Supplementary Information (SI) for Chemical Science.

Supplementary Information

Radical Pathways for 2,4-Chromandione Synthesis via Photoexcitation of 4-Hydroxycoumarins

Sumitava Mallik,[†] Enrico Sfreddo,[†] Hailong Wang,[†] Paolo Melchiorre[†]*

[†]University of Bologna, Department of Industrial Chemistry '*Toso Montanari*'
via Piero Gobetti 85, 40129 Bologna, Italy

*Correspondence to: p.melchiorre@unibo.it

Table of Contents

A. General Information

The NMR spectra were recorded at 400 MHz and 600 MHz for ^{1}H, 101 or 150 MHz for ^{13}C and 376 MHz for ^{19}F{^{1}H}. The chemical shift (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvents ($CHCl_3$ @ 7.26 ppm ^{1}H NMR and 77.16 ppm ^{13}C NMR). Coupling constants are given in Hertz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; q, quartet; m, multiplet; br, broad signal

High resolution mass spectra (HRMS) were obtained from High Resolution Mass Spectra (HMRS) were obtained from the Mass Facility unit on a Waters Xevo Q Tof spectrometer with electrospray ionization (ESI). UV-vis measurements were carried out on a Cary 3500 Multicell UV-vis spectrophotometer. Cyclic voltammetry studies were carried out on a CHI660C potentiostat, offering compliance voltage up to ± 100 V (available at the counter electrode), ± 10 V scan range and ±2 A current range. Fluorescence measurements were carried out on an Edinburgh FLSP920 spectrometer equipped with a 450 W xenon arc lamp, double excitation and single emission monochromators, and a Peltier-cooled Hamamatsu R928P photomultiplier tube (185−850 nm).

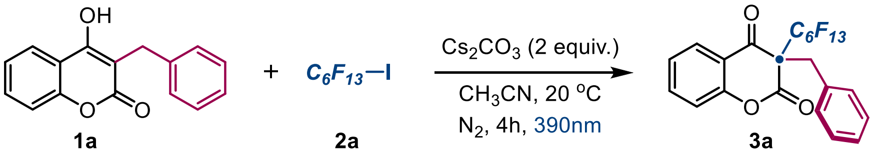
Yields refer to isolated materials of >95% purity as determined by ^{1}H NMR analysis.

General Procedures. All reactions were set up under an argon atmosphere in oven-dried glassware. Synthesis grade and anhydrous solvents were used as purchased from commercial sources. Chromatographic purification of products was accomplished using forced-flow chromatography (FC) on silica gel (230-400 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were employed, using UV light as the visualizing agent and an acidic mixture of vanillin or basic aqueous potassium permanganate ($KMnO_4$) stain solutions, and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotatory evaporator.

Materials. Commercial grade reagents and solvents were purchased at the highest quality from commercial suppliers and used as received, unless otherwise stated.

B1. Optimization Studies

Table S1. Optimization of the model reaction[a]



Entry	Deviation	NMRy **3a**[b]
1	none	82
2	no base, no light	0
3	in arial condition instead of N_2	0
4	in 427nm, 440nm, and 456nm	0
5	DMSO, DMF instead of CH_3CN	<15
6	DCM, DCE instead of CH_3CN	5 / 30
7	CH_3OH, HFIP instead of CH_3CN	0
8	Na_2CO_3, K_2CO_3 instead of Cs_2CO_3	56 / 70
9	DBU, DABCO instead of Cs_2CO_3	16 / 24
10	TMG instead of Cs_2CO_3	78
11	**2a** (2 equiv.) or (1 equiv.)	40 / 15
12	1equiv. Cs_2CO_3 instead of 2 equiv.	37

[a] Reactions performed over 4 hours in 1 mL of CH_3CN using 0.15 mmol of **1a**, 0.45 mmol of **2a**, and base (2 equiv.) under irradiation by a Kessil lamp (λ_{max} = 390 nm, irradiance = 100 mW/cm^2). [b] Yield of **3a** determined by ^{1}H NMR analysis of the crude mixture using dibromomethane as the internal standard.

B2. Unsuccessful Substrates

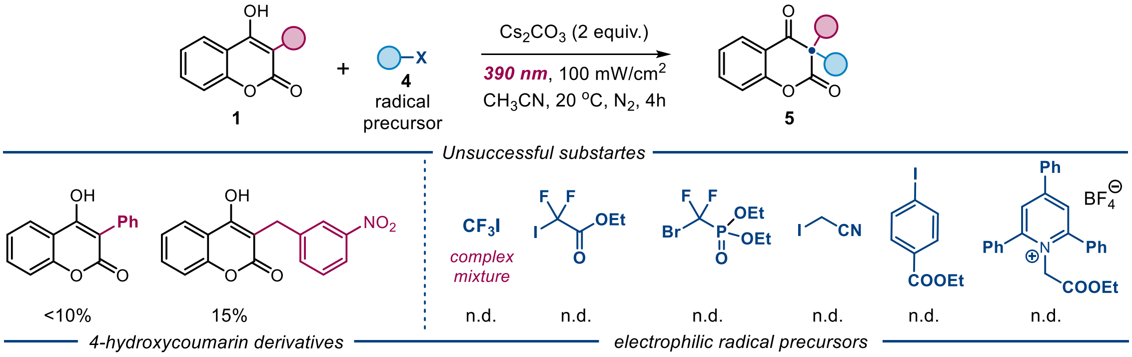
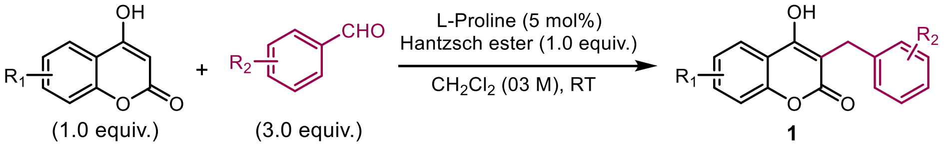


Figure S1. Unsuccessful and poorly reactive 4-hydroxycoumarins and radical precursors; radical precursors were reacted with substrate **1a**; n.d. = product not detected

C. Synthesis of 4-Hydroxycoumarin Substrates

Compound **1a** and the similar substrates detailed in Figure S2 were synthesized according to previously reported procedures,[1-2] with slight modifications as outlined below.

General Procedure A:



An oven-dried flask was charged with 4-hydroxycoumarin (1.0 equiv.), aldehyde (3.0 equiv.), Hantzsch ester (1.0 equiv.), and proline (0.05 equiv.), which were dissolved in 0.3 M dichloromethane. The reaction mixture was stirred at room temperature overnight. The reaction was monitored by TLC analysis, and the excess solvent was evaporated using a rotary evaporator. The crude reaction mixture was purified by flash column chromatography on silica gel, using 50% ethyl acetate in hexanes as the eluent, to afford the final benzylated 4-hydroxycoumarin substrate **1** as a white solid.

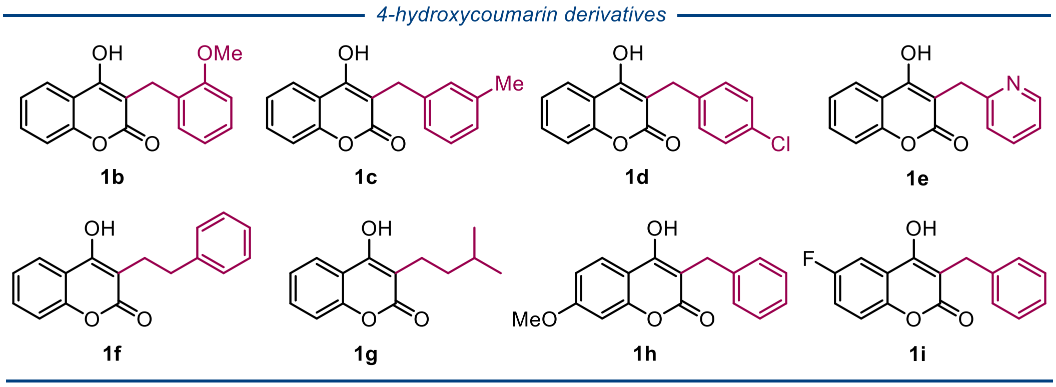
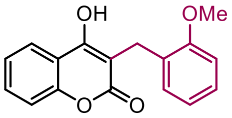


Figure S2: Starting materials synthesized according to procedure **A**.

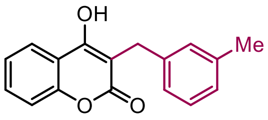
Characterization of substrates 1b –1i:



1b

4-hydroxy-3-(2-methoxybenzyl)-2H-chromen-2-one (1b): Synthesized according to the general procedure **A** using 4-hydroxycoumarin (250 mg, 1.54 mmol, 1.0 equiv.), 2-methoxybenzaldehyde (630 mg, 4.63 mmol, 3.0 equiv.) and Hantzsch ester (391 mg, 1.54 mmol, 1.0 equiv.), and L-proline (8.9 mg, 0.077 mmol, 0.05 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane:EtOAc = 1:1 as eluent) to afford **1b** (292 mg, 67% yield) as a light yellow solid.

^{1}H NMR (400 MHz, DMSO) δ 7.99 – 7.92 (m, 1H), 7.62 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.42 – 7.33 (m, 2H), 7.17 (ddd, *J* = 8.1, 7.2, 1.9 Hz, 1H), 6.97 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.89 – 6.75 (m, 2H), 3.83 (s, 3H), 3.81 (s, 2H).
^{13}C NMR (151 MHz, DMSO) δ 162.8, 161.1, 157.1, 152.1, 131.8, 127.3, 127.7, 126.9, 123.9, 123.3, 120.1, 116.3, 116.2, 110.3, 102.3, 55.3, 23.8.



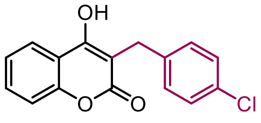
1c

4-hydroxy-3-(3-methylbenzyl)-2H-chromen-2-one (1c): Synthesized according to the general procedure **A** using 4-hydroxycoumarin (250 mg, 1.54 mmol, 1.0 equiv.), 3-methylbenzaldehyde (556 mg, 4.63 mmol, 3.0 equiv.) and Hantzsch ester (391 mg, 1.54 mmol, 1.0 equiv.), and L-proline (8.9mg, 0.077

mmol, 0.05 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane:EtOAc = 1:1 as eluent) to afford **1c** (337 mg, 82% yield) as a white solid.

^{1}H NMR (400 MHz, DMSO) δ 7.96 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.63 – 7.54 (m, 1H), 7.38 – 7.29 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.06 – 6.89 (m, 3H), 3.82 (s, 2H), 2.23 (s, 3H).

^{13}C NMR (151 MHz, DMSO) δ 163.0, 161.4, 152.1, 140.1, 137.1, 131.6, 128.7, 128.0, 126.4, 125.2, 123.7, 123.5, 116.8, 116.1, 103.8, 29.1, 21.0.

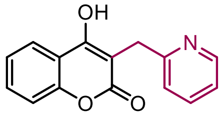


1d

3-(4-chlorobenzyl)-4-hydroxy-2H-chromen-2-one (1d): Synthesized according to the general procedure **A** using 4-hydroxycoumarin (1.0 g, 6.17 mmol, 1.0 equiv.), 4-chlorobenzaldehyde 2.6 g, 18.5 mmol, 3.0 equiv.) and Hantzsch ester (1.56 g, 6.17 mmol, 1.0 equiv.), and L-proline (35.5 mg, 0.31 mmol, 0.05 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane:EtOAc = 1:1 as eluent) to afford **1d** (1.15 g, 65% yield) as a white solid.

^{1}H NMR (600 MHz, DMSO) δ 8.00 – 7.95 (m, 1H), 7.61 (ddd, *J* = 8.7, 7.4, 1.6 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 3.86 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 162.8, 160.8, 152.1, 138.9, 132.0, 130.5, 130.0, 128.1, 124.0, 123.4, 116.3, 116.2, 103.8, 28.6.

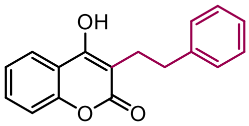


1e

4-hydroxy-3-(pyridin-2-ylmethyl)-2H-chromen-2-one (1e): Synthesized according to the general procedure **A** using 4-hydroxycoumarin (250 mg, 1.54 mmol, 1.0 equiv.), 2-pyridinecarboxaldehyde (495 mg, 4.63 mmol, 3.0 equiv.) and Hantzsch ester (391 mg, 1.54 mmol, 1.0 equiv.), and L-proline (8.9 mg, 0.077 mmol, 0.05 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane:EtOAc = 1:1 as eluent) to afford **1e** (206 mg, 53% yield) as a light yellow solid.

^{1}H NMR (400 MHz, DMSO) δ 8.56 (ddd, *J* = 5.1, 1.8, 0.9 Hz, 1H), 7.93 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.88 (td, *J* = 7.7, 1.8 Hz, 1H), 7.60 (ddd, *J* = 8.4, 7.3, 1.7 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.30 (m, 3H), 4.10 (s, 2H).

^{13}C NMR (151 MHz, DMSO) δ 163.8, 162.9, 159.2, 152.2, 147.1, 139.0, 131.8, 123.8, 123.4, 123.3, 122.4, 117.3, 116.0, 100.7, 31.8.

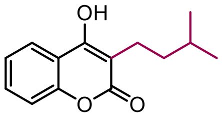


1f

4-hydroxy-3-phenethyl-2H-chromen-2-one (1f): Synthesized according to the general procedure **A** using 4-hydroxycoumarin (250 mg, 1.54 mmol, 1.0 equiv.), 2-phenylacetaldehyde (556 mg, 4.63 mmol, 3.0 equiv.) and Hantzsch ester (391 mg, 1.54 mmol, 1.0 equiv.), and L-proline (8.9 mg, 0.077 mmol, 0.05 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane:EtOAc = 1:1 as eluent) to afford **1f** (211 mg, 51% yield) as a white solid.

^{1}H NMR (600 MHz, DMSO) δ 7.92 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.58 (ddd, *J* = 8.5, 7.3, 1.6 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.30 – 7.24 (m, 4H), 7.23 – 7.11 (m, 1H), 2.82 – 2.76 (m, 2H), 2.76 – 2.70 (m, 2H).

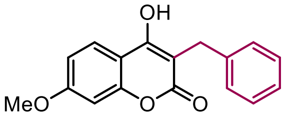
^{13}C NMR (151 MHz, DMSO) δ 162.8, 160.2, 151.9, 141.6, 131.6, 128.3, 128.2, 125.8, 123.8, 123.3, 116.5, 116.1, 104.2, 33.6, 25.7.



1g

4-hydroxy-3-isopentyl-2H-chromen-2-one (1g): Synthesized according to the general procedure **A** using 4-hydroxycoumarin (250 mg, 1.54 mmol, 1.0 equiv.), isovaleraldehyde (398 mg, 4.63 mmol, 3.0 equiv.) and Hantzsch ester (391 mg, 1.54 mmol, 1.0 equiv.), and L-proline (8.9 mg, 0.077 mmol, 0.05 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane:EtOAc = 1:1 as eluent) to afford **1g** (283 mg, 79% yield) as a white solid.

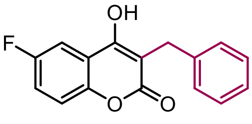
^{1}H NMR (400 MHz, DMSO) δ 7.92 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.37 – 7.28 (m, 2H), 1.56 (dp, *J* = 13.3, 6.7 Hz, 1H), 1.37 – 1.27 (m, 2H), 0.91 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (151 MHz, DMSO) δ 162.8, 159.8, 151.8, 131.4, 123.7, 123.1, 116.5, 116.0, 105.5, 36.9, 27.6, 22.5, 21.7.



1h

3-benzyl-4-hydroxy-7-methoxy-2H-chromen-2-one (1h): Synthesized according to the general procedure **A** using 4-hydroxy-7-methoxycoumarin (150 mg, 0.78 mmol, 1.0 equiv.), benzaldehyde (249 mg, 2.34 mmol, 3.0 equiv.) and Hantzsch ester (198 mg, 0.78 mmol, 1.0 equiv.), and L-proline (4.5 mg, 0.04 mmol, 0.05 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane:EtOAc = 1:1 as eluent) to afford **1h** (159 mg, 72% yield) as a light brown solid.

^{1}H NMR (400 MHz, DMSO) δ 7.88 (d, *J* = 9.5 Hz, 1H), 7.27 – 7.20 (m, 5H), 7.24 – 7.09 (m, 1H), 6.96 – 6.88 (m, 2H), 3.83 (s, 3H), 3.81 (s, 2H).
^{13}C NMR (151 MHz, DMSO) δ 163.4, 162.1, 153.89, 140.6, 128.1, 128.1, 125.6, 124.7, 111.5, 110.1, 101.0, 100.3, 55.8, 29.1.



1i

3-benzyl-6-fluoro-4-hydroxy-2H-chromen-2-one (1i): Synthesized according to the general procedure **A** using 6-fluoro-4-hydroxycoumarin (200 mg, 1.11 mmol, 1.0 equiv.), benzaldehyde (353 mg, 3.33 mmol, 3.0 equiv.) and Hantzsch ester (281 mg, 1.11 mmol, 1.0 equiv.), and L-proline (6.40 mg, 0.056 mmol, 0.05 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane:EtOAc = 1:1 as eluent) to afford **1i** (247 mg, 82% yield) as a white solid.

^{1}H NMR (600 MHz, DMSO) δ 7.69 (dd, *J* = 9.2, 3.0 Hz, 1H), 7.43 (td, *J* = 8.6, 3.0 Hz, 1H), 7.38 (dd, *J* = 9.0, 4.5 Hz, 1H), 7.25 – 7.20 (m, 4H), 7.13 (tt, *J* = 5.6, 2.5 Hz, 1H), 3.83 (s, 2H).
^{13}C NMR (151 MHz, DMSO) δ 162.9, 161.2, 158.7, 157.1, 148.5, 140.2, 128.1 (2×C), 125.7, 118.8, 118.7, 118.2, 118.1, 109.1, 109.0, 104.0, 29.3.
^{19}F NMR (565 MHz, DMSO) δ -118.43.

D. Experimental Procedures

D1. General Procedure for the 3,3-disubstituted 2,4-chromandiones

- ***Photochemical Set-up 1*** *390 nm Kessil lamp setup* with PhotoRedOx Box TC™ (Figure S3)

The reactions were performed using a PhotoRedOx Box TC™ reactor under the illumination of a *Kessil* lamp (max 52 W, λ_{max} = 390 nm, positioned 2-3 cm away from the vial), with a fan to maintain a cool temperature. Under these conditions, the reaction temperature within the vessel was measured to be between 20-22 °C.

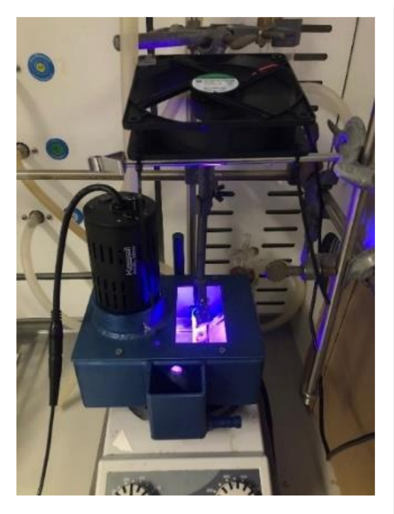
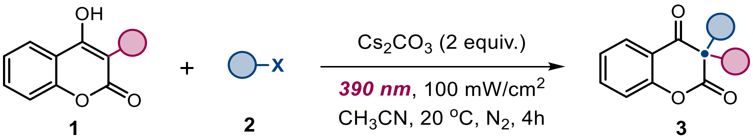
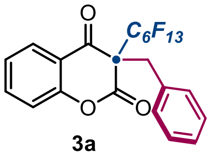


Figure S3. Reaction setup using PhotoRedOx Box TC™ reactor with 390 nm *Kessil lamp*.



To a 4 mL glass vial, 4-hydroxycoumarins **1** (0.2 mmol, 1.0 equiv.) and Cs_2CO_3 (0.4 mmol, 2 equiv.) were sequentially added. The vial was sealed with a screw-top cap with septum and then vacuumed and backfilled with nitrogen for 3 times. Afterwards, fluoroalkyl halides **2** (0.6 mmol, 3 equiv.), followed by argon-sparged CH_3CN (0.2 M, 1.0 mL) were added *via* syringe. The vial was sealed with Parafilm and then stirred under the irradiation of 390 nm *Kessil* lamp with PhotoRedOx Box TC™ reactor for 4 hours using ***Set-up 1*** detailed in **Figure S3**. After the reaction was completed, the reaction mixture was transferred to an extraction funnel, 10 mL of H_2O and 2 mL of brine were added, and the organic layer was extracted with EtOAc. The organic layer was washed with brine twice. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The crude residue was purified by column chromatography to afford the corresponding product **3**.

D2. Characterization of Products

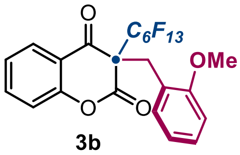


3a

3-Benzyl-3-(perfluorohexyl)-chromane-2,4-dione (3a): Synthesized according to the General Procedure using **1a** (50 mg, 0.2 mmol, 1.0 equiv.), **2a** (268 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 99: 1 as eluent) to afford **3a** (91 mg, 80% yield) as a colourless oil.

^{1}H NMR (400 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 7.22 (td, *J* = 7.6, 1.1 Hz, 1H), 7.10 (q, *J* = 3.4 Hz, 5H), 6.99 (dd, *J* = 8.2, 1.0 Hz, 1H), 4.36 – 3.37 (m, 2H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 185.7, 162.6, 153.7, 138.2, 131.4, 130.8, 128.9, 128.2, 127.4, 125.7, 118.8, 117.6, 63.1, 39.1.
^{19}F NMR (376 MHz, CDCl$_3$) δ -80.81 (t, *J* = 10.0 Hz), -108.55 – -112.32 (m), -116.1 – -117.9 (m), -121.71 (bs), -122.6 – -122.8 (m), -124.18 – -129.13 (m).

HRMS: calculated for $C_{22}H_{12}F_{13}O_3$ ($M+Na^+$): 593.0398, found 593.0399.

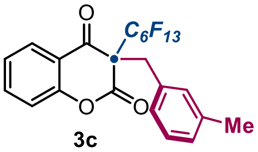


3b

3-(2-Methoxybenzyl)-3-(perfluorohexyl)-chromane-2,4-dione (3b): Synthesized according to the General Procedure using **1a** (56 mg, 0.2 mmol, 1.0 equiv.), **2b** (268 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 99: 1 as eluent) to afford **3b** (90 mg, 75% yield) as a colourless oil.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.87 – 7.83 (m, 1H), 7.58 (ddd, *J* = 8.3, 7.3, 1.7 Hz, 1H), 7.28 – 7.19 (m, 1H), 7.15 – 7.08 (m, 2H), 7.07 – 7.02 (m, 1H), 6.82 (td, *J* = 7.4, 1.1 Hz, 1H), 6.54 (dt, *J* = 8.1, 0.8 Hz, 1H), 3.90 – 3.77 (m, 1H), 3.40 (s, 3H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 184.9, 162.4, 157.0, 153.9, 137.3, 132.7, 129.5, 127.3, 125.2, 121.3, 121.0, 119.0, 117.3, 109.9, 54.2, 29.9.
^{19}F NMR (565 MHz, CDCl$_3$) δ -80.8 (t, *J* = 9.9 Hz), -107.0 – -113.8 (m), -114.5 – -118.2 (m), -119.2 – -123.8 (m), -126.1 (dt, *J* = 47.3, 14.1 Hz).

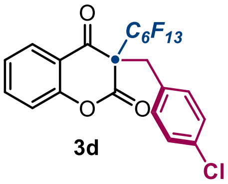
HRMS: calculated for $C_{23}H_{13}F_{13}O_4$ ($M+Na^+$): 623.0498, found 623.0504.



3c

3-(3-Methylbenzyl)-3-(perfluorohexyl)-chromane-2,4-dione (3c): Synthesized according to the General Procedure using **1a** (53 mg, 0.2 mmol, 1.0 equiv.), **2c** (268 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 99: 1 as eluent) to afford **3c** (69 mg, 58% yield) as a colourless oil.**^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.90 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.57 (ddd, *J* = 8.3, 7.3, 1.7 Hz, 1H), 7.22 (ddd, *J* = 8.1, 7.3, 1.1 Hz, 1H), 7.02 – 6.95 (m, 2H), 6.93 – 6.83 (m, 3H), 4.42 – 3.31 (m, 2H), 2.16 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 185.8, 162.6, 153.8, 138.6, 138.1, 135.0, 131.5, 131.3, 128.9, 128.7, 127.7, 127.3, 125.6, 117.6, 63.1, 39.1, 21.3. **^{19}F NMR (565 MHz, CDCl$_3$)** δ -80.8 (t, *J* = 9.8 Hz), -108.1 – -111.2 (m), -114.5 – -118.7 (m), -121.7 (ddd, *J* = 56.1, 27.9, 13.3 Hz), -122.3 – -123.7 (m), -125.1 – -127.8 (m).

HRMS: calculated for $C_{23}H_{13}F_{13}O_3$ ($M+Na^+$): 607.0549, found 607.0555.

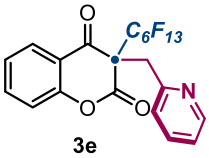


3d

3-(4-Chlorobenzyl)-3-(perfluorohexyl)-chromane-2,4-dione (3d): Synthesized according to the General Procedure using **1a** (57 mg, 0.2 mmol, 1.0 equiv.), **2d** (268 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 99: 1 as eluent) to afford **3d** (79 mg, 65% yield) as a colourless oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.62 (ddd, *J* = 8.3, 7.3, 1.7 Hz, 1H), 7.33 – 7.23 (m, 1H), 7.14 – 7.08 (m, 2H), 7.04 (dd, *J* = 8.4, 1.4 Hz, 3H), 4.13 – 3.51 (m, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 185.5, 162.4, 153.7, 138.5, 134.4, 132.3, 130.1, 129.1, 127.4, 126.0, 118.7, 117.8, 63.1, 37.9.

^{19}F NMR (565 MHz, CDCl$_3$) δ -80.8 (t, *J* = 10.0 Hz), -100.2 – -114.3 (m), -114.51 – -119.1 (m), -120.3 – -122.1 (m), -122.1 – -123.7 (m), -126.1 (dtd, *J* = 121.5, 15.6, 7.7 Hz). **HRMS:** calculated for $C_{22}H_{12}F_{13}O_3$ (M+Na$^+$): 627.0009, found 627.0009.



3e

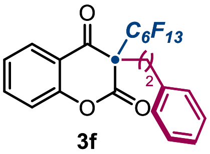
3-(Pyridin-2-ylmethyl)-3-(perfluorohexyl)-chromane-2,4-dione (3e): Synthesized according to the General Procedure using **1a** (51 mg, 0.2 mmol, 1.0 equiv.), **2e** (268 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.32 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 98: 2 as eluent) to afford **3e** (102 mg, 89% yield) as a colourless oil.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.92 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.86 (ddd, *J* = 5.0, 1.7, 1.0 Hz, 1H), 7.70 (ddd, *J* = 8.1, 7.3, 1.7 Hz, 1H), 7.58 (td, *J* = 7.7, 1.7 Hz, 1H), 7.33 – 7.25 (m, 3H), 6.98 (ddd, *J* = 7.4, 5.0, 1.1 Hz, 1H), 4.84 – 3.65 (m, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 185.2, 163.4, 154.2, 154.0, 147.3, 137.0, 136.7, 127.1, 125.0, 123.0, 121.9, 120.3, 117.6, 60.9, 39.8.

^{19}F NMR (565 MHz, CDCl$_3$) δ -80.8 (t, *J* = 9.7 Hz), -109.4 (ddtt, *J* = 40.4, 20.9, 11.2, 5.1 Hz), -115.7 – -120.1 (m), -121.4 (t, *J* = 18.3 Hz), -122.7 (dddq, *J* = 19.9, 15.1, 10.2, 5.5 Hz), -126.1 (dt, *J* = 41.9, 14.0 Hz).

HRMS: calculated for $C_{21}H_{10}F_{13}N_1O_3$ (M+Na$^+$): 594.0345, found 594.0351.



3f

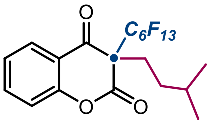
3-Phenethyl-3-(perfluorohexyl)-chromane-2,4-dione (3f): Synthesized according to the General Procedure using **1a** (53 mg, 0.2 mmol, 1.0 equiv.), **2f** (268 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 98: 2 as eluent) to afford **3f** (80 mg, 68% yield) as a colourless oil.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.98 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.74 (ddd, *J* = 8.4, 7.3, 1.7 Hz, 1H), 7.43 – 7.30 (m, 2H), 7.25 – 7.20 (m, 2H), 7.19 – 7.14 (m, 1H), 7.13 – 7.07 (m, 2H), 2.95 (td, *J* = 12.2, 5.4 Hz, 1H), 2.78 (ddd, *J* = 12.8, 11.7, 4.7 Hz, 1H), 2.60 – 2.53 (m, 1H), 2.50 – 2.39 (m, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 185.4, 162.8, 154.3, 138.9, 138.4, 128.8, 128.7, 127.7, 127.0, 125.9, 119.0, 117.9, 62.2, 35.0, 30.6.

^{19}F NMR (565 MHz, CDCl$_3$) δ -80.8 (t, *J* = 10.1 Hz), -108.8 – -111.9 (m), -116.2 – -119.0 (m), -120.6 – -121.9 (m), -122.1 – -123.6 (m), -126.1 (dt, *J* = 98.1, 16.0 Hz).

HRMS: calculated for $C_{23}H_{13}F_{13}O_3$ (M+Na$^+$): 607.0549, found 607.0555.

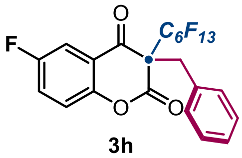


3g

3-Isopentyl-3-(perfluorohexyl)-chromane-2,4-dione (3g): Synthesized according to the General Procedure using **1a** (46 mg, 0.2 mmol, 1.0 equiv.), **2g** (268 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 99: 1 as eluent) to afford **3g** (97 mg, 88% yield) as a colourless oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.74 (ddd, *J* = 8.8, 7.4, 1.7 Hz, 1H), 7.35 (td, *J* = 7.7, 1.1 Hz, 1H), 7.29 – 7.22 (m, 1H), 2.85 – 2.53 (m, 1H), 2.46 (td, *J* = 12.5, 4.3 Hz, 1H), 1.15 – 1.01 (m, 1H), 0.87 – 0.84 (m, 6H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 185.9, 163.1, 154.3, 138.3, 127.6, 125.9, 119.0, 118.0, 62.2, 32.8, 29.9, 28.4, 22.2, 22.2.
^{19}F NMR (565 MHz, CDCl$_3$) δ -80.8 (t, *J* = 10.0 Hz), -109.3 – -111.7 (m), -116.5 – -118.7 (m), -121.7 (ddd, *J* = 37.0, 25.2, 12.8 Hz), -122.0 – -123.6 (m), -125.1 – -127.1 (m).

HRMS: calculated for $C_{20}H_{15}F_{13}O_3$ (M+Na$^+$): 573.0706, found 573.0711.

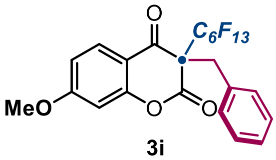


3h

3-Benzyl-6-fluoro-3-(perfluorohexyl)-chromane-2,4-dione (3h): Synthesized according to the General Procedure using **1a** (54 mg, 0.2 mmol, 1.0 equiv.), **2h** (268 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 99: 1 as eluent) to afford **3h** (85 mg, 72% yield) as a pale-yellow liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53 (dd, *J* = 7.6, 3.1 Hz, 1H), 7.33 – 7.25 (m, 1H), 7.17 – 7.11 (m, 3H), 7.10 – 7.06 (m, 2H), 7.00 (dd, *J* = 9.0, 4.0 Hz, 1H), 4.08 – 3.50 (m, 2H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 185.2, 160.2, 158.6, 149.8, 131.1, 130.8, 129.0, 128.4, 125.7, 125.5, 119.7, 112.8, 77.4, 76.9, 68.1, 39.3.
^{19}F NMR (565 MHz, CDCl$_3$) δ -80.8 (t, *J* = 9.7 Hz), -106.5 – -112.0 (m), -113.1 – -115.5 (m), -115.7 – -118.1 (m), -121.2 – -122.2 (m), -122.3 – -123.3 (m), -124.8 – -127.7 (m).

HRMS: calculated for $C_{22}H_{10}F_{14}O_3$ (M+Na$^+$): 611.0304, found 611.0304.

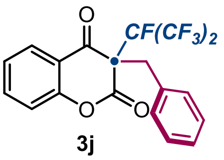


3i

3-Benzyl-7-methoxy-3-(perfluorohexyl)-chromane-2,4-dione (3i): Synthesized according to the General Procedure using **1a** (56 mg, 0.2 mmol, 1.0 equiv.), **2i** (268 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 99: 1 as eluent) to afford **3i** (84 mg, 70% yield) as a colourless oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, *J* = 8.9 Hz, 1H), 7.18 – 7.06 (m, 5H), 6.73 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.40 (d, *J* = 2.3 Hz, 1H), 3.92 (d, *J* = 12.3 Hz, 1H), 3.82 (s, 3H), 3.71 (d, *J* = 12.5 Hz, 1H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 207.1, 167.5, 162.9, 155.8, 131.7, 130.8, 129.3, 128.8, 128.1, 113.6, 112.5, 101.1, 62.6, 56.2, 31.1.
^{19}F NMR (376 MHz, CDCl$_3$) δ -80.7 – -81.0 (m), -109.9 – -110.4 (m), -117.4 (dtd, *J* = 53.5, 16.6, 8.8 Hz), -121.6 – -121.8 (m, *J* = 44.9 Hz), -122.1 – -123.4 (m), -125.3 – -126.9 (m).

HRMS: calculated for $C_{23}H_{13}F_{13}O_4$ (M+Na$^+$): 623.0498, found 623.0504.

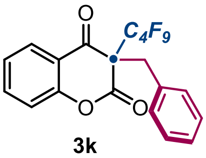


3j

3-Benzyl-3-(perfluoroisopropyl)-chromane-2,4-dione (3j): Synthesized according to the General Procedure using **1a** (50 mg, 0.2 mmol, 1.0 equiv.), **2j** (178 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 99: 1 as eluent) to afford **3j** (35 mg, 41% yield) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (ddd, *J* = 7.9, 1.8, 0.4 Hz, 1H), 7.56 (ddd, *J* = 8.3, 7.3, 1.7 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.15 – 7.03 (m, 5H), 7.01 – 6.94 (m, 1H), 4.07 – 3.75 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 207.6, 186.6, 162.9, 153.5, 138.1, 131.7, 131.3, 128.8, 128.1, 127.4, 1257, 118.7, 117.4, 77.4, 62.5, 39.9, 30.3.
^{19}F NMR (565 MHz, $CDCl_3$) δ -68.6 (td, *J* = 11.1, 6.0 Hz), -69.1 (qd, *J* = 11.1, 5.8 Hz), -177.8 (p, *J* = 6.0 Hz).

HRMS: calculated for $C_{19}H_{11}F_7O_3$ (M+Na$^+$): 443.0409, found 443.0494.

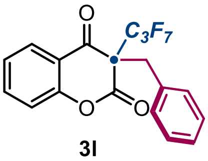


3k

3-Benzyl-3-(perfluorobutyl)-chromane-2,4-dione (3k): Synthesized according to the General Procedure using **1a** (50 mg, 0.2 mmol, 1.0 equiv.), **2k** (208 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 99: 1 as eluent) to afford **3k** (72 mg, 77% yield) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.57 (ddd, *J* = 8.3, 7.3, 1.7 Hz, 1H), 7.22 (ddd, *J* = 8.1, 7.3, 1.1 Hz, 1H), 7.17 – 7.05 (m, 5H), 6.99 (dd, *J* = 8.3, 1.0 Hz, 1H), 3.94 – 3.37 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 207.5, 185.7, 162.5, 153.7, 138.2, 131.4, 130.8, 128.9, 128.2, 127.4, 125.7, 118.8, 118.7, 117.7, 63.0, 39.0.
^{19}F NMR (565 MHz, $CDCl_3$) δ -80.8 (t, *J* = 9.7 Hz), -109.1 – -111.7 (m), -116.6 – -119.4 (m), -124.8 – -126.9 (m).

HRMS: calculated for $C_{20}H_{11}F_9O_3$ (M+Na$^+$): 493.0457, found 493.0462.

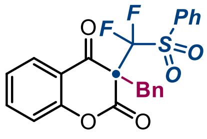


3l

3-Benzyl-3-(perfluoropropyl)-chromane-2,4-dione (3l): Synthesized according to the General Procedure using **1a** (50 mg, 0.2 mmol, 1.0 equiv.), **2l** (178 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 99: 1 as eluent) to afford **3l** (48 mg, 57% yield) as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.57 (ddd, *J* = 8.3, 7.3, 1.7 Hz, 1H), 7.22 (ddd, *J* = 8.1, 7.4, 1.0 Hz, 1H), 7.16 – 7.07 (m, 5H), 6.99 (dd, *J* = 8.3, 1.0 Hz, 1H), 4.79 – 3.01 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 185.7, 162.5, 153.8, 138.2, 131.5, 130.8, 128.9, 128.2, 127.4, 125.7, 118.8, 117.6, 63.0, 38.8.
^{19}F NMR (565 MHz, $CDCl_3$) δ -75.6 – -88.1 (m), -107.3 – -112.1 (m), -119.5 – -123.7 (m).

HRMS: calculated for $C_{19}H_{11}F_7O_3$ (M+Na$^+$): 443.0489, found 443.0494.

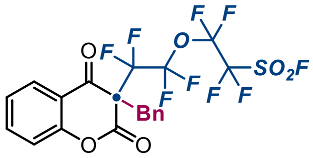


3m

3-Benzyl-3-(difluoro(phenylsulfonyl)methyl) -chromane-2,4-dione (3m): Synthesized according to the General Procedure using **1a** (50 mg, 0.2 mmol, 1.0 equiv.), **2m** (191 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 98: 2 as eluent) to afford **3m** (28 mg, 32% yield) as a white semi-solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (ddd, *J* = 8.1, 6.0, 1.6 Hz, 3H), 7.82 – 7.74 (m, 1H), 7.66 – 7.59 (m, 2H), 7.55 (ddd, *J* = 8.6, 7.3, 1.7 Hz, 1H), 7.22 (ddd, *J* = 8.3, 7.3, 1.0 Hz, 1H), 7.15 – 7.07 (m, 5H), 7.00 (dd, *J* = 8.3, 1.0 Hz, 1H), 4.42 – 3.17 (m, 2H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 186.0, 163.0, 154.0, 137.7, 136.1, 132.1, 131.6, 131.3, 131.0, 130.7, 129.7, 129.6, 128.8, 128.2, 127.4, 125.4, 117.6, 62.6, 39.9.
^{19}F NMR (565 MHz, CDCl$_3$) δ -95.88 (d, *J* = 226.9 Hz), -99.02 (d, *J* = 226.9 Hz).

HRMS: calculated for $C_{23}H_{16}F_2O_5S$ (M+Na$^+$): 465.0579, found 465.0584.

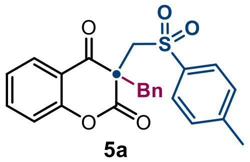


3n

3-Benzyl-3-(1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoroethoxy) ethane-1-sulfonylfluoride)-chromane-2,4-dione (3n): Synthesized according to the General Procedure using **1a** (50 mg, 0.2 mmol, 1.0 equiv.), **2n** (256 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 99: 1 as eluent) to afford **3n** (68 mg, 62% yield) as a colourless oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.59 (dddd, *J* = 8.2, 7.3, 1.8, 0.8 Hz, 1H), 7.23 (ddd, *J* = 8.1, 7.3, 1.0 Hz, 1H), 7.18 – 7.02 (m, 5H), 7.00 (dd, *J* = 8.3, 1.0 Hz, 1H), 4.60 – 3.08 (m, 2H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 185.5, 162.2, 153.8, 138.4, 131.7, 130.8, 129.0, 128.9, 128.2, 127.5, 125.8, 118.6, 118.6, 117.7, 63.0, 38.7.
^{19}F NMR (565 MHz, CDCl$_3$) δ 51.4 – 38.0 (m), -63.0 – -91.3 (m), -111.9, -112.2 – -117.2 (m).

HRMS: calculated for $C_{20}H_{11}F_9O_6S$ (M+Na$^+$): 573.0025, found 573.0031.

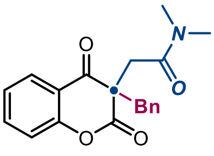


5a

3-Benzyl-3-(tosylmethyl)-chromane-2,4-dione (5a): Synthesized according to the General Procedure using **1a** (50 mg, 0.2 mmol, 1.0 equiv.), 1-((iodomethyl)sulfonyl)-4-methylbenzene **4a** (178 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 98: 2 as eluent) to afford **5a** (74 mg, 88% yield) as a white solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.88 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.84 – 7.79 (m, 1H), 7.73 – 7.63 (m, 1H), 7.53 – 7.47 (m, 1H), 7.39 – 7.30 (m, 3H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.08 – 7.02 (m, 2H), 6.98 – 6.90 (m, 3H), 4.53 – 3.98 (m, 2H), 3.14 (q, *J* = 12.9 Hz, 2H), 2.44 (s, 3H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 191.6, 168.9, 145.1, 138.1, 137.2, 131.7, 130.1, 129.9, 129.8, 128.5, 128.2, 127.9, 127.5, 127.0, 125.0, 117.5, 62.9, 60.1, 46.4, 21.8.

HRMS: calculated for $C_{24}H_{20}O_5S$ (M+Na$^+$): 443.0924, found 443.0929.

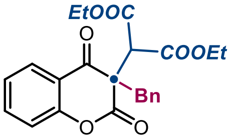


5b

2-(3-benzyl-2,4-dioxo-3-chroman-3-yl)-N,N-dimethylacetamide (5b): Synthesized according to the General Procedure using **1a** (50 mg, 0.2 mmol, 1.0 equiv.), 2-bromo-N,N-dimethylacetamide **4b** (100 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 70: 30 as eluent) to afford **5b** (37 mg, 55% yield) as a colourless oil liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.79 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.40 (ddd, *J* = 8.3, 7.2, 1.7 Hz, 1H), 7.14 – 7.06 (m, 1H), 7.05 – 7.00 (m, 3H), 6.99 – 6.92 (m, 2H), 6.87 (dd, *J* = 8.4, 1.1 Hz, 1H), 3.68 – 3.34 (m, 2H), 3.16 (s, 2H), 3.05 (s, 3H), 2.83 (s, 3H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 194.4, 171.3, 169.7, 154.4, 136.3, 133.3, 129.7, 128.3, 127.7, 126.5, 124.4, 119.7, 117.3, 59.4, 44.9, 43.4, 37.4, 35.6.

HRMS: calculated for $C_{20}H_{19}NO_4$ (M+Na$^+$): 360.1206, found 360.1212.



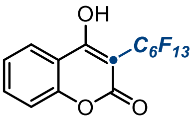
5c

Diethyl-2-(3-benzyl-2,4-dioxo-3-chroman-3-yl)malonate (5c): Synthesized according to the General Procedure using **1a** (50 mg, 0.2 mmol, 1.0 equiv.), diethyl bromomalonate **4c** (143 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (Hexane: EtOAc = 98: 2 as eluent) to afford **5c** (37 mg, 45% yield) as a pale-yellow liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.79 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.46 (ddd, *J* = 8.3, 7.3, 1.7 Hz, 1H), 7.14 (td, *J* = 7.6, 1.0 Hz, 1H), 7.09 – 6.99 (m, 5H), 6.91 (dd, *J* = 8.3, 1.1 Hz, 1H), 4.34 (s, 1H), 4.31 – 4.22 (m, 4H), 3.69 – 3.42 (m, 2H), 1.28 (td, *J* = 7.2, 4.7 Hz, 6H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 192.76, 169.25, 168.31, 168.19, 154.20, 136.94, 132.85, 130.14, 128.36, 127.87, 126.86, 124.86, 119.20, 117.29, 62.69, 62.44, 62.40, 56.60, 43.74, 13.99.

HRMS: calculated for $C_{23}H_{22}O_7$ (M+Na$^+$): 433.1258, found 433.1263.

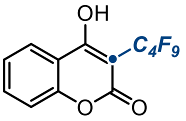
Note: The synthesized compounds **7a-d**, derived from unsubstituted 4-hydroxycoumarin **6**, were found to be unstable on silica. Therefore, the reactions leading to these compounds were quenched, and given the complete conversion of the products, no chromatography was performed. Instead, an aqueous workup and extraction were carried out, delivering pure fluorinated products **7a-d** in high yields.



7a

3-(perfluorohexyl)-4-hydroxycoumarin (7a): Synthesized according to the General Procedure using **6a** (32 mg, 0.2 mmol, 1.0 equiv.), perfluorohexyl iodide **2a** (268 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). After the reaction was completed, the reaction mixture was transferred to an extraction funnel, 10 mL of H_2O and 2 mL of brine were added, and the organic layer was extracted with EtOAc. The organic layer was washed with brine twice. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness to get product **7a** (89 mg, 93% yield) as a sticky yellow solid.

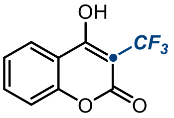
^{1}H NMR (400 MHz, MeOD) δ 7.97 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.3, 7.2, 1.7 Hz, 1H), 7.26 – 7.13 (m, 2H).
^{13}C NMR (101 MHz, MeOD) δ 177.8, 165.4, 155.1, 133.2, 126.4, 124.1, 123.5, 117.0, 89.7.
^{19}F NMR (376 MHz, MeOD) δ -82.5 (t, *J* = 10.1 Hz), -105.9 – -106.2 (m), -122.5, -123.7 (tdd, *J* = 14.1, 6.7, 3.4 Hz), -127.0 – -127.6 (m).
HRMS: calculated for $C_{15}H_5F_{13}O_3$ (M+Na$^+$): 502.9923, found 502.9929.



7b

3-(perfluorobutyl)-4-hydroxycoumarin (7b): Synthesized according to the General Procedure using **6b** (32 mg, 0.2 mmol, 1.0 equiv.), perfluorobutyl iodide **2k** (208 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). After the reaction was completed, the reaction mixture was transferred to an extraction funnel, 10 mL of H_2O and 2 mL of brine were added, and the organic layer was extracted with EtOAc. The organic layer was washed with brine twice. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness to get product **7b** (73 mg, 96% yield) as a sticky yellow solid.

