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SUPPORTING INFORMATION

Tandem synthesis of 4-aminoxanthones is controlled by a water-assisted tautomerization: A general straightforward reaction

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TABLE OF CONTENTS

EXPERIMENTAL PROCEDURES

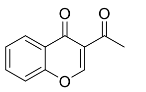
General Synthetic Techniques

Liquid reagents were measured using positive-displacement micropipettes with disposable tips and pistons. Thin layer chromatography was performed on aluminum plates, using 254 nm UV light or a mixture of *p*-anisaldehyde (2.5%), acetic acid (1%) and H_2SO_4 (3.4%) in 95% ethanol, as developer.

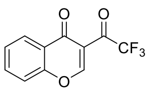
Materials. Isocyanides and dienophiles were purchased from commercial sources. Methyl 2-(6-methyl-4-oxo-4*H*-chromen-3-yl)-2-oxoacetate (**1a**), methyl 2-oxo-2-(4-oxo-4*H*-chromen-3-yl)acetate (**1b**), methyl 2-(7-methoxy-4-oxo-4*H*-chromen-3-yl)-2-oxoacetate (**1c**), methyl 2-(6-chloro-4-oxo-4*H*-chromen-3-yl)-2-oxoacetate (**1d**) and 1,1'-(4,4'-dihydroxy-[1,1'-biphenyl]-3,3'-diyl)bis(ethan-1-one) (**9**) were prepared according to literature procedures.[1]

Instrumentation. Melting points are uncorrected. IR spectra were recorded as KBr pellets. Proton and carbon-13 nuclear magnetic resonance (^{1}H NMR or ^{13}C NMR) spectra were obtained on a 400 MHz or 500 MHz spectrometer. Mass spectra (MS) and High Resolution Mass Spectra (HRMS) were recorded using Electron Impact (EI, 70 eV), Chemical Ionization (CI) with CH_4, or ESI-FIA-TOF. The assignments of signals in ^{13}C NMR were made by DEPT. Experiments under microwave irradiation were performed in closed vials, using a focused single-mode microwave reactor CEM Discover BenchMate, provided with an IR internal thermal probe.

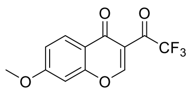
Synthesis and characterization of chromones (1f-1j)



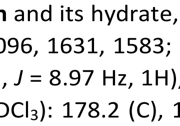
3-Acetyl-4*H*-chromen-4-one (1f):[2] A solution of (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **9a** (214 mg, 1.16 mmol) in pyridine (1 mL) and two drops of piperidine was cooled in ice-bath and then acetic anhydride **10a** (1 mL, 9 mmol) was added dropwise. The reaction was let to slowly reach the room temperature overnight and then it was heated at 120 ºC until the starting material was consumed (2 hours). The residue was washed with saturated aqueous Brine (3 x1 5 mL) and $CuSO_4$ (3 x1 5 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The organic phase was dried over Na_2SO_4 and concentrated, and the crude was purified by column chromatography (silica gel, hexane-EtOAc gradient), giving the desired chromone **1f** (129 mg, 59%), obtained as a white solid; mp: 128-132 ºC (lit.[2] 125-128 ºC).



3-(2,2,2-Trifluoroacetyl)-4*H*-chromen-4-one (1g):[3] A solution of (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **9a** (214 mg, 1.12 mmol) in dry 1,2-dichloroethane (2 mL) was cooled in ice-bath and then a solution of trifluoroacetic anhydride **10b** (468 µL, 3.37 mmol) in 1,2-dichloroethane was added dropwise. The reaction was let to slowly reach the room temperature overnight and then it was heated at 100 ºC until the starting material was consumed (4 hours). The residue was washed with saturated aqueous $NaHCO_3$ (3 x 15 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The organic phase was dried over Na_2SO_4 and concentrated, and the precipitate was washed with hexane, giving the product as a mixture of chromone **1g** and its hydrate, in a 0.2:1 ratio (203 mg, 75%), obtained as a white solid; mp: 145 ºC (lit.[3] 124-125 ºC)

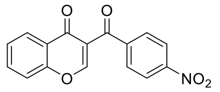


7-Methoxy-3-(2,2,2-trifluoroacetyl)-4*H*-chromen-4-one (1h): A solution of (*E*)-3-(dimethylamino)-1-(2-hydroxy-4-methoxyphenyl)prop-2-en-1-one **9b** (221 mg, 1.0 mmol) in dry 1,2-dichloroethane (2 mL) was cooled in ice-bath and then a solution of trifluoroacetic anhydride **10b** (417 µL, 3 mmol) in 1,2-dichloroethane was added dropwise. The reaction was let to slowly reach the room temperature overnight and then it was stirred at room temperature until the starting material was consumed (12 hours). The residue was washed with saturated aqueous $NaHCO_3$ (3 x 15 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The organic phase was dried over Na_2SO_4 and concentrated, and the precipitate was washed with hexane, giving the product as a mixture of chromone **1h** and its hydrate, in a 1:3 ratio (193 mg. 71%), obtained as a brown solid; mp: 112-117 ºC; IR (cm^{-1}): 3329, 3096, 1631, 1583; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.54 (s, 0.2H), 8.31 (s, 1H), 8.21 (d, *J* = 8.92 Hz, 0.2H), 8.14 (d, *J* = 8.97 Hz, 1H), 7.09-7.06 (m, 1H), 6.93-6.91 (m, 1H), 6.25 (s, 1H), 3.95 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 178.2 (C), 165.3 (C), 158.5 (C), 157.6 (CH), 127.4 (CH), 117.1 (C), 116.9 (C), 116.1 (CH), 116.0 (CH), 101.0 (CH), 100.4 (CH), 100.1 (C), 56.2 (CH_3) ppm; MS (CI) m/z (%) 274 (M+2, 12), 273 (M+1, 100), 272 (M$^+$, 6), 177 (12), 149 (35), 99 (28).



3-(2-Nitrobenzoyl)-4*H*-chromen-4-one (1i):[4] To a solution of 4*H*-chromen-4-one **11** (184 mg, 1.25 mmol) and *o*-nitrobenzaldehyde **12a** (158 mg ,1 mmol) in dry methanol (0.5 mL), sodium *tert*-butoxide (27 mg, 0.267 mmol) in methanol was added dropwise

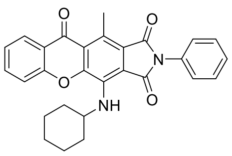
under a nitrogen atmosphere. Once the chromone **11** was consumed (72 hours), a solution of HCl 1N (2 mL) was added to the reaction mixture. The solvents were removed in the rotary evaporator, and the residue was re-dissolved in ethyl acetate and washed with H2O (3 x 15 mL). The organic phase was dried over Na_2SO_4 and concentrated, and the resulting solid was washed with methanol and ethyl acetate, giving the Baylis-Hillman intermediate 3-(hydroxy(2-nitrophenyl)methyl)-4*H*-chromen-4-one (196 mg, 66%), as a white solid.
A solution of 3-(hydroxy(2-nitrophenyl)methyl)-4*H*-chromen-4-one (96 mg, 0.38 mmol) and MnO2 (667 mg ,7.7 mmol) in CH_2Cl_2 (6 mL) was stirred at room temperature under a nitrogen atmosphere until the starting material was consumed (1.25 hours). Then the mixture was filtered over celite, washing with CH_2Cl_2 (20 mL), and the organic residue was evaporated, giving a white solid, which was washed with cyclohexane affording **1i** (103 mg, 92%).



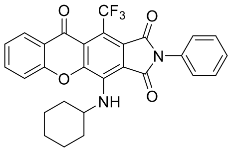
3-(4-nitrobenzoyl)-4*H*-chromen-4-one (1j):[4] To a solution of 4*H*-chromen-4-one **11** (200 mg, 1.37 mmol) and *p*-nitrobenzaldehyde **12b** (176 mg ,1.16 mmol) in dry methanol (4 mL), a freshly prepared sodium methoxide solution in methanol was added dropwise under a nitrogen atmosphere. Once the chromone **11** was consumed (36 hours), a solution of HCl 1N (2 mL) was added to the reaction mixture. The solvents were removed in the rotary evaporator, and the residue was re-dissolved in ethyl acetate and washed with H2O (3 x 15 mL). The organic phase was dried over Na_2SO_4 and concentrated, and the resulting solid was washed with methanol and ethyl acetate, giving the Baylis-Hillman intermediate 3-(hydroxy(4-nitrophenyl)methyl)-4*H*-chromen-4-one (279 mg, 81%), as a white solid.
A solution of 3-(hydroxy(4-nitrophenyl)methyl)-4*H*-chromen-4-one (173 mg, 0.58 mmol) and MnO2 (1.01 g ,11.64 mmol) in CH_2Cl_2 (6 mL) was stirred at room temperature under a nitrogen atmosphere until the starting material was consumed (1.25 hours). Then the mixture was filtered over celite, washing with CH_2Cl_2 (20 mL), and the organic residue was evaporated, giving a bright-green solid, which was washed with cyclohexane affording **1j** (138 mg, 81%).

General procedure for the synthesis of xanthones (8a-bk)

Isocyanide **2a-g** (1.2 mmol) and dienophile **3a-f** (1.2 mmol) are successively added to a solution of chromenone **1a-m** (1 mmol) in the appropriate solvent (2 mL). The resulting mixture is stirred at the appropriate temperature under a nitrogen atmosphere until the chromone (**1**) is consumed. HCl 1N (2 mL) is then added to the reaction mixture, and after 30 minutes, the crude is washed with brine (15 mL), and extracted with CH_2Cl_2 (3 x 15 mL). The organic phase is dried over Na_2SO_4 and concentrated. The resulting residue is purified by column chromatography (silica gel, hexane-EtOAc gradient), giving the desired product **8**.

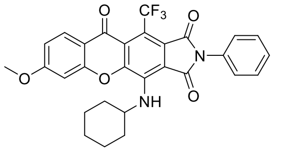


4-(Cyclohexylamino)-11-methyl-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8ak): To a solution of chromenone **1f** (188 mg, 1 mmol) in dry THF (2mL), cyclohexylisocyanide **2a** (151 µL, 1.2 mmol) and *N*-phenylmaleimide **3a** (208 mg, 1.2 mmol) were added. The resulting mixture was heated at 80ºC (bath temperature) under a nitrogen atmosphere until the chromone **1f** was consumed (40.2 hours). HCl 1N (2 mL) was then added to the reaction mixture, and after 30 minutes, the crude was washed with brine (15 mL), and extracted with CH_2Cl_2 (3 x 15 mL). The organic phase was dried over Na_2SO_4 concentrated and the crude was purified by column chromatography (silica gel, hexane-EtOAc gradient), giving the desired product **8ak** (429 mg, 95%), obtained as a yellow solid; mp: 214 ºC; IR (cm^{-1}): 3430, 2922, 2853, 1754, 1694, 1656, 1611; ^1H NMR (500 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.53-7.50 (m, 2H), 7.45-7.39 (m, 5H), 6.77 (bs, 1H, NH), 4.27 (m, 1H), 3.19 (s, 3H), 2.13 (m, 2H), 1.84 (m, 2H), 1.67-1.25 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 178.8 (C), 168.3 (C), 167.1 (C), 154.5 (C), 151.7 (C), 137.1 (C), 135.1 (CH), 131.8 (C), 131.6 (C), 129.1 (CH), 128.8 (CH), 128.3 (CH), 127.1 (CH), 126.8 (CH), 125.3 (CH), 125.0 (C), 123.0 (C), 122.6 (C), 117.3 (CH), 114.2 (C), 54.6 (CH), 34.9 (CH_2), 25.8 (CH_2), 24.9 (CH_2), 15.9 (CH_3) ppm; MS (CI) m/z (%) 453 (M+1, 39), 452 (M^+, 13), 375 (22), 347 (93), 298 (100); HRMS (EI) Calcd for $C_{28}H_{24}N_2O_4$: 452.17361. Found: 452.1735.

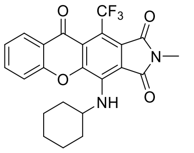


4-(Cyclohexylamino)-2-phenyl-11-(trifluoromethyl)chromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8al): The general procedure described for the synthesis of **8ak** was applied to a mixture of chromone **1g** (62 mg, 0.26 mmol), isocyanide **2a** (38 µL, 0.31 mmol) and *N*-phenylmaleimide **3a** (56 mg, 0.31 mmol) in THF, affording xanthone **8al** (21 hours, 80 mg, 61 %), obtained as a yellow solid; mp: 255 ºC; IR (cm^{-1}): 3314, 2931, 2850, 1762, 1705, 1665, 1612; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.7 Hz, 1H), 7.79

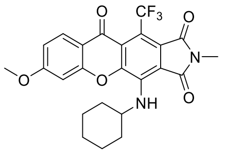
(t, J = 7.5 Hz, 1H), 7.64 (bs, NH, 1H), 7.53-7.43 (m, 7H), 4.46 (m, 1H), 2.19 (m, 2H), 1.88 (m, 2H), 1.72–1.26 (m, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9 (C), 168.2 (C), 162.9 (C), 154.1 (C), 149.1 (C), 140.7 (C), 135.4 (CH), 131.5 (C), 129.2 (CH), 128.5 (CH), 127.2 (CH), 126.8 (CH), 125.8 (CH), 123.2 (C), 117.1 (CH), 111.9 (C), 54.7 (CH), 35.0 (CH_2), 25.5 (CH_2), 24.8 (CH_2) ppm; HRMS (EI) Calcd for $C_{28}H_{21}F_3N_2NaO_4$: 529.1337. Found: 529.1346.



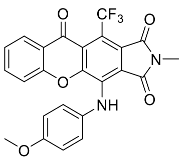
4-(Cyclohexylamino)-7-methoxy-2-phenyl-11-(trifluoromethyl) chromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8am): The general procedure described for the synthesis of **8ak** was applied to a mixture of chromone **1h** (51 mg, 0.187 mmol), isocyanide **2a** (28 µL, 0.22 mmol) and *N*-phenylmaleimide **3a** (38.1 mg, 0.22 mmol) in THF, affording xanthone **8am** (13 hours, 58 mg, 58 %), obtained as a yellow solid; mp: 296 ºC; IR (cm^{-1}): 3452, 2926, 1762, 1711, 1668, 1613; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, J = 8.9 Hz, 1H), 7.59 (bs, 1H), 7.53-7.49 (m, 2H), 7.45-7.40 (m, 3H), 7.04 (d, J = 8.9 Hz, 1H) 6.79 (d, J = 2.3 Hz, 1H), 4.42 (m, 1H), 3.97 (s, 3H), 2.18 (m, 2H), 1.90 (m, 2H), 1.60-1.25 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 174.9 (C), 168.2 (C), 165.5 (C), 163.0 (C), 155.8 (C), 149.1 (C), 140.6 (C), 131.5 (C), 129.3 (CH), 128.8 (CH), 128.5 (CH), 127.1 (C), 126.8 (CH), 117.0 (C), 114.4 (CH), 111.8 (C), 56.1 (CH_3), 54.7 (CH), 34.9 (CH_2), 25.5 (CH_2), 24.8 (CH_2) ppm; MS (CI) m/z (%) 537 (M+1, 16), 536 (M^+, 23), 517 (96), 174 (100); HRMS (EI) Calcd for $C_{29}H_{23}F_3N_2O_5$: 536.1559. Found: 536.1558.



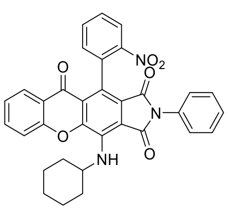
4-(Cyclohexylamino)-2-methyl-11-(trifluoromethyl)chromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8an): The general procedure described for the synthesis of **8ak** was applied to a mixture of chromone **1g** (56 mg, 0.231 mmol), isocyanide **2a** (34 µL,0.278 mmol) and *N*-methylmaleimide **3b** (32 mg, 0.289 mmol) in THF, affording xanthone **8an** (17 hours, 27 mg, 26 %), obtained as a yellow solid; mp: 197 ºC; IR (cm^{-1}): 3326, 2939, 2851, 1763, 1702, 1671, 1609; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, J = 7.7 Hz, 1H), 7.78 (t, J = 7.4 Hz, 1H), 7.48-7.42 (m, 3H), 4.41 (m, 1H), 3.17 (s, 3H), 2.17 (m, 2H), 1.88-1.34 (m, 8H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 175.8 (C), 168.9 (C), 164.0 (C), 153.8 (C), 148.9 (C), 140.0 (C), 136.0 (C), 135.2 (CH), 127.4 (C), 127.0 (CH), 125.6 (CH), 124.7 (C), 123.5 (C), 122.9 (C), 116.9 (CH), 112.3 (C), 54.5 (CH), 34.8 (CH_2), 25.4 (CH_2), 24.6 (CH_2), 24.2 (CH_3) ppm; MS (CI) m/z (%) 445 (M+1, 10), 444 (M^+, 18), 426 (28), 425 (100); HRMS (EI) Calcd for $C_{23}H_{19}F_3N_2O_4$: 444.1297. Found: 444.1296.



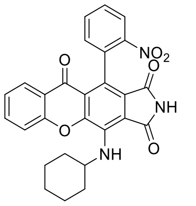
4-(Cyclohexylamino)-7-methoxy-2-methyl-11-(trifluoromethyl) chromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8ao): The general procedure described for the synthesis of **8ak** was applied to a mixture of chromone **1h** (54 mg, 0.197 mmol), isocyanide **2a** (29 µL, 0.233 mmol) and *N*-methylmaleimide **3b** (26 mg, 0.234 mmol) in THF, affording xanthone **8ao** (31 hours, 55 mg, 59 %), obtained as a dark yellow solid; mp: 249 ºC; IR (cm^{-1}): 3443, 2919, 1759, 1701, 1666, 1616; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 8.9 Hz, 1H), 7.36 (bs, 1H), 7.00 (d, J = 8.9 Hz, 1H), 6.75 (d, J = 1.9 Hz, 1H), 4.36 (m, 1H), 3.95 (s, 3H), 3.16 (s, 3H), 2.17 (m, 2H), 1.88-1.47 (m, 8H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 174.9 (C), 169.3 (C), 165.4 (C), 164.2 (C), 155.7 (C), 149.0 (C), 140.0 (C), 128.7 (CH), 116.9 (C), 114.3 (CH), 112.5 (C), 99.8 (CH), 56.1 (CH), 54.6 (CH_3), 34.9 (CH_2), 25.5 (CH_2), 24.78 (CH_2), 24.35 (CH_3) ppm; MS (CI) m/z (%) 475 (M+1, 29), 455 (15), 341 (18), 226 (37); HRMS (EI) Calcd for $C_{24}H_{21}F_3N_2O_5$: 474.1403. Found: 474.1418.



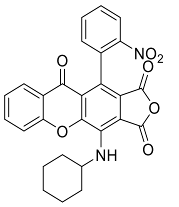
4-((4-Methoxyphenyl)amino)-2-methyl-11-(trifluoromethyl)chromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8ap): The general procedure described for the synthesis of **8ak** was applied to a mixture of chromone **1g** (60 mg, 0.247 mmol), isocyanide **2f** (39 mg, 0.293 mmol) and *N*-methylmaleimide **3b** (35 mg, 0.304 mmol) in THF, affording xanthone **8ap** (31 hours, 61 mg, 53 %), obtained as an orange solid; mp: 189 ºC; IR (cm^{-1}): 3317, 1764, 1691, 1614; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.17 (d, J = 7.2 Hz, 1H), 7.59 (m, 2H), 7.38 (m, 1H), 7.19 (d, J = 7.8 Hz, 1H), 6.95 (m, 3H), 6.53 (d, J = 7.91 Hz, 1H), 3.90 (s, 3H), 3.23 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 175.6 (C), 168.5 (C), 157.9 (C), 153.3 (C), 149.3 (C), 137.6 (C), 135.1 (CH), 135.1 (CH), 133.4 (C), 127.4 (CH), 125.9 (CH), 125.4 (CH), 122.7 (C), 117.0 (CH), 114.5 (CH), 114.2 (CH), 55.7 (CH_3), 24.5 (CH_3) ppm; MS (CI) m/z (%) 468 (M^+, 62), 448 (26), 321 (22), 229 (53); HRMS (EI) Calcd for $C_{24}H_{15}F_3N_2O_5$: 468.0933. Found: 468.0929.



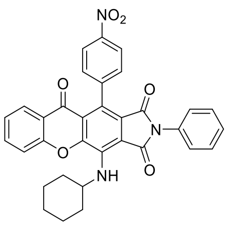
4-(Cyclohexylamino)-11-(2-nitrophenyl)-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8aq): The general procedure described for the synthesis of **8ak** was applied to a mixture of chromone **1i** (56 mg, 0.191 mmol), isocyanide **2a** (28 µL, 0.225 mmol) and *N*-phenylmaleimide **3a** (40 mg, 0.283 mmol) in THF, affording xanthone **8aq** (6,5 hours, 82 mg, 77 %), obtained as an orange solid; mp: 230 ºC; IR (cm^{-1}): 3342, 2929, 1759, 1698, 1659, 1610; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 8.3, 1.1 Hz, 1H), 8.11 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.68 (t, *J* = 7.5, 1H), 7.60 (m, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.44-7.31 (m, 7H), 7.02 (bs, NH, 1H), 4.45 (m, 1H), 2.22 (m, 2H), 1.90 (m, 2H), 1.71-1.26 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 177.0 (C), 168.3 (C), 165.4 (C), 155.0 (C), 150.7 (C), 147.6 (C), 138.7 (C), 135.5 (CH), 133.8 (C), 133.4 (CH), 131.4 (C), 131.0 (CH), 129.1 (CH), 128.5 (CH), 128.2 (CH), 127.1 (CH), 126.5 (CH), 125.7 (C), 125.4 (CH), 124.9 (CH), 123.8 (C), 122.5 (C), 122.2 (C), 117.6 (CH), 112.8 (C), 54.7 (CH), 35.14 (CH_2), 35.06 (CH_2), 25.7 (CH_2), 24.9 (CH_2) ppm; MS (CI) m/z (%) 560 (M+1, 16), 559 (M^+, 9), 512 (10), 478 (10), 174 (17); HRMS (EI) Calcd for $C_{33}H_{25}N_3O_6$: 559.1743. Found: 559.1743.



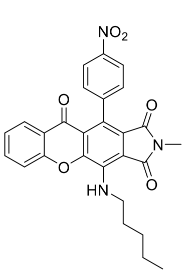
4-(Cyclohexylamino)-11-(2-nitrophenyl)chromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8ar): The general procedure described for the synthesis of **8ak** was applied to a mixture of chromone **1i** (128 mg, 0.433 mmol), isocyanide **2a** (65 μL, 0.523 mmol) and maleimide **3d** (52 mg, 0.534 mmol) in THF, affording xanthone **8ar** (31 hours, 77 mg, 37 %), obtained as a dark yellow solid; mp: 279 ºC (dec); IR (cm^{-1}): 3218, 2926, 2851, 1757, 1704, 1662, 1608; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.9 Hz, 1H), 8.09 (d, *J* = 7.4 Hz, 1H), 7.77-7.61 (m, 4H), 7.48-7.29 (m, 3H), 6.80 (bs, NH, 1H), 4.40 (m, 1H), 2.20 (m, 2H), 1.89 – 1.36 (m, 8H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 177.0 (C), 168.7 (C), 165.8 (C), 154.8 (C), 150.5 (C), 147.6 (C), 138.6 (C), 135.5 (CH), 133.6 (C), 133.3 (CH), 131.0 (CH), 128.6 (CH), 127.1 (CH), 125.47 (C), 125.43 (CH), 124.8 (CH), 123.8 (C), 123.5 (C), 122.2 (C), 117.5 (CH), 113.8 (C), 54.8 (CH), 35.2 (CH_2), 35.1 (CH_2), 25.7 (CH_2), 25.0 (CH_2) ppm; MS (CI) m/z (%) 485 (M+2, 93), 484 (M+1, 100), 483 (M^+, 3), 464 (18), 437 (24); HRMS (EI) Calcd for $C_{27}H_{21}N_3O_6$: 483.1430. Found: 483.1427.



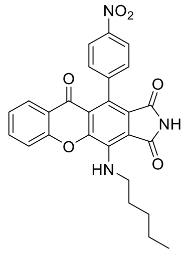
4-(Cyclohexylamino)-11-(2-nitrophenyl)-1*H*-furo[3,4-*b*]xanthene-1,3,10-trione (8as): The general procedure described for the synthesis of **8ak** was applied to a mixture of chromone **1i** (130 mg, 0.441 mmol), isocyanide **2a** (66 μL, 0.531 mmol) and maleic anhydride **3c** (57 mg, 0.577 mmol) in THF, affording xanthone **8as** (22 hours, 188 mg, 88 %), obtained as an orange solid; mp: 318 ºC (dec); IR (cm^{-1}): 3359, 2936, 1825, 1742, 1663, 1628, 1610; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 7.6 Hz, 1H), 7.79 (t, *J* = 7.4 Hz, 1H), 7.71 (t, *J* = 7.3 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 1H), 6.50 (d, *J* = 7.7 Hz, NH, 1H), 4.52 (m, 1H), 2.24 (m, 2H), 1.91 (m, 2H), 1.76-1.26 (m, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): 176.6 (C), 163.6 (C), 161.1 (C), 154.8 (C), 150.4 (C), 147.5 (C), 139.4 (C), 135.9 (CH), 133.7 (CH), 132.5 (C), 130.9 (CH), 129.1 (CH), 127.2 (CH), 127.0 (C), 125.9 (CH), 125.0 (CH), 124.4 (C), 122.2 (C), 117.6 (CH), 110.8 (C), 55.0 (CH), 35.06 (CH_2), 35.01 (CH_2), 25.6 (CH_2), 24.9 (CH_2) ppm; MS (CI) m/z (%) 485 (M+1, 14), 484 (M^+, 36), 438 (15), 403 (100); HRMS (EI) Calcd for $C_{27}H_{20}N_2O_7$: 484.1271. Found: 484.1274.



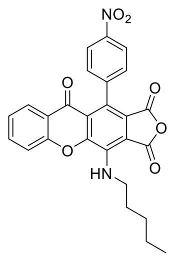
4-(Cyclohexylamino)-11-(4-nitrophenyl)-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8at): The general procedure described for the synthesis of **8ak** was applied to a mixture of chromone **1j** (50 mg, 0.171 mmol), isocyanide **2a** (26 μL, 0.209 mmol) and *N*-phenylmaleimide **3a** (37 mg, 0.211 mmol) in THF, affording xanthone **8at** (35 hours, 90 mg, 93 %), obtained as a dark yellow solid; mp: 314 ºC (dec); IR (cm^{-1}): 3430, 2931, 1757, 1706, 1664, 1608; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.47-7.35 (m, 8H), 7.12 (bs, NH, 1H), 4.47 (m, 1H), 2.22 (m, 2H), 1.90 (m, 2H), 1.73–1.26 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 176.8 (C), 168.3 (C), 165.2 (C), 154.7 (C), 150.6 (C), 147.2 (C), 144.6 (C), 139.0 (C), 135.7 (CH), 131.3 (C), 129.6 (CH), 129.1 (CH), 128.3 (CH), 127.1 (CH), 126.9 (C), 126.5 (CH), 125.7 (CH), 123.8 (C), 123.5 (C), 123.2 (CH), 122.4 (C), 117.6 (CH), 112.7 (C), 54.7 (CH), 35.0 (CH_2), 25.6 (CH_2), 24.8 (CH_2) ppm; MS (CI) m/z (%) 560 (M+1, 74), 559 (M^+, 100), 558 (30), 311 (9), 167 (10); HRMS (EI) Calcd for $C_{33}H_{25}N_3O_6$: 559.1743. Found: 559.1747.



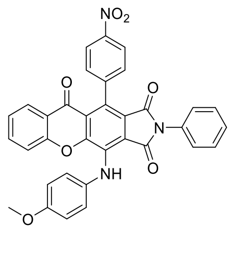
2-Methyl-11-(4-nitrophenyl)-4-(pentylamino)chromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8au): The general procedure described for the synthesis of **8ak** was applied to a mixture of chromone **1j** (51 mg, 0.173 mmol), isocyanide **2e** (26 μL, 0.208 mmol) and *N*-methylmaleimide **3b** (24 mg, 0.216 mmol) in THF, affording xanthone **8au** (20 hours, 57 mg, 68 %), obtained as a yellow solid; mp: 242 ºC; IR (cm^{-1}): 3400, 2927, 1756, 1700, 1660, 1607; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.43–7.39 (m, 3H), 6.87 (bs, NH, 1H), 3.97 (t, *J* = 7.1 Hz, 2H), 3.06 (s, 3H), 1.82 (q, *J* = 7.4 Hz, 2H), 1.54–1.42 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 177.4 (C), 169.6 (C), 167.0 (C), 155.2 (C), 151.2 (C), 147.6 (C), 145.1 (C), 139.6 (C), 135.9 (CH), 129.9 (CH), 127.3 (CH), 126.8 (C), 125.9 (CH), 124.3 (C), 123.5 (C), 123.4 (CH), 122.6 (C), 117.8 CH), 113.4 (C), 46.6 (CH_2), 30.9 (CH_2), 28.8 (CH_2), 23.6 (CH_3), 22.3 (CH_2), 13.81 (CH_3) ppm; MS (CI) m/z (%) 487 (M+2, 6), 486 (M+1, 26), 469 (7), 428 (5); HRMS (EI) Calcd for $C_{27}H_{23}N_3O_6$: 485.1587. Found: 485.1585.



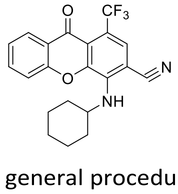
11-(4-Nitrophenyl)-4-(pentylamino)chromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8av): The general procedure described for the synthesis of **8ak** was applied to a mixture of chromone **1j** (54 mg, 0.183 mmol), isocyanide **2e** (27 µL, 0.217 mmol) and maleimide **3d** (23 mg, 0.237 mmol) in THF, affording xanthone **8av** (5 days, 57 mg, 66 %), obtained as a yellow solid; mp: 291 ºC; IR (cm^{-1}): 3433, 2920, 1760, 1693, 1660, 1607; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.67 (bs, NH, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.43–7.40 (m, 3H), 6.91 (bs, NH, 1H), 3.97 (t, *J* = 7.2 Hz, 2H), 1.82 (q, *J* = 7.4 Hz, 2H), 1.53–1.42 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 176.8 (C), 168.5 (C), 165.6 (C), 154.7 (C), 150.7 (C), 147.3 (C), 144.4 (C), 139.7 (C), 135.7 (CH), 129.6 (CH), 127.1 (CH), 126.8 (C), 125.7 (CH), 124.4 (C), 123.7 (C), 123.2 (CH), 122.4 (C), 117.6 (CH), 113.4 (C), 46.8 (CH_2), 31.2 (CH_2), 29.2 (CH_2), 22.6 (CH_2), 14.2 (CH_3) ppm; MS (CI) m/z (%) 472 (M+1, 100), 471 (M$^+$, 39), 455 (24), 351 (34); HRMS (EI) Calcd for $C_{26}H_{21}N_3O_6$: 471.1430. Found: 471.1434.



11-(4-Nitrophenyl)-4-(pentylamino)-1*H*-furo[3,4-*b*]xanthene-1,3,10-trione (8aw): The general procedure described for the synthesis of **8ak** was applied to a mixture of chromone **1j** (58 mg, 0.196 mmol), isocyanide **2e** (30 µL, 0.238 mmol) and maleic anhydride **3c** (25 mg, 0.250 mmol) in THF, affording xanthone **8aw** (5.4 days, 55 mg, 59 %), obtained as a yellow solid; mp: 272 ºC (dec); IR (cm^{-1}): 3382, 2955, 1812, 1764, 1664, 1608; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.5 Hz, 2H), 8.12 (d, *J* = 6.8 Hz, 1H), 7.83 (t, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 6.60 (t, *J* = 5.2 Hz, NH, 1H), 4.05 (c, *J* = 6.7 Hz, 2H), 1.85 (q, *J* = 7.2 Hz, 2H), 1.54–1.44 (m, 4H), 0.98 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 176.3 (C), 163.4 (C), 160.7 (C), 154.6 (C), 150.5 (C), 147.6 (C), 143.2 (C), 140.6 (C), 136.0 (CH), 129.5 (CH), 128.1 (C), 127.2 (CH), 126.1 (CH), 124.3 (C), 123.4 (CH), 123.1 (C), 122.4 (C), 118.5 (C), 117.6 (CH), 110.6 (C), 47.1 (CH_2), 31.0 (CH_2), 29.0 (CH_2), 22.6 (CH_2), 14.2 (CH_3) ppm; MS (CI) m/z (%) 474 (M+2, 22), 473 (M+1, 76), 472 (M$^+$, 52), 295 (6); HRMS (EI) Calcd for $C_{26}H_{20}N_2O_7$: 472.1271. Found: 472.1273.

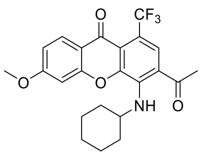


4-((4-Methoxyphenyl)amino)-11-(4-nitrophenyl)-2-phenylchromeno [2,3-*f*] isoindole-1,3,10(2*H*)-trione (8ax): The general procedure described for the synthesis of **8ak** was applied to a mixture of chromone **1j** (45 mg, 0.152 mmol), isocyanide **2f** (25 mg, 0.188 mmol) and *N*-phenylmaleimide **3a** (35 mg, 0.202 mmol) in THF, affording xanthone **8ax** (6 days, 45 mg, 51 %), obtained as a dark orange solid; mp: 296 ºC; IR (cm^{-1}): 3363, 1762, 1713, 1661, 1607; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.33 (d, *J* = 8.8 Hz, 2H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.50–7.44 (m, 4H), 7.39–7.31 (m, 4H), 7.23 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 1H), 3.89 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): 176.6 (C), 168.0 (C), 165.1 (C), 157.8 (C), 154.2 (C), 151.0 (C), 147.4 (C), 144.1 (C), 136.2 (C), 135.6 (CH), 134.2 (C), 131.3 (C), 129.5 (CH), 129.2 (CH), 128.4 (CH), 126.7 (CH), 126.5 (CH), 125.56 (CH), 125.53 (C), 123.9 (C), 123.3 (CH), 123.0 (C), 122.3 (C), 117.7 (CH), 115.1 (C), 114.1 (CH), 55.86 (CH_3) ppm; MS (CI) m/z (%) 584 (M+1, 71), 583 (M$^+$, 17), 580 (27), 242 (14); HRMS (EI) Calcd for $C_{34}H_{21}N_3O_7$: 583.1380. Found: 583.1362.

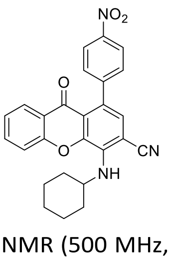


4-(Cyclohexylamino)-9-oxo-1-(trifluoromethyl)-9H-xanthene-3-carbonitrile (8ay): A solution of chromone **1g** (56 mg, 0.232 mmol), isocyanide **2a** (35 µL, 0.282 mmol) and acrylonitrile **3e** (20 µL, 0.301 mmol) in THF (2 mL) was irradiated with MW in a sealed vial at 100 ºC until the chromone **1g** was consumed (2 hours). Then DBU (69 µL, 0.462 mmol) was added and the mixture was irradiated 20 minutes. The crude was elaborated as the general procedure affording the xanthone **8ay** (25 mg, 28 %), obtained as a yellow solid; mp: 250 ºC; IR (cm^{-1}): 3424, 3351, 2927, 2855, 2214, 1672, 1609, 1563; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.73 (s, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 5.63 (d, *J* = 8.6 Hz, NH, 1H), 4.37 (m, 1H), 2.24 (m, 2H), 1.84 (m, 2H), 1.74 (m, 1H), 1.52 – 1.28 (m, 5H) ppm; ^{13}C NMR (126

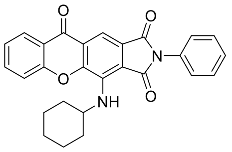
MHz, $CDCl_3$): 174.9 (C), 154.5 (C), 146.7 (C), 143.0 (C), 135.7 (CH), 129.4 (CH), 127.7 (CH), 126.0 (CH), 122.8 (C), 121.1 (C), 118.5 (C), 117.5 (CH), 92.2 (C), 52.2 (CH), 34.02 (CH_2), 25.2 (CH_2), 24.0 (CH_2) ppm; MS (CI) m/z (%) 387 (M+1, 19), 386 (M^+, 18), 370 (50), 367 (76), 351 (25); HRMS (EI) Calcd for $C_{21}H_{17}F_3N_2O_2$: 386.1242. Found: 386.1239.



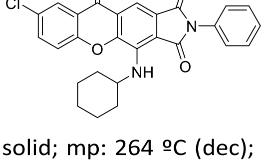
3-Acetyl-4-(cyclohexylamino)-6-methoxy-1-(trifluoromethyl)-9*H*-xanthen-9-one (8az): A solution of chromone **1h** (50 mg, 0.184 mmol), isocyanide **2a** (27 µL, 0.217 mmol) and methyl vinylketone **3f** (18 µL, 0.221 mmol) in THF (2 mL) was irradiated with MW in a sealed vial at 100ºC until the chromone **1h** was consumed (2 hours). Then DBU (55 µL, 0.369 mmol) was added and the mixture was irradiated 30 minutes. The crude was elaborated as the general procedure affording the xanthone **8az** (32 mg , 41 %), obtained as a yellow solid; mp: 206 ºC; IR (cm^{-1}): 3441, 2916, 2846, 1669, 1644, 1623; ^1H NMR (400 MHz, $CDCl_3$) δ 10.00 (d, *J* = 6.6 Hz, NH, 1H), 8.23 (d, *J* = 8.9 Hz, 1H), 8.07 (s, 1H), 6.98 (dd, *J* = 9.0, 2.3 Hz, 1H), 6.75 (d, *J* = 2.3 Hz, 1H), 4.35 (m, 1H), 3.95 (s, 3H), 2.68 (s, 3H), 2.15 (m, 2H), 1.88-1.25 (m, 8H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 201.0 (C), 174.6 (C), 165.8 (C), 156.6 (C), 148.7 (C), 145.6 (C), 129.1 (CH), 127.7 (CH), 122.8 (C), 117.7 (C), 116.8 (C), 114.3 (CH), 99.6 (CH), 55.9 (CH), 55.2 (CH_3), 34.8 (CH_2), 28.4 (CH_3), 25.4 (CH_2), 24.7 (CH_2) ppm; MS (CI) m/z (%) 435 (M+1, 14), 434 (M^+, 100), 428 (25), 414 (65), 383 (95); HRMS (EI) Calcd for $C_{23}H_{22}F_3NO_4$: 433.1501. Found: 433.1509.



