

Sulfonic acid containing cation-exchanger resin “INDION-770” & copper(I) salts: A novel reusable catalyst for N-arylation of NH-heterocycles with haloarenes

P. J. Amal Joseph, S. Priyadarshini, M. Lakshmi Kantam and H. Maheswaran*

Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology,
Hyderabad, India

Tel: +91 40 27191532; Fax: +91 40 27193510; E-mail: maheswaran_dr@yahoo.com

Supporting information

Table of contents

| | |
|--|---------|
| Experimental section ----- | S2-S4 |
| SEM images----- | S5 |
| XPS spectra----- | S6-S7 |
| Analytical data ----- | S8-S11 |
| ¹ H & ¹³ C NMR spectra ----- | S12-S38 |

Experimental Section

General Remarks

All chemicals were purchased from Sigma Aldrich and were used as received. All solvents used were analytical grade and were used as received from Merck India Pvt. Ltd. The INDION-770 resin was purchased from Ion Exchange India Ltd. The Thin Layer Chromatography (TLC) was carried out on Merck silica gel 60 F₂₅₄ plates using ethyl acetate and hexanes as eluting agents. Purification of products was carried out by flash chromatography using silica gel (60-100 mesh) and a mixture of ethyl acetate and hexane as eluting agent. All products were characterized by ¹H-NMR spectroscopy. The ¹H and ¹³C spectra of samples were acquired on a Bruker-Avance-300 MHz or a Varian 500 MHz Spectrometer using TMS as an internal standard in CDCl₃ or DMSO-d₆ as solvent. Mass spectra (EI MS) were acquired with an Agilent Technologies 6890 N instrument with an Agilent 5973 N mass detector (EI). The copper content determination analyses were carried out using Thermo Intrepid XSP DUO, ICP OES equipment using standard procedures. X-ray photoelectron spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg K α anode. SEM images of the catalyst were acquired on a Hitachi S-2560 SEM.

General procedure for Cuprous Iodide and INDION-770 resin catalyzed direct N-arylation of imidazole and benzimidazole with haloarenes. Cuprous iodide (38 mg; 0.2 mmol; 10 mol % relative to haloarene) and INDION-770 resin (200 mg; ~ 0.8 mmol of active sulfonic acid groups) were stirred in DMSO (3 mL) at 110 °C for 10 minutes. To this was added K₂CO₃ (4 mmol), haloarene (2 mmol) and NH-Heterocycle (2.6 mmol) respectively. The reaction mixture is then stirred at 125 °C for the indicated period as described in Table 1 and 2 in the main manuscript. The progress of the reaction was monitored by TLC studies using a mixture of ethyl acetate and hexane as eluting agent. After the completion of reaction, the reaction mixture was filtered through a sintered funnel, and the filtrate was diluted with water and extracted with ethyl acetate (3 X 50 mL). The combined organic extracts were dried over anhydrous sodium sulfate, and

filtered. Then, the solvent was evaporated under reduced pressure to give the crude product which was purified by flash column chromatography to afford the desired products in good yields.

General procedure for Cuprous Oxide and INDION-770 resin catalyzed direct N-arylation pyrazole with haloarenes. Cuprous oxide (29 mg; 0.2 mmol; 10 mol % relative to aryl halide) and INDION-770 resin (200 mg; ~ 0.8 mmol of active sulfonic acid groups) were stirred in DMSO (3 mL) at 110 °C for 10 minutes. To this was added Cs₂CO₃ (4 mmol), haloarene (2 mmol) and pyrazole (2.6 mmol) respectively. The reaction mixture is stirred at 125 °C for the indicated period as described in Table 1 and 2 in the main manuscript. The progress of the reaction was monitored by TLC studies using a mixture of ethyl acetate and hexane as eluting agent. After the completion of reaction, the reaction mixture was filtered through a sintered funnel, and the filtrate was diluted with water and extracted with ethyl acetate (3 X 50 mL). The combined organic extracts were dried over anhydrous sodium sulfate, and filtered. Then, the solvent was evaporated under reduced pressure to give the crude product which was purified by flash column chromatography to afford the desired products in good yields.

Procedure for preparation of Copper exchanged INDION-770 catalyst. Cuprous iodide (0.2 mmol, 38 mg) and INDION-770 resin (200 mg) were stirred in DMSO (3 mL) at 110 °C for 15 minutes to form copper exchanged INDION-770. It is filtered through a sintered funnel, washed with DMSO and methanol respectively, and oven dried to yield around 210 mg of Copper exchanged INDION-770 catalyst.

Procedure for recycling studies for N-arylation of imidazole with 4-iodoanisole catalyzed by Copper exchanged INDION-770 catalyst. Copper exchanged INDION-770 catalyst (210 mg), K₂CO₃ (4 mmol), 4-iodoanisole (2 mmol) and imidazole (2.6 mmol) were stirred in DMSO (3 mL) at 125 °C for 24 h. The progress of the reaction was monitored by TLC studies using a mixture of ethyl acetate and hexane as eluting agent. After the completion of reaction, the reaction mixture was filtered through a sintered funnel, and the filtrate was diluted with water and extracted with ethyl acetate (3 X 50

mL). The combined organic extracts were dried over anhydrous sodium sulfate, and filtered. Then, the solvent was evaporated under reduced pressure to give the crude product which was purified by flash column chromatography to afford the desired products in good yields. The spent copper exchanged INDION-770 resin catalyst was washed first with ethyl acetate and then with water, and then oven dried and reused under as is condition for the next cycle.

Procedure for ICP OES analysis of Copper exchanged INDION-770 catalyst. Copper exchanged INDION-770 catalyst (210 mg) (in case of used catalyst, it is washed first with ethyl acetate and then with water) is taken in a pressure tube; to this was added 10 mL of 1:1 con HCl/HNO₃, and stirred at room temperature for 30 minutes. It is then heated at 100 °C for 24 h. It is then cooled, diluted with water, filtered through a whatmann no. 40 filter paper, and transferred into a 100 mL standard flask. This solution is diluted 1000 times and analyzed for copper content using ICP OES using standardized procedure.

Procedure for ICP OES analysis of reaction solution. The reaction solution is diluted with water. It is then filtered through a Whatmann no. 40 filter paper, and quantitatively transferred to 10 mL standard flask. This solution is then analyzed using ICP OES.

SEM images of Copper exchanged INDION-770 catalyst

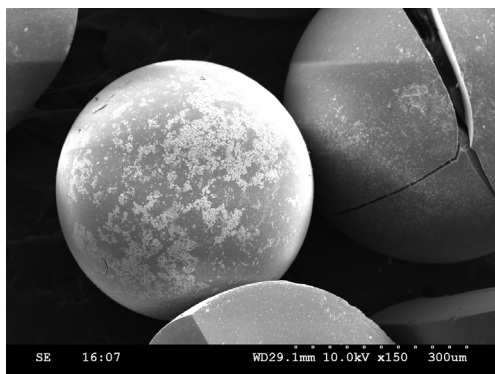


Fig. 1, Copper exchanged INDION-770 catalyst (fresh)

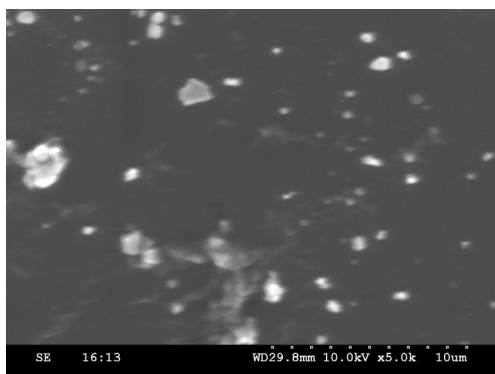


Fig. 2, Copper exchanged INDION-770 catalyst (fresh)

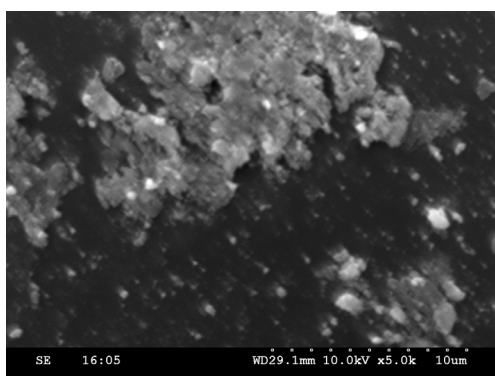


Fig. 3, Spent copper exchanged INDION-770 catalyst (after 2nd recycle)

XPS spectrum of Copper exchanged INDION-770 catalyst

X-ray photoelectron spectroscopic (XPS) investigation of Copper exchanged INDION-770 catalyst (fresh; see Figure 4) and spent catalyst (after 2nd-recycle; see Figure 5) at the Cu 2p level shows 2p_{3/2} line at 933.4 and 933.6 eV, respectively, which corresponds to +1 oxidation state of copper. Notably, the XPS spectra of the spent catalyst (after 4th cycle, see Figure 6) at the Cu 2p level shows 2p_{3/2} line at 933.0 and 934.6 eV, which shows the presence of copper in both +1 and +2 oxidation states with the former being dominant in the copper exchanged INDION-770 resin.

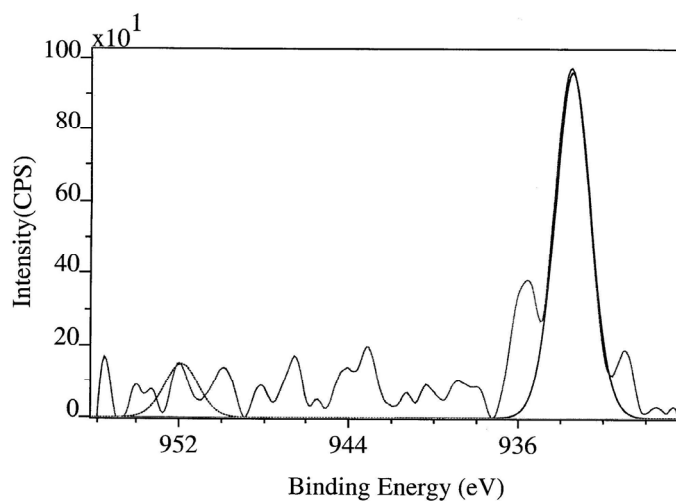


Fig. 3

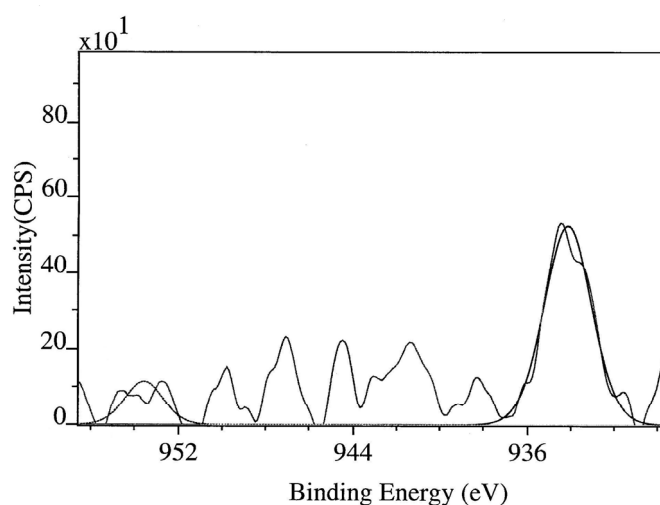


Fig. 4

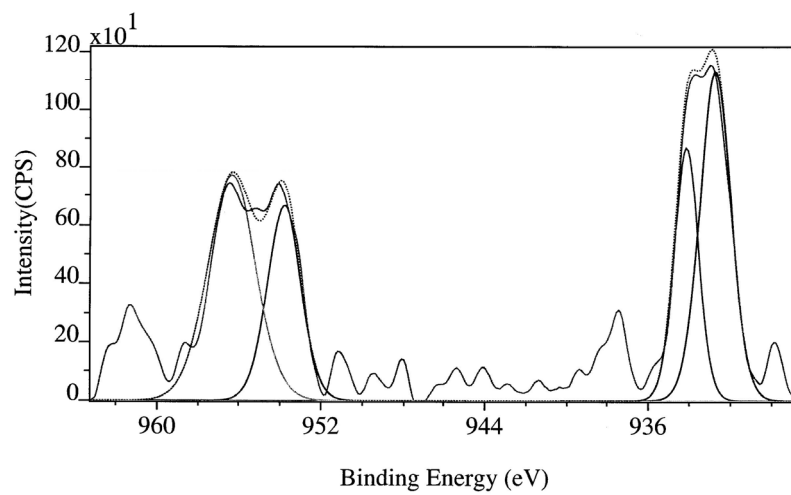


Fig. 5

Analytical Data

1-Phenyl-1H-imidazole (Table 2, Entries 1, 4 & 22); ^1H NMR (500 MHz, CDCl_3): δ = 7.80 (br s, 1H), 7.50-7.42 (m, 2H), 7.40-7.30 (m, 3H), 7.23 (s, 1H), 7.15 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 137.3, 135.6, 130.4, 129.8, 127.4, 121.4, 118.3; EI-MS: m/z = 144 (M^+)

1-(4-Nitro-phenyl)-1H-imidazole (Table 2, Entries 2, 5 & 20); ^1H NMR (300 MHz, DMSO-d_6): δ = 8.49 (s, 1H), 8.34 (d, 2H, J = 9.1 Hz), 7.96 (d, 3H, J = 8.9 Hz), 7.19 (br s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 146.3, 141.9, 135.4, 131.7, 125.7, 121.0, 117.6; EI-MS: m/z = 189 (M^+)

1-(4-Methoxy-phenyl)-1H-imidazole (Table 2, Entries 3 & 11); ^1H NMR (300 MHz, CDCl_3): δ = 7.71 (br s, 1H), 7.27 (d, 2H, J = 9.1 Hz), 7.15 (br s, 2H), 6.93 (d, 2H, J = 9.1 Hz), 3.83 (s, 3H). EI-MS: m/z = 174 (M^+)

1-(2-Nitro-phenyl)-1H-imidazole (Table 2, Entries 6 & 19); ^1H NMR (300 MHz, DMSO-d_6): δ = 8.05 (d, 1H, J = 8.1 Hz), 7.79 (t, 1H, J = 7.7 Hz), 7.66 (t, 2H, J = 7.9 Hz), 7.57 (d, 1H, J = 7.8 Hz), 7.13 (d, 2H, J = 7.8 Hz); EI-MS: m/z = 189 (M^+)

1-(4-Trifluoromethyl-phenyl)-1H-imidazole (Table 2, Entries 7 & 17); ^1H NMR (500 MHz, CDCl_3): δ = 7.95 (s, 1H), 7.78-7.73 (m, 2H), 7.58-7.52 (m, 2H), 7.32 (s, 1H), 7.24 (s, 1H); EI-MS: m/z = 212 (M^+)

1-(4-imidazol-1-yl-phenyl)-ethanone (Table 2, Entry 8); ^1H NMR (500 MHz, CDCl_3): δ = 8.06 (d, 2H, J = 8.8 Hz), 7.90 (s, 1H), 7.49 (d, 2H, J = 8.8 Hz), 7.30 (s, 1H), 7.20 (s, 1H), 2.62 (s, 3H); EI-MS: m/z = 186 (M^+)

1-(4-Chlorophenyl)-1H-imidazole (Table 2, Entry 9); ^1H NMR (300 MHz): δ = 7.77 (br s, 1H), 7.47 – 7.38 (m, 2 H), 7.36-7.29 (m, 2H), 7.24-7.10 (m, 2H); EI-MS: m/z 178 (M^+), 180 (M^+).

