RSC Advances

Supporting information

Silica gel promoted environment-friendly synthesis of α-amino amidines and regioselective transformation of α-amino amidines into amidino substituted indazoles

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Experimental Section

General: IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in $CDCl_3$; chemical shifts (δ in ppm) and coupling constants (J in Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H = 0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in $CDCl_3$; chemical shifts (δ in ppm) are reported relative to $CHCl_3$ (δ_C = 77.00 ppm). In the ^{1}H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet and br s = broad singlet, sept = septet. The assignment of signals were confirmed by ^{1}H and ^{13}C spectral data. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF using multimode source.

All small scale reactions were carried out in 10 ml stoppered round bottom flask (RBF). Reactions were monitored by silica gel TLC plates, using a mixture of petroleum ether and ethyl acetate as eluents. All solvents were distilled prior use; petroleum ether with a boiling range of 60 to 80^{o}C, dichloromethane (DCM), ethyl acetate, purchased from locally available commercial sources were used. Aromatic amines and aldehydes were purchased from locally available commercial sources and few of them from Sigma Aldrich. Azido aldehydes were prepared according to literature procedure.[1]

1. Experimental Procedure for the Synthesis of α-Amino amidines using silica gel (Table 2, 4a-o): To a solution of 2-Azido benzaldehyde **1** (1 mmol) in dichloromethane (6 mL), amine (2 mmol) and silica gel (0.5 g mesh 100-200) were added and the resulting mixture was stirred for 30 minutes. Then isocyanide (1 mmol) was added to above reaction mixture and stirring was continued for appropriate time until the starting materials were completely consumed. The solvent was removed under reduced pressure and the slurry so formed was purified by column chromatography on silica (petroleum ether/ethyl acetate as eluant). The silica was activated by washing with 5N HCl, water followed by Ethyl acetate and dried in oven for 14 h at 100 ^{o}C. All the compounds were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR and HR-MS Spectral analyses. Among 16 compounds, 10 (**4a-j**) are unknown and 6 (**4**k-**p**) are known. We gave FTIR, ^{1}H NMR & ^{13}C NMR spectral data for known compounds and FTIR, ^{1}H NMR, ^{13}C NMR & HR-MS spectral data for unknown compounds.

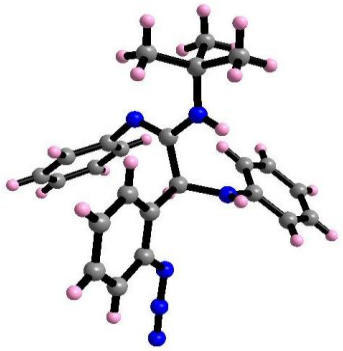
2. Experimental Procedure for the Synthesis of amidino substituted indazoles using $FeCl_3$ (Table 4, 5a-j): α-amino amidines **4** (1 mmol), $FeCl_3$ (20 mol %) and dimethyl formamide (2 mL) were taken in a two-necked round bottom flask, and the mixture was refluxed at 120 ^{o}C under nitrogen atmosphere for

appropriate time until the starting material was completely consumed. After completion of the reaction (monitored by TLC), added 25 mL water to the reaction mixture and extracted with EtOAc. The extract was dried over anhydrous Na_2SO_4.The residue was purified by column chromatography on silica gel (60-120 mesh, petroleum ether/EtOAc as eluant) to yield the desired products. All the compounds (**5a-j)** were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR and HR-MS Spectral analyses.

3. General Procedure for the large scale Synthesis of N-cyclohexyl-N', 2-diphenyl-2-(phenylamino) acetimidamide (Scheme 3, 4l): To a solution of benzaldehyde **1l** (9.41 mmol) in dichloromethane (50 mL), aniline **2l** (18.82 mmol) and silica gel (5 g mesh 100-200) were added and the resulting mixture was stirred for 30 minutes. Then cyclohexyl isocyanide **3l** (9.41 mmol) was added to above reaction mixture and stirring was continued for appropriate time until the starting materials were completely consumed. The reaction mixture was filtered, washed with EtOAc (20 mL), concentrated under reduced pressure and purified by column chromatography on silica gel (eluent: nhexane/EtOAc = 10:0.3) to give the *α*-amino amidine **4l** in 62% yield.

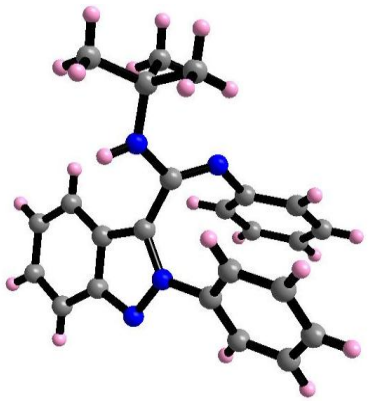
4. General Procedure for the recycling of silica gel in the Synthesis of N-cyclohexyl-N', 2-diphenyl-2-(phenylamino) acetimidamide (Table 5, 4l): To a solution of benzaldehyde **1l** (0.68 mmol) in dichloromethane (50 mL), aniline **2l** (1.36 mmol) and silica gel (0.5 g mesh 100-200) were added and the resulting mixture was stirred for 30 minutes. Then cyclohexyl isocyanide **3l** (0.68 mmol) was added to above reaction mixture and stirring was continued for appropriate time until the starting materials were completely consumed. The reaction mixture was filtered, washed with EtOAc (20 mL), concentrated under reduced pressure and purified by column chromatography on silica gel (eluent: nhexane/EtOAc = 10:0.3). The filtered silica gel was activated by washing with 5N HCl, water followed by Ethyl acetate and dried in oven for 14 h at 100 ^{o}C then used for the next cycle of the reaction.

3. X-ray crystal structure data for 2-(2-azidophenyl)-N-tert-butyl-N'-phenyl-2 (phenylamino)acetimidamide (4a) CCDC 1044390



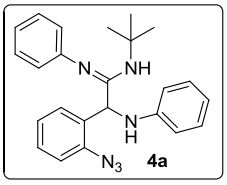
Operator	K. Ravikumar
Empirical formula	$C_{24}H_{26}N_6$
Formula weight	398.51
Temperature/K	566(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.920(2)
b/Å	9.0785(9)
c/Å	15.7191(19)
α/°	90
β/°	110.502(13)
γ/°	90
Volume/Å^3	2261.6(5)
Z	4
ρ_{calc}mg/mm^3	1.170
m/mm^{-1}	0.568
F(000)	848.0
Crystal size/mm^3	0.20 × 0.18 × 0.16
2Θ range for data collection	11.166 to 145.73°
Index ranges	$-19 \leq h \leq 20$, $-10 \leq k \leq 9$, $-19 \leq l \leq 18$
Reflections collected	8360
Independent reflections	4306[R(int) = 0.0348]
Data/restraints/parameters	4306/0/276
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0927, wR_2 = 0.2269
Final R indexes [all data]	R_1 = 0.1465, wR_2 = 0.3260
Largest diff. peak/hole / e Å^{-3}	0.30/-0.51

4. X-ray crystal structure data for N-tert-butyl-N'2-diphenyl-2H-indazole-3-carboximidamide (5a) CCDC 1044391

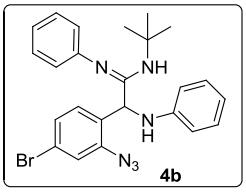


Operator	K. Ravikumar
Empirical formula	$C_{24}H_{24}N_4$
Formula weight	368.47
Temperature/K	566(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.5010(11)
b/Å	11.7613(15)
c/Å	18.1827(15)
α/°	81.571(9)
β/°	78.506(7)
γ/°	61.154(12)
Volume/Å^3	2107.5(4)
Z	4
ρ_{calc}mg/mm^3	1.161
m/mm^{-1}	0.544
F(000)	784.0
Crystal size/mm^3	0.19 × 0.17 × 0.15
2Θ range for data collection	8.598 to 142.156°
Index ranges	$-14 \leq h \leq 11$, $-14 \leq k \leq 14$, $-22 \leq l \leq 16$
Reflections collected	15456
Independent reflections	7849[R(int) = 0.0505]
Data/restraints/parameters	7849/0/513
Goodness-of-fit on F^2	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0622, wR_2 = 0.2160
Final R indexes [all data]	R_1 = 0.1264, wR_2 = 0.2400
Largest diff. peak/hole / e Å^{-3}	0.12/-0.14

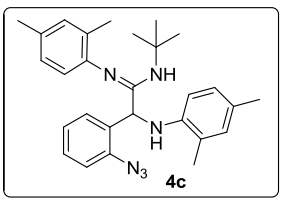
Spectral Data of all Compounds (4a-p & 5a-j)



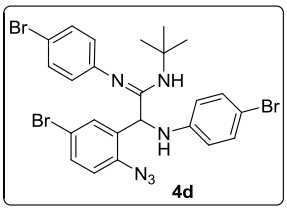
2-(2-azidophenyl)-N-tert-butyl-N'-phenyl-2-(phenylamino) acetimidamide (4a): Brown solid (80%), Mp 128-130 °C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3378, 3052, 3023, 2963, 2921, 2123, 2095, 1633, 1483, 1298, 1183, 898, 748, 695. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.53 (d, J = 7.3 Hz, 1H), 7.32 (td, J_a = 7.7, J_b = 1.2 Hz, 1H), 7.23 (m, 2H), 7.14 (m, 1H), 7.01 (t, J = 7.6, 2H), 6.94 (d, J = 7.8 Hz, 1H), 6.83 (m, 2H), 6.68 (d, J = 7.8 Hz, 2H), 6.4 (d, J = 7.8 Hz, 2H), 5.99 (s, 1H), 5.14 (d, J = 1.5 Hz, 1H), 3.53 (s, 1H), 1.47 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 154, 150.7, 147, 138.7, 130.8, 129.7, 129, 128.8, 128, 125, 122, 121, 119.5, 118, 113.8, 54, 51, 28. HR-MS (ESI+) m/z calculated for $[C_{24}H_{27}N_6]^+$ = $[M+H]^+$: 399.2292; found: 399.2312.



2-(2-azido-4-bromophenyl)-N-tert-butyl-N'-phenyl-2-(phenylamino) acetimidamide (4b): Brown solid (77%), Mp 93-95 °C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3376.1, 3052.1, 2962, 2926.2, 2113.6, 1634.5, 1591.9, 1498.6, 1422.8, 1315.1, 1259.3, 1182.6, 750.2, 696.3. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.51 (d, J = 8.3 Hz, 1H), 7.25 (m, 2H), 7.04 (t, J = 7.8 Hz, 2H), 6.85 (m, 3H), 6.68 (d, J = 7.8 Hz, 2H), 6.53 (d, J = 2 Hz, 1H), 6.42 (d, J = 7.3 Hz, 2H), 5.97 (s, 1H), 5.09 (d, J = 2 Hz, 1H), 3.5 (s, 1H), 1.44 (br. s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 154, 150.7, 147, 141.5, 140, 130, 129, 128, 127, 122, 121, 119.7, 115, 113.8, 108.8, 53.9, 51, 28. HR-MS (ESI+) m/z calculated for $[C_{24}H_{26}BrN_6]^+$ = $[M+H]^+$: 477.1397; found: 477.1466.

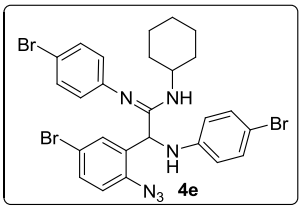


2-(2-azidophenyl)-N-tert-butyl-N'-(2,4-dimethylphenyl)-2-(2,4-dimethylphenylamino)acetimidamide (4c): Brown solid (68%), Mp 118-120 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3381.3, 2959.9, 2918, 2123.2, 1634.9, 1508.6, 1488.9, 1450.1, 1297.7, 1256, 1223.6, 1186, 1042, 829, 809.7, 752.9, 69.7. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.6 (d, *J* = 7.3 Hz, 1H), 7.35 (m, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.8, 1H), 6.93 (s, 1H), 6.82-6.75 (m, 3H), 6.38 (d, *J* = 7.8 Hz, 1H), 6.09 (br s, 1H), 5.25 (s, 1H), 3.33 (br s, 1H), 2.31 (s, 3H), 2.25 (s, 3H), 2.07 (s, 3H), 1.69 (s, 3H), 1.52, (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 153.7, 146.3, 143.3, 138.6, 131, 130.6, 130.5, 129.9, 129.5, 128.7, 128.4, 127.6, 126.3, 125.1, 122.7, 121.7, 118.3, 115.1, 112.2, 54.3, 50.8, 28.6, 20.7, 20.5, 17.7, 17.5. HR-MS (ESI+) m/z calculated for $[C_{24}H_{27}N_6]^+ = [M+H]^+$: 455.2918; found: 455.2925.



4d

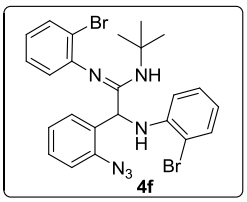
2-(2-azido-5-bromophenyl)-N-tert-butyl-N'-(4-bromophenyl)-2-(4-bromophenylamino) acetimidamide (4d): Brown solid (75%), Mp 133-135 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3377.8, 2962.1, 2123, 2094.7, 1631.1, 1476.8, 1291.1, 1181.7, 1070.4, 842.4, 811.2, 738.1, 587.8. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.49 (d, *J* = 2.4 Hz, 1H), 7.38 (dd, *J* = 8.6, *J* = 2.2 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.07 (s, 1H), 6.79 (d, *J* = 8.3 Hz, 2H), 6.46 (s, 2H), 6.21 (d, *J* = 8.8 Hz, 2H), 5.82 (s, 1H), 4.97 (s, 1H), 3.51 (s, 1H), 1.37 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 153, 149.5 145.8, 137.9, 132.9, 132, 131.8, 131, 123.8 119.9, 117.8, 115, 114, 111.9, 54, 51, 28. HR-MS (ESI+) m/z calculated for $[C_{24}H_{24}Br_3N_6]^+ = [M+H]^+$: 632.9607; found: 632.9599.



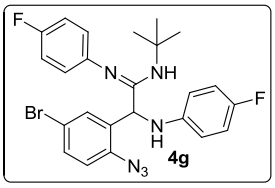
4e

2-(2-azido-5-bromophenyl)-N-cyclohexyl-N'-(4-bromophenyl)-2-(4-bromophenylamino) acetimidamide (4e): Brown solid (78%), Mp 120-122 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3380.9, 2962, 2927.4, 2124.9, 2098, 1632.7, 1580.8, 1489.9, 1390.7, 1361, 1181.4, 1070.5, 1004.9, 842.2, 814, 754.5, 673.6. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.52 (br. s, 1H), 7. 46 (dd, J_a = 8.6, J_b = 2.2 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.26 (s, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.53 (s, 3H), 6.31 (d, *J* = 7.3 Hz, 2H), 5.93 (d, *J* = 6.4 Hz, 1H), 5.1 (br. s, 1H), 3.9 (br. s, 1H), 3.62 (br s, 1H), 2.11 (br. s, 1H),

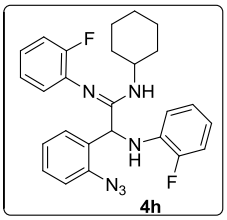
1.99 (br. s, 1H), 1.69 (m, 4H), 1.41 (d, J = 8.3 Hz, 2H), 1.17 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 154.6, 149, 145.8, 137.8, 132.9, 132, 131.8, 131.5, 124, 119.8, 117.9, 115, 114.5, 11.9, 53.8, 48.8, 33, 326, 25.7, 24.9, 24.8. HR-MS (ESI+) m/z calculated for $[C_{26}H_{26}\ Br_3N_6]^+$ = $[M+H]^+$: 658.9764; found: 658.9759.



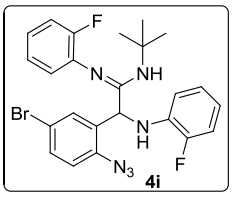
2-(2-azidophenyl)-N'-(2-bromophenyl)-2-(2-bromophenylamino)-N-tert-butyl-acetimidamide (4f): White solid (82%), Mp 102-103 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3383, 3059, 2960.8, 2926, 2124.3, 2098.4, 1633.2, 1581.1, 1491, 1461.2, 1299.8, 1184.6, 1022.6, 745.2, 675.7. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.5 (d, J = 7.8 Hz, 1H), 7.42 (d, J = 7.8, Hz, 2H), 7.35 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.17 (m, 1H), 7.08 (d, J = 8.3 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 6.83 (t, J = 7.3 Hz, 1H), 6.71 (m, 2H), 6.14 (d, J = 7.8 Hz, 1H), 5.95 (br s, 1H), 5.02 (br s, 1H), 4.23 (br s, 1H), 1.5 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 153.7, 148.6, 143.9, 138, 132.4, 132.3, 129.9, 128.8, 128.7, 126.9, 125, 123.7, 122.5, 120, 118, 117.6, 114, 110, 55, 51, 28.6. HR-MS (ESI+) m/z calculated for $[C_{24}H_{25}Br_2N_6]^+$ = $[M+H]^+$: 555.0502; found: 555.0499.



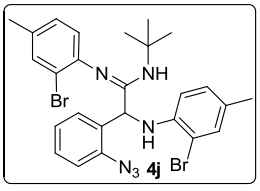
2-(2-azido-5-bromophenyl)-N-tert-butyl-N'-(4-fluorophenyl)-2-(4-fluorophenylamino) acetimidamide (4g): Brown solid (80%), Mp 113-115 ^{o}C IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3386.1, 3068, 2962.6, 2927.1, 2129, 2107, 1634.4, 1509, 1485, 1297, 1120.2, 1103.4, 1035.9, 809.5, 745. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.59 (d, J = 2 Hz, 1H), 7.45 (dd, J_a = 8.6, J_b = 2.2 Hz, 1H), 7.16 (m, 1H), 6.99 (m, 3H), 6.83 (m, 3H), 6.75 (td, J_a = 7.6, J_b = 1 Hz,, 2H), 6.27 (m, 1H), 6.12 (s, 1H), 5.04 (d, J = 2 Hz, 1H), 3.86 (br.s, 1H), 1.5 (br. s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 155, 154.7, 152.8, 152.7, 150, 137.9, 137.8, 135, 132.8, 131.8, 131.6, 125, 124.8, 123.7, 117.8, 115, 114.5, 114, 54.5, 51.5, 28. HR-MS (ESI+) m/z calculated for $[C_{24}H_{24}Br\,F_2N_6]^+$ = $[M+H]^+$: 513.1208; found: 513.1223.



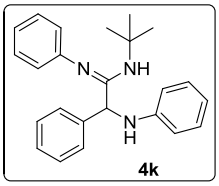
2-(2-azidophenyl)-N-cyclohexyl-N'-(2-fluorophenyl)-2-(2-fluorophenylamino) acetimidamide (**4h**) White solid (78%), Mp 105-107 °C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3397.6, 3055.3, 2930.3, 2853.5, 2128.5, 1630.8, 1509.7, 1485.7, 1299.7, 1263.9, 894.1, 736.5, 703.3. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.45 (d, J = 7.3 Hz, 1H), 7. 33 (m, 1H), 7.15 (t, J = 7.3 Hz, 2H), 7.02-6.92 (m, 4H), 6.85-6.80 (dd, J_a = 14.4, J_b = 7.1 Hz, 2H), 6.72 (t, J = 7.3 Hz, 1H), 6.21 (m, 2H), 5.16 (br s, 1H), 4.04 (m, 1H), 3.89 (br. s, 1H), 2.21 (d, J = 9.8 Hz, 1H), 2.1 (br s, 1H), 1.76 (d, J = 12.7 Hz, 1H), 1.64 (m, 2H), 1.43 (m, 2H), 1.3 (d, J = 11.7 Hz, 1H), 1.16 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 156.6, 155.6, 153.2, 152.7, 150.3, 138.5, 138, 137.9, 135.4, 135.3, 130, 129.5, 128.6, 125.3, 125, 123.6, 122.6, 122.5, 119.3, 119.2, 118, 115.4, 115.2, 114.6, 114.4, 113.9, 54.47, 49, 32.9, 32.5, 25.8, 25, 24.8. HR-MS (ESI+) m/z calculated for $[C_{26}H_{27}F_2N_6]^+ = [M+H]^+$: 461.2260; found: 461.2271.



2-(2-azido-5-bromophenyl)-N-tert-butyl-N'-(2-fluorophenyl)-2-(2-fluorophenylamino) acetimidamide (4i): Brown solid (82%), Mp 140-142 °C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3363.3, 2965.3, 2128, 1627.2, 1509.5, 1496.4, 1391.3, 1214, 1188.1, 1091.8, 834.2, 803.5, 663.6, 518.7. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.62 (d, J = 2 Hz, 1H), 7.47 (dd, J_a = 8.6, J_b = 2.2 Hz, 1H), 6.97 (t, J = 8.6, 2H), 6.88 (d, J = 8.8, 1H), 6.77 (d, J = 17.6, 2H), 6.61 (m, 2H), 6.36 (m, 2H), 6.01 (s, 1H), 5.04 (d, J = 1.5 Hz, 1H), 3.48 (s, 1H), 1.48 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 159, 158, 157, 155.9, 154, 146.5, 143, 137.7, 132.7, 132, 131.9, 123, 119.8, 117.8, 116, 115, 114.9, 114.7, 114.6, 54, 51, 28. HR-MS (ESI+) m/z calculated for $[C_{26}H_{27}F_2N_6]^+ = [M+H]^+$: 513.1208; found: 513.1228.

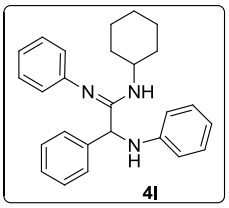


2-(2-azidophenyl)-N'-(2-bromo4-methylphenyl)-2-(2-bromo4-methylphenyl)-N-tert-butyl acetimidamide (4j): White solid (77%), Mp 117-119 °C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3401.9, 2958.8, 2925.8, 2835.4, .^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.51 (d, *J* = 6.8 Hz, 1H), 7.35 (m, 1H), 7.24 (m, 2H), 7.16 (m, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.98 (dd, J_a = 7.8, J_b = 4.4 Hz, 2H), 6.64 (m, 1H), 6.02 (br. s, 1H), 5.98 (s, 1H), 4.98 (d, *J* = 2.4 Hz, 1H), 4.07 (d, *J* = 1.5 Hz, 1H), 2.2 (s, 3H), 2.2 (s, 1H), 1.49 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 154.2, 145.8, 141.8, 138.6, 132.7, 132.6, 132.2, 130.3, 130, 129.9, 129.3, 128.7, 127.8, 125.3, 123.5, 118.5, 117.3, 114.2, 110.3, 55.2, 51.3, 20.3, 20.2. HR-MS (ESI+) m/z calculated for $[C_{26}H_{29}N_6Br_2]^+ = [M+H]^+$: 583.0815; found: 583.0809.



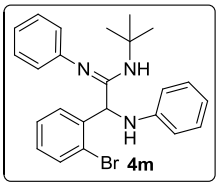
4k

N-tert-butyl-N', 2-diphenyl-2-(phenylamino) acetimidamide (4k):[2] White solid (90%), Mp 133-135 °C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3381.3, 3053.7, 2961.7, 2925.4, 1638.3, 1592.2, 1498.6, 1485.7, 1452.1, 1263.6, 1183.8, 1263.6, 1183.8, 1070.6, 732.2, 698.8. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.28-7.21 (m, 4H), 7.14 (dd, J_a = 7.6, J_b = 1.7 Hz, 2H), 7.03 (m, 2H), 6.83 (m, 2H), 6.69 (d, *J* = 7.8 Hz, 2H), 6.49 (d, *J* = 7.8 Hz, 2H), 5.89 (br s, 1H), 4.92 (s, 1H), 3.71 (br s, 1H), 1.46 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 153.9, 150.7, 147.2, 139.9, 129.3, 128.8, 128.5, 128.3, 128.1, 122.3, 121.2, 119.4, 113.8, 59.9, 50.9, 28.4.

