Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electronic Supplementary Information

Visible light-induced Iridium(III)-sensitized [2+2] and [3+2] photocycloadditions of 2-cyanochromone with alkenes

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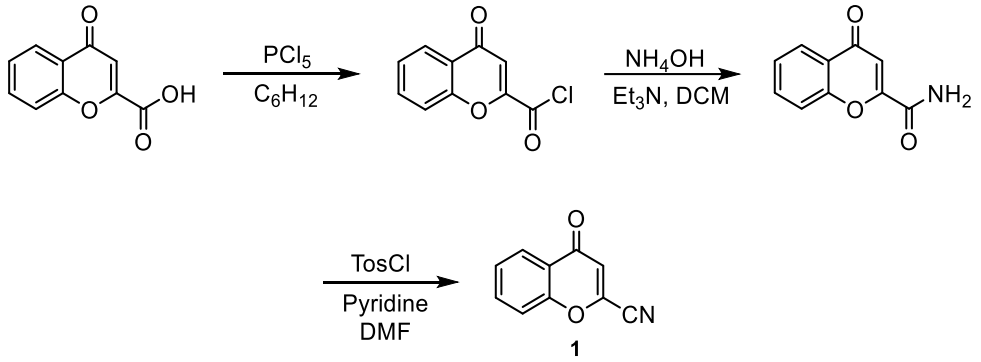
Contents:

1 General information

Commercially available chemicals were used as received from suppliers unless otherwise noted. Dry solvents used were obtained from suppliers in serum-cap quality. Solvents for chromatographic separation were distilled twice prior to use. Thin-layer chromatography was carried out using silica-coated aluminium plates, silica 60 F_{254}, *Merck*. Column chromatography was performed with silica 60 (230-400 mesh, *Macherey-Nagel*). NMR spectra were recorded on *Bruker AVANCE 500 NEO* and *Bruker AVANCE 300 III* instruments, and spectra were calibrated against the (residual) solvent resonances of $CDCl_3$ (δ^H = 7.26 ppm, δ^C = 77.16 ppm).^{1}H- and ^{13}C-NMR peak assignments were made based on 2D NMR spectra. ESI-TOF HRMS spectrometry was performed using an *Agilent* 1200/6210 Time-of-Flight LC-MS instrument. EI HR mass spectra were obtained from a Thermo Electron MAT 95-XP instrument. X-Ray crystallographic analyses were performed on *Apex Kappa-II* and *D8 QUEST* instruments by *Bruker-AXS*.

2 Synthesis of 2-cyanochromone (1)

2-Cyanochromone (**1**) was synthesized in a three-step process according to protocols described earlier.[1],[2] Initially, 2-chromone carboxylic acid was converted into its acyl chloride with PCl_5 followed aminolysis to give the 2-chromone carboxamide. Dehydration with the aid of tosyl chloride led to 2-cyanochromone (**1**).

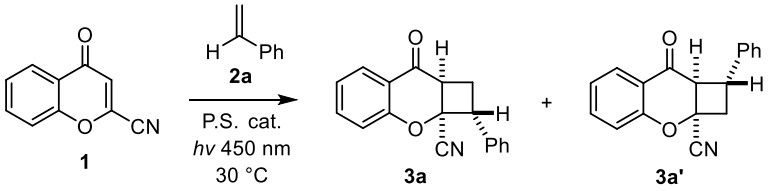


Scheme 1. Synthesis of 2-cyanochromone (**1**)

[1] F. Bousejra-ElGarah, B. Lajoie, J.-P. Souchard, G. Baziard, J. Bouajila, S. El Hage, *Med. Chem. Res.*, 2016, **25**, 2547-2556.

[2] G. P. Ellis, D. Shaw, *J. Med. Chem.*, 1972, **15**, 865-867.

3 Reaction optimization



#	Sens (cat.)	cat. (mol %)	2a (eq.)	time [h]	solvent	conv. 1 [%][a]	yield. 3a [%][a]	yield 3a' [%][a]
1	1,5-diamino AQ	10	20	24	MeCN	10	3	1
2	thioxanthone	10	20	24	MeCN	70	42	8
3	4CzIPN	2	20	24	MeCN	40	17	5
4	Eosin Y[b]	2	20	24	MeCN	32	0	0
5	Rose bengal[b]	2	20	24	MeCN	18	0	0
6	$Ir(ppy)_3$	2	20	24	MeCN	35	0	0
7	$[Ir(ppy)_2dt(bpy)]PF_6$	2	20	24	MeCN	55	13	5
8	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	2	20	24	MeCN	70	43	12
9	$Ru(bpy)(PF_6)_2$	2	20	24 h	MeCN	3	0	0
10	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	1	20	24	MeCN	50	32	10
11	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	3	20	24	MeCN	79	58	11
12	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	4	20	24	MeCN	70	41	10
13	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	3	20	36	MeCN	93	64	13
14	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	3	15	36	MeCN	80	62	13
15	**$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$**	**3**	**10**	**36**	**MeCN**	**96**	**72 (71%)[c]**	**14**
16	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	3	5	36	MeCN	87	64	14
17	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	3	10	36	Acetone	85	48	13
18	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	3	10	36	$CHCl_3$	64	39	18
19	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	3	10	36	DCM	89	43	15
20	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	3	10	36	DMF	67	30	9
21	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ [d]	3	10	36	MeCN	2	0	0
22	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ [e]	3	10	36	MeCN	4	0	0
23	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ [f]	3	10	36	MeCN	72	57	n.d.

Reactions were performed on 0.1 mmol scale of **1** and with 450 nm LED irradiation (30 W). [a] Determined by ^1H NMR-analysis using CH_2Br_2 as the internal standard. [b] Reaction performed with 530 nm LED irradiation (30 W). [c] Isolated yield. [d] Without irradiation. [e] Without sensitizer. [f] Under oxygen atmosphere.

4 Ir(III)-sensitized [2+2] photocycloadditions

General procedure 1

A 10 mL crimp cap vial was charged with 4-oxo-4*H*-chromene-2-carbonitrile **1** (1.0 equiv.) and (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3 mol-%) and the vial was sealed. Dry MeCN (5.00 mL) and alkene **2** or **4** (10.0 equiv., freshly distilled) were added via syringe and the reaction mixture was saturated with argon for 5 minutes (via cannula). The reaction mixture was stirred vigorously for 36 h, while irradiated with blue LEDs (34 W, λ_{em} = 450 nm, solution temperature 30 C). The solvent was evaporated and the crude mixture was purified by column chromatography (silica gel) to afford the products **3** or **5**.

(*Note:* regioisomer ratio was determined from crude ^{1}H-NMR spectra; in several cases regioisomers could not be entirely separated by column chromatography).

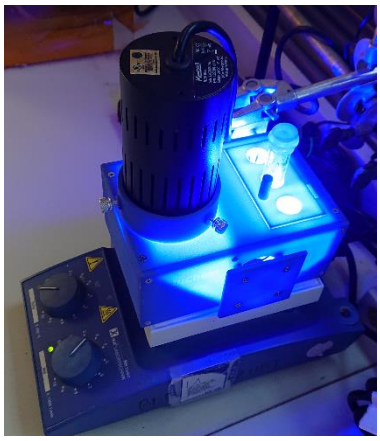
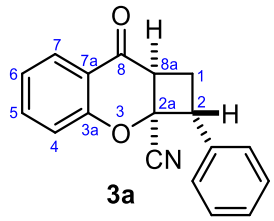


Figure S1. Irradiation setup, EvoluChem™ PhotoRedOx Box, 450 nm / 30 W blue LED.

(2*R,2a*R**,8a*S**)-8-Oxo-2-phenyl-1,2,8,8a-tetrahydro-2a*H*-cyclobuta[*b*]chromene-2a-carbonitrile (3a)**



3a

According to the General Procedure 1, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and styrene (**2a**, 114.6 µL, 104.1 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **3a** as a colorless solid (19.5 mg, 71%).

R_f = 0.38 (EtOAc /heptane 1:3). **m.p.:** 118-119 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.99 (ddd, *J* = 7.9, 1.8, 0.4 Hz, 1 H, 7-H), 7.62 (ddd, *J* = 8.4, 7.2, 1.8 Hz, 1 H, 5-H), 7.46-7.31 (m, 3 H, Ar-H), 7.30-7.26 (m, 2 H, Ar-H), 7.18 (ddd, *J* = 7.9, 7.2, 1.1 Hz, 1 H, 6-H), 7.10 (ddd, *J* = 8.4, 1.1, 0.4 Hz, 1 H, 4-H), 4.40 (m_c, 1 H, 2-H), 3.71 (ddd, *J* = 9.4, 2.7, 1.1 Hz, 1 H, 8a-H), 2.81 (ddd, *J* = 11.9, 11.4, 9.4 Hz, 1 H, 1-H), 2.69 (ddd, *J* = 11.9, 9.6, 2.7 Hz, 1 H, 1-H) ppm.

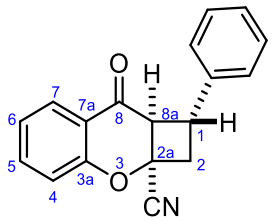
^{13}C NMR (75 MHz, $CDCl_3$) δ = 190.5 (C-8), 157.4 (C-3a), 137.6 (C-5), 136.0 (Ar), 129.0 (Ar), 128.4 (Ar), 127.5 (C-7), 127.0 (Ar), 123.3 (C-6), 119.1 (C-7a), 118.8 (C-4), 116.4 (CN), 78.6 (C-2a), 48.4 (C-2), 45.6 (C-8a), 25.4 (C-1) ppm.

IR: $\tilde{\nu}$ = 2930, 2860, 1685, 1610, 1450, 1310, 1220, 750, 695 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{18}H_{14}NO_2^+$ $[M+H]^+$: 276.1024, found: 276.1021.

Combining a number of smaller scaled reactions allowed for the isolation of a clean sample of the regioisomeric product (brown oil):

(1*R,2a*R**,8a*S**)-8-Oxo-1-phenyl-1,2,8,8a-tetrahydro-2a*H*-cyclobuta[*b*]chromene-2a-carbonitrile (3a')**



3a'

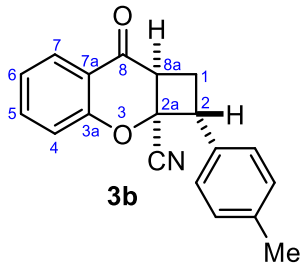
R_f = 0.40 (EtOAc /heptane 1:3).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.96 (dd, *J* = 7.8, 1.7 Hz, 1 H, 7-H), 7.61 (ddd, *J* = 9.0, 7.4, 1.7 Hz, 1 H, 5-H), 7.42-7.37 (m, 2 H, Ar-H), 7.36-7.33 (m, 2 H, Ar-H), 7.33-7.28 (m, 1 H, Ar-H), 7.21 (ddd, *J* = 7.8, 7.4, 1.0 Hz, 1 H, 6-H), 7.15 (dd, *J* = 9.2, 1.0 Hz, 1 H, 4-H), 4.21 (q, *J* = 9.2 Hz, 1 H, 1-H), 3.72 (d, *J* = 9.6 Hz, 1 H, 8a-H), 3.14 (ddd, *J* = 12.6, 8.3, 1.0 Hz, 1 H, 2-H), 3.00 (dd, *J* = 12.6, 8.3 Hz, 1 H, 2-H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 187.8 (C-8), 159.0 (C-3a), 140.0 (Ar), 137.1 (C-5), 129.0 (Ar), 127.7 (Ar), 127.7(C-7), 126.5 (Ar), 124.0 (C-6), 120.2 (C-7a), 118.8 (C-4), 117.5 (CN), 70.5 (C-2a), 53.3 (C-8a), 41.0 (C-1), 40.6 (C-2) ppm.

HRMS (EI): *m/z* calc.: $C_{18}H_{13}NO_2^+$ $[M]^+$: 275.0941, found: 275.0943.

(2*R,2a*R**,8a*S**)-8-Oxo-2-(p-tolyl)-1,2,8,8a-tetrahydro-2a*H*-cyclobuta[*b*]chromene-2a-carbonitrile (3b)**



3b

According to the General Procedure 1, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and 4-methylstyrene (**2b**, 131.7 µL, 118.1 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **3b** as a yellow solid (22.0 mg, 76%).

R_f = 0.36 (EtOAc /heptane 1:3). **m.p.:** 118-120 °C.

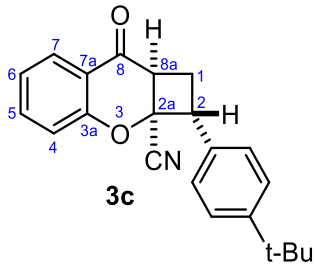
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98 (dd, *J* = 7.9, 1.8 Hz, 1 H, 7-H), 7.61 (ddd, *J* = 8.4, 7.3, 1.8 Hz, 1 H, 5-H), 7.21 (d, *J* = 8.1 Hz, 2 H, Ar-H), 7.19-7.14 (m, 3 H, 6-H, Ar-H), 7.09 (dd, *J* = 8.4, 0.7 Hz, 1 H, 4-H), 4.35 (m_c, 1 H, 2-H), 3.69 (ddd, *J* = 9.5, 2.6, 1.0 Hz, 1 H, 8a-H), 2.79 (td, *J* = 11.6, 9.5 Hz, 1 H,1-H), 2.66 (ddd, *J* = 11.6, 9.5, 2.6 Hz, 1 H, 1-H), 2.36 (s, 3 H, CH_3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 190.6 (C-8), 157.4 (C-3a), 138.2 (Ar), 137.6 (C-5), 133.0 (Ar), 129.7 (Ar), 127.5 (C-7), 126.9 (Ar), 123.3 (C-6), 119.1 (C-7a), 118.8 (C-4), 116.5 (CN), 78.8 (C-2a), 48.2 (C-2), 45.6 (C-8a), 25.5 (C-1), 21.3 (CH_3) ppm.

IR: $\tilde{\nu}$ = 2960, 2920, 1680, 1610, 1480, 1315, 1120, 815, 750, 480 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{19}H_{15}NNaO_2^+$ $[M+Na]^+$: 312.1000, found: 312.1006.

(2*R,2a*R**,8a*S**)-2-(4-(T*ert*-butyl)phenyl)-8-oxo-1,2,8,8a-tetrahydro-2a*H* cyclobuta[*b*] chromene-2a-carbonitrile (3c)**



3c

According to the General Procedure 1 ,4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and 4-*tert*-butylstyrene (**2c**, 183.2 µL, 160.2 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **3c** as a yellow solid (22.2 mg, 67%).

R_f = 0.37 (EtOAc /heptane 1:3). **m.p.:** 127-130 °C.

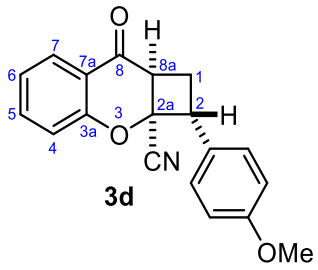
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.99 (dd, *J* = 7.9, 1.8 Hz, 1 H, 7-H), 7.62 (ddd, *J* = 8.3, 7.2, 1.8 Hz, 1 H, 5-H), 7.42 (m_c, 2 H, Ar-H), 7.22 (m_c, 2 H, Ar-H), 7.17 (ddd, *J* = 7.9, 7.2, 1.0 Hz, 1 H, 6-H), 7.08 (dd, *J* = 8.3, 1.0 Hz, 1 H, 4-H), 4.35 (m_c, 1 H, 2-H), 3.70 (ddd, *J* = 9.6, 2.6, 1.1 Hz, 1 H, 8a-H), 2.80 (td, *J* = 11.7, 9.6 Hz, 1 H, 1-H), 2.67 (ddd, *J* = 11.7, 9.6, 2.6 Hz, 1 H, 1-H), 1.33 (s, 9 H, *t*-Bu) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 190.6 (C-8), 157.5 (C-3a), 151.4 (Ar), 137.6 (C-5), 132.9 (Ar), 127.5 (C-7), 126.9 (Ar), 125.9 (Ar), 123.3 (C-6), 119.1 (C-7a), 118.8 (C-4), 116.5 (CN), 78.7 (C-2a), 48.2 (C-2), 45.6 (C-8a), 34.7 (*t*-Bu), 31.4 (*t*-Bu), 25.7 (C-1) ppm.

IR: $\tilde{\nu}$ = 2960, 1687, 1610, 1460, 1220, 1120, 830, 760 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{22}H_{22}NO_2^+$ $[M+H]^+$: 332.1651, found: 332.1656.

(2R*,2a*R,8a*S**)-2-(4-Methoxyphenyl)-8-oxo-1,2,8,8a-tetrahydro-2a*H*-cyclobuta[*b*] chromene-2a-carbonitrile (3d)**



3d

According to the General Procedure 1, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and 4-methoxystyrene (**2d**, 122.0 µL, 134.1 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **3d** as a brown solid (19.2 mg, 63%).

R_f = 0.34 (EtOAc /heptane 1:3). **m.p.:** 124-127 °C.

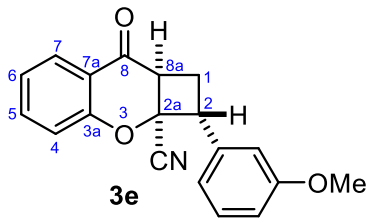
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98 (dd, *J* = 7.9, 1.7 Hz, 1 H, 7-H), 7.61 (ddd, *J* = 8.4, 7.2, 1.7 Hz, 1 H, 5-H), 7.20 (m_c, 2 H, Ar-H), 7.17 (ddd, *J* = 7.9, 7.2, 1.1 Hz, 1 H, 6-H), 7.08 (dd, *J* = 8.4, 1.1 Hz, 1 H, 4-H), 6.93 (m_c, 2 H, Ar-H), 4.34 (m_c, 1 H, 2-H), 3.81 (s, 3 H, OCH_3), 3.69 (ddd, *J* = 9.5, 2.7, 1.1 Hz, 1 H, 8a-H), 2.77 (td, *J* = 12.3, 9.5 Hz, 1 H 1-H), 2.66 (ddd, *J* = 12.3, 9.5, 2.7 Hz, 1 H 1-H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 190.6 (C-8), 159.7 (Ar), 157.5 (C-3a), 137.6 (C-5), 128.3 (Ar), 128.0 (Ar), 127.5 (C-7), 123.3 (C-6), 119.1 (C-7a), 118.8 (C-4), 116.5 (CN), 114.4 (Ar), 78.9 (C-2a), 55.4 (OCH_3), 48.0 (C-2), 45.5 (C-8a), 25.7 (C-1) ppm.

IR: $\tilde{\nu}$ = 2960, 2840, 1690, 1520, 1460, 1240, 1120, 810, 755, 505 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{19}H_{16}NO_3^+$ $[M+H]^+$: 306.1130, found: 306.1136.

(2*R,2a*R**,8a*S**)-2-(3-Methoxyphenyl)-8-oxo-1,2,8,8a-tetrahydro-2a*H*-cyclobuta[*b*] chromene-2a-carbonitrile (3e)**



3e

According to the General Procedure 1, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and 3-methoxystyrene (**2e**, 122.0 µL, 134.1 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **3e** as a colorless solid (19.5 mg, 64%).

R_f = 0.34 (EtOAc /heptane 1:3). **m.p.:** 128-130 °C.

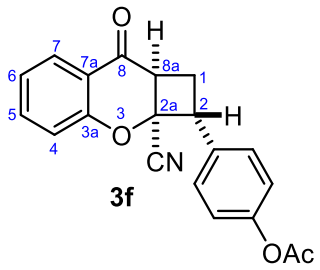
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98 (dd, *J* = 7.9, 1.7 Hz, 1 H, 7-H), 7.62 (ddd, *J* = 9.0, 7.2, 1.7 Hz, 1 H, 5-H), 7.33 (m_c, 1 H, Ar-H), 7.17 (ddd, *J* = 7.9, 7.2, 1.1 Hz, 1 H, 6-H), 7.09 (dd, *J* = 9.0, 1.1 Hz, 1 H, 4-H), 6.90-6.84 (m, 2 H, Ar-H), 6.79 (m_c, 1 H, Ar-H), 4.37 (m_c, 1 H, 2-H), 3.83 (s, 3 H, OCH_3), 3.69 (ddd, *J* = 9.5, 2.6, 1.1 Hz, 1 H, 8a-H), 2.78 (td, *J* = 12.1, 9.5 Hz, 1 H 1-H), 2.67 (ddd, *J* = 12.1, 9.5, 2.6 Hz, 1 H 1-H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 190.5 (C-8), 160.0 (Ar), 157.4 (C-3a), 137.6 (C-5), 137.6 (Ar), 130.1 (Ar), 127.5 (C-7), 123.3 (C-6), 119.2 (C-7a), 119.1 (Ar), 118.8 (C-4), 116.4 (CN), 113.4 (Ar), 113.1 (Ar), 78.5 (C-2a), 55.4 (OCH_3), 48.3 (C-2), 45.6 (C-8a), 25.4 (C-1) ppm.

IR: $\tilde{\nu}$ = 2960, 2920, 1690, 1460, 1130, 1055, 755, 690 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{19}H_{16}NO_3^+$ $[M+H]^+$: 306.1130, found: 306.1130.

4-[(2*R,2a*R**,8a*S**)-2a-Cyano-8-oxo-2,2a,8,8a-tetrahydro-1*H*-cyclobuta[*b*]chromen-2-yl] phenyl acetate (3f)**



3f

According to the General Procedure 1, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and 4-acetoxyoxystyrene (**2f**, 153.0 µL, 162.2 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **3f** as a colorless solid (19.3 mg, 58%).

R_f = 0.30 (EtOAc /heptane 1:3). **m.p.:** 128-131 °C.

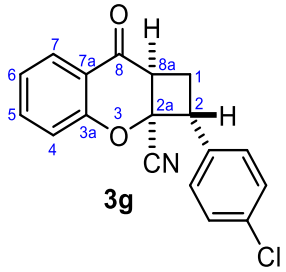
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98 (dd, *J* = 7.9, 1.7 Hz, 1 H, 7-H), 7.62 (ddd, *J* = 9.0, 7.3, 1.7 Hz, 1 H, 5-H), 7.29 (m_c, 2 H, Ar-H), 7.18 (ddd, *J* = 7.9, 7.3, 1.1 Hz, 1 H, 6-H), 7.15 (m_c, 2 H, Ar-H), 7.08 (dd, *J* = 9.0, 1.1 Hz, 1 H, 4-H), 4.37 (m_c, 1 H, 2-H), 3.70 (ddd, *J* = 9.4, 2.5, 1.0 Hz, 1 H, 8a-H), 2.77 (td, *J* = 12.2, 9.4 Hz, 1 H, 1-H), 2.69 (ddd, *J* = 12.2, 9.4, 2.5 Hz, 1 H, 1-H), 2.30 (s, 3 H, CH_3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 190.3 (C-8), 169.4 (OAc), 157.3 (C-3a), 150.7 (Ar), 137.7 (C-5), 133.5 (Ar), 128.2 (Ar), 127.5 (C-7), 123.4 (C-6), 122.2 (Ar), 119.1 (C-7a), 118.8 (C-4), 116.3 (CN), 78.5 (C-2a), 47.9 (C-2), 45.6 (C-8a), 25.6 (C-1), 21.3 (CH_3) ppm.