1-*p*-Tolyl-1H-imidazole (Table 2, Entry 10); ^1H NMR (300 MHz, CDCl_3): δ = 7.83 (br s, 1H), 7.30-7.16 (m, 6H), 2.41 (s, 3H); EI-MS: m/z = 158 (M^+)

1-(3-Methoxy-phenyl)-1H-imidazole (Table 2, Entry 12); ^1H NMR (500 MHz, CDCl_3): δ = 7.81 (s, 1 H), 7.33 (d, 1H, J = 8.3 Hz), 7.28-6.99 (m, 2H), 6.94 (d, 1H, 7.9 Hz), 6.91-6.81 (m, 2H), 3.83 (s, 3H); EI-MS: m/z = 174 (M^+)

1-(2-Methoxy-phenyl)-1H-imidazole (Table 2, Entry 13); ^1H NMR (500 MHz, DMSO-d_6): δ = 7.74 (brs, 1H) 7.36-7.29 (m, 2H), 7.25 (s, 1H), 7.11 (d, J = 8.4 Hz, 1H) 7.05-7.00 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ = 152.2, 137.5, 128.7, 128.5, 126.2, 125.2, 120.8, 120.1, 112.1, 55.5; EI-MS: m/z = 174 (M^+)

1-Naphthalen-2-yl-1H-imidazole (Table 2, Entry 14); ^1H NMR (500 MHz, DMSO- d_6): δ = 8.12 (s, 1H), 8.01-7.95 (m, 2H), 7.89 (t, 2H, J = 9.4 Hz), 7.66 (d, 1H, J = 8.4 Hz), 7.61-7.48 (m, 3H), 7.13 (s, 1H) ^{13}C NMR (75 MHz, DMSO- d_6): δ = 136.3, 134.9, 133.7, 131.9, 130.5, 130.3, 128.2, 127.7, 126.6, 120.0, 118.6, 117.8. EI-MS: m/z = 194 (M^+)

4-Imidazol-1-yl-phenylamine (Table 2, Entry 15); ^1H NMR (300 MHz, DMSO- d_6): δ = 7.76 (s, 1H), 7.26 (s, 1H), 7.11 (d, 2H, J = 8.6 Hz), 7.03 (s, 1H), 6.67 (d, 2H, J = 8.6 Hz), 3.8 (br s, 2H); EI-MS: m/z = 159 (M^+)

1-(4-Methylsulfanyl-phenyl)-1H-imidazole (Table 2, Entry 16); ^1H NMR (300 MHz, DMSO- d_6): δ = 7.90 (br s, 1H), 7.43-7.27 (m, 5H), 7.13 (s, 1H), 2.51 (s, 3H); EI-MS: m/z = 190 (M^+)

4-imidazol-1-yl-benzonitrile (Table 2, Entry 18); ^1H NMR (500 MHz, DMSO- d_6): δ = 7.96 (s, 1H), 7.85-7.76 (m, 2H), 7.57-7.52 (m, 2H), 7.32 (s, 1H), 7.22 (s, 1H); EI-MS: m/z = 169 (M^+)

1-Phenyl-1H-benzimidazole (Table 2, Entry 23); ^1H NMR (300 MHz, CDCl_3): δ = 8.08 (s, 1H), 7.91-7.81 (m, 1H), 7.64-7.49 (m, 5H), 7.48-7.41 (m, 1H), 7.37-7.24 (m, 2H); ^{13}C NMR (75 MHz, DMSO- d_6): δ = 143.8, 143.2, 135.9, 133.0, 130.0, 127.7, 123.6, 123.4, 122.4, 119.9, 110.6; EI-MS: m/z = 194 (M^+)

1-(2-Methoxy-phenyl)-1H-benzimidazole (Table 2, Entry 24); ^1H NMR (500 MHz, CDCl_3): δ = 7.98 (s, 1H), 7.81 (d, 1H, J = 8.8 Hz), 7.39 (d, 3H, J = 8.8 Hz), 7.29-7.22 (m, 2H), 7.02 (d, 2H, J = 8.8 Hz), 3.87 (s, 1H); ^{13}C NMR (75 MHz, DMSO- d_6): δ = 153.6, 144.3, 143.0, 134.2, 130.0, 127.4, 124.0, 122.9, 121.8, 120.9, 119.5, 117.0, 112.9, 110.8, 55.7; EI-MS: m/z = 224 (M^+)

1-(4-Methoxyphenyl)-1H-benzimidazole (Table 2, Entry 25); ^1H NMR (300 MHz, CDCl_3): δ = 8.02 (s, 1H), 7.85 (d, 1H, J = 7.55 Hz), 7.46-7.37 (m, 3H), 7.33-7.25 (m, 2H), 7.08-7.02 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ = 158.6, 143.5, 143.3, 133.5, 128.7, 125.3, 123.2, 122.1, 119.8, 115.0, 110.4, 55.4; EI-MS: m/z = 224 (M^+)

1-m-Tolyl-1H-benzimidazole (Table 2, Entry 26); ^1H NMR (300 MHz, CDCl_3): δ = 8.05 (s, 1H), 7.83 (s, 1H), 7.60-7.21 (m, 7H), 2.48 (s, 1H); ^{13}C NMR (75 MHz, DMSO- d_6): δ = 143.8, 143.2, 139.7, 135.8, 129.7, 128.3, 124.0, 123.3, 122.3, 120.6, 119.9, 110.6, 20.8; EI-MS: m/z = 208 (M^+)

1-Naphthalen-2-yl-1H-benzimidazole (Table 2, Entry 27); ^1H NMR (500 MHz, CDCl_3): δ = 8.11 (s, 1H), 7.94 (d, 1H, J = 8.8 Hz), 7.90-7.81 (m, 4 H), 7.58-7.49 (m, 4H), 7.32-7.24 (m, 2H); ^{13}C NMR (75 MHz, DMSO- d_6): δ = 143.9, 143.4, 133.4, 133.2, 131.8, 129.9, 127.9, 127.7, 127.0, 126.5, 123.4, 122.4, 122.1, 121.3, 119.9, 110.7; EI-MS: m/z = 244 (M^+)

1-(4-Nitrophenyl)-1H-benzimidazole (Table 2, Entry 28); ^1H NMR (300 MHz, DMSO- d_6): δ = 8.49-8.42 (m, 3H), 7.96-7.89 (m, 2H), 7.80-7.76 (m, 1H), 7.69-7.64 (m, 1H),

7.39-7.29 (m, 2H); ^{13}C NMR (75MHz, DMSO- d_6): δ = 145.6, 144.1, 143.1, 141.3, 132.2, 125.4, 124.0, 123.6, 123.1, 120.2, 110.9; EI-MS: m/z = 239 (M^+).

1-Phenyl-1H-pyrazole (Table 2, Entry 29); ^1H NMR (300 MHz, CDCl_3): δ = 7.89 (d, 1H, J = 2.3 Hz), 7.69 (d, 1H, J = 1.5 Hz), 7.68-7.64 (m, 2H), 7.42 (t, 2H, J = 7.9 Hz), 7.24 (d, 1H, J = 6.8 Hz), 6.42 (t, 1H, J = 2.3 Hz); ^{13}C NMR (75 MHz, CDCl_3): δ = 141.0, 140.1, 129.4, 126.7, 126.4, 119.1, 107.5; EI-MS: m/z = 144 (M^+)

1-(4-Methoxy-phenyl)-1H-pyrazole (Table 2, Entry 30); ^1H NMR (300 MHz, CDCl_3): δ = 7.79 (bs, 1H), 7.62 (s, 1H), 7.56 (d, 2H, J = 9.1 Hz), 6.92 (d, 2H, J = 9.1 Hz), 6.39 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ = 158.2, 140.5, 134.0, 126.7, 120.8, 114.4, 107.1, 55.5; EI-MS: m/z = 174 (M^+)

1-(2-Methoxy-phenyl)-1H-pyrazole (Table 2, Entry 31); ^1H NMR (300 MHz, CDCl_3): δ = 8.01(s, 1H), 7.74 (d, 1H, J = 8.3 Hz), 7.62 (s, 1H), 7.26-7.20 (m, 1H), 7.02 (d, 2H, J = 7.5 Hz), 6.36 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ = 151.3, 140.0, 131.4, 129.6, 127.9, 125.1, 121.1, 112.2, 106.1, 55.8; EI-MS: m/z = 174 (M^+)

1-(3-Methoxy-phenyl)-1H-pyrazole (Table 2, Entry 32); ^1H NMR (300 MHz, CDCl_3): δ = 7.89 (bs, 1H), 7.65 (s, 1H), 7.33-7.26 (m, 2H), 7.18 (d, 1H, J = 8.1 Hz), 6.78 (d, 1H, J = 8.1 Hz), 6.41 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 160.4, 141.3, 140.9, 130.0, 126.8, 112.3, 111.0, 107.5, 105.0, 55.3; EI-MS: m/z = 174 (M^+)

1-*p*-Tolyl-1H-pyrazole (Table 2, Entry 33); ^1H NMR (300 MHz, CDCl_3): δ = 7.86 (bs, 1H), 7.64 (s, 1H), 7.55 (d, 2H, J = 8.3 Hz), 7.21 (d, 2H, J = 8.3 Hz), 6.41 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ = 140.8, 138.0, 136.2, 129.9, 126.7, 119.1, 107.3, 20.9; EI-MS: m/z = 158 (M^+)

1-Naphthalen-2yl-1H-pyrazole (Table 2, Entry 34); ^1H NMR (300 MHz, CDCl_3): δ = 8.04 (s, 1H), 7.98 (d, 1H, J = 2.3 Hz), 7.85 (d, 2H, J = 1.5 Hz), 7.79 (t, 2H, J = 7.6 Hz), 7.70 (s, 1H), 7.49-7.37 (m, 2H), 6.43 (t, 1H, J = 2.3 Hz); ^{13}C NMR (75 MHz, CDCl_3): δ = 141.2, 137.6, 133.5, 131.7, 129.4, 127.9, 127.7, 126.9, 125.8, 118.5, 116.2, 107.7; EI-MS: m/z = 194 (M^+)

1-(4-Chlorophenyl)-1H-pyrazole (Table 2, Entry 35); ^1H NMR (300 MHz, CDCl_3): δ = 7.85 (d, J = 2.3 Hz, 1 H), 7.67-7.61 (m, 3 H), 7.42-7.37 (m, 2 H), 6.43 (t, 1H, J = 2.3 Hz); EI-MS: m/z = 178 (M^+), 180 (M^+).

1-(4-Methylsulfanyl-phenyl)-1H-pyrazole (Table 2, Entry 36); ^1H NMR (300 MHz, CDCl_3): δ = 7.84 (bs, 1H), 7.64 (s, 1H), 7.61 (s, 1H), 7.58 (s, 1H), 7.31 (s, 1H), 7.27 (s, 1H), 6.40 (s, 1H), 2.48 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ = 140.9, 137.6, 136.4, 127.6, 126.5, 119.5, 107.5, 16.1; EI-MS: m/z = 190 (M^+)

1-(4-Aminophenyl)-1H-pyrazole (Table 2, Entry 37); ^1H NMR (300 MHz, CDCl_3): δ = 7.73 (s, 1H), 7.59 (s, 1H), 7.40 (d, 2H, J = 8.3 Hz), 6.67 (d, 2 H, J = 9.1 Hz), 6.35 (s, 1H), 3.57 (brs, 2 H); EI-MS: m/z = 159 (M^+)

1-(4-pyrazol-1-yl-phenyl)-ethanone (Table 2, Entry 38); ^1H NMR (300 MHz, CDCl_3): δ = 8.06-7.95 (m, 2 H), 8.01 (d, 1 H, J = 2.5, Hz), 7.82-7.74 (m, 2 H), 7.70 (s, 1 H), 6.46 (s, 1 H), 2.59 (s, 3 H); EI-MS: m/z = 186 (M^+)

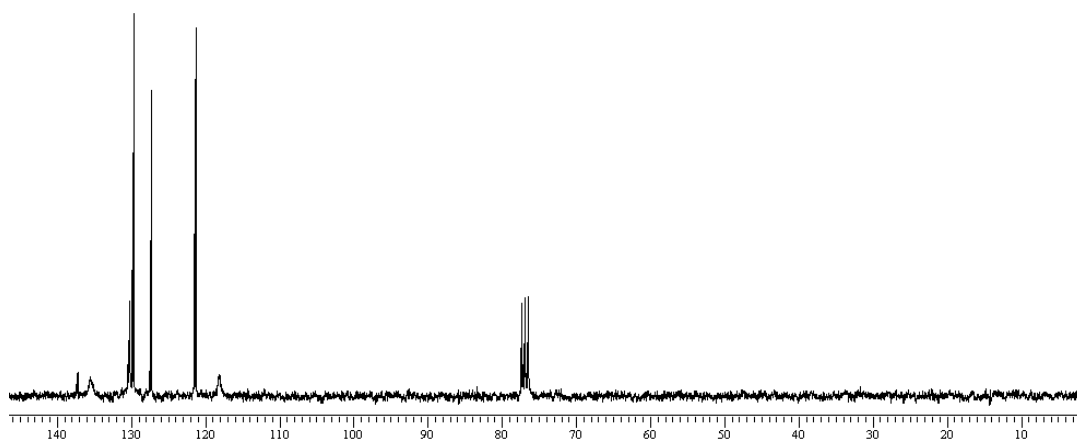
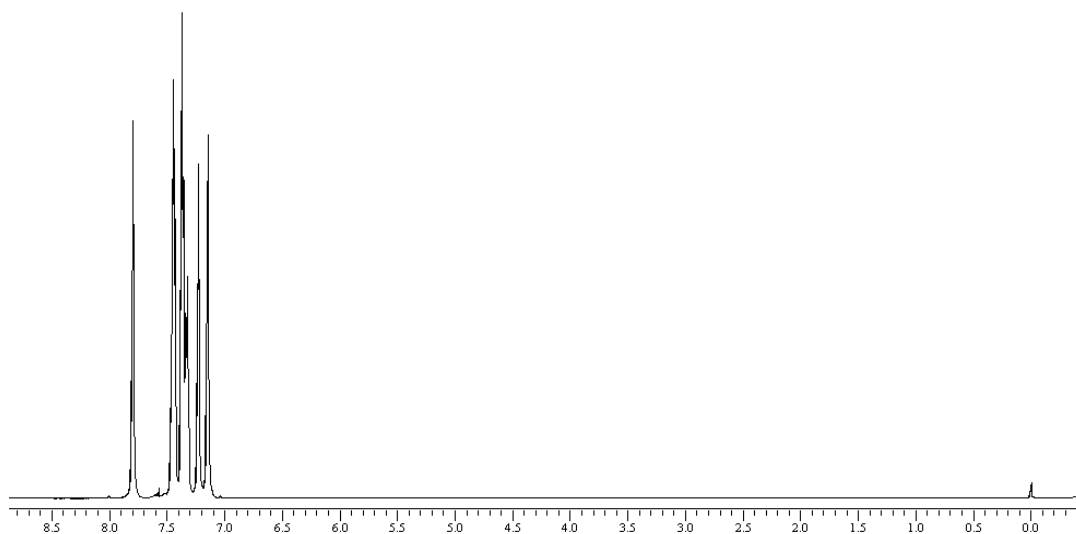
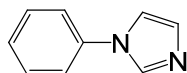
1-(2-Nitro-phenyl)-1H-pyrazole (Table 2, Entry 39); ^1H NMR (500 MHz, CDCl_3): δ = 7.83 (d, 1H, J = 7.8 Hz), 7.70-7.65 (m, 2H), 7.63 (d, 1H, J = 7.8 Hz), 7.58 (d, 1H, J = 7.8 Hz), 7.48 (t, 1 H, J = 7.8 Hz), 6.45 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 144.5, 142.2, 133.3, 132.9, 129.6, 128.3, 126.1, 124.9, 108.1; EI-MS: m/z = 189 (M^+)

1-(4-Trifluoromethyl-phenyl)-1H-pyrazole (Table 2, Entry 40); ^1H NMR (300 MHz, CDCl_3) δ = 7.89-7.71 (m, 3 H), 7.51-7.43 (m, 3 H), 6.47 (t, 1 H, J = 2.3 Hz); EI-MS: m/z = 212 (M^+)

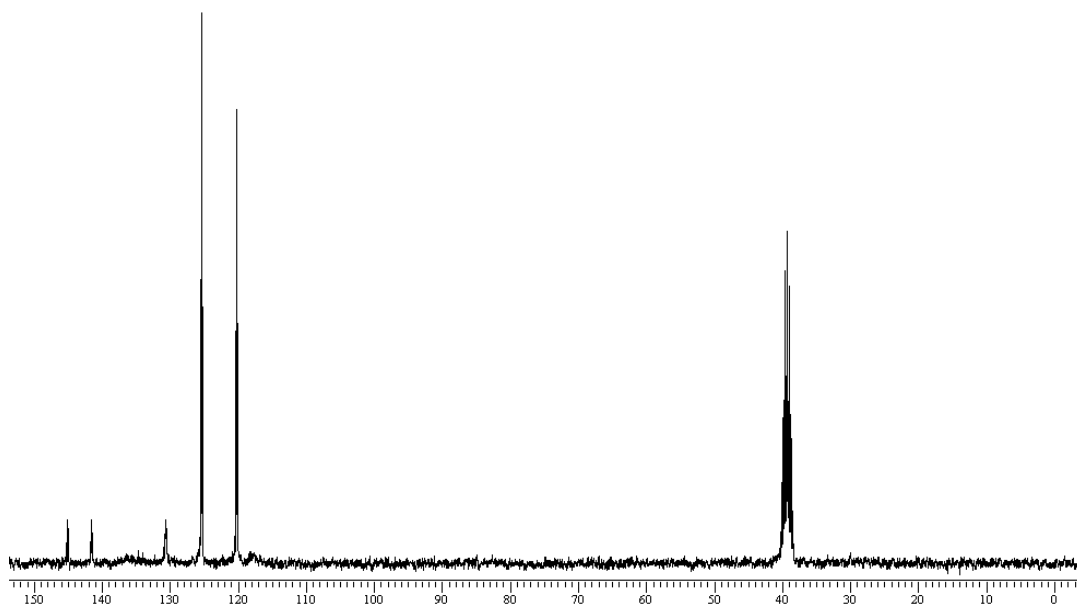
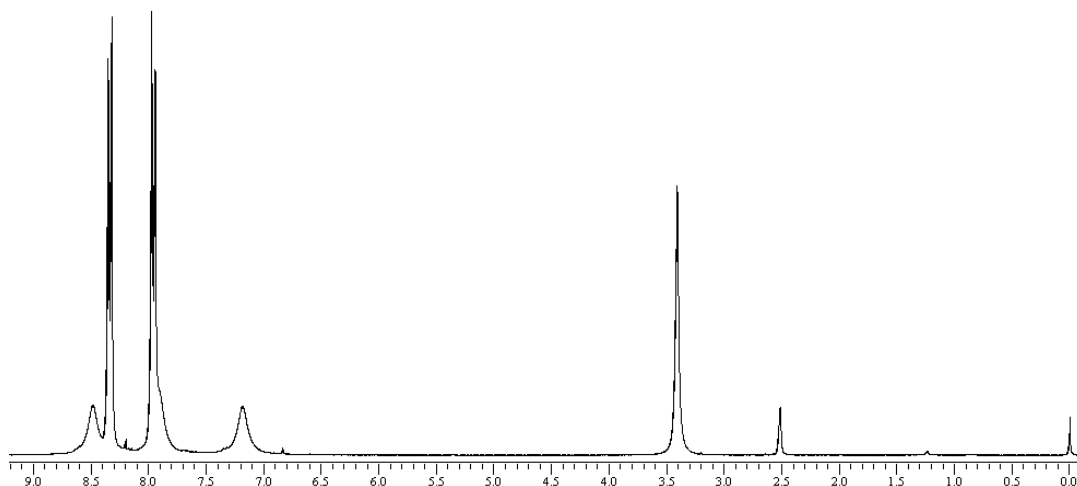
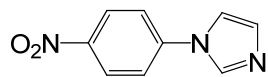
1-(4-Nitro-phenyl)-1H-pyrazole (Table 2, Entry 42); ^1H NMR (500 MHz, DMSO-d_6): δ = 8.42 (s, 1 H), 8.31 (d, 2H, J = 8.8 Hz), 8.05 (d, 2 H, J = 8.8 Hz), 7.73 (s, 1 H), 6.53 (s, 1 H); EI-MS: m/z = 189 (M^+)

