Supplementary Material (ESI) for Chemical Communications

Formation of 4,5-disubstituted 1,3-dimethyl-3,4-dihydropyrimidin-2(*1H*)-ones

General Procedure – Homocoupling Reaction

To a suspension of 1,3-dimethylurea (0.22g, 2.5mmol) in anhydrous toluene (3ml) over 4Å molecular sieves, the desired aldehyde was added (5mmol) and the solution stirred under nitrogen at room temperature. To this solution, boron trifluoride diethylethereate (63µL, 0.25mmol, 10mol%) was added and the solution heated to reflux and stirred for between 2 and 4 hours and followed by TLC.
The reaction solution was diluted to approximately three times the volume with ethyl acetate and the molecular sieves removed. The solvent was removed *in vacuo* and the resulting oil purified by column chromatography without work-up.

Modification: In the case of low yielding reaction or when using monosubstituted ureas, 3eq. of aldehyde was added to refluxing solution of urea, $BF_3.Et_2O$ in toluene.

General Procedure – Cross-over Reaction

To a suspension of the 1,3-dimethylurea (0.22g, 2.5mmol) in anhydrous toluene (3ml) over 4Å molecular sieves, the desired aldehydes were added (both at 2.5mmol) and the solution stirred under nitrogen at room temperature. To this solution, boron trifluoride diethylethereate (63µL, 0.25mmol, 10mol%) was added and the solution heated to reflux and stirred for between 2 and 4 hours and followed by TLC.
The reaction solution was diluted to approximately three times the volume with ethyl acetate and the molecular sieves removed. The solvent was removed *in vacuo* and the resulting oil purified by column chromatography without work-up.

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Scheme 2: Three-component coupling of monosubstituted ureas with aliphatic aldehydes and benzaldehyde

To a suspension of the desired monosubstituted urea (2.5mmol) in anhydrous toluene (3ml) over 4Å molecular sieves, the desired aliphatic aldehyde was added (2.5mmol) followed by benzaldehyde (0.51ml, 5mmol) and the solution stirred under nitrogen at room temperature. To this solution, boron trifluoride diethylethereate (63µL, 0.25mmol, 10mol%) was added and the solution heated to reflux and stirred for 4 hours and followed by TLC.

The reaction solution was diluted to approximately three times the volume with ethyl acetate and the molecular sieves removed. The solvent was removed *in vacuo* and the resulting oil purified by column chromatography without work-up.

Pyrimidinone formation by Enamide Disproportionation

To degassed DME (3ml) Enamide **1** (0.325g, 1.7mmol, 1eq.) was dissolved and the solution heated to 60°C under an atmosphere of nitrogen. To the heated solution $BF_3.Et_2O$ (43µL, 0.17mmol, 10mol%) was added and the reaction stirred at 60°C for 4 hours and followed by TLC.

At complete reaction, water was added and the product extracted to ethyl acetate. The organic phase was isolated and dried over $MgSO_4$. The resulting organic solution was evaporated under reduced pressure to yield a yellow oil which was purified by column chromatography.

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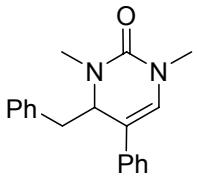
Spectroscopic Data



2 (92%)

^{1}H NMR (270MHz, Toluene-d_8) δ = 7.20-6.90 (m, 10H, Ar**H**), 5.82 (s, 1H, C=C**H**N), 4.26 (app. dd, 1H, PhCH$_2$C**H**), 2.82 (s, 3H, CH$_2$CHNC**H**$_3$), 2.72 (dd, J=3.96, 13.86, 1H, PhC**H**$_2$), 2.49 (s, 3H, C=CHNC**H**$_3$), 2.43 (dd, J=4.62, 13.53, 1H, PhC**H**$_2$); ^{13}C NMR (68MHz, $CDCl_3$) δ = 154.1(C), 136.5 (C), 135.9 (C), 130.0 (CH), 128.9 (CH), 127.8 (CH), 127.7(CH), 126.6 (CH), 126.3 (CH), 124.1 (CH), 112.0 (CH), 61.5 (CH), 37.5 (CH$_2$), 35.0 (CH$_3$), 34.5 (CH$_3$); IR (cm^{-1}), 2923 (br), 1650 (br), 1598, 1494, 1452, 1341; HRMS: *m/z* (CI), 293.1654 [M+H]$^+$

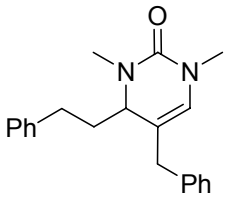


Table 1: Entry 2 (86%)

^{1}H NMR (400MHz, Benzene-d_6) δ = 7.2-6.95 (m, 10H, Ar**H**), 5.36 (s, 1H, C=C**H**N) 3.53 (app. dd, 1H, NC**H**CH$_2$), 3.00 (s, 2H, PhC**H**$_2$C=CH), 2.78 (s, 3H, NC**H**$_3$), 2.67 (s, 3H, NC**H**$_3$), 2.53 (m, 2H, CHCH$_2$C**H**$_2$), 1.67 (m, 1H, CHC**H**$_2$CH$_2$), 1.52 (m, 1H, CHC**H**$_2$CH$_2$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 154.7(C), 141.9 (C), 138.6 (C), 129.0 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 127.9 (CH), 126.8 (CH), 126.0 (CH), 111.4 (C), 66.9 (CH), 37.5 (CH$_2$), 34.9 (CH$_3$), 33.9 (CH$_3$), 32.7 (CH$_2$), 29.4 (CH$_2$); IR (cm^{-1}), 2924 (br), 1550, 1497; HRMS *m/z* (CI), 321.1967 [M+H]$^+$

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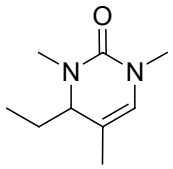

Table 1: Entry 3 (74%)

^{1}H NMR (400MHz, $CDCl_3$) δ = 5.70 (s, 1H, NC**H**=C), 3.77 (app. dd, 1H, CH_2C**H**N), 2.93 (s, 3H, NC**H**$_3$), 2.86 (s, 3H, NC**H**$_3$), 1.68 (m, 1H, NCHC**H**$_2$), 1.56 (s, 3H, NCHCC**H**$_3$), 1.45 (m, 1H, NCHC**H**$_2$), 0.78 (t, J = 7.3, 3H, NCHCH$_2$C**H**$_3$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 155.0 (C), 126.2 (CH), 107.8 (C), 63.8 (CH), 34.8 (CH_3), 33.8 (CH_3), 23.1 (CH_2), 17.0 (CH_3), 7.1 (CH_3); IR (cm^{-1}), 3373 (br, w), 2940, 1704, 1627, 1458; HRMS *m/z* (CI), 169.1341 $[M+H]^+$

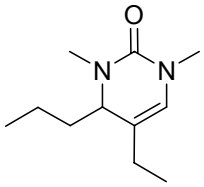

Table 1: Entry 4 (70%)

^{1}H NMR (400MHz, $CDCl_3$) δ = 5.65 (s, 1H, NC**H**=C), 3.76 (app. dd, 1H, CH_2C**H**N) 2.96 (s, 3H, NC**H**$_3$), 2.88 (s, 3H, NC**H**$_3$), 1.94 (m, 2H, NCHCC**H**$_2$), 1.59 (m, 1H, NCHC**H**$_2$), 1.40 (m, 1H, NCHC**H**$_2$), 1.26 (m, 1H, NCHCH$_2$C**H**$_2$), 1.00 (t, J= 7.3, 3H, CCH$_2$C**H**$_3$), 0.86 (t, J = 7.3, 3H, CHCH$_2$CH$_2$C**H**$_3$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 155.2 (C), 126.2 (CH), 124.9 (CH), 114.9 (C), 61.8 (CH), 35.0 (CH_3), 34.2 (CH_3), 33.8 (CH_2), 23.9 (CH_2), 16.8 (CH_2), 14.5 (CH_3), 12.4 (CH_3); IR (cm^{-1}), 3931 (w), 1647, 1464, 1239; HRMS *m/z* (CI), 197.1654 $[M+H]^+$

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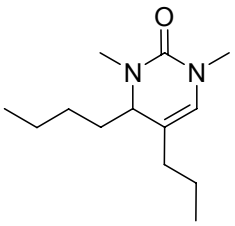


Table 1: Entry 5 (87%)

^{1}H NMR (400MHz, $CDCl_3$) δ = 5.72 (s, 1H, NC**H**=C), 3.82 (app. dd, 1H, NC**H**CH_2), 3.02 (s, 3H, NC**H**$_3$), 2.94 (s, 3H, NC**H**$_3$), 1.94 (m, 2H, NCHCC**H**$_2$), 1.7-1.2 (m, 8H, 4 x CH_2), 0.94 (t, J=7.1, 3H, CCH_2CH_2C**H**$_3$), 0.90 (t, J=7.1, 3H, $CHCH_2CH_2CH_2C$**H**$_3$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 155.0 (C) 125.5 (CH), 112.8 (C), 61.4 (CH), 34.8 (CH_3), 34.0 (CH_3), 32.8 (CH_2), 30.8 (CH_2), 25.3 (CH_2), 23.0 (CH_2), 20.8 (CH_2), 14.1 (CH_3), 13.9 (CH_3); IR (cm^{-1}), 2926, 1651, 1466, 1246, 1061; HRMS *m/z* (CI), 225.1967 $[M+H]^+$

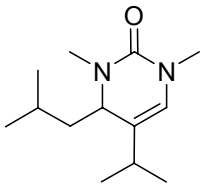


Table 1: Entry 6 (62%)

^{1}H NMR (400MHz, $CDCl_3$) δ = 5.68 (s, 1H, NC**H**=C), 3.72 (app. dd, 1H, NC**H**CH_2), 3.05 (s, 3H, NC**H**$_3$), 2.99 (s, 3H, NC**H**$_3$), 2.21 (m, 1H, CH=CC**H**$(CH_3)_2$), 1.73 (m, 1H, CH_2C**H**$(CH_3)_2$), 1.52 (m, 1H, NCHC**H**$_2$), 1.38 (m, 1H, NCHC**H**$_2$), 1.09 (d, J=6.6, 3H, CCH(C**H**$_3)_2$), 1.06 (d, J=6.6, 3H, CCH(C**H**$_3)_2$), 0.94 (d, J=6.6, 3H, CH_2CH(C**H**$_3)_2$), 0.91 (d, J=6.6, 3H, CH_2CH(C**H**$_3)_2$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 155.3 (C), 123.7 (CH), 122 (C), 58.9 (CH), 42.4 (CH), 35.2 (CH_3), 34.8 (CH_3), 29.0 (CH_2), 24.6 (CH_3), 22.9 (2xCH_3), 20.6 (CH_3); IR (cm^{-1}), 2955, 2344 (w, br), 1651, 1464, 1242, 1045; HRMS *m/z* (CI), 225.1967 $[M+H]^+$

Supplementary Material (ESI) for Chemical Communications

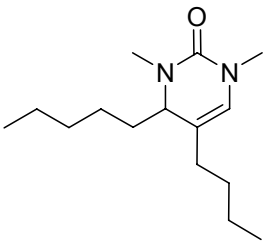


Table 1: Entry 7 (88%)

^{1}H NMR (400MHz, $CDCl_3$) δ = 5.72 (s, 1H, NC**H**=C), 3.82 (app. dd, 1H, NC**H**CH_2), 3.01 (s, 3H, NC**H**$_3$), 2.93 (s, 3H, NC**H**$_3$), 1.94 (m, 2H, NCHCC**H**$_2$), 1.7-1.2 (m, 12H, 6 x C**H**$_2$), 0.93 (t, J=7.1, 3H, CCH_2CH_2C**H**$_3$), 0.89 (t, J=7.1, 3H, $CHCH_2CH_2CH_2C$**H**$_3$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 155.0 (C) 125.3 (CH), 113.0 (C), 61.5 (CH), 34.8 (CH_3), 34.0 (CH_3), 32.1 (CH_2), 31.0 (CH_2), 30.4 (CH_2), 29.8 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.5 (CH_2), 14.2 (CH_3), 14.0 (CH_3); IR (cm^{-1}), 2926, 1650, 1465, 1246, 1061; HRMS m/z (CI), 253.2280 $[M+H]^+$

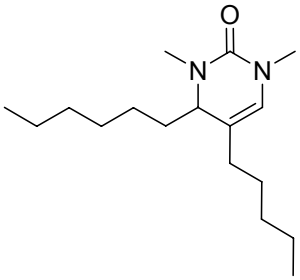


Table 1: Entry 8 (86%)

^{1}H NMR (400MHz, $CDCl_3$) δ = 5.72 (s, 1H, NC**H**=C), 3.82 (app. dd, 1H, NC**H**CH_2), 3.01 (s, 3H, NC**H**$_3$), 2.93 (s, 3H, NC**H**$_3$), 1.92 (m, 2H, NCHCC**H**$_2$), 1.7-1.2 (m, 16H, 8 x C**H**$_2$), 0.92 (t, J=7, 3H, CCH_2CH_2C**H**$_3$), 0.89 (t, J=7, 3H, $CHCH_2CH_2CH_2C$**H**$_3$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 155.0 (C) 125.3 (CH), 113.0 (C), 61.5 (CH), 34.8 (CH_3), 34.0 (CH_3), 31.9 (CH_2), 31.6 (CH_2), 31.1 (CH_2), 30.7 (CH_2), 29.6 (CH_2), 27.3 (CH_2), 23.1 (CH_2), 22.8 (CH_2), 22.6 (CH_2), 14.2 (CH_3), 14.1 (CH_3); IR (cm^{-1}), 2928, 1650, 1465, 1256, 1058; HRMS m/z (CI), 281.2593 $[M+H]^+$

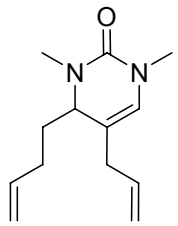
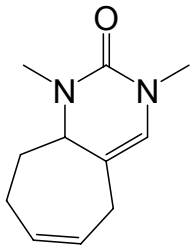


Table 1: Entry 9 (76%)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.80-5.65 (m, 2H, 2xCH_2=C**H**), 5.75 (s, 1H, NC**H**=C), 5.1-4.9 (m, 4H, 2xC**H**$_2$=CH), 3.82 (app. dd, 1H, NC**H**CH_2), 2.97 (s, 3H, NC**H**$_3$), 2.89 (s, 3H, NC**H**$_3$), 2.66 (m, 2H, CC**H**$_2$), 2.03 (m, 2H, CH2=CHC**H**$_2$$CH_2$), 1.72 (m, 1H, NCHC**H**$_2$), 1.54 (m, 1H, CCHC**H**$_2$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 154.2 (C), 138.0 (CH), 135.1 (CH), 126.8 (CH), 117.0 (CH_2), 114.7 (CH_2), 60.7 (CH), 35.3 (CH_2), 34.8 (CH_3), 34.0 (CH_3), 29.9 (CH_2), 27.3 (CH_2); IR (cm^{-1}), 3348 (w, br), 2930 (w), 1737, 1635, 1485, 1262, 910; HRMS *m/z* (CI), 221.1654 $[M+H]^+$



15 (70%)

^{1}H NMR (400 MHz, $CDCl_3$) δ= 5.68 (m, 2H, CHCCH_2C**H**C**H**), 5.65 (s, 1H, NC**H**=C), 3.76 (dd, J=9.7, 3.17, 1H, NC**H**CH_2), 2.99 (s, 3H, NC**H**$_3$), 2.92 (s, 3H, NC**H**$_3$), 2.64 (m, 2H, NCHCC**H**$_2$), 2.01 (m, 1H, NCHC**H**$_2$), 1.98 (m, 2H, NCHCH_2C**H**$_2$), 1.46 (m, 1H, NCHC**H**$_2$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 154.0 (C), 129.9 (CH), 129.4 (CH), 124.4 (CH), 112.2 (C), 64.8 (CH), 34.7 (CH_3), 33.6 (CH_3), 31.9 (CH_2), 31.4 (CH_2), 24.8 (CH_2); IR (cm^{-1}), 3385 (w, br), 2928 (w), 1699, 1634 (s), 1482, 1419, 1266; HRMS *m/z* (CI), 192.1341 $[M+H]^+$

Supplementary Material (ESI) for Chemical Communications

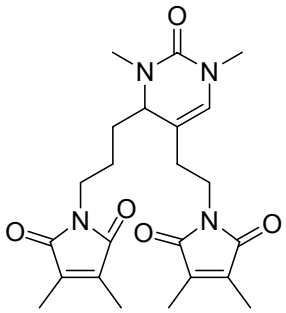


Table `1: Entry 10 (25%)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.69 (s, 1H, NC**H**=C), 3.87 (app. dd, 1H, NC**H**CH_2), 3.60-3.35 (m, 4H, 2xNC**H**$_2$), 2.90 (s, 3H, NC**H**$_3$), 2.83 (s, 3H, NC**H**$_3$), 2.78-2.63 (m, 2H, CH=CC**H**$_2$), 2.23 (m, 2H, $CHCH_2$C**H**$_2$), 1.89 (s, 6H, COCC**H**$_3$), 1.88 (s, 6H, COCC**H**$_3$), 1.8-1.4 (m, 2H, NCHC**H**$_2$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 172.3 (C), 172.1 (C), 154.5 (C), 137.2 (C), 137.1 (C), 128.2 (CH), 108.0 (C), 59.8 (CH), 37.8 (CH_2), 35.9 (CH_2), 34.7 (CH_3), 34.0 (CH_3), 29.5 (CH_2), 28.4 (CH_2), 22.9 (CH_2), 8.8 (2xCH_3); IR (cm^{-1}), 2943 (w), 1694, 1644, 1404, 728; HRMS *m/z* (CI), 443.2294 $[M+H]^+$

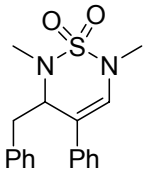


Table 1: Entry 11 (51%)

^{1}H NMR (400 MHz, Acetone-d_6) δ = 7.30-6.95 (m, 10H, Ar**H**), 5.51 (s, 1H, C=C**H**), 4.16 (dd, J= 3.4, 11.6, 1H, NCHC**H**$_2$), 3.67 (dd, J= 11.7, 13.9, 1H, NC**H**CH_2), 2.66 (dd, J= 3.2, 11.6, 1H, NCHC**H**$_2$), 2.64 (s, 3H, NC**H**$_3$), 2.37 (s, 3H, NC**H**$_3$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 138.5 (C), 137.5 (C), 129.4 (CH), 128.9 (CH), 128.5 (CH), 128.3 (CH), 127.4 (CH), 126.4 (CH), 126.3 (CH), 125.6 (CH), 116.3 (C), 69.6 (CH), 40.5 (CH_3), 37.4 (CH_2), 36.2 (CH_3); IR (cm^{-1}), 3061 (w), 1738 (w, br), 1638, 1335, 1253, 1146; HRMS *m/z* (CI), 329.1323 $[M+H]^+$

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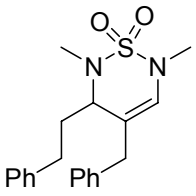


Table 1: Entry 12 (53%)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30-6.95 (m, 10H, Ar**H**), 5.57 (s, 1H, C=C**H**), 3.30 (m, 1H, NC**H**CH_2), 2.96 (s, 3H, NC**H**$_3$), 2.81 (m, 2H, NCHCH_2C**H**$_2$), 2.51 (m, 2H, CHCC**H**$_2$), 2.49 (s, 3H, NC**H**$_3$), 2.35 (m, 1H, NCHC**H**$_2$), 1.84 (m, 1H, NCHC**H**$_2$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 141.3 (C), 138.3 (C), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 127.4 (CH), 126.6 (CH), 125.9 (CH), 114.8 (C), 64.7 (CH), 38.4 (CH_3), 37.9 (CH_2), 35.6 (CH_3), 32.0 (CH_2), 31.5 (CH_2); IR (cm^{-1}), 2927 (w, br), 1662 (w), 1494, 1453, 1344, 1163; HRMS *m/z* (CI), 357.1636 $[M+H]^+$

