Supporting Information

3*H*-Phenothiazin-3-one: A Photocatalyst for the Mild Oxidation of Boronic Acids Under Green LED Irradiation

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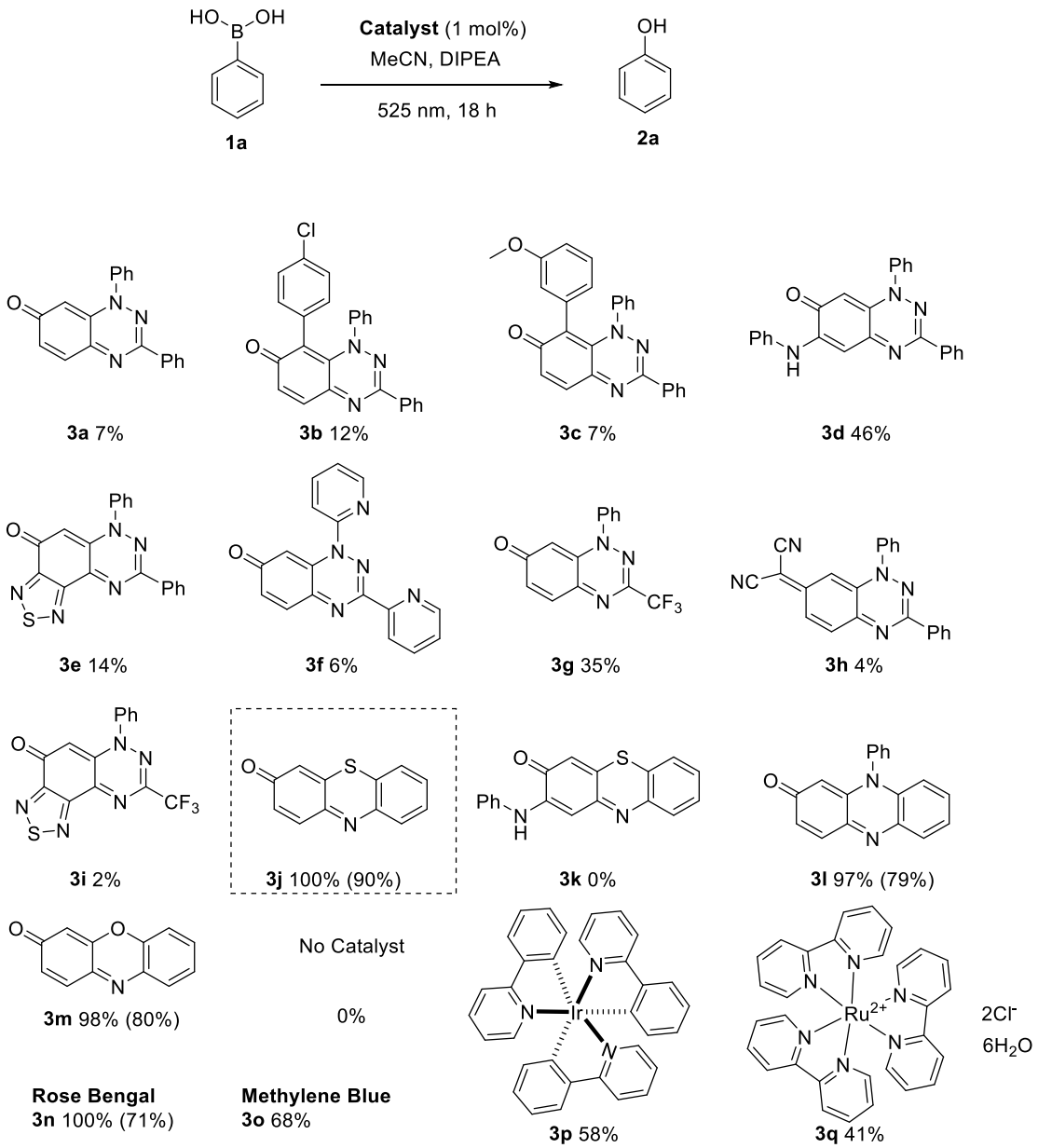
S.1 General Methods

Chromatographic purification of products was accomplished using forced-flow chromatography on Merck® Kieselgel 230-400 mesh. Thin-layer chromatography (TLC) was performed on aluminum backed silica plates (0.2 mm, 60 F_{254}). Visualization of the developed chromatogram was performed by fluorescence quenching, using phosphomolybdic acid, anisaldehyde or potassium permanganate stains. Mass spectra (ESI) were recorded on a Finnigan® Surveyor MSQ LC-MS spectrometer. ^{1}H, ^{13}C, ^{11}B and ^{19}FNMR spectra were recorded on a Bruker® Avance (400 MHz, 100 MHz, 128 MHz and 376 MHz, respectively). Data for ^{1}H-NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constant and assignment. Data for ^{13}C-, ^{11}B- and ^{19}F-NMR are reported in terms of chemical shift (δ ppm). ^{19}F- and ^{11}B-NMR spectra are internally referenced to trifluoroacetic acid and $BF_3.OEt_2$, respectively. Mass spectra and conversions of the reactions were recorded on a Shimadzu® GCMS-QP2010 Plus Gas Chromatograph Mass Spectrometer utilizing a MEGA® column (MEGA-5, F.T.: 0.25 μm, I.D.: 0.25 mm, L.: 30 m, T_{max}: 350 ºC, Column ID# 11475). A Varian® Cary 50 UV-Vis spectrophotometer was used for the quantum yield measurements and UV-Vis mechanistic studies. Cyclic Voltammetry studies were performed on a Princeton Applied Research Potentiostat/Galvanostat 263A. The concentration of boronic acid or *N*,*N'*-diisopropylethylamine, were 1 mM in MeCN containing *n*-Bu_4NPF_6 (0.1 M) as the electrolyte. For cyclic voltammetry, three-electrode electrochemical cell was used with glassy carbon disk as working electrode, Pt wire as the counter electrode and Ag/AgCl (1 M KCl) as reference electrode. Scan rate 100 mV s^{-1}, Temperature = 20 °C, Fc/Fc^+ (E_{Fc/Fc^+}= 0.40 V *vs* SCE) was used as the internal reference. MeCN was distilled over CaH_2. Samples were deaerated by passing argon through the solvent, prior to measuring the cyclic voltammogram. For all measurements, blank samples (only electrolyte in the system) were taken to ensure the correct operation of the electrochemical cell. Upon each measurement, ferrocene was added and the cyclic voltammogram was run again. All redox potentials ($E_{1/2}$) are referenced according to the ferrocene's value (E_{Fc/Fc^+}= 0.40 V *vs* SCE).

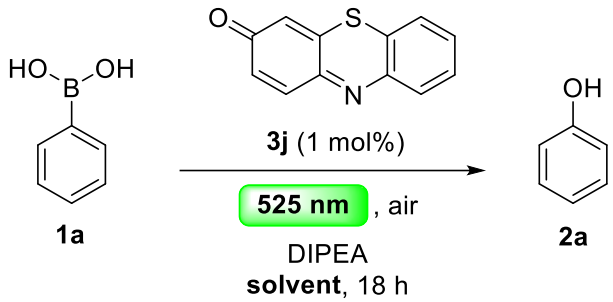
S.2 Optimization of the Reaction Conditions for the Aerobic Photochemical Oxidation of Phenyl Boronic Acid Under Green LED Irradiation

Photocatalyst Optimization[a]



All reactions were carried out using phenylboronic acid (**1a**) (24 mg, 0.20 mmol, 1.0 equiv.), *N,N'*-diisopropylethylamine (DIPEA) (26 mg, 0.20 mmol, 1.0 equiv.) and catalyst (1 mol%) in MeCN (1 mL) under irradiation at 525 nm for 18 h. [a] Conversion determined by ^{1}H-NMR, yield of isolated product after column chromatography in parenthesis.

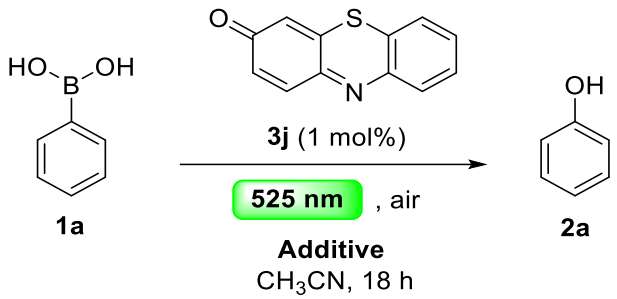
Solvent Optimization



Entry	Solvent	Conversion (%)[a]	Yield (%)[b]
1	MeCN	100	90
2	CH_2Cl_2	57	-
3	$CHCl_3$	29	-
4	AcOEt	60	-
5	EtOH	65	-
6	Isopropanol	0	-
7	Dioxane	55	-
8	THF	32	-
9	Petroleum Eth. (40-60 °C)	7	-
10	Cyclohexane	14	-
11	Benzene	65	-
12	Toluene	87	58
13	Xylene	84	79
14	DMSO	0	-
15	DMF	90	61
16	DMAc	82	-
17	H_2O	2	-
18	H_2O-MeCN (1:1)	85	80

Table S1. All reactions were carried out using phenylboronic acid (**1a**) (24 mg, 0.20 mmol, 1.0 equiv.), *N,N'*-diisopropylethylamine (DIPEA) (26 mg, 0.20 mmol, 1.0 equiv.) and catalyst (**3j**) (0.4 mg, 0.002 mmol, 1 mol%) in solvent (1 mL) under irradiation at 525 nm for 18 h. [a] Conversion determined by ^{1}H-NMR. [b] Yield after column chromatography.

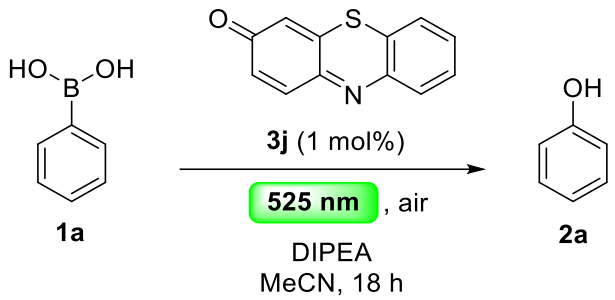
Additive Optimization



Entry	Additive	Equiv.	Conversion (%)[a]	Yield (%)[b]
1	DIPEA	1.0	100	90
2	DIPEA	0.75	63	-
3	DIPEA	0.5	50	-
4	Propylamine	1.0	5	-
5	Triethylamine	1.0	76	-
6	Morpholine	1.0	18	-
7	*N*-Methylmorpholine	1.0	27	-
8	Hantzsch ester	1.0	46	-
9	K_2CO_3	1.0	0	-

Table S2. All reactions were carried out using phenylboronic acid (**1a**) (24 mg, 0.20 mmol, 1.0 equiv.), additive and catalyst (**3j**) (0.4 mg, 0.002 mmol, 1 mol%) in MeCN (1 mL) under irradiation at 525 nm for 18 h. [a] Conversion determined by ^{1}H-NMR. [b] Yield after column chromatography.

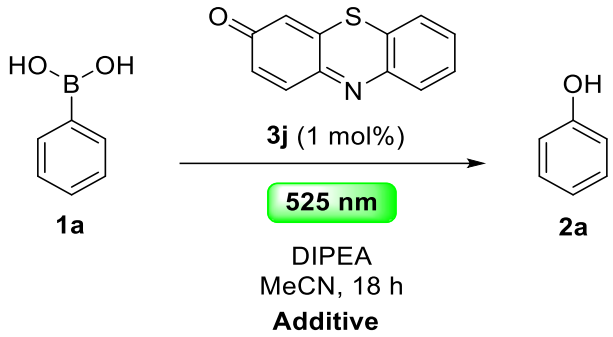
S.3 Control Experiments for the Aerobic Photochemical Oxidation of Phenyl Boronic Acid Under Green LED Irradiation



Entry	Deviation from standard conditions	Conversion (%)[a]
1	No catalyst	0
2	No DIPEA	0
3	Argon atmosphere	0
4	Under darkness	0
5	Under darkness at 40 °C	0

Table S3. All reactions were carried out using phenylboronic acid (**1a**) (24 mg, 0.20 mmol, 1.0 equiv.), *N*,*N'*-diisopropylethylamine (DIPEA) (26 mg, 0.20 mmol, 1.0 equiv.) and catalyst (**3j**) (0.4 mg, 0.002 mmol, 1 mol%) in MeCN (1 mL) under irradiation at 525 nm for 18 h. [a] Conversion determined by ^{1}H-NMR.

S.4 Mechanistic Investigations with Quenchers for the Aerobic Photochemical Oxidation of Phenyl Boronic Acid Under Green LED Irradiation



Entry	Additive	Conversion (%)[a]
1	TEMPO	0
2	BHT	20

Table S4. All reactions were carried out using phenylboronic acid (**1a**) (24 mg, 0.20 mmol, 1.0 equiv.), *N*,*N'*-diisopropylethylamine (DIPEA) (26 mg, 0.20 mmol, 1.0 equiv.), catalyst (**3j**) (0.4 mg, 0.002 mmol, 1 mol%) and quencher (0.20 mmol, 1.0 equiv.) in MeCN (1 mL) under irradiation at 525 nm for 18 h. [a] Conversion determined by ^{1}H-NMR.

S.5 UV-Vis Studies

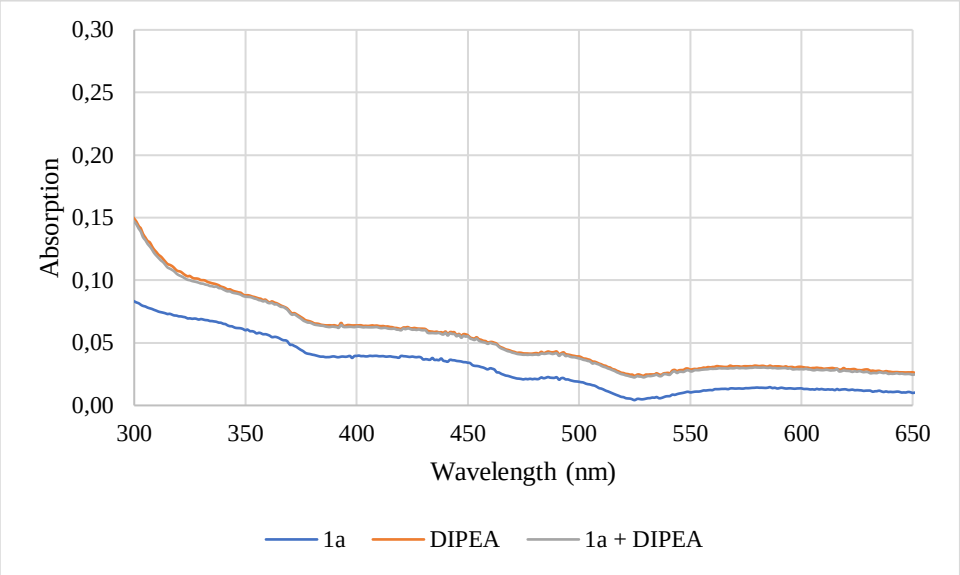


Figure S1. UV-Vis absorption spectra of phenylboronic acid (**1a**) (10^{-2} M), *N*,*N'*-diisopropylethylamine (DIPEA) (10^{-2} M) and their mixture (10^{-2} M) in MeCN.

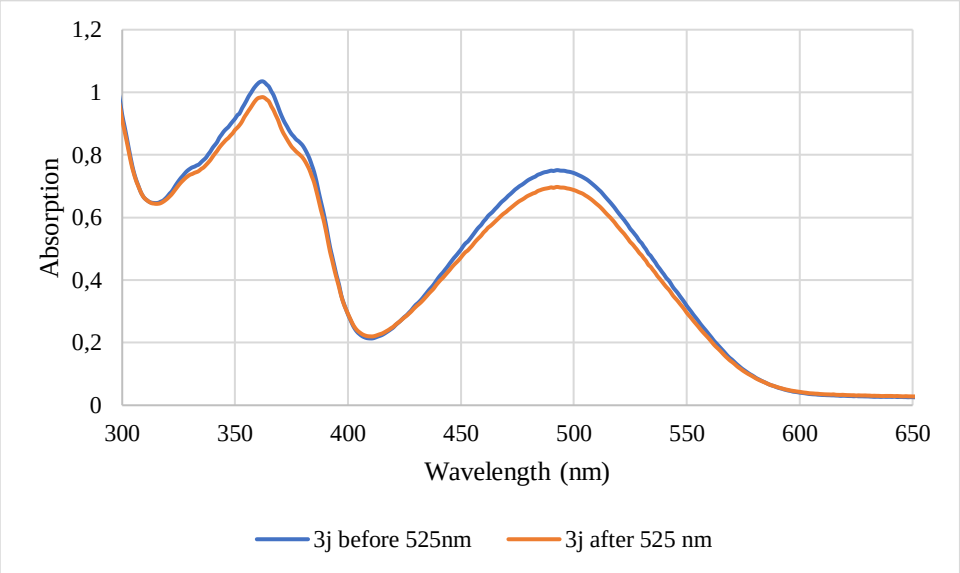


Figure S2. UV-Vis absorption spectra of **3j** (10^{-4} M) in MeCN, **before** and **after** irradiation at 525 nm for 120 s.

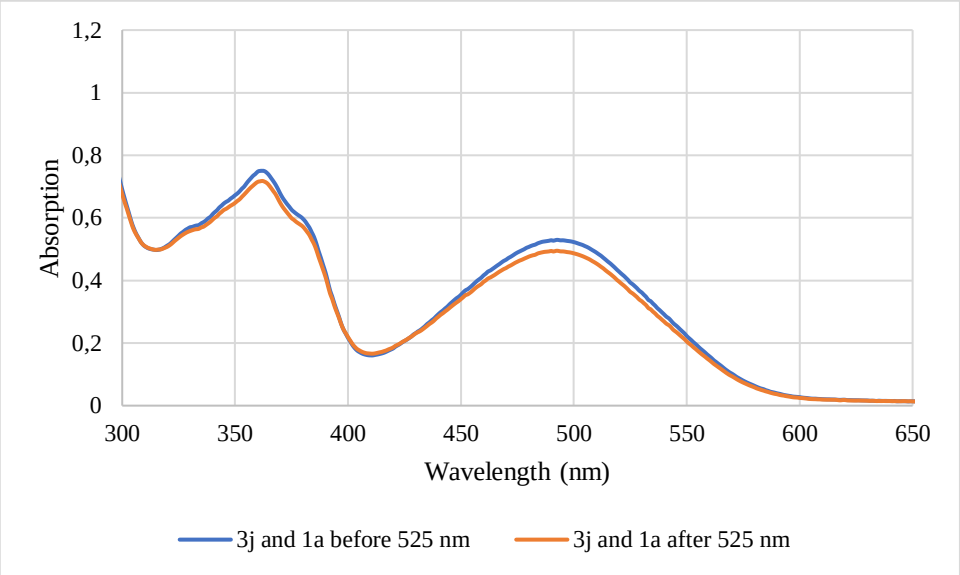


Figure S3. UV-Vis absorption spectra of a mixture of **3j** (10^{-4} M) and phenylboronic acid (**1a**) (10^{-2} M) in MeCN, **before** and **after** irradiation at 525 nm for 120 s.

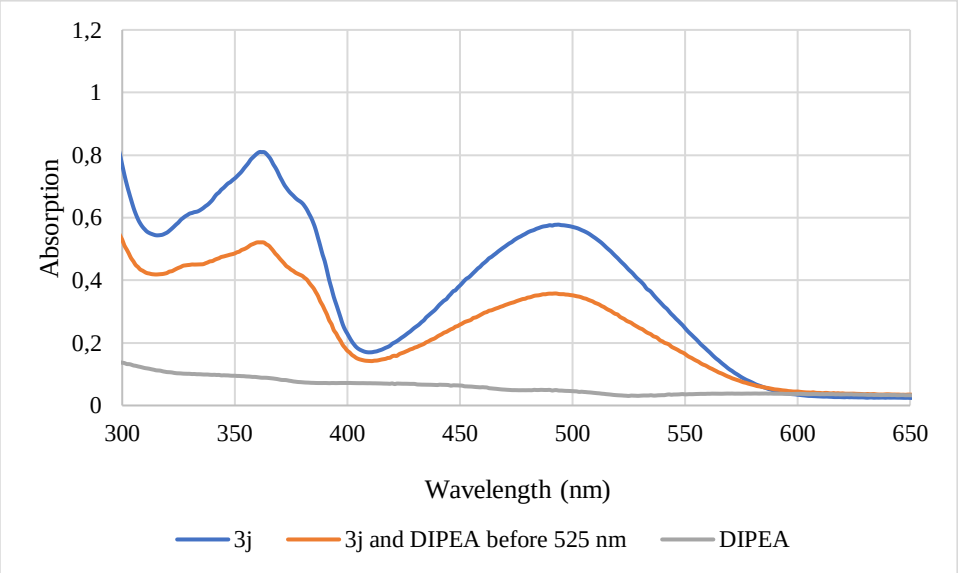


Figure S4. UV-Vis absorption spectra of **3j**, *N*,*N'*-diisopropylethylamine and a mixture of **3j** (10^{-4} M) with *N*,*N'*-diisopropylethylamine (10^{-2} M) in MeCN.

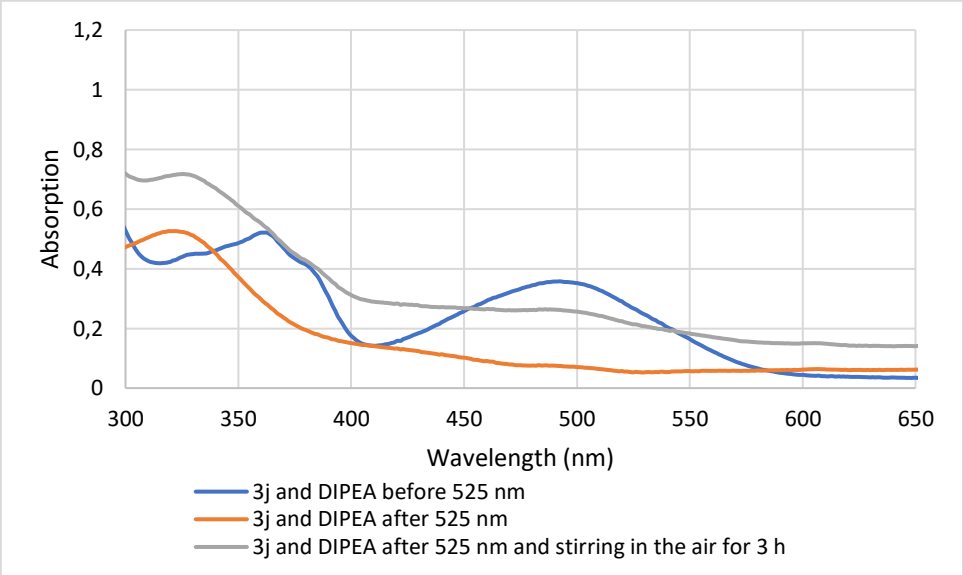


Figure S5. UV-Vis absorption spectra of a mixture of **3j** (10^{-4} M) with *N,N'*-diisopropylethylamine (DIPEA) (10^{-2} M) in MeCN, **before** and **after** irradiation at 525 nm for 120 s, and **after stirring** for 3 h under open air.

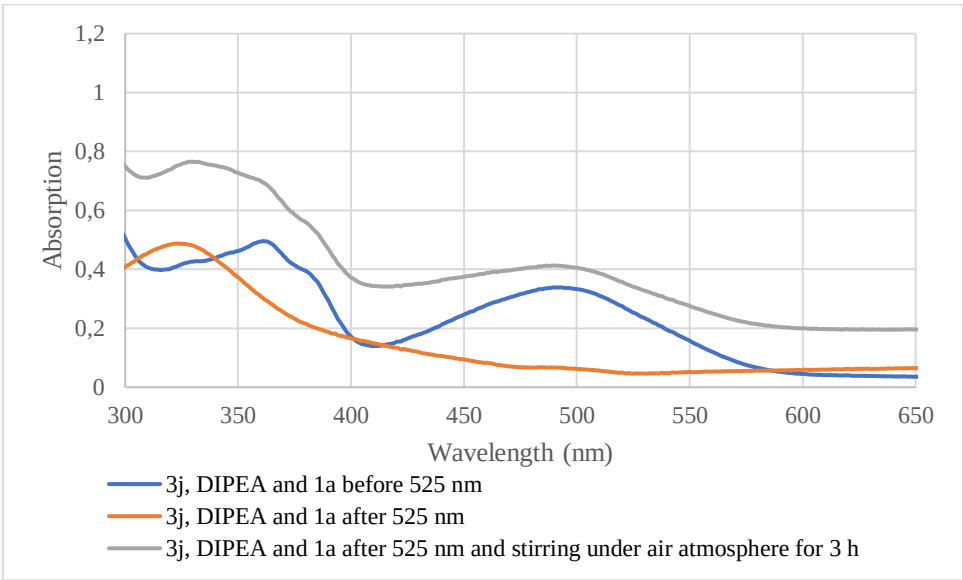


Figure S6. UV-Vis absorption spectra of a mixture of **3j** (10^{-4} M), *N,N'*-diisopropylethylamine (DIPEA) (10^{-2} M) and phenylboronic acid (**1a**) (10^{-2} M) in MeCN, **before** and **after** irradiation at 525 nm for 120 s, and **after stirring** for 3 h under open air.

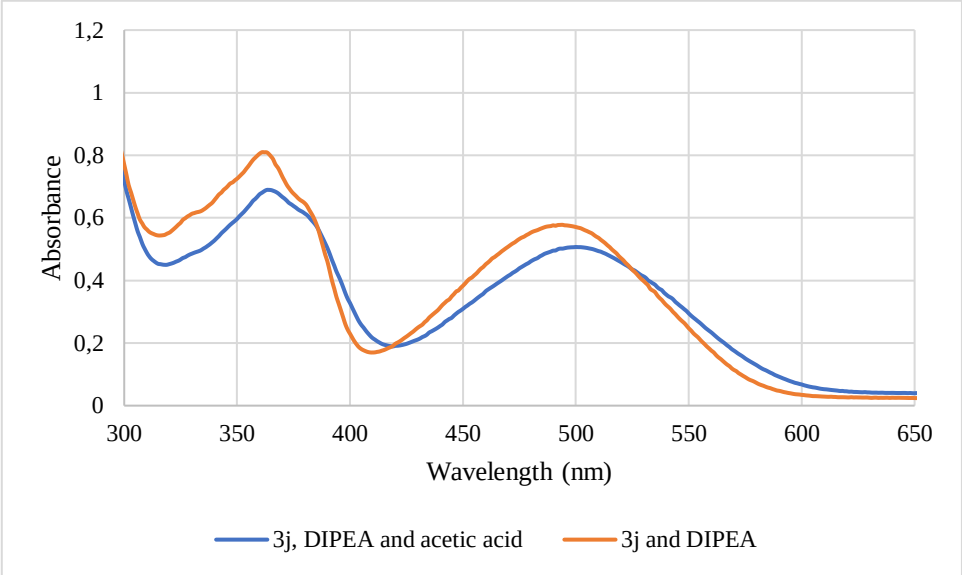


Figure S7. UV-Vis absorption spectra of mixture of **3j** (10^{-4} M), *N,N'*-diisopropylethylamine (DIPEA) (10^{-2}) and acetic acid (10^{-2} M) in MeCN, **before** and **after** irradiation at 525 nm for 120 s.