4-(Cyclohexylamino)-1-(4-nitrophenyl)-9-oxo-9*H*-xanthene-3-carbonitrile (8ba): A solution of chromone **1j** (48 mg, 0.161 mmol), isocyanide **2a** (24 µL, 0.193 mmol) and acrylonitrile **3e** (20 µL, 0.301 mmol) in THF (2 mL) was irradiated with MW in a sealed vial at 100 ºC until the chromone **1j** was consumed (5 hours). Then DBU (69 µL, 0.462 mmol) was added and the mixture was irradiated 15 minutes. The crude was elaborated as the general procedure, affording xanthone **8ba** (t_1 5 hours, t_2 15 minutes, 39 mg, 56 %), obtained as a yellow solid; mp: 245 ºC; IR (cm^{-1}): 3394, 2920, 2213, 1655, 1606, 1560; ^1H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.44–7.41 (m, 3H), 7.13 (s, 1H), 5.33 (bs, NH, 1H), 4.32 (m, 1H), 2.26 (m, 2H), 1.88-1.25 (m, 8H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 176.4 (C), 154.8 (C), 147.7 (C), 147.0 (C), 146.3 (C), 140.5 (C), 135.4 (CH), 130.4 (CH), 129.9 (CH), 127.1 (CH), 125.4 (CH), 123.1 (CH), 122.4 (C), 120.9 (C), 118.6 (C), 117.6 (CH), 94.7 (C), 52.6 (CH), 34.4 (CH_2), 25.6 (CH_2), 24.5 (CH_2) ppm; MS (CI) m/z (%) 440 (M+1, 41), 439 (M^+, 8), 284 (14), 257 (14); HRMS (EI) Calcd for $C_{26}H_{21}N_3O_4$: 439.1532. Found: 439.1532.

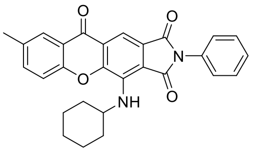


4-(Cyclohexylamino)-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8bb): A solution of chromone **1k** (67 mg, 0.383 mmol), isocyanide **2a** (57 µL, 0.459 mmol) and *N*-phenylmaleimide **3a** (83 mg, 0.479 mmol) in toluene (2 mL) was heated at 110 ºC (bath temperature) under a nitrogen atmosphere until the chromone **1k** was consumed (41 hours). HCl 1N (2 mL) was then added to the reaction mixture, and after 30 minutes, the crude was washed with brine (15 mL), and extracted with CH_2Cl_2 (3 x 15 mL). The organic phase was dried over Na_2SO_4 concentrated and the crude was purified by column chromatography (silica gel, hexane-EtOAc gradient), giving the desire product **8bb** (41 hours, 149 mg, 89 %), obtained as a yellow solid; mp: 202 ºC; IR (cm^{-1}): 3333, 2924, 1753, 1701, 1664, 1608; ^1H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.9 Hz, 1H), 8.06 (s, 1H), 7.77 (t, *J* = 8.6 Hz, 1H), 7.52 – 7.38 (m, 7H), 6.80 (d, *J* = 8.4 Hz, NH, 1H), 4.36 (m, 1H), 2.16 (m, 2H), 1.85 (m, 2H), 1.54 – 1.25 (m, 6H) (m, 8H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 176.3 (C), 168.6 (C), 166.0 (C), 155.2 (C), 149.4 (C), 138.5 (C), 135.5 (CH), 131.7 (C), 129.2 (CH), 128.1 (CH), 126.9 (CH), 126.5 (CH), 126.4 (C), 126.0 (C), 125.3 (CH), 121.4 (C), 117.9 (CH), 113.1 (C), 109.9 (CH), 54.4 (CH), 34.9 (CH_2), 25.6(CH_2), 24.8 (CH_2) ppm; MS (CI) m/z (%) 440 (M+1, 22), 439 (M+1, 100), 438 (M^+, 18), 357 (39), 285 (17); HRMS (EI) Calcd for $C_{27}H_{22}N_2O_4$: 438.1580. Found: 438.1582.

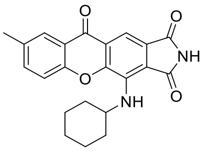


8-Chloro-4-(cyclohexylamino)-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8bc): The general procedure described for the synthesis of **8bb** was applied to a mixture of chromone **1l** (67 mg, 0.321 mmol), isocyanide **2a** (48 µL, 0.387 mmol) and *N*-phenylmaleimide **3a** (69 mg, 0.397 mmol) in toluene (2 mL), affording xanthone **8bc** (25 hours, 140 mg, 92 %), obtained as an orange-red solid; mp: 264 ºC (dec); IR (cm^{-1}): 3337, 3068, 2931, 1757, 1700, 1656, 1614; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 2.6 Hz, 1H), 8.09 (s, 1H), 7.72 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.56 – 7.37 (m, 6H), 6.84 (d, *J* = 7.9 Hz, NH, 1H), 4.36 (m, 1H), 2.15 (m, 2H), 1.86 (m, 2H), 1.69 (m, 1H), 1.53–1.31 (m, 5H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 175.4 (C), 168.6 (C), 165.9 (C), 153.6 (C), 149.4 (C), 138.6 (C), 135.8 (CH), 131.7 (C), 131.4 (C), 129.3

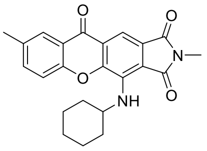
(CH), 128.3 (CH), 126.8 (C), 126.5 (CH), 126.3 (CH), 125.8 (C), 122.4 (C), 119.8 (CH), 113. (C), 109.9 (CH), 54.5 (CH), 34.8 (CH_2), 25.7 (CH_2), 24.7 (CH_2) ppm; MS (CI) m/z (%) 473 (M+1, 21), 472 (M^+, 100), 437 (12), 392 (12); HRMS (EI) Calcd for $C_{27}H_{21}ClN_2O_4$: 472.1190. Found: 472.1190.



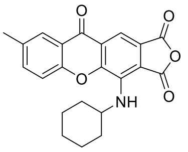
4-(Cyclohexylamino)-8-methyl-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8bd): The general procedure described for the synthesis of **8bb** was applied to a mixture of chromone **1m** (65 mg, 0.343 mmol), isocyanide **2a** (51 µL, 0.411 mmol) and *N*-phenylmaleimide **3a** (71 mg, 0.410 mmol) in toluene (2 mL), affording xanthone **8bd** (60 hours, 135 mg, 87 %), obtained as a dark yellow solid; mp: 232 ºC; IR (cm^{-1}): 3342, 2922, 1755, 1693, 1660, 1615; ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 5.5 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.55 – 7.32 (m, 6H), 6.80 (bs, NH, 1H), 4.39 (m, 1H), 2.49 (s, 3H), 2.16 (m, 2H), 1.85 (m, 2H), 1.74–1.23 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 176.6 (C), 168.7 (C), 166.2 (C), 153.7 (C), 149.6 (C), 138.6 (C), 136.8 (CH), 135.4 (C), 131.8 (C), 129.3 (CH), 128.1 (CH), 126.7 (CH), 126.4 (CH), 126.3 (C), 125.9 (C), 121.3 (C), 117.8 (CH), 113.0 (C), 110.2 (CH), 54.5 (CH), 35.0 (CH_2), 25.7 (CH_2), 24.7 (CH_2), 21.14 (CH_3) ppm; MS (CI) m/z (%) 454 (M+2, 15), 452 (M^+, 29), 371 (24), 293 (46); HRMS (EI) Calcd for $C_{28}H_{24}N_2O_4$: 452.1736. Found: 452.1737.



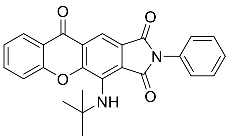
4-(Cyclohexylamino)-8-methylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8be): The general procedure described for the synthesis of **8bb** was applied to a mixture of chromone **1m** (68 mg, 0.360 mmol), isocyanide **2a** (54 µL, 0.435 mmol) and maleimide **3d** (43 mg, 0.446 mmol) in toluene (2 mL), affording xanthone **8be** (48 hours, 118 mg, 87 %), obtained as an orange solid; mp: 239 ºC (dec); IR (cm^{-1}): 3227, 2929, 1754, 1707, 1649, 1616; ^1H NMR (400 MHz, DMSO) δ 11.19 (bs, NH, 1H), 7.88 (s, 1H), 7.70–7.54 (m, 3H), 6.56 (d, *J* = 8.5 Hz, NH, 1H), 4.33 (m, 1H), 2.43 (s, 3H), 2.04 (m, 2H), 1.83–1.25 (m, 8H) ppm; ^{13}C NMR (101 MHz, DMSO): 175.3 (C), 169.6 (C), 167.4 (C), 152.9 (C), 148.5 (C), 137.3 (C), 136.7 (CH), 134.7 (C), 127.5 (C), 124.7 (CH), 124.2 (C), 120.1 (C), 117.9 (CH), 113.5 (C), 106.9 (CH), 53.5 (CH), 33.8 (CH_2), 25.0 (CH_2), 24.0 (CH_2), 20.2 (CH_3) ppm; MS (CI) m/z (%) 378 (M+2, 51), 377 (M+1, 67), 350 (10), 334 (30), 256 (40); HRMS (EI) Calcd for $C_{22}H_{20}N_2O_4$: 376.1423. Found: 376.1425.



4-(Cyclohexylamino)-2,8-dimethylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8bf): The general procedure described for the synthesis of **8bb** was applied to a mixture of chromone **1m** (64 mg, 0.339 mmol), isocyanide **2a** (51 µL, 0.411 mmol) and *N*-methylmaleimide **3b** (47 mg, 0.424 mmol) in toluene (2 mL), affording xanthone **8bf** (59 hours, 93 mg, 70 %), obtained as a red solid; mp: 234 ºC (dec); IR (cm^{-1}): 3337, 2926, 2850, 1747, 1697, 1655, 1612; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (m, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, NH, 1H), 4.33 (m, 1H), 3.15 (s, 3H), 2.48 (s, 3H), 2.14 (m, 2H), 1.84 (m, 2H), 1.59–1.19 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 176.4 (C), 169.5 (C), 167.2 (C), 153.5 (C), 149.4 (C), 137.9 (C), 136.6 (CH), 135.2 (C), 126.7 (C), 126.1 (CH), 125.4 (C), 121.1 (C), 117.6 (CH), 113.7 (C), 109.7 (CH), 54.2 (CH), 34.8 (CH_2), 25.6 (CH_2), 24.7 (CH_2), 23.9 (CH_3), 20.9 (CH_3) ppm; MS (CI) m/z (%) 391 (M+1, 51), 390 (M^+, 15), 347 (11), 309 (14), 257 (19); HRMS (EI) Calcd for $C_{23}H_{22}N_2O_4$: 390.1580. Found: 390.1580.

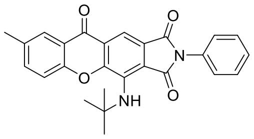


4-(Cyclohexylamino)-8-methyl-1*H*-furo[3,4-*b*]xanthene-1,3,10-trione (8bg): The general procedure described for the synthesis of **8bb** was applied to a mixture of chromone **1m** (70 mg, 0.369 mmol), isocyanide **2a** (55 µL, 0.443 mmol) and maleic anhydride **3c** (44 mg, 0.448 mmol) in toluene (2 mL), affording xanthone **8bg** (62 hours, 64 mg, 46 %), obtained as a yellow solid; mp: 291 ºC (dec); IR (cm^{-1}): 3358, 2933, 1815, 1759, 1662, 1615; ^1H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 2H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 6.34 (d, *J* = 7.7 Hz, NH, 1H), 4.49 (m, 1H), 2.51 (s, 3H), 2.18 (m, 2H), 1.86 (m, 2H), 1.77–1.25 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 176.1 (C), 164.0 (C), 162.4 (C), 153.6 (C), 149.3 (C), 139.6 (C), 137.2 (CH), 136.0 (C), 126.6 (C), 126.5 (CH), 125.5 (C), 121.2 (C), 117.8 (CH), 111.7 (CH), 54.7 (CH), 34.9 (CH_2), 25.5 (CH_2), 24.8 (CH_2), 21.1 (CH_3) ppm; MS (CI) m/z (%) 379 (M+2, 24), 378 (M+1, 58), 377 (M^+, 80), 373 (13), 350 (10); HRMS (EI) Calcd for $C_{22}H_{19}NO_5$: 377.1263. Found: 377.1256.

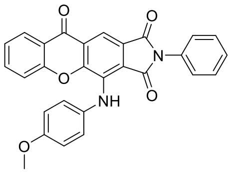


4-(*tert*-Butylamino)-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8bh): The general procedure described for the synthesis of **8bb** was applied to a mixture of chromone **1k** (61 mg, 0.351 mmol), isocyanide **2b** (48 µL, 0.426 mmol) and *N*-phenylmaleimide **3a** (76 mg, 0.438 mmol) in toluene (2 mL), affording xanthone **8bh** (124 hours, 84 mg, 58 %), obtained as a yellow solid; mp: 201 ºC; IR (cm^{-1}):

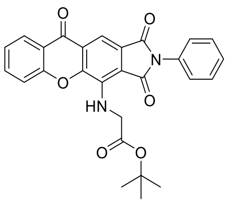
3333, 2958, 1754, 1707, 1666, 1608; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.9 Hz, 1H), 8.24 (s, 1H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.54-7.41 (m, 6H), 7.13 (bs, NH, 1H), 1.64 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 176.6 (C), 169.1 (C), 165.9 (C), 155.4 (C), 150.2 (C), 139.6 (C), 135.6 (CH), 131.6 (C), 129.3 (CH), 128.3 (CH), 127.2 (CH), 126.6 (C), 126.5 (CH), 126.3 (C), 125.4 (CH), 121.6 (C), 117.6 (CH), 116.6 (C), 111.8 (CH), 54.9 (C), 31.8 (CH_3) ppm; MS (CI) m/z (%) 414 (M+2, 10), 413 (M+1, 38), 385 (15), 357 (43); HRMS (EI) Calcd for $C_{25}H_{20}N_2O_4$: 412.1423. Found: 412.1422.



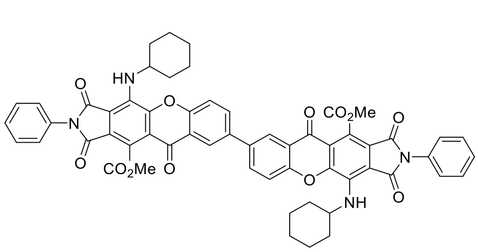
4-(*tert*-Butylamino)-8-methyl-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8bi): The general procedure described for the synthesis of **8bb** was applied to a mixture of chromone **1m** (68 mg, 0.360 mmol), isocyanide **2b** (49 µL, 0.434 mmol) and *N*-phenylmaleimide **3a** (78 mg, 0.449 mmol) in toluene (2 mL), affording xanthone **8bi** (29 hours, 51 mg, 33 %), obtained as a yellow solid; mp: 266 ºC (dec); IR (cm^{-1}): 3340, 2969, 1757, 1705, 1657, 1615; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.15 (s, 1H), 7.62 (m, 1H), 7.53 (m, 3H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 2.51 (s, 3H), 1.63 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 176.7 (C), 169.2 (C), 165.9 (C), 153.7 (C), 150.3 (C), 139.7 (C), 136.9 (CH), 135.5 (C), 131.7 (C), 129.3 (CH), 128.3 (CH), 126.6 (CH), 126.5 (C), 126.4 (CH), 126.1 (C), 121.3 (C), 117.5 (CH), 116.4 (C), 111.9 (CH), 54.9 (C), 31.8 (CH_3), 21.1 (CH_3) ppm; MS (CI) m/z (%) 427 (M+1, 40), 426 (M^+, 13), 371 (32), 313 (40), 267 (39); HRMS (EI) Calcd for $C_{26}H_{22}N_2O_4$: 426.1580. Found: 426.1581.



4-((4-Methoxyphenyl)amino)-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8bj): The general procedure described for the synthesis of **8bb** was applied to a mixture of chromone **1k** (62 mg, 0.358 mmol), isocyanide **2f** (65 mg, 0.488 mmol) and *N*-phenylmaleimide **3a** (78 mg, 0.450 mmol) in toluene (2 mL), affording xanthone **8bj** (41 hours, 69 mg, 42 %), obtained as a dark orange solid; mp: 253 ºC; IR (cm^{-1}): 3336, 1762, 1703, 1652, 1609; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.28 (s, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.55–7.46 (m, 4H), 7.42 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 8.4, 0.6 Hz, 1H), 3.87 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 176.4 (C), 168.6 (C), 166.0 (C), 157.6 (C), 154.9 (C), 150.0 (C), 135.8 (C), 135.6 (CH), 134.2 (C), 131.7 (C), 129.3 (CH), 128.3 (CH), 126.7 (CH), 126.6 (CH), 126.4 (C), 126.0 (C), 125.4 (CH), 125.3 (CH), 121.4 (C), 118.1 (CH), 115.7 (C), 114.0 (CH), 112.4 (CH), 55.8 (CH_3) ppm; MS (CI) m/z (%) 464 (M+2, 16), 463 (M+1, 40), 462 (M^+, 11), 307 (9), 225 (13); HRMS (EI) Calcd for $C_{28}H_{18}N_2O_5$: 462.1216. Found: 462.1216.

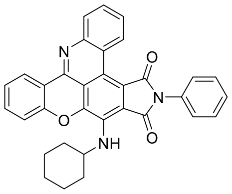


***tert*-Butyl (1,3,10-trioxo-2-phenyl-1,2,3,10-tetrahydrochromeno[2,3-*f*]isoindol-4-yl) glycinate (8bk)**: The general procedure described for the synthesis of **8bb** was applied to a mixture of chromone **1k** (64 mg, 0.365 mmol), isocyanide **2g** (64 µL, 0.440 mmol) and *N*-phenylmaleimide **3a** (78 mg, 0.450 mmol) in toluene (2 mL), affording xanthone **8bk** (95 hours, 146 mg, 85 %), obtained as a dark yellow solid; mp: 276 ºC; IR (cm^{-1}): 3295, 1755, 1737, 1702, 1654, 1612; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.0 Hz, 1H), 8.18 (s, 1H), 7.80 (t, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.54–7.44 (m, 5H), 7.44–7.38 (m, 1H), 7.12 (t, *J* = 5.9 Hz, NH, 1H), 4.60 (d, *J* = 6.0 Hz, 2H), 1.45 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 176.3 (C), 169.6 (C), 167.9 (C), 166.1 (C), 155.3 (C), 149.6 (C), 138.1 (C), 135.5 (CH), 131.8 (C), 129.2 (CH), 128.2 (CH), 127.1 (CH), 126.7 (CH), 126.6 (C), 125.6 (C), 125.5 (CH), 121.5 (C), 118.2 (CH), 113.6 (C), 110.9 (CH), 82.8 (C), 48.7 (CH_2), 28.2 (CH_3) ppm; MS (CI) m/z (%) 471 (M+1, 27), 415 (15), 307 (9), 225 (13); HRMS (EI) Calcd for $C_{27}H_{22}N_2O_6$: 470.1478. Found: 470.1480.

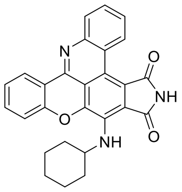


Dimethyl 4,4'-bis(cyclohexylamino)-1,1',3,3',10,10'-hexaoxo-2,2'-diphenyl-1,1',2,2',3,3',10,10'-octahydro-[8,8'-bichromeno[2,3-*f*]isoindole]-11,11'-dicarboxylate (19): To a solution of bischromone **18** (139 mg, 0.3 mmol) in dry THF (2 mL), isocyanide **2a** (89 µL ,0.72 mmol) and *N*-phenylmaleimide **3a** (208 mg ,1.2 mmol) were added. The resulting mixture was heated at 80 ºC (bath temperature) under a nitrogen atmosphere until the chromone **18** was consumed (6 hours). HCl 1N (2 mL) was then added to the reaction mixture, and after 30 minutes, the crude was washed with brine (15 mL), and extracted with CH_2Cl_2 (3 x 15 mL). The organic phase was dried over Na_2SO_4 and concentrated, and the solid was washed with hexane and ethyl acetate, giving the desired product **20** (234 mg, 79 %), obtained as a yellow solid; mp: 355 ºC (dec); IR (cm^{-1}): 3455, 2929, 1762, 1701, 1664, 1614; ^{1}H NMR (500 MHz, $CDCl_3$) δ

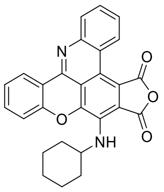
8.16 (s, 2H), 8.01 (d, *J* = 7.9 Hz, 2H), 7.59-7.42 (m, 11H), 6.78 (s, 2H), 4.34 (s, 2H), 4.18 (s, 6H), 4.12 (s, 1H), 2.15-1.30 (m, 20H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): 175.1 (C), 167.7 (C), 166.8 (C), 164.7 (C), 154.2 (C), 148.8 (C), 138.7 (C), 136.2 (C), 134.4 (CH), 131.4 (C), 129.3 (CH), 128.4 (CH), 126.6 (CH), 124.2 (CH), 123.7 (C), 122.4 (C), 121.3 (C), 119.3 (CH), 118.2 (C), 112.6 (C), 54.4 (CH), 53.4 (CH_3), 34.4 (CH_2), 25.6 (CH_2), 24.5 (CH_2) ppm; HRMS (ESI-ICP-Q-TOF) Calcd for $C_{58}H_{46}N_4O_{12}$ H^-: 989.3039. Found: 989.3069.



8-(Cyclohexylamino)-6-phenyl-5*H*-chromeno[4,3,2-gh]pyrrolo[3,4-k]phenanthridine-5,7(6*H*)-dione (20aq): A solution of xanthone **8aq** (25 mg, 0.044 mmol) and iron (18 mg, 0.323 mmol) in acetic acid (1 mL) was heated at 130 ºC under nitrogen until the starting xanthone was consumed. Then the organic phase was filter over celite, and extracted with NaOH 2M (3 x 20 mL), dried over Na_2SO_4 and purified by chromatographic column (gradient AcOEt:hexane) yielding the desired product **13aq** (15 hours, 12 mg, 54 %), obtained as a red solid; mp: 190 ºC; IR (cm^{-1}): 3423, 2924, 2849, 1745, 1693, 1586; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.82 (d, *J* = 8.4 Hz, 1H), 8.53 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.58–7.41 (m, 8H), 7.30 (t, *J* = 7.1 Hz, 1H), 7.15 (bs, NH, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 4.17 (m, 1H), 2.16 (m, 2H), 1.86 (m, 2H), 1.60-1.38 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): 168.9 (C), 166.8 (C), 152.3 (C), 145.9 (C), 144.9 (C), 144.7 (C), 134.6 (C), 132.4 (CH), 131.9 (C), 129.9 (CH), 129.4 (CH), 129.2 (CH), 128.9 (CH), 128.3 (CH), 127.1 (CH), 126.4 (CH), 125.6 (CH), 125.2 (CH), 124.3 (C), 122.3 (C), 121.0 (C), 119.0 (C), 118.4 (C), 117.8 (C), 116.6 (CH), 54.1 (CH), 35.1 (CH_2), 25.8 (CH_2), 24.9 (CH_2) ppm; MS (CI) m/z (%) 513 (M+2, 33), 512 (M+1, 59), 511 (M^+, 41), 478 (14), 350 (10); HRMS (EI) Calcd for $C_{33}H_{25}N_3O_3$: 511.1896. Found: 511.1892.



8-(Cyclohexylamino)-5*H*-chromeno[4,3,2-*gh*]pyrrolo[3,4-*k*]phenanthridine-5,7(6*H*)-dione (20ar): The general procedure described for the synthesis of **13aq** was applied to a mixture of xanthone **8ar** (35 mg, 0.071 mmol) and iron (30 mg, 0.531 mmol) in acetic acid (2 mL), yielding the desired product **13ar** (12 hours, 13 mg, 43 %), obtained as a red solid; mp: 303 ºC; IR (cm^{-1}): 3442, 2922, 1696, 1637; ^{1}H NMR (500 MHz, Acetone) δ 10.05 (d, *J* = 8.4, Hz, 1H), 8.63 (d, *J* = 7.9 Hz, 1H), 7.95 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.74 – 7.61 (m, 2H), 7.54 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.49 – 7.36 (m, 2H), 7.16 (t, *J* = 25.2 Hz, 1H), 4.34 (dt, *J* = 14.0, 4.7 Hz, 1H), 2.26 – 2.14 (m, 2H), 1.84 (ddd, *J* = 23.7, 13.9, 9.7 Hz, 2H), 1.74 – 1.64 (m, 2H), 1.62 – 1.50 (m, 2H), 1.48 – 1.33 (m, 3H). The low solubility of this compound in the usual solvents made impossible to obtain ^{13}C-NMR data; HRMS (ESI-ICP-Q-TOF) Calcd for $C_{27}H_{21}N_3O_3$ H^+: 436.1656 Found: 436.1656.



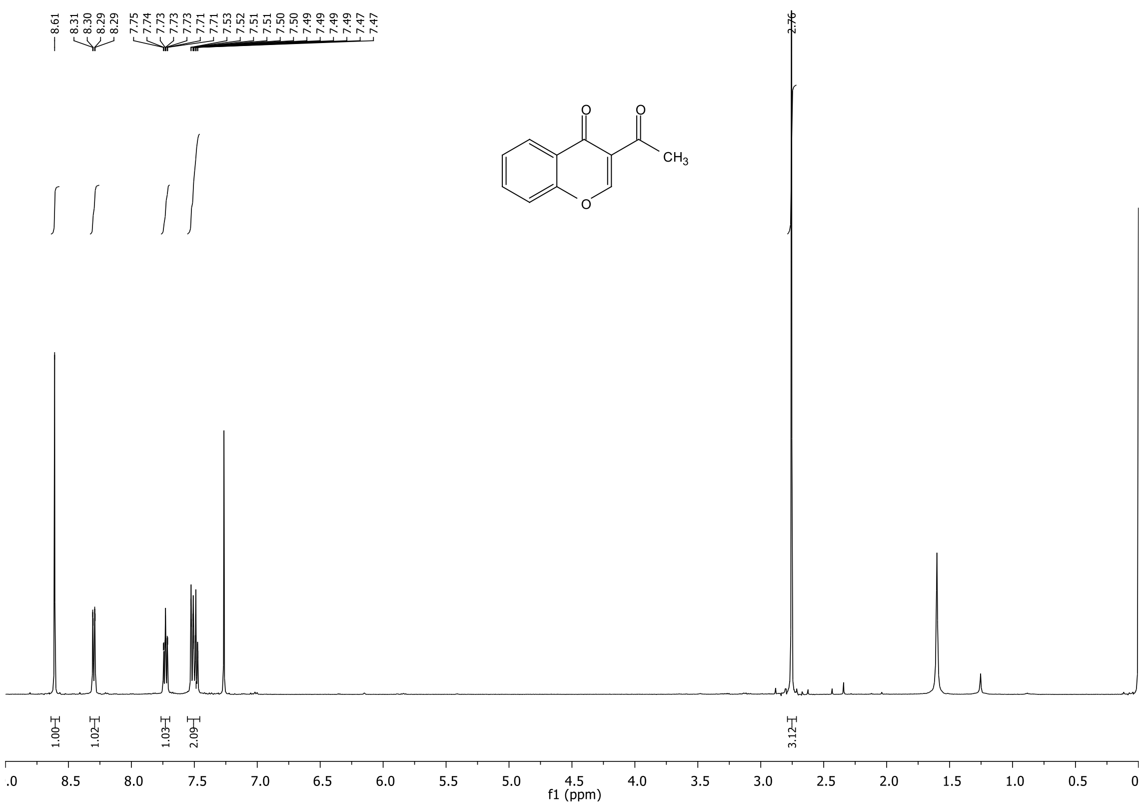
8-(Cyclohexylamino)chromeno[4,3,2-*gh*]furo[3,4-*k*]phenanthridine-5,7-dione (20as): The general procedure described for the synthesis of **13aq** was applied to a mixture of xanthone **8as** (49 mg, 0.100 mmol) and iron (47 mg, 0.845 mmol) in acetic acid (2 mL), yielding the desired product **13as** (50 hours, 19 mg, 43 %), obtained as a red solid; mp: 339 ºC (dec); IR (cm^{-1}): 3358, 2933, 1815, 1759, 1662, 1615; The low solubility of this compound in the usual solvents made impossible to obtain NMR data ; HRMS (ESI-ICP-Q-TOF) Calcd for $C_{27}H_{20}N_2O_4$ H^+: 437.1496. Found: 437.1496.

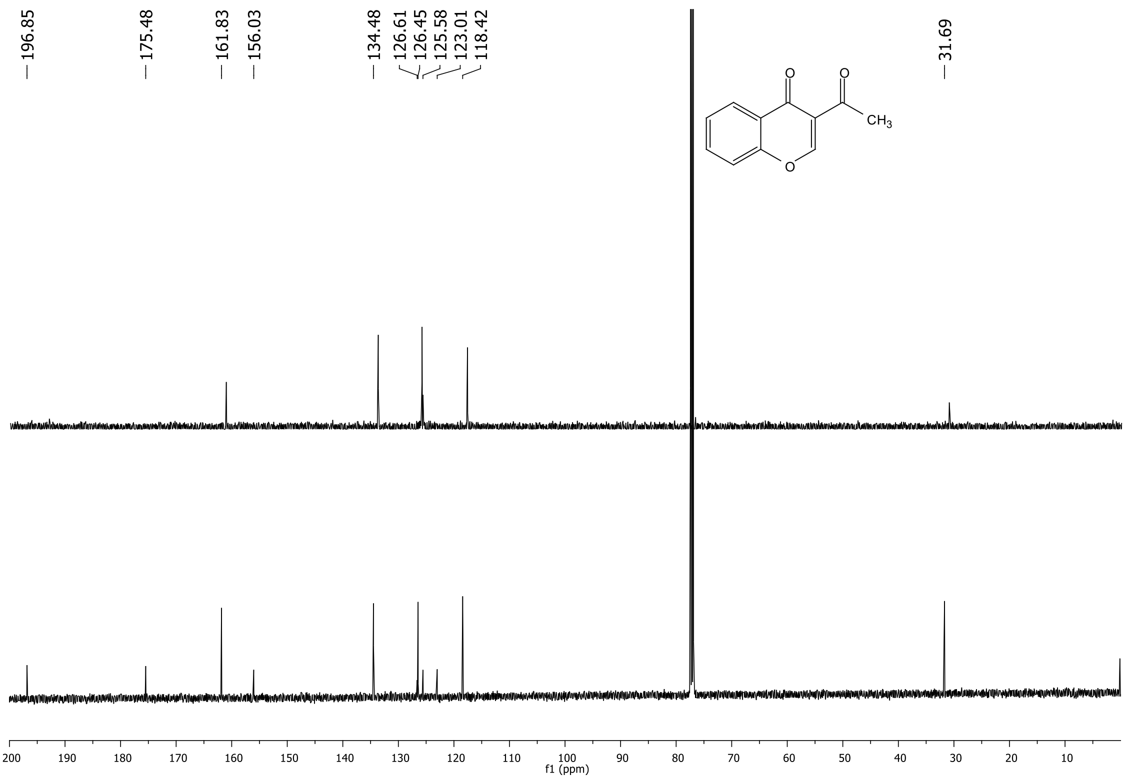
References

1. (a) A. Bornadiego, J. Diaz and C. F. Marcos, *Adv. Synth. Catal.*, 2014, **356**, 718-722; (b) G. Sagrera, A. Bertucci, A. Vazquez and G. Seoane, *Bioorg. Med. Chem.*, 2011, **19**, 3060-3073.
2. L. A. Stubbing, F. F. Li, D. P. Furkert, V. E. Caprio and M. A. Brimble, *Tetrahedron*, 2012, **68**, 6948-6956.
3. V. Y. Sosnovskikh and R. A. Irgashev, *Synlett*, 2005, 1164-1166.
4. V. O. Iaroshenko, I. Savych, A. Villinger, V. Y. Sosnovskikh and P. Langer, *Org. Biomol. Chem.*, 2012, **10**, 9344-9348.

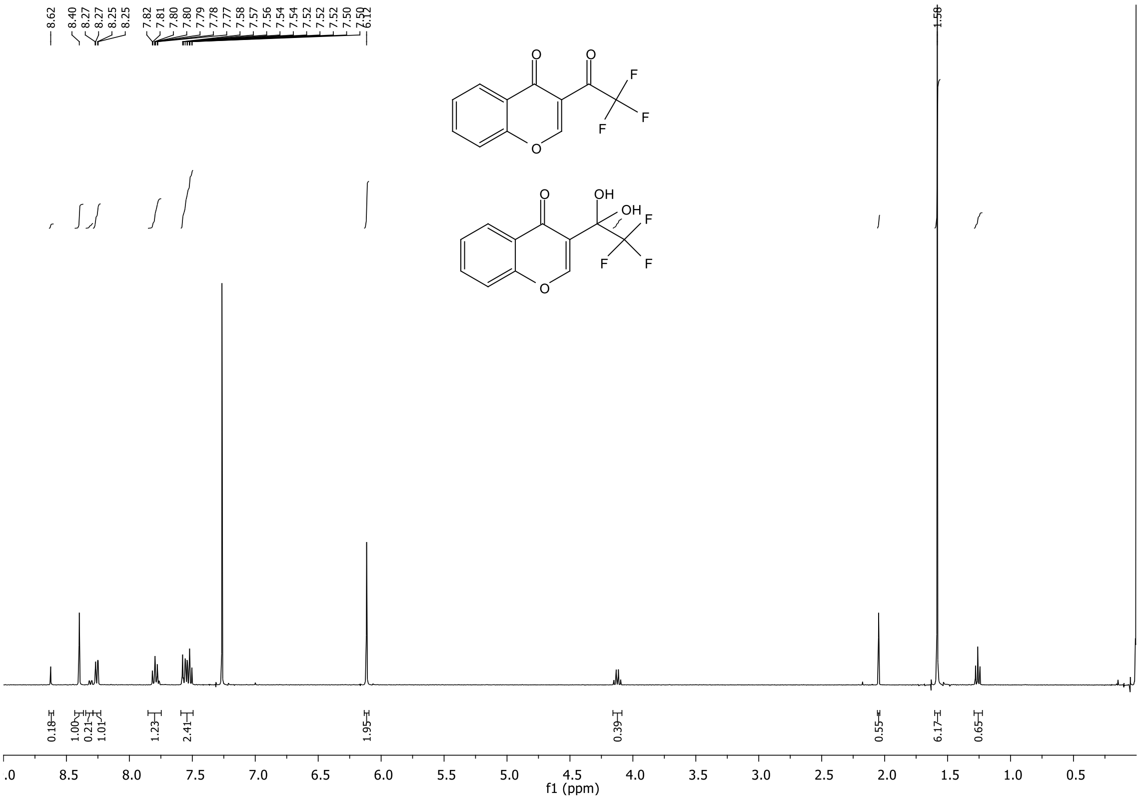
NMR SPECTRA

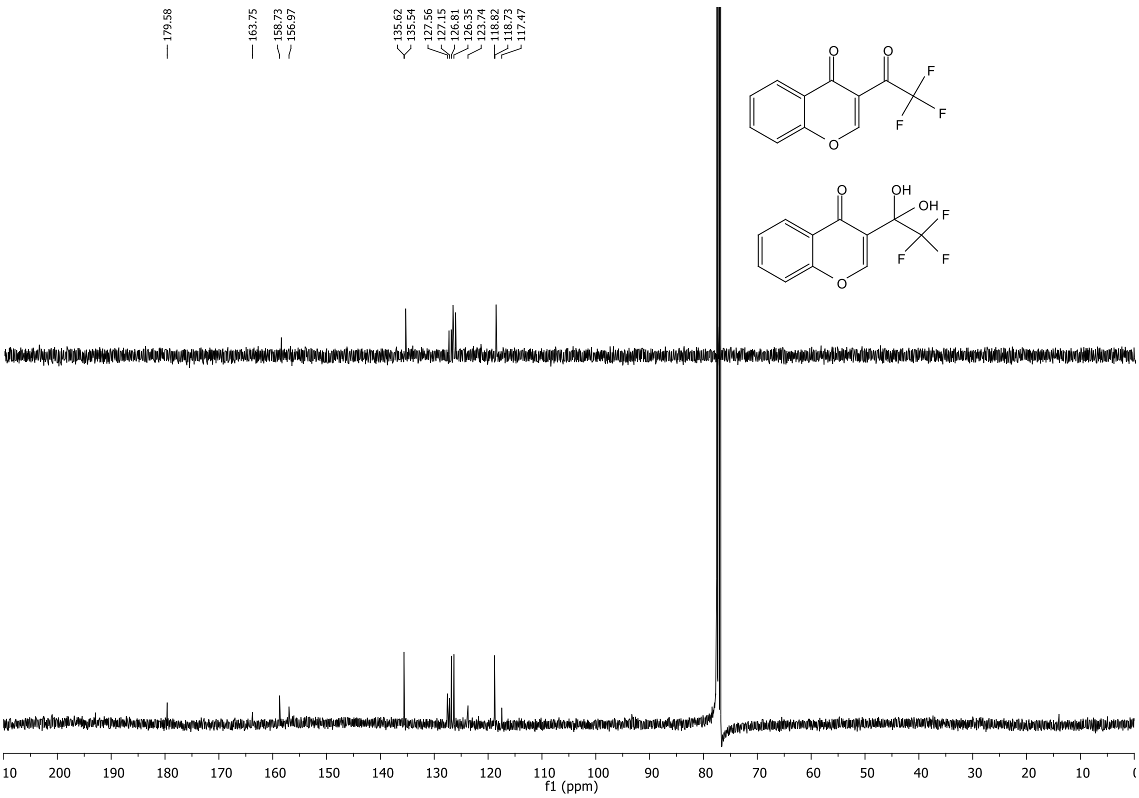
3-Acetyl-4*H*-chromen-4-one (1f)



