Supplementary Information for

Atom economical synthesis of *N*-alkylbenzamides *via* iron(III) sulfate catalyzed rearrangement of 2-alkyl-3-aryloxaziridines in water and in the presence of surfactant

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General methods

NMR spectra were acquired using $CDCl_3$ as solvent, running at 300 and 400 MHz for ^1H, and at 75 and 100 MHz for ^{13}C. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CHCl_3$, 7.28 ppm and H_2O 1.61 ppm for ^1H NMR; $CDCl_3$, 76.5 ppm for ^{13}C NMR). In all ^1H NMR spectra, multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet). Coupling constant values (in Hertz) and number of protons for each signal are also indicated. The IR spectra were recorded on Perkin-Elmer FT-IR spectrometer. Melting points were determined on a Büchi SMP-20 capillary apparatus and are uncorrected. TLC was carried out on Merck 60F-254 precoated silica gel plates (0.25 mm). Dimethyl carbonate (Reagent plus®, 99%), hydrogen peroxide (30 % wt in water), were purchased from Sigma-Aldrich. All starting materials purchased from commercial suppliers were used without further purification, except alkylamines and aromatic aldehydes which were distilled or recrystallized (solid reagents) before use.

Synthesis of *N*-alkyloxaziridines

N-Alkyloxaziridines were prepared according to the green method developed by our group.[1]

General procedure: To a solution of the aldehyde (1 mmol) in DMC (1 mL) was added the *N*-alkylamine (1.5 mmol). The mixture was stirred for 10 mn. A 5 mmol of hydrogen peroxide solution (30 % wt) was then added over a period of 5 mn. The mixture was stirred at room temperature until disappearance of aldehyde (15 h, reaction monitored by TLC). Then, the mixture was washed with 3 mL of aqueous saturated solution of sodium sulfite, centrifuged (5 mn, 4000 rpm, Figure 1) to separate the organic and the aqueous phases, and further extracted with 2×1 mL of DMC (we extracted the oxaziridine with 2 mL of DMC instead of 11 mL of ethyl acetate[1]). The combined organic phases were concentrated under reduced pressure to yield pure oxaziridine.

N-*tert*-Butyloxaziridines **1a-f** were obtained in the *trans*-isomer form (100%)[1]. Oxaziridines with smaller substituents (**1g-q)** were obtained as mixtures of *trans* and *cis*-isomers (*trans/cis* ratio: from 92:8 to 88:12).

Oxaziridines **1a**,[1] **1b**,[2] **1c**,[3] **1d**,[1] **1e**,[4] **1f**,[3] **1g**,[1] **1h**,[5] **1i**,[5] **1j**,[6] **1k**,[1] **1l**,[1] **1m**,[7] **1n**,[8] **1o**,[4] **1p**,[9] and **1q**[1] are known compounds.

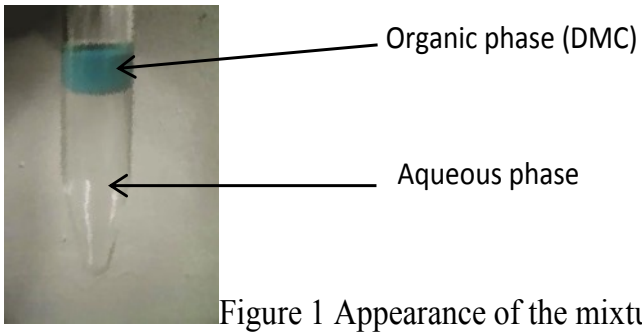


Figure 1 Appearance of the mixture after centrifugation.

Synthesis of *N*-alkylbenzamides

General procedure: A mixture of H_2O (1 mL), $Fe_2(SO_4)_3.5H_2O$ (2.5 mol%), SDS (15 mol%) was stirred for 5 mn at room temperature. After that, oxaziridine (0.5 mmol) was added and the reaction was stirred in a 5 mL sealed vial at 70 °C until disappearance of the oxaziridine (TLC). After completion of the reaction, the mixture was extracted with 3×1 mL portions of ethyl acetate, filtered through a short pad of silica gel and concentrated under reduced pressure to yield pure *N*-alkylbenzamide.

N-Alkylbenzamides **2a**,[10] **2b**,[10] **2c**,[10] **2d**,[11] **2e**,[12] **2f**,[11] **2g**,[11] **2h**,[13] **2i**,[13] **2j**,[14] **2k**,[11] **2l**,[15] **2m**,[15] **2n**,[16] **2o**,[17] **2p**,[18] and **2q** [18] are known compounds.

***N-(tert*-Butyl)benzamide 2a:** According to the general procedure, the product was isolated as white solid (m.p. = 134–135 °C); ν_{max} (KBr)/cm^{-1} 3332 (NH), 1643 (C=O); δ_H (400 MHz; $CDCl_3$) 7.70 (2 H, m), 7.45–7.37 (3 H, m), 5.97 (1 H, br s), 1.46 (9 H, s); δ_C (100 MHz; $CDCl_3$) 166.9, 135.8, 131.0, 128.4, 126.6, 51.5, 28.8.

***N-(tert*-Butyl)-4-methoxybenzamide 2b:** According to the general procedure, the product was isolated as white solid (m.p. = 117–118 °C); ν_{max} (KBr)/cm^{-1} 3330 (NH), 1646 (C=O); δ_H (400 MHz; $CDCl_3$) 7.67 (2 H, d, *J* = 8.8 Hz), 6.88 (2 H, d, *J* = 8.8 Hz), 5.89 (1 H, br s), 3.82 (3 H, s), 1.45 (9 H, s); δ_C (100 MHz; $CDCl_3$) 166.4, 161.8, 128.4, 128.1, 113.5, 55.3, 51.4, 28.9.

4-Bromo-*N-(tert*-butyl)benzamide 2c: According to the general procedure, the product was isolated as yellow solid (m.p. = 130–131 °C); ν_{max} (KBr)/cm^{-1} 3355 (NH), 1652 (C=O); δ_H (300 MHz; $CDCl_3$) 7.60–7.54 (4H, m), 5.99 (1 H, br s), 1.47 (9 H, s); δ_C (75 MHz; $CDCl_3$) 165.9, 134.7, 131.6, 128.3, 125.6, 51.7, 28.8.

***N*-(*tert*-Butyl)-4-nitrobenzamide 2d:** According to the general procedure, the product was isolated as yellow solid (m.p. = 157–158 °C); ν_{max} (KBr)/cm^{-1} 3330 (NH), 1643 (C=O); δ_H (300 MHz; $CDCl_3$) 8.22 (2 H, d, *J* = 8.7 Hz), 7.87 (2 H, d, *J* = 8.7 Hz), 6.16 (1 H, br s), 1.48 (9 H, s); δ_C (75 MHz; $CDCl_3$) 164.9, 149.2, 141.5, 127.9, 123.6, 52.2, 28.7.

***N*-(*tert*-Butyl)-2-chlorobenzamide 2e:** According to the general procedure, the product was isolated as yellow solid (m.p. = 109–110 °C); ν_{max} (KBr)/cm^{-1} 3385 (NH), 1651 (C=O); δ_H (400 MHz; $CDCl_3$) 7.58–7.56 (1 H, m), 7.35–7.26 (3 H, m), 5.92 (1 H, br s), 1.46 (9 H, s); δ_C (100 MHz; $CDCl_3$) 165.8, 136.4, 130.7, 130.3, 130.0, 129.6, 126.9, 52.1, 28.7.

***N*-(*tert*-Butylpicolinamide 2f:** According to the general procedure, the product was isolated as yellow solid (m.p. = 36–37 °C); ν_{max} (KBr)/cm^{-1} 3383 (NH), 1677 (C=O); δ_H (300 MHz; $CDCl_3$) 8.52–8.49 (1 H, m), 8.19–8.15 (1 H, m), 8.0 (1 H, br), 7.85–7.79 (1 H, m), 7.43–7.36 (1 H, m), 1.49 (9 H, s); δ_C (75 MHz; $CDCl_3$) 163.3, 150.7, 147.7, 137.3, 125.8, 121.6, 50.8, 28.7.

***N*-Cyclohexylbenzamide 2g:** According to the general procedure, the product was isolated as white solid (m.p. = 153–154 °C); ν_{max} (KBr)/cm^{-1} 3322 (NH), 1634 (C=O); δ_H (300 MHz; $CDCl_3$) 7.78–7.77 (2 H, m), 7.49–7.40 (3 H, m), 6.13 (1H, br), 4.03–3.93 (1H, m), 2.05–1.18 (10 H, m); δ_C (75 MHz; $CDCl_3$) 166.6, 135.0, 131.2, 128.4, 126.8, 48.6, 33.2, 25.5, 24.9.

***N*-Cyclohexyl-4-methoxybenzamide 2h:** According to the general procedure, the product was isolated as white solid (m.p. = 160–162 °C); ν_{max} (KBr)/cm^{-1} 3315 (NH), 1639 (C=O); δ_H (300 MHz; $CDCl_3$) 7.73 (2 H, d, *J* = 8.1 Hz), 6.92 (2 H, d, *J* = 8.1 Hz), 6.01 (1H, br), 4.10–3.85 (1H, m), 3.85 (3 H, s), 2.05–1.18 (10 H, m); δ_C (75 MHz; $CDCl_3$) 166.1, 161.9, 128.5, 127.3, 113.6, 55.3, 48.6, 33.2, 25.5, 24.9.

4-Chloro-*N*-Cyclohexylbenzamide 2i: According to the general procedure, the product was isolated as yellow solid (m.p. = 188–190 °C); ν_{max} (KBr)/cm^{-1} 3305 (NH), 1631 (C=O); δ_H (300 MHz; $CDCl_3$) 7.70 (2 H, d, *J* = 8.4 Hz), 7.38 (2 H, d, *J* = 8.4 Hz), 6.14 (1H, br), 4.05–3.88 (1H, m), 2.03–1.17 (10 H, m); δ_C (75 MHz; $CDCl_3$) 165.5, 137.3, 133.4, 128.6, 128.3, 48.8, 33.1, 25.5, 24.9.

***N*-Cyclohexyl-2-nitrobenzamide 2j:** According to the general procedure, the product was isolated as yellow solid (m.p. = 156–157 °C); ν_{max} (KBr)/cm^{-1} 3411 (NH), 1660 (C=O); δ_H (300 MHz; $CDCl_3$) 8.06 (2 H, m), 7.69–7.50 (3 H, m), 5.82 (1H, br), 3.99 (1H, m), 2.11–1.22 (10 H, m); δ_C (75 MHz; $CDCl_3$) 165.6, 146.3, 133.6, 133.3, 130.2, 124.4, 49.0, 32.7, 25.4, 24.8.

***N*-Isopropylbenzamide 2k:** According to the general procedure, the product was isolated as white solid (m.p. = 101–103 °C); ν_{max} (KBr)/cm^{-1} 3290 (NH), 1630 (C=O); δ_H (400 MHz; $CDCl_3$) 7.75–7.73 (2 H, m), 7.45–7.38 (3 H, m), 6.12 (1 H, br s), 4.32–4.20 (1 H, m), 1.23 (6 H, d, J = 6.8 Hz); δ_C (100 MHz; $CDCl_3$) 166.7, 134.9, 131.1, 128.4, 126.8, 41.8, 22.7.

***N*-Isopropyl-4-methoxybenzamide 2l:** According to the general procedure, the product was isolated as white solid (m.p. = 119–120 °C); ν_{max} (KBr)/cm^{-1} 3290 (NH), 1635 (C=O); δ_H (300 MHz; $CDCl_3$) 7.73 (2 H, d, J = 8.7 Hz), 6.90 (2 H, d, J = 8.7 Hz), 6.01 (1 H, br s), 4.31–4.24 (1 H, m), 3.84 (3 H, s), 1.25 (6 H, d, J = 6.6 Hz); δ_C (75 MHz; $CDCl_3$) 166.2, 161.9, 128.5, 127.2, 113.6, 55.3, 41.7, 22.8.

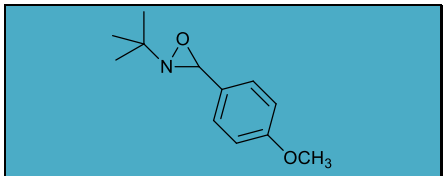
***N*-Isopropyl-4-nitrobenzamide 2m:** According to the general procedure, the product was isolated as yellow solid (m.p. = 150–152 °C); ν_{max} (KBr)/cm^{-1} 3275 (NH), 1630 (C=O); δ_H (300 MHz; $CDCl_3$) 8.25 (2 H, d, J = 8.4 Hz), 7.92 (2 H, d, J = 8.7 Hz), 6.33 (1 H, br s), 4.34–4.23 (1 H, m), 1.28 (6 H, d, J = 6.6 Hz); δ_C (75 MHz; $CDCl_3$) 164.7, 149.3, 140.5, 128.1, 123.6, 42.4, 22.6.

***N*-(*sec*-Butyl)benzamide 2n:** According to the general procedure, the product was isolated as white solid (m.p. = 87–90 °C); ν_{max} (KBr)/cm^{-1} 3285 (NH), 1632 (C=O); δ_H (300 MHz; $CDCl_3$) 7.77 (2 H, m), 7.48–7.40 (3 H, m), 6.14 (1 H, br s), 4.19–4.05 (1 H, m), 1.62–1.53 (2 H, m), 1.22 (3 H, d, J = 6.3 Hz), 0.96 (3 H, t, J = 7.2 Hz); δ_C (75 MHz; $CDCl_3$) 166.9, 135.0, 131.2, 128.4, 126.8, 47.1, 29.7, 20.4, 10.4.

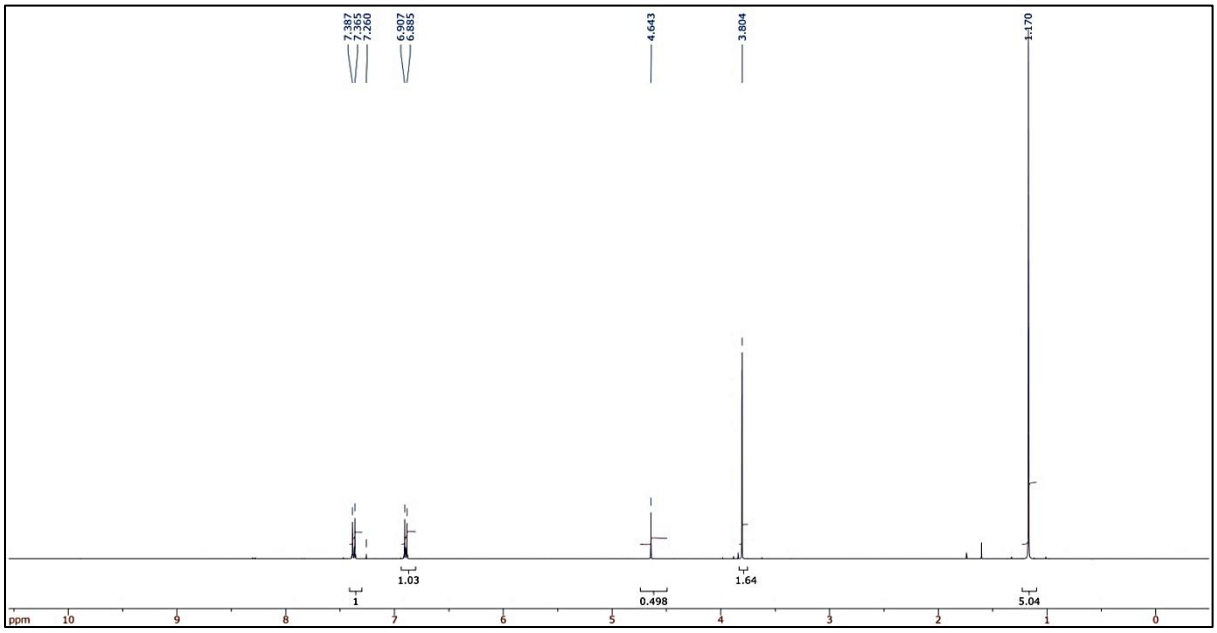
***N*-(3-Methylbutan-2yl)benzamide 2o:** According to the general procedure, the product was isolated as white solid (m.p. = 73–75 °C); ν_{max} (KBr)/cm^{-1} 3290 (NH), 1635 (C=O); δ_H (300 MHz; $CDCl_3$) 7.78–7.75 (2 H, m), 7.49–7.39 (3 H, m), 6.11 (1 H, br s), 4.14–4.02 (1 H, m), 0.98 (3 H, d, J = 6.9 Hz), 0.96 (3 H, d, J = 6.9 Hz); δ_C (75 MHz; $CDCl_3$) 166.8, 135.2, 131.1, 128.4, 126.7, 50.4, 33.1, 18.6, 18.5, 17.6.