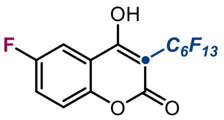
^{1}H NMR (400 MHz, MeOD) δ 7.97 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.50 (ddd, *J* = 8.2, 7.2, 1.7 Hz, 1H), 7.26 – 7.13 (m, 2H).
^{13}C NMR (151 MHz, DMSO) δ 173.4, 160.7, 153.6, 131.3, 125.1, 122.6, 122.1,115.5, 85.2.
^{19}F NMR (376 MHz, MeOD) δ -82.5 (ddd, *J* = 13.2, 6.5, 2.9 Hz), -105.7 (ddt, *J* = 16.5, 14.0, 2.9 Hz), -123.7 (ddt, *J* = 12.5, 10.0, 4.8 Hz), -127.2 – -127.4 (m).
HRMS: calculated for $C_{13}H_5F_9O_3$ (M+Na$^+$): 402.9987, found 402.9993.



7c

3-(trifluoromethyl)-4-hydroxycoumarin (7c): Synthesized according to the General Procedure with some modification, using **6c** (32 mg, 0.2 mmol, 1.0 equiv.) and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.) were taken in a Schlenk tube and degassed 3 times with argon. Then 1ml dry CH_3CN was added and the Schlenk tube was cooled using a liquid nitrogen bath. After that trifluoromethyl iodide **2c** (117 mg, 0.6 mmol, 3.0 equiv.) was added via syringe. Once addition of trifluoromethyl iodide was over, the Schlenk tube was placed under the irradiation of 390 nm *Kessil* lamp with PhotoRedOx Box TC™ reactor for 4 hours. After the reaction was completed, the reaction mixture was transferred to an extraction funnel, 10 mL of H_2O and 2 mL of brine were added, and the organic layer was extracted with EtOAc. The organic layer was washed with brine twice. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness to get product **7c** (72 mg, 79% yield) as a sticky yellow solid.

^{1}H NMR (400 MHz, DMSO) δ 7.83 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.43 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H), 7.17 – 7.05 (m, 2H).
^{13}C NMR (101 MHz, DMSO) δ 172.9, 160.7, 153.6, 131.4, 125.1, 122.6, 122.2, 115.6, 87.9.
^{19}F NMR (376 MHz, DMSO) δ -52.9.
HRMS: calculated for $C_{10}H_5F_3O_3$ (M$^+$): 230.0191, found 230.0113.



7d

3-(perfluorohexyl)-6-fluoro-4-hydroxycoumarin (7d): Synthesized according to the General Procedure using **6d** (36 mg, 0.2 mmol, 1.0 equiv.), perfluorohexyl iodide **2a** (268 mg, 0.6 mmol, 3.0 equiv.), and cesium carbonate (130 mg, 0.4 mmol, 2.0 equiv.). After the reaction was completed, the reaction mixture was transferred to an extraction funnel, 10 mL of H_2O and 2 mL of brine were added, and the organic layer was extracted with EtOAc. The organic layer was washed with brine twice. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness to get product **7d** (98 mg, 98% yield) as a sticky red solid.

^{1}H NMR (400 MHz, DMSO) δ 7.47 (dd, *J* = 9.0, 3.2 Hz, 1H), 7.28 (ddd, *J* = 8.9, 8.2, 3.2 Hz, 1H), 7.14 (dd, *J* = 8.9, 4.4 Hz, 1H).
^{13}C NMR (101 MHz, DMSO) δ 172.3, 160.6, 158.8, 156.4, 149.8, 123.9, 118.4, 117.5, 110.2, 85.5.
^{19}F NMR (376 MHz, DMSO) δ -80.58 (tt, *J* = 9.6, 2.7 Hz), -102.97 (tt, *J* = 13.8, 3.7 Hz), -121.08 (td, *J* = 8.6, 4.6 Hz), -121.48 (ddd, *J* = 21.5, 11.4, 4.9 Hz), -121.98 (t, *J* = 15.1 Hz), -122.53 – -122.75 (m), -126.02 (td, *J* = 13.8, 5.6 Hz).
HRMS: calculated for $C_{15}H_4F_{14}O_3$ (M+Na$^+$): 520.9829, found 520.9835.

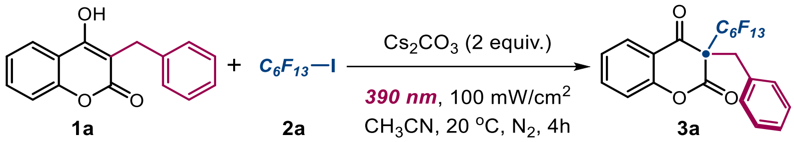
D3. Gram scale synthesis

- ***Set-up 2*** Gram scale experiment (Figure S4)

The gram scale reaction was performed using an PhotoRedOx Box TC™ reactor with 390 nm *Kessil lamp* (max 52W, λ_{max}= 390 nm, 2-3 cm away from the vial), and a fan to cool down the temperature.

Figure S4. Setup for the gram-scale experiment using PhotoRedOx Box TC™ reactor with 390 nm *Kessil lamp*

General Procedure for the gram scale synthesis of 3a



To a 100 mL Schlenk tube, 3-benzyl-4-hydroxycoumarin **1a** (1.01g, 4 mmol, 1.0 equiv.) and Cs_2CO_3 (2.6g, 8 mmol, 2 equiv.) were sequentially added. The vial was sealed with a screw-top cap with septum and then vacuumed and backfilled with nitrogen for 3 times. Afterwards, perfluorohexyl iodide **2a** (5.4 g, 12 mmol, 3 equiv.), followed by argon-sparged CH_3CN (0.2M, 20 mL) were added *via* syringe. The vial was sealed with Parafilm and then stirred under the irradiation of 390 nm *Kessil* lamp with PhotoRedOx Box TC™ reactor for 4 hours using ***Set-up 2*** detailed in **Figure S3** After the reaction was completed, the reaction mixture was transferred to an extraction funnel, 20 mL of H_2O and 10 mL of brine were added, and the organic layer was extracted with EtOAc. The organic layer was washed with brine twice. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The crude residue was purified by column chromatography to afford the corresponding product **3a** (1.1 g, 50% yield) as a colourless oil liquid.

E. Photophysical Studies

Sample Preparation:

Three 25 mL glass vials, each containing either **1a**, **2a**, or a mixture of **1a** and Cs_2CO_3, were sealed with septa, degassed, and then dry CH_3CN (20 mL) was added to each vial to prepare 0.1 M solutions. From these stock solutions, **1a** (10^{-4} M), **2a** (10^{-4} M), and **1a** with Cs_2CO_3 (10^{-4} M) were prepared accordingly. Then, 2.5 mL of each solution was transferred into an argon-filled quartz cuvette (10 x 10 mm light path) equipped with a septum.

E1. UV-Absorption Studies

UV-Vis measurements were carried out on an Cary 3500 Multicell UV-Vis spectrophotometer equipped with two silicon diode detectors, double beam optics and Xenon pulse light (Figure S5).

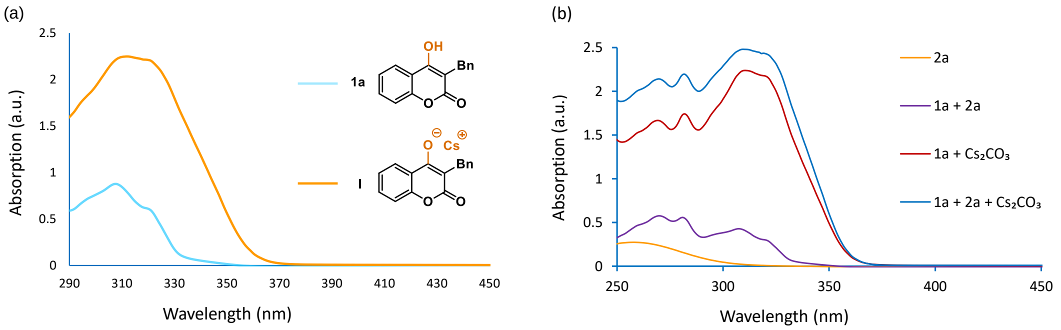


Figure S5. (a) Absorption spectra recorded for **1a** (10-4 M; blue line) and **Ia** (in situ generated mixing **1a** with Cs_2CO_3; red line) measured in CH_3CN. (b) All samples in CH3CN. *Yellow line*: [**2a**] = 10^{-4} M; *purple line*: [**1a**] = 10^{-4} M and [**2a**] =3. 10^{-4} M; *red line*: [**1a**] = 10^{-4} M and [Cs2CO3] = 2x10^{-4} M; and *blue line*: [**1a**] = 1x10^{-4} M, [**2a**] = 3x10^{-4} M, and [Cs2CO3] = 2x10^{-4} M.

E2. Emission Studies

Fluorescence measurements were carried out on an Edinburgh FLSP920 spectrometer equipped with a 450 W xenon arc lamp, double excitation and single emission monochromators, and a Peltier-cooled Hamamatsu R928P photomultiplier tube (185–850 nm). The emission spectrum of the deprotonated substrate **Ia** (formed in situ form **1a** upon addition of Cs_2CO_3 in degassed CH_3CN according to the same procedure mentioned before) was recorded from 320 nm to 600 nm after excitation with a 314 nm laser (Figure S6).

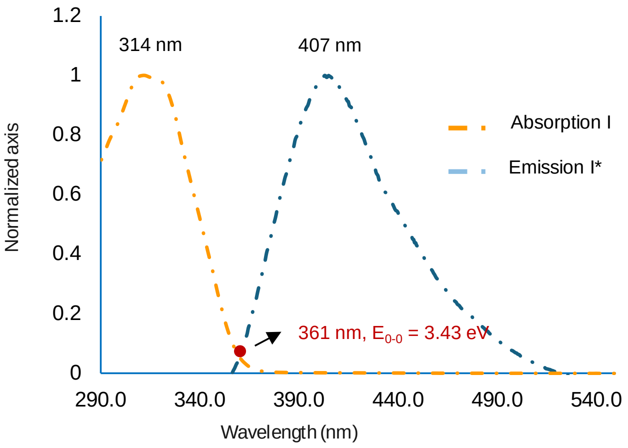


Figure S6. Stern-Volmer quenching studies of the photoactive species **Ia** (formed upon deprotonation of **1a**) in CH_3CN using **2a** as quencher.

E3. Stern-Volmer quenching studies

Fluorescence measurements were carried out on an Edinburgh FLSP920 spectrometer equipped with a 450 W xenon arc lamp, double excitation and single emission monochromators. A 0.025 M solution of the quencher substrate (**2a**) in degassed CH_3CN (HPLC grade) was prepared and 20 μL of this stock solution were added to the solution of the deprotonated photoactive species **Ia**, prepared according to the procedure detailed at the beginning of section E. The addition of the substrate solution **2a** was repeated for four times. After each addition, the solution was mixed and the emission spectra of the excited catalyst was acquired from 320 nm to 600 nm (the excitation wavelength was fixed at 314 nm). A solvent blank was subtracted from all the measurements. The excitation wavelength was chosen in order to avoid saturation of the emission detector.

The results shown in Figure S6 indicates that all substrates quenched the excited state emission of the deprotonated substrate **Ia**. The Stern-Volmer plot shows a linear correlation between the amounts of substrates and the ratio I_0/I, following the relationship: $I_0/I = 1 + KSV[Q]$ (Q = Quencher) (Figure S7).

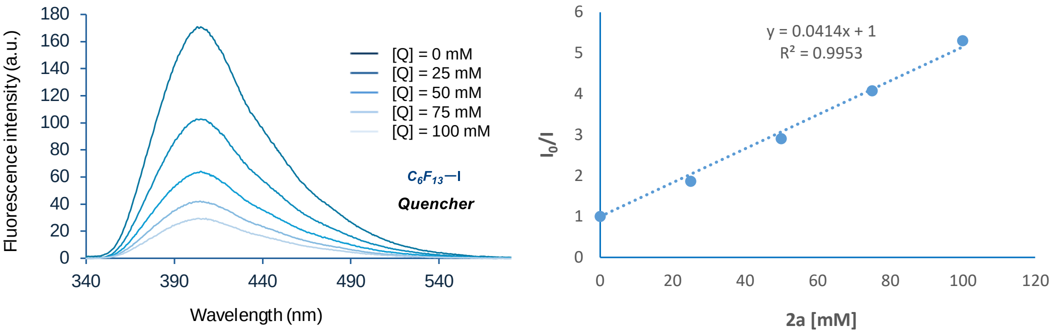


Figure S7. Stern-Volmer quenching studies using perfluorohexyl iodide (**2a**) as the quencher Q

E4. Electrochemical Studies

Cyclic voltammetry (CV) measurements were carried out on a CHI660C instrument with a glassy carbon disk electrode (diameter: 3 mm) as working electrode. A silver wire coated with AgCl immersed in a 3.0 M aqueous solution of KCl and separated from the analyte by a fritted glass disk was employed as the reference electrode and a Pt wire counter-electrode completed the electrochemical setup. The scan rate was 100 mV/s unless otherwise stated. The substrates were measured at concentration of 0.02 M in CH_3CN with $TBAPF_6$ (0.1 M) as electrolyte. The deprotonated substrate **Ia** was at a concentration of 0.02 M. Potentials are quoted with the following notation: E_p^C (E_{Red}) refers to the cathodic peak potential, E_p^A (E_{Ox}) refers to the anodic peak potential (Figure S8 and S9).

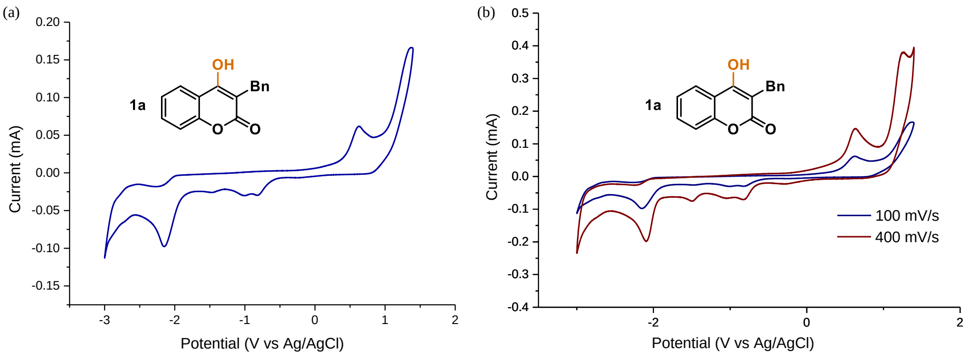


Figure S8: (left) CV of the 4-hydroxycoumarin substrate **1a** in CH_3CN starting with the oxidation, reversible oxidation and reduction, E_p^A = 0.61 V and E_p^C = -2.13 V; (right) CV of **1a** in CH_3CN starting with the oxidation with a sweep rates of 100 and 400 mV/s.

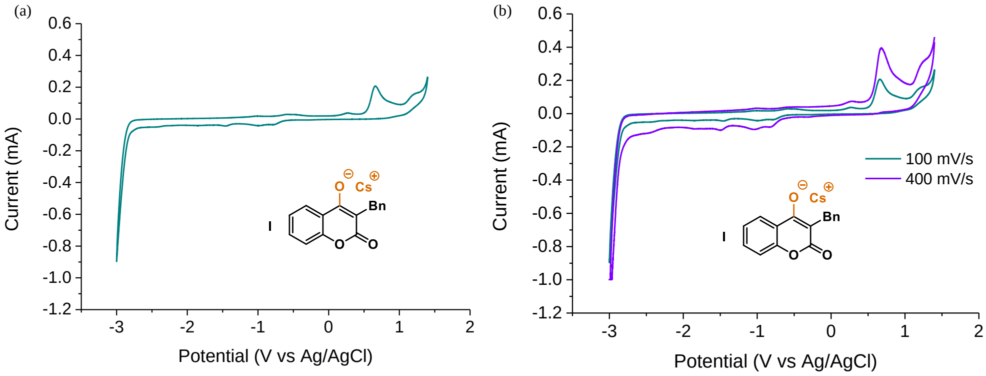


Figure S9. (left) CV of the in situ deprotonated species **Ia** in CH_3CN starting with the oxidation, reversible oxidation and reduction, E_p^A = 0.66 V and E_p^C = -2.44 V; (right) CV of **Ia** in CH_3CN starting with the oxidation with a sweep rates of 100 and 400 mV/s.

E4.1. Conversion of the potential from Ag/AgCl to SCE

The conversion of the redox potential from Ag/AgCl to SCE was done according to the literature by measuring the redox potential of ferrocene as reference in CH_3CN (Figure S10).[3]

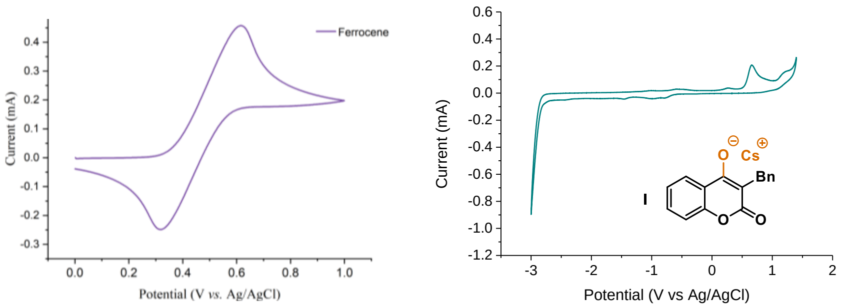


Figure S10. (left) CV of ferrocene in CH_3CN, reversible reduction and oxidation $E_{1/2}$ = 0.46 V. (right) CV of deprotonated substrate **Ia** in CH_3CN, reversible oxidation E_p^A = 0.66 V.

With the reference CV, the redox potential *vs.* SCE in CH_3CN was calculated using the following equations:

$$E_p^A\,(\text{Ag/AgCl to Fc/Fc}^+) = 0.66 - 0.46 = 0.20\ \text{V}\ vs.\ \text{Fc/Fc}^+$$
$$E_p^A\ (\text{Fc/Fc}^+\ \text{to SCE}) = 0.20 + 0.38 = 0.58\ \text{V}\ vs.\ \text{SCE}$$

E4.2. Evaluation of the excited-state potential of the excited deprotonated substrate 1a

Using the data collected from the CV studies (**Figure S7-S9**) and from the absorption and emission spectra (**Figure S5**) of deprotonated substrate **Ia**, we could estimate the redox potential of the excited state with the following Equation:[4]

$$\mathrm{E}(\mathbf{Ia}^{\bullet+}/\ \mathbf{Ia}^{*}) = \mathrm{E}(\mathbf{Ia}^{\bullet+}/\ \mathbf{Ia}) - \mathrm{E}_{0\text{-}0}(\mathbf{Ia}^{*})/(\ \mathbf{Ia})$$

Since the electrochemical oxidation of deprotonated substrate **Ia** is reversible (**Figure S8**), the reversible peak potential E_p anode was used for $E(Pc^{\bullet+}/Pc)$. The oxidation potential was calculated to be 0.58 V *vs.* SCE (in ACN). $E_{0\text{-}0}(\mathbf{Ia}^{*})/(\mathbf{Ia})$ was approximately determined spectroscopically from the tail of absorption spectrum (roughly at 314 nm for deprotonated substrate **Ia**) to have values of 3.43 eV.

The oxidation potential of the excited **Ia***:

$$E(\mathbf{Ia}^{\bullet+}/\,\mathbf{Ia}^{*}) = 0.66 - 3.43 = \boldsymbol{\mathit{-2.77\ V\ vs.\ Ag/AgCl}}$$

$$E(\mathbf{Ia}^{\bullet+}/\,\mathbf{Ia}^{*}) = 0.58 - 3.43 = \boldsymbol{\mathit{-2.85\ V\ vs.\ SCE}}$$

E5. Time-resolved Emission Decay

Emission lifetimes (τ) were determined with the single photon counting technique (TCSPC) with the same Edinburgh FLSP920 spectrometer using pulsed picosecond LED (EPLED 365, FWHM < 800ps) as the excitation source, with repetition rates between 1 kHz and 1 MHz, and the above-mentioned R928P PMT as detector. The goodness of fit was assessed by minimizing the reduced $\chi 2$ function and by visual inspection of the weighted residuals (Figure S11).

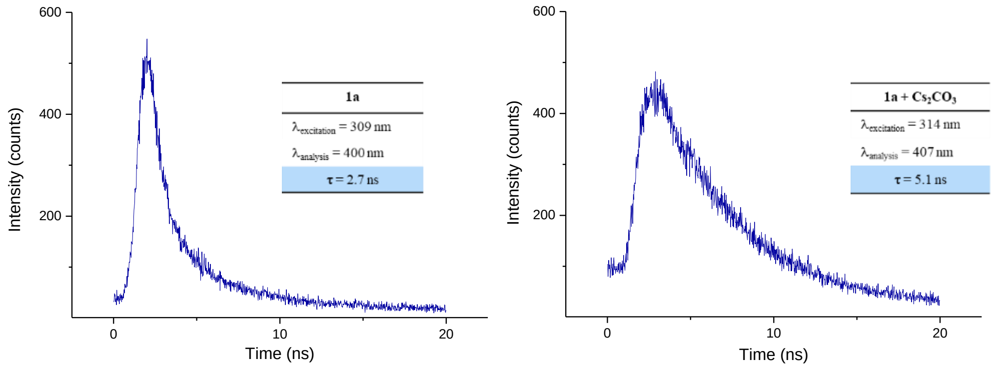


Figure S11. (left) Time-resolved emission decay (excitation at 309 nm, analysis at 400 nm) of **1a** ($1 \cdot 10^{-4}$ M) in CH_3CN solution measured by TC-SPC (τ = 2.7 ns, from deconvolution and single-exponential fitting, X^2= 1.319) (right) Time-resolved emission decay (excitation at 314 nm, analysis at 407 nm) of **1a** with Cs_2CO_3 ($1 \cdot 10^{-4}$ M) in CH_3CN solution measured by TC-SPC (τ = 5.1 ns, from deconvolution and single-exponential fitting, X^2= 1.047).

E6. Quantum Yield Determination

-Experimental Setup

The experiments for the quantum yield determination were conducted under illumination by a 390 Kessil lamp (setup depicted in Figure S12), using a 3D printed photoreactor. The intensity was fixed to the maximum value.

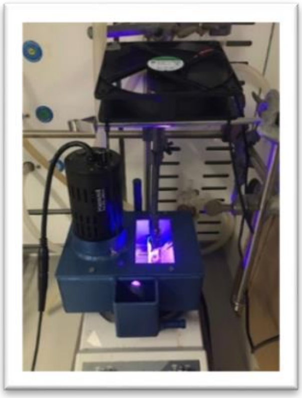


Figure S12. Kessil lamp set-up for the quantum yield determination

General Procedure for photon Flux (F) determination:[5]

$$\textbf{(1)} \quad \Phi = M / (F \bullet t \bullet f)$$

$$\textbf{(2)} \quad f = 1\text{-}10^{-A}$$

M is the moles of product formed (mol), **F** is the number of photons emitted per second (einstein s−1), **t** is the time (s) and **f** is fraction of light absorbed which can be calculated using eq. 2, where **A** is the measured absorbance at 390 nm.

The number of photons emitted per second was determined using azobenzene as actinometer.[6-7] Using the reaction setup depicted in Figure S11, a glass vial was filled with a solution of Z-azobenzene (0.1 mmol) in CD_3OD (0.1M) and irradiated at 390 nm. The trans-cis isomerization was monitored by ^{1}H-NMR using dibromomethane as internal standard (Figure S13**)**.

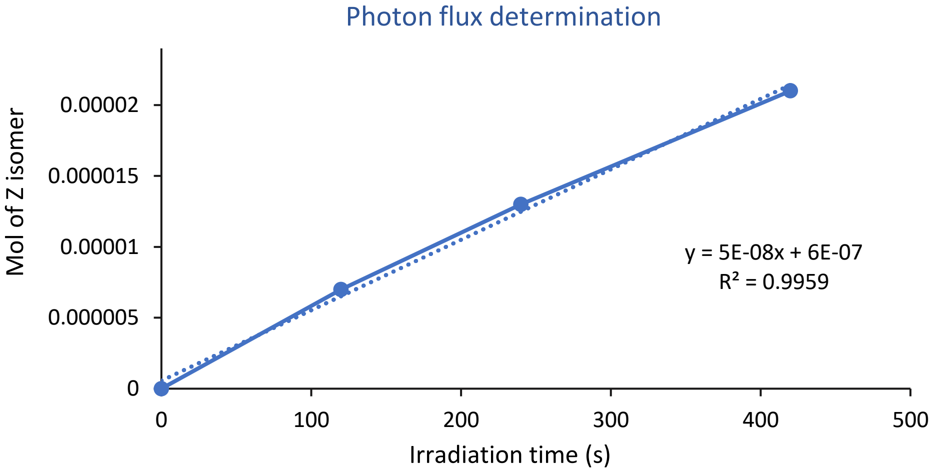


Figure S13. Plot of moles of *cis*-azobenzene formed vs irradiation time (s)

The actinometer solution was irradiated for 0 min, 2 min, 4 min, and 7 min. According to the eq. (**1**), (**2**) and estimated quantum yield of trans-cis isomerization process at 390 nm (Φ = 0.262), the number of photons emitted per time unit (**F**) was determined (2.08 x 10^{-8} mol s^{-1}).

Quantum Yield Determination:

Following the general procedure, three model perfluoroalkylation reactions between **1a**, and **2a** using Cs_2CO_3 were performed separately. Each reaction mixture was irradiated for 0 min, 3 min, 6 min, 9 min and 12 min. After irradiation reactions were worked up and the amount of product **3a** formed was determined by ^{1}H NMR analysis of the crude using dibromomethane as the internal standard. Fraction of light absorbed *f* was recognized as 1. The moles of the formed product **3a** are plotted against the number of incident photons (Figure S14). The quantum yield was calculated to be $\Phi = 8.4$ based on the slope and eq. (**1**), (**2**).

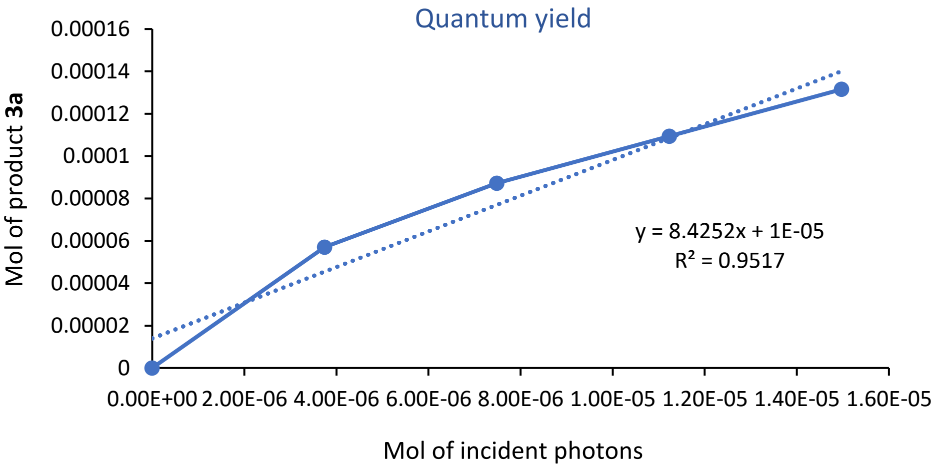


Figure S14. Plot of moles of incident photons vs moles of product **3a** formed.

E. Flow photocatalysis

-Experimental Setup

Figure S15 details a schematic representation of the photoflow catalysis setup. In this setup, a 4 mL glass vial containing **1a** (0.2 mmol, 1 equiv.) and tetramethyl guanidine (0.2 mmol, 1 equiv.) was sealed with a screw-top cap with a septum, then evacuated and backfilled with argon three times. Next, electrophilic radical precursors **2** (0.6 mmol, 3 equiv.) were added, followed by 2 mL of argon-sparged CH_3CN via syringe. The resulting solution was drawn into a 5 mL syringe, which was then connected to a flow reactor equipped with two 390 nm Kessil lamps. The temperature of the photoreactor was maintained at 20 °C using a temperature controller connected to an external chiller. The syringe pump delivered the solution at a flow rate of 0.5 mL/min for 10 minutes, and the crude product mixture was collected in a separate vial.

After the reaction, the mixture was transferred to an extraction funnel, and 10 mL of H_2O and 2 mL of brine were added. The organic layer was then extracted with EtOAc and washed with brine twice. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The crude residue was purified by column chromatography to yield the corresponding products **3a**, **3k**, and **5a**.

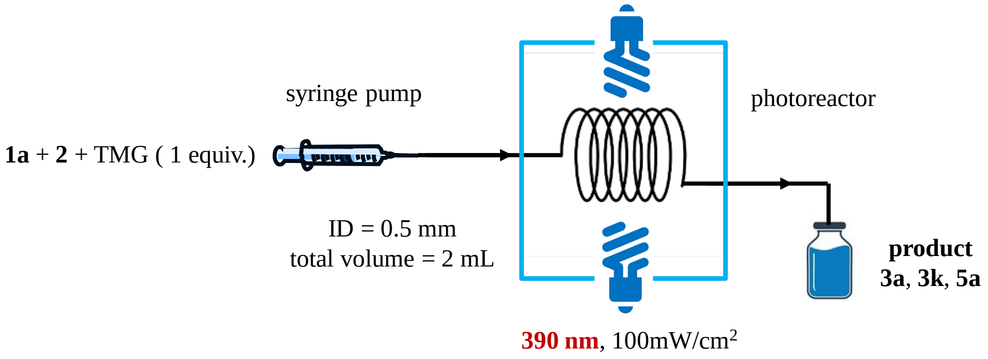


Figure S15. Schematic representation of the flow setup. ID = internal diameter.

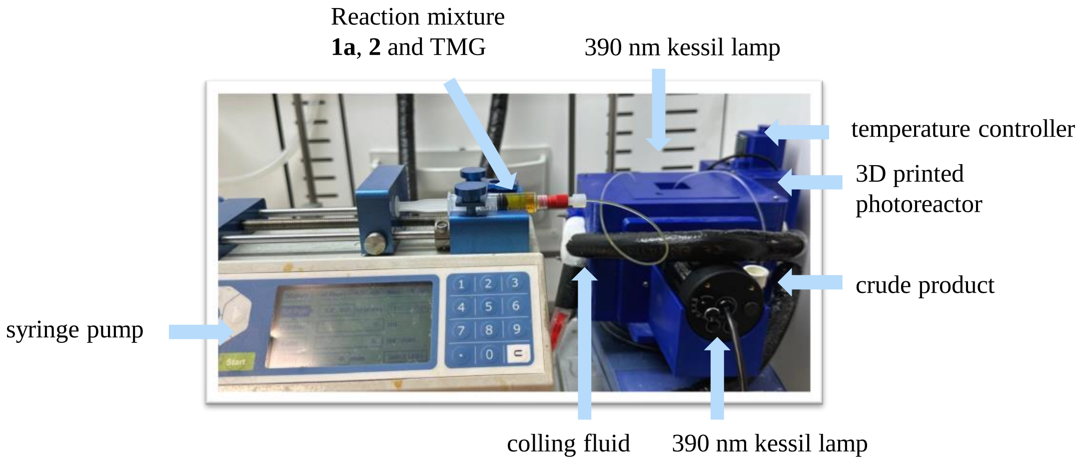
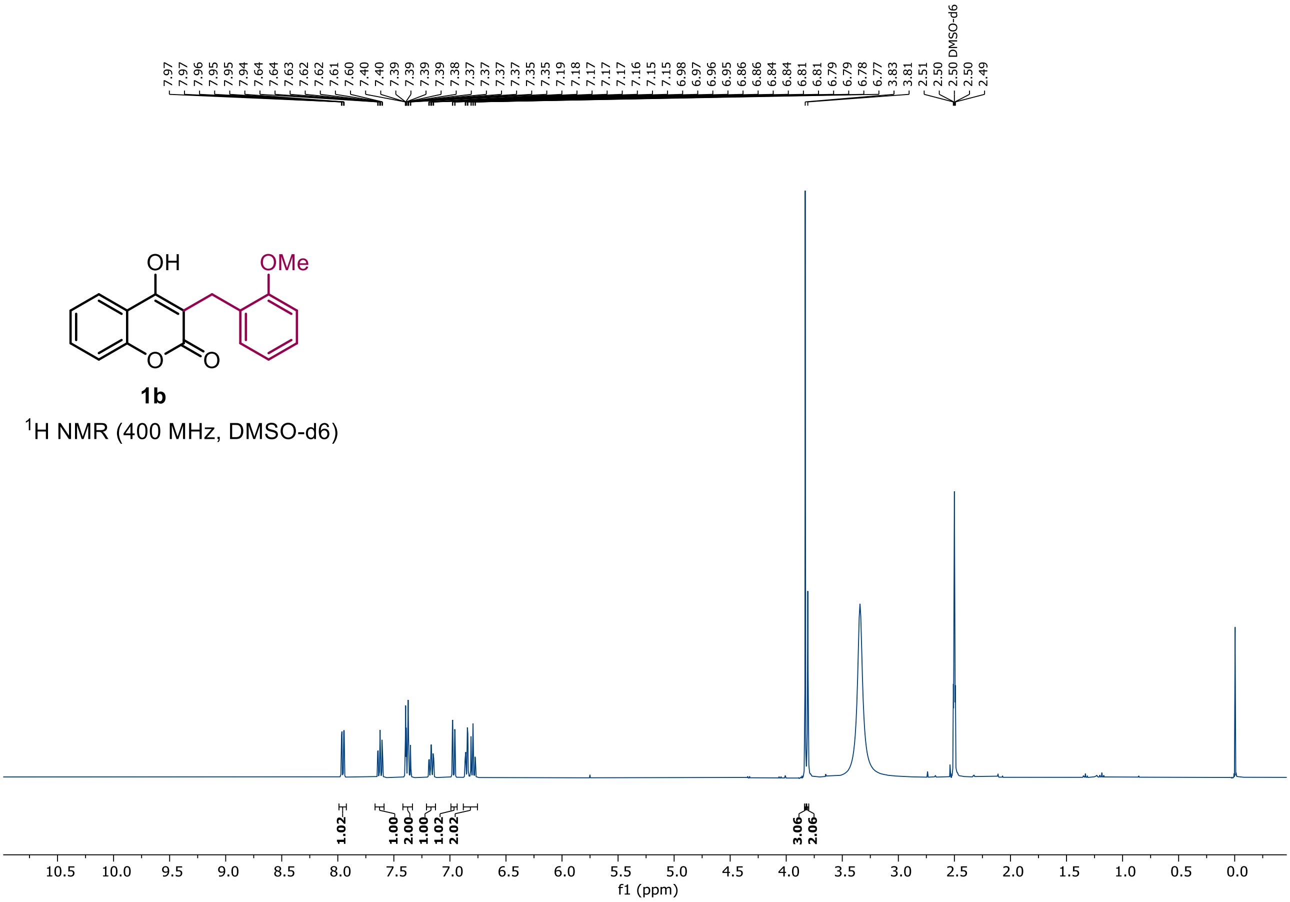


Figure S16. The photoreactor shown in Figure S15 was formed by a 3D-printed holding a cylindrical flow coil with 2 Kessil 390 nm LEDs pointing toward the flow coil inside the reactor. The distance between the LEDs is 2 cm and the tubing is 2 mm.

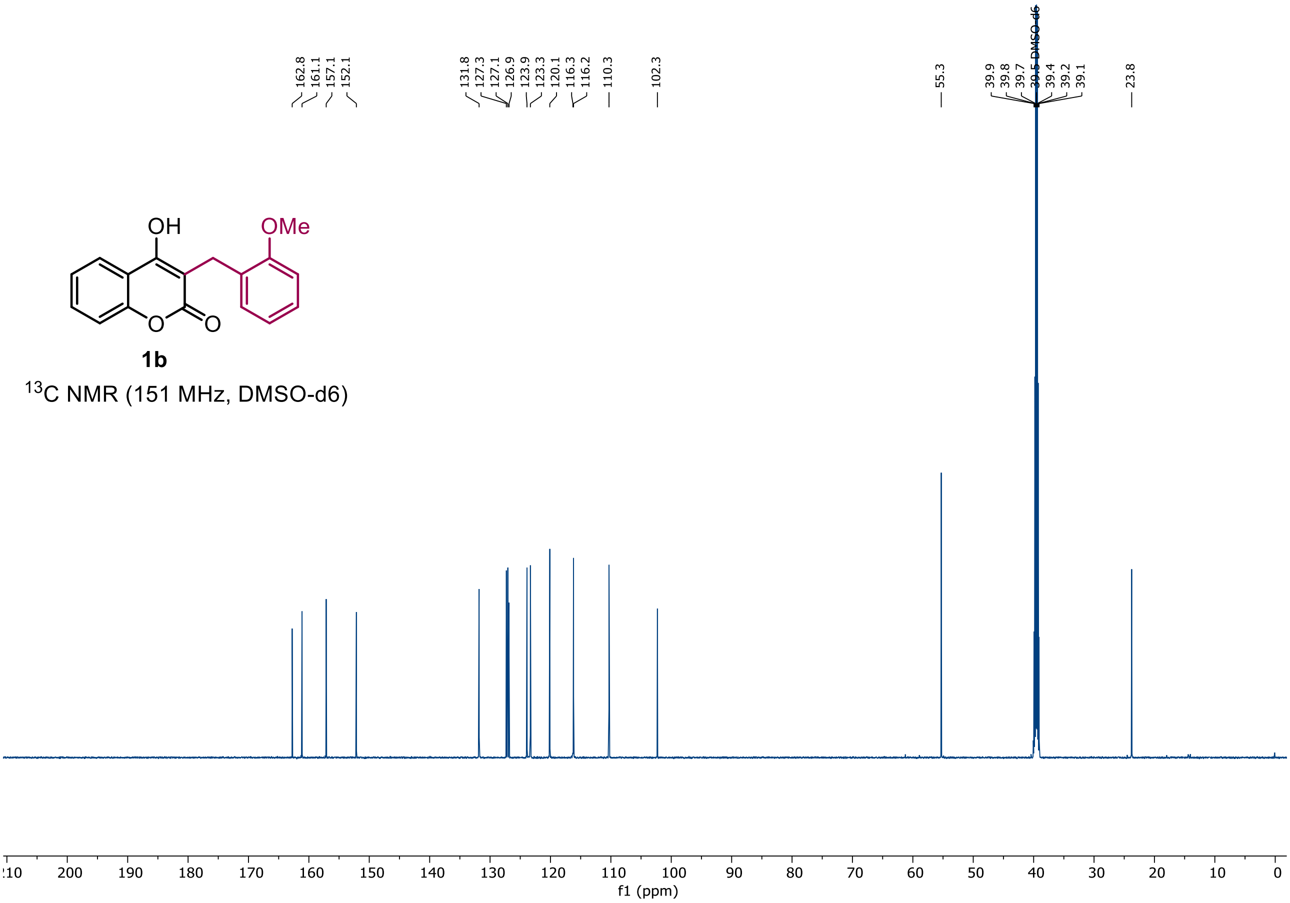
F. References

1. D. B. Ramachary, M. Kishor, *Org. Biomol. Chem.* **2010**, *8*, 2859.
2. A. Montagut-Romans, M. Boulven, M. Lemaire, F. Popowycz *RSC Adv.* **2016**, *6*, 4540.
3. V. V. Pavlishchuk, A. W. Addison, *Inorganica Chim. Acta.* **2000**, *298*, 97.
4. L. Buzzetti, G. E. M. Crisenza, P. Melchiorre, *Angew. Chem. Int. Ed.* **2019**, *58*, 3730; *Angew. Chem.* **2019**, *131*, 3768.
5. M. A. Cismesia, T. P. Yoon, *Chem. Sci*. **2015**, *6*, 5426.
6. T. v. Leeuwen, L. Buzzetti, L. A. Perego, P. Melchiorre, *Angew. Chem. Int. Ed.* **2019**, *58*, 4953; *Angew. Chem.* **2019**, *131*, 5007.
7. V., Ladányi, P. Dvořák, J. A. Anshori, Ľ. Vetráková, J. Wirz, D. Heger, Photochem. *Photobiol. Sci.* **2017**, *16*, 1757.