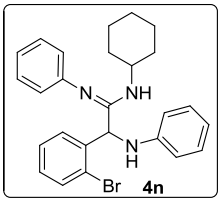


4l

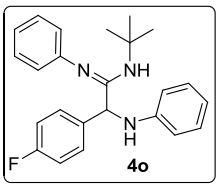
N-cyclohexyl-N', 2-diphenyl-2-(phenylamino) acetimidamide (4l):[2] Pale yellow solid (86%), Mp 147-149 °C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3382.8, 3053.1, 3027.7, 2926.9, 2852, 1626.8, 1590.1, 1482.5, 1311.6, 1251.2, 1105.1, 1071.3, 892.8, 750.5, 695.6. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.3-7.21 (m, 5H), 7.11 (d, *J* = 6.8 Hz, 2H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.84 (t, *J* = 7.3 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 2H), 6.5 (d, *J* = 7.8 Hz, 2H), 5.96 (d, *J* = 7.3 Hz, 1H), 4.97 (s, 1H), 3.72 (br s, 1H), 2.1 (m, 2H), 1.65 (m, 3H), 1.4 (m, 2H), 1.18 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 155.1, 150.5, 147.1, 139.5, 129.3, 128.8, 128.4, 128.4, 128.3, 128.1, 122.7, 121.5, 119.4, 113.8, 59.9, 48.6, 33.1, 32.6, 25.9, 25, 24.8.



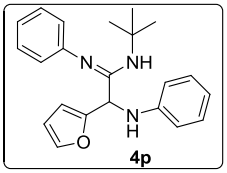
2-(2-bromophenyl)-N-tert-butyl-N'-phenyl-2-(phenylamino) acetimidamide (4m):[2] White solid (80%), Mp 108-110 °C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3377.9, 3052.5, 2961.4, 2925.5, 1635.2, 1592.4, 1513, 1485.3, 1389, 1295.4, 1257.3, 1183.2, 1025.9, 899.1, 825.4, 776.4, 751.9, 696. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.66 (dd, J_a = 7.6, J_b = 1.2 Hz, 1H), 7.43 (dd, J_a = 7.8, J_b = 1 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.23 (m, 2H), 7.16 (td, J_a = 7.6, J_b = 1.5 Hz, 1H), 7.01 (t, J = 7.8 Hz, 2H), 6.85 (t, J = 7.3 Hz, 1H), 6.79 (m, 1H), 6.7 (d, J = 7.8 Hz, 2H), 6.41, (d, J = 7.3 Hz, 2H), 5.97 (s, 1H), 5.22 (d, J = 1.5 Hz, 1H), 3.58 (s, 1H), 1.49 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 153.9, 150.5, 147, 139, 133, 129.8, 129, 128.6, 127.8, 125.5, 121.9, 121, 119.6, 113.8, 59.6, 51, 28.



2-(2-bromophenyl)-N-cyclohexyl-N'-phenyl-2-(phenylamino) acetimidamide (4n):[2] Pale yellow solid (75%), Mp 114-116 °C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3383, 3052.4, 2927, 2851.9, 1626.7, 1590.7, 1499.7, 1482.5, 1303.8, 1252.3, 1201.5, 1181.7, 1119.8, 1070.9, 1025.2, 950.4, 893.7, 750.5, 695.2, 561.9. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.6 (d, J = 7.3 Hz, 1H), 7.4 (d, J = 7.8 Hz, 1H), 7.3 (m, 1H), 7.2 (m, 2H), 7.13 (m, 2H), 7.0 (t, J = 7.3 Hz, 2H), 6.81 (m, 2H), 6.67 (d, J = 7.8 Hz, 2H), 6.44, (d, J = 7.8 Hz, 2H), 5.99 (d, J = 7.8 Hz, 1H), 5.29 (br s, 1H), 3.99 (br s, 1H), 3.61 (br s, 1H), 2.17 (d, J = 9.8 Hz, 1H), 2.06 (d, J = 10.8 Hz, 1H), 1.72 (m, 1H), 1.61(m, 2H), 1.41 (m, 2H), 1.27 (d, J = 8.3 Hz, 1H), 1.12 (m, 2H) ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 155.1, 150.4, 147.4, 138.8, 137.9, 133.1, 129.9, 129.4, 129.3, 128.7, 127.8, 125.5, 122.3, 121.7, 119.6, 118.5, 117.3, 115, 113.8, 59.4, 48.8, 33.2, 32.6, 25.9, 25.1, 24.9.

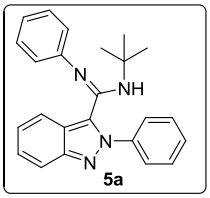


2-(4-fluorophenyl)-N-tert-butyl-N'-phenyl-2-(phenylamino) acetimidamide (4o):[2] Pale yellow solid (70%), Mp 70-72 °C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3382.2, 3052.7, 2962.1, 1636.4, 1590.9, 1499.3, 1485.9, 1360.4, 1263.3, 1182.1, 1091, 896.3, 734, 699.8, 545.4. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.23 (m, 4H), 7.06 (m, 4H), 6.84 (m, 2H), 6.68 (d, *J* = 7.8 Hz, 2H), 6.49 (d, *J* = 7.3 Hz, 2H), 7.01 (t, *J* = 7.8 Hz, 2H), 6.85 (t, *J* = 7.3 Hz, 1H), 6.79 (m, 1H), 6.7 (d, *J* = 7.8 Hz, 2H), 6.41, (d, *J* = 7.3 Hz, 2H), 5.85 (s, 1H), 4.91 (s, 1H), 3.66 (s, 1H), 1.45 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 153.5, 150.4, 146.9, 138.3, 134.2, 129.5, 129.4, 129, 128.6, 122.2, 121.3, 119.6, 113.8, 59.2, 51, 28.4.



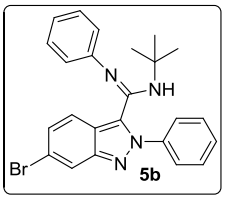
4p

N-tert-butyl-2-(furan-2-yl)N'-phenyl-2-(phenylamino) acetimidamide (4p):[2] Pale yellow solid (74%), Mp 104-106 °C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3385.7, 3025.4, 2962.1, 2927.1, 1641.7, 1591.7, 1501.1, 1360.5, 1245.6, 1183.9, 1070.3, 745.9, 696.7. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.33 (s, 1H), 7.22 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 2H), 6.85 (dt, J_a = 10.8, J_b = 7.3 Hz, 2H), 6.68 (m, 4H), 6.27 (d, *J* = 3.4 Hz, 2H), 5.73 (br s, 1H), 5.04 (s, 1H), 3.98 (br s, 1H), 1.43 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 152.2, 151.9, 150.4, 146.7, 142.4, 129.3, 128.6, 121.9, 121.4, 119.5, 113.9, 110.5, 108.9, 53.5, 51, 28.3.

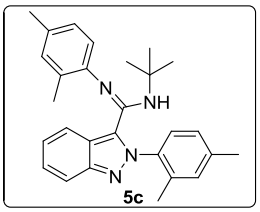


5a

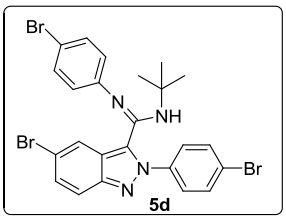
N-tert-butyl-N'2-diphenyl-2H-indazole-3-carboximidamide (5a): white solid (75%), Mp 130-131 °C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3402.1, 3284.1, 3057, 2962.5, 2927, 1617.9, 1502.3, 1451.1, 1363.2, 1309.5, 1250.2, 1218.5, 1192.6, 1120.78, 1072.1, 907.8, 832.8, 751, 690.5. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.74 (dd, J_a = 10.5, J_b = 9 Hz, 2H), 7.33 (m, 4H), 7.22 (m, 4H), 6.73 (m, 2H), 6.66 (d, *J* = 6.8 Hz, 1H), 5.96 (d, *J* = 7.8 Hz, 2H), 4.75 (s, 1H), 1.6 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 128.7, 128.3, 128, 126.9, 124, 123, 121.4, 121.3, 119.5, 118, 52.7, 28.8. HR-MS (ESI+) m/z calculated for $[C_{24}H_{25}N_4]^+ = [M+H]^+$: 369.2074; found: 369.2084.



6-bromo- N-tert-butyl-N'2-diphenyl-2H-indazole-3-carboximidamide (5b): Red solid (70%), Mp 170-171 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3406, 2962.7, 2928.3, 1620.5, 1592.5, 1502.9, 1362.7, 1275.4, 1218.7, 908, 757.4, 693.3. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.69 (d, *J* = 8.8 Hz, 1H), 7.33 (m, 4H), 7.24 (t, *J* = 6.1 Hz, 2H), 6.86 (m, 2H), 6.74 (m, 2H), 6.66 (m, 1H), 5.97 (d, *J* = 7.8 Hz, 2H), 4.7 (s, 1H), 1.58 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 148.9, 148, 145, 139.4, 139.1, 129, 128.8, 128.5, 128, 123.9, 121.6, 121.4, 121.3120.9, 117, 105.7, 52.8, 28.7. HR-MS (ESI+) m/z calculated for $[C_{24}H_{24}BrN_4]^+$ = $[M+H]^+$: 447.1179; found: 447.1169.

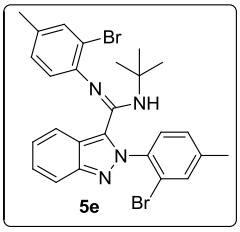


N-tert-butyl-N'2-bis(2,4-dimethylphenyl)-2H-indazole-3-carboximidamide (5c): Brown solid (69%), Mp 180-181 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3403.3, 2958.3, 2923.6, 2855.3, 1633.9, 1511.9, 1451.2, 1362.9, 1218.9, 1102.3, 814.9, 747.1, 567.6. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.74 (d, *J* = 8.3 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.29 (m, 1H), 7.16 (m, 1H), 6.89 (s, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.58 (s, 1H), 6.32 (d, *J* = 7.8 Hz, 1H), 5.74 (d, *J* = 7.8 Hz, 1H), 4.55 (s, 1H), 2.28 (s, 3H), 2.04 (s, 3H), 1.47 (s, 9H), 1.47 (s, 3H), 1.33 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 148, 145, 144, 138.9, 136, 132, 131.5, 131, 130, 126.5, 126.4, 126.2, 126.1, 122.8, 122, 119.6, 119.5, 118, 52.5, 21, 20.6, 17.4, 16.9. HR-MS (ESI+) m/z calculated for $[C_{28}H_{33}N_4]^+$ = $[M+H]^+$: 425.2700; found: 425.2715.

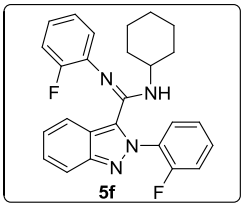


5-bromo-N',2-bis(4-bromophenyl)-N-tert-butyl-2H-indazole-3-carboximidamide (5d): White solid (71%), Mp 175-177 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3410.5, 3293.7, 2961.7, 1627.1, 1616.7, 1493.8, 1390.9, 1316.9, 1249.9, 1216.3, 1190.6, 1070.1, 1010.3, 826.6, 803.2, 709.2. ^{1}H NMR ($CDCl_3$,

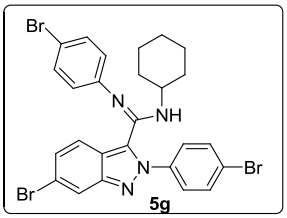
400 MHz): δ_H = 7.85 (d, *J* = 1 Hz, 1H), 7.6 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.3 Hz, 2H), 5.76 (d, *J* = 8.8 Hz, 2H), 4.87 (s, 1H), 1.62 (br. s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 147.8, 146.8, 145, 138, 131.9, 131, 130.9, 127.6, 125, 124, 122.9, 122.7, 121, 120, 117, 114.6, 53, 28.7. HR-MS (ESI+) m/z calculated for $[C_{24}H_{22}Br_3N_4]^+$ = $[M+H]^+$: 604.9387; found: 604.9370.



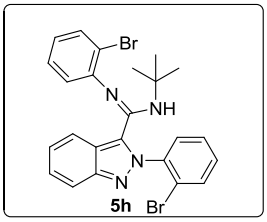
N',2-bis(2-bromo-4-methylphenyl)-N-tert-butyl-2H-indazole-3-carboximidamide (5e): White solid (65%), Mp 162-163 °C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3416.8, 3057.3, 2959. 9, 2921.7, 1616, 1505.9, 1481.3, 1361.9, 1247.8, 1215, 1195.4, 1037.4, 901.9, 812.7, 735.2, 702.9, 600.5. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.76 (dd, J_a = 19.8, J_b = 8.6 Hz, 2H), 7.44 (s, 1H), 7.36 (m, 1H), 7.21 (m, 1H), 7.13 (s, 1H), 6.95 (d, *J* = 7.3, 1H), 6.54 (m, 1H), 6.39 (br. s, 1H), 5.9 (d, *J* = 7.8, 1H), 4.83 (s, 1H), 2.42 (s, 3H), 2.15 (s, 3H), 1.52 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 148.4, 145.1, 145, 141.6, 136.4, 133.2, 132.8, 132.5, 130.9, 128.6, 128.2, 128, 127.1, 123.4, 122.3, 120.8, 120.1, 120, 118.3, 52.7, 28.8, 21.01, 20.3. HR-MS (ESI+) m/z calculated for $[C_{26}H_{27}Br_2N_4]^+$ = $[M+H]^+$: 553.0597; found: 553.0589.



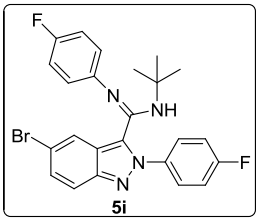
N-cyclohexyl-N'2-bis(2-fluorophenyl)-2H-indazole-3-carboximidamide (5f): Brown solid (62%), Mp 132-134 °C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3397.2, 3271.4, 2928.5, 2853.2, 1608.5, 1511.9, 1493.8, 1367.8, 1218.5, 1152, 1093.3, 832.7, 801.2, 748.7, 681.1, 625.4. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.7 (dd, J_a = 12, J_b = 8.6 Hz, 2H), 7.35 (d, *J* = 15.7 Hz, 1H), 7.15 (m, 1H), 7.06 (m, 2H), 6.98 (m, 2H), 6.43 (t, *J* = 8.8 Hz, 2H), 5.84 (dd, J_a = 8.3, J_b = 4.9 Hz, 2H), 5.04 (d, *J* = 7.8 Hz, 1H), 4.13 (m, 1H), 2.28 (br. s, 1H), 1.82 (d, *J* = 11.2 Hz, 2H), 1.7 (m, 1H), 1.38 (m, 4) ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 163.6, 161, 159.6, 157, 148, 146.9, 145, 135.6, 127.8, 127, 125.5, 123.5, 123, 122.5, 119, 118, 115.8, 115.6, 114.6, 49.9, 33, 32.7, 29.7, 25.8, 25, 24.9. HR-MS (ESI+) m/z calculated for $[C_{26}H_{25}F_2N_4]^+$ = $[M+H]^+$: 431.2024; found: 431.2064.



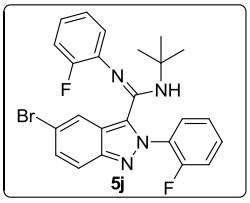
6-bromo-N', 2-bis(4-bromophenyl) N-cyclohexyl -2H-indazole-3-carboximidamide (5g) : Brown solid (75%), Mp 160-162 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3399.6, 3269.8, 2926.4, 2852.5, 1609.9, 1492.7, 1341.7, 1316.9, 1248.4, 1204.8, 1128.4, 1070.1, 1009.7, 826, 803.3, 737.6, 566.3. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.87 (s, 1H), 7.61 (d, *J* = 9.3 Hz, 1H), 7.41 (d, *J* = 1.5 Hz, 3H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.77 (d, *J* = 8.8 Hz, 2H), 4.98 (d, *J* = 7.3 Hz, 1H) 4.12 (d, *J* = 4.9 Hz, 1H), 2.29 (br. s, 2H), 1.84 (d, *J* = 12.2 Hz, 2H), 1.71 (m, 2H), 1.38 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 147.7, 146.9, 146, 138, 132, 131.2, 131, 127, 125.2, 124, 123, 122.8, 121, 120, 117.5, 114.8, 50, 33, 32.6, 25.7, 24.9. HR-MS (ESI+) m/z calculated for $[C_{26}H_{24}Br_3N_4]^+$ = $[M+H]^+$: 630.9536; found: 630.9526.



N'2-bis(2-bromophenyl)-N-tert-butyl-2H-indazole-3-carboximidamide(5h): Brown solid (58%), Mp 120-122 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3415.9, 3059.6, 2959.7, 2923.2, 1616.3, 1579..4, 1507.4, 1465.2, 1363.7, 1216.5, 1194.6, 1072.9, 1025.3, 898.3, 747.5, 656.4. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.8 (d, *J* = 8.3 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.64 (dd, *J* = 8.3 Hz, 1H), 7.31 (m, 4H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.75 (td, *J* = 7.6, *J* = 1.5 Hz, 1H), 6.65 (td, *J* = 7.6, *J* = 1.5 Hz, 1H), 6.01 (dd, *J* = 7.8, *J* = 1 Hz), 4.91 (s, 1H), 1.53 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 148.5, 147.6, 145, 139, 132.9, 132.6, 131, 130.6, 128.7, 128, 127.3, 12.6, 122.8, 122, 121, 120.5, 120, 119.9, 118, 52.9, 28.8. HR-MS (ESI+) m/z calculated for $[C_{24}H_{23}Br_2N_4]^+$ = $[M+H]^+$: 527.0265; found: 527.0292.



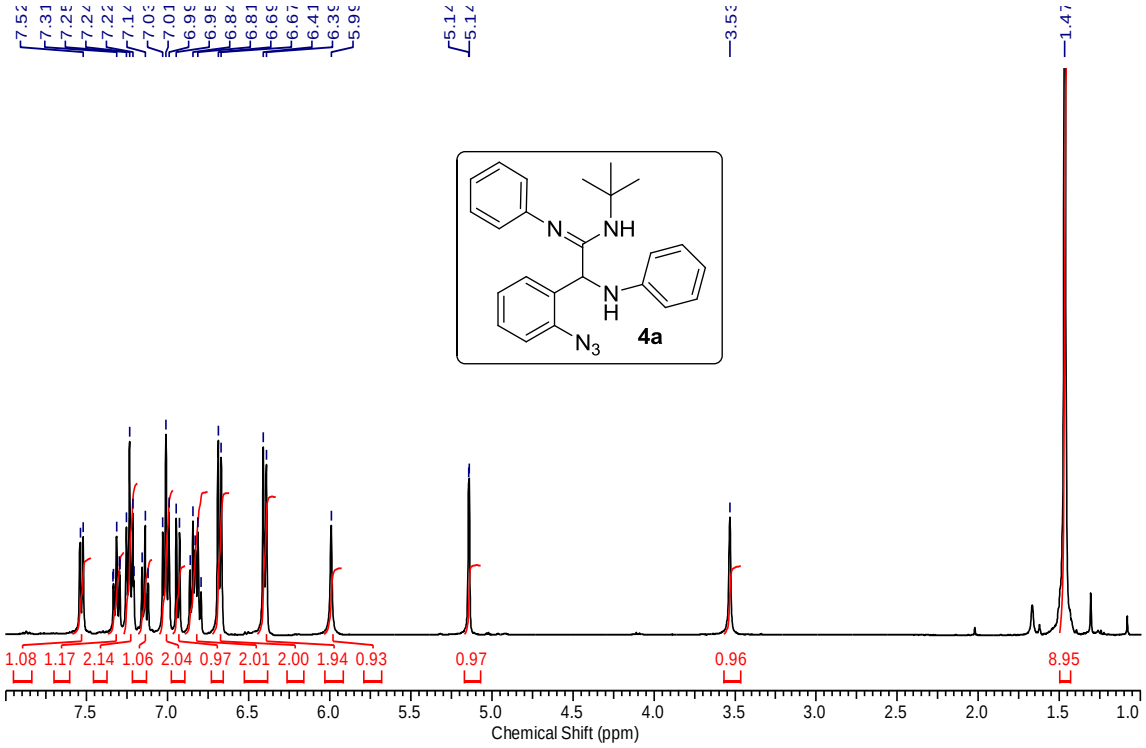
5-bromo-N-tert-butyl-N'-2-bis(4-fluorophenyl)-2H-indazole-3-carboximidamide (5i): Pale yellow solid (65%), Mp 138-140 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3415.1, 2964.1, 2927.7, 1628.1, 1506, 1450.6, 1392, 1362.2, 1316.7, 1250.4, 1216.9, 1093.1, 1060.3, 942.1, 900.2, 848.3, 804.3, 750.6, 672, 607.4. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.95 (d, *J* = 1.5 Hz, 1H), 7.61 (d, *J* = 9.3 Hz, 1H), 7.4 (m, 2H), 7.18 (m, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.86 (m, 1H), 6.61 (m, 3H), 5.96 (m, 1H), 4.84 (s, 1H) 1.57 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 157, 156, 154.6, 153.7, 147, 146, 137, 131, 130.8, 130.6, 127.6, 127.5, 124.6, 123.5, 123, 122.6, 122.5, 122, 119.9, 117, 116, 115, 52.9, 28.6. HR-MS (ESI+) m/z calculated for $[C_{24}H_{22}BrF_2N_4]^+ = [M+H]^+$: 485.0973; found: 485.0988.



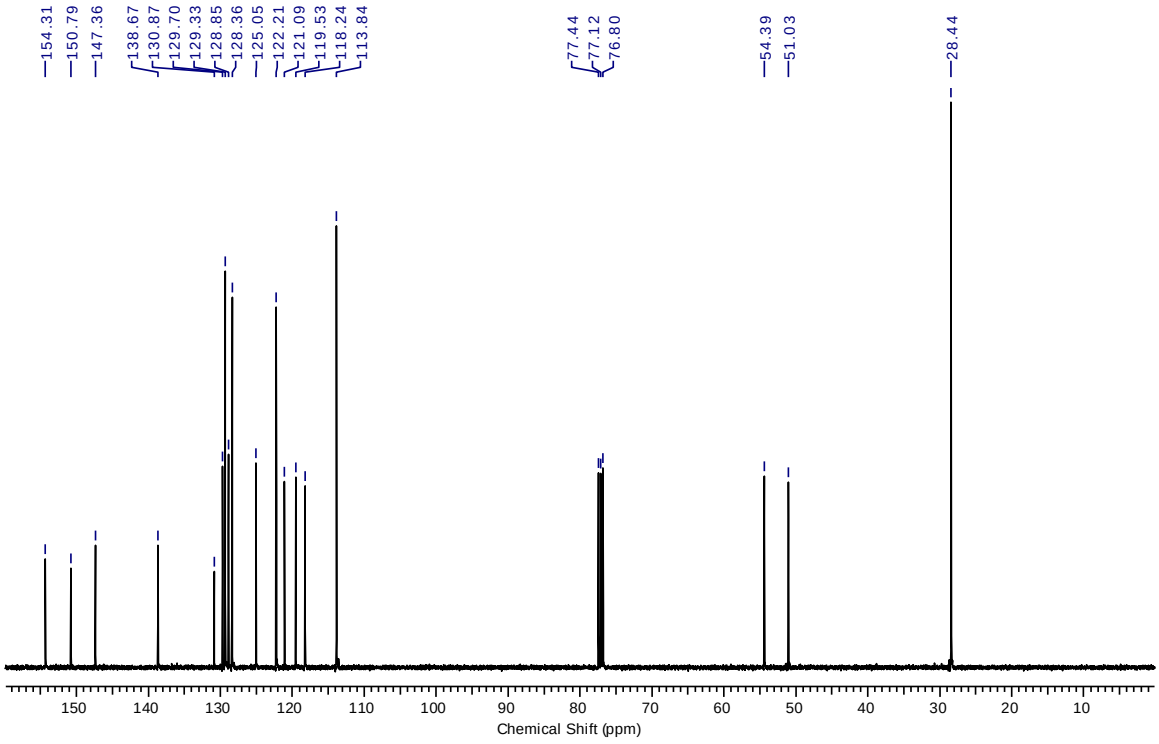
5j

5-bromo-N-tert-butyl-N'-2-bis(4-fluorophenyl)-2H-indazole-3-carboximidamide(5j): Brown solid (69%), Mp 129-131 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3412.4, 3291.6, 2964.5, 2928.7, 1628.3, 1510.5, 1498.7, 1452.2, 1215.7, 1188.7, 1153.8, 1122.1, 1093.4, 1063.4, 901.2, 834.6, 804, 737.9, 663.5, 519.9. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.86 (d, *J* = 1, Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.41 (dd, *J* = 9.3, *J* = 2 Hz, 1H), 7.14 (m, 2H), 7.01 (m, 2H), 6.45 (d, *J* = 17.6 Hz, 2H), 5.84 (m, 2H), 4.81 (s, 1H), 1.6 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 163.8, 161, 159.5, 157, 146.6, 145, 144.8, 135, 131, 127.9, 125.5, 122, 121, 119, 117, 115.8, 115.6, 114.8, 114.5, 53, 28.8. HR-MS (ESI+) m/z calculated for $[C_{24}H_{22}BrF_2N_4]^+ = [M+H]^+$: 485.0973; found: 485.0992.