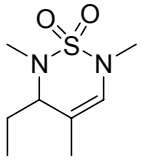


Table 1: Entry 13 (52%)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.57 (s, 1H, C=C**H**), 3.67 (dd, J= 4.4, 11, 1H, NC**H**CH_2), 2.98 (s, 3H, NC**H**$_3$), 2.66 (s, 3H, NC**H**$_3$), 1.75 (m, 2H, NCHC**H**$_2$), 1.61 (s, 3H, CHCC**H**$_3$), 0.99 (t, J= 7.3, 3H, NCHCH_2C**H**$_3$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 126.1 (CH), 112.3 (C), 68.2 (CH), 36.1 (CH_3), 35.7 (CH_3), 23.0 (CH_2), 17.7 (CH_3), 10.4 (CH_3); IR (cm^{-1}), 2971 (w), 1738 (w), 1455, 1339, 1161; HRMS *m/z* (CI), 205.1010 $[M+H]^+$

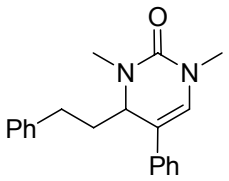


Table 2: Entry 2 (76%)

^{1}H NMR (270MHz, $CDCl_3$) δ = 7.31-7.03 (m, 10H, Ar**H**), 6.40 (s, 1H, PhC=C**H**), 4.58 (app dd, 1H, CH_3NC**H**), 3.16 (s, 3H, PhCCHNC**H**$_3$), 3.09 (s, 3H, $PhCH_2CH_2CHNC$**H**$_3$), 2.60 (m, 2H PhC**H**$_2$), 1.92 (m, 2H, $PhCH_2C$**H**$_2$); ^{13}C NMR (68MHz, $CDCl_3$) δ = 154.5 (C), 141.5 (C), 136.4 (C), 128.9 (CH), 128.4 (CH), 128.3 (CH), 127.8 (CH), 126.6 (CH), 125.9 (CH), 124.7 (CH), 112.9 (C), 60.3 (CH), 35.3 (CH_3), 34.6 (CH_3), 33.9 (CH_2), 29.9 (CH_2); IR (cm^{-1}) 2927, 1703, 1646, 1599, 1446, 1342; HRMS *m/z* (CI), 307.1810 $[M+H]^+$

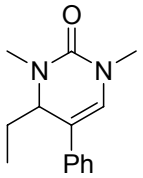


Table 2: Entry 4 (55%)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32-7.12 (m, 5H, Ar**H**), 6.38 (s, 1H, C=C**H**), 4.46(app. dd, 1H, NC**H**CH_2), 3.09 (s, 3H, NC**H**$_3$), 3.00 (s, 3H, NC**H**$_3$), 1.72 (m, 1H, CHC**H**$_2$), 1.50 (m, 1H, CHC**H**$_2$), 0.81 (t, J= 7.3, 3H, $NCHCH_2C$**H**$_3$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 154.5 (C), 136.4 (C), 128.7 (CH), 127.5 (CH), 126.3 (CH), 124.4 (CH), 112.3 (C), 61.0 (CH), 35.1 (CH_3), 34.2 (CH_3), 24.4 (CH_2), 7.5 (CH_3); IR (cm^{-1}), 2963 (w), 1646, 1462, 1337, 1254, 1062; HRMS *m/z* (CI), 231.1497 $[M+H]^+$

Supplementary Material (ESI) for Chemical Communications

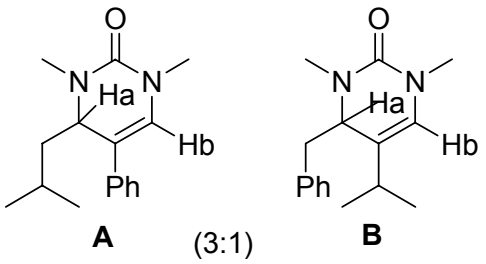


Table 2: Entry 5 (45% NMR Yield)

NMR data for mixture of products and only quoted data for diagnostic protons, **a** and **b**. ^{1}H NMR (400MHz, $CDCl_3$) δ = 6.34 (s, **A,** NC**Hb**=C), 6.23 (s, **B**, NC**Hb**=C), 4.63 (app. t, **B**, NC**Ha**CH2), 4.35 (app. t, **A**, NC**Ha**CH_2)

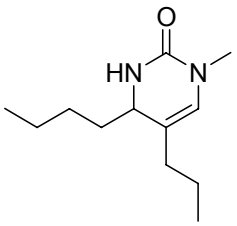


Table 3: Entry 1 (67%)

^{1}H NMR (400MHz, $CDCl_3$) δ = 5.59 (s, 1H, NC**H**=C), 5.14 (br.s, 1H, N**H**), 3.82 (app.t, 1H, NHC**H**), 2.92 (s, 3H, NC$\mathbf{H}_3$), 1.81 (m, 2H, NHCHC$\mathbf{H}_2$), 1.25-1.05 (m, 8H, 4 x C$\mathbf{H}_2$), 0.88 (t, J=7.3, 3H, CHCC$H_2CH_2C\mathbf{H}_3$), 0.86 (t, J=7.3, 3H, NCH$CH_2CH_2CH_2C\mathbf{H}_3$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 154.7 (C), 124.6 (CH), 114.2 (C), 54.3 (CH), 35.1 (CH_2), 34.0 (CH_3), 32.3 (CH_2), 25.9 (CH_2), 22.5 (CH_2), 20.5 (CH_2), 14.0 (CH_3), 13.7 (CH_3); IR (cm^{-1}), 3313 (w, br), 2957, 2871, 1697 (s), 1464; HRMS *m/z* (CI), $[M+H]^+$

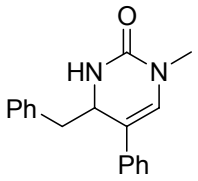


Table 3: Entry 2 (59%)

^{1}H NMR (400MHz, $CDCl_3$) δ = 7.4-7.15 (m, 10H, Ar**H**), 6.32 (s, 1H, NC**H**=C), 5.01 (br.s, 1H, N**H**), 4.65 (app. dt, J=5.9, 2.8, 1H, NHC**H**), 3.02 (s, 3H, NCH_3), 2.90 (dd, J=13.6, 3.0, 1H, NCHC**H**$_2$), 2.70 (dd, J=13.6, 8.7, 1H, NCHC**H**$_2$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 153.9 (C), 136.6 (C), 135.8 (C), 129.6 (CH), 128.9 (CH), 128.5 (CH), 127.1 (CH), 126.8 (CH), 126.7 (CH), 124.5 (CH), 114.1 (C), 55.3 (CH), 42.4 (CH_2), 34.4 (CH_3); IR (cm^{-1}), 3233 (w), 2511 (w, br), 2159, 2027, 1976, 1666 (s), 1452, 1266; HRMS *m/z* (CI), 279.1497 $[M+H]^+$

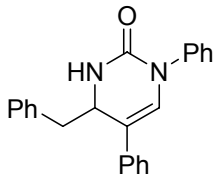


Table 3: Entry 3 (56%)

^{1}H NMR (400MHz, $CDCl_3$) δ = 7.4-7.05 (m, 15H, Ar**H**), 6.56 (s, 1H, NC**H**=C), 5.31 (br.s, 1H, N**H**), 4.84 (ddd, J=3.75, 3.42, 2.69, 1H, NHC**H**), 2.95 (dd, J=13.5, 3.63, 1H, NCHC**H**$_2$), 2.84 (dd, J=13.5, 7.26, 1H, NCHC**H**$_2$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 153 (C), 140.6 (C), 136.5 (C), 135.9 (C), 130.1 (CH), 129.1 (CH), 129.0 (CH), 128.6 (CH), 127.3 (CH), 127.1 (CH), 127.0 (CH), 127.0 (CH), 126.5 (CH), 125.0 (CH), 114.7 (C), 55.2 (CH), 42.7 (CH_2); IR (cm^{-1}), 3663 (w, br), 3219 (w, br), 2513 (br), 2160, 1030, 1977, 1682, 1230, 749; HRMS *m/z* (CI), 341.1654 $[M+H]^+$

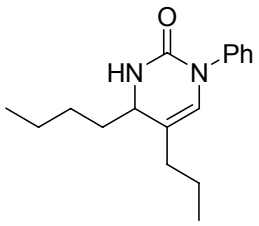
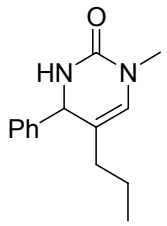


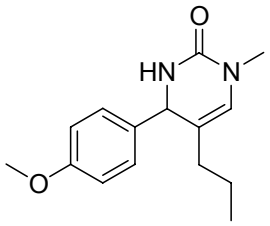
Table 3: Entry 4 (62%)

^{1}H NMR (400MHz, $CDCl_3$) δ = 7.38-7.20 (m, 5H, Ar**H**), 6.02 (s, 1H, C**H**NPh), 4.98 (br.s, 1H, N**H**), 4.00 (app. dt, J=6.1, 2.9, 1H, NHC**H**), 1.97 (m, 2H, NHCHC$\mathbf{H}_2$), 1.65-1.3 (m, 8H, 4 x C$\mathbf{H}_2$), 0.93 (t, J=7.1, 3H, $NCHCH_2CH_2CH_2C\mathbf{H}_3$), 0.92 (t, J=7.1, $NCHCCH_2CH_2C\mathbf{H}_3$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 153.4 (C), 141.2 (C), 129.0 (CH), 126.4 (CH), 126.2 (CH), 124.7 (CH), 115.3 (C), 54.6 (CH), 35.4 (CH_2), 32.5 (CH_2), 26.1 (CH_2), 22.7 (CH_2), 20.7 (CH_2), 14.2 (CH_3), 13.9 (CH_3); IR (cm^{-1}), 2928 (w), 1694, 1673, 1419, 1267, 1233, 755; HRMS *m/z* (CI), 273.1967 $[M+H]^+$



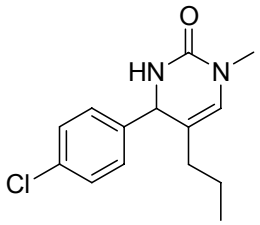
13 (Table 4, Entry1) (60%)

^{1}H NMR (400MHz, $CDCl_3$) δ = 7.4-7.25 (m, 5H, Ar**H**), 5.80 (s, 1H, MeNC**H**=C), 4.94 (s, 1H, NHC**H**), 4.92 (br.s, 1H, N**H**), 3.11 (s, 3H, NC$\mathbf{H}_3$), 1.75 (m, 2H, NCHCC$\mathbf{H}_2$), 1.37 (m, 2H, $NCHCCH_2C\mathbf{H}_2$), 0.87 (t, J=7.3, 3H, $NCHCCH_2CH_2C\mathbf{H}_3$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 153.4 (C), 143.0 (C), 129.0 (CH), 128.3 (CH), 127.1 (CH), 124.5 (CH), 113.9 (C), 60.0 (CH), 34.4 (CH_3), 32.5 (CH_2), 20.4 (CH_2), 13.8 (CH_3); IR (cm^{-1}), 3213 (w), 1255, 1667, 1449, 1401, 1236; HRMS *m/z* (CI), 230.1419 $[M+H]^+$



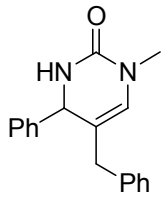
13 (Table 4, Entry 3) (51%)

^{1}H NMR (400MHz, $CDCl_3$) δ = 7.20 (d, J=8.7, 2H, Ar), 6.86 (d, J=8.7, 2H, Ar), 5.76 (s, 1H, MeNC**H**=C), 4.88 (brs, 2H, N**H**C**H**), 3.80 (s, 3H, OC**H**$_3$), 3.08 (s, 3H, NC**H**$_3$), 1.72 (m, 2H, CHCC**H**$_2$CH$_2$), 1.35 (m, 2H, CHCCH$_2$C**H**$_2$) 0.84 (t, J=7.3, 3H, NCHCCH$_2$CH$_2$C**H**$_3$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 159.4 (C), 153.2 (C), 135.1 (C), 128.1 (CH), 124.2 (CH), 114.0 (CH), 59.2 (CH), 55.3 (CH_3), 34.2 (CH_3), 32.4 (CH_2), 20.2 (CH_2), 13.6 (CH_3); IR (cm^{-1}), 3214 (w), 2953 (w), 1673 (s), 1512, 1478, 1404, 1245, 1173, 1030; HRMS *m/z* (CI), 261.1600$[M+H]^+$



13 (Table 4, Entry 2) (59%)

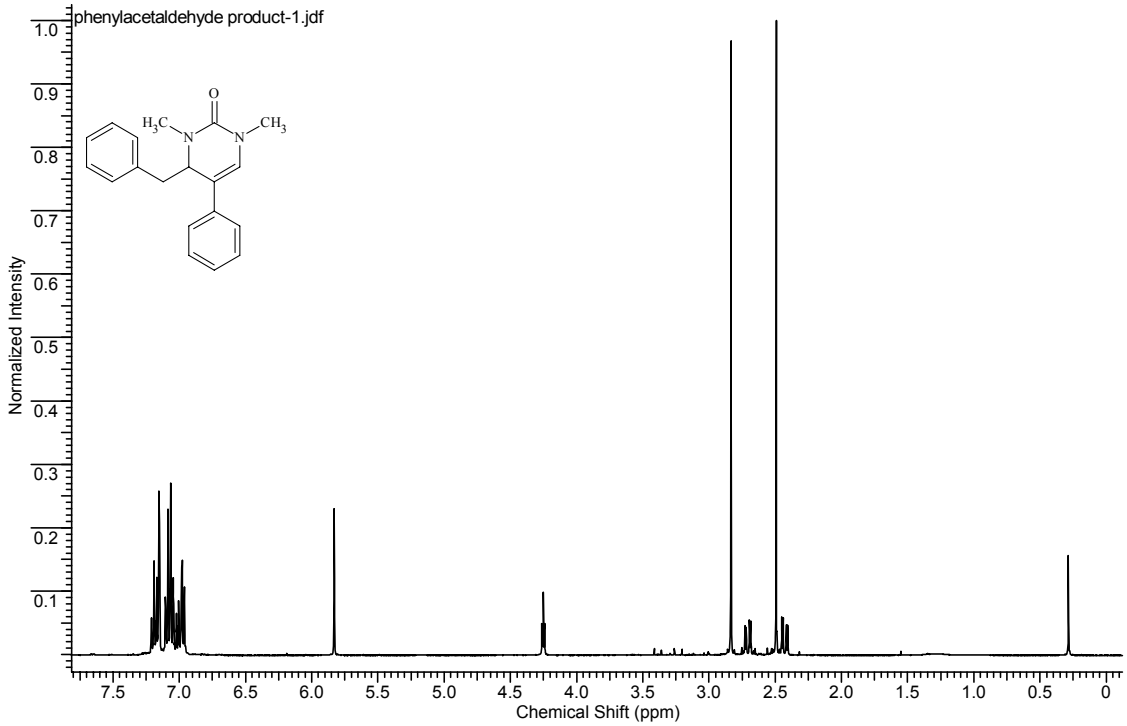
^{1}H NMR (400MHz, $CDCl_3$) δ = 7.32 (d, J=8.2, 2H, Ar), 7.22 (d, J=8.4, 2H, Ar), 5.78 (s, 1H, MeNC**H**=C),, 5.11 (br. s, 1H, N**H**), 4.91 (s, 1H, NHC**H**), 3.08 (s, 3H, NC**H**$_3$), 1.70 (m, 2H, CHCC**H**$_2$CH$_2$), 1.33 (m, 2H, CHCCH$_2$C**H**$_2$) 0.85 (t, J=7.3, 3H, NCHCCH$_2$CH$_2$C**H**$_3$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 153.3 (C), 141.5 (C), 134.0 (C), 129.1 (CH), 128.5 (CH), 124.8 (CH), 113.4 (C), 59.3 (CH), 34.4 (CH_3), 32.4 (CH_2), 20.3 (CH_2), 13.7 (CH_3); IR (cm^{-1}), 3208 (w), 2957 (w), 1673 (s), 1481, 1401, 1266, 1086; HRMS *m/z* (CI), 265.1101 $[M+H]^+$

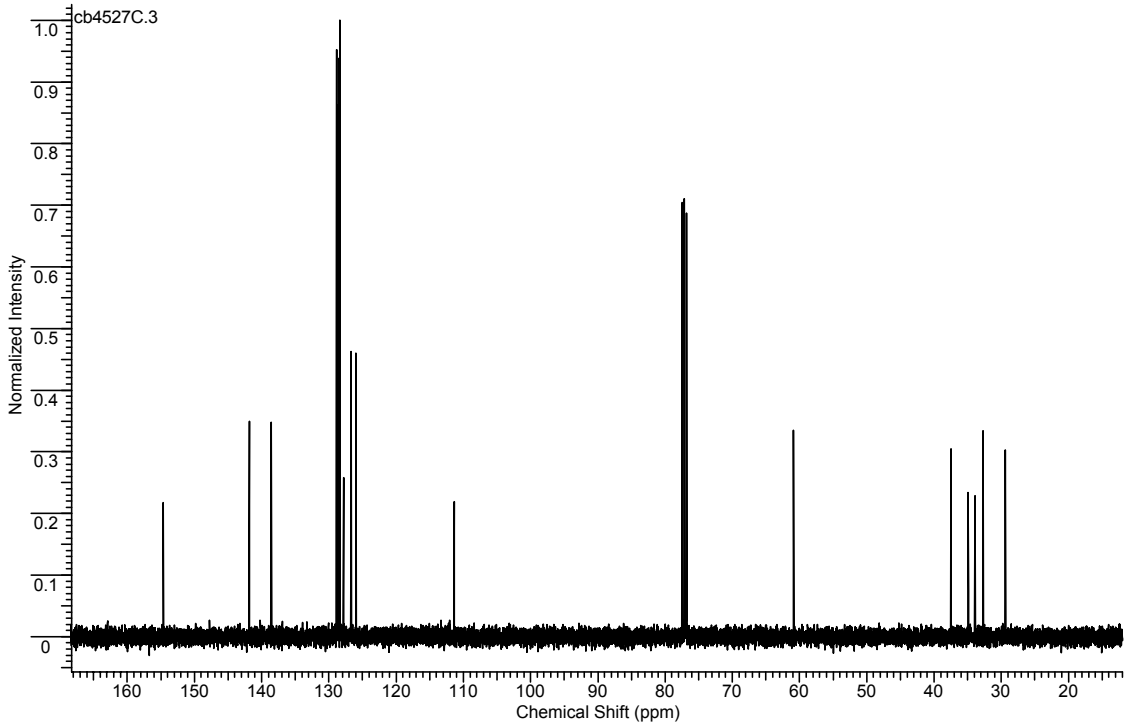


13 (Table 4, Entry 4) (60%)

^{1}H NMR (400MHz, $CDCl_3$) δ = 7.40-7.10 (m, 10H, Ar**H**), 5.80 (s, 1H, NC**H**=C), 5.08 (br.s, 1H, N**H**), 4.80 (br. s, 1H, NHC**H**), 3.17 (d, J=15.5, 1H, CH=CC**H**$_2$), 3.09 (s, 3H, NC**H**$_3$), 2.95 (d, J=15.4, 1H, CH=CC**H**$_2$); ^{13}C NMR (100MHz, $CDCl_3$) δ = 153.2 (C), 142.6 (C), 138.2 (C), 129.0 (CH), 128.9 (CH), 128.6 (CH), 128.3 (CH), 127.2 (CH), 126.7 (CH), 126.2 (CH), 113.6 (C), 59.3 (CH), 36.9 (CH_2), 34.4 (CH_3); IR (cm^{-1}), 3212 (w), 1699 (s), 1668 (s), 1450, 1404, 760; HRMS *m/z* (CI), 279.1493 $[M+H]^+$