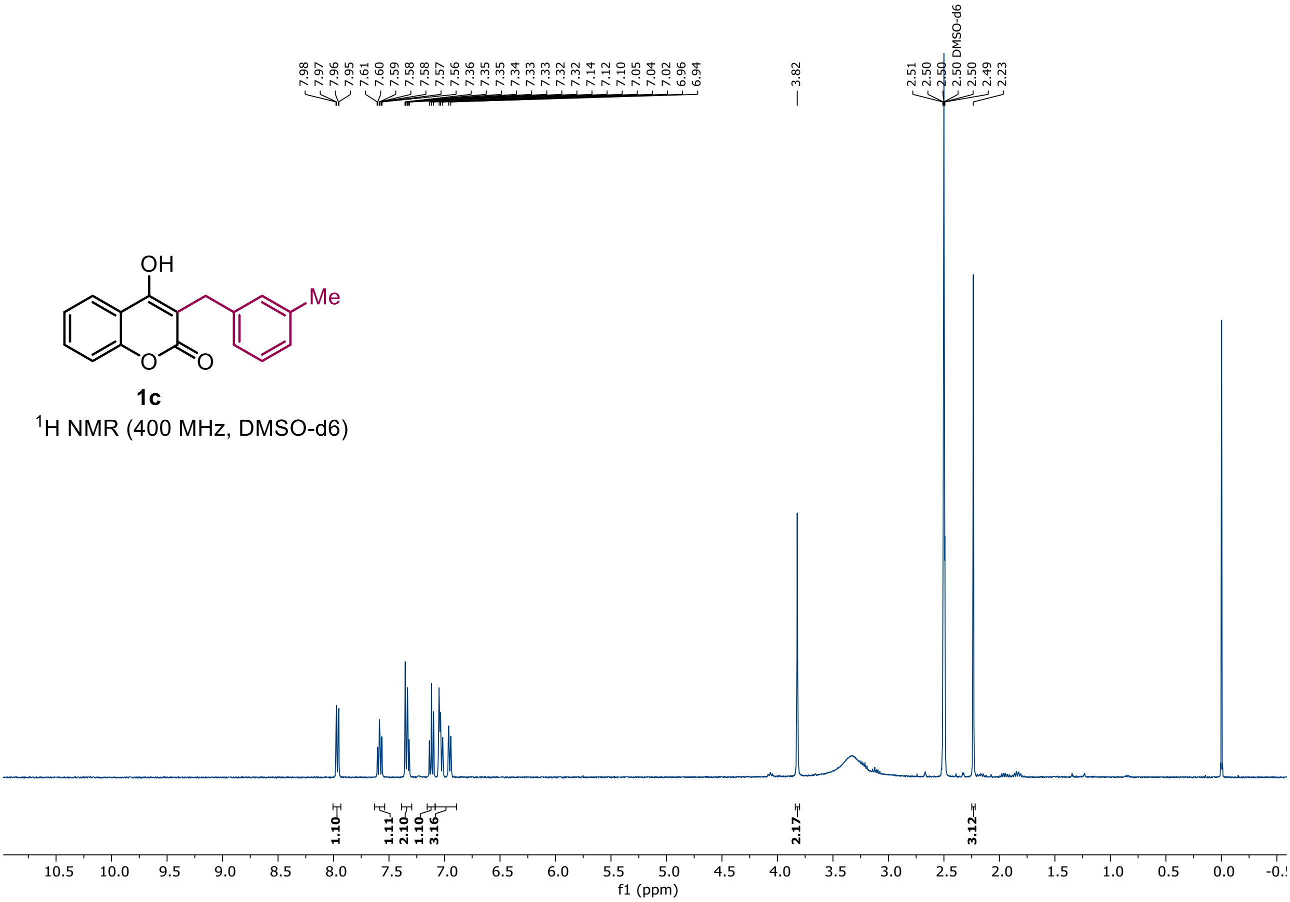
1b

^{1}H NMR (400 MHz, DMSO-d6)



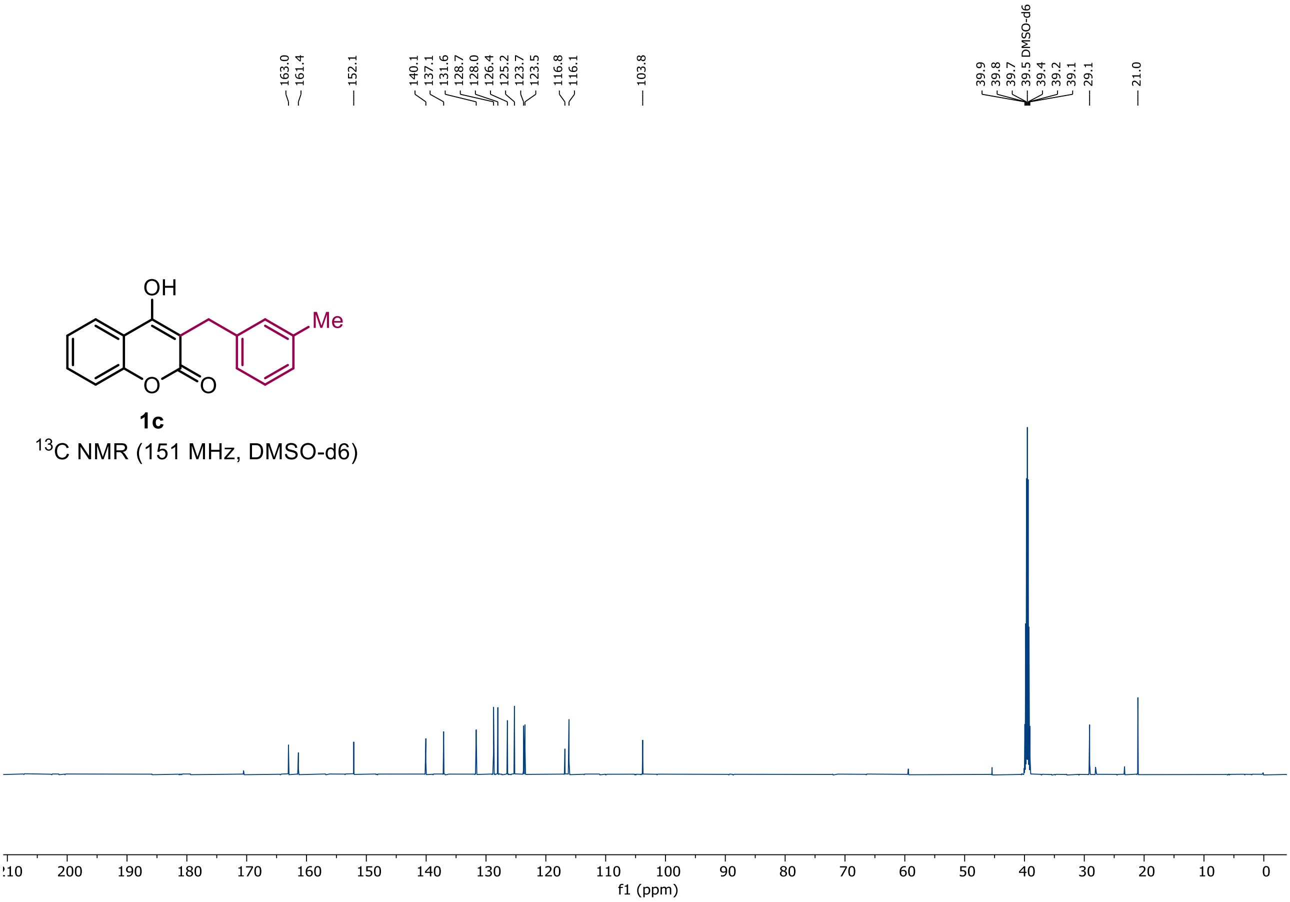
1b

^{13}C NMR (151 MHz, DMSO-d6)



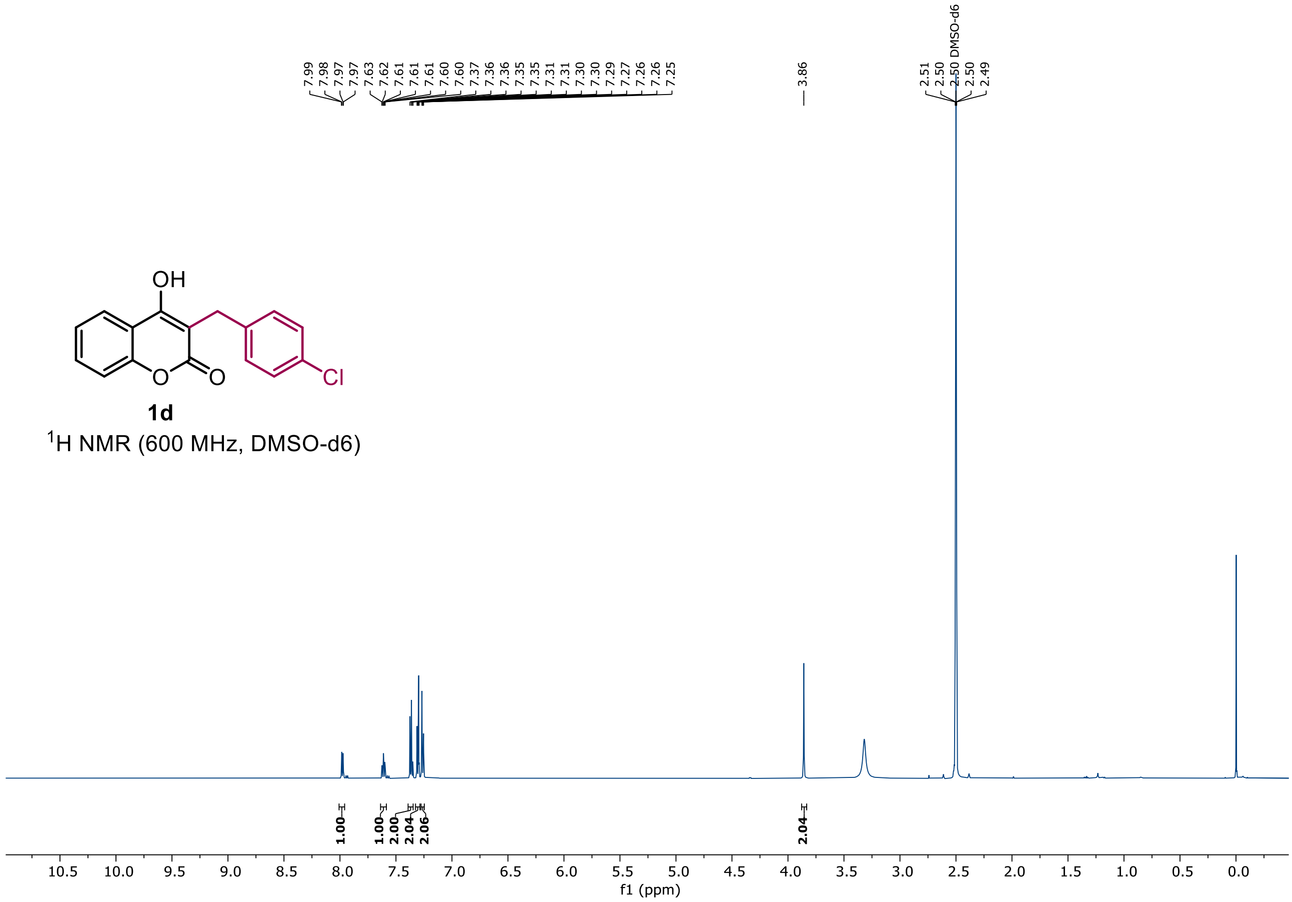
1c

^{1}H NMR (400 MHz, DMSO-d6)



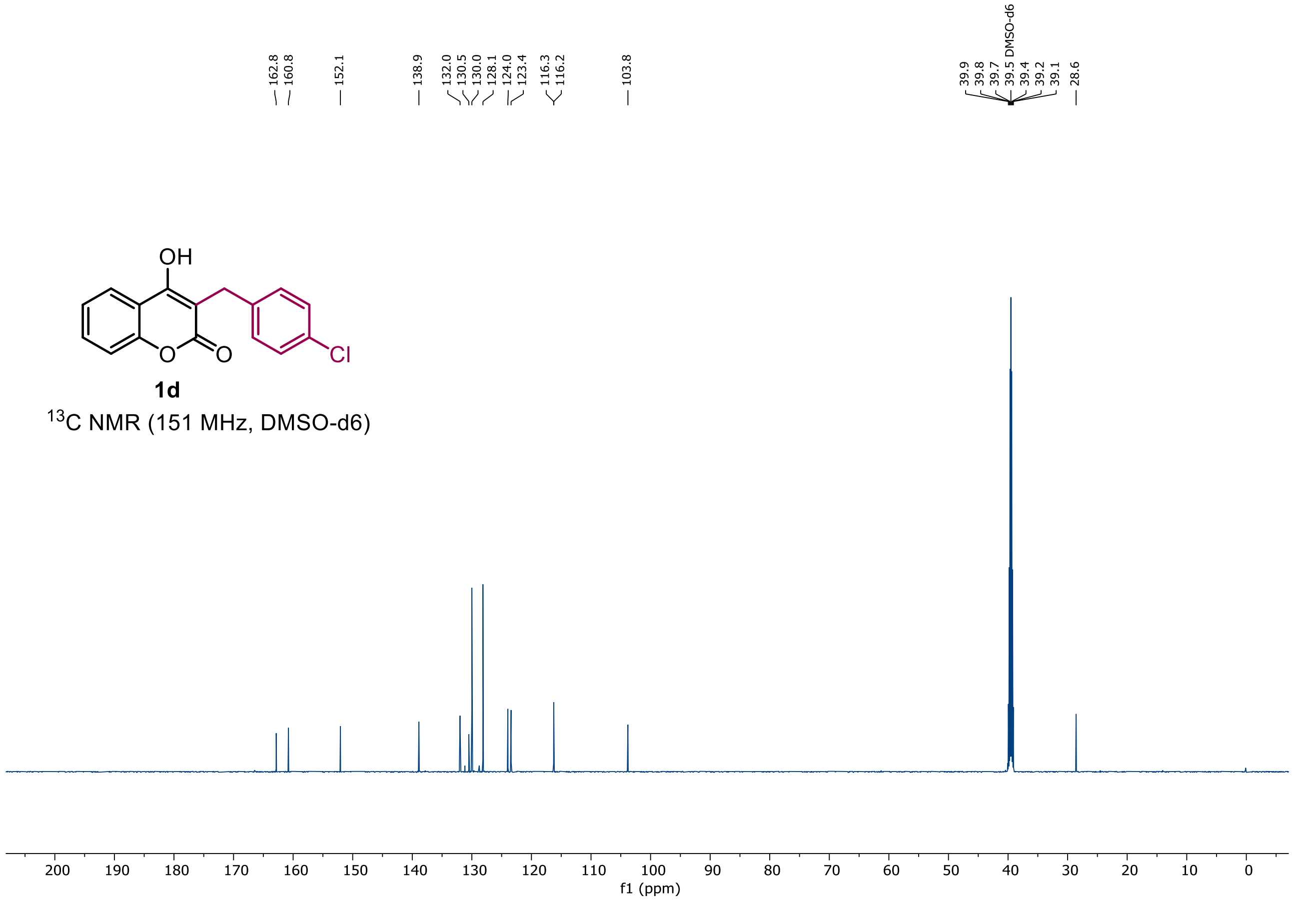
1c

^{13}C NMR (151 MHz, DMSO-d6)



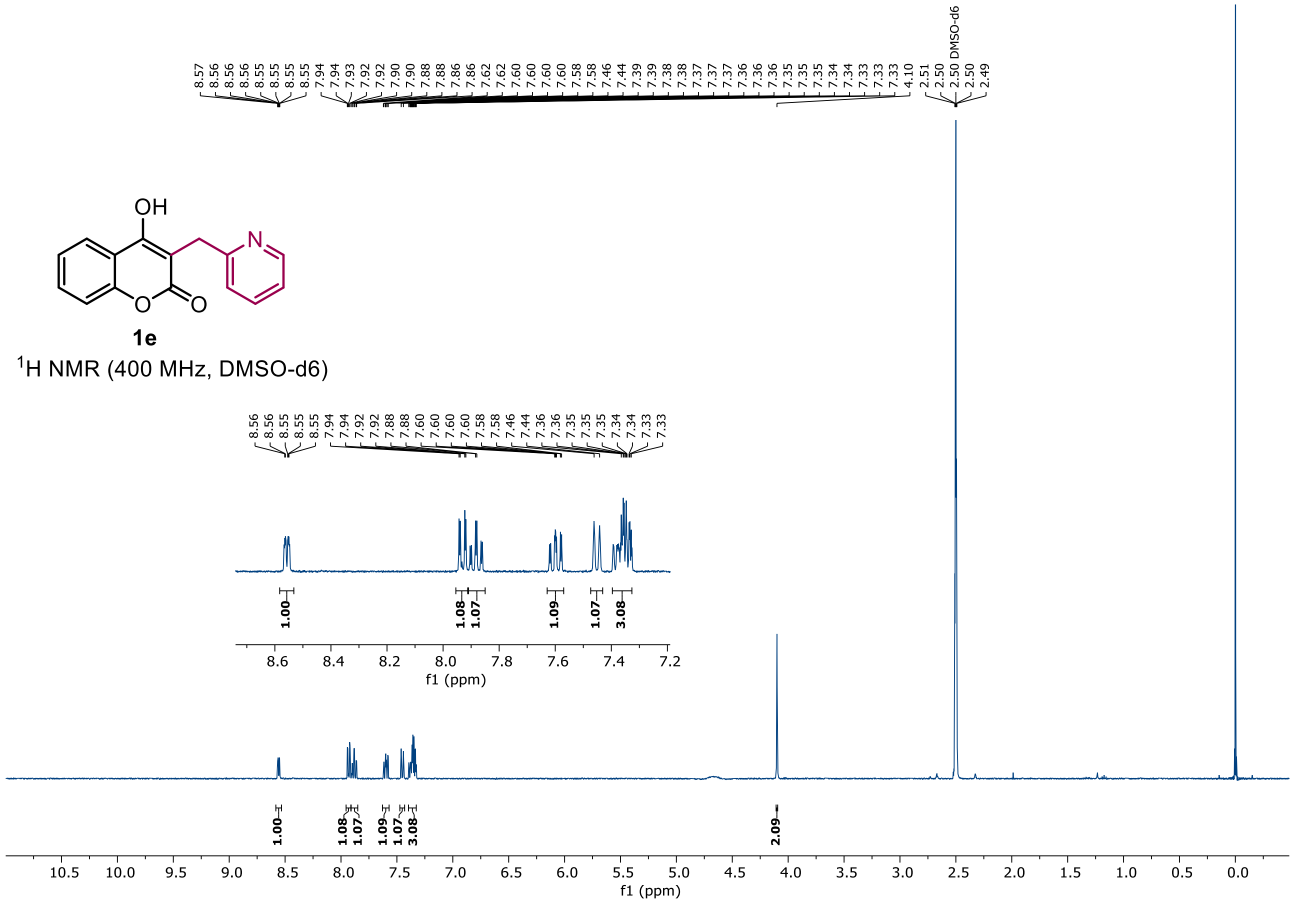
1d

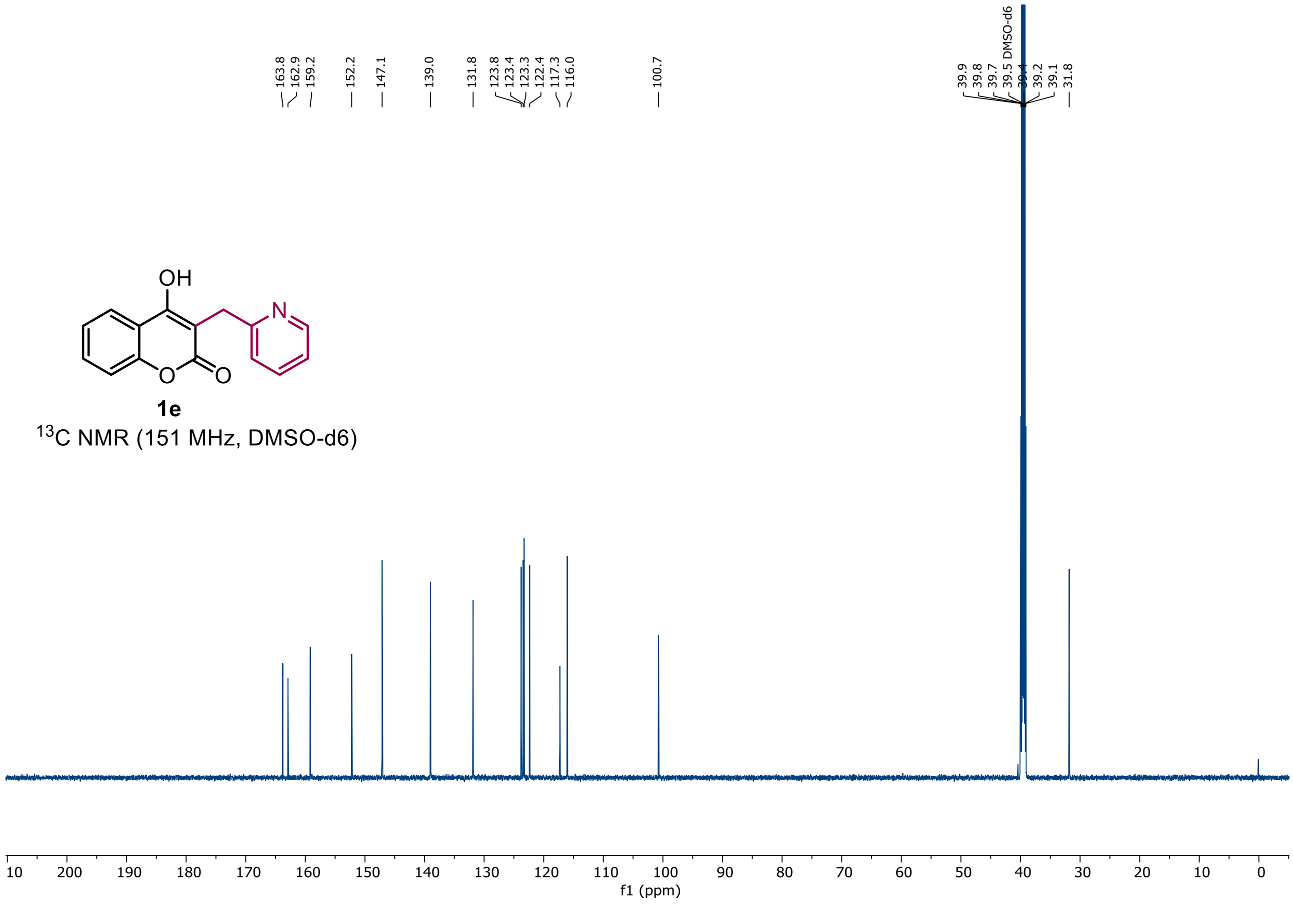
^{1}H NMR (600 MHz, DMSO-d6)

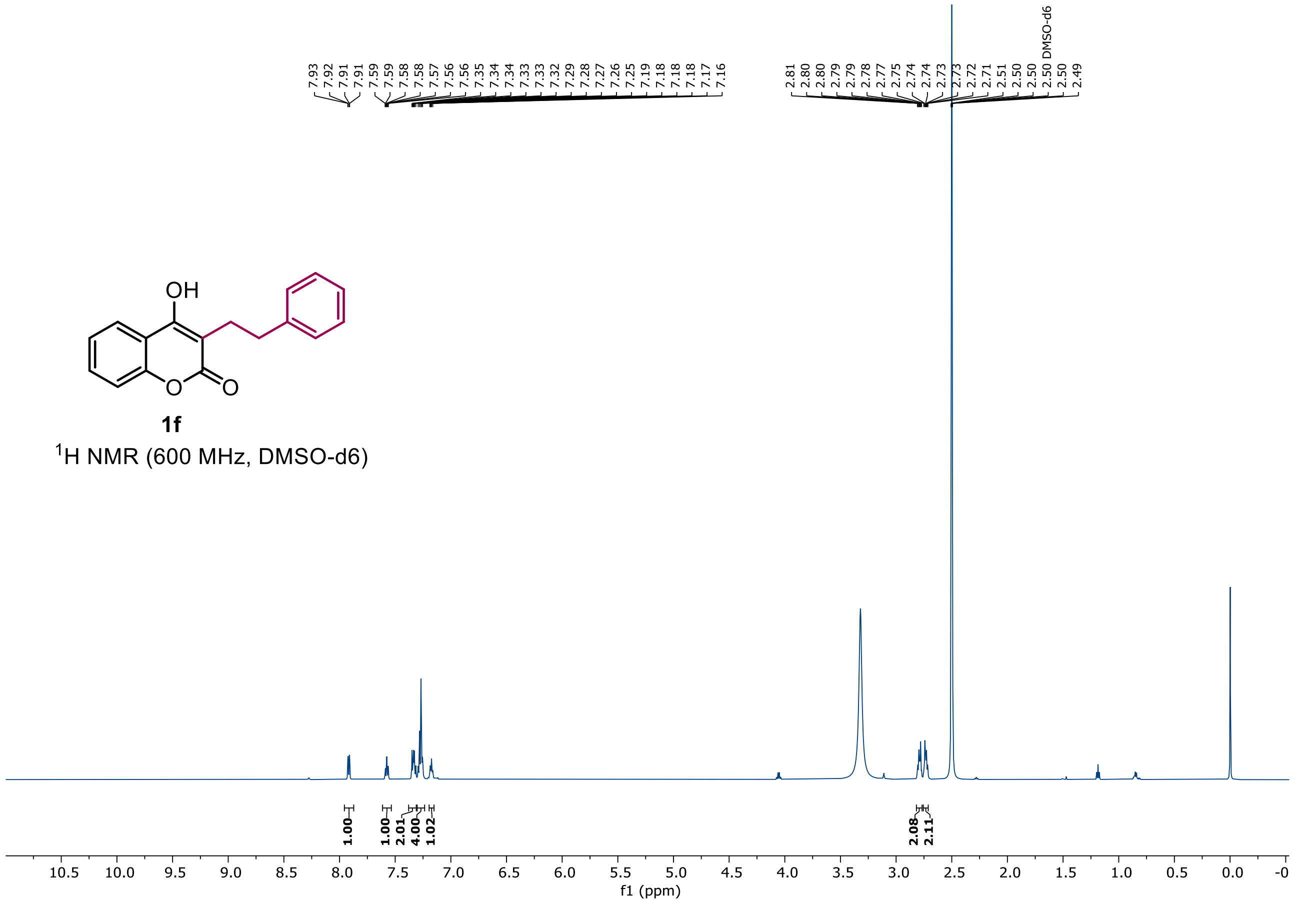


1d

^{13}C NMR (151 MHz, DMSO-d6)

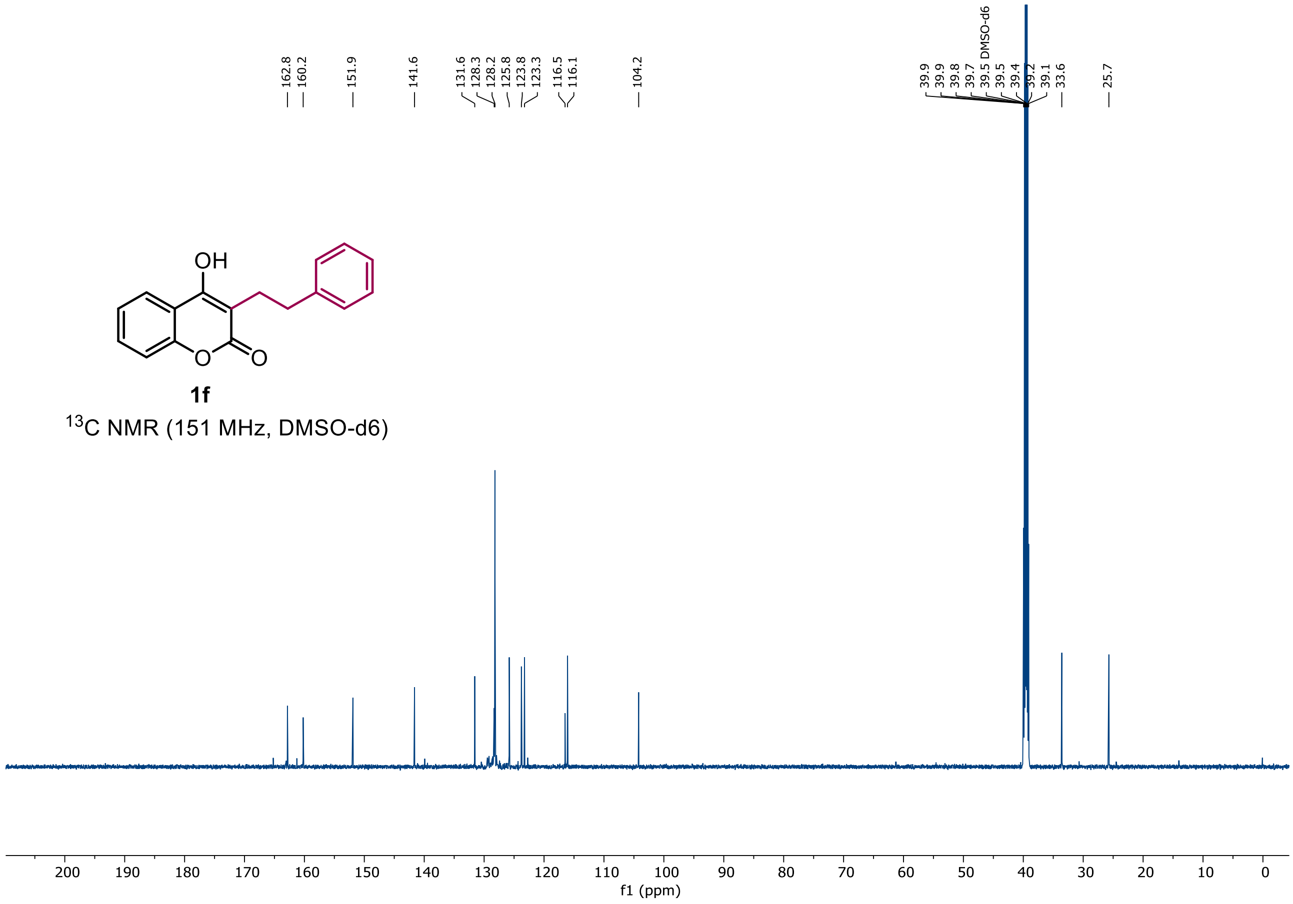

8.57
8.56
8.56
8.56
8.55
8.55
8.55
8.55
7.94
7.94
7.93
7.92
7.92
7.90
7.90
7.88
7.88
7.86
7.86
7.62
7.62
7.60
7.60
7.60
7.60
7.58
7.58
7.46
7.44
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.33
7.33
4.10
2.51
2.50
2.50 DMSO-d6
2.50
2.49
OH
N
O
O
1e
^{1}H NMR (400 MHz, DMSO-d6)
8.56
8.56
8.55
8.55
8.55
7.94
7.94
7.92
7.92
7.88
7.88
7.60
7.60
7.60
7.60
7.58
7.46
7.44
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.33
1.00
1.08
1.07
1.09
1.07
3.08
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
f1 (ppm)
1.00
1.08
1.07
1.09
1.07
3.08
2.09
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.8
162.9
159.2
152.2
147.1
139.0
131.8
123.8
123.4
123.3
122.4
117.3
116.0
100.7
39.9
39.8
39.7
39.5 DMSO-d6
39.4
39.2
39.1
31.8
OH
N
O
O
1e
^{13}C NMR (151 MHz, DMSO-d6)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



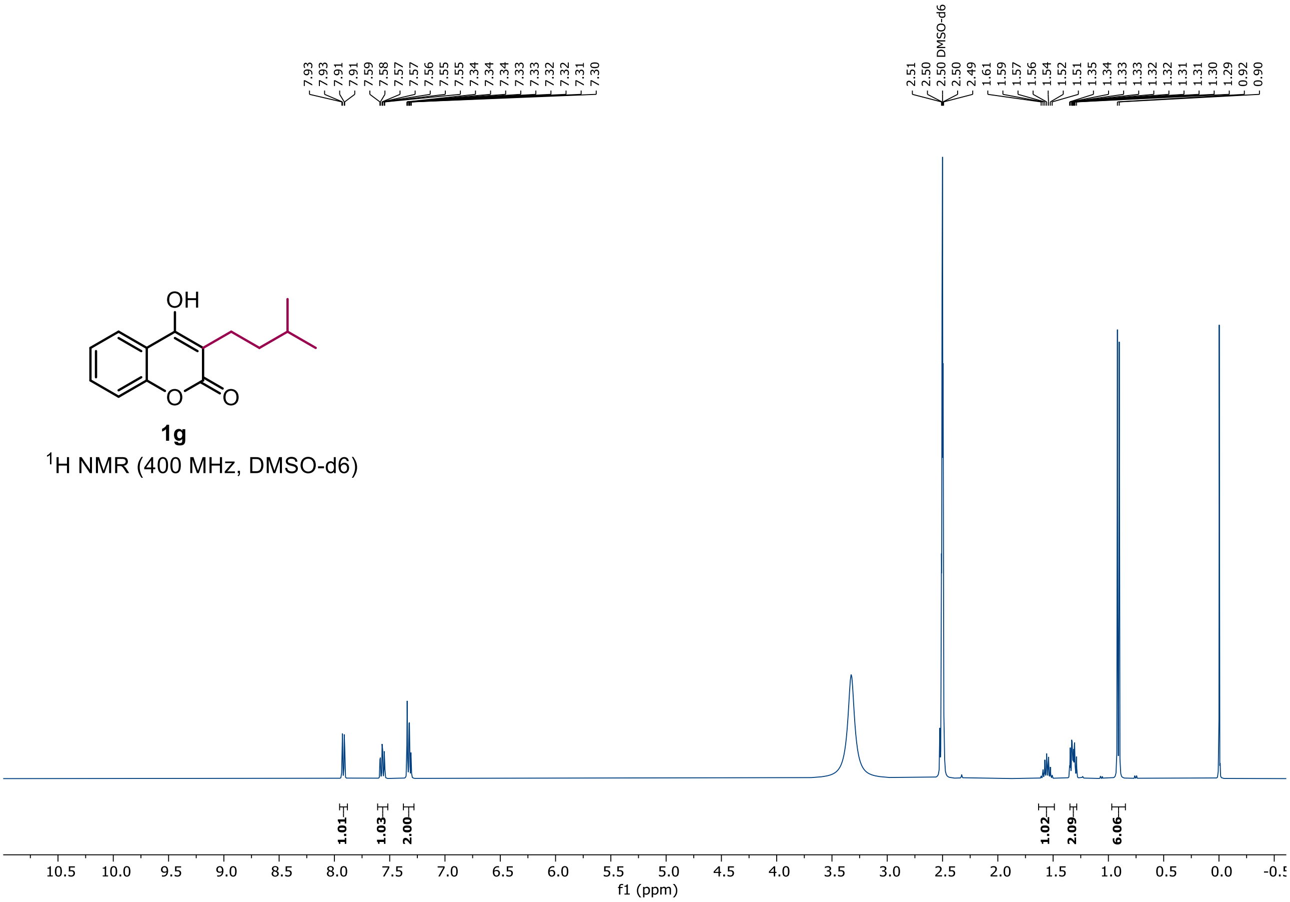
1f

^{1}H NMR (600 MHz, DMSO-d6)



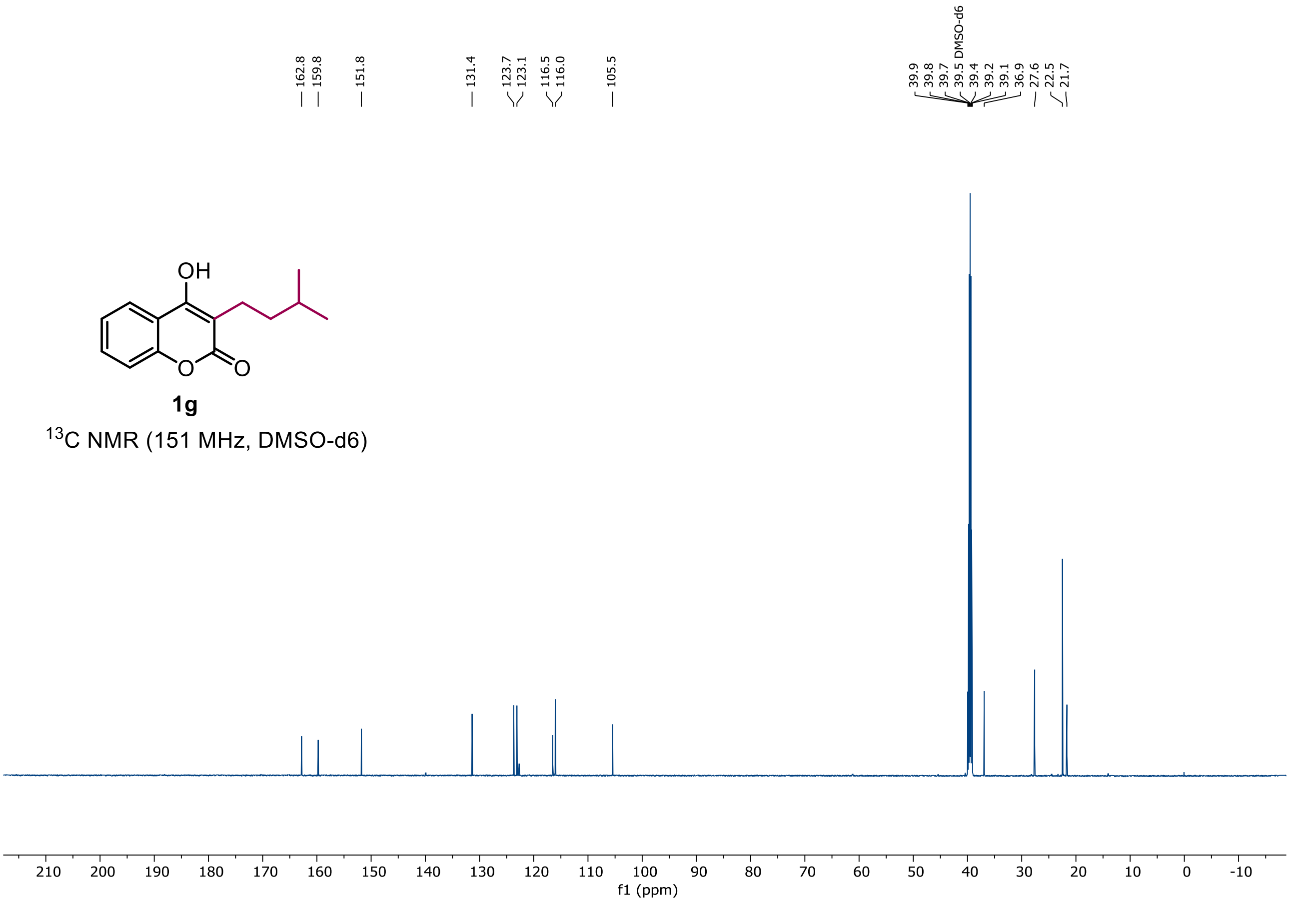
1f

^{13}C NMR (151 MHz, DMSO-d6)



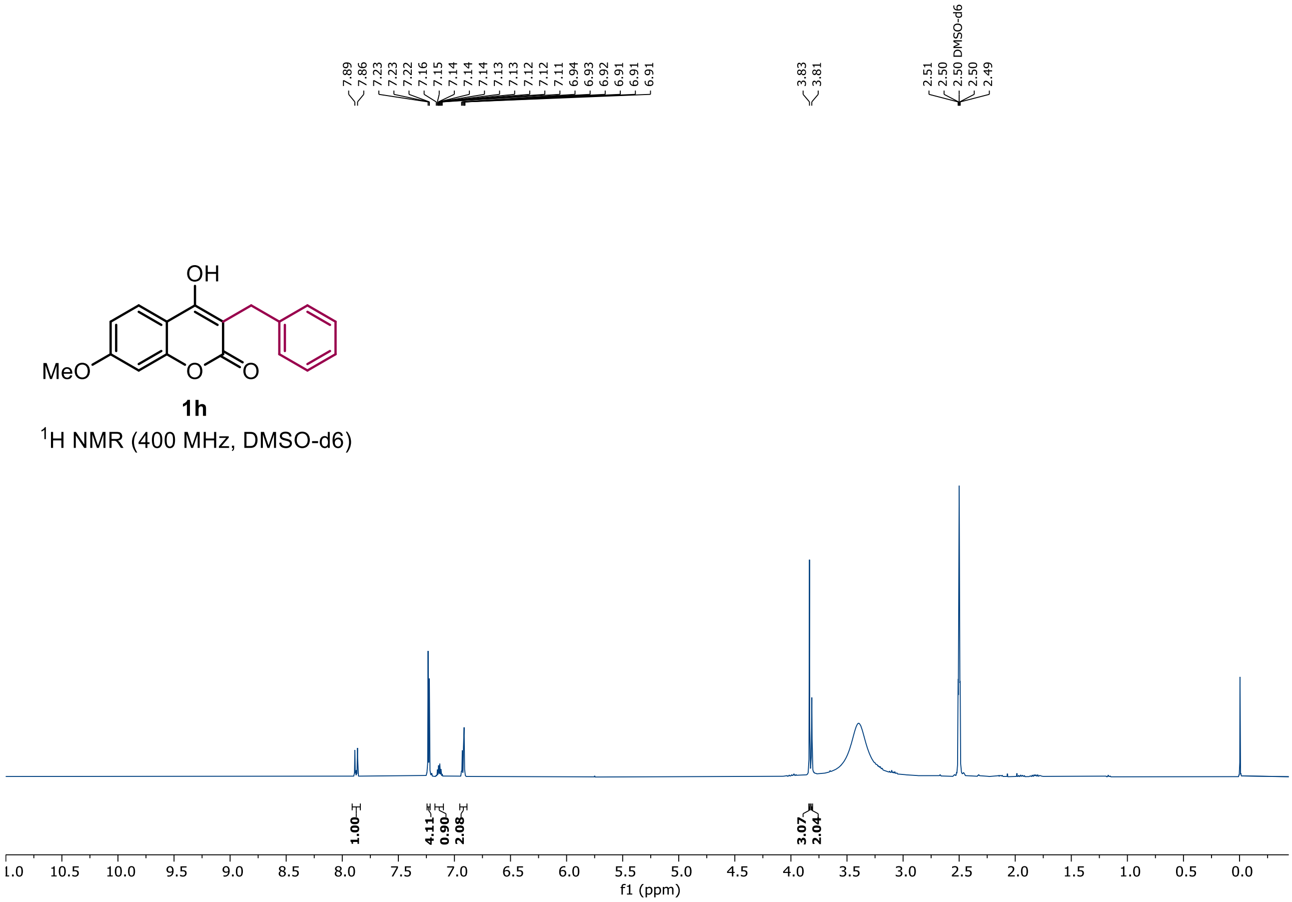
1g

^{1}H NMR (400 MHz, DMSO-d6)



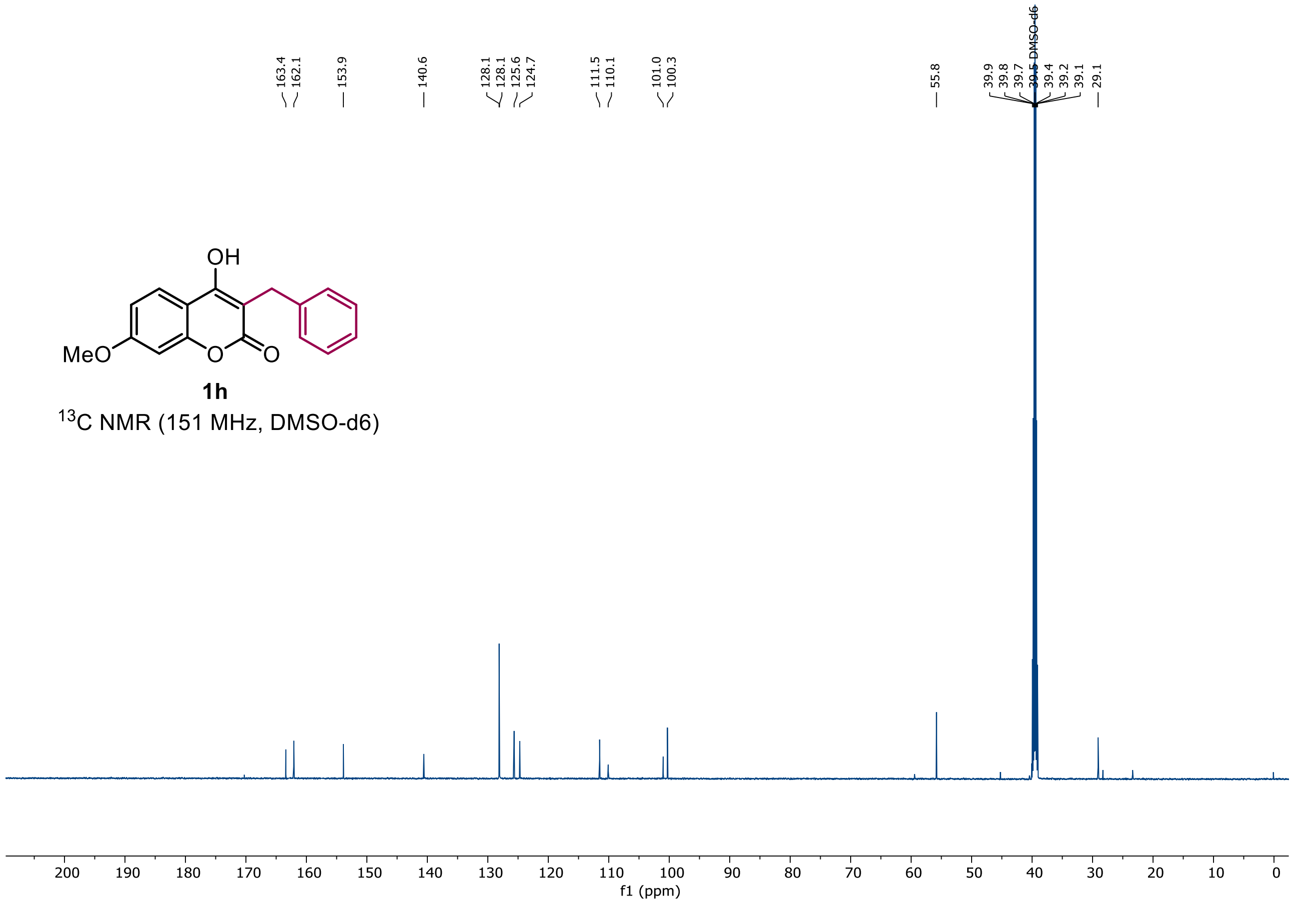
1g

^{13}C NMR (151 MHz, DMSO-d6)



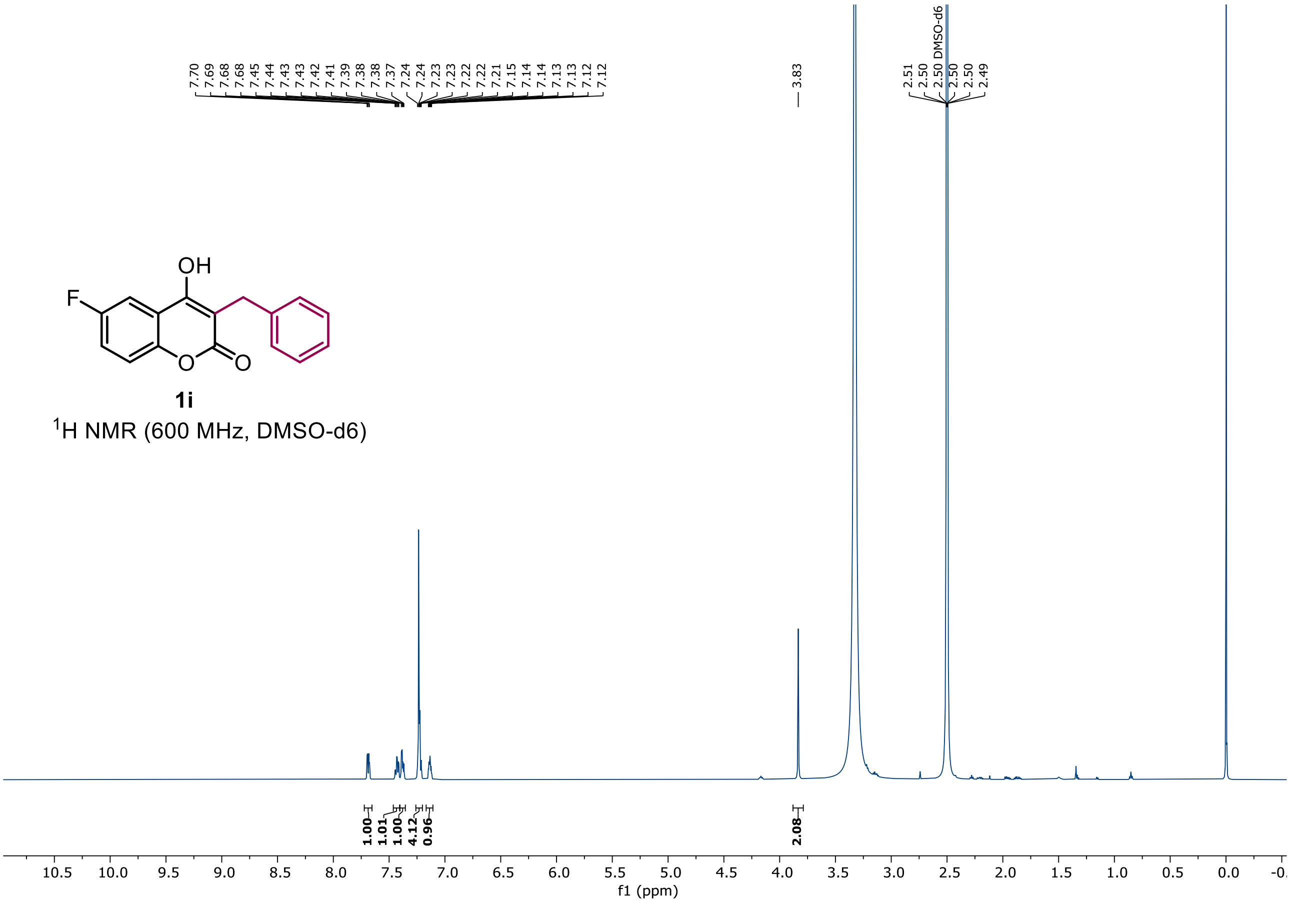
1h

^{1}H NMR (400 MHz, DMSO-d6)