^1H NMR & ^{13}C NMR Spectra

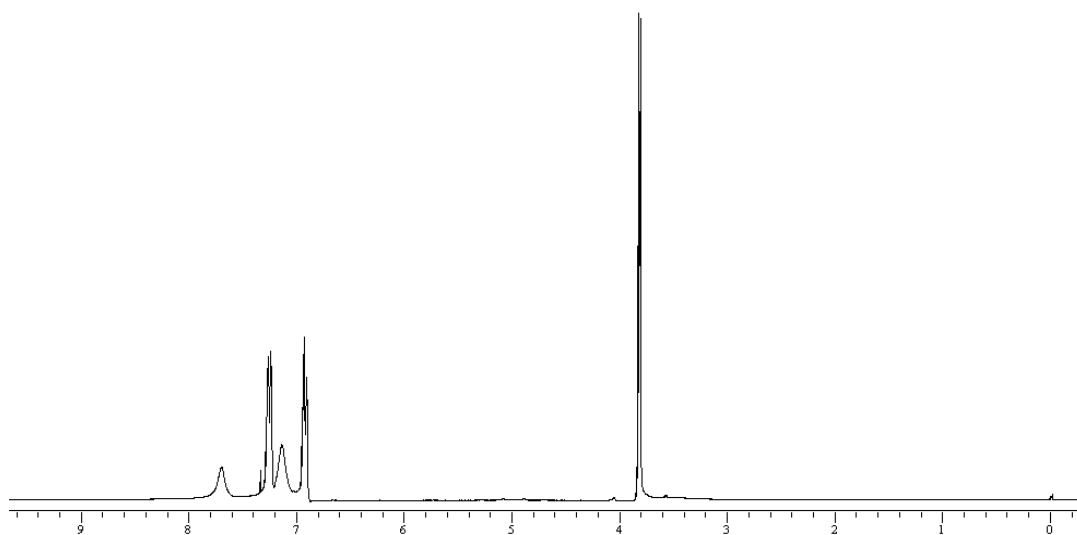
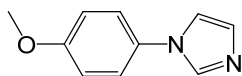
1-Phenyl-1H-imidazole (Table 2, Entries 1, 4 & 22)



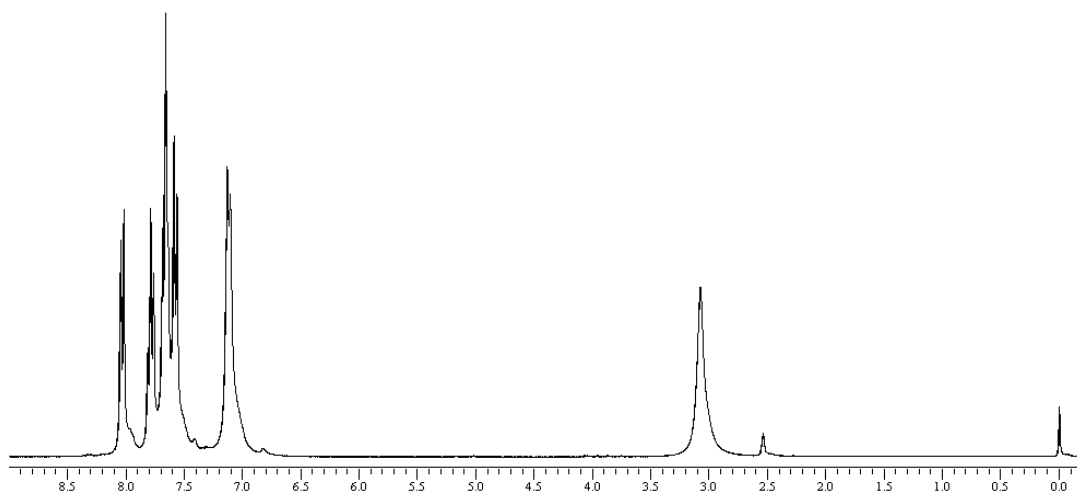
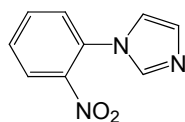
1-(4-Nitro-phenyl)-1H-imidazole (Table 2, Entries 2, 5 & 20)



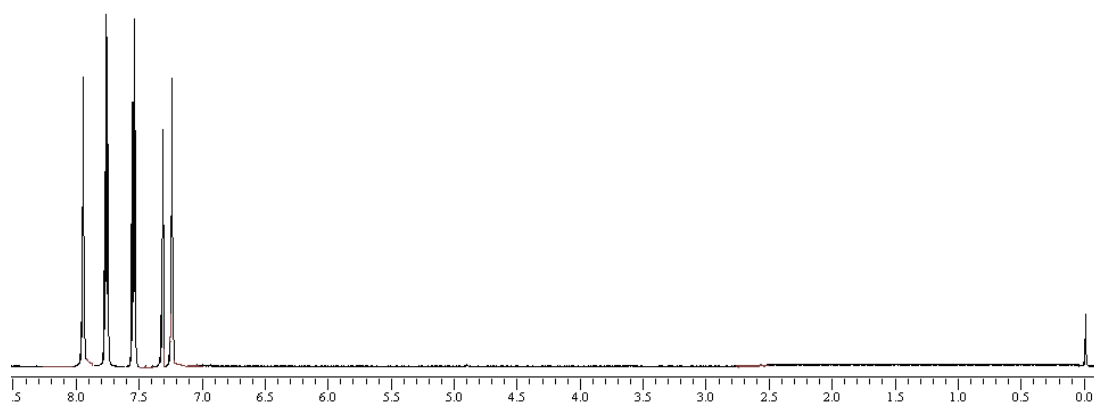
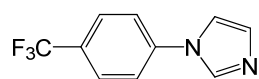
1-(4-Methoxy-phenyl)-1H-imidazole (Table 2, Entries 3 & 11)



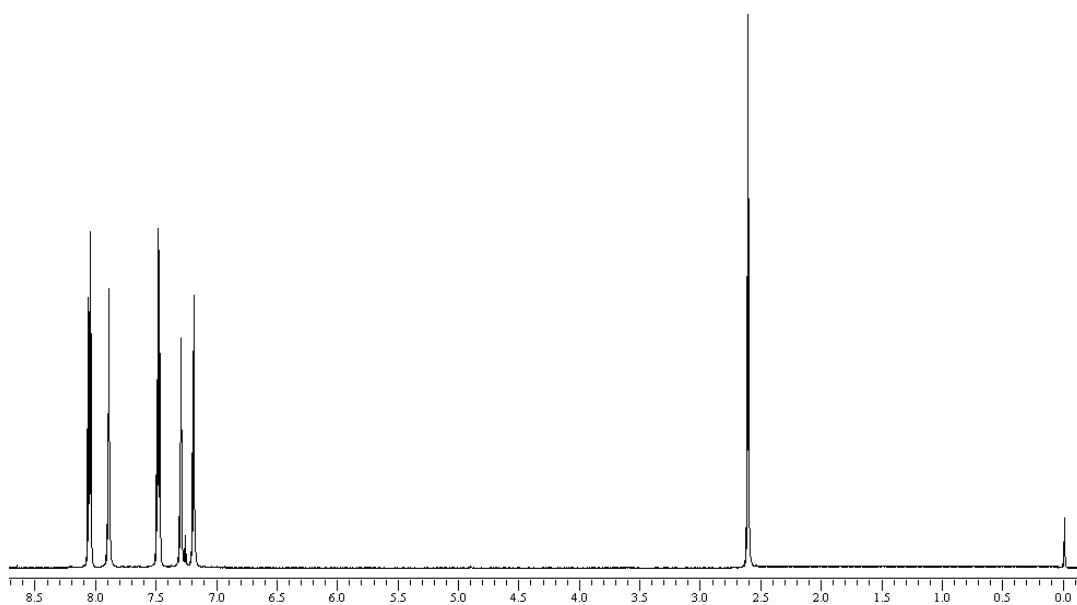
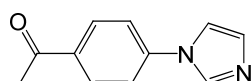
1-(2-Nitro-phenyl)-1H-imidazole (Table 2, Entries 6 & 19)



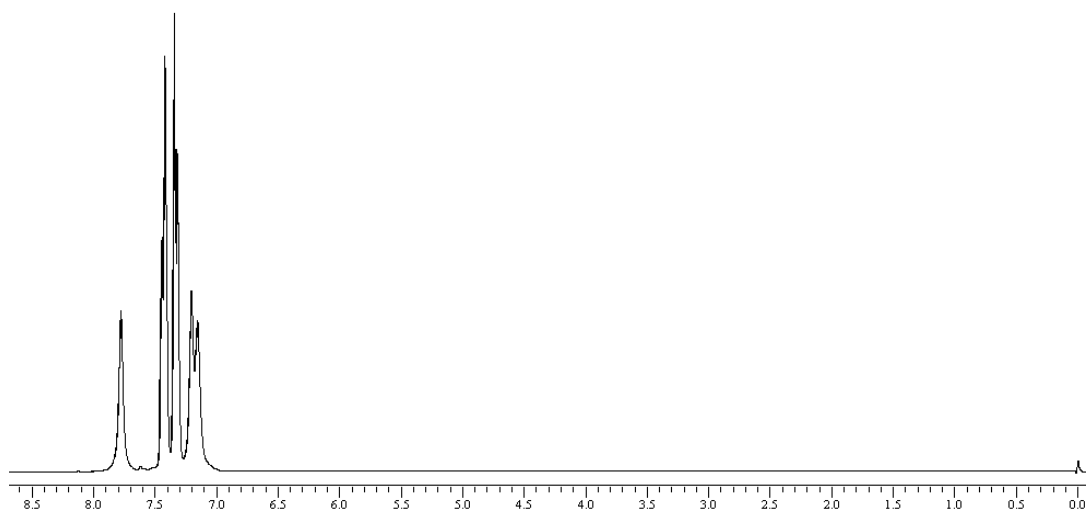
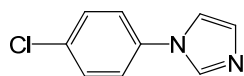
1-(4-Trifluoromethyl-phenyl)-1H-imidazole (Table 2, Entries 7 & 17)



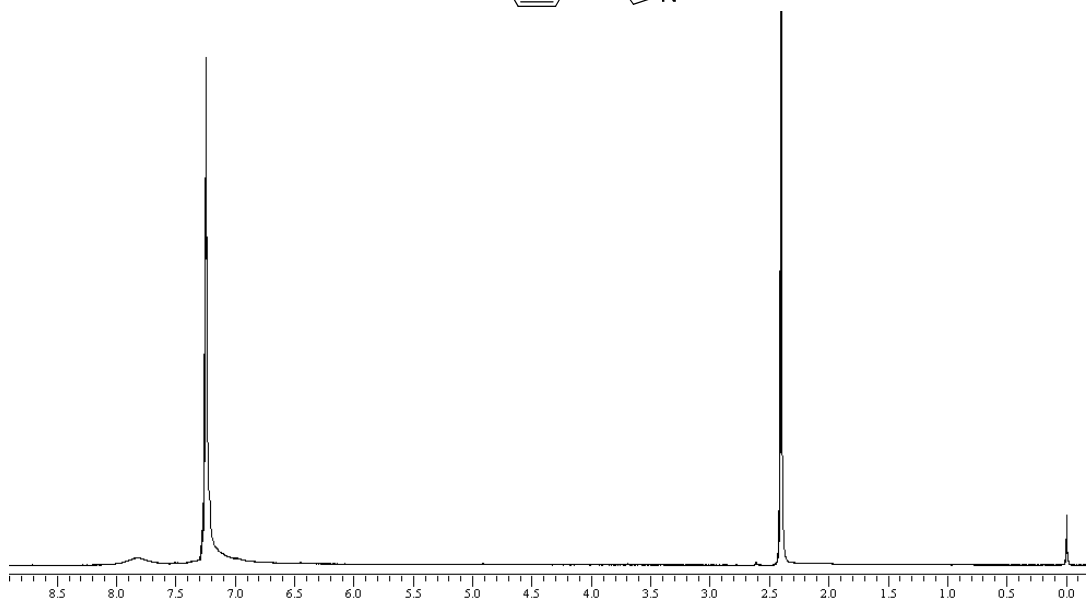
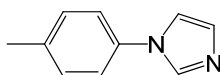
1-(4-imidazol-1-yl-phenyl)-ethanone (Table 2, Entry 8)



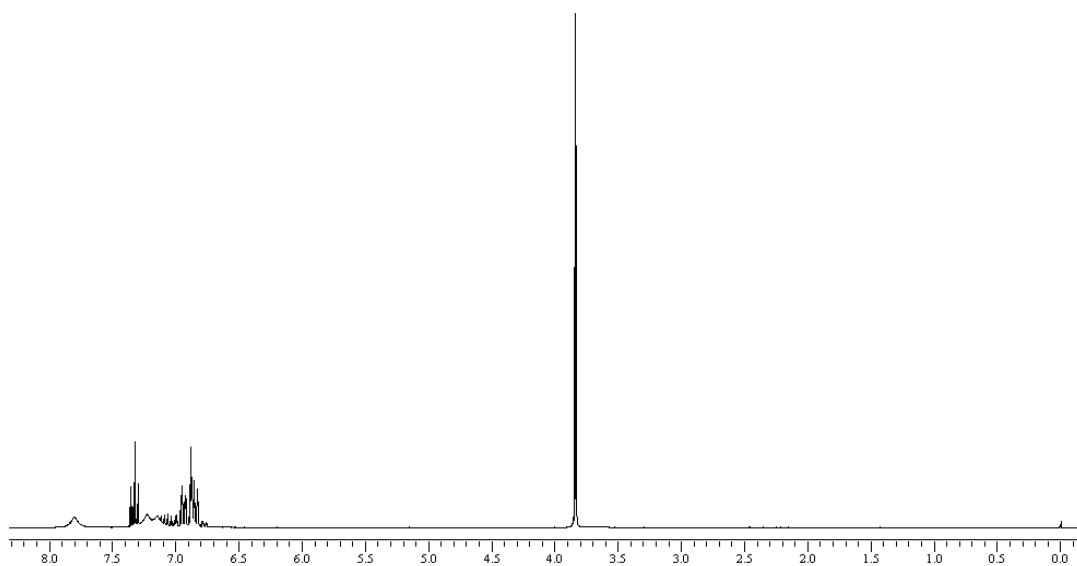
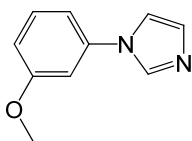
1-(4-Chlorophenyl)-1H-imidazole (Table 2, Entry 9)



