Electronic Supporting Information

Benzylamine promoted direct C–H arylation of arenes and heteroarenes via excitation with heat or light

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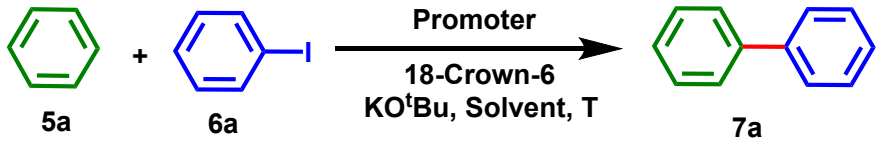
1. Optimization of the 1-promoted C–H arylation of benzene with iodobenzene under heating condition:

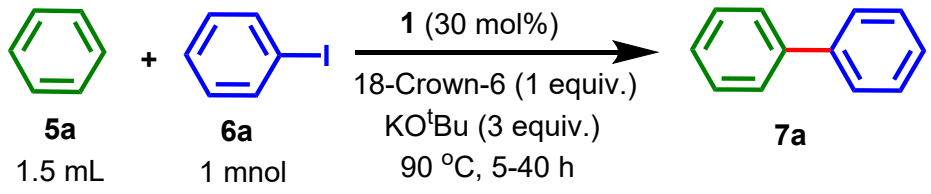


Scheme S1. 1-promoted C–H arylation of benzene with iodobenzene.

In a pressure tube, KO^{t}Bu (0-3 mmol) promotor **1-4** (0-0.3 mmol) and benzene (1.5 mL) were added under inert condition. An instant colour change from colorless to red was observed. After that, substrate iodobenzene (1 mmol) and 18-crown-6 (0-1 mmol) were added, and then the resulting mixture was stirred for 30-36 h at 80-90 °C under an inert atmosphere. Next, the reaction mixture was cooled down to room temperature and quenched with water (4 mL). After quenching, the biphenyl product **7a** was extracted with 30 mL (3 x 10 mL) of ethyl acetate and the combined organic part was dried over anhydrous sodium sulfate. The organic part was evaporated under reduced pressure leads to the crude **7a** which was further purified by column chromatography on silica gel using hexane as eluent to get the pure **7a**.

2. Kinetic Study

Table S1. Yield of benzylamine hydrochloride salt (**4a**) at different time intervals.



Entry	Reaction time	Yield (%)[a]
1	5 h	18
2	10 h	39
3	15 h	57
4	20 h	68
5	25 h	76
6	30 h	82
7	35 h	86
8	40 h	86

[a] Isolated yield.

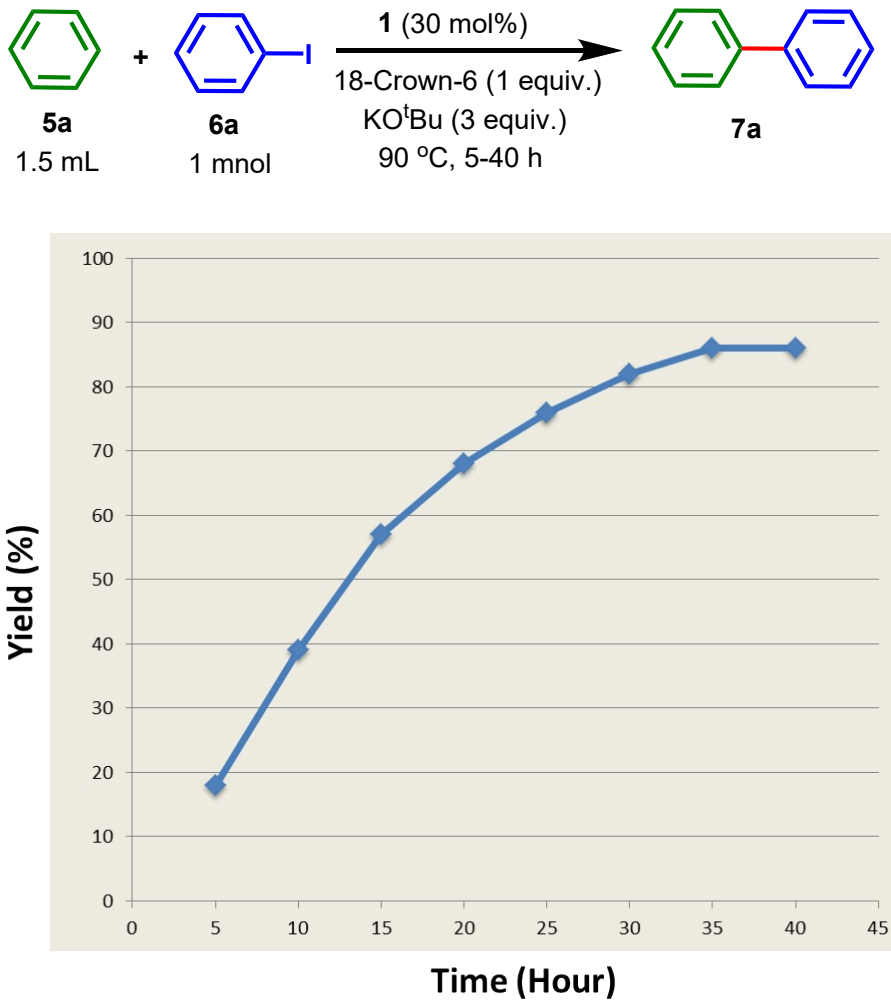
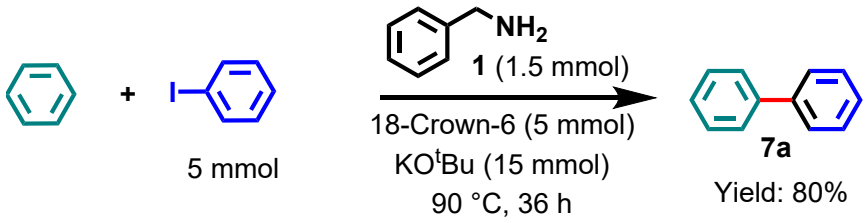


Figure S1. Graphical representation of yield of C–H arylation of benzene (**7a**) *vs* time.

3. Procedure for gram-scale synthesis of 7a:

In a pressure tube, KO^{t}Bu (1.68 g, 15 mmol, 3.0 equiv.), promotor 1 (161 mg, 1.5 mmol) and benzene (7.5 mL) were added under inert condition. After that, iodobenzene (1.02 g, 5 mmol) and 18-crown-6 (1.32 g, 5 mmol) were added, and then the resulting mixture was stirred for 36 h at 90 °C under an inert atmosphere. Next, the reaction mixture was cooled down to room temperature and quenched with water (20 mL). After quenching, the arylated products were extracted with 150 mL (3 x 50 mL) of ethyl acetate and the combined organic part was dried over anhydrous sodium sulfate. The organic part was evaporated under reduced pressure leads to the crude arylated product which was further purified by column chromatography on silica gel using hexane as eluent. The yield of the isolated pure compound is 618 mg (80 %).

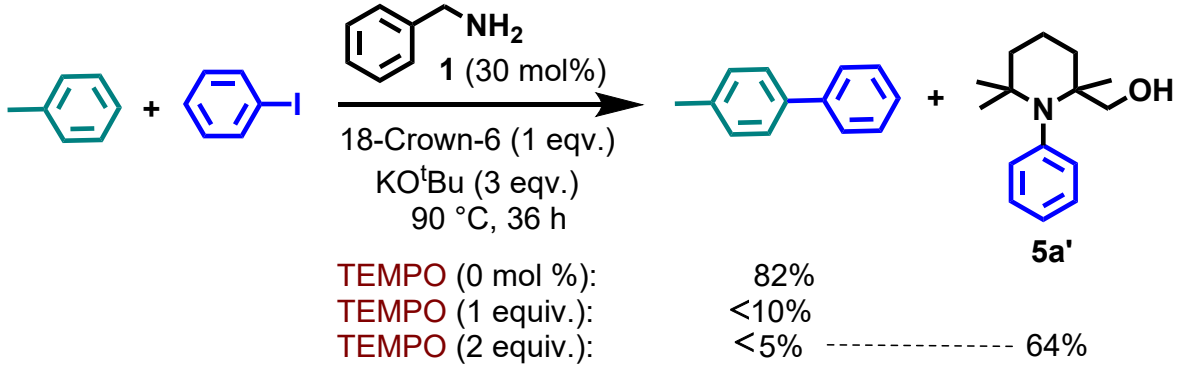


Scheme S2: 1-promoted C–H arylation of benzene in gram-scale.

4. Mechanistic studies

4.1. 1-promoted C–H arylation of toluene using iodobenzene in presence of excess TEMPO:

In a pressure tube, KO^{t}Bu (336 mg, 3 mmol, 3.0 equiv.), promotor **1** (32 mg, 30 mol %) and toluene (1.5 mL) were added under inert condition. After that, TEMPO (0-2 mmol), iodobenzene (1 mmol) and 18-crown-6 (264 mg, 1 equiv.) were added, and then the resulting mixture was stirred for 36 h at 90 °C under an inert atmosphere. Next, the reaction mixture was cooled down to room temperature and quenched with water (4 mL). After quenching, the arylated products were extracted with 30 mL (3 x 10 mL) of ethyl acetate and the combined organic part was dried over anhydrous sodium sulfate. The organic part was evaporated under reduced pressure leads to the crude mixture of phenyl-toluene and TEMPO-trapped radical. Further purification by column chromatography on silica gel using hexane/ethylacetate as eluent leads to the pure phenyl-toluene product and TEMPO-trapped radical (**5a'**). The **5a'** was isolated with 64% yield when 2 equivalent TEMPO was used in the reaction mixture.



Scheme S3. 1-catalysed C–H arylation of furan in presence of TEMPO.

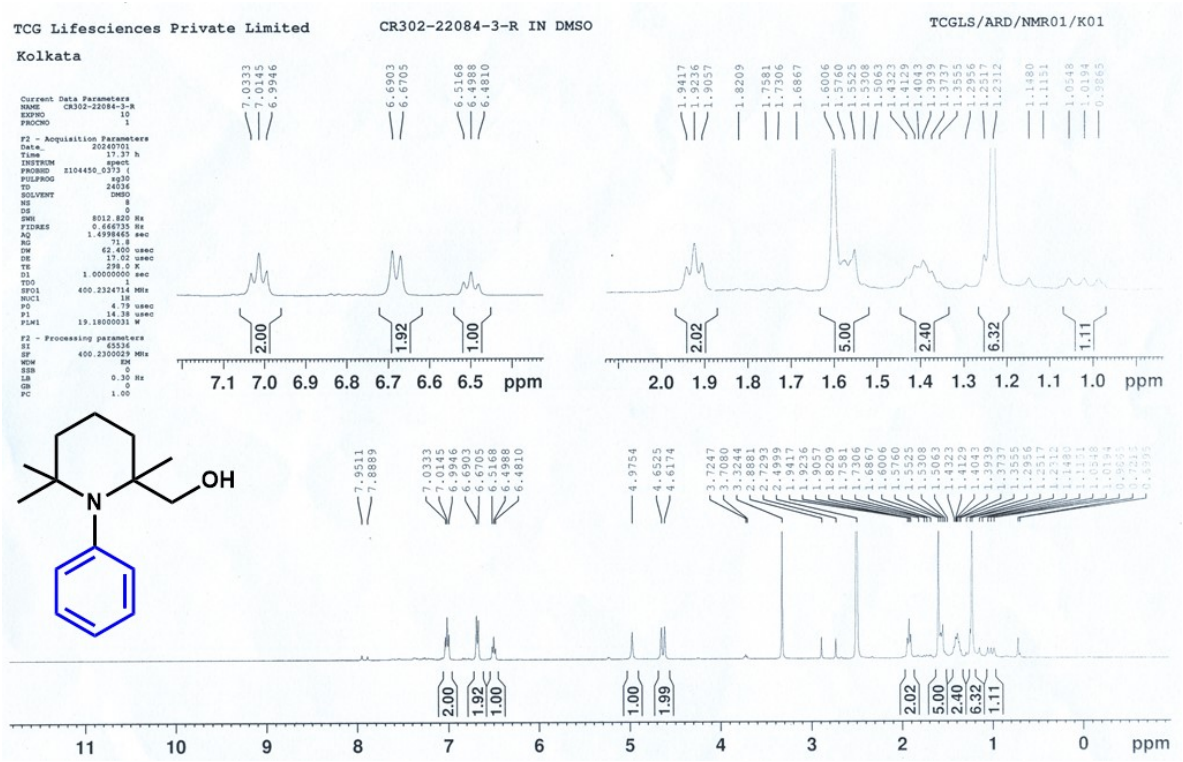


Figure S2: ^{1}H NMR spectrum of **5a'**.

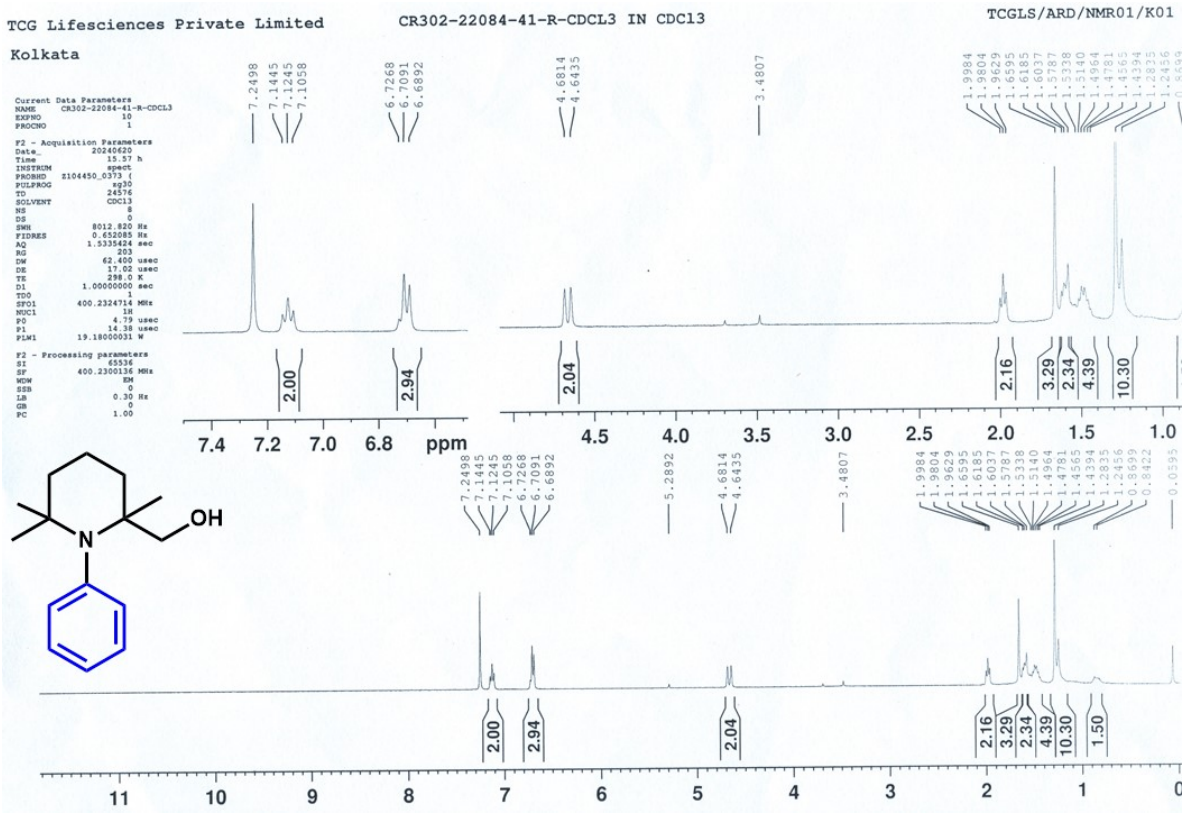


Figure S3: ^{13}C {^{1}H} NMR spectrum of **5a'**.

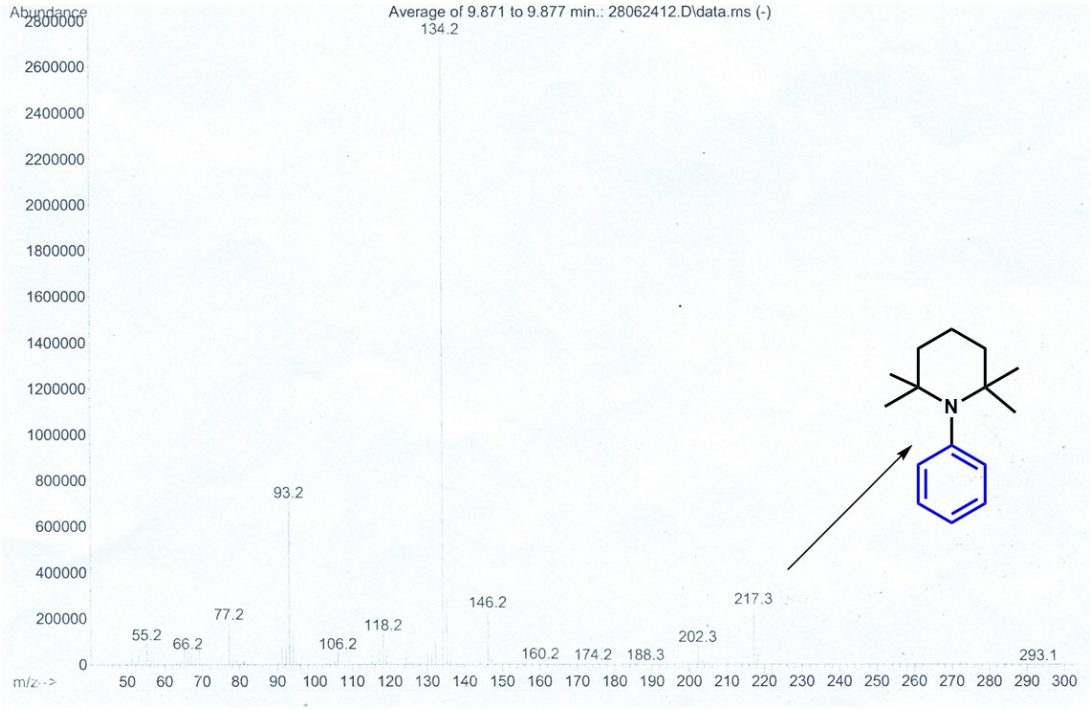
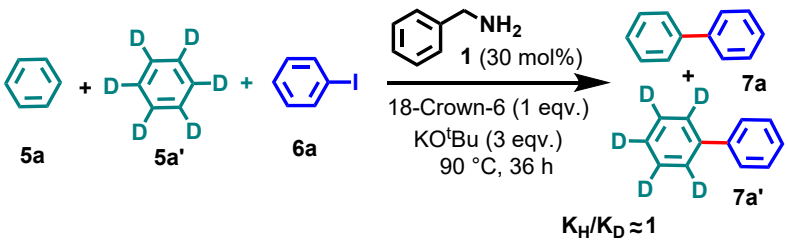


Figure S4: GC-MS spectrum of **5a'**.

4.2. Kinetic isotope effect experiment.

In a pressure tube, KO^{t}Bu (336 mg, 3 mmol, 3.0 equiv.), promotor **1** (32 mg, 30 mol %) and 1:1 mixture of benzene and benzene-d6 (0.75 mL + 0.75 mL) were added under inert condition. After that, iodobenzene (1 mmol) and 18-crown-6 (264 mg, 1 equiv.) were added, and then the resulting mixture was stirred for 36 h at 90 °C under an inert atmosphere. Next, the reaction mixture was cooled down to room temperature and quenched with water (4 mL). After quenching, the arylated products were extracted with 30 mL (3 x 10 mL) of ethyl acetate and the combined organic part was dried over anhydrous sodium sulfate. The organic part was evaporated under reduced pressure and then purified by column chromatography on silica gel using hexane as eluent. The GC-MS analysis indicates the formation of 1:1 mixture of phenyl-benzene **7a** and deuterated phenyl-benzene **7a'**.



Scheme S4. Kinetic isotope effect experiment.

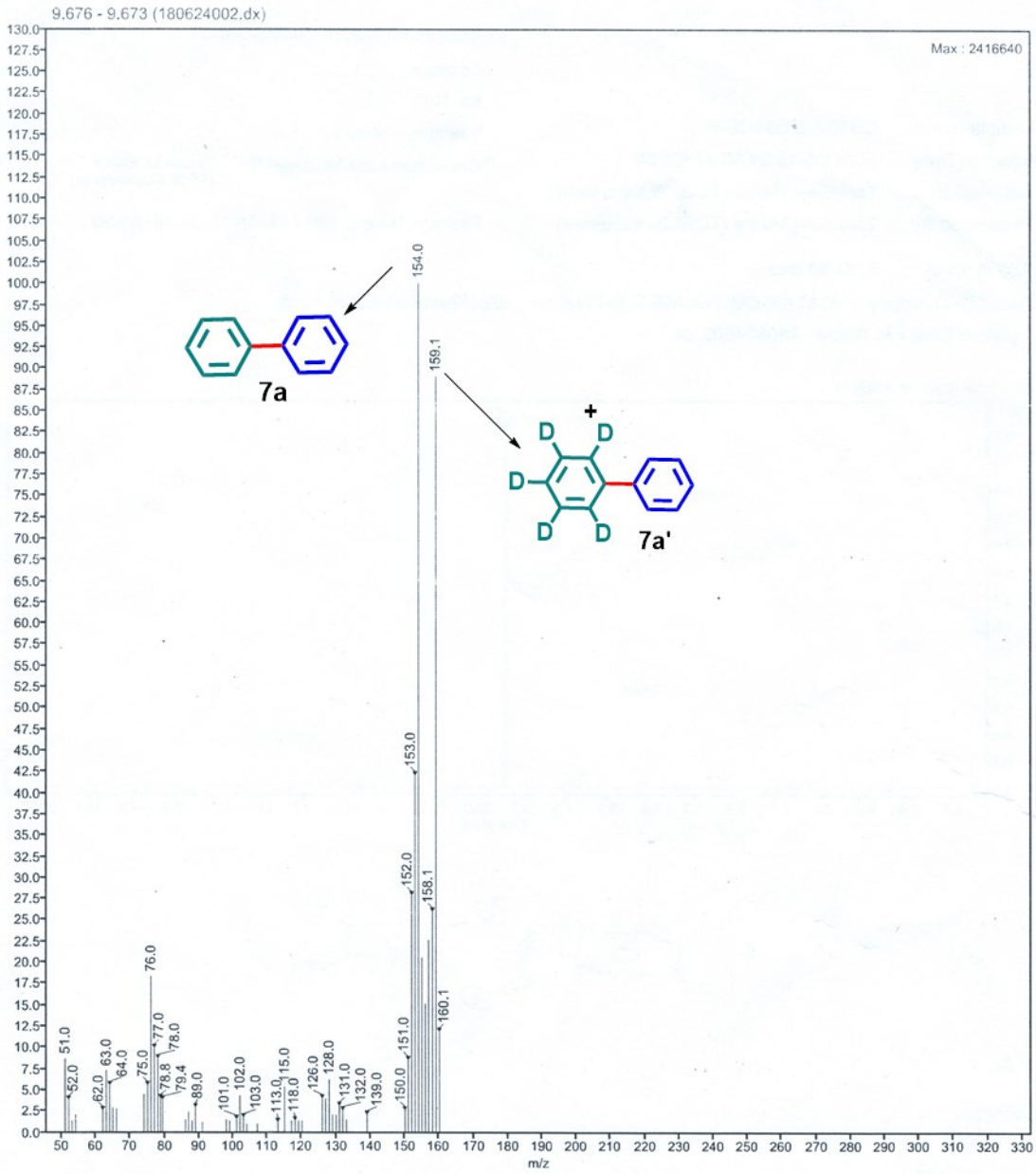
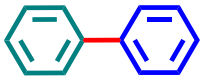


Figure S5: GC-MS spectrum of the mixture of **7a** and **7a'**.

5. The analytical and spectroscopic characterization data of the products:

Phenylbenzene, 7a[1]



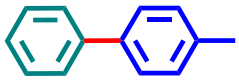
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.65 (d, J = 7.1 Hz, 4H), 7.46 (t, J = 7.6 Hz, 4H), 7.36 (t, J = 7.7 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 140.09, 128.82, 127.52, 127.31, 126.59.

GC-MS: calc. for **7a**: 154.2; found: 154.2.

4-Methylphenylbenzene, 7b[2]



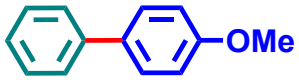
White crystalline solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.72-7.68 (m, 2H), 7.63 (d, J = 7.3 Hz, 2H), 7.46 (t, J = 8 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.29 (t, J = 8.3 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 140.00, 137.20, 136.58, 129.40, 128.76, 126.99, 126.38, 126.30, 20.54.

GC-MS: calc. for **7b**: 168.2; found: 168.2.

4-Methoxybiphenyl, 7c[3]



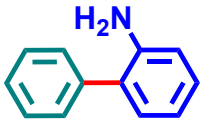
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.60 (m, 4H), 7.42 (t, J = 8 Hz, 2H), 7.31 (t, J = 8 Hz, 1H), 7.01 (d, J = 6 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 158.80, 139.74, 132.43, 128.76, 127.65, 126.60, 126.08, 114.26, 55.06.

GC-MS: calc. for **7c**: 184.2; found: 184.2.

2-Aminobiphenyl, 7d[4]



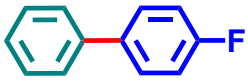
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.43 (m, 4H), 7.33 (t, J = 6.9 Hz, 1H), 7.04 (t, J = 7.3 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 6.76 (d, J = 7.8 Hz, 1H), 6.64 (t, J = 7.3 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 145.58, 138.95, 128.49, 127.16, 125.05, 124.38, 120.44, 116.85, 115.51, 115.02.

GC-MS: calc. for **7d**: 169.1; found: 169.1.

4-Fluorobiphenyl, 7e[5]



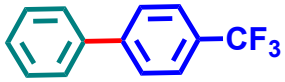
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.43 (m, 4H), 7.33 (t, J = 6.9 Hz, 1H), 7.04 (t, J = 7.3 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 6.76 (d, J = 7.8 Hz, 1H), 6.64 (t, J = 7.3 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 139.06, 136.58, 136.55, 128.86, 128.61, 128.53, 127.31, 126.55, 115.72, 115.50.

GC-MS: calc. for **7e**: 172.2; found: 172.2.

4-(Trifluoromethyl)biphenyl, 7f[6]



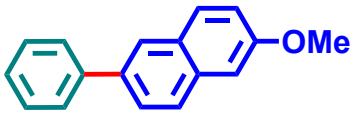
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.89 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 7.6 Hz, 2H), 7.52 (t, J = 7.2 Hz, 2H), 3.79 (s, 3H), 7.45 (t, J = 7.2 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 144.07, 138.50, 129.00, 128.33, 127.91, 127.59, 127.36, 126.93, 125.65, 125.61.

GC-MS: calc. for 8h: 222.2; found: 222.2.

2-Methoxy-6-phenylnaphthalene, 7g[7]



White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 8.14 (s, 1H), 7.90 (d, J = 8.8 Hz, 2H), 7.79 (t, J = 7.2 Hz, 3H), 7.49 (t, J = 7.8 Hz, 2H), 7.35 (m, 2H), 7.19 (dd, J = 8.9 and 2.4 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 157.32, 140.00, 135.06, 133.45, 129.63, 128.78, 128.66, 127.25, 127.09, 126.59, 125.35, 124.96, 119.61, 105.94, 55.17, 55.11.

GC-MS: calc. for **7f**: 234.2; found: 234.2.

p-Terphenyl, 7h[8]

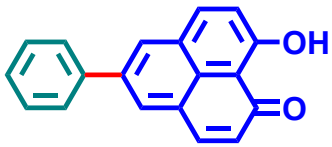
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.78 (s, 4H), 7.72 (d, J = 7.7 Hz, 4H), 7.49 (t, J = 7.6 Hz, 4H), 7.39 (t, J = 7.8 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 139.50, 139.04, 128.89, 127.42, 127.08, 126.46.

GC-MS: calc. for **7g**: 234.2; found: 234.2.

9-Hydroxy-5-phenyl-1H-phenalen-1-one, 7i[9]



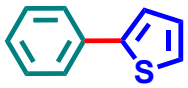
Yellow solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane/DCM.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 14.08 (s, 1H), 8.66 (s, 2H), 8.49 (d, J = 8.2 Hz, 2H), 7.90 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.9 Hz, 2H), 7.45 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 9.3 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 178.36, 142.24, 138.86, 136.35, 131.64, 129.09, 127.82, 126.93, 125.60, 125.04, 123.37.

GC-MS: calc. for **7h**: 273.1; found: 273.1.

2-phenylthiophene, 7j[10]



Yellow solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.87 (s, 1H), 7.71 (d, J = 7.8 Hz, 2H), 7.64 (t, J = 2.8 Hz, 1H), 7.56 (d, J = 4.8 Hz, 1H), 7.41 (t, J = 8.0 Hz, 2H), 7.29 (t, J = 6.3 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 141.33, 135.02, 128.76, 126.98, 126.96, 126.05, 125.95, 120.82.

GC-MS: calc. for **7i**: 160.2; found: 160.2.

4-Phenylpyridine, 7k[11]

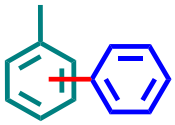
Yellow solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 8.72 (d, J = 4.8 Hz, 1H), 8.08 (t, J = 8.0 Hz, 1H), 7.97 (m, 3H), 7.68 (m, 2H), 7.55 (d, J = 8.0 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 148.47, 137.57, 132.89, 130.48, 128.11, 126.63. 124.09.

GC-MS: calc. for **7j**: 155.0; found: 155.0.

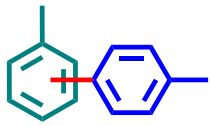
n-(Pphenyl)toluene, 8a



After completion of the reaction followed by quenching with water, product was extracted in 30 mL ethyl acetate and then dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure. All isomeric products (ortho, meta and para) were collected together from other reaction impurities by column chromatography over silica gel (100-200 mesh) using 3% EtOAc in hexane mixture. Total yield was calculated by taking weight of obtained mixture of products. This mixture of products was subjected to NMR

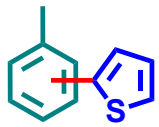
and GC-MS spectroscopic characterization. Analysis of NMR data suggests the presence of three regio-isomers in the product.

n-(Methylphenyl)toluene, 8b



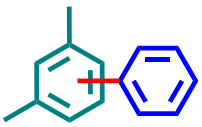
The same procedure mentioned above for **8a** was followed for the isolation of the product **8b**. Total yield was calculated by taking weight of obtained mixture of products. The mixture of product isomers was subjected to NMR and GC-MS spectroscopic characterization. Analysis of NMR data suggests the presence of three regio-isomers in the product.

n-(Thiophen-2-yl)toluene, 8c



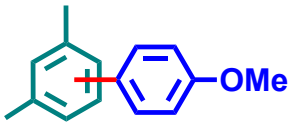
The 8c was synthesized and isolated according to the procedures mentioned for **8a**. Total yield was calculated by taking weight of obtained mixture of products. The mixture of product isomers was subjected to NMR and GC-MS spectroscopic characterization. Analysis of NMR data suggests the presence of three regio-isomers in the product.

n-(Phenyl)-m-xylene, 8d



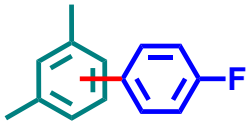
The **8d** was synthesized and isolated according to the procedures mentioned for **8a**. The purification was carried out by column chromatography over silica gel (100-200 mesh) using hexane. Total yield was calculated by taking weight of obtained mixture of products. The mixture of product isomers was subjected to NMR and GC-MS spectroscopic characterization. Analysis of NMR data suggests the presence of three regio-isomers in the product.

n-(4-Methoxyphenyl)-m-xylene, 8e



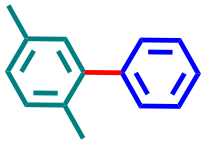
The **8e** was synthesized and isolated according to the procedures mentioned for **8a**. The purification was carried out by column chromatography over silica gel (100-200 mesh) using hexane. Total yield was calculated by taking weight of obtained mixture of products. The mixture of product isomers was subjected to NMR and GC-MS spectroscopic characterization. Analysis of NMR data suggests the presence of three regio-isomers in the product.

n-(4-Fluorophenyl)-m-xylene, 8f



The **8e** was synthesized and isolated according to the procedures mentioned for **8a**. The purification was carried out by column chromatography over silica gel (100-200 mesh) using hexane. Total yield was calculated by taking weight of obtained mixture of products. The mixture of product isomers was subjected to NMR and GC-MS spectroscopic characterization. Analysis of NMR data suggests the presence of three regio-isomers in the product.

2,5-Dimethylbiphenyl, 8g[12]



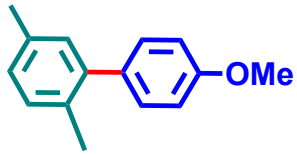
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.47 (t, J = 8.1 Hz, 1H), 7.42 (d, J = 7.2 Hz, 1H), 7.35 (m, 1H), 7.31 (d, J = 6.8 Hz, 2H), 7.16 (d, J = 7.6 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 7.00 (s, 1H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 141.37, 141.02, 137.04, 134.56 (d), 131.32, 130.20 (d), 128.71 (d), 128.08 (d), 127.76, 126.69, 20.41, 19.57.

GC-MS: calc. for **8g**: 183.2; found: 183.2.

4′-Methoxy-2,5-dimethyl-1,1′-biphenyl, 8h[13]



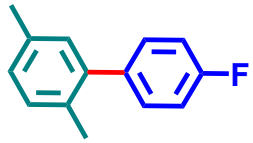
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.23 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 7.6 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.97 (d, J = 8.0 Hz, 3H), 3.79 (s, 3H), 2.28 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 157.98, 140.61, 134.45, 133.51, 131.31, 129.96, 129.78, 127.28, 113.40, 54.75 (d), 20.28, 19.50.

GC-MS: calc. for 8h: 212.2; found: 212.2.

4′-Fluoro-2,5-dimethyl-1,1′-biphenyl, 8i[13]



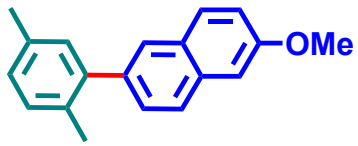
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.36 (m, 2H), 7.25 (d, J = 8.8 Hz, 2H), 7.07 (m, 1H), 7.00 (s, 1H), 2.28 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 162.35, 159.94, 139.96, 137.62, 127.58, 134.74, 131.44, 130.72 (d), 130.11(d), 127.91, 114.85 (d), 20.41 (d), 19.53.

GC-MS: calc. for **8i**: 200.2; found: 200.2.

2-(2,5-Dimethylphenyl)-6-methoxynaphthalene, 8j



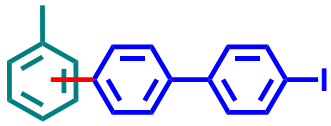
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.85 (m, 2H), 7.76 (s, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.36 (s, 1H), 7.18 (m, 2H), 7.10 (m, 1H), 3.68 (s, 3H), 2.31 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 157.22, 140.99, 136.50, 134.67, 132.96, 131.57, 130.16 (d), 129.32, 128.24, 127.72 (d), 127.09, 126.24, 124.48, 120.95, 118.68, 117.62, 55.11, 20.42, 19.67.

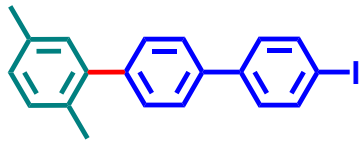
GC-MS: calc. for **8j**: 262.1; found: 262.1.

2-(2,5-Dimethylphenyl)-6-methoxynaphthalene, 8k



The **8k** was synthesized and isolated according to the procedures mentioned for **8a**. The purification was carried out by column chromatography over silica gel (100-200 mesh) using hexane. Total yield was calculated by taking weight of obtained mixture of products. The mixture of product isomers was subjected to NMR and GC-MS spectroscopic characterization. Analysis of NMR data suggests the presence of three regio-isomers in the product.

4''-iodo-2,5-dimethyl-1,1':4',1''-terphenyl, 8l



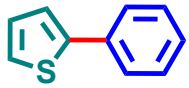
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.72 (d, J = 8.4 Hz, 3H), 7.55-7.36 (m, 5H), 7.19 (d, J = 7.6 Hz, 1H), 7.08 (m, 2H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 140.53, 140.43, 139.70, 138.49, 134.77, 131.44, 130.25, 130.04, 129.44, 128.89, 128.67, 128.13, 127.89, 127.37, 126.54, 126.37.

GC-MS: calc. for **8l**: 384.1; found: 384.1.

2-phenylthiophene, 9a[10]



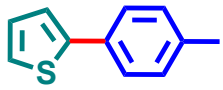
Colorless oil. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.66 (d, J = 7.6 Hz, 2H), 7.54 (dd, J = 4.8 Hz, and J = 0.8 Hz, 1H), 7.52 (d, J = 3.6 Hz, 1H), 7.42 (t, J = 8.0 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.14 (m, 1H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 143.22, 113.64, 129.01, 128.77, 128.38, 127.45, 125.56, 125.30, 123.58.

GC-MS: calc. for **9a**: 160.1; found: 160.1.

2-(4-Methylphenyl)thiophene, 9b[14]



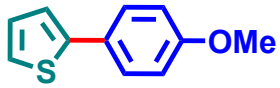
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.54 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 4.8 Hz, 1H), 7.45 (d, J = 2.0 Hz, 1H), 7.22 (d, J = 7.6 Hz, 2H), 7.11 (t, J = 4.8 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 143.22, 113.64, 129.01, 128.77, 128.38, 127.45, 125.56, 125.30, 123.58.

GC-MS: calc. for **9b**: 174.2; found: 174.2.

2-(4-Methoxyphenyl)thiophene, 9c[15]



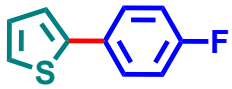
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane. The product contain small amount of another region isomer.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.59 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 4.8 Hz, 1H), 7.36 (d, J = 3.6 Hz, 1H), 7.09 (t, J = 4.0 Hz, 1H), 6.97 (d, J = 8.8 Hz, 1H), 3.74 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 158.71, 143.19, 128.15, 127.08, 126.59, 124.26, 122.28, 114.33, 54.96.

GC-MS: calc. for **9c**: 190.2; found: 190.2.

2-(4-Fluorophenyl)thiophene, 9d[16]



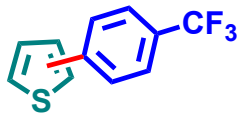
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.69 (t, J = 5.6 Hz, 2H), 7.54 (d, J = 3.2 Hz, 1H), 7.48 (d, J = 2.8 Hz, 1H), 7.25 (t, J = 8.4 Hz, 2H), 7.13 (t, J = 3.6 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 162.72, 160.28, 142.07, 130.30 (d), 128.45, 127.34 (d), 125.63, 123.77, 116.01, 115.79.

GC-MS: calc. for **9d**: 178.0; found: 178.0.

n-[4-(Trifluoromethyl)phenyl]thiophene, 9e



The **9e** was synthesized and isolated according to the procedures mentioned for **8a**. The purification was carried out by column chromatography over silica gel (100-200 mesh) using hexane. Total yield was calculated by taking weight of obtained mixture of products. The mixture of product isomers was subjected to NMR and GC-MS spectroscopic characterization. Analysis of NMR data suggests the presence of two regio-isomers, 2-[4-(Trifluoromethyl)phenyl]thiophene and 3-[4-(Trifluoromethyl)phenyl]thiophene in the product.

2-[1,1′-Biphenyl]-4-ylthiophene, 9f[17]

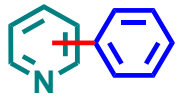
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.77-7.70 (m, 6H), 7.58 (m, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.17 (t, J = 7.2 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 142.81, 139.30, 139.04, 132.78, 128.92, 128.54, 127.51, 127.22, 126.38, 125.83, 125.74, 123.75.

GC-MS: calc. for **9e**: 236.2; found: 236.2.

n-Phenylpyridine, 9g[18]



White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane. Two isomers are formed in our catalytic condition and isolated them separately during the column purification. Both isomers were subjected to NMR and GC-MS spectroscopic characterization.

2-Phenylpyridine: Yield 42%.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 8.67 (d, J = 5.2 Hz, 1H), 8.08 (d, J = 7.6 Hz, 2H), 7.96 (d, J = 8.0 Hz, 1H), 7.87 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.2 Hz, 2H), 7.43 (t, J = 6.8 Hz, 1H), 7.35 (t, J = 4.8 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 155.88, 149.44, 138.58, 137.13, 128.93, 128.64, 126.40, 122.50, 120.12.

GC-MS: calc. for **9f**: 155.1; found: 155.2.

3-Phenylpyridine: Yield 47%.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 8.89 (s, 1H), 8.57 (d, J = 4.4 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.23 (d, J = 7.6 Hz, 2H), 7.50 (q, J = 7.6 Hz, 3H), 7.43 (t, J = 7.2 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 148.38, 147.56, 136.98, 135.45, 134.00, 129.02, 128.02, 126.78, 123.75.

GC-MS: calc. for **9f**: 155.1; found: 155.1.

n-(4-Methoxyphenyl)pyridine, 9h[19]

White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane. Two isomers are formed in our catalytic condition and isolated them separately during the column purification. Both isomers were subjected to NMR and GC-MS spectroscopic characterization.

2-(4-Methoxyphenyl)pyridine: Yield 40%.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 8.60 (d, J = 4.4 Hz, 1H), 8.04 (d, J = 8.8 Hz, 2H), 7.88 (d, J = 8.0 Hz, 1H), 7.81 (t, J = 7.6 Hz, 1H), 7.27 (t, J = 6.0 Hz, 1H), 7.04 (d, J = 8.8 Hz, 2H), 3.81 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 160.00, 155.64, 149.21, 136.90, 131.04, 127.68, 121.60, 119.21, 113.97, 55.07.

GC-MS: calc. for **9g**: 185.2; found: 185.2.

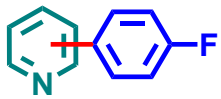
3-(4-Methoxyphenyl)pyridine: Yield 45%.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 8.51 (d, J = 1.2 Hz, 1H), 8.51 (d, J = 2.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.8 Hz, 2H), 7.44 (q, J = 4.4 Hz, 1H), 7.06 (d, J = 8.8 Hz, 2H), 3.81 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 159.32, 147.66, 147.13, 135.11, 133.38, 129.21, 127.93, 123.68, 114.50, 55.13.

GC-MS: calc. for **9g**: 185.2; found: 185.2.

n-(4-Fluorophenyl)pyridine, 9i[20]



White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane. Two isomers are formed in our catalytic condition and isolated them separately during the column purification. Both isomers were subjected to NMR and GC-MS spectroscopic characterization.

2-(4-Fluorophenyl)pyridine: Yield 43%.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 8.65 (d, J = 4.4 Hz, 1H), 8.42 (t, J = 6.0 Hz, 2H), 7.95 (d, J = 8.0 Hz, 1H), 7.88 (t, J = 7.6 Hz, 1H), 7.33 (m, 3H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 163.98, 161.53, 154.86, 149.43, 137.20, 128.56 (d), 122.44, 119.96, 115.48 (d).

GC-MS: calc. for **9h**: 173.2; found: 173.2.

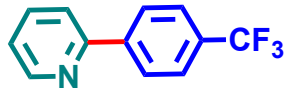
3-(4-Fluorophenyl)pyridine: Yield 46%.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 8.88 (s, 1H), 8.56 (d, J = 4.8 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.78 (t, J = 5.2 Hz, 2H), 7.48 (m, 1H), 7.34 (t, J = 8.8 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 163.36, 160.93, 148.30, 147.44, 134.44, 133.90, 133.42 (d), 128.84 (d), 123.66, 115.92, 115.71.

GC-MS: calc. for 9h: 173.2; found: 173.2.

2-(4-(Trifluoromethyl)phenyl)pyridine, 9j[21]



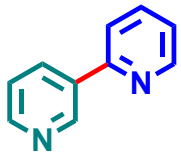
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane/EtOAc (20:1).

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 8.72 (s, 1H), 8.31 (d, J = 8.0 Hz, 2H), 8.09 (d, J = 7.8 Hz, 1H), 7.95 (t, J = 6.0 Hz, 1H), 7.86 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 7.6 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 154.25, 149.71, 142.38, 137.45, 127.15, 125.58, 125.54, 123.49, 120.88.

GC-MS: calc. for **9j**: 223.1; found: 223.1.

2,3′-Bipyridine, 9k[22]



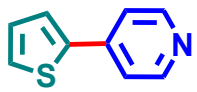
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 8.72 (d, J = 8.0 Hz, 1H), 8.07 (td, J = 7.6 Hz and J = 1.2 Hz, 1H), 8.01-7.95 (m, 2H), 7.68 (m, 2H), 7.55 (t, J = 7.6 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 154.51, 148.50, 137.61, 135.91, 132.93, 130.52, 128.15, 126.67, 124.08.

GC-MS: calc. for **9i**: 156.1; found: 156.1.

4-(2-Thienyl)pyridine, 9l[23]



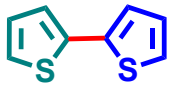
White solid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 8.57 (m, 2H), 7.81 (d, J = 2.8 Hz, 1H), 7.75 (d, J = 5.2 Hz, 1H), 7.65 (m, 2H), 7.22 (t, J = 4.0 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 150.26, 140.41, 140.15, 128.77, 128.17, 127.07 (d), 126.34, 119.39.

GC-MS: calc. for **9j**: 161.1; found: 161.1.

2,2′-Bithiophene, 9m[24]



Colorless liquid. The crude product was purified by column chromatography using Merck silica gel 100-200 mesh with hexane.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.49 (d, J = 5.2 Hz, 2H), 7.29 (d, J = 3.2 Hz, 2H), 7.08 (t, J = 4.8 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 136.38, 128.15, 125.18, 123.88.

GC-MS: calc. for **9k**: 166.0; found: 166.0.

6. ^{1}H NMR and ^{13}C NMR spectra of the products:

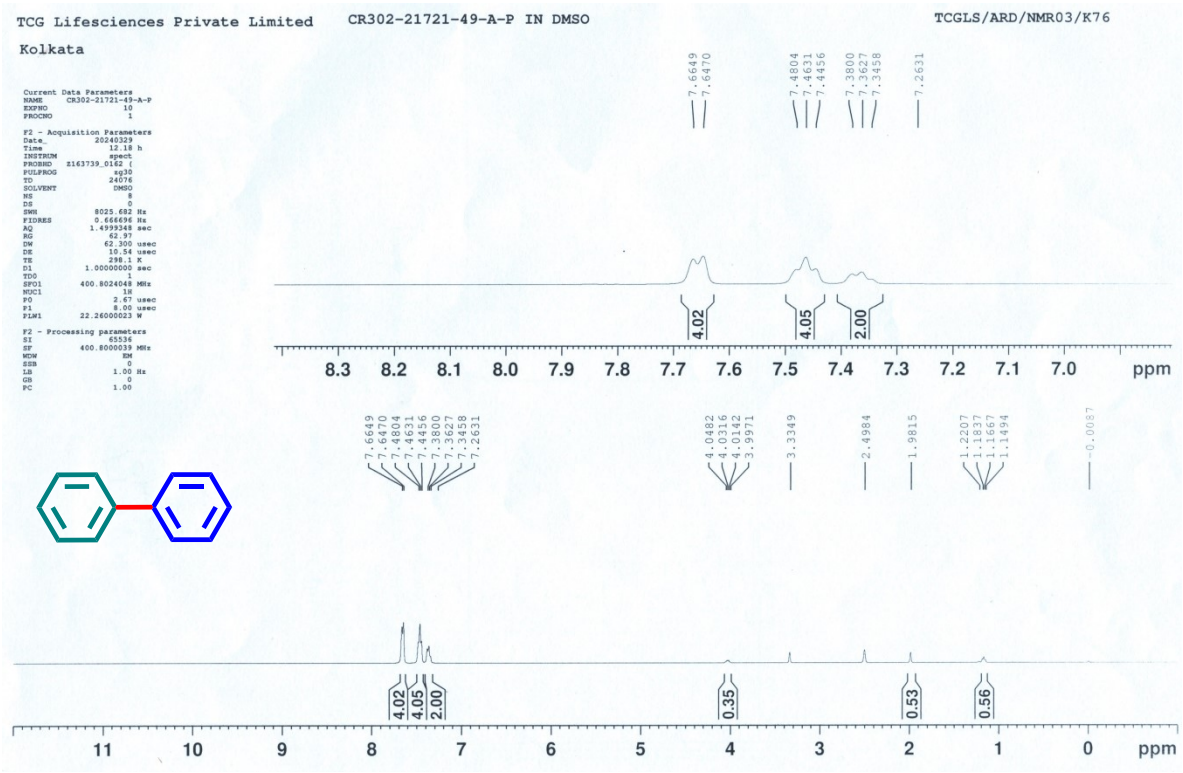


Figure S6: ^{1}H NMR spectrum of **7a**.

