Supporting Information

Palladium Nanoparticles on a Pyridinium Supported Ionic Liquid Phase: a Recyclable and Low-Leaching Palladium Catalyst for Aminocarbonylation Reactions

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Figure S1 ^{13}C CP MAS spectrum of **SILP-1** (below) and **SILP-2** (above) (spinning rate: 5000 Hz, * indicates rotational sidebands)

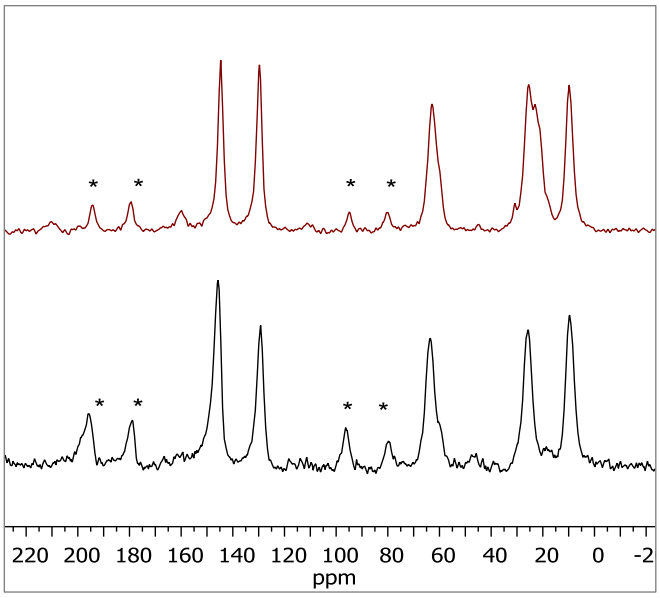


Figure S2 ^{29}Si CP MAS spectrum of **SILP-1** (T_2: $Si(OSi)_2ROH$, T_3: $Si(OSi)_3R$, Q_3: $Si(OSi)_3OH$, and Q_4: $Si(OSi)_4$).

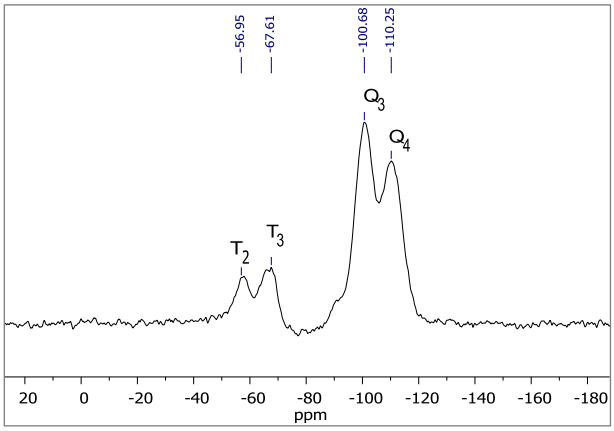


Figure S3 ^{13}C CP MAS spectrum of **CAT-1** (spinning rate 8000 Hz, * indicates rotational sidebands)

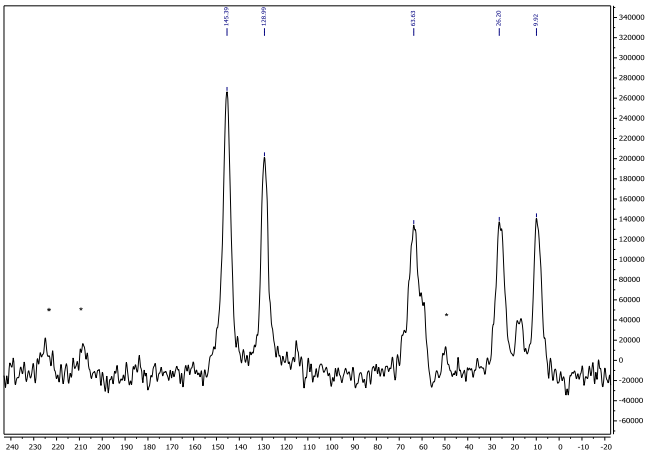


Figure S4 ^{29}Si CP MAS spectrum of **CAT-1**

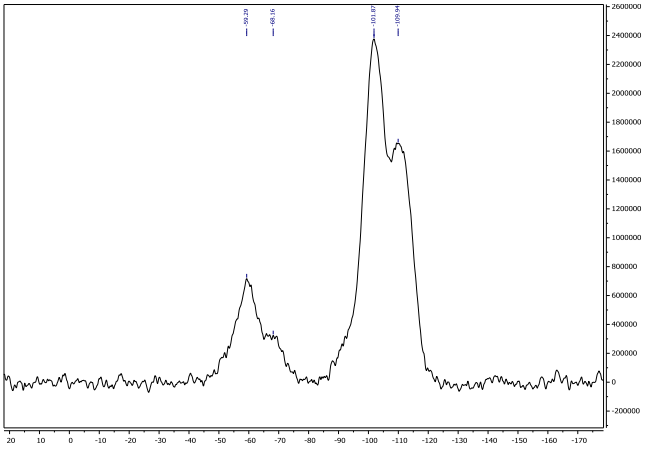


Figure S5 FT-IR spectra of ionic liquids (**1**, **2**) and SILPs (**SILP-1** and **SILP-2**)

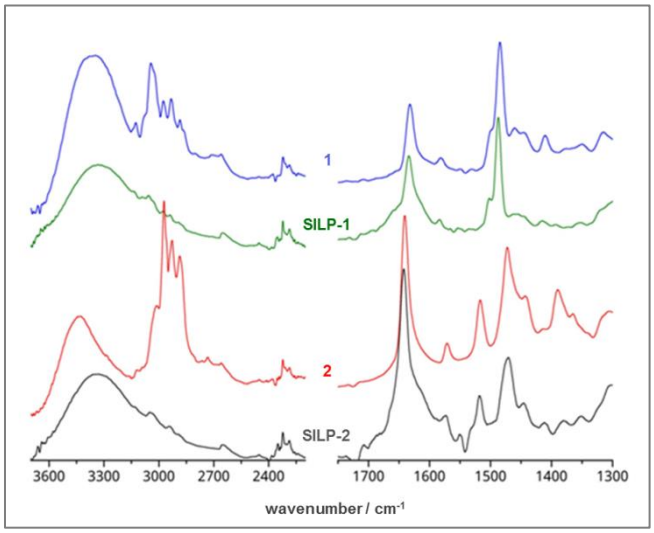


Figure S6 TGA (above) and DTG (below) curves of **SILP-1** and **SILP-2**

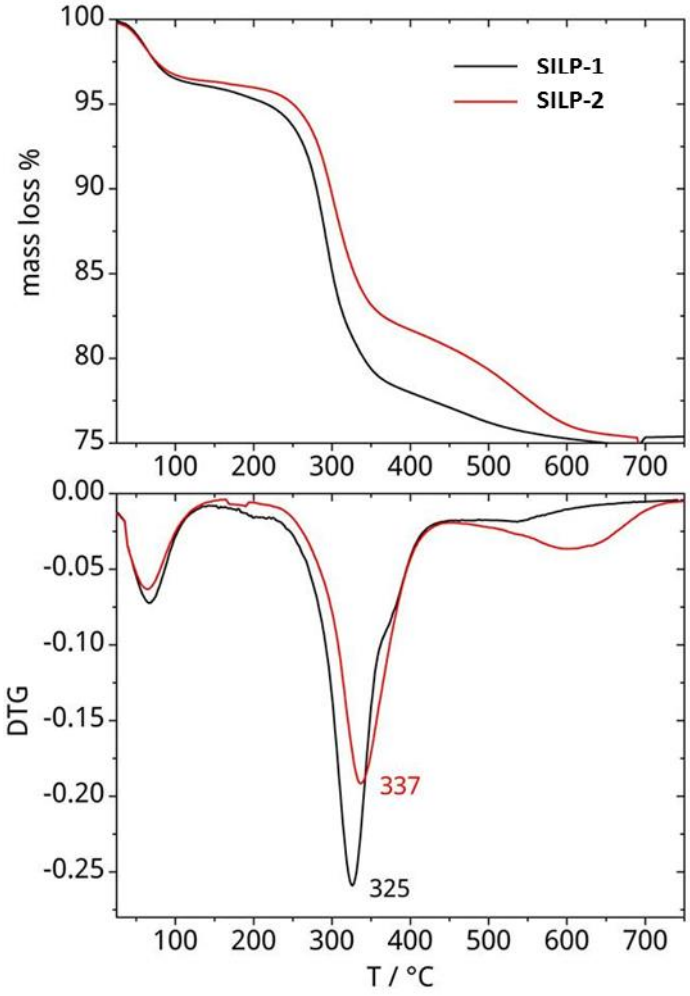
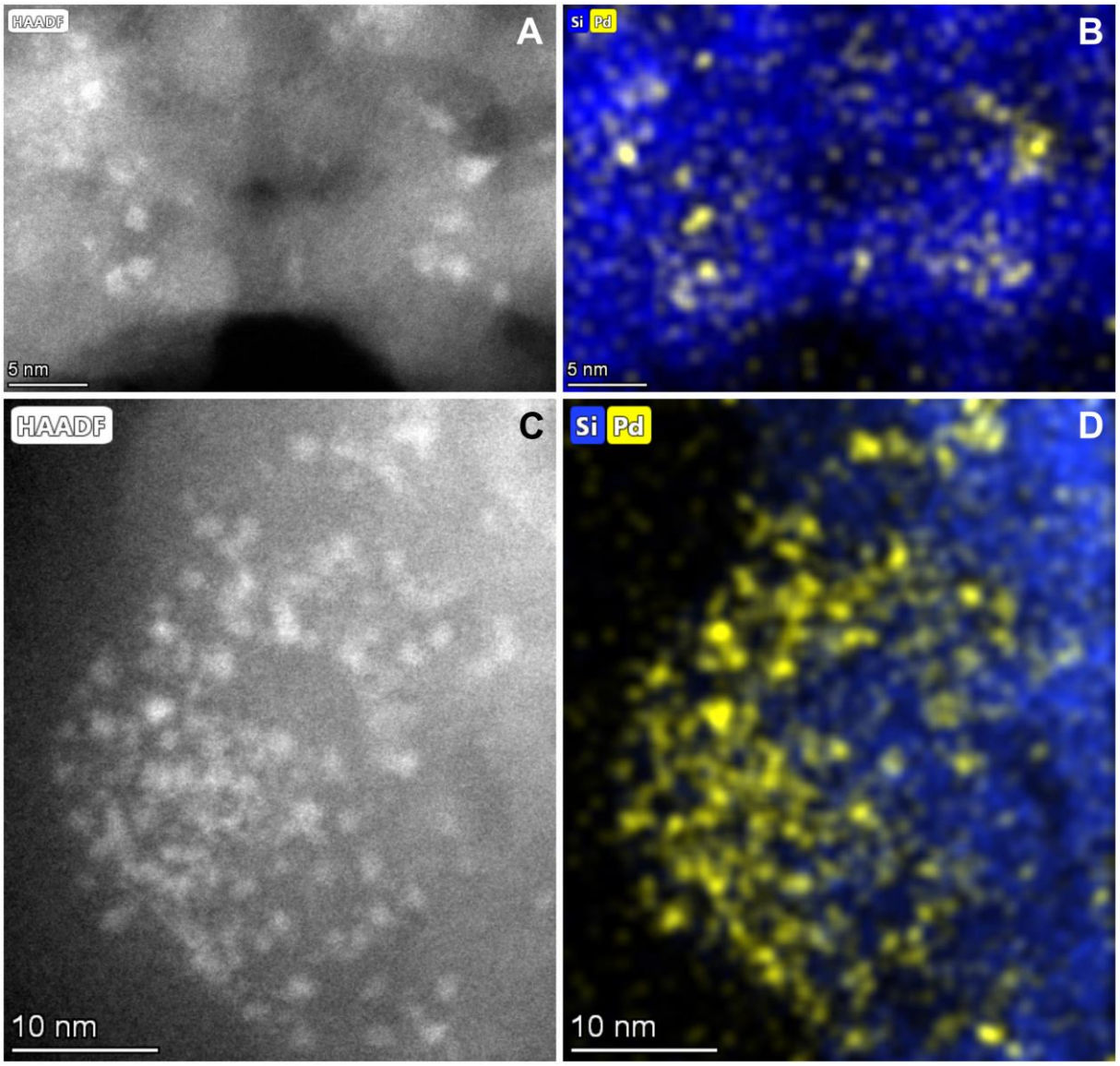


Figure S7 STEM HAADF images and Si-Pd eds elemental maps of the fresh (A-B) and spent (C-D) **CAT-1** samples where the bright grains appear as Pd nanoparticles (yellow) on the silica support (blue).



Characterisation of the products

1-(3-Triethoxysilyl)-pyridinium iodide (1): ^{1}H NMR (400.13 MHz, DMSO-d_6): 9.05-9.11 (m, 1H); 8.62 (t, J= 7.6 Hz, 1H); 8.17 (t, J= 7.6 Hz, 2H); 4.58 (t, J= 7.3 Hz, 1H); 3.73 (q, J= 7.0 Hz, 6H); 1.92-1.99 (m, 2H); 1.13 (t, J= 7.0 Hz, 9H); 0.52-0.56 (m 2H). ^{13}C NMR (100.62 MHz, DMSO-d_6): 146.0; 145.2, 128.6; 63.3; 58.4; 25.4; 18.6; 7.1.

4-Methyl-1-(3-triethoxysilyl)-pyridinium iodide (2): ^{1}H NMR (400.13 MHz, DMSO-d_6): 8.86 (d, J= 6.6 Hz, 2H); 7.95 (d, J= 6.6 Hz, 2H); 4.45 (t, J= 7.2 Hz, 2H); 3.71 (q, J= 7.0 Hz, 6H); 2.58 (s, 3H); 1.85-1.93 (m, 2H); 1.11 (t, J= 7.0 Hz, 9H); 0.46-0.51 (m, 2H).