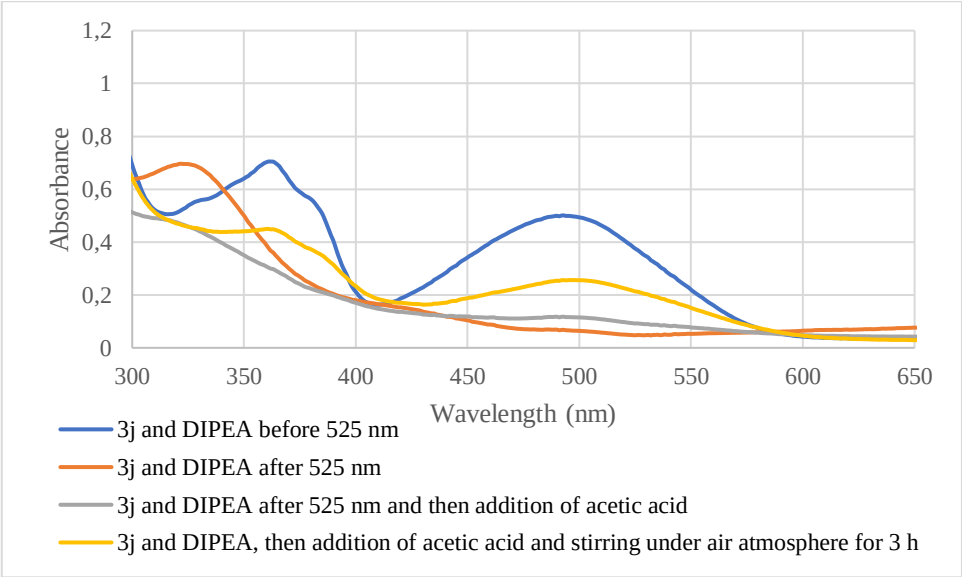
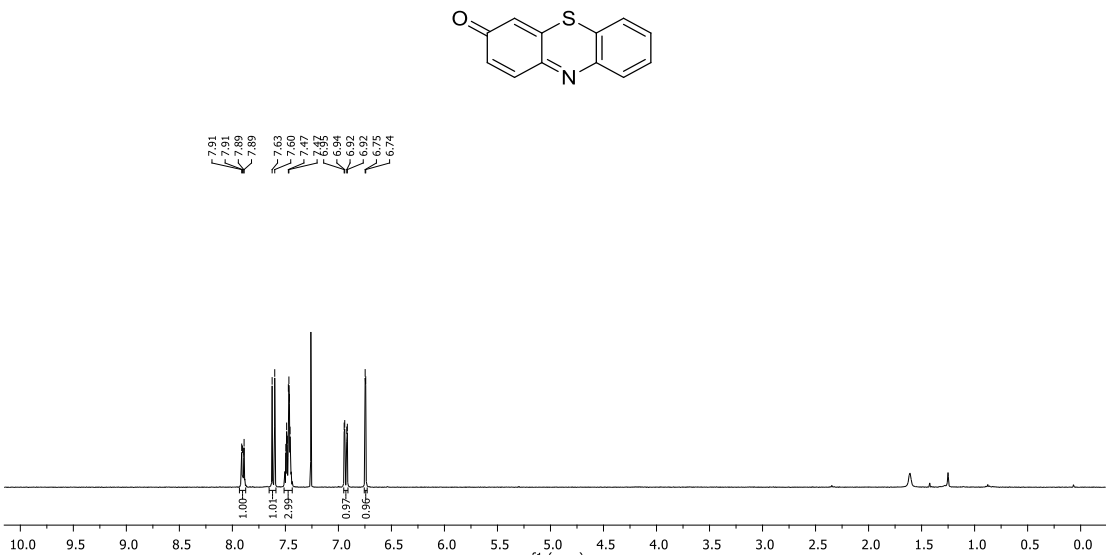
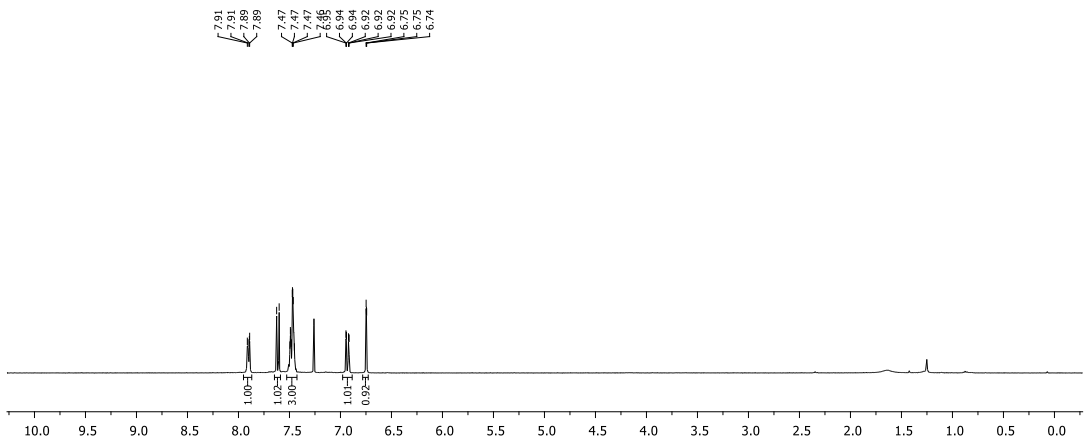


Figure S8. UV-Vis absorption spectra of a mixture of **3j** (10^{-4} M) and *N,N'*-diisopropylethylamine (DIPEA) (10^{-2}) in MeCN, **before** and **after** irradiation at 525 nm for 120 s and then after **addition** of acetic acid (10^{-2} M) and **stirring** under open air for 3 h.

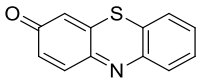
S.6 NMR Studies



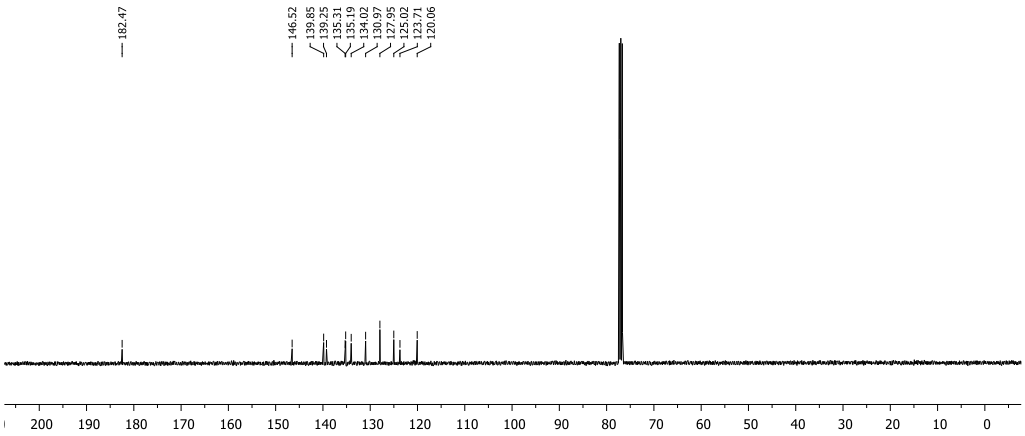
^{1}H NMR (400 MHz, $CDCl_3$) of **3j** (5 mg, 0.02 mmol) before irradiation.



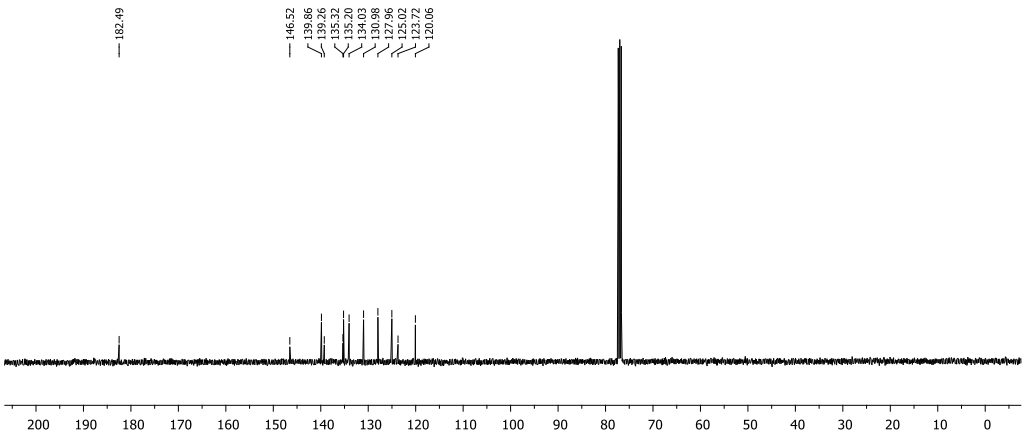
^{1}H NMR (400 MHz, $CDCl_3$) of **3j** (5 mg, 0.02 mmol) after irradiation at 525 nm for 3 h.



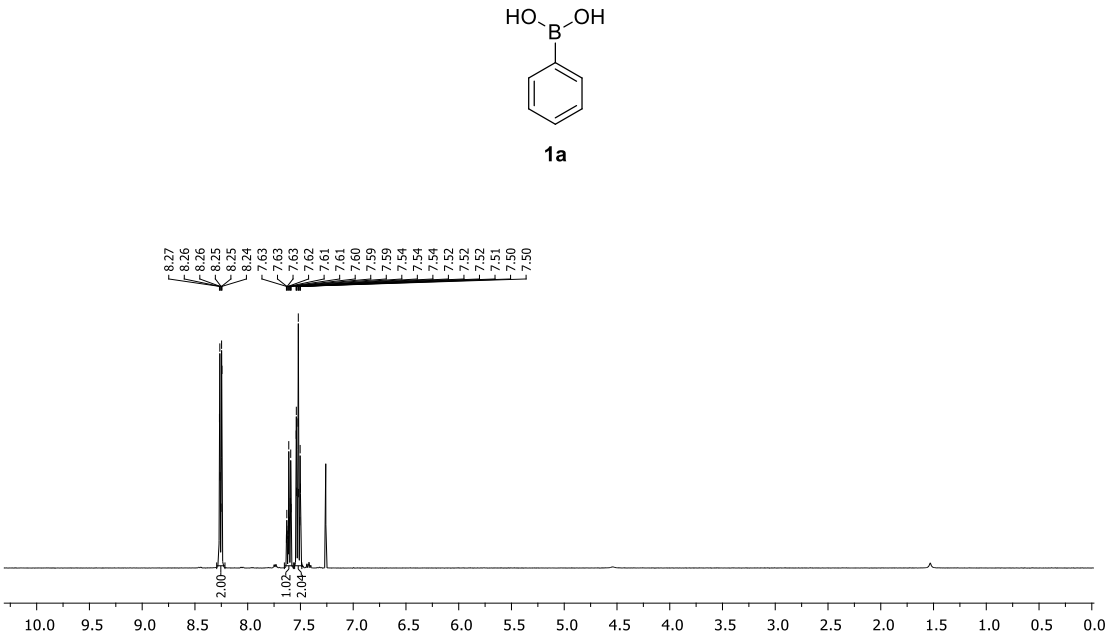
3j



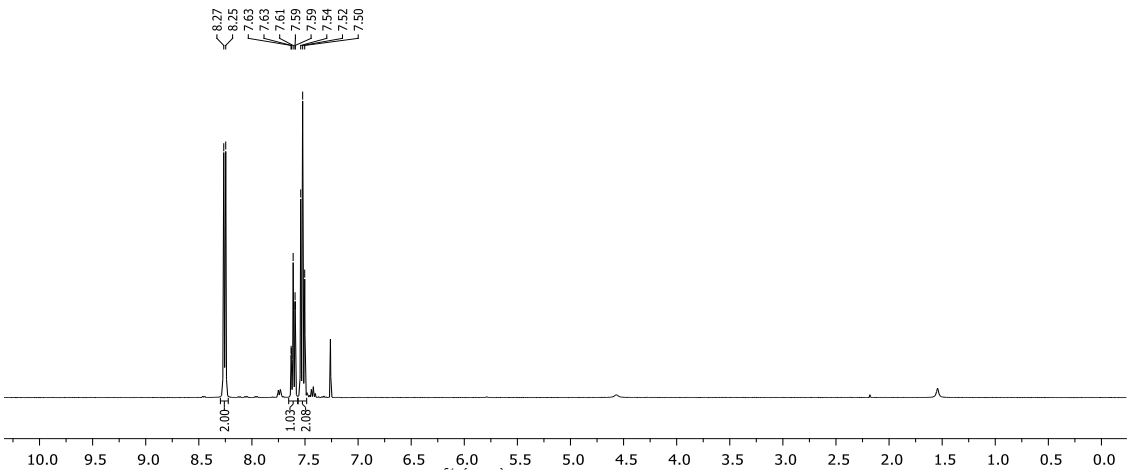
^{13}C NMR (100 MHz, $CDCl_3$) of **3j** (5 mg, 0.02 mmol) before irradiation.



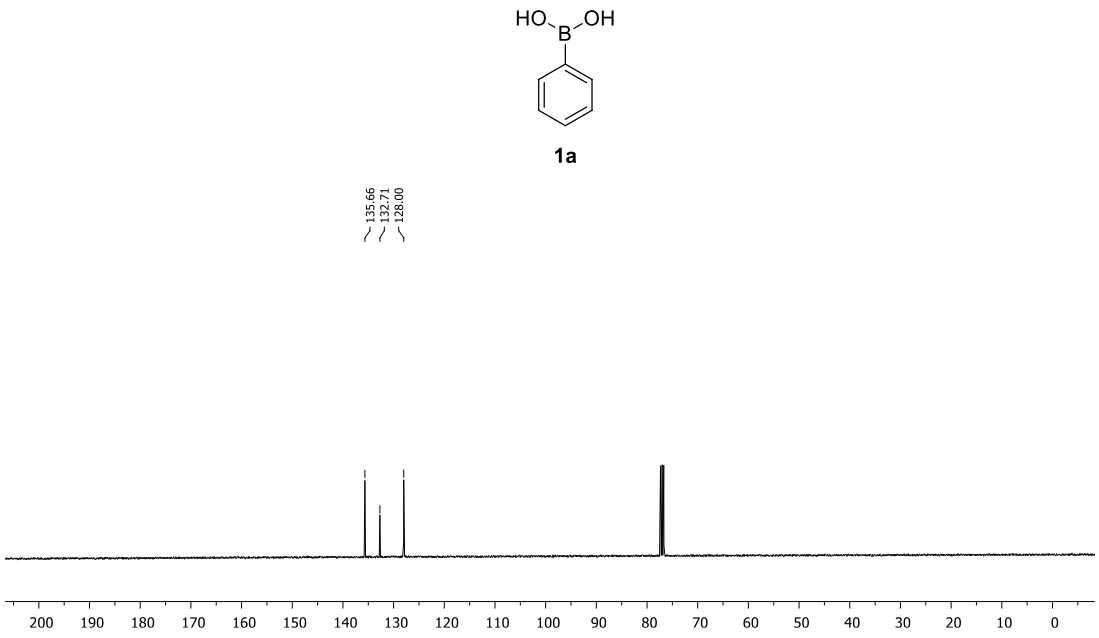
^{13}C NMR (100 MHz, $CDCl_3$) of **3j** (5 mg, 0.02 mmol) after irradiation at 525 nm for 3 h.



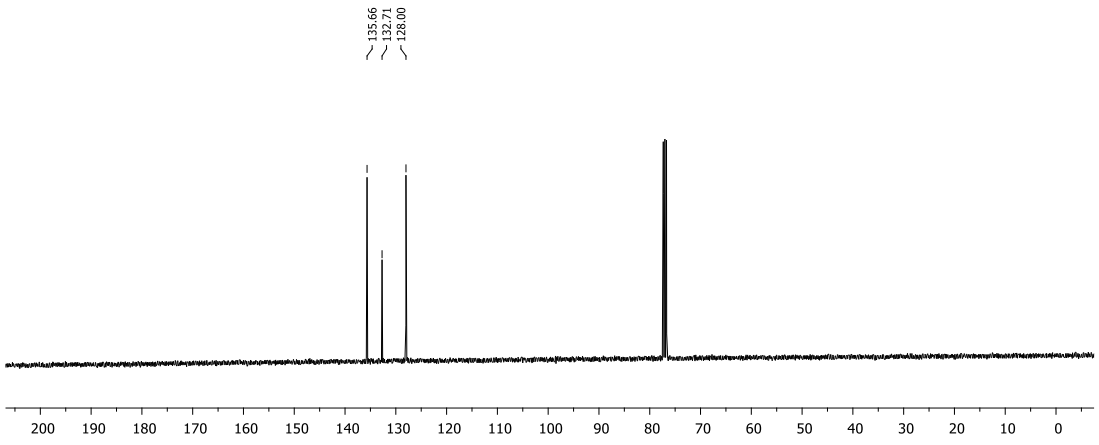
^{1}H NMR (400 MHz, $CDCl_3$) of phenylboronic acid (**1a**) (12 mg, 0.10 mmol) before irradiation.



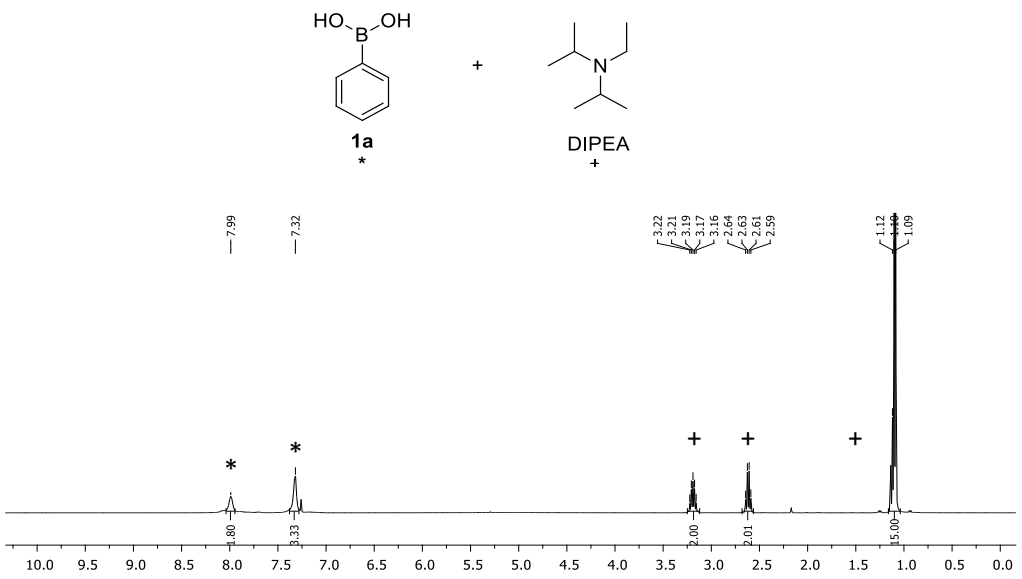
^{1}H NMR (400 MHz, $CDCl_3$) of phenylboronic acid (**1a**) (12 mg, 0.10 mmol) after irradiation at 525 nm for 3 h.



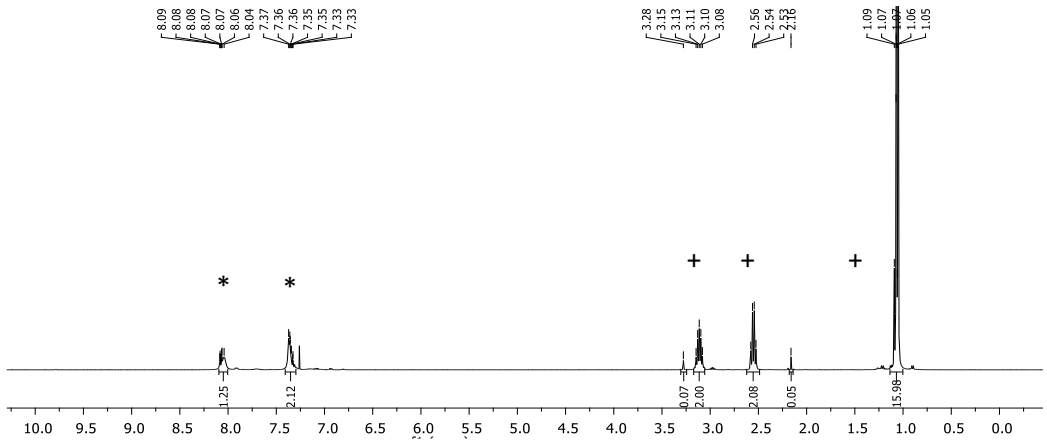
^{13}C NMR (100 MHz, $CDCl_3$) of phenylboronic acid (**1a**) (12 mg, 0.10 mmol) before irradiation.



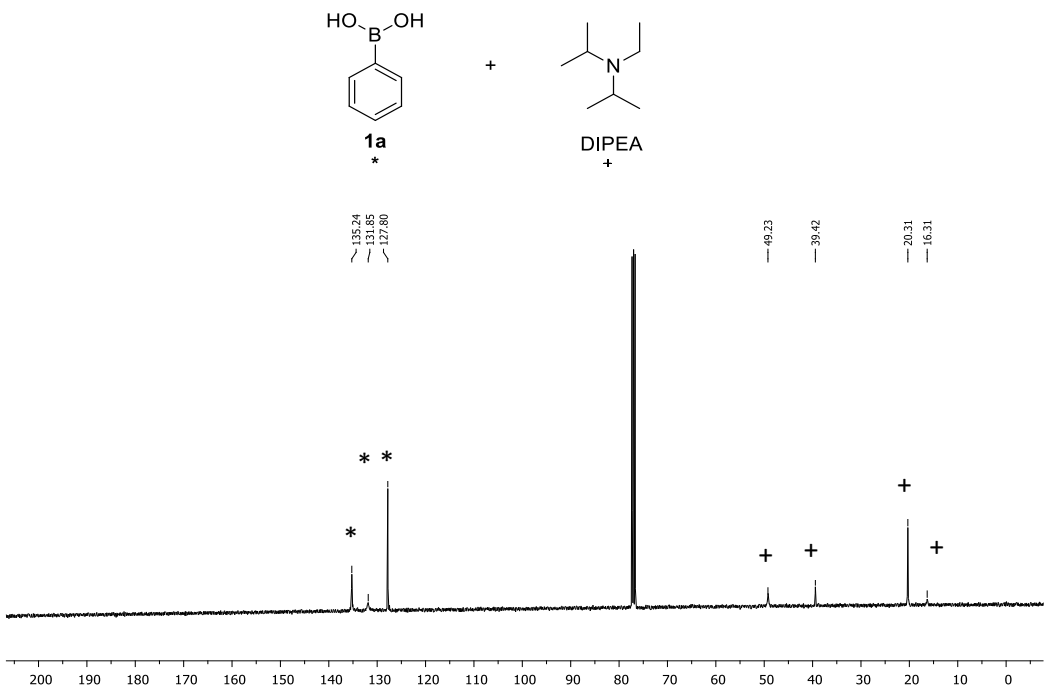
^{13}C NMR (100 MHz, $CDCl_3$) of phenylboronic acid (**1a**) (12 mg, 0.10 mmol) after irradiation at 525 nm for 3 h.



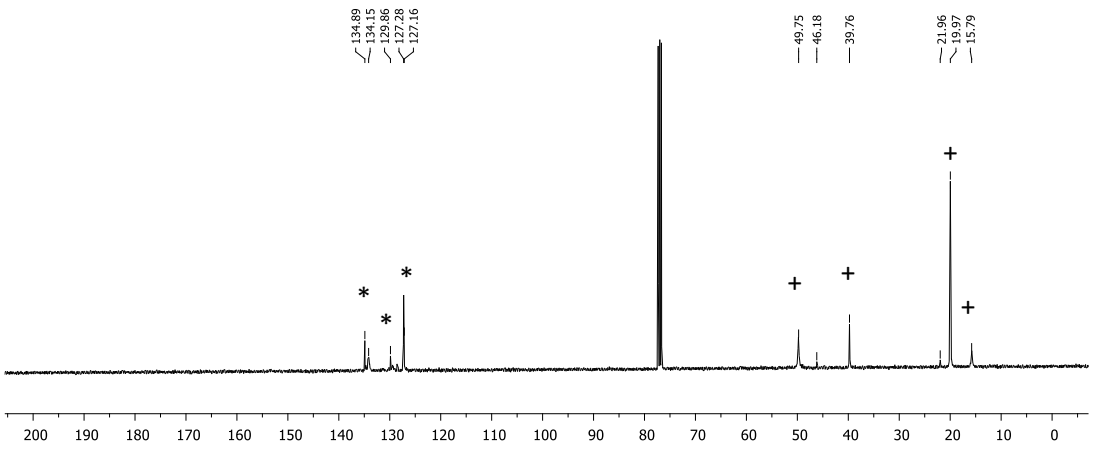
^{1}H NMR (400 MHz, $CDCl_3$) of a mixture of phenylboronic acid (**1a**) (12 mg, 0.10 mmol) with *N,N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) before irradiation.