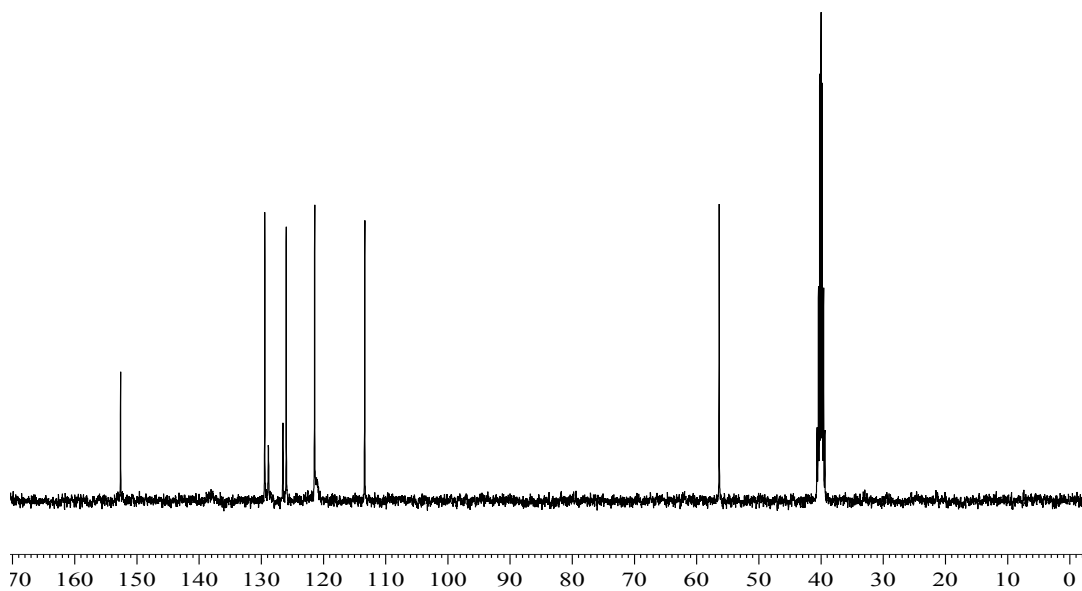
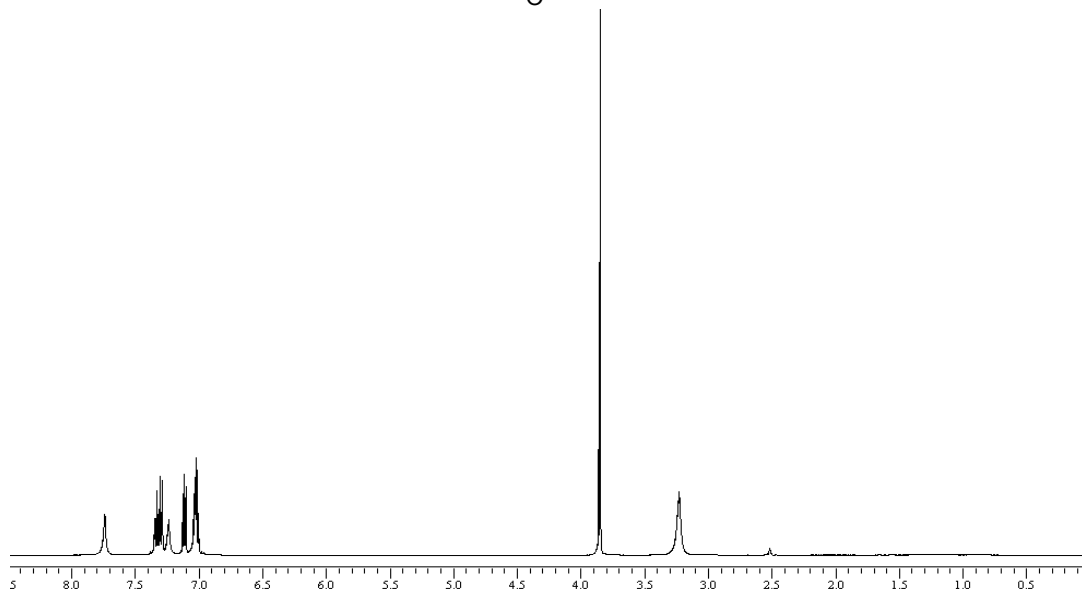
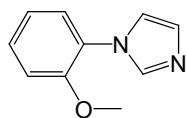
1-*p*-Tolyl-1H-imidazole (Table 2, Entry 10)



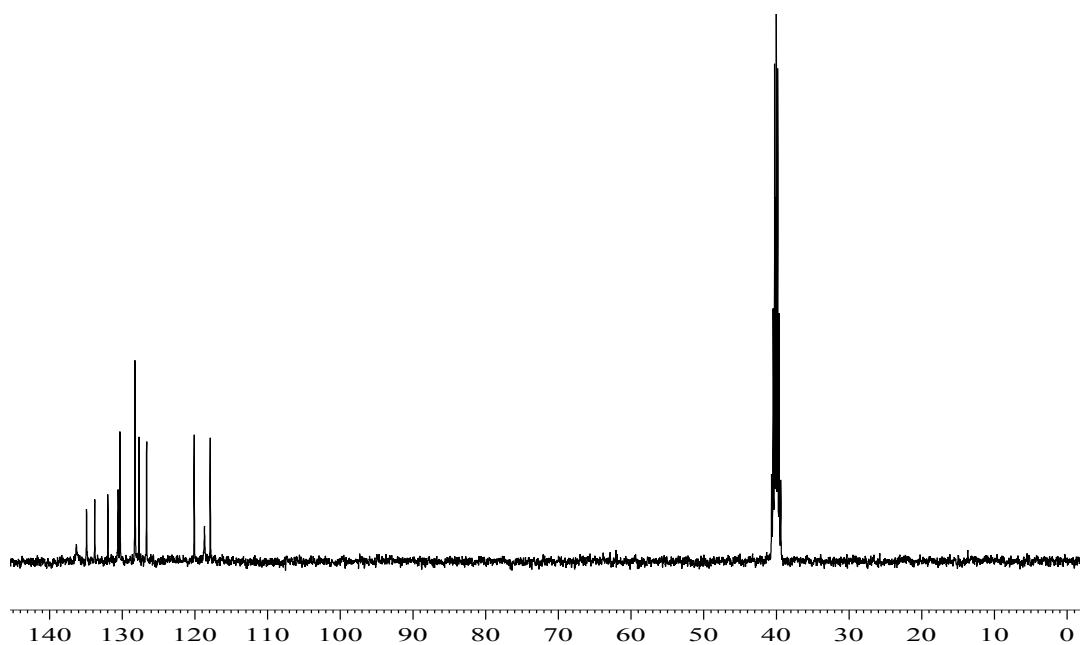
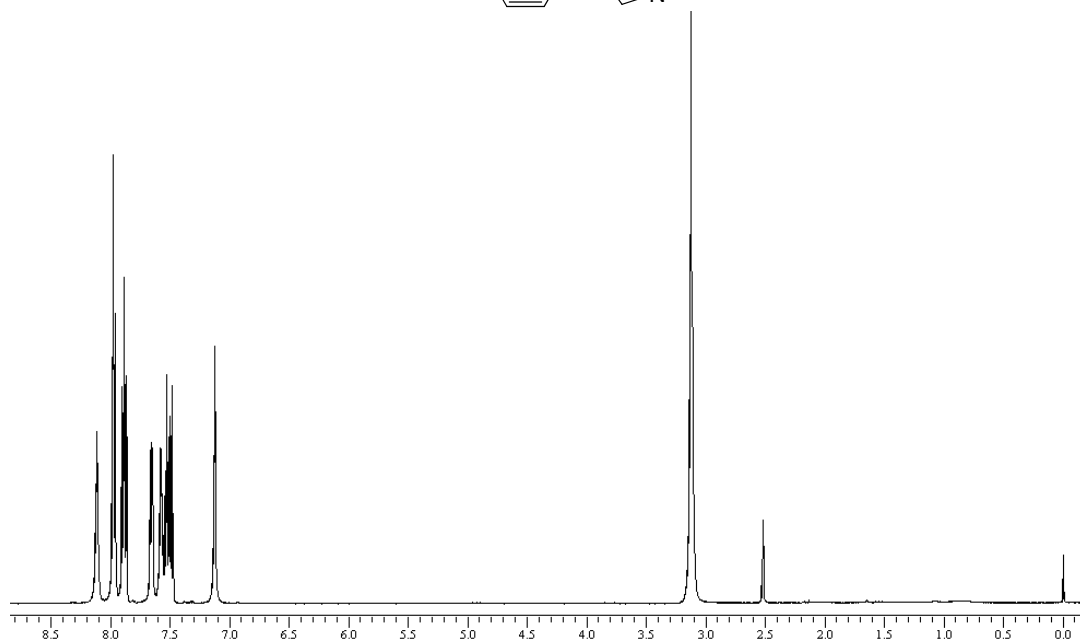
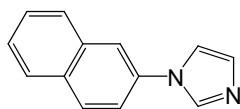
1-(3-Methoxy-phenyl)-1H-imidazole (Table 2, Entry 12)



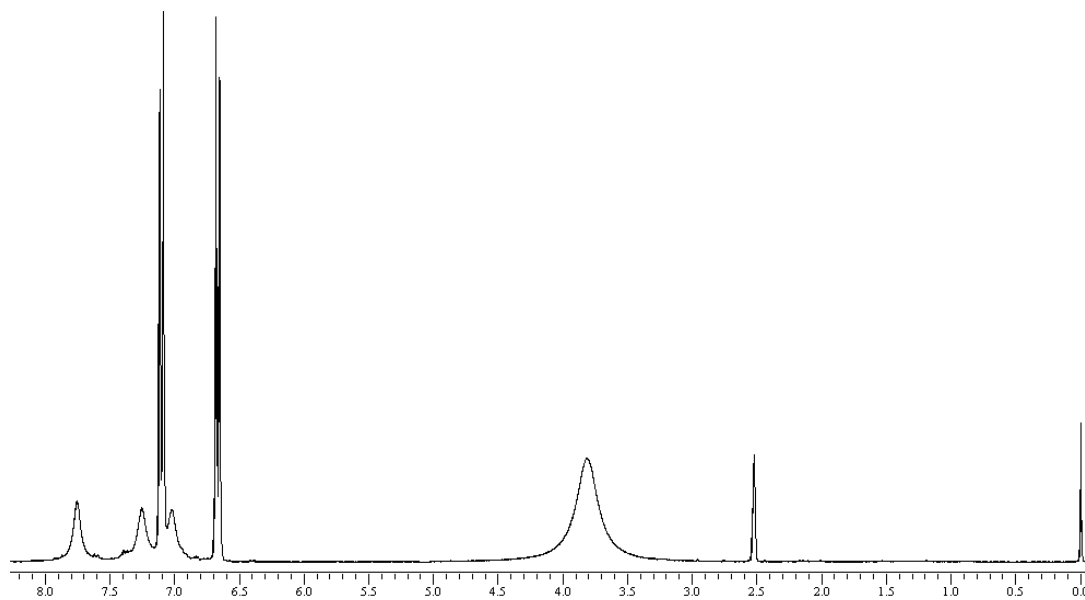
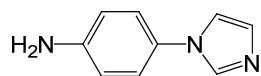
1-(2-Methoxy-phenyl)-1H-imidazole (Table 2, Entry 13)



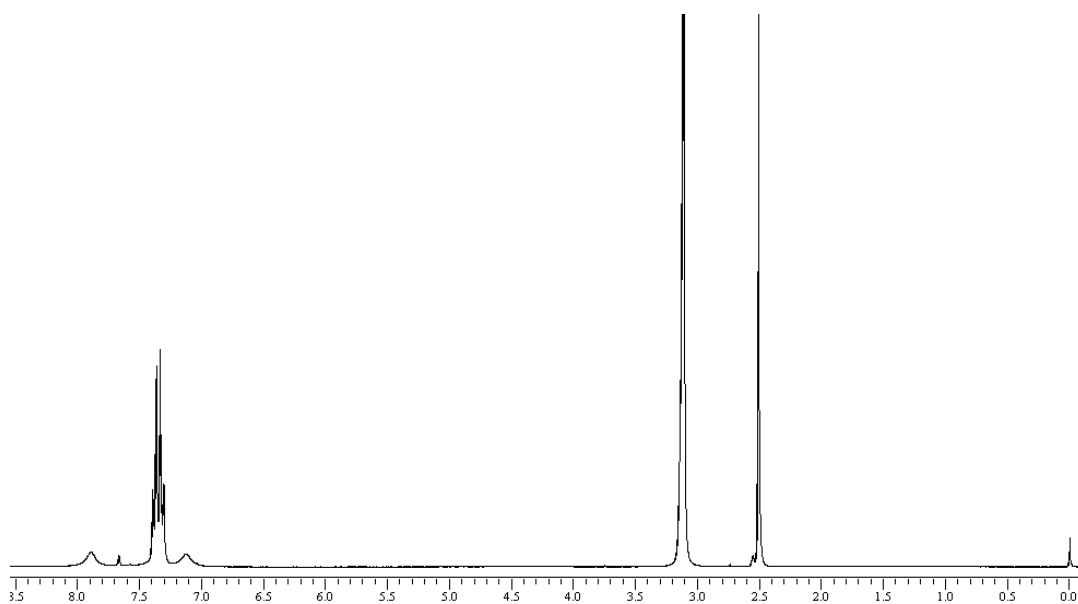
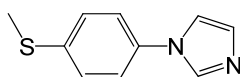
1-Naphthalen-2-yl-1H-imidazole (Table 2, Entry 14)



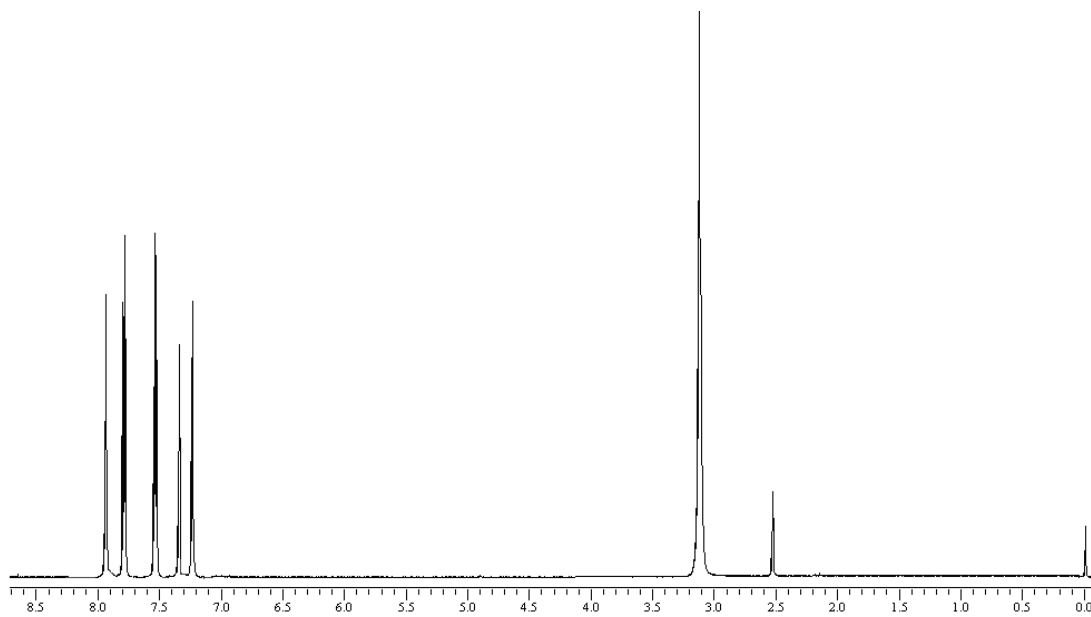
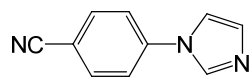
4-Imidazol-1-yl-phenylamine (Table 2, Entry 15)