Morpholino(phenyl)methanone (5a): ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.33–7.46 (m, 5H); 3.55–3.88 (m, 6H); 3.35–3.55 (m, 2H). ^{13}C NMR (125.78 MHz, $CDCl_3$):170.6; 135.5; 130.0; 128.7; 127.2; 67.0; 48.1; 42.5. MS(m/z/rel.int.): 191(M^+)/11; 190/34; 176/9; 160/6; 105/100; 86/12; 77/68; 51/24

1-Morpholino-2-phenylethane-1,2-dione (6a, Table 3, entry 1): ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.96 (dd, J = 8.2, J = 1.1 Hz, 2H); 7.66 (tt, J = 7.4, J = 1.1 Hz, 1H); 7.50-7.55 (m, 2H), 3.78 -3.82 (m, 4H); 3.64-3.67 (m, 2H); 3.37-3.40 (m, 2H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 191.3; 165.6; 135.1; 133.3; 129.8; 129.3; 66.9; 66.8; 46.4; 41.8. MS(m/z/rel.int.): 219 (M^+)/6; 114/11; 105/100; 86/4; 77/54; 70/26; 51/22.

***N,N*-diethyl-2-oxo-2-phenylacetamide (7):** MS(m/z/rel.int.): 205(M^+)/5; 105/61; 100/100; 77/42; 72/74; 51/21.

1-Phenyl-2-(piperidin-1-yl)ethane-1,2-dione (Table 3, entry 2): ^{1}H NMR (400.13 MHz, $CDCl_3$): 7.92-7.95 (m, 2H); 7.60-7.64 (m, 1H); 7.47-7.51 (m, 2H); 3.67-3.71 (m, 2H); 3.25-3.28 (m, 2H); 1.64-1.71 (m, 4H); 1.50-1.55 (m, 2H). ^{13}C NMR (100.62 MHz, $CDCl_3$): 192.0; 165.5; 134.6; 133.3, 129.6; 129.0; 47.0; 42.1; 26.2; 25.4; 24.4. MS(m/z/rel.int.): 217(M^+)/5; 112/100; 105/50; 84/10; 77/33; 69/60; 41/25.

Phenyl(piperidin-1-yl)methanone: MS(m/z/rel.int.): 189(M^+)/36; 188/100; 105/97; 84/9; 77/56; 51/12.

1-Phenyl-2-(pyrrolidin-1-yl)ethane-1,2-dione (Table 3, entry 3): ^{1}H NMR (400.13 MHz, $CDCl_3$): 7.97-8.01 (m, 2H); 77.60-7.65 (m, 1H); 7.47-7.52 (m, 2H); 3.64-3.68 (m, 2H); 3.41-3.45 (m, 2H); 1.90-1.99 (m, 4H). ^{13}C NMR (100.62 MHz, $CDCl_3$): 191.2; 165.1; 134.7; 133.1; 130.0; 129.1; 46.8; 45.4; 26.1; 24.2. MS(m/z/rel.int.): 203(M^+)/5; 202/7; 105/70; 98/100; 77/54; 70/30; 55/55.

Phenyl(pyrrolidin-1-yl)methanone: MS(m/z/rel.int.): 175(M^+)/46; 174/35; 164/19; 105/100; 77/58; 51/12.

***N,N*-Dibutylbenzamide:** MS(m/z/rel.int.): 233(M^+)/10; 190/14; 148/5; 105/100; 77/28; 51/3.

***N,N*-Dibutyl-2-oxo-2-phenylacetamide:** MS(m/z/rel.int.): 261(M^+)/3; 218/2; 156/78; 105/69; 77/45; 57/100.

***N*-Phenylbenzamide (Table 3, entry 5):** ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.90-7.98 (brs, 1H); 7.87 (d, J=7.5Hz, 2H); 7.65 (d, J=7.5Hz, 2H); 7.54 (t, J=7.5Hz, 1H); 7.47 (t, J=7.5Hz, 2H); 7.37 (t, J=7.5Hz, 2H); 7.15 (t, J=7.5Hz, 1H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 166.0; 138.1; 135.1; 132.0; 129.2; 128.9; 127.2; 124.8; 120.4. MS(m/z/rel.int.): 197(M^+)/40; 105/100; 77/55; 51/12.

***N*-(4-Methylphenyl)benzamide (Table 3, entry 6):** ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.89 (d, J = 7.6 Hz, 2H); 7.78-7.83 (brs, 1H); 7.49-7.59 (m, 5H); 7.20 (d, J = 7.6 Hz, 2H); 2.37 (s, 3H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 165.6; 135.4; 135.1; 134.3; 131.7; 129.6; 128.8; 127.0; 120.3; 20.9. MS(m/z/rel.int.): 211(M^+)/39; 150/100; 77/47; 51/9.

***N*-(4-Butylphenyl)benzamide (Table 3, entry 7):** ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.87 (d, J=8.4 Hz, 2H); 7.75-7.80 (brs, 1H); 7.51-7.57 (m, 3H); 7.49 (t, J=7.5 Hz, 2H); 7.18 (d, J=8.4 Hz, 2H); 2.60 (t, J=7.8 Hz, 2H); 1.54-1.64 (m, 4H); 1.36 (sext, J=7.1 Hz, 2H); 0.93 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 165.8; 139.6; 135.7; 135.3; 131.9; 129.1; 128.9; 127.1; 120.4; 35.2; 33.8; 22.4; 14.1. MS(m/z/rel.int.): 253(M^+)/52; 210/34; 105/100; 77/45; 51/8.

1-Morpholino-2-(4-methoxyphenyl)ethane-1,2-dione (Table 3, entry 8): ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.93 (d, J=8.9 Hz, 2H); 6.99 (d, J=8.9 Hz, 2H); 3.90 (s, 3H); 3.74-3.82 (m, 4H); 3.63-3.66 (m, 2H); 3.37-3.39 (m, 2H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 190.0; 166.0; 165.2; 132.3; 126.4; 114.6; 67.0; 66.9; 55.8; 46.5; 41.7. MS(m/z/rel.int.): 249(M^+)/3; 135/100; 92/10; 77/15; 70/8.

Morpholino(4-methoxyphenyl)methanone: MS(m/z/rel.int.): 221(M^+)/10; 220/16, 135/100; 92/10; 77/15

1-(3,4-Dimethylphenyl)-2-morpholinoethane-1,2-dione (Table 3, entry 9): ^{1}H NMR (400.13 MHz, $CDCl_3$): 7.71-7.73 (brs, 1H); 7.68 (dd, J = 7.9, 1.7 Hz, 1H); 7.27 (d, J = 7.9 Hz, 1H); 3.75-3.82 (m, 4H); 3.61-3.67 (m, 2H); 3.34-3.38 (m, 2H); 2.34 (s, 3H); 2.33 (s, 3H). ^{13}C NMR (100.62 MHz, $CDCl_3$): 191.3; 165.9; 145.2; 137.8; 131.1; 130.5; 130.4; 127.6; 66.8; 66.7; 46.3; 41.6; 20.4; 19.8. MS(m/z/rel.int.): 247(M^+)/4; 133/100; 105/24; 79/11; 77/10; 70/9.

Morpholino(3,4-dimethylphenyl)methanone: MS(m/z/rel.int.): 219(M^+)/11; 218/17; 133/100; 105/20; 79/11; 77/12.

Morpholino(4-nitrophenyl)methanone (Table 3, entry 10): ^{1}H NMR (500.15 MHz, $CDCl_3$): 8.29 (d, J=8.9 Hz, 2H); 7.59 (d, J=8.9 Hz, 2H); 3.72-3.88 (brs, 4H); 3.46-3.58 brs, 2H); 3.33-3.46 (brs, 2H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 168.2; 148.7; 141.6; 128.3; 124.1; 66.9; 48.2; 42.8. MS(m/z/rel.int.): 236(M^+)/10; 235/14; 150/40; 86/37; 76/43; 56/100.

Morpholino(4-aminophenyl)methanone (8): MS(m/z/rel.int.): 206(M^+)/12; 205/8; 120/100; 92/20; 65/22.

1-Morpholino-2-(4-aminophenyl)ethane-1,2-dione (9): MS(m/z/rel.int.): 234(M^+)/3; 120/100; 92/17; 70/6; 65/16

1-(1,4-Benzodioxan-6-ylcarbonyl)piperidine (11): ^{1}H NMR (400.13 MHz, $CDCl_3$): 6.91 (d, J = 1.8 Hz, 1H); 6.86 (dd, J = 8.2 Hz; 1.8 Hz, 1H); 6.825 (d, J = 8.32 Hz, 1H); 4.23 (brs, 4H); 3.30-3.70 (m, 4H); 1.60-1.69 (m, 2H). 1.42-1.60 (m, 4H). ^{13}C NMR (100.62 MHz, $CDCl_3$): 169.9; 144.7; 143.3; 129.7; 120.5; 117.3; 116.5; 64.5; 64.4; 49.0; 43.4; 26.4; 25.9; 24.7. MS (m/z/rel.int.): 247(M^+)/3; 163/100; 135/23; 112/14; 79/12; 51/23

1-(1,4-Benzodioxan-6-yl)-2-(piperidin-1-yl)ethane-1,2-dione (12): ^{1}H NMR (400.13 MHz, $CDCl_3$): 7. 45 (dd, J = 0.3 Hz, 2.1 Hz, 1H); 7.43 (dd, J = 2.1 Hz, 8.1 Hz, 1H); 6.91 (dd, J = 0.3 Hz, 8.1 Hz, 1H); 4.23-4.32 (m, 4H); 3.63-3.69 (m, 2H); 3.22-3.28 (m, 2H); 1.62-1.70 (m, 4H); 1.48-1.54 (m, 2H). ^{13}C NMR (100.62 MHz, $CDCl_3$): 190.7; 165.7; 149.6; 143.8; 127.1; 124.0; 118.7; 117.8; 64.8; 64.1; 47.1; 42.1; 26.2; 25.5; 24.4. MS (m/z/rel.int.): 275(M^+)/4; 163/100; 135/14; 112/12; 107/22; 84/9; 79/14; 51/18

4-Chloro-N-(2-morpholinoethyl)benzamide (15): ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.71 (d, J =8,5 Hz, 2H); 7.41 (d, J = 8,5 Hz, 2H); 3.69-3.78(m, 4H); 3.54 (dd, J = 11.2 Hz, J = 5.6 Hz, 2H); 2.61 (t, J = 6.0 Hz, 2H); 2.47-2.56 (m, 4H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 166.4; 137.8; 133.1; 129.0; 128.5, 67.1 (2C); 57.0; 53.5 (2C); 36.2. MS (m/z/rel.int.): 269(M^+)/9; 139/7; 113/11; 100/100; 75/4; 70/5; 56/12

***N*-(2-Morpholinoethyl)-2-oxo-2-(4-chloro-phenyl)acetamide (16):** MS (m/z/rel.int.): 297(M^+)/15; 157/3; 139/6; 113/7; 111/6; 100/100; 70/6; 56/10

***N,N*-Diethylnicotinamide (19):** ^{1}H NMR (400.13 MHz, DMSO-d_6): 8.51-8.70 (m, 2H); 7.75-7.80 (m, 1H); 7.42-7.45 (m,1H); 3.37-3.52 (m, 2 H); 3.06-3.23 (m, 2H); 1.09-1.20 (m, 3H), 0.96-1.09 (m, 3H). ^{13}C NMR (100.62 MHz, DMSO-d_6): 167.6; 150.0; 146.8; 133.9; 133.0; 123.6; 42.9; 38.9; 14.0; 12.8. MS (m/z/rel.int.): 178(M^+)/5; 177/10; 106/100; 78/57; 51/55.

1-(*N,N*-diethylamino)-2 (pyridin-3-yl)ethane-1,2-dione (20): MS (m/z/rel.int.): 178 (M^+-CH_2=CH_2)/12; 106/23; 100/83; 78/70; 72/100; 51/88; 44/50.

17-(*N*-t-Butyl-carbamoyl)-4-aza-5α-androst-16-en-3-one (23): ^{1}H NMR (400.13 MHz, $CDCl_3$): 6.16-6.19 (m, 1H); 5.80-5.86 (brs, 1H); 5.42-5.47 (brs, 1H); 3.05-3.12 (m, 1H); 2.38-2.45 (m, 2H); 0.80-2.20 (m, H); 1.37 (s, 9H); 0.99 (s, 3H); 0.93 (s, 3H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 172.3; 165.8; 152.0; 133.8; 61.0; 56.3; 51.9; 51.3; 46.9;36.2, 34.7; 33.6; 33.4; 31.5; 29.6; 29.1; 28.7; 27.5; 21.2; 16.7; 11.5. MS (m/z/rel.int.): 372(M^+)/100; 357/39; 317/12; 300/73; 284/7; 272/29; 124/23; 105/31; 91/39; 79/34; 57/74; 41/57.