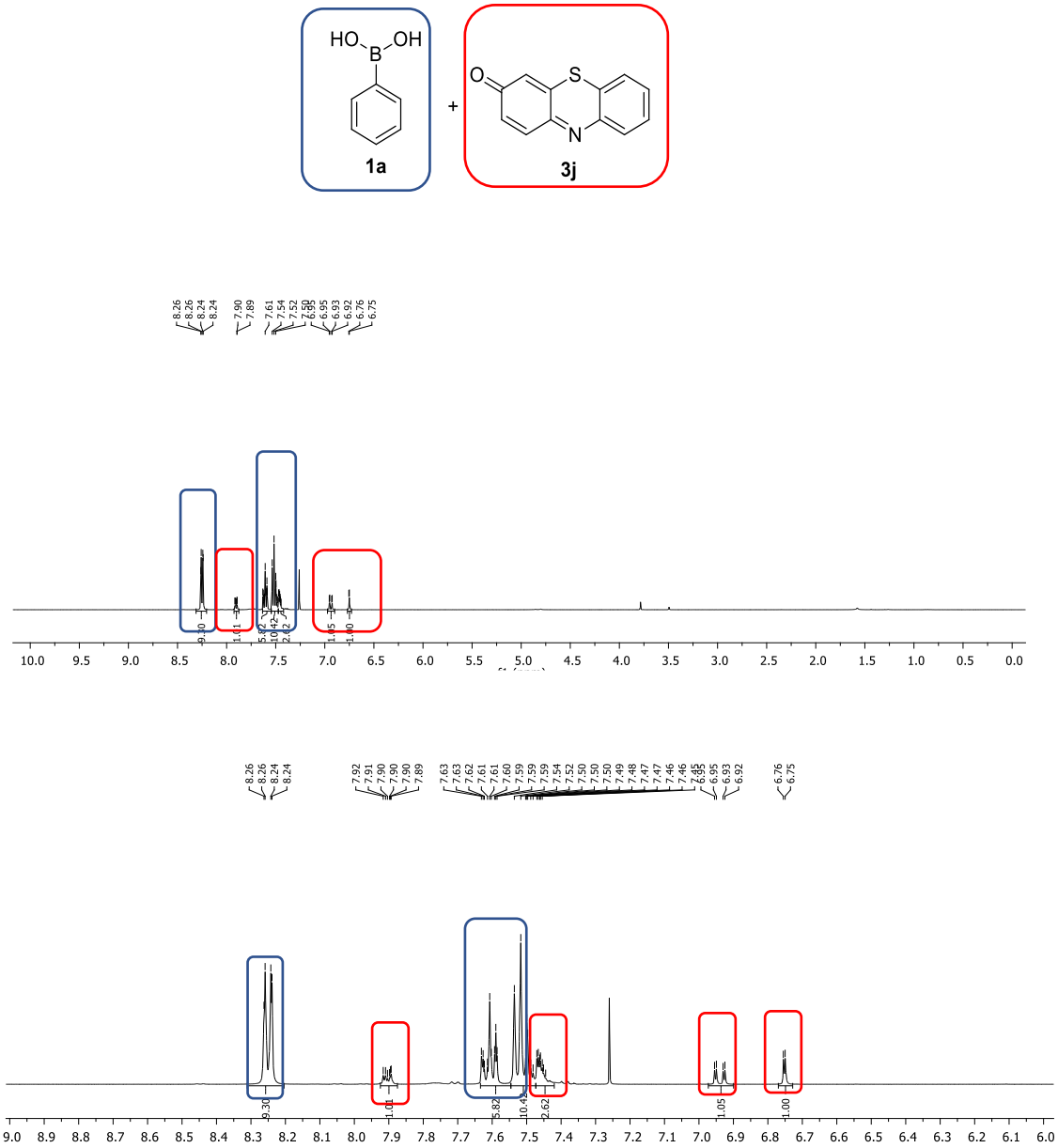
^{1}H NMR (400 MHz, $CDCl_3$) of a mixture of phenylboronic acid (**1a**) (12 mg, 0.10 mmol) with *N,N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) after irradiation at 525 nm for 3 h.



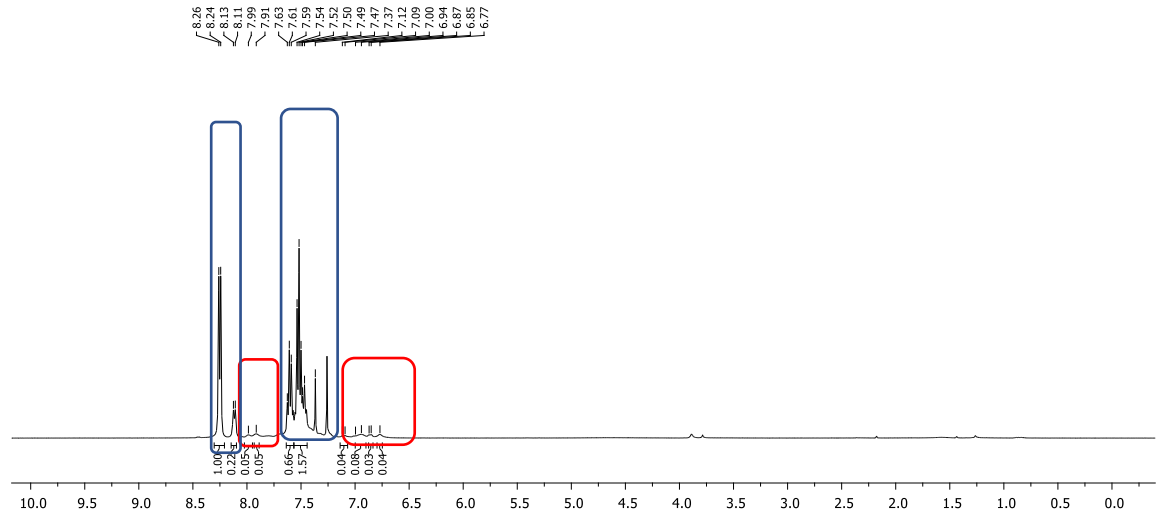
^{13}C NMR (100 MHz, $CDCl_3$) of a mixture of phenylboronic acid (**1a**) (12 mg, 0.10 mmol) with *N*,*N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) before irradiation.

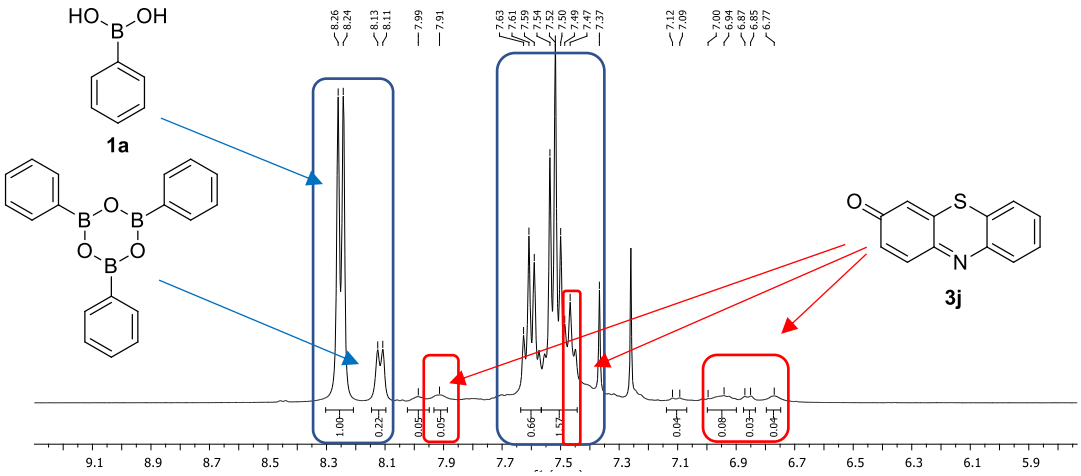


^{13}C NMR (100 MHz, $CDCl_3$) of a mixture of phenylboronic acid (**1a**) (12 mg, 0.10 mmol) with *N*,*N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) after irradiation at 525 nm for 3 h.

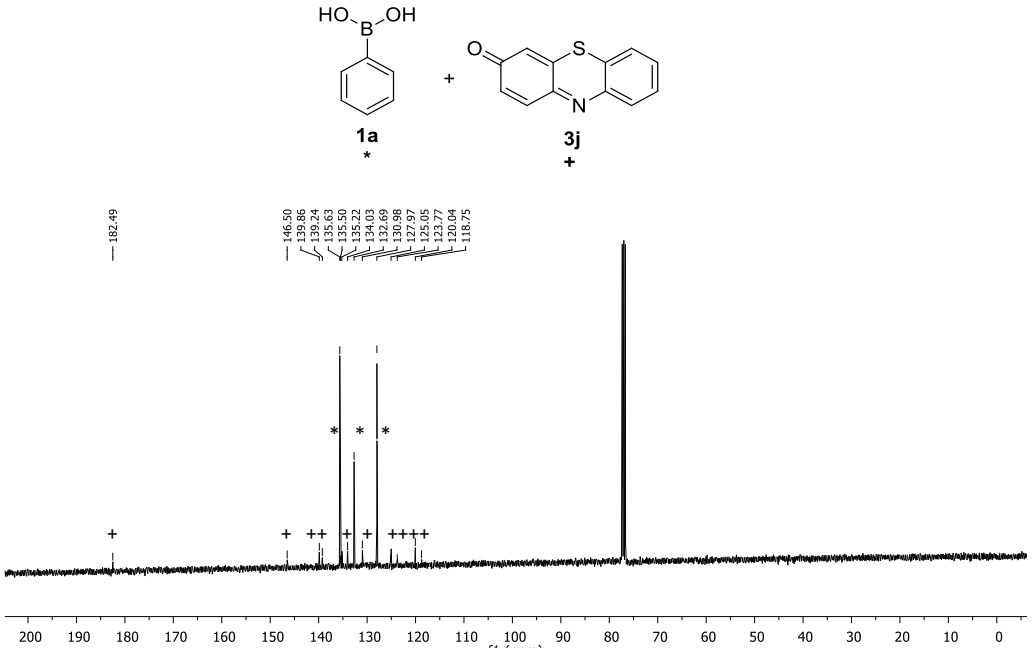


^{1}H NMR (400 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol) with phenylboronic acid (**1a**) (12 mg, 0.10 mmol) before irradiation and zoom in 9.0-6.0 ppm.

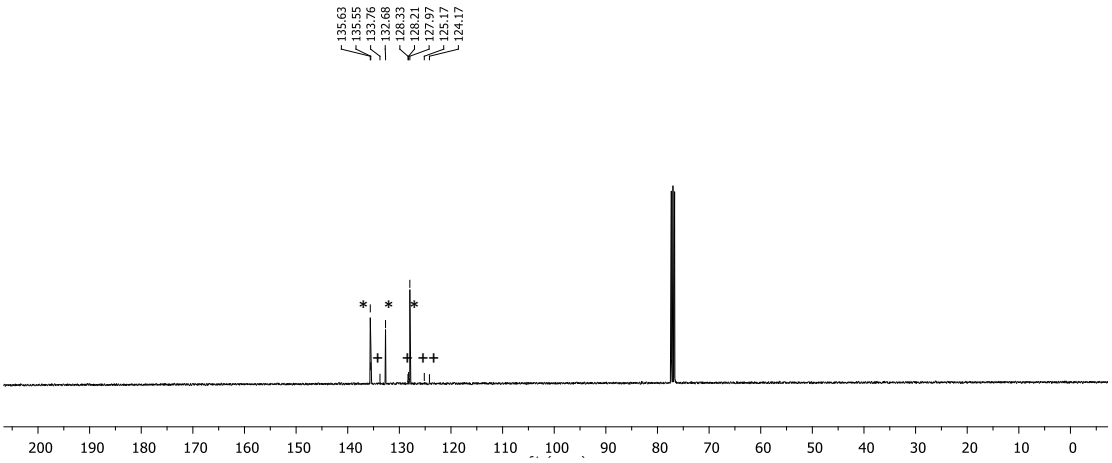




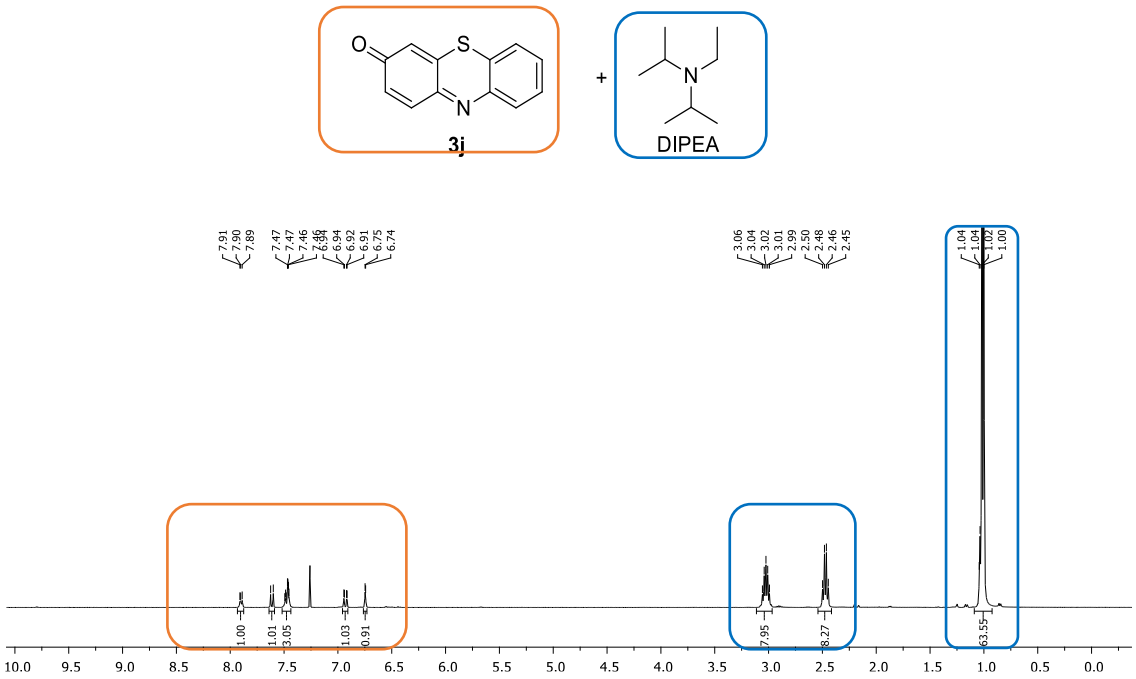
^{1}H NMR (400 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol) with phenylboronic acid (**1a**) (12 mg, 0.10 mmol) after irradiation at 525 nm for 3 h.



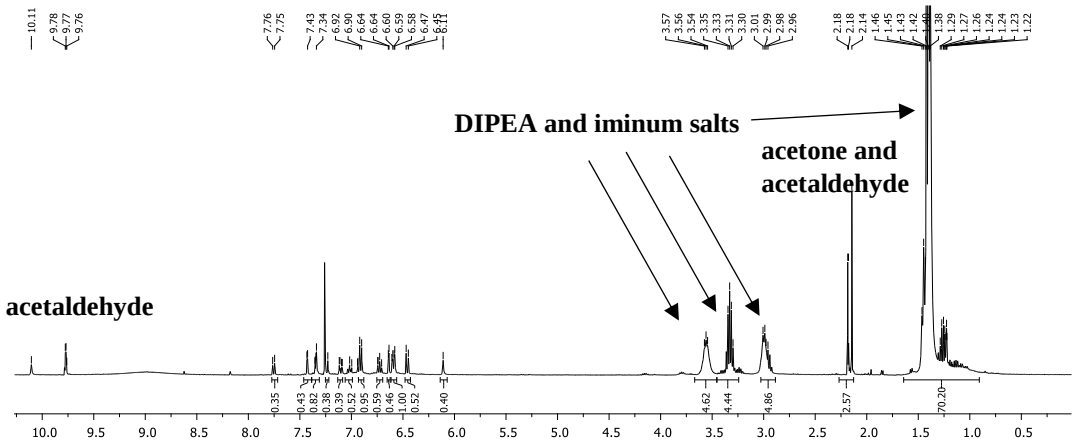
^{13}C NMR (100 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol) with phenylboronic acid (**1a**) (12 mg, 0.10 mmol) before irradiation.



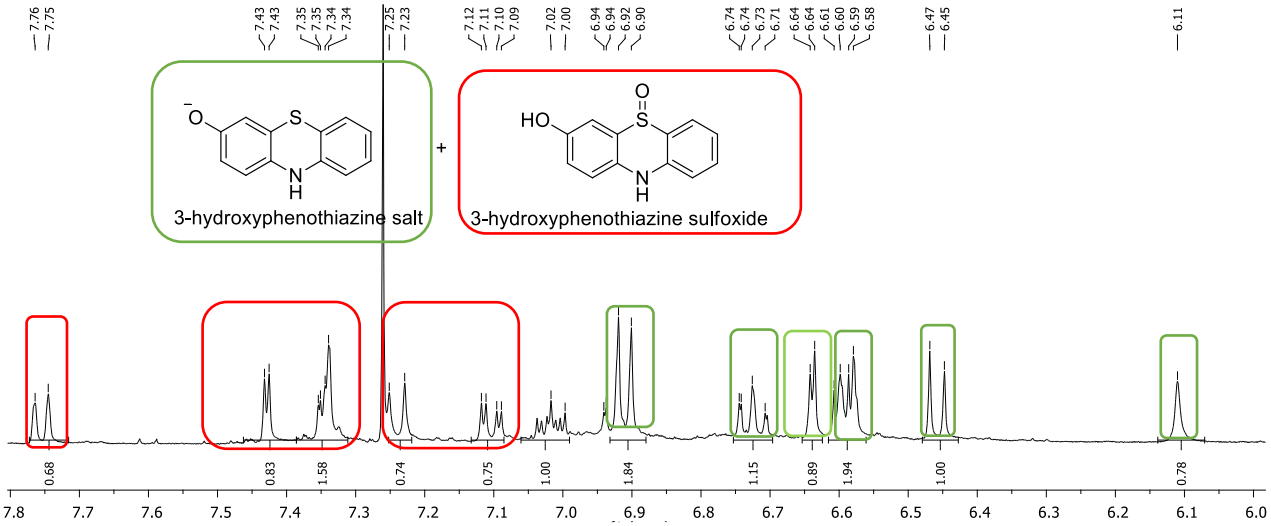
^{13}C NMR (100 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol) with **1a** (12 mg, 0.10 mmol) after irradiation at 525 nm for 3 h.



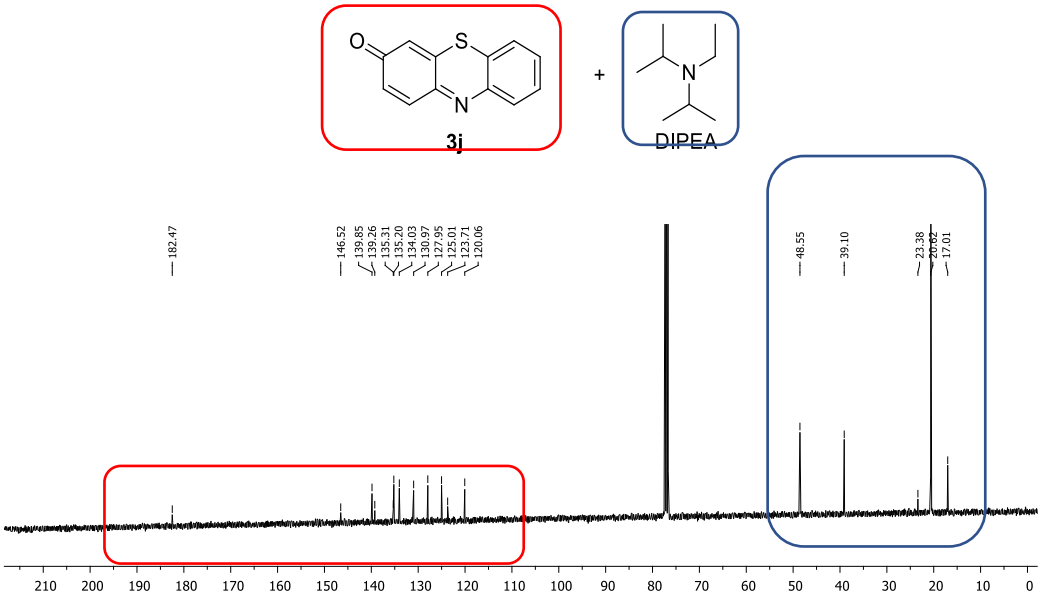
^{1}H NMR (400 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol) with *N*,*N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) before irradiation.



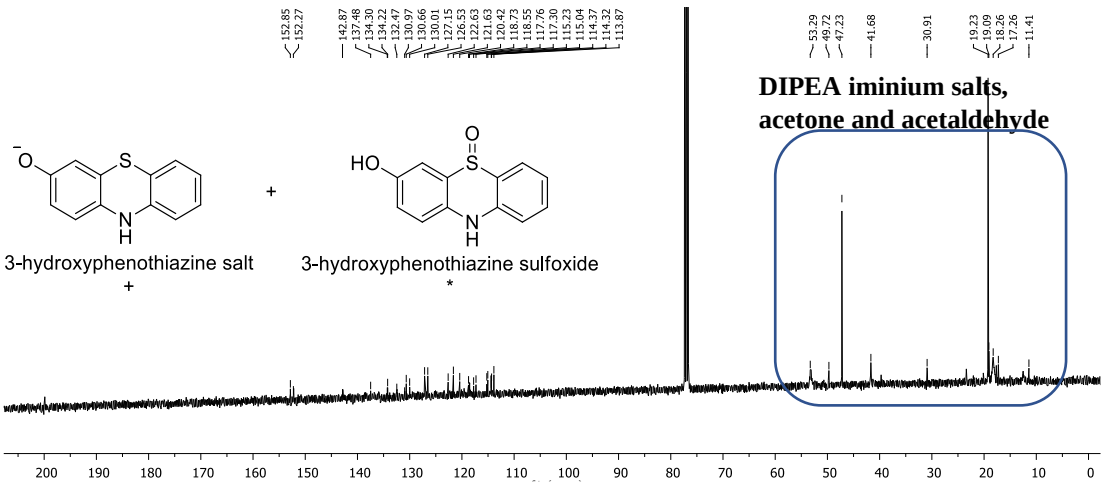
^{1}H NMR (400 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol) with *N*,*N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) after irradiation at 525 nm for 3 h.



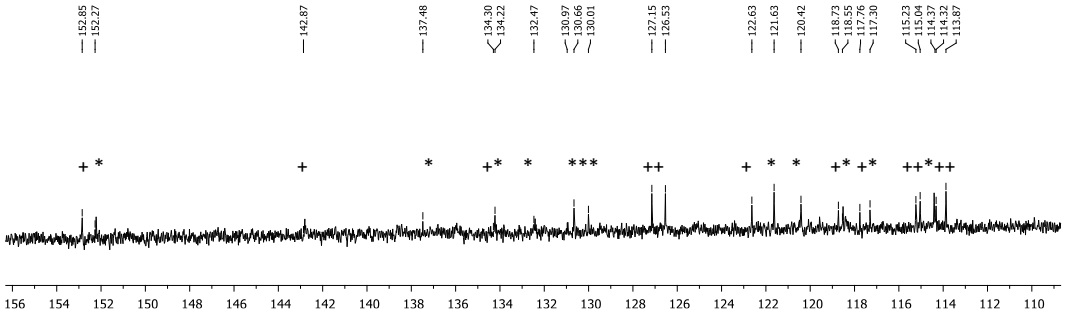
^{1}H NMR (400 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol) with *N*,*N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) after irradiation at 525 nm for 3 h.



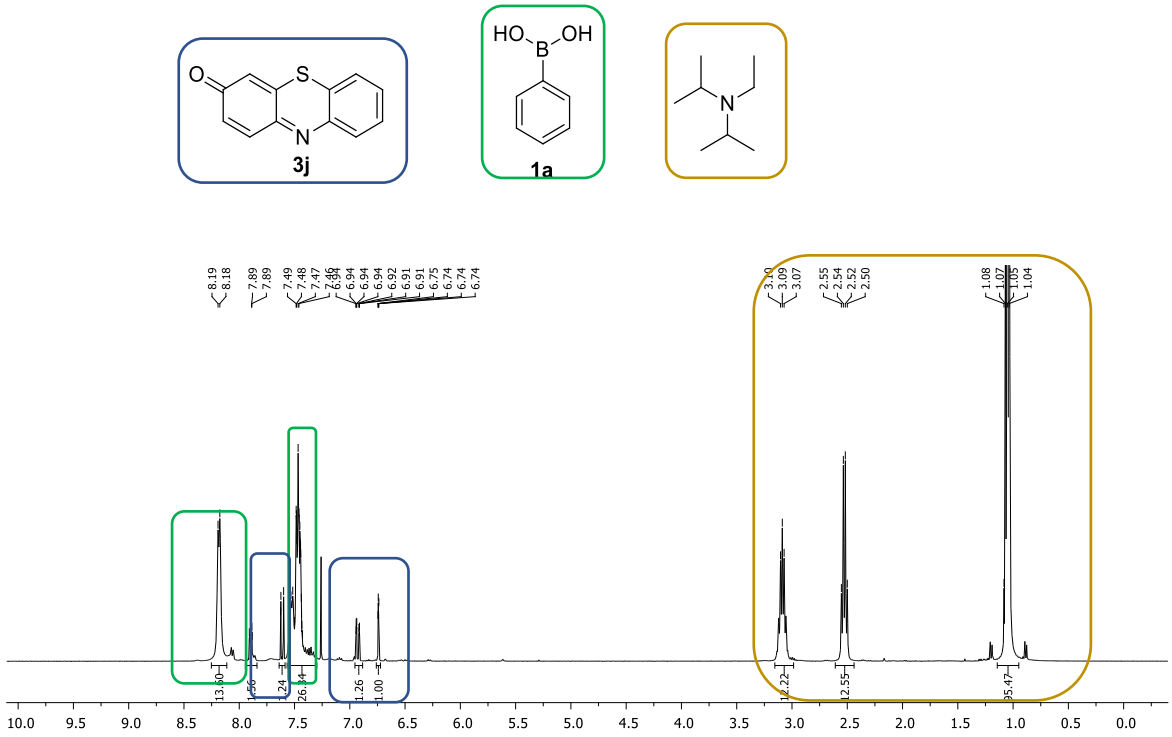
^{13}C NMR (100 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol) with *N*,*N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) before irradiation.



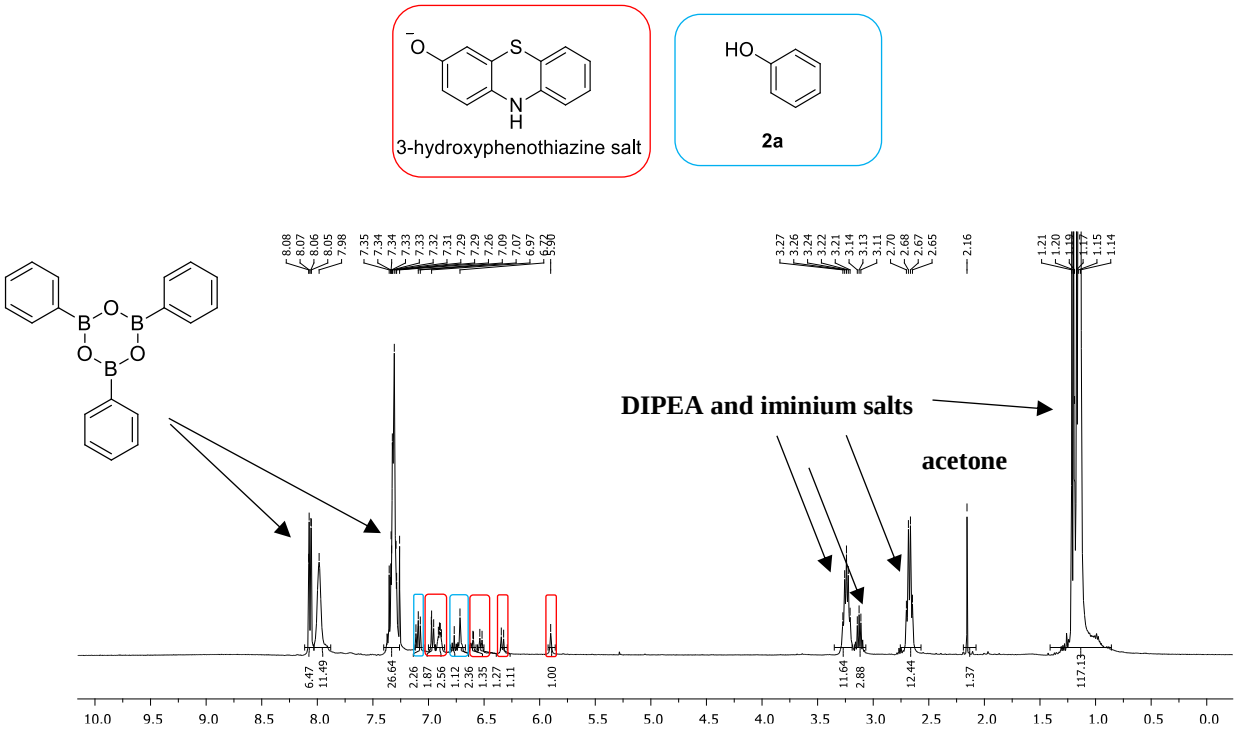
^{13}C NMR (100 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol) with *N*,*N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) after irradiation at 525 nm for 3 h.