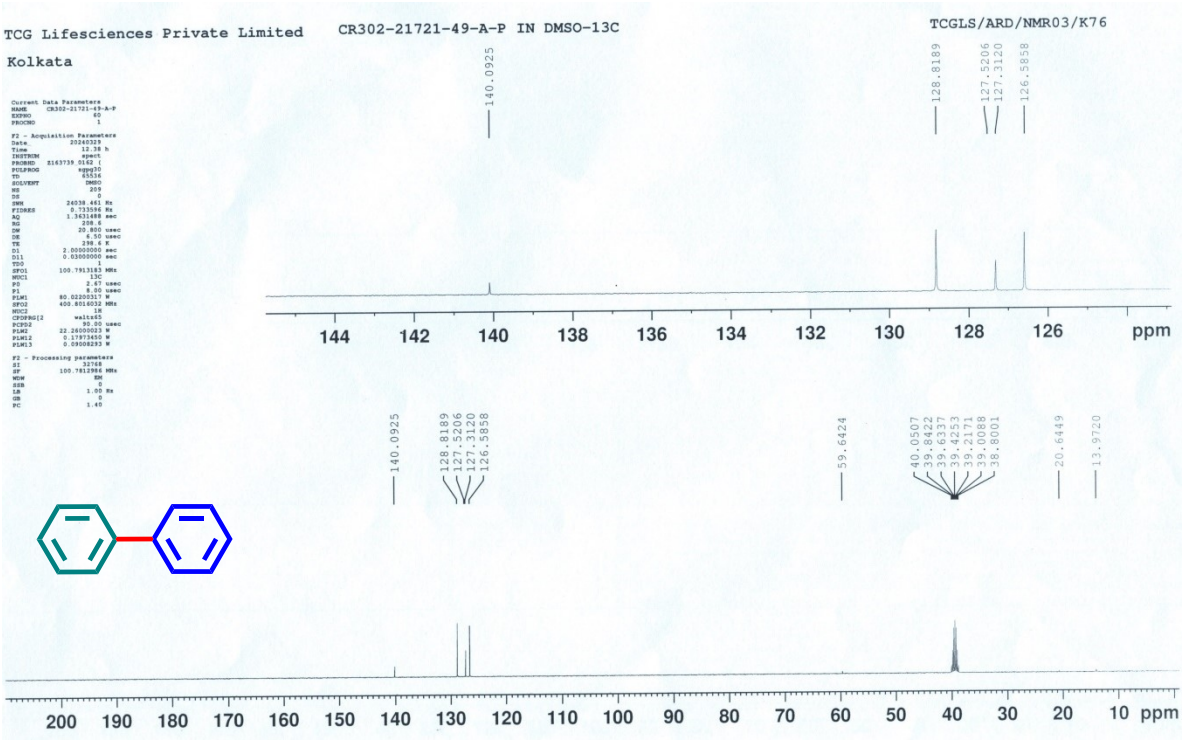


Figure S7: ^{13}C {^{1}H} NMR spectrum of **7a**.

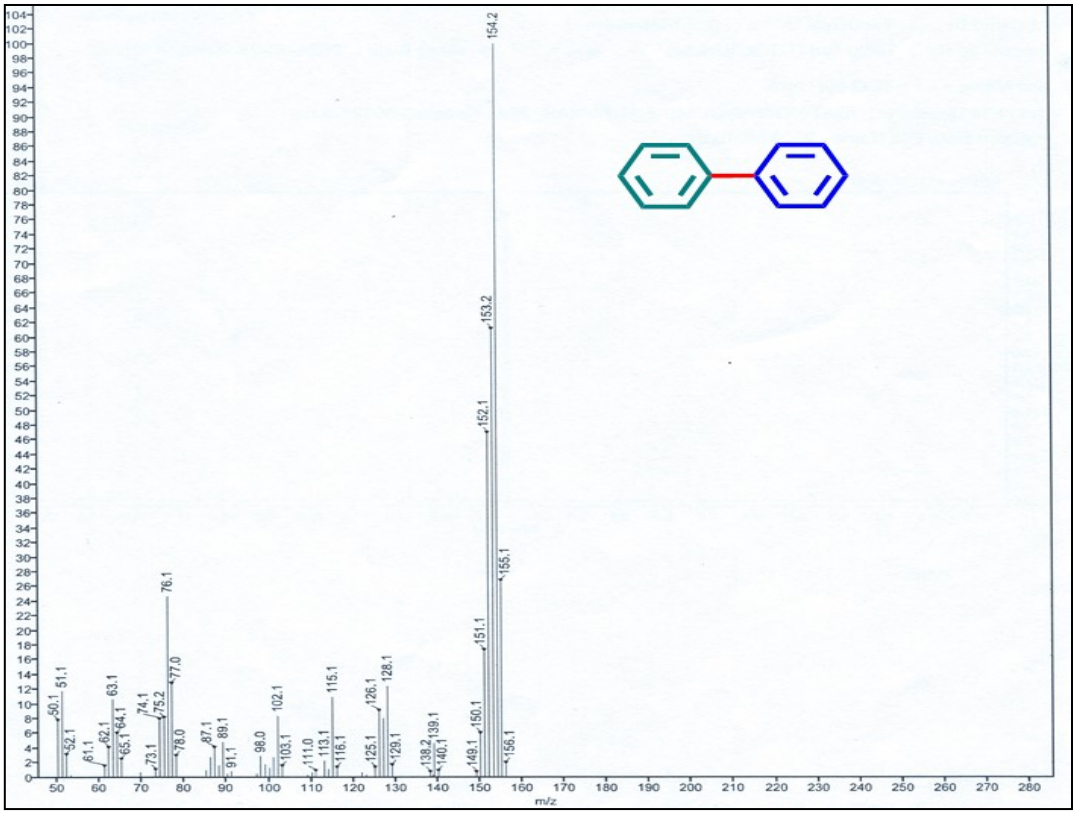


Figure S8: GC-MS spectrum of **7a**.

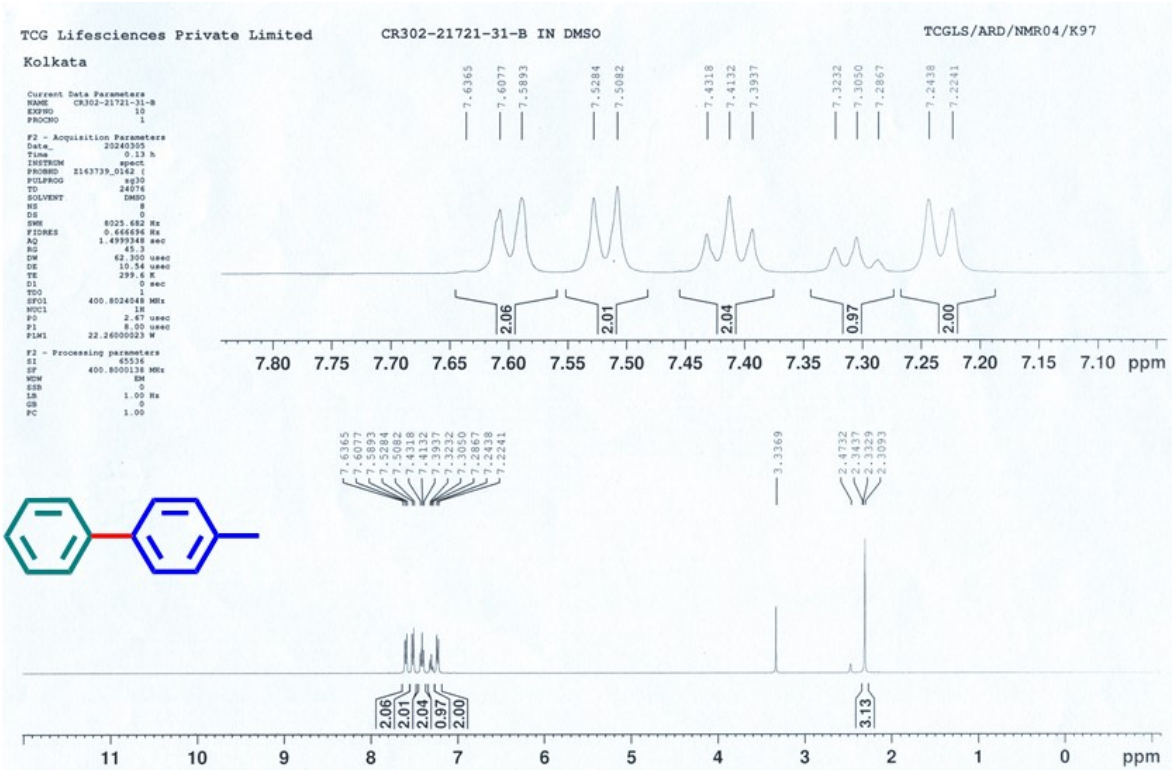


Figure S9: ^{1}H NMR spectrum of **7b**.

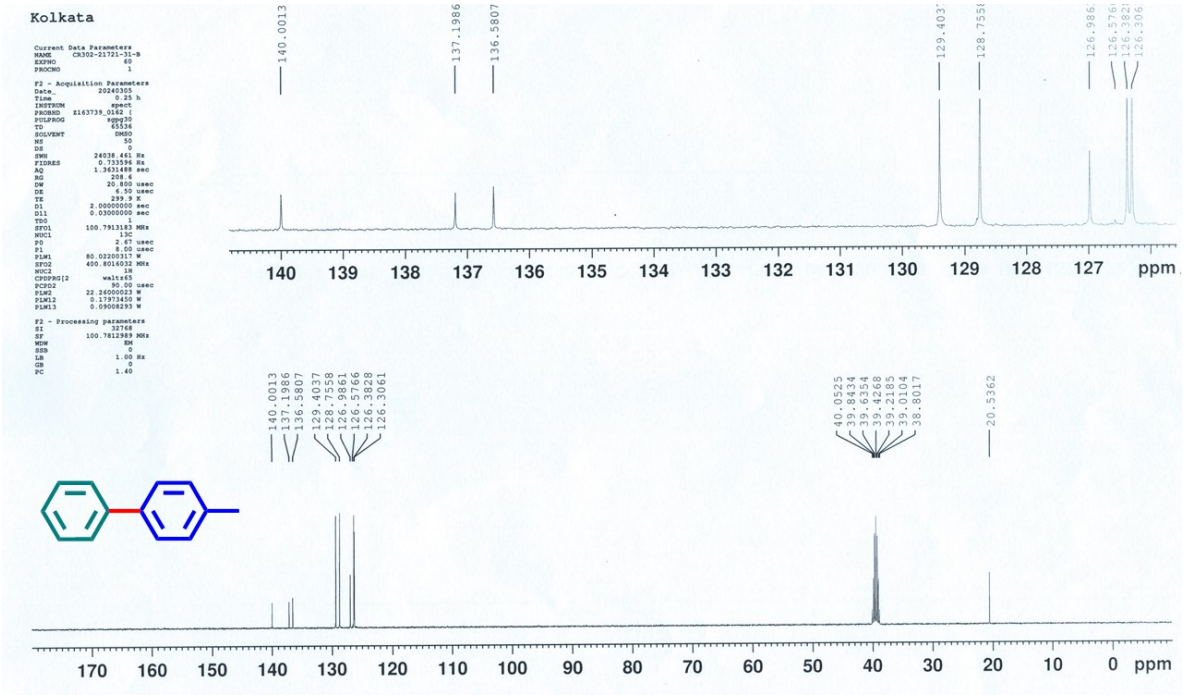


Figure S10: ^{13}C {^{1}H} NMR spectrum of **7b**.

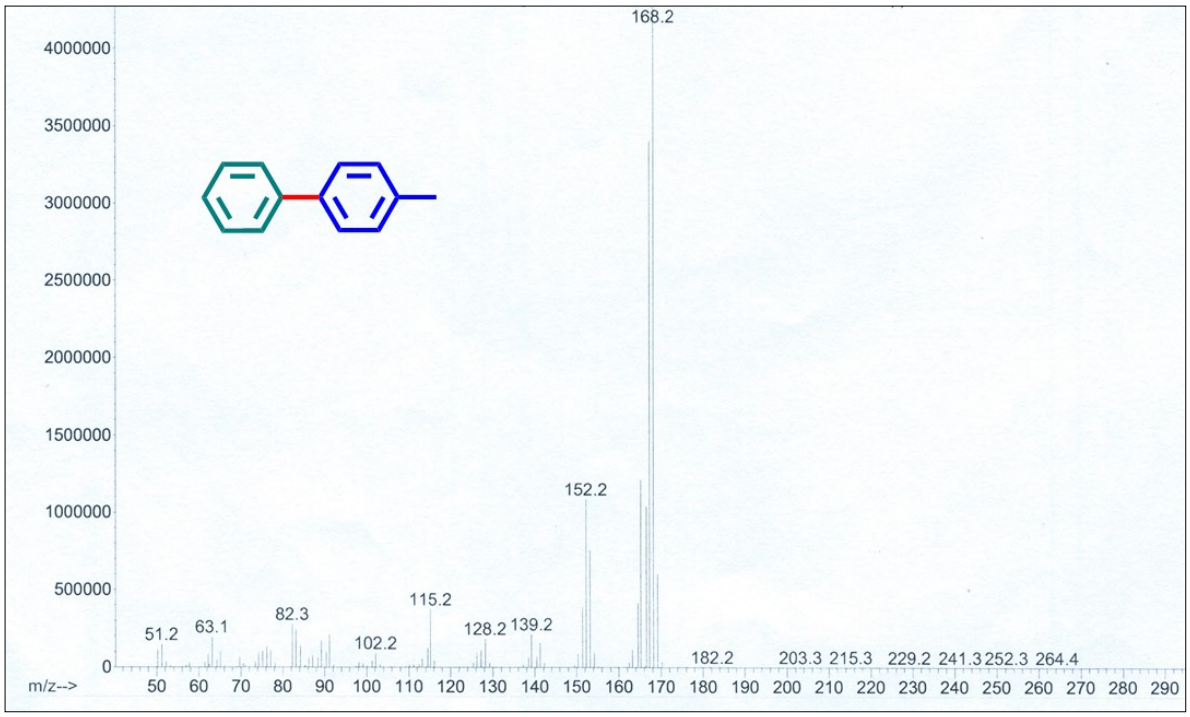


Figure S11: GC-MS spectrum of **7b**.

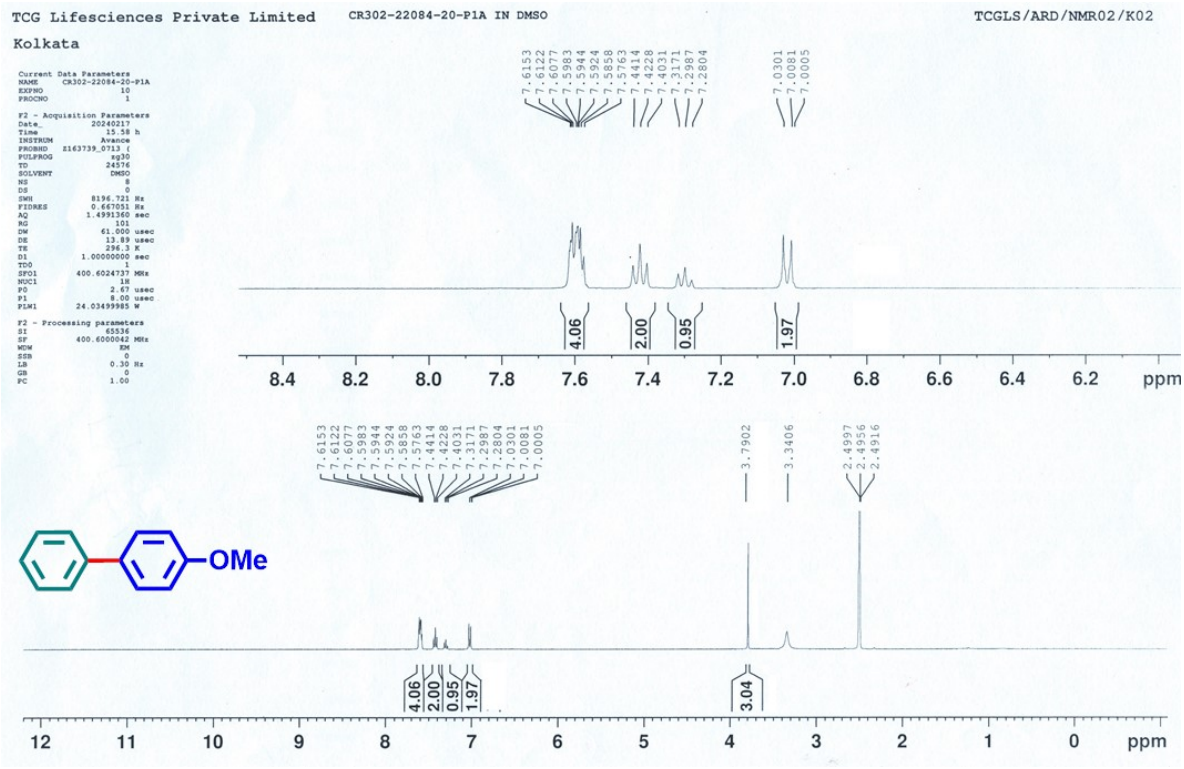


Figure S12: ^{1}H NMR spectrum of **7c**.

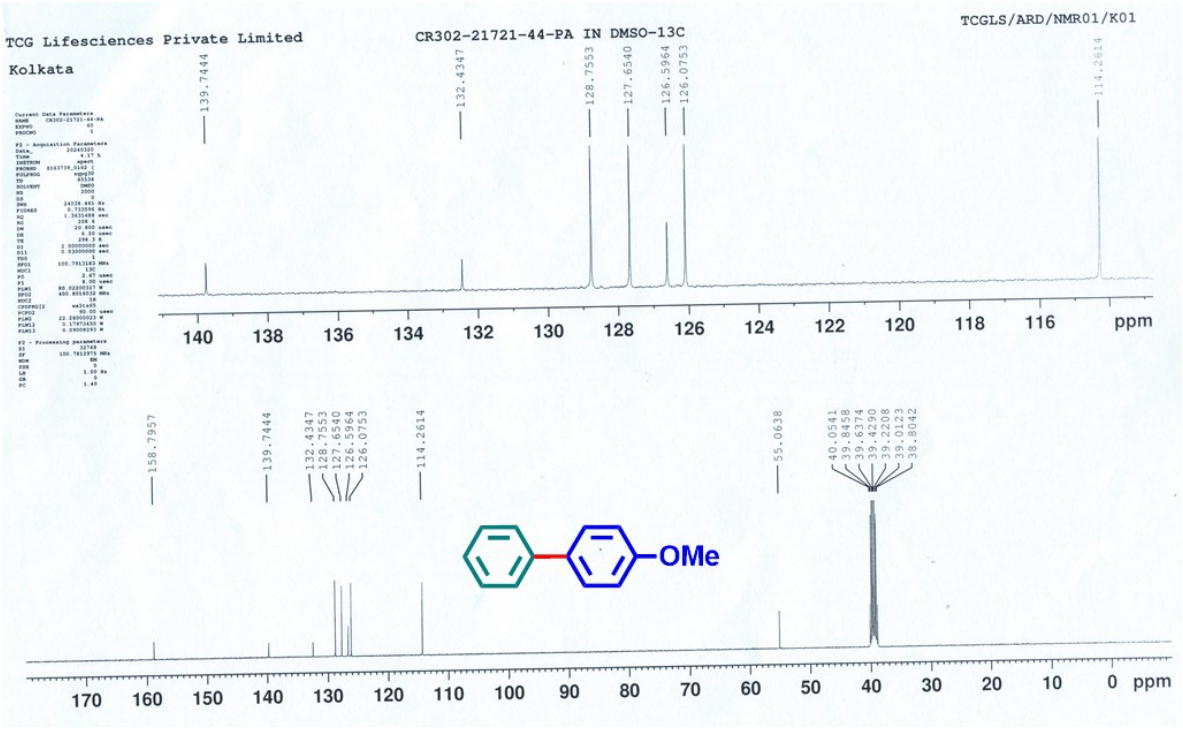


Figure S13: ^{13}C {^{1}H} NMR spectrum of **7c**.

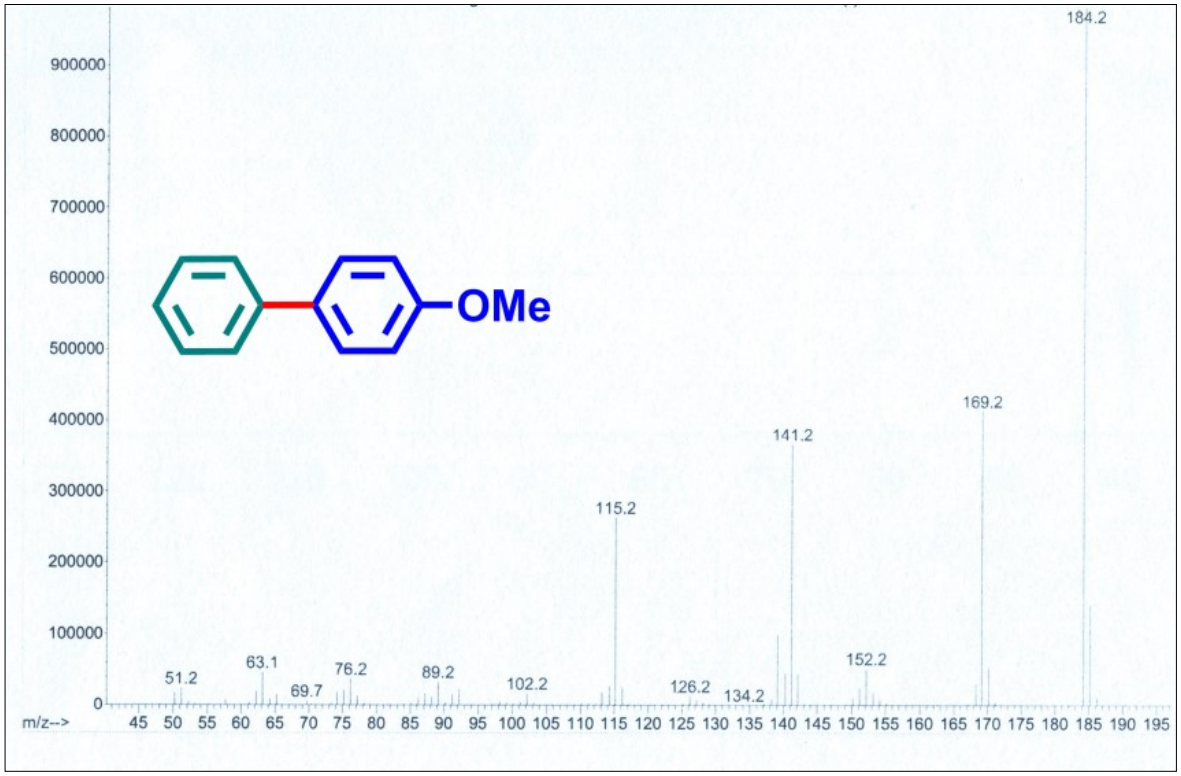


Figure S14: GC-MS spectrum of **7c**.

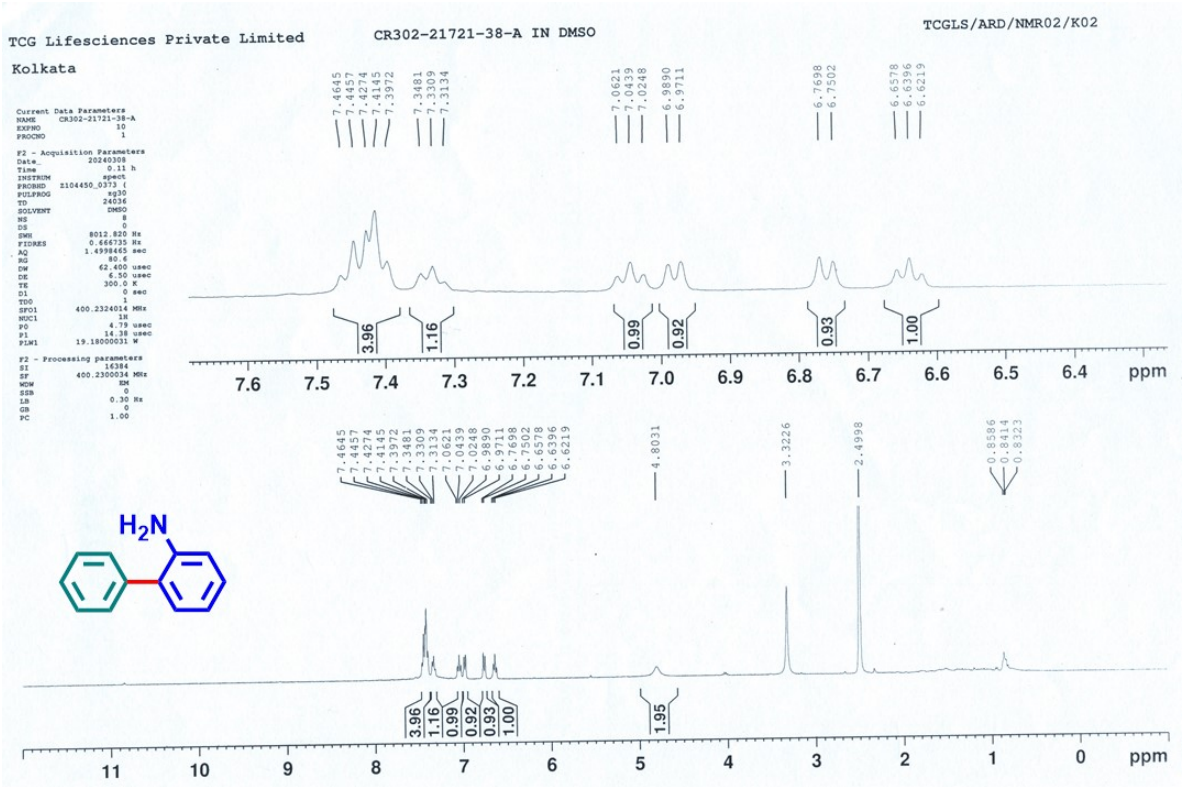


Figure S15: ^{1}H NMR spectrum of **7d**.

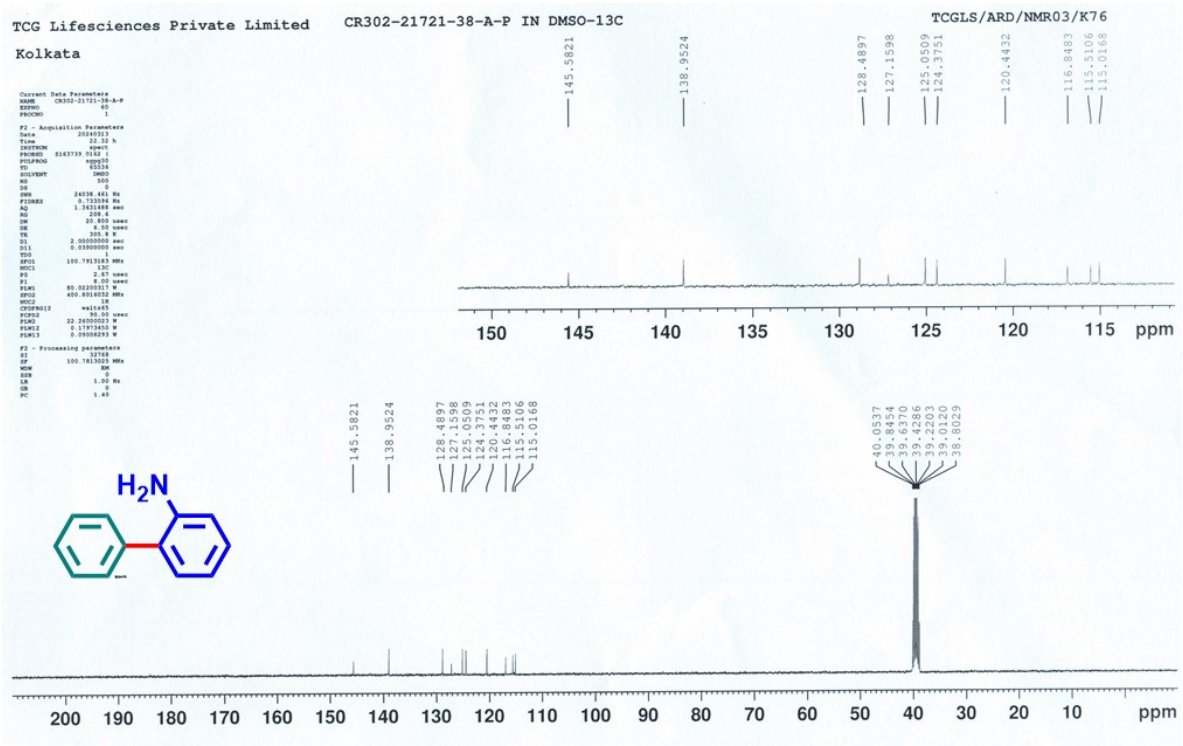


Figure S16: ^{13}C {^{1}H} NMR spectrum of **7d**.

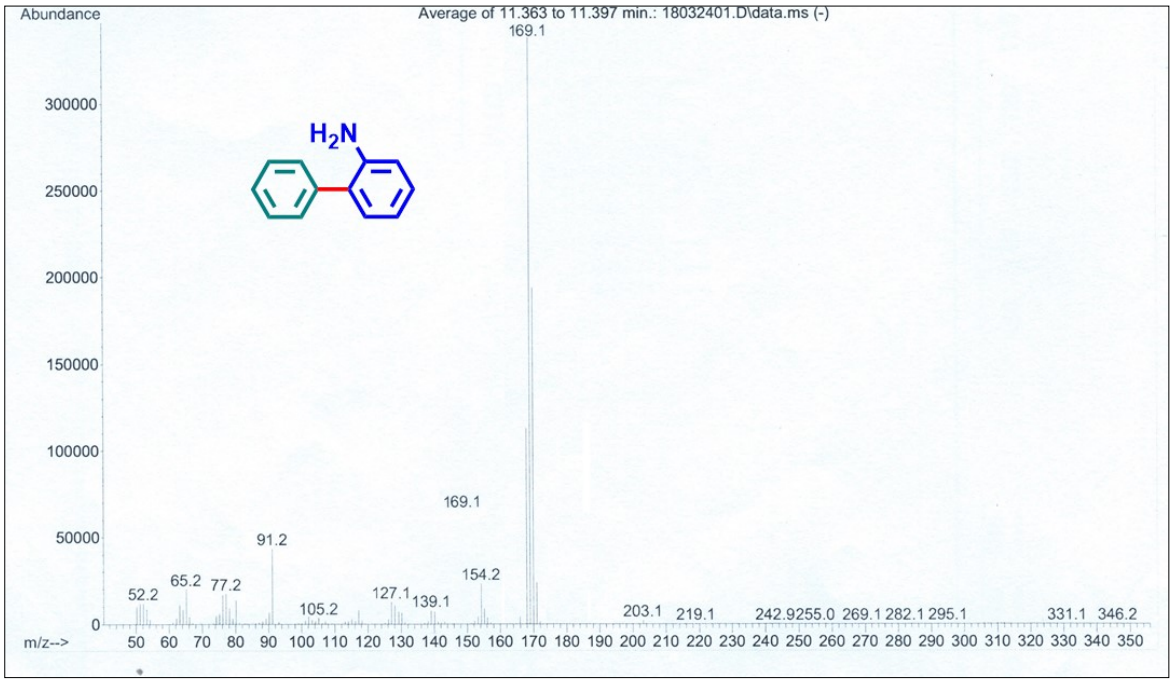


Figure S17: GC-MS spectrum of **7d**.

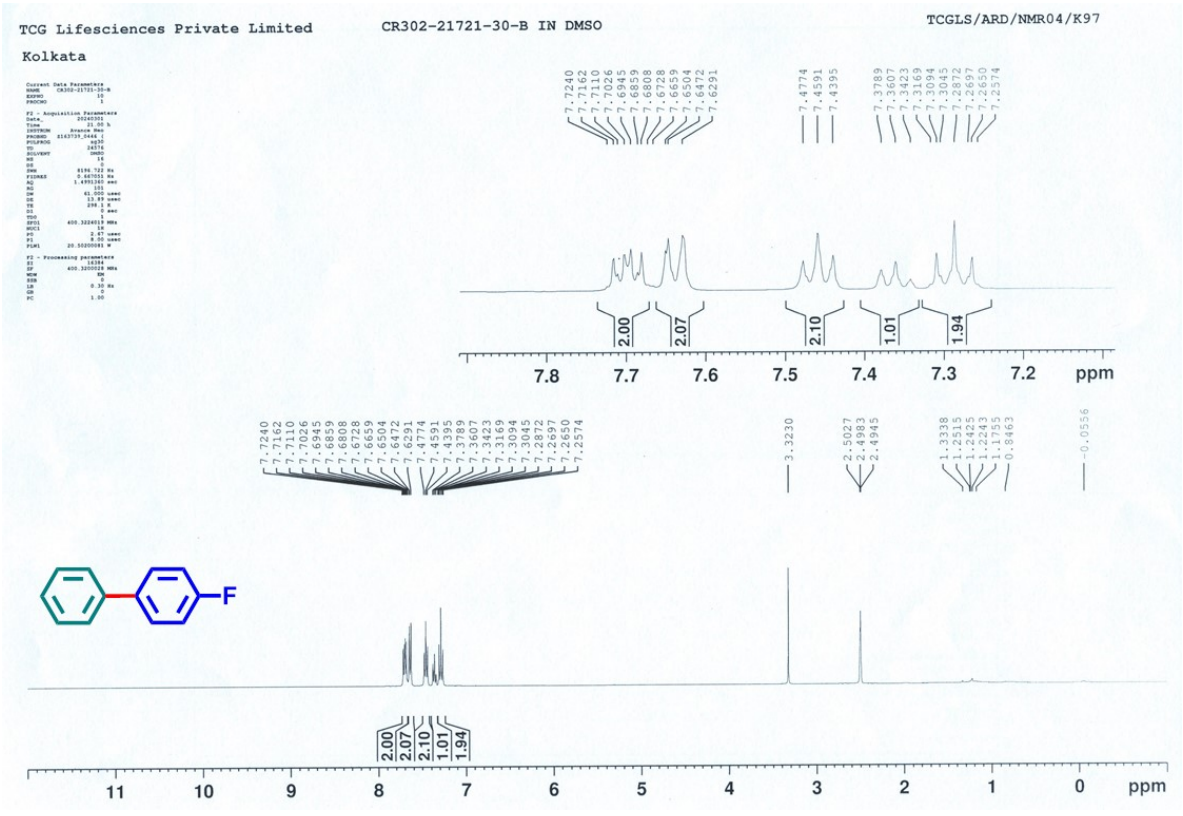


Figure S18: ^{1}H NMR spectrum of **7e**.

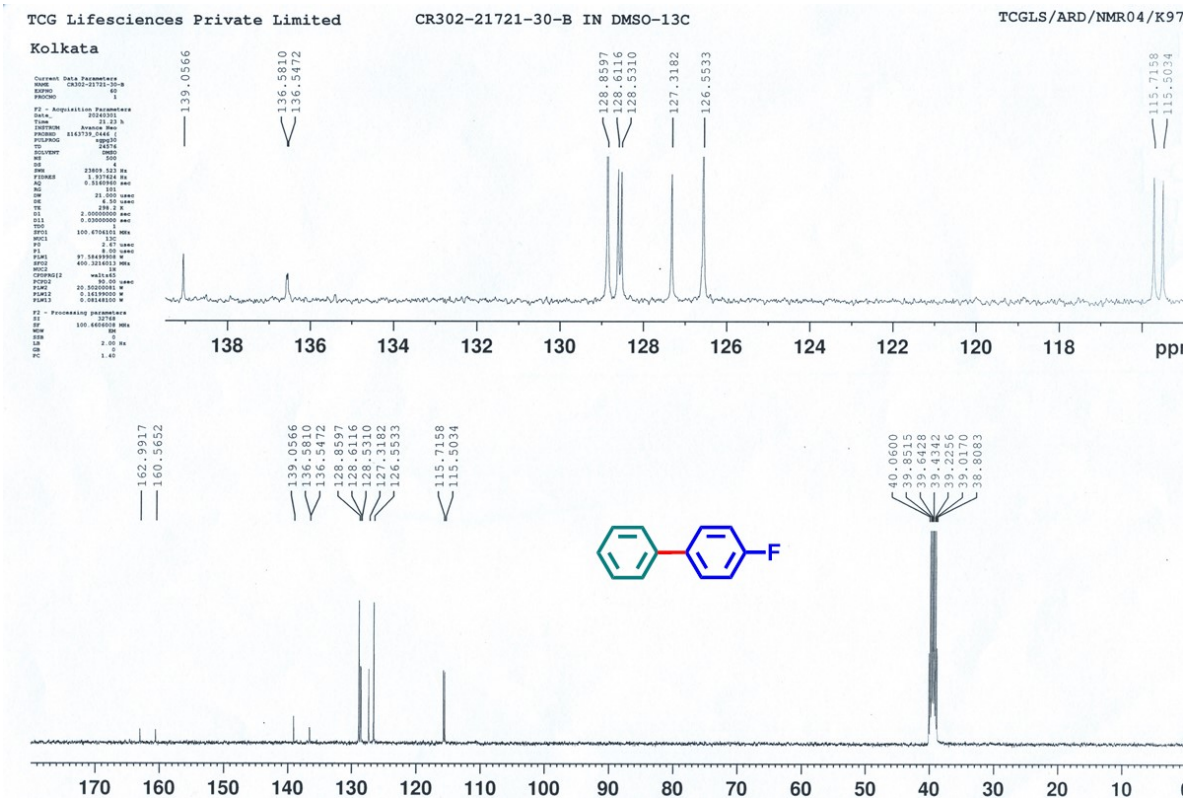


Figure S19: ^{13}C {^{1}H} NMR spectrum of **7e**.

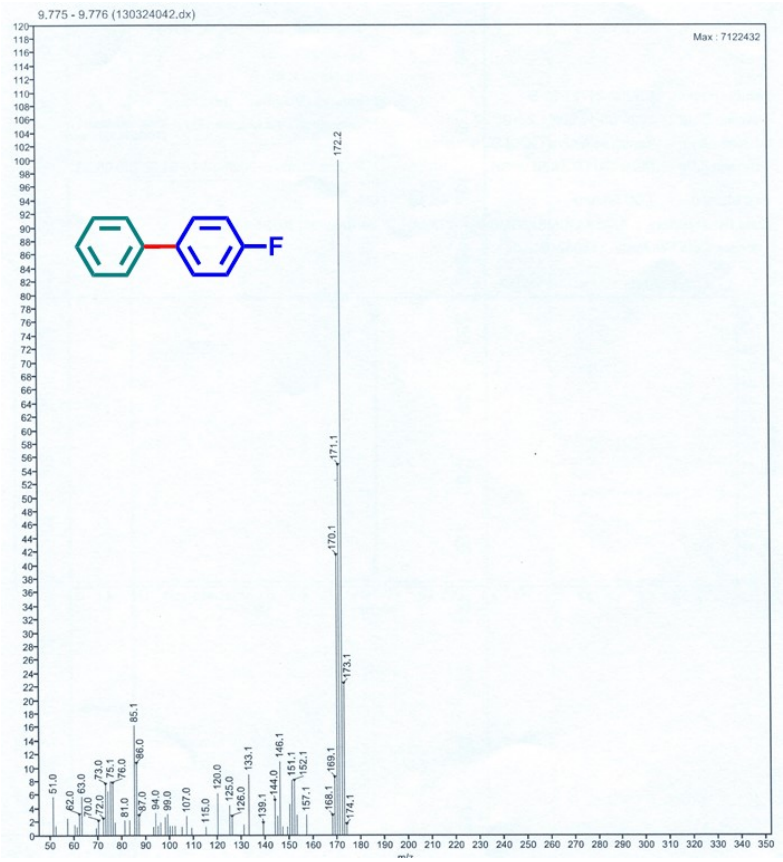


Figure S20: GC-MS spectrum of **7e**.

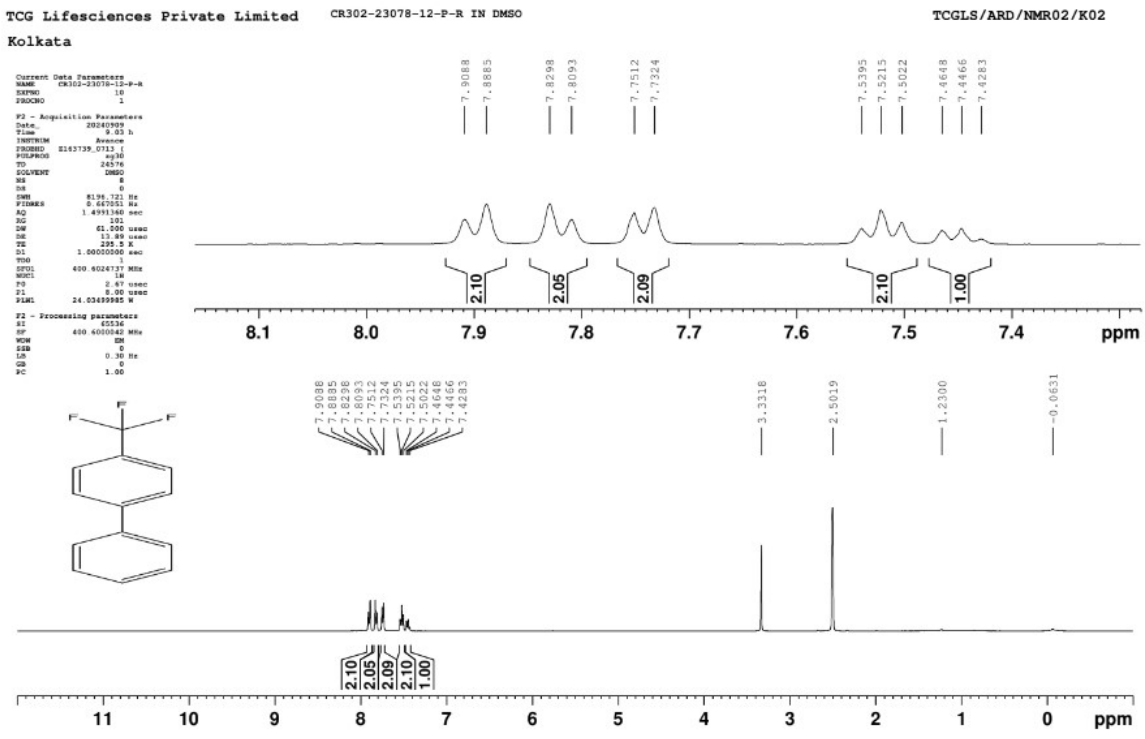


Figure S21: ^{1}H NMR spectrum of **7f**.

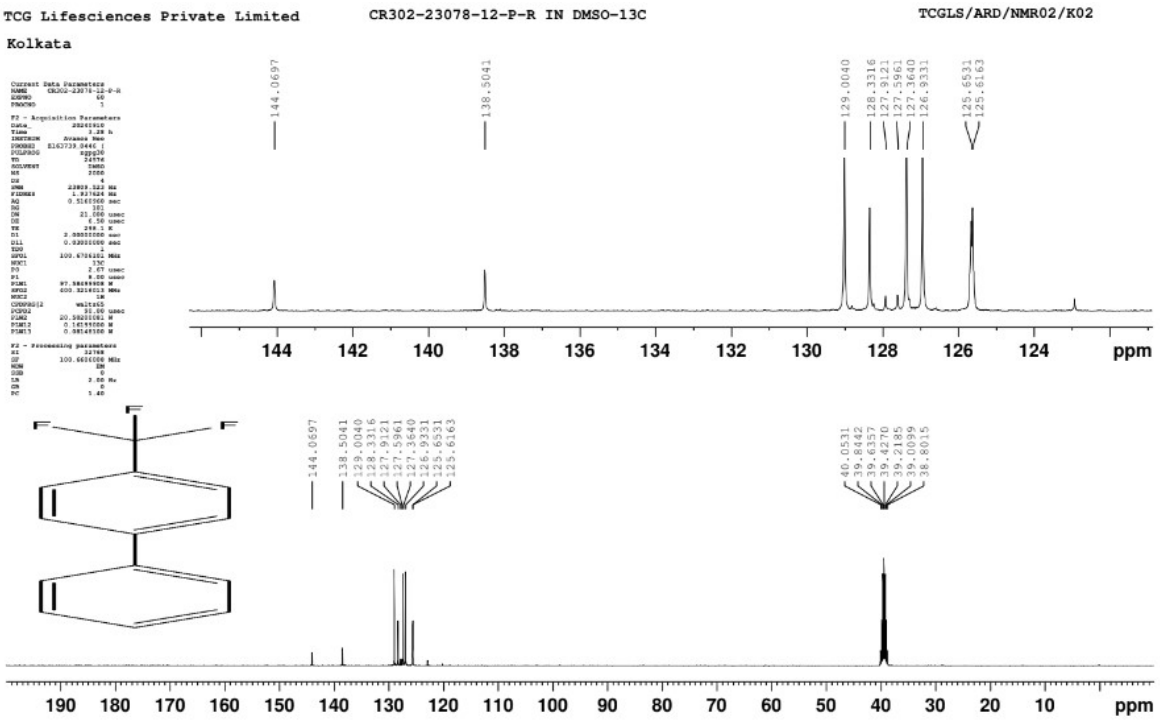


Figure S22: ^{13}C {^{1}H} NMR spectrum of **7f**.

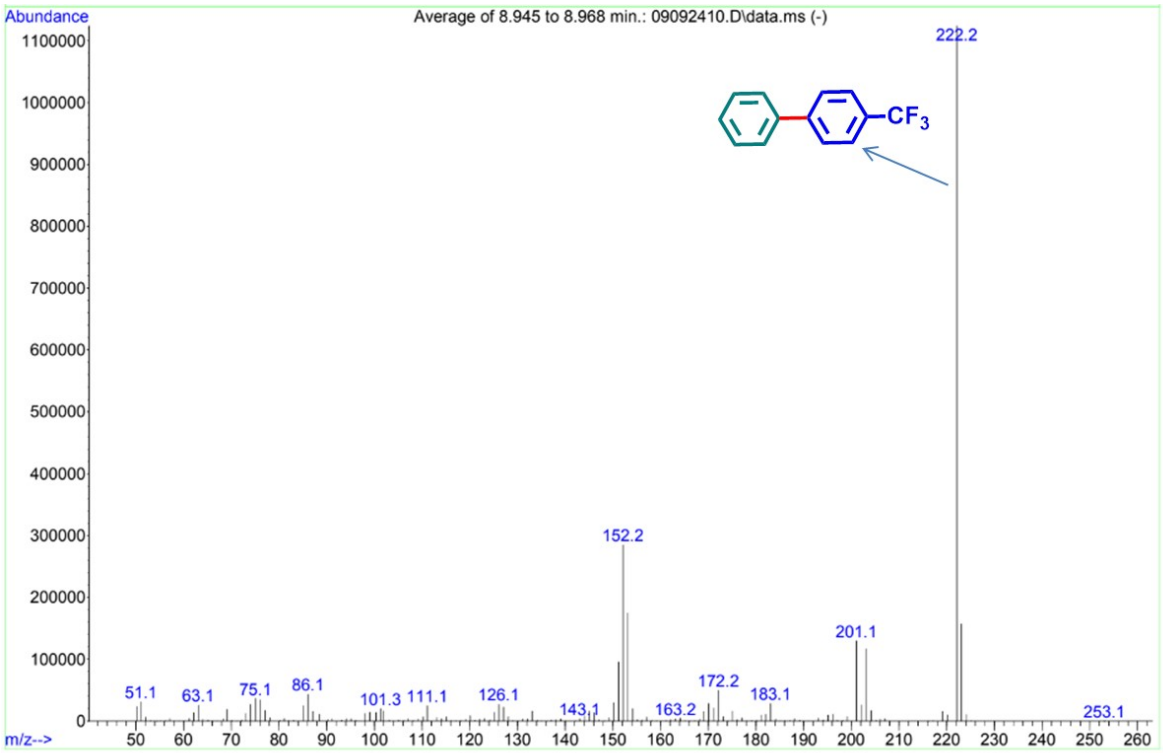


Figure S23: GC-MS spectrum of **7f**.

