Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Choline chloride based eutectic solvents: Direct C-3 alkenylation/alkylation of indoles with 1,3-dicarbonyl compounds

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Spectroscopic data for 3b-3n

(*E*)-3-(2-Methyl-1*H*-indol-3-yl)-1,3-diphenylprop-2-en-1-one (3b)

Orange solid, mp 192-194 ^{o}C; IR υ = 2910, 2852, 1626, 1592, 1551, 1459, 1223, 1210, 769 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.05 (s, 3H, CH_3), 6.67 (d, 1H, C7'-H, *J* = 8 Hz), 6.75 (t, 1H, PhH, *J* = 7 Hz), 6.93 (t, 1H, *J* = 7 Hz, PhH), 7.11 (s, 1H, C2-H), 7.18 (d, 1H, *J* = 8 Hz), 7.27 (t, 2H, PhH, *J* = 8 Hz), 7.36-7.46 (m, 6H, PhH), 7.77 (d, 2H, *J* = 8 Hz), 11.15 (bs, 1H, NH); ESI-MS: *m/z* calculated for $C_{24}H_{19}NO$ 337.41, found $[M+H]^+$ 338.2

3-(2-Methyl-1*H*-indol-3-yl)cyclohex-2-enone (3c)

Pink solid, mp 199-200 ^{o}C; IR υ = 3179, 2934, 2861, 1629, 1614, 1557, 1455, 1251, 1165, 741 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 2.17 (quintet, 2H, CH_2, *J* = 7 Hz), 2.52-2.56 (m, 5H, CH_3 & CH_2), 2.90 (t, 2H, CH_2, *J* = 7 Hz), 6.24 (apparent triplet, 1H, CH), 7.10-7.20 (m, 2H, C5'-H & C6'-H), 7.32 (dd, 1H, C7'-H, *J* = 2 & 8 Hz), 7.68 (dd, 1H, C4'-H, *J* = 2 & 8 Hz), 8.58 (bs, 1H, NH); ESI-MS: *m/z* calculated for $C_{15}H_{15}NO$ 225.29, found $[M+H]^+$ 226.3

5,5-Dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclohex-2-enone (3d)

Pale yellow solid, mp 195-196 ^{o}C; IR υ = 3213, 2965, 2862, 1626, 1615, 1568, 1455, 1243, 1144, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.17 (s, 6H, 2xCH_3), 2.39 (s, 2H, CH_2CO), 2.53 (s, 3H, CH_3), 2.79 (s, 2H, CH_2), 6.22 (s, 1H, CH), 7.11-7.20 (m, 2H, C5'-H & C6'-H), 7.32 (dd, 1H, C7'-H, *J* = 2 & 8.1 Hz), 7.67 (dd, 1H, C4'-H, *J* = 2 & 8 Hz), 8.54 (bs, 1H, NH); ESI-MS: *m/z* calculated for $C_{17}H_{19}NO$ 253.34, found $[M+H]^+$ 254.3

(*E*)-Methyl 3-(2-methyl-1*H*-indol-3-yl)but-2-enoate (3e)

White solid, mp 136-138 ^{o}C; IR υ = 3332, 2945, 2845, 1676, 1600, 1535, 1423, 1257, 1172, 736 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.49 (s, 3H, CH_3), 2.67 (d, 3H, CH_3, *J* = 1.5 Hz), 3.76 (s, 3H, OCH_3), 5.94 (q, 1H, C2-H, *J* = 1.5 Hz), 7.09-7.18 (m, 2H, C5'-H & C6'-H), 7.28 (dd, 1H, C7'-H, *J* = 2 & 8 Hz), 7.64 (dd, 1H, C4'-H, *J* = 2 & 8 Hz), 8.10 (bs, 1H, NH); ESI-MS: *m/z* calculated for $C_{14}H_{15}NO_2$ 229.27, found $[M+H]^+$ 230.1

(*E*)-Ethyl 3-(2-methyl-1*H*-indol-3-yl)but-2-enoate (3f)

Grey solid, mp 123-124 ^{o}C; IR υ = 3326, 2978, 2893, 1677, 1587, 1568, 1422, 1144, 741 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.33 (t, 3H, CH_3, *J* = 7 Hz), 2.51 (s, 3H, CH_3), 2.66 (d, 3H, CH_3, *J* = 0.4 Hz), 4.23 (q, 2H, CH_2, *J* = 7 Hz), 5.93 (d, 1H, C2-H, *J* = 0.4 Hz), 7.10-7.18 (m, 2H,

C5'-H & C6'-H), 7.29 (dd, 1H, C7'-H, *J* = 2 & 8 Hz), 7.65 (d, 1H, C4'-H, *J* = 8 Hz), 8.02 (bs, 1H, NH); ESI-MS: *m/z* calculated for $C_{15}H_{17}NO_2$ 243.30, found $[M+H]^+$ 244.2

(*E*)-*tert*-Butyl 3-(2-methyl-1*H*-indol-3-yl)but-2-enoate (3g)

Brown sticky mass.; IR υ = 2978, 1699, 1678, 1606, 1457, 1276, 1135, 739 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 1.54 (s, 9H, 3 x CH_3), 2.47 (s, 3H, CH_3), 2.61 (d, 3H, CH_3, *J* = 1.3 Hz), 5.85 (d, 1H, C2-H, *J* = 1.3 Hz), 7.10-7.17 (m, 2H, C5'-H & C6'-H), 7.27 (dd, 1H, C7'-H, *J* = 2 & 8 Hz), 7.63 (dd, 1H, C4'-H, *J* = 2 & 8 Hz), 8.06 (bs, 1H, NH); ESI-MS: *m/z* calculated for $C_{17}H_{21}NO_2$ 271.35, found $[M+H]^+$ 272.4

(*E*)-3-(2-Methyl-1*H*-indol-3-yl)-*N*-phenylbut-2-enamide (3h)

Yellow brown solid, mp 74-76 °C; IR υ = 3390, 3285, 2921, 2854, 1649, 1593, 1529, 1433, 1256, 1164, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 2.46 (s, 3H, CH_3), 2.60 (d, 3H, CH_3, *J* = 0.4 Hz), 6.15 (d, 1H, C2-H, *J* = 0.4 Hz), 6.99-7.07 (m, 3H, C5'-H & C6'-H), 7.27-7.31 (m, 3H, C7'-H, *J* = 2 & 8 Hz), 7.63 (d, 1H, C4'-H, *J* = 8 Hz), 7.67 (d, 2H, *J* = 8 Hz), 9.90 (bs, 1H, NH), 11.24 (bs,1H, NH); ESI-MS: *m/z* calculated for $C_{19}H_{18}N_2O$ 290.36, found $[M+H]^+$ 291.2

(*E*)-*N*-(2-Chlorophenyl)-3-(2-methyl-1*H*-indol-3-yl)but-2-enamide (3i)

Pink solid, mp 153-156 °C; IR υ = 3405, 3305, 3065, 2955, 1665, 1603, 1587, 1427, 1294, 1202, 1150, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 2.48 (s, 3H, CH_3), 2.61 (d, 3H, CH_3, *J* = 0.9 Hz), 6.31 (s, 1H, C2-H), 7.01-7.06 (m, 2H, C5'-H & C6'-H), 7.16 (td, 1H, C7'-H, *J* = 1.2 & 8 Hz), 7.30 (d, 1H, *J* = 8 Hz), 7.33 (dt, 1H, *J* = 2 & 8 Hz), 7.48 (dd, 1H, *J* = 8 & 1.4 Hz), 7.63 (d, 1H, *J* = 8 Hz), 7.83 (d, 1H, *J* = 7.1 Hz), 9.47 (bs, 1H, NH), 11.25 (bs, 1H, NH); ESI-MS: *m/z* calculated for $C_{19}H_{17}ClN_2O$ 324.80, found $[M+H]^+$ 325.6

