Supporting Information

Unconventional titania photocatalysis: direct deployment of carboxylic acids in alkylations and annulations.

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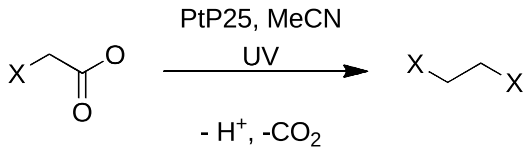
General Experimental Section

All reagents and solvents were purchased from either Sigma Aldrich or Alfa Aesar and used without further purification. Acetonitrile and methanol were dried over calcium hydride prior to use. Column chromatography was carried out using Silica 60A (particle size 40-63 µm, Silicycle, Canada) as the stationary phase, and TLC was performed on precoated silica gel plates (0.20 mm thick, Sil G UV_{254}, Macherey-Nagel, Germany) and observed under UV light unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV III 500, Bruker AV II 400 and Bruker AV 300 instruments. Chemical shifts are reported in parts per million (ppm) from low to high frequency and referenced to the residual solvent resonance. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, br = broad. Melting points (M.p.) were determined using a Sanyo Gallenkamp apparatus and are reported uncorrected. Mass spectrometry was carried out at the EPSRC National Mass Spectrometry Service Centre, Swansea, UK.

Platinised TiO_2 (Pt-TiO_2) was prepared in accordance with the literature.[1] P25 was used and the Pt loading was 0.1% (wt/wt).

General Procedure A: Preparations by Semiconductor Photocatalysis - Dimerisations

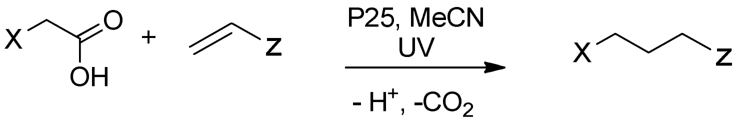
To a 5 mg ml^{-1} dispersion of semiconductor in MeCN (freshly distilled over CaH_2) was added a known amount of the desired carboxylic acid. The resulting mixture was degassed by bubbling with argon for 20 minutes. The mixture was then irradiated by two banks of six 29 cm 15 W Philips Cleo tubes (λ = 350 nm) for the desired reaction time with mechanical stirring. Following irradiation the semiconductor powder was removed by filtration through celite. The solvent was removed under reduced pressure and the crude reaction mixture was purified if necessary.



Scheme S1. General procedure for the Pt-TiO_2 photosensitised dimerisation of carboxylic acids.

General Procedure B: Preparations by Semiconductor Photocatalysis – Intermolecular Additions

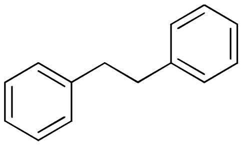
To a 1 mg ml^{-1} suspension of semiconductor in MeCN (freshly distilled over CaH_2) was added known amounts of desired reagents. The resulting mixture was degassed by bubbling with argon for 20 minutes. The mixture was then irradiated with eight 29 cm 15 W Philips Cleo tubes (λ = 350 nm) for the desired reaction time. Following irradiation the semiconductor powder was removed by filtration through celite. The solvent was removed under reduced pressure and the crude reaction mixture was purified if necessary. Unless otherwise stated all reagents were commercially available and used without further modification.



Scheme S2. General procedure for the TiO_2 photosensitised intermolecular addition of carboxylic acids to acceptors.

Synthesis and Experimental Section

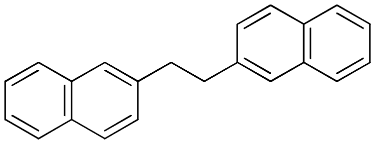
Bibenzyl 2a



2a

Phenylacetic acid (54.5 mg, 0.4 mmol), and Pt-TiO_2 (P-25, 250 mg, 3.1 mmol) were reacted in accordance with the general procedure A. Following irradiation for 19 h **2a** was obtained as a colourless solid (29.7 mg, 81%) without further purification. ^1H NMR (500 MHz, $CDCl_3$, 298 K): $\delta = 2.95$ (s, 4H, C*H*$_2$) 7.21-7.24 (m, 6H, Ar-*H*), 7.30-7.33 (m, 4H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 296 K): δ = 38.0, 126.0, 128.4, 128.5, 141.8. Consistent with literature.[2]

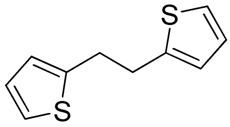
1,2-Di(naphthalen-2-yl)ethane 2b



2b

(Naphthalen-2-yl)acetic acid (58.3 mg, 0.31 mmol), and 0.1% (w/w) Pt-TiO_2 (P-25, 200 mg, 2.5 mmol) for 52 h in accordance with the general procedure A. ^1H NMR analysis of the resultant mixture revealed **2b** (0.087 mmol, 56%). 2-methylnaphthalene (0.125 mmol, 40%) was also observed. These data are consistent with literature.[3]

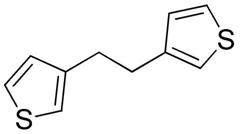
1,2-Di(thiophen-2-yl)ethane 2c



2c

2-Thiopheneacetic acid (27 mg, 0.19 mmol), and Pt-TiO_2 (P-25, 120 mg, 1.5 mmol) were reacted in accordance with the general procedure A. Following irradiation for 20 h **2c** was obtained as a colourless solid (15.3 mg, 83%) without further purification. ^{1}H NMR (300 MHz, $CDCl_3$, 296 K): δ = 3.20 (s, 4H, C*H*$_2$), 6.80 (d, *J* = 3.4 Hz, 2H, Ar*H*), 6.91-6.94 (m, 2H, Ar*H*), 7.14 (d, *J* = 5.2 Hz, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 296 K): δ = 32.2, 123.4, 124.7, 126.8, 143.7. Consistent with literature.[4]

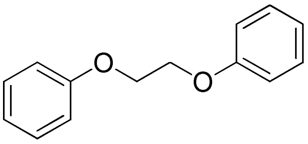
1,2-Di(thiophen-3-yl)ethane 2d



2d

3-Thiopheneacetic acid (27 mg, 0.19 mmol), and Pt-TiO_2 (P-25, 120 mg, 1.5 mmol) were reacted in accordance with the general procedure A. Following irradiation for 20 h **2d** was obtained as a colourless solid (14.3 mg, 78%) without further purification. ^{1}H NMR (300 MHz, $CDCl_3$, 296 K): δ = 2.96 (s, 4H, C*H*$_2$), 6.93 (m, 4H, Ar*H*), 7.24 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 296 K): δ = 31.3, 120.4, 125.3, 128.2, 142.1. Consistent with literature.[5]

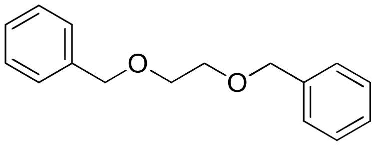
1,2-Diphenoxyethane 2e



2e

Phenoxyacetic acid (60 mg, 0.4 mmol), and (P-25, 250mg, 3.1 mmol) were reacted in accordance with the general procedure A. Following irradiation for 21 h the crude reaction mixture was purified by column chromatography on silica gel (eluent: 50% CH_2Cl_2 in Petrol 40/60) to yield **2e** as a colourless solid (22.5 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 4.34 (s, 4H, C*H*$_2$), 6.95-7.00 (m, 6H, Ar-*H*), 7.28-7.34 (m, 4H, Ar-*H*); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ = 66.5, 114.7, 121.1, 129.5, 158.7. Consistent with literature.[6] Analysis of the ^{1}H NMR prior to chromatography revealed phenoxyacetone (11% w.r.t. **2e**), phenol (6% w.r.t. **2e**) and 3-phenoxypropanenitrile (3% w.r.t. **2e**). These data were consistent with literature.[7]

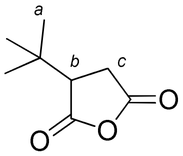
1,2-Bis(benzyloxy)ethane 2f



2f

Benzyloxyacetic acid (66 mg, 0.4 mmol), and Pt-TiO_2 (P-25, 250 mg, 3.1 mmol) were reacted in accordance with the general procedure A. Following irradiation for 21 h the crude reaction mixture was purified by column chromatography on silica gel (eluent: CH_2Cl_2) to yield **2f** as a colourless oil (18.6 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ = 3.67 (s, 4H, O-C*H*$_2$) 4.59 (s, 4H, Ph-C*H*$_2$), 7.27-7.39 (m, 10H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 296 K): δ = 69.5, 73.3, 127.6, 127.8, 128.4, 138.3. Consistent with literature.[8]

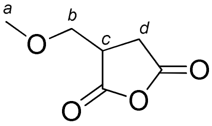
tert-Butylsuccinic anhydride 3a



3a

Pivalic acid (43 mg, 0.42 mmol), maleic anhydride (167 mg, 1.68 mmol) and TiO_2 (50 mg, 0.63 mmol) were reacted in accordance with the general procedure B. Following irradiation for 26 h the crude mixture was purified by column chromatography on silica gel (eluent: 20% EtOAc in Petrol 40/60) to yield **3a** as a clear oil (10.7mg, 16%). ^{1}H NMR (300 MHz, $CDCl_3$, 297 K): $\delta = 1.09$ (s, 9H, H_a), 2.77-3.03 (m, 3H, $H_{b,c}$); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): $\delta =$ 27.0, 29.7, 31.5, 51.1, 170.1, 171.7. Consistent with literature.[9] Succinic anhydride was also isolated as a white powder (33.8 mg, 20%). ^{1}H NMR (300 MHz, $CDCl_3$, 296 K): $\delta = 2.99$ (s, 4H, H_a). Consistent with literature.[10]

(Methoxymethyl)succinic anhydride 3b

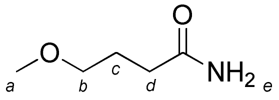


3b

Methoxyacetic acid (60 mg, 0.66 mmol), maleic anhydride (259 mg, 2.64 mmol) and TiO_2 (80 mg, 1.00 mmol) were reacted in accordance with the general procedure B. Following irradiation for 18 h the crude mixture was purified by column chromatography on silica gel (eluent: 5% EtOAc in DCM) to yield **3b** as a clear oil (51.4mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): $\delta = 2.94$-3.07 (m, 2H, H_d), 3.23-3.29 (m, 1H, H_c), 3.35 (s, 3H, H_a), 3.55 (dd, $J = 3.1, 9.2$ Hz, 1H, H_b), 3.81 (dd, $J = 3.3, 9.2$ Hz, 1H, $H_{b'}$); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): $\delta = 31.2$, 42.1, 59.3, 70.0, 170.4, 172.8; LR-ESIMS: $m/z = 162$ $[MNH_4]^+$; HR-ESIMS:

m/z = 162.0761 (calcd. for $C_6H_{12}NO_3$, 162.0766). Succinic anhydride was also isolated as a white powder (33.8 mg, 16%).

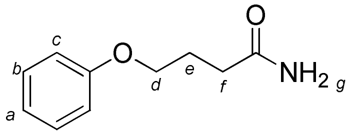
4-Methoxybutanamide 4a



4a

Methoxyacetic acid (282 mg, 3.13 mmol), acrylamide (45 mg, 0.63 mmol) and TiO_2 (75 mg, 0.94 mmol) were reacted in accordance with the general procedure B. Following irradiation for 38 h the reaction mixture was purified by column chromatography on silica gel (eluent: gradient of 2-10% MeOH in CH_2Cl_2; visualised by staining with vanillin) to yield **4a** as an off-white solid (48.9 mg, 67%). Mp: 39-40˚C. ^{1}H NMR (500 MHz, *d6*-acetone, 295 K): δ = 1.76-1.82 (m, 2H, H_c), 2.21 (t, *J* = 7.5 Hz, 2H, H_d), 3.24 (s, 3H, H_a), 3.34 (t, *J* = 6.4 Hz, 2H, H_b) 6.25 (br-s, 1H, H_e) 6.76 (br-s, 1H, $H_{e'}$); ^{13}C NMR (75 MHz, *d6*-acetone, 296 K): δ = 26.2, 32.6, 58.4, 72.5, 175.0; LR-EIMS: *m/z* = 117 $[M]^+$; HR-ESIMS: *m/z* = 117.0782 (calcd. for $C_5H_{11}O_2N_1$, 117.0790).

4-Phenoxybutanamide 4b

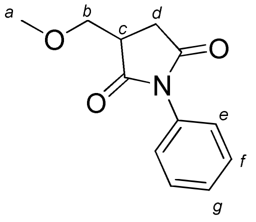


4b

Phenoxyacetic acid (507 mg, 3.33 mmol), acrylamide (47 mg, 0.66 mmol) and TiO_2 (80 mg, 1.0 mmol) were reacted in accordance with the general procedure B. Following irradiation for 62 h the reaction mixture was purified by column chromatography on silica gel (eluent: 2% MeOH in CH_2Cl_2) to yield **4b** as a white powder (97.3 mg, 82%). Mp: 110 ˚C. ^{1}H NMR (300

MHz, $CDCl_3$, 294 K): δ = 2.13 (m, 2H, H_e), 2.45 (t, *J* = 7.2 Hz, 2H, H_f), 4.02 (t, *J* = 6.0 Hz, 2H, H_d), 5.63 (br-s, 1H, H_g), 5.82 (br-s, 1H, $H_{g'}$), 6.90 (d, *J* = 8.8 Hz, 2H, H_c), 6.95 (t, *J* = 7.4 Hz, 1H, H_a), 7.29 (t, *J* = 7.4 Hz, 2H, H_b); ^{13}C NMR (75 MHz, $CDCl_3$, 295 K): δ = 25.4, 32.6, 67.1, 114.9, 121.2, 129.9, 159.2, 175.4; LR-EIMS: *m/z* = 202 $[MNa]^+$;HR-ESIMS: *m/z* = 202.0838 (calcd. for $C_{10}H_{13}NO_2Na$, 202.0844).

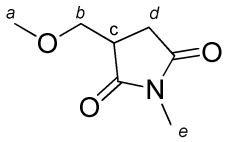
3-(Methoxymethyl)-1-phenylpyrrolidine-2,5-dione 5a



5a

Methoxyacetic acid (54.4 mg, 0.63 mmol), *N*-phenylmaleimide (433.6 mg, 2.50 mmol) and TiO_2 (75 mg, 0.94 mmol) were reacted together in accordance with the general procedure B. Following irradiation for 18 h the reaction mixture was purified by column chromatography on silica gel (eluent: 30% EtOAc in Petroleum Ether 40-60) to yield **5a** as a white powder (74.4 mg, 54%). Mp: 109-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 299 K) δ = 2.86-2.99 (m, 2H, H_d, $H_{d'}$), 3.08-3.15 (m, 1H, H_c), 3.38 (s, 3H, H_a), 3.36 (dd, J= 3.3 Hz, 9.1 Hz, 1H, H_b), 3.91 (dd, J= 3.9 Hz, 9.1 Hz, 1H, $H_{b'}$), 7.26-7.30 (m, 2H, H_f), 7.36-7.41 (m, 1H, H_g), 7.44-7.49 (m, 2H, H_e); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ = 31.9, 41.2, 59.3, 70.8, 126.6, 128.6, 129.1, 132.1, 175.8, 177.3; LR-ESIMS: *m/z* = 221 $[MH]^+$; HR-EIMS: *m/z* = 220.0969 (calcd. for $C_{12}H_{14}O_3N_1$, 220.0974). *N*-phenyl succinimide was also isolated as an off-white solid (61.3 mg, 14 %). ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 2.81 (s, 4H, H_a), 7.24 (m, 2H, *Ar*-H), 7.37 (m, 1H, *Ar*-H), 7.44 (m, 2H, *Ar*-H); ^{13}C NMR (100 MHz, $CDCl_3$, 297 K): δ = 28.4, 126.5, 128.7, 129.2, 132.0, 176.3. Consistent with literature.[11]

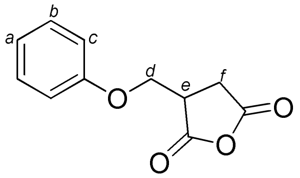
3-(Methoxymethyl)-1-methylpyrrolidine-2,5-dione 5b



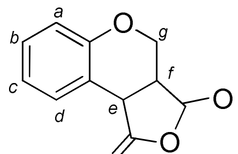
5b

Methoxyacetic acid (60 mg, 0.66 mmol), *N*-methylmaleimide (296 mg, 2.64 mmol) and TiO_2 (80 mg, 1.0 mmol) were reacted in accordance with the general procedure B for 16 h. Following irradiation the reaction mixture was purified by column chromatography on silica gel (eluent: 50% EtOAc in Petrol 40/60) to yield **5b** as a colourless oil (60.3 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ = 2.68-2.80 (m, 2H, H_d), 2.93-3.00 (m, 1H, H_c), 2.98 (s, 3H, H_e), 3.32 (s, 3H, H_a), 3.54 (dd, *J* = 3.4, 9.2 Hz, 1H, H_b), 3.79 (dd, *J* = 4.2, 9.2 Hz, 1H, $H_{b'}$); ^{13}C NMR (75 MHz, $CDCl_3$, 296 K): δ = 25.3, 32.1, 41.5, 59.6, 70.8, 177.3, 178.6; LR-ESIMS: *m/z* = 158 [M*H*]$^+$; HR-ESIMS: *m/z* = 158.0811 (calcd. for $C_7H_{12}NO_3$, 158.0817). *N*-methyl succinimde was also observed by ^{1}H NMR (10% w.r.t. **A**). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 2.69 (s, 4H, 2xCH_2), 2.97 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 299 K): δ = 28.2, 177.3 Consistent with literature.[12]

(Phenoxymethyl)succinic anhydride 7a & 3a,4-dihydro-1*H*-furo[3,4-*c*]chromene-1,3(9b*H*)-dione 8a



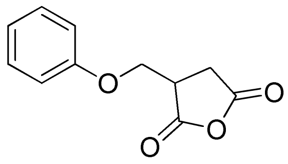
7a



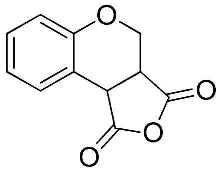
8a

Phenoxyacetic acid (100 mg, 0.65 mmol), maleic anhydride (130 mg, 1.3 mmol) and TiO_2 (75 mg, 0.98 mmol) were reacted in accordance with the general procedure B. Following irradiation for 26 h the crude mixture was purified by column chromatography on silica gel (eluent: 5% EtOAc in DCM) to yield **7a** as a white crystalline solid (45.3 mg, 34%). Mp. 91-93˚C. ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 3.15 (d, *J* = 7.9 Hz, 1H, H_f), 3.46 – 3.52 (m, 1H, H_e), 4.17 (dd, J = 3.1, 9.2 Hz, 1H, H_d), 4.44 (dd, J = 3.6, 9.3 Hz, 1H, H_d), 6.88 (d, *J* = 7.8 Hz, 2H, H_c), 7.01 (t, *J* = 7.4 Hz, 1H, H_a), 7.30 (t, *J* = 8.4 Hz, 1H, H_b); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ = 31.4, 41.7, 65.6, 114.7, 122.1, 129.7, 157.7, 169.8, 171.9; LR-EIMS: *m/z* = 207 $[MH]^+$; HR-ESIMS: *m/z* = 207.0646 (calcd. for $C_{11}H_{11}O_4$, 207.0657). As above to yield **8a** as a yellow oil (34.5mg, 26%). ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 3.67-3.72 (m, 1H, H_f), 4.08 (dd, *J* = 4.1, 11.6 Hz, 1H, H_g), 4.36 (d, *J* = 9.9 Hz, 1H, H_e), 4.59 (dd, *J* = 3.5, 11.6 Hz, 1H, $H_{g'}$), 6.95 (d, *J* = 8.3 Hz, 1H, H_d), 7.09 (t, *J* = 7.6 Hz, 1H, H_c), 7.27 (m, 1H, Ar-H), 7.53 (d, *J* = 7.7 Hz, 1H, H_a); ^{13}C NMR (75 MHz, $CDCl_3$, 299 K): δ = 40.2, 42.6, 63.0, 114.5, 114.7, 118.3, 123.3, 129.7, 154.9, 169.9, 170.6; LR-EIMS: *m/z* = 204 $[M]^+$; HR-ESIMS: *m/z* = 204.0415 (calcd. for $C_{11}H_8O_4$, 204.0423). Succinic anhydride was also isolated as a colourless solid (43 mg, 33%).

