Supporting Information for

Calcium mediated efficient synthesis of N-arylamidines from Organic Nitriles and Amines

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Table of Contents

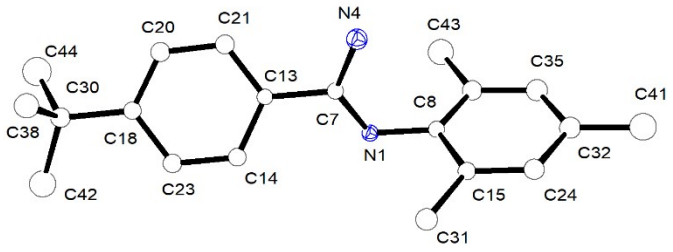


Figure FS1. Solid-state structure of product **3p** obtained from 4-(tert-butyl)benzonitrile and **1b**, drawn with 30% thermal ellipsoids.

Table TS1. Crystallographic data and refinement parameters of **3d**, **3j**, **4a** and **4c**.

Crystal Parameters	**3d**	**3j**	**4a**	**4c**
CCDC No.	1997732	1997733	1997734	1997735
Empirical formula	$C_{19}H_{23}BrN_2$	$C_{21}H_{29}N_3$	$C_{26}H_{28}ClN_3O$	$C_{27}H_{30}ClN_3O_2$
Formula weight	359.30	323.48	433.98	464.01
T (K)	298(2)	113	113	113
λ (Å)	0.71073	0.71075	0.71073	0.71075
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\,2_1/c$	$P\,2_1/n$	$P\,2_1/n$	$P\,2_1/n$
a (Å)	19.7432(16)	8.5523(11)	12.988(2)	18.7816(14)
b (Å)	18.485(2)	10.6764(14)	15.255(2)	29.0379(17)
c (Å)	10.3179(10)	20.418(3)	14.374(2)	19.9928(15)
α (°)	90	90	90	90
β (°)	99.181(8)	93.693(4)	104.275(4)	115.493(14)
γ (°)	90	90	90	90
V (Å^3)	3717.3(7)	1860.5(4)	2760.0(7)	9842.0(12)
Z	8	4	5	17
Density (mg/m^3)	1.284	1.155	1.305	1.331
μ (mm^{-1}) (mm^{-1})	2.211	0.068	0.196	0.195
F (000)	1488	704	1150	4182
Theta range for data collection	3.468 to 29.588	3.056 to 27.545	3.10 to 27.50	3.024 to 27.543
Limiting indices	-20<=h<= 27 -25<=k<= 17 -13<=l<= 12	-11<=h<= 11 -13<=k<= 13 -26<=l<= 26	-16 <=h<= 16 -19 <=h<= 19 -18 <=h<= 18	-24 <=h<= 24 -37 <=k<= 37 -25 <=h<= 25
Reflections collected/unique	8825/3647 [R(int) = 0.0281]	21956/4271 [R(int) = 0.0417]	38432/6357 [R(int) = 0.1199]	22653/1221 [R(int) = 0.0532]
Completeness to theta	99.7%	99.9%	99.8%	99.9%

Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
Max. and min. transmission	6.936 to 59.176	6.112 and 55.09	6.20 and 55.0	6.048 and 55.086
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restrains/ parameters	8825/0/414	4271/0/223	6357/0/316	22653/0/1221
Goodness-of-fit on F^2	1.027	1.065	1.71	1.032
Final R indices [I>=2σ (I)]	R1 = 0.0710, wR2 = 0.1999	R1 = 0.0426, wR2 = 0.1073	R1 = 0.1398, wR2 = 0.4069	R1 = 0.0462, wR2 = 0.1113
R indices (all data)	R1 = 0.1642, wR2 = 0.2609	R1 = 0.0600, wR2 = 0.1149	R1 = 0.1178, wR2 = 0.3791	R1 = 0.0714, wR2 = 0.1228
Largest diff. peak/ hole (e $Å^{-3}$)	0.74/-0.80	0.25/-0.25	-	0.99/-1.05

Experimental

General. All manipulations involving air- and moisture-sensitive compounds were carried out under argon using the standard Schlenk technique or argon-filled M. Braun glove box. Hydrocarbon solvents (*n*-hexane, toluene, benzene) were distilled under nitrogen atmosphere from $LiAlH_4$ and stored inside the glove box. THF was dried and deoxygenated by distillation over sodium benzophenone under argon and then distilled and dried over CaH_2 prior to being stored in the glove box. ^1H NMR (400 MHz) and $^{13}C\{^1H\}$ (100 MHz) spectra were recorded on the BRUKER ADVANCE III-400 spectrometer. All nitriles and alkynes were purchased from Sigma Aldrich, Alfa Aesar or TCI Chemicals (India) Pvt. Ltd and stored in the glove box. The amines were purchased from Sigma Aldrich and distilled prior to use. $LiN(SiMe_3)_2$, $NaN(SiMe_3)_2$ and $KN(SiMe_3)_2$ were purchased from Sigma Aldrich and used as received. Calcium bis(trimethylsilyl) amide $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ was prepared according to procedure prescribed in the literature.[1] NMR solvent ($CDCl_3$) was purchased from Merck and distilled over molecular sieves.

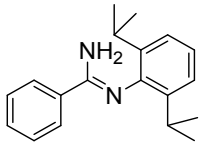
General procedure for catalytic synthesis of N-arylamidines (3a-3zd). In the glove box, the preferred catalyst $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ (20 mg, 0.05 mmol, 5 mol %) was taken and the corresponding amine (0.997 mmol) were added to a Schlenk tube followed by the addition of nitriles (1.108 mmol). The Schlenk tube was taken out and the reaction mixture was stirred in an oil bath at 65°C for 12 h. TLC was moinitored and after the desired reaction time, the resulting reaction mixtures were further purified by

column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate (5:2.5 - 5:4). The isolated products were characterised by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy.

Procedure for gram-scale synthesis of N-(2,6-diisopropylphenyl)benzimidamide (3a). In the glove box, the preferred catalyst $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ (350 mg, 0.97 mmol, 5 mol %) was taken and 2,6-diisopropylaniline (17.5 mmol, 3 g) were added to a 50 mL Schlenk tube followed by the addition of benzonitrile (19.4 mmol, 2 g). The Schlenk tube was taken out and the reaction mixture was stirred in an oil bath at 65 °C for 12 hours in neat condition. TLC was moinitored and the resulting reaction mixture was purified from column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate (5:2.5). The product was isolated as white solid (Yield = 4.5 g, 84%).

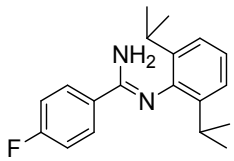
Procedure for gram-scale synthesis of N-(2,6-diisopropylphenyl)-4-bromobenzimidamide (3d). The procedure was followed as mentioned above. The product was isolated as white solid (Yield = 3.2 g, 81%).

NMR data of N-arylamidines 3a-3zd.



N-(2,6-diisopropylphenyl)benzimidamide (**3a**).[2-4]

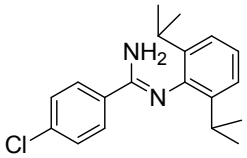
Yield (289.2 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.94 - 7.92 (m, 2H, Ar-*H*), 7.52 - 7.48 (m, 3H, Ar-*H*), 7.19 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.11 - 7.08 (m, 1H, Ar-*H*), 4.62 (s, 2H, N*H*$_2$), 3.12 - 3.02 (sept, 2H, C*H*), 1.21 (dd, *J* = 4.0 Hz, 12H, C*H*$_3$) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ_C 153.3, 144.1, 139.2, 135.8, 130.4, 128.6, 126.7, 123.3, 28.2, 23.6 (d, *J* = 9.0 Hz) ppm. Elemental analysis $C_{19}H_{24}N_2$ (280.40). Calcd (found) C 81.38 (81.13), H 8.63 (8.49), N 9.99 (9.74).



N-(2,6-diisopropylphenyl)-4-fluorobenzimidamide (**3b**).

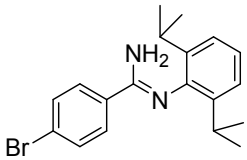
Yield (297.8 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.92 - 7.89 (m, 2H, Ar-*H*), 7.17 - 7.12 (m, 4H, Ar-*H*), 7.09 - 7.05 (m, 1H, Ar-*H*), 4.56 (s, 2H, N*H*$_2$), 3.06 - 2.95 (sept, 2H, C*H*), 1.18 (dd, *J* = 4.0 Hz, 12H, C*H*$_3$) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ_C 164.2 (d, *J* = 251.0 Hz), 152.3, 144.0, 139.2, 128.8

(d, J = 8.0 Hz), 123.4 (d, J = 10.0 Hz), 115.5 (d, J = 22.0 Hz), 28.2, 23.6 (d, J = 4.0 Hz) ppm. Elemental analysis $C_{19}H_{23}FN_2$ (298.39). Calcd (found) C 76.48 (76.32), H 7.77 (7.59), N 9.39 (9.08).



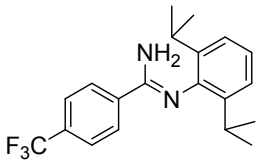
4-chloro-N'-(2,6-diisopropylphenyl)benzimidamide (**3c**).[2-4]

Yield (317.7 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.85 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.43 (d, J = 12.0 Hz, 2H, Ar-*H*), 7.17 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.05 (q, J = 8.0 Hz, 1H, Ar-*H*), 4.60 (s, 2H, NH_2), 3.05 - 2.94 (sept, 2H, C*H*), 1.19 (dd, J = 4.0 Hz, 12H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 152.3, 143.8, 139.1, 136.5, 134.0, 128.7, 128.1, 123.5 (d, J = 17.0 Hz), 122.7, 28.2, 23.5 (d, J = 5.0 Hz), 22.4 ppm. Elemental analysis $C_{19}H_{23}ClN_2$ (314.85). Calcd (found) C 72.48 (72.22), H 7.36 (7.19), N 8.90 (8.68).



4-bromo-N'-(2,6-diisopropylphenyl)benzimidamide (**3d**).

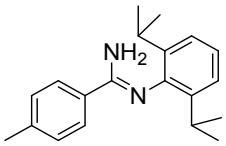
Yield (362.6 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.79 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.59 (d, J = 12.0 Hz, 2H, Ar-*H*), 7.15 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.07 (t, J = 8.0 Hz, 1H, Ar-*H*), 4.57 (s, 2H, NH_2), 3.03 - 2.93 (sept, 2H, C*H*), 1.18 (dd, J = 4.0 Hz, 12H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 152.3, 143.8, 139.1, 134.5, 131.8, 128.3, 124.9, 123.5 (d, J = 17.0 Hz), 28.2, 23.5 (d, J = 5.0 Hz) ppm. Elemental analysis $C_{19}H_{23}BrN_2$ (359.30). Calcd (found) C 63.51 (63.37), H 6.45 (6.29), N 7.80 (7.63).



N-(2,6-diisopropylphenyl)-4-(trifluoromethyl)benzimidamide (**3e**).

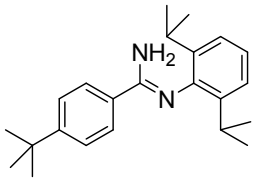
Yield (324.5 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.03 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.71 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.18 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.10 (t, J = 8.0 Hz, 1H, Ar-*H*), 4.69 (s, 2H, NH_2), 3.05 - 2.94 (sept, 2H, C*H*), 1.19 (t, J = 8.0 Hz, 12H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 152.1, 143.6, 139.0, 132.3 (d, J = 32.0 Hz), 127.2, 125.6 (d, J = 12.0 Hz), 124.3 (q, J = 270.0 Hz), 123.6 (d, J =

28.0 Hz), 28.3, 23.5 (d, J = 3.0 Hz) ppm. Elemental analysis $C_{20}H_{23}F_3N_2$ (348.40). Calcd (found) C 68.95 (68.83), H 6.65 (6.51), N 8.04 (7.87).



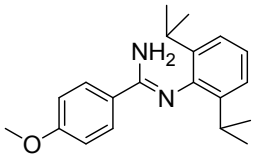
N-(2,6-diisopropylphenyl)-4-methylbenzimidamide (**3f**).

Yield (280.8 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.81 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.27 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.15 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.08 - 7.04 (m, 1H, Ar-*H*), 4.56 (s, 2H, NH_2), 3.09 - 2.99 (sept, 2H, C*H*), 2.42 (s, 3H, CH_3), 1.17 (d, J = 8.0 Hz, 12H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 153.2, 144.2, 140.7, 139.3, 132.9, 129.2, 126.6, 123.3, 28.2, 23.6 (d, J = 10.0 Hz), 21.4 ppm. Elemental analysis $C_{20}H_{26}N_2$ (294.43). Calcd (found) C 81.59 (81.39), H 8.90 (8.77), N 9.51 (9.45).



4-(tert-butyl)-N'-(2,6-diisopropylphenyl)benzimidamide (**3g**).

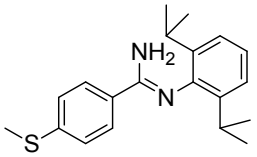
Yield (320.9 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.89 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.51 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.18 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.09 (t, J = 8.0 Hz, 1H, Ar-*H*), 4.62 (s, 2H, NH_2), 3.12 - 3.02 (sept, 2H, C*H*), 1.39 (s, 9H, (CH_3)$_3$), 1.20 (d, J = 8.0 Hz, 12H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 153.4 (d, J = 64.0 Hz), 144.3, 139.3, 132.8, 126.4, 125.5, 123.3, 34.8, 31.2, 28.1, 23.6 (d, J = 14.0 Hz) ppm. Elemental analysis $C_{23}H_{32}N_2$ (336.51). Calcd (found) C 82.09 (81.79), H 9.58 (9.43), N 8.32 (8.27).



N-(2,6-diisopropylphenyl)-4-methoxybenzimidamide (**3h**).[2-4]

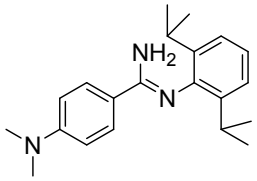
Yield (251.3 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.87 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.16 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.09 - 7.06 (m, 1H, Ar-*H*), 6.96 (d, J = 8.0 Hz, 2H, Ar-*H*), 4.56 (s, 2H, NH_2), 3.86 (s, 3H, OCH_3), 3.10 - 3.00 (sept, 2H, C*H*), 1.18 (dd, J = 8.0 Hz, 12H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz,

$CDCl_3$): δ_C 161.4, 144.3, 139.3, 128.2, 123.3, 113.8, 55.4, 28.1, 23.6 (d, *J* = 12.0 Hz) ppm. Elemental analysis $C_{20}H_{26}N_2O$ (310.43). Calcd (found) C 77.38 (77.12), H 8.44 (8.36), N 9.02 (8.85).



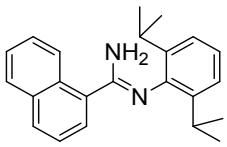
N-(2,6-diisopropylphenyl)-4-(methylthio)benzimidamide (**3i**).

Yield (264.3 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.83 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.28 (d, *J* = 12.0 Hz, 2H, Ar-*H*), 7.17 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.09 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 4.63 (s, 2H, NH_2), 3.08 - 2.98 (sept, 2H, C*H*), 2.52 (s, 3H, SCH_3), 1.19 (dd, *J* = 4.0 Hz, 12H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 152.7, 144.1, 141.6, 139.2, 132.0, 127.0, 125.7, 123.3, 28.1, 23.5 (d, *J* = 10.0 Hz), 15.3 ppm. Elemental analysis $C_{20}H_{26}N_2S$ (326.49). Calcd (found) C 73.57 (73.41), H 8.03 (7.82), N 8.58 (8.32).



N-(2,6-diisopropylphenyl)-4-(dimethylamino)benzimidamide (**3j**).

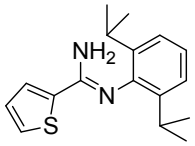
Yield (290.5 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.86 (d, *J* = 12.0 Hz, 2H, Ar-*H*), 7.21 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.11 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 6.76 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 4.55 (s, 2H, NH_2), 3.18 - 3.08 (sept, 2H, C*H*), 3.04 (s, 6H, N(CH_3)$_2$), 1.23 (d, *J* = 4.0 Hz, 12H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 153.1, 151.8, 144.5, 139.5, 127.7, 123.1, 122.8 (d, *J* = 16.0 Hz), 111.4, 40.1, 28.0, 23.5 (d, *J* = 19.0 Hz) ppm. Elemental analysis $C_{21}H_{29}N_3$ (323.47). Calcd (found) C 77.97 (77.84), H 9.04 (8.91), N 12.99 (12.87).



(Z)-N'-(2,6-diisopropylphenyl)-1-naphthimidamide (**3k**).

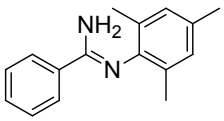
Yield (340.8 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.33 (s, 1H, Ar-*H*), 8.10 (dd, *J* = 4.0 Hz, 1H, Ar-*H*), 7.95 - 7.88 (m, 3H, Ar-*H*), 7.57 - 7.53 (m, 2H, Ar-*H*), 7.19 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.10 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 4.72 (s, 2H, NH_2), 3.15 - 3.05 (sept, 2H, C*H*), 1.21 (dd, *J* = 4.0 Hz, 12H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 153.4, 139.3, 134.4, 132.9 (d, *J* = 13.0 Hz), 128.6, 128.4, 127.7,

127.1, 126.5, 126.1, 124.3, 123.4, 28.3, 23.6 (d, J = 11.0 Hz) ppm. Elemental analysis $C_{23}H_{26}N_2$ (330.46). Calcd (found) C 83.59 (83.43), H 7.93 (7.84), N 8.48 (8.38).



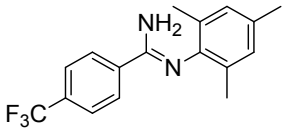
N-(2,6-diisopropylphenyl)thiophene-2-carboximidamide (**3l**).

Yield (295.4 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42 (d, J = 4.0 Hz, 1H, Ar-*H*), 7.37 (d, J = 4.0 Hz, 1H, Ar-*H*), 7.16 (d, J = 4.0 Hz, 2H, Ar-*H*), 7.11 - 7.07 (m, 2H, Ar-*H*), 4.61 (s, 2H, NH_2), 3.10 - 3.00 (sept, 2H, C*H*), 1.19 (dd, J = 4.0 Hz, 12H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 148.2, 143.3, 140.4, 139.4, 128.8, 127.2, 125.4, 123.4 (d, J = 32.0 Hz), 28.2, 26.8, 23.5 (d, J = 24.0 Hz) ppm. Elemental analysis $C_{17}H_{22}N_2S$ (286.43). Calcd (found) C 71.28 (71.19), H 7.74 (7.63), N 9.78 (9.61).



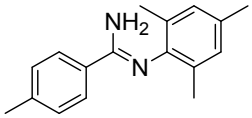
N-mesitylbenzimidamide (**3m**).

Yield (240.5 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.85 (d, J = 4.0 Hz, 2H, Ar-*H*), 7.49 - 7.39 (m, 3H, Ar-*H*), 6.86 (s, 2H, Ar-*H*), 4.99 (s, 2H, NH_2), 2.26 (s, 3H, CH_3), 2.07 (s, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 154.5, 142.1, 135.0, 132.5, 130.6, 128.8 (d, J = 22.0 Hz), 128.5, 126.8, 29.6, 20.7, 17.6 ppm. Elemental analysis $C_{16}H_{18}N_2$ (238.32). Calcd (found) C 80.63 (8.54), H 7.61 (7.48), N 11.75 (11.62).



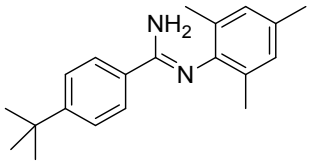
N-mesityl-4-(trifluoromethyl)benzimidamide (**3n**).

Yield (305.7 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.93 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.63 (d, J = 8.0 Hz, 2H, Ar-*H*), 6.88 (s, 2H, Ar-*H*), 4.79 (s, 2H, NH_2), 2.28 (s, 3H, CH_3), 2.07 (s, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 152.5, 143.0, 138.9, 132.1 (d, J = 39.0 Hz), 128.6 (d, J = 58.0 Hz), 127.1, 125.3 (d, J = 11.0 Hz), 123.8 (q, J = 270.0 Hz), 20.6, 17.5 ppm. Elemental analysis $C_{17}H_{17}F_3N_2$ (306.32). Calcd (found) C 66.66 (66.46), H 5.59 (5.41), N 9.14 (9.02).



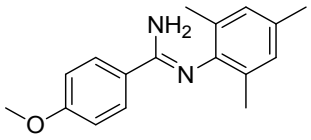
N-mesityl-4-methylbenzimidamide (**3o**).

Yield (251.8 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.77 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.22 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.86 (s, 2H, Ar-*H*), 4.56 (s, 2H, NH_2), 2.39 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.09 (s, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 153.1, 140.5, 132.8, 131.7, 128.9 (d, *J* = 35.0 Hz), 21.3, 20.7, 17.6 ppm. Elemental analysis $C_{17}H_{20}N_2$ (252.35). Calcd (found) C 80.91 (80.78), H 7.99 (7.83), N 11.10 (10.98).



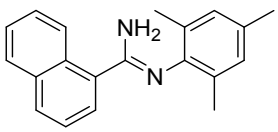
4-(tert-butyl)-N-mesitylbenzimidamide (**3p**).

Yield (284.0 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.85 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.47 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.89 (s, 2H, Ar-*H*), 4.54 (s, 2H, NH_2), 2.28 (s, 3H, CH_3), 2.12 (s, 6H, CH_3), 1.37 (s, 9H, (CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 153.4, 143.6, 132.7, 131.7, 128.7 (d, *J* = 13.0 Hz), 126.4, 125.3, 34.7, 31.2, 20.7, 17.6 ppm. Elemental analysis $C_{20}H_{26}N_2$ (294.43). Calcd (found) C 81.59 (81.47), H 8.90 (8.73), N 9.51 (9.45).



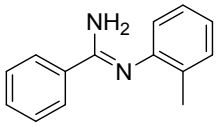
N-mesityl-4-methoxybenzimidamide (**3q**).

Yield (253.0 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.83 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.92 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.86 (s, 2H, Ar-*H*), 4.67 (s, 2H, NH_2), 3.83 (s, 3H, OCH_3), 2.26 (s, 3H, CH_3), 2.10 (s, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 161.3, 153.0, 143.5, 131.7, 128.7, 128.0 (d, *J* = 16.0 Hz), 113.6, 55.2, 29.6, 20.6, 17.6 ppm. Elemental analysis $C_{17}H_{20}N_2O$ (268.35). Calcd (found) C 76.09 (75.91), H 7.51 (7.37), N 10.44 (10.38).



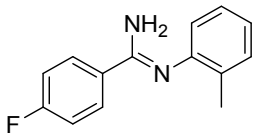
N-mesityl-1-naphthimidamide (**3r**).

Yield (278.2 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.31 (s, 1H, Ar-*H*), 8.07 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.88 (t, *J* = 8.0 Hz, 3H, Ar-*H*), 7.56 - 7.50 (m, 2H, Ar-*H*), 6.91 (s, 2H, Ar-*H*), 4.74 (s, 2H, NH_2), 2.30 (s, 3H, CH_3), 2.16 (s, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 153.3, 143.6, 134.3, 132.8 (d, *J* = 18.0 Hz), 128.7 (d, *J* = 25.0 Hz), 127.9 (d, *J* = 55.0 Hz), 126.9, 126.2 (d, *J* = 31.0 Hz), 124.2, 20.7, 17.7 ppm. Elemental analysis $C_{20}H_{20}N_2$ (288.38). Calcd (found) C 83.30 (83.12), H 6.99 (6.83), N 9.71 (9.63).



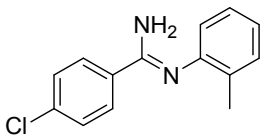
N-(o-tolyl)benzimidamide (**3s**). [4-5]

Yield (216.8 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.85 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.49 - 7.40 (m, 3H, Ar-*H*), 7.23 - 7.15 (m, 2H, Ar-*H*), 6.99 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 6.86 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 4.69 (s, 2H, NH_2), 2.19 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 130.6 (d, *J* = 22.0 Hz), 128.4, 126.8 (d, *J* = 5.0 Hz), 123.1, 121.2, 17.6 ppm. Elemental analysis $C_{14}H_{14}N_2$ (210.27). Calcd (found) C 79.97 (79.82), H 6.71 (6.59), N 13.32 (13.14).



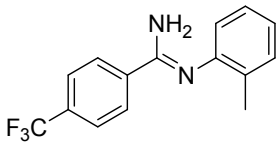
4-fluoro-N-(o-tolyl)benzimidamide (**3t**).

Yield (230.3 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.84 - 7.81 (m, 2H, Ar-*H*), 7.21 - 7.14 (m, 2H, Ar-*H*), 7.07 (t, *J* = 8.0 Hz, 2H, Ar-*H*), 6.98 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 6.82 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 4.64 (s, 2H, NH_2), 2.15 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 164.0 (d, *J* = 250.0 Hz), 153.2, 147.5, 133.6 (d, *J* = 14.0 Hz), 131.6, 130.7, 129.1 (d, *J* = 59.0 Hz), 126.8, 123.2, 121.0, 117.5, 115.3 (d, *J* = 22.0 Hz), 114.2, 17.5 ppm. Elemental analysis $C_{14}H_{13}FN_2$ (228.26). Calcd (found) C 73.66 (73.51), H 5.74 (5.63), N 12.27 (12.10).



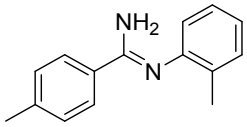
4-chloro-N-(o-tolyl)benzimidamide (**3u**).

Yield (250.0 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.79 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.38 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.22 - 7.15 (m, 2H, Ar-*H*), 7.00 - 6.97 (m, 1H, Ar-*H*), 6.83 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 4.73 (s, 2H, N*H*$_2$), 2.15 (s, 3H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 152.9, 147.6, 136.5, 134.0, 130.8, 129.4, 128.3 (d, *J* = 49.0 Hz), 126.9, 123.2, 120.9, 17.5 ppm. Elemental analysis $C_{14}H_{13}ClN_2$ (244.71). Calcd (found) C 68.71 (68.62), H 5.35 (5.29), N 11.45 (11.38).



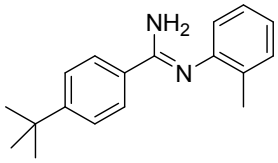
N-(o-tolyl)-4-(trifluoromethyl)benzimidamide (**3v**).

Yield (274.6 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.96 (d, *J* = 4.0 Hz, 2H, Ar-*H*), 7.67 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.23 - 7.16 (m, 2H, Ar-*H*), 7.00 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 6.84 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 4.82 (s, 2H, N*H*$_2$), 2.17 (s, 3H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 152.7, 147.5, 139.0, 132.2 (d, *J* = 33.0 Hz), 130.9, 127.1 (d, *J* = 27.0 Hz), 125.4 (d, *J* = 3.0 Hz), 125.0 (q, *J* = 270.0 Hz), 123.4, 17.5 ppm. Elemental analysis $C_{15}H_{13}F_3N_2$ (278.27). Calcd (found) C 64.74 (64.65), H 4.71 (4.62), N 10.07 (9.88).



4-methyl-N-(o-tolyl)benzimidamide (**3w**).

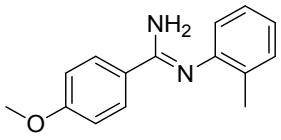
Yield (223.8 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.69 (d, *J* = 4.0 Hz, 2H, Ar-*H*), 7.20 - 7.12 (m, 4H, Ar-*H*), 6.99 - 6.96 (m, 1H, Ar-*H*), 6.82 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 5.12 (s, 2H, N*H*$_2$), 2.38 (s, 3H, C*H*$_3$), 2.17 (s, 3H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 140.5, 130.5, 128.9, 127.3, 126.6, 123.1, 121.4, 21.2, 17.4 ppm. Elemental analysis $C_{15}H_{16}N_2$ (224.30). Calcd (found) C 80.32 (80.21), H 7.19 (7.07), N 12.49 (12.33).



4-(tert-butyl)-N-(o-tolyl)benzimidamide (**3x**).

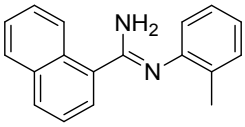
Yield (251.1 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.80 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.42 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.21 - 7.13 (m, 2H, Ar-*H*), 6.97 - 6.94 (m, 1H, Ar-*H*), 6.84 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 4.70

(s, 2H, NH_2), 2.15 (s, 3H, CH_3), 1.34 (s, 9H, (CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 153.7, 148.2, 132.7, 130.6, 129.4, 126.6 (d, J = 33.0 Hz), 125.3, 122.9, 121.1, 34.7, 31.1, 17.5 ppm. Elemental analysis $C_{18}H_{22}N_2$ (266.38). Calcd (found) C 81.16 (81.01), H 8.32 (8.17), N 10.52 (10.43).



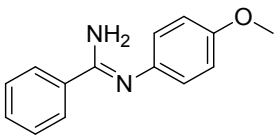
4-methoxy-N-(o-tolyl)benzimidamide (**3y**).

Yield (221.2 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.80 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.21 - 7.13 (m, 2H, Ar-*H*), 6.97 (t, J = 8.0 Hz, 1H, Ar-*H*), 6.91 (d, J = 8.0 Hz, 2H, Ar-*H*), 6.84 (d, J = 8.0 Hz, 1H, Ar-*H*), 4.65 (s, 2H, NH_2), 3.83 (s, 3H, OCH_3), 2.17 (s, 9H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 161.4, 130.6, 129.6, 128.2, 126.7, 122.9, 121.3, 113.6, 55.3, 17.6 ppm. Elemental analysis $C_{15}H_{16}N_2O$ (240.30). Calcd (found) C 74.97 (79.78), H 6.71 (6.62), N 11.66 (11.57).



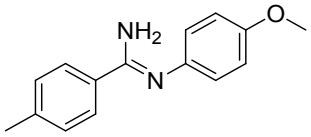
N-(o-tolyl)-1-naphthimidamide (**3z**).

