Electronic supplementary information

Amine modified mesoporous Al_2O_3 @MCM-41: An efficient, synergetic and recyclable catalyst for the formylation of amines using carbon dioxide and DMAB under solvent free and mild reaction condition

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Experimental section

General

All the chemicals and reagents were of AR grade procured from Sigma Aldrich, Alfa Aesar, Merck and S. D. fine chemicals Ltd., India and were used without further purification/pre-treatment. DMAB (Dimethylamine-borane complex) procured from Sigma Aldrich, India. All the substrates of amines were obtained from Sigma-Aldrich (purity >99.99+%). CO_2 was obtained from Rakhangi Gases Ltd., Mumbai, India with a purity of 99.99+%. All the reactions were monitored by using thin layer chromatography using Merck silica gel 60 F254 plates (TLC) and Perkin Elmer Clarus 400 gas chromatography equipped with flame ionization detector with a capillary column (Elite - 1, 30 m × 0.32 mm × 0.25 μm). All the isolated products (**2a-ff**) were confirmed by GC-MS, ^{1}H NMR and ^{13}C NMR analysis techniques. GC-MS (Shimadzu QP 2010) instrument (Rxt-17, 30 m × 25 mm, film thickness (df) = 0.25 μm) (column flow 2 mL min^{-1}, 80 °C to 240 °C at 10 °C / min rise). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 and 500 MHz NMR spectrometer with $CDCl_3$ as a solvent. The chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (TMS) as an internal standard. *J* (coupling constant) values were reported in Hz. Splitting patterns of proton are described as s (singlet), d (doublet), dd (doublet of doublets), t (triplet) and m (multiplet).

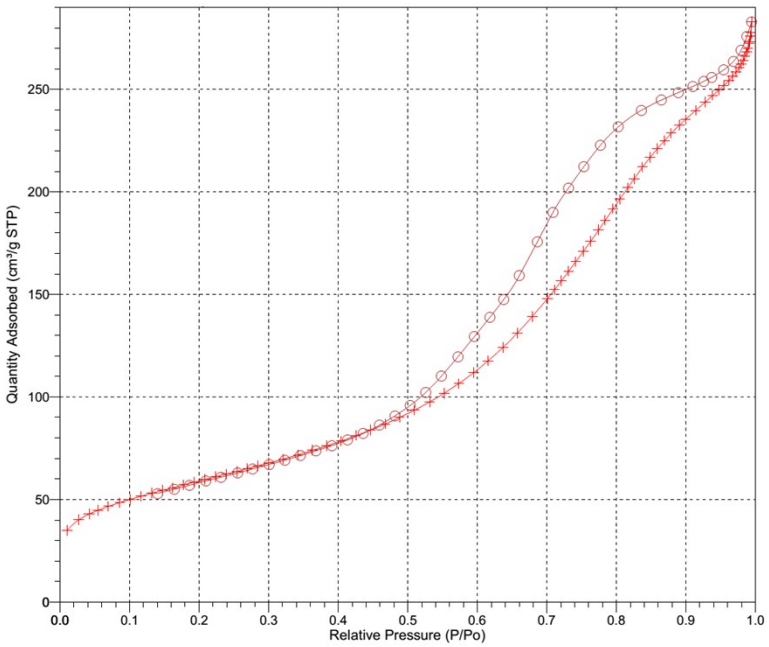
BET Surface area characterization data

Table S1 Surface characterization of MCM-41, meso Al_2O_3, meso Al_2O_3@MCM-41 and 16 wt% APTES meso Al_2O_3@MCM-41

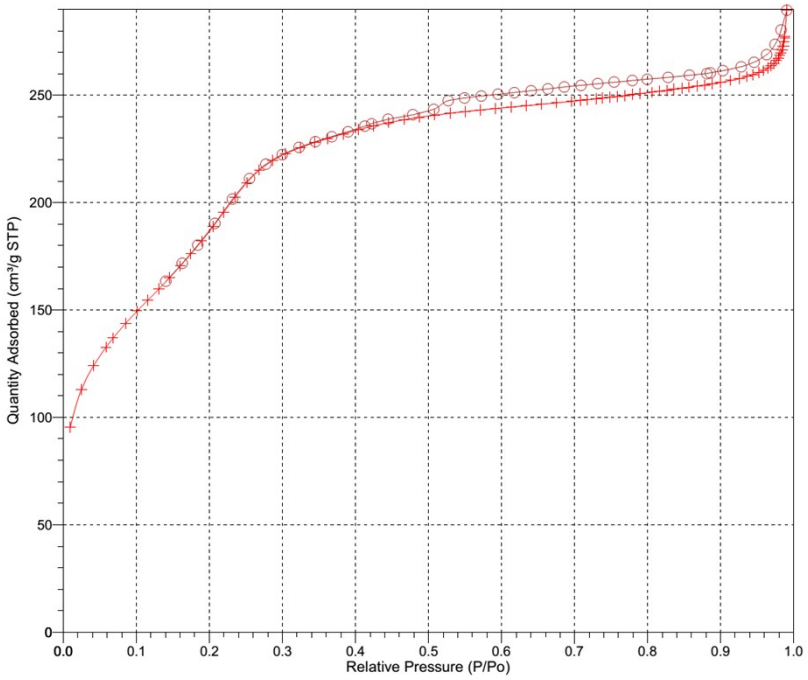
Sr. No.	Sample	BET surface area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
1	Meso-Al_2O_3	213	0.42	7.8
2	MCM-41	878	0.65	2.5
3	Meso-Al_2O_3/MCM-41	1045	1.64	2.6
4	16 wt% APTES meso Al_2O_3@MCM-41	720	0.36	2.8

N_2 adsorption-desorption isotherms (Figure S1(**a-c**))

(a)



(b)



(c)

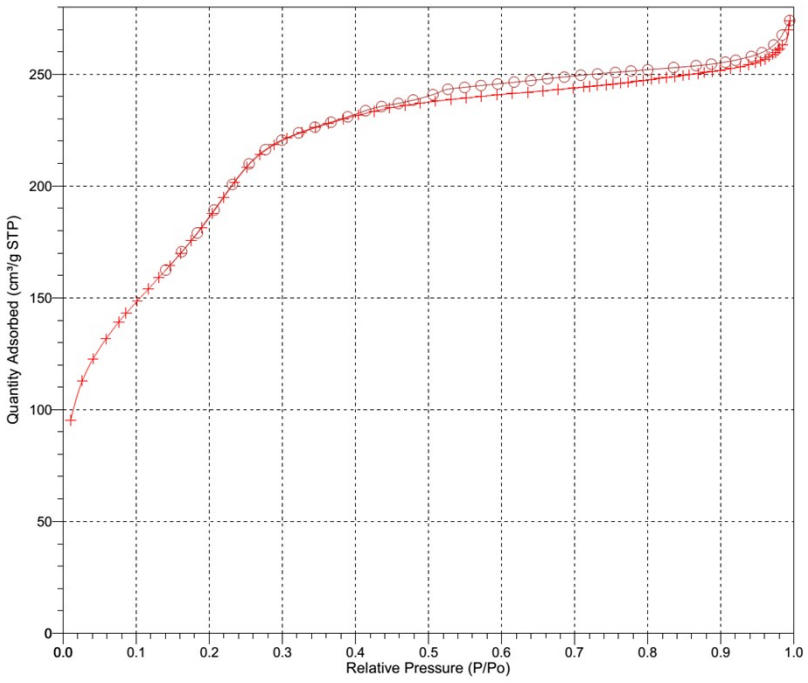


Figure S1 N_2 adsorption-desorption isotherms of **(a)** 0 wt%, **(b)** Fresh 16 wt% and **(c)** Reused 16 wt% amine modified meso Al_2O_3@MCM-41.

Pore size distribution curve (Figure S2)

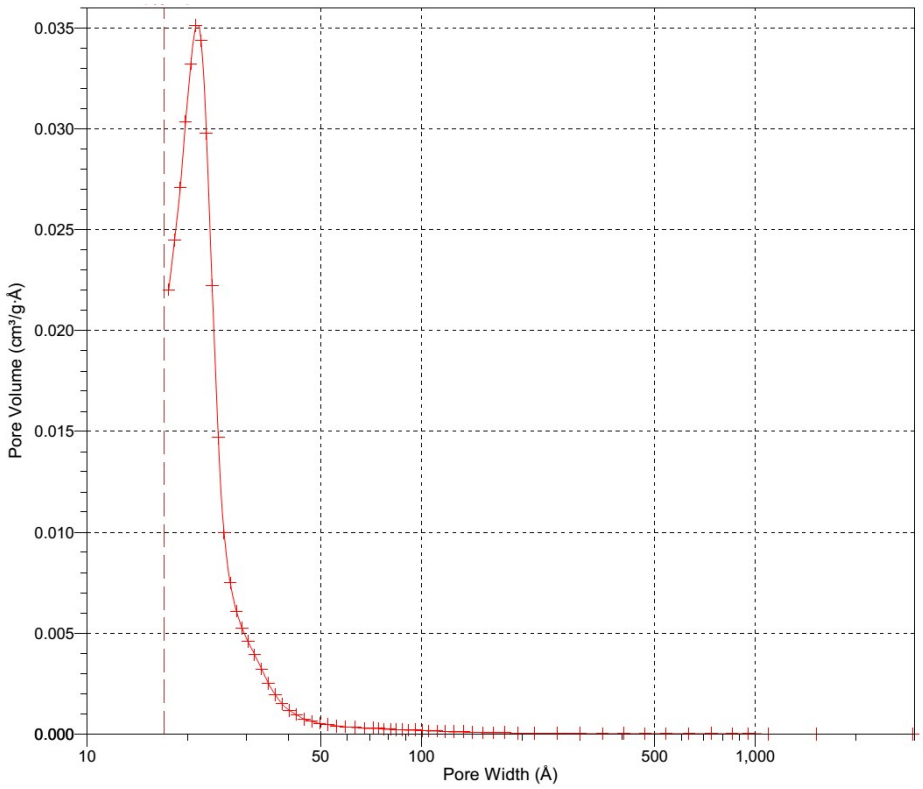


Figure S2 Pore size distribution curve of 16 wt% amine modified meso Al_2O_3@MCM-41.