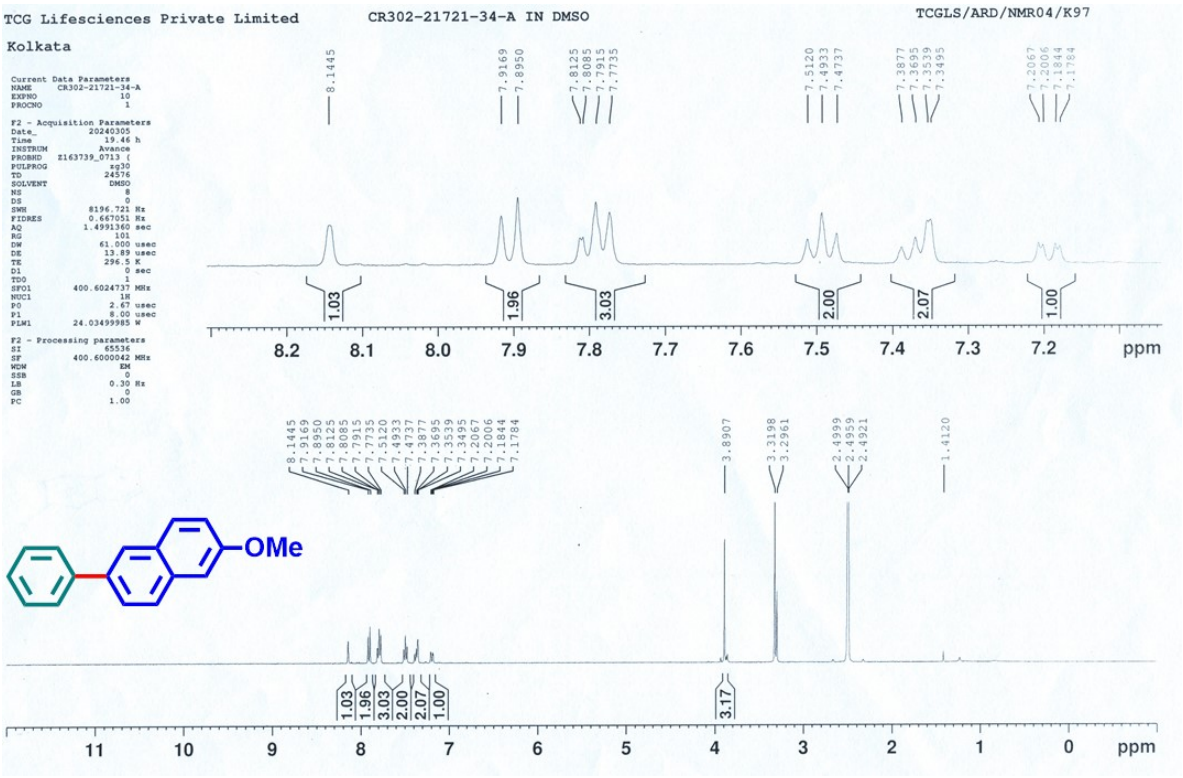


Figure S24: ^{1}H NMR spectrum of **7g**.

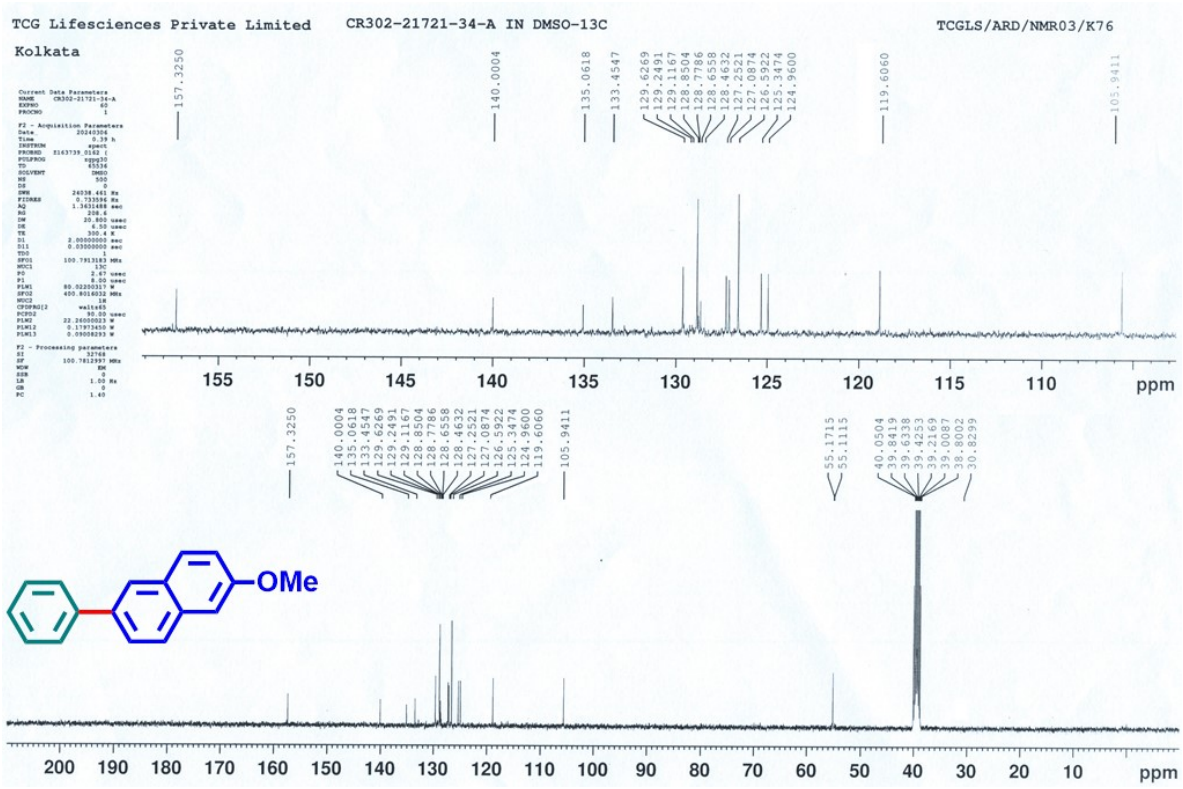


Figure S25: ^{13}C {^{1}H} NMR spectrum of **7g**.

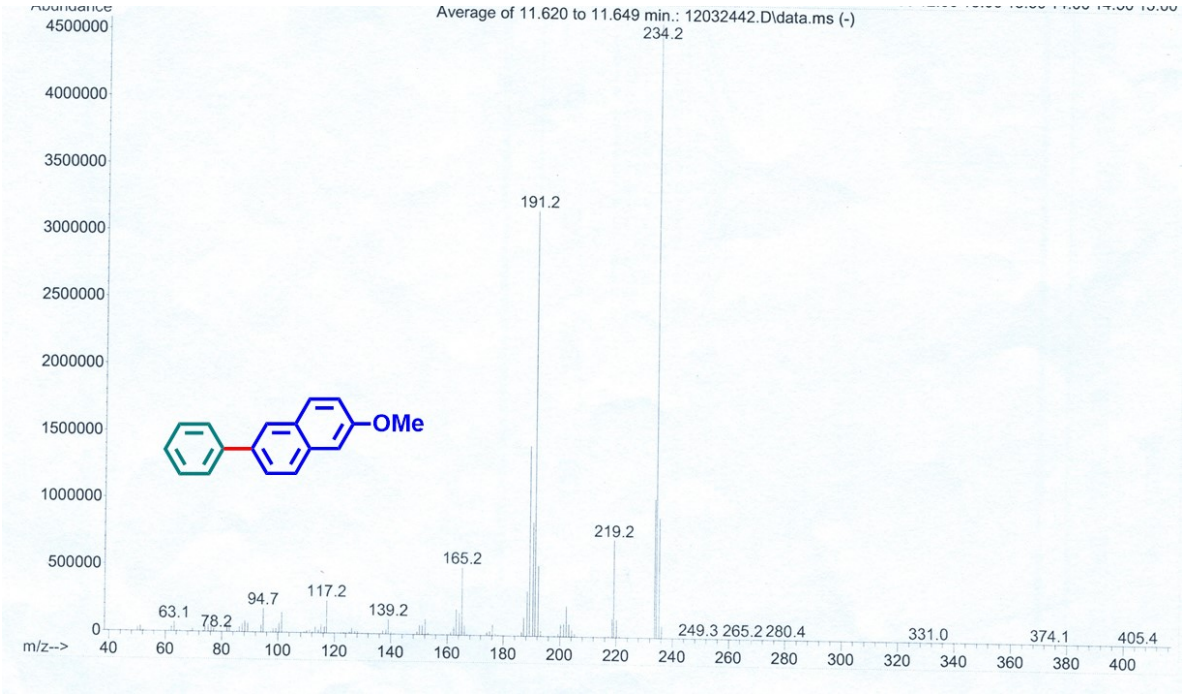


Figure S26: GC-MS spectrum of **7g**.

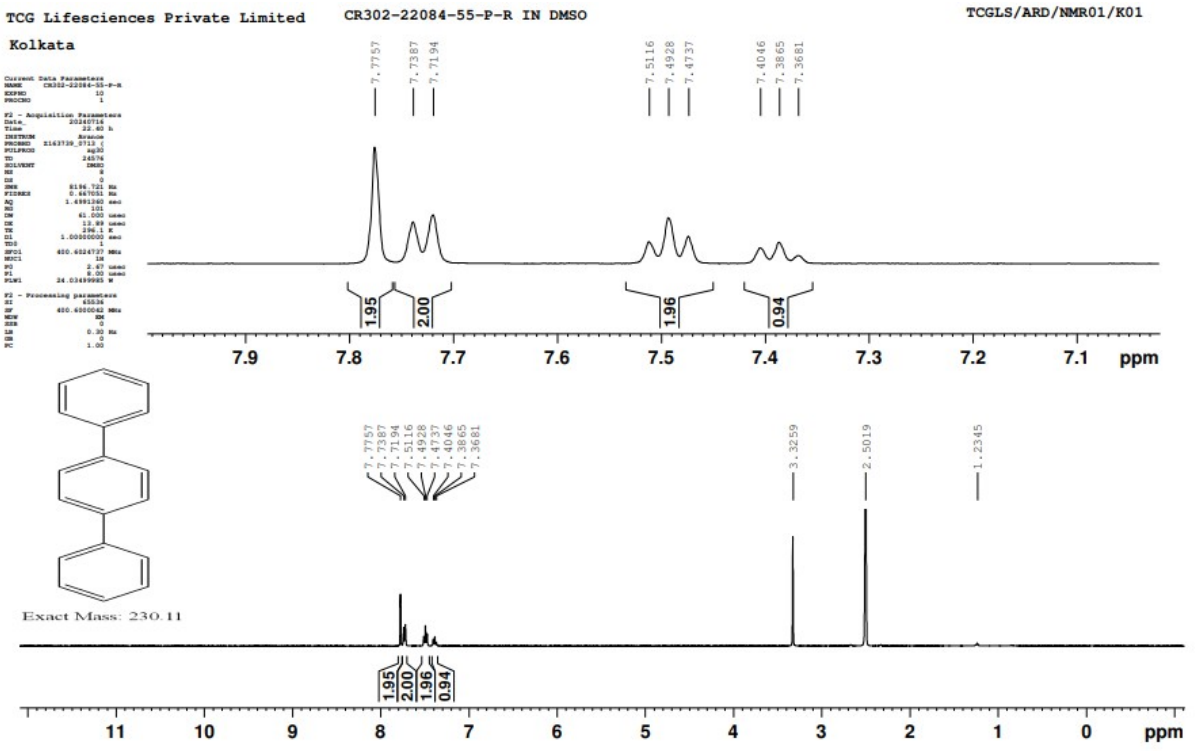


Figure S27: ^{1}H NMR spectrum of **7h**.

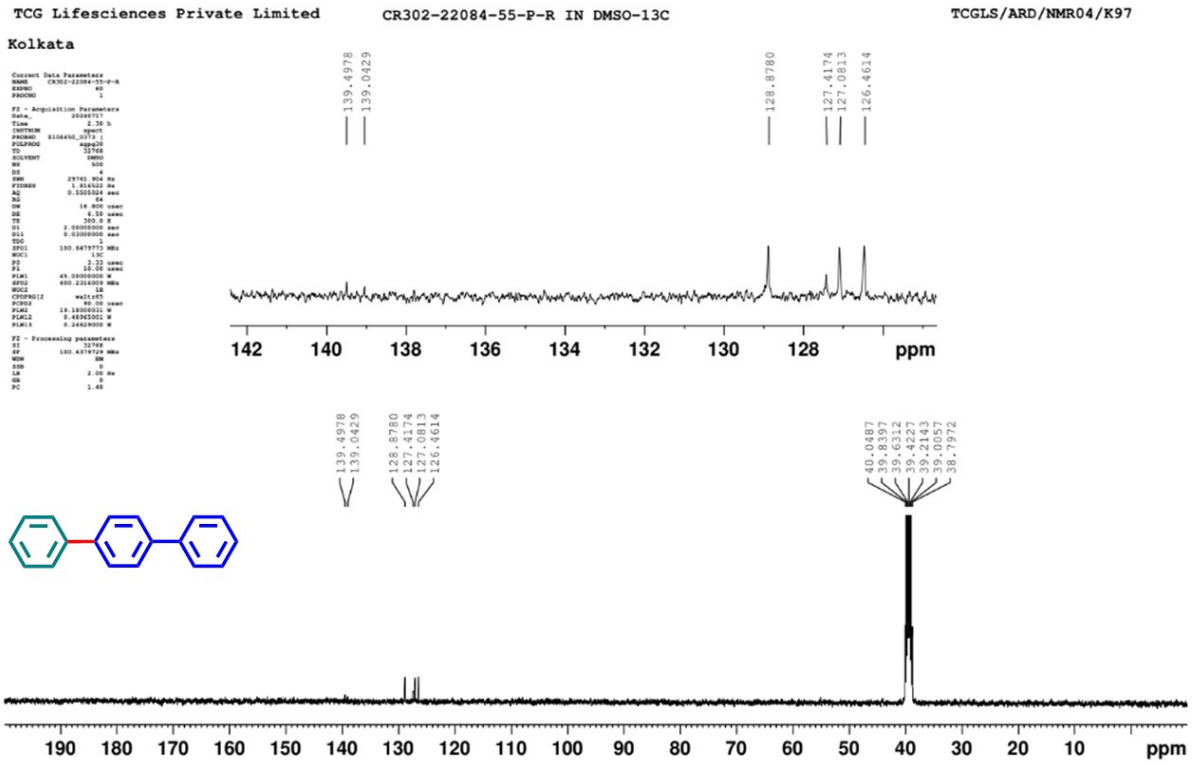


Figure S28: ^{13}C {^{1}H} NMR spectrum of **7h**.

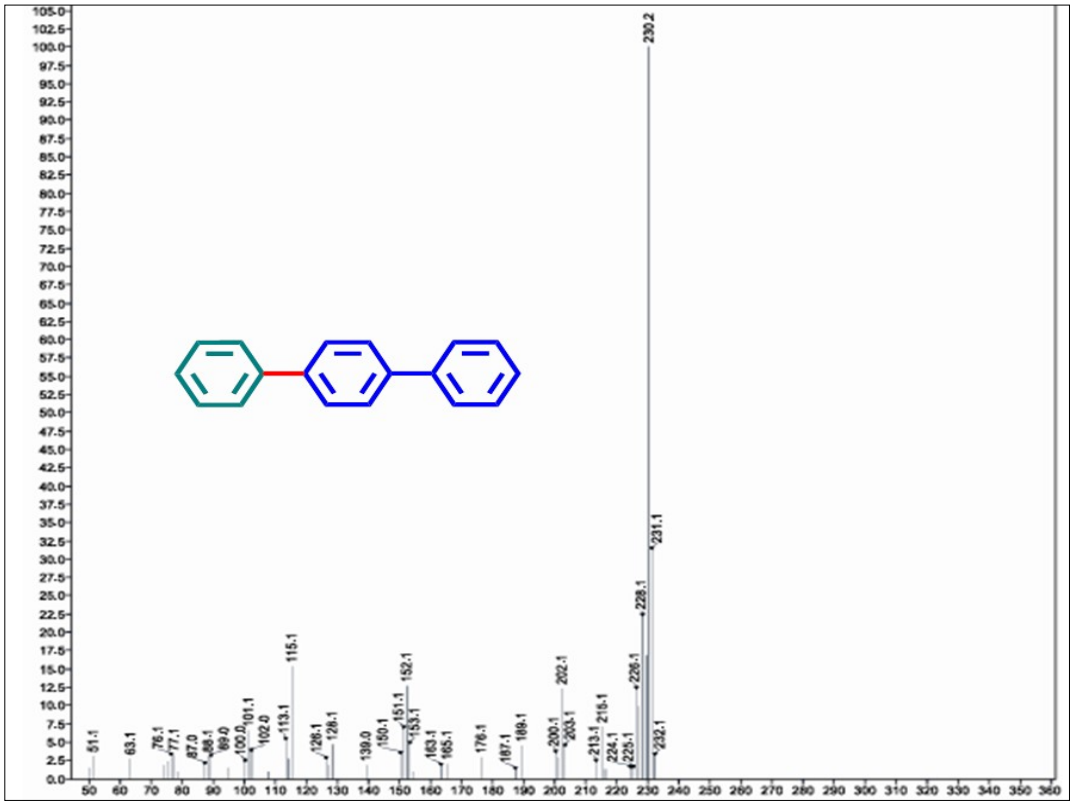


Figure S29: GC-MS spectrum of **7h**.

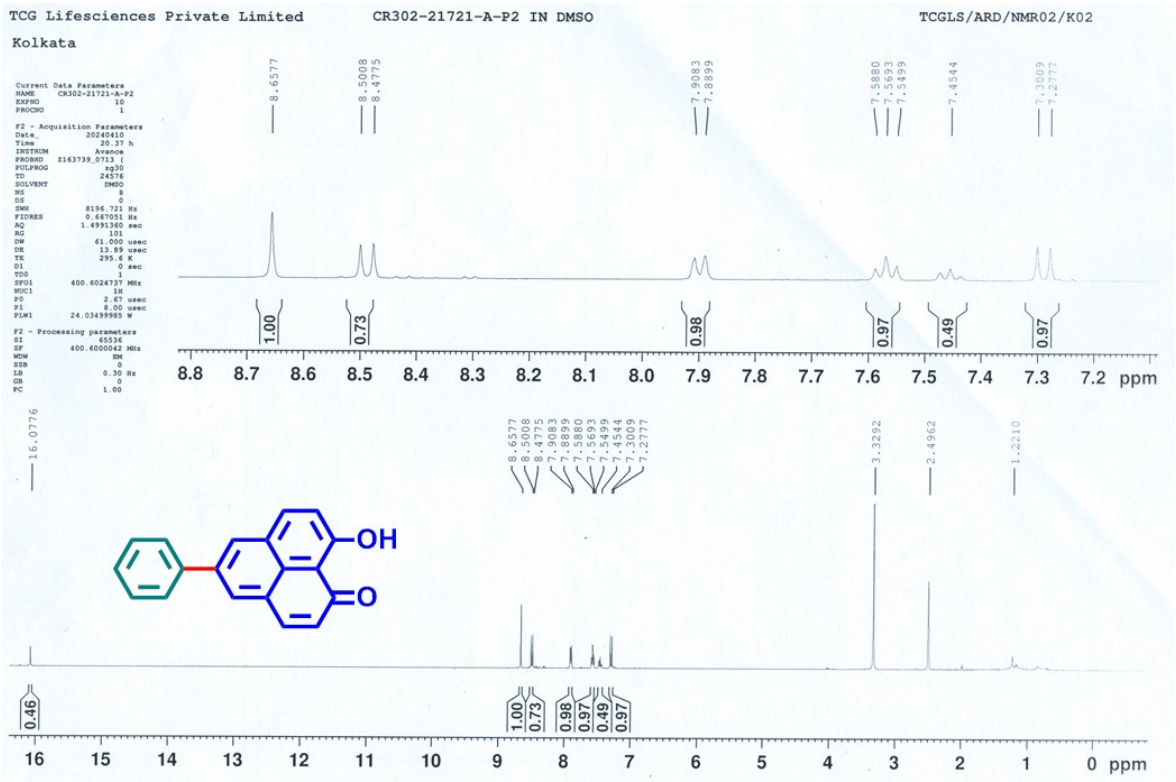


Figure S30: [1]H NMR spectrum of **7i**.

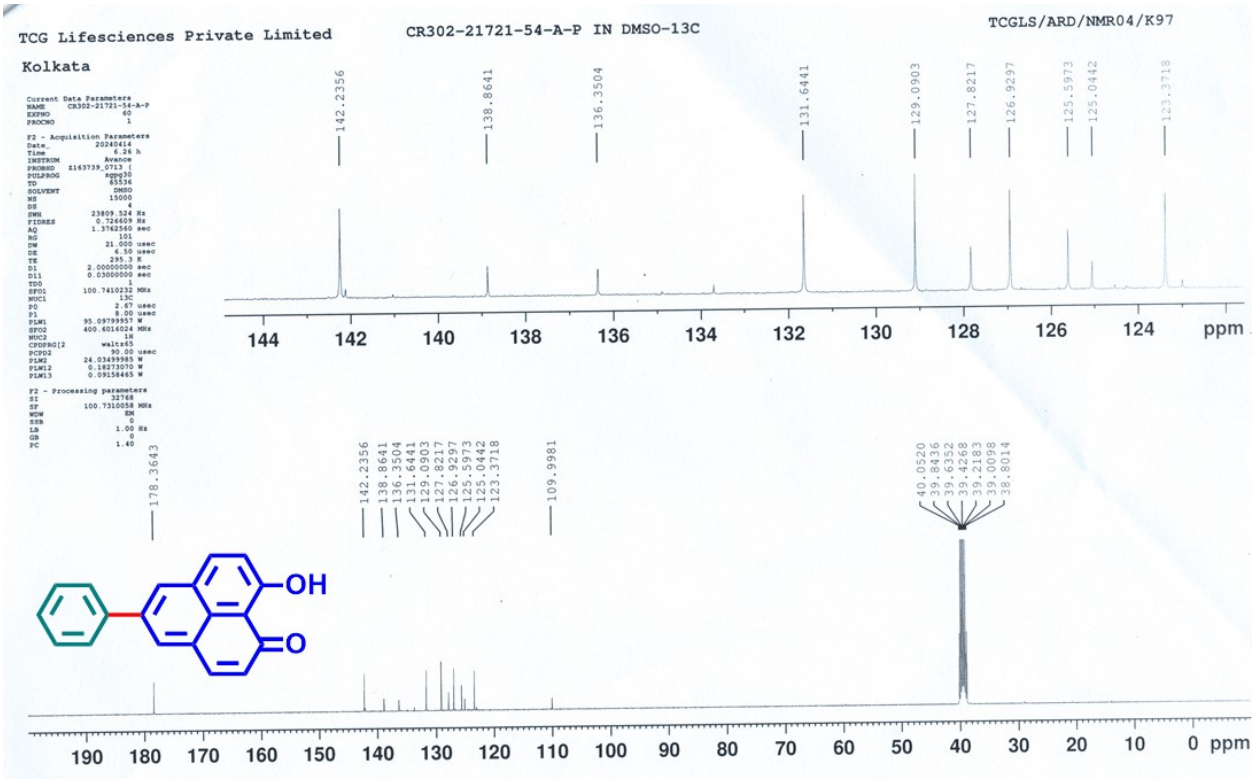


Figure S31: ^{13}C {^{1}H} NMR spectrum of **7i**.

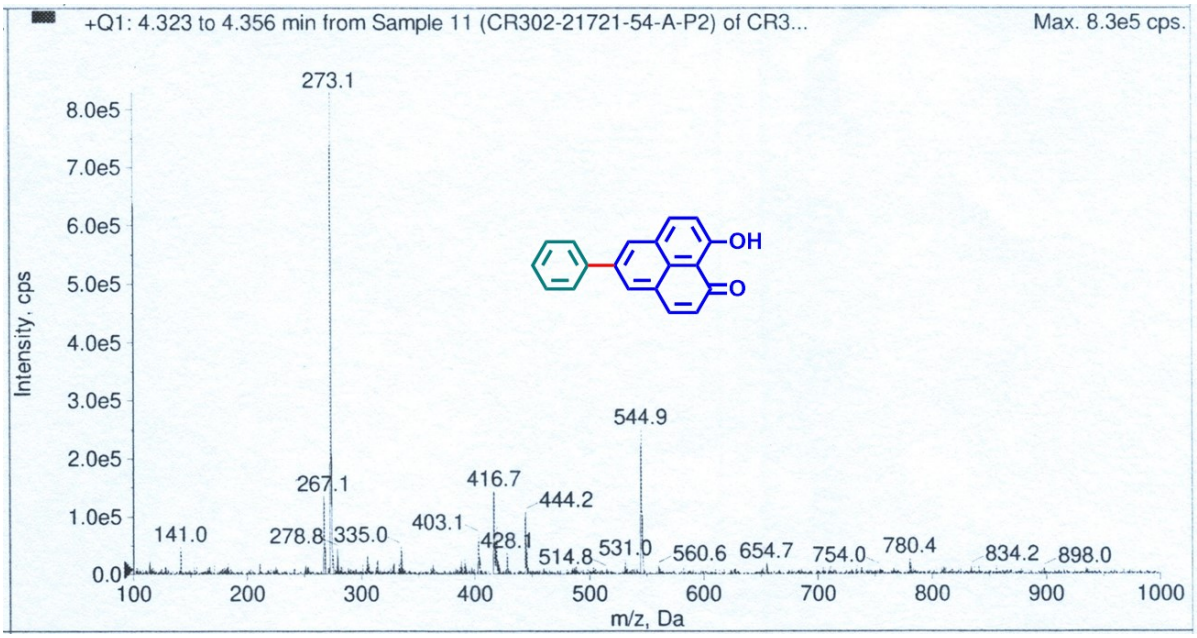


Figure S32: GC-MS spectrum of **7i**.

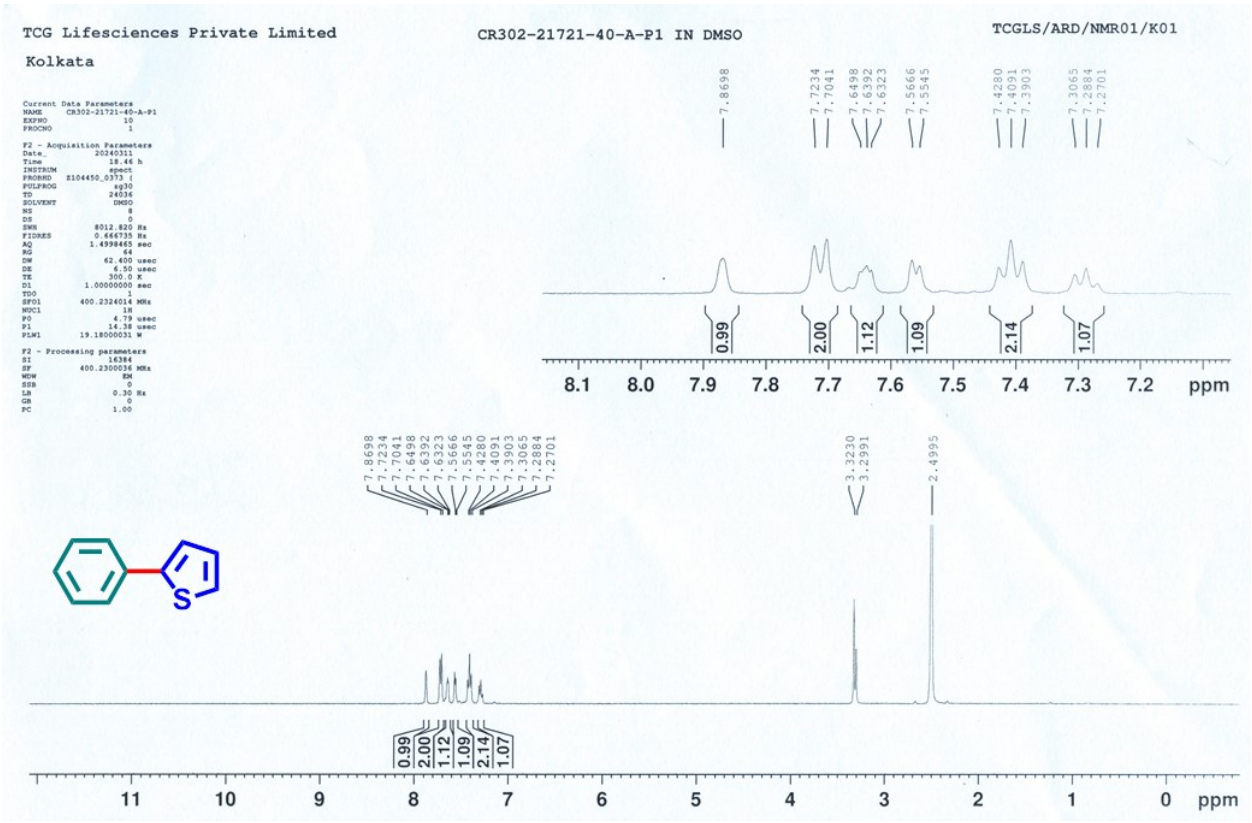


Figure S33: ^{1}H NMR spectrum of **7j**.

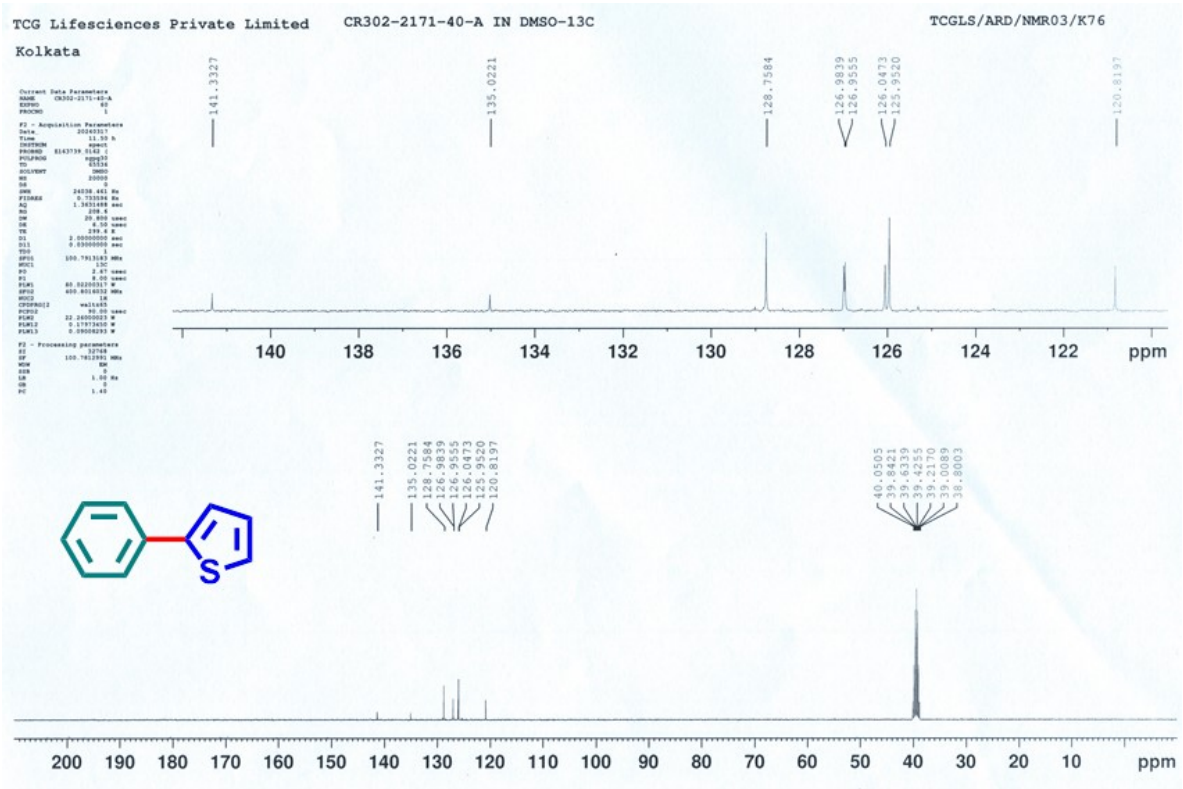


Figure S34: ^{13}C {^{1}H} NMR spectrum of **7j**.

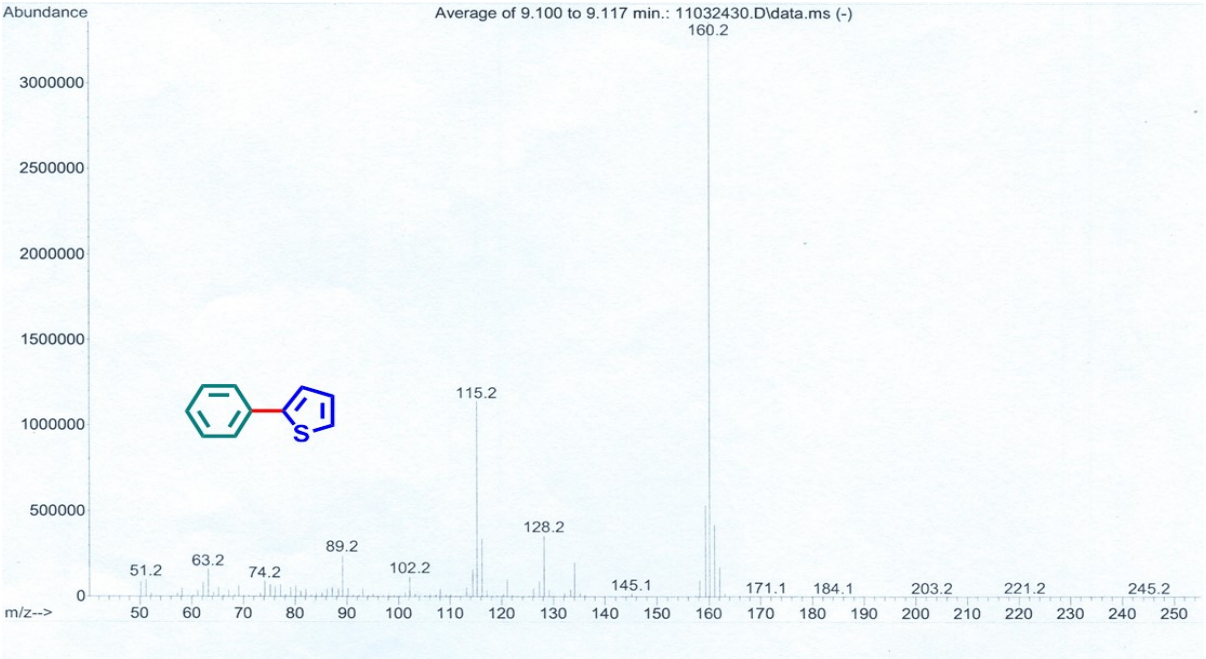


Figure S35: GC-MS spectrum of **7j**.

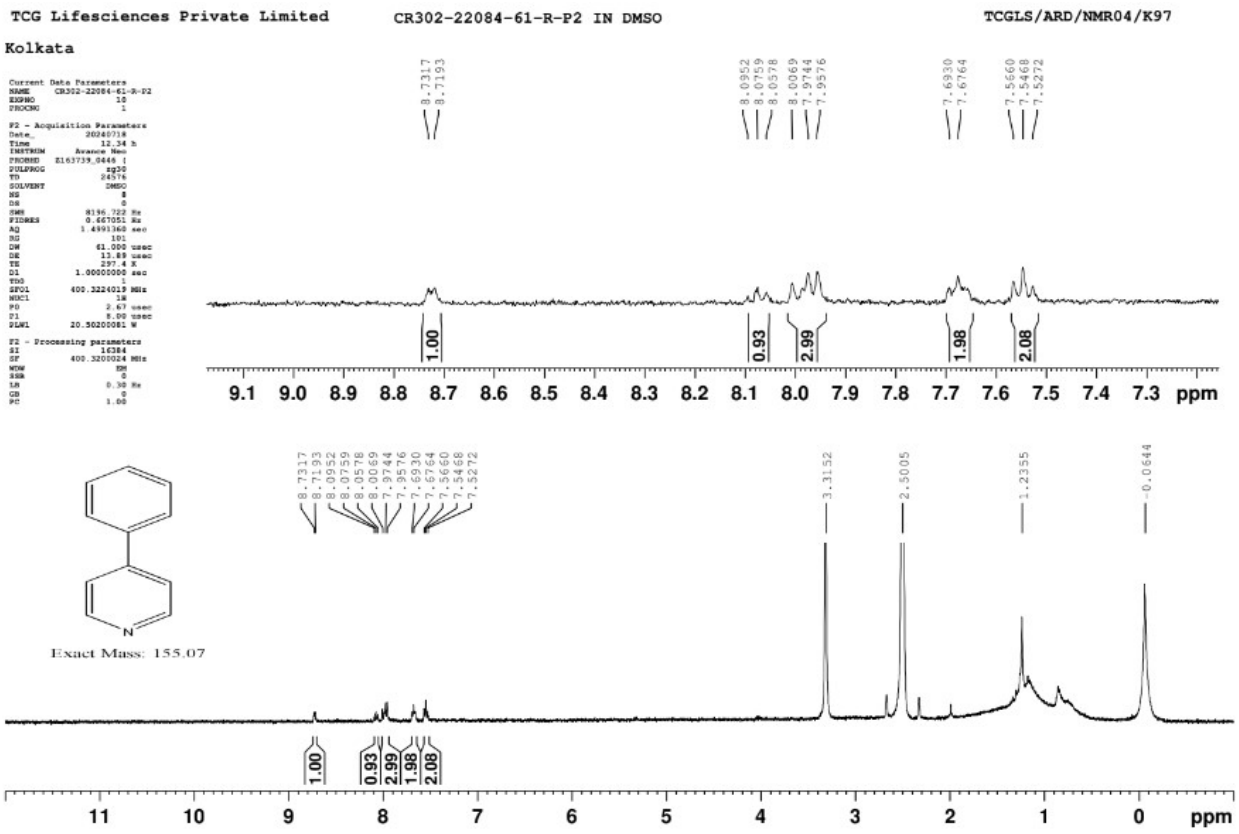


Figure S36: ^{1}H NMR spectrum of **7k**.

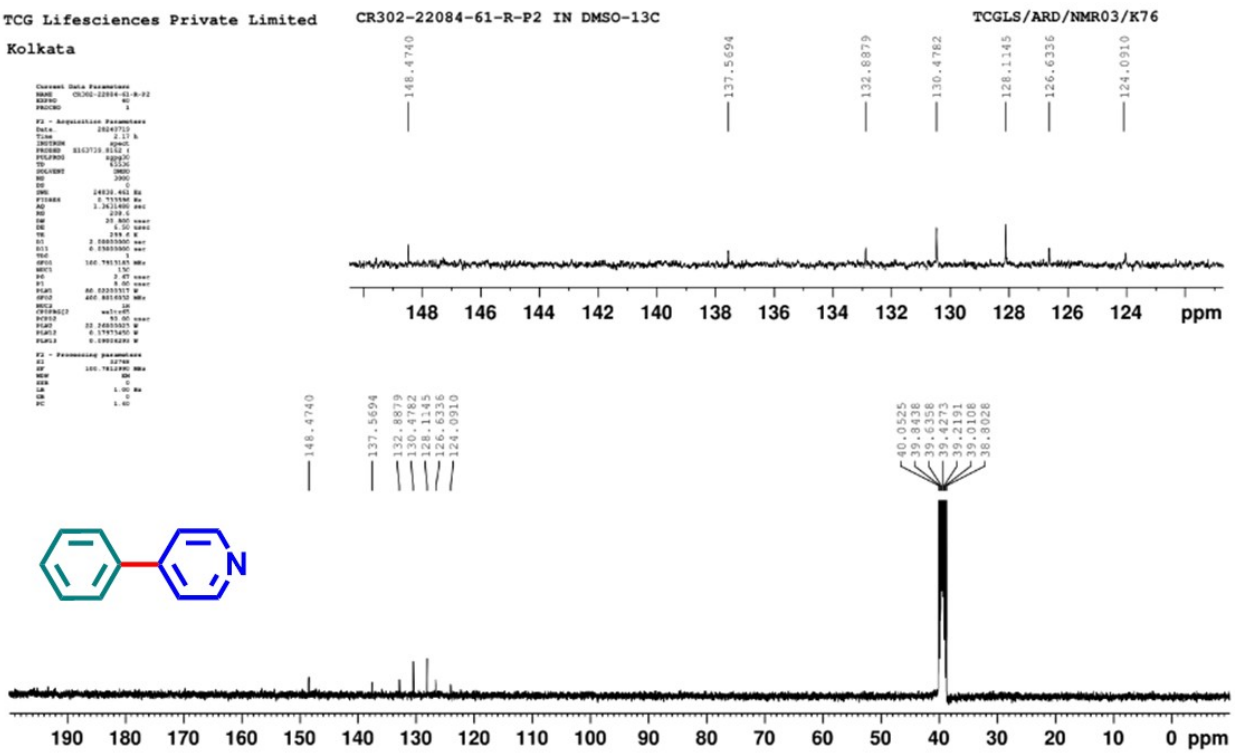


Figure S37: ^{13}C {^{1}H} NMR spectrum of **7k**.

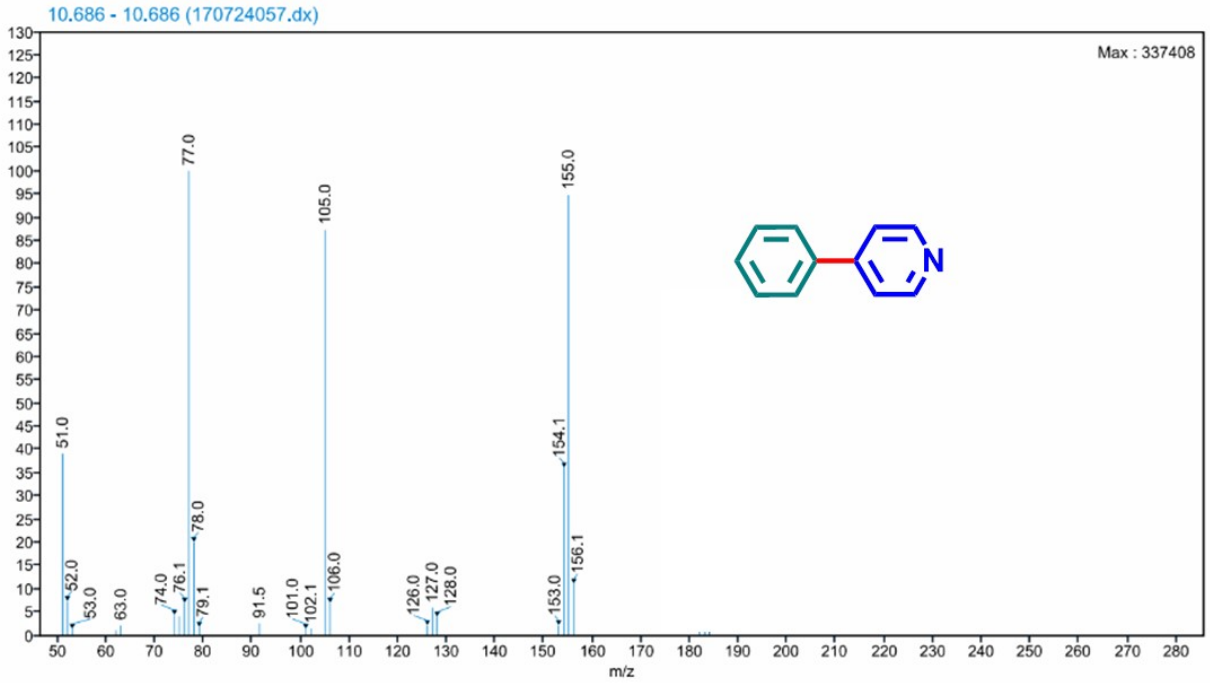


Figure S38: GC-MS spectrum of **7k**.

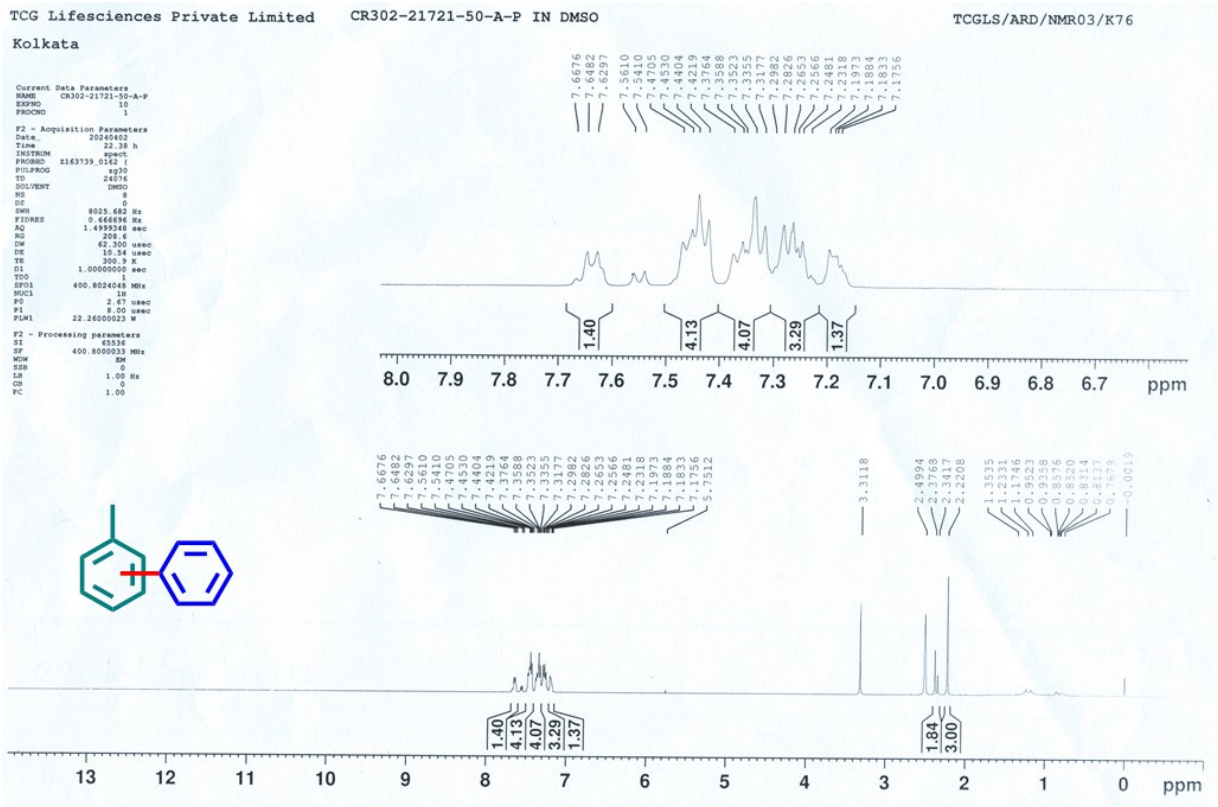


Figure S39: ^{1}H NMR spectrum of **8a**.

