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Synthesis of Substituted Isoquinolines *via* Iminoalkynes Cyclization using Ag(I) Exchanged K10-Montmorillonite Clay as Reusable Catalyst

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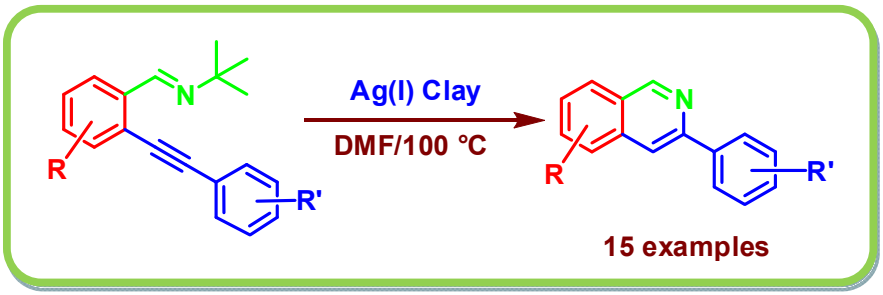


Contents

1. General information

Methods

NMR spectra were registered on Bruker DRX spectrometer operating at 300 or 400 MHz for ^{1}H and 75 or 100 MHz for ^{13}C. All ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ with TMS as the internal standard. Chemical shifts are expressed in ppm and J values are given in Hz (Coupling constants are calculated according to the actual values given in NMR spectrums, here the decimals are reduced). Purifications by column chromatography were performed on silica gel 60-120 mesh. The XRD pattern of the catalyst samples was measured with a PW3050/60 (XPERT-PRO Diffractometer system) instrument using a Cu Kα radiation at room temperature.

Table S1: Chapter V: Synthesis of substituted isoquinolines via iminoalkynes cyclization using Ag(I)-exchanged Montmorillonite clay as reusable catalyst

The following aldehydes, alkynes and *t*-butylamine are used in this chapter.

Chemicals	**Suppliers**	**Chemicals**	**Suppliers**
2-Bromobenzaldehyde	Aldrich	3-Methoxyphenylacetylene	Aldrich
2-Bromo-5-chlorobenzaldehyde	Aldrich	4-Trifluoromethyl-phenylacetylene	Aldrich
2-Bromo-5-nitrobenzaldehyde	Aldrich	3-Fluorophenylacetylene	Aldrich
2-Bromo-3-methoxy-benzaldehyde	Aldrich	2-Methylphenylacetylene	Aldrich
2-Methoxyphenylacetylene	Aldrich	3-Trifluoromethyl-phenylacetylene	Aldrich
Phenylacetylene	Aldrich	Cyclopropylacetylene	Lancaster
t-Butylamine	Aldrich	Copperiodide	Spectrochem

Preparation and characterization of catalysts

Preparation of Na^+ exchanged montmorillonite clay

A sample of 1 g of K10 montmorillonite clay (K10-clay) was stirred with 1 M sodium chloride solution at RT for 72 h, then filtered and washed repeatedly with water to remove excess sodium chloride. This was dried at 90 °C under vacuum for overnight. Various cation exchanged clays[1,2] were prepared from the above sodium exchanged clay with appropriate salt (nitrate or chloride) solutions as mentioned above.

Preparation and characterization of Ag^I exchanged K10 montmorillonite clay

K10 montmorillonite clay (Fluka) was used as received. The silver ions were exchanged into K10 montmorillonite clay (5 g) by stirring with silver nitrate (1 M in 25 ml of water for 1 g of clay) solution at room temperature for 72 h. The clay was filtered, washed thoroughly with distilled water. This was dried at 100 °C under vacuum tray drying for overnight. Ag(I) exchanged K10 clay was characterized by powder XRD, SEM with EDX , UV-DRS and ICP-OES analyses.

Silver-exchanged clay was prepared by ion-exchange method[1] and was characterized by powder XRD, EDX, UV-DRS and ICP-OES analyses. X-ray powder diffraction pattern for Ag(I) clay is shown in Figure **S1**. The structure of K10 clay is retained as observed from the retention of all the characteristic peaks in XRD patterns after Ag(I) ion exchange process.

XRD analysis

X-ray powder diffraction pattern for Ag^{I}-K10 clay is shown in Figure S1. The structure of K10-clay is intact as observed from the retention of all the characteristic peaks in XRD patterns after Ag(I) ion exchange process.

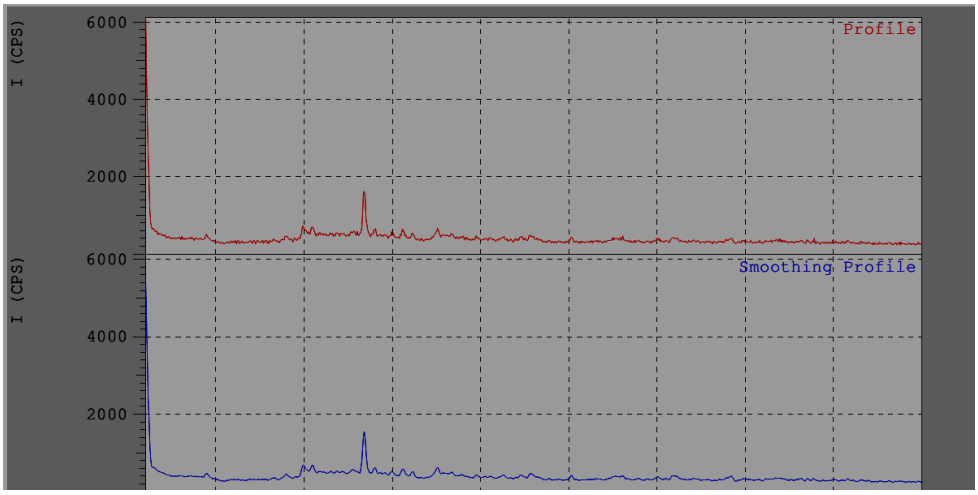


Figure S1. *XRD data for Ag^{I}-K10 clay.*

SEM and EDX analyses

SEM images (Figure. S2) of Ag^{I}-K10 clay show that the surface consists of aluminium sheets. The total silver content in the sample was determined by EDX analysis and it was found to be 4.57 weight %.

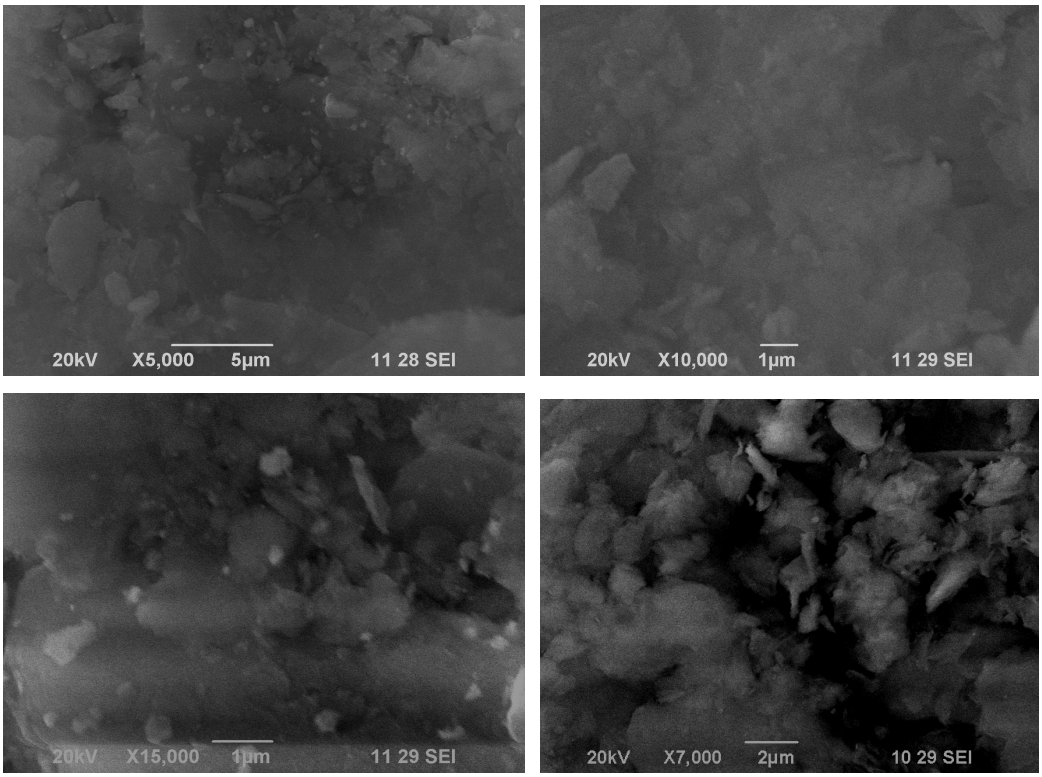


Figure S2. *SEM image of Ag(I) exchanged K10-clay.*

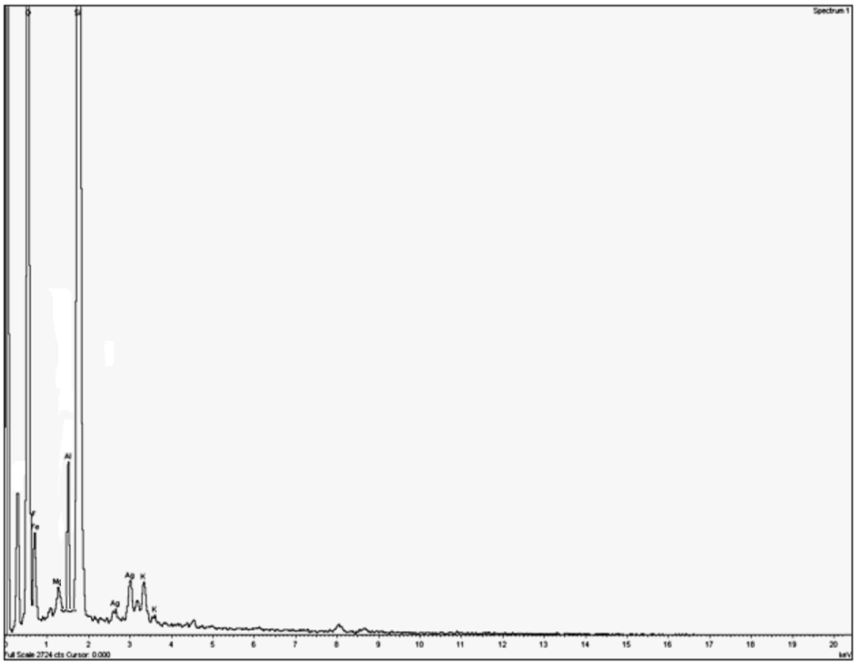


Figure S3. *EDX spectrum of Ag^{I}-K10 clay.*

UV-DRS analysis

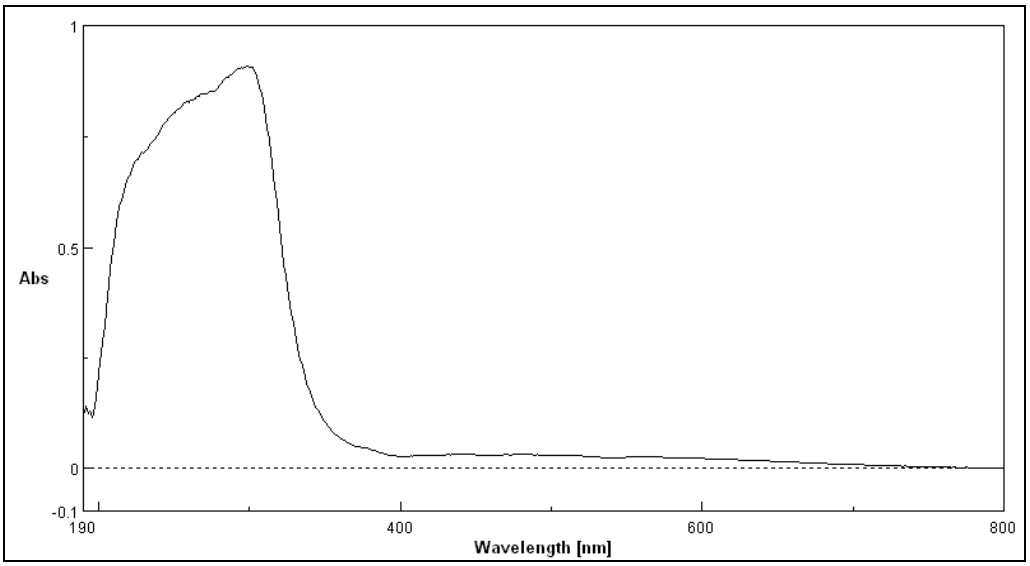


Figure S4. *UV–Visible diffuse reflectance spectra of Ag^{I}-K10 clay.*

The total silver content in the samples was determined by EDX analysis and it was found to be 4.57 % of weight.

Table S2: Percentage of elements present in Ag^{I}-K10 clay

Element	App Conc.	Intensity Corrn.	Weight %	Weight % Sigma	Atomic %
O K	117.55	0.7644	55.83	0.87	69.42
Mg K	0.99	0.7227	0.38	0.06	0.26
Al K	11.57	0.8293	1.85	0.12	1.42
Si K	52.45	0.8631	35.69	0.35	24.04
K K	2.50	1.0085	0.68	0.06	0.30
Fe K	2.93	0.8103	1.00	0.09	0.30
Ag K	6.80	0.7698	4.57	0.15	4.27
Totals			100.00		

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) Analysis

1. From ICP-OES analysis silver concentration in silver exchanged clay is found to be 4.57 %.

Element Symbol	Concentration (%)
Ag 328.068	4.57

2. Ag^{I}-K10 clay is added (0.02 g) to a mixture of iminoalkyne (1 mmol) in DMF (5 mL) and stirred at 100 °C for 6 h. After completion of reaction, the catalyst is filtered. The recovered catalyst is used for recycled upto fifth cycle. After the five cycles, the filtrate and reused Ag^{I}-K10 clay are analyzed with ICP-OES.

Filtrate:

Element Symbol	Concentration (%)
Ag 328.068	BDL

BDL : BELOW DETECTABLE LIMIT

Reused Ag^{I}-K10 clay (after the five cycle):

Element Symbol	Concentration (%)
Ag 328.068	4.56

3. Iminoalkyne (1 mmol) in DMF (5 mL) is treated with 20 mg of Ag^{I}-K10 at 100 °C for 6 h. Thus, the reaction mixture after 6 h at 100 °C is filtered and removed the catalyst. Iminoalkyne (0.5 mmol) is further added to the filtrate, and the reaction mixture is heated at 100 °C for 6 h. In addition, ICP-OES analysis of the reaction mixture after removing the catalyst indicated the presence of Ag^{I} below the detection limit

Element Symbol	Concentration (%)
Ag 328.068	BDL

BDL : BELOW DETECTABLE LIMIT

4. Ag^{I}-K10 clay and DMF (5 mL) are stirred at 100 °C for 6 h. The catalyst is filtered and the filtrate is analyzed with ICP-OES.

Element Symbol	**Concentration (%)**
Ag 328.068	BDL

BDL : BELOW DETECTABLE LIMIT

This result shows that that no leaching of silver has taken place from the solid to the liquid phase. This proves that catalyst is heterogeneous in nature.

Typical procedure for synthesis of substituted isoquinolines

Step-1: General procedure for the preparation of 2-(1-alkynyl)benzaldehyde

To a solution of 2-bromobenzaldehyde (1 eq) and alkyne (1.2 eq) in Et_3N (10 volume) was added $PdCl_2(PPh_3)_2$ (2 mol%). The mixture was stirred for 5 min, and CuI (1 mol%) was added. The resulting mixture was then heated under a nitrogen atmosphere at 50° C for 4 h. The reaction was monitored by TLC to establish completion. The reaction mixture was allowed to cool to room temperature, and the ammonium salt was removed by filtration. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate as an eluent to afford 2-(1-alkynyl)benzaldehyde.

Step-2: General procedure for the preparation of iminoalkynes

To a mixture of 2-(1-alkynyl)benzaldehyde (1 eq) was added *tert*-butylamine (6 eq). The mixture was then stirred under an Ar atmosphere at room temperature for 24 h. The resulting mixture was extracted with ether. The combined organic layers were dried over Na_2SO_4 and filtered. Removal of the solvent afforded an iminoalkyne.

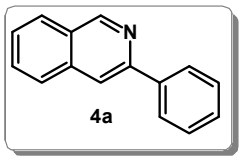
Step-3: General procedure for the cyclization of iminoalkynes

To a solution of iminoalkyne (1 mmol) in DMF (5 mL) was added Ag^{I}-K10 clay (20 mg) and the solution was flushed with nitrogen. The reaction mixture was heated to 100 °C for 6 h. The reaction mixture was cooled to room temperature, and then filtered

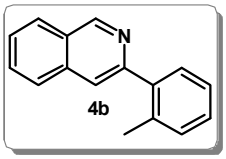
and concentrated. The crude product was purified through column chromatography by using *n*-hexane/ethyl acetate as an eluent to afford as substituted isoquinolines. The recovered catalyst was thoroughly washed with ethyl acetate and reused for next run. The purified products were characterized by their ^{1}H, ^{13}C-NMR as well as by mass spectral data.

2. Characterization Data

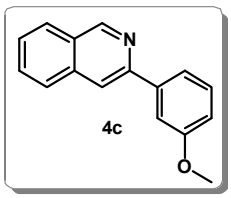
Spectral data of substituted isoquinolines



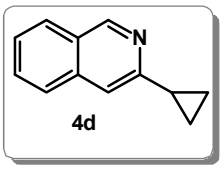
3-Phenylisoquinoline[3] (4a) (Table 2, entry 1): Compound **4a** was prepared according to the general procedure and purified by column chromatography. Offwhite solid; m.p. 103.4-104.4 °C. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 7.41-7.45 (m, 1H), 7.50-7.58 (m, 2H), 7.60-7.62 (m, 1H), 7.69-7.73 (m, 1H), 7.78-7.90 (d, 1H), 8.00-8.02 (d, 1H), 8.08 (s, 1H), 8.13-8.15 (t, 2H), 9.36 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 116.5, 126.9, 127.0, 127.0, 127.5, 127.7, 128.5, 128.7, 130.5, 136.6, 139.5, 151.2, 152.3 ppm; **LC MS (ESI-MS):** m/z calcd for $C_{15}H_{11}N$ $(M+H)^+$: 206.2; Found: 206.1 $(M+H)^+$.



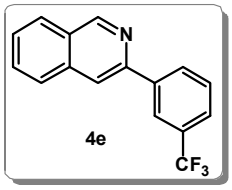
3-(2-Methylphenyl)isoquinoline[4] (4b) (Table 2, entry 2): Compound **4b** was prepared according to the general procedure and purified by column chromatography. Yellow solid; m.p. 80.4-81.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ =2.43 (s, 3H),7.27-7.33 (q, 3H), 7.51-7.52 (d, 1H), 7.61-7.65 (m, 1H), 7.71-7.75 (m, 1H), 7.76 (s, 1H), 7.86-7.88 (d, 1H), 8.02-8.04 (d, 1H), 9.36 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 20.3, 120.0, 125.8, 126.6, 127.0, 127.1, 127.4, 128.0, 129.9, 130.4, 130.6, 136.07, 136.07, 136.1, 140.4, 151.7, 153.6 ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{13}N$ $(M+H)^+$: 220.2; Found: 220.1 $(M+H)^+$.



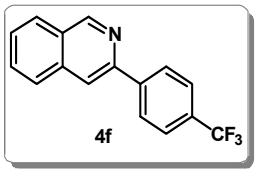
3-(3-Methoxyphenyl)isoquinoline[5] (4c) (Table 2, entry 3): Compound **4c** was prepared according to the general procedure and purified by column chromatography. Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ =3.93 (s, 3H), 6.97-6.99 (m, 1H), 7.00-7.44 (t, 1H), 7.57-7.61 (t, 1H), 7.68-7.74 (m, 3H), 7.86-7.89 (d, 1H), 7.98-8.00 (d, 1H), 8.07 (s, 1H), 9.36 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 55.4, 112.1, 114.6, 116.7, 119.3, 126.9, 127.1, 127.5, 127.8, 129.7, 130.5, 136.6, 141.0, 151.0, 152.3, 160.1 ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{13}NO$ $(M+H)^+$: 236.2; Found: 236.1 $(M+H)^+$.



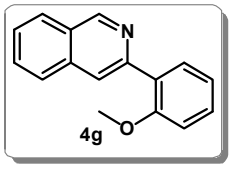
3-Cyclopropylisoquinoline[6] (4d) (Table 2, entry 4): Compound **4d** was prepared according to the general procedure and purified by column chromatography. White solid; m.p. 62.3-63.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 1.05-1.10 (m, 2H), 1.11-1.13 (m, 2H), 2.16- 2.22 (m, 1H), 7.46-7.50 (m, 2H), 7.60-7.64 (m, 1H), 7.70-7.72 (d, 1H), 7.88-7.90 (d, 1H), 9.12 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 9.1, 16.9, 116.3, 125.6, 126.9, 127.4, 130.17, 136.3, 152.1, 156.0 ppm; **LC MS (ESI-MS):** m/z calcd for $C_{12}H_{11}N$ $(M+H)^+$: 170.2; Found: 170.1 $(M+H)^+$.



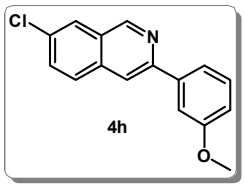
3-[3-Trifluoromethyl)phenyl]isoquinoline[7] (4e) (Table 2, entry 5): Compound **4e** was prepared according to the general procedure and purified by column chromatography. Pale yellow solid; m.p. 70.1-71.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 7.61-7.68 (m, 3H), 7.71-7.75 (t, 1H), 7.90-7.92 (d, 1H), 8.01-8.03 (d, 1H), 8.11 (s, 1H), 8.31-8.33 (d, 1H), 8.42 (s, 1H), 9.35 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 112.1, 119.0, 119.0, 120.2, 122.2, 122.8, 122.8, 123.2, 124.4, 125.3, 125.9, 131.7, 135.5, 144.8, 147.8 ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{10}F_3N$ $(M+H)^+$: 274.2; Found: 274.2 $(M+H)^+$.



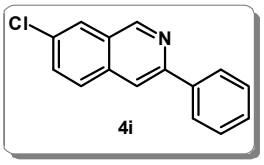
3-[4-(Trilfluoromethyl)phenyl]isoquinoline (4f) (Table 2, entry 6): Compound **4f** was prepared according to the general procedure and purified by column chromatography. Off white solid; m.p. 165.8-167.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 7.63-7.66 (m, 1H), 7.72-7.78 (m, 3H), 7.90-7.92 (d, 1H), 8.02-8.04 (d, 1H), 8.12 (s, 1H), 8.24-8.27 (d, 1H), 9.36 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 117.3, 125.6, 125.70, 125.74, 125.77, 127.0, 127.1, 127.6, 127.7, 128.0, 130.8, 136.4, 149.5, 152.6 ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{10}F_3N$ $(M+H)^+$: 274.2; Found: 274.1 $(M+H)^+$.



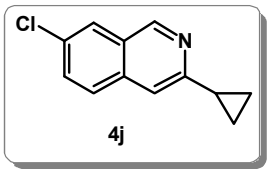
3-(2-Methoxyphenyl)isoquinoline[7] (4g) (Table 2, entry 7): Compound **4g** was prepared according to the general procedure and purified by column chromatography. Yellowish liquid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 3.91 (s, 3H), 7.05-7.07 (d, 1H), 7.11-7.15 (m, 1H), 7.38-7.42 (m, 1H), 7.57-7.61 (m, 1H), 7.67-7.71 (m, 1H), 7.86-7.88 (d, 1H), 7.91-7.92 (d, 1H), 8.01-8.02 (d, 1H), 8.2 (s, 1H), 9.36 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 55.7, 111.4, 121.0, 121.1, 127.00, 127.03, 127.3, 127.4, 129.0, 129.5, 130.2, 131.4, 136.2, 149.2, 151.8, 157.0 ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{13}NO$ $(M+H)^+$: 236.2; Found: 236.1 $(M+H)^+$.



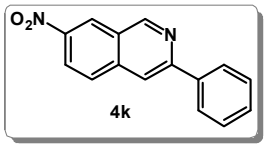
7-Chloro-3-(3-methoxyphenyl)isoquinoline (4h) (Table 2, entry 8): Compound **4h** was prepared according to the general procedure and purified by column chromatography. White solid; m.p. 118.2-119.6 °C. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 3.93 (s, 3H), 6.97-7.00 (m, 1H), 7.40-7.44 (t, 1H), 7.62-7.68 (m, 2H), 7.71 (s, 1H), 7.81-7.83 (d, 1H), 7.97 (s, 1H), 8.04 (s, 1H), 9.26 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 55.4, 112.1, 114.1, 116.3, 119.3, 126.3, 128.2, 128.6, 129.8, 131.5, 132.6, 134.8, 140.6, 151.2, 151.4, 160.1 ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{12}ClNO$ $(M+H)^+$: 270.7; Found: 270.8 $(M+H)^+$.



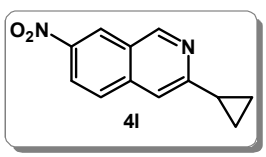
7-Chloro-3-phenylisoquinoline[8] (4i) (Table 2, entry 9): Compound **4i** was prepared according to the general procedure and purified by column chromatography. White solid; m.p. 152.5 -153.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 7.42-7.454 (m, 1H), 7.50-7.54 (m, 2H), 7.62-7.65 (q, 1H), 7.81-7.84 (d, 1H), 7.97-7.98 (d, 1H), 8.05 (s, 1H), 8.11-8.13 (m, 2H), 9.27 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 116.1, 126.3, 126.9, 128.1, 128.6, 128.8, 131.6, 132.5, 134.9, 139.0, 151.35, 151.6 ppm; **LC MS (ESI-MS):** m/z calcd for $C_{15}H_{10}ClN$ $(M+H)^+$: 240.6; Found: 240.8 $(M+H)^+$.



7-Chloro-3-cyclopropylisoquinoline (4j) (Table 2, entry 10): Compound **4j** was prepared according to the general procedure and purified by column chromatography. White solid; m.p. 106.4-107.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 1.03-1.05 (q, 2H), 1.08-1.11 (q, 2H), 2.13- 2.19 (m, 1H), 7.44 (s, 1H), 7.53-7.56 (m, 1H), 7.64-7.66 (d, 1H), 7.86 (s, 1H), 9.03 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 9.4, 17.0, 116.2, 126.2, 127.3, 127.4, 131.2, 131.2, 134.6, 151.1, 156.6 ppm; **LC MS (ESI-MS):** m/z calcd for $C_{12}H_{10}ClN$ $(M+H)^+$: 204.6; Found: 204.1 $(M+H)^+$.

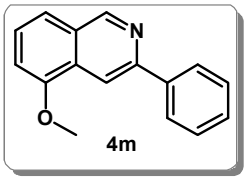


7-Nitro-3-phenylisoquinoline (4k) (Table 2, entry 11): Compound **4k** was prepared according to the general procedure and purified by column chromatography. Light yellow solid; m.p. 192.8-195.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 7.47-7.50 (t, 1H), 7.53-7.56 (t, 2H), 8.00-8.02 (d, 1H), 8.16-8.18 (d, 3H), 8.45-8.47 (t, 1H), 8.95 (s, 1H), 9.52 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 115.9, 123.9, 124.5, 126.1, 127.3, 128.7, 129.0, 129.6, 138.3, 139.1, 145.9, 154.1, 154.8 ppm; **LC MS (ESI-MS):** m/z calcd for $C_{15}H_{10}N_2O_2$ $(M+H)^+$: 251.2; Found: 251.1 $(M+H)^+$.