Yield (225.2 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.31 (s, 1H, Ar-*H*), 8.03 (d, J = 8.0 Hz, 1H, Ar-*H*), 7.90 - 7.87 (m, 3H, Ar-*H*), 7.58 - 7.51 (m, 2H, Ar-*H*), 7.27 - 7.19 (m, 2H, Ar-*H*), 7.04 - 7.01 (m, 1H, Ar-*H*), 6.93 (d, J = 8.0 Hz, 1H, Ar-*H*), 4.75 (s, 2H, NH_2), 2.24 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 134.3, 132.7, 130.7, 129.6, 128.4 (d, J = 37.0 Hz), 127.7, 126.9 (d, J = 22.0 Hz), 126.4 (d, J = 11.0 Hz), 124.2, 123.2, 121.2, 17.6 ppm. Elemental analysis $C_{18}H_{16}N_2$ (260.33). Calcd (found) C 83.04 (82.87), H 6.19 (6.05), N 10.76 (10.68).



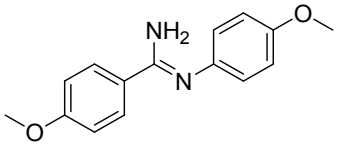
N-(4-methoxyphenyl)benzimidamide (**3za**).

Yield (223.3 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.76 (d, J = 4.0 Hz, 2H, Ar-*H*), 7.43 - 7.34 (m, 3H, Ar-*H*), 6.86 (s, 4H, Ar-*H*), 4.94 (s, 2H, NH_2), 3.74 (s, 3H, OCH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 155.3, 142.0, 135.5, 130.2, 128.2, 126.6, 122.4, 114.6, 55.2 ppm. Elemental analysis $C_{14}H_{14}N_2O$ (226.27). Calcd (found) C 74.31 (74.21), H 6.24 (6.19), N 12.38 (12.26).



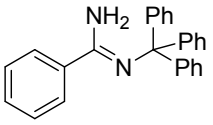
N-(4-methoxyphenyl)-4-methylbenzimidamide (**3zb**).

Yield (223.8 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.68 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.18 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.87 (s, 4H, Ar-*H*), 4.81 (s, 2H, NH_2), 3.76 (s, 3H, OCH_3), 2.37 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 155.4, 142.3, 140.5, 132.8, 129.0, 127.3, 126.6, 122.6, 114.7, 55.3, 21.2 ppm. Elemental analysis $C_{15}H_{16}N_2O$ (240.30). Calcd (found) C 74.97 (74.83), H 6.71 (6.58), N 11.66 (11.49).



4-methoxy-N-(4-methoxyphenyl)benzimidamide (**3zc**).

Yield (224.5 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.76 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.91 - 6.88 (m, 6H, Ar-*H*), 4.72 (s, 2H, NH_2), 3.82 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 161.4, 155.5, 128.3, 122.7, 114.7, 113.7, 55.3 (d, *J* = 9.0 Hz) ppm. Elemental analysis $C_{15}H_{16}N_2O_2$ (256.29). Calcd (found) C 70.29 (70.13), H 6.29 (6.11), N 10.93 (10.87).



N-tritylbenzimidamide (**3zd**).

Yield (325.5 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.95 (d, *J* = 4.0 Hz, 2H, Ar-*H*), 7.55 (d, *J* = 8.0 Hz, 6H, Ar-*H*), 7.50 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.40 (t, *J* = 8.0 Hz, 7H, Ar-*H*), 7.33 (d, *J* = 8.0 Hz, 3H, Ar-*H*), 4.72 (s, 2H, NH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 148.4, 146.1, 138.2, 129.9, 128.9, 128.3, 127.9, 126.5 ppm. Elemental analysis $C_{26}H_{22}N_2$ (362.46). Calcd (found) C 86.15 (86.01), H 6.12 (5.93), N 7.73 (7.67).

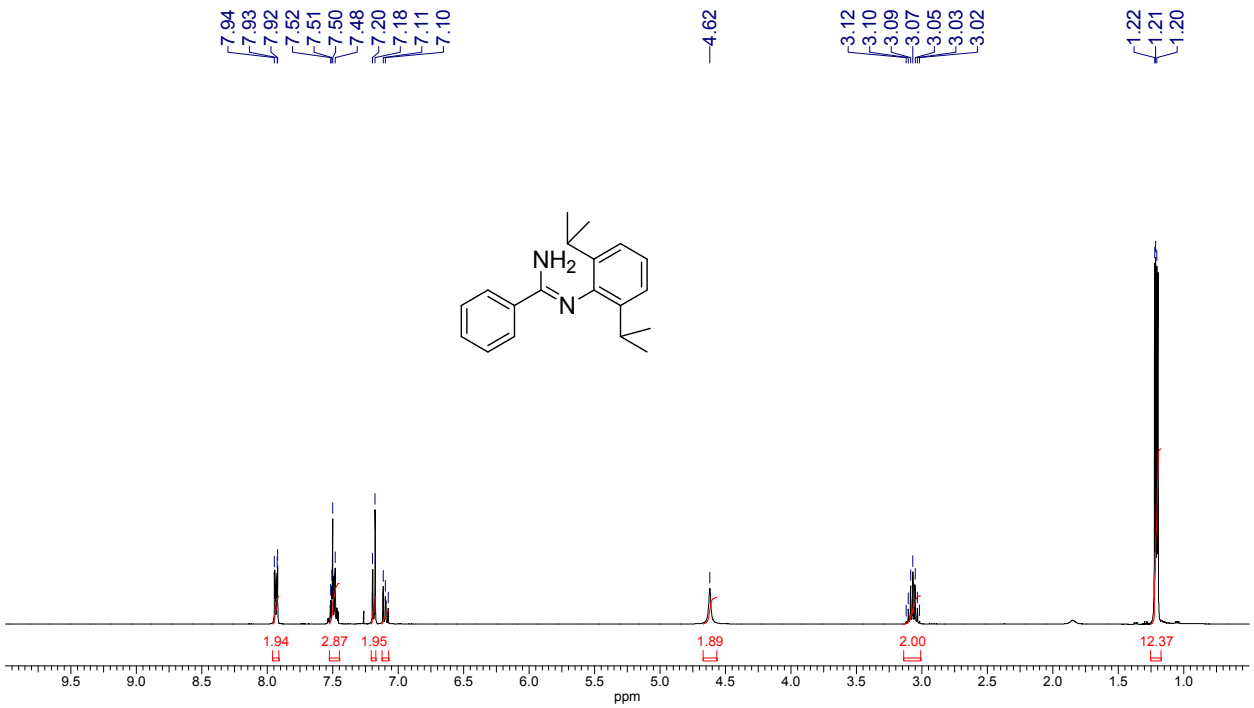


Figure FS2. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**.

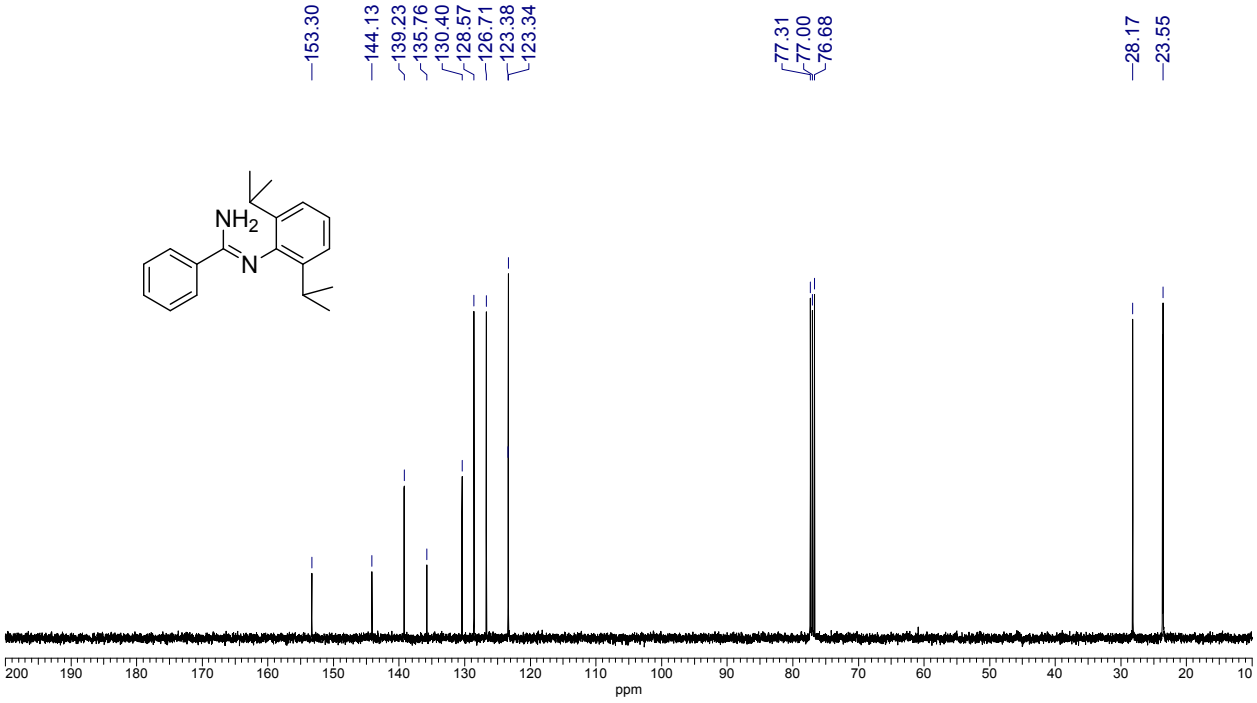


Figure FS3. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3a**.

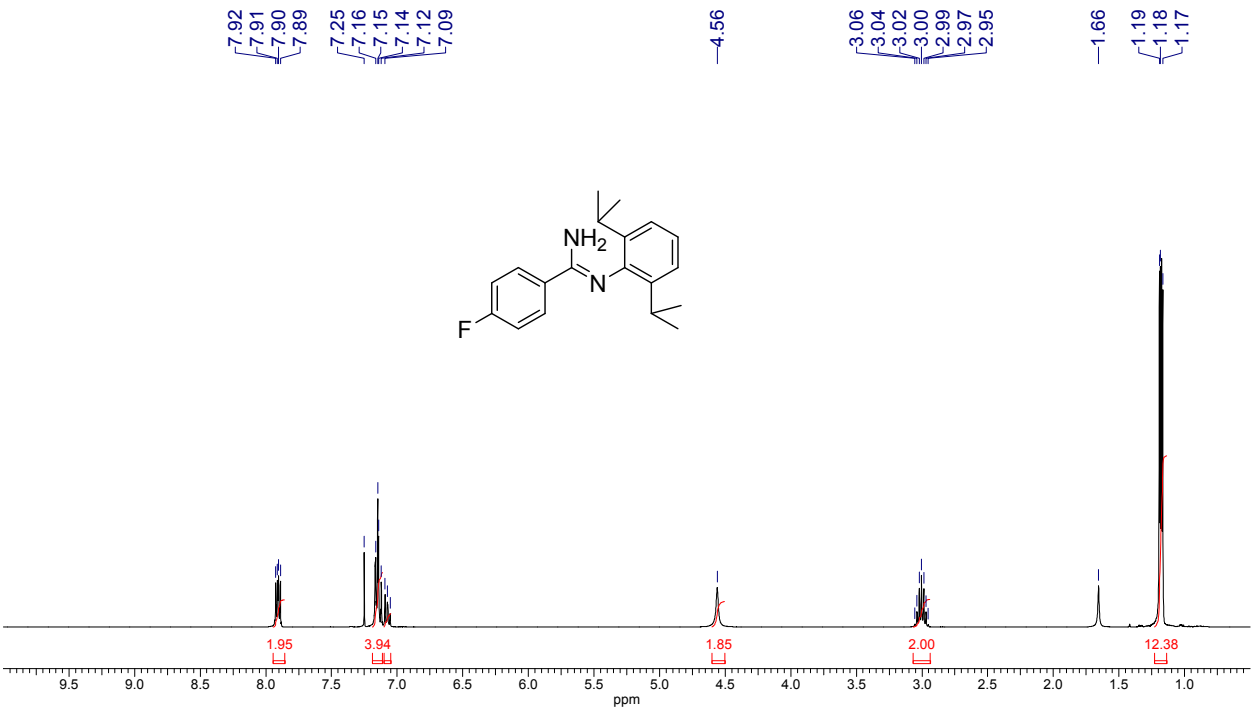


Figure FS4. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b**.

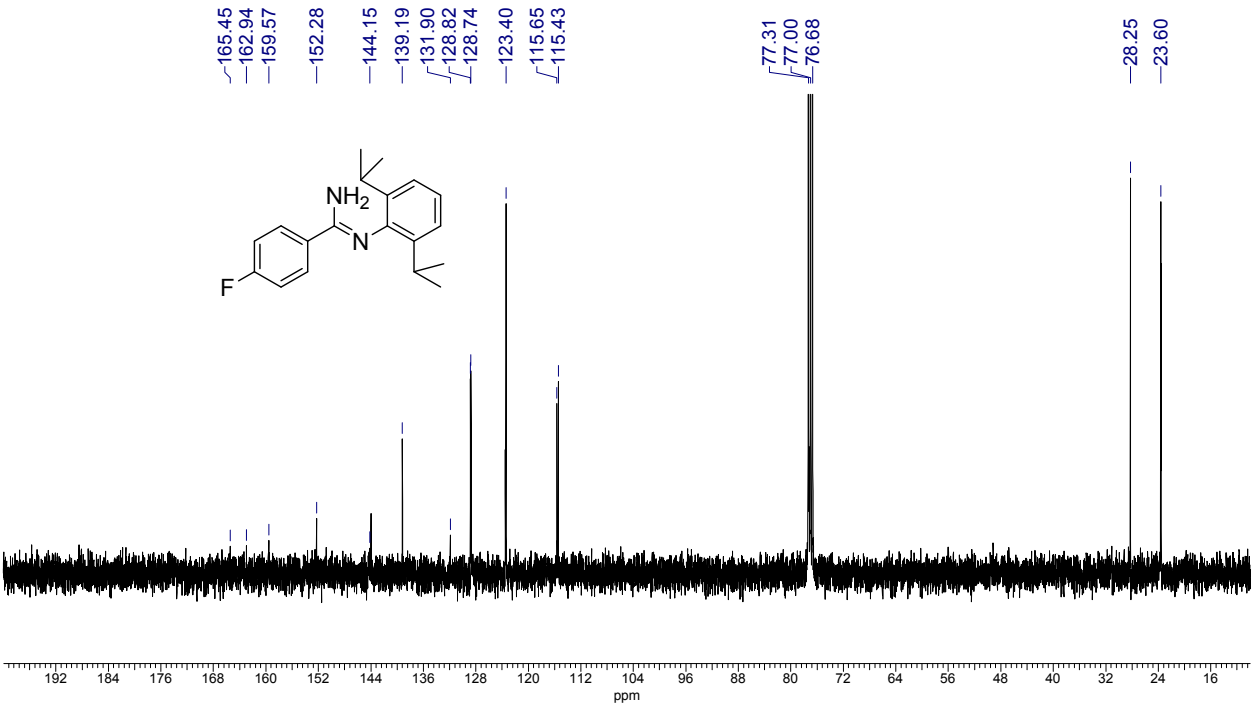


Figure FS5. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3b**.

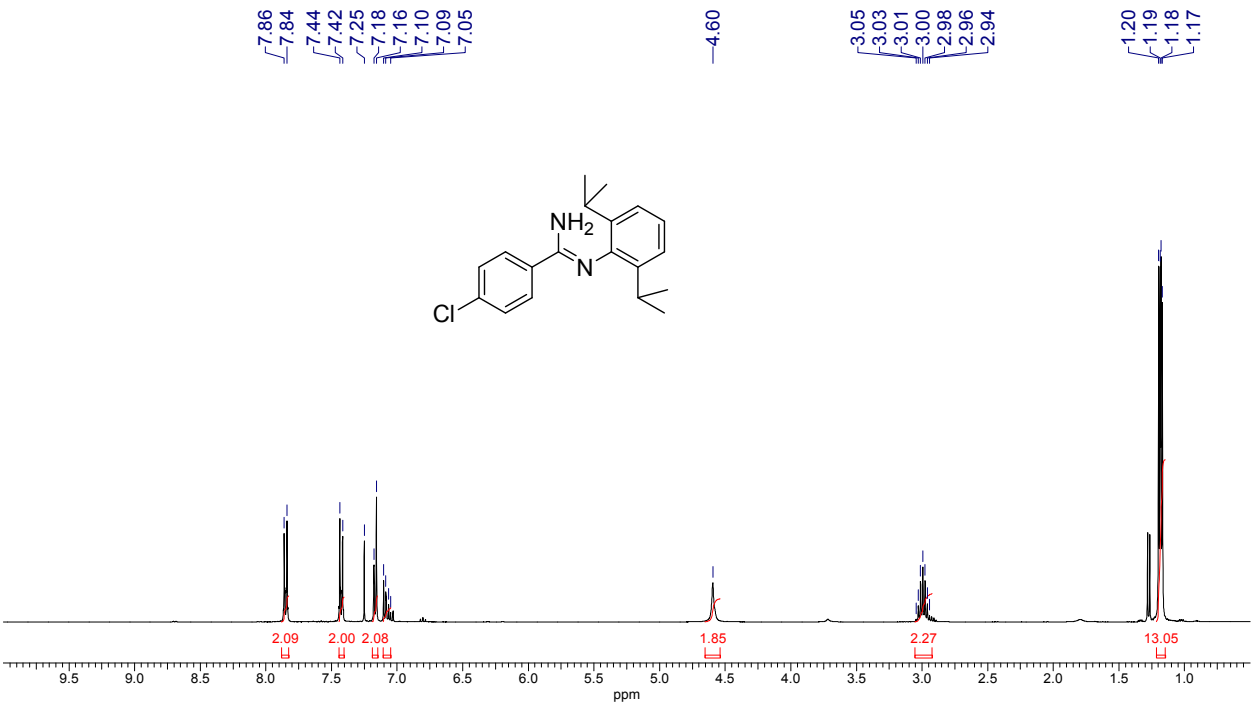


Figure FS6. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c**.

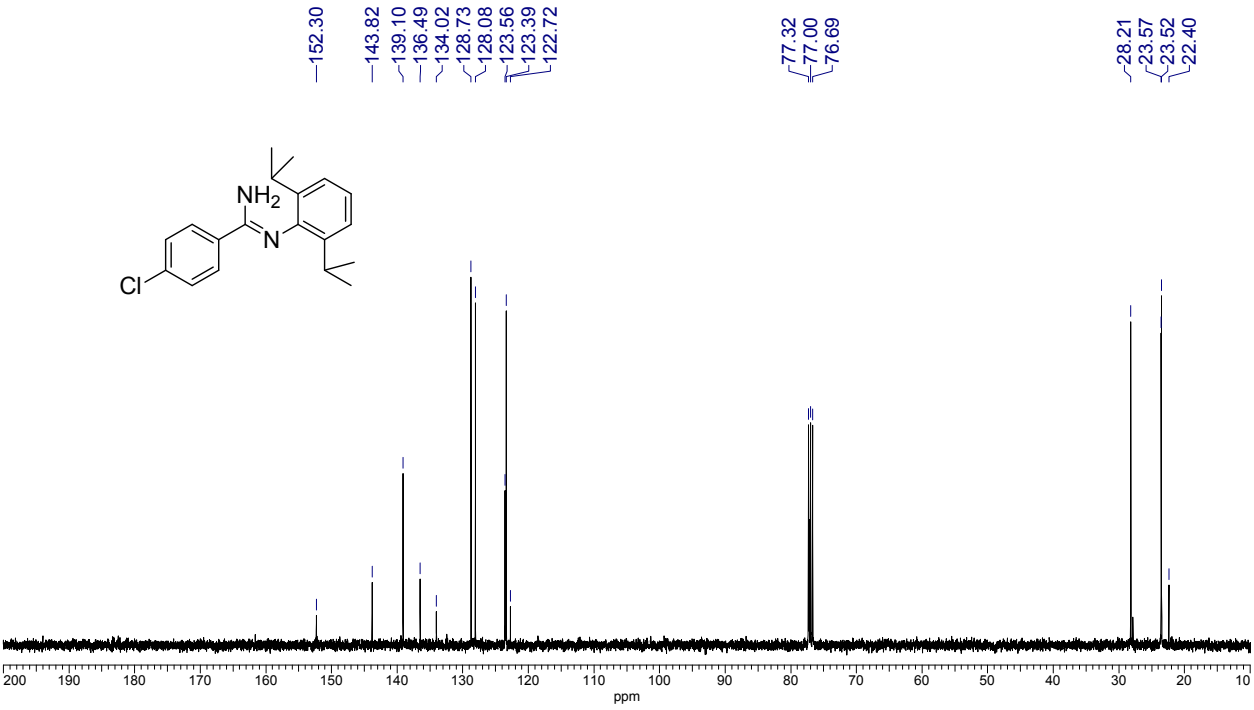


Figure FS7. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3c**.

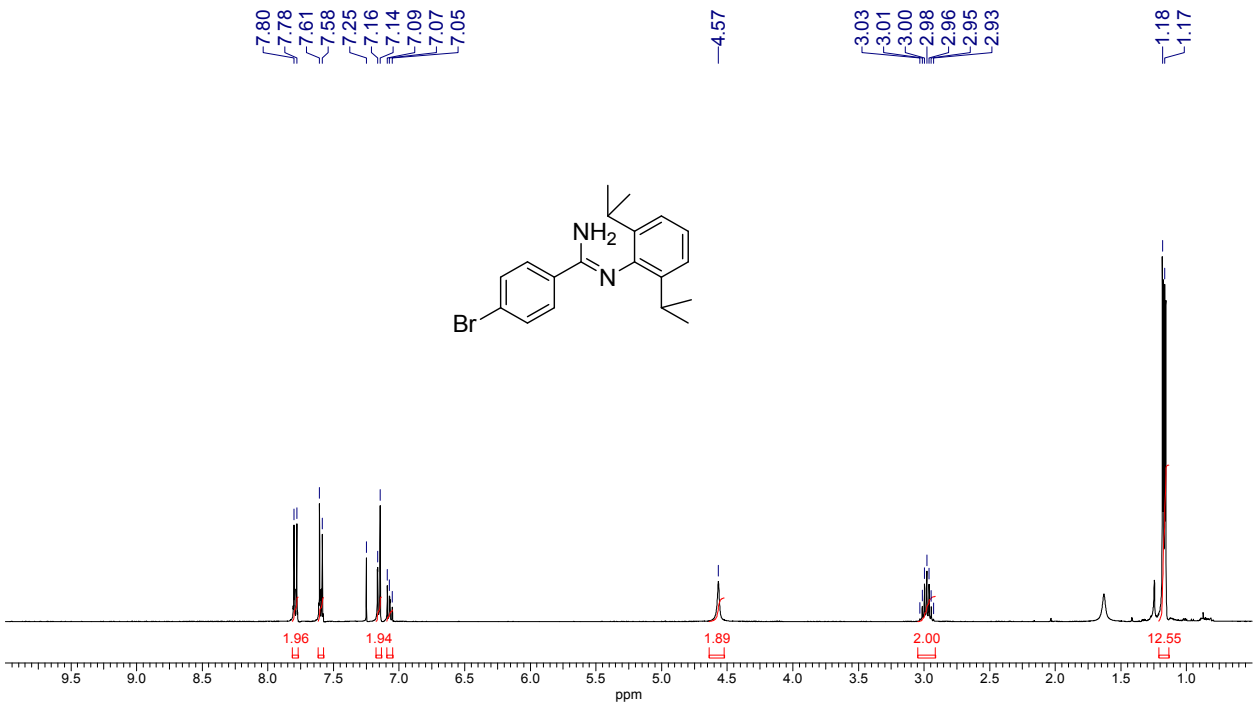


Figure FS8. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3d**.

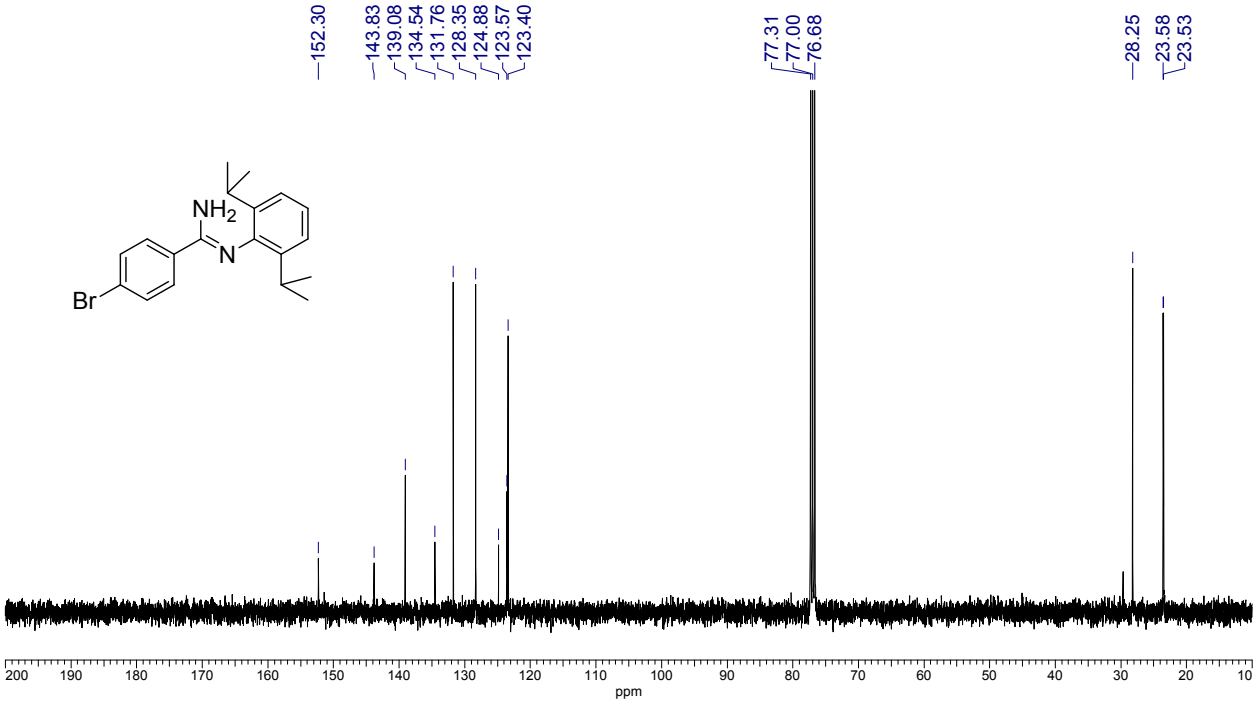


Figure FS9. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3d**.

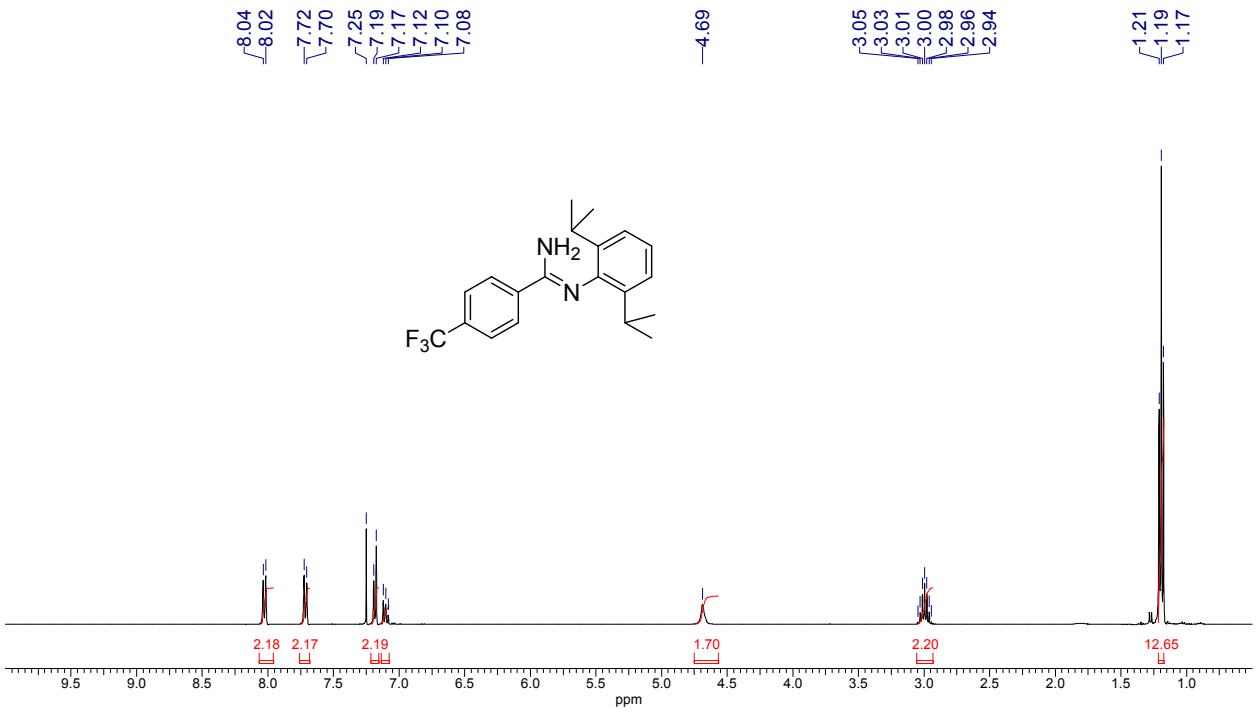


Figure FS10. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3e**.