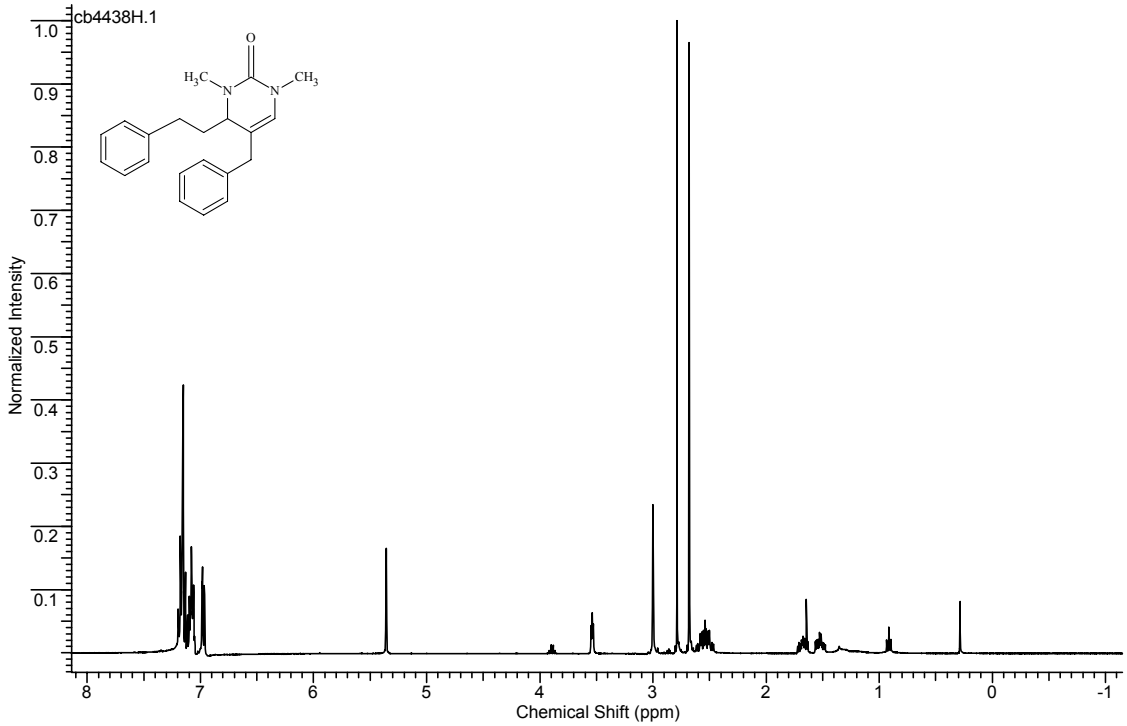
Table 1: Entry 1 (2)