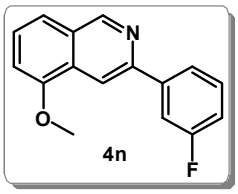


3-Cyclopropyl-7-nitroisoquinoline (4l) (Table 2, entry 12): Compound **4l** was prepared according to the general procedure and purified by column chromatography.Yellow solid; m.p. 137.4-138.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 1.11-1.15 (q, 2H), 1.17-1.21 (q, 2H), 2.18- 2.24 (m,

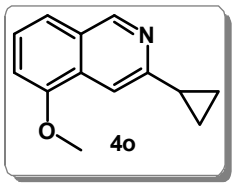
1H), 7.58 (s, 1H), 7.81-7.84 (d, 1H), 8.36-8.39 (d, 1H), 8.85 (s, 1H), 9.27 (s, 1H) ppm; **^{13}C NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 10.4, 17.49, 116.4, 123.6, 124.5, 125.2, 127.4, 138.6, 145.1, 154.0, 160.9 ppm; **LC MS (ESI-MS):** m/z calcd for $C_{12}H_{10}N_2O_2$ $(M+H)^+$: 215.2; Found: 215.1 $(M+H)^+$.



5-Methoxy-3-phenylisoquinoline (4m) (Table 2, entry 13): Compound **4m** was prepared according to the general procedure and purified by column chromatography. Light brown solid; m.p. 88.1-89.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 4.06 (s, 3H), 7.00-7.02 (d, 1H), 7.40-7.42 (m, 1H), 7.42-7.58 (m, 4H), 8.16-8.18 (q, 2H), 8.47 (s, 1H), 9.30 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 55.5, 107.6, 111.0, 119.2, 126.9, 127.0, 128.2, 128.3, 128.6, 129.1, 139.7, 150.8, 151.6, 154.71 ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{13}NO$ $(M+H)^+$: 236.2; Found: 236.1 $(M+H)^+$.

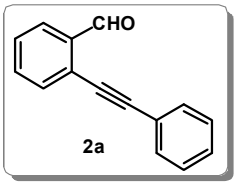


3-(3-Fluorophenyl)-5-methoxyisoquinoline (4n) (Table 2, entry 14): Compound **4n** was prepared according to the general procedure and purified by column chromatography. Light yellow solid; m.p. 97.7-99.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 4.04 (s, 3H), 6.99-7.01 (d, 1H), 7.07-7.12 (m, 1H), 7.44-7.56 (m, 3H), 7.89-7.93 (m, 2H), 8.43 (s, 1H), 9.28 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 55.6, 107.8, 111.3, 113.9, 115.2, 119.2, 122.4, 127.5, 128.6, 129.0, 130.1, 142.1, 149.4, 151.8, 154.8, 164.6 ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{13}NO$ $(M+H)^+$: 254.2; Found: 254.1 $(M+H)^+$.

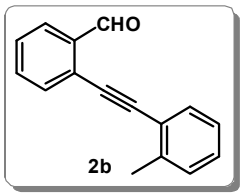


3-Cyclopropyl-5-methoxyisoquinoline (4o) (Table 2, entry 15): Compound **4o** was prepared according to the general procedure and purified by column chromatography. Yellowish liquid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 1.04-1.09 (q, 2H), 1.09-1.12 (q, 2H), 2.18-2.24 (m, 1H), 3.97 (s, 3H), 6.88-6.90 (d, 1H), 7.33-7.37 (t, 1H), 7.43-7.45 (d, 1H), 7.81 (s, 1H), 9.06 (s, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 9.2, 17.2, 55.4, 107.2, 110.7, 119.1, 125.7, 127.6, 128.9, 151.4, 153.7, 155.8 ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{13}NO$ $(M+H)^+$: 200.2; Found: 200.1 $(M+H)^+$.

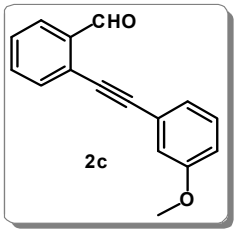
Step-1 intermediate:



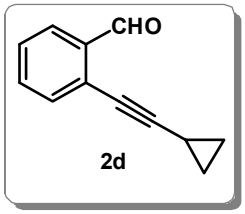
2-(Phenylethynyl)benzaldehyde[9] (2a): Compound **2a** was prepared according to the general procedure and purified by column chromatography. Brown solid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 7.38-7.41 (m, 3H), 7.45-7.48 (t, 1H), 7.56-7.67 (m, 4H), 7.95-7.97 (dd, 1H), 10.66 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{15}H_{10}O$ $(M+H)^+$: 207.2; Found: 207.3 $(M+H)^+$.



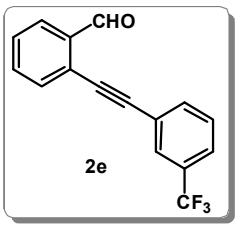
2-[(2-Methylphenyl)ethynyl]benzaldehyde (2b): Compound **2b** was prepared according to the general procedure and purified by column chromatography. Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 2.55 (s, 3H), 7.21-7.24 (m, 1H), 7.27-7.30 (m, 2H), 7.46-7.48 (t, 1H), 7.54-7.56 (d, 1H), 7.60-7.62 (t, 1H), 7.66-7.68 (m, 1H), 7.96-7.98 (dd, 1H), 10.69 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{12}O$ $(M+H)^+$: 221.2; Found: 221.1 $(M+H)^+$.



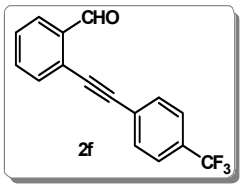
2-[(3-Methoxyphenyl)ethynyl]benzaldehyde (2c): Compound **2c** was prepared according to the general procedure and purified by column chromatography. Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 3.85 (s, 3H), 6.95-6.97 (d, 1H), 7.09 (s, 1H), 7.17-7.19 (t, 1H), 7.27-7.33 (m, 1H), 7.47-7.49 (t, 1H), 7.60-7.62 (t, 1H), 7.65-7.67 (t, 1H), 7.96-7.97 (dd, 1H), 10.66 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{12}O_2$ $(M+H)^+$: 237.2; Found: 237.1 $(M+H)^+$.



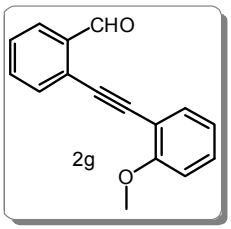
2-(Cyclopropylethynyl)benzaldehyde[10] (2d): Compound **2d** was prepared according to the general procedure and purified by column chromatography. Colorless liquid. **^{1}H NMR (300 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 0.92-0.95 (m, 2H), 0.95-0.98 (m, 2H), 1.47-1.56 (m, 1H), 7.34-7.39 (m, 1H), 7.43-7.53 (m, 2H), 7.88-7.90 (d, 1H), 10.49 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{12}H_{10}O$ $(M+H)^+$: 171.2; Found: 171.1 $(M+H)^+$.



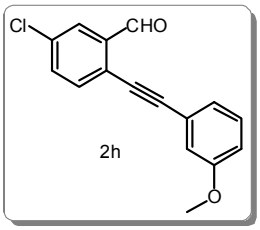
2-{[3-(Trifluoromethyl)phenyl]ethynyl}benzaldehyde[7] (2e): Compound **2e** was prepared according to the general procedure and purified by column chromatography. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 7.50-7.56 (m, 2H), 7.61-7.69 (m, 3H), 7.74-7.76 (d, 1H), 7.84 (s, 1H), 7.97-7.99 (dd, 1H), 10.64 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_9F_3O$ $(M+H)^+$: 275.2; Found: 275.1 $(M+H)^+$.



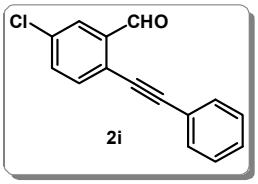
2-{[4-(Trifluoromethyl)phenyl]ethynyl}benzaldehyde[10] (2f): Compound **2f** was prepared according to the general procedure and purified by column chromatography. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 7.49-7.53 (t, 1H), 7.60-7.69 (m, 6H), 7.97-7.99 (dd, 1H), 10.63 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_9F_3O$ $(M+H)^+$: 275.2; Found: 275.1 $(M+H)^+$.



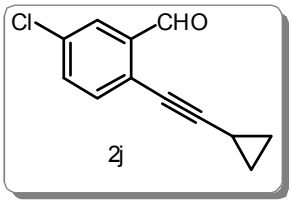
2-[(2-Methoxyphenyl)ethynyl]benzaldehyde[7] (2g): Compound **2g** was prepared according to the general procedure and purified by column chromatography. Brown oil. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 3.94 (s, 3H), 6.92-6.97 (m, 2H), 7.34-7.39 (m, 1H), 7.42-7.46 (t, 1H), 7.51-7.53 (m, 1H), 7.56-7.58 (t, 1H), 7.60-7.67 (t, 1H), 7.94-7.97 (dd, 1H), 10.74 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{12}O_2$ $(M+H)^+$: 237.2; Found: 237.1 $(M+H)^+$.



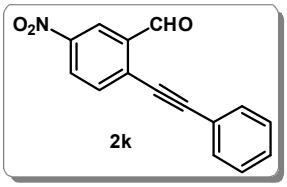
5-Chloro-2-[(3-methoxyphenyl)ethynyl]benzaldyde (2h): Compound **2h** was prepared according to the general procedure and purified by column chromatography. Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 3.85 (s, 3H), 6.95-6.98 (m, 1H), 7.07 (s, 1H), 7.15-7.17 (t, 1H), 7.27-7.32 (m, 1H), 7.54-7.61 (m, 2H), 7.91-7.92 (dd, 1H), 10.59 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{11}ClO_2$ $(M+H)^+$: 271.7; Found: 271.6 $(M+H)^+$.



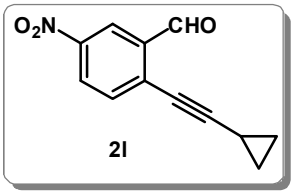
5-Chloro-2-(phenylethynyl)benzaldehyde (2i): Compound **2i** was prepared according to the general procedure and purified by column chromatography. Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 7.37-7.42 (m, 3H), 7.54-7.61 (m, 4H), 7.922-7.927 (d, 1H), 10.59 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{15}H_9ClO$ $(M+H)^+$: 241.6; Found: 241.6 $(M+H)^+$.



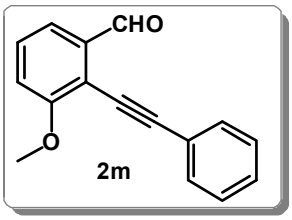
5-Chloro-2(cyclopropylethynyl)benzaldehyde (2j): Compound **2j** was prepared according to the general procedure and purified by column chromatography. Colorless liquid. **^{1}H NMR (300 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 0.93-0.95 (m, 2H), 0.95-0.98 (m, 2H), 1.48-1.54 (m, 1H), 7.40-7.42 (d, 1H), 7.44-7.47 (t, 1H), 7.82-7.83 (d, 1H), 10.41 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{12}H_9O$ $(M+H)^+$: 205.6; Found: 205.1 $(M+H)^+$.



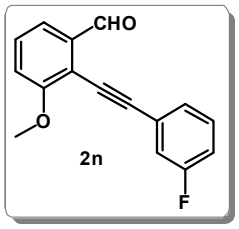
5-Nitro-2-(phenylethynyl)benzaldehyde (2k): Compound **2k** was prepared according to the general procedure and purified by column chromatography. Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 7.43-7.47 (m, 3H), 7.60-7.62 (dd, 2H), 7.82-7.84 (d, 1H), 8.41-8.44 (dd, 1H), 8.77-8.78 (d, 1H), 10.66 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{15}H_9NO_3$ $(M+H)^+$: 252.2; Found: 252.0 $(M+H)^+$.



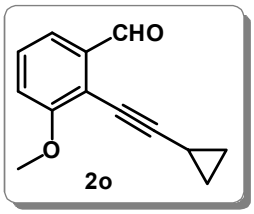
(2-cyclopropylethynyl)-5-nitrobenzaldehyde (2l): Compound **2l** was prepared according to the general procedure and purified by column chromatography. Colorless liquid. **^{1}H NMR (300 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 0.96-0.98 (m, 2H), 1.02-1.07 (m, 2H), 1.55-1.60 (m, 1H), 7.62-7.64 (d, 1H), 8.32-8.34 (dd, 1H), 8.68-8.69 (d, 1H), 10.48 (s, 1H) ppm; **GC MS:** m/z calcd for $C_{12}H_9NO_3$ $(M+H)^+$: 216.2; Found: 216.0 (M+H).



3-methoxy-2-(phenylethynyl)benzaldehyde (2m): Compound **2m** was prepared according to the general procedure and purified by column chromatography. Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 3.98 (s, 3H), 7.14-7.16 (t, 1H), 7.37-7.44 (m, 4H), 7.56-7.62 (m, 3H), 10.67 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{12}FO_2$ $(M+H)^+$: 237.2; Found: 237.1 $(M+H)^+$.

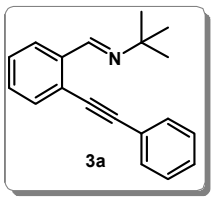


2-[(3-Fluorophenyl)ethynyl]-3-methoxybenzaldehyde (2n): Compound **2n** was prepared according to the general procedure and purified by column chromatography. Pale yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 3.98 (s, 3H), 7.06-7.07 (m, 1H), 7.11-7.16 (m, 1H), 7.28-7.30 (m, 1H), 7.32-7.38 (m, 2H), 7.41-7.45 (t, 1H), 7.55-7.57 (dd, 1H), 10.62 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{11}FO_2$ $(M+H)^+$: 255.2; Found: 255.1 $(M+H)^+$.

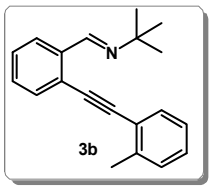


2-(Cyclopropylethynyl)-3-methoxybenzaldehyde (2o): Compound **2o** was prepared according to the general procedure and purified by column chromatography. Colorless liquid. **^{1}H NMR (300 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 0.90-0.92 (m, 2H), 0.95-0.98 (m, 2H), 3.92 (s, 3H), 7.06-7.09 (d, 1H), 7.29-7.35 (m, 1H), 7.47-7.50 (d, 1H), 10.49 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{13}H_{12}O_2$ $(M+H)^+$: 201.2; Found: 201.1 $(M+H)^+$.

Step-2 intermediate

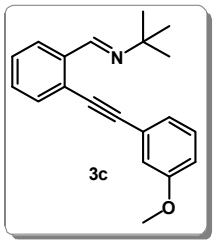


***tert*-Butyl{(1E)-[2-(phenylethynyl)phenyl]methylene}amine[9] (3a):** Brown solid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 1.35 (s, 9H), 7.36-7.39 (m, 5H), 7.53-7.56 (m, 3H), 8.06-8.93 (dd, 1H), 8.93 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{19}H_{19}N$ $(M+H)^+$: 262.3; Found: 262.1 $(M+H)^+$.

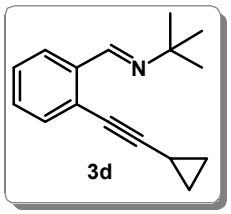


***tert*-Butyl((1E)-{2-[(2-methylphenyl)ethynyl]phenyl}methylene)amine (3b):** Yellow Solid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 1.34 (s, 9H), 2.56 (s, 3H), 7.20-7.27 (m, 1H),

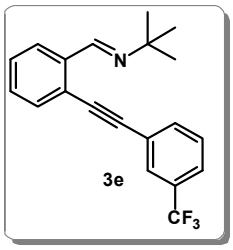
7.27-7.28 (t, 1H), 7.37- 7.40 (m, 2H), 7.51-7.53 (d, 1H), 7.56-7.59 (m, 1H), 8.09-8.10 (dd, 1H), 8.93 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{20}H_{21}N$ (M^+): 276.3; Found: 276.1 $(M+H)^+$.



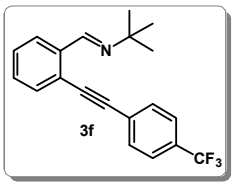
***N*-((1E)-{2-[3-Methoxyphenyl)ethynyl]phenyl}methylene)-2-methyl propan-2-amine (3c):** Yellowish oil. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 1.35 (s, 9H), 3. 84 (s, 3H), 6.93-6.95 (t, 1H), 7.07 (s, 1H), 7.13-7.15 (d, 1H), 7.27-7.31 (m, 1H), 7.37-7.39 (m, 2H), 7.55-7.57 (t, 1H), 7.65-7.67 (t, 1H), 8.07-8.09 (dd, 1H), 8.93 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{20}H_{21}NO$ $(M+H)^+$: 292.3; Found: 292.2 $(M+H)^+$.



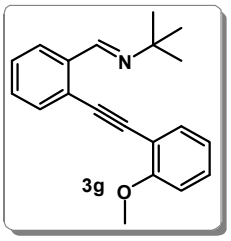
1-(Cyclopropylethynyl)-2-[(1E)-3,3-dimethylbut-1-en-1-yl]benzene (3d): Colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 0.90-0.92 (m, 2H), 0.93-0.95 (m, 2H), 1.31 (s, 9H), 1.46-1.53 (m, 1H), 7.25-7.31 (m, 1H), 7.36-7.40 (m, 2H), 7.97-8.01 (m, 1H), 8.75 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{19}N$ $(M+H)^+$: 226.3; Found: 226.2 $(M+H)^+$.



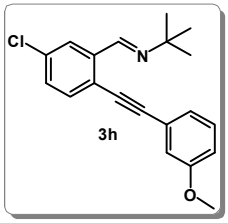
***tert*-Butyl[(1E)-(2-{[3-(trifluoromethyl)phenyl]ethynyl}phenyl)methylene]amine (3e):** Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 1.36 (s, 9H), 7.38-7.39 (m, 2H), 7.51-7.53 (t, 1H), 7.55-7.57 (d, 1H), 7.58-7.63 (m, 1H), 7.69-7.71 (d, 1H), 7.80 (s, 1H), 8.08-8.10 (dd, 1H), 8.93 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{20}H_{18}F_3N$ $(M+H)^+$: 330.3; Found: 330.0 $(M+H)^+$.



***tert*-Butyl[(1E)-(2-{[4-(trifluoromethyl)phenyl]ethynyl}phenyl)methylene]amine[10] (3f):** Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 1.37 (s, 9H), 7.39-7.42 (m, 2H), 7.56-7.58 (t, 1H), 7.62-7.68 (m, 4H), 8.08-8.10 (dd, 1H), 8.89 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{20}H_{18}F_3N$ $(M+H)^+$: 330.3; Found: 330.0 $(M+H)^+$.

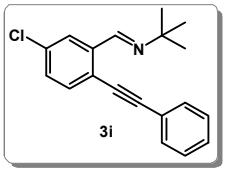


***N*-((1E)-{2-{(2-Methoxyphenyl)ethynyl]phenyl}methylene)-2-methyl propan-2-amine[11] (3g):** Yellowish oil. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 1.35 (s, 9H), 3.90 (s, 3H), 6.92-6.98 (m, 2H), 7.32-7.37 (m, 3H), 7.50-7.52 (t, 1H), 7.56-7.58 (t, 1H), 8.07-8.09 (dd, 1H), 9.01 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{20}H_{21}NO$ $(M+H)^+$: 292.3; Found: 292.2 $(M+H)^+$.

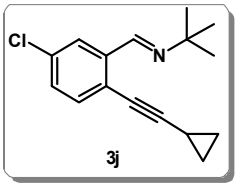


***N*-((1E)-{5-chloro-2-{(3-methoxyphenyl)ethynyl]phenyl}methylene)-2-methylpropan-2-amine (3h):** White solid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300K, TMS = 0 ppm):** δ = 1.34 (s, 9H), 3.83 (s, 3H), 6.92-6.94 (m, 1H), 7.04 (s, 1H), 7.11-7.12 (d, 1H), 7.29-7.35 (m, 2H), 7.46-7.49 (d, 1H), 8.063-8.068 (d, 1H), 8.83 (s, 1H) ppm;

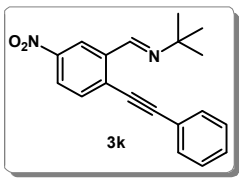
LC MS (ESI-MS): m/z calcd for $C_{20}H_{20}ClNO$ $(M+H)^+$: 326.8; Found: 326.2 $(M+H)^+$.



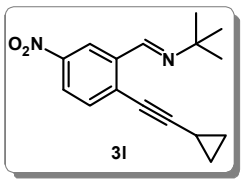
***N*-{(1E)-{5-Chloro-2-(phenylethynyl)phenyl]methylene}-2-methyl propan-2-amine (3i):** Pale yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 1.34 (s, 9H), 7.32-7.39 (m, 4H), 7.47-7.53 (m, 3H), 8.05-8.06 (d, 1H), 8.84 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{19}H_{18}ClN$ $(M+H)^+$: 296.8; Found: 296.2 $(M+H)^+$.



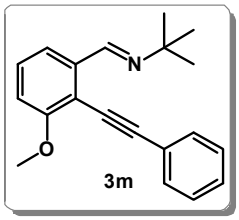
***N*-{(1E)-{5-Chloro-2-(cyclopropylethynyl)phenyl]methylene}-2-methylpropan-2-amine (3j):** Light brown solid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 0.91-0.92 (m, 2H), 0.93-0.95 (m, 2H), 1.30 (s, 9H), 1.47-1.51 (m, 1H), 7.22-7.26 (m, 1H), 7.26-7.31 (t, 1H), 7.97 (s, 1H), 8.65 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{16}H_{18}ClN$ $(M+H)^+$: 260.7; Found: 260.1 $(M+H)^+$.



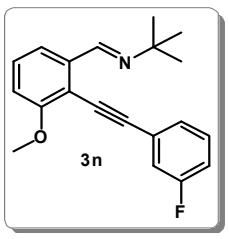
***tert*-Butyl{(1E)-[5-nitro-2-(phenylethynyl)phenyl]methylene} amine (3k):** Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 1.36 (s, 9H), 7.41-7.44 (m, 3H), 7.55-7.57 (dd, 2H), 7.68-7.70 (d, 1H), 8.19-8.21 (dd, 1H), 8.88 (s, 1H), 8.92 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{19}H_{18}N_2O_2$ $(M+H)^+$: 307.3; Found: 307.0 $(M+H)^+$.



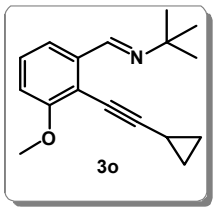
***N*-{(1E)-[2-(Cyclopropylethynyl)-5-nitrophenyl]methylene}-2-methylpropan-2-amine (3l):** Colorless liquid. **^{1}H NMR (300 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 0.96-0.98 (m, 2H), 1.02-1.03 (m, 2H), 1.32 (s, 9H), 1.53-1.57 (m, 1H), 7.49-7.51 (d, 1H), 8.10-8.13 (dd, 1H), 8.68 (s, 1H), 8.83 (s, 1H) ppm; **GC MS:** m/z calcd for $C_{16}H_{18}N_2O_2$ $(M+H)^+$: 271.3; Found: 271.0 $(M+H)^+$.



***N*-{(1E)-(3-Methoxy-2-(phenylethynyl)phenyl]methylene}-2-methyl propan-2-amine (3m):** Yellowish oil. **^{1}H NMR (300 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm):** δ = 1.34 (s, 9H), 3.94 (s, 3H), 6.92-6.95 (d, 1H), 7.32-7.38 (m, 4H), 7.55-7.58 (t, 2H), 7.66-7.69 (d, 1H), 8.93 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{17}H_{21}NO$ $(M+H)^+$: 256.3; Found: 256.2 $(M+H)^+$.



***N*-((1E)-{2-[(3-Fluorophenyl)ethynyl]-3-methoxyphenyl}methyl ene)-2-methylpropan-2-amine (3n):** Pale yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$, T = 300 K, TMS = 0 PPM):** δ = 1.34 (s, 9H), 3.98 (s, 3H), 6.93-6.95 (d, 1H), 7.02-7.09 (m, 1H), 7.23-7.26 (m, 1H), 7.29-7.37 (m, 3H), 7.66-7.69 (d, 1H), 8.88 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{20}H_{20}FNO$ $(M+H)^+$: 310.3; Found: 310.1 $(M+H)^+$.



***N*-{(1E)-[2-(Cyclopropylethynyl)-3-methoxyphenyl]methylene-2-methylpropan-2-amine (3o):** Colorless liquid. **^{1}H NMR (300 MHz, $CDCl_3$, T = 300 K, TMS = 0 PPM):** δ = 0.90-0.92 (m, 2H), 0.94-0.97 (m, 2H), 1.26 (s, 9H), 1.51-1.63 (m, 1H), 3.92 (s, 3H), 6.86-6.88 (d, 1H), 7.21-7.26 (t, 1H), 7.58-7.61 (d, 1H), 8.73 (s, 1H) ppm; **LC MS (ESI-MS):** m/z calcd for $C_{17}H_{21}NO$ $(M+H)^+$: 256.3; Found: 256.0 $(M+H)^+$.