IR: $\tilde{\nu}$ = 2930, 1760, 1690, 1460, 1220, 1130, 760, 510 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{20}H_{16}NO_4^+$ $[M+H]^+$: 334.1079, found: 334.1081.

(2*R,2a*R**,8a*S**)-2-(4-Chlorophenyl)-8-oxo-1,2,8,8a-tetrahydro-2a*H*-cyclobuta[*b*] chromene-2a-carbonitrile (3g)**



3g

According to the General Procedure 1, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and 4-chlorostyrene (**2g**, 120.0 µL, 138.6 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **3g** as a colorless solid (21.4 mg, 69%).

R_f = 0.34 (EtOAc /heptane 1:3). **m.p.:** 126-128 °C.

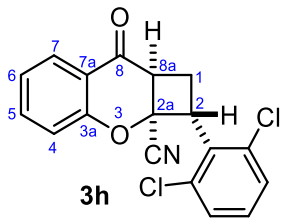
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98 (dd, *J* = 7.9, 1.8 Hz, 1 H, 7-H), 7.62 (ddd, *J* = 9.0, 7.2, 1.8 Hz, 1 H, 5-H), 7.38 (m_c, 2 H, Ar-H), 7.22-7.19 (m, 2 H, Ar-H), 7.17 (ddd, *J* = 7.9, 7.2, 1.0 Hz, 1 H, 6-H), 7.09 (dd, *J* = 9.0, 1.0 Hz, 1 H, 4-H), 4.37 (m_c, 1 H, 2-H), 3.70 (ddd, *J* = 9.3, 2.6, 1.0 Hz, 1 H, 8a-H), 2.70 (td, *J* = 12.1, 9.3 Hz, 1 H, 1-H), 2.69 (ddd, *J* = 12.1, 9.3, 2.6 Hz, 1 H, 1-H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 190.2 (C-8), 157.3 (C-3a), 137.7 (C-5), 134.5 (Ar), 134.4 (Ar), 129.2 (Ar), 128.4 (Ar), 127.5 (C-7), 123.5 (C-6), 119.1 (C-7a), 118.8 (C-4), 116.5 (CN), 78.5 (C-2a), 47.9 (C-2), 45.5 (C-8a), 25.3 (C-1) ppm.

IR: $\tilde{\nu}$ = 2920, 2855, 1685, 1610, 1460, 1310, 1110, 810, 760, 510 cm^{-1}.

Elemental analysis: $C_{18}H_{12}ClNO_2$, calc.: C 69.80, H 3.91, N 4.52, found: C 68.81, H 3.90, N 4.28.

(2*R,2a*R**,8a*S**)-2-(2,6-Dichlorophenyl)-8-oxo-1,2,8,8a-tetrahydro-2a*H*-cyclobuta[*b*] chromene-2a-carbonitrile (3h)**



3h

According to the General Procedure 1, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and 2,6-dichlorostyrene (**2h**, 136.6 µL, 173.0 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **3h** as a colorless solid (9.6 mg, 28%).

R_f = 0.37 (EtOAc /heptane 1:3). **m.p.:** 125-127 °C.

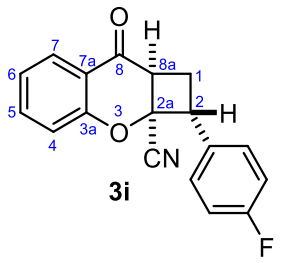
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.97 (dd, *J* = 7.9, 1.7 Hz, 1 H, 7-H), 7.61 (ddd, *J* = 9.0, 7.3, 1.7 Hz, 1 H, 5-H), 7.36 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.23-7.16 (m, 2 H, Ar-H, 6-H), 7.06 (dd, *J* = 9.0, 1.0 Hz, 1 H, 4-H), 5.10 (m_c, 1 H, 2-H), 3.96-3.86 (m, 2 H, 1-H, 8a-H), 2.77 (ddd, *J* = 11.9, 8.6, 2.9 Hz, 1 H, 1-H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 190.5 (C-8), 157.5 (C-3a), 137.5 (C-5), 136.6 (Ar), 130.4 (Ar), 130.1 (Ar), 130.0 (Ar), 127.3 (C-7), 123.5 (C-6), 119.5 (C-7a), 119.1 (C-4), 116.7 (CN), 77.7 (C-2a), 46.5 (C-2), 45.7 (C-8a), 27.1 (C-1) ppm.

IR: $\tilde{\nu}$ = 2970, 1690, 1610, 1460, 1310, 1110, 785, 745 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{18}H_{12}Cl_2NO_2^+$ $[M+H]^+$: 344.0245, found: 344.0243.

(2*R,2a*S**,8a*S**)-2-(4-Fluorophenyl)-8-oxo-1,2,8,8a-tetrahydro-2a*H*-cyclobuta[*b*] chromene-2a-carbonitrile (3i)**



3i

According to the General Procedure, 1,4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and 4-fluorostyrene (**2i**, 119.2 µL, 122.1 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **3i** as a pale yellow oil (17.9 mg, 61%, containing 7% of its regioisomer that could not be separated).

R_f = 0.38 (EtOAc /heptane 1:3).

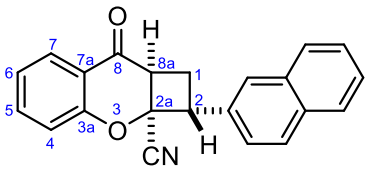
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98 (dd, *J* = 7.8, 1.8 Hz, 1 H, 7-H), 7.62 (ddd, *J* = 9.1, 7.2, 1.8 Hz, 1 H, 5-H), 7.24 (m_c, 2 H, Ar-H), 7.18 (ddd, *J* = 7.8, 7.2, 1.0 Hz, 1 H, 6-H), 7.12-7.07 (m, 3 H, 4-H, Ar-H), 4.37 (m_c, 1 H, 2-H), 3.70 (ddd, *J* = 9.4, 2.6, 0.9 Hz, 1 H, 8a-H), 2.76 (td, *J* = 12.1, 9.6 Hz, 1 H, 1-H), 2.69 (ddd, *J* = 12.1, 9.6, 2.7 Hz, 1 H, 1-H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 190.3 (C-8), 162.7 ($^{1}J_{C,F}$ = 246.9 Hz, Ar), 157.3 (C-3a), 137.7 (C-5), 131.8 ($^{4}J_{C,F}$ = 3.3 Hz, Ar), 128.8 ($^{3}J_{C,F}$ = 8.4 Hz, Ar), 127.5 (C-7), 123.4 (C-6), 119.1 (C-7a), 118.7 (C-4), 116.3 (CN), 116.0 ($^{2}J_{C,F}$ = 21.6 Hz, Ar) 78.6 (C-2a), 47.8 (C-2), 45.5 (C-8a), 25.5 (C-1) ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ = -113.43 (s, 1 F, Ar-F) ppm.

Elemental analysis: $C_{18}H_{12}FNO_2$, calc.: C 73.71, H 4.12, N 4.78, found: C 71.35, H 4.60, N 4.32.

(1*R,2a*R**,8a*S**)-2-(Naphthalen-2-yl)-8-oxo-1,2,8,8a-tetrahydro-2a*H*-cyclobuta[*b*] chromene-2a-carbonitrile (3j)**



3j

According to the General Procedure, 1,4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and 2-vinylnaphthalene (**2j**, 154.2 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **3j** as a colorless oil (23.1 mg, 71%, containing 19% of its regioisomer that could not be separated).

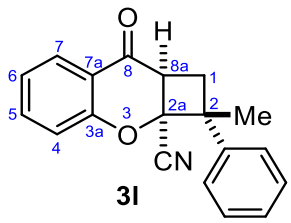
R_f = 0.41 (EtOAc /heptane 1:3).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.01 (dd, *J* = 7.9, 1.8 Hz, 1 H, 7-H), 7.91-7.82 (m, 3 H, Ar-H), 7.69 (s, 1 H, Ar-H), 7.65 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1 H, 5-H), 7.54-7.48 (m, 2 H, Ar-H), 7.39 (dd, *J* = 8.6, 1.9 Hz, 1 H, Ar-H), 7.20 (ddd, *J* = 8.4, 7.2, 1.0 Hz, 1 H, 6-H), 7.15 (dd, *J* = 8.4, 1.0 Hz, 1 H, 4-H), 4.56 (m_c, 1 H, 2-H), 3.75 (ddd, *J* = 9.5, 2.5, 1.0 Hz, 1 H, 8a-H), 2.94 (td, *J* = 12.0, 9.5 Hz, 1 H, 1-H), 2.78 (ddd, *J* = 12.0, 9.5, 2.5 Hz, 1 H, 1-H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 190.5 (C-8), 157.4 (C-3a), 137.7 (C-5), 128.9 (Ar), 128.1 (Ar), 127.9 (Ar), 127.5 (C-7), 126.7 (Ar), 126.5 (Ar), 125.9 (Ar), 124.7 (Ar), 123.4 (C-6), 119.1 (C-7a), 118.8 (C-4), 116.4 (CN), 78.6 (C-2a), 48.6 (C-2), 45.6 (C-8a), 25.4 (C-1) ppm.

Elemental analysis: $C_{22}H_{15}NO_2$, calc.: C 81.21, H 4.65, N 4.30, found: C 81.75, H 5.10, N 3.72.

(2*R,2a*S**,8a*S**)-2-Methyl-8-oxo-2-phenyl-1,2,8,8a-tetrahydro-2a*H*-cyclobuta[*b*] chromene-2a-carbonitrile (3l)**



3l

According to the General Procedure 1, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and α-methylstyrene (**2l**, 129.9 µL, 118.2 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **3l** as a colorless solid (10.4 mg, 36%).

R_f = 0.36 (EtOAc /heptane 1:3). **m.p.:** 138-139 °C.

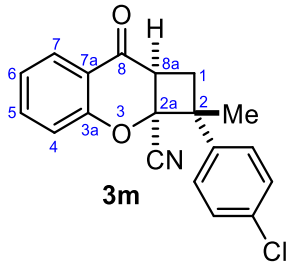
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.90 (dd, *J* = 7.9, 1.8 Hz, 1 H, 7-H), 7.59 (ddd, *J* = 9.1, 7.4, 1.8 Hz, 1 H, 5-H), 7.46-7.41 (m, 2 H, Ar-H), 7.36-7.30 (m, 3 H, Ar-H), 7.14 (ddd, *J* = 7.9, 7.4, 1.1 Hz, 1 H, 6-H), 7.11 (dd, *J* = 9.1, 1.1 Hz, 1 H, 4-H), 3.71 (dd, *J* = 10.2, 4.3 Hz, 1 H, 8a-H), 3.14 (dd, *J* = 12.1, 10.2 Hz, 1 H, 1-H), 2.69 (dd, *J* = 12.1, 4.3 Hz, 1 H, 1-H), 1.51 (s, 3 H, CH_3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 190.6 (C-8), 159.7 (C-3a), 143.7 (Ar), 137.3 (C-5), 129.0 (Ar), 127.8 (Ar), 127.2 (C-7), 125.2 (Ar), 123.0 (C-6), 119.1 (C-7a), 118.1 (C-4), 117.9 (CN), 79.3 (C-2a), 55.1 (C-2), 43.7 (C-8a), 33.6 (C-1), 25.4 (CH_3) ppm.

IR: $\tilde{\nu}$ = 2980, 1690, 1605, 1455, 1320, 1130, 760, 695 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{19}H_{16}NO_2^+$ $[M+H]^+$: 290.1181, found: 290.1178.

(2*R,2a*S**,8a*S**)-2-(4-Chlorophenyl)-2-methyl-8-oxo-1,2,8,8a-tetrahydro-2a*H*-cyclobuta [*b*]chromene-2a-carbonitrile (3m)**



3m

According to the General Procedure 1, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and 4-chloro-α-methylstyrene (**2m**, 142.3 µL, 152.6 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **3m** as a colorless solid (11.0 mg, 34%).

R_f = 0.35 (EtOAc /heptane 1:3). **m.p.:** 143-146°C.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.89 (dd, *J* = 7.9, 1.8 Hz, 1 H, 7-H), 7.60 (ddd, *J* = 8.9, 7.3, 1.8 Hz, 1 H, 5-H), 7.40 (m_c, 2 H, Ar-H), 7.25 (m_c, 2 H, Ar-H), 7.15 (ddd, *J* = 7.9, 7.3, 1.0 Hz, 1 H,

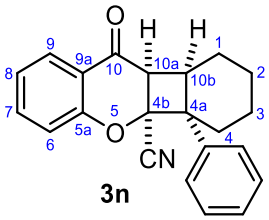
6-H), 7.10 (dd, *J* = 8.9, 1.0 Hz, 1 H, 4-H), 3.71 (dd, *J* = 10.2, 4.2 Hz, 1 H, 8a-H), 3.08 (dd, *J* = 12.2, 10.2 Hz, 1 H, 1 H, 1-H), 2.69 (dd, *J* = 12.2, 4.2 Hz, 1 H, 1 H, 1-H), 1.48 (s, 3 H CH_3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 190.4 (C-8), 159.5 (C-3a), 142.3 (Ar), 137.4 (C-5), 133.7 (Ar), 129.3 (Ar), 127.2 (C-7), 126.7 (Ar), 123.1 (C-6), 119.0 (C-7a), 118.0 (C-4), 117.8 (CN), 79.1 (C-2a), 54.8 (C-2), 43.5 (C-8a), 33.5 (C-1), 25.3 (CH_3) ppm.

IR: $\tilde{\nu}$ = 2980, 2940, 1690, 1610, 1310, 1090, 820, 755, 505 cm^{-1}.

Elemental analysis: $C_{19}H_{14}ClNO_2$, calc.: C 70.48, H 4.36, N 4.33, found: C 70.28, H 5.00, N 4.37.

(4a*R,4b*S**,10a*S**,10b*R**)-10-Oxo-4a-phenyl-1,2,3,4,4a,10,10a,10b-octahydro-4b*H*-benzo[3,4]cyclobuta[1,2-*b*]chromene-4b-carbonitrile (3n)**



3n

According to the General Procedure 1, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and 1-phenyl-1-cyclohexene (**2n**, 159.5 µL, 158.2 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **3n** as a colorless solid (21.7 mg, 66%).

R_f = 0.40 (EtOAc /heptane 1:3). **m.p.:** 128-130 °C.

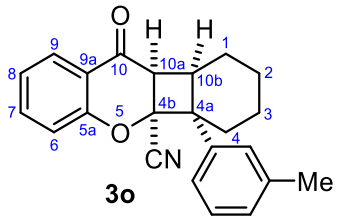
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.88 (dd, *J* = 7.8, 1.7 Hz, 1 H, 9-H), 7.45 (ddd, *J* = 9.0, 7.3, 1.7 Hz, 1 H, 7-H), 7.40 (m_c, 2 H, Ar-H), 7.33-7.27 (m, 3 H, Ar-H), 7.10 (m_c, 1 H, 8-H), 6.87 (dd, *J* = 8.4, 0.7 Hz, 1 H, 6-H), 3.62 (d, *J* = 10.8 Hz, 1 H, 10a-H), 3.46 (dd, *J* = 10.8, 5.6 Hz, 1 H, 10b-H), 2.24 (dt, *J* = 14.1, 3.5 Hz, 1 H, 4-H), 2.14 (td, *J* = 13.1, 3.5 Hz, 1 H, 4-H), 2.02 (m_c, 1 H, 1-H), 1.95-1.82 (m, 2 H, 1-H, 2-H), 1.70-1.55 (m, 2 H, 2-H, 3-H), 1.16 (m_c, 1 H, 3-H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 189.0 (C-10), 159.3 (C-5a), 141.1 (Ar), 136.7 (C-7), 128.5 (Ar), 127.2 (C-9), 127.2 (Ar), 126.7 (Ar), 123.6 (C-8), 120.1 (C-9a), 118.9 (C-6), 116.8 (CN), 77.3 (C-4b), 53.1 (C-4a), 44.9 (C-10a), 40.0 (C-10b), 34.9 (C-4), 24.4 (C-1), 21.0 (C-2), 20.0 (C-3) ppm.

IR: $\tilde{\nu}$ = 2940, 2860, 1690, 1450, 1300, 1115, 760, 705, 540 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{22}H_{20}NO_2^+$ $[M+H]^+$: 330.1494, found: 330.1493.

(4a*R,4b*S**,10a*S**,10b*R**)-10-Oxo-4a-(*m*-tolyl)-1,2,3,4,4a,10,10a,10b-octahydro-4b*H*-benzo[3,4]cyclobuta[1,2-*b*]chromene-4b-carbonitrile (3o)**



According to the General Procedure 1, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and 3'-methyl-2,3,4,5-tetrahydro-1,1'-biphenyl (**2o**, 172.3 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **3o** as a pale yellow solid (16.9 mg, 49%).

R_f = 0.41 (EtOAc /heptane 1:3). **m.p.:** 127-129 °C.

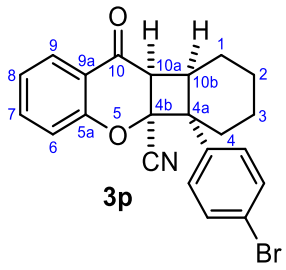
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.88 (dd, *J* = 7.8, 1.8 Hz, 1 H, 9-H), 7.45 (ddd, *J* = 9.0, 7.3, 1.8 Hz, 1 H, 7-H), 7.27 (t, *J* = 7.5 Hz, 1 H, Ar-H), 7.09 (m_c, 4 H, Ar-H, 8-H), 6.89 (d, *J* = 9.0 Hz, 1 H, 6-H), 3.61 (d, *J* = 10.3 Hz, 1 H, 10a-H), 3.45 (dd, *J* = 10.3, 5.5 Hz, 1 H, 10b-H), 2.39 (s, 3 H, CH_3), 2.23 (dt, *J* = 14.0, 3.3 Hz 1 H, 4-H), 2.12 (td, *J* = 14.0, 3.1 Hz, 1 H, 4-H), 2.03-1.98 (m, 1 H, 1-H), 1.93-1.81 (m, 2 H,1-H, 2-H), 1.68-1.59 (m, 2-H, 3-H), 1.16 (m_c, 3-H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 189.1 (C-10), 159.3 (C-5a), 141.1 (Ar), 138.1 (Ar), 136.7 (C-7), 128.4 (Ar), 128.0 (Ar), 127.3 (Ar), 127.2 (C-9), 123.9 (Ar), 123.6 (C-8), 120.1 (C-9a), 119.0 (C-6), 116.8 (CN), 77.3 (C-4b), 53.0 (C-4a), 45.0 (C-10a), 40.0 (C-10b), 34.9 (C-4), 24.4 (C-1), 21.8 (CH_3), 21.1 (C-2), 20.0 (C-3) ppm.

IR: $\tilde{\nu}$ = 2940, 2860, 1690, 1610, 1460, 1305, 1110, 760, 710, 540 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{23}H_{22}NO_2^+$ $[M+H]^+$: 344.1650, found: 344.1646.

(4a*R,4b*S**,10aS*,10b*R**)-4a-(4-Bromophenyl)-10-oxo-1,2,3,4,4a,10,10a,10b-octahydro-4b*H*-benzo[3,4]cyclobuta[1,2-*b*]chromene-4b-carbonitrile (3p)**



According to the General Procedure 1, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and 4'-bromo-2,3,4,5-tetrahydro-1,1'-biphenyl (**2p**, 237.1 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **3p** as a colorless solid (28.2 mg, 69%).

R_f = 0.40 (EtOAc /heptane 1:3). **m.p.:** 136-138 °C.

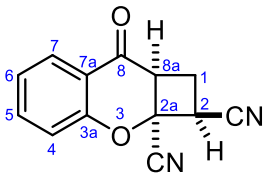
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.88 (dd, *J* = 7.9, 1.8 Hz, 1 H, 9-H), 7.52 (m_c, 2 H, Ar-H), 7.47 (ddd, *J* = 9.0, 7.3, 1.8 Hz, 1 H, 7-H), 7.15 (m, 2 H, Ar-H), 7.11 (ddd, *J* = 7.9, 7.3, 1.0 Hz, 1 H, 8-H), 6.88 (dd, *J* = 9.0, 1.0 Hz, 1 H, 6-H), 3.60 (d, *J* = 10.8 Hz, 1 H, 10a-H), 3.40 (dd, *J* = 10.8, 5.3 Hz, 1 H, 10b-H), 2.18 (dt, *J* = 13.9 , 3.5 Hz, 1 H, 4-H), 2.12 (td, *J* = 13.9, 3.2 Hz, 1 H, 4-H), 2.07-1.96 (m, 1 H, 1-H), 1.90-1.79 (m, 2 H, 1-H, 2-H), 1.70-1.59 (m, 2 H, 2-H, 3-H), 1.12 (m_c, 1 H, 3-H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 188.7 (C-10), 159.1 (C-5a), 140.2 (Ar), 136.8 (C-7), 131.7 (Ar), 128.5 (Ar), 127.2 (C-9), 123.8 (C-8), 121.3 (Ar), 120.0 (C-9a), 118.9 (C-6), 116.5 (CN), 77.1 (C-4b), 52.7 (C-4a), 44.8 (C-10a), 39.9 (C-10b), 34.7 (C-4), 24.3 (C-1), 20.9 (C-2), 19.9 (C-3) ppm.

IR: $\tilde{\nu}$ = 2940, 2865, 1690, 1610, 1460, 1310, 1115, 765, 740, 530 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{22}H_{19}BrNO_2^+$ $[M+H]^+$: 408.0599, found: 408.0595.

(2*S,2a*R**,8a*S**)-8-Oxo-1,2,8,8a-tetrahydro-2a*H*-cyclobuta[*b*]chromene-2,2a-dicarbo nitrile (5a)**



5a

According to the General Procedure 1, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (3.4 mg, 3.0 µmol, 3 mol-%) and acrylonitrile (**4a**, 66.0 µL, 54.0 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **5a** as a yellow solid (13.7 mg, 61%).

R_f = 0.38 (EtOAc /heptane 1:3). **m.p.:** 154-156 °C.