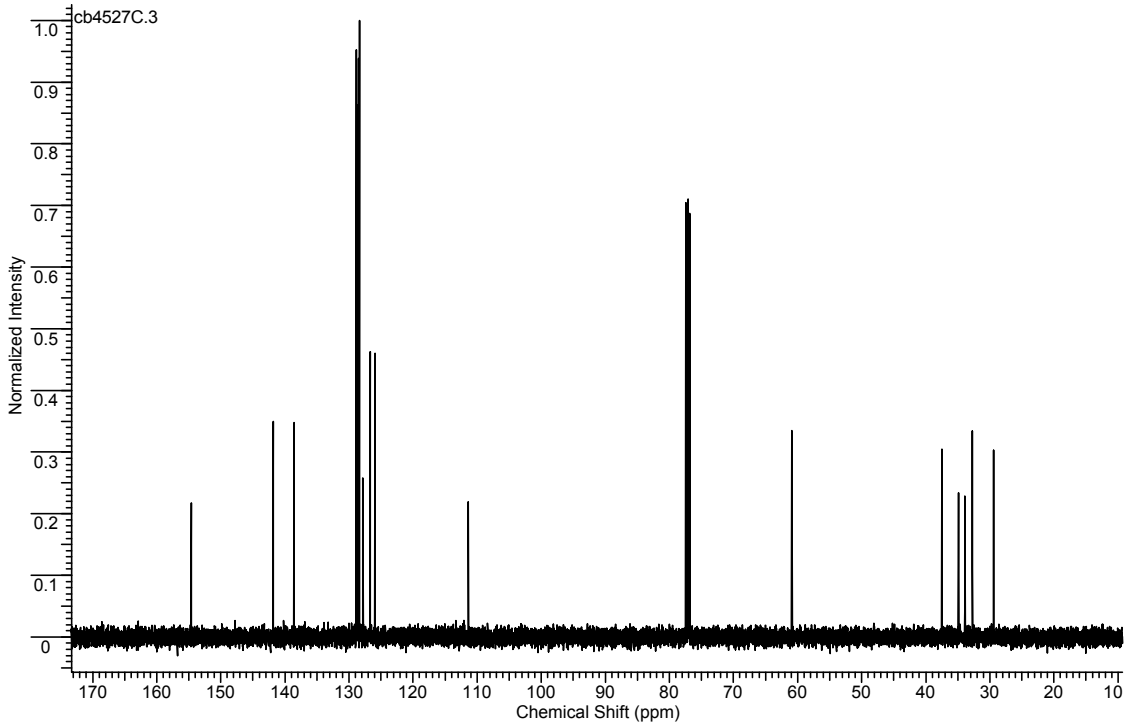




Supplementary Material (ESI) for Chemical Communications

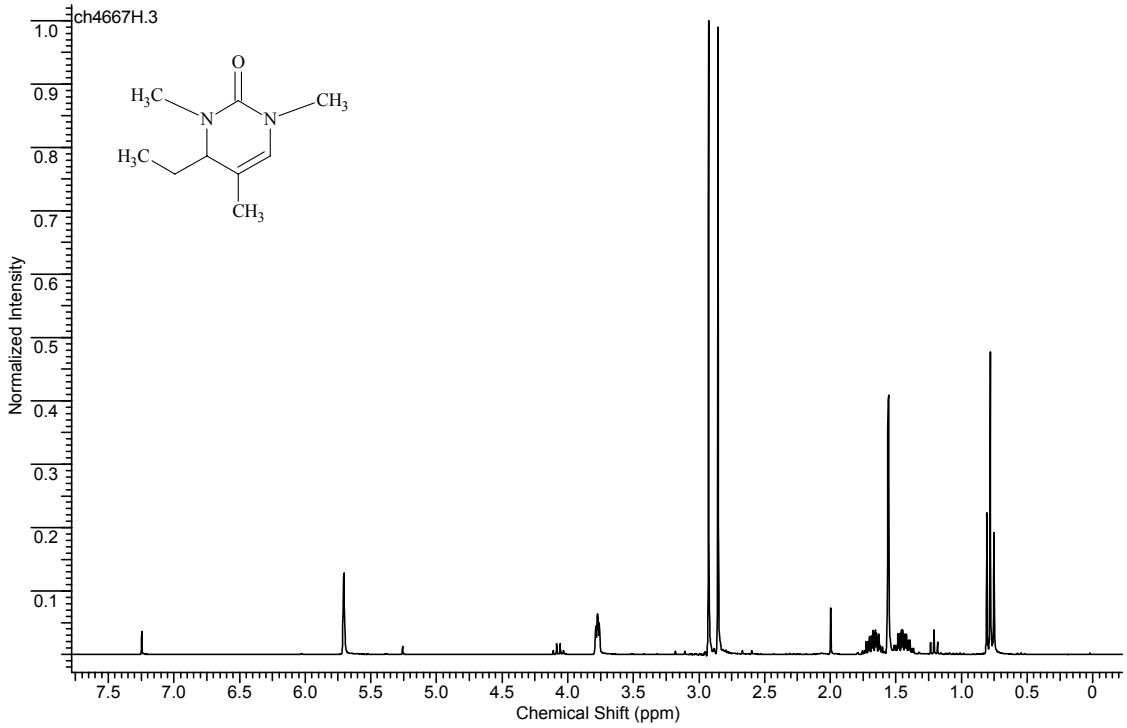
Table 1: Entry 2

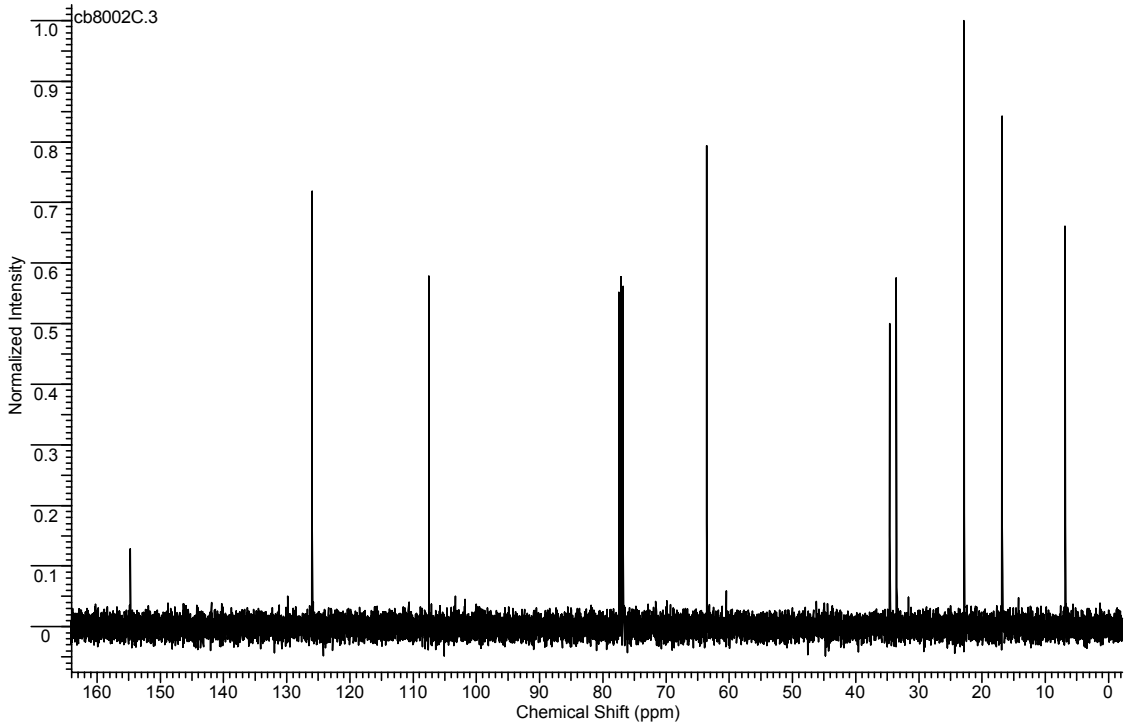




Supplementary Material (ESI) for Chemical Communications

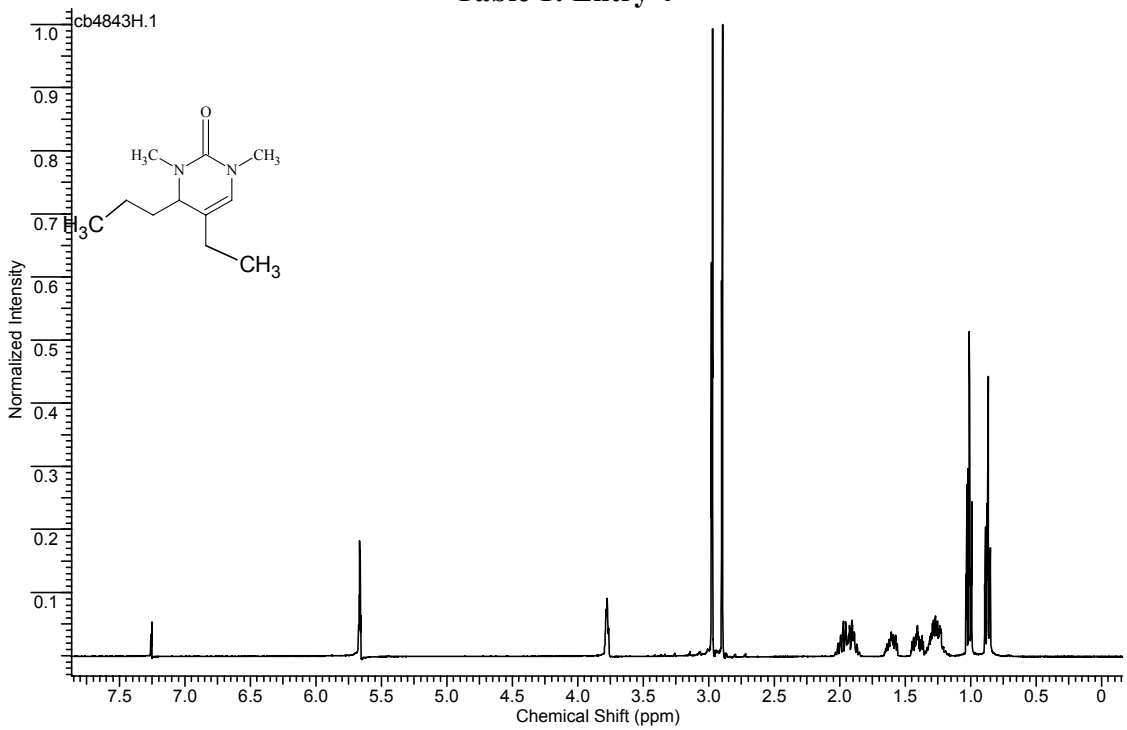
Table 1: Entry 3

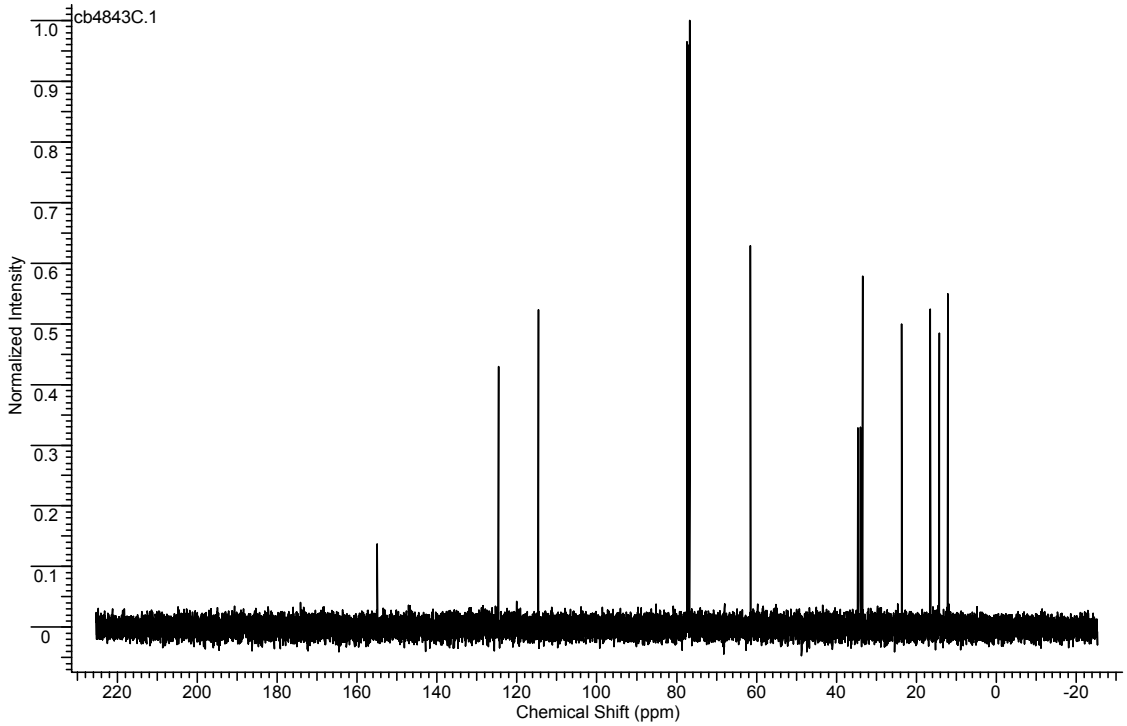




Supplementary Material (ESI) for Chemical Communications

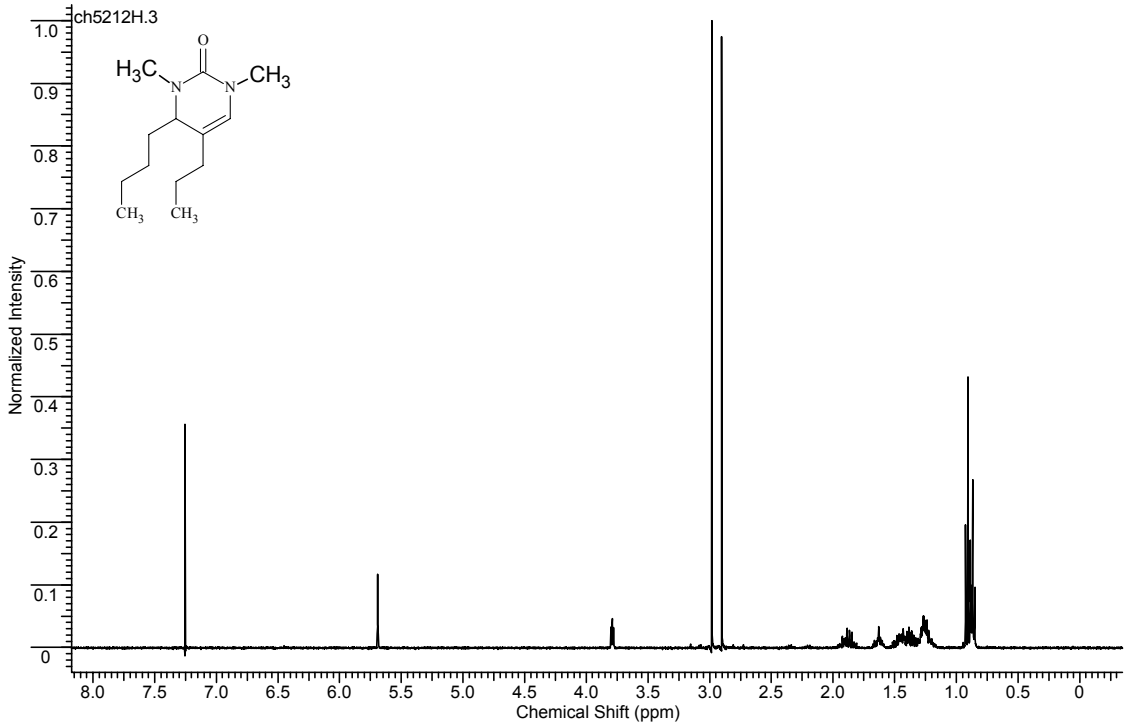
Table 1: Entry 4

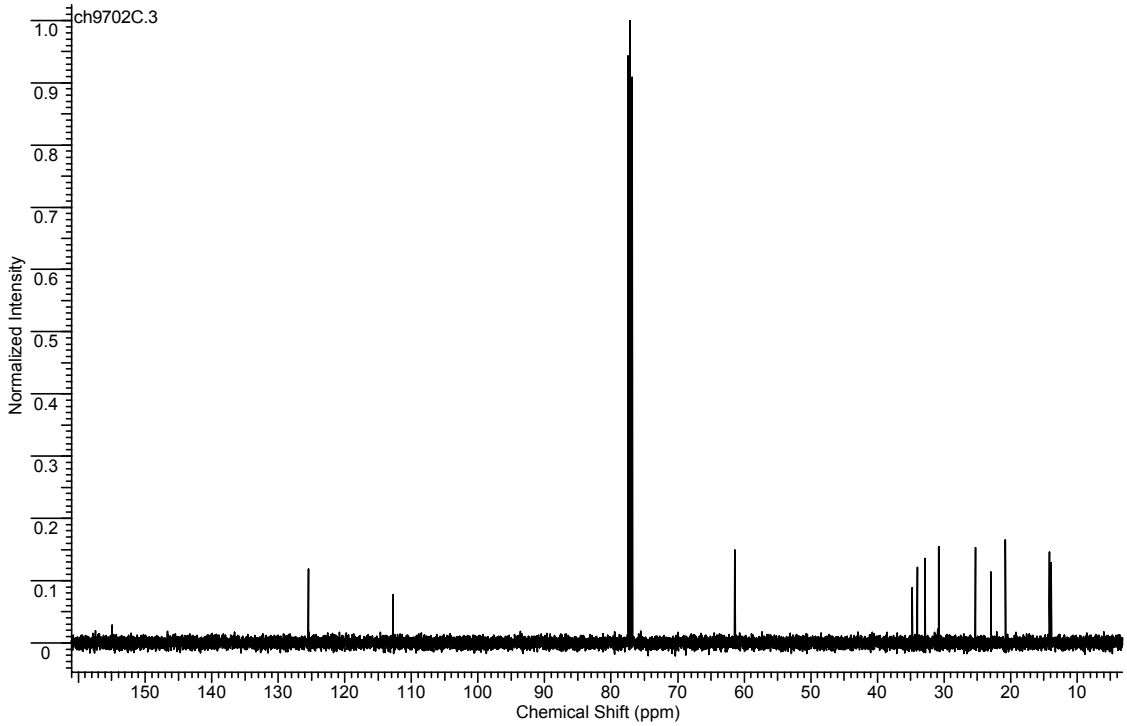




Supplementary Material (ESI) for Chemical Communications

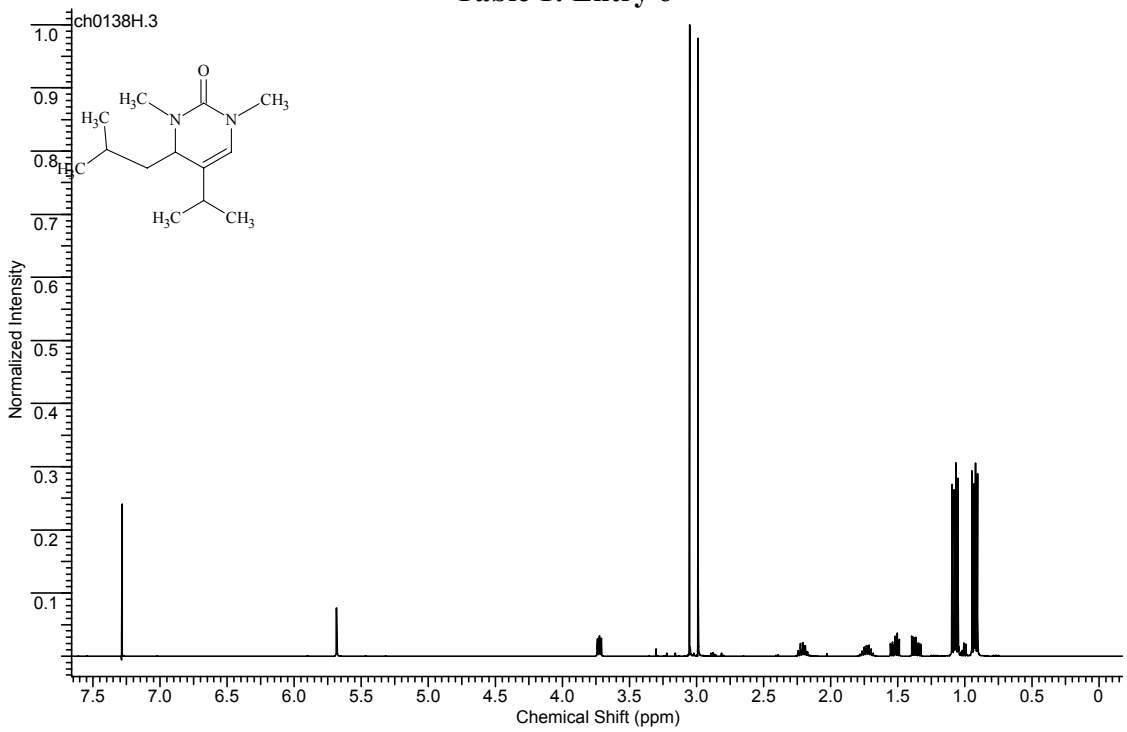
Table 1: Entry 5





Supplementary Material (ESI) for Chemical Communications

Table 1: Entry 6



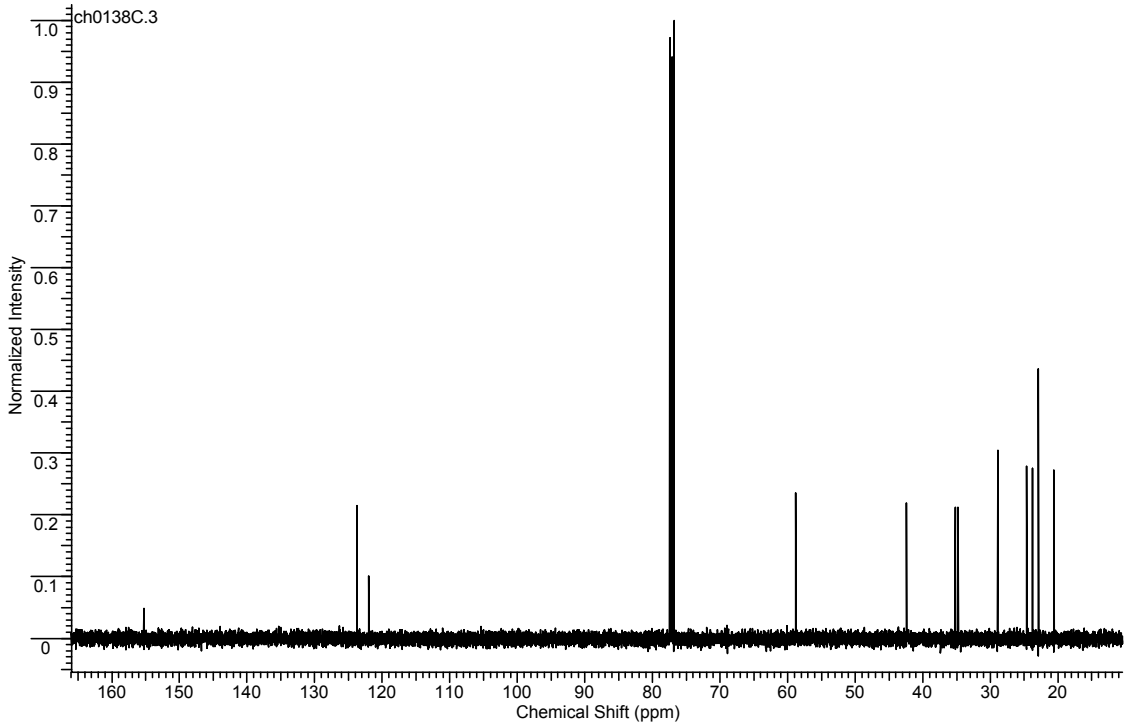
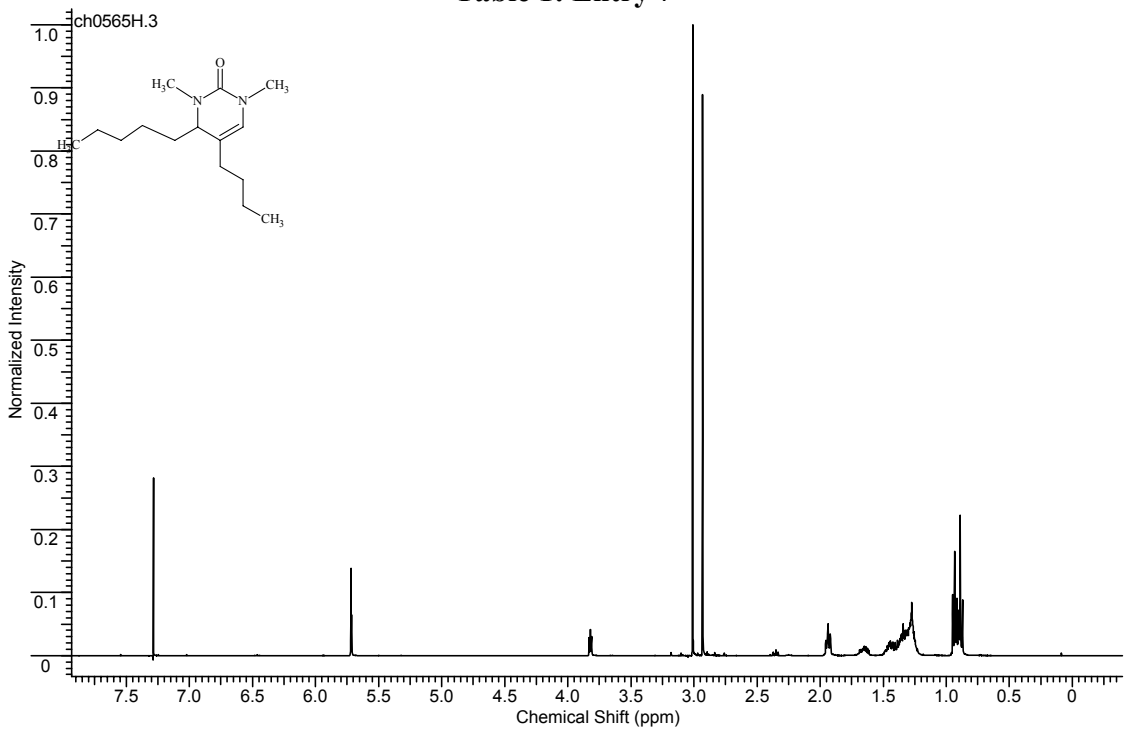


Table 1: Entry 7



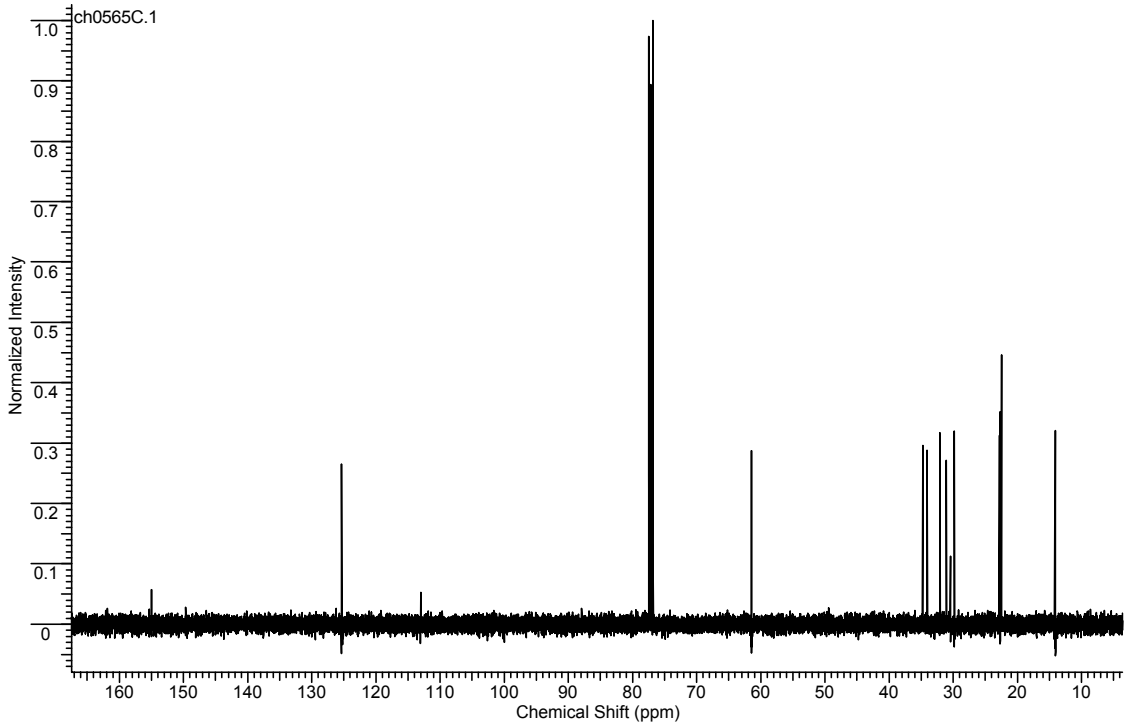
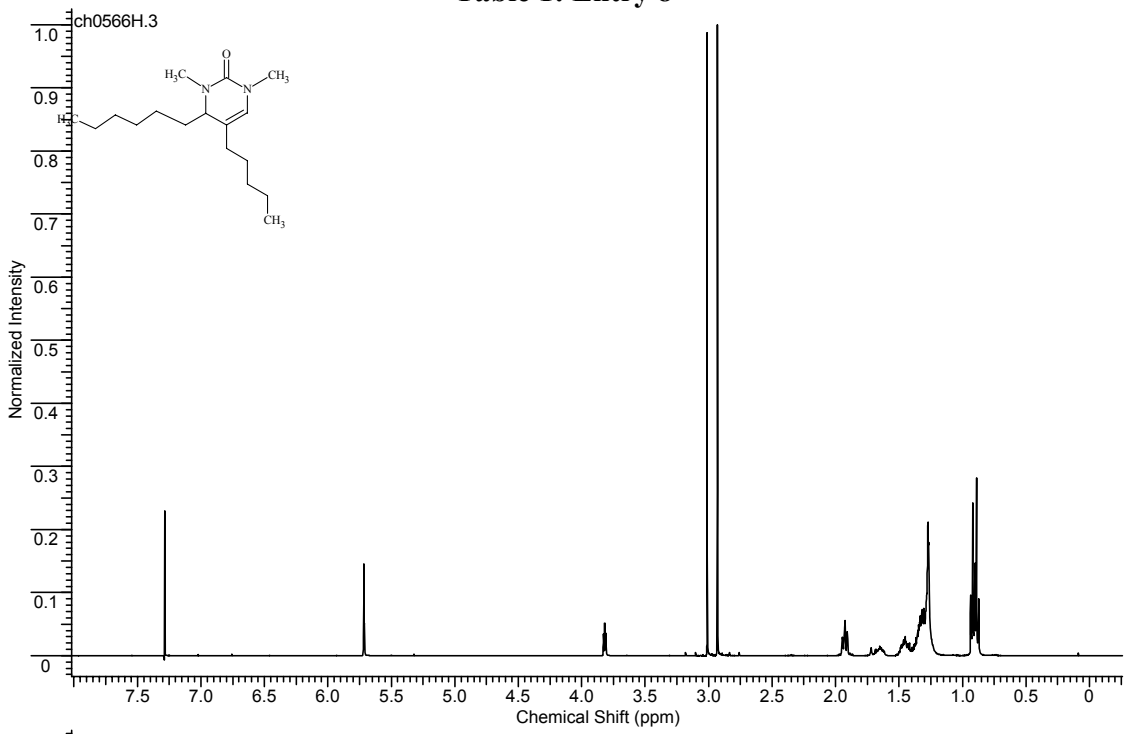
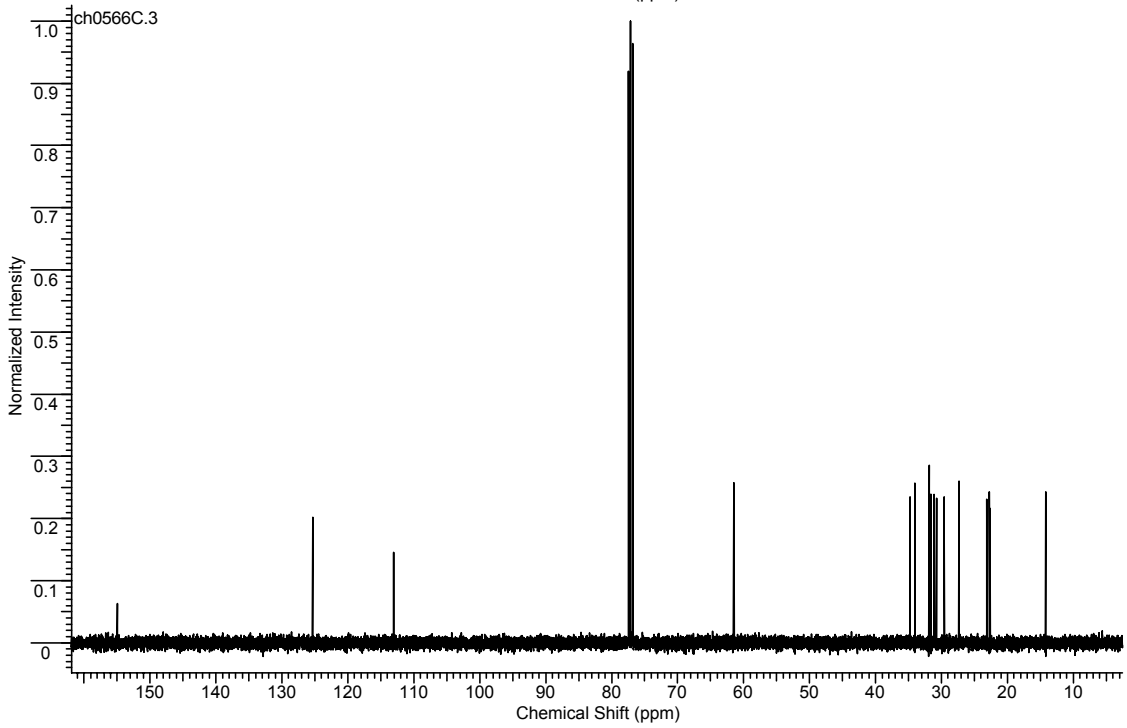