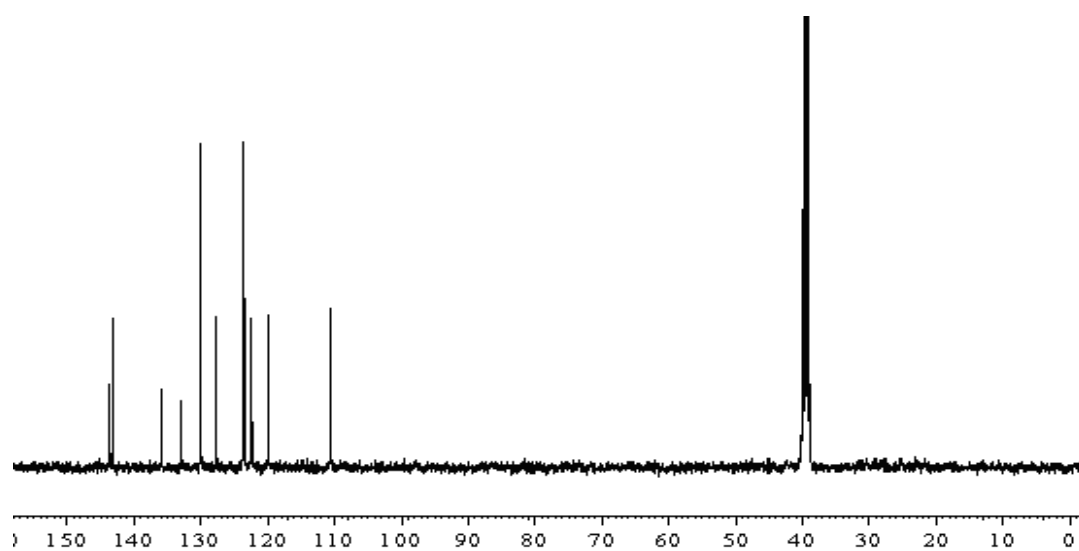
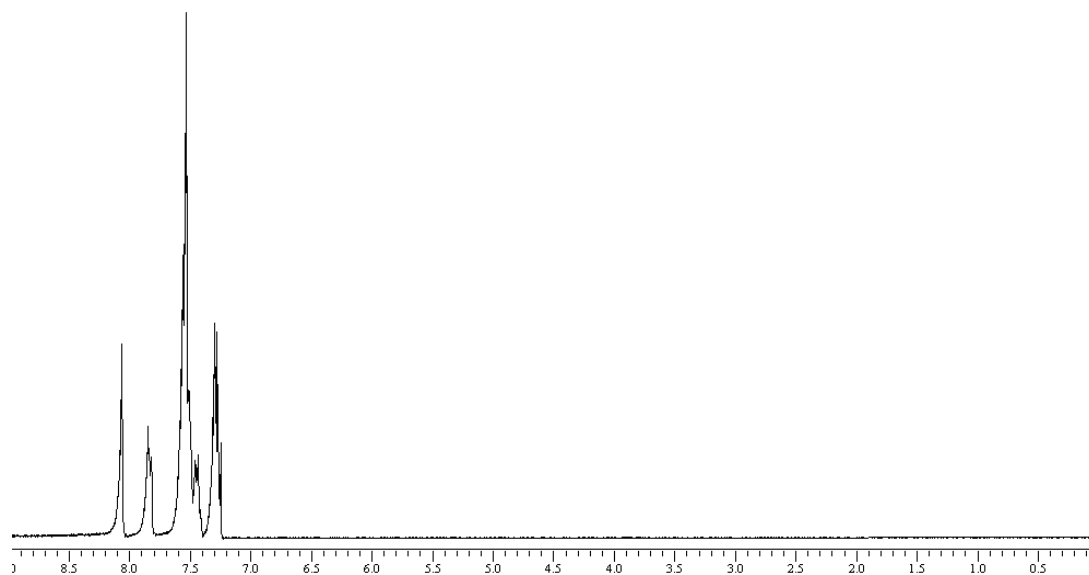
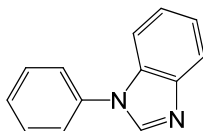
1-(4-Methylsulfonyl-phenyl)-1H-imidazole (Table 2, Entry 16)



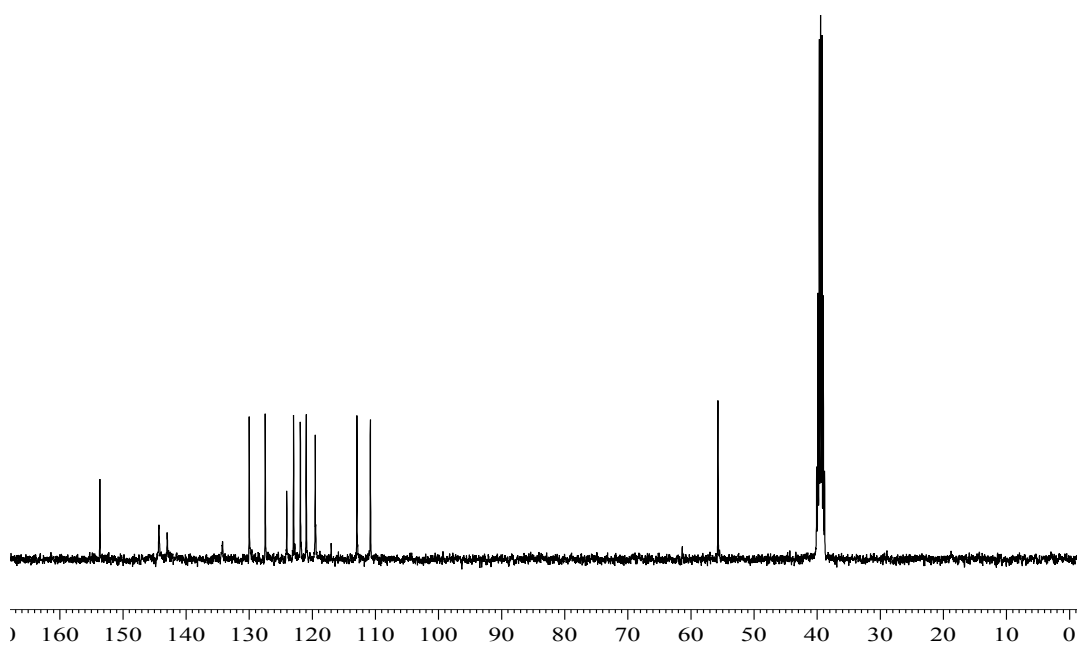
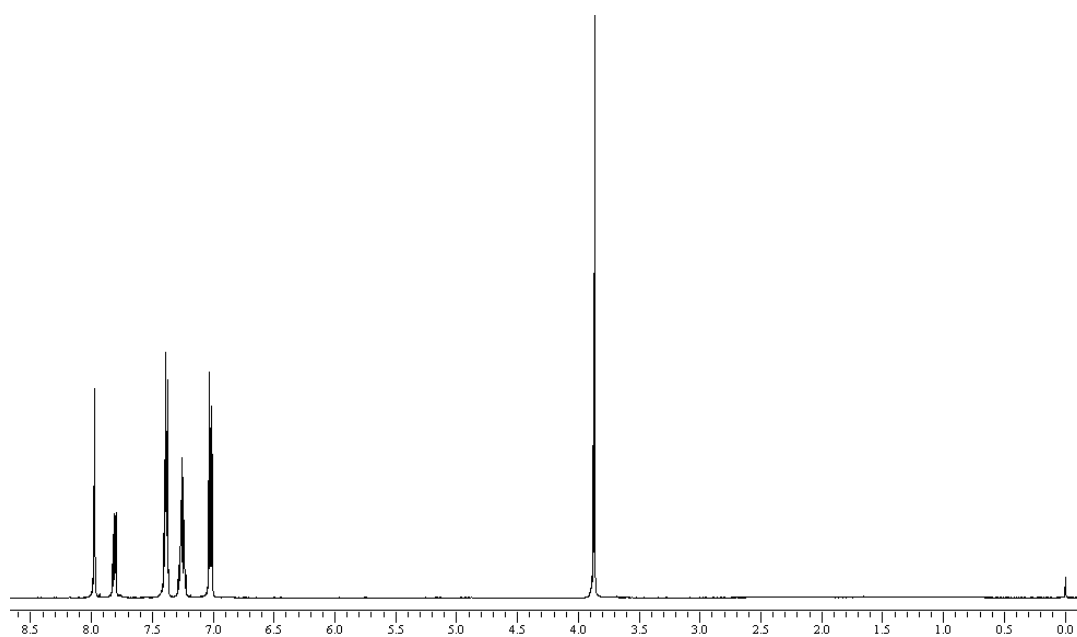
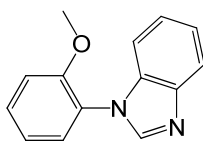
4-imidazol-1-yl-benzonitrile (Table 2, Entry 18)



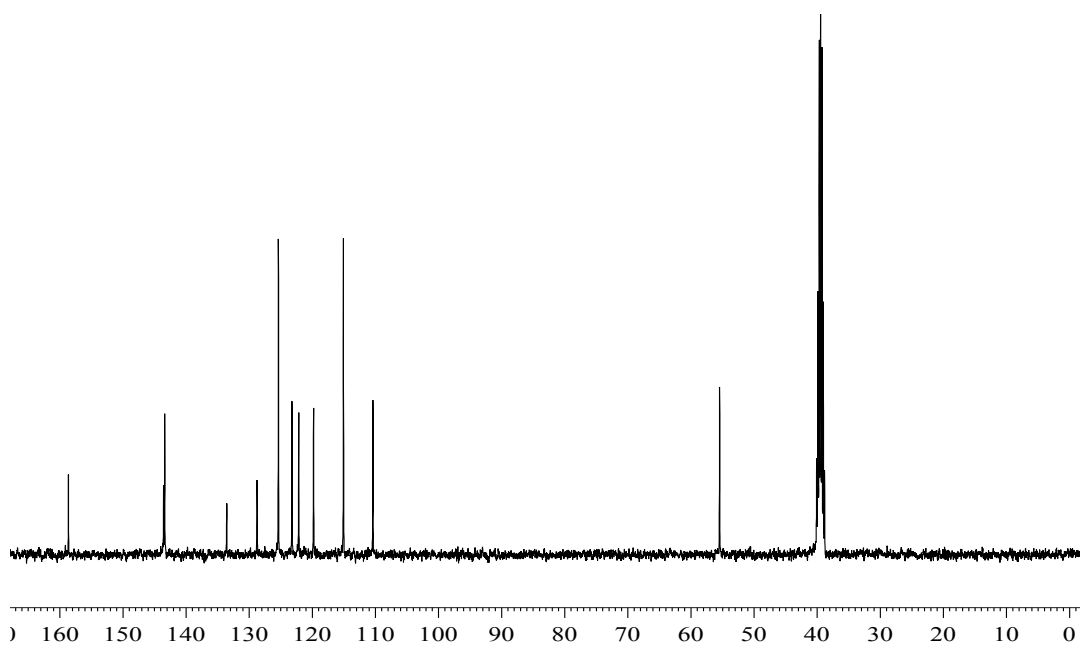
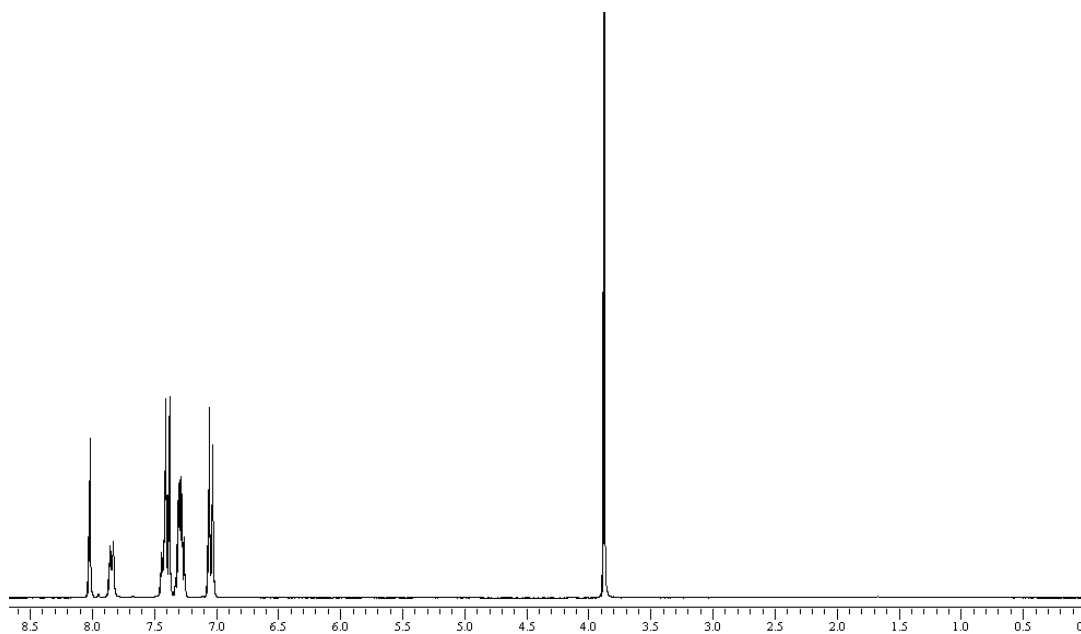
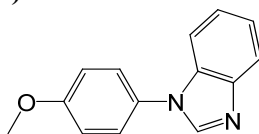
1-Phenyl-1H-benzimidazole (Table 2, Entry 23)



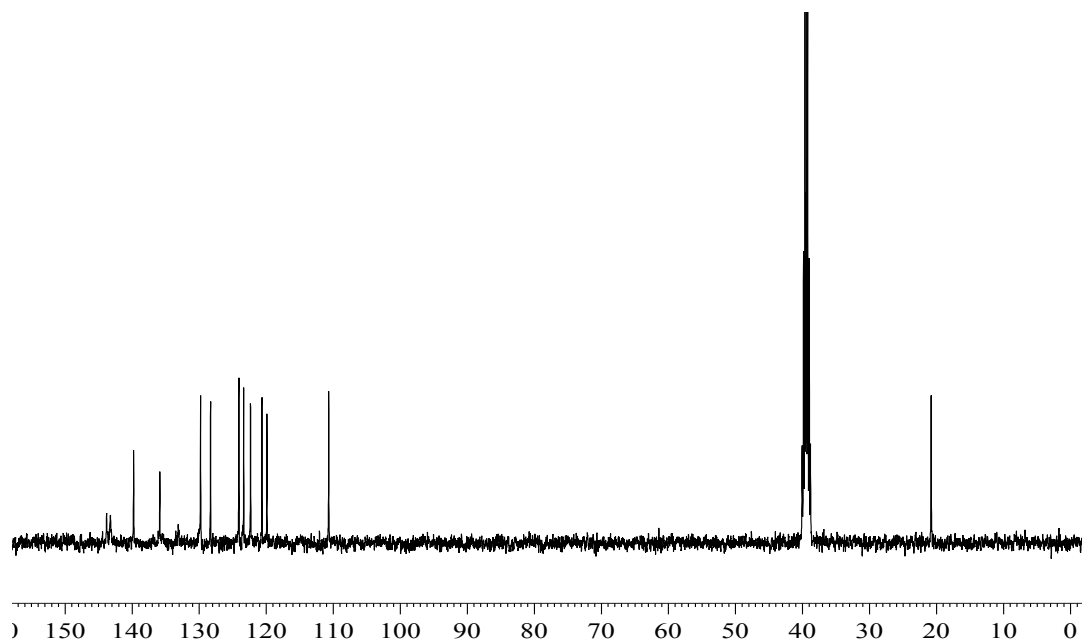
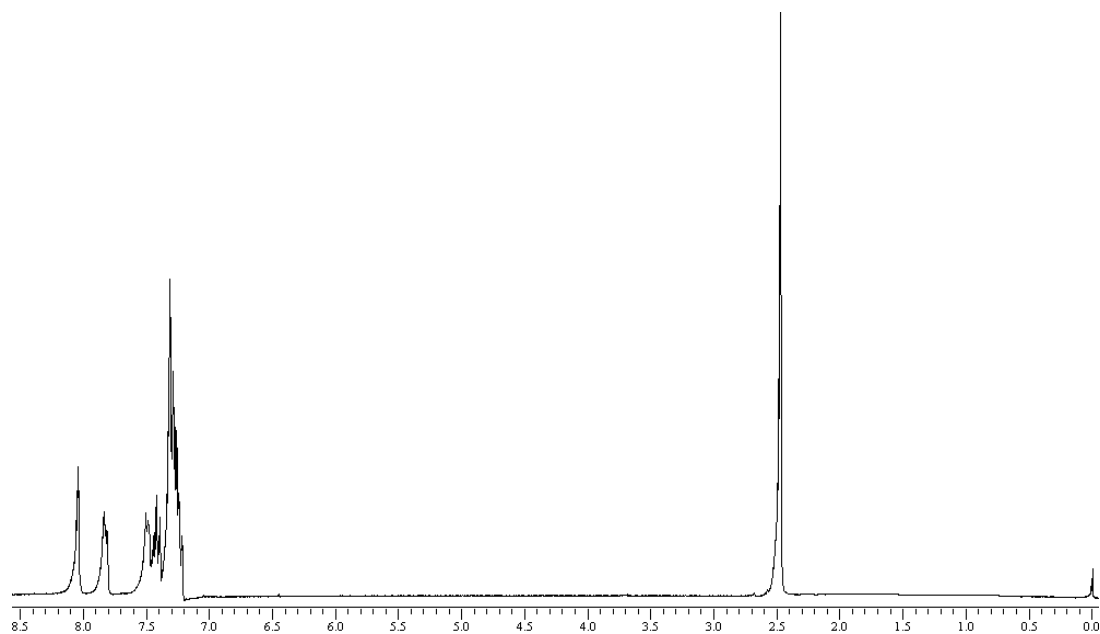
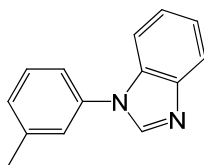
1-(2-Methoxy-phenyl)-1H-benzimidazole (Table 2, Entry 24)