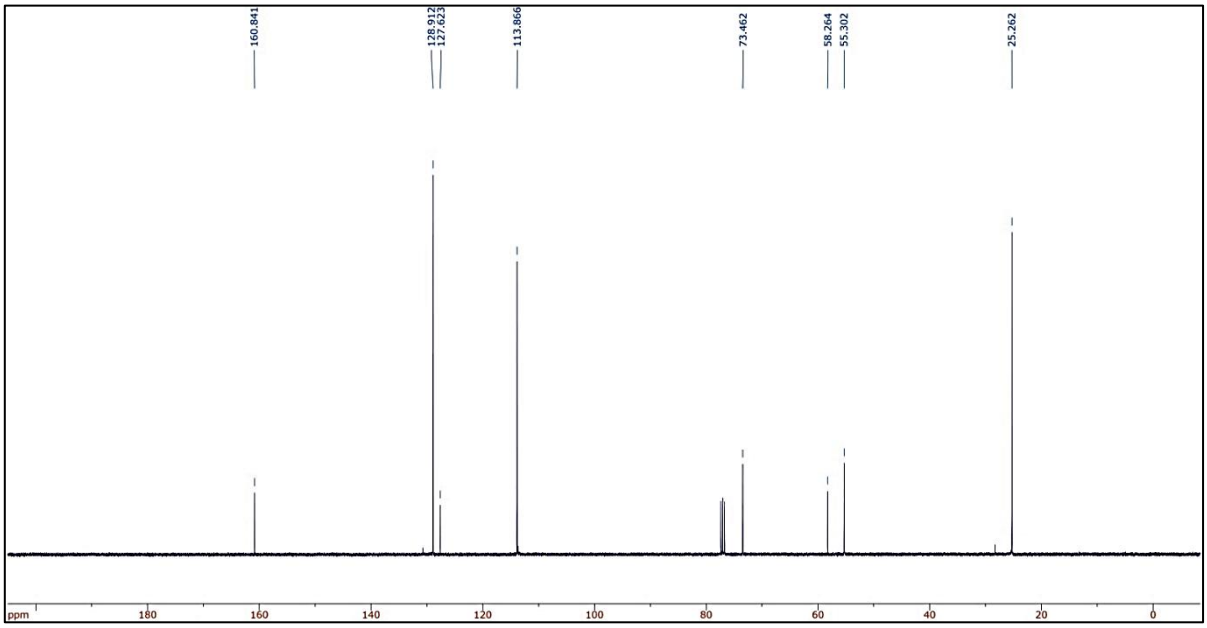
***N*-(*n*-Butyl)benzamide 2p:** The product was recrystallized in *n*-hexane and isolated as white solid (m.p. = 39–41 °C); ν_{max} (KBr)/cm^{-1} 3290 (NH), 1635 (C=O); δ_H (300 MHz; $CDCl_3$) 7.77 (2 H, m), 7.48–7.40 (3 H, m), 6.47 (1 H, br s), 3.47–3.41 (2 H, m), 1.62–1.34 (4 H, m), 0.94 (3 H, t, *J* = 6.9 Hz); δ_C (75 MHz; $CDCl_3$) 167.7, 134.7, 131.2, 128.4, 126.8, 39.8, 31.7, 20.1, 13.8.

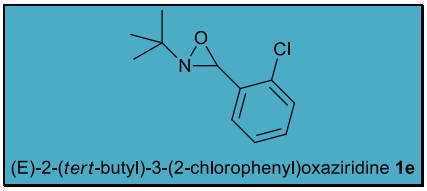
***N*-(*n*-Propyl)benzamide 2q:** The product was recrystallized in *n*-hexane and isolated as white solid (m.p. = 83–84 °C); ν_{max} (KBr)/cm^{-1} 3270 (NH), 1630 (C=O); δ_H (300 MHz; $CDCl_3$) 7.78 (2 H, d, *J* = 7.5 Hz), 7.50–7.41 (3 H, m), 6.31 (1 H, br s), 3.43 (2 H, q, *J* = 6.6 Hz), 1.65 (2 H, q, *J* = 7.2 Hz), 1.00 (3 H, t, *J* = 7.2 Hz); δ_C (75 MHz; $CDCl_3$) 167.6, 134.8, 131.2, 128.5, 126.8, 41.7, 22.9, 11.4.



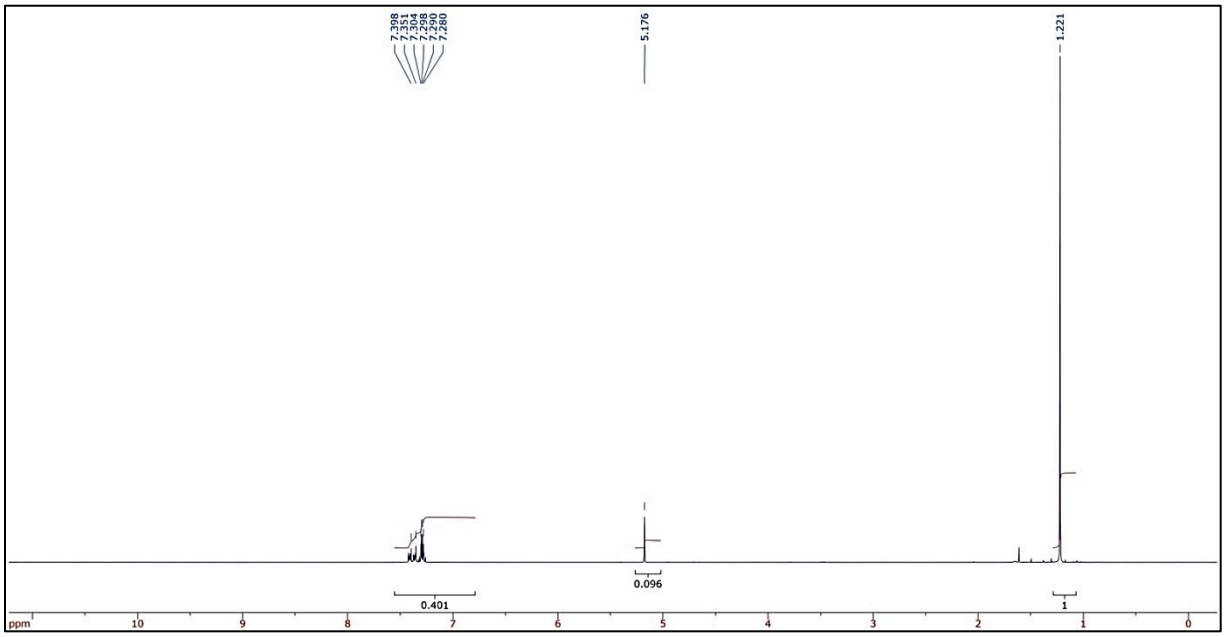
(E)-2-(*tert*-butyl)-3-(4-methoxyphenyl)oxaziridine **1b**

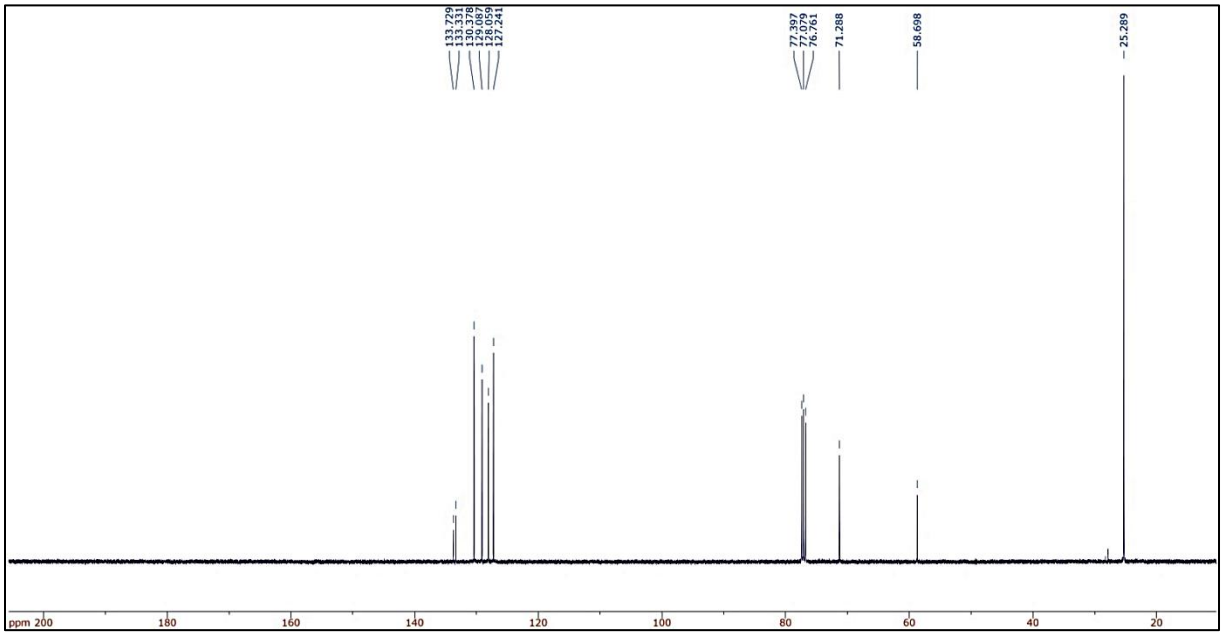


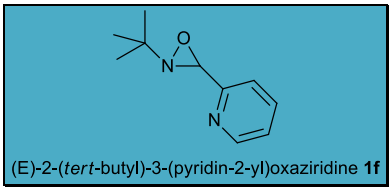




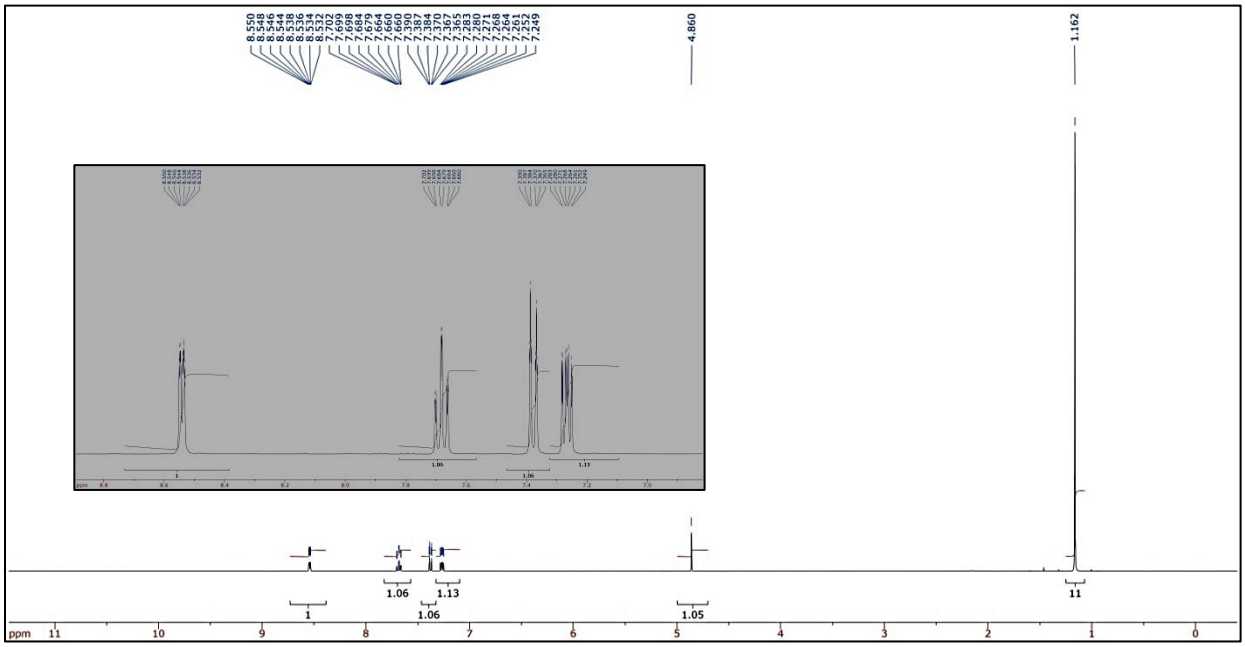
(E)-2-(*tert*-butyl)-3-(2-chlorophenyl)oxaziridine **1e**

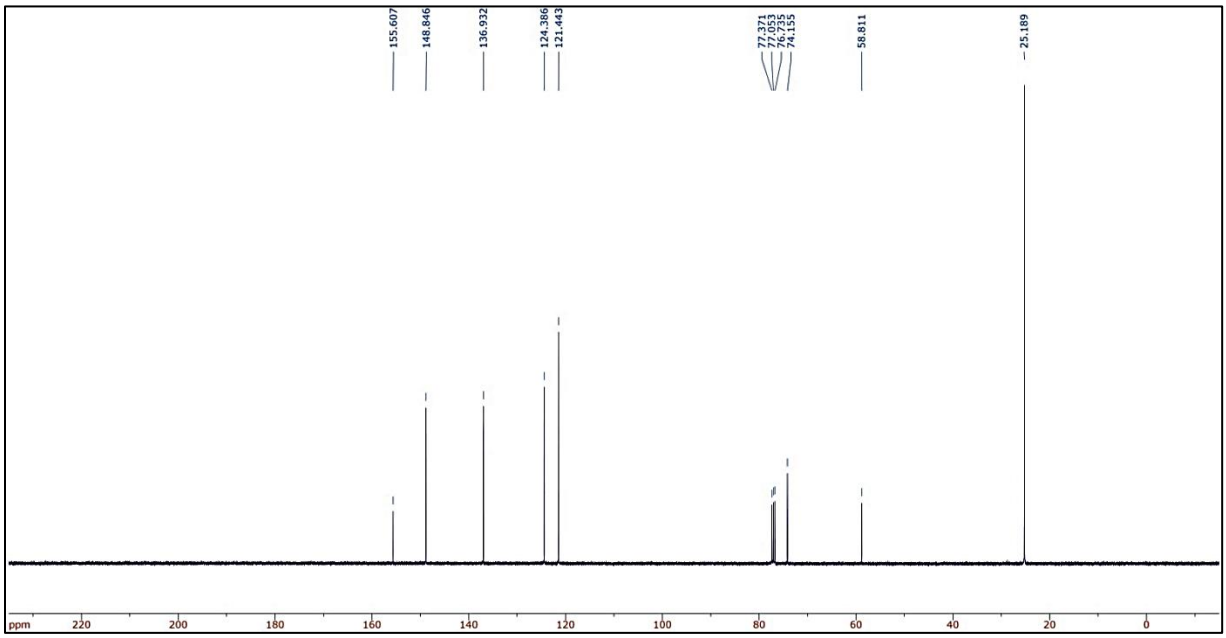


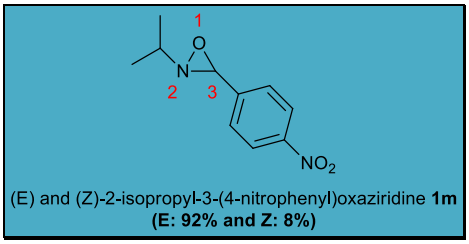




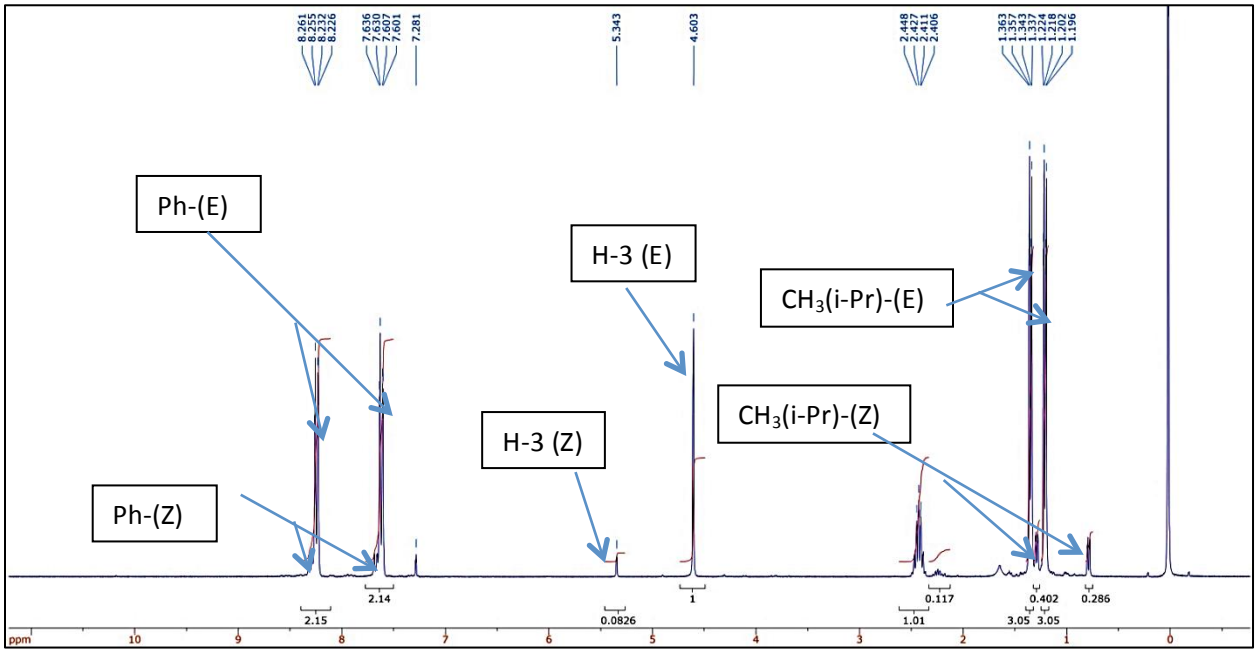
(E)-2-(*tert*-butyl)-3-(pyridin-2-yl)oxaziridine **1f**