^{1}H- and ^{13}C NMR spectra of isolated products

Figure S8 ^{1}H NMR spectrum of morpholino(phenyl)methanone (**5a**) in $CDCl_3$

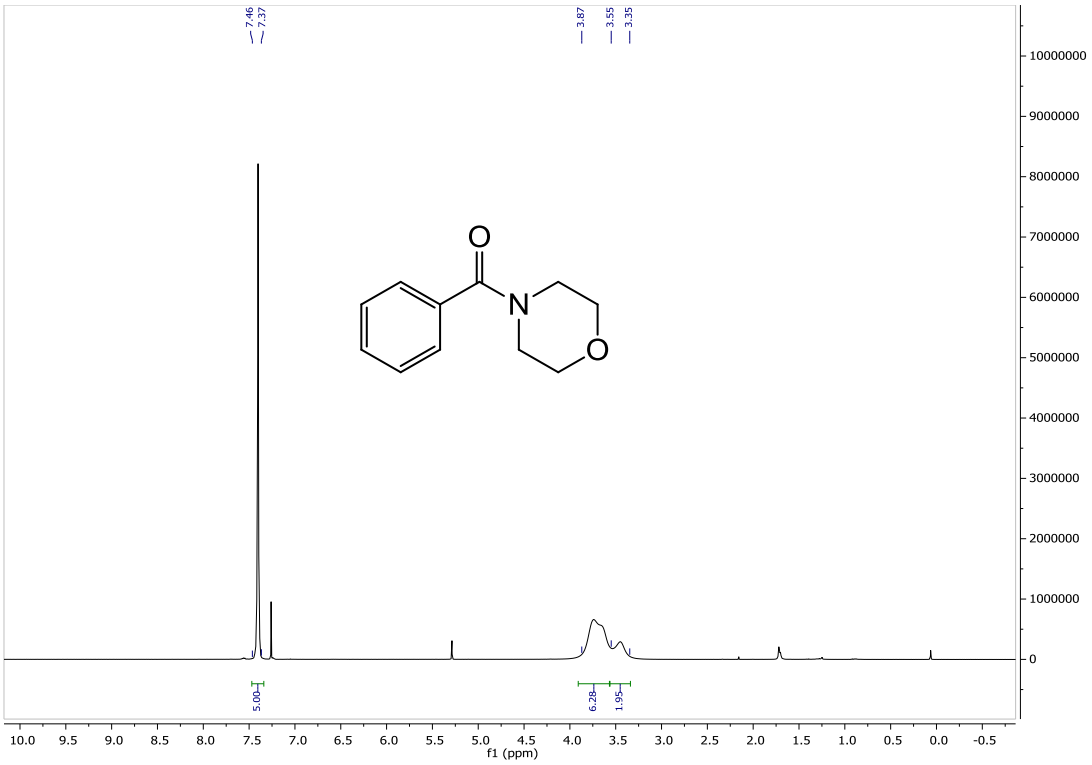


Figure S9 ^{13}C NMR spectrum of morpholino(phenyl)methanone (**5a**) in $CDCl_3$

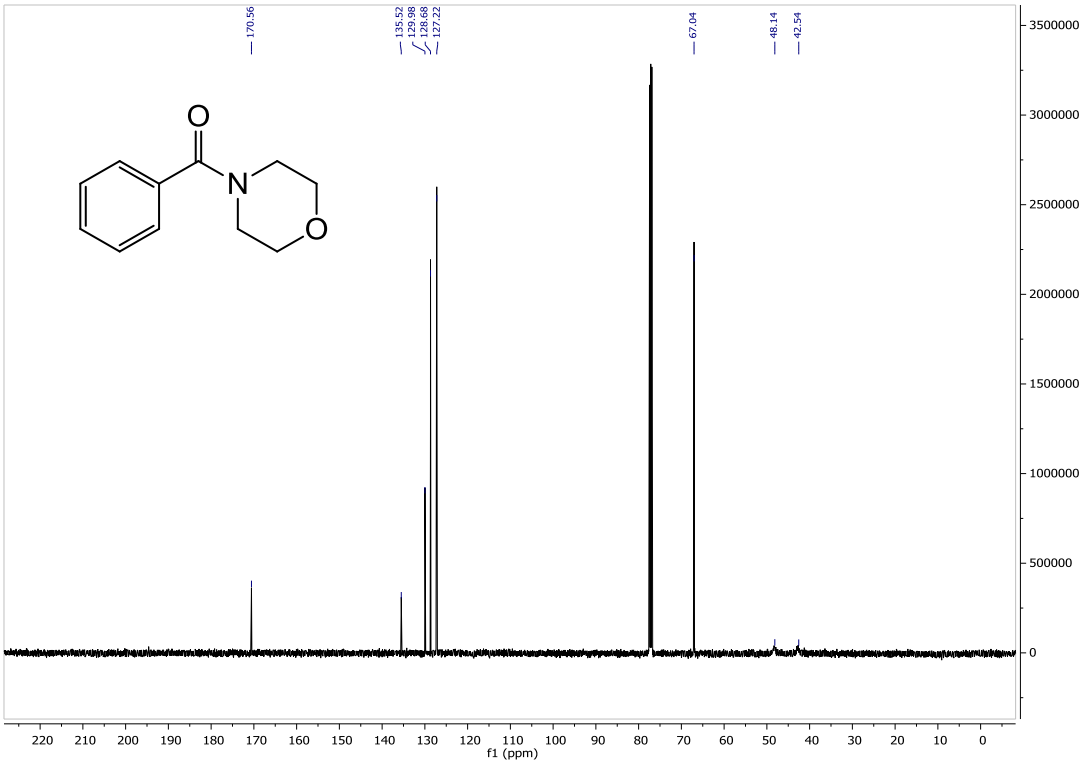


Figure S10 ^{1}H NMR spectrum of 1-morpholino-2-phenylethane-1,2-dione (**6a**) in $CDCl_3$

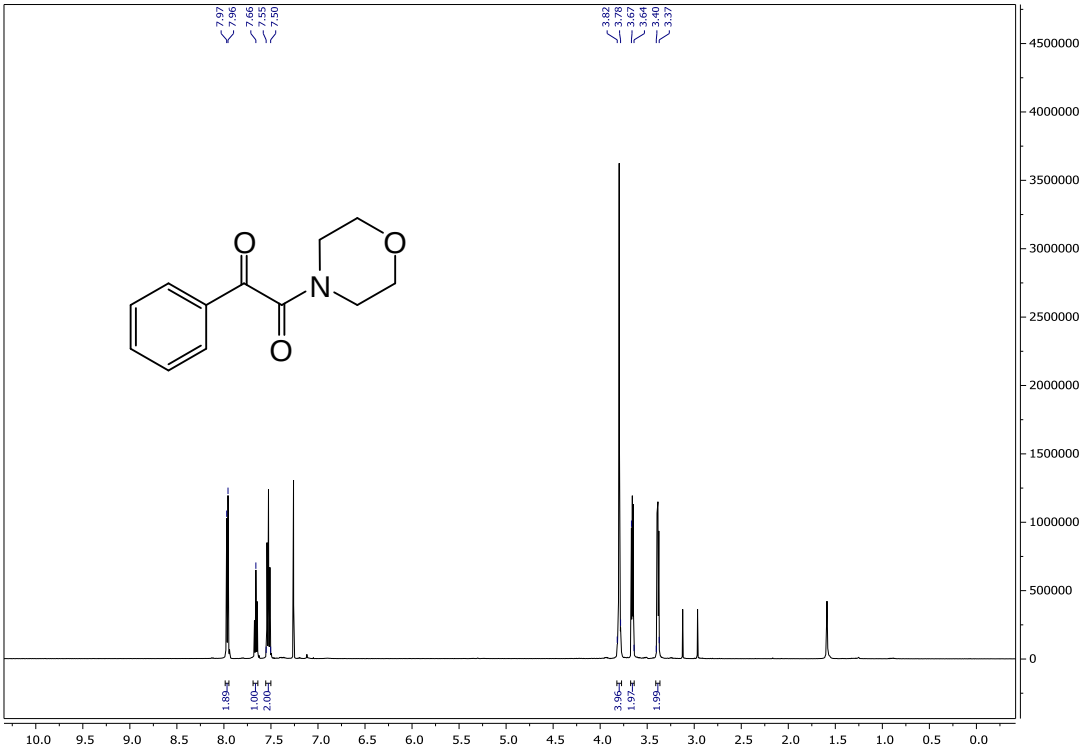


Figure S11 ^{13}C NMR spectrum of 1-morpholino-2-phenylethane-1,2-dione (**6a**) in $CDCl_3$

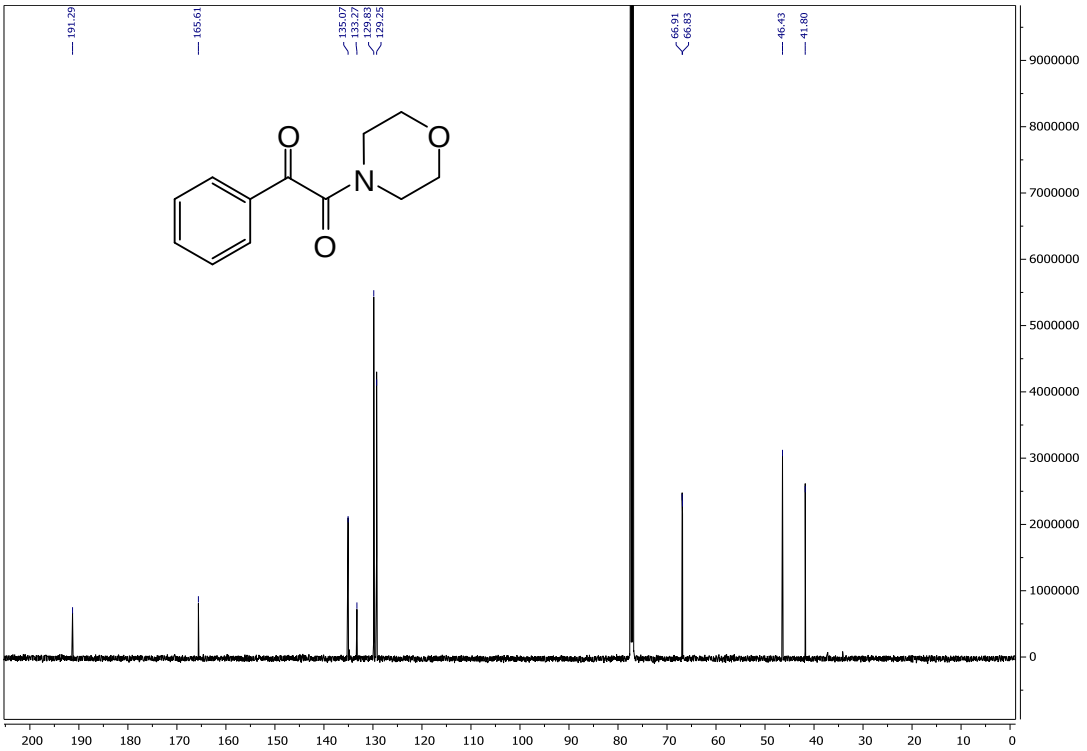


Figure S12 ^{1}H NMR spectrum of 1-phenyl-2-(piperidin-1-yl)ethane-1,2-dione (Table 3, entry 2) in $CDCl_3$

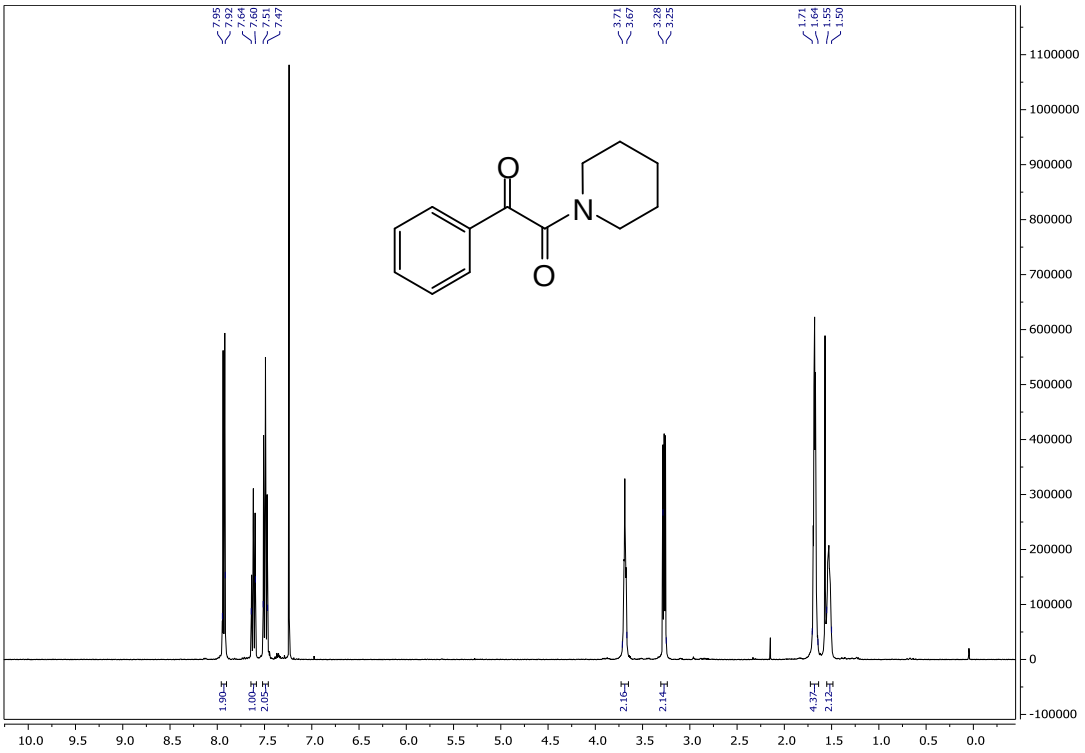


Figure S13 ^{13}C NMR spectrum of 1-phenyl-2-(piperidin-1-yl)ethane-1,2-dione (Table 3, entry 2) in $CDCl_3$