FT-IR analysis of various amines modified meso Al_2O_3@MCM-41 catalysts (Figure S3)

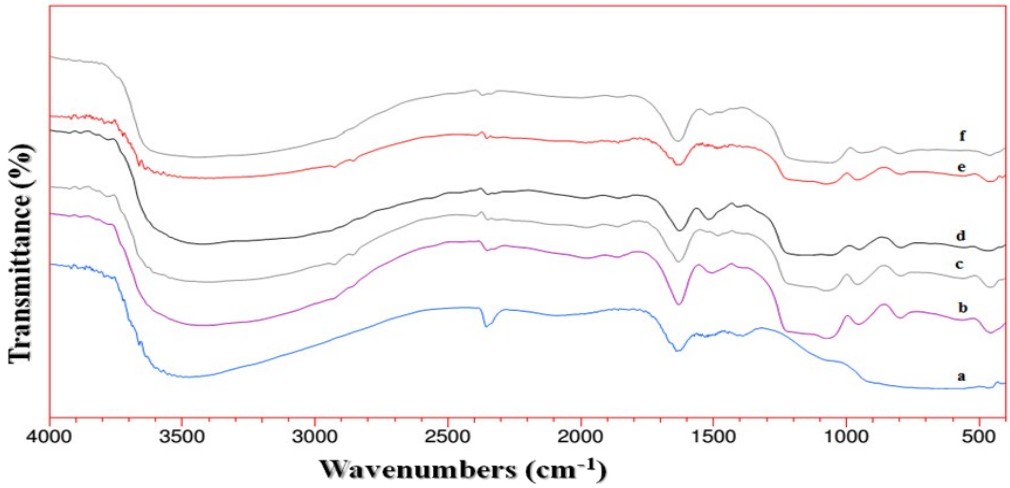
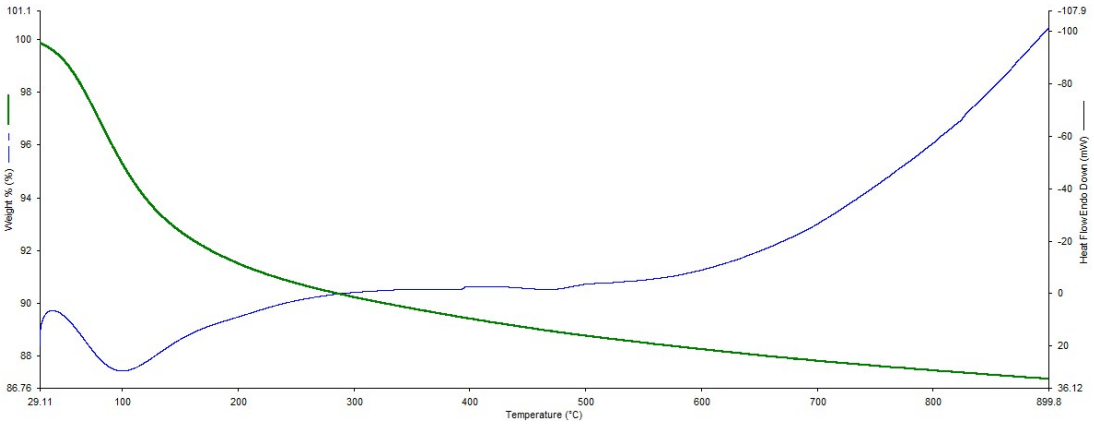


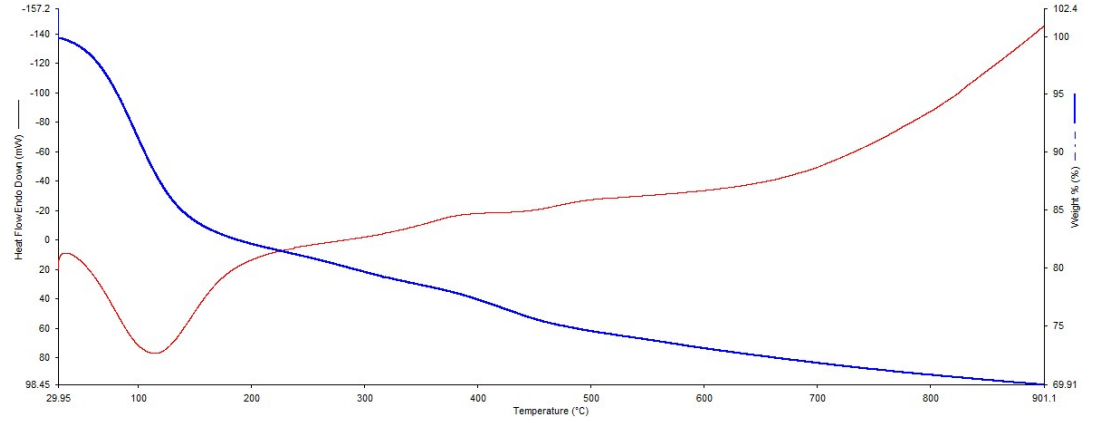
Figure S3 FT-IR of (a) 0, (b) 3.2, (c) 6.4, (d) 12.8, (e) 16.0 and (f) 20.0 wt% amine modified meso Al_2O_3@MCM-41 catalysts

TGA/DSC analysis of various amines loaded on meso Al_2O_3@MCM-41 (Figure S4)

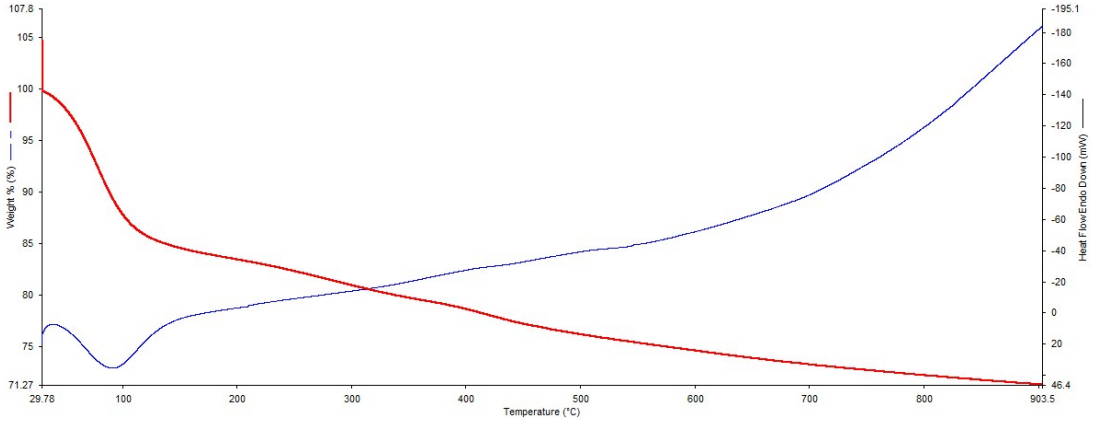
a)



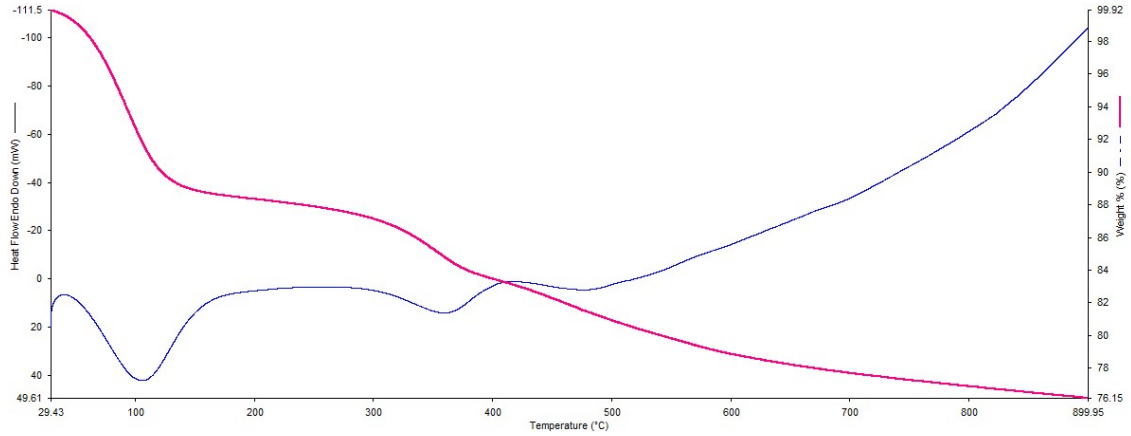
b)



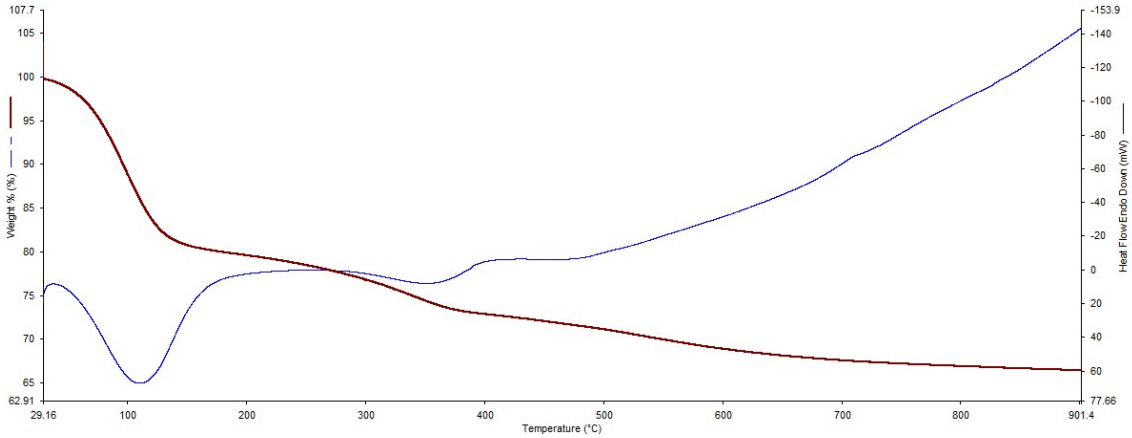
c)



d)



e)



f)

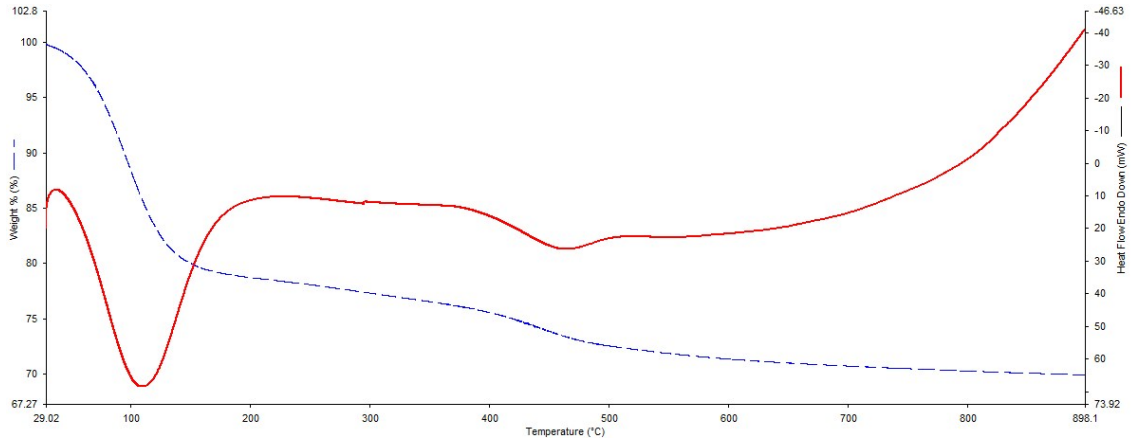


Figure S4 TGA/DSC analyses of (a) 0, (b) 3.2, (c) 6.4, (d) 12.8, (e) 16.0, and (f) 20.0 wt% amines loaded on meso Al_2O_3@MCM-41 catalysts.