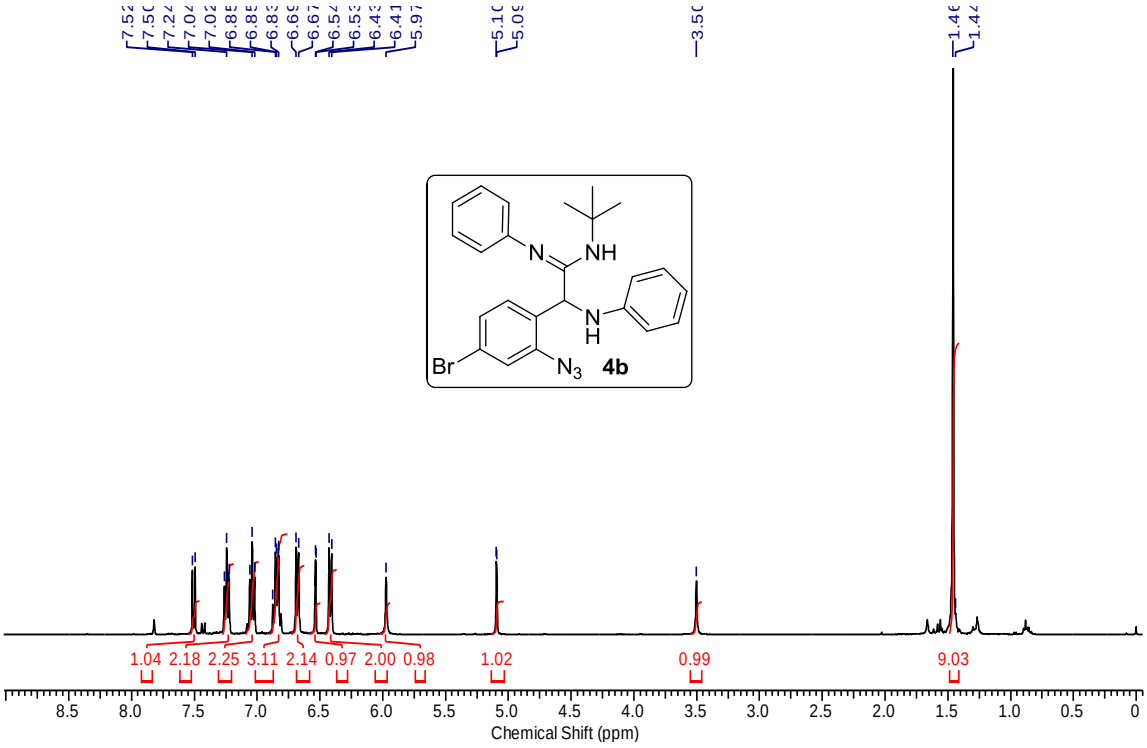
Copies of ^{1}H NMR & ^{13}C NMR Spectra of all Compounds (4a-o & 5a-j)



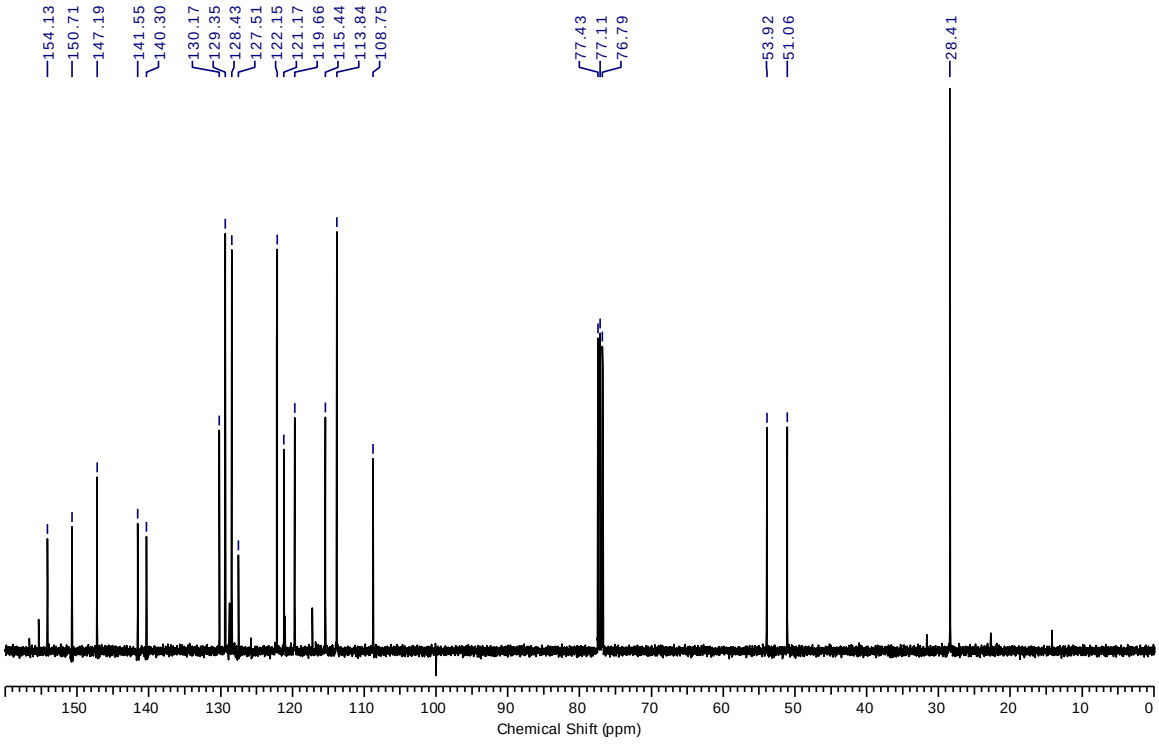
^{1}H NMR (400 MHz) spectrum of compound **4a** in $CDCl_3$



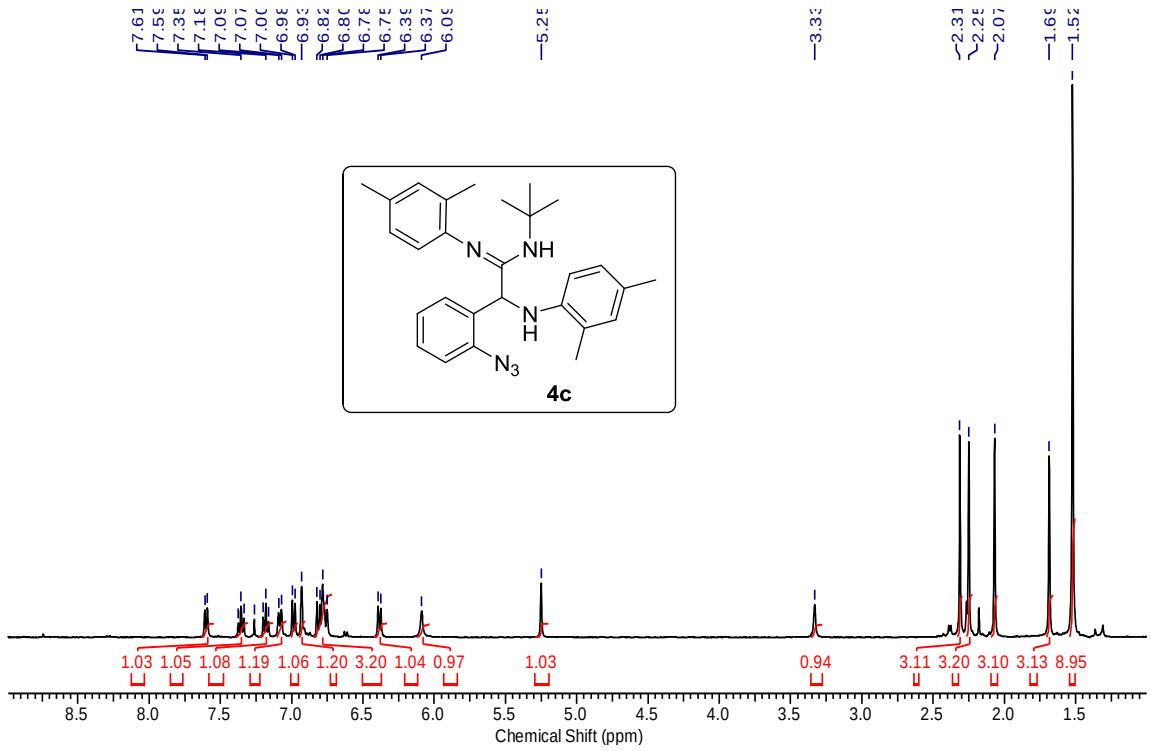
^{13}C NMR (100 MHz) spectrum of compound **4a** in $CDCl_3$



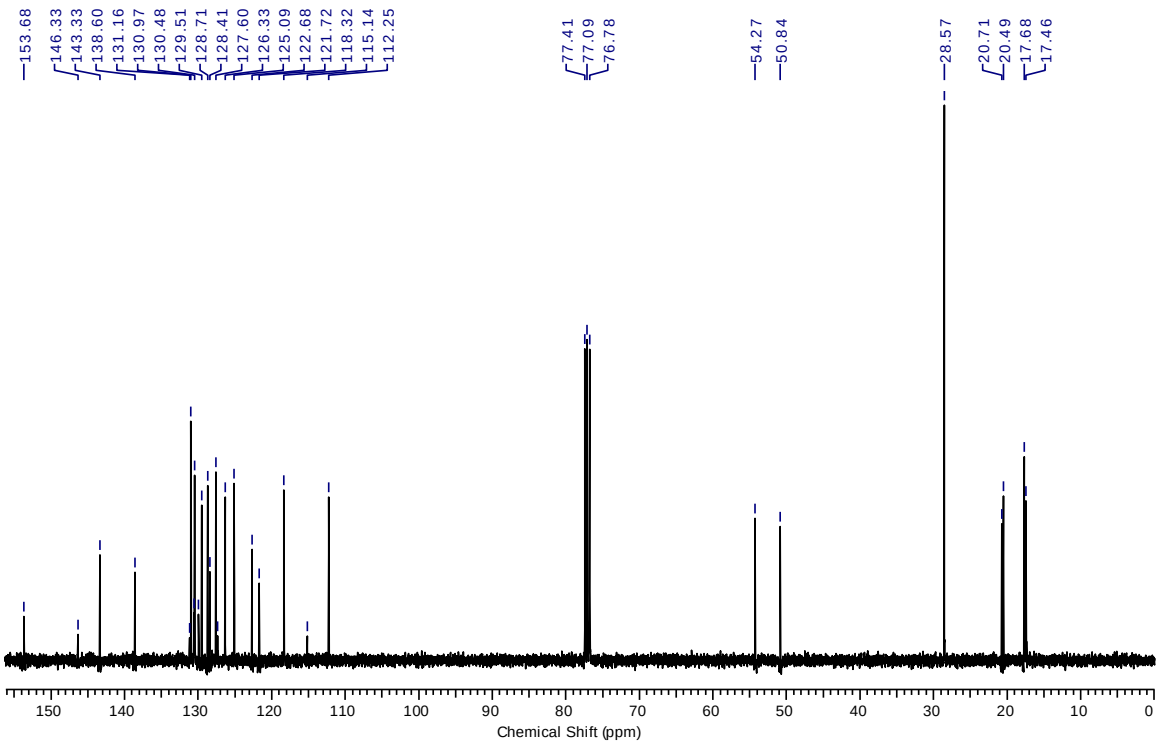
^{1}H NMR (400 MHz) spectrum of compound **4b** in $CDCl_3$



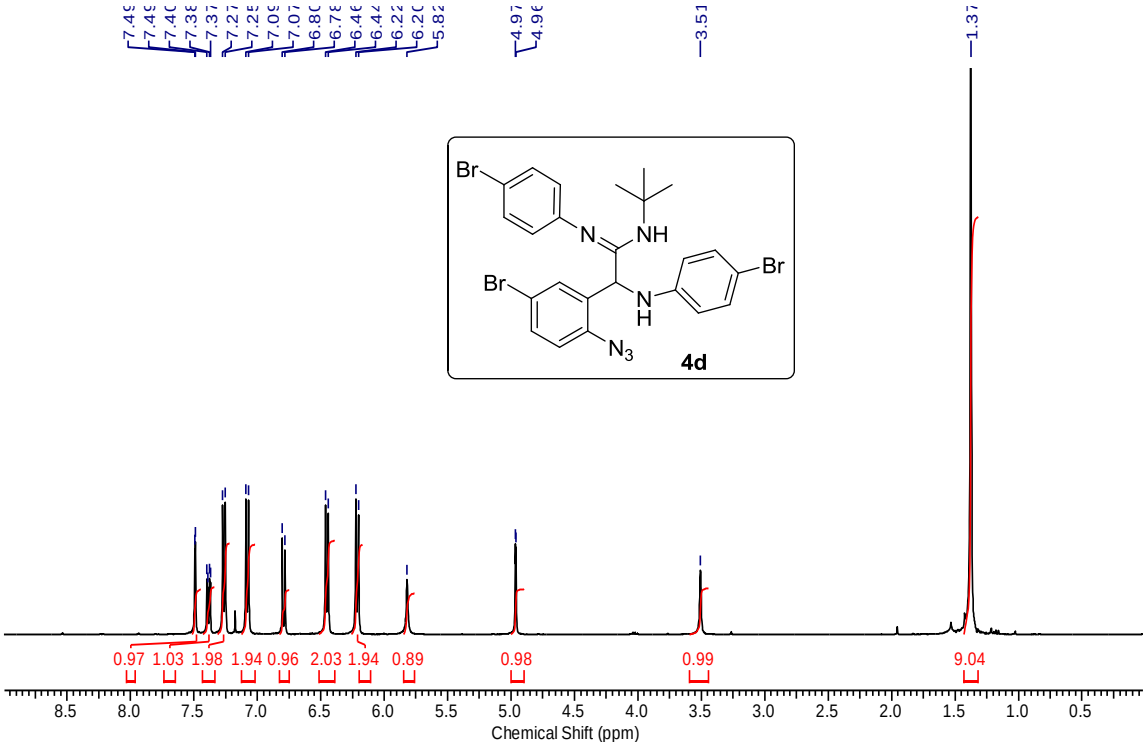
^{13}C NMR (100 MHz) spectrum of compound **4b** in $CDCl_3$



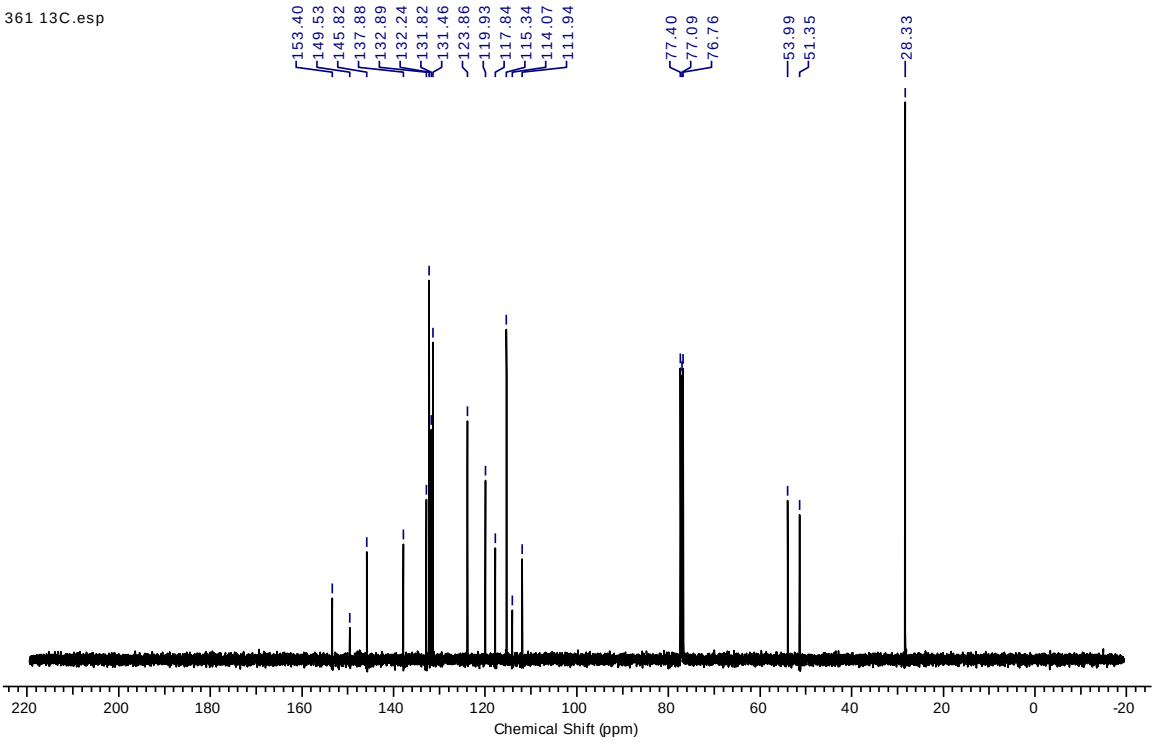
^{1}H NMR (400 MHz) spectrum of compound **4c** in $CDCl_3$



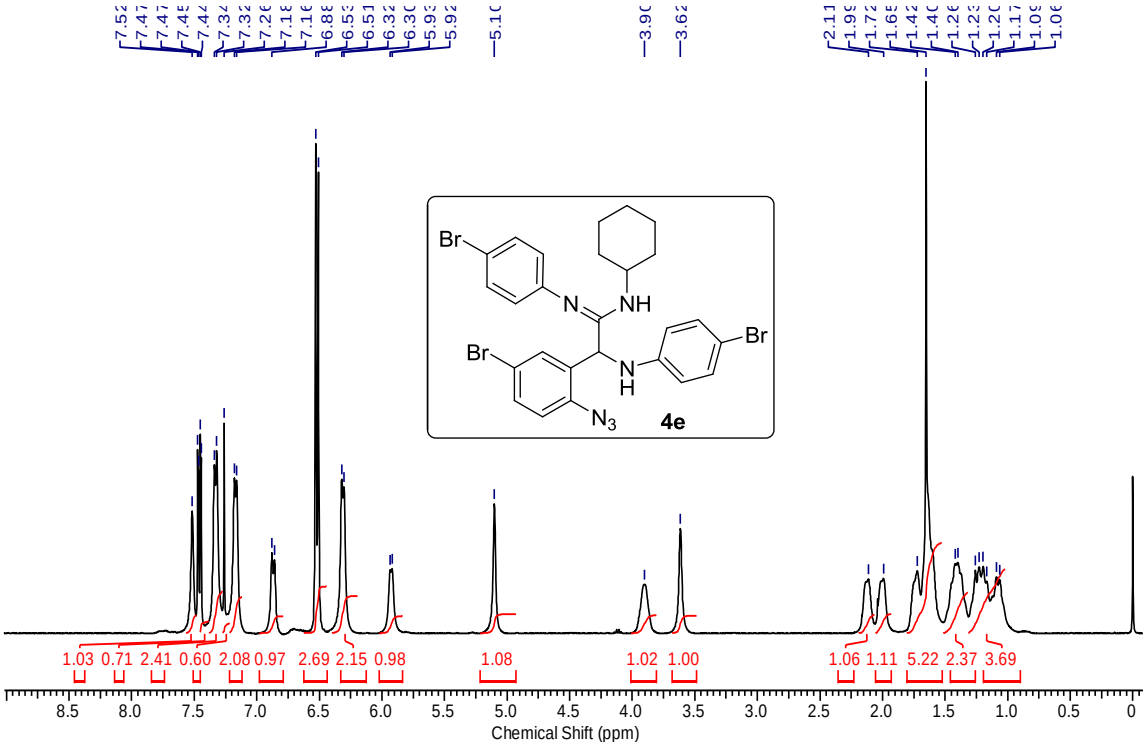
^{13}C NMR (100 MHz) spectrum of compound **4c** in $CDCl_3$



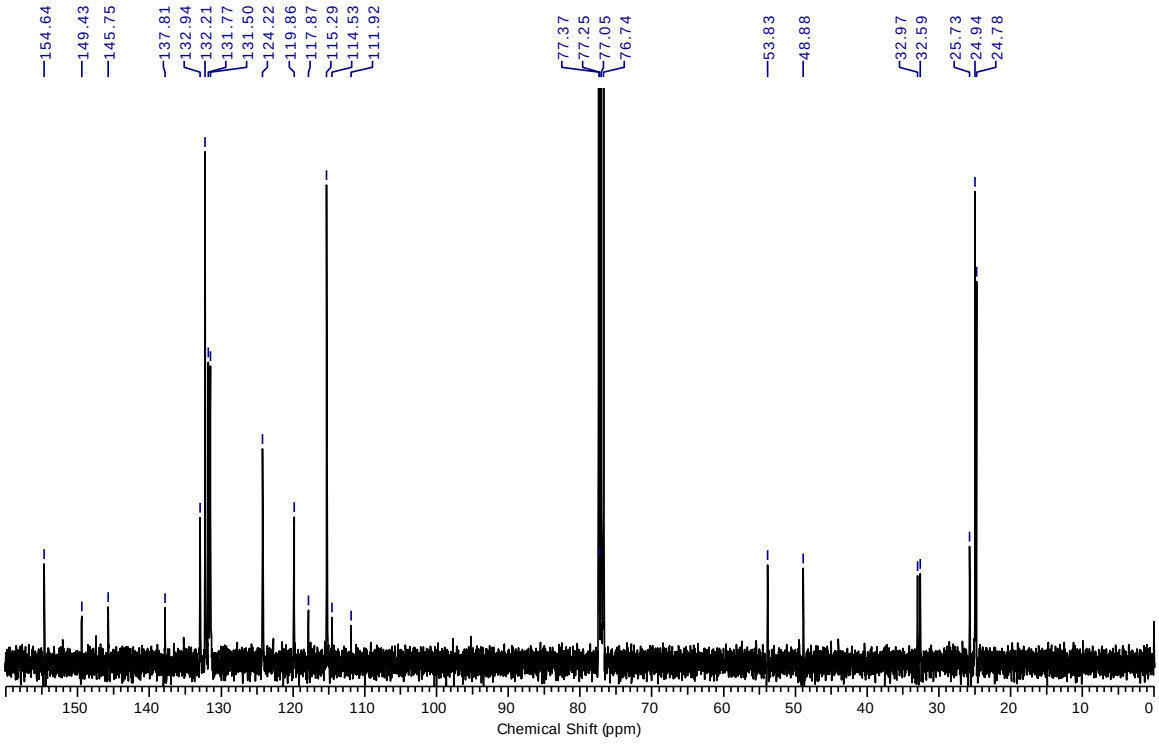
^{1}H NMR (400 MHz) spectrum of compound **4d** in $CDCl_3$