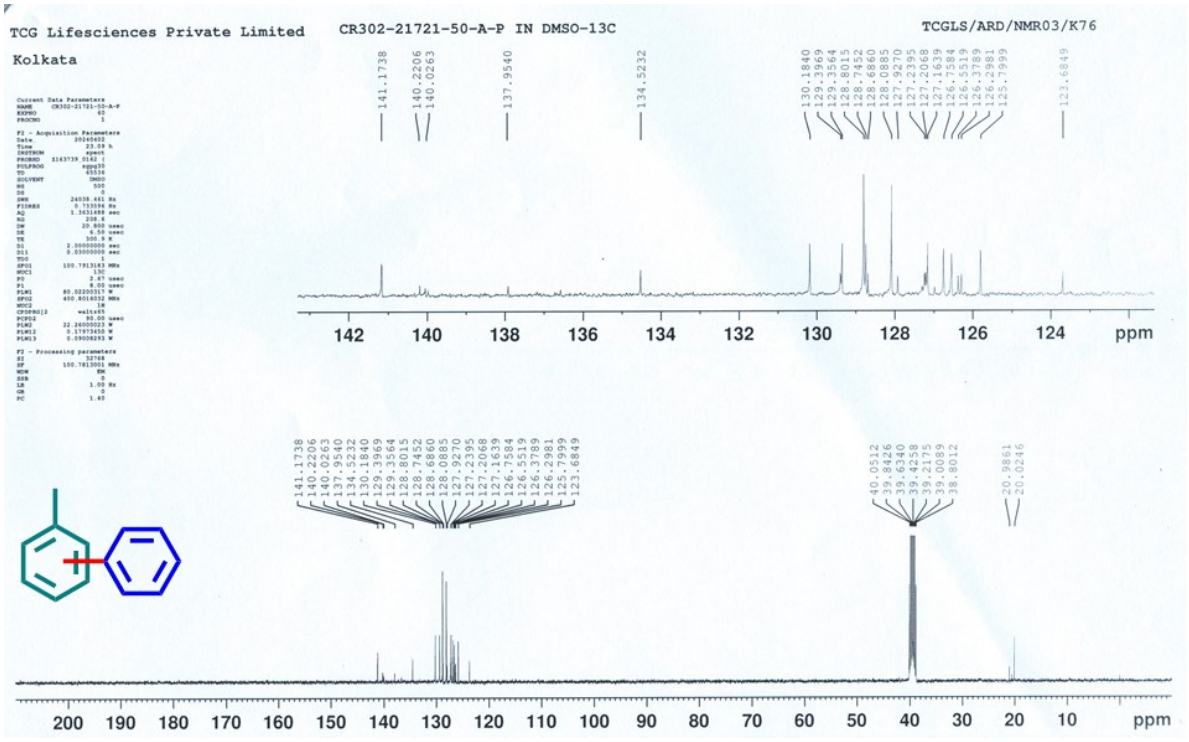


Figure S40: ^{13}C {^{1}H} NMR spectrum of **8a**.

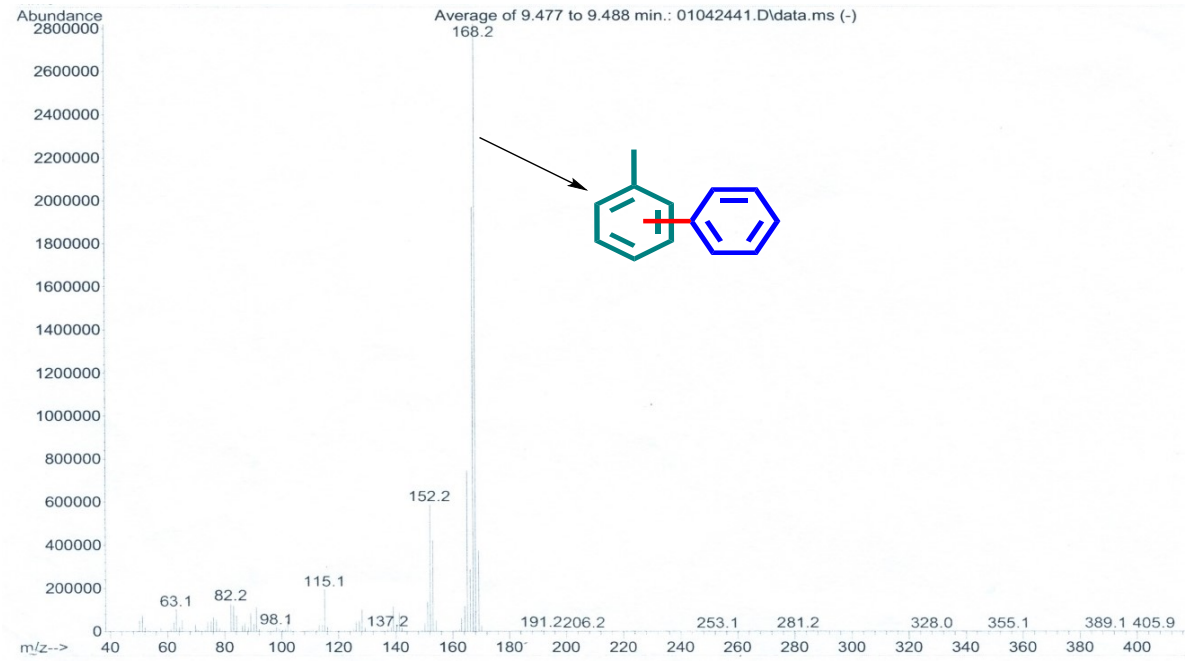


Figure S41: GC-MS spectrum of **8a**.

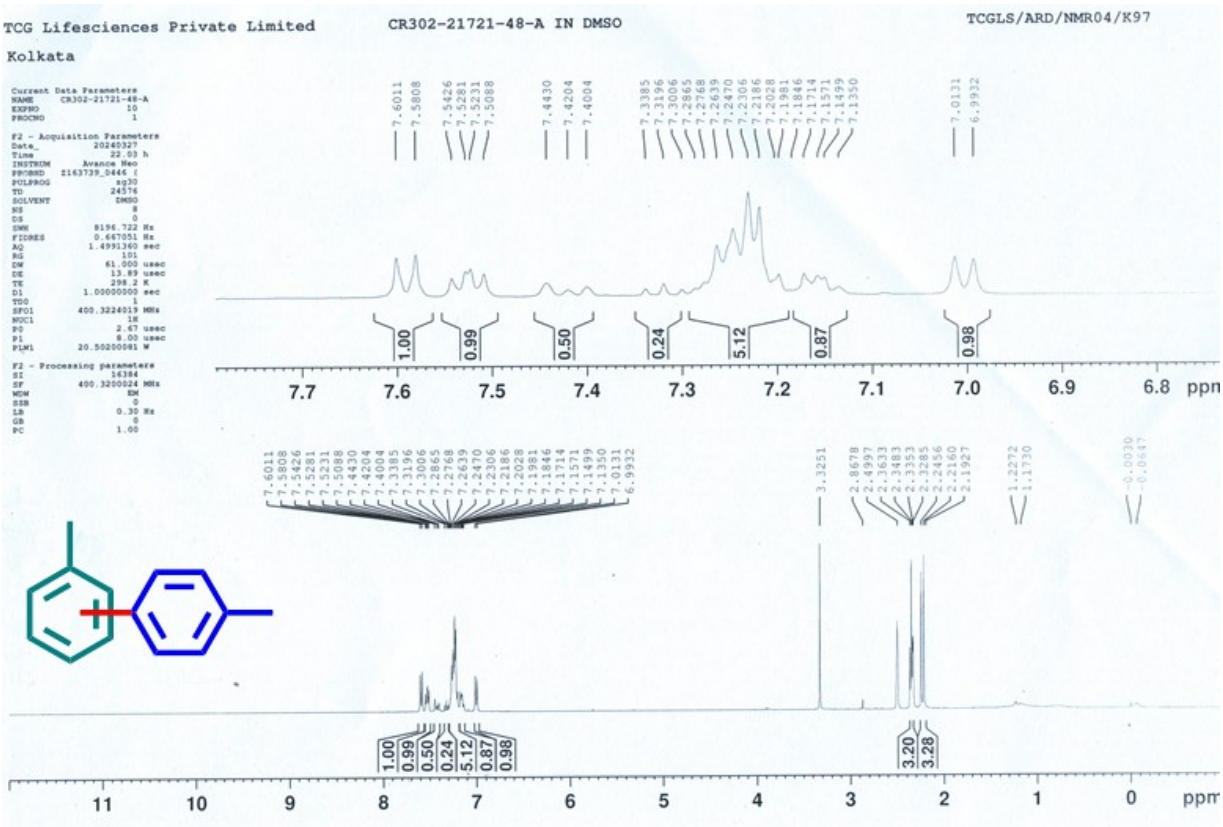


Figure S42: ^{1}H NMR spectrum of **8b**.

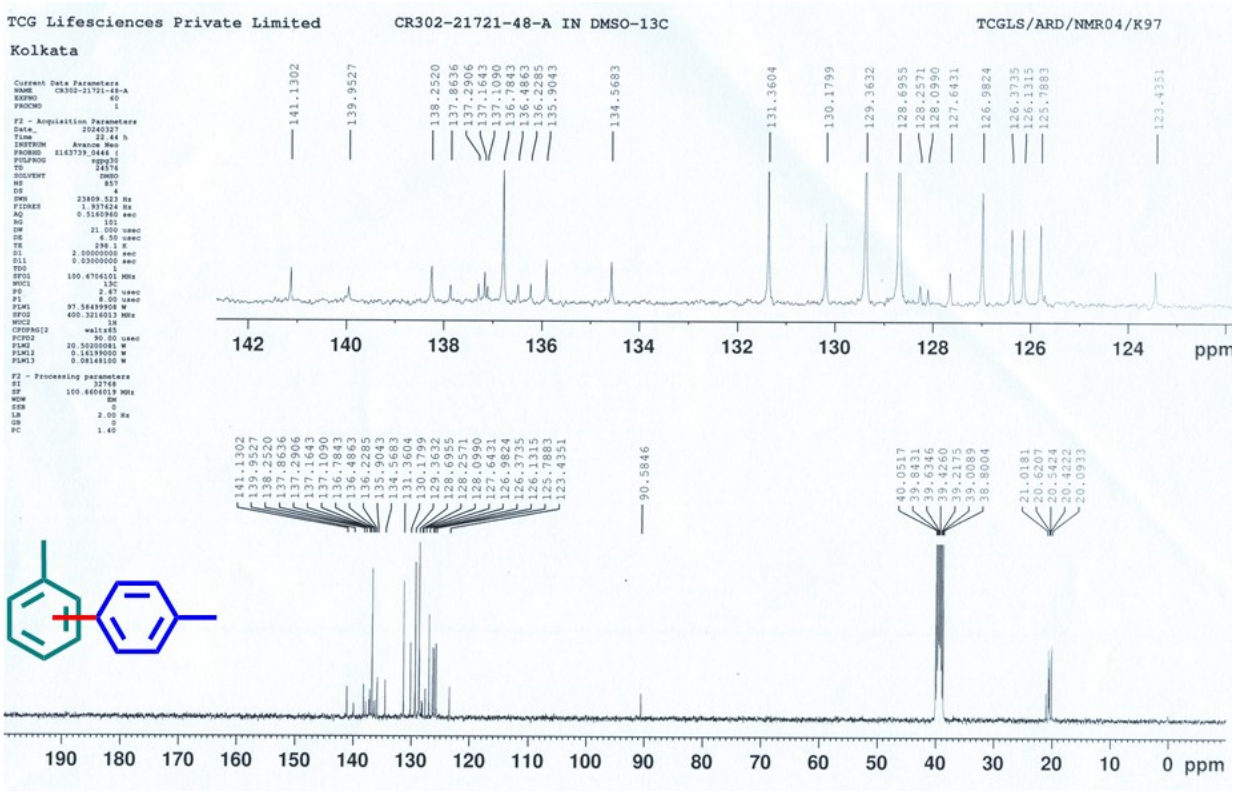


Figure S43: ^{13}C {^{1}H} NMR spectrum of **8b**.

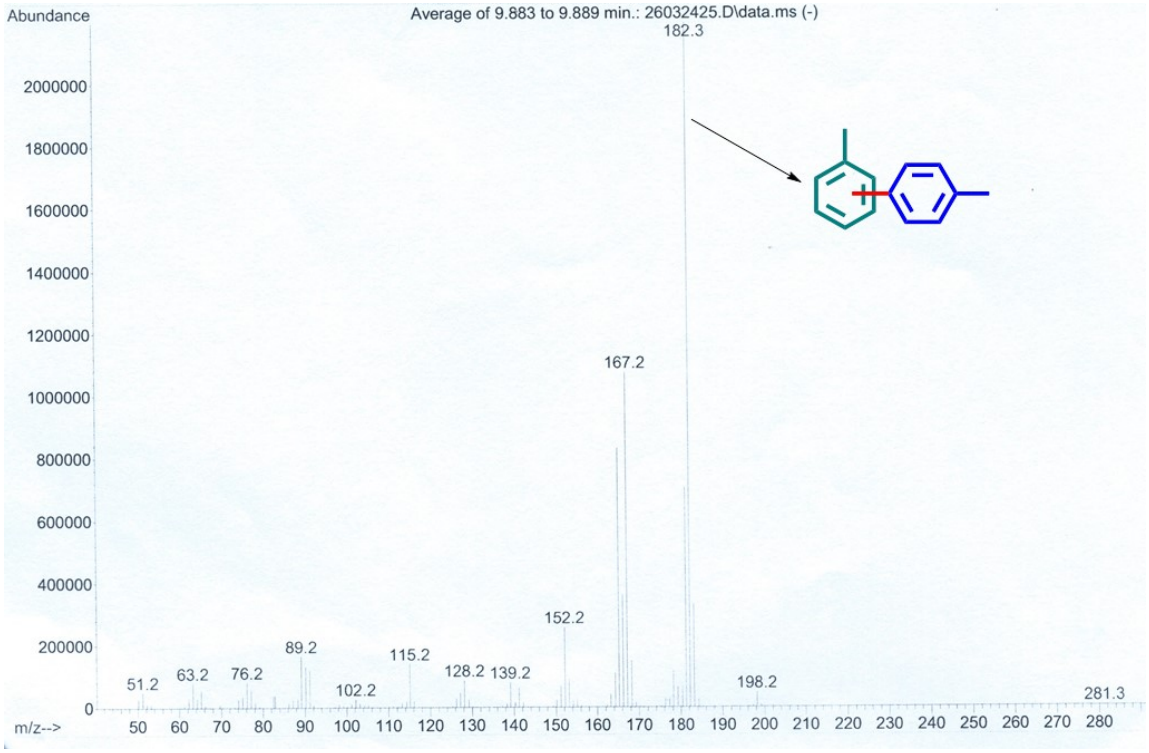


Figure S44: GC-MS spectrum of **8b**.

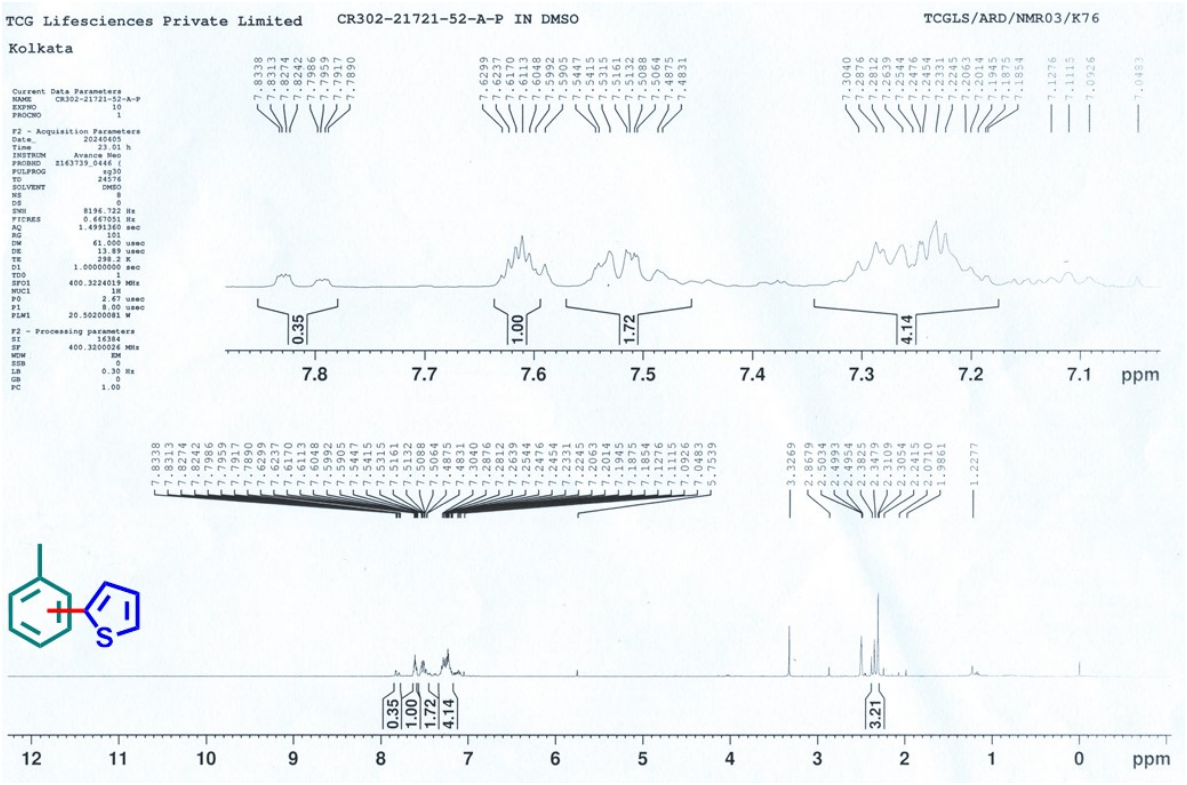


Figure S45: ^{1}H NMR spectrum of **8c**.

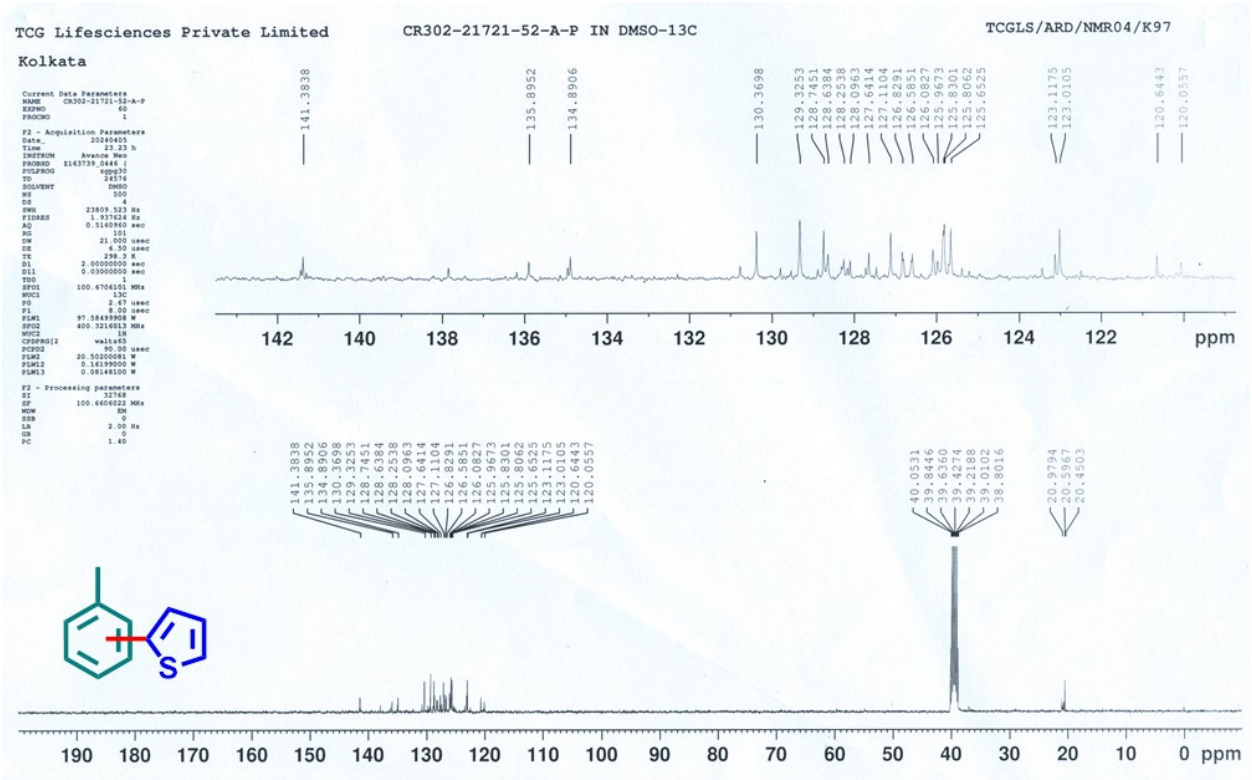


Figure S46: ^{13}C {^{1}H} NMR spectrum of **8c**.

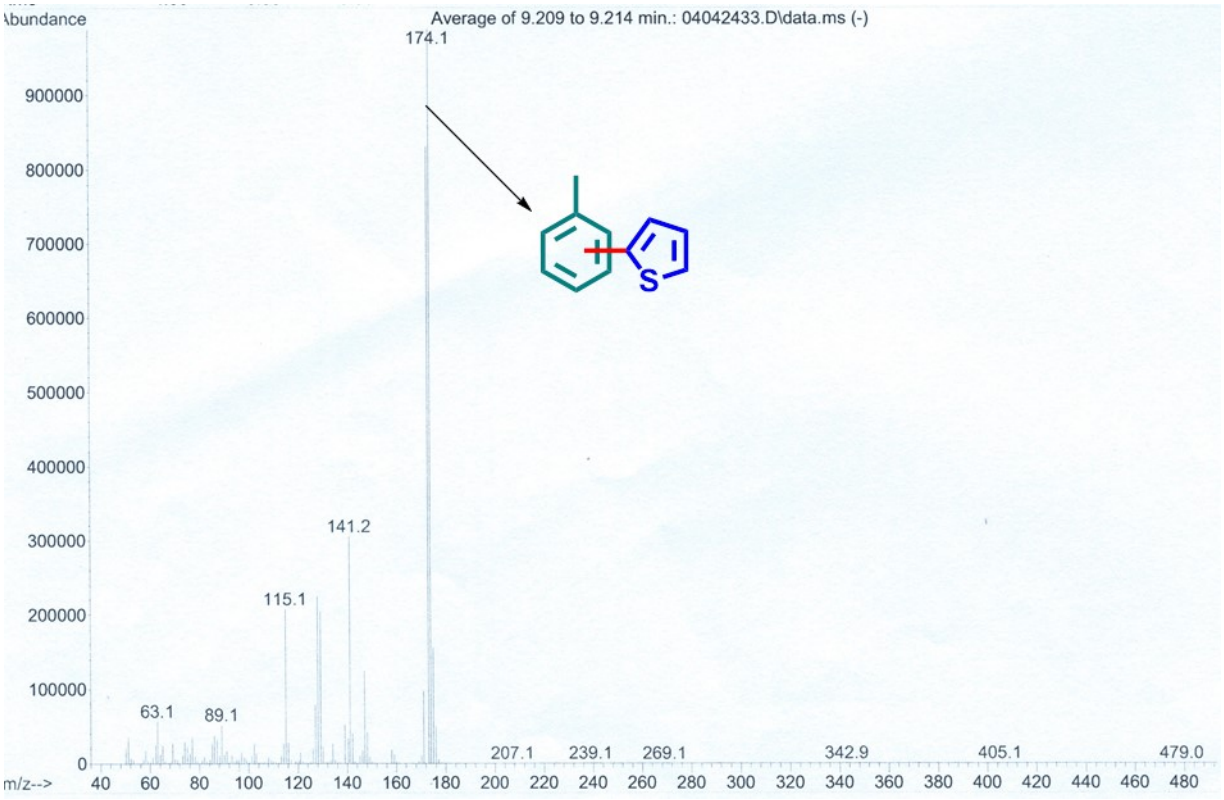


Figure S47: GC-MS spectrum of **8c**.

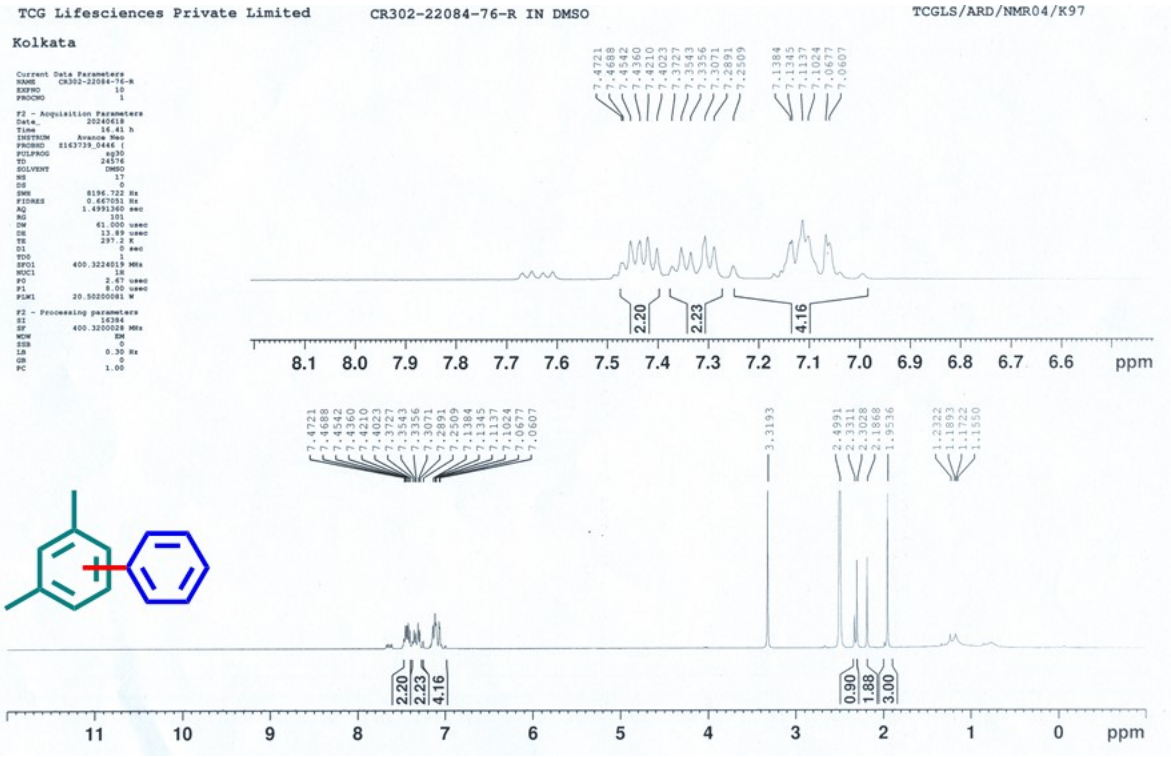


Figure S48: ^{1}H NMR spectrum of **8d**.

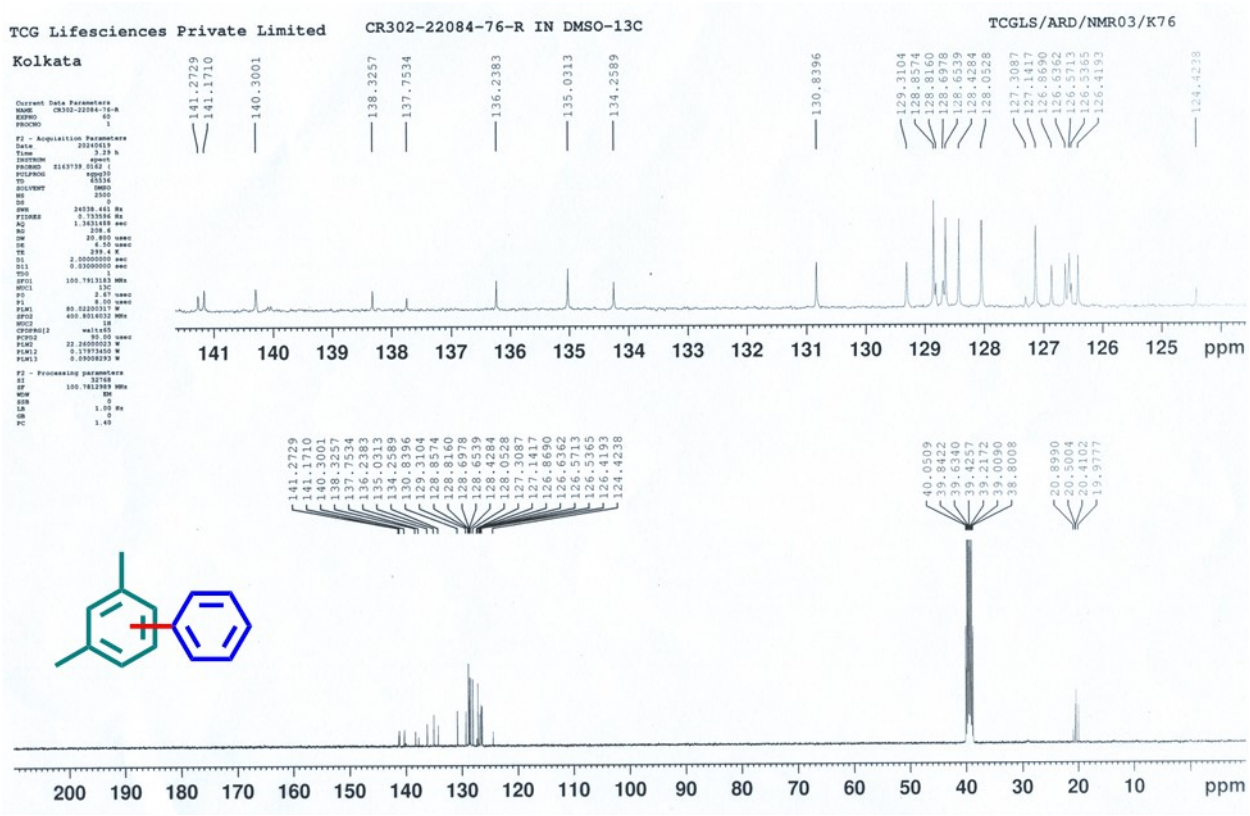


Figure S49: ^{13}C {^{1}H} NMR spectrum of **8d**.

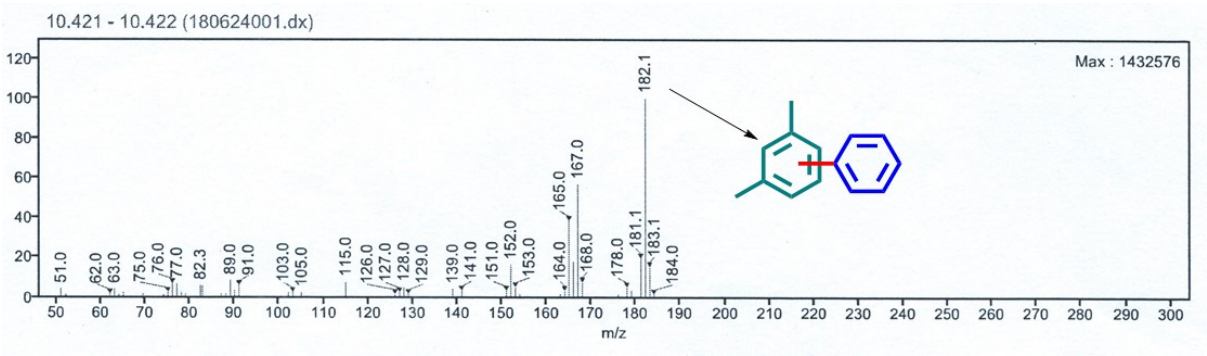


Figure S50: GC-MS spectrum of **8d**.

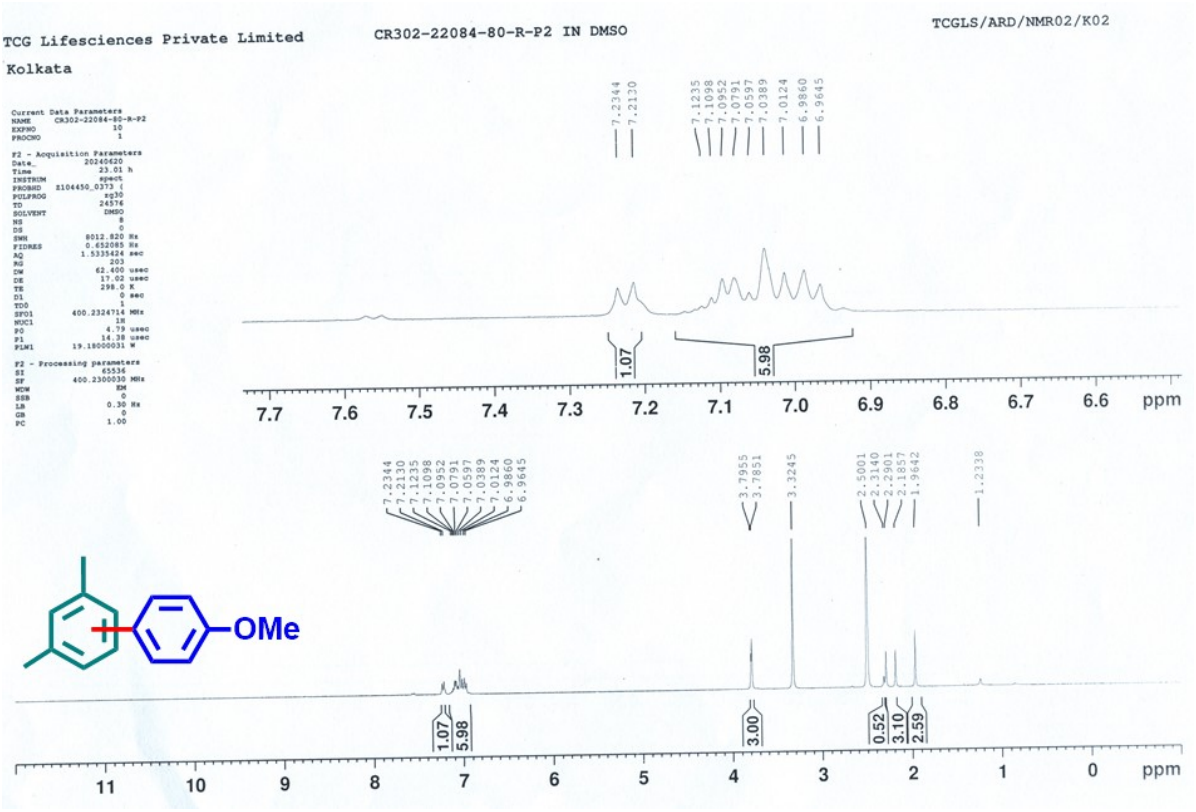


Figure S51: ^{1}H NMR spectrum of **8e**.

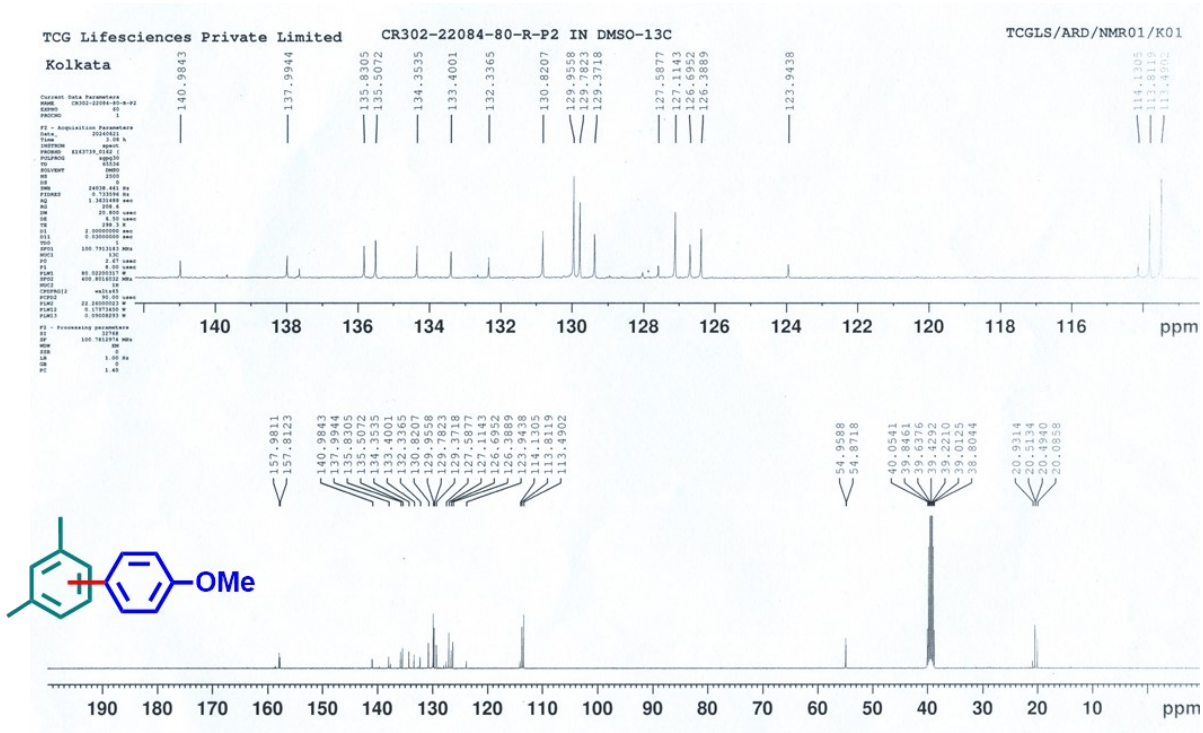


Figure S52: ^{13}C {^{1}H} NMR spectrum of **8e**.

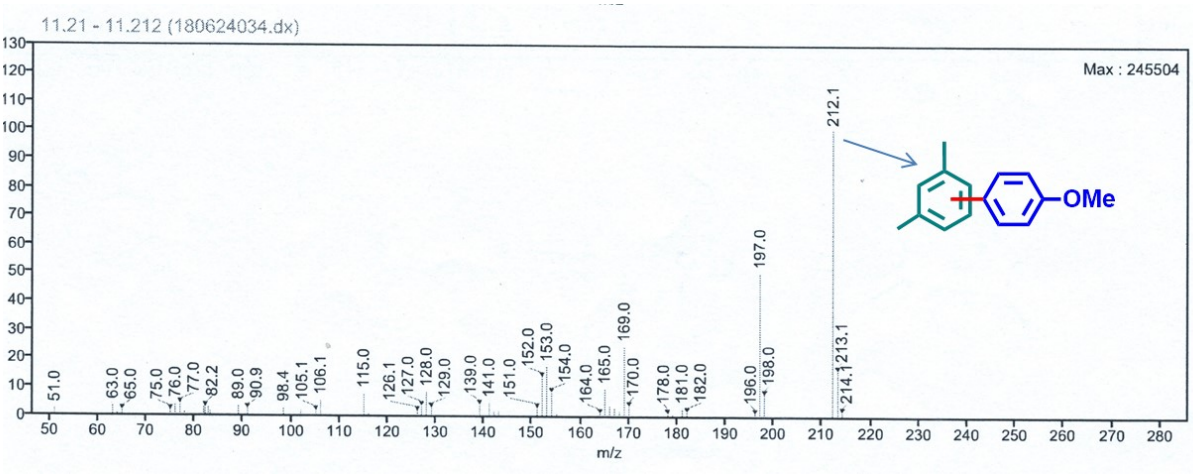


Figure S53: GC-MS spectrum of **8e**.

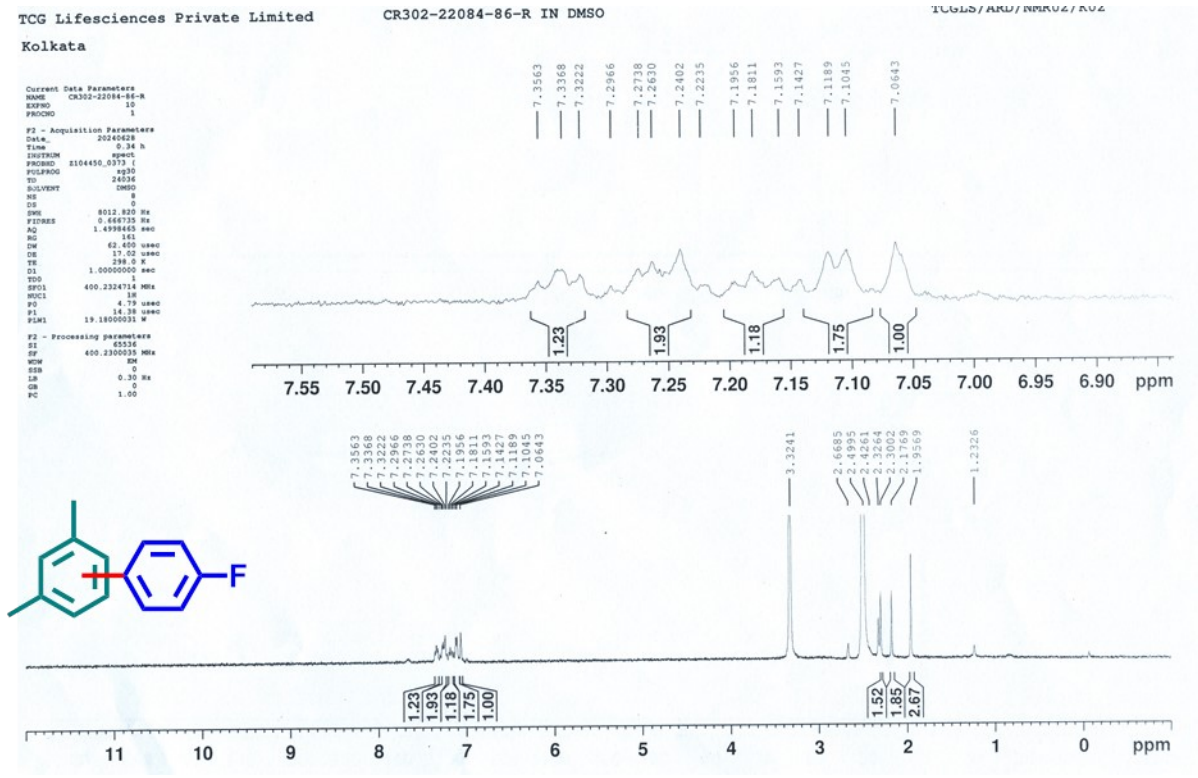


Figure S54: ^{1}H NMR spectrum of **8f**.

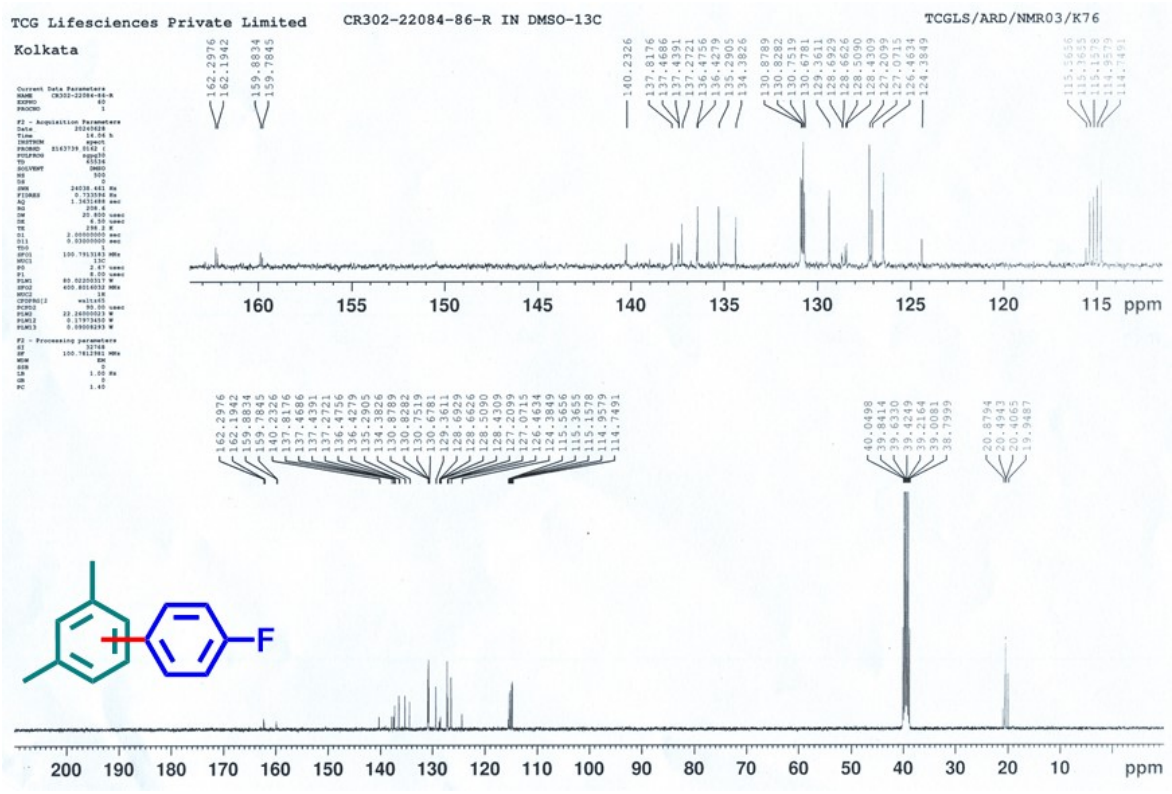


Figure S55: ^{13}C {^{1}H} NMR spectrum of **8f**.

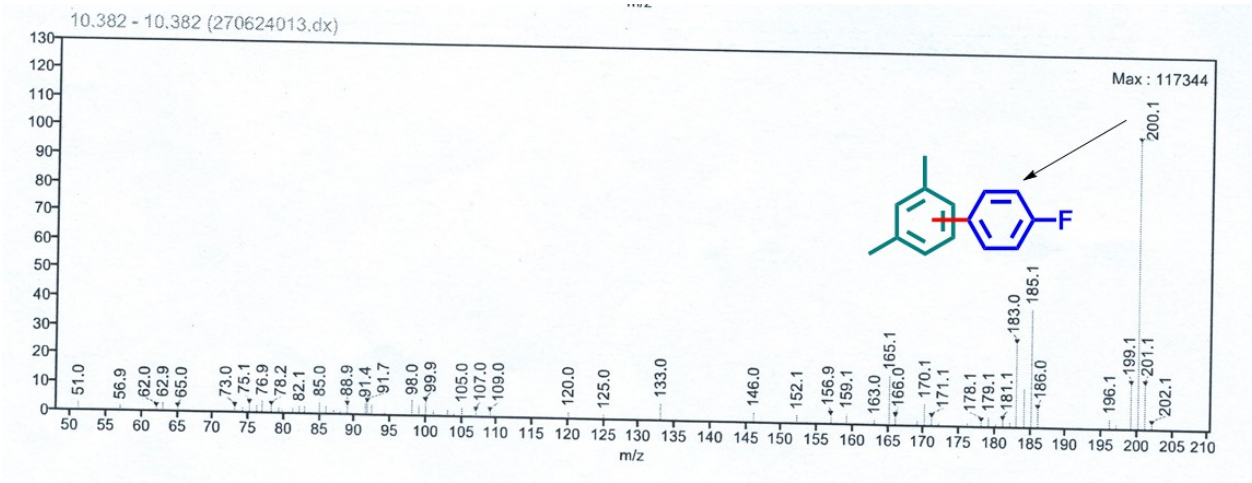


Figure S56: GC-MS spectrum of **8f**.