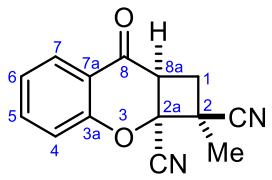
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 (dd, *J* = 7.8, 1.6 Hz, 1 H, 7-H), 7.67 (ddd, *J* = 8.3, 7.4, 1.6 Hz, 1 H, 5-H), 7.26 (m_c, 2 H, 6-H, 4-H), 3.87 (t, *J* = 9.1 Hz, 1 H, 2-H), 3.69 (t, *J* = 9.8 Hz, 1 H, 8a-H), 3.05 (ddd, *J* = 11.9, 9.8, 9.1 Hz, 1 H, 1-H), 2.94 (ddd, *J* = 11.9, 9.8, 9.1 Hz, 1 H, 1-H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 186.1 (C-8), 158.1 (C-3a), 137.8 (C-5), 127.6 (C-7), 124.9 (C-6), 119.8 (C-7a), 119.0 (C-4), 115.5 (CN), 113.9 (CN), 71.4 (C-2a), 44.6 (C-8a), 33.3 (C-2), 28.0 (C-1).

IR: $\tilde{\nu}$ = 2990, 1690, 1600, 1460, 1300, 755, 740cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{13}H_8N_2NaO_2^+$ $[M+Na]^+$: 247.0478, found: 247.0483.

(2*S,2a*S**,8a*S**)-2-Methyl-8-oxo-1,2,8,8a-tetrahydro-2a*H*-cyclobuta[*b*]chromene-2,2a-dicarbonitrile (5b)**



5b

According to the General Procedure 1, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and methacrylonitrile (**4b**, 84.0 µL, 68.0 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after 36 h reaction time and column chromatography (silica, EtOAc/heptane 1:3), compound **5b** as a colorless solid (23.5 mg, 99%).

R_f = 0.39 (EtOAc /heptane 1:3). **m.p.:** 152-154°C.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.91 (dd, *J* = 7.9, 1.8 Hz, 1 H, 7-H), 7.65 (ddd, *J* = 8.5, 7.3, 1.8 Hz, 1 H, 5-H), 7.24 (m_c, 2 H, 6-H, 4-H), 3.69 (dd, *J* = 10.2, 9.2 Hz, 1 H, 8a-H), 3.06 (dd, *J* = 12.2, 9.2 Hz, 1 H, 1-H), 2.67 (dd, *J* = 12.2, 10.2 Hz, 1 H, 1-H), 1.87 (s, 3 H, CH_3) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 186.7 (C-8), 158.1 (C-3a), 137.8 (C-5), 127.5 (C-7), 124.7 (C-6), 119.6 (C-7a), 118.9 (C-4), 117.5 (CN), 114.3 (CN), 76.1 (C-2a), 42.5 (C-8a), 40.4 (C-2), 34.6 (C-1), 21.7 (CH_3) ppm.

IR: $\tilde{\nu}$ = 2945, 2875, 1620, 1450, 1315, 1115, 760, 530 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{14}H_{11}N_2NaO_2^+$ $[M+Na]^+$: 261.0639, found: 261.0640.

5 Ir(III)-sensitized [2+2] and [3+2] photocycloadditions

General procedure 2

A 10 mL crimp cap vial was charged with 4-oxo-4*H*-chromene-2-carbonitrile **1** (1.0 equiv.) and (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3 mol-%) and the vial was sealed. Dry MeCN (5.00 mL) and alkene **2** (10.0 equiv., freshly distilled) were added via syringe and the reaction mixture was saturated with argon for 5 minutes (via cannula). The reaction mixture was stirred vigorously for 48 h, while irradiated with blue LEDs (34 W, λ_{em} = 450 nm, solution temperature 30 °C). The solvent was evaporated. The dry residue was dissolved in acetone (3.00 mL) and 1 M HCl aq. (1.00 mL) was added. The mixture was stirred overnight, then poured into $NaHCO_3$ (aq.) and the aqueous layer was extracted with Et_2O (3×). The organic phase was dried over $MgSO_4$, filtered and evaporated to dryness. Column chromatography provided the products **3** and/or **6**.

Modification:

Reactions that were run at 65 °C or -10 °C were conducted under identical conditions but using a setup consisting of a 10 W / 450 nm LED that was mounted on a glass fiber, which was immersed into the reaction mixture, inside a small glass tube (ø ca. 5 mm). The reaction vial was either heated in an oil bath or cooled in a cooling bath (*i*-PrOH and crygenerator), see Figure S2.

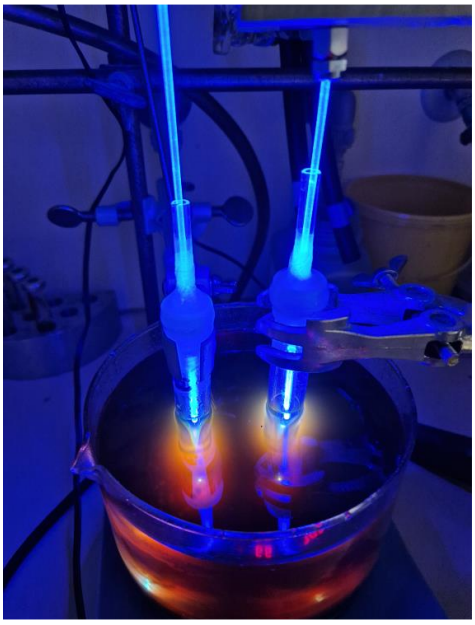
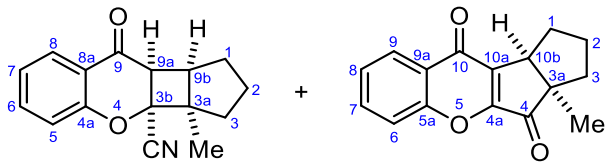


Figure S2. Irradiation setup for heated and cooled reactions, 450 nm / 10 W blue LED.

(3a*R,3b*S**,9a*S**,9b*R**)-3a-Methyl-9-oxo-2,3,3a,9,9a,9b-hexahydrocyclopenta[3,4]cyclobuta[1,2-*b*]chromene-3b(1*H*)-carbonitrile (3s)**

and

(3a*R,10b*S**)-3a-Methyl-2,3,3a,10b-tetrahydro-1*H*-pentaleno[2,1-*b*]chromene-4,10-dione (6s)**



3s **6s**

According to the General Procedure 2, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ (3.4 mg, 3.0 µmol, 3 mol-%) and 1-methyl-1-cyclopentene (**2s**, 105.3 µL 82.1 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after column chromatography (silica, EtOAc/heptane 1:3), compound **3s** as a brown solid (4.6 mg, 18%) and compound **6s** as a yellow solid (7.2 mg, 28%).

Analytical data for **3s**:

R$_f$ = 0.40 (EtOAc /heptane 1:3). **m.p.:** 131-133 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.86 (dd, *J* = 7.8, 1.7 Hz, 1 H, 8-H), 7.56 (ddd, *J* = 9.1, 7.4, 1.7 Hz, 1 H, 6-H), 7.13 (ddd, *J* = 7.8, 7.4, 1.0 Hz, 1 H, 7-H), 7.07 (dd, *J* = 9.1, 1.0 Hz, 1 H, 5-H), 3.11 (d, *J* = 6.6 Hz, 1 H, 9a-H), 2.72 (t, *J* = 6.6 Hz, 1 H, 9b-H), 2.31-2.24 (m, 1 H, 3-H), 2.06-1.97 (m, 2 H, 2-H), 1.97-1.88 (m, 1 H, 1-H), 1.85-1.74 (m, 1 H, 1-H), 1.69-1.60 (m, 1 H, 3-H), 1.30 (s, 3 H, CH_3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 189.5 (C-9), 159.1 (C-4a), 137.0 (C-6), 127.2 (C-8), 123.3 (C-7), 119.8 (C-8a), 118.5 (C-5), 116.7 (CN), 76.4 (C-3b), 54.4 (C-3a), 49.9 (C-9b), 47.7 (C-9a), 38.0 (C-3), 32.2 (C-1), 25.7 (C-2), 19.6 (CH_3) ppm.

IR: $\tilde{\nu}$ = 2960, 1680, 1610, 1450, 1315, 1020, 760 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{16}H_{16}NO_2^+$ $[M+H]^+$: 254.1181, found: 254.1181.

Analytical data for **6s**:

R$_f$ = 0.38 (EtOAc /heptane 1:3). **m.p.:** 118-121 °C.

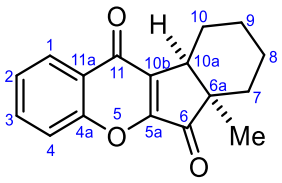
^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.27 (dd, *J* = 8.0, 1.7 Hz, 1 H, 9-H), 7.75 (ddd, *J* = 8.5, 7.1, 1.7 Hz, 1 H, 7-H), 7.63 (dd, *J* = 8.5, 1.0 Hz, 1 H, 6-H), 7.47 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1 H, 8-H), 3.32 (dd, *J* = 8.7, 2.4 Hz, 1 H, 10b-H), 2.11-2.06 (m, 1 H, 3-H), 2.06-2.02 (m, 1 H, 1-H), 2.01-1.95 (m, 1 H, 1-H), 1.76-1.68 (m, 1 H, 2-H), 1.57-1.49 (m, 1 H, 3-H), 1.36 (s, 3 H, CH_3), 1.33-1.24 (m, 1 H, 2-H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 206.9 (C-4), 178.1 (C-10), 156.4 (C-4a), 156.4 (C-5a), 141.3 (C-10a), 135.1 (C-7), 126.3 (C-9), 125.9 (C-8), 125.4 (C-9a), 119.4 (C-6), 55.3 (C-3a), 46.3 (C-10b), 38.2 (C-3), 29.1 (C-1), 25.4 (C-2), 22.5 (CH_3) ppm.

IR: $\tilde{\nu}$ = 2960, 2870, 1715, 1650, 1460, 1060, 760, 695 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{16}H_{15}O_3^+$ [M+H]$^+$: 255.1021, found: 255.1021.

(6a*R,10a*S**)-6a-Methyl-6a,7,8,9,10,10a-hexahydroindeno[2,1-*b*]chromene-6,11-dione (6t)**



6t

According to the General Procedure 2, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ (3.4 mg, 3.0 µmol, 3 mol-%) and 1-methyl-1-cyclohexene (**2t**, 118.6 µL 96.2 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after column chromatography (silica, EtOAc/heptane 1:3), compound **6t** as a yellow solid (12.1 mg, 44%).

R$_f$ = 0.40 (EtOAc /heptane 1:3). **m.p.:** 103-105 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.26 (dd, *J* = 8.0, 1.6 Hz, 1 H, 1-H), 7.75 (ddd, *J* = 8.8, 7.1, 1.6 Hz, 1 H, 3-H), 7.63 (dd, *J* = 8.8, 1.0 Hz, 1 H, 4-H), 7.47 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1 H, 2-H), 3.11 (t, *J* = 6.2 Hz, 1 H, 10a-H), 2.21-2.12 (m, 1 H, 10-H), 1.94-1.82 (m, 2 H, 10-H, 7-H), 1.63-1.54 (m, 2 H, 7-H, 8-H), 1.54-1.46 (m, 1 H, 8-H), 1.41-1.31 (m, 2 H, 9-H), 1.25 (s, 3 H, CH_3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 206.3 (C-6), 178.2 (C-11), 156.4 (C-5a), 156.3 (C-4a), 141.4 (C-10b), 135.0 (C-3), 126.3 (C-1), 125.9 (C-2), 125.4 (C-11a), 119.3 (C-4), 47.8 (C-6a), 42.0 (C-10a), 30.6 (C-7), 25.1 (C-10), 24.5 (CH_3), 19.5 (C-8), 19.5 (C-9) ppm.

IR: $\tilde{\nu}$ = 2940, 2870, 1720, 1650, 1465, 1290, 1070,760, 695 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{17}H_{17}O_3^+$ [M+H]$^+$: 269.1178, found: 269.1177.

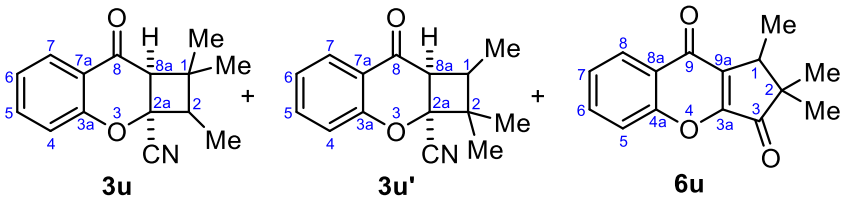
(2a*R,8a*S**)-1,1,2-Trimethyl-8-oxo-1,2,8,8a-tetrahydro-2a*H*-cyclobuta[*b*]chromene-2a-carbonitrile (3u)**

and

(2a*S,8a*S**)-1,2,2-Trimethyl-8-oxo-1,2,8,8a-tetrahydro-2a*H*-cyclobuta[*b*]chromene-2a-carbonitrile (3u')**

and

1,2,2-Trimethyl-1,2-dihydrocyclopenta[*b*]chromene-3,9-dione (6u)



3u **3u'** **6u**

According to the General Procedure 2, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and 2-methyl-2-butene (**2u**, 106.0 µL 70.1 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after column chromatography (silica, EtOAc/heptane 1:3), compounds **3u** and **3u'** as a colorless oil (1.9 mg, 8%, inseparable mixture of isomers) and compound compound **6u** as a pale yellow oil (5.8 mg, 24%).

Analytical data for **3u**/**3u'**:

R_f = 0.40 (EtOAc /heptane 1:3).

The complicated NMR spectrum did not allow for peak assignments.

HRMS (EI): *m/z* calc.: $C_{15}H_{15}NO_2^+$ $[M]^+$: 241.1097, found: 241.1096.

Analytical data for **6u**:

R_f = 0.38 (EtOAc /heptane 1:3).

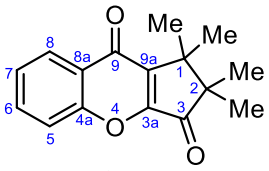
^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.26 (dd, *J* = 8.1, 1.7 Hz, 1 H, 8-H), 7.75 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1 H, 6-H), 7.62 (dd, *J* = 8.7, 1.0 Hz, 1 H, 5-H), 7.47 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1 H, 7-H), 3.14 (q, *J* = 7.2 Hz, 1 H, 1-H), 1.38 (d, *J* = 7.2 Hz, 1 H, CH_3), 1.26 (s, 3 H, CH_3), 1.19 (s, 3 H, CH_3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 206.3 (C-3), 178.2 (C-9), 156.3 (C-4a), 155.5 (C-3a), 142.1 (C-9a), 135.0 (C-6), 126.2 (C-8), 125.9 (C-7), 125.5 (C-8a), 119.3 (C-5), 47.4 (C-2), 40.6 (C-1), 26.8 (CH_3), 19.9 (CH_3), 14.9 (CH_3) ppm.

IR: $\tilde{\nu}$ = 2970, 2860, 1720, 1655, 1455, 1010, 760 cm^{-1}.

HRMS (ESI+): *m/z* calc.: $C_{15}H_{15}O_3^+$ $[M+H]^+$: 243.1021, found: 243.1017.

1,1,2,2-Tetramethyl-1,2-dihydrocyclopenta[*b*]chromene-3,9-dione (6v)



6v

According to the General Procedure, 2, 4-oxo-4*H*-chromene-2-carbonitrile (**1**, 17.1 mg, 0.10 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (3.4 mg, 3.0 µmol, 3 mol-%) and 2,3-dimethyl-2-butene (**2v**, 119.0 µL 84.2 mg, 1.00 mmol) in MeCN (5.00 mL) gave, after column chromatography (silica, EtOAc/heptane 1:3), compound **6v** as a colorless oil (10.5 mg, 41%).

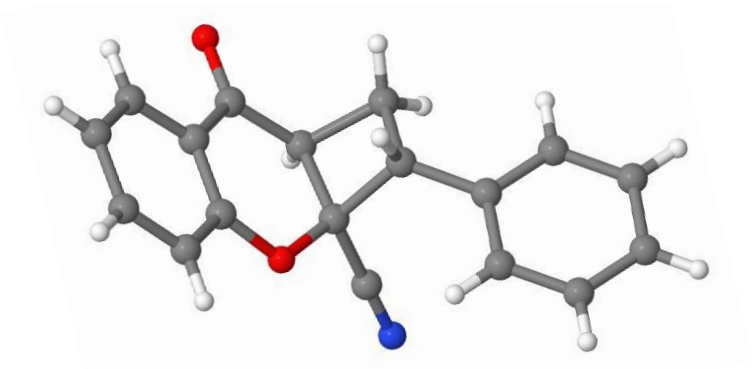
R_f = 0.38 (EtOAc /heptane 1:3).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.24 (dd, *J* = 8.0, 1.7 Hz, 1 H, 8-H), 7.73 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1 H, 6-H), 7.61 (dd, *J* = 8.6, 0.9 Hz, 1 H, 5-H), 7.46 (ddd, *J* = 8.0, 7.1, 0.9 Hz, 1 H, 7-H), 1.43 (s, 6 H, CH_3), 1.18 (s, 6 H, CH_3) ppm.

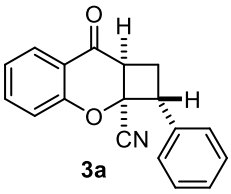
^{13}C NMR (126 MHz, $CDCl_3$) δ = 206.3 (C-3), 177.9 (C-9), 156.0 (C-4a), 155.3 (C-3a), 144.0 (C-9a), 134.9 (C-6), 126.3 (C-8), 125.9 (C-7), 125.8 (C-8a), 119.2 (C-5), 51.9 (C-2), 43.1 (C-1), 23.8 (2× CH_3), 21.8 (2× CH_3) ppm.

HRMS (ESI+): *m/z* calc.: $C_{16}H_{17}O_3^+$ $[M+H]^+$: 257.1178, found: 257.1180.

6 X-Ray crystal structures

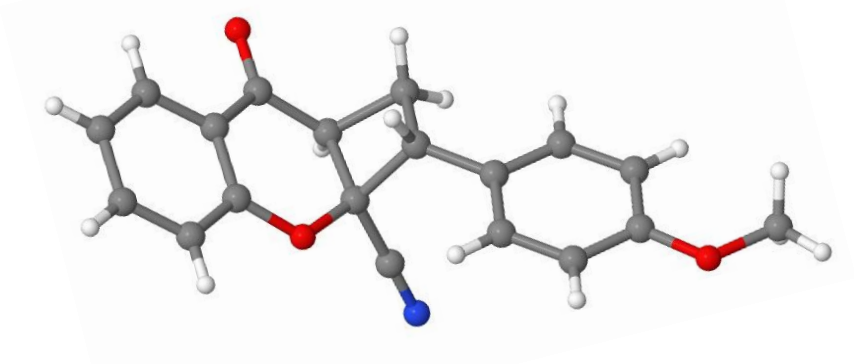


Crystal data	
Unit cell lengths (Å)	9.931 11.526 31.731
Unit cell angles (deg)	90.580 92.359 109.744
Space group Hall symbol	-P 1
Space group HM symbol	P -1
Crystal class	Triclinic
International tables #	2
Space group multiplicity	2

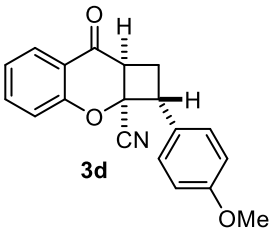


3a

Figure S3. X-Ray crystal structure of compound **3a**, CCDC No. 2250461. The crystal structure data can be retrieved from the Cambridge Crystallographic Data Centre, www.ccdc.cam.ac.uk.

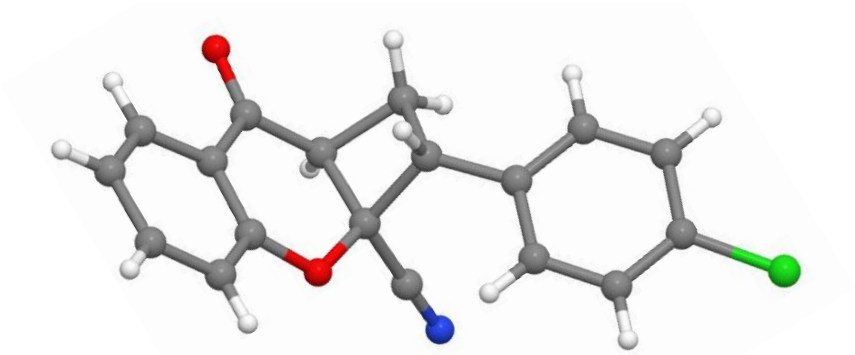


Crystal data	
Unit cell lengths (Å)	14.645 6.393 17.586
Unit cell angles (deg)	90.000 112.361 90.000
Space group Hall symbol	-P 2yn
Space group HM symbol	P 1 21/n 1
Crystal class	Monoclinic
International tables #	14
Space group multiplicity	4



3d

Figure S4. X-Ray crystal structure of compound **3d**, CCDC No. 2250462. The crystal structure data can be retrieved from the Cambridge Crystallographic Data Centre, www.ccdc.cam.ac.uk.



Crystal data	
Unit cell lengths (Å)	8.063 9.882 10.105
Unit cell angles (deg)	114.137 98.043 97.708
Space group Hall symbol	-P 1
Space group HM symbol	P -1
Crystal class	Triclinic
International tables #	2
Space group multiplicity	2

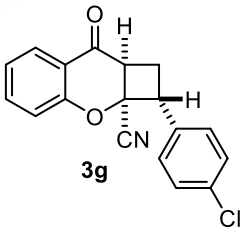
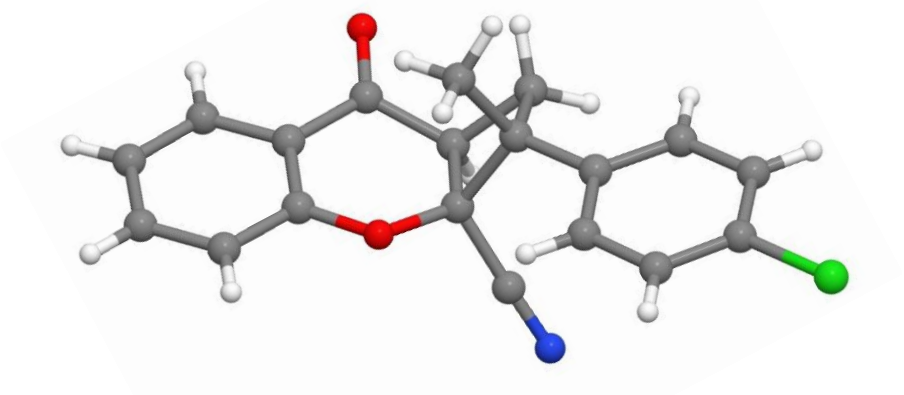


Figure S5. X-Ray crystal structure of compound **3g**, CCDC No. 2250463. The crystal structure data can be retrieved from the Cambridge Crystallographic Data Centre, www.ccdc.cam.ac.uk.