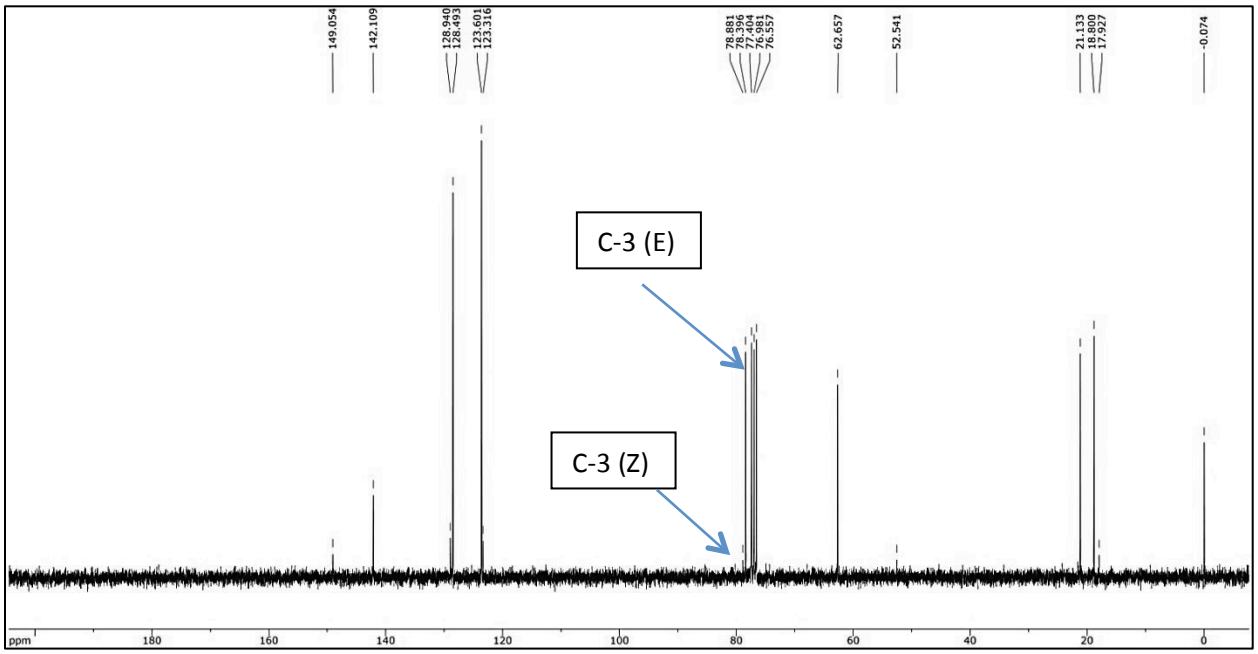


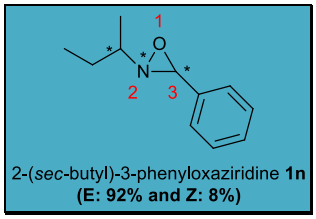




(E) and (Z)-2-isopropyl-3-(4-nitrophenyl)oxaziridine **1m**
(E: 92% and Z: 8%)



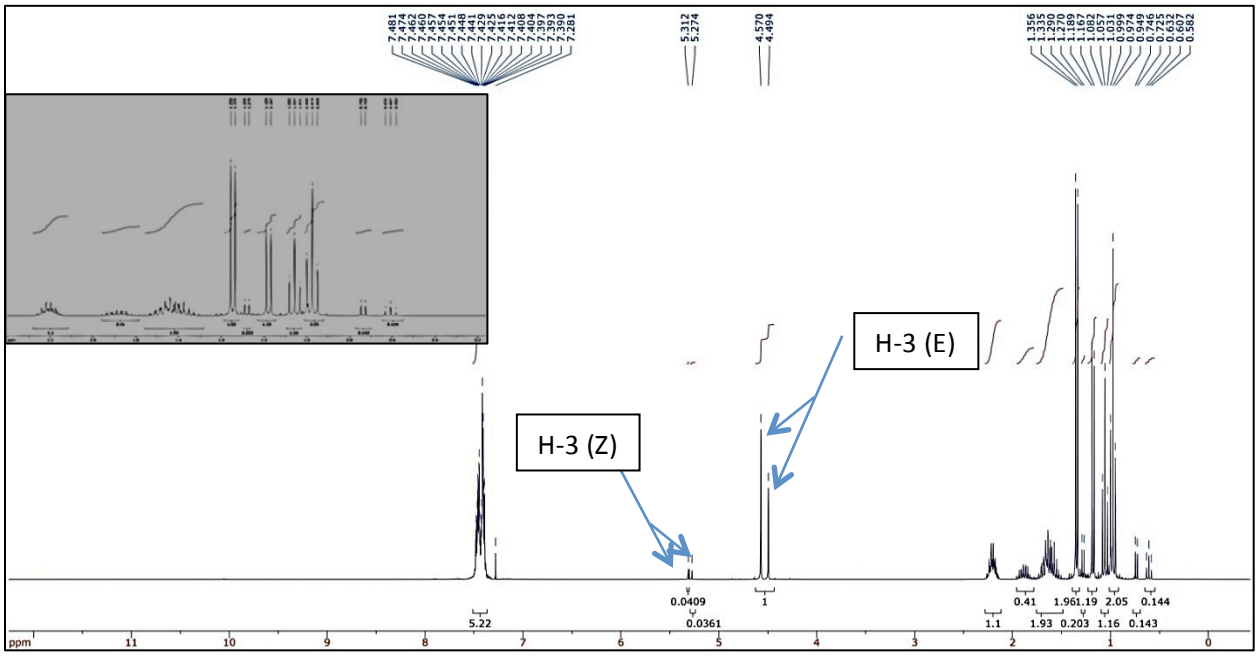


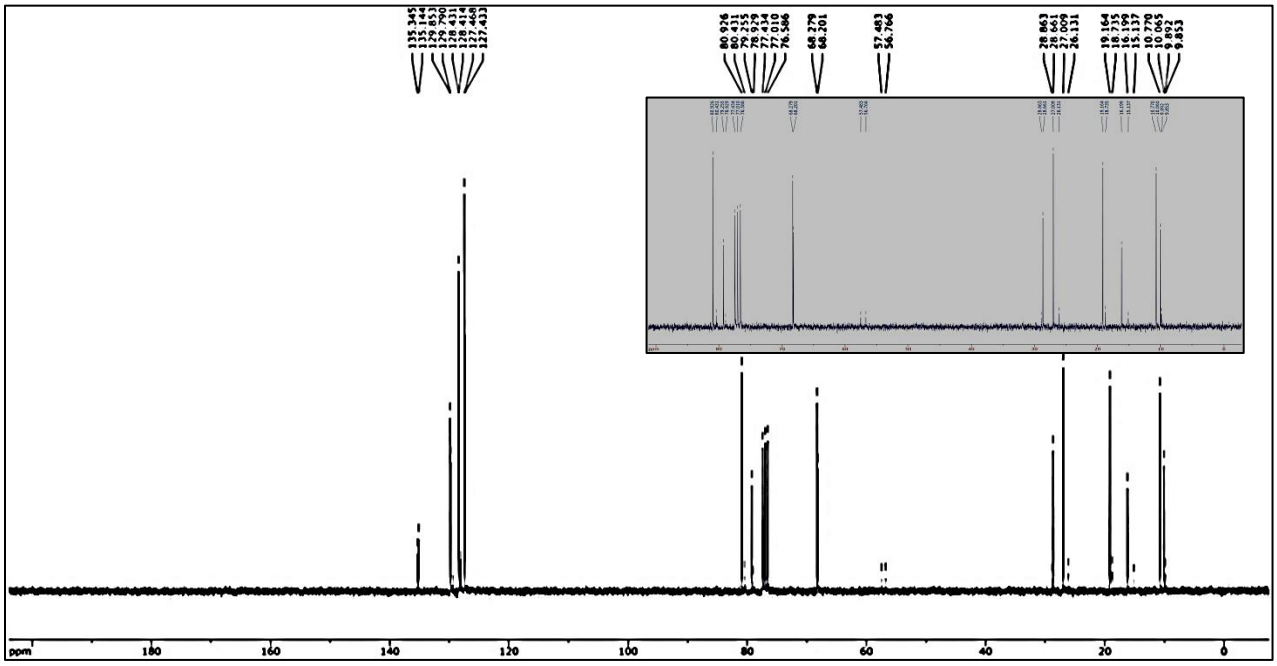


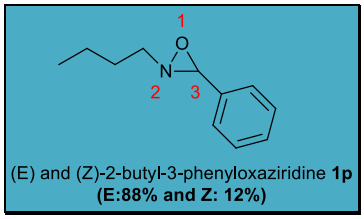
2-(*sec*-butyl)-3-phenyloxaziridine **1n**
(E: 92% and Z: 8%)

(E) = [(R,R,R)+(S,S,S)]+[(R,S,S)+(S,R,R)]

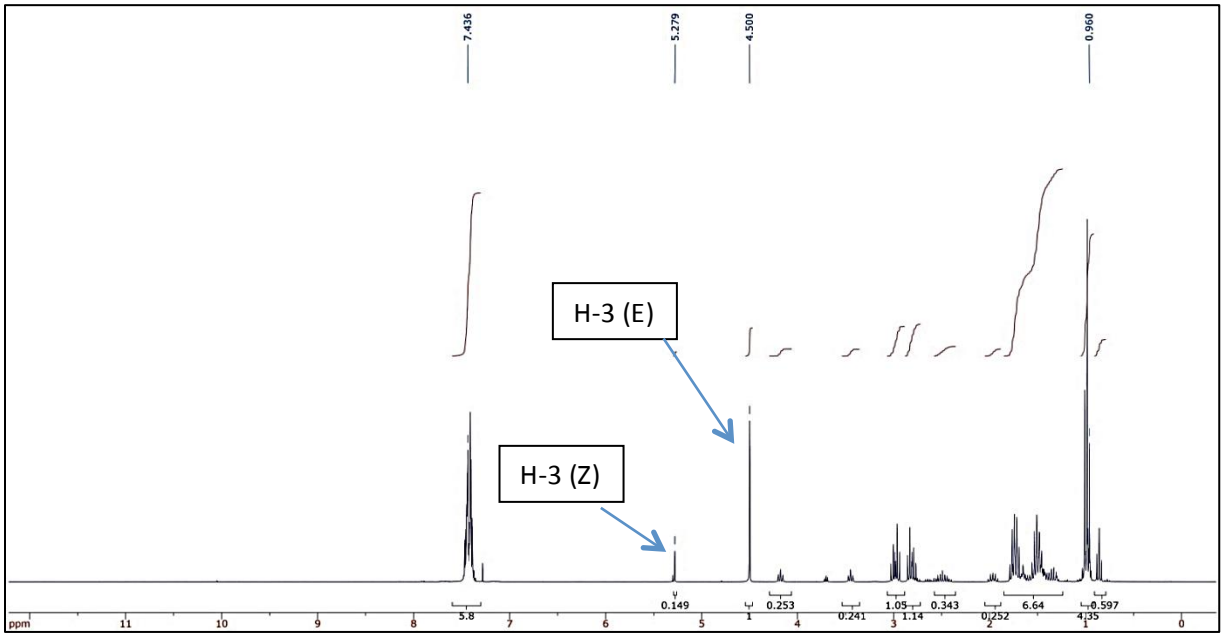
(Z) = [(R,S,R)+(S,R,S)]+[(R,R,S)+(S,S,R)]

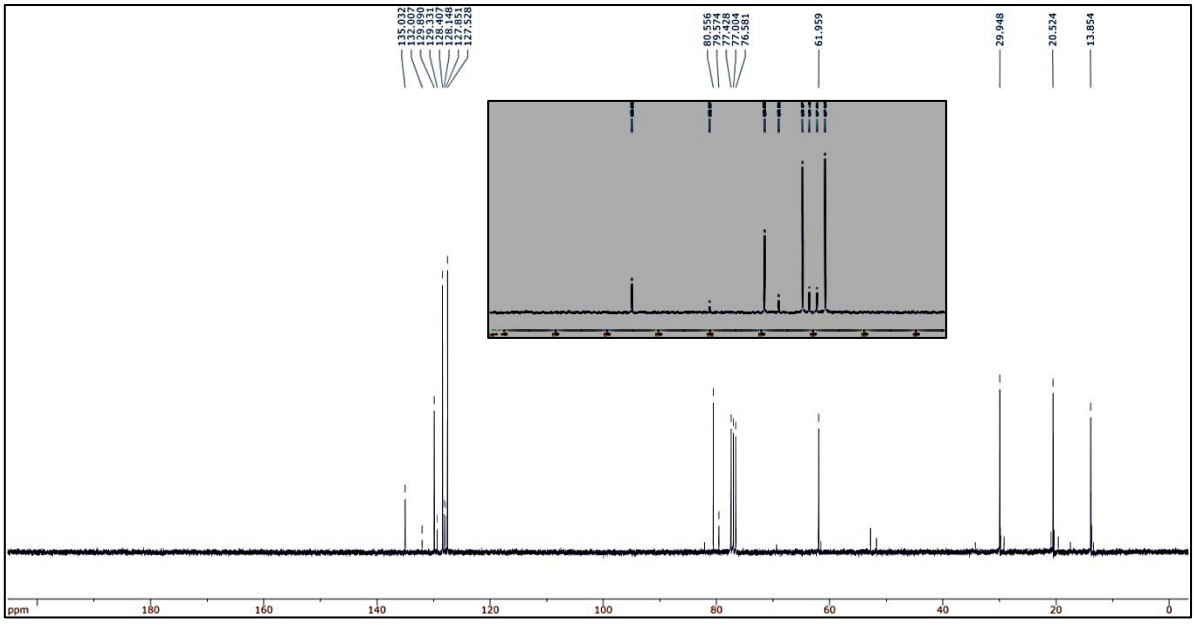


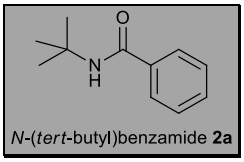




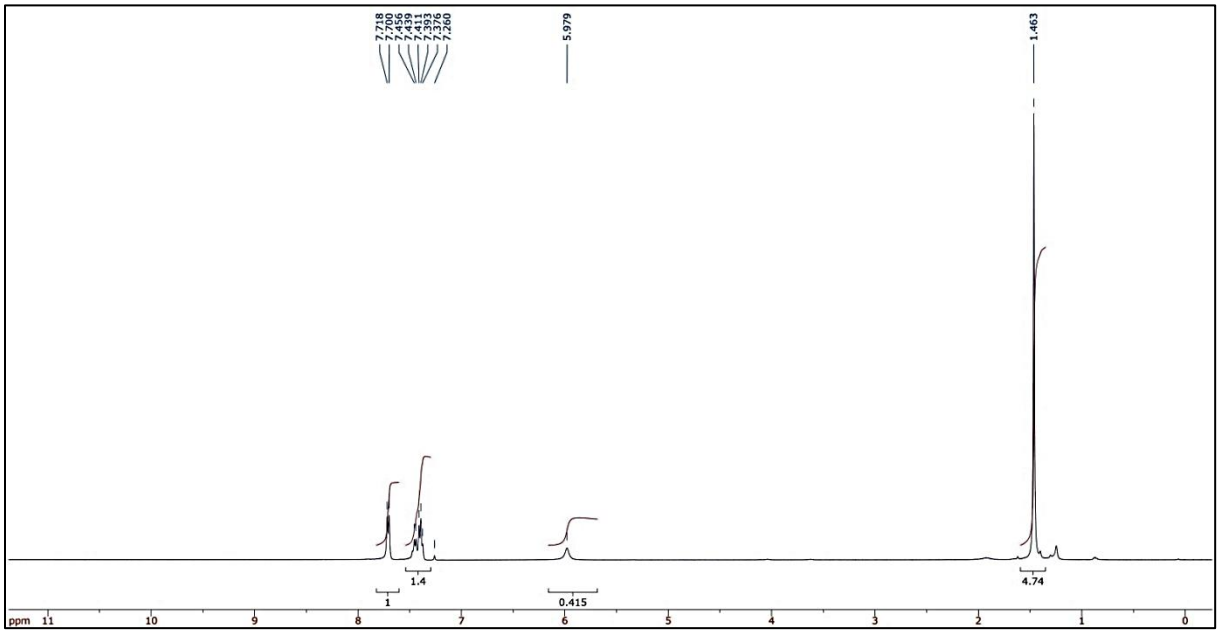
(E) and (Z)-2-butyl-3-phenyloxaziridine **1p**
(E:88% and Z: 12%)