3. ^{1}H & ^{13}C NMR spectra of substituted isoquinolines

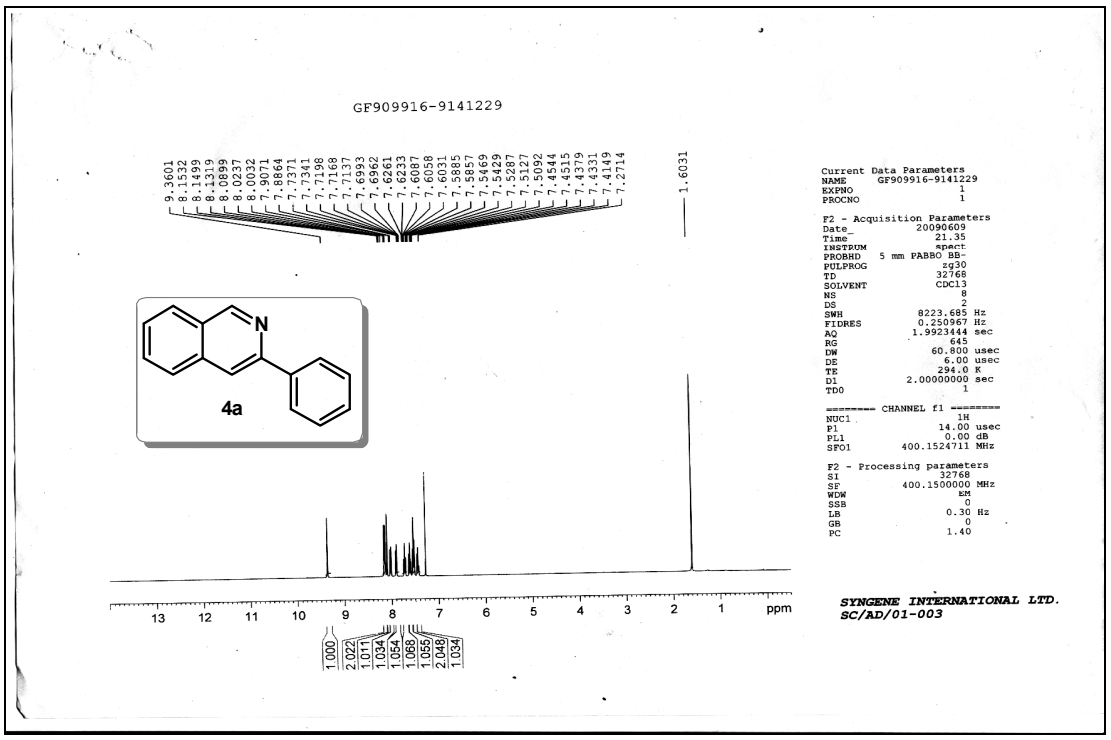


Figure S5. *^{1}H-NMR spectrum of 3-phenylisoquinoline* ***(4a)*** *(Table 1, entry 1).*

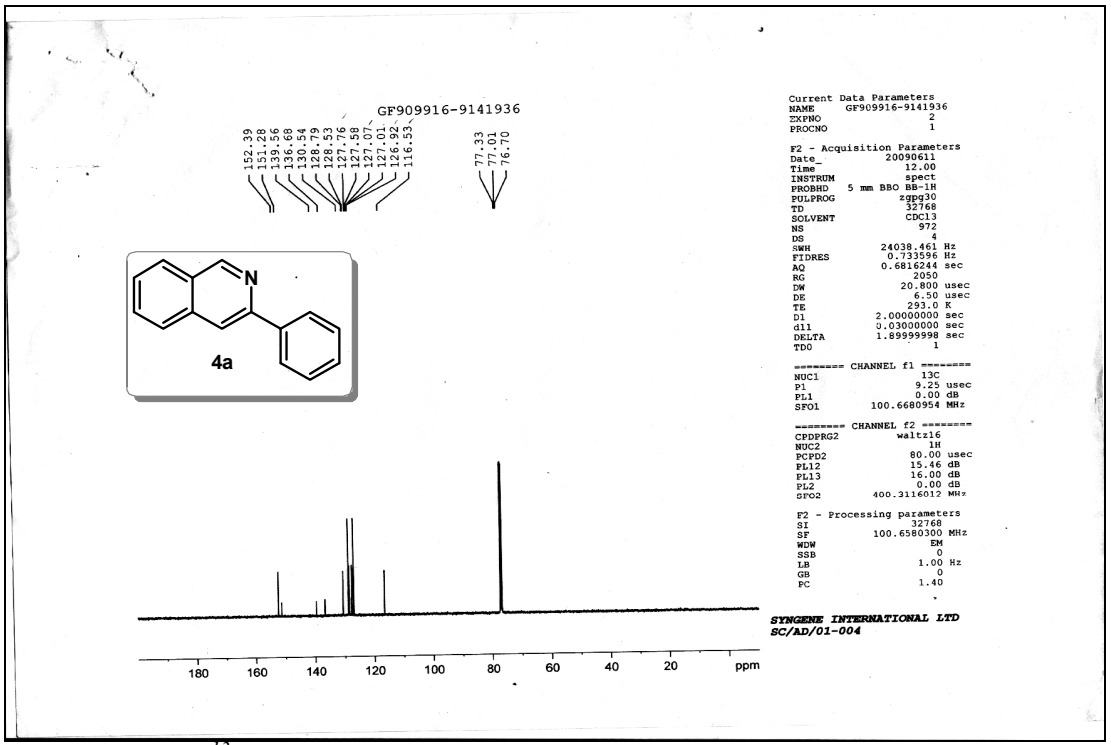


Figure S6. *^{13}C-NMR spectrum of 3-phenylisoquionline* ***(4a)*** *(Table 2, entry 1).*

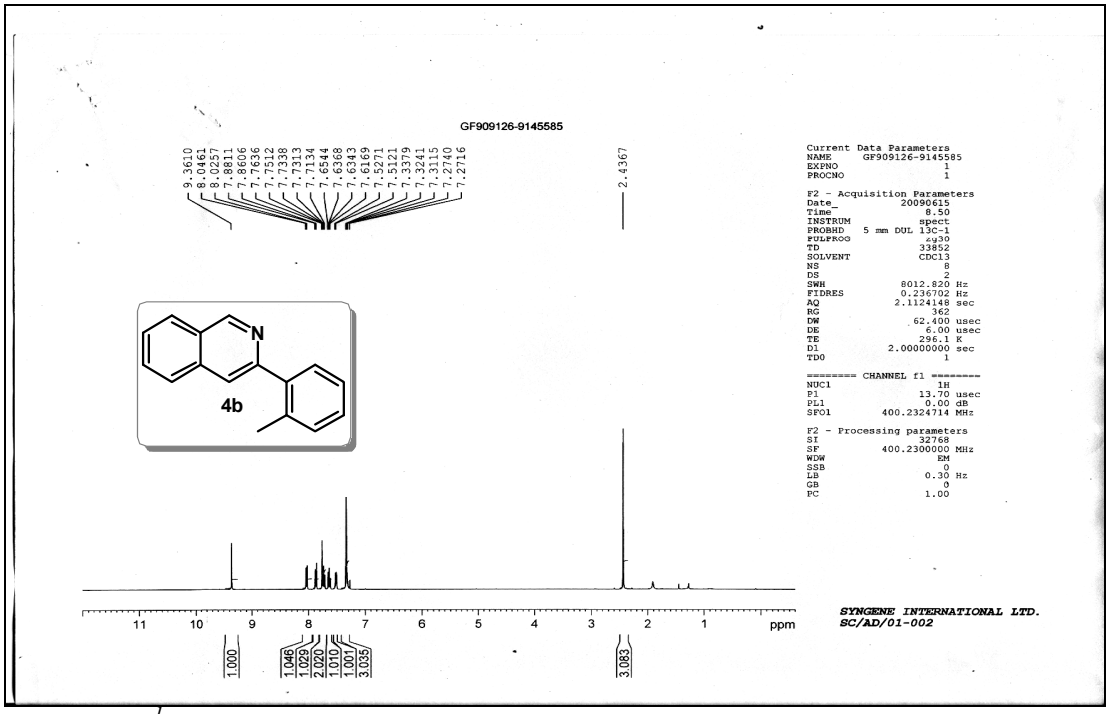


Figure S7. *^{1}H-NMR spectrum of 3-(2-methylphenyl)isoquinoline* ***(4b)*** *(Table 2, entry 2)*

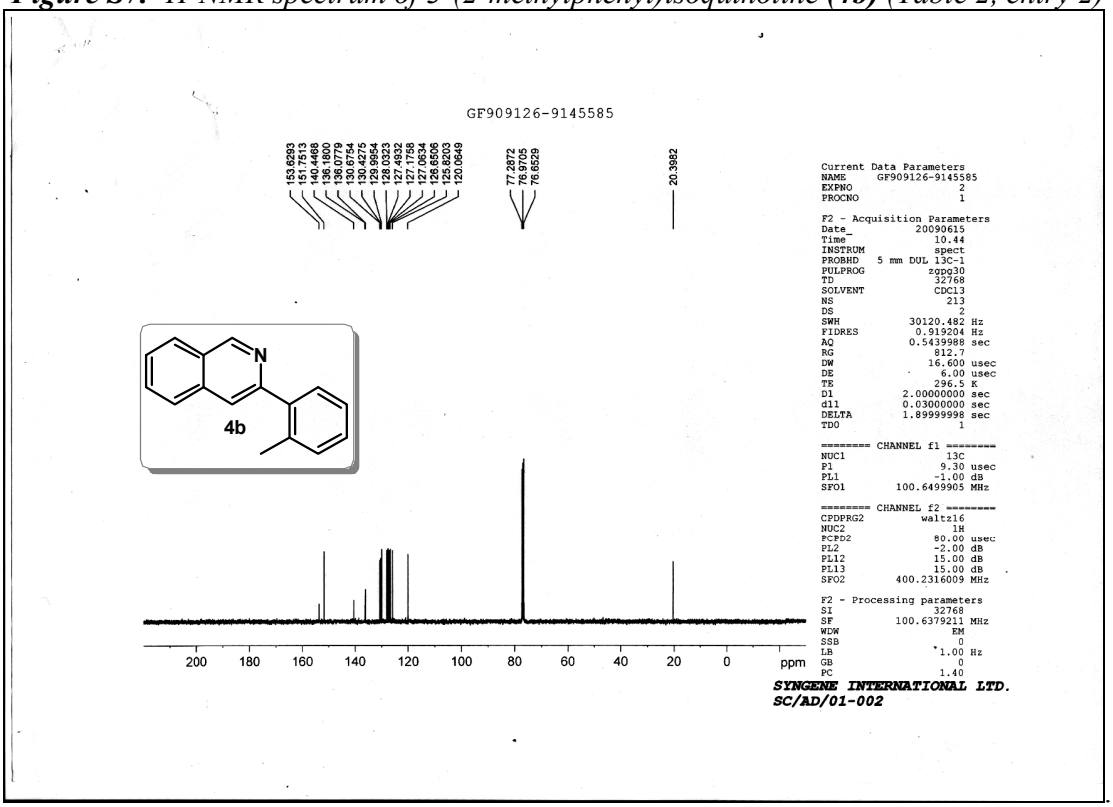


Figure S8. *^{13}C-NMR spectrum of 3-(2-methylphenyl)isoquinoline* ***(4b)*** *(Table 2, entry 2)*

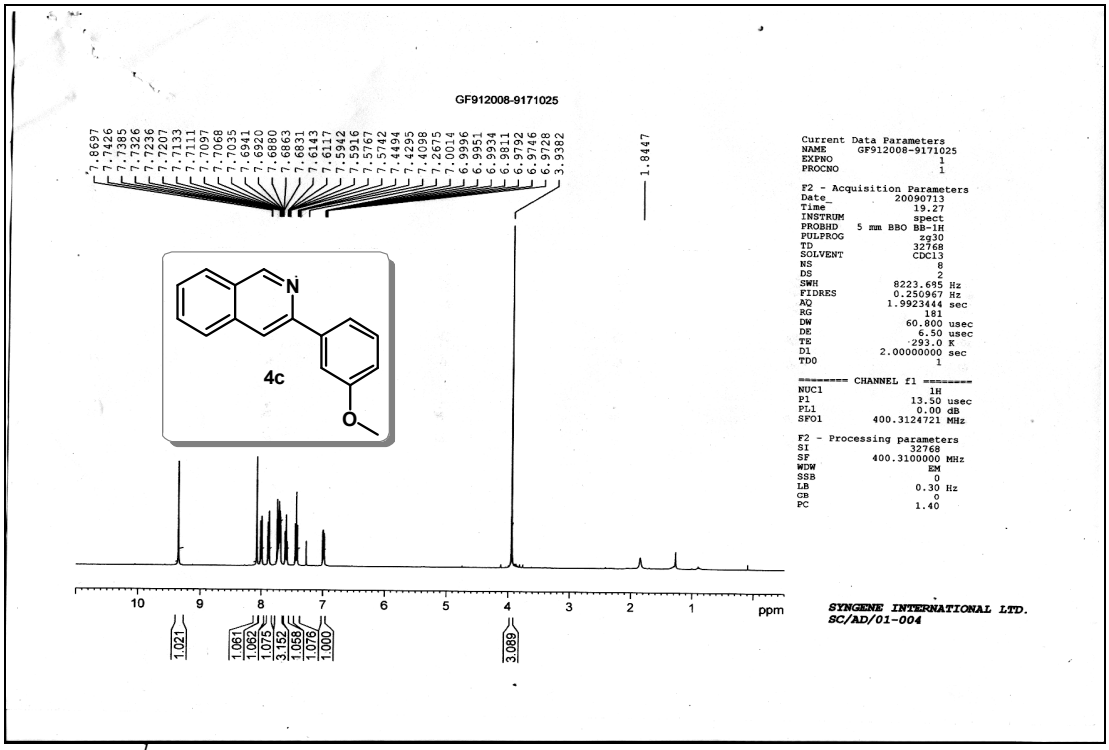


Figure S9. *^{1}H-NMR spectrum of 3-(3-methoxyphenyl)isoquinoline* ***(4c)*** *(Table 3, entry 3).*

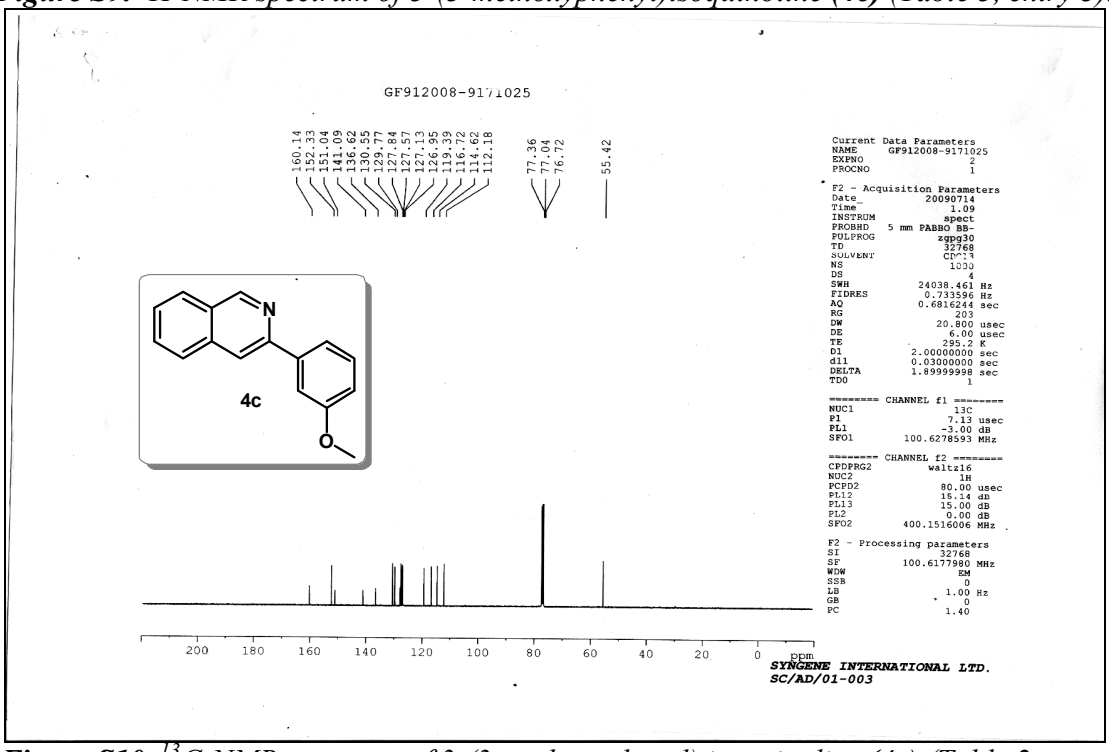


Figure S10. *^{13}C-NMR spectrum of 3-(3-methoxyphenyl) isoquinoline* ***(4c)*** *(Table 2, entry 3).*

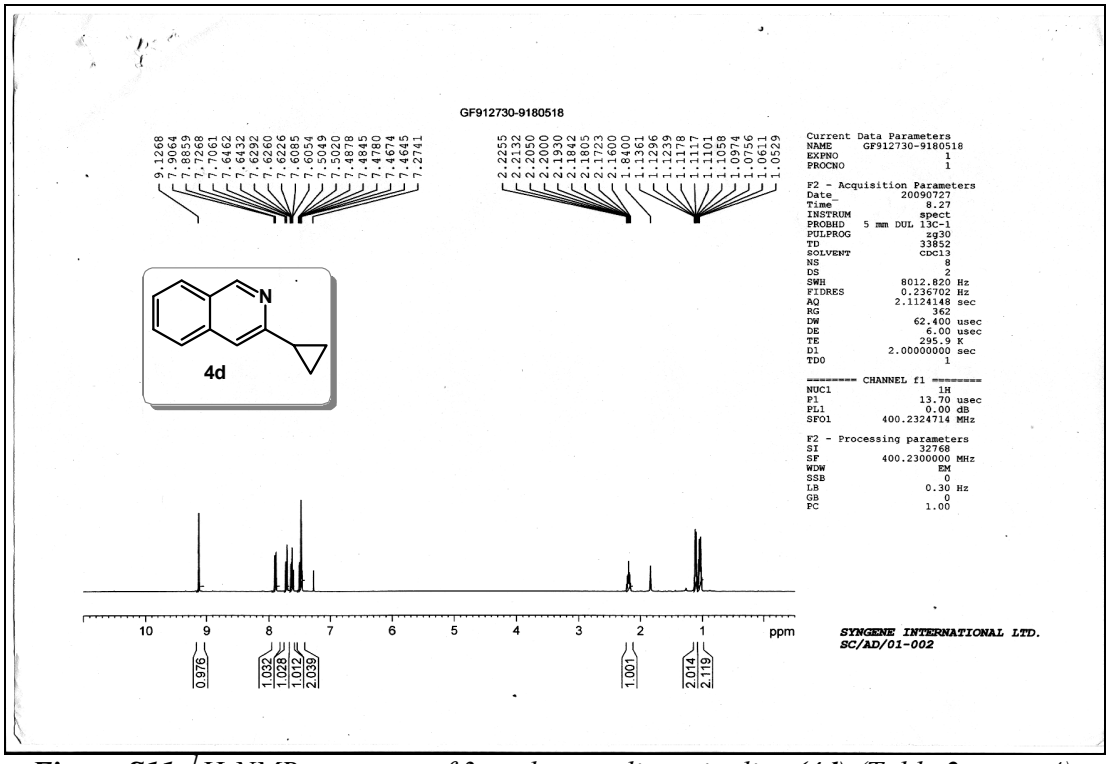


Figure S11. *^{1}H-NMR spectrum of 3-cyclopropylisoquinoline* ***(4d)*** *(Table 2, entry 4).*

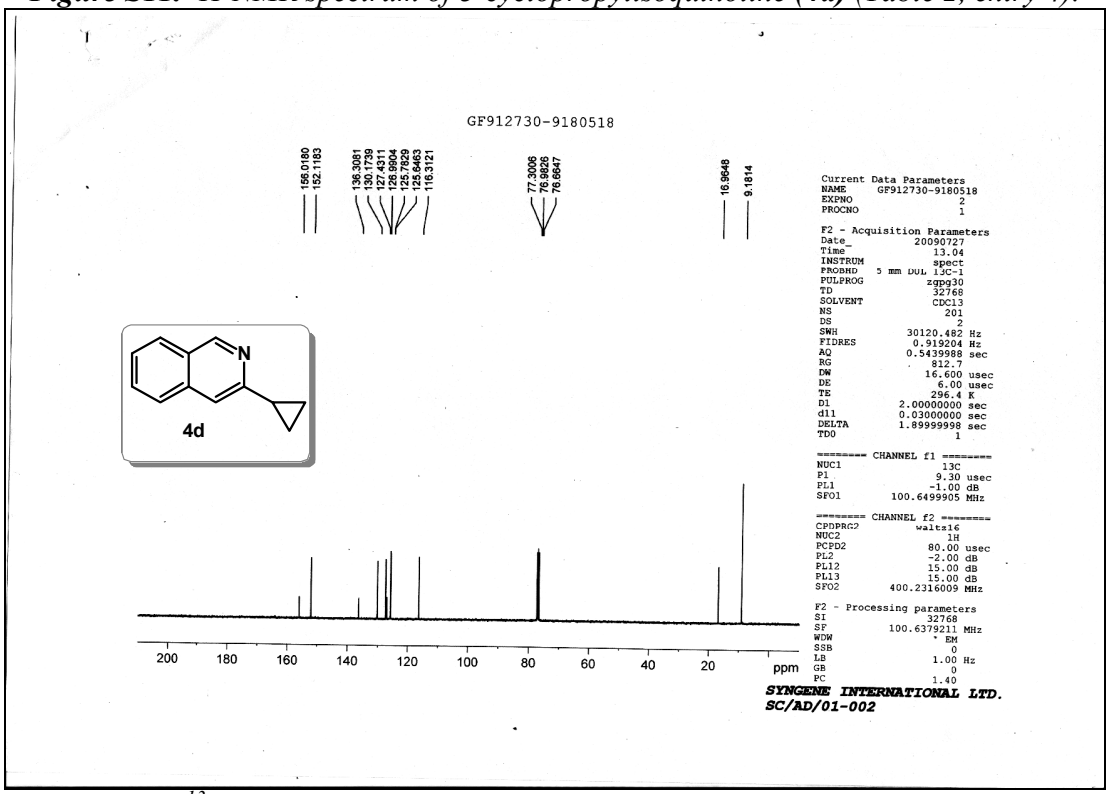


Figure S12. *^{13}C-NMR spectrum of 3-cyclopropylisoquinoline* ***(4d)*** *(Table 2, entry 4).*

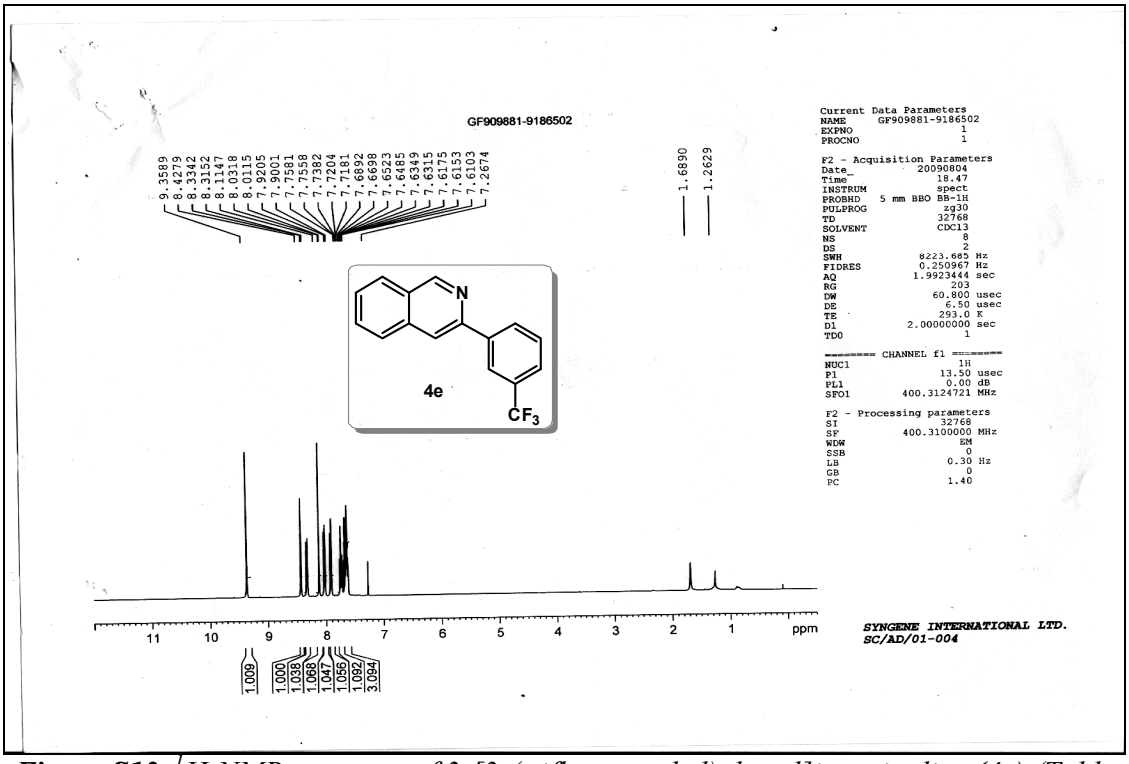


Figure S13. *^{1}H-NMR spectrum of 3-[3-(trifluoromethyl)phenyl]isoquinoline* ***(4e)*** *(Table 2, entry 5).*

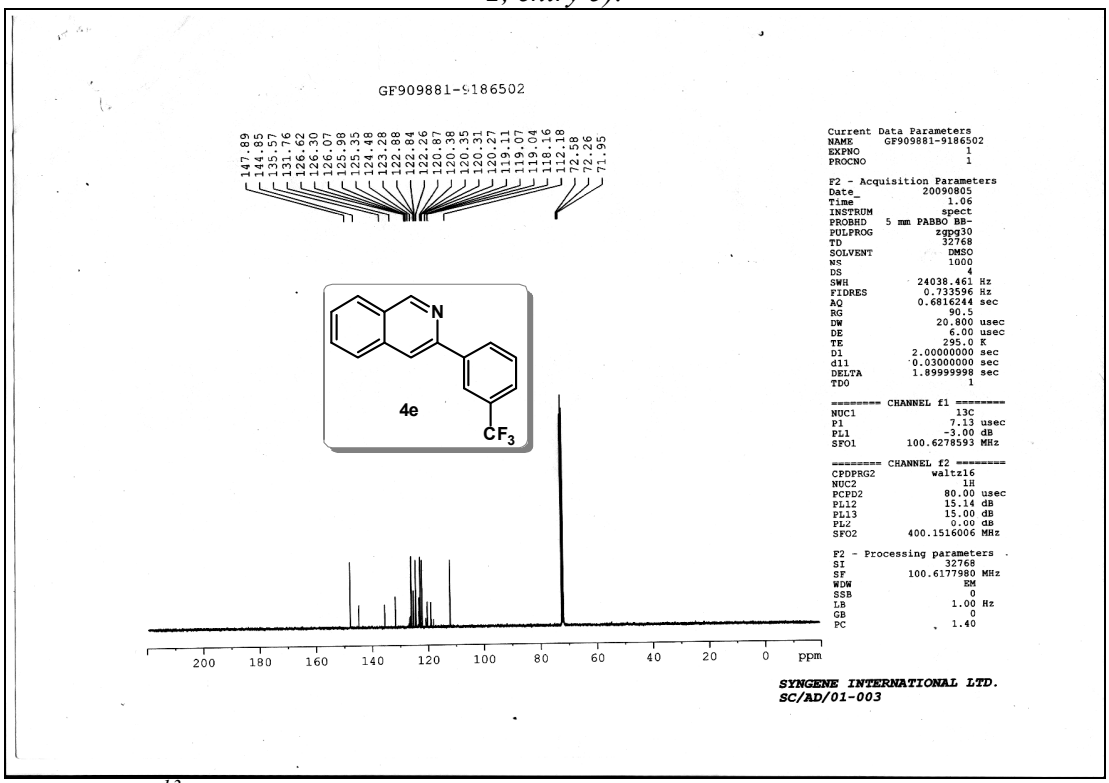


Figure S14. *^{13}C-NMR spectrum of 3-[3-(trifluoromethyl)phenyl]isoquinoline* ***(4e)*** *(Table 2, entry 5).*

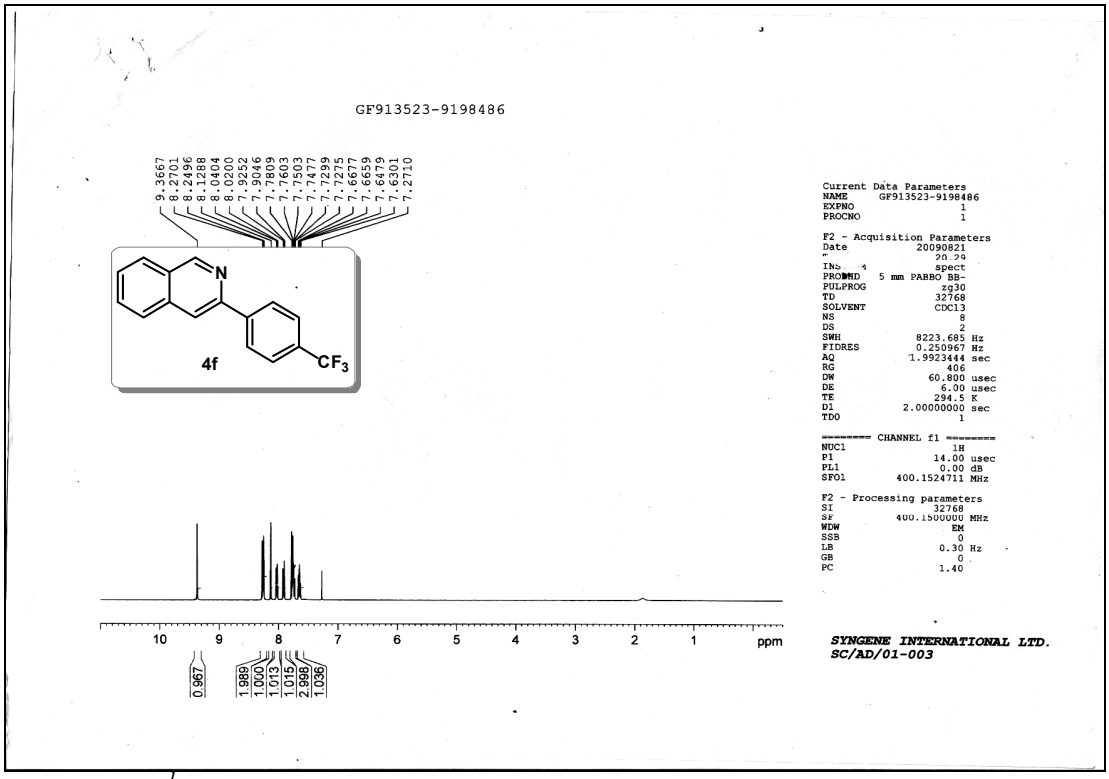


Figure S15. *^{1}H-NMR spectrum of 3-[4-(trifluoromethyl)phenyl]isoquinoline* ***(4f)*** *(Table 2, entry 6).*