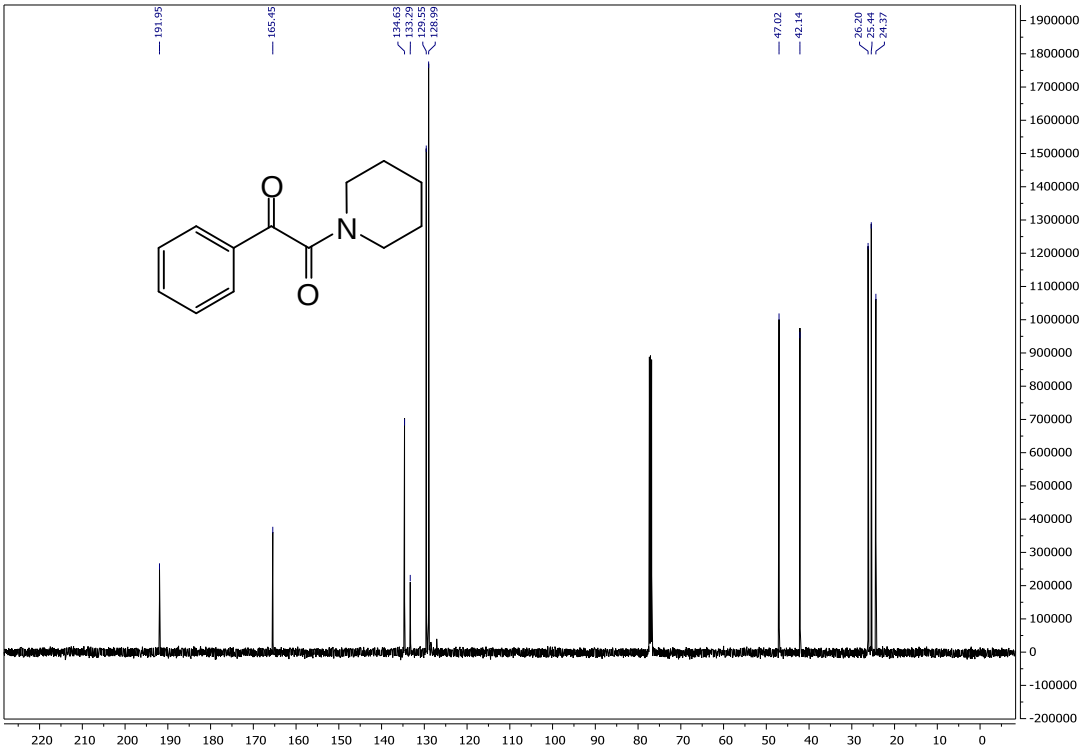


Figure S14 ^{1}H NMR spectrum of 1-phenyl-2-(pyrrolidin-1-yl)ethane-1,2-dione (Table 3, entry 3) in $CDCl_3$

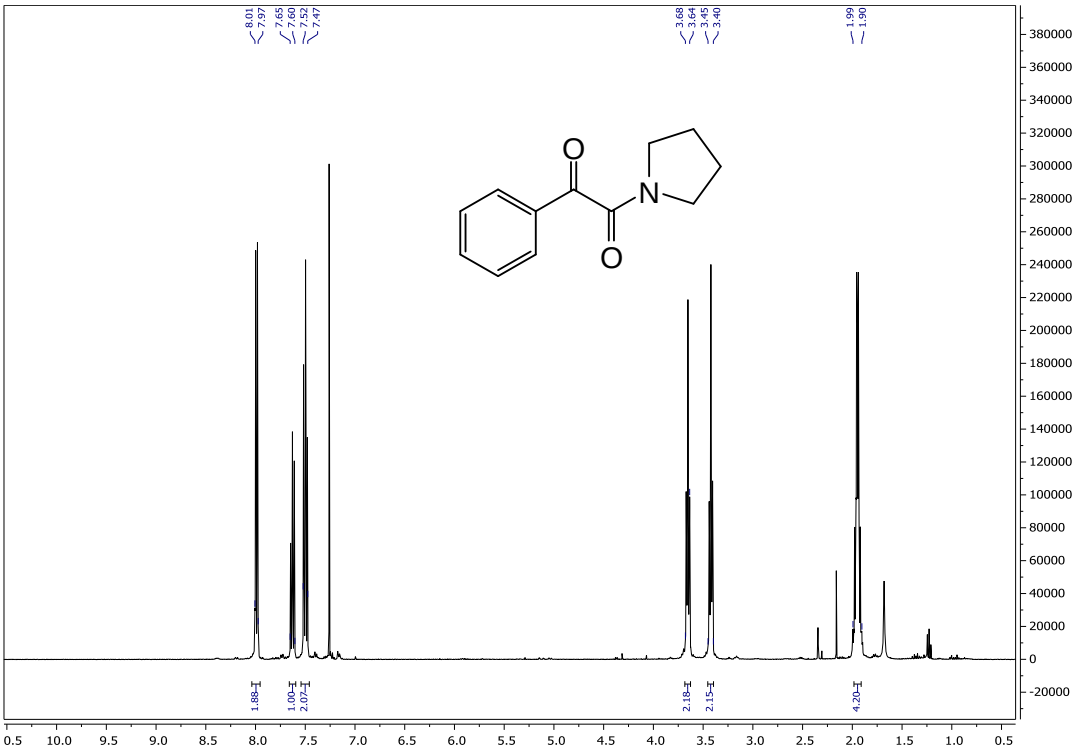


Figure S15 ^{13}C NMR spectrum of 1-phenyl-2-(pyrrolidin-1-yl)ethane-1,2-dione (Table 3, entry 3) in $CDCl_3$

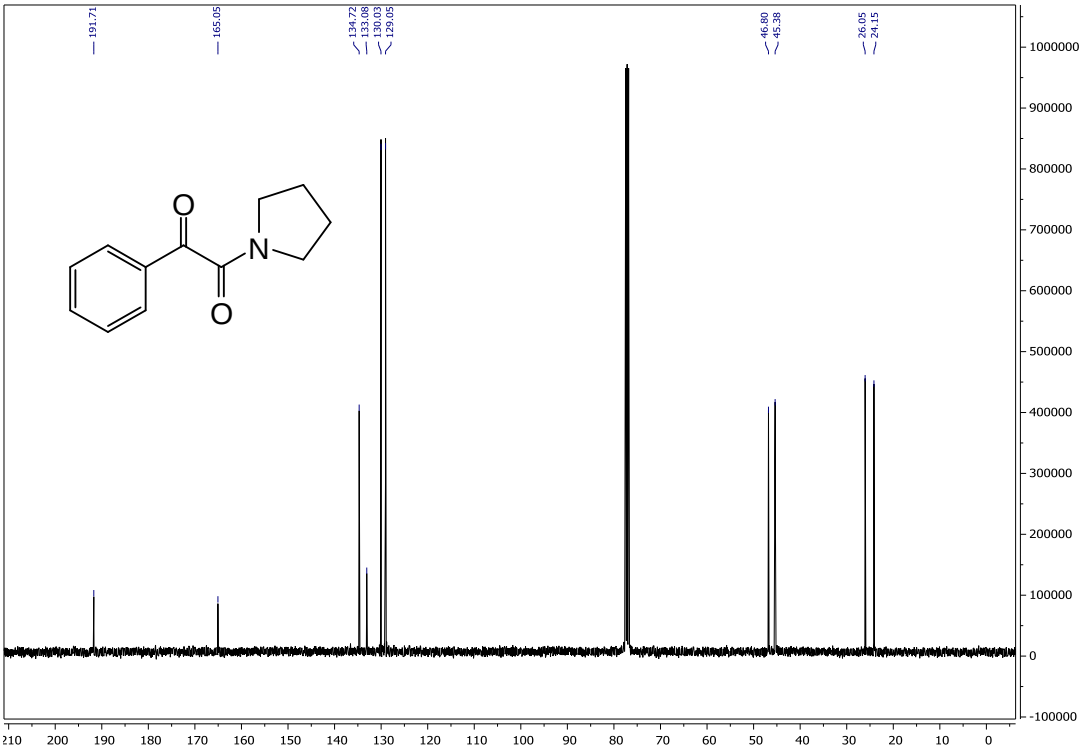


Figure S16 ^{1}H NMR spectrum of *N*-phenylbenzamide (Table 3, entry 5) in $CDCl_3$

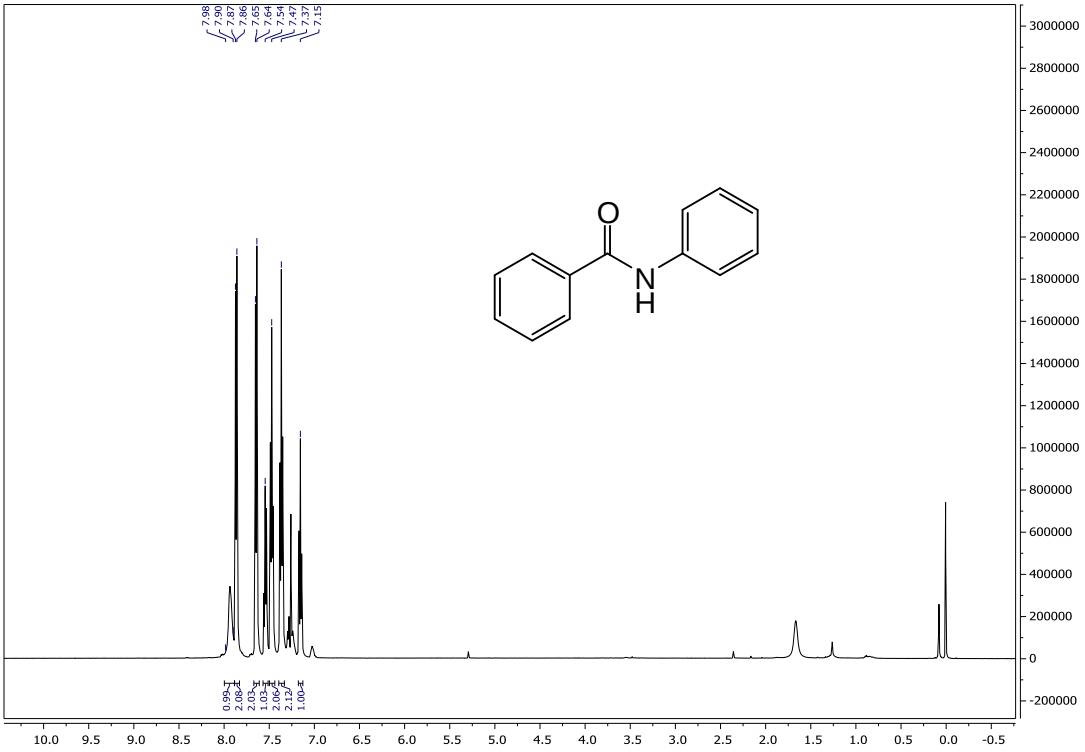


Figure S17 ^{13}C NMR spectrum of *N*-phenylbenzamide (Table 3, entry 5) in $CDCl_3$

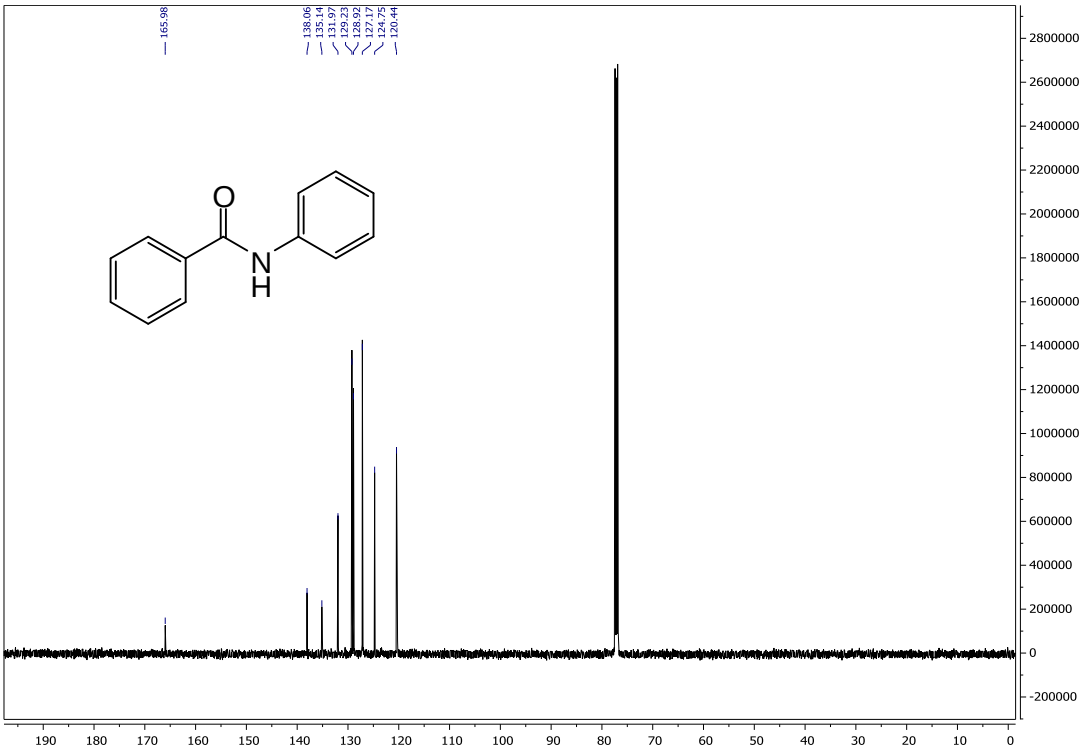


Figure S18 ^{1}H NMR spectrum of *N*-(4-methylphenyl)benzamide (Table 3, entry 6) in $CDCl_3$

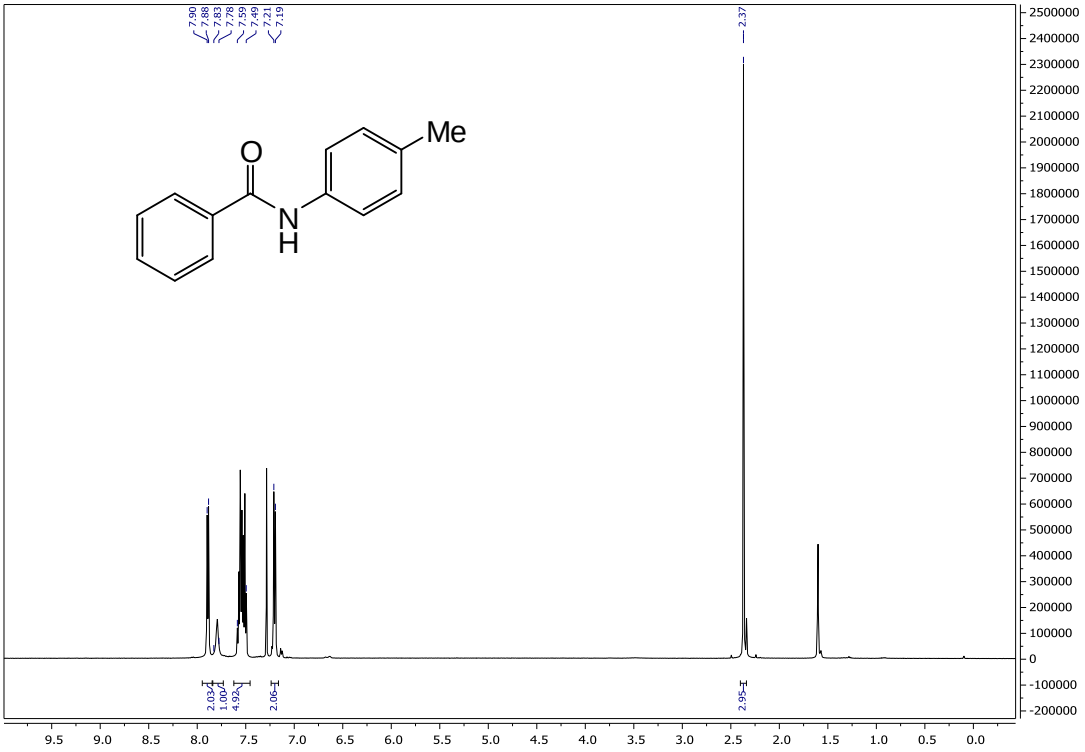


Figure S19 ^{13}C NMR spectrum of *N*-(4-methylphenyl)benzamide (Table 3, entry 6) in $CDCl_3$