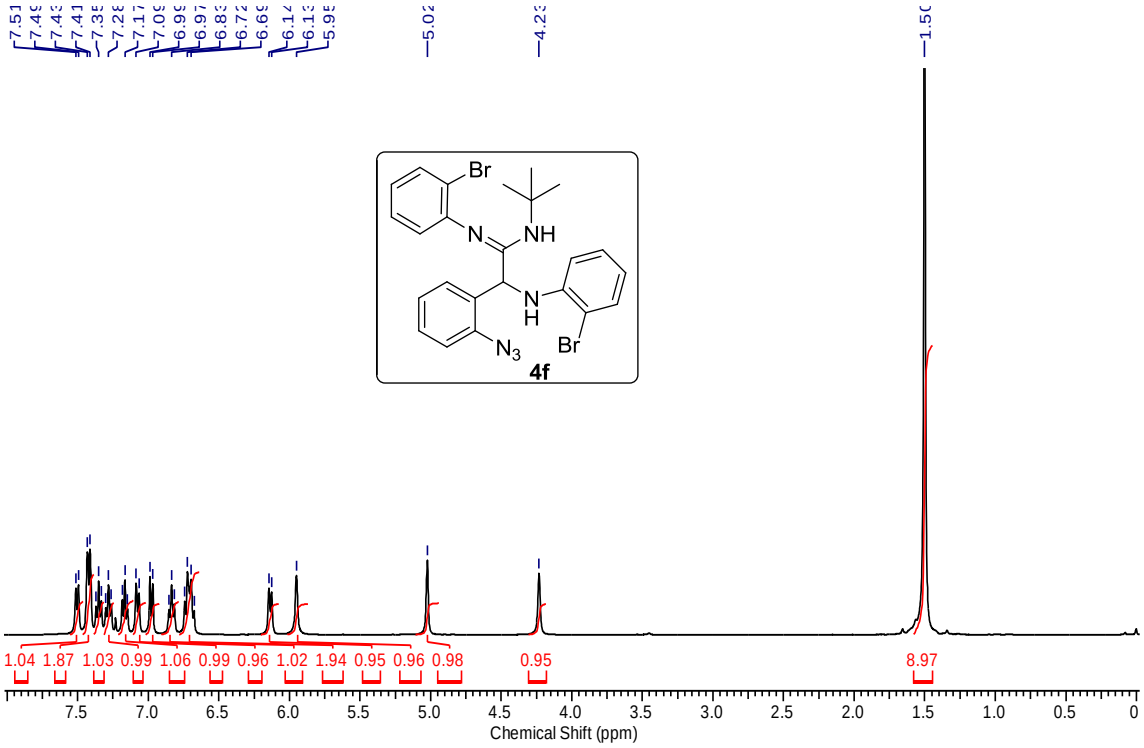
^{13}C NMR (100 MHz) spectrum of compound **4d** in $CDCl_3$



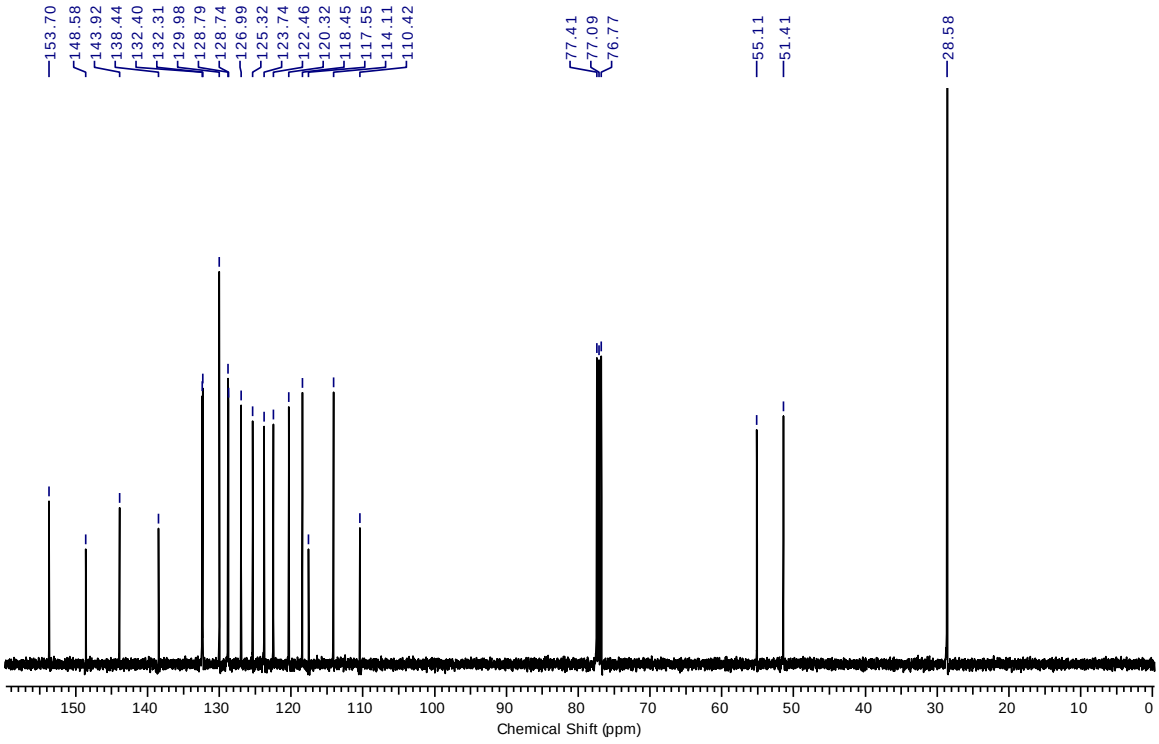
^{1}H NMR (400 MHz) spectrum of compound **4e** in $CDCl_3$



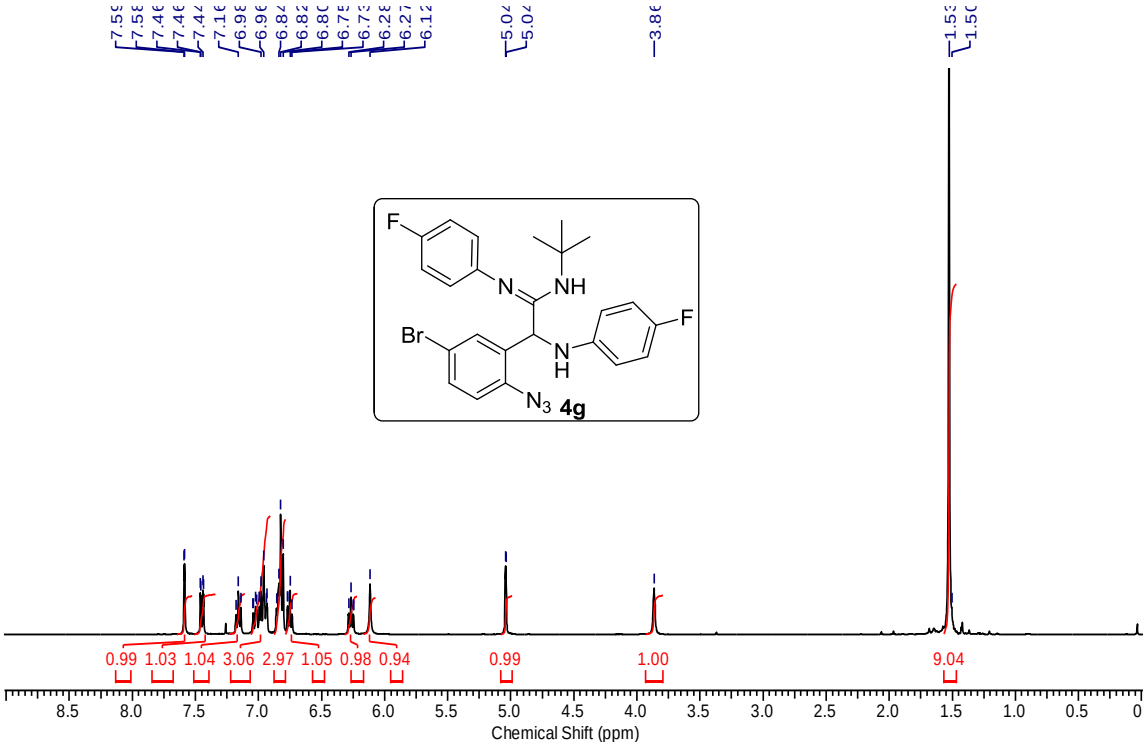
^{13}C NMR (100 MHz) spectrum of compound **4e** in $CDCl_3$



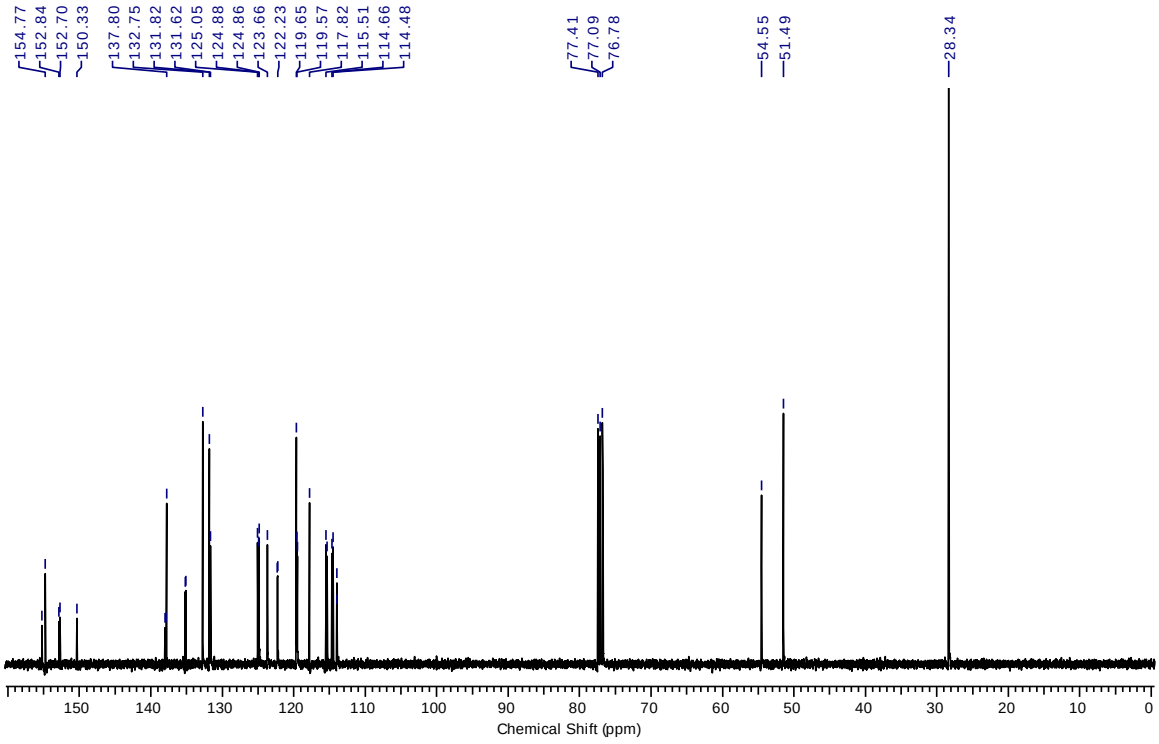
^{1}H NMR (400 MHz) spectrum of compound **4f** in $CDCl_3$



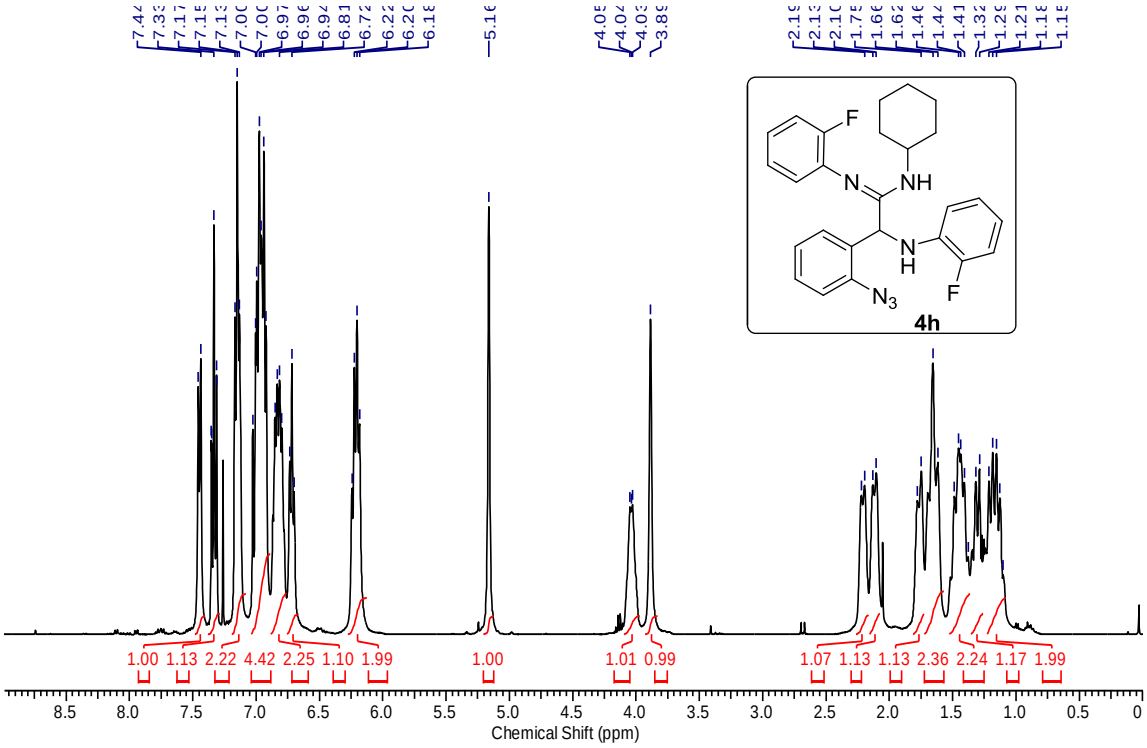
^{13}C NMR (100 MHz) spectrum of compound **4f** in $CDCl_3$



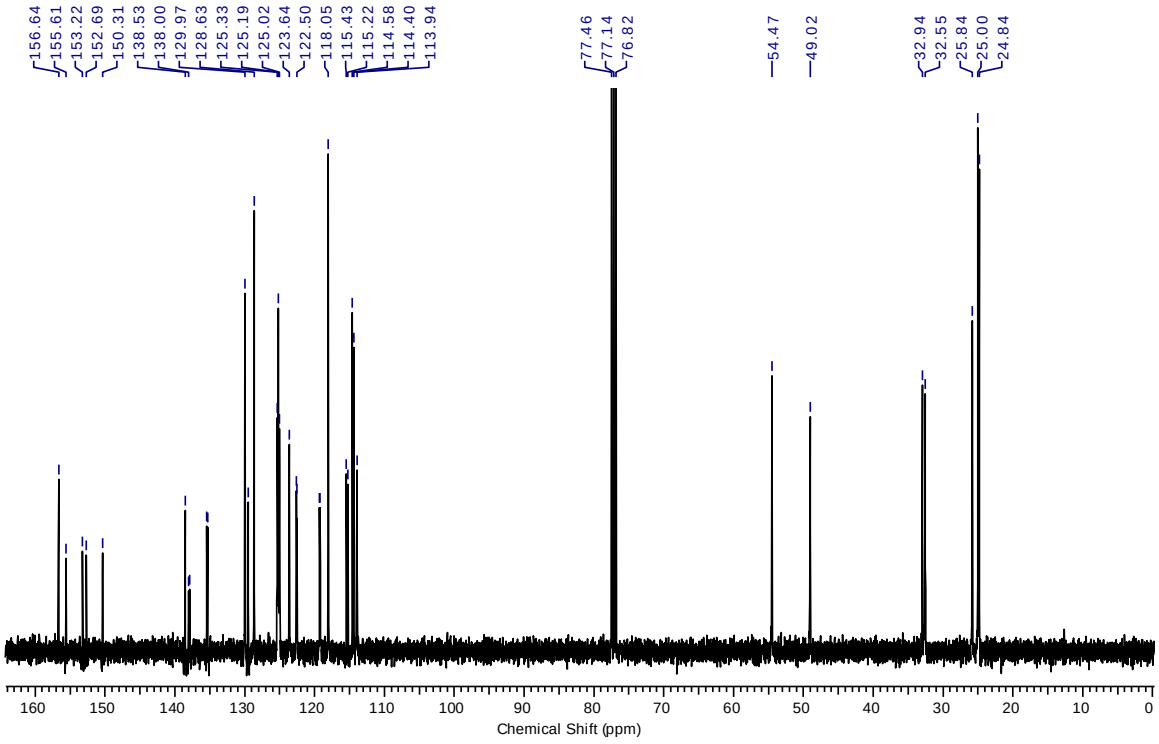
^{1}H NMR (400 MHz) spectrum of compound **4g** in $CDCl_3$



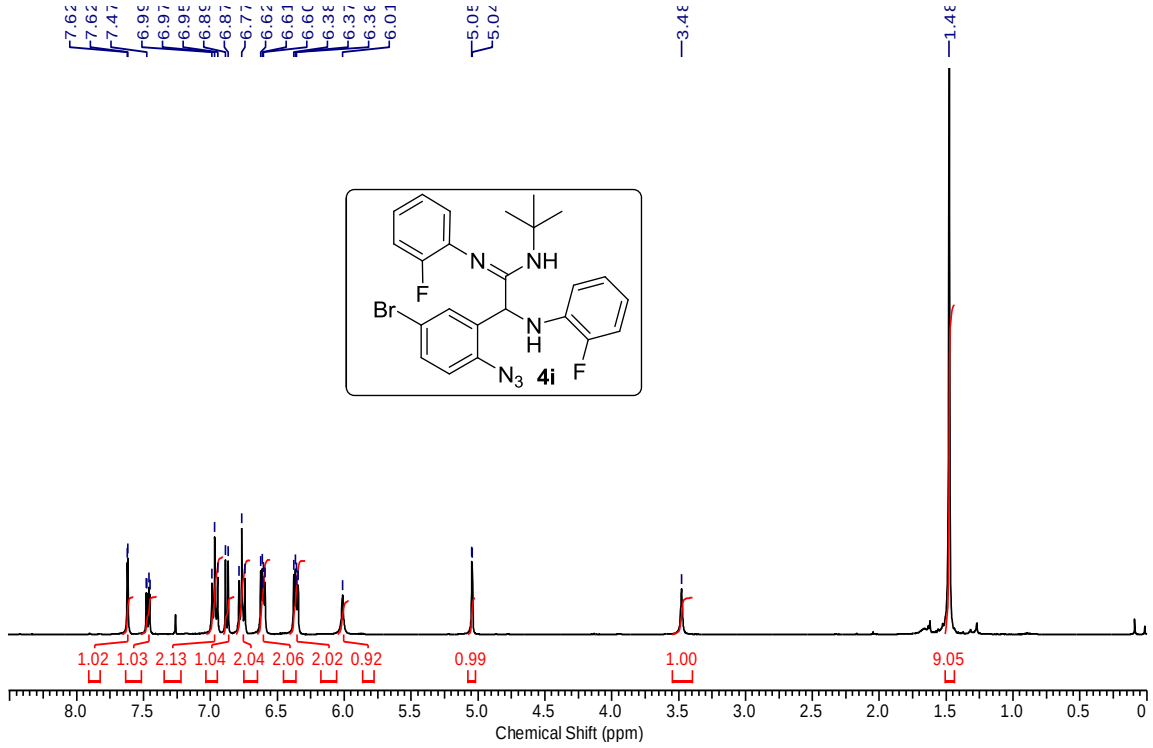
^{13}C NMR (100 MHz) spectrum of compound **4g** in $CDCl_3$



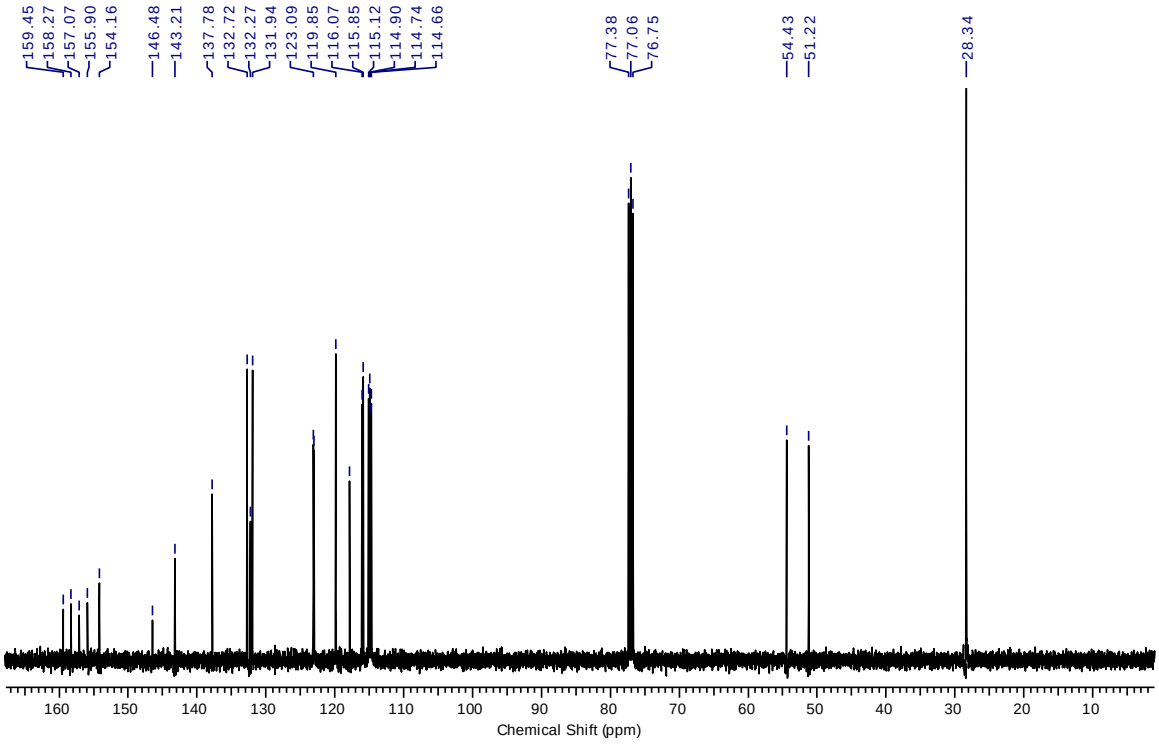
^{1}H NMR (400 MHz) spectrum of compound **4h** in $CDCl_3$



