Transamidation catalysed by magnetically separable Fe_3O_4 nano catalyst under solvent-free condition.

Pranila B. Thale[‡a], Pravin N. Borase[‡a] and Dr. Ganapati S. Shankarling*[a].
[a]Dyestuff technology Department, Institute of Chemical Technology, Mumbai 400019, India.
Tel: 91-22-33612708, Fax: +91-22-33611020
E-mail address: gsshankarling@gmail.com

Supporting Information

1. General experimental procedure:

1.1 Materials and Methods:

The catalyst ZnO, MgO and Al_2O_3 were procured from S.D. Fine chemicals Ltd, Mumbai, India. All the commercially available chemicals and regents were used without further purification. The progress of the reaction was monitored by thin layer chromatography. All the products were purified by column chromatography using hexane: ethyl acetate as eluent. TEM images of the catalyst were taken on Philips CM 200 kV instrument. SEM micrographs were obtained on JEOL JSM-7600F model instrument. The XRD study was performed on a Shimadzu XRD-6100 with Cu-kα (1.54˚A). ^{1}H NMR spectra were recorded on Agilent 500 MHz spectrometer in $CDCl_3$ solvent. Mass spectral data were acquired from a Finnigan LCQ Advantage max spectrometer. The IR spectra of the synthesized compound were recorded on Jasco FT-IR ATR-PRO/4100 spectrophotometer.

1.2 General procedure for synthesis of the Fe_3O_4 catalyst:

The Fe_3O_4 nano catalyst was prepared according to previously reported literature method[1].A mixture of 5.0 g of ferric chloride and 1.85 g of ferrous chloride salts were dissolved in distilled water and heated at 90˚C for 1 h under nitrogen atmosphere. The solution turned brown. Then, the aqueous solution of ammonia (25%) was added in a drop wise manner over a period of 30 min. The mixture was cooled to room temperature and magnetic nano particles were collected with magnet. It was rinsed thoroughly with distilled water to remove excess of ammonia and then with acetone.

2. X-ray diffraction spectra: The catalyst was characterised by X-ray diffractometer scanning rate of 2°/min and 2 theta angle ranging from 20°-60° with current 30mA and 40kV voltage.

3. Spectroscopic data for compounds:

(2a) *N*-benzylbenzamide: m.p. 96˚C; IR (in cm^{-1}): 3276, 3033, 1633 ; ^{1}H NMR (δ in ppm, $CDCl_3$) (500 MHz): 7.80 (2H, d, aromatic CH), 7.52-7.49 (1H, m, aromatic CH), 7.45-7.42 (2H, m, aromatic CH), 7.37-7.29 (5H, m, aromatic CH), 6.42 (1H, s, NH), 4.66 (2H, d); m/z (EI) 211 (M^+); $C_{14}H_{12}FNO$ calculated m/z: 211.

(2b) *N*-(4-methoxybenzyl)benzamide: m.p. 96°C; IR (in cm^{-1}): 3227, 3069, 1628; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 7.79-7.77 (2H, m, aromatic CH), 7.51-7.48 (1H, m, aromatic CH), 7.44-7.41 (2H, m, aromatic CH), 7.30 (2H, d, J = 8.6 Hz), 6.89 (2H, d, J = 8.6 Hz), 6.32 (1H, s, NH), 4.59 (2H, d), 3.81 (3H, s); m/z (EI) 241 (M^+); $C_{15}H_{15}NO_2$ calculated m/z: 241.

(2c) *N*-(4-fluorobenzyl)benzamide: m.p. 114°C; IR (in cm^{-1}): 3289, 3061, 1634; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 7.80- 7.78 (2H, m, aromatic CH), 7.52 (1H, t, *J* = 7.5, aromatic CH), 7.44 (2H, t, *J* = 7.5 aromatic CH), 7.35-7.27 (2H, m, aromatic CH), 7.06-7.03 (2H, m, aromatic CH), 6.39 (1H, s, NH), 4.62 (2H, d); m/z (EI) 229 (M^+); $C_{14}H_{12}FNO$ calculated m/z: 229.

(2d) *N*-dodecylbenzamide: m.p. 55°C; IR (in cm^{-1}): 3338, 3042, 1629; m/z (EI) 289 (M^+); $C_{19}H_{31}NO$ calculated m/z: 289.

(2e) *N*-phenethylbenzamide: m.p. 114°C; IR (in cm^{-1}): 3335, 3019, 1632; m/z (EI) 225 (M^+); $C_{15}H_{15}NO$ calculated m/z: 225.

(2f) *(S)*-*N*-(1-phenylethyl)benzamide: m.p. 116°C IR (in cm^{-1}): 3328, 3025, 1632 ; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 7.78 (2H, d, *J* = 7.5 Hz, aromatic CH), 7.50 (1H, t, *J* = 7.5 Hz, aromatic CH), 7.44-7.35 (6H, m, aromatic CH), 7.30-7.29 (1H, m, aromatic CH), 6.31 (s, 1H, NH), 5.35 (1H, p, *J* = 7 Hz), 1.62 (3H, d, *J* = 7 Hz); m/z (EI) 225 (M^+); $C_{15}H_{15}NO$ calculated m/z: 225.

(2g) *N*-butylbenzamide: m.p. 39°C; IR (in cm^{-1}): 3309, 3066, 1635; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 7.76-7.48(2H, m, aromatic CH), 7.49-7.46 (1H, m, aromatic CH), 7.42-7.39 (2H, m, aromatic CH), 6.25 (1H, S), 3.44 (2H, q), 1.59 (2H, p), 1.41 (2H, sex) 0.95 (3H, t); m/z (EI) 177 (M^+); $C_{15}H_{15}NO$ calculated m/z: 177.