(*E*)-4-(2-Methyl-1-propyl-1*H*-indol-3-yl)pent-3-en-2-one (3j)

White solid, mp 100-101 °C; IR υ = 2930, 2871, 1666, 1561, 1411, 1177, 747 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 0.98 (t, 3H, CH_3, *J* = 6.5 Hz), 1.78 (quintet, 2H, CH_2, *J* = 6.5 Hz), 2.28 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 2.64 (d, 3H, CH_3, *J* = 1.6 Hz), 4. 05 (t, 2H, *N*-CH_2, *J* = 6.5 Hz), 6.32 (s, 1H, C3-H), 7.11-7.19 (m, 2H, C5'-H & C6'-H), 7.29 (d, 1H, C7'-H, *J* = 7.8 Hz), 7.64 (d, 1H, C4'-H, *J* = 8 Hz); ESI-MS: *m/z* calculated for $C_{17}H_{21}NO$ 255.35, found $[M+H]^+$ 256.4

(*E*)-Methyl 3-(2-methyl-1-propyl-1*H*-indol-3-yl)but-2-enoate (3k)

Brown sticky mass; IR υ = 2965, 2874, 1707, 1608, 1465, 1412, 1232, 1136, 894, 739 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 0.93 (t, 3H, CH_3, *J* = 7 Hz), 1.71 (sextet, 2H, CH_2, *J* = 7 Hz), 2.48 (s, 3H, CH_3), 2.63 (d, 3H, CH_3, *J* = 1.2 Hz), 3.70 (s, 3H, OCH_3), 4.09-4.17 (t, 2H, *N*-CH_2, *J* = 7 Hz), 5.85 (d, 1H, C2-H, *J* = 1.2 Hz), 7.08 (dt, 1H, C5'-H, *J* = 1.6 & 8 Hz), 7.16 (dt, 1H, C6'-H, *J* = 1.6 & 8 Hz), 7.49 (d, 1H, C7'-H, *J* = 8 Hz), 7.59 (d, 1H, C4'-H, *J* = 8 Hz); ESI-MS: *m/z* calculated for $C_{17}H_{21}NO_2$ 271.35, found $[M+H]^+$ 272.5

(*E*)-4-(1-Butyl-2-methyl-1*H*-indol-3-yl)pent-3-en-2-one (3l)

Brown sticky mass; IR υ = 3052, 2958, 2922, 2868, 1671, 1580, 1566, 1464, 1413, 1236, 1090, 894, 739 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 0.96 (t, 3H, CH_3, *J* = 6.5 Hz), 1.41 (sextet, 2H, CH_2, *J* = 6.5 Hz), 1.74 (quintet, 2H, CH_2, *J* = 6.5 Hz), 2.28 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 2.64 (s, 3H), 4.08 (t, 2H, *N*-CH_2, *J* = 6.5 Hz), 6.32 (s, 1H, C3-H), 7.14 (t, 1H, C5'-H, *J* = 8 Hz), 7.18 (dt, 1H, C6'-H, *J* = 1.2 & 8 Hz), 7.28 (d, 1H, C7'-H, *J* = 8 Hz), 7.64 (d, 1H, C4'-H, *J* = 8 Hz); ESI-MS: *m/z* calculated for $C_{18}H_{23}NO$ 269.38, found $[M+H]^+$ 270.5

4,4-Di(1*H*-indol-3-yl)pentan-2-one (3m)

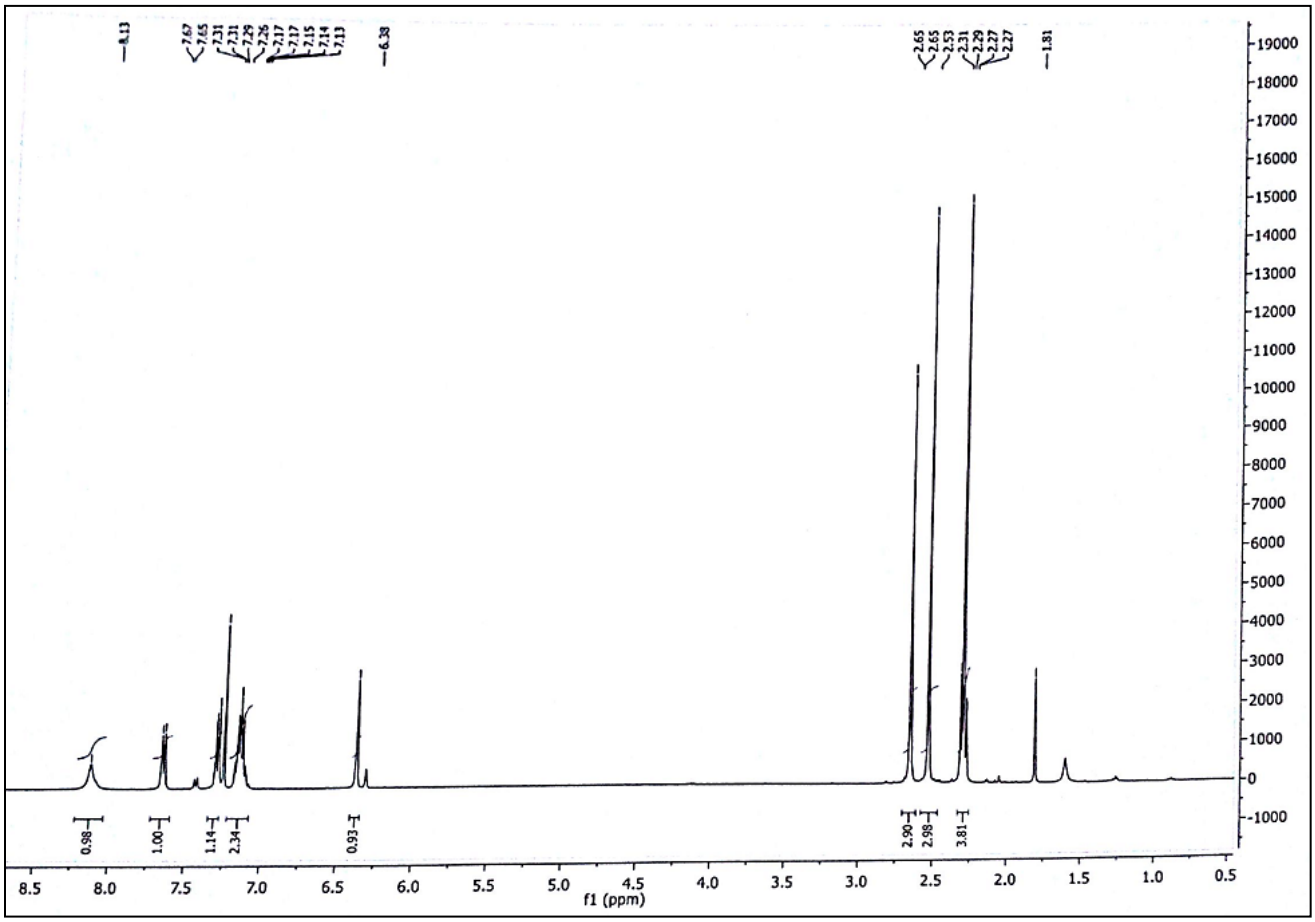
mp 231-233 ^oC; IR υ = 1698, 1609, 1575, 1513, 1352, 1252, 1192, 1132 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 1.84 (s, 3H, CH_3), 3.32 (s, 3H, CH_3), 3.41 (s, 2H, CH_2), 6.65 (dt, 2H, C5'-H, *J* = 1.2 & 7.3 Hz), 6.89 (dt, 2H, C6'-H, *J* = 1.2 & 7.3 Hz), 7.11 (d, 2H, C7'-H, *J* = 7.5 Hz), 7.25 (d, 2H, C4'-H, *J* = 7.5 Hz), 10.81 (bs, 2H, NH); ESI-MS: *m/z* calculated for $C_{21}H_{20}N_2O$ 316.40, found $[M+H]^+$ 317.5