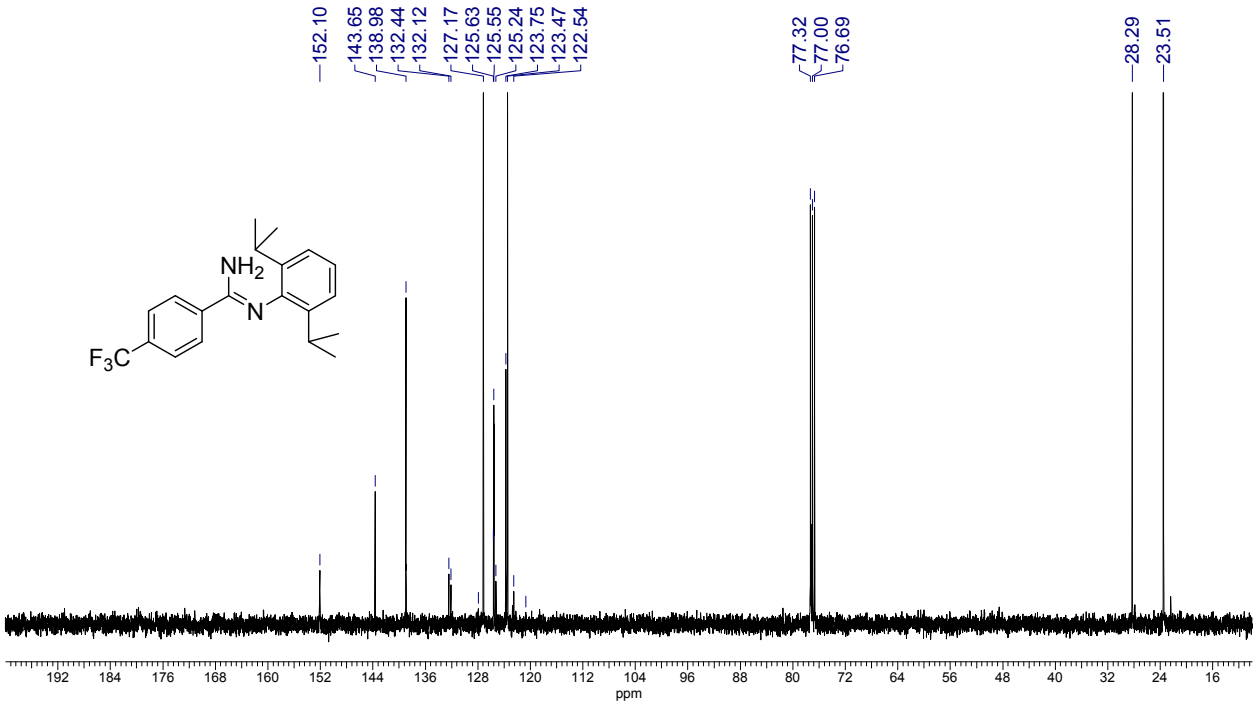


Figure FS11. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3e**.

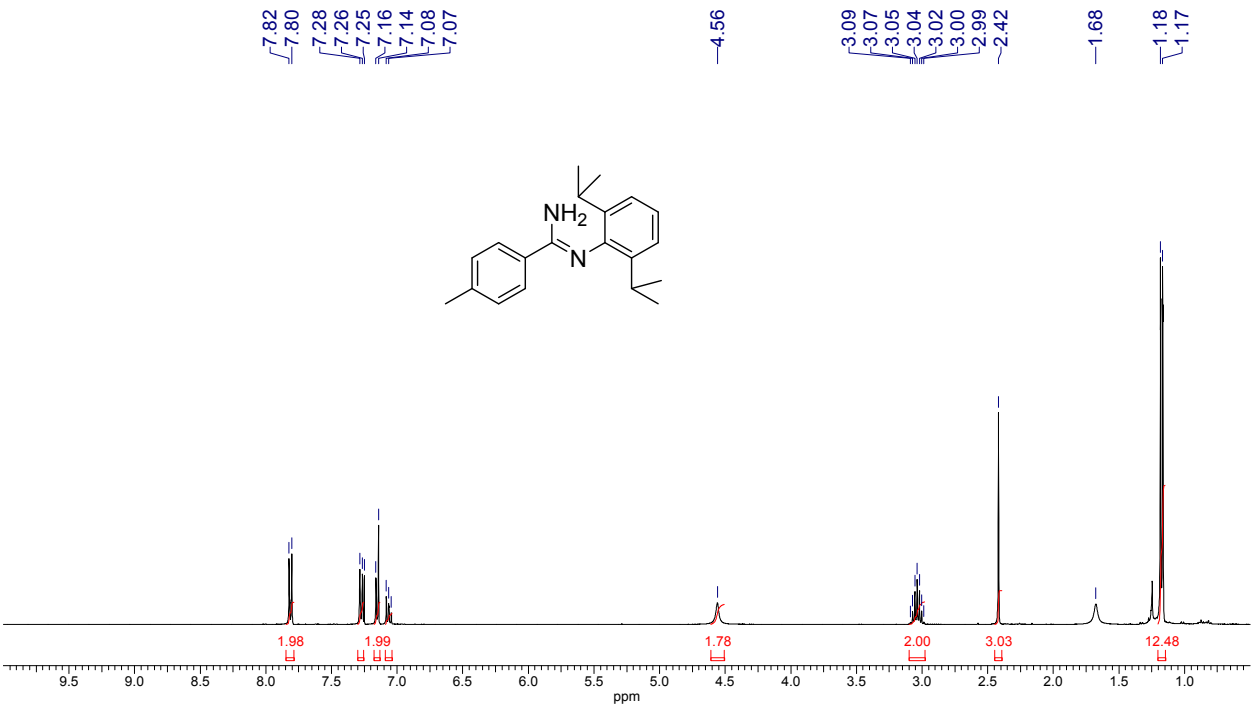


Figure FS12. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3f**.

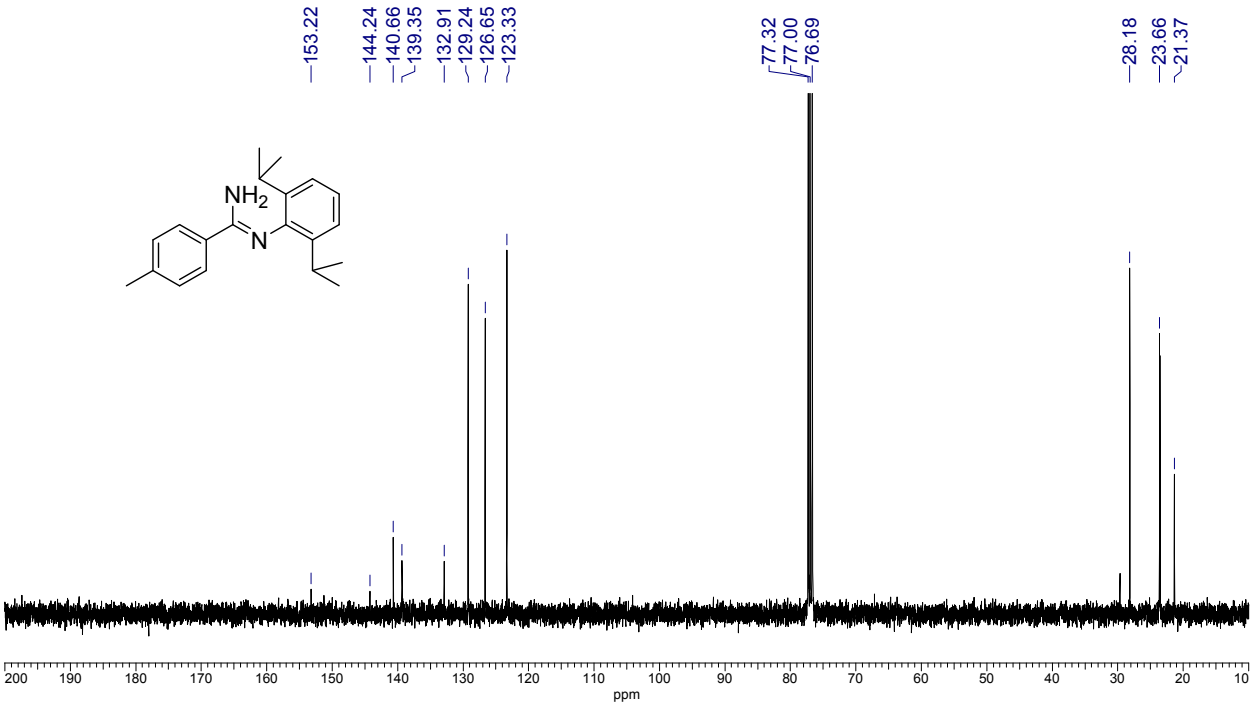


Figure FS13. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3f**.

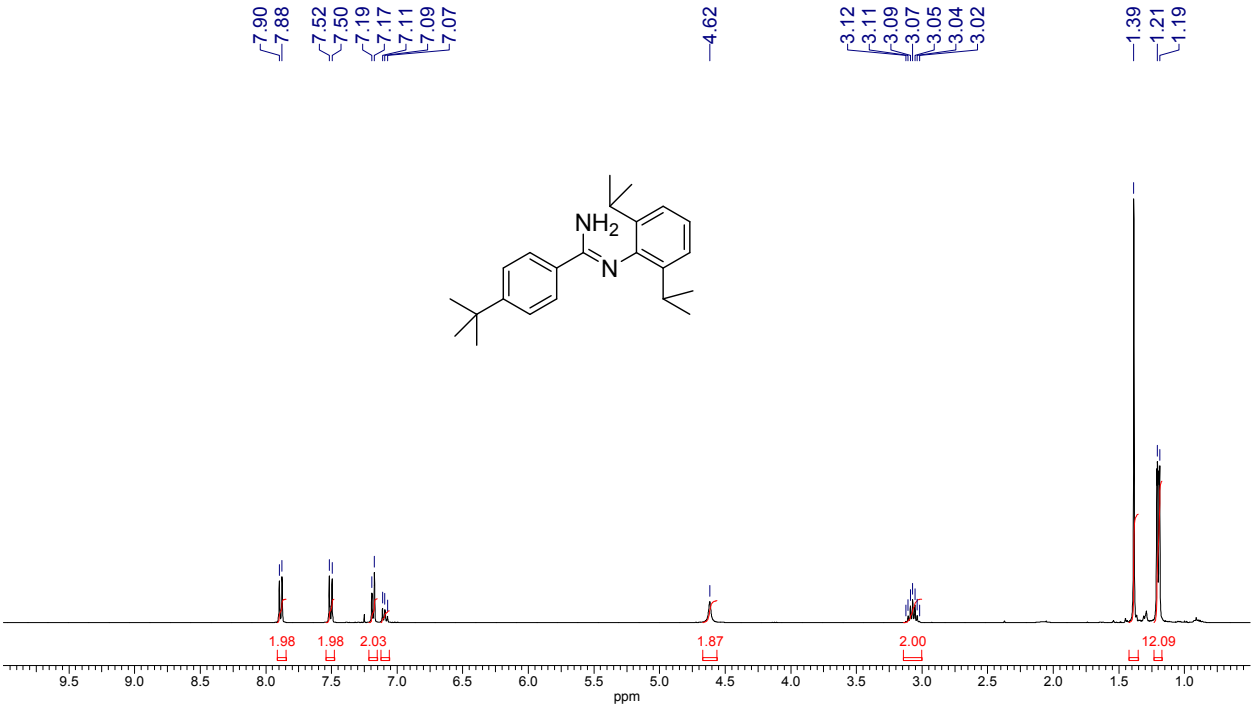


Figure FS14. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3g**.

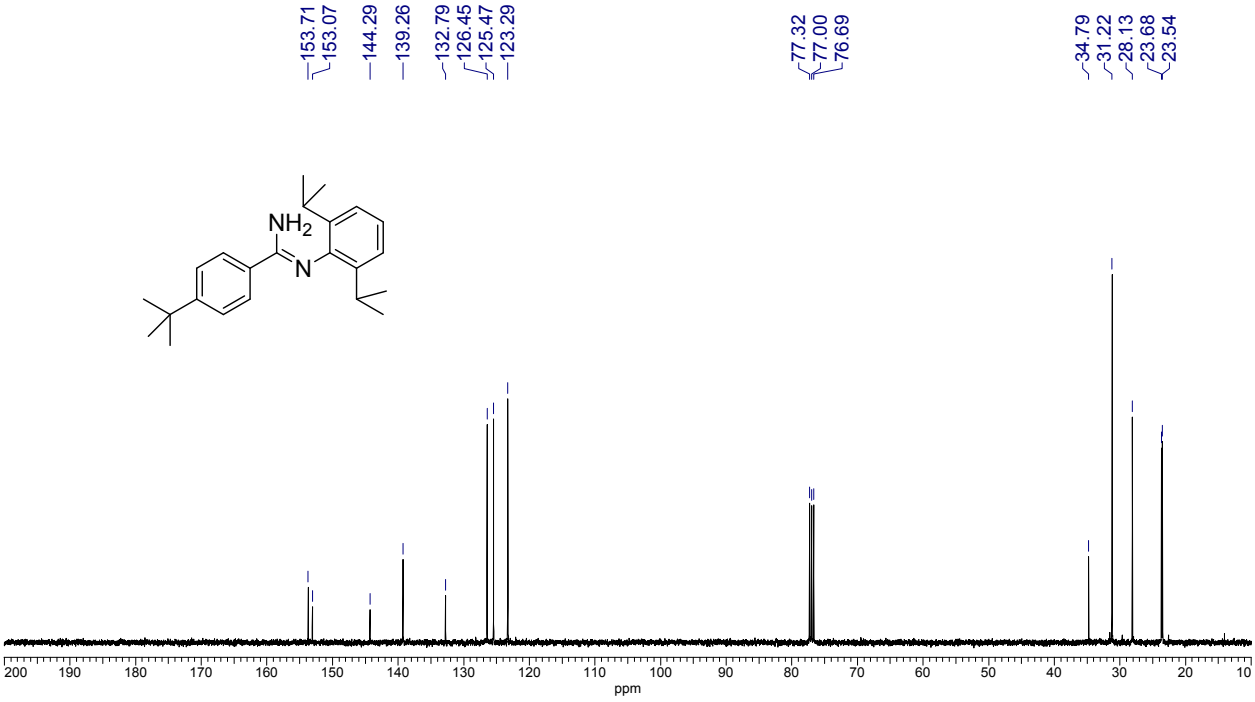


Figure FS15. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3g**.

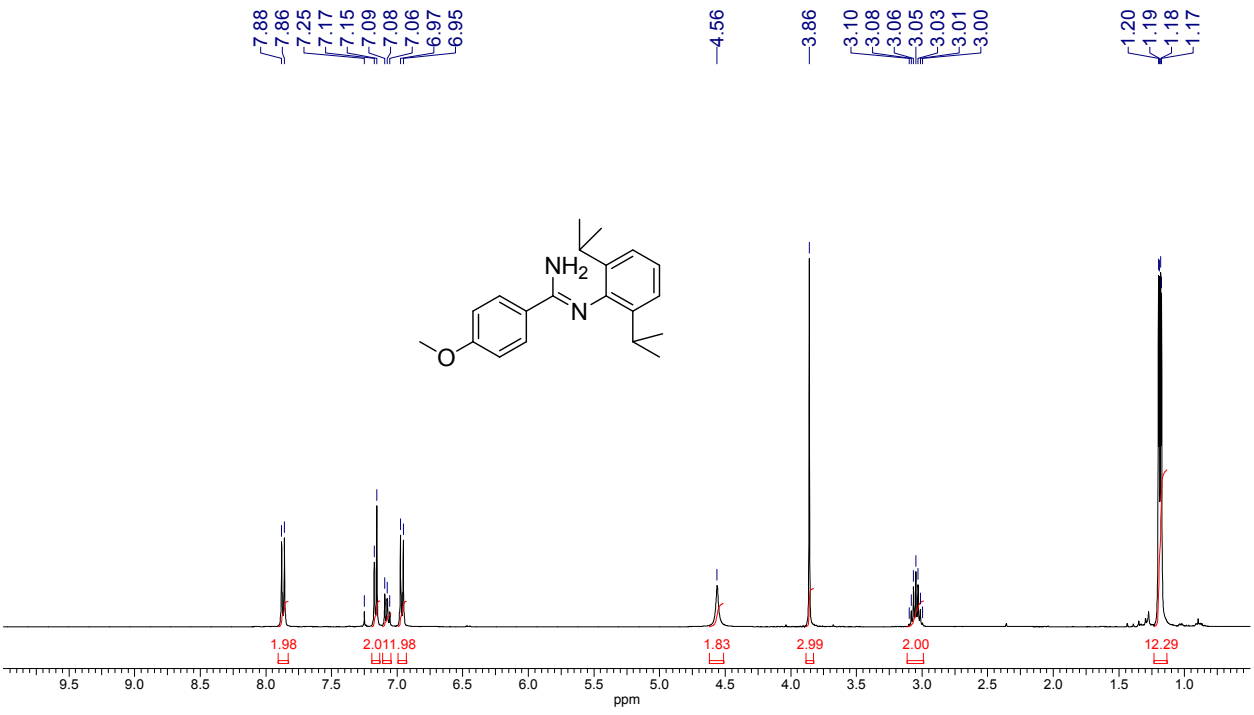


Figure FS16. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3h**.

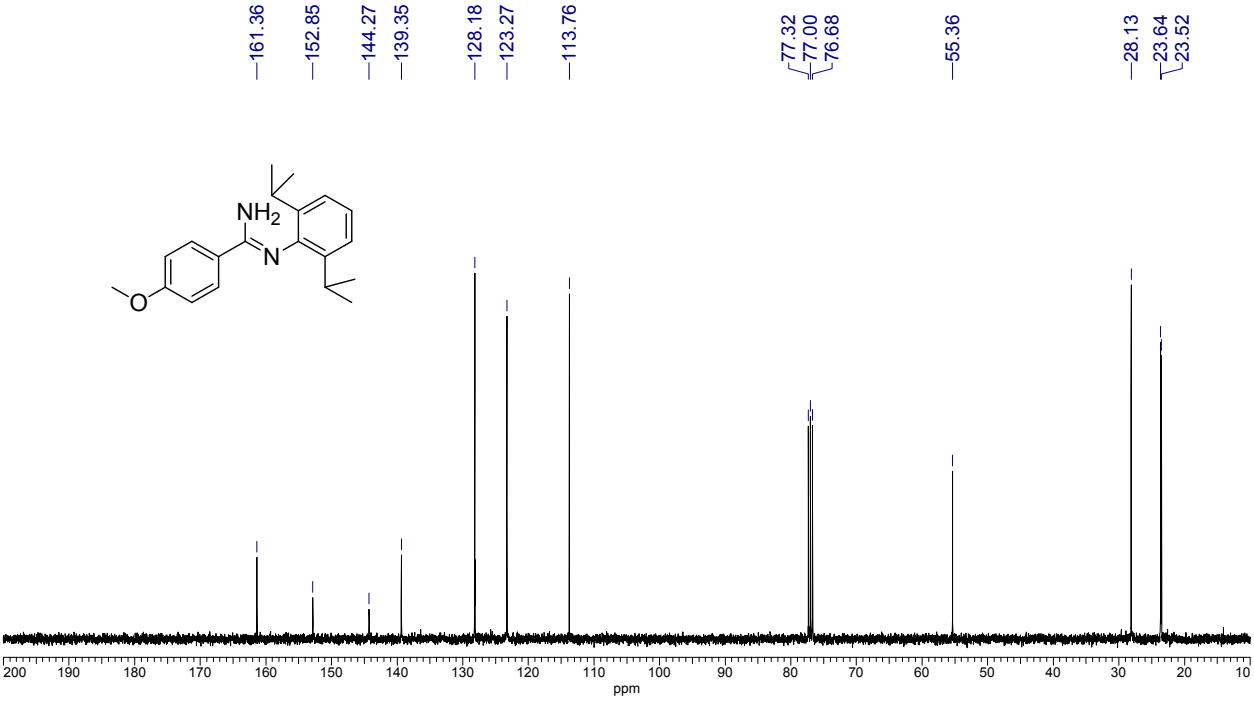


Figure FS17. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3h**.

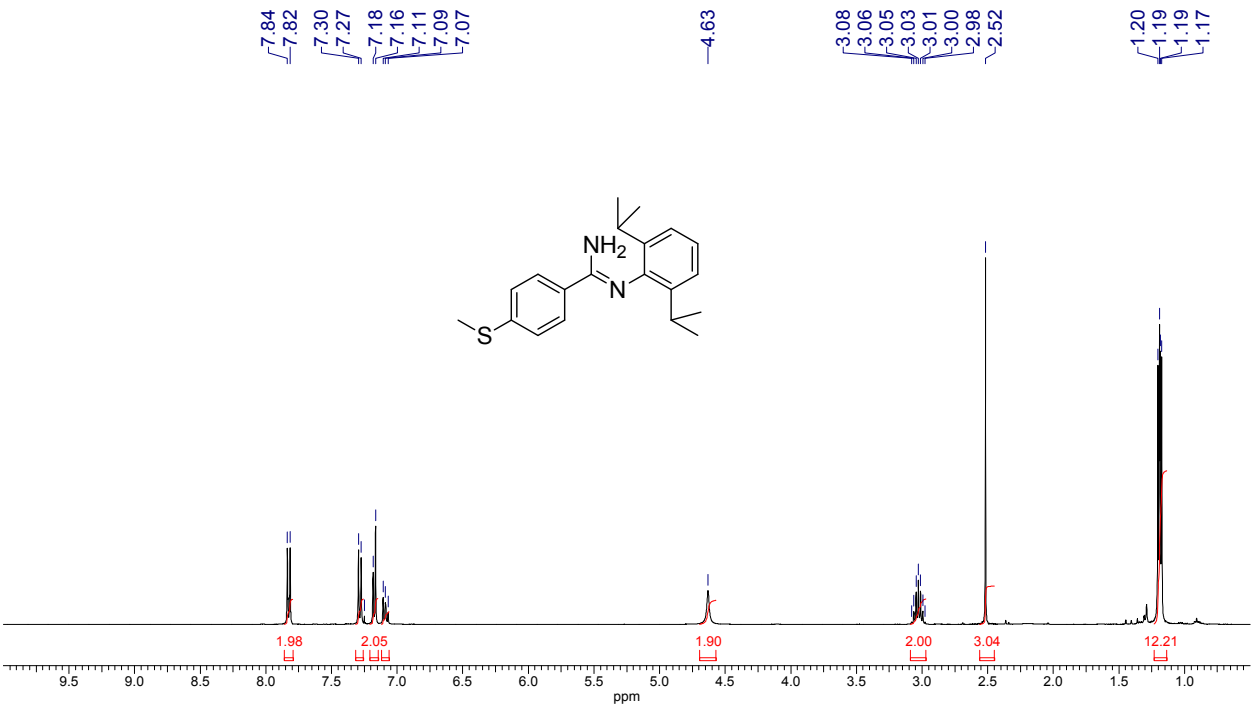


Figure FS18. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3i**.

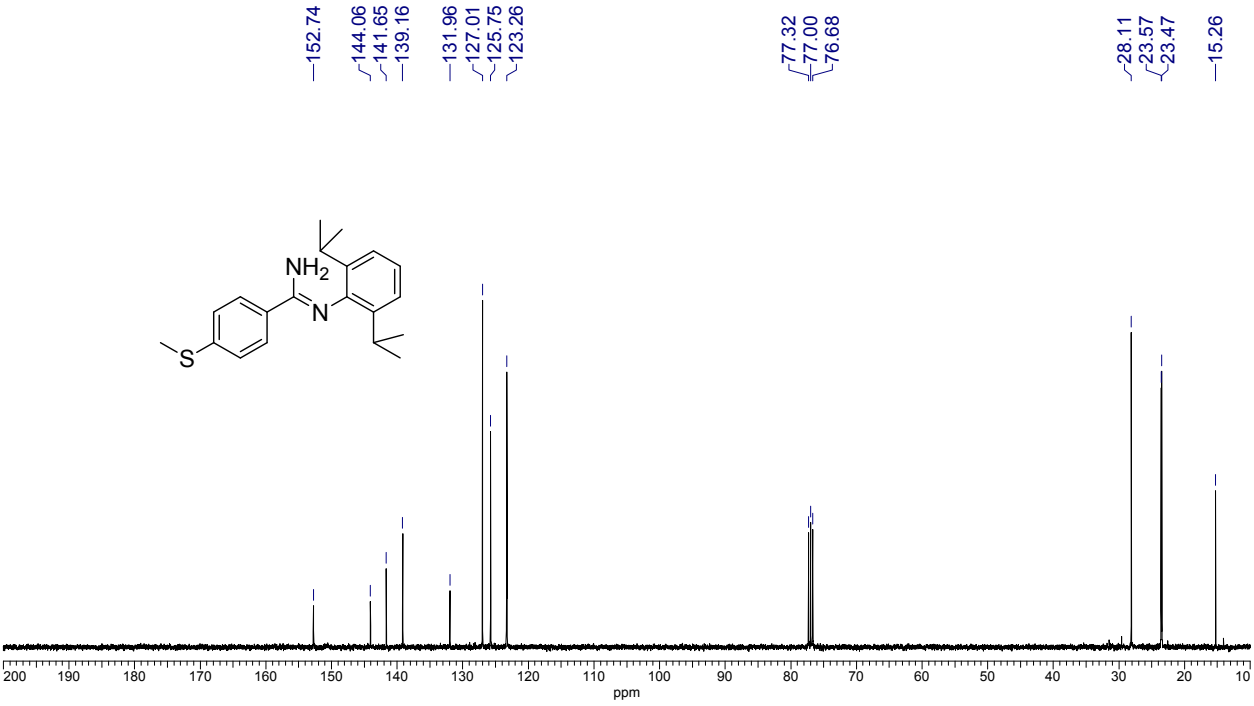


Figure FS19. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3i**.

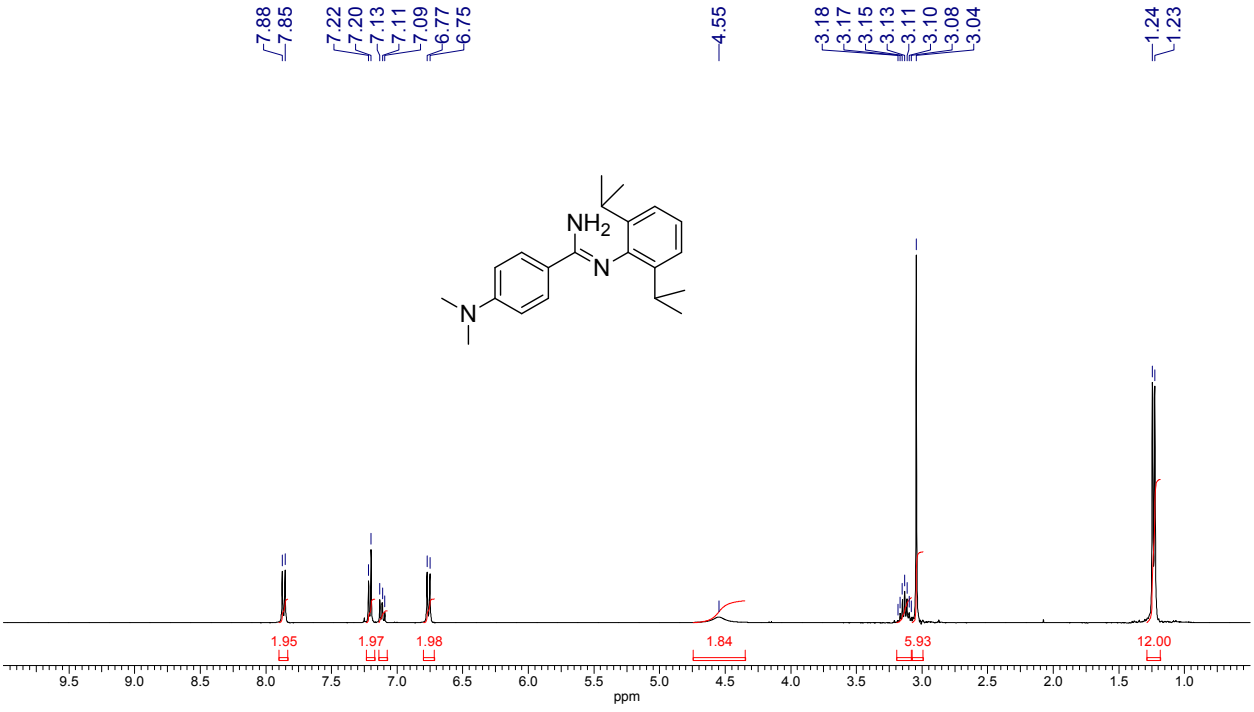


Figure FS20. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3j**.

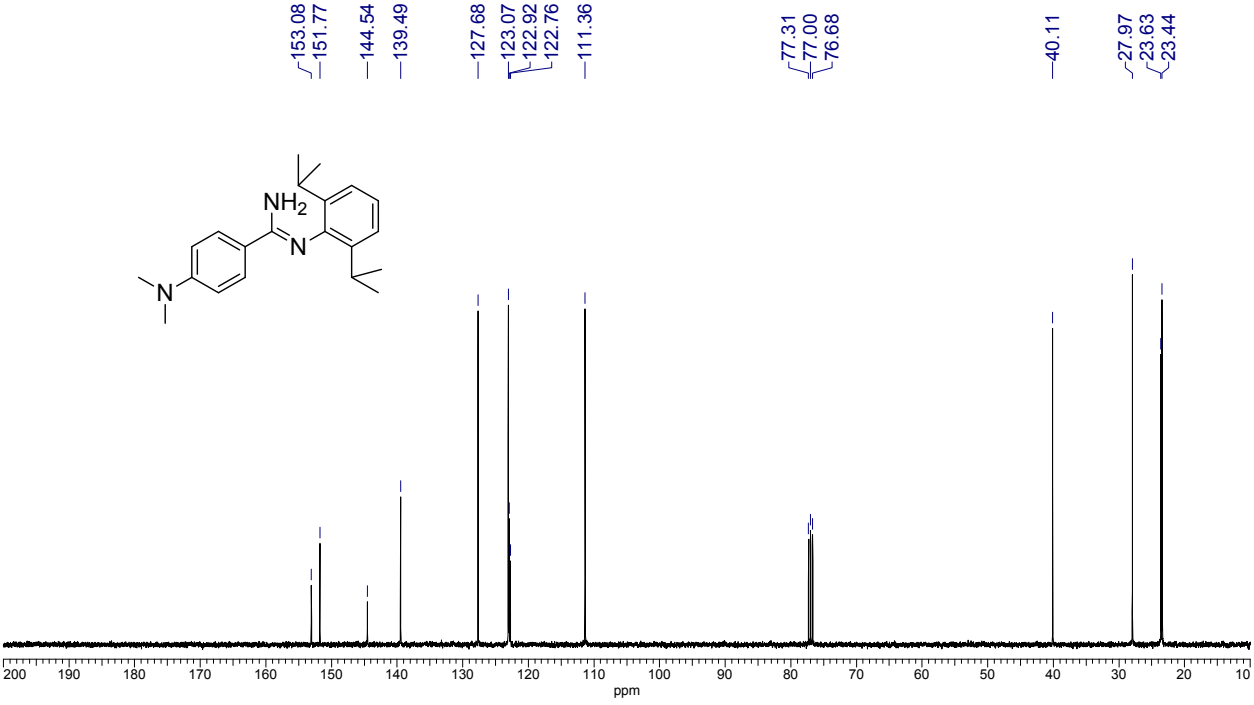


Figure FS21. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3j**.

