Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Synthesis of Imines from the Coupling Reaction of Alcohols and Amines Catalyzed by Phosphine Free Cobalt(II) Complexes

Jharna Mahato,[a] Partha Sarathi Bera,[a] and Tanmoy Kumar Saha[a,*]

[a]Department of Chemistry, National Institute of Technology Durgapur, West Bengal, India-713209. Corresponding Author Email: tksaha.ch@nitdgp.ac.in.

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1. General experimental procedure:

Materials and Reagents

All the required chemicals like 4,5-dichloro-*o*-phenylenediamine, 4-(diethylamino)salicylaldehyde, $CoCl_2 \cdot 6H_2O$, substituted benzyl alcohols, substituted amines, *t*-BuOK were purchased from Sigma-Aldrich and used without additional purification. The solvents were purified according to the standard procedure.

Physical measurements

Merck pre-coated silica gel 60 F254 aluminium sheets were used for thin-layer chromatography, with detection using UV light at a wavelength of 254 nm. Chromatographic separations were performed using Merck silica gel (100−200 mesh). ^{1}H, ^{13}C NMR (Nuclear magnetic resonance) spectra were recorded at 500/400 MHz and 126 MHz respectively, using $CDCl_3$ and DMSO-d6 as the solvent. ^{1}H, ^{13}C NMR chemical shifts were reported in ppm. Multiplicity is abbreviated as: s, singlet; d, doublet; t, triplet; m, multiplate. IR spectra were recorded on Thermo Fisher Scientific FTIR spectrometer. GC spectra were recorded on Shimadzu GC-2010 Plus spectrometer [HP-Molesieve column (TCD) 30 meter from Agilent]. HRMS were obtained from mass spectrometer (ESI).

2. Experimental Methods:

(a) Synthesis of 2,2'-(1,2-phenylenebis(azaneylylidene))bis(methaneylylidene))diphenol (L^1H_2)

o-phenylenediamine (0.1081 g, 1 mmol) in 10 mL methanol was added dropwise to salicylaldehyde (0.2442 g, 2 mmol) in 10 mL methanol. The reaction mixture was refluxed for 6 hours in open air and yellow colour precipitate was obtained. The yellow precipitate was filtered and the isolated solid was washed with cold methanol. The isolated compound was characterised by IR and NMR and ESI-HRMS spectroscopic studies. Yield: (0.2713 g, 84%) Selected **IR** data: (ATR, ν/cm^{-1}): 1613 (C=N), 1558, 1479, 1360, 1273, 1190, 1149, 906,832, 754, 658. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (C*H*=N, s, 2H), 7.40-7.34 (Ar*H*, m, 5H), 7.25-7.23 (Ar*H*, t, 1H), 7.09-6.90 (Ar*H*, m, 6H). **HR-MS**: m/z: calcd for $[C_{20}H_{16}N_2O_2+H\ ]^+$: 317.13; found: 317.1290.

(b) Synthesis of N,N-Bis(4-diethylaminosalicylidene)-4,5-dichloro-1,2-phenylenediamine (L^2H_2)

4,5-dichloro-*o*-phenylenediamine (0.1770 g, 1 mmol) in 20 mL dichloromethane was added dropwise to 4-(diethylamino)salicylaldehyde (0.3864 g, 2 mmol) in 20 mL dichloromethane under stirring condition. The reaction mixture was stirred for 24 hours at room temperature in open air. Then the solvent of the reaction mixture was removed from the reaction mixture under reduced pressure. Upon removal of solvent yellow, the residue was washed with hot ethanol and dried, yellow colour solid was obtained. The compound was characterized by IR and NMR and ESI-HRMS spectroscopic studies. Yield: (0.3323 g, 63%) Selected **IR** data: (ATR, ν/cm^{-1}): 3403, 3318, 2968, 1629 (C=N), 1590, 1516, 1483, 1341, 1231, 1126, 1071, 868, 813, 740, 676, 606. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.34 (C*H*=N, s, 2H), 7.19-7.17 (Ar*H*, d, 2H), 7.04 (Ar*H* , s, 2H), 6.82 (Ar*H* , s, 2H), 6.29-6.26 (Ar*H* , d, 2H), 6.19- 6.18 (Ar*H* , d, 2H), 3.43-3.39 (CH_2, q, 8H), 1.23-1.20 (CH_3, t, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.08 (Ar*C*-OH), 161.56 (*C*H=N), 152.19 (Ar*C*), 142.51 (Ar*C*), 134.06 (Ar*C*), 128.88 (Ar*C*), 120.52 (Ar*C*), 109.27 (Ar*C*), 103.93 (Ar*C*), 98.00 (Ar*C*), 44.63 (*C*H_2), 12.68 (*C*H_3). **HR-MS**: m/z: calcd for $[C_{28}H_{33}Cl_2N_4O_2+H\ ]^+$: 527.20; found: 527.1981.

(c) Synthesis of Cobalt complex (1a)

To 10 mL of ethanol/chloroform (1:1) solution of ligand **L1** (0.3222 g, 1 mmol) a batch of $CoCl_2{\cdot}6H_2O$ (0.2378 g, 1 mmol) in 4 mL of ethanol was added. The reaction mixture was refluxed for 6 h. After cooling the reaction mixture, brown solid was obtained. The brown solid was filtered and washed with methanol. The compound was characterised by IR, and ESI-MS analysis. Yield: (0.2088 g, 56%) Selected **IR** data: (ATR, ν/cm^{-1}): 1609 (C=N), 1578, 1532, 1457, 1438, 1378, 1309, 1185, 1148, 1130, 928, 744, 642, 619. **HR-MS** m/z: calcd for $[C_{20}H_{14}CoN_2O_2]^+$: 373.04; found 373.0468 for $[C_{20}H_{14}CoN_2O_2]^+$

(d) Synthesis of Cobalt complex 1b

To 10 mL of ethanol/chloroform (1:1) solution of ligand **L2** (0.2637 g, 0.5 mmol) a batch of $CoCl_2{\cdot}6H_2O$ (0.1189 g, 0.5 mmol) in 4 mL of ethanol was added. The reaction mixture was stirred for 5 h at room temperature in open air and brown colour precipitate was obtained. The brown precipitate was filtered and the isolated solid was washed with ethanol. The compound was characterised by IR, and ESI-MS analysis. Yield: 0.2390 g (82%) Selected **IR** data: (ATR, ν/cm^{-1}): 2966, 2866, 1611 (C=N), 1590,1557, 1483, 1405, 1341, 1245, 1143, 1066, 781, 616.

HR-MS m/z: calcd for $[C_{28}H_{30}Cl_2CoN_4O_2]^+$: 583.11; found: 583.1210 for $[C_{28}H_{30}Cl_2CoN_4O_2]^+$

(e) General Procedure for imine synthesis

Amine (1.0 mmol), alcohol (1.0 mmol), *t*-BuOK (1.0 mmol), and catalyst **1b** (1 mol%) were taken with 4 mL of *ortho*-xylene solvent in a 50 mL round-bottom flask containing with a stirring bar under aerobic conditions. The flask was equipped with a condenser and refluxed at 90°C for 8 h in a preheated oil bath. After that the reaction mixture was cooled at room temperature and the solvent was concentrated under reduced pressure. Then, the residue was purified using silica gel (100-200 mesh) column chromatography with 2-15% ethyl acetate in hexane as an eluent to get a pure compound.

(f) General Procedure for benzimidazole derivative synthesis

Diamine (1.0 mmol), alcohol (1.0 mmol), *t*-BuOK (1.0 mmol), and catalyst **1b** (1 mol%) were taken with 4 mL of *ortho*-xylene solvent in a 50 mL round-bottom flask containing with a stirring bar under aerobic conditions. The flask was equipped with a condenser and refluxed at 90°C for 8 h in a preheated oil bath. After that the reaction mixture was cooled at room temperature and the solvent was concentrated under reduced pressure. Then, the residue was purified using silica gel (100-200 mesh) column chromatography with 5-20% ethyl acetate in hexane as an eluent to get a pure compound.

(g) Procedure for hydrogen gas detection

Aniline (0.5 mmol), benzyl alcohol (0.5 mmol), *t*-BuOK (0.5 mmol) and catalyst **1b** (1 mol%) were taken with 4 mL of *ortho*-xylene solvent in a round bottom flask. The reaction mixture was refluxed at 90°C for 8 h in a preheated oil bath. After 8 h the gas mixture was injected into Gas chromatography instrument and H_2 gas was determined.

3. Characterization data for synthesized imine and benzimidazole derivative

***N*-Benzylidene aniline (4a):**

Following the general procedure, the product was isolated as yellow solid. Yield: 161 mg (89%). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ ppm: 8.39 (C*H*=N, s, 1H), 7.84-7.82 (Ar*H*, m, 2H), 7.41-7.40 (Ar*H*, m, 3H), 7.34-7.31 (Ar*H* , t, 2H), 7.18-7.13 (Ar*H* , m, 3H). **HR-MS**: m/z= 182.0970 $[M+H]^+$. NMR data are in accordance with literature values.

***N*-Benzylidene 4-(methyl) aniline (4b):**

Following the general procedure, the product was isolated as yellow liquid. Yield: 181 mg (93%). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ ppm: 8.48 (C*H*=N, s, 1H), 7.92-7.89 (Ar*H*, m, 2H), 7.48 (Ar*H*, m, 3H), 7.22-7.15 (Ar*H*, dd, 4H), 2.39 (CH_3, s, 3H). **GC-MS**: m/z= 195 $[M]^+$. NMR data are in accordance with literature values.

***N*-Benzylidene 4-(methoxy) aniline (4c):**

Following the general procedure, the product was isolated as light-yellow solid. Yield: 179mg (85%). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ ppm: 8.49 (C*H*=N, s, 1H), 7.91-7.87 (Ar*H*, m, 2H), 7.47-7.46 (Ar*H*, m, 3H), 7.25-7.23 (Ar*H*, d, 2H), 6.95-6.93 (Ar*H*, d, 2H), 3.84 (Ar*H*, s, 3H). **GC-MS**: m/z= 211 $[M]^+$. NMR data are in accordance with literature values.

***N*-Benzylidene-2,4,6-(trimethyl) aniline (4d):**

Following the general procedure, the product was isolated as yellow liquid. Yield: 172 mg (77%). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ ppm: 8.21 (C*H*=N, s, 1H), 7.66-7.63 (Ar*H*, t, 1H), 7.56-7.53 (Ar*H*, t, 2H), 7.50-7.49 (Ar*H*, m, 2H), 6.89 (Ar*H*, s, 2H), 2.29 (CH_3, s, 3H), 2.12 (CH_3, s, 6H). **GC-MS**: m/z= 223 $[M]^+$. NMR data are in accordance with literature values.

***N*-Benzylidene 2,6-(dipropyl) aniline (4e):**

Following the general procedure, the product was isolated as yellow liquid. Yield: 238 mg (90%). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ ppm: 8.2 (C*H*=N, s, 1H), 7.93-7.92 (Ar*H*, m, 2H), 7.53-7.51 (Ar*H*, m, 3H), 7.18-7.16 (Ar*H*, d, 2H), 7.13-7.10 (Ar*H*, t, 1H), 3.03-2.95 (C*H*, m, 2H), 1.19-1.17 (CH_3, d, 12H). **HR-MS**: m/z= 266.1919 $[M+H]^+$. NMR data are in accordance with literature values.

1-phenyl-N-(pyridin-2-yl)methanimine (4g):

Following the general procedure, the product was isolated as white solid. Yield: 145 mg (80%). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 9.15 (C*H*=N, s, 1H), 8.51-8.50 (Ar*H*, d, 1H), 8.00-7.99 (Ar*H*, d, 2H), 7.78-7.75 (Ar*H*, t, 1H), 7.53-7.47 (Ar*H*, m, 3H), 7.45-7.42 (Ar*H*, t, 1H), 7.34-7.33 (Ar*H*, d, 1H). **HR-MS**: m/z= 183.0922 $[M+H]^+$. NMR data are in accordance with literature values.

N,N'-(pyridine-2,6-diyl)bis(1-phenylmethanimine) (4i):

Following the general procedure, the product was isolated as yellow solid. Yield: 216 mg (76%). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 10.03 (C*H*=N, s, 2H), 8.05-8.03 (Ar*H*, d, 2H), 7.90-7.88 (Ar*H*, d, 2H), 7.66-7.63 (Ar*H*, t, 1H), 7.56-7.45 (Ar*H*, m, 4H), 7.38-7.34 (Ar*H*, m, 3H), 7.18-7.17 (Ar*H*, d, 1H). **HR-MS**: m/z= 286.1341 $[M+H]^+$. NMR data are in accordance with literature values.

1-(4-methoxyphenyl)-*N*-phenylmethanimine (4l):

Following the general procedure, the product was isolated as yellow solid. Yield: 192 mg (91%). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ ppm: 8.38 (C*H*=N, s, 1H), 7.87-7.83 (Ar*H*, m, 3H), 7.39-7.37 (Ar*H*, d, 1H), 7.22-7.20 (Ar*H*, d, 2H), 7.00-6.97 (Ar*H*, m, 3H), 3.86 (CH_3, s, 3H). **GC-MS**: m/z= 211 $[M]^+$. NMR data are in accordance with literature values.

1-(3-chlorophenyl)-*N*-phenylmethanimine (4o):

Following the general procedure, the product was isolated as yellow liquid. Yield: 165 mg (77%). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.44 (C*H*=N, s, 1H), 7.99 (Ar*H*, t, 1H), 7.80-7.77 (Ar*H*, d, 2H), 7.64-7.62 (Ar*H*, m, 1H), 7.52-7.40 (Ar*H*, m, 5H). **GC-MS**: m/z= 215 $[M]^+$. NMR data are in accordance with literature values.