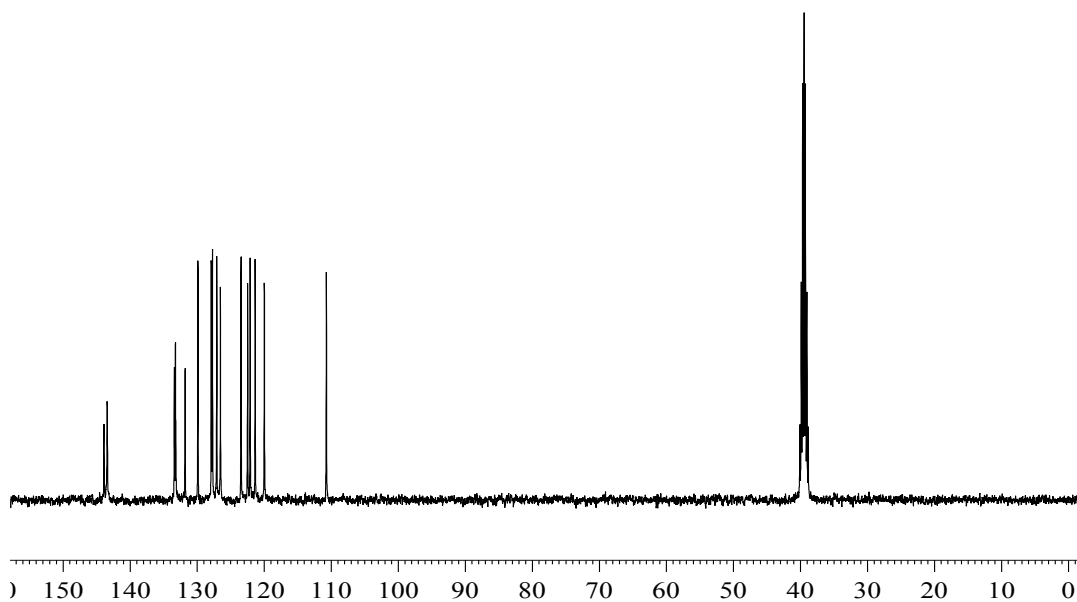
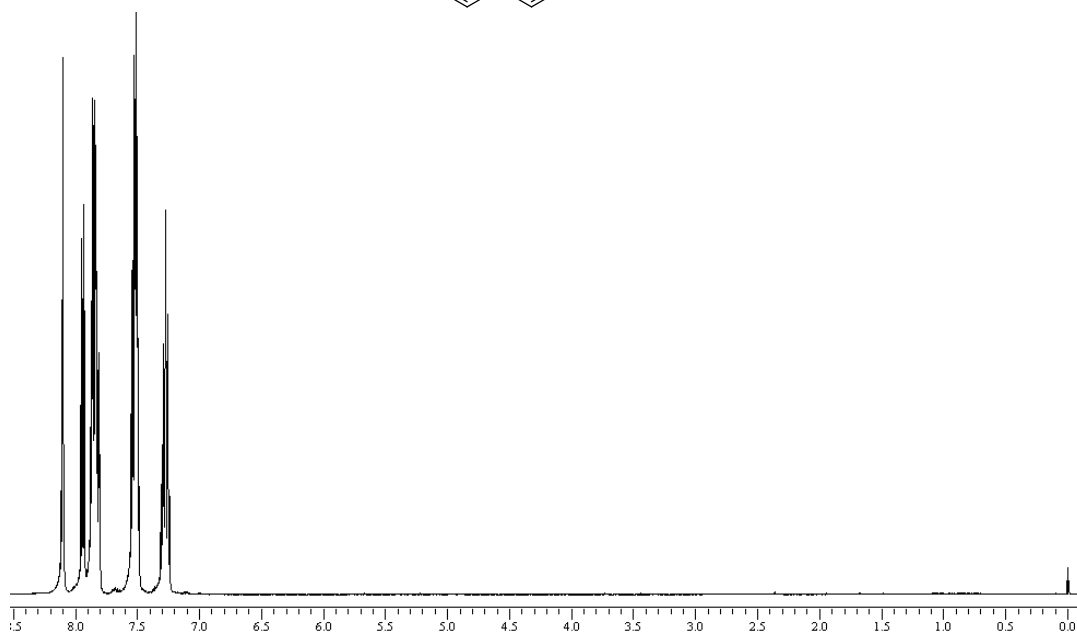
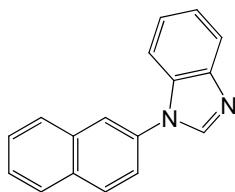
1-(4-Methoxyphenyl)-1H-benzimidazole (Table 2, Entry 25)



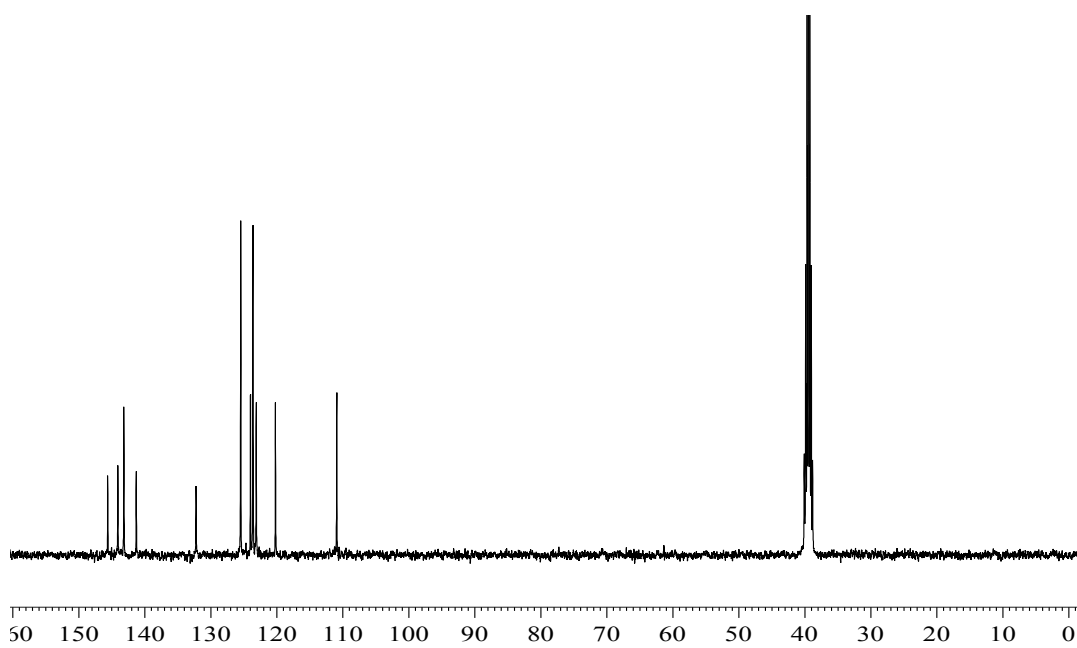
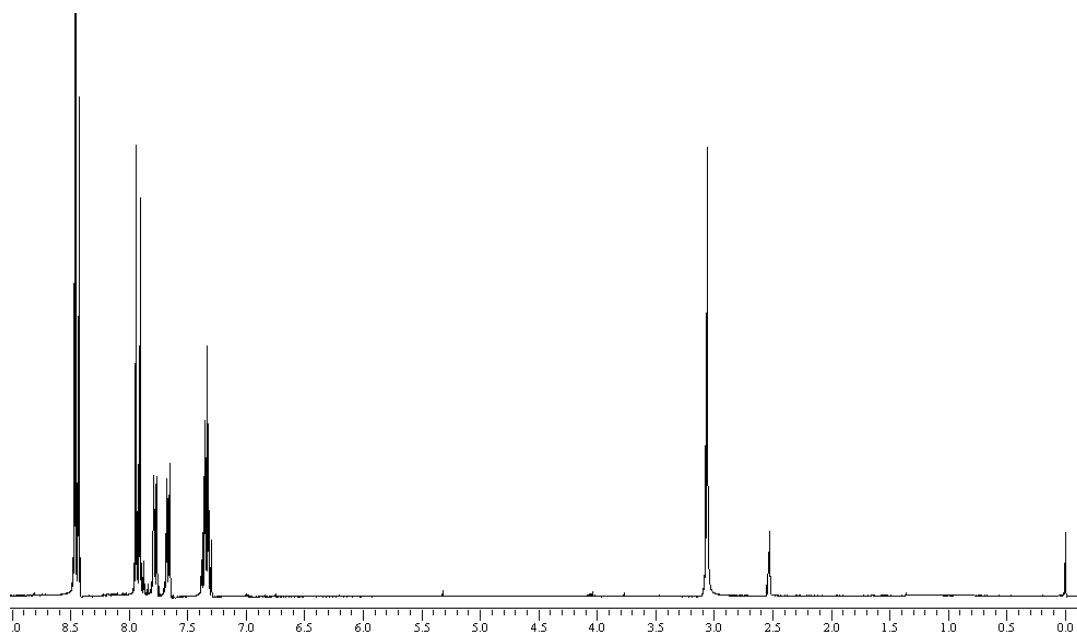
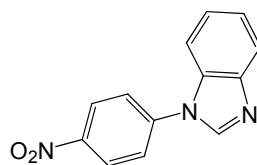
1-m-Tolyl-1H-benzimidazole (Table 2, Entry 26)



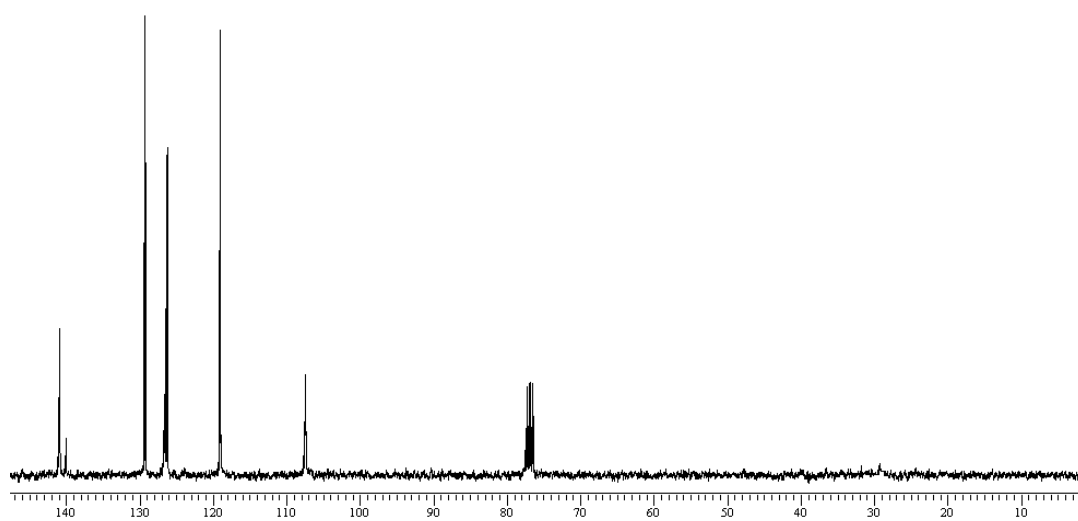
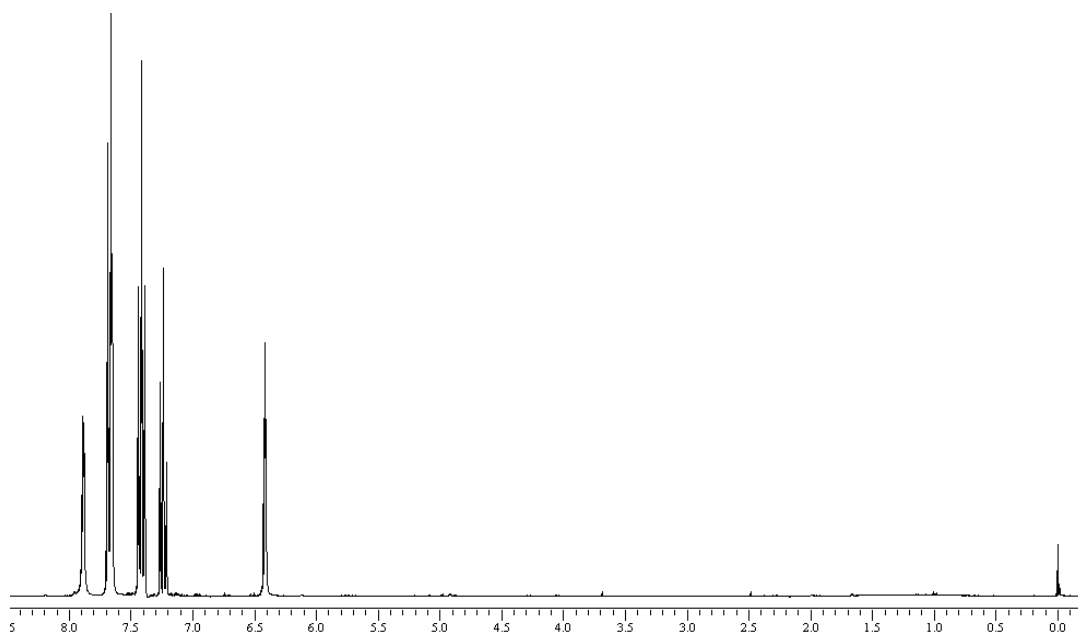
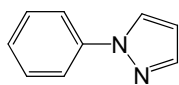
1-Naphthalen-2-yl-1H-benzimidazole (Table 2, Entry 27)



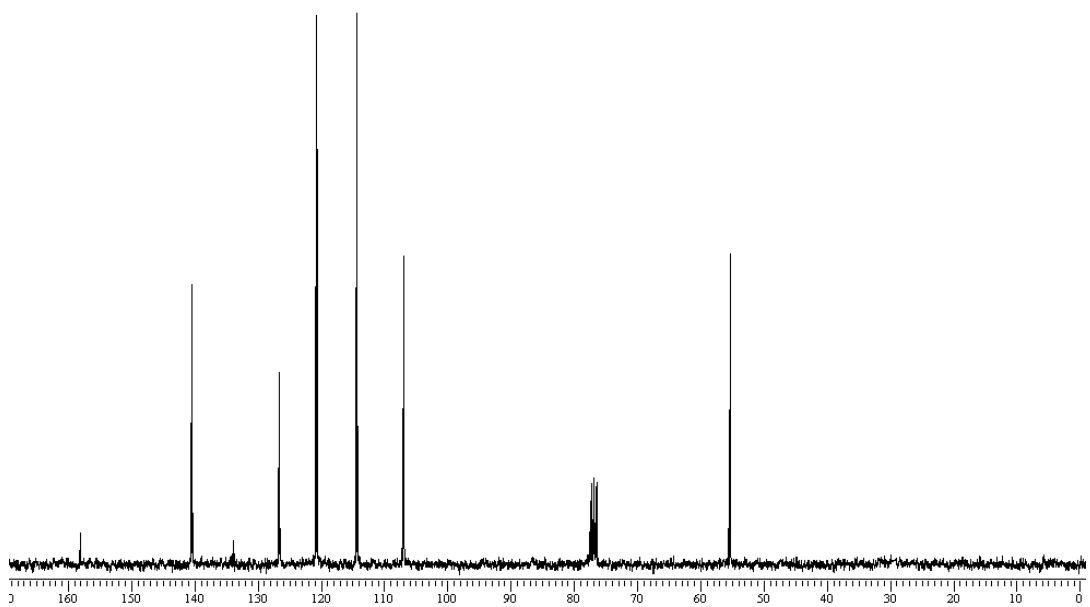
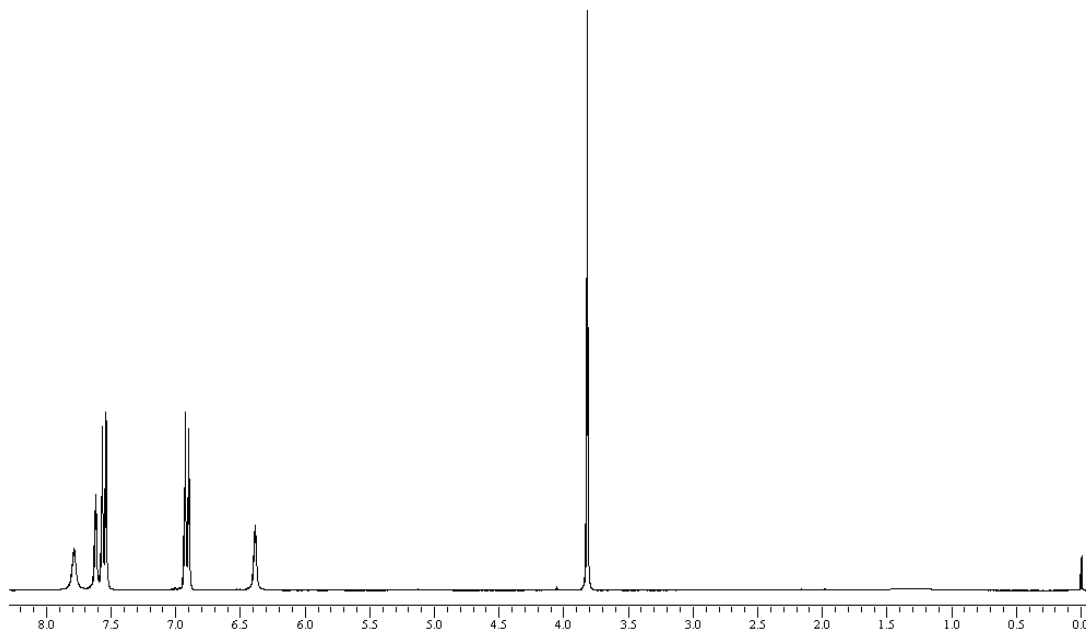
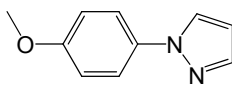
1-(4-Nitrophenyl)-1*H*-benzimidazole (Table 2, Entry 28)