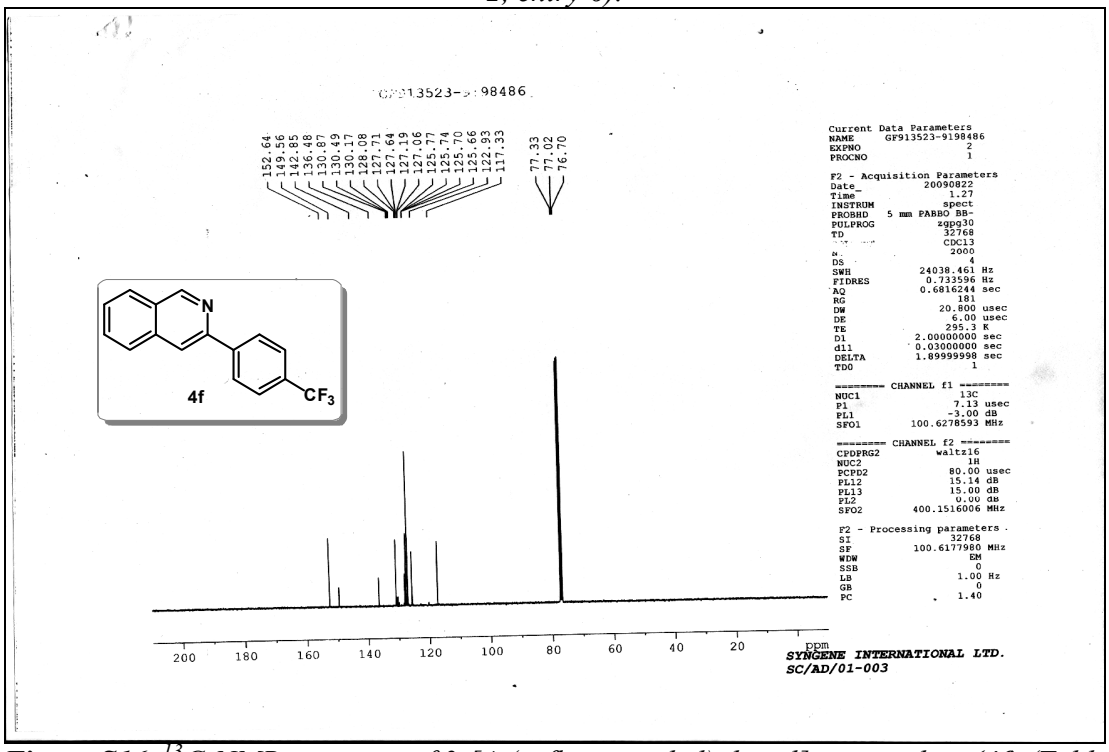


Figure S16. *^{13}C-NMR spectrum of 3-[4-(trifluoromethyl)phenyl]isoquinoline* ***(4f)*** *(Table 2, entry 6).*

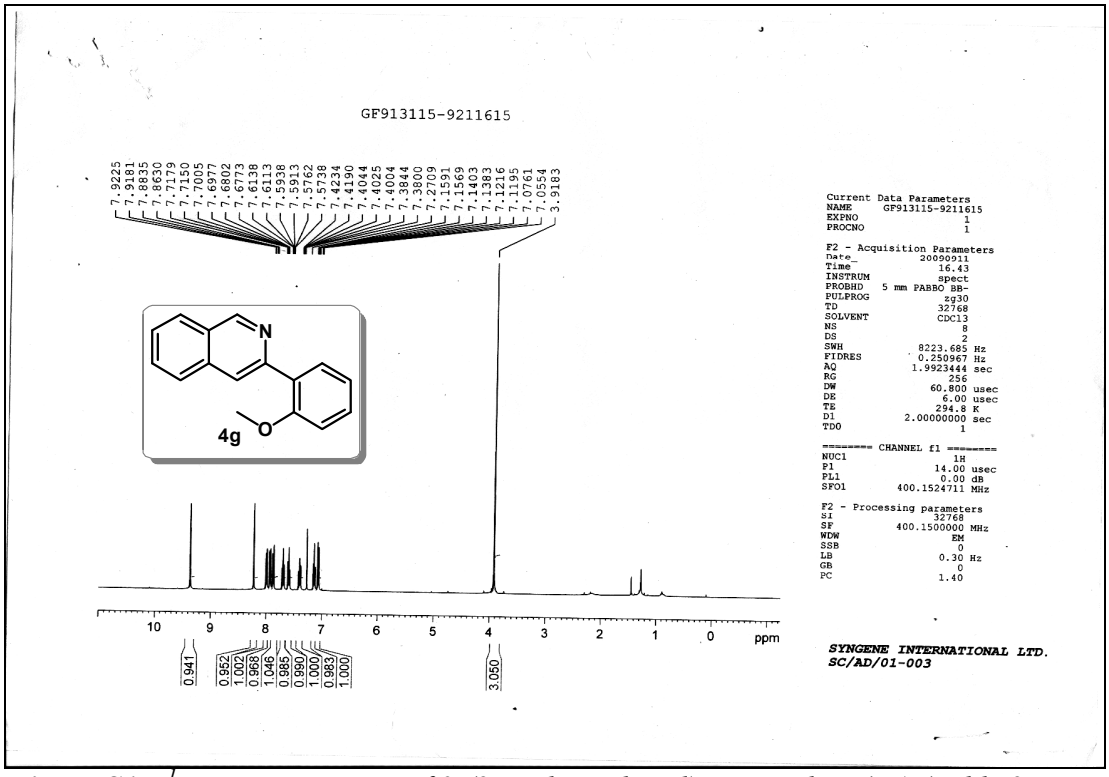


Figure S17. *^{1}H-NMR spectrum of 3-(2-methoxyphenyl)isoquinoline* ***(4g)*** *(Table 2, entry 7).*

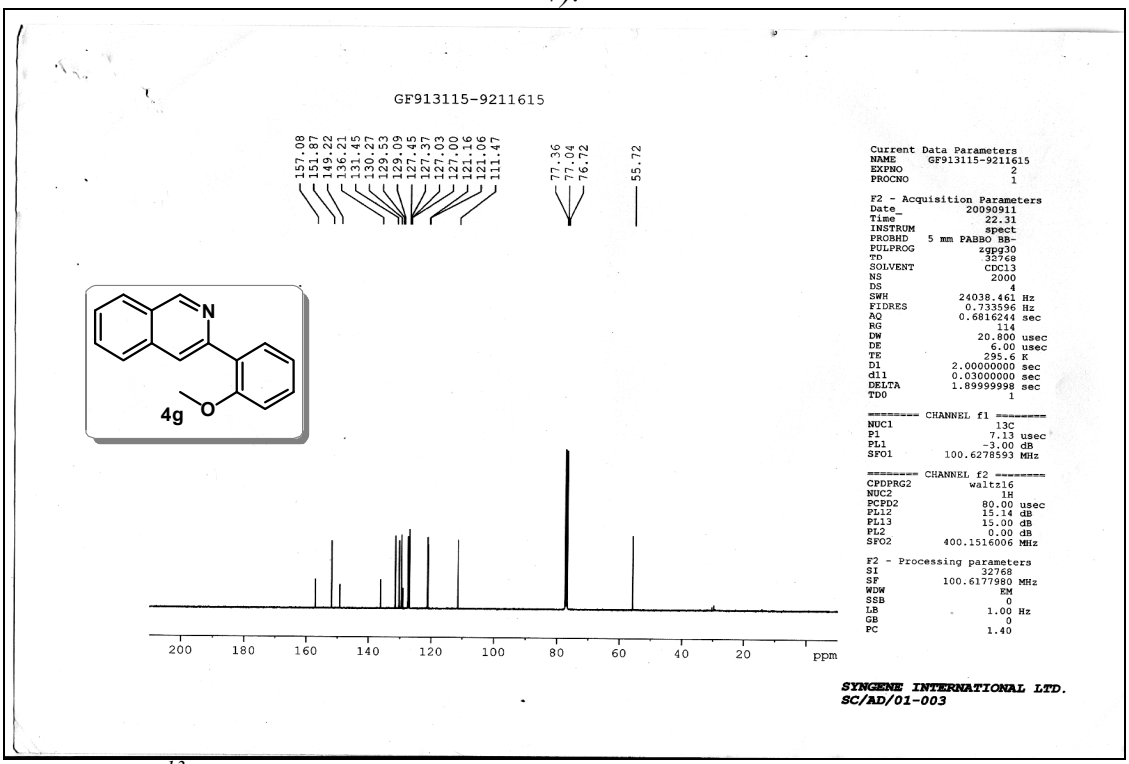


Figure S18. *^{13}C-NMR spectrum of* ***3-(2-methoxyphenyl)isoquinoline (4g)*** *(Table 2, entry 7).*

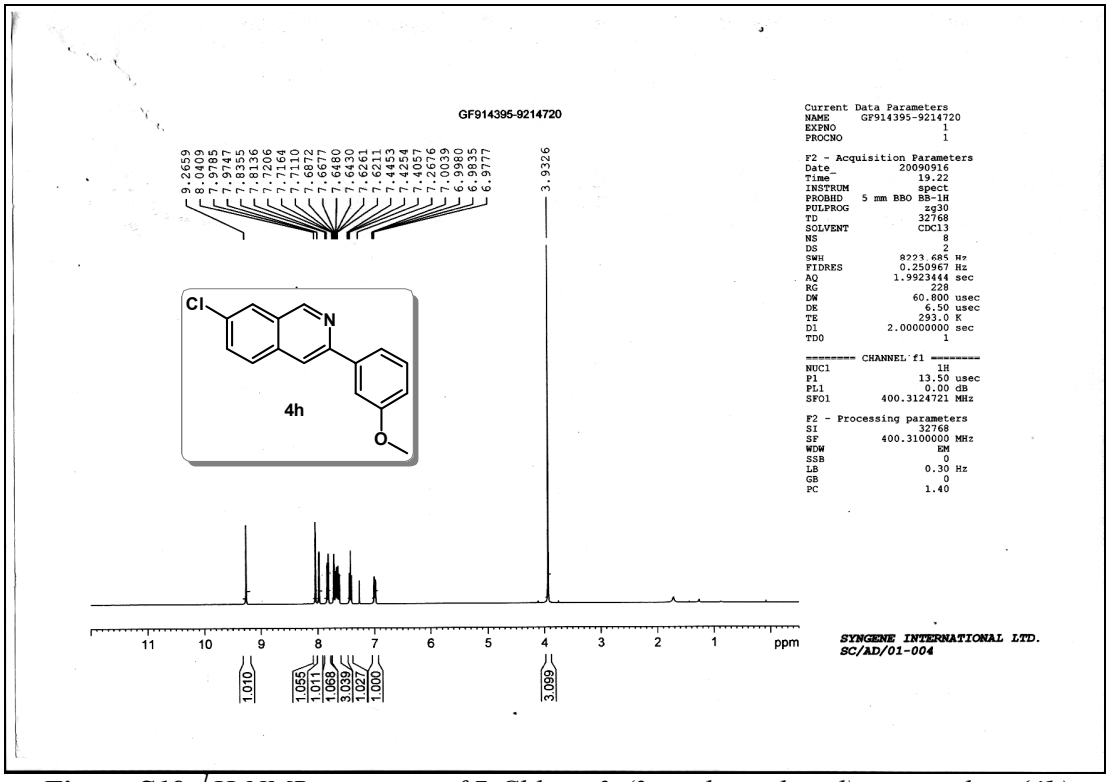


Figure S19. *^{1}H-NMR spectrum of 7-Chloro-3-(3-methoxyphenyl)isoquinoline* ***(4h)*** *(Table 2, entry 8).*

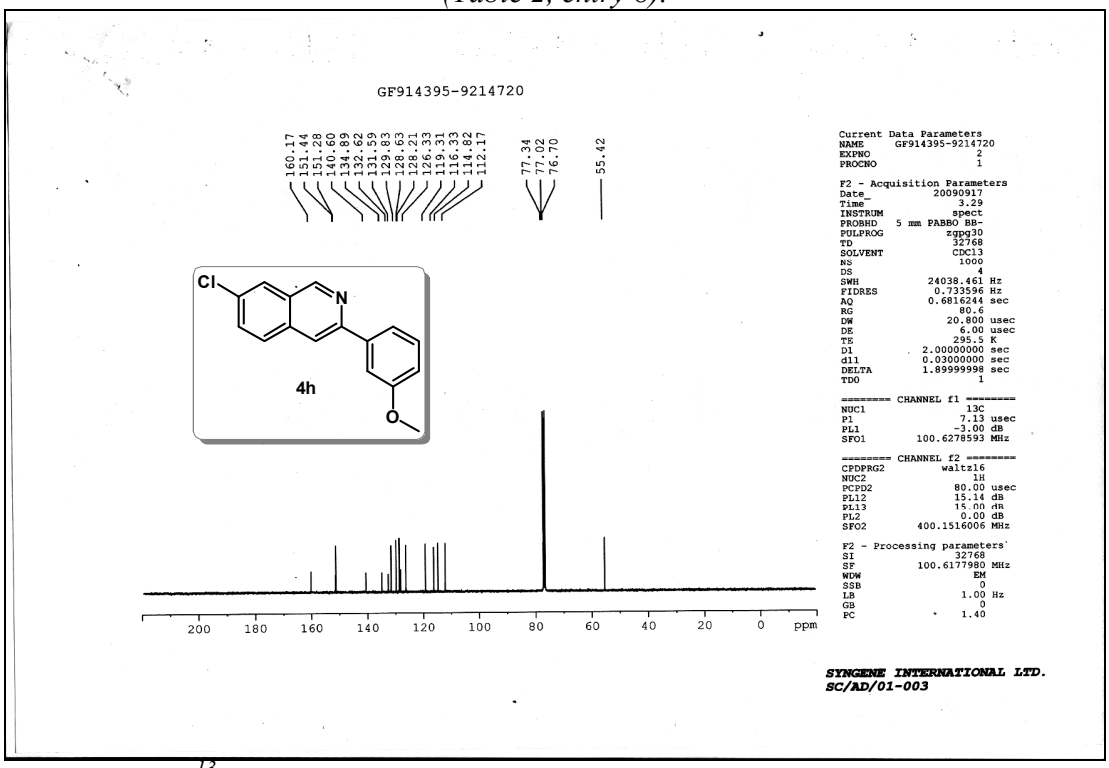


Figure S20. *^{13}C-NMR spectrum of 7-Chloro-3-(3-methoxyphenyl)isoquinoline* ***(4h)*** *(Table 2, entry 8).*

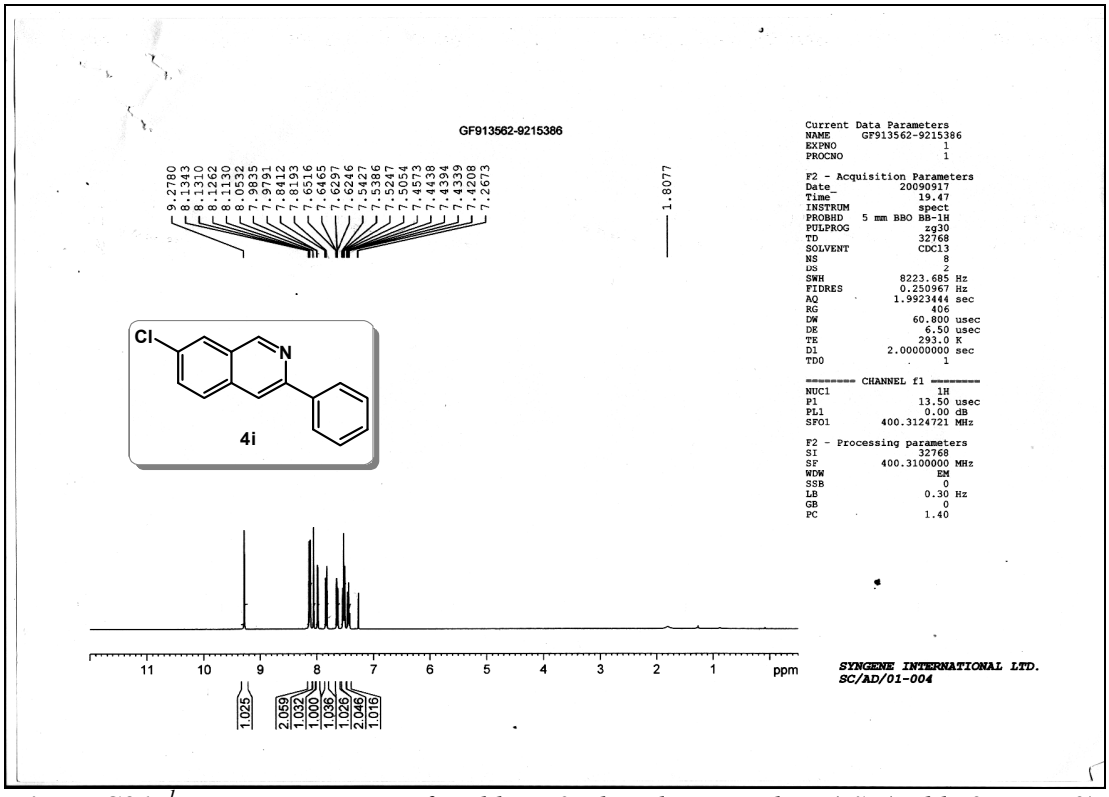


Figure S21. *[1]H-NMR spectrum of 7-chloro-3-phenylisoquinoline* ***(4i)*** *(Table 2, entry 9).*

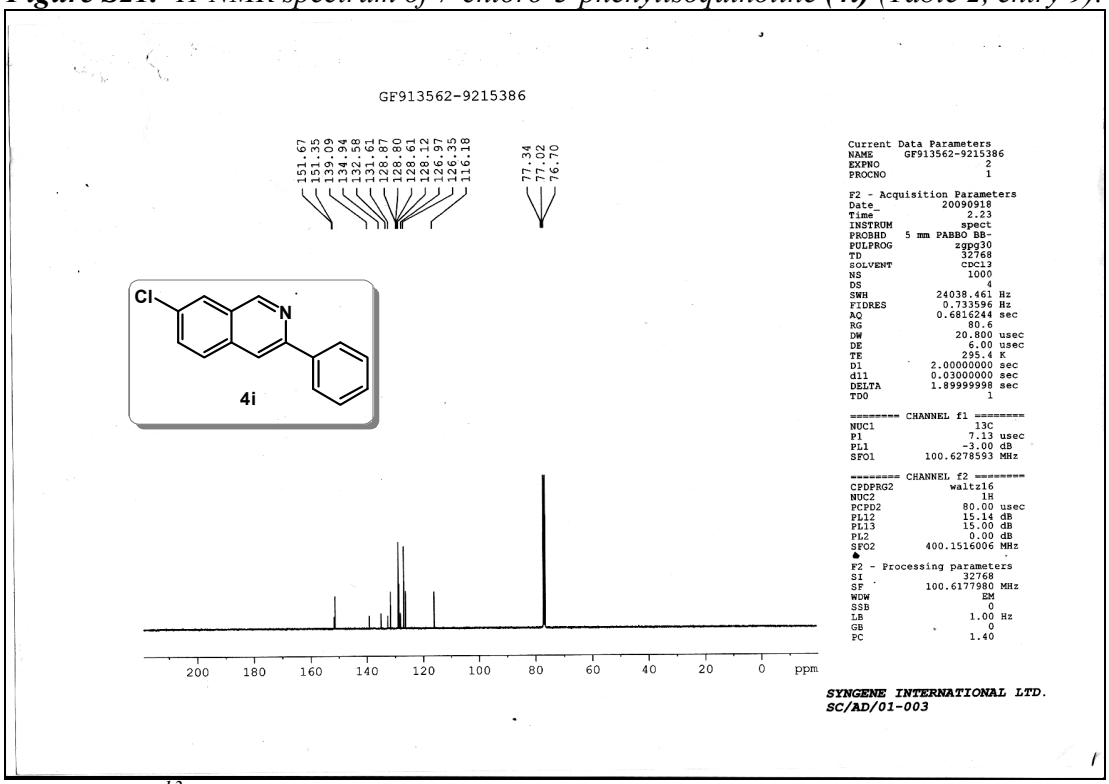


Figure S22. *[13]C-NMR spectrum of 7-chloro-3-phenylisoquinoline* ***(4i)*** *(Table 2, entry 9).*

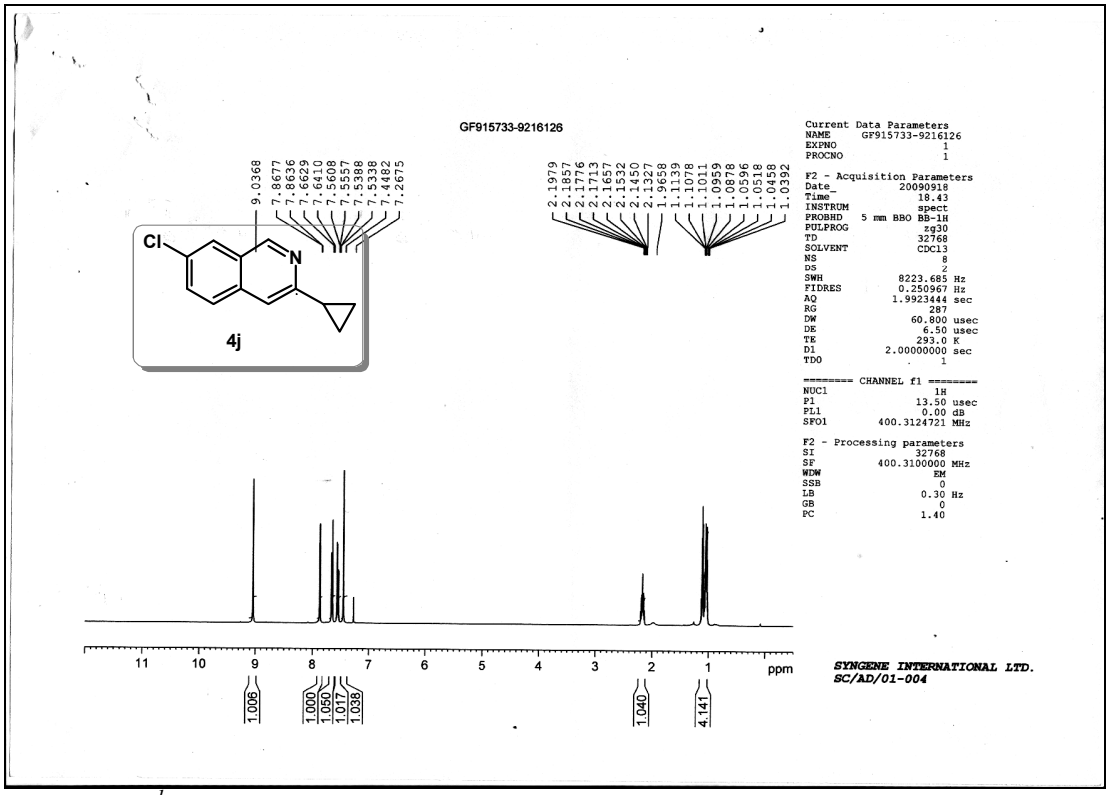


Figure S23. *^{1}H-NMR spectrum of 7-chloro-3-cyclopropylisoquinoline* ***(4j)*** *(Table 2, entry 10).*

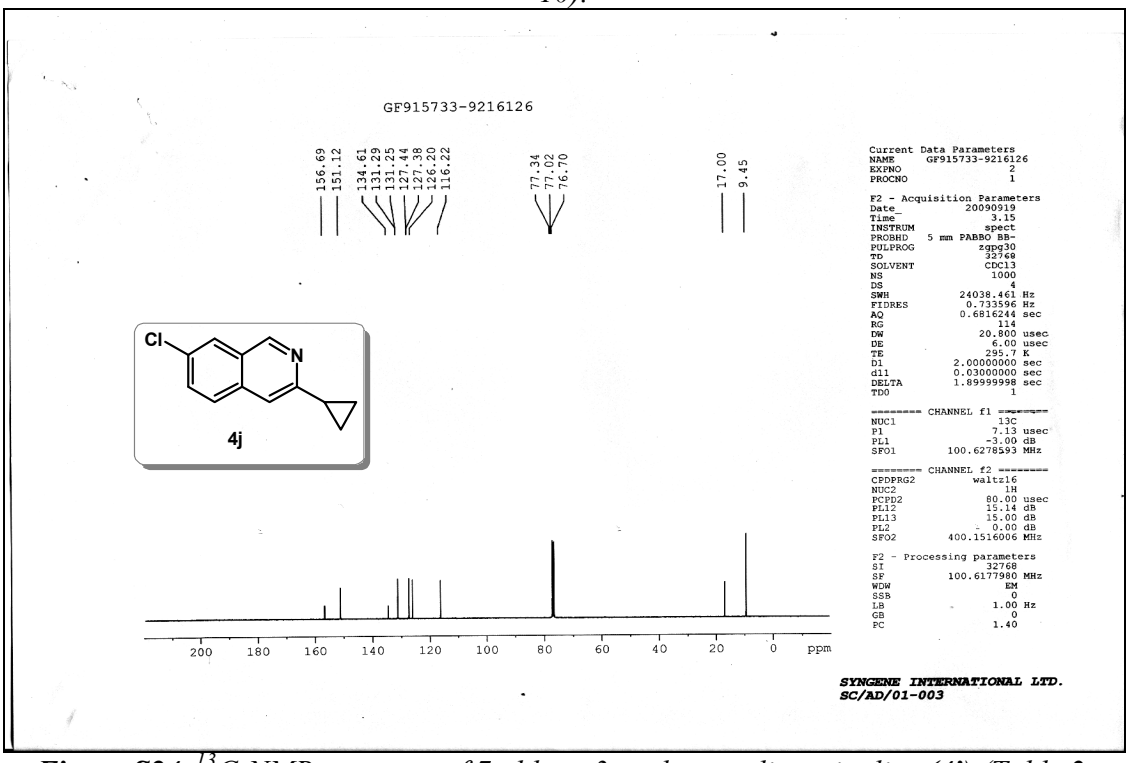


Figure S24. *^{13}C-NMR spectrum of 7-chloro-3-cyclopropylisoquinoline* ***(4j)*** *(Table 2, entry 10).*

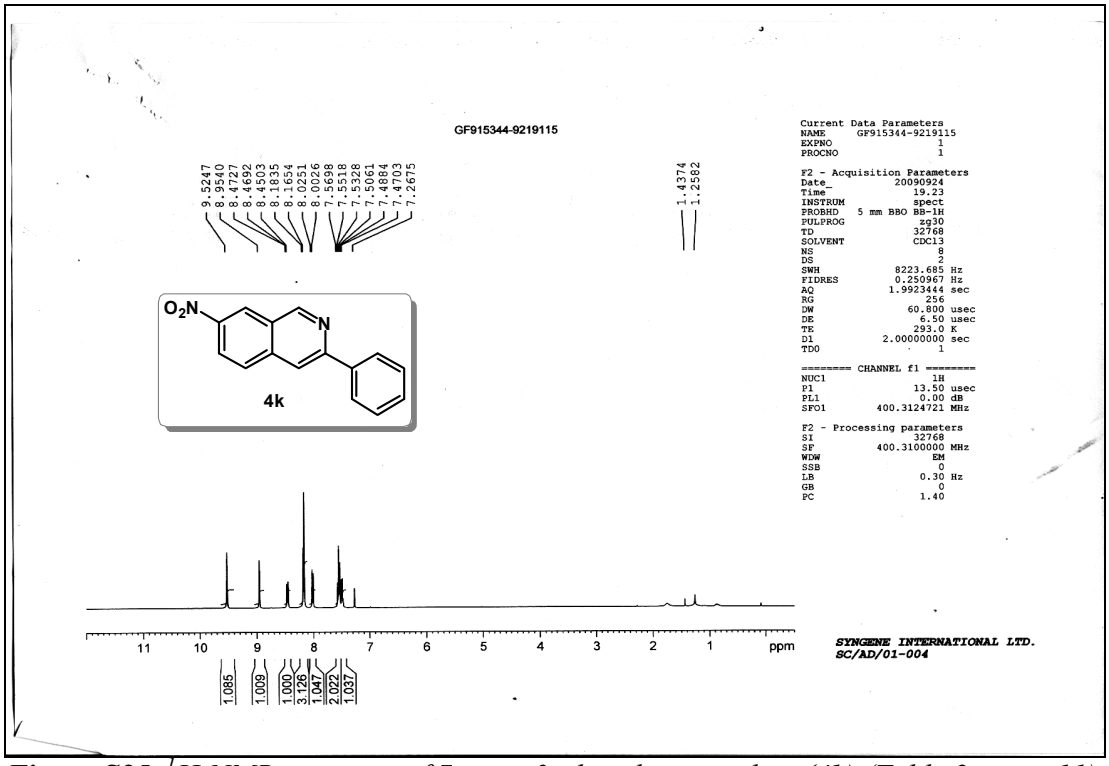


Figure S25. *^{1}H-NMR spectrum of 7-nitro-3-phenylisoquinoline* ***(4k)*** *(Table 2, entry 11).*