Spectroscopic data of some selected compounds[1-4]

i. ***N-benzyl-N-methyl formamide (2a)(Table 3, entry 1):*** Colourless oil; Yield: 99%; ^{1}H NMR ($CDCl_3$, 400 MHz, 30 °C, TMS) δ = 8.26 (major rotamer, s, 1H), 8.13 (minor rotamer, s, 1H), 7.37-7.17 (m, 5H), 4.50 (minor rotamer, s, 2H), 4.37 (major rotamer, s, 2H), 2.82 (minor rotamer, s, 3H), 2.76 (major rotamer, s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 30 °C, TMS) δ = 162.74 (major rotamer), 162.57 (minor rotamer), 135.96 (minor rotamer), 135.69 (major rotamer), 128.88 (major rotamer), 128.67 (minor rotamer), 128.21 (major rotamer), 128.08 (minor rotamer), 127.62 (minor rotamer), 127.36 (major rotamer), 53.47 (major rotamer), 47.74 (minor rotamer), 34.05 (major rotamer), 29.44 (minor rotamer). GC-MS (EI) (% relative intensity): *m/z* = 149 (100) $[M]^+$.

ii. ***N-benzyl-N-(tert-butyl)formamide (2c)(Table 3, entry 3):*** Light yellow solid; Yield: 86%; ^{1}H NMR ($CDCl_3$, 500 MHz, 30 °C, TMS) δ = 8.65 (s, 1H), 7.28-7.19 (m, 5H), 4.62 (s, 2H), 1.32 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz, 30 °C, TMS) δ = 164.73 (minor rotamer), 162.45 (major rotamer), 138.89, 130.79, 128.75 (minor rotamer), 128.72 (major rotamer), 128.39, 126.80 (major rotamer), 126.71 (minor rotamer), 126.31, 55.90, 44.01, 30.05. GC-MS (EI) (% relative intensity): *m/z* = 191 (100) $[M]^+$.

iii. ***N-methyl-N-phenyl formamide (2d)(Table 3, entry 4):*** Brownish oil; Yield: 97%; ^{1}H NMR ($CDCl_3$, 400 MHz, 30 °C, TMS) δ = 8.39 (s, 1H), 7.33 (t, *J* = 8 Hz, 2H), 7.20 (t, *J* = 8 Hz, 1H), 7.10 (d, *J* = 4 Hz, 2H), 3.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 30 °C, TMS) δ = 162.27 (major rotamer), 162.17 (minor rotamer), 142.08, 129.55, 128.96, 126.32 (major rotamer), 126.16 (minor rotamer), 123.53, 122.26, 31.95. GC-MS (EI) (% relative intensity): *m/z* = 135 (85) $[M]^+$.

iv. ***N,N-diphenylformamide (2f)(Table 3, entry 6):*** Light violet colour; yield: 45%; ^{1}H NMR ($CDCl_3$, 500 MHz, 30 °C, TMS) δ = 8.68 (s, 1H), 7.43-7.18 (m, 10H). ^{13}C NMR ($CDCl_3$, 125 MHz, 30 °C, TMS) δ = 161.73, 141.79, 139.62, 139.26, 129.68, 129.17, 127.03,

126.86, 126.11, 125.08, 118.49, 114.04. GC-MS (EI) (% relative intensity): *m/z* = 197 (100) $[M]^+$.

v. ***Indoline-1-carbaldehyde (2g)(Table 3, entry 7&8):*** Brown solid; Yield: 84% & 98%; ^1H NMR ($CDCl_3$, 400 MHz, 30 °C, TMS) δ = 8.92 (major rotamer, s, 1H), 8.50 (minor rotamer, s, 1H), 7.24–7.14 (m, 3H), 7.05–7.01 (m, 1H), 4.05 (t, *J* = 8 Hz, 2H), 3.14 (t, *J* = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 30 °C, TMS) δ = 157.58, 140.93, 127.57, 126.06, 125.13, 124.28, 109.38, 44.64, 27.17. GC-MS (EI) (% relative intensity): *m/z* = 147 (65) $[M]^+$.

vi. ***Morpholine-4-carbaldehyde (2j)(Table 3, entry 10):*** Colourless oil; yield: 99%; ^1H NMR ($CDCl_3$, 400 MHz, 30 °C, TMS): δ = 7.92 (s, 1H), 3.58-3.52 (m, 4H), 3.44 (t, *J* = 4 Hz, 2H), 3.28 (t, *J* = 4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 30 °C, TMS): δ = 160.81, 67.08, 66.26, 45.67, 40.44. GC-MS (EI) (% relative intensity): m/z = 115 (100) $[M]^+$.

vii. ***N,N-dimethyl formamide (2r)(Table 3, entry 18):*** Colourless liquid; yield: 98%; ^1H NMR ($CDCl_3$, 400 MHz, 30 °C, TMS): δ = 7.54 (s, 1H), 2.52 (s, 3H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 30 °C, TMS): δ = 162.05, 35.95, 30.78. GC-MS (EI) (% relative intensity): *m/z* = 73 (100) $[M]^+$.

viii. ***N,N-diethyl formamide (2s)(Table 3, entry 19):*** Colourless liquid; yield: 90%; ^1H NMR ($CDCl_3$, 400 MHz, 30 °C, TMS): δ = 7.81 (s, 1H), 3.16-3.04 (m, 4H), 0.98-0.88 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, 30 °C, TMS): δ = 161.97, 41.62, 36.33, 14.62, 12.49. GC-MS (EI) (% relative intensity): *m/z* = 101 (100) $[M]^+$.

ix. ***N,N-dibutyl formamide (2v)(Table 3, entry 22):*** Colourless oil; yield: 91%; ^1H NMR ($CDCl_3$, 400 MHz, 30 °C, TMS) δ = 7.95 (s, 1H), 3.20 (t, *J* = 8 Hz, 2H), 3.12 (t, *J* = 8 Hz, 2H), 1.43 (t, *J* = 4 Hz, 4H), 1.23 (t, *J* = 8 Hz, 4H), 0.87-0.83 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, 30 °C, TMS) δ = 162.61, 47.08, 41.76, 30.64, 29.29, 20.06, 19.54, 13.70, 13.54. GC-MS (EI) (% relative intensity): *m/z* = 157 (36) $[M]^+$.

x. ***N-cyclohexyl formamide (2x)(Table 3, entry 24):*** Colourless oil; Yield: 89%; ^{1}H NMR ($CDCl_3$, 400 MHz, 30 °C, TMS) δ = 8.04 (minor rotamer, s, 1H), 8.00 (major rotamer, s, 1H), 6.25 (br, s, 1H), 3.79-3.72 (major rotamer, m, 1H), 3.23-3.21 (minor rotamer, m, 1H), 1.85-1.53 (m, 5H), 1.34-1.06 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz, 30 °C, TMS) δ = 163.76 (minor rotamer), 160.55 (major rotamer), 51.09, 47.02, 34.52, 32.84, 25.33, 24.92 (minor rotamer), 24.68 (major rotamer). GC-MS (EI) (% relative intensity): *m/z* = 127 (15) $[M]^+$.

xi. ***N-tert-butyl formamide (2y)(Table 3, entry 25):*** Yellow oil; Yield: 80%; ^{1}H NMR ($CDCl_3$, 400 MHz, 30 °C, TMS) δ = 8.11 (minor rotamer, s, 1H), 8.08 (major rotamer, s, 1H), 7.86 (major rotamer, s, 1H), 7.85 (minor rotamer, 1H), 1.22 (major rotamer, s, 9H), 1.19 (minor rotamer, s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz, 30 °C, TMS) δ = 163.29 (minor rotamer), 160.89 (major rotamer), 50.98 (major rotamer), 50.22 (minor rotamer), 30.60 (minor rotamer), 28.69 (major rotamer). GC-MS (EI) (% relative intensity): *m/z* = 101 (18) $[M]^+$.

xii. ***N-phenyl formamide (2z)(Table 3, entry 26):*** Brown oil; Yield: 91%; ^{1}H NMR ($CDCl_3$, 400 MHz, 30 °C, TMS) δ = 9.22 (minor rotamer, br, s, 1H), 8.68 (major rotamer, s, 1H), 8.65 (minor rotamer, s, 1H), 8.29 (major rotamer, s, 1H), 7.54 (d, *J* = 8 Hz, 1H), 7.32-7.25 (m, 2H), 7.16-7.06 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 30 °C, TMS) δ = 163.28 (major rotamer), 159.95 (minor rotamer), 137.07 (major rotamer), 136.83 (minor rotamer), 129.69, 129.02, 125.24 (minor rotamer), 124.75 (major rotamer), 120.22, 118.76. GC-MS (EI) (% relative intensity): *m/z* = 121 (100) $[M]^+$.

xiii. ***N-mesitylformamide (2aa)(Table 3, entry 27):*** White solid; Yield: 75%; ^{1}H NMR ($CDCl_3$, 500 MHz, 30 °C, TMS) δ = 8.40-8.04 (m, 1H), 6.93 (m, 2H), 2.29-2.22 (m, 6H), 1.25 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, 30 °C, TMS) δ = 165.07, 159.59, 137.77 (minor rotamer), 137.66 (major rotamer), 135.35 (major rotamer), 135.16 (minor

rotamer), 130.52, 129.80, 129.49, 129.15. GC-MS (EI) (% relative intensity): *m/z* = 163 (100) $[M]^+$.

xiv. ***N-(3-methoxyphenyl)formamide (2bb)(Table 3, entry 28):*** Yellow oil; Yield: 83%; ^{1}H NMR ($CDCl_3$, 500 MHz, 30 °C, TMS) δ = 8.82 (br, s, 1H), 8.33 (s, 1H), 7.30-7.03 (m, 2H), 6.72-6.63 (m, 2H), 3.79 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, 30 °C, TMS) δ = 162.89, 160.65 (minor rotamer), 159.47 (major rotamer), 138.21, 130.56 (major rotamer), 129.76 (minor rotamer), 112.20, 110.87 (minor rotamer), 110.41 (major rotamer), 105.99, 104.87, 55.37. GC-MS (EI) (% relative intensity): *m/z* = 151 (100) $[M]^+$.

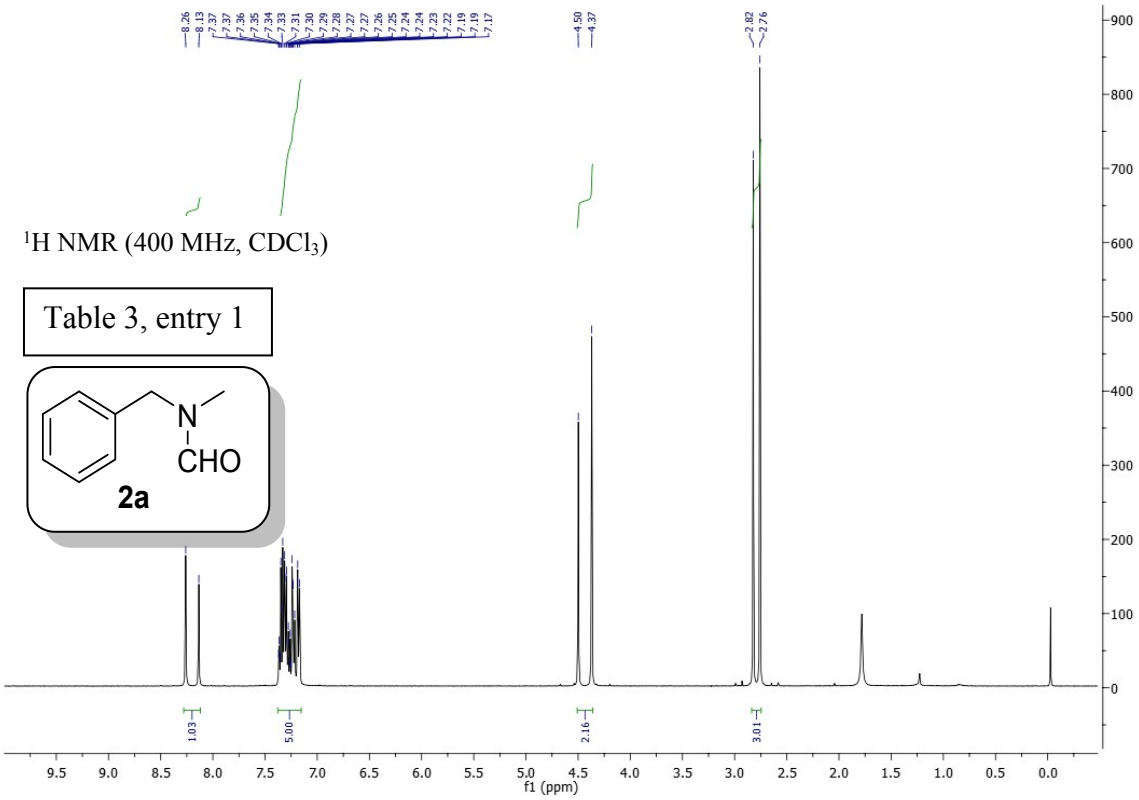
xv. ***N-(3,4-dimethoxyphenyl)formamide (2cc)(Table 3, entry 29):*** Yellow oil; Yield: 85%; ^{1}H NMR ($CDCl_3$, 500 MHz, 30 °C, TMS) δ = 8.54 (s, 1H), 8.03 (br, s, 1H), 7.58-7.34 (m, 1H), 7.00-6.62 (m, 2H), 3.98-3.85 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, 30 °C, TMS) δ = 162.97, 158.86, 151.42, 149.79 (minor rotamer), 149.08 (major rotamer), 147.20 (minor rotamer), 146.18 (major rotamer), 130.49 (major rotamer), 129.87 (minor rotamer), 120.09, 112.09 (major rotamer), 110.48 (minor rotamer), 105.05, 102.02, 56.08. GC-MS (EI) (% relative intensity): *m/z* = 181 (100) $[M]^+$.

