Visible light-mediated arylation of *ortho*-hydroxyarylenaminones: Direct access to isoflavones.

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Table of Contents

(A)	Experimental Section	3
(B)	Characterization of products	-9
(C)	Copies ¹ H and ¹³ C NMR spectra	-27

(A) Experimental Section.

Commercially available starting materials, reagents, catalysts, anhydrous and degassed solvents were used without further purification. Flash column chromatography was performed with Merck Silica gel 60 (230-400 mesh). The solvents for column chromatography were distilled before the use. Thin layer chromatography was carried out using Merck TLC Silica gel 60 F₂₅₄ and visualized by short-wavelength ultraviolet light or by treatment with potassium permanganate (KMnO₄) stain. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Bruker 250 and 500 MHz at 20°C. All ¹H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for CHCl₃ (7.26 ppm) and DMSO (2.50 ppm). All ¹³C NMR spectra were reported in ppm relative to residual CHCl₃ (77.00 ppm) or DMSO (39.70 ppm) and were obtained with ¹H decoupling. Coupling constants, *J*, are reported in Hertz (Hz). Gas chromatographic analyses was performed on Gas Chromatograph Mass Spectrometer GCMS-QP2010 Ultra instrument.

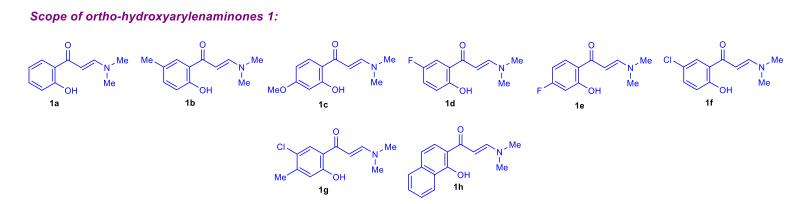
The optimal reaction conditions were identified by Microscale High-Throughput Experimentation Screening. Parallel synthesis was accomplished in an MBraun glovebox operating with a constant Ar-purge (oxygen and water <5 ppm). Screening reactions were carried out in 10 mL vials using suitable heating blocks. Liquid chemicals were dosed using gas tight micro syringes. Isolation of obtained compounds was achieved by column chromatography on Silica gel.

General procedure for the synthesis of aryl diazonium tetrafluoroborates starting from commercial anilines.

An appropriate aniline (20 mmol) was added dropwise to the mixture of aqueous HBF₄ 48% (40 mmol, 5.2 mL) and absolute EtOH (7 mL) placed in 50 mL round bottom-flask. Subsequently, the reaction mixture was stirred until total homogeneity, followed by the slow addition of *t*-BuONO 90% (40 mmol, 5.4 mL) at 0°C. Afterwards, the mixture was stirred intensively for 10 minutes at 0°C and additionally for 30 minutes at room temperature. Finally, addition of Et₂O (20 mL) caused precipitation of the title diazonium salt which was filtrated and washed 4 times with Et₂O, then dried in vacuum. Aryl part:

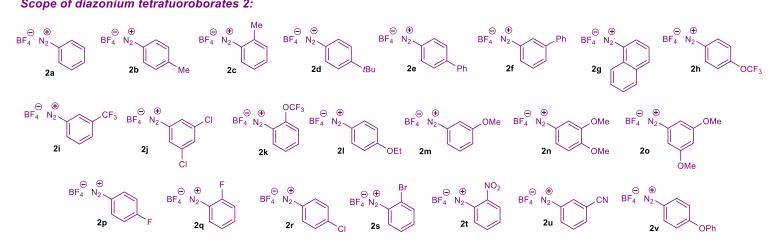
d OCF₃ g .CF₃ .CI _OMe ,OMe .OMe i OEt n `OMe 0 m .CN u р OPh

Scheme 1. List of aryl substituents.

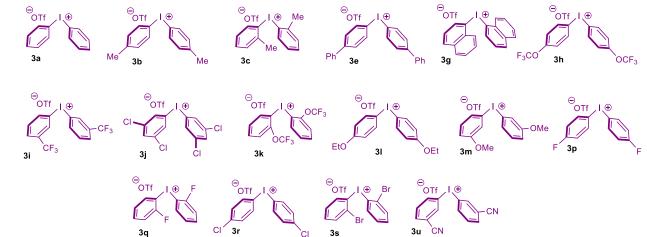


Scheme 2. List of *ortho*-hydroxyarylenaminones 1 used for preparation of 3-arylchromones.

Scope of diazonium tetrafuoroborates 2:



Scheme 3. List of diazonium tetrafuoroborates 2 used for preparation of 3-arylchromones.

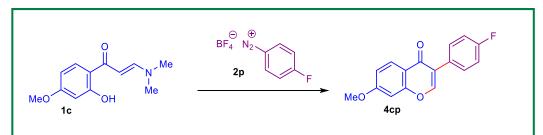


Scope of diaryliodonium triflates 3:

Scheme 4. List of diaryliodonium triflates 3 used for preparation of 3-arylchromones.

1. Reaction condition screening for arylation of *ortho*-hydroxyarylenaminones.

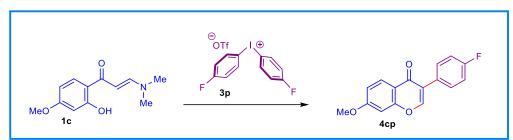
Table S1. Optimization of the reaction conditions.



Reaction (a) ^b								
entry	catalysts (equiv.)/reagent (equiv.)/additive	light source	Solvent/temperature/time	yield (%) 4cp ^a				
1	Eosin Y (0.03)/diazonium salt (1.5)	Green LED	MeOH/10h	52				
2	Eosin Y (0.03)/diazonium salt (1.5)	Green LED	CH ₃ CN/10h	44				
3	Eosin Y (0.03)/diazonium salt (1.5)	Green LED	DMSO/10h	87				
4	Eosin Y (0.03)/diazonium salt (1.3)	Green LED	DMSO/3h	86				
5	Eosin Y (0.03)/diazonium salt (1.3)	NO	DMSO/3h	0 ^c				
6	diazonium salt (1.3)	Green LED	DMSO/3h	0 ^c				
7	Eosin Y (0.03)/diazonium salt (1.3)/TEMPO (1.5)	Green LED	DMSO/3h	0 ^c				
8	Porphyrin (0.015)/diazonium salt (1.5)	Blue LED	DMSO/10h	33				
9	fac-Ir(ppy)₃ (0.01)/diazonium salt (1.3)	Blue LED	CH ₃ CN/10h	75				
10	fac-Ir(ppy)₃ (0.01)/diazonium salt (1.3)	Blue LED	DMSO/10h	79				
11	Ru(bpy)₃Cl₂*6H₂O (0.02)/diazonium salt (1.5)	Blue LED	DMSO/10h	43				
12	Ru(bpm) ₃ Cl ₂ *6H ₂ O (0.02)/diazonium salt (1.5)	Blue LED	DMSO/10h	47				

^a Isolated yield. ^b All reactions were conducted at room temperature in inert atmosphere. ^c These experiments were analyzed by both ¹H NMR and GC/MS techniques.

Table S2. Optimization of the reaction conditions.



Reaction (b) ^b								
entry	catalysts (equiv.)/reagent (equiv.)	light source	solvent/time	yield (%) 4cp				
1	fac-Ir(ppy)₃ (0.01)/diaryliodonium salt (1.5)	Blue LED	MeOH/12h	61				
2	fac-Ir(ppy)₃ (0.01)/diaryliodonium salt (1.5)	Blue LED	DMSO /12h	77				
3	Ru(bpy) ₃ Cl ₂ *6H ₂ O (0.02)/diaryliodonium salt (1.5)	Blue LED	DMSO/12h	57				
4	Ru(bpy) ₃ Cl ₂ *6H ₂ O (0.02)/diaryliodonium salt (1.5)	Blue LED	MeOH/12h	28				
5	Ru(bpy) ₃ Cl ₂ *6H ₂ O (0.02)diaryliodonium salt (1.5)	Blue LED	CH₃CN/12h	79				
6	Ru(bpy) ₃ Cl ₂ *6H ₂ O (0.02)/diaryliodonium salt (1.5)	Blue LED	CH₃CN/4h	80				
7	Ru(bpy) ₃ Cl ₂ *6H ₂ O (0.02)/diaryliodonium salt (1.8)	Blue LED	CH₃CN/4h	80				
8	Ru(bpy) ₃ Cl ₂ *6H ₂ O (0.02)/diaryliodonium salt (1.3)	Blue LED	CH₃CN/4h	69				
9	Ru(bpy) ₃ Cl ₂ *6H ₂ O (0.02)/diaryliodonium salt (1.5)	NO	CH₃CN/4h	0 ^c				
10	diaryliodonium salt (1.5)	Blue LED	CH₃CN/4h	0 ^c				
11	Ru(bpy) ₃ Cl ₂ *6H ₂ O (0.02)/diaryliodonium salt (1.5)/TEMPO (1.7)	Blue LED	CH₃CN/4h	0 ^c				
12	Ru(bpm) ₃ Cl ₂ *6H ₂ O (0.02)/diaryliodonium salt (1.5)	Blue LED	CH₃CN/4h	64				
13	Ru(bpz) ₃ Cl ₂ *6H ₂ O(0.02)/diaryliodonium salt (1.5)	Blue LED	CH₃CN/4h	60				
14	[Cu(dpp) ₂]PF ₆ (0.02)/diaryliodonium salt (1.5)	Green LED	CH₃CN/12h	0				
15	[Cu(dpp) ₂]PF ₆ (0.02)/diaryliodonium salt (1.5)	Green LED	DMSO/12h	0				
16	[Cu(dap) ₂]PF ₆ (0.02)/diaryliodonium salt (1.5)	Green LED	CH₃CN/12h	0				

^a Isolated yield. ^b All reactions were conducted at room temperature in inert atmosphere. ^c These experiments were analyzed by both ¹H NMR and GC/MS techniques.

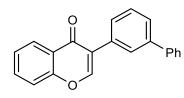
2. Reaction procedures with optimised reaction conditions.

Protocol A: *General procedure for the synthesis of 3-arylchromones 4 by reaction of ortho-hydroxyarylenaminones with aryl diazonium tetrafluoroborates.* Under inert atmosphere (glovebox operating with a constant Ar-purge) to a 10 mL vial equipped with a stir bar was placed photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), appropriate *ortho*-hydroxyarylenaminone (1.0 mmol, 1.0 equiv.) and appropriate aryl diazonium tetrafluoroborate (1.3 mmol, 1.3 equiv.). Afterwards, dry DMSO (0.2 mmol/mL) was added and the reaction vial was properly capped by Teflon Mininert Valve. Finally, the reaction vial was removed from the glovebox and subjected to irradiation under vigorous stirring using 24 W green (525±5 nm) LED strips for 3 hours. The reaction was controlled by both GC MS and TLC. After completion the reaction mixture was evaporated till the dryness using an oil pump and the crude was directly subjected to gradient flash chromatography on silica gel using appropriate mixture of hexane/ethyl acetate as eluent to isolate the desired chromone derivative. The gram scale synthesis was conducted on 10 mmol of the starting *ortho*-hydroxyarylenaminone.

Protocol B: *General procedure for the synthesis of 3-arylchromones 4 by reaction of ortho-hydroxyarylenaminones with diaryliodonium triflates.* Under inert atmosphere (glovebox operating with a constant Ar-purge) to a 20 mL vial equipped with a stir bar was placed photocatalyst Ru(bpy)₃Cl_{2*6}H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), appropriate *ortho*-hydroxyarylenaminone (1.0 mmol, 1.0 equiv.) and appropriate diaryliodonium triflate (1.5 mmol, 1.5 equiv.). Afterwards, dry CH₃CN (0.12 mmol/mL) was added and the reaction vial was properly capped by Teflon Mininert Valve. Finally, the reaction vial was removed from the glovebox and subjected to irradiation under vigorous stirring using 34 W blue LED lamps (Kessil KSH150B Blue LED Grow Light; 5 cm - 6 cm away, with cooling fan on top to keep the reaction mixture at room temperature) for 4 hours. The reaction was controlled by both GC MS and TLC. After completion the reaction mixture was evaporated till the dryness using rotary evaporator and the crude was directly subjected to gradient flash chromatography on silica gel using appropriate mixture of hexane/ethyl acetate as eluent to isolate the desired chromone derivative. Compounds **4bg**, **4ci**, **4cp**, **4db**, **4fa**, **4hq** were prepared starting from corresponding diaryliodonium hexafluorophosphates following the same procedure. The gram scale synthesis was conducted on 10 mmol of the starting *ortho*-hydroxyarylenaminone.

(B) Characterization of products.

3-([1,1'-biphenyl]-3-yl)-4H-chromen-4-one (4af).



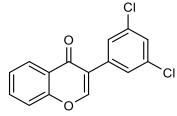
The title compound was prepared by following *protocol A* starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (191 mg, 1.0 mmol, 1.0 equiv.), [1,1'-biphenyl]-3-diazonium diazonium tetrafluoroborate **2f** (348 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate

5:1 to 3:1 as eluent to isolate the desired chromone derivative 4af (256 mg, 0.86 mmol, 86%).

Light yellow solid, mp 184-185 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.35 – 7.38 (m, 1H, CH_{Ar}), 7.44 – 7.47 (m, 3H, CH_{Ar}), 7.50 – 7.58 (m, 3H, CH_{Ar}), 7.62 – 7.67 (m, 3H, CH_{Ar}), 7.69 – 7.72 (m, 1H, CH_{Ar}), 7.81 – 7.82 (m, 1H, CH_{Ar}), 8.09 (s, 1H, CH_{Ar}), 8.34 (dd, 1H, ³*J* = 8.0 Hz, ⁴*J* = 1.4 Hz, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 118.1, 124.6, 125.3, 125.4, 126.5, 127.1, 127.4, 127.5, 127.8, 127.9, 128.8, 129.0, 132.4, 133.7, 141.0, 141.6, 153.2, 156.3, 176.3.

HRMS (TOF MS ES+): Calcd for C₂₁H₁₅O₂ (M+H) 299.1076. Found 299.1072.

3-(3,5-dichlorophenyl)-4H-chromen-4-one (4aj).



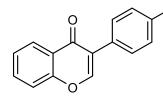
The title compound was prepared by following **protocol A** starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (191 mg, 1.0 mmol, 1.0 equiv.), 3,5-dichlorobenzenediazonium tetrafluoroborate **2j** (338 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl

acetate 15:1 to 12:1 as eluent to isolate the desired chromone derivative 4aj (232 mg, 0.80 mmol, 80%).

Alternatively the title compound was prepared by following **protocol B** starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (191 mg, 1.0 mmol, 1.0 equiv.) and bis(3,5-dichlorophenyl)iodonium

triflate **3j** (852 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 15:1 to 12:1 as eluent to isolate the desired chromone derivative **4aj** (215 mg, 0.74 mmol, 74%). Light yellow solid, mp 129-130 °C. ¹H NMR (500 MHz, CDCl₃): 7.38 (d, 1H, ⁴*J* = 1.9 Hz, CH_{Ar}), 7.45 – 7.48 (m, 1H, CH_{Ar}), 7.49 (d, 2H, ⁴*J* = 1.8 Hz, CH_{Ar}), 7.51 (d, 1H, ³*J* = 8.4 Hz, CH_{Ar}), 7.71 – 7.74 (m, 1H, CH_{Ar}), 8.50 (s, 1H, CH_{Ar}), 8.30 (dd, 1H, ³*J* = 7.9 Hz, ⁴*J* = 1.5 Hz, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 118.1, 124.3, 125.7, 126.4, 127.3, 128.3, 134.1, 134.7, 135.0, 153.6, 156.1, 175.6. HRMS (TOF MS ES+): Calcd for C₁₅H₉O₂Cl₂ (M+H) 290.9982. Found 290.9980.