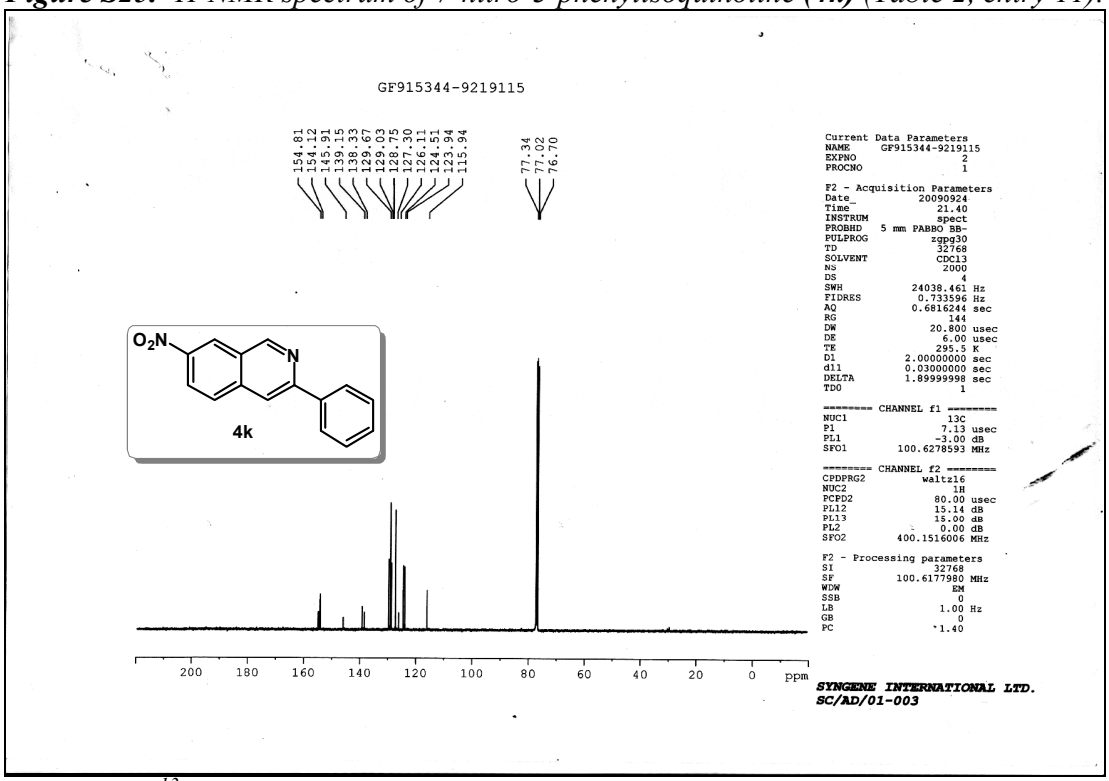


Figure S26. *^{13}C-NMR spectrum of 7-Nitro-3-phenylisoquinoline* ***(4k)*** *(Table 2, entry 11).*

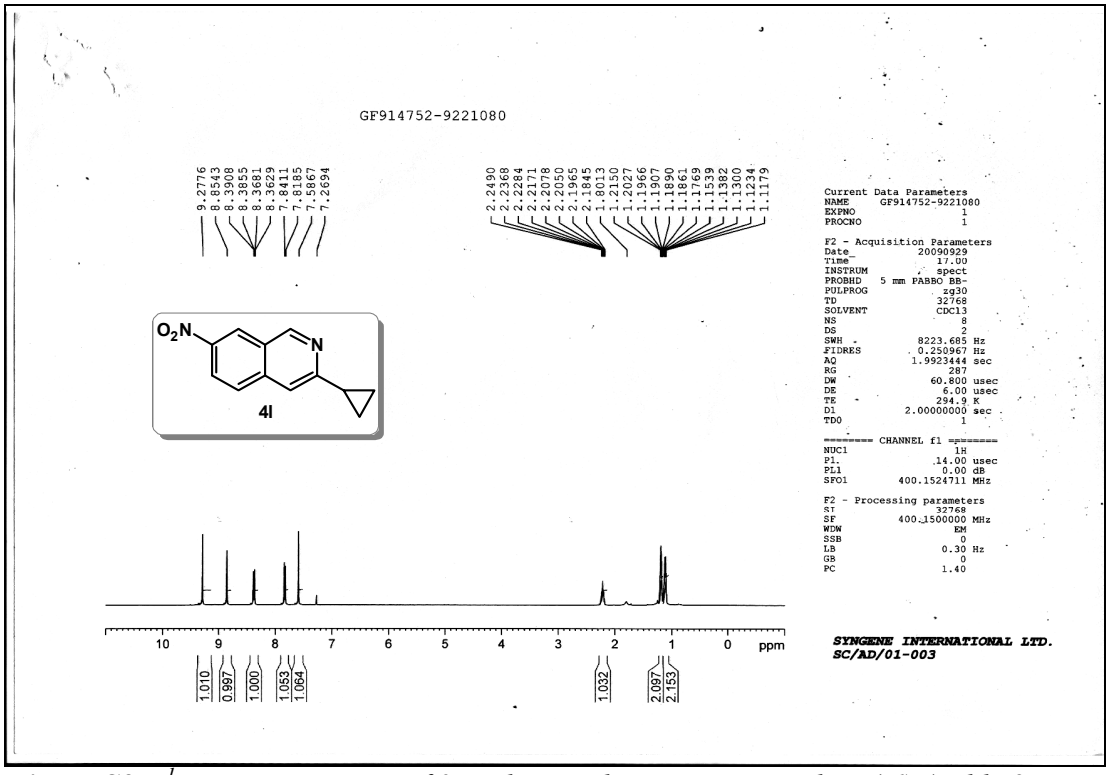


Figure S27. *^{1}H-NMR spectrum of 3-cyclopropyl-7-nitroisoquinoline* ***(4l)*** *(Table 2, entry 12).*

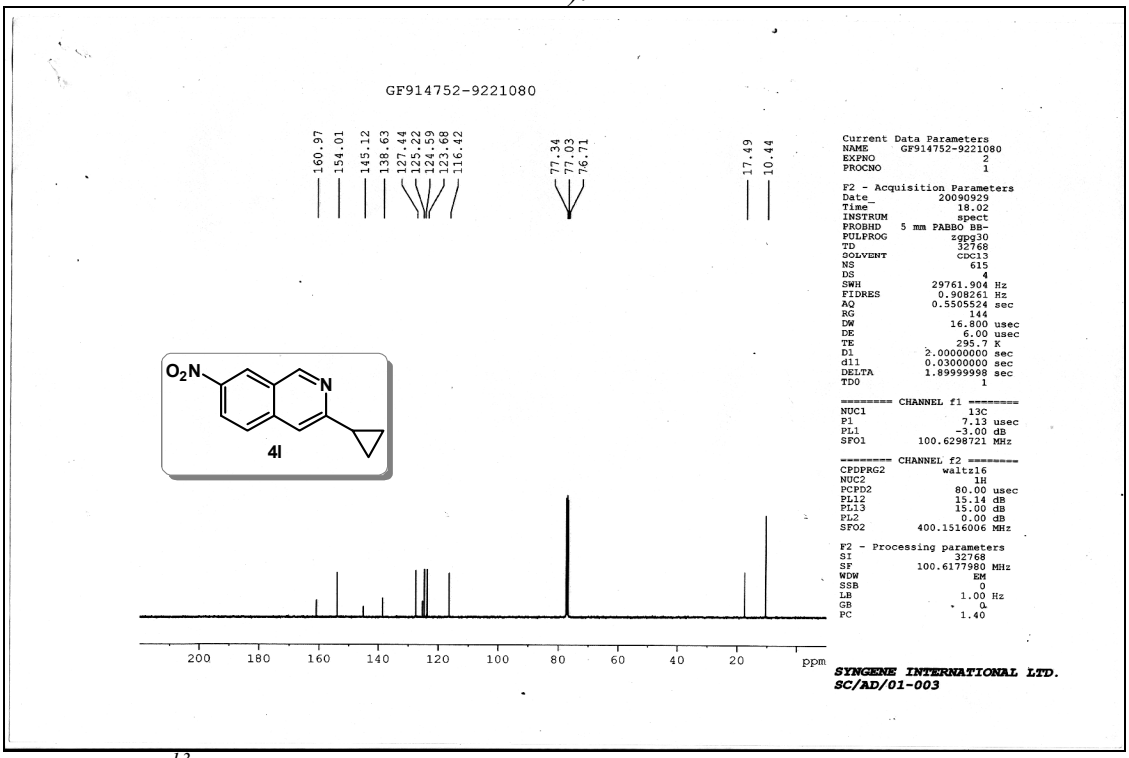


Figure S28. *^{13}C-NMR spectrum of 3-cyclopropyl-7-nitroisoquinoline* ***(4l)*** *(Table 3, entry 12).*

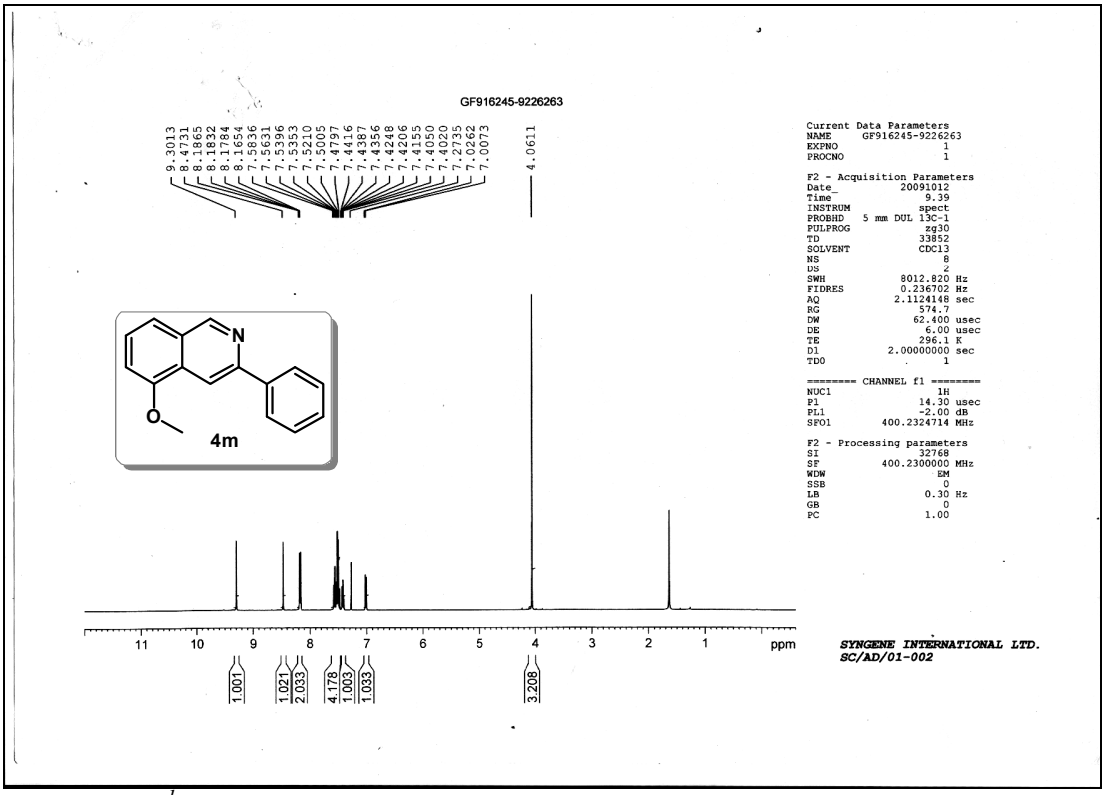


Figure S29. *[1]H-NMR spectrum of 5-methoxy-3-phenylisoquinoline* ***(4m)*** *(Table 2, entry 13).*

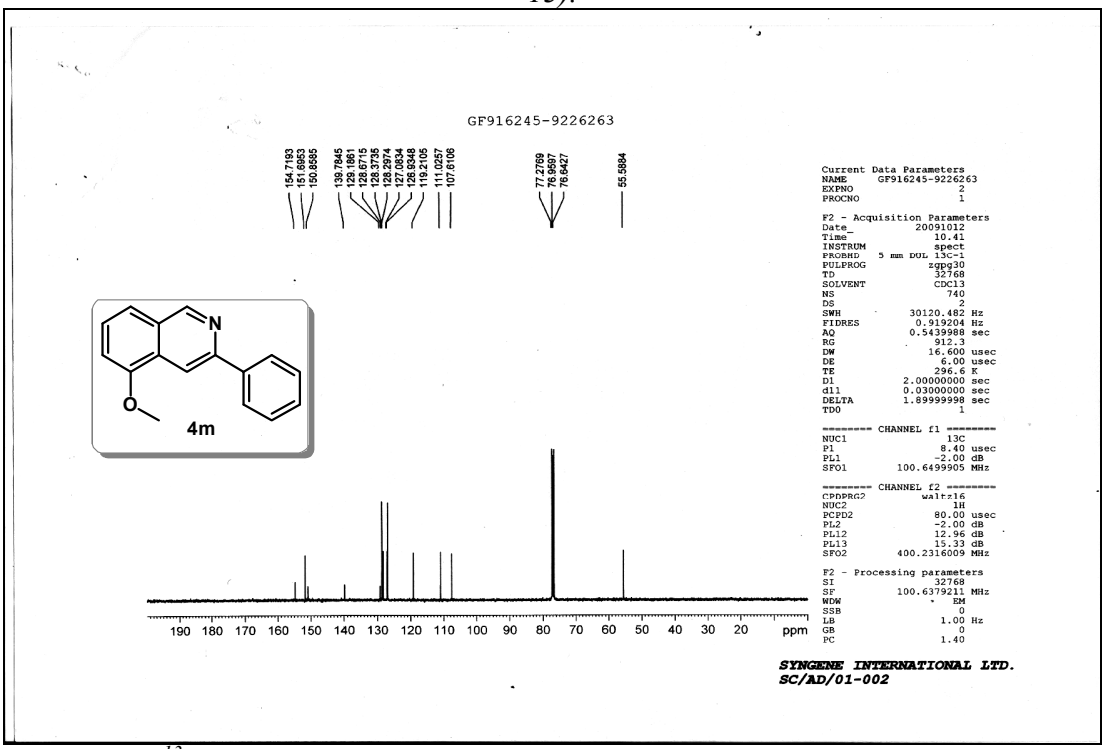


Figure S30. *[13]C-NMR spectrum of 5-methoxy-3-phenylisoquinoline* ***(4m)*** *(Table 2, entry 13).*

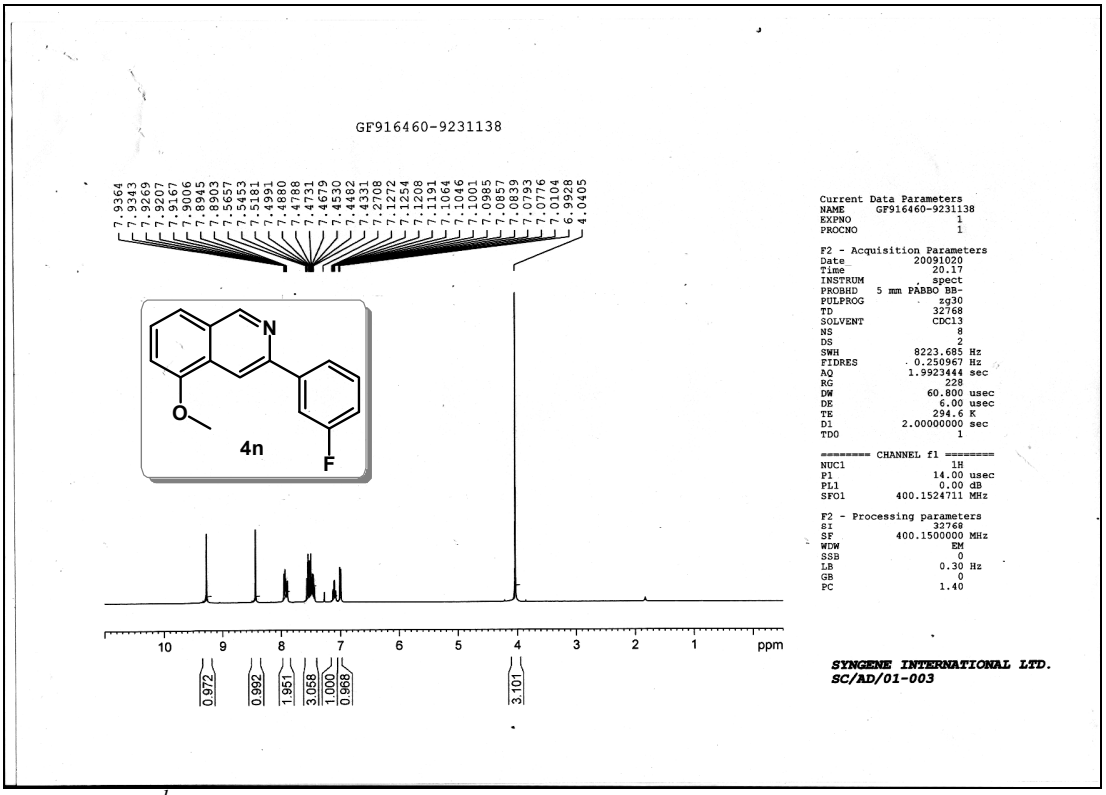


Figure S31. *^{1}H-NMR spectrum of 3-(3-fluorophenyl)-5-methoxyisoquinoline* ***(4n)*** *(Table 2, entry 14).*

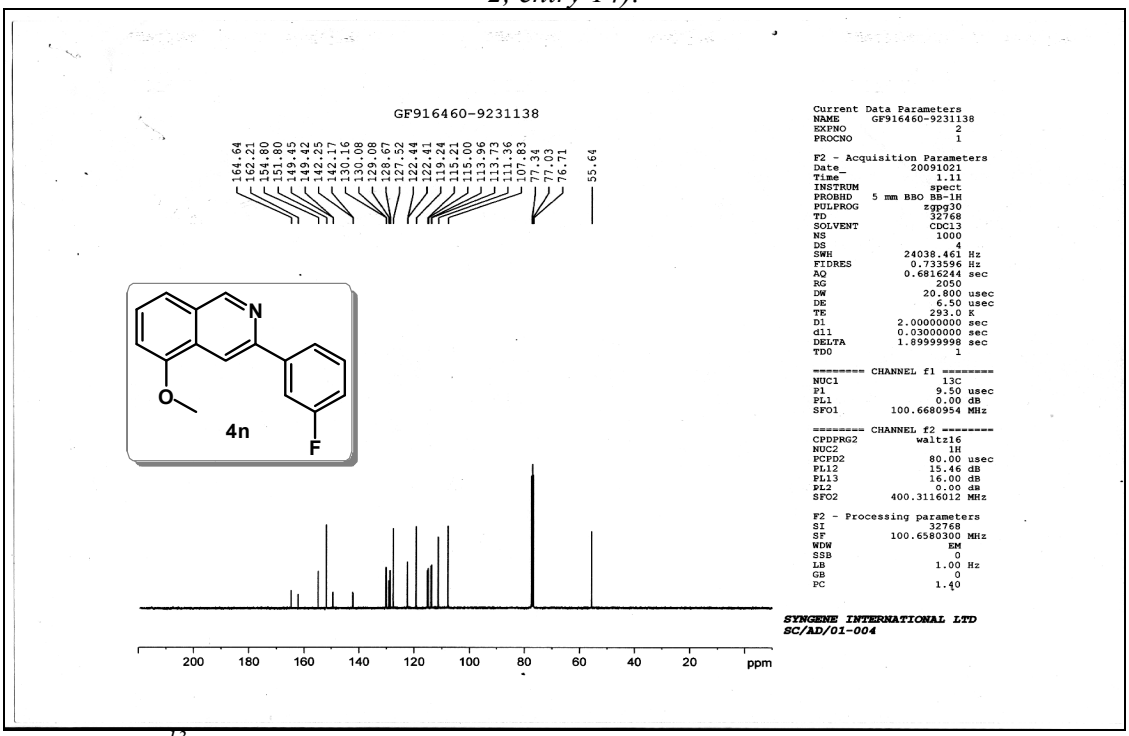


Figure S32. *^{13}C-NMR spectrum of 3-(3-fluorophenyl)-5-methoxyisoquinoline* ***(4n)*** *(Table 2, entry 14).*

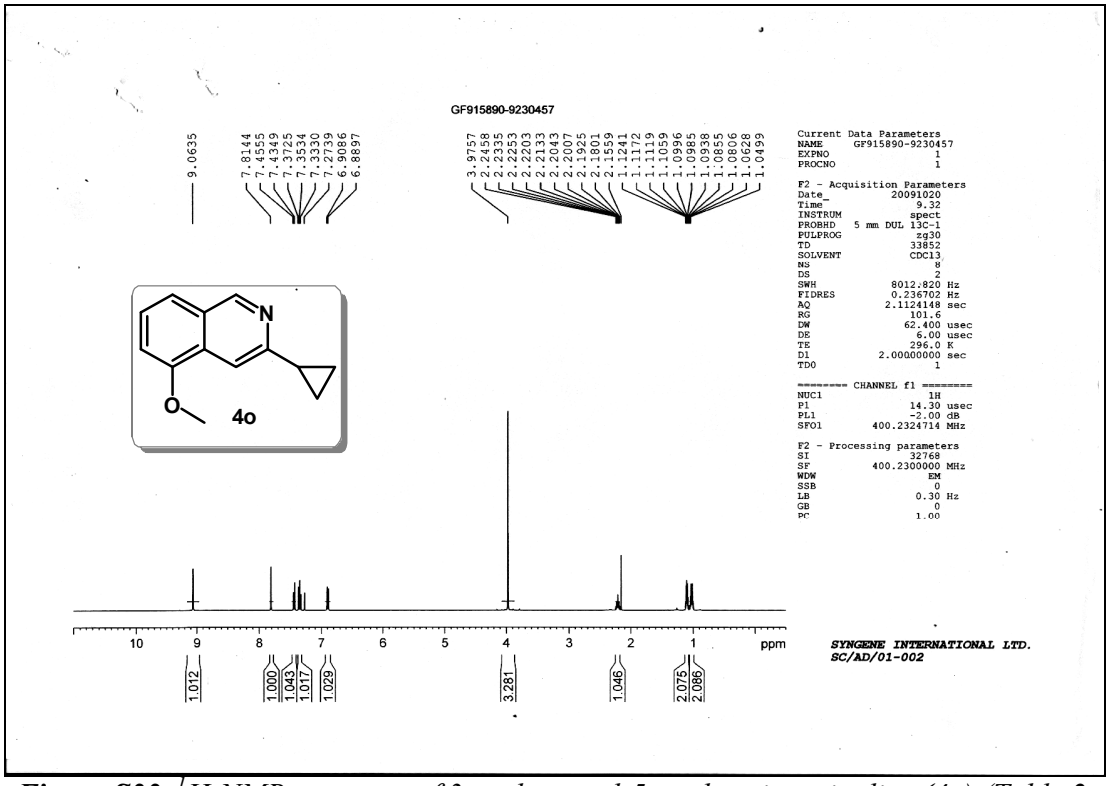


Figure S33. *^{1}H-NMR spectrum of 3-cyclopropyl-5-methoxyisoquinoline* ***(4o)*** *(Table 2, entry 15).*

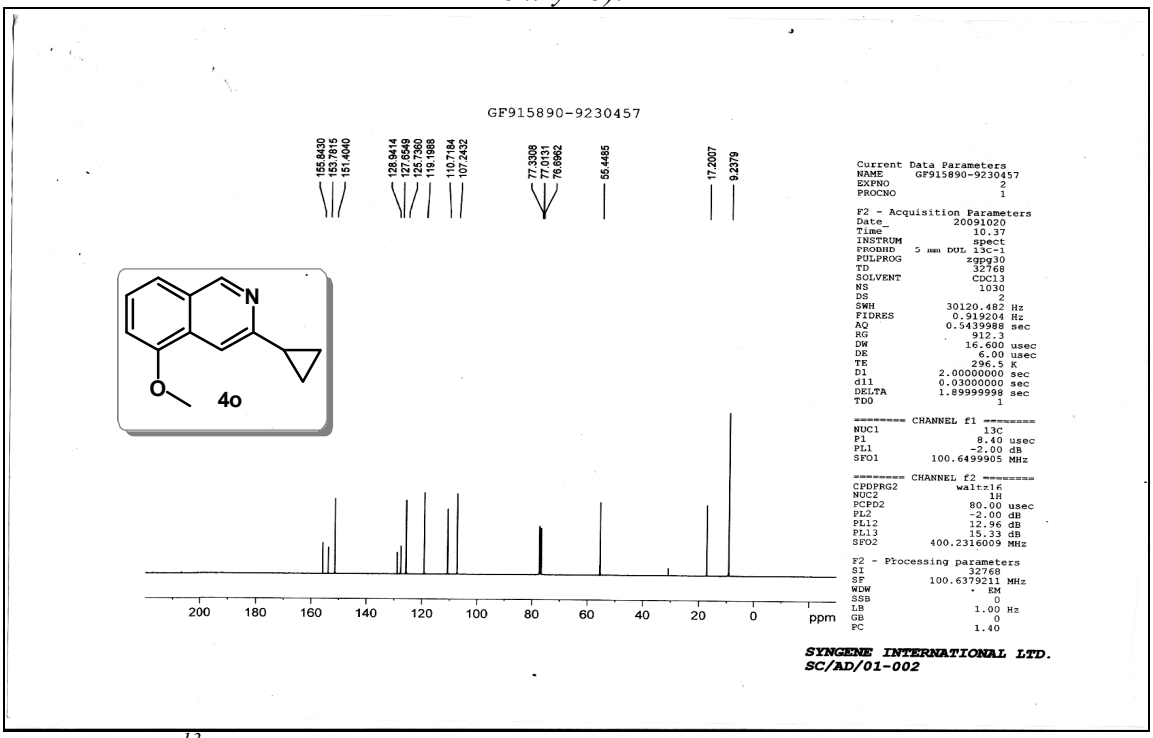


Figure S34. *^{13}C-NMR spectrum of 3-cyclopropyl-5-methoxyisoquinoline* ***(4o)*** *(Table 2, entry 15).*