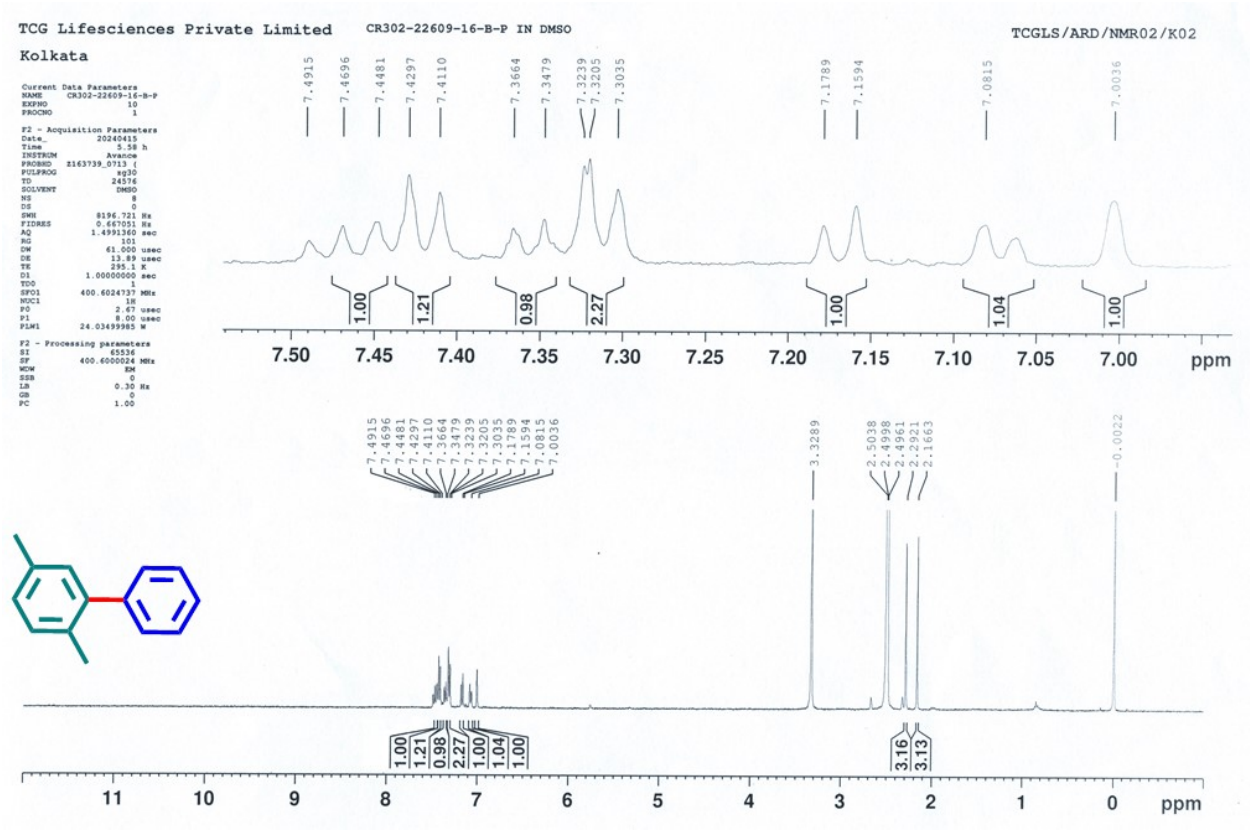


Figure S57: ^{1}H NMR spectrum of **8g**.

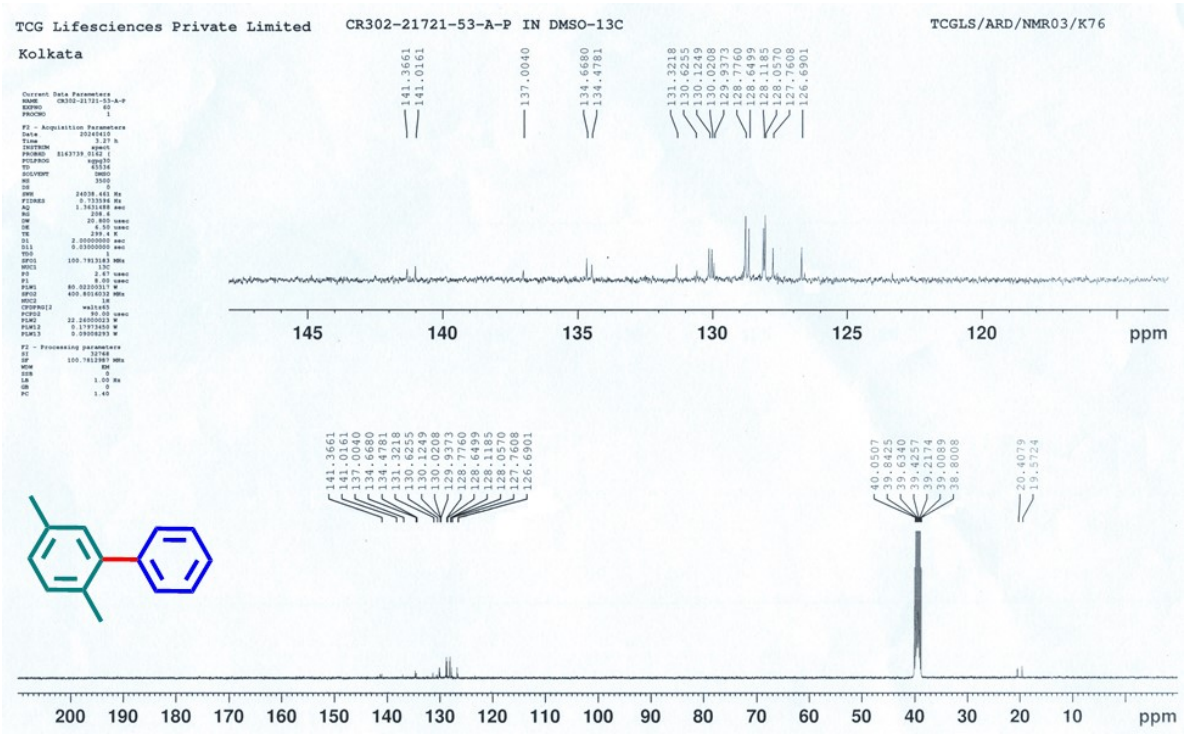


Figure S58: ^{13}C {^{1}H} NMR spectrum of **8g**.

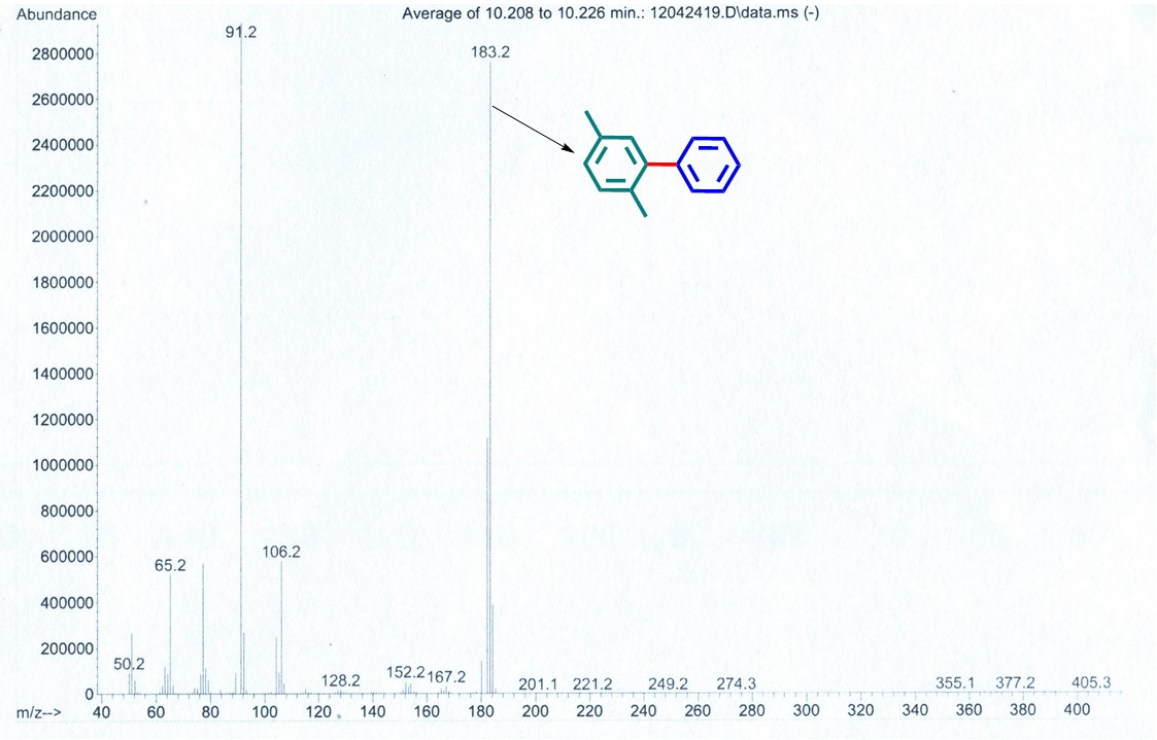


Figure S59: GC-MS spectrum of **8g**.

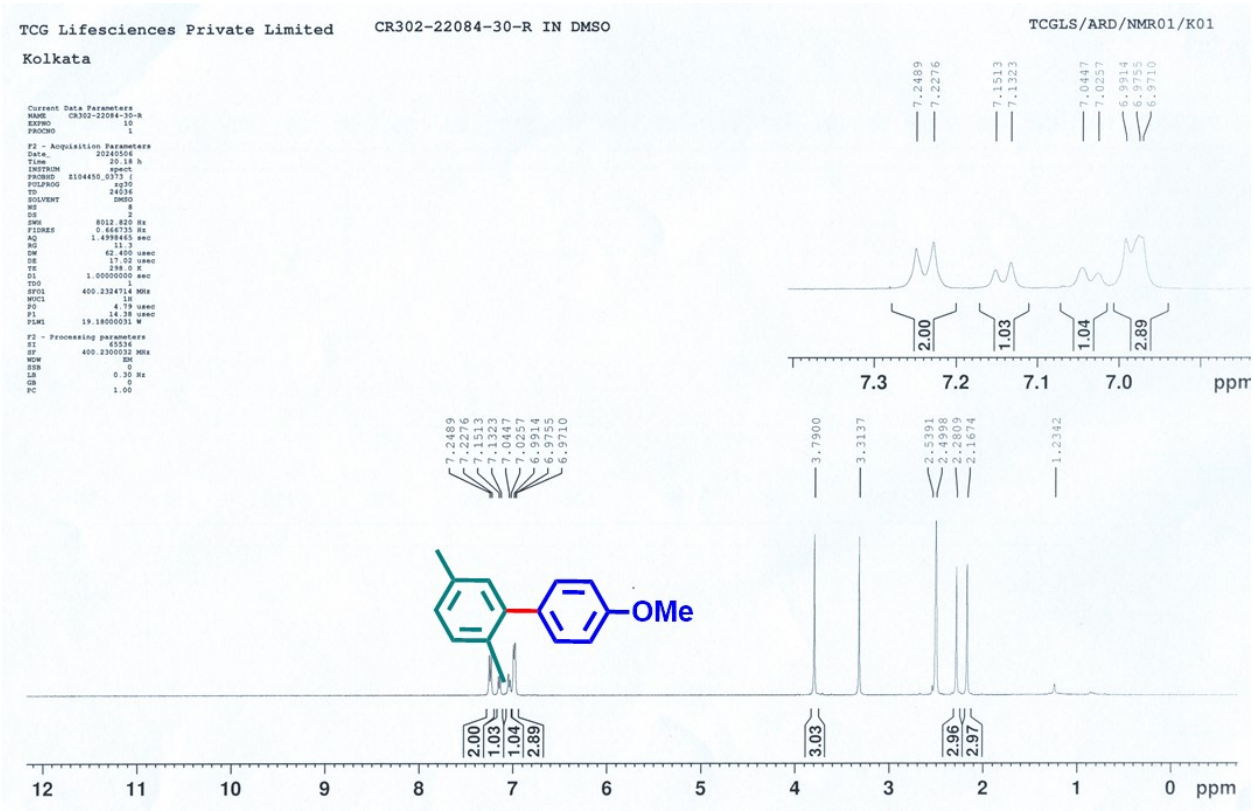


Figure S60: ^{1}H NMR spectrum of **8h**.

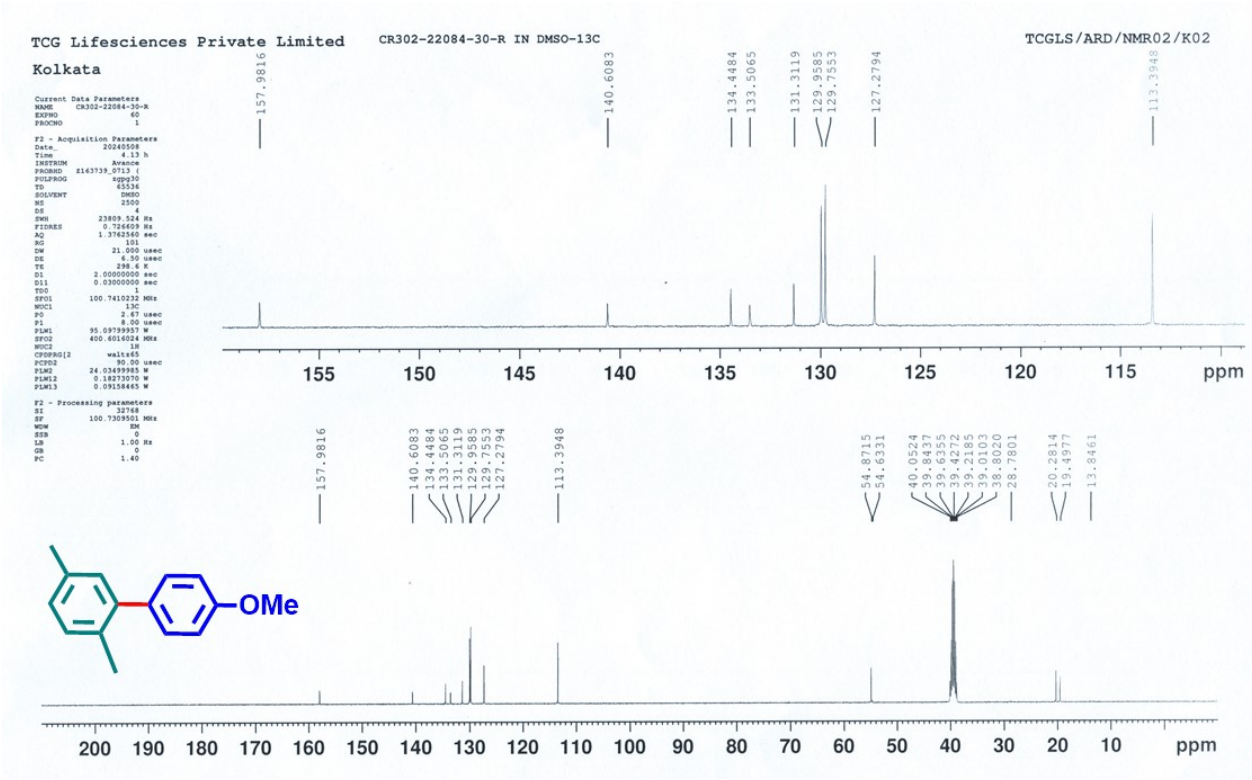


Figure S61: ^{13}C {^{1}H} NMR spectrum of **8h**.

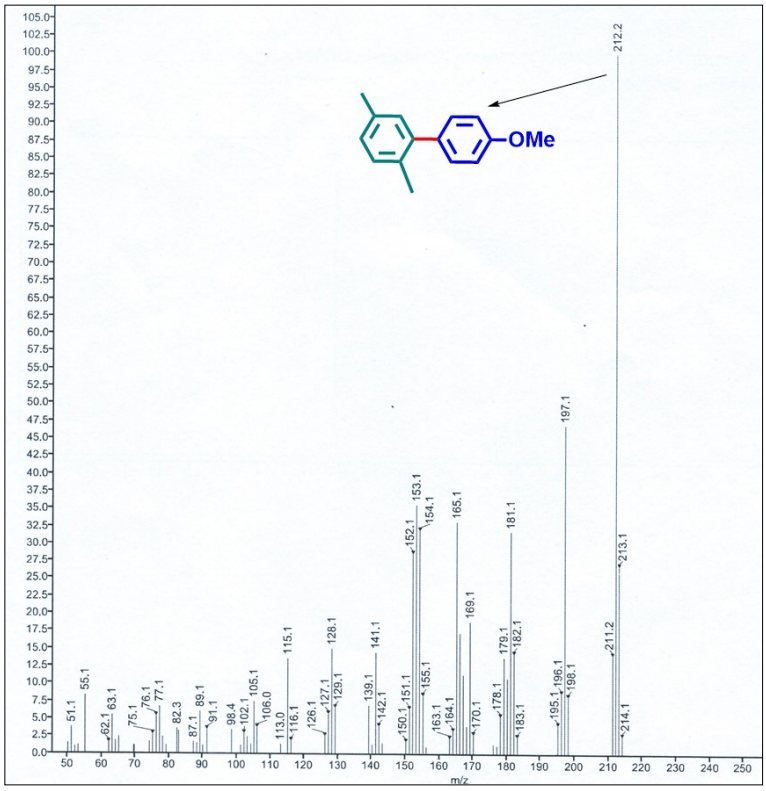


Figure S62: GC-MS spectrum of **8h**.

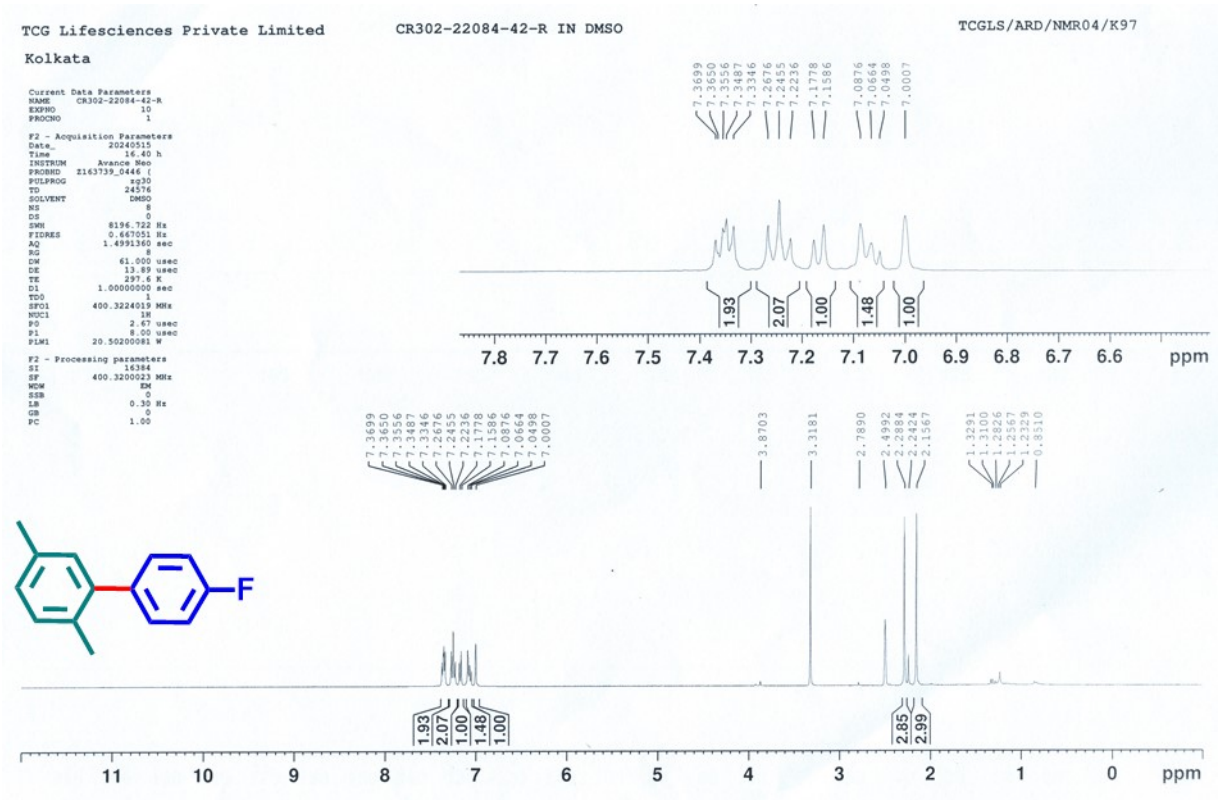


Figure S63: ^{1}H NMR spectrum of **8i**.

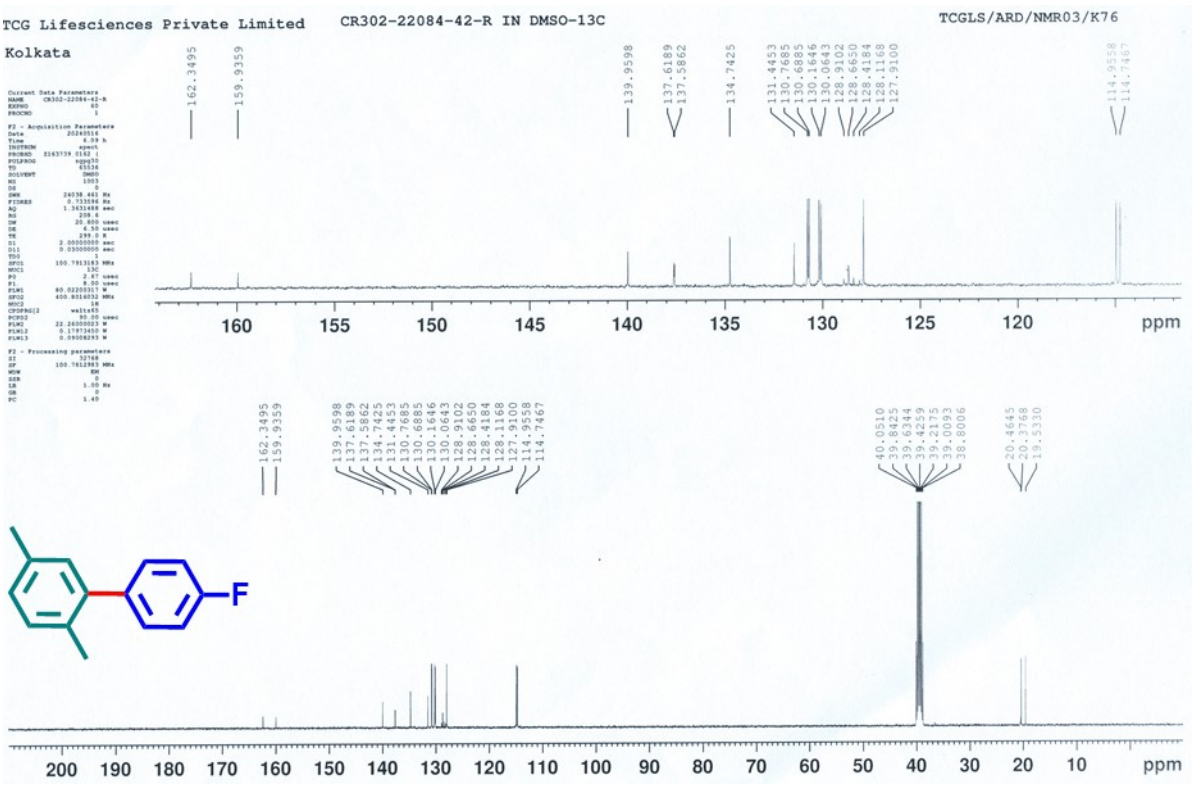


Figure S64: ^{13}C {^{1}H} NMR spectrum of **8i**.

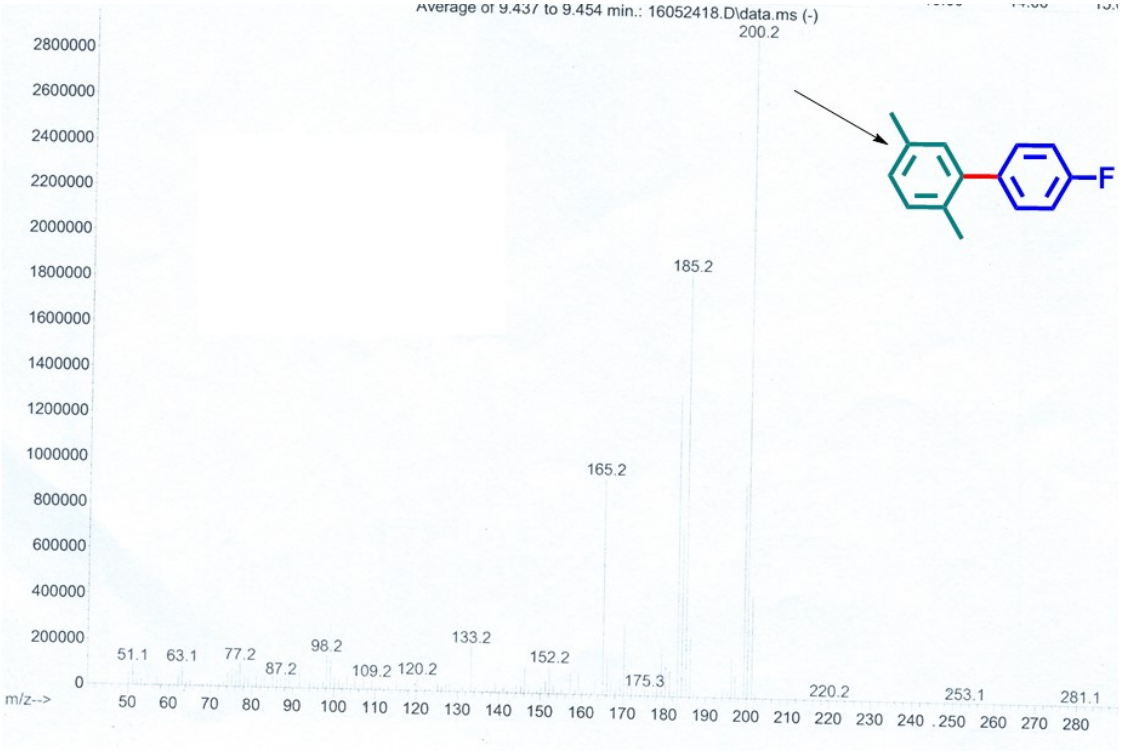


Figure S65: GC-MS spectrum of **8i**.

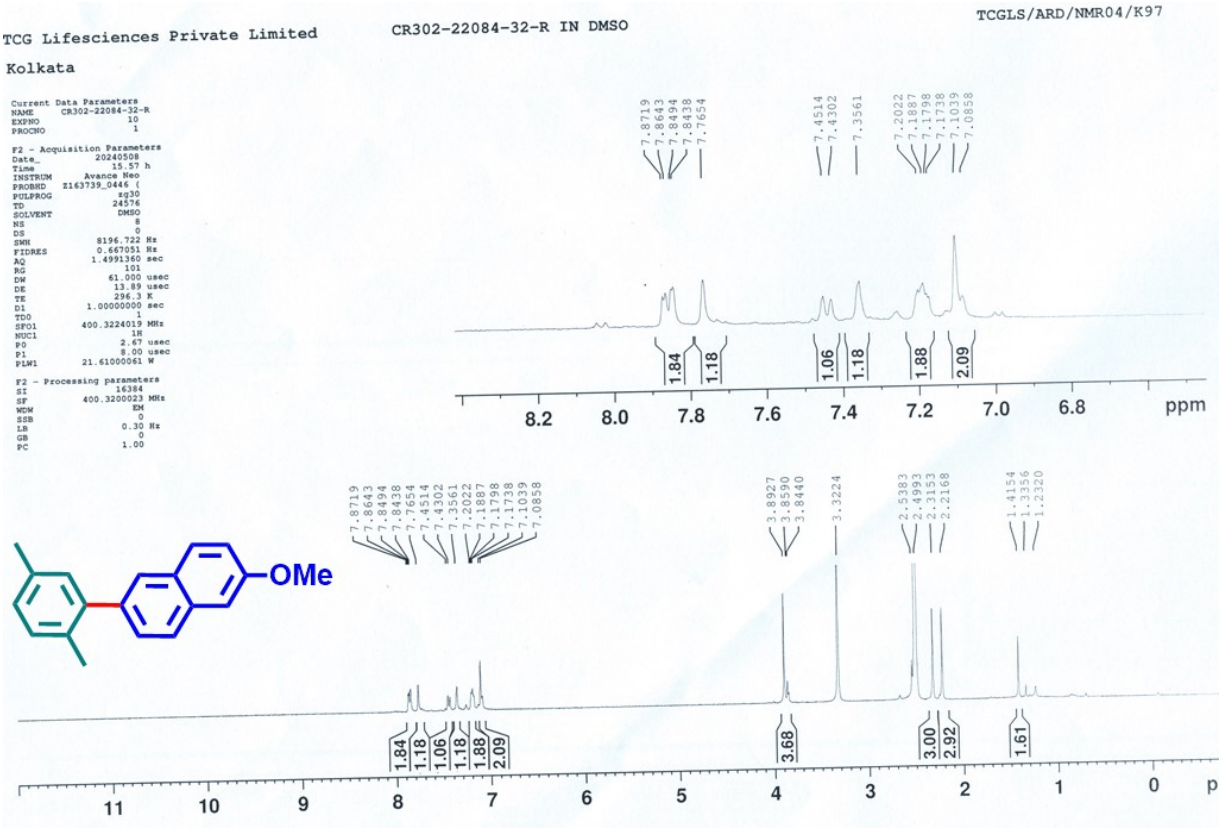


Figure S66: ^{1}H NMR spectrum of **8j**

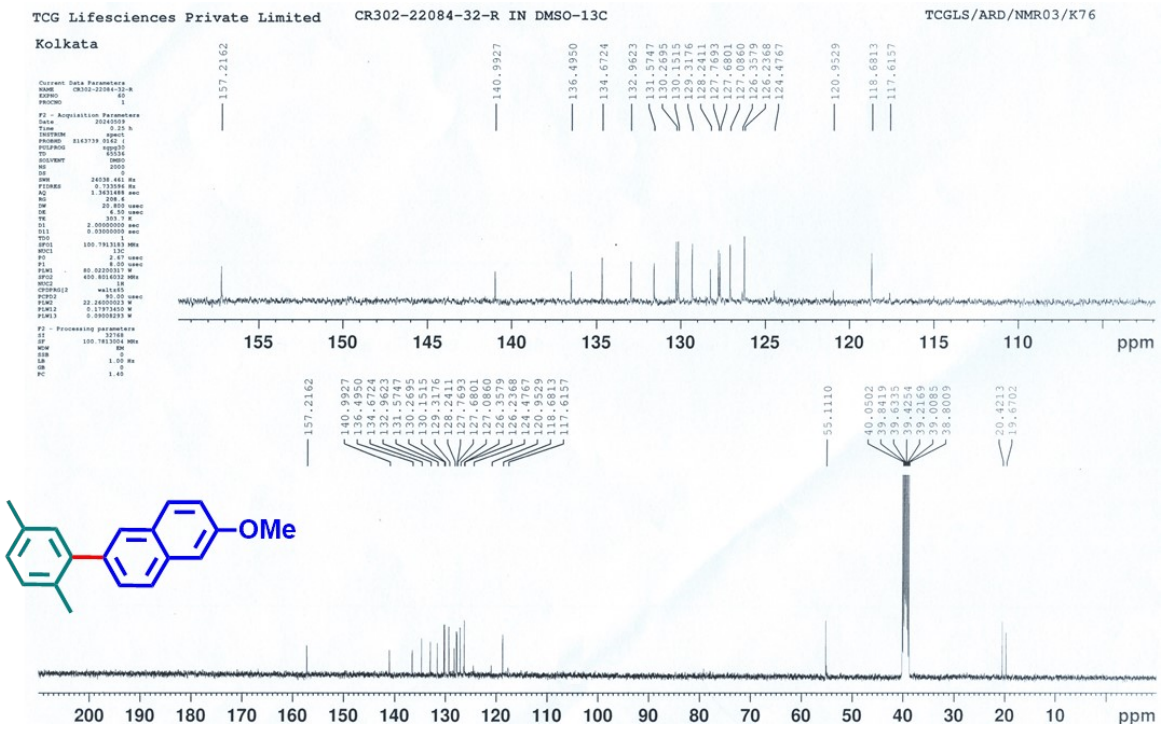


Figure S67: ^{13}C {^{1}H} NMR spectrum of **8j**.

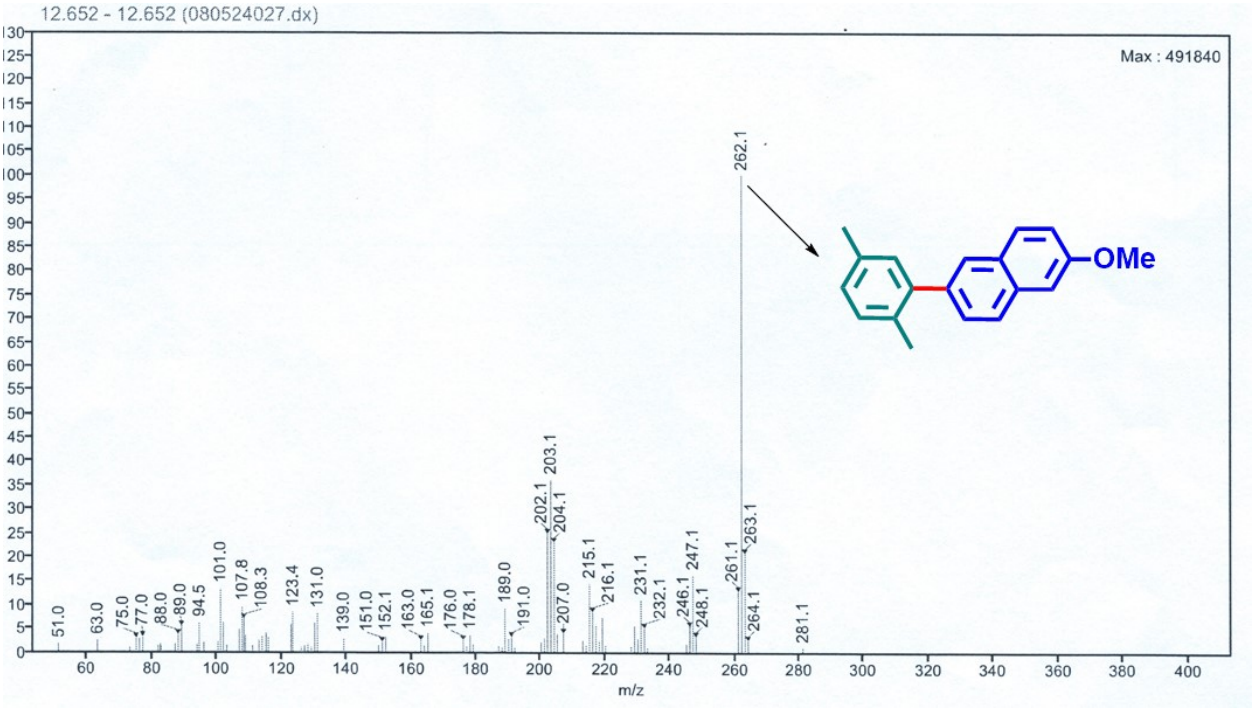


Figure S68: GC-MS spectrum of **8j**.

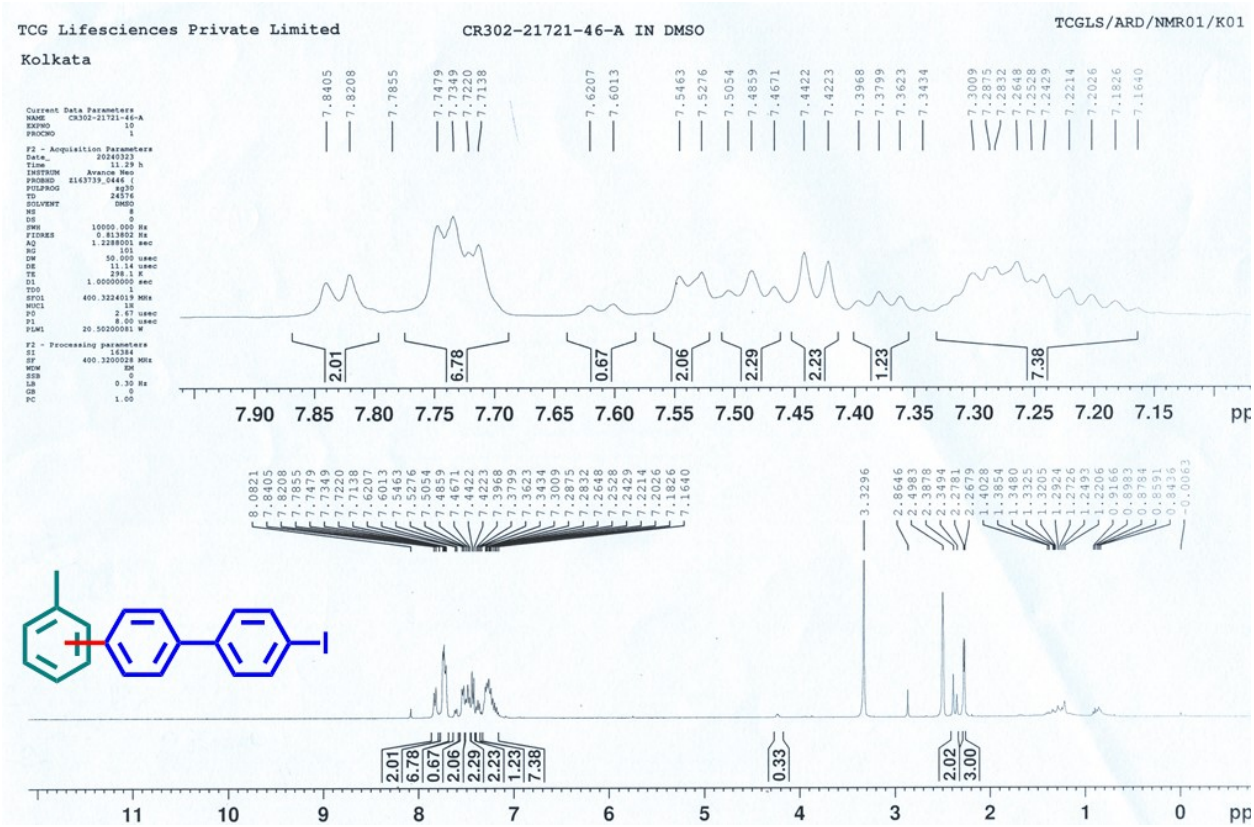


Figure S69: ^{1}H NMR spectrum of **8k**.

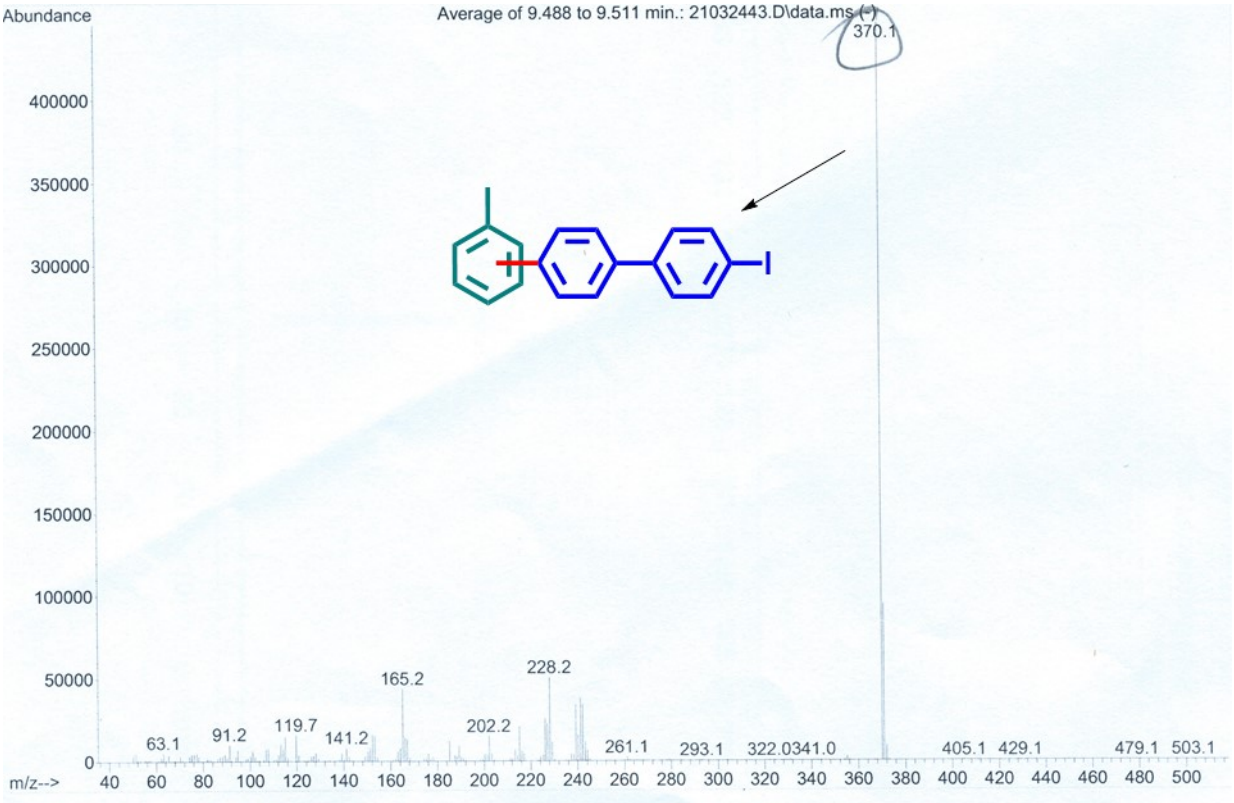


Figure S70: GC-MS spectrum of **8k**.

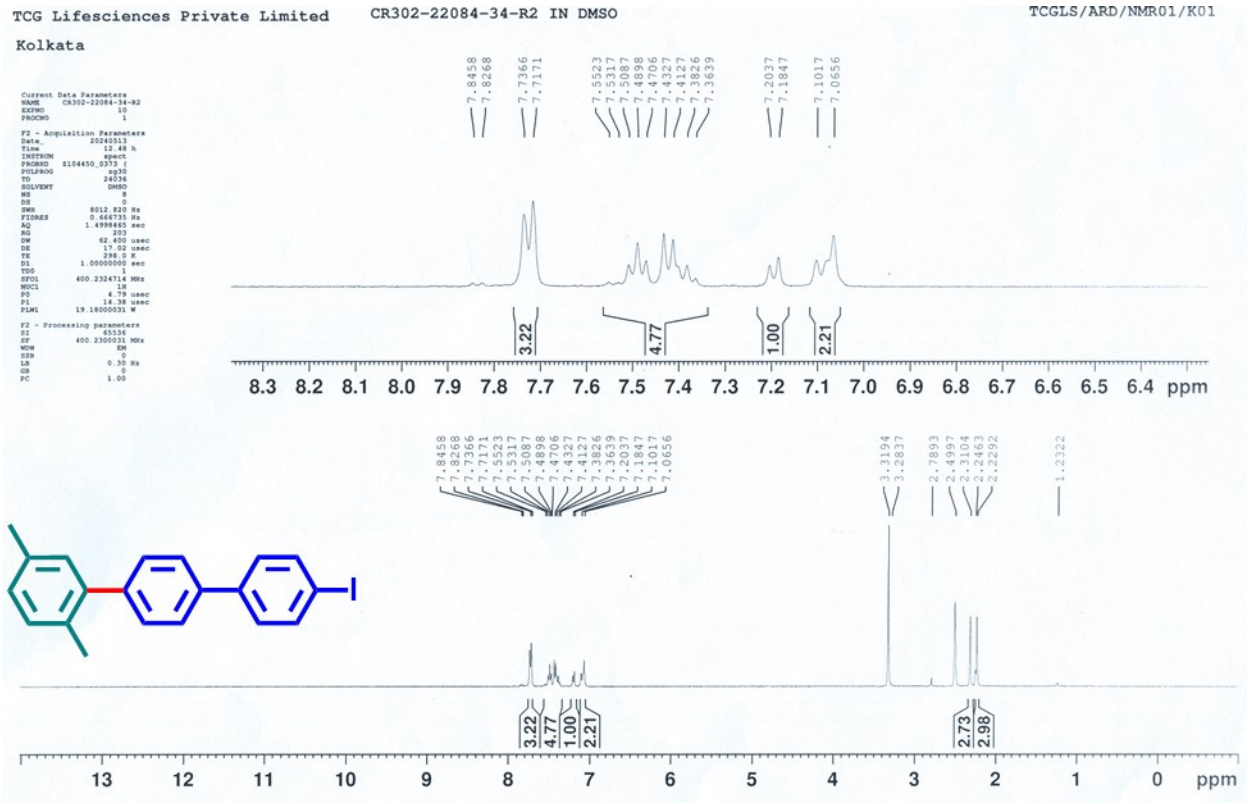


Figure S71: ^{1}H NMR spectrum of **8l**.

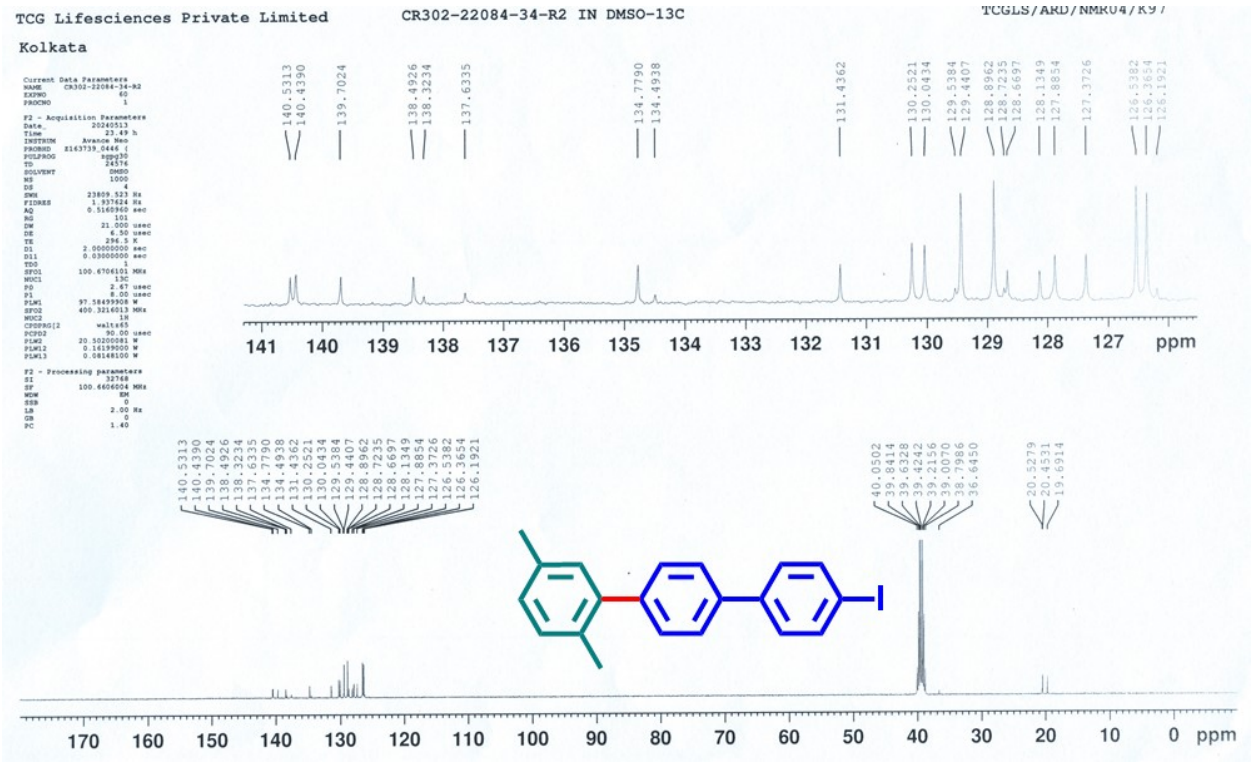


Figure S72: ^{13}C {^{1}H} NMR spectrum of **8l**.

