

## ZrO<sub>2</sub>-β-cyclodextrin catalyzed synthesis of 2,4,5-trisubstituted imidazoles and 1,2-disubstituted benzimidazoles under solvent free conditions and evaluation of their antibacterial study

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### 1. Experimental Section

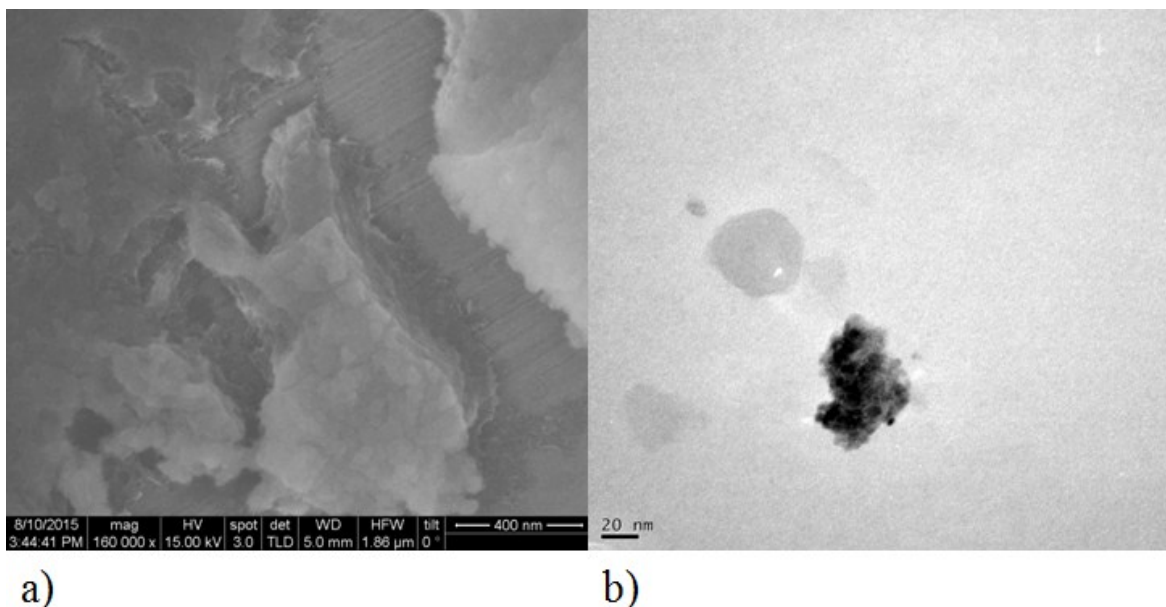
#### General Methods

Zirconium oxychloride (ZrOCl<sub>2</sub>.8H<sub>2</sub>O, >99.0%), ammonia (NH<sub>3</sub>.H<sub>2</sub>O, 25%) was purchased from S.D. FINE-CHEM LTD, India. β-cyclodextrin was purchased from Sigma-Aldrich India, deionized water was used for all workup procedures. Melting points were measured on secor INDIA apparatus and are uncorrected. <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded on VNMRS-400

(Agilent Technologies) NMR spectra in CDCl<sub>3</sub>. Tetramethylsilane (TMS;  $\delta = 0.00$  ppm) served as internal standards for <sup>1</sup>H NMR. The corresponding residual non-deuterated solvent signal (CDCl<sub>3</sub>:  $\delta = 77.00$  ppm) was used as internal standards for <sup>13</sup>C NMR. Performed Column chromatography on silica gel 60-120 mesh (Merck). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Mass spectra were measured with Micromass Q-ToF (HRESI-MS). DMF was dried over CaH<sub>2</sub> for 2 h and filtered. The catalyst was characterized by ATR-Fourier transform infrared (ATR-IR) were recorded using a Thermo Nicolet FTIR spectrometer (Model 5700, Madison, WI) fitted with a single bounce attenuated total reflectance (ATR) accessory with a ZnSe crystal of range 400-4000cm<sup>-1</sup>. X-ray powder diffraction (PXRD) was carried out on a XRD 7000, Shimadzu diffractometer with CuK $\alpha$  radiation. Scanning electron microscopy (SEM) images were obtained using a JEOL JXA-8530F microscope. Transmission electron microscopy (TEM) images were performed on PHILIPS CM200 electron microscopes at an acceleration voltage of 20-200kv. TGA thermograms of the nanoparticles were obtained under nitrogen on a Perkin–Elmer TGA 7 analyzer at a heating rate of 20°C min<sup>-1</sup>.

Approximately (20 ml) of sterile molten nutrient agar media was aseptically poured into petriplates and allowed to solidify. Around 0.1 ml of the inoculums was seeded on the plates and spread using a sterile spreader. 0.2 mg of the derivatives was dissolved in 1000 $\mu$ l of DMSO/MeOH (1-14, in DMSO and 15-25 in MeOH). Then 25-50  $\mu$ l of that suspension with final concentration 0.2 mg/ml per disc were loaded on paper disc and then placed aseptically on the surface of inoculated plates. The plates were incubated overnight for 24 hours at 37 °C. Streptomycin (10  $\mu$ g / disc) and MeOH (50  $\mu$ l) were used as positive control. The diameter of

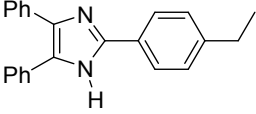
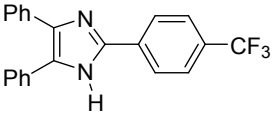
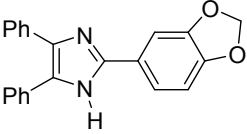
inhibition zone was measured in millimeter (mm) scale and was recorded. The mean values of the diameter of the inhibition zone of the triplicates were taken as the final value.

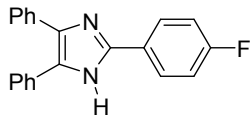
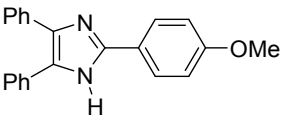
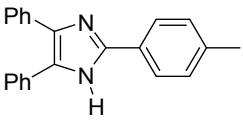
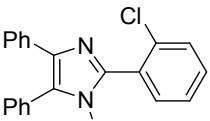


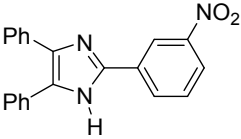
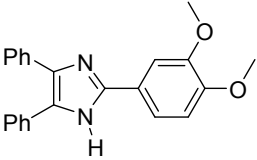
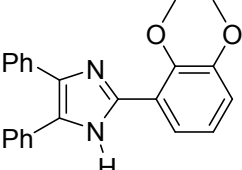
2. **Fig. 1** (a) SEM and (b) TEM of recovered ZrO<sub>2</sub>-supported -β-cyclodextrin nanoparticles.

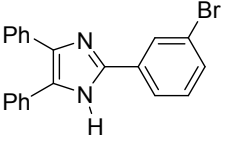
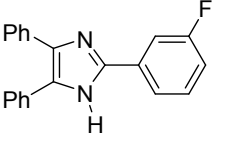
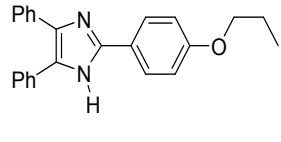
3. **Characterization data of isolated triazole molecules 3(a-n) and 5(a-k):**

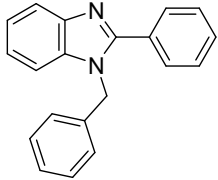
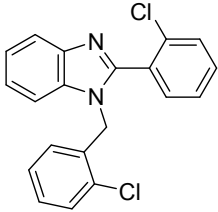
Entry	Product	NMR data
1	<p><b>3a</b></p>	<p><b>2,4,5-Triphenyl-1H-imidazole (3a):</b> White solid; mp: 270-276°C (lit.<sup>[57]</sup> 269 - 275 °C ); <b>FT-IR</b> (KBr, cm<sup>-1</sup>): 3442, 1630, 1582; <b><sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400MHz):</b> δ 12.61 ( s, 1H), 7.37-8.13 (m, 15H); <b><sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100MHz):</b> δ 143.96, 130.76, 127.58, 126.49, 125.39, 123.73; <b>HRMS (ESI) m/z</b> Calculated for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub> (M+1) + 297.1313, Found 297.1320</p>

2	 <p style="text-align: center;"><b>3b</b></p>	<p><b>2-(4-Ethylphenyl)-4,5-diphenyl-1H-imidazole (3b):</b> White solid; mp: (lit.<sup>[57]</sup>); <b>FT-IR</b> (KBr): 3445, 3068, 2970, 1590, 1582; <b><sup>1</sup>H NMR(400 MHz, DMSO-d<sub>6</sub>):</b> <math>\delta</math> 12.55 (s, 1H), 7.98-7.96 (d, <math>J = 8.0</math> Hz, 2H, ArH), 7.53-7.19 (m, 12H, ArH), 2.63-2.62 (q, 2H, CH<sub>2</sub>), 1.21-1.17 (t, 3H, CH<sub>3</sub>); <b><sup>13</sup>C NMR (100MHz, DMSO-d<sub>6</sub>):</b> <math>\delta</math> 146.1, 144.3, 137.3, 135.7, 132.1, 131.6, 128.9, 128.5, 128.3, 127.5, 127.4, 126.8, 125.7, 125.6, 28.4, 15.8, 15.7; HRMS (ESI) <math>m/z</math> Calculated for C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> (M+1)<sup>+</sup> 356.1525, Found 357.1532. <math>m/z</math> Calculated for C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> (M+1)<sup>+</sup> 357.1525, Found 357.1532.</p>
3	 <p style="text-align: center;"><b>3c</b></p>	<p><b>4,5-Diphenyl-2-(4-(trifluoromethyl)phenyl)-1H-imidazole (3c):</b> White solid; m.p.: 264-266 °C (lit.<sup>[58]</sup> 262-264<sup>0</sup>C); <b>FT-IR</b> (KBr) (<math>\nu_{\text{max}}/\text{cm}^{-1}</math>): 3435, 1618, 1580; <b><sup>1</sup>H NMR(400 MHz, DMSO-d<sub>6</sub>):</b> <math>\delta</math> 8.28-8.25 (d, <math>J = 8.0</math> Hz, 2H, ArH), 7.83-7.81 (d, <math>J = 8.4</math> Hz, 2H, ArH), 7.55-7.49 (m, 5H, ArH), 7.45-7.37 (m, 5H, ArH)</p>
4	 <p style="text-align: center;"><b>3d</b></p>	<p><b>2-(Benzo[d][1,3]dioxol-4-yl)-4,5-diphenyl-1H-imidazole (3d):</b> White solid; mp 207-208 °C (lit. <sup>[58]</sup> 206-207 °C); <b>FT-IR</b> (KBr): 3445, 3068, 2970, 1590, 1582; <b><sup>1</sup>H NMR(400 MHz, DMSO-d<sub>6</sub>):</b> <math>\delta</math> 12.47 (s, 1H), 7.61-7.59 (d, <math>J = 6.8</math> Hz, 2H, ArH), 7.53-7.51 (d, <math>J = 7.2</math> Hz, 2H, ArH), 7.47-7.46 (d, <math>J = 7.2</math> Hz, 2H, ArH), 7.42-7.38 (t, <math>J = 7.6</math> Hz, 2H, ArH), 7.35-7.33 (d, <math>J = 7.2</math> Hz, 1H, ArH), 7.28-7.25 (t, <math>J = 7.6</math> Hz, 2H, ArH), 7.20-7.18 (t, <math>J = 7.6</math> Hz, 1H, ArH), 7.01-6.98 (t, <math>J = 8.8</math> Hz, 1H, ArH), 6.05 (s, 2H, CH<sub>2</sub>); <b><sup>13</sup>C NMR (100MHz, DMSO-d<sub>6</sub>):</b> <math>\delta</math> 148.0, 147.8, 145.8, 137.2, 135.6, 131.5, 129.0, 128.8, 128.7, 128.6, 128.2, 127.5, 127.4, 126.8, 125.1, 119.7, 119.6, 109.0, 108.9, 106.0, 105.9, 101.7; HRMS (ESI) <math>m/z</math> Calculated for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> (M+1)<sup>+</sup> 341.1212, Found 341.1217.</p>
		<p><b>2-(4-Fluorophenyl)-4,5-diphenyl-1H-imidazole (3e):</b> White solid; m.p.: 260–262 °C (lit.<sup>[58]</sup> 262-264<sup>0</sup>C); <b>FT-IR</b> (KBr):</p>

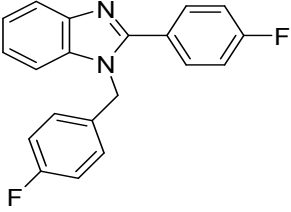
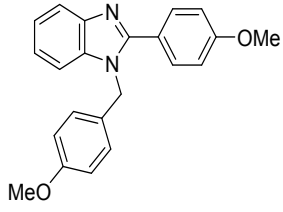
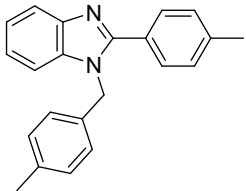
5	 <p style="text-align: center;"><b>3e</b></p>	<p>3060, 3028, 1615, 1500, 1460 <math>\text{cm}^{-1}</math>; <b><math>^1\text{H}</math> NMR(400 MHz, DMSO-d<sub>6</sub>):</b> <math>\delta</math> 12.72 (s, 1H), 8.16-8.14 (d, <math>J</math> = 8.0 Hz, 2H, ArH), 8.10-8.08 d, <math>J</math> = 8.2Hz, 2H, ArH), 7.56-7.54 (t, <math>J</math> = 7.6Hz, 2H), 7.40-7.22 (m, 6H); <b><math>^{13}\text{C}</math> NMR (100MHz, DMSO-d<sub>6</sub>):</b> <math>\delta</math> 146.4, 130.2, 130.1, 129.7, 129.1, 128.6, 127.2, 127.1, 126.5, 125.6, 125.3, 123.4, 116.4; HRMS (ESI) <math>m/z</math> Calculated for <math>\text{C}_{21}\text{H}_{15}\text{FN}_2</math> (M+1)<sup>+</sup> 315.1219 Found 315.1225.</p>
6	 <p style="text-align: center;"><b>3f</b></p>	<p><b>2-(4-Methoxyphenyl)-4,5-diphenyl-1H-imidazole (3f):</b> White solid: mp: 231-233 °C (lit.<sup>[58]</sup> 230-233 °C ); <b>FT-IR</b> (KBr, <math>\text{cm}^{-1}</math>): 3429, 3032, 2962, 1630, 1504 <math>\text{cm}^{-1}</math>; <b><math>^1\text{H}</math> NMR(400 MHz, DMSO-d<sub>6</sub>):</b> <math>\delta</math> 12.51 (s, 1H), 8.06-8.04 (d, <math>J</math> = 8.1 Hz, 2H), 7.52-7.35 (m, 10H), 7.06-7.04 (d, <math>J</math> = 8.4 Hz, 2H), 3.84 (s, 3H, OMe), <b><math>^{13}\text{C}</math> NMR (100MHz, DMSO-d<sub>6</sub>):</b> <math>\delta</math> 159.6, 145.8, 137.7, 137.0, 135.3, 131.2, 129.4, 128.6, 128.2, 127.9, 126.6, 125.3, 123.4, 114.2, 55.3; HRMS (ESI) <math>m/z</math> Calculated for <math>\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}</math> (M+1)<sup>+</sup> 327.1419, Found 327.1439.</p>
7	 <p style="text-align: center;"><b>3g</b></p>	<p><b>4,5-Diphenyl-2-(p-tolyl)-1H-imidazole (3g):</b> White solid: mp: 230-232 °C (lit.<sup>[58]</sup> 231-233 °C ); <b>FT-IR</b> (KBr, <math>\text{cm}^{-1}</math>): 3429, 3032, 2962, 1630, 1504 <math>\text{cm}^{-1}</math>; <b><math>^1\text{H}</math> NMR(400 MHz, DMSO-d<sub>6</sub>):</b> <math>\delta</math> 12.58 (s, 1H), 8.06-8.04 (d, <math>J</math> = 8.0 Hz, 2H), 7.53-7.20 (m, 10H), 7.08-7.06 (d, <math>J</math> = 8.0 Hz, 2H), 2.32 (s, 3H, CH<sub>3</sub>), <b><math>^{13}\text{C}</math> NMR (100MHz, DMSO-d<sub>6</sub>):</b> <math>\delta</math> 145.7, 137.5, 137.0, 135.3, 131.2, 129.4, 128.7, 128.3, 128.0, 127.8, 127.5, 127.1, 126.5, 125.0, 21.1; HRMS (ESI) <math>m/z</math> Calculated for <math>\text{C}_{22}\text{H}_{18}\text{N}_2</math> (M+1)<sup>+</sup> 310.1470, Found 310.1477.</p>
8	 <p style="text-align: center;"><b>3h</b></p>	<p><b>2-(2-Chlorophenyl)-4,5-diphenyl-1H-imidazole (3h):</b> White solid: mp: 202-204 °C (lit.<sup>[58]</sup> 201-202 °C ); <b>FT-IR</b> (KBr, <math>\text{cm}^{-1}</math>): 3442, 3072, 2960, 1615; <b><math>^1\text{H}</math> NMR (DMSO-d<sub>6</sub>, 400MHz):</b> <math>\delta</math> 12.47(s, 1H), 8.04-8.00 (m, 1H), 7.52-7.21 (m, 13H); <b><math>^{13}\text{C}</math> NMR (100 MHz, DMSO-d<sub>6</sub>):</b> <math>\delta</math> 145.7, 128.6, 128.4, 128.3, 128.2, 127.4, 127.2, 126.9, 126.6, 123.4, 114.3; HRMS (ESI) <math>m/z</math></p>