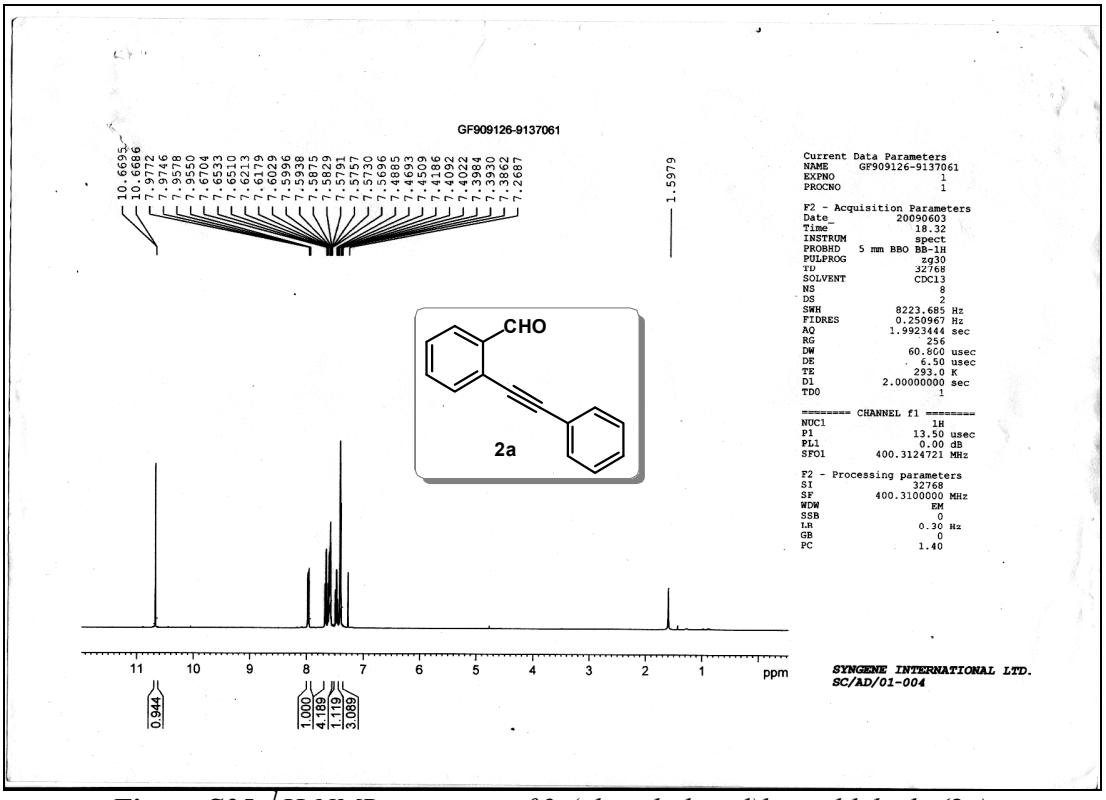


Figure S35. *^{1}H-NMR spectrum of 2-(phenylethynyl)benzaldehyde* ***(2a)****.*

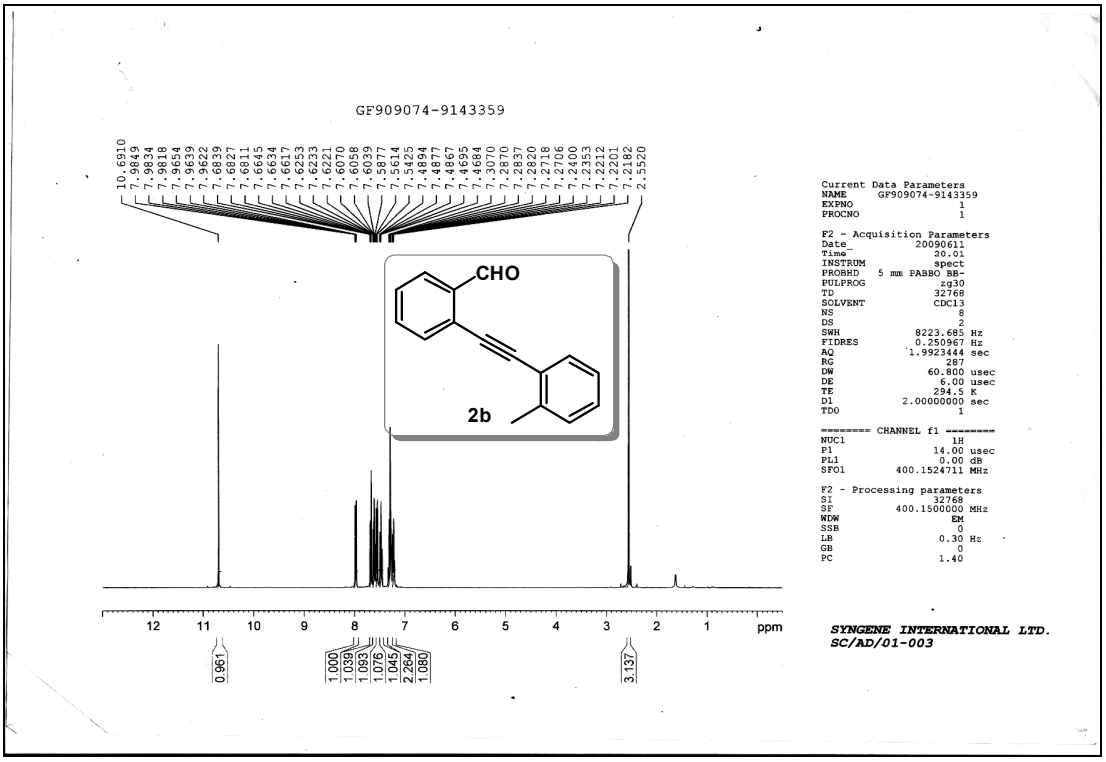


Figure S36. *^{1}H-NMR spectrum of 2-[(2-methylphenyl)ethynyl]benzaldehyde* ***(2b).***

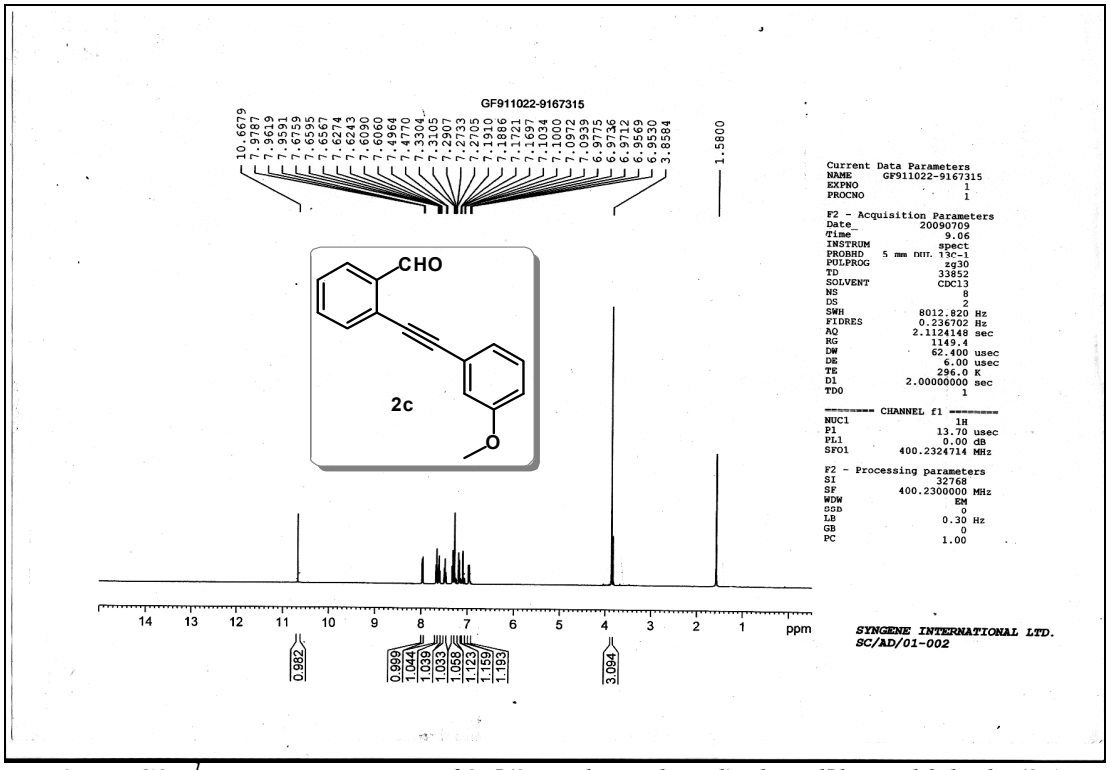


Figure S37. *^{1}H-NMR spectrum of 2-[(3-methoxyphenyl)ethynyl]benzaldehyde* ***(2c).***

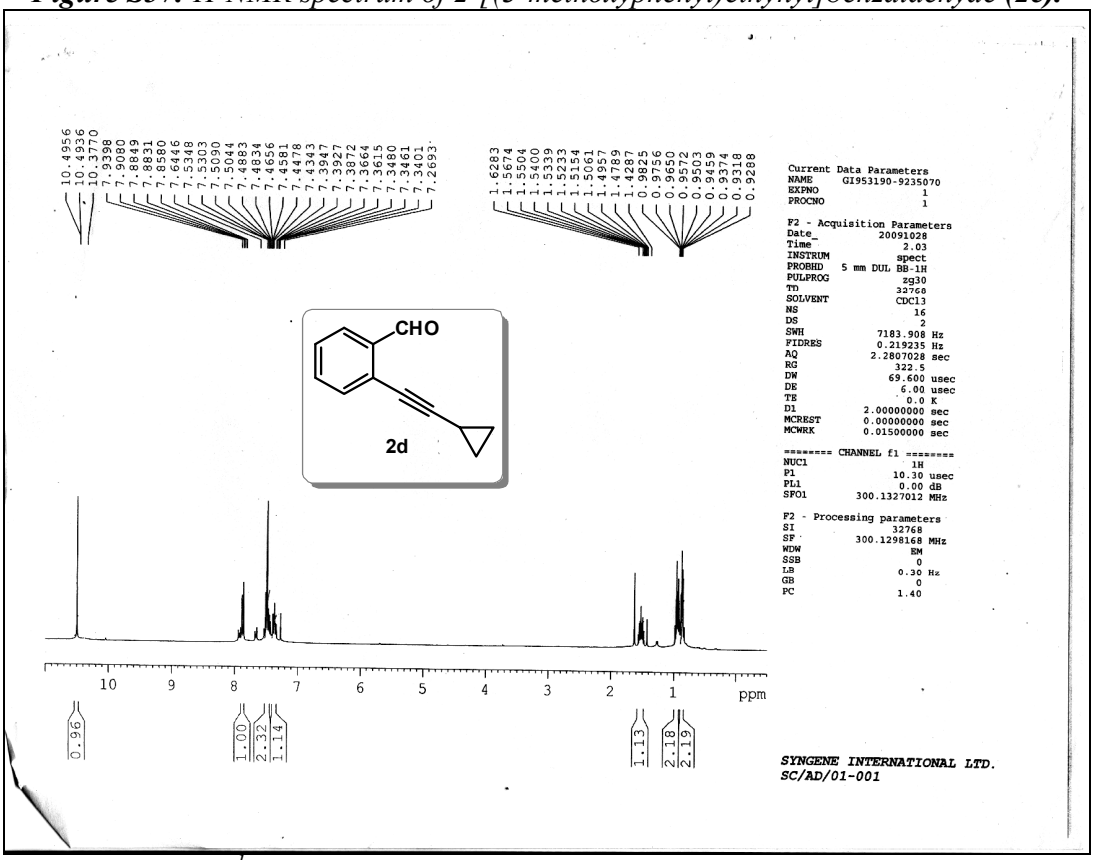


Figure. S38. *^{1}H-NMR spectrum of 2-(cyclopropylethynyl)benzaldehyde* ***(2d).***

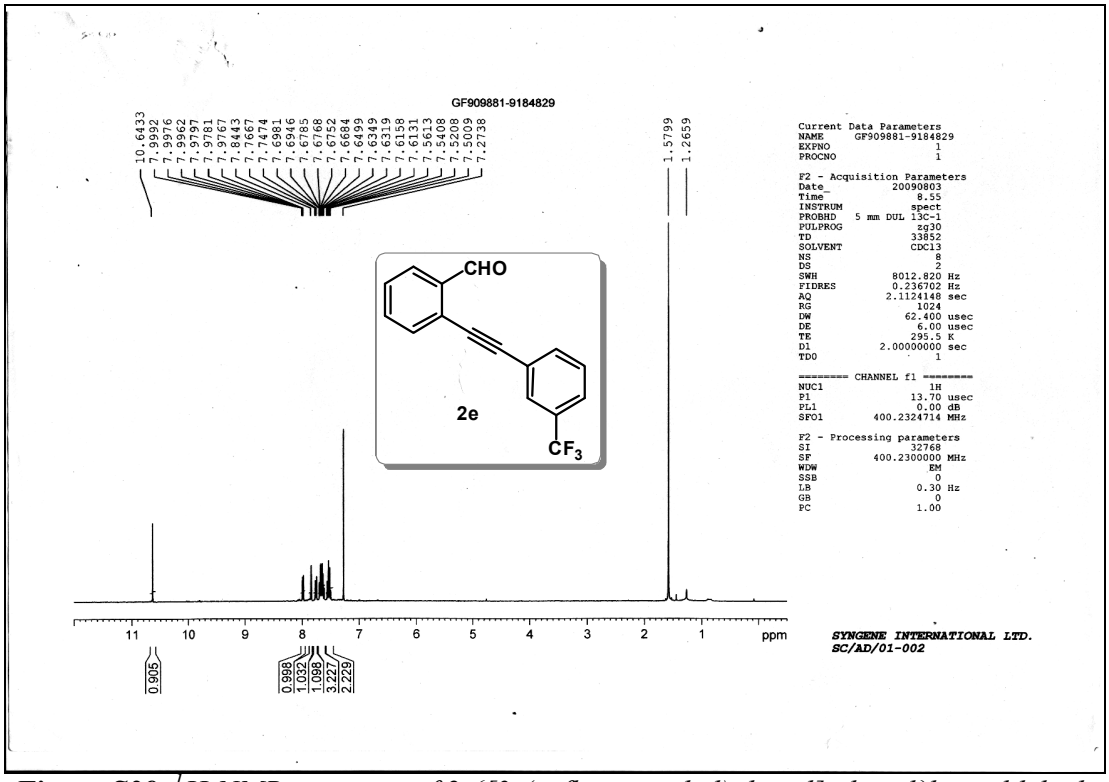


Figure S39. *^{1}H-NMR spectrum of 2-{[3-(trifluoromethyl)phenyl]ethynyl}benzaldehyde* ***(2e)****.*

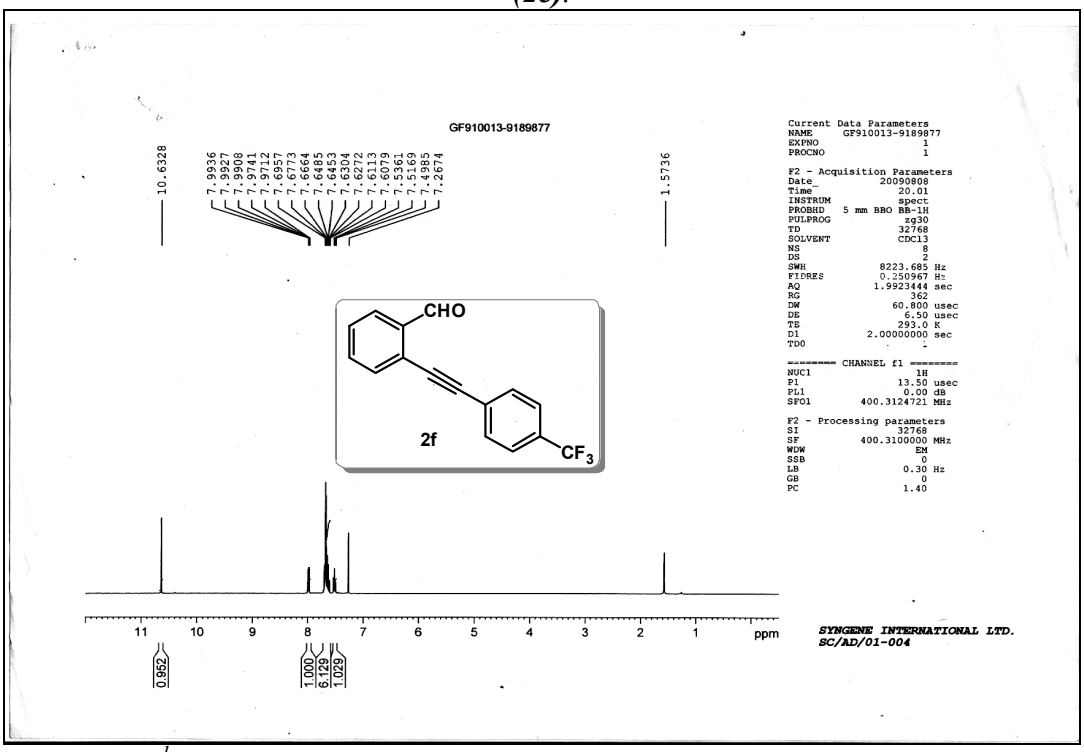


Figure S40. *^{1}H-NMR spectrum of 2-{[4-(trifluoromethyl)phenyl]ethynyl}benzaldehyde* ***(2f)***

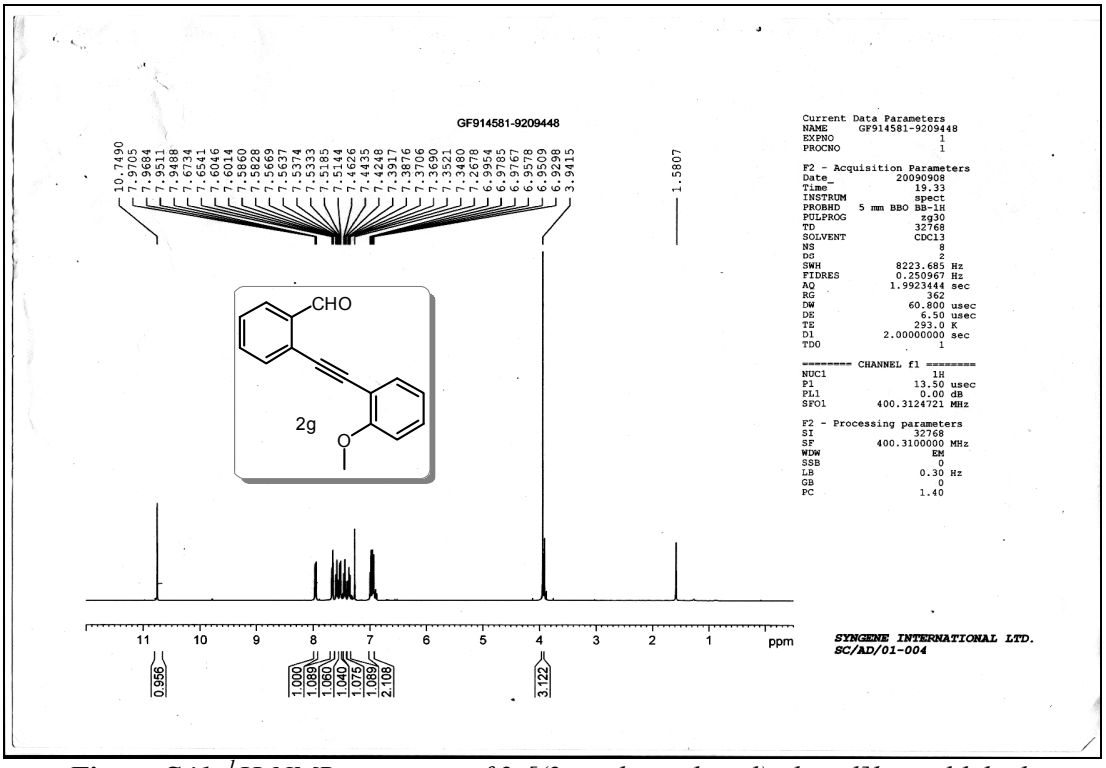


Figure S41. *[1]H-NMR spectrum of 2-[(2-methoxyphenyl)ethynyl]benzaldehyde* ***(2g)***.

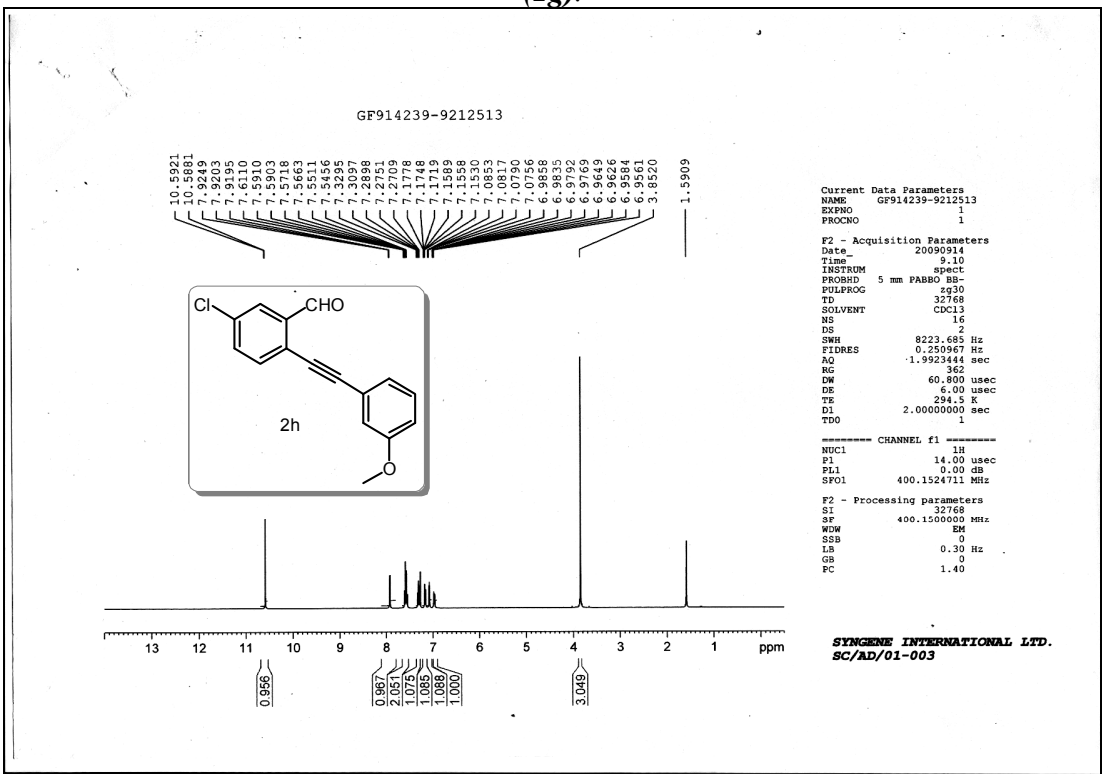


Figure S42. *[1]H-NMR spectrum of 5-chloro-2-[(3-methoxyphenyl)ethynyl]benzaldyde* ***(2h)***.

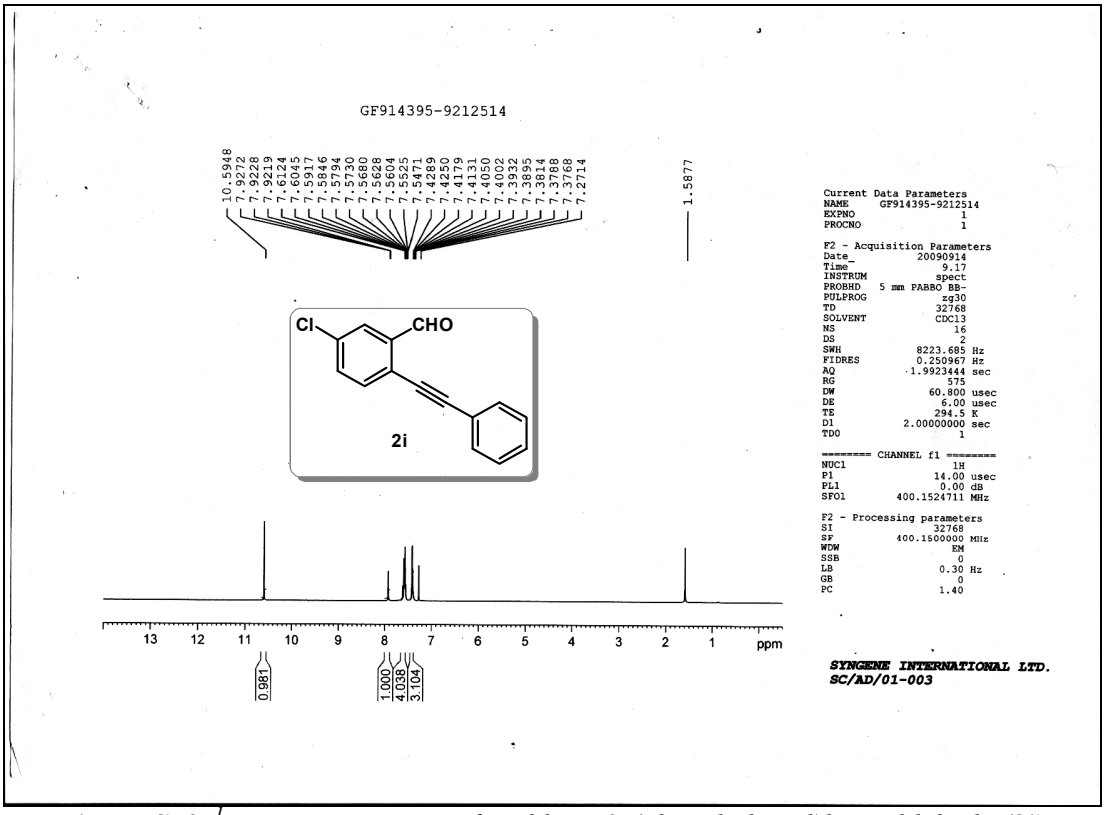


Figure S43. *^{1}H-NMR spectrum of 5-chloro-2-(phenylethynyl)benzaldehyde* ***(2i)***.

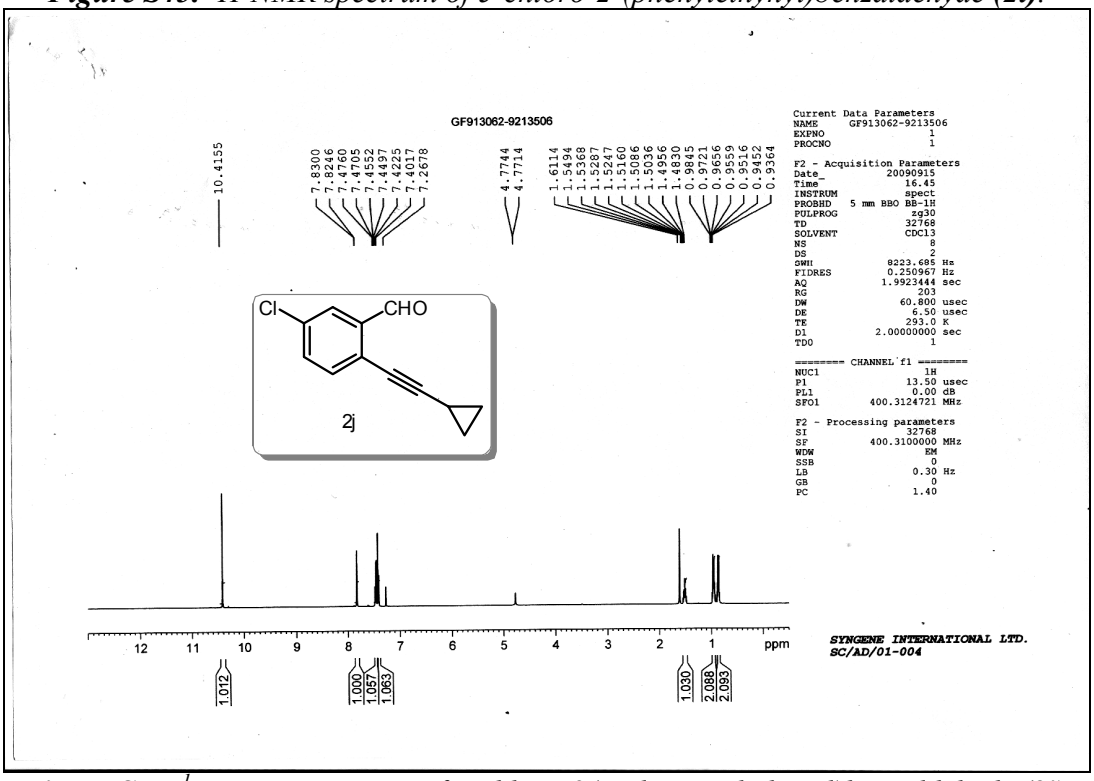


Figure S44. *^{1}H-NMR spectrum of 5-chloro-2(cyclopropylethynyl)benzaldehyde* ***(2j)***.