Methyl 3,3-di(1*H*-indol-3-yl)butanoate (3n)

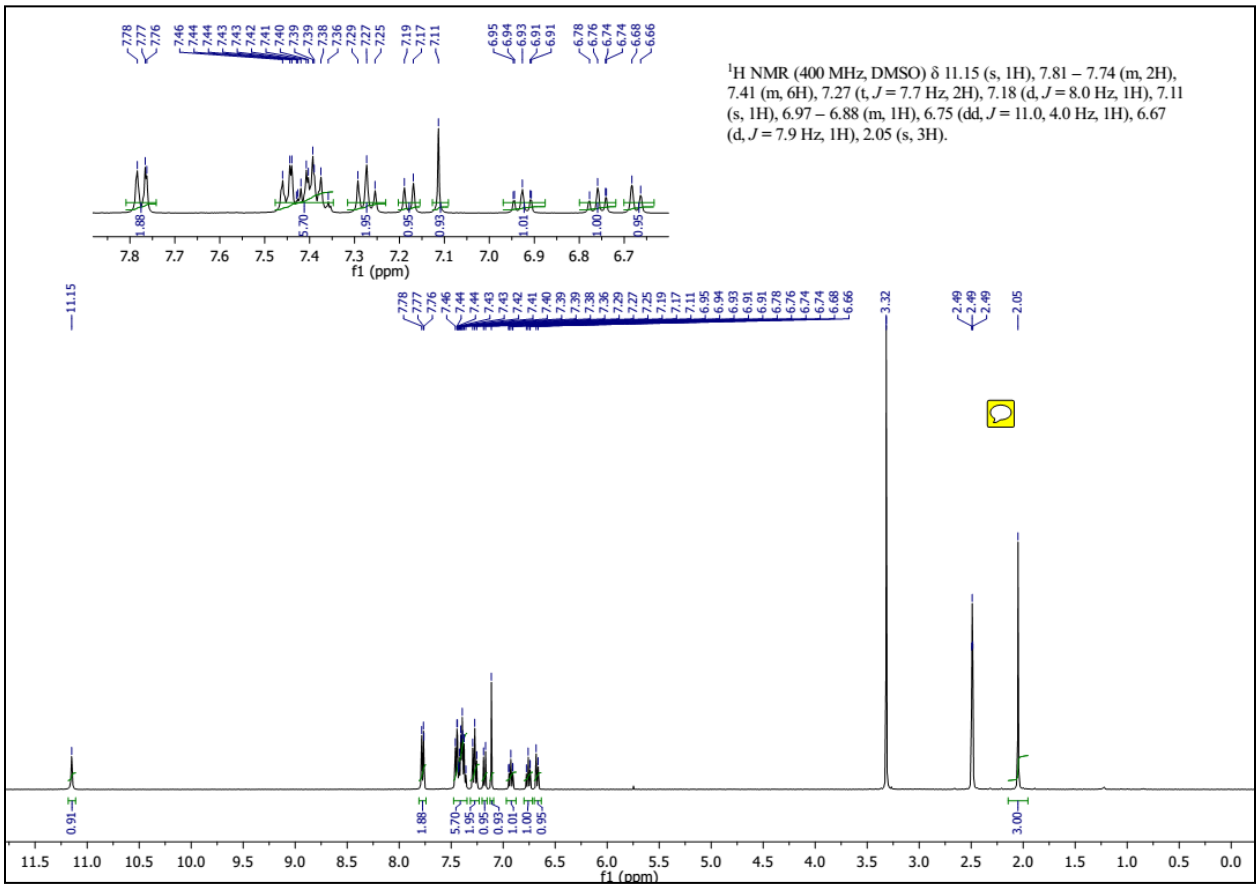
White solid, mp 180-181^oC; IR υ = 3052, 2958, 2822, 2868, 1671, 1580, 1566, 1464, 1413, 1236, 1090, 894, 739 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 1.95 (s, 3H, CH_3), 3.32 (s, 2H, CH_2), 3.36 (s, 3H, CH_3), 6.64 (t, 2H, C5'-H, *J* = 7.3 Hz), 6.90 (t, 2H, C6'-H, *J* = 7.3 Hz), 7.05 (d, 2H, C7'-H, *J* = 7.8 Hz), 7.28 (t, 2H, C4'-H, *J* = 7.8 Hz), 10.80 (s, 2H, NH); ESI-MS: *m/z* calculated for $C_{21}H_{20}N_2O_2$ 332.40, found $[M+H]^+$ 333.3

^{1}H NMR Data (3a-3n)

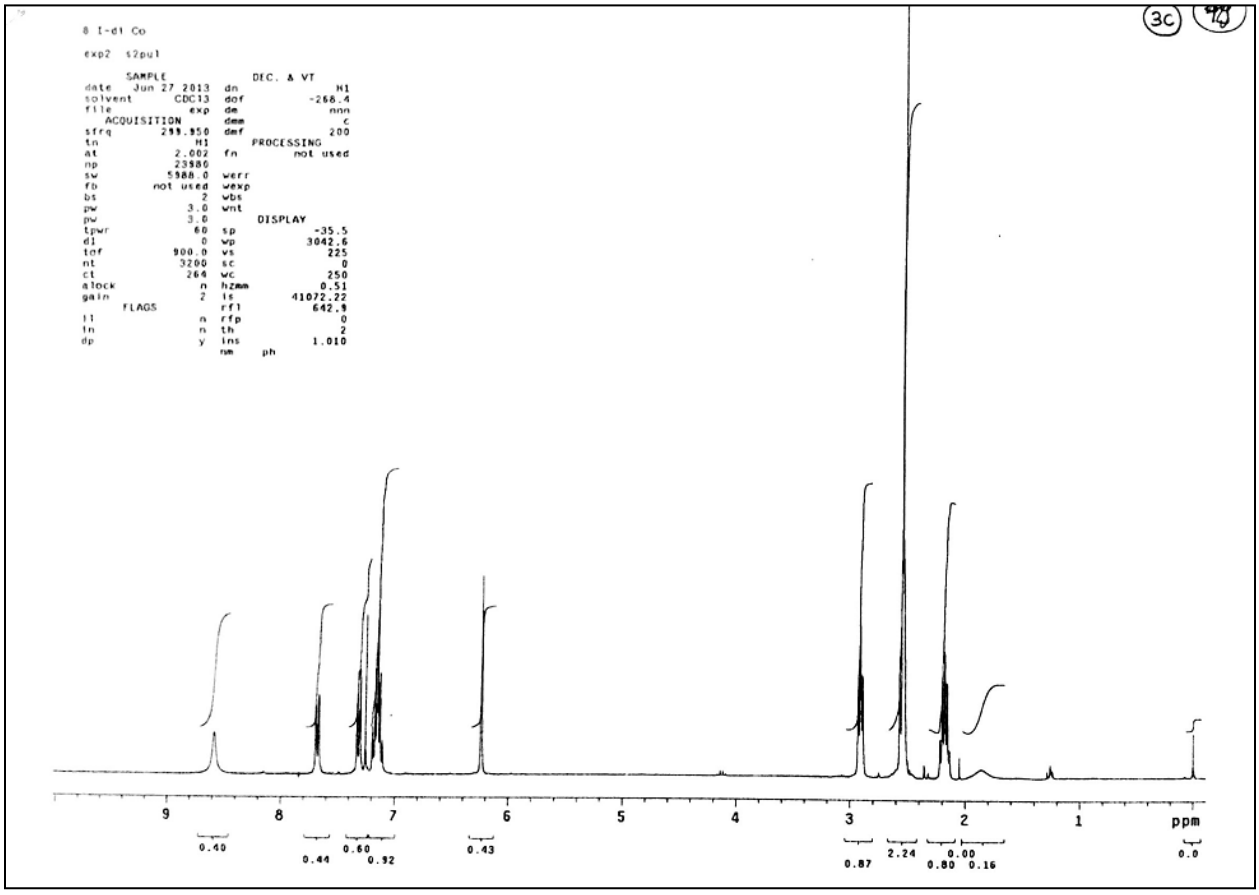
(*E*)-4-(2-methyl-1*H*-indol-3-yl)pent-3-en-2-one (3a)