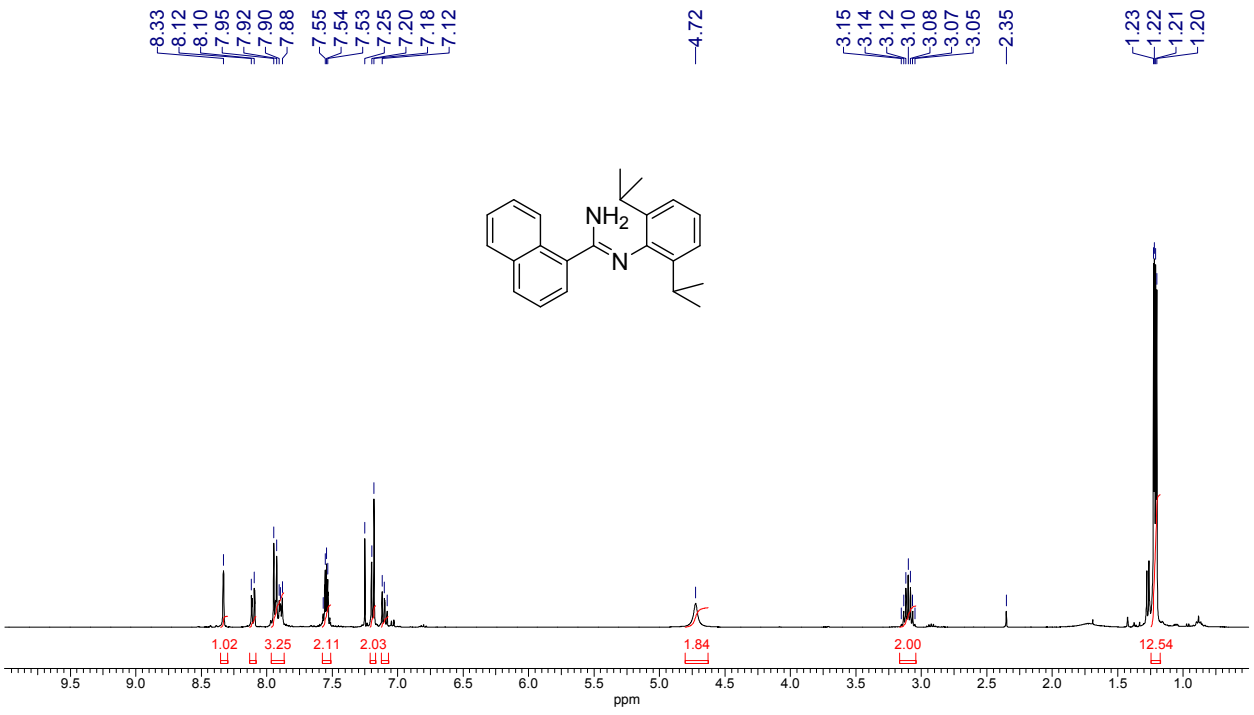


Figure FS22. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3k**.

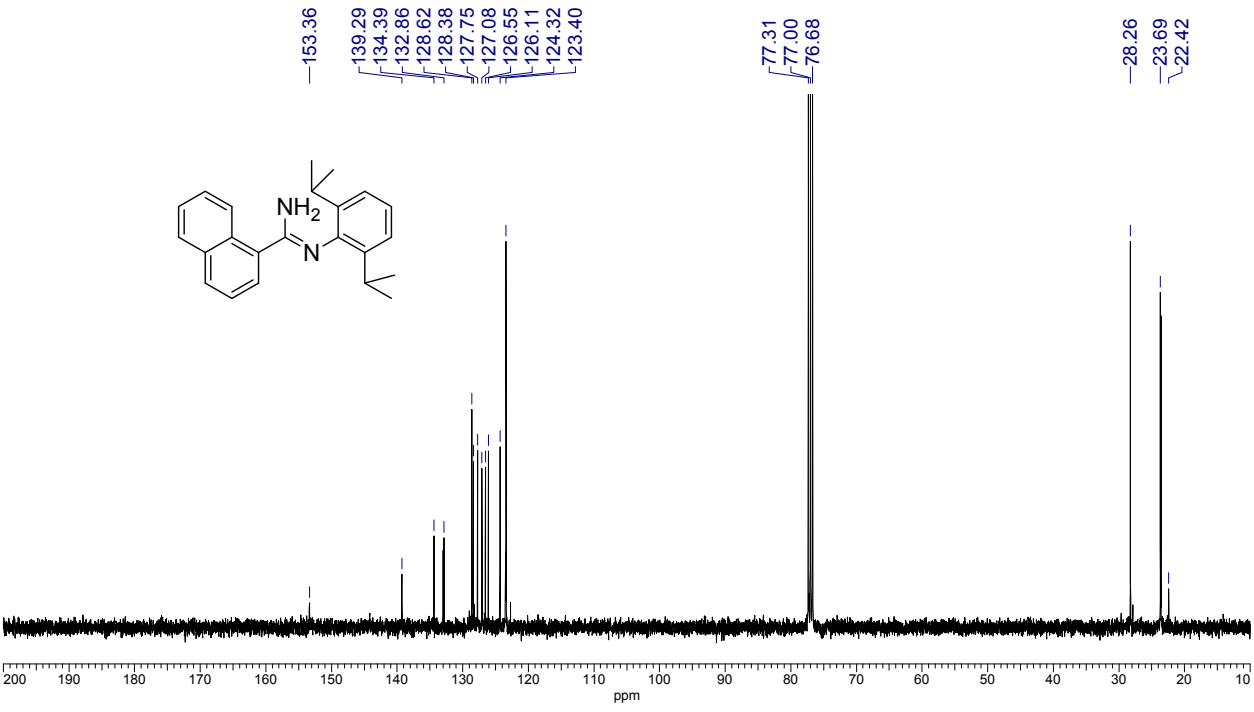


Figure FS23. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3k**.

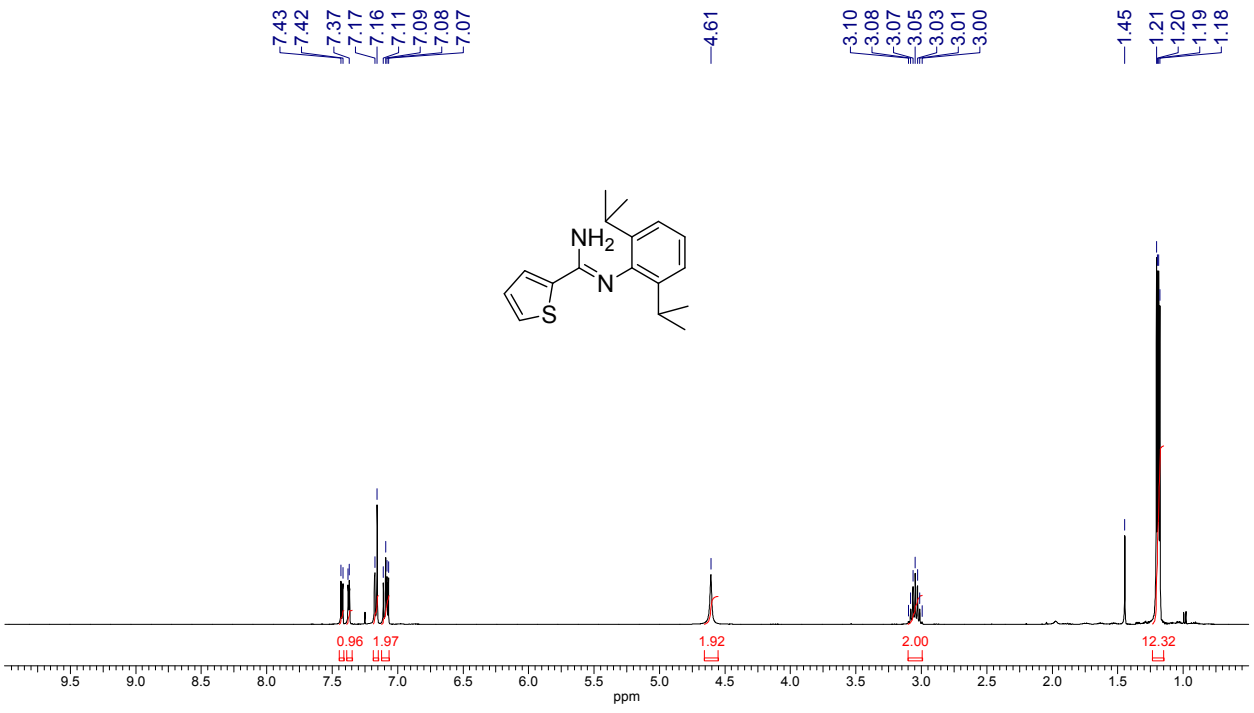


Figure FS24. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3l**.

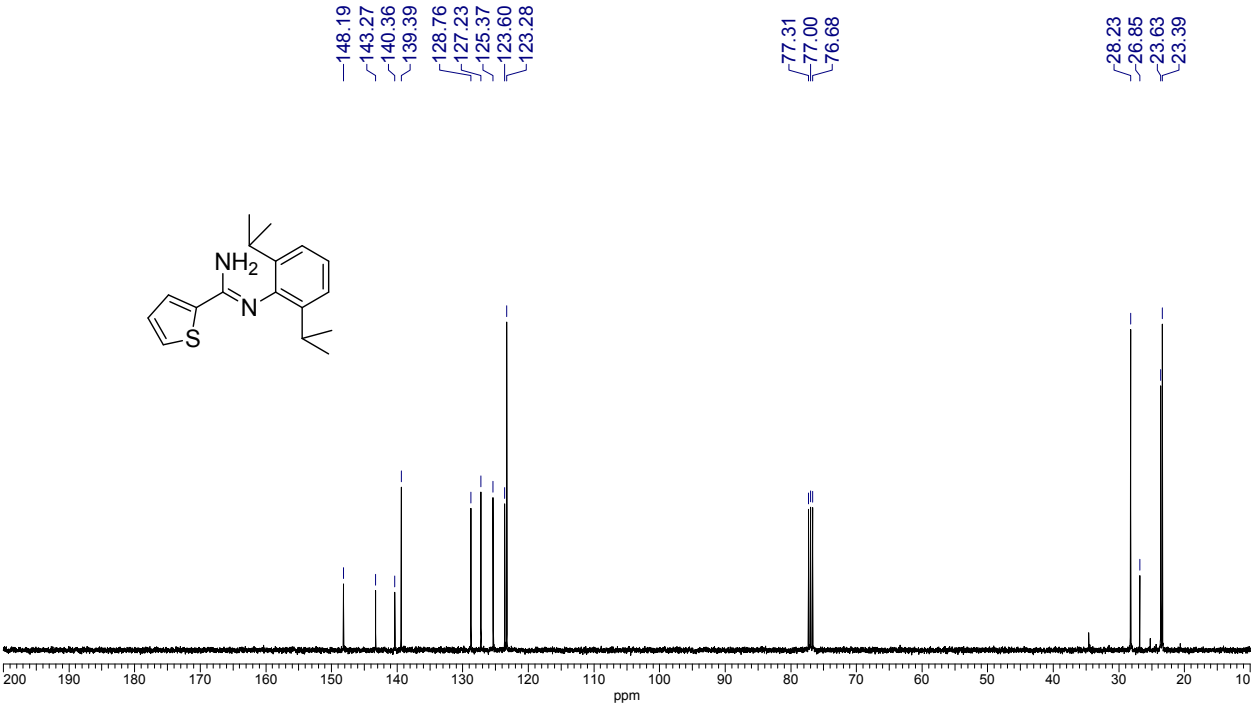


Figure FS25. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3l**.

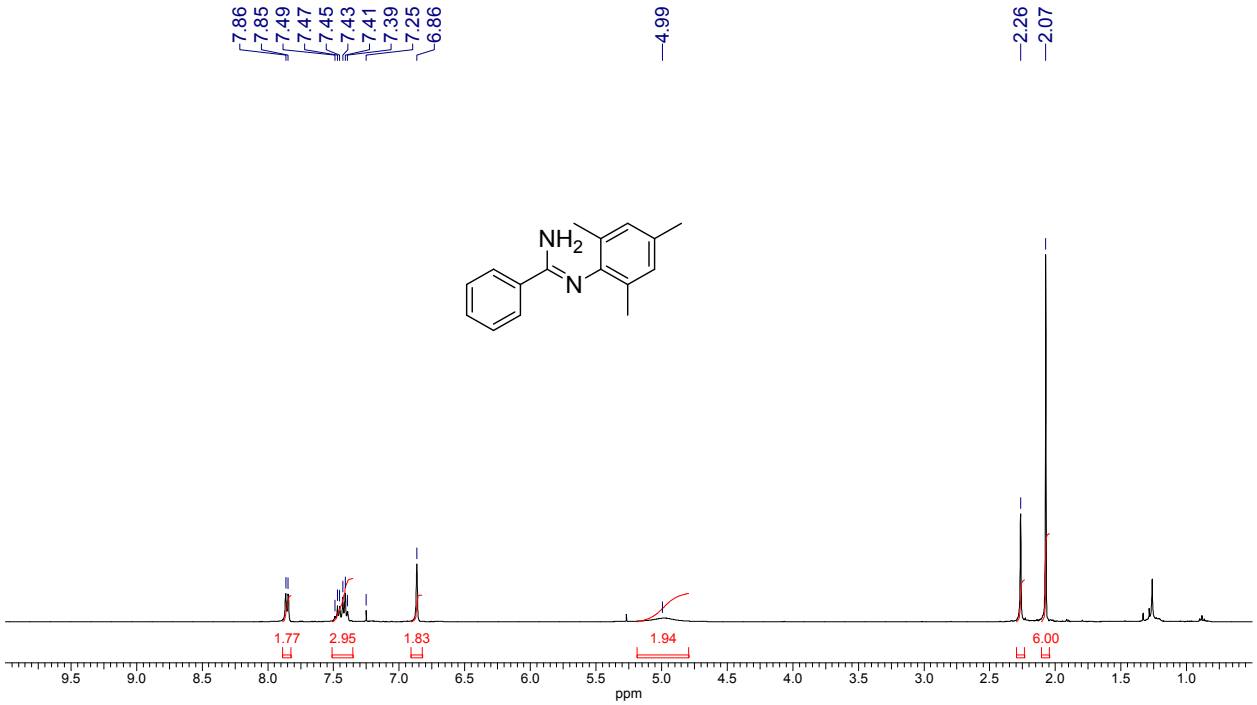


Figure FS26. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3m**.

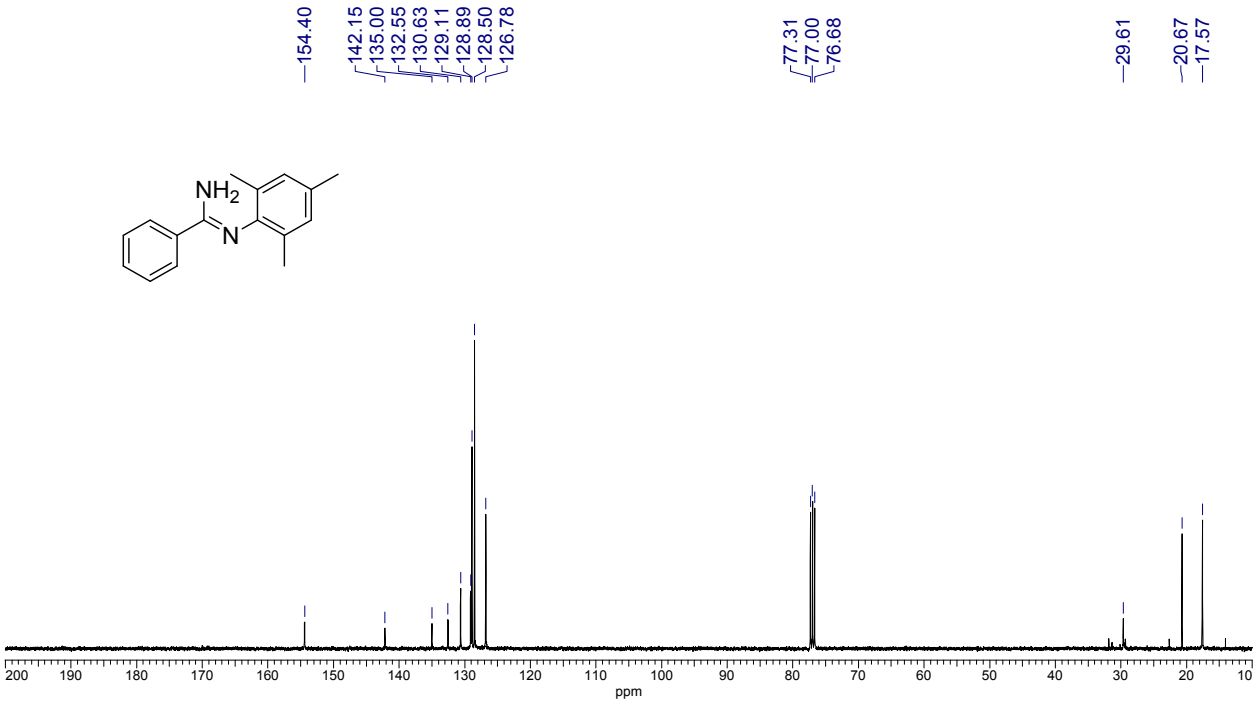


Figure FS27. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3m**.

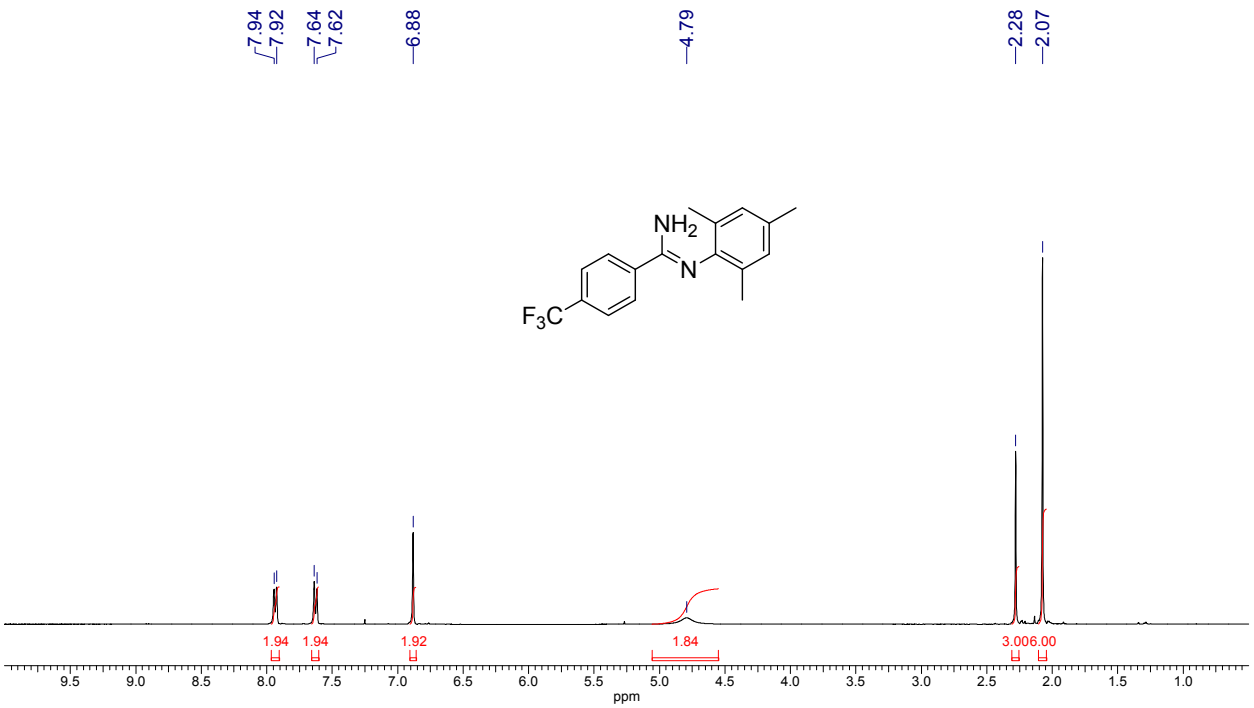


Figure FS28. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3n**.

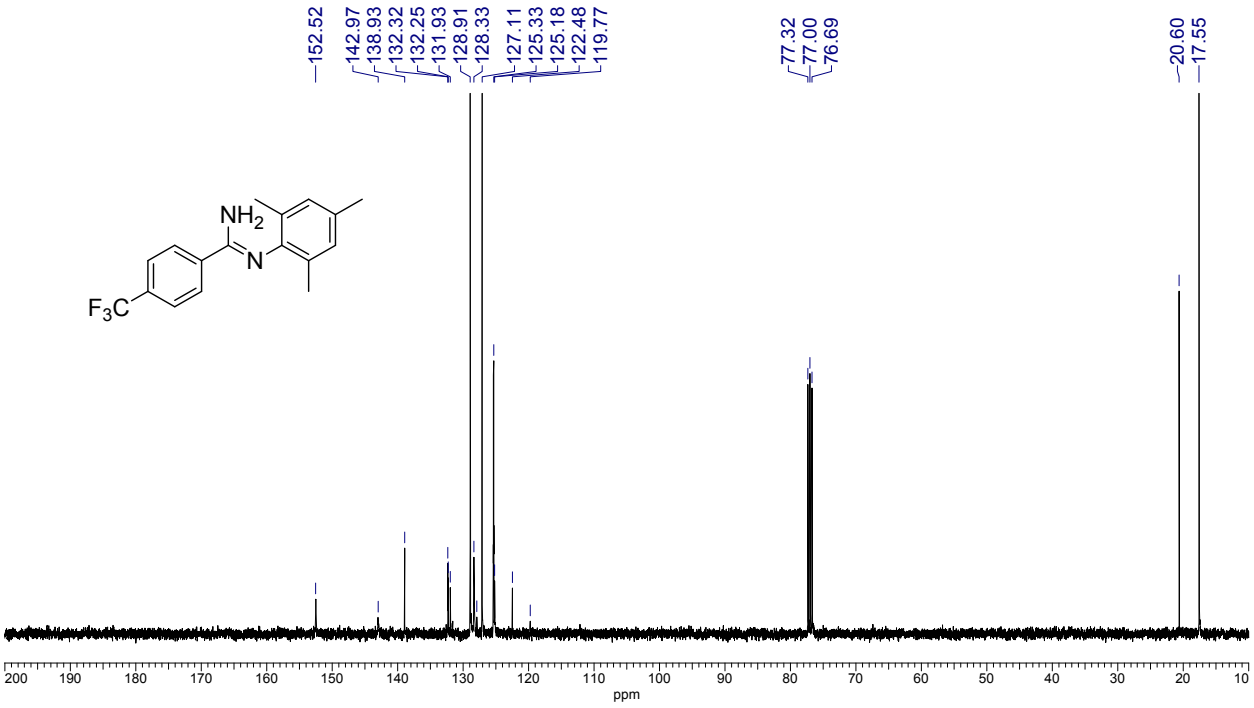


Figure FS29. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3n**.

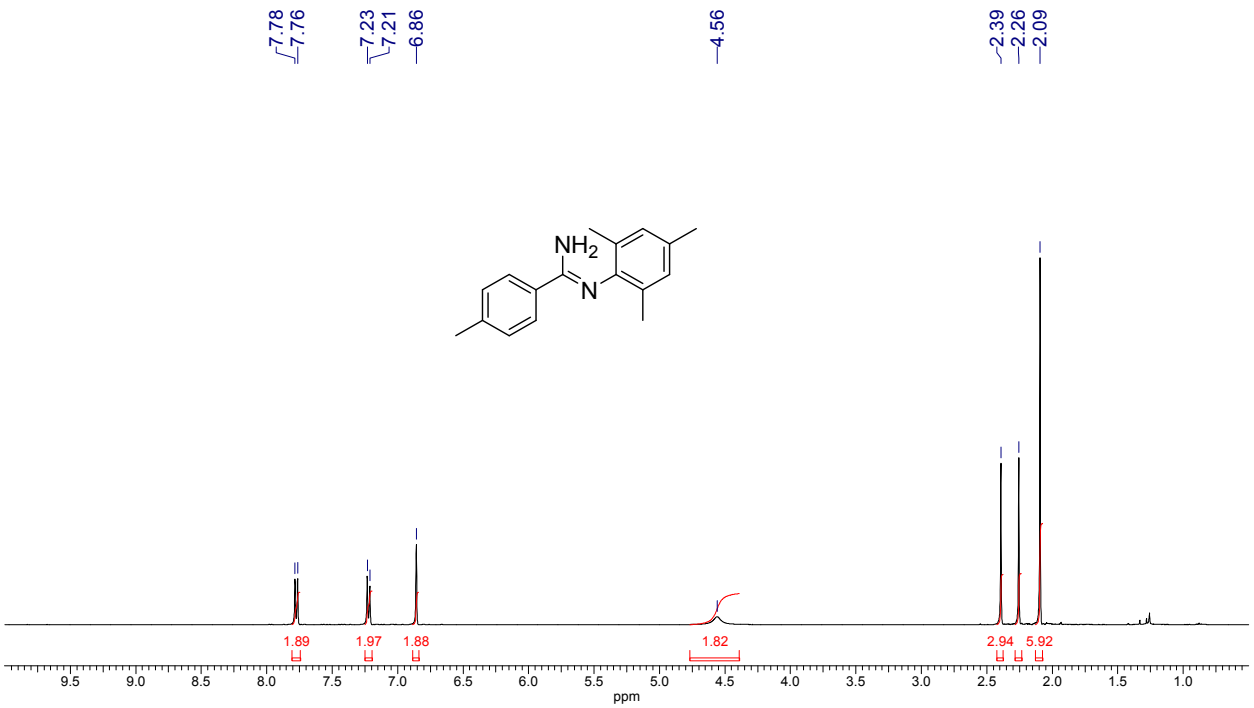


Figure FS30. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3o**.

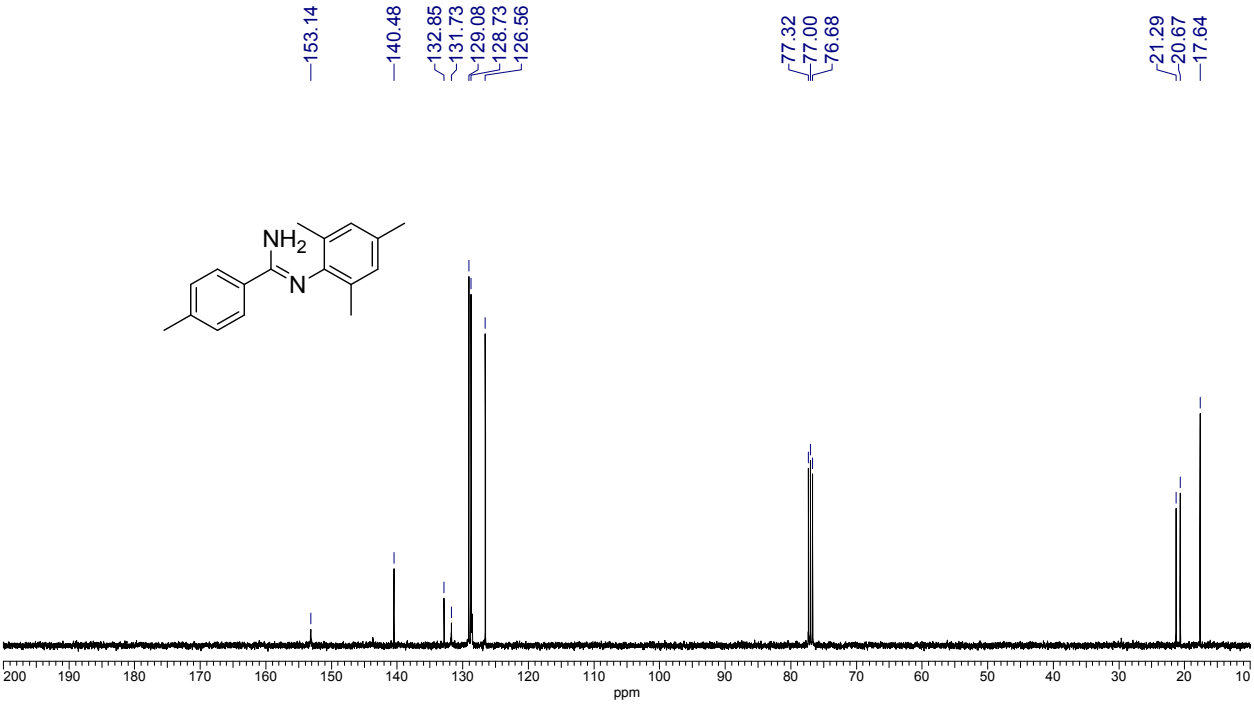


Figure FS31. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3o**.