(2h) *N*-phenylbenzamide: m.p. 162°C; IR (in cm^{-1}): 3334, 3036, 1648; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 7.89-7.87 (2H, m, aromatic CH), 7.84 (1H, s, NH), 7.65 (2H, d, *J* = 7.5 Hz, aromatic CH), 7.56 (2H, t, *J* = 7.5 Hz, aromatic CH), 7.49 (2H, t, *J* = 7.5 Hz, aromatic CH), 7.38 (2H, t, aromatic CH), 7.16 (1H, t, *J* = 7.5 Hz, aromatic CH); m/z (EI) 197 (M^+); $C_{13}H_{11}NO$ calculated m/z: 197.

(2i) *N*-(p-tolyl)benzamide: m.p. 156°C; IR (in cm^{-1}): 3309, 3074, 1647; m/z (EI) 211 (M^+); $C_{13}H_{11}NO$ calculated m/z: 211.

(3a) *N*-benzylacetamide: m.p. 62°C; IR (in cm^{-1}): 3279, 3088, 1619; m/z (EI) 149 (M^+); $C_9H_{11}NO$ calculated m/z: 149.

(3b) *N*-(4-methoxybenzyl)acetamide: m.p. 95°C; IR (in cm^{-1}): 3279, 3091, 1619; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 7.22- 7.20 (2H, m, aromatic CH), 6.87-6.86 (2H, m, aromatic CH), 5.70 (1H, s, NH), 4.35 (2H, d), 3.80 (3H, s), 2.01 (3H, s); m/z (EI) 179 (M^+); $C_{10}H_{13}NO_2$ calculated m/z: 179.

(3c) *N*-(4-fluorobenzyl)acetamide: m.p. 96°C; IR (in cm^{-1}): 3278, 1632, 3069 ; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 7.26- 7.23 (2H, m, aromatic CH), 7.01 (2H, t , *J* = 8.5, aromatic CH), 5.82 (1H, s, NH), 4.39 (2H, d), 2.02 (3H, s); m/z (EI) 167 (M^+); $C_9H_{10}FNO$ calculated m/z: 167.

(3d) *N*-benzylformamide: m.p. 63˚C

(3e) *N*-(4-methoxybenzyl)formamide: m.p. 78˚C

(3f) *N*-(4-fluorobenzyl)formamide: m.p. 59˚C

(4a) 2-benzylisoindoline-1,3-dione: m.p. 133˚C; IR (in cm^{-1}): 3440, 1693, 3047 ; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 7.86- 7.84 (2H, m, aromatic CH), 7.72-7.70 (2H, m, aromatic CH), 7.44(2H, d, J = 8.5, aromatic CH), 7.33-7.27 (3H, m, aromatic CH), 4.85 (2H, s); m/z (EI) 237 (M^+); $C_{15}H_{11}NO_2$ calculated m/z: 237.

(4b) 2-(4-methoxybenzyl) isoindoline-1,3-dione: m.p. 130˚C; IR (in cm^{-1}): 3435, 3050, 1604; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 7.84- 7.82 (2H, m, aromatic CH), 7.70-7.68 (2H, m, aromatic CH), 7.39 (2H, d, J = 8.5, aromatic CH),6.84 (2H, d, J = 8.5 Hz, aromatic CH), 4.79 (2H, s), 3.77 (3H,s); m/z (EI) 267 (M^+); $C_{16}H_{13}NO_3$ calculated m/z: 267.

(4c) 2-(4-fluorobenzyl) isoindoline-1,3-dione: m.p. 132˚C; IR (in cm^{-1}):3454, 3050, 1690; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 7.86- 7.84 (2H, m, aromatic CH), 7.72-7.70 (2H, m, aromatic CH), 7.44-7.41 (2H, m, aromatic CH), 7.01-6.98 (2H, m, aromatic CH), 4.81(1H, s); m/z (EI) 255 (M^+); $C_{16}H_{13}NO_2$ calculated m/z: 255.

(4d) 2-phenethylisoindoline-1,3-dione: : m.p. 130˚C; IR (in cm^{-1}): 3440, 3019, 1697 ; m/z (EI) 251 (M^+); $C_{16}H_{13}NO_2$ calculated m/z: 251.

(4e) 2-butylisoindoline-1,3-dione : m.p. 28˚C; IR (in cm^{-1}): 3469, 3050, 1611; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 7.81- 7.80 (2H, m, aromatic CH), 7.69- 7.67 (2H, m, aromatic CH), 3.66 (2H, t, J = 7.5Hz), 1.66-1.60 (2H, m, J = 7.5Hz), 1.38-1.30(2H, m, J = 7.5Hz), 0.92 (3H, t, J = 7.5Hz); m/z (EI) 203 (M^+); $C_{12}H_{13}NO_2$ calculated m/z: 203.

(4f) 2-(cyclohexylmethyl)isoindoline-1,3-dione: m.p. 168˚C; IR (in cm^{-1}): 3450, 1691, 3074 ; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 7.82- 7.80 (2H, m, aromatic CH), 7.70-7.67 (2H, m, aromatic CH), 4.11 (1H, tt), 2.21 (2H, qd), 1.88-1.85 (2H, m), 1.74-1.71 (3H, m), 1.41-1.26 (3H, m); m/z (EI) 229 (M^+); $C_{15}H_{17}NO_2$ calculated m/z: 229.

(5a) *N*-benzylformamide: m.p. 63˚C; IR (in cm^{-1}): 3270, 3042, 1637; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 8.26 (1H, s, aromatic CH), 7.38-7.29 (5H, m, aromatic CH), 5.91 (1H, s, NH), 4.49 (2H, d); m/z (EI) 135 (M^+); C_8H_9NO calculated m/z: 135.

(5b) *N*-(4-fluorobenzyl)formamide: m.p. 59˚C; IR (in cm^{-1}): 3270, 3037, 1644; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 8.25(1H, s), 7.27-7.25 (2H, m, aromatic CH), 7.04-7.01 (2H, m, aromatic CH), 5.96 (1H, s), 4.45 (2H, d); m/z (EI) 153 (M^+); C_8H_8FNO calculated m/z: 153.