3-(4-chlorophenyl)-4H-chromen-4-one (4ar).



The title compound was prepared by following *protocol A* starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (191 mg, 1.0 mmol, 1.0 equiv.), 4-chlorobenzenediazonium tetrafluoroborate **2r** (294 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate

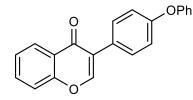
12:1 to 10:1 as eluent to isolate the desired chromone derivative 4ar (213 mg, 0.83 mmol, 83%).

Alternatively the title compound was prepared by following *protocol B* starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (191 mg, 1.0 mmol, 1.0 equiv.), bis(4-chlorophenyl)iodonium triflate **3r** (748 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 12:1 to 10:1 as eluent to isolate the desired chromone derivative **4ar** (203 mg, 0.79 mmol, 79%). Light brown solid, mp 186-187°C. ¹H NMR (500 MHz, CDCl₃): δ 7.40 – 7.45 (m, 3H, CH_{Ar}), 7.48 – 7.53 (m, 3H, CH_{Ar}), 7.68 – 7.71 (m, 1H, CH_{Ar}), 8.02 (s, 1H, CH_{Ar}), 8.30 (dd, 1H, ³J = 8.0 Hz, ⁴J = 1.6 Hz, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 118.1, 124.3, 124.4, 125.4, 126.4, 128.7, 130.1, 130.2, 133.8, 134.2, 153.0, 156.1, 176.0.

HRMS (TOF MS ES+): Calcd for C₁₅H₁₀O₂Cl (M+H) 257.0376. Found 257.0369.

3-(4-phenoxyphenyl)-4H-chromen-4-one (4av).



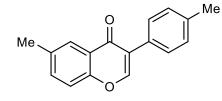
The title compound was prepared by following **protocol A** starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (191 mg, 1.0 mmol, 1.0 equiv.), 4-phenoxybenzenediazonium tetrafluoroborate **2v** (269 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl

acetate 10:1 to 8:1 as eluent to isolate the desired chromone derivative 4av (254 mg, 0.81 mmol, 81%).

White solid, mp 158-159 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.06 – 7.09 (m, 4H, CH_{Ar}), 7.11 – 7.15 (m, 1H, CH_{Ar}), 7.35 (d, 1H, ³*J* = 8.6 Hz, CH_{Ar}), 7.37 (d, 1H, ³*J* = 8.6 Hz, CH_{Ar}), 7.43 (dt, 1H, ³*J* = 7.9 Hz, ⁴*J* = 1.0 Hz, CH_{Ar}), 7.49 (d, 1H, ³*J* = 8.4 Hz, CH_{Ar}), 7.55 (td, 2H, ³*J* = 8.9 Hz, ⁴*J* = 2.2 Hz, CH_{Ar}), 7.69 – 7.70 (m, 1H, CH_{Ar}), 8.03 (s, 1H, CH_{Ar}), 8.32 (dd, 1H, ³*J* = 7.9 Hz, ⁴*J* = 1.4 Hz, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 118.0, 118.6, 119.2, 123.5, 124.4, 124.7, 125.2, 126.4, 126.6, 129.8, 130.3, 133.6, 156.1, 156.8, 157.4, 176.3. HRMS (TOF MS ES+): Calcd for C₂₁H₁₅O₃ (M+H) 315.1030. Found 315.1021.

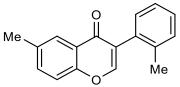
6-methyl-3-(p-tolyl)-4H-chromen-4-one (4bb).



The title compound was prepared by following **protocol A** starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxy-5-methylphenyl)prop-2-en-1-one **1b** (205 mg, 1.0 mmol, 1.0 equiv.), 4-methylbenzenediazonium tetrafluoroborate **2b** (268 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a

mixture of hexane/ethyl acetate 7:1 to 5:1 as eluent to isolate the desired chromone derivative **4bb** (225 mg, 0.90 mmol, 90%). White solid, mp 138-139 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.47 2.39 (s, 3H, Me), 2.47 (s, 3H, Me), 7.25 (d, 2H, ³*J* = 7.5 Hz, CH_{Ar}), 7.36 (d, 1H, ³*J* = 8.1 Hz, CH_{Ar}), 7.30 – 7.33 (m, 2H, CH_{Ar}), 7.45 (d, 2H, ³*J* = 8.1 Hz, CH_{Ar}), 7.49 (dd, 1H, ³*J* = 8.8 Hz, ⁴*J* = 2.0 Hz, CH_{Ar}), 7.98 (s, 1H, CH_{Ar}), 8.09 (br.s, 1H, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 21.0, 21.2, 117.7, 124.2, 125.1, 125.6, 128.8, 129.0, 129.2, 134.8, 135.1, 137.9, 152.7, 154.4, 176.4. HRMS (TOF MS ES+): Calcd for C₁₇H₁₅O₂ (M+H) 251.1082. Found 251.1072.

6-methyl-3-(o-tolyl)-4H-chromen-4-one (4bc).



The title compound was prepared by following protocol A starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol,

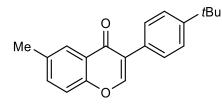
0.03 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxy-5-methylphenyl)prop-2-en-1-one **1b** (205 mg, 1.0 mmol, 1.0 equiv.), 2-methylbenzenediazonium tetrafluoroborate **2c** (294 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of

hexane/ethyl acetate 8:1 to 7:1 as eluent to isolate the desired chromone derivative **4bc** (175 mg, 0.70 mmol, 70%).

Alternatively the title compound was prepared by following **protocol B** starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxy-5-methylphenyl)prop-2-en-1-one **1b** (205 mg, 1.0 mmol, 1.0 equiv.), di-o-tolyliodonium triflate **3c** (687 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 8:1 to 7:1 as eluent to isolate the desired chromone derivative **4bc** (152 mg, 0.61 mmol, 61%).

Light brown solid, mp 221-222 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.27 (s, 3H, Me), 2.49 (s, 3H, Me), 7.19 (d, 1H, ³*J* = 7.37 Hz, CH_{Ar}), 7.23 – 7.26 (m, 1H, CH_{Ar}), 7.30 – 7.33 (m, 2H, CH_{Ar}), 7.40 (d, 1H, ³*J* = 8.7 Hz, CH_{Ar}), 7.50 (dd, 1H, ³*J* = 8.6 Hz, ⁴*J* = 2.1 Hz, CH_{Ar}), 7.86 (s, 1H, CH_{Ar}), 8.10 (br.s, 1H, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 19.9, 20.8, 117.8, 123.9, 125.5, 125.7, 126.1, 128.5, 130.1, 130.4, 131.7, 134.8, 135.1, 138.0, 153.4, 154.6, 175.9. HRMS (TOF MS ES+): Calcd for C₁₇H₁₅O₂ (M+H) 251.1074. Found 251.1072.

3-(4-(tert-butyl)phenyl)-6-methyl-4H-chromen-4-one (4bd).

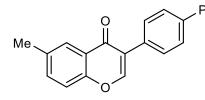


The title compound was prepared by following **protocol A** starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxy-5-methylphenyl)prop-2-en-1-one **1b** (205 mg, 1.0 mmol, 1.0 equiv.), 4-(tert-butyl)benzenediazonium tetrafluoroborate **2d** (322 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using

a mixture of hexane/ethyl acetate 8:1 to 7:1 as eluent to isolate the desired chromone derivative **4bd** (239 mg, 0.82 mmol, 82%). White solid, mp 133-134 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.36 (s, 9H, *t*Bu), 2.48 (s, 3H, Me), 7.37 (d, 1H, ³*J* = 8.6 Hz, CH_{Ar}), 7.46 – 7.50 (m, 3H, CH_{Ar}), 7.51 – 7.53 (m, 2H, CH_{Ar}), 8.02 (s, 1H, CH_{Ar}), 8.11 (br s, 1H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 21.0, 31.3, 34.6, 117.7, 124.2, 125.0, 125.5, 125.7, 128.6, 129.0, 134.8, 135.1, 151.0, 152.9, 154.4, 176.4. HRMS (TOF MS ES+): Calcd for C₂₀H₂₁O₂ (M+H) 293.1547. Found 293.1542.

6-methyl-3-(4-phenoxyphenyl)-4H-chromen-4-one (4be).

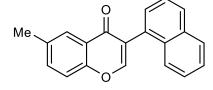


The title compound was prepared by following **protocol A** starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxy-5-methylphenyl)prop-2-en-1-one **1b** (205 mg, 1.0 mmol, 1.0 equiv.), [1,1'-biphenyl]-4-diazonium tetrafluoroborate **2e** (348 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a

mixture of hexane/ethyl acetate 4:1 to 2:1 as eluent to isolate the desired chromone derivative **4be** (287 mg, 0.92 mmol, 92%). Alternatively the title compound was prepared by following *protocol B* starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxy-5-methylphenyl)prop-2-en-1-one **1b** (205 mg, 1.0 mmol, 1.0 equiv.), di([1,1'-biphenyl]-4-yl)iodonium triflate **3e** (873 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 4:1 to 2:1 as eluent to isolate the desired chromone derivative **4be** (262 mg, 0.84 mmol, 84%). Yellow solid, mp 182-183 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.49 (s, 3H, Me), 7.35 – 7.38 (m, 1H, CH_{Ar}), 7.40 (d, 1H, ³*J* = 8.6 Hz, CH_{Ar}), 7.45 – 7.48 (m, 2H, CH_{Ar}), 7.51 (dd, 1H, ³*J* = 8.6 Hz, ⁴*J* = 2.0 Hz, CH_{Ar}), 7.62 – 7.69 (m, 6H, CH_{Ar}), 8.07 (s, 1H, CH_{Ar}), 8.12 (d, 1H, ⁴*J* = 0.9 Hz, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 21.0, 117.8, 118.7, 119.2, 123.5, 124.2, 124.6, 125.7, 126.8, 129.8, 130.4, 134.9, 135.2, 152.7, 154.5, 156.9, 157.4, 176.4.

HRMS (TOF MS ES+): Calcd for C₂₂H₁₇O₂ (M+H) 313.1235. Found 313.1229.

6-methyl-3-(naphthalen-1-yl)-4H-chromen-4-one (4bg).



The title compound was prepared by following *protocol A* starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxy-5-methylphenyl)prop-2-en-1-one **1b** (205 mg, 1.0 mmol, 1.0 equiv.), naphthalene-1-diazonium tetrafluoroborate **2g** (315 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of

hexane/ethyl acetate 12:1 to 10:1 as eluent to isolate the desired chromone derivative 4bg (226 mg, 0.79 mmol, 79%).

Alternatively the title compound was prepared by following *protocol B* starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxy-5-methylphenyl)prop-2-en-1-one **1b** (205 mg, 1.0 mmol, 1.0 equiv.), di(naphthalen-1-yl)iodonium

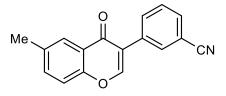
triflate **3g** (795 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 12:1 to 10:1 as eluent to isolate the desired chromone derivative **4bg** (180 mg, 0.63 mmol, 63%). This compound (171 mg, 0.60 mmol, 60%) can be prepared following the same protocol starting from di(naphthalen-1-yl)iodonium hexafluorophosphate (789 mg, 1.5 mmol, 1.5 equiv.).

Light greenish, mp 120-121 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.50 (s, 3H, Me), 7.43 – 7.48 (m, 3H, CH_{Ar}), 7.51 – 7.55 (m, 3H, CH_{Ar}), 7.76 (d, 1H, ³*J* = 8.2 Hz, CH_{Ar}), 7.92 (t, 2H, ³*J* = 8.5 Hz, CH_{Ar}), 8.00 (s, 1H, CH_{Ar}), 8.16 (br. s, 1H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 20.9, 117.8, 123.9, 125.0, 125.2, 125.3, 125.5, 125.6, 125.8, 126.2, 128.1, 128.3, 129.9, 132.3, 133.5, 134.9, 135.2, 154.0, 154.6, 176.5.

HRMS (TOF MS ES+): Calcd for C₂₀H₁₅O₂ (M+H) 287.1080. Found 287.1072.

3-(6-methyl-4-oxo-4H-chromen-3-yl)benzonitrile (4bu).



The title compound was prepared by following **protocol A** starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxy-5-methylphenyl)prop-2-en-1-one **1b** (205 mg, 1.0 mmol, 1.0 equiv.), 3-cyanobenzenediazonium tetrafluoroborate **2u** (282 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a

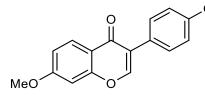
mixture of hexane/ethyl acetate 10:1 to 8:1 as eluent to isolate the desired chromone derivative 4bu (201 mg, 0.77 mmol, 77%).

Alternatively the title compound was prepared by following *protocol B* starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxy-5-methylphenyl)prop-2-en-1-one **1b** (205 mg, 1.0 mmol, 1.0 equiv.), bis(3-cyanophenyl)iodonium triflate **3u** (720 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 10:1 to 8:1 as eluent to isolate the desired chromone derivative **4bu** (185 mg, 0.71 mmol, 71%). White solid, mp 191 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.49 (s, 3H, Me), 7.41 (d, 1H, ³J = 8.1 Hz, CH_{Ar}), 7.52 – 7.54 (m, 1H, CH_{Ar}), 7.55 (d, 1H, ³J = 7.8 Hz, CH_{Ar}), 7.65 (dt, 1H, ³J = 7.3 Hz, ⁴J = 1.3 Hz, CH_{Ar}), 7.83 (dt, 1H, ³J = 7.7 Hz, ⁴J = 1.3 Hz, CH_{Ar}), 7.88 – 7.89 (m, 1H, CH_{Ar}), 8.04 (s, 1H, CH_{Ar}), 8.07 (d, 1H, ⁴J = 1.0 Hz, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 21.0, 112.7, 117.9, 118.6, 123.3, 124.0, 125.6, 129.3, 131.6, 132.4, 133.3, 133.4, 135.4, 135.8, 153.4, 154.5, 175.7.

HRMS (TOF MS ES+): Calcd for C₁₇H₁₂NO₂ (M+H) 262.0868. Found 262.0868.

7-methoxy-3-(4-(trifluoromethoxy)phenyl)-4H-chromen-4-one (4ch).



OCF₃ The title compound was prepared by following *protocol A* starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxy-4-methoxyphenyl)prop-2-en-1-one 1c (221 mg, 1.0 mmol, 1.0 equiv.), 4-(trifluoromethoxy)benzenediazonium tetrafluoroborate 2h (359 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography

on silica gel using a mixture of hexane/ethyl acetate 5:1 to 1:1 as eluent to isolate the desired chromone derivative **4ch** (292 mg, 0.87 mmol, 87%).

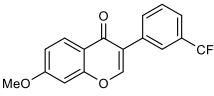
Alternatively the title compound was prepared by following *protocol B* starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxy-4-methoxyphenyl)prop-2-en-1-one **1c** (221 mg, 1.0 mmol, 1.0 equiv.), bis(4-(trifluoromethoxy)phenyl)iodonium triflate **3h** (897 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 5:1 to 1:1 as eluent to isolate the desired chromone derivative **4ch** (276 mg, 0.82 mmol, 82%).