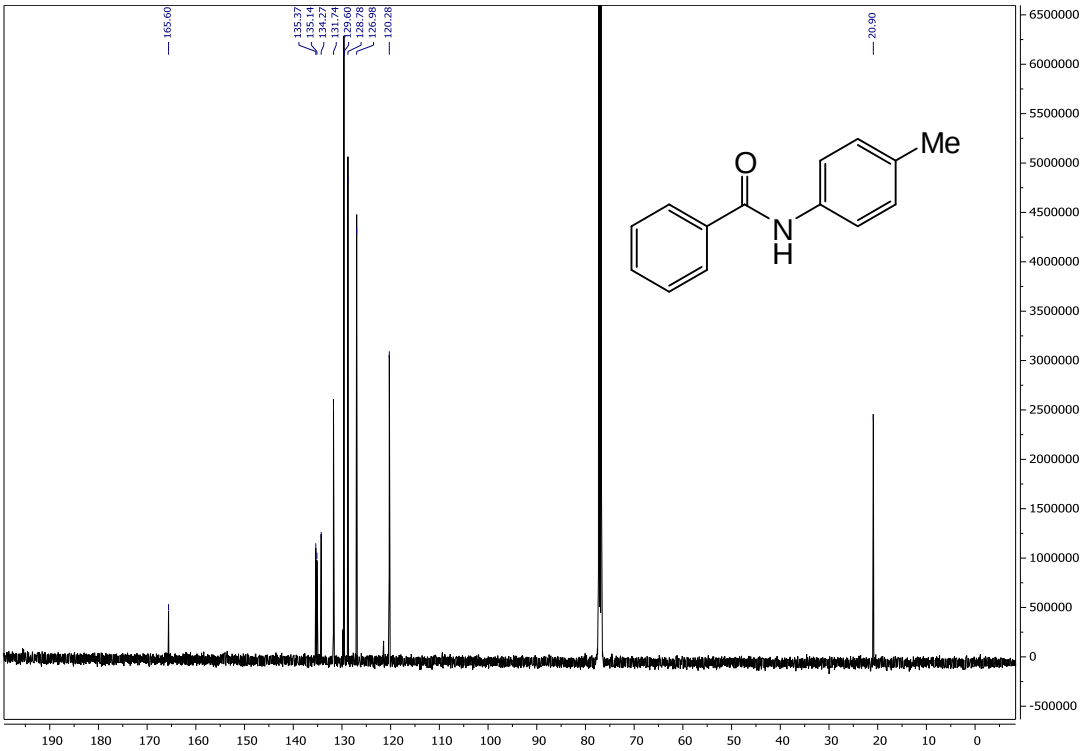


Figure S20 ^{1}H NMR spectrum of *N*-(4-butylphenyl)benzamide (Table 3, entry 7) in $CDCl_3$

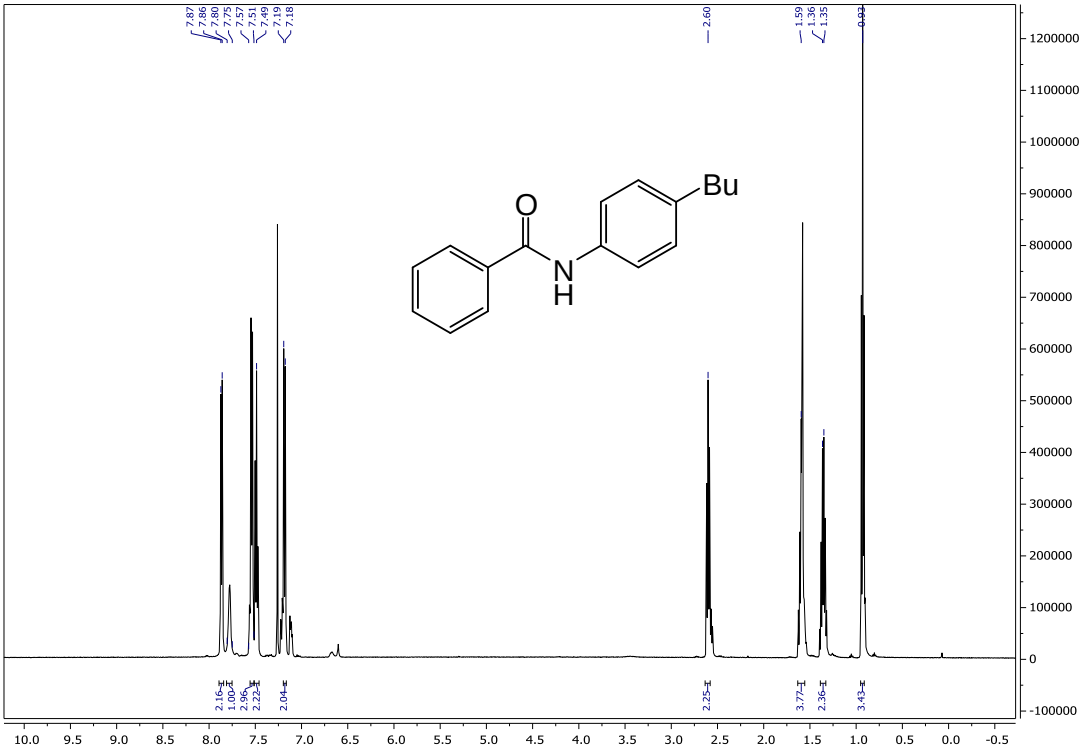


Figure S21 ^{13}C NMR spectrum of *N*-(4-butylphenyl)benzamide (Table 3, entry 7) in $CDCl_3$

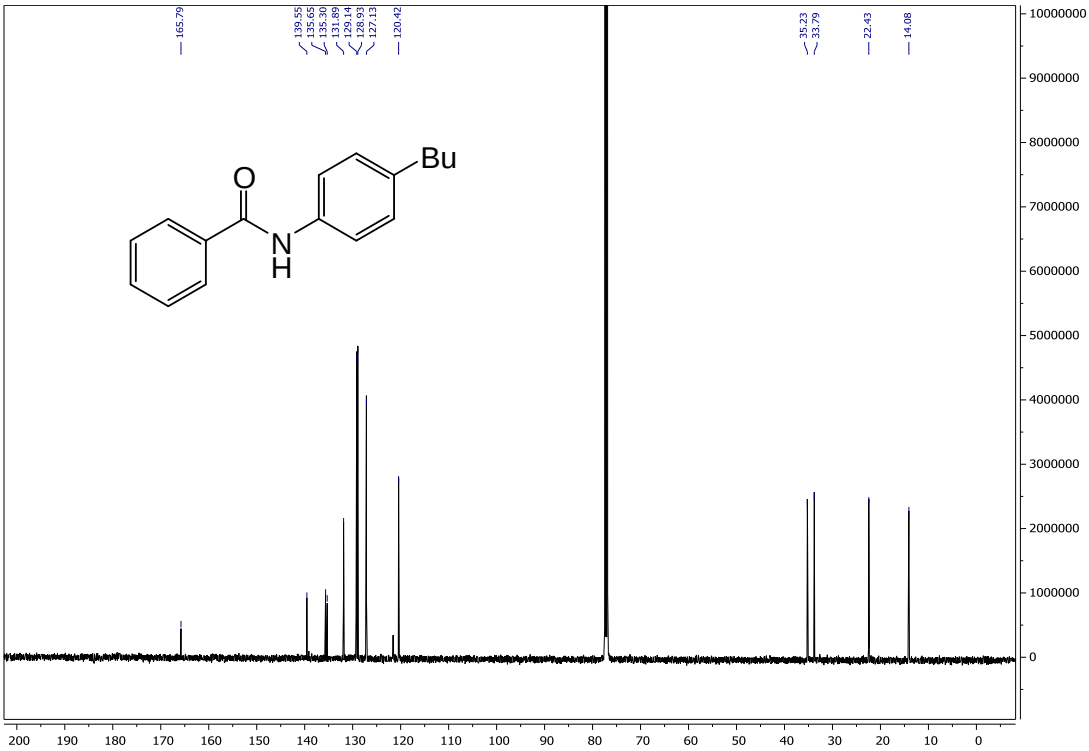


Figure S22 ^{1}H NMR spectrum of 1-morpholino-2-(4-methoxyphenyl)ethane-1,2-dione (Table 3, entry 8) in $CDCl_3$

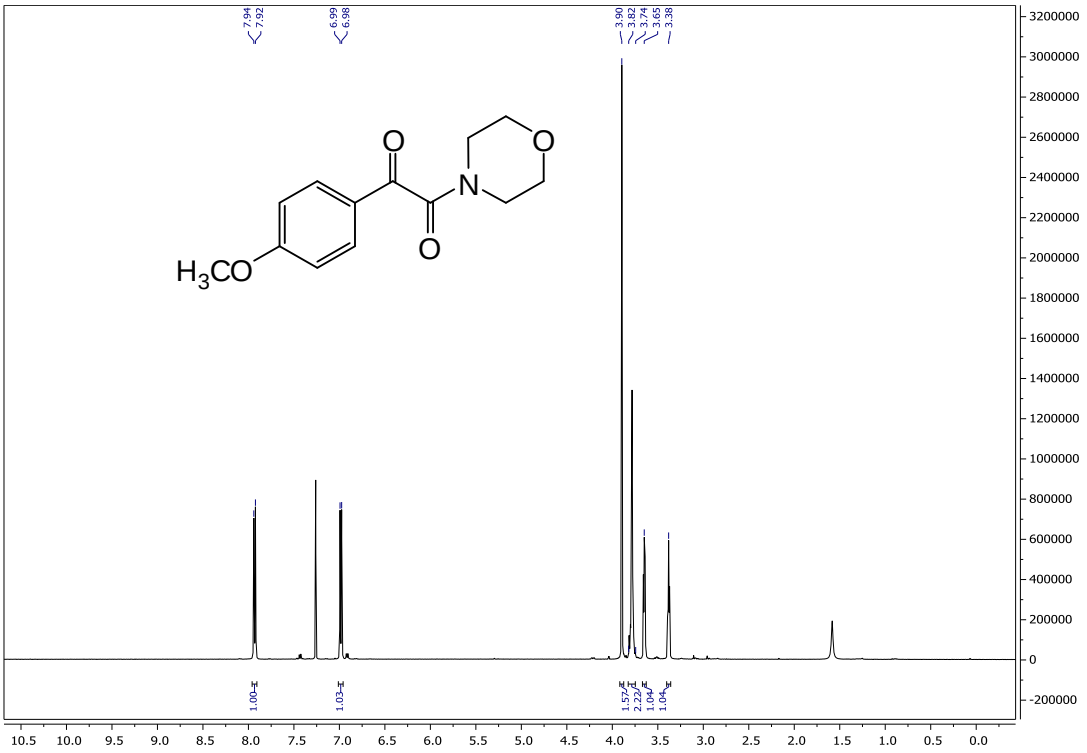


Figure S23 ^{13}C NMR spectrum of 1-morpholino-2-(4-methoxyphenyl)ethane-1,2-dione (Table 3, entry 8) in $CDCl_3$

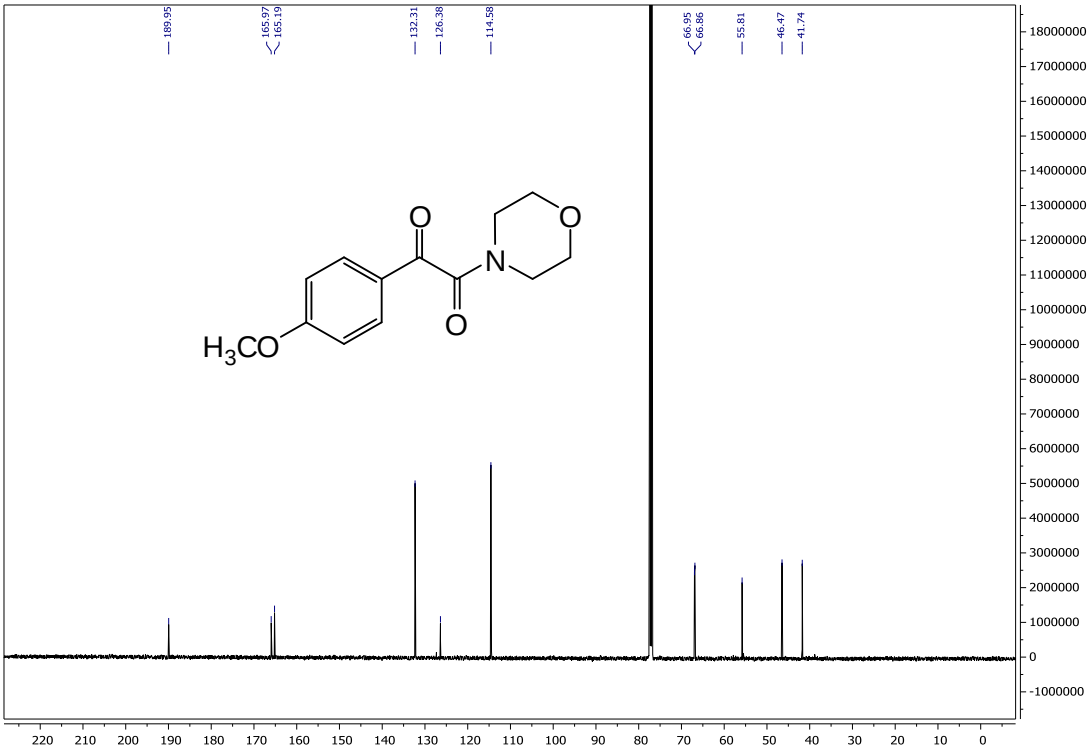


Figure S24 ^{1}H NMR spectrum of 1-(3,4-dimethylphenyl)-2-morpholinoethane-1,2-dione (Table 3, entry 9) in $CDCl_3$