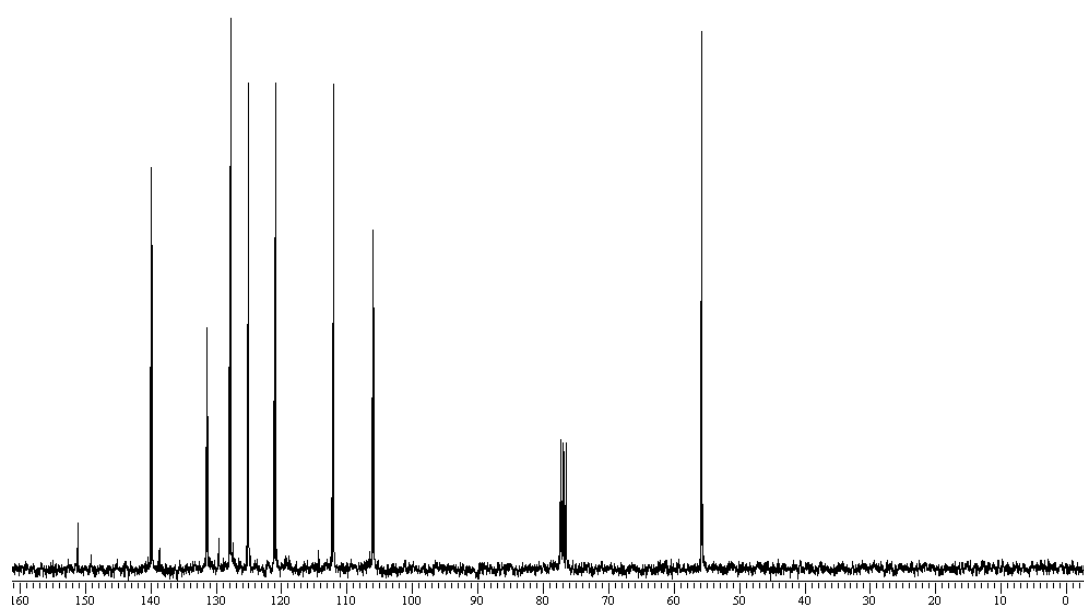
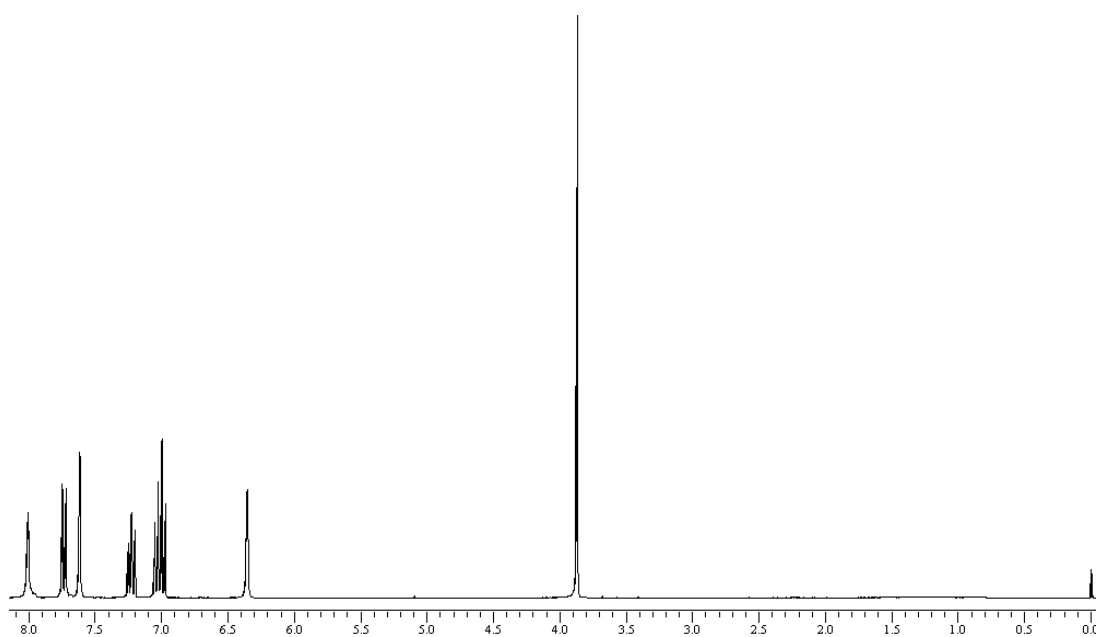
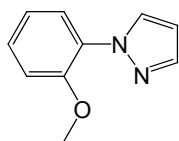
1-Phenyl-1H-pyrazole (Table 2, Entry 29)



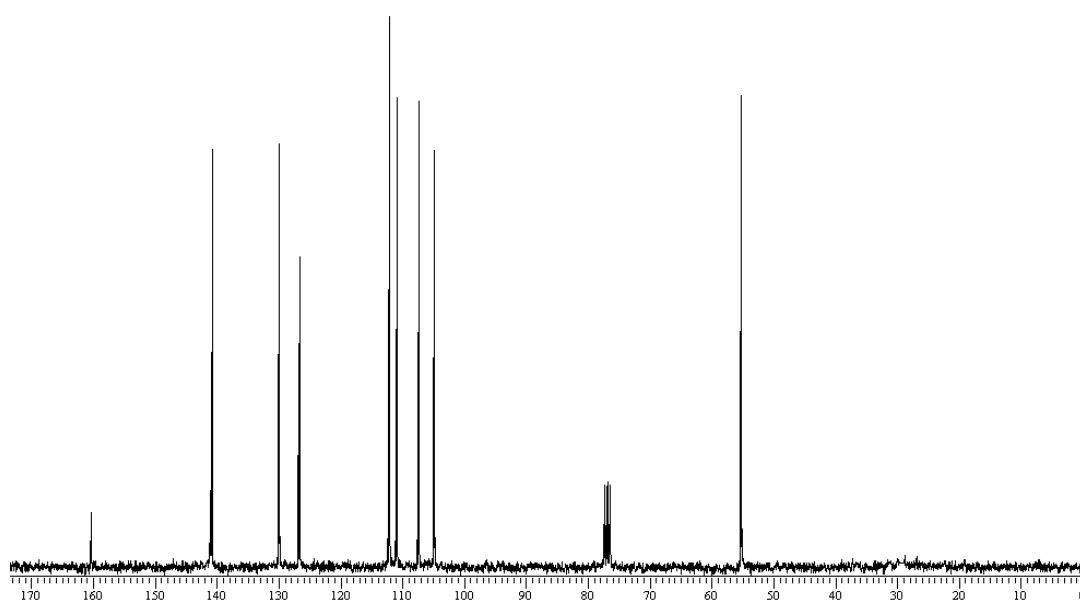
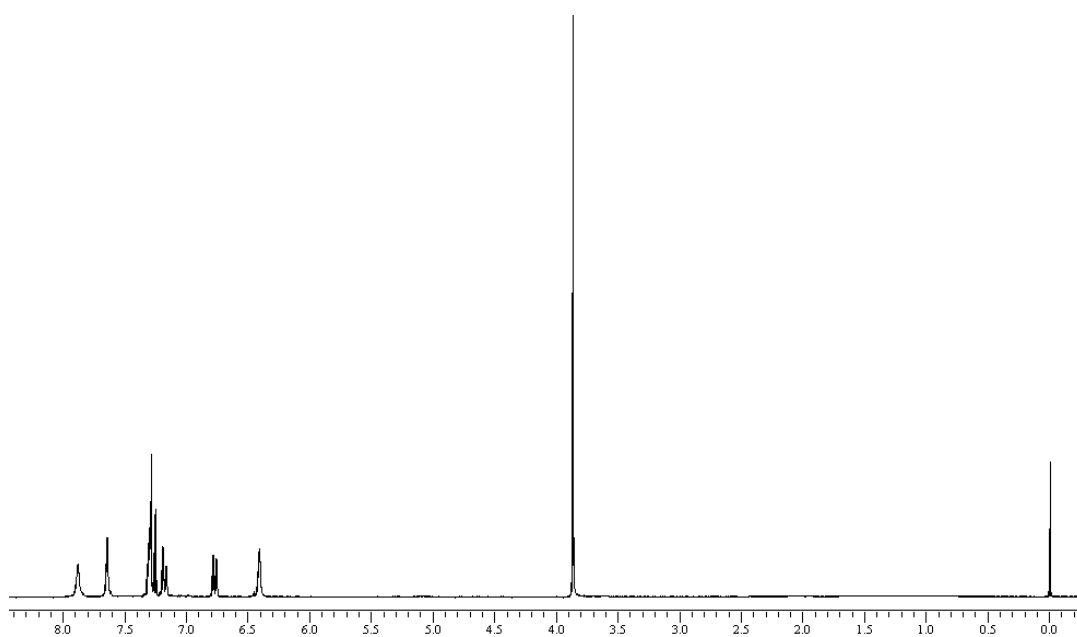
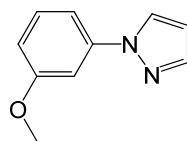
1-(4-Methoxy-phenyl)-1H-pyrazole (Table 2, Entry 30)



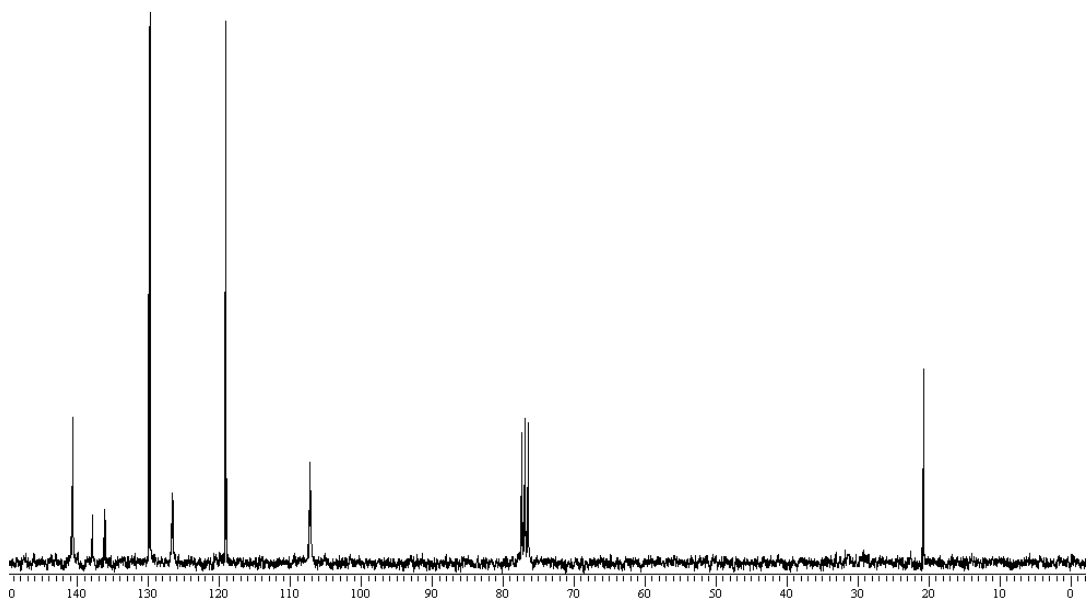
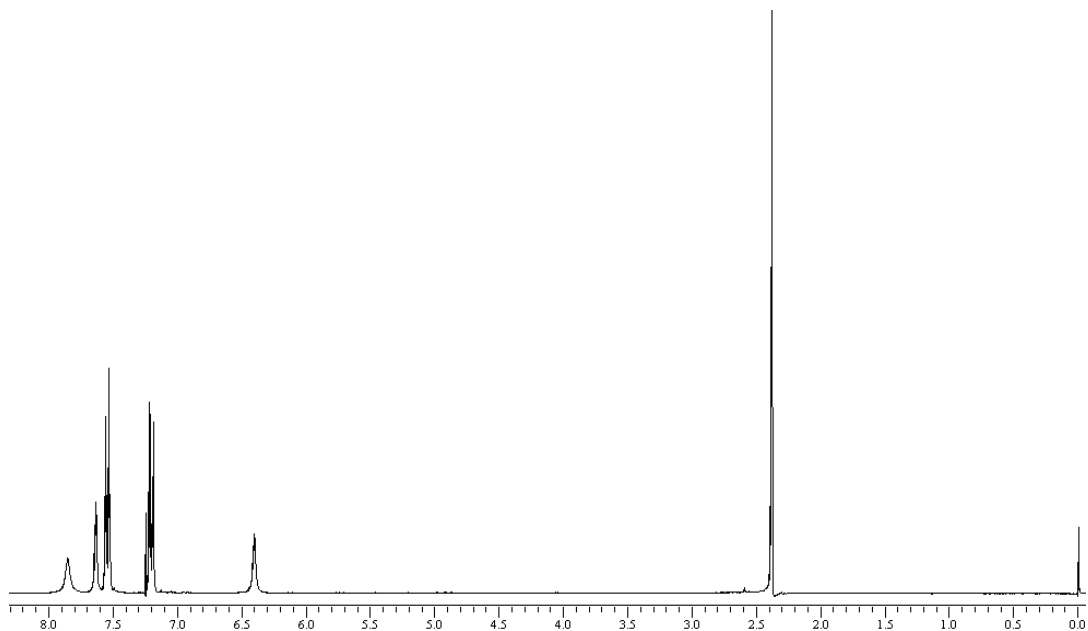
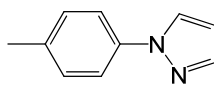
1-(2-Methoxy-phenyl)-1H-pyrazole (Table 2, Entry 31)



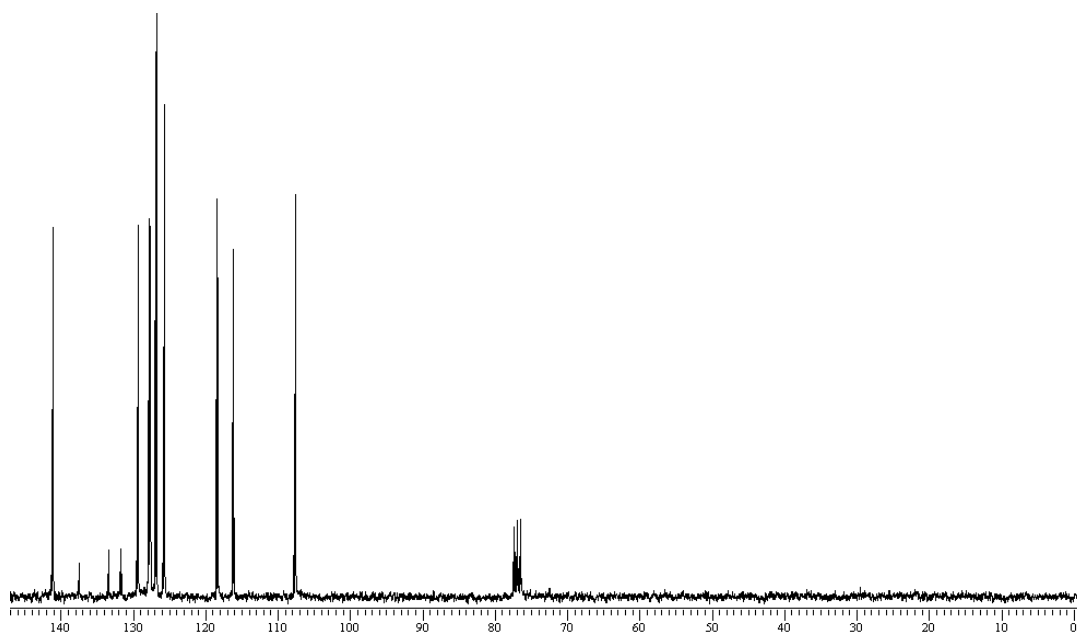
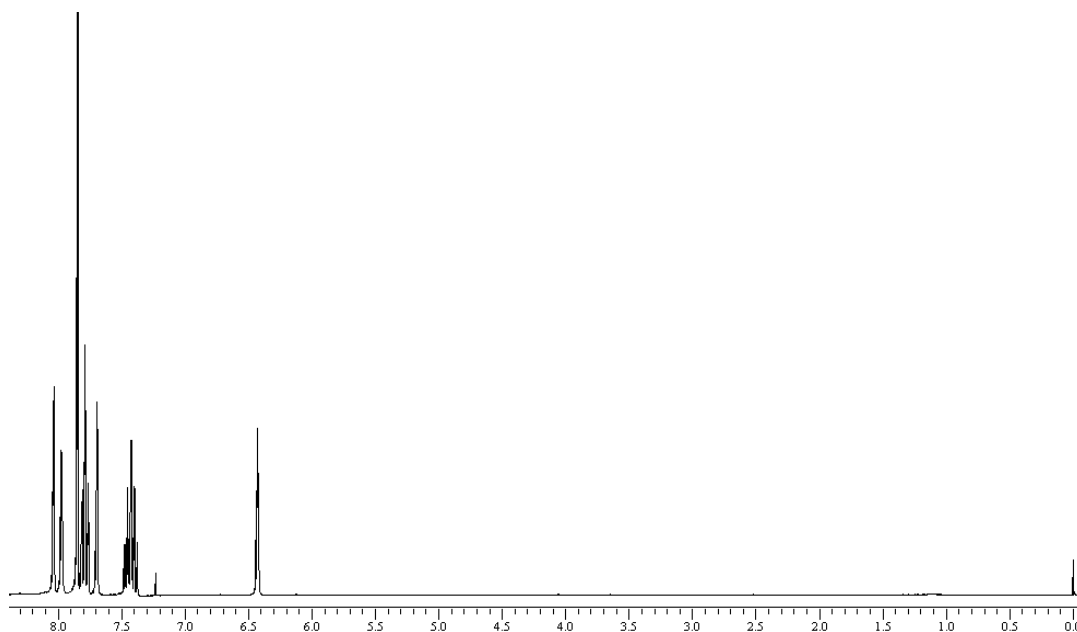
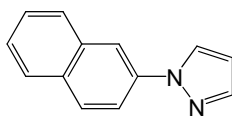
1-(3-Methoxy-phenyl)-1H-pyrazole (Table 2, Entry 32)