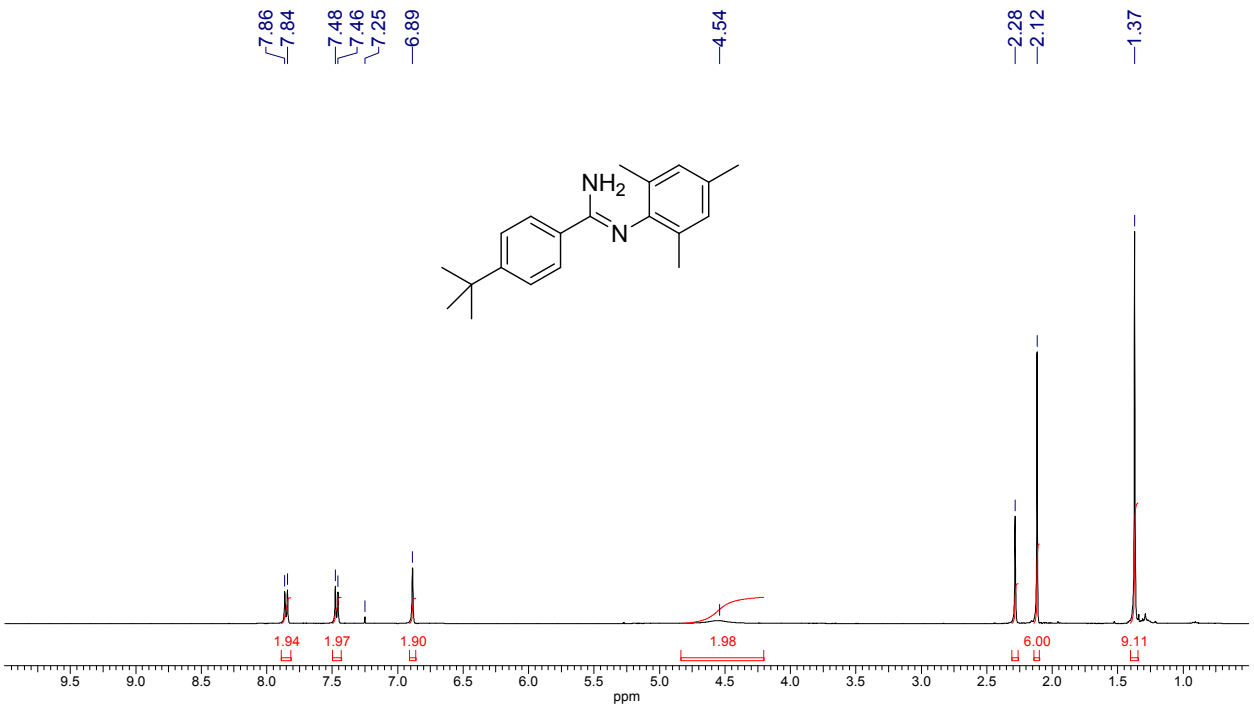


Figure FS32. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3p**.

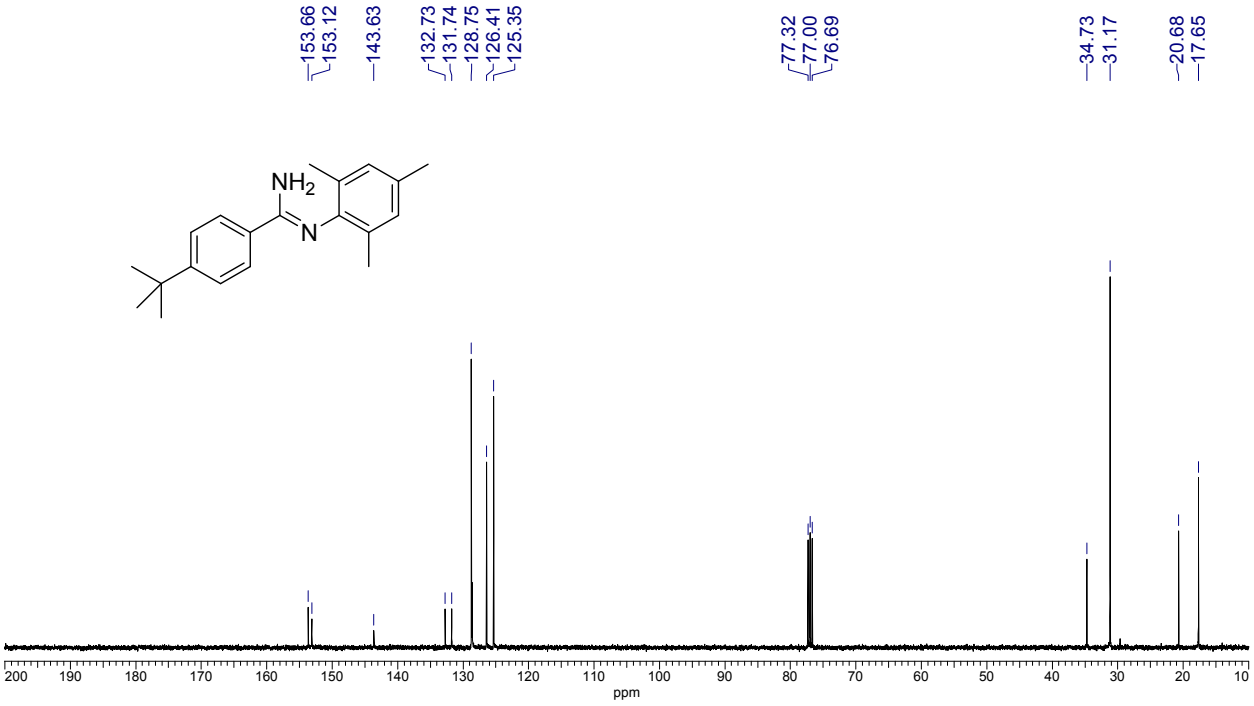


Figure FS33. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3p**.

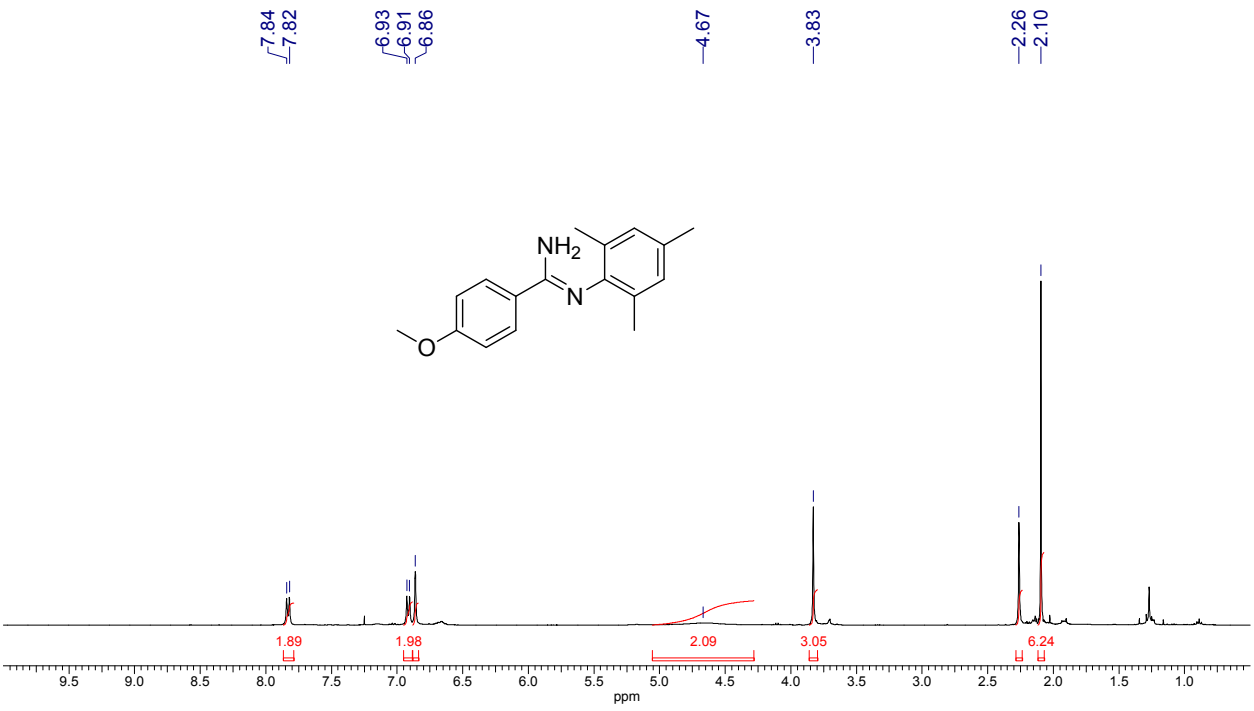


Figure FS34. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3q**.

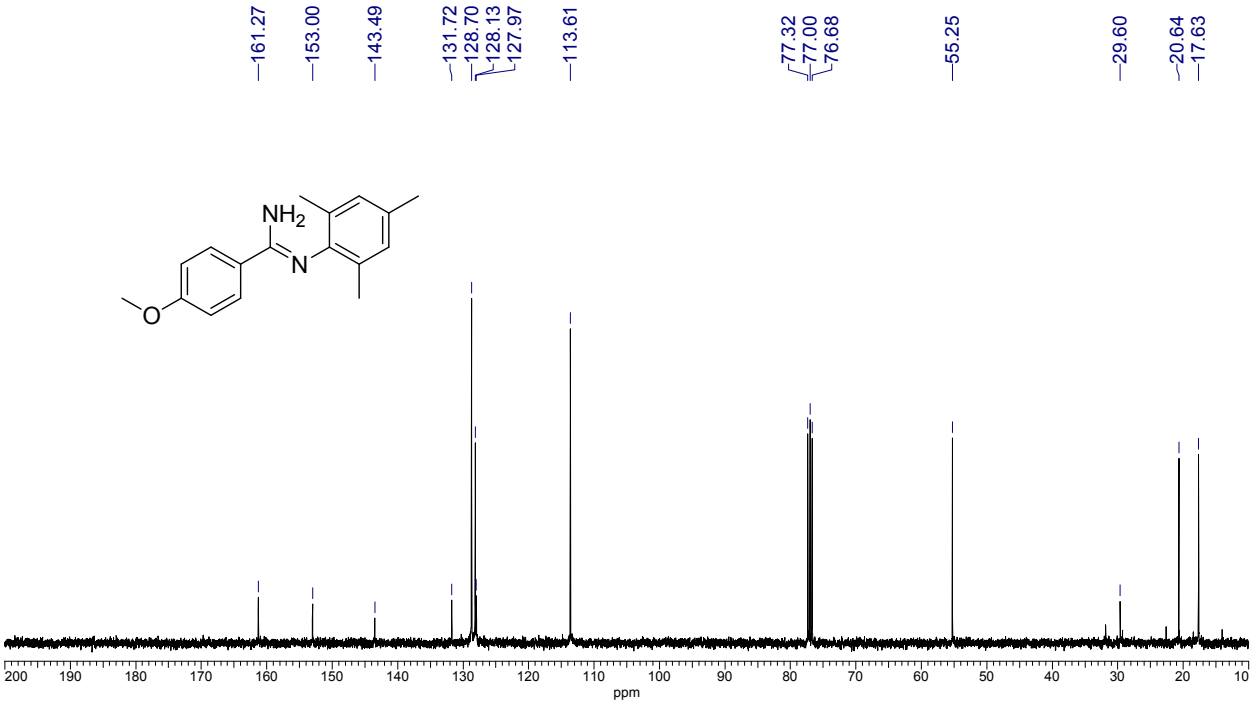


Figure FS35. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3q**.

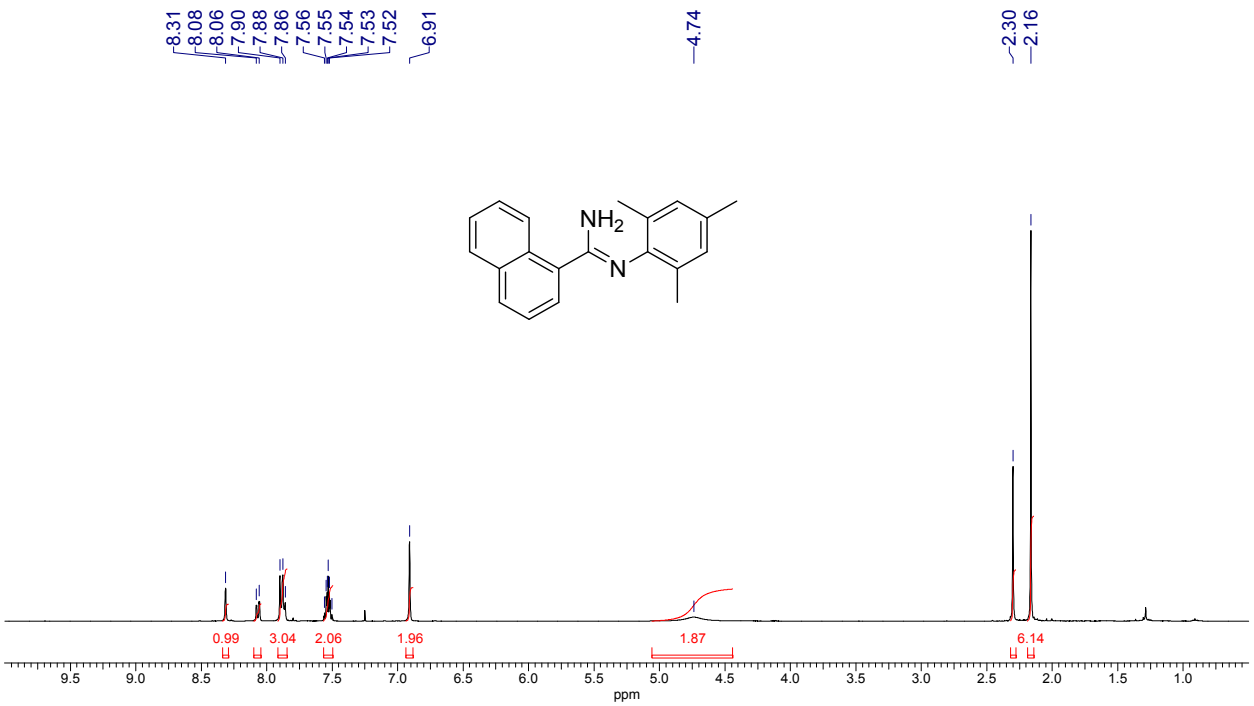


Figure FS36. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3r**.

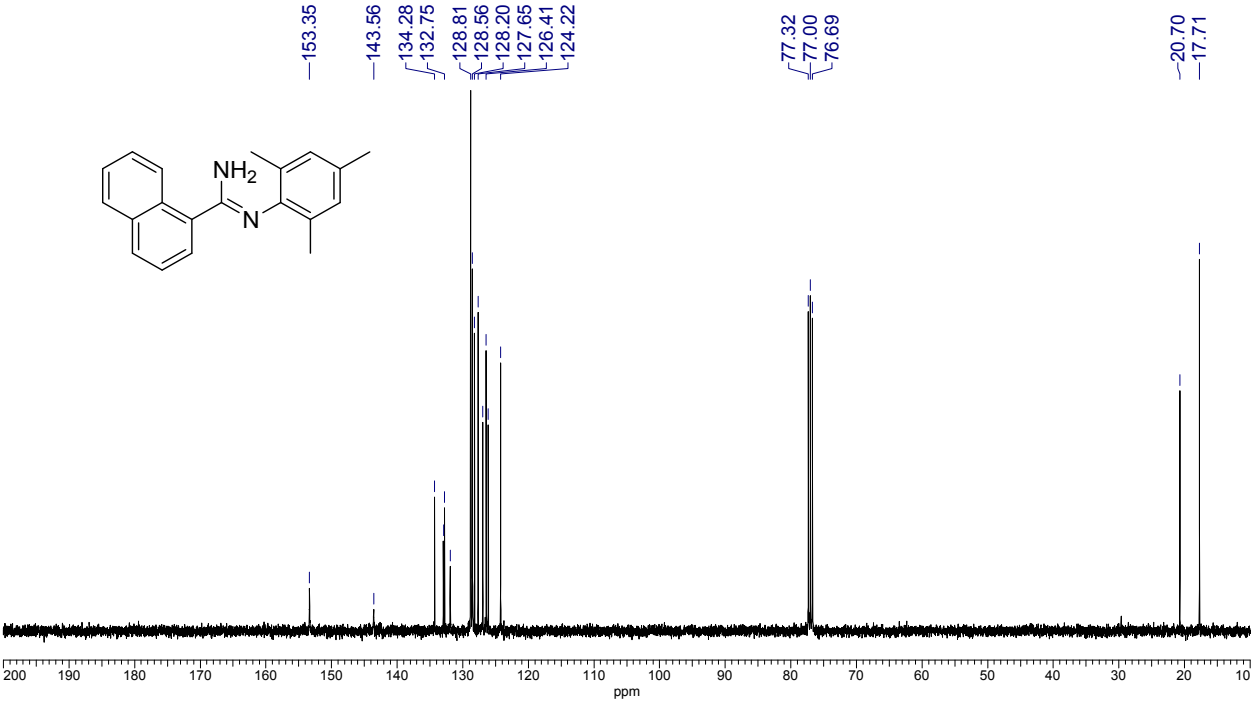


Figure FS37. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3r**.

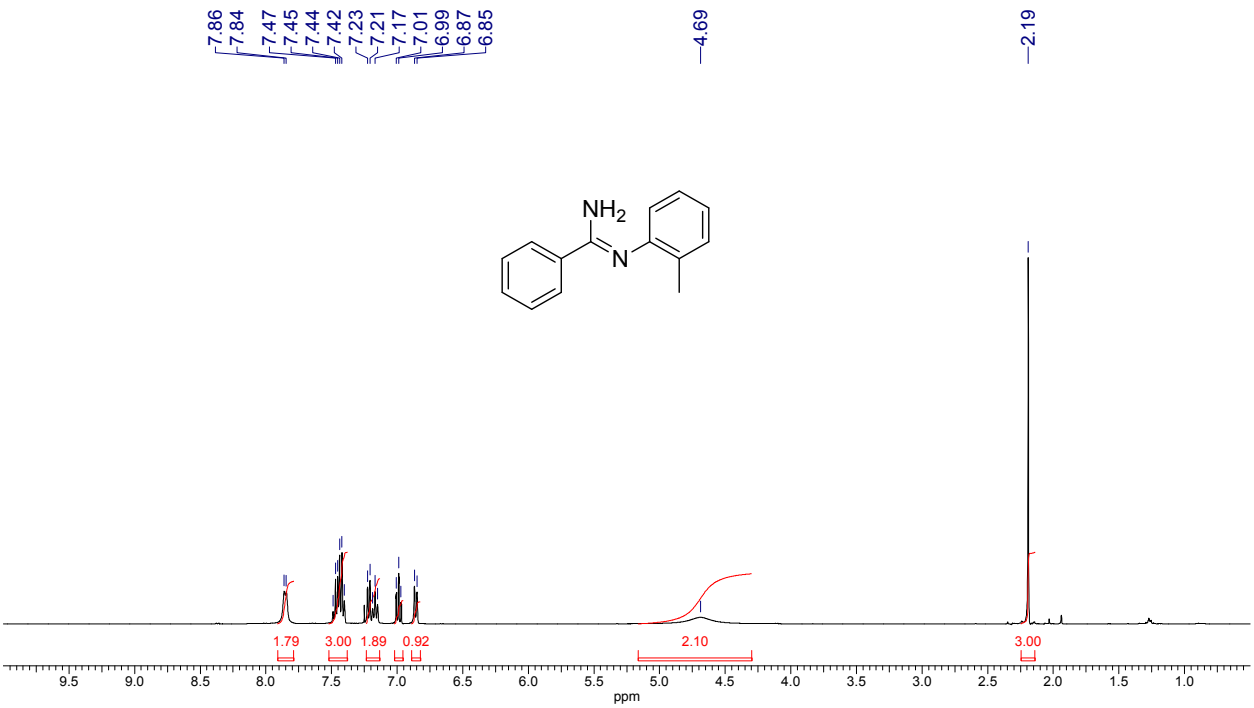


Figure FS38. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3s**.

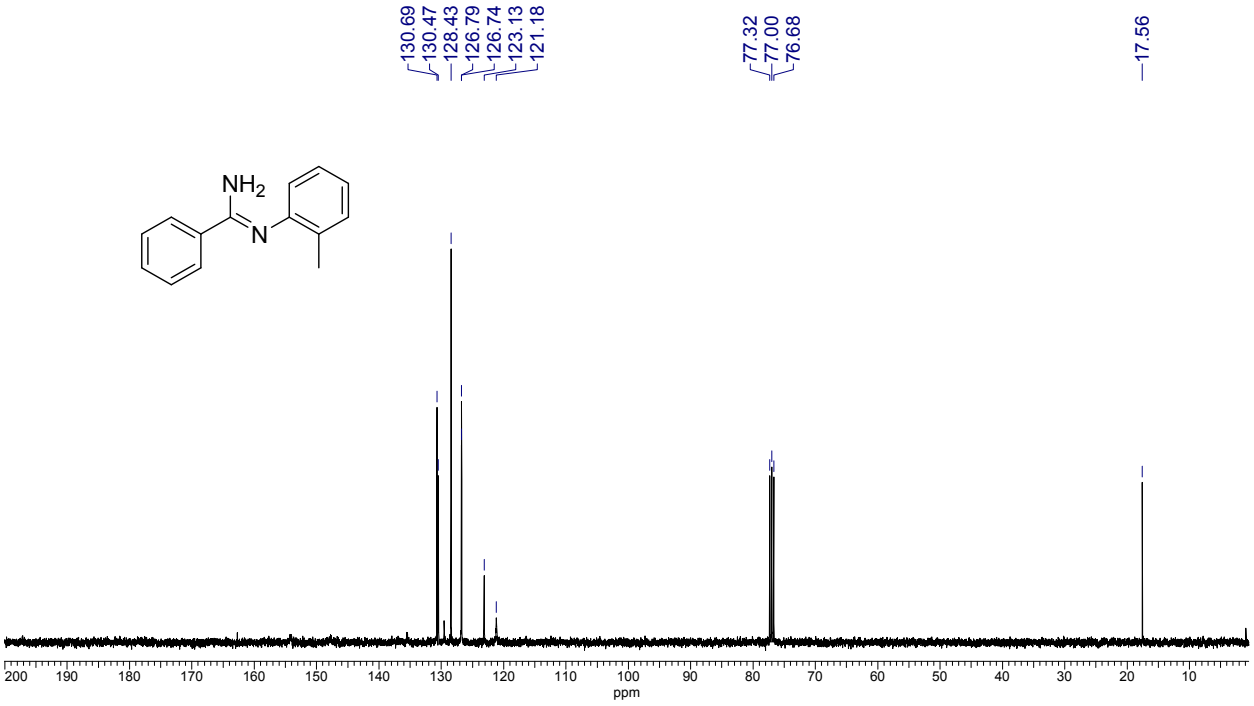


Figure FS39. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3s**.

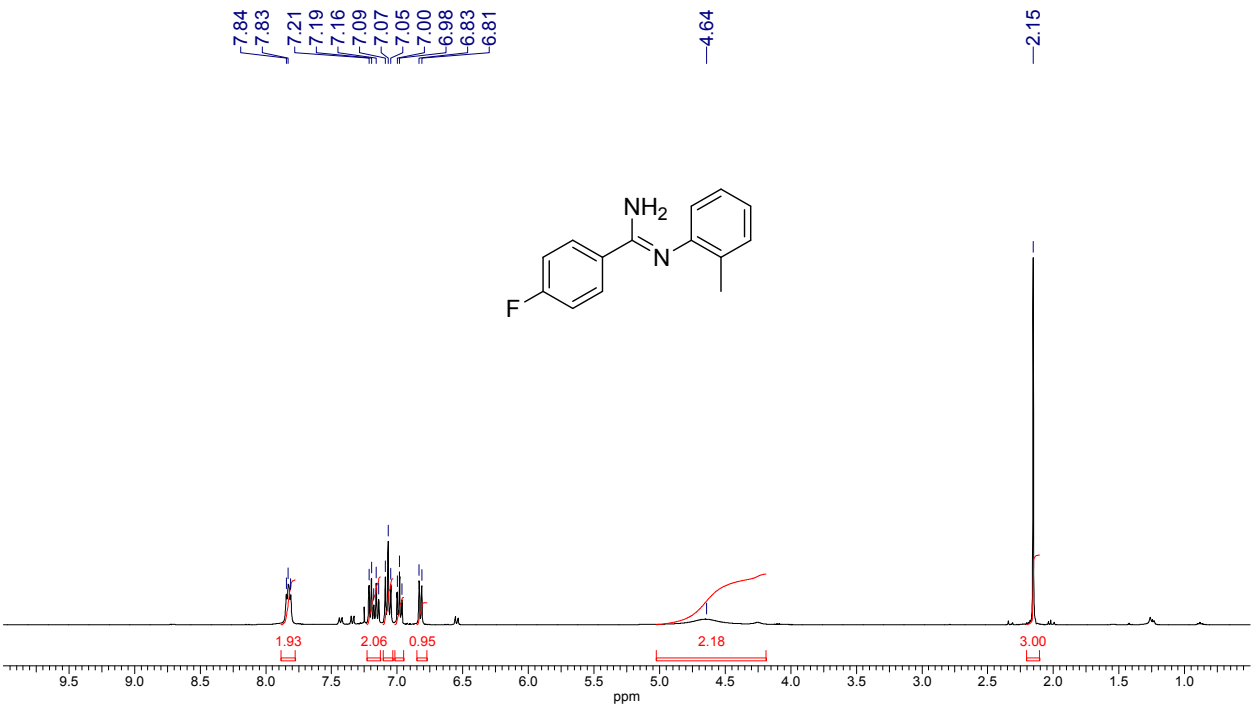


Figure FS40. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3t**.

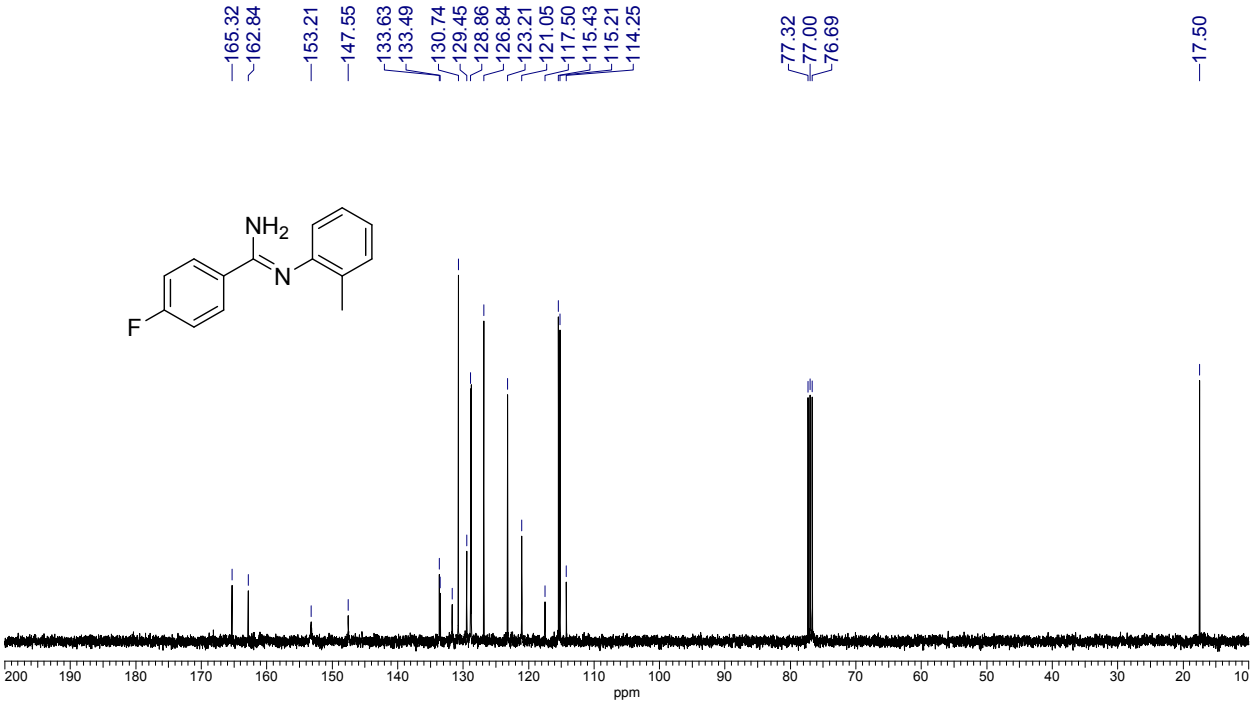


Figure FS41. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3t**.

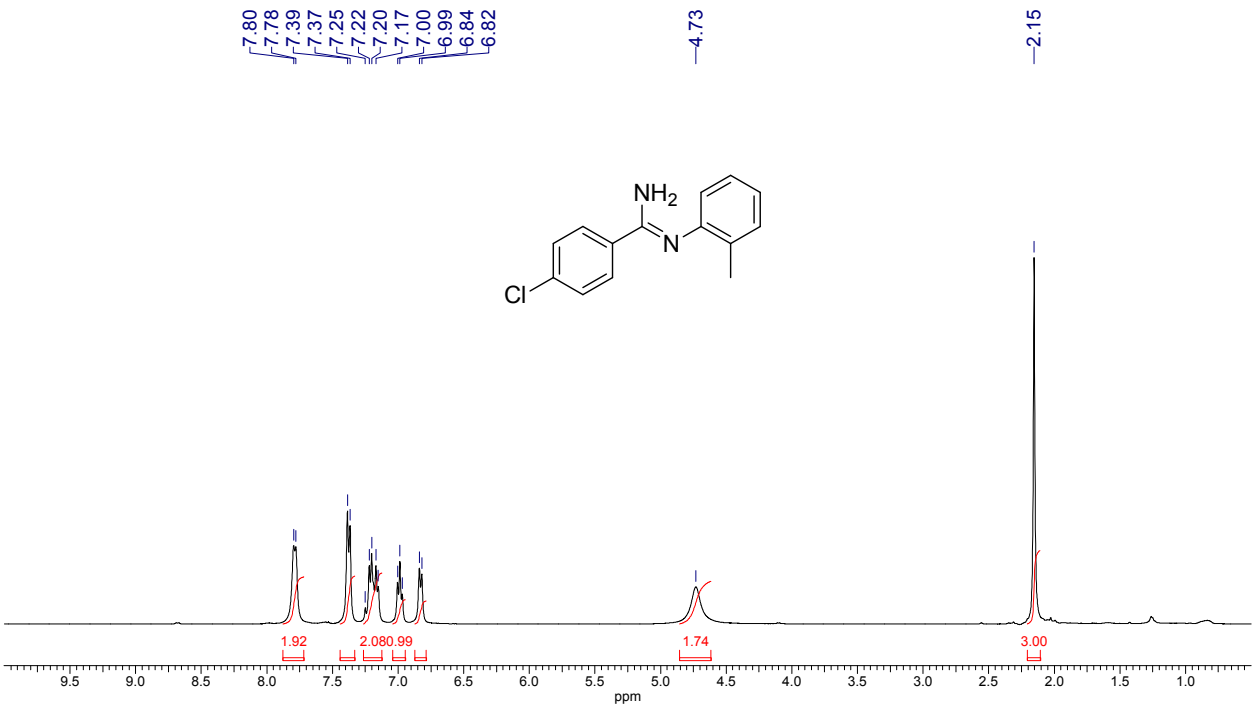


Figure FS42. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3u**.