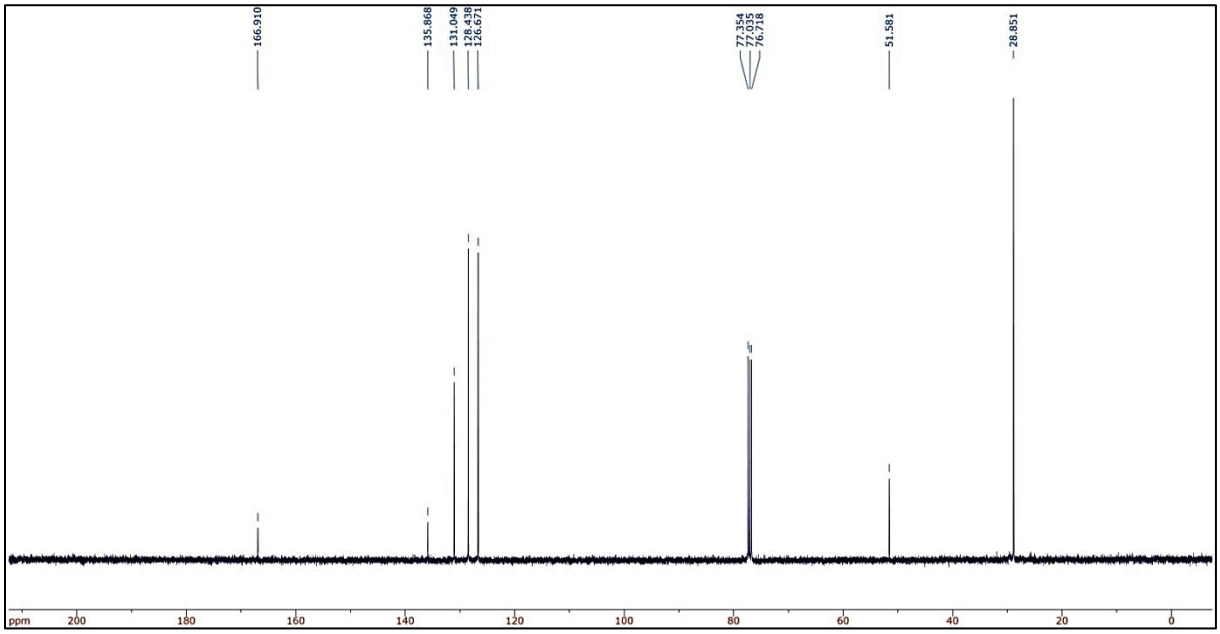


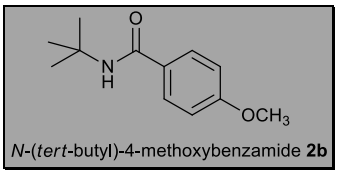




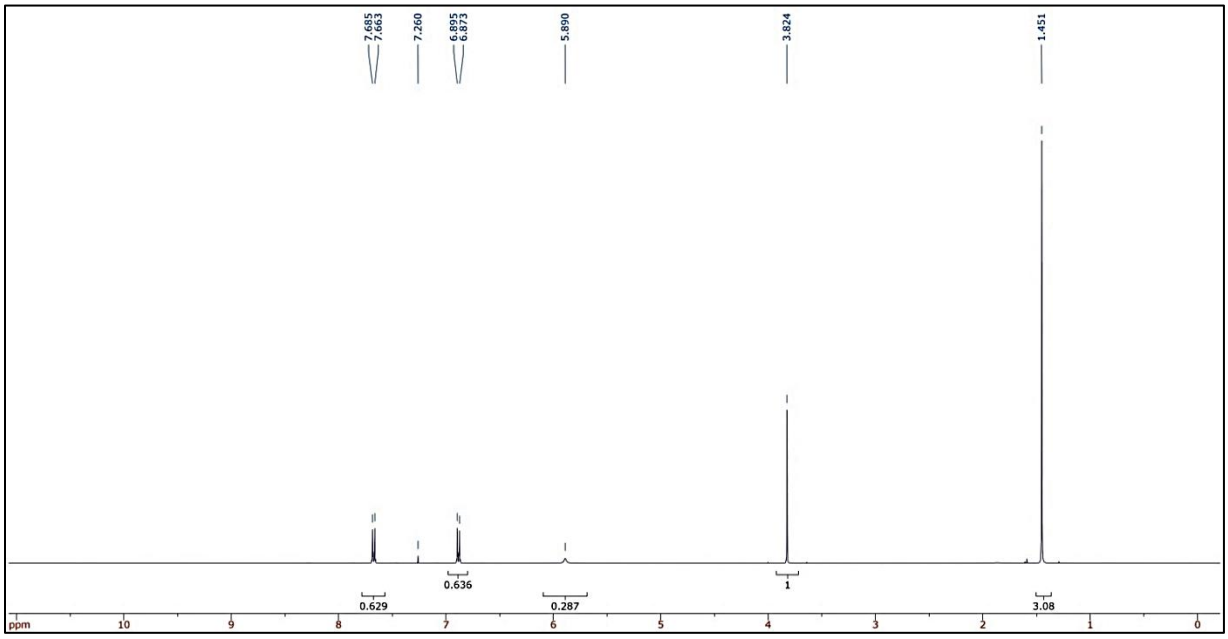
N-(*tert*-butyl)benzamide **2a**

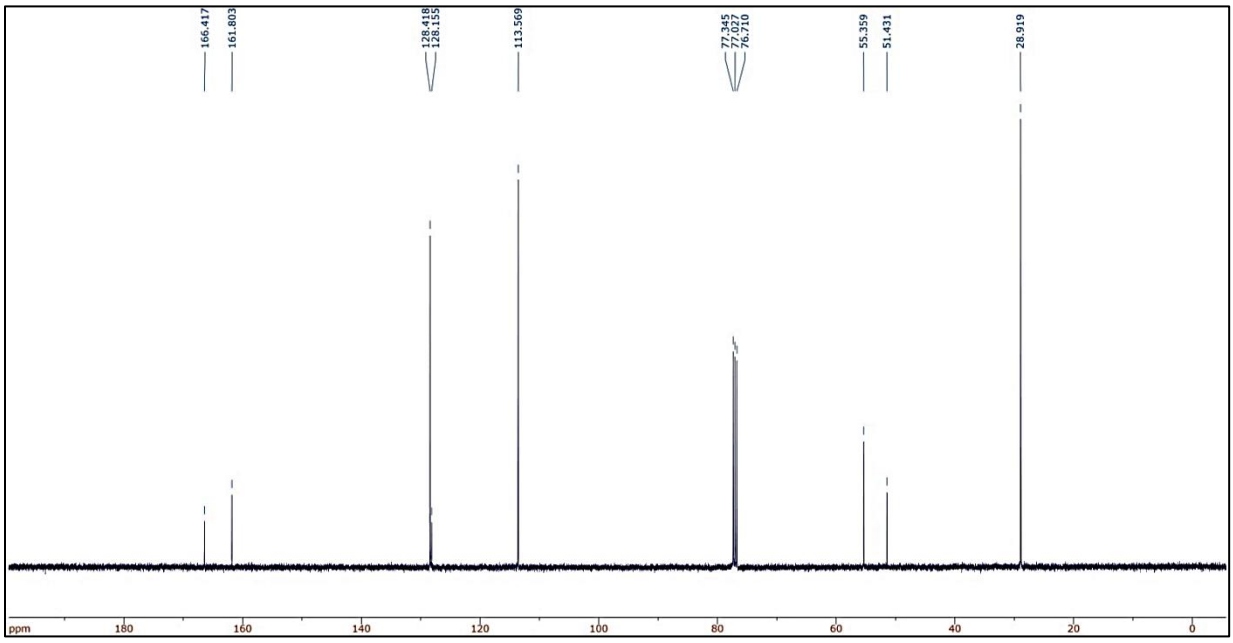


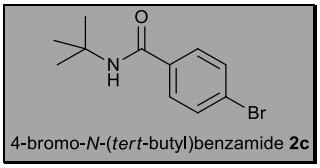




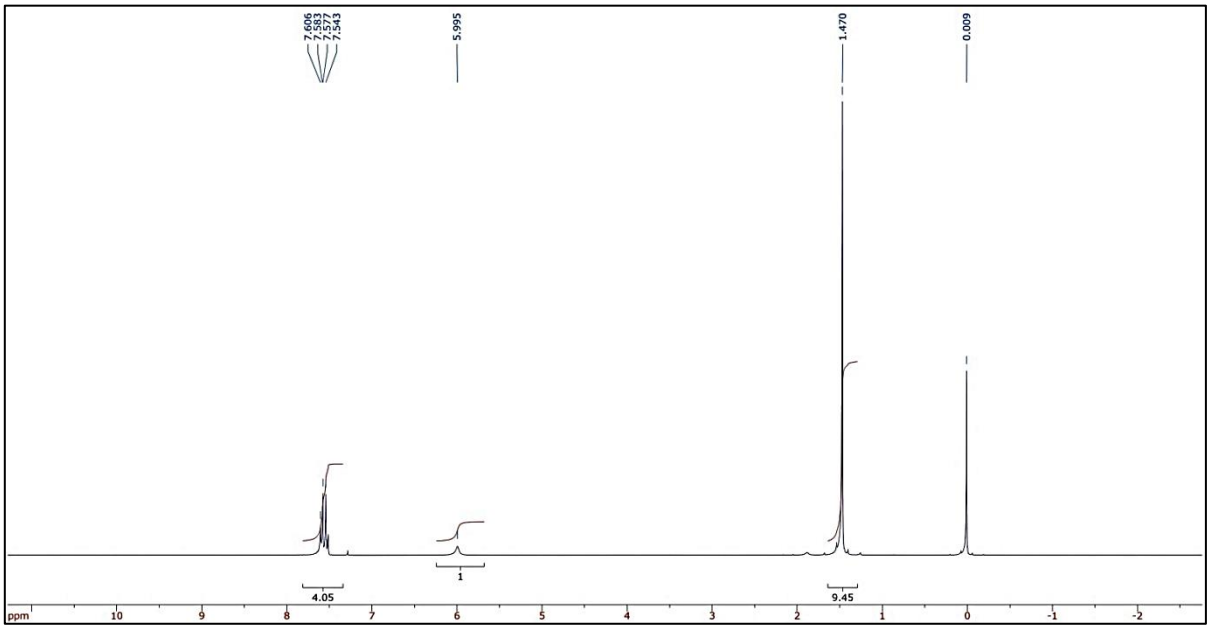
N-(*tert*-butyl)-4-methoxybenzamide **2b**

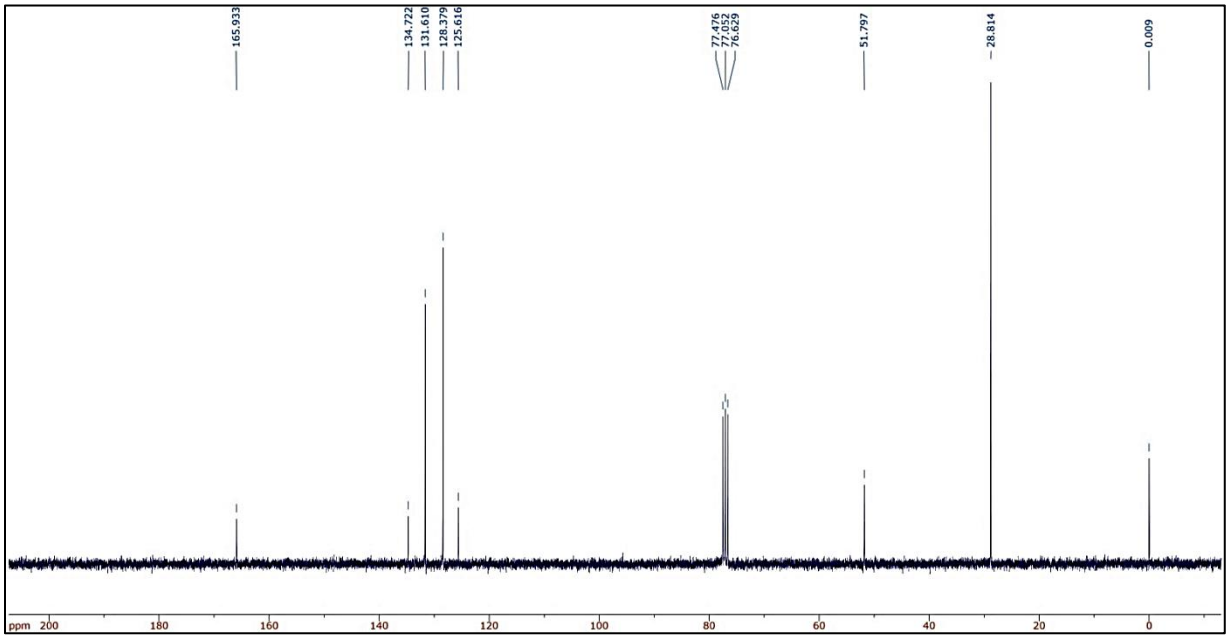


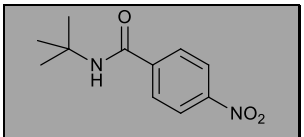




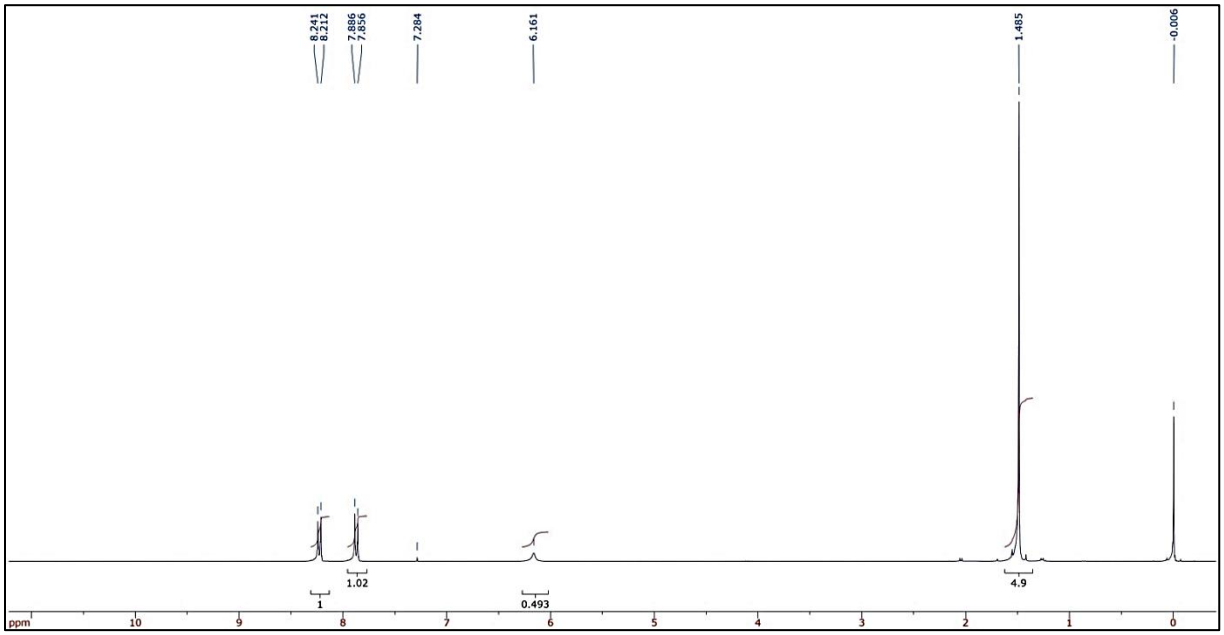
4-bromo-*N*-(*tert*-butyl)benzamide **2c**