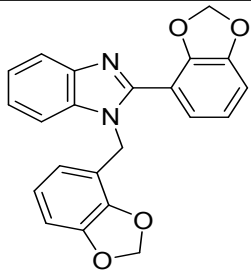
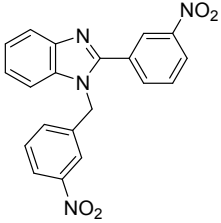
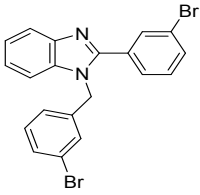
		Calculated for C <sub>21</sub> H <sub>15</sub> N <sub>2</sub> Cl (M+1) <sup>+</sup> 331.0924, (M+3) <sup>+</sup> 333.0824, Found 331.0620 (M+1) <sup>+</sup> , 333.0874 (M+3) <sup>+</sup>
9	 <p style="text-align: center;"><b>3i</b></p>	<b>2-(3-Nitrophenyl)-4,5-diphenyl-1H-imidazole (3i):</b> Yellow solid; mp: 268-270 °C (lit. <sup>[58]</sup> 265-267 °C ); <b>FT-IR</b> (KBr): 3450, 1652, 1600, 1530, 1330 cm <sup>-1</sup> ; <b><sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):</b> δ 12.87 (s, 1H), 8.89 (s, 1H), 8.58-8.56 (t, <i>J</i> =7.6 Hz, 1H), 8.25-8.23 (d, 1H, <i>J</i> =8.0 Hz), 7.81-7.79 (d, 1H, <i>J</i> =8.0 Hz), 7.54–7.30 (m, 10H); <b><sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):</b> δ 148.6, 142.5, 132.9, 131.3, 130.5, 128.9, 128.3, 127.2, 123.5, 119.3; HRMS (ESI) <i>m/z</i> Calculated for C <sub>21</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> (M+1) <sup>+</sup> 342.1164, Found 342.1172.
10	 <p style="text-align: center;"><b>3j</b></p>	<b>2-(3,4-Dimethoxyphenyl)-4,5-diphenyl-1H-imidazole (3j):</b> White solid; mp 214-216 °C (lit. <sup>[59]</sup> 213-216 °C ); <b>FT-IR</b> (KBr): 3430, 2982, 2900, 2460, 1629, 1210 cm <sup>-1</sup> ; <b><sup>1</sup>H NMR(400 MHz, DMSO-d<sub>6</sub>):</b> δ 12.54 (s, 1H), 8.08-8.06 (d, <i>J</i> = 8.8 Hz, 2H, ArH), 7.65-7.29 (m, 10H, ArH), 7.00-6.98 (d, <i>J</i> = 8.8 Hz, 1H, ArH), 3.89 (s, 6H); <b><sup>13</sup>C NMR (100MHz, DMSO-d<sub>6</sub>):</b> δ 150.2, 148.1, 145.2, 133.2, 129.6, 129.2, 129.0, 128.9, 128.8, 127.4, 124.3, 121.0, 115.9, 112.4, 56.4; HRMS (ESI) <i>m/z</i> Calculated for C <sub>23</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> (M+1) <sup>+</sup> 356.1525, Found 357.1532.
11	 <p style="text-align: center;"><b>3k</b></p>	<b>2-(2,3-Dimethoxyphenyl)-4,5-diphenyl-1H-imidazole (3k):</b> White solid; mp 214-216 °C (lit.213-216 <sup>0</sup> C ); <b>FT-IR</b> (KBr): 3430, 2982, 2900, 2460, 1629, 1210 cm <sup>-1</sup> ; <b><sup>1</sup>H NMR(400 MHz, DMSO-d<sub>6</sub>):</b> δ 12.52 (s, 1H), 8.04-8.02 (d, <i>J</i> = 8.0 Hz, 1H, ArH), 7.65-7.29 (m, 10H, ArH), 7.14-7.12 (t, <i>J</i> = 8.0 Hz, 1H, ArH), 7.00-6.98 (d, <i>J</i> = 8.0 Hz, 1H, ArH), 3.82 (s, 6H, OMe), <b><sup>13</sup>C NMR (100MHz, DMSO-d<sub>6</sub>):</b> δ 148.3, 147.9, 147.5,138.2, 131.5, 129.6, 129.2, 129.0, 128.9, , 125.4, , 123.3, 119.0, 118.4, 60.2, 56.4; HRMS (ESI) <i>m/z</i> Calculated for C <sub>23</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> (M+1) <sup>+</sup> 357.1525, Found 357.1532.

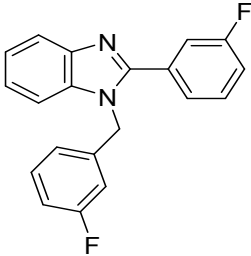
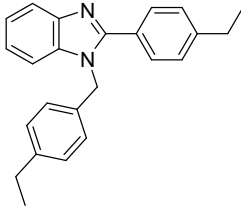
12	 <p style="text-align: center;"><b>3l</b></p>	<p><b>2-(3-Bromophenyl)-4,5-diphenyl-1H-imidazole (3l):</b> White solid; mp: 301-304 °C (lit. [60] 302-303 °C ); <b>FT-IR</b> (KBr): 3430, 3050, 1607, 1585, 1327 cm<sup>-1</sup>; <b><sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):</b> δ 12.85 (s, 1H), 8.30 (s, 1H), 8.56-8.54 (d, <i>J</i>=8.0 Hz, 1H), 8.20-8.18 (d, 1H, <i>J</i>=8.0 Hz), 7.54–7.30 (m, 10H), 7.30-7.28 (t, 1H, <i>J</i>=8.0 Hz); <b><sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):</b> δ 148.6, 142.5, 132.9, 131.3, 130.5, 128.9, 128.3, 127.2, 123.5, 119.3; HRMS (ESI) <i>m/z</i> Calculated for C<sub>21</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub> (M+1)<sup>+</sup> 375.1164, (M+3)<sup>+</sup> 377.1164, Found 375.6172 (M+1)<sup>+</sup>, 375.8464 (M+3)<sup>+</sup>.</p>
13	 <p style="text-align: center;"><b>3m</b></p>	<p><b>2-(3-Fluorophenyl)-4,5-diphenyl-1H-imidazole (3m):</b> White solid; mp: 221-223 °C (lit.[29] 220-222 °C ); <b>FT-IR</b> (KBr): 3058, 2692, 1614, 1578 cm<sup>-1</sup>; <b><sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):</b> δ 12.76 ( s, 1H), 7.92-7.90 (d, <i>J</i> = 8.0 Hz, 1H, ArH), 7.86-7.83 (d, <i>J</i> = 12.0 Hz, 1H, ArH), 7.53-7.47 (m, 5H, ArH), 7.44-7.40 (t, <i>J</i> = 7.4 Hz, 2H, ArH), 7.38-7.36 (d, <i>J</i> = 7.2 Hz, 1H, ArH), 7.30-7.26 (t, <i>J</i> = 7.4 Hz, 2H, ArH), 7.22-7.17 (m, 2H, ArH); <b><sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):</b> δ 178.9, 163.4, 139.2, 132.0, 129.4, 129.2, 127.2, 123.0, 115.0; HRMS (ESI) <i>m/z</i> Calculated for C<sub>21</sub>H<sub>15</sub>FN<sub>2</sub> (M+1)<sup>+</sup> 315.1219 Found 315.1225 (M+1)<sup>+</sup>.</p>
14	 <p style="text-align: center;"><b>3n</b></p>	<p><b>1-(4-Propoxybenzyl)-2-(4-propoxyphenyl)-1H benzo[d]imidazoles (3n):</b> White solid; mp: 156-161 °C; <b>FT-IR</b> (KBr): 3029, 2989, 1615, 1567, 1480, 1290, 1130, 1156, 1012 cm<sup>-1</sup>; <b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):</b> δ 7.82-7.80 (d, <i>J</i> = 8.4Hz, 1H, ArH), 7.61-7.59 (d, <i>J</i> = 9.2Hz, 2H, ArH), 7.25-7.24 (d, <i>J</i> = 1.6Hz, 1H, ArH), 7.21-7.19 (d, <i>J</i> = 8.0Hz, 2H, ArH), 7.01-6.99 (d, <i>J</i> = 8.8 Hz, 2H), 6.94-6.90 (m, 2H), 6.84-6.82 (d, <i>J</i> = 8.4 Hz, 2H), 5.36 (s, 2H), 3.95-3.92 (t, 2H, CH<sub>2</sub>), 3.89-3.86 (t, 2H, CH<sub>2</sub>), 1.83-1.73 (st, 6H, CH<sub>2</sub>), 1.05-0.99 (t, 6H, CH<sub>3</sub>); <b><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):</b> δ 160.5, 160.4, 158.7, 154.2, 152.4, 143.0, 136.0, 130.7, 130.5, 128.3, 128.3, 128.2, 127.1, 122.7, 122.4, 122.0, 119.5, 119.4, 114.9, 114.7, 110.5, 47.9, 22.5, 10.4;</p>

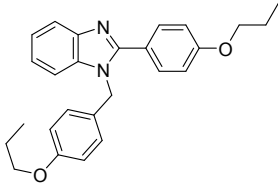
		HRMS (ESI) m/z Calculated for C <sub>26</sub> H <sub>28</sub> N <sub>2</sub> O <sub>2</sub> (M+1) <sup>+</sup> 401.2151 Found 401.2155.
15	 <p style="text-align: center;"><b>5a</b></p>	<b>1-Benzyl-2-phenyl-1H-benzo[d]imidazole (5a):</b> Pale yellow solid; mp: 130-132 <sup>o</sup> C (lit. <sup>[14]</sup> 130 <sup>o</sup> C ); <b>FT-IR</b> (KBr): 3035, 2928, 1609, 1587, 1497, 1271, 1150, 1110, 1020 cm <sup>-1</sup> ; <b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):</b> δ 7.87-7.85 (d, <i>J</i> = 7.6 Hz, 1H), 7.70 – 7.67(m, 2H); 7.48 – 7.41 (m, 3H); 7.32 – 7.19 (m, 6H); 7.10-7.08 (d, <i>J</i> = 8.0 Hz, 2H); 5.44 (s, 2H); <b><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):</b> δ 155.01, 142.9, 136.25, 135.9, 129.91, 129.81, 129.15, 128.93, 128.63, 127.98, 127.65, 125.84, 122.94, 122.59, 119.85, 110.43, 48.23: HRMS (ESI) m/z Calculated for C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> (M+1) <sup>+</sup> 284.1313, Found 284.1317.
16	 <p style="text-align: center;"><b>5b</b></p>	<b>1-(2-Chlorobenzyl)-2-(2-chlorophenyl)-1H-benzo[d]imidazoles (5b):</b> Pale yellow crystal; mp: 159-160 <sup>o</sup> C (lit. <sup>[14]</sup> 158 - 159 °C ); <b>FT-IR</b> (KBr): 3030, 2945, 1619, 1576, 1492, 1277, 1130, 1130, 1010, 650 cm <sup>-1</sup> ; <b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):</b> δ 7.80-7.78 (d, 1H, <i>J</i> = 8.2 Hz), 7.65-7.63 (d, 1H, <i>J</i> = 7.6 Hz), 7.58-7.56 (t, 1H, <i>J</i> = 8.0 Hz), 7.50-7.48(d, 2H, <i>J</i> = 8.0 Hz), 7.44-7.42 (t, 1H, <i>J</i> = 7.6 Hz), 7.39-7.37 (d, 1H, <i>J</i> = 8.0 Hz), 7.32-7.30 (t, 2H, <i>J</i> = 4.0 Hz), 7.28-7.26 (d, 1H, <i>J</i> = 7.6 Hz), 7.19-7.17 (t, 1H, <i>J</i> = 7.6 Hz), 6.68-6.66 (d, 1H, <i>J</i> = 8.0 Hz), 5.45 (s, 2H, CH <sub>2</sub> ); <b><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):</b> δ 151.9, 144.7, 136.2, 134.6, 134.4, 133.4, 133.1, 132.8, 130.9, 130.7, 130.6, 130.5, 129.8, 128.6, 128.50, 125.3, 124.4, 120.8, 113.2, 46.3; HRMS (ESI) m/z Calculated for C <sub>20</sub> H <sub>14</sub> Cl <sub>2</sub> N <sub>2</sub> (M+1) <sup>+</sup> 353.0534, (M+3) <sup>+</sup> 355.0534, (M+5) <sup>+</sup> 357.0534, Found 353.0539 (M+1) <sup>+</sup> . 355.0649 (M+3) <sup>+</sup> . 357.0833 (M+5) <sup>+</sup> .
		<b>1-(4-Fluorobenzyl)-2-(4-fluorophenyl)-1Hbenzo[d]imidazoles (5c):</b> Yellow solid; mp: 111-113 °C (lit. <sup>[15]</sup> 111 °C ); <b>FT-IR</b>