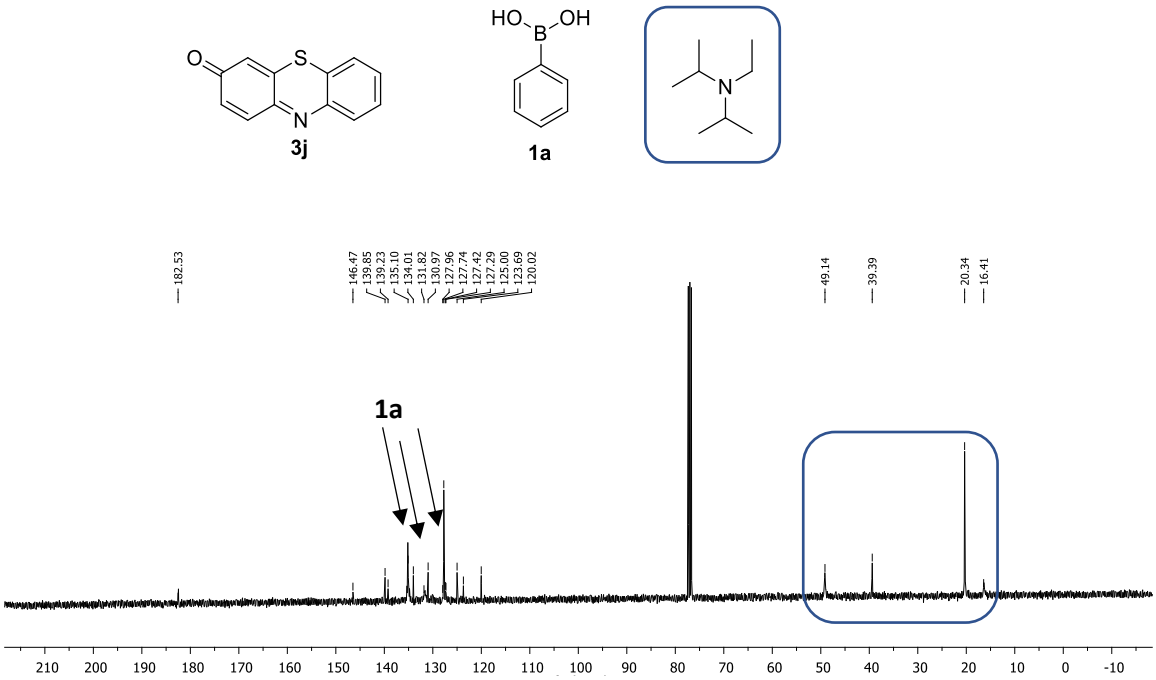
^{13}C NMR (100 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol) with *N*,*N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) after irradiation at 525 nm for 3 h.



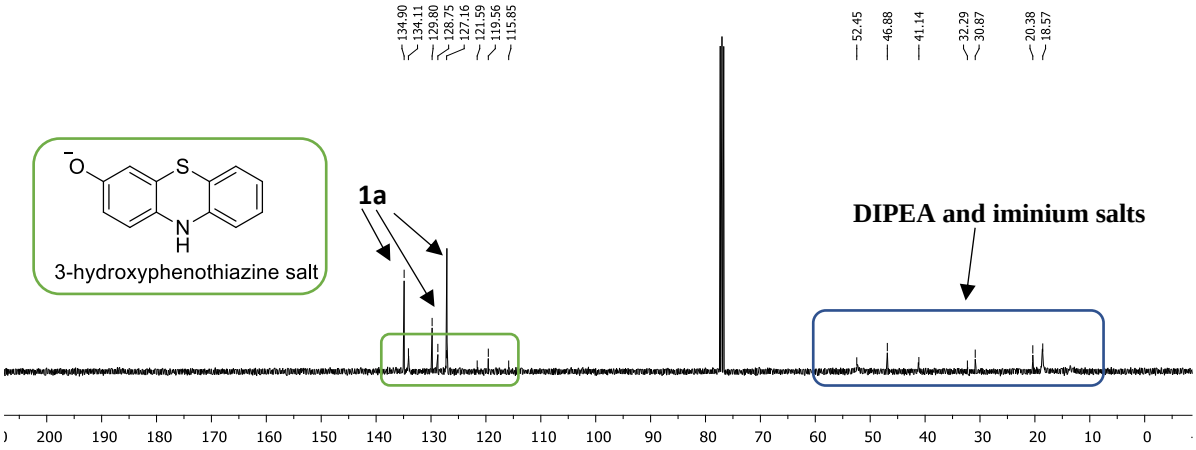
^{1}H NMR (400 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol), phenylboronic acid (**1a**) (12 mg, 0.10 mmol) and *N*,*N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) before irradiation.



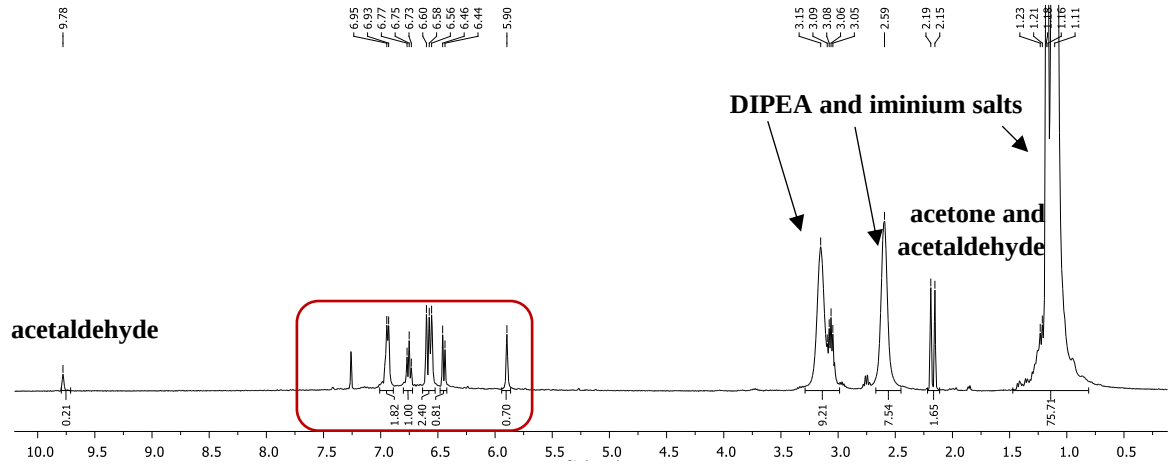
^{1}H NMR (400 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol), phenylboronic acid (**1a**) (12 mg, 0.10 mmol) and *N*,*N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) after irradiation at 525 nm for 3 h.



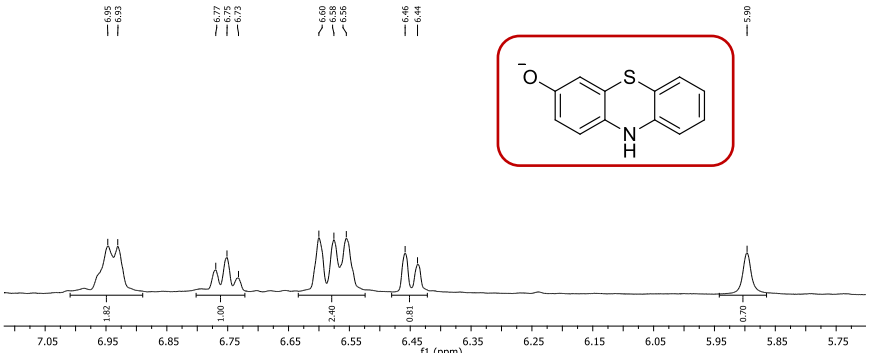
^{13}C NMR (100 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol), phenylboronic acid (**1a**) (12 mg, 0.10 mmol) and *N*,*N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) before irradiation.



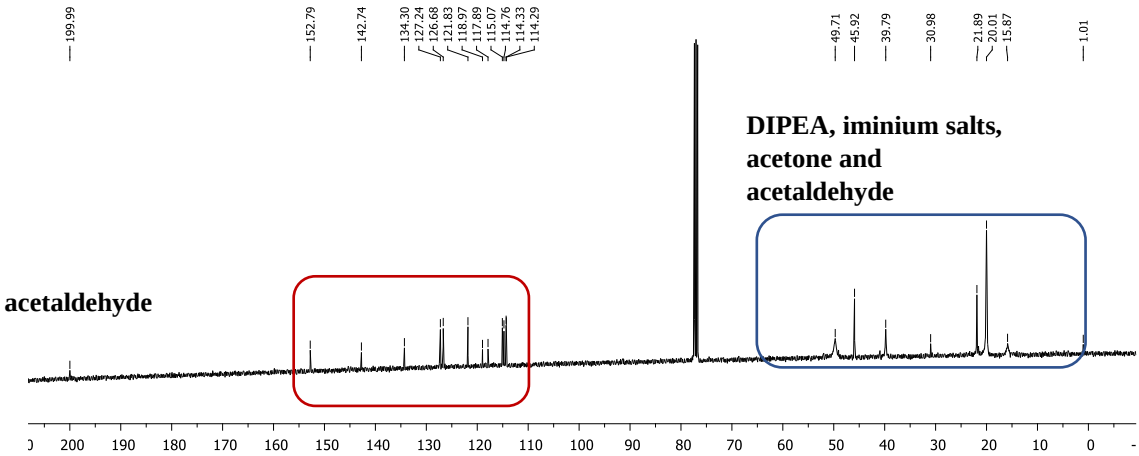
^{13}C NMR (100 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol), phenylboronic acid (**1a**) (12 mg, 0.10 mmol) and *N*,*N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) after irradiation at 525 nm for 3 h.



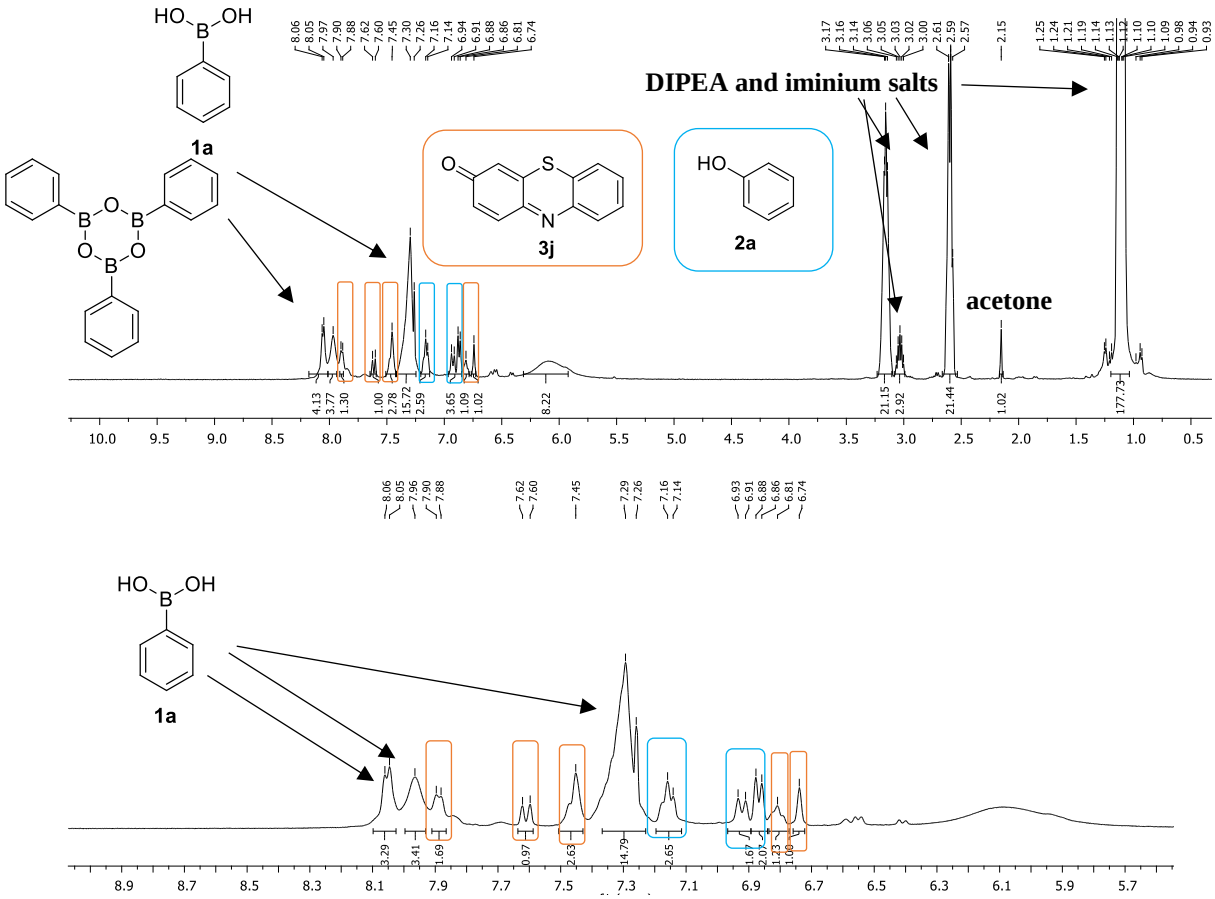
^{1}H NMR (400 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol) and *N*,*N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) after irradiation at 525 nm for 3 h under argon atmosphere.



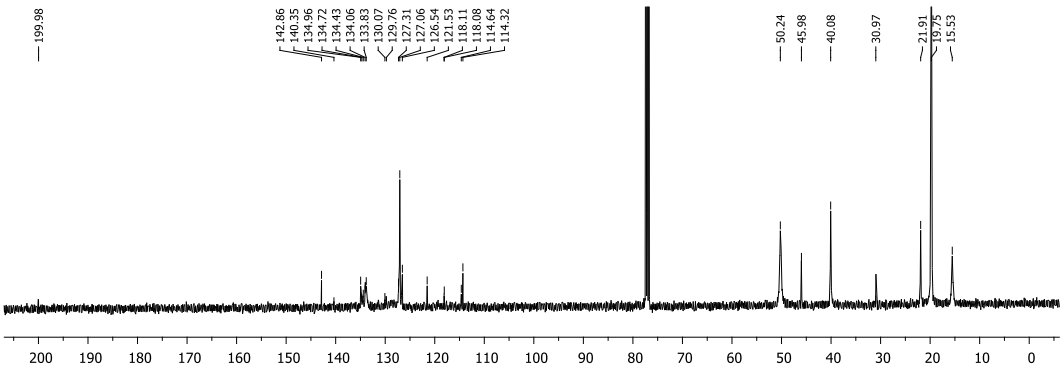
^{1}H NMR (400 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol), and *N*,*N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) after irradiation at 525 nm for 3 h under argon atmosphere.



^{13}C NMR (100 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol) with *N,N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) after irradiation at 525 nm for 3 h under argon atmosphere.



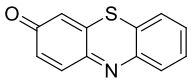
^{1}H NMR (400 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol) with *N,N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) after irradiation at 525 nm for 3 h under argon atmosphere, followed by the addition of phenylboronic acid (**1a**) (12 mg, 0.10 mmol) and stirring under dark and open air conditions for 18 h.



^{13}C NMR (100 MHz, $CDCl_3$) of a mixture of **3j** (5 mg, 0.02 mmol) with *N*,*N'*-diisopropylethylamine (DIPEA) (13 mg, 0.10 mmol) after irradiation at 525 nm for 3 h under argon atmosphere, followed by the addition of phenylboronic acid (**1a**) (12 mg, 0.10 mmol) and stirring under dark and open air conditions for 18 h.

NMR data of intermediates

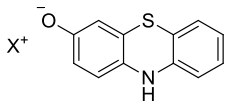
3H-Phenothiazin-3-one (3j)



The NMR data are in accordance with the literature.[1]

^{1}H NMR ($CDCl_3$, 400 MHz): 7.91-7.89 (1H, m, ArH), 7.61 (1H, d, *J* = 9.9 Hz, ArH), 7.50-7.45 (3H, m, ArH), 6.93 (1H, dd, *J* = 9.9 and 2.1 Hz, ArH), 6.75 (1H, d, *J* = 2.1 Hz, ArH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 182.5, 146.5, 139.9, 139.3, 135.3, 135.2, 134.0 131.0, 128.0, 125.0, 123.7, 120.1; **HRMS (ESI)** for $C_{12}H_7NOS$ $[M+H]^+$: calculated 214.0312, found 214.0324.

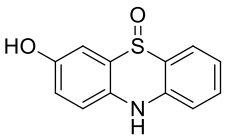
3-Hydroxyphenothiazine salt



The NMR data are in accordance with the literature.[2]

^{1}H NMR ($CDCl_3$, 400 MHz): 6.94 (2H, d, *J* = 7.5 Hz, ArH), 6.75 (1H, t, *J* = 7.5 Hz, ArH), 6.64 (1H, d, *J* = 2.6 Hz, ArH), 6.60-6.56 (2H, m, ArH), 6.45 (1H, d, *J* = 8.1 Hz, ArH), 5.90 (1H, s, NH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.9, 142.9, 134.3, 127.2, 126.6, 122.7, 118.7, 117.8, 115.2, 115.0, 114.4, 113.9; **HRMS (ESI)** for $C_{12}H_8NOS$ $[M+H]^+$: calculated 215.0339, found 215.0395.

3-Hydroxyphenothiazine sulfoxide



The NMR data are in accordance with the literature.[1]

^{1}H NMR ($CDCl_3$, 400 MHz): 10.11 (1H, s, NH or OH), 7.75 (1H, *J* = 7.6 Hz, ArH), 7.43 (1H, d, *J* = 2.7 Hz, ArH), 7.35-7.34 (1H, m, ArH), 7.24 (1H, d, *J* = 8.9 Hz, ArH),

7.12-7.09 (2H, m, ArH), 7.02-7.00 (1H, m, ArH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.3, 137.5, 134.2, 132.5, 131.0, 130.7, 130.0, 121.6, 120.4, 118.6, 117.3, 114.3; **HRMS (ESI)** for $C_{12}H_9NO_2S$ $[M+Na]^+$: calculated 254.0246, found 254.0235.

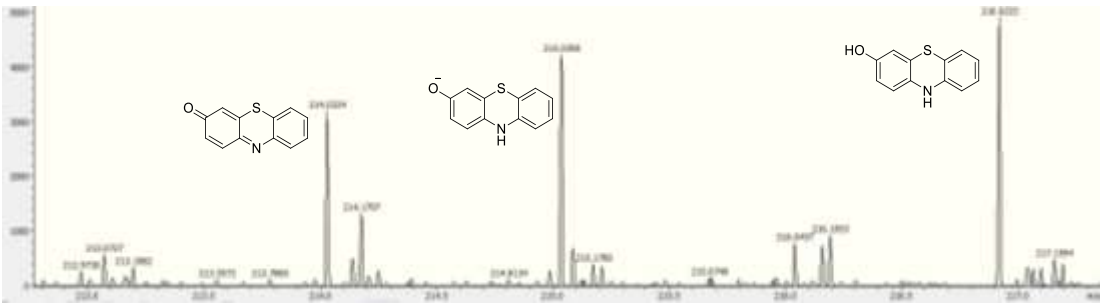
S.7 HRMS Studies

Instrumentation

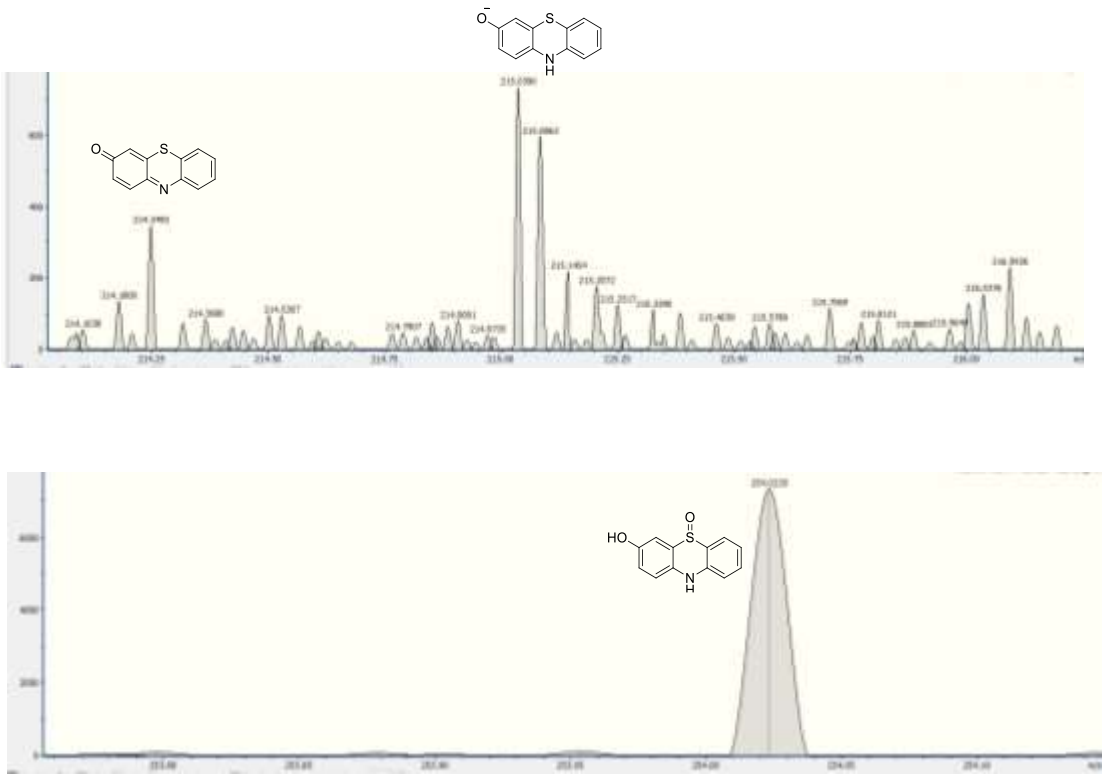
High Resolution Mass Spectra were recorded with a Q-TOF (Time of Flight Mass Spectrometer) Bruker Maxis Impact with electrospray ionization (ESI) source. N_2 was used as the collision gas and positive ionization mode was used for all MS experiments. The data acquisition was carried out with Data Analysis from Bruker Daltonics (version4.1). Acetonitrile LC-MS gradient was obtained from Carlo Erba Reagents (Chausséedu Vexin, France). Source conditions: End plate offset 500V, Capillary 4500V, Nebulizer 0.4 bar, dry gas 4.0 L/min, dry temperature 180 ^{o}C and Quadrupole conditions: Ion energy 5 eV, Collision energy 10 eV, Transfer time 143 μs, Collision ion RF 3500 vpp, Pre pulse storage 1μs.

HRMS studies were performed with an ESI source in negative-ionization mode. The annotation of the intermediates was based on the exact mass high accuracy (mass error lower than 5 ppm) and in most cases on the isotopic distribution similarity (mSigma values lower than 50).

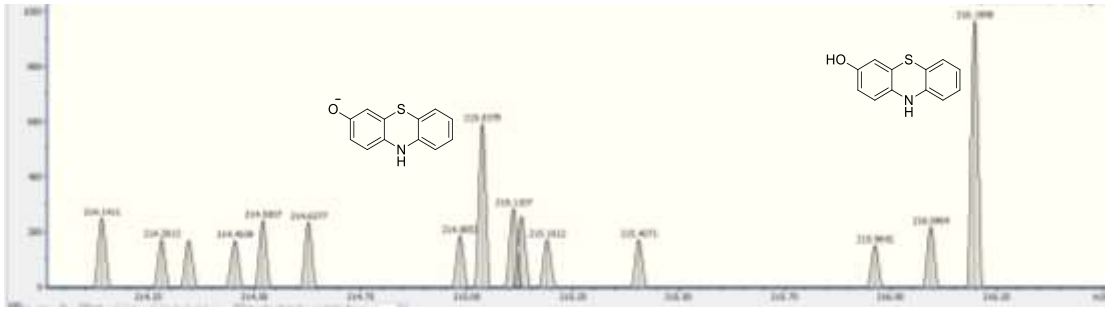
A) In a glass vial, *N*,*N*'-diisopropylethylamine (26 mg, 0.20 mmol) and **3j** (0.4 mg, 1 mol%, 0.002 mmol) in MeCN (1.0 mL) were added. The reaction mixture was left stirring under irradiation by Kessil lamp 525 nm and Ar atm for 3 h. Sample of the reaction mixture (20 μL) was dissolved in MeOH (980 μL) and 100 μL of that sample were further diluted with 900 μL of MeOH. Finally, 100 μL were directly injected to the ESI source of Q-TOF for analysis.



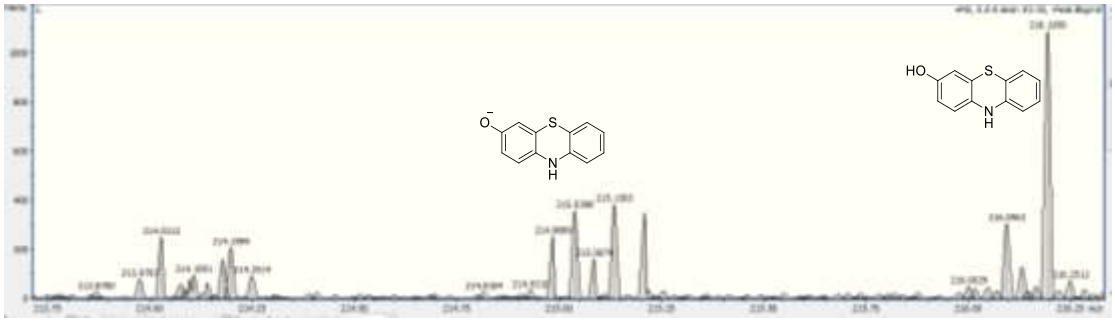
B) In a glass vial *N*,*N*'-diisopropylethylamine (26 mg, 0.20 mmol) and **3j** (0.4 mg, 1 mol%, 0.002 mmol) in MeCN (1.0 mL) were added. The reaction mixture was left stirring under irradiation by Kessil lamp 525 nm for 3 h. Sample of the reaction mixture (20 μL) was dissolved in MeOH (980 μL) and 100 μL of that sample were further diluted with 900 μL of MeOH. Finally, 100 μL were directly injected to the ESI source of Q-TOF for analysis.