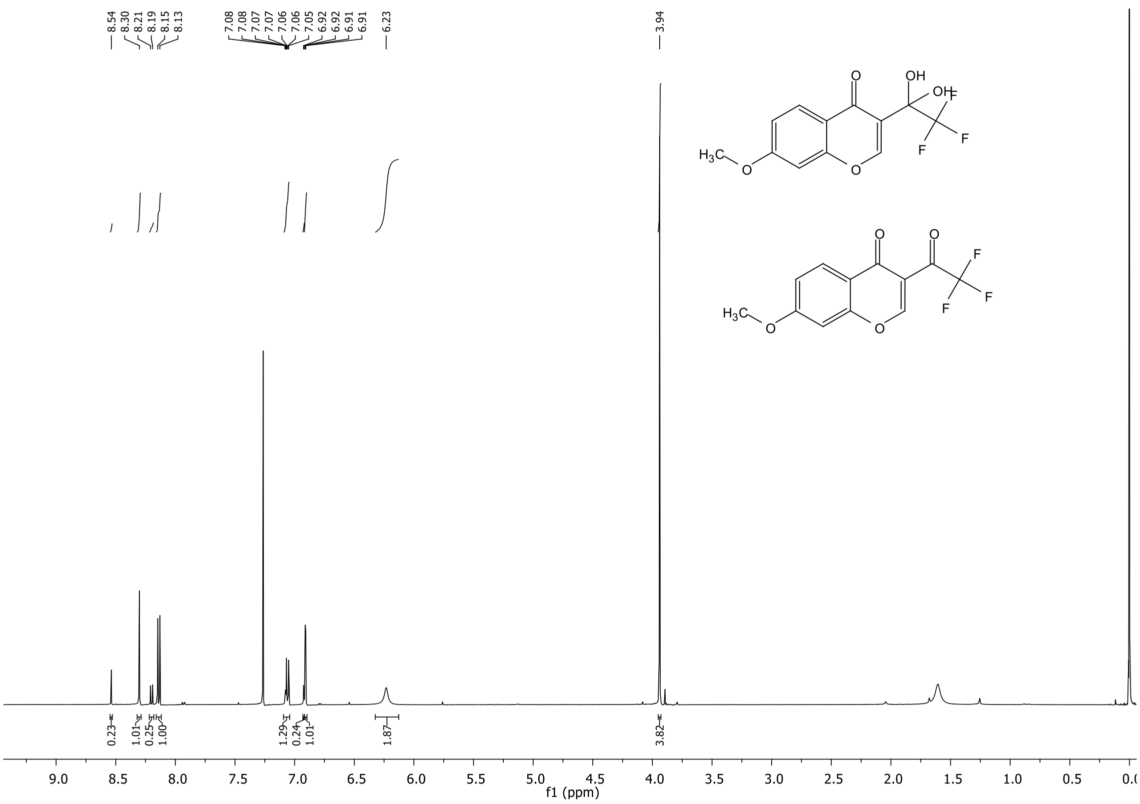


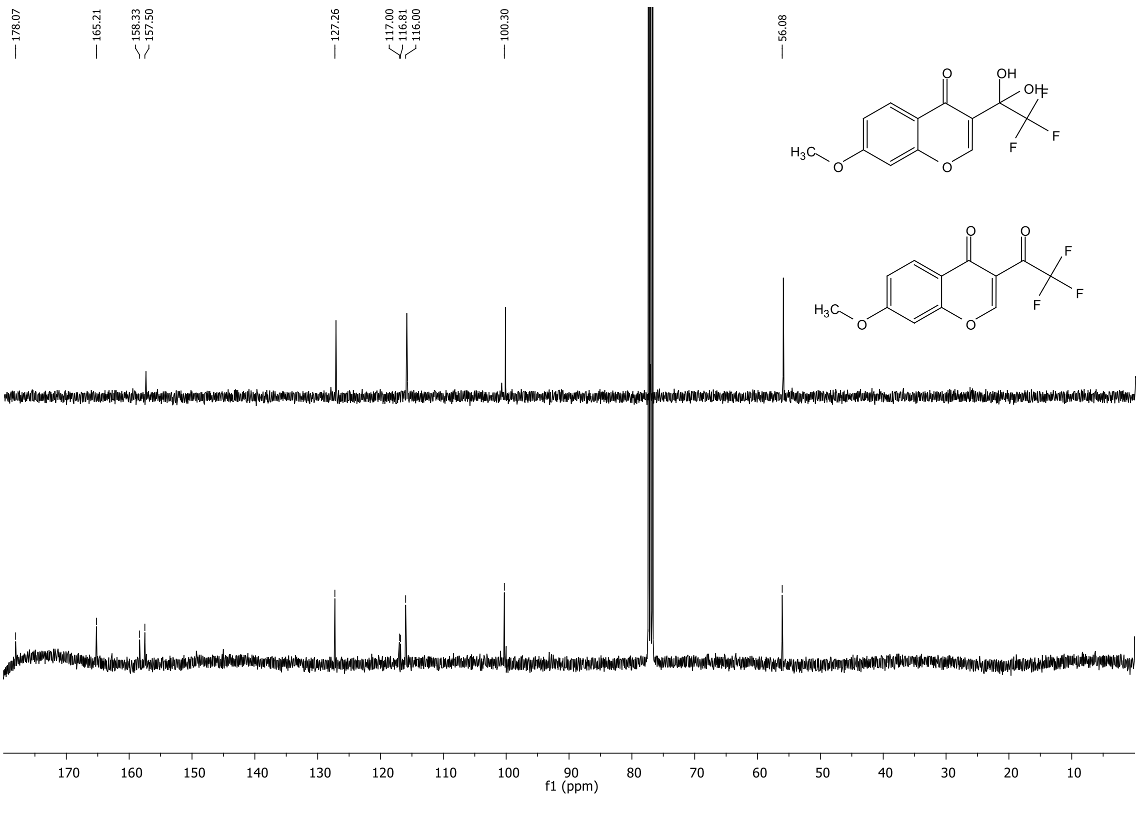
3-(2,2,2-Trifluoroacetyl)-4*H*-chromen-4-one (1g)



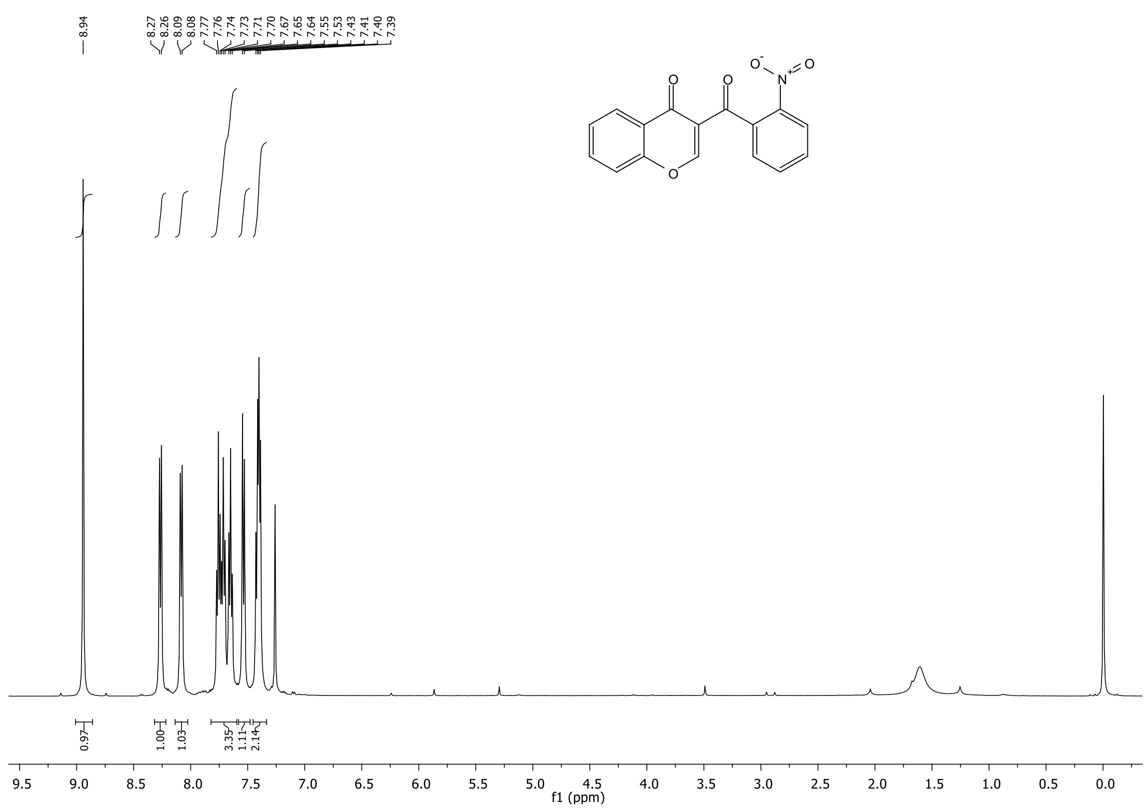


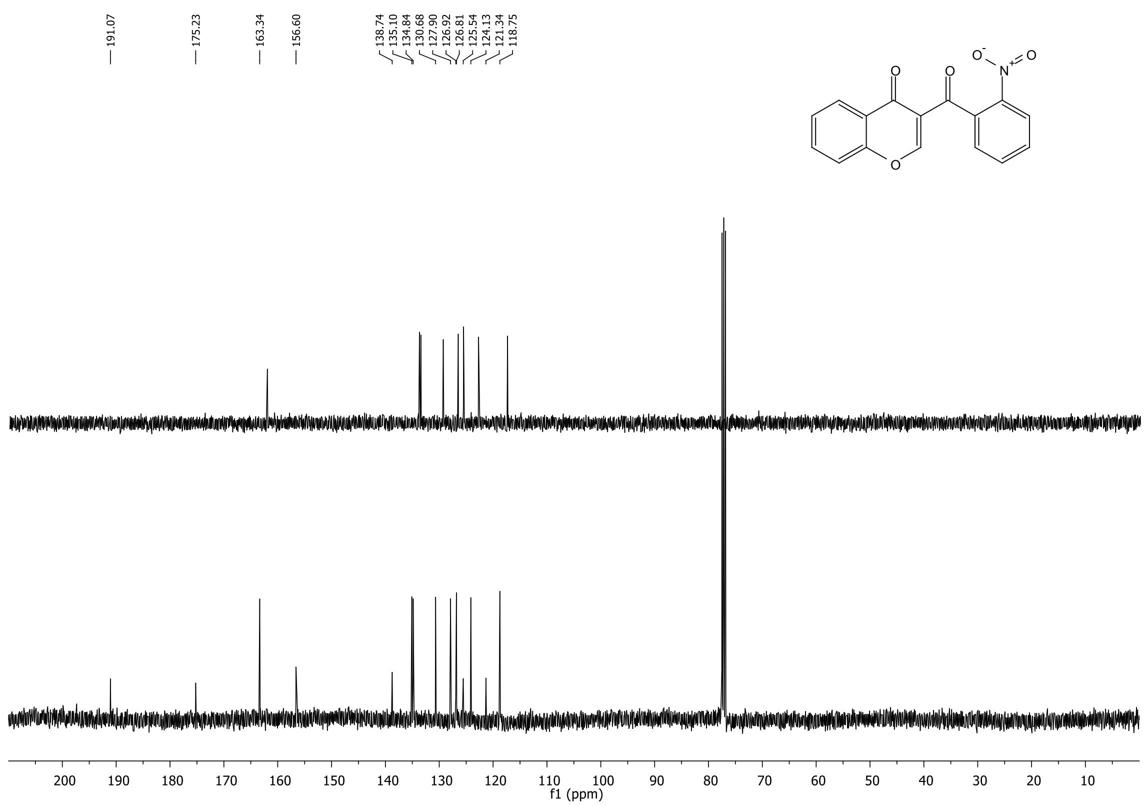
7-Methoxy-3-(2,2,2-trifluoroacetyl)-4*H*-chromen-4-one (1h)



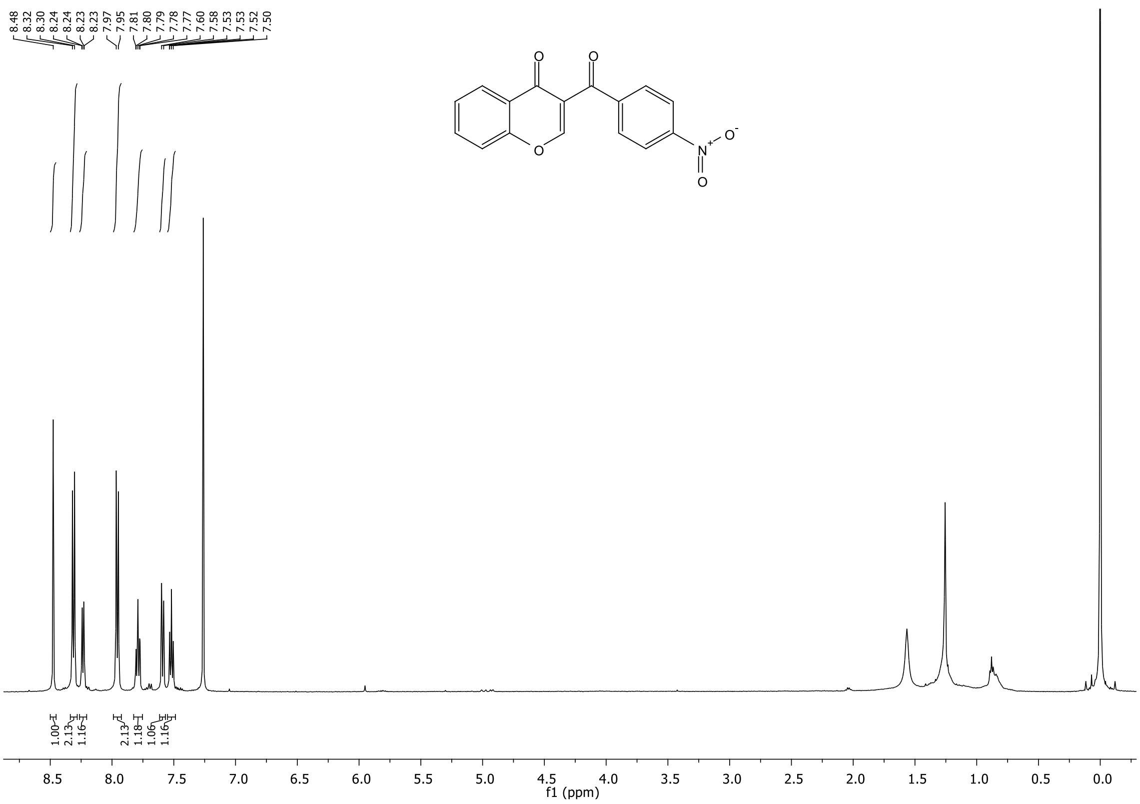


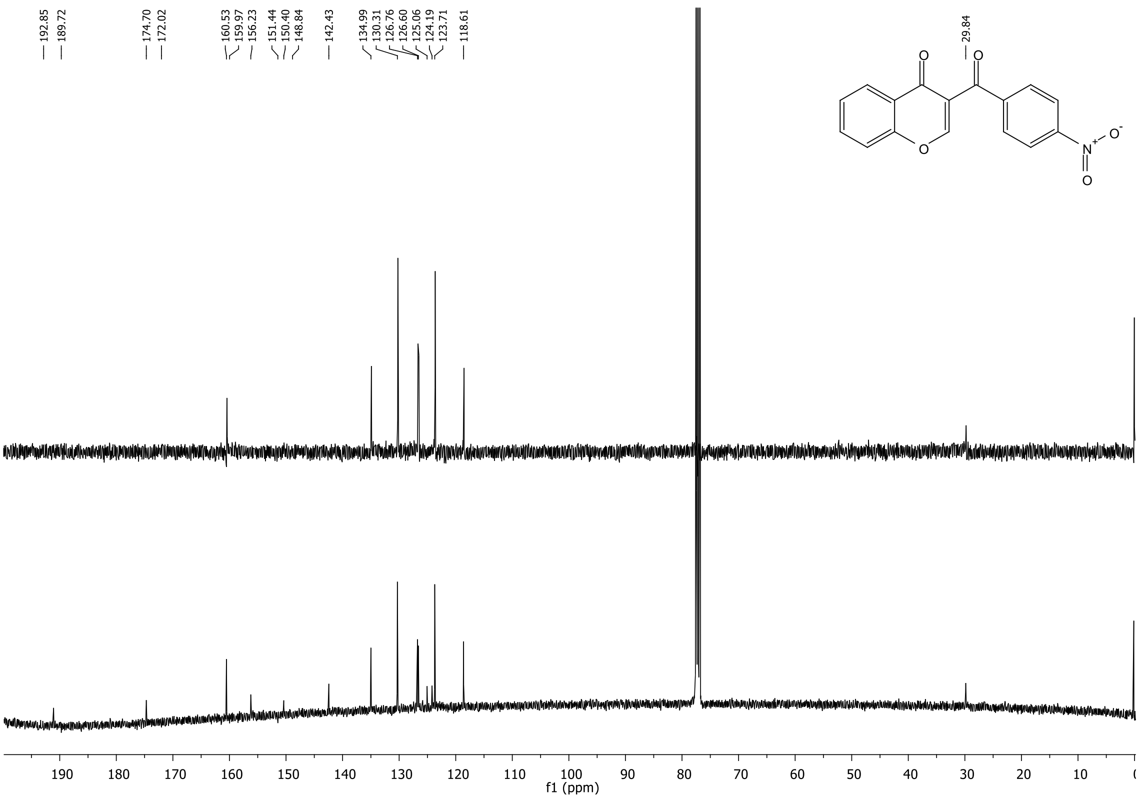
3-(2-Nitrobenzoyl)-4*H*-chromen-4-one (1i)



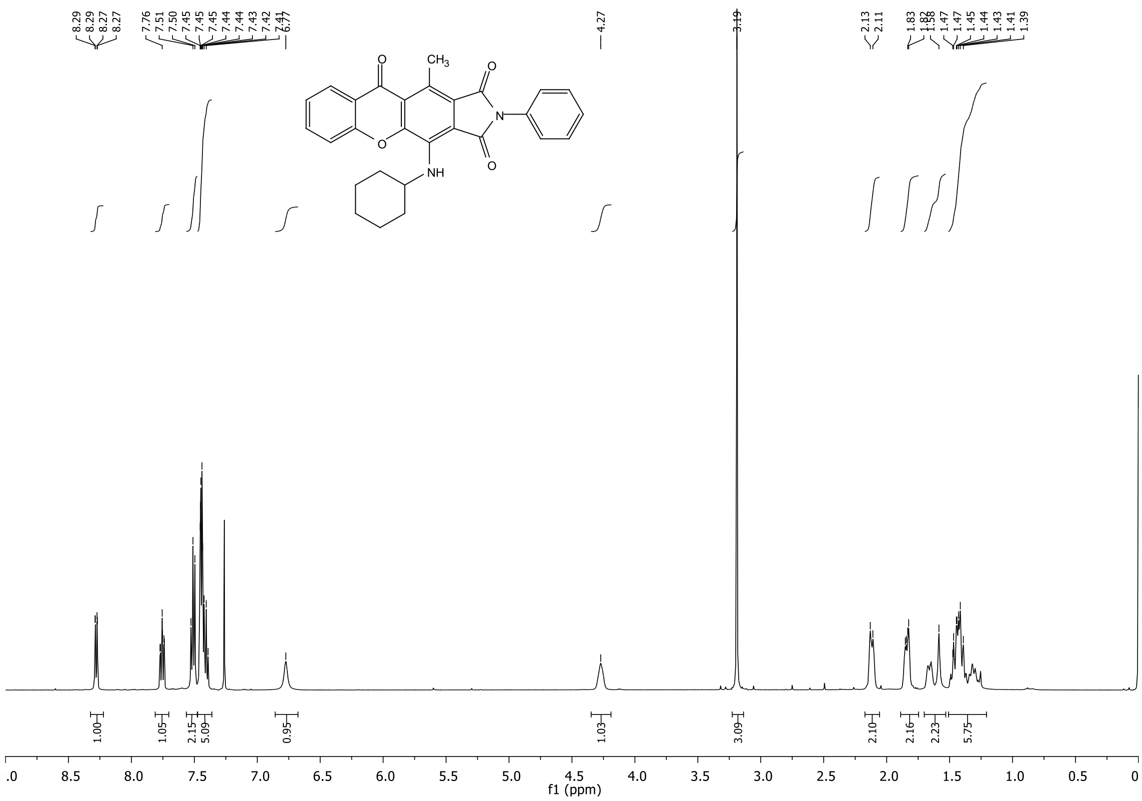


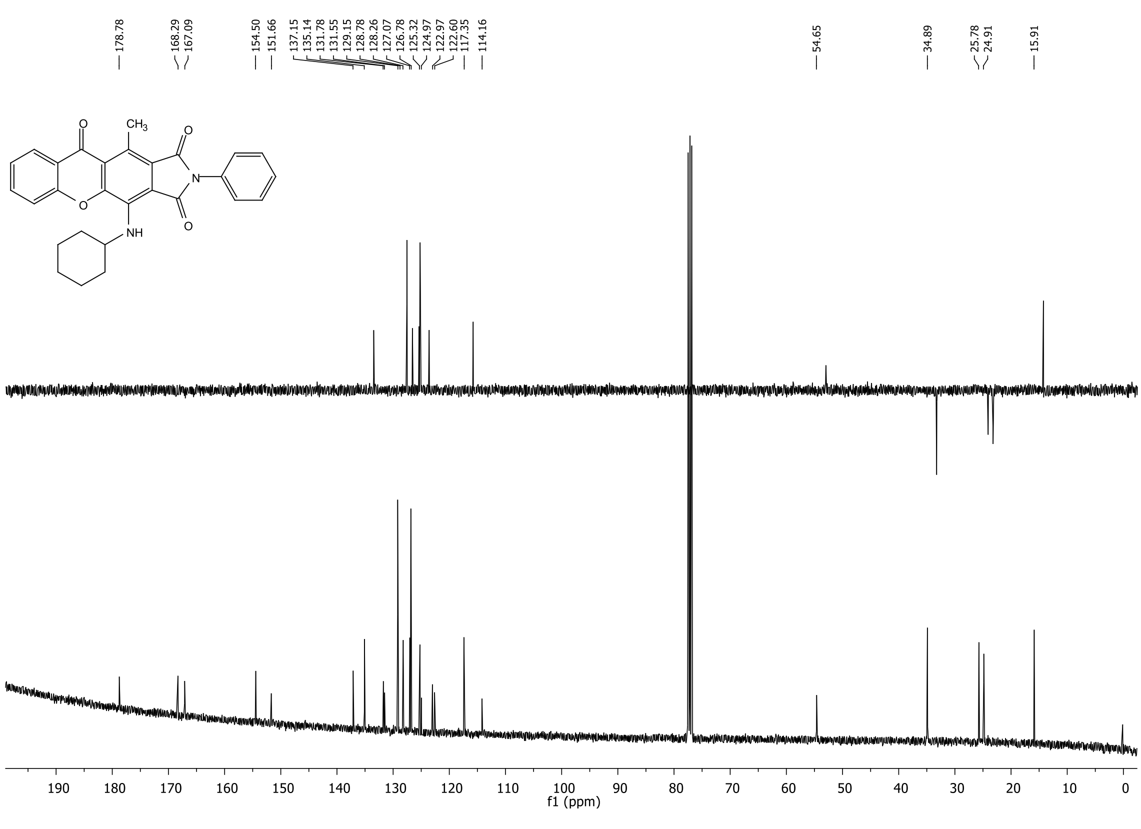
3-(4-nitrobenzoyl)-4*H*-chromen-4-one (1j)



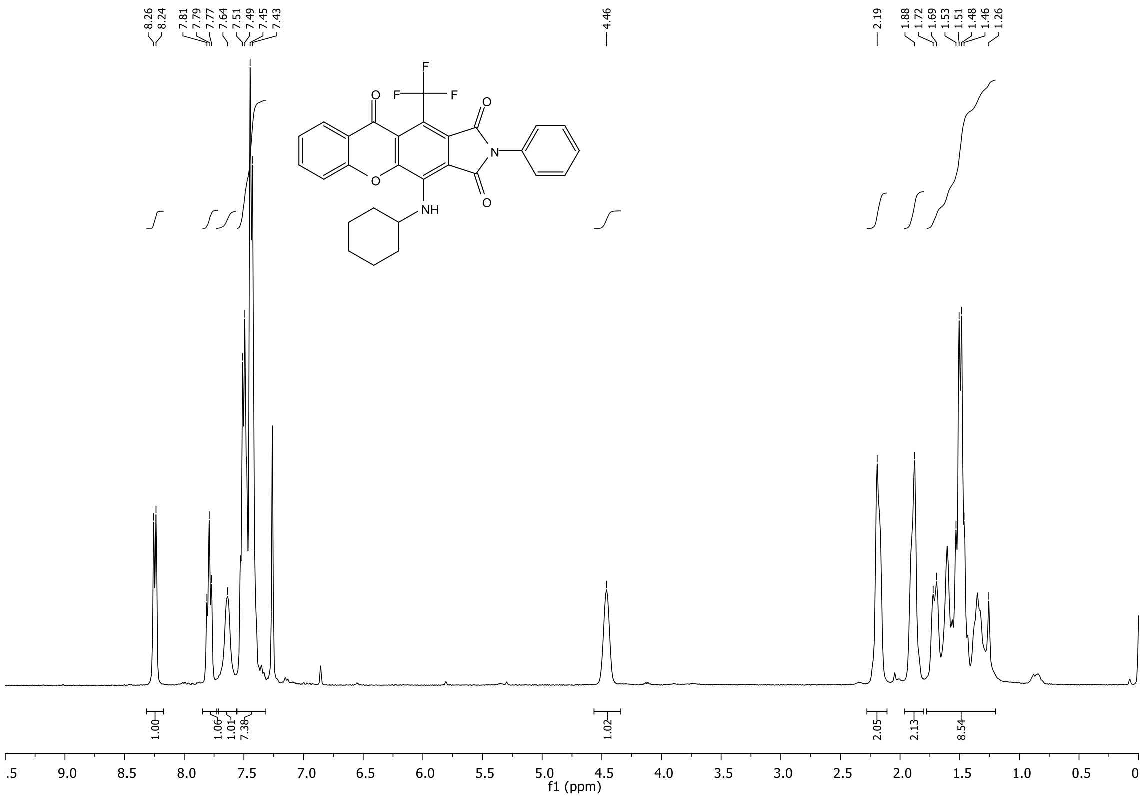


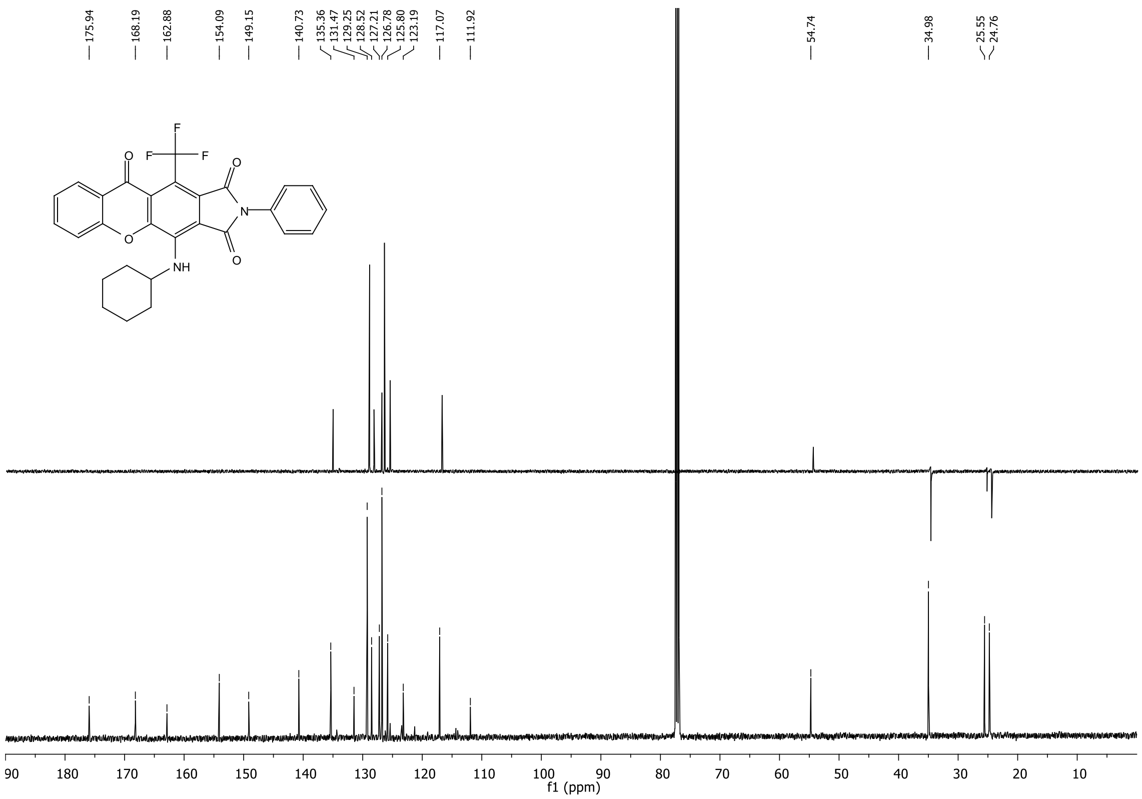
4-(Cyclohexylamino)-11-methyl-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8ak)



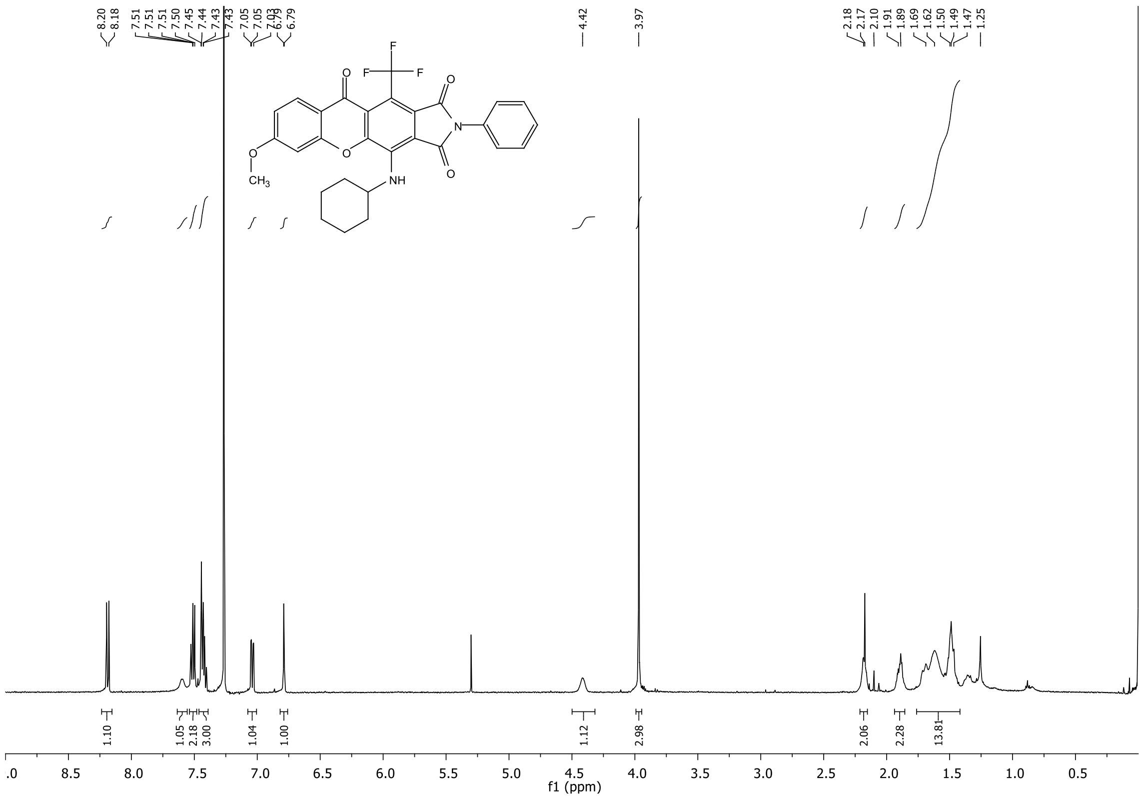


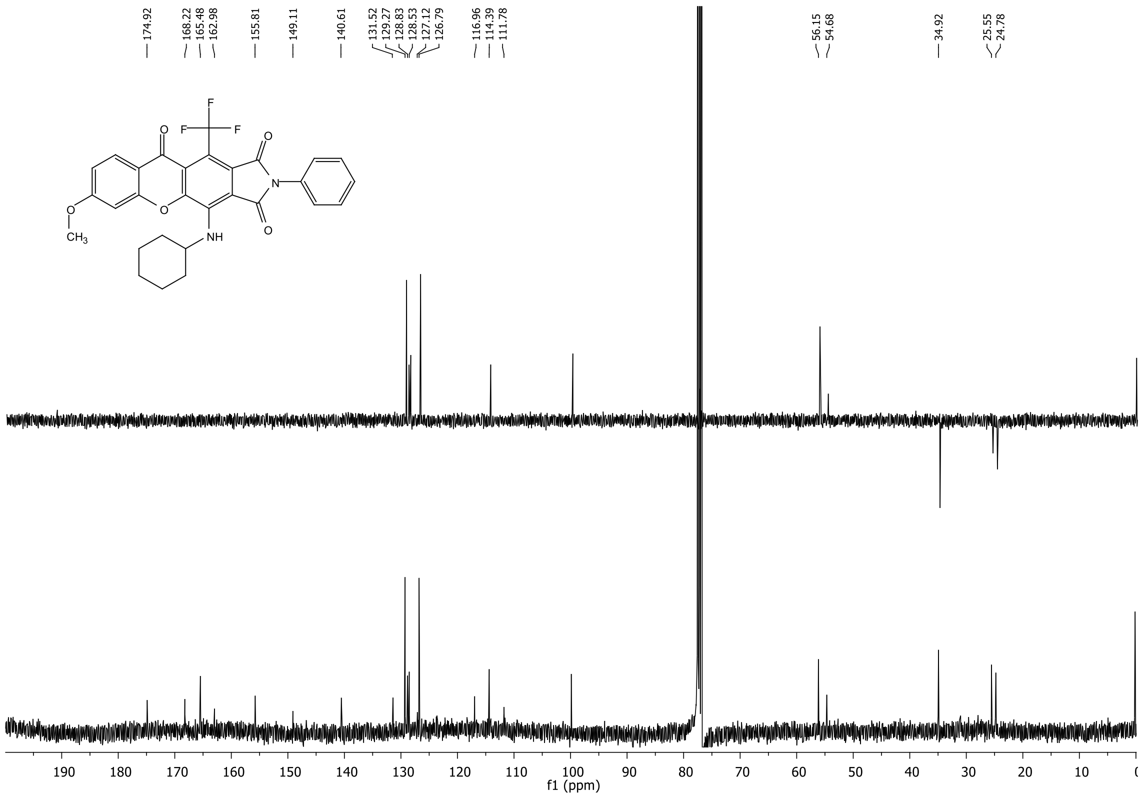
4-(Cyclohexylamino)-2-phenyl-11-(trifluoromethyl)chromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8al)



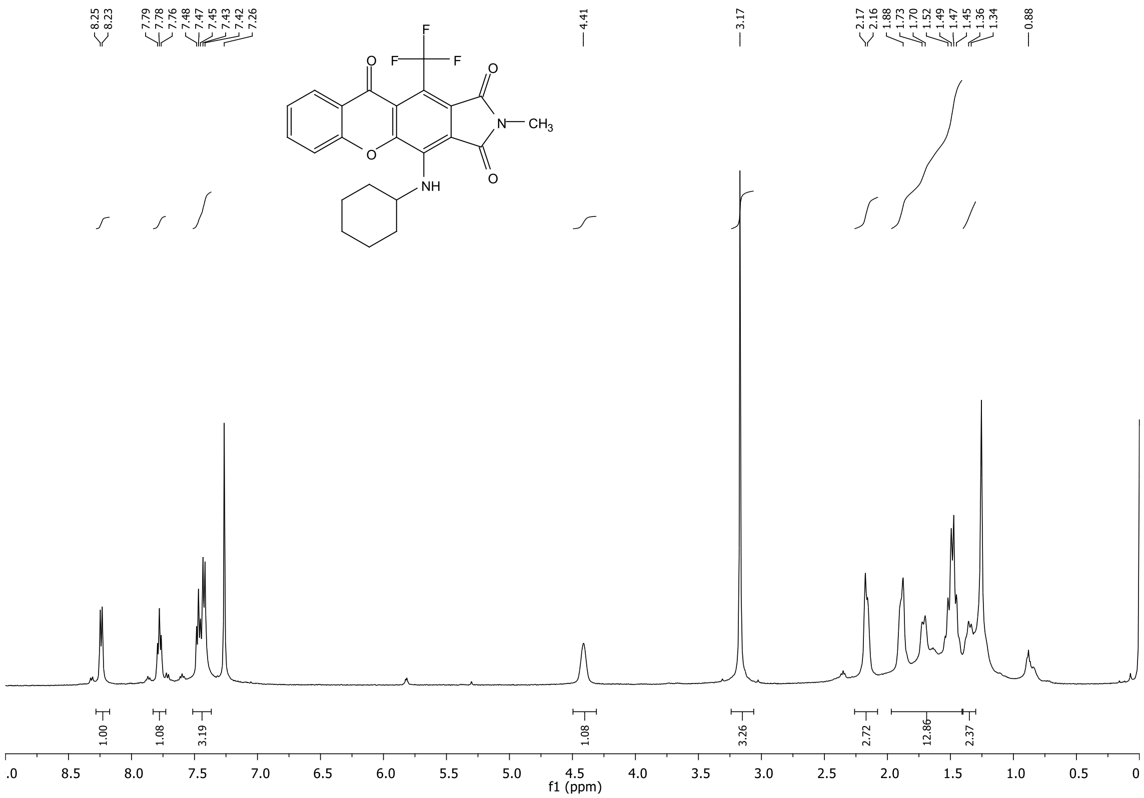


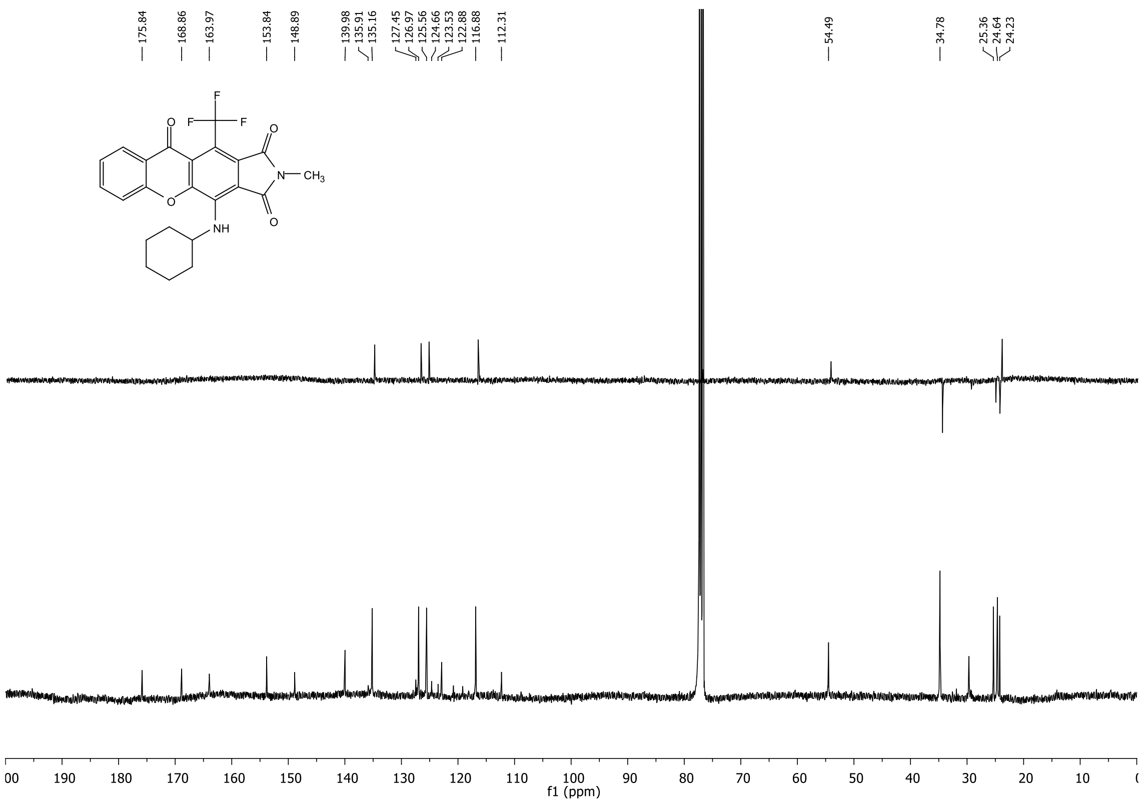
4-(Cyclohexylamino)-7-methoxy-2-phenyl-11-(trifluoromethyl) chromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8am)