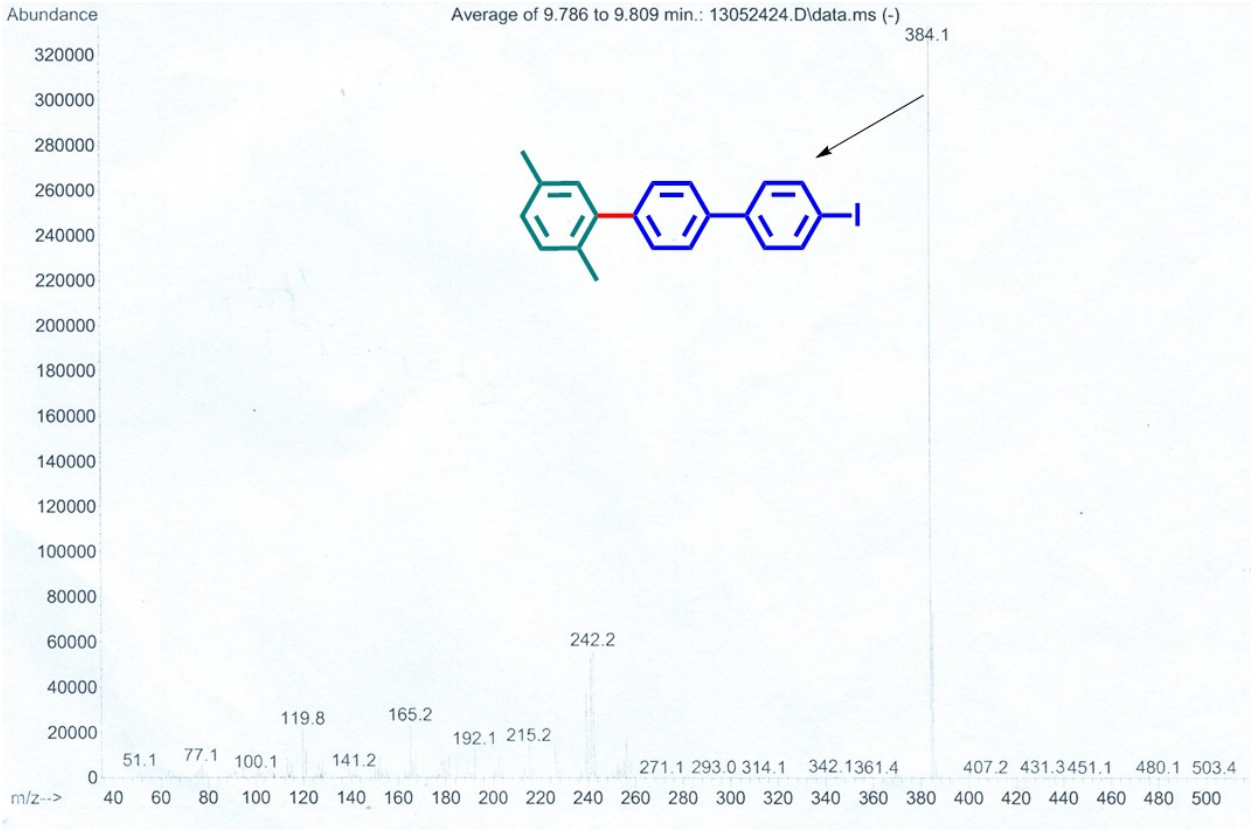


Figure S73: GC-MS spectrum of **8l**.

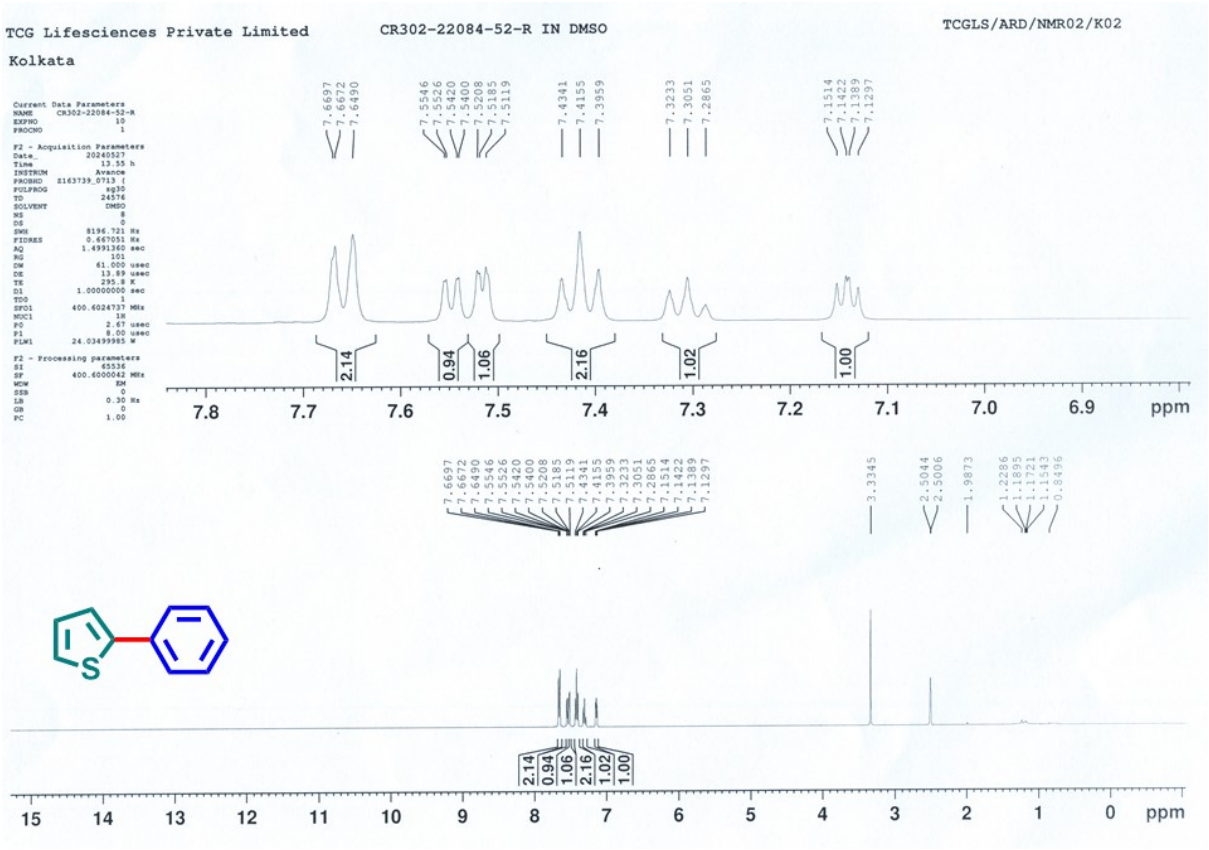


Figure S74: ^{1}H NMR spectrum of **9a**.

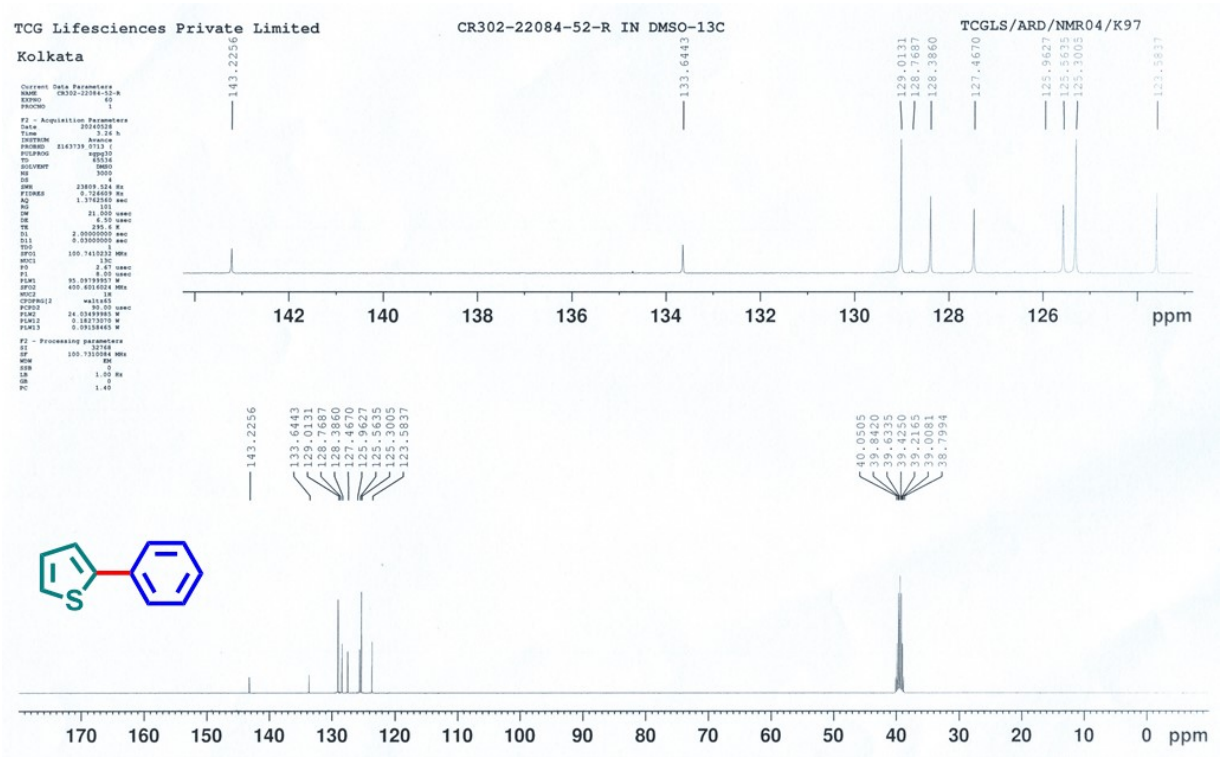


Figure S75: ^{13}C {^{1}H} NMR spectrum of **9a**.

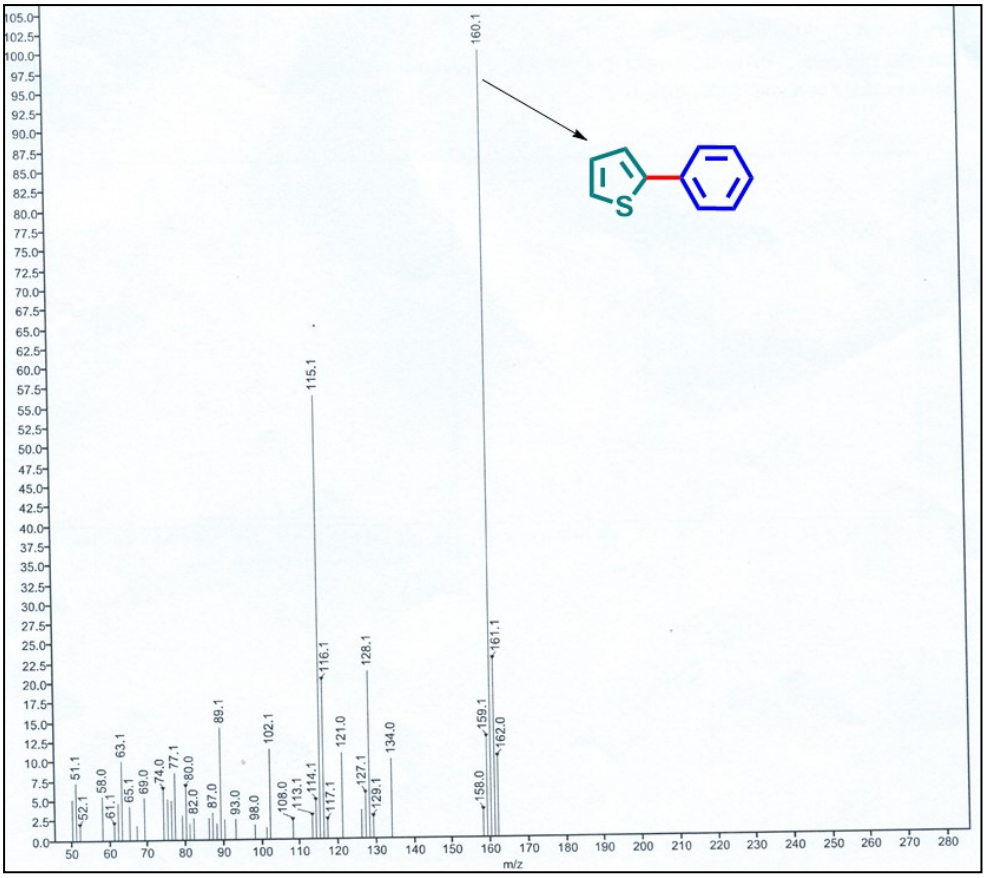


Figure S76: GC-MS spectrum of **9a**.

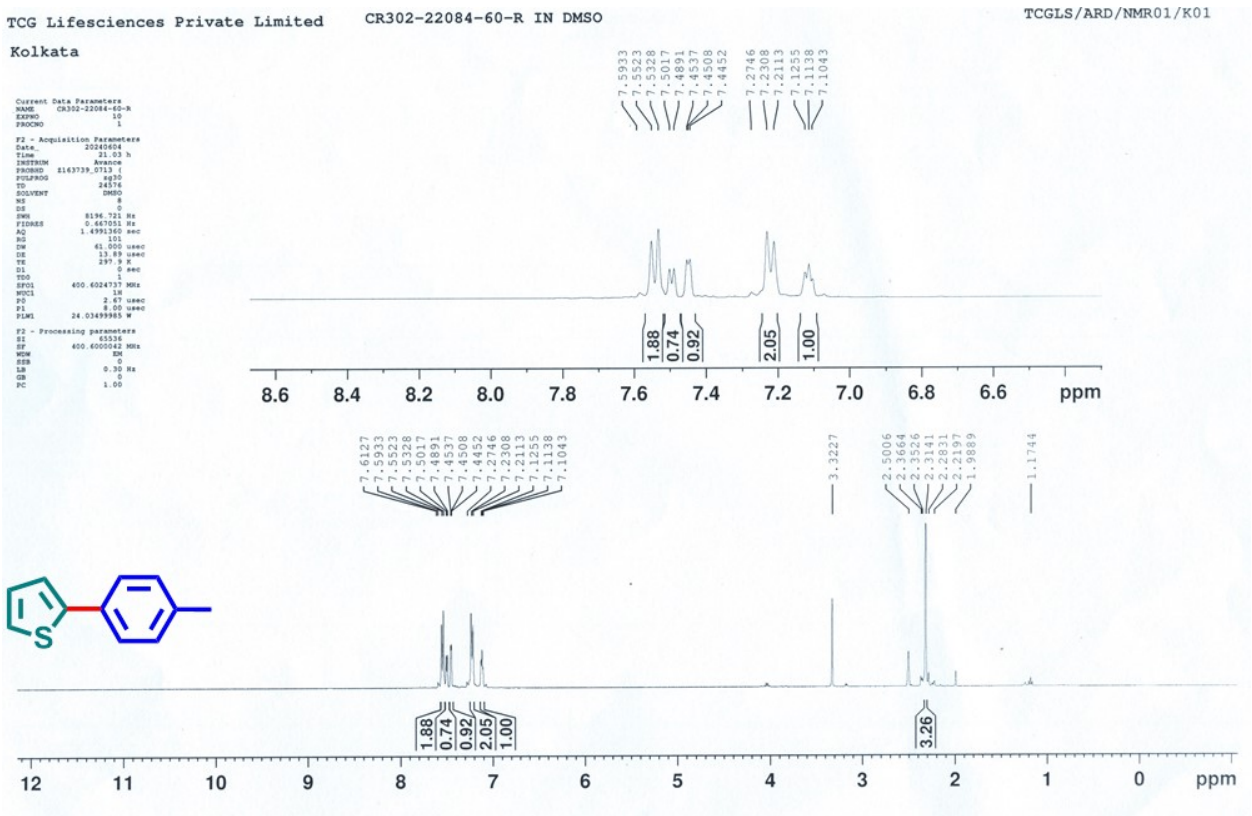


Figure S77: ^{1}H NMR spectrum of **9b**.

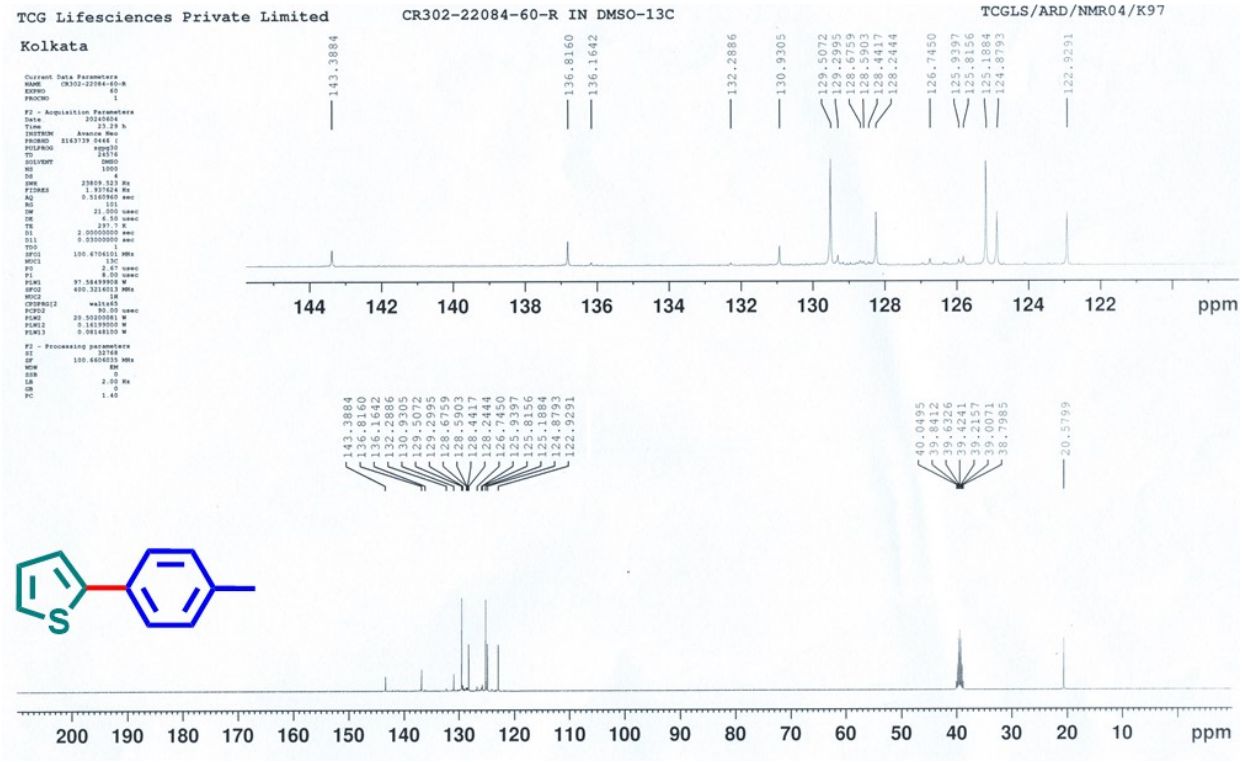


Figure S78: ^{13}C {^{1}H} NMR spectrum of **9b**.

Figure S79: GC-MS spectrum of **9b**.

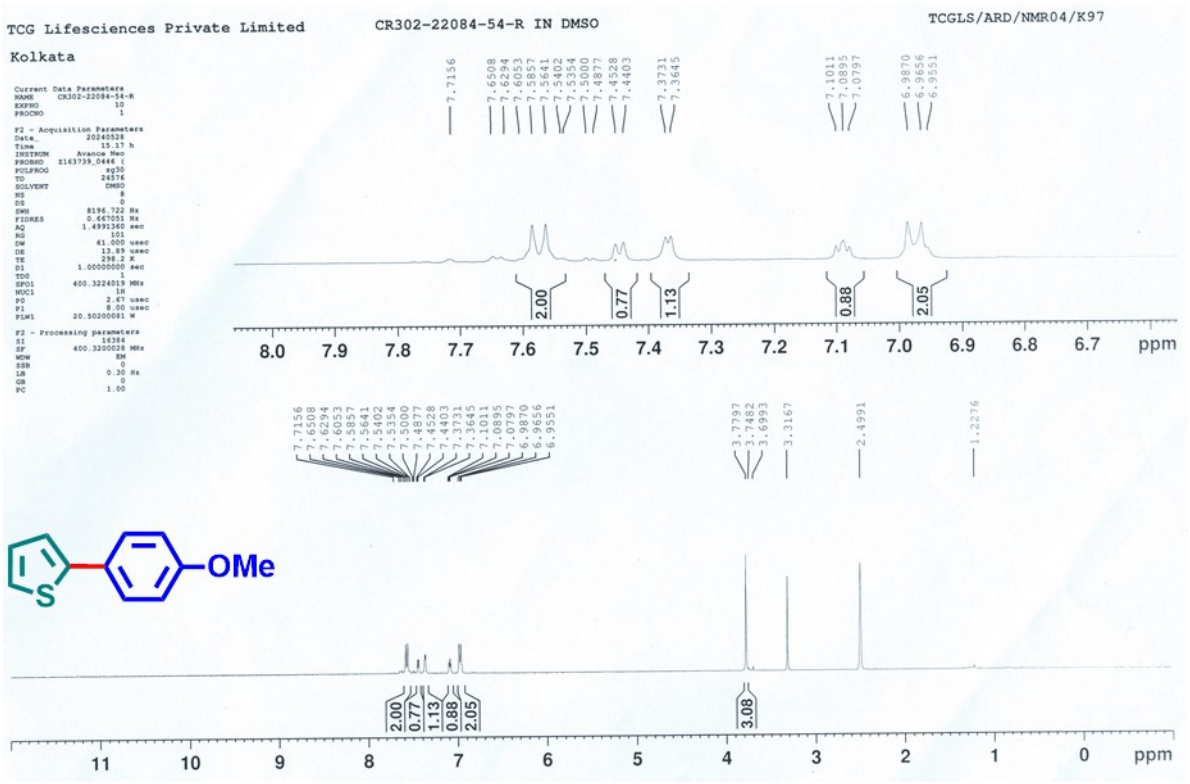


Figure S80: ^{1}H NMR spectrum of **9c**.

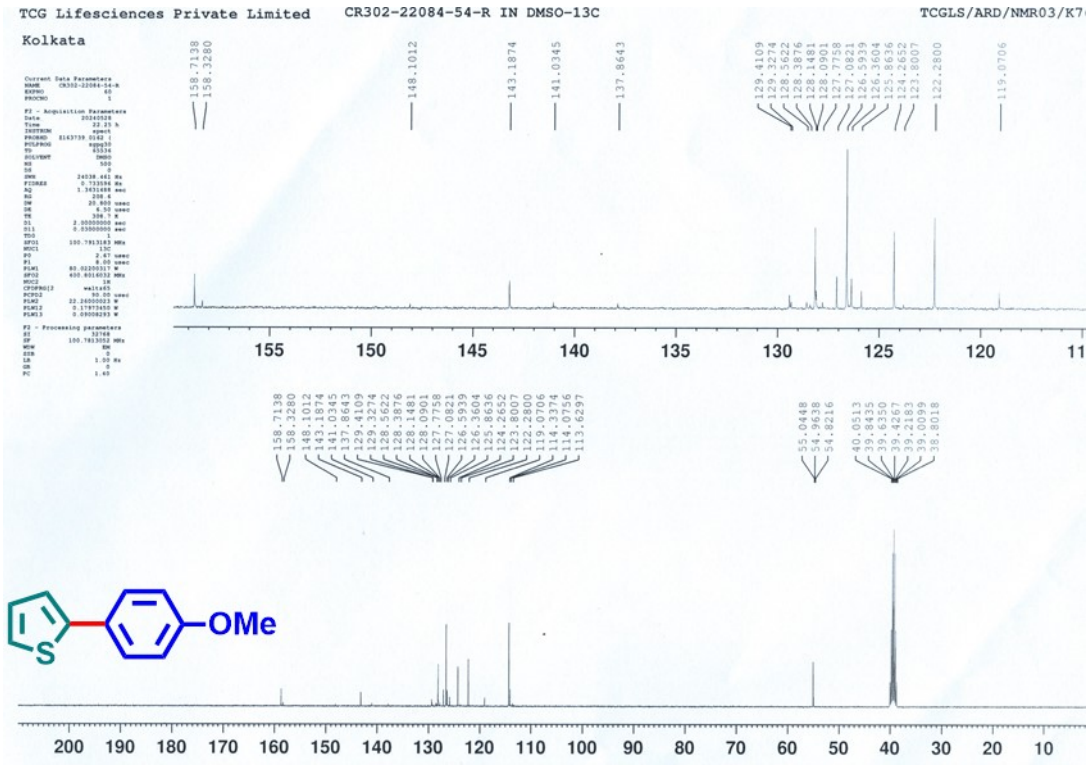


Figure S81: ^{13}C {^{1}H} NMR spectrum of **9c**.

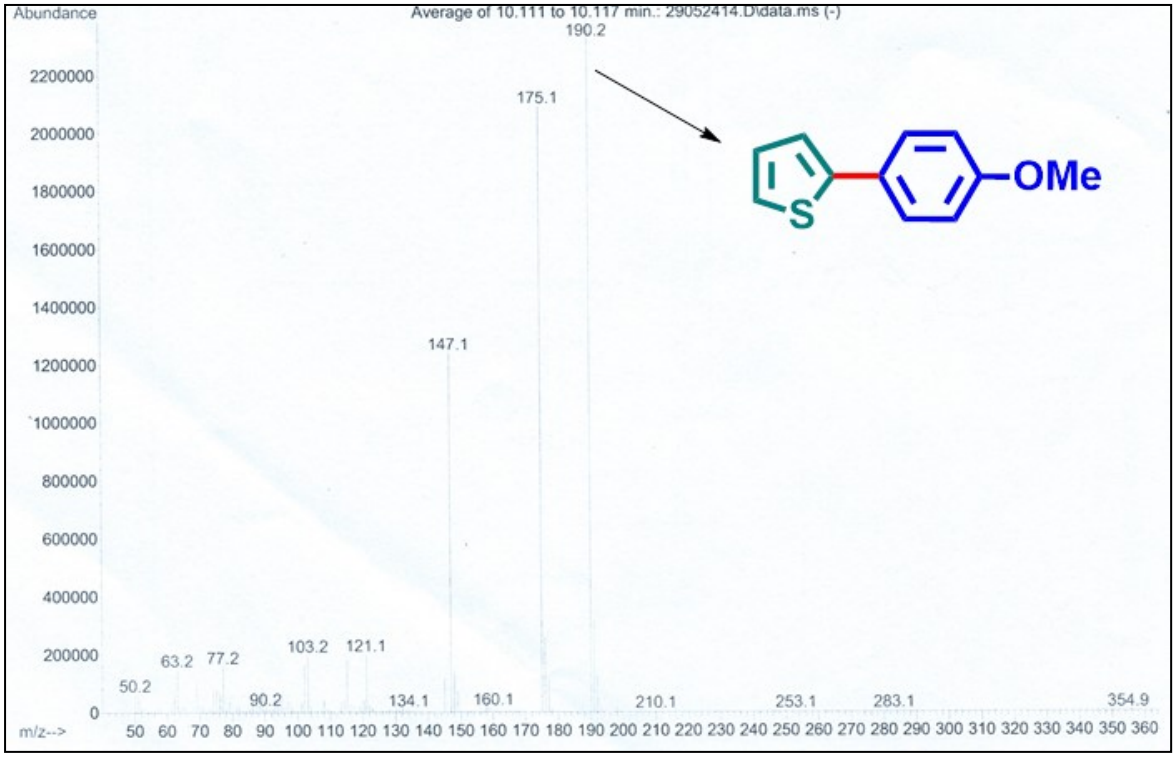


Figure S82: GC-MS spectrum of **9c**.

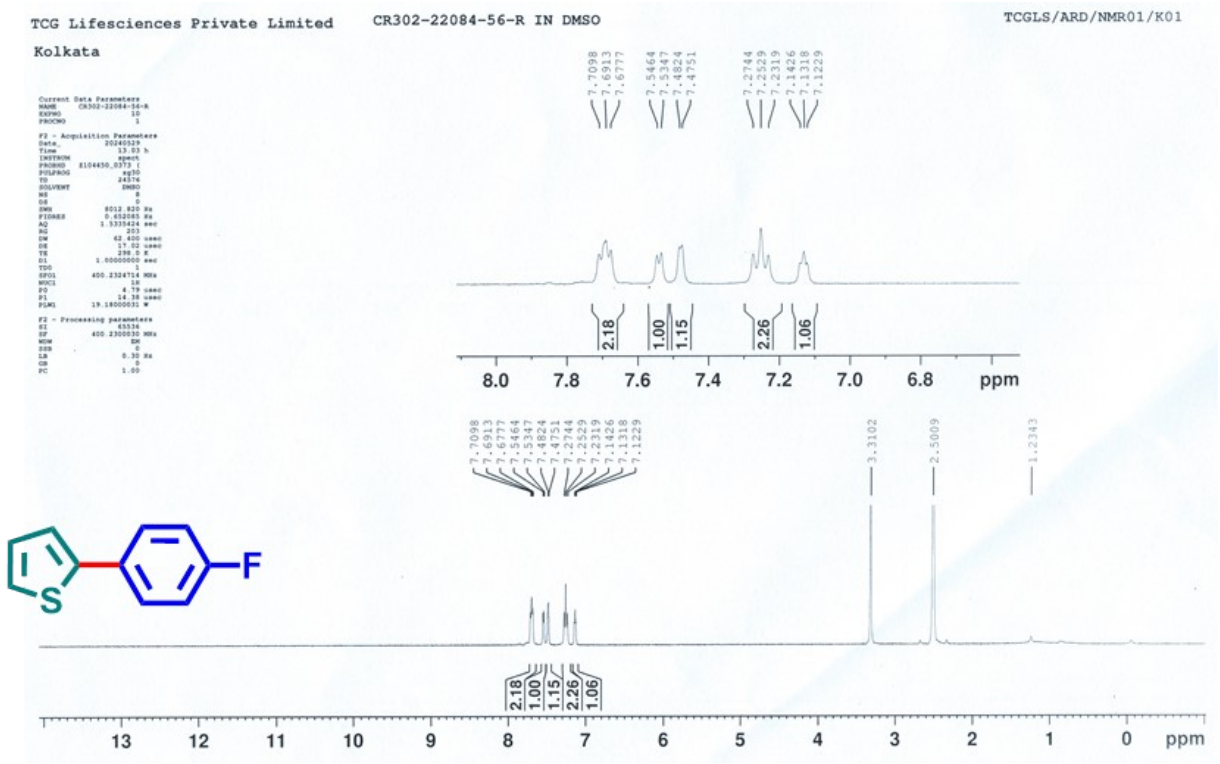


Figure S83: ^{1}H NMR spectrum of **9d**.

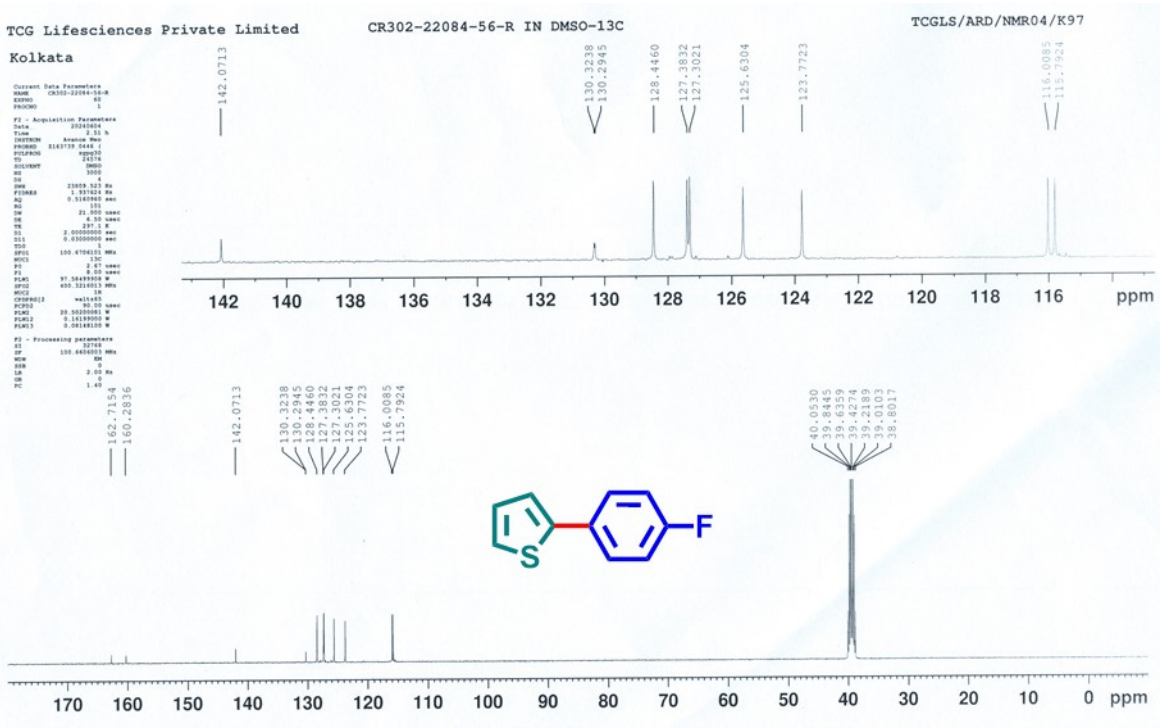


Figure S84: ^{13}C {^{1}H} NMR spectrum of **9d**.

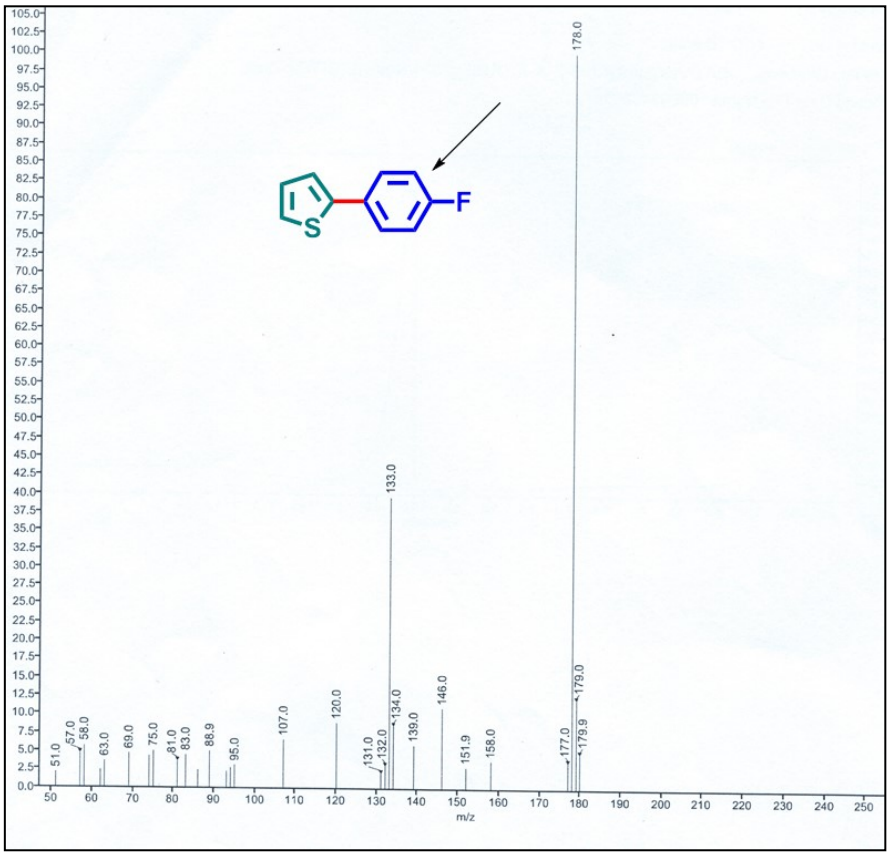


Figure S85: GC-MS spectrum of **9d**.

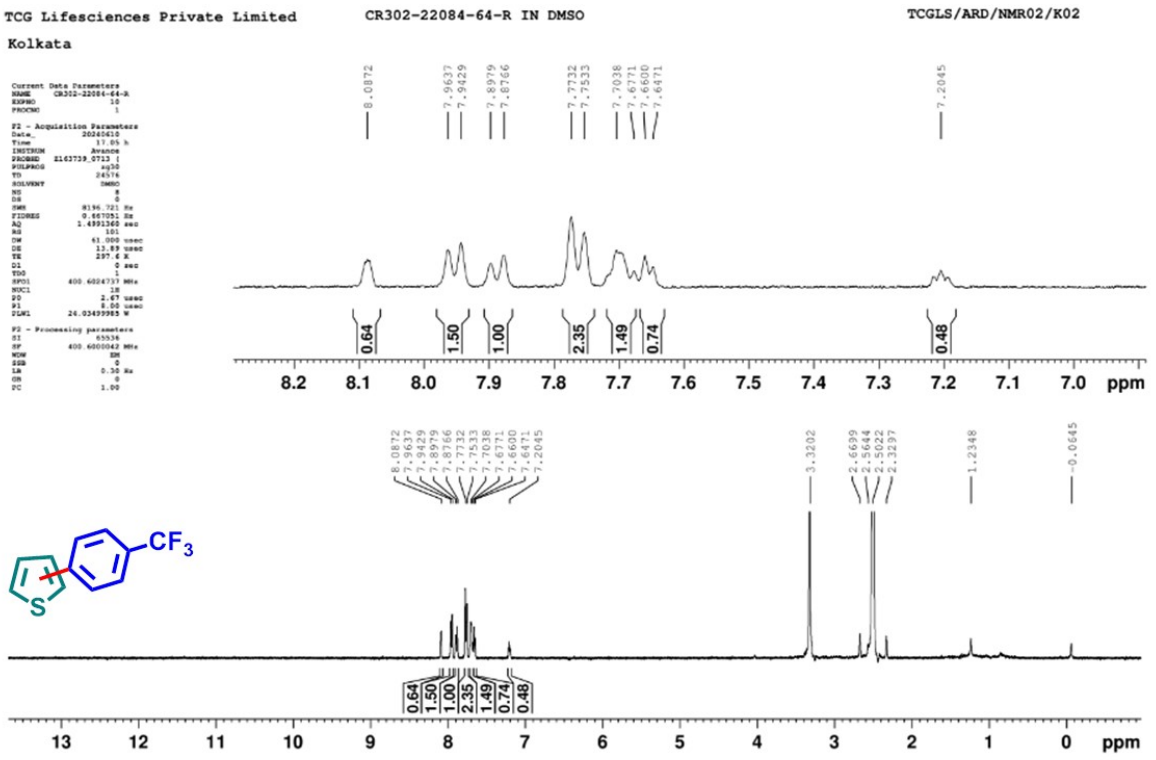


Figure S86: ^{1}H NMR spectrum of **9e**.

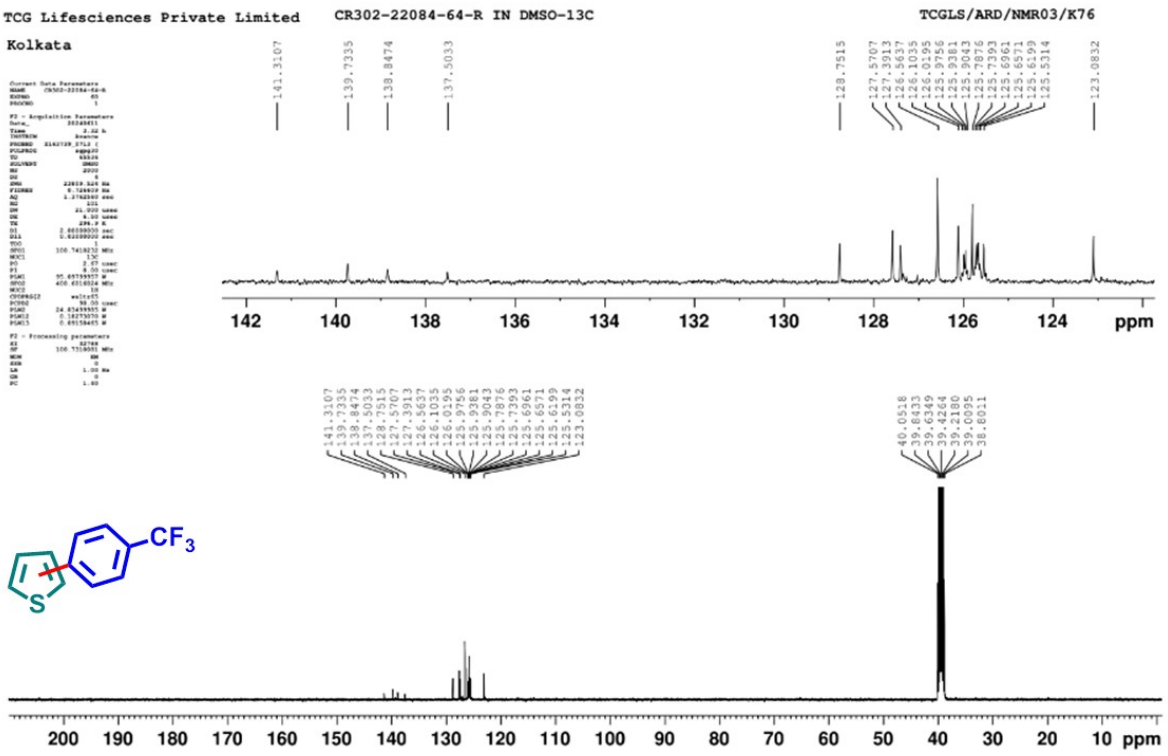


Figure S87: ^{13}C {^{1}H} NMR spectrum of **9e**.

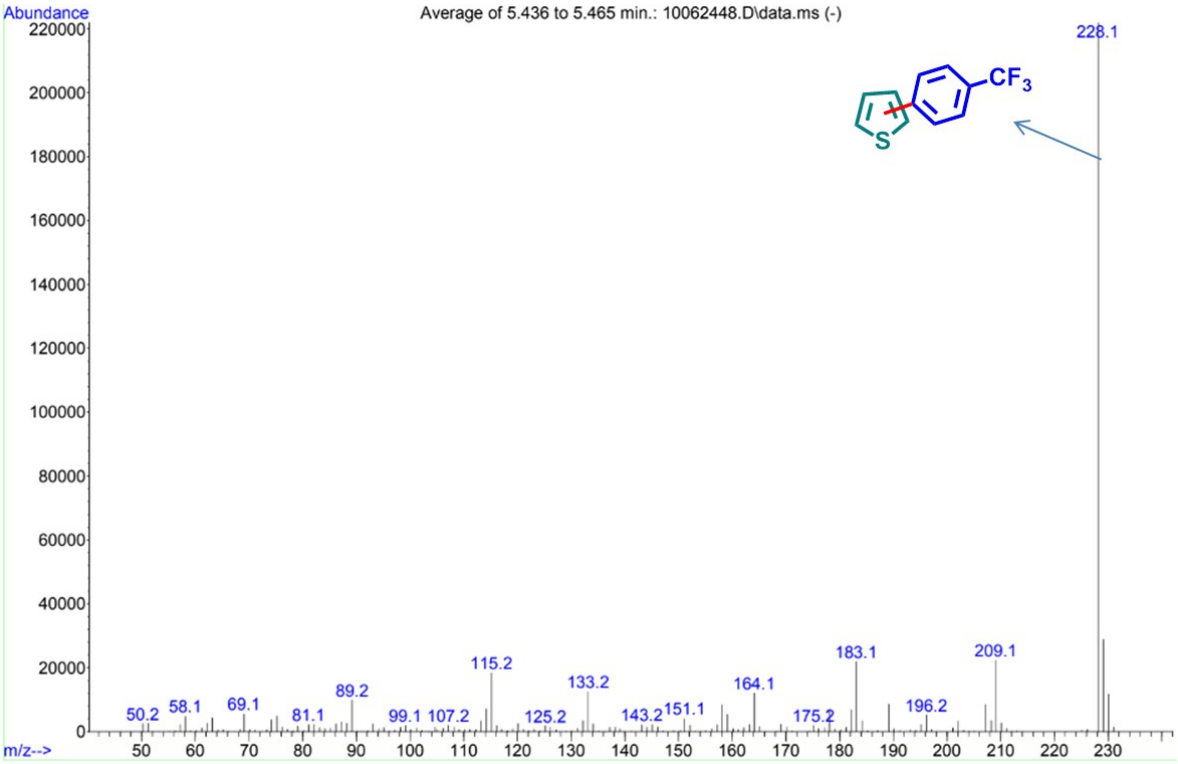


Figure S88: GC-MS spectrum of **9e**.

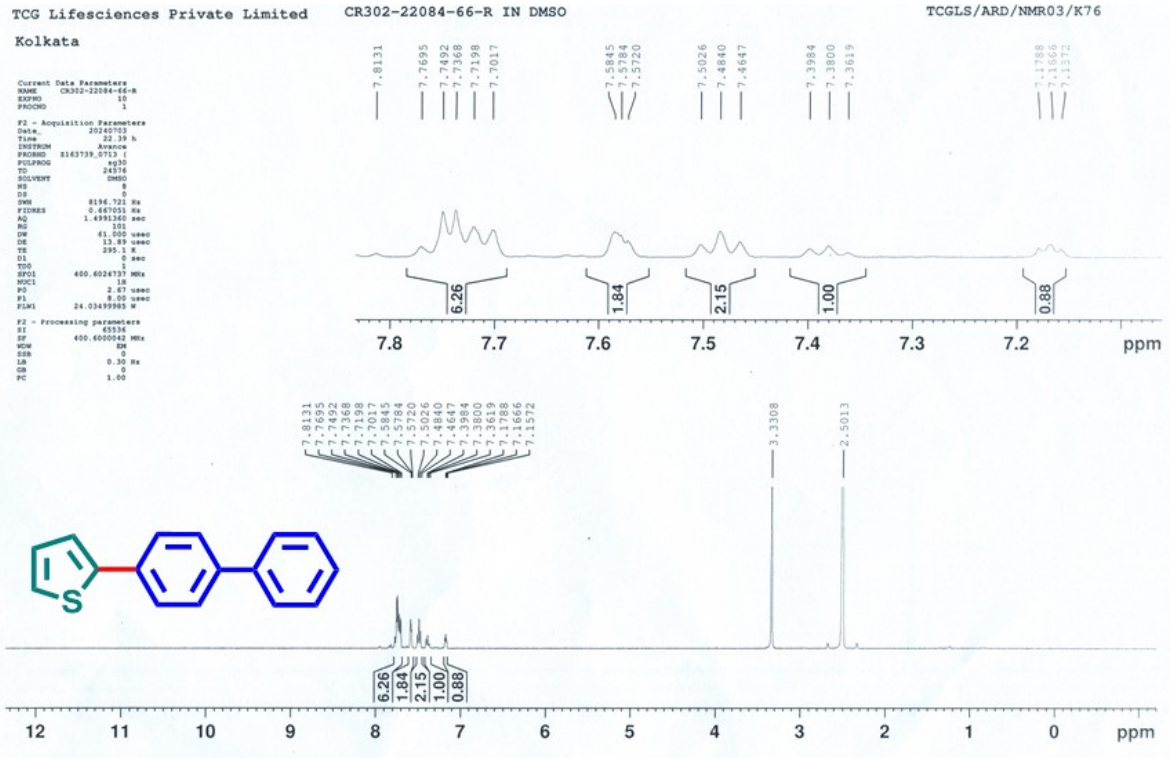


Figure S89: ^{1}H NMR spectrum of **9f**.