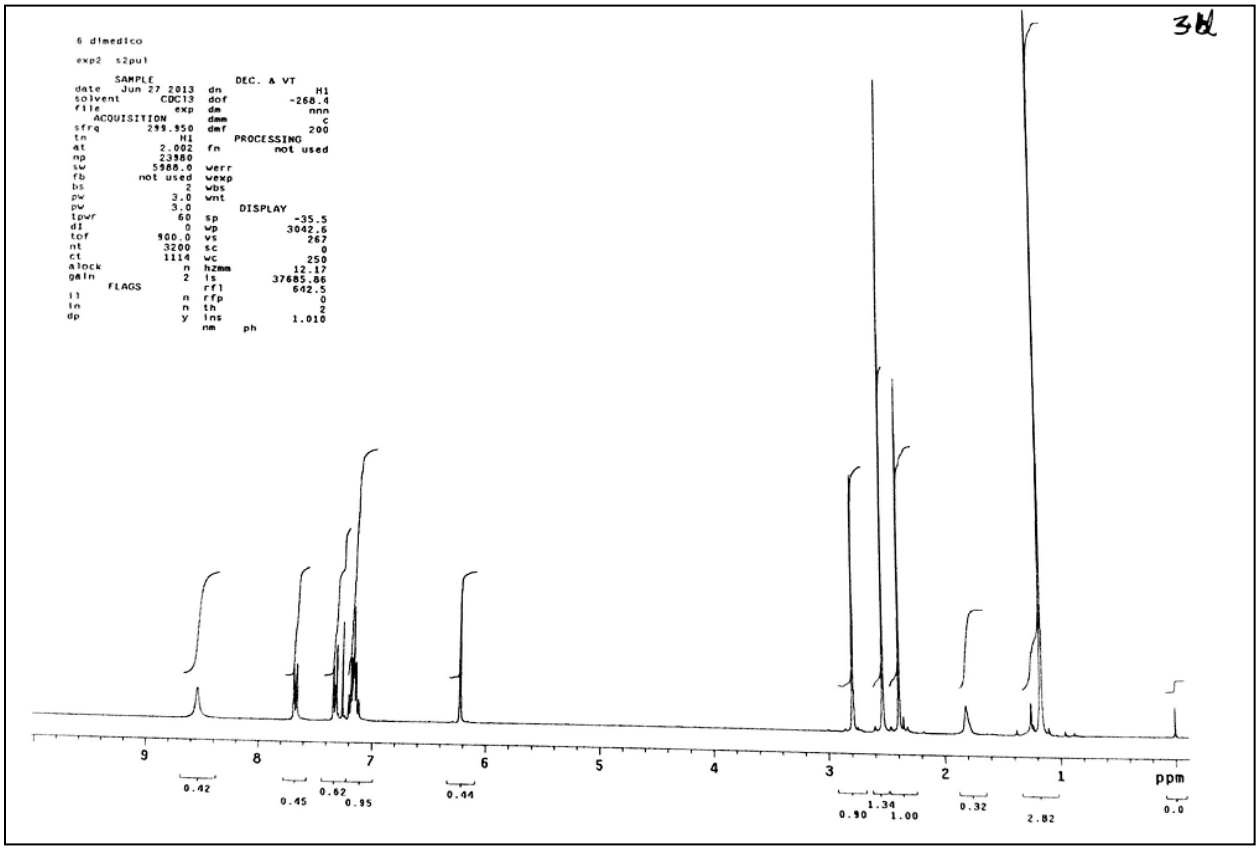
(*E*)-3-(2-methyl-1*H*-indol-3-yl)-1,3-diphenylprop-2-en-1-one (3b)



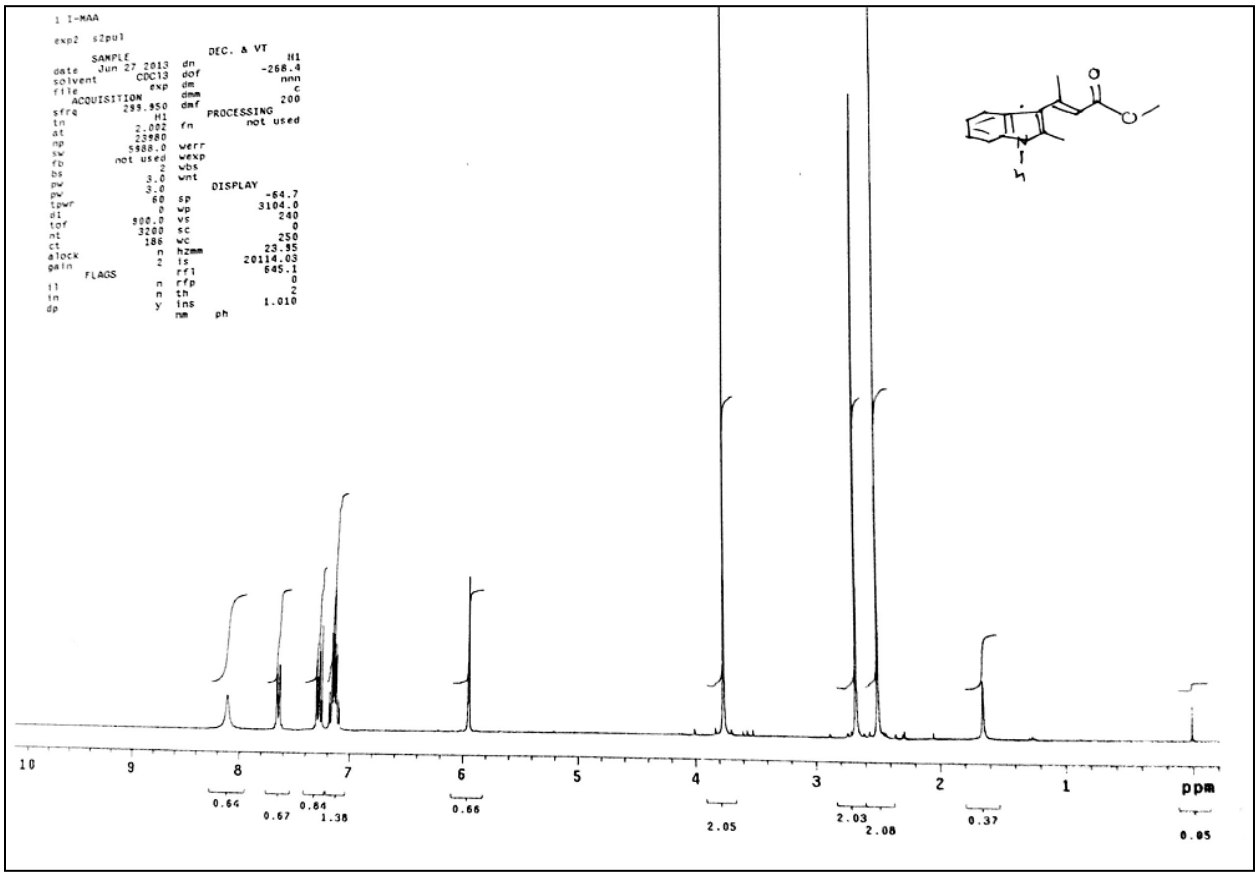
3-(2-methyl-1*H*-indol-3-yl)cyclohex-2-enone (3c)