(Phenoxymethyl)succinic anhydride 7a & 3a,4-dihydro-1*H*-furo[3,4-*c*]chromene-1,3(9b*H*)-dione 8a



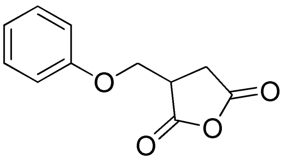
7a

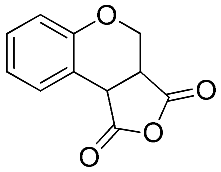


8a

Phenoxyacetic acid (20 mg, 0.13 mmol), maleic anhydride (26 mg, 0.26 mmol) and 0.1% Pt-TiO_2 (P-25, 16 mg, 0.2 mmol) were reacted in accordance with the general procedure A for 17 h. ^{1}H NMR analysis (w.r.t. CH_2Br_2 standard) of the resultant mixture revealed: **7a** (0.06 mmol, 48%) and **8a** (0.01 mmol, 8%).

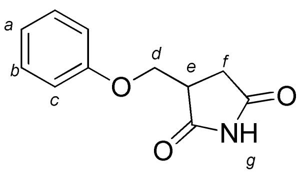
(Phenoxymethyl)succinic anhydride 7a & 3a,4-dihydro-1*H*-furo[3,4-*c*]chromene-1,3(9b*H*)-dione 8a


7a

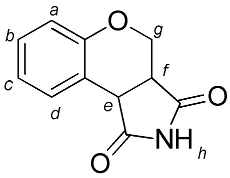

8a

Phenoxyacetic acid (15.2 mg, 0.1 mmol), maleic anhydride (19.6 mg, 0.2 mmol) and TiO_2 (P-25, 12 mg, 0.15 mmol) in MeCN (2.4 mL – 5 mg mL^{-1} dispersion) were reacted in accordance with the general procedure A for 45 h. ^1H NMR analysis (w.r.t. CH_2Br_2 standard) of the resultant mixture revealed: **7a** (0.02 mmol, 16%) and **8a** (0.05 mmol, 47%).

1-Methyl-3-(phenoxymethyl)pyrrolidine-2,5-dione 7b & 3a,4-dihydrochromeno[3,4-*c*]pyrrole-1,3(2*H*,9b*H*)-dione 8b



7b

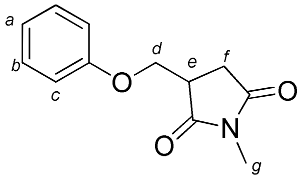


8b

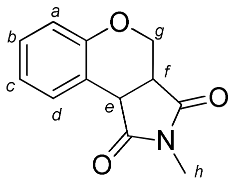
Phenoxyacetic acid (100 mg, 0.65 mmol), maleimide (127 mg, 1.3 mmol) and TiO_2 (75 mg, 0.98 mmol) were reacted in accordance with the general procedure B. Following irradiation for 17 h the crude mixture was purified by column chromatography on silica gel (eluent: 20% EtOAc in Petrol 40/60) to yield **7b** as a clear oil (41.7 mg, 31%). ^1H NMR (400 MHz, $CDCl_3$, 296 K): δ = 2.88 (d, J = 7.6 Hz, 2H, H_f), 3.18 – 3.24 (m, 1H, H_e), 4.18 (dd, J = 3.3, 9.2 Hz, 1H, H_d), 4.37 (dd, J = 4.3, 9.2 Hz, 1H, $H_{d'}$), 6.86 (d, J = 8.8 Hz, 2H, H_c), 6.96 (t, J = 8.3 Hz, 1H, H_a), 7.26 (t, J = 7.9 Hz, 2H, H_b), 9.55 (br-s, 1H, H_g); ^{13}C NMR (75 MHz, $CDCl_3$, 296 K): δ = 32.8, 42.0, 65.8, 114.6, 121.6, 129.6, 158.1, 177.2, 178.3; LR-ESIMS: m/z = 206 $[MH]^+$;

HR-ESIMS: *m/z* = 206.0809 (calcd. for $C_{11}H_{12}NO_3$, 206.0817). As above to yield **8b** as a colourless solid (63.1 mg, 48%). Mp: 158-160 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ = 3.44-3.47 (m, 1H, H_f), 4.01 (dd, *J* = 4.2, 11.5 Hz 1H, H_g), 4.11 (d, *J* = 9.2 Hz, 1H, H_e), 4.59 (dd, *J* = 3.1, 11.4 Hz 1H, $H_{g'}$), 6.92 (d, *J* = 8.2 Hz, 1H, H_d), 7.06 (t, *J* = 8.2 Hz, 1H, H_c), 7.23 (t, *J* = 8.0 Hz, 1H, H_b), 7.54 (d, *J* = 7.8 Hz, 1H, H_a), 7.72 (br-s, 1H, H_h); ^{13}C NMR (75 MHz, $CDCl_3$, 297 K): δ = 40.9, 43.4, 63.7, 117.1, 117.9, 122.9, 129.2, 130.0, 155.3, 175.7, 176.3; LR-ESIMS: *m/z* = 204 $[MH]^+$; HR-ESIMS: *m/z* = 204.0649 (calcd. for $C_{11}H_{10}NO_3$, 204.0661). Succinimide was also isolated as a white powder (52.1 mg, 41%). ^{1}H NMR (300 MHz, $CDCl_3$, 296 K): δ = 2.75 (s, 4H, 2xCH_2), 8.84 (br-s, 1H, N*H*); ^{13}C NMR (75 MHz, $CDCl_3$, 299 K): δ = 29.6, 177.9. Consistent with literature.[13]

N-Methyl-3-(phenoxymethyl)pyrrolidine-2,5-dione 7c & *N*-methyl-3a,4-dihydrochromeno[3,4-*c*]pyrrole-1,3(2*H*,9b*H*)-dione 8c



7c

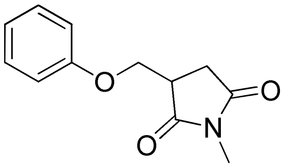


8c

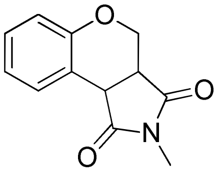
Phenoxyacetic acid (100 mg, 0.65 mmol), *N*-methylmaleimide (145 mg, 1.3 mmol) and TiO_2 (75 mg, 0.98 mmol) were reacted in accordance with the general procedure B. Following irradiation for 20 h the crude mixture was purified by column chromatography on silica gel (eluent: 20% EtOAc in Petrol 40/60) to yield **7c** as a colourless oil (32.6mg, 23%). ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 2.88–2.90 (m, 2H, H_f), 3.04 (s, 3H, H_g), 3.17–3.23 (m, 1H, H_e), 4.17 (dd, *J* = 3.4, 9.2 Hz, 1H, H_d), 4.40 (dd, *J* = 4.4, 9.2 Hz, 1H, H_d), 6.87 (d, *J* = 8.8 Hz, 2H, H_a), 6.98 (t, *J* = 7.4 Hz, 1H, H_b), 7.28 (t, *J* = 7.4 Hz, 2H, H_c); ^{13}C NMR (75 MHz, $CDCl_3$, 297 K): δ = 25.4, 32.1, 41.1, 66.4, 115.1, 122.0, 130.0, 158.5, 177.0 178.0; LR-MS: *m/z* =

219 [M]$^+$; HR-MS: m/z = 219.0892 (calcd. for $C_{12}H_{13}NO_3$, 219.0895). As above to yield **8c** as a white powder (77.8mg, 55%). Mp: 125-127 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ = 3.00 (s, 3H, H_h), 3.36 - 3.40 (m, 1H, H_f), 4.01 (dd, J = 4.2, 11.4 Hz, 1H, H_g), 4.07 (d, J = 9.2 Hz, 1H, H_e), 4.62 (dd, J = 2.9, 11.4 Hz, 1H, $H_{g'}$), 6.89 (d, J = 8.2 Hz, 1H, H_d), 7.05 (t, J = 7.5 Hz, 1H, H_c), 7.21 (t, J = 7.7 Hz, 1H, H_b), 7.58 (d, J = 7.4 Hz, 1H, H_a); ^{13}C NMR (75 MHz, $CDCl_3$, 297 K): δ = 27.8, 40.1, 42.7, 64.3, 118.1, 118.3, 123.2, 129.4, 130.5, 155.7, 176.6, 177.2; LR-MS: m/z = 217 [M]$^+$; HR-MS: m/z = 217.0733 (calcd. for $C_{12}H_{11}NO_3$, 217.0739). *N*-methylsuccinimde was also isolated as an off-white powder (57.2 mg, 39%).

N-Methyl-3-(phenoxymethyl)pyrrolidine-2,5-dione 7c & *N*-methyl-3a,4-dihydrochromeno[3,4-*c*]pyrrole-1,3(2*H*,9b*H*)-dione 8c



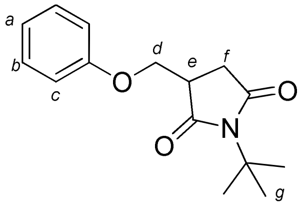
7c



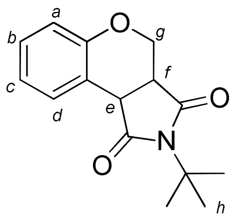
8c

Phenoxyacetic acid (15.2 mg, 0.1 mmol), *N*-methylmaleimide (22.2 mg, 0.2 mmol) and TiO_2 (P-25, 12 mg, 0.15 mmol) in MeCN (2.4 mL – 5 mg mL^{-1} dispersion) were reacted in accordance with the general procedure B for 45 h. ^{1}H NMR analysis (w.r.t. CH_2Br_2 standard) of the resultant mixture revealed: **7c** (0.01 mmol, 7%) and **8c** (0.07 mmol, 68%).

N-(*tert*-Butyl)-3-(phenoxymethyl)pyrrolidine-2,5-dione 7d & *N*-(tert-butyl)-3a,4-dihydrochromeno[3,4-*c*]pyrrole-1,3(2*H*,9b*H*)-dione 8d



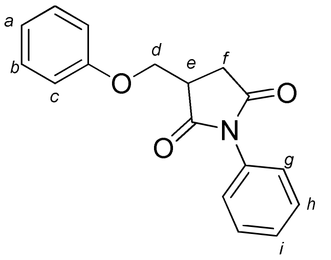
7d



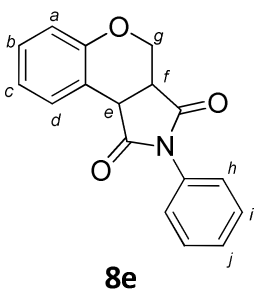
8d

Phenoxyacetic acid (100 mg, 0.65 mmol), *N*-(tert-butyl)-maleimide (199 mg, 1.3 mmol) and TiO_2 (75 mg, 0.98 mmol) were reacted in accordance with the general procedure B. Following irradiation for 12 h the crude mixture was purified by column chromatography on silica gel (eluent: 10% EtOAc in Petrol 40/60) to yield **7d** as a clear oil (57mg, 34%). ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 1.58 (s, 9H, H_g), 2.70-2.81 (m, 2H, H_f), 2.99-3.03 (m, 1H, H_e), 4.12 (dd, *J* = 3.2, 9.0 Hz, 1H, $H_{d'}$), 4.35 (dd, *J* = 4.8, 9.0 Hz 1H, H_d), 6.86 (d, *J* = 7.7 Hz, 2H, H_c), 6.97 (t, *J* = 7.3 Hz, 1H, H_a), 7.28 (t, *J* = 7.4 Hz, 1H, H_b); ^{13}C NMR (75 MHz, $CDCl_3$, 297 K): δ = 28.4, 32.3, 40.4, 58.6, 66.7, 114.6, 121.5, 129.5, 158.2, 176.1, 178.3; LR-MS: *m/z* = 262 [M*H*]$^+$; HR-MS: *m/z* = 262.1431 (calcd. for $C_{15}H_{20}NO_3$, 262.1433). As above to yield **8d** as a white solid (55.7 mg, 33%). Mp = 80-81 ˚C ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 1.54 (s, 9H, H_h), 3.20-3.25 (m, 1H, H_f), 3.89 (d, *J* = 9.4 Hz, 1H, H_e), 3.99 (dd, *J* = 4.2, 11.3 Hz, 1H, H_g), 3.49 (dd, *J* = 3.6, 11.3 Hz, 1H, $H_{g'}$), 6.89 (d, *J* = 8.2 Hz, 1H, H_d), 7.03 (t, *J* = 7.6 Hz, 1H, H_c), 7.20 (t, *J* = 7.5 Hz, 1H, H_b), 7.54 (d, *J* = 7.7 Hz, 1H, H_a); ^{13}C NMR (75 MHz, $CDCl_3$, 297 K): δ = 28.3, 39.8, 41.9, 59.0, 64.2, 117.7, 117.9, 122.6, 128.8, 130.2, 155.1, 177.1; LR-MS: *m/z* = 260 [M*H*]$^+$; HR-MS: *m/z* = 260.1277 (calcd. for $C_{15}H_{18}NO_3$, 260.1287). Analysis of the crude reaction mixture revealed *N*-(tert-butyl)succinimde (11 % w.r.t. **7d** & **8d**).

3-(Phenoxymethyl)-1-phenylpyrrolidine-2,5-dione 7e & *N*-phenyl-3a,4-dihydrochromeno[3,4-*c*]pyrrole-1,3(2*H*,9b*H*)-dione 8e



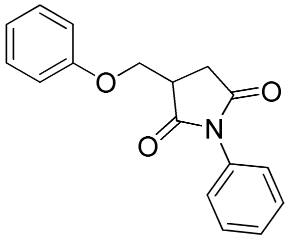
7e



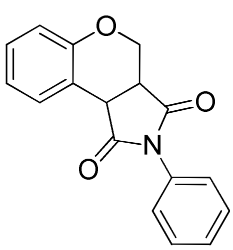
8e

Phenoxyacetic acid (100 mg, 0.65 mmol), *N*-phenyl maleimide (230 mg, 1.3 mmol) and TiO_2 (75 mg, 0.98 mmol) were reacted in accordance with the general procedure B. Following irradiation for 11 h the crude mixture was purified by column chromatography on silica gel (eluent: 20% EtOAc in Petrol 40/60) to yield **7e** as a yellow oil (71.5 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 3.01-3.07 (m, 2H, H$_f$), 3.33-3.39 (m, 1H, H$_e$), 4.28 (dd, *J* = 3.2, 9.0 Hz, 1H, H$_d$), 4.55 (dd, *J* = 4.1, 9.1 Hz, 1H, H$_{d'}$), 6.91 (d, *J* = 8.8 Hz, 2H, H$_b$), 7.00 (t, *J* = 7.3 Hz, 1H, H$_a$), 7.28-7.33 (m, 2H, *Ar*-H), 7.41 (t, *J* = 7.4 Hz, 1H, H$_i$), 7.48 (d, *J* = 7.2, 2H, H$_g$); ^{13}C NMR (75 MHz, $CDCl_3$, 297 K): δ = 32.4, 41.1, 66.9, 115.1, 122.1, 127.0, 129.2, 129.7, 130.0, 132.4, 158.5, 175.9, 177.1; LR-MS: *m/z* = 282 [M*H*]$^+$; HR-MS: *m/z* = 282.1125 (calcd. for $C_{17}H_{16}NO_3$, 282.1130). As above to yield **8e** as a white powder (72.8mg, 40%). Mp: 143-145 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 3.54-3.58 (m, 1H, H$_f$), 4.11, (dd, *J* = 4.4, 11.4 Hz, 1H, H$_g$), 4.23 (d, *J* = 9.3 Hz, 1H, H$_f$), 4.7 (dd, *J* = 3.3, 11.4 Hz, 1H, H$_{g'}$), 6.94 (d, *J* = 8.2 Hz, 1H, H$_d$), 7.07 (t, *J* = 7.5 Hz, 1H, H$_c$), 7.22-7.27 (m, 2H, *Ar*-H), 7.37 (t, *J* = 7.4 Hz, 2H, H$_i$), 7.44 (t, *J* = 7.1 Hz, 1H, H$_b$), 7.63 (d, *J* = 7.4 Hz, 1H, H$_a$); ^{13}C NMR (75 MHz, $CDCl_3$, 297 K): δ = 40.2, 42.6, 64.4, 77.1, 77.5, 77.9, 117.7, 118.3, 123.3, 126.7, 129.2, 129.5, 129.6, 130.7, 132.1 155.7 175.5, 176.1; LR-MS: *m/z* = 280 [M*H*]$^+$; HR-MS: m/z = 280.0971 (calcd. for $C_{17}H_{14}NO_3$, 280.0974). *N*-phenyl succinimde was also isolated (59.4 mg, 26%).