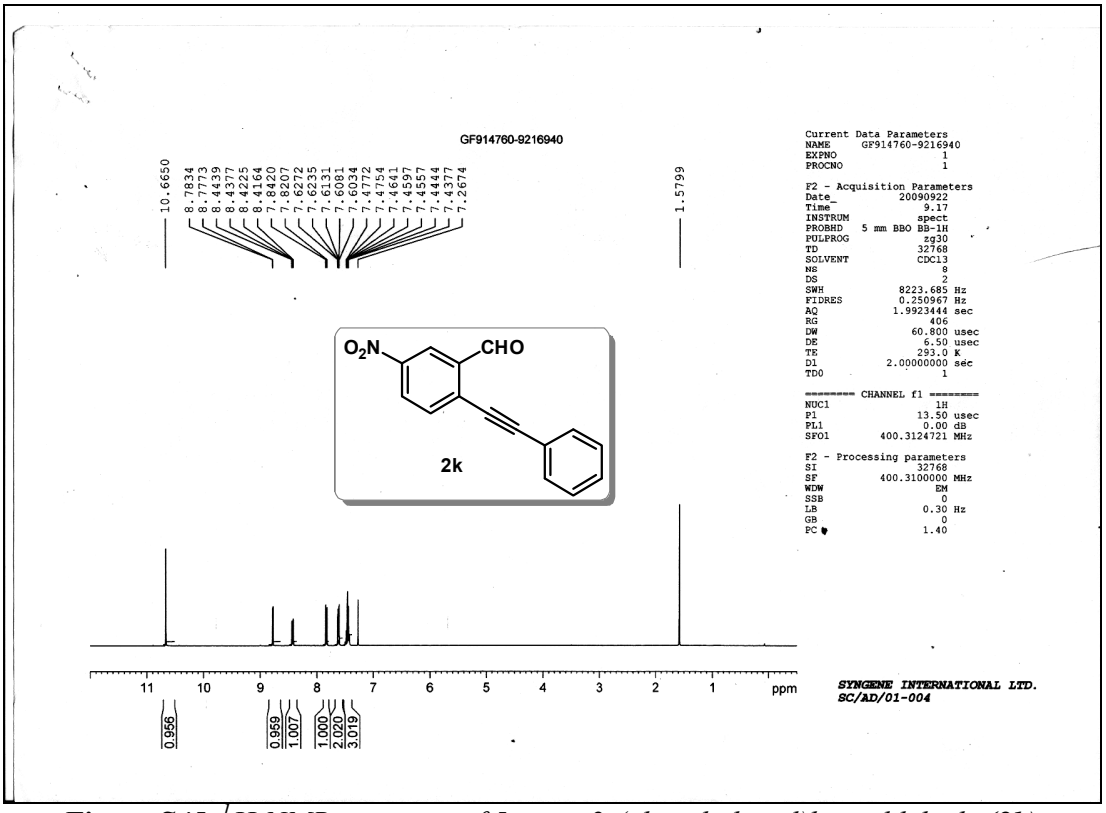


Figure S45. *^{1}H-NMR spectrum of 5-nitro-2-(phenylethynyl)benzaldehyde* ***(2k)****.*

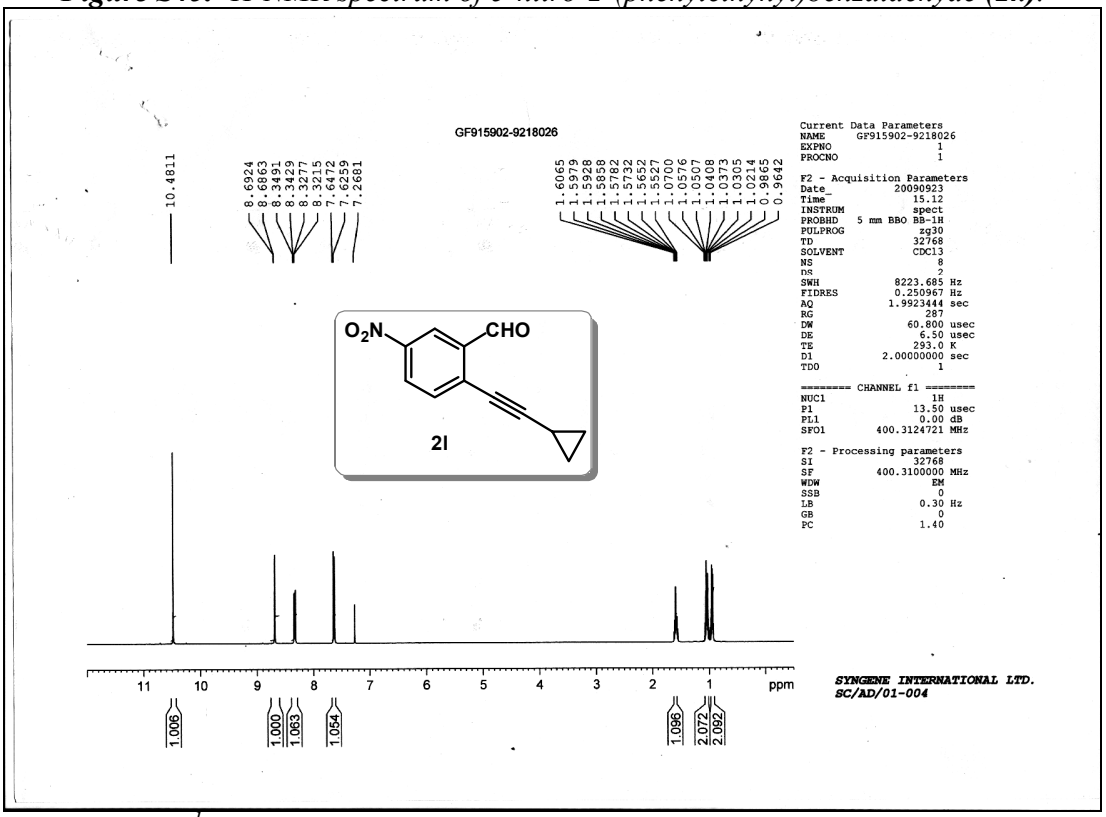


Figure S46. *^{1}H-NMR spectrum of (2-cyclopropylethynyl)-5-nitrobenzaldehyde* ***(2l)****.*

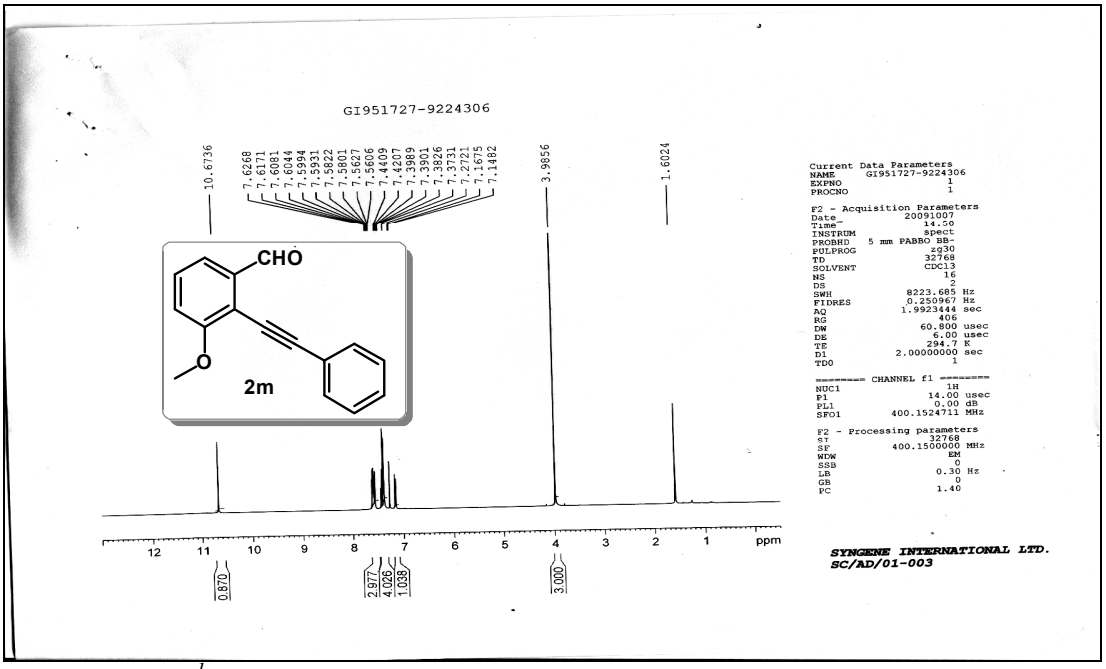


Figure S47. *^{1}H-NMR spectrum of 3-methoxy-2-(phenylethynyl)benzaldehyde* ***(2m)****.*

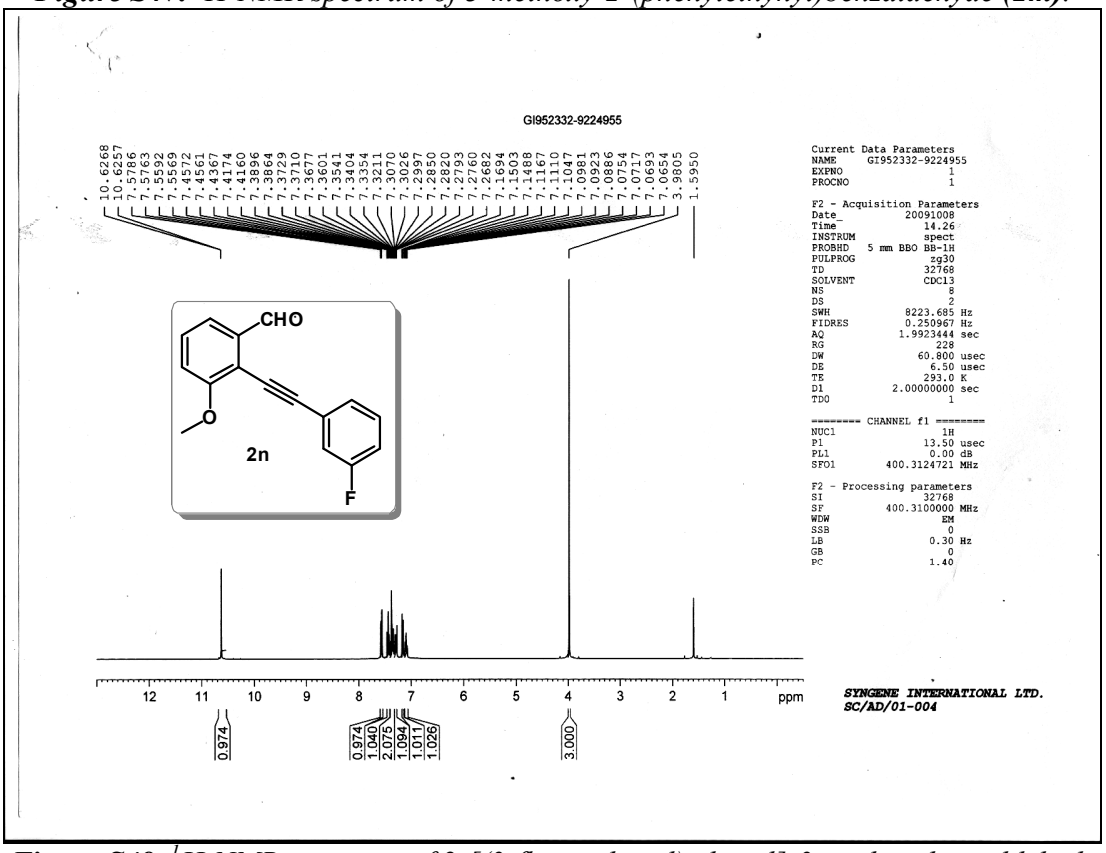


Figure S48. *^{1}H-NMR spectrum of 2-[(3-fluorophenyl)ethynyl]-3-methoxybenzaldehyde* ***(2n)****.*

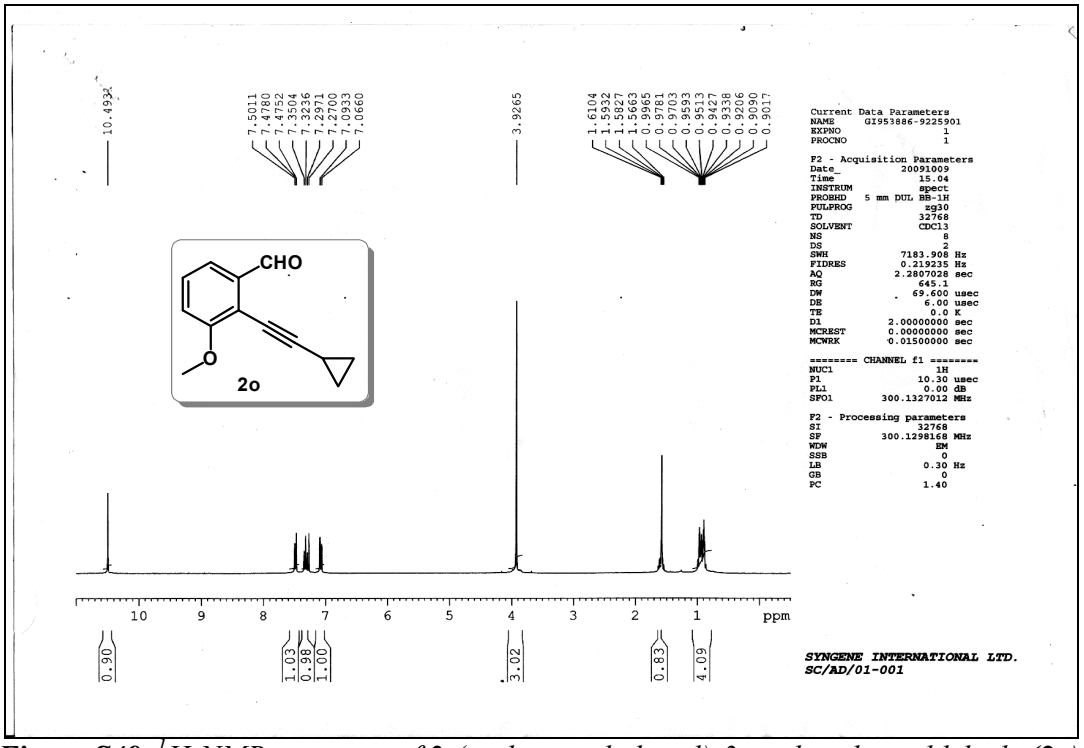


Figure S49. *^{1}H-NMR spectrum of 2-(cyclopropylethynyl)-3-methoxybenzaldehyde* ***(2o)***.

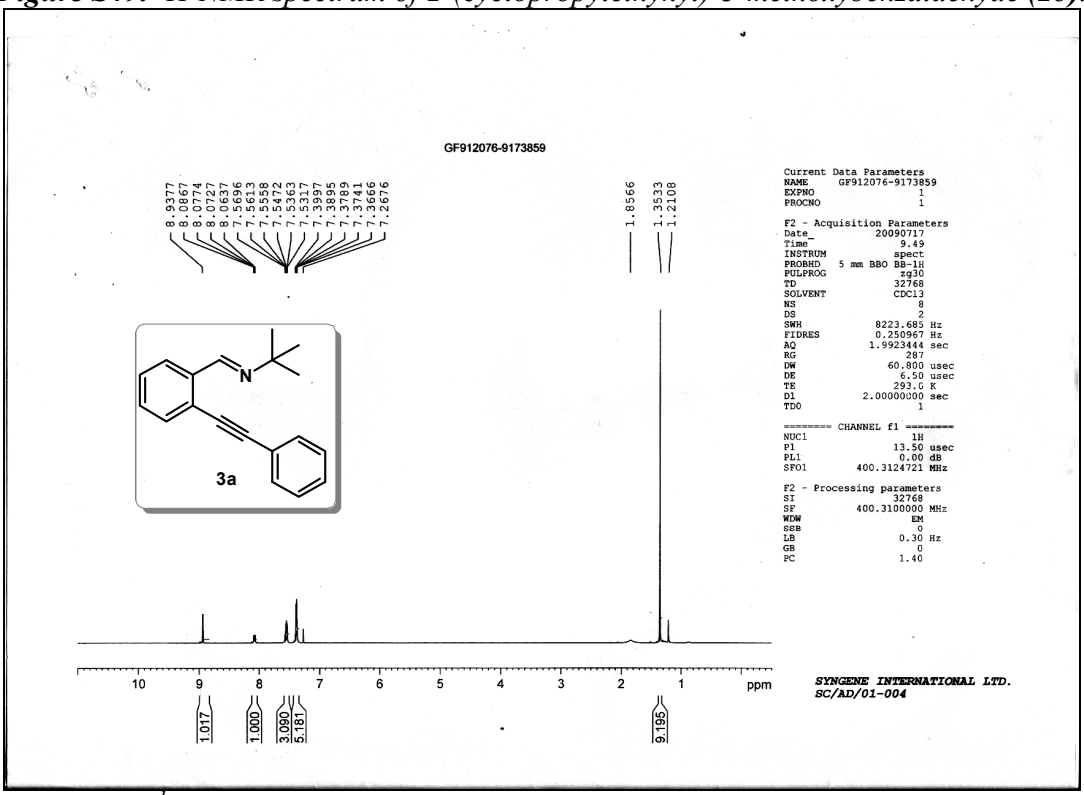


Figure S50. *^{1}H-NMR spectrum of tert-butyl{(1E)-[2-(phenylethynyl)phenyl]methylene} amine* ***(3a)***.

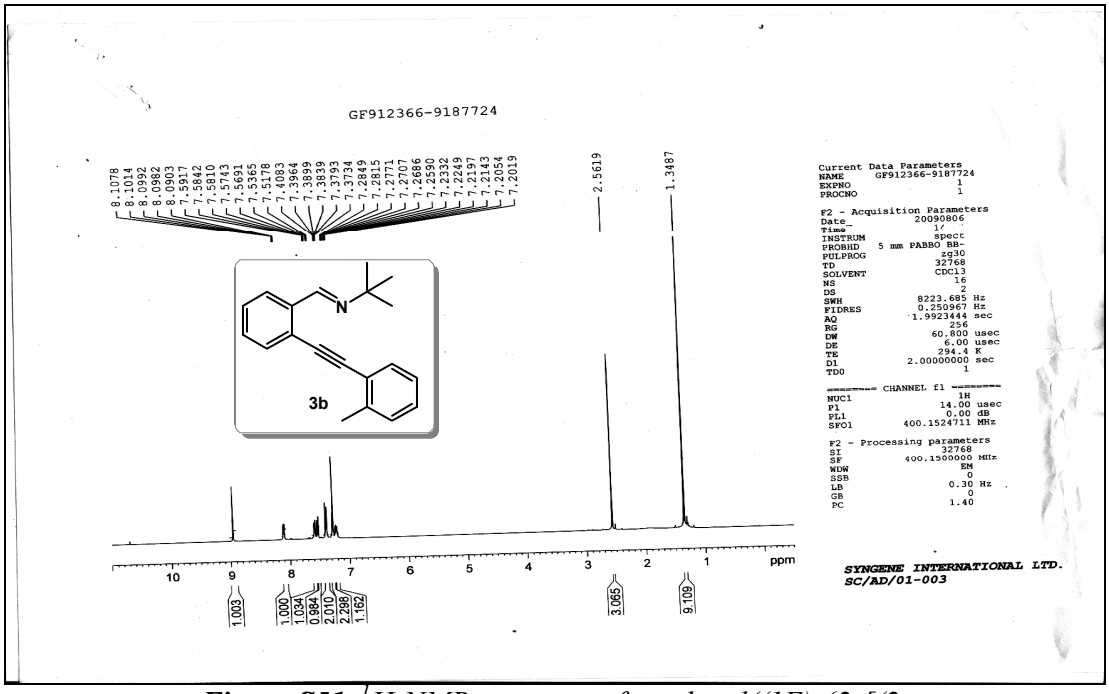


Figure S51. *^{1}H-NMR spectrum of tert-butyl((1E)-{2-[(2-ethylphenyl)ethynyl]phenyl}methylene)amine* ***(3b).***

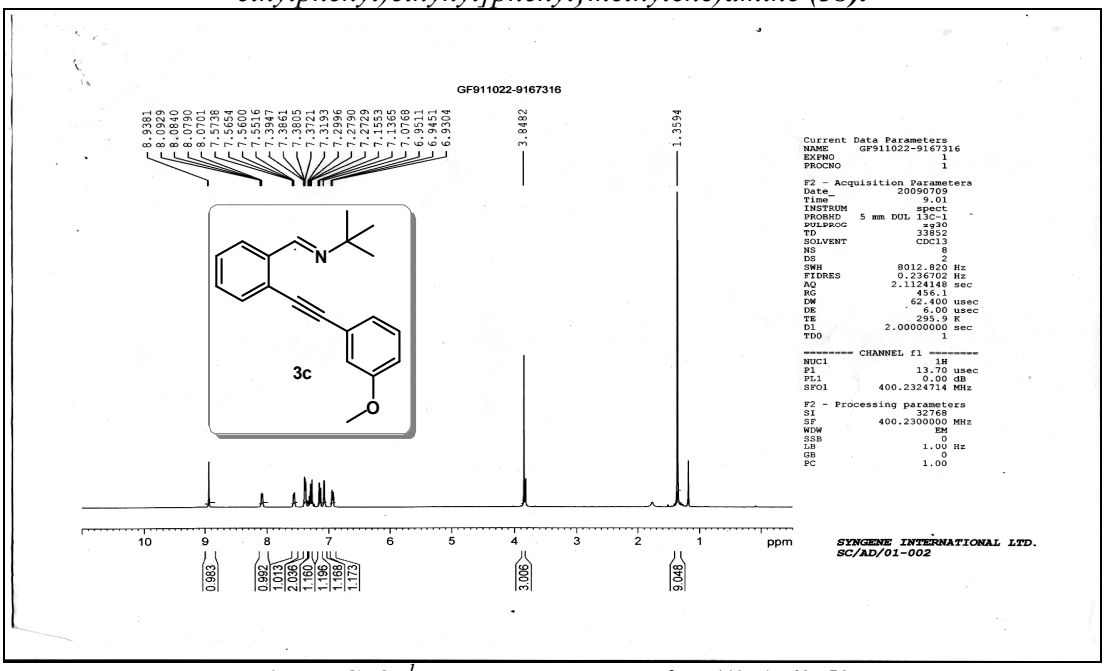


Figure S52. *^{1}H-NMR spectrum of N-((1E)-{2-[3-methoxyphenyl)ethynyl]phenyl}methylene)-2-methylpropan-2-amine* ***(3c)***.

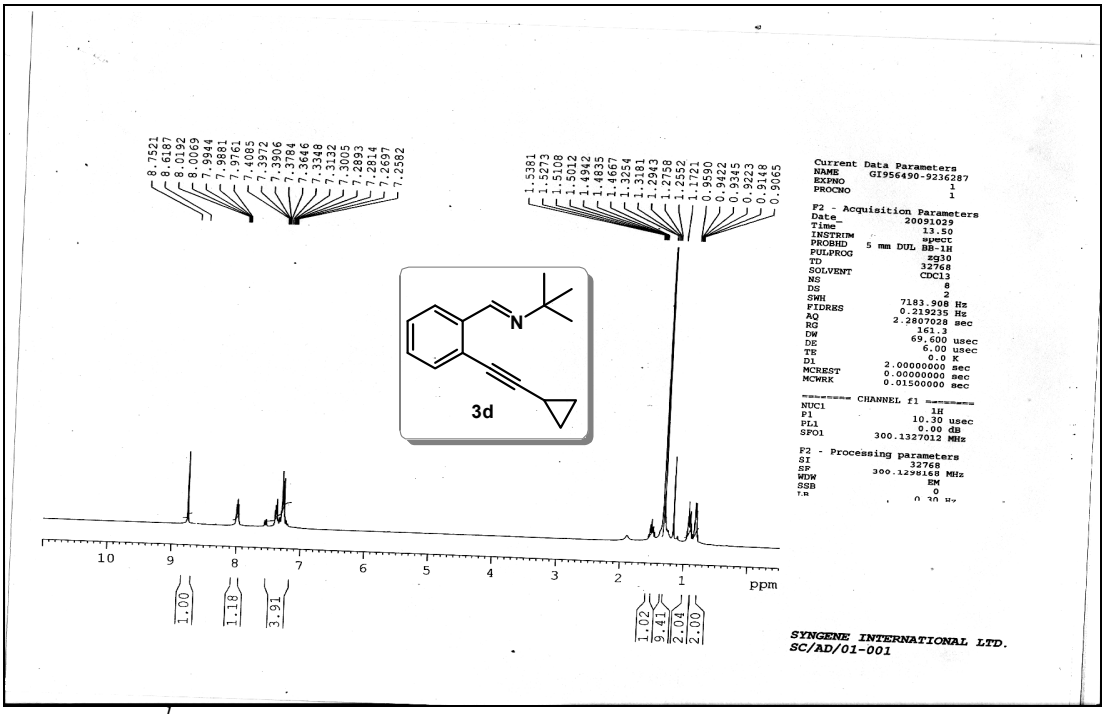


Figure S53. *^{1}H-NMR spectrum of 1-(cyclopropylethynyl)-2-[(1E)-3,3-dimethylbut-1-en-1- yl]benzene* ***(3d)****.*

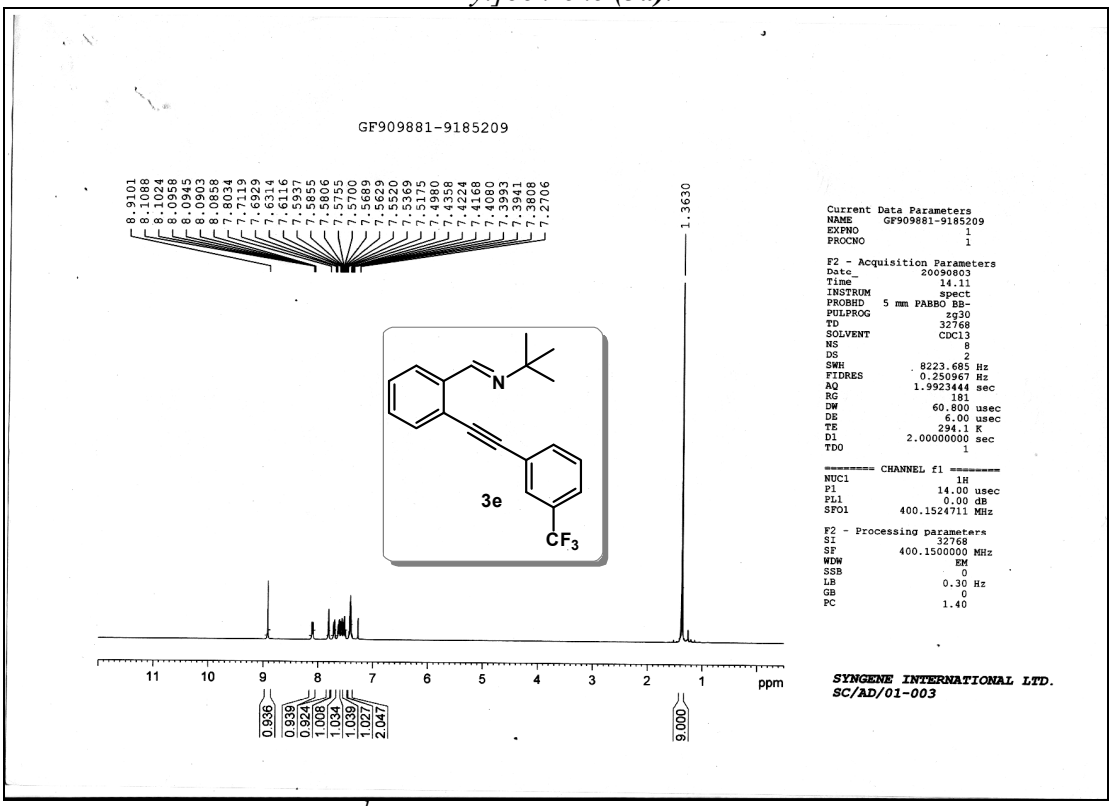


Figure S54. *^{1}H-NMR spectrum of tert-butyl[(1E)-(2-{[3-(trifluoromethyl)phenyl]ethynyl}phenyl)methylene]amine* ***(3e)****.*

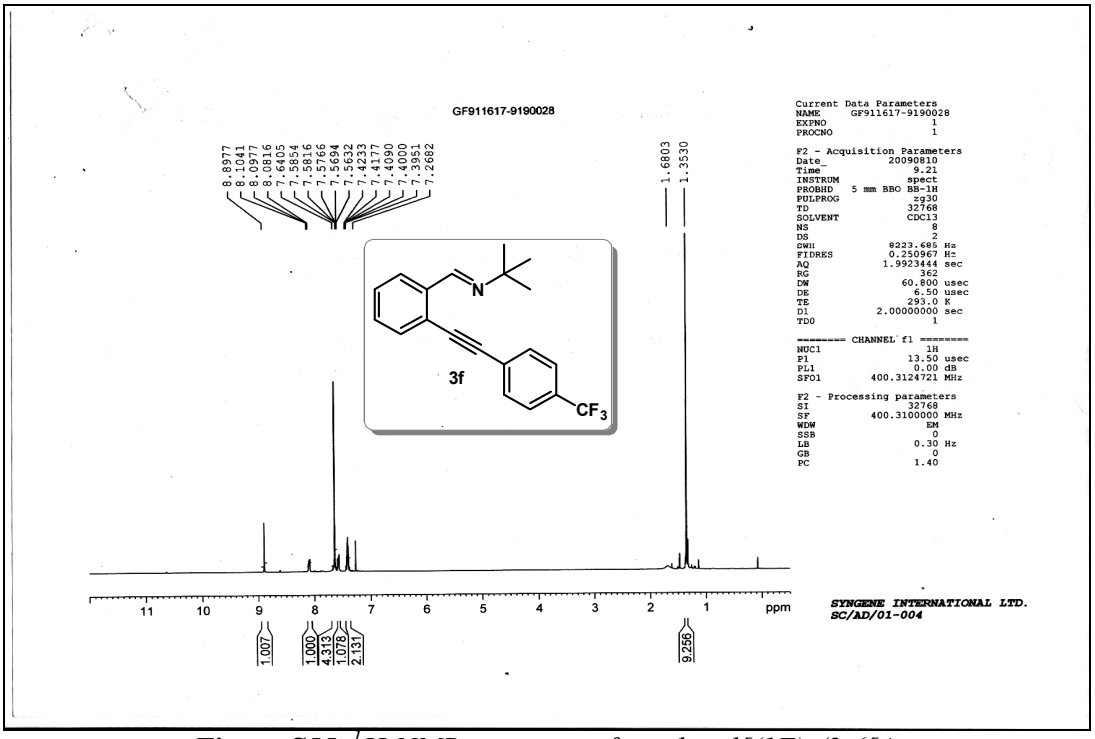


Figure S55. *^{1}H-NMR spectrum of tert-butyl[(1E)-(2-{[4-(trifluoromethyl)phenyl]ethynyl}phenyl)methylene]amine* ***(3f)***.