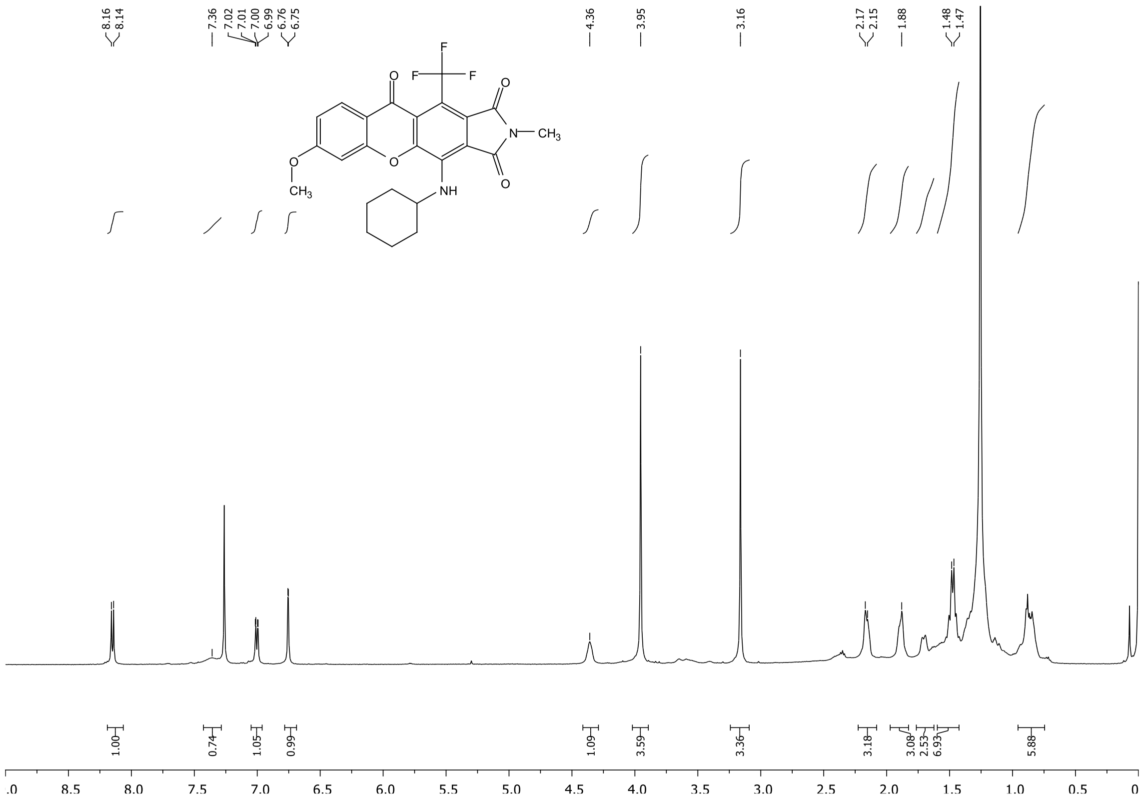


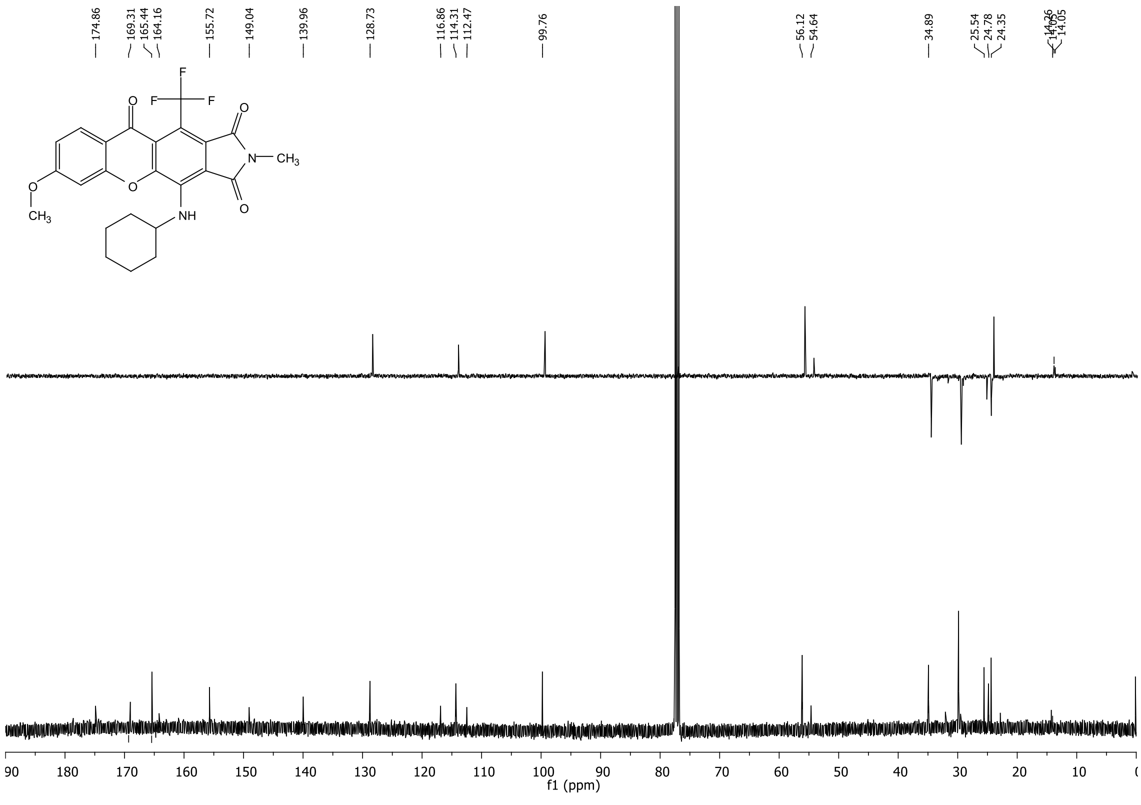
4-(Cyclohexylamino)-2-methyl-11-(trifluoromethyl)chromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8an)



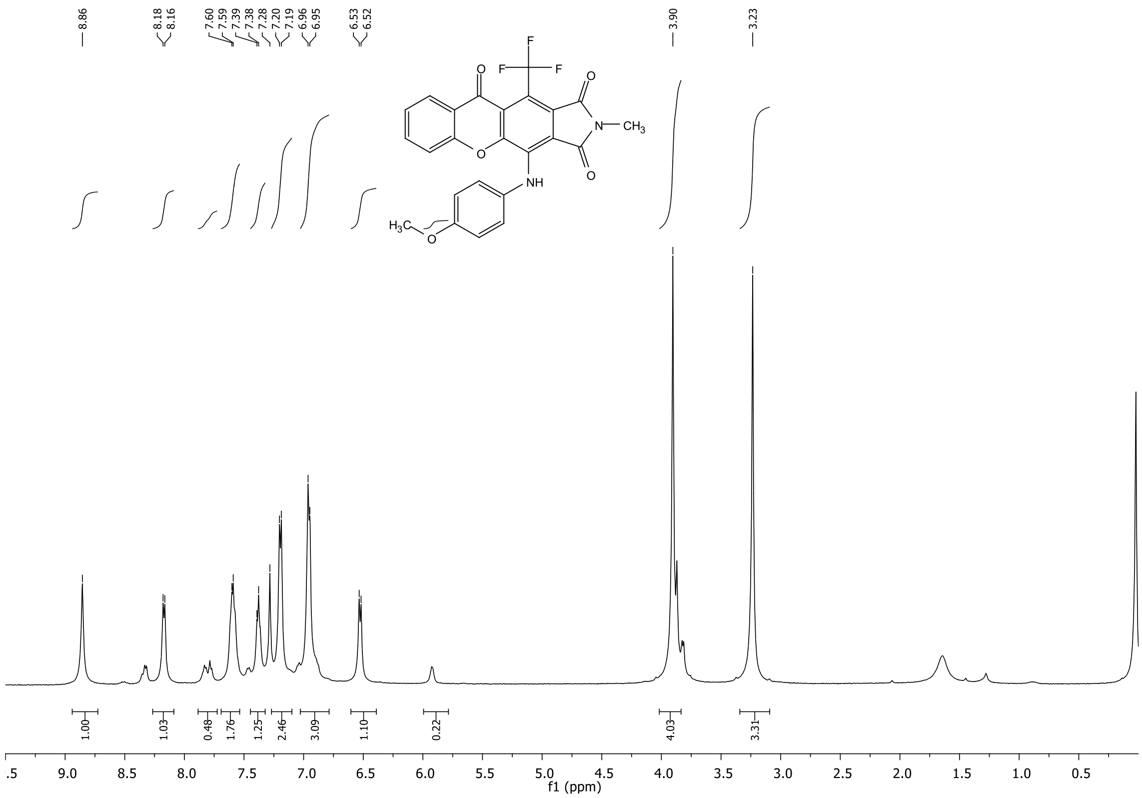


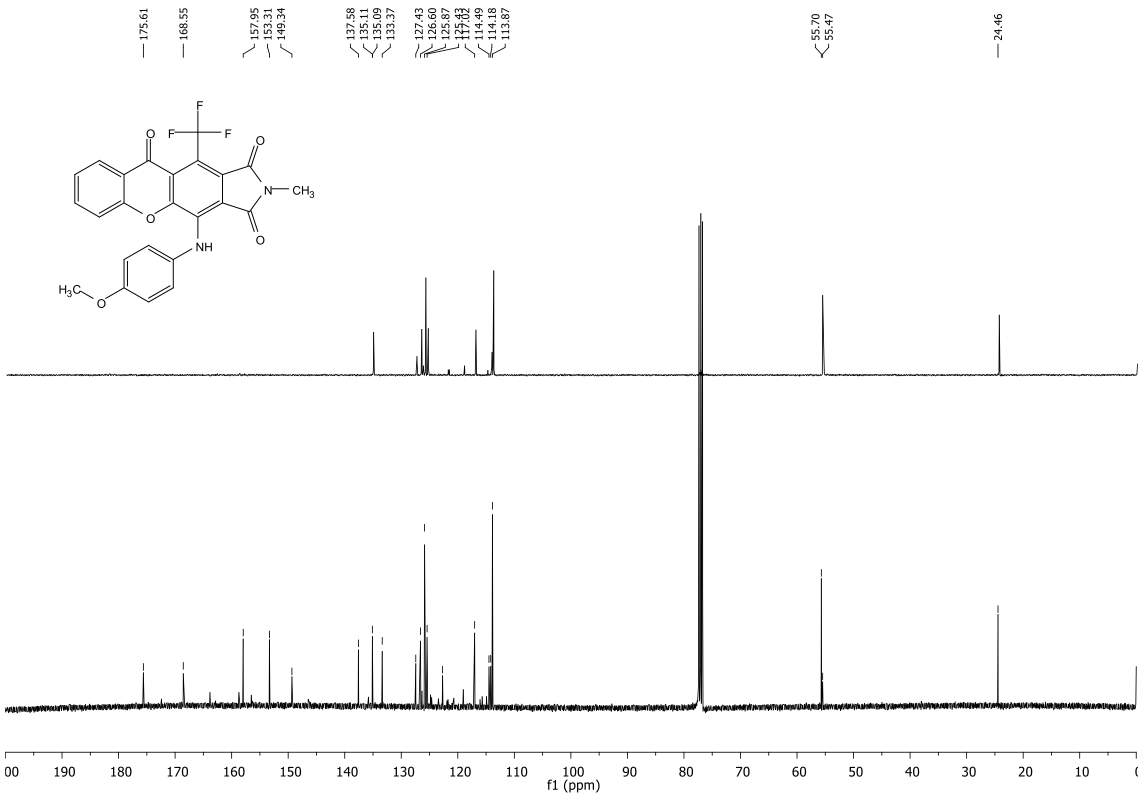
4-(Cyclohexylamino)-7-methoxy-2-methyl-11-(trifluoromethyl) chromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8ao)



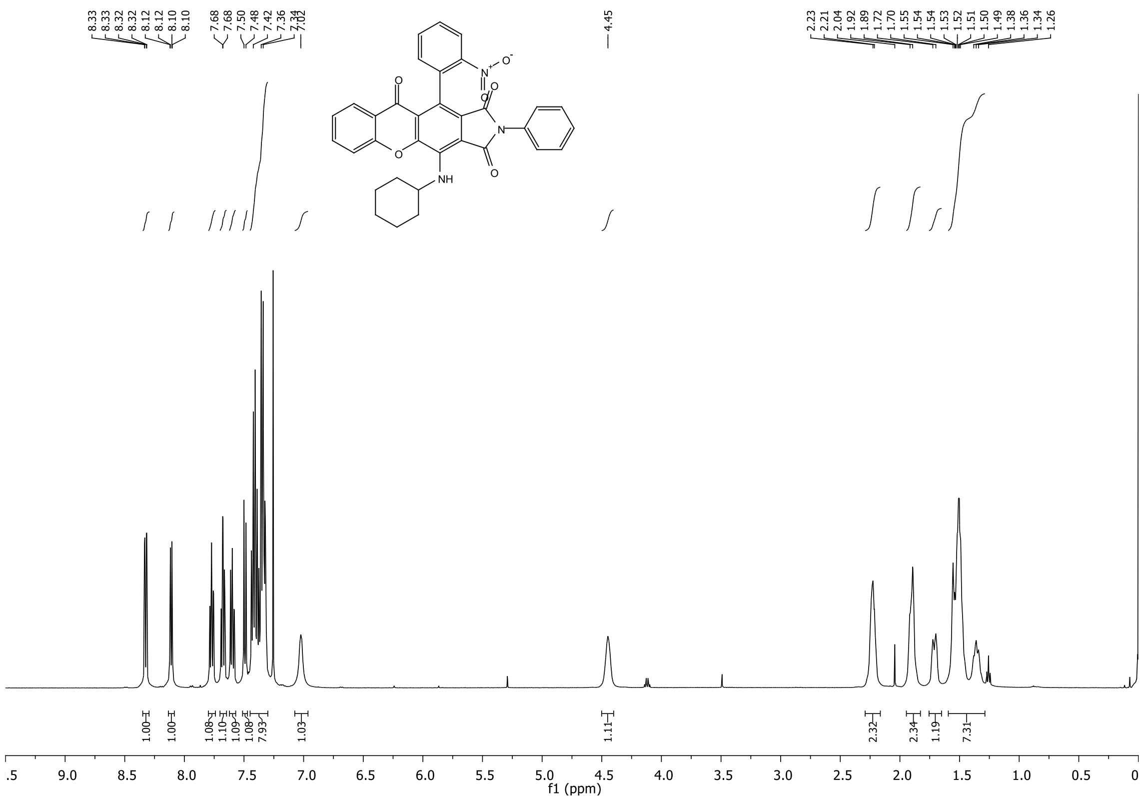


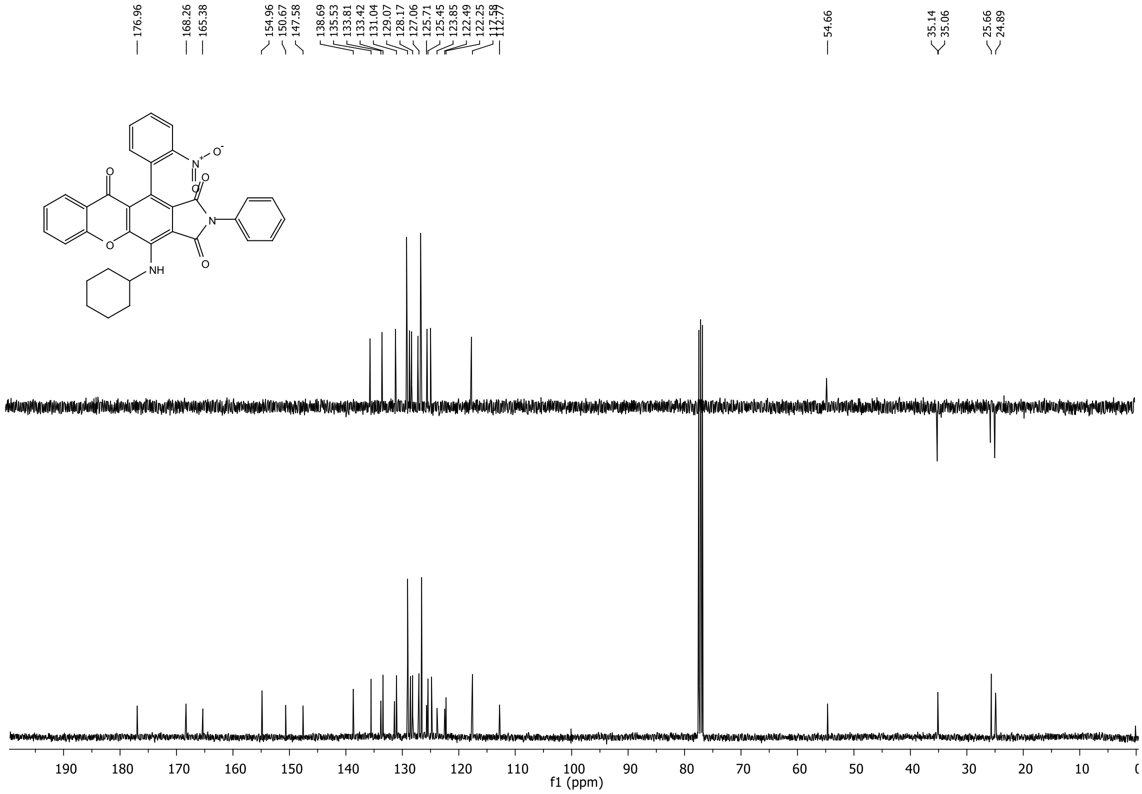
4-((4-Methoxyphenyl)amino)-2-methyl-11-(trifluoromethyl)chromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8ap)



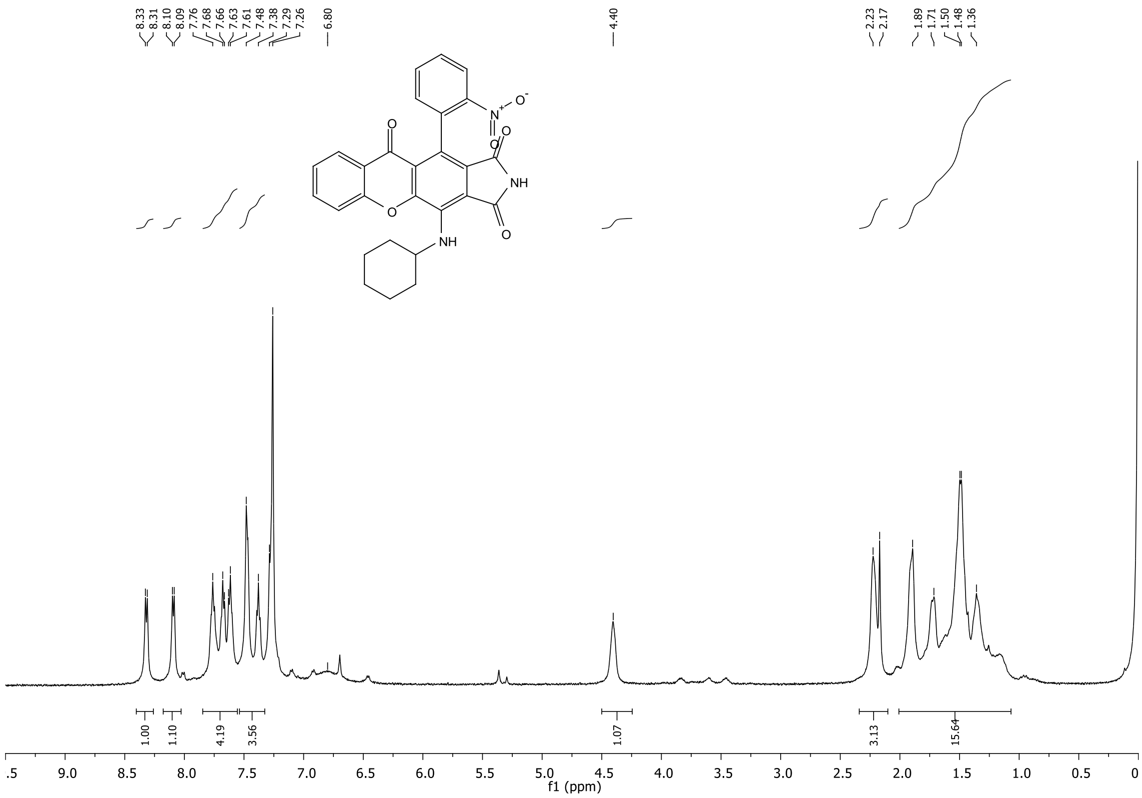


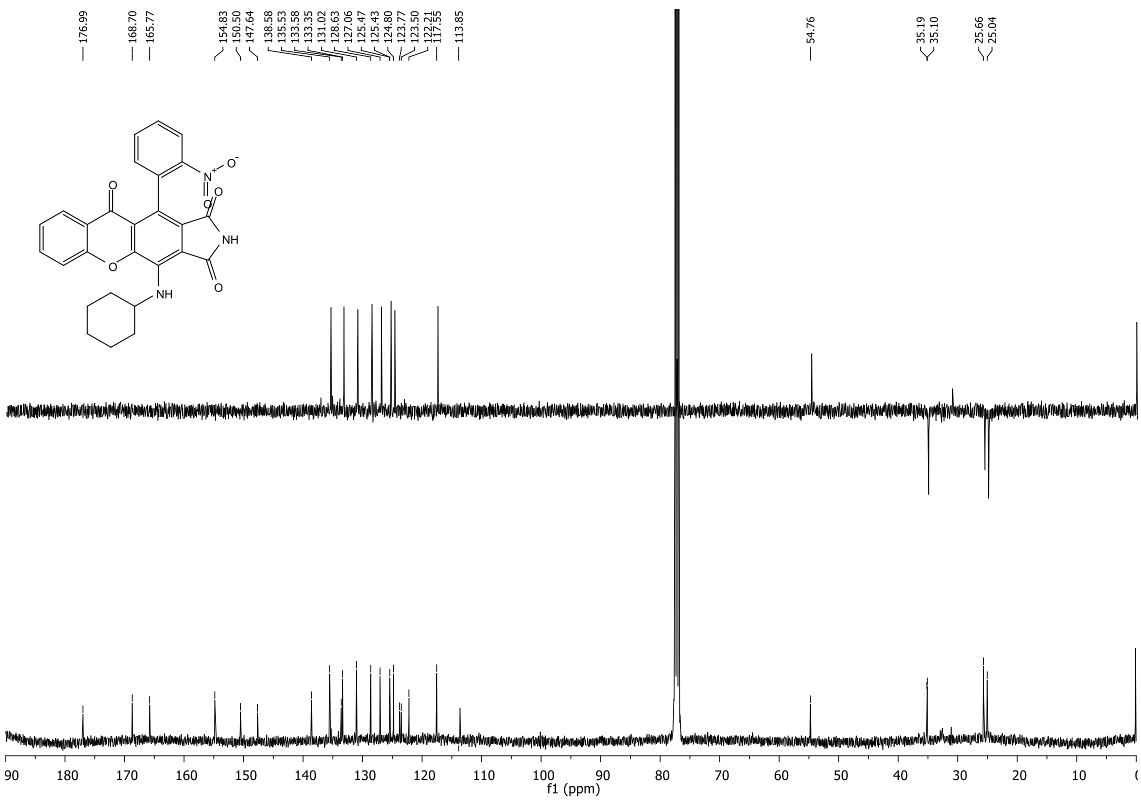
4-(Cyclohexylamino)-11-(2-nitrophenyl)-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8aq)



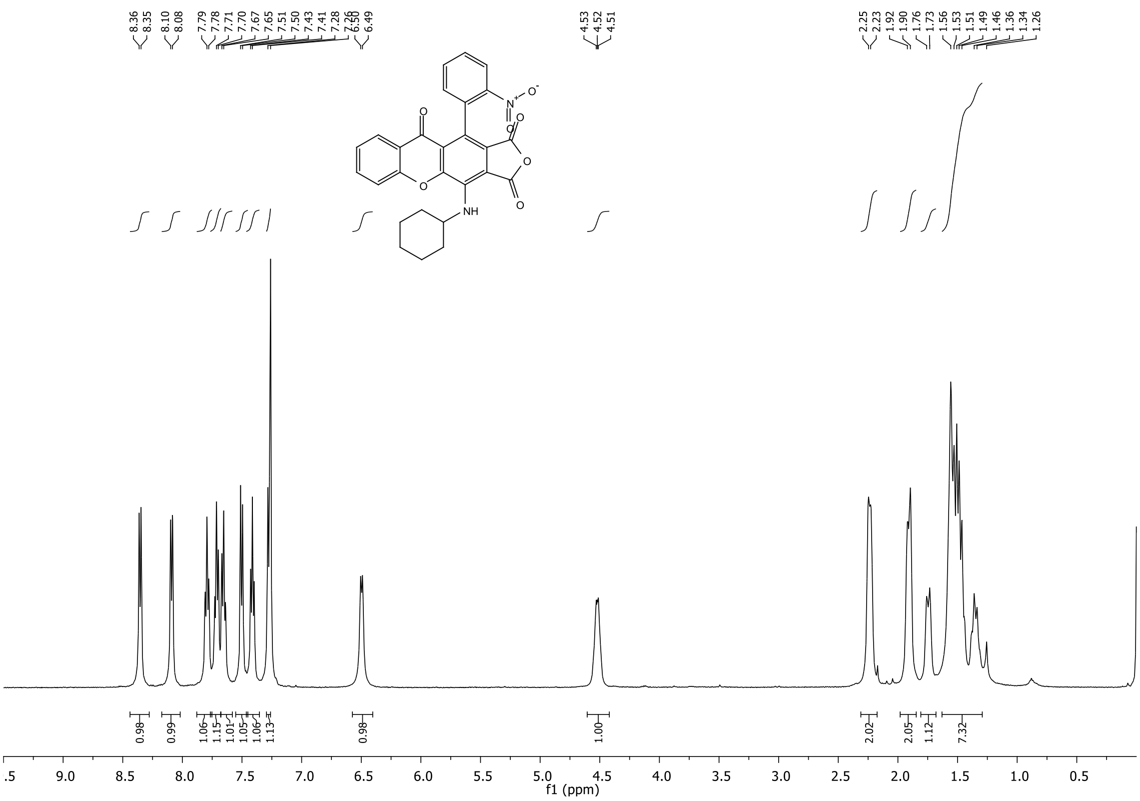


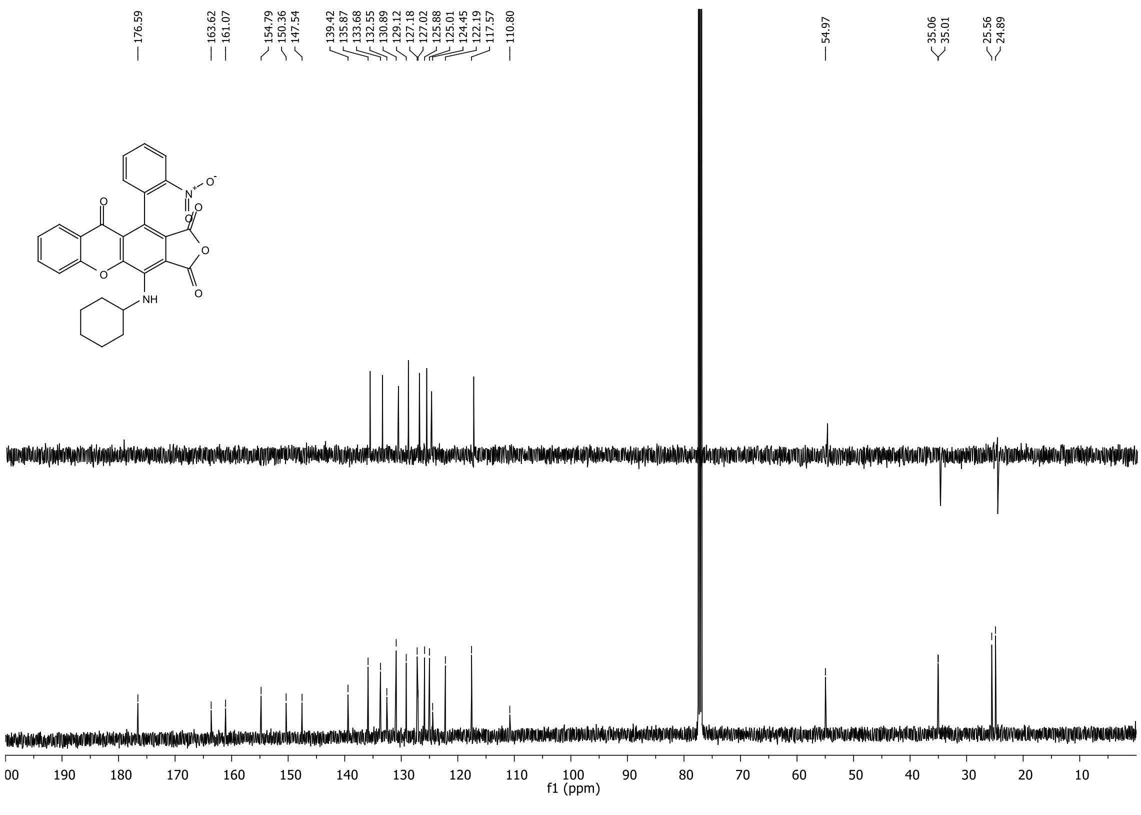
4-(Cyclohexylamino)-11-(2-nitrophenyl)chromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8ar)



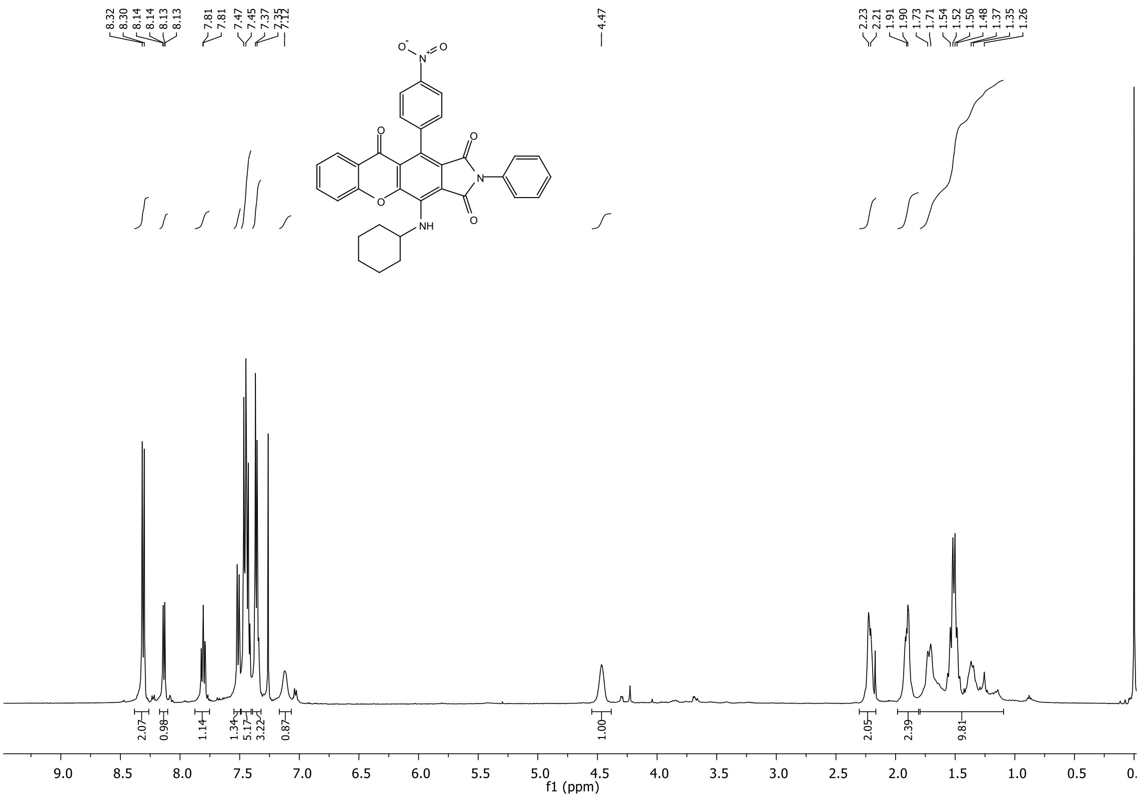


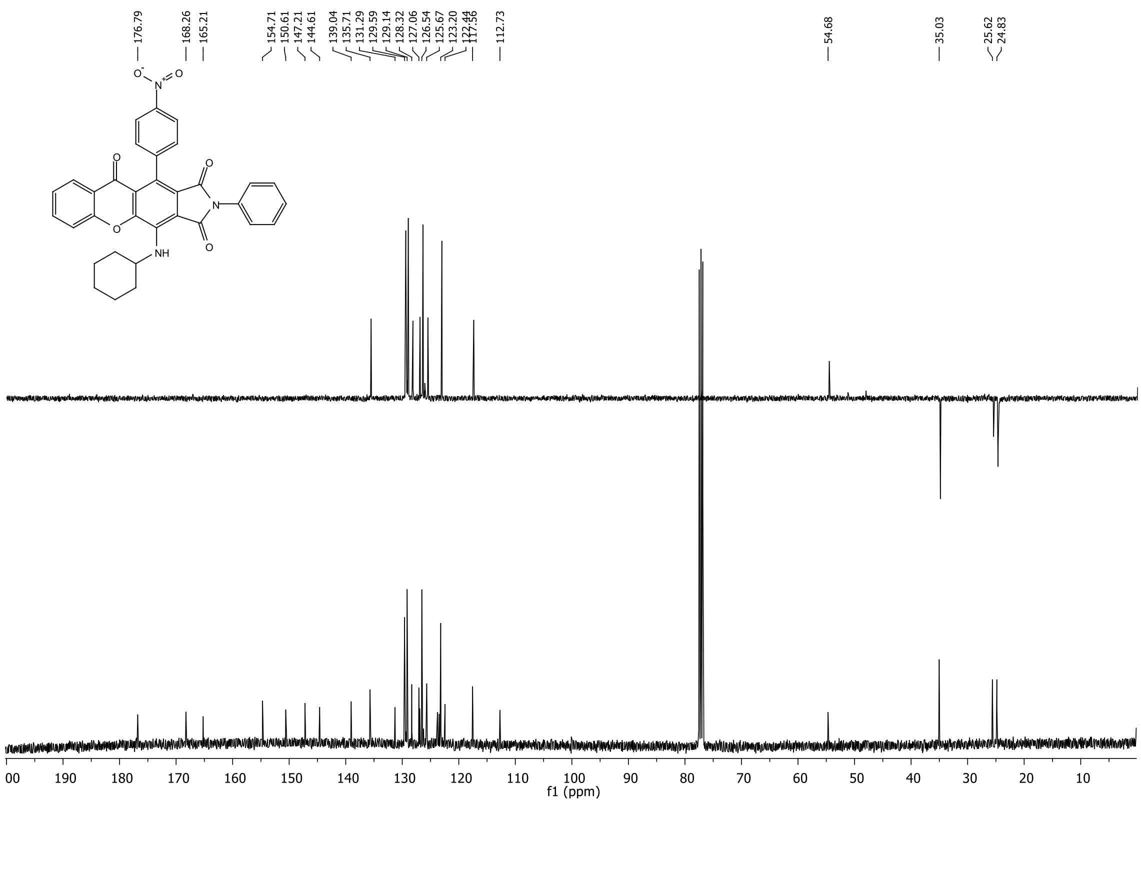
4-(Cyclohexylamino)-11-(2-nitrophenyl)-1*H*-furo[3,4-*b*]xanthene-1,3,10-trione (8as)