3-(Phenoxymethyl)-1-phenylpyrrolidine-2,5-dione 7e & *N*-phenyl-3a,4-dihydrochromeno[3,4-*c*]pyrrole-1,3(2*H*,9b*H*)-dione 8e



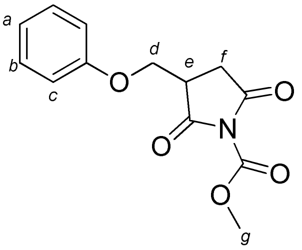
7e



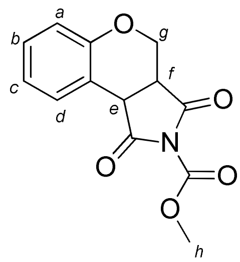
8e

Phenoxyacetic acid (20 mg, 0.13 mmol), *N*-phenylmaleimide (22.2 mg, 0.2 mmol) and 0.1% Pt-TiO_2 (P-25, 16 mg, 0.2 mmol) were reacted in accordance with the general procedure A for 16 h. ^{1}H NMR analysis (w.r.t. a CH_2Br_2 standard) of the resultant mixture revealed: **7e** (0.01 mmol, 8%) and **8e** (0.07 mmol, 69%).

Methyl 2,5-dioxo-3-(phenoxymethyl)pyrrolidine-1-carboxylate 7f & methyl 1,3-dioxo-1,3a,4,9b-tetrahydrochromeno[3,4-*c*]pyrrole-2(3*H*)-carboxylate 8f



7f

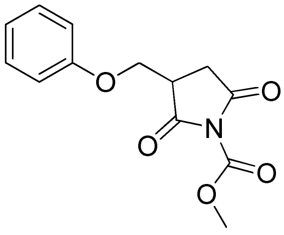


8f

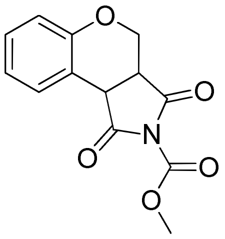
Phenoxyacetic acid (100 mg, 0.65 mmol), *N*-methoxycarbonylmaleimide (202 mg, 1.3 mmol) and TiO_2 (75 mg, 0.98 mmol) were in accordance with the general procedure B. Following irradiation for 12 h the crude mixture was purified by column chromatography on silica gel (eluent: 20% EtOAc in Petrol 40/60) to yield **7f** as a clear oil (59.7 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 3.00 (d, J = 7.3 Hz, 1H, H_f), 3.28 (m, 1H, H_e), 4.00 (s, 3H, H_g), 4.16 (dd, J = 3.3, 9.2Hz, 1H, H_d), 4.45 (d, J = 4.0, 9.2 Hz 1H, $H_{d'}$), 6.88 (d, J = 8.9 Hz, 2H, H_c), 6.99 (t, J = 7.4 Hz, 1H, H_a), 7.29 (t, J = 7.4 Hz, 2H, H_b); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ = 32.0, 41.0, 55.0, 65.8, 114.7, 121.9, 129.6, 148.6, 157.9, 171.7, 173.2; LR-MS: *m/z* = 281 $[\mathrm{M}NH_4]^+$; HR-MS: *m/z* = 281.1131 (calcd. for $C_{13}H_{17}N_2O_5$, 281.1137). As above to yield **8f** as white solid (56.4 mg, 33%). Mp: 82-85 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 3.45-3.49 (m, 1H, H_f), 3.95 (s, 3H, H_h), 4.03 (dd, J = 3.9, 11.4 Hz, 1H, H_g), 4.16 (d, J = 9.6 Hz, 1H, H_e), 4.63 (dd, J = 3.2, 11.4 Hz 1H, $H_{g'}$), 6.91 (d, J = 8.2 Hz, 1H, H_d), 7.05 (t, J = 7.5 Hz, 1H, H_c), 7.23 (t, J = 8.1 Hz, 1H, H_b), 7.56 (d, J = 7.8 Hz, 1H, H_a). ^{13}C NMR (75 MHz,

$CDCl_3$, 298 K): δ = 40.0, 42.3, 55.1, 63.2, 115.9, 118.1, 123.0, 129.5, 130.0, 148.4, 155.1, 171.6, 172.1; LR-MS: *m/z* = 284 [M*Na*]$^+$; HR-MS: *m/z* = 284.0531 (calcd. for $C_{13}H_{11}NO_5Na$, 284.0535). Analysis of the crude reaction mixture revealed *N*-methoxycarbonylsuccinimide (19 % w.r.t. **7f** & **8f**).

Methyl 2,5-dioxo-3-(phenoxymethyl)pyrrolidine-1-carboxylate 7f & methyl 1,3-dioxo-1,3a,4,9b-tetrahydrochromeno[3,4-*c*]pyrrole-2(3*H*)-carboxylate 8f



7f



8f

Phenoxyacetic acid (20 mg, 0.13 mmol), *N*-carboxymethylmaleimide (31 mg, 0.2 mmol) and 0.1% Pt-TiO_2 (P-25, 16 mg, 0.2 mmol) were reacted in accordance with the general procedure A for 16 h. ^{1}H NMR analysis (w.r.t. a CH_2Br_2 standard) of the resultant mixture revealed: **7f** (0.02 mmol, 24%) and **8f** (0.05 mmol, 50%).

EPR Spectroscopy

Isotropic EPR spectra were obtained with a Bruker EMX 10/12 spectrometer fitted with a rectangular ER4122 SP resonant cavity and operating at 9.5 GHz with 100 kHz modulation. Stock solutions of each carboxylic acid (2 to 15 mg) in *tert*-butylbenzene or benzene (0.5 mL) were prepared and sonicated if necessary. An aliquot (0.2 mL), to which any additional reactant had been added, was placed in a 4 or 5 mm o.d. quartz tube, de-aerated by bubbling nitrogen for 15 min, and photolysed in the resonant cavity by unfiltered light from a 500 W super pressure mercury arc lamp. In all cases where spectra were obtained, hfs were assigned with the aid of computer simulations using the Bruker SimFonia and NIEHS Winsim2002 software packages. EPR signals were digitally filtered and double integrated using the Bruker WinEPR software and radical concentrations were calculated by reference to the double integral of the signal from a known concentration of the stable radical DPPH [1×10^{-3} M in PhMe], run under identical conditions, as described previously. The majority of EPR spectra were recorded with 2.0 mW power, 0.8 G_{pp} modulation intensity and a gain of *ca.* 10^6.

Anisotropic EPR spectra were obtained using a Jeol JES-FA200 spectrometer, with an X band microwave unit. Temperature control was achieved with an Oxford Instruments ESR900 cryostat, with an ITC 5035 Intelligent Temperature Controller operating with liquid nitrogen. The light source was a 500 watt Hg-Xe arc lamp, filtered through pyrex and water to remove UV and IR components. Samples were prepared by placing the organic material in a side arm, and titania (100mg) in a second side arm, attached to an EPR quartz tube, sealed by a Young's tap. Air and physisorbed water were then removed from the sample by attaching the cell to a vacuum line and degassing overnight. The organic material (0.5ml, 2.3M in acetonitrile) was then degassed using the freeze pump thaw method. Once degassed the sample cell was sealed and removed from the vacuum line. The titania was moved into the EPR tube attachment, followed by the organic material, by opening the Young's tap. Experiments were run firstly in the dark, then using a 1% light filter along with a 400nm attenuated filter. The 1% filter was then removed to give 400nm light, followed by full broadband (320-900nm). The sample was then also measured in the dark and the temperature dependence of radicals was investigated. The usual EPR settings were: field centre; 325mT, sweep width; +/- 15mT, microwave power; 5mW, Amplitude; 500, modulation frequency; 100kHz, modulation width; 0.1mT, time constant: 1.0 s; sweep time; 8min.

The g for the *t*-butyl radical was 2.0022 with a hyperfine splitting of 2.26mT.

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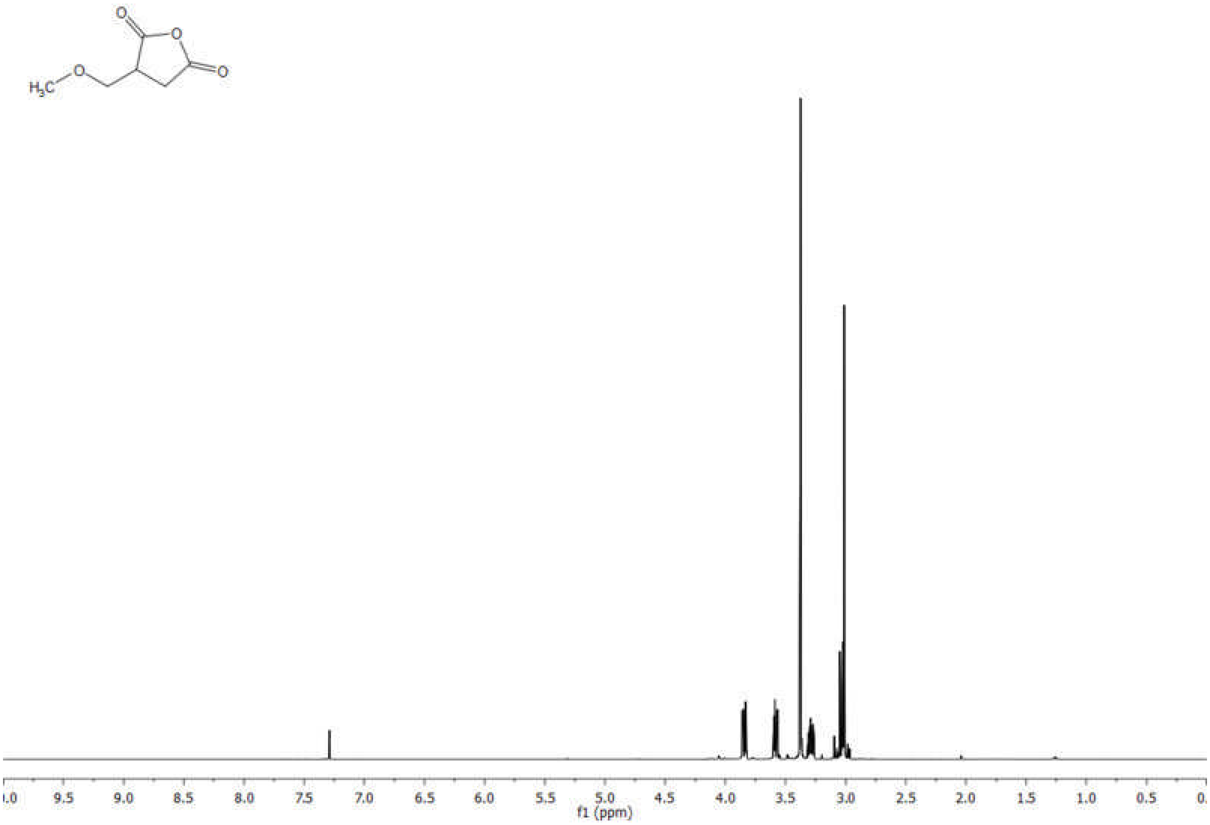
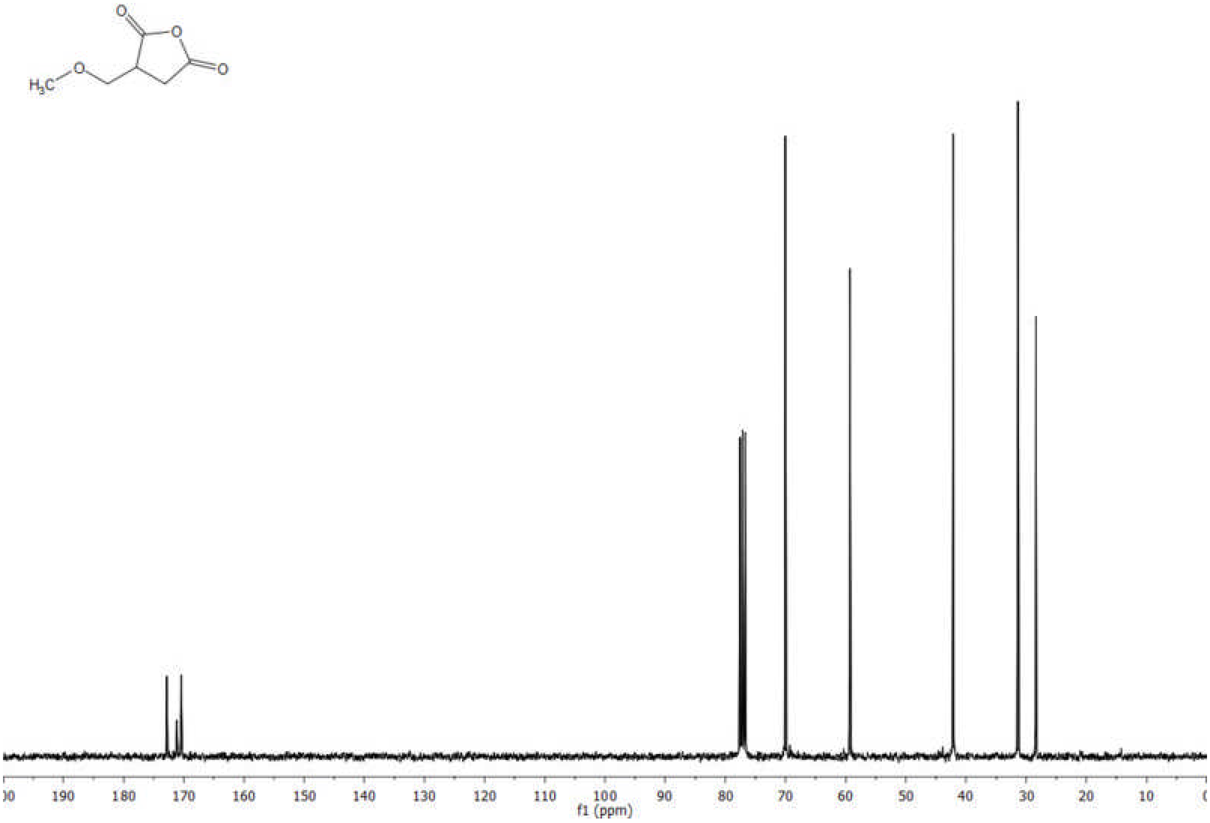
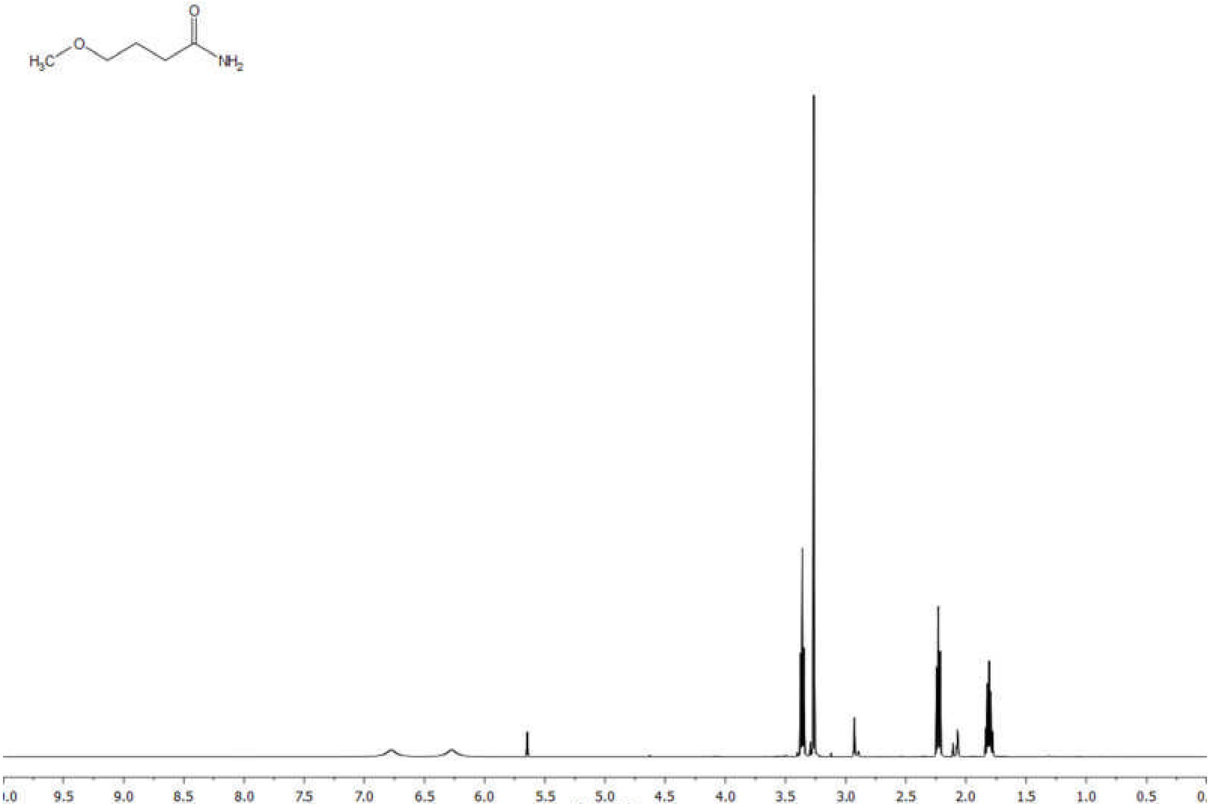
^{1}H and ^{13}C NMR spectra of novel compounds