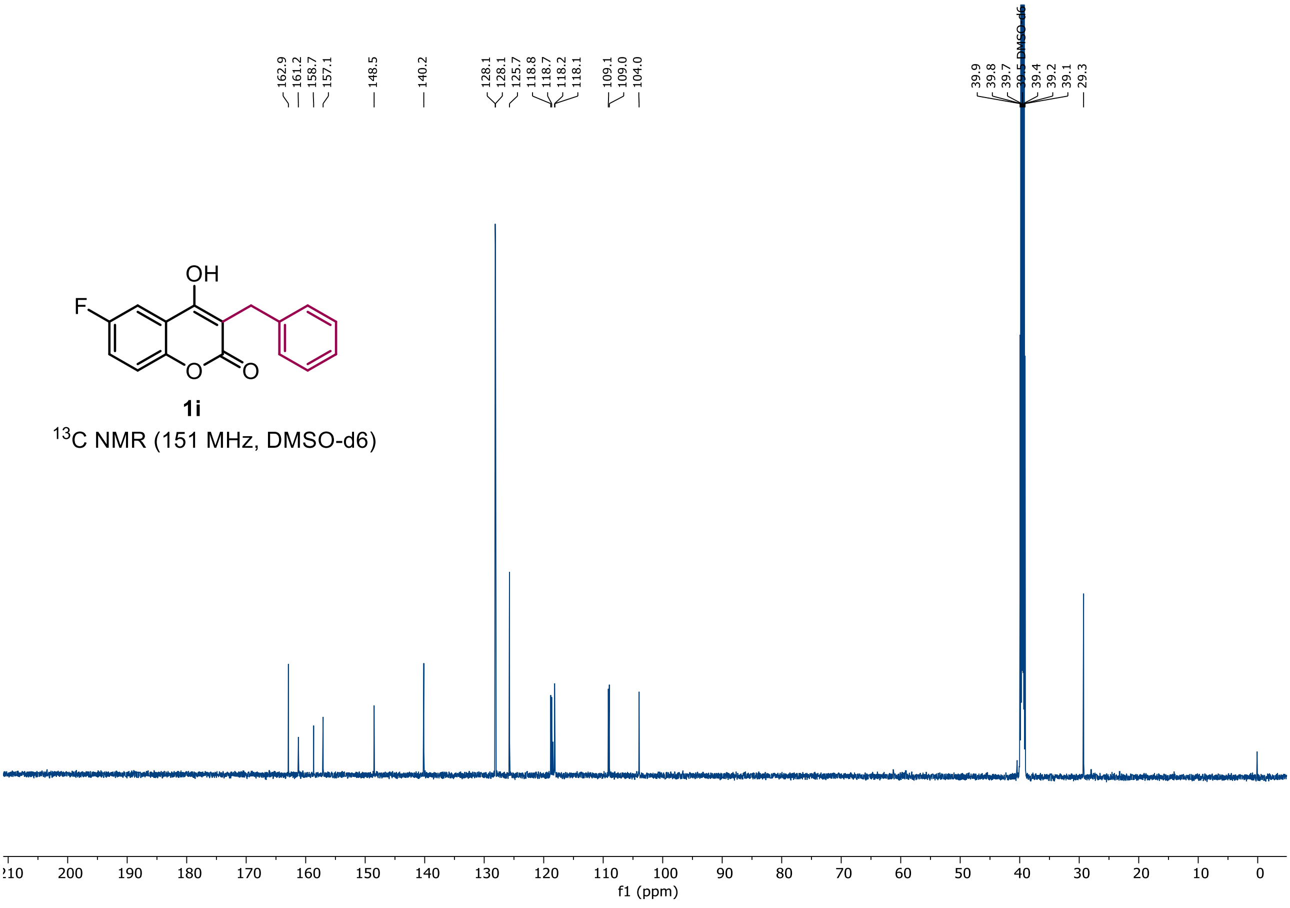


1h

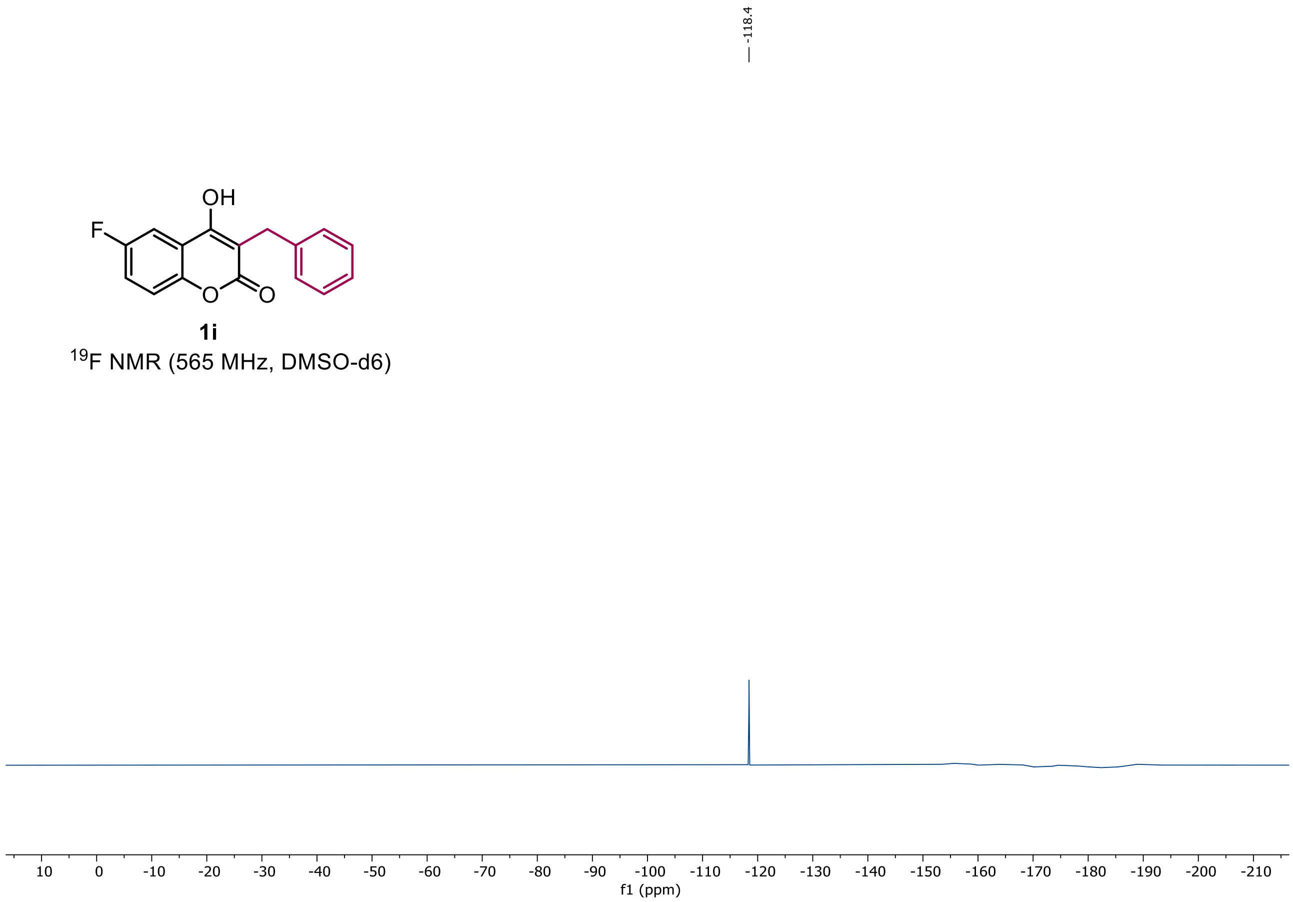
^{13}C NMR (151 MHz, DMSO-d6)



7.70
7.69
7.68
7.45
7.44
7.43
7.42
7.41
7.39
7.38
7.38
7.37
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.15
7.14
7.14
7.13
7.13
7.12
7.12
3.83
2.51
2.50
2.50 DMSO-d6
2.50
2.50
2.49
OH
F
O
O
1i
^{1}H NMR (600 MHz, DMSO-d6)
1.00
1.01
1.00
4.12
0.96
2.08
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

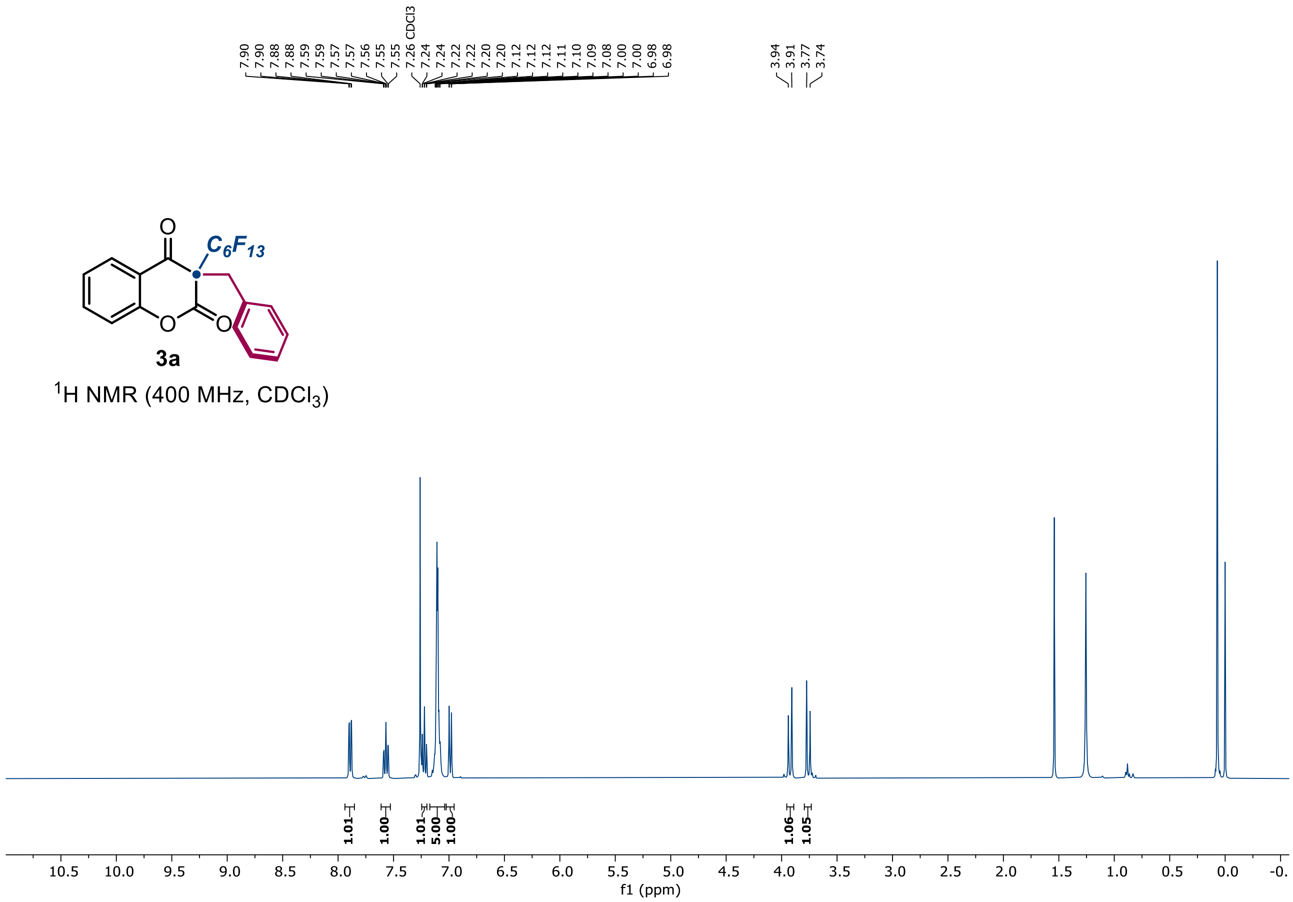


162.9
161.2
158.7
157.1
148.5
140.2
128.1
128.1
125.7
118.8
118.7
118.2
118.1
109.1
109.0
104.0
39.9
39.8
39.7
39.5 DMSO-d6
39.4
39.2
39.1
29.3
OH
F
O
O
1i
^{13}C NMR (151 MHz, DMSO-d6)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



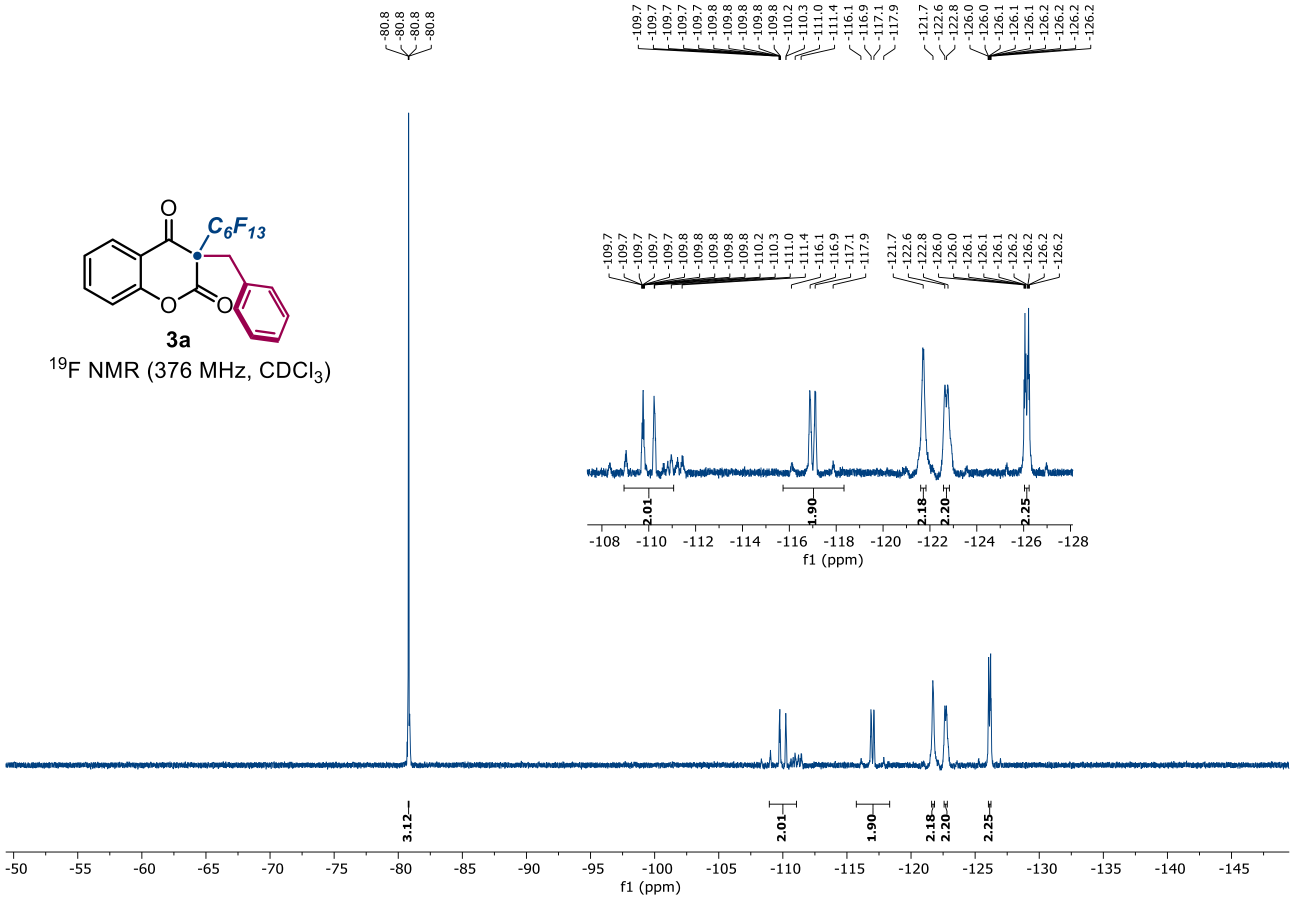
1i

^{19}F NMR (565 MHz, DMSO-d6)



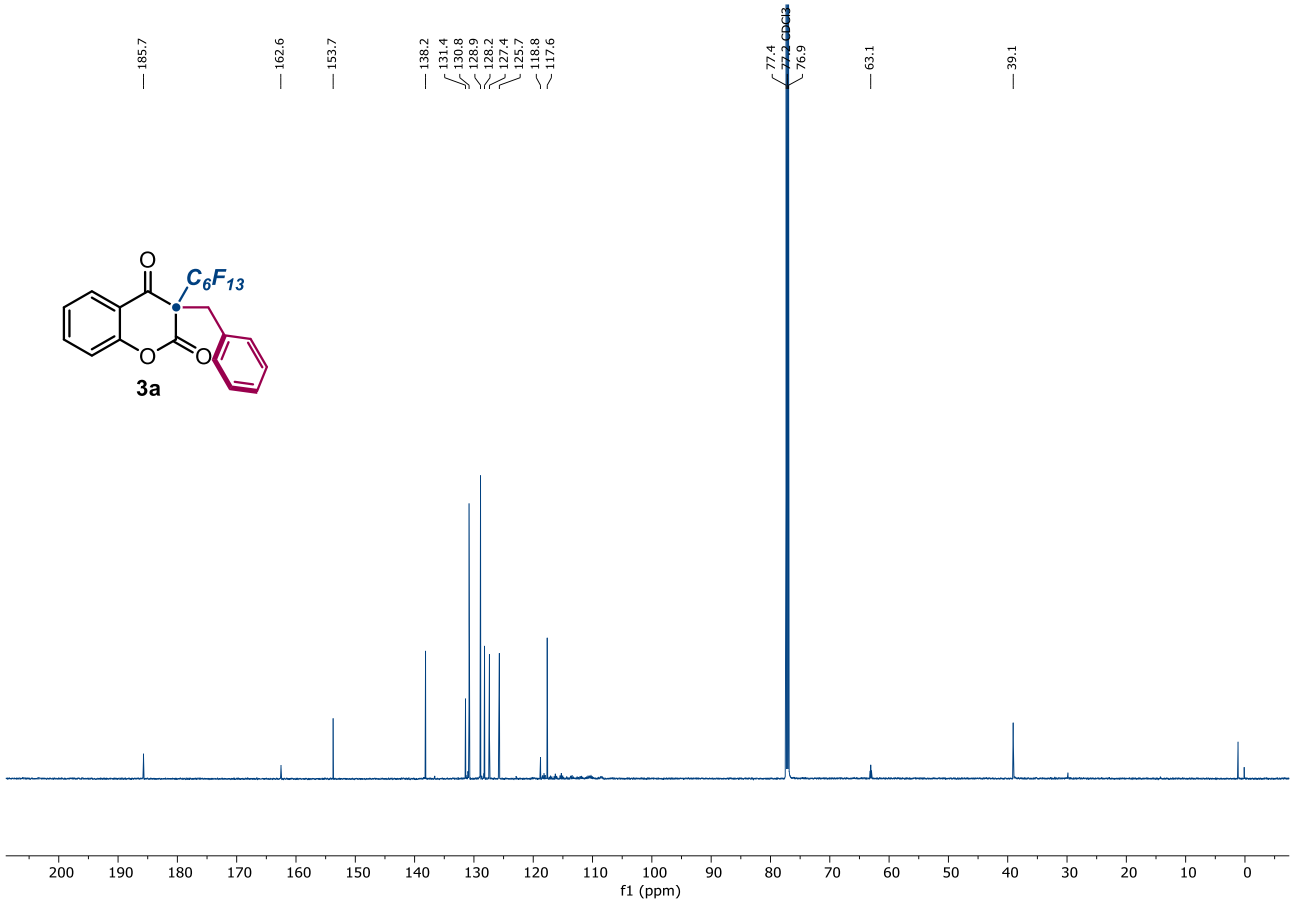
3a

^{1}H NMR (400 MHz, $CDCl_3$)

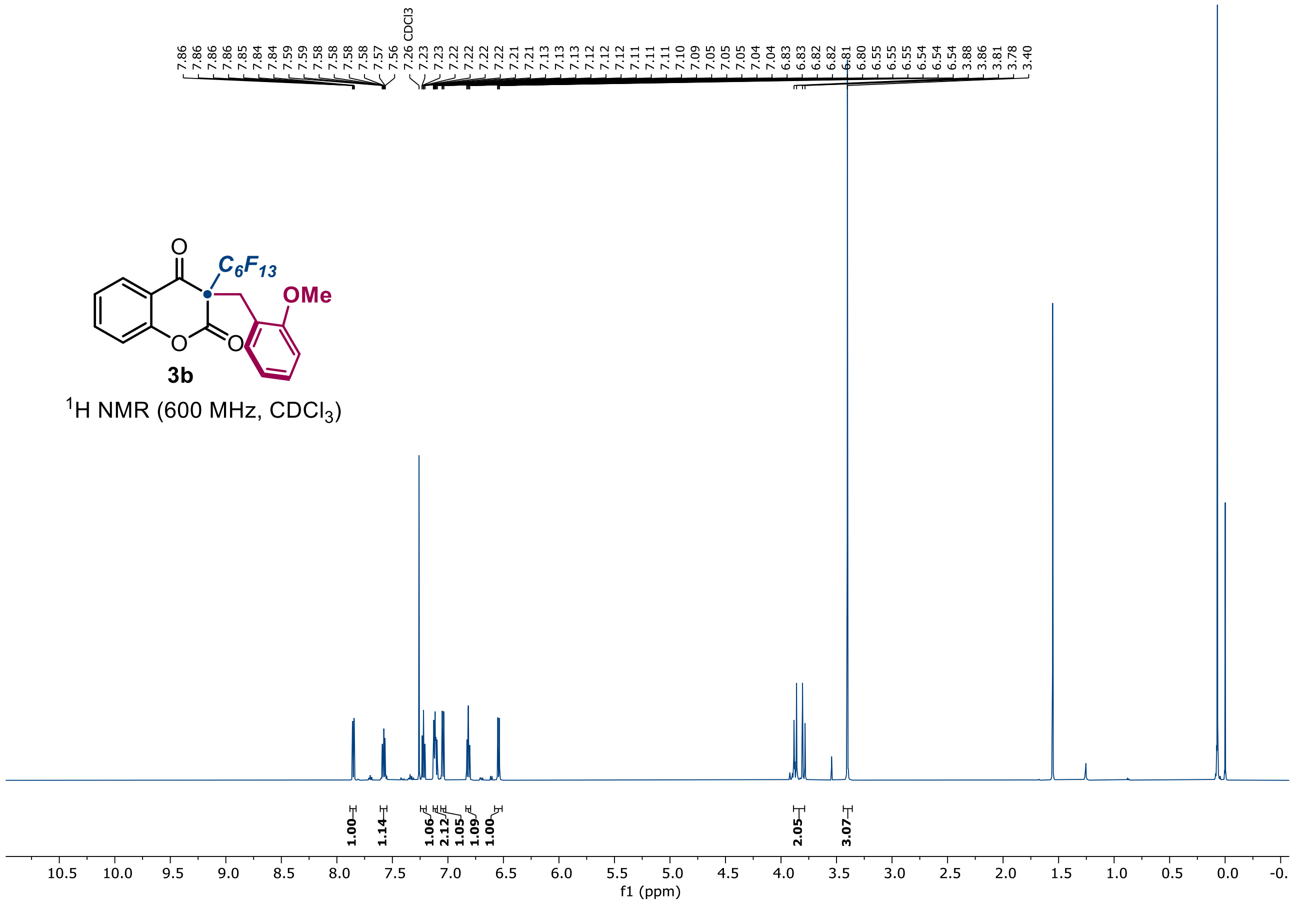


3a

^{19}F NMR (376 MHz, $CDCl_3$)

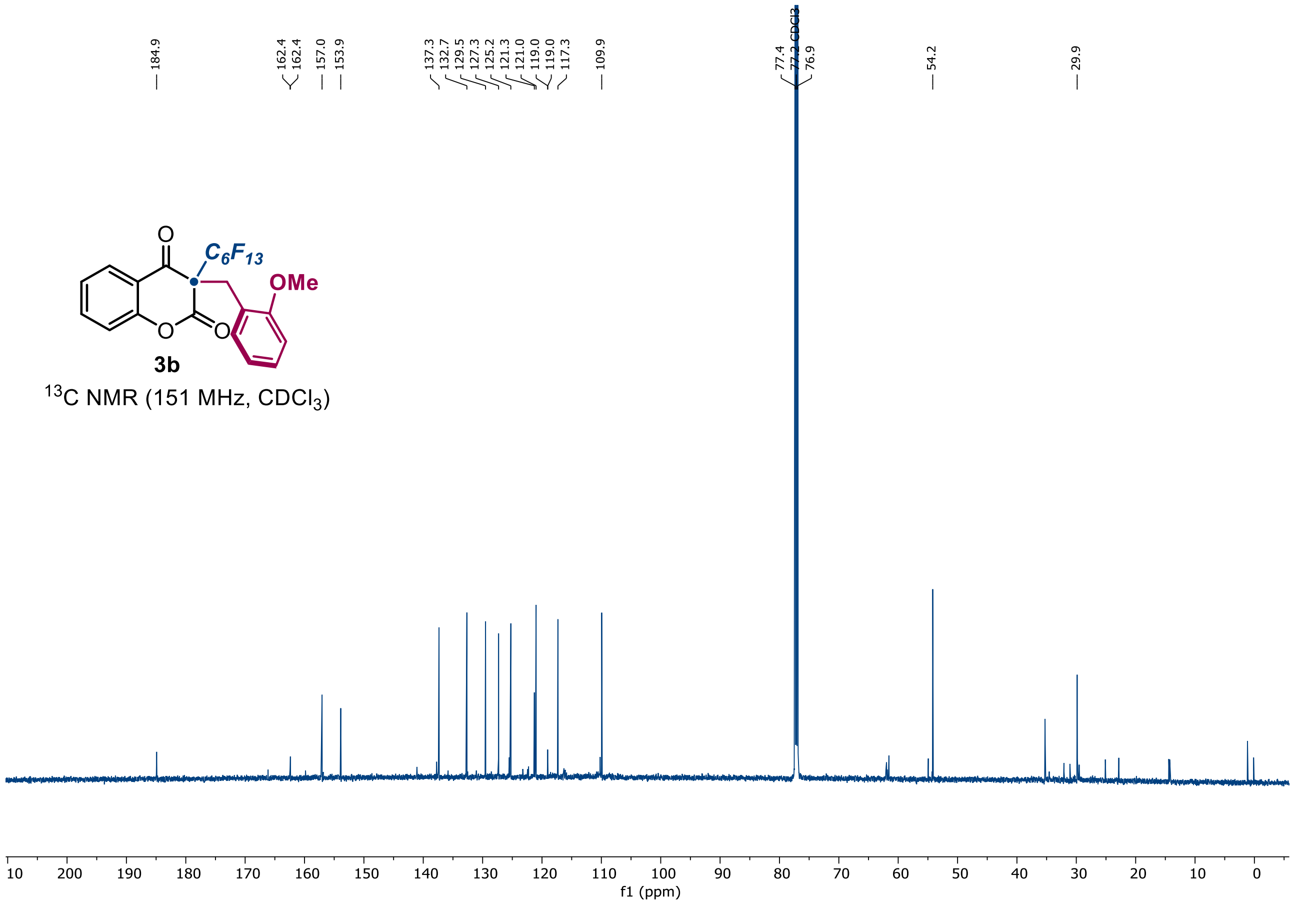


3a



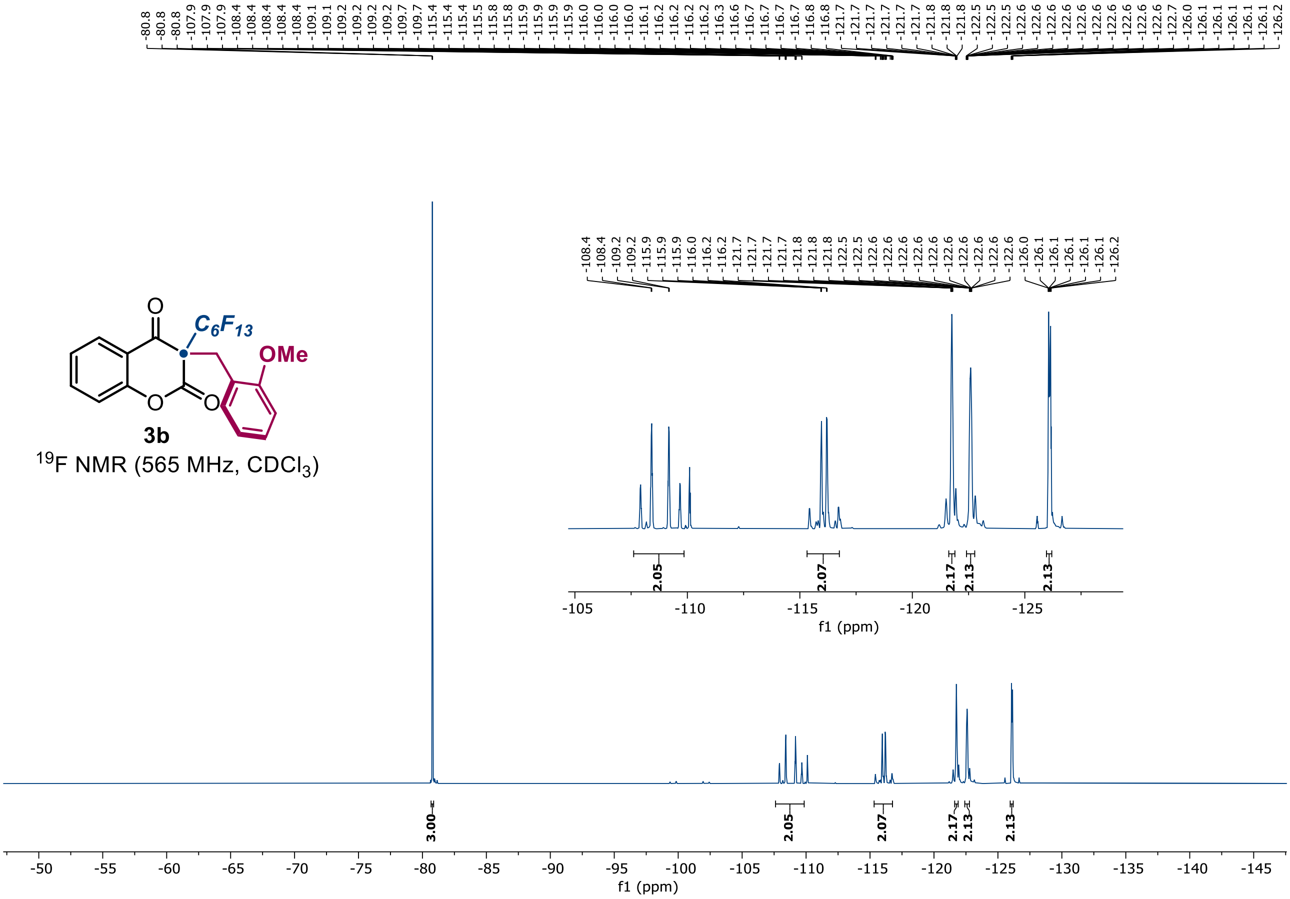
3b

^{1}H NMR (600 MHz, CDCl$_3$)



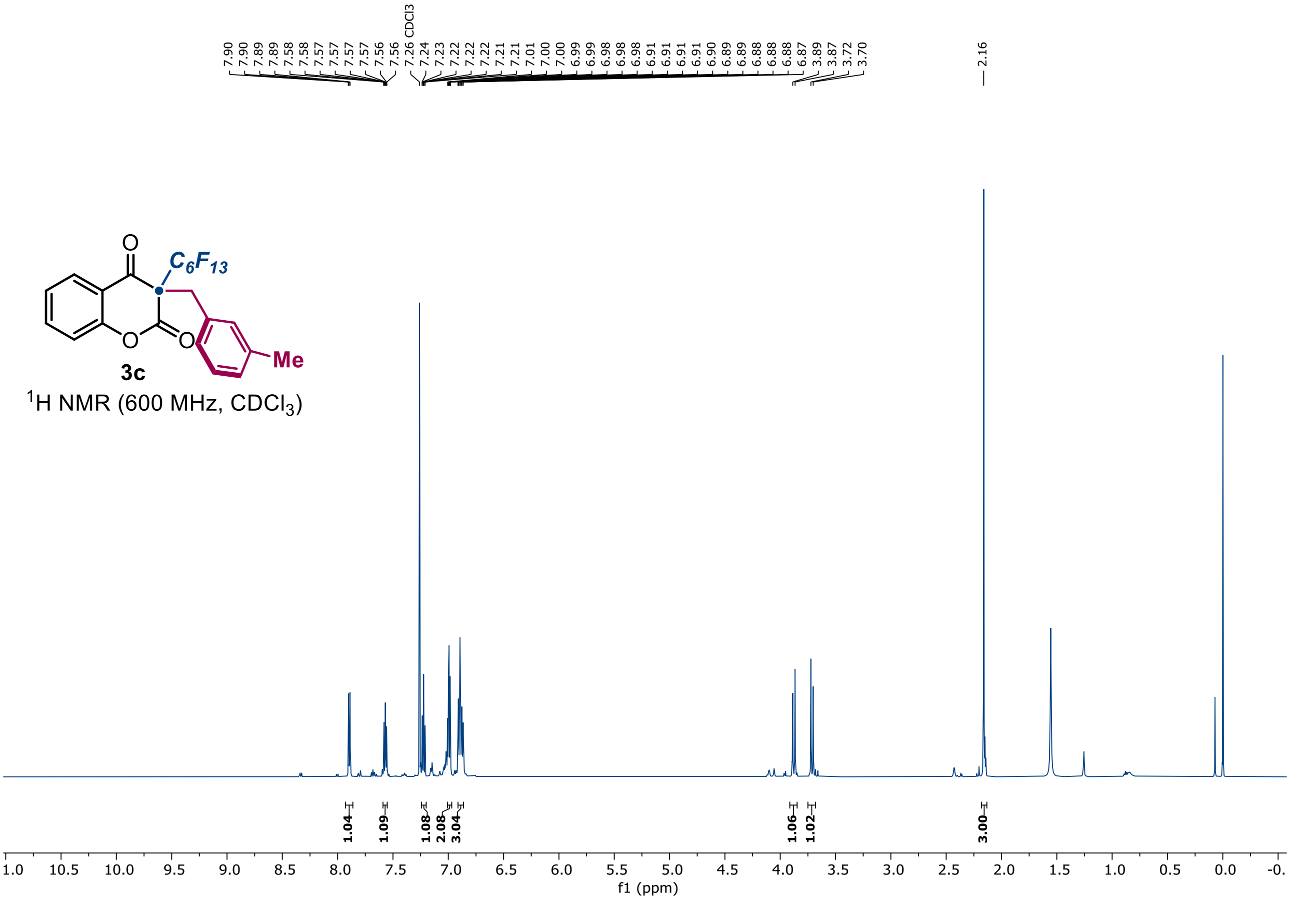
3b

^{13}C NMR (151 MHz, CDCl$_3$)



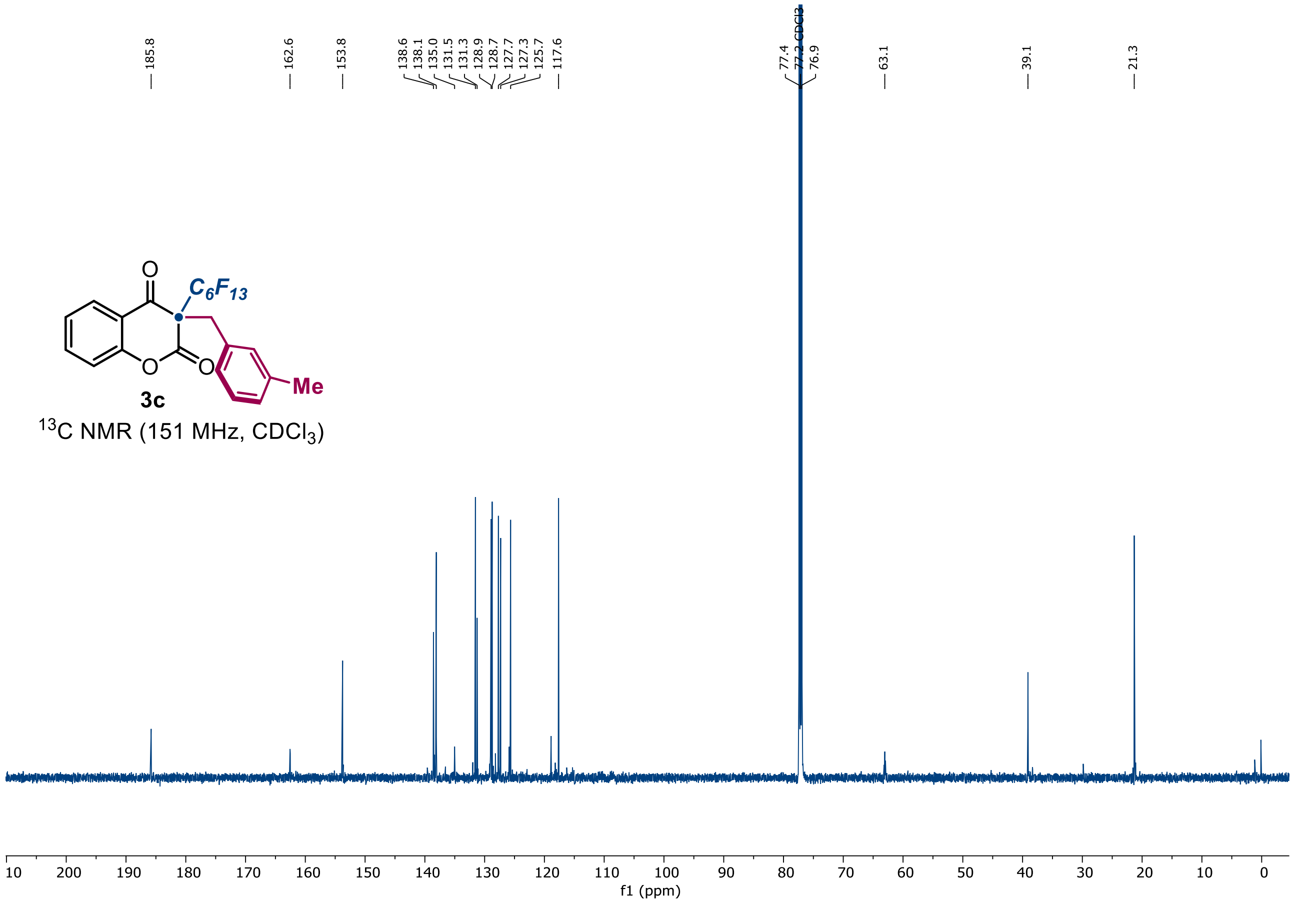
3b

^{19}F NMR (565 MHz, CDCl$_3$)



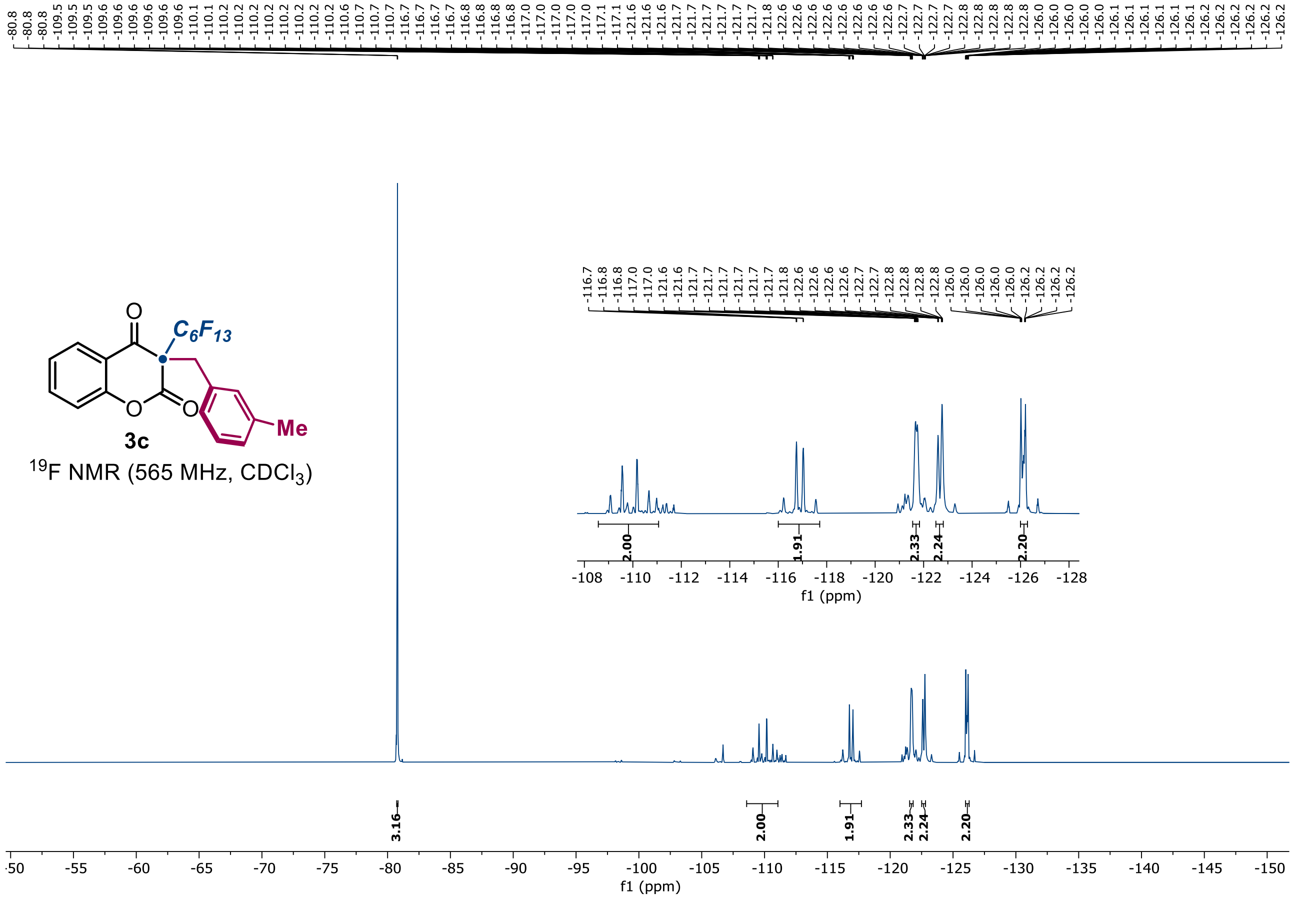
3c

^{1}H NMR (600 MHz, CDCl$_3$)



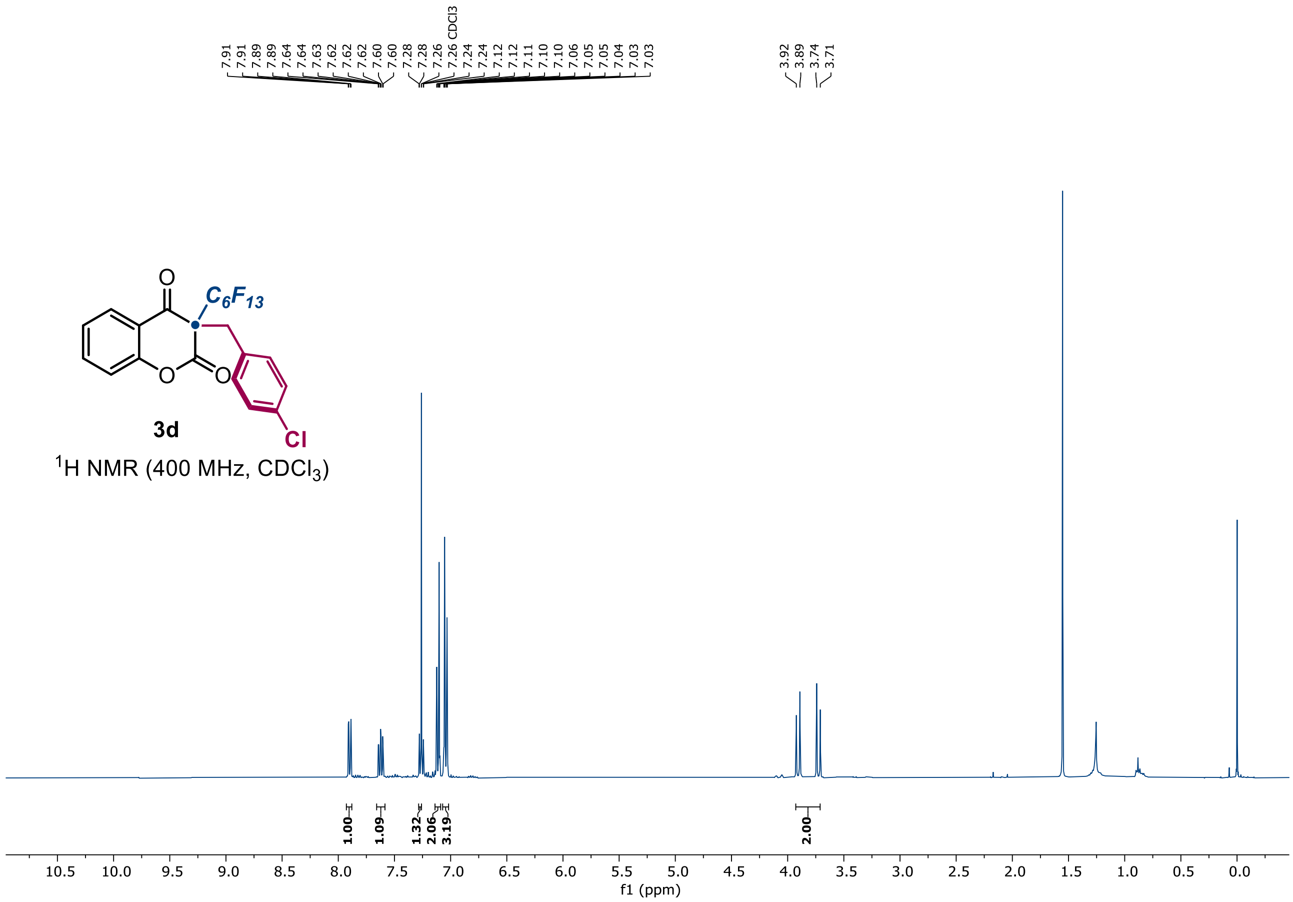
3c

^{13}C NMR (151 MHz, CDCl$_3$)



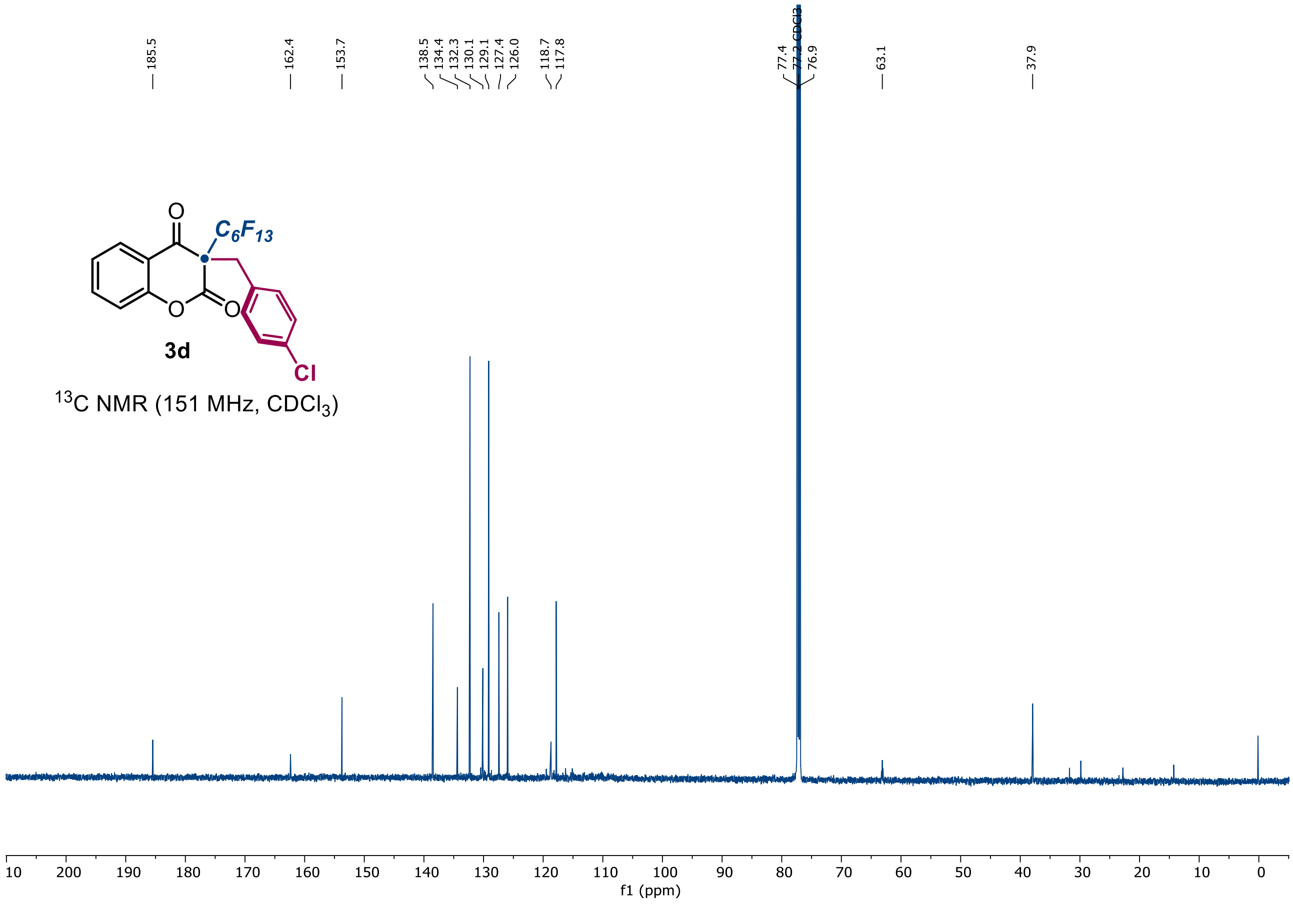
3c

^{19}F NMR (565 MHz, CDCl$_3$)