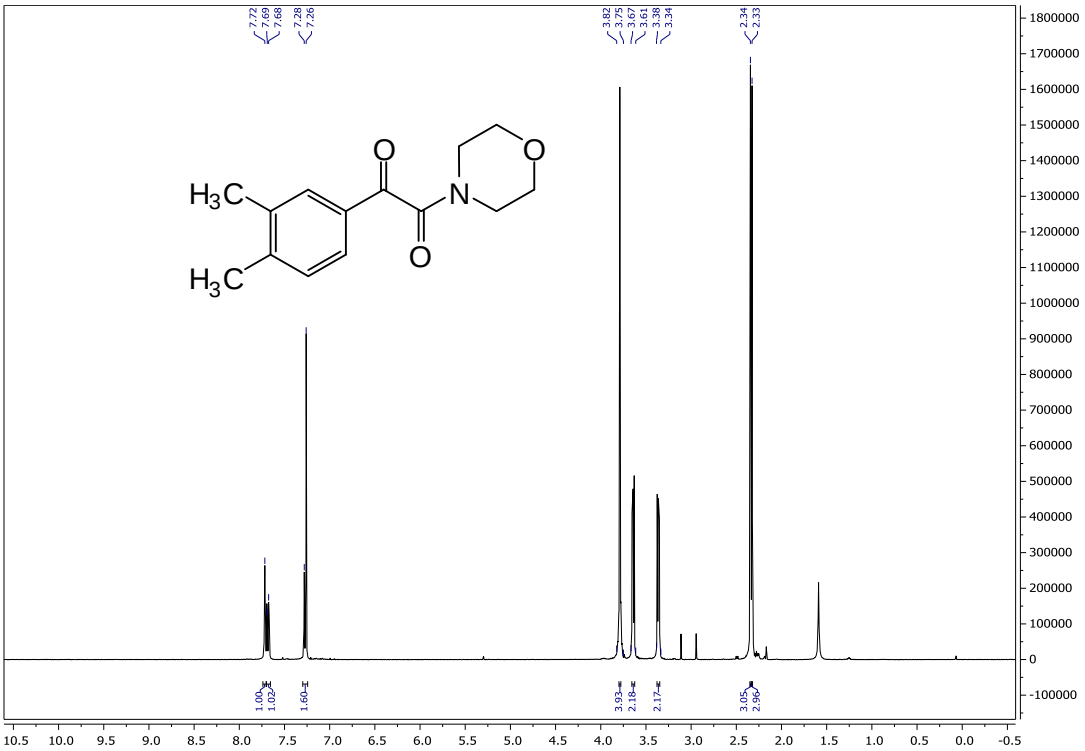


Figure S25 ^{13}C NMR spectrum of 1-(3,4-dimethylphenyl)-2-morpholinoethane-1,2-dione (Table 3, entry 9) in $CDCl_3$

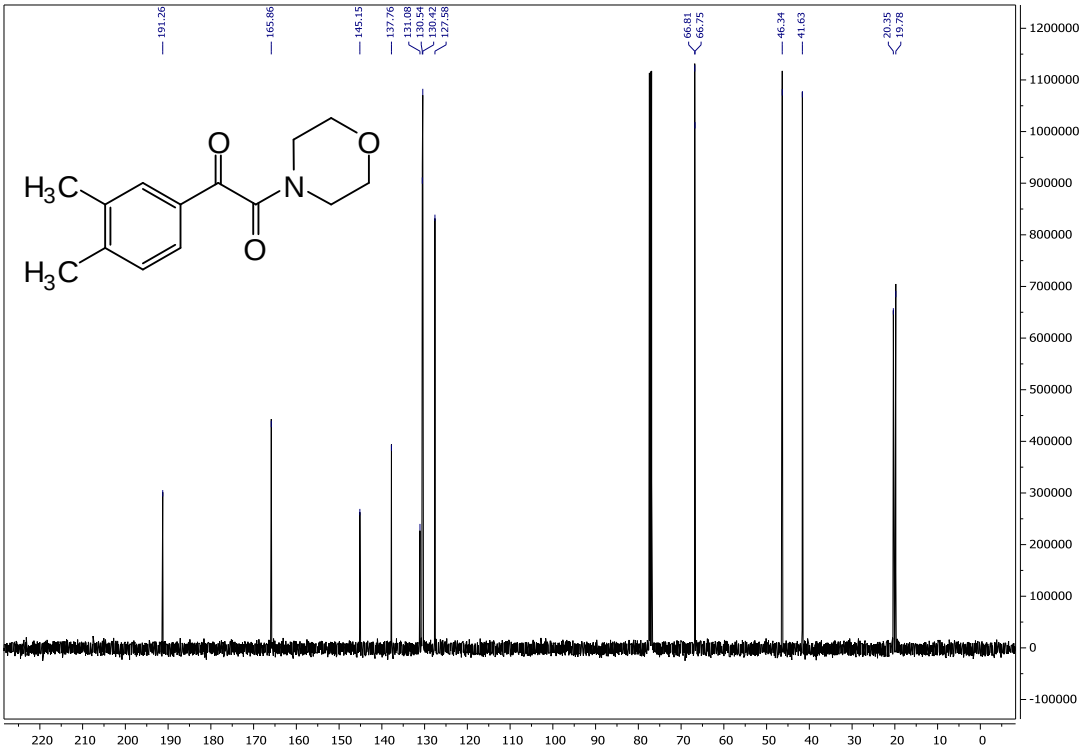


Figure S26 ^{1}H NMR spectrum of morpholino(4-nitrophenyl)methanone (Table 3, entry 10) in $CDCl_3$

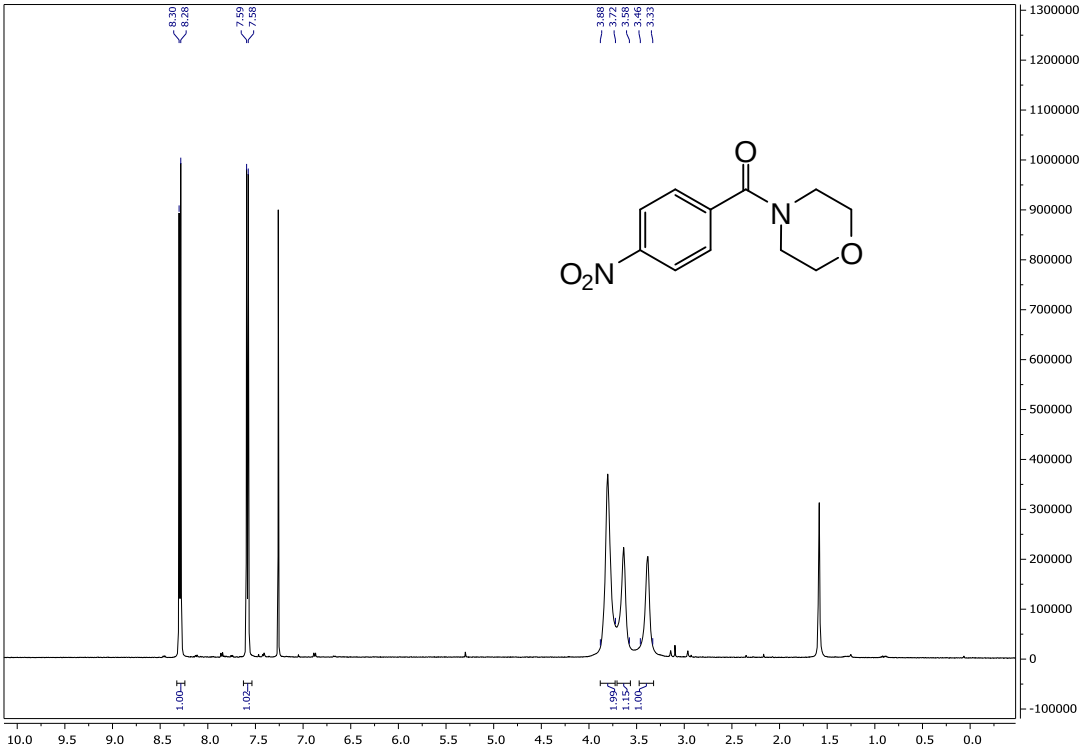


Figure S27 ^{13}C NMR spectrum of morpholino(4-nitrophenyl)methanone (Table 3, entry 10) in $CDCl_3$

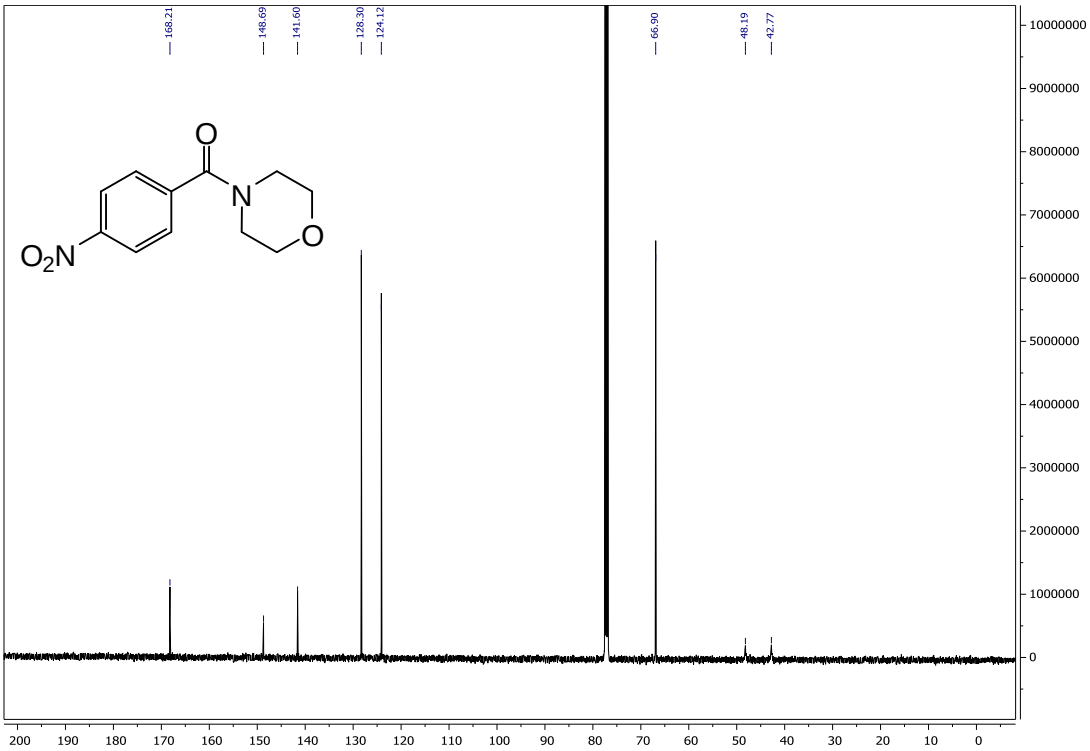


Figure S28 ^{1}H NMR spectrum of (2,3-dihydrobenzo[b][1,4]dioxin-6-yl)(piperidin-1-yl)methanone (**11**) in $CDCl_3$ at 55 °C

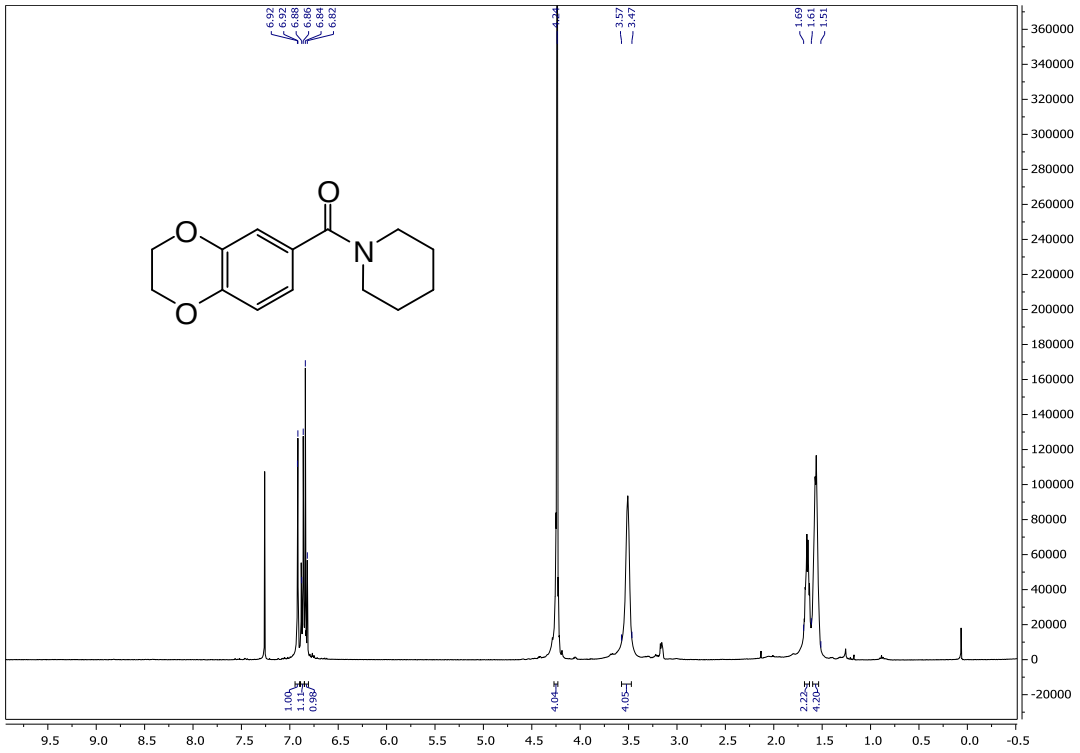


Figure S29 ^{1}H NMR spectrum of (2,3-dihydrobenzo[b][1,4]dioxin-6-yl)(piperidin-1-yl)methanone (**11**) in $CDCl_3$ at 25 °C