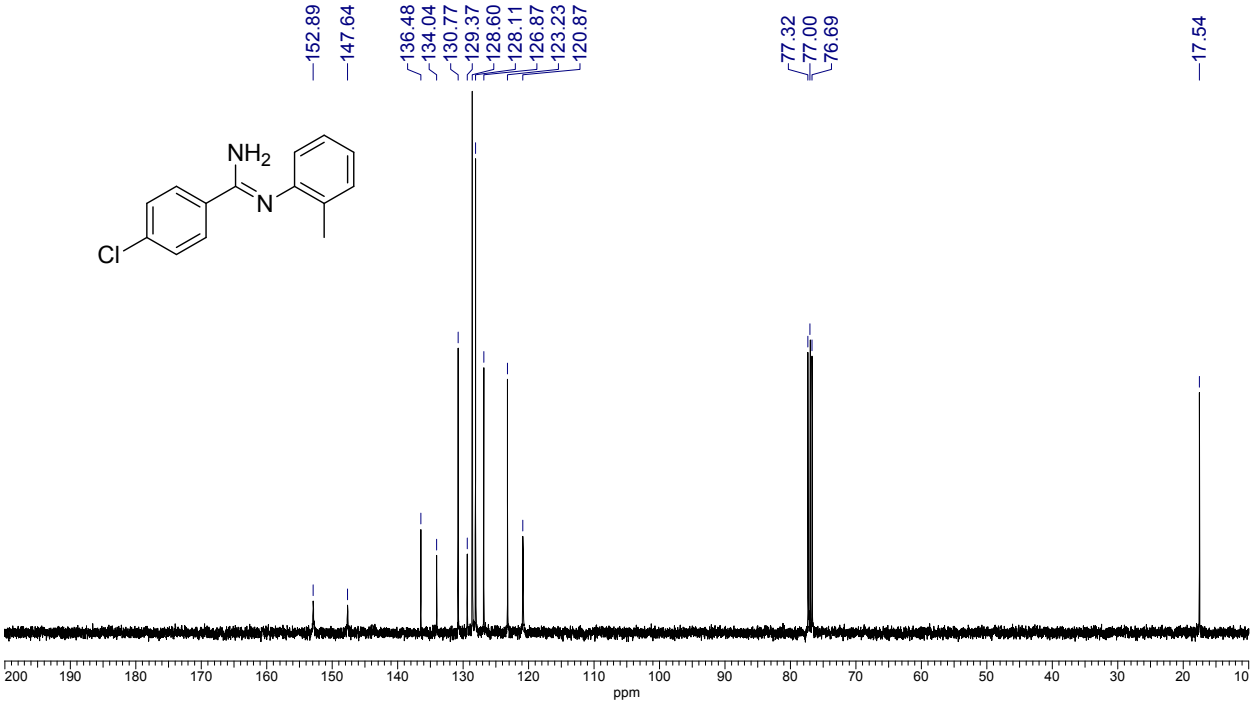


Figure FS43. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3u**.

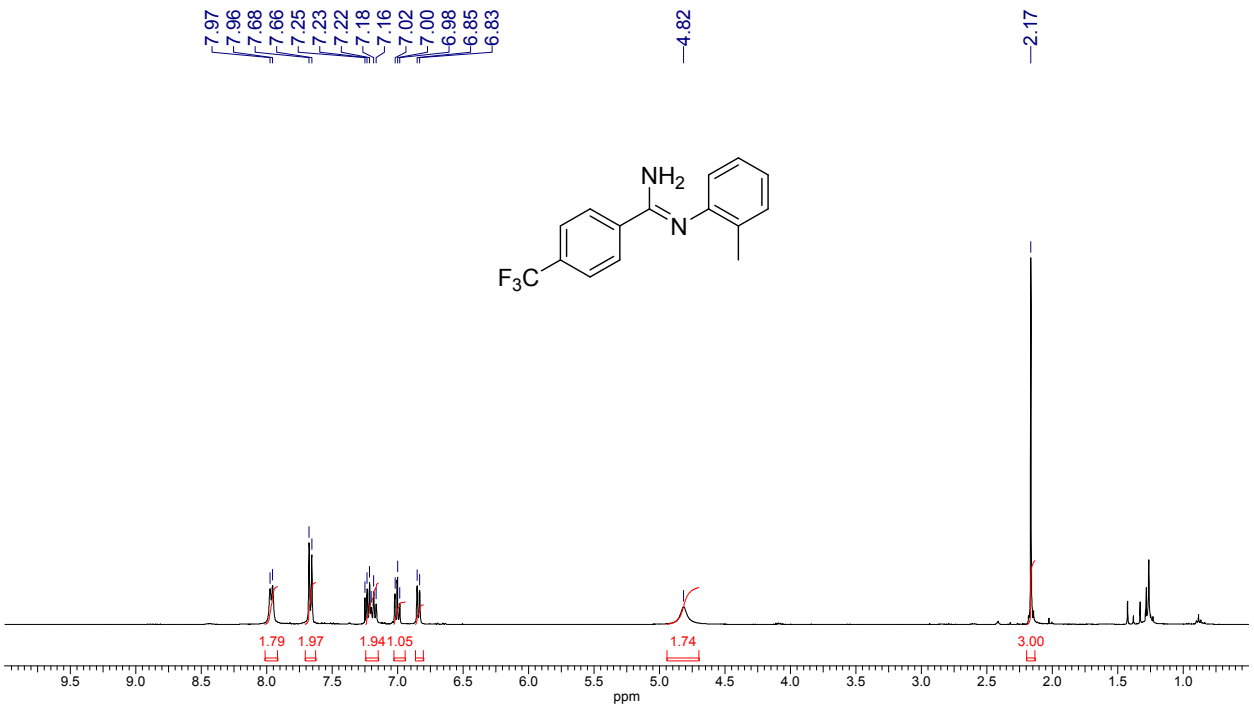


Figure FS44. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3v**.

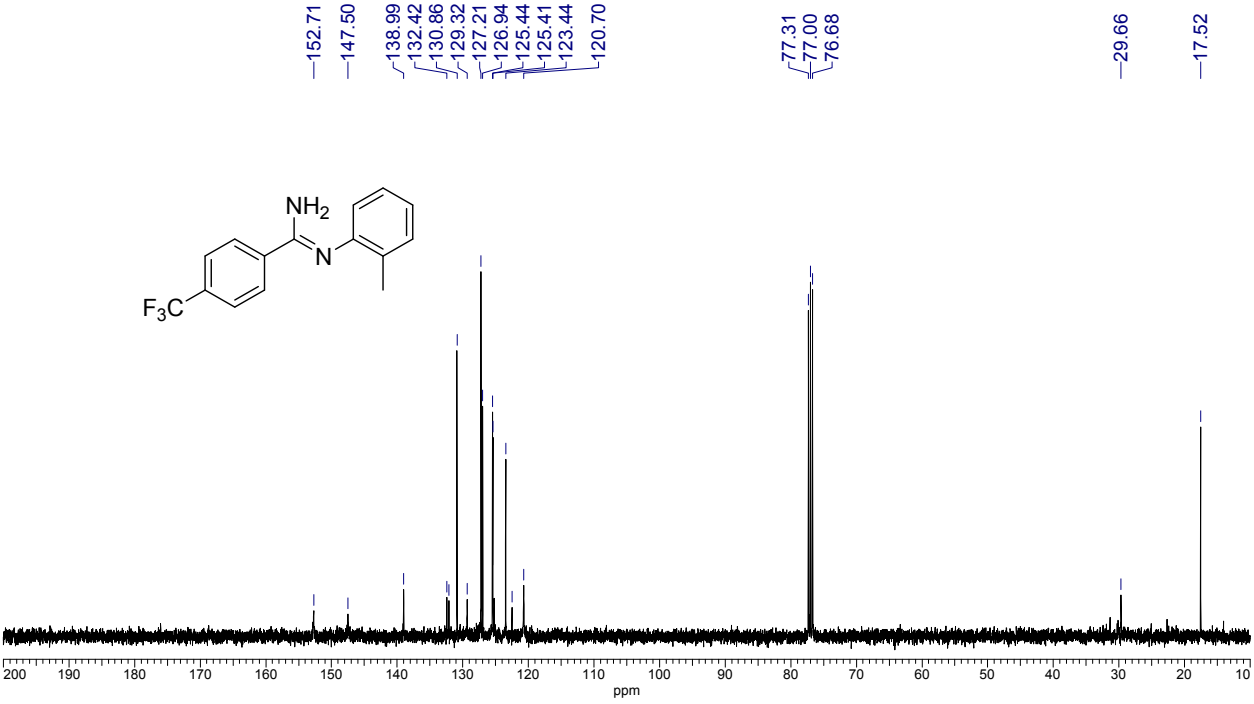


Figure FS45. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3v**.

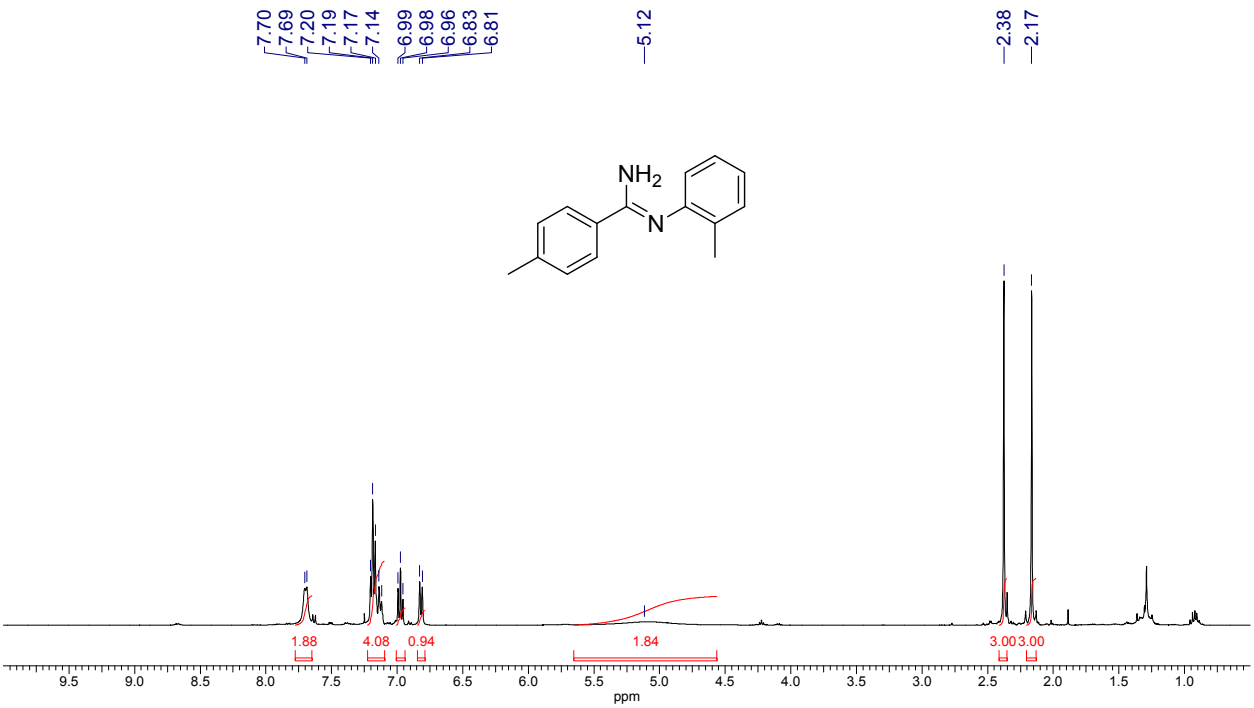


Figure FS46. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3w**.

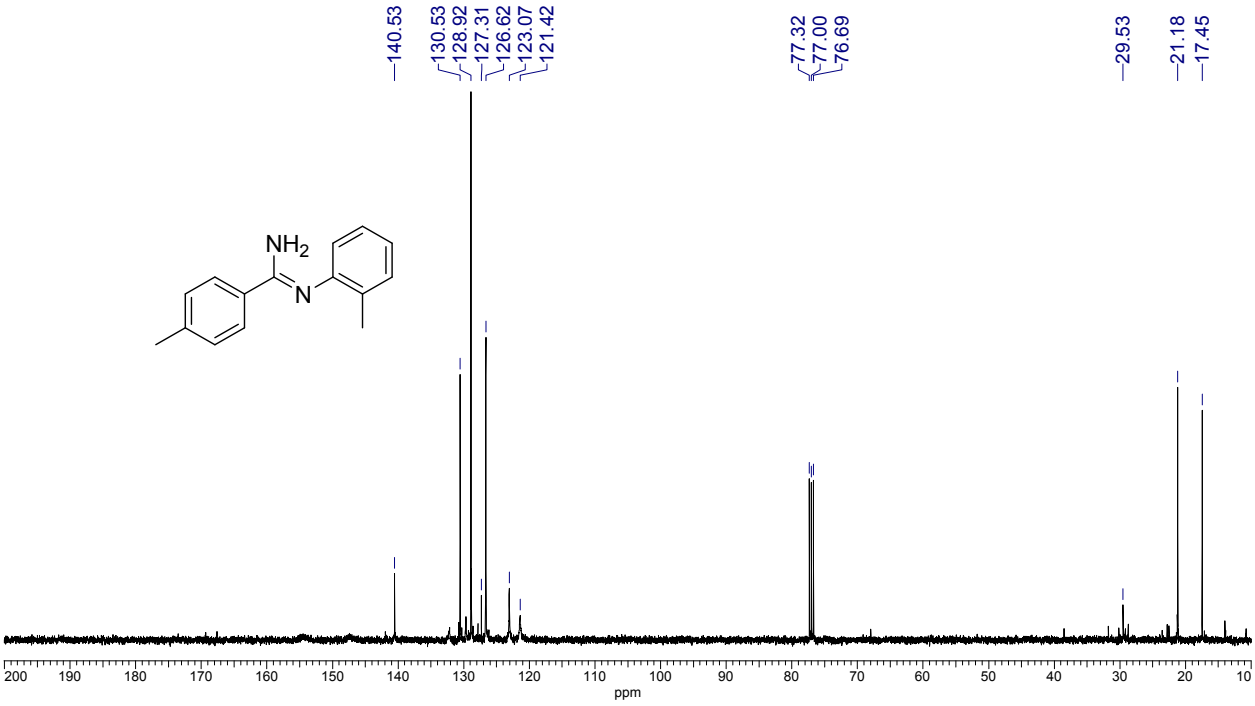


Figure FS47. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3w**.

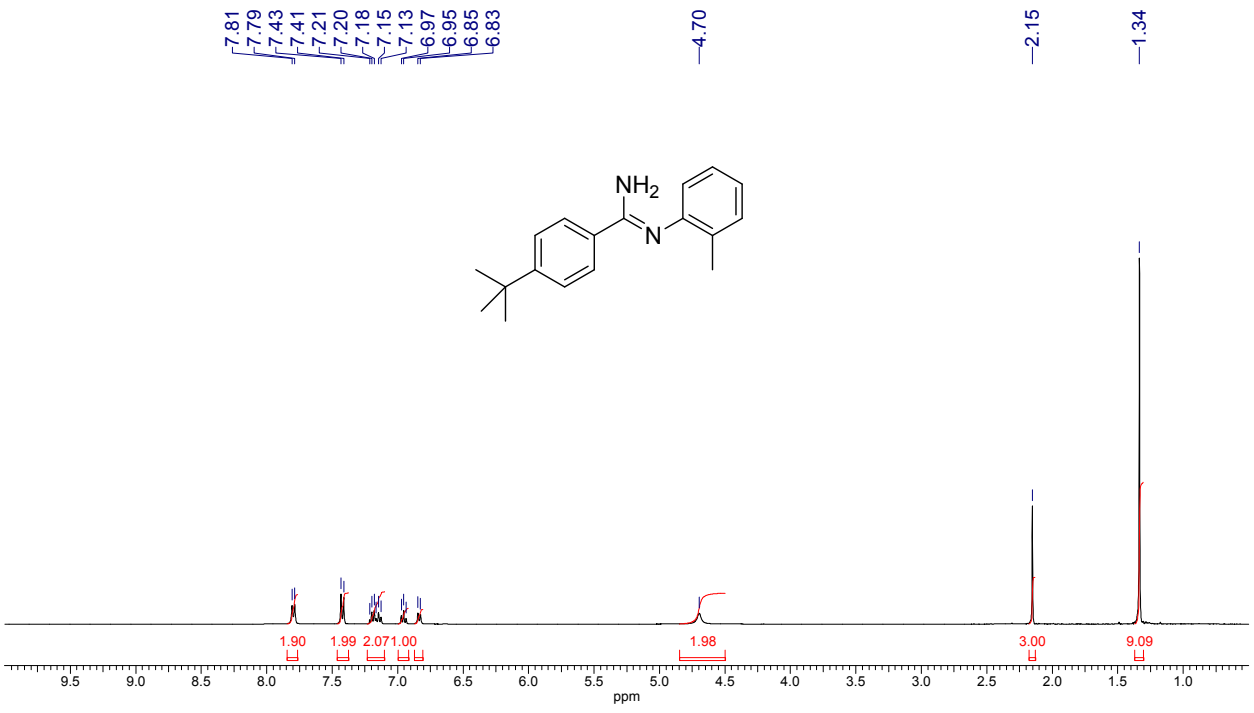


Figure FS48. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3x**.

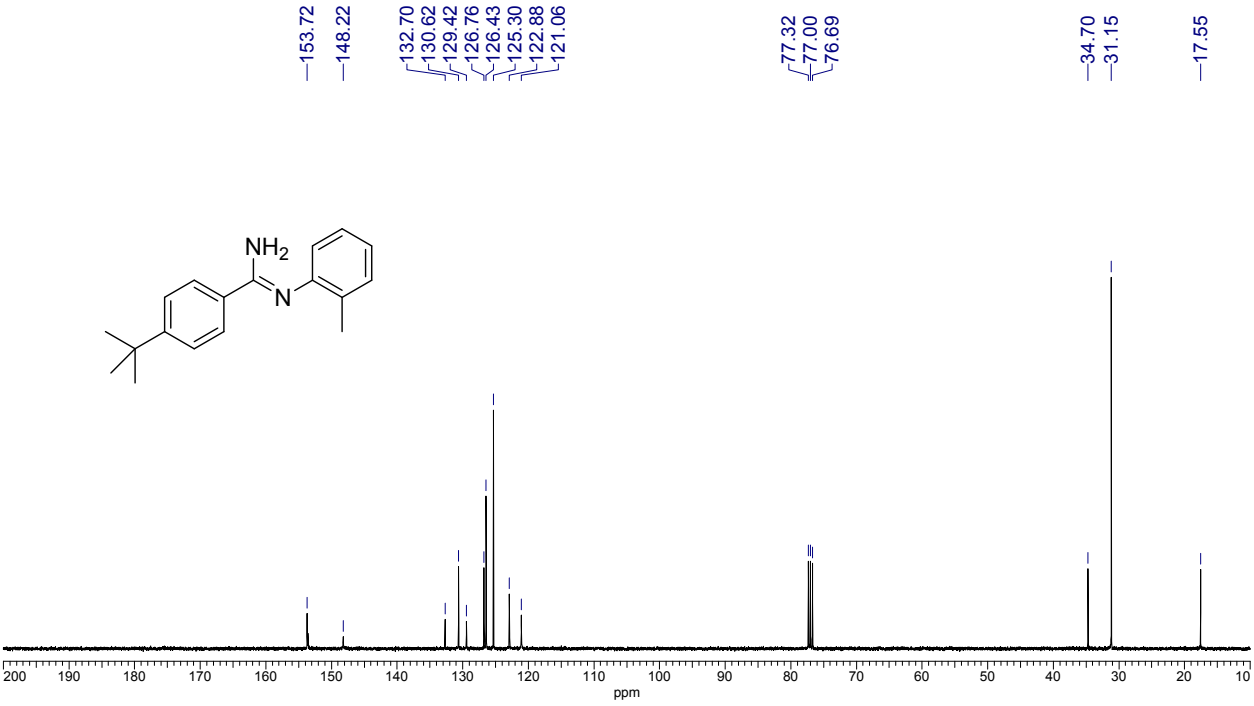


Figure FS49. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3x**.

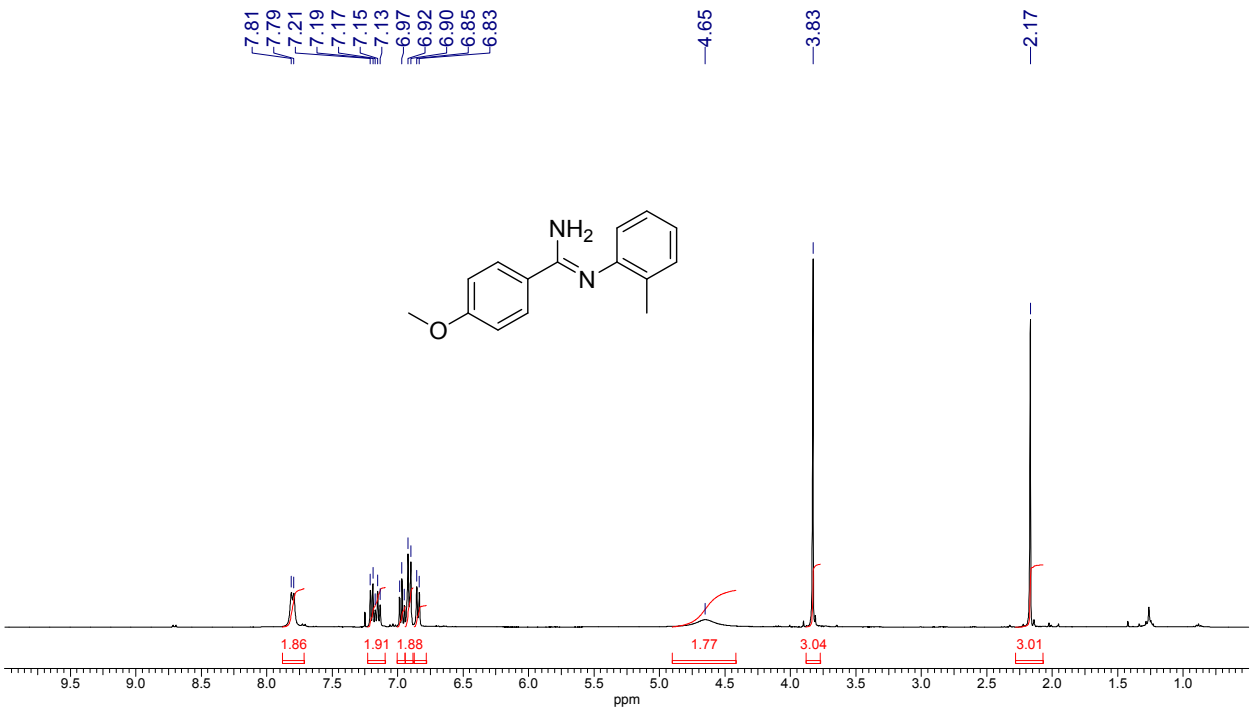


Figure FS50. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3y**.

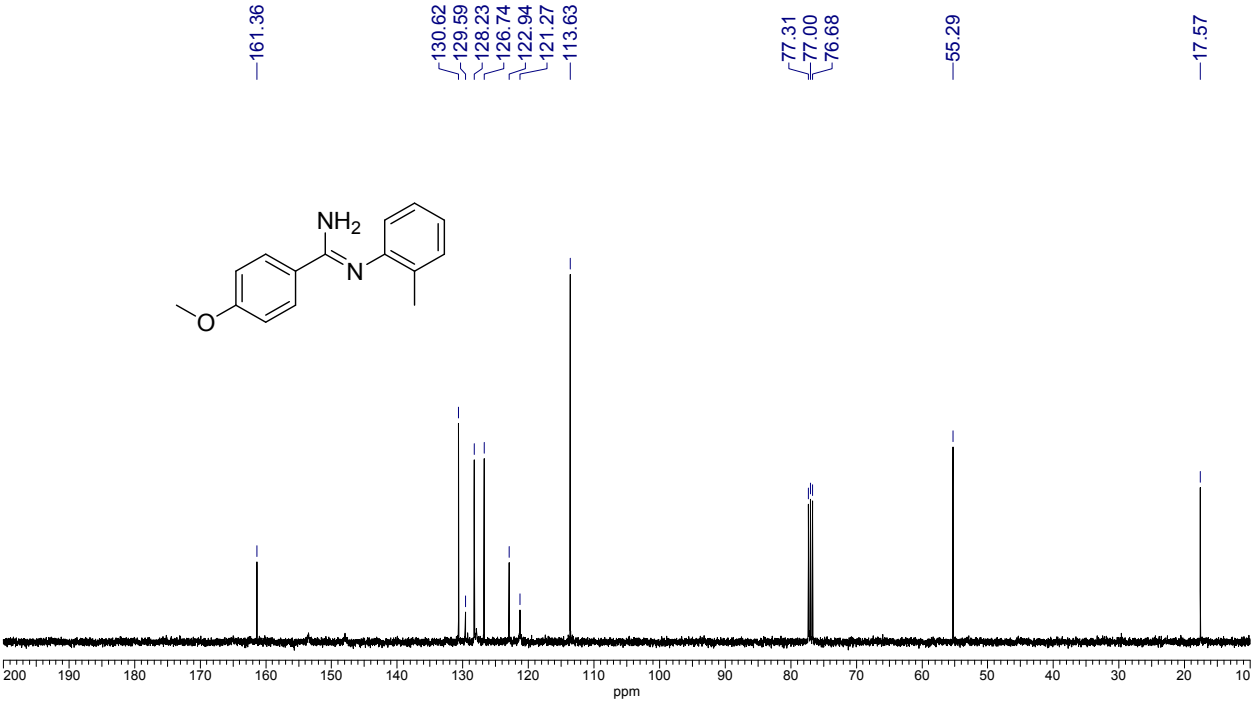


Figure FS51. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3y**.

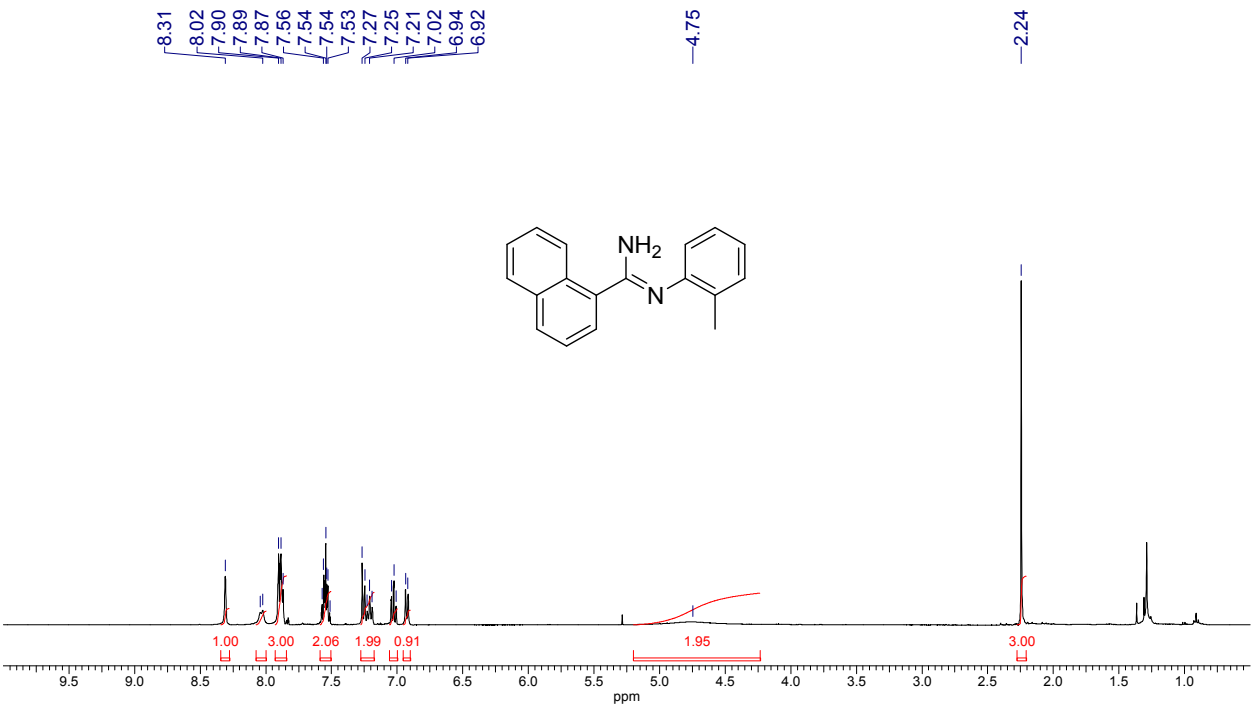


Figure FS52. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3z**.