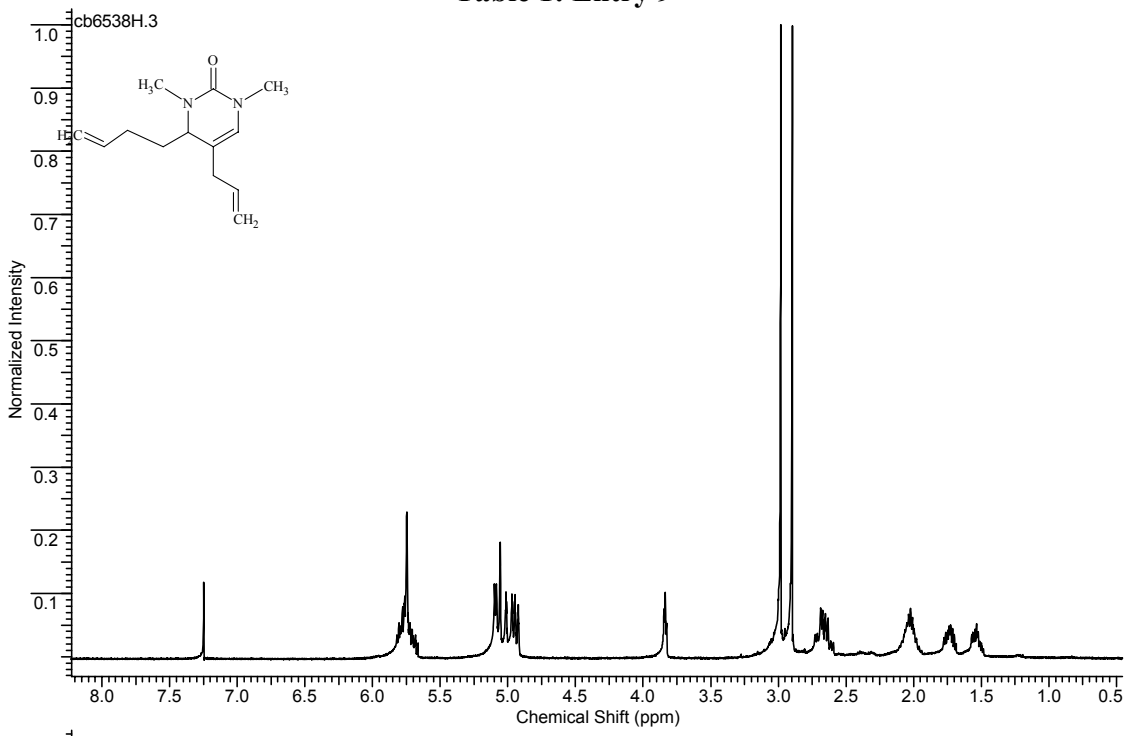
Table 1: Entry 8





Supplementary Material (ESI) for Chemical Communications

Table 1: Entry 9



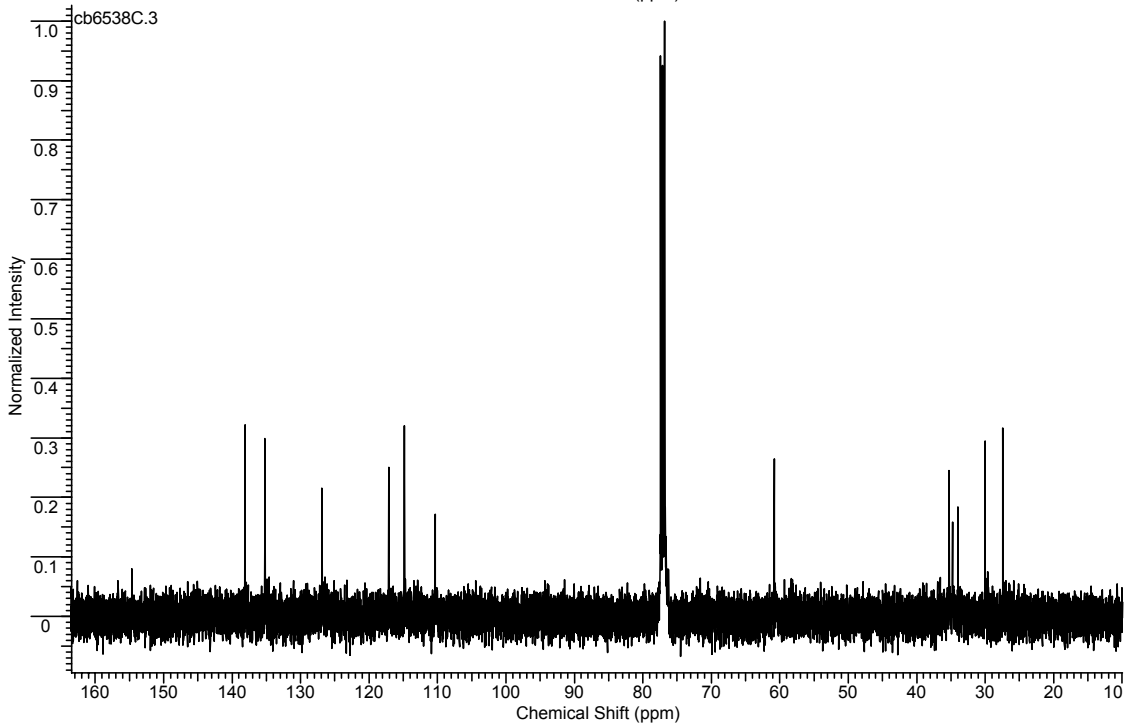


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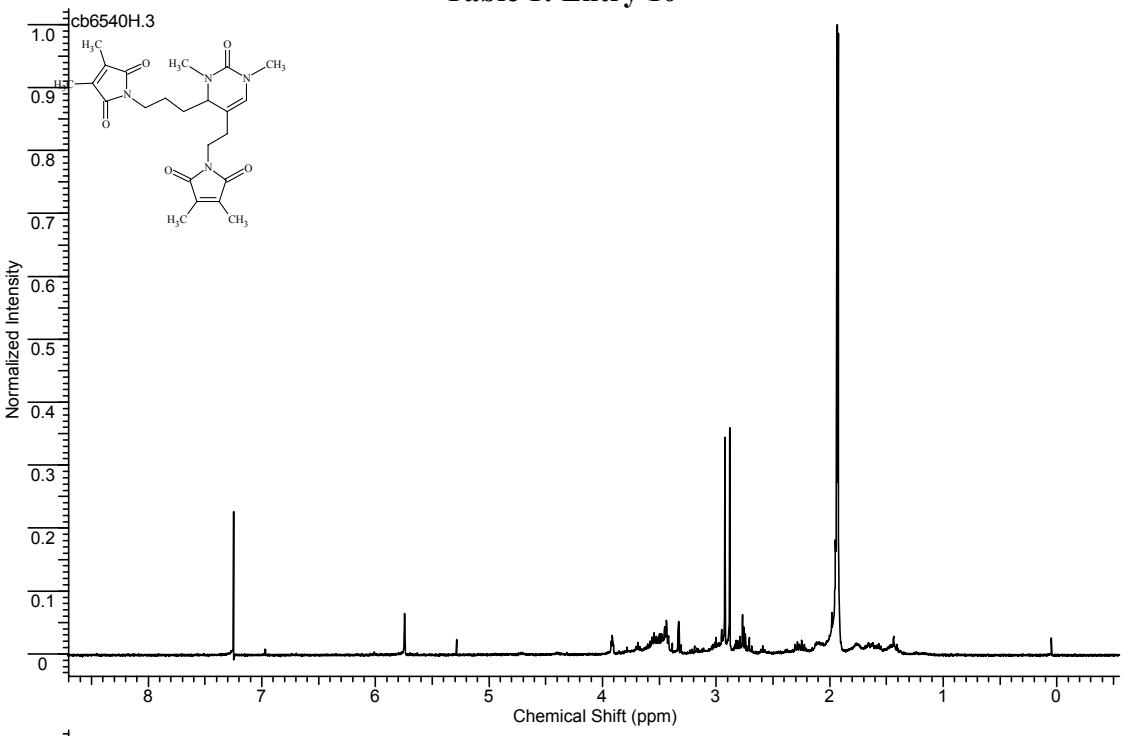
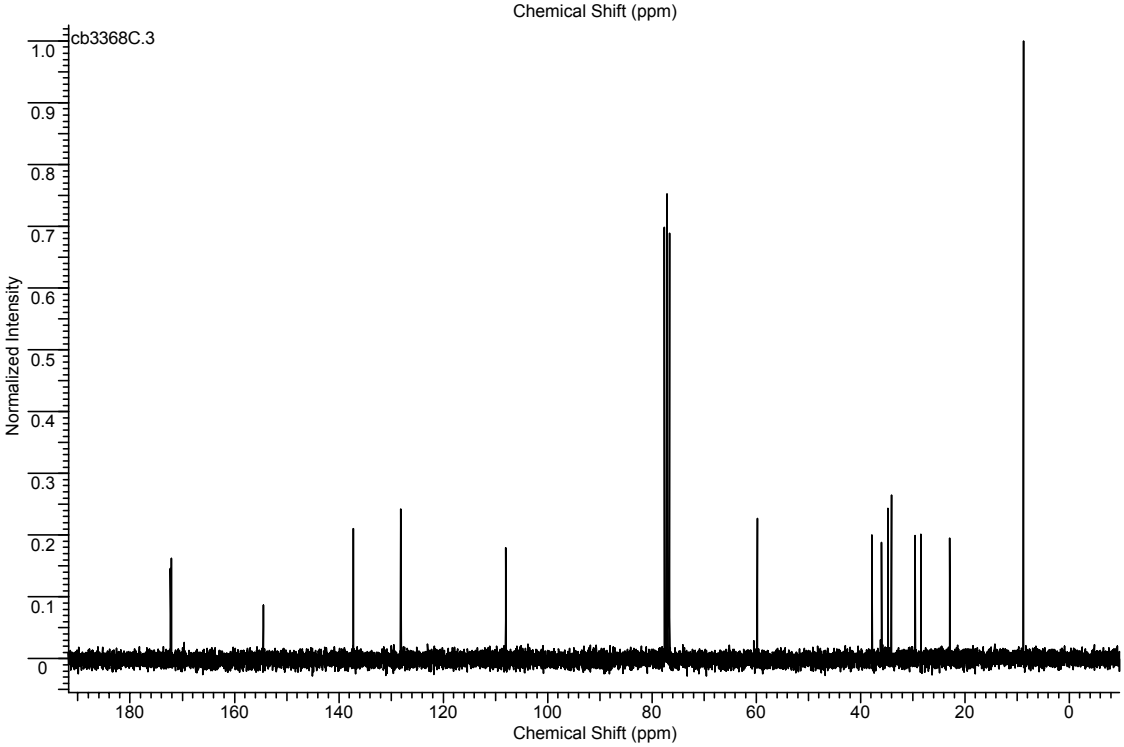
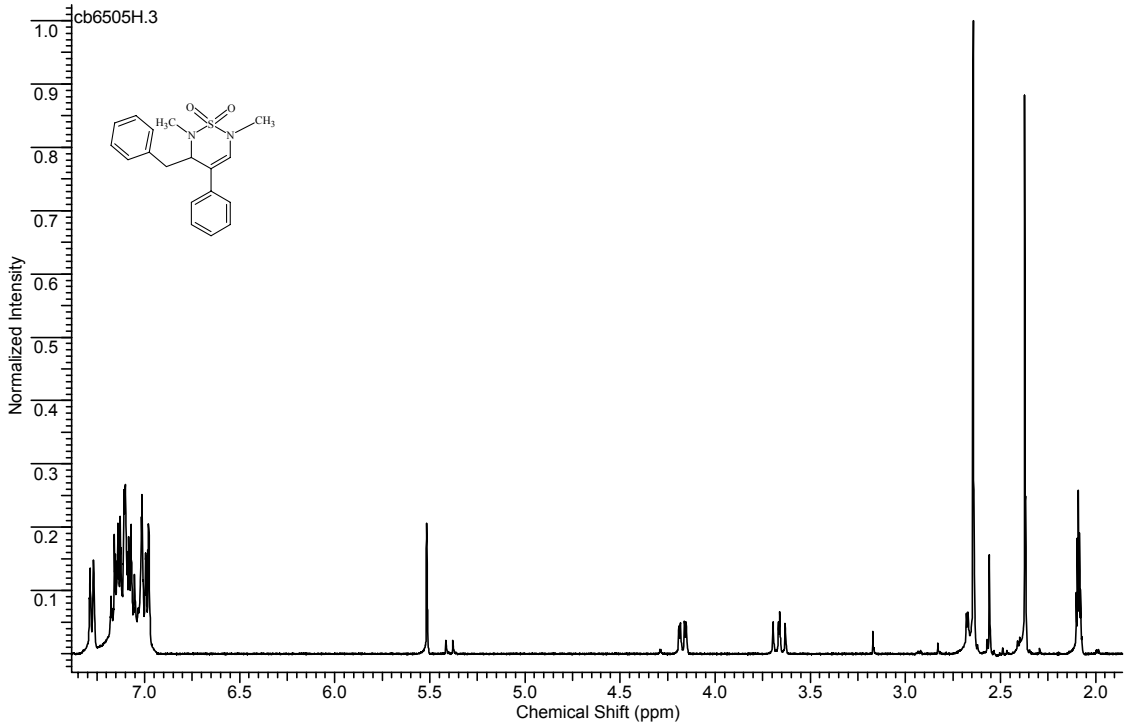
Table 1: Entry 10