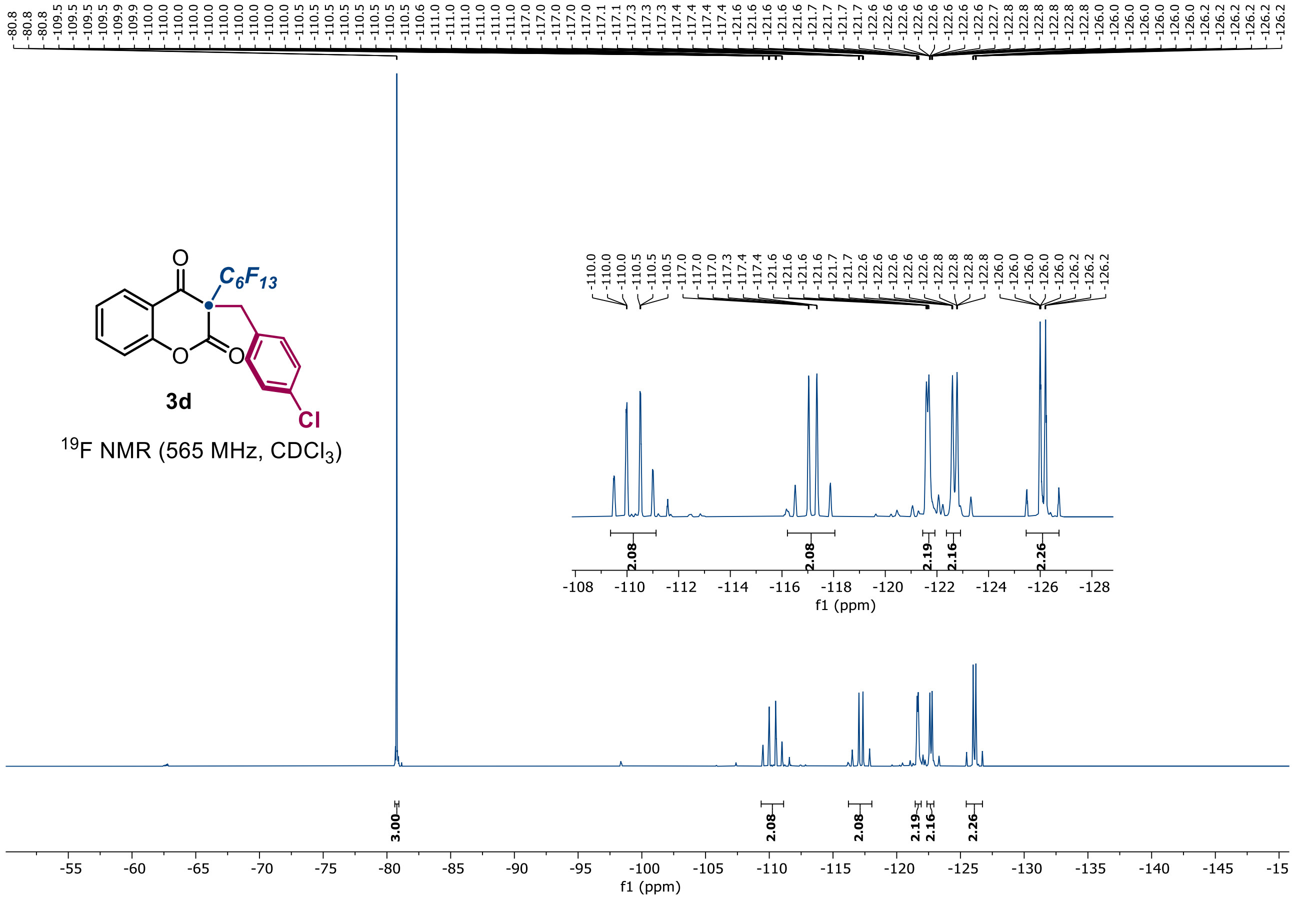
3d

^{1}H NMR (400 MHz, CDCl$_3$)



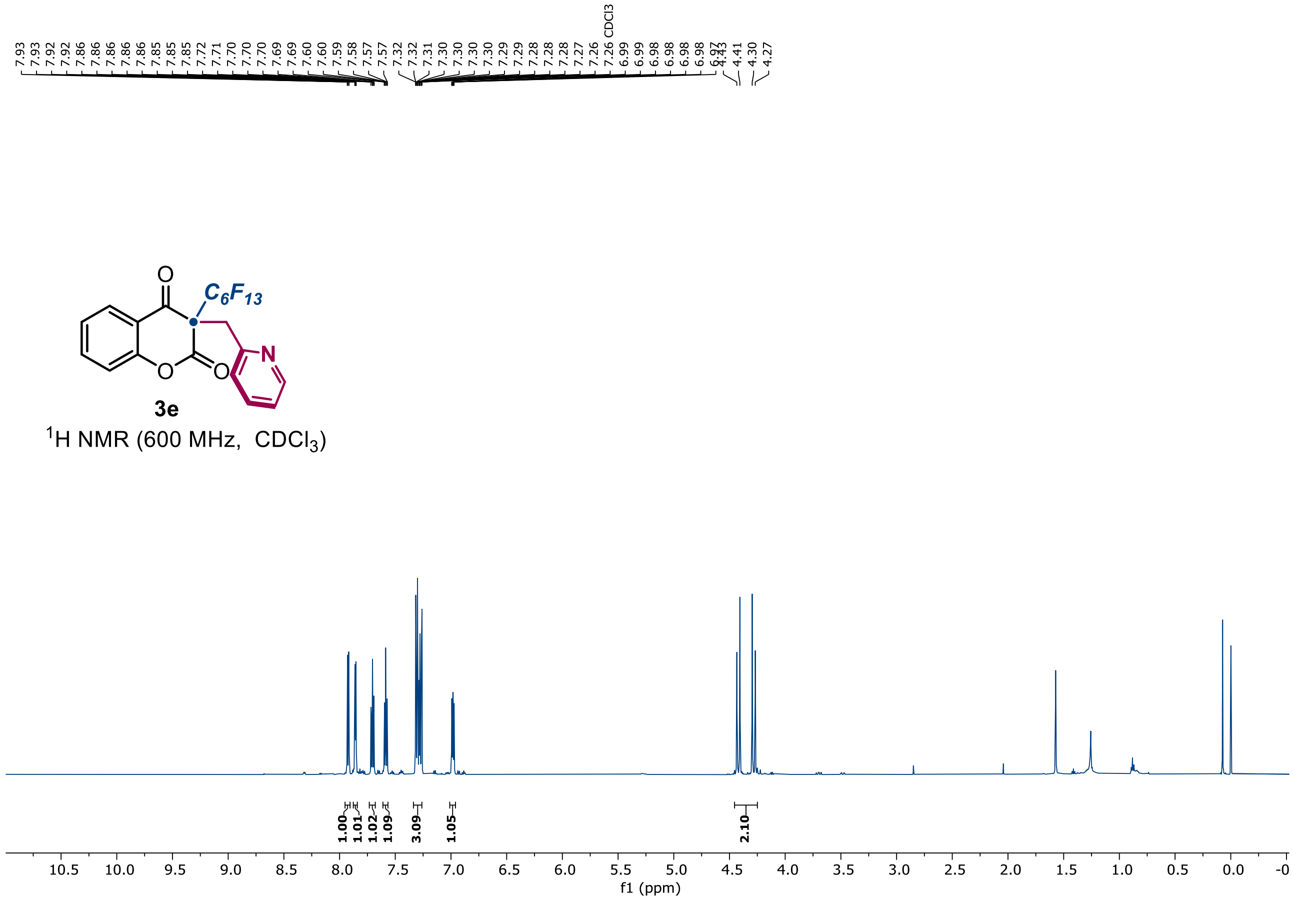
3d

^{13}C NMR (151 MHz, CDCl$_3$)



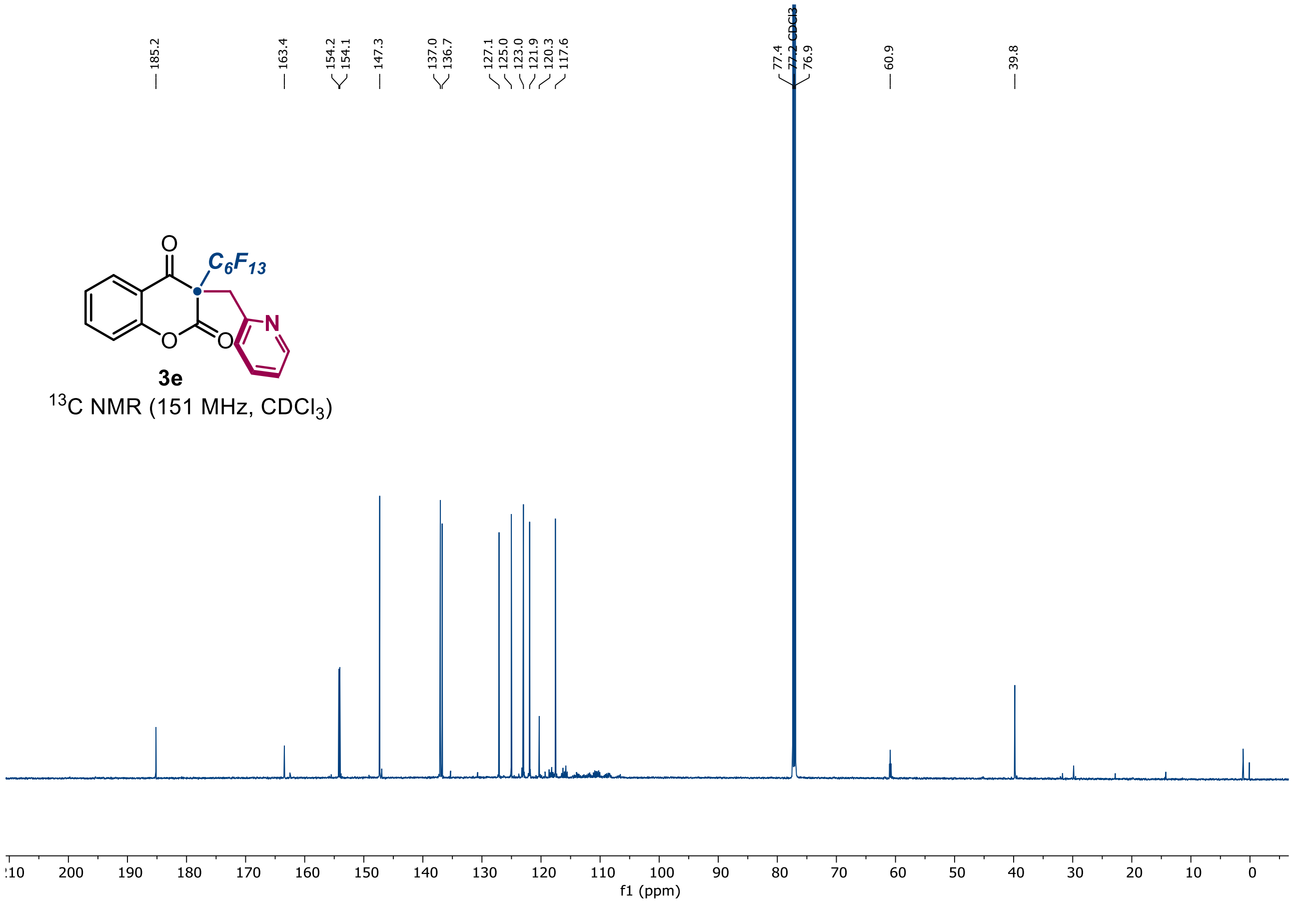
3d

^{19}F NMR (565 MHz, $CDCl_3$)



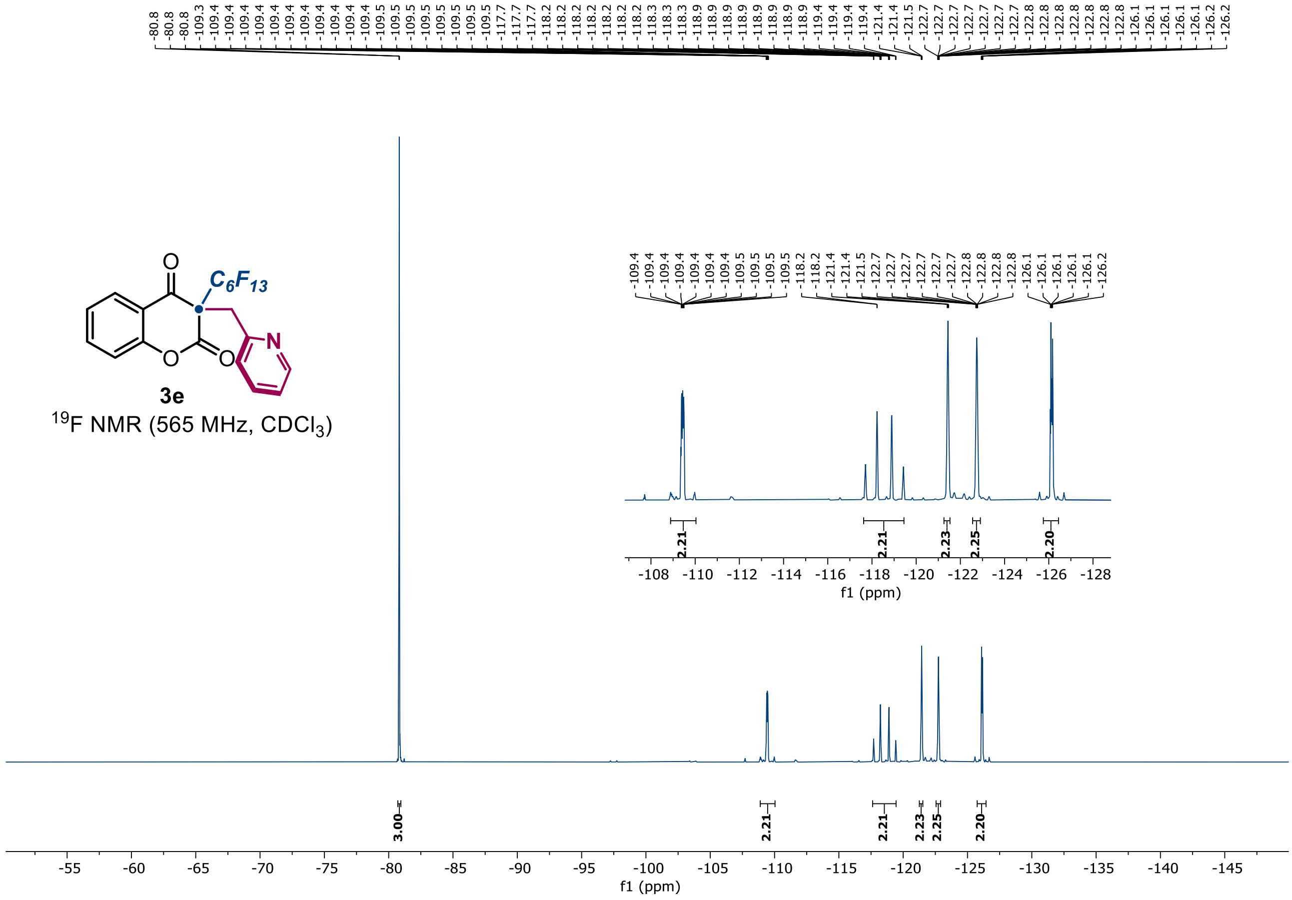
3e

^{1}H NMR (600 MHz, $CDCl_3$)



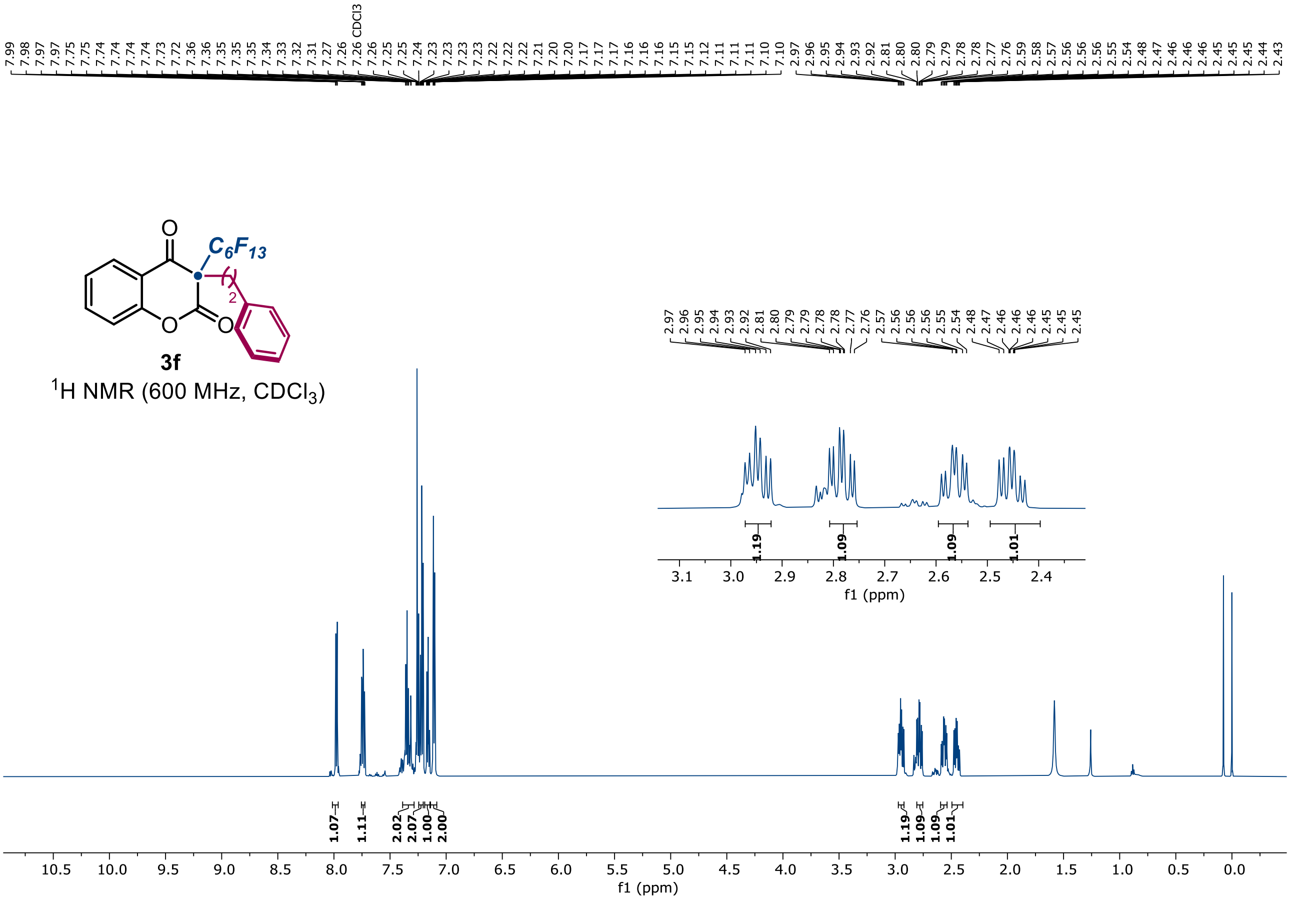
3e

^{13}C NMR (151 MHz, CDCl$_3$)



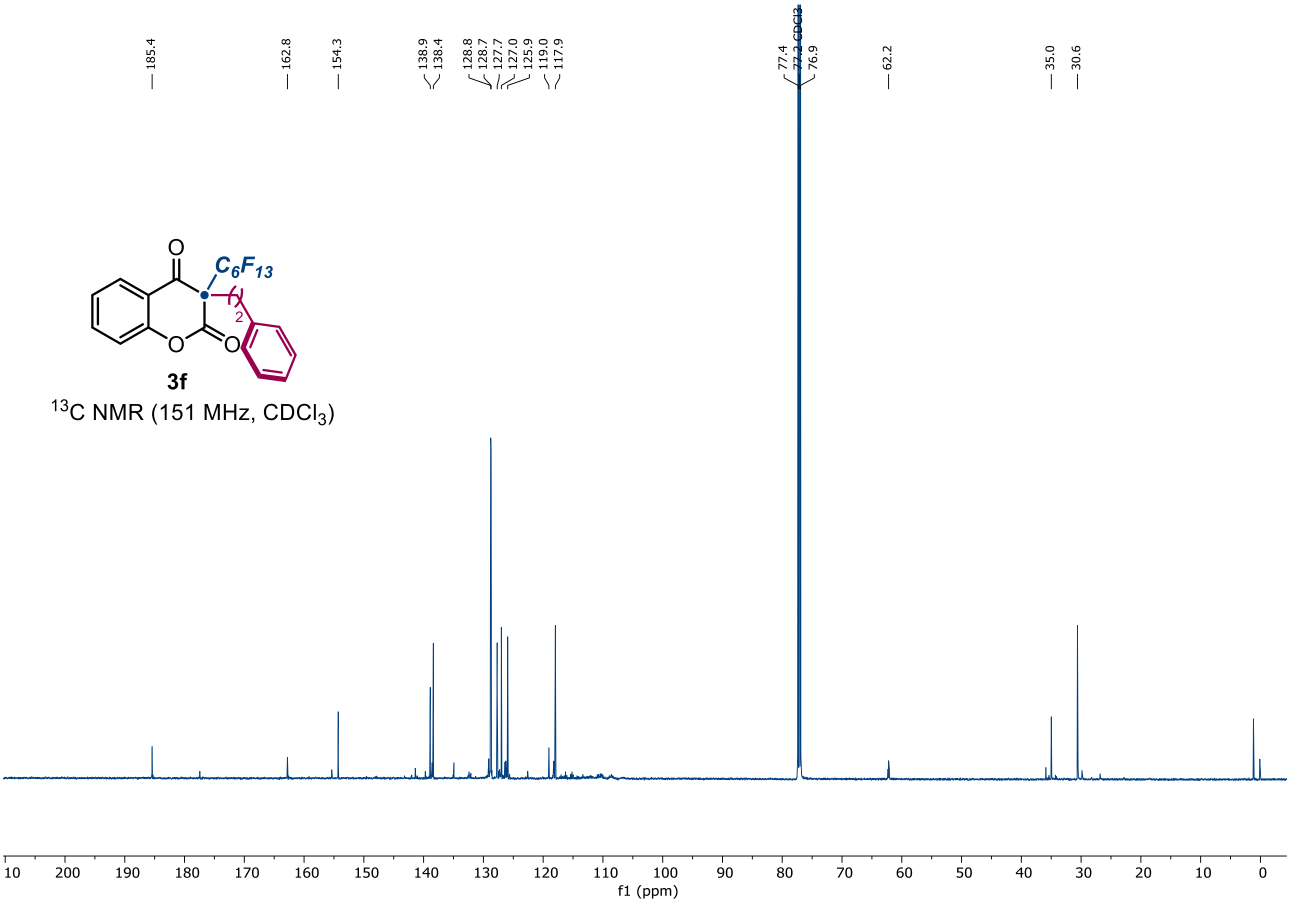
3e

^{19}F NMR (565 MHz, CDCl$_3$)



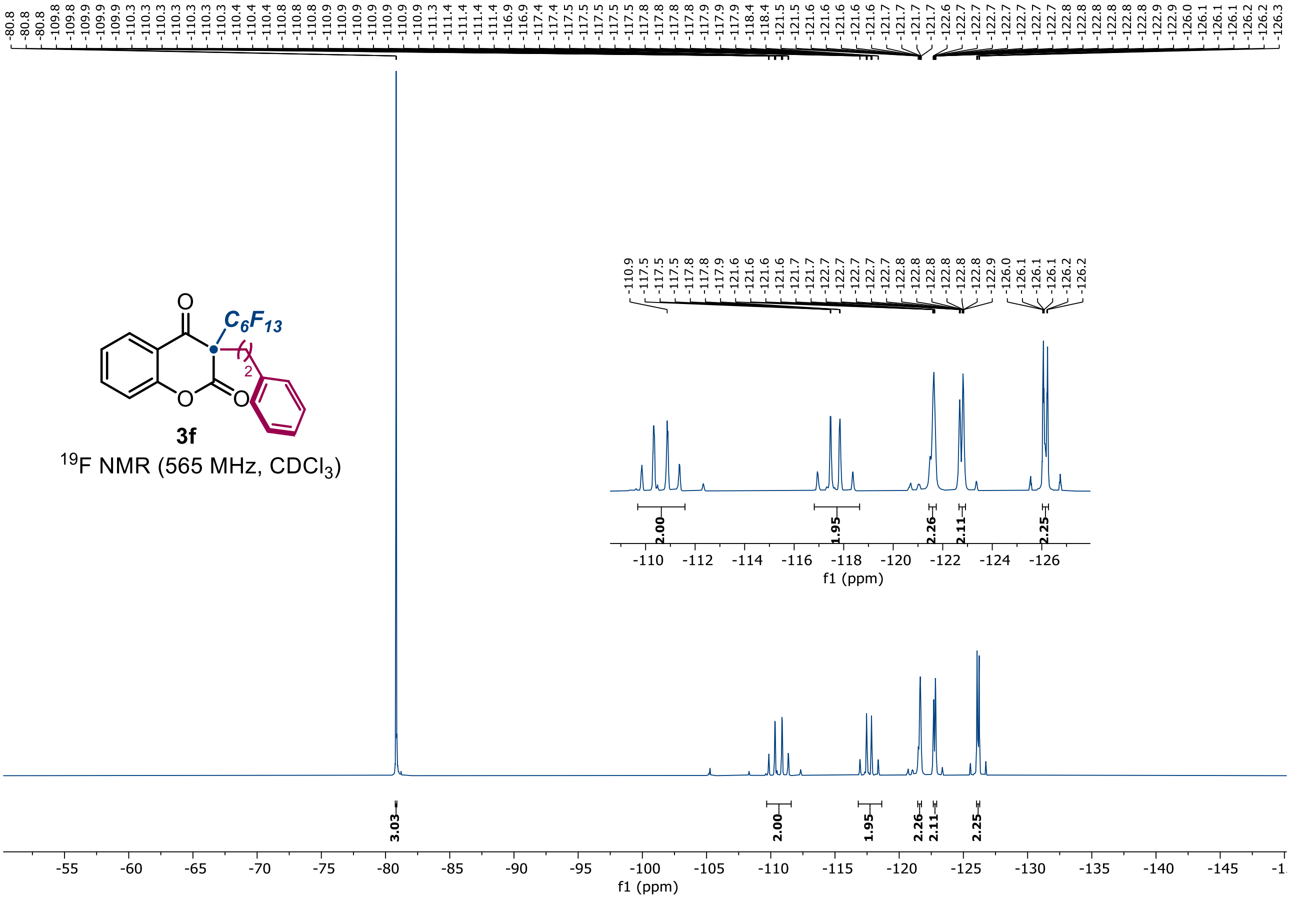
3f

^{1}H NMR (600 MHz, CDCl$_3$)



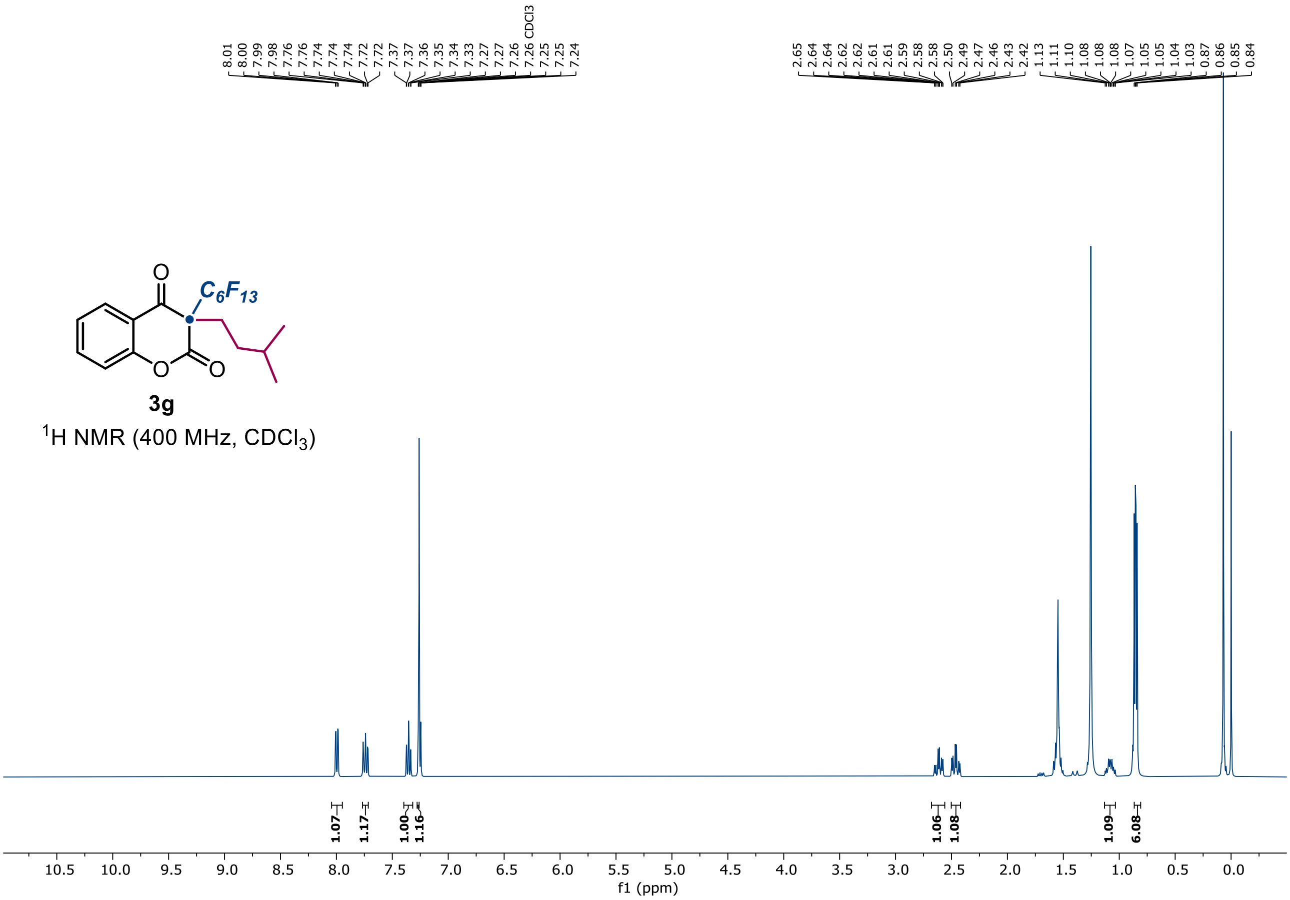
3f

^{13}C NMR (151 MHz, CDCl$_3$)



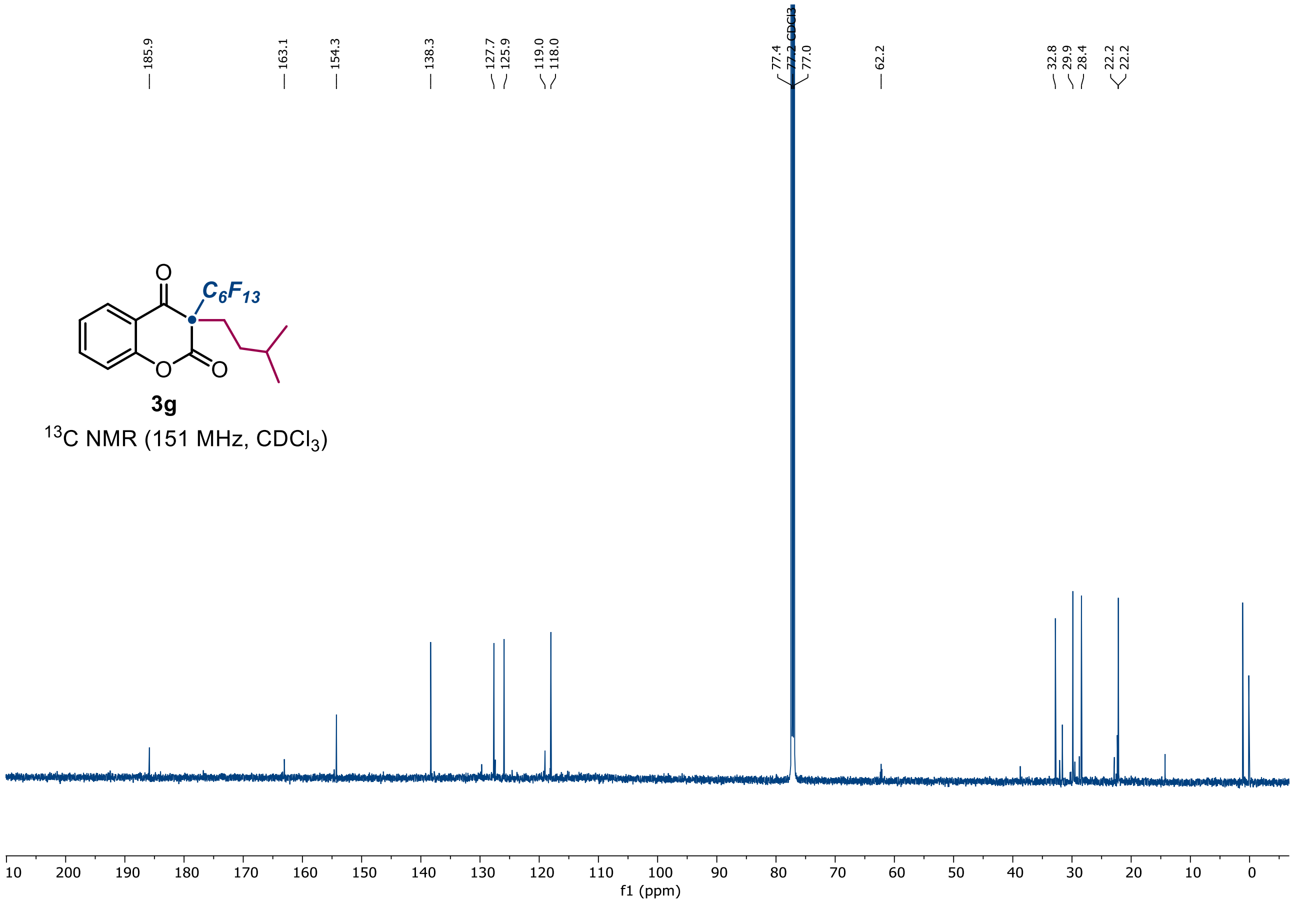
3f

^{19}F NMR (565 MHz, CDCl$_3$)



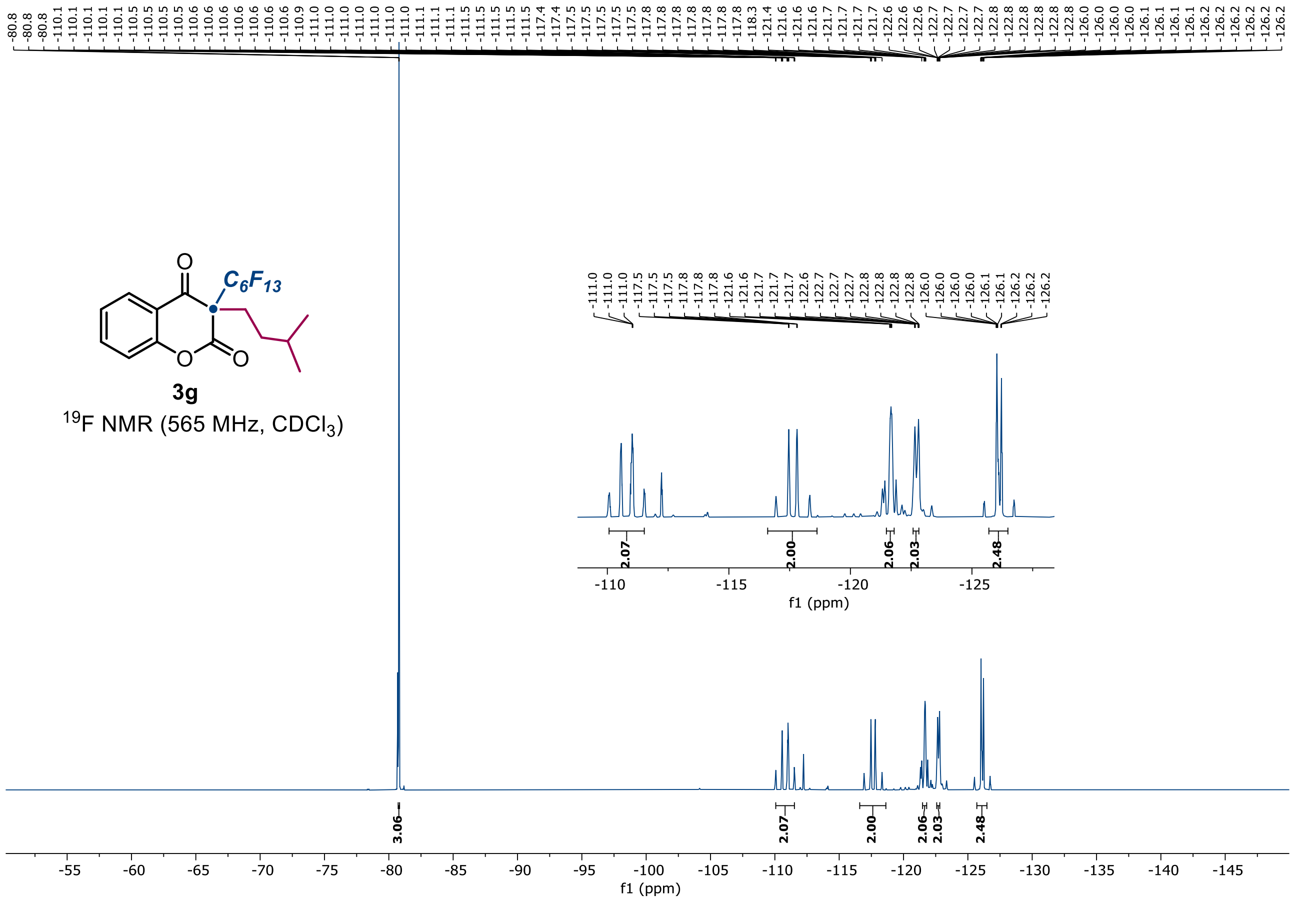
3g

^{1}H NMR (400 MHz, CDCl$_3$)



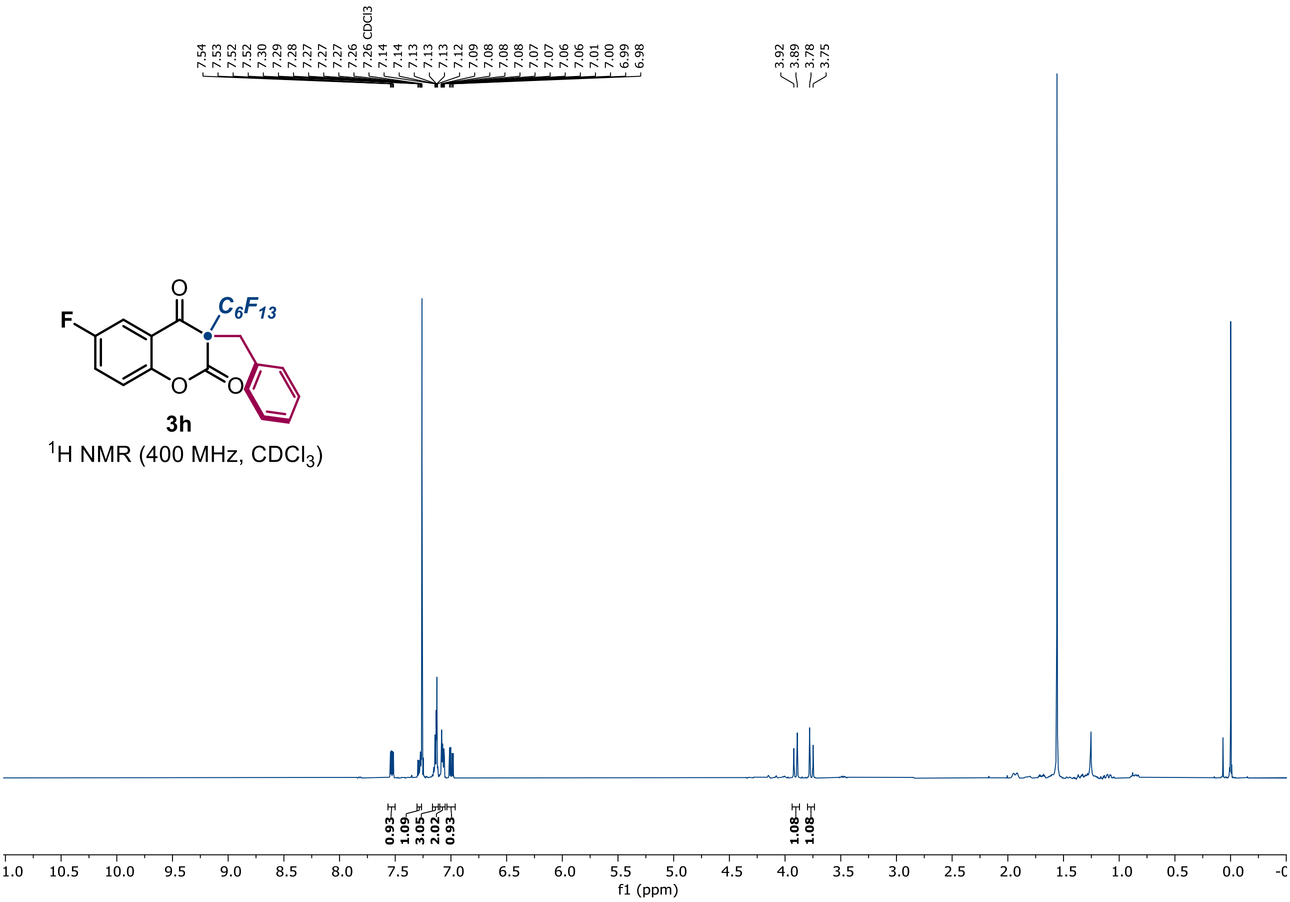
3g

^{13}C NMR (151 MHz, CDCl$_3$)



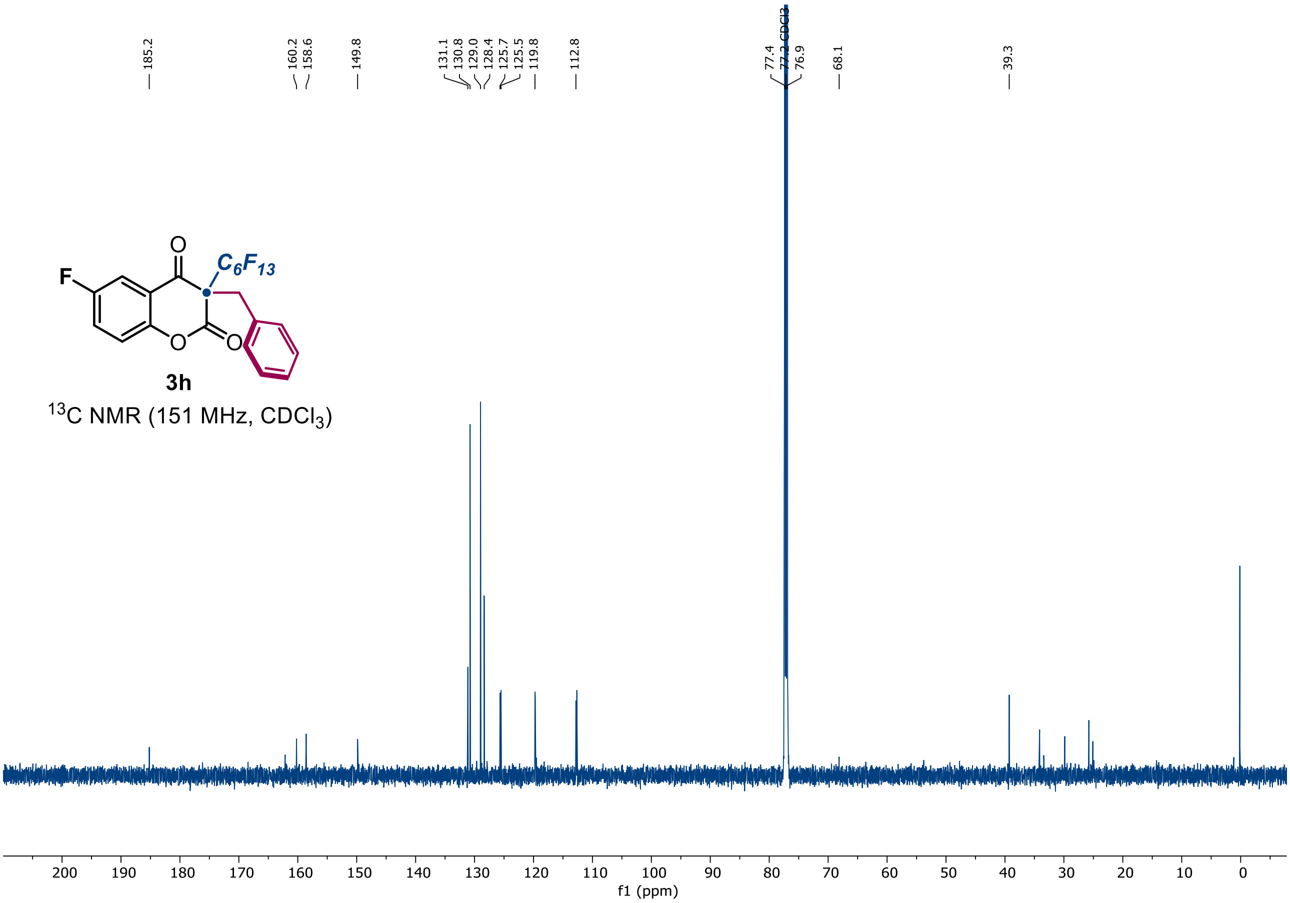
3g

^{19}F NMR (565 MHz, CDCl$_3$)