xvi. ***N-(2,6-diethylphenyl)formamide (2dd)(Table 3, entry 30):*** White solid; Yield: 51%; ^{1}H NMR ($CDCl_3$, 500 MHz, 30 °C, TMS) δ = 8.35-8.04 (s, 1H), 7.68 (br, s, 1H), 7.27-7.11 (m, 3H), 2.69-2.57 (m, 4H), 1.23-1.17 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, 30 °C, TMS) δ = 165.36, 160.31, 141.92 (major rotamer), 141.36 (minor rotamer), 131.77 (major rotamer), 131.19 (minor rotamer), 128.43, 126.88 (major rotamer), 126.36 (minor rotamer), 24.94, 14.75 (major rotamer), 14.39 (minor rotamer). GC-MS (EI) (% relative intensity): *m/z* = 177 (100) $[M]^+$.

xvii. ***N-(4-(difluoromethoxy)phenyl)formamide (2ee)(Table 3, entry 31):*** Yellow oil; Yield: 69%; ^{1}H NMR ($CDCl_3$, 500 MHz, 30 °C, TMS) δ = 8.80-8.60 (s, 1H), 8.33-8.03 (s, 1H), 7.53 (d, *J* = 10 Hz, 3H), 7.11-7.07 (m, 3H), 6.62-6.31 (td, *J* = 5, 10 Hz, 1H). ^{13}C NMR

($CDCl_3$, 125 MHz, 30 °C, TMS) δ = 162.92, 159.37, 148.24 (minor rotamer), 147.58 (major rotamer), 134.35, 121.49 (major rotamer), 120.45 (minor rotamer), 117.94, 115.87, 113.80. GC-MS (EI) (% relative intensity): *m/z* = 187 (100) $[M]^+$.

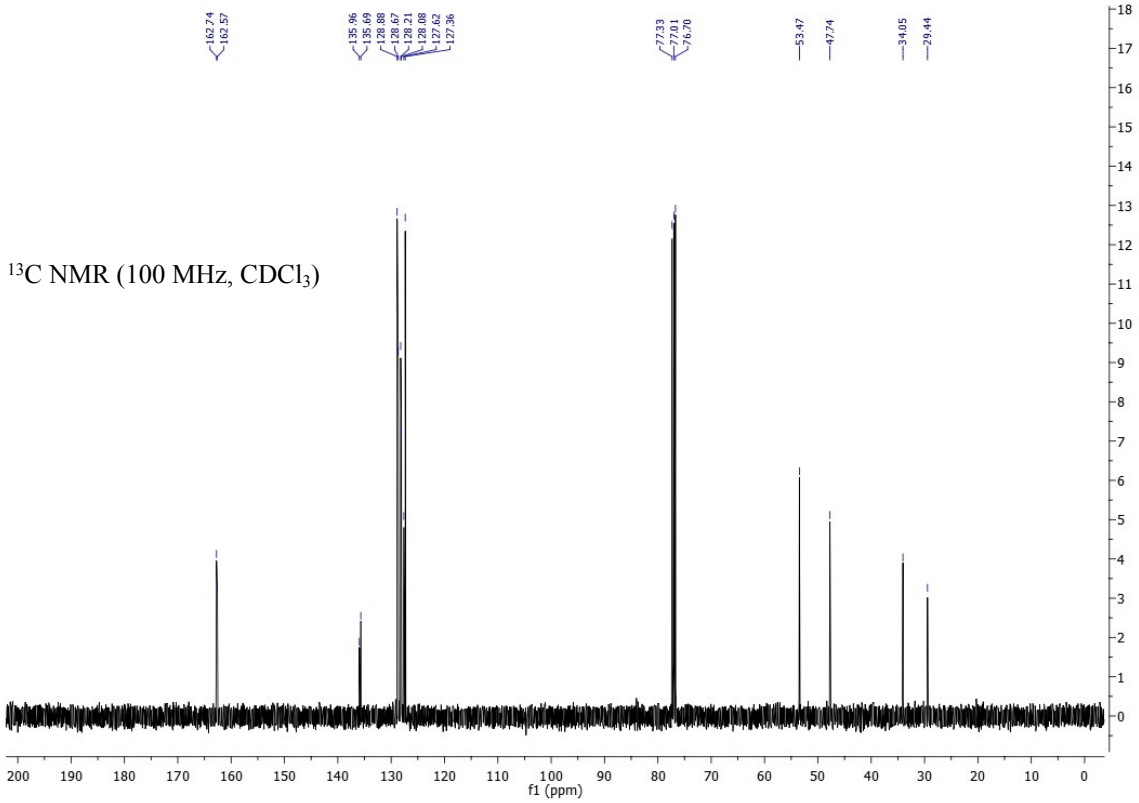
1. ^{1}H and ^{13}C NMR spectra of some selected products



^{1}H NMR (400 MHz, $CDCl_3$)

Table 3, entry 1

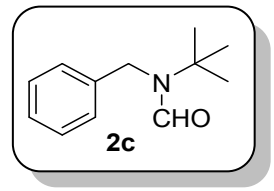
2a



^{13}C NMR (100 MHz, $CDCl_3$)

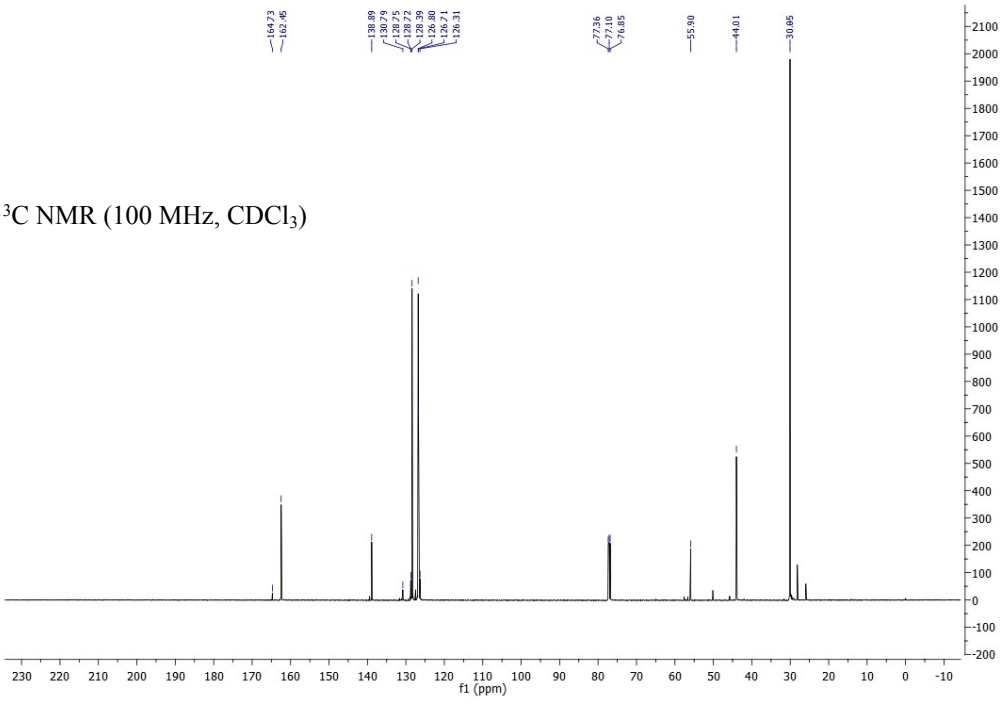
^{1}H NMR (400 MHz, $CDCl_3$)

Table 3, entry 3



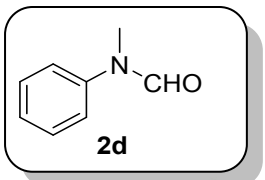
2c

^{13}C NMR (100 MHz, $CDCl_3$)



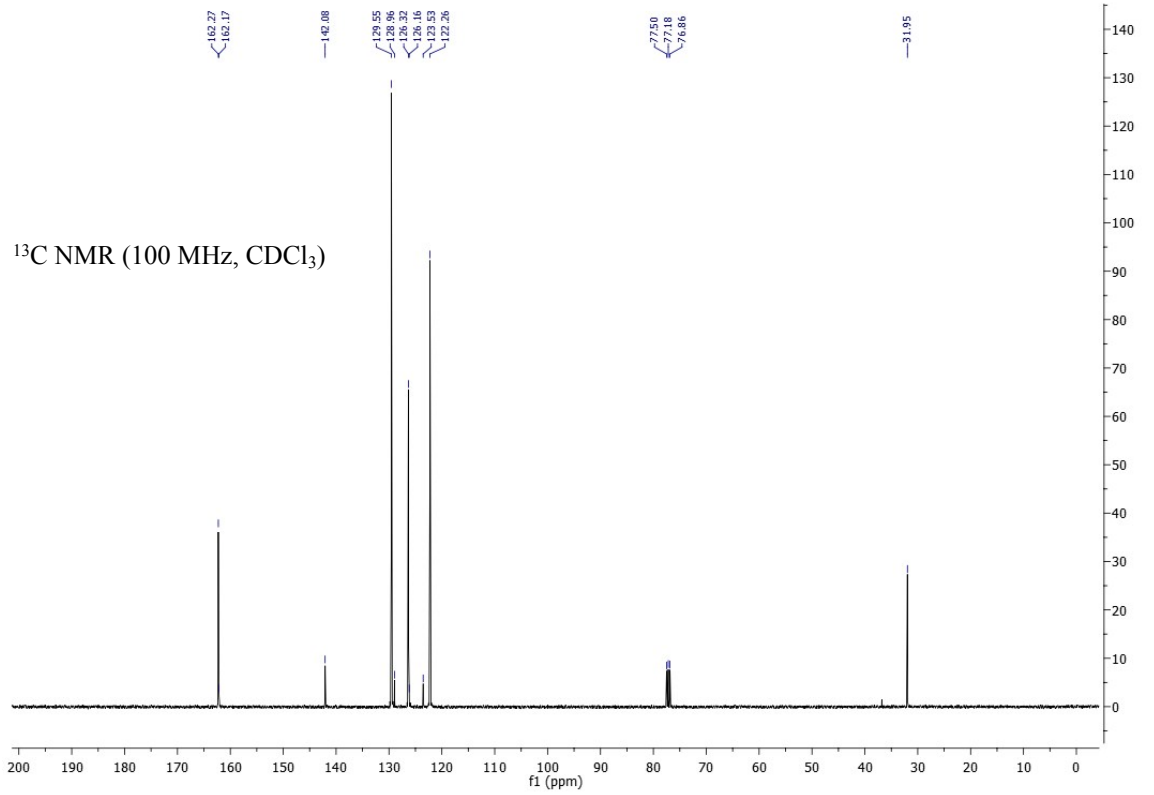
^{1}H NMR (400 MHz, $CDCl_3$)