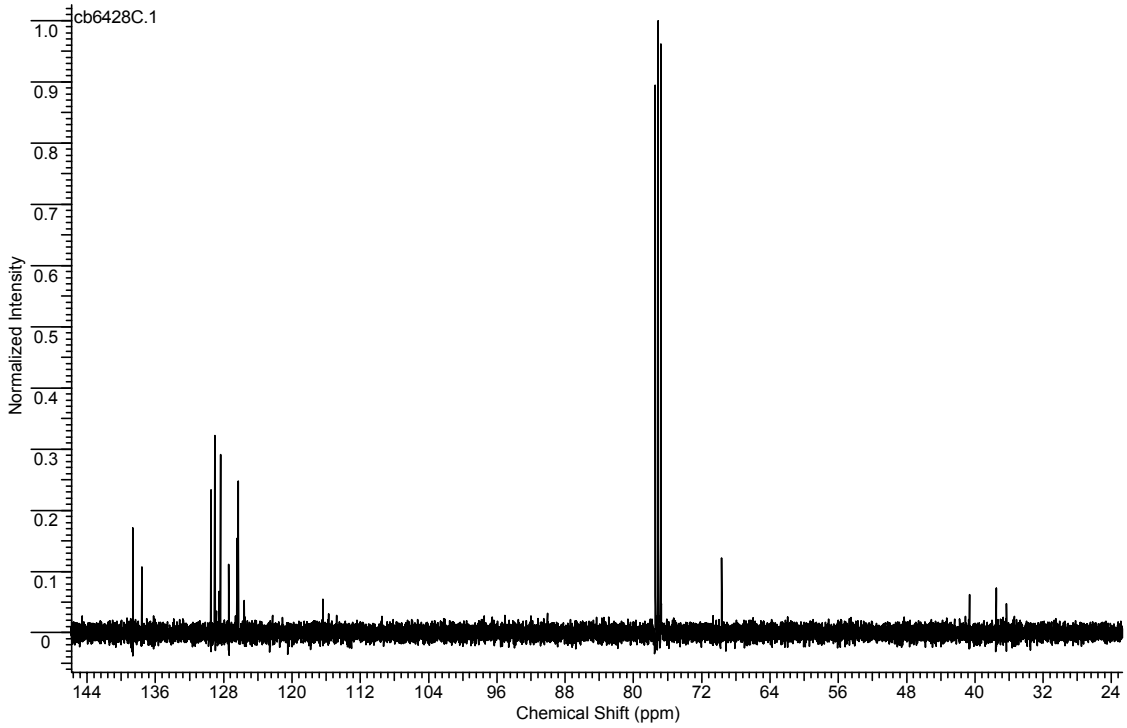




Supplementary Material (ESI) for Chemical Communications

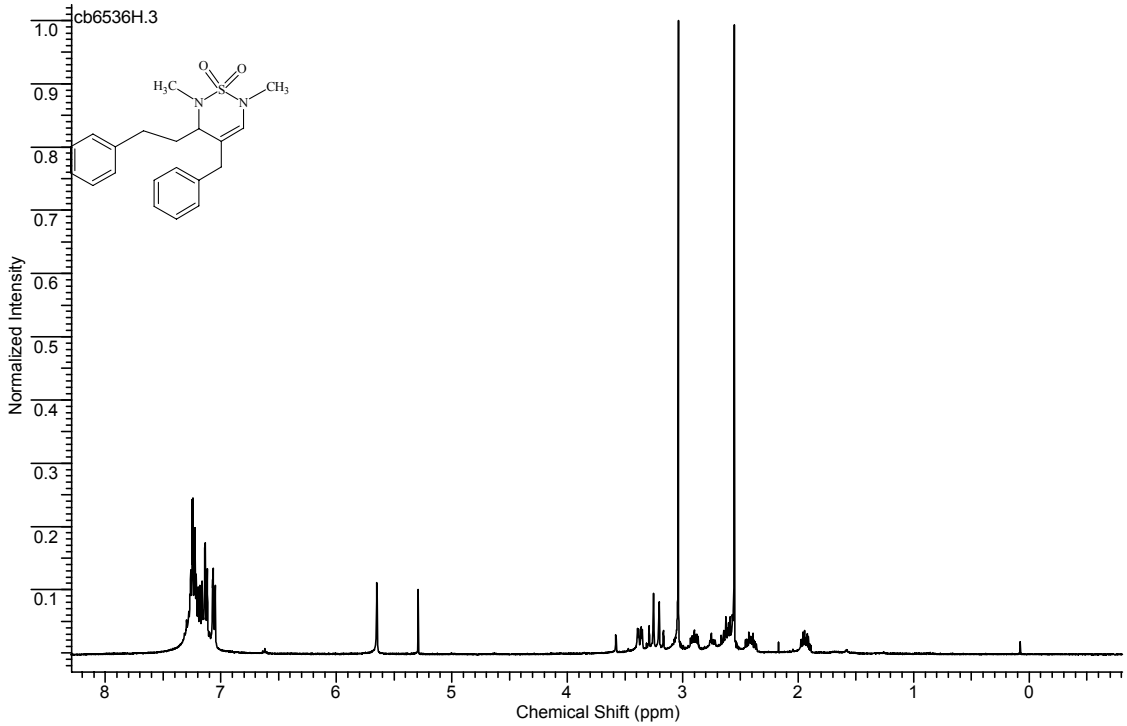
Table 1: Entry 11

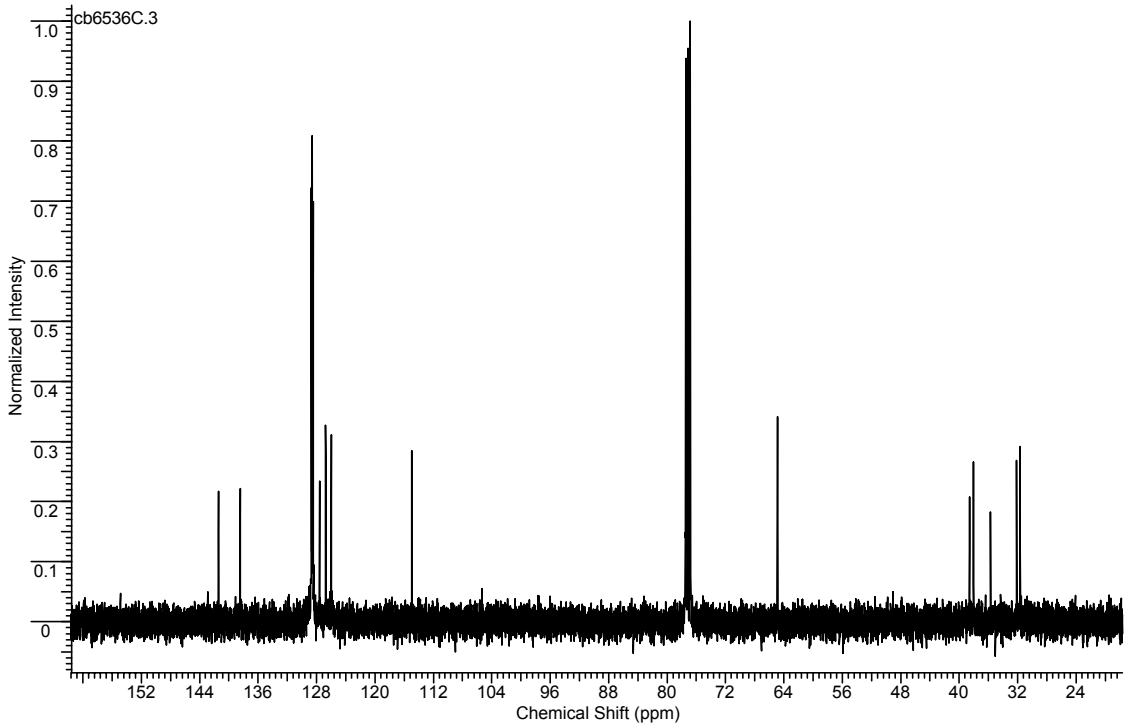




Supplementary Material (ESI) for Chemical Communications

Table 1: Entry 12





Supplementary Material (ESI) for Chemical Communications

Table 1: Entry 13

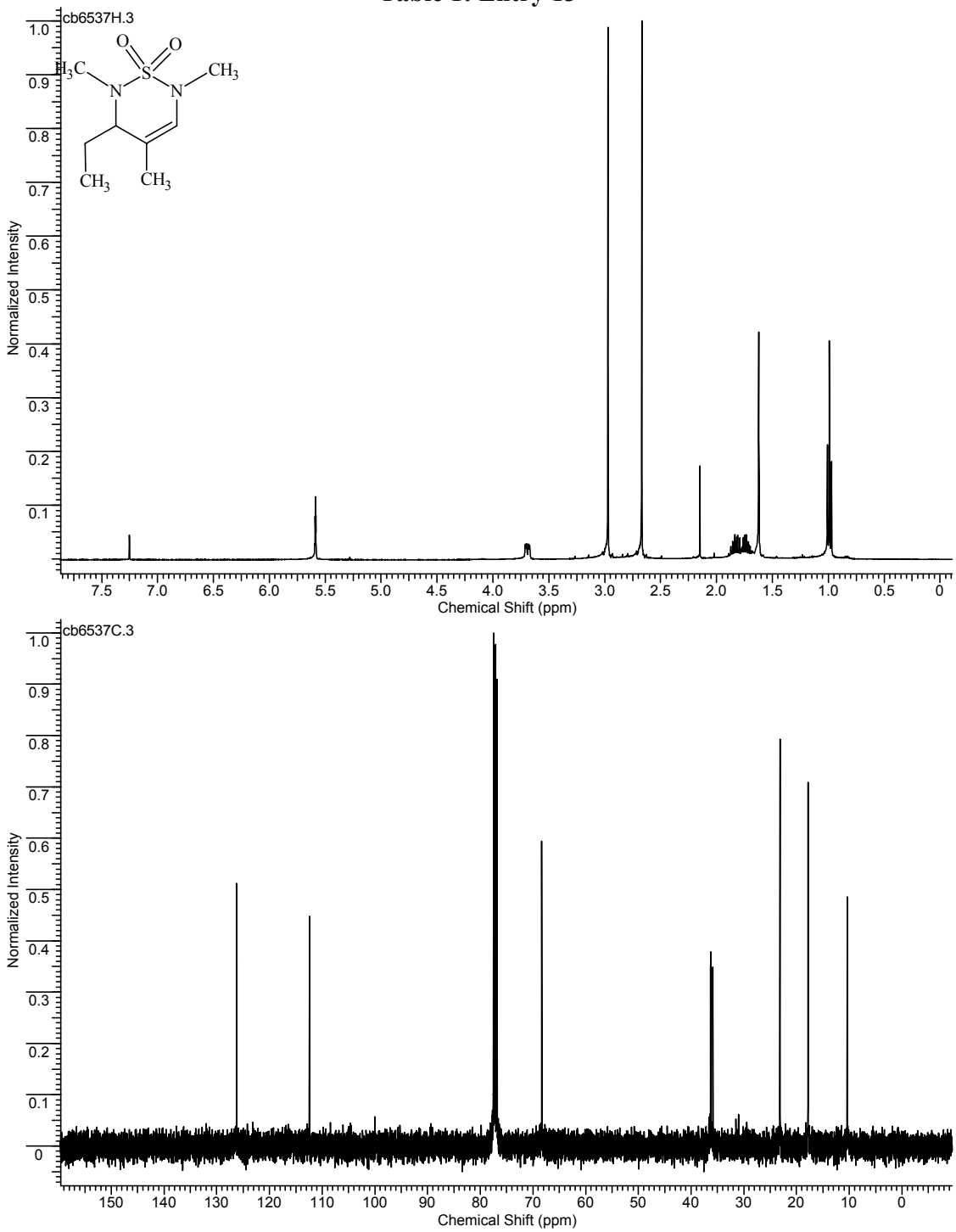
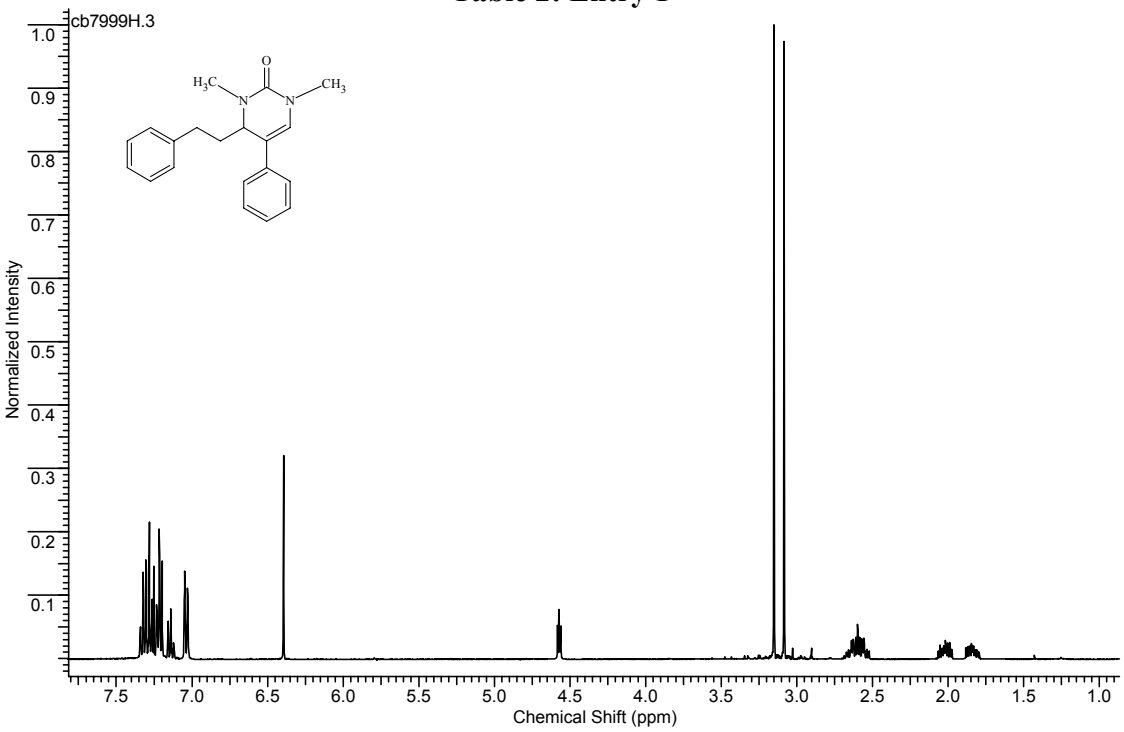


Table 2: Entry 1



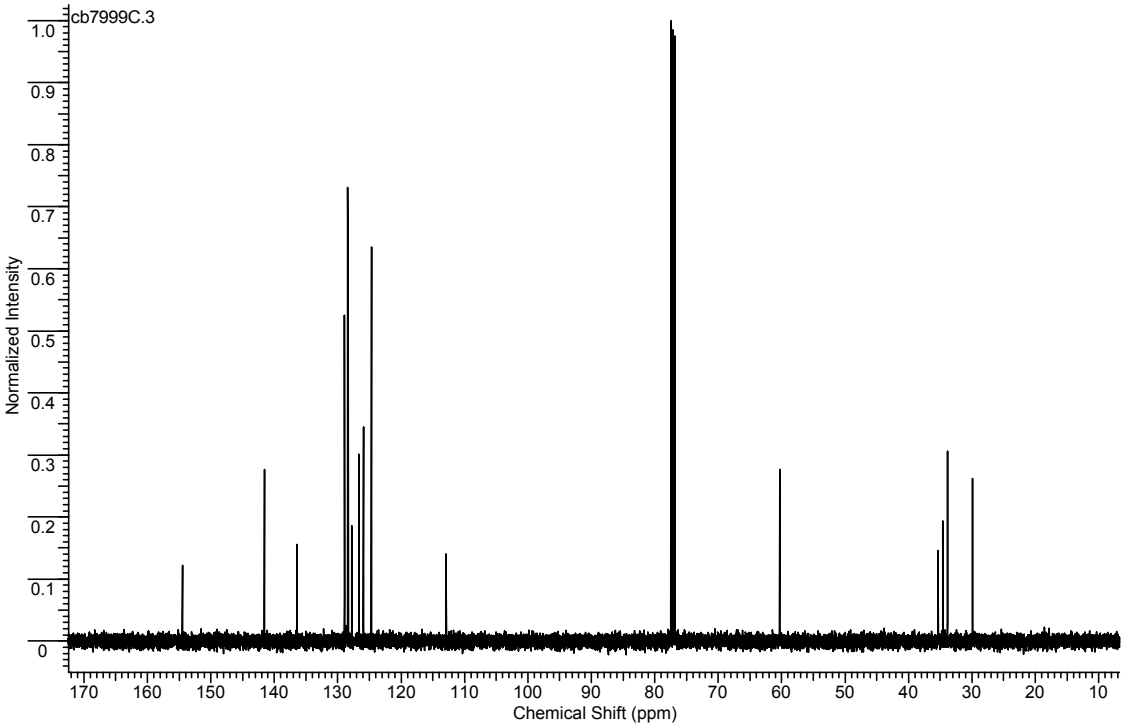
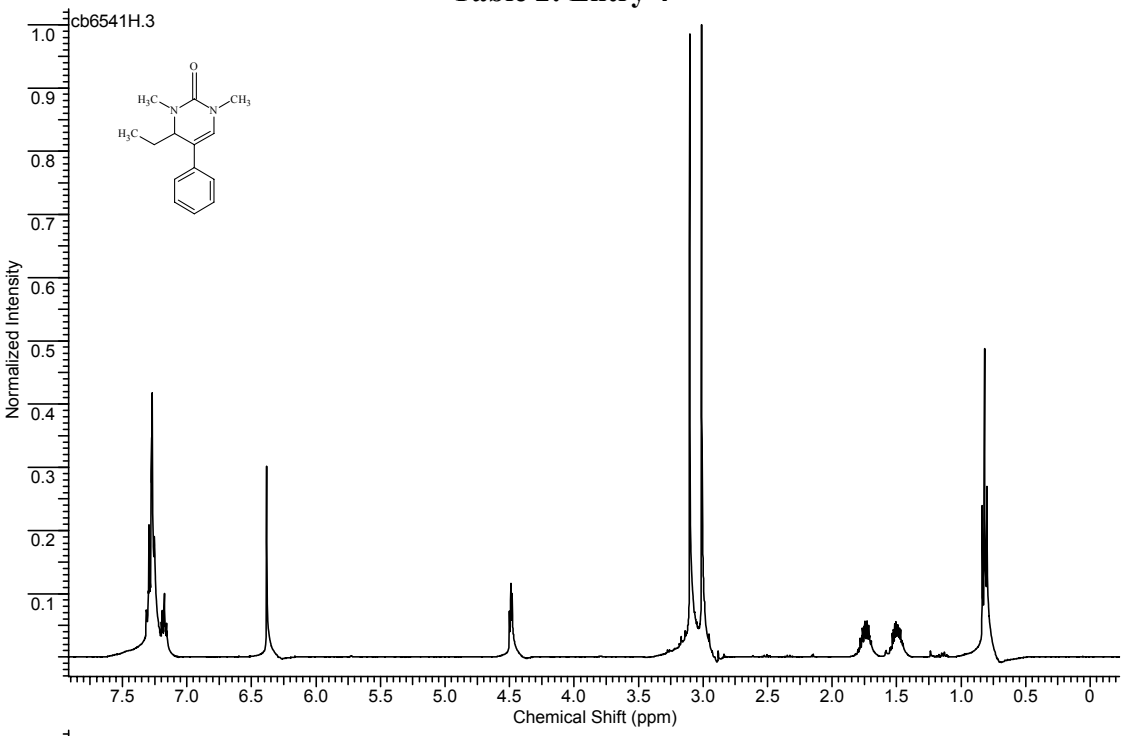


Table 2: Entry 4



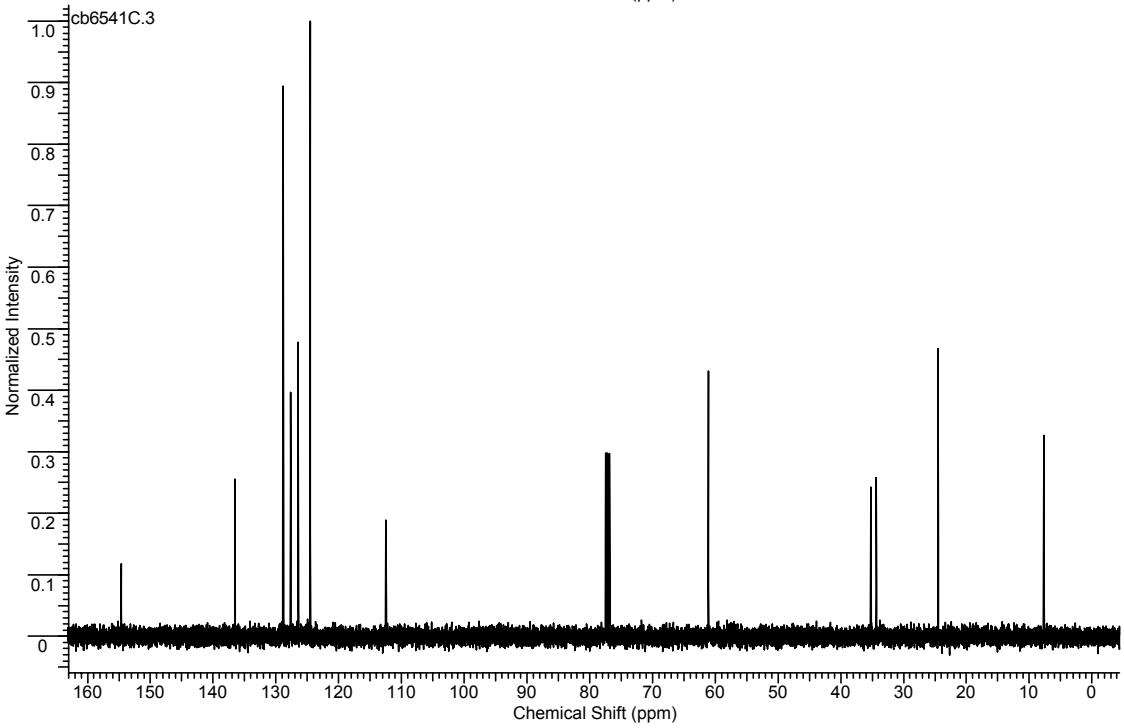


Table 2: Entry 5

As 3:1 mixture of regioisomers

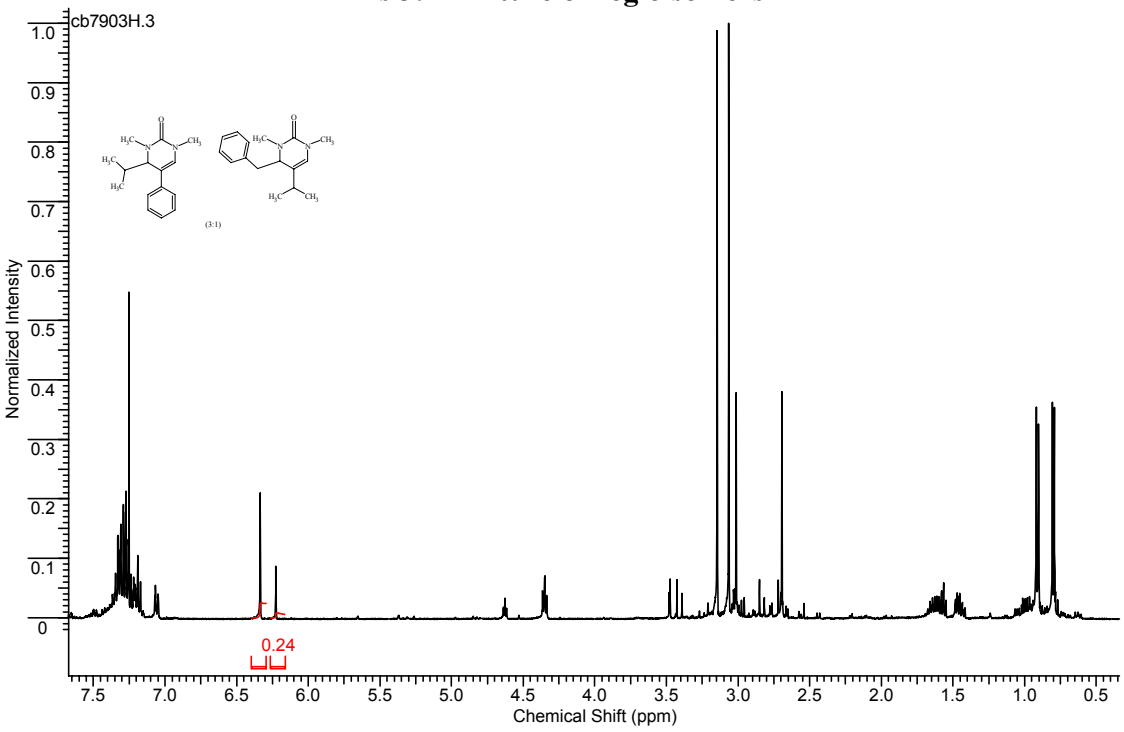
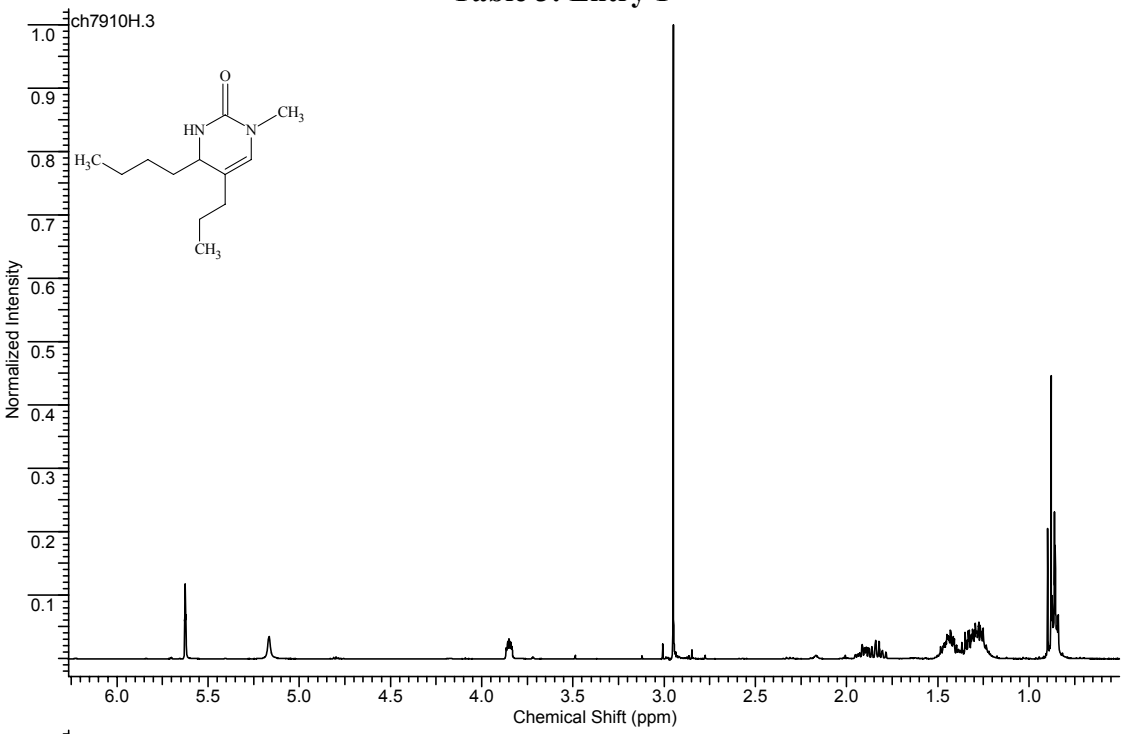


Table 3: Entry 1



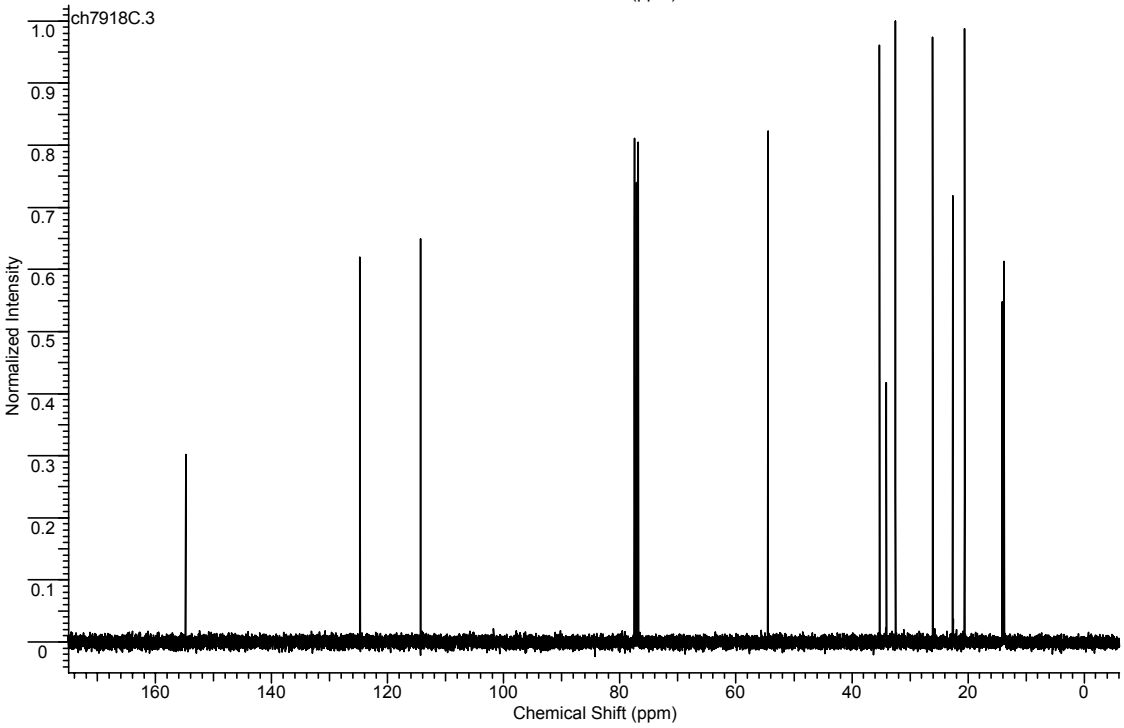
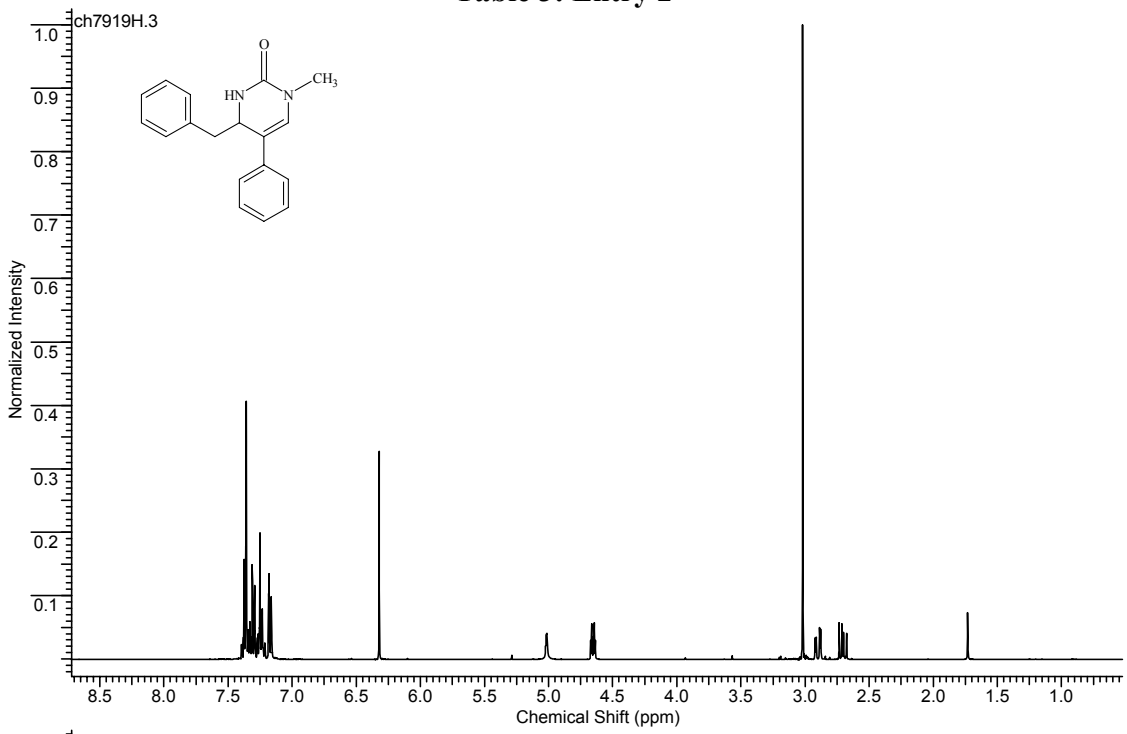