C) In a glass vial *N*,*N*'-diisopropylethylamine (26 mg, 0.20 mmol), **3j** (0.4 mg, 1 mol%, 0.002 mmol) and **1a** (24 mg, 0.20 mmol) in MeCN (1.0 mL) were added. The reaction mixture was left stirring under irradiation by Kessil lamp 525 nm and Ar atm for 3 h. Sample of the reaction mixture (20 μL) was dissolved in MeOH (980 μL) and 100 μL of that sample were further diluted with 900 μL of MeOH. Finally, 100 μL were directly injected to the ESI source of Q-TOF for analysis.



D) In a glass vial *N*,*N*'-diisopropylethylamine (26 mg, 0.20 mmol), **3j** (0.4 mg, 1 mol%, 0.002 mmol) and **1a** (24 mg, 0.20 mmol) in MeCN (1.0 mL) were added. The reaction mixture was left stirring under irradiation by Kessil lamp 525 nm for 3 h. Sample of the reaction mixture (20 μL) was dissolved in MeOH (980 μL) and 100 μL of that sample were further diluted with 900 μL of MeOH. Finally, 100 μL were directly injected to the ESI source of Q-TOF for analysis.



S.8 Test for the Detection of H_2O_2 Production

A) Test for the detection of H_2O_2 from catalyst 3j

In a glass vial, catalyst **3j** (0.4 mg, 0.002 mmol) was added in MeCN (1.0 mL). The solution was left stirring under irradiation at 525 nm for 18 h.

KI-glacial acetic acid test solution preparation: 30 mg of potassium iodide was dissolved in 3 mL of glacial acetic acid.

H_2O_2 generation test: The irradiated solution was added to the KI-glacial acetic acid test solution.

Figure S9. A) **3j** after irradiation at 525 nm for 18 h; **B)** KI-glacial acetic acid test solution; **C)** Solution resulting upon the addition of the irradiated **3j** to the KI-glacial acetic acid test solution (***negative result***).

B) Test for the detection of H_2O_2 from the mixture of catalyst (3j) with DIPEA

In a glass vial, *N*,*N*'-diisopropylethylamine (26 mg, 0.20 mmol) and catalyst **3j** (0.4 mg, 0.002 mmol) were added in MeCN (1.0 mL). The reaction mixture was left stirring under irradiation at 525 nm for 18 h.

KI-glacial acetic acid test solution preparation: 30 mg of potassium iodide was dissolved in 3 mL of glacial acetic acid.

H_2O_2 generation test: The irradiated reaction mixture was added to the KI-glacial acetic acid test solution, where immediate dark color appearance indicated the generation of H_2O_2 during the reaction.

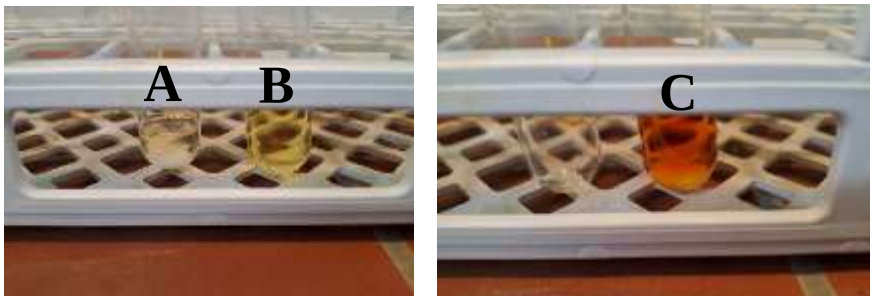


Figure S10. A) Reaction mixture after irradiation at 525 nm for 18 h; **B)** KI-glacial acetic acid test solution; **C)** Solution resulting upon the addition of the irradiated reaction mixture to the KI-glacial acetic acid test solution (***positive result***).

S.9 Cyclic Voltammetry Studies

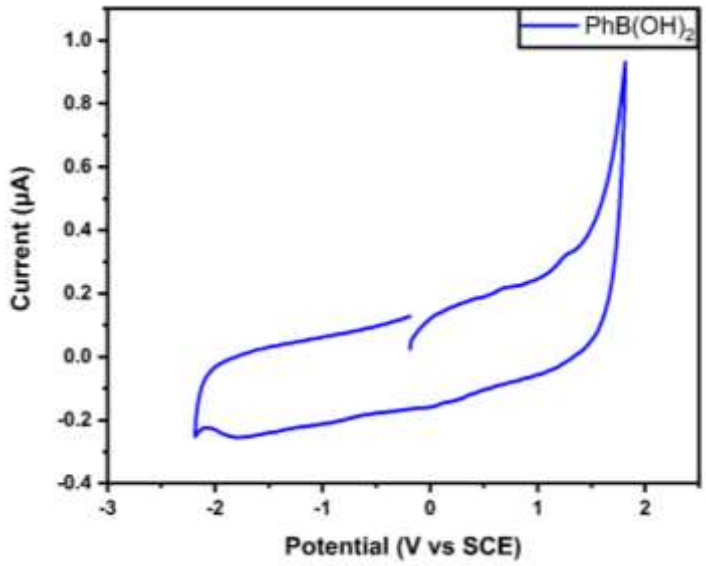


Figure S11. Cyclic voltammogram of $PhB(OH)_2$ (**1a**) in MeCN, electrolyte: *n*-Bu_4NPF_6 (0.1 M). Electrodes: working: glassy carbon disk (⌀ 3 mm); counter: Pt wire; reference: Ag/AgCl (1M KCl. Scan rate 100 $mV \cdot s^{-1}$, temp 20 °C, internal reference: Fc/Fc^+ (0.40 V).

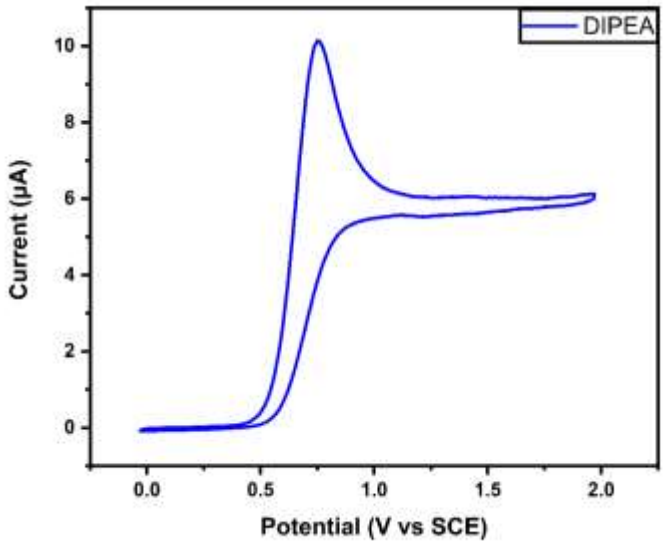


Figure S12. Cyclic voltammogram of *N,N'*-diisopropylethylamine in MeCN, electrolyte: *n*-Bu_4NPF_6 (0.1 M). Electrodes: working: glassy carbon disk (⌀ 3 mm); counter: Pt wire; reference: Ag/AgCl (1M KCl. Scan rate 100 $mV \cdot s^{-1}$, temp 20 °C, internal reference: Fc/Fc^+ (0.40 V).

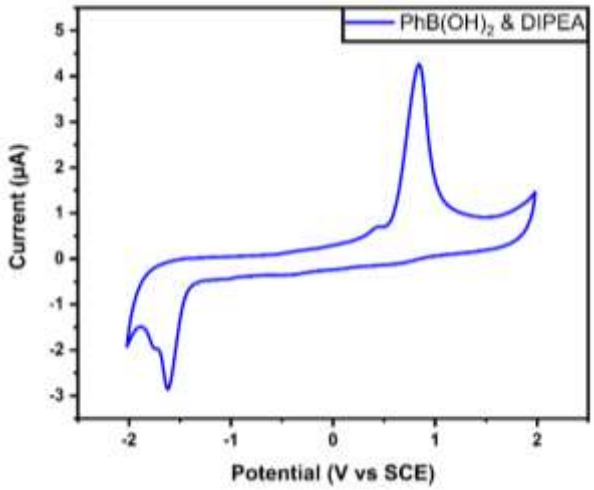


Figure S13. Cyclic voltammogram of $PhB(OH)_2$ (**1a**) mixed with DIPEA in MeCN, electrolyte: *n*-Bu_4NPF_6 (0.1 M). Electrodes: working: glassy carbon disk (⌀ 3 mm); counter: Pt wire; reference: Ag/AgCl (1M KCl. Scan rate 100 $mV \cdot s^{-1}$, temp 20 °C, internal reference: Fc/Fc^+ (0.40 V). Oxidation potentials: $E_{1/2}^{0/+1}$ = 0.70 V, reduction potential: $E^{0/-1}$ = -1.62 V and $E^{-1/-2}$= -1.74 V.

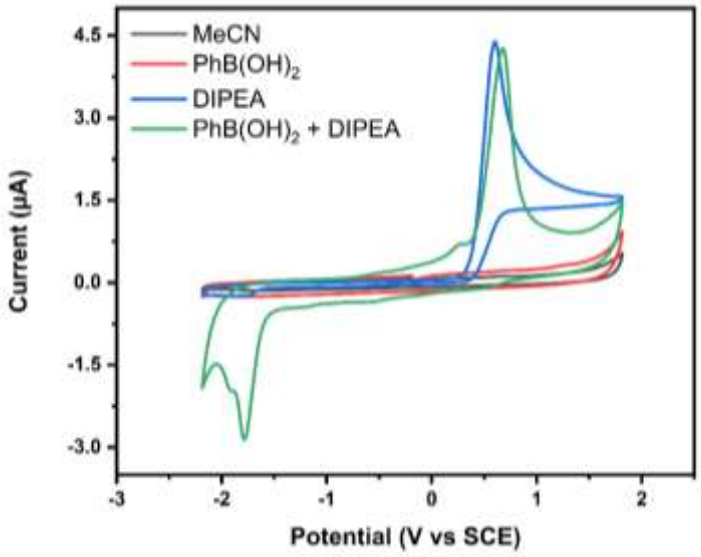


Figure S14. Cyclic voltammograms of a blank (grey line) $PhB(OH)_2$ (**1a**) (red line), DIPEA (blue line), and a mixture of $PhB(OH)_2$ (**1a**) with DIPEA (green line), in MeCN, electrolyte: *n*-Bu_4NPF_6 (0.1 M). Electrodes: working: glassy carbon disk (⌀ 3 mm); counter: Pt wire; reference: Ag/AgCl (1M KCl. Scan rate 100 $mV \cdot s^{-1}$, temp 20 °C, internal reference: Fc/Fc^+ (0.40 V).

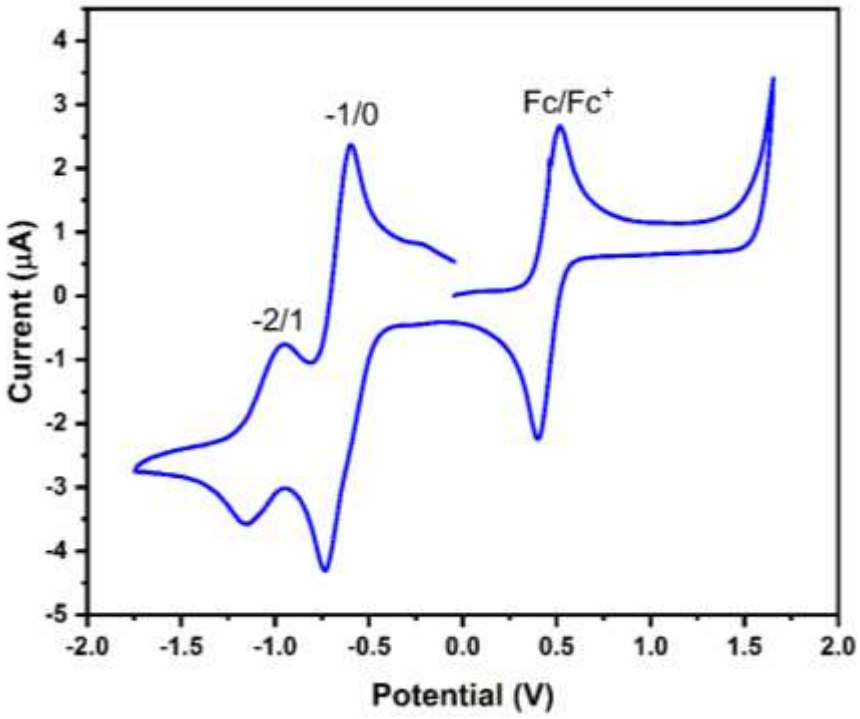


Figure S15. Cyclic voltammograms data of **3j** in MeCN, electrolyte: *n*-Bu_4NPF_6 (0.1 M). Electrodes: working: glassy carbon disk (⌀ 3 mm); counter: Pt wire; reference: Ag/AgCl (1M KCl. Scan rate 100 $mV \cdot s^{-1}$, temp 20 °C, internal reference: Fc/Fc^+ (0.40 V).: Oxidation potentials $E_{1/2}^{-1/0}$ = -0.664 V, $E_{1/2}^{-2/-1}$ = -1.056 V.

S.10 Determination of the Quantum Yield

S.10.1 Determination of the photon flux

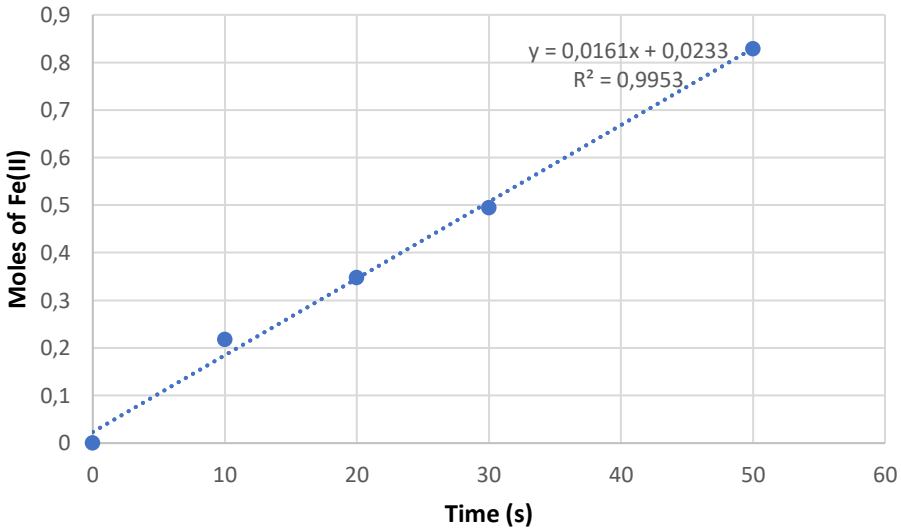
A ferrioxalate actinometer solution was prepared following the Hammond variation of the Hatchard and Parker procedure[3] outlined in the Handbook of Photochemistry.[4] Ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed. The values of the quantum yield of potassium ferrioxalate are related to the concentration and wavelength. The solutions were prepared and stored under dark:

1. Potassium ferrioxalate solution 0.012M: 147.4 mg of potassium ferrioxalate and 69.5 μL of sulfuric acid (96%) were added to a 25 mL volumetric flask and filled to the mark with water (HPLC grade).
2. Phenanthroline solution: 0.2% by weight of 1,10-phenanthroline in water (100 mg in 50 mL volumetric flask or 50 mg in 25 mL).
3. Buffer solution: to a 100 mL volumetric flask 4.94 g of NaOAc and 1.0 mL of sulfuric acid (96%) were added and filled to the mark with water (HPLC grade).

A cuvette was loaded with 1.0 mL of potassium ferrioxalate solution and placed under Kessil 525 nm lamp irradiation. Four different actinometer solutions were irradiated in sequence for 10 s, 20 s, 30 s and 50 s, respectively. After each irradiation, the actinometer solutions were carefully transferred into a 10 mL volumetric flask, then 0.5 mL of phenanthroline solution and 2.0 mL of buffer solution were added and the flask was filled up with water. The absorbance of the final solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured. The moles of Fe^{2+} formed for each sample are determined using Beer's Law (Eq. 1):

$$Moles\ of\ Fe(II) = \frac{V_1 \times V_3 \times \Delta A(510\ nm)}{10^3 \times V_2 \times 1 \times \varepsilon(510\ nm)} \quad \text{(Eq. 1)}$$

where V_1 is the irradiated volume (1 mL), V_2 is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), V_3 is the final volume after complexation with phenanthroline (10 mL), l is the optical path-length of the irradiation cell (1 cm), ΔA (510 nm) is the optical difference in absorbance between the irradiated solution and the one stored in the dark, ε (510 nm) is the extinction coefficient the complex $Fe(phen)_3^{2+}$ at 510 nm (11100 L mol^{-1} cm^{-1}). The moles of Fe^{2+} formed (x) are plotted as a function of time (t).



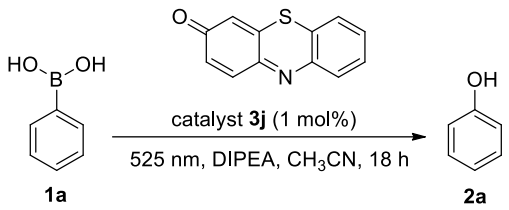
The slope of this line was correlated to the moles of incident photons by unit of time ($q^0_{n,p}$) by the use of the following Equation 2:

$$\Phi(\lambda) = \frac{dx/dt}{q^0{}_{np} \times [1 - 10^{-A(\lambda)}]}$$

where dx/dt is the rate of change of a measurable quantity (spectral or any other property), the quantum yield (Φ) for Fe^{2+} at 525 nm is 0.64,[5] $[1\text{-}10^{-A(\lambda)}]$ is the ratio of absorbed photons by the solution, and A(λ) is the absorbance of the actinometer at the wavelength used to carry out the experiments (525 nm). The absorbance at 525 nm

(A(525)) was 0.2136. The photon flux, which is $q^0_{n,p}$, was determined to be $4{,}02 \times 10^{-8}$ einstein s^{-1}.

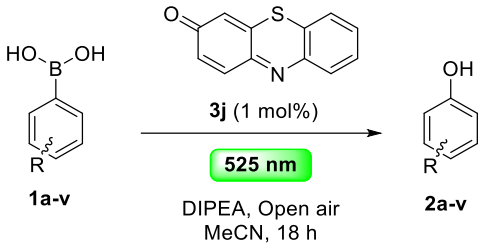
S.10.2 Determination of the quantum yield for the photochemical oxidation of 1a at 525 nm



In a glass vial, *N*,*N'*-Diisopropylethylamine (DIPEA) (1.0 equiv, 26 mg, 0.20 mmol), **1a** (1.0 equiv., 24 mg, 0.20 mmol), photocatalyst **3j** (1 mol%, 0.4 mg, 0.002 mmol) and MeCN (1 mL) was added. The reaction mixture was left stirring under irradiation by Kessil lamp 525 nm and air atmosphere for 7200 s. After irradiation, the solvent was removed, and the yield of the product was determined by ^{1}H NMR (16%). The quantum yield was determined with the following equation:

$$\Phi(\lambda) = \frac{mole\ of\ product}{flux \times t \times f} = \frac{0.032 \times 10^{-3}}{4.02 \times 10^{-8} einstein\ s^{-1} \times 7200\ s\ \times 0.3885} = 0.28$$

S.11 Experimental Procedures for the Photochemical Oxidation of Boronic Acids Under Green LED Irradiation



General Experimental Procedure:

In a glass vial containing the corresponding boronic acid (1.0 equiv., 0.50 mmol) and catalyst **3j** (1 mg, 1 mol%, 0.005 mmol) in acetonitrile (2.5 mL), *N,N'*-diisopropylethylamine (65 mg, 1.0 equiv., 0.50 mmol) was added. The reaction mixture was stirred and irradiated with LED lamps (Kessil PR 160L, 525 nm) for 18 h. Upon reaction completion, the reaction mixture was evaporated *in vacuo* until dry. The desired product was purified by column chromatography.

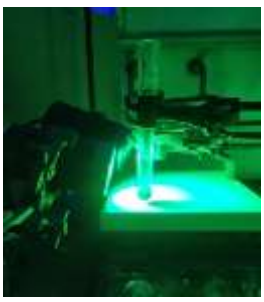
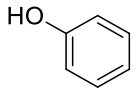
A)  **B)** 

Figure S16 A). Reaction setup: the reaction mixture is placed symmetrically 5 cm away from the irradiation source, **B).** Reaction mixture under LED lamp (Kessil PR 160L, 525 nm) irradiation set up.

Experimental Data:

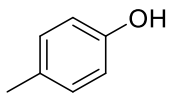
Phenol (2a)[6]



Yield: **90%**; Colourless solid; m.p. 40-41 °C; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26 (2H, t, J = 7.9 Hz, ArH), 6.94 (1H, t, J = 7.9 Hz, ArH), 6.84 (2H, d, J = 7.9 Hz, ArH), 4.27 (1H, br s, OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 155.7, 130.0, 121.1, 115.6; **MS** (ESI) *m/z* 93 $[M-H]^-$.

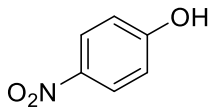
p-Cresol (2b)[6]



Yield: **63%**; Colourless solid; m.p. 34-35 °C; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.06 (2H, d, J = 8.2 Hz, ArH), 6.78 (2H, d, J = 8.2 Hz, ArH), 6.99 (1H, br s, OH), 2.30 (1H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 153.6, 130.4, 130.3, 115.4, 20.7; **MS** (ESI) *m/z* 107 $[M-H]^-$.

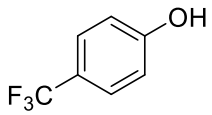
4-Nitrophenol (2c)[6]



Yield: **83%**; Yellow solid; m.p. 109-113 °C; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (2H, d, J = 9.1 Hz, ArH), 6.93 (2H, d, J = 9.1 Hz, ArH), 6.06 (1H, br s, OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 116.7, 142.0, 126.6, 116.0; **MS** (ESI) *m/z* 140 $[M+H]^+$.

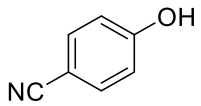
4-(Trifluoromethyl)phenol (2d)[7]



Yield: **94%**; Colourless solid; m.p. 45-47 °C; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (2H, d, J = 8.4 Hz, ArH), 6.90 (2H, d, J = 8.4 Hz, ArH), 5.40 (1H, br s, OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 158.5, 127.2 (q, J = 3.8 Hz), 124.4 (q, J = 271.0 Hz), 123.2 (q, J = 32.7 Hz), 115.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -61.5; **MS** (ESI) *m/z* 161 $[M-H]^-$.

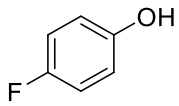
4-Hydroxybenzonitrile (2e)[6]



Yield: **60%**; Brown solid; m.p. 98-101 °C; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (2H, d, J = 8.9 Hz, ArH), 6.94 (2H, d, J = 8.9 Hz, ArH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 160.7, 134.6, 119.6, 116.8, 103.2; **MS** (ESI) *m/z* 120 $[M+H]^+$.

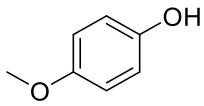
4-Fluorophenol (2f)[6]



Yield: **61%**; Red solid; m.p. 43-45 °C; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.92 (2H, t, J = 8.5 Hz, ArH), 6.77 (2H, dd, J = 8.5 and 4.2 Hz, ArH), 4.12 (1H, br s, OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 157.3 (d, J = 237.9 Hz), 151.4 (d, J = 2.1 Hz), 116.3 (d, J = 8.0 Hz), 116.0 (d, J = 23.2 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -124.2; **MS** (ESI) *m/z* 111 $[M-H]^-$.

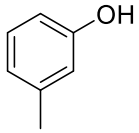
4-Methoxyphenol (2g)[6]



Yield: **82%**; Colourless solid; m.p. 55-57 °C; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.79 (2H, d, J = 9.1 Hz, ArH), 6.76 (2H, d, J = 9.1 Hz, ArH), 3.76 (3H, s, OCH_3), 1.26 (1H, br s, OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 153.9, 149.4, 116.0, 114.8, 55.8; **MS** (ESI) *m/z* 123 $[M-H]^-$.

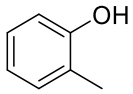
m-Cresol (2h)[6]



Yield: **71%**; Colourless oil; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14 (1H, t, J = 7.7 Hz, ArH), 6.78 (1H, d, J = 7.7 Hz, ArH), 6.70-6.64 (2H, m, ArH), 4.98 (1H, br s, OH), 2.32 (3H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 155.3, 139.8, 129.4, 121.6, 116.0, 112.3, 21.3; **MS** (ESI) *m/z* 107 $[M-H]^-$.

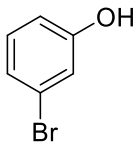
o-Cresol (2i)[6]



Yield: **64%**; Colourless oil; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.13 (1H, d, J = 7.5 Hz, ArH), 7.09 (1H, t, J = 7.5 Hz, ArH), 6.85 (1H, t, J = 7.5 Hz, ArH), 6.78 (1H, d, J = 7.5 Hz, ArH), 4.84 (1H, br s, OH), 2.27 (3H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 153.8, 131.1, 127.2, 123.7, 120.8, 114.9, 15.7; **MS** (ESI) *m/z* 107 $[M-H]^-$.

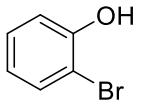
3-Bromophenol (2j)[6]



Yield: **71%**; Colourless semisolid; mp 30-32 °C; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.12-7.06 (2H, m, ArH), 7.03-7.02 (1H, m, ArH), 6.79-6.76 (1H, m, ArH), 4.69 (1H, br, OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 156.2, 130.8, 124.0, 122.8, 118.8, 114.2; **MS** (ESI) *m/z* 171/173 $[M+H]^+$.

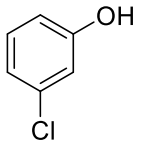
2-Bromophenol (2k)[6]



Yield: **87%**; Yellow oil; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (1H, d, J = 8.1 Hz, ArH), 7.22 (1H, t, J = 8.1 Hz, ArH), 7.03 (1H, d, J = 8.1 Hz, ArH), 6.81 (1H, t, J = 8.1 Hz, ArH), 5.49 (1H, br s, OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.3, 132.1, 129.2, 121.8, 116.2, 110.2; **MS** (ESI) *m/z* 171/173 $[M+H]^+$.