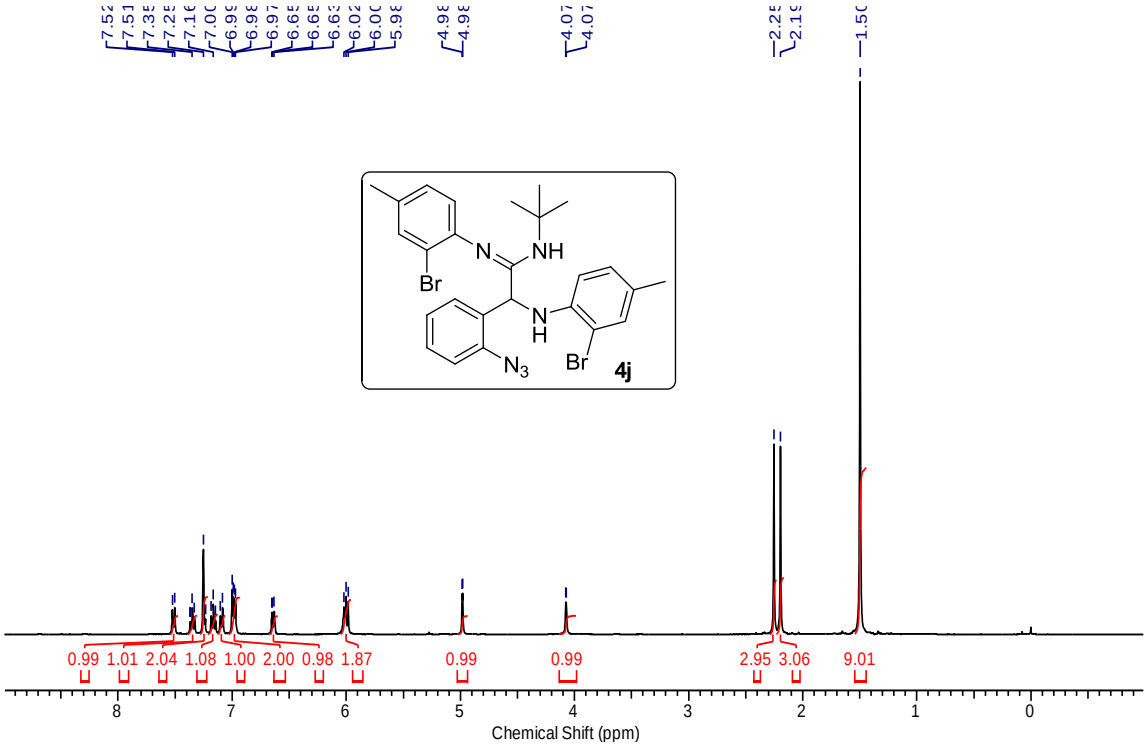
^{13}C NMR (100 MHz) spectrum of compound **4h** in $CDCl_3$



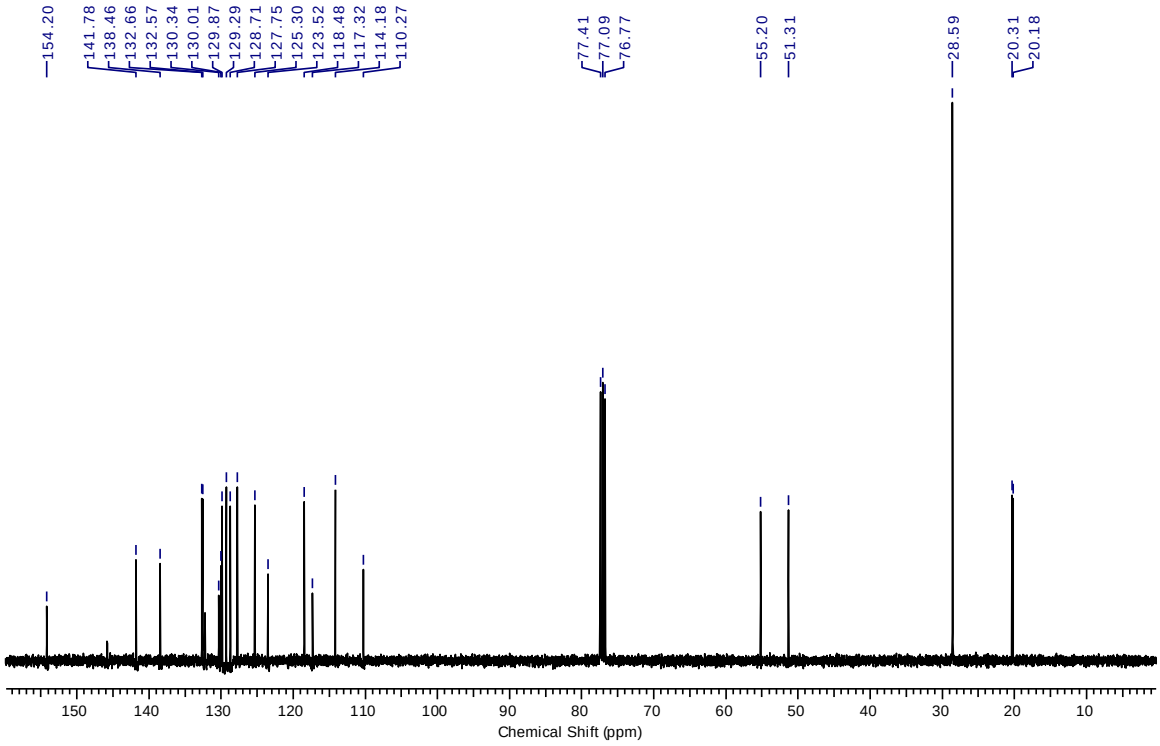
^{1}H NMR (400 MHz) spectrum of compound **4i** in $CDCl_3$



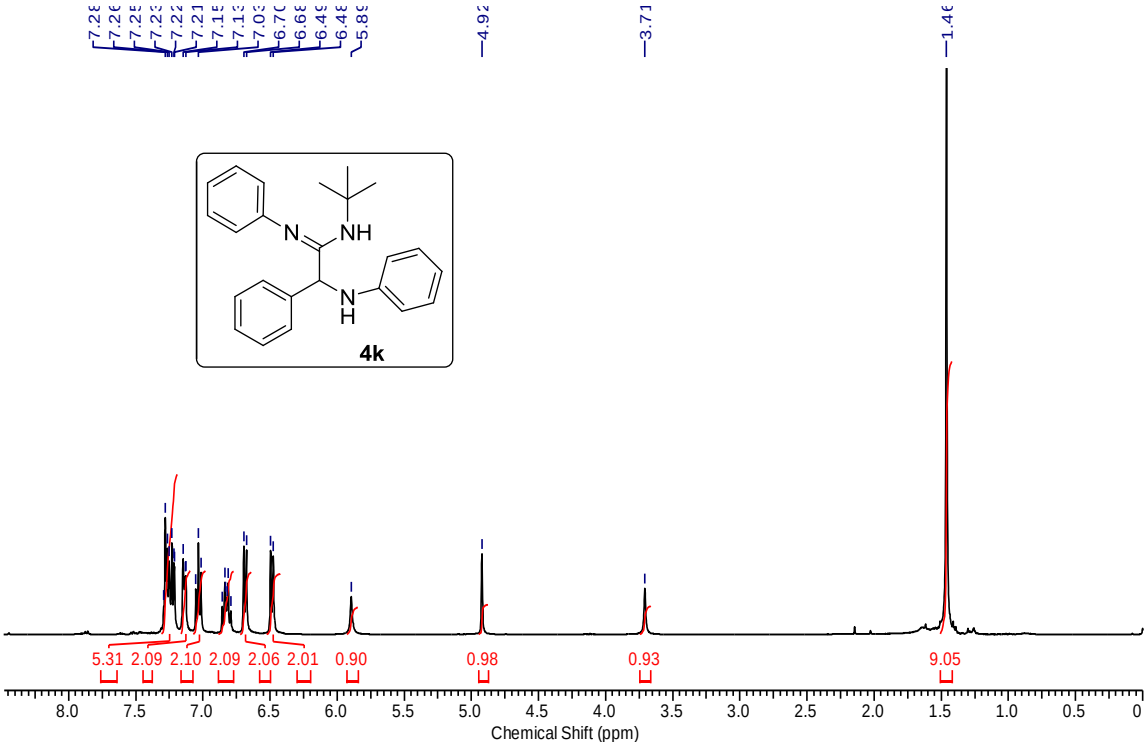
^{13}C NMR (100 MHz) spectrum of compound **4i** in $CDCl_3$



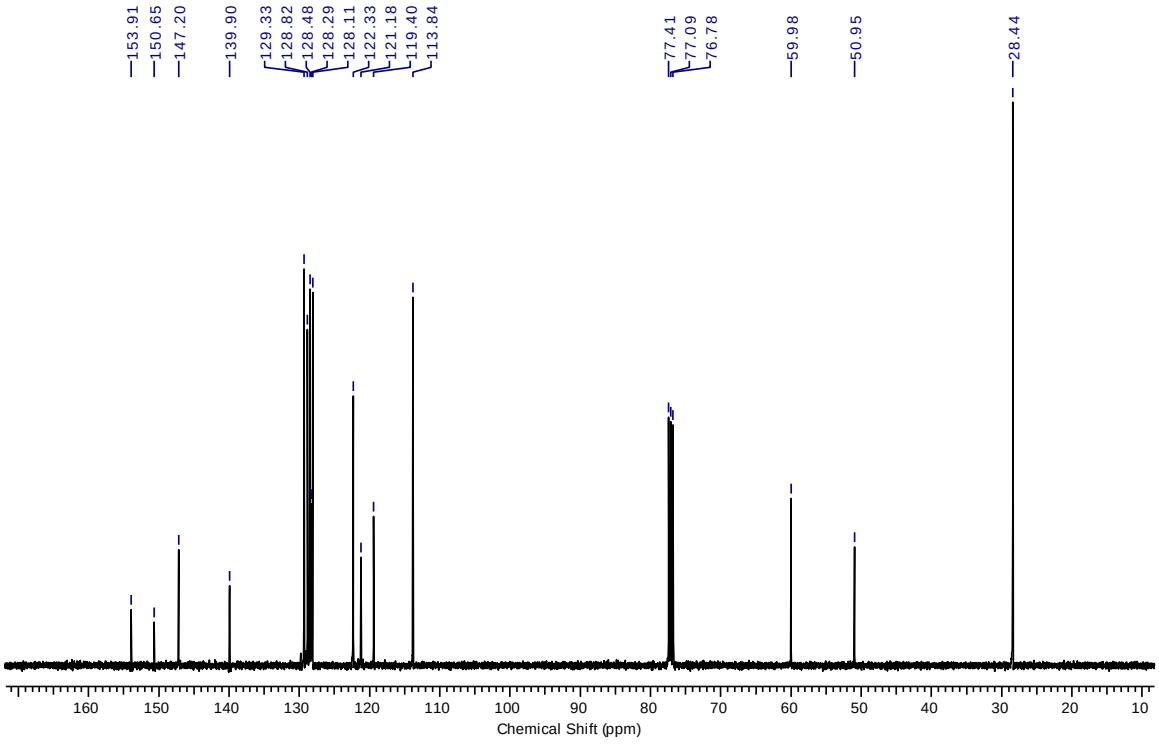
^{1}H NMR (400 MHz) spectrum of compound **4j** in $CDCl_3$



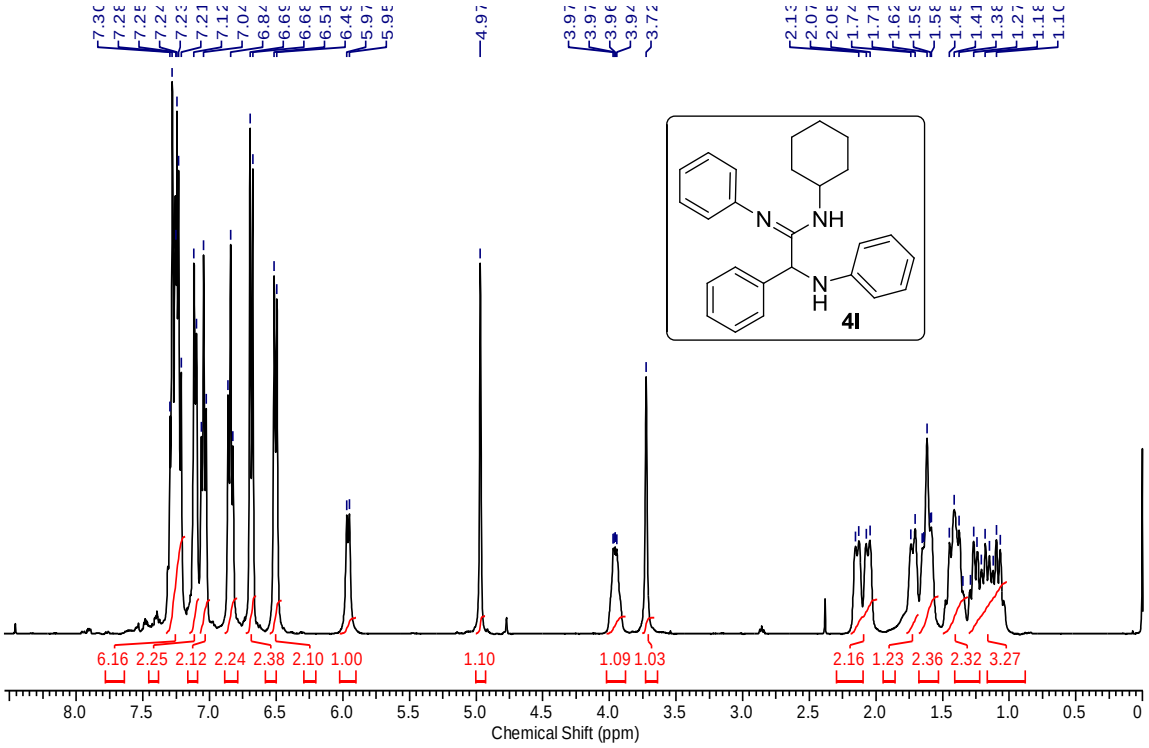
^{13}C NMR (100 MHz) spectrum of compound **4j** in $CDCl_3$



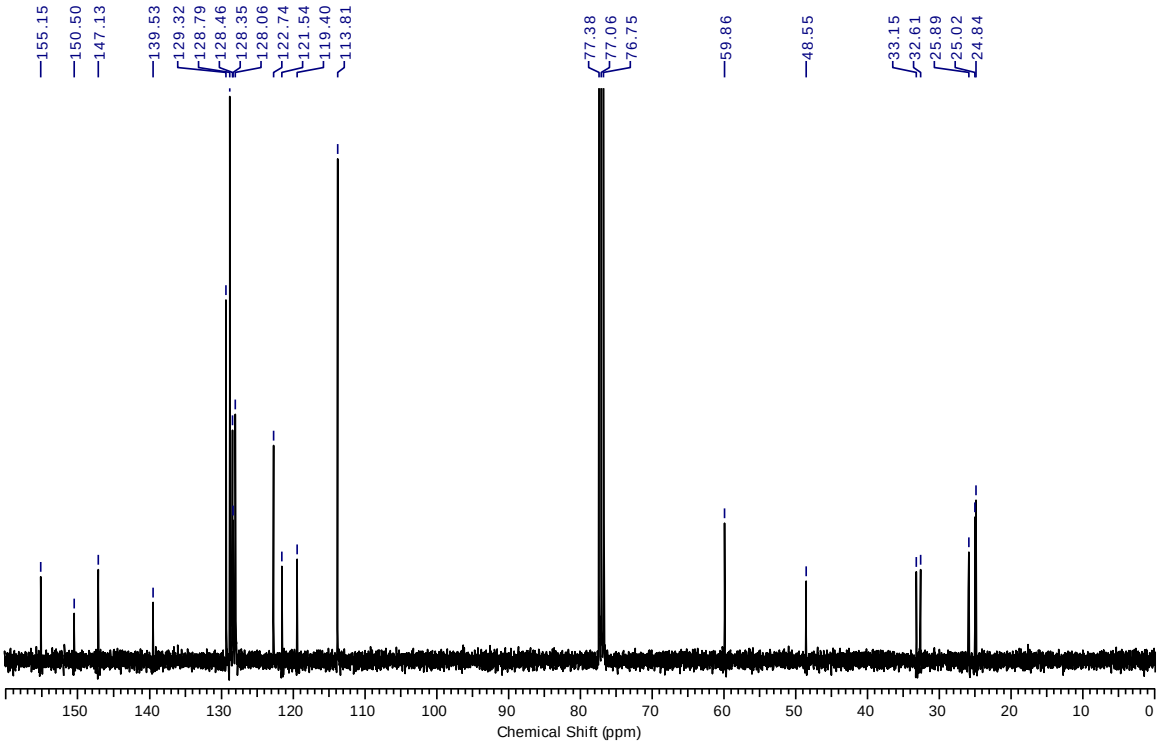
^{1}H NMR (400 MHz) spectrum of compound **4k** in $CDCl_3$



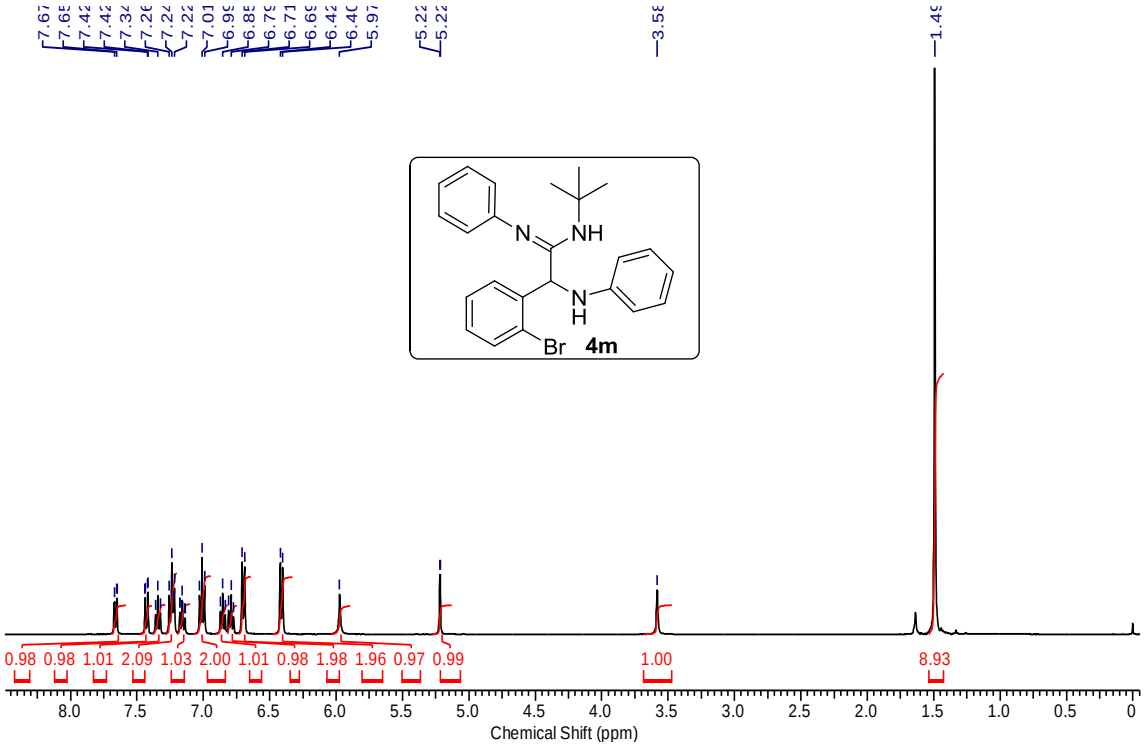
^{13}C NMR (100 MHz) spectrum of compound **4k** in $CDCl_3$



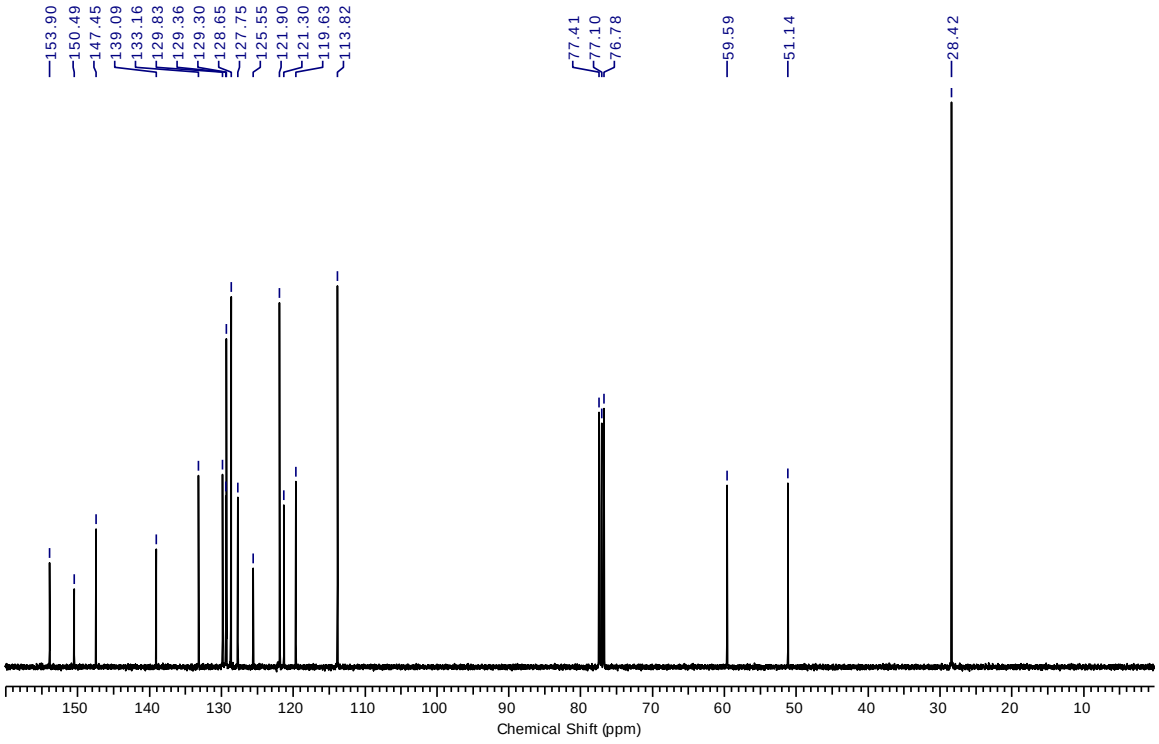
^{1}H NMR (400 MHz) spectrum of compound **4l** in $CDCl_3$



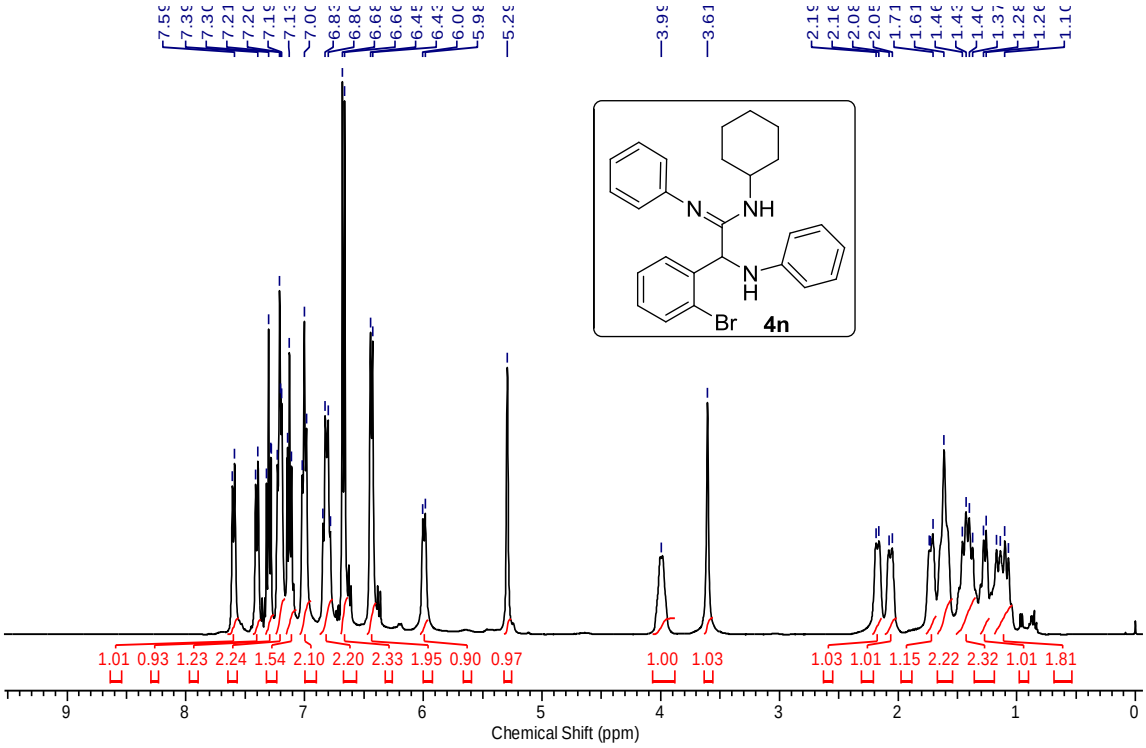
^{13}C NMR (100 MHz) spectrum of compound **4l** in $CDCl_3$