***N*-phenyl-9H-fluoren-9-imine (4s):**

Following the general procedure, the product was isolated as orange liquid. Yield: 178 mg (70%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.94-7.91 (Ar*H*, 2H, d), 7.61-7.59 (Ar*H*, 1H, d), 7.55-7.31 (Ar*H*, m, 6H), 7.24-7.20 (Ar*H*, t, 1H), 7.03-7.00 (Ar*H*, d, 1H), 6.94-6.90 (Ar*H*, t, 1H), 6.57-6.55 (Ar*H*, d, 1H). **GC-MS**: m/z= 255 $[M]^+$.

5,6-dichloro-2-phenyl-1H-benzo[d]imidazole (5a):

Following the general procedure, the product was isolated as grey solid. Yield: 223 mg (85%). **^{1}H-NMR** (500 MHz, DMSO) δ 13.28 (N*H*, s, 1H), 8.17- 8.16 (Ar*H*, d, 2H), 7.94 (Ar*H*, s, 1H), 7.77 (Ar*H*, s, 1H), 7.63-7.61 (Ar*H*, t, 1H), 7.57-7.55 (Ar*H*, m, 1H), 7.52-7.49 (Ar*H*, t, 1H). **HR-MS**: m/z= 263.0143 $[M+H]^+$.

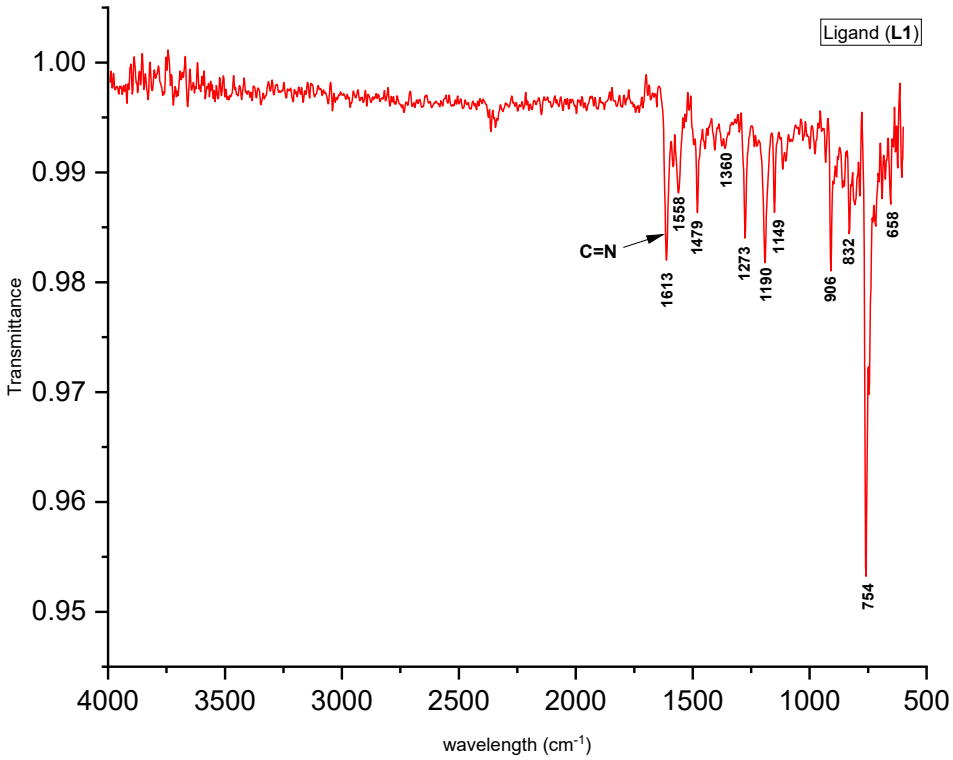

Figure S1. FTIR Spectrum of L**1** in ATR mode, taken in the range 4000 cm^{-1}–500 cm^{-1}

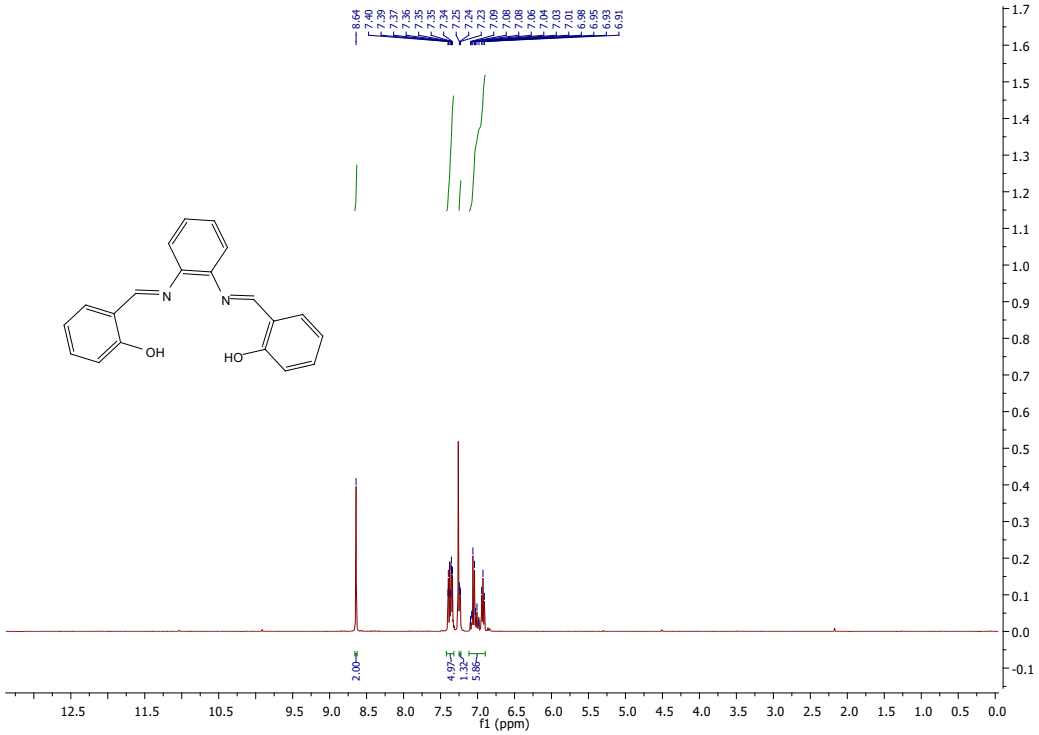

Figure S2. ^{1}H NMR of ligand (**L1**)

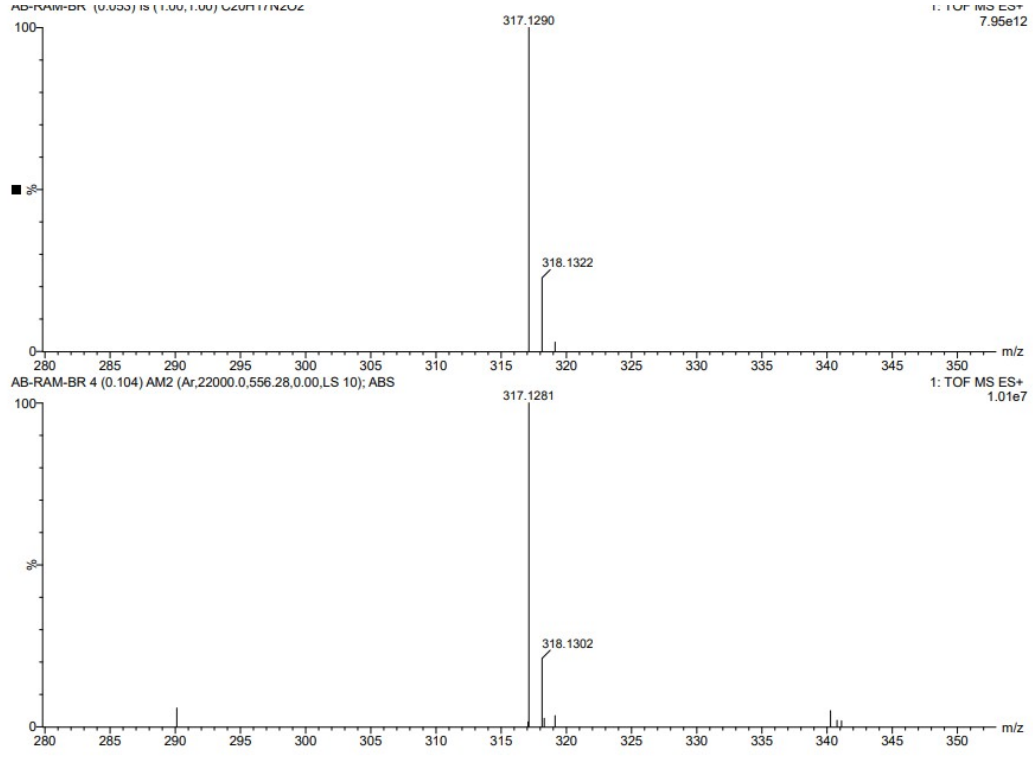

Figure S3. HRMS of ligand (**L1**) taken in methanol

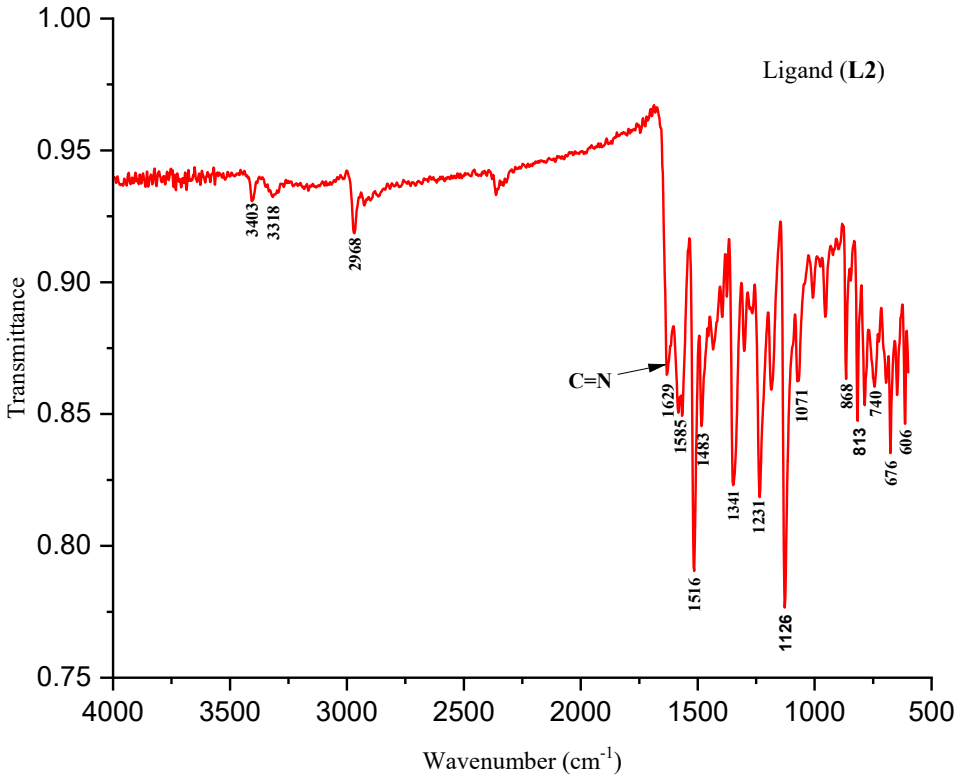

Figure S4. FTIR Spectrum of L**2** in ATR mode, taken in the range 4000 cm^{-1}–500 cm^{-1}

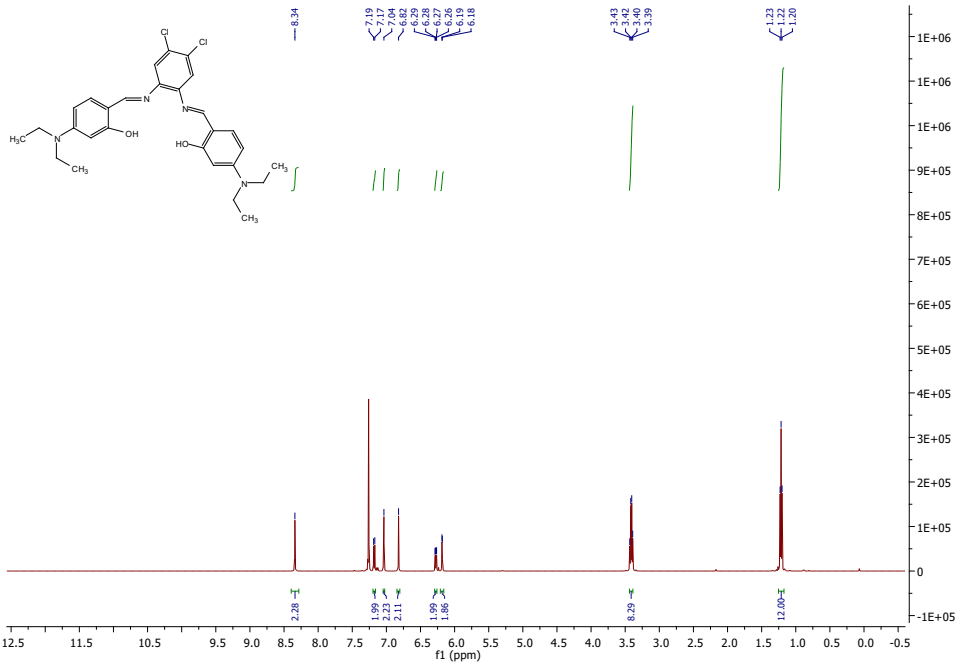

Figure S5. ^{1}H NMR of ligand (**L2**)