(5c) *N*-(4-methoxybenzyl) formamide: m.p. 78˚C; IR (in cm^{-1}): 3277, 3013, 1637; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 8.22 (1H, s, aromatic CH), 7.22-7.18 (2H, m, aromatic CH), 6.90-6.82 (2H, m, aromatic CH), 5.88 (1H, s), 4.41 (2H, d), 3.80 (3H, s); m/z (EI) 165 (M^+); $C_9H_{11}NO_2$ calculated m/z: 165.

(5d) *N*-(3-methoxybenzyl)formamide: Yellow liquid; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 8.23 (1H, S), 6.87-6.79 (4H, m, aromatic CH), 6.06 (1H, s), 4.44 (2H, d), 3.79

(3H, t); IR (in cm^{-1}): 3281, 3049, 1658; m/z (EI) 165 (M^+); $C_9H_{11}NO_2$ calculated m/z: 165.

(5e) (*S*)-*N*-(1-phenylethyl)formamide: Yellow liquid; IR (in cm^{-1}): 3267, 3036, 1653; m/z (EI) 149 (M^+); $C_9H_{11}NO$ calculated m/z: 149.

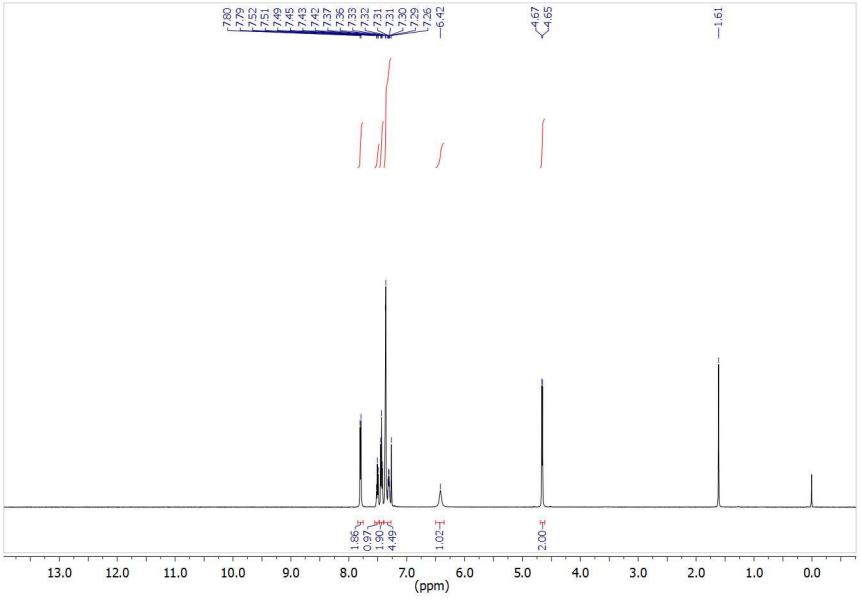
(5f) *N*-phenethylformamide: Yellow liquid; IR (in cm^{-1}): 3268, 3036, 1652; m/z (EI) 149 (M^+); $C_9H_{11}NO$ calculated m/z: 149.

(5g) *N*-dodecylformamide: m.p. 28-30°C; IR (in cm^{-1}): 3287, 3034, 1638 ; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 8.16 (1H, s), 5.59 (1H, s, NH), 3.29 (2H, q), 1.52 (2H, p), 1.28-1.25 (18H, m), 0.88 (3H, t); m/z (EI) 212 (M-1); $C_{13}H_{27}NO$ calculated m/z: 213.

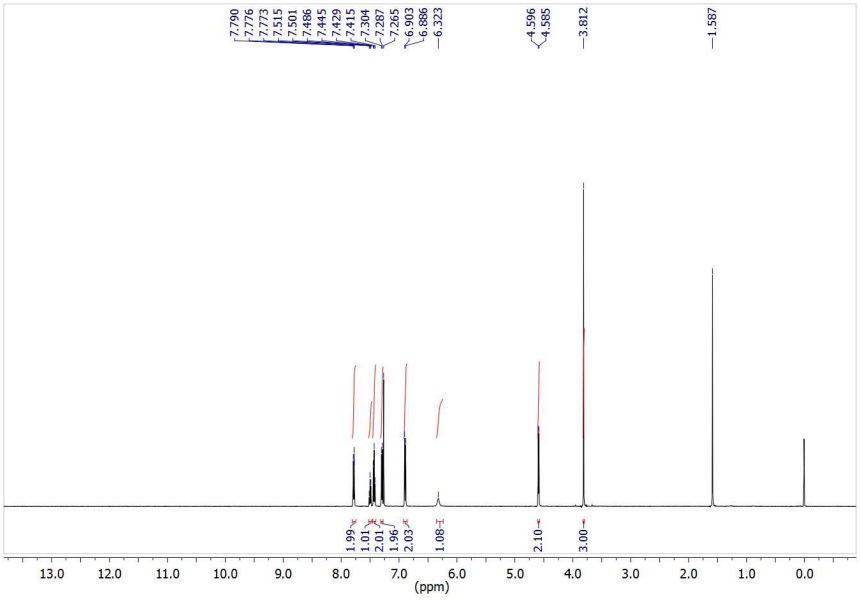
(5h) *N*-(4-cyanobenzyl)formamide: m.p. 127°C; IR (in cm^{-1}): 3271, 3033, 2219, 1644 ; ^1H NMR (δ in ppm, $CDCl_3$) (500 MHz): 8.33 (1H, s), 7.63 (2H, m, J = 8.0 Hz, aromatic CH), 7.41 (2H, m, J = 8.0 Hz, aromatic CH), 5.99 (1H, s), 4.56 (2H, d), m/z (EI) 160 (M^+); $C_9H_8N_2O$ calculated m/z: 160.