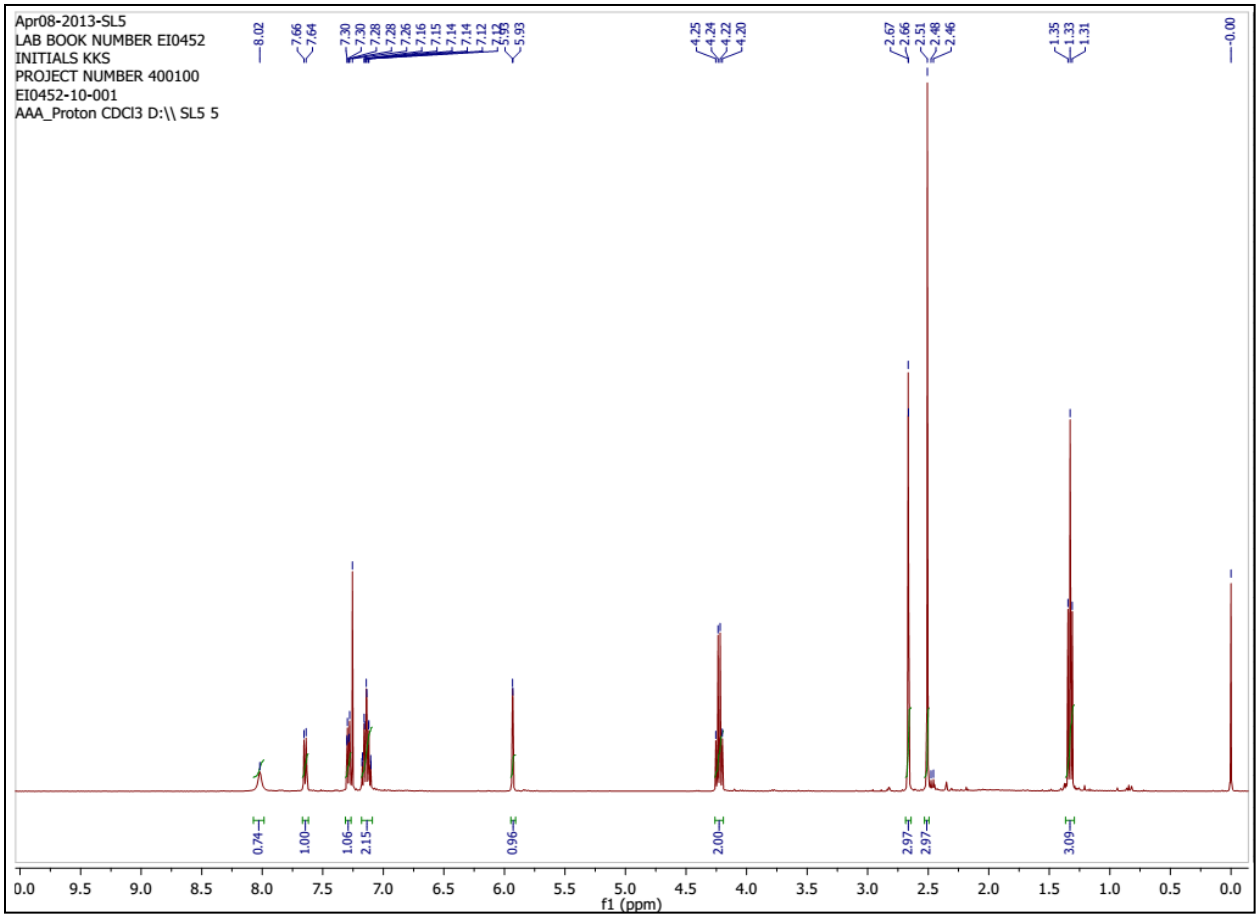
5,5-dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclohex-2-enone (3d)



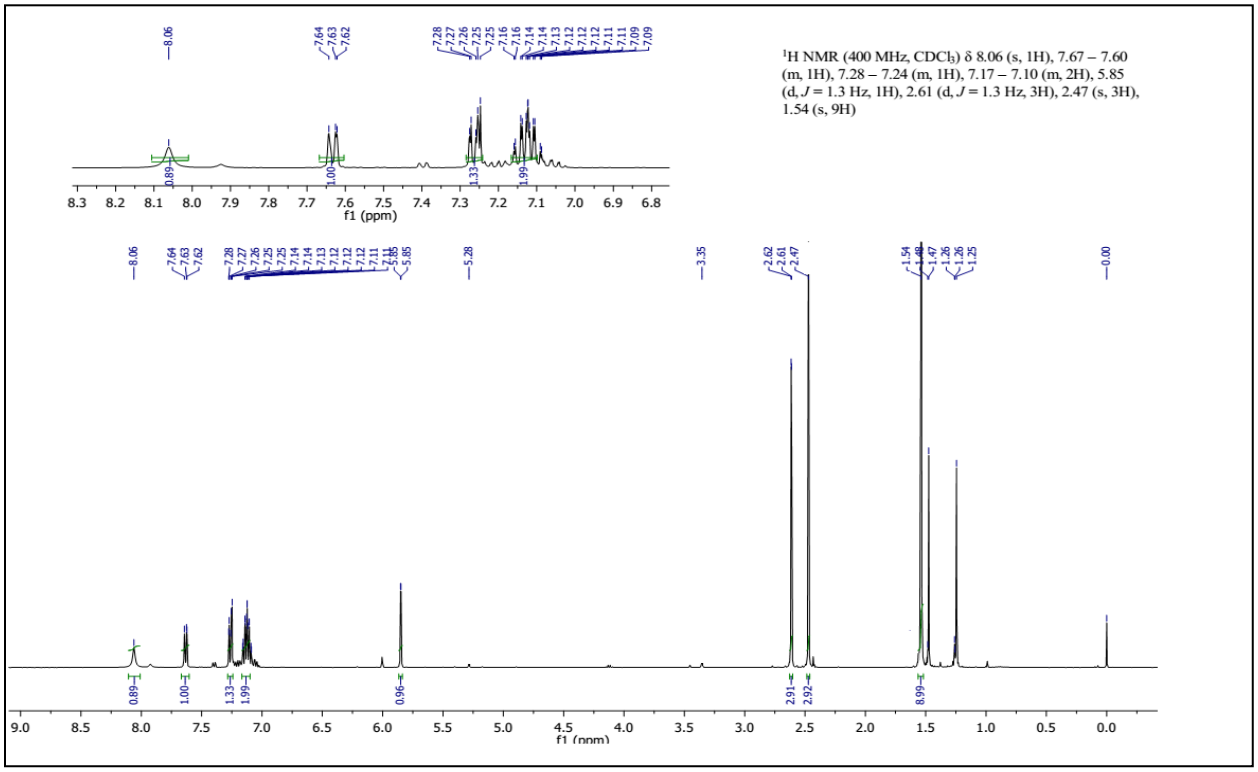
(*E*)-methyl 3-(2-methyl-1*H*-indol-3-yl)but-2-enoate (3e)