Crystal data	
Unit cell lengths (Å)	9.497 10.788 15.316
Unit cell angles (deg)	90.000 104.883 90.000
Space group Hall symbol	-P 2yn
Space group HM symbol	P 1 21/n 1
Crystal class	Monoclinic
International tables #	14
Space group multiplicity	4

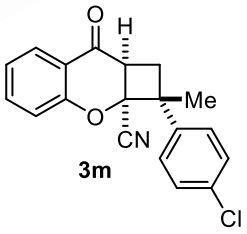
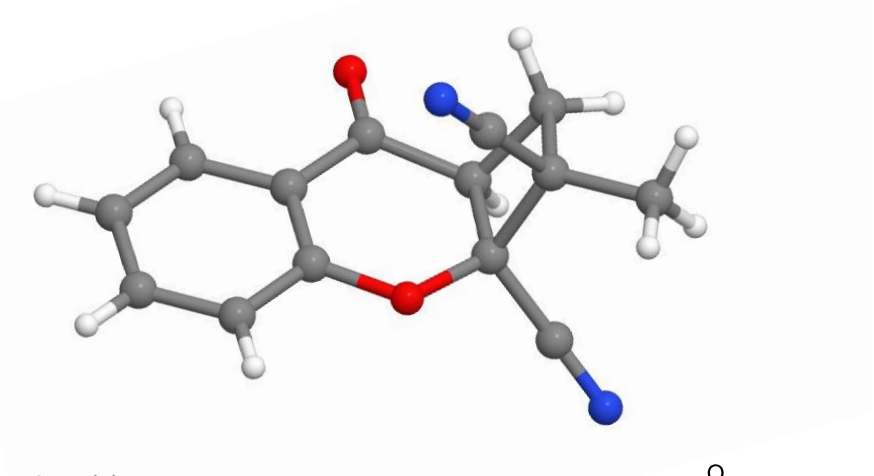
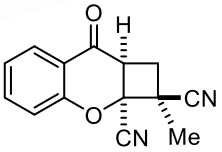


Figure S6. X-Ray crystal structure of compound **3m**, CCDC No. 2250464. The crystal structure data can be retrieved from the Cambridge Crystallographic Data Centre, www.ccdc.cam.ac.uk.



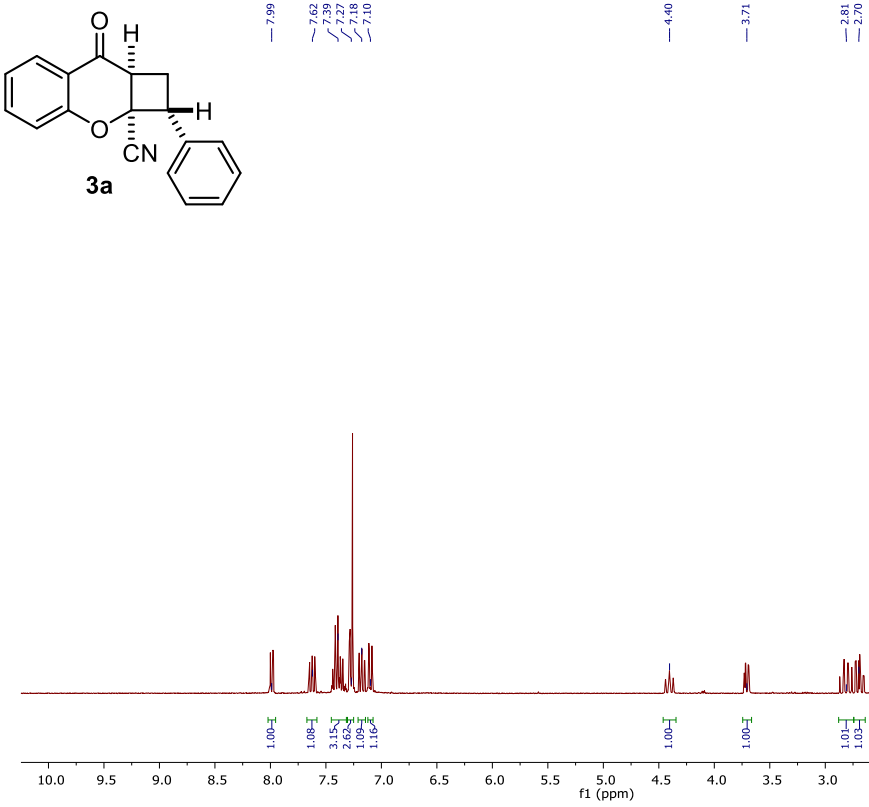
Crystal data			
Unit cell lengths (Å)	10.255	6.279	18.091
Unit cell angles (deg)	90.000	100.081	90.000
Space group Hall symbol	-P 2yn		
Space group HM symbol	P 1 21/n 1		
Crystal class	Monoclinic		
International tables #	14		
Space group multiplicity	4		



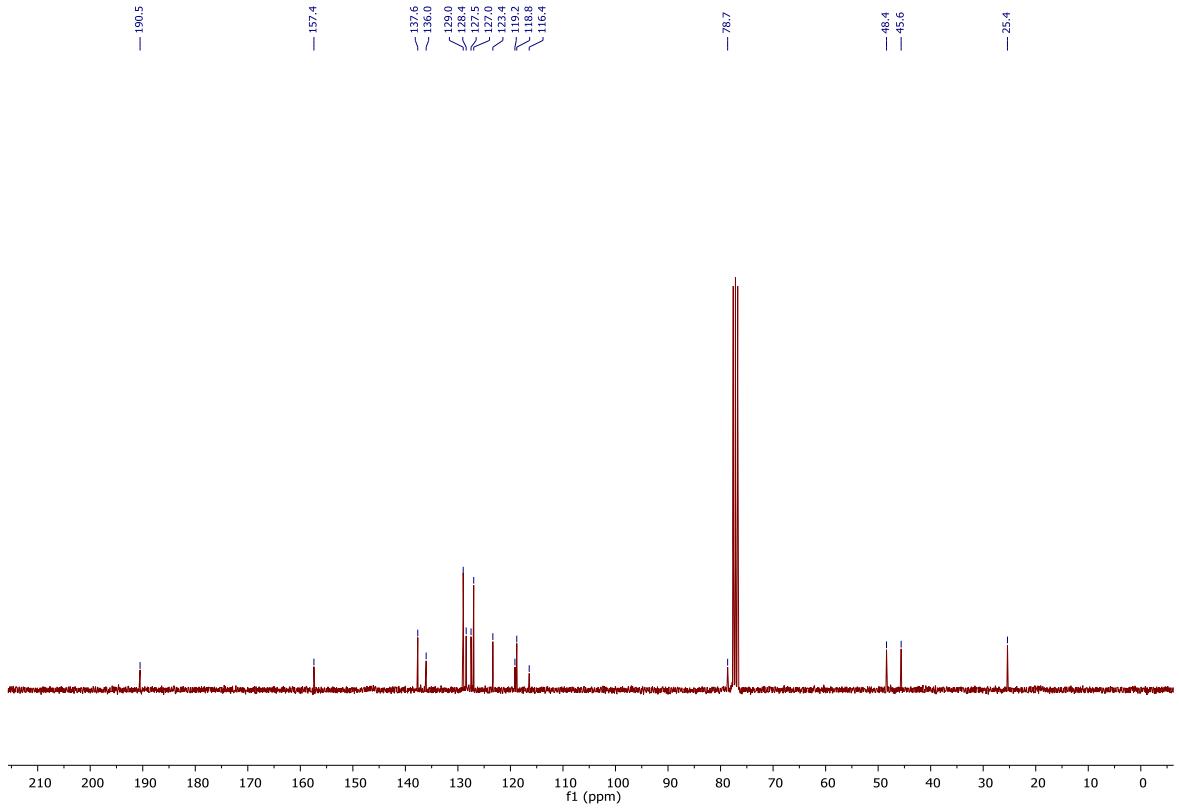
5b

Figure S7. X-Ray crystal structure of compound **5b**, CCDC No. 2250465. The crystal structure data can be retrieved from the Cambridge Crystallographic Data Centre, www.ccdc.cam.ac.uk.

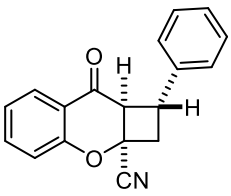
7 NMR spectra



^{1}H-NMR (300 MHz, $CDCl_3$)

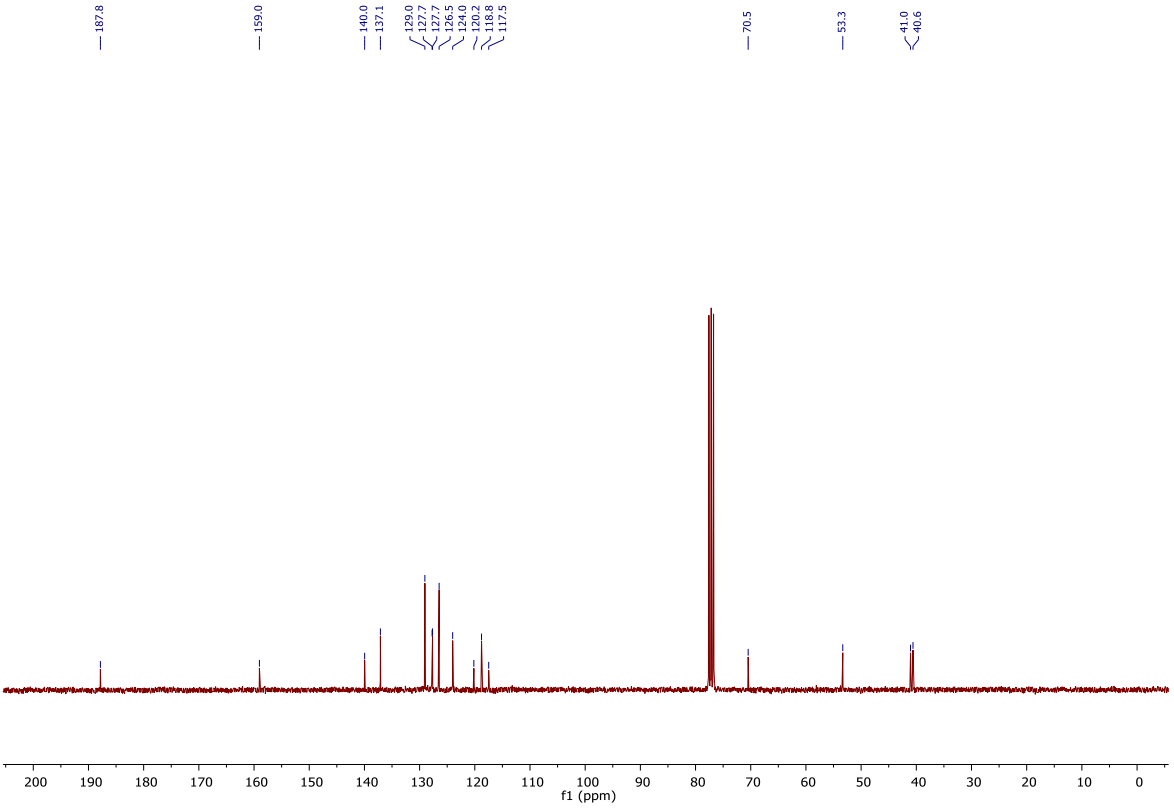


^{13}C-NMR (75 MHz, $CDCl_3$)

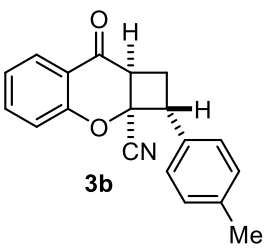


3a'

^{1}H-NMR (500 MHz, $CDCl_3$)

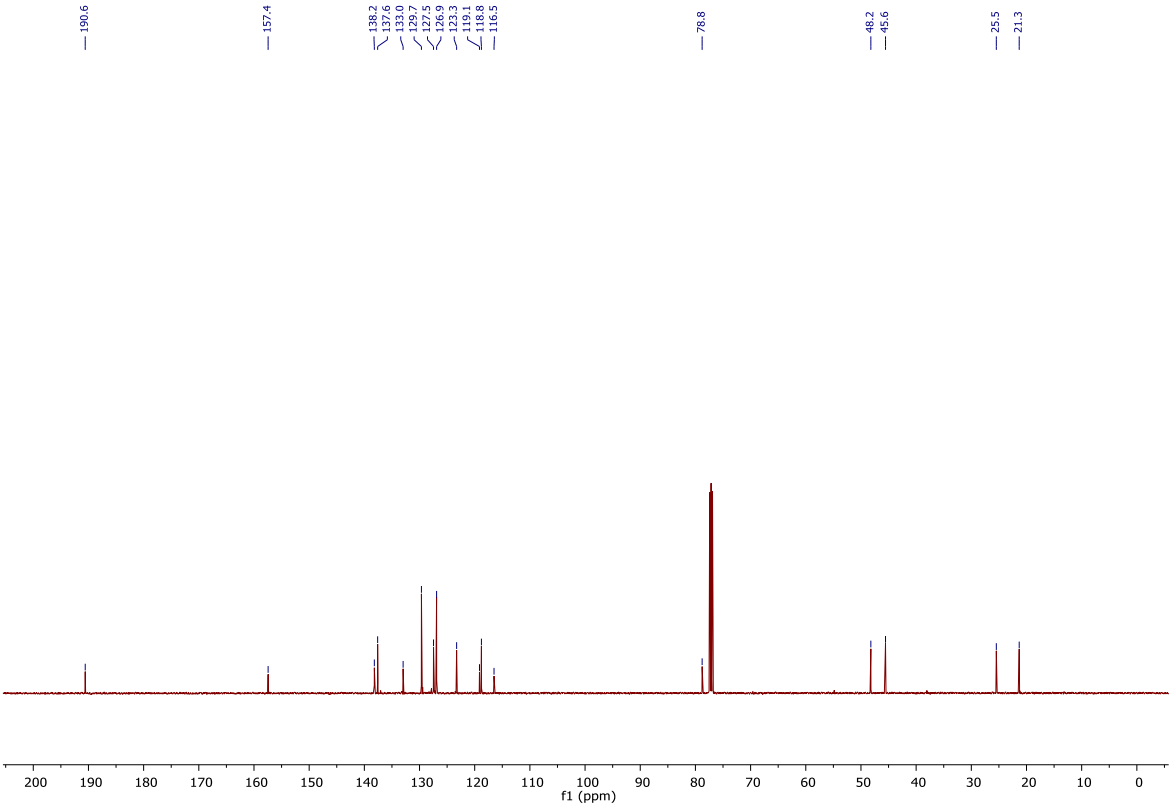


^{13}C-NMR (75 MHz, $CDCl_3$)

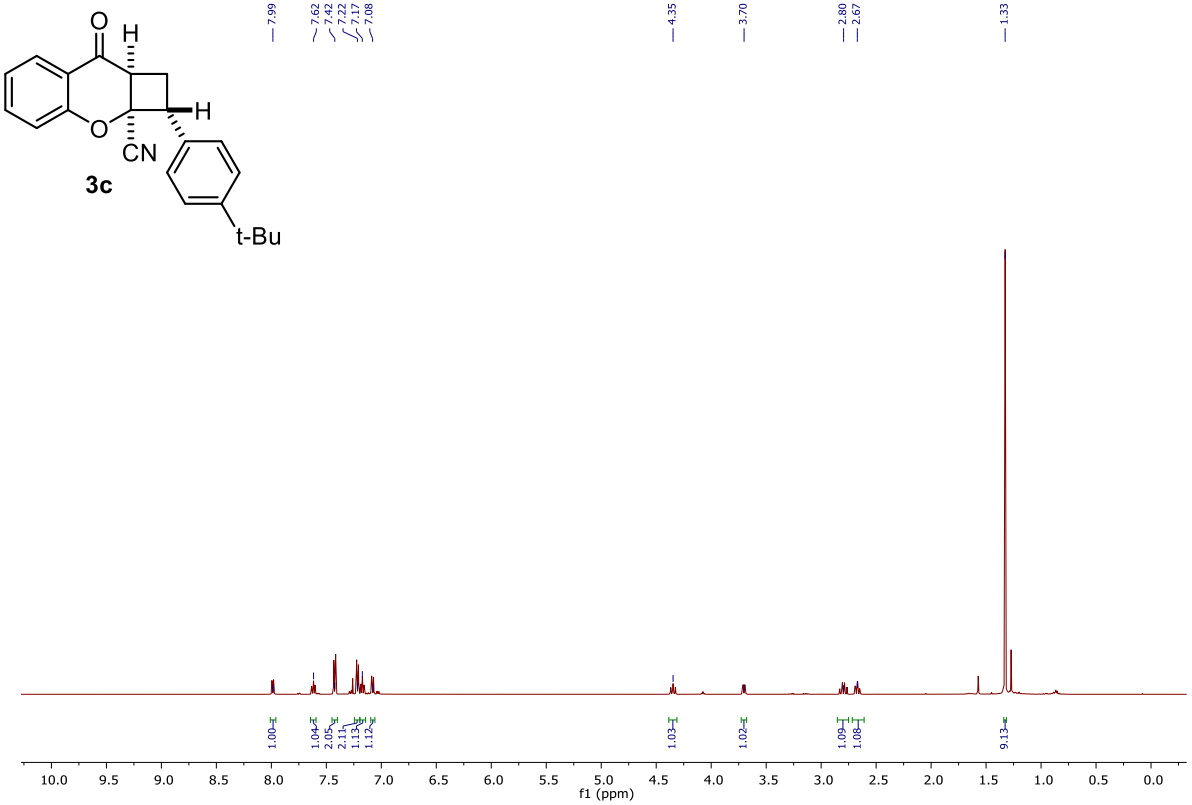


3b

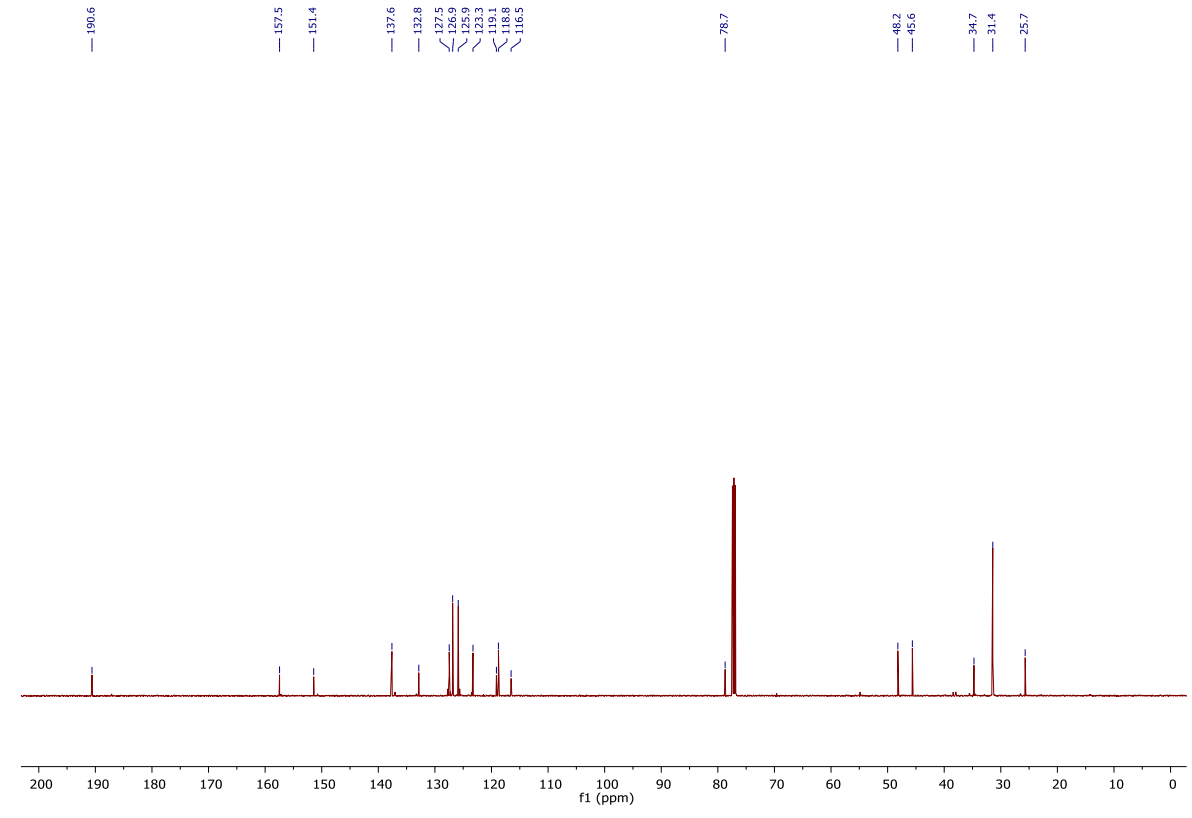
^{1}H-NMR (500 MHz, $CDCl_3$)