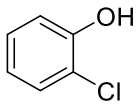
3-Chlorophenol (2l)[6]



Yield: **84%**; Colourless solid; m.p. 32-34 °C; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16 (1H, t, J = 8.1 Hz, ArH), 6.92 (1H, d, J = 8.1 Hz, ArH), 6.86 (1H, s, ArH), 6.72 (1H, d, J = 8.1, ArH), 5.09 (1H, br s, OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 156.3, 135.0, 130.5, 121.1, 116.0, 113.8; **MS** (ESI) *m/z* 127/129 $[M-H]^-$.

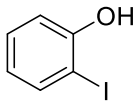
2-Chlorophenol (2m)[7]



Yield: **64%**; Colourless oil; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (1H, d, J = 8.2 Hz, ArH), 7.20-7.16 (1H, m, ArH), 7.02 (1H, d, J = 8.2 Hz, ArH), 6.87 (1H, t, J = 8.2 Hz, ArH), 5.53 (1H, br s, OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 151.3, 129.0, 128.4, 121.3, 119.9, 116.2; **MS** (ESI) *m/z* 127/129 $[M-H]^-$.

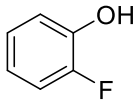
2-Iodophenol (2n)[8]



Yield: **79%**; Yellow solid; m.p. 32-34 ^{o}C; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (1H, dd, J = 7.9 and 1.5 Hz, ArH), 7.26 -7.22 (1H, m, ArH), 7.00 (1H, dd, J = 7.9 and 1.5 Hz, ArH), 6.69-6.65 (1H, m, ArH), 5.28 (1H, br s, OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 154.8, 138.3, 130.2, 122.4, 115.2, 85.7; **MS** (ESI) *m/z* 221 $[M+H]^+$.

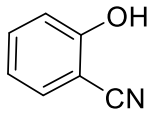
2-Fluorophenol (2o)[7]



Yield: **67%**; Colourless oil; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.10-6.98 (3H, m, ArH), 6.88-6.82 (1H, m, ArH), 5.10 (1H, br s, OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 151.1 (d, J = 237.3 Hz), 143.6 (d, J = 14.2 Hz), 124.9 (d, J = 3.8 Hz), 120.8 (d, J = 6.5 Hz), 117.2, 115.5 (d, J = 18.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -141.4; **MS** (ESI) *m/z* 111 $[M-H]^-$.

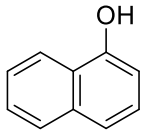
2-Hydroxybenzonitrile (2p)[6]



Yield: **66%**; Pale yellow solid; m.p. 86-90 °C; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51-7.44 (2H, m, ArH), 7.02 (2H, d, J = 8.4 Hz, ArH), 6.82 (1H, br s, OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 158.6, 134.7, 132.9, 120.9, 116.6, 116.4, 99.5; **MS** (ESI) *m/z* 120 $[M+H]^+$.

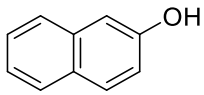
Naphthalen-1-ol (2q)[6]



Yield: **71%**; Colourless solid; m.p. 119-122 °C; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20-8.18 (1H, m, ArH), 7.84-7.81 (1H, m, ArH), 7.51-7.49 (2H, m, ArH), 7.45 (1H, d, J = 7.8 Hz, ArH), 7.31 (1H, t, J = 7.8 Hz, ArH), 6.82 (1H, d, J = 7.8 Hz, ArH), 5.30 (1H, br s, OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 151.4, 134.8, 127.7, 126.5, 125.8, 125.3, 124.4, 121.5, 120.7, 108.6; **MS** (ESI) *m/z* 143 $[M-H]^-$

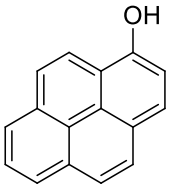
Naphthalen-2-ol (2r)[6]



Yield: **78%**; Colourless solid; m.p. 94-96 °C; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (2H, t, J = 8.5 Hz, ArH), 7.68 (1H, d, J = 8.5 Hz, ArH), 7.44 (1H, t, J = 8.5 Hz, ArH), 7.34 (1H, t, J = 8.5 Hz, ArH), 7.13 (2H, t, J = 8.5 Hz, ArH), 4.49 (1H, br s, OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 153.3, 134.6, 129.8, 128.9, 127.7, 126.5, 126.4, 123.6, 117.7, 109.5; **MS** (ESI) *m/z* 143 $[M-H]^-$.

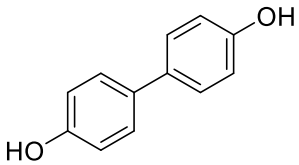
Pyren-1-ol (2s)[6]



Yield: **71%**; Brown solid; m.p. 169-171 °C; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (1H, d, J = 8.9 Hz, ArH), 8.11 (2H, d, J = 7.3 Hz, ArH), 8.04 (2H, t, J = 8.3 Hz, ArH), 7.97 (2H, dd, J = 8.3 and 7.3 Hz, ArH), 7.90 (1H, d, J = 8.9 Hz, ArH), 7.47 (1H, d, J = 8.3 Hz, ArH), 5.50 (1H, br s, OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 149.7, 131.7, 131.6, 127.2, 126.6, 126.2, 126.1, 125.7, 125.5, 125.0, 124.5, 124.2, 120.5, 118.6, 113.0; **MS** (ESI) *m/z* 219 $[M+H]^+$.

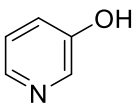
[1,1'-Biphenyl]-4,4'-diol (2t)[9]



Yield: **60%**; White solid; m.p. 280-283 °C; Eluent: Dichloromethane / Methanol 9:1; NMR data in accordance with reported literature.[9]

^{1}H NMR (400 MHz, CD_3OD) δ: 9.37 (2H, br s, OH), 7.34 (4H, d, J = 8.6 Hz, ArH), 6.77 (4H, d, J = 8.6 Hz, ArH); **^{13}C NMR** (100 MHz, CD_3OD) δ: 156.2, 131.2, 127.0, 115.6; **MS** (ESI) *m/z* 187 $[M+H]^+$

Pyridin-3-ol (2u)[10]

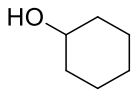


Yield: **53%**; Colourless solid; m.p. 119-121 °C; Eluent: Dichloromethane / Methanol 9:1; NMR data in accordance with reported literature.[10]

^{1}H NMR (400 MHz, CD_3OD) δ: 8.32 (1H, d, J = 2.8 Hz, ArH), 8.09 (1H, dd, J = 4.7 and 1.4 Hz, ArH), 7.36 (1H, ddd, J = 8.4, 2.8 and 1.4 Hz, ArH), 7.29 (1H, dd, J = 8.4 and 4.7 Hz, ArH),

5.76 (1H, br s, OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 155.3, 138.6, 136.0, 125.6, 125.3; **MS** (ESI) *m/z* 96 $[M+H]^+$.

Cyclohexanol (2v)[6]



Yield: **71%**; Colourless oil; Eluent: Petroleum ether / Ethyl acetate 6:1; NMR data in accordance with reported literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.61-3.58 (1H, m, C*H*OH), 1.91-1.86 (2H, m, 2 x C*H*H), 1.76-1.70 (2H, m, C*H*H and OH), 1.56-1.51 (1H, m, C*H*H), 1.30-1.23 (6H, m, 6 x C*H*H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 69.9, 35.3, 25.3, 24.0; **MS** (ESI) *m/z* 101 $[M+H]^+$.

Colorless oil (71%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.64-3.61 (1H, m, OC*H*), 1.92-1.88 (2H, m, 2 x C*H*H), 1.77-1.74 (2H, m, 2 x C*H*H), 1.58-1.55 (1H, m, C*H*H), 1.33-1.17 (6H, m, 6 x C*H*H and OH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 70.1, 35.4, 25.4, 24.2; **MS** (ESI) *m/z* 101 $[M+H]^+$.

S.12 References

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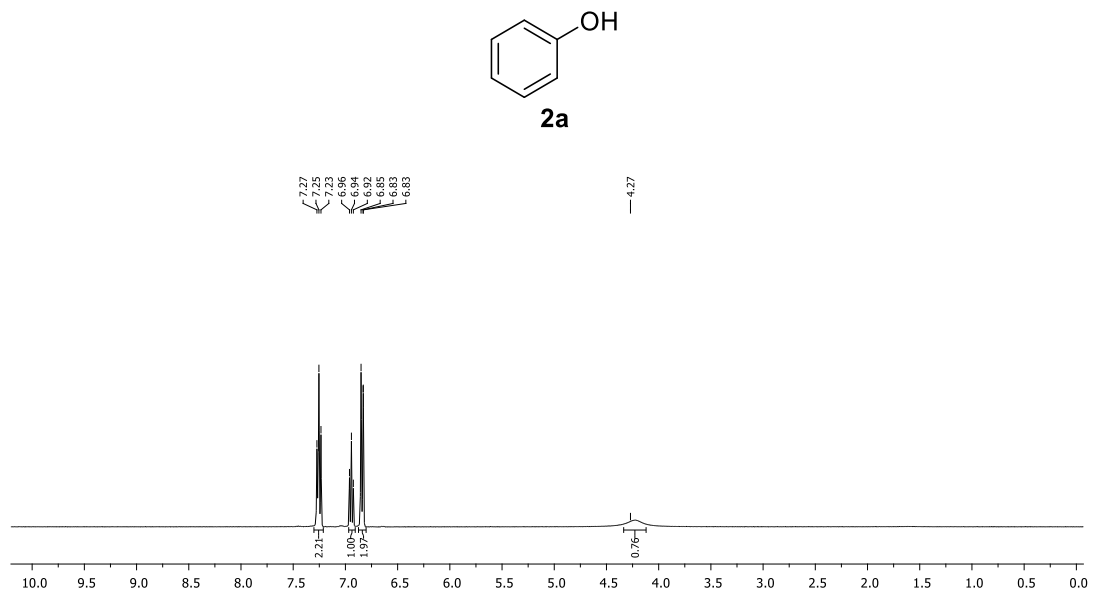
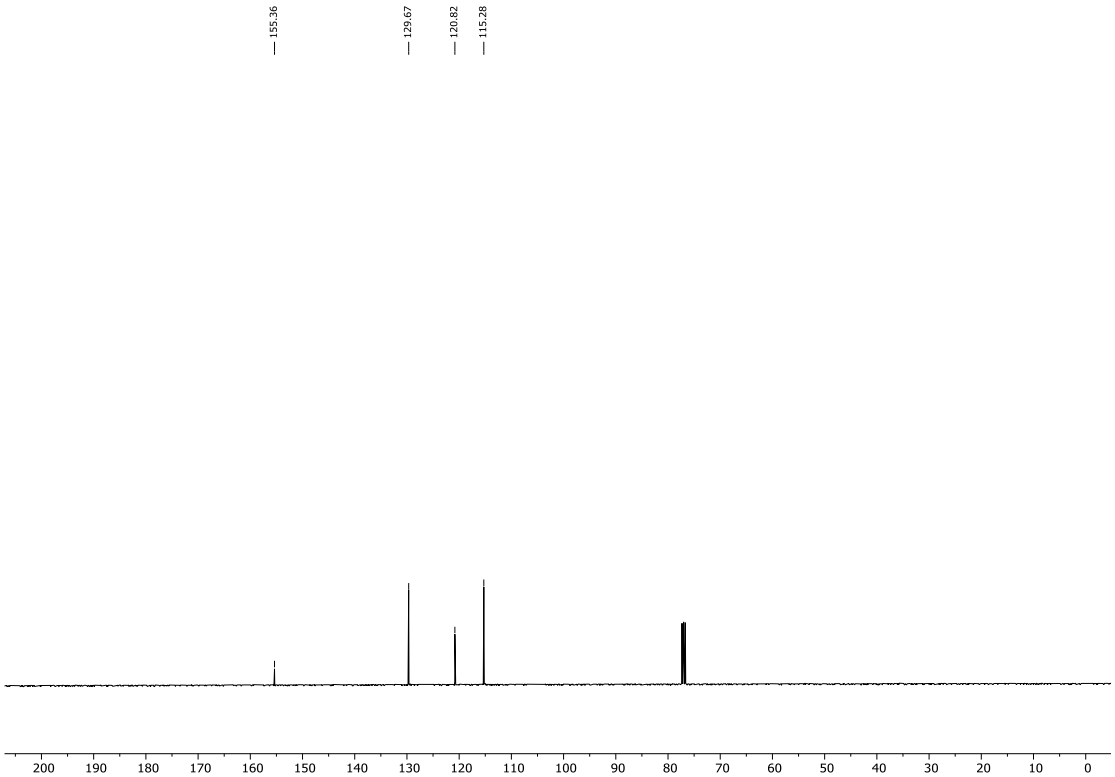
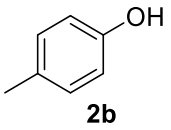
S.13 NMR Spectra



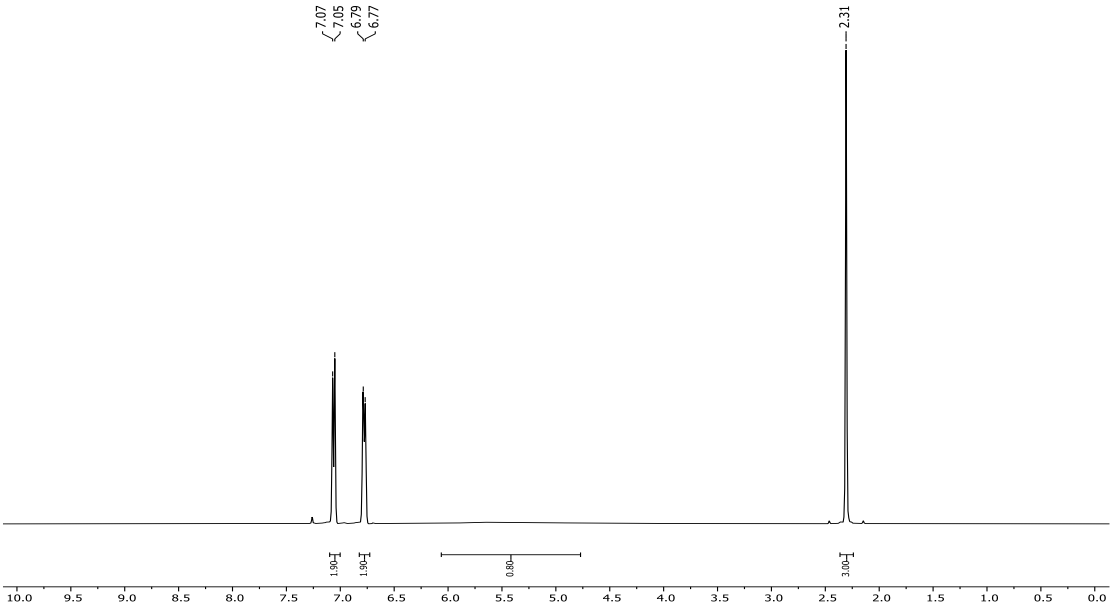
^{1}H-NMR (400 MHz) of compound **2a** in $CDCl_3$



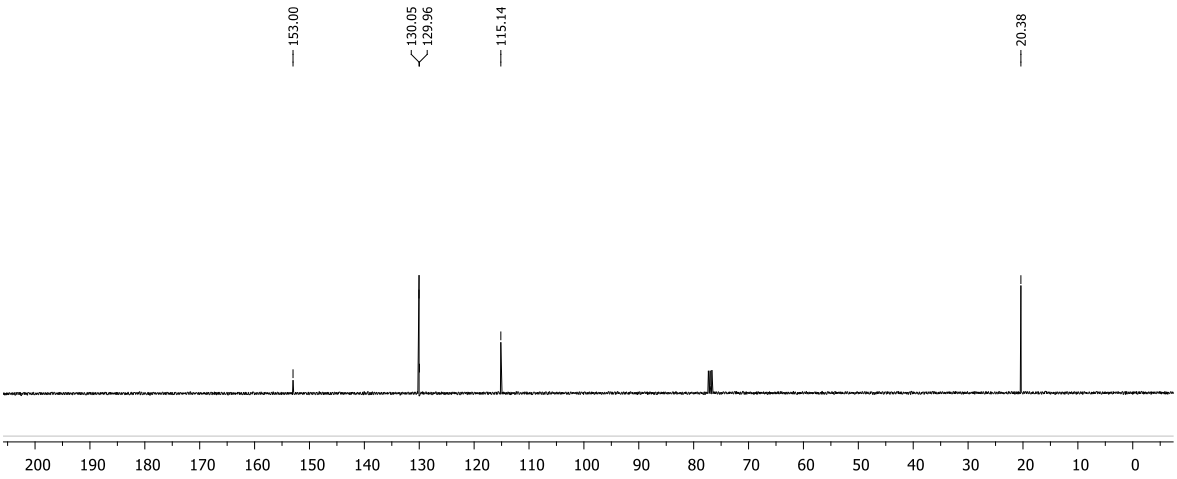
^{13}C-NMR (100 MHz) of compound **2a** in $CDCl_3$



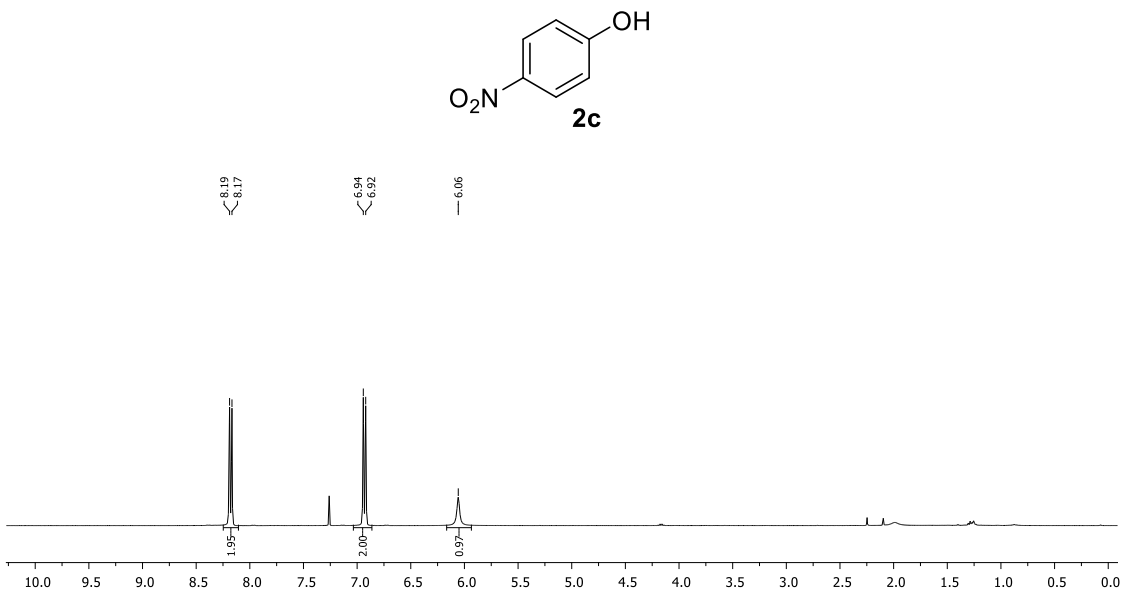
2b



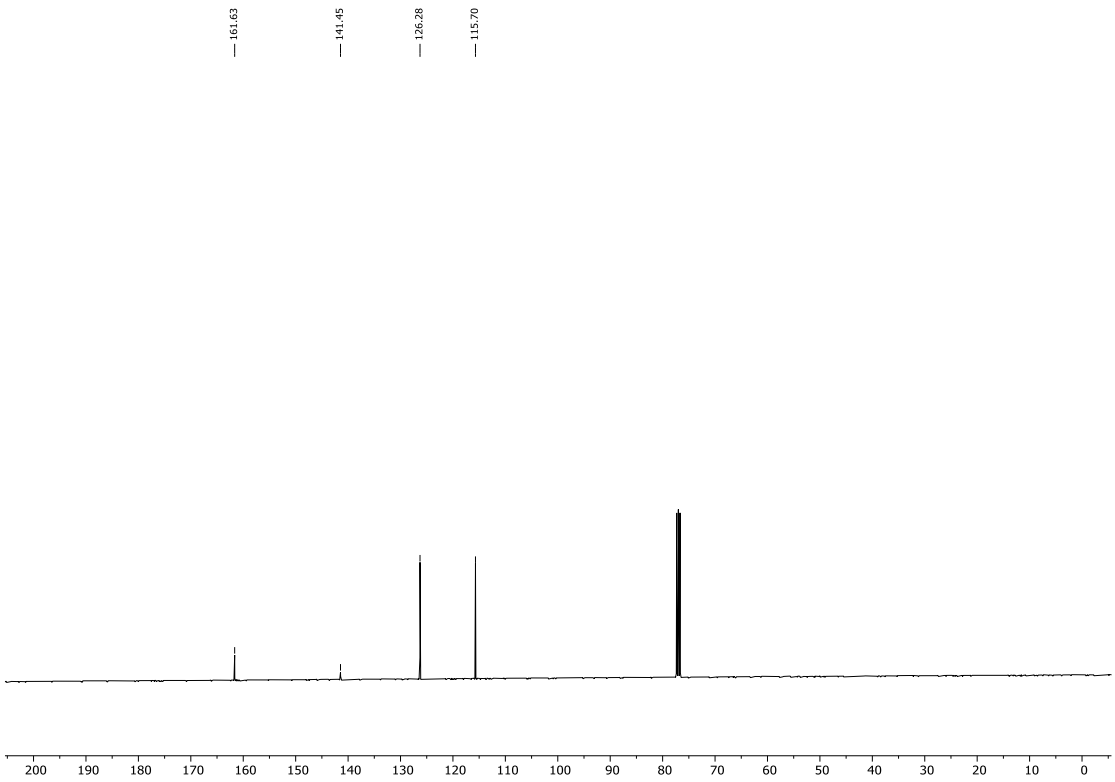
^{1}H-NMR (400 MHz) of compound **2b** in $CDCl_3$



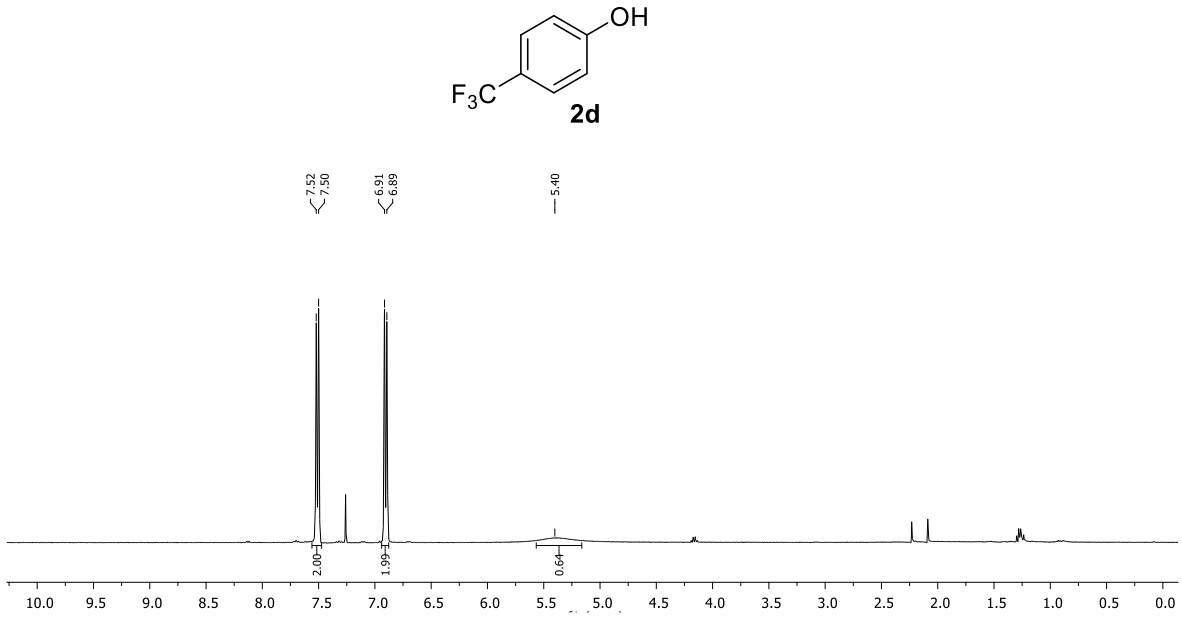
^{13}C-NMR (100 MHz) of compound **2b** in $CDCl_3$



^{1}H-NMR (400 MHz) of compound **2c** in $CDCl_3$



^{13}C-NMR (100 MHz) of compound **2c** in $CDCl_3$



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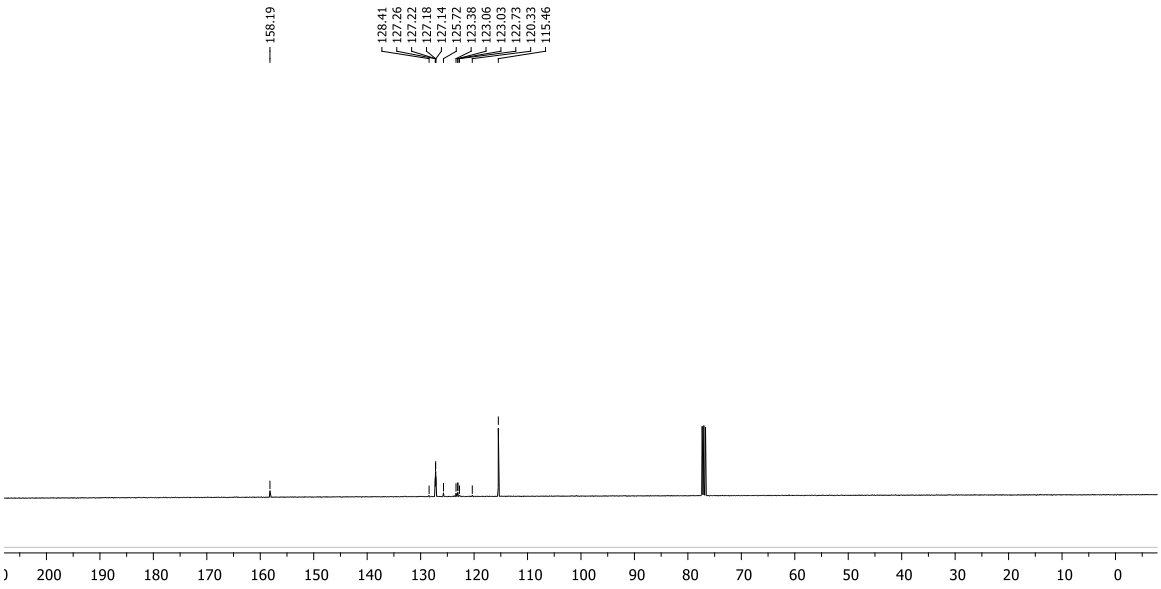
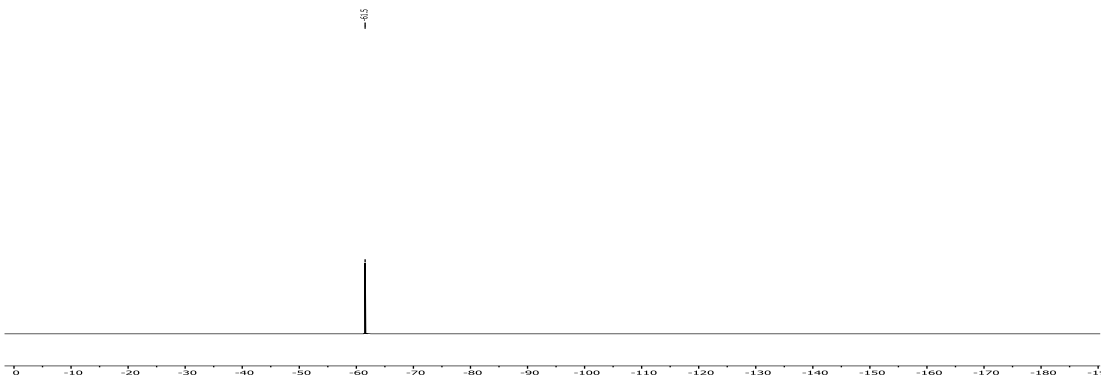
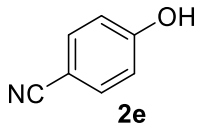