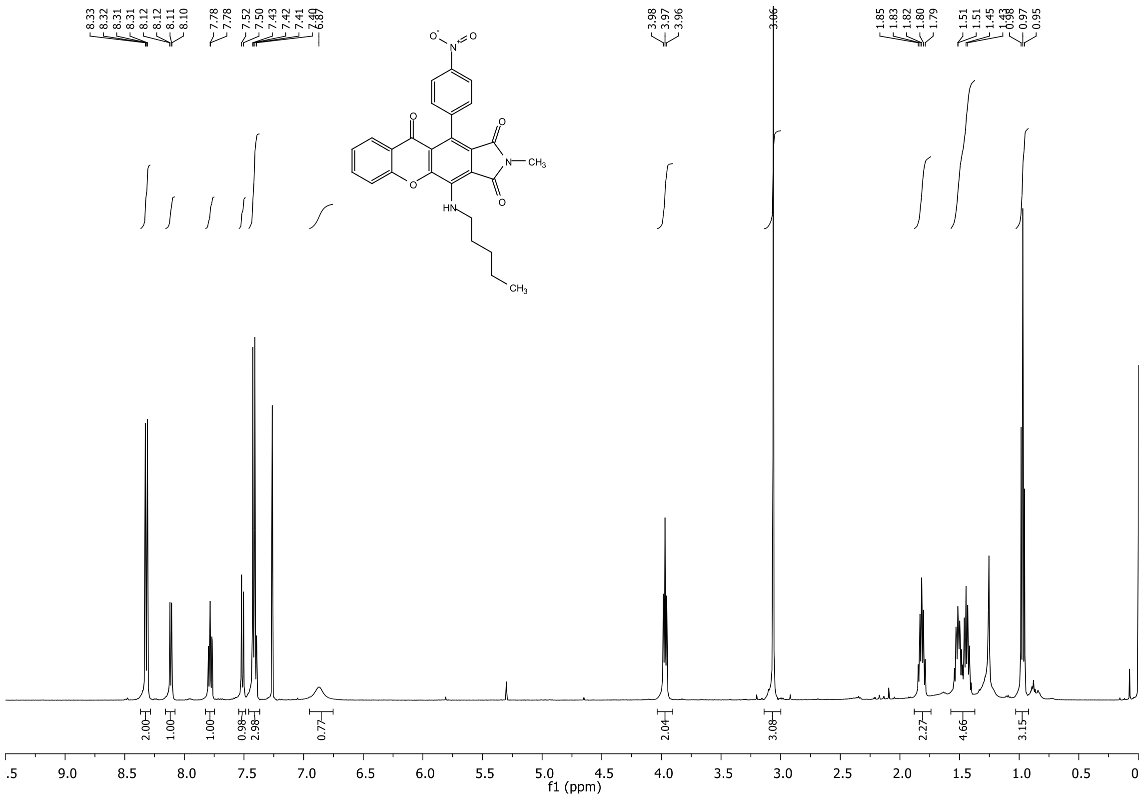


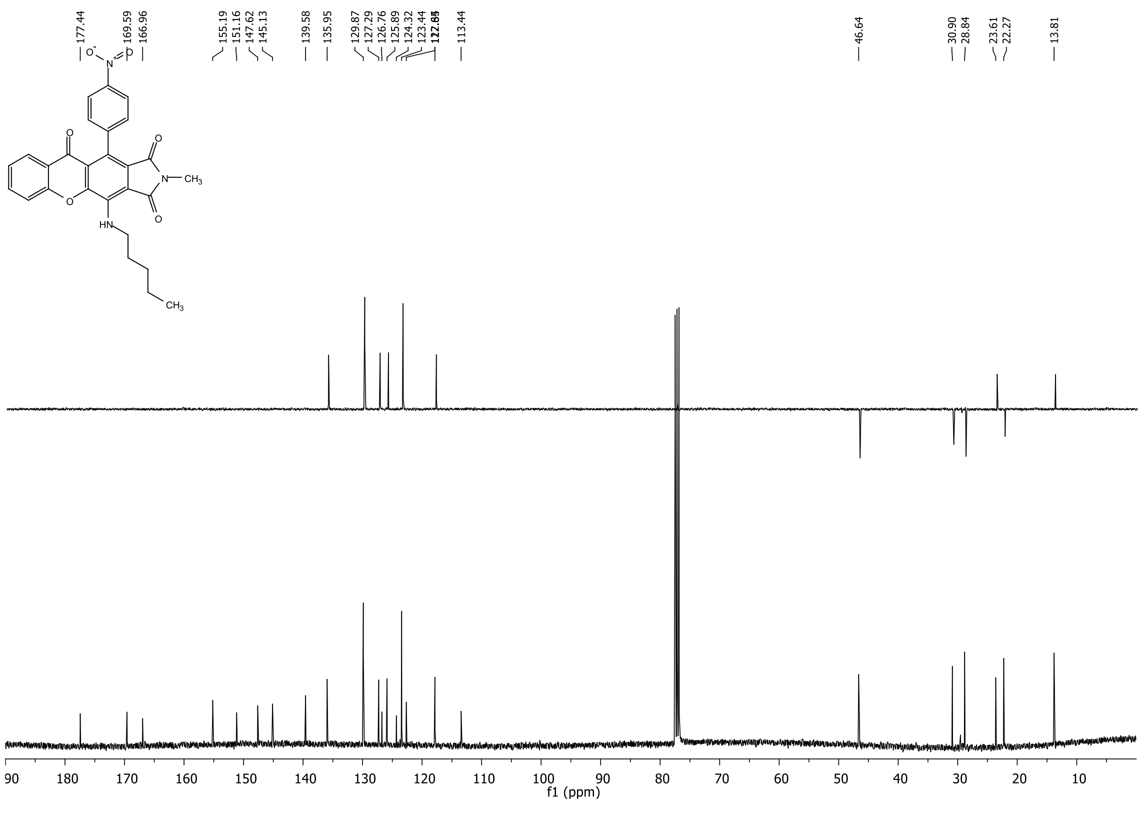
4-(Cyclohexylamino)-11-(4-nitrophenyl)-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8at)



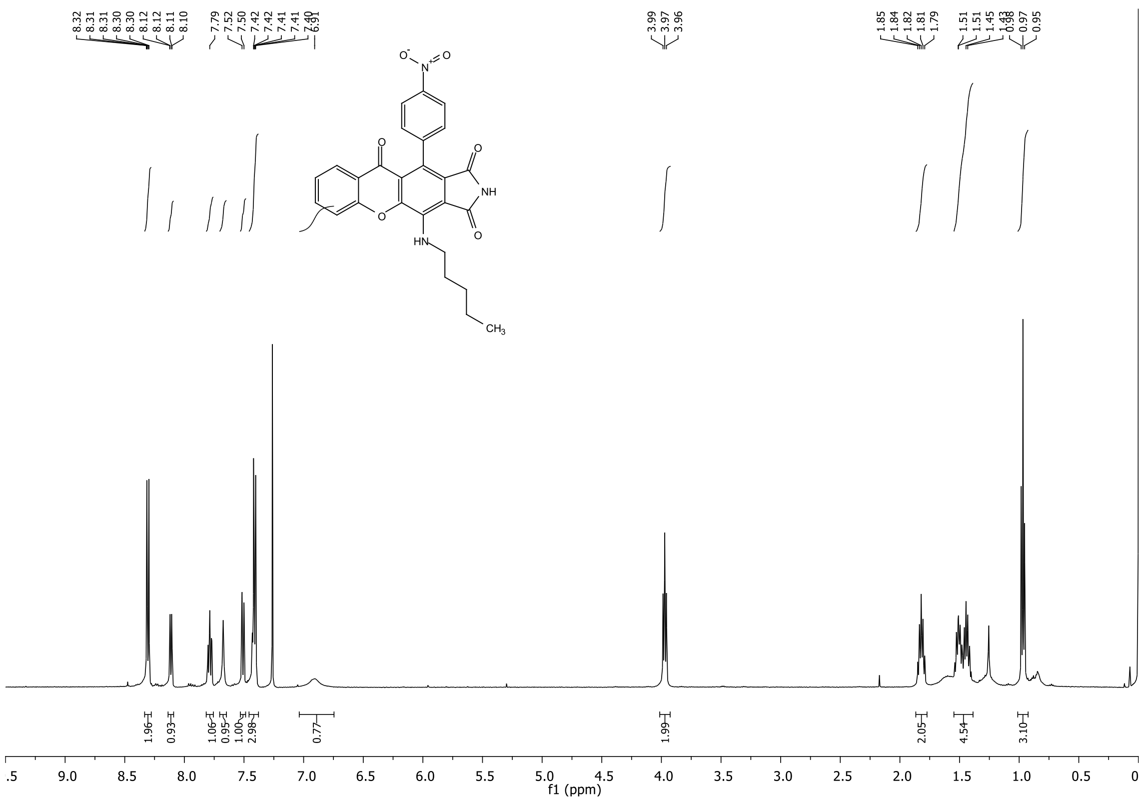


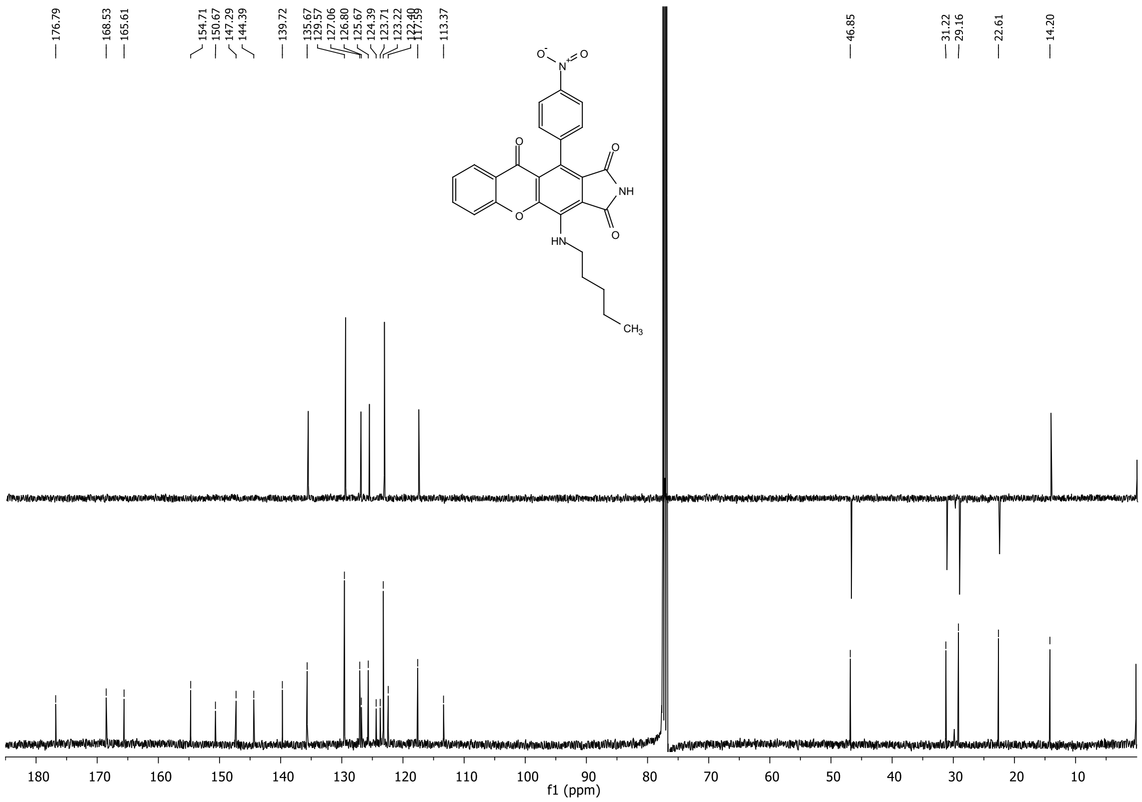
2-Methyl-11-(4-nitrophenyl)-4-(pentylamino)chromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8au)



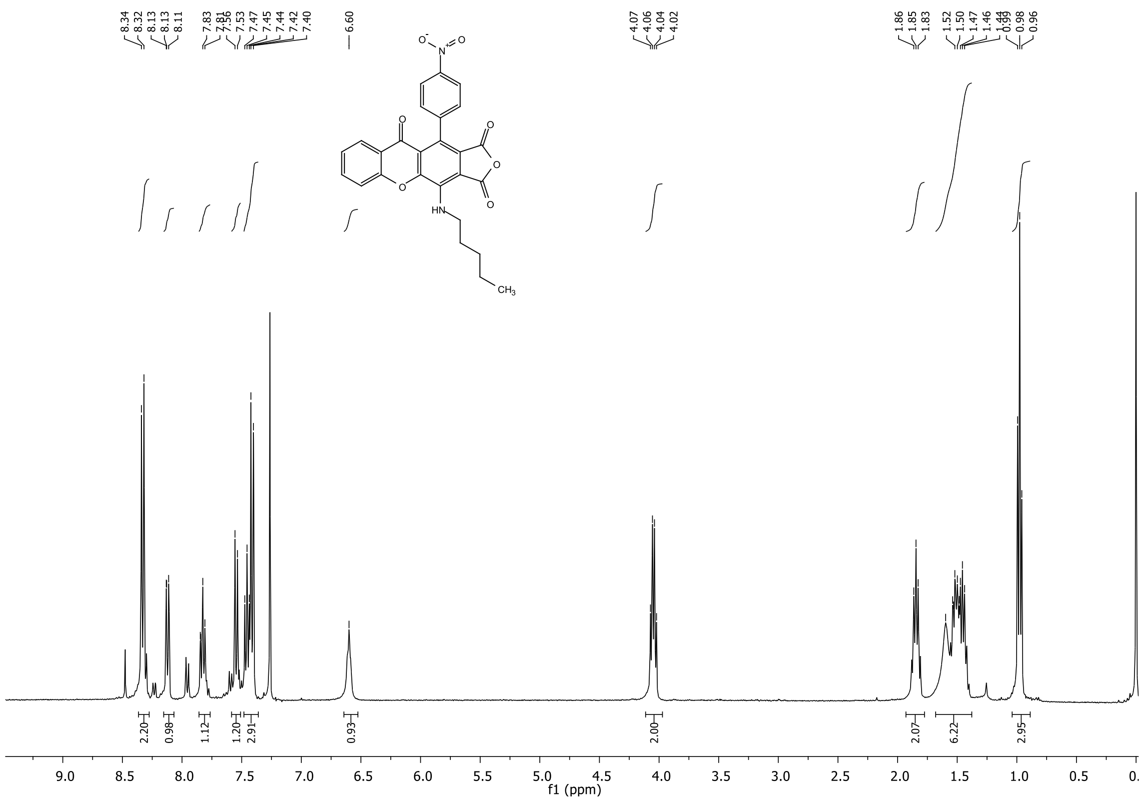


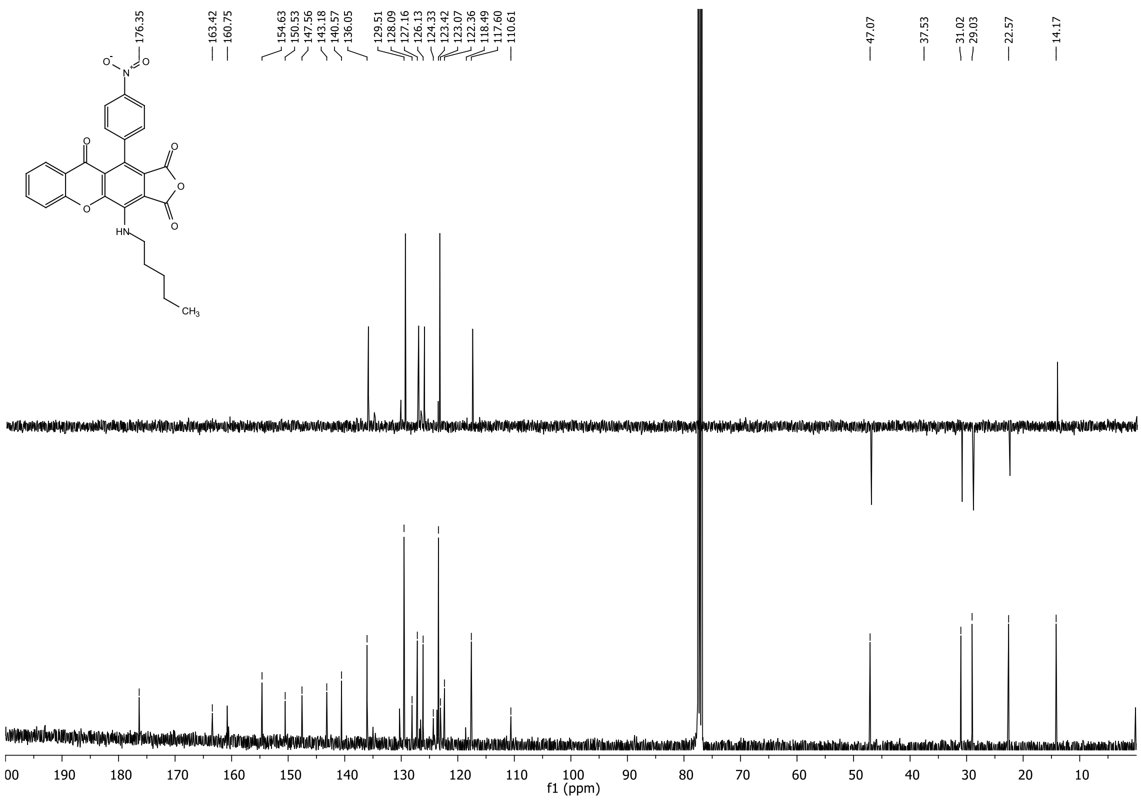
11-(4-Nitrophenyl)-4-(pentylamino)chromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8av)



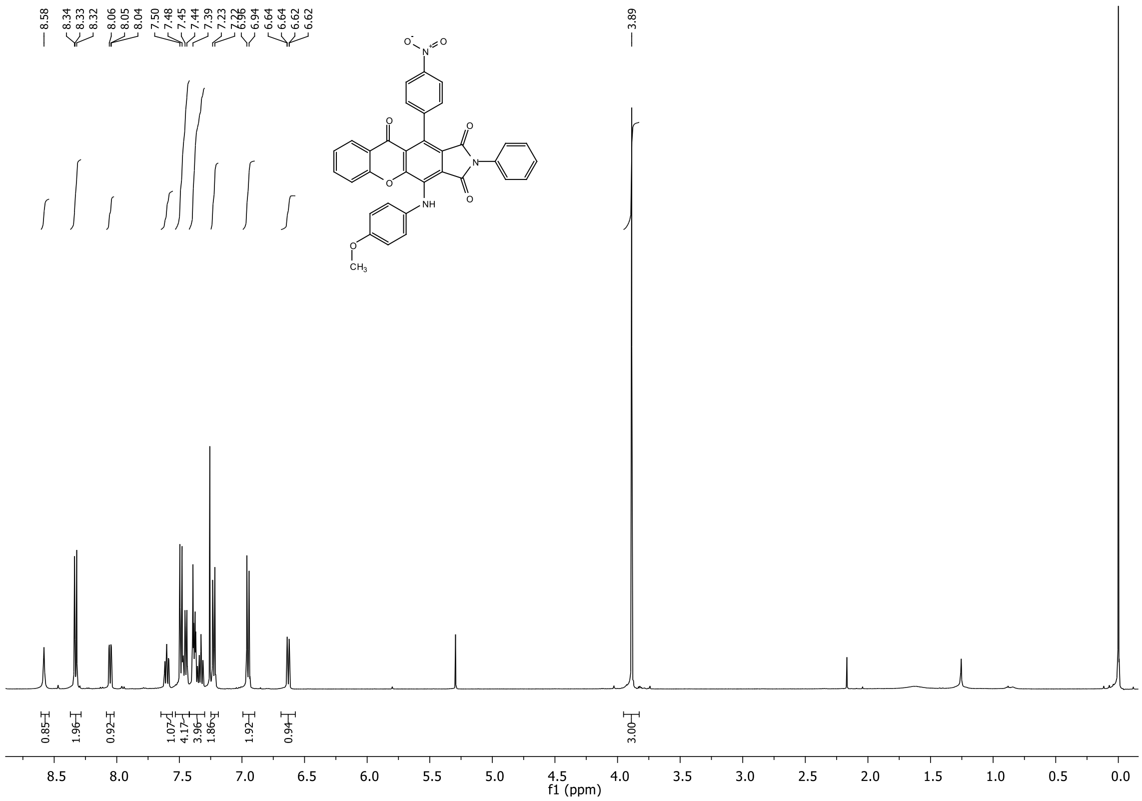


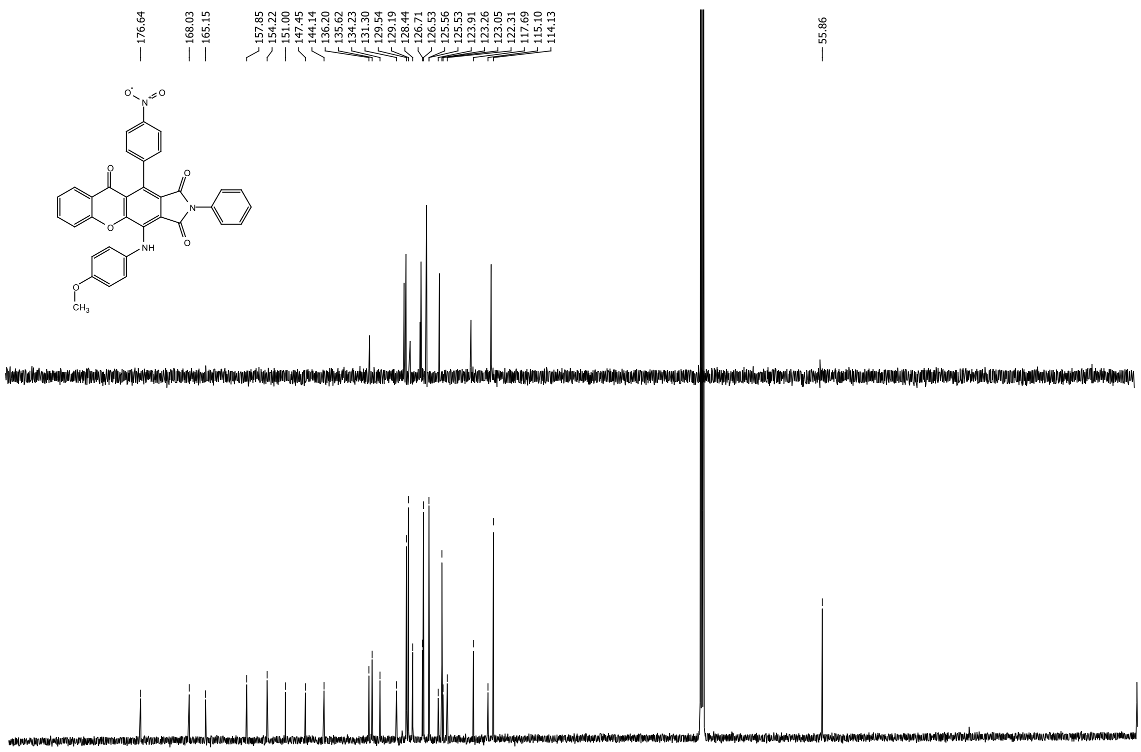
11-(4-Nitrophenyl)-4-(pentylamino)-1*H*-furo[3,4-*b*]xanthene-1,3,10-trione (8aw)



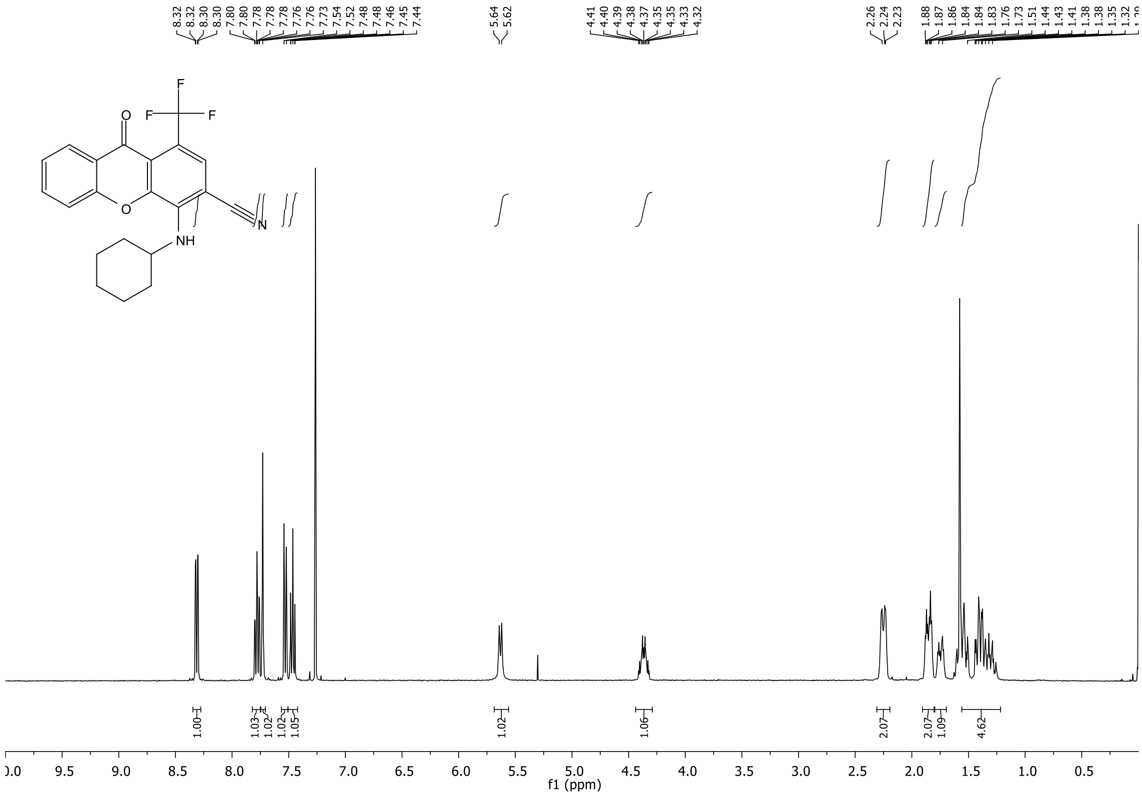


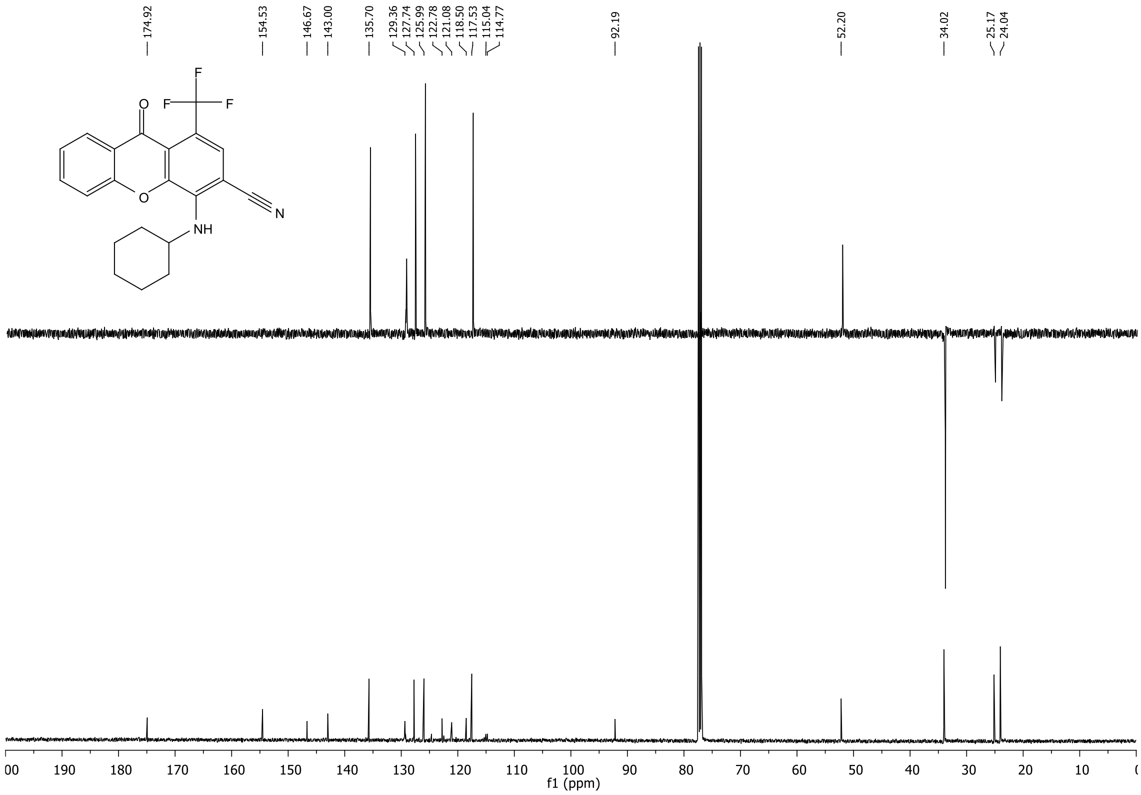
4-((4-Methoxyphenyl)amino)-11-(4-nitrophenyl)-2-phenylchromeno [2,3-*f*] isoindole-1,3,10(2*H*)-trione (8ax)



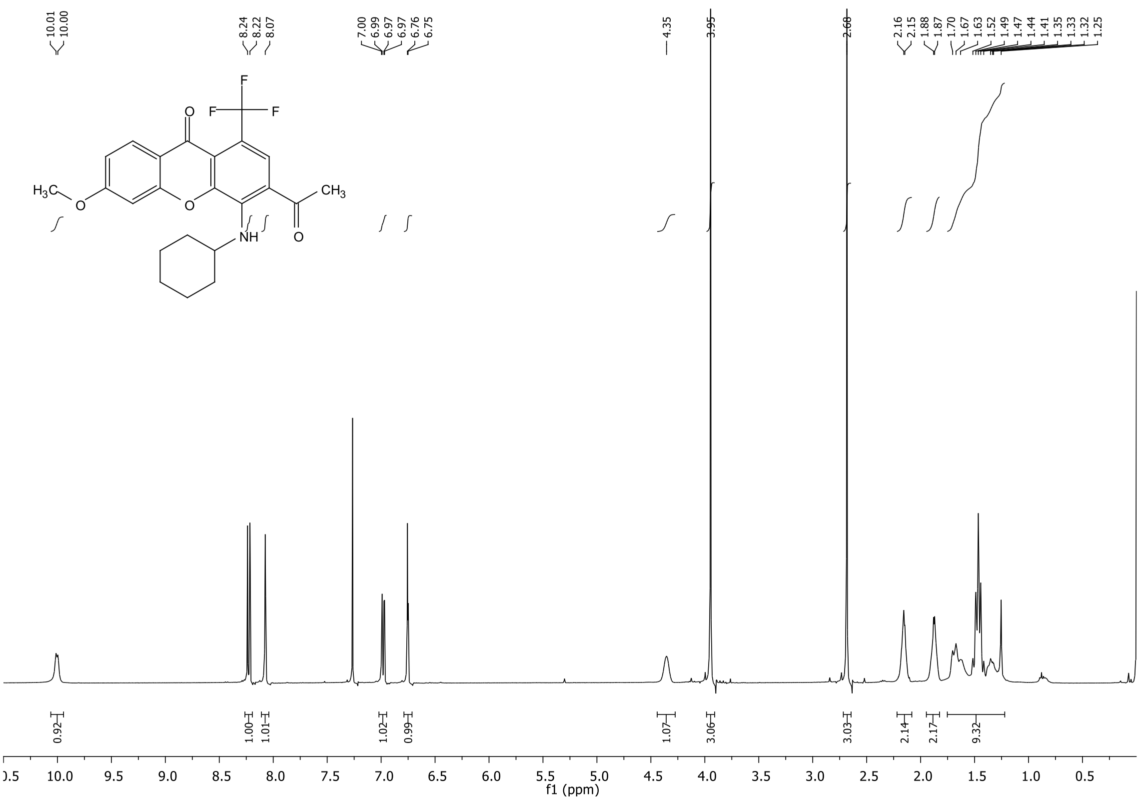


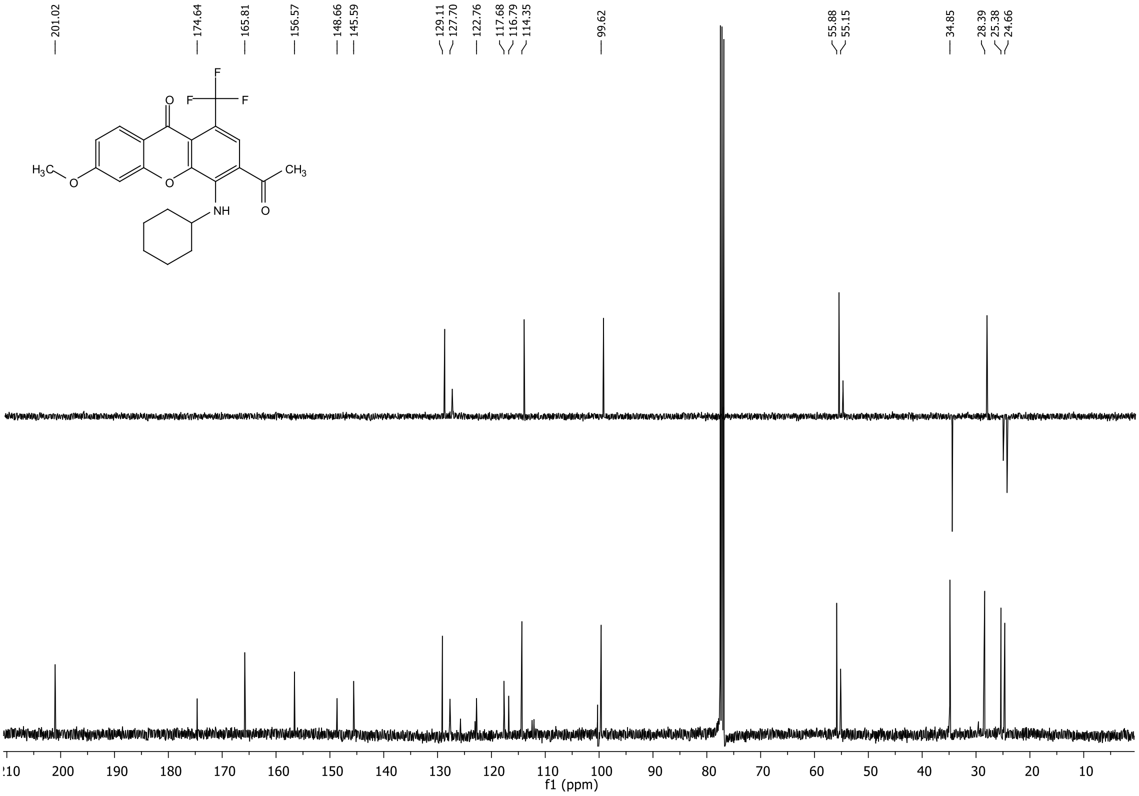
4-(Cyclohexylamino)-9-oxo-1-(trifluoromethyl)-9H-xanthene-3-carbonitrile (8ay)



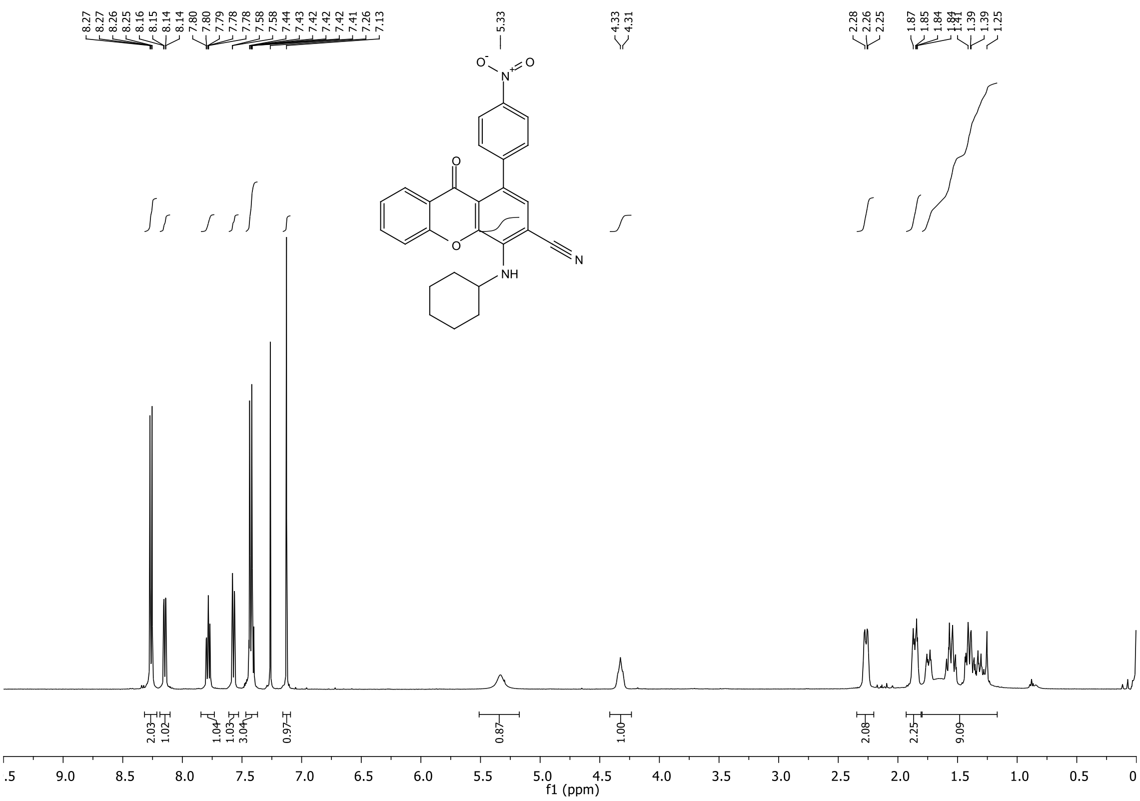


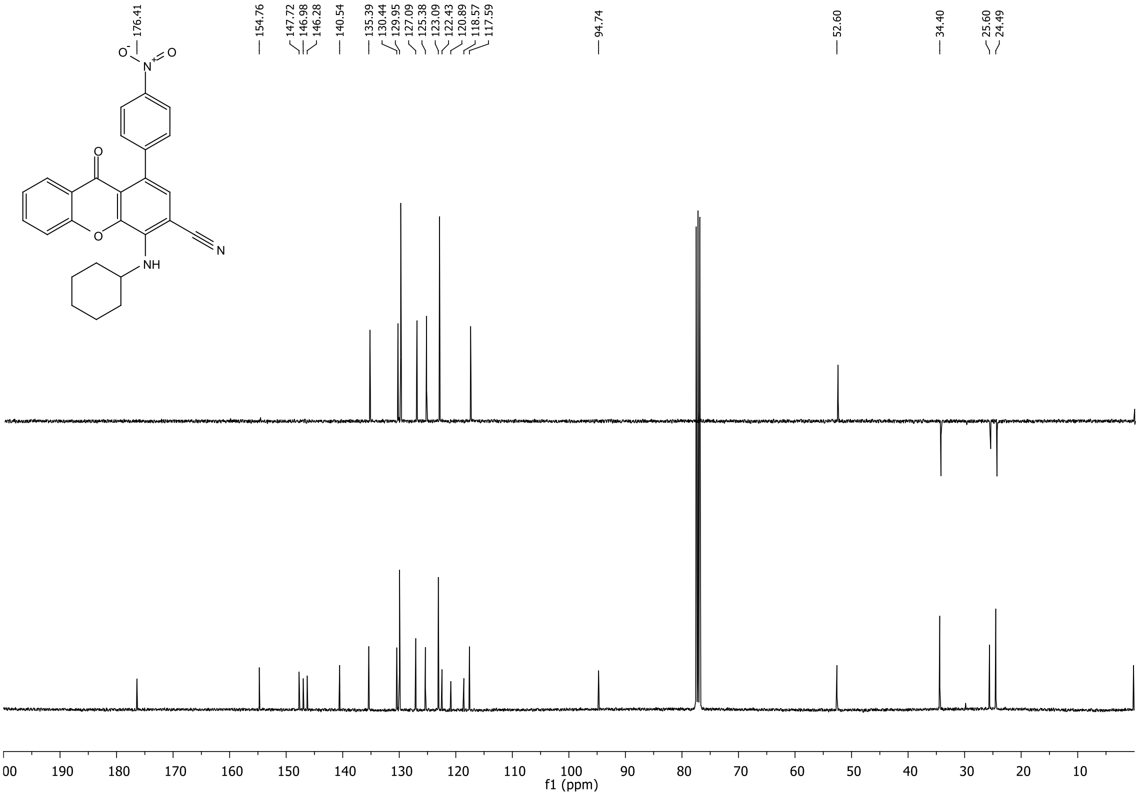
3-Acetyl-4-(cyclohexylamino)-6-methoxy-1-(trifluoromethyl)-9*H*-xanthen-9-one (8az)