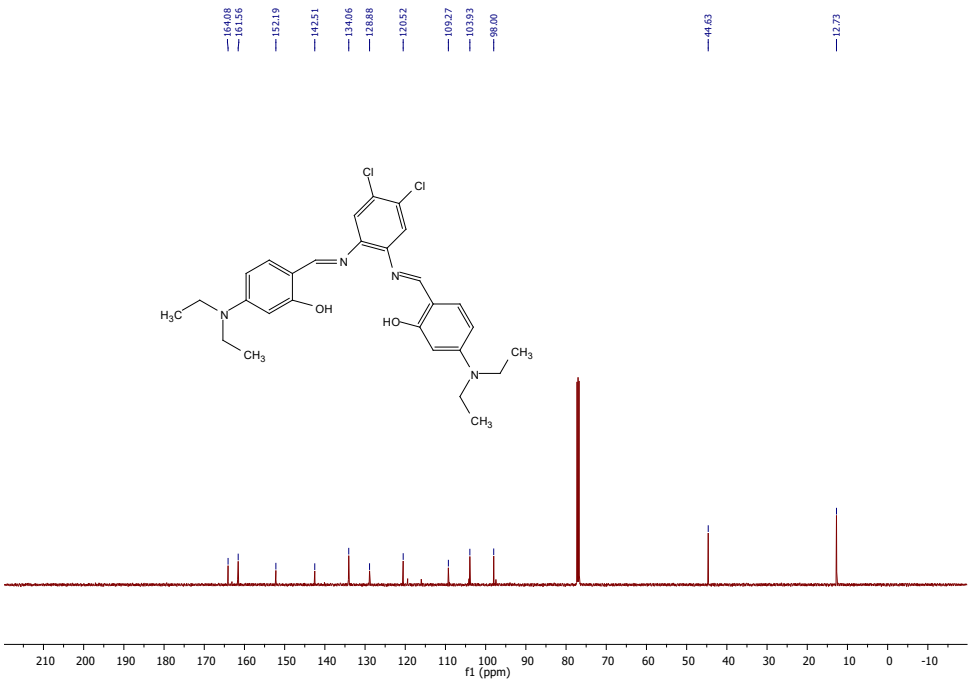

Figure S6. ^{13}C NMR of ligand (**L2**)

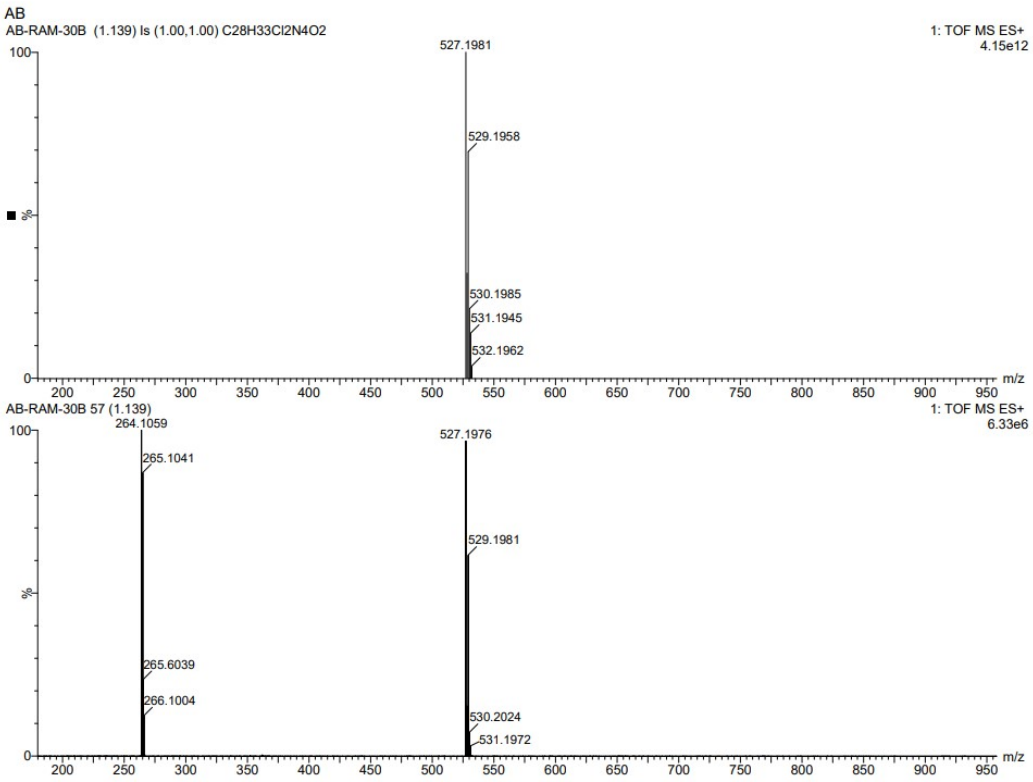

Figure S7. HRMS of ligand (**L2**) taken in methanol

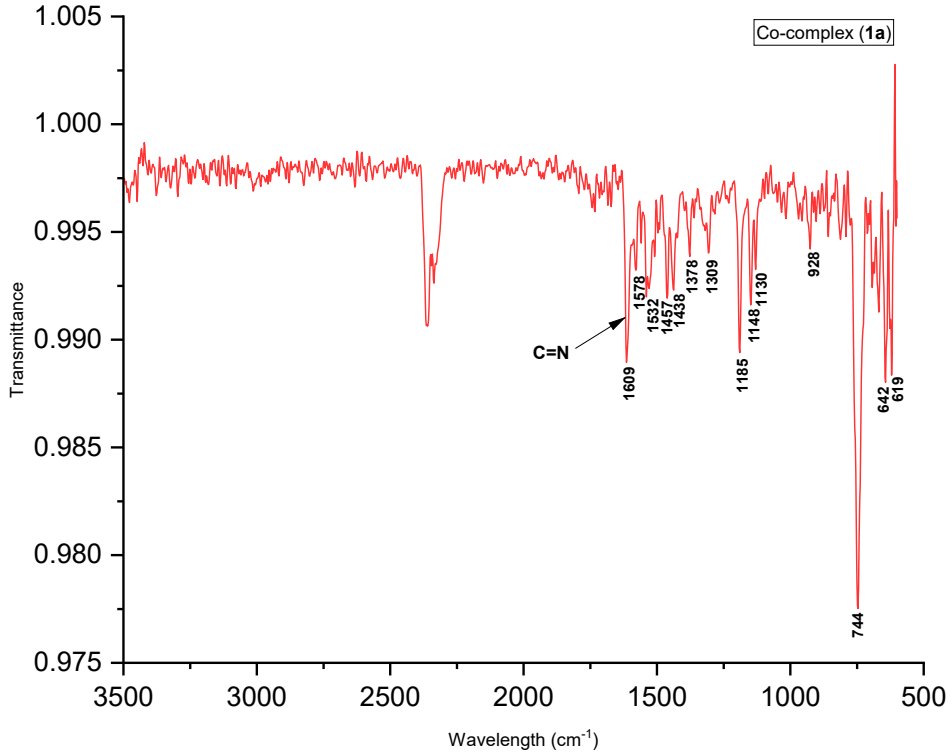

Figure S8. FTIR Spectrum of **1a** in ATR mode, taken in the range 3500 cm^{-1}–500 cm^{-1}

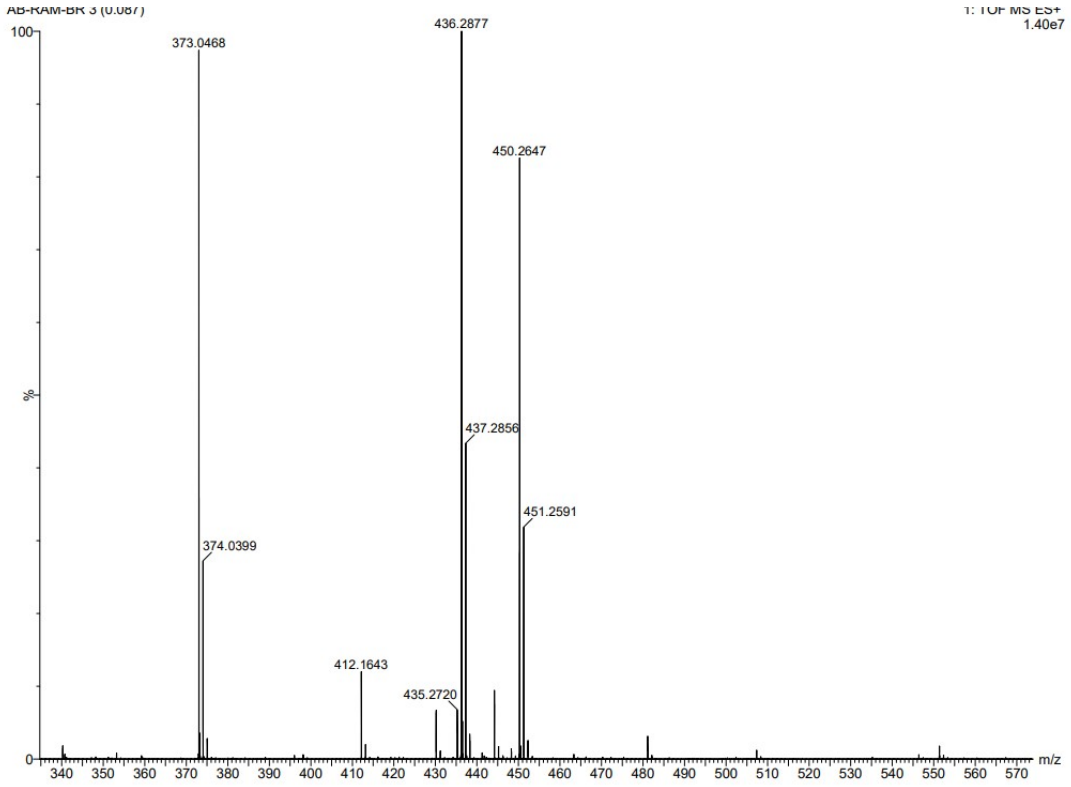

Figure S9. HRMS of **1a** taken in Methanol.

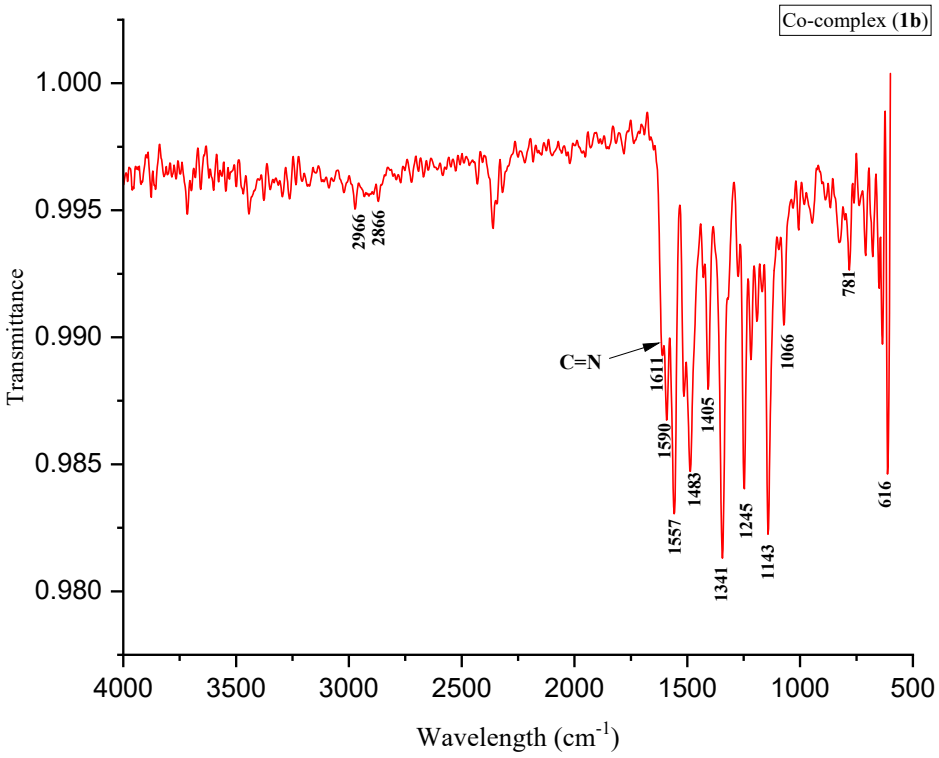

Figure S10. FTIR Spectrum of **1b** in ATR mode, taken in the range 4000 cm^{-1}–500 cm^{-1}

Figure S11. HRMS of **1b** taken in Methanol.