Table 3, entry 4



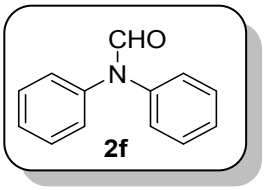
2d

^{13}C NMR (100 MHz, $CDCl_3$)



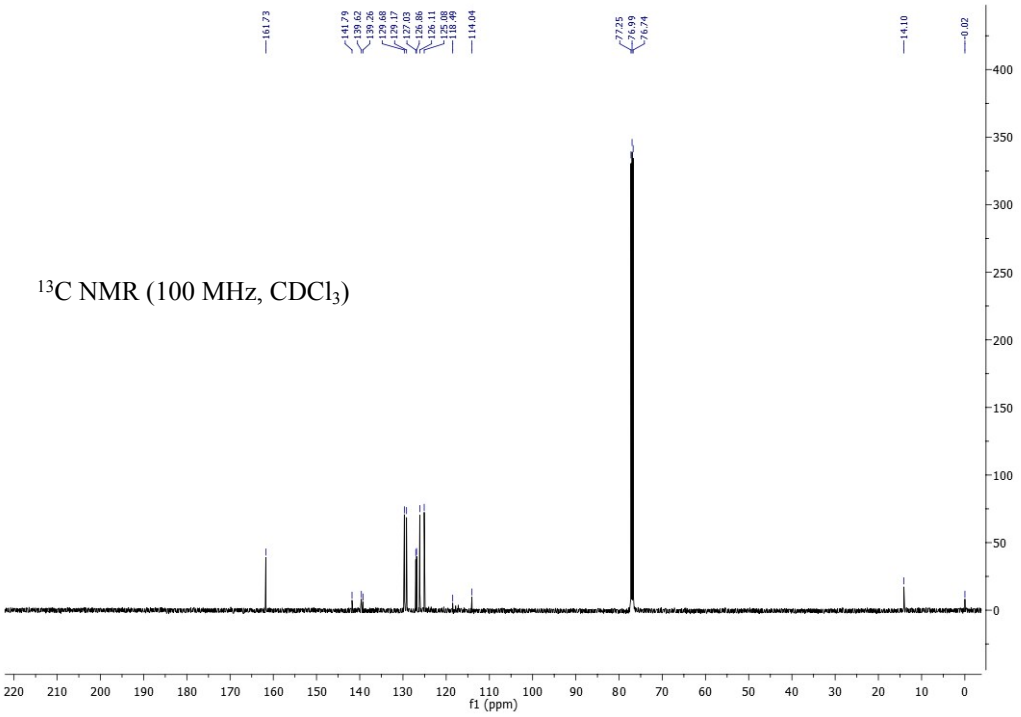
^{1}H NMR (500 MHz, $CDCl_3$)

Table 3, entry 6



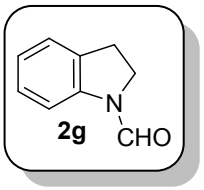
2f

^{13}C NMR (100 MHz, $CDCl_3$)



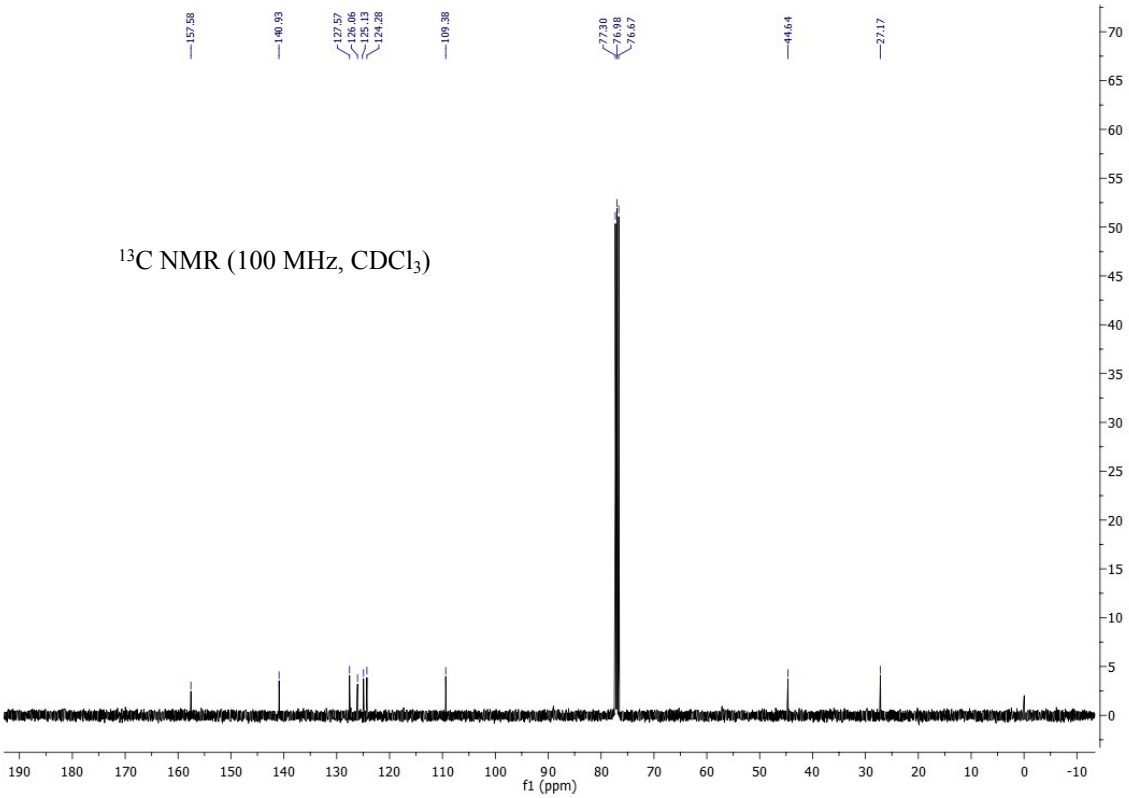
^{1}H NMR (400 MHz, $CDCl_3$)

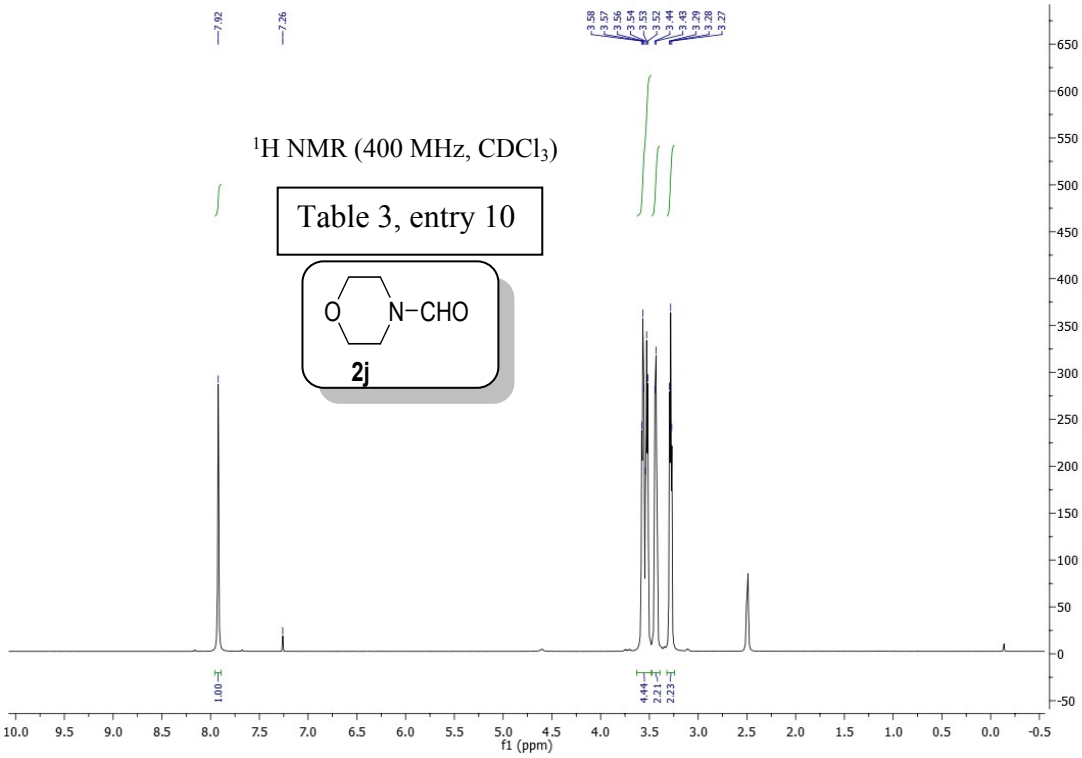
Table 3, entry 7 & 8



2g

^{13}C NMR (100 MHz, $CDCl_3$)

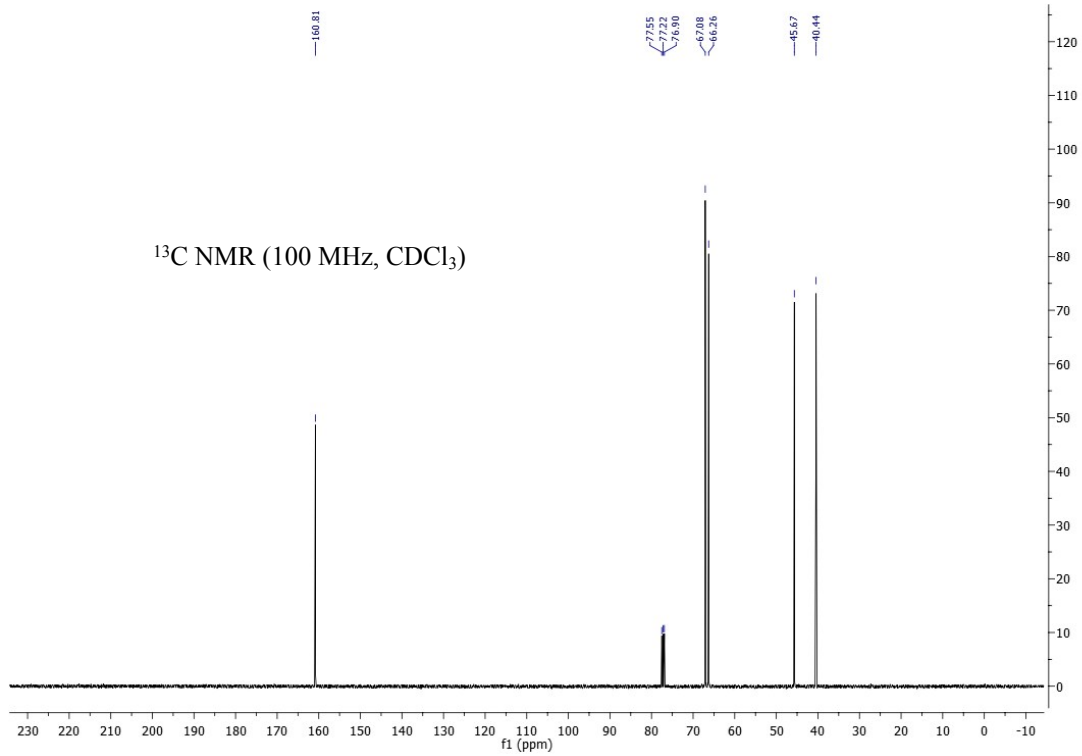




^{1}H NMR (400 MHz, $CDCl_3$)