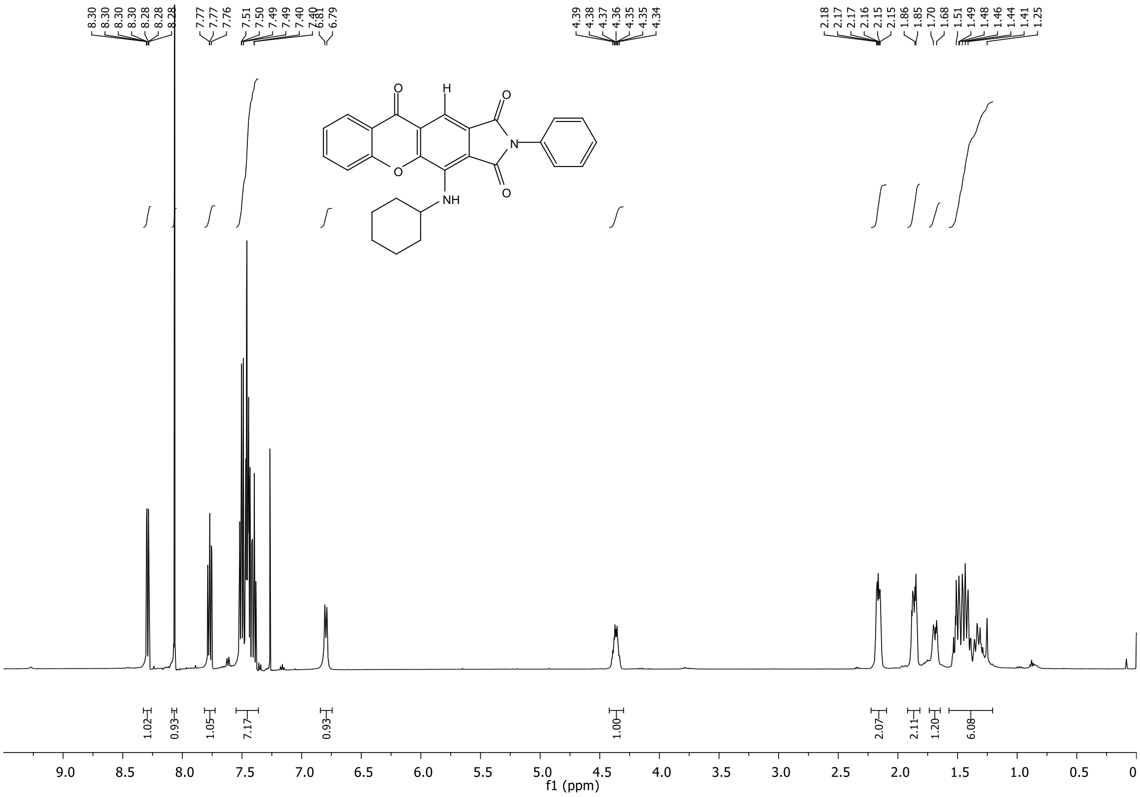


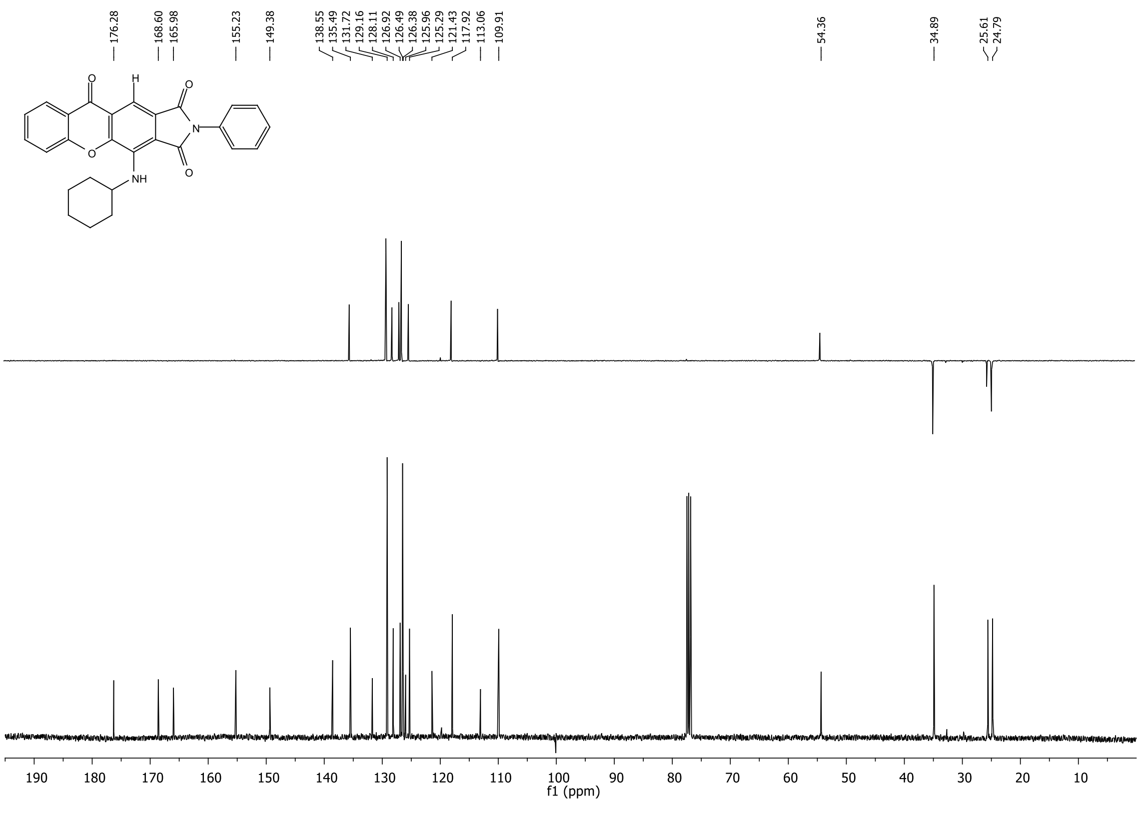
4-(Cyclohexylamino)-1-(4-nitrophenyl)-9-oxo-9*H*-xanthene-3-carbonitrile (8ba)



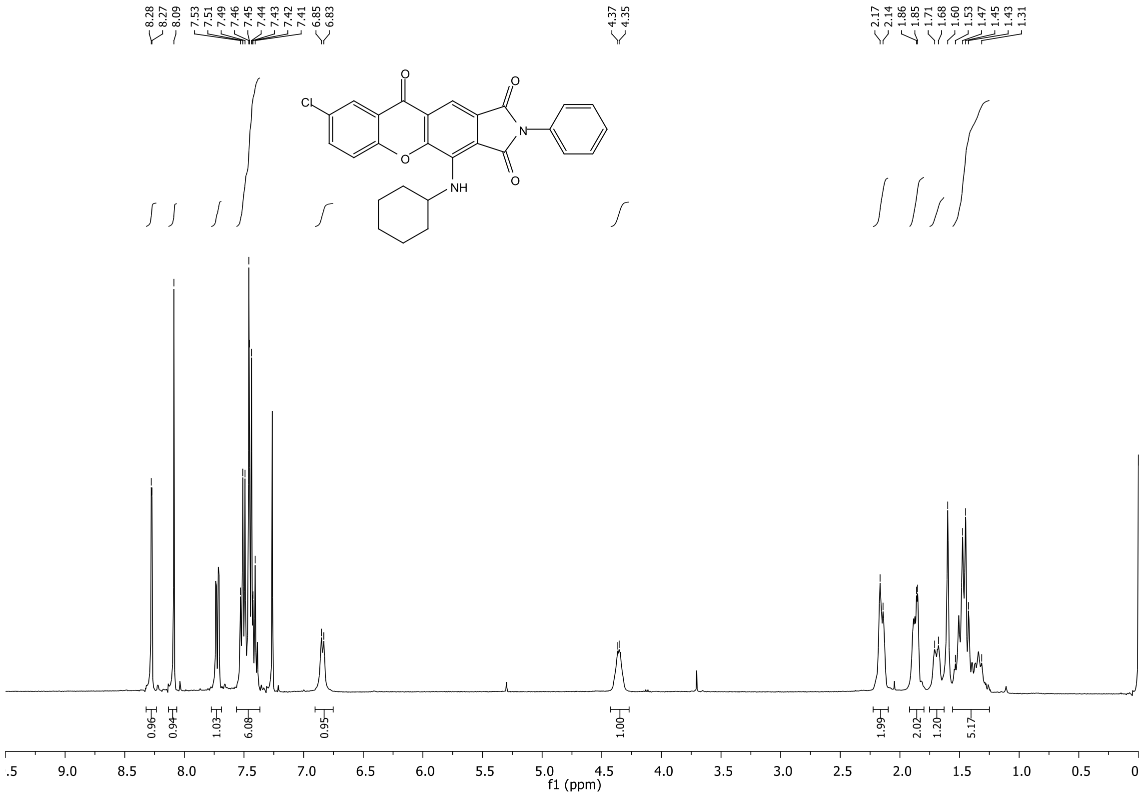


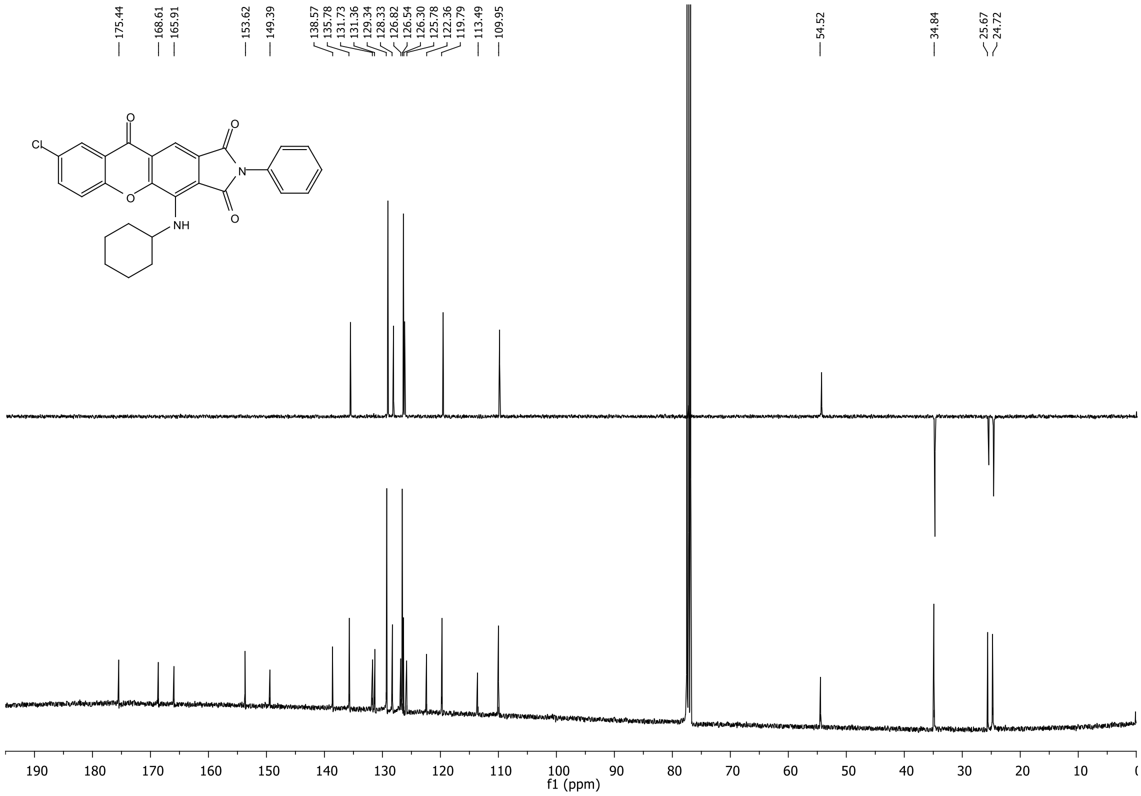
4-(Cyclohexylamino)-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8bb)



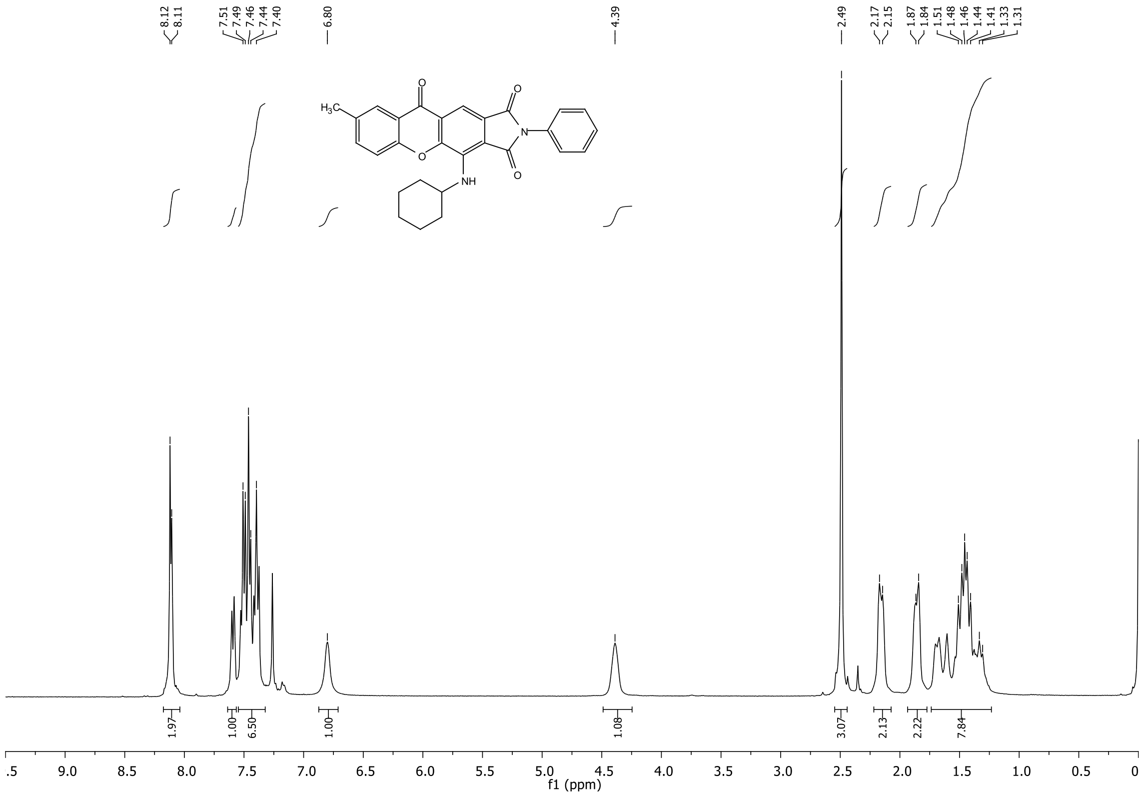


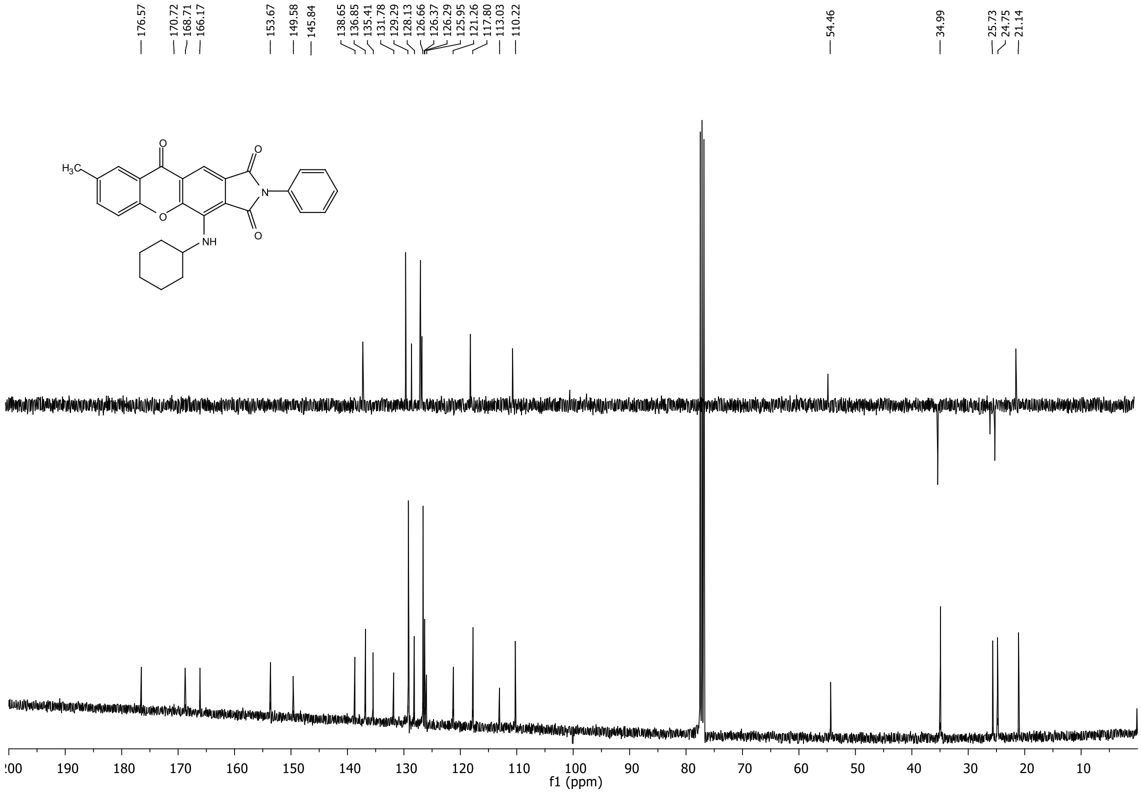
8-Chloro-4-(cyclohexylamino)-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8bc)



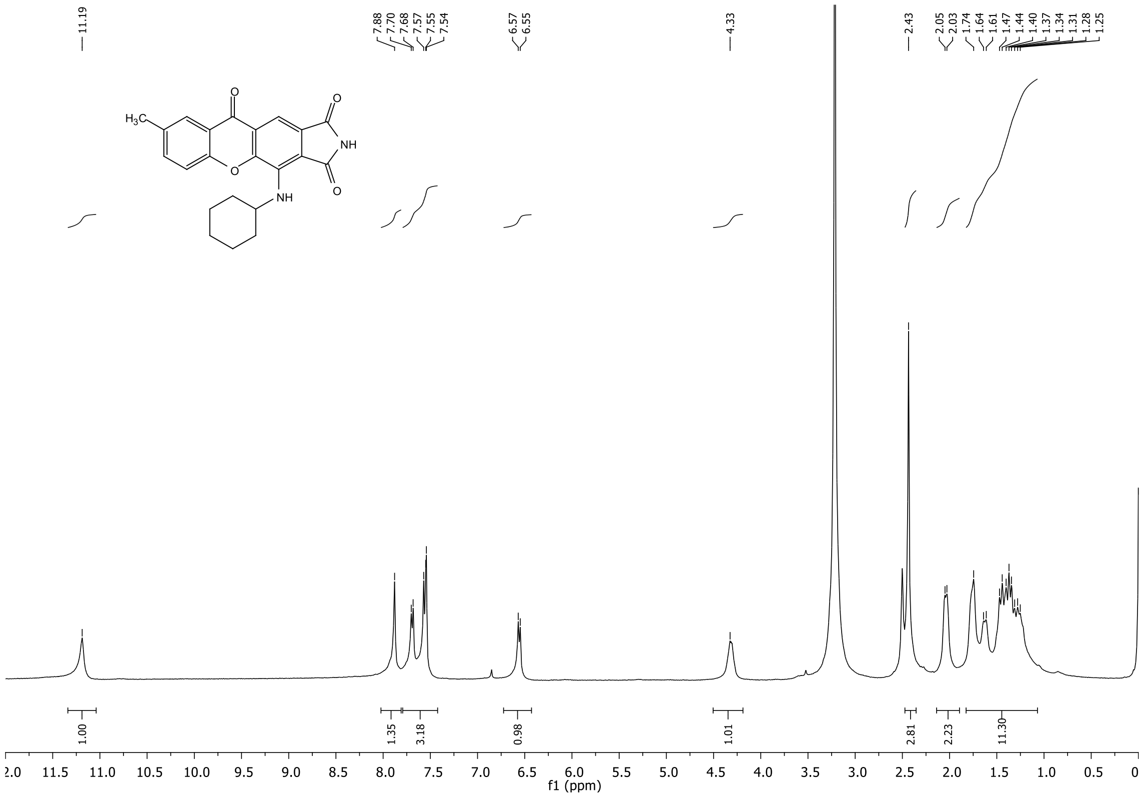


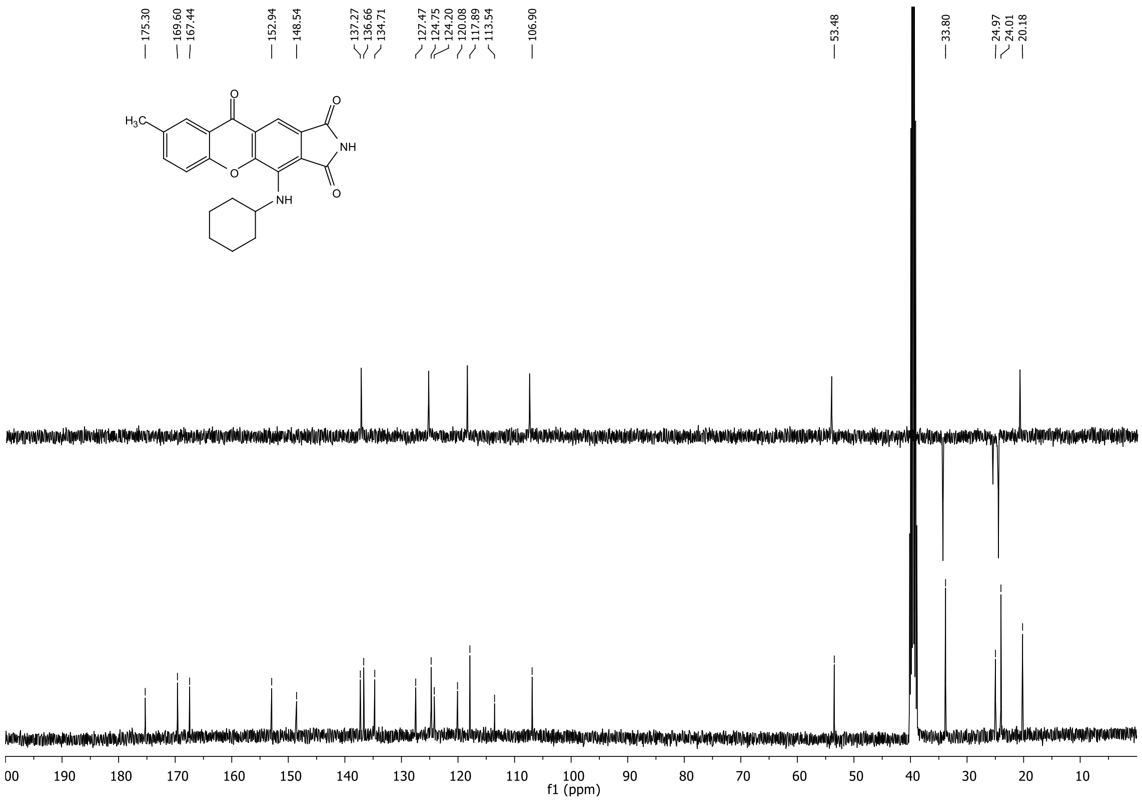
4-(Cyclohexylamino)-8-methyl-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8bd)



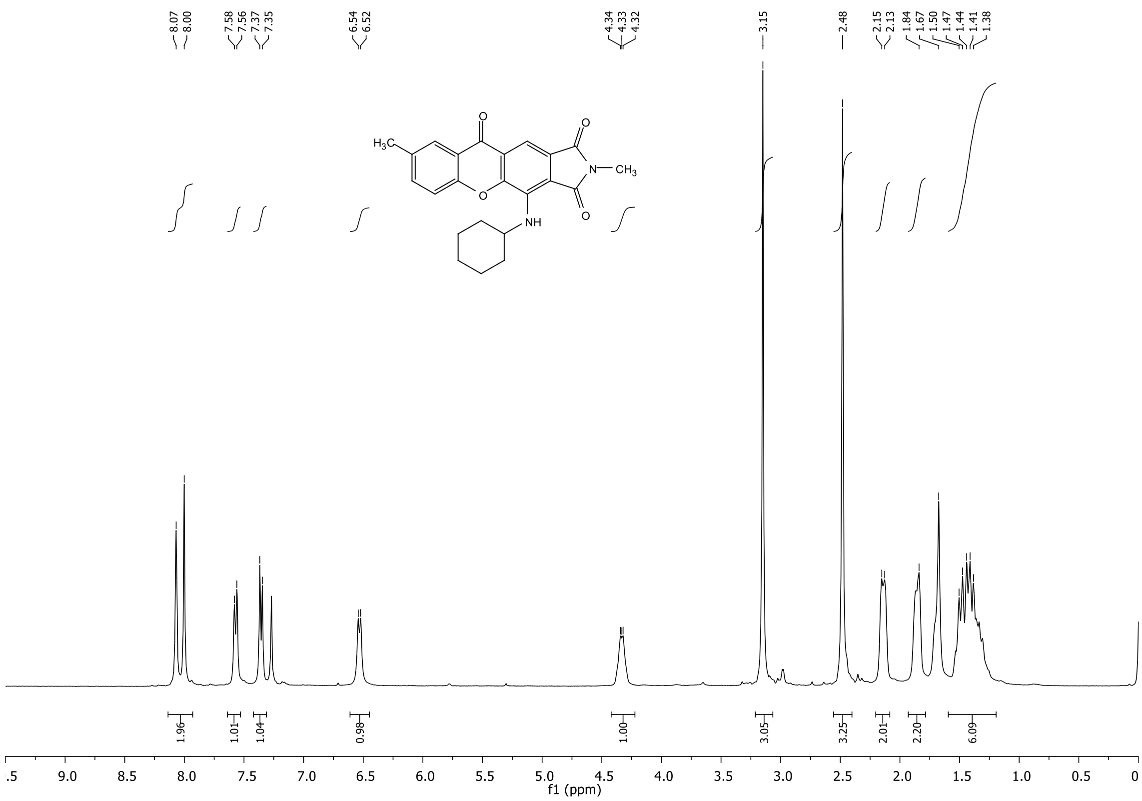


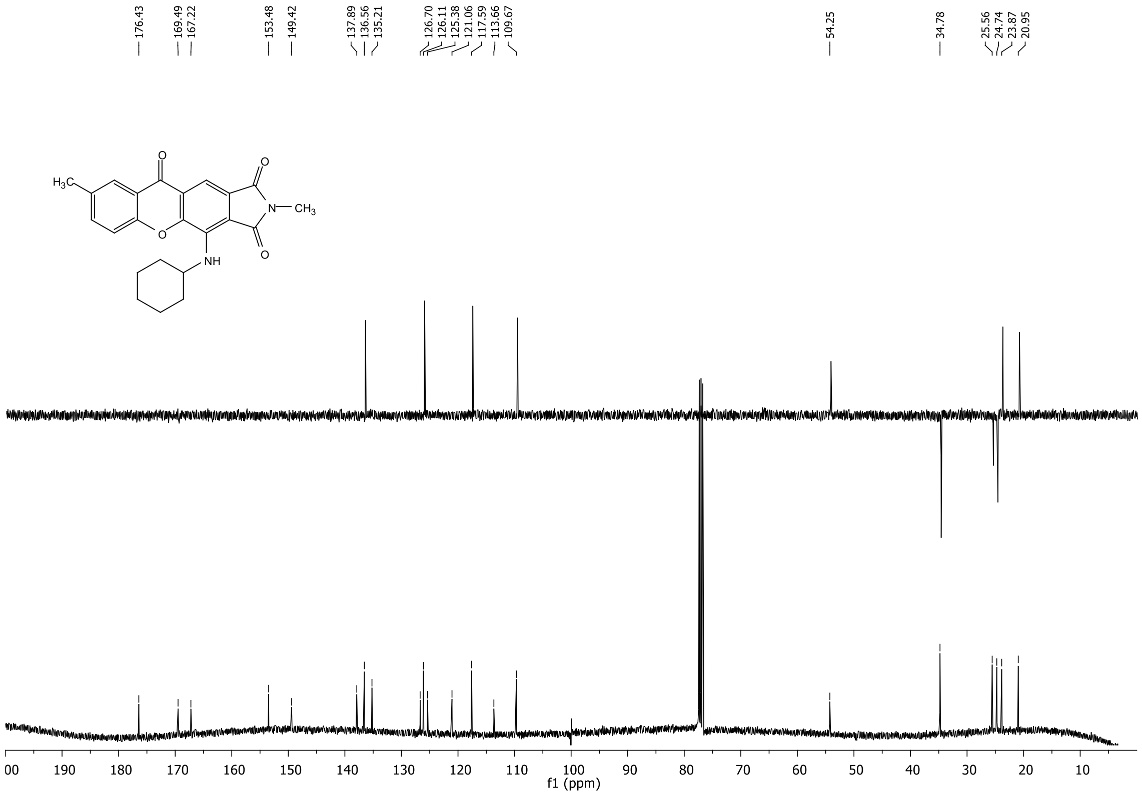
4-(Cyclohexylamino)-8-methylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8be)



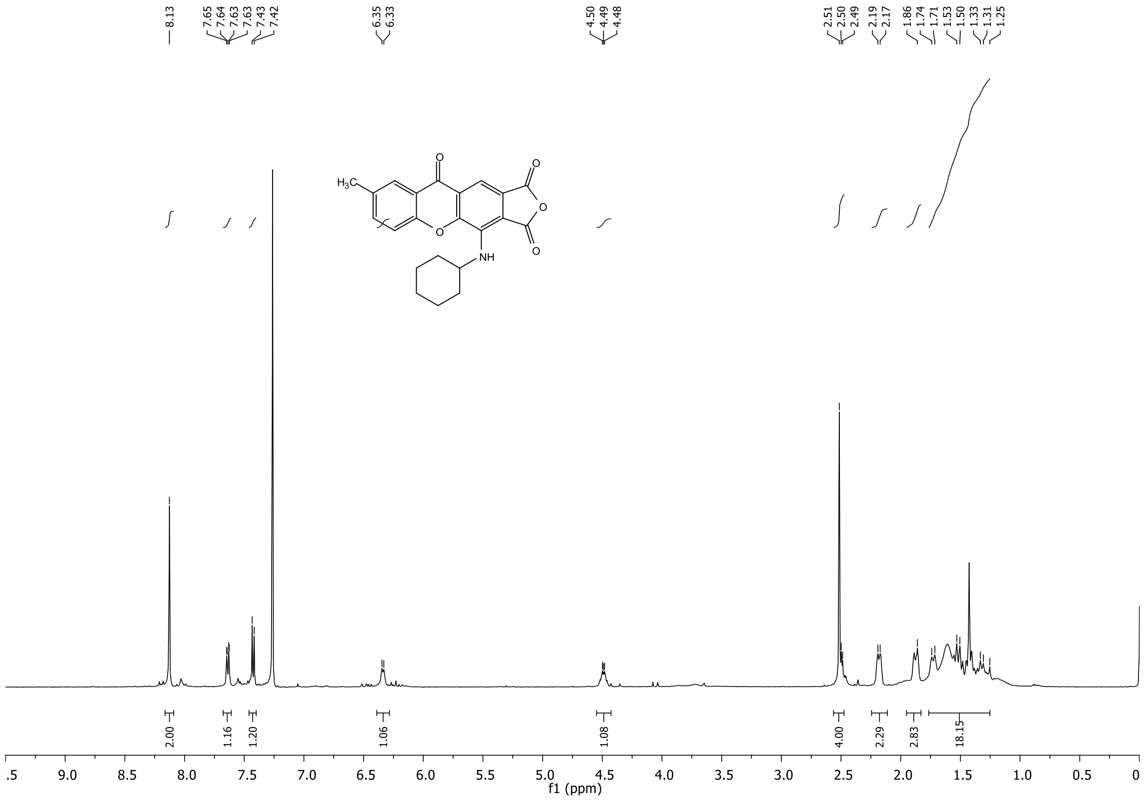


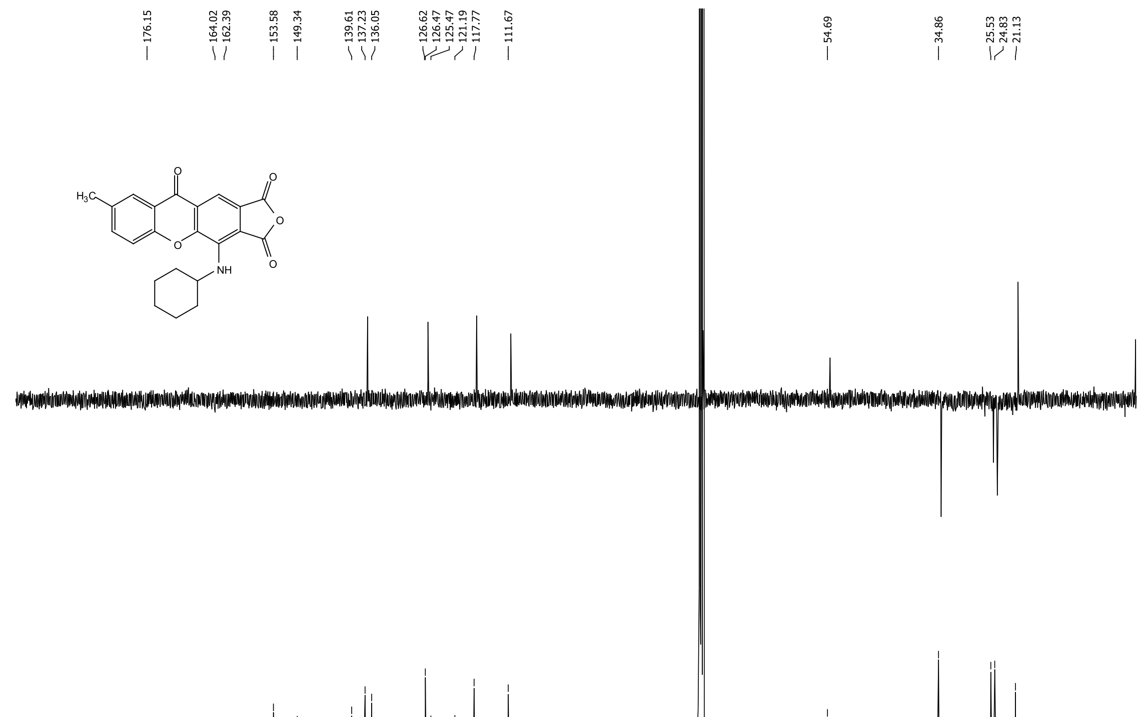
4-(Cyclohexylamino)-2,8-dimethylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8bf)