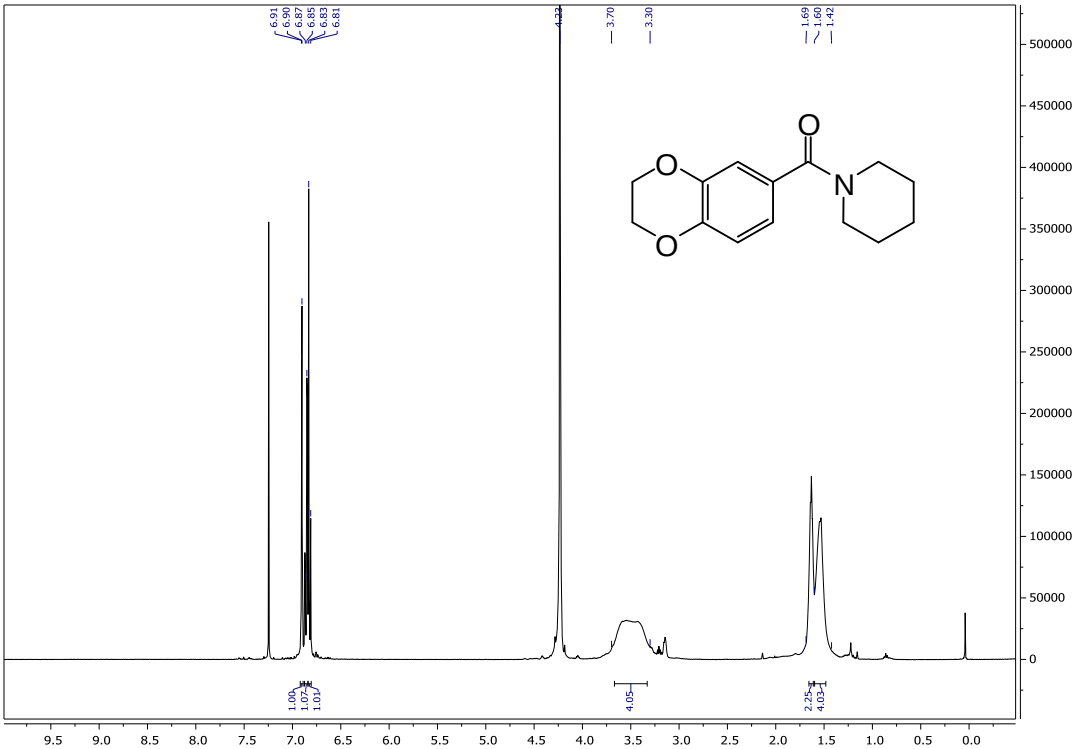


Figure S30 ^{13}C NMR spectrum of (2,3-dihydrobenzo[b][1,4]dioxin-6-yl)(piperidin-1-yl)methanone (**11**) in $CDCl_3$

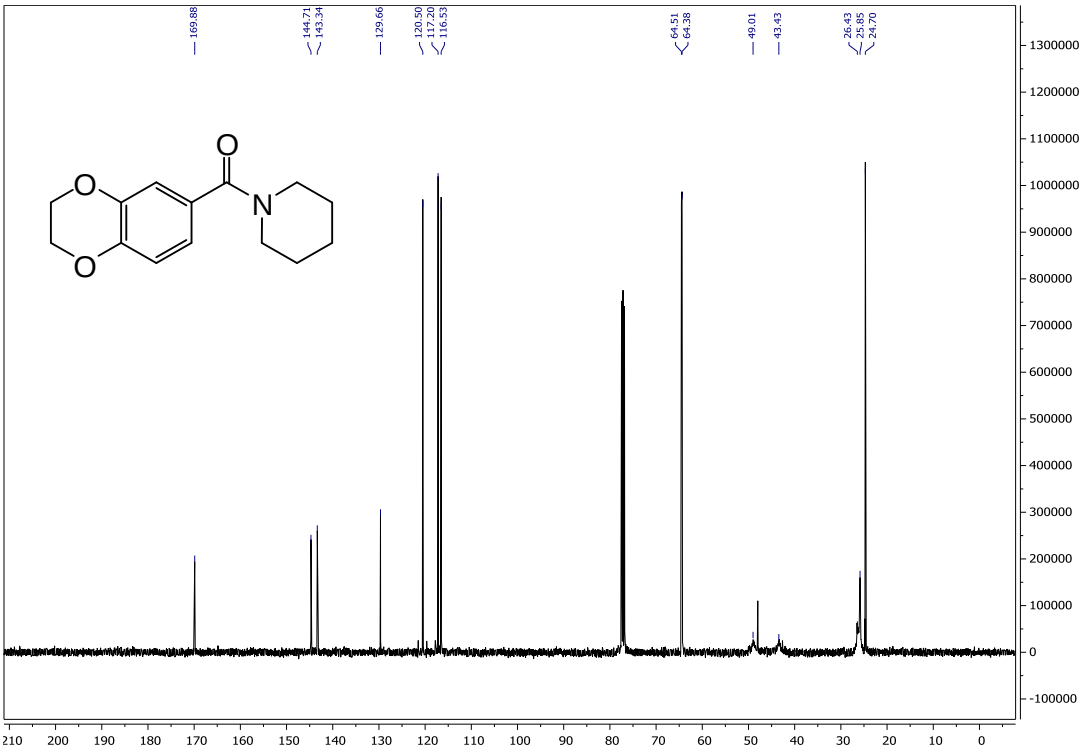


Figure S31 ^{1}H NMR spectrum of 1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-(piperidin-1-yl)ethane-1,2-dione (**12**) in $CDCl_3$

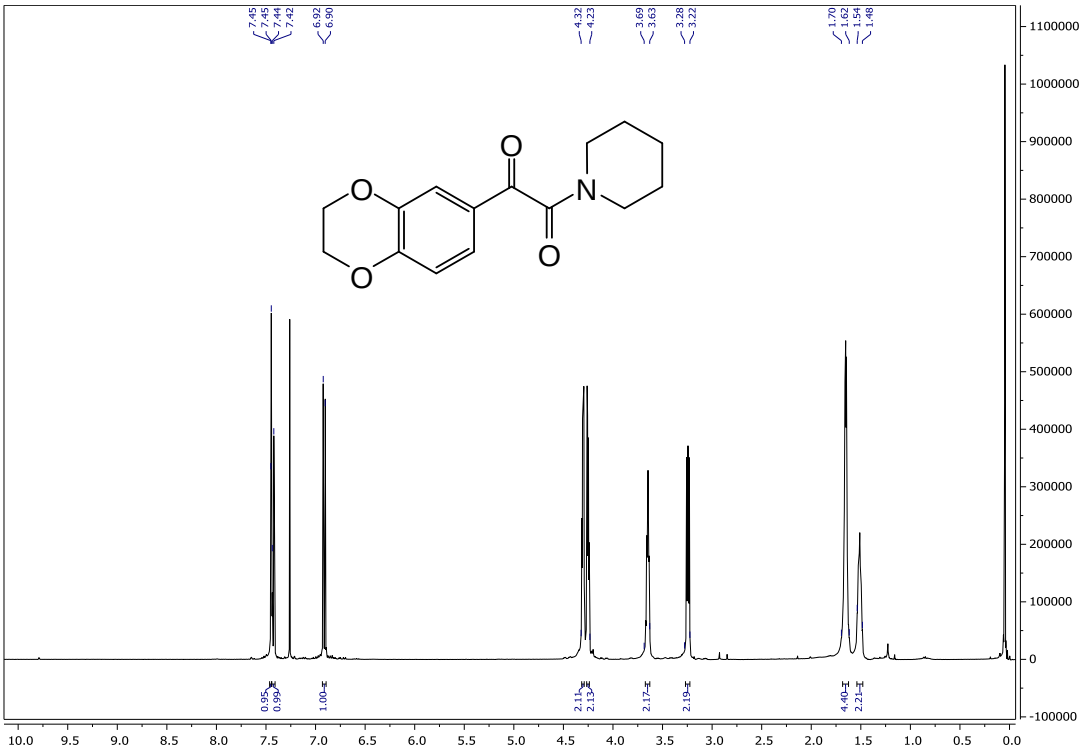


Figure S32 ^{13}C NMR spectrum of 1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-(piperidin-1-yl)ethane-1,2-dione (**12**) in $CDCl_3$

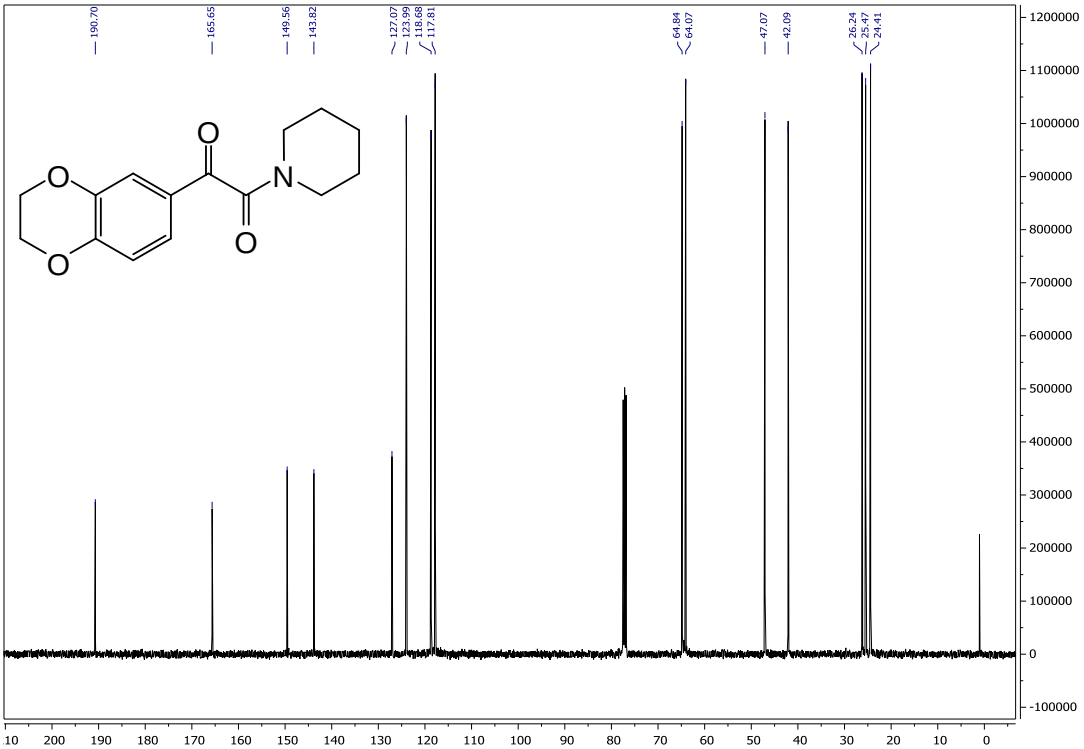


Figure S33 ^{1}H NMR spectrum of 4-chloro-*N*-(2-morpholinoethyl)benzamide (**15**) in $CDCl_3$

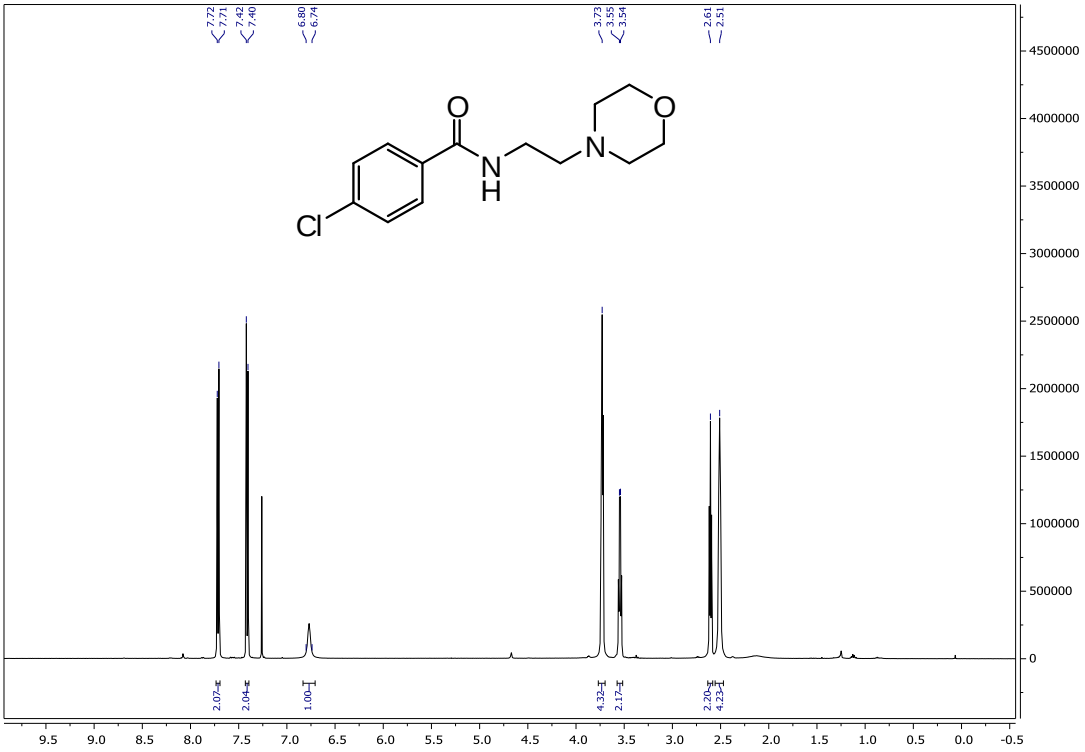


Figure S34 ^{13}C NMR spectrum of 4-chloro-*N*-(2-morpholinoethyl)benzamide (**15**) in $CDCl_3$