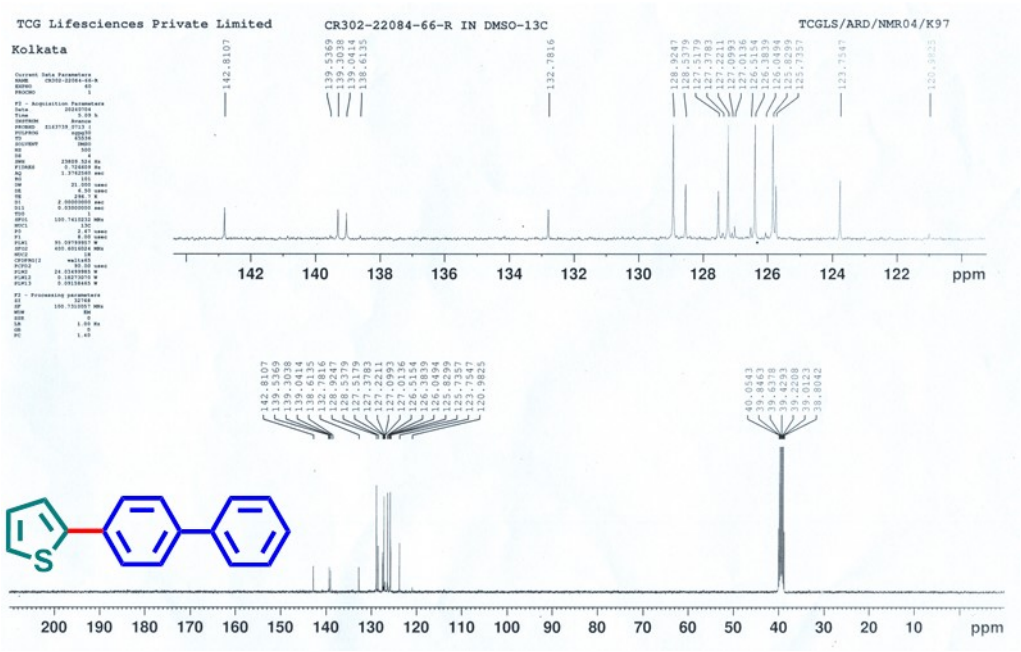


Figure S90: ^{13}C {^{1}H} NMR spectrum of **9f**.

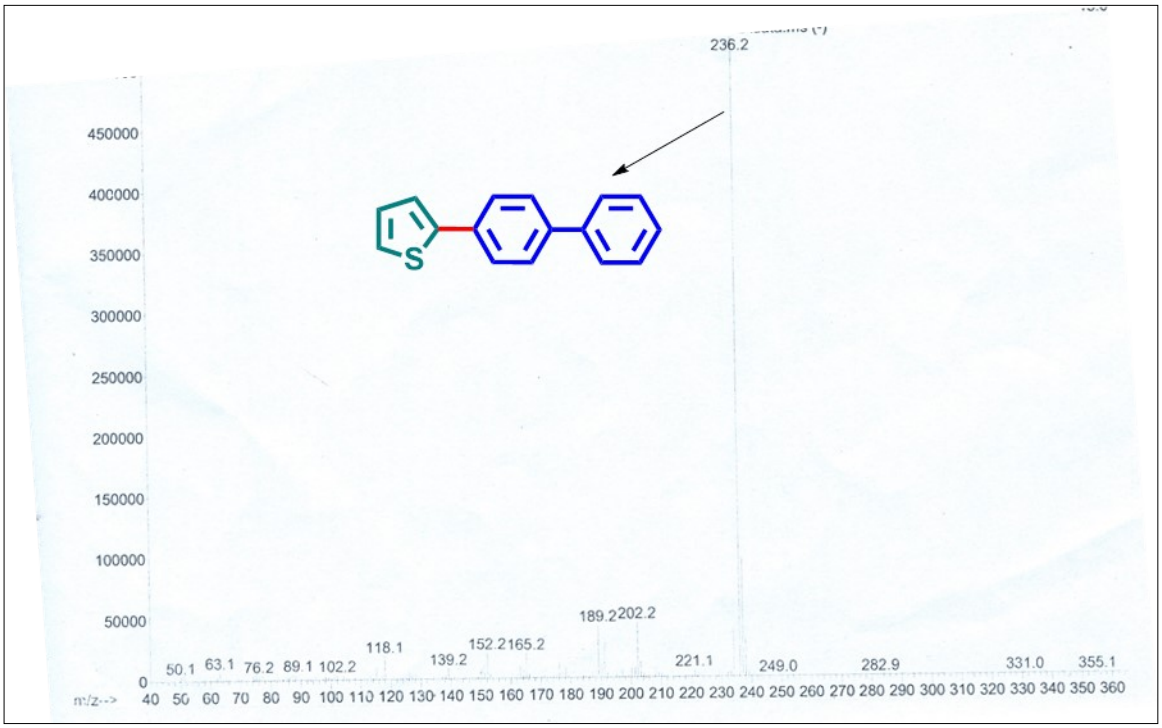


Figure S91: GC-MS spectrum of **9f**.

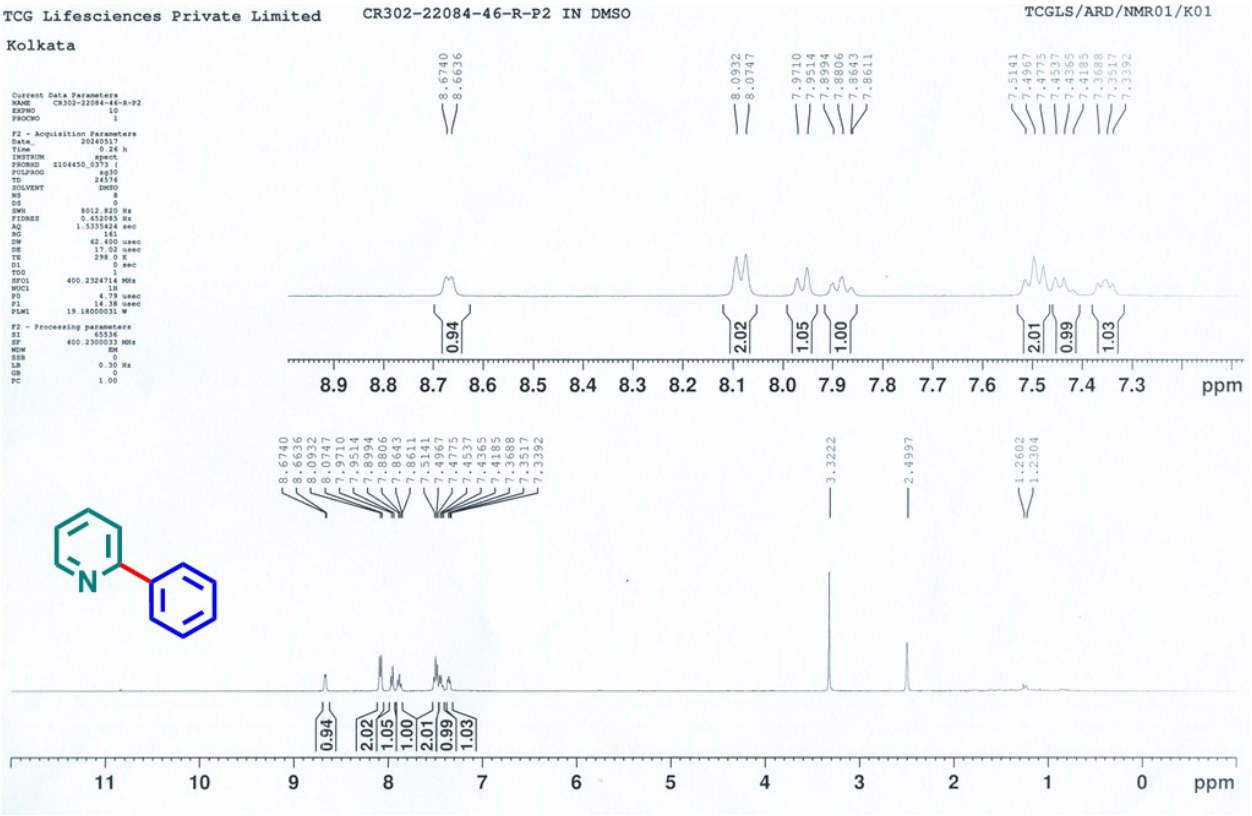


Figure S92: ^{1}H NMR spectrum of **9g**.

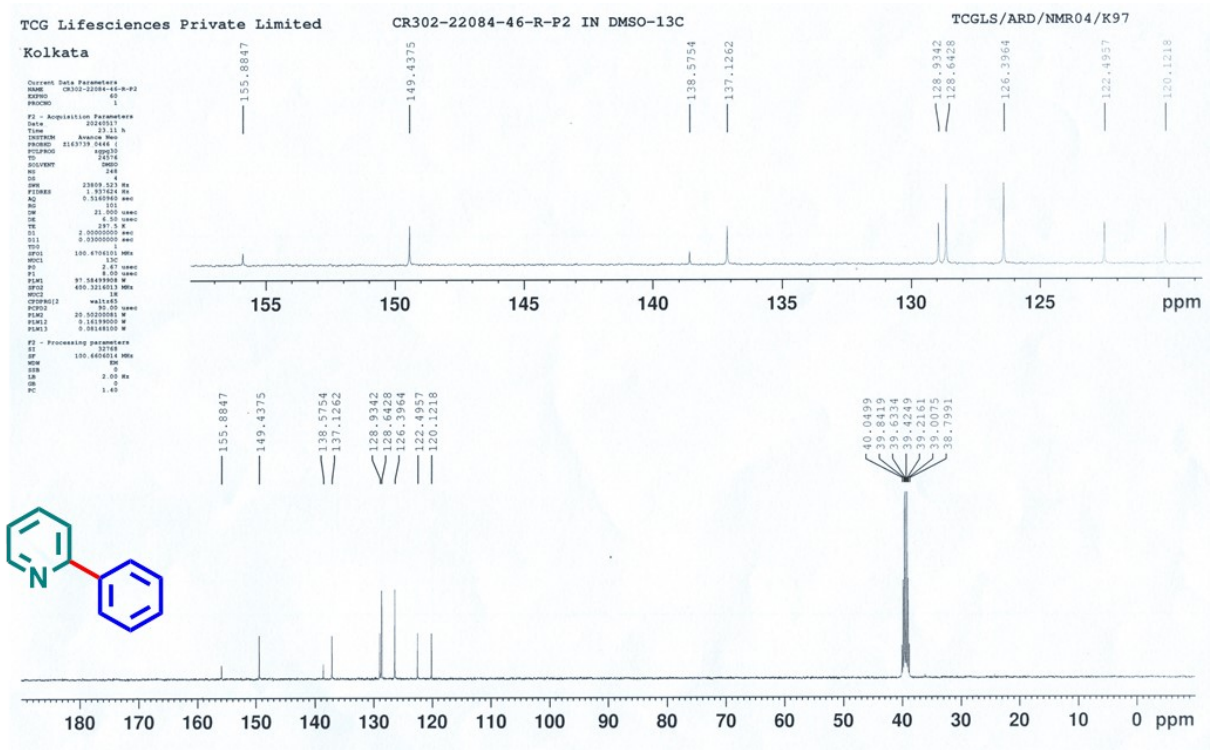


Figure S93: ^{13}C {^{1}H} NMR spectrum of **9g**.

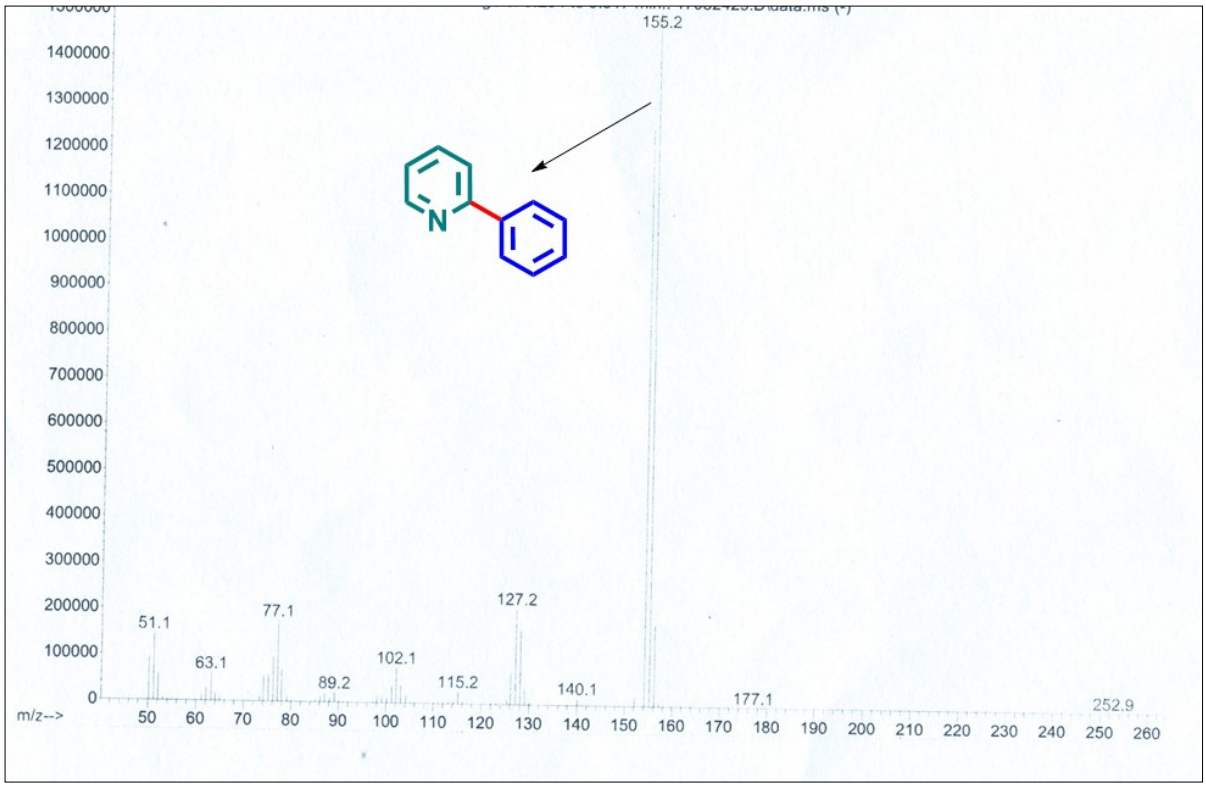


Figure S94: GC-MS spectrum of **9g**.

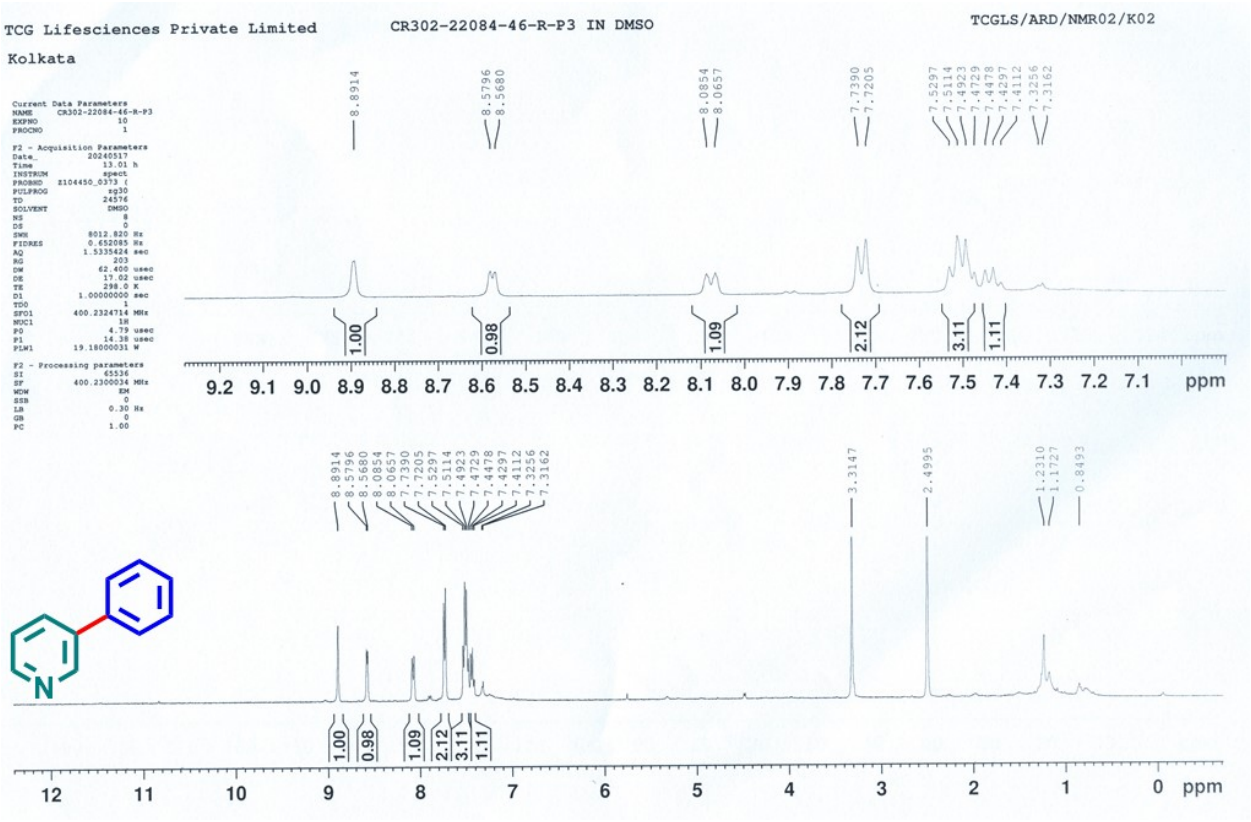


Figure S95: ^{1}H NMR spectrum of **9g**.

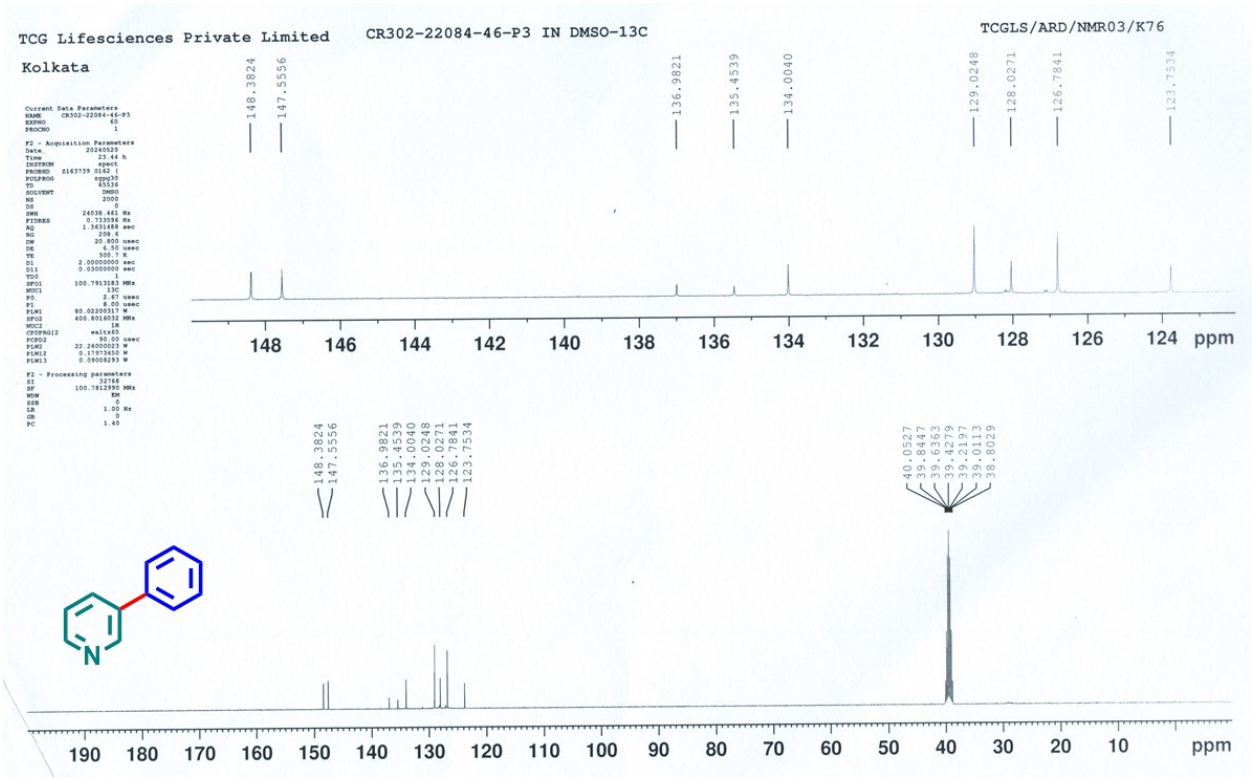


Figure S96: ^{13}C {^{1}H} NMR spectrum of **9g**.

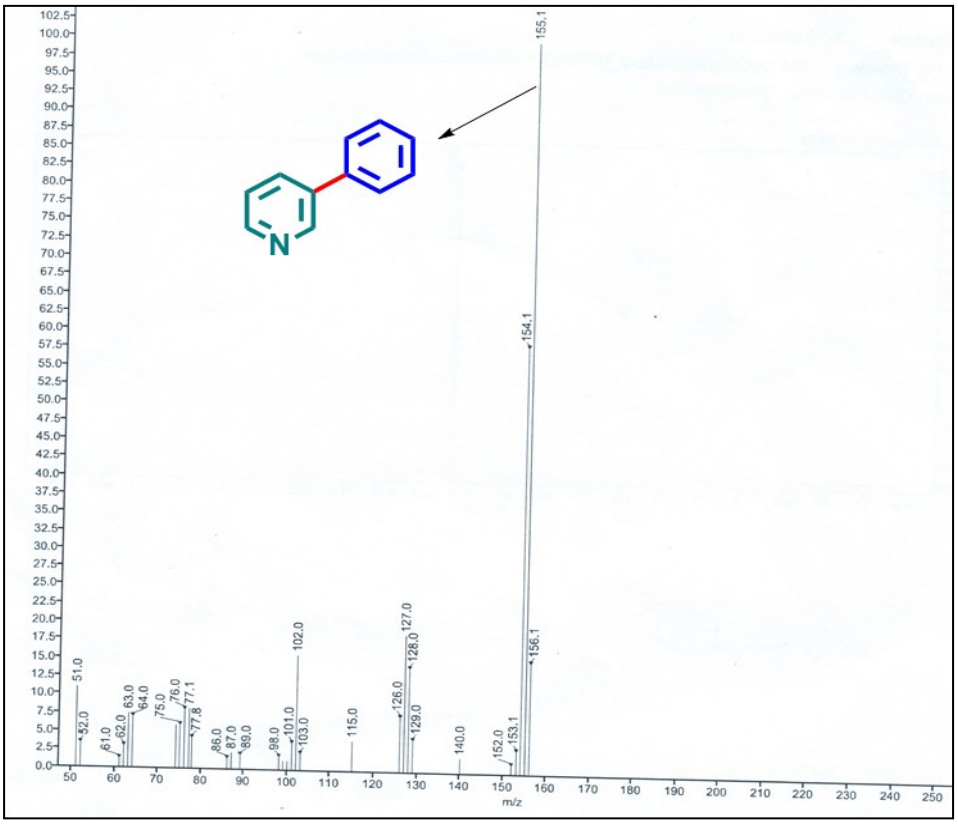


Figure S97: GC-MS spectrum of **9g**.

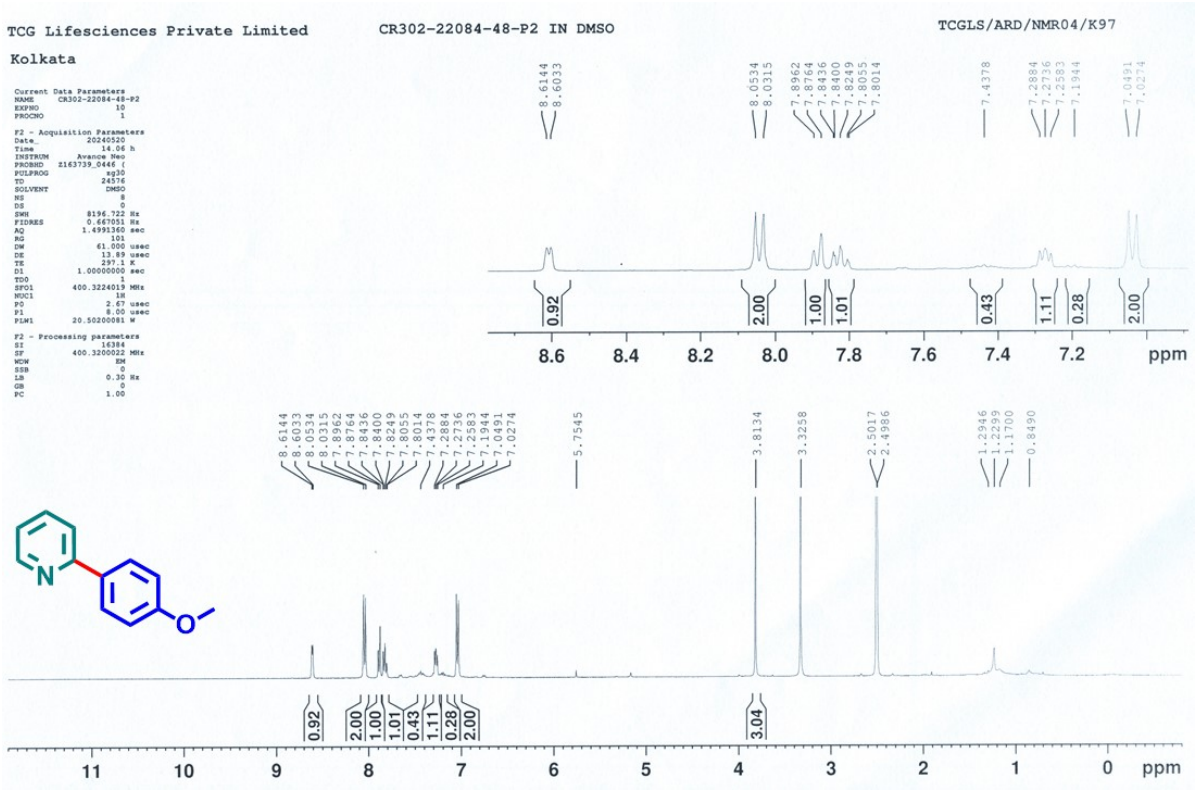


Figure S98: ^{1}H NMR spectrum of **9h**.

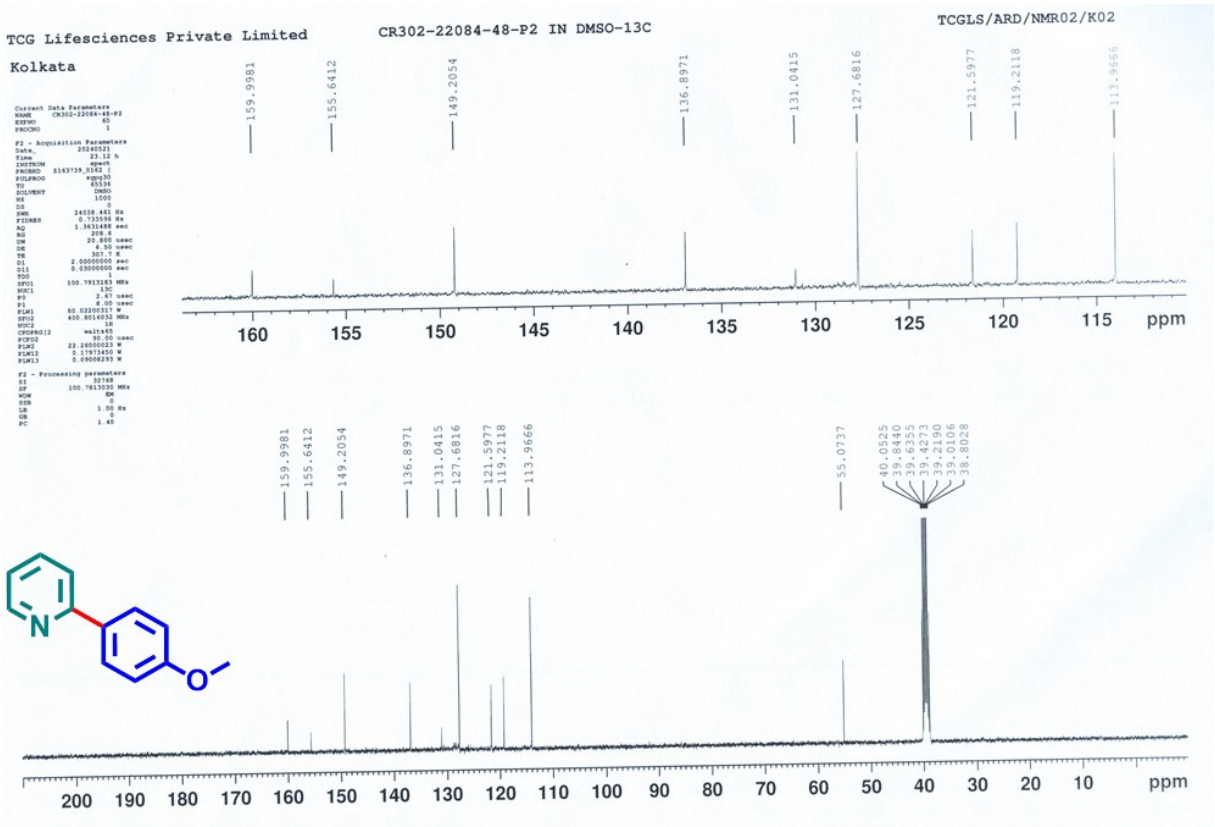


Figure S99: ^{13}C {^{1}H} NMR spectrum of **9h**.

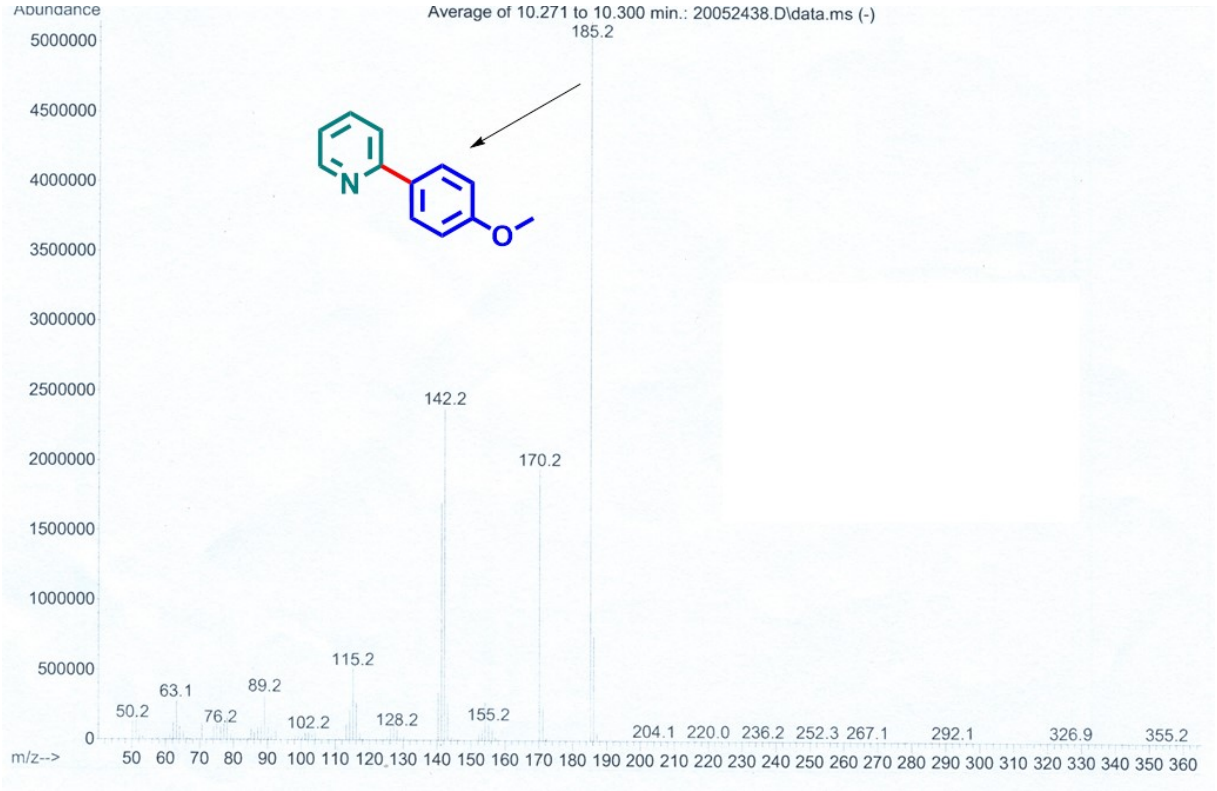


Figure S100: GC-MS spectrum of **9h**.

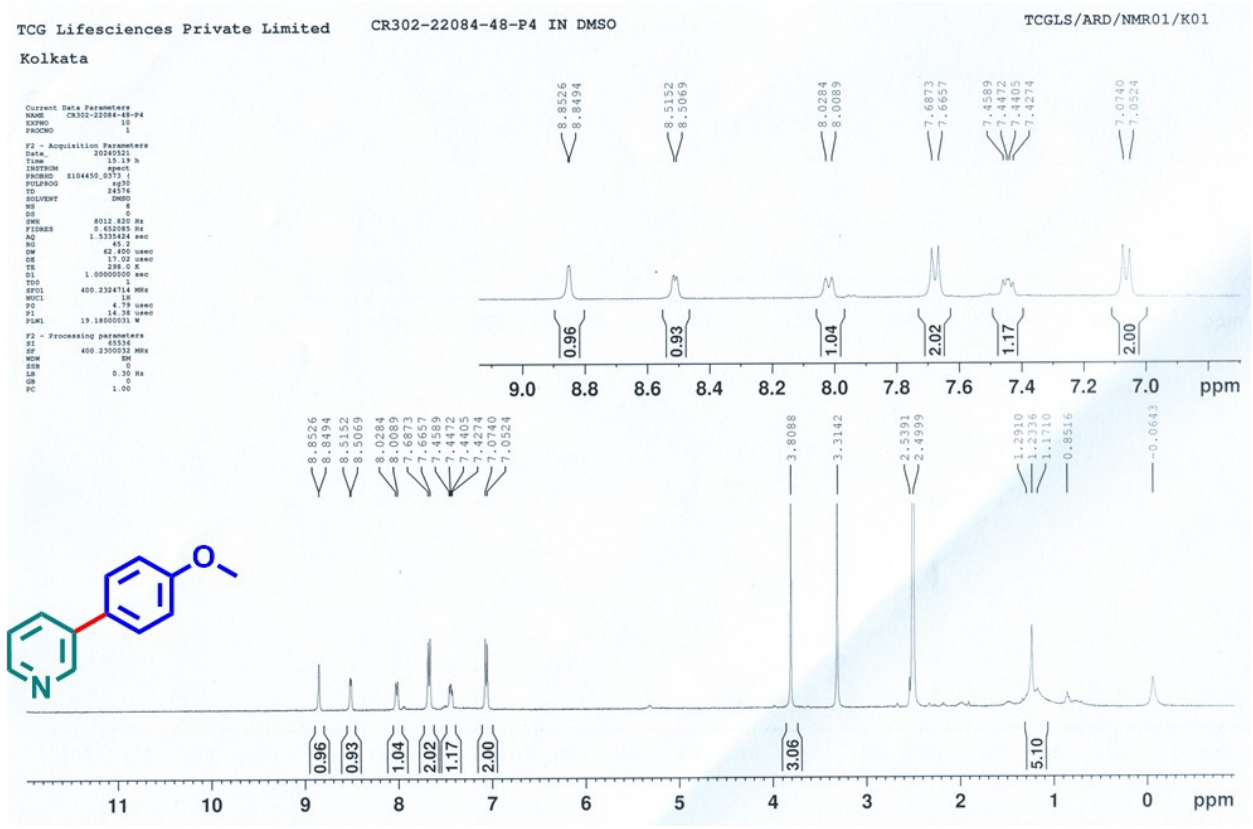


Figure S101: ^{1}H NMR spectrum of **9h**.

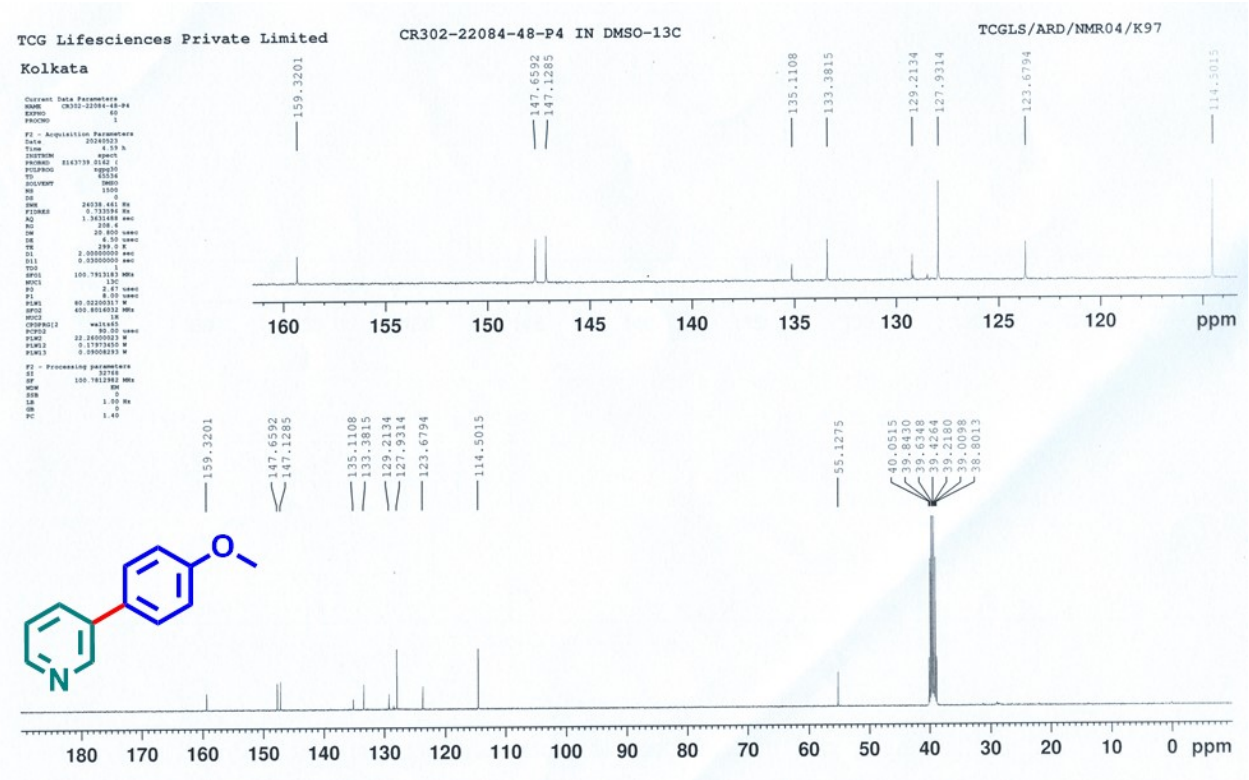


Figure S102: ^{13}C {^{1}H} NMR spectrum of **9h**.

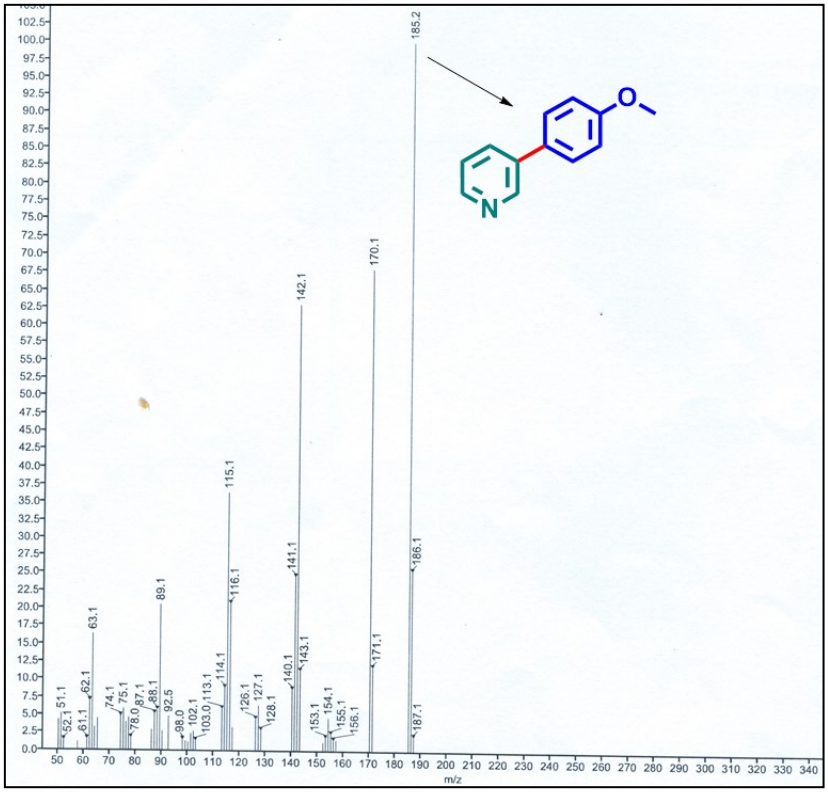


Figure S103: GC-MS spectrum of **9h**.

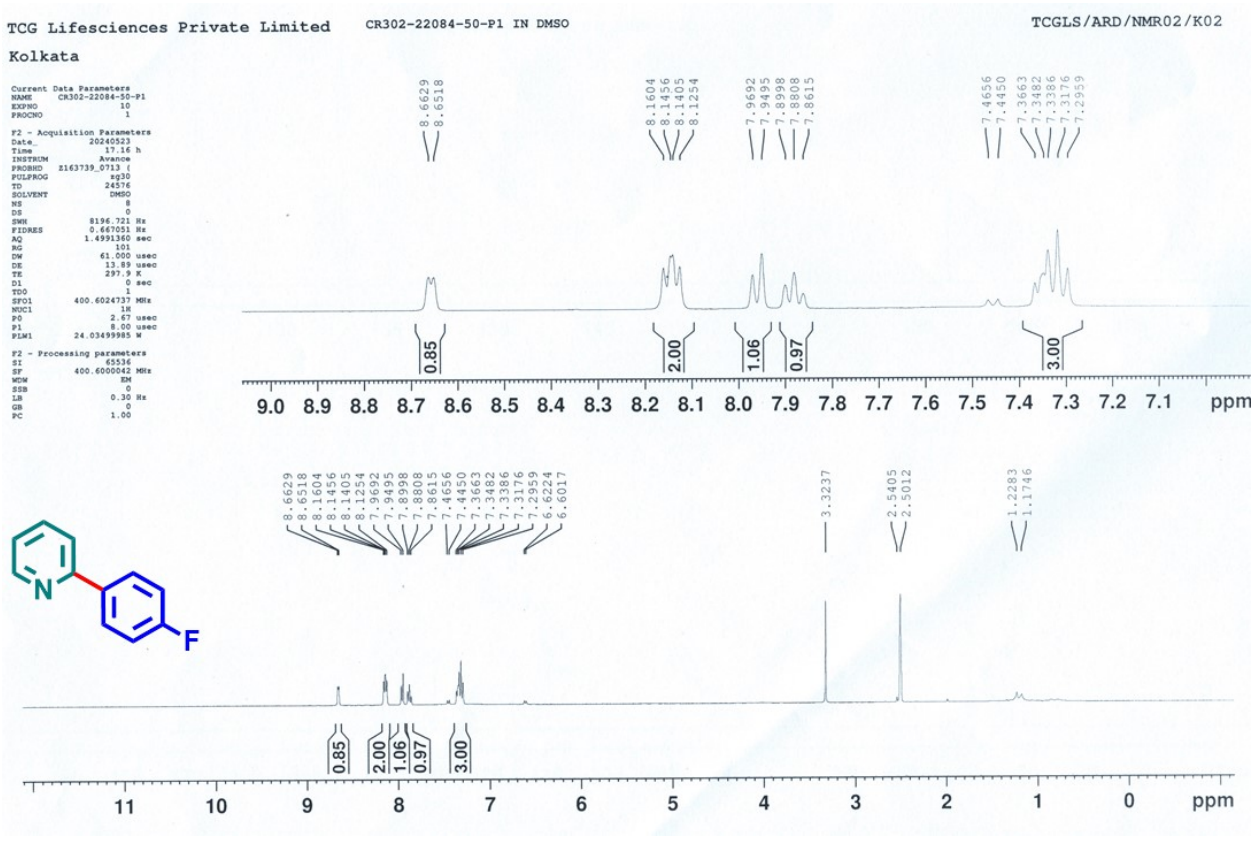


Figure S104: ^{1}H NMR spectrum of **9i**.

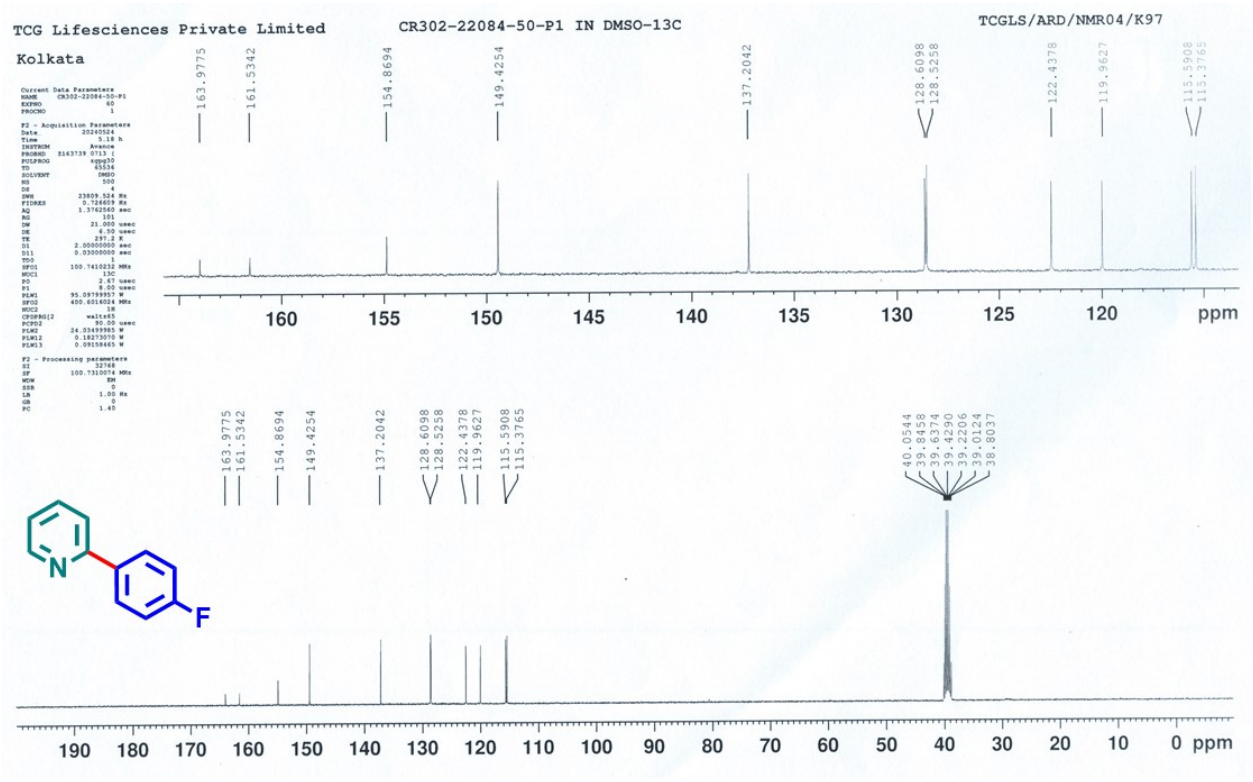


Figure S105: ^{13}C {^{1}H} NMR spectrum of **9i**.