Table 3, entry 10

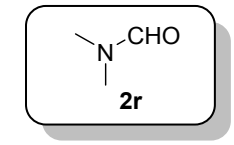
2j



^{13}C NMR (100 MHz, $CDCl_3$)

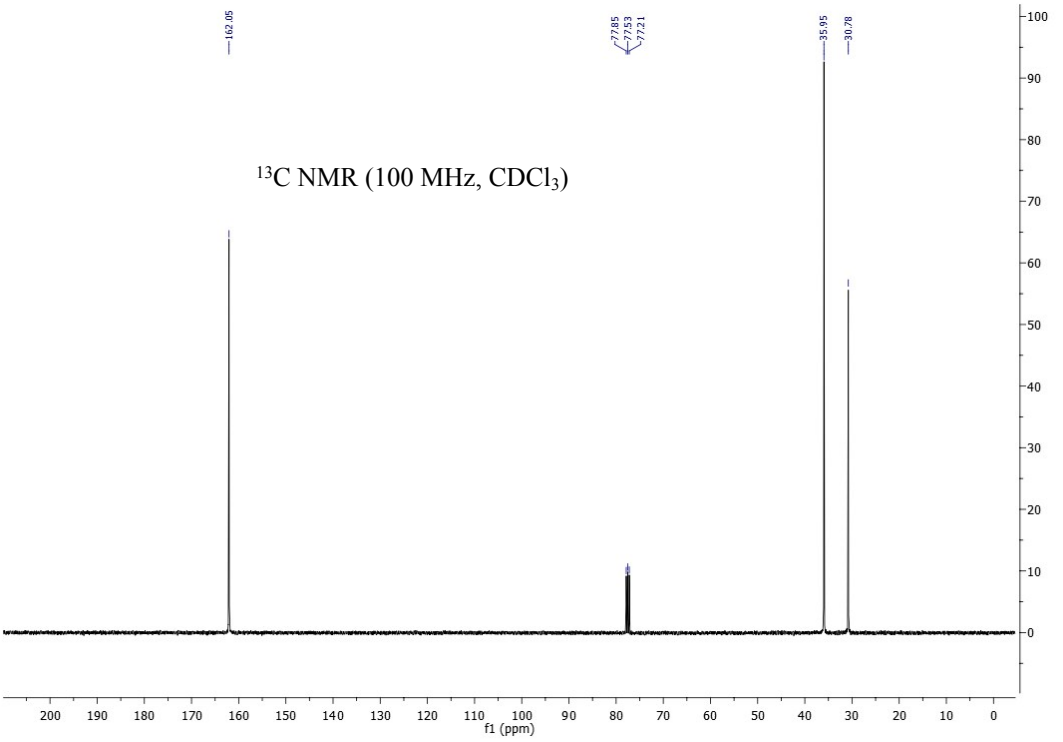
^{1}H NMR (400 MHz, $CDCl_3$)

Table 3, entry 18



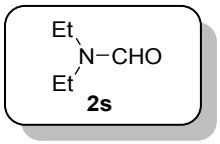
2r

^{13}C NMR (100 MHz, $CDCl_3$)



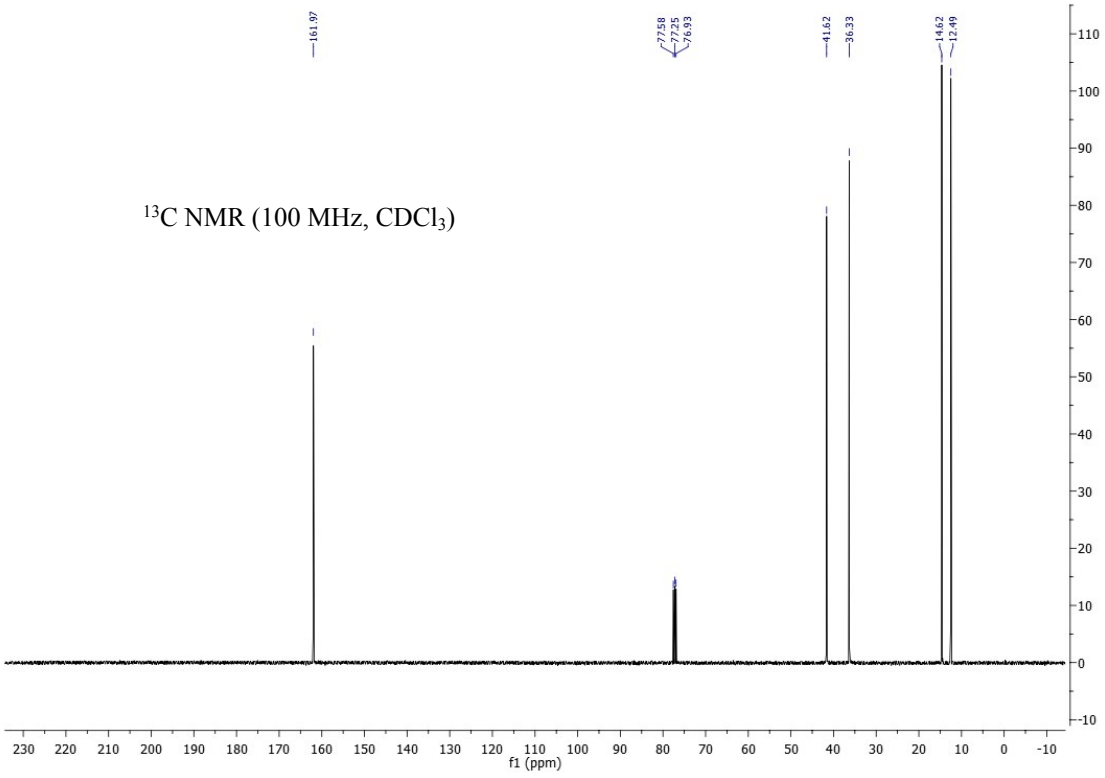
^{1}H NMR (400 MHz, $CDCl_3$)

Table 3, entry 19



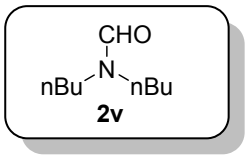
2s

^{13}C NMR (100 MHz, $CDCl_3$)



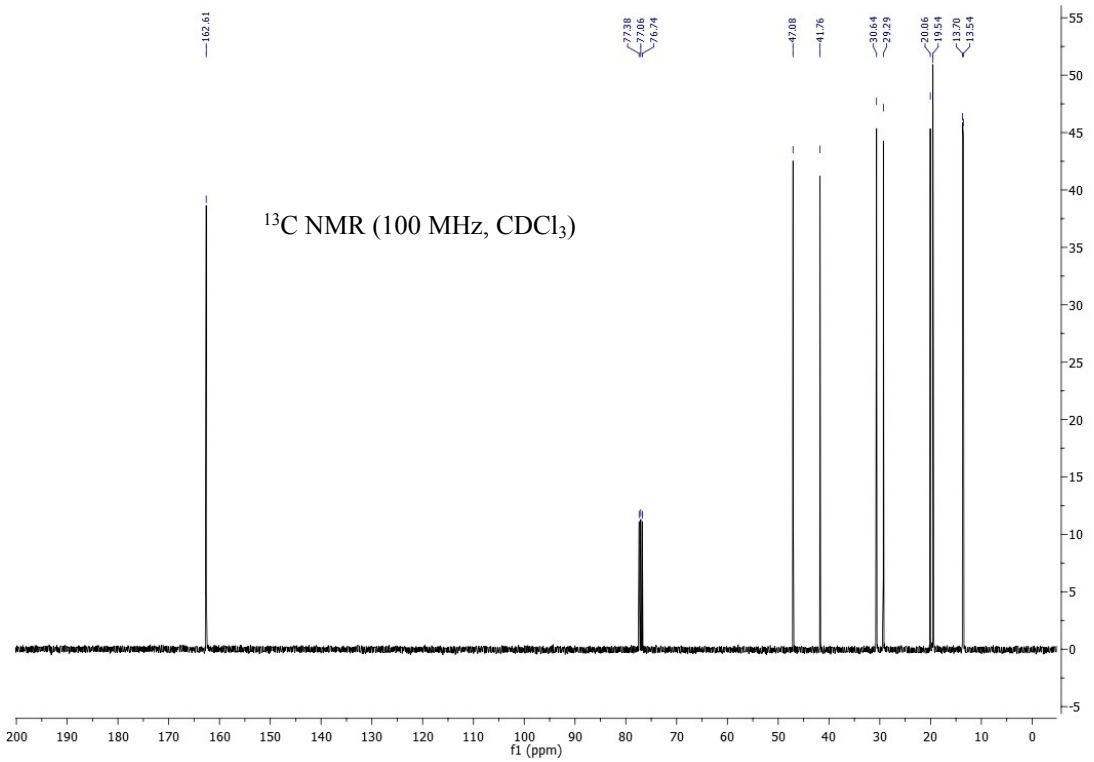
^{1}H NMR (400 MHz, $CDCl_3$)

Table 3, entry 22



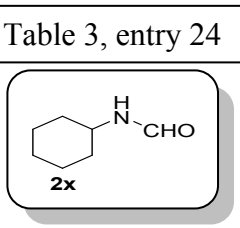
2v

^{13}C NMR (100 MHz, $CDCl_3$)



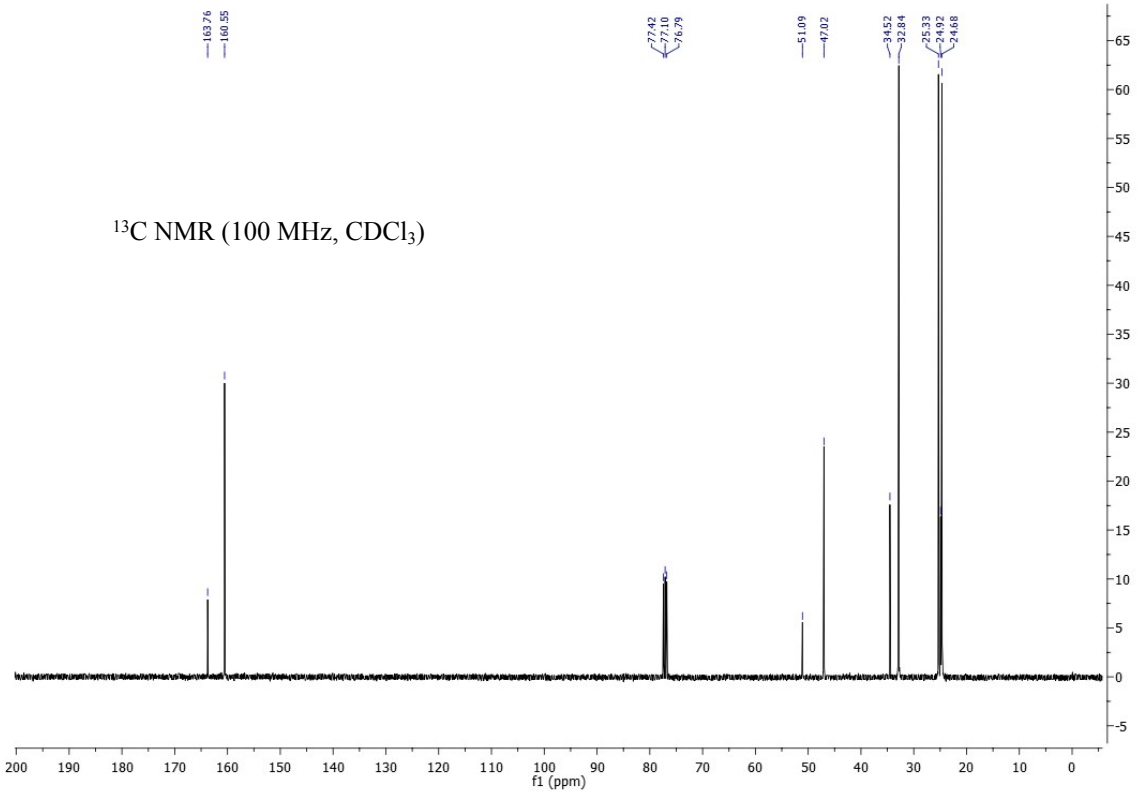
^{1}H NMR (400 MHz, $CDCl_3$)