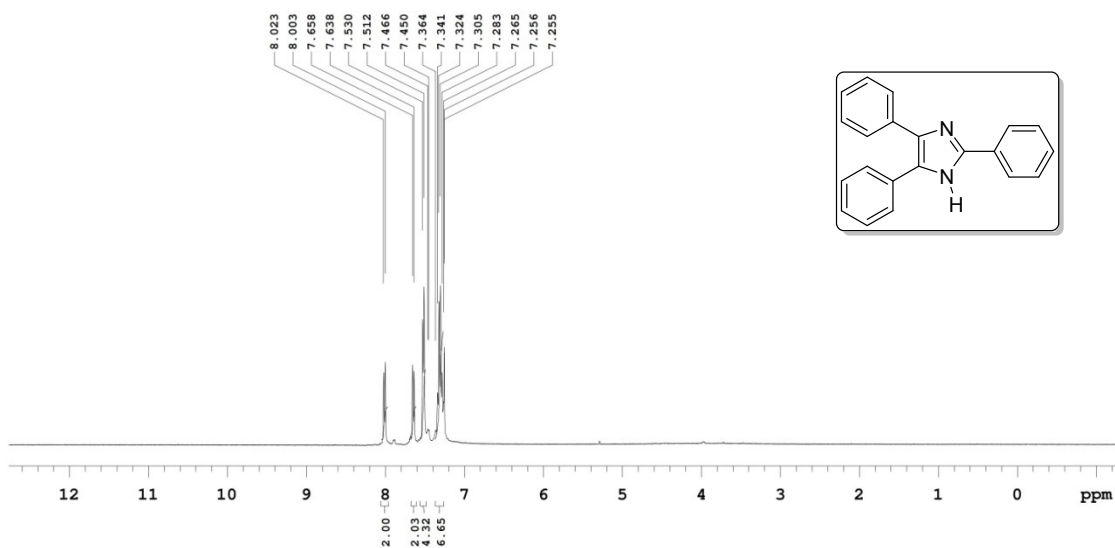


17	 <p style="text-align: center;"><b>5c</b></p>	<p>(KBr): 3029, 2955, 1615, 1595, 1478, 1271, 1150, 1130, 1025, 780 cm<sup>-1</sup>; <b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):</b> δ 7.81-7.76 (m, 3 H), 7.54-7.56 (d, 1H, <i>J</i> = 8.8 Hz), 7.38-7.36 (t, 2H, <i>J</i> = 8.4 Hz), 7.28-7.26 (m, 2H), 7.12-7.10 (t, 2H, <i>J</i> = 8.4 Hz), 7.08-7.04 (m, 2H), 5.48 (s, 2H); <b><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):</b> δ 165.1, 163.5, 163.2, 161.5, 153.5, 143.8, 137.1, 134.2, 132.7, 129.5, 127.8, 123.9, 123.6, 120.6, 117.1 (m), 112.2, 47.9 HRMS (ESI) <i>m/z</i> Calculated for C<sub>20</sub>H<sub>14</sub>F<sub>2</sub>N<sub>2</sub> (M+1)<sup>+</sup> 321.1125 Found 321.1129 (M+1)<sup>+</sup>.</p>
18	 <p style="text-align: center;"><b>5d</b></p>	<p><b>1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzo[d]imidazoles (5d):</b> mp: 128-130°C (lit. [16] 130-131°C ); <b>FT-IR</b> (KBr): 3010, 2935, 1600, 1570, 1480, 1271, 1150, 1123, 1050 cm<sup>-1</sup>; <b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):</b> δ 7.72-7.70 (d, 3 H, <i>J</i> = 8.2 Hz), 7.44-7.42 (d, 1H, <i>J</i> = 8.0 Hz), 7.35-7.28 (m, 2H), 7.12-7.10 (d, 2H, <i>J</i> = 8.4 Hz), 7.00-6.98 (d, 2H, <i>J</i> = 8.2 Hz), 6.92-6.90 (d, 2H, <i>J</i> = 8.4 Hz), 5.47 (s, 2H), 3.80 (s, 3H), 3.65 (s, 3H); <b><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):</b> δ 161.6, 159.7, 154.3, 143.91, 136.2, 131.6, 130.2, 128.8, 123.7, 123.6, 123.3, 120.3, 116.50, 115.4, 112.6, 56.6, 56.2, 48.2 HRMS (ESI) <i>m/z</i> Calculated for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> (M+1)<sup>+</sup> 345.1525 Found 345.1530.</p>
19	 <p style="text-align: center;"><b>5e</b></p>	<p><b>1-(4-Methylbenzyl)-2-p-tolyl-1H-benzo[d]imidazole (5e):</b> White solid; mp: 130-131°C (lit.[16] 129 -130°C ); <b>FT-IR</b> (KBr): 3046, 2900, 1612, 1567, 1487, 1268, 1143, 1134, 1028 cm<sup>-1</sup>; <b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):</b> δ 7.73-7.71 (d, 1H, <i>J</i> = 7.2 Hz), 7.65-7.63 (d, 2H, <i>J</i> = 7.6 Hz), 7.42-7.40 (d, 1H, <i>J</i> = 7.6Hz), 7.32-7.30 (d, 2H, <i>J</i> = 7.8Hz), 7.26-7.19 (m, 2H), 7.10-7.08 (d, 2H, <i>J</i> = 7.6 Hz), 6.88-6.86 (d, 2H, <i>J</i> = 7.6 Hz), 5.49 (s, 2H), 2.32 (s, 3H), 2.18 (s, 3H); <b><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):</b> δ 154.5, 143.9, 140.6, 137.9, 137.1, 135.2, 131.5, 130.1, 128.3, 126.2, 124.7, 122.3, 120.1, 113.4, 47.4, 22.3, 21.6; HRMS (ESI) <i>m/z</i> Calculated for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub> (M+1)<sup>+</sup> 313.1626 Found 313.1630;</p>

		HPLC 97.9 %.
20	 <p style="text-align: center;"><b>5f</b></p>	<p><b>2-(Benzo[d][1,3]dioxol-5-yl)-1-(benzo[d][1,3]dioxol-5-ylmethyl)-1H-benzo[d]imidazoles (5f):</b> White solid; mp: 161-164<sup>o</sup>C (lit.<sup>[17]</sup> 162<sup>o</sup>C );<b>FT-IR</b> (KBr): 3023, 2934, 1616, 1590, 1497, 1285, 1150, 1120, 1030 1 cm<sup>-1</sup>; <b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):</b> δ 7.82-7.80 (d, <i>J</i> = 7.6Hz, 1H, ArH), δ 7.30-7.11 (m, 5H, ArH), 6.85-6.83 (d, <i>J</i> = 8.0Hz, 1H, ArH), 6.74-6.72 (d, <i>J</i> = 8.0Hz, 1H, ArH), 6.55-6.54 (m, 2H), 5.99 (s, 2H), 5.92 (s, 2H), 5.33 (s, 2H); <b><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):</b> δ 153.8, 149.1, 148.3, 148.0, 147.2, 142.9, 135.9, 130.0, 124.5, 123.6, 123.5, 123.0, 122.7, 122.6, 119.7, 110.4, 109.6, 109.5, 108.6, 106.5, 101.6, 48.1; HRMS (ESI) <i>m/z</i> Calculated for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub> (M+1)<sup>+</sup> 373.1110 Found 373.1117: HPLC 97.2 %.</p>
21	 <p style="text-align: center;"><b>5g</b></p>	<p><b>1-(3-Nitrobenzyl)-2-(3-nitrophenyl)-1H-benzo[d]imidazoles (5g):</b> Pale yellow solid; mp: 168-169<sup>o</sup>C (lit. <sup>[18]</sup> 167 - 168 <sup>o</sup>C );<b>FT-IR</b> (KBr): 3027, 2947, 1616, 1594, 1491, 1264, 1129, 1110, 1043 cm<sup>-1</sup>; <b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):</b> δ 8.43 (s, 1H), 8.40-8.38 (d, 1 H, <i>J</i> = 8.2Hz), 8.20-8.18 (d, 1H, <i>J</i> = 7.6 Hz), 8.14-8.12 (d, 1H, <i>J</i> = 8.0 Hz), 7.98 (s, 1H), 7.84-7.78 (m, 2H), 7.65-7.56 (m, 2H), 7.42-7.40 (d, 1H, <i>J</i> = 7.6 Hz), 7.35-7.33 (m, 2H), 5.80 (s, 2H); <b><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):</b> δ 152.4, 152.4, 149.2, 149.3, 143.8, 140.4, 137.3, 136.7, 134.2, 132.4, 132.1, 132.9, 125.1, 125.3, 124.3, 123.8, 122.6, 121.3, 112.6, 48.3; HRMS (ESI) <i>m/z</i> Calculated for C<sub>20</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub> (M+1)<sup>+</sup> 375.1015 Found 375.1019.</p>
22	 <p style="text-align: center;"><b>5h</b></p>	<p><b>1-(3-Bromobenzyl)-2-(3-bromophenyl)-1H-benzo[d]imidazoles (5h):</b> White solid; mp: 176-199<sup>o</sup>C (lit. <sup>[19]</sup> 175 - 178 <sup>o</sup>C ); <b>FT-IR</b> (KBr): 3035, 2928, 1609, 1587, 1497, 1271, 1150, 1110, 1020, 730, 720 cm<sup>-1</sup>; <b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):</b> δ 7.89-7.85 (m, 2 H), 7.60-7.47 (m, 5 H), 7.35-7.32 (t, 2H, <i>J</i> = 8.0 Hz), 7.25-7.22 (m, 2H), 7.10-7.08 (d, 1H, <i>J</i> = 7.6</p>

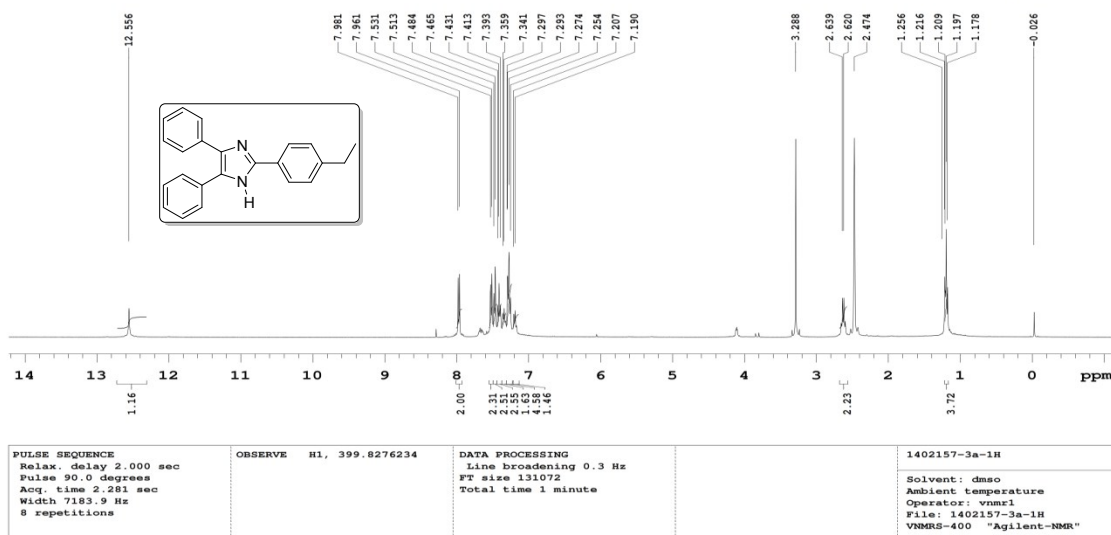
	<b>5h</b>	Hz), 5.43 (s, 2 H); <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ 154.5, 143.6, 136.3, 136.2, 134.3, 134.6, 133.7, 133.6, 132.7, 131.2, 129.6, 129.5, 129.3, 124.8, 124.6, 124.1, 123.2, 121.2, 112.5, 49.1; HRMS (ESI) m/z Calculated for C <sub>20</sub> H <sub>14</sub> Br <sub>2</sub> N <sub>2</sub> (M+1) <sup>+</sup> 443.9524, (M+3) <sup>+</sup> 445.9524, (M+5) <sup>+</sup> 447.9524, Found 443.9629 (M+1) <sup>+</sup> , 445.962 (M+3) <sup>+</sup> , 447.9513 (M+5) <sup>+</sup> .
23	 <p><b>5i</b></p>	<b>1-(3-Fluorobenzyl)-2-(3-fluorophenyl)-1H-benzo[d]imidazole (5i):</b> White solid; mp: 178-180 °C ; FT-IR (KBr): 3062, 2700, 1618, 1582 cm <sup>-1</sup> ; <sup>1</sup> H NMR (400 MHz, DMSO-d <sub>6</sub> ): δ 7.77-7.70 (m, 1H, ArH), 7.57-7.48 (m, 4H, ArH), 7.38-7.31 (m, 1H, ArH), 7.30-7.21 (m, 3H, ArH), 7.06-7.01 (dt, J = 2.2 Hz, 1H, ArH), 6.84-6.82 (d, J = 10.0 Hz, 1H, ArH), 6.75-6.36 (d, 1H, ArH), 2.47 (s, 2H, CH <sub>2</sub> ) ; <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ 178.9, 163.4, 139.2, 132.0, 129.4, 129.2, 127.2, 123.0, 115.0; <sup>13</sup> C NMR (100 MHz, DMSO-d <sub>6</sub> ) δ: 163.0, 162.9, 153.5, 143.5, 138.0, 132.4, 130.1, 127.9, 123.4, 123.3, 123.2, 119.7, 119.4, 116.2, 116.0, 113.4, 50.1; HRMS (ESI) m/z Calculated for C <sub>20</sub> H <sub>14</sub> F <sub>2</sub> N <sub>2</sub> (M+1) <sup>+</sup> 321.1125, Found 321.1130 (M+1) <sup>+</sup> .
24	 <p><b>5j</b></p>	<b>1-(4-Ethylbenzyl)-2-(4-ethylphenyl)-1H-benzo[d]imidazole (5j):</b> Yellow solid; mp: 97-99 °C; FT-IR (KBr): 3025, 2940, 1600, 1574, 1550, 1271, 1140, 1129, 1020 cm <sup>-1</sup> ; <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ): δ 7.86-7.85 (d, J = 8.4 Hz, 1H, ArH), δ 7.63-7.61 (d, J = 8.4 Hz, 2H, ArH), 7.28 – 7.25 (m, 3H), 7.21 – 7.19 (m, 2H), 7.15 – 7.13 (d, J = 8.0 Hz, 2H), 7.03-7.00 (d, J = 8.4 Hz, 2H), 5.42 (s, 2H), 2.70-2.68 (q, 2H, CH <sub>2</sub> ), 2.63-2.62 (q, 2H, CH <sub>2</sub> ), 1.27-1.20 (t, 6H, CH <sub>3</sub> ); <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ 154.3, 146.2, 143.7, 143.1, 136.0, 133.6, 129.3, 129.1, 128.49, 128.43, 128.2, 128.1, 127.3, 125.9, 122.8, 122.5, 122.4, 119.8, 119.7, 110.5, 48.2, 28.7, 15.4; : HRMS (ESI) m/z Calculated for C <sub>24</sub> H <sub>24</sub> N <sub>2</sub> (M+1) <sup>+</sup> 341.1939, Found 341.1945 (M+1) <sup>+</sup> .