3b





4a



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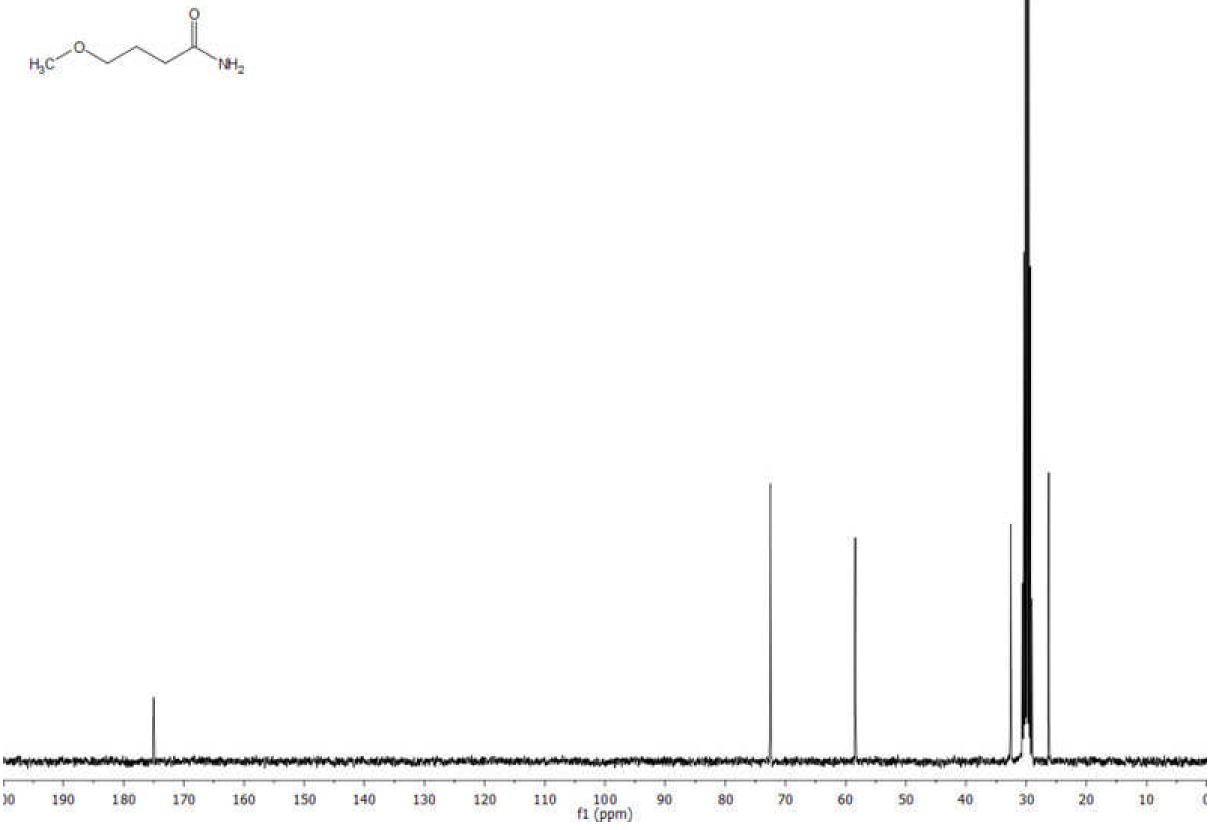
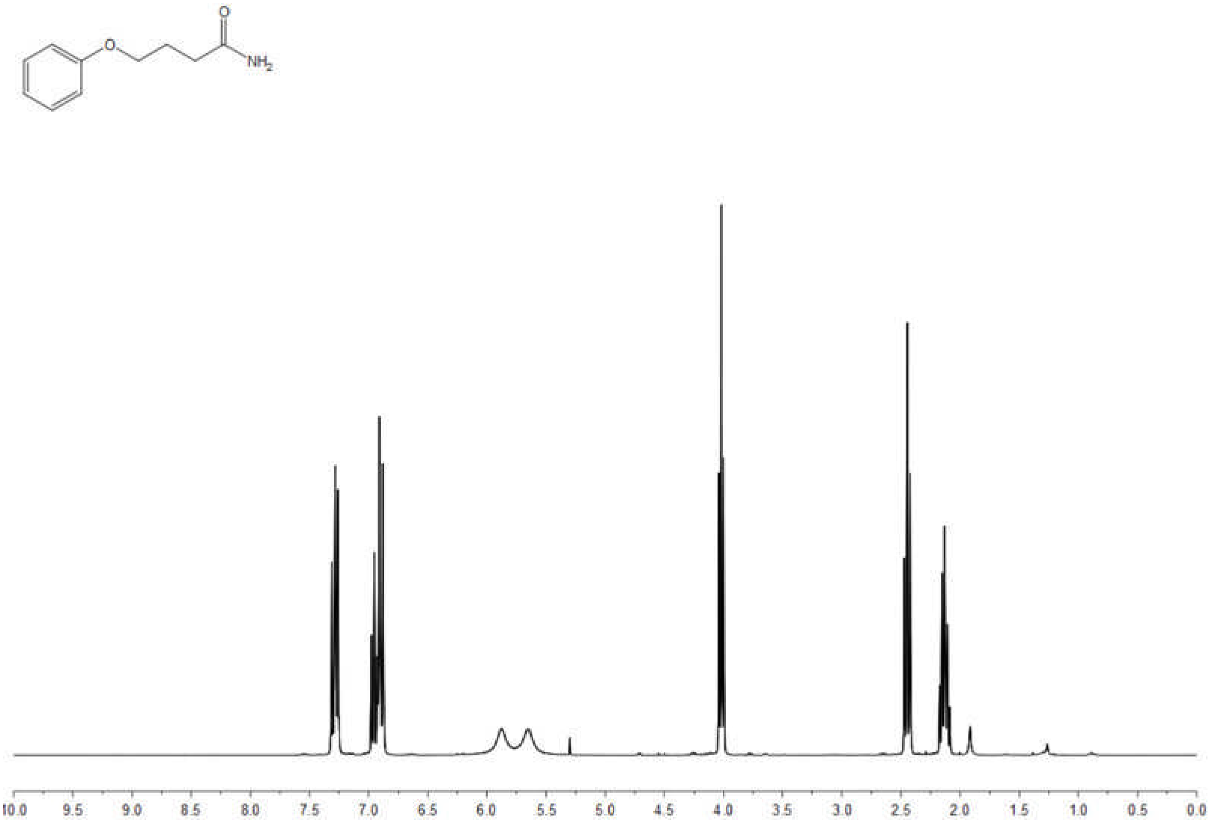
H$_3$C
O
NH$_2$
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



O
H$_3$C
O
NH$_2$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

4b



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NH2
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7.0
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6.0
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4.0
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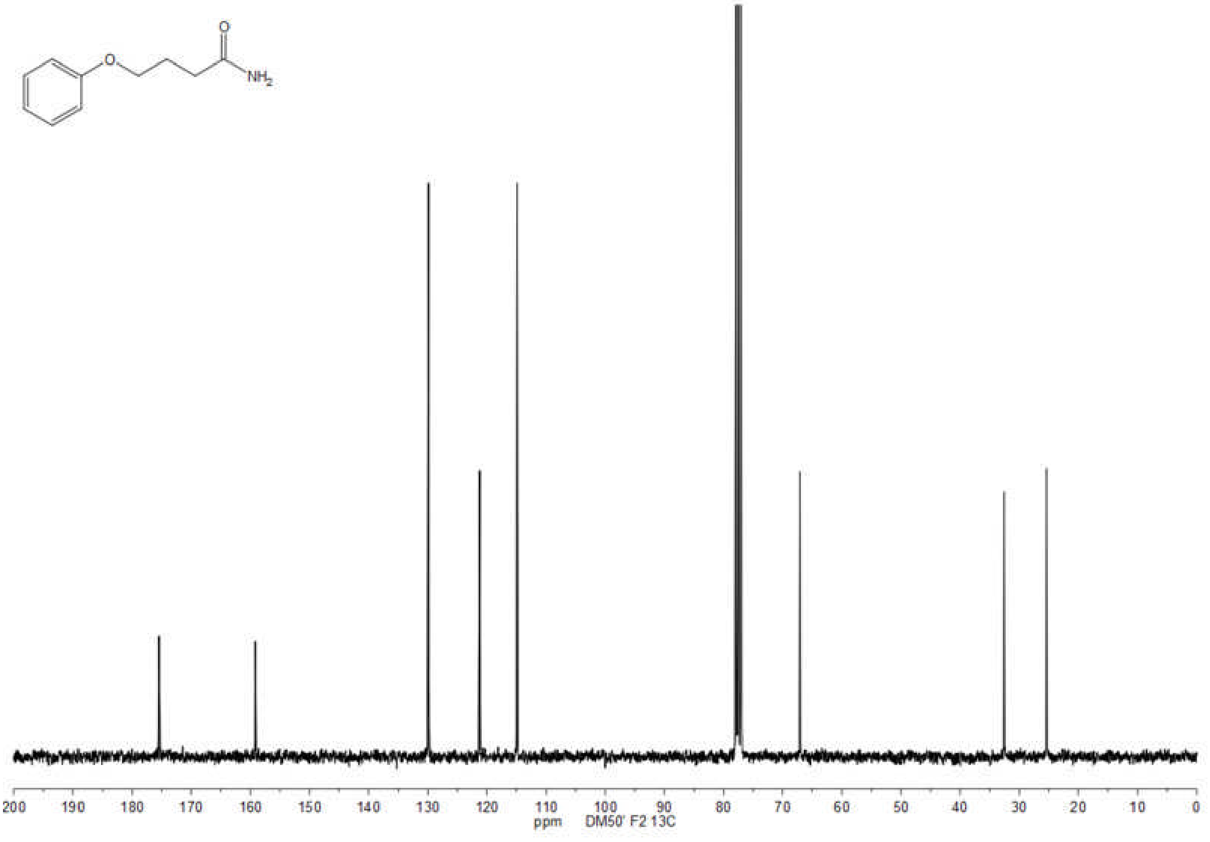
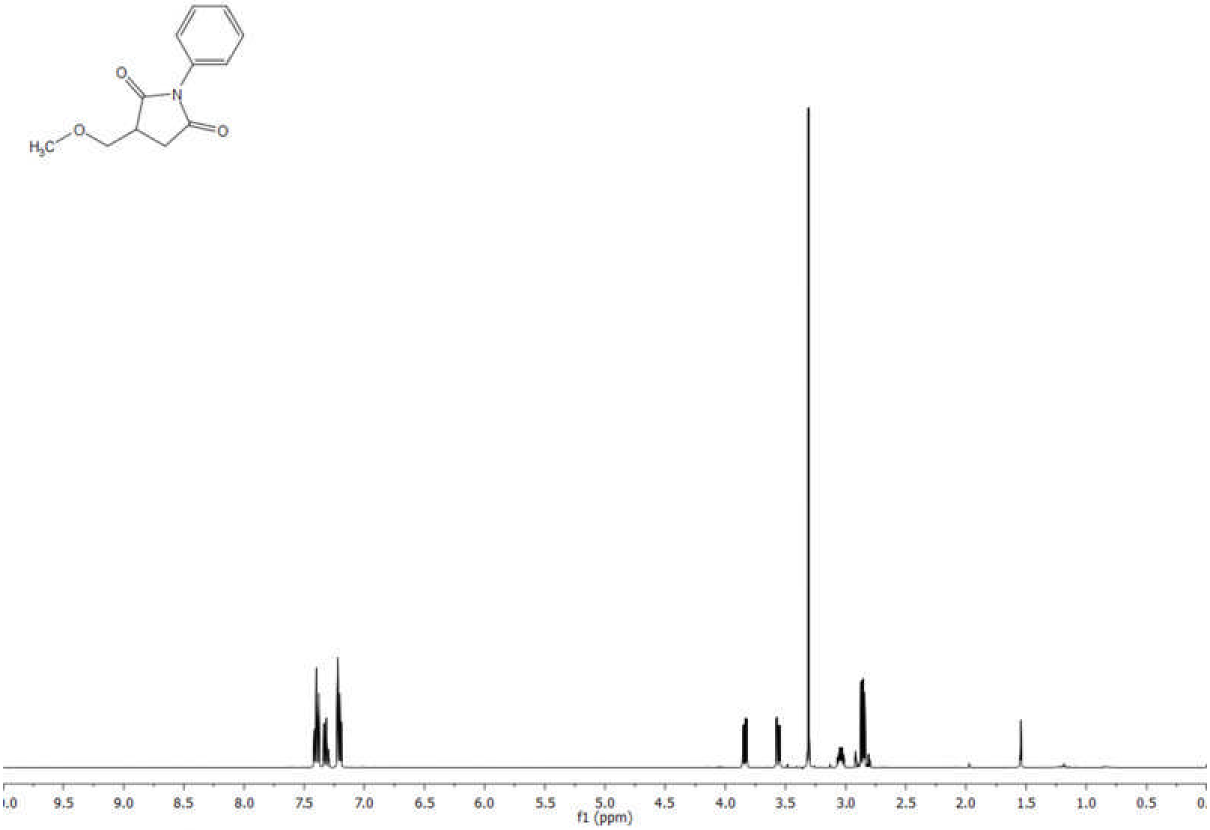
3.0
2.5
2.0
1.5
1.0
0.5
0.0



O
NH2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
DM50' F2 13C

5a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N
O
O
H3C
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8.5
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7.5
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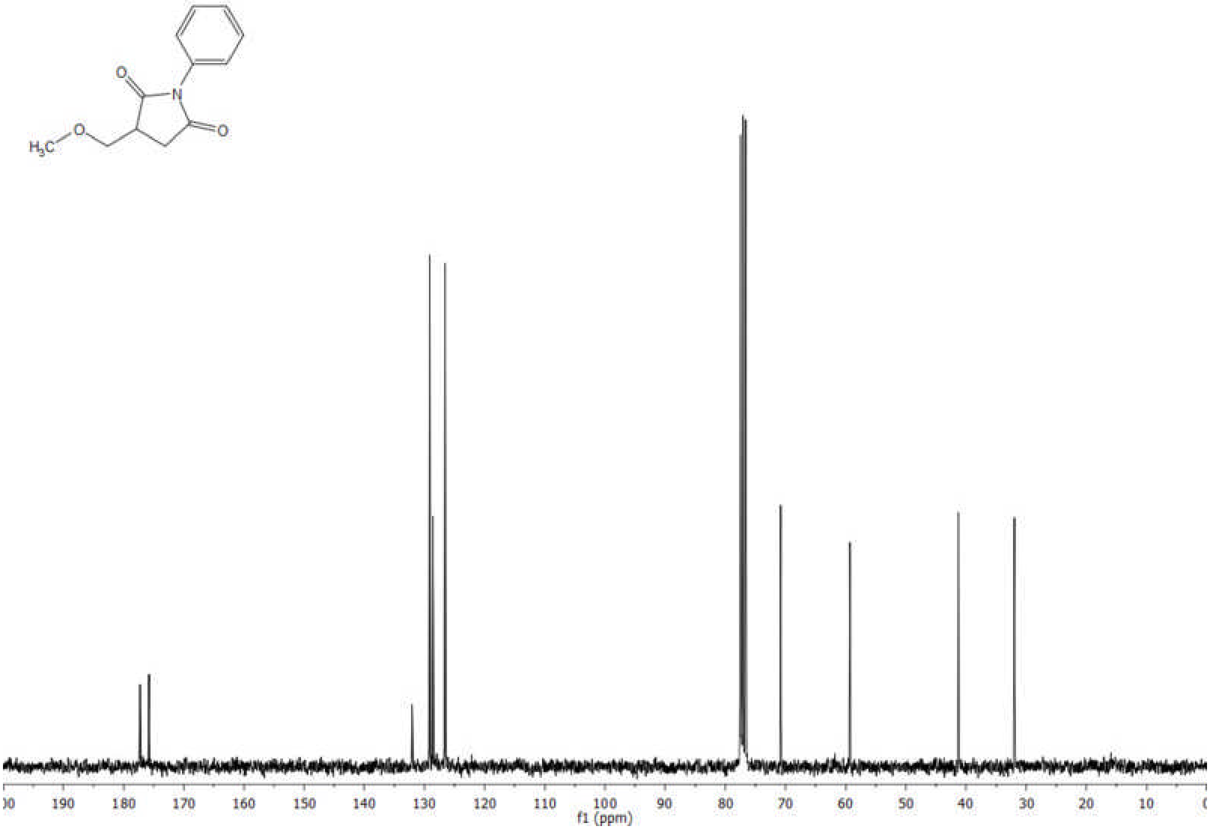
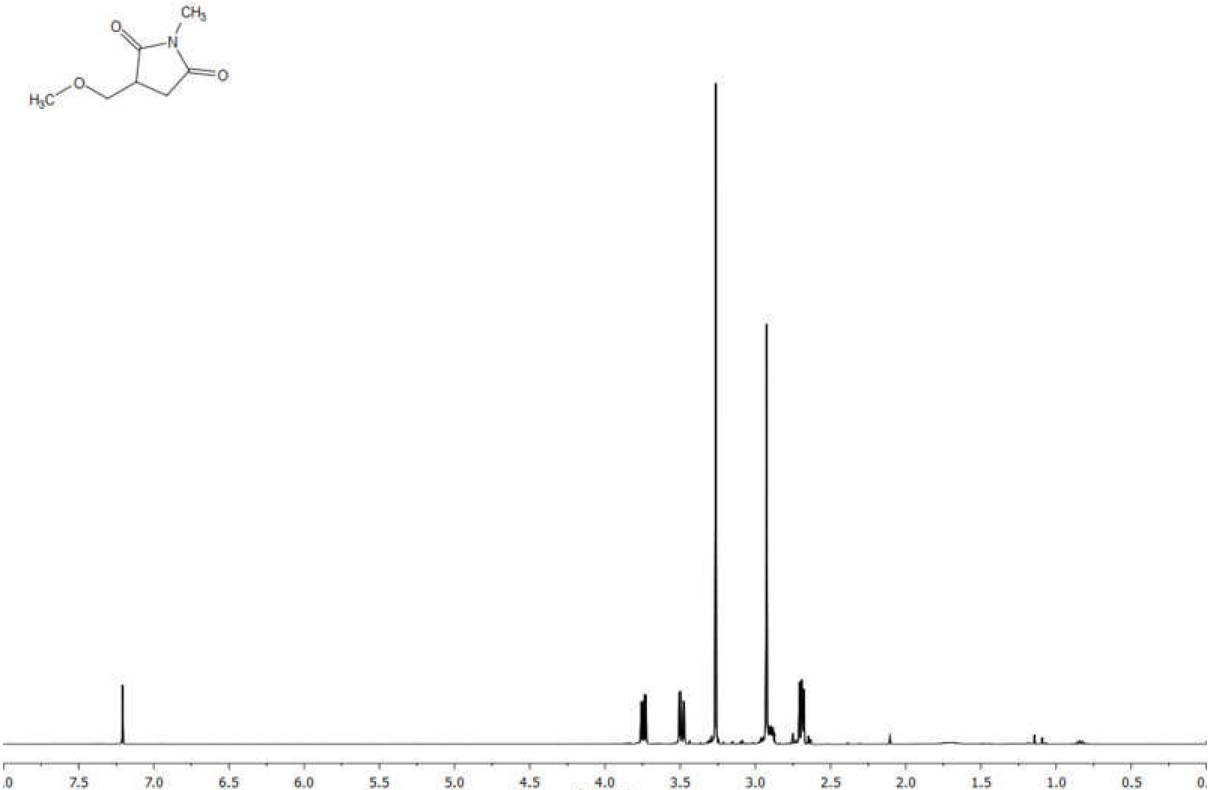
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