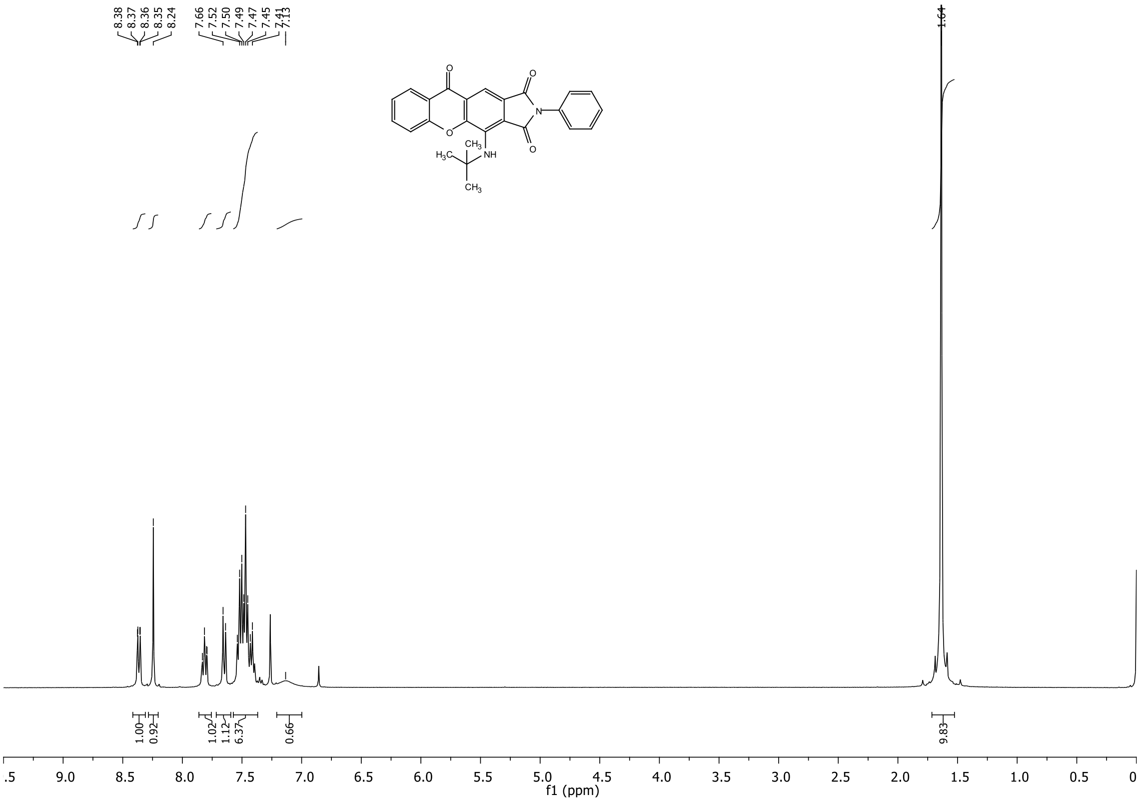


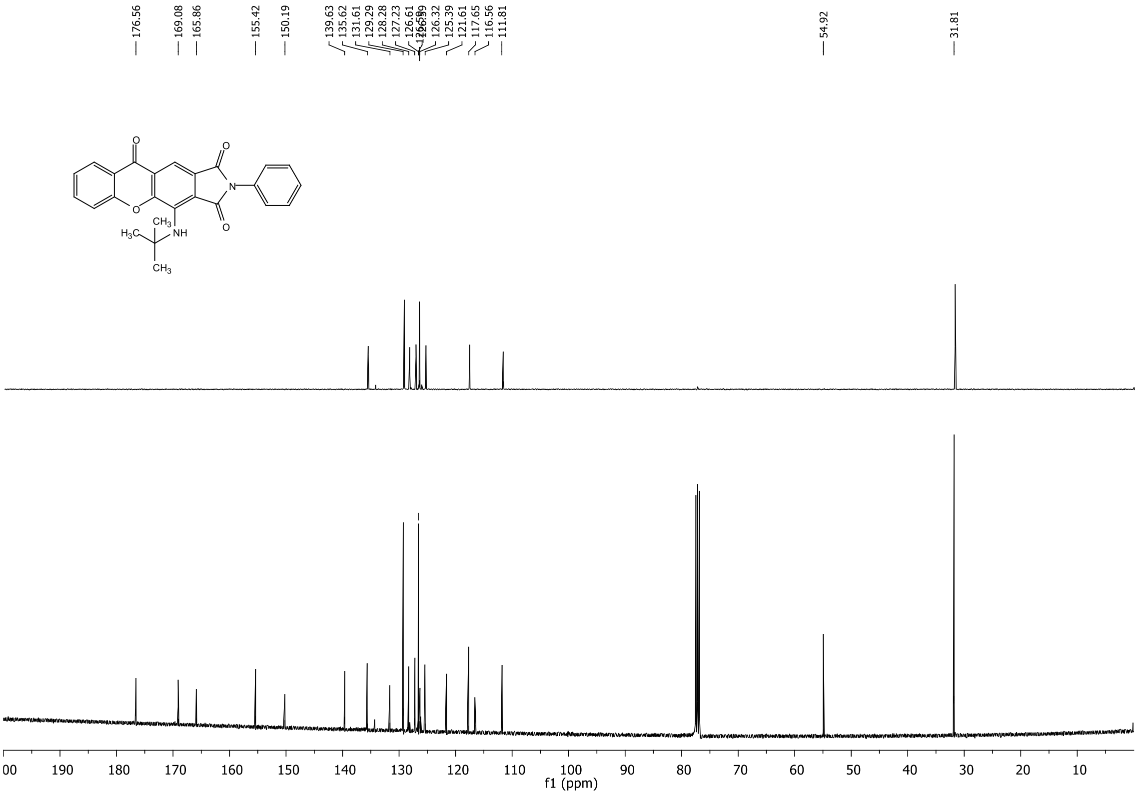
4-(Cyclohexylamino)-8-methyl-1*H*-furo[3,4-*b*]xanthene-1,3,10-trione (8bg)



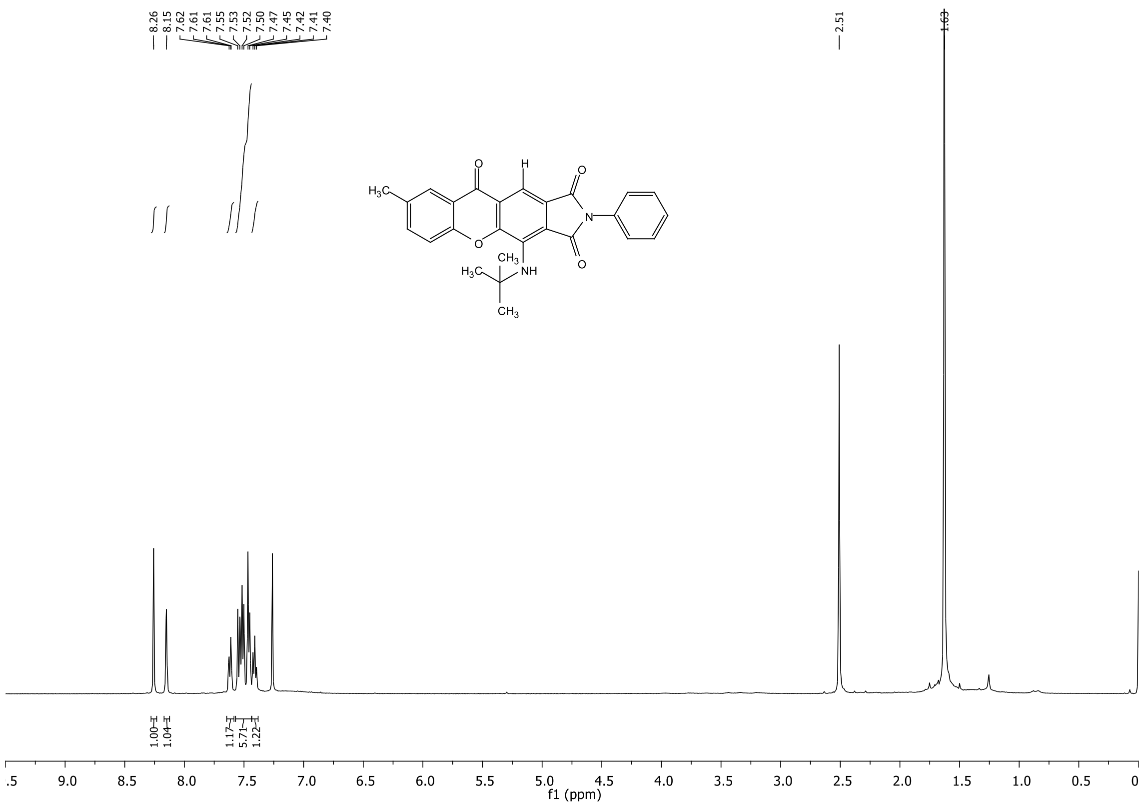


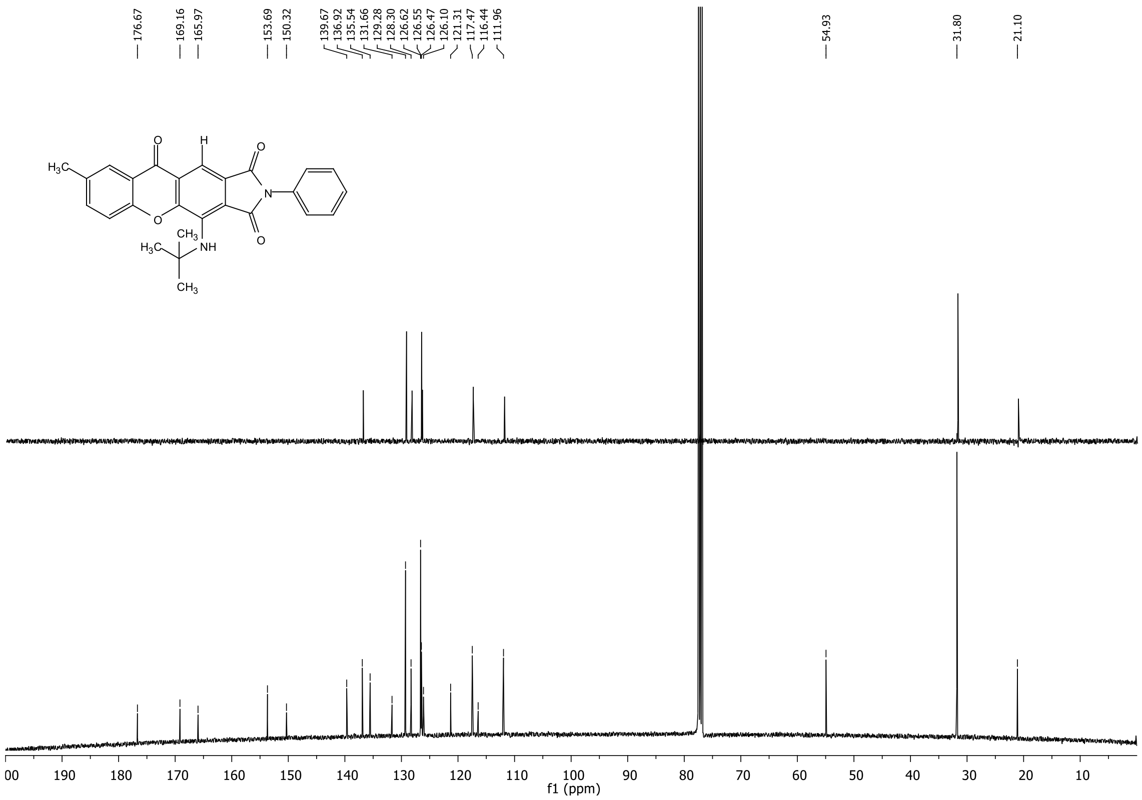
4-(*tert*-Butylamino)-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8bh)



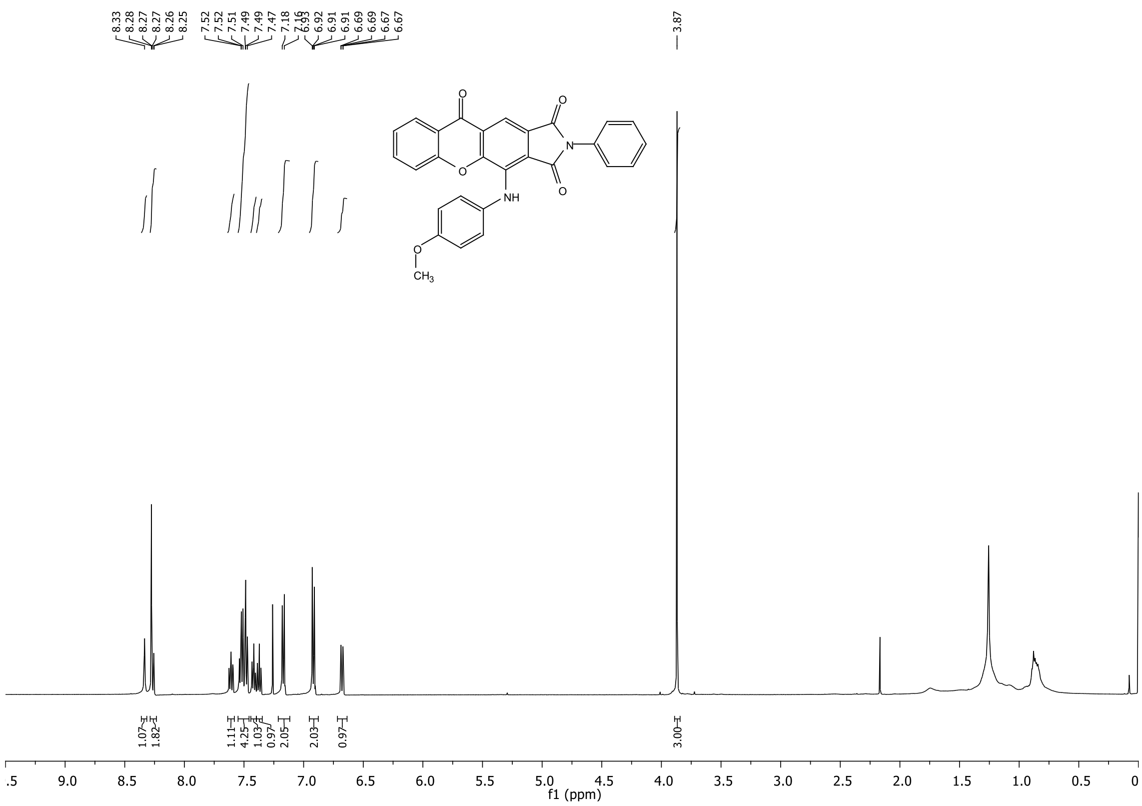


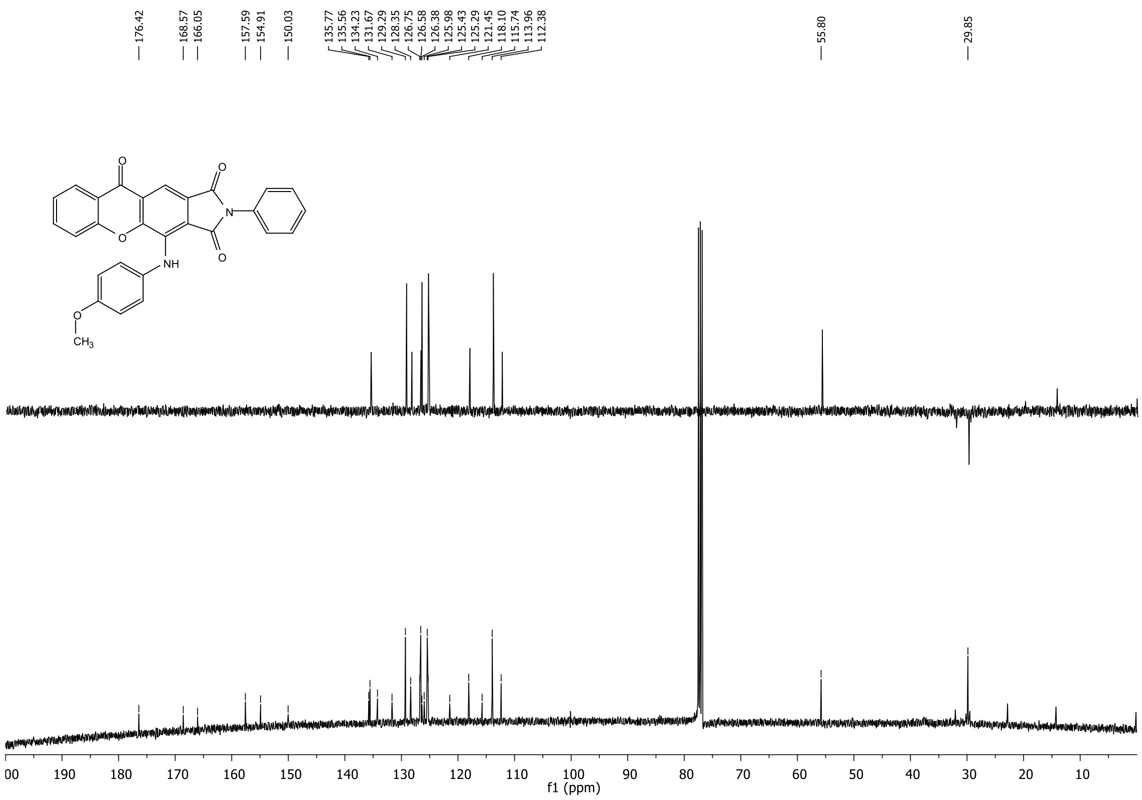
4-(*tert*-Butylamino)-8-methyl-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8bi)



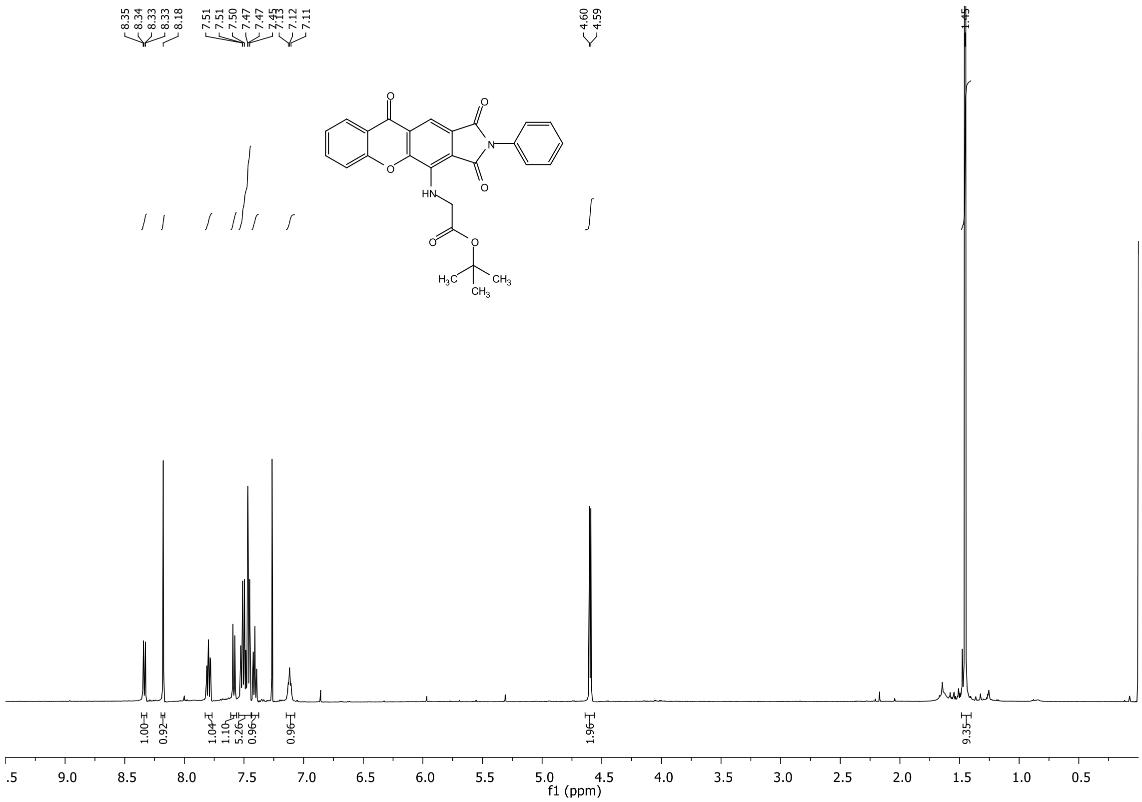


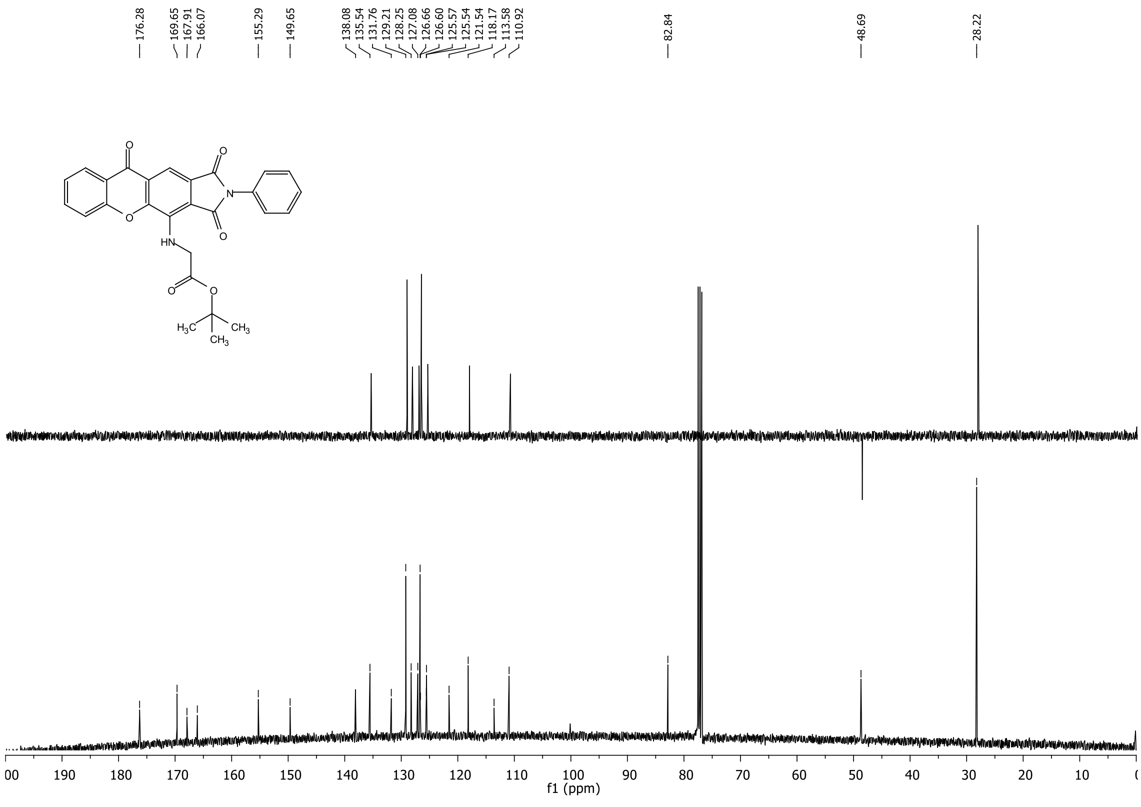
4-((4-Methoxyphenyl)amino)-2-phenylchromeno[2,3-*f*]isoindole-1,3,10(2*H*)-trione (8bj)



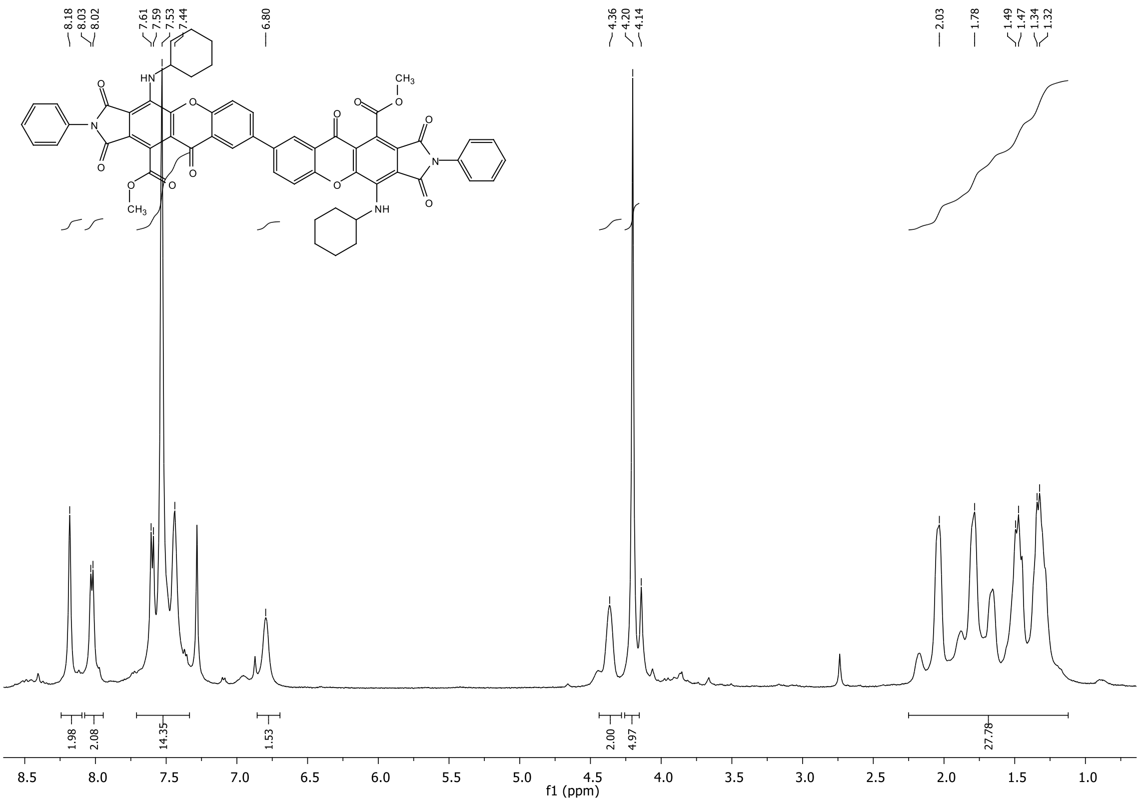


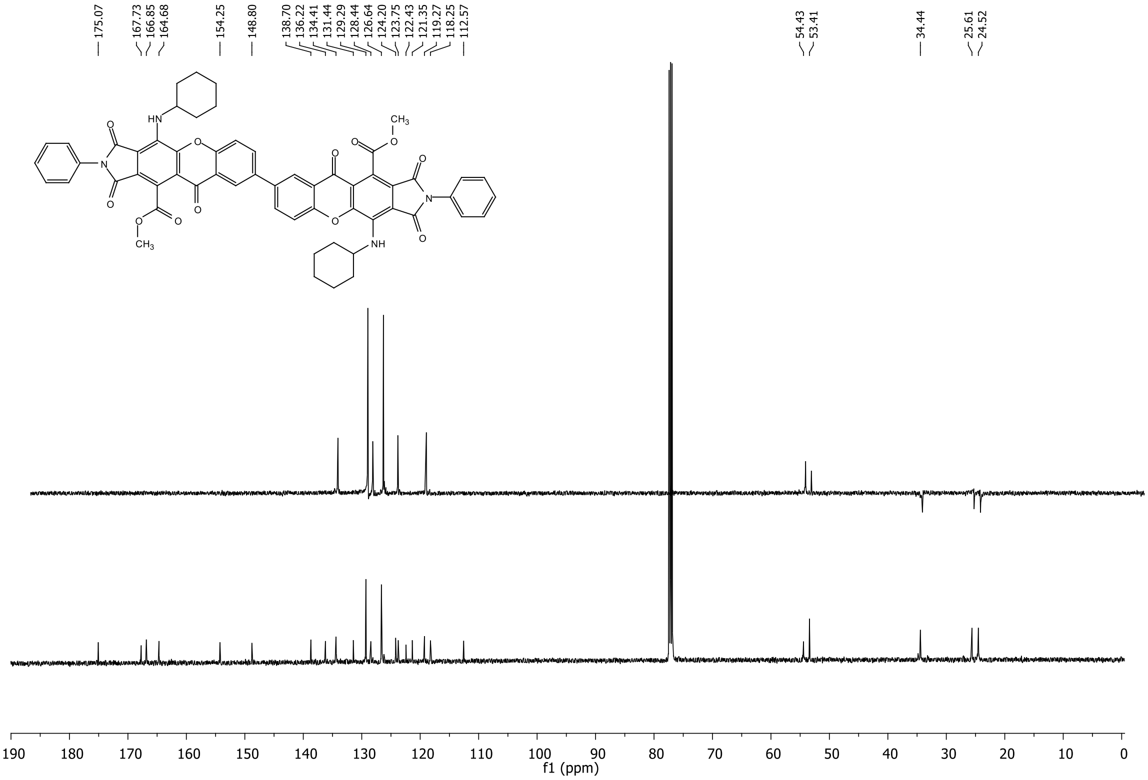
***tert*-Butyl (1,3,10-trioxo-2-phenyl-1,2,3,10-tetrahydrochromeno[2,3-*f*]isoindol-4-yl) glycinate (8bk)**



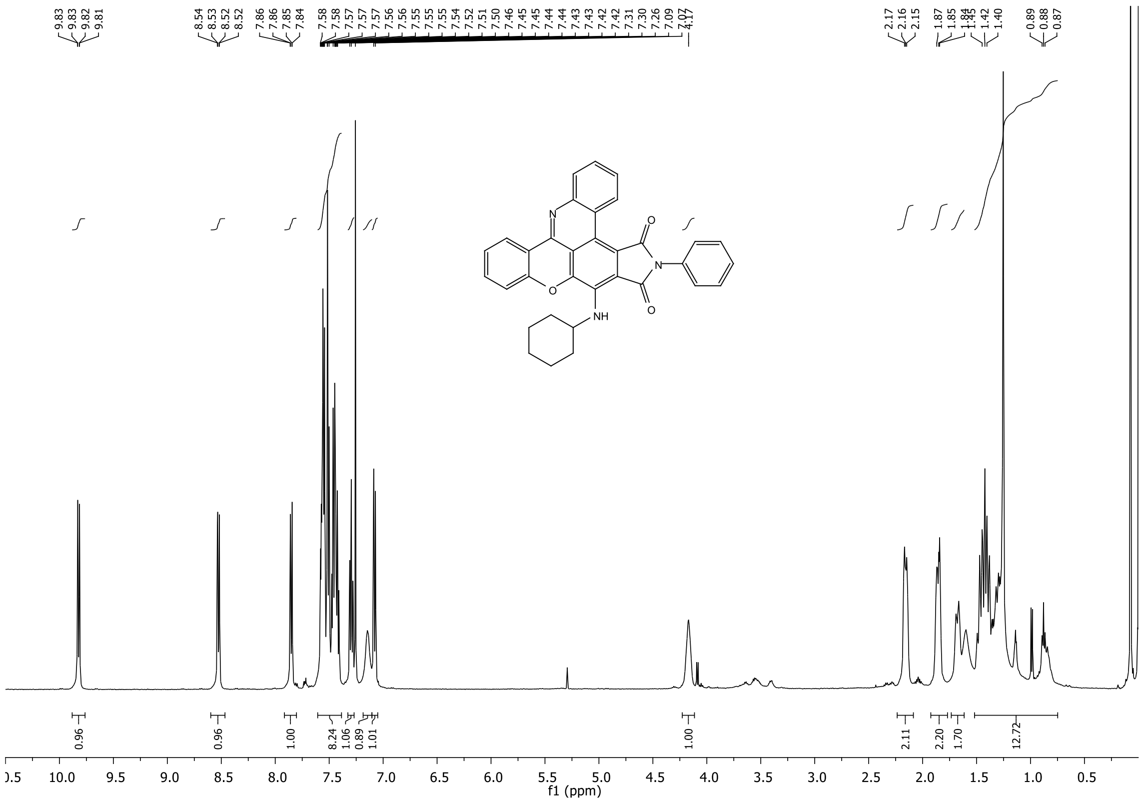


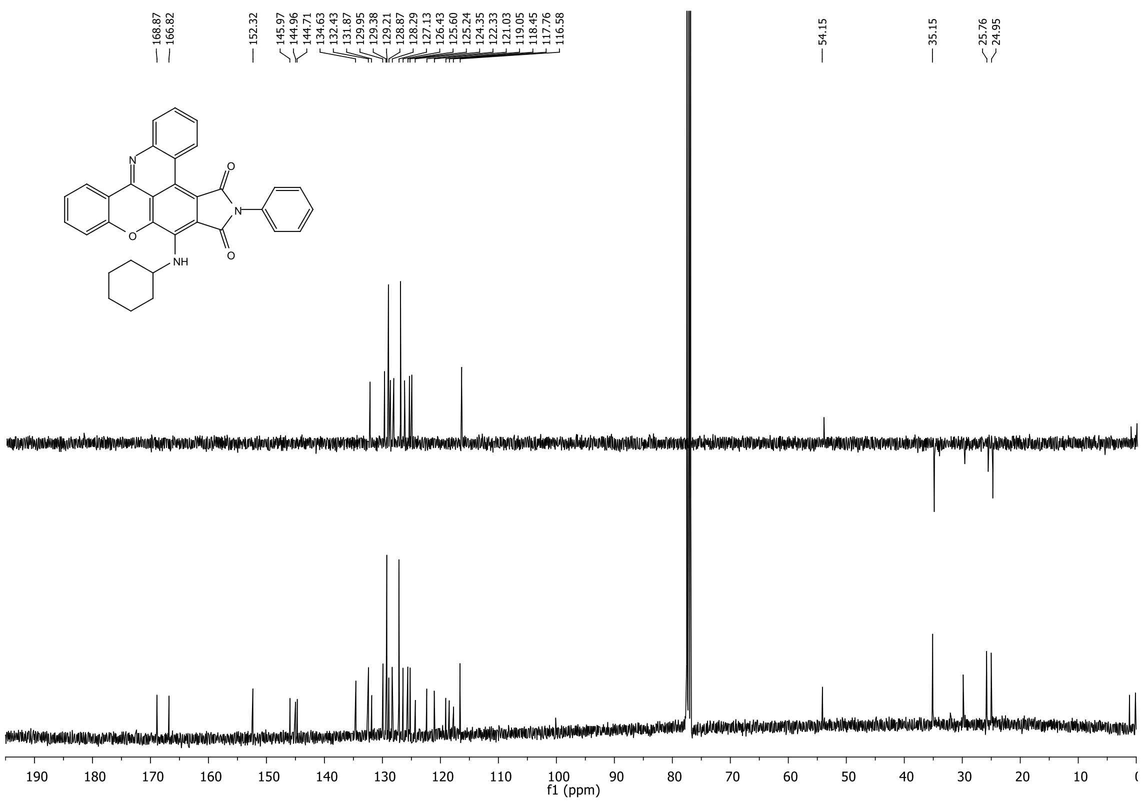
Dimethyl 4,4'-bis(cyclohexylamino)-1,1',3,3',10,10'-hexaoxo-2,2'-diphenyl-1,1',2,2',3,3',10,10'-octahydro-[8,8'-bichromeno[2,3-*f*]isoindole]-11,11'-dicarboxylate (19)



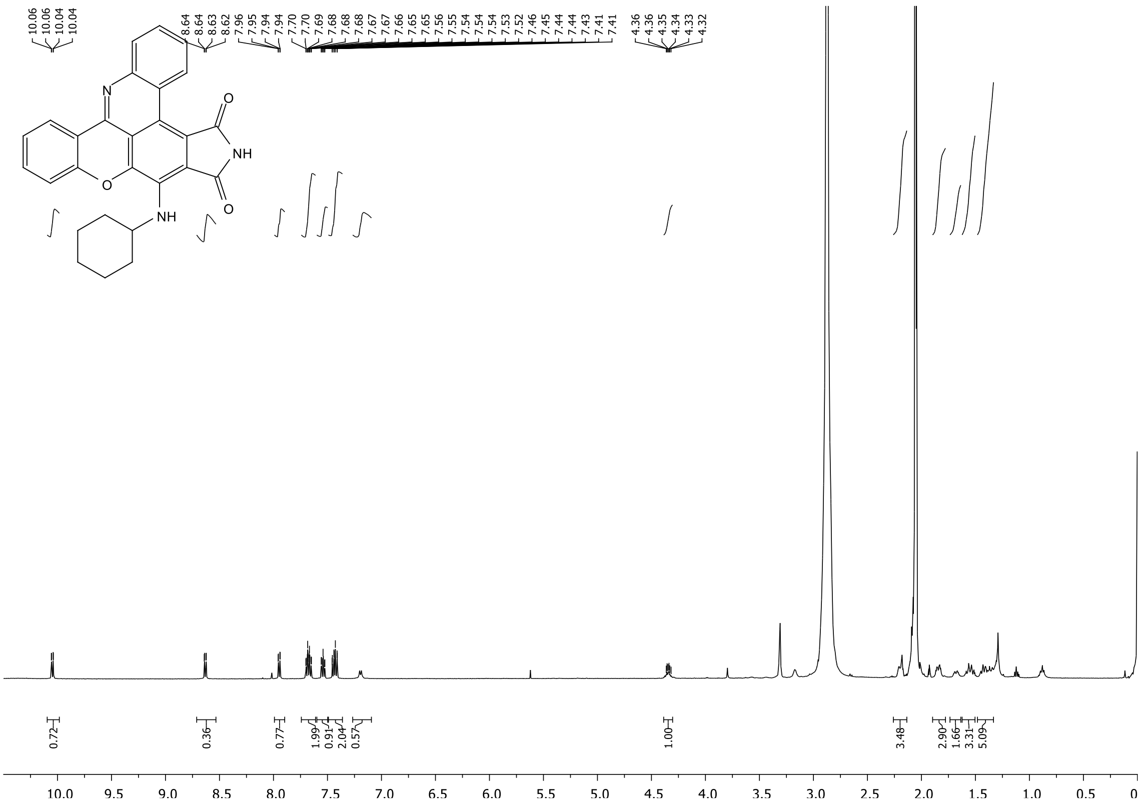


8-(Cyclohexylamino)-6-phenyl-5*H*-chromeno[4,3,2-gh]pyrrolo[3,4-k]phenanthridine-5,7(6*H*)-dione (20aq)