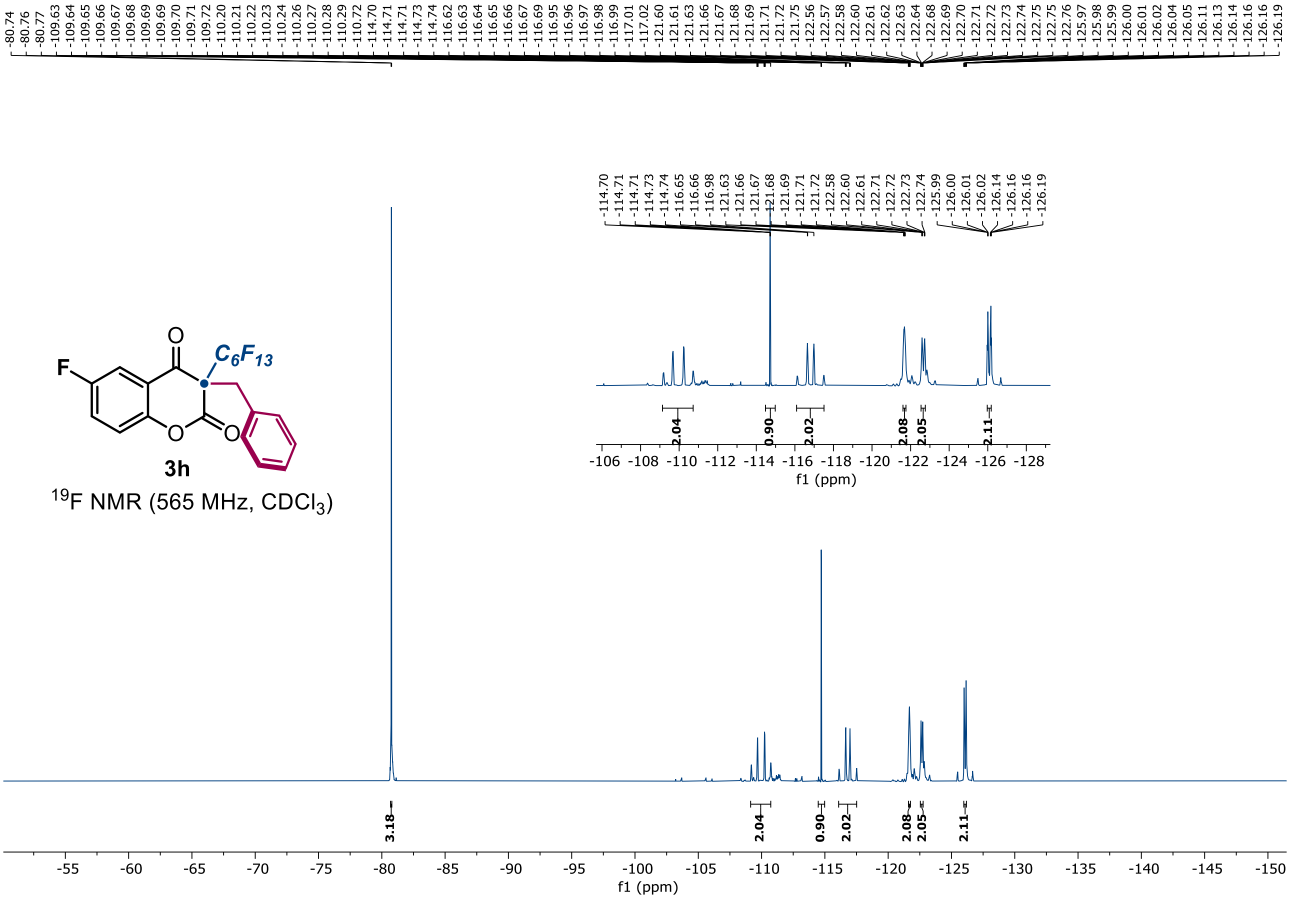
3h

^{1}H NMR (400 MHz, $CDCl_3$)



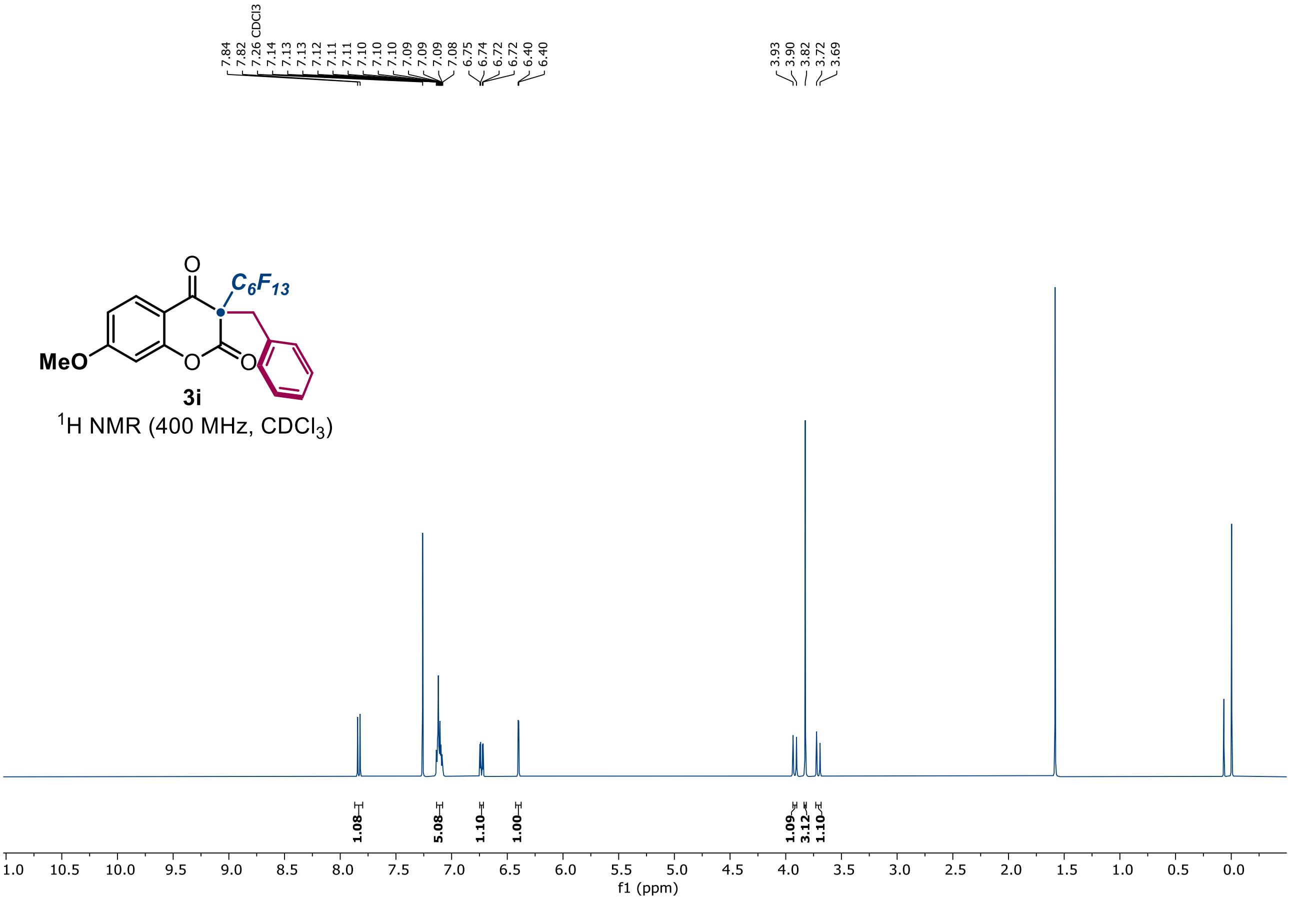
3h

^{13}C NMR (151 MHz, $CDCl_3$)



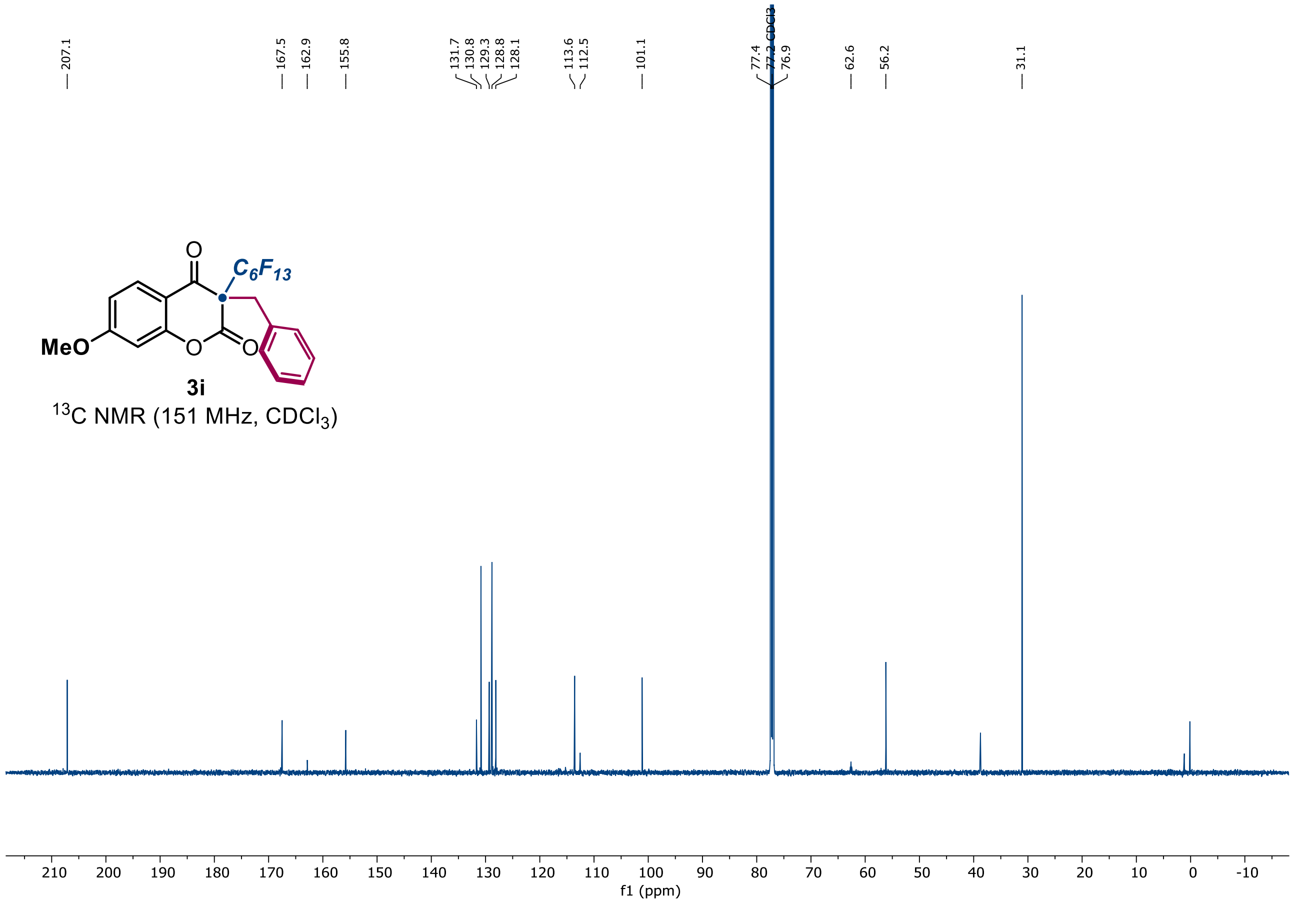
3h

^{19}F NMR (565 MHz, CDCl$_3$)



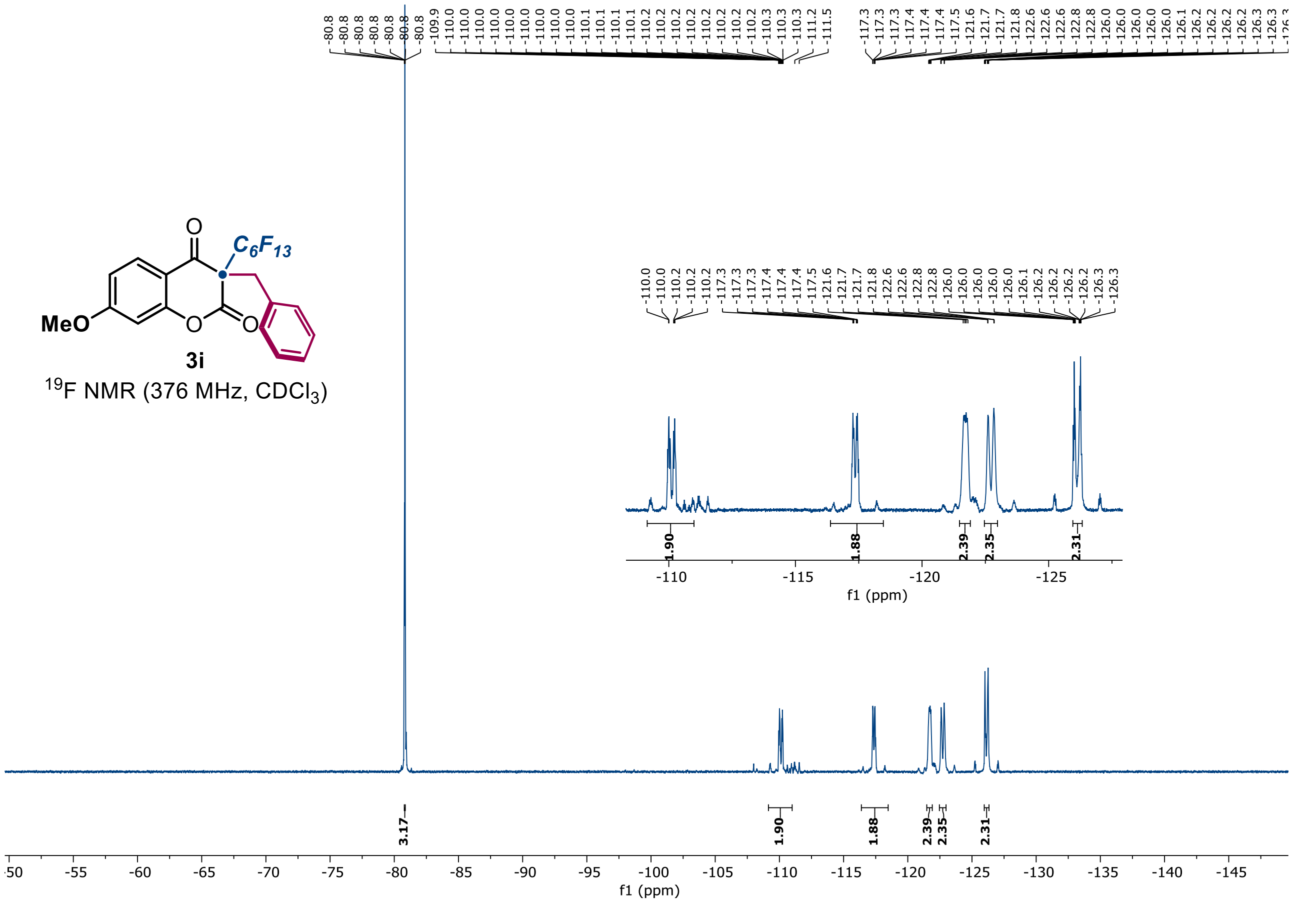
3i

^{1}H NMR (400 MHz, CDCl$_3$)



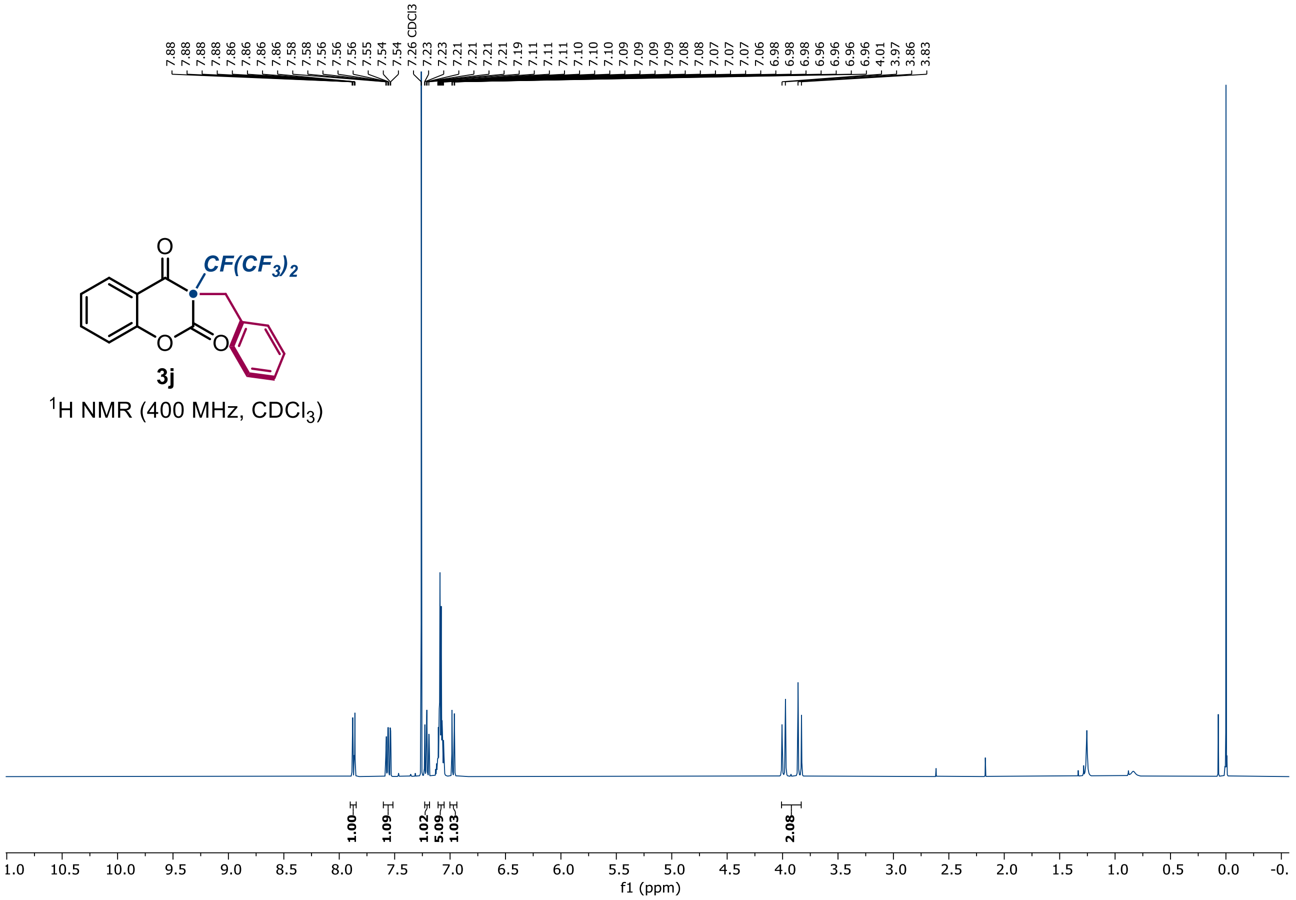
3i

^{13}C NMR (151 MHz, CDCl$_3$)



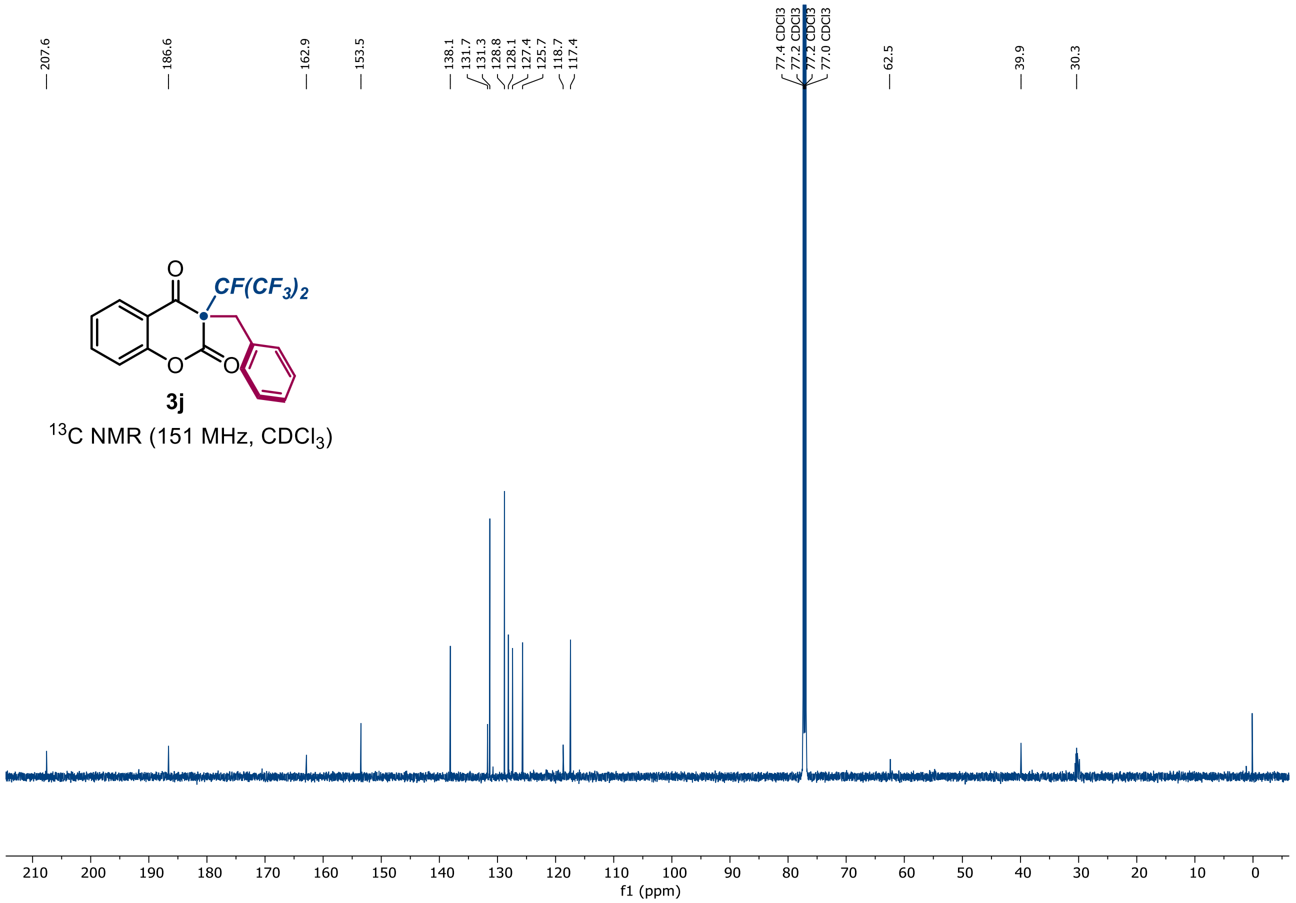
3i

^{19}F NMR (376 MHz, CDCl$_3$)



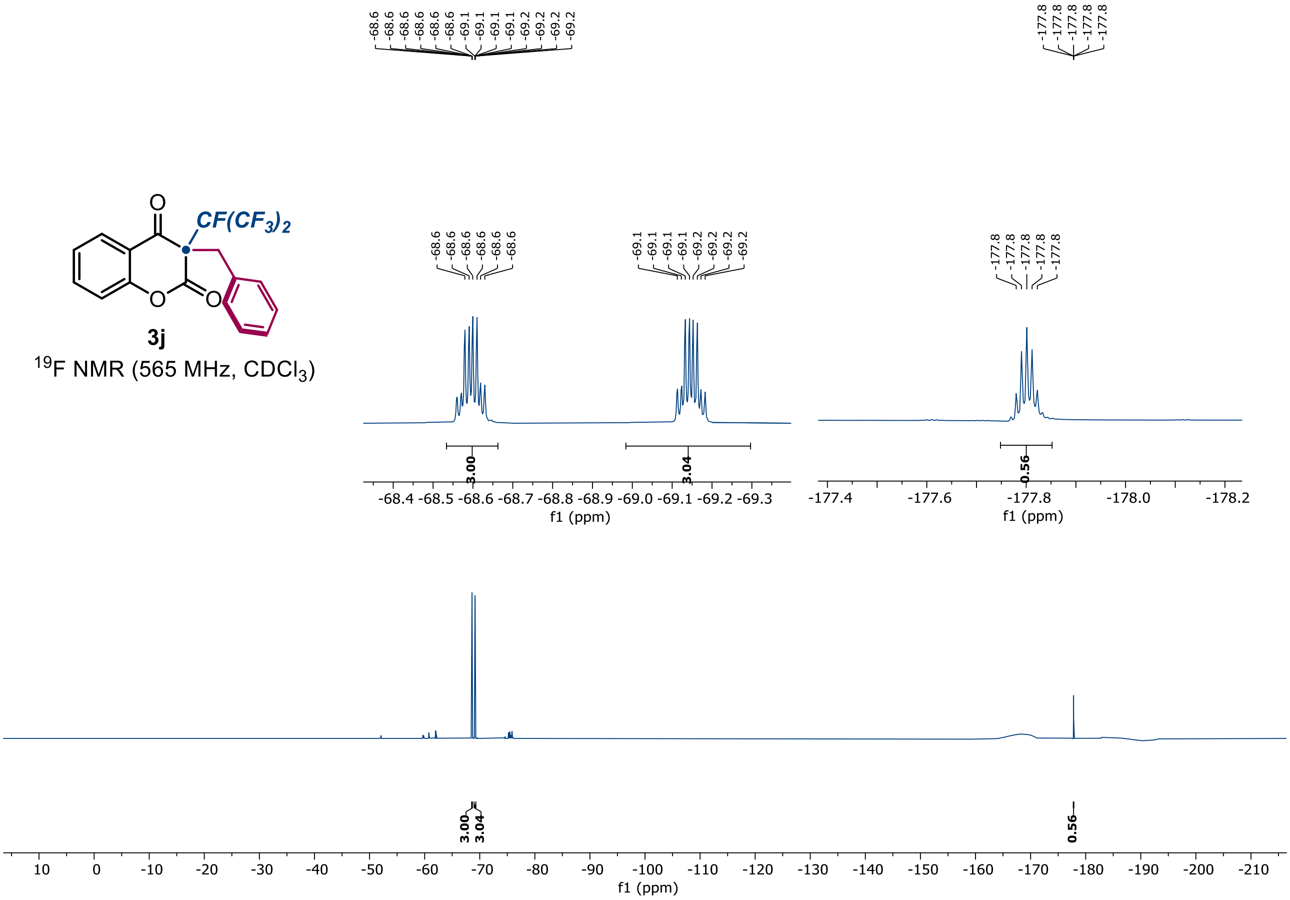
3j

^{1}H NMR (400 MHz, CDCl$_3$)



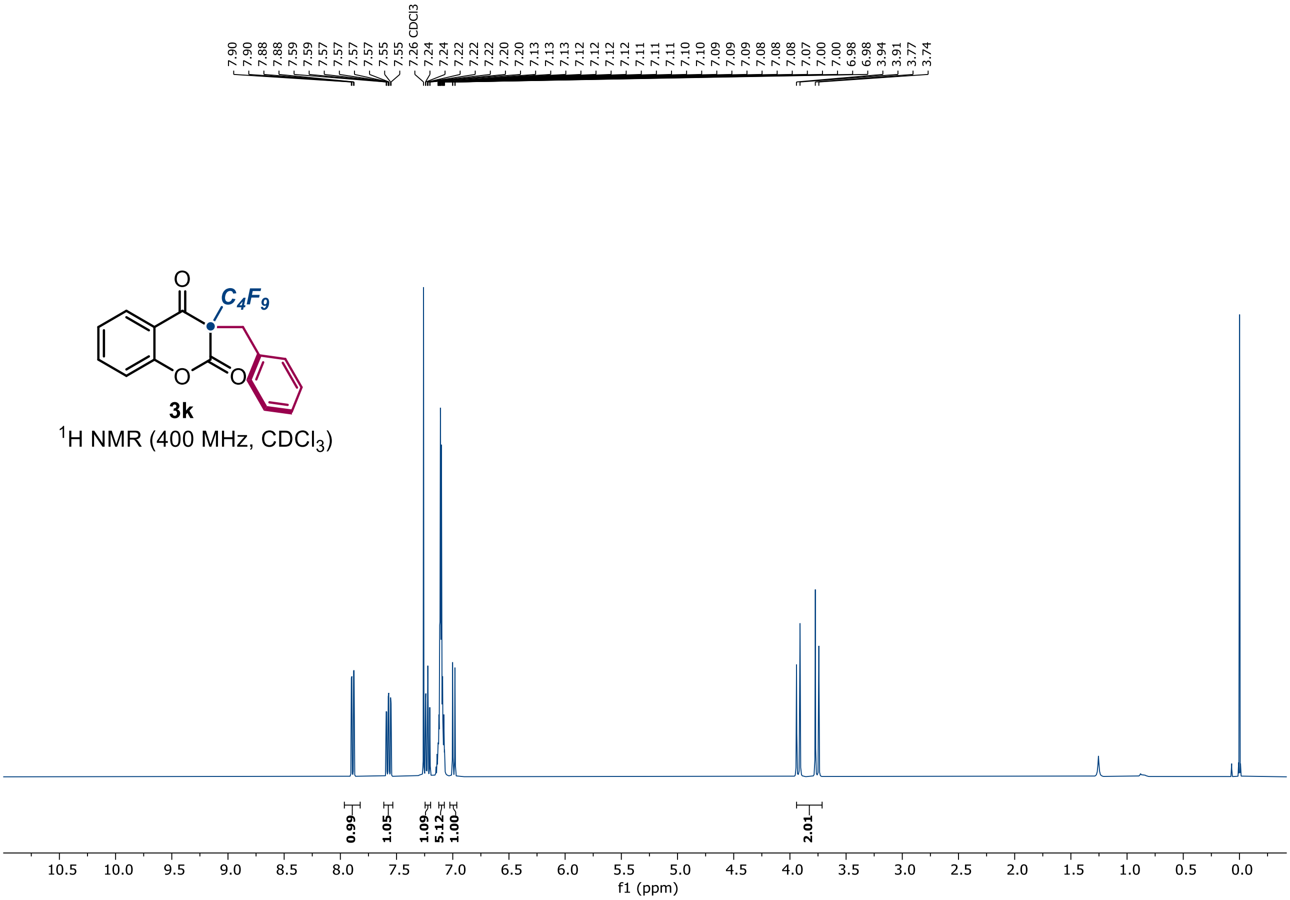
3j

^{13}C NMR (151 MHz, CDCl$_3$)



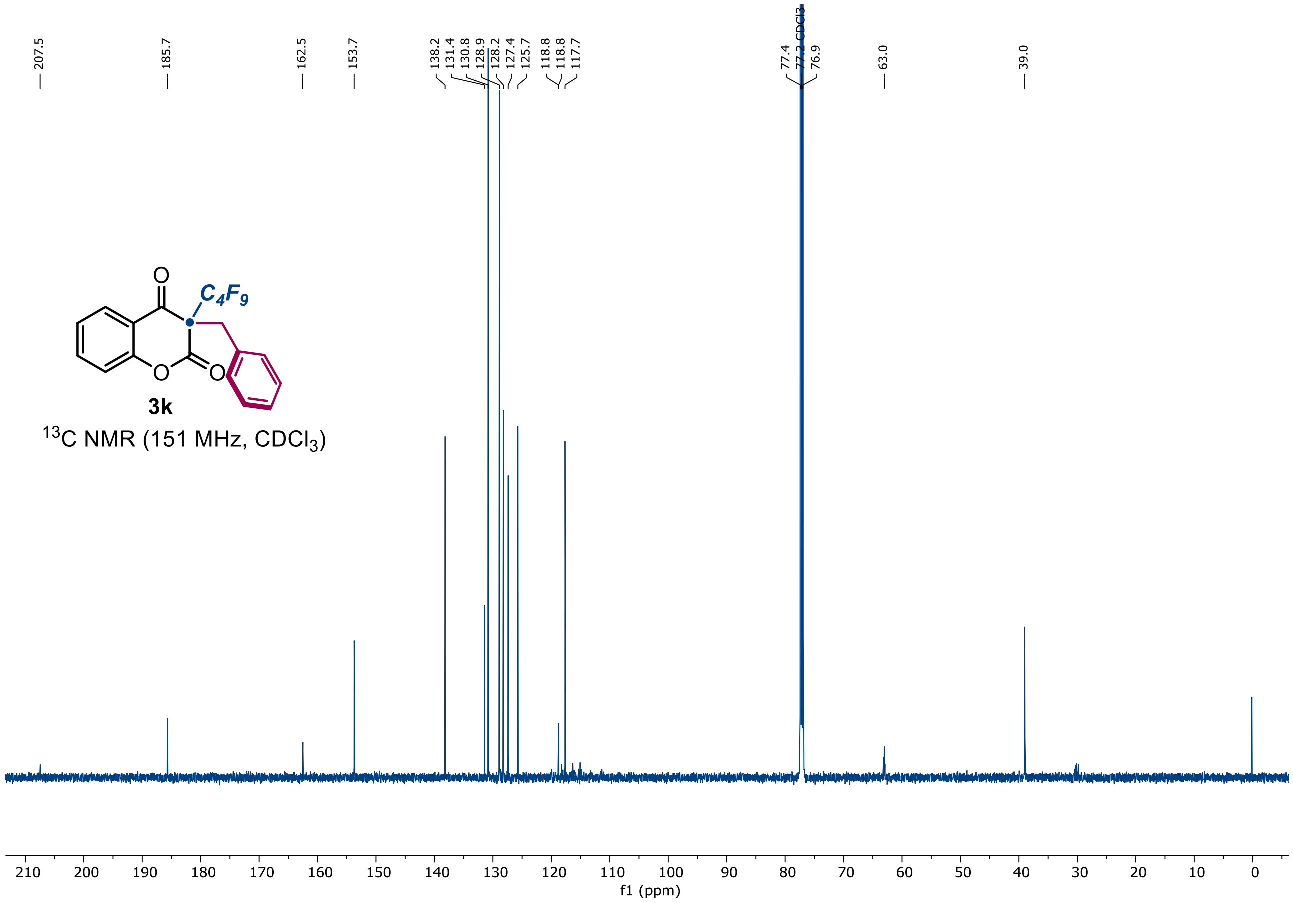
3j

^{19}F NMR (565 MHz, CDCl$_3$)



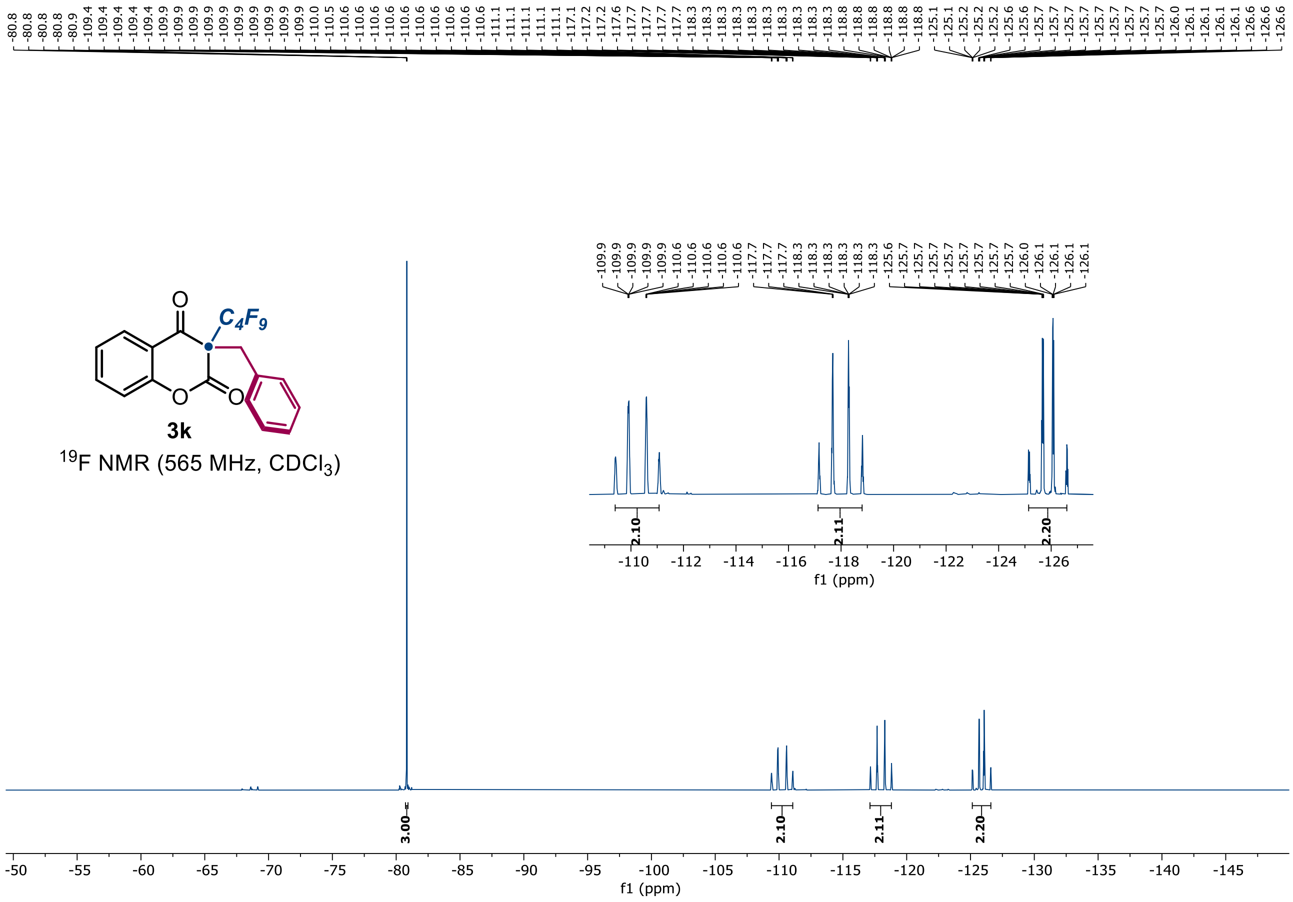
3k

^{1}H NMR (400 MHz, CDCl$_3$)



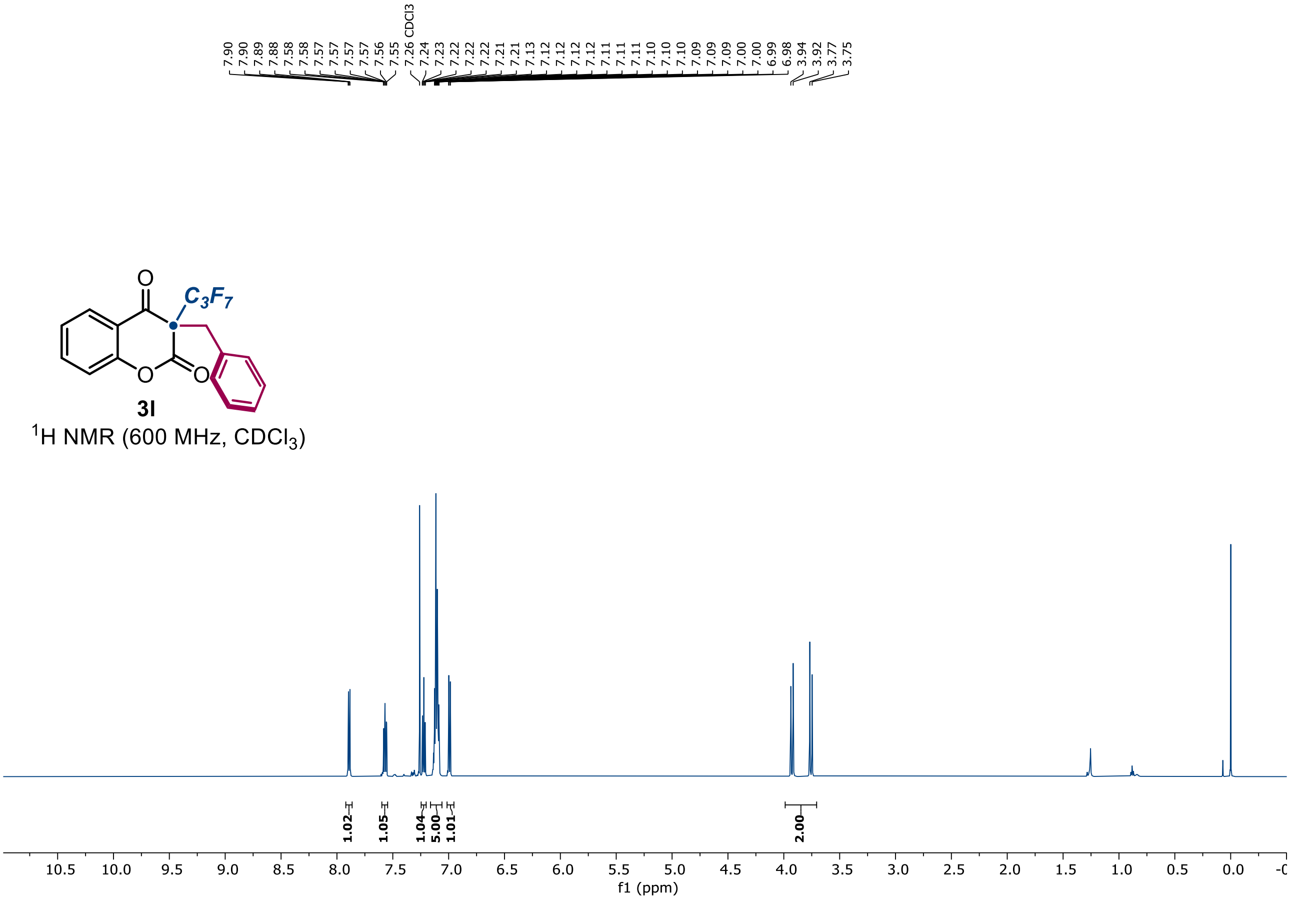
3k

^{13}C NMR (151 MHz, CDCl$_3$)



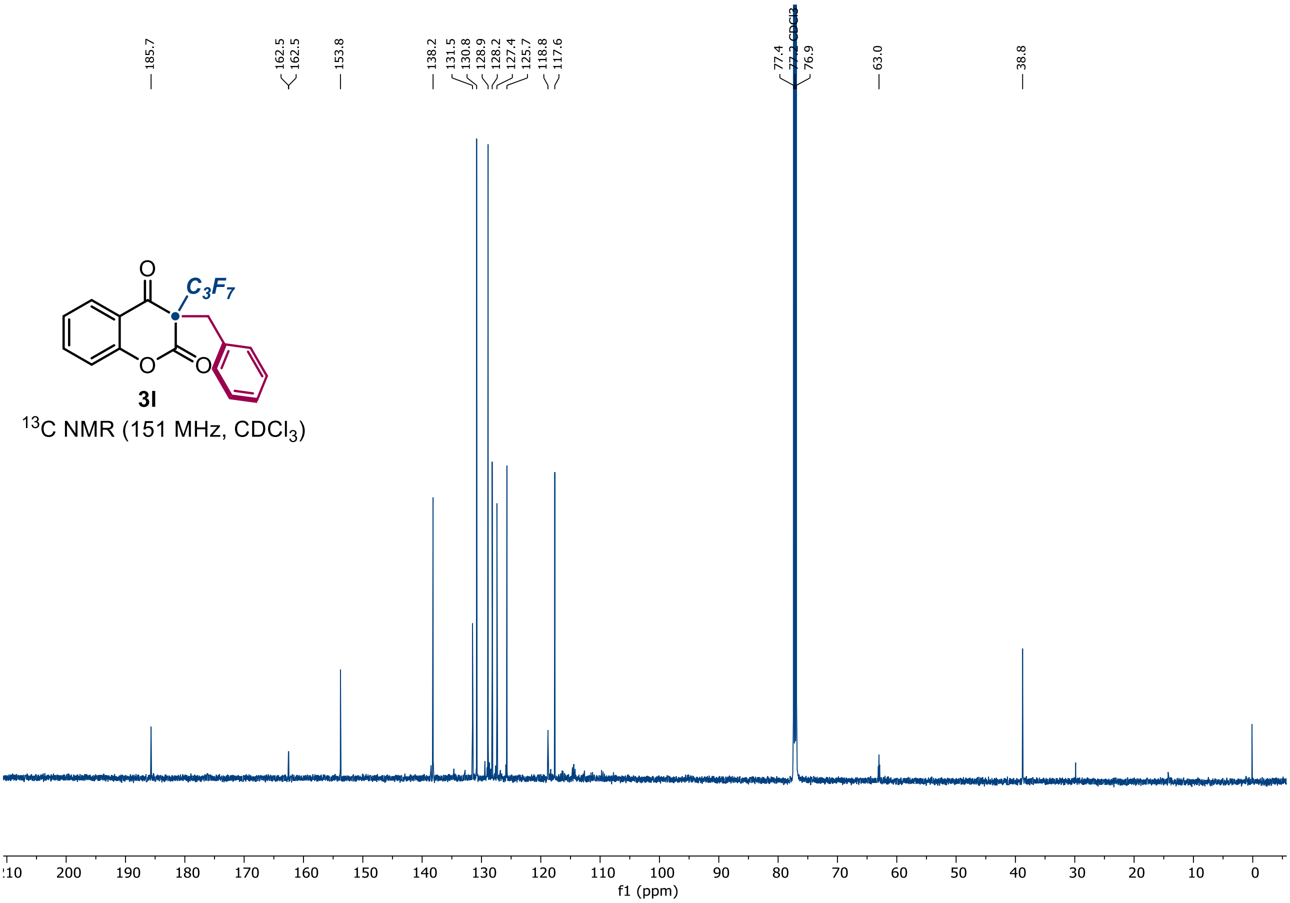
3k

^{19}F NMR (565 MHz, CDCl$_3$)