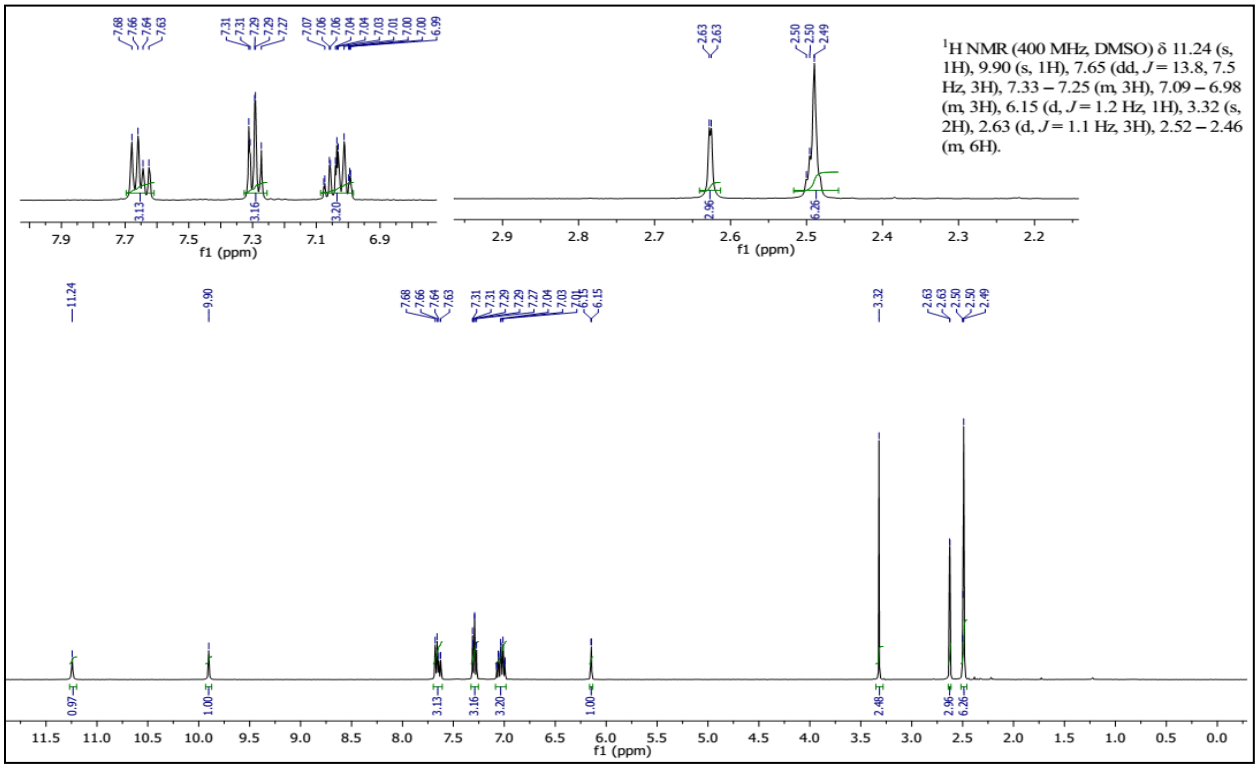
(*E*)-ethyl 3-(2-methyl-1*H*-indol-3-yl)but-2-enoate (3f)



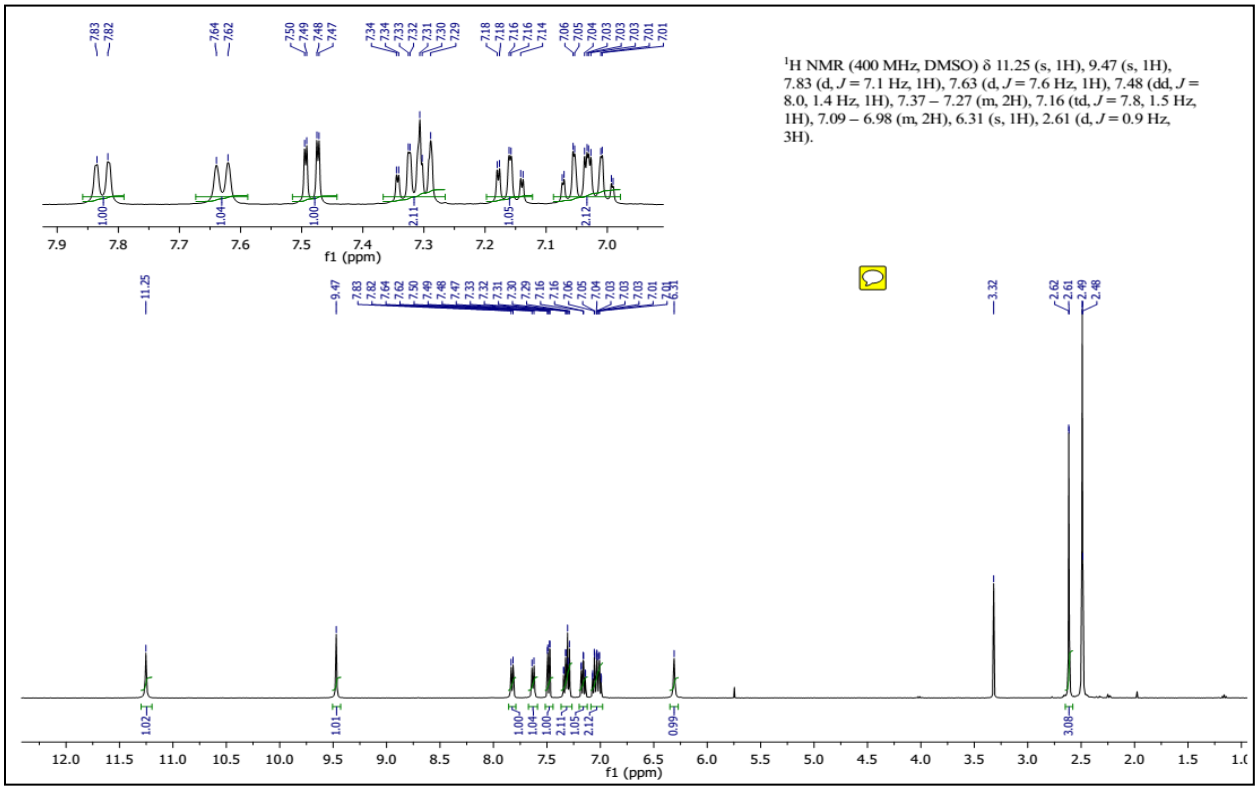
(*E*)-*tert*-butyl 3-(2-methyl-1*H*-indol-3-yl)but-2-enoate (3g)