O
N
O
O
H3C
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

5b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O
N
O
H3C
O
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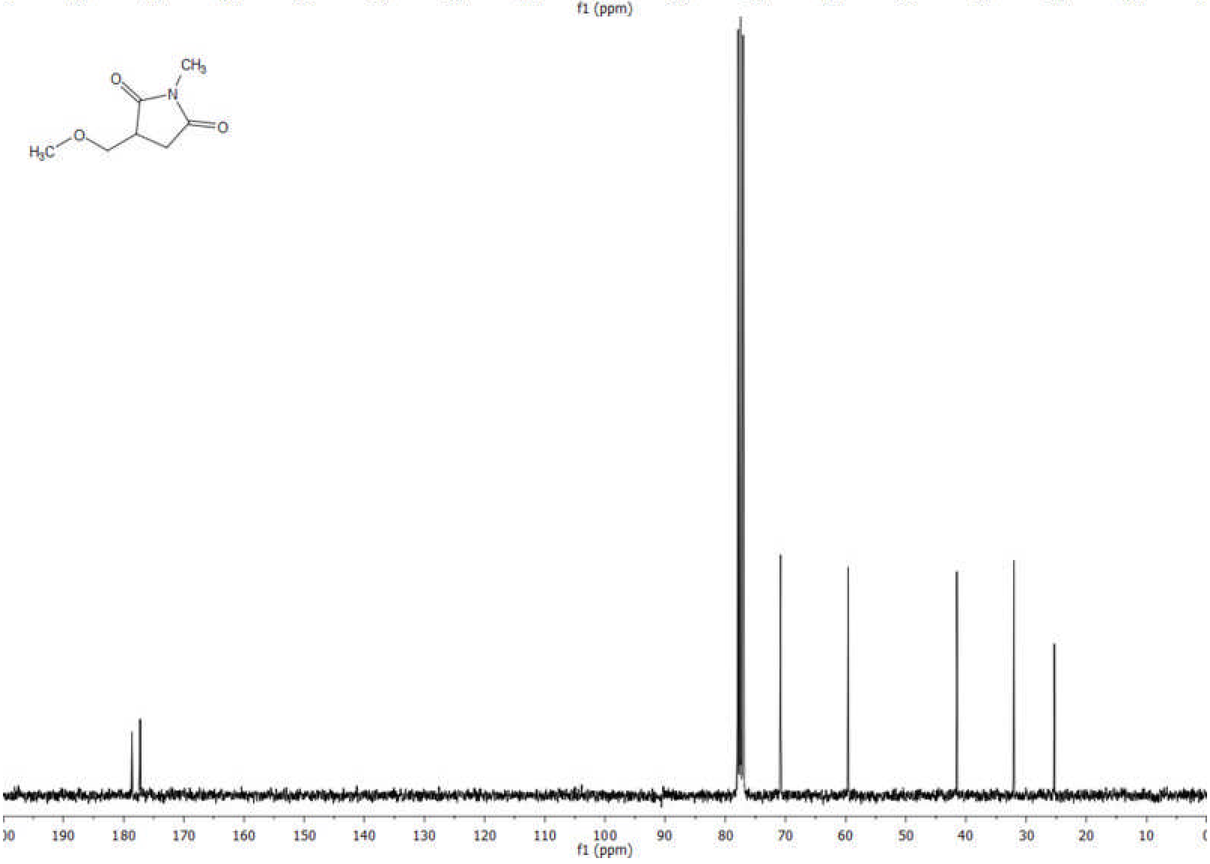
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


CH3
O
N
O
H3C
O
190
180
170
160
150
140
130
120
110
100
90
80
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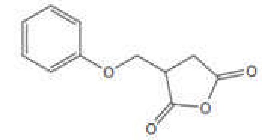
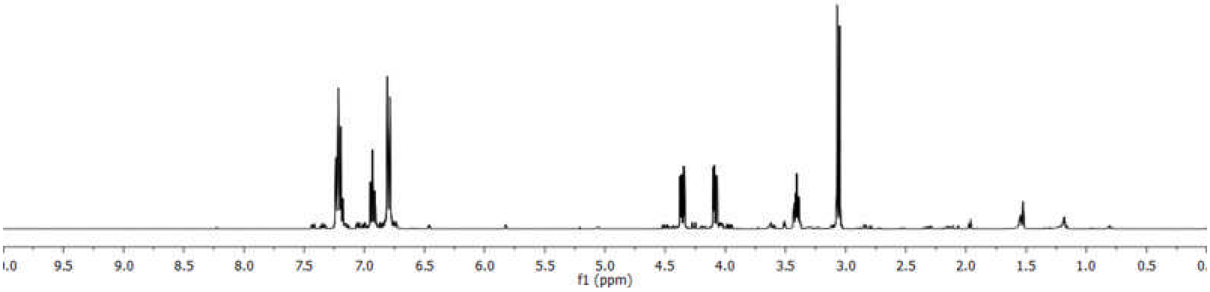
30
20
10
f1 (ppm)

7a


O
O
O
O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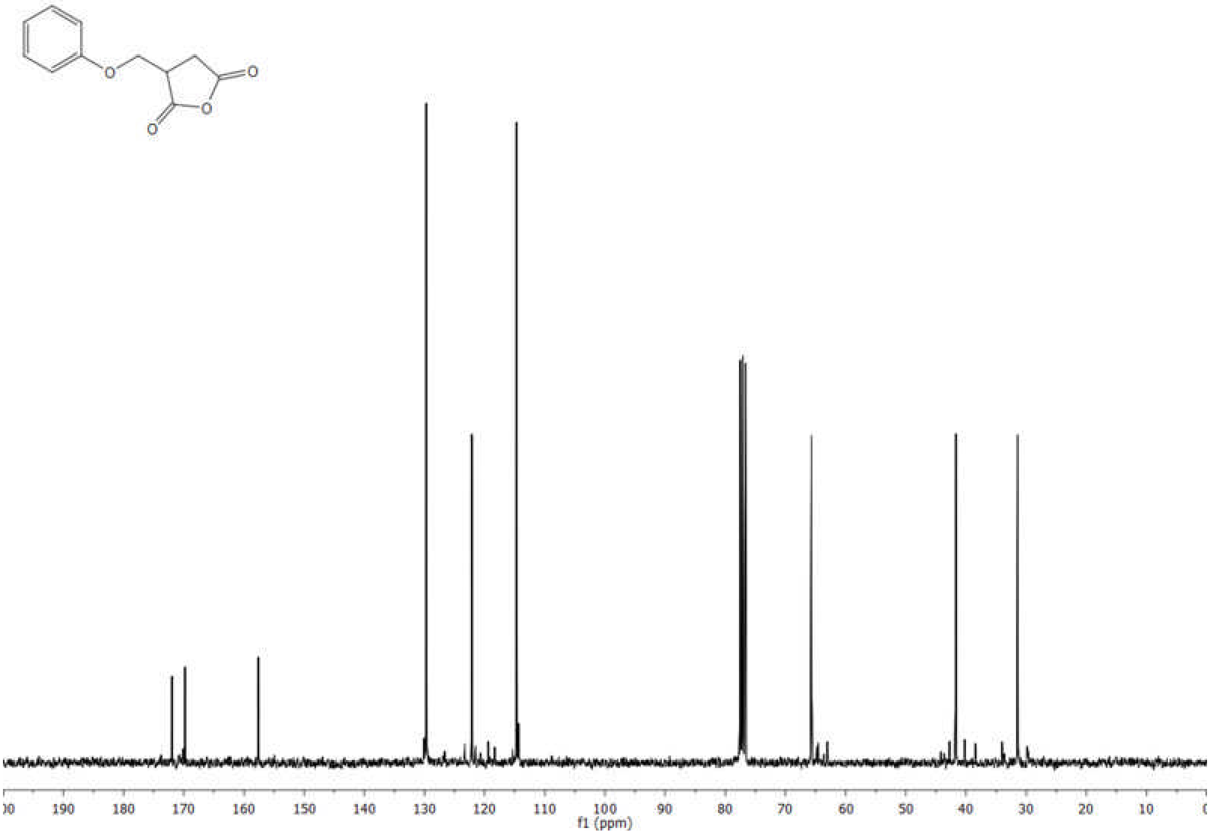
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


O
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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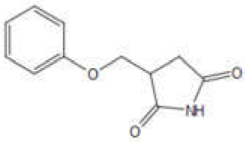
30
20
10
f1 (ppm)

7b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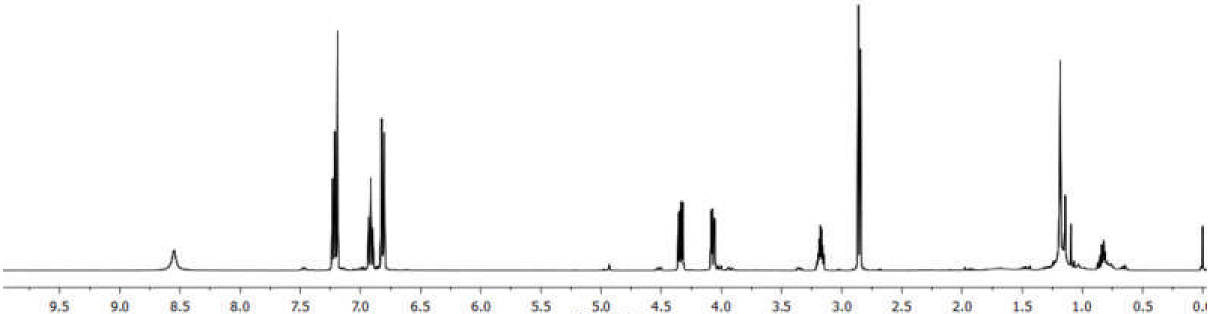
O
NH
O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9.0
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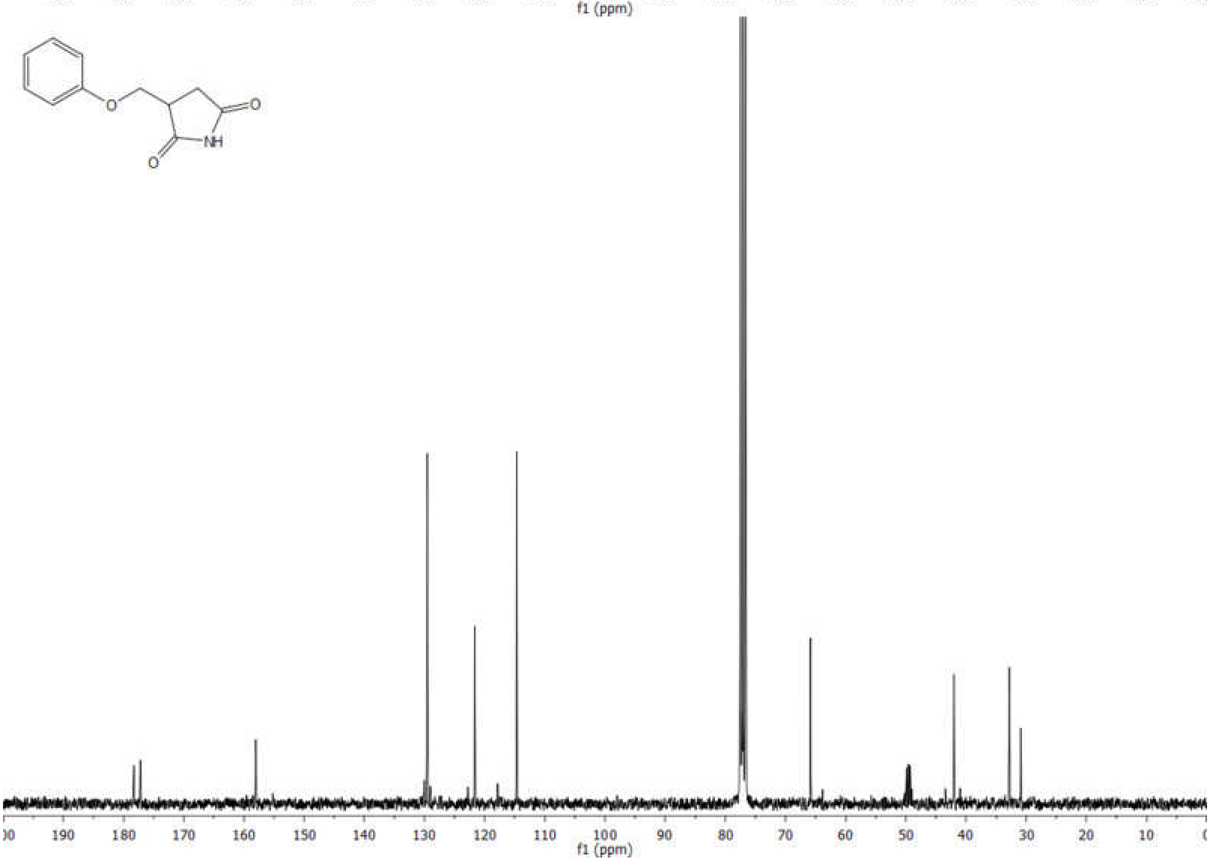
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


O
O
NH
O
190
180
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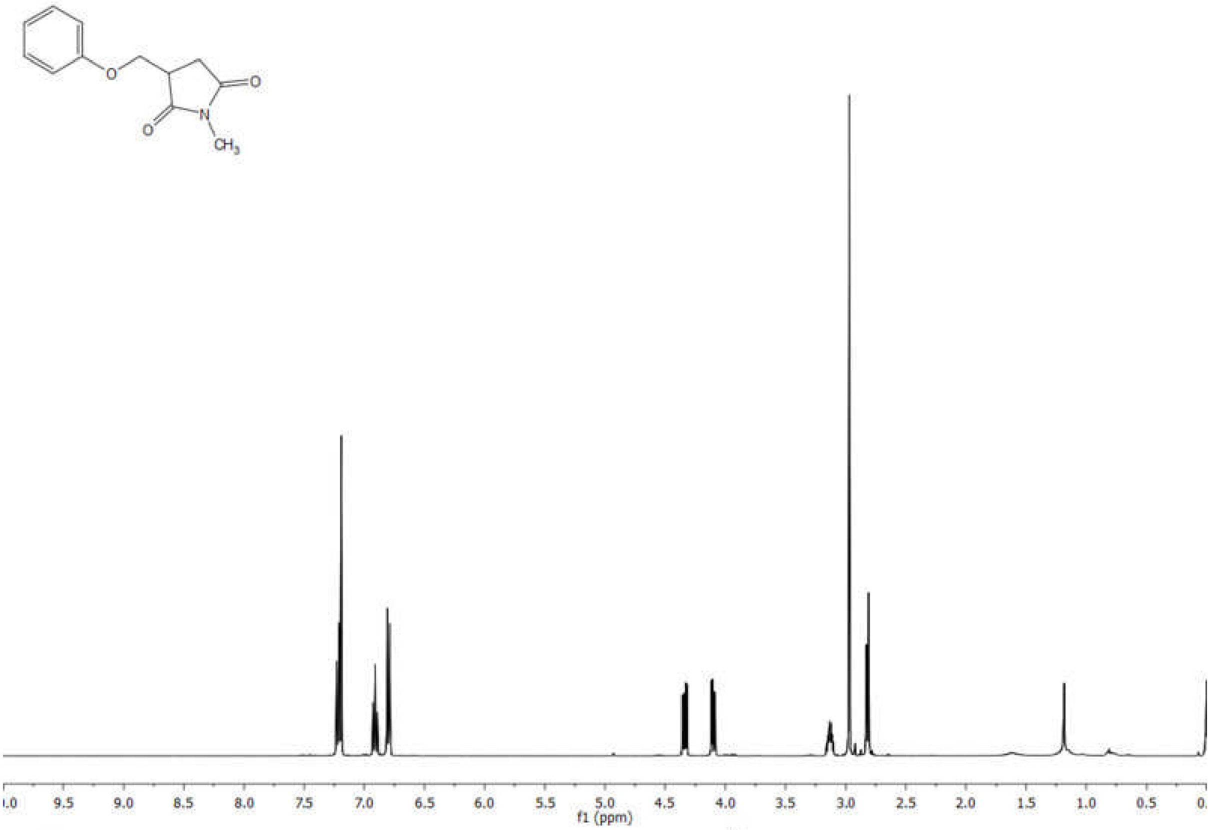
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