4. ^{1}HNMR of compounds:

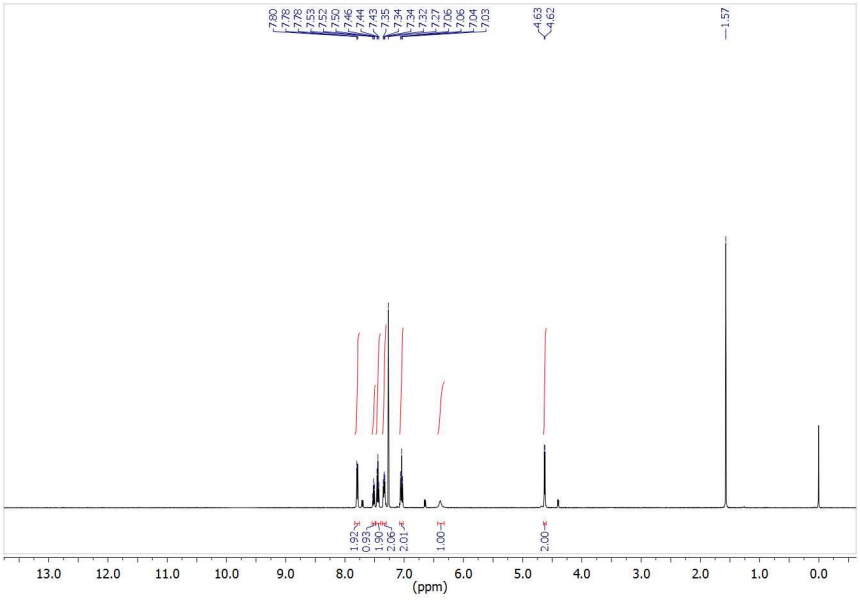
2a) *N*-benzylbenzamide:



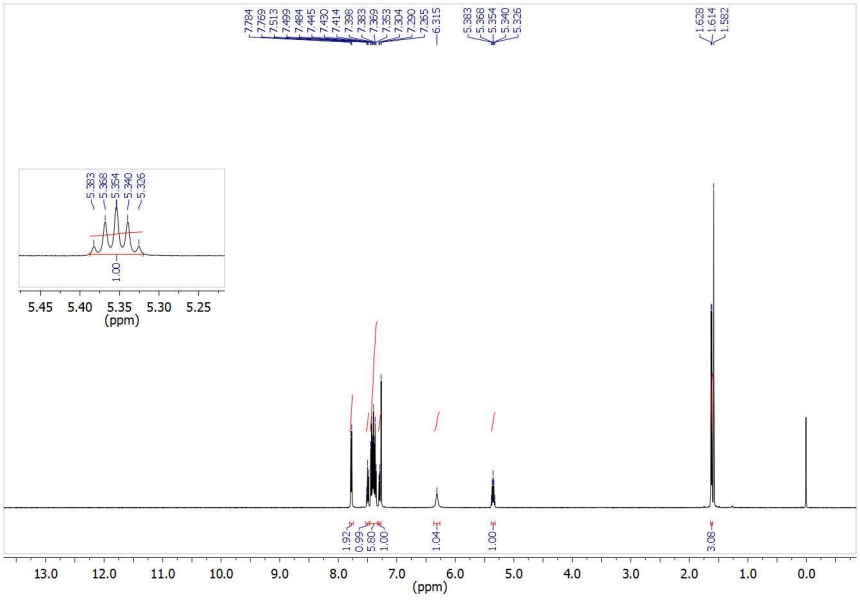
2b) *N*-(4-methoxybenzyl)benzamide:



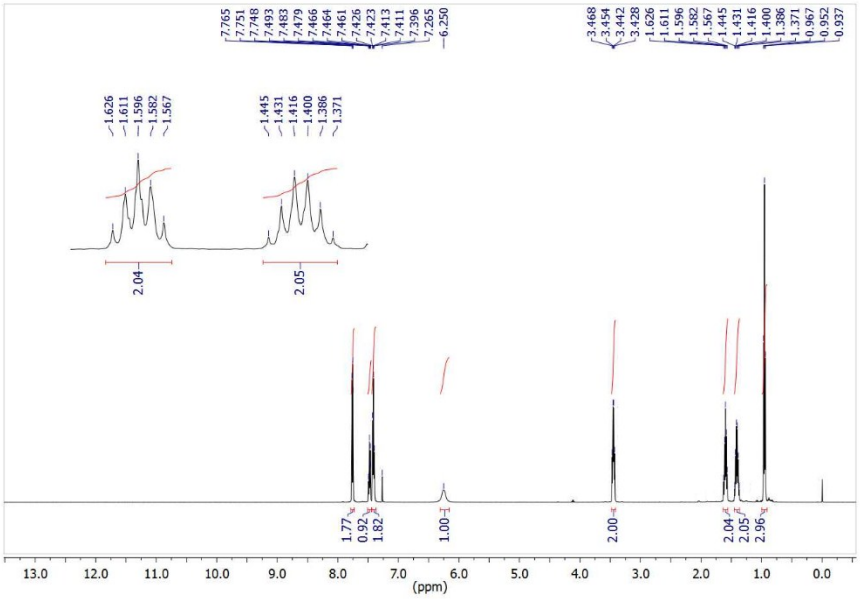
2c) *N*-(4-fluorobenzyl)benzamide:



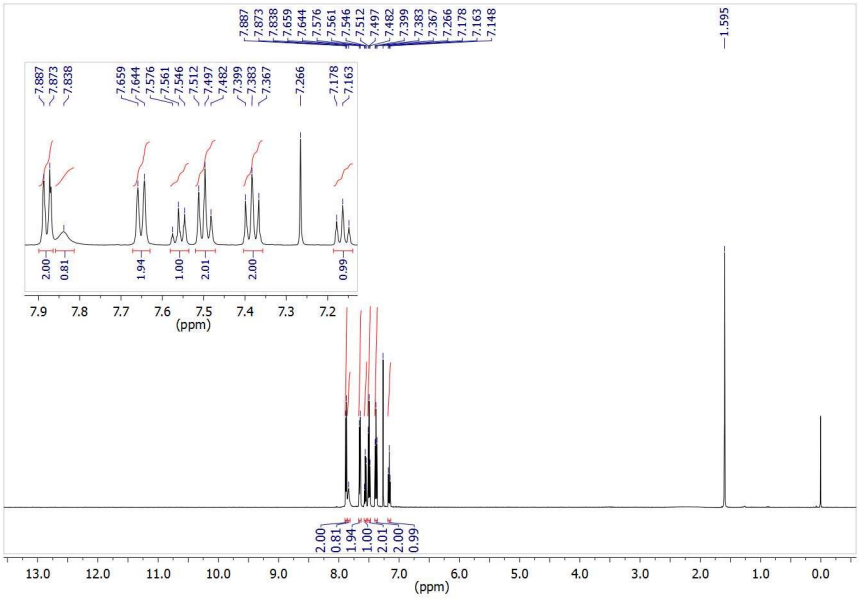
2f) *(S)-N*-(1-phenylethyl)benzamide:



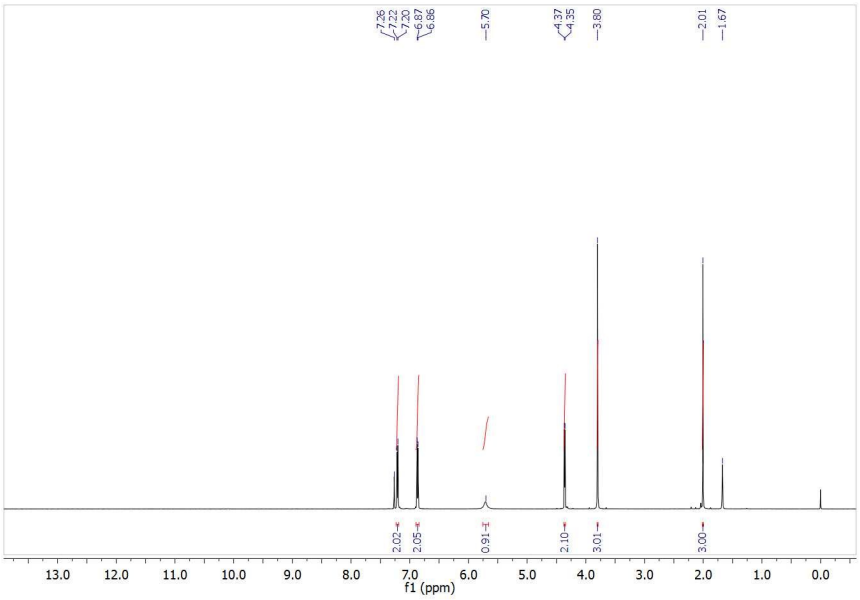
2g) *N*-butylbenzamide:



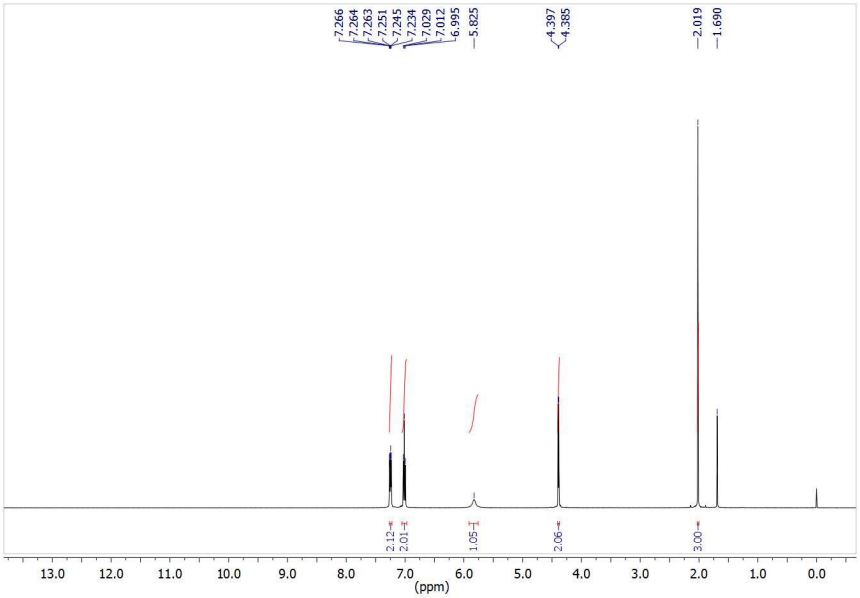
2h) *N*-phenylbenzamide:



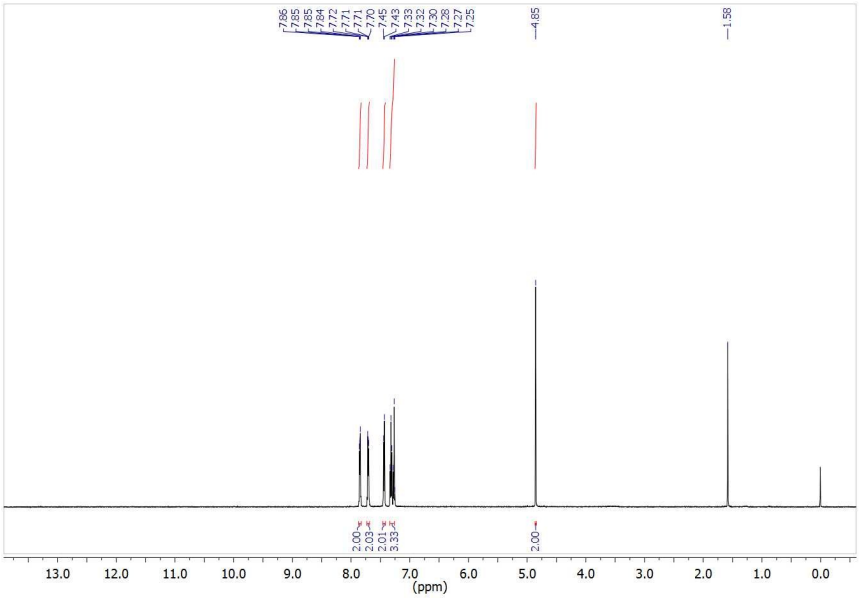
3b) *N*-(4-methoxybenzyl)acetamide:



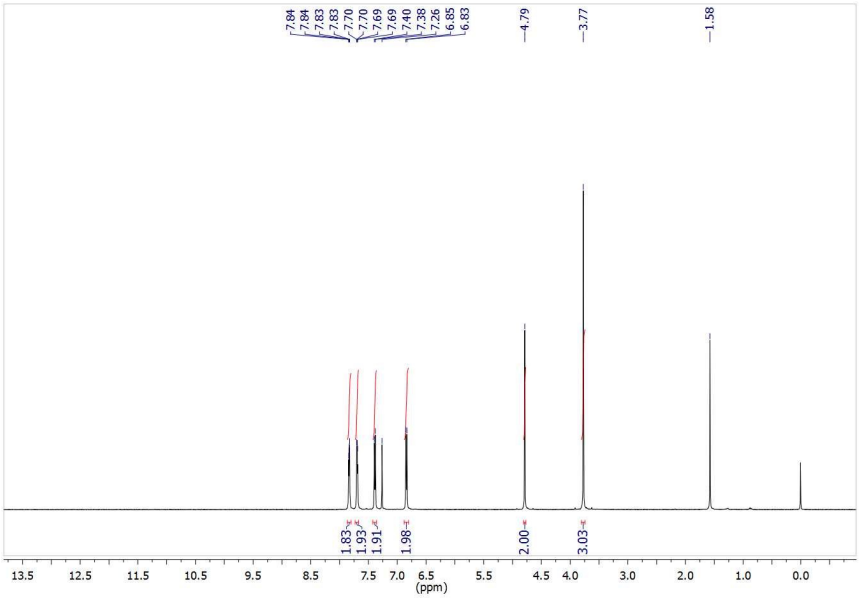
3c) *N*-(4-fluorobenzyl)acetamide:



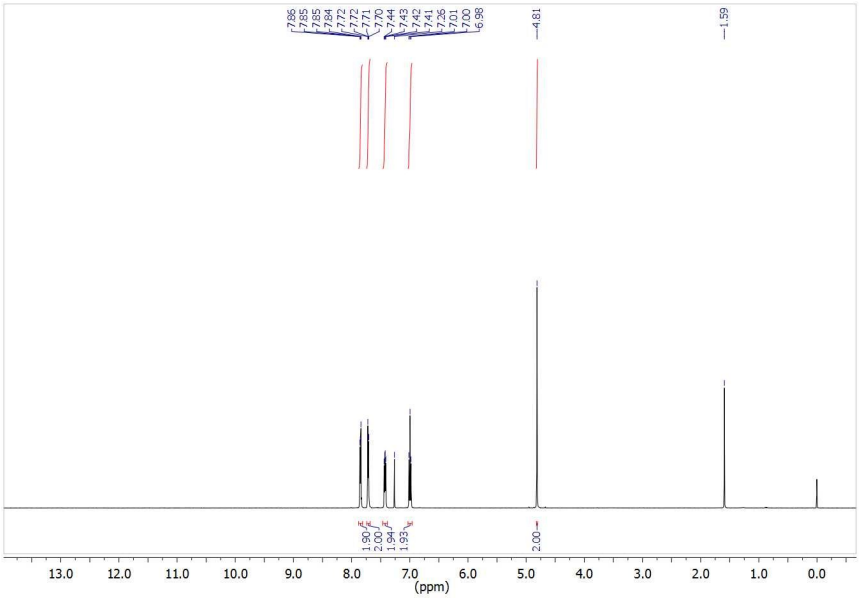
4a) 2-benzylisoindoline-1,3-dione:



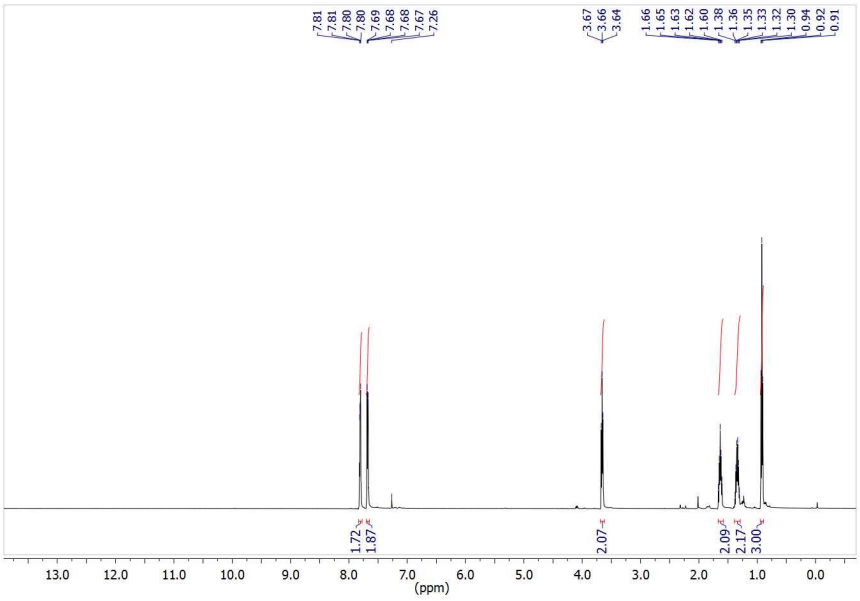
4b) 2-(4-methoxybenzyl) isoindoline-1,3-dione:



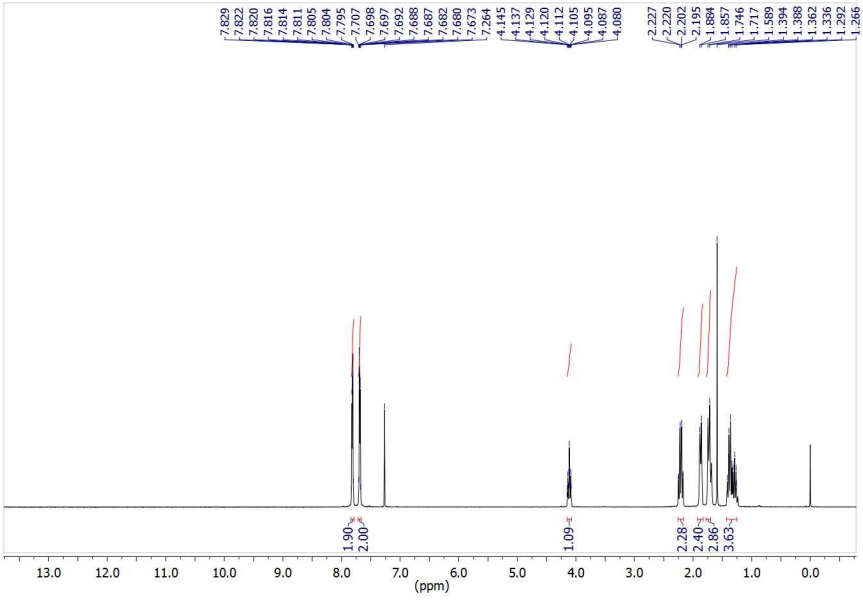
4c) 2-(4-fluorobenzyl) isoindoline-1,3-dione:



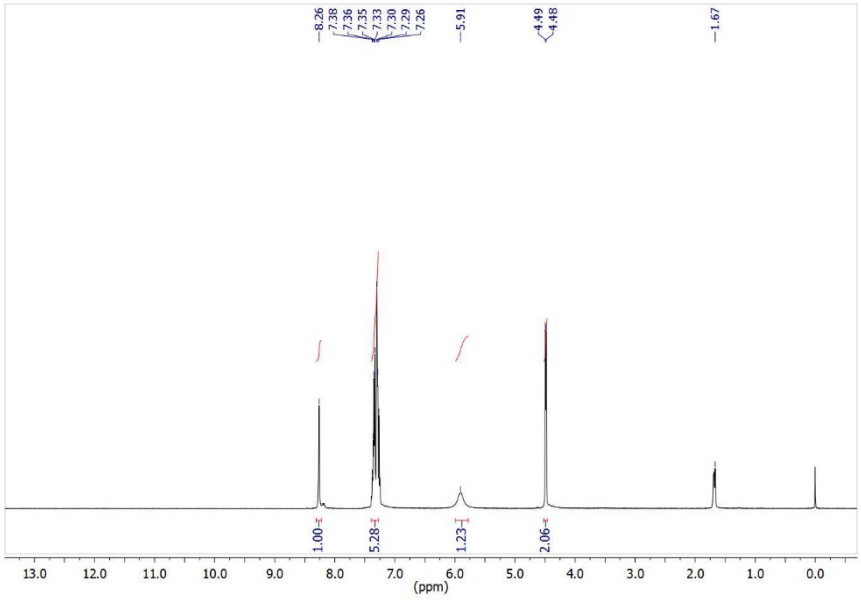
4e) 2-butylisoindoline-1,3-dione :



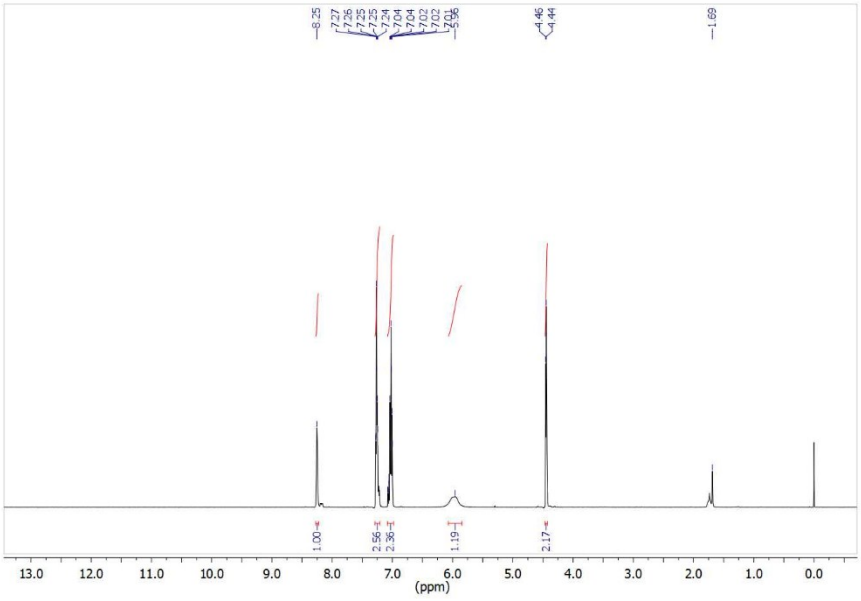
4f) 2-(cyclohexylmethyl)isoindoline-1,3-dione:



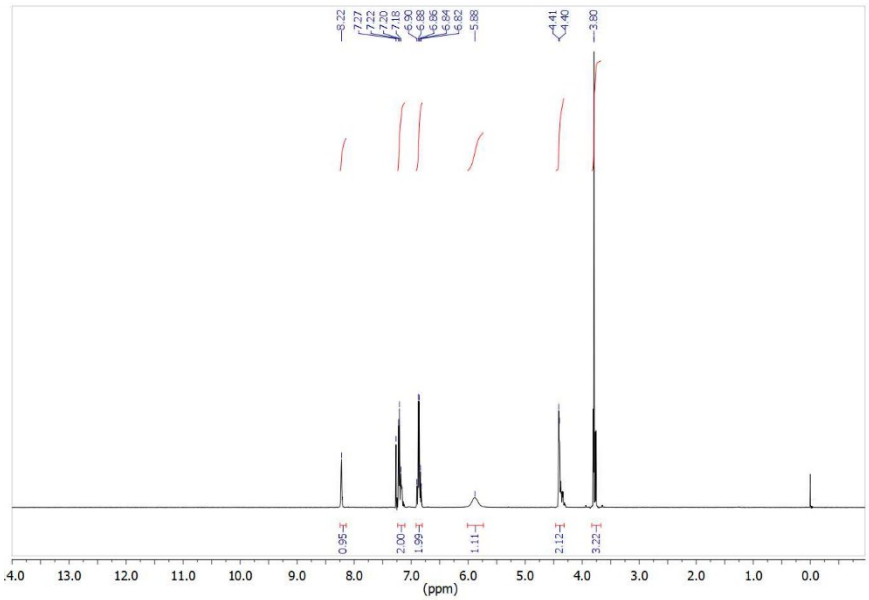
5a) *N*-benzylformamide:



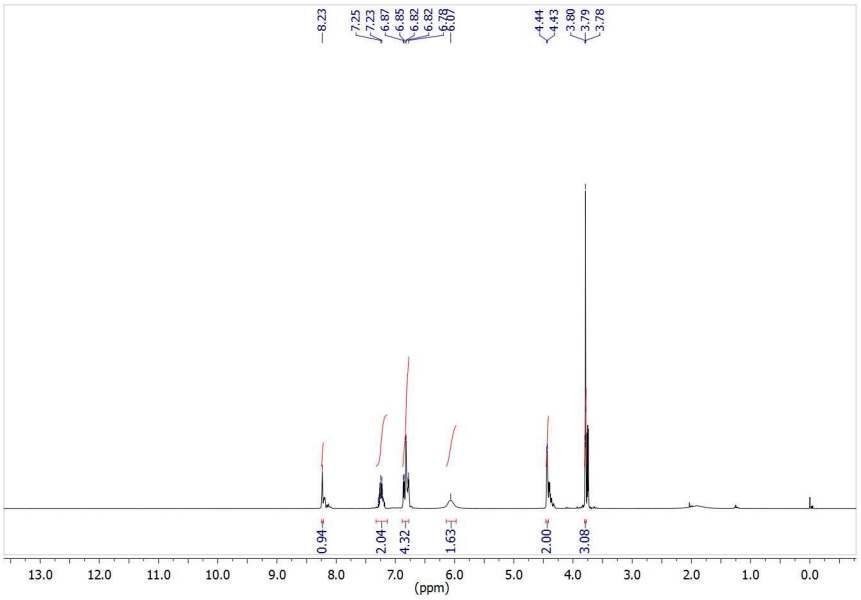
5b) *N*-(4-fluorobenzyl)formamide:



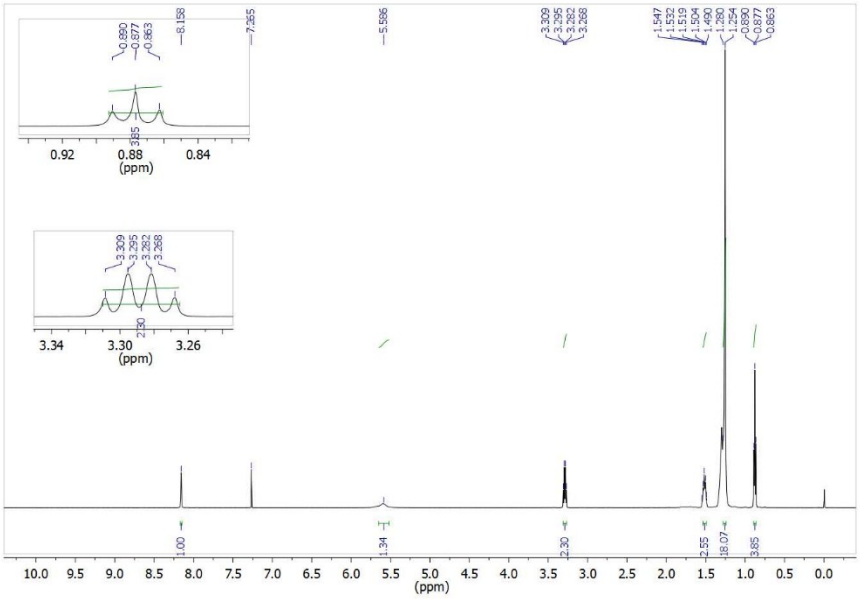
5c) *N*-(4-methoxybenzyl) formamide:



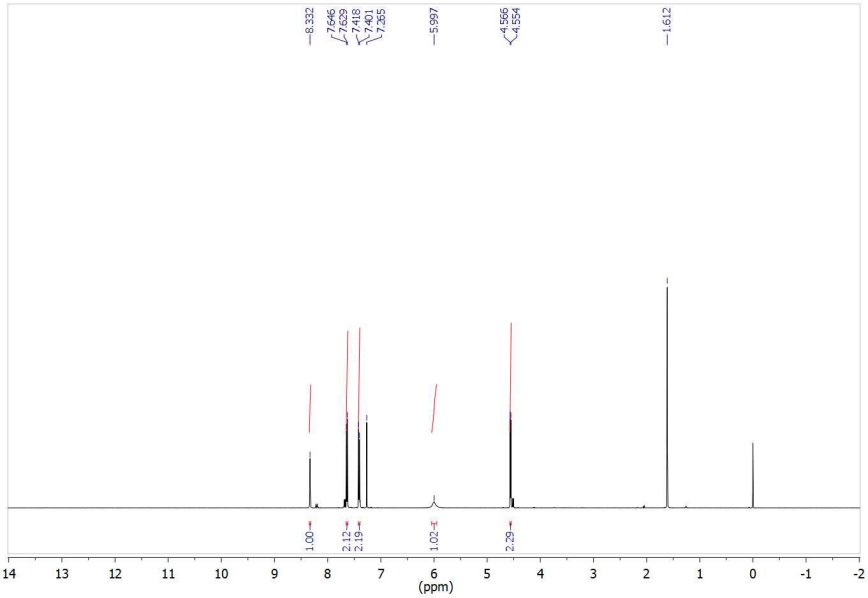
5d) *N*-(3-methoxybenzyl)formamide:



5g) *N*-dodecylformamide:



5h) *N*-(4-cyanobenzyl)formamide:



Reference:

1) F. Nemati, M. Heravi, and R. S. RAD, Chinese J. Catal., 2012, **33**, 1825–1831.