Light yellow solid, mp 149-150 °C. ¹H NMR (500 MHz, CDCl₃): δ 3.92 (s, 3H, OMe), 6.86 (d, 1H, ⁴*J* = 2.4 Hz, CH_{Ar}), 7.00 (dd, 1H, ³*J* = 8.7 Hz, ⁴*J* = 2.4 Hz, CH_{Ar}), 7.27 (d, 2H, ³*J* = 8.3 Hz, CH_{Ar}), 7.59 (d, 2H, ³*J* = 9.0 Hz, CH_{Ar}), 7.95 (s, 1H, CH_{Ar}), 7.59 (d, 1H, ³*J* = 8.7 Hz, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 55.9, 100.2, 114.8, 118.3, 120.4 (d, ¹*J_{CF}* = 253.3 Hz), 121.1, 124.1, 127.8, 130.4, 130.7, 149.1, 152.7, 158.0, 164.2, 175.4.

HRMS (TOF MS ES+): Calcd for $C_{17}H_{12}O_4F_3$ (M+H) 337.0703. Found 337.0699.

7-methoxy-3-(3-(trifluoromethyl)phenyl)-4H-chromen-4-one (4ci).



The title compound was prepared by following **protocol A** starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxy-4-methoxyphenyl)prop-2-en-1-one **1c** (221 mg, 1.0 mmol, 1.0 equiv.), 3-(trifluoromethyl)benzenediazonium tetrafluoroborate **2i** (338 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography

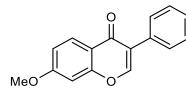
on silica gel using a mixture of hexane/ethyl acetate 7:1 to 3:1 as eluent to isolate the desired chromone derivative **4ci** (256 mg, 0.83 mmol, 83%). Alternatively the title compound was prepared by following *protocol B* starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxy-4-methoxyphenyl)prop-2-en-1-one **1c** (221 mg, 1.0 mmol, 1.0 equiv.), bis(3-(trifluoromethyl)phenyl)iodonium triflate **3i** (849 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 7:1 to 3:1 as eluent to isolate the desired chromone derivative **4ci** (246 mg, 0.77 mmol, 77%). This compound (243 mg, 0.76 mmol, 76%) can be prepared following the same protocol starting from bis(3-(trifluoromethyl)phenyl)iodonium hexafluorophosphate (843 mg, 1.5 mmol, 1.5 equiv.).

White solid, mp 124 - 125 °C. ¹H NMR (500 MHz, CDCl₃): δ 3.92 (s, 3H, OMe), 6.87 (d, 1H, ⁴*J* = 2.3 Hz, CH_{Ar}), 7.01 (dd, 1H, ³*J* = 8.9 Hz, ⁴*J* = 2.3 Hz, CH_{Ar}), 7.55 (t, 1H, ³*J* = 7.7 Hz, CH_{Ar}), 7.63 (d, 1H, ³*J* = 7.7 Hz, CH_{Ar}), 7.77 (d, 1H, ³*J* = 7.7 Hz, CH_{Ar}), 7.82 (s, 1H, CH_{Ar}), 7.99 (s, 1H, CH_{Ar}), 8.20 (d, 1H, ³*J* = 8.8 Hz, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 55.9, 100.2, 118.2, 124.0 (q, ¹*J*_{CF} = 273.3 Hz, CF₃), 124.1, 124.8 (m), 125.6 (m), 127.7, 128.9, 130.9 (q, ²*J*_{CF} = 32.0 Hz, CCF₃), 132.3, 132.8, 152.9, 158.0, 164.3, 175.2.

HRMS (TOF MS ES+): Calcd for C₁₇H₁₂O₃F₃ (M+H) 321.0746. Found 321.0739.

3-(4-fluorophenyl)-7-methoxy-4H-chromen-4-one (4cp).



The title compound was prepared by following **protocol A** starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxy-4-methoxyphenyl)prop-2-en-1-one **1c** (221 mg, 1.0 mmol, 1.0 equiv.), 4-fluorobenzenediazonium tetrafluoroborate **2p** (273 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a

mixture of hexane/ethyl acetate 5:1 to 3:1 as eluent to isolate the desired chromone derivative 4cp (232 mg, 0.86 mmol, 86%).

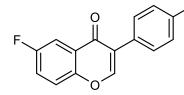
Alternatively the title compound was prepared by following *protocol B* starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-3-(dimethylamino)-1-(2-hydroxy-4-methoxyphenyl)prop-2-en-1-one **1c** (221 mg, 1.0 mmol, 1.0 equiv.), bis(4-fluorophenyl)iodonium triflate **3p** (699 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 5:1 to 3:1 as eluent to isolate the desired chromone derivative **4cp** (216 mg, 0.80 mmol, 80%). This compound (224 mg, 0.83 mmol, 83 %) can be prepared following the same protocol starting from bis(4-fluorophenyl)iodonium hexafluorophosphate (693 mg, 1.5 mmol, 1.5 equiv.).

Yellow solid, mp 138 - 139 °C. ¹H NMR (500 MHz, CDCl₃): δ 3.91 (s, 3H, OMe), 6.85 (d, 1H, ⁴J = 2.4 Hz, CH_{Ar}), 7.01 (dd, 1H, ³J = 8.9 Hz, ⁴J = 2.3 Hz, CH_{Ar}), 7.05 – 7.09 (m, 1H, CH_{Ar}), 7.31 – 7.39 (m, 3H, CH_{Ar}), 7.96 (s, 1H, CH_{Ar}), 8.20 (d, 1H, ³J = 8.7 Hz, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 55.9, 100.1, 114.8, 115.0 (d, J_{CF} = 20.8 Hz), 116.0 (d, J_{CF} = 20.8 Hz), 118.3, 124.1 (m), 124.4 (d, J_{CF} = 2.9 Hz), 127.8, 129.9 (d, J_{CF} = 8.3 Hz), 134.0 (d, J_{CF} = 8.6 Hz), 152.8, 157.9, 162.7 (d, ¹ J_{CF} = 245.0 Hz, CF), 164.1, 175.2.

HRMS (TOF MS ES+): Calcd for C₁₆H₁₂O₃F (M+H) 271.0772. Found 271.0770.

6-fluoro-3-(p-tolyl)-4H-chromen-4-one (4db).



Me The title compound was prepared by following *protocol A* starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(5-fluoro-2-hydroxyphenyl)prop-2-en-1-one 1d (209 mg, 1.0 mmol, 1.0 equiv.), 4-methylbenzenediazonium tetrafluoroborate 2b (268 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of

hexane/ethyl acetate 7:1 to 5:1 as eluent to isolate the desired chromone derivative **4db** (206 mg, 0.81 mmol, 81%).

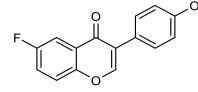
Alternatively the title compound was prepared by following *protocol B* starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-3-(dimethylamino)-1-(5-fluoro-2-hydroxyphenyl)prop-2-en-1-one **1d** (209 mg, 1.0 mmol, 1.0 equiv.), di-p-tolyliodonium triflate **3b** (687 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 7:1 to 5:1 as eluent to isolate the desired chromone derivative **4db** (185 mg, 0.73 mmol, 73%). This compound (180 mg, 0.71 mmol, 71 %) can be prepared following the same protocol starting from di-p-tolyliodonium hexafluorophosphate (681 mg, 1.5 mmol, 1.5 equiv.).

White solid, mp 160-161 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.41 (s, 3H, Me), 7.27 (d, 2H, ³*J* = 8.0 Hz, CH_{Ar}), 7.39 – 7.43 (m, 1H, CH_{Ar}), 7.46 – 7.51 (m, 3H, CH_{Ar}), 7.95 (dd, 1H, ³*J* = 8.3 Hz, ⁴*J* = 3.1 Hz, CH_{Ar}), 8.02 (s, 1H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 21.2, 111.1 (d, J_{CF} = 24.0 Hz), 120.1 (d, J_{CF} = 8.1 Hz), 121.7 (d, J_{CF} = 25.3 Hz), 124.5, 125.5 (d, J_{CF} = 7.0 Hz), 128.4, 128.7, 129.2, 138.2, 152.3, 152.9, 159.5 (d, $^{1}J_{CF}$ = 252.0 Hz), 175.5.

HRMS (TOF MS ES+): Calcd for C₆₁H₁₂O₂F (M+H) 255.0822. Found 255.0821.

3-(4-ethoxyphenyl)-6-fluoro-4H-chromen-4-one (4dl).



The title compound was prepared by following **protocol A** starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(5-fluoro-2-hydroxyphenyl)prop-2-en-1-one **1d** (209 mg, 1.0 mmol, 1.0 equiv.), 4-ethoxybenzenediazonium tetrafluoroborate **2l** (307 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of

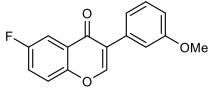
hexane/ethyl acetate 5:1 to 3:1 as eluent to isolate the desired chromone derivative 4dl (227 mg, 0.80 mmol, 80%).

Alternatively the title compound was prepared by following *protocol B* starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-3-(dimethylamino)-1-(5-fluoro-2-hydroxyphenyl)prop-2-en-1-one **1d** (209 mg, 1.0 mmol, 1.0 equiv.), bis(4-ethoxyphenyl)iodonium triflate **3l** (777 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 5:1 to 3:1 as eluent to isolate the desired chromone derivative **4dl** (224 mg, 0.79 mmol, 79%). White solid, mp 163-164 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.43 (t, 3H, ³J = 6.7 Hz, OCH₂CH₃), 4.06 (q, 2H, ³J = 6.7 Hz, OCH₂CH₃), 6.96 (d, 2H, ³J = 8.9 Hz, CH_{Ar}), 7.37 – 7.42 (m, 1H, CH_{Ar}), 7.47 – 7.50 (m, 3H, CH_{Ar}), 7.93 (dd, 1H, ³J = 8.3 Hz, ⁴J = 3.0 Hz, CH_{Ar}), 8.00 (s, 1H, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 14.8, 63.5, 111.1 (d, *J_{CF}* = 22.0 Hz), 120.11 (d, *J_{CF}* = 7.8 Hz), 121.7 (d, *J_{CF}* = 25.9 Hz), 123.5, 124.4, 125.5 (d, *J_{CF}* = 7.6

Hz), 130.0, 152.4, 152.7, 159.1, 159.5 (d, ¹J_{CF} = 249.5 Hz), 160.7, 175.7.

HRMS (TOF MS ES+): Calcd for C₁₇H₁₄O₃F (M+H) 285.0931. Found 285.0927.

6-fluoro-3-(3-methoxyphenyl)-4H-chromen-4-one (4dm).



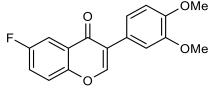
The title compound was prepared by following **protocol A** starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(5-fluoro-2-hydroxyphenyl)prop-2-en-1-one **1d** (209 mg, 1.0 mmol, 1.0 equiv.), 3-methoxybenzenediazonium tetrafluoroborate **2m** (288 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a

mixture of hexane/ethyl acetate 5:1 to 3:1 as eluent to isolate the desired chromone derivative **4dm** (210 mg, 0.78 mmol, 78%). Alternatively the title compound was prepared by following *protocol B* starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-3-(dimethylamino)-1-(5-fluoro-2-hydroxyphenyl)prop-2-en-1-one **1d** (209 mg, 1.0 mmol, 1.0 equiv.), bis(3-methoxyphenyl)iodonium triflate **3m** (735 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 5:1 to 3:1 as eluent to isolate the desired chromone derivative **4dm** (192 mg, 0.71 mmol, 71%). White solid, mp 133-134 °C. ¹H NMR (500 MHz, CDCl₃): δ 3.83 (s 3H, OMe), 6.91 (dd, 1H, ³J = 8.4 Hz, ⁴J = 2.1 Hz, CH_{Ar}), 7.09 (d, 1H, ³J = 7.7 Hz, CH_{Ar}), 7.13 – 7.14 (m, 1H, CH_{Ar}), 7.33 (d, 1H, ³J = 8.0 Hz, CH_{Ar}), 7.37 – 7.41 (m, 1H, CH_{Ar}), 7.46 – 7.49 (m, 1H, CH_{Ar}), 7.91 (dd, 1H, ³J = 8.5 Hz, ⁴J = 3.0 Hz, CH_{Ar}), 8.02 (s, 1H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 55.2, 111.0 (d, J_{CF} = 23.5 Hz), 114.2 (d, J_{CF} = 48.8 Hz), 120.1 (d, J_{CF} = 7.9 Hz), 121.0, 121.6 (d, J_{CF} = 25.1 Hz), 124.4, 125.5 (d, J_{CF} = 7.2 Hz), 129.5, 132.7, 152.3, 153.3, 159.5, 159.52 (d, ¹ J_{CF} = 244.6 Hz), 175.3.

HRMS (TOF MS ES+): Calcd for C₁₆H₁₂O₃F (M+H) 271.0778. Found 271.0770.

3-(3,4-dimethoxyphenyl)-6-fluoro-4H-chromen-4-one (4dn).



The title compound was prepared by following *protocol A* starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(5-fluoro-2-hydroxyphenyl)prop-2-en-1-one 1d (209 mg, 1.0 mmol, 1.0 equiv.), 3,4-dimethoxybenzenediazonium tetrafluoroborate 2n (327 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using

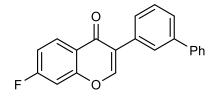
a mixture of hexane/ethyl acetate 3:1 to pure ethyl acetate as eluent to isolate the desired chromone derivative 4dn (264 mg, 0.88 mmol, 88%).

Light brown solid, mp 152 - 153 °C. ¹H NMR (500 MHz, CDCl₃): δ 3.91 (s, 3H, OMe), 3.93 (s, 3H, OMe), 6.92 (d, 1H, ³*J* = 8.4 Hz, CH_{Ar}), 7.05 (dd, 1H, ³*J* = 8.4 Hz, ⁴*J* = 1.9 Hz, CH_{Ar}), 7.18 (d, 1H, ⁴*J* = 2.0 Hz, CH_{Ar}), 7.39 – 7.43 (m, 1H, CH_{Ar}), 7.48 – 7.51 (m, 1H, CH_{Ar}), 7.93 (dd, 1H, ³*J* = 8.3 Hz, ⁴*J* = 3.0 Hz, CH_{Ar}), 8.03 (s, 1H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 55.92, 55.93, 111.0 (d, *J_{CF}* = 24.5 Hz), 111.2, 112.3, 120.1 (d, *J_{CF}* = 8.0 Hz), 121.0, 121.8 (d, *J_{CF}* = 25.6 Hz), 124.1, 124.4, 125.5 (d, *J_{CF}* = 7.7 Hz), 148.8, 149.2, 152.4, 152.9, 159.6 (d, ¹*J_{CF}* = 248.8 Hz), 175.7.

HRMS (TOF MS ES+): Calcd for C₁₇H₁₄O₄F (M+H) 301.0874. Found 301.0876.

3-([1,1'-biphenyl]-3-yl)-7-fluoro-4H-chromen-4-one (4ef).



The title compound was prepared by following **protocol A** starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(4-fluoro-2-hydroxyphenyl)prop-2-en-1-one **1e** (209 mg, 1.0 mmol, 1.0 equiv.), [1,1'-biphenyl]-3-diazonium tetrafluoroborate **2f** (348 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of

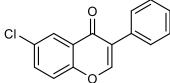
hexane/ethyl acetate 7:1 to 3:1 as eluent to isolate the desired chromone derivative 4ef (287 mg, 0.91 mmol, 91%).