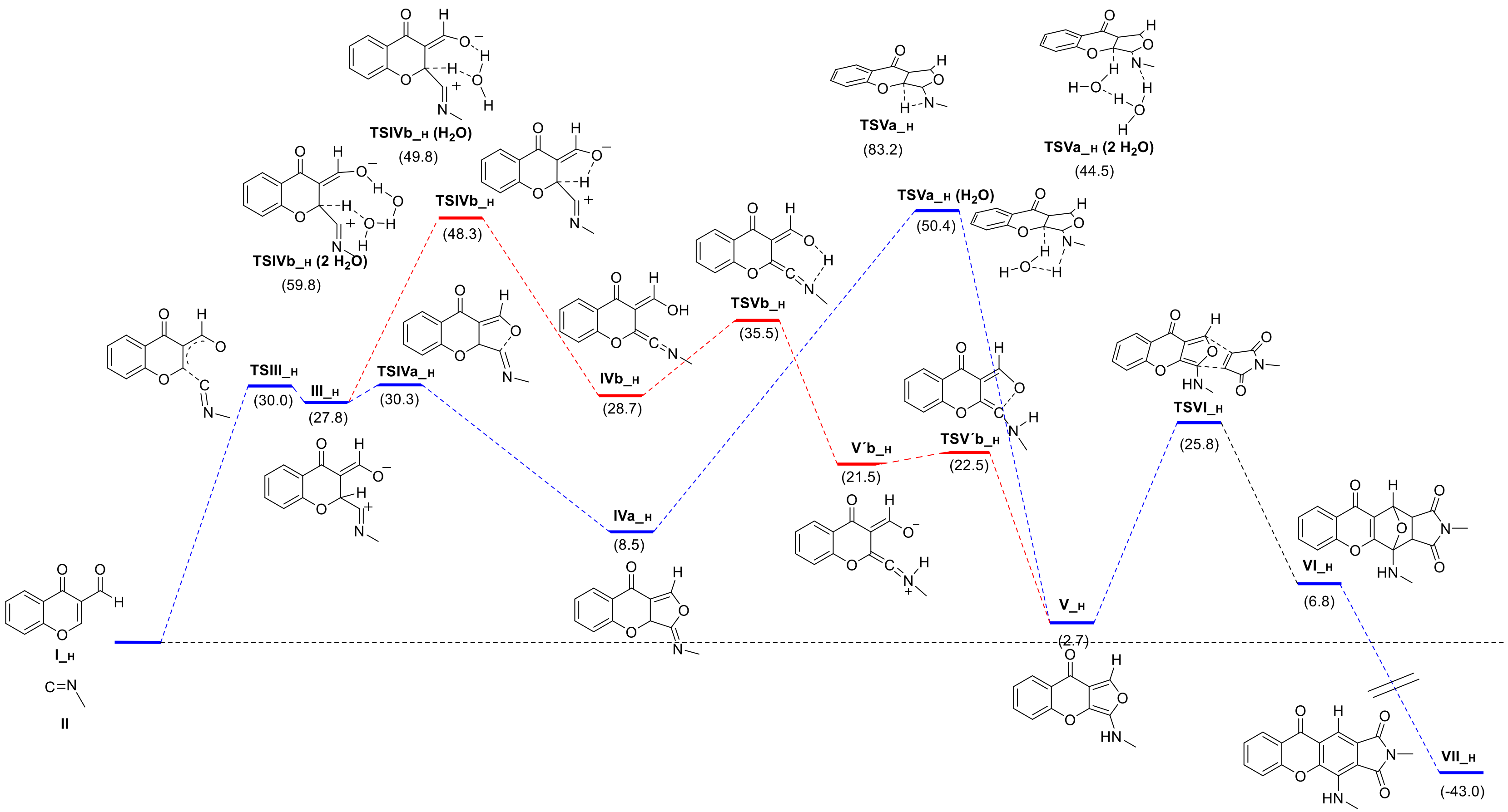




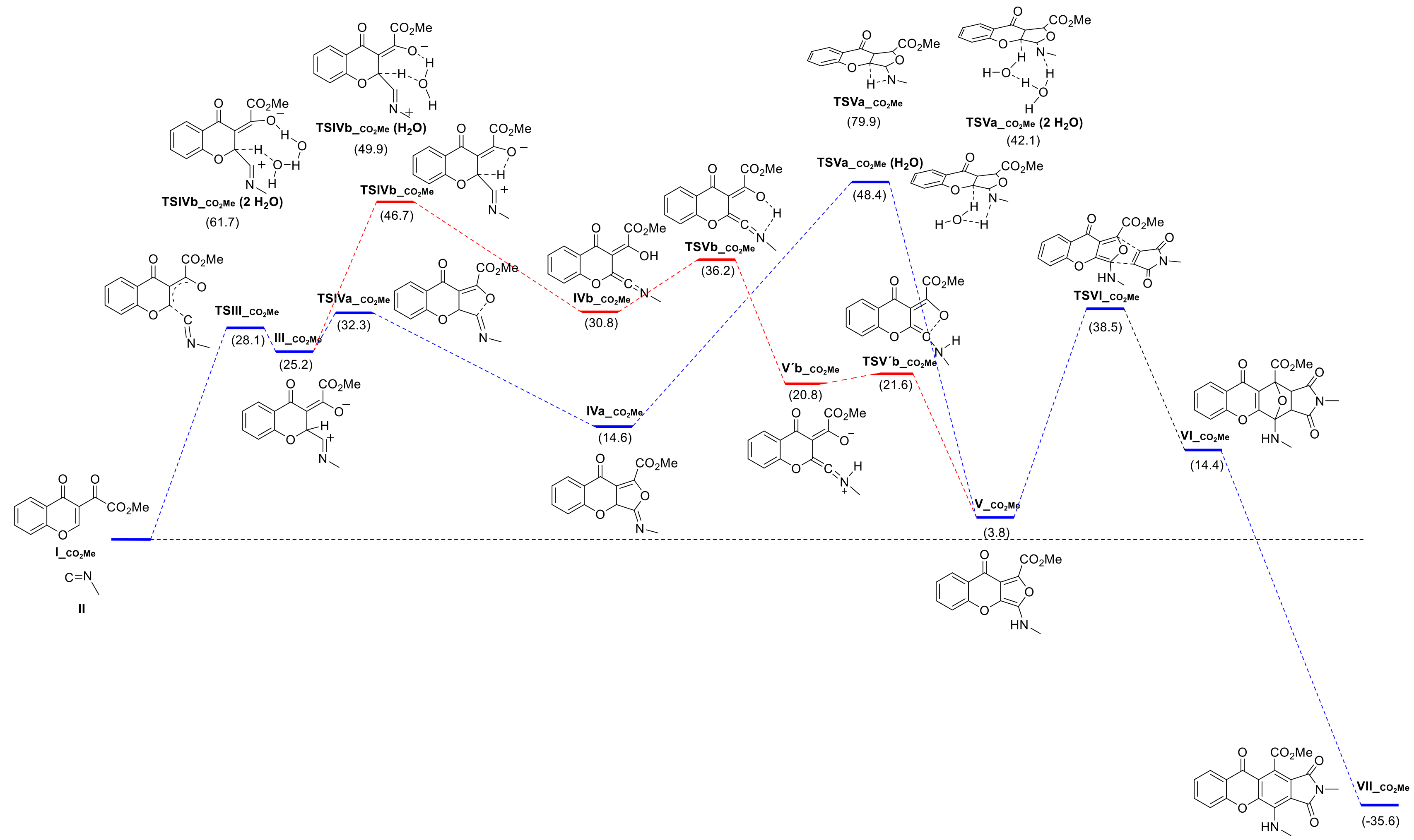
8-(Cyclohexylamino)-5*H*-chromeno[4,3,2-*gh*]pyrrolo[3,4-*k*]phenanthridine-5,7(6*H*)-dione (20ar)



COMPUTATIONAL DETAILS



Scheme S1. Reaction profile for two possible mechanisms for the multicomponent synthesis of xanthones **VII**, starting from chromone **1k**, calculated in THF at PCM-B3LYP/6-31+G(d) level of theory (Gaussian 16). Mechanism A: blue; mechanism B: red.



Scheme S2. Reaction profile for two possible mechanisms for the multicomponent synthesis of xanthones **VII**, starting from chromone **1a**, calculated in THF at PCM-B3LYP/6-31+G(d) level of theory (Gaussian 16). Mechanism A: blue; mechanism B: red.

Table S1. Energies of the principal transition states and intermediates for mechanism A, calculated in THF at PCM-B3LYP/6-31+G(d) level of theory (Gaussian 16)

Mechanism A	TS_{III}	Zwiterion (III)	TS_{IVa}	Iminolactone (IVa)	TS_{Va}	TS_{Va} (H_2O)	TS_{Va} (2 H_2O)	Aminofuran (V)	TS_{VI}	Xanthone (VII)
1k (H)	30.0	27.8	30.3	8.5	83.2	50.4	44.5	2.7	25.8	-43.0
1a (CO_2Me)	28.1	25.2	32.3	14.6	79.9	48.4	42.1	3.8	38.5	-35.6

Table S2. Energies of the principal transition states and intermediates for mechanism B, calculated in THF at PCM-B3LYP/6-31+G(d) level of theory (Gaussian 16)

Mechanism B	TS_{III}	Zwiterion (III)	TS_{IVb}	TS_{IVb} (H_2O)	TS_{IVb} ($2H_2O$)	Iminoketene (IVb)	TS_{Vb}	V'_b	$TS_{V'b}$	Aminofuran (V)	TS_{VI}	Xanthone (VII)
1k (H)	30.0	27.8	48.3	49.8	59.8	28.7	35.5	21.5	22.5	2.7	25.8	-43.0
1a (CO_2Me)	28.1	25.2	46.7	49.9	61.7	30.8	36.2	20.8	21.6	3.8	38.5	-35.6

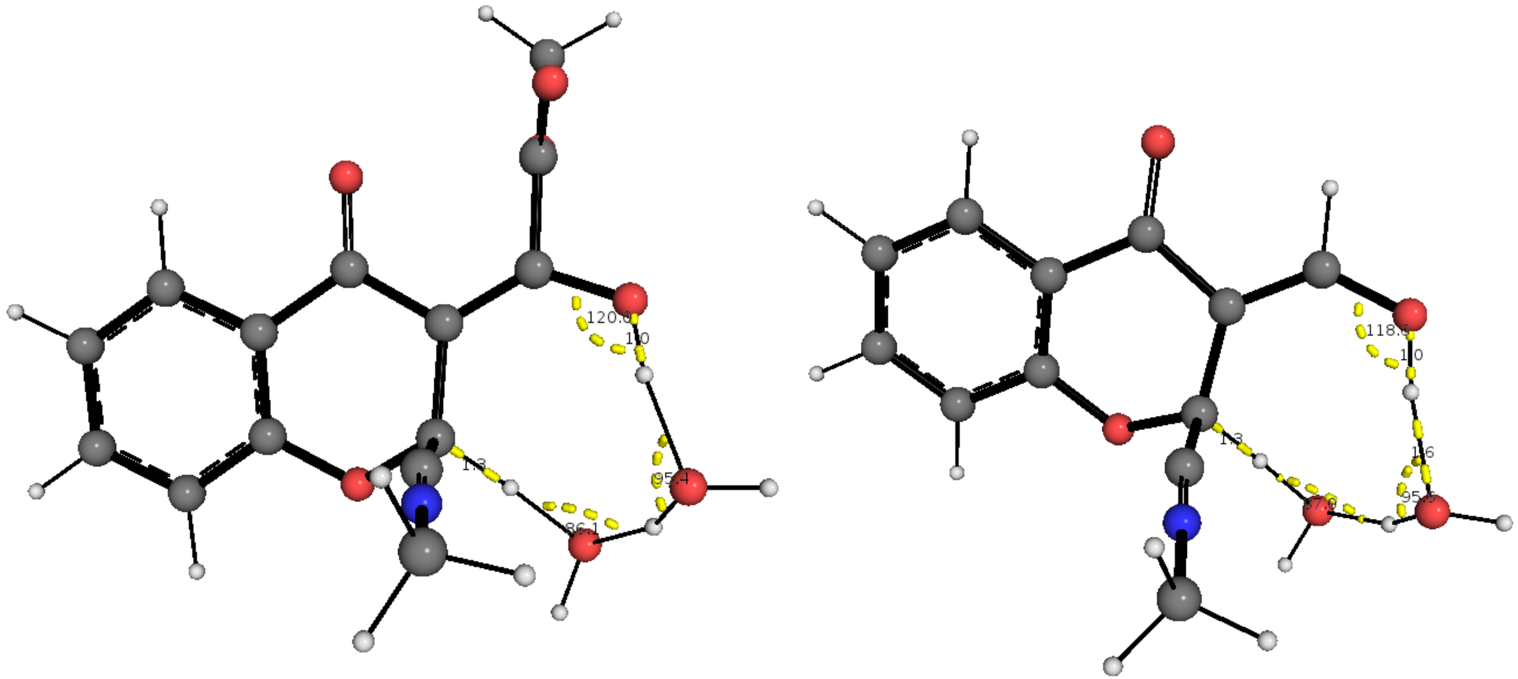


Figure S1. Computational geometry located for **TSIVb** (for **1a** and **1k**) including two molecules of water to assist the proton transfer.

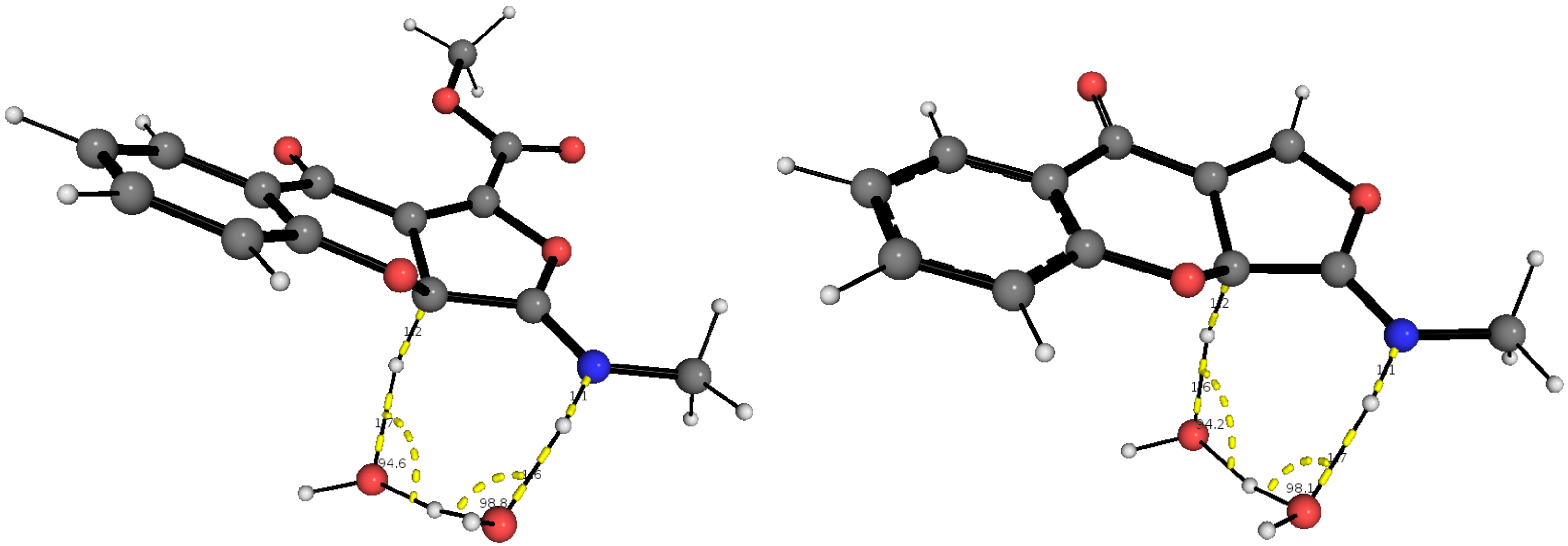


Figure S2. Computational geometry located for **TSVa** (for **1a** and **1k**) including two molecules of water to assist the proton transfer.

Table S3. Electronic energies and thermodynamical magnitudes of the critical structures involved in multicomponent reaction of chromone **I** (**1k**) with methylisocyanide and *N*-methylmaleimide (NMM) in THF at the PCM-B3LYP/6-31+G(d) theory level (298K), done in Gaussian 16.

	E (hartree)	**H (hartree)**	**S(cal/Kmol)**	**G(hartree)**	**H (hartree)**	**S(cal/Kmol)**	**G(hartree)**	**ΔE (kcal/mol)**	**ΔH (kcal/mol)**	**ΔS (kcal/mol)**	**ΔG (kcal/mol)**
I	-610,36652	0,14778	97,70000	0,10136	-610,21874	97,70000	-610,26516				
II	-132,73217	0,05024	60,61500	0,02144	-132,68193	60,61500	-132,71073				
H_2O	-76,42967	0,02481	45,13800	0,00337	-76,40486	45,13800	-76,42630				
NMM	-398,77046	0,10437	85,05300	0,06396	-398,66608	85,05300	-398,70650				
TSIII	-743,06885	0,19890	122,25500	0,14081	-742,86995	122,25500	-742,92804	18,72641	19,28051	-10,74588	30,03225
III	-743,07453	0,20025	120,74000	0,14288	-742,87428	120,74000	-742,93165	15,16142	16,56202	-11,19735	27,76495
TSIV	-743,07142	0,19936	116,83100	0,14385	-742,87206	116,83100	-742,92757	17,11187	17,95712	-12,36223	30,32596
IV	-743,11076	0,20178	112,21000	0,14847	-742,90898	112,21000	-742,96229	-7,57367	-5,20984	-13,73929	8,53701
V	-743,12101	0,20248	111,74600	0,14939	-742,91853	111,74600	-742,97163	-14,00572	-11,20515	-13,87756	2,67975
TSV (H_2O)	-819,48780	0,22363	121,47400	0,16592	-819,26417	121,47400	-819,32189	25,45281	25,95796	-24,42974	50,39945
TSV ($2H_2O$)	-895,94690	0,25181	131,41100	0,18937	-895,69509	131,41100	-895,75752	6,98863	9,60534	-34,91964	44,54256
TSV	-742,98502	0,19487	111,76400	0,14177	-742,79014	111,76400	-742,84325	71,33444	69,36155	-13,87220	83,24143
TSVI	-1141,87605	0,30771	153,64200	0,23471	-1141,56835	153,64200	-1141,64135	-4,32950	-0,99366	-26,73835	25,75895
VI	-1141,91502	0,31179	143,72800	0,24350	-1141,60322	143,72800	-1141,67151	-28,77967	-22,87857	-29,69272	6,82961
VII	-1065,53827	0,28240	144,56400	0,21372	-1065,25587	144,56400	-1065,32455	-61,98934	-58,96224	-15,99247	-42,96075

Table S4. Electronic energies and thermodynamical magnitudes of the critical structures involved in multicomponent reaction of chromone **I** (**1k**) with methylisocyanide and *N*-methylmaleimide (NMM) in toluene at the PCM-B3LYP/6-31+G(d) theory level (298K), done in Gaussian 16.

	E (hartree)	H (hartree)	S(cal/Kmol)	G(hartree)	H (hartree)	S(cal/Kmol)	G(hartree)	ΔE (kcal/mol)	ΔH (kcal/mol)	ΔS (kcal/mol)	ΔG (kcal/mol)
I	-610,36232	0,14782	97,64700	0,10142	-610,21451	97,64700	-610,26090				
II	-132,72978	0,05022	60,66300	0,02139	-132,67957	60,66300	-132,70839				
H_2O	-76,42668	0,02483	45,13300	0,00339	-76,40185	45,13300	-76,42329				
NMM	-398,76698	0,10444	84,85500	0,06413	-398,66254	84,85500	-398,70285				
TSIII	-743,06068	0,19892	121,88900	0,14101	-742,86175	121,88900	-742,91966	19,72363	20,28462	-10,85346	31,14367
III	-743,06312	0,20009	122,23100	0,14202	-742,86303	122,23100	-742,92111	18,18862	19,48255	-10,75154	30,23931
TSIV	-743,06165	0,19936	116,91600	0,14381	-742,86229	116,91600	-742,91784	19,11182	19,94515	-12,33541	32,28638
IV	-743,10654	0,20185	112,06200	0,14861	-742,90468	112,06200	-742,95793	-9,05433	-6,65536	-13,78190	7,13354
V	-743,11709	0,20256	111,74900	0,14946	-742,91453	111,74900	-742,96763	-15,67584	-12,83385	-13,87518	1,04791
TSV (H_2O)	-819,48014	0,22320	120,73200	0,16584	-819,25694	120,73200	-819,31430	24,25055	24,46391	-24,64788	49,12377
TSV ($2H_2O$)	-895,93794	0,25076	131,46900	0,18829	-895,68718	131,46900	-895,74965	4,72193	6,64273	-34,89789	41,55799
TSV	-742,98119	0,19493	111,72400	0,14185	-742,78626	111,72400	-742,83934	69,60068	67,65665	-13,88263	81,54595
TSVI	-1141,86791	0,30798	151,58900	0,23596	-1141,55993	151,58900	-1141,63196	-5,53809	-2,08114	-27,28965	25,22180
VI	-1141,90737	0,31188	144,05600	0,24344	-1141,59549	144,05600	-1141,66393	-30,29972	-24,39422	-29,53448	5,15520
VII	-1065,53248	0,28257	145,26200	0,21355	-1065,24991	145,26200	-1065,31893	-62,79625	-59,70325	-15,72546	-43,97033

Table S5. Electronic energies and thermodynamical magnitudes of the critical structures involved in multicomponent reaction of chromone **I** (**1k**) with methylisocyanide and *N*-methylmaleimide (NMM) in THF at the PCM-M062X/6-31+G(d,p) theory level (298K), done in Gaussian 09.

	E (hartree)	H (hartree)	S(cal/Kmol)	G(hartree)	H (hartree)	S(cal/Kmol)	G(hartree)	ΔE (kcal/mol)	ΔH (kcal/mol)	ΔS (kcal/mol)	ΔG (kcal/mol)
I	-610,12458	0,14927	97,53200	0,10293	-609,97531	97,53200	-610,02165				
II	-132,67295	0,05050	60,46100	0,02177	-132,62246	60,46100	-132,65118				
H_2O	-76,40186	0,02531	45,09300	0,00389	-76,37655	45,09300	-76,39797				
NMM	-398,60766	0,10516	84,08200	0,06521	-398,50250	84,08200	-398,54245				
TSIII	-742,77302	0,20063	121,94800	0,14269	-742,57239	121,94800	-742,63033	15,38514	15,92606	-10,74141	26,67278
III	-742,77926	0,20234	122,29600	0,14424	-742,57691	122,29600	-742,63502	11,46926	13,08636	-10,63771	23,72955
TSIV	-742,77525	0,20124	116,40700	0,14594	-742,57400	116,40700	-742,62931	13,98639	14,91323	-12,39263	27,31219
IV	-742,82043	0,20406	111,71000	0,15098	-742,61638	111,71000	-742,66946	-14,37043	-11,67967	-13,79233	2,11989
V	-742,83356	0,20450	112,76000	0,15092	-742,62906	112,76000	-742,68264	-22,60541	-19,63729	-13,47943	-6,15023
TSV (H_2O)	-819,16932	0,22385	118,08800	0,16774	-818,94547	118,08800	-819,00158	18,87474	18,10164	-25,32940	43,44424
TSV	-742,69654	0,19732	111,71000	0,14425	-742,49922	111,71000	-742,55229	63,37633	61,84207	-13,79233	75,64163
TSVI	-1141,43943	0,31068	146,83000	0,24092	-1141,12875	146,83000	-1141,19851	-21,48210	-17,87015	-28,38301	10,52716
VI	-1141,49646	0,31474	142,01900	0,24727	-1141,18172	142,01900	-1141,24920	-57,27043	-51,11080	-29,81669	-21,27900
VII	-1065,12677	0,28481	143,27000	0,21674	-1064,84196	143,27000	-1064,91003	-77,45545	-74,19428	-16,00618	-58,17961

Table S6. Electronic energies and thermodynamical magnitudes of the critical structures involved in multicomponent reaction of chromone **I** (**1a**) with methylisocyanide and *N*-methylmaleimide (NMM) in THF at the PCM-B3LYP/6-31+G(d) theory level (298K), done in Gaussian 16.

	E (hartree)	H (hartree)	S(cal/Kmol)	G(hartree)	H (hartree)	S(cal/Kmol)	G(hartree)	ΔE (kcal/mol)	ΔH (kcal/mol)	ΔS (kcal/mol)	ΔG (kcal/mol)
I	-838,24566	0,19510	122,45600	0,13692	-838,05055	122,45600	-838,10874				
II	-132,73217	0,05024	60,61500	0,02144	-132,68193	60,61500	-132,71073				
H_2O	-76,42967	0,02481	45,13800	0,00337	-76,40486	45,13800	-76,42630				
NMM	-398,77046	0,10437	85,05300	0,06396	-398,66608	85,05300	-398,70650				
TSIII	-970,95112	0,24625	146,92100	0,17644	-970,70488	146,92100	-970,77468	16,75622	17,32663	-10,77270	28,10410
III	-970,95784	0,24761	145,44900	0,17850	-970,71024	145,44900	-970,77935	12,53917	13,96174	-11,21136	25,17784
TSIV	-970,94826	0,24657	139,68000	0,18020	-970,70169	139,68000	-970,76806	18,55559	19,32617	-12,93052	32,26290
IV	-970,98024	0,24876	136,07700	0,18410	-970,73148	136,07700	-970,79614	-1,51252	0,63293	-14,00421	14,64334
V	-970,99850	0,24954	135,78100	0,18502	-970,74896	135,78100	-970,81348	-12,97245	-10,33691	-14,09242	3,76197
TSV (H_2O)	-1047,37034	0,27077	145,50900	0,20163	-1047,09957	145,50900	-1047,16871	23,31413	23,70256	-24,64460	48,35866
TSV	-970,86954	0,24207	136,17200	0,17737	-970,62747	136,17200	-970,69217	67,95161	65,89965	-13,97590	79,88182
TSV ($2H_2O$)	-1123,82779	0,29797	158,30100	0,22276	-1123,52982	158,30100	-1123,60503	5,88184	7,77127	-34,28371	42,07094
TSVI	-1369,73933	0,35499	168,92300	0,27473	-1369,38434	168,92300	-1369,46460	5,61603	8,92991	-29,56190	38,50632
VI	-1369,78381	0,35836	163,28000	0,28078	-1369,42546	163,28000	-1369,50304	-22,29500	-16,86956	-31,24351	14,38920
VII	-1293,40725	0,32943	165,53300	0,25078	-1293,07782	165,53300	-1293,15647	-55,62106	-52,77907	-17,12099	-35,64932

Table S7. Electronic energies and thermodynamical magnitudes of the critical structures involved in multicomponent reaction of chromone **I** (**1i**) with methylisocyanide and *N*-methylmaleimide (NMM) in THF at the PCM-B3LYP/6-31+G(d) theory level (298K), done in Gaussian 16.

	E (hartree)	H (hartree)	S(cal/Kmol)	G(hartree)	H (hartree)	S(cal/Kmol)	G(hartree)	ΔE (kcal/mol)	ΔH (kcal/mol)	ΔS (kcal/mol)	ΔG (kcal/mol)
I	-1045,93794	0,23814	136,84000	0,17313	-1045,69979	136,84000	-1045,76481				
II	-132,73217	0,05024	60,61500	0,02144	-132,68193	60,61500	-132,71073				
H_2O	-76,42967	0,02481	45,13800	0,00337	-76,40486	45,13800	-76,42630				
NMM	-398,77046	0,10437	85,05300	0,06396	-398,66608	85,05300	-398,70650				
TSIII	-1178,63931	0,28918	161,50600	0,21244	-1178,35013	161,50600	-1178,42687	19,32356	19,82557	-10,71280	30,54343
III	-1178,64740	0,29048	161,97600	0,21352	-1178,35692	161,97600	-1178,43388	14,25166	15,57005	-10,57274	26,14798
TSIV	-1178,64472	0,28964	156,62600	0,21522	-1178,35508	156,62600	-1178,42950	15,93132	16,72135	-12,16704	28,89441
IV	-1178,68469	0,29200	150,80200	0,22035	-1178,39268	150,80200	-1178,46433	-9,14710	-6,87426	-13,90259	7,03512
V	-1178,69727	0,29266	150,17200	0,22131	-1178,40461	150,17200	-1178,47596	-17,04195	-14,35683	-14,09033	-0,25983
TSV (H_2O)	-1255,06314	0,31389	159,77400	0,23798	-1254,74925	159,77400	-1254,82517	22,98860	23,42660	-24,68006	48,11910
TSV	-1178,56088	0,28513	150,65000	0,21355	-1178,27575	150,65000	-1178,34733	68,54310	66,50055	-13,94789	80,45574
TSV (2H2O)	-1331,52240	0,34219	170,17900	0,26133	-1331,18021	170,17900	-1331,26107	4,42432	7,04920	-35,03050	42,09623
TSVI	-1577,43876	0,39796	186,59300	0,30930	-1577,04080	186,59300	-1577,12946	1,13528	4,39896	-28,58267	32,99582
VI	-1577,47786	0,40138	181,22300	0,31527	-1577,07648	181,22300	-1577,16259	-23,40177	-17,99075	-30,18293	12,20751
VII	-1501,10042	0,37251	180,77100	0,28662	-1500,72791	180,77100	-1500,81380	-56,17453	-53,30933	-16,86650	-36,43371

Table S8. Electronic energies and thermodynamical magnitudes of the critical structures involved in multicomponent reaction of chromone **I** (**1j**) with methylisocyanide and *N*-methylmaleimide (NMM) in THF at the PCM-B3LYP/6-31+G(d) theory level (298K), done in Gaussian 16.

	E (hartree)	H (hartree)	S(cal/Kmol)	G(hartree)	H (hartree)	S(cal/Kmol)	G(hartree)	ΔE (kcal/mol)	ΔH (kcal/mol)	ΔS (kcal/mol)	ΔG (kcal/mol)
I	-1045,94377	0,23828	137,15800	0,17311	-1045,70549	137,15800	-1045,77066				
II	-132,73217	0,05024	60,61500	0,02144	-132,68193	60,61500	-132,71073				
H_2O	-76,42967	0,02481	45,13800	0,00337	-76,40486	45,13800	-76,42630				
NMM	-398,77046	0,10437	85,05300	0,06396	-398,66608	85,05300	-398,70650				
TSIII	-1178,64607	0,28938	161,13100	0,21282	-1178,35669	161,13100	-1178,43324	18,74853	19,28944	-10,91932	30,21438
III	-1178,65209	0,29068	161,62400	0,21389	-1178,36140	161,62400	-1178,43820	14,97134	16,32927	-10,77240	27,10737
TSIV	-1178,65060	0,28981	154,46900	0,21641	-1178,36079	154,46900	-1178,43419	15,90309	16,71321	-12,90459	29,62359
IV	-1178,69461	0,29223	152,06800	0,21998	-1178,40238	152,06800	-1178,47463	-11,71464	-9,38344	-13,62009	4,24293
V	-1178,71206	0,29288	150,81600	0,22122	-1178,41918	150,81600	-1178,49083	-22,66156	-19,92437	-13,99319	-5,92400
TSV (H_2O)	-1255,07362	0,31413	160,00800	0,23810	-1254,75949	160,00800	-1254,83552	20,07735	20,57810	-24,70509	45,29508
TSV	-1178,57226	0,28534	151,11900	0,21353	-1178,28692	151,11900	-1178,35872	65,06296	63,06622	-13,90289	76,97623
TSV ($2H_2O$)	-1331,53224	0,34223	170,63800	0,26116	-1331,19001	170,63800	-1331,27108	1,90897	4,47736	-34,98848	39,48235
TSVI	-1577,45229	0,39811	187,80800	0,30888	-1577,05418	187,80800	-1577,14341	-3,69422	-0,41799	-28,31536	27,91155
VI	-1577,49393	0,40153	180,62300	0,31571	-1577,09240	180,62300	-1577,17822	-29,82303	-24,40448	-30,45649	6,06738
VII	-1501,10522	0,37248	182,73600	0,28566	-1500,73274	182,73600	-1500,81957	-55,52962	-52,76733	-16,37570	-36,38305

Table S9. Electronic energies and thermodynamical magnitudes of the critical structures involved in multicomponent reaction of chromone **I** (**1k**) with methylisocyanide and NMM in THF at the PCM-B3LYP/6-31+G(d) theory level (298K), done in Gaussian 16 for two possible mechanisms.

	E (hartree)	H (hartree)	S(cal/Kmol)	G(hartree)	H (hartree)	S(cal/Kmol)	G(hartree)	ΔE (kcal/mol)	ΔH (kcal/mol)	ΔS (kcal/mol)	ΔG (kcal/mol)
I	-610,36652	0,14778	97,70000	0,10136	-610,21874	97,70000	-610,26516				
II	-132,73217	0,05024	60,61500	0,02144	-132,68193	60,61500	-132,71073				
H_2O	-76,42967	0,02481	45,13800	0,00337	-76,40486	45,13800	-76,42630				
NMM	-398,77046	0,10437	85,05300	0,06396	-398,66608	85,05300	-398,70650				
TSIII	-743,06885	0,19890	122,25500	0,14081	-742,86995	122,25500	-742,92804	18,72641	19,28051	-10,74588	30,03225
III	-743,07453	0,20025	120,74000	0,14288	-742,87428	120,74000	-742,93165	15,16142	16,56202	-11,19735	27,76495
TSIVa	-743,07142	0,19936	116,83100	0,14385	-742,87206	116,83100	-742,92757	17,11187	17,95712	-12,36223	30,32596
TSIVb	-743,03757	0,19540	119,42600	0,13866	-742,84217	119,42600	-742,89891	38,35705	36,71423	-11,58892	48,30935
TSIVb (H_2O)	-819,48267	0,22070	128,09100	0,15984	-819,26196	128,09100	-819,32282	28,67606	27,34386	-22,45788	49,81309
TSIVb (H_2O)	-895,91521	0,24885	140,69900	0,18200	-895,66636	140,69900	-895,73321	26,87376	27,63242	-32,15182	59,79981
IVa	-743,11076	0,20178	112,21000	0,14847	-742,90898	112,21000	-742,96229	-7,57367	-5,20984	-13,73929	8,53701
IVb	-743,07444	0,20054	118,49900	0,14423	-742,87390	118,49900	-742,93020	15,22273	16,80468	-11,86517	28,67591
TSVa (H_2O)	-819,48780	0,22363	121,47400	0,16592	-819,26417	121,47400	-819,32189	25,45281	25,95796	-24,42974	50,39945
TSVa (H_2O)	-895,94690	0,25181	131,41100	0,18937	-895,69509	131,41100	-895,75752	6,98863	9,60534	-34,91964	44,54256
TSVa	-742,98502	0,19487	111,76400	0,14177	-742,79014	111,76400	-742,84325	71,33444	69,36155	-13,87220	83,24143
TSVb	-743,06177	0,19544	111,66000	0,14238	-742,86633	111,66000	-742,91939	23,16998	21,55163	-13,90319	35,46226
V´b	-743,08735	0,20114	116,50900	0,14578	-742,88622	116,50900	-742,94158	7,11584	9,07304	-12,45819	21,53789
TSV´b	-743,08694	0,20016	112,19900	0,14685	-742,88678	112,19900	-742,94009	7,37321	8,71859	-13,74257	22,46858
V	-743,12101	0,20248	111,74600	0,14939	-742,91853	111,74600	-742,97163	-14,00572	-11,20515	-13,87756	2,67975
TSVI	-1141,8760	0,30771	153,64200	0,23471	-1141,56835	153,64200	-1141,64135	-4,32950	-0,99366	-26,73835	25,75895
VI	-1141,9150	0,31179	143,72800	0,24350	-1141,60322	143,72800	-1141,67151	-28,77967	-22,87857	-29,69272	6,82961
VII	-1065,5382	0,28240	144,56400	0,21372	-1065,25587	144,56400	-1065,32455	-61,98934	-58,96224	-15,99247	-42,96075

Table S10. Electronic energies and thermodynamical magnitudes of the critical structures involved in multicomponent reaction of chromone **I** (**1a**) with methylisocyanide and *N*-methylmaleimide (NMM) in THF at the PCM-B3LYP/6-31+G(d) theory level (298K), done in Gaussian 16 for two possible mechanisms.

	E (hartree)	H (hartree)	S(cal/Kmol)	G(hartree)	H (hartree)	S(cal/Kmol)	G(hartree)	ΔE (kcal/mol)	ΔH (kcal/mol)	ΔS (kcal/mol)	ΔG (kcal/mol)
I	-838,24566	0,19510	122,45600	0,13692	-838,05055	122,45600	-838,10874				
II	-132,73217	0,05024	60,61500	0,02144	-132,68193	60,61500	-132,71073				
H_2O	-76,42967	0,02481	45,13800	0,00337	-76,40486	45,13800	-76,42630				
NMM	-398,77046	0,10437	85,05300	0,06396	-398,66608	85,05300	-398,70650				
TSIII	-970,95112	0,24625	146,92100	0,17644	-970,70488	146,92100	-970,77468	16,75622	17,32663	-10,77270	28,10410
III	-970,95784	0,24761	145,44900	0,17850	-970,71024	145,44900	-970,77935	12,53917	13,96174	-11,21136	25,17784
TSIVa	-970,94826	0,24657	139,68000	0,18020	-970,70169	139,68000	-970,76806	18,55559	19,32617	-12,93052	32,26290
TSIVb	-970,91850	0,24253	145,42900	0,17344	-970,67597	145,42900	-970,74506	37,22858	35,46842	-11,21732	46,69080
TSIVb (H_2O)	-1047,3609	0,26684	151,98300	0,19462	-1047,09408	151,98300	-1047,16629	29,23189	27,15233	-22,71535	49,87821
TSIVb ($2H_2O$)	-1123,79128	0,29511	163,17000	0,21758	-1123,49618	163,17000	-1123,57370	28,79209	28,88308	-32,83275	61,73132
IVa	-970,98024	0,24876	136,07700	0,18410	-970,73148	136,07700	-970,79614	-1,51252	0,63293	-14,00421	14,64334
IVb	-970,95034	0,24741	141,83300	0,18002	-970,70293	141,83300	-970,77032	17,24809	18,54891	-12,28892	30,84308
TSVa (H_2O)	-1047,3703	0,27077	145,50900	0,20163	-1047,09957	145,50900	-1047,16871	23,31413	23,70256	-24,64460	48,35866
TSVa ($2H_2O$)	-1123,82779	0,29797	158,30100	0,22276	-1123,52982	158,30100	-1123,60503	5,88184	7,77127	-34,28371	42,07094
TSVa	-970,86954	0,24207	136,17200	0,17737	-970,62747	136,17200	-970,69217	67,95161	65,89965	-13,97590	79,88182
TSVb	-970,93964	0,24239	135,68100	0,17792	-970,69726	135,68100	-970,76172	23,96033	22,10792	-14,12222	36,23630
V´b	-970,96802	0,24842	140,55900	0,18164	-970,71960	140,55900	-970,78639	6,15089	8,08613	-12,66858	20,75994
TSV´b	-970,96784	0,24745	136,17900	0,18275	-970,72038	136,17900	-970,78509	6,26919	7,59574	-13,97382	21,57603
V	-970,99850	0,24954	135,78100	0,18502	-970,74896	135,78100	-970,81348	-12,97245	-10,33691	-14,09242	3,76197
TSVI	-1369,7393	0,35499	168,92300	0,27473	-1369,38434	168,92300	-1369,46460	5,61603	8,92991	-29,56190	38,50632
VI	-1369,7838	0,35836	163,28000	0,28078	-1369,42546	163,28000	-1369,50304	-22,29500	-16,86956	-31,24351	14,38920
VII	-1293,4072	0,32943	165,53300	0,25078	-1293,07782	165,53300	-1293,15647	-55,62106	-52,77907	-17,12099	-35,64932