Table 3: Entry 2



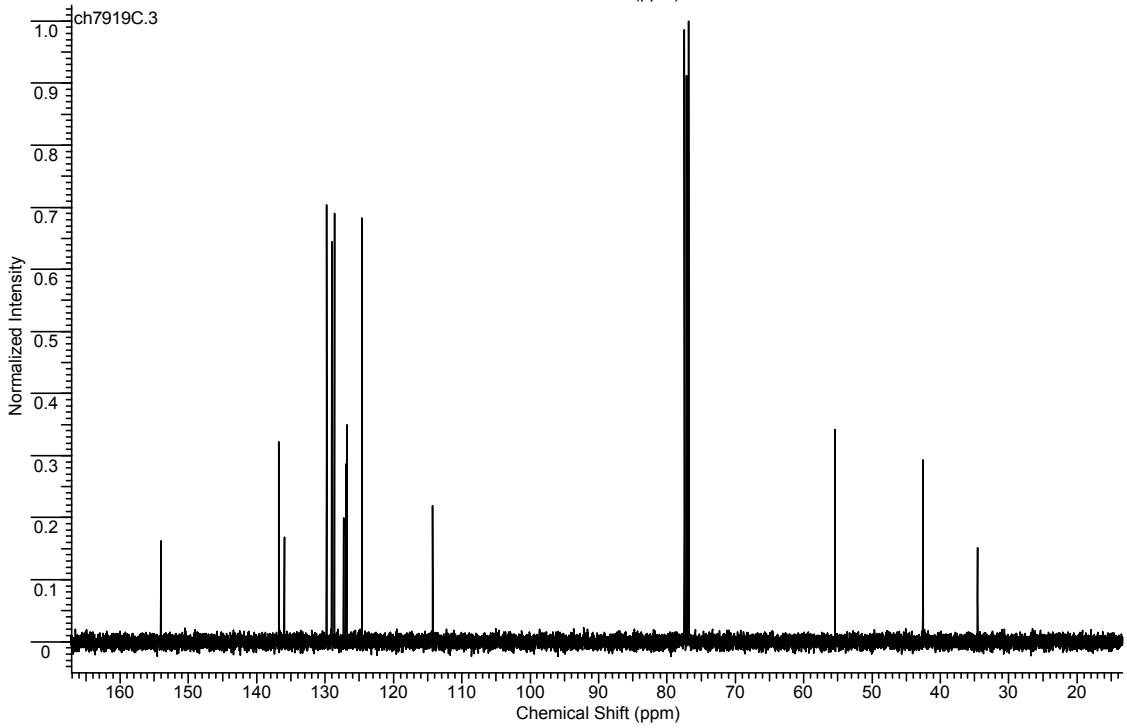
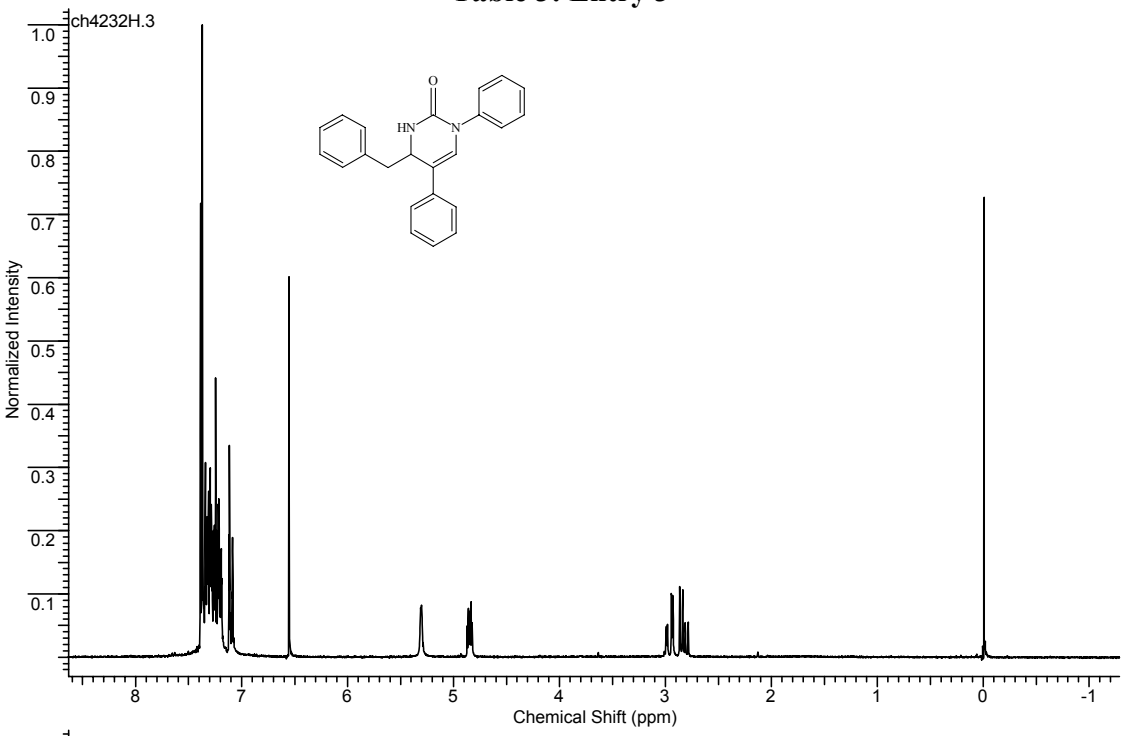


Table 3: Entry 3



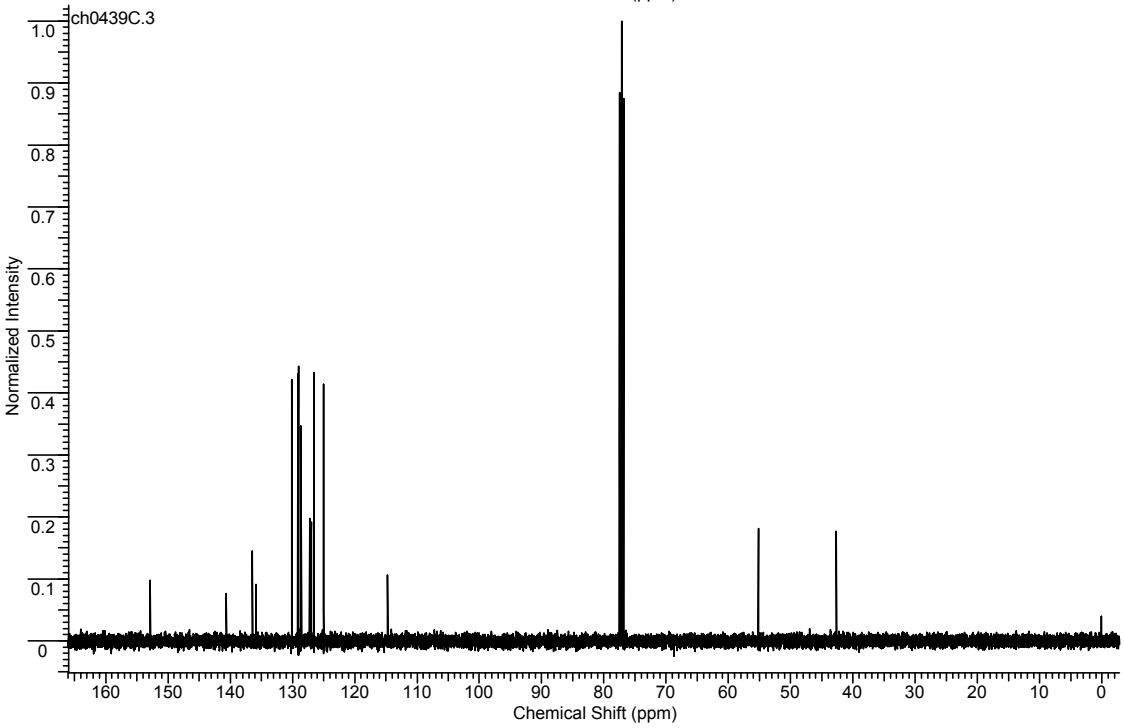
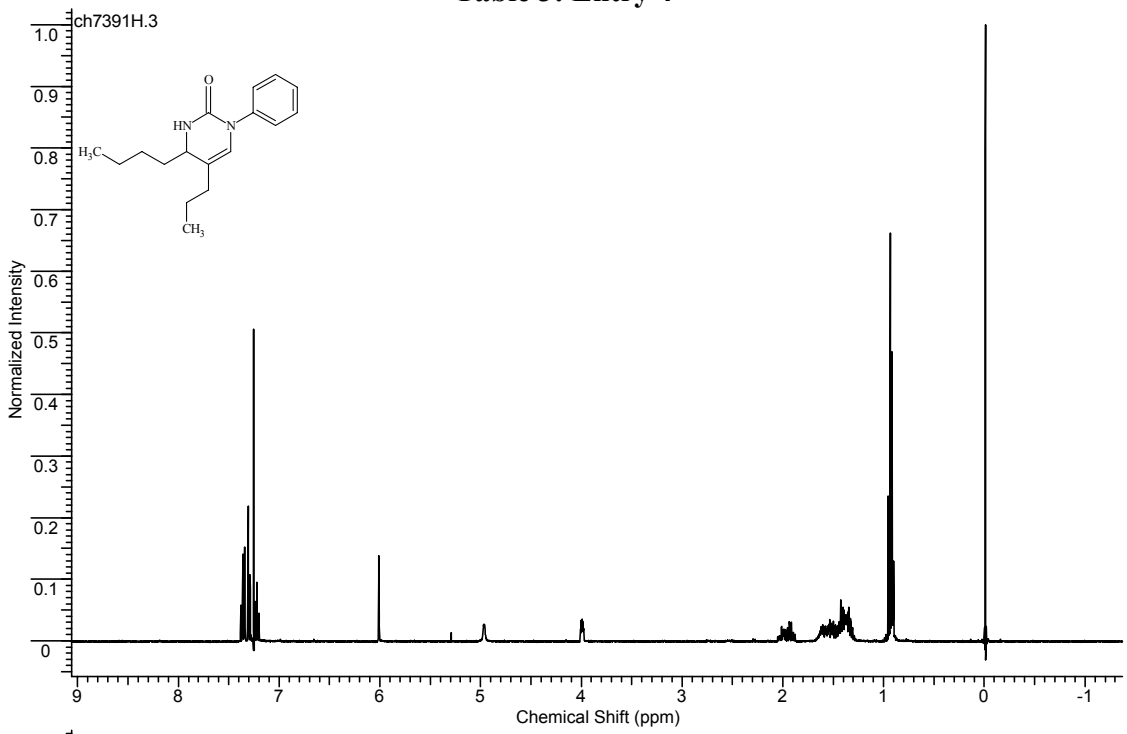
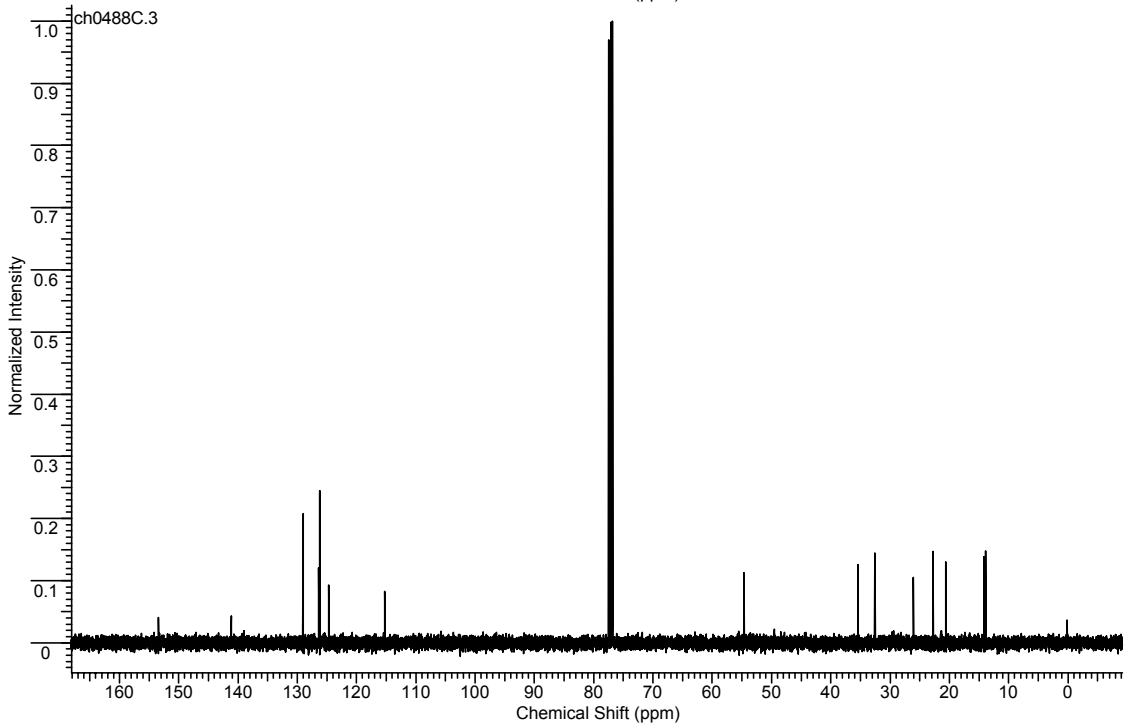
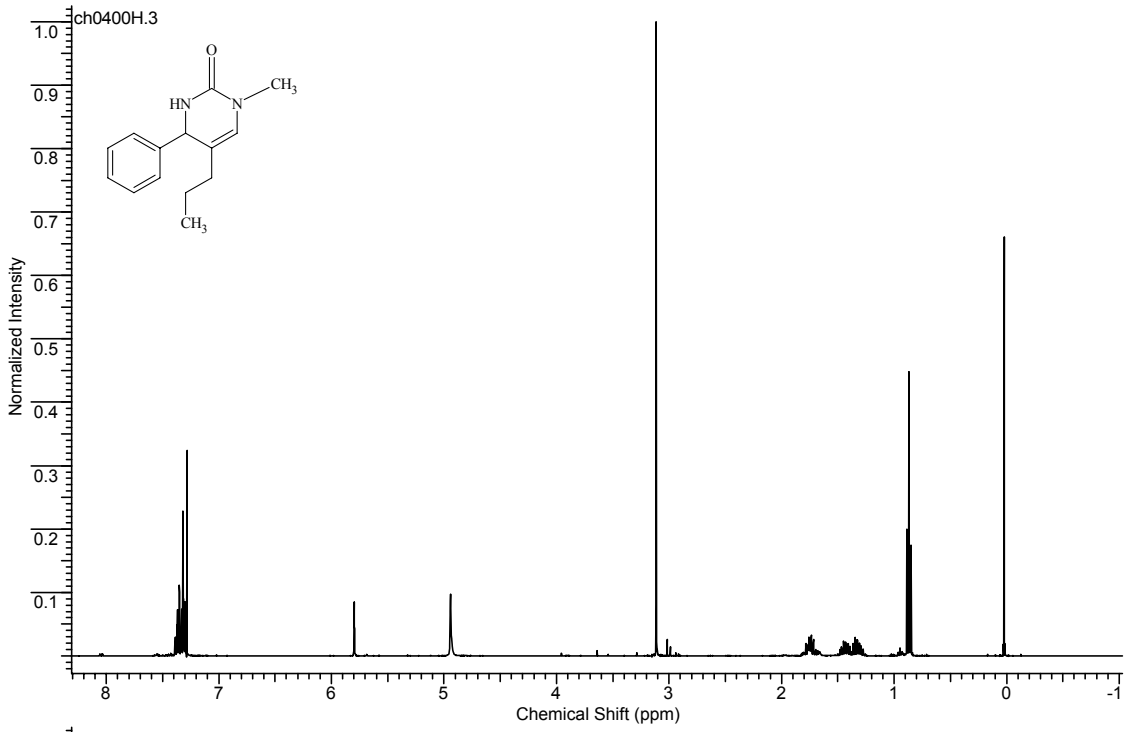