25	 <p style="text-align: center;"><b>5k</b></p>	<p><b>1-(4-Propoxybenzyl)-2-(4-propoxyphenyl)-1H-benzo[d]imidazoles (5k):</b> White solid; mp: 156-161°C; <b>FT-IR</b> (KBr): <b>FT-IR</b> (KBr): 3029, 2989, 1615, 1567, 1480, 1290, 1130, 1156, 1012 cm<sup>-1</sup>; <b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):</b> δ 7.82-7.80 (d, <i>J</i> = 8.4Hz, 1H, ArH), 7.61-7.59 (d, <i>J</i> = 9.2Hz, 2H, ArH), 7.25-7.24 (d, <i>J</i> = 1.6Hz, 1H, ArH), 7.21-7.19 (d, <i>J</i> = 8.0Hz, 2H, ArH), 7.01-6.99 (d, <i>J</i> = 8.8 Hz, 2H), 6.94-6.90 (m, 2H), 6.84-6.82 (d, <i>J</i> = 8.4 Hz, 2H), 5.36 (s, 2H), 3.95-3.92 (t, 2H, CH<sub>2</sub>), 3.89-3.86 (t, 2H, CH<sub>2</sub>), 1.83-1.73 (st, 6H, CH<sub>2</sub>), 1.05-0.99 (t, 6H, CH<sub>3</sub>), <b><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):</b> δ 160.5, 160.4, 158.7, 154.2, 152.4, 143.0, 136.0, 130.7, 130.5, 128.3, 128.3, 128.2, 127.1, 122.7, 122.4, 122.0, 119.5, 119.4, 114.9, 114.7, 110.5, 47.9, 22.5, 10.4; HRMS (ESI) <i>m/z</i> Calculated for C<sub>26</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub> (M+1)<sup>+</sup> 401.2151 Found 401.2155 (M+1)<sup>+</sup>.</p>
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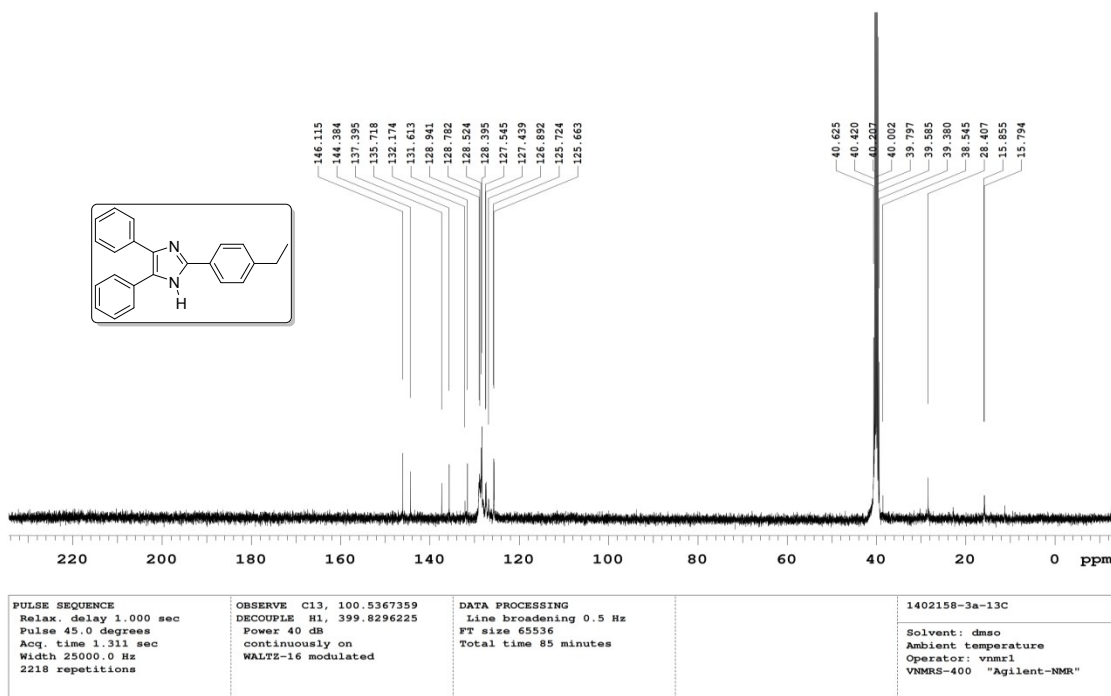


<p>PULSE SEQUENCE</p> <p>Relax. delay 2.000 sec</p> <p>Pulse 90.0 degrees</p> <p>Acq. time 2.281 sec</p> <p>Width 7183.9 Hz</p> <p>8 repetitions</p>	<p>OBSERVE H1, 399.8257202</p>	<p>DATA PROCESSING</p> <p>Line broadening 0.3 Hz</p> <p>FT size 131072</p> <p>Total time 1 minute</p>	<p>1401676-P2-1H</p> <p>Solvent: cdcl3</p> <p>Ambient temperature</p> <p>Operator: vnmr1</p> <p>File: 1401676-P2-1H</p> <p>VNMR5-400 "Agilent-NMR"</p>
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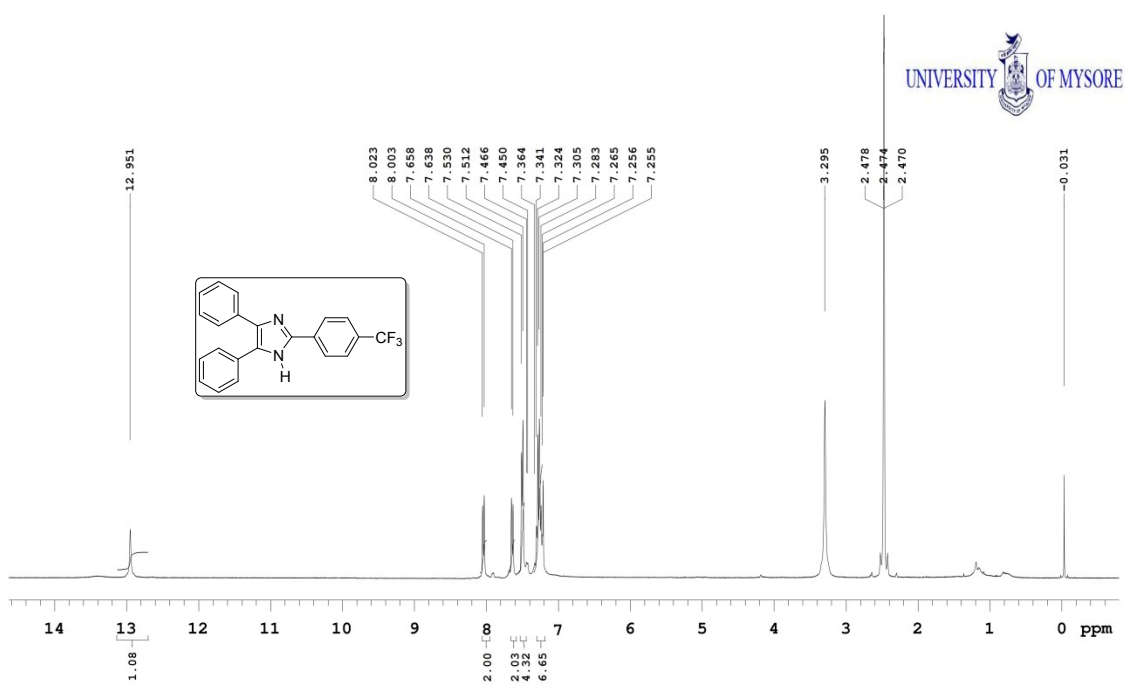
**<sup>1</sup>H NMR spectrum of compound 3a**



**<sup>1</sup>H NMR spectrum of compound entry 3b**

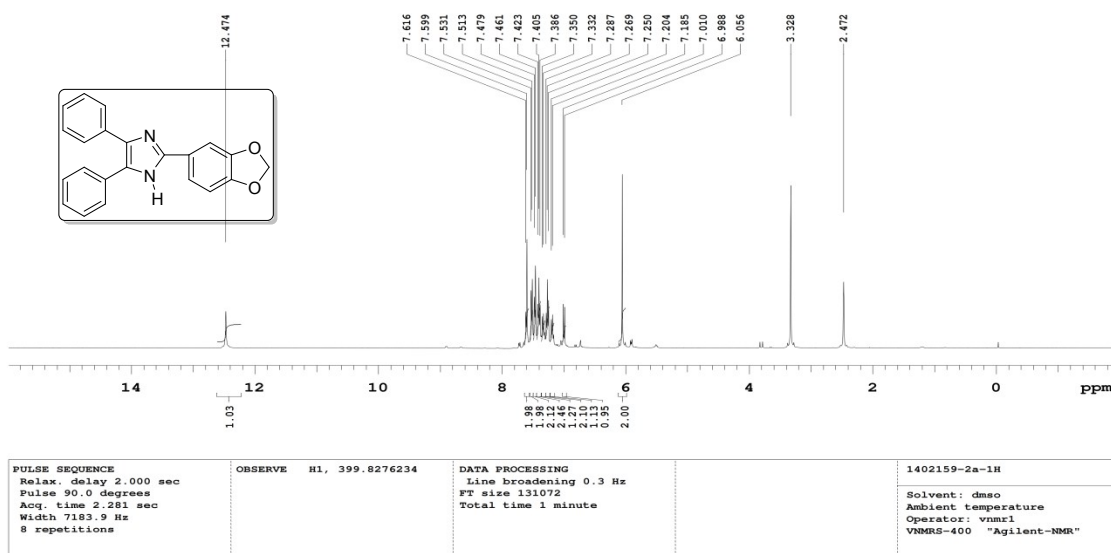


**<sup>13</sup>C NMR spectrum of compound entry 3b**

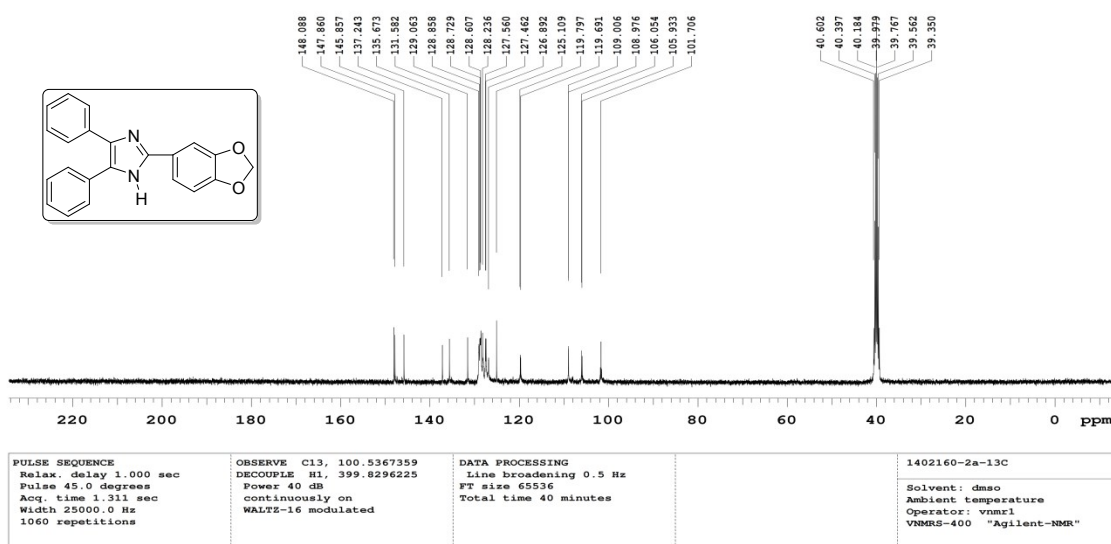


<b>PULSE SEQUENCE</b> Relax. delay 2.000 sec Pulse 90.0 degrees Acq. time 2.281 sec Width 7183.9 Hz 8 repetitions	<b>OBSERVE</b> H1, 399.8276234	<b>DATA PROCESSING</b> Line broadening 0.3 Hz FT size 131072 Total time 1 minute	1402156-1a-1H Solvent: dmsd Ambient temperature Operator: vmmr1 File: 1402156-1a-1H VMRS-400 "Agilent-NMR"
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**<sup>1</sup>H NMR spectrum of compound entry 3c**