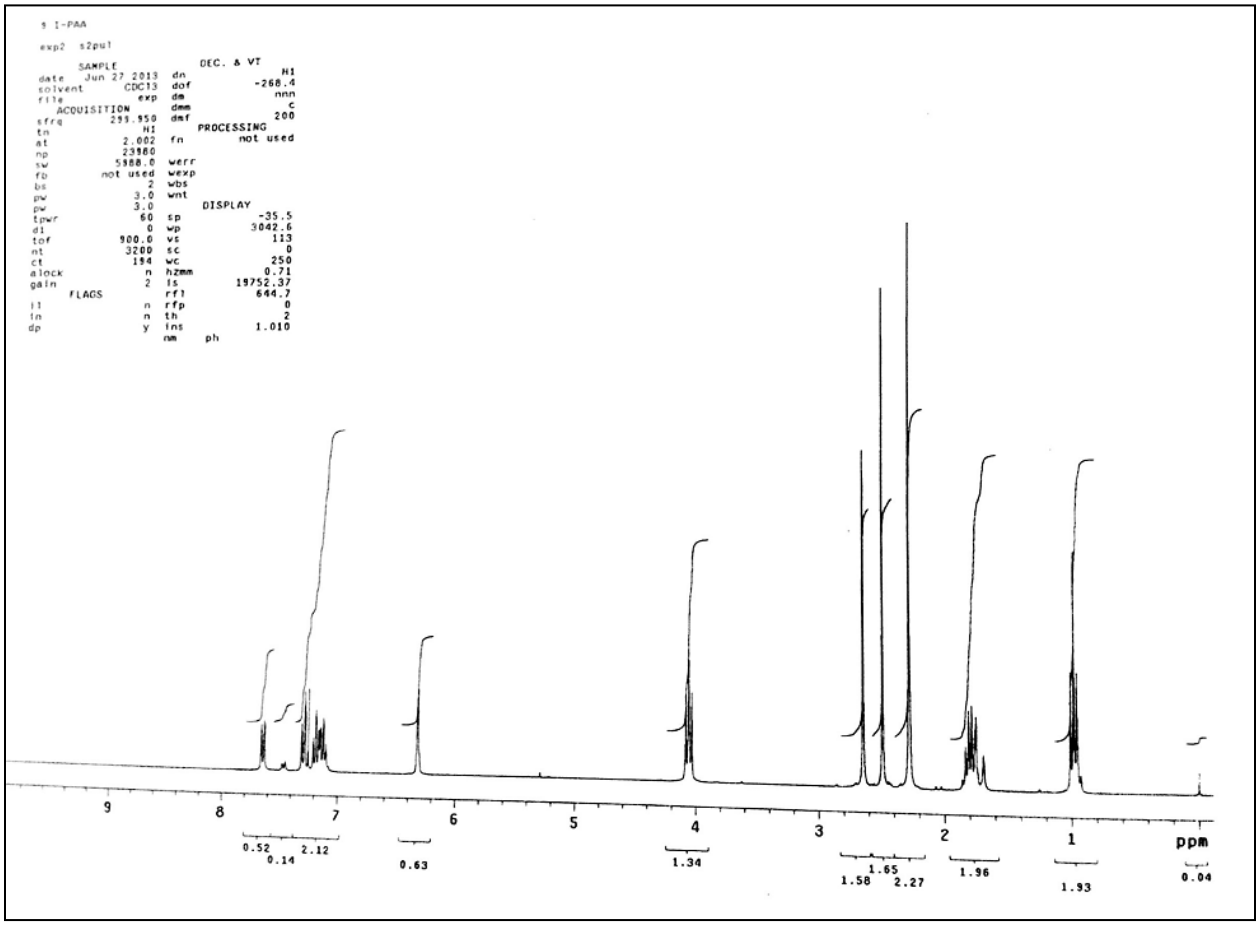
(*E*)-3-(2-methyl-1*H*-indol-3-yl)-*N*-phenylbut-2-enamide (3h)



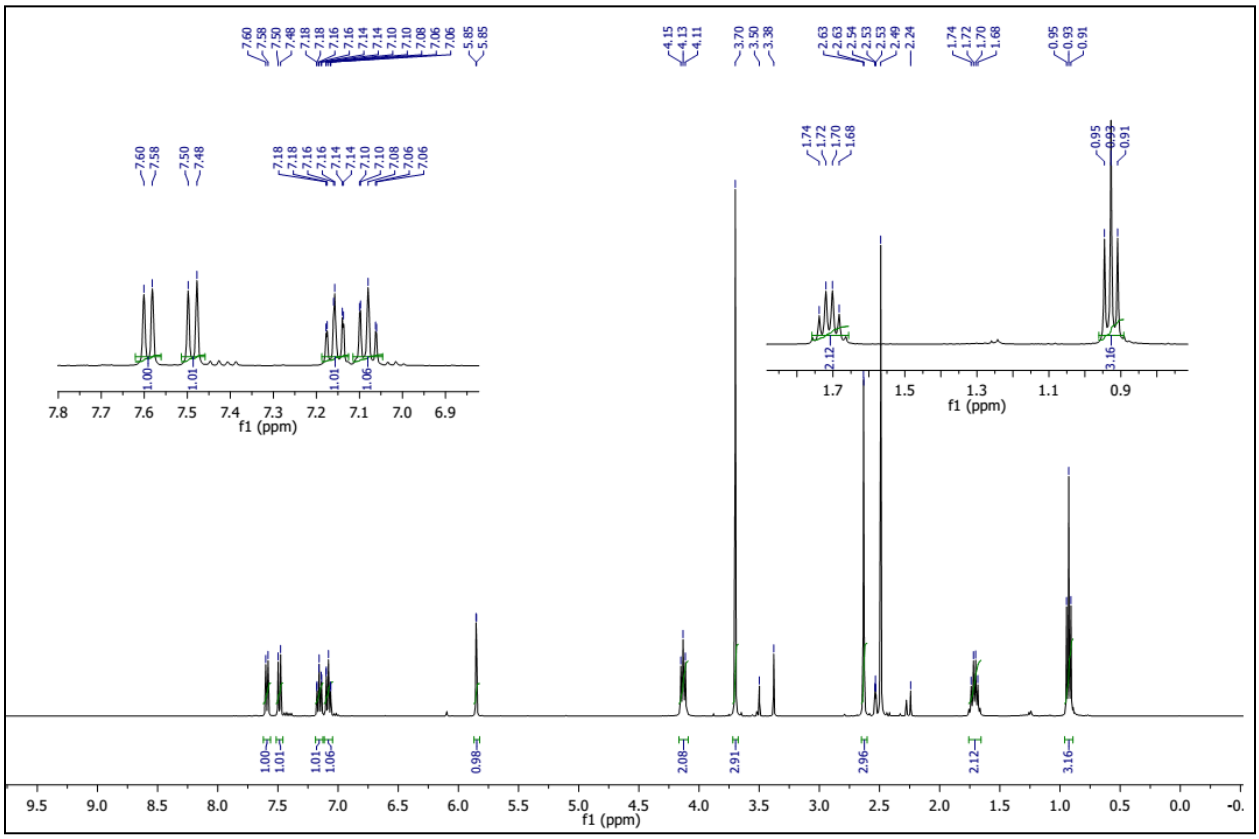
(*E*)-*N*-(2-chlorophenyl)-3-(2-methyl-1*H*-indol-3-yl)but-2-enamide (3i)