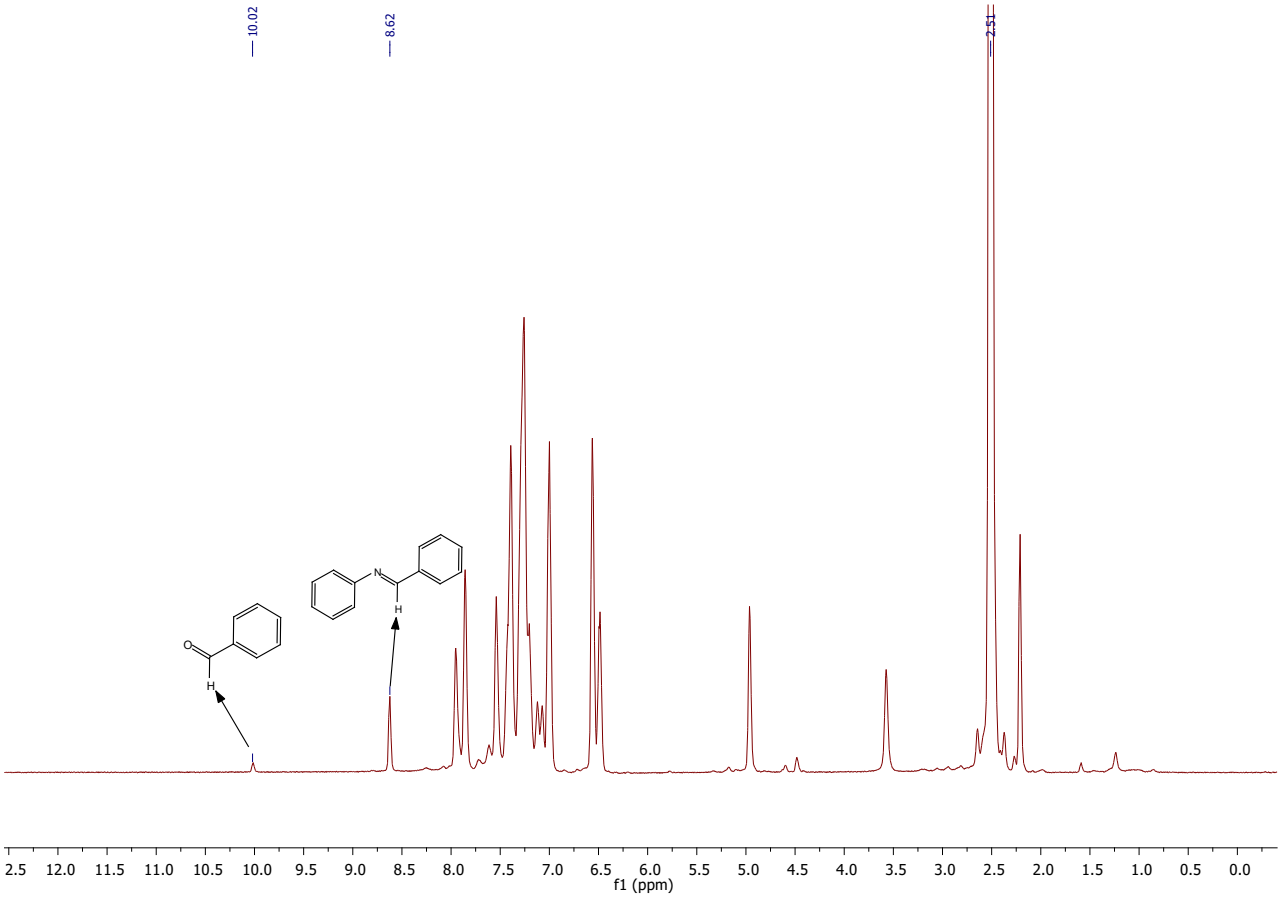

Figure S12. ^{1}H NMR of reaction mixture of Benzyl alcohol with aniline under optimized reaction condition at 30 min.

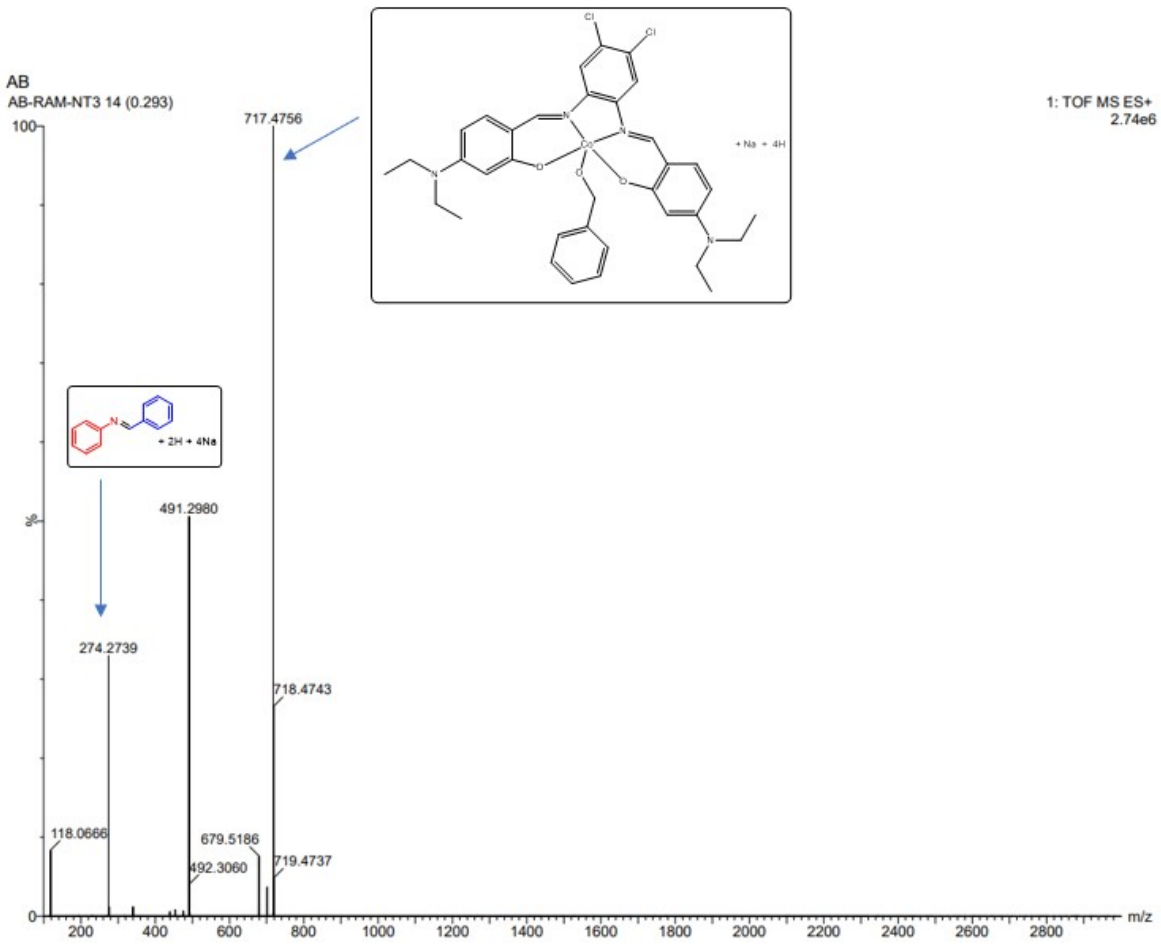

Figure S13. HRMS of reaction mixture of Benzyl alcohol with aniline under optimized reaction condition at 10 min.

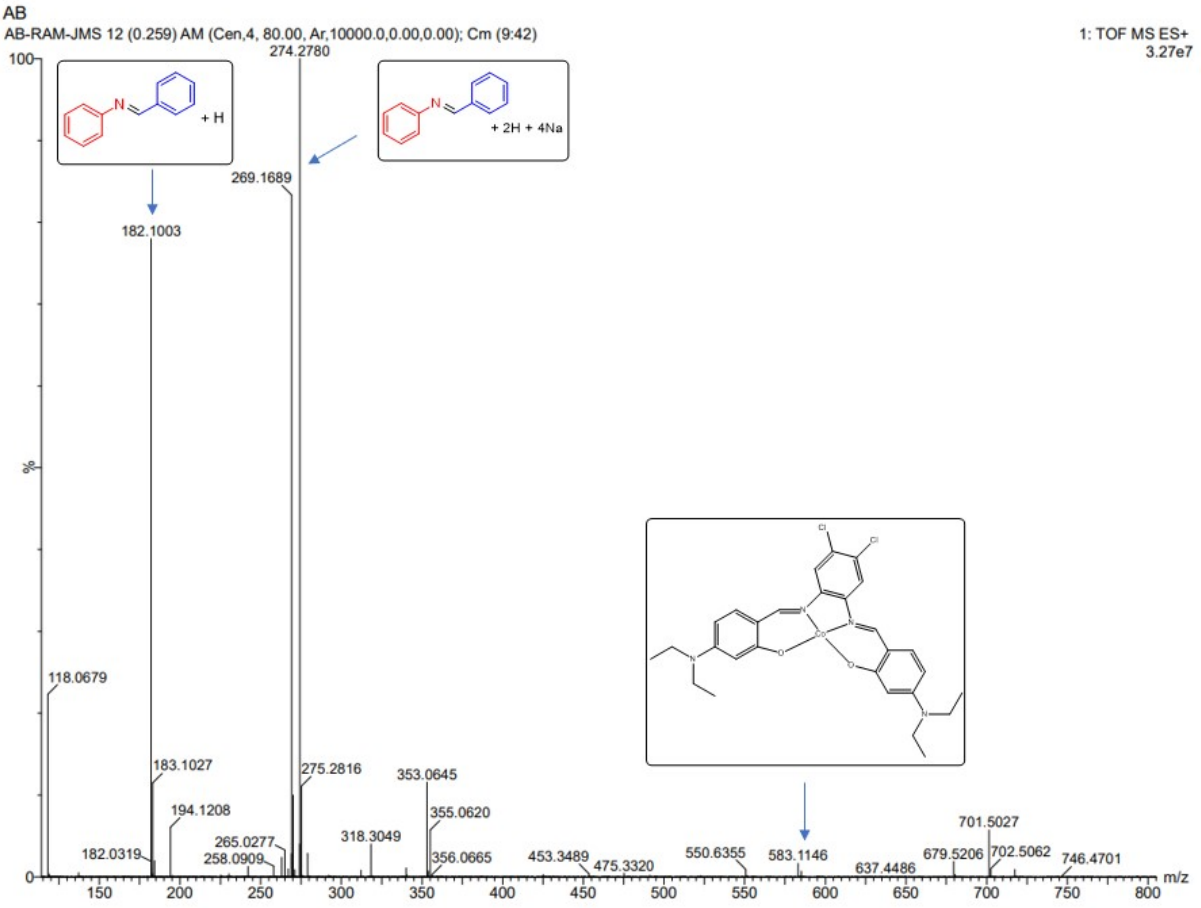

Figure S14. HRMS of reaction mixture of Benzyl alcohol with aniline under optimized reaction condition at 4 hours.

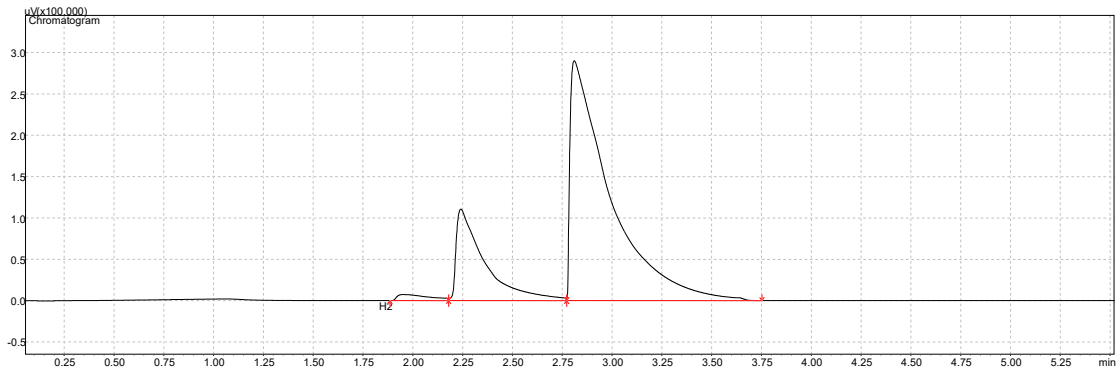

Figure S14. GC of the reaction mixture of benzyl alcohol with aniline catalyzed by **1b**, showing the evolution of H_2 gas.