7c


O
O
N
O
CH3
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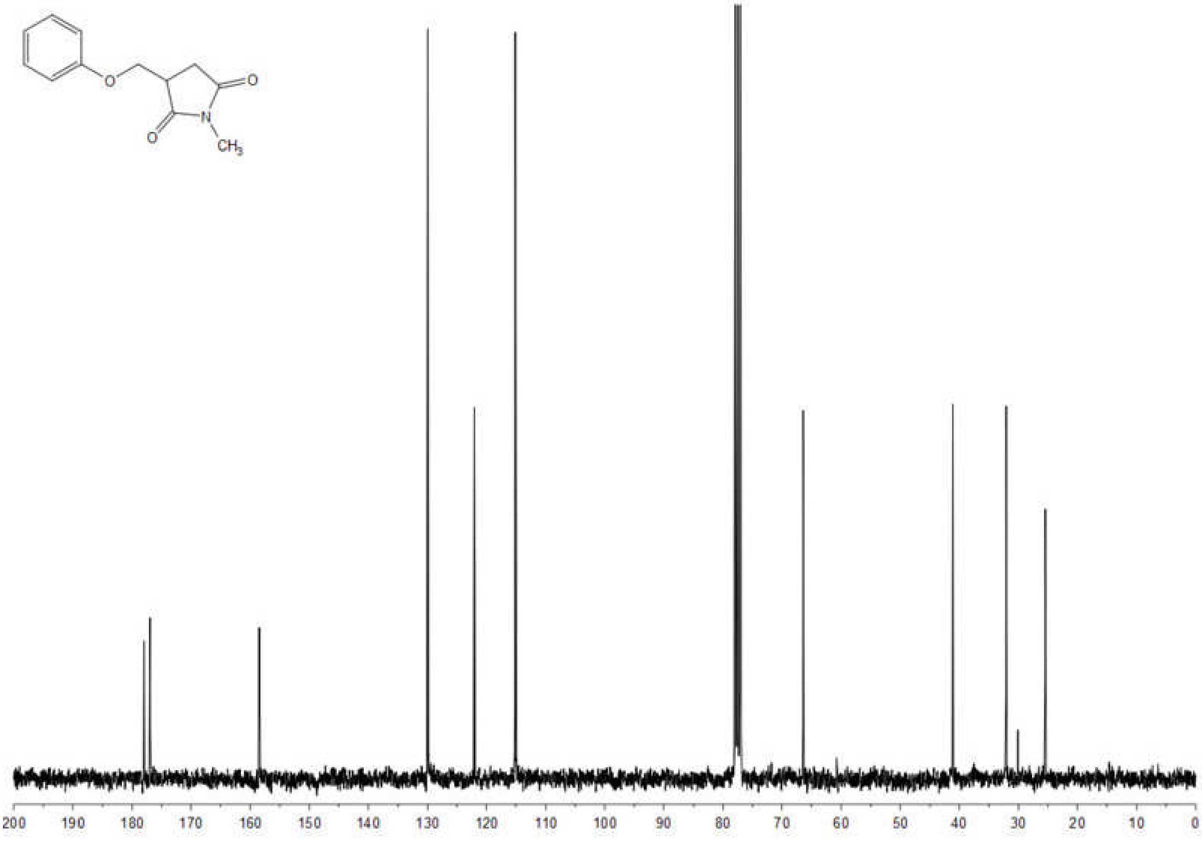
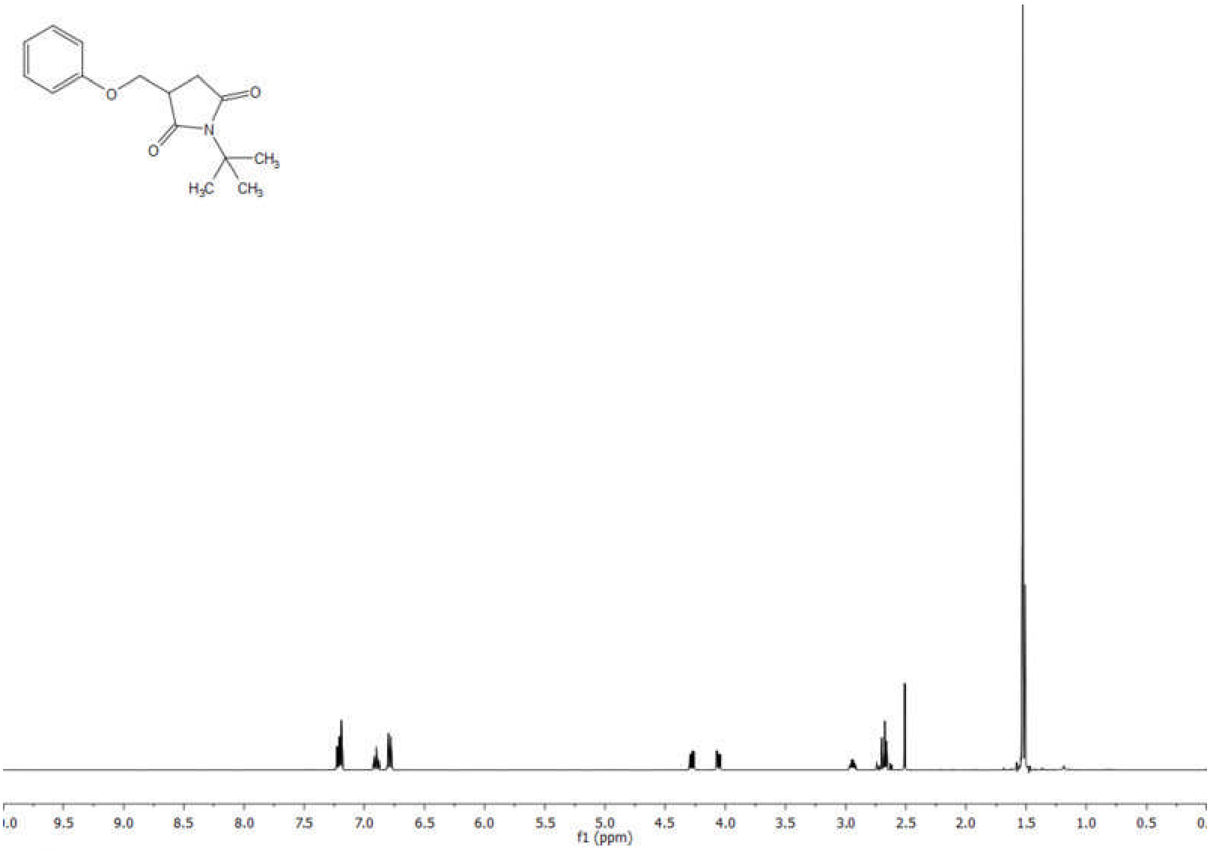
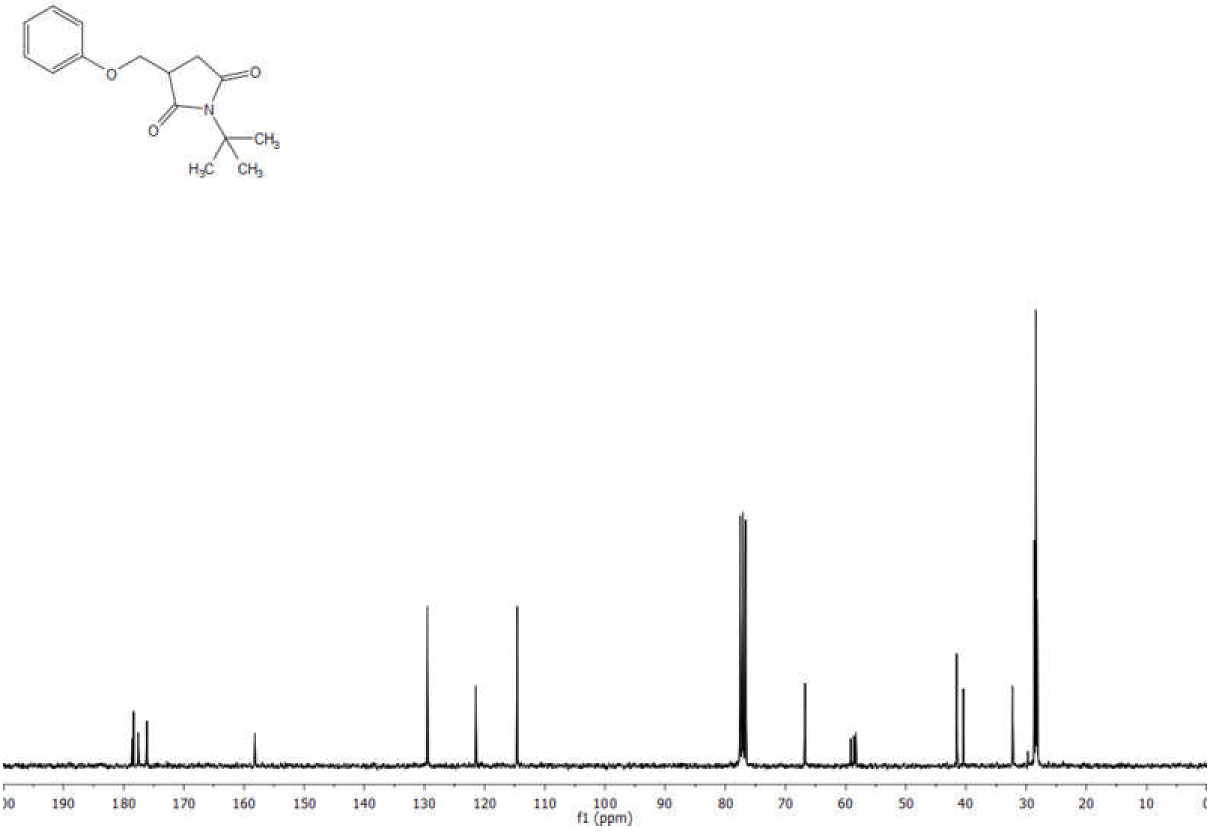
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


O
O
N
O
CH3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

7d

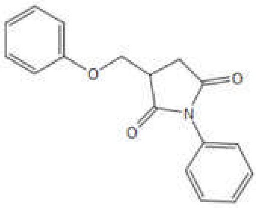


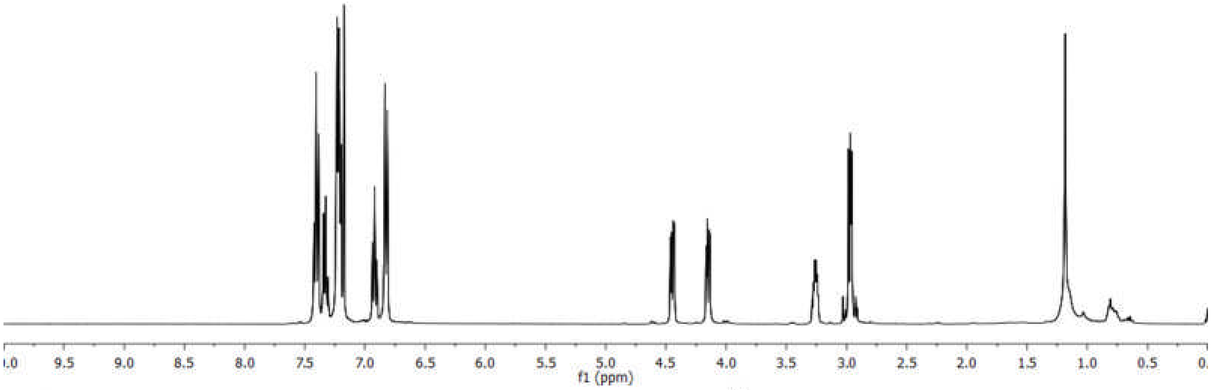
O
O
N
O
CH3
H3C
CH3
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)



O
O
N
O
CH3
H3C
CH3
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(
f1 (ppm)

7e


O
O
N
O


.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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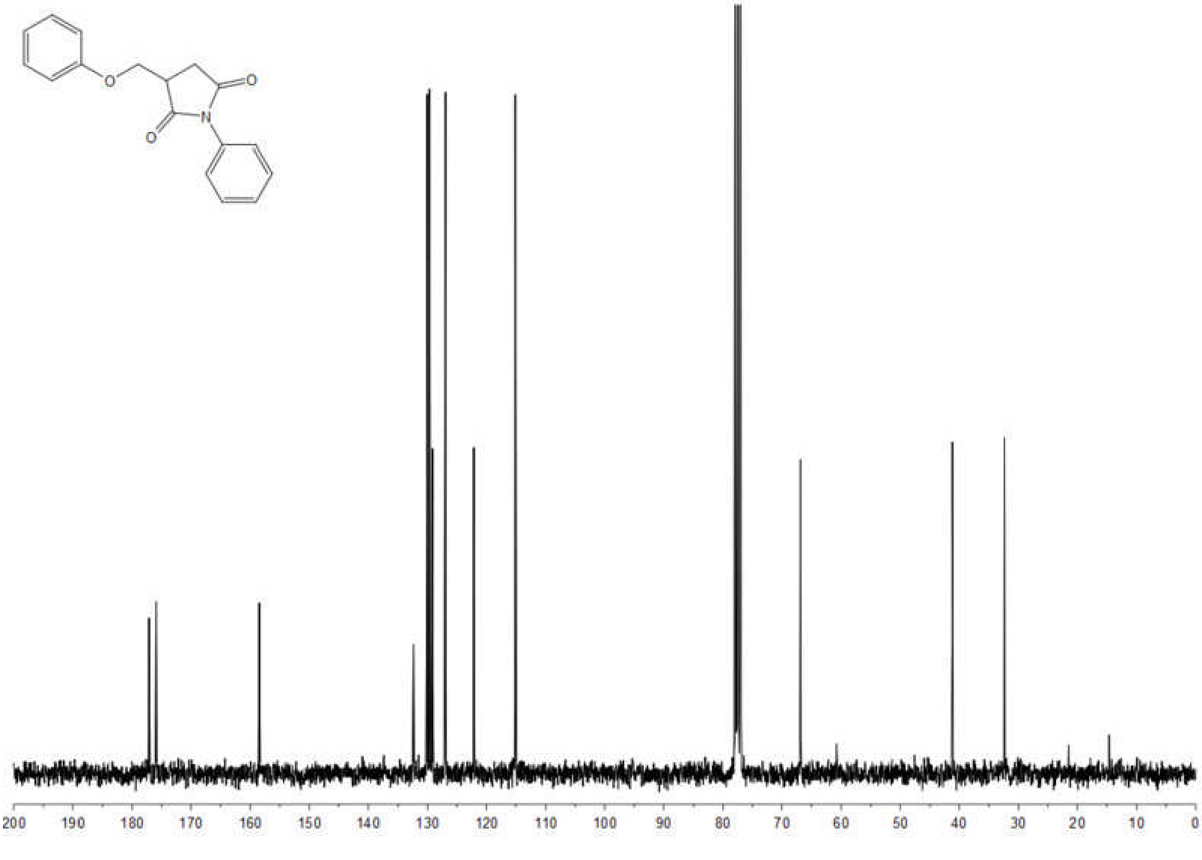
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


O
O
N
O
200
190
180
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160
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140
130
120
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100
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80
70
60
50
40
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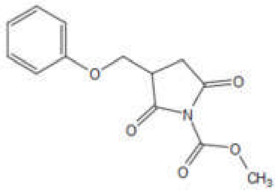
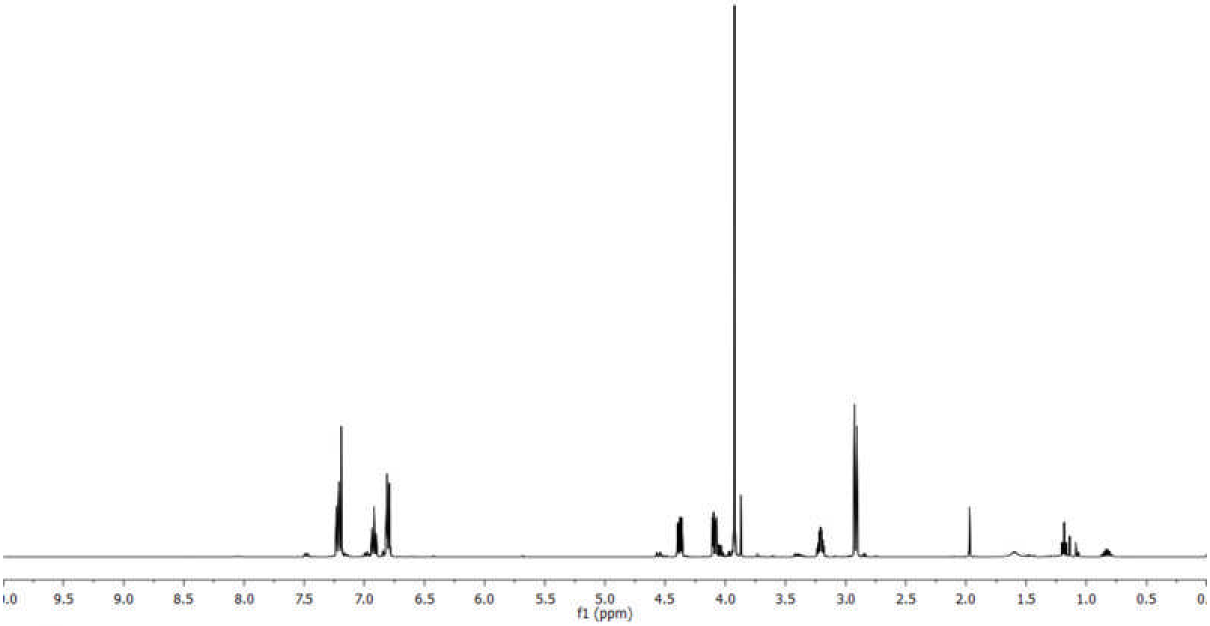
20
10
0

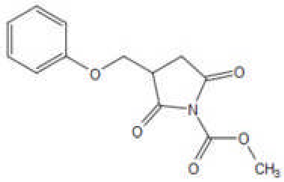
7f



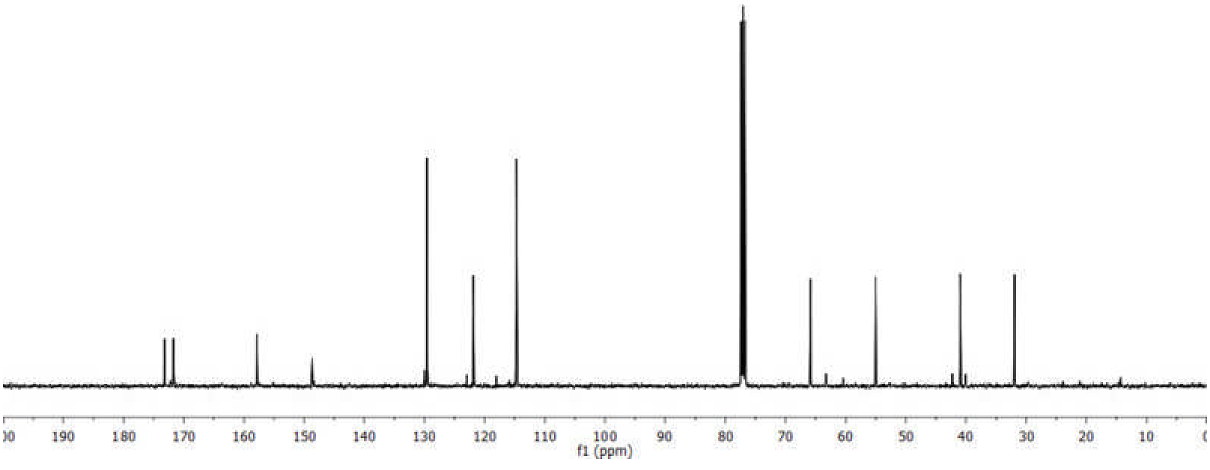
O
O
O
N
O
O
CH3



.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.