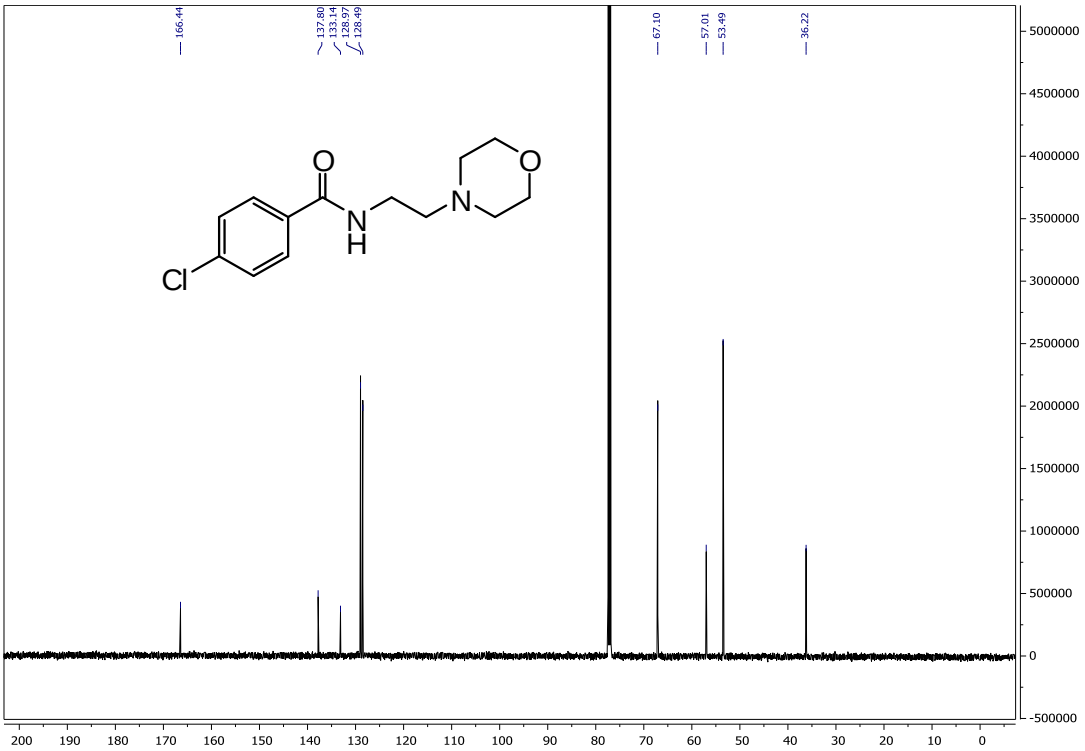


Figure S35 ^{1}H NMR spectrum of *N,N*-diethylnicotinamide (**19**) in DMSO-d_6

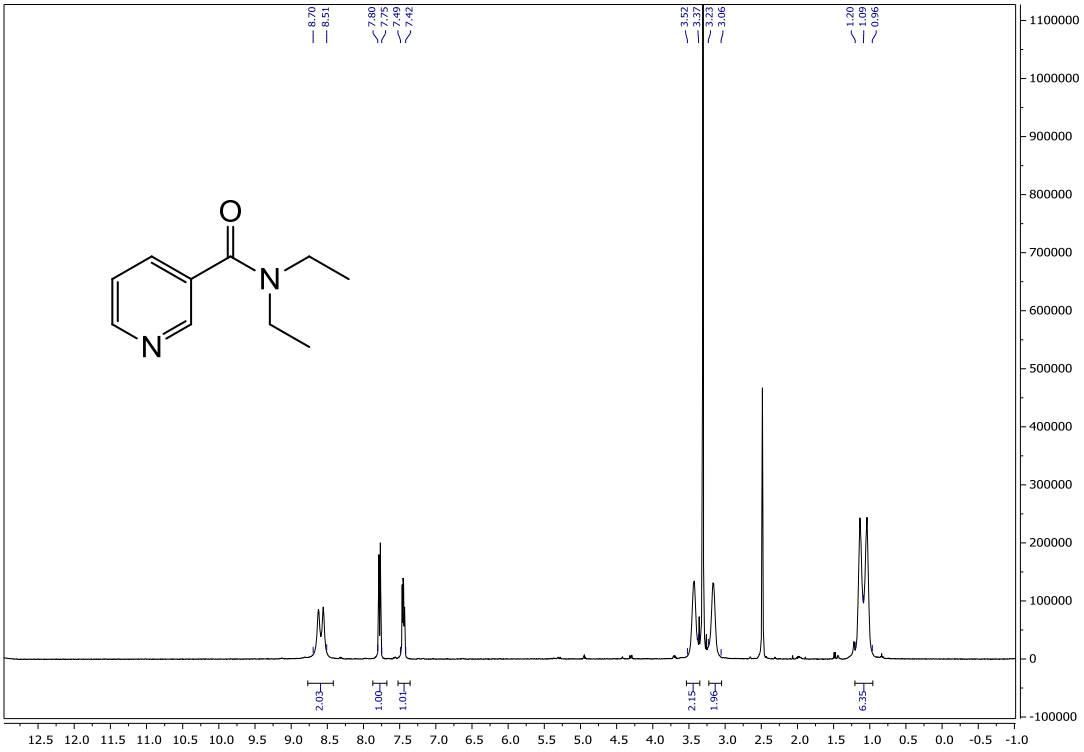


Figure S36 ^{13}C NMR spectrum of *N,N*-diethylnicotinamide (**19**) in DMSO-d_6

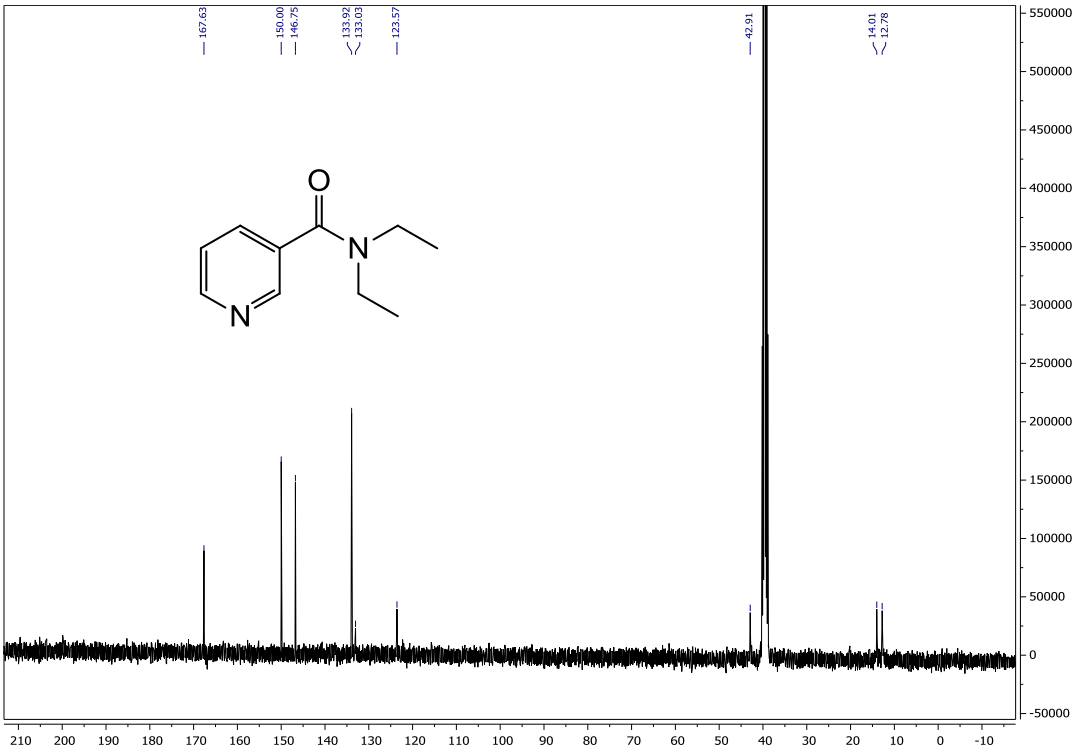


Figure S37 DEPT spectrum of *N,N*-diethylnicotinamide (**19**) in DMSO-d_6

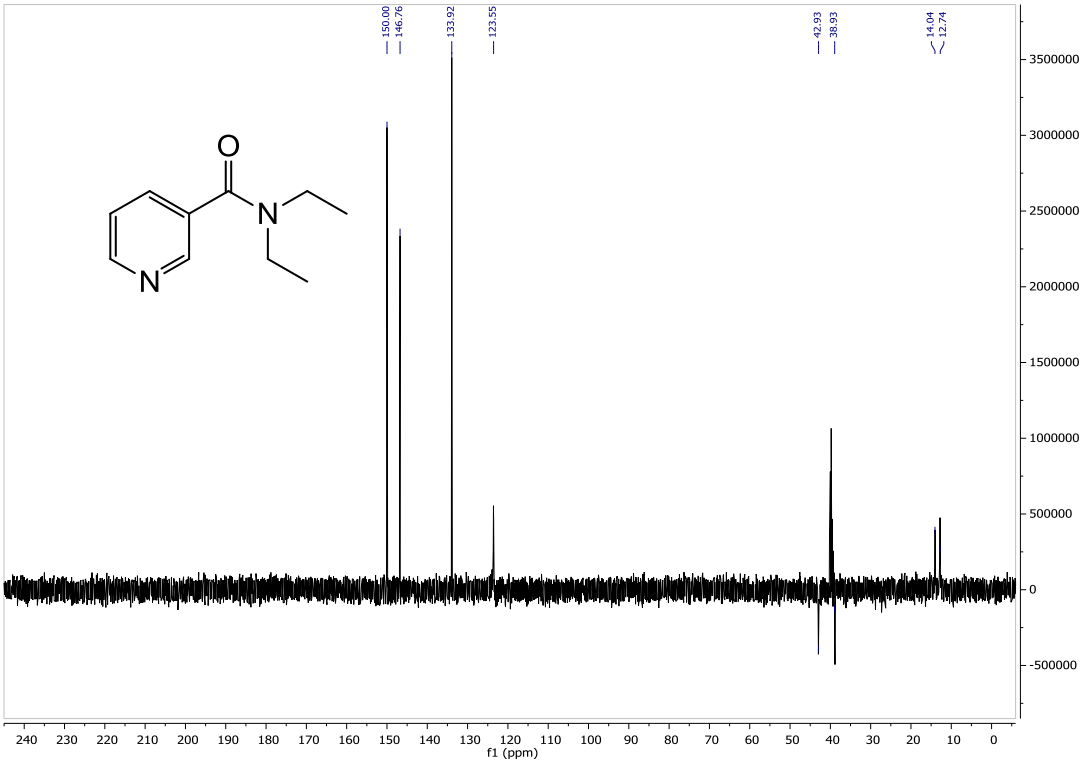


Figure S38 ^{1}H NMR spectrum of 17-(*N*-*t*-butyl-carbamoyl)-4-aza-5α-androst-16-en-3-one (**23**) in $CDCl_3$

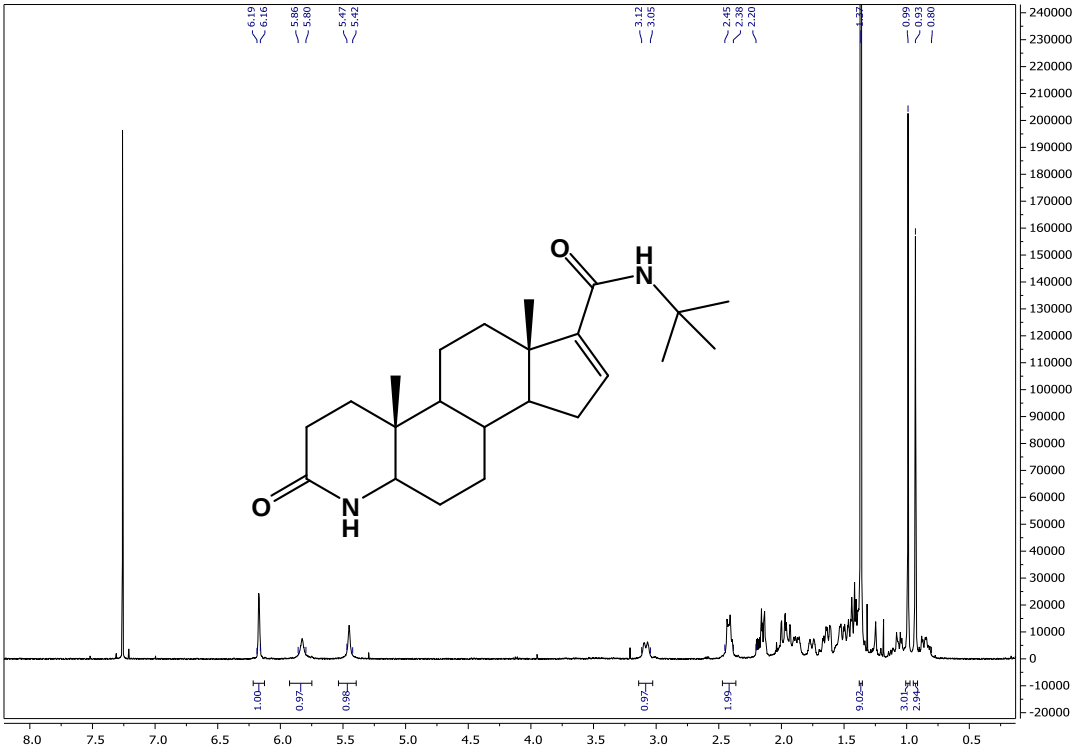


Figure S39 ^{13}C NMR spectrum of 17-(*N*-*t*-butyl-carbamoyl)-4-aza-5α-androst-16-en-3-one (**23**) in $CDCl_3$