Table 3, entry 24



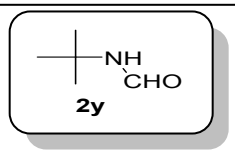
2x

^{13}C NMR (100 MHz, $CDCl_3$)



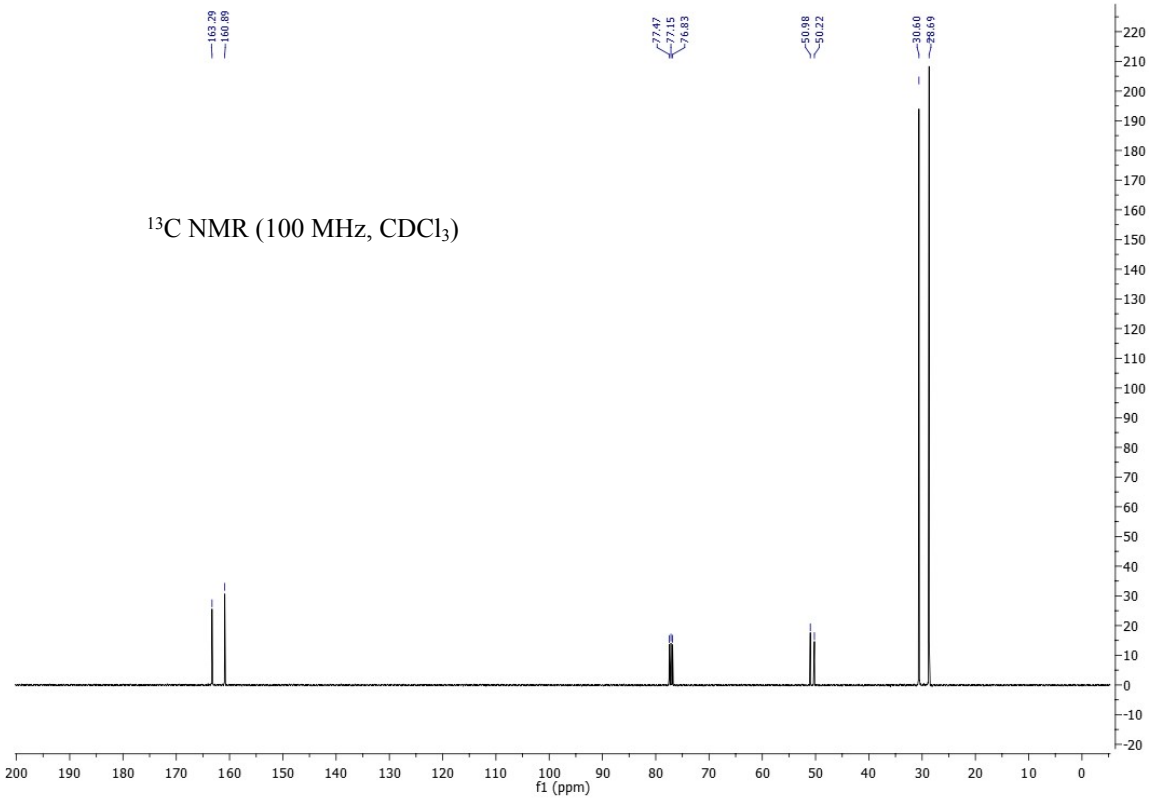
^{1}H NMR (400 MHz, $CDCl_3$)

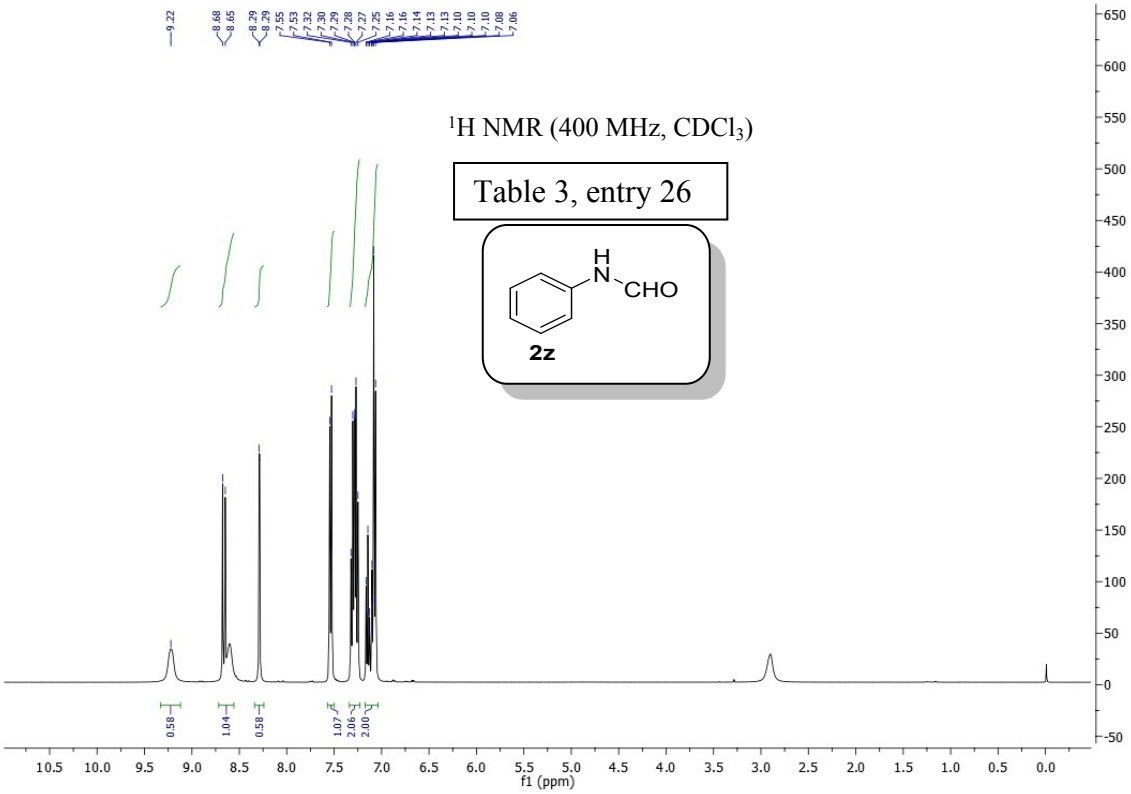
Table 3, entry 25



2y

^{13}C NMR (100 MHz, $CDCl_3$)

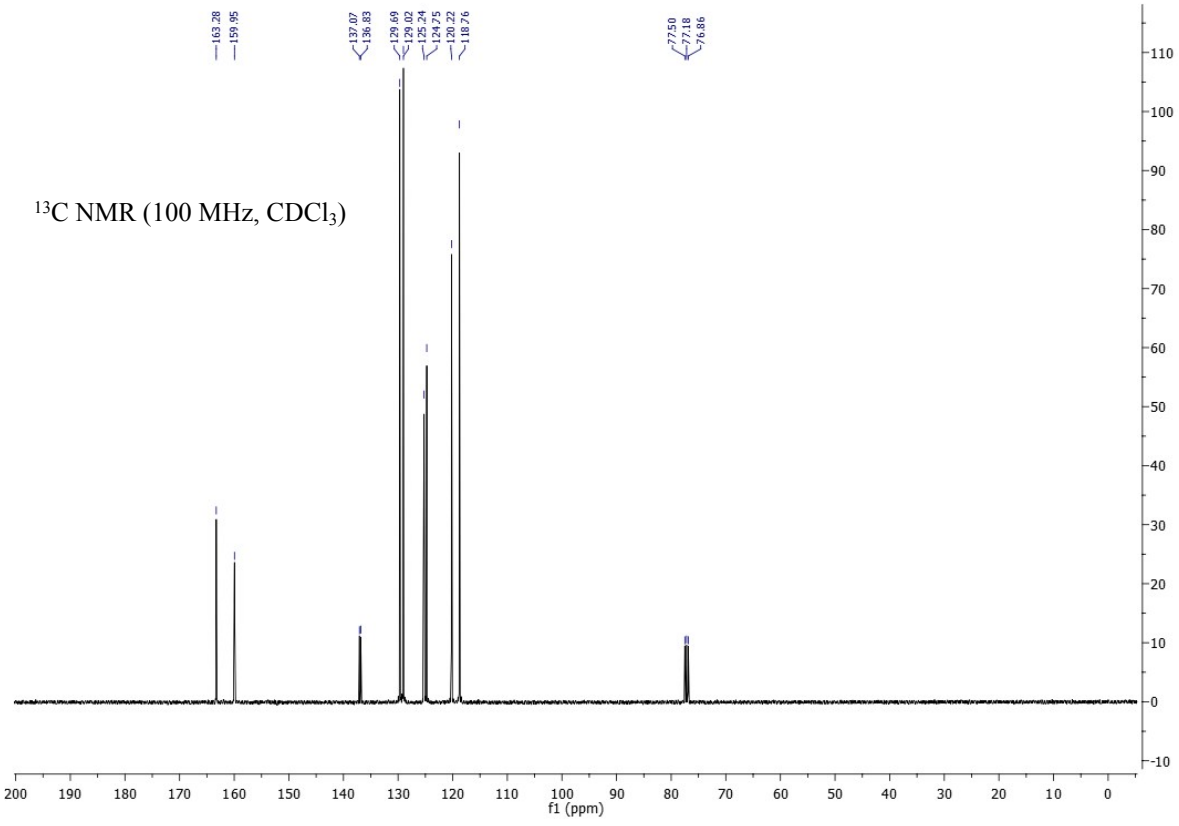




^{1}H NMR (400 MHz, $CDCl_3$)

Table 3, entry 26

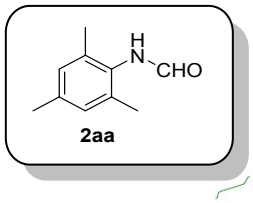
2z



^{13}C NMR (100 MHz, $CDCl_3$)