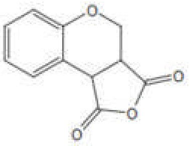


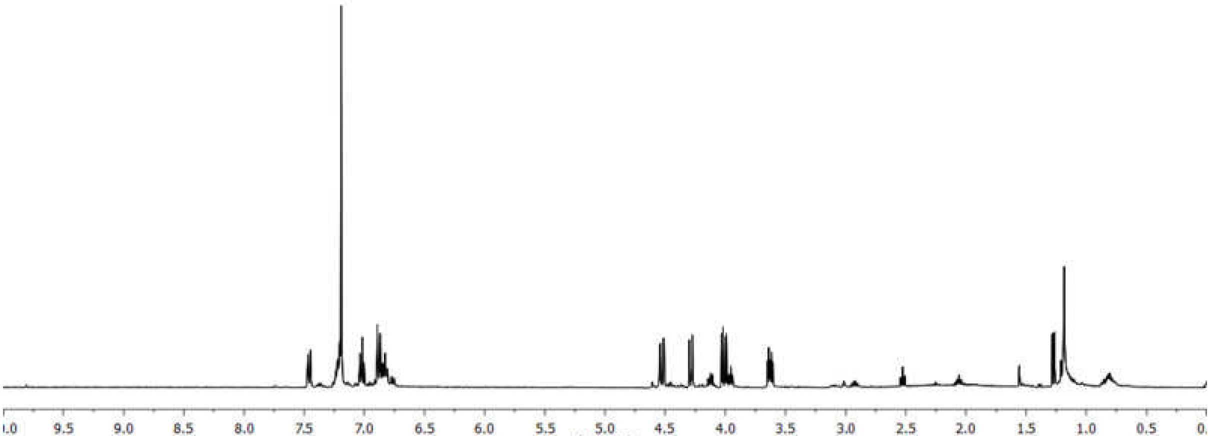
O
O
O
N
O
O
CH3



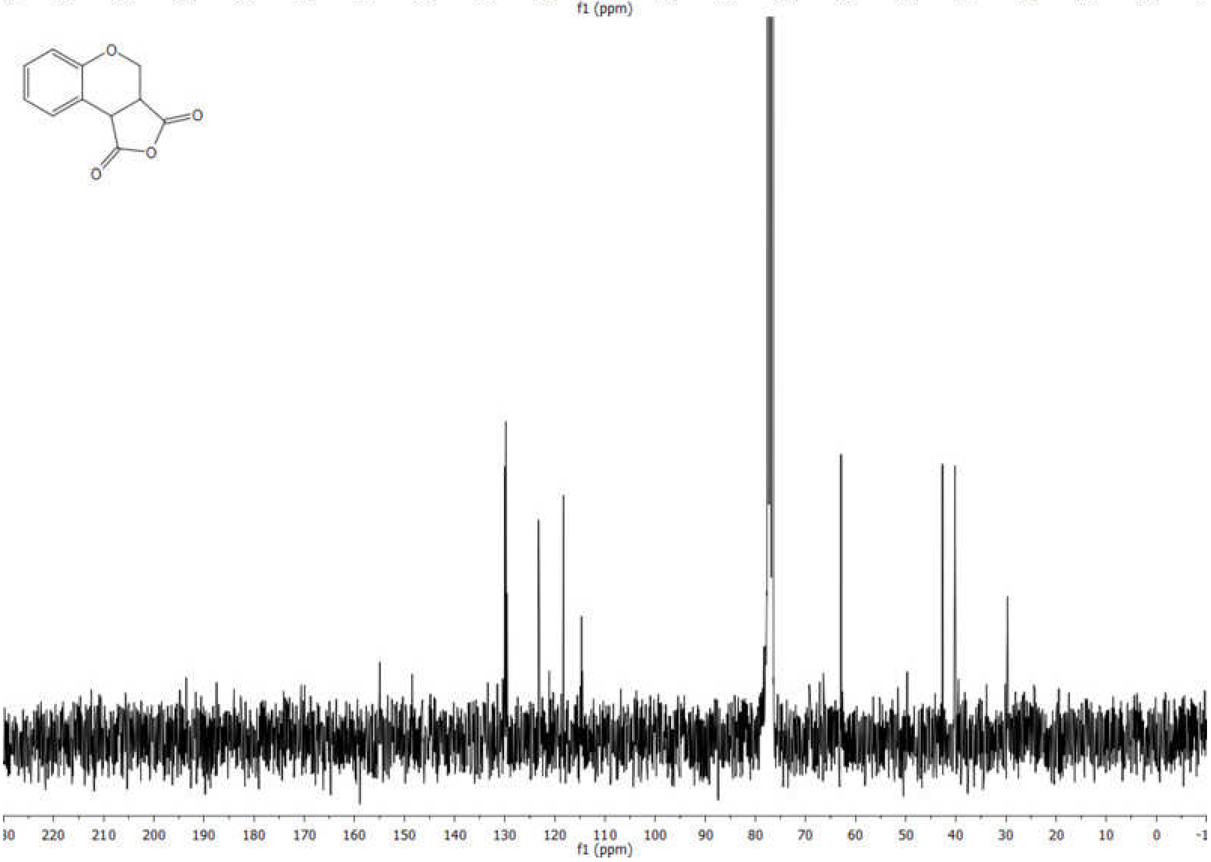
00
190
180
170
160
150
140
130
120
110
100
f1 (ppm)
90
80
70
60
50
40
30
20
10

8a





9.5
9.0
8.5
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
f1 (ppm)



220
210
200
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180
170
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100
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70
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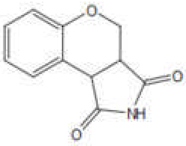
30
20
10
0
f1 (ppm)

8b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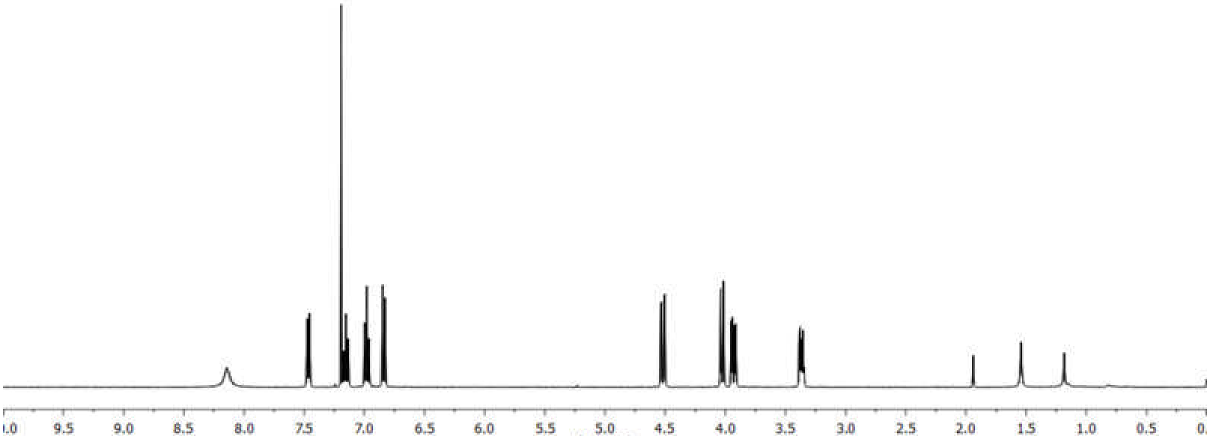
O
NH
O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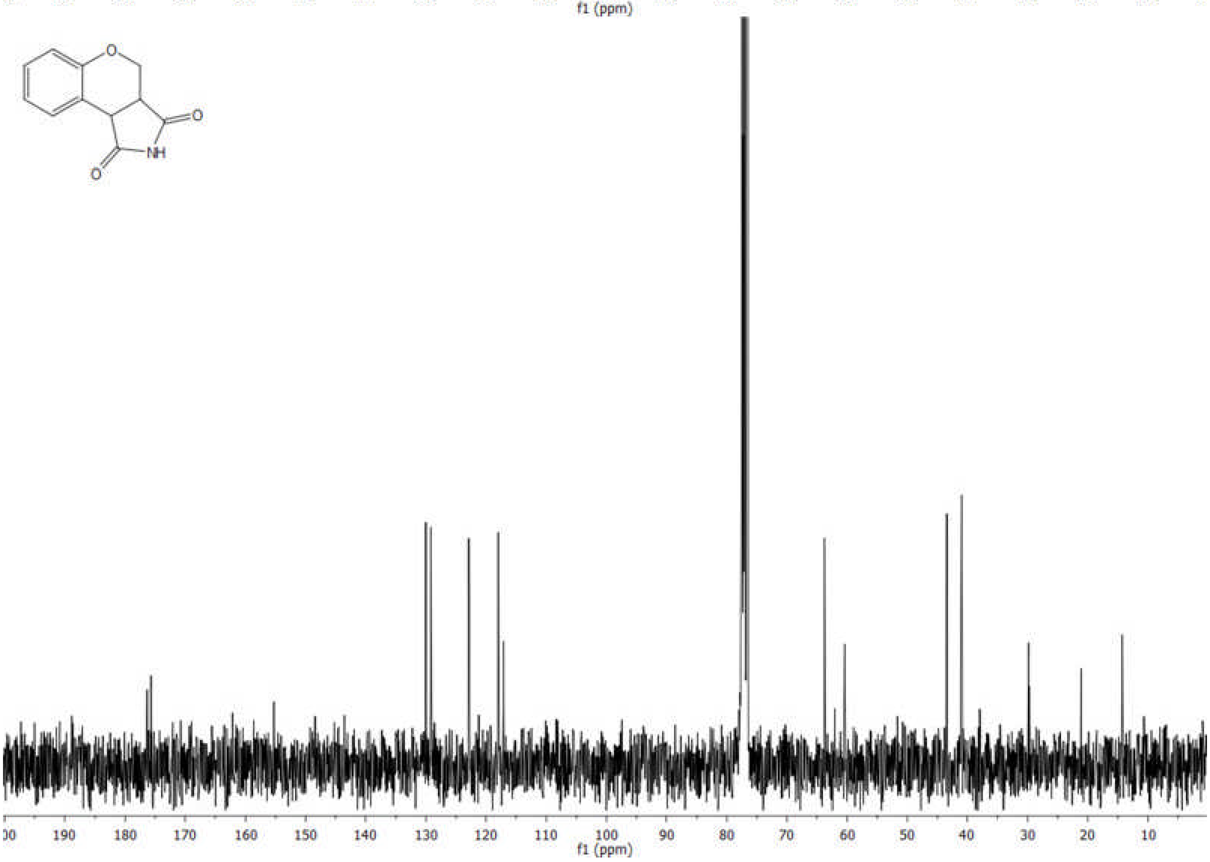
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


O
O
NH
O
190
180
170
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150
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130
120
110
100
90
80
70
60
50
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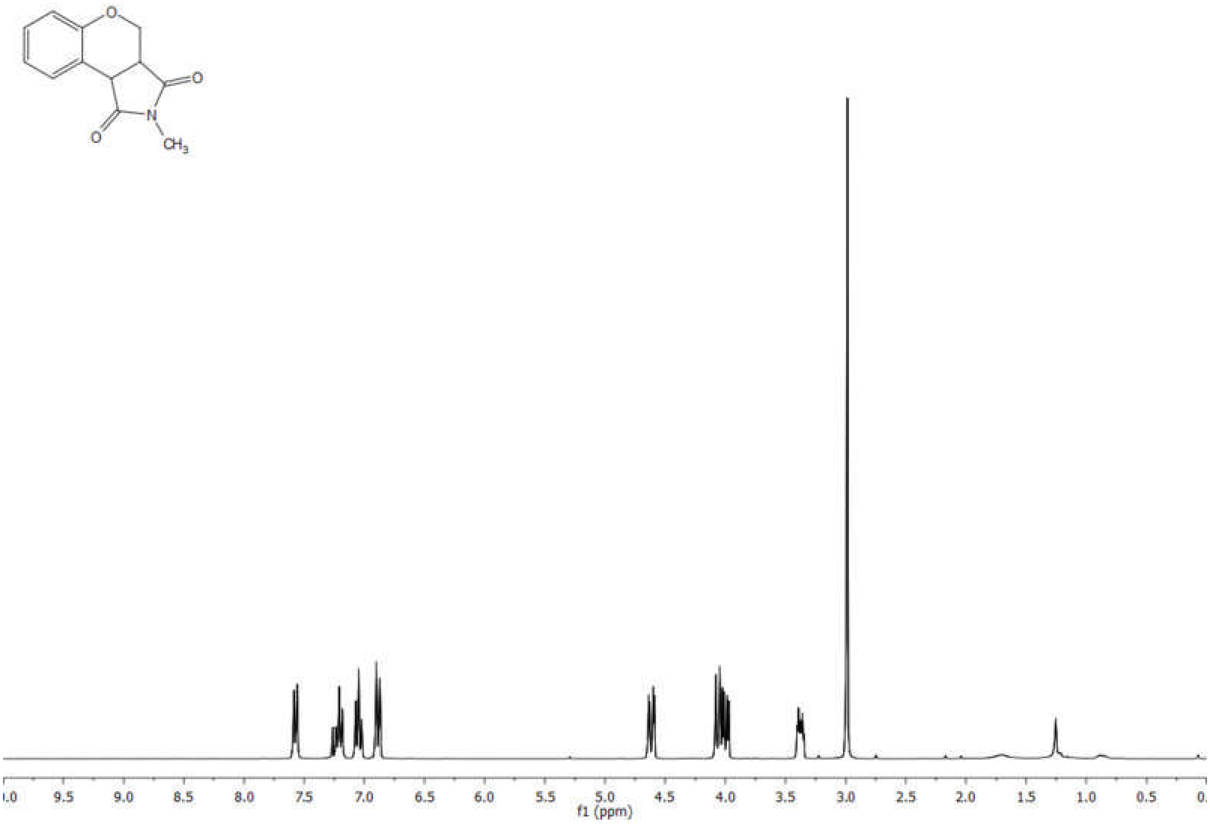
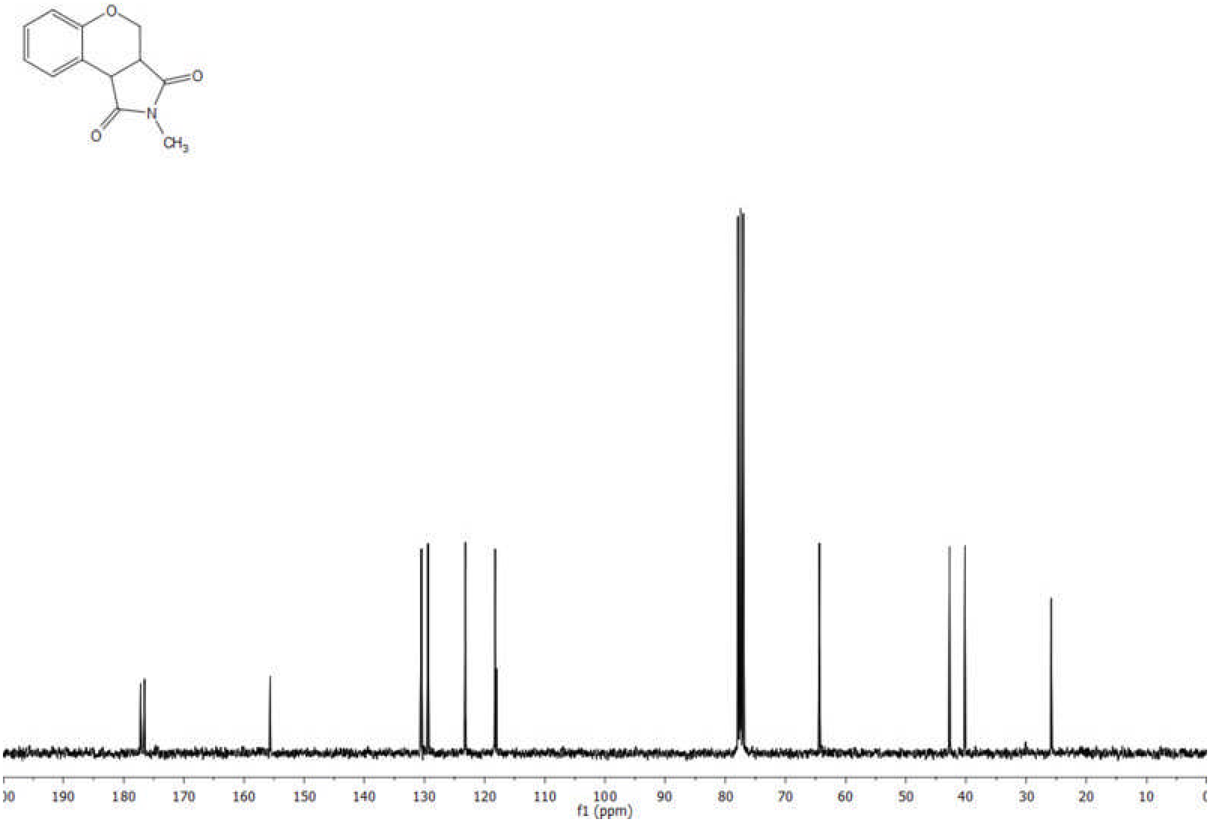
30
20
10
f1 (ppm)