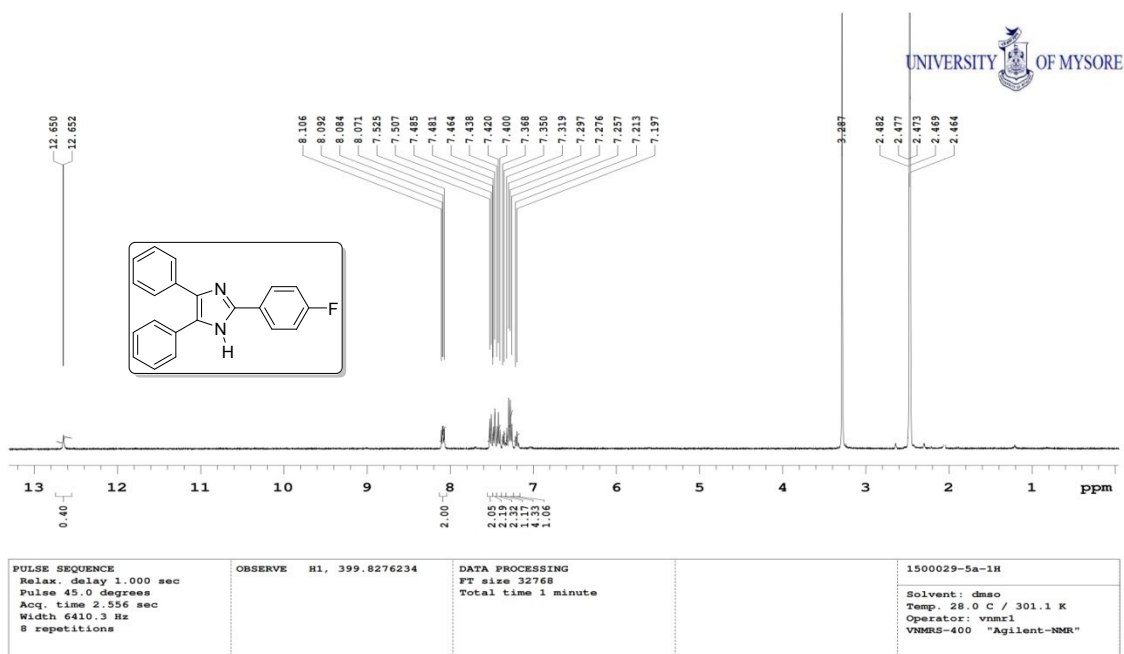


**<sup>1</sup>H NMR spectrum of compound entry 3d**

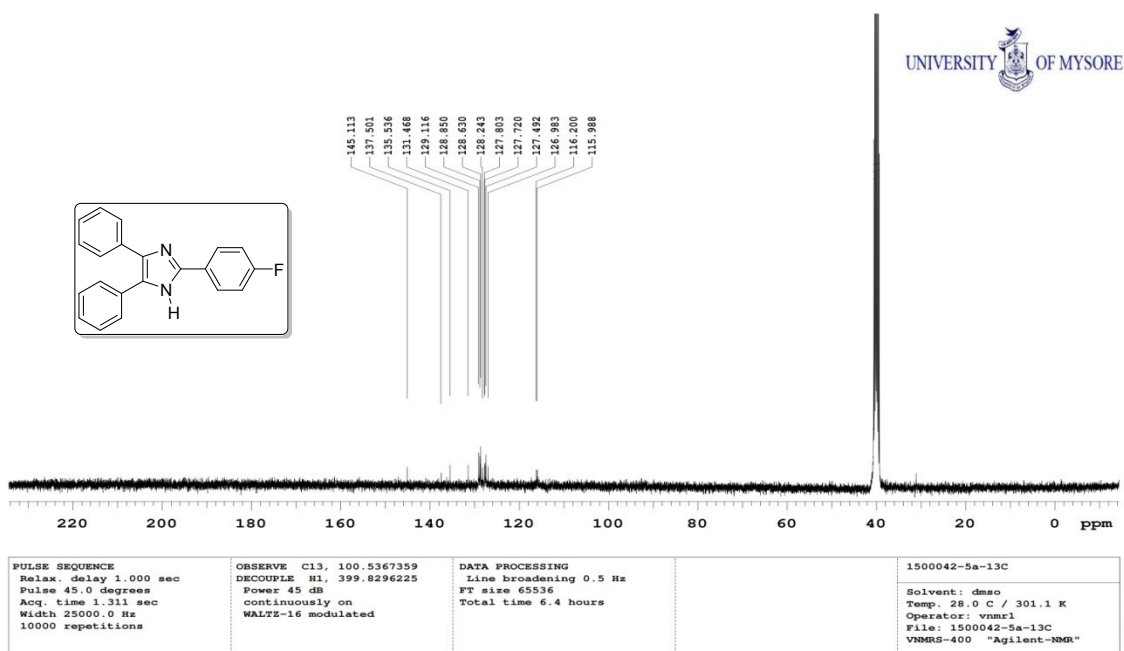


**<sup>13</sup>C NMR spectrum of compound entry 3d**

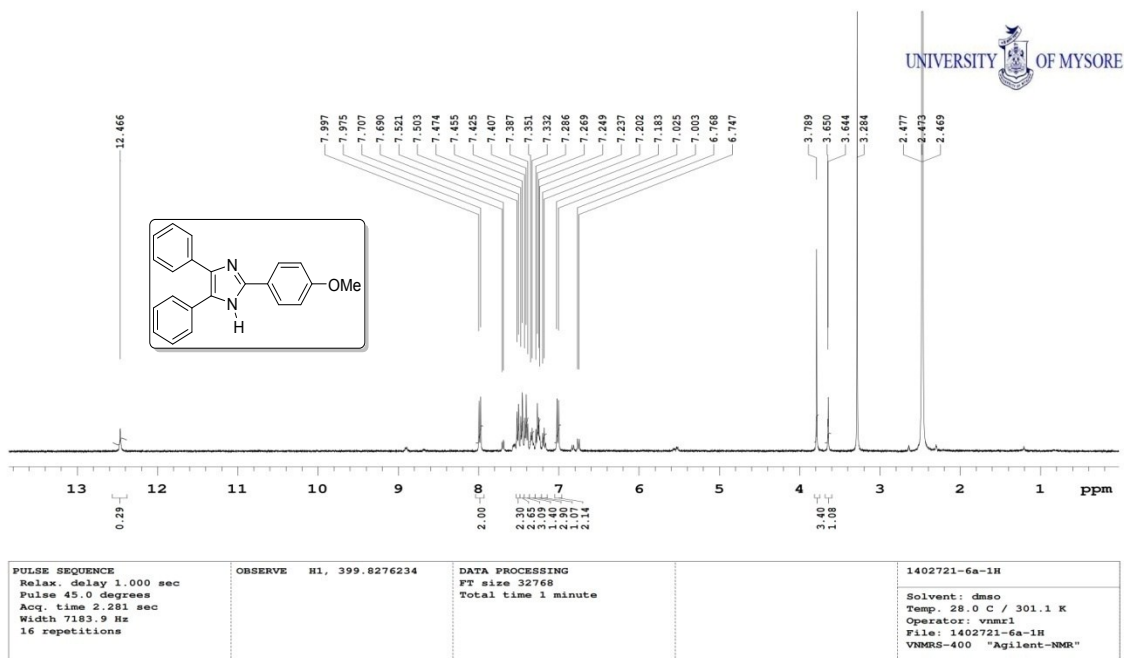




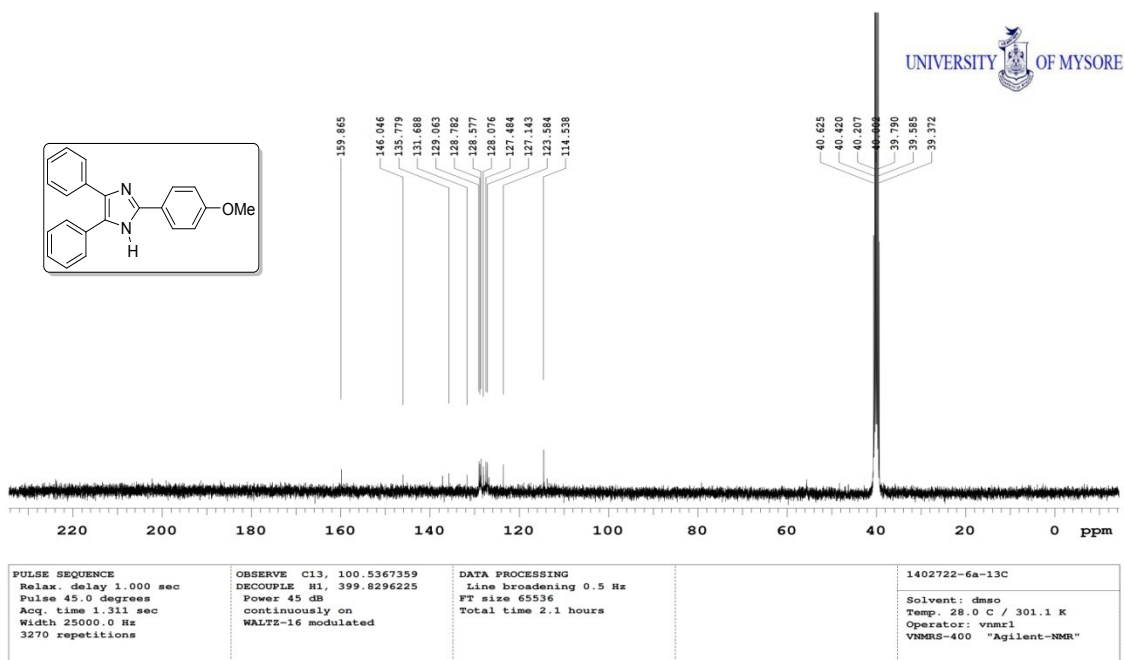
**<sup>1</sup>H NMR spectrum of compound entry 3e**



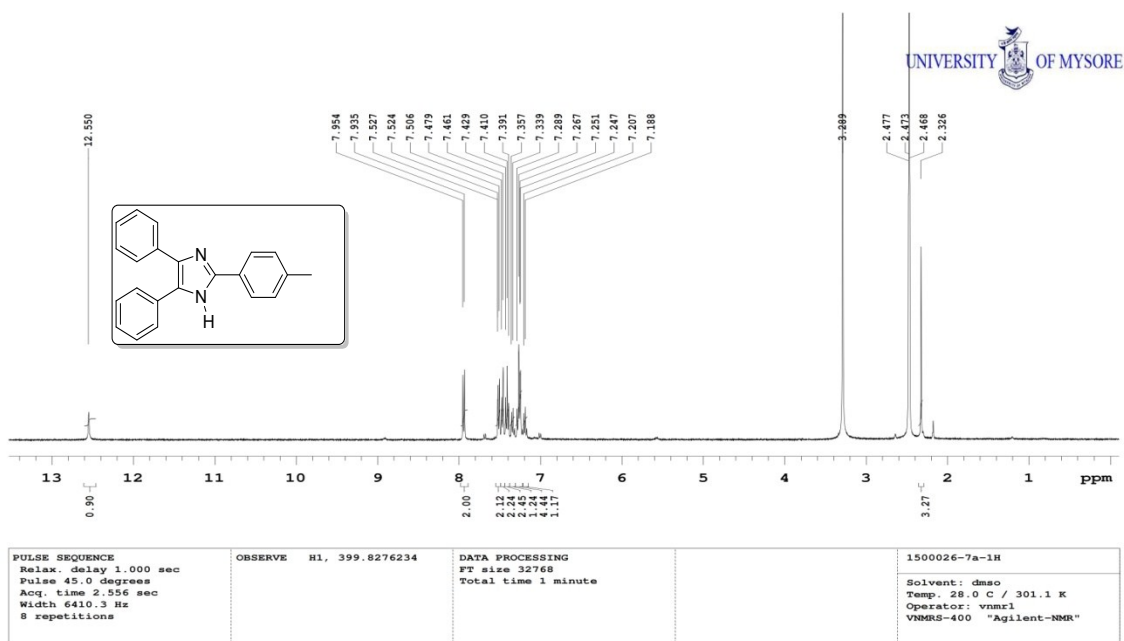
**<sup>13</sup>C NMR spectrum of compound entry 3e**



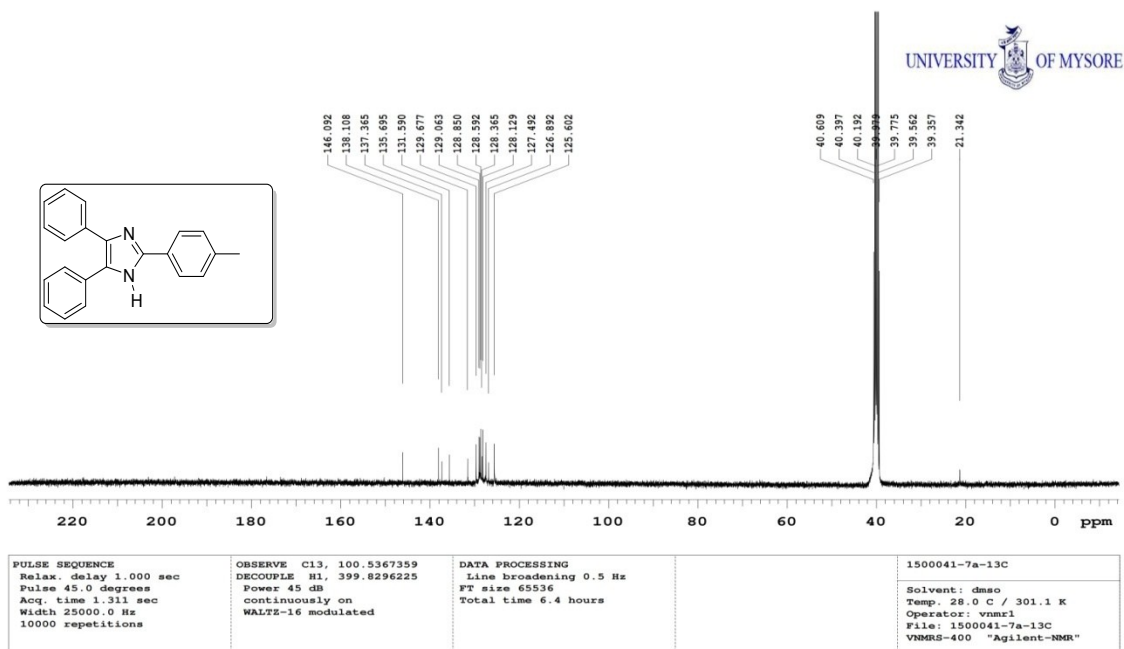
**<sup>1</sup>H NMR spectrum of compound entry 3f**



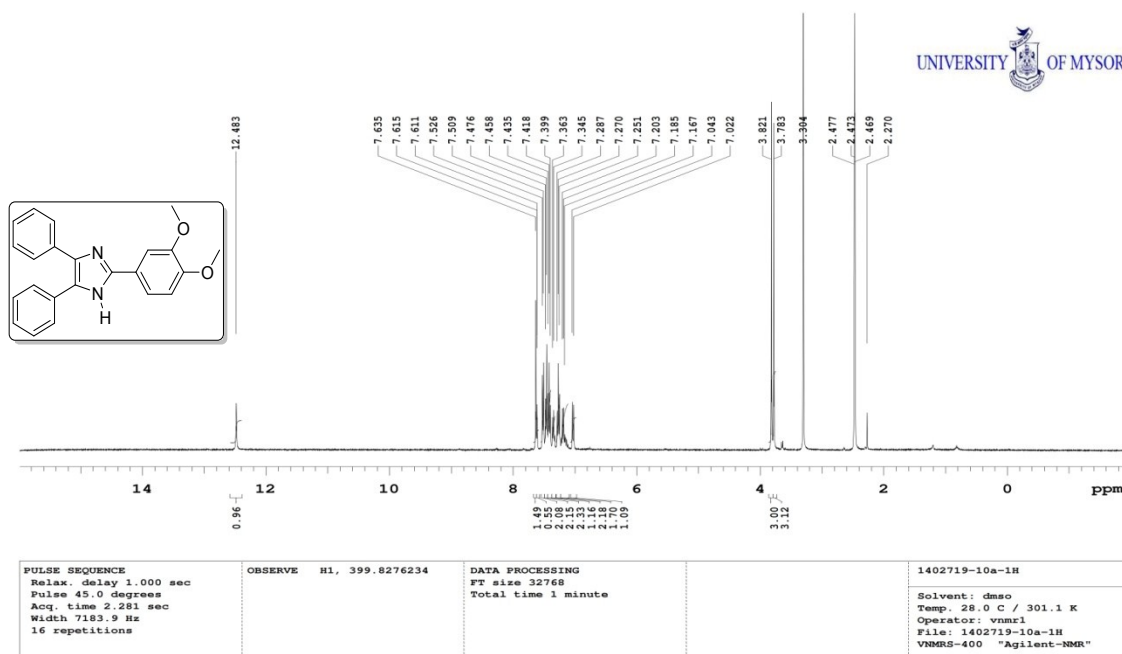
**<sup>13</sup>C NMR spectrum of compound entry 3f**



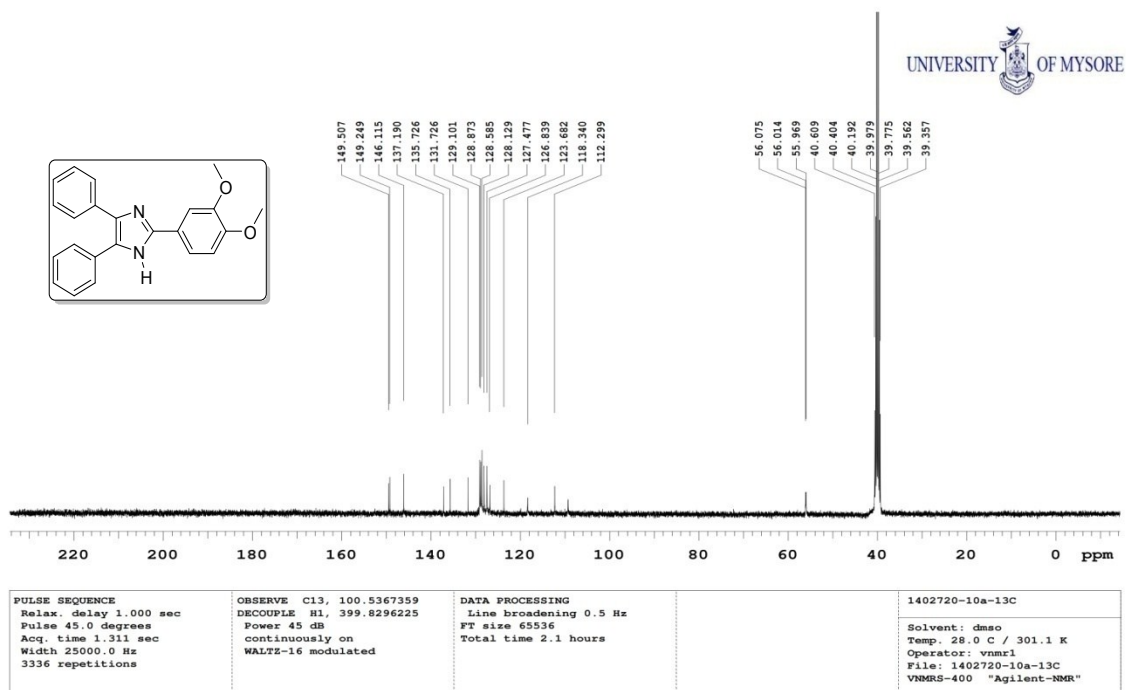
<sup>1</sup>H NMR spectrum of compound entry 3g



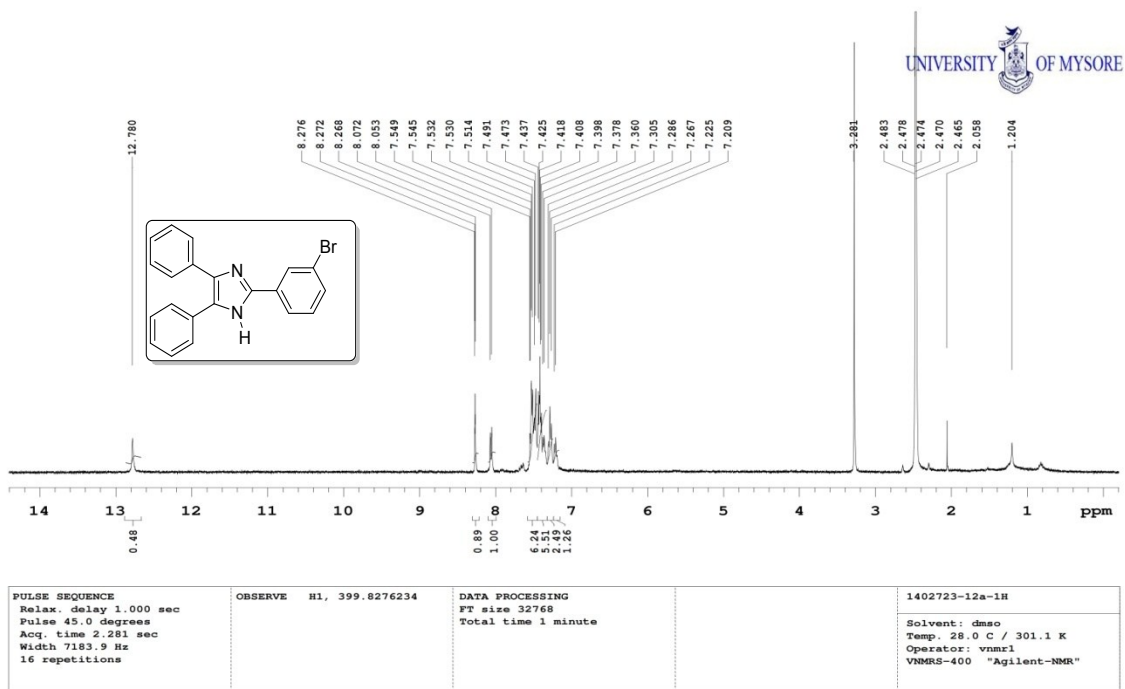
<sup>13</sup>C NMR spectrum of compound entry 3g