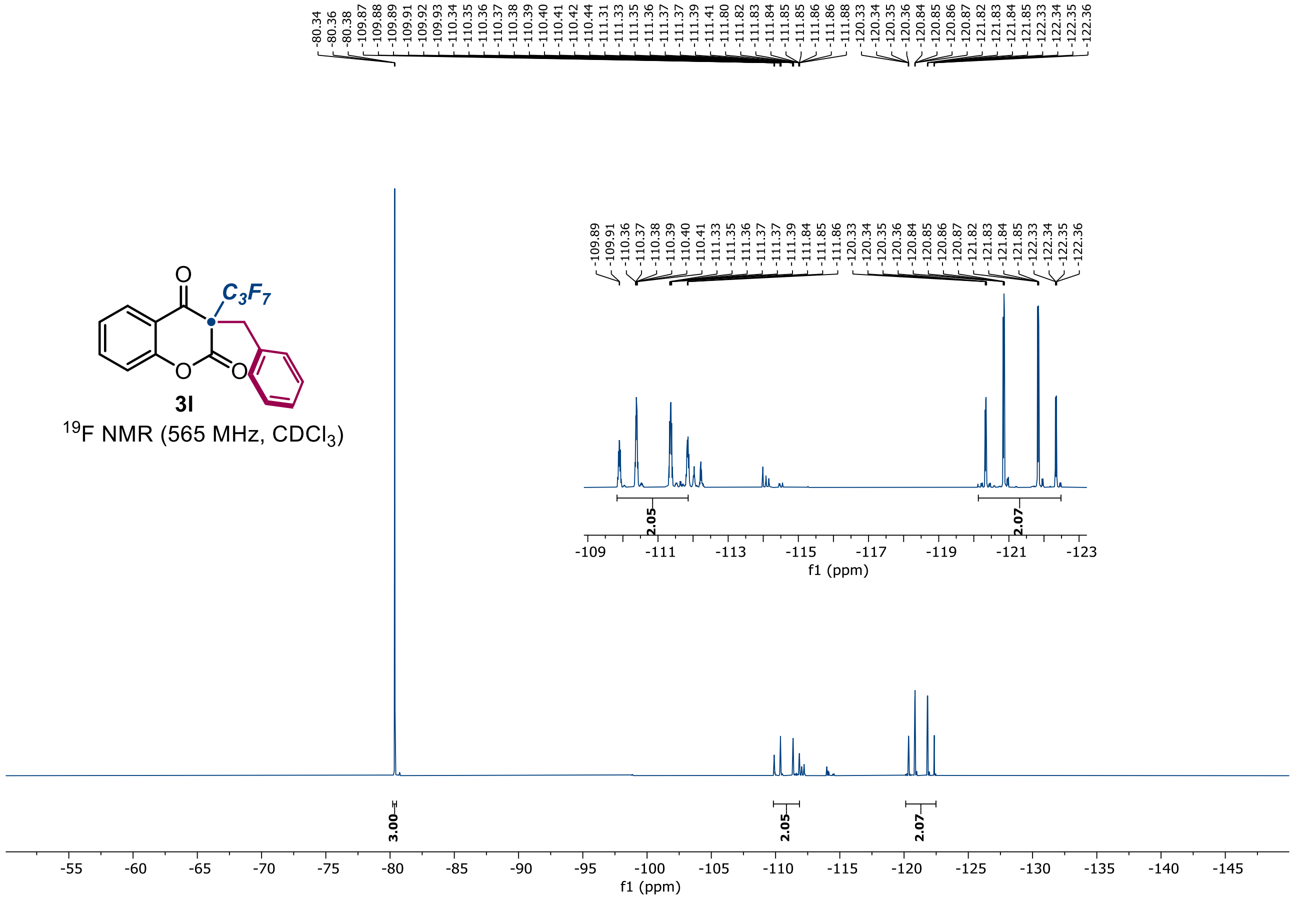
3l

^{1}H NMR (600 MHz, $CDCl_3$)



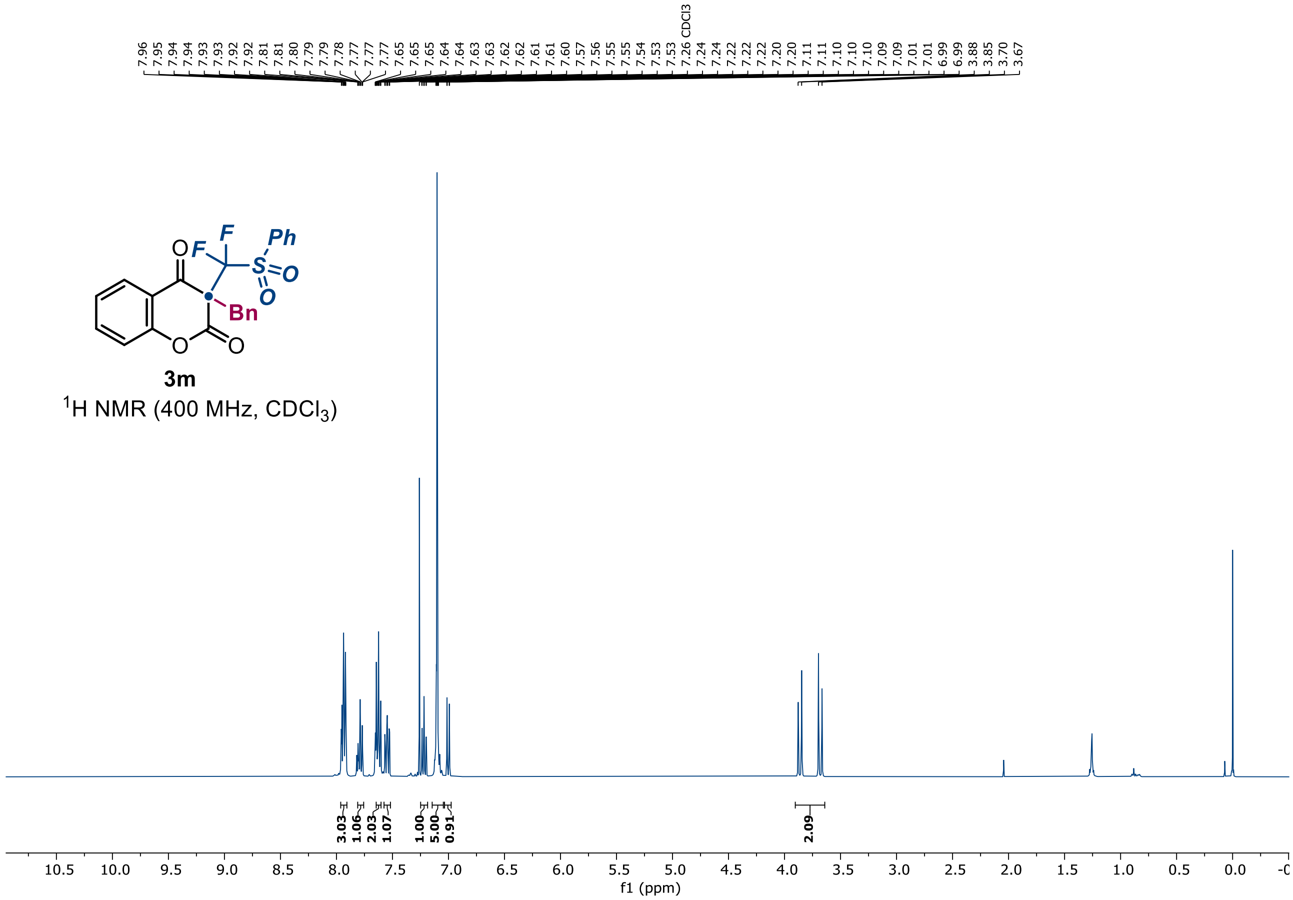
3l

^{13}C NMR (151 MHz, $CDCl_3$)



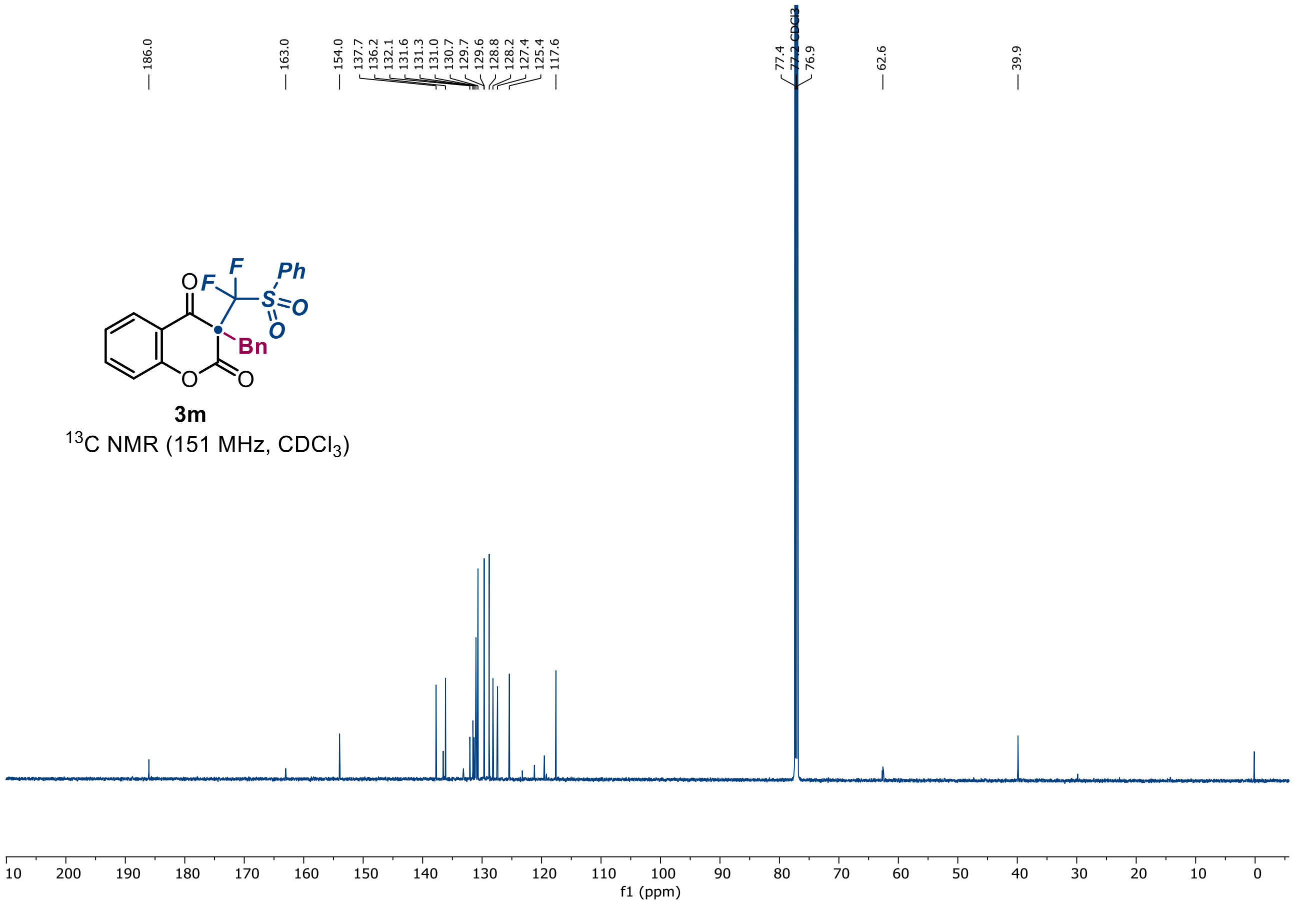
3l

^{19}F NMR (565 MHz, $CDCl_3$)



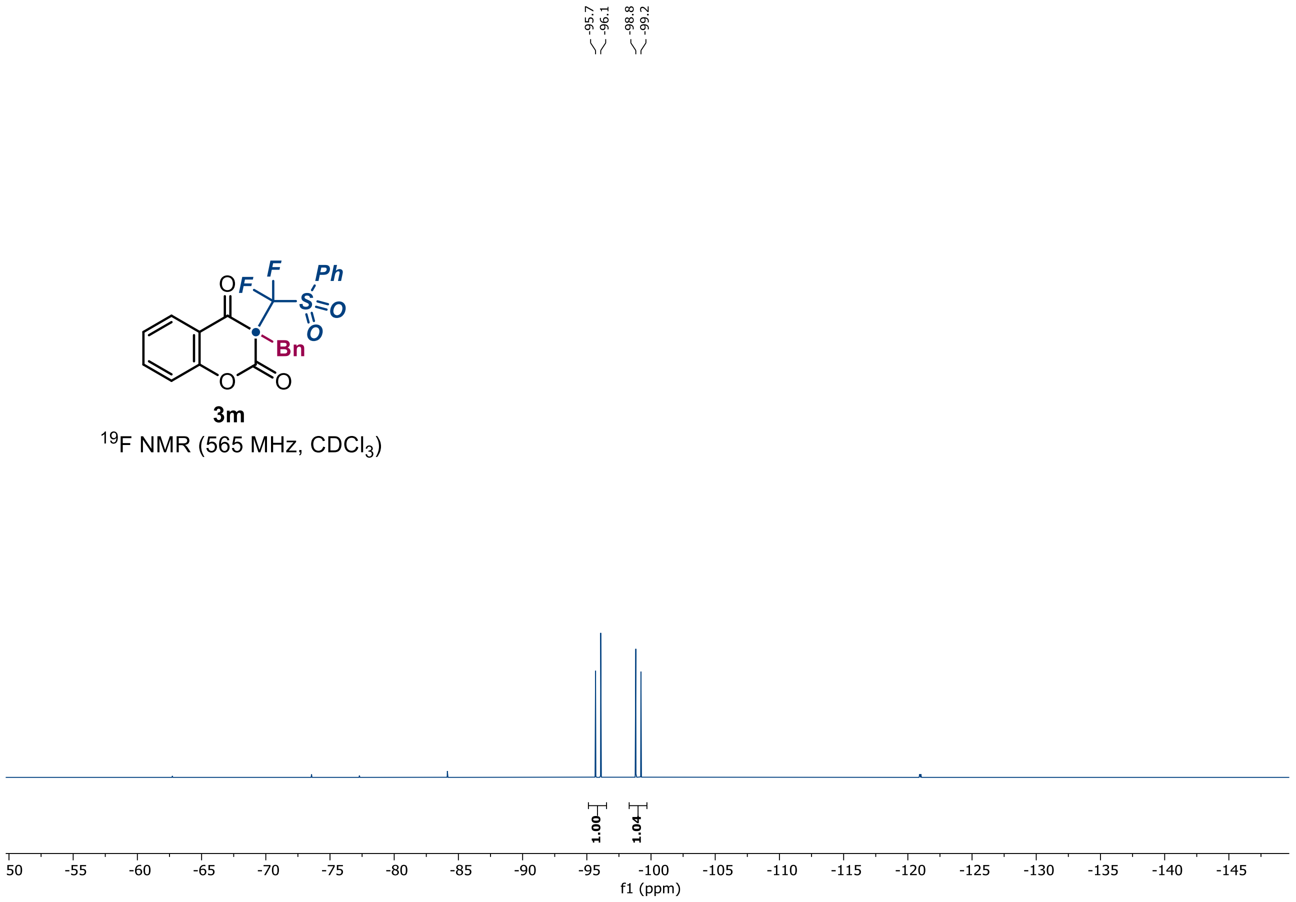
3m

^{1}H NMR (400 MHz, $CDCl_3$)



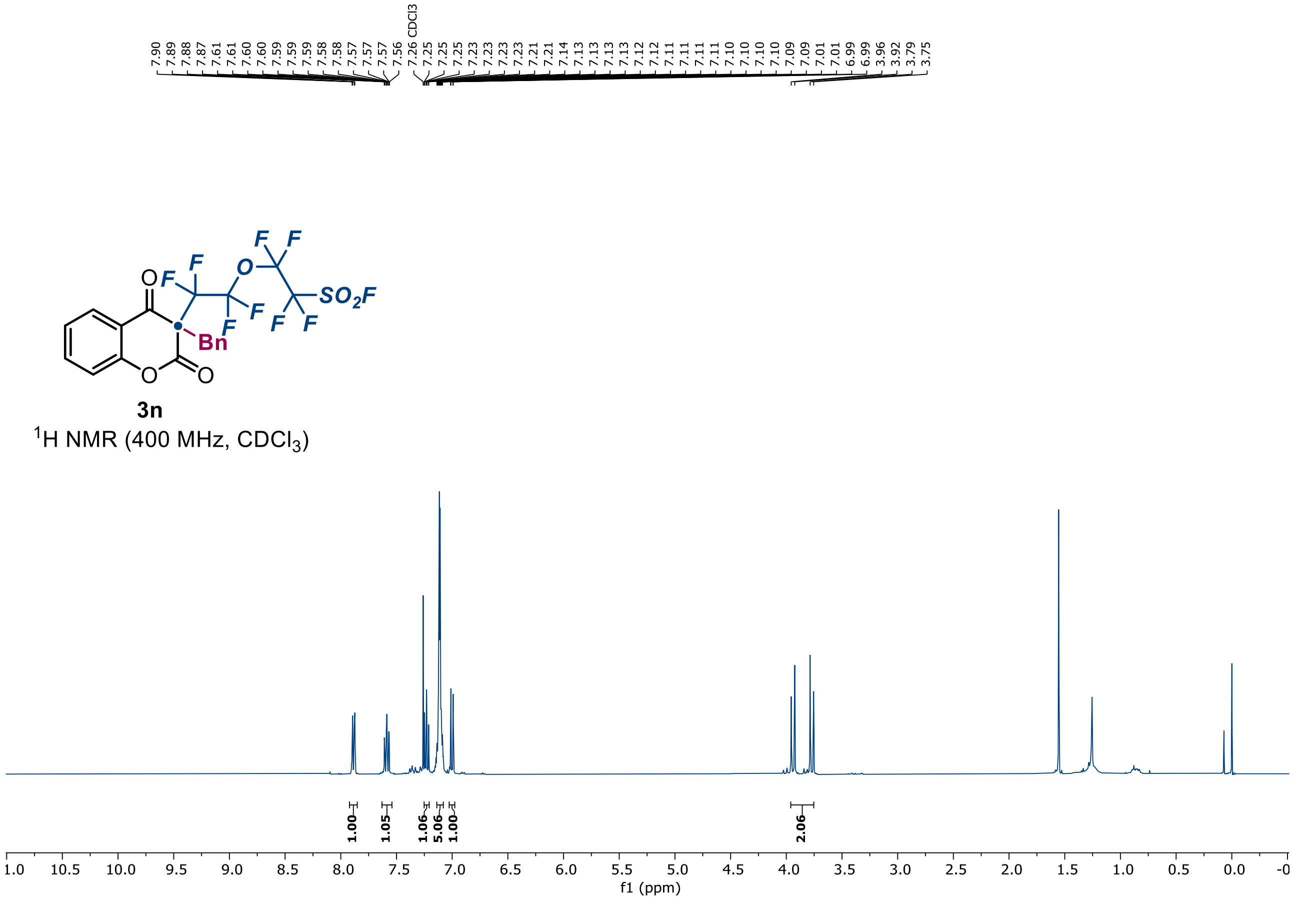
3m

^{13}C NMR (151 MHz, $CDCl_3$)



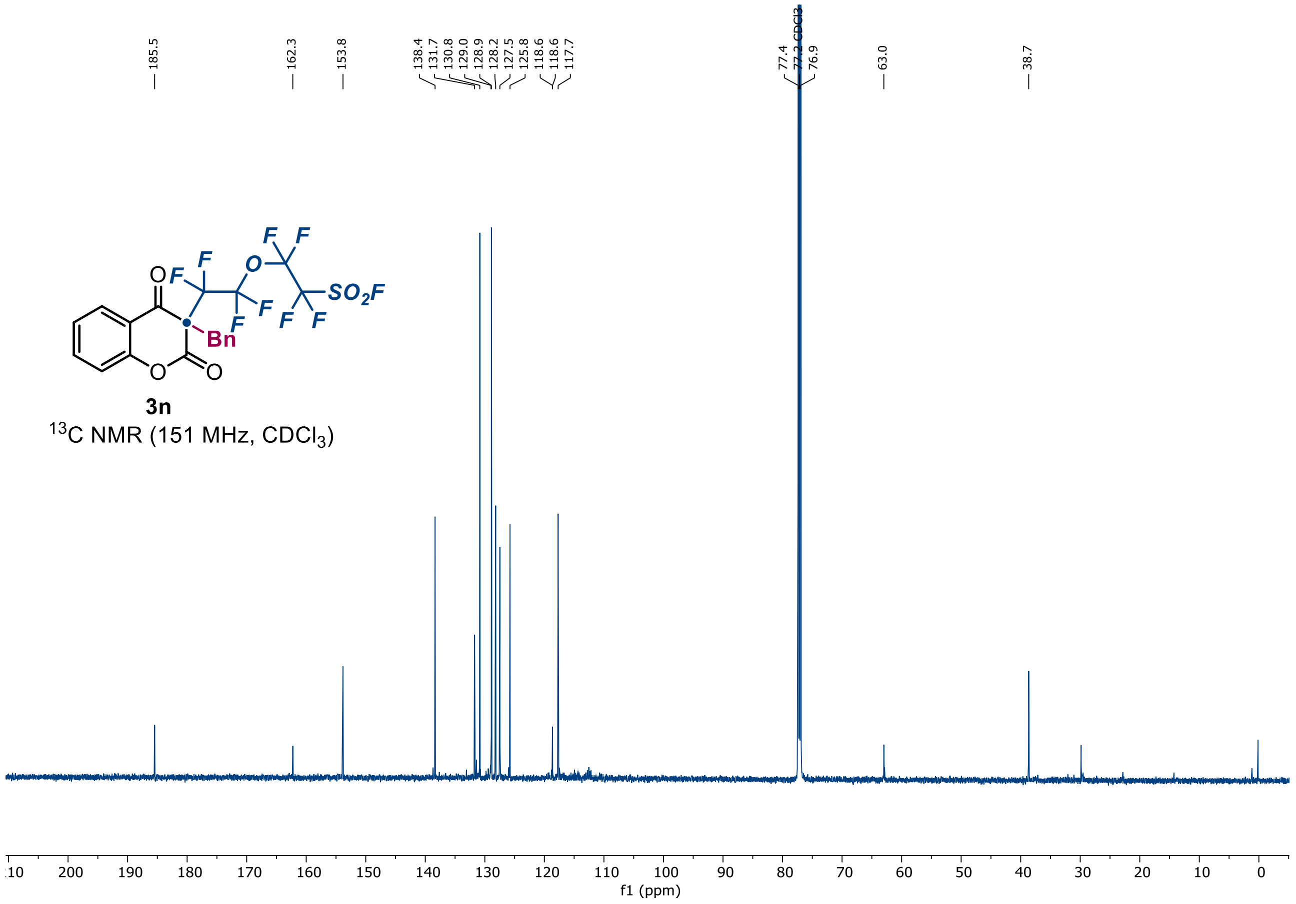
3m

^{19}F NMR (565 MHz, $CDCl_3$)



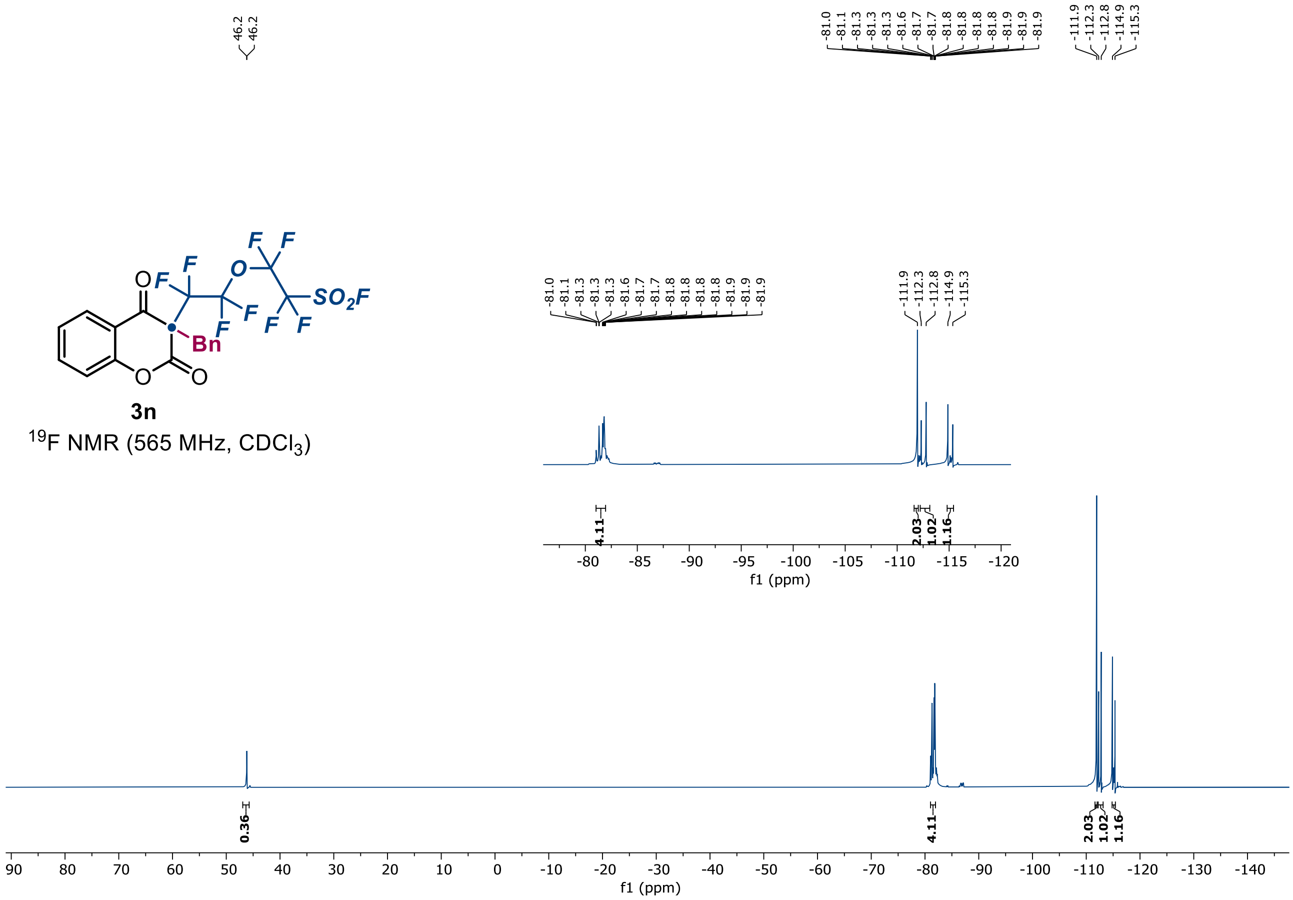
3n

^{1}H NMR (400 MHz, CDCl$_3$)



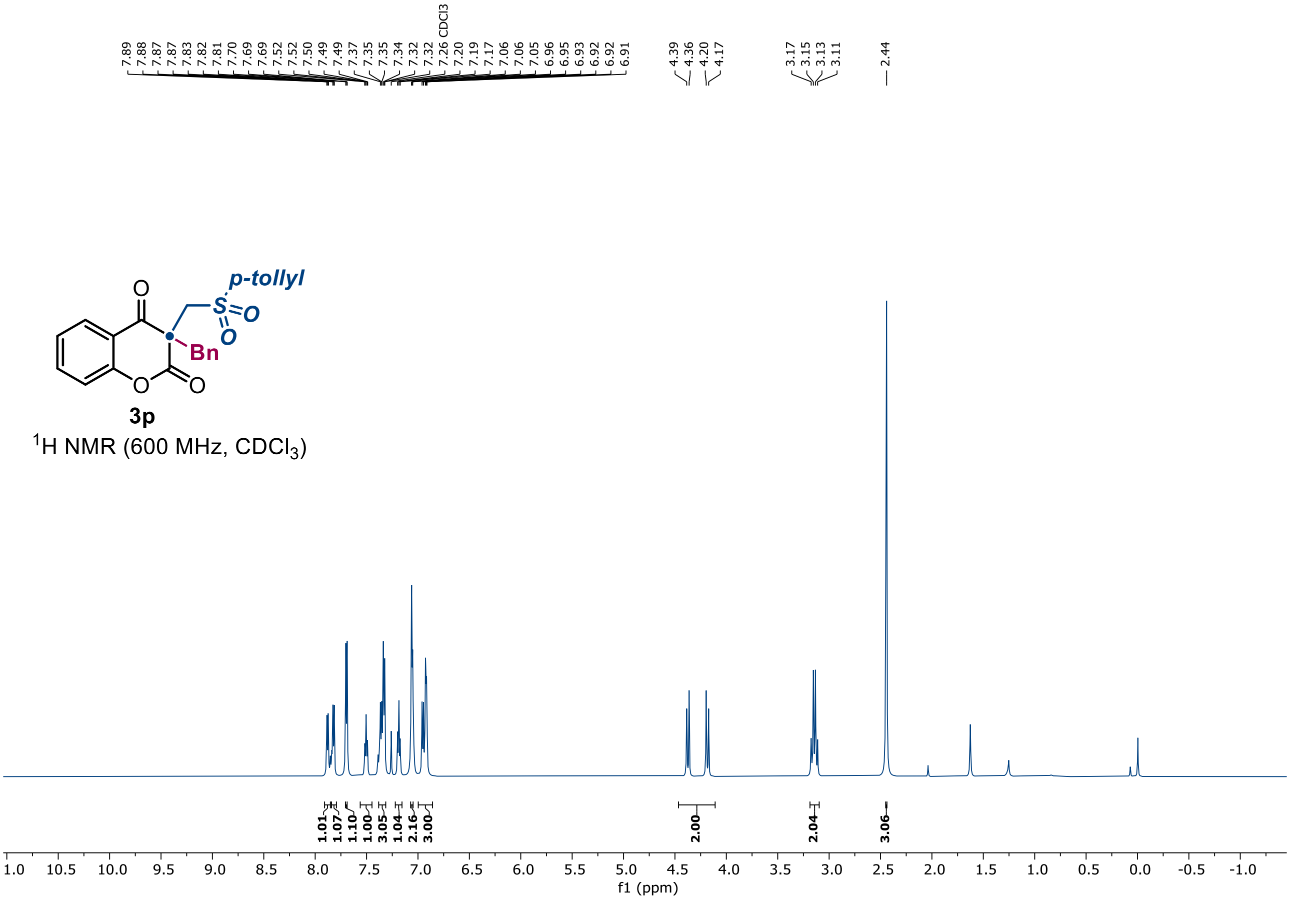
3n

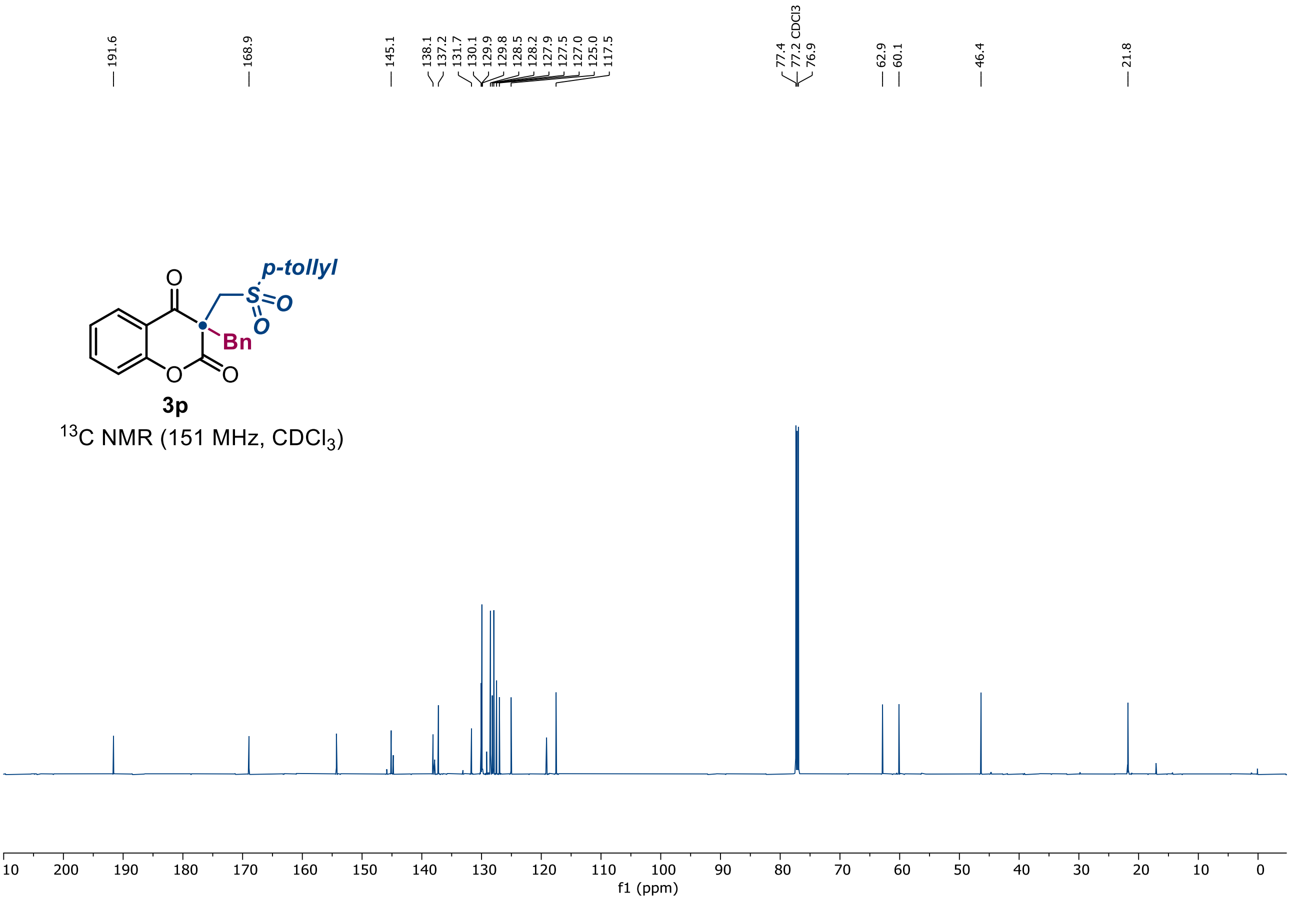
^{13}C NMR (151 MHz, CDCl$_3$)

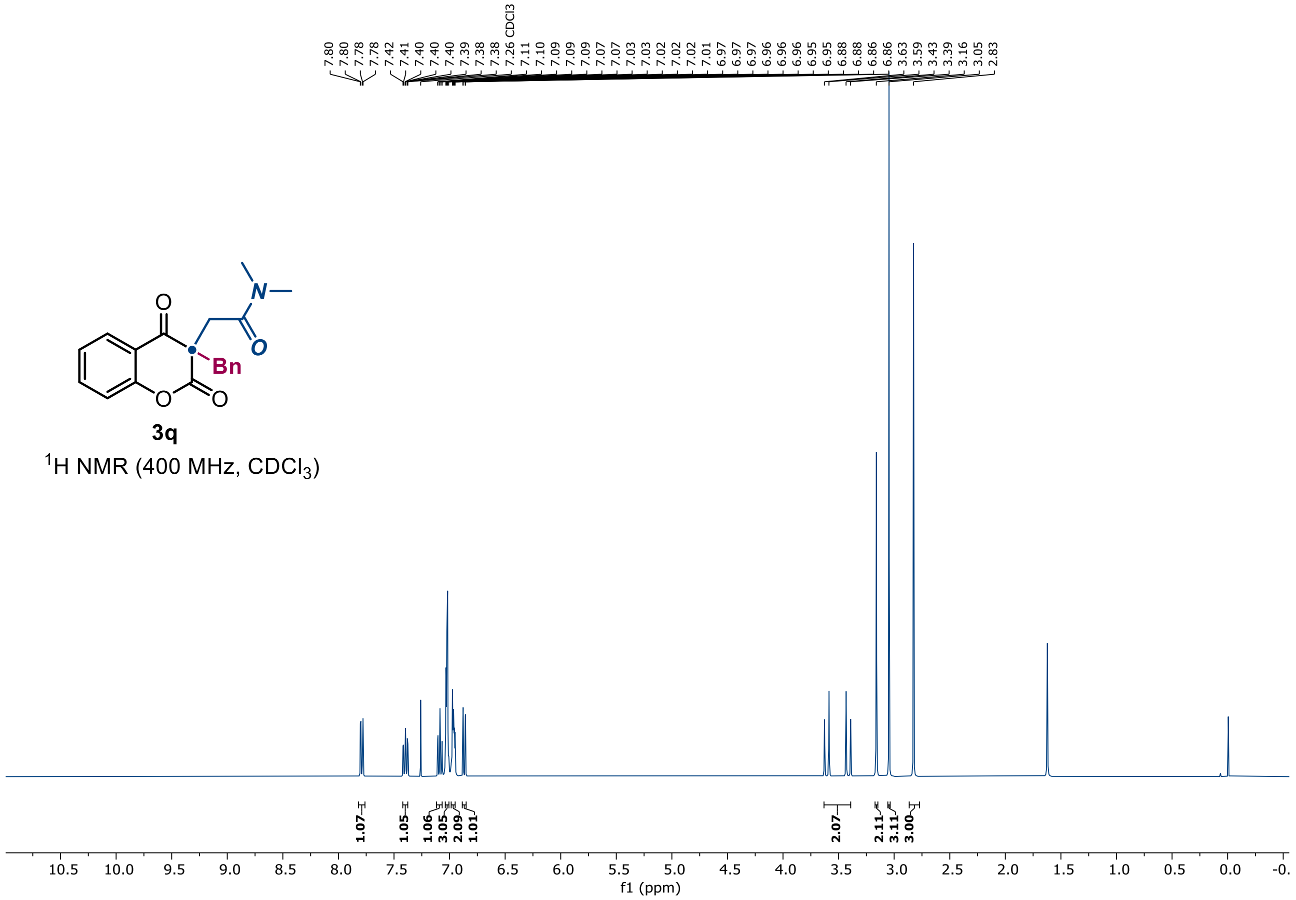


3n

^{19}F NMR (565 MHz, $CDCl_3$)

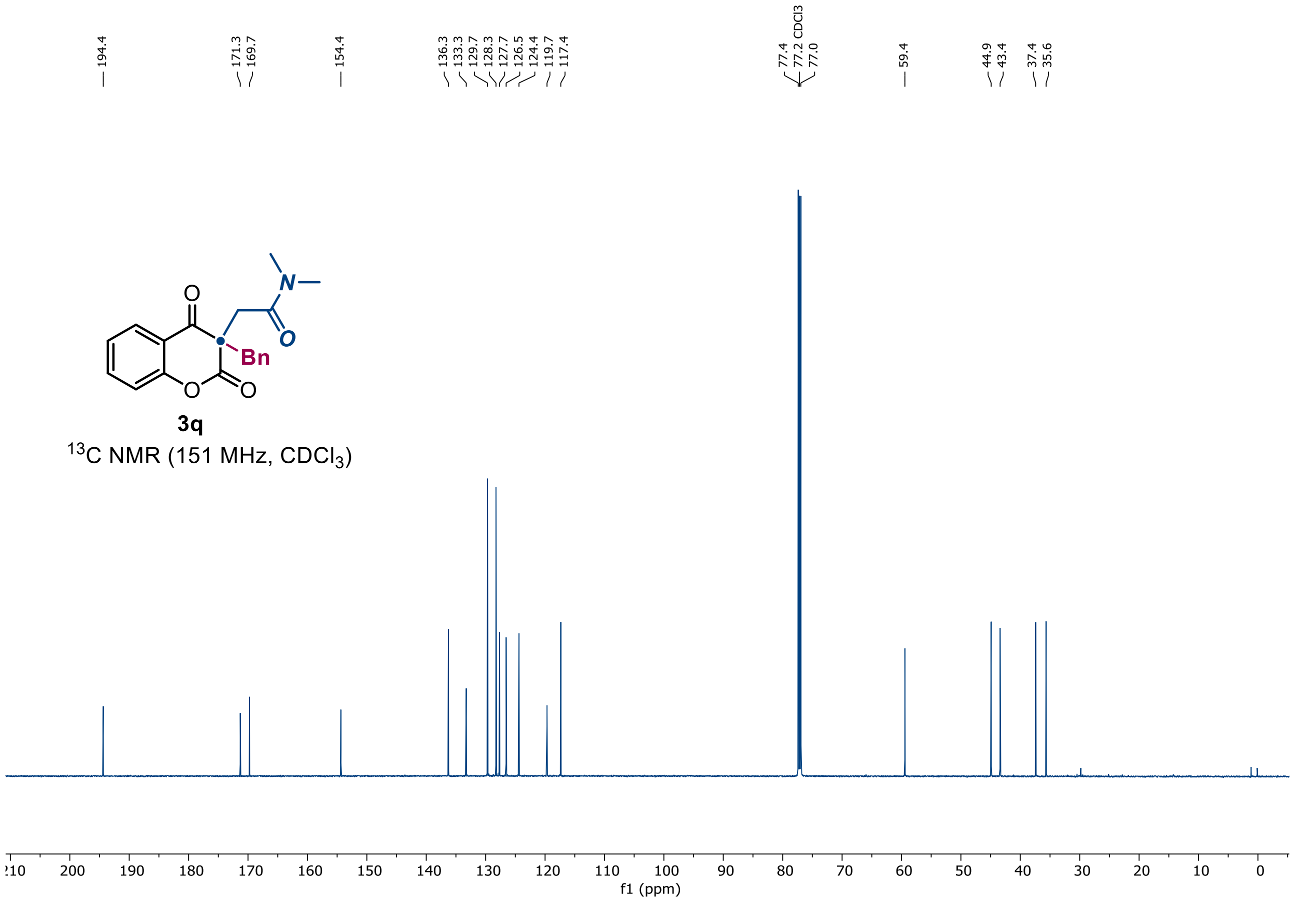

7.89
7.88
7.87
7.87
7.83
7.82
7.81
7.70
7.69
7.69
7.52
7.50
7.49
7.49
7.37
7.35
7.35
7.34
7.32
7.32
7.26 CDCl3
7.20
7.19
7.17
7.06
7.05
6.96
6.95
6.93
6.92
6.92
6.91
4.39
4.36
4.20
4.17
3.17
3.15
3.13
3.11
2.44
p-tollyl
Bn
3p
1H NMR (600 MHz, CDCl3)
1.01
1.07
1.10
1.00
3.05
1.04
2.16
3.00
2.00
2.04
3.06
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


191.6
168.9
145.1
138.1
137.2
131.7
130.1
129.9
129.8
128.5
128.2
127.9
127.5
127.0
125.0
117.5
77.4
77.2 CDCl3
76.9
62.9
60.1
46.4
21.8
p-tollyl
Bn
3p
13C NMR (151 MHz, CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



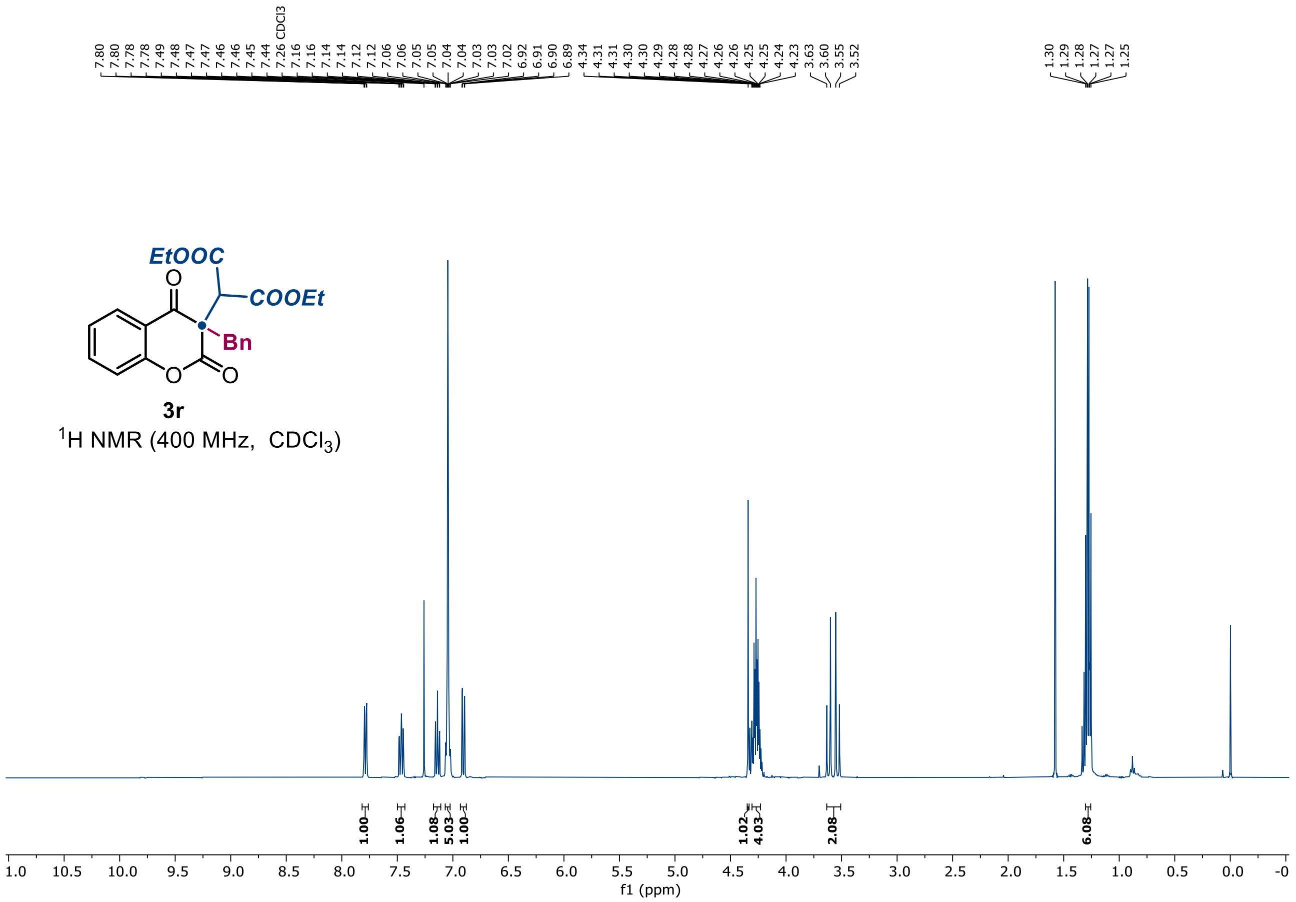
3q

^{1}H NMR (400 MHz, CDCl$_3$)