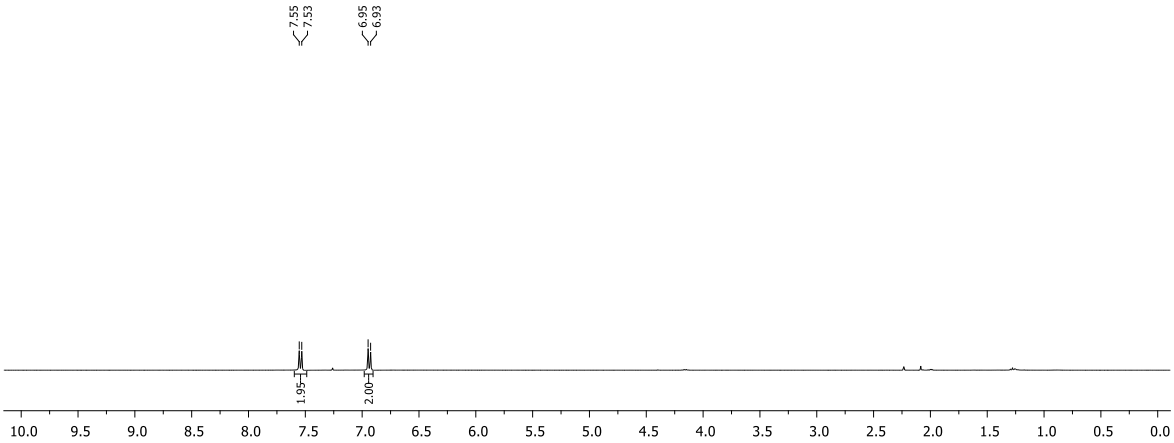
^{13}C-NMR (100 MHz) of compound **2d** in $CDCl_3$



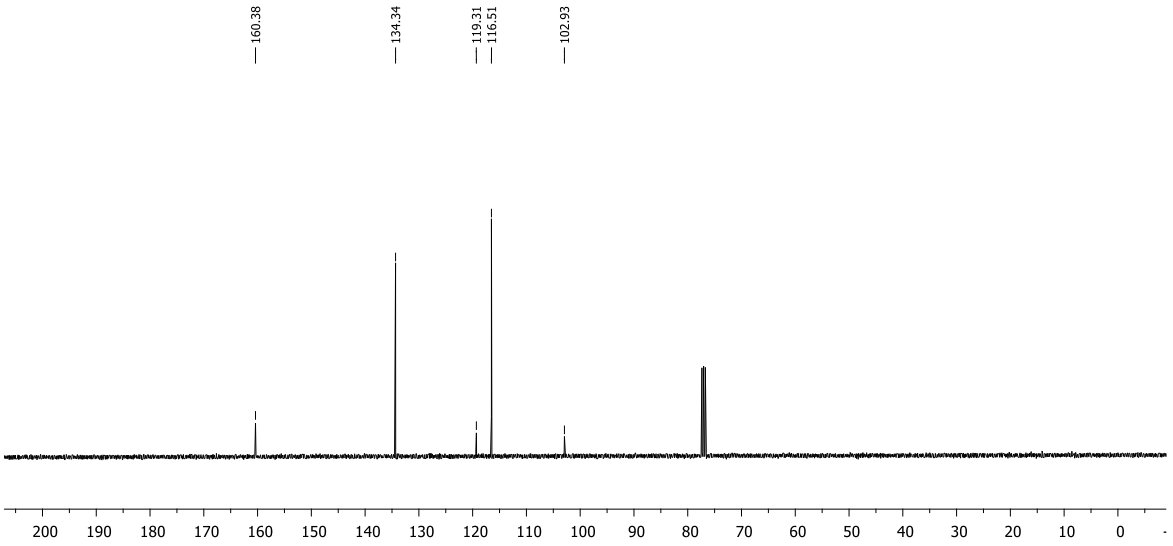
^{19}F-NMR (376 MHz) of compound **2d** in $CDCl_3$



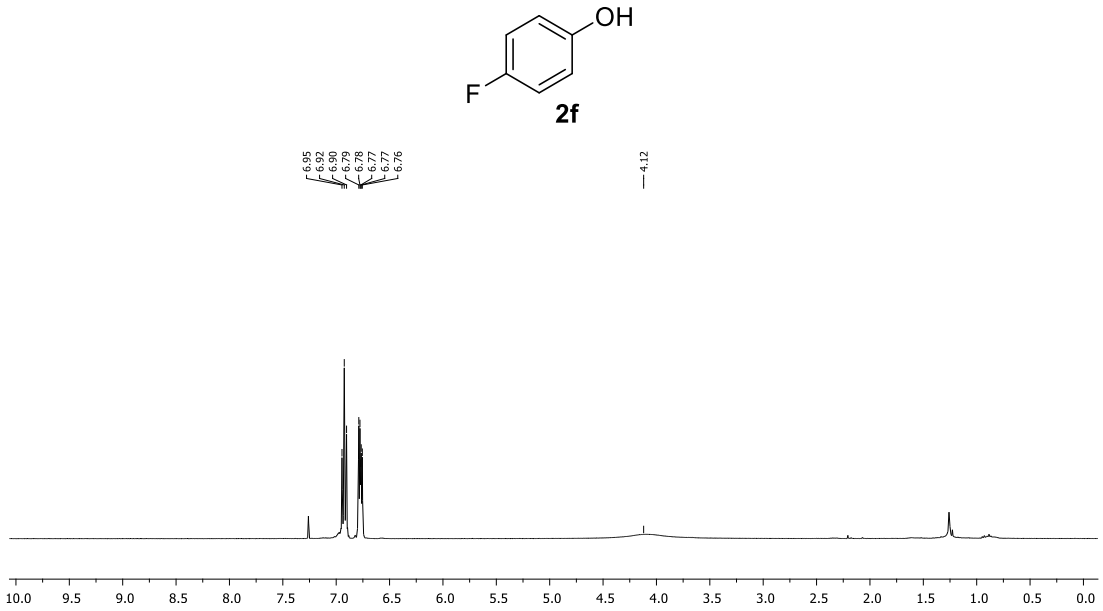
2e



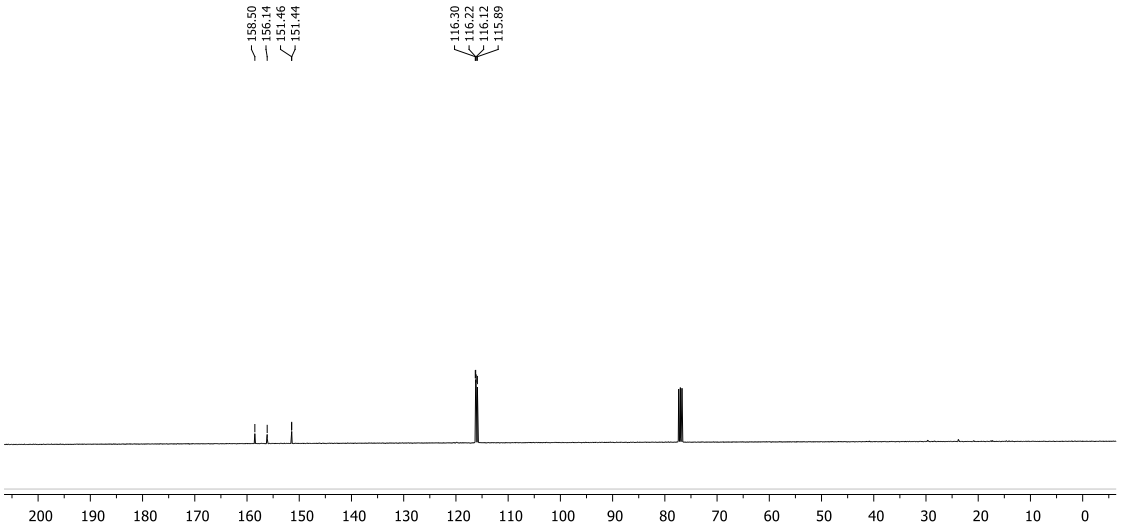
^{1}H-NMR (400 MHz) of compound **2e** in $CDCl_3$



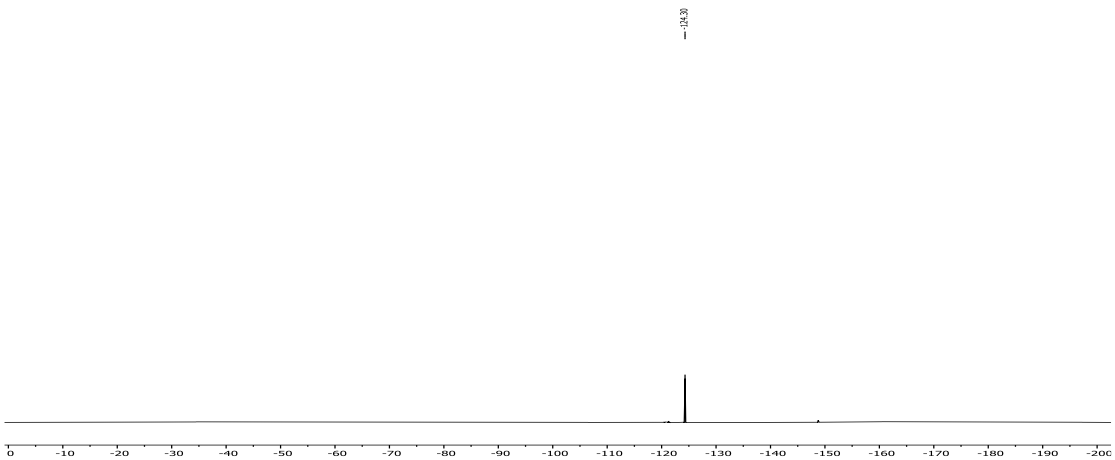
^{13}C-NMR (100 MHz) of compound **2e** in $CDCl_3$



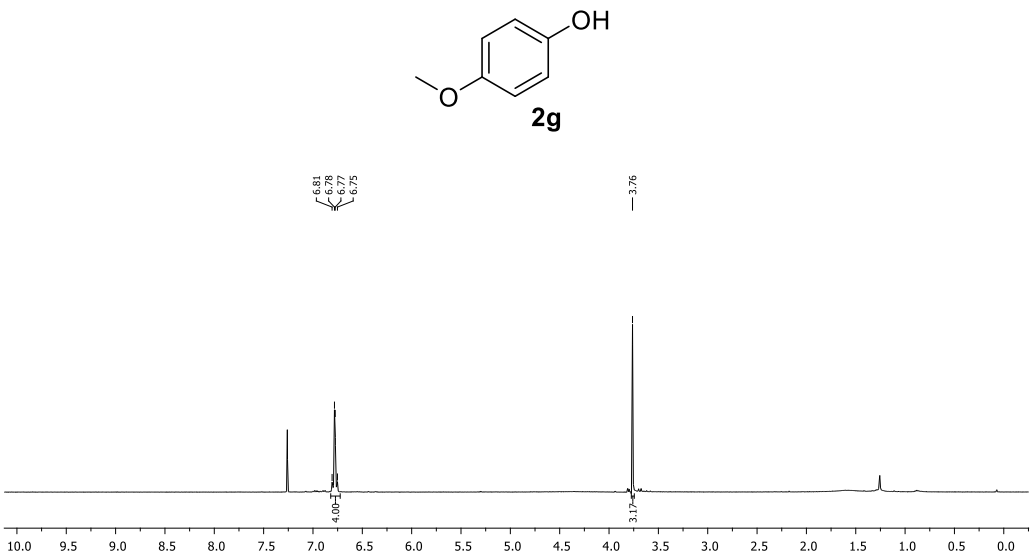
^{1}H-NMR (400 MHz) of compound **2f** in $CDCl_3$



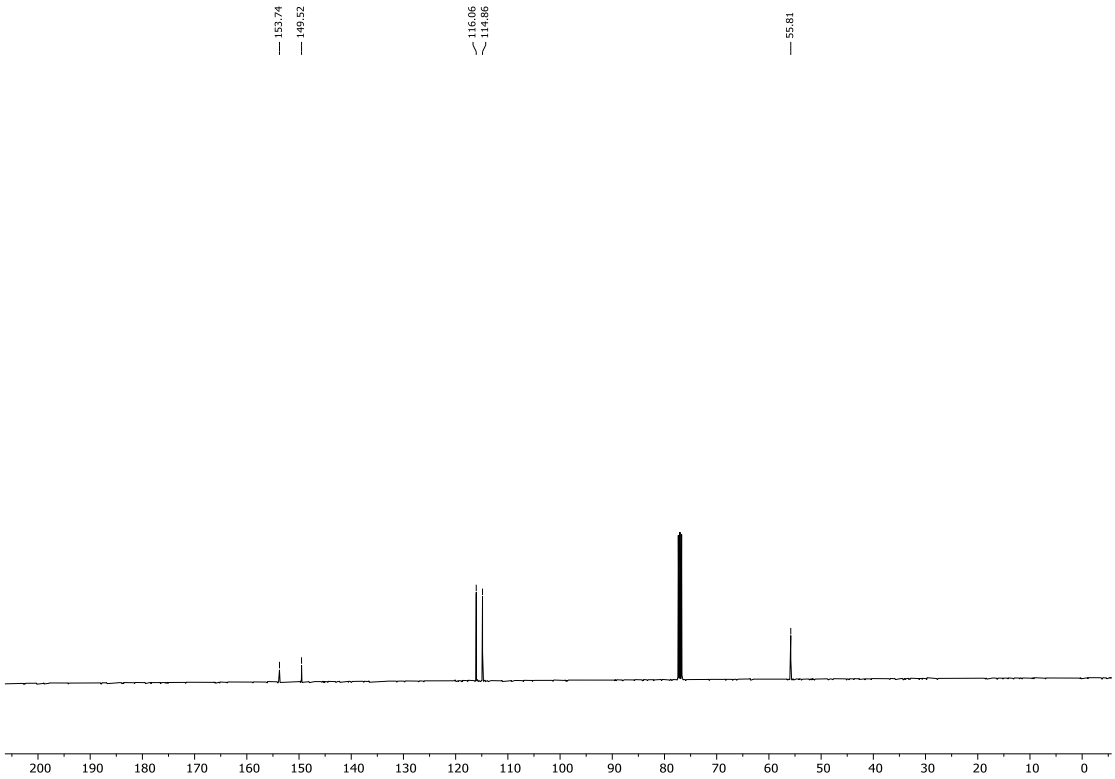
^{13}C-NMR (100 MHz) of compound **2f** in $CDCl_3$



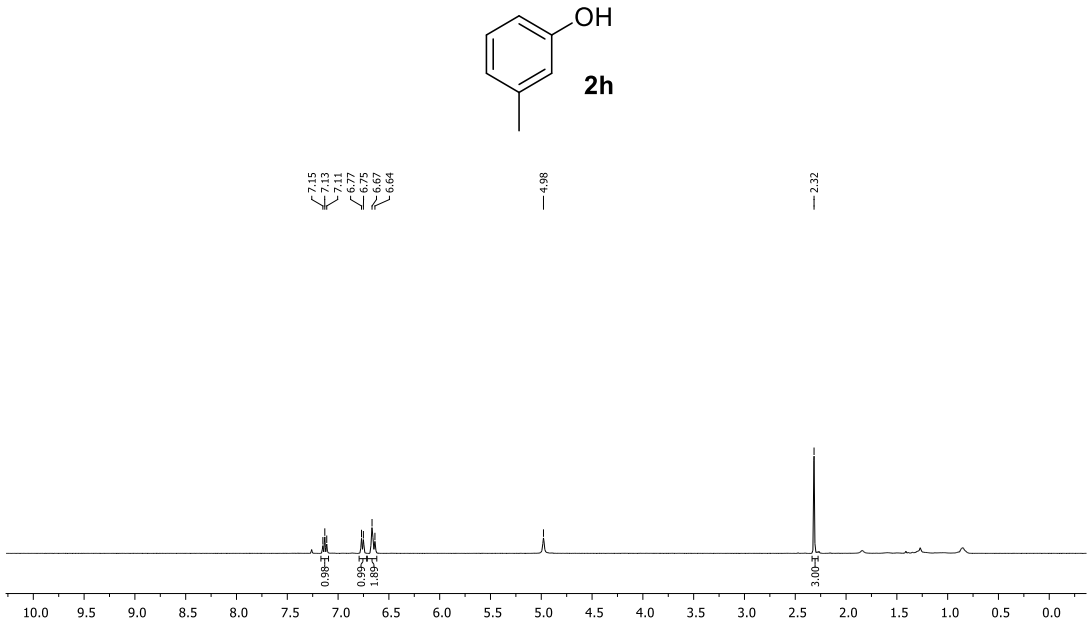
^{19}F-NMR (376 MHz) of compound **2f** in $CDCl_3$



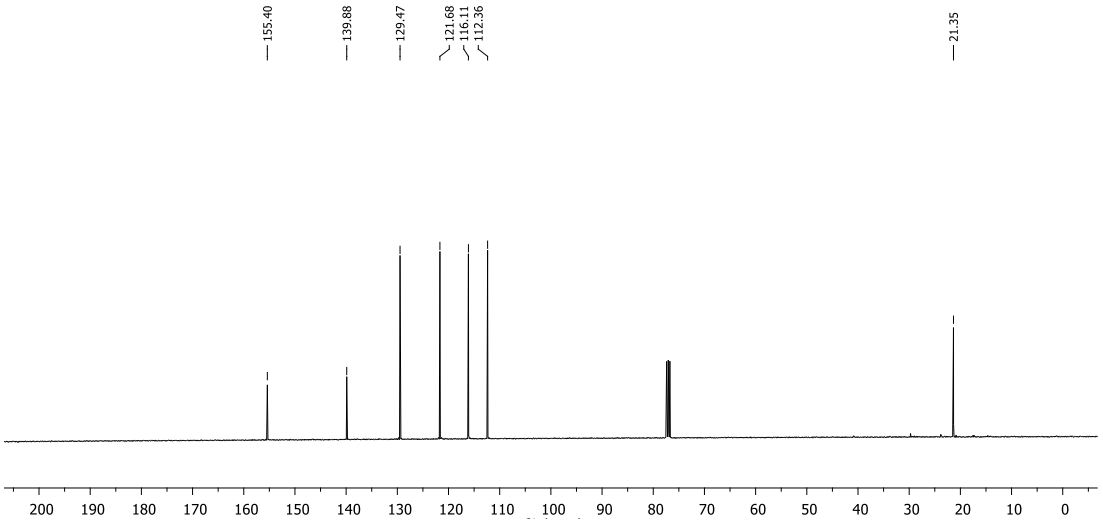
^{1}H-NMR (400 MHz) of compound **2g** in $CDCl_3$



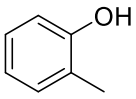
^{13}C-NMR (100 MHz) of compound **2g** in $CDCl_3$



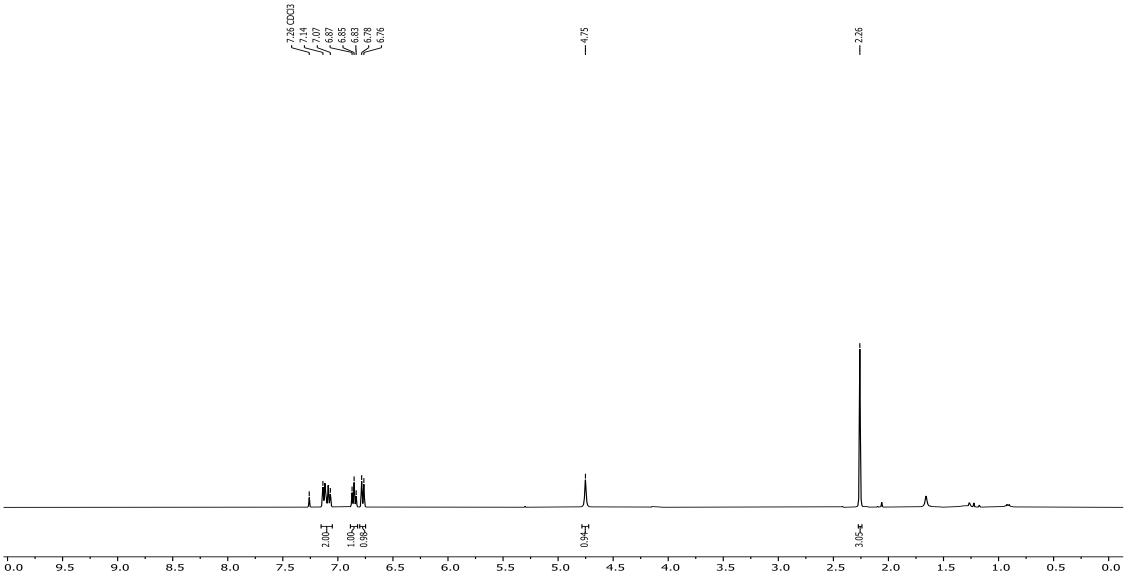
^{1}H-NMR (400 MHz) of compound **2h** in $CDCl_3$



^{13}C-NMR (100 MHz) of compound **2h** in $CDCl_3$



2i



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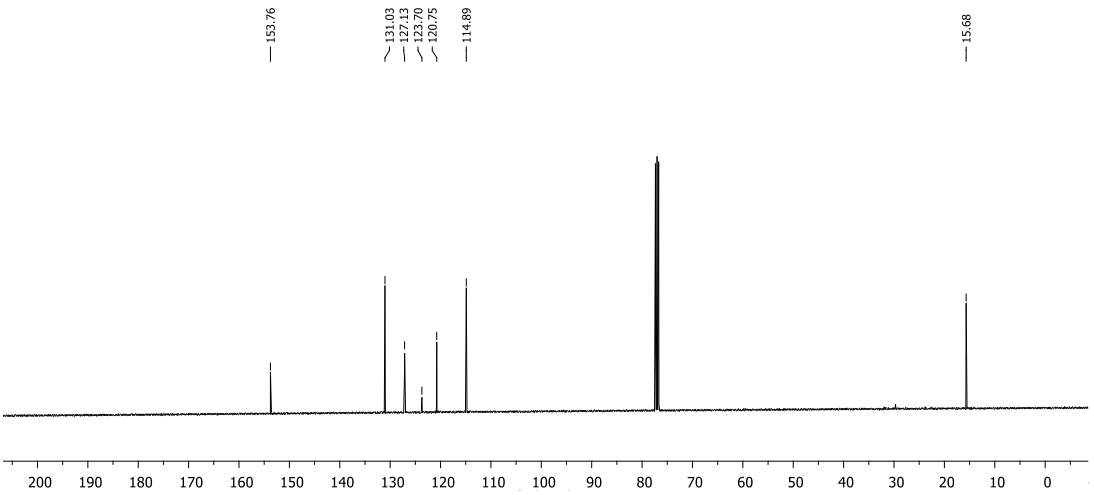
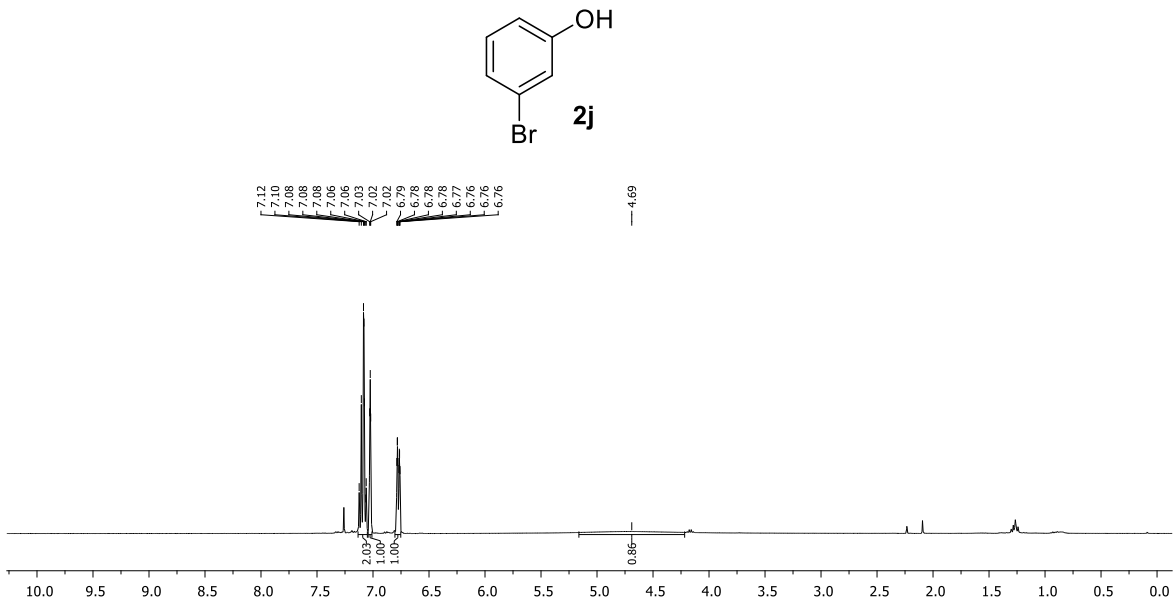
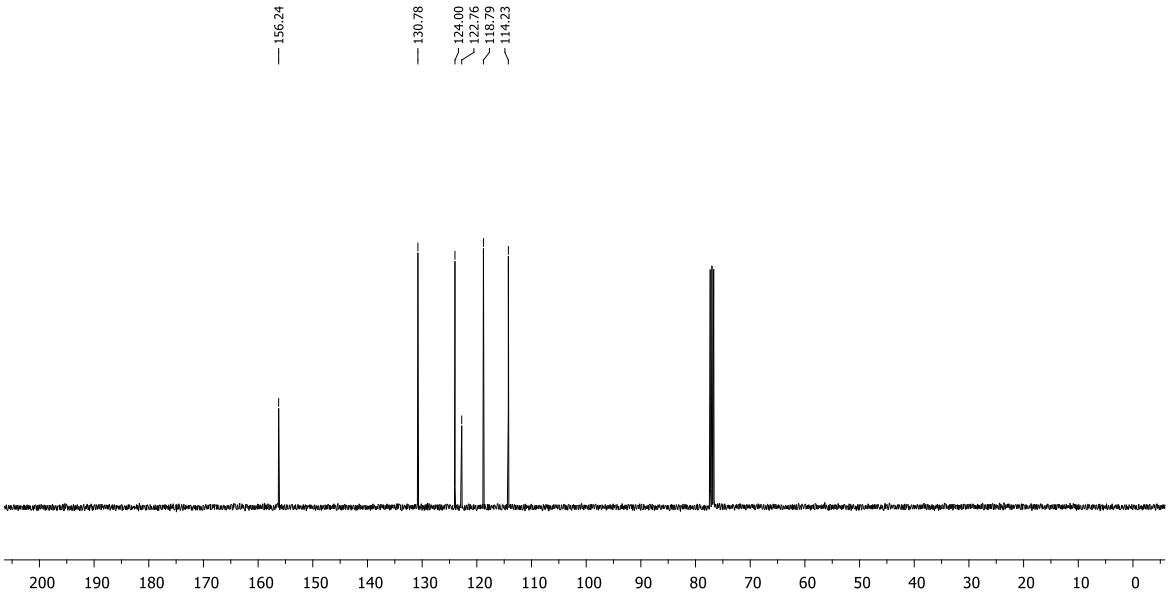