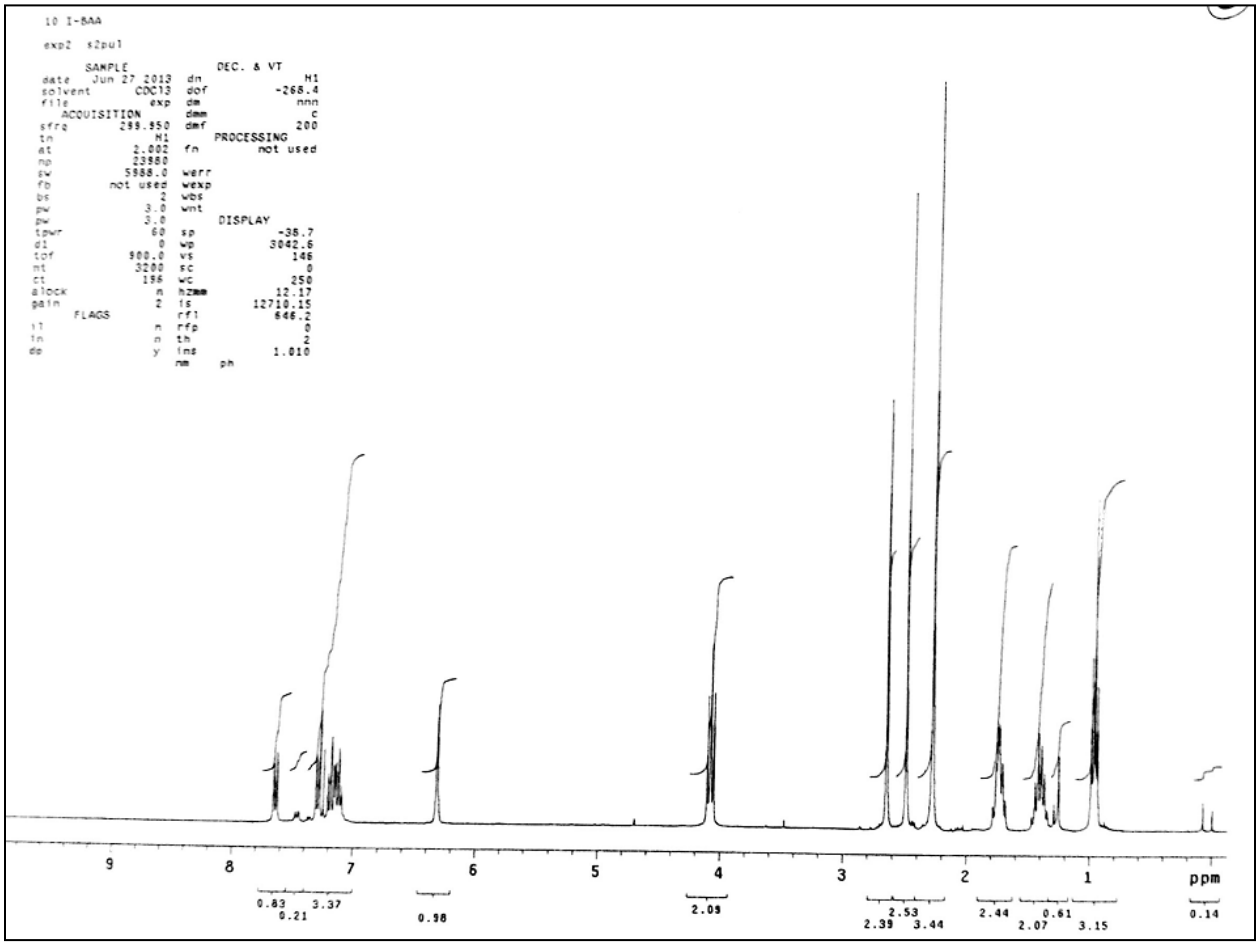
(*E*)-4-(2-methyl-1-propyl-1*H*-indol-3-yl)pent-3-en-2-one (3j)



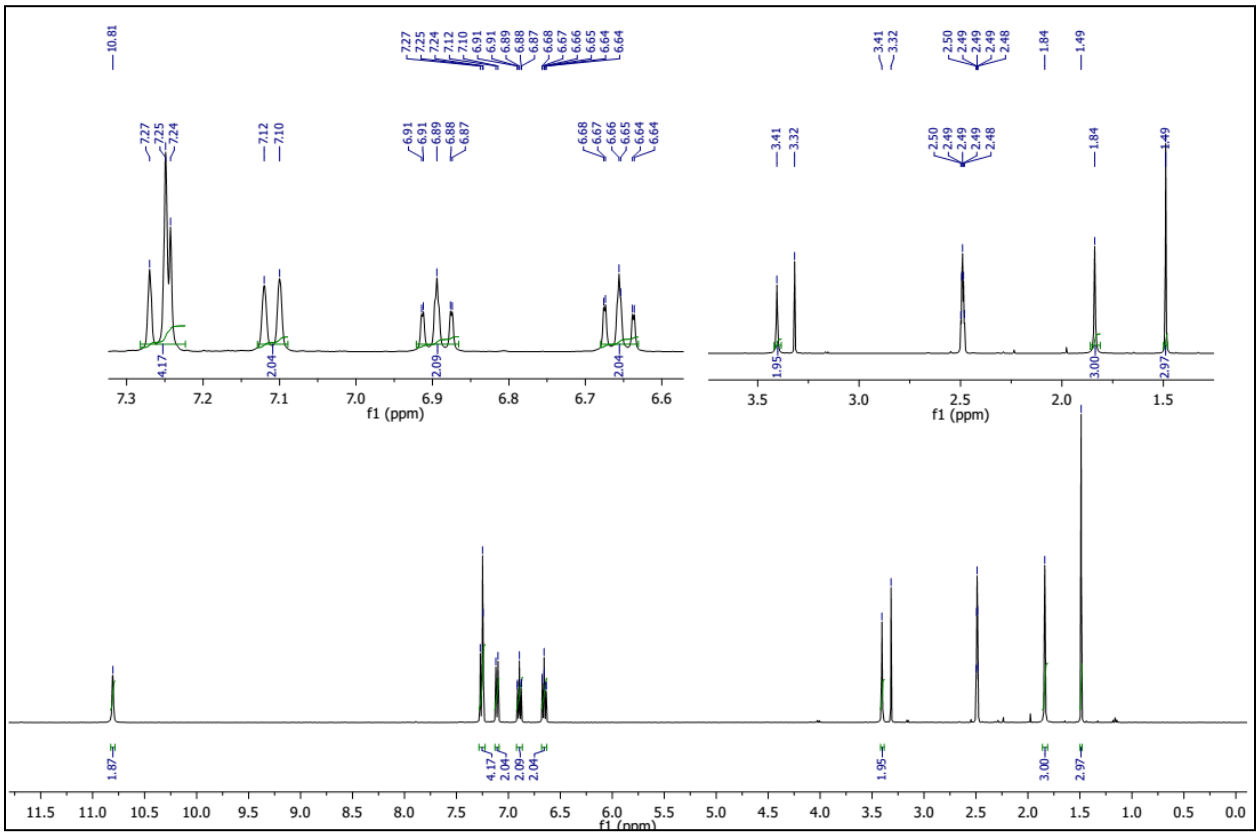
(*E*)-methyl 3-(2-methyl-1-propyl-1*H*-indol-3-yl)but-2-enoate (3k)



(*E*)-4-(1-butyl-2-methyl-1*H*-indol-3-yl)pent-3-en-2-one (3l)



4,4-di(1*H*-indol-3-yl)pentan-2-one (3m)



Methyl 3,3-di(1*H*-indol-3-yl)butanoate (3n)