White solid, mp 131-132 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.16 – 7.19 (m, 2H, CH_{Ar}), 7.35 – 7.38 (m, 2H, CH_{Ar}), 7.44 – 7.47 (m, 2H, CH_{Ar}), 7.52 – 7.53 (m, 2H, CH_{Ar}), 7.62 – 7.65 (m, 3H, CH_{Ar}), 7.79 (s, 1H, CH_{Ar}), 8.04 (s, 1H, CH_{Ar}), 8.34 – 8.37 (m, 1H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 104.6 (d, *J_{CF}* = 27.0 Hz), 114.1 (d, *J_{CF}* = 23.0 Hz), 121.4, 125.5, 127.1, 127.2, 127.4, 127.8 (d, ¹*J_{CF}* = 3.1 Hz), 128.7, 128.9, 129.0, 131.8, 140.7, 141.5, 153.2, 157.1 (d, *J_{CF}* = 11.7 Hz), 165.5 (d, ¹*J_{CF}* = 251.7 Hz), 175.3.

HRMS (TOF MS ES+): Calcd for C₂₁H₁₄O₂F (M+H) 317.0987. Found 317.0978.

6-chloro-3-phenyl-4H-chromen-4-one (4fa).



The title compound was prepared by following **protocol A** starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-1-(5-chloro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1f** (225 mg, 1.0 mmol, 1.0 equiv.), benzenediazonium tetrafluoroborate **2a** (249 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification

was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 9:1 to 7:1 as eluent to isolate the desired chromone derivative **4fa** (208 mg, 0.81 mmol, 81%).

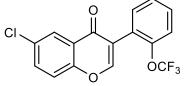
Alternatively the title compound was prepared by following *protocol B* starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-1-(5-chloro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1f** (225 mg, 1.0 mmol, 1.0 equiv.), diphenyliodonium triflate **3a** (645 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 9:1 to 7:1 as eluent to isolate the desired chromone derivative **4fa** (192 mg, 0.75 mmol, 75%). This compound (187 mg, 0.73 mmol, 73 %) can be prepared following the same protocol starting from diphenyliodonium hexafluorophosphate (639 mg, 1.5 mmol, 1.5 equiv.).

White solid, mp 179-180°C. ¹H NMR (500 MHz, CDCl₃): δ 7.40 – 7.47 (m, 4H, CH_{Ar}), 7.55 (m, 2H, CH_{Ar}), 7.62 (dd, 1H, ³*J* = 8.9 Hz, ⁴*J* = 2.6 Hz, CH_{Ar}) 8.02 (s, 1H, CH_{Ar}), 8.27 (d, 1H, ⁴*J* = 2.6 Hz, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 119.8, 125.4, 125.5, 125.8, 128.4, 128.6, 128.9, 131.2, 131.3, 133.9, 153.2, 154.5, 175.1.

HRMS (TOF MS ES+): Calcd for C₁₅H₁₀O₂Cl (M+H) 257.0374. Found 257.0369.

6-chloro-3-(2-(trifluoromethoxy)phenyl)-4H-chromen-4-one (4fk).



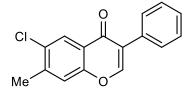
The title compound was prepared by following **protocol A** starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-1-(5-chloro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1f** (225 mg, 1.0 mmol, 1.0 = equiv.), 2-(trifluoromethoxy)benzenediazonium tetrafluoroborate **2k** (359 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of

hexane/ethyl acetate 7:1 to 5:1 as eluent to isolate the desired chromone derivative **4fk** (265 mg, 0.78 mmol, 78%). Alternatively the title compound was prepared by following *protocol B* starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-1-(5-chloro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1f** (225 mg, 1.0 mmol, 1.0 equiv.), bis(2-(trifluoromethoxy)phenyl)iodonium triflate **3k** (897 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 7:1 to 5:1 as eluent to isolate the desired chromone derivative **4fk** (204 mg, 0.60 mmol, 60%). White solid, mp 140-141 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.35 – 7.38 (m, 2H, CH_{Ar}), 7.43 – 7.48 (m, 3H, CH_{Ar}), 7.63 (dd, 1H, ³*J* = 8.9 Hz, ⁴*J* = 2.6 Hz, CH_{Ar}), 7.98 (s, 1H, CH_{Ar}), 8.24 (d, 1H, ⁴*J* = 2.5 Hz, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 119.9, 120.3 (d, ¹*J_{CF}* = 258.3 Hz), 120.8, 121.5, 124.7, 125.1, 125.7, 126.8, 130.1, 131.4, 132.4, 134.0, 147.3, 154.4, 154.6, 174.3.

HRMS (TOF MS ES+): Calcd for C₁₆H₉O₃F₃Cl (M+H) 341.0197. Found 341.0192.

6-chloro-7-methyl-3-phenyl-4H-chromen-4-one (4ga).



The title compound was prepared by following *protocol A* starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-1-(5-chloro-2-hydroxy-4-methylphenyl)-3-(dimethylamino)prop-2-en-1-one **1g** (239 mg, 1.0 mmol, 1.0 equiv.), benzenediazonium tetrafluoroborate **2a** (249 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl

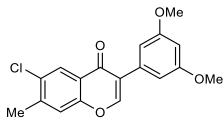
acetate 10:1 to 7:1 as eluent to isolate the desired chromone derivative 4ga (243 mg, 0.90 mmol, 90%).

Alternatively the title compound was prepared by following *protocol B* starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-1-(5-chloro-2-hydroxy-4-methylphenyl)-3-(dimethylamino)prop-2-en-1-one **1g** (239 mg, 1.0 mmol, 1.0 equiv.), diphenyliodonium triflate **3a** (645 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 10:1 to 7:1 as eluent to isolate the desired chromone derivative **4ga** (214 mg, 0.79 mmol, 79%). Light yellow solid, mp 193-194°C. ¹H NMR (500 MHz, CDCl₃): δ 2.52 (s, 3H, Me), 7.37 – 7.46 (m, 4H, CH_{Ar}), 7.54 – 7.56 (m, 2H, CH_{Ar}), 7.96 (s, 1H, CH_{Ar}), 8.26 (s, 1H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 20.8, 119.8, 123.6, 125.3, 126.0, 128.3, 128.6, 128.9, 131.6, 132.0, 142.9, 153.0, 154.5, 175.1.

HRMS (TOF MS ES+): Calcd for C₁₆H₁₂O₂Cl (M+H) 271.0529. Found 271.0526.

6-chloro-3-(3,5-dimethoxyphenyl)-7-methyl-4H-chromen-4-one (4go).

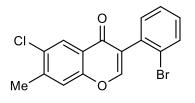


The title compound was prepared by following **protocol A** starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-1-(5-chloro-2-hydroxy-4-methylphenyl)-3-(dimethylamino)prop-2-en-1-one **1g** (239 mg, 1.0 mmol, 1.0 equiv.), 3,5-dimethoxybenzenediazonium tetrafluoroborate **2o** (327 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on

silica gel using a mixture of hexane/ethyl acetate 10:1 to 7:1 as eluent to isolate the desired chromone derivative **4go** (268 mg, 0.81 mmol, 81%). Light yellow solid, mp 158-159°C. ¹H NMR (500 MHz, CDCl₃): δ 2.51 (s, 3H, Me), 3.82 (s, 6H, 2xOMe), 6.49 (s, 1H, CH_{Ar}), 7.40 (s, 1H, CH_{Ar}), 6.69 (d, 1H, ⁴J = 2.0 Hz, CH_{Ar}), 7.36 (s, 1H, CH_{Ar}), 7.99 (s, 1H, CH_{Ar}), 8.24 (br. s, 1H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 20.8, 55.4, 100.6, 107.0, 119.8, 123.6, 125.1, 126.0, 132.0, 126.0, 132.0, 133.5, 143.0, 153.1, 154.4, 160.7, 175.0. HRMS (TOF MS ES+): Calcd for C₁₈H₁₆O₄Cl (M+H) 331.0745. Found 331.0737.

3-(2-bromophenyl)-6-chloro-7-methyl-4H-chromen-4-one (4gs).



The title compound was prepared by following *protocol A* starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-1-(5-chloro-2-hydroxy-4-methylphenyl)-3-(dimethylamino)prop-2-en-1-one **1g** (239 mg, 1.0 mmol, 1.0 equiv.), 2-bromobenzenediazonium tetrafluoroborate **2s** (352 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of

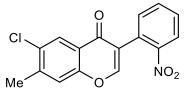
hexane/ethyl acetate 10:1 to 8:1 as eluent to isolate the desired chromone derivative **4gs** (182 mg, 0.52 mmol, 52%).

Alternatively the title compound was prepared by following *protocol B* starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-1-(5-chloro-2-hydroxy-4-methylphenyl)-3-(dimethylamino)prop-2-en-1-one **1g** (239 mg, 1.0 mmol, 1.0 equiv.), bis(2-bromophenyl)iodonium triflate **3s** (882 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 10:1 to 8:1 as eluent to isolate the desired chromone derivative **4gs** (108 mg, 0.31 mmol, 31%).

Light brown solid, mp 186-187°C. ¹H NMR (500 MHz, CDCl₃): δ 2.51 (s, 3H, Me), 7.24 – 7.28 (m, 1H, CH_{Ar}), 7.31 (dd, 1H, ³*J* = 7.8 Hz, ⁴*J* = 1.9 Hz, CH_{Ar}), 7.36 (dd, 1H, ³*J* = 7.6 Hz, ⁴*J* = 0.9 Hz, CH_{Ar}), 7.39 (s, 1H, CH_{Ar}), 7.66 (dd, 1H, ³*J* = 8.9 Hz, ⁴*J* = 0.9 Hz, CH_{Ar}), 7.90 (s, 1H, CH_{Ar}), 8.24 (br. s, 1H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 20.8, 119.9, 123.4, 124.7, 125.7, 126.0, 127.4, 130.1, 132.0, 132.1, 132.6, 133.0, 143.1, 154.3, 154.6, 174.3. HRMS (TOF MS ES+): Calcd for C₁₆H₁₁O₂ClBr (M+H) 348.9637. Found 348.9631.

6-chloro-7-methyl-3-(2-nitrophenyl)-4H-chromen-4-one (4gt).



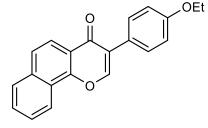
The title compound was prepared by following *protocol A* starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-1-(5-chloro-2-hydroxy-4-methylphenyl)-3-(dimethylamino)prop-2-en-1-one **1g** (239 mg, 1.0 mmol, 1.0 equiv.), 2-nitrobenzenediazonium tetrafluoroborate **2t** (308 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2

mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 7:1 to 3:1 as eluent to isolate the desired chromone derivative **4gt** (218 mg, 0.69 mmol, 69%).

Yellow solid, mp 189-190°C. ¹H NMR (500 MHz, CDCl₃): δ 2.52 (s, 3H, Me), 7.37 (dd, 1H, ³*J* = 7.5 Hz, ⁴*J* = 1.0 Hz, CH_{Ar}), 7.40 (s, 1H, CH_{Ar}), 7.58 (dd, 1H, ³*J* = 7.1 Hz, ⁴*J* = 1.0 Hz, CH_{Ar}), 7.67 (dd, 1H, ³*J* = 7.5 Hz, ⁴*J* = 1.4 Hz, CH_{Ar}), 8.01 (s, 1H, CH_{Ar}), 8.10 (dd, 1H, ³*J* = 8.0 Hz, ⁴*J* = 1.3 Hz, CH_{Ar}), 8.19 (br. s, 1H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 20.9, 119.9, 122.7, 124.5, 124.9, 126.1, 126.6, 129.7, 132.0, 132.3, 133.3, 143.5, 149.6, 152.0, 154.7, 174.0. HRMS (TOF MS ES+): Calcd for C₁₆H₁₁NO₄Cl (M+H) 316.0381. Found 316.0377.

3-(4-ethoxyphenyl)-4H-benzo[h]chromen-4-one (4hl).



The title compound was prepared by following *protocol* **A** starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(1-hydroxynaphthalen-2-yl)prop-2-en-1-one **1h** (241 mg, 1.0 mmol, 1.0 equiv.), 4-ethoxybenzenediazonium tetrafluoroborate **2l** (307 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 7:1 to 5:1 as eluent to isolate the desired chromone derivative **4hl** (265 mg, 0.84 mmol,

84%).

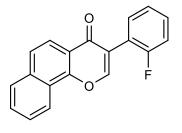
Alternatively the title compound was prepared by following *protocol B* starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-3-(dimethylamino)-1-(1-hydroxynaphthalen-2-yl)prop-2-en-1-one **1h** (241 mg, 1.0 mmol, 1.0 equiv.), bis(4-ethoxyphenyl)iodonium

triflate **3I** (777 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 7:1 to 5:1 as eluent to isolate the desired chromone derivative **4hl** (227 mg, 0.72 mmol, 72%). Light yellow solid, mp 159 - 160 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.44 (t, 3H, ³*J* = 8.5 Hz, OCH₂CH₃), 4.08 (q, 2H, ³*J* = 7.3 Hz, OCH₂CH₃), 6.98 (d, 2H, ³*J* = 8.0 Hz, CH_{Ar}), 7.57 (d, 2H, ³*J* = 8.8 Hz, CH_{Ar}), 7.67 – 7.72 (m, 2H, CH_{Ar}), 7.76 (d, 1H, ³*J* = 8.7 Hz, CH_{Ar}), 7.92 (d, 1H, ³*J* = 7.8 Hz, CH_{Ar}), 8.17 (s, 1H, CH_{Ar}), 8.23 (d, 1H, ³*J* = 8.6 Hz, CH_{Ar}), 8.48 (d, 1H, ³*J* = 7.8 Hz, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 14.8, 63.5, 114.5, 120.8, 121.3, 122.2, 123.8, 124.0, 125.2, 126.2, 127.1, 128.1, 129.2, 130.1, 135.6, 151.6, 153.5,

159.1, 176.3.

HRMS (TOF MS ES+): Calcd for C₂₁H₁₇O₃ (M+H) 317.1176. Found 317.1178.

3-(2-fluorophenyl)-4H-benzo[h]chromen-4-one (4hq).



The title compound was prepared by following **protocol A** starting from photocatalyst Eosin Y (19.5 mg, 0.03 mmol, 0.03 equiv.), (E)-3-(dimethylamino)-1-(1-hydroxynaphthalen-2-yl)prop-2-en-1-one **1h** (241 mg, 1.0 mmol, 1.0 equiv.), 2-fluorobenzenediazonium tetrafluoroborate **2q** (273 mg, 1.3 mmol, 1.3 equiv.) and dry DMSO (0.2 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 7:1 to 3:1 as eluent to isolate the desired chromone derivative **4hq** (232 mg, 0.80 mmol, 80%).

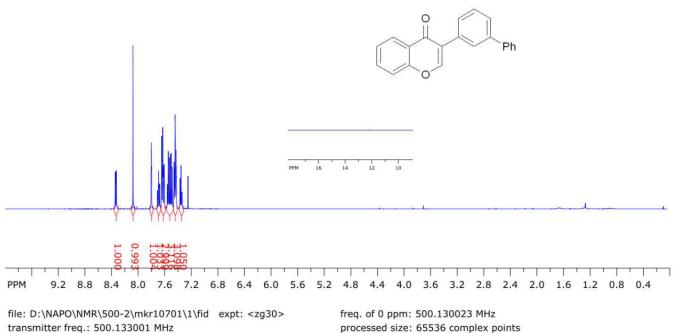
Alternatively the title compound was prepared by following *protocol B* starting from photocatalyst Ru(bpy)₃Cl_{2*}6H₂O (15.0 mg, 0.02 mmol, 0.02 equiv.), (E)-3-(dimethylamino)-1-(1-hydroxynaphthalen-2-yl)prop-2-en-1-one **1h** (241 mg, 1.0 mmol, 1.0 equiv.), bis(2-fluorophenyl)iodonium triflate **3q** (699 mg, 1.5 mmol, 1.5 equiv.) and dry CH₃CN (0.12 mmol/mL). Purification was accomplished by gradient flash chromatography on silica gel using a mixture of hexane/ethyl acetate 7:1 to 3:1 as eluent to isolate the desired chromone derivative **4hq** (188 mg, 0.63 mmol, 63%). This compound (185 mg, 0.64 mmol, 64 %) can be prepared following the same protocol starting from bis(2-fluorophenyl)iodonium hexafluorophosphate (693 mg, 1.5 mmol, 1.5 equiv.).