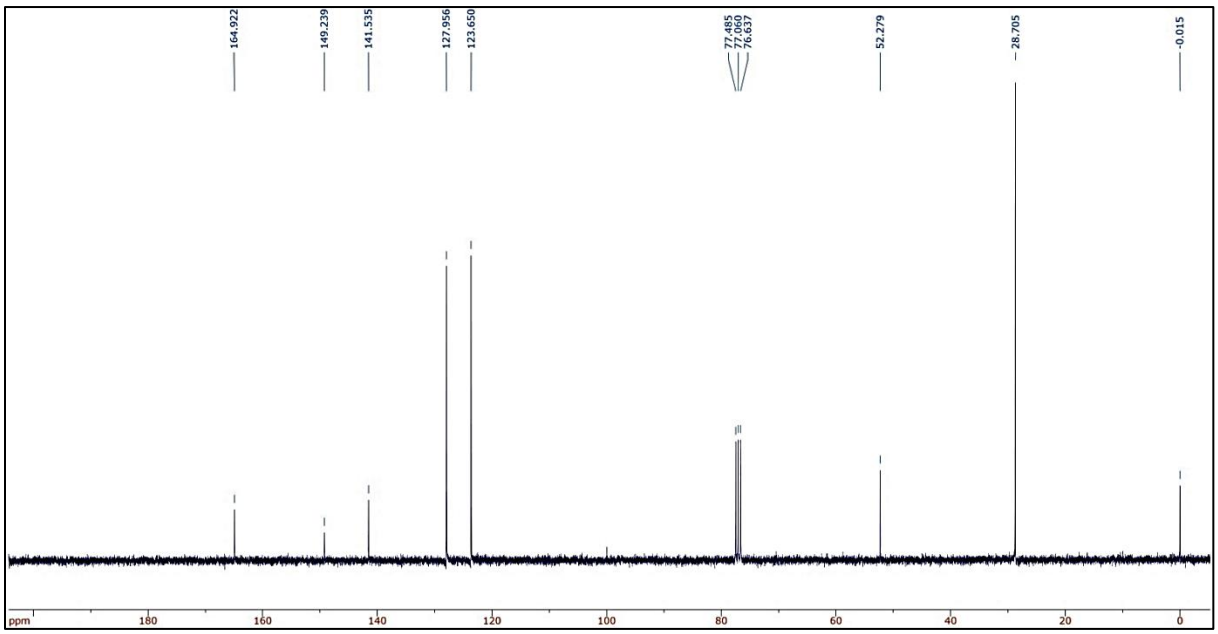


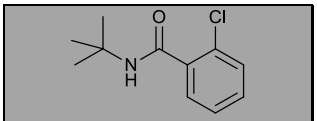




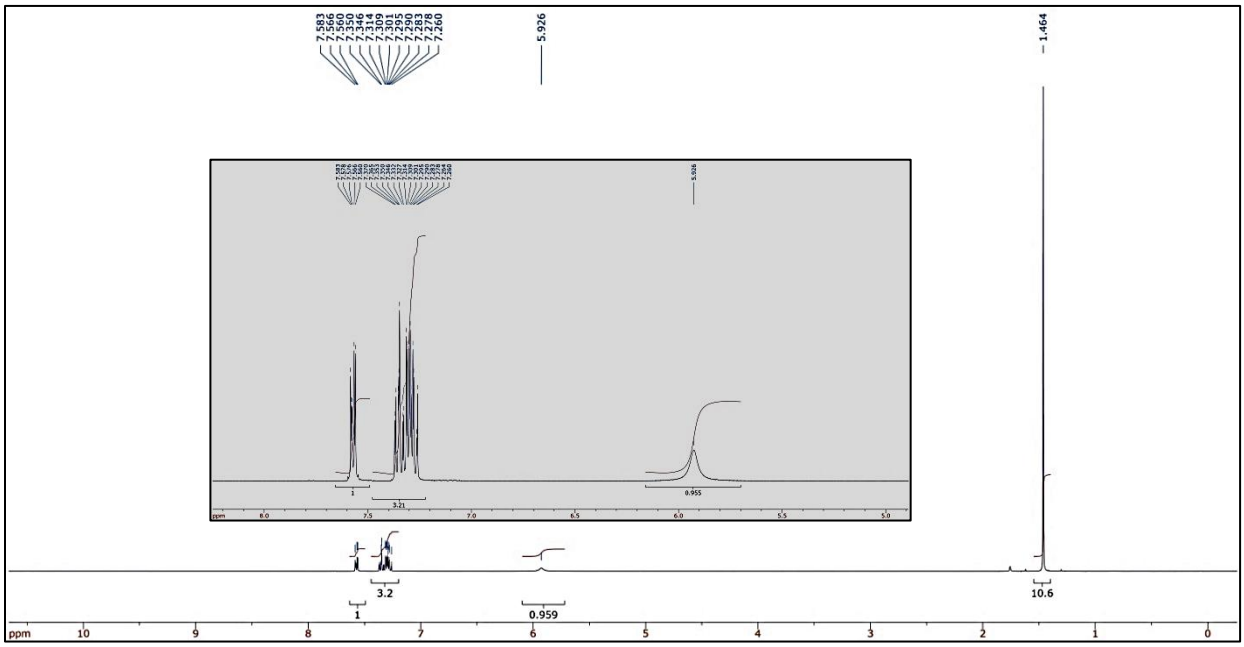
N-(*tert*-butyl)-4-nitrobenzamide **2d**

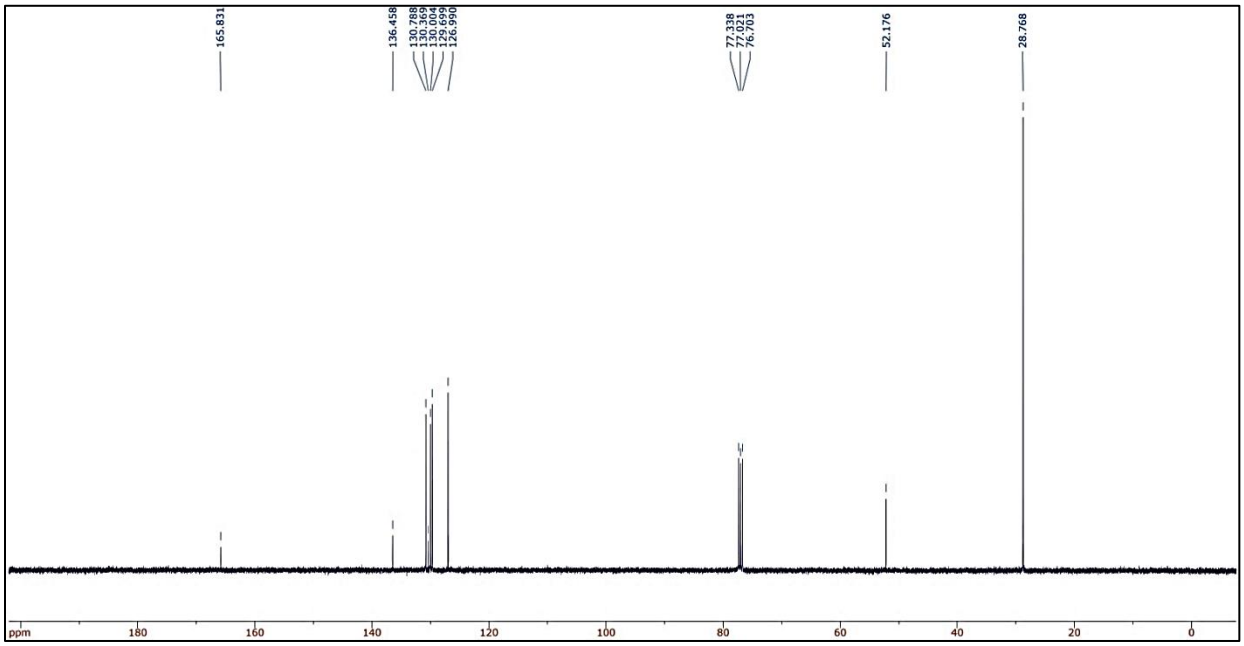


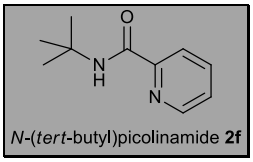




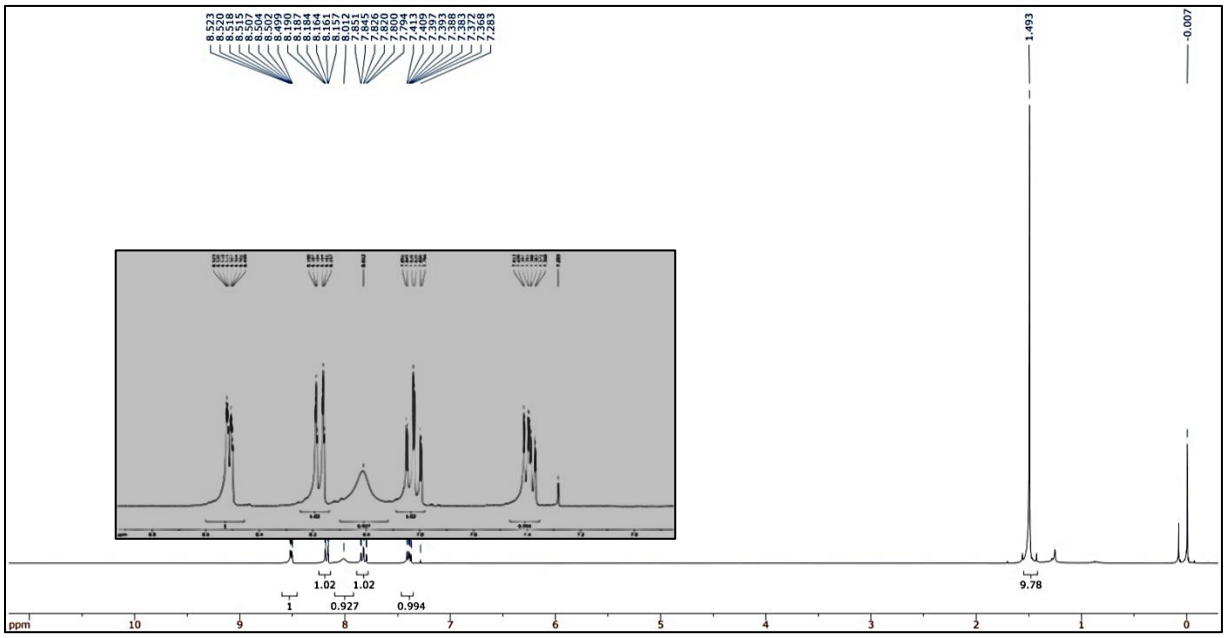
N-(*tert*-butyl)-2-chlorobenzamide **2e**