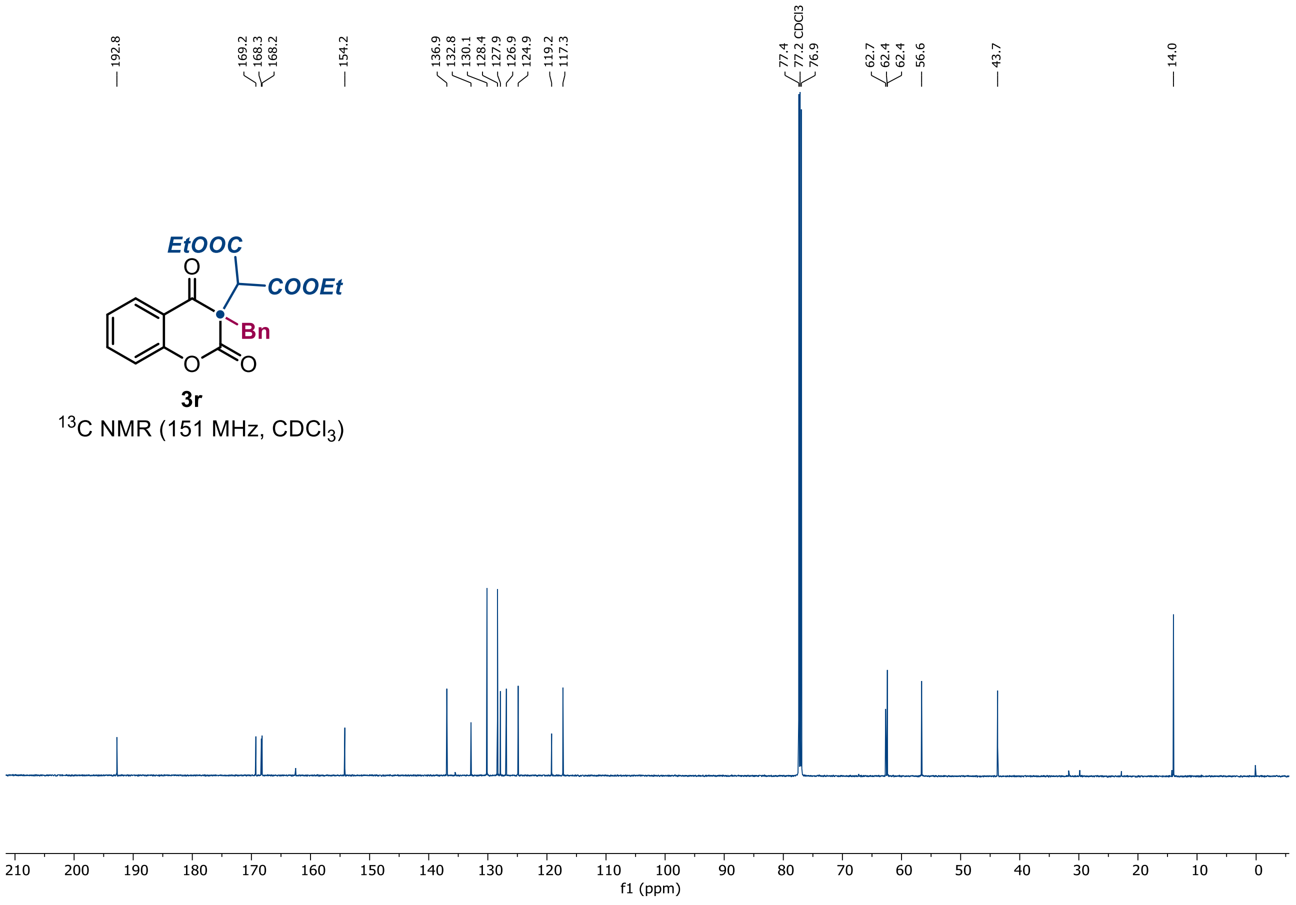
3q

^{13}C NMR (151 MHz, CDCl$_3$)



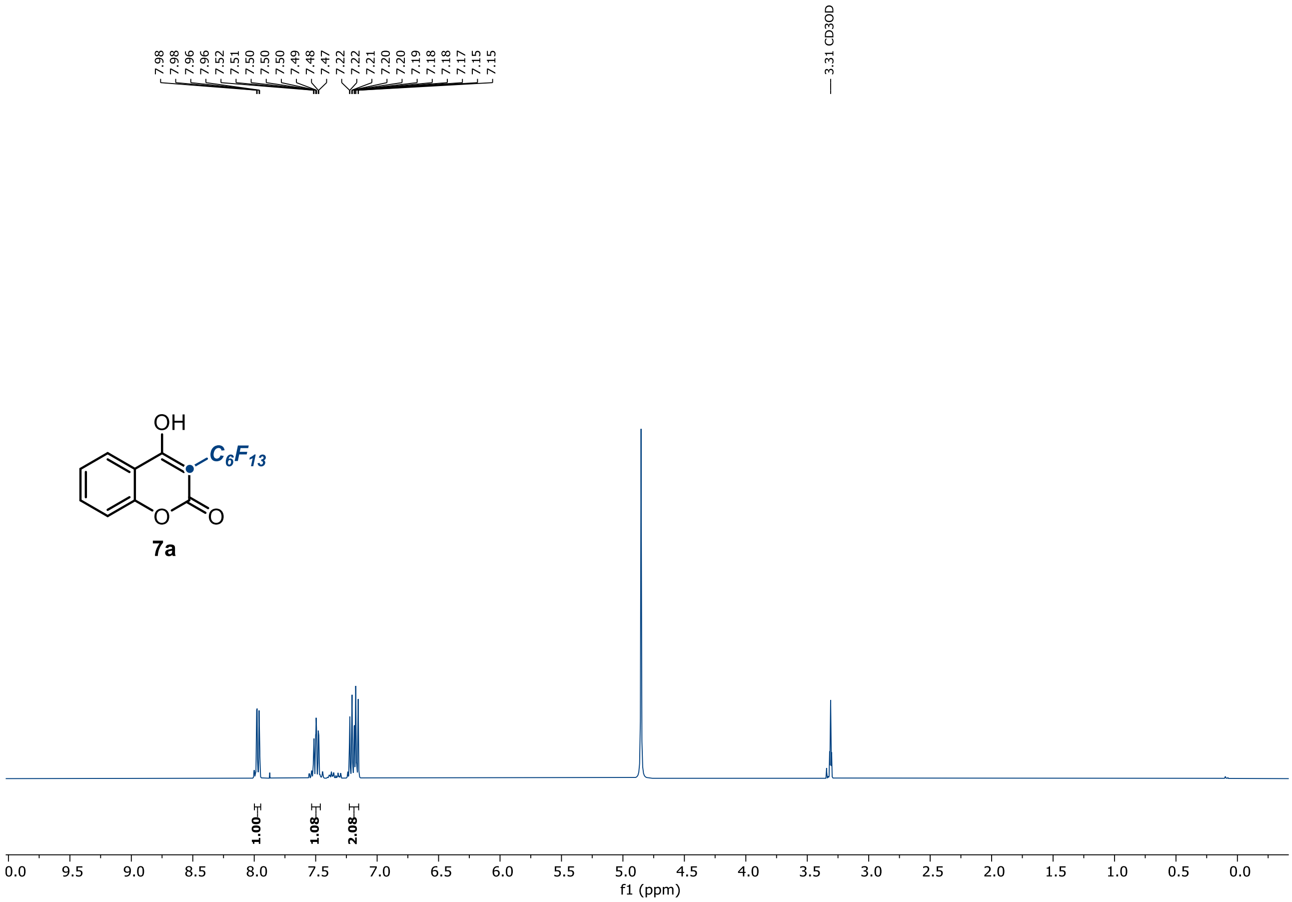
3r

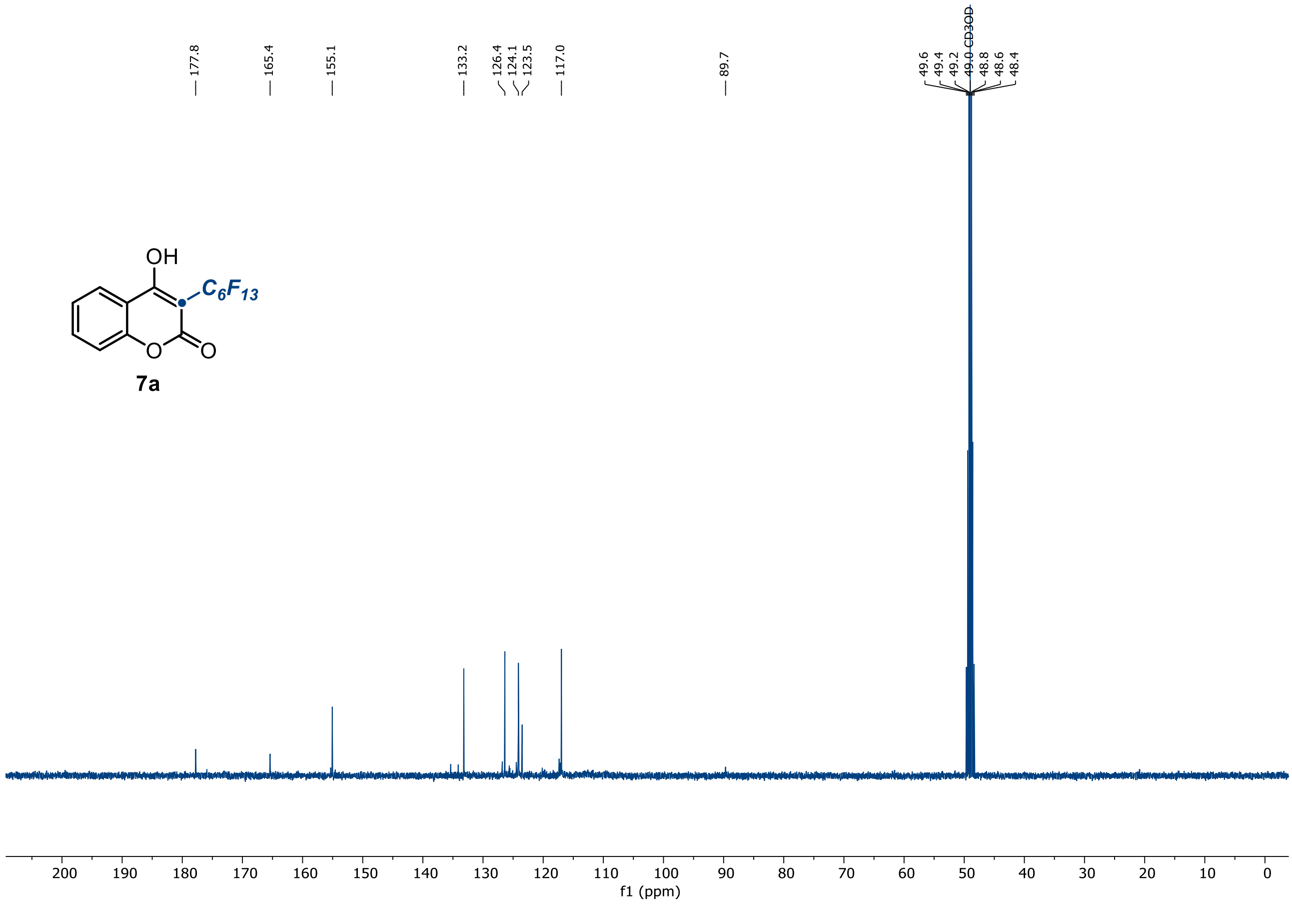
^{1}H NMR (400 MHz, CDCl$_3$)

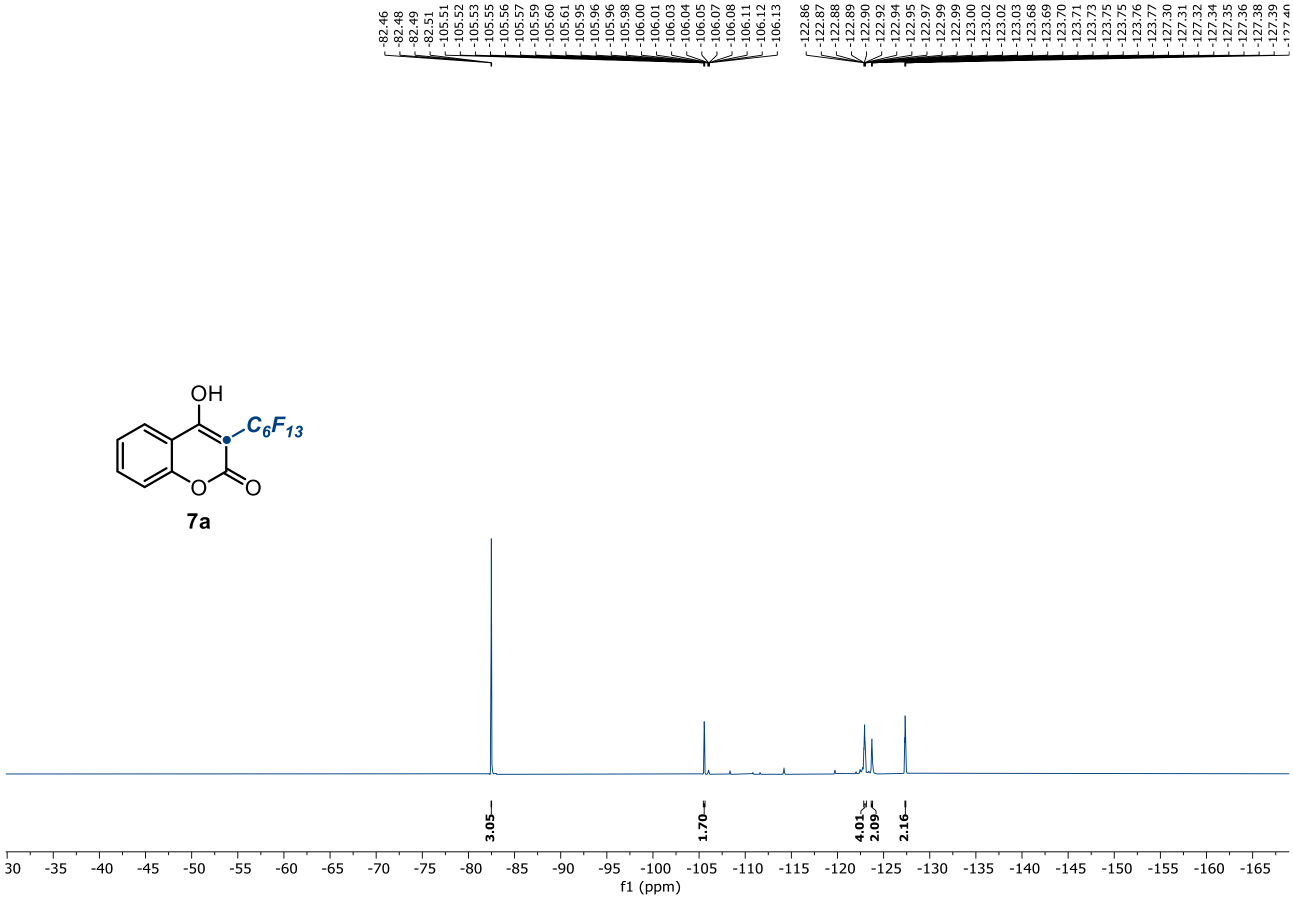


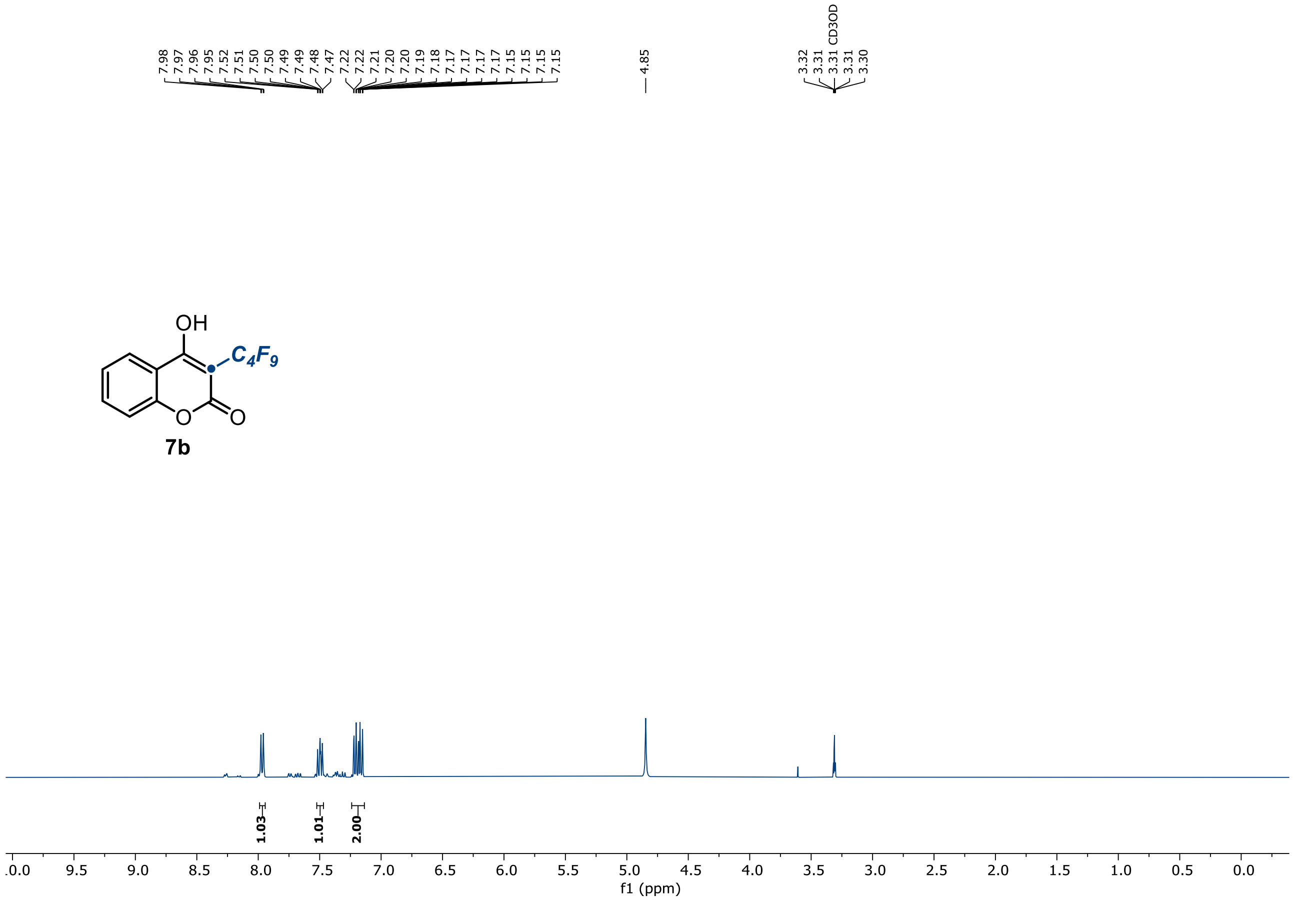
3r

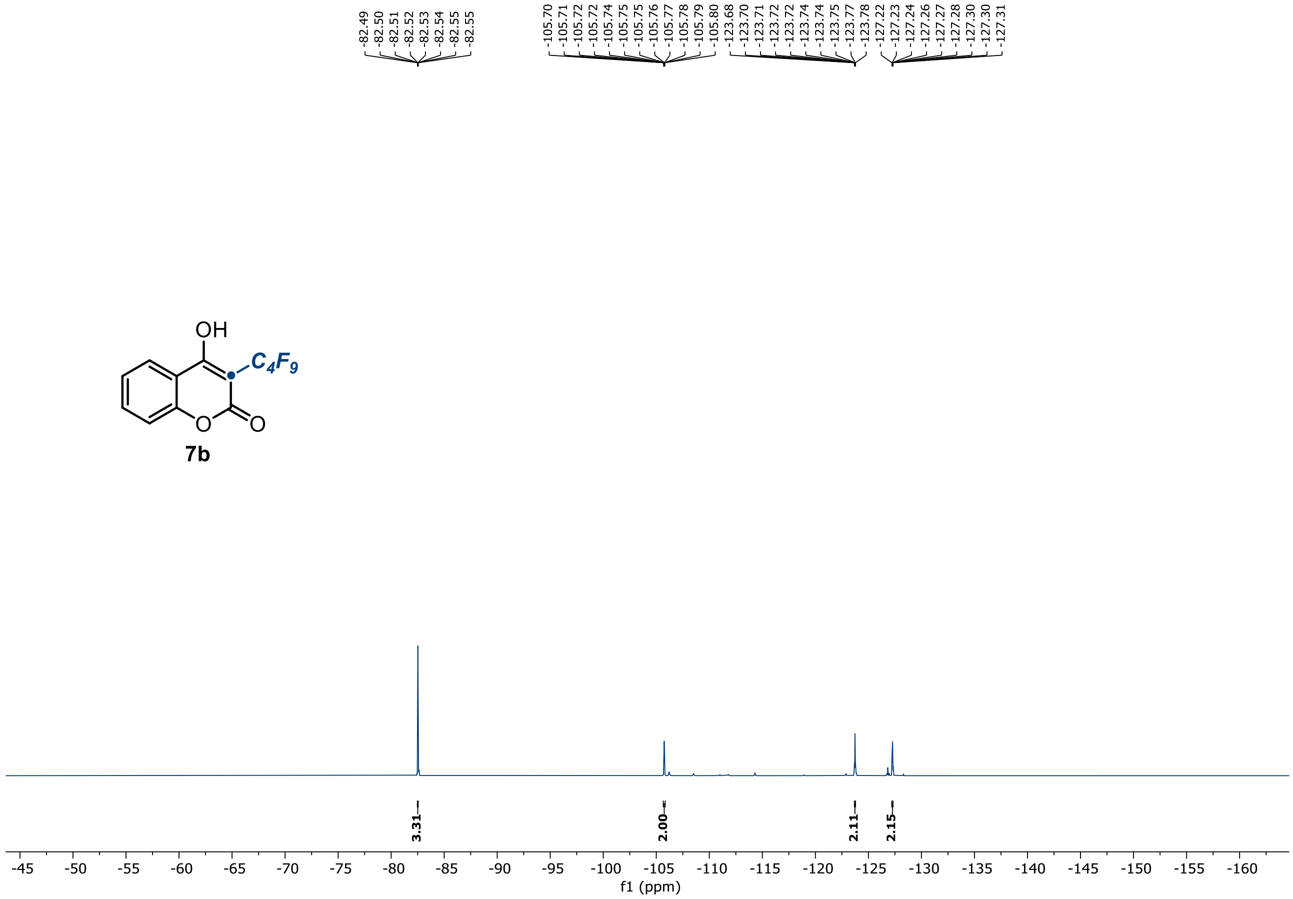
^{13}C NMR (151 MHz, CDCl$_3$)

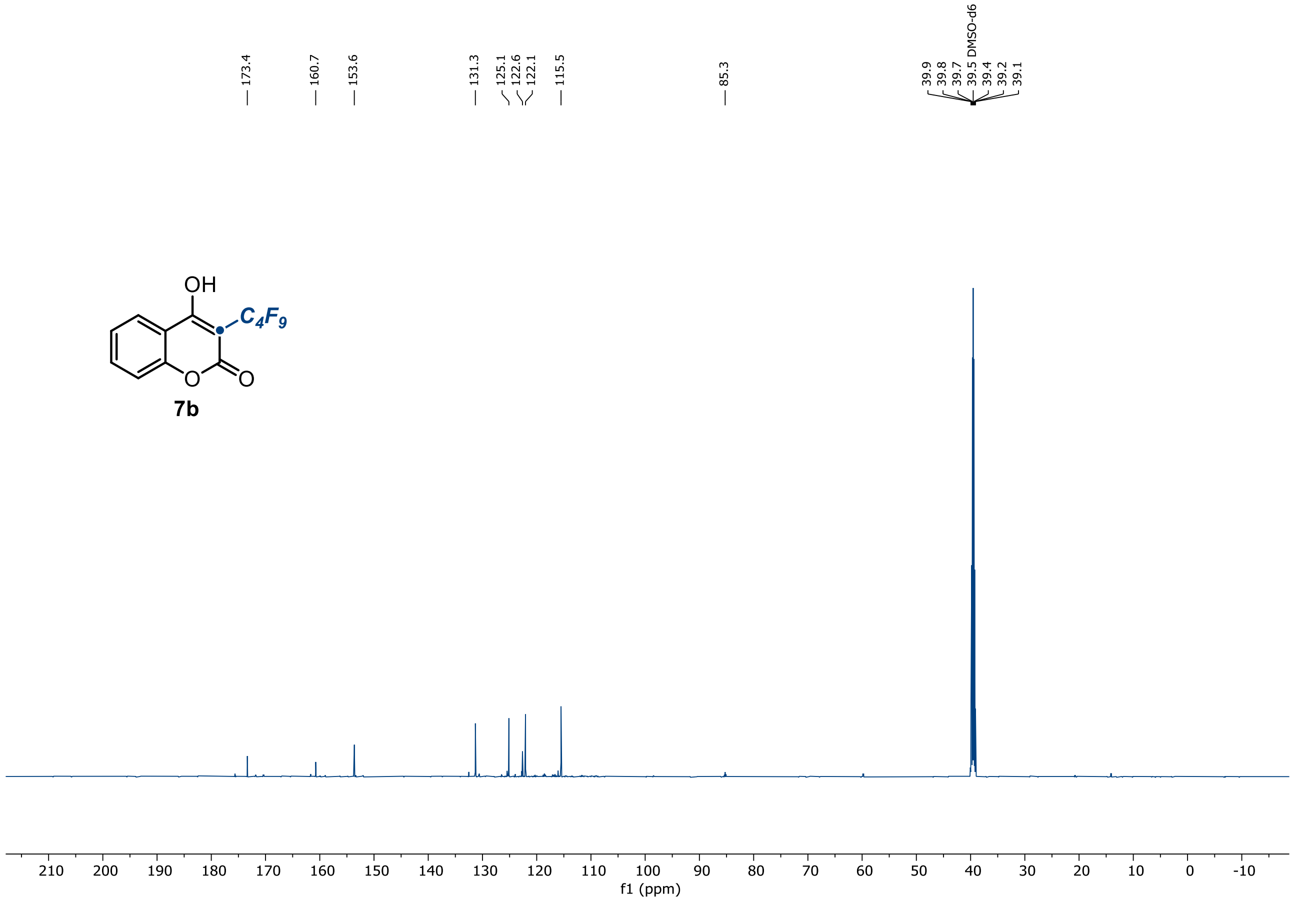

7.98
7.98
7.96
7.96
7.52
7.51
7.50
7.50
7.50
7.49
7.48
7.47
7.22
7.22
7.21
7.20
7.20
7.19
7.18
7.18
7.17
7.15
7.15
3.31 CD3OD
OH
C6F13
O
O
7a
1.00
1.08
2.08
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

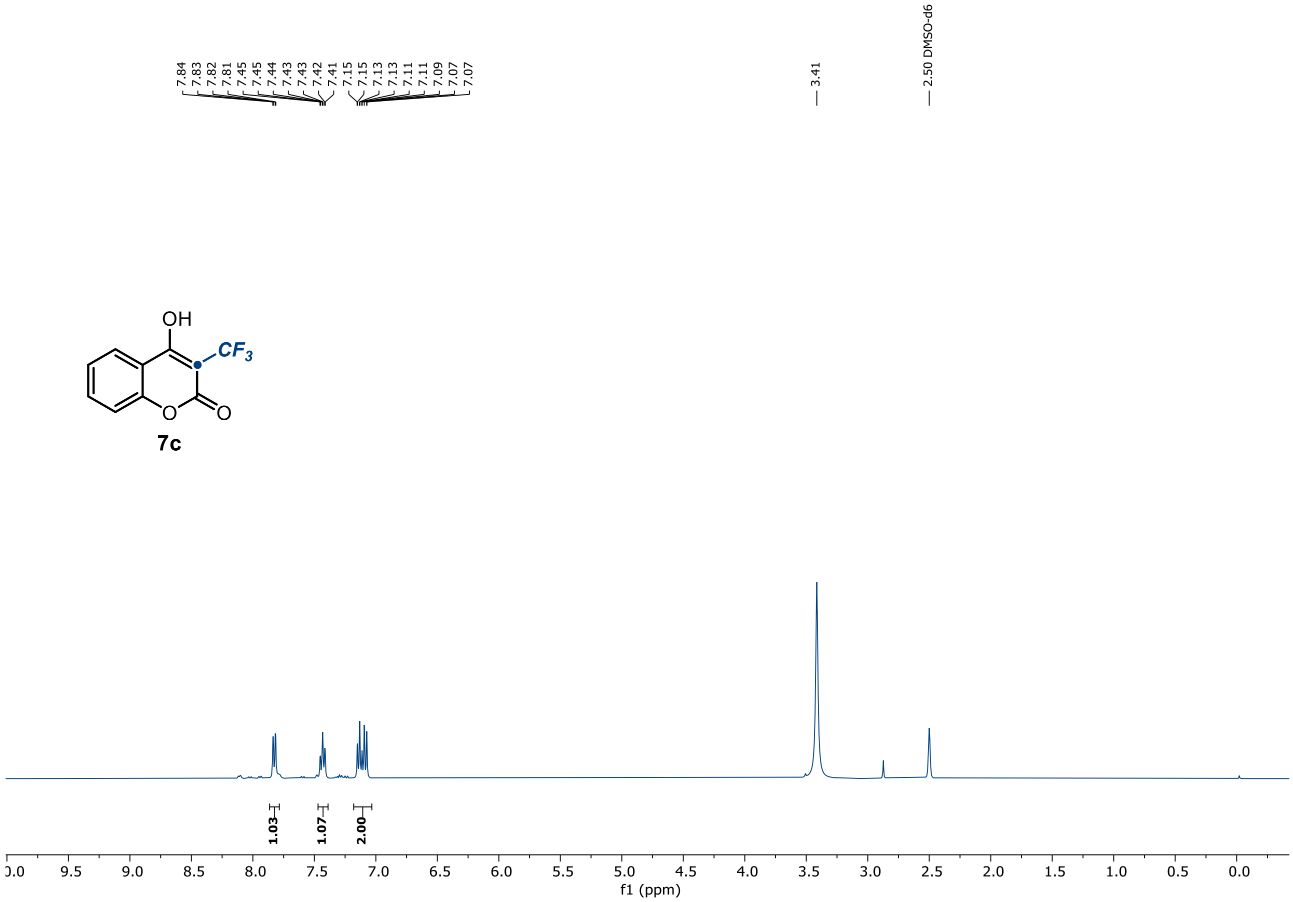

177.8
165.4
155.1
133.2
126.4
124.1
123.5
117.0
89.7
49.6
49.4
49.2
49.0 CD3OD
48.8
48.6
48.4
OH
C6F13
O
O
7a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

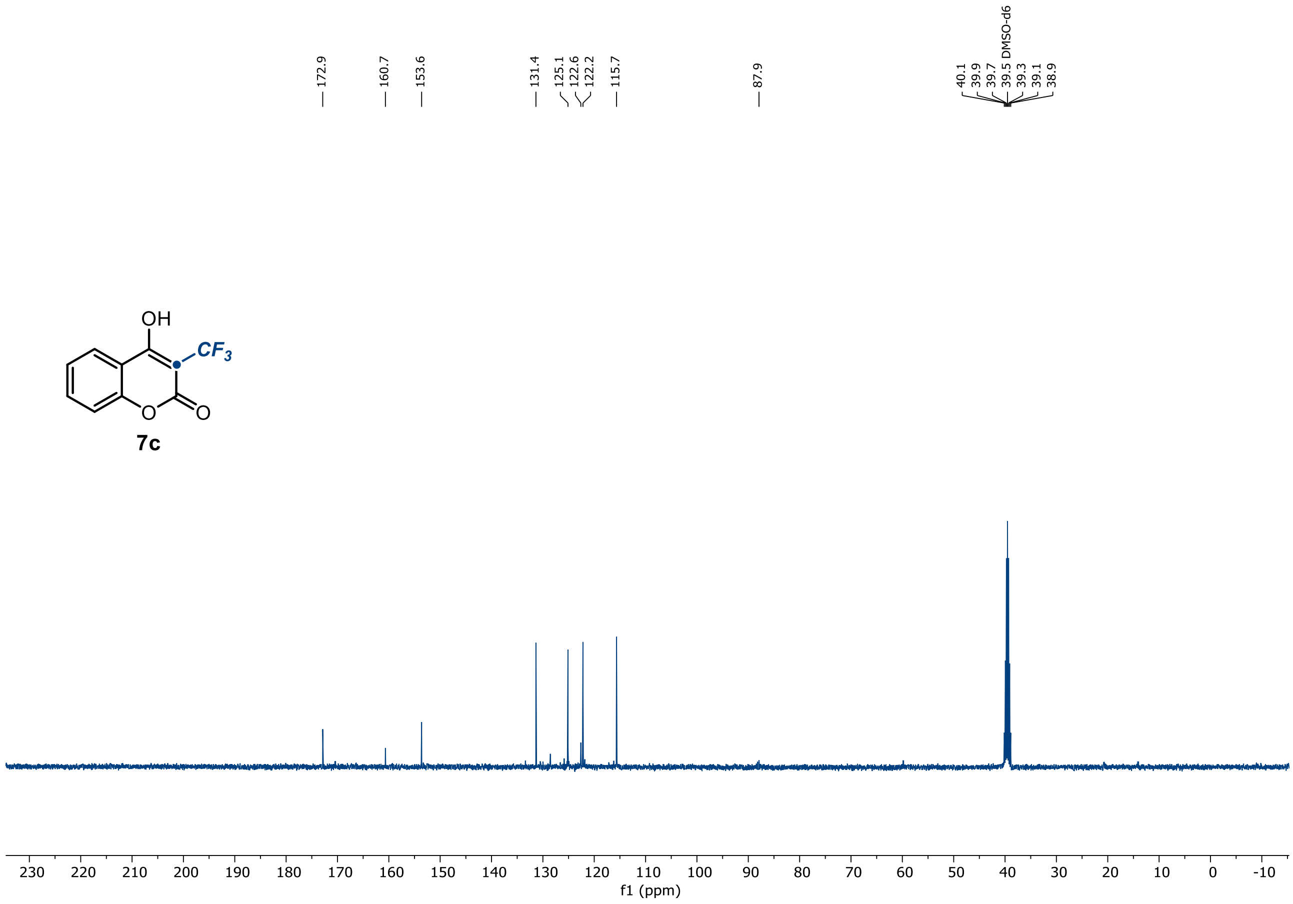

-82.46
-82.48
-82.49
-82.51
-105.51
-105.52
-105.53
-105.55
-105.56
-105.57
-105.59
-105.60
-105.61
-105.95
-105.96
-105.96
-105.98
-106.00
-106.01
-106.03
-106.04
-106.05
-106.07
-106.08
-106.11
-106.12
-106.13
-122.86
-122.87
-122.88
-122.89
-122.90
-122.92
-122.94
-122.95
-122.97
-122.99
-122.99
-123.00
-123.02
-123.03
-123.68
-123.69
-123.70
-123.71
-123.73
-123.75
-123.76
-123.77
-127.30
-127.31
-127.32
-127.34
-127.35
-127.36
-127.38
-127.39
OH
C6F13
O
O
7a
3.05
1.70
4.01
2.09
2.16
30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
f1 (ppm)

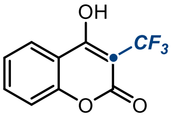

7.98
7.97
7.96
7.95
7.52
7.51
7.50
7.50
7.49
7.49
7.48
7.47
7.22
7.22
7.21
7.20
7.20
7.19
7.18
7.17
7.17
7.17
7.17
7.15
7.15
7.15
7.15
4.85
3.32
3.31
3.31 CD3OD
3.31
3.30
OH
C4F9
O
O
7b
1.03
1.01
2.00
.0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-82.49
-82.50
-82.51
-82.52
-82.53
-82.54
-82.55
-82.55
-105.70
-105.71
-105.72
-105.72
-105.74
-105.75
-105.75
-105.76
-105.77
-105.78
-105.79
-105.80
-123.68
-123.70
-123.71
-123.72
-123.72
-123.74
-123.75
-123.77
-123.78
-127.22
-127.23
-127.24
-127.26
-127.27
-127.28
-127.30
-127.30
-127.31
OH
C4F9
O
O
7b
3.31
2.00
2.11
2.15
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
f1 (ppm)

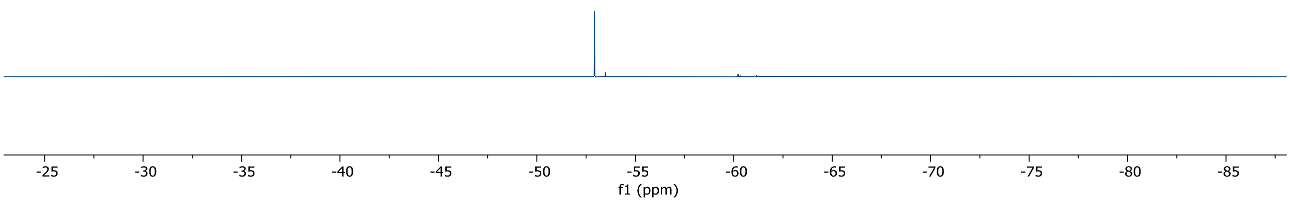

173.4
160.7
153.6
131.3
125.1
122.6
122.1
115.5
85.3
39.9
39.8
39.7
39.5 DMSO-d6
39.4
39.2
39.1
OH
C4F9
O
O
7b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

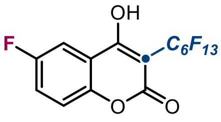

7.84
7.83
7.82
7.81
7.45
7.45
7.44
7.43
7.43
7.42
7.41
7.15
7.15
7.13
7.13
7.11
7.11
7.09
7.07
7.07
3.41
2.50 DMSO-d6
OH
CF3
O
O
7c
1.03
1.07
2.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


172.9
160.7
153.6
131.4
125.1
122.6
122.2
115.7
87.9
40.1
39.9
39.7
39.5 DMSO-d6
39.3
39.1
38.9
OH
CF3
O
O
7c
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

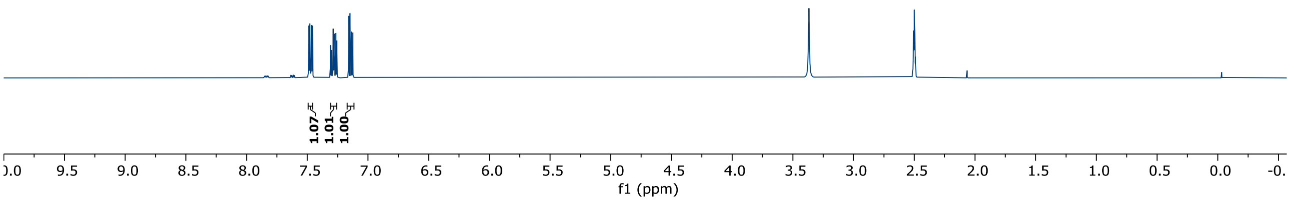


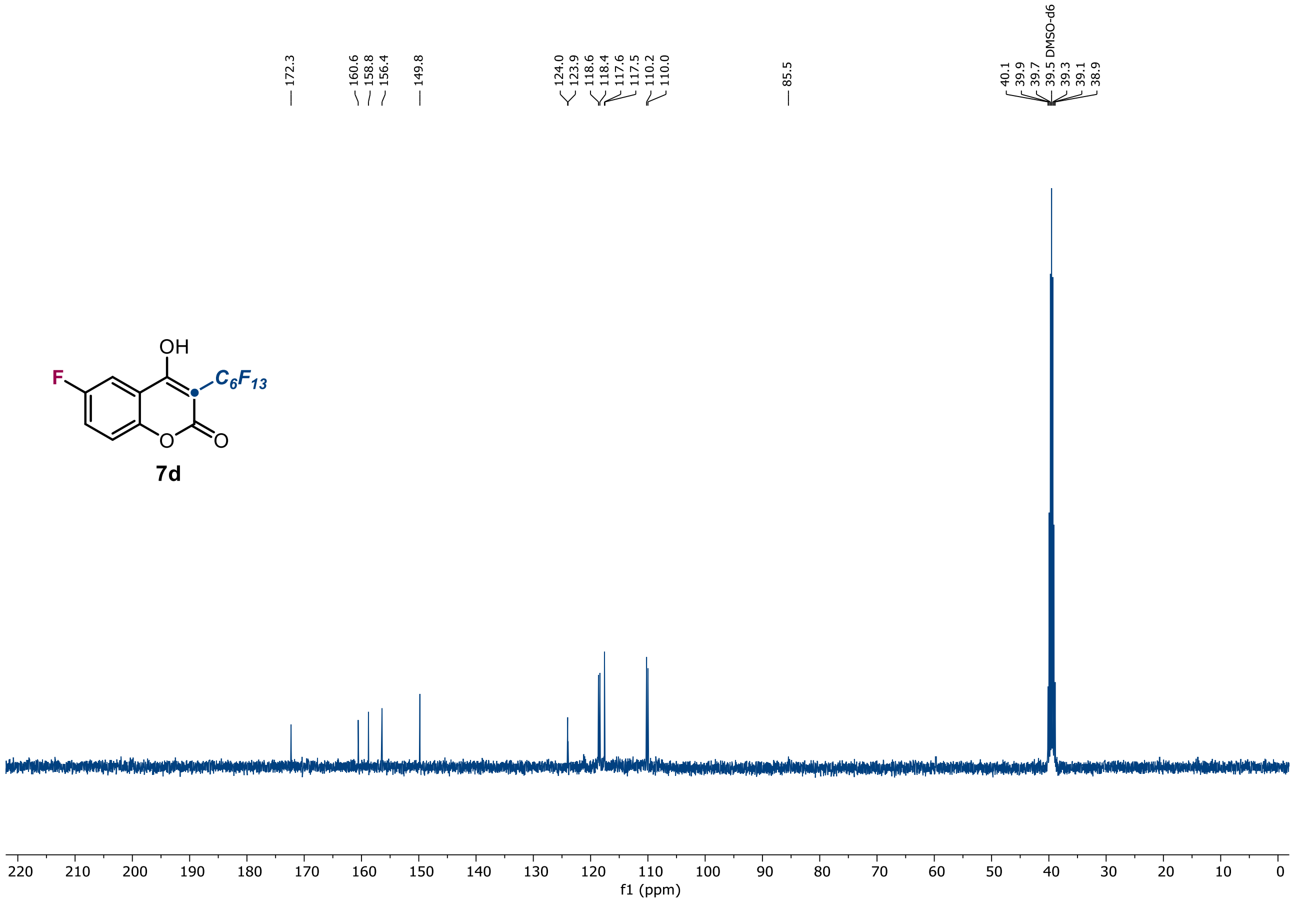
7c

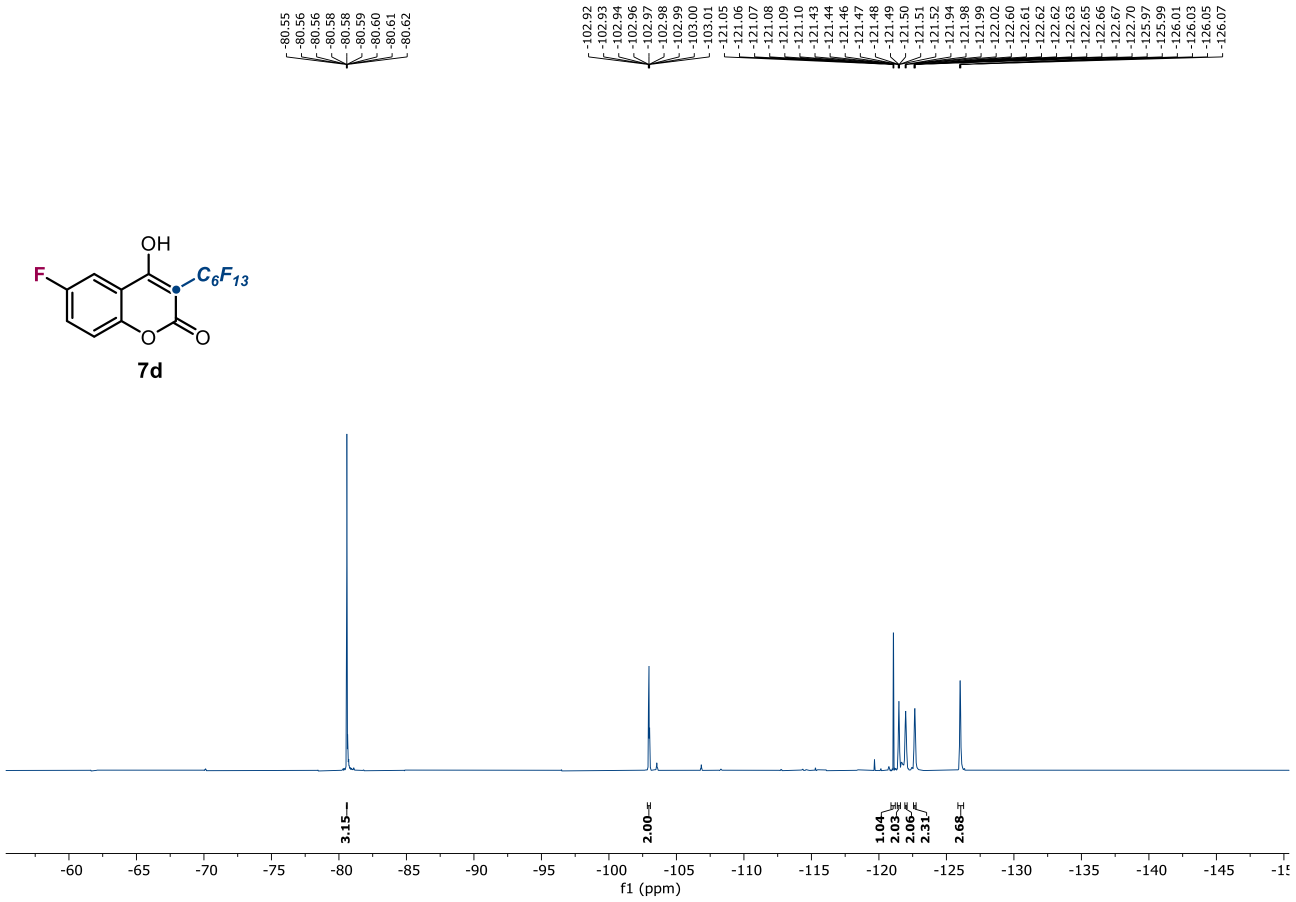

-52.9
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
f1 (ppm)



7d


7.49
7.48
7.47
7.46
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.16
7.15
7.14
7.13
3.37
2.51
2.50
2.50 DMSO-d6
2.50
2.49
1.07
1.01
1.00
).0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


172.3
160.6
158.8
156.4
149.8
124.0
123.9
118.6
118.4
117.6
117.5
110.2
110.0
85.5
40.1
39.9
39.7
39.5 DMSO-d6
39.3
39.1
38.9
OH
F
C6F13
O
O
7d
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-80.55
-80.56
-80.56
-80.58
-80.58
-80.59
-80.60
-80.61
-80.62
-102.92
-102.93
-102.94
-102.96
-102.97
-102.98
-102.99
-103.00
-103.01
-121.05
-121.06
-121.07
-121.08
-121.09
-121.10
-121.43
-121.44
-121.46
-121.47
-121.48
-121.49
-121.50
-121.51
-121.52
-121.94
-121.98
-121.99
-122.02
-122.60
-122.61
-122.62
-122.62
-122.63
-122.65
-122.66
-122.67
-122.70
-125.97
-125.99
-126.01
-126.03
-126.05
-126.07
OH
F
C6F13
O
O
7d
3.15
2.00
1.04
2.03
2.06
2.31
2.68
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)