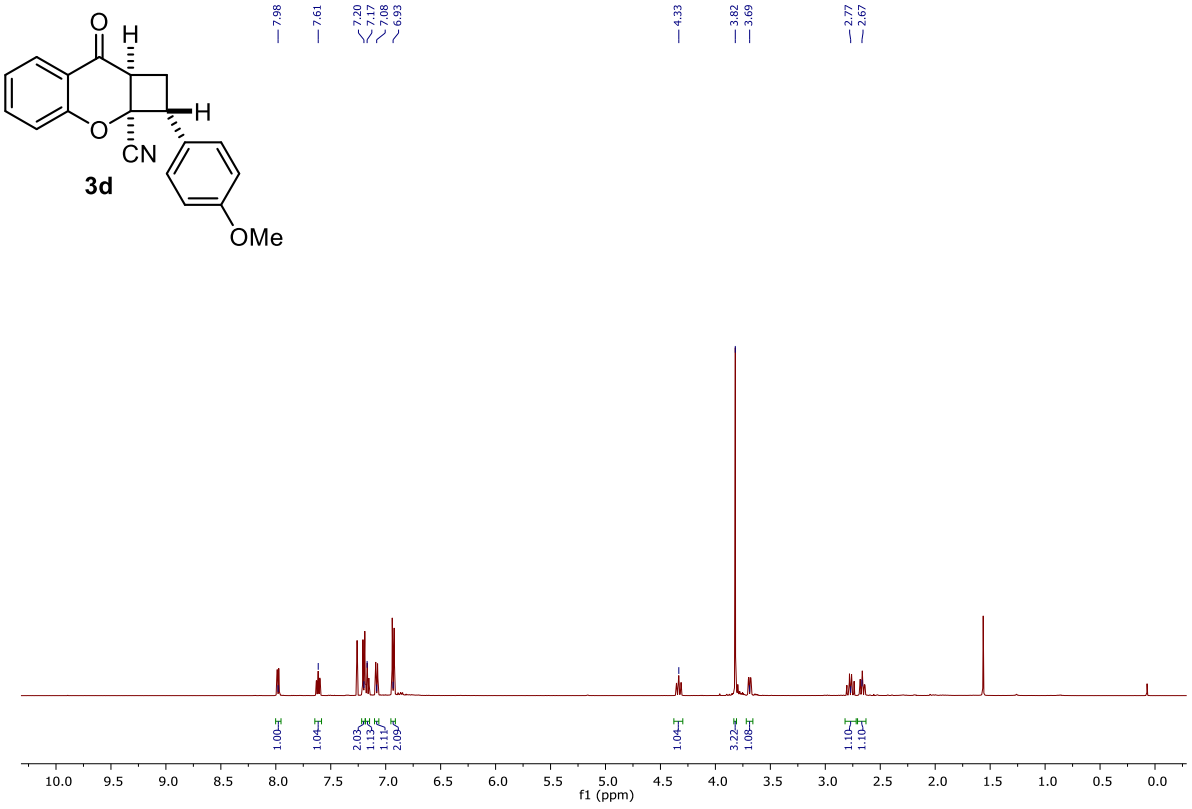
^{13}C-NMR (126 MHz, $CDCl_3$)



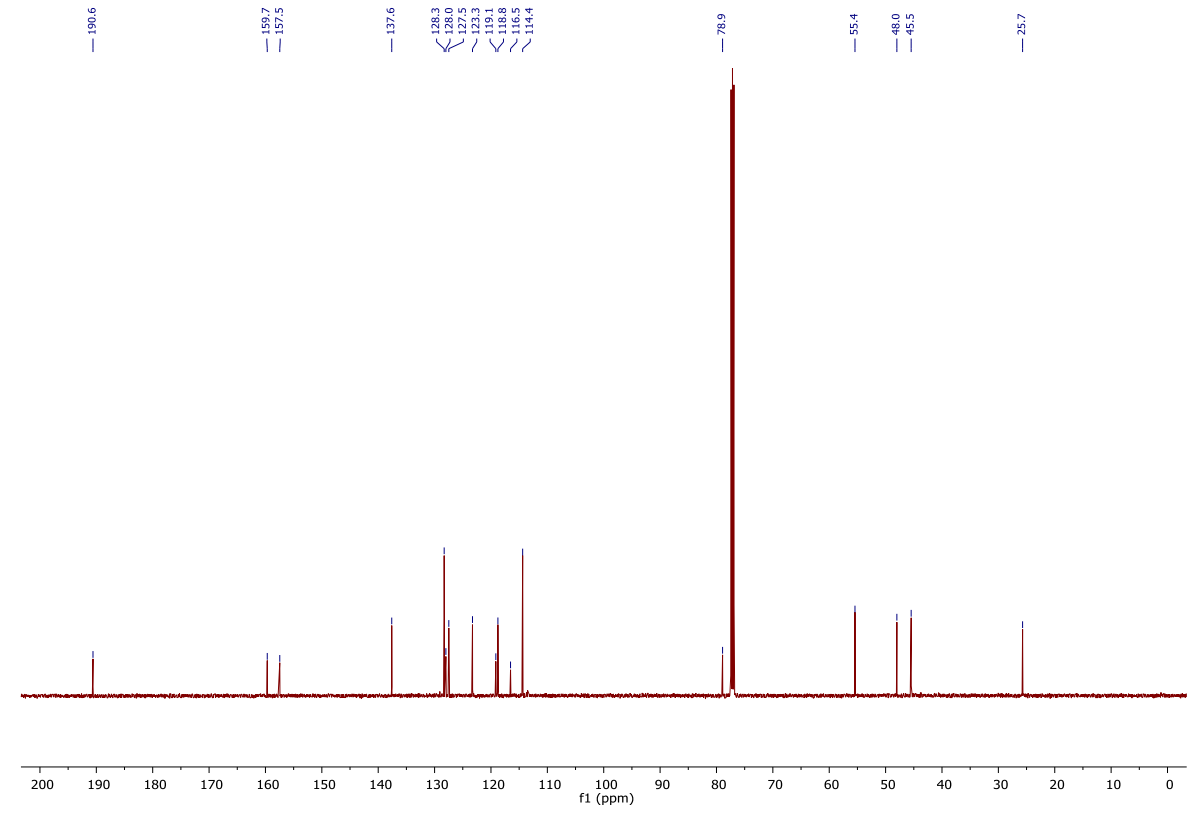
^{1}H-NMR (500 MHz, $CDCl_3$)



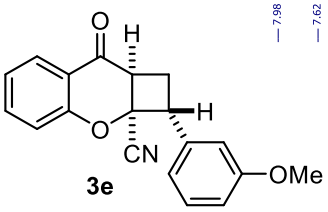
^{13}C-NMR (126 MHz, $CDCl_3$)



^{1}H-NMR (500 MHz, $CDCl_3$)

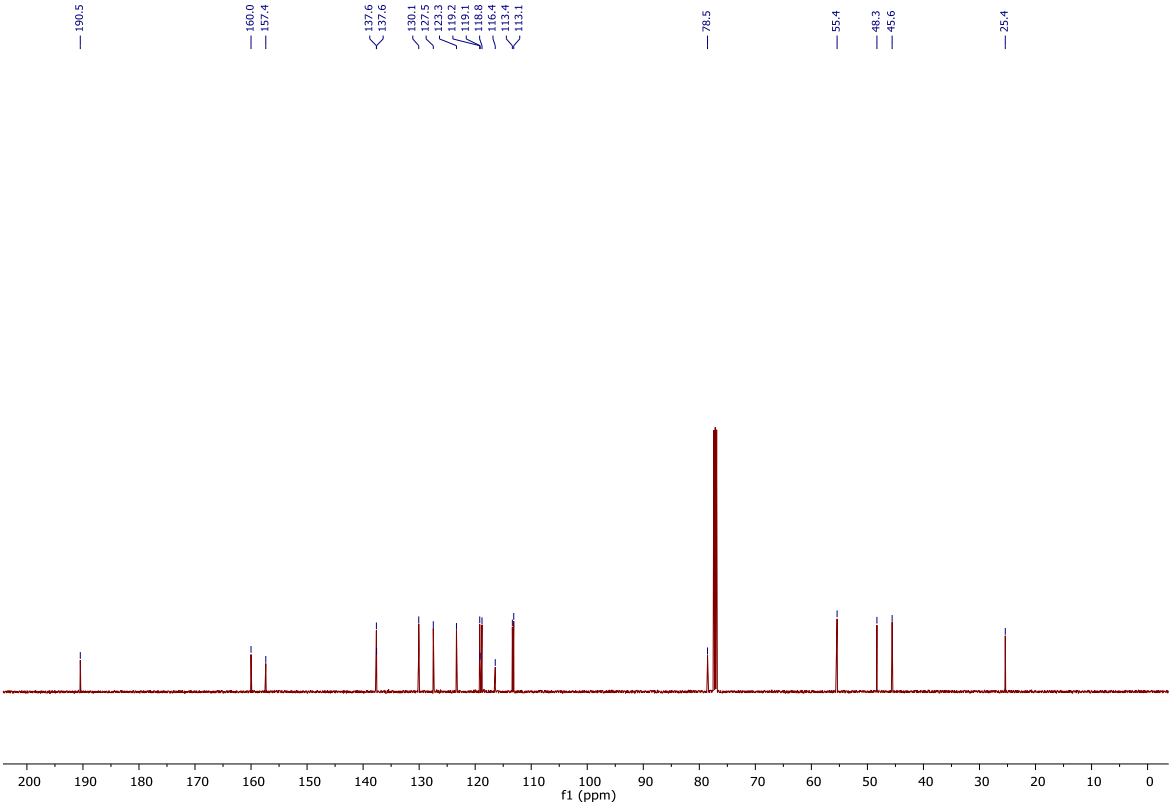


^{13}C-NMR (126 MHz, $CDCl_3$)

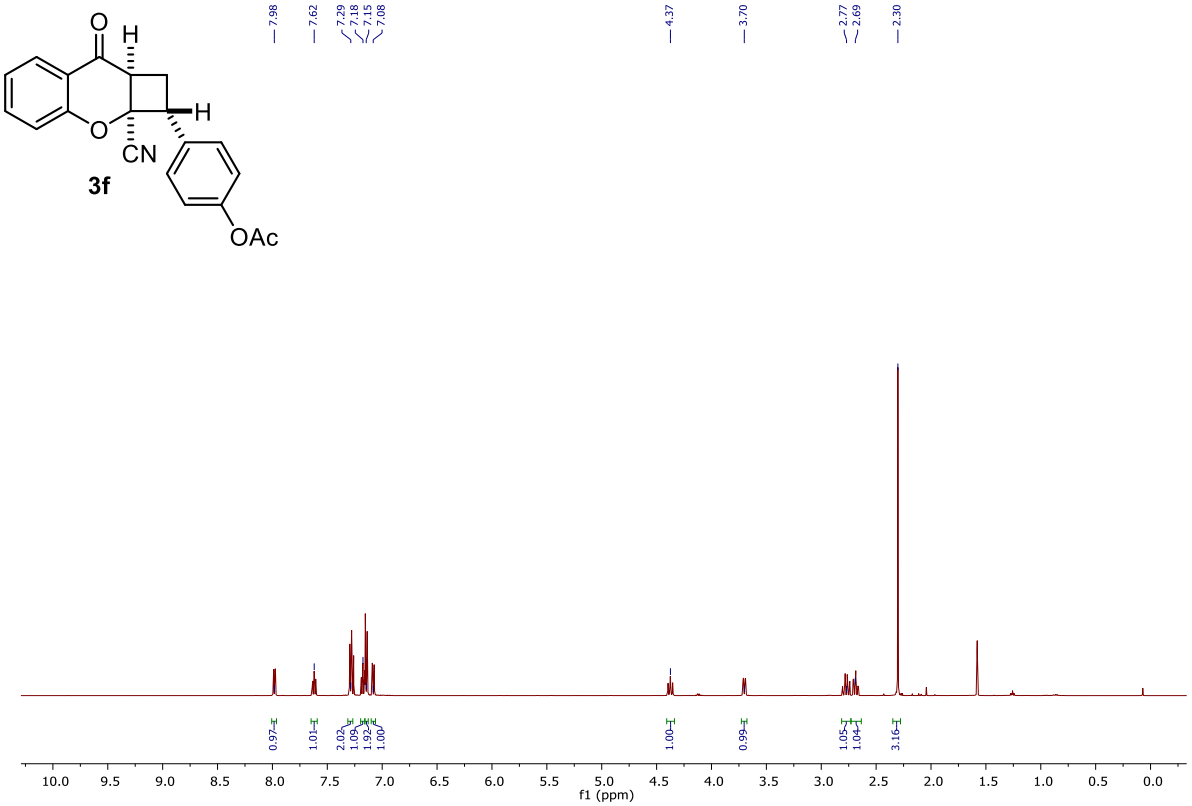


3e

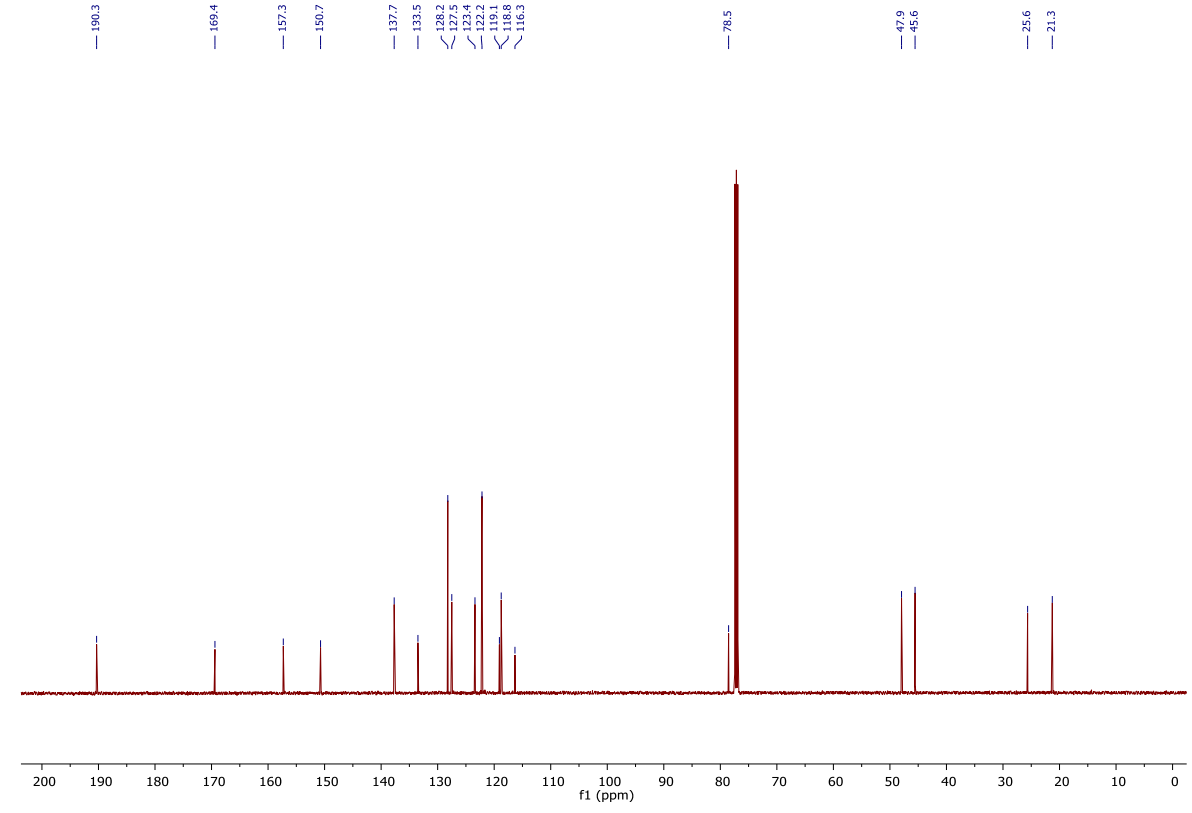
^{1}H-NMR (500 MHz, $CDCl_3$)



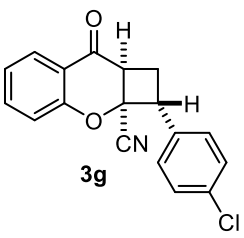
^{13}C-NMR (126 MHz, $CDCl_3$)



^{1}H-NMR (500 MHz, $CDCl_3$)

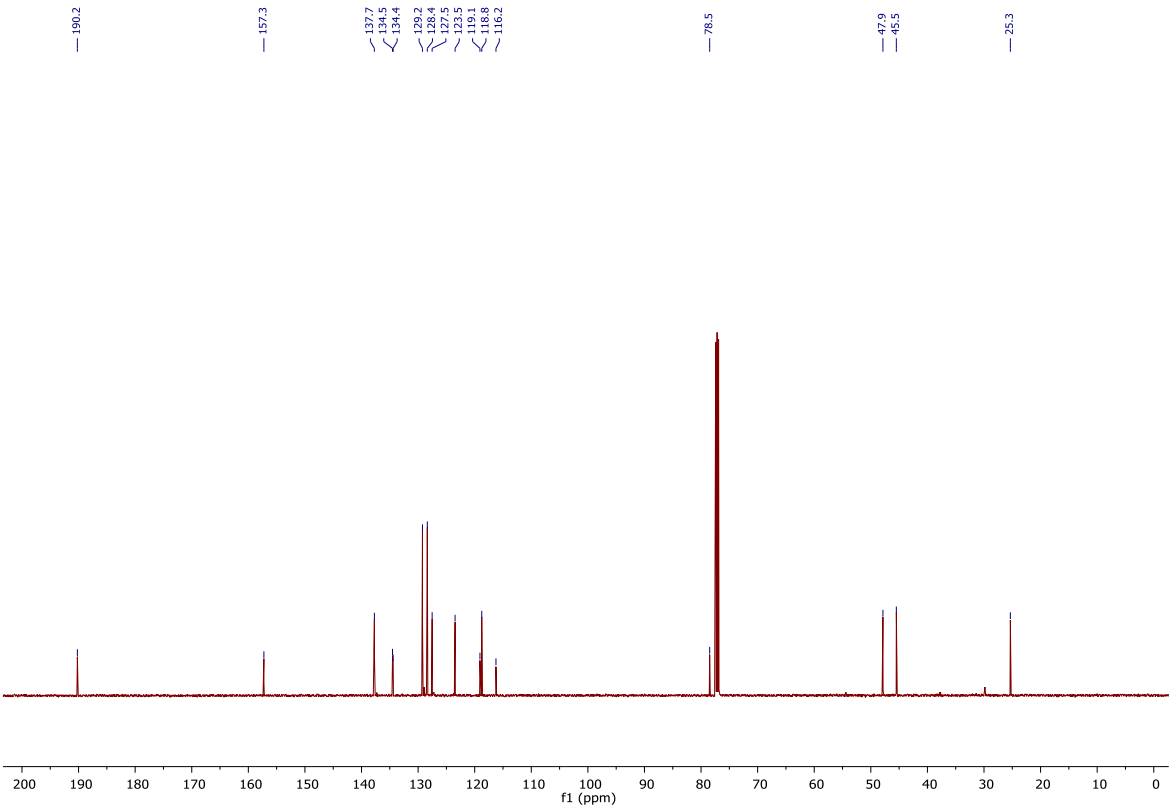


^{13}C-NMR (126 MHz, $CDCl_3$)

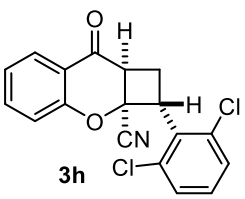


3g

^{1}H-NMR (500 MHz, $CDCl_3$)

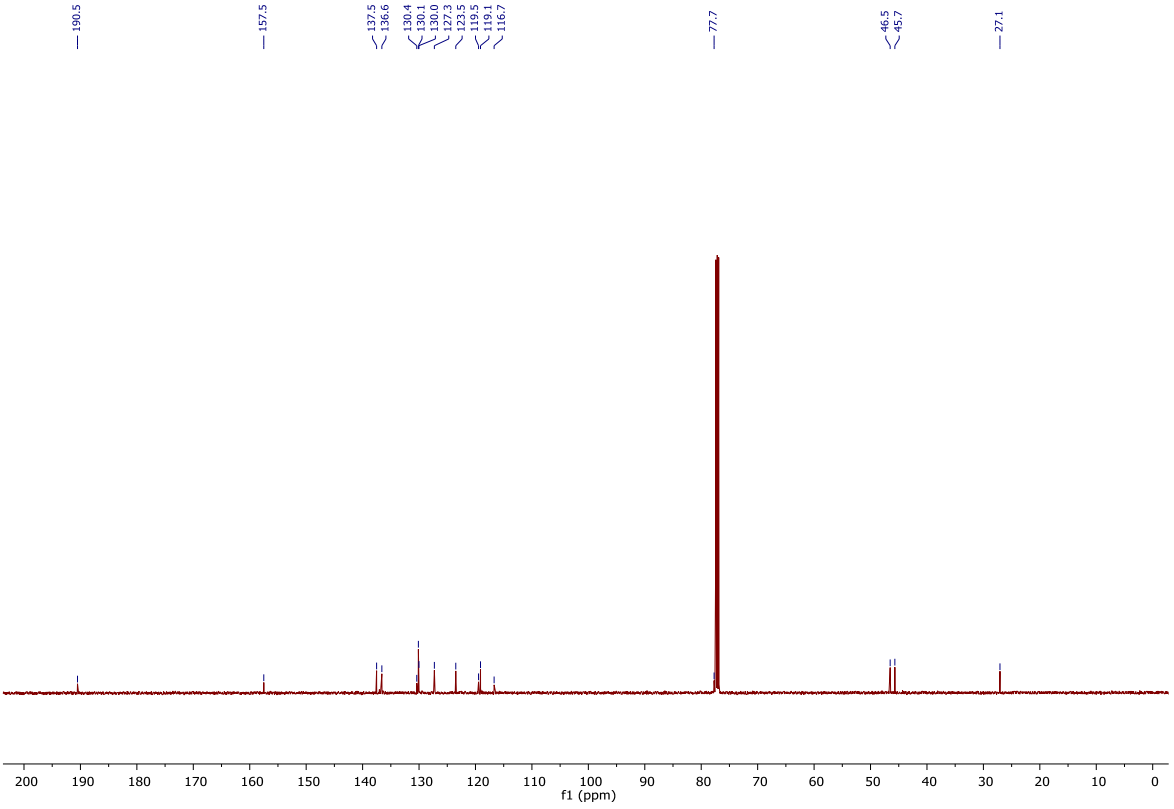


^{13}C-NMR (126 MHz, $CDCl_3$)