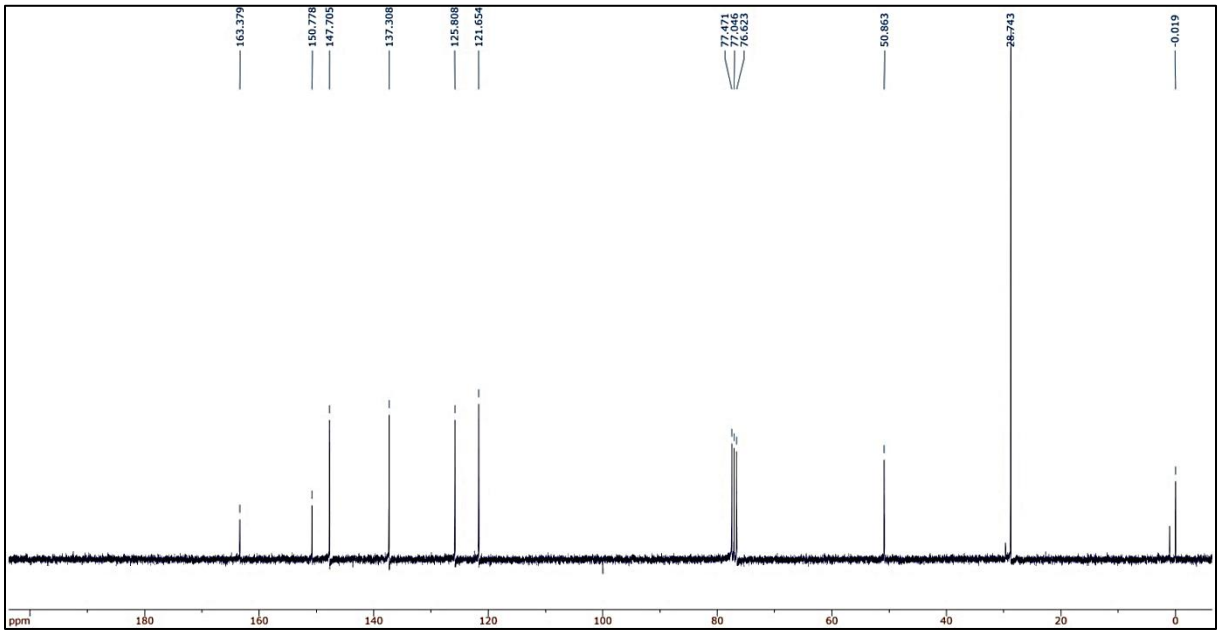


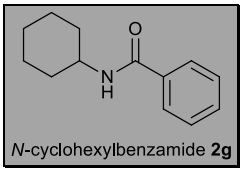




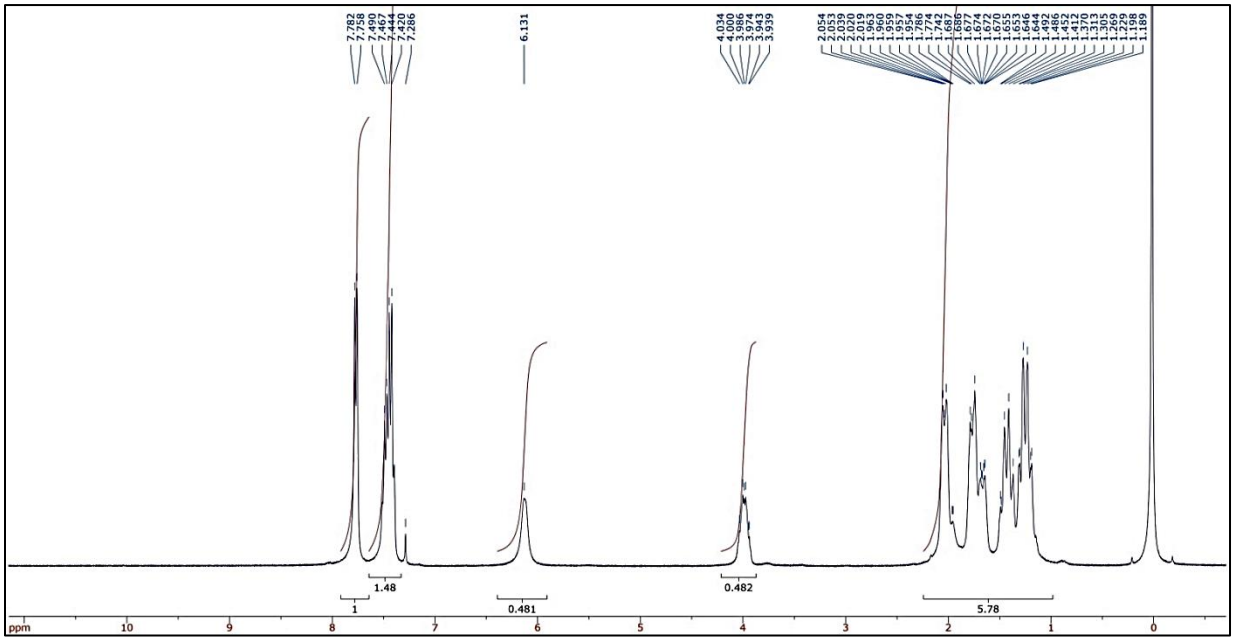
N-(*tert*-butyl)picolinamide **2f**

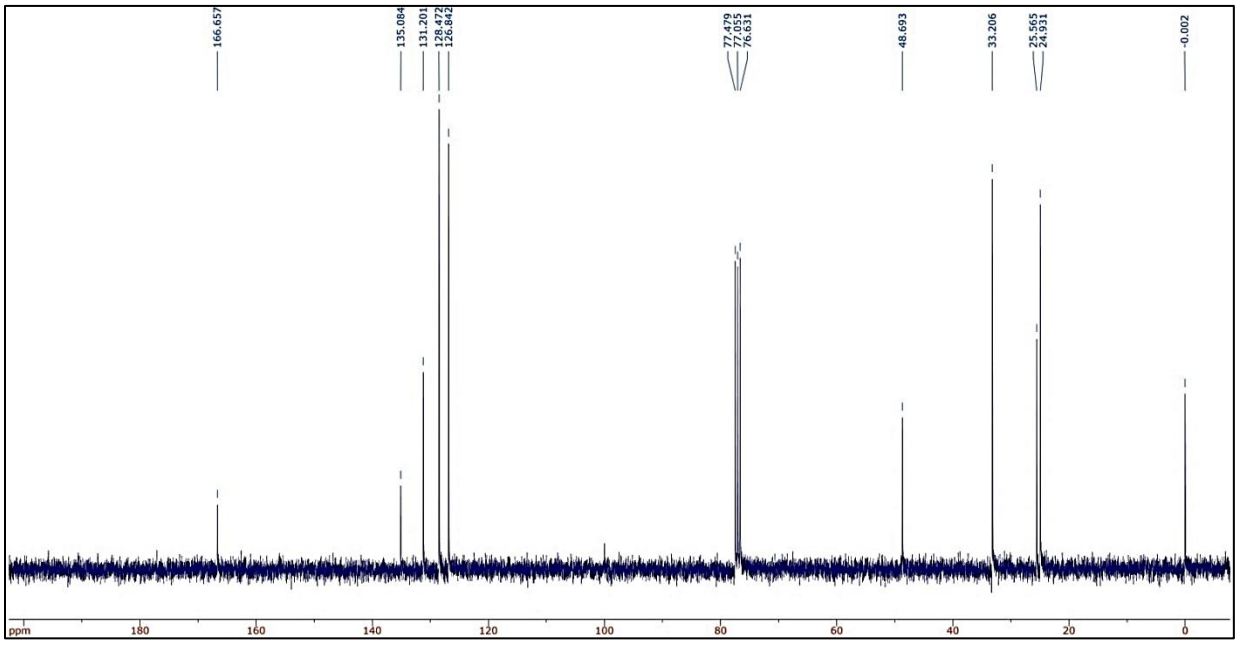


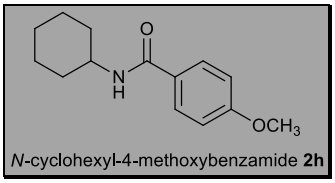




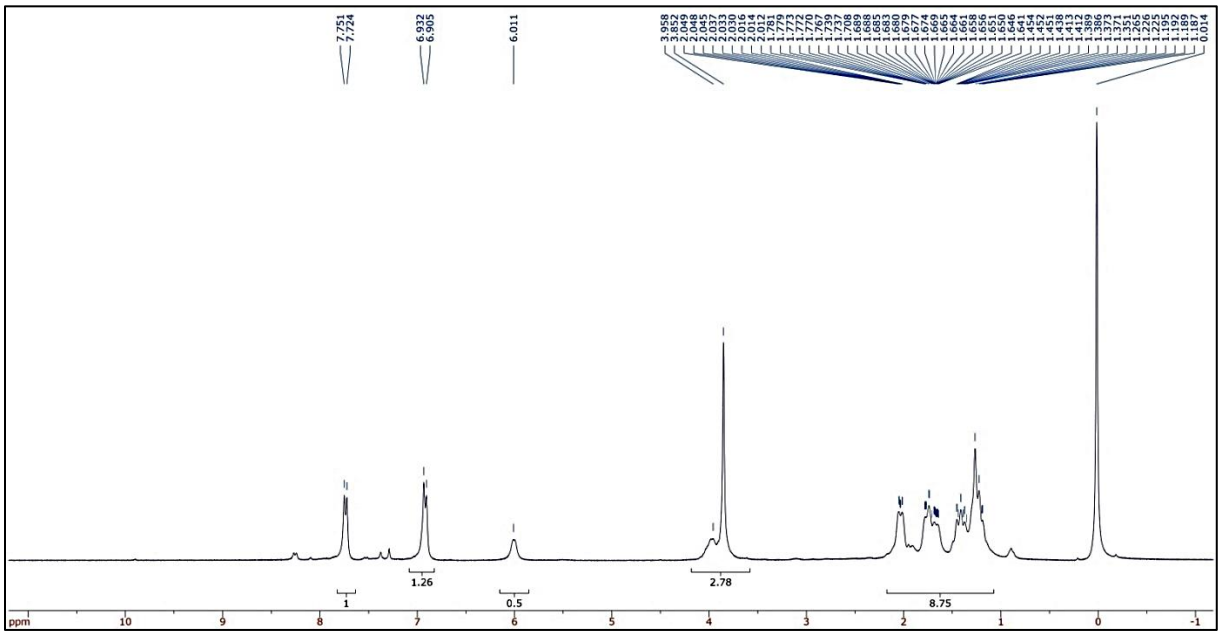
N-cyclohexylbenzamide **2g**

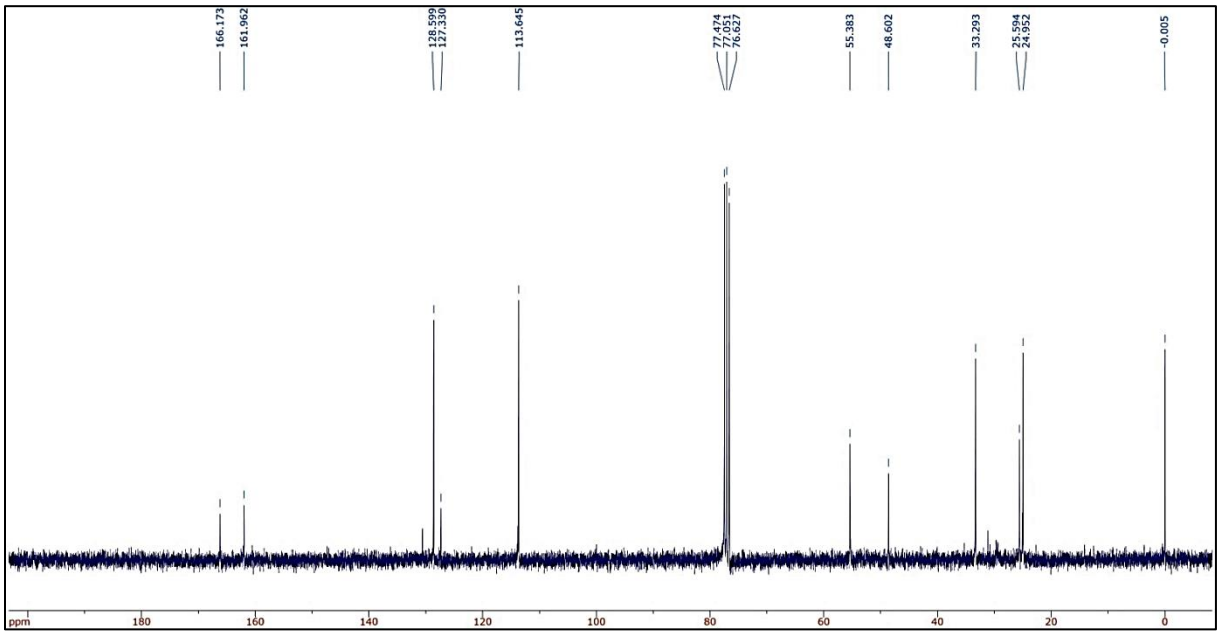


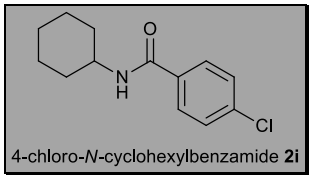




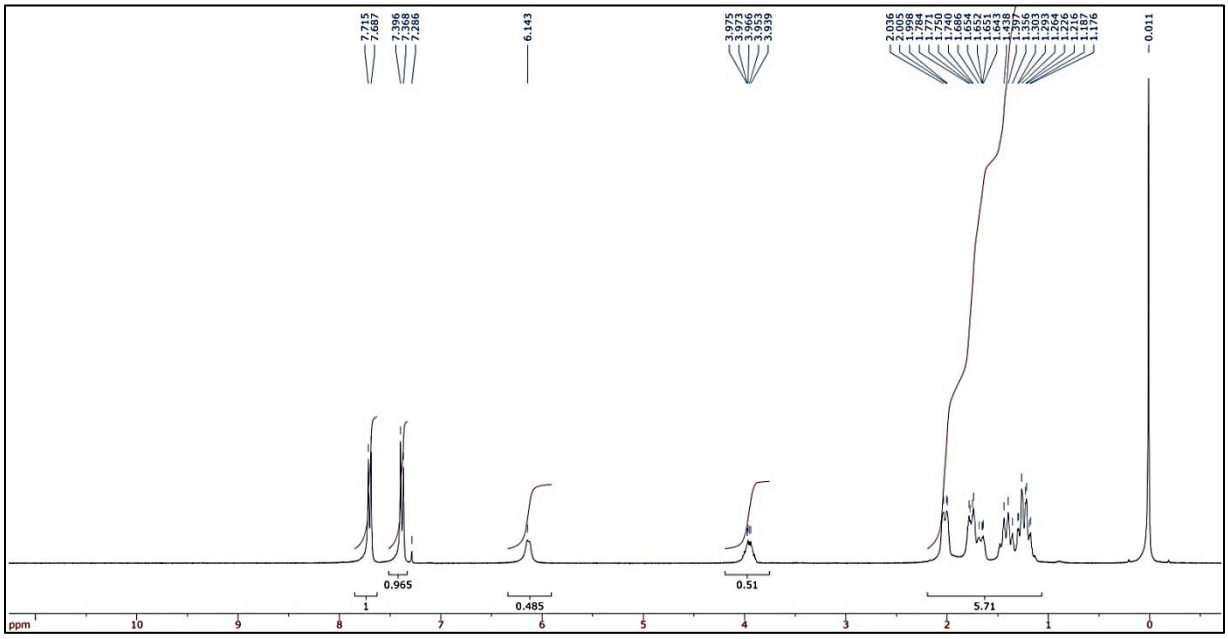
N-cyclohexyl-4-methoxybenzamide **2h**

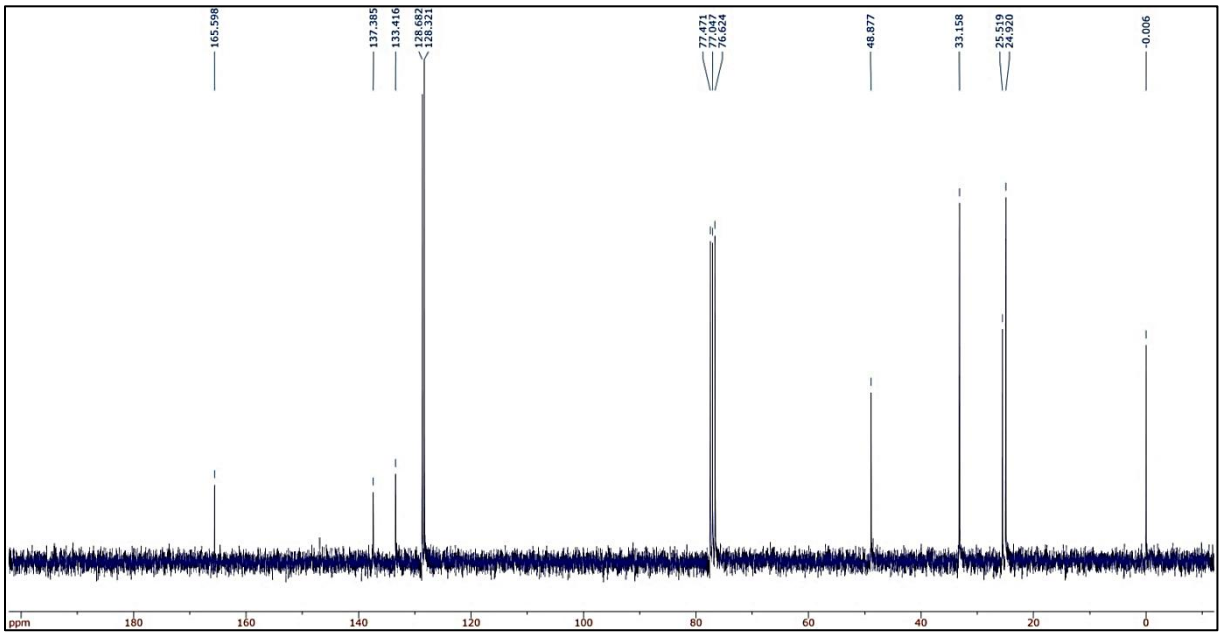


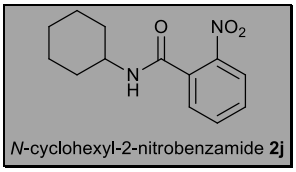




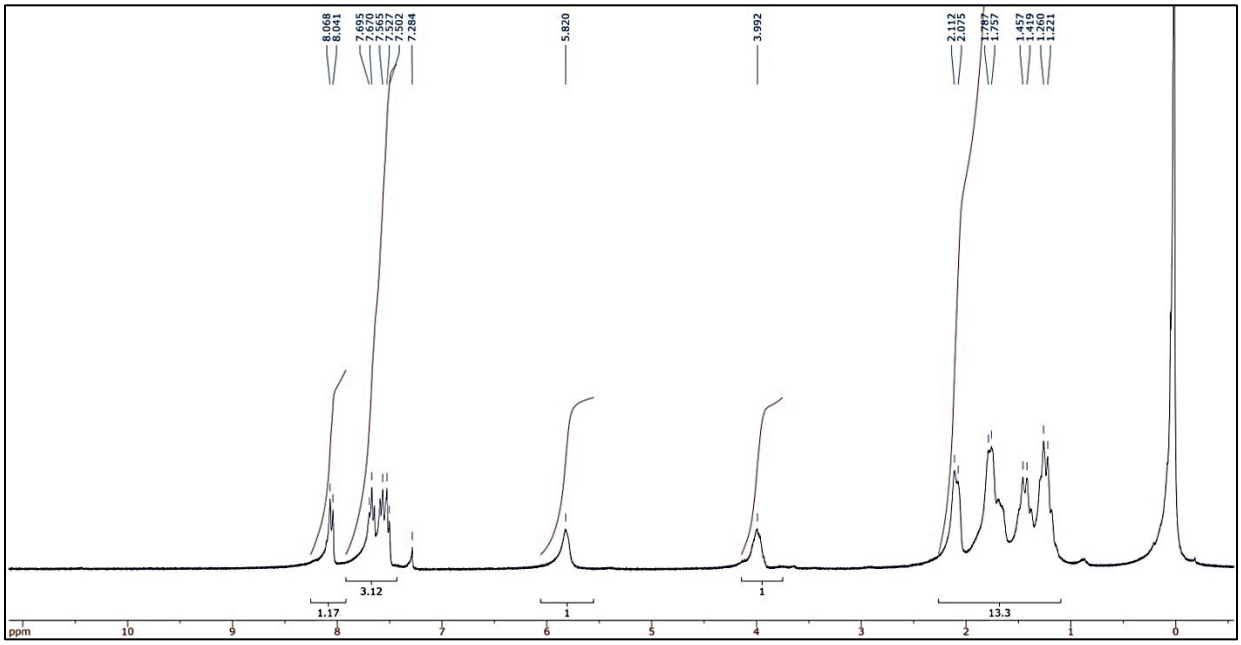
4-chloro-*N*-cyclohexylbenzamide **2i**