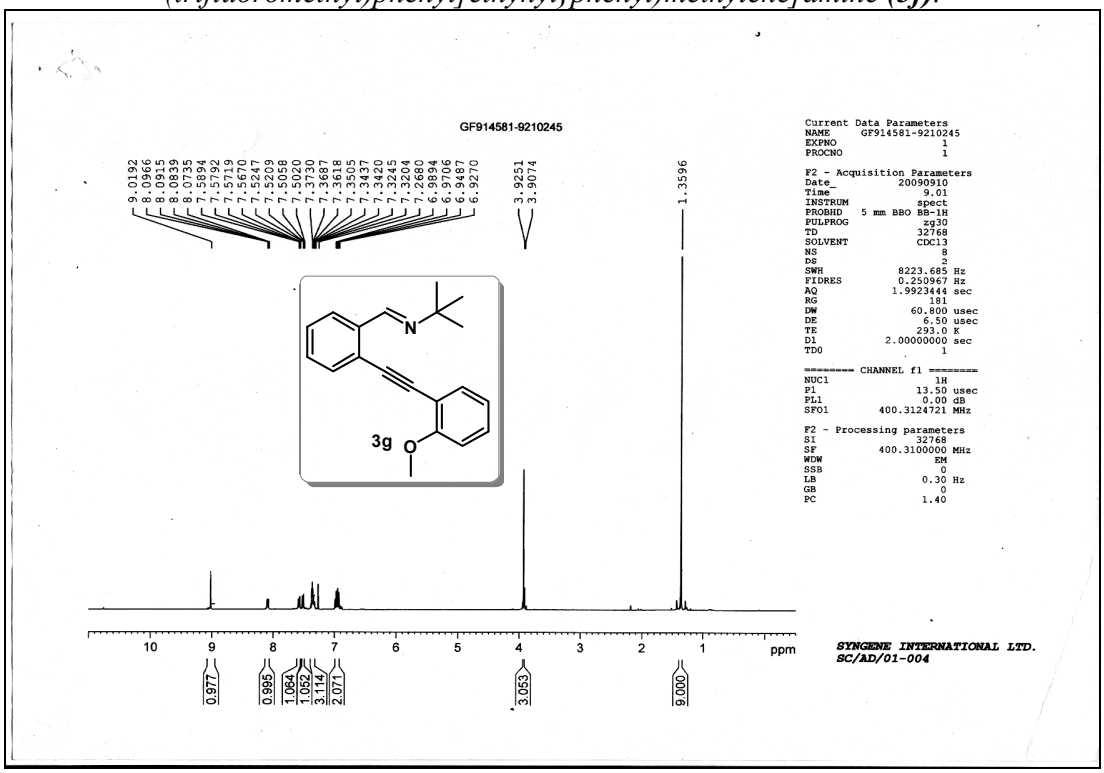


Figure S56. *^{1}H-NMR spectrum of N-((1E)-{2-{(2-methoxyphenyl)ethynyl]phenyl}methylene)-2-methylpropan-2-amine* ***(3g)***.

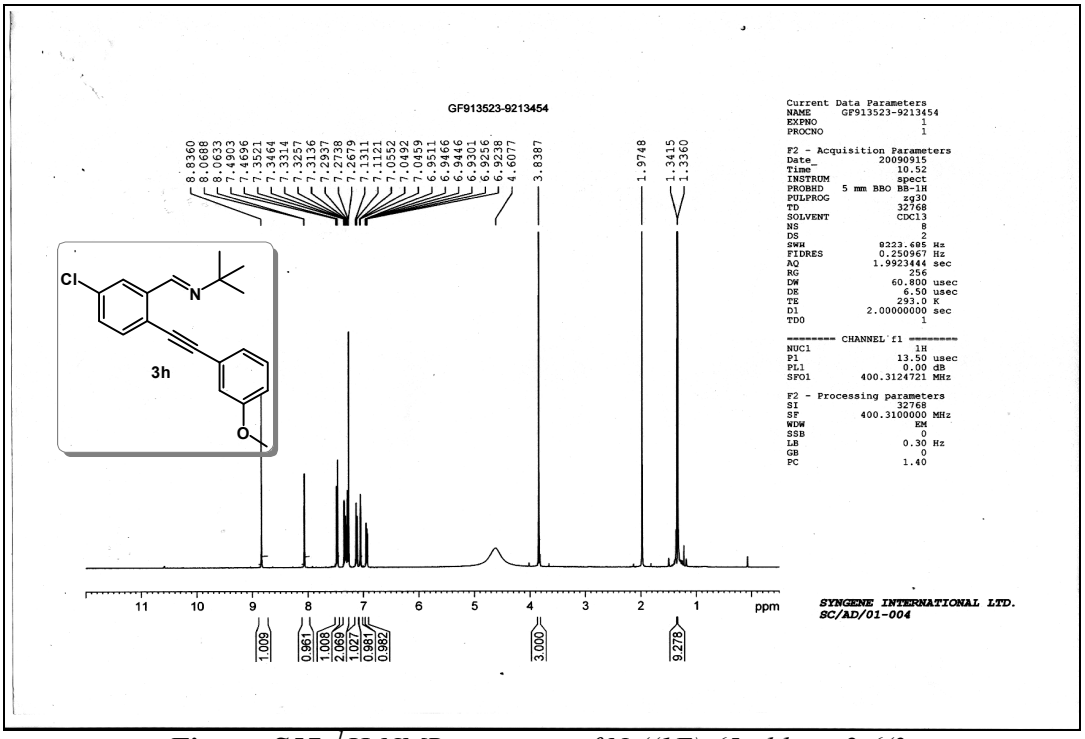


Figure. S57. *^{1}H-NMR spectrum of N-((1E)-{5-chloro-2-{(3-methoxyphenyl)ethynyl]phenyl}methylene)-2-methylpropan-2-amine (3h).*

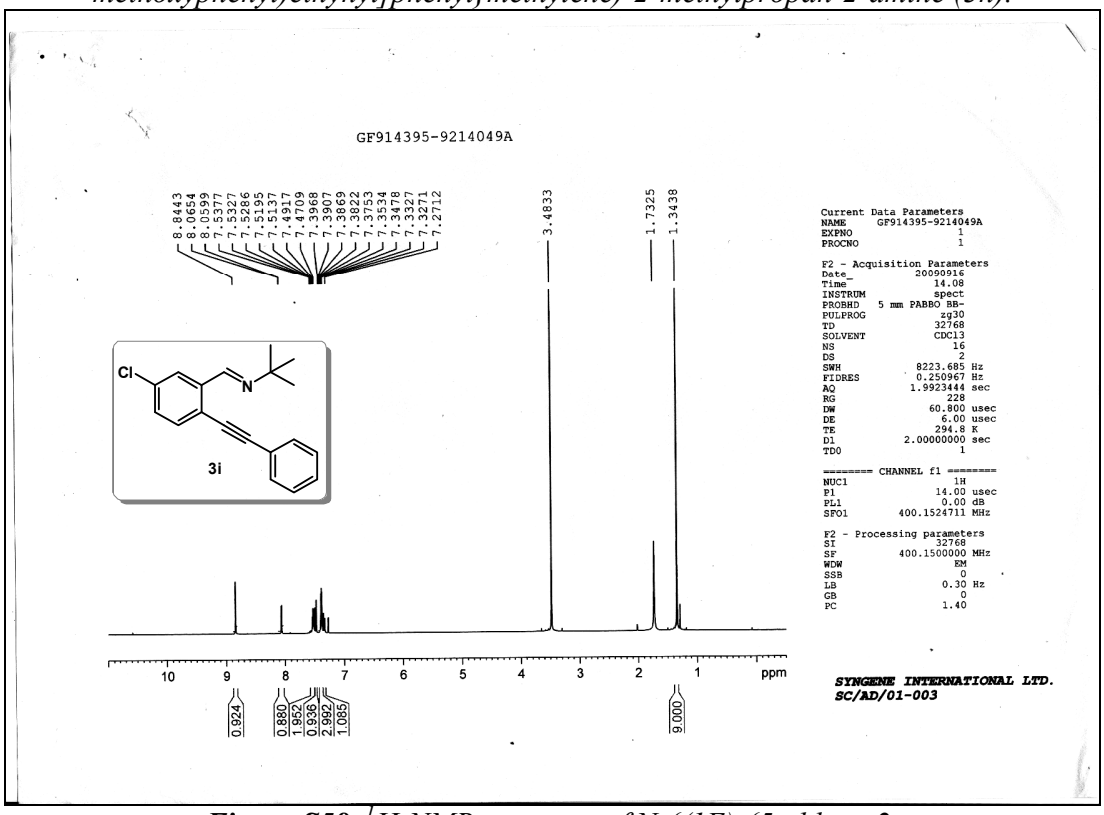


Figure S58. *^{1}H-NMR spectrum of N-{(1E)-{5-chloro-2-(phenylethynyl)phenyl]methylene}-2-methylpropan-2-amine* ***(3i)****.*

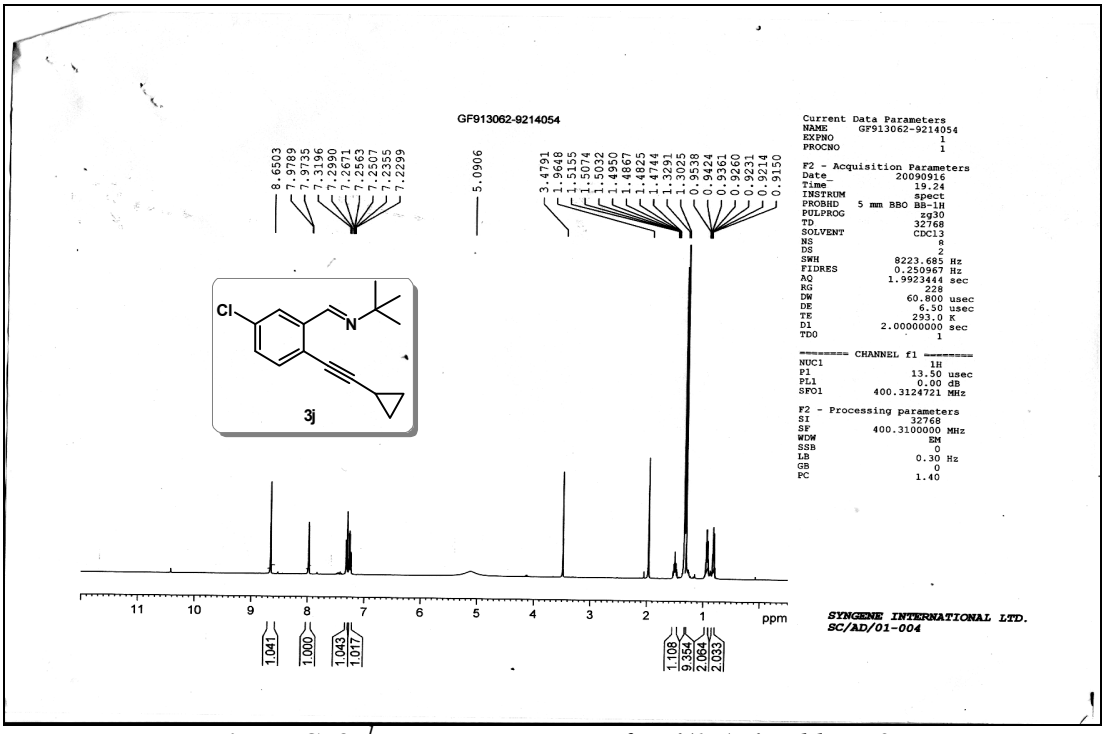


Figure S59. *^{1}H-NMR spectrum of N-{(1E)-{5-chloro-2-(cyclopropylethynyl)phenyl]methylene}-2-methylpropan-2-amine* ***(3j)****.*

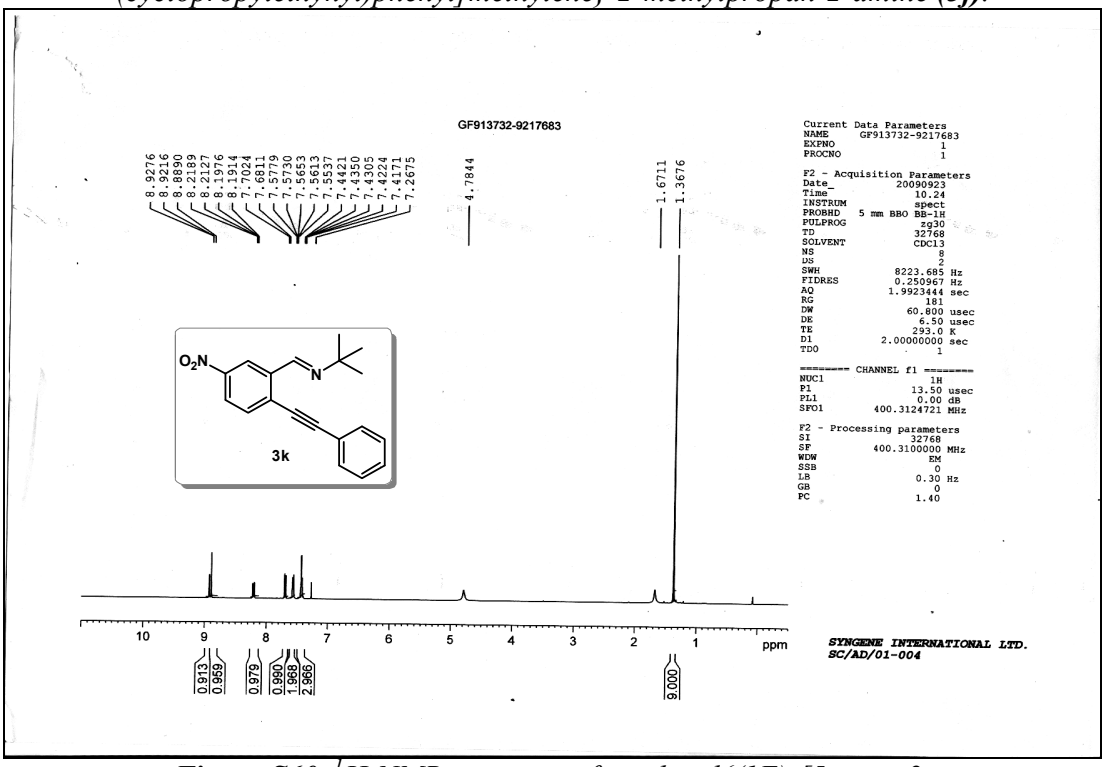


Figure S60. *^{1}H-NMR spectrum of tert-butyl{(1E)-[5-nitro-2-(phenylethynyl)phenyl]methylene}amine* ***(3k)****.*

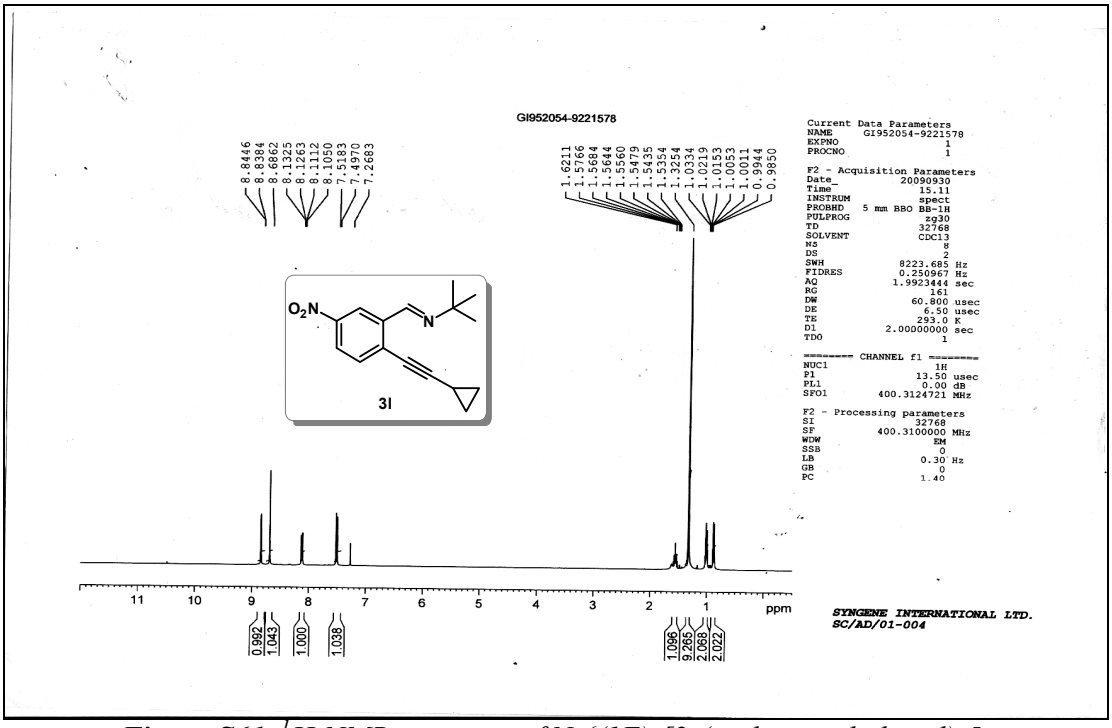


Figure S61. *^{1}H-NMR spectrum of N-{(1E)-[2-(cyclopropylethynyl)-5-nitrophenyl]methylene}-2-methylpropan-2-amine* ***(3l)***.

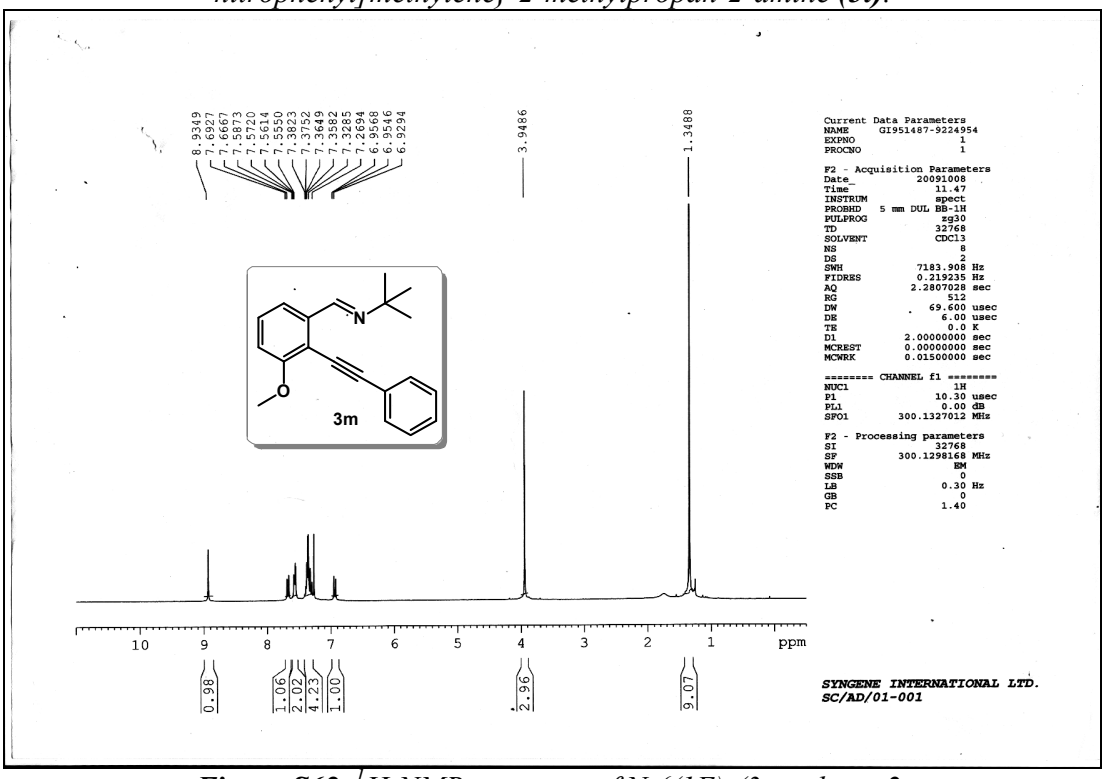


Figure S62. *^{1}H-NMR spectrum of N-{(1E)-(3-methoxy-2-(phenylethynyl)phenyl]methylene}-2-methylpropan-2-amine* ***(3m)***.

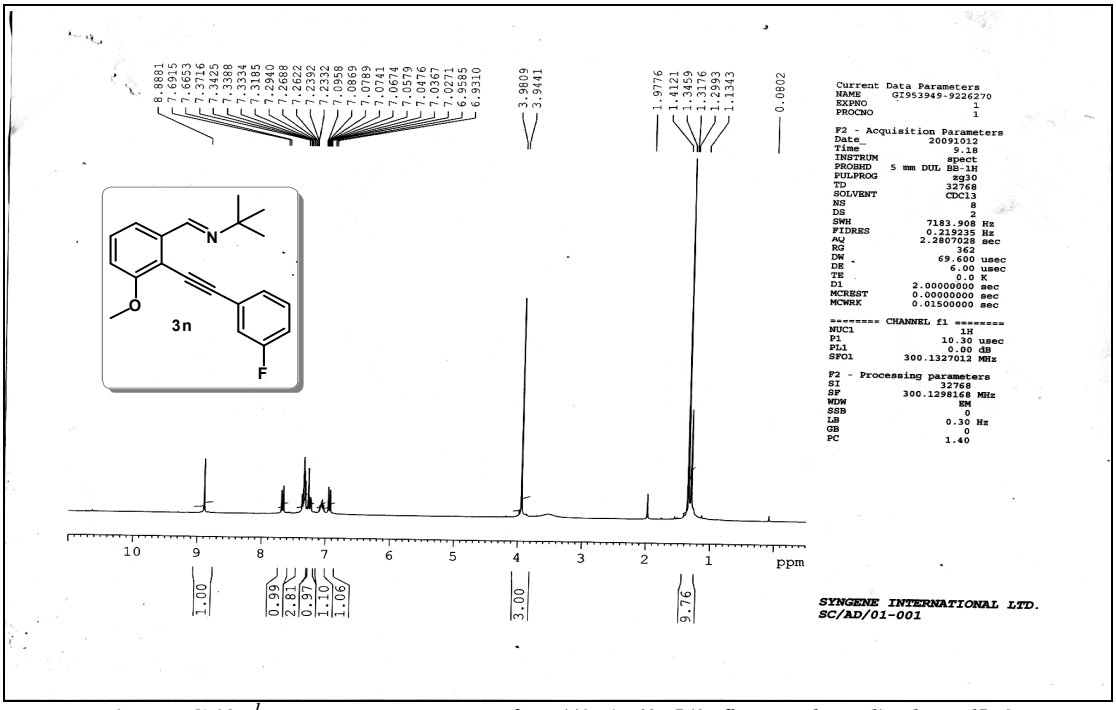


Figure S63. *^{1}H-NMR spectrum of N-((1E)-{2-[(3-fluorophenyl)ethynyl]-3-methoxyphenyl}methylene)-2-methylpropan-2-amine* ***(3n)****.*

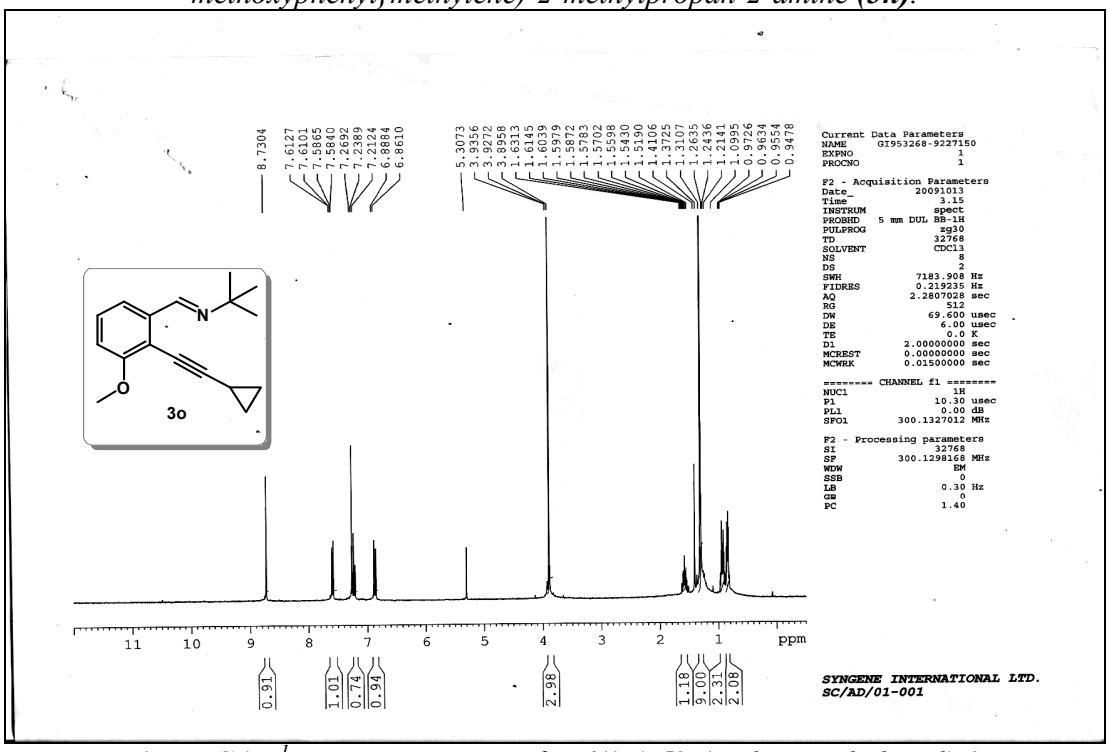


Figure S64. *^{1}H-NMR spectrum of N-{(1E)-[2-(cyclopropylethynyl)-3-methoxyphenyl]methylene-2-methylpropan-2-amine* ***(3o)****.*

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