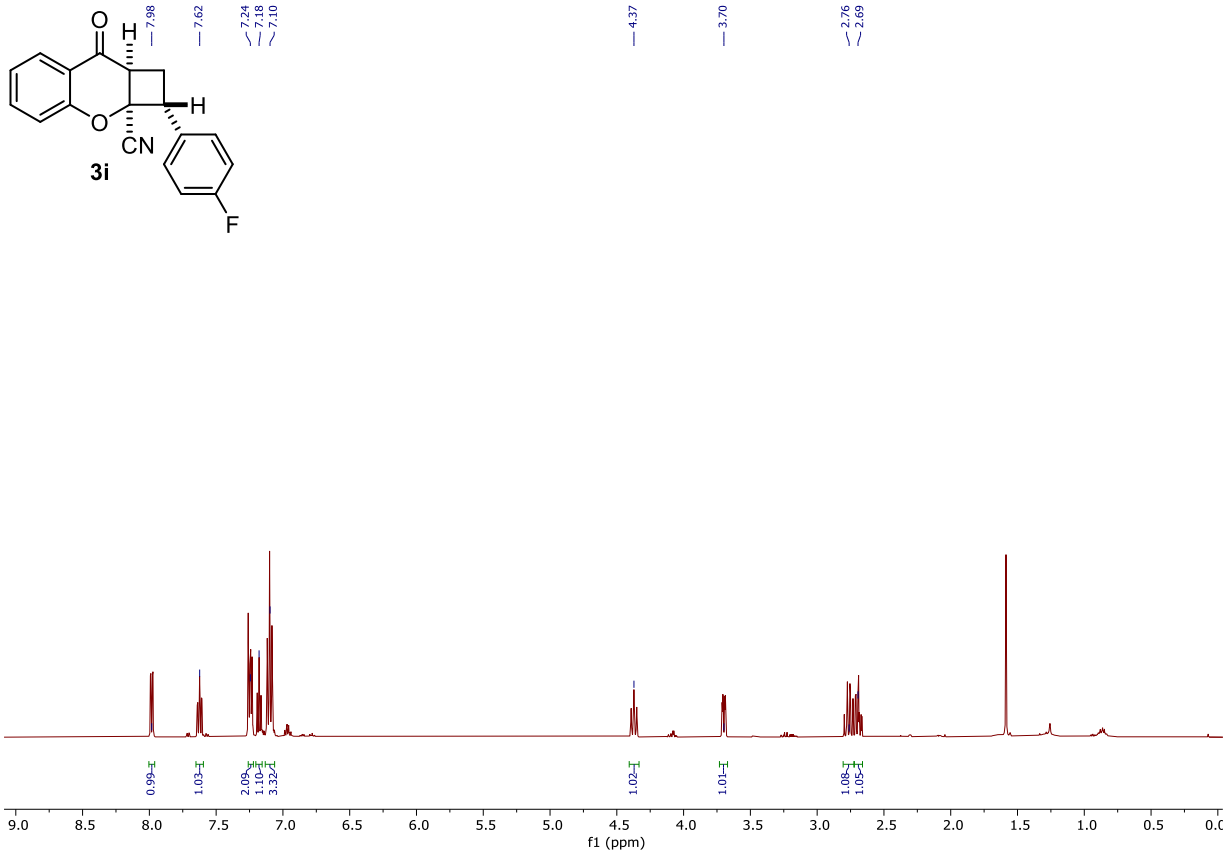


3h

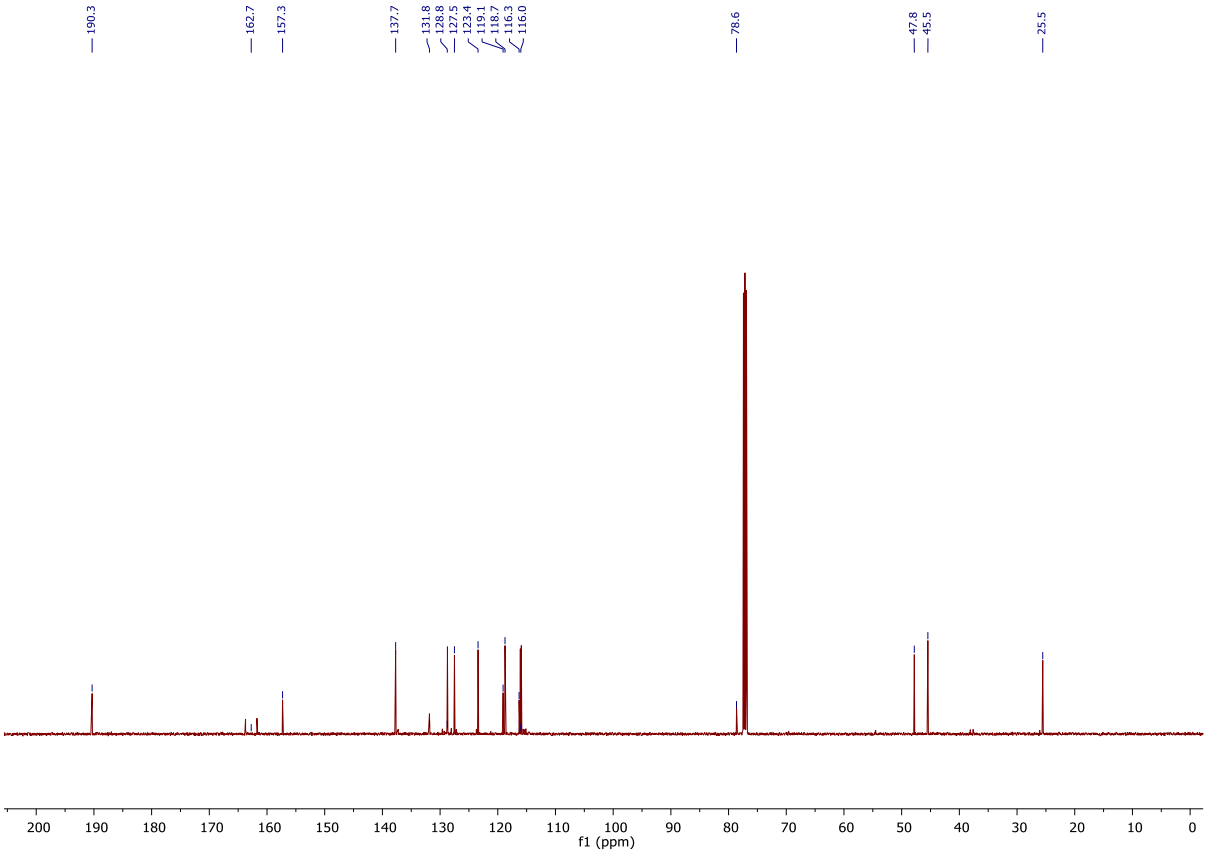
^{1}H-NMR (500 MHz, $CDCl_3$)



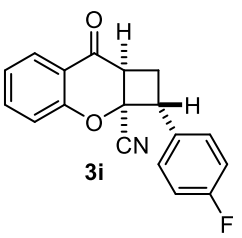
^{13}C-NMR (126 MHz, $CDCl_3$)



^{1}H-NMR (500 MHz, $CDCl_3$)

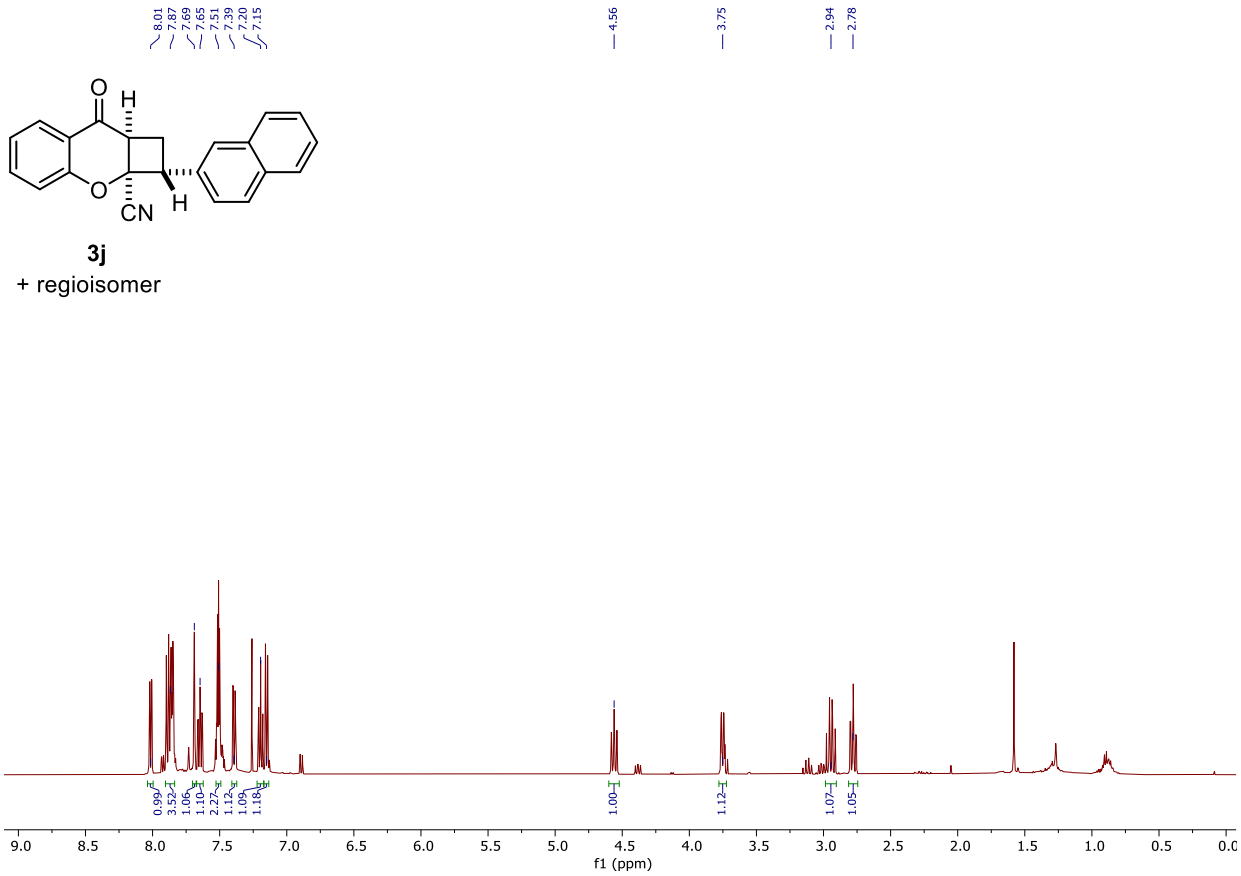


^{13}C-NMR (126 MHz, $CDCl_3$)



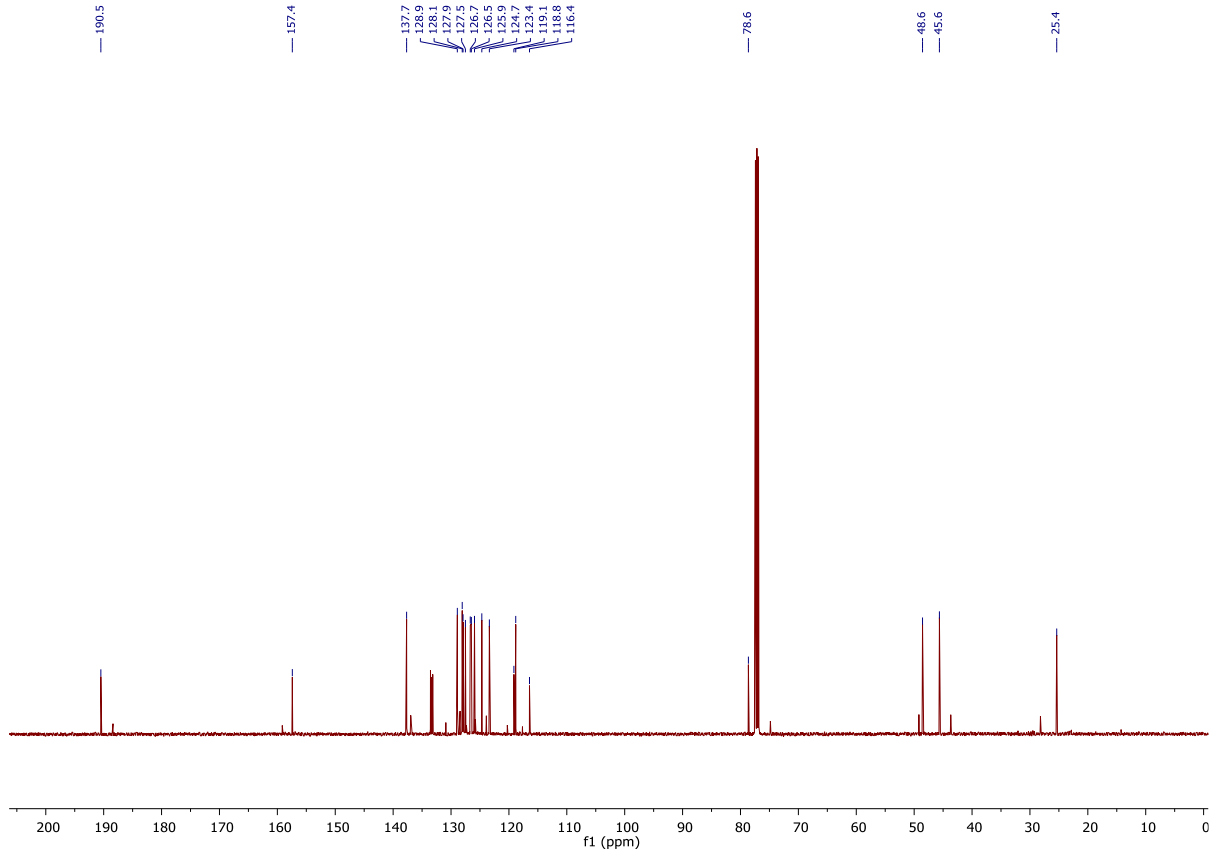
3i

^{19}F-NMR (282 MHz, $CDCl_3$)

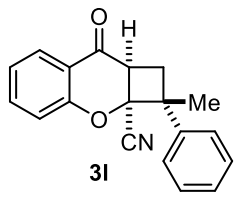


3j
+ regioisomer

^{1}H-NMR (500 MHz, $CDCl_3$)

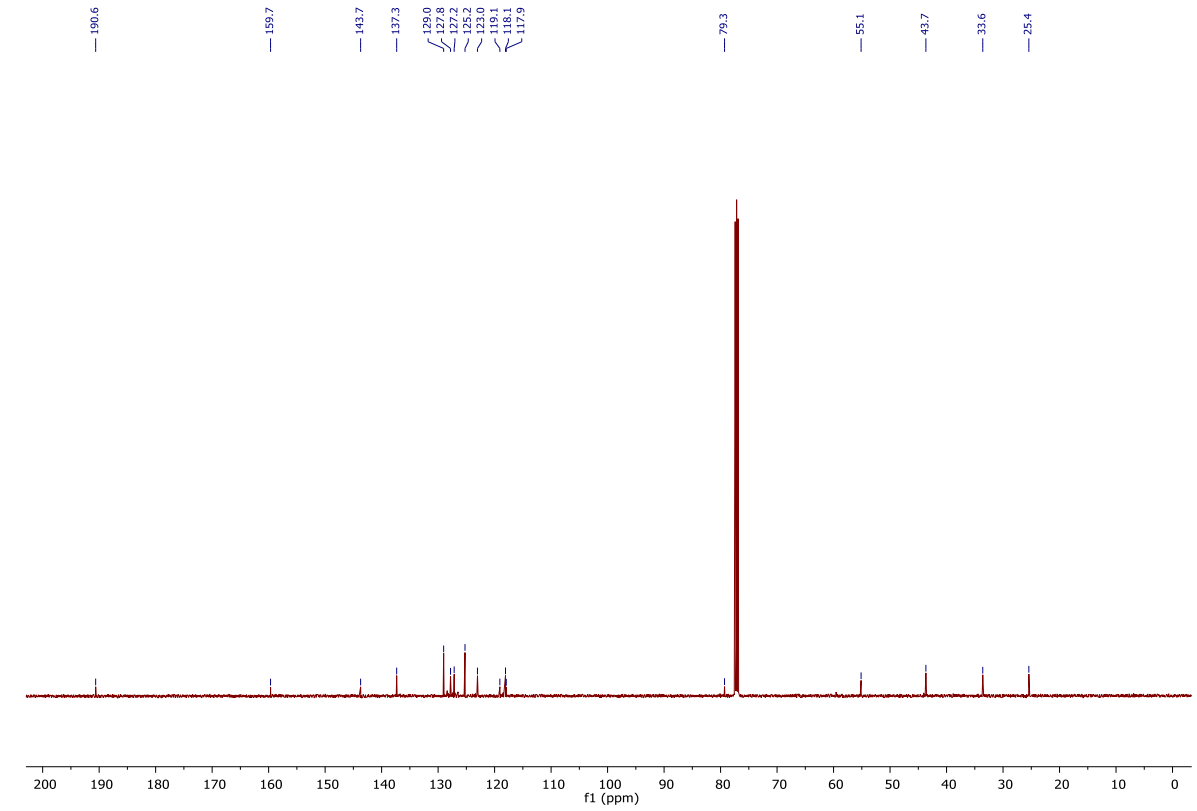


^{13}C-NMR (126 MHz, $CDCl_3$)

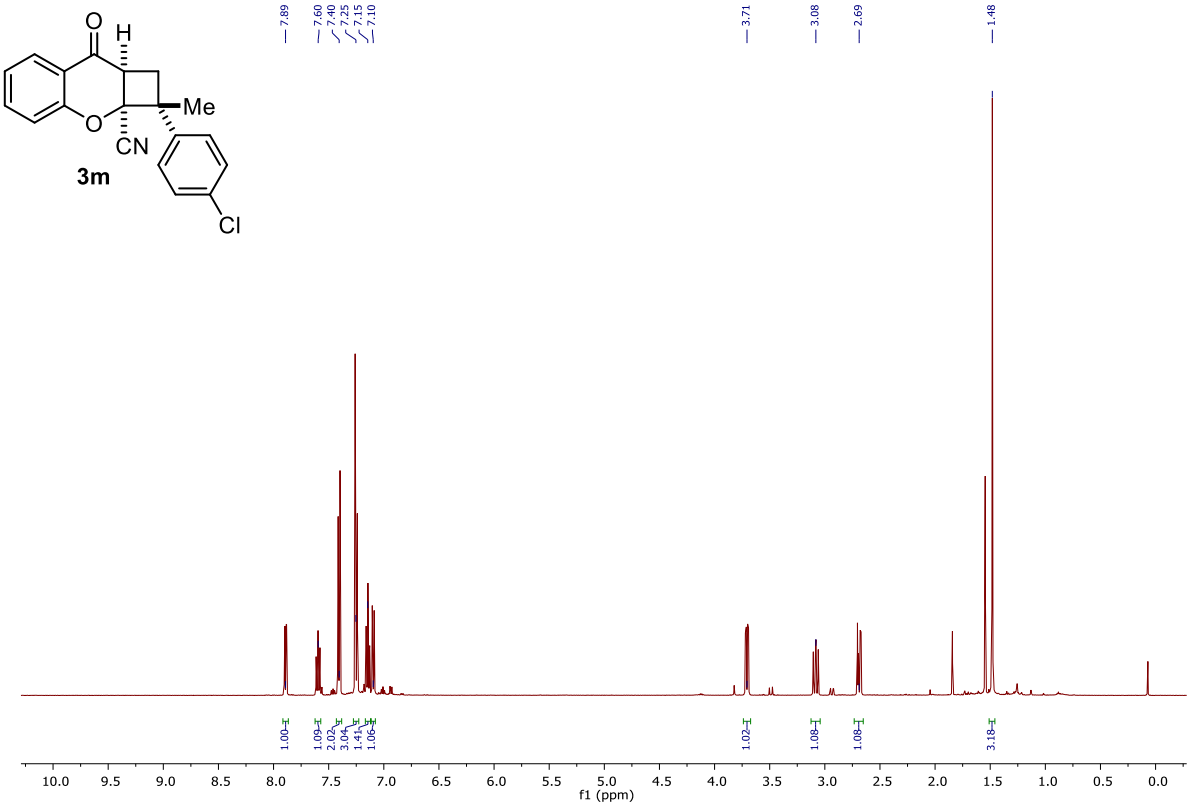


3l

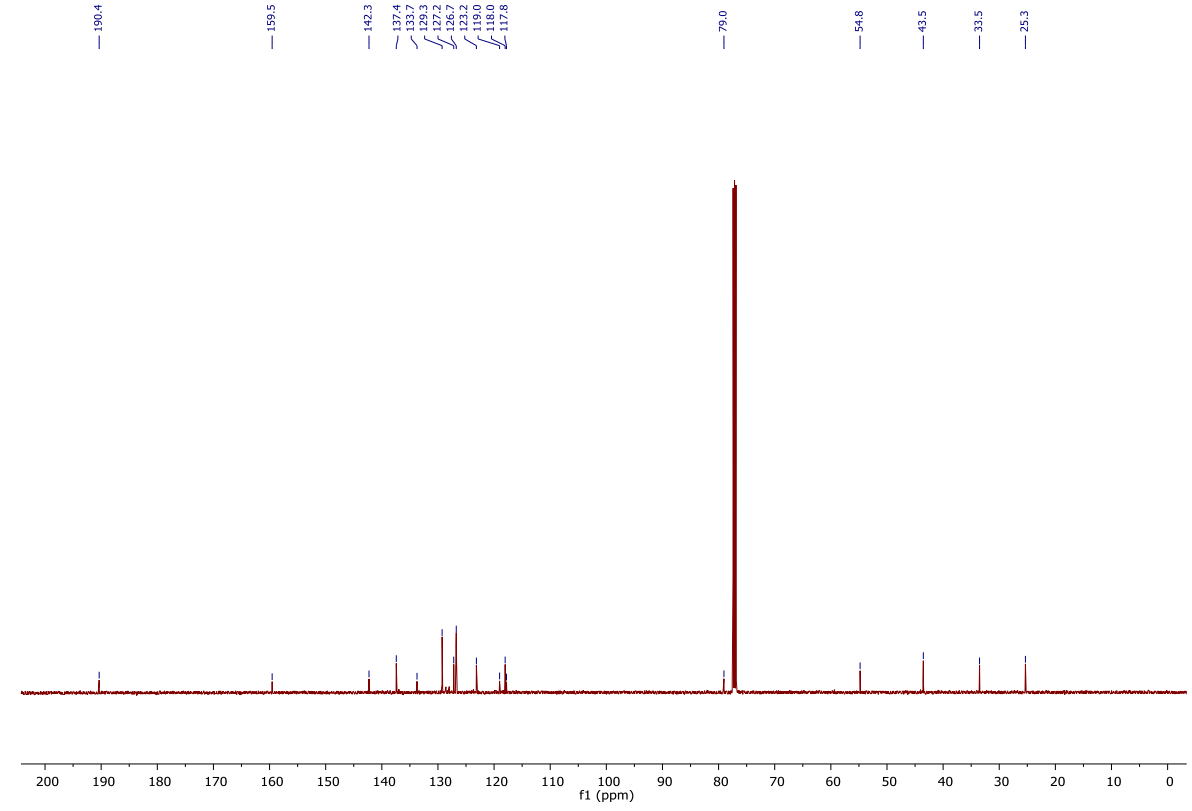
^{1}H-NMR (500 MHz, $CDCl_3$)



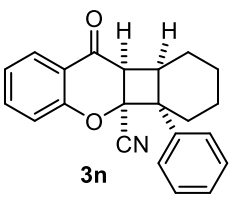
^{13}C-NMR (126 MHz, $CDCl_3$)



^{1}H-NMR (500 MHz, $CDCl_3$)