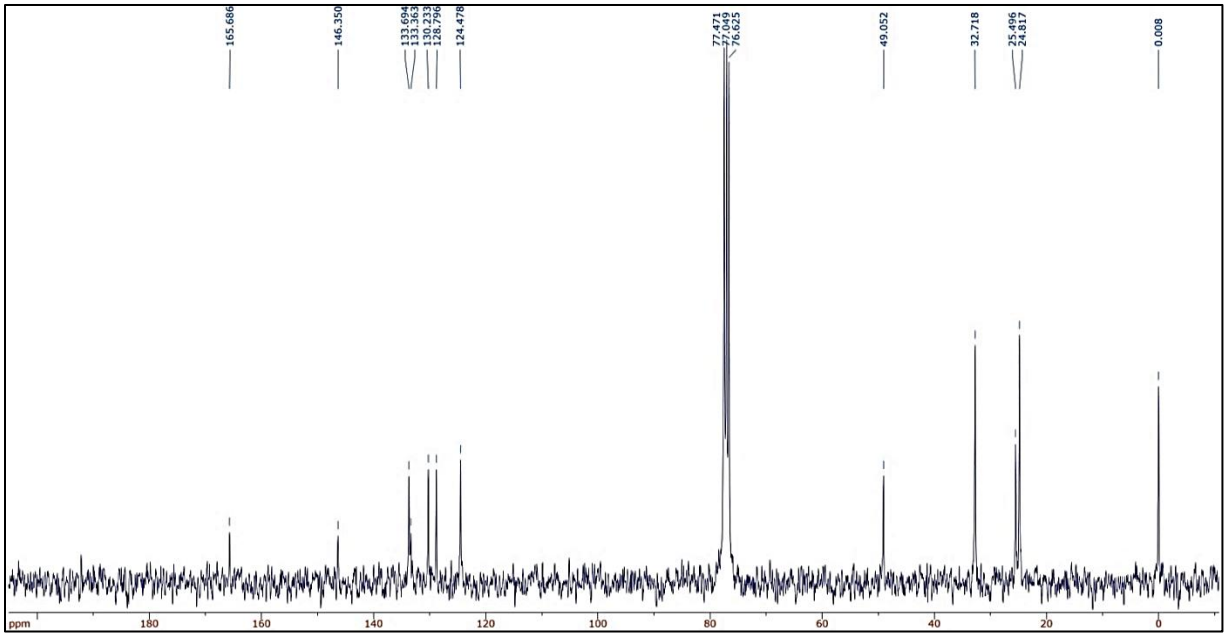


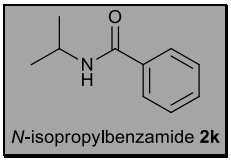




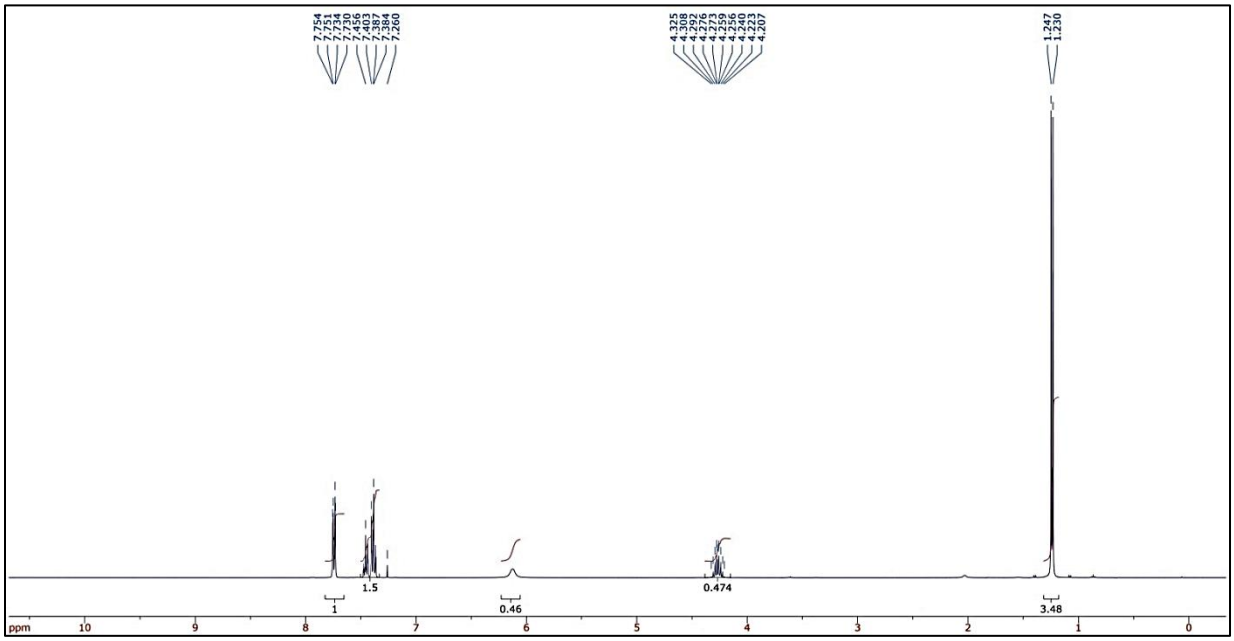
N-cyclohexyl-2-nitrobenzamide **2j**

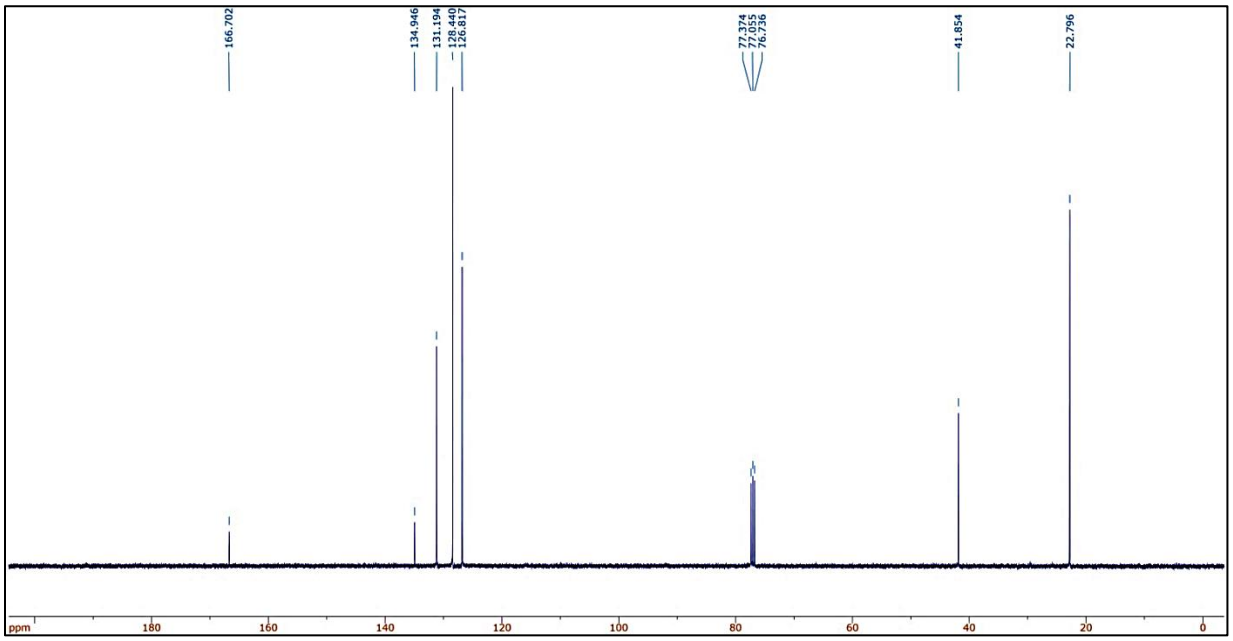


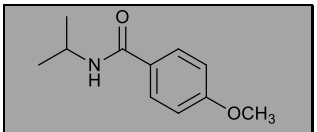




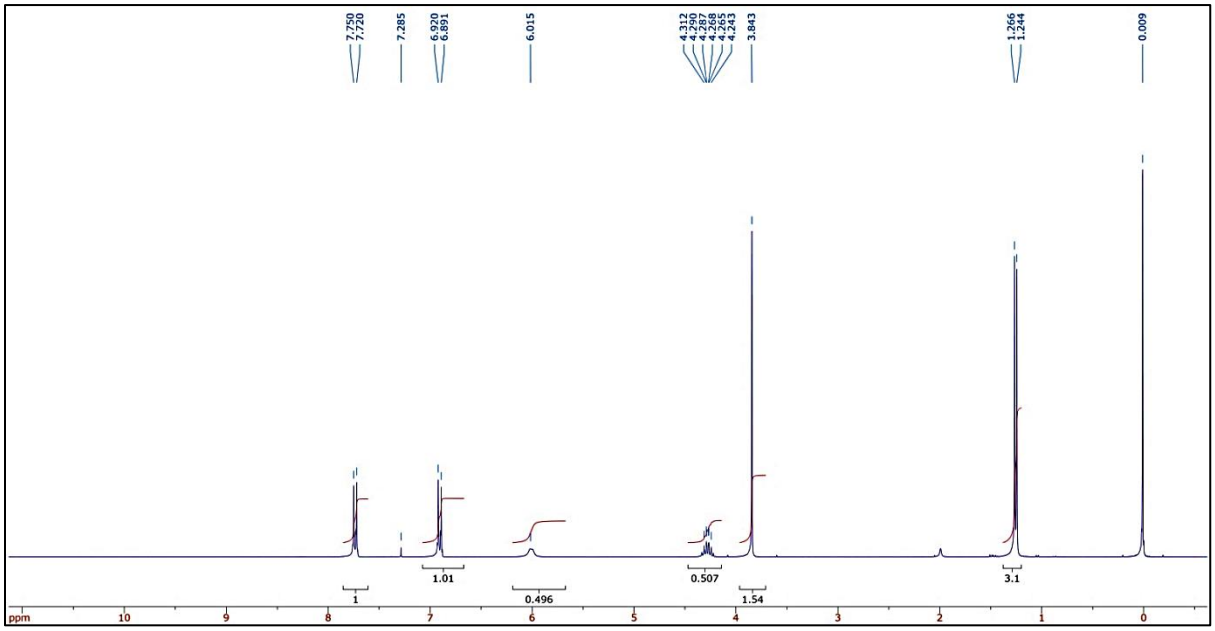
N-isopropylbenzamide **2k**

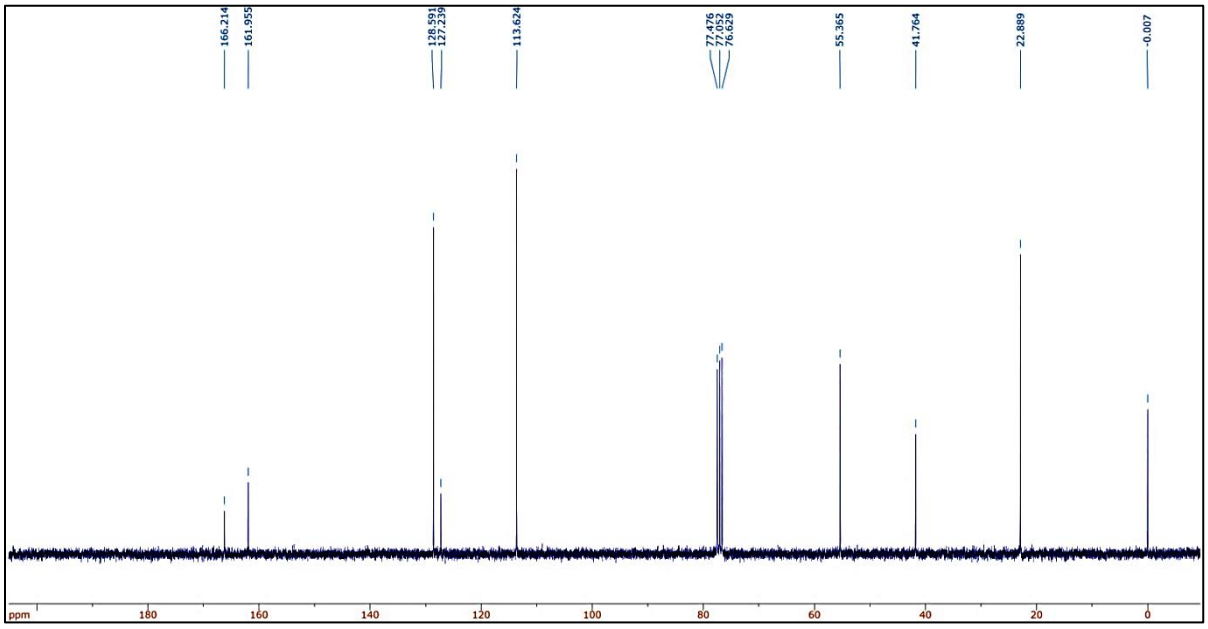


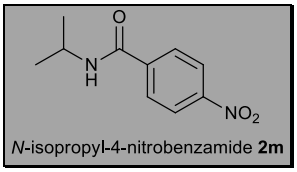




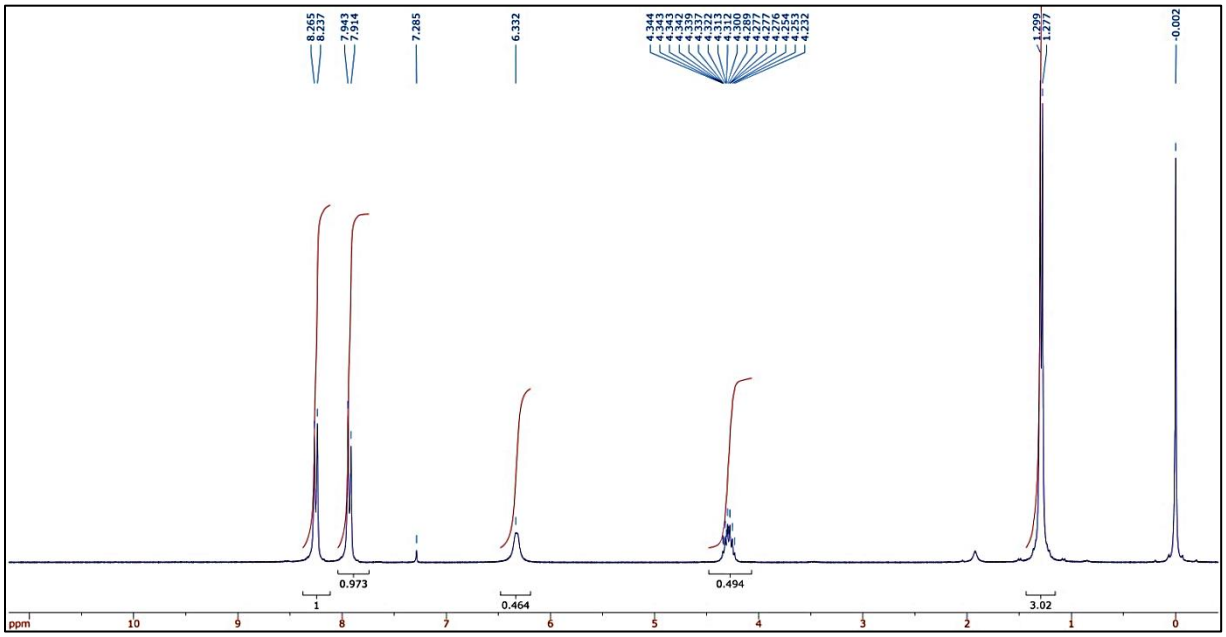
N-isopropyl-4-methoxybenzamide **2l**

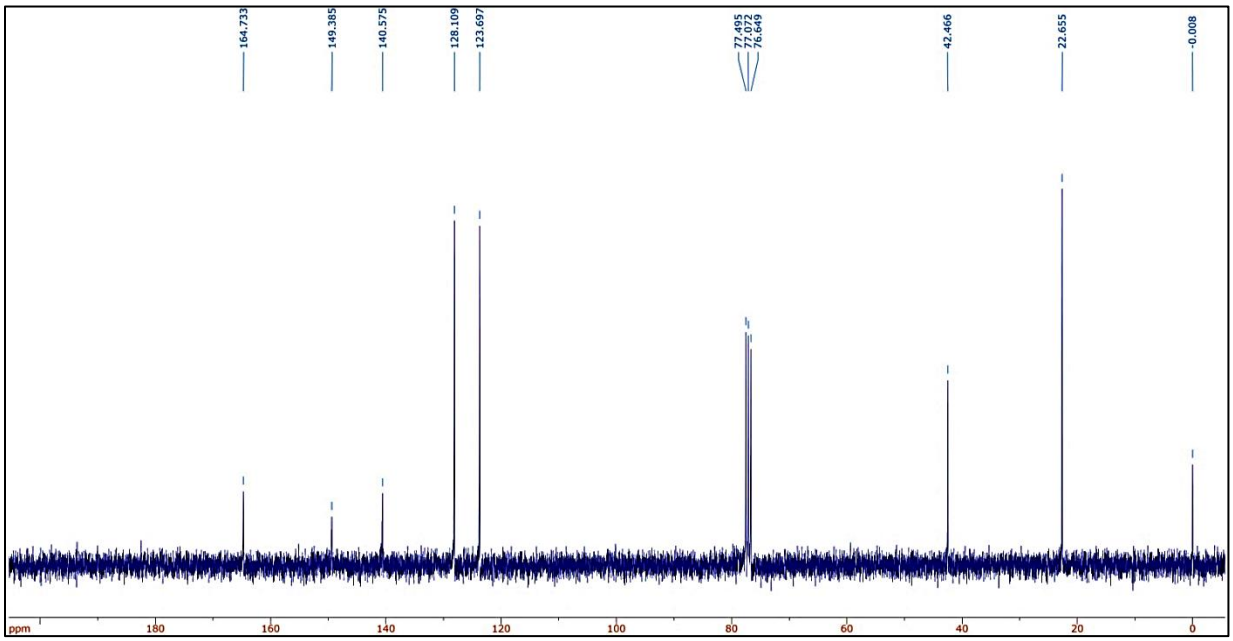


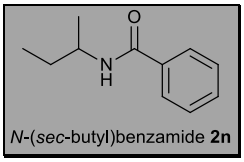




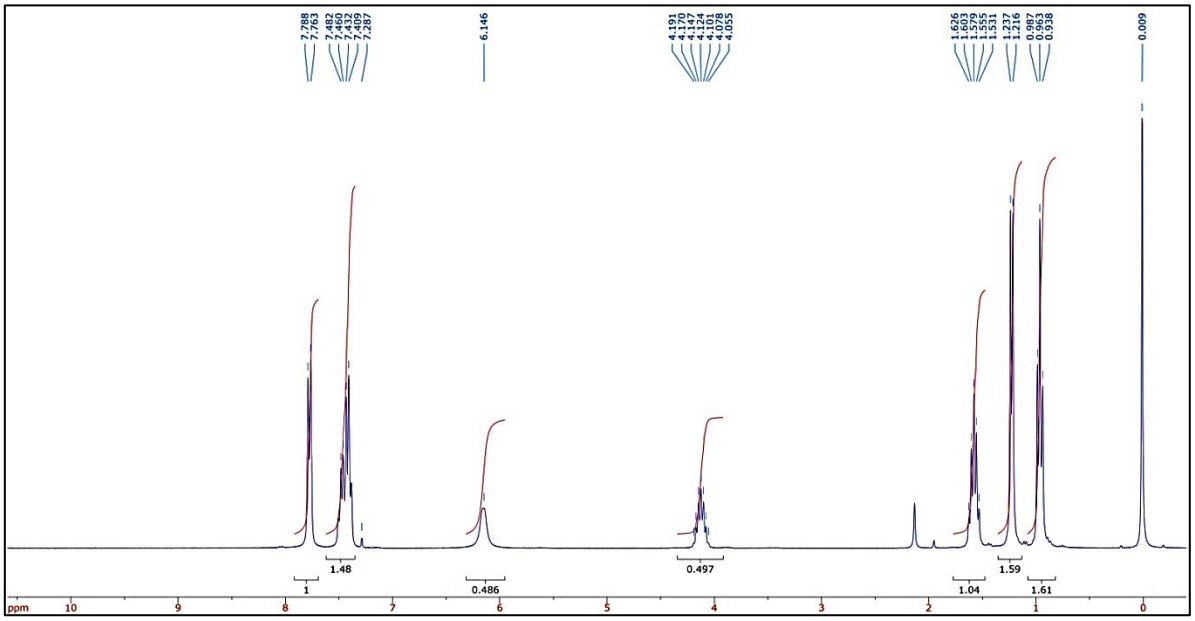