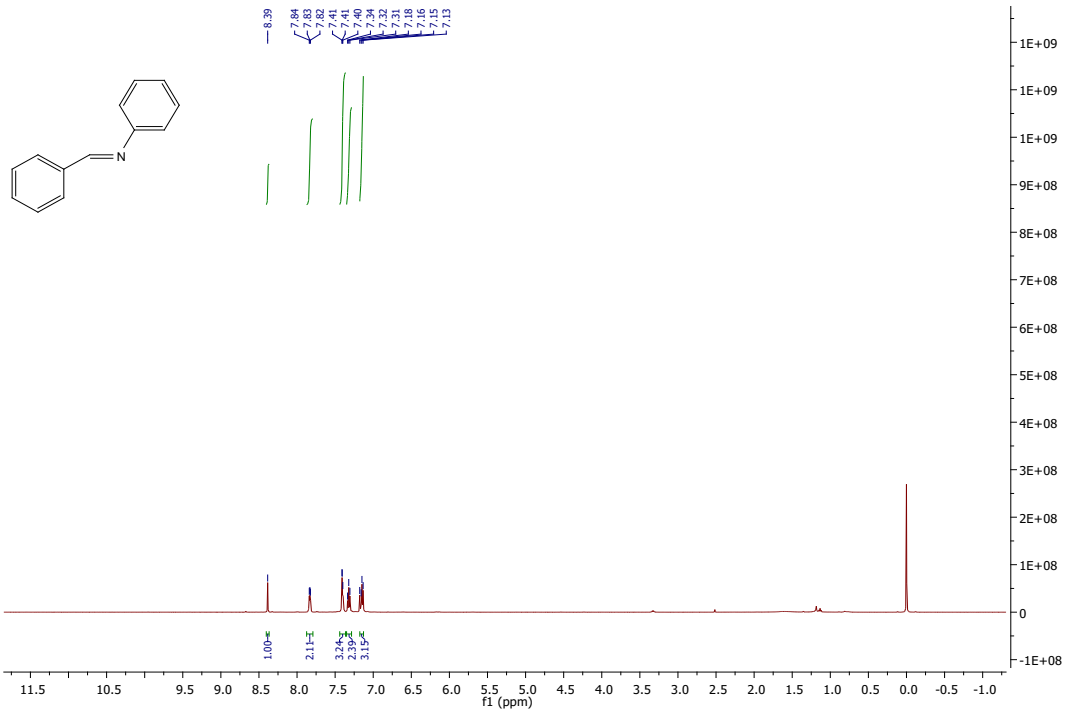

Figure S16. [1]H NMR of Compound **4a**

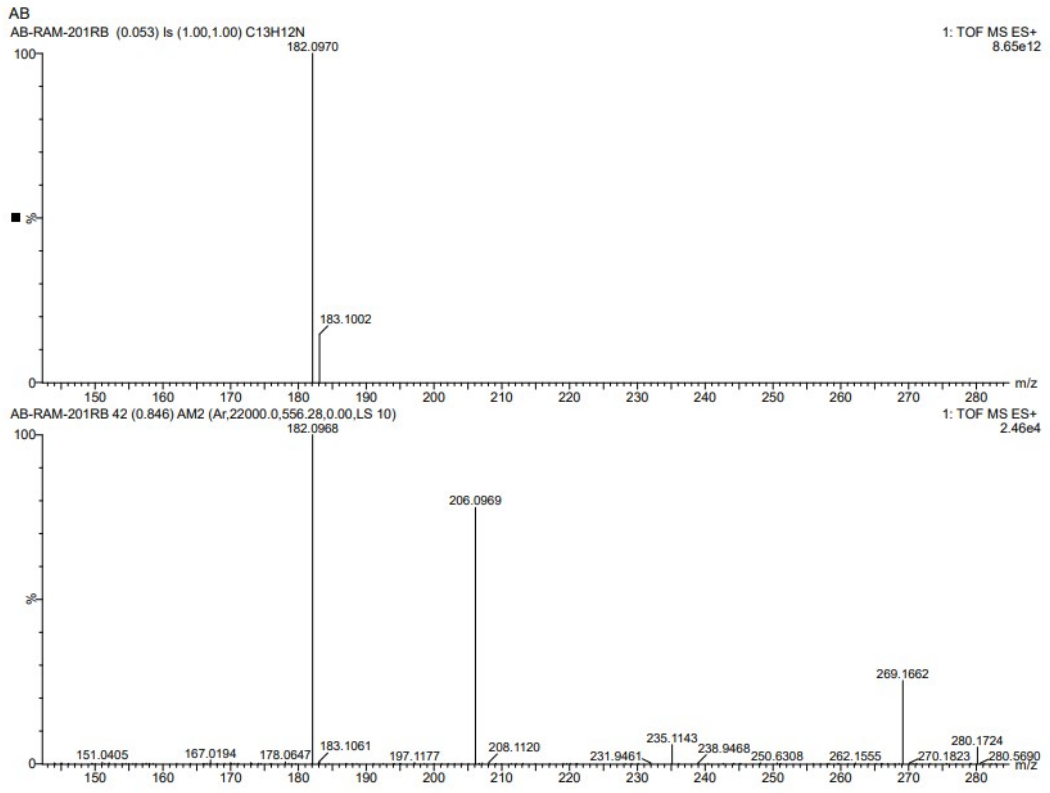

Figure S17. HRMS of Compound **4a**

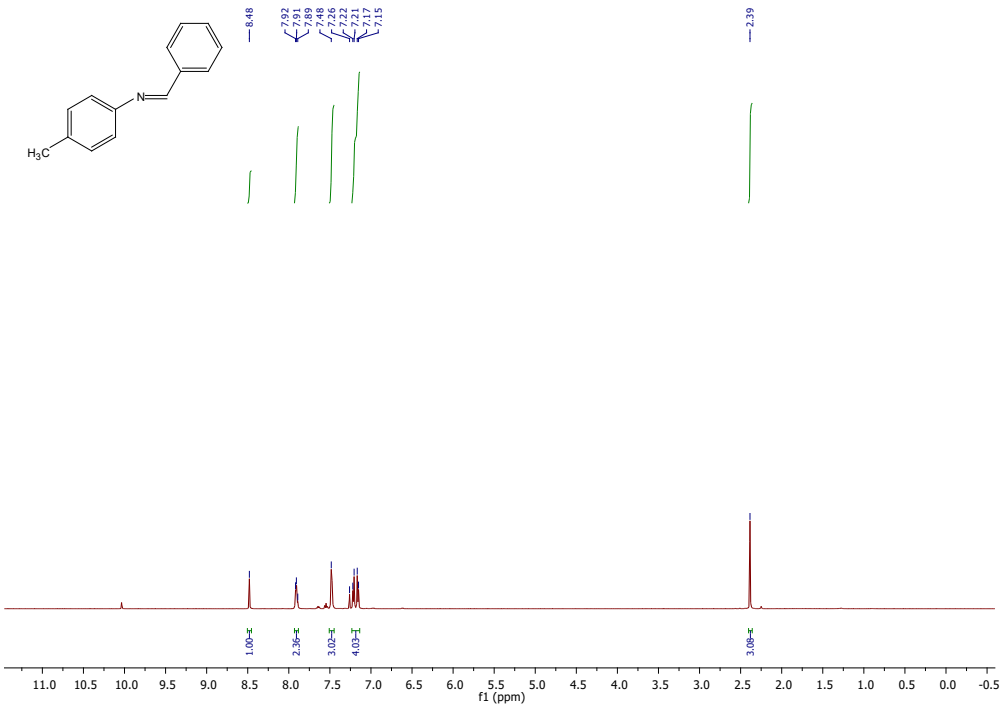

Figure S18. ^{1}H NMR of Compound **4b**

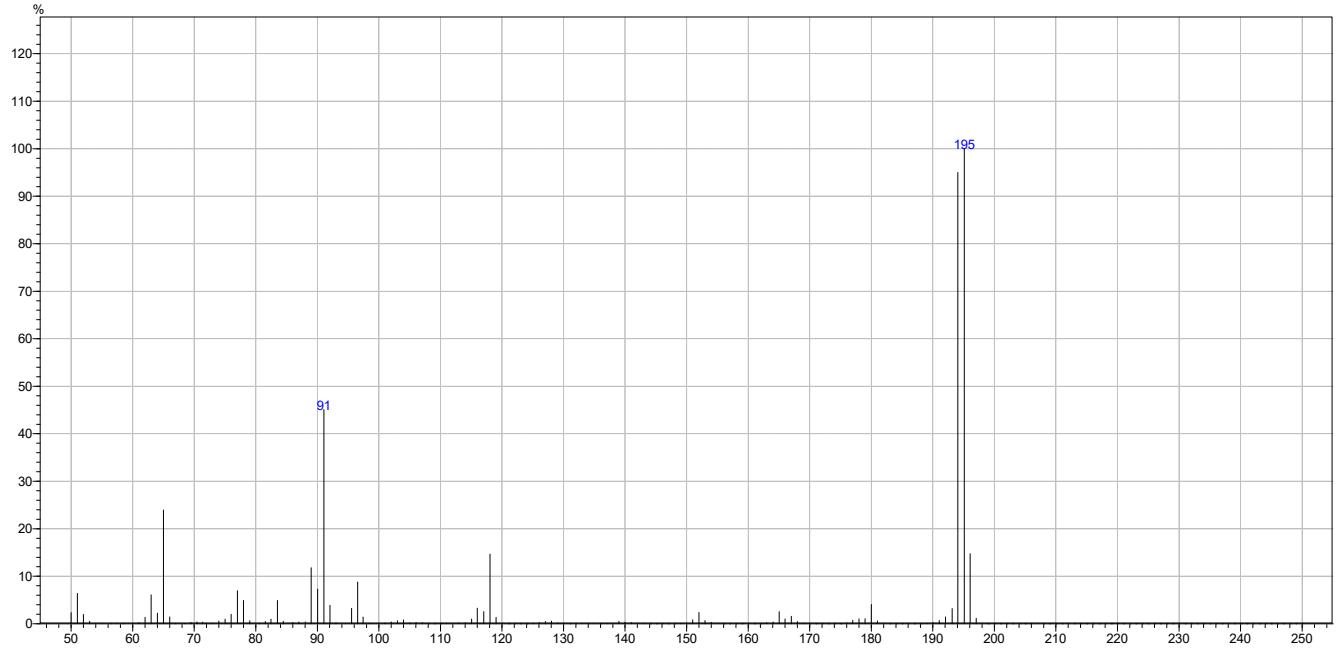

Figure S19. GC-MS of Compound **4b**

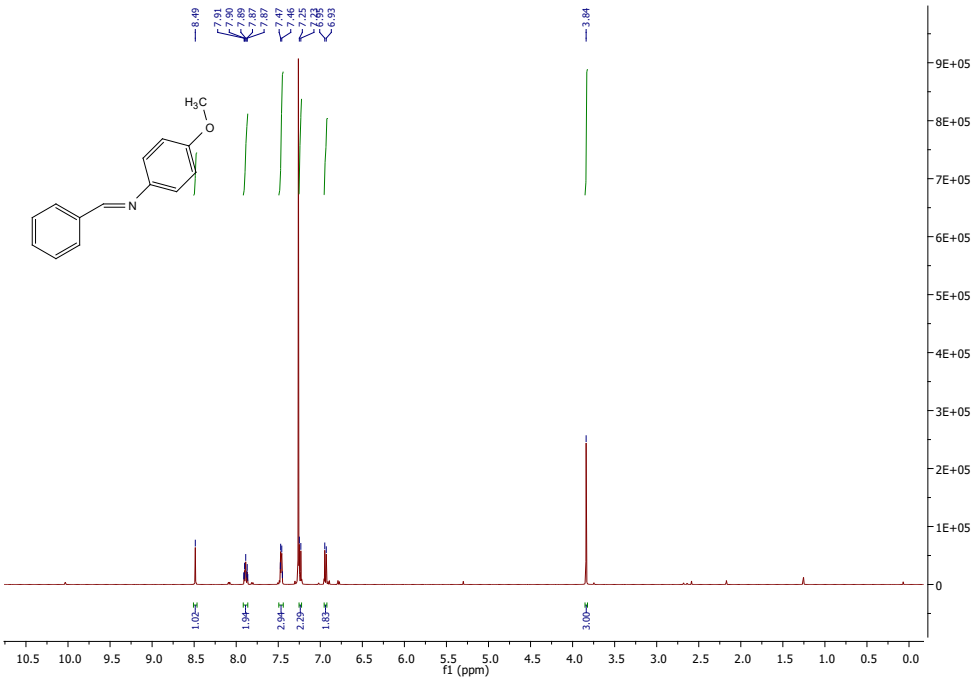

Figure S20. ^{1}H NMR of Compound **4c**

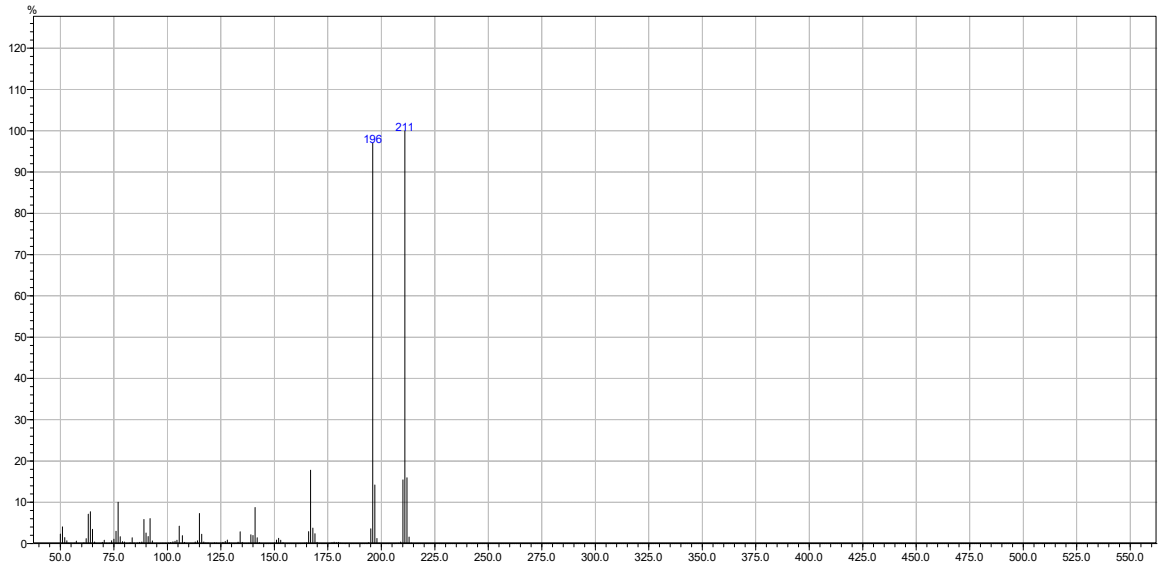