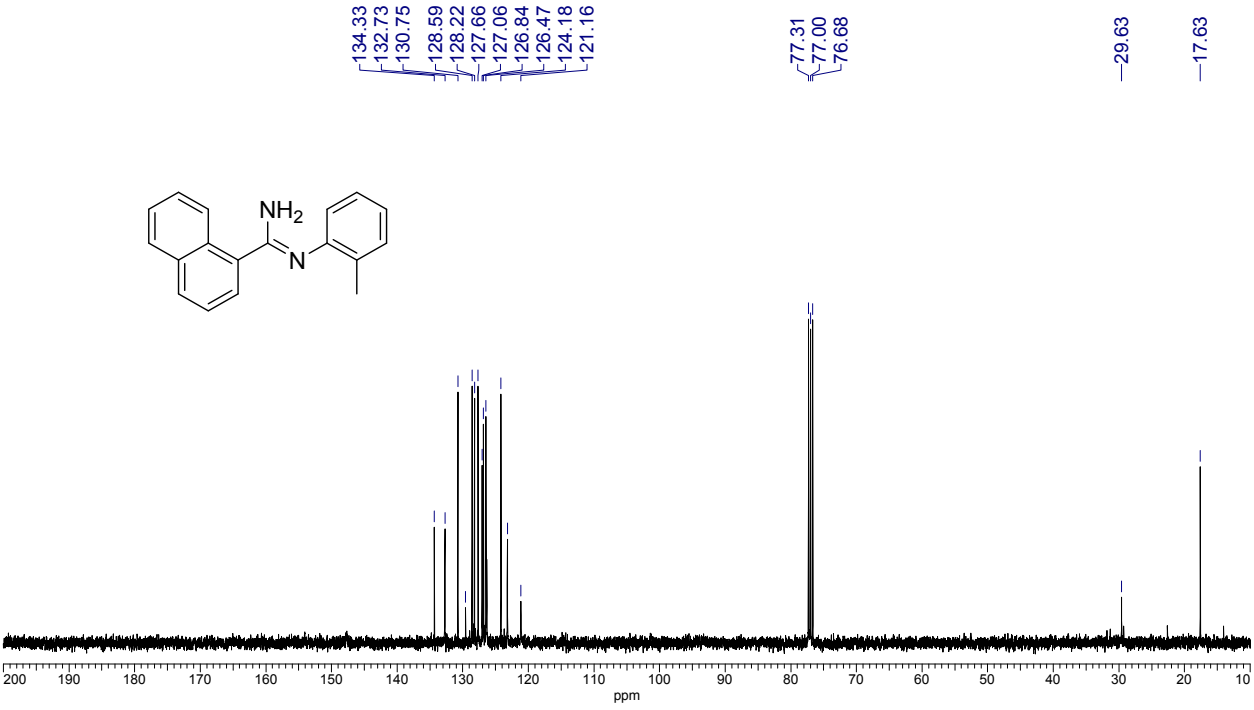


Figure FS53. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3z**.

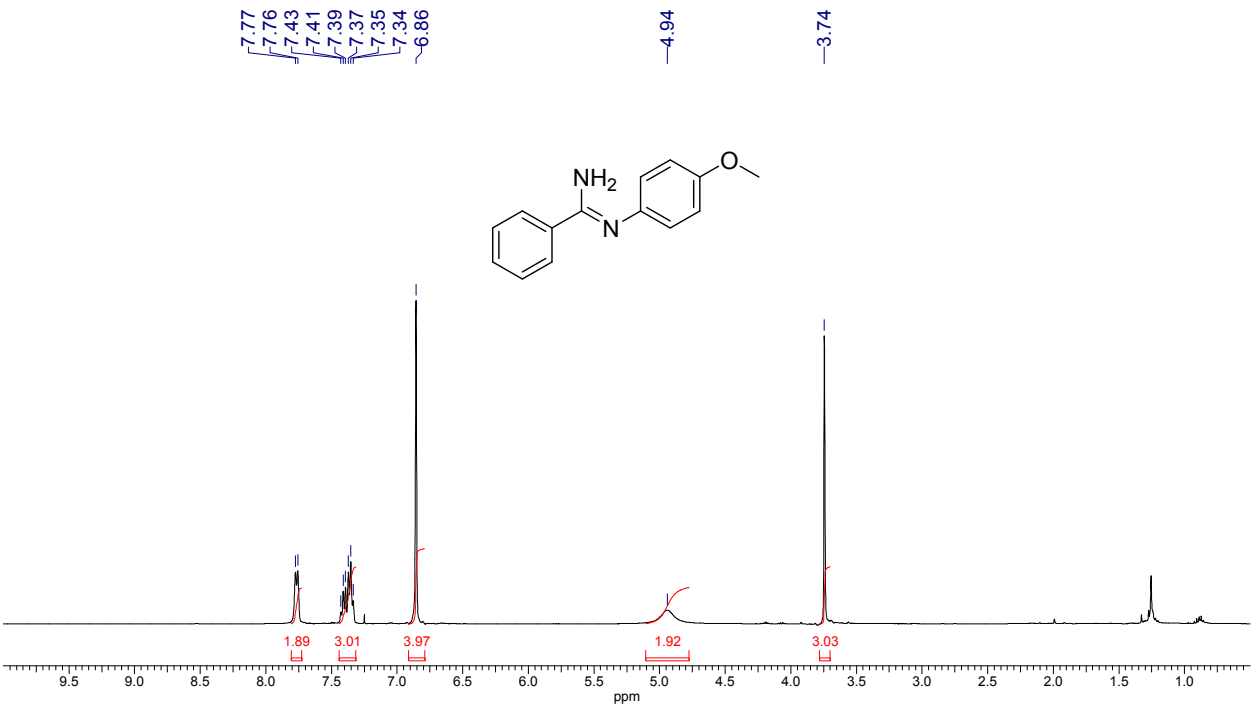


Figure FS54. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3za**.

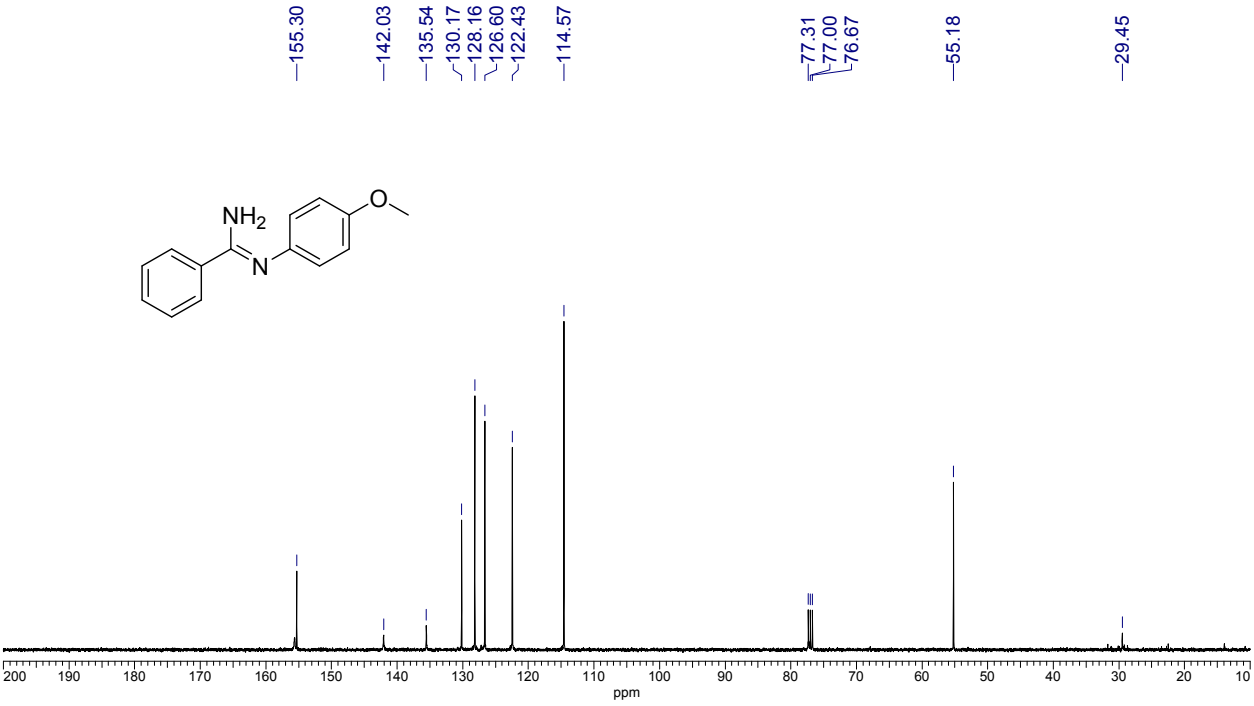


Figure FS55. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3za**.

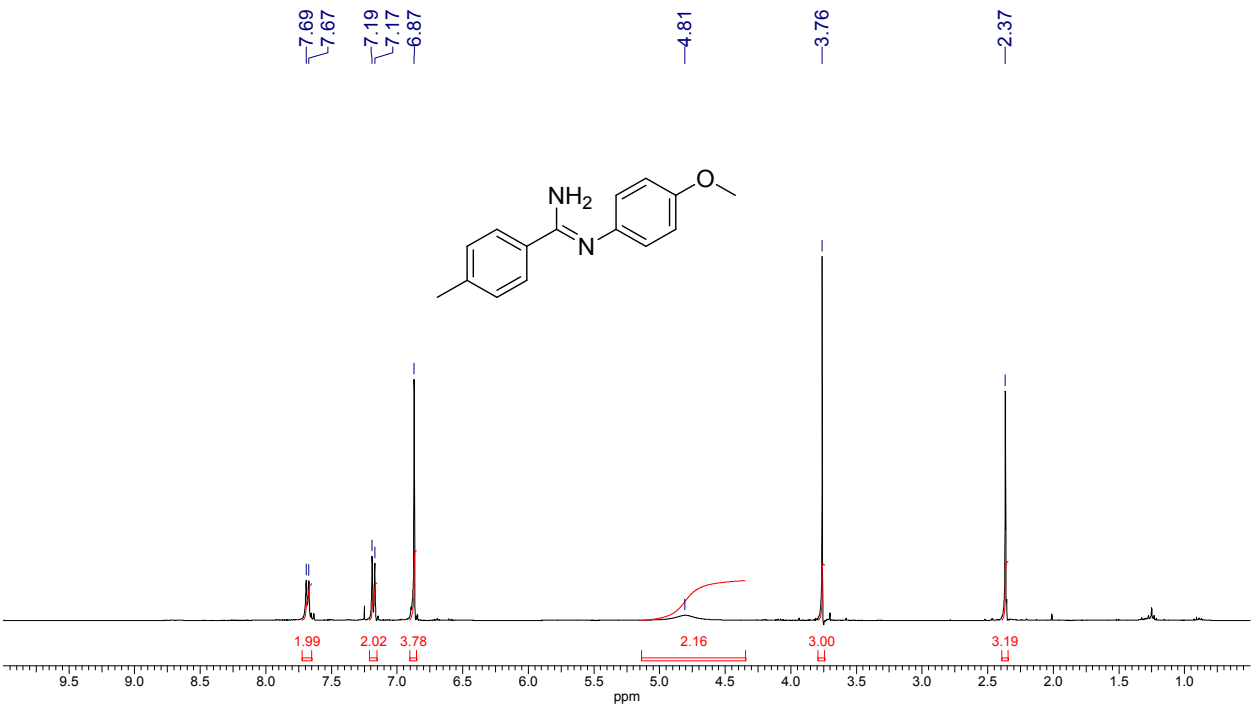


Figure FS56. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3zb**.

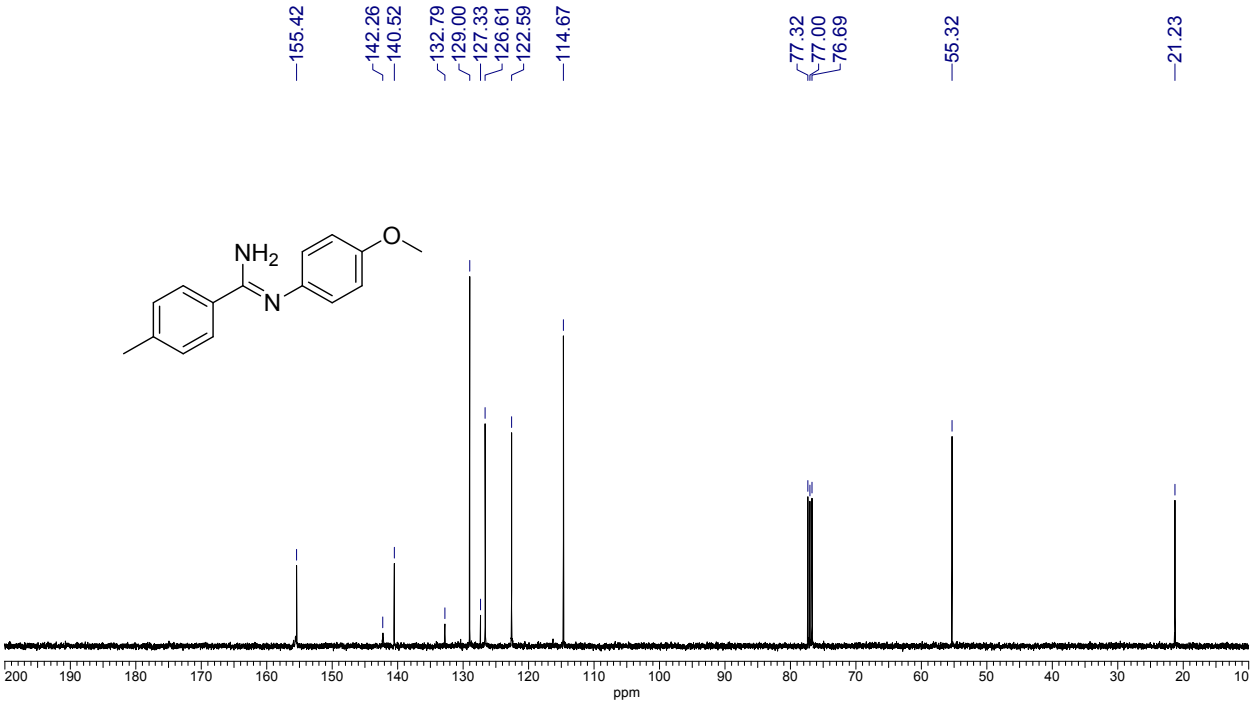


Figure FS57. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3zb**.

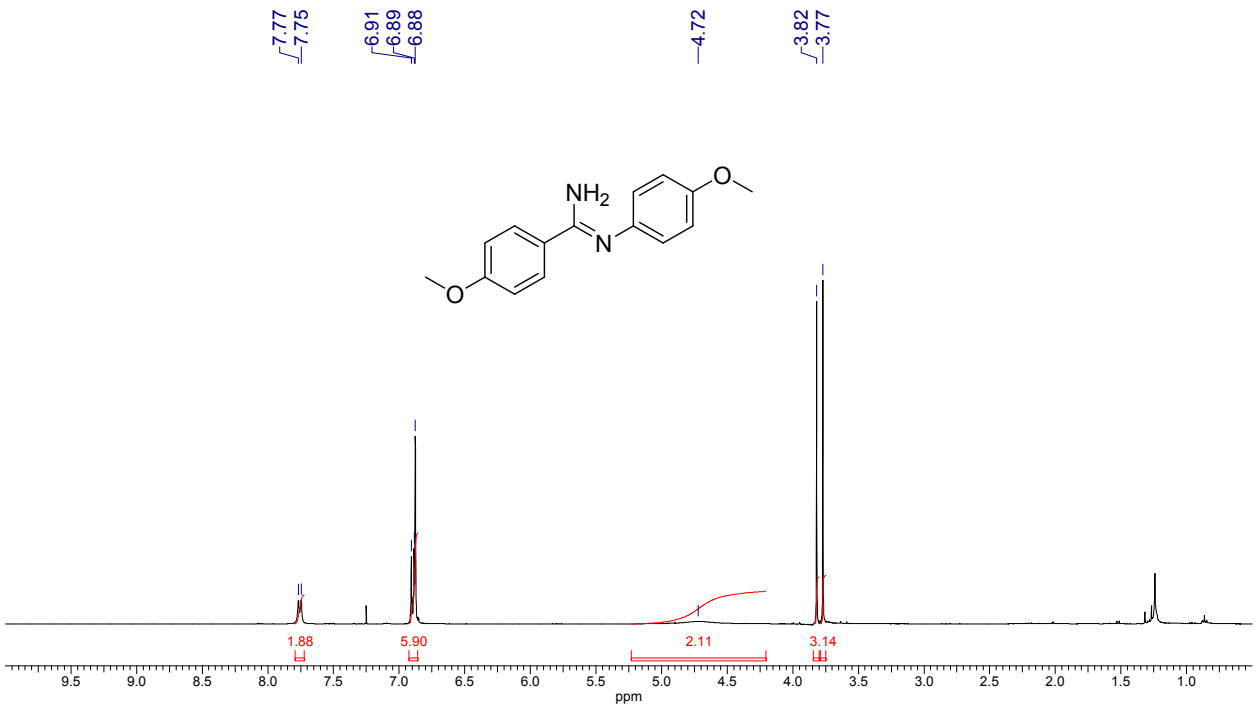


Figure FS58. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3zc**.

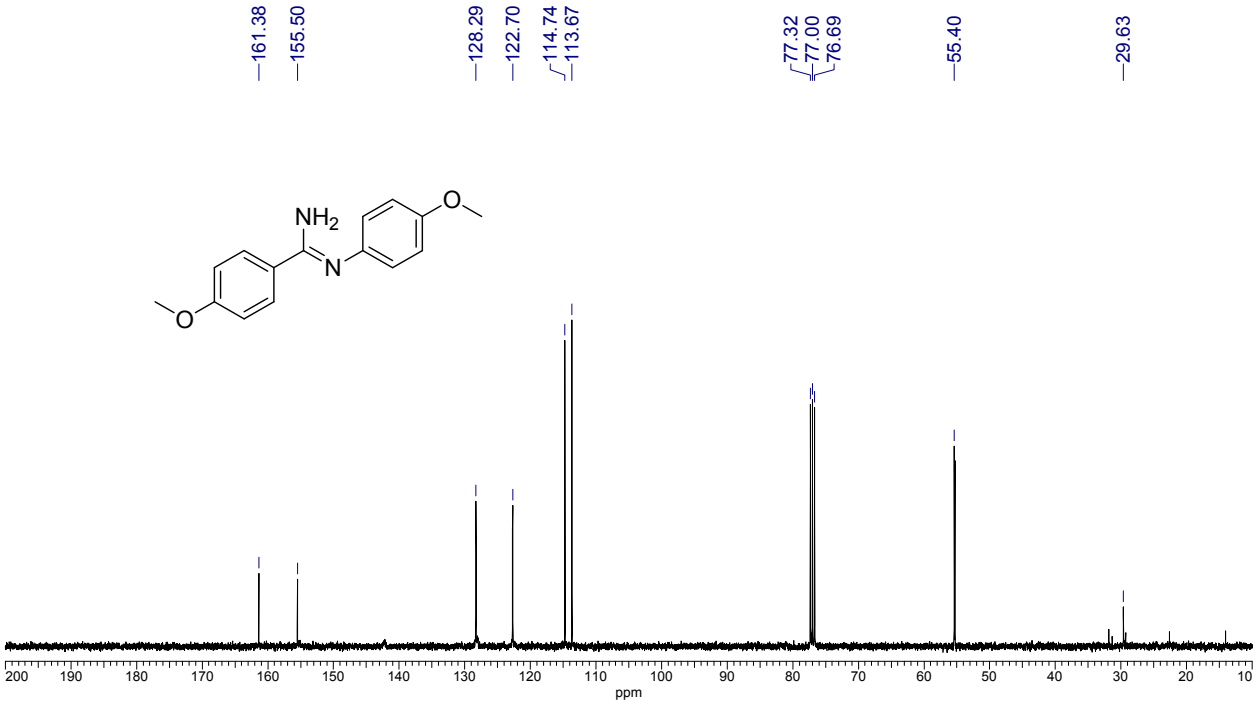


Figure FS59. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3zc**.

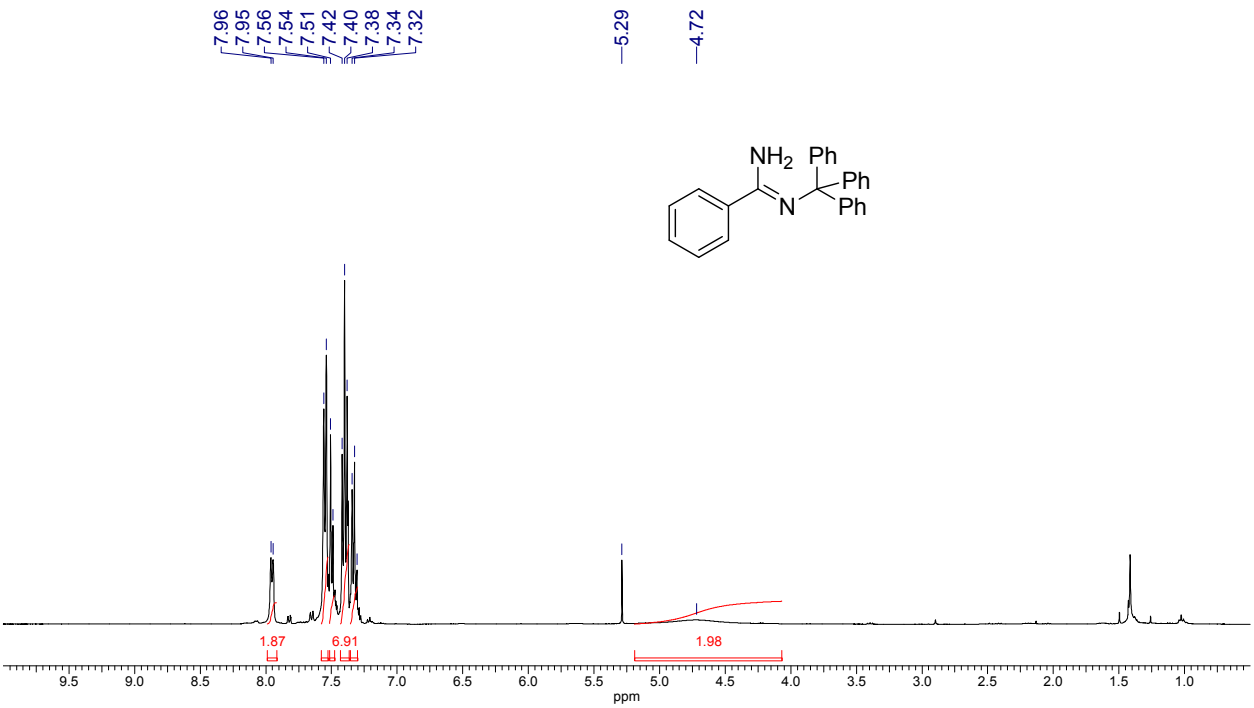


Figure FS60. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3zd**.

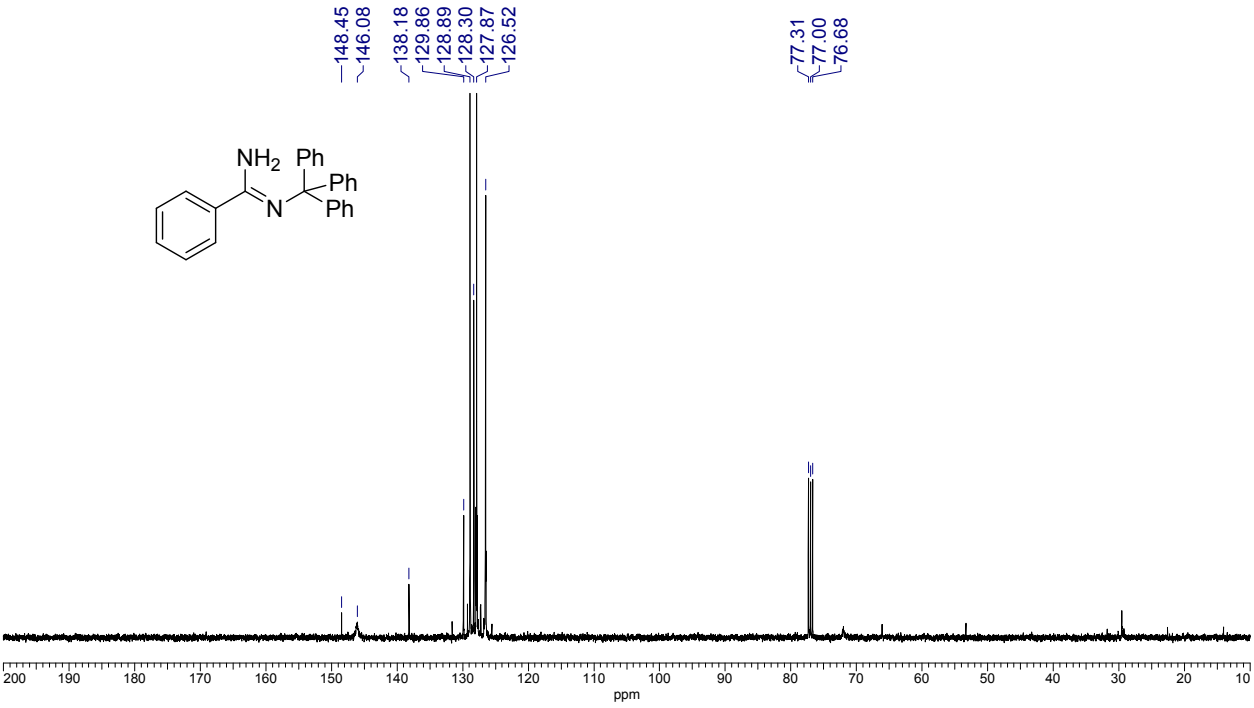
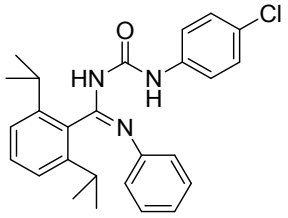


Figure FS61. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3zd**.

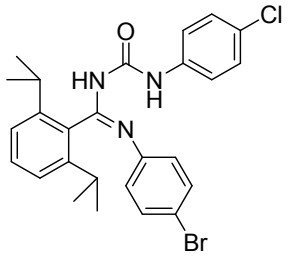
General procedure for synthesis of urea derivatives from N-arylamidines (4a-4f). In a dry Schlenk tube, the desired amidine (0.2 mmol) was taken followed by the addition of the respective substituted phenyl isocyanate (0.2 mmol). Minimum amount of toluene was added and the resulting mixture was allowed to stir at room temperature for 12 h. The solvent was then evaporated under vacuo to obtain the resulting product. The crude mixture was washed with n-hexane (3 x 5 ml) and dried to acquire the urea derivatives as white product. The isolated products were characterised by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy.

NMR data for urea derivatives 4a-4f.



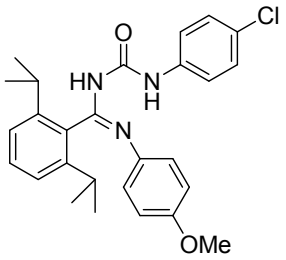
N-((4-chlorophenyl)carbamoyl)-2,6-diisopropyl-N'-phenylbenzimidamide (**4a**).

Yield (79.0 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 12.37 (s, 1H, N*H*), 8.21 (s, 1H, N*H*), 7.34 (d, *J* = 12.0 Hz, 2H, Ar-*H*), 7.27 (q, *J* = 8.0 Hz, 1H, Ar-*H*), 7.21 - 7.14 (m, 6H, Ar-*H*), 6.95 (s, 3H, Ar-*H*), 2.94 - 2.84 (sept, 2H, C*H*), 1.06 (d, *J* = 8.0 Hz, 6H, CH_3), 0.87 (d, *J* = 4.0 Hz, 6H, CH_3) ppm. Elemental analysis $C_{26}H_{28}ClN_3O$ (433.97). Calcd (found) C 71.96 (71.82), H 6.50 (6.39), N 9.68 (9.58).



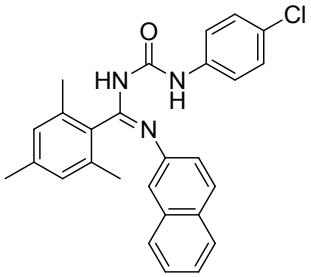
N'-(4-bromophenyl)-N-((4-chlorophenyl)carbamoyl)-2,6-diisopropylbenzimidamide (**4b**).

Yield (91.3 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 12.36 (s, 1H, N*H*), 8.77 (s, 1H, N*H*), 7.41 - 7.34 (m, 4H, Ar-*H*), 7.30 - 7.23 (m, 4H, Ar-*H*), 7.09 (q, *J* = 8.0 Hz, 2H, Ar-*H*), 7.03 (s, 2H, Ar-*H*), 2.96 - 2.85 (sept, 2H, C*H*), 1.11 (d, *J* = 4.0 Hz, 6H, CH_3), 0.97 (d, *J* = 8.0 Hz, 6H, CH_3) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ_C 153.0, 138.1, 136.6, 131.6, 129.4, 128.9, 124.6, 123.2, 121.0, 28.7, 24.5, 21.8 ppm. Elemental analysis $C_{26}H_{27}BrClN_3O$ (512.86). Calcd (found) C 60.89 (60.81), H 5.31 (5.22), N 8.19 (8.17).



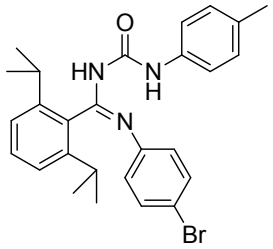
N-((4-chlorophenyl)carbamoyl)-2,6-diisopropyl-N'-(4-methoxyphenyl)benzimidamide (**4c**).