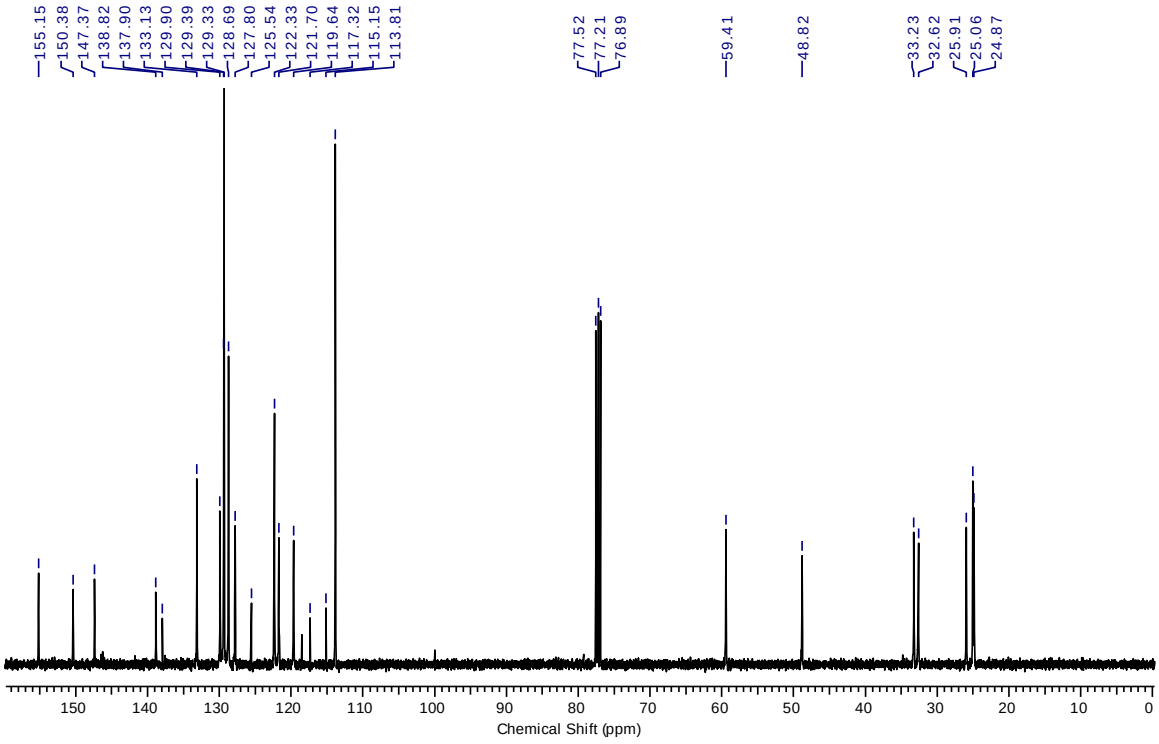
^{1}H NMR (400 MHz) spectrum of compound **4m** in $CDCl_3$



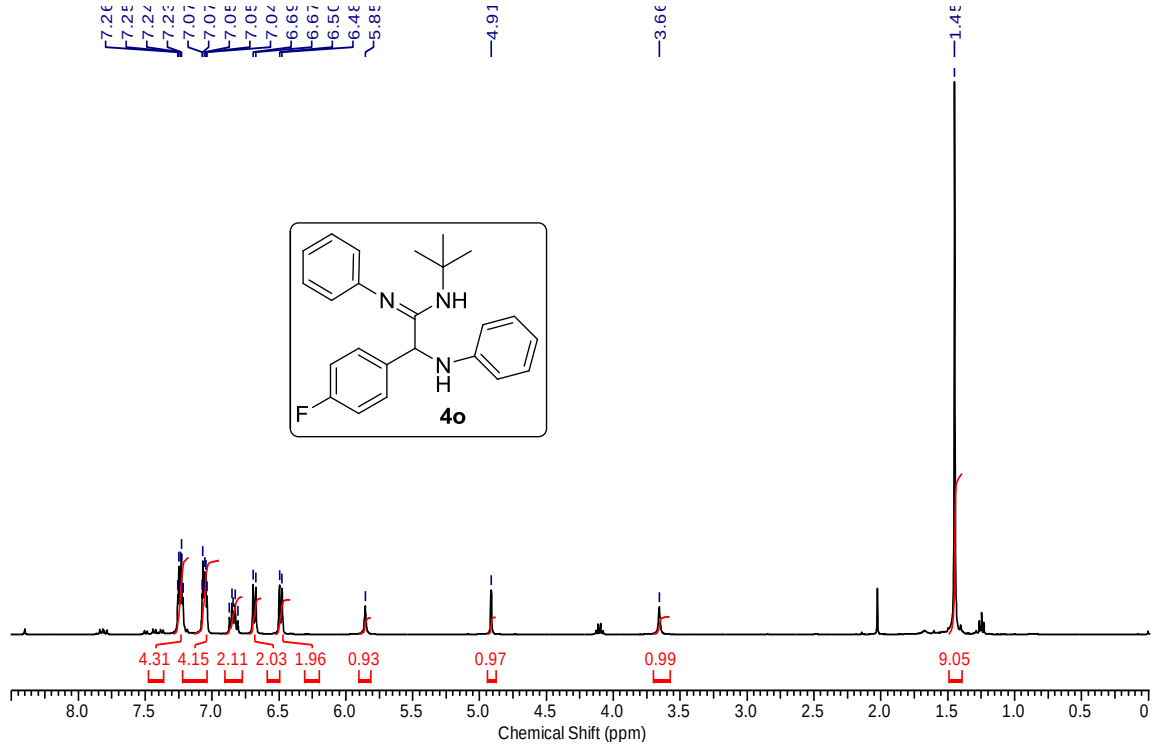
^{13}C NMR (100 MHz) spectrum of compound **4m** in $CDCl_3$



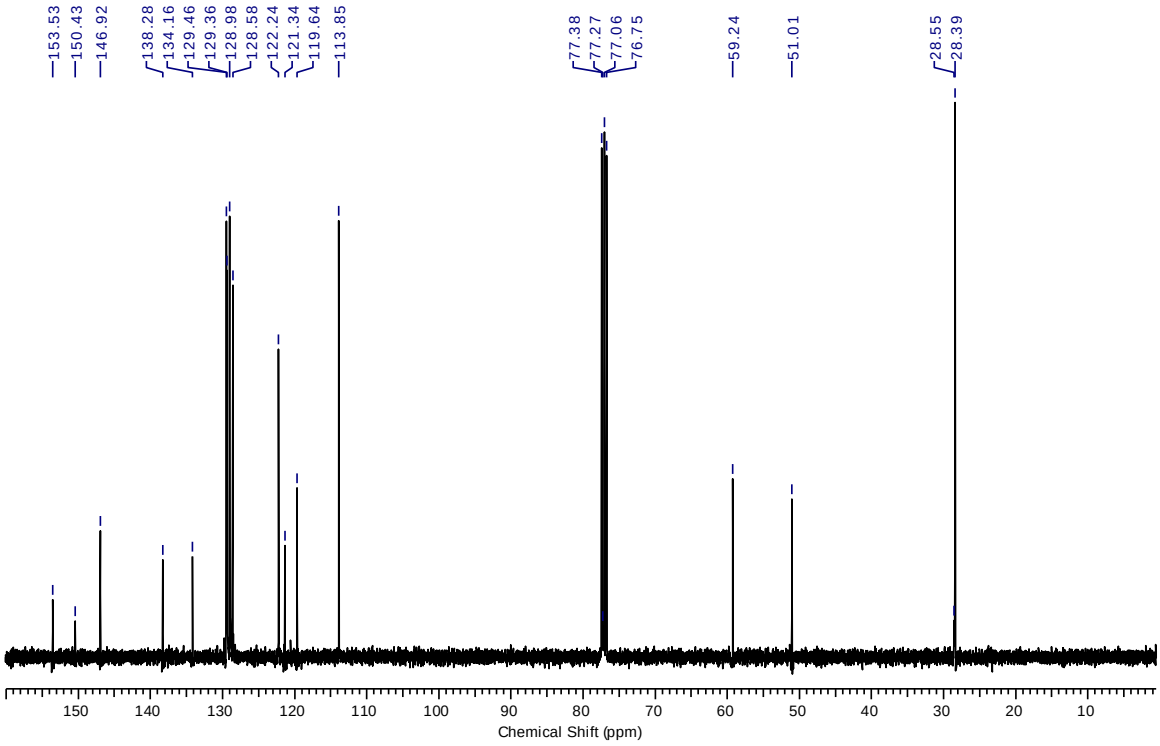
^{1}H NMR (400 MHz) spectrum of compound **4n** in $CDCl_3$



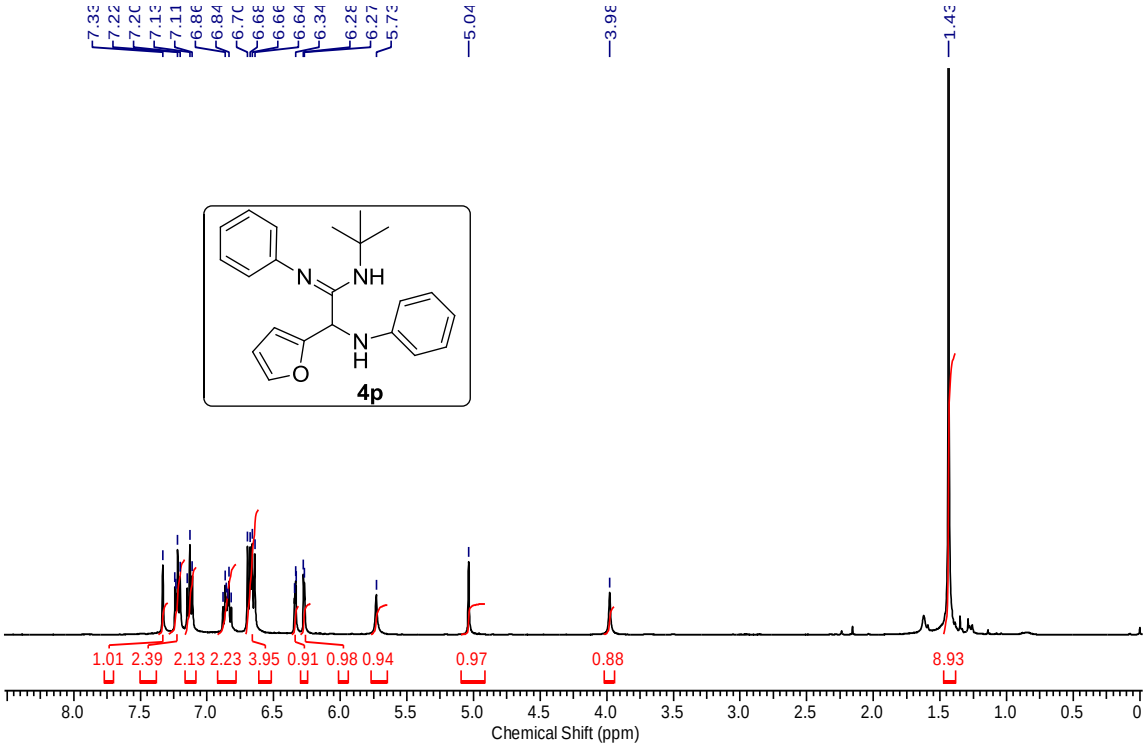
^{13}C NMR (100 MHz) spectrum of compound **4n** in $CDCl_3$



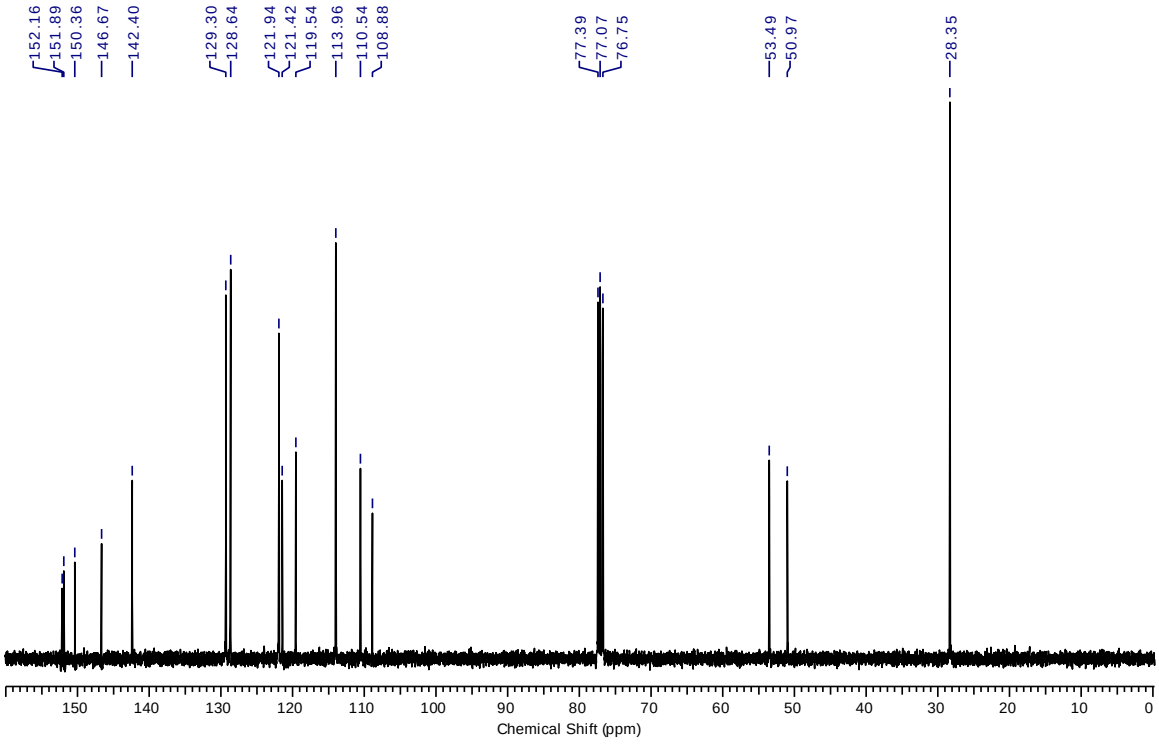
^{1}H NMR (400 MHz) spectrum of compound **4o** in $CDCl_3$



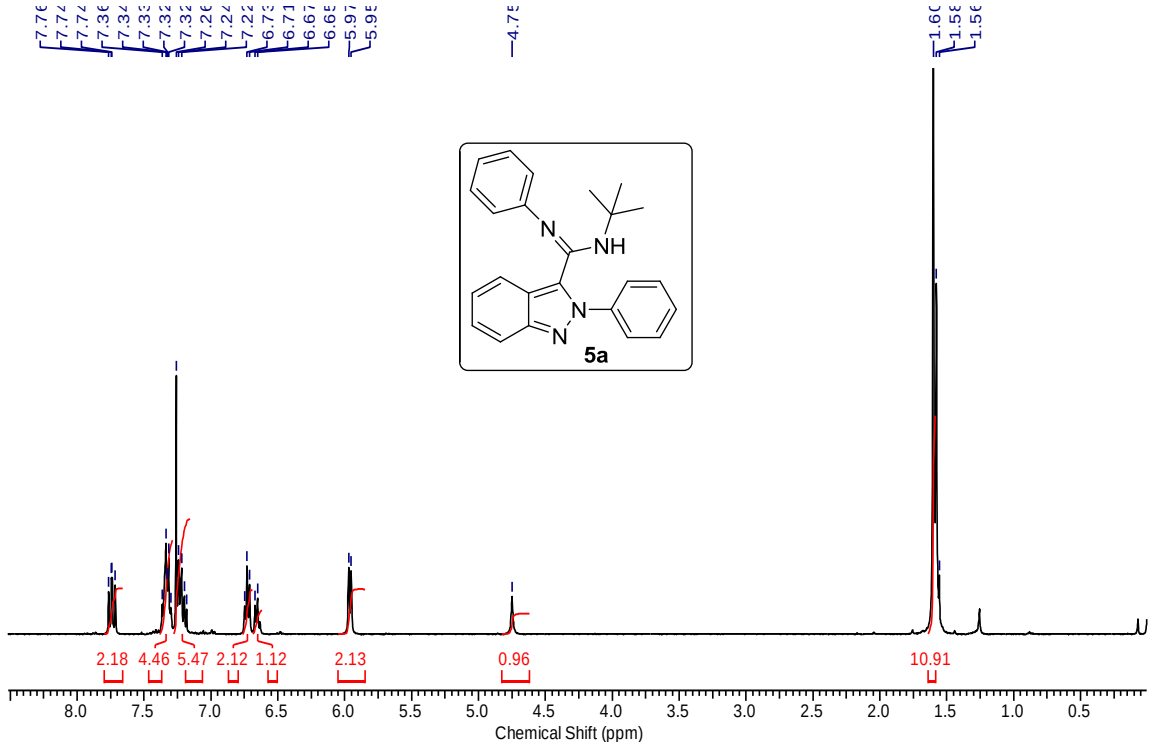
^{13}C NMR (100 MHz) spectrum of compound **4o** in $CDCl_3$



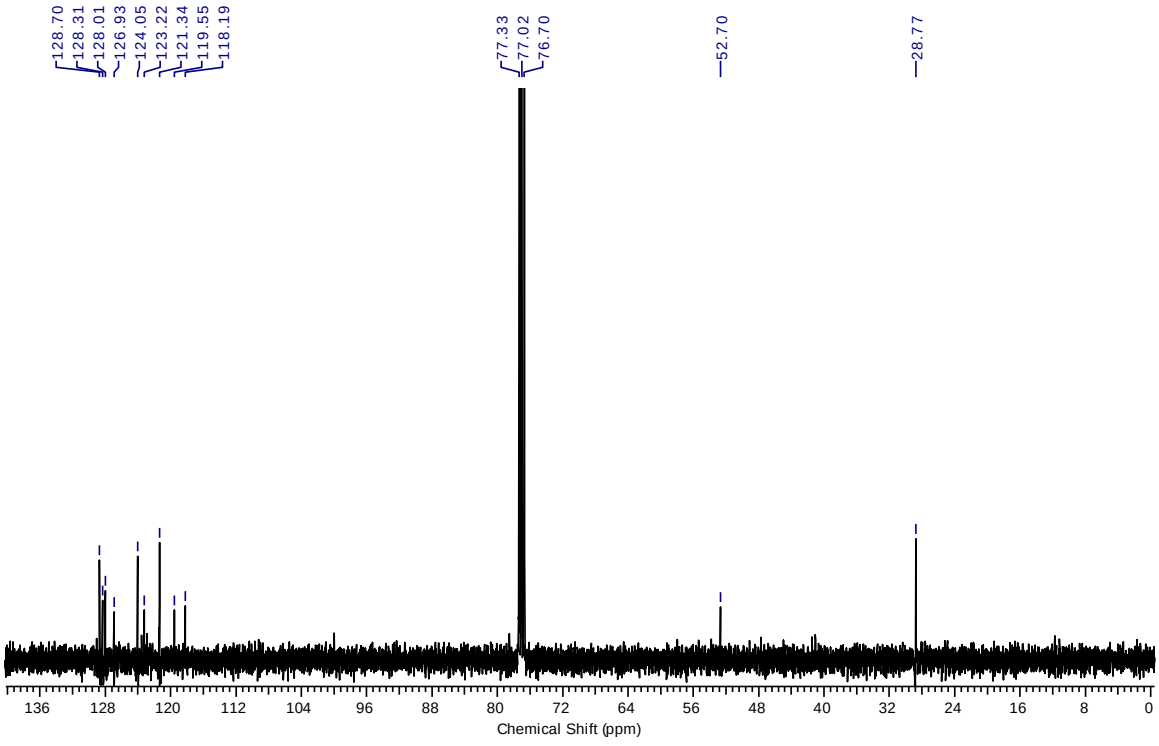
^{1}H NMR (400 MHz) spectrum of compound **4p** in $CDCl_3$



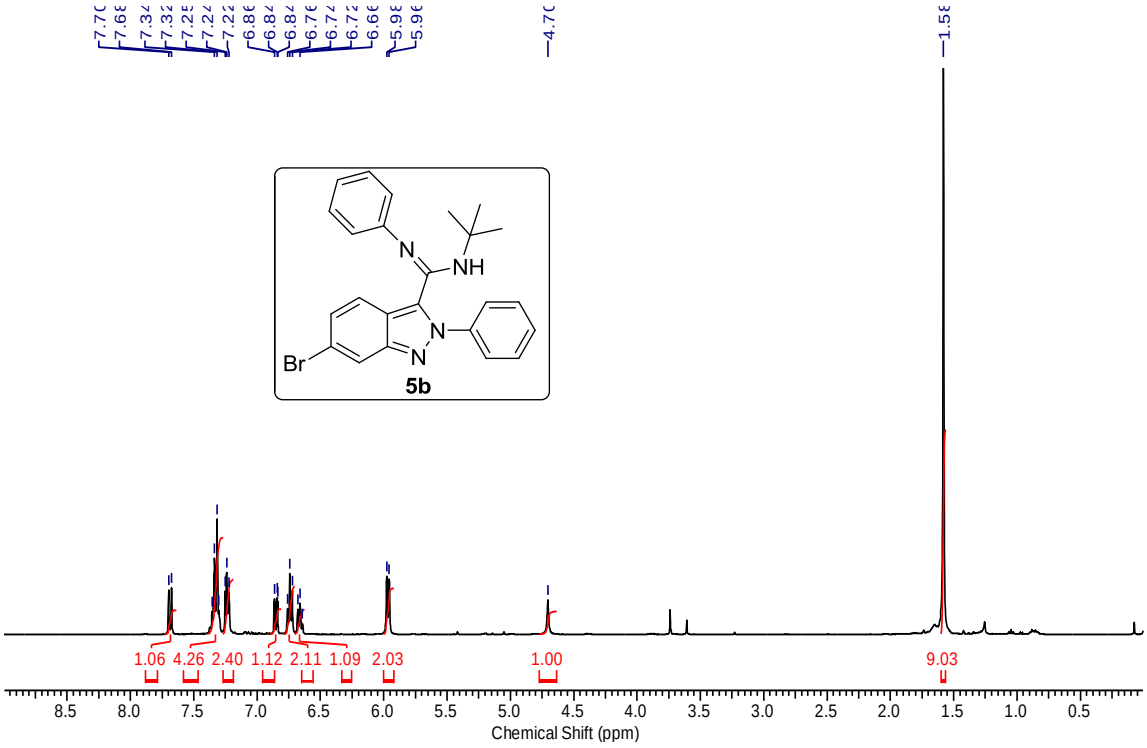
^{13}C NMR (100 MHz) spectrum of compound **4p** in $CDCl_3$