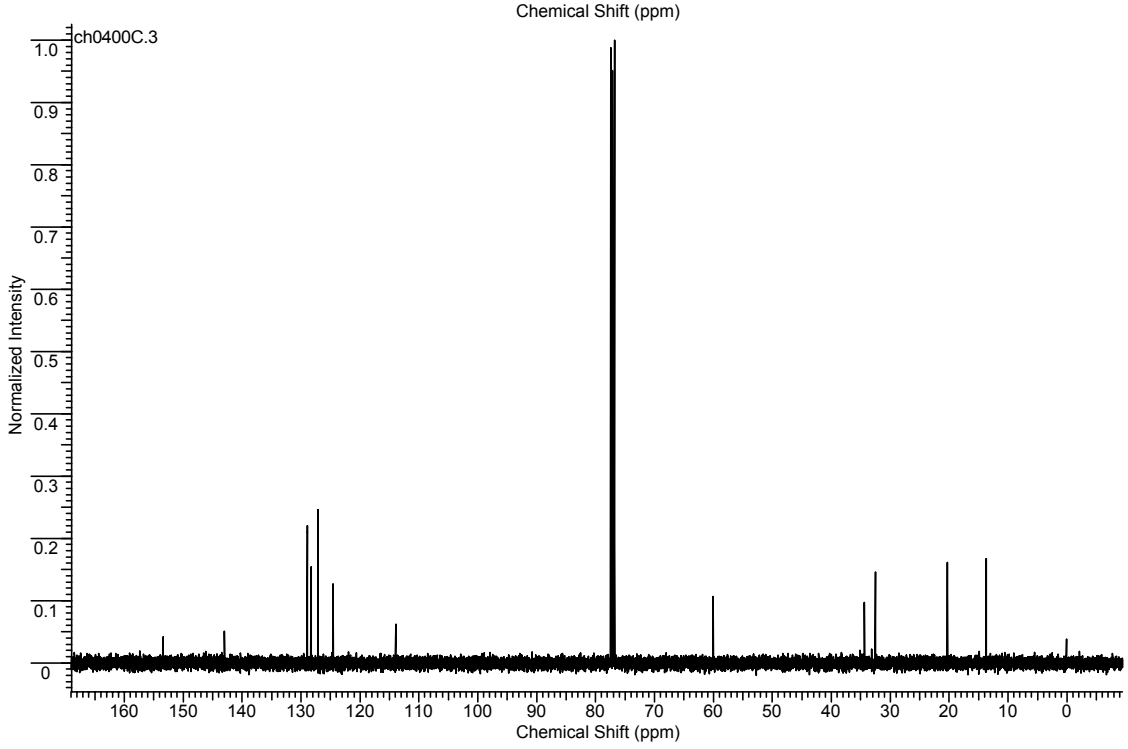
Table 3: Entry 4



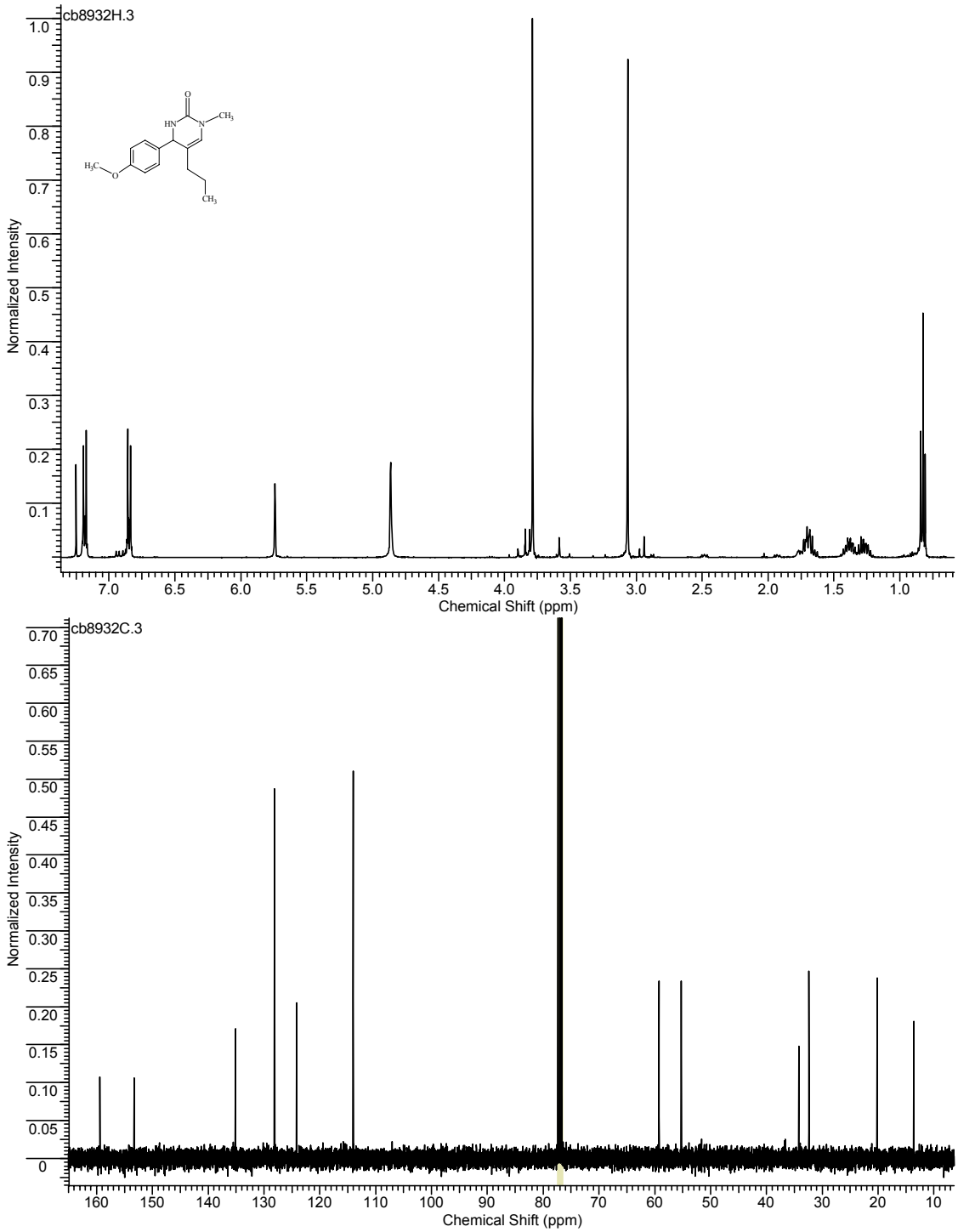


13 (Table 4, Entry1)

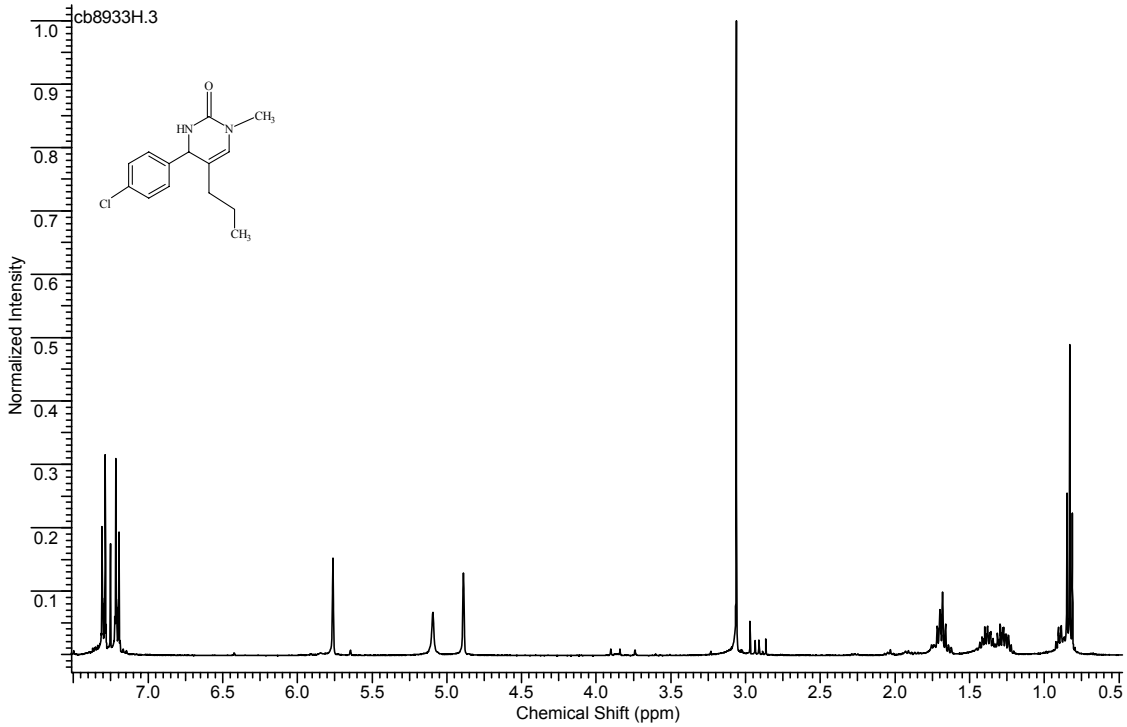


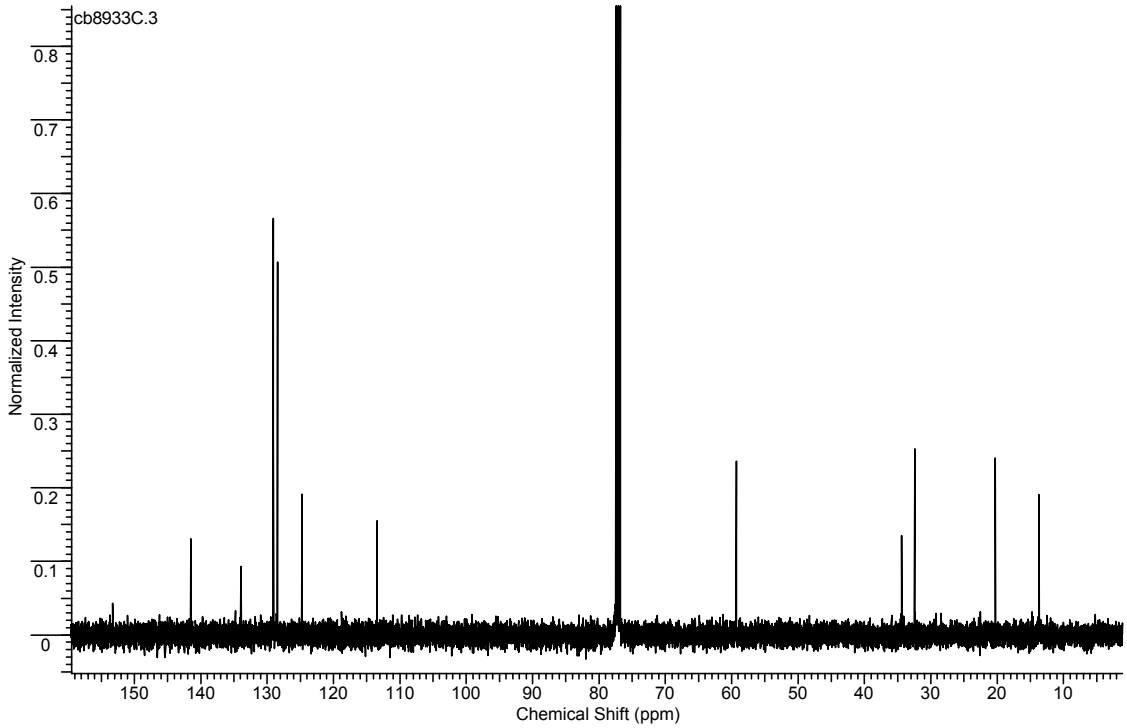


13 (Table 4, Entry3)

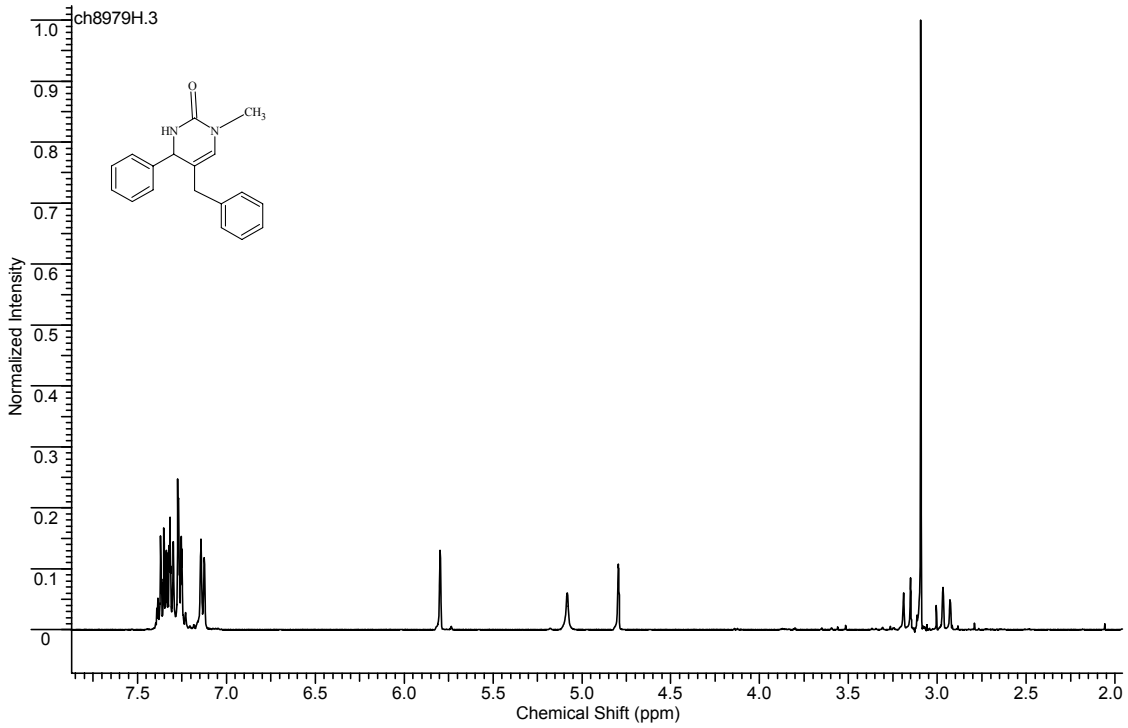


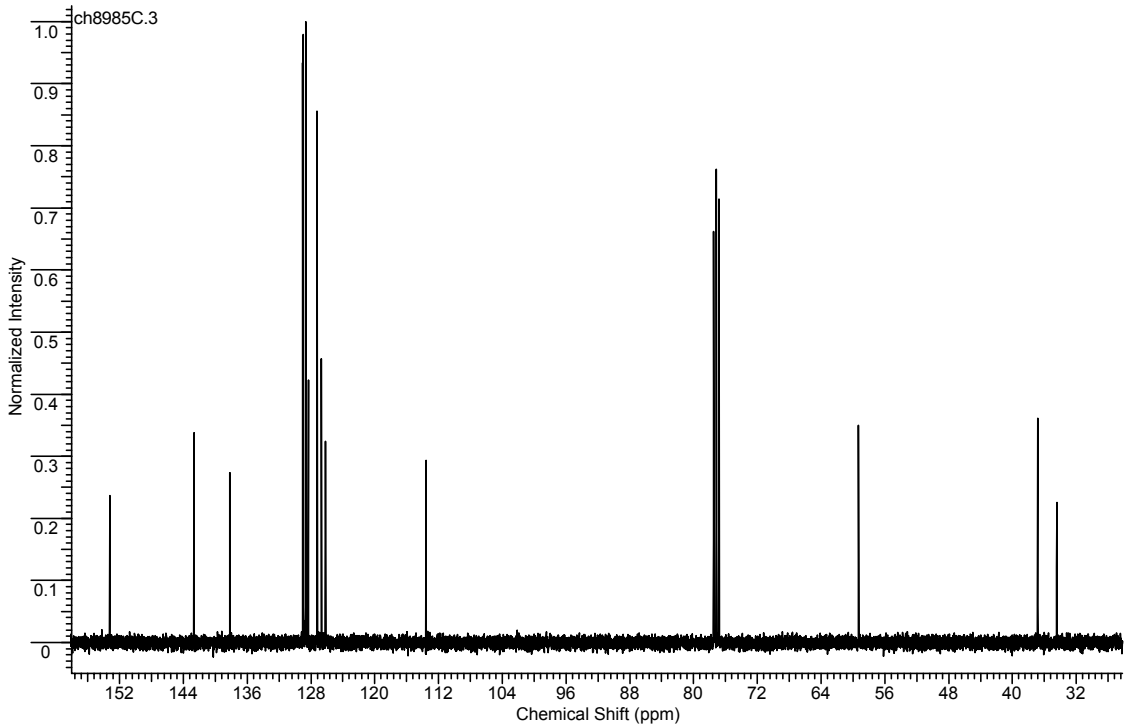
13 (Table 4, Entry2)



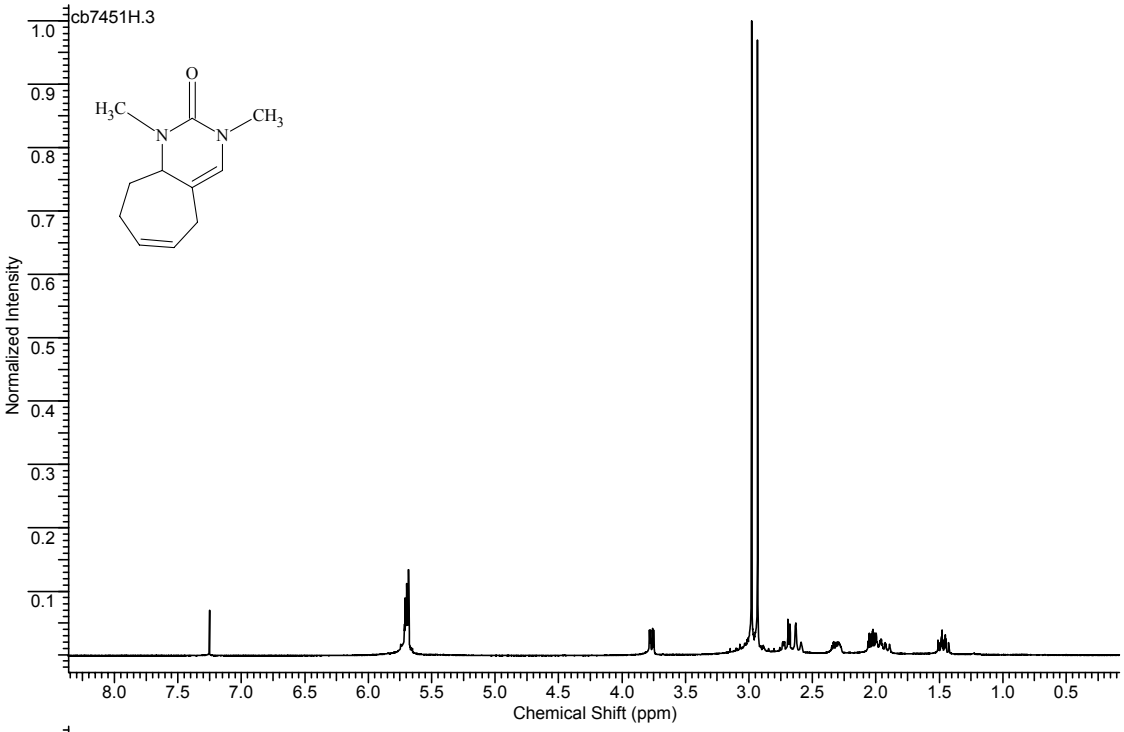


13 (Table 4, Entry4)





15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O
H3C
N
N
CH3
Normalized Intensity
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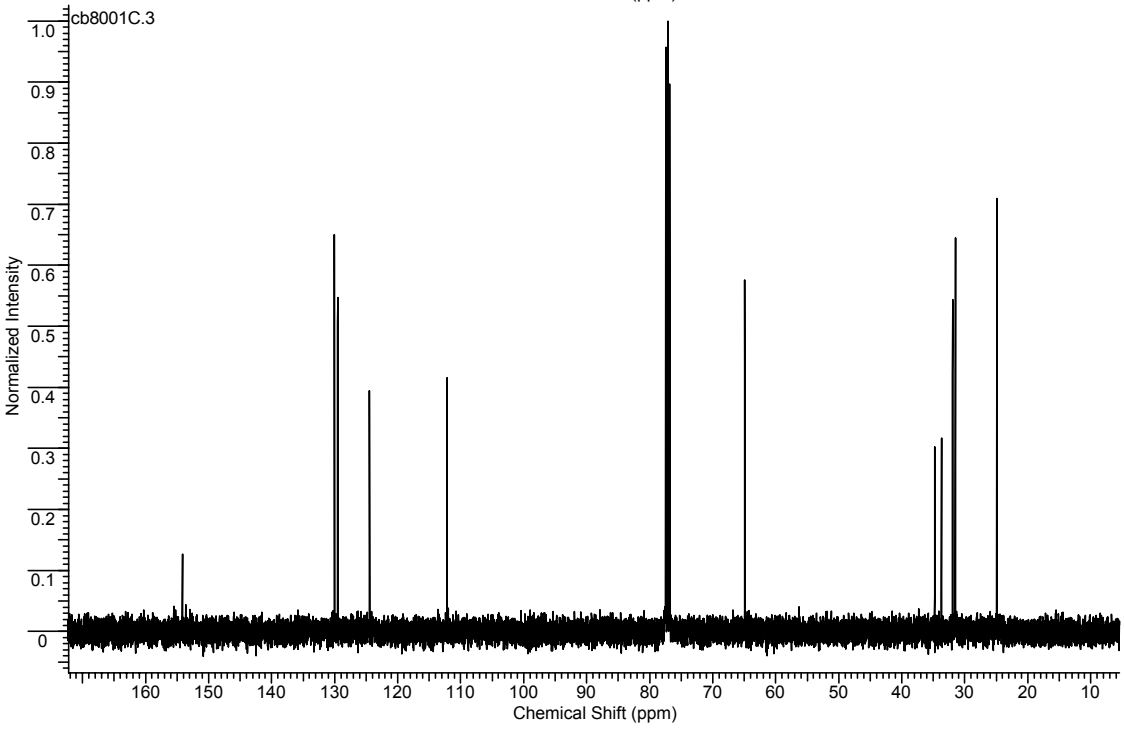
0.7
0.6
0.5
0.4
0.3
0.2
0.1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


cb8001C.3
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0.6
0.5
0.4
0.3
0.2
0.1
0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)