Light yellow solid, mp 181-182 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.19 – 7.27 (m, 2H, CH_{Ar}), 7.39 – 7.42 (m, 1H, CH_{Ar}), 7.58 (dt, 1H, ³*J* = 7.4 Hz, ⁴*J* = 1.6 Hz, CH_{Ar}), 7.68 – 7.74 (m, 2H, CH_{Ar}), 7.79 (d, 1H, ³*J* = 8.7 Hz, CH_{Ar}), 7.94 (d, 1H, ³*J* = 7.8 Hz, CH_{Ar}), 8.24 (d, 1H, ³*J* = 8.8 Hz, CH_{Ar}), 8.25 (s, 1H, CH_{Ar}), 8.50 (d, 1H, ³*J* = 8.0 Hz, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 115.8 (d, J_{CF} = 22.3 Hz), 119.4 (d, J_{CF} = 14.1 Hz), 120.7, 121.2, 121.5, 122.2, 123.9, 124.1 (d, ¹ J_{CF} = 3.5 Hz), 125.5, 127.2, 128.1, 129.4, 130.1 (d, J_{CF} = 8.4 Hz), 132.0 (d, J_{CF} = 2.8 Hz), 135.8, 153.6, 153.7 (d, J_{CF} = 3.2 Hz), 160.3 (d, ¹ J_{CF} = 247.6 Hz), 175.4. HRMS (TOF MS ES+): Calcd for C₁₉H₁₂O₂F (M+H) 291.0828. Found 291.0821. (C) Copies ¹H and ¹³C NMR spectra

Compound 4af

SpinWorks 4: ISM 113-1 1H

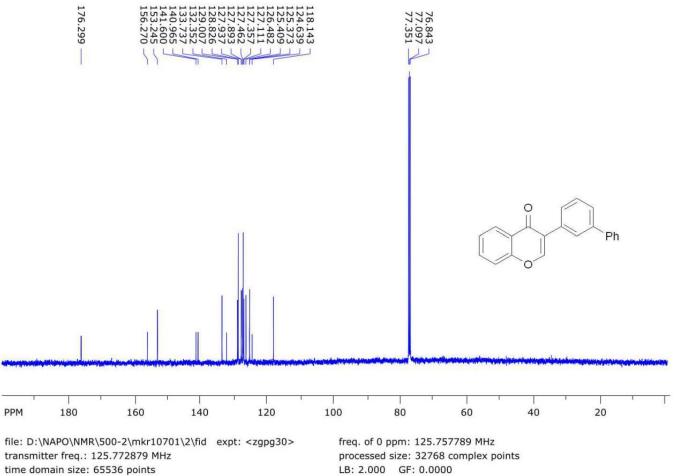


time domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 24 freq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 199.770 ppm/cm: 0.39943 **Compound 4af**

SpinWorks 4: ISM 113 13C

width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt

number of scans: 512

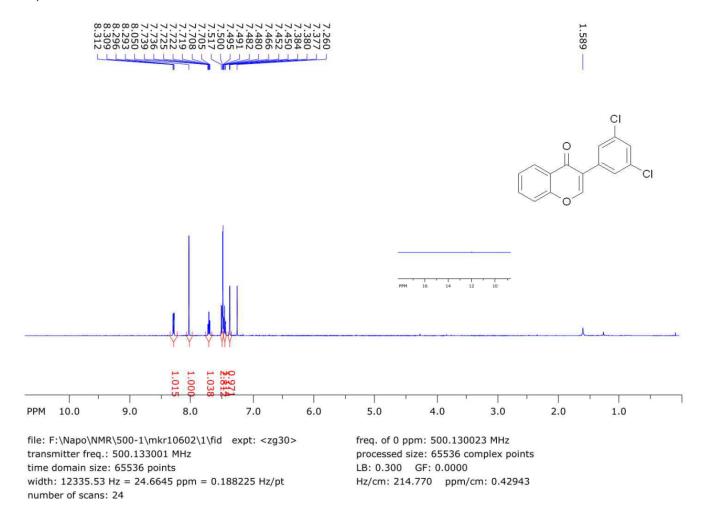


Hz/cm: 1011.530 ppm/cm: 8.04251

29

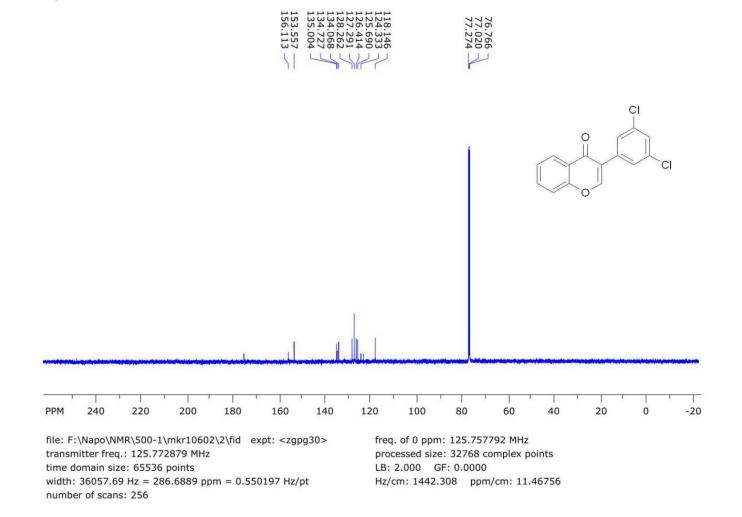
Compound 4aj

SpinWorks 4: ISM 17 1H



30

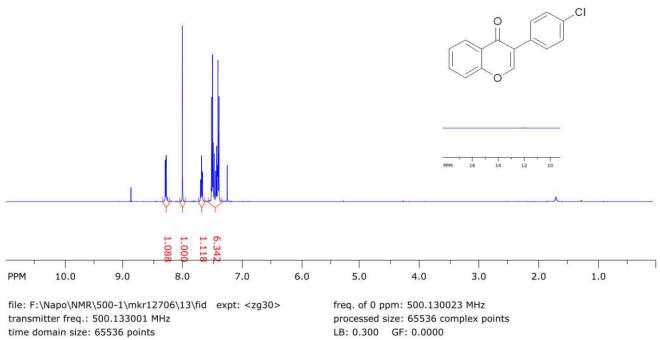
Compound 4aj



Compound 4ar

SpinWorks 4: ISM 70R



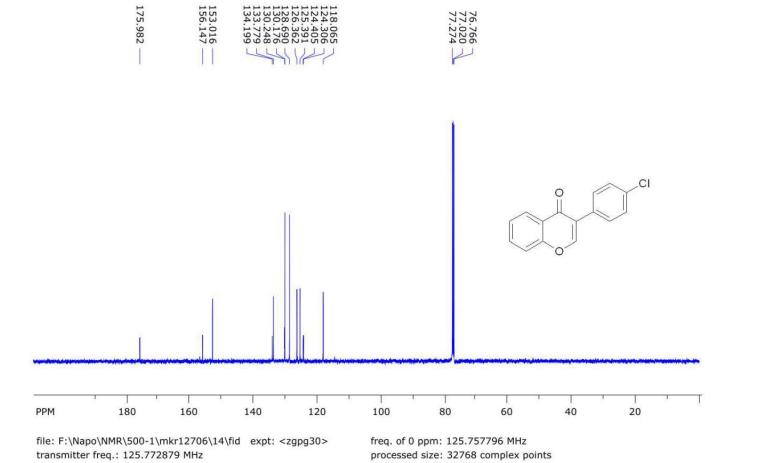


width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/ptnumber of scans: 32

Hz/cm: 219.727 ppm/cm: 0.43934

Compound 4ar

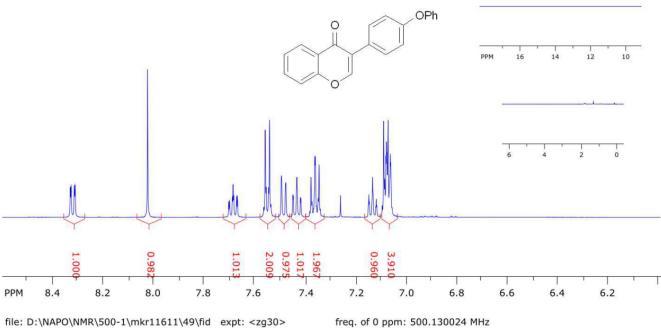
SpinWorks 4: ISM 70R



time domain size: 65536 points width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt number of scans: 368 processed size: 32768 complex points LB: 2.000 GF: 0.0000 Hz/cm: 1057.585 ppm/cm: 8.40869 **Compound 4av**

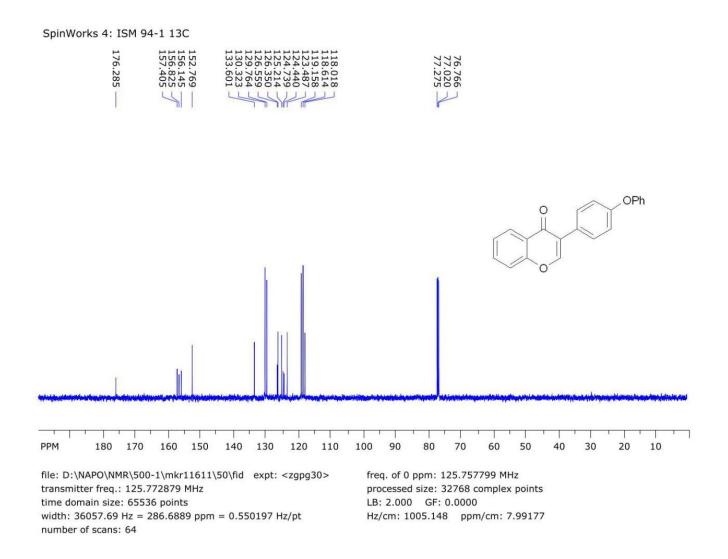
SpinWorks 4: ISM 94-1 1H





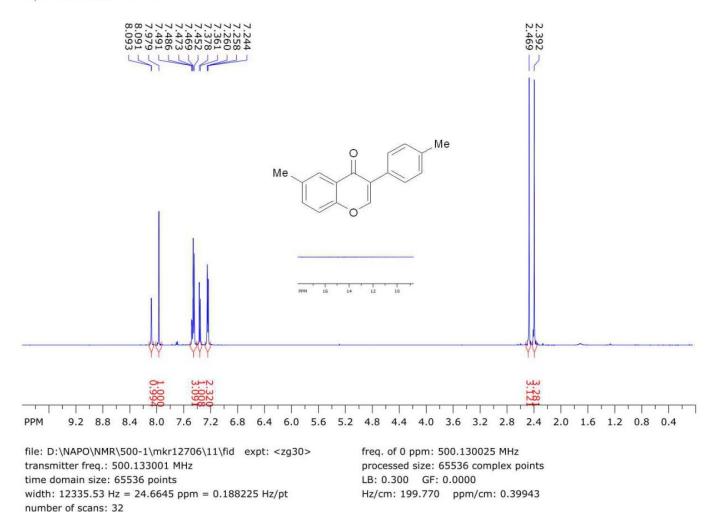
transmitter freq.: 500.133001 MHztime domain size: 65536 pointswidth: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/ptnumber of scans: 24 freq. of 0 ppm: 500.130024 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 52.290 ppm/cm: 0.10455

Compound 4av



Compound 4bb

SpinWorks 4: ISM 78 1H

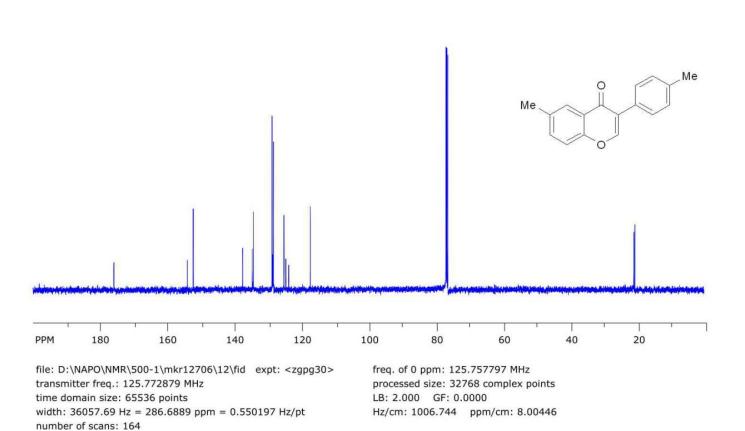


36

Compound 4bb

SpinWorks 4: ISM 78 13C

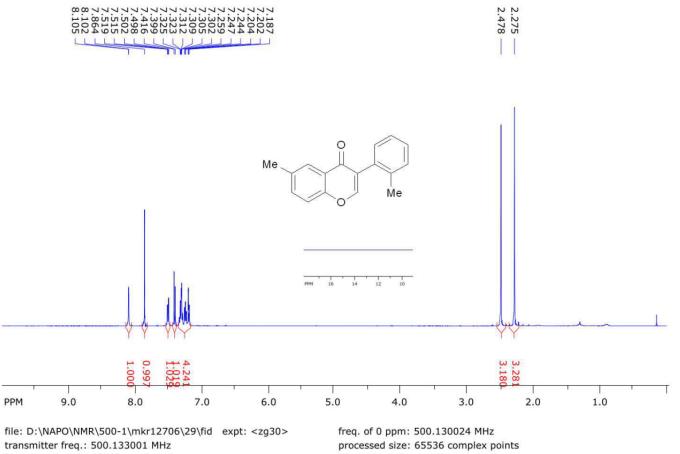




37

Compound 4bc

SpinWorks 4: ISM 75 1H



time domain size: 65536 points

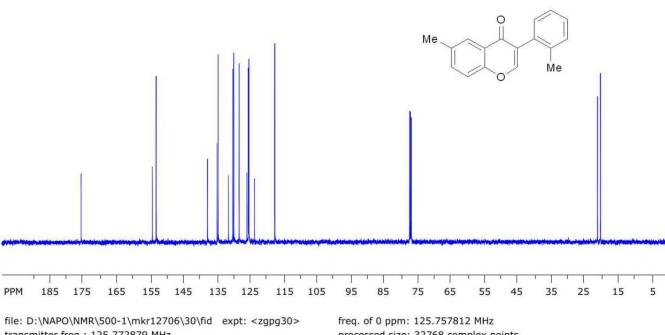
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 16

LB: 0.300 GF: 0.0000 Hz/cm: 200.862 ppm/cm: 0.40162

Compound 4bc

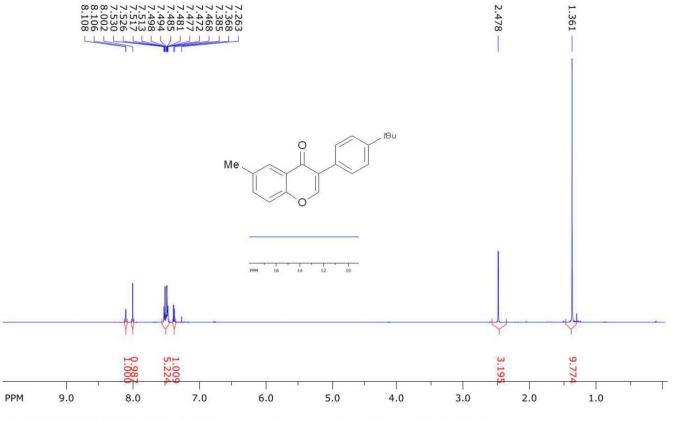
SpinWorks 4: ISM 75 13C





transmitter freq.: 125.772879 MHz time domain size: 65536 points width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt number of scans: 128 freq. of 0 ppm: 125.757812 MHz processed size: 32768 complex points LB: 2.000 GF: 0.0000 Hz/cm: 1003.553 ppm/cm: 7.97909 **Compound 4bd**