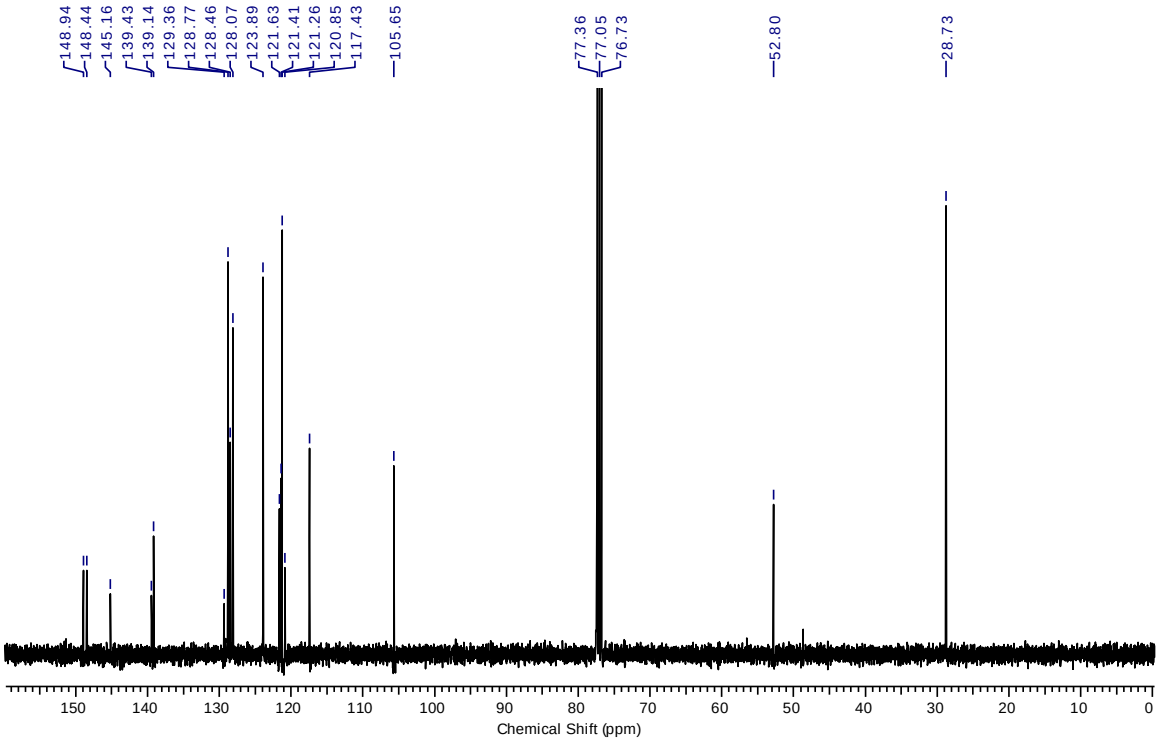
^{1}H NMR (400 MHz) spectrum of compound **5a** in $CDCl_3$



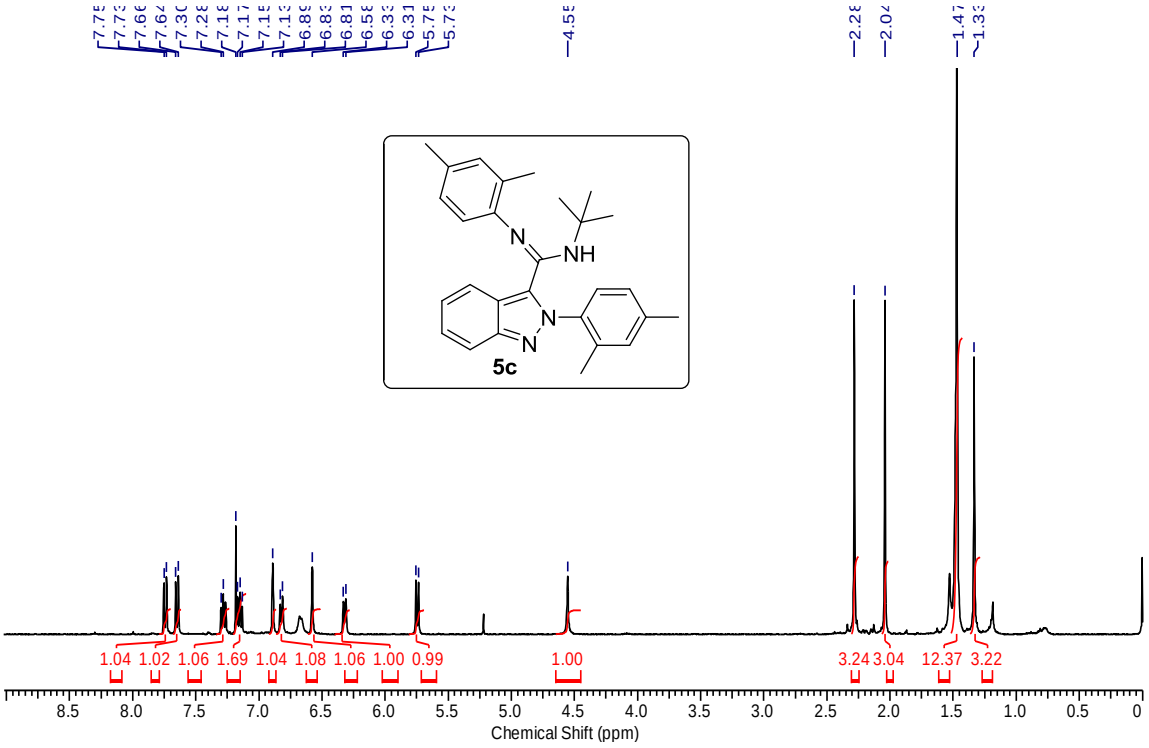
^{13}C NMR (100 MHz) spectrum of compound **5a** in $CDCl_3$



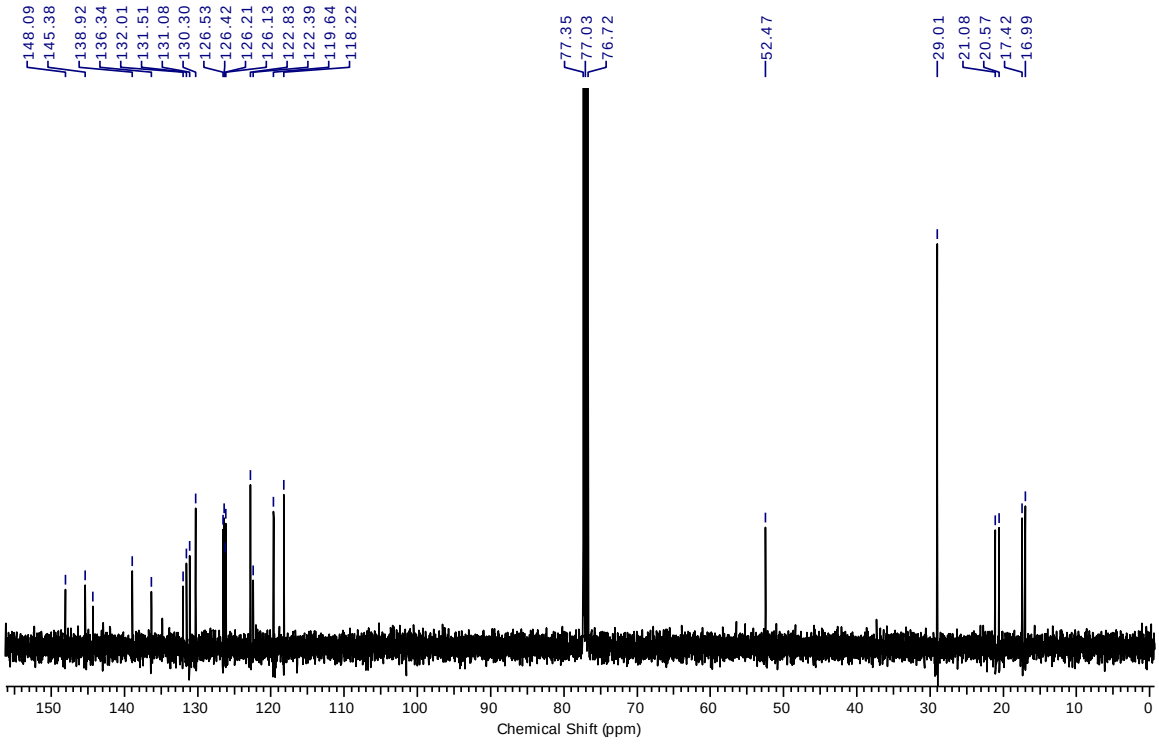
^{1}H NMR (400 MHz) spectrum of compound **5b** in $CDCl_3$



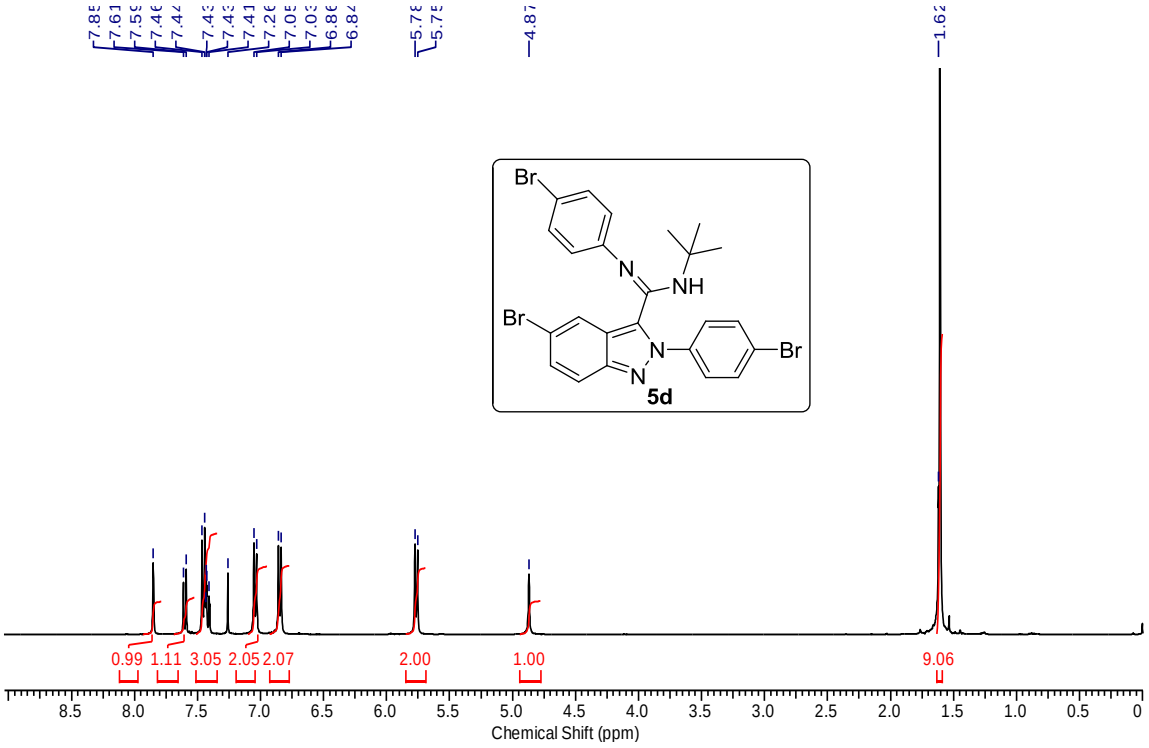
^{13}C NMR (100 MHz) spectrum of compound **5b** in $CDCl_3$



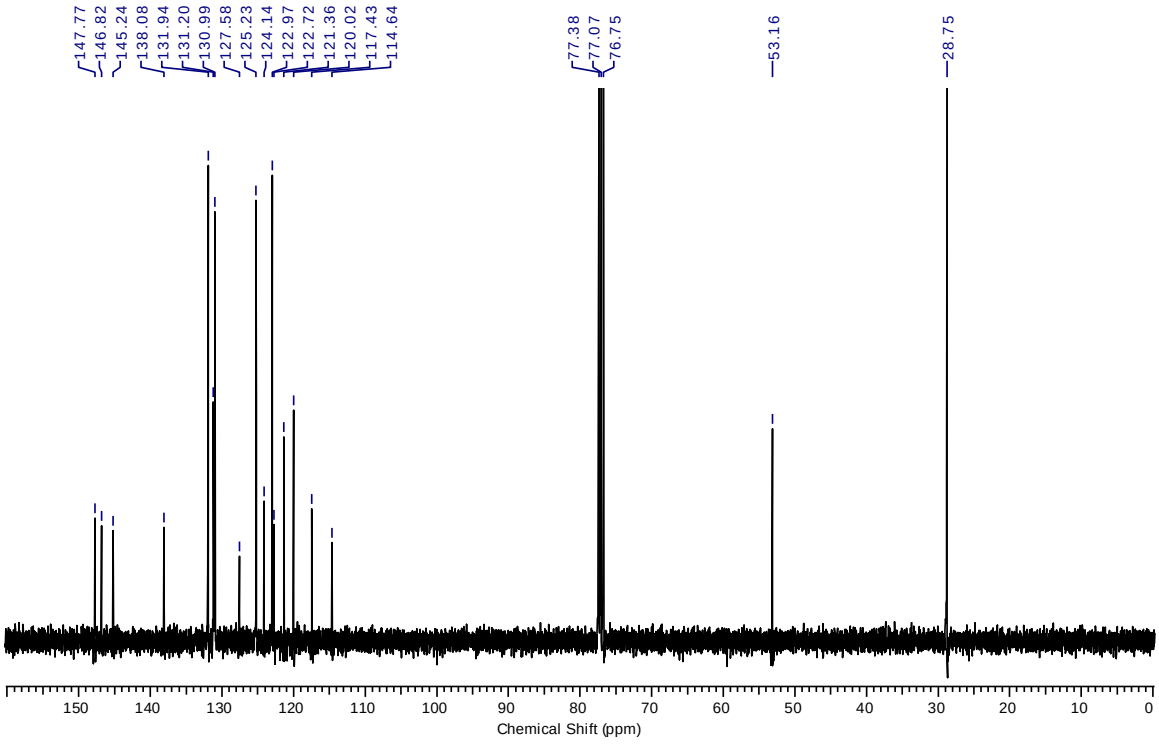
^{1}H NMR (400 MHz) spectrum of compound **5c** in $CDCl_3$



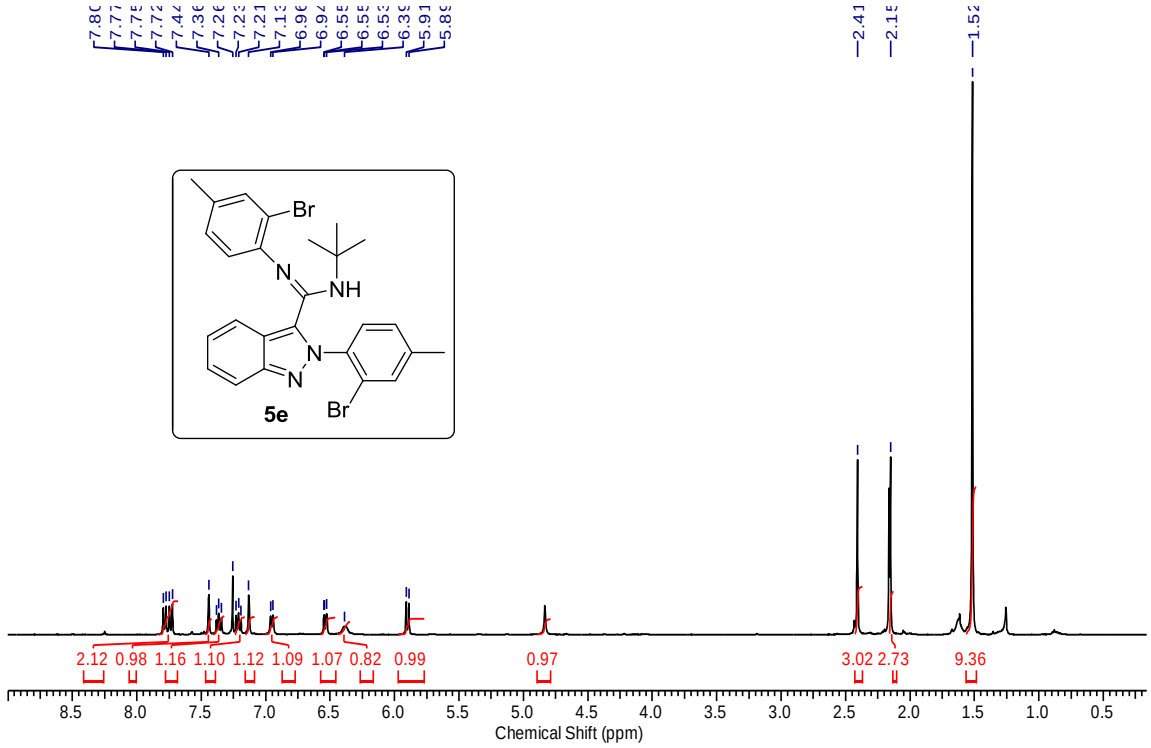
^{13}C NMR (100 MHz) spectrum of compound **5c** in $CDCl_3$



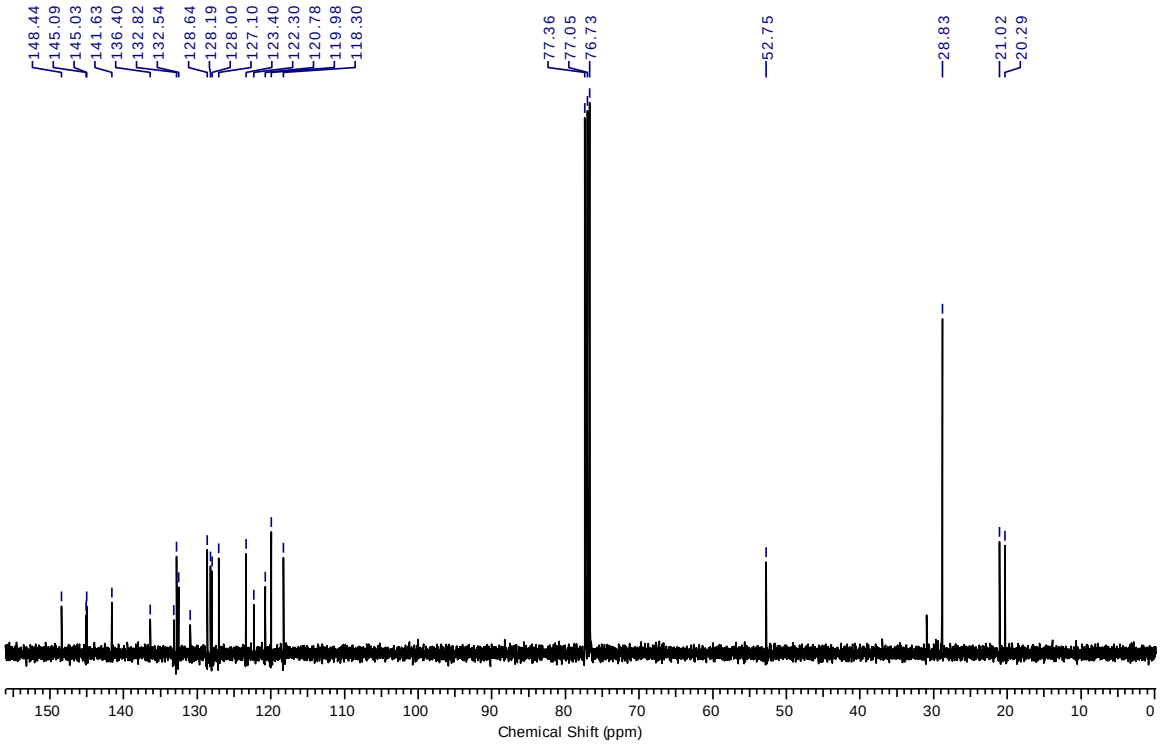
^{1}H NMR (400 MHz) spectrum of compound **5d** in $CDCl_3$



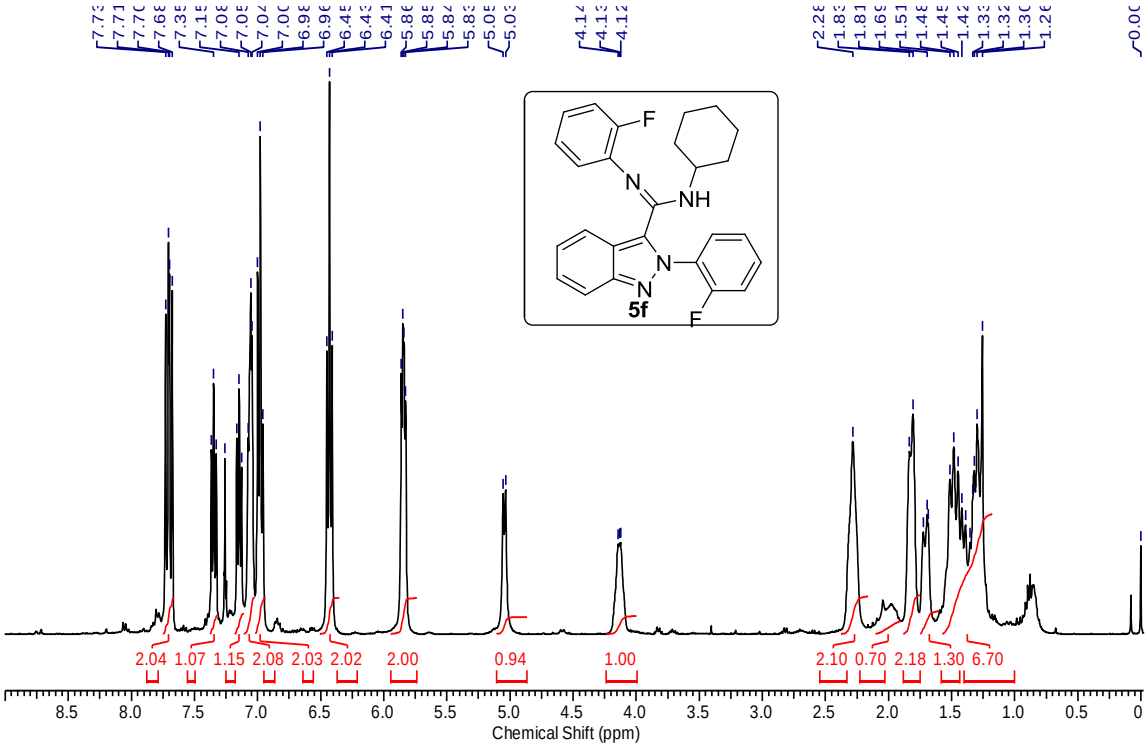
^{13}C NMR (100 MHz) spectrum of compound **5d** in $CDCl_3$



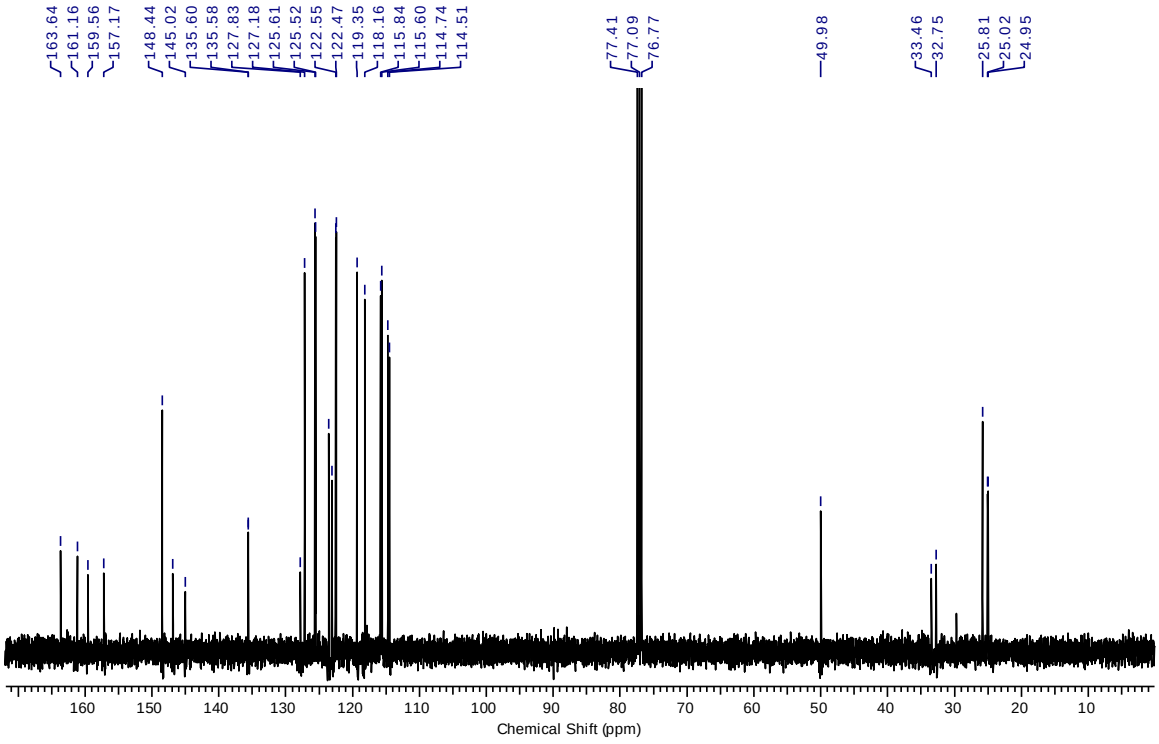
^{1}H NMR (400 MHz) spectrum of compound **5e** in $CDCl_3$