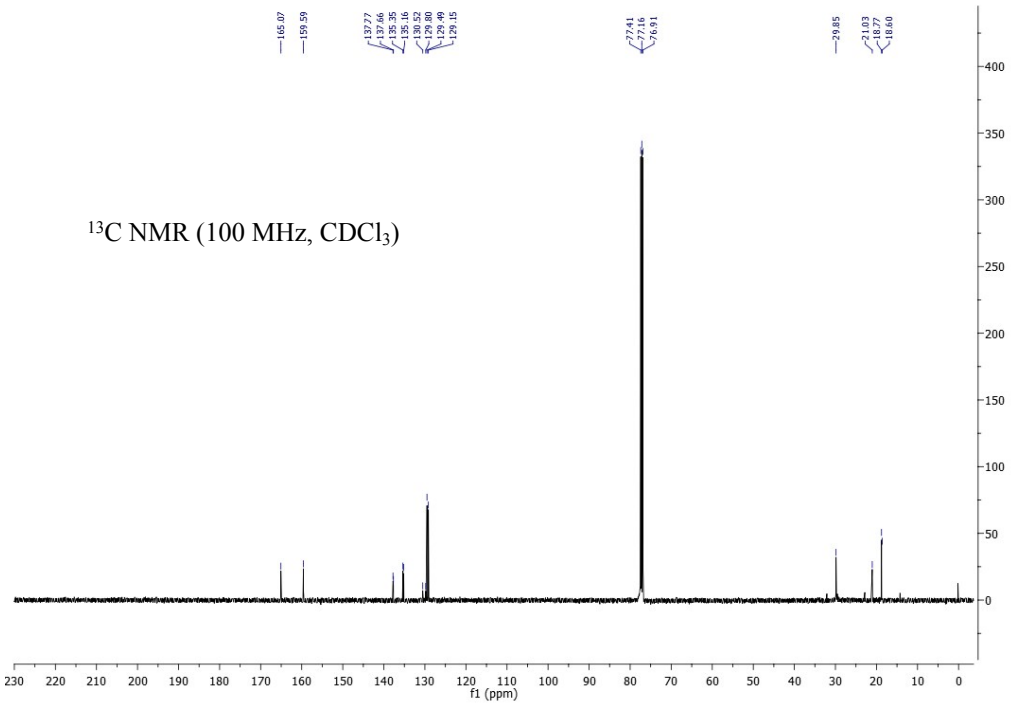
^{1}H NMR (500 MHz, $CDCl_3$)

Table 3, entry 27



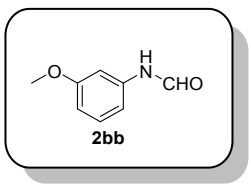
2aa

^{13}C NMR (100 MHz, $CDCl_3$)



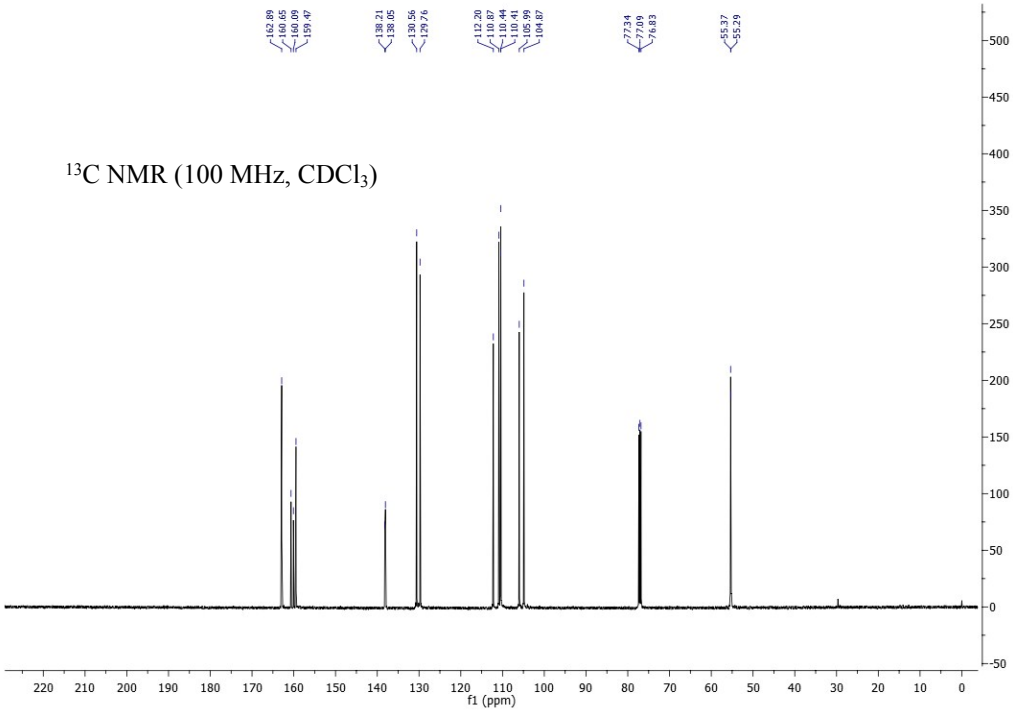
^{1}H NMR (500 MHz, $CDCl_3$)

Table 3, entry 28



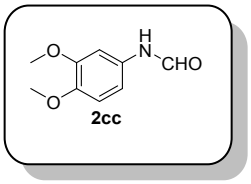
2bb

^{13}C NMR (100 MHz, $CDCl_3$)



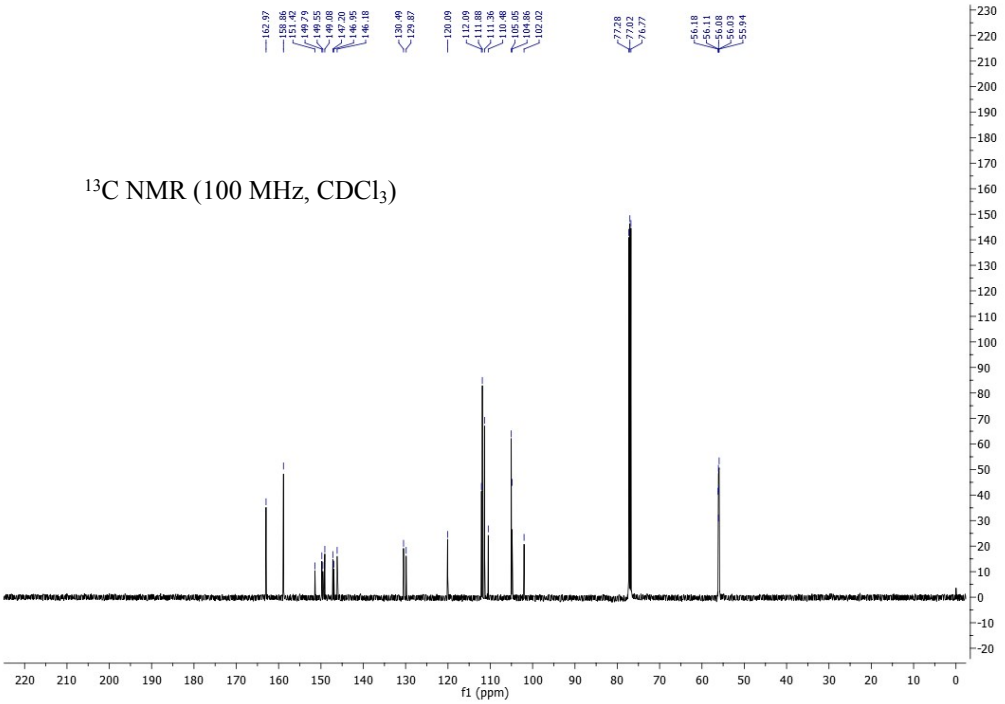
^{1}H NMR (500 MHz, $CDCl_3$)

Table 3, entry 29



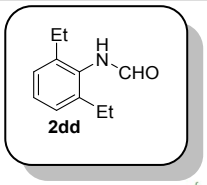
2cc

^{13}C NMR (100 MHz, $CDCl_3$)



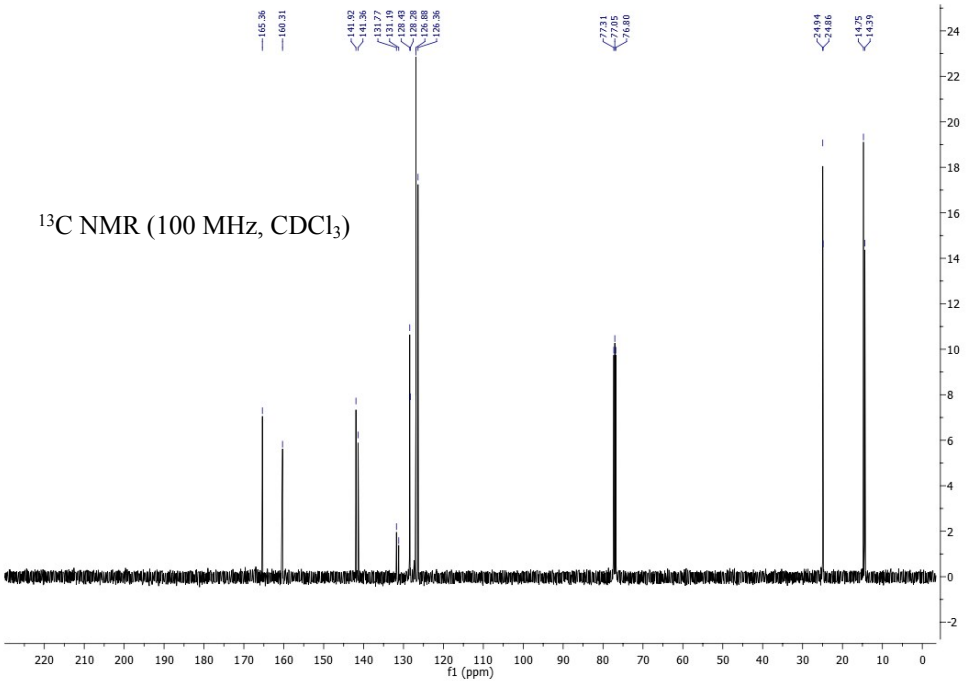
^{1}H NMR (500 MHz, $CDCl_3$)

Table 3, entry 30



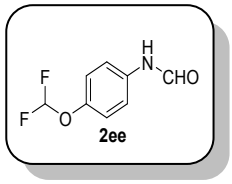
2dd

^{13}C NMR (100 MHz, $CDCl_3$)



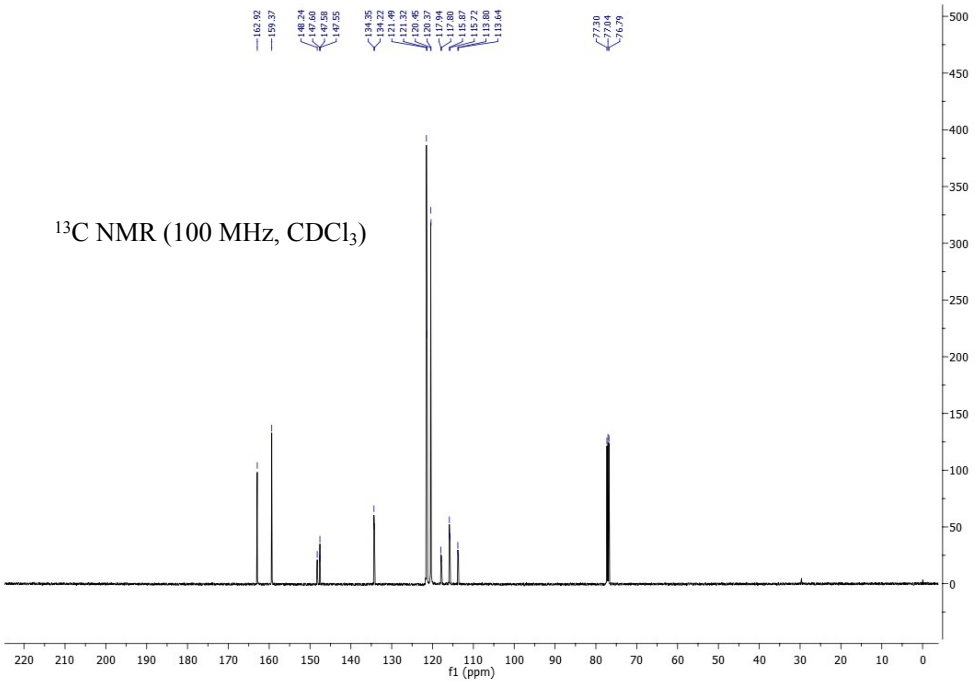
^{1}H NMR (500 MHz, $CDCl_3$)

Table 3, entry 31



2ee

^{13}C NMR (100 MHz, $CDCl_3$)



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