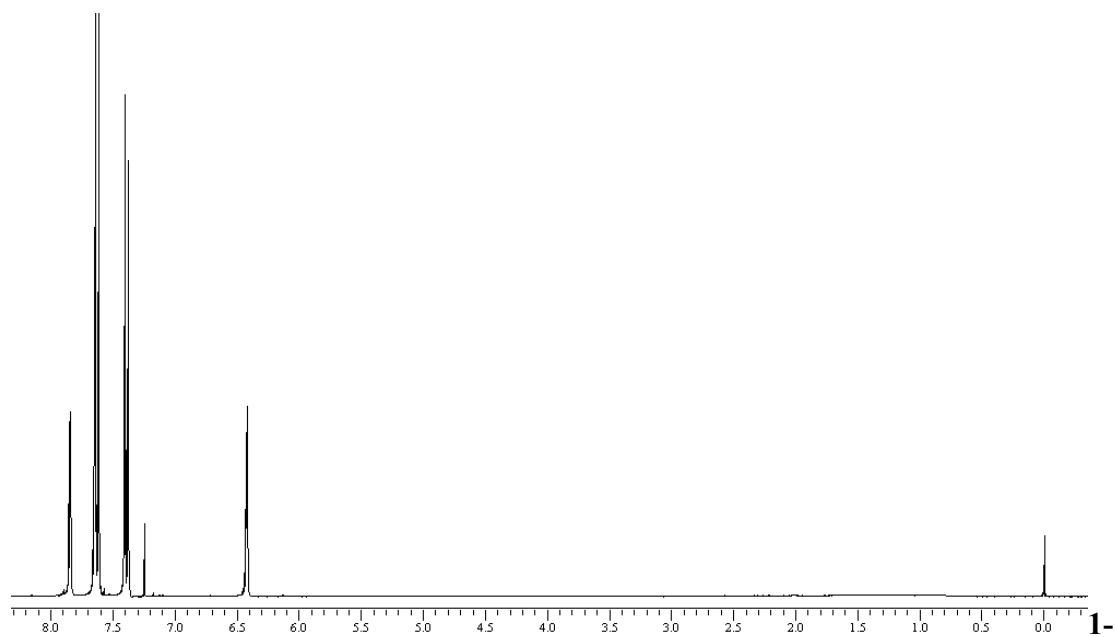
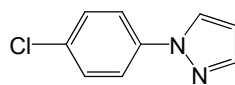
1-*p*-Tolyl-1H-pyrazole (Table 2, Entry 33)



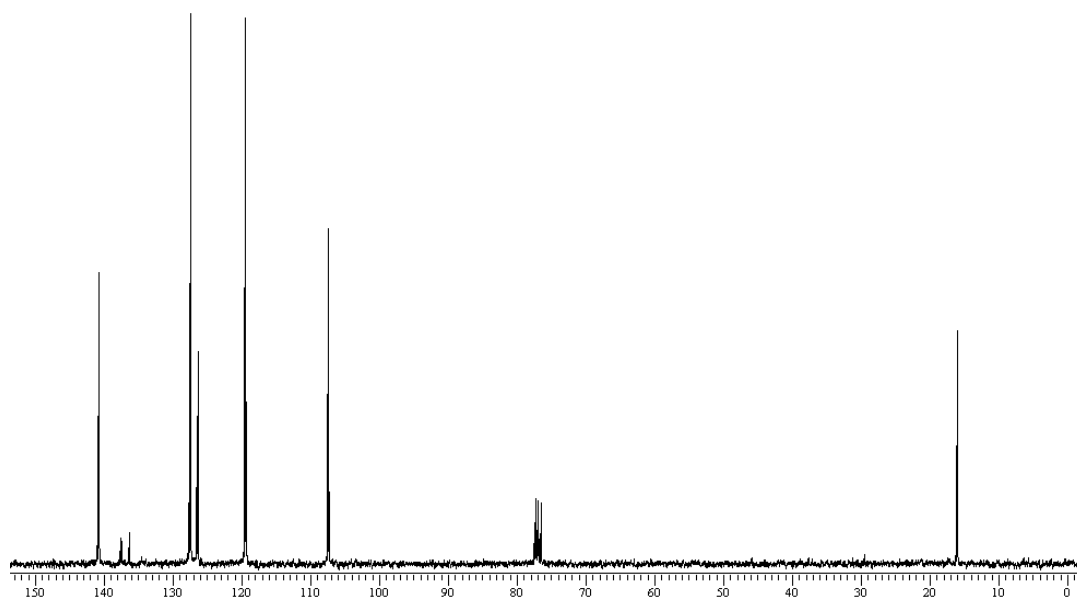
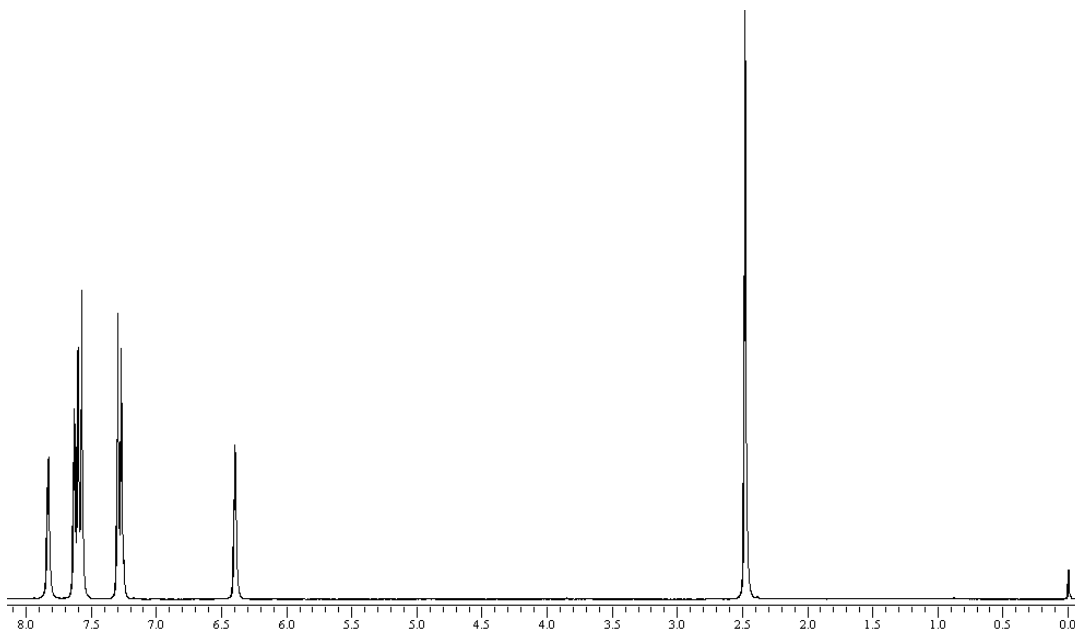
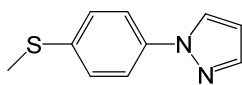
1-Naphthalen-2yl-1H-pyrazole (Table 2, Entry 34)



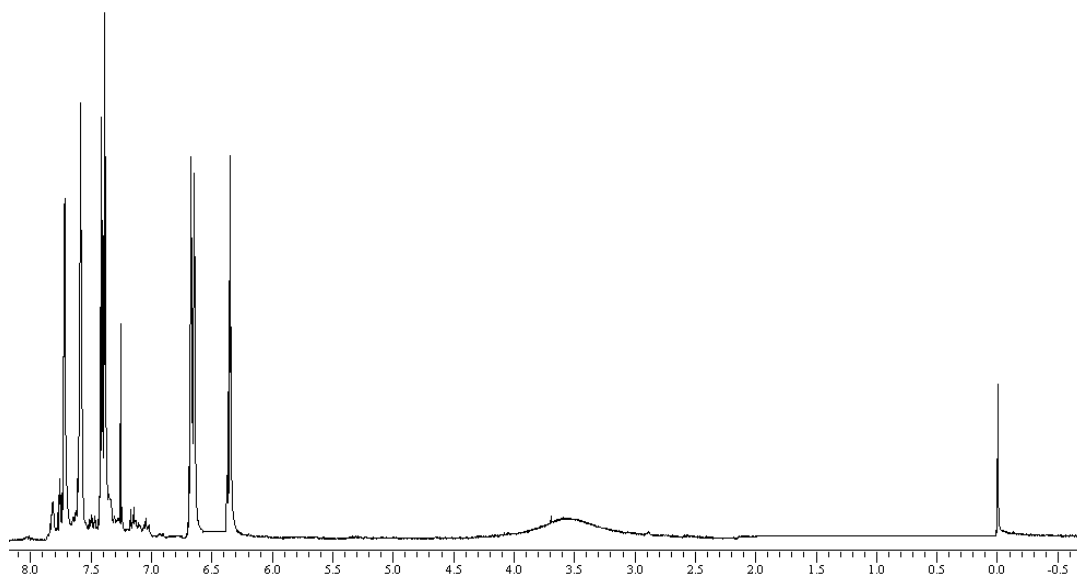
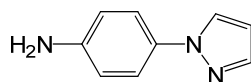
1-(4-Chlorophenyl)-1H-pyrazole (Table 2, Entry 35)



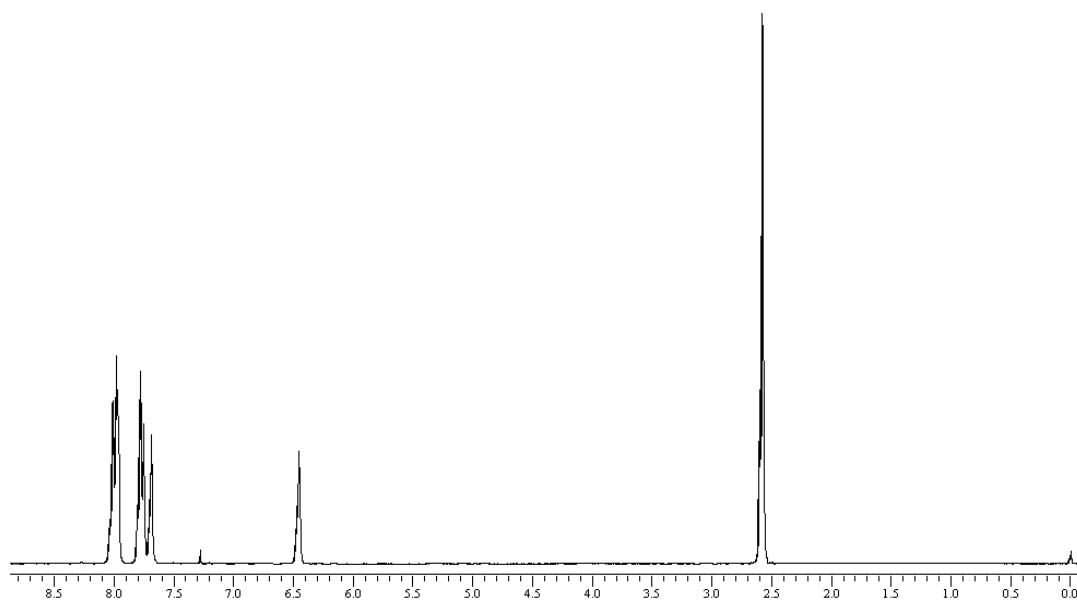
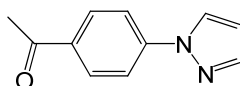
(4-Methylsulfanyl-phenyl)-1H-pyrazole (Table 2, Entry 36)



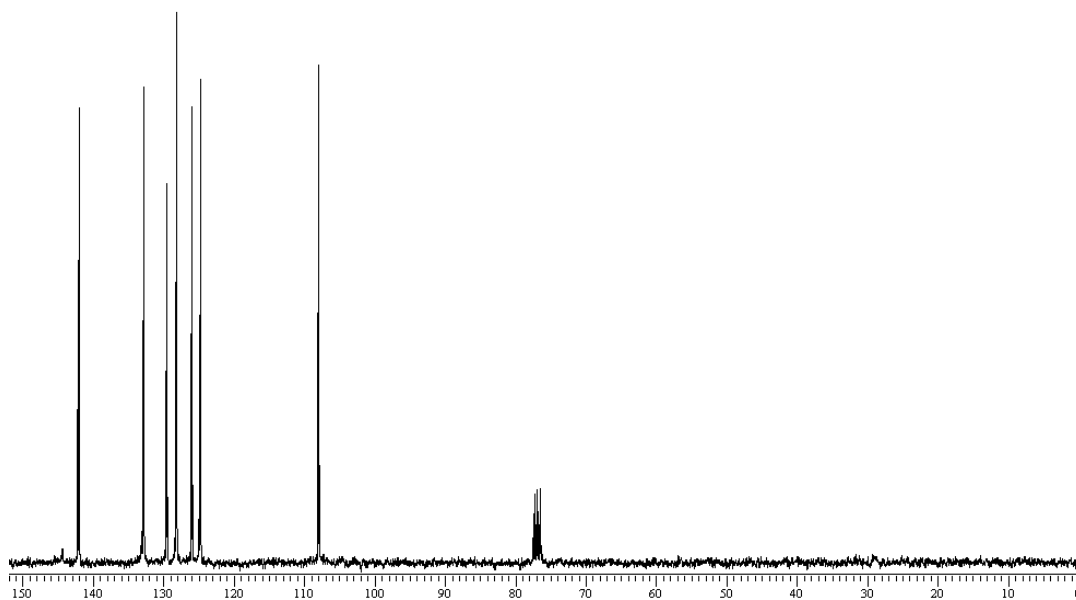
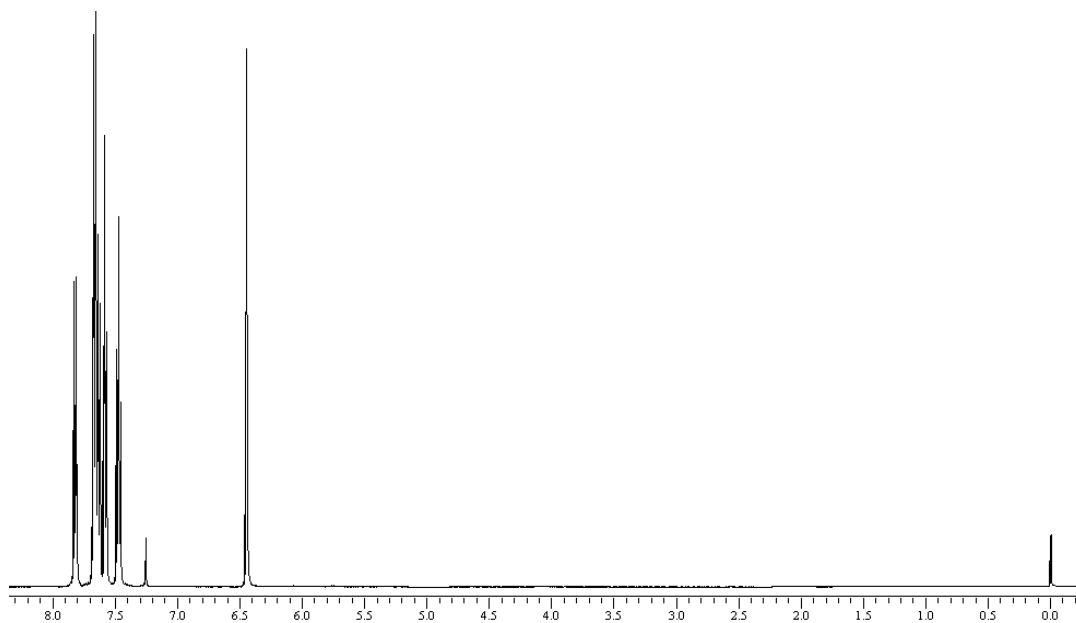
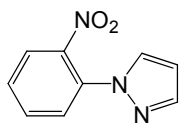
1-(4-Aminophenyl)-1*H*-pyrazole (Table 2, Entry 37)



1-(4-pyrazol-1-yl-phenyl)-ethanone (Table 2, Entry 38)



1-(2-Nitro-phenyl)-1H-pyrazole (Table 2, Entry 39)



1-(4-Trifluoromethyl-phenyl)-1H-pyrazole (Table 2, Entry 40)