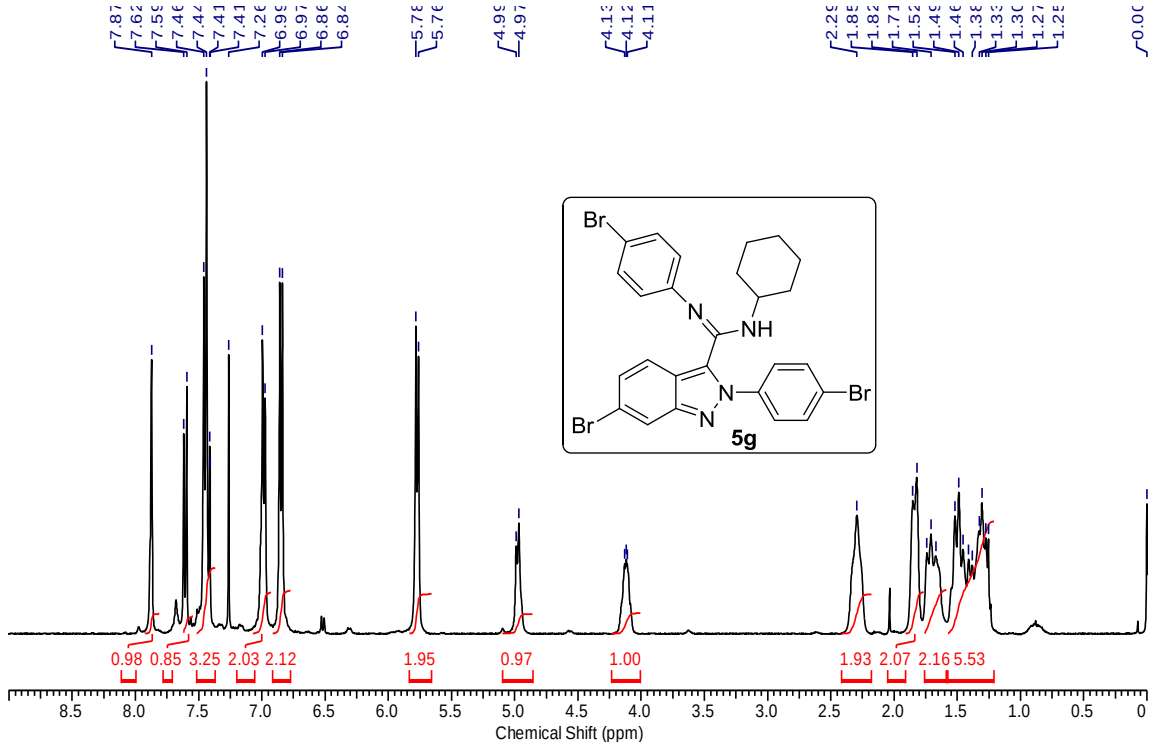
^{13}C NMR (100 MHz) spectrum of compound **5e** in $CDCl_3$



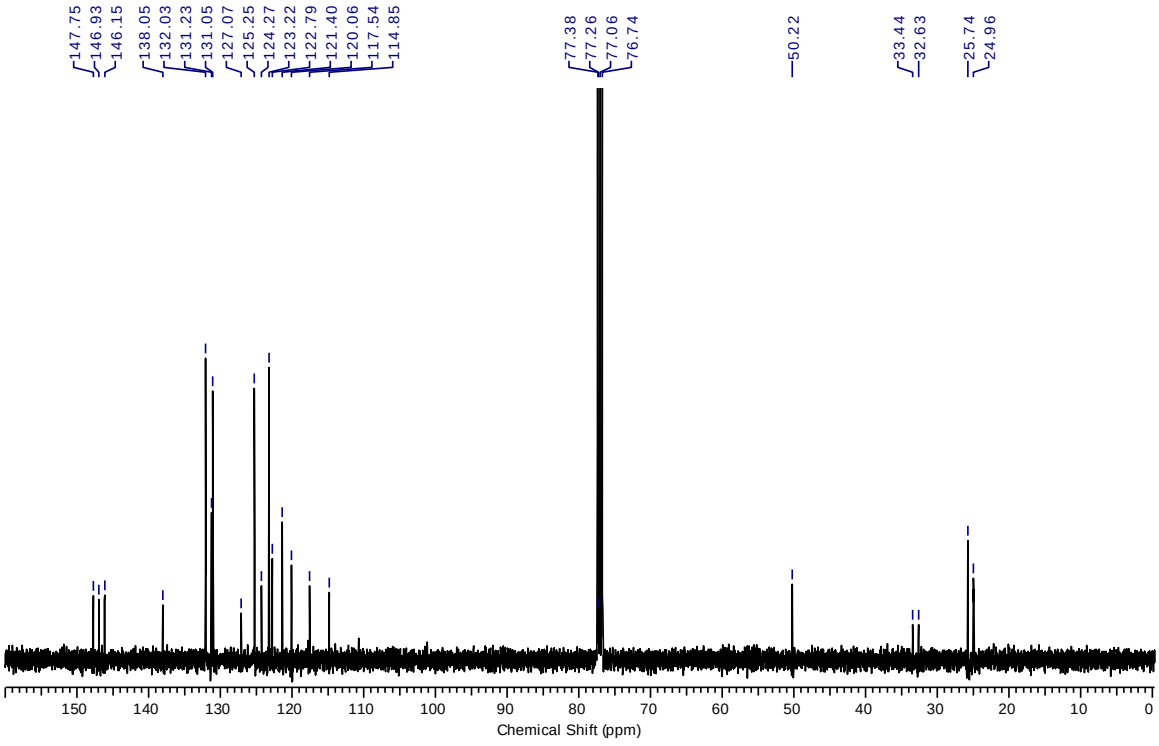
^{1}H NMR (400 MHz) spectrum of compound **5f** in $CDCl_3$



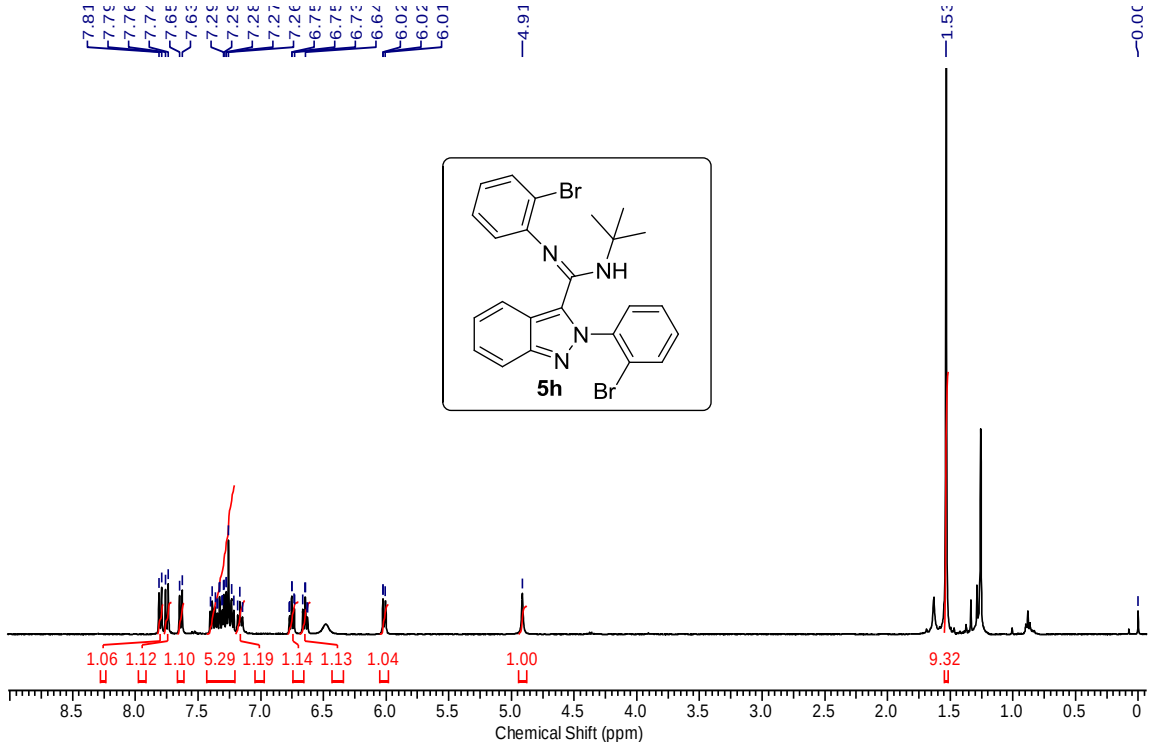
^{13}C NMR (100 MHz) spectrum of compound **5f** in $CDCl_3$



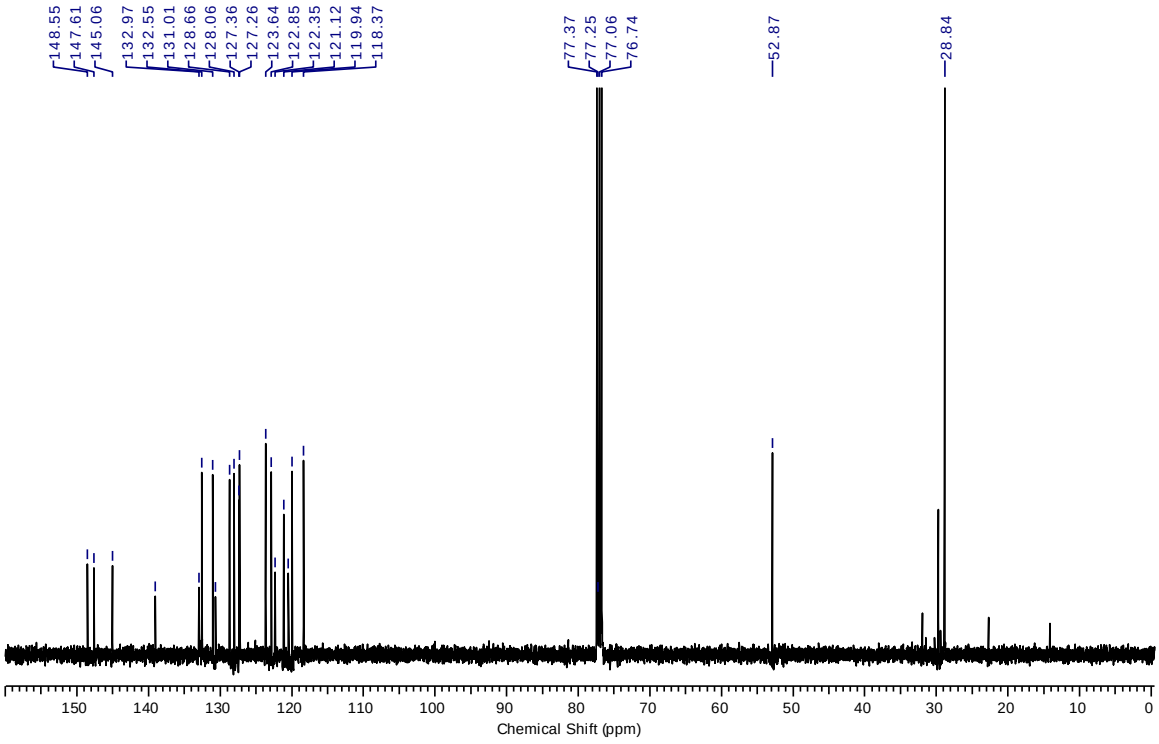
^{1}H NMR (400 MHz) spectrum of compound **5g** in $CDCl_3$



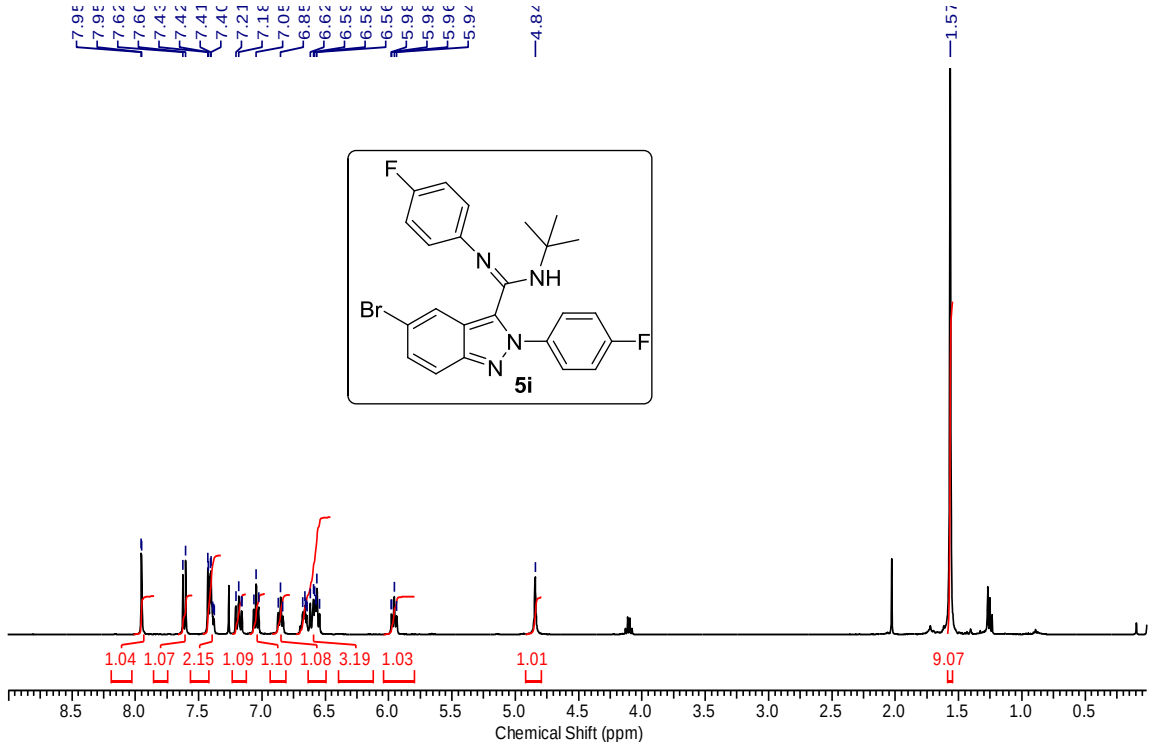
^{13}C NMR (100 MHz) spectrum of compound **5g** in $CDCl_3$



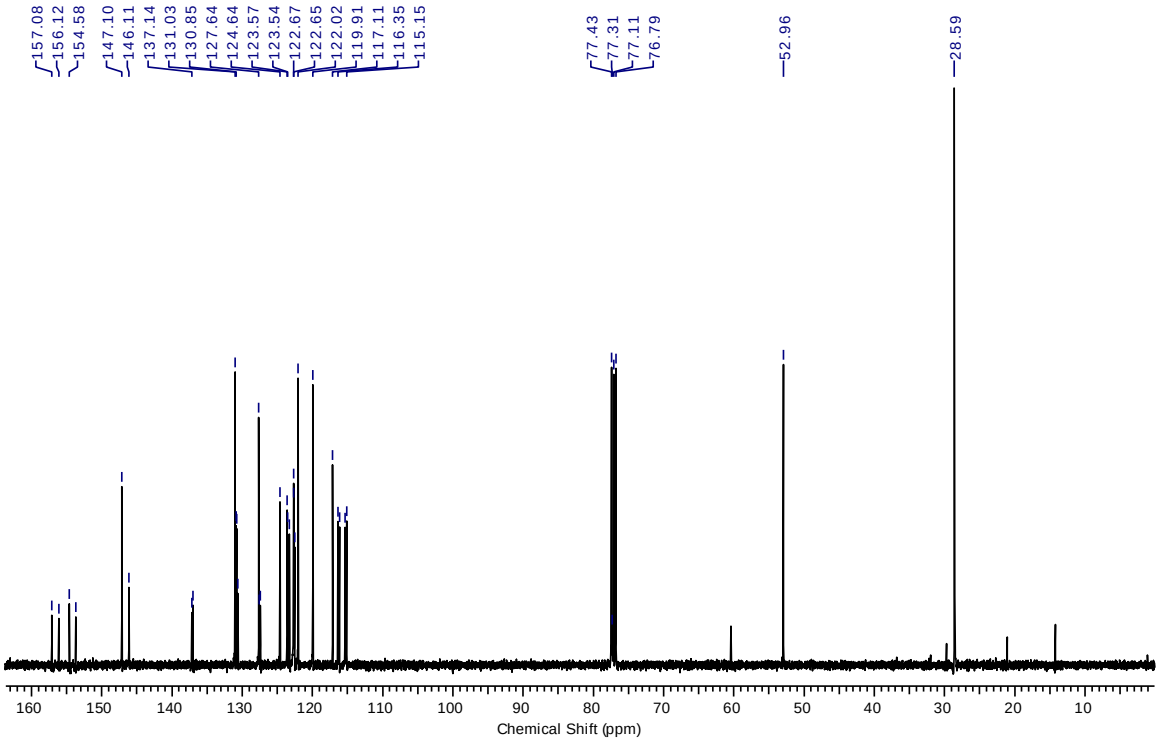
^{1}H NMR (400 MHz) spectrum of compound **5h** in $CDCl_3$



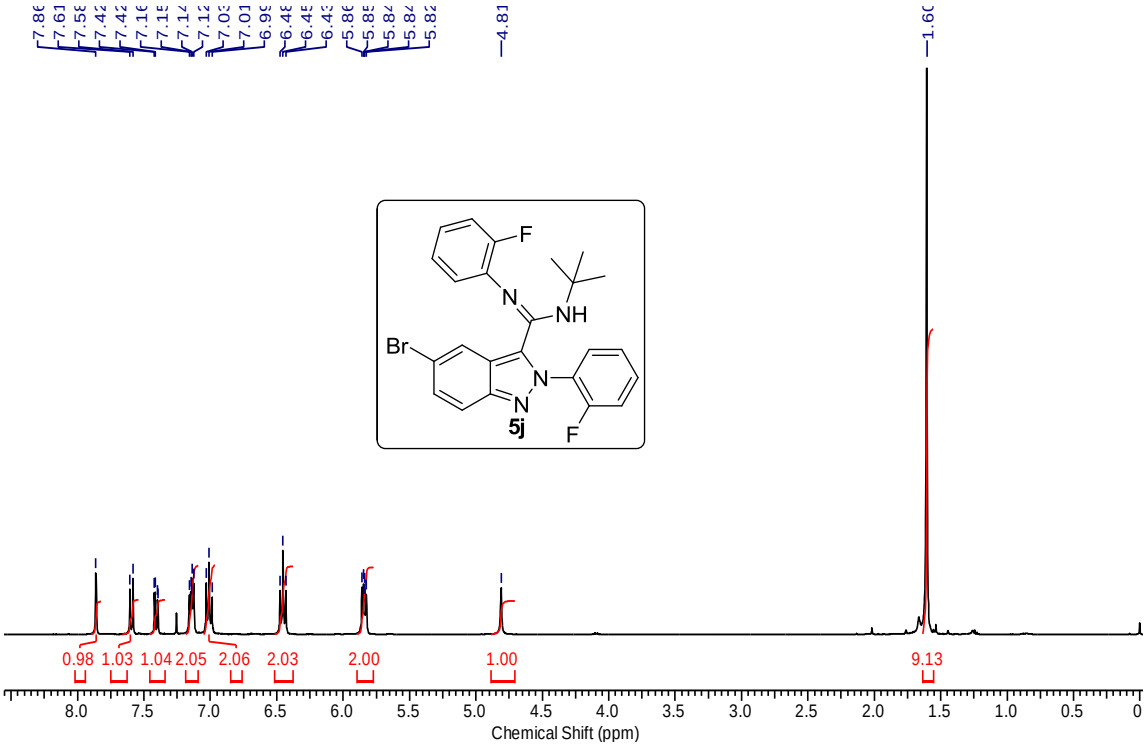
^{13}C NMR (100 MHz) spectrum of compound **5h** in $CDCl_3$



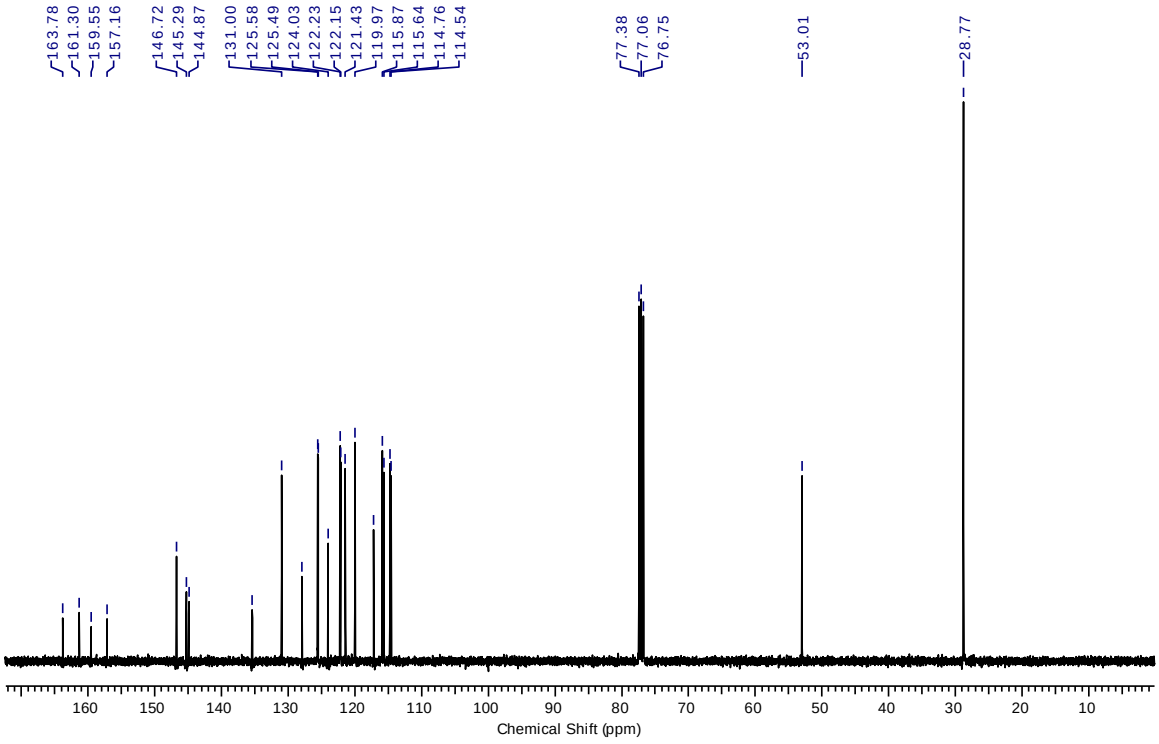
^{1}H NMR (400 MHz) spectrum of compound **5i** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of compound **5i** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of compound **5j** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of compound **5j** in $CDCl_3$

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1. M. Shen and T. G. Driver, *Org Lett*., 2010, **12**, 2884.
2. A. T. Khan, R. S. Basha, M. Lal, M. Mohammad, *RSC Advances*., 2012, **2**, 5506.