SpinWorks 4: ISM 131 1H



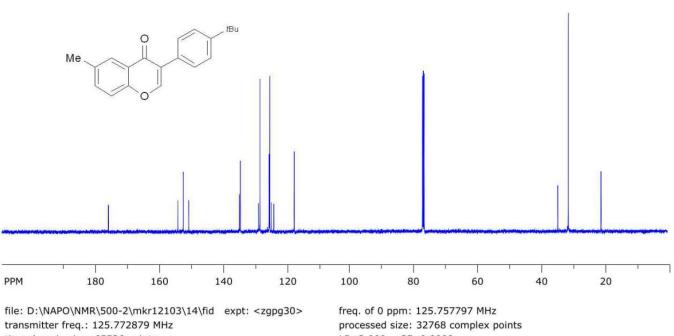
file: D:\NAPO\NMR\500-2\mkr12103\13\fid expt: <zg30> transmitter freq.: 500.133001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 24

freq. of 0 ppm: 500.130022 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 200.316 ppm/cm: 0.40053

Compound 4bd

SpinWorks 4: ISM 131 13C



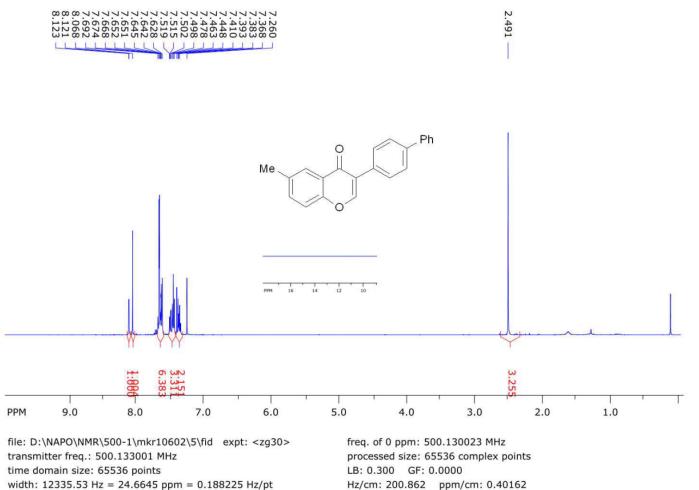


time domain size: 65536 points width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt number of scans: 512

processed size: 32768 complex points LB: 2.000 GF: 0.0000 Hz/cm: 1056.203 ppm/cm: 8.39770 Compound 4be

SpinWorks 4: ISM 19 1H

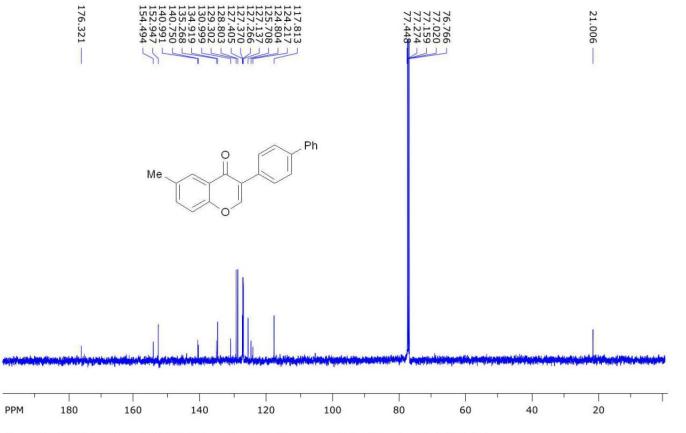
number of scans: 24



Hz/cm: 200.862 ppm/cm: 0.40162

Compound 4be

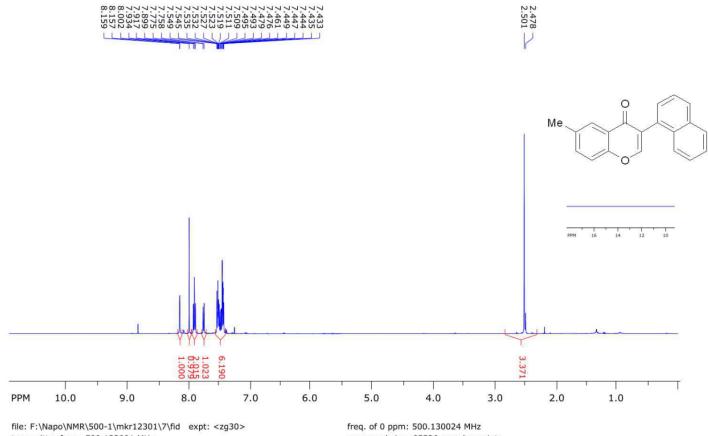
SpinWorks 4: ISM 19 13C



file: D:\NAPO\NMR\500-1\mkr10602\6\fid expt: <zgpg30> transmitter freq.: 125.772879 MHz time domain size: 65536 points width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt number of scans: 256

freq. of 0 ppm: 125.757793 MHz processed size: 32768 complex points LB: 2.000 GF: 0.0000 Hz/cm: 1011.530 ppm/cm: 8.04251 **Compound 4bg**

SpinWorks 4: ISM 14-1 1H

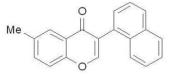


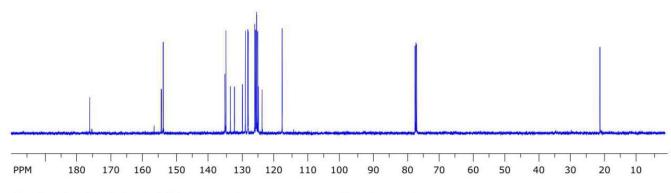
transmitter freq.: 500.133001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 24

freq. of 0 ppm: 500.130024 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 219.727 ppm/cm: 0.43934 **Compound 4bg**

SpinWorks 4: ISM 14-1 13C

176.461	154.053 154.640	1117,810 1125,232 1125,232 1125,232 1125,232 1125,592 1125,592 1125,592 1125,592 1125,592 1125,592 1125,592 1125,592 1125,592 1125,292 112	76.766 77.020 77.274	20.877
	4		K	l.

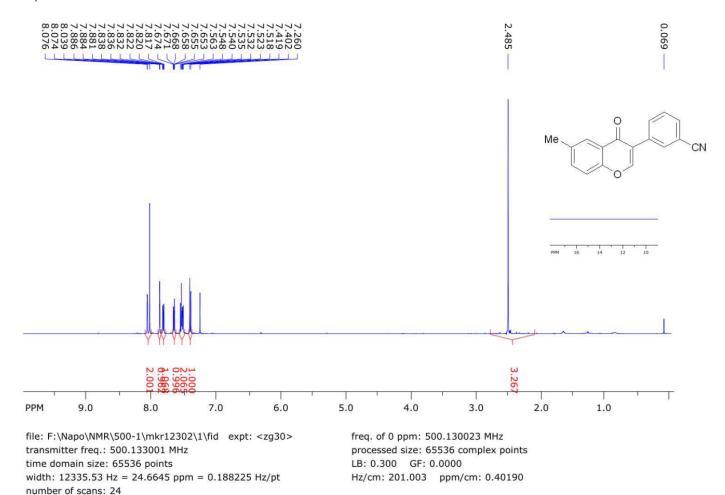




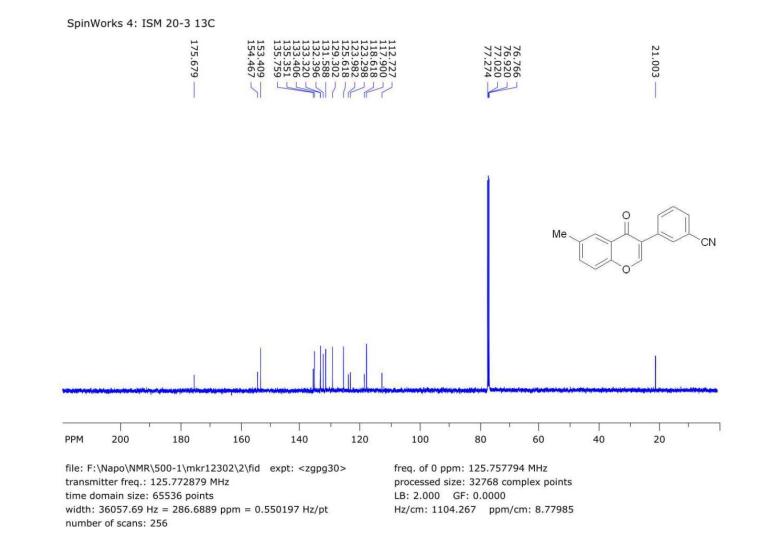
file: F:\Napo\NMR\500-1\mkr12301\8\fid expt: <zgpg30> transmitter freq.: 125.772879 MHz time domain size: 65536 points width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt number of scans: 256

freq. of 0 ppm: 125.757813 MHz processed size: 32768 complex points LB: 2.000 GF: 0.0000 Hz/cm: 1002.855 ppm/cm: 7.97354 **Compound 4bu**

SpinWorks 4: ISM 20-3 1H



Compound 4bu



Compound 4ch

3.919

SpinWorks 4: ISM 100 1H

.196

88 11111111066

0.98 2.03 1.00 1.02 2.29 3.23 1.00 PPM 9.2 8.8 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4 file: D:\NAPO\NMR\500-1\mkr12611\29\fid expt: <zg30> transmitter freq.: 500.133001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 24

freq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 199.224 ppm/cm: 0.39834

1

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0

14

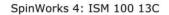
16

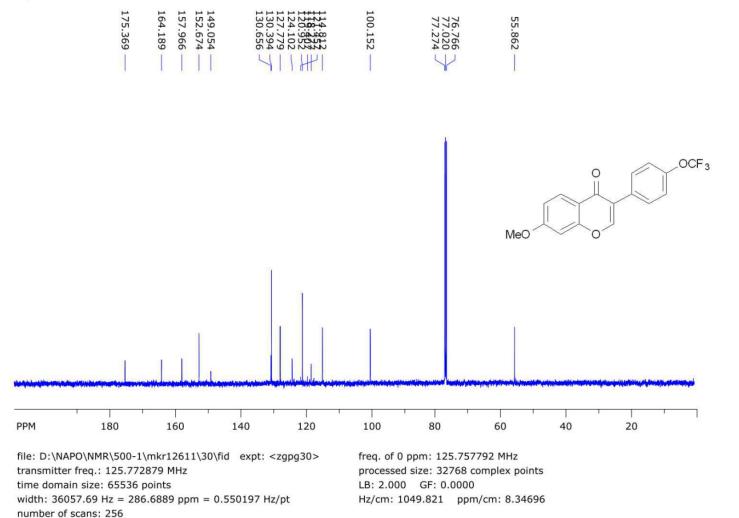
12

10

MeC

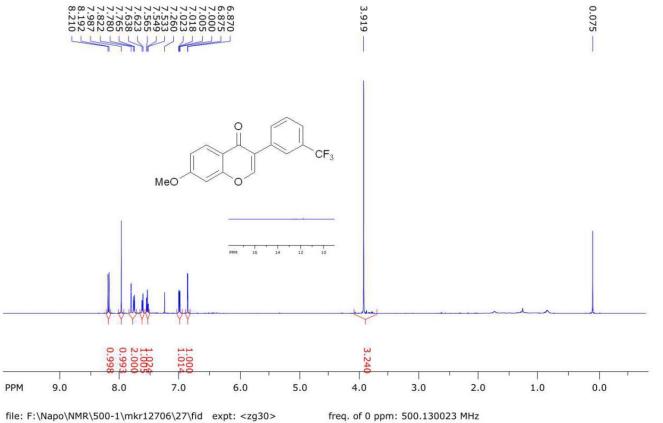
Compound 4ch





Compound 4ci

SpinWorks 4: ISM 67

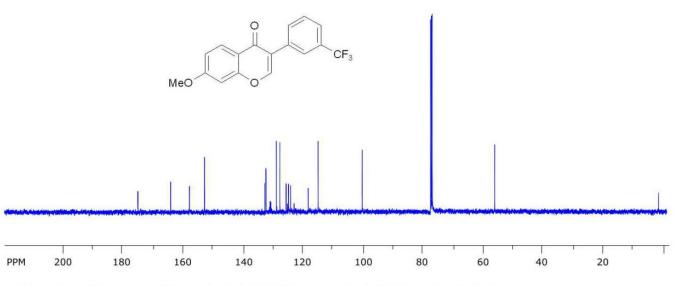


transmitter freq.: 500.133001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 24 freq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 215.872 ppm/cm: 0.43163

Compound 4ci

SpinWorks 4: ISM 67

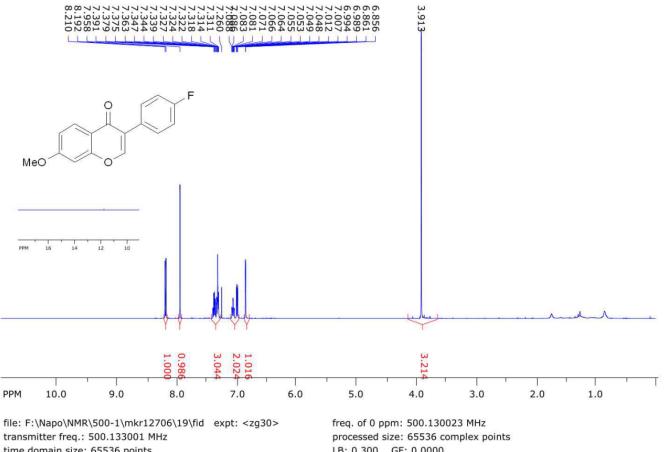




file: F:\Napo\NMR\500-1\mkr12706\28\fid expt: <zgpg30> transmitter freq.: 125.772879 MHz time domain size: 65536 points width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt number of scans: 270

freq. of 0 ppm: 125.757793 MHz processed size: 32768 complex points LB: 2.000 GF: 0.0000 Hz/cm: 1113.925 ppm/cm: 8.85664 **Compound 4cp**

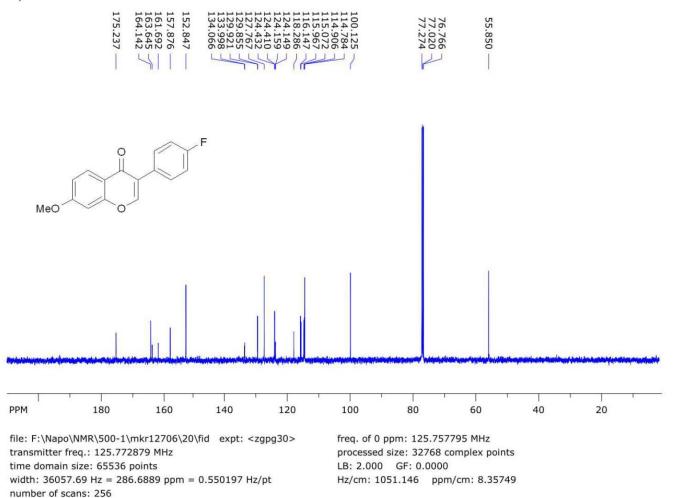
SpinWorks 4: ISM 69



time domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 32

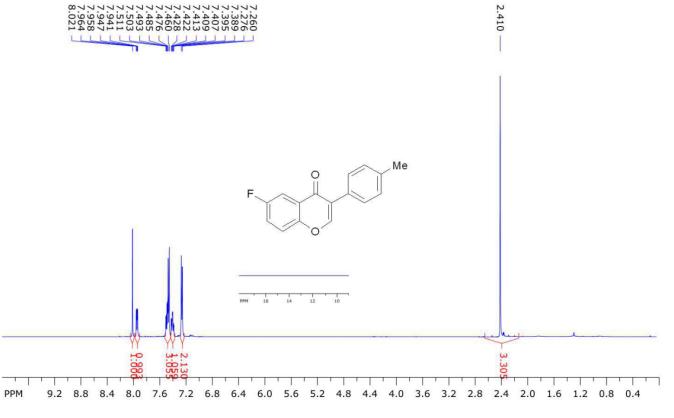
LB: 0.300 GF: 0.0000 Hz/cm: 219.727 ppm/cm: 0.43934 **Compound 4cp**