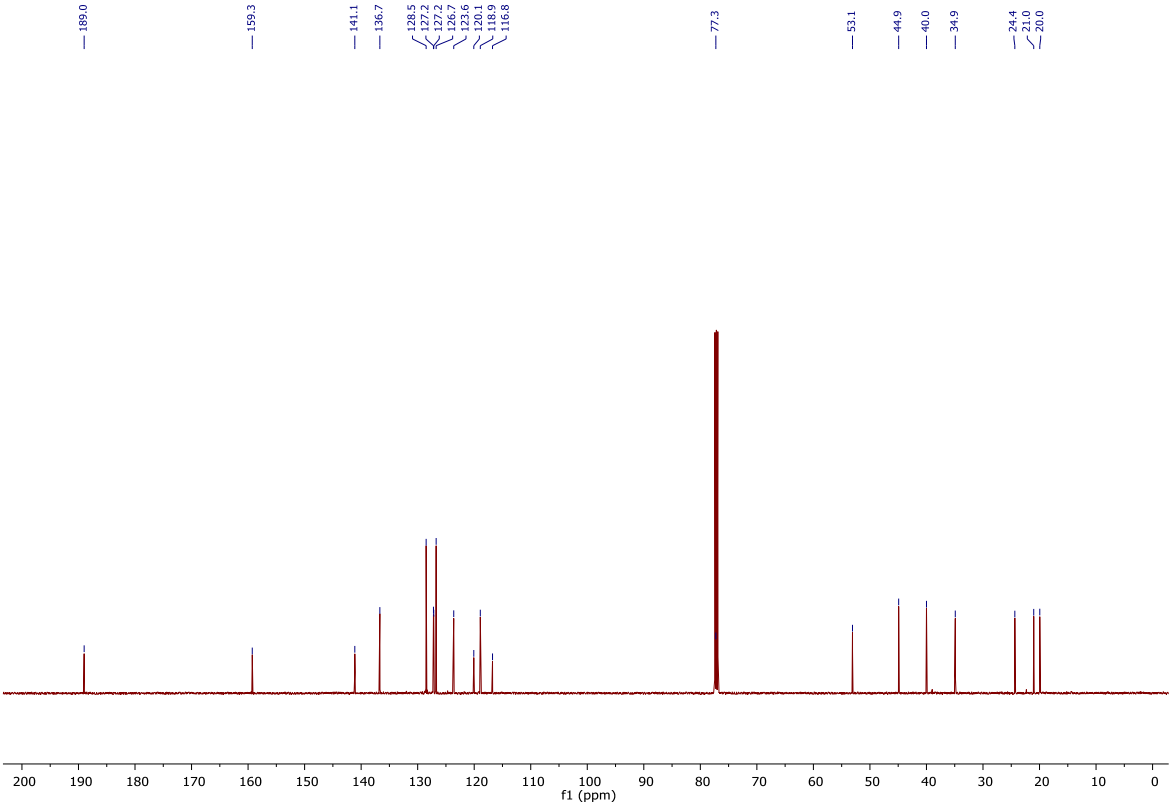


^{13}C-NMR (126 MHz, $CDCl_3$)

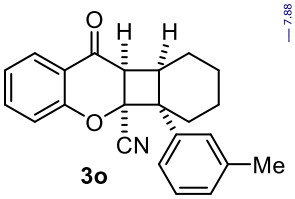


3n

^{1}H-NMR (500 MHz, $CDCl_3$)

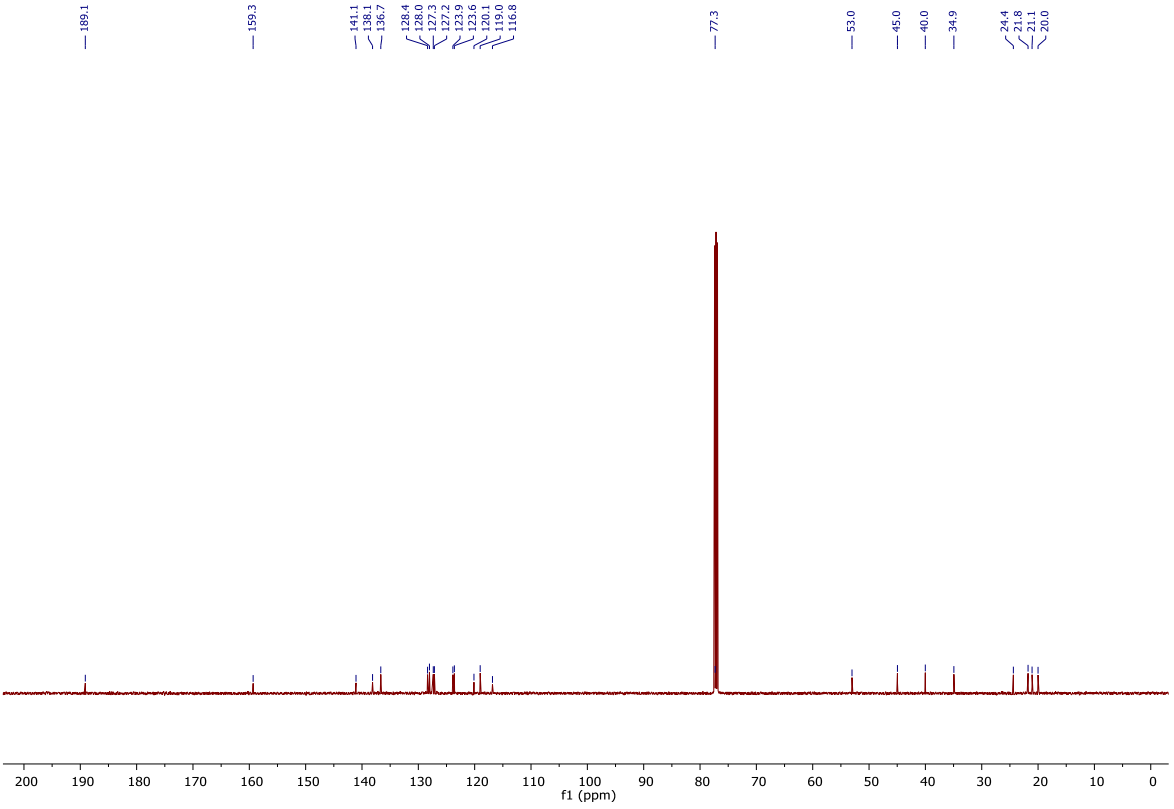


^{13}C-NMR (126 MHz, $CDCl_3$)

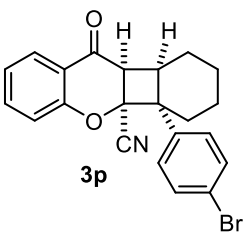


3o

^{1}H-NMR (500 MHz, $CDCl_3$)

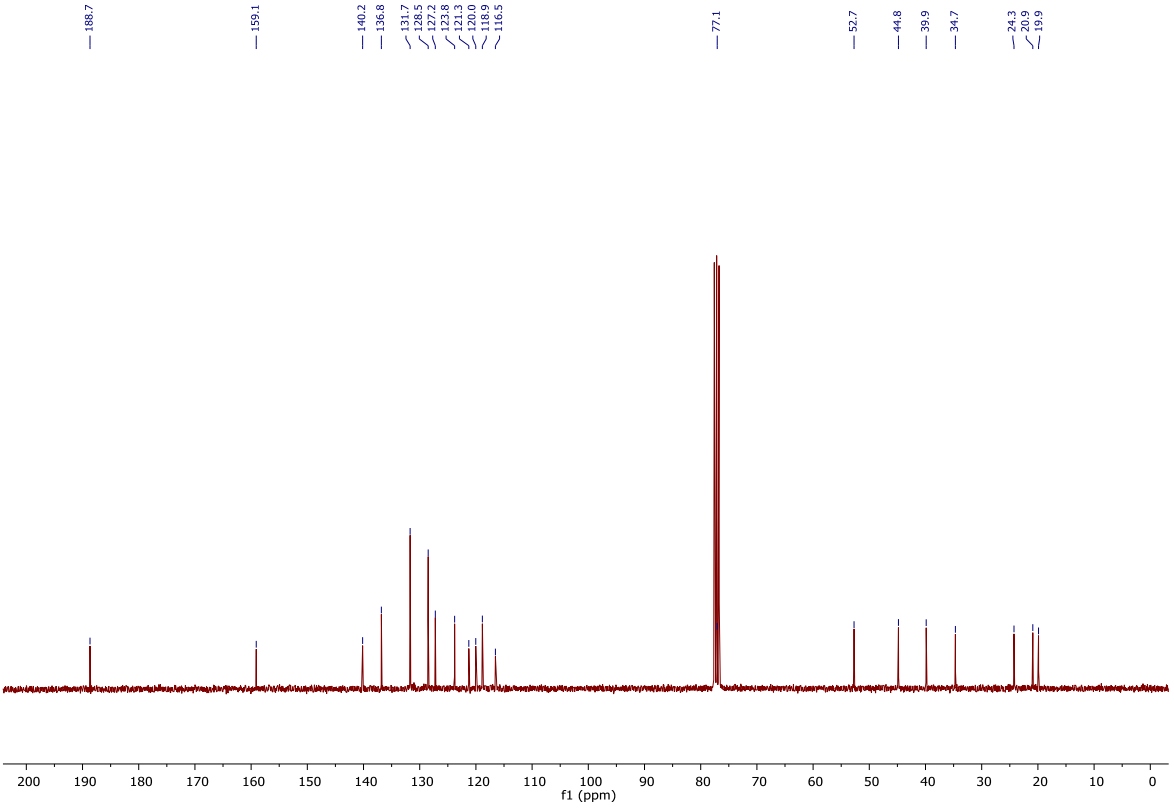


^{13}C-NMR (126 MHz, $CDCl_3$)

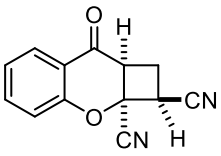


3p

^{1}H-NMR (500 MHz, $CDCl_3$)

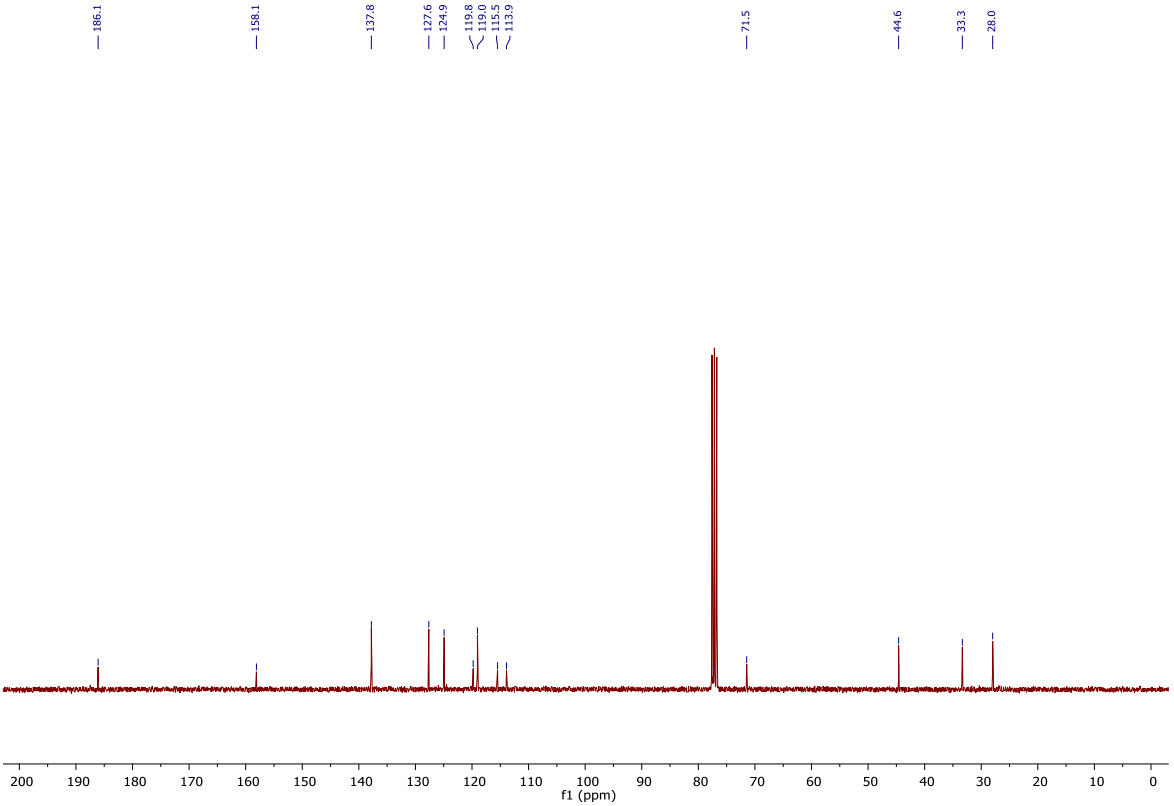


^{13}C-NMR (75 MHz, $CDCl_3$)

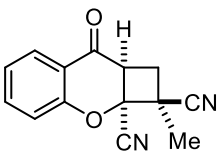


5a

^{1}H-NMR (500 MHz, $CDCl_3$)

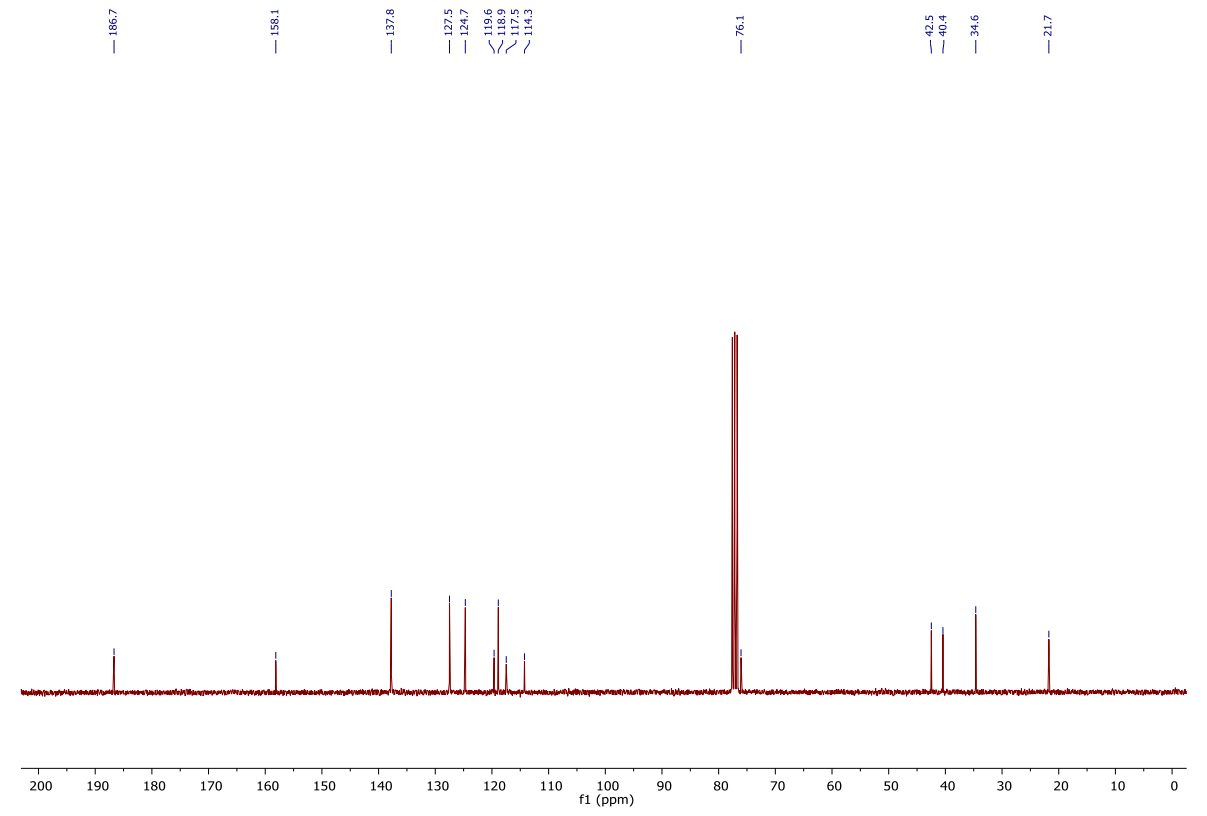


^{13}C-NMR (75 MHz, $CDCl_3$)

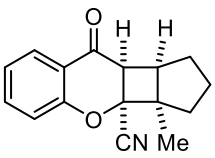


5b

^{1}H-NMR (300 MHz, $CDCl_3$)

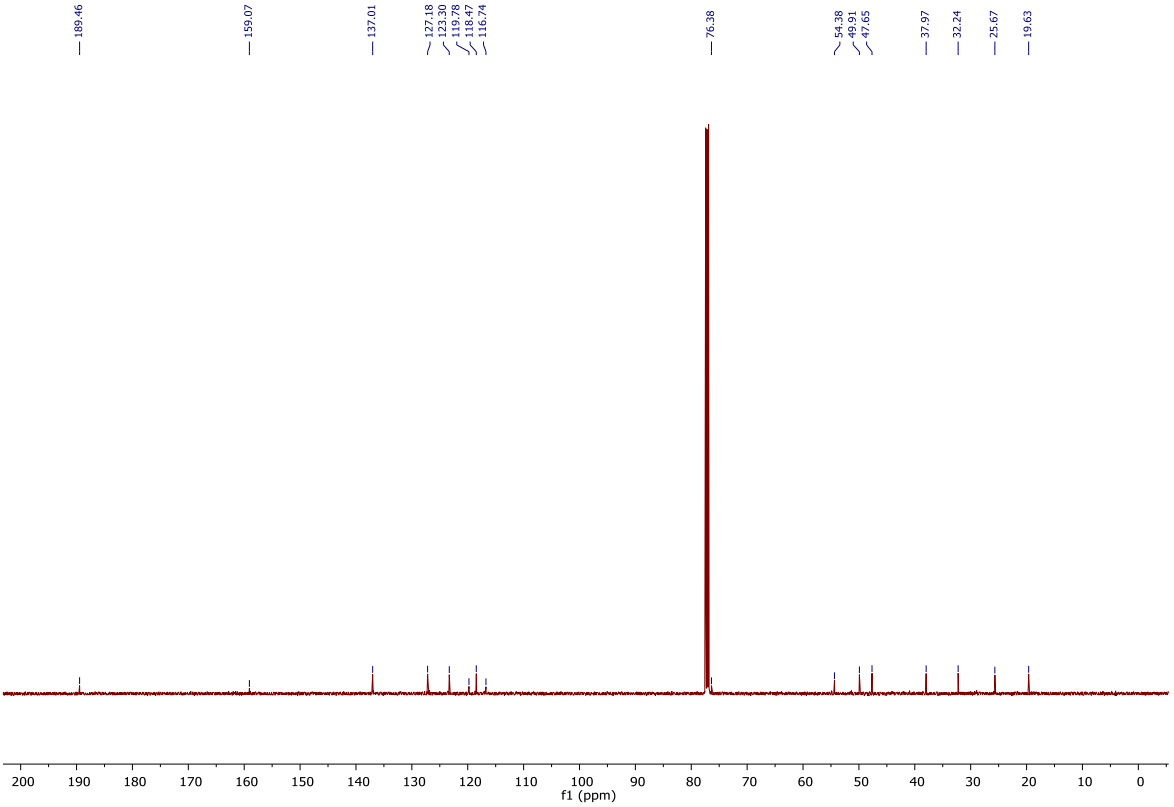


^{13}C-NMR (75 MHz, $CDCl_3$)