Yield (83.5 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 12.47 (s, 1H, N*H*), 8.62 (s, 1H, N*H*), 7.32 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.18 - 7.11 (m, 4H, Ar-*H*), 6.96 (s, 3H, Ar-*H*), 6.67 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 3.69 (s, 3H, OCH_3), 2.94 - 2.83 (sept, 2H, C*H*), 1.05 (d, *J* = 8.0 Hz, 6H, CH_3), 0.88 (d, *J* = 8.0 Hz, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 161.0, 153.5 (d, *J* = 22.0 Hz), 141.8, 138.3, 136.9, 129.6, 128.6 (d, *J* = 50.0 Hz), 124.3 (d, *J* = 35.0 Hz), 123.1, 121.0, 113.6, 55.2, 28.4, 24.4, 21.9 ppm. Elemental analysis $C_{27}H_{30}ClN_3O_2$ (463.99). Calcd (found) C 69.89 (69.83), H 6.52 (6.41), N 9.06 (8.95).



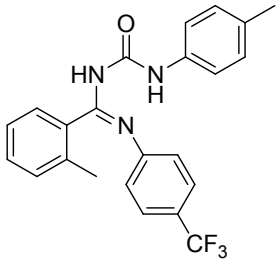
N-((4-chlorophenyl)carbamoyl)-2,4,6-trimethyl-N'-(naphthalen-2-yl)benzimidamide (**4d**).

Yield (80.4 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 12.45 (s, 1H, N*H*), 8.33 (s, 1H, N*H*), 7.82 - 7.73 (m, 3H, Ar-*H*), 7.64 - 7.49 (m, 3H, Ar-*H*), 7.39 - 7.29 (m, 1H, Ar-*H*), 7.14 - 7.07 (m, 2H, Ar-*H*), 6.71 (s, 2H, Ar-*H*), 2.17 (s, 3H, CH_3), 2.02 (s, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 154.4, 153.1, 141.9, 136.6, 133.8, 132.7 (d, *J* = 56.0 Hz), 128.8 (d, *J* = 11.0 Hz), 128.1, 127.7 (d, *J* = 11.0 Hz), 126.8, 123.6, 121.2, 20.6, 18.7 ppm. Elemental analysis $C_{27}H_{24}ClN_3O$ (441.95). Calcd (found) C 73.38 (73.24), H 5.47 (5.33), N 9.51 (9.42).



N'-(4-bromophenyl)-2,6-diisopropyl-N-(p-tolylcarbamoyl)benzimidamide (**4e**).

Yield (87.6 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 12.21 (s, 1H, N*H*), 9.11 (s, 1H, N*H*), 7.40 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.28 (d, *J* = 8.0 Hz, 3H, Ar-*H*), 7.14 - 7.08 (m, 3H, Ar-*H*), 7.03 (s, 3H, Ar-*H*), 2.99 - 2.89 (sept, 2H, C*H*), 2.30 (s, 3H, CH_3), 1.12 (d, *J* = 8.0 Hz, 6H, CH_3), 0.97 (d, *J* = 8.0 Hz, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 153.2 (d, *J* = 34.0 Hz), 141.5, 138.2, 135.4, 133.3, 131.3 (d, *J* = 42.0 Hz), 129.5, 124.6 (d, *J* = 49.0 Hz), 123.1, 119.7, 28.4, 24.4, 21.8, 20.8 ppm. Elemental analysis $C_{27}H_{30}BrN_3O$ (492.45). Calcd (found) C 65.85 (65.73), H 6.14 (6.05), N 8.53 (8.42).



2-methyl-N-(p-tolylcarbamoyl)-N'-(4-(trifluoromethyl)phenyl)benzimidamide (**4f**).

Yield (66.6 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 12.00 (s, 1H, N*H*), 8.23 (s, 1H, N*H*), 7.55 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.34 (t, *J* = 8.0 Hz, 3H, Ar-*H*), 7.16 (d, *J* = 12.0 Hz, 3H, Ar-*H*), 7.09 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 6.91 (t, *J* = 4.0 Hz, 2H, Ar-*H*), 6.36 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 2.30 (d, *J* = 8.0 Hz, 6H, merged CH_3) ppm. Elemental analysis $C_{23}H_{20}F_3N_3O$ (411.41). Calcd (found) C 67.14 (67.09), H 4.90 (4.83), N 10.21 (10.15).

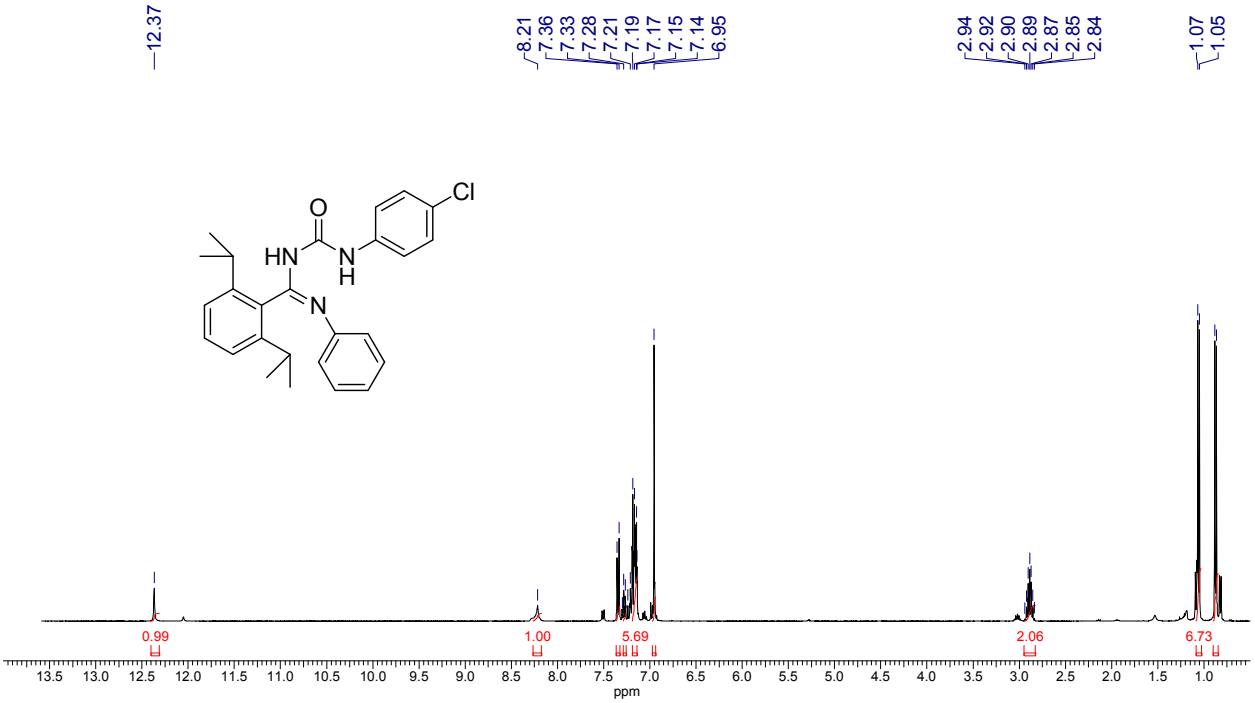


Figure FS62. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a**.

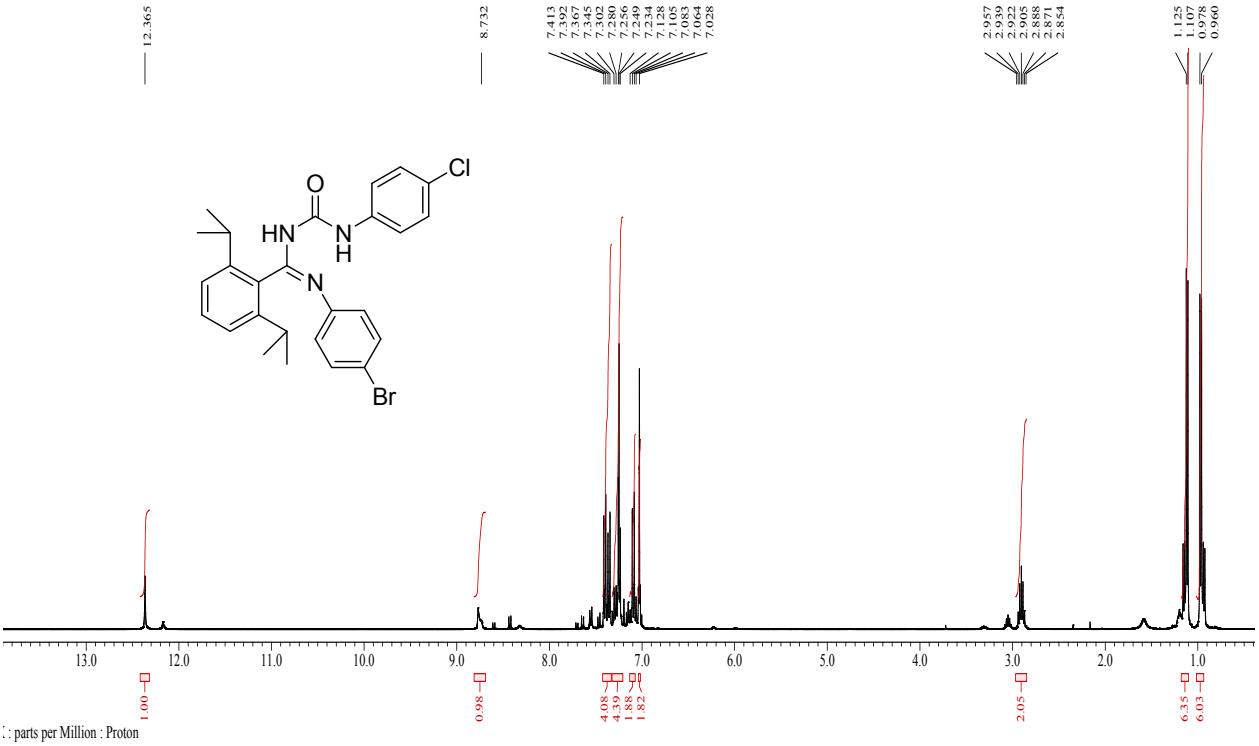


Figure FS63. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4b**.

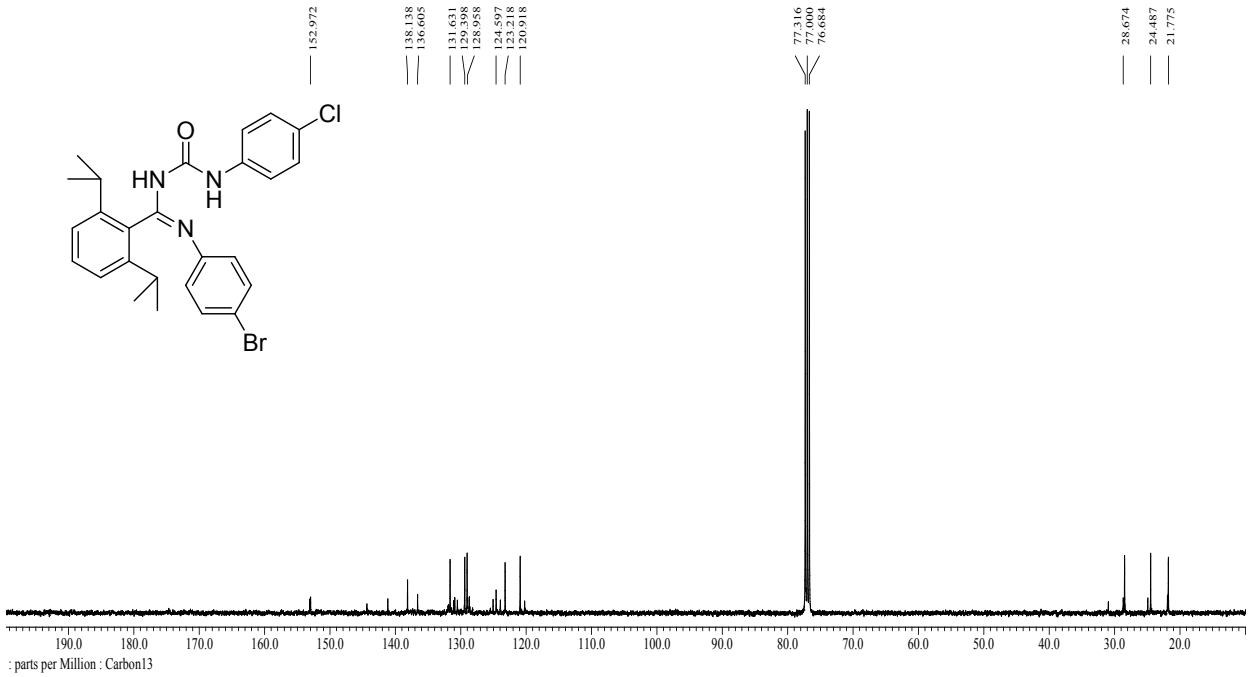


Figure FS64. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4b**.

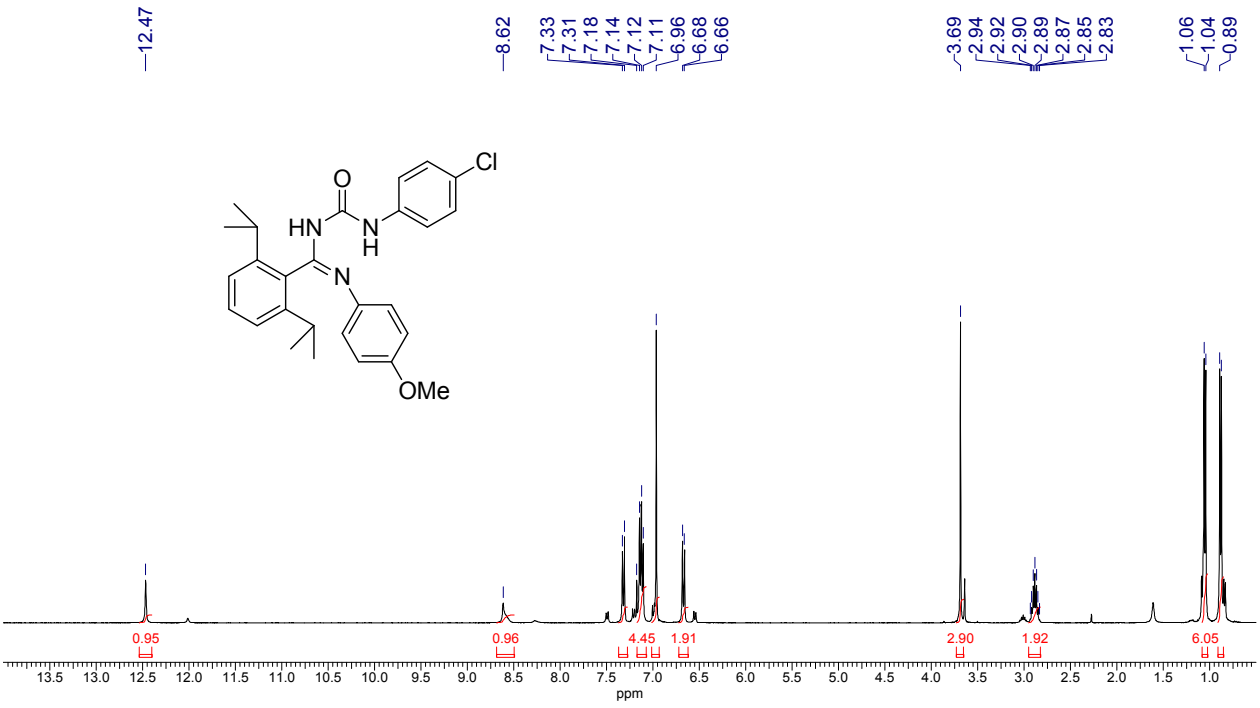


Figure FS65. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4c**.

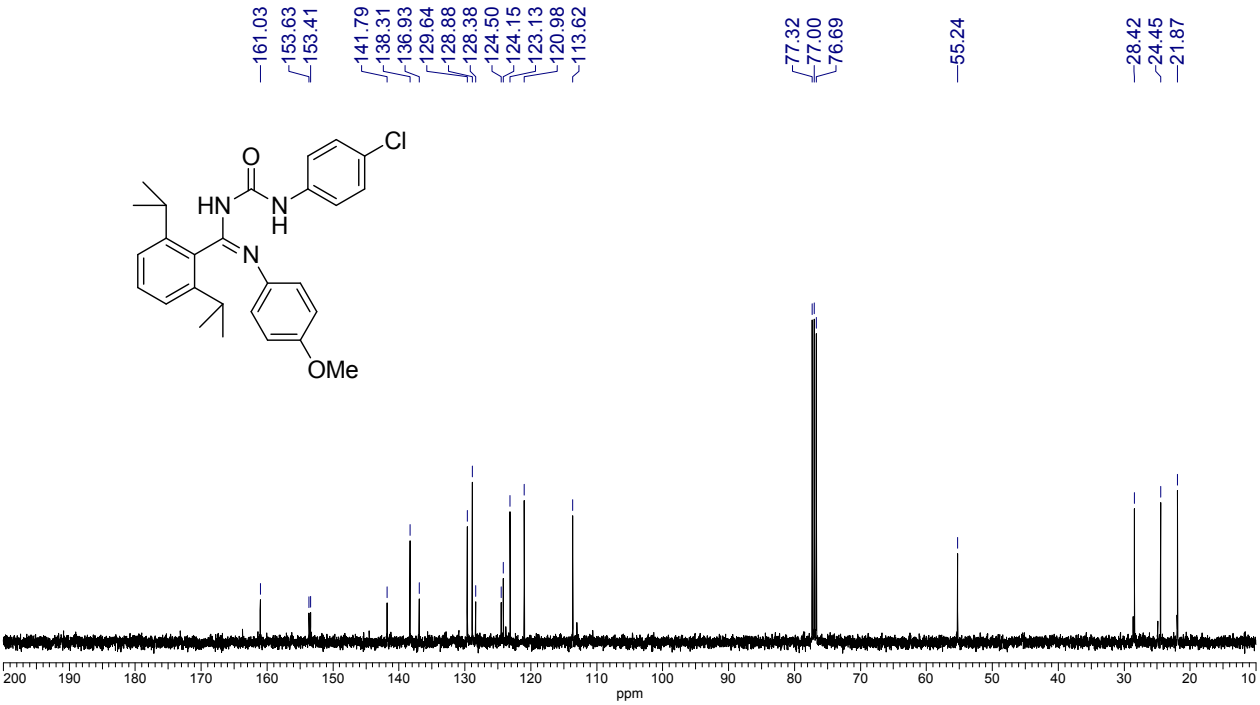


Figure FS66. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4c**.

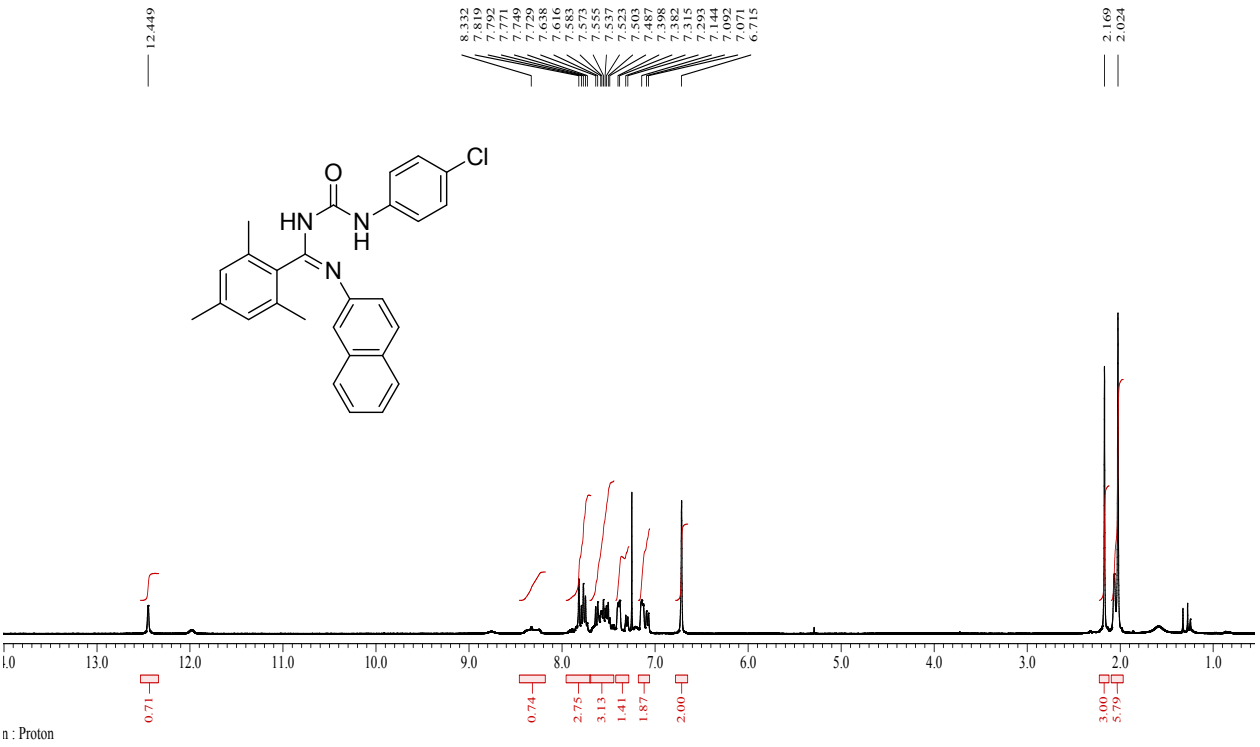


Figure FS67. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4d**.

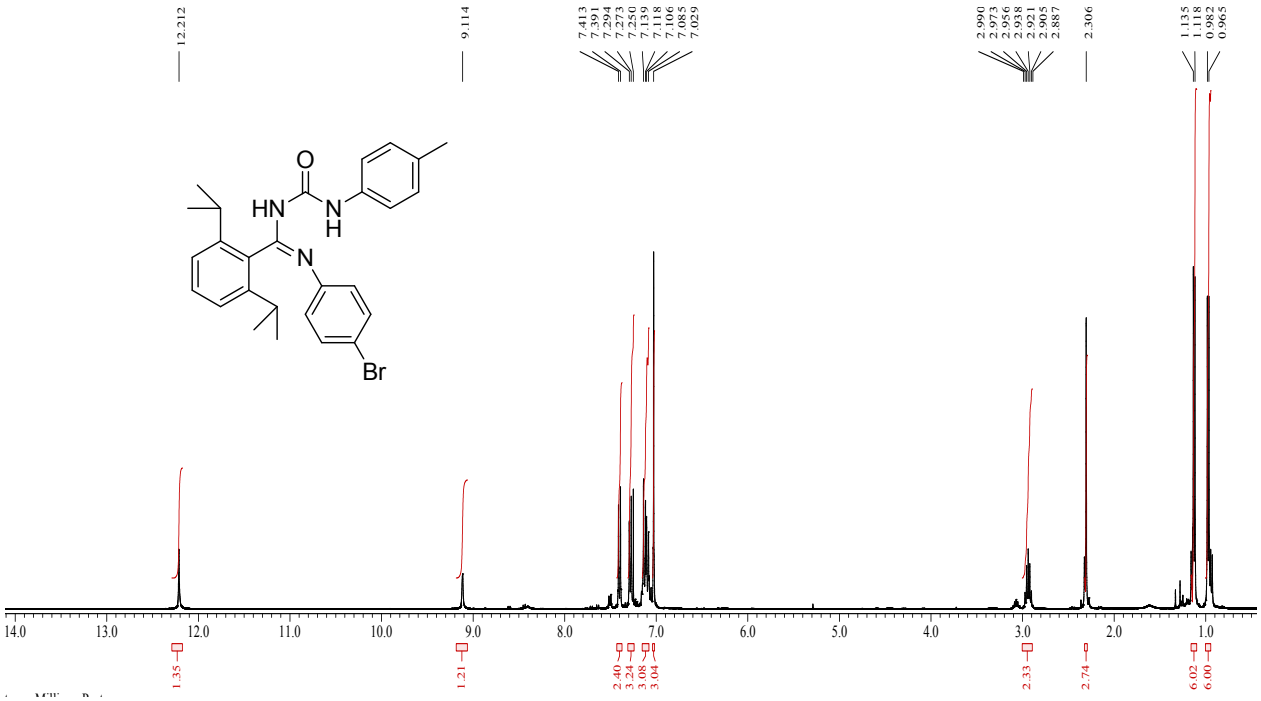


Figure FS68. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4e**.

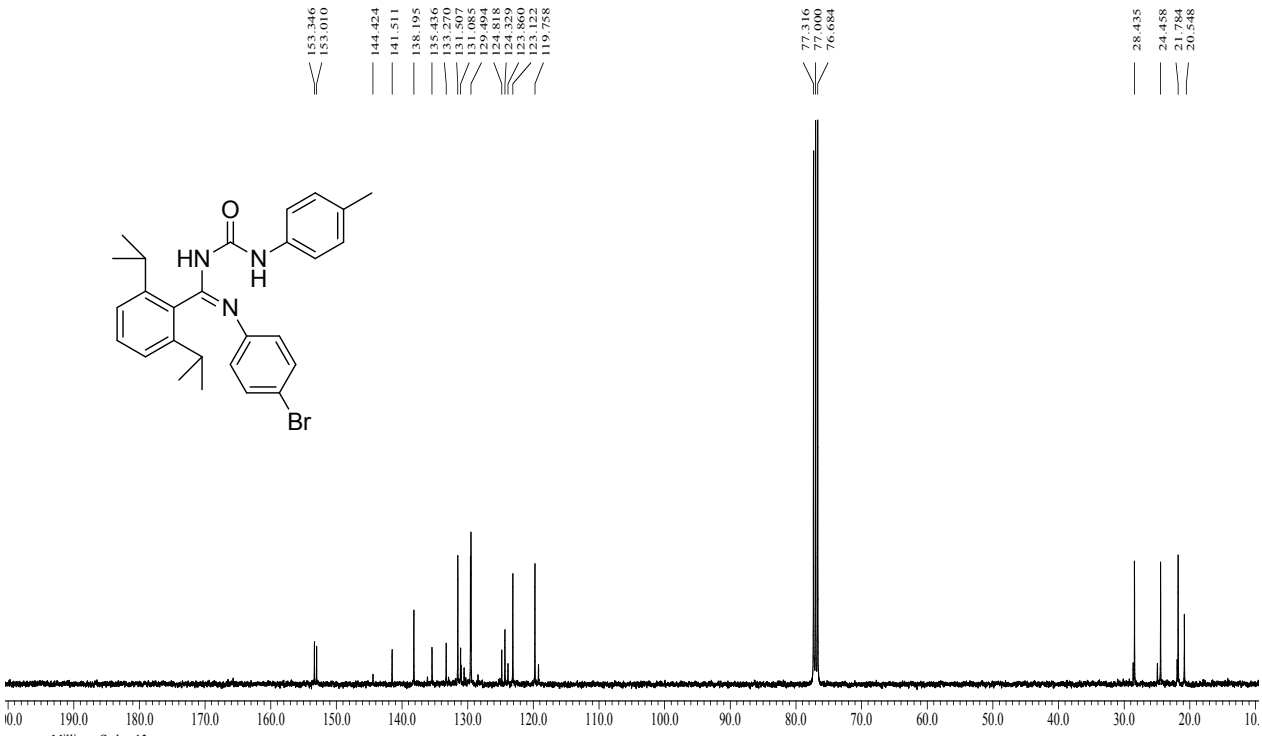


Figure FS69. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4e**.

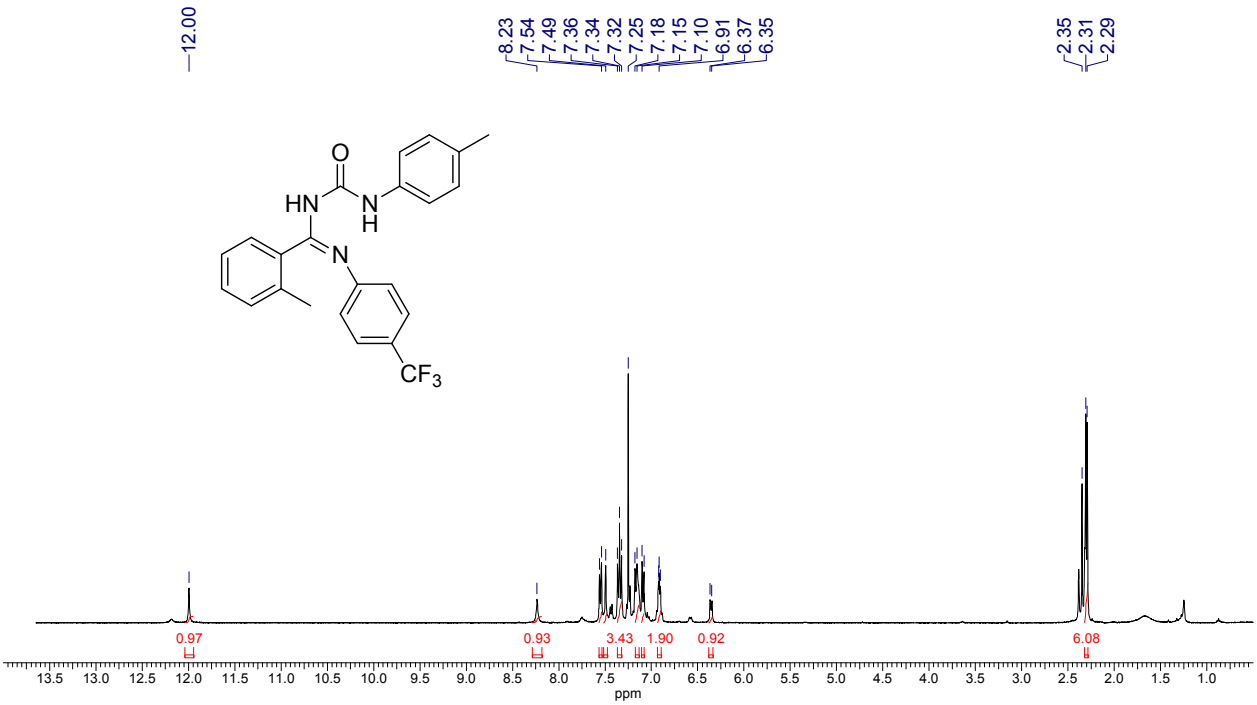


Figure FS70. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4f**.

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