N-isopropyl-4-nitrobenzamide **2m**

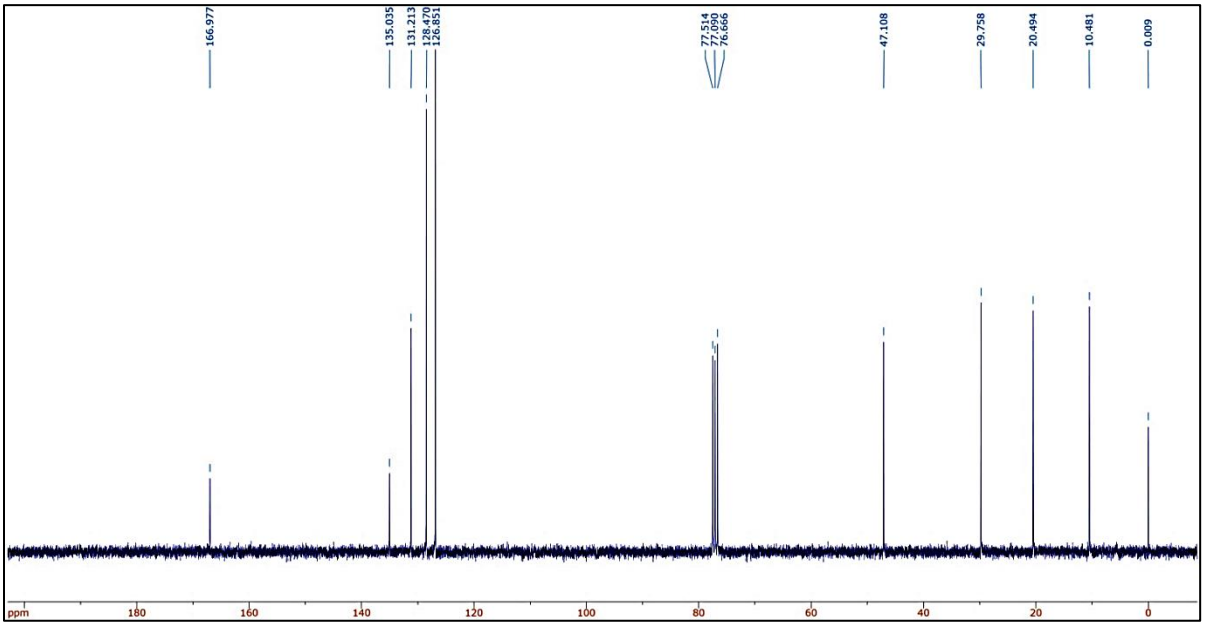


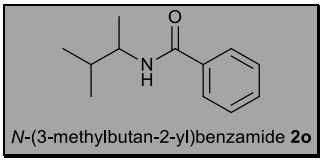




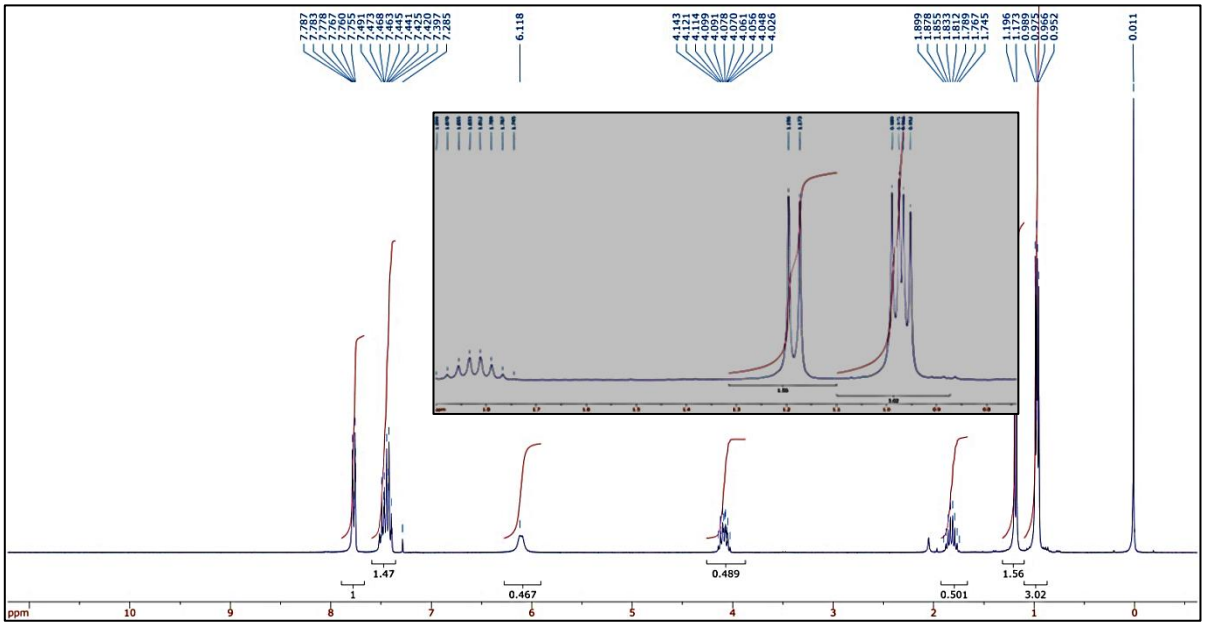
N-(*sec*-butyl)benzamide **2n**

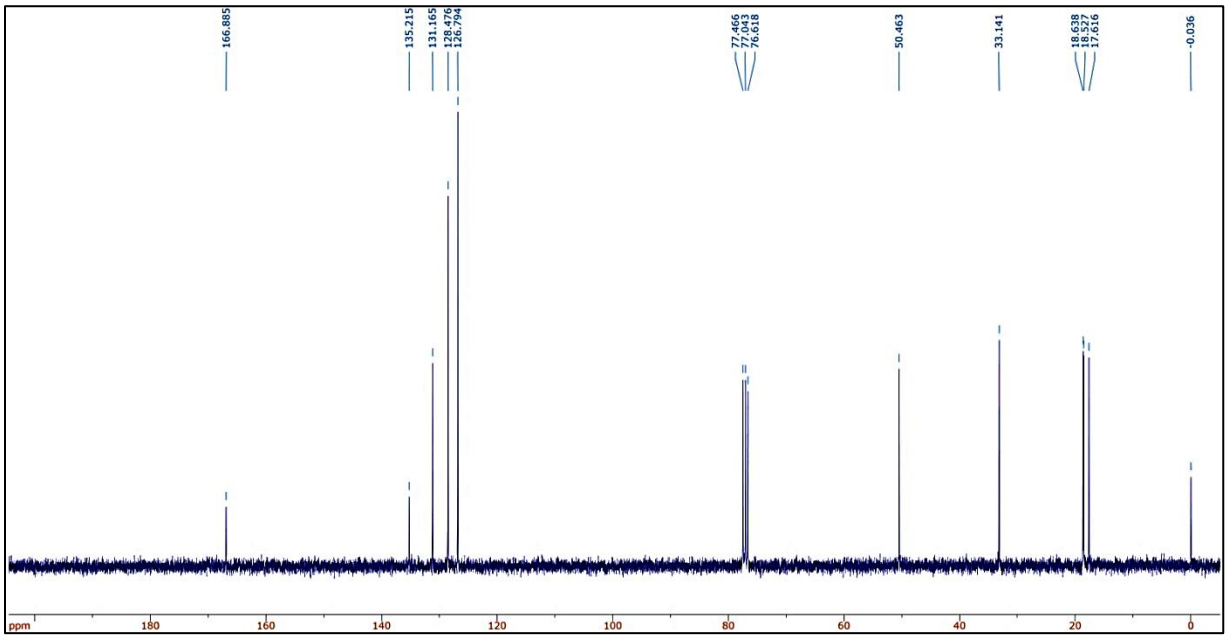


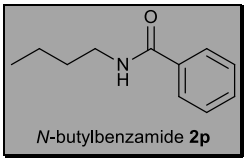




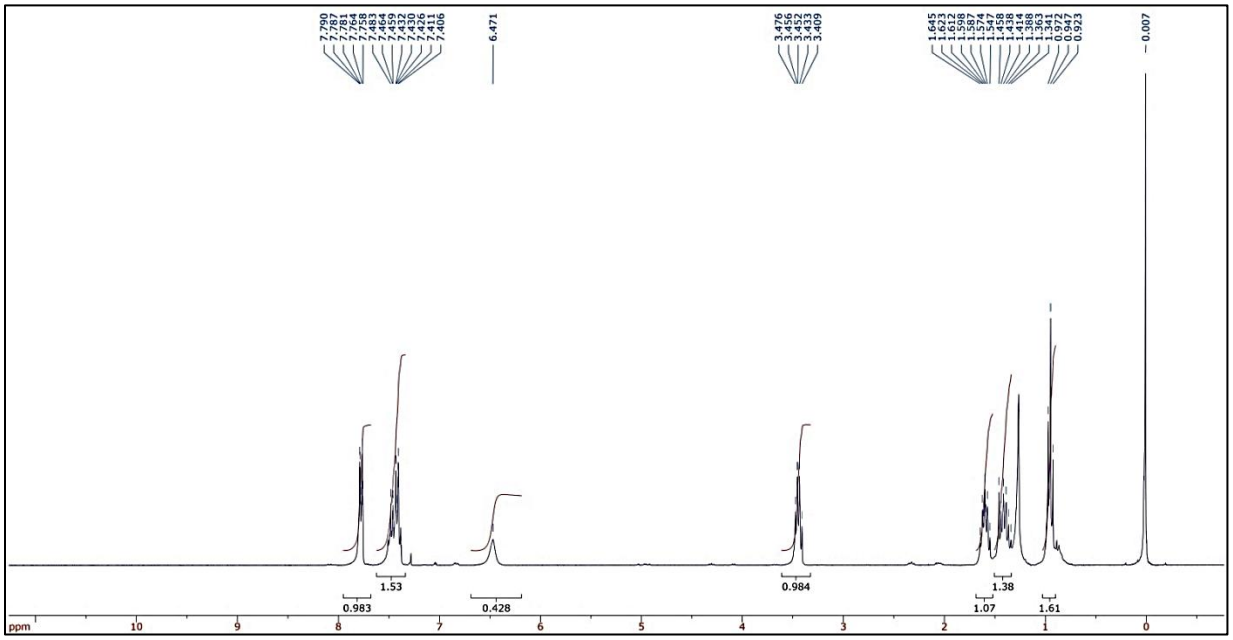
N-(3-methylbutan-2-yl)benzamide **2o**

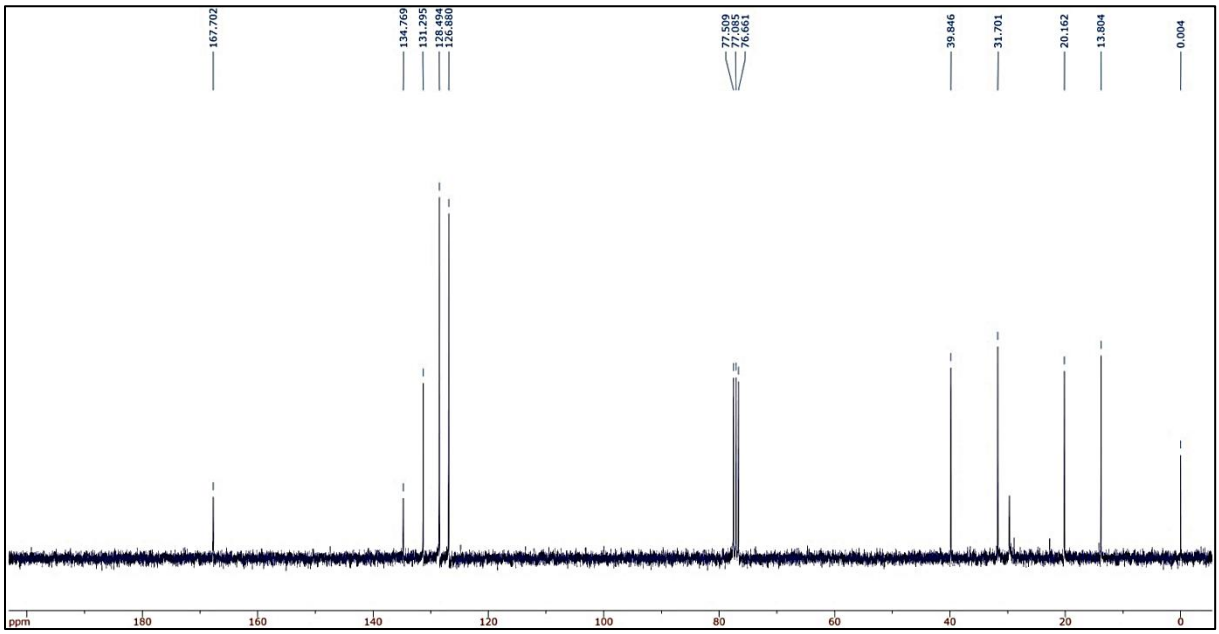


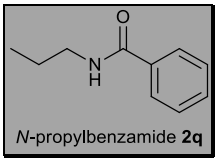




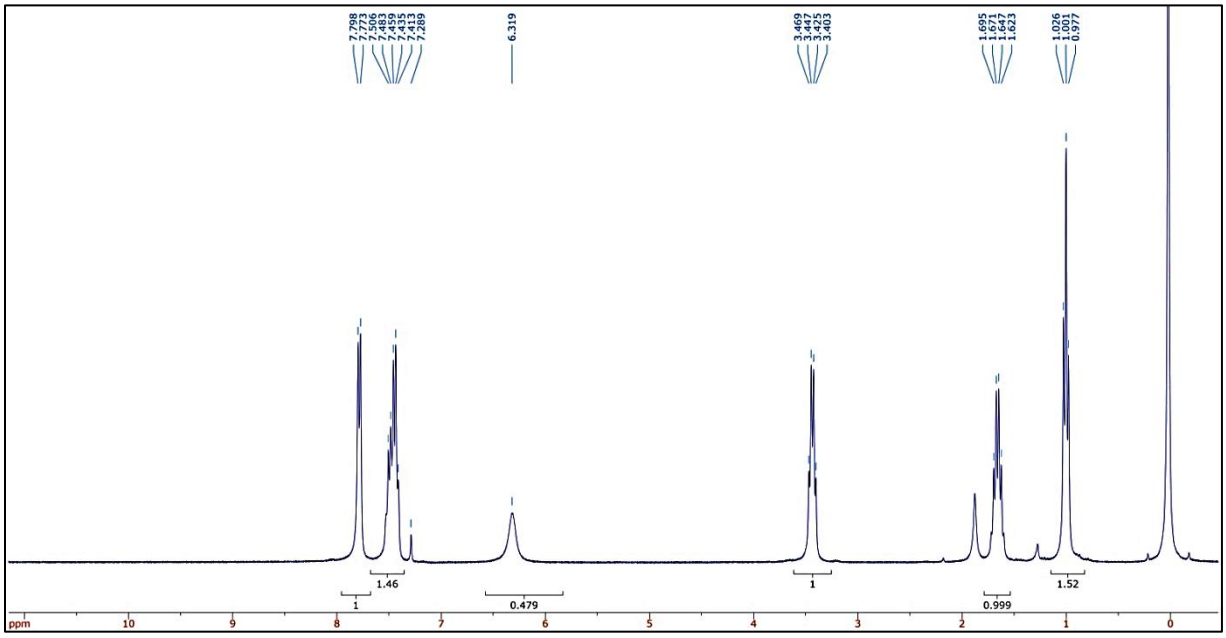
N-butylbenzamide **2p**

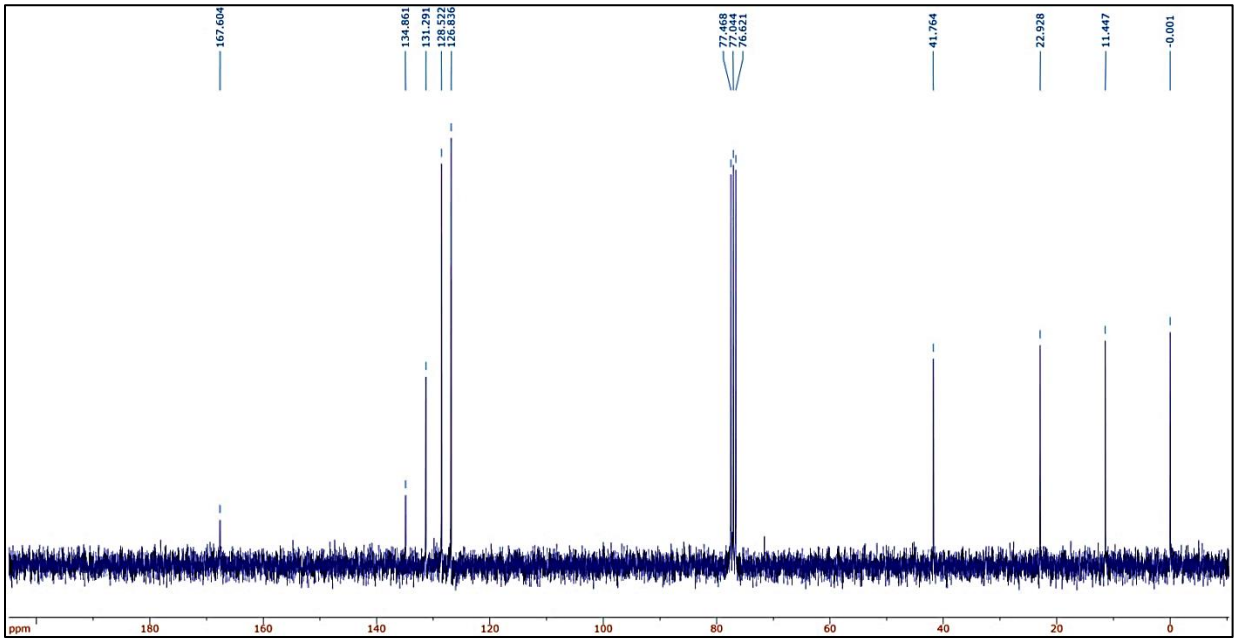






N-propylbenzamide **2q**





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