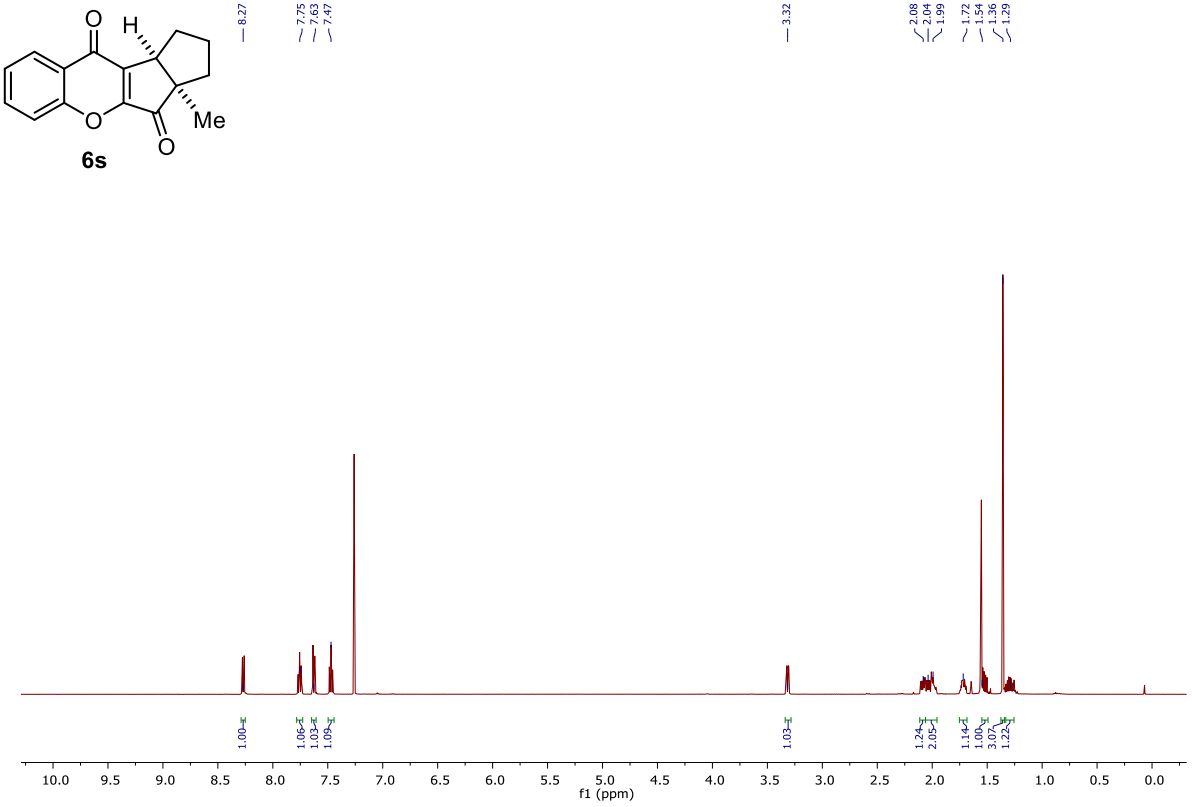


3s

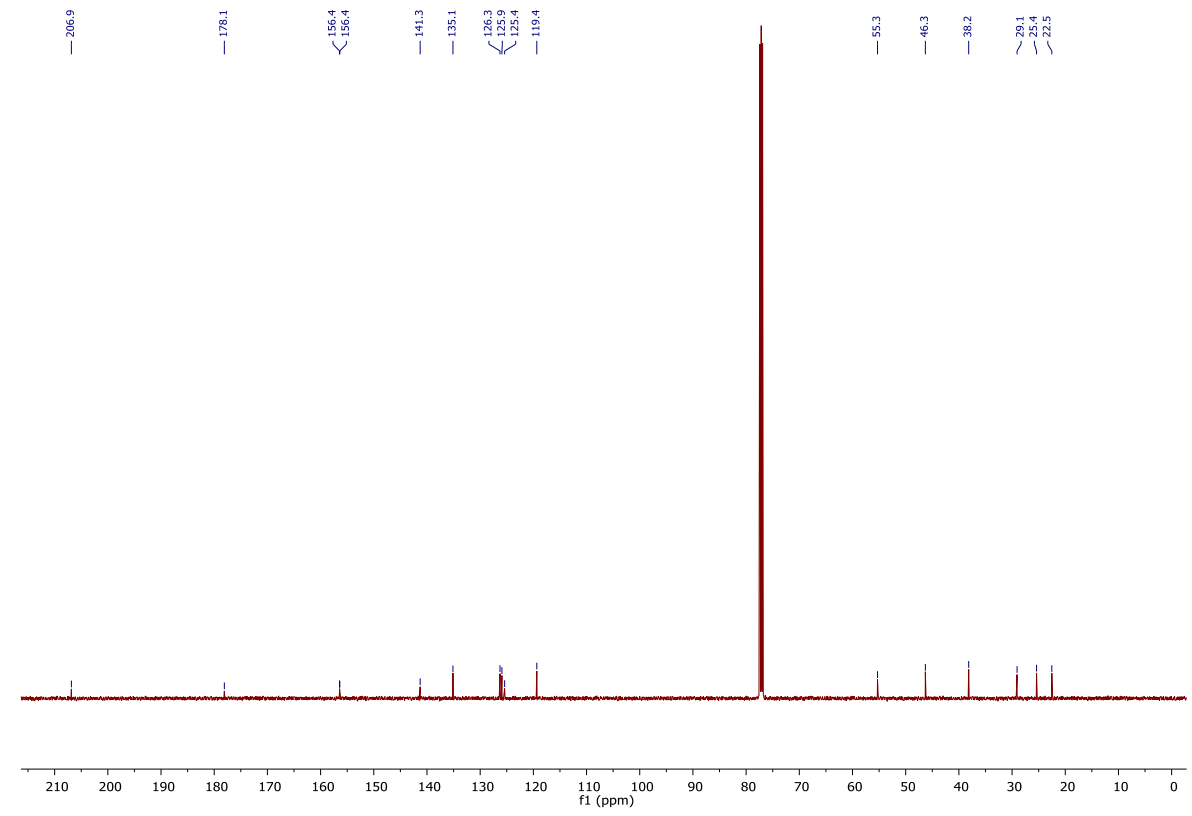
^{1}H-NMR (500 MHz, $CDCl_3$)



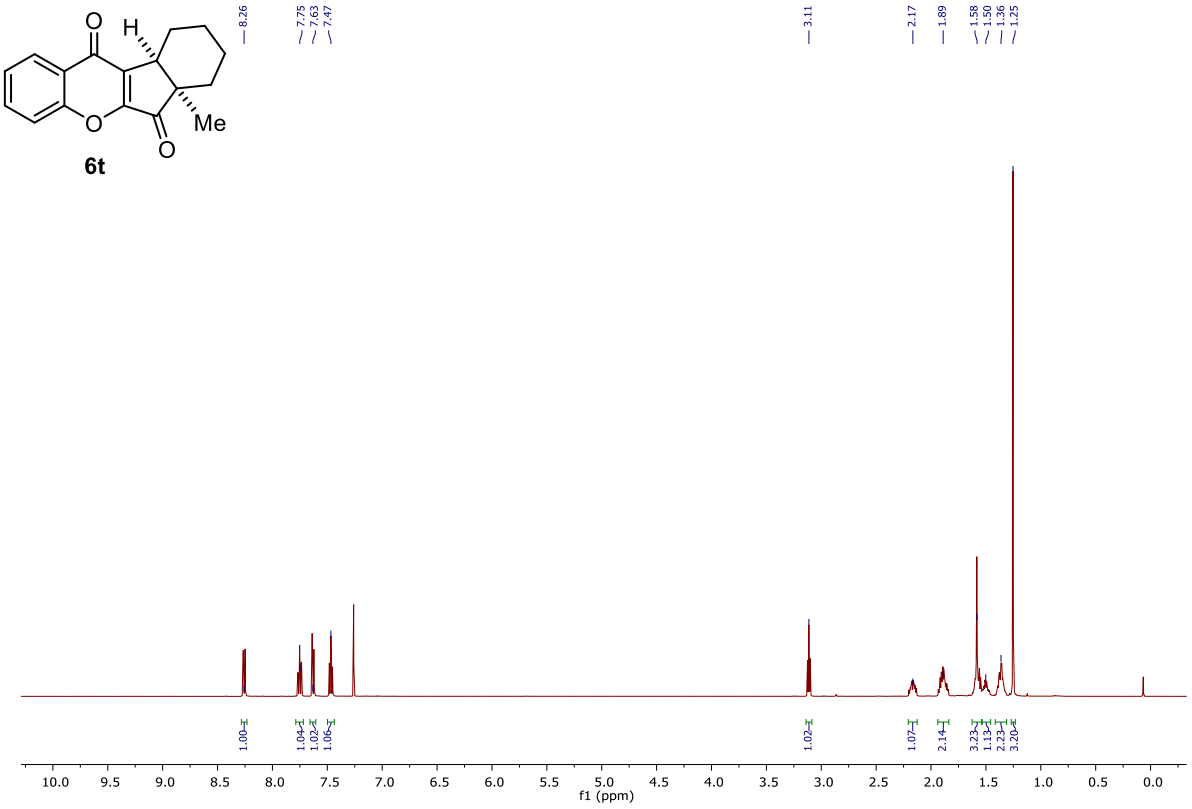
^{13}C-NMR (126 MHz, $CDCl_3$)



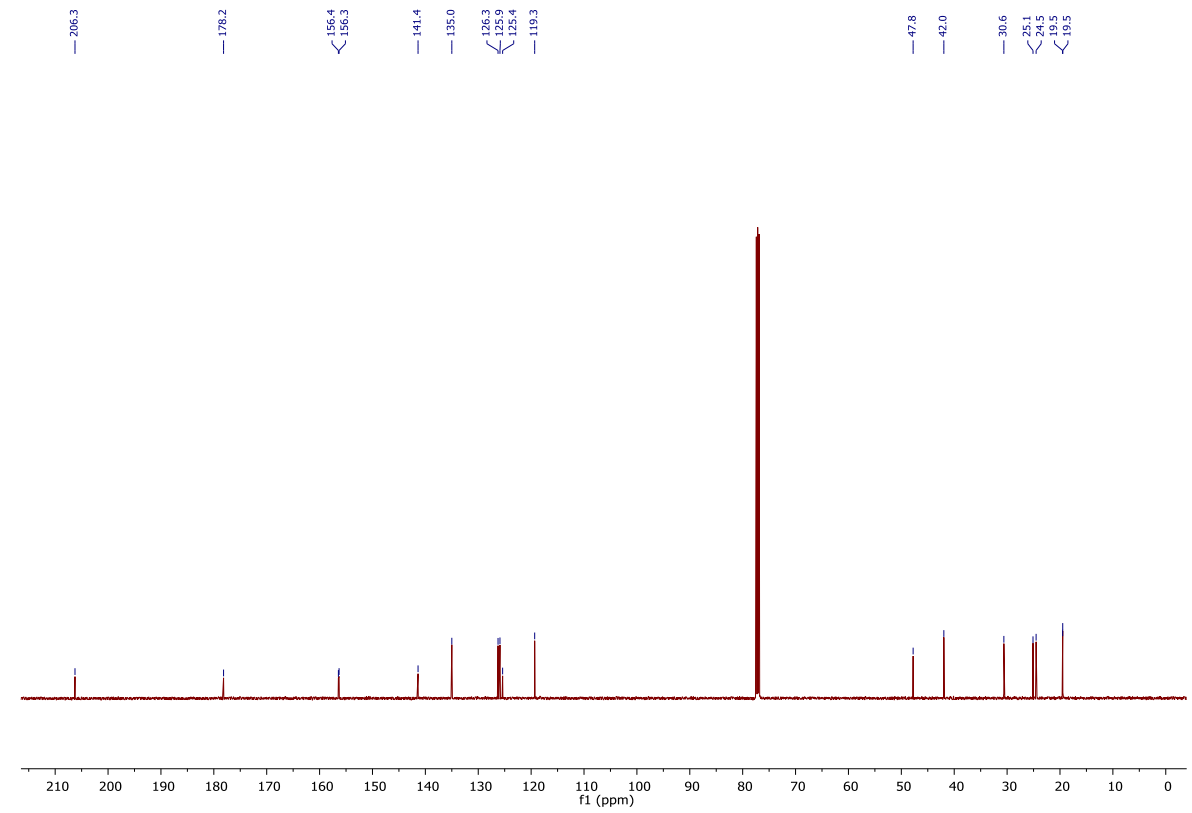
^{1}H-NMR (500 MHz, $CDCl_3$)



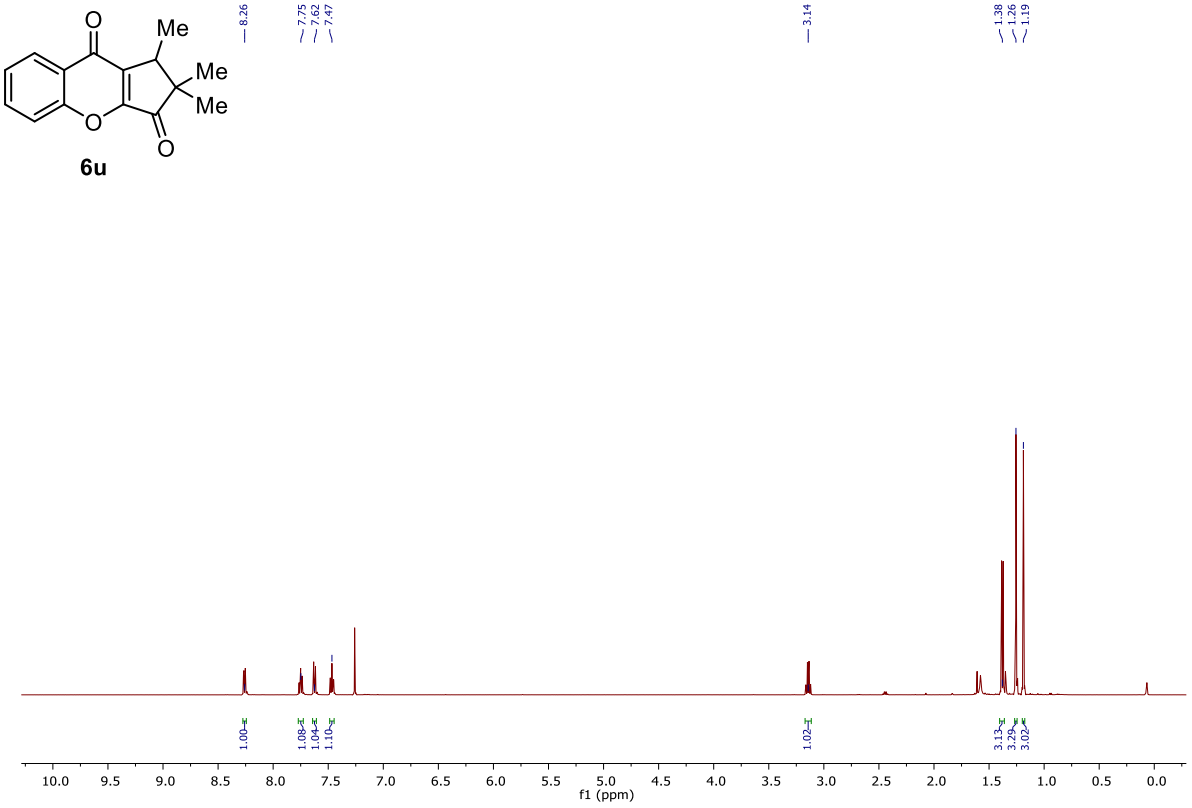
^{13}C-NMR (126 MHz, $CDCl_3$)



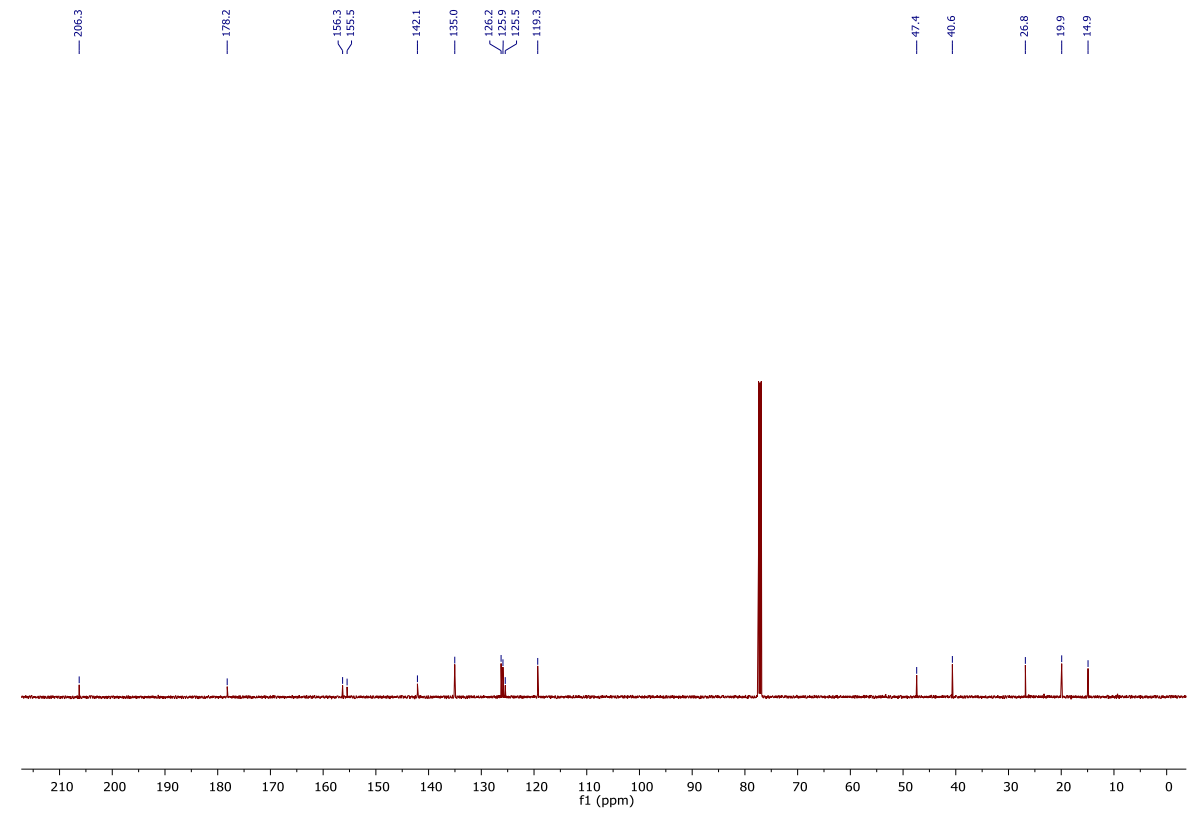
^{1}H-NMR (500 MHz, $CDCl_3$)



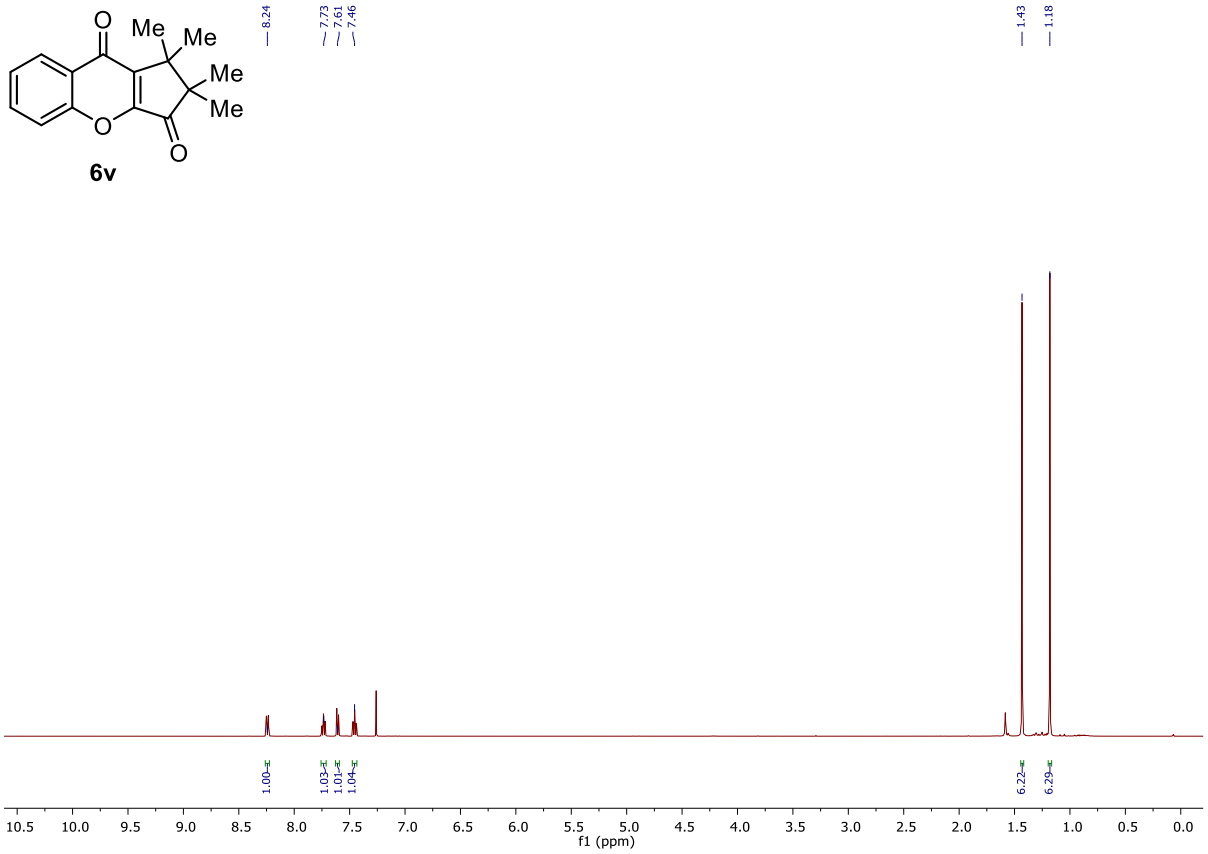
^{13}C-NMR (126 MHz, $CDCl_3$)



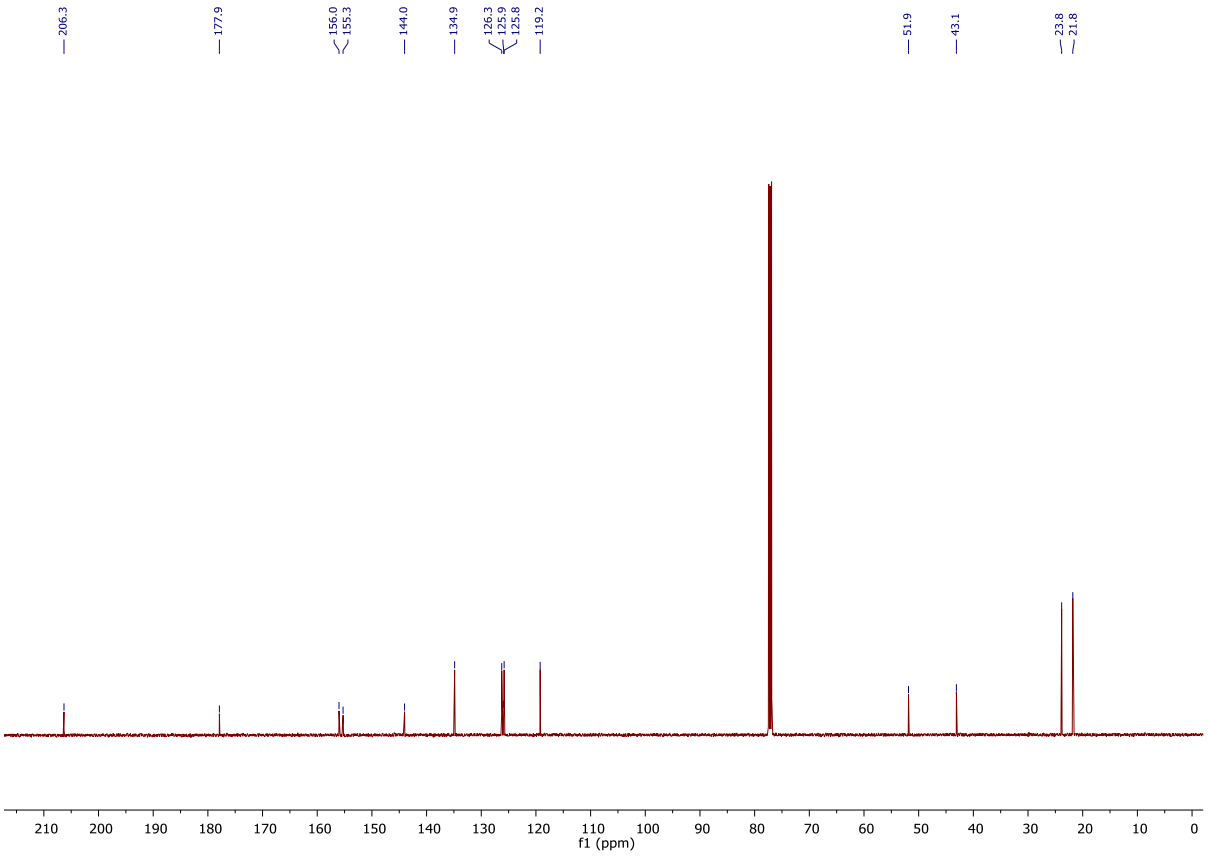
^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (126 MHz, $CDCl_3$)



^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (126 MHz, $CDCl_3$)