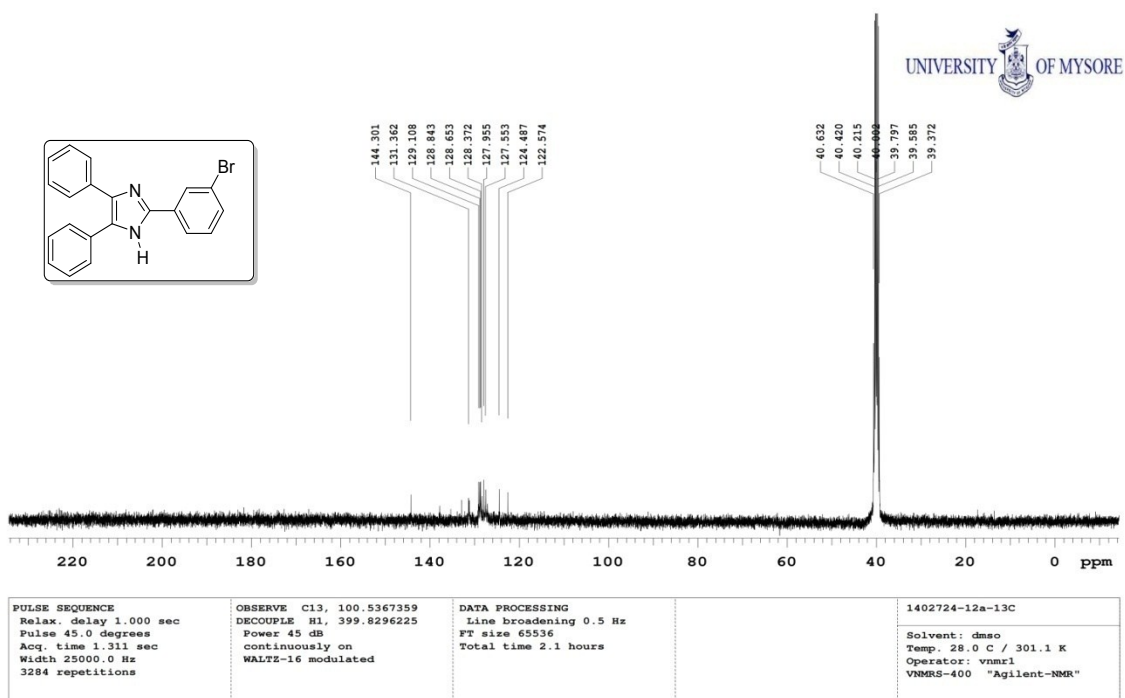
**<sup>1</sup>H NMR spectrum of compound entry 3j**



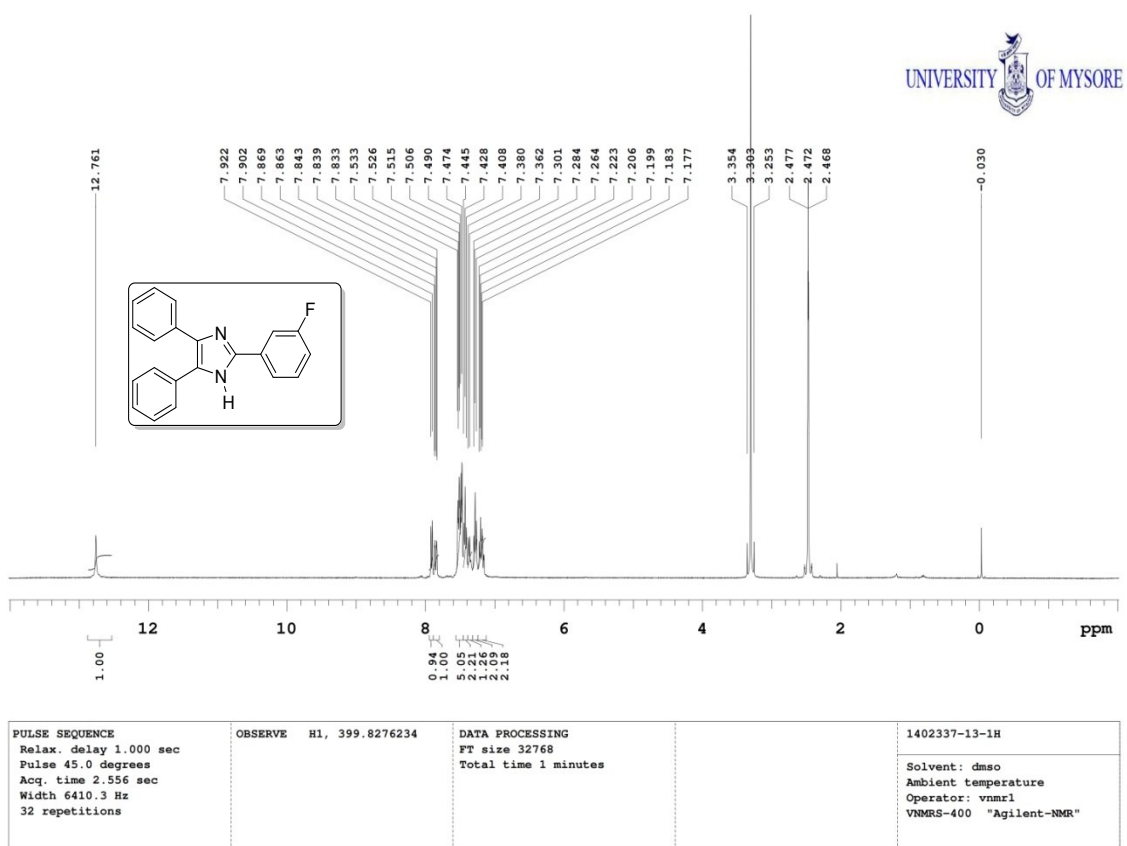
**<sup>13</sup>C NMR spectrum of compound entry 3j**



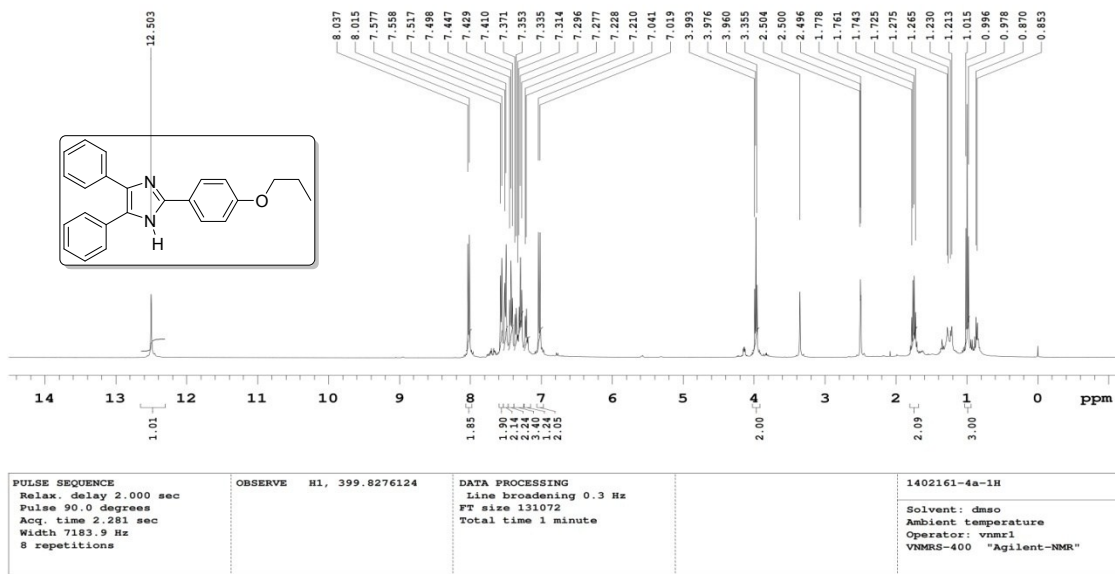
**<sup>1</sup>H NMR spectrum of compound entry 31**



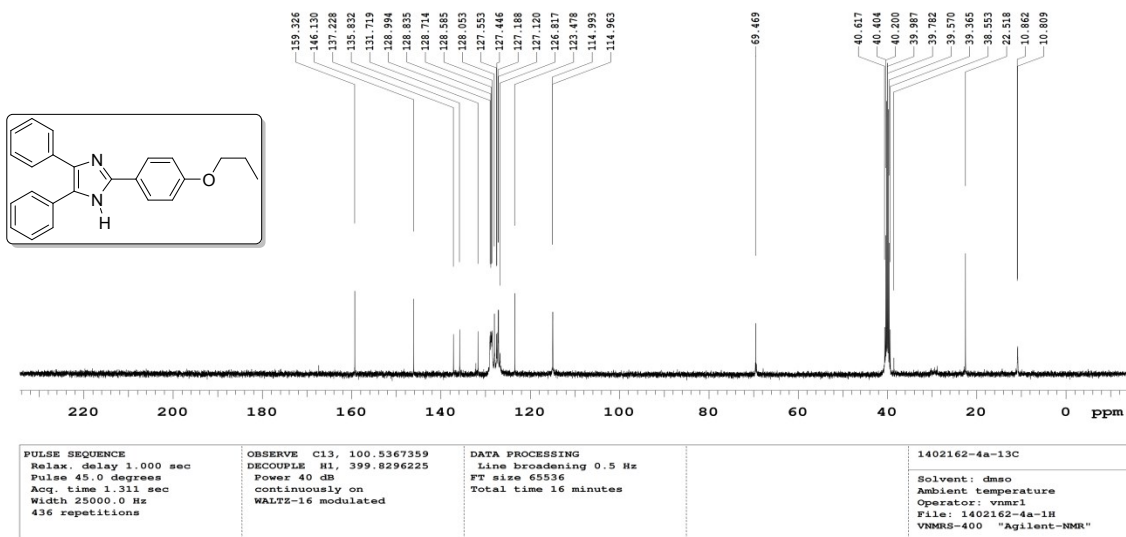
**<sup>13</sup>C NMR spectrum of compound entry 31**



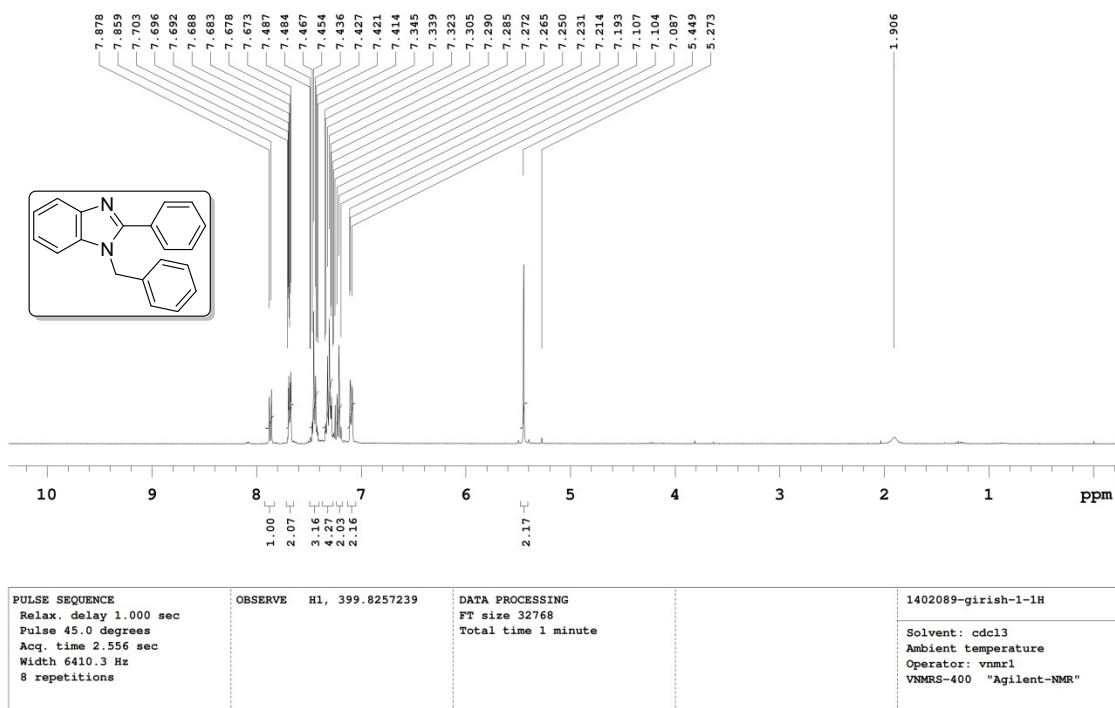
<sup>1</sup>H NMR spectrum of compound entry 3m