SpinWorks 4: ISM 69



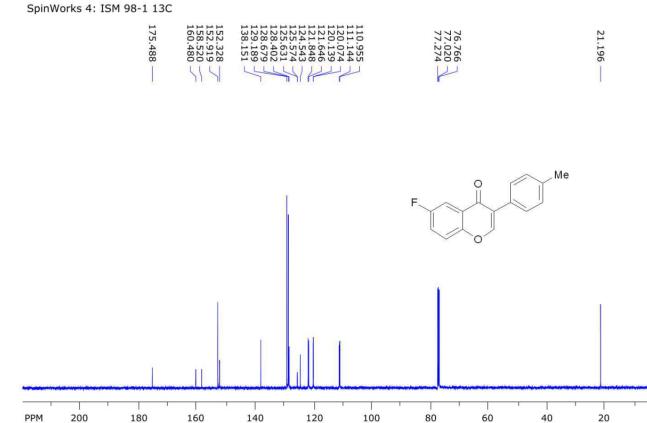
Compound 4db

SpinWorks 4: ISM 98-1 1H



file: D:\NAPO\NMR\500-1\mkr12611\25\fid expt: <zg30> transmitter freq.: 500.133001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 24

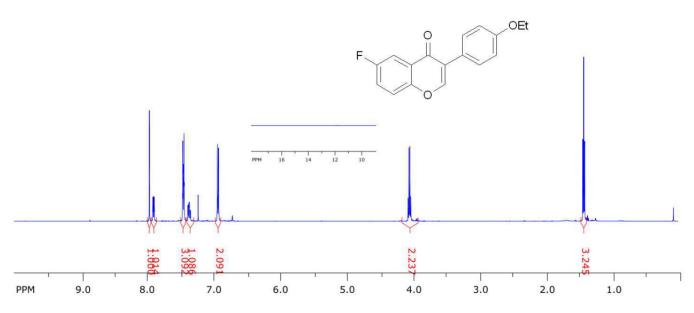
freq. of 0 ppm: 500.130014 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 199.770 ppm/cm: 0.39943 **Compound 4db**



file: D:\NAPO\NMR\500-1\mkr12611\26\fid expt: <zgpg30> transmitter freq.: 125.772879 MHz time domain size: 65536 points width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt number of scans: 256 freq. of 0 ppm: 125.757802 MHz processed size: 32768 complex points LB: 2.000 GF: 0.0000 Hz/cm: 1113.640 ppm/cm: 8.85437 Compound 4dl

SpinWorks 4: ISM 104 1H



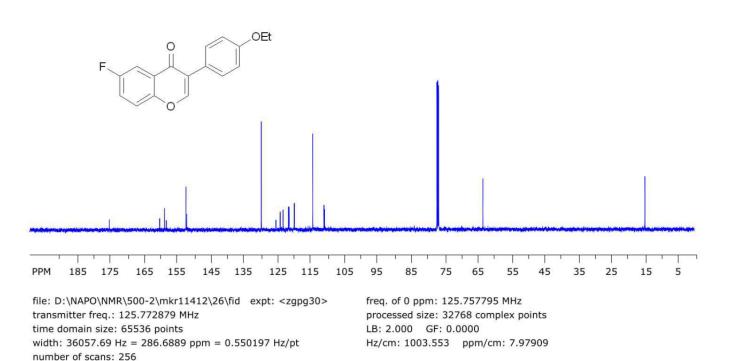


file: D:\NAPO\NMR\500-2\mkr11412\25\fid expt: <zg30> transmitter freq.: 500.133001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 24

freq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 200.862 ppm/cm: 0.40162 Compound 4dl

SpinWorks 4: ISM 104 13C

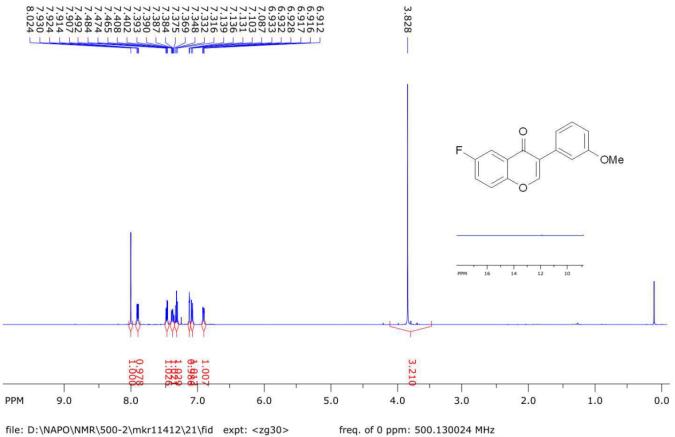




57

Compound 4dm

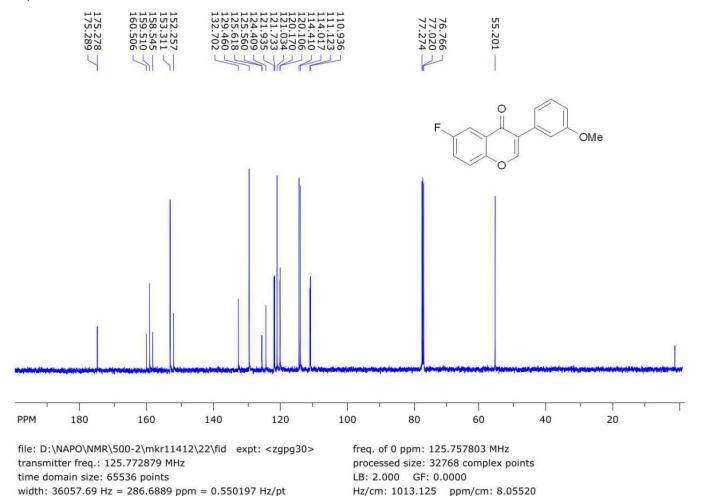
SpinWorks 4: ISM 107-1 1H



transmitter freq.: 500.133001 MHztime domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/ptnumber of scans: 24 freq. of 0 ppm: 500.130024 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 201.407 ppm/cm: 0.40271 **Compound 4dm**

SpinWorks 4: ISM 107-1 13C

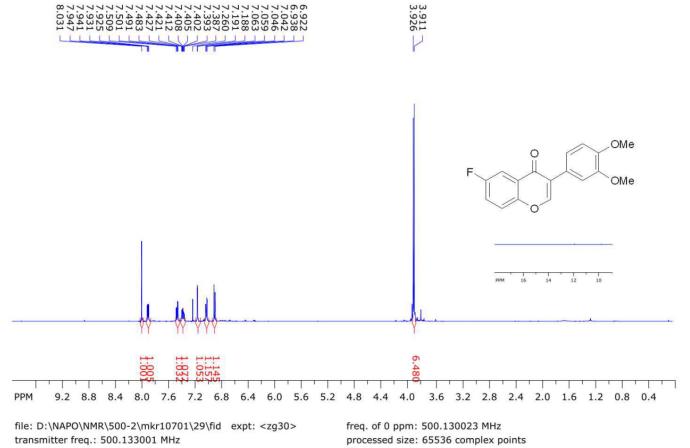
number of scans: 256



59

Compound 4dn

SpinWorks 4: ISM 111-1 1H

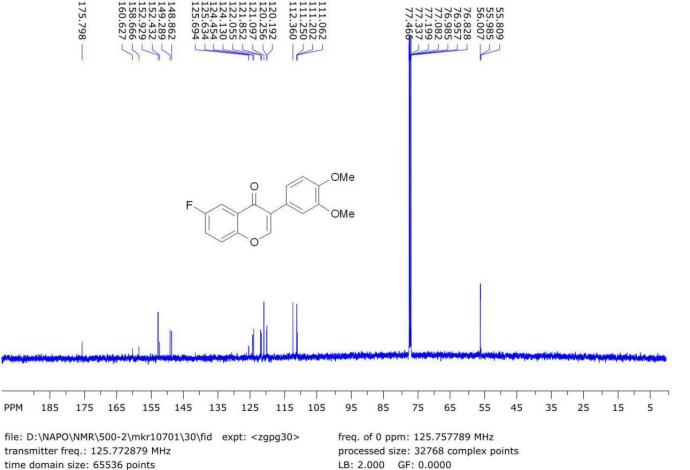


transmitter freq.: 500.133001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 16 rreq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 199.770 ppm/cm: 0.39943 **Compound 4dn**

SpinWorks 4: ISM 111-1 13C

width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt

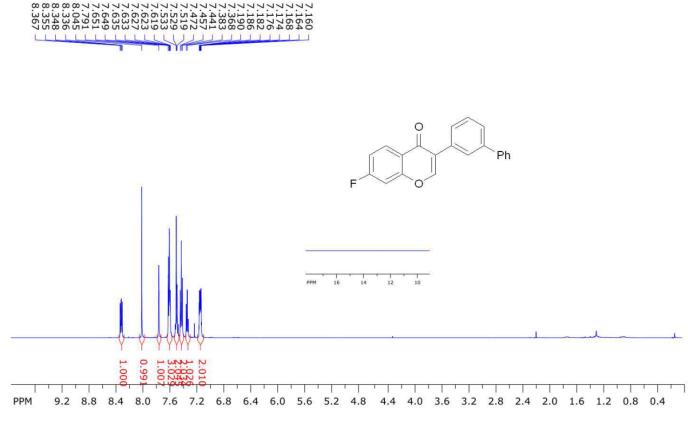
number of scans: 512



Hz/cm: 1005.148 ppm/cm: 7.99177

Compound 4ef

SpinWorks 4: ISM 125 1H

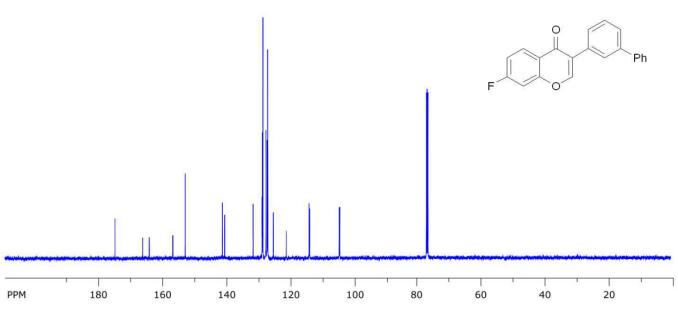


file: D:\NAPO\NMR\500-2\mkr12103\11\fid expt: <zg30> transmitter freq.: 500.133001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 24

freq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 199.770 ppm/cm: 0.39943 **Compound 4ef**

SpinWorks 4: ISM 125 13C

	$ \rightarrow \rightarrow$	
V	004440000000000000000000000000000000000	レレレ
S	444444000000000000000000000000000000000	776
N	00000000000000000000000000000000000000	NON
9	60 55825220000000000000000000000000000000	726
96		406
0.		+00.

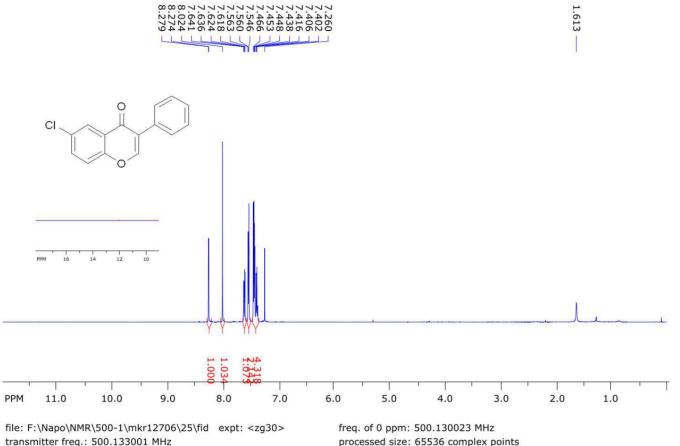


file: D:\NAPO\NMR\500-2\mkr12103\12\fid expt: <zgpg30> transmitter freq.: 125.772879 MHz time domain size: 65536 points width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt number of scans: 512

freq. of 0 ppm: 125.757801 MHz processed size: 32768 complex points LB: 2.000 GF: 0.0000 Hz/cm: 1054.608 ppm/cm: 8.38502

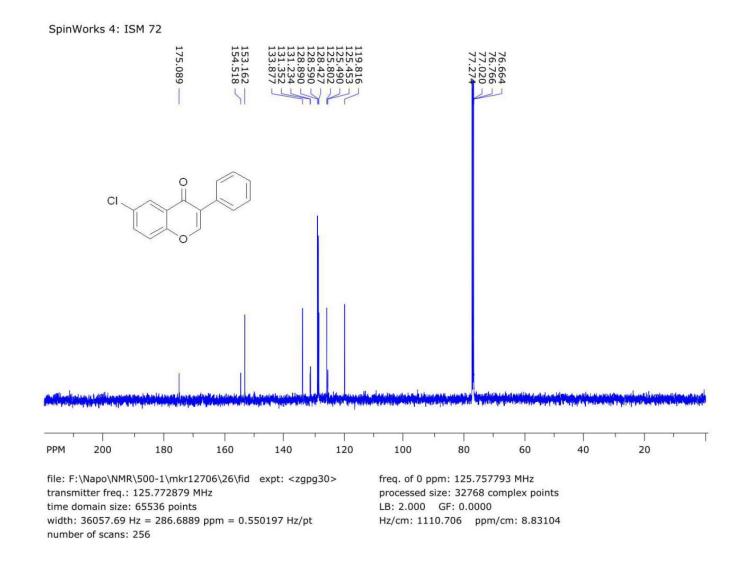
Compound 4fa

SpinWorks 4: ISM 72



transmitter freq.: 500.133001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 32 freq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 240.653 ppm/cm: 0.48118

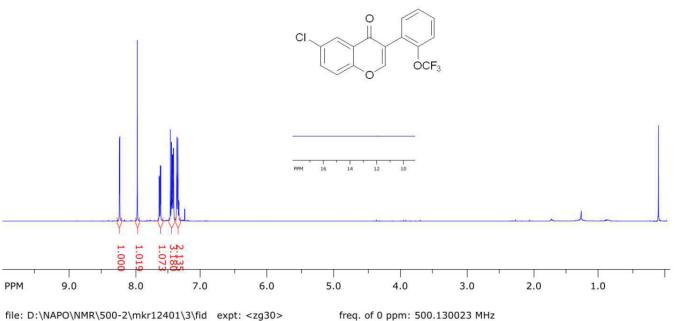
Compound 4fa



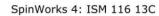
Compound 4fk

SpinWorks 4: ISM 116 1H

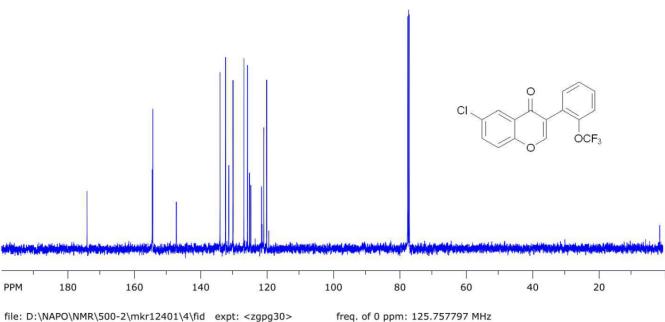




transmitter freq.: 500.133001 MHztime domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/ptnumber of scans: 24 freq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 201.407 ppm/cm: 0.40271 **Compound 4fk**