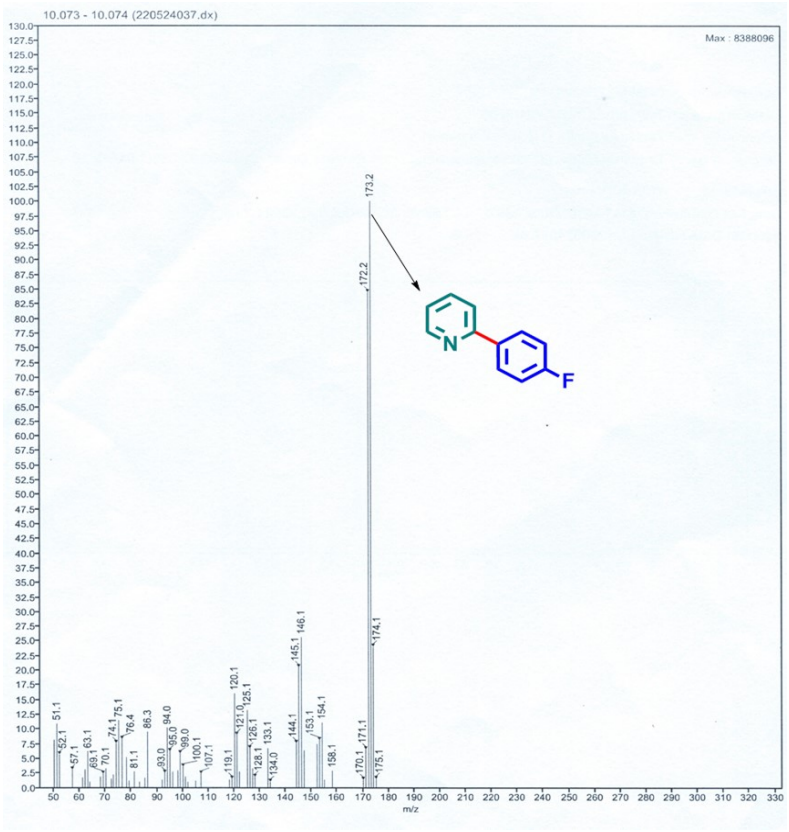


Figure S106: GC-MS spectrum of **9i**.

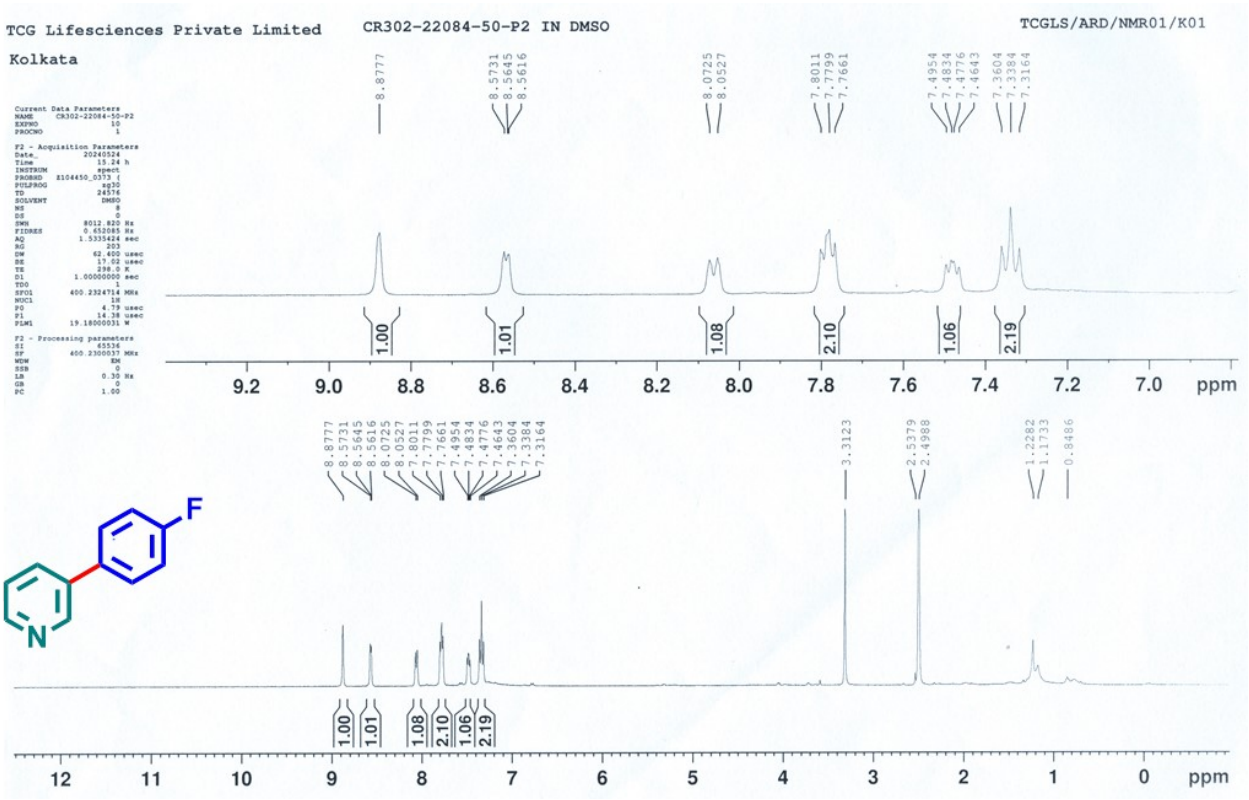


Figure S107: ^{1}H NMR spectrum of **9i**.

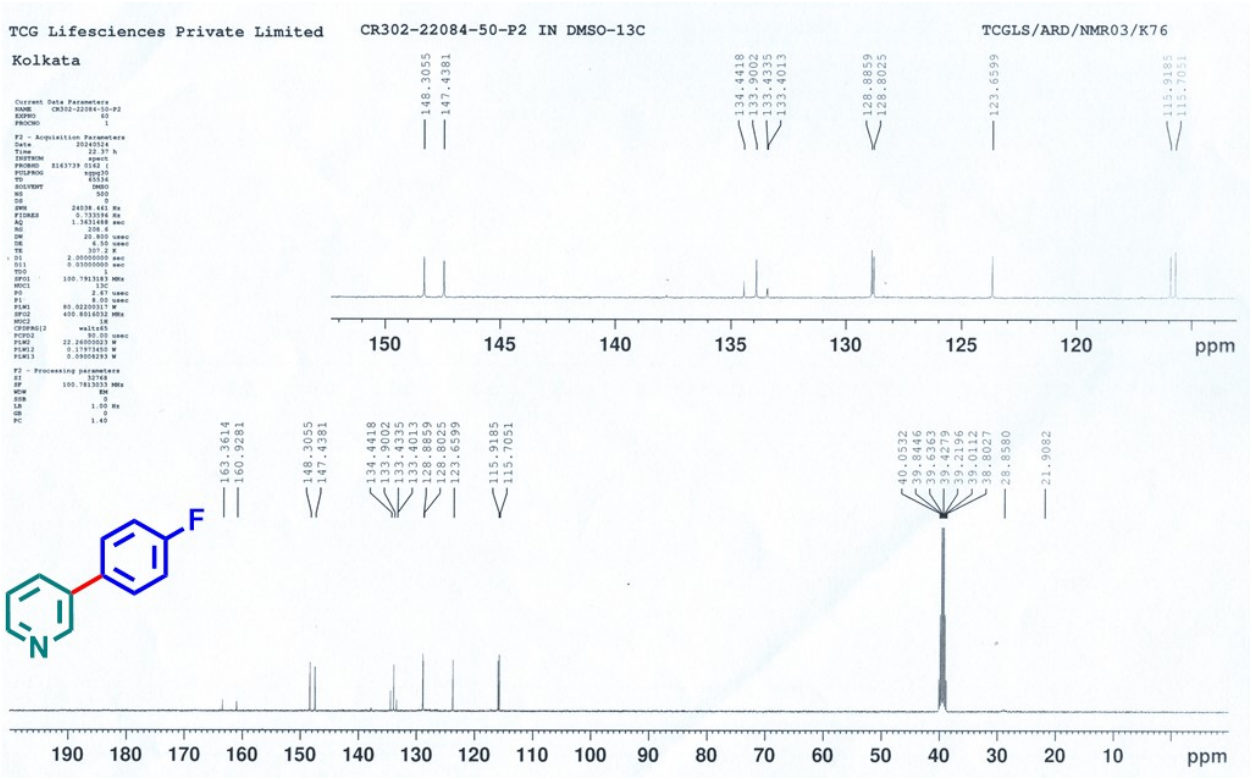


Figure S108: ^{13}C {^{1}H} NMR spectrum of **9i**.

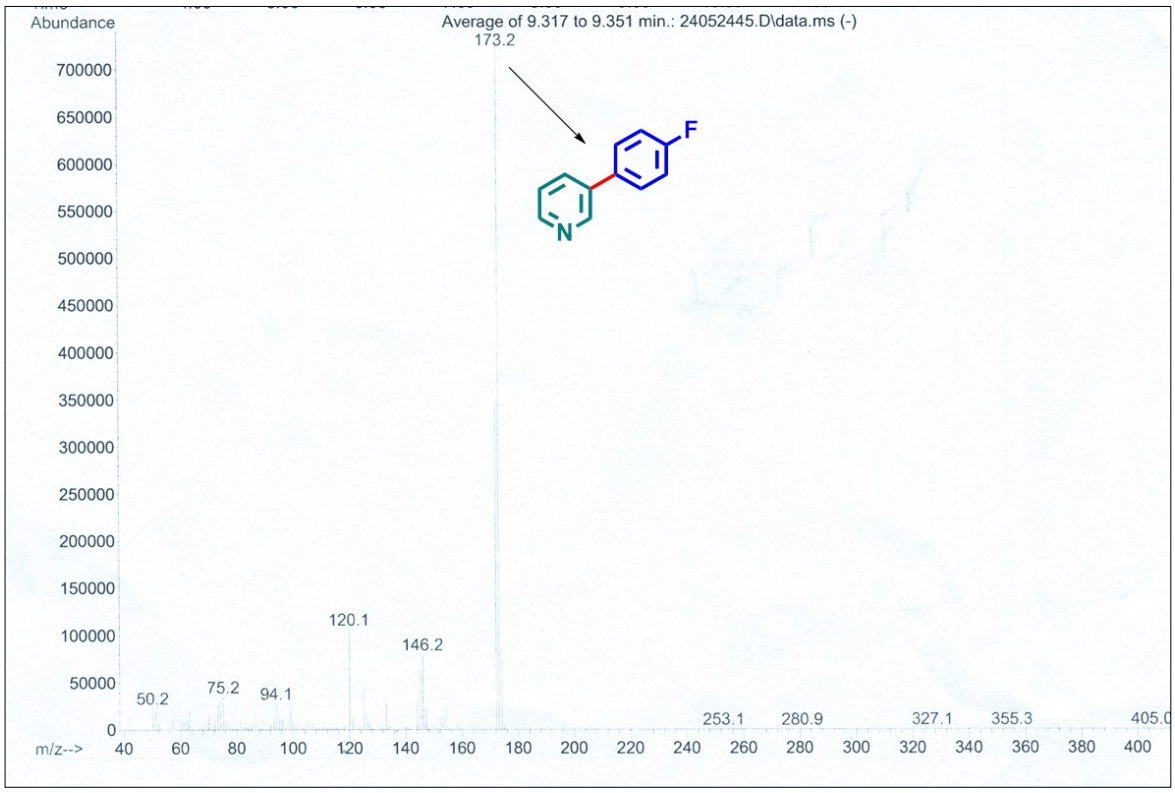


Figure S109: GC-MS spectrum of **9i**.

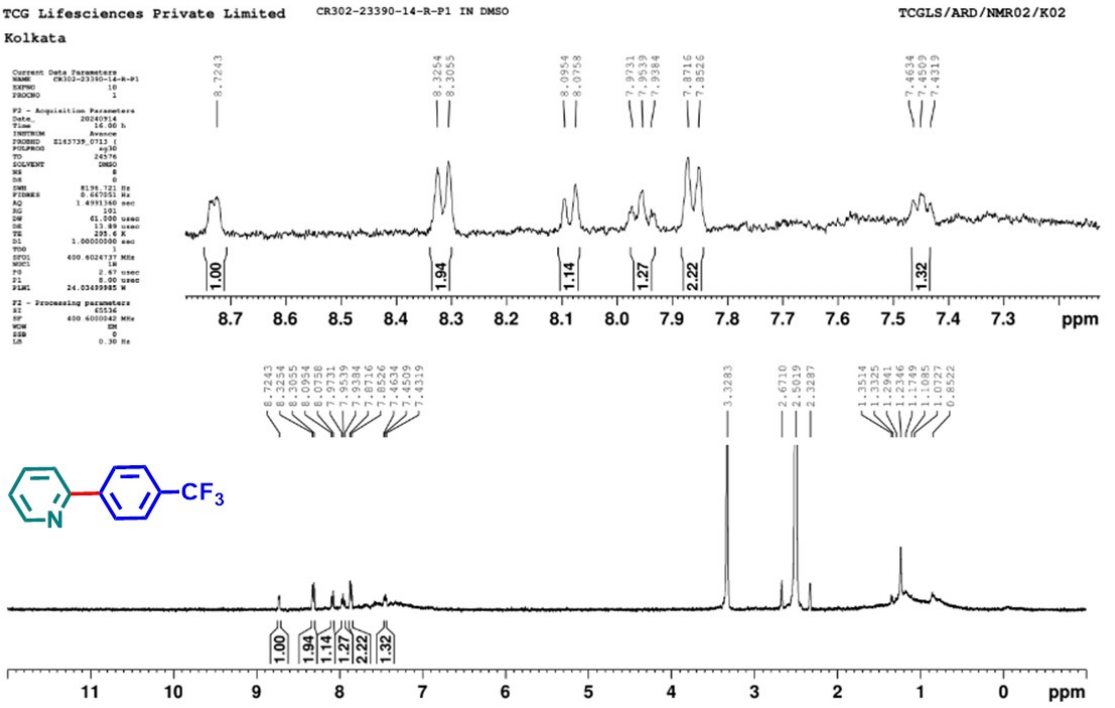


Figure S110: ^{1}H NMR spectrum of **9j**.

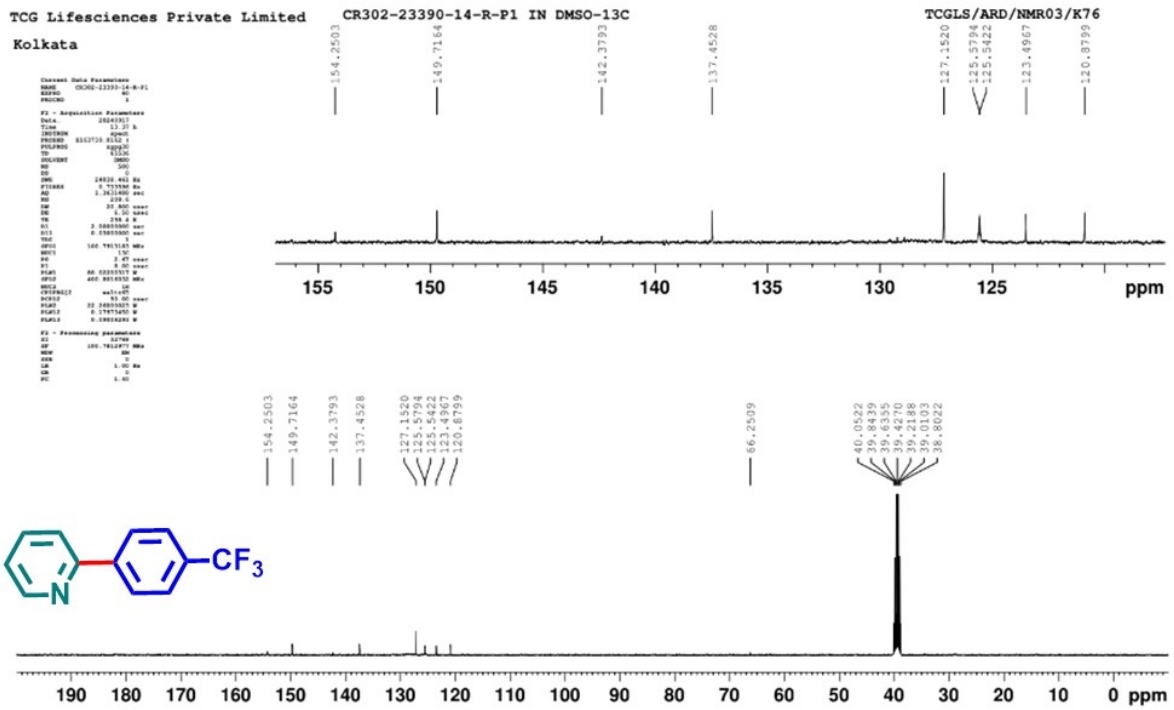


Figure S111: ^{13}C {^{1}H} NMR spectrum of **9j**.

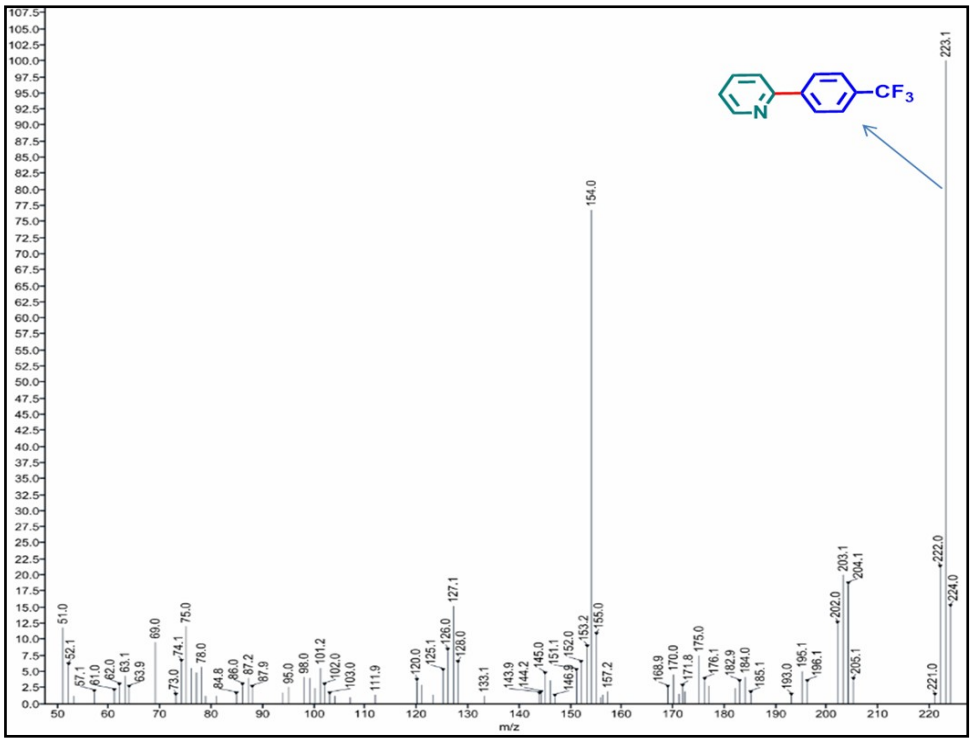


Figure S112: GC-MS spectrum of **9j**.

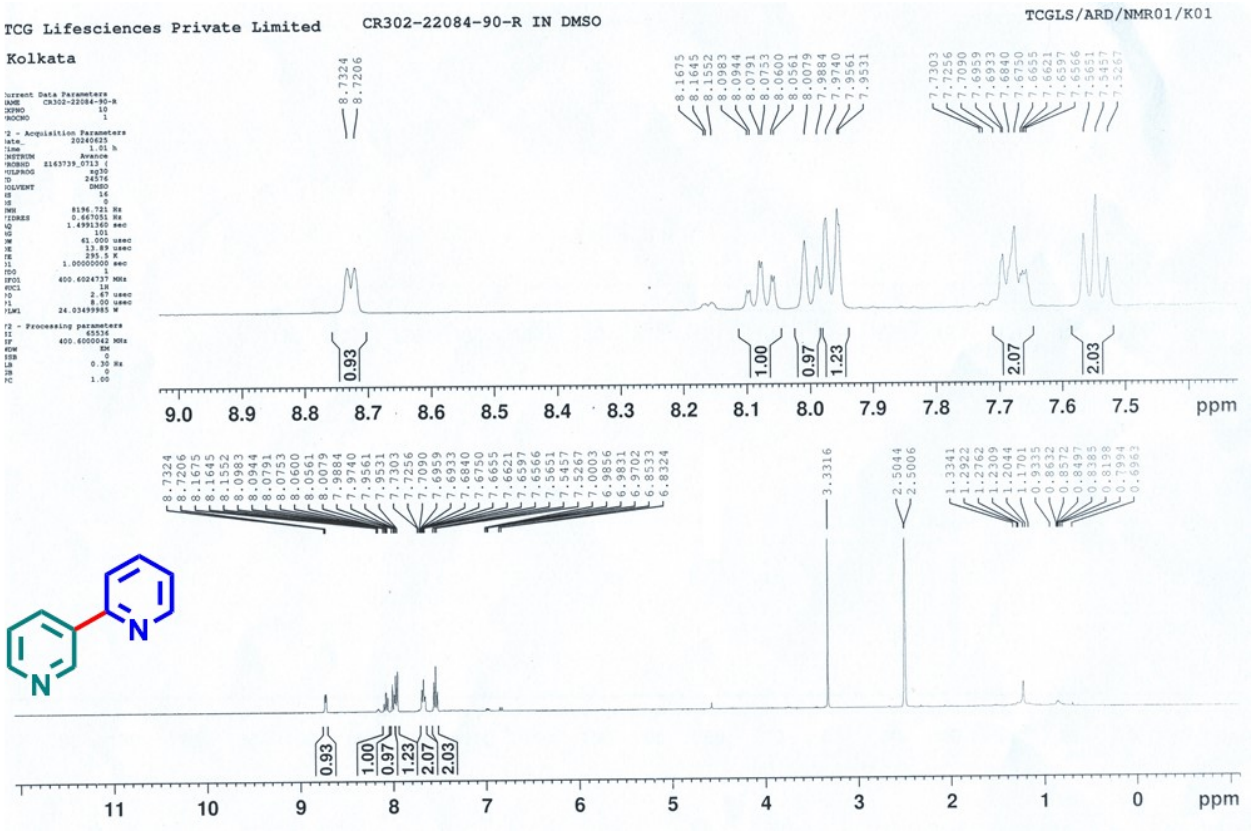


Figure S113: ^{1}H NMR spectrum of **9k**.

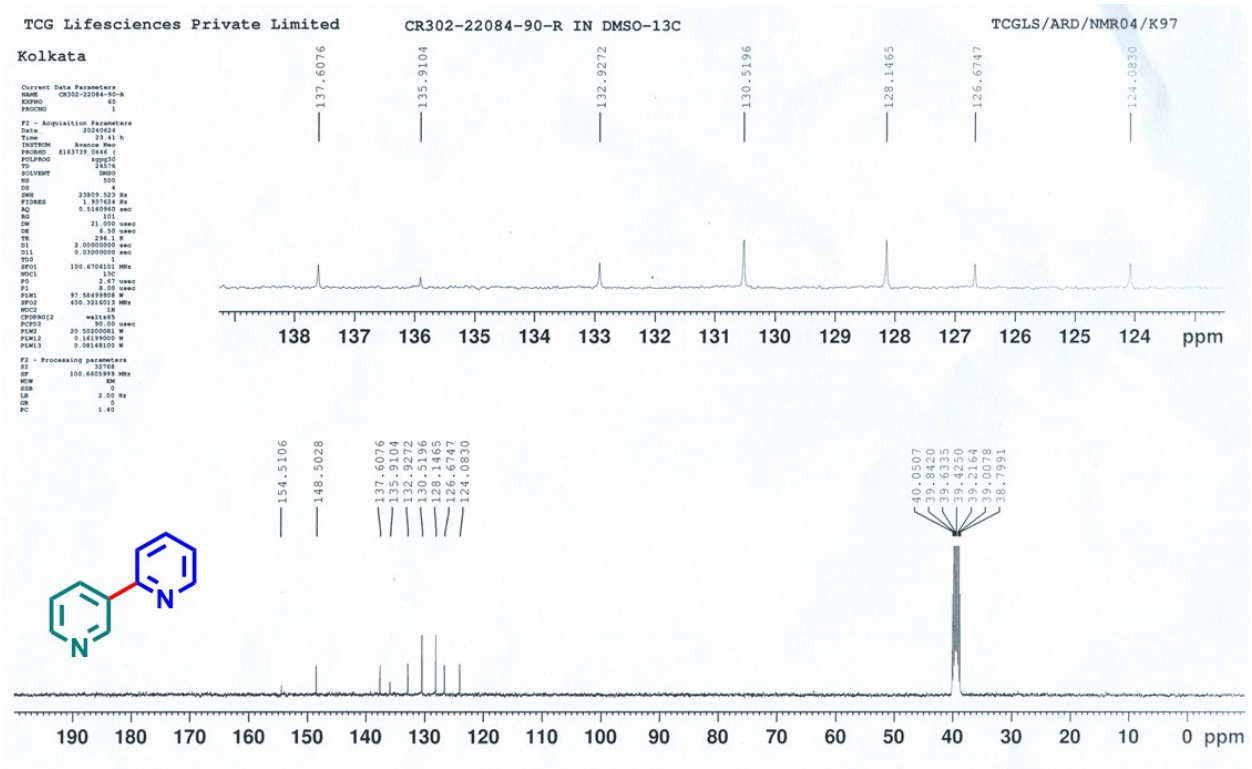


Figure S114: ^{13}C {^{1}H} NMR spectrum of **9k**.

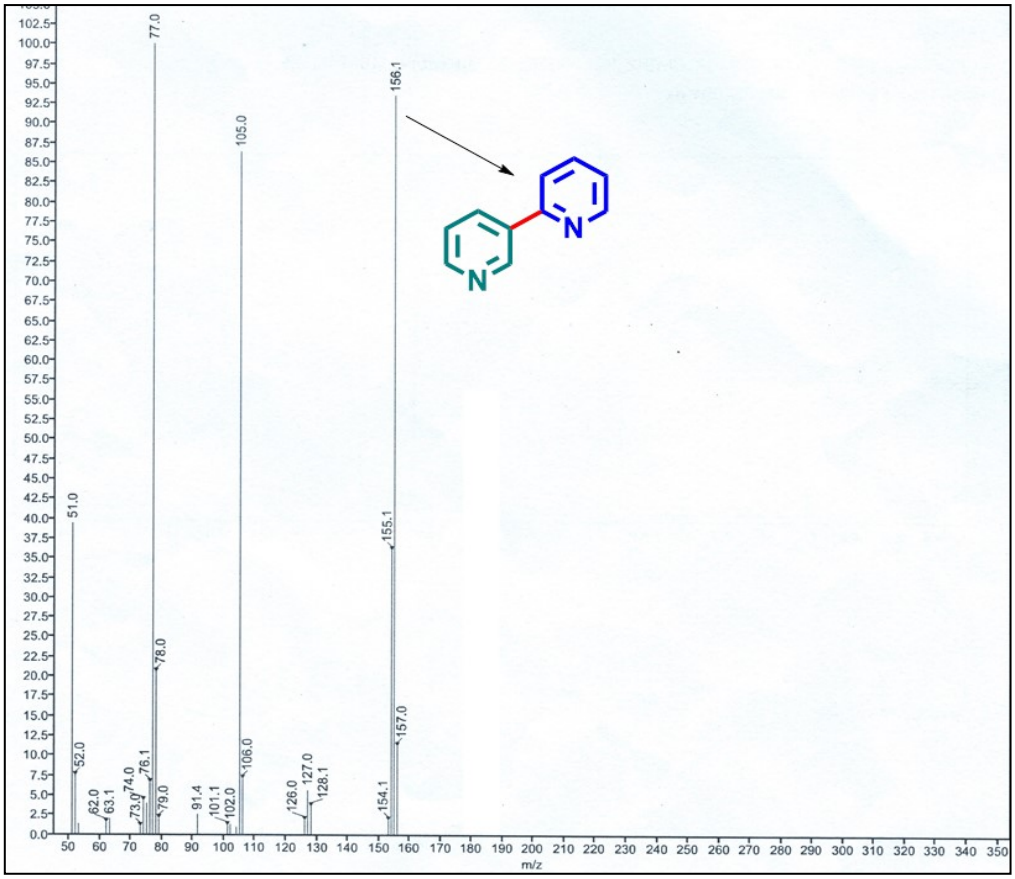


Figure S115: GC-MS spectrum of **9k**.

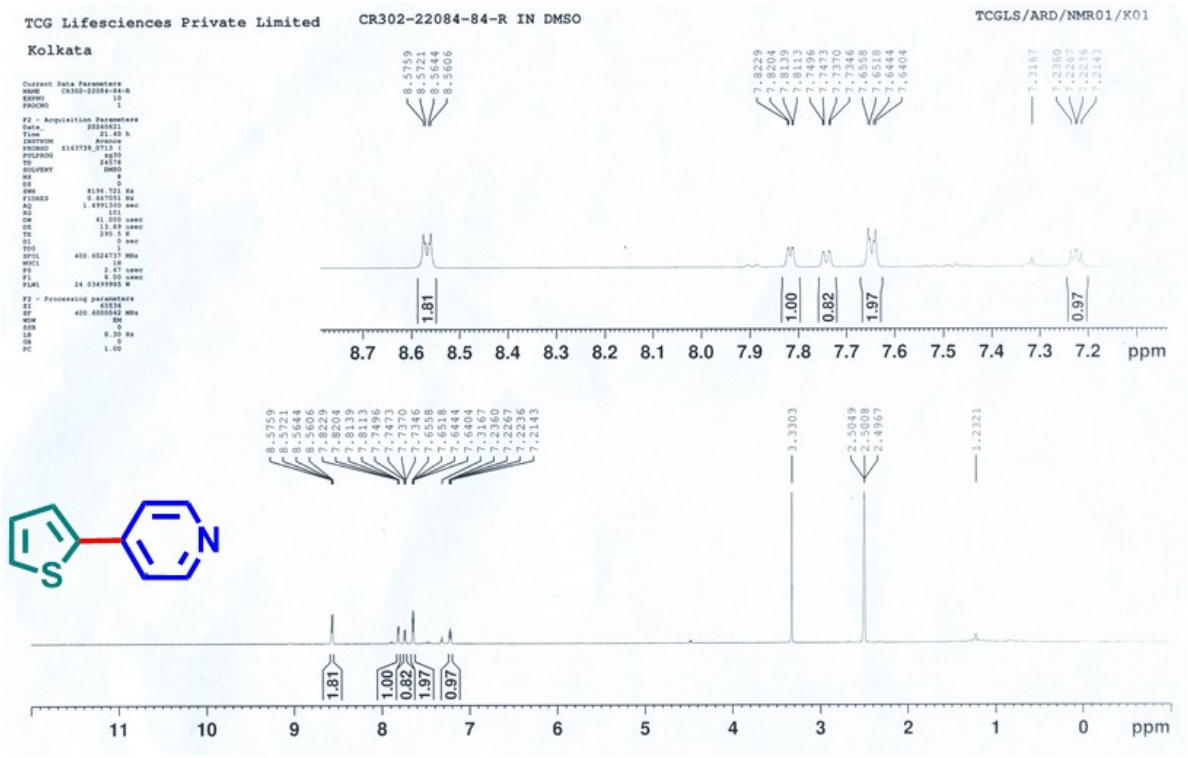


Figure S116: ^{1}H NMR spectrum of **9l**.

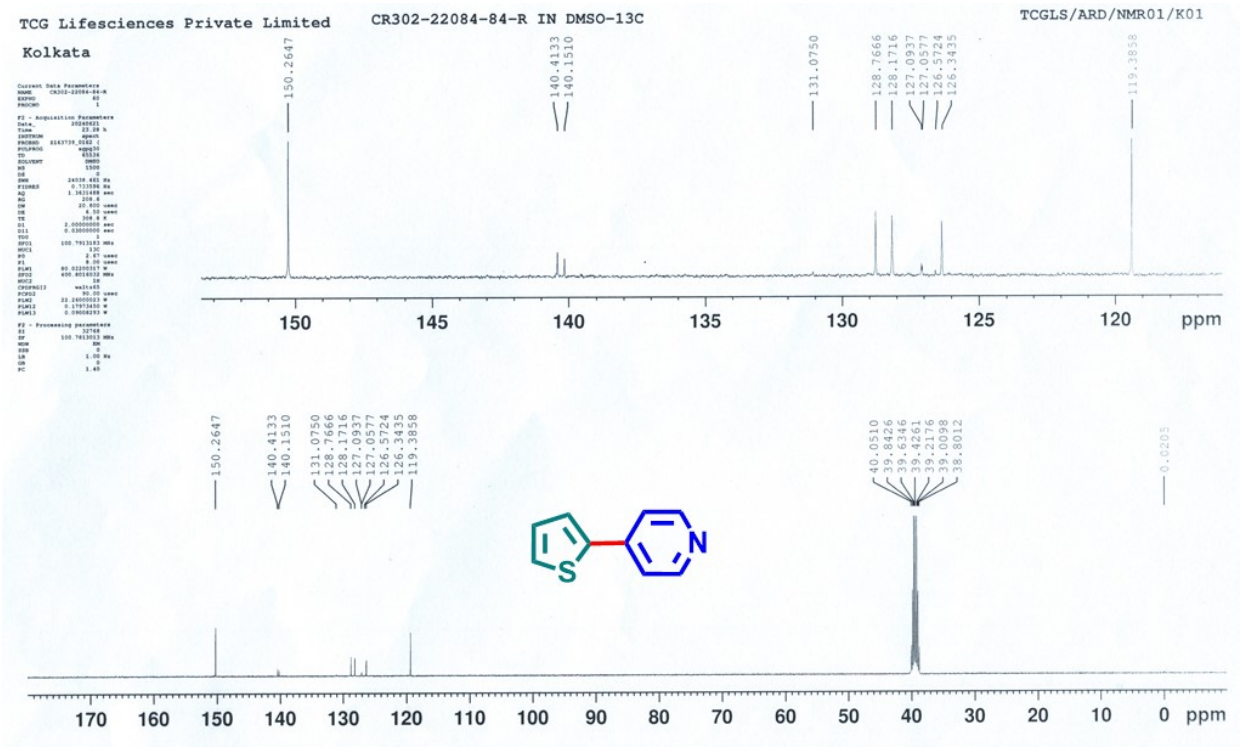


Figure S117: ^{13}C {^{1}H} NMR spectrum of **9l**.

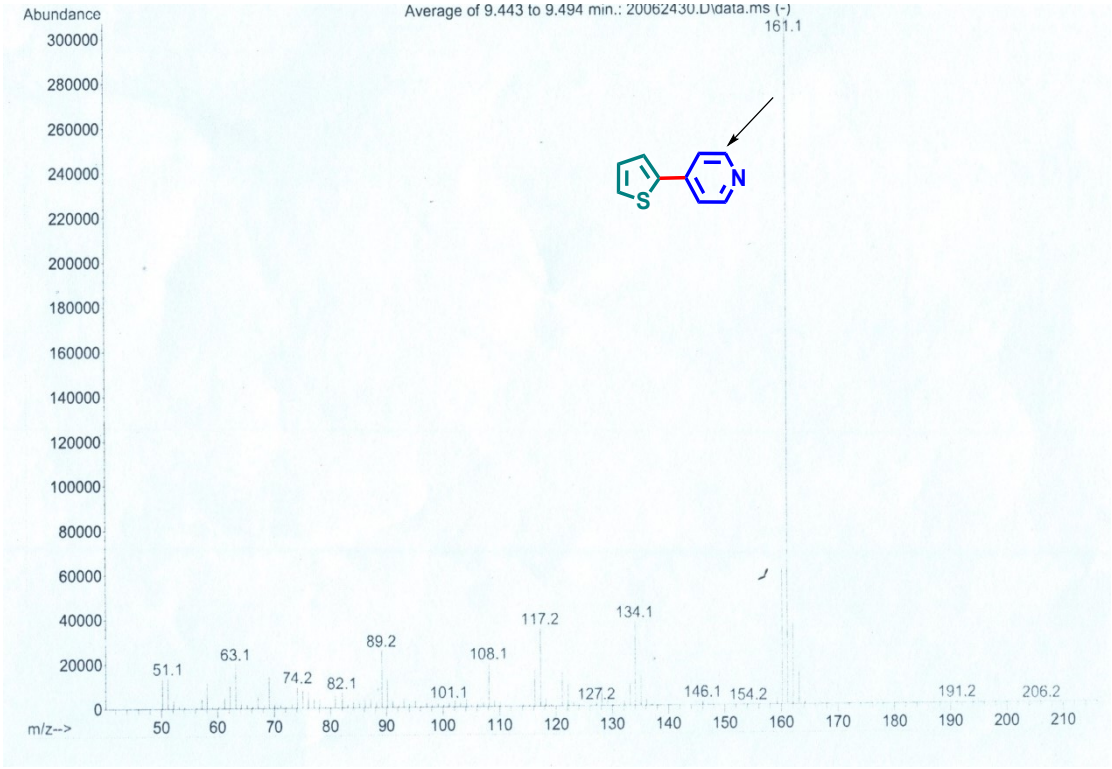


Figure S118: GC-MS spectrum of **9l**.

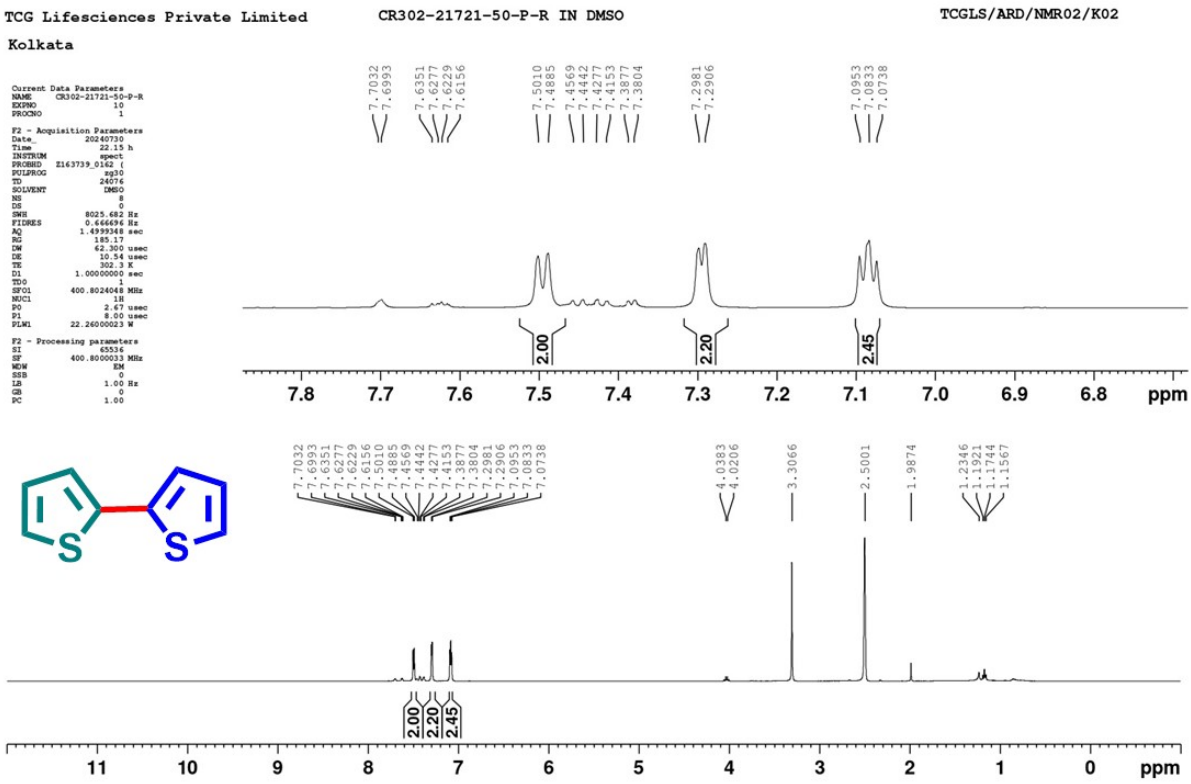


Figure S119: ^{1}H NMR spectrum of **9m**.

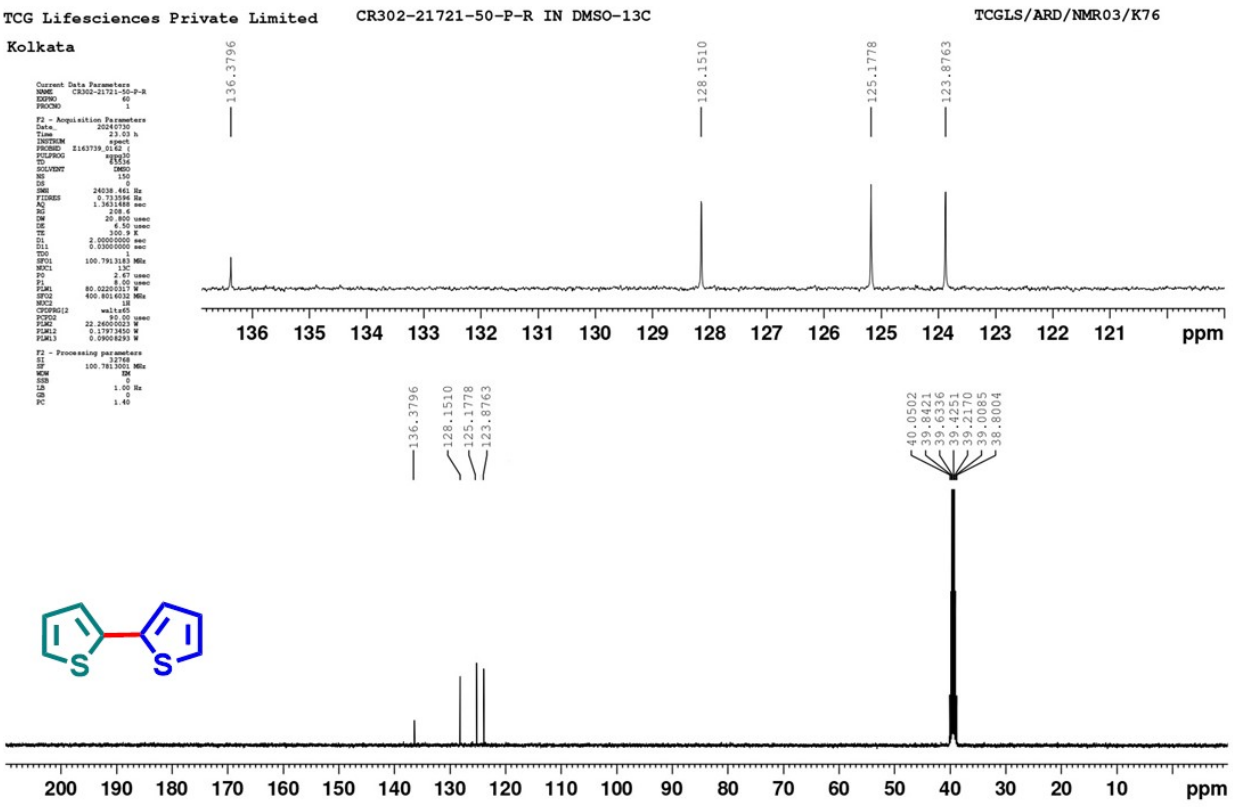


Figure S120: ^{13}C {^{1}H} NMR spectrum of **9m**.

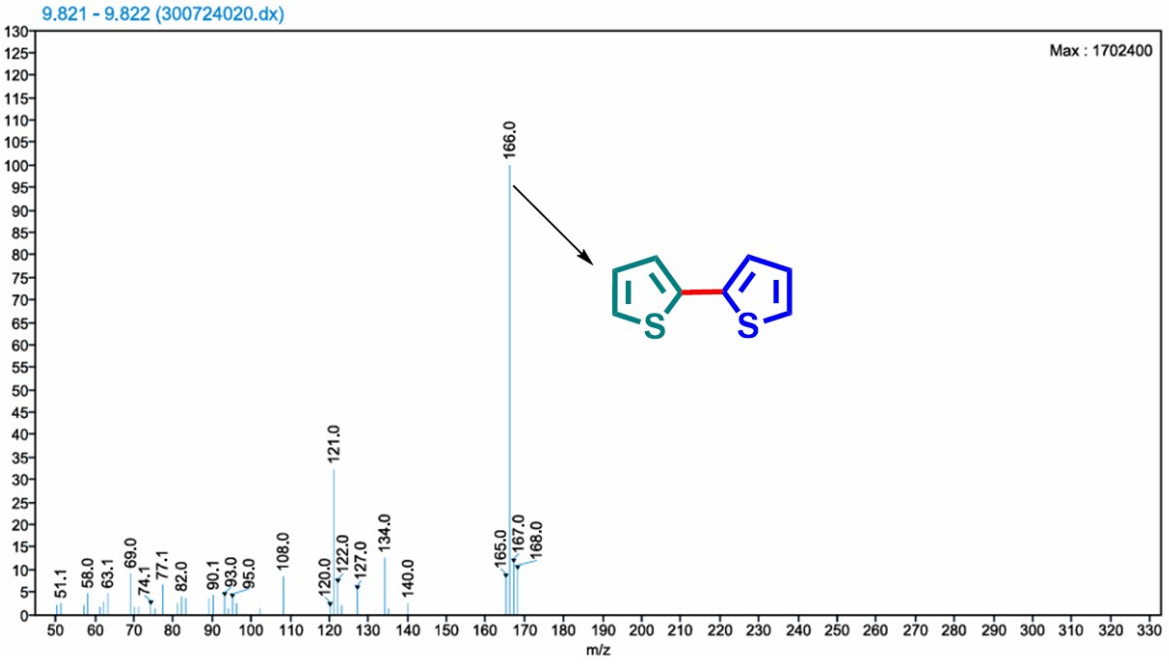
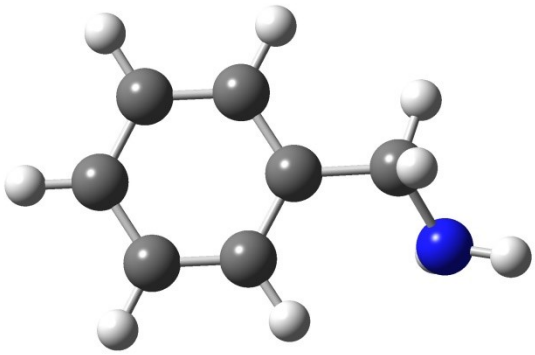


Figure S121: GC-MS spectrum of **9m**.

7. Theoretical calculation:

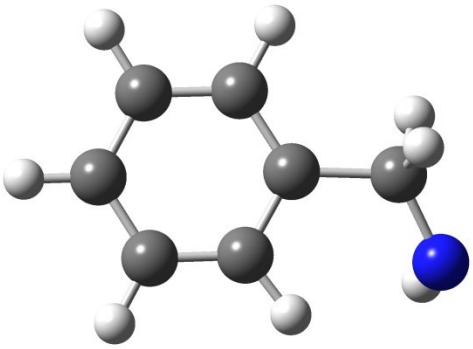
Geometry optimization of the compound **1** and **1a** were carried out with the help of Gaussian16 at ub3lyp level of theory with basis 6-31g(d) for all the elements.

Coordinates of optimized structure **1**:



C	-2.23856	0.30268	0.09986
C	-1.31436	1.33526	-0.10883
C	0.04727	1.03791	-0.25532
C	0.4847	-0.29202	-0.19311
C	-0.4395	-1.3246	0.01558
C	-1.80113	-1.02725	0.16207
H	-3.2782	0.52971	0.2117
H	-1.64835	2.35069	-0.15633
H	0.75292	1.8263	-0.41466
H	-0.10551	-2.34003	0.06308
H	-2.50678	-1.81565	0.32141
C	1.981	-0.61878	-0.35409
N	2.78471	0.50608	0.14555
H	3.75633	0.2939	0.04103
H	2.57908	0.65928	1.11212
H	2.20103	-0.7827	-1.38831
H	2.21561	-1.50066	0.20461

Coordinates of optimized structure **1a**:



C	2.18459	-0.00803	0.25956
C	1.50704	-1.22816	0.13256
C	0.13677	-1.2415	-0.1609
C	-0.55595	-0.0347	-0.32735
C	0.1216	1.18543	-0.20034
C	1.49187	1.19876	0.09312
H	3.23081	0.00215	0.48362
H	2.03594	-2.14958	0.25965
H	-0.38055	-2.17309	-0.25787
H	-0.4073	2.10685	-0.32743
H	2.00919	2.13036	0.19009
C	-2.06173	-0.04935	-0.64983
N	-2.83123	-0.03381	0.60258
H	-2.45666	0.4148	1.41403
H	-2.29933	-0.93362	-1.20347
H	-2.31025	0.81342	-1.23186

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