<sup>1</sup>H NMR spectrum of compound entry 3n

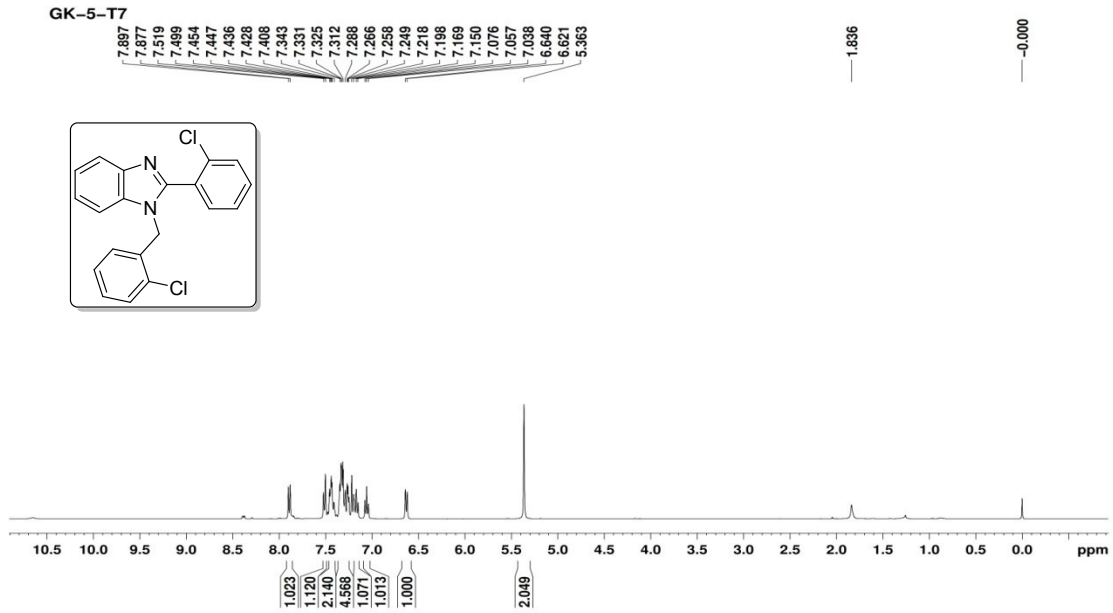


<sup>13</sup>C NMR spectrum of compound entry 3n

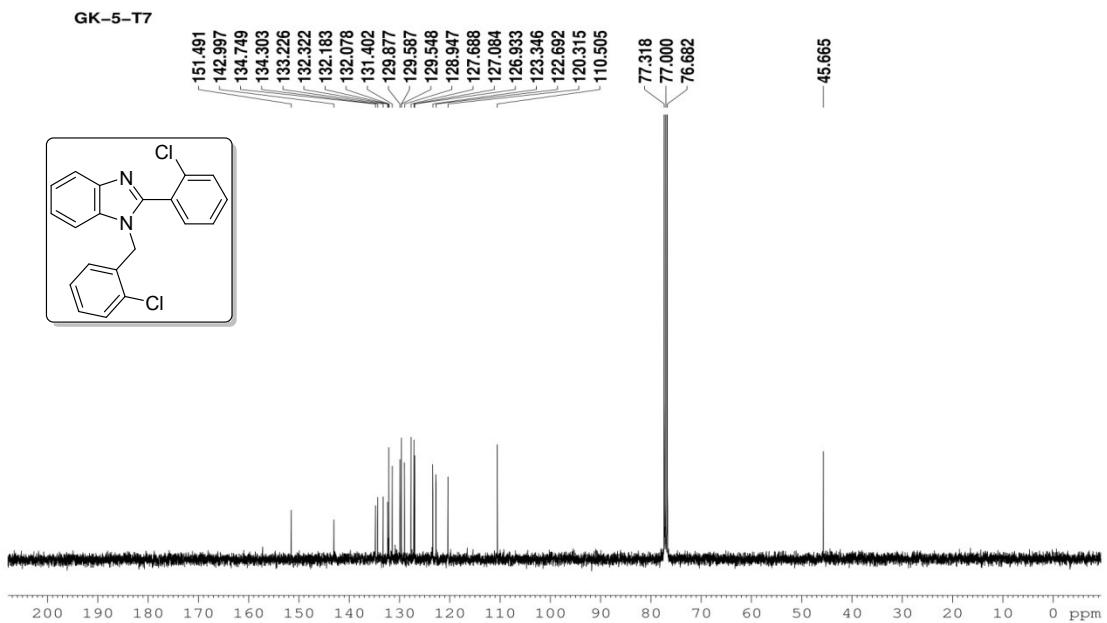


<sup>1</sup>H NMR spectrum of compound entry 5a

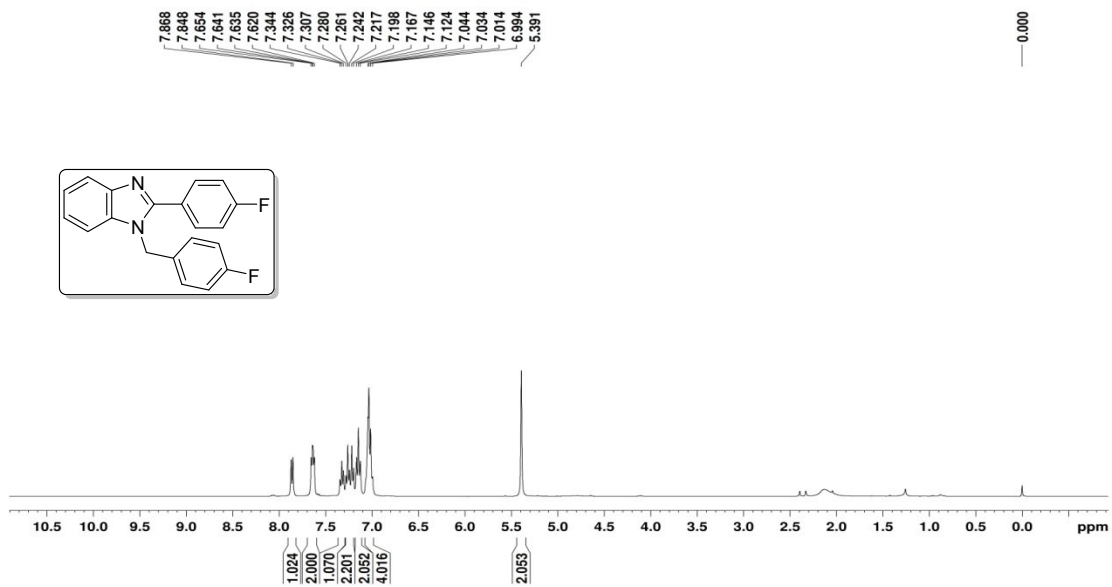




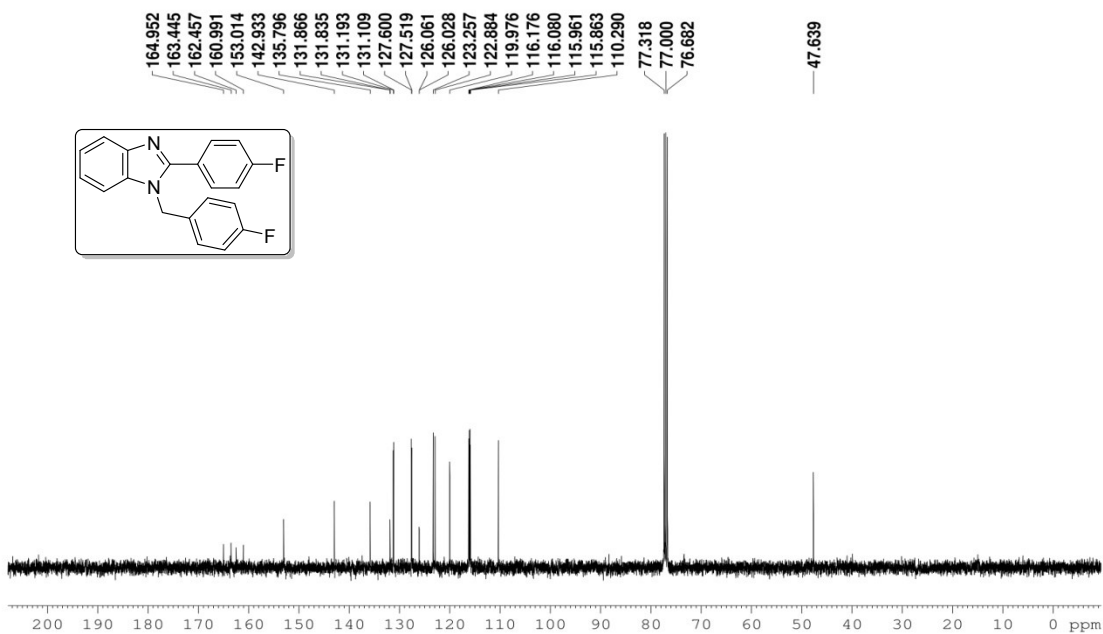
$^1\text{H}$  NMR spectrum of compound entry 5b



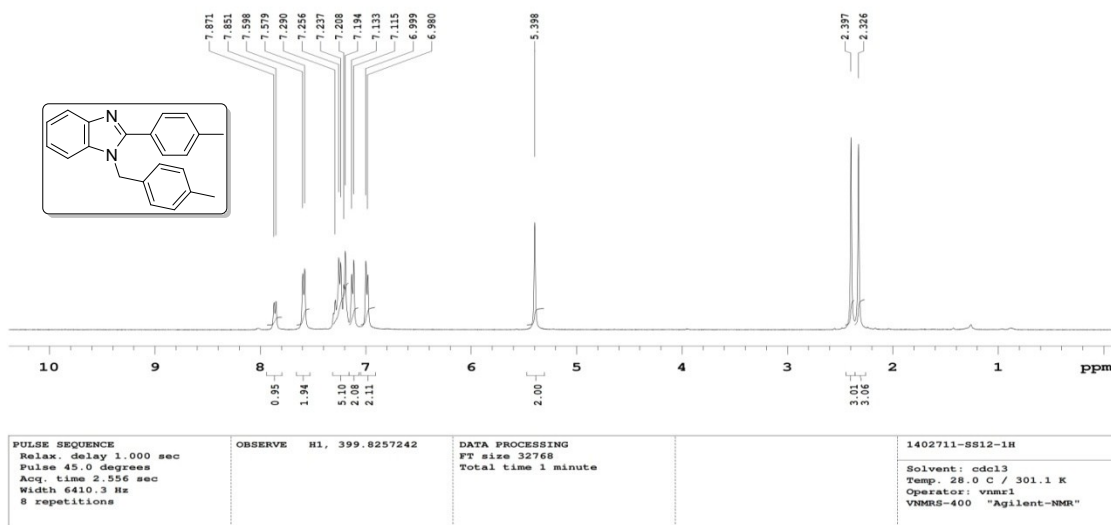
$^{13}\text{C}$  NMR spectrum of compound entry 5b



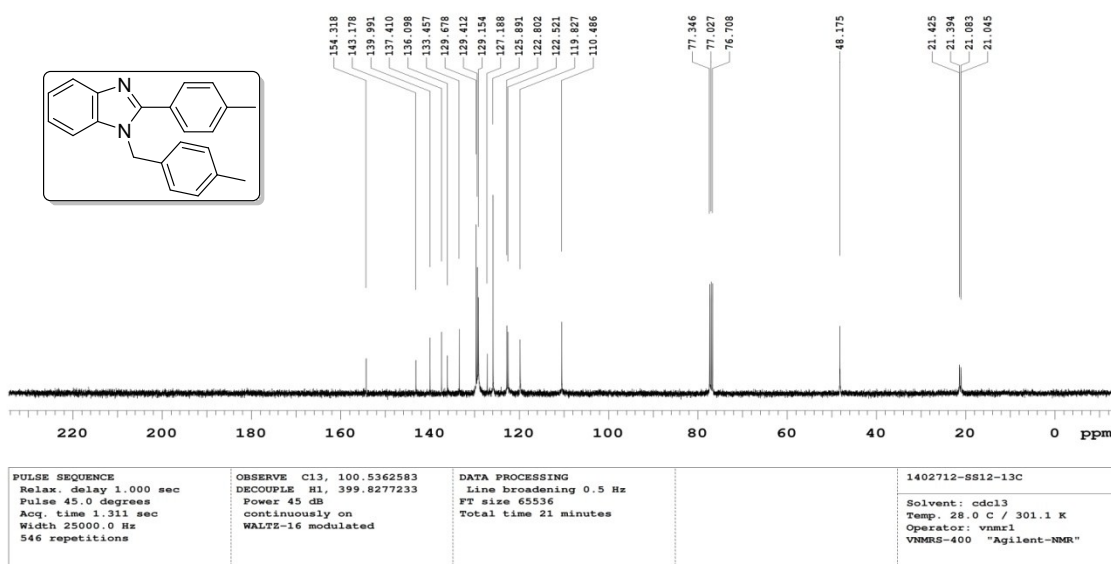
**<sup>1</sup>H NMR spectrum of compound entry 5c**



**<sup>13</sup>C NMR spectrum of compound entry 5c**



<sup>1</sup>H NMR spectrum of compound entry 5e



<sup>13</sup>C NMR spectrum of compound 5e

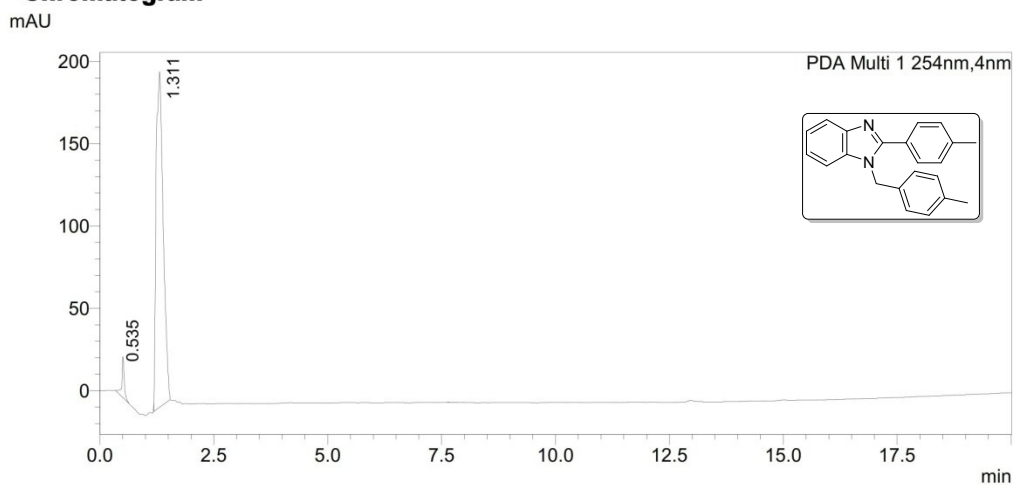
# Analysis Report

## <Sample Information>

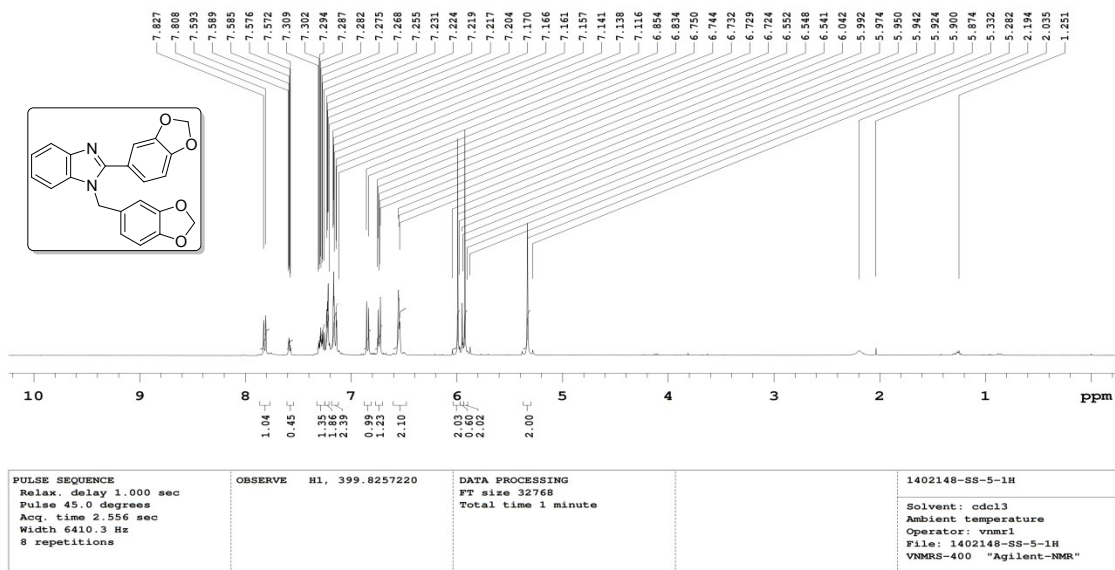
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Sample ID : RSK-1  
Data Filename : RSK-1.lcd  
Method Filename : Method C18 200-450.lcm  
Batch Filename : 06092013.lcb  
Vial # : 1-2  
Injection Volume : 50 uL  
Date Acquired : 8/8/2015 12:41:45 PM  
Date Processed : 8/8/2015 1:01:49 PM

Sample Type : Unknown  
Level : 1  
Acquired by : System Administrator  
Processed by : System Administrator