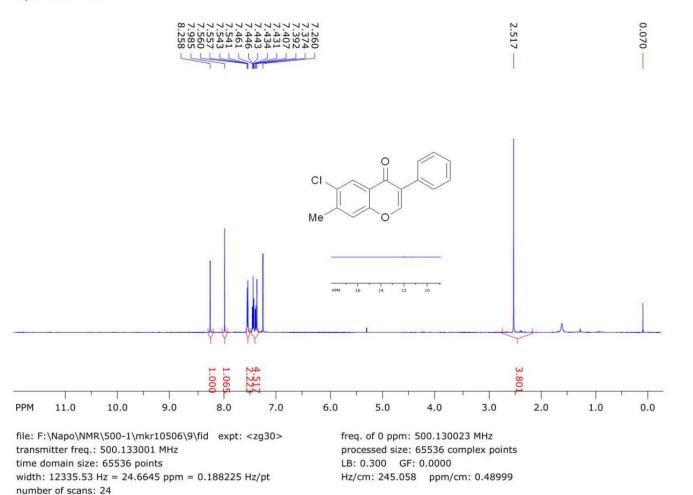






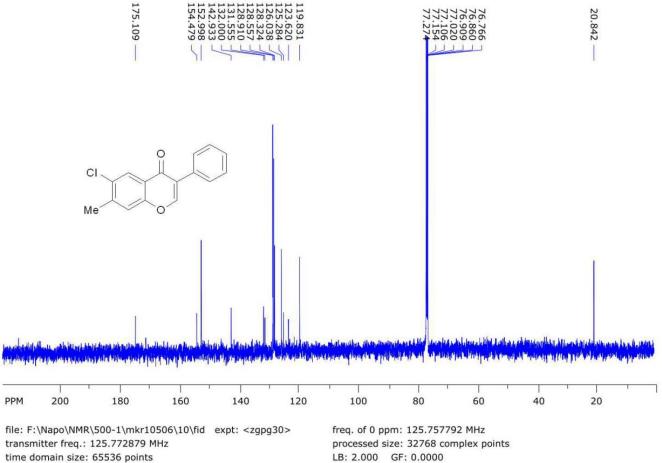
file: D:\NAPO\NMR\500-2\mkr12401\4\fid expt: <zgpg30> transmitter freq.: 125.772879 MHz time domain size: 65536 points width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt number of scans: 96 freq. of 0 ppm: 125.757797 MHz processed size: 32768 complex points LB: 2.000 GF: 0.0000 Hz/cm: 1006.744 ppm/cm: 8.00446 **Compound 4ga**

SpinWorks 4: ISM 71



Compound 4ga

SpinWorks 4: ISM 71



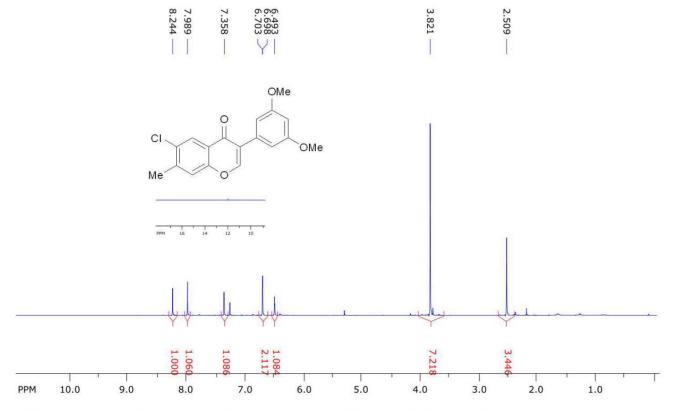
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt Hz/cm: 1102.657 ppm/cm: 8.76705

number of scans: 512

69

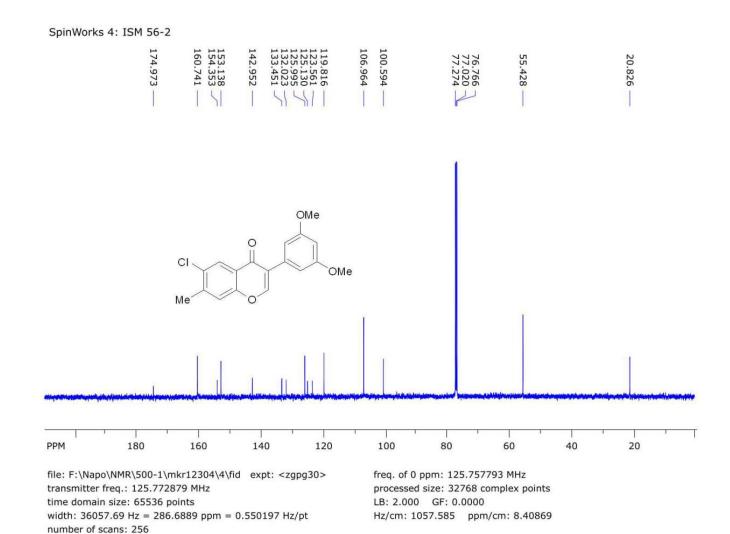
Compound 4go

SpinWorks 4: ISM 56-2



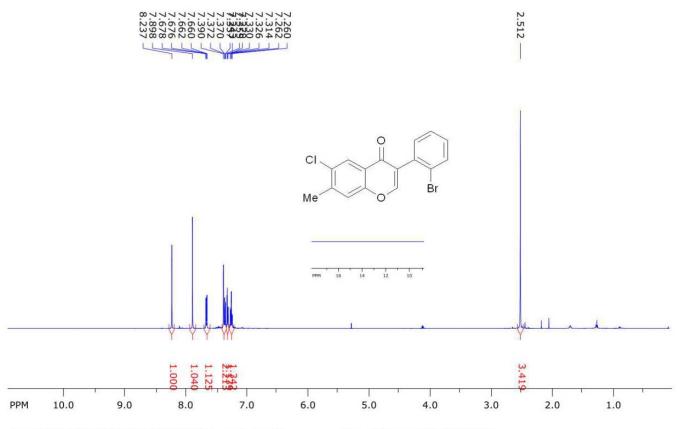
file: F:\Napo\NMR\500-1\mkr12304\3\fid expt: <zg30> transmitter freq.: 500.133001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 24 freq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 220.277 ppm/cm: 0.44044

Compound 4go



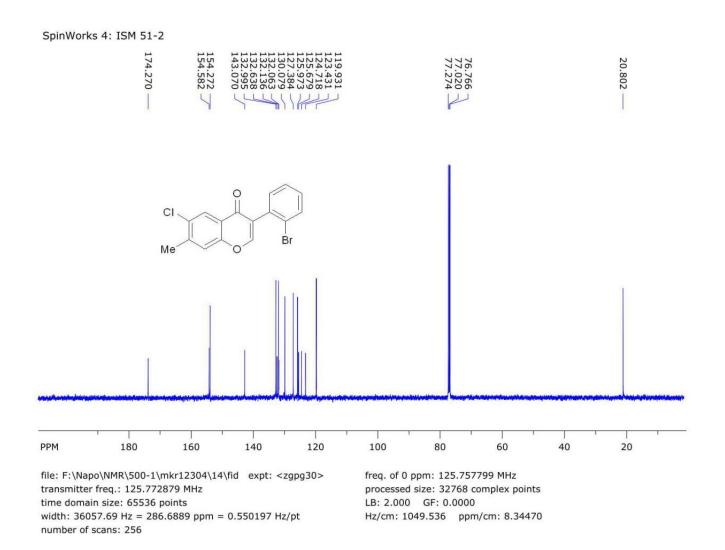
Compound 4gs

SpinWorks 4: IVA 51-2



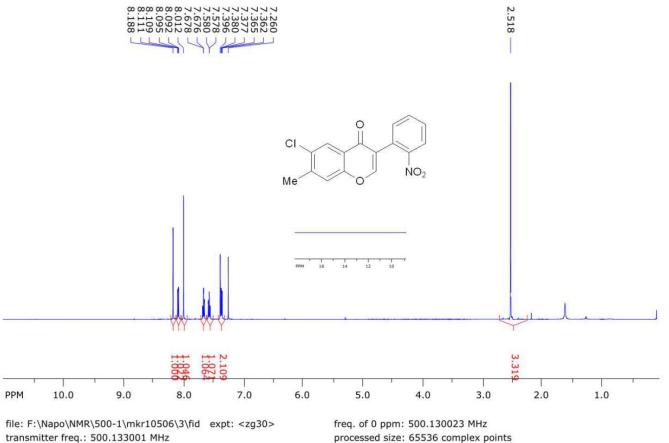
file: F:\Napo\NMR\500-1\mkr12304\13\fid expt: <zg30> transmitter freq.: 500.133001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 24

freq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 217.524 ppm/cm: 0.43493 **Compound 4gs**



Compound 4gt

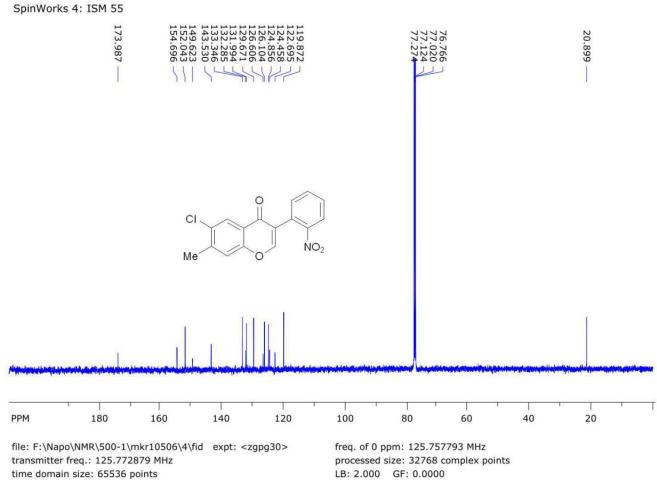
SpinWorks 4: ISM 55



time domain size: 65536 points

width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 24 freq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 219.727 ppm/cm: 0.43934

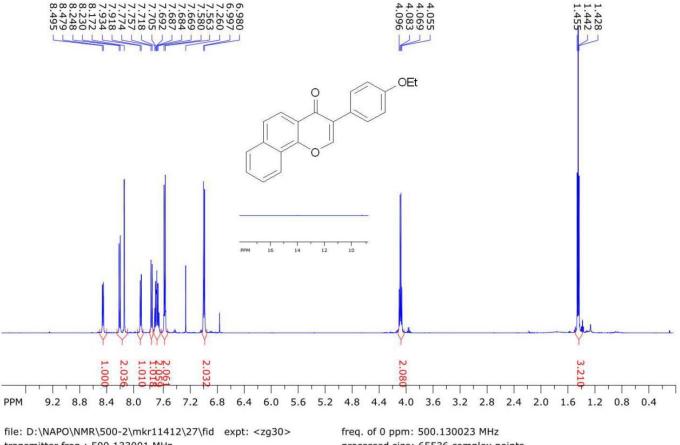
Compound 4gt



width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt number of scans: 512

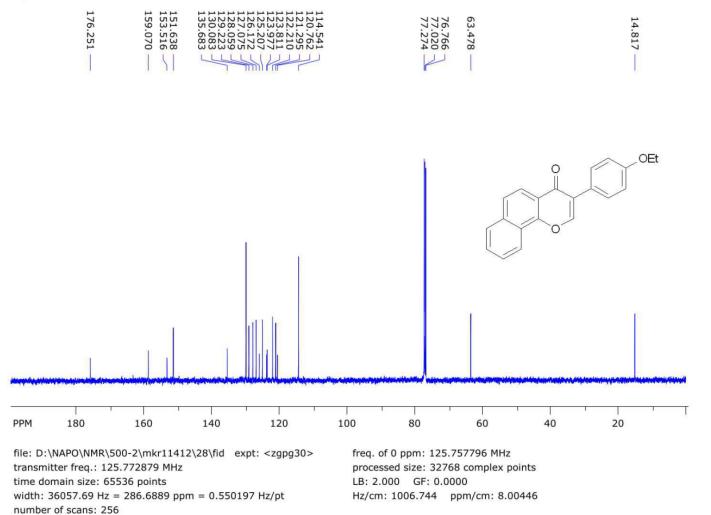
LB: 2.000 GF: 0.0000 Hz/cm: 1057.585 ppm/cm: 8.40869 Compound 4hl

SpinWorks 4: ISM 103 1H



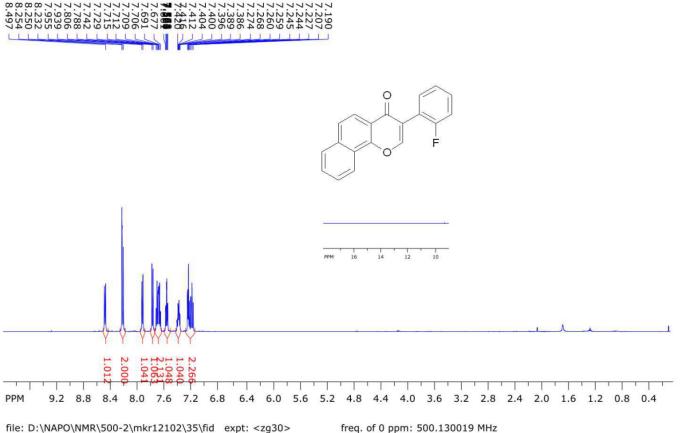
transmitter freq.: 500.133001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 24 freq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 199.224 ppm/cm: 0.39834 Compound 4hl

SpinWorks 4: ISM 103 13C

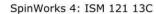


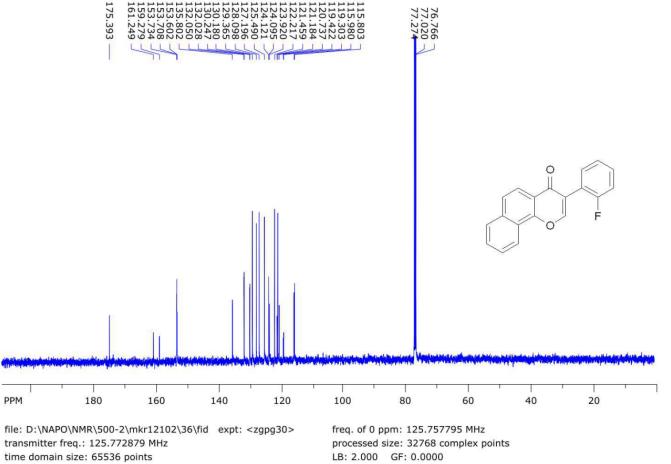
Compound 4hq

SpinWorks 4: ISM 121 1H



The D: (NAPO(MMR(500-2(MRF12102(55))) d expt: <2g3transmitter freq.: 500.133001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt number of scans: 24 freq. of 0 ppm: 500.130019 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 199.224 ppm/cm: 0.39834 **Compound 4hq**





width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt number of scans: 512

Hz/cm: 1056.203 ppm/cm: 8.39770