Figure S21. GC-MS of Compound **4c**

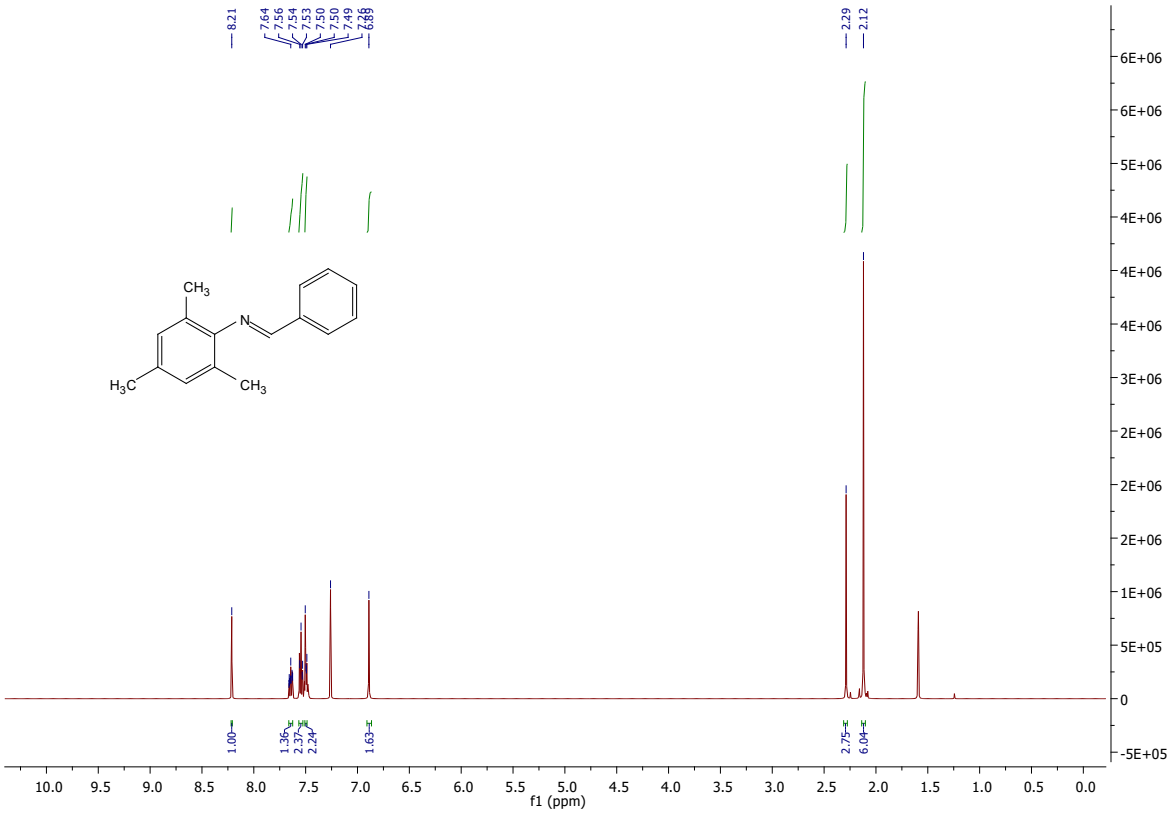

Figure S22. ^{1}H NMR of Compound **4d**

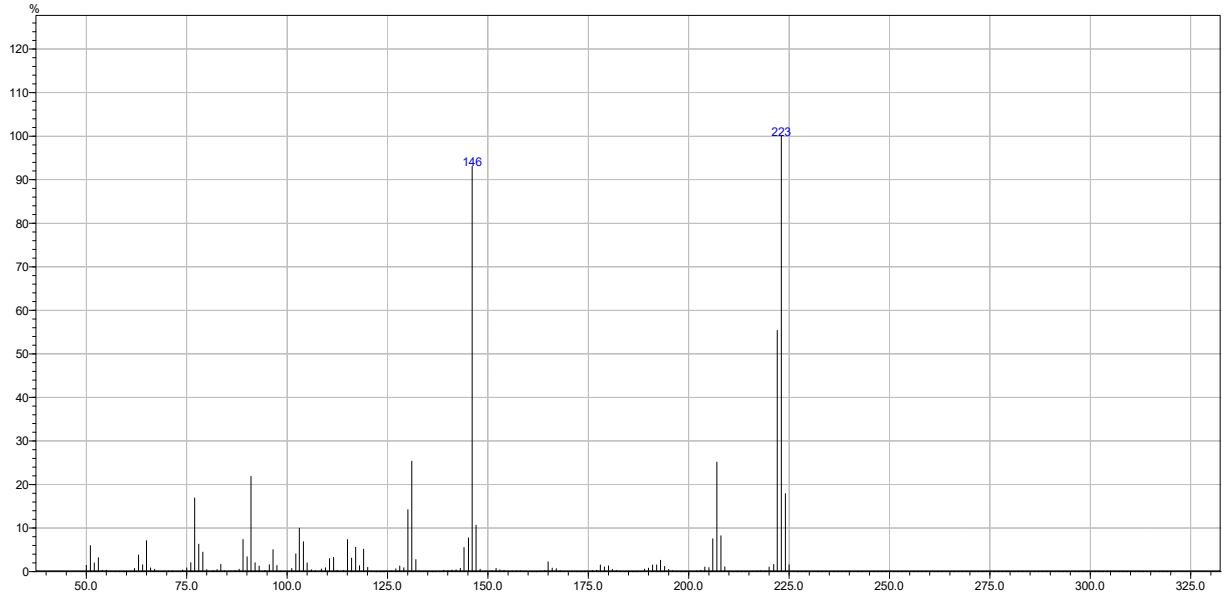

Figure S23. GC-MS of Compound **4d**

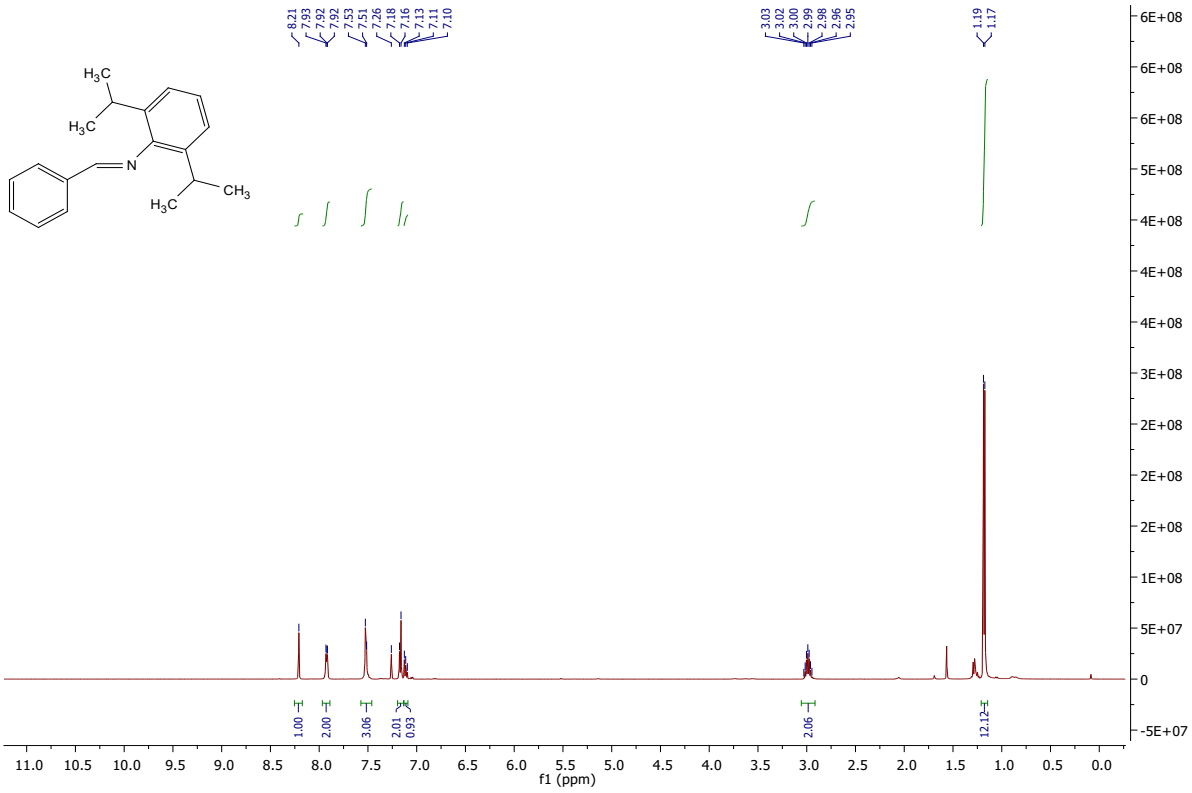

Figure S24. [1]H NMR of Compound **4e**

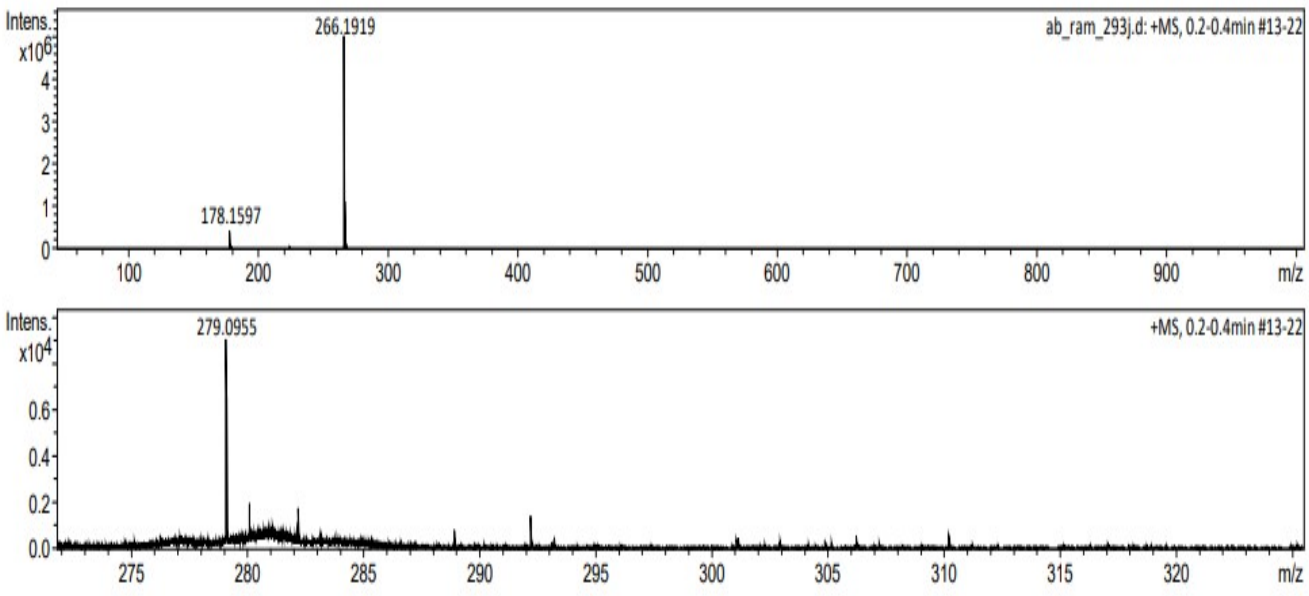

Figure S25. HRMS of Compound **4e**

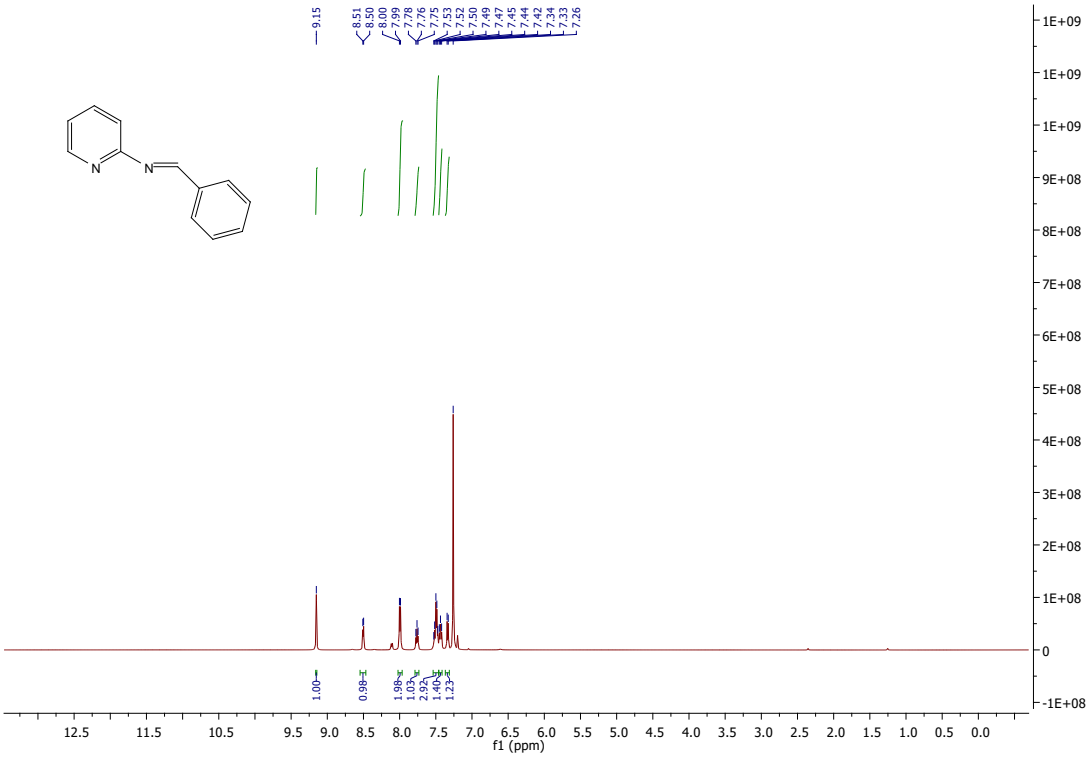

Figure S26. [1]H NMR of Compound **4g**

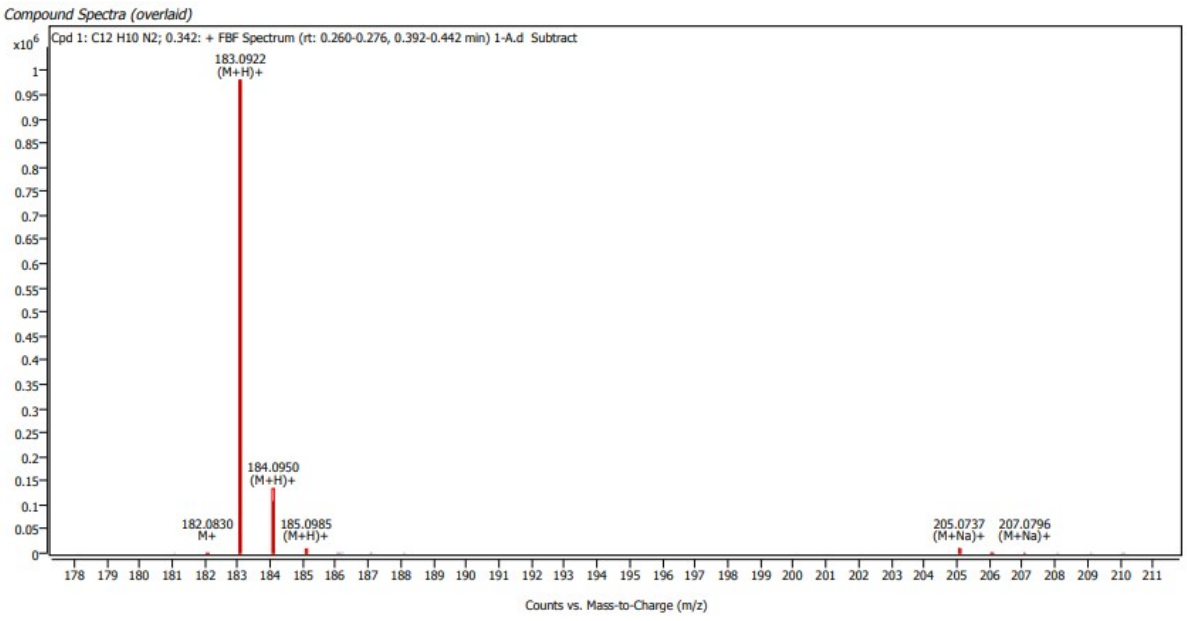