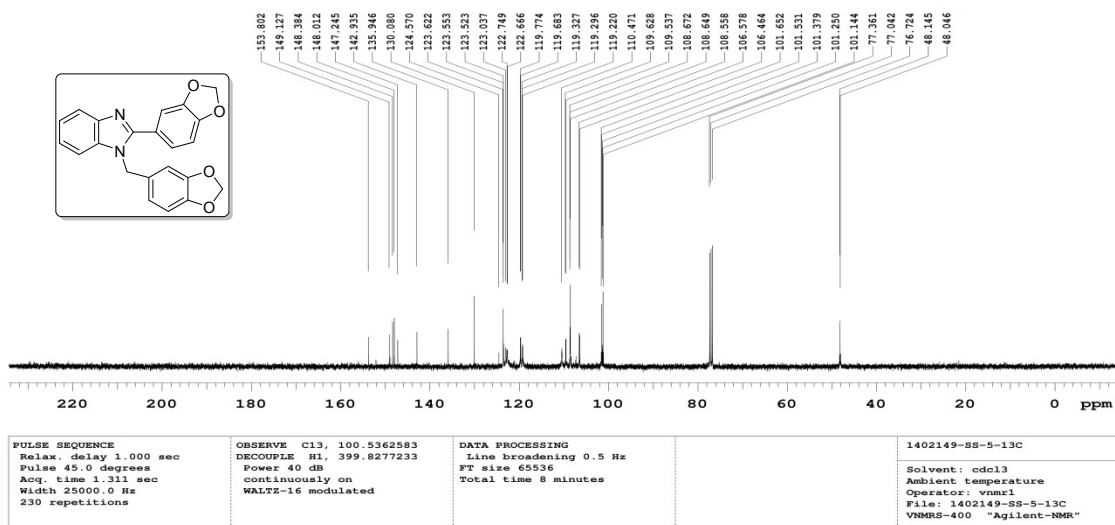
## <Chromatogram>



## HPLC report of compound 5e



**<sup>1</sup>H NMR spectrum of compound entry 5f**



**<sup>13</sup>C NMR spectrum of compound entry 5f**

# Analysis Report

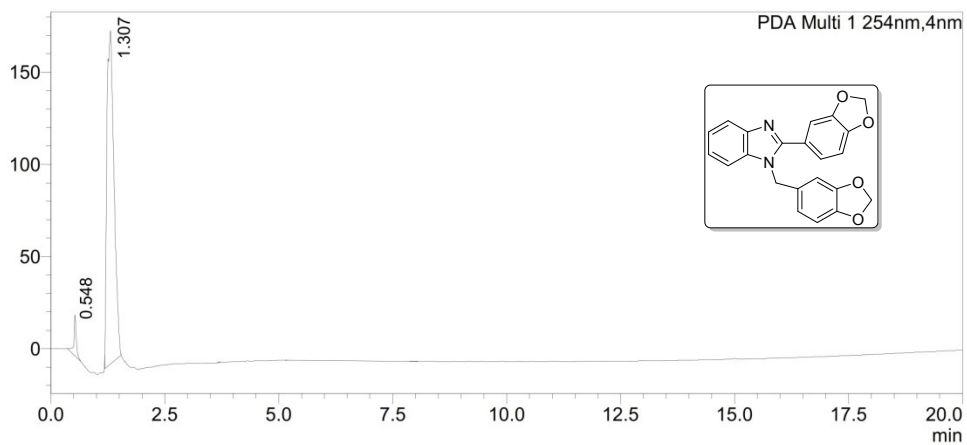
## <Sample Information>

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Batch Filename : 06092013.lcb  
Vial # : 1-3  
Injection Volume : 50 uL  
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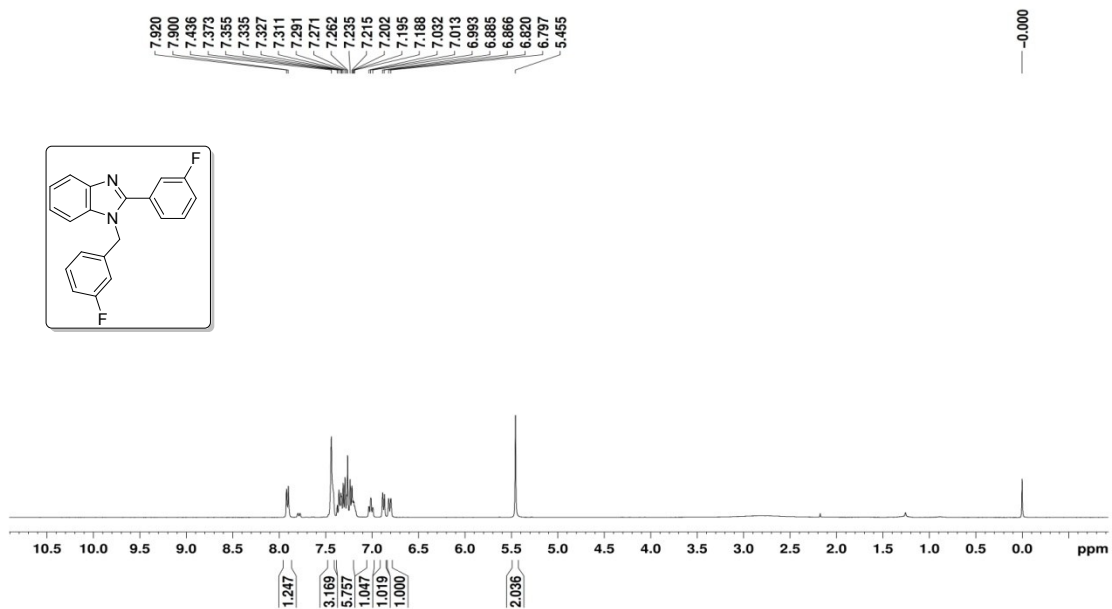
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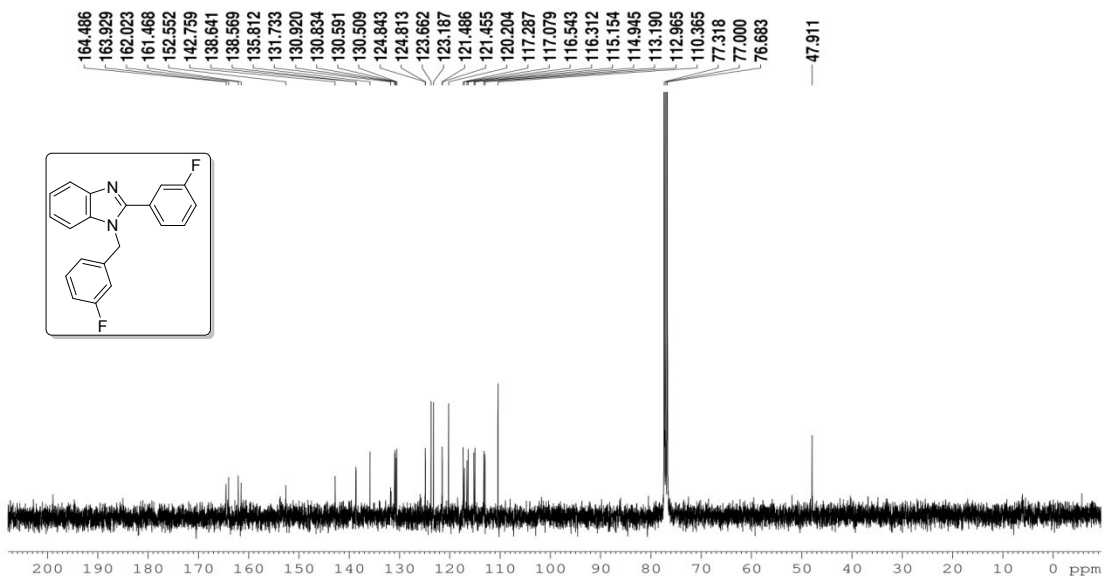
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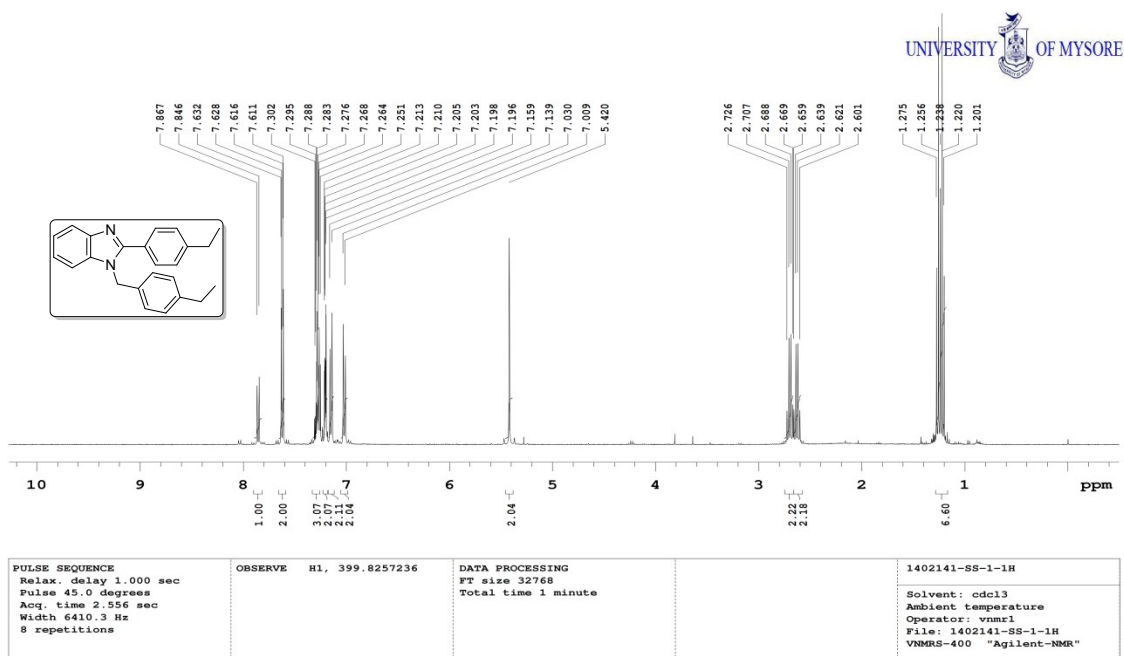
## HPLC report of compound 5f



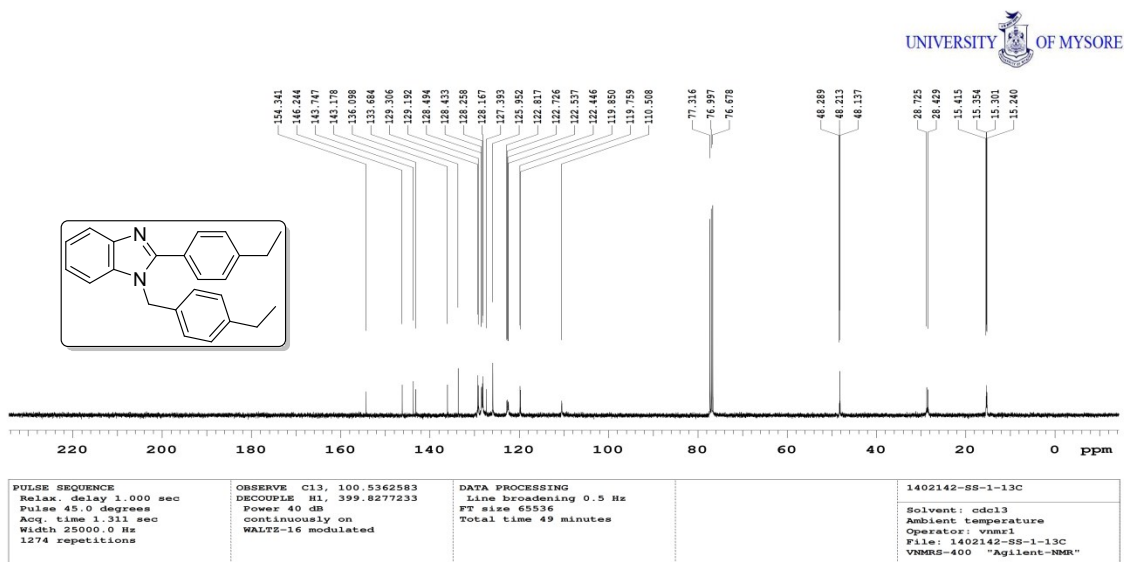
<sup>1</sup>H NMR spectrum of compound entry 5i



<sup>13</sup>C NMR spectrum of compound entry 5i

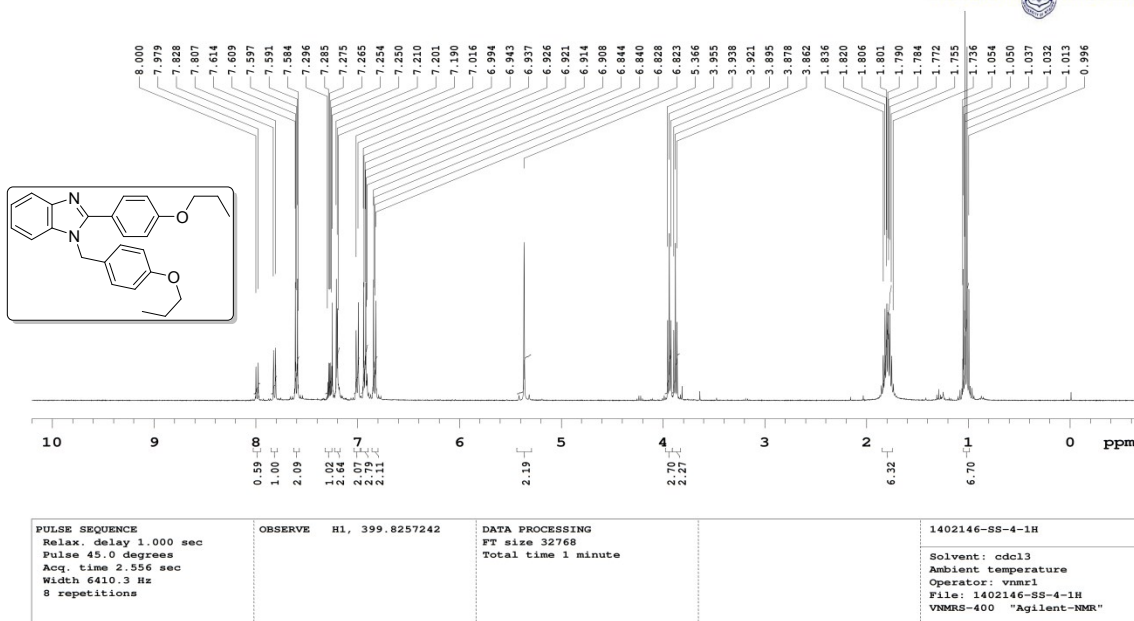


**<sup>1</sup>H NMR spectrum of compound entry 5j**

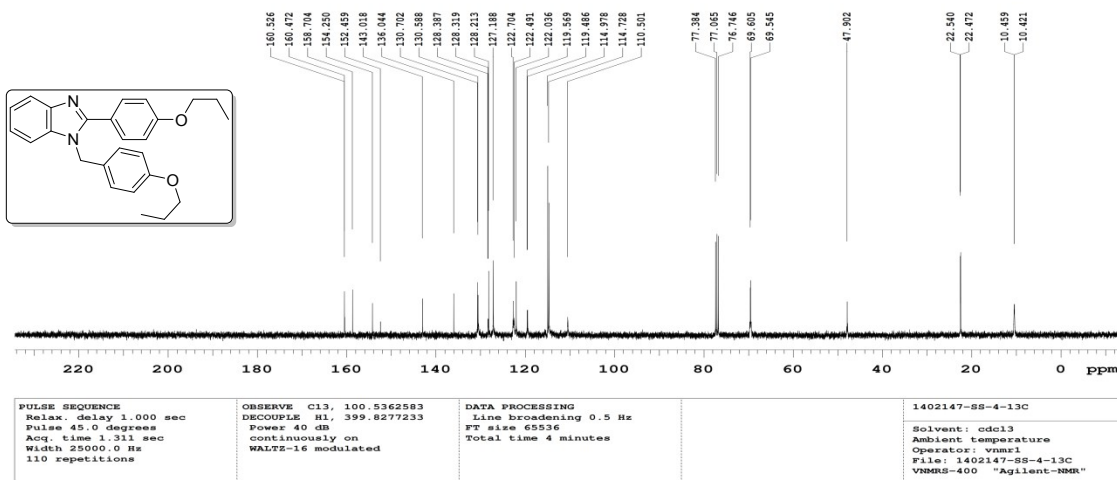


**<sup>13</sup>C NMR spectrum of compound entry 5j**





**<sup>1</sup>H NMR spectrum of compound entry 5k**



**<sup>13</sup>C NMR spectrum of compound entry 5k**