8c

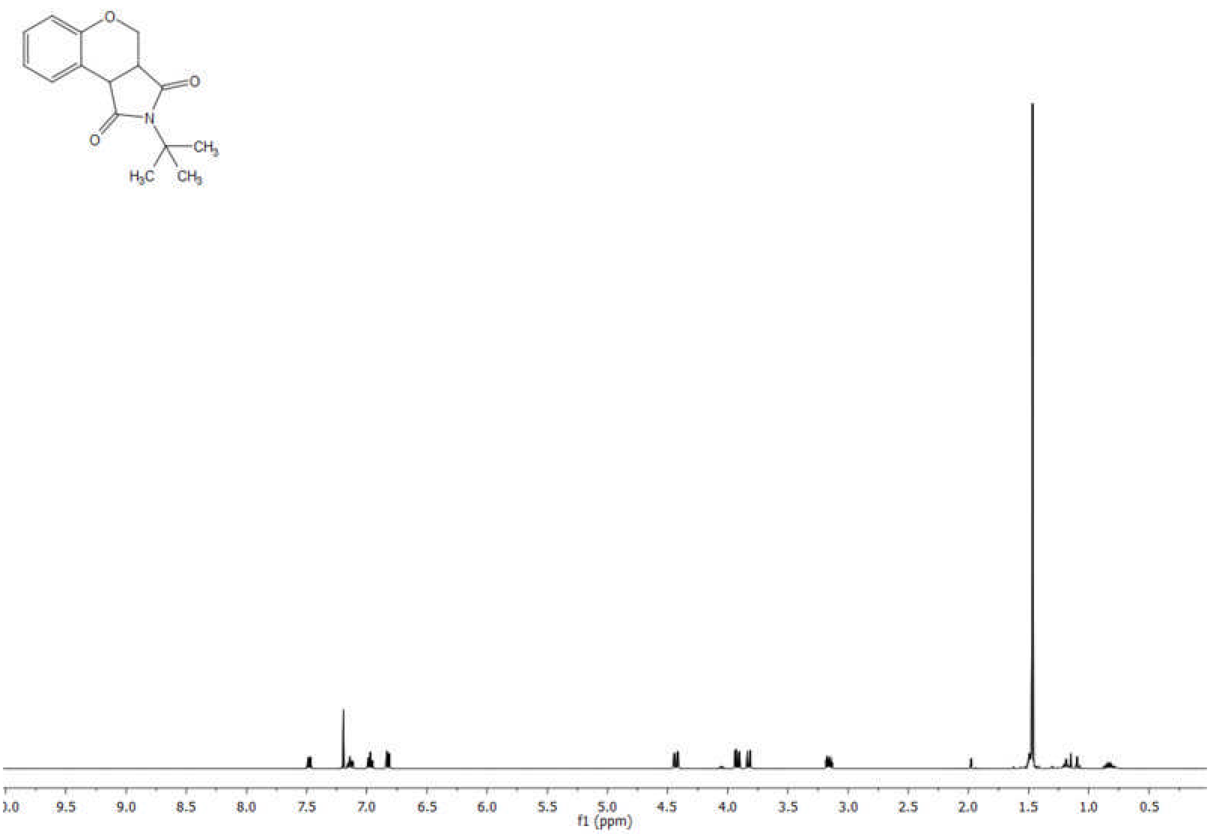


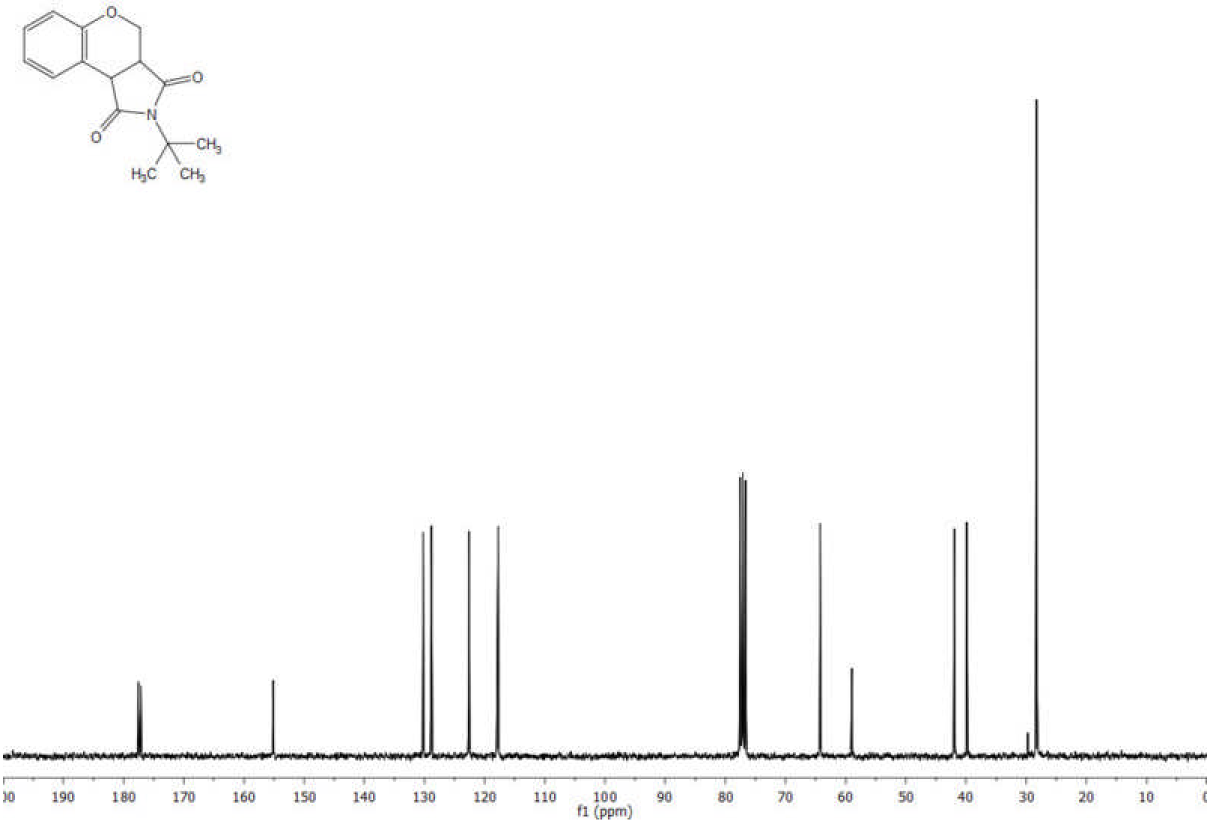
O
O
N
O
CH3
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)



O
O
N
O
CH3
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(
f1 (ppm)

8d


O
O
N
O
CH3
H3C
CH3
9.5
9.0
8.5
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
f1 (ppm)


O
O
N
O
CH3
H3C
CH3
190
180
170
160
150
140
130
120
110
100
90
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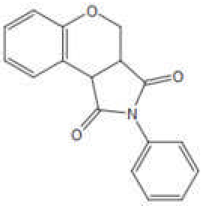
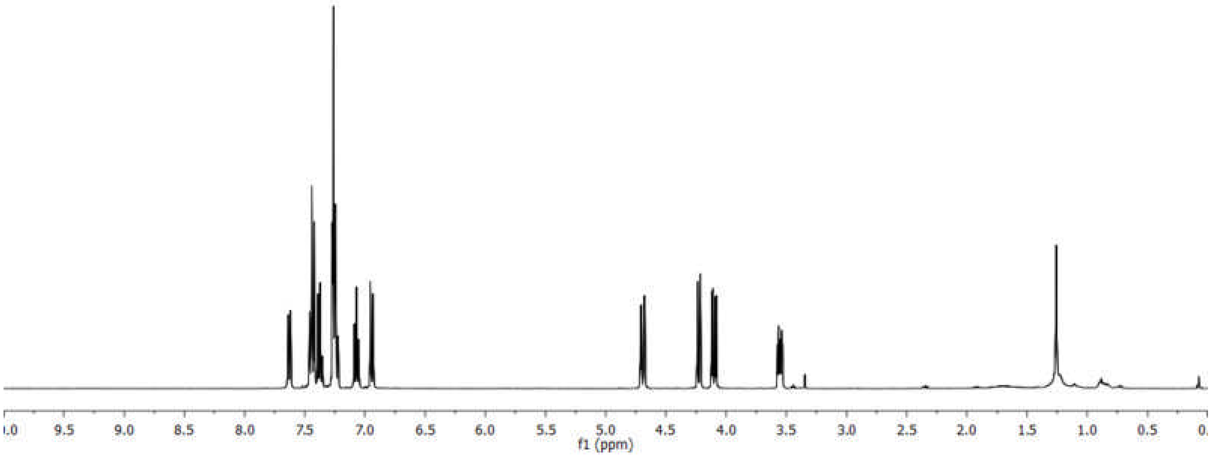
30
20
10
f1 (ppm)

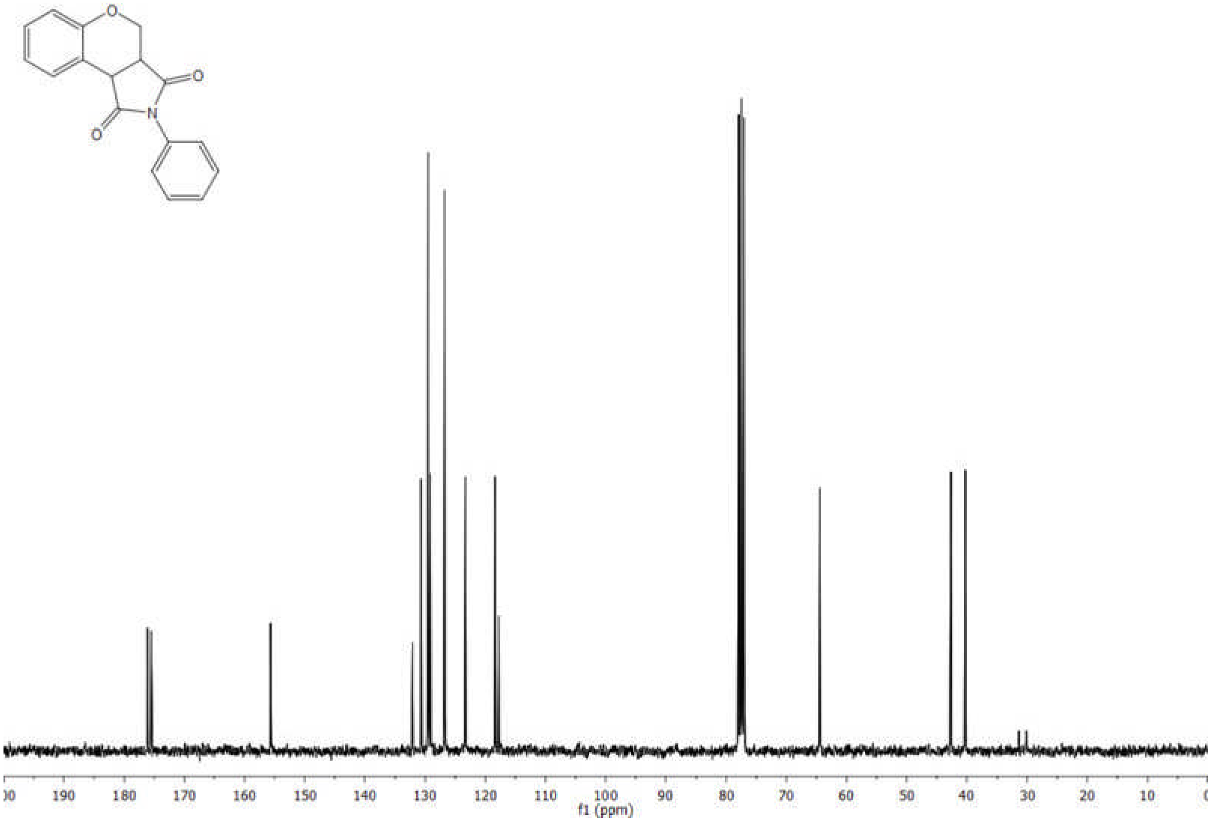
8e



O
O
N
O

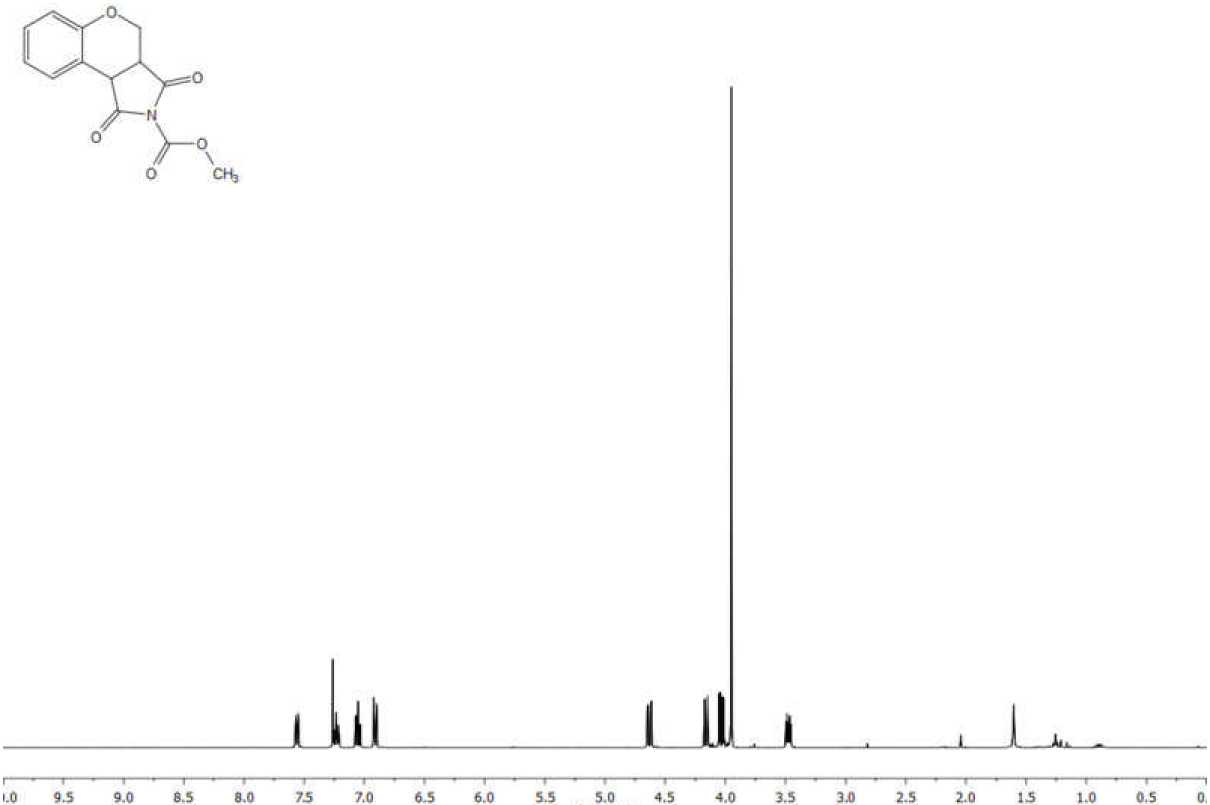


.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

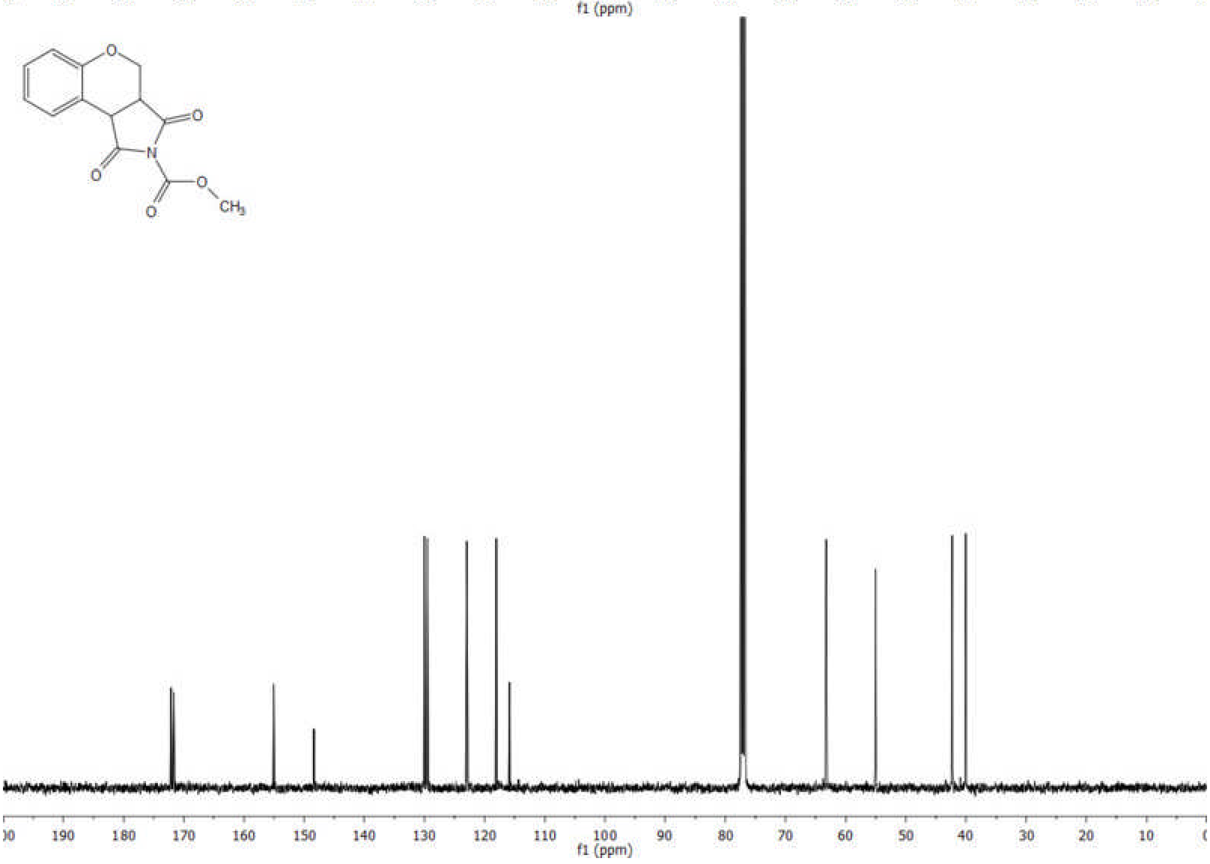


O
O
N
O
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

8f



O
N
O
O
O
O
CH3
.0
9.5
9.0
8.5
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
0.
f1 (ppm)



O
N
O
O
O
O
CH3
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(
f1 (ppm)