Figure S27. HRMS of Compound **4g**

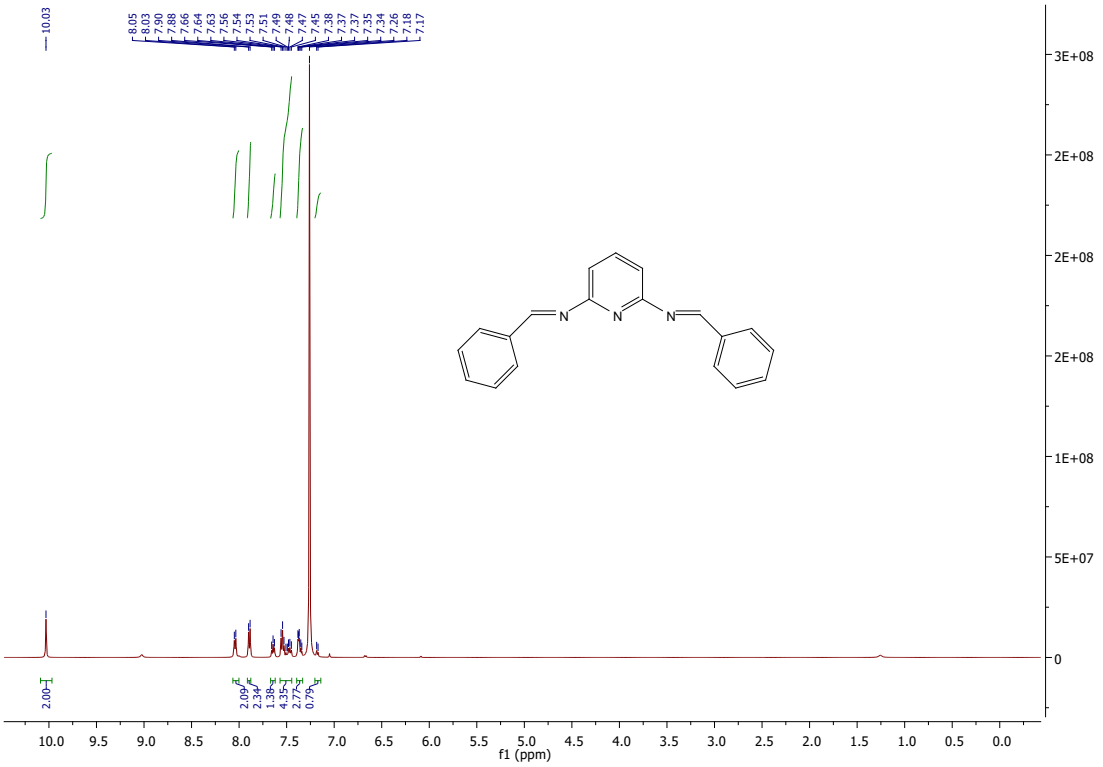

Figure S28. ^{1}H NMR of Compound **4i**

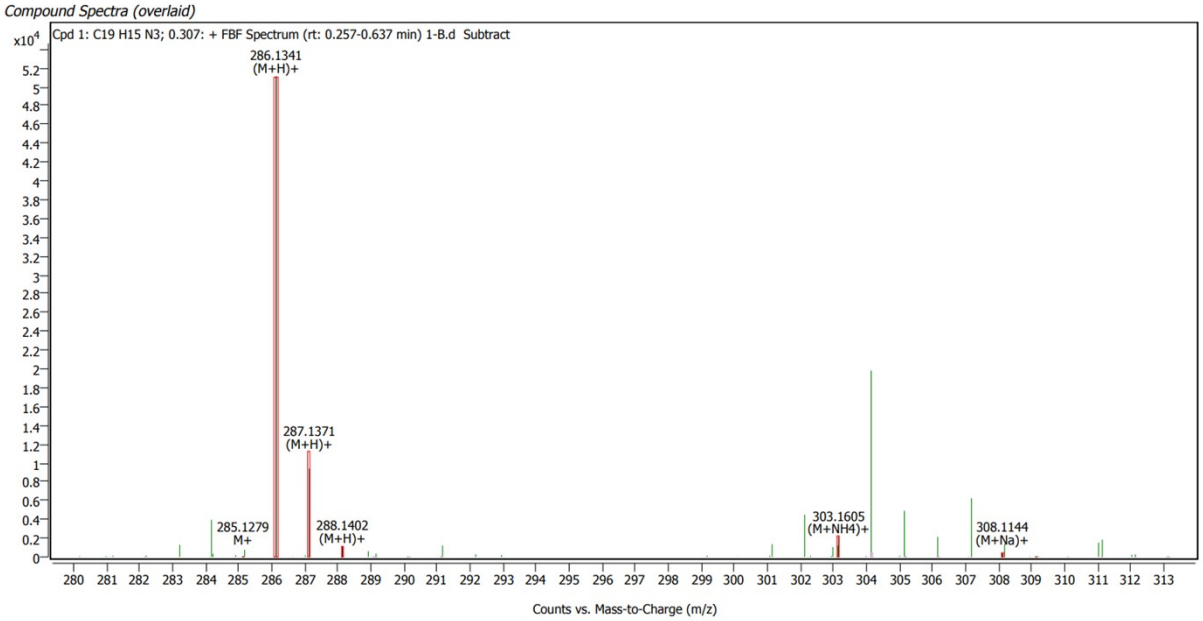

Figure S29. HRMS of Compound **4i**

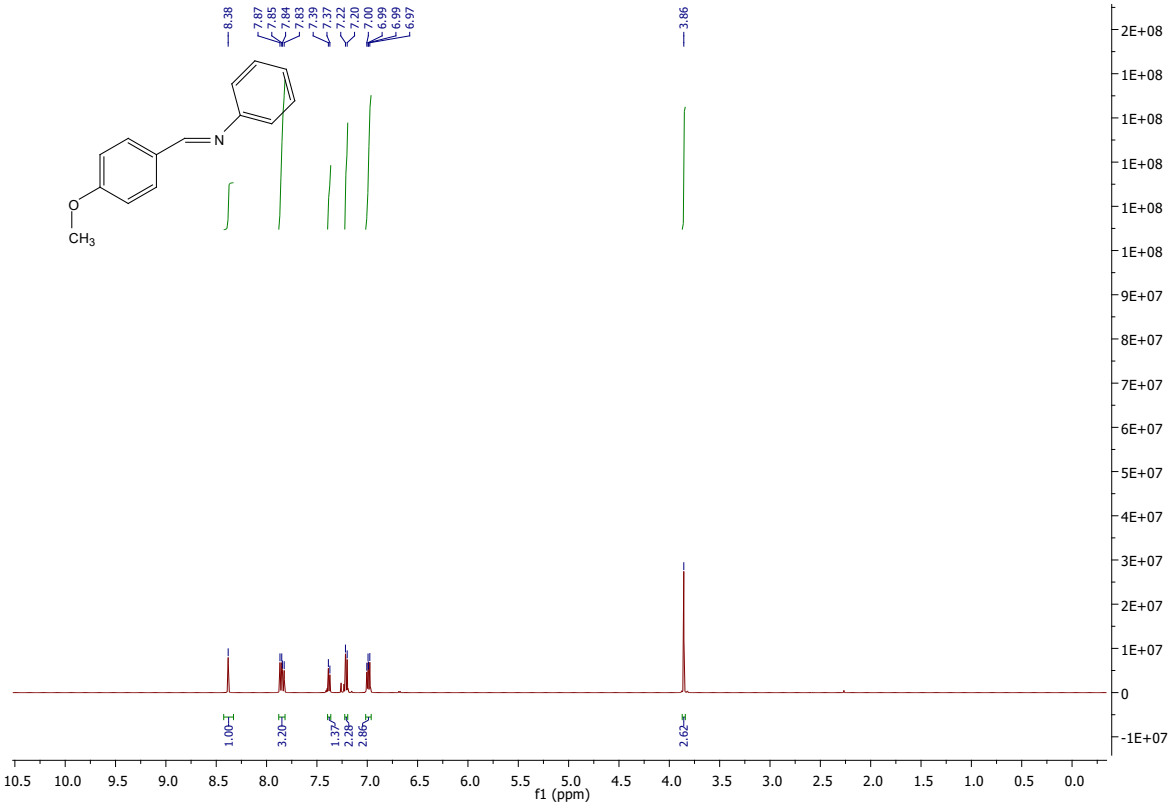

Figure S30. ^{1}H NMR of Compound **4l**

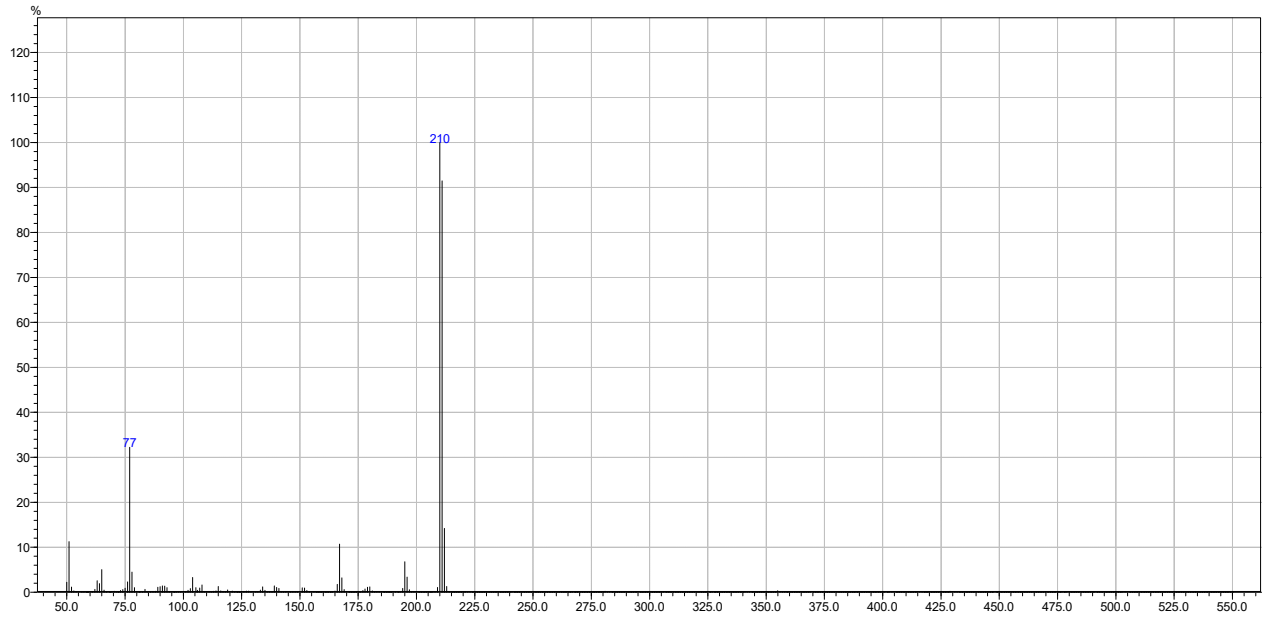

Figure S31. GC-MS of Compound **4l**

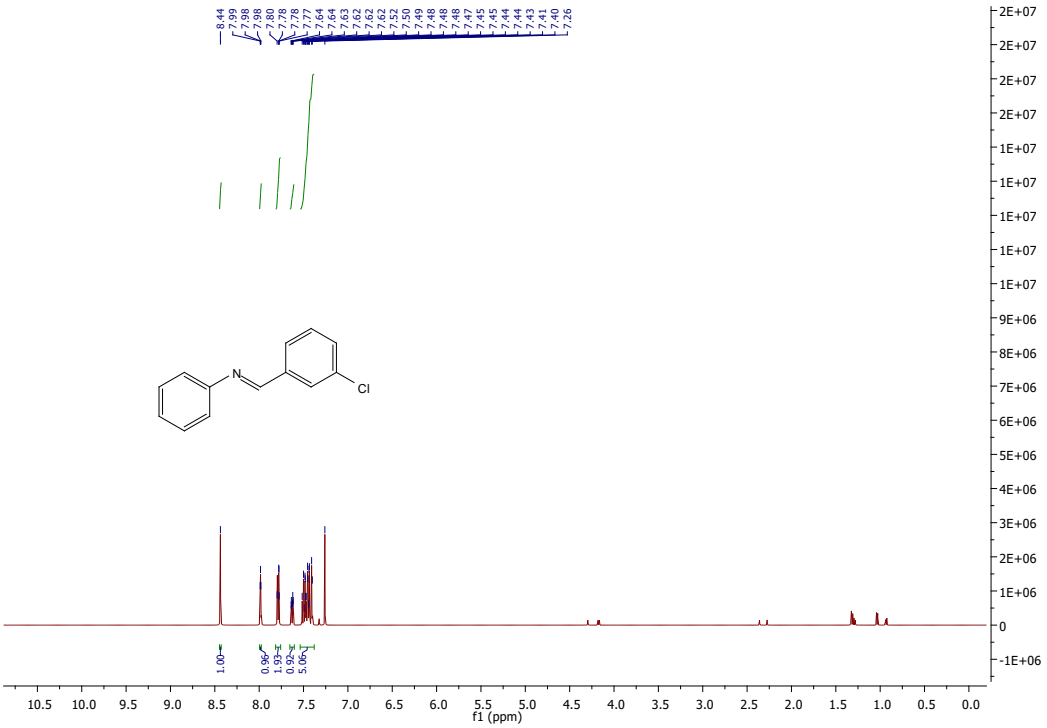

Figure S32. ^{1}H NMR of Compound **4o**

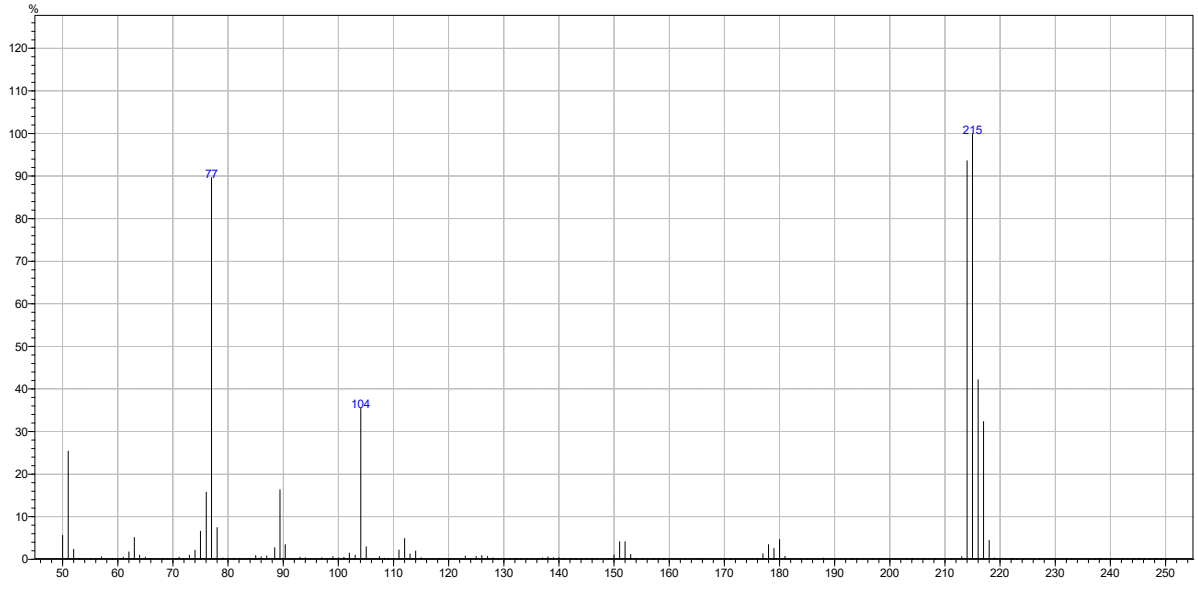

Figure S33. GC-MS of Compound **4o**

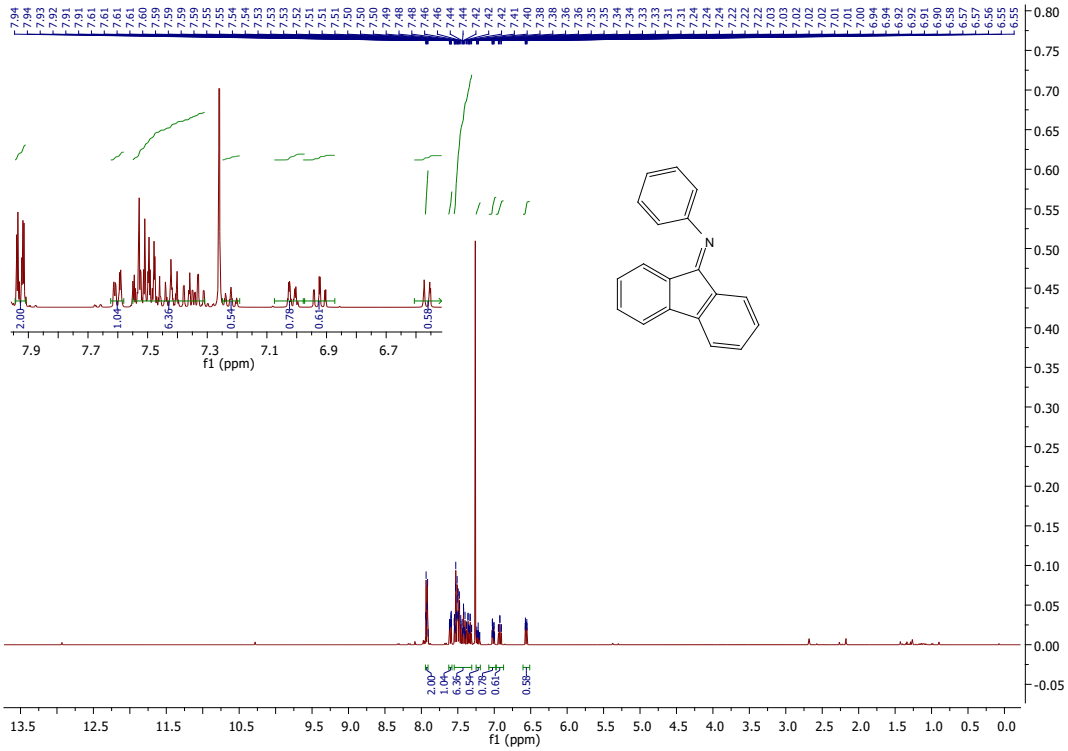

Figure S34. ^{1}H NMR of Compound **4s**

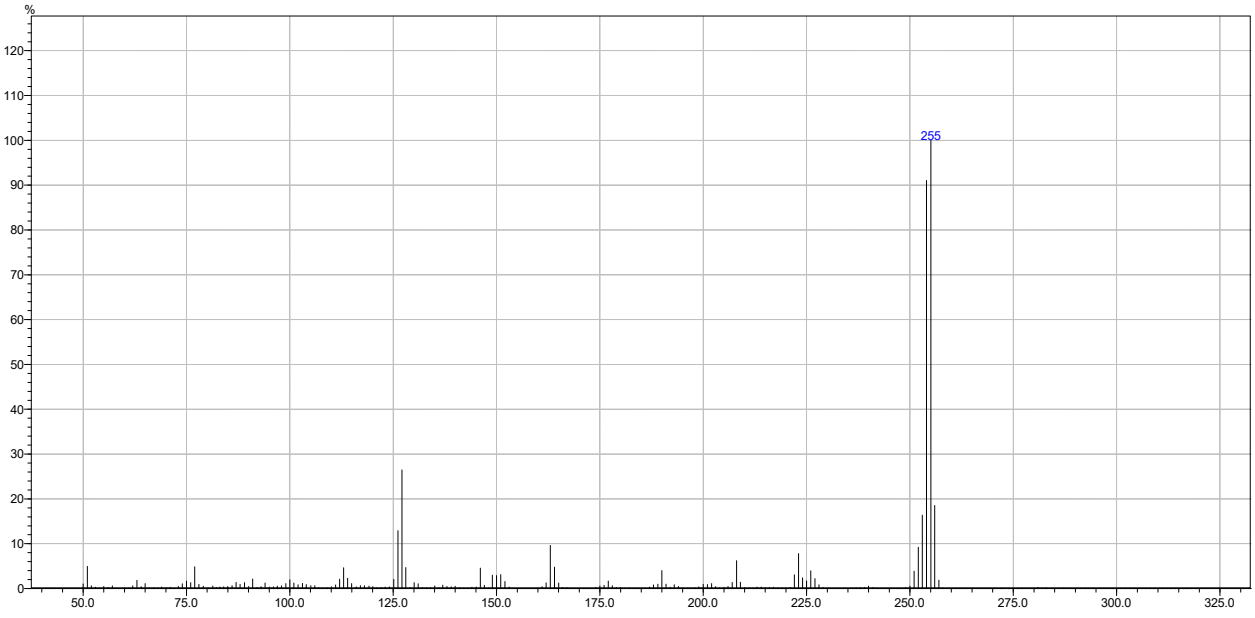

Figure S35. GC-MS of Compound **4s**

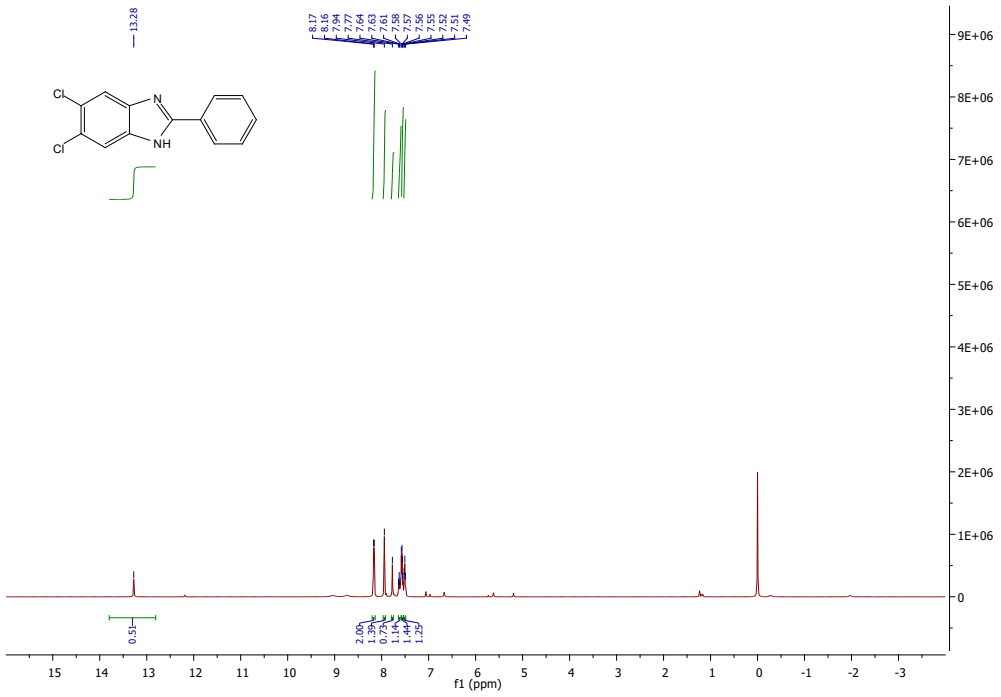

Figure S36. ^{1}H NMR of Compound **5a**

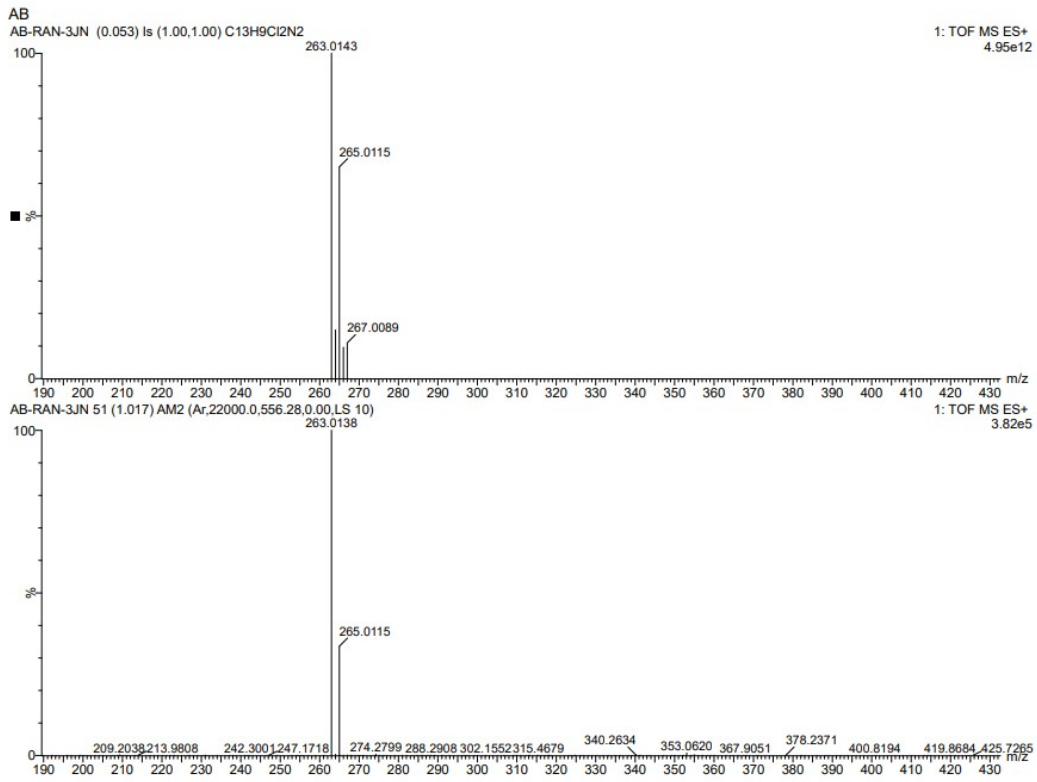

Figure S37. HRMS of Compound **5a**

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