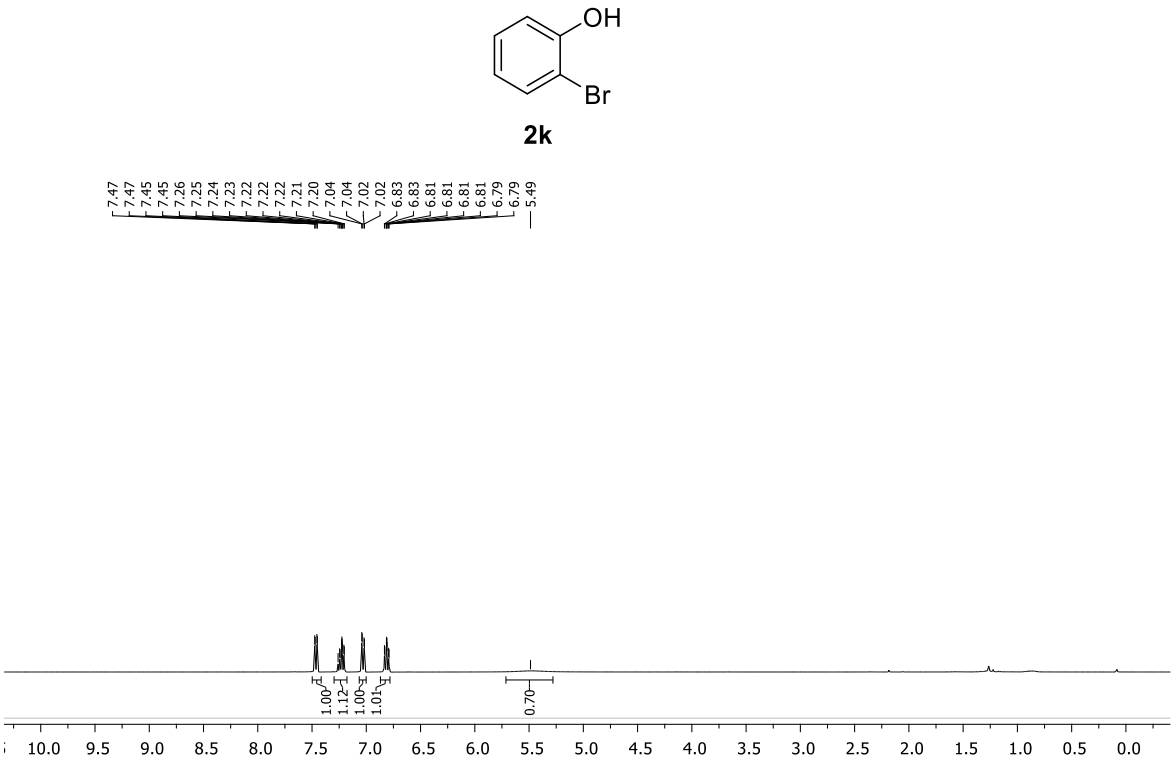
^{13}C-NMR (100 MHz) of compound **2i** in $CDCl_3$



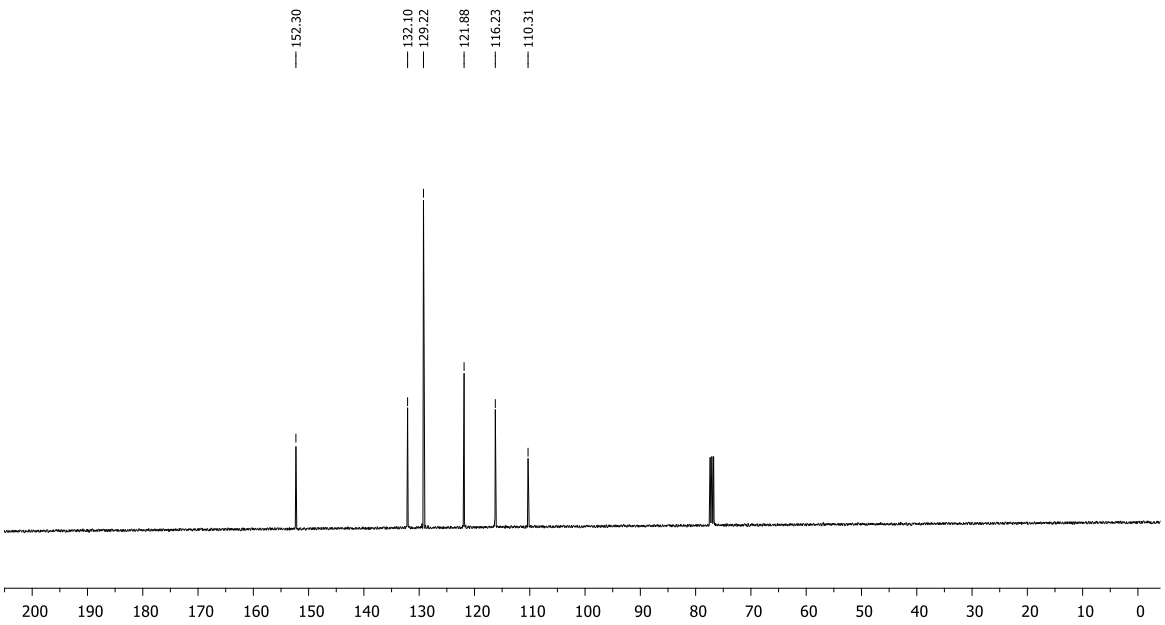
^{1}H-NMR (400 MHz) of compound **2j** in $CDCl_3$



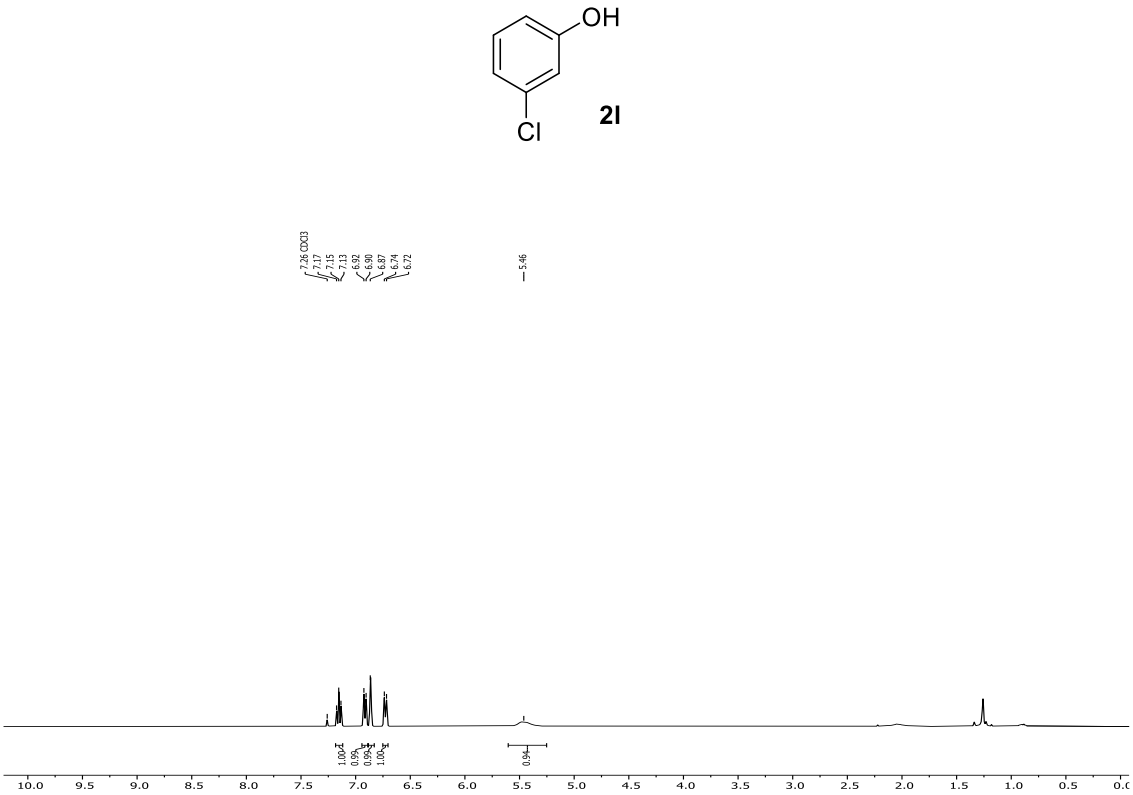
^{13}C-NMR (100 MHz) of compound **2j** in $CDCl_3$



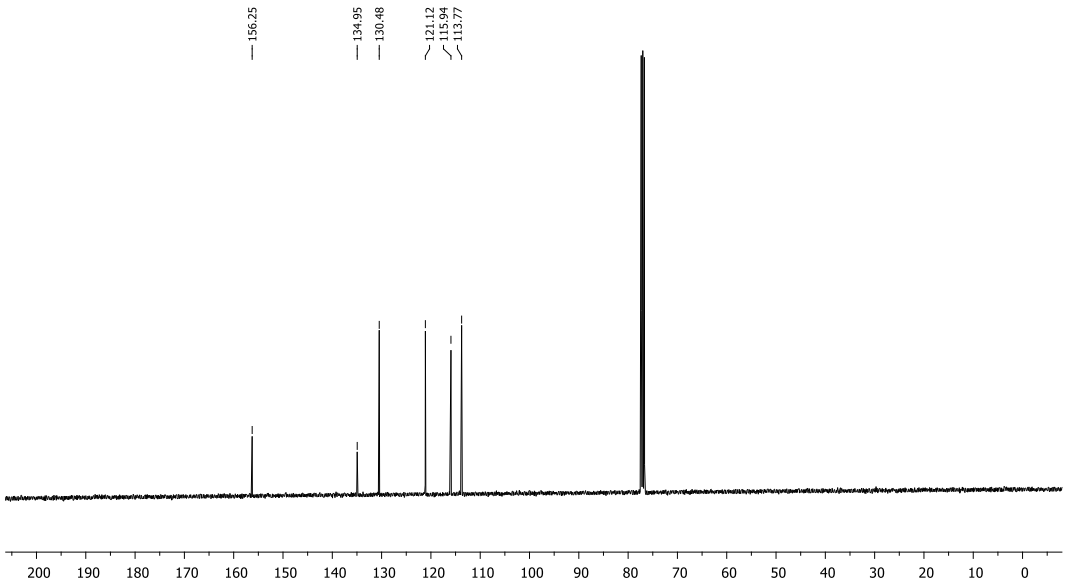
^{1}H-NMR (400 MHz) of compound **2k** in $CDCl_3$



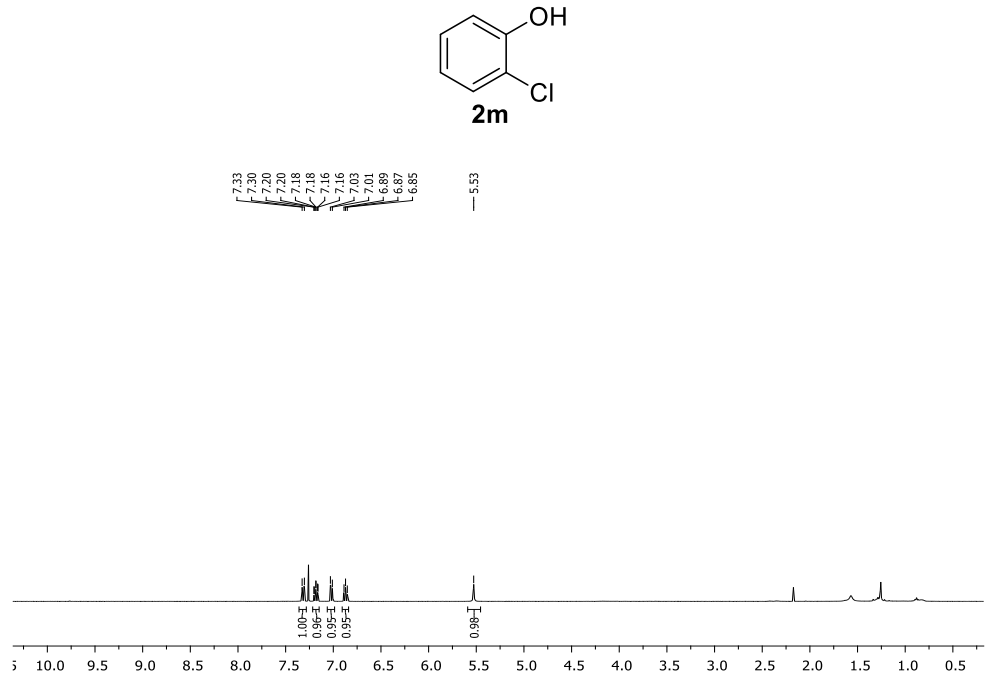
^{13}C-NMR (100 MHz) of compound **2k** in $CDCl_3$



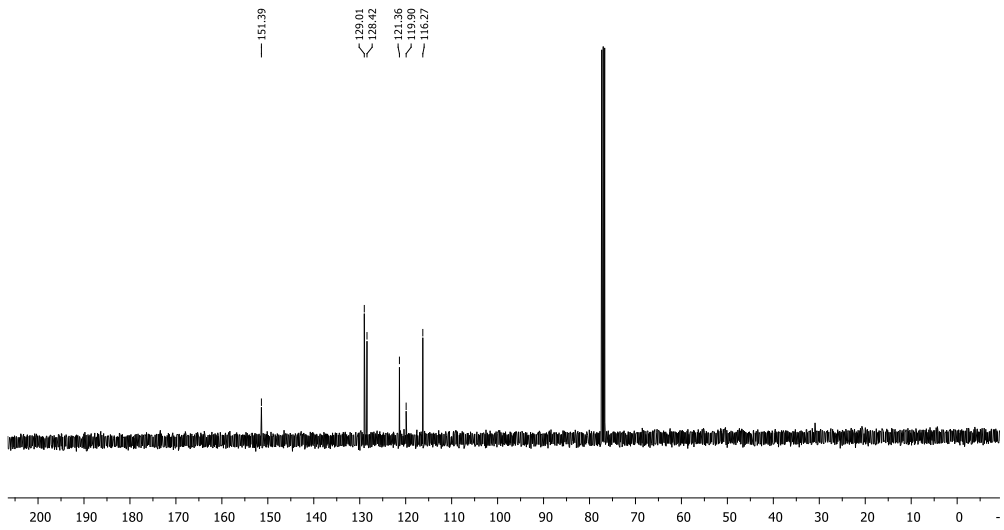
^{1}H-NMR (400 MHz) of compound **2l** in $CDCl_3$



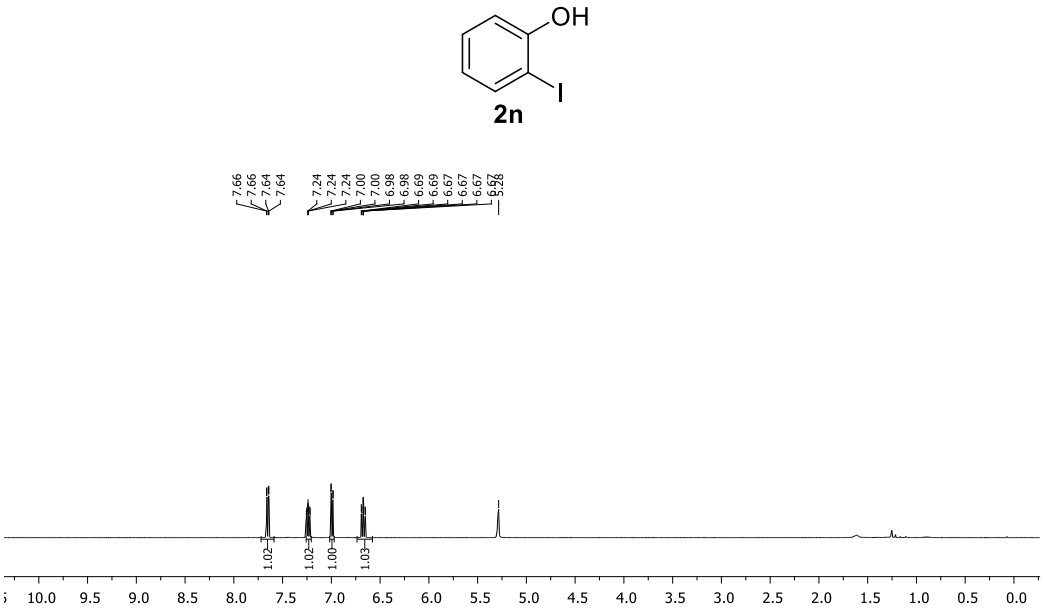
^{13}C-NMR (100 MHz) of compound **2l** in $CDCl_3$



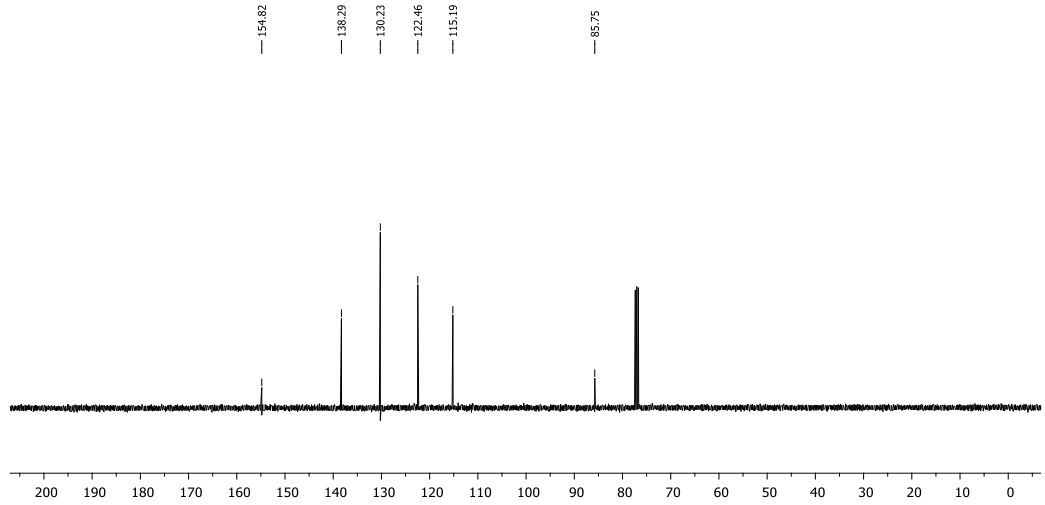
^{1}H-NMR (400 MHz) of compound **2m** in $CDCl_3$



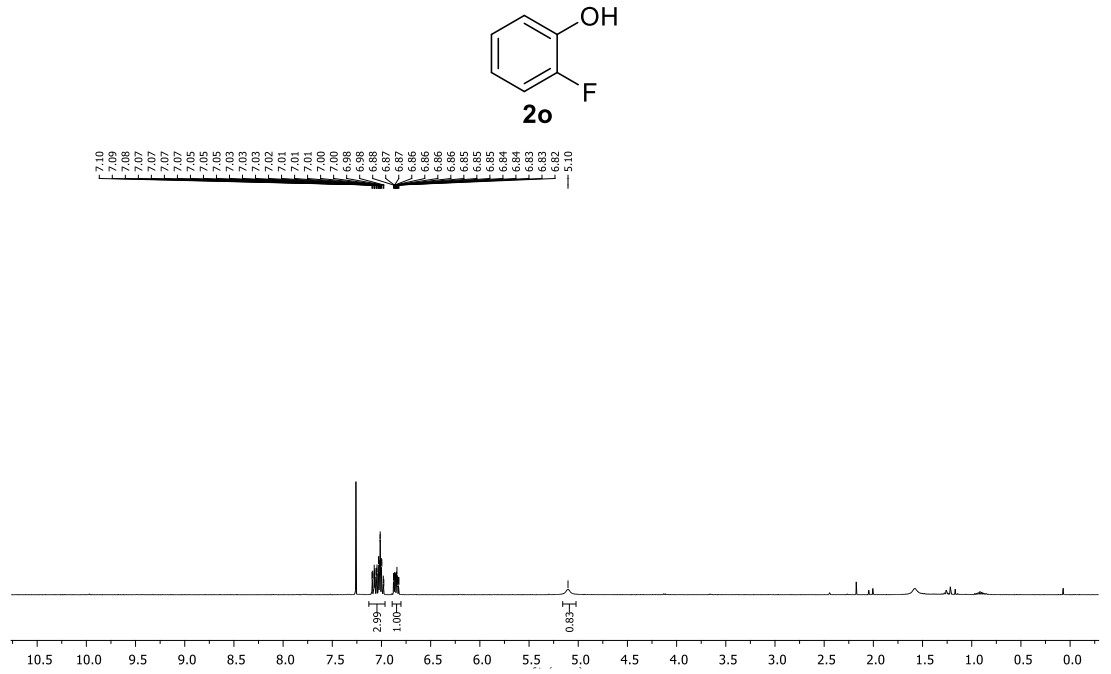
^{13}C-NMR (100 MHz) of compound **2m** in $CDCl_3$



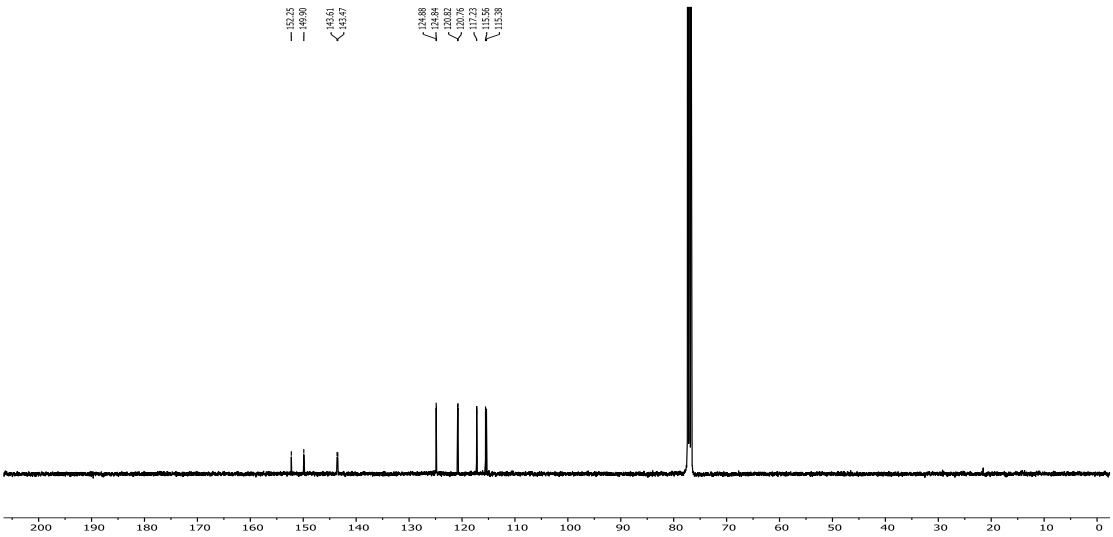
^{1}H-NMR (400 MHz) of compound **2n** in $CDCl_3$



^{13}C-NMR (100 MHz) of compound **2n** in $CDCl_3$

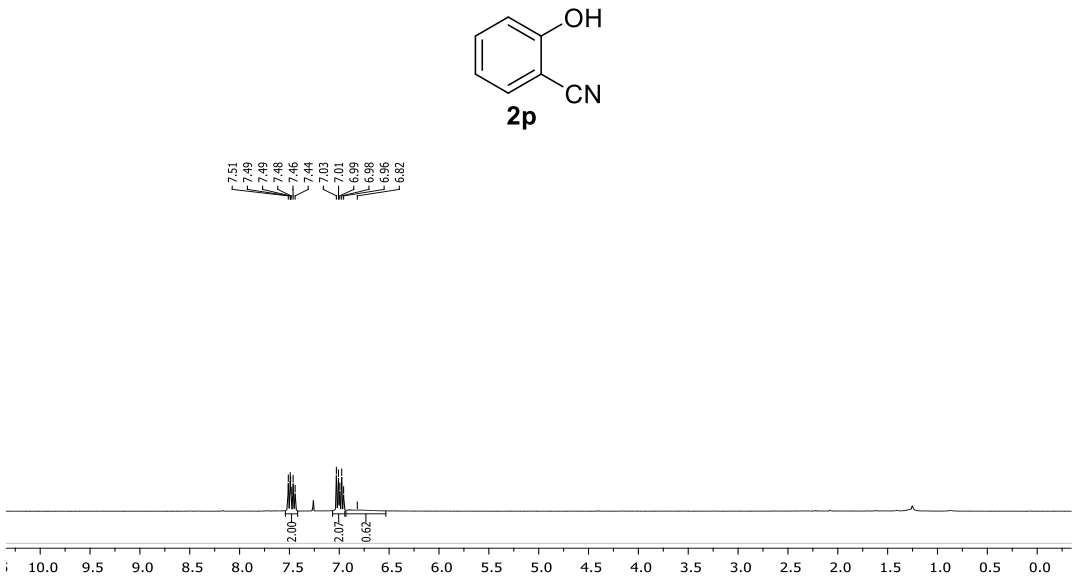


^{1}H-NMR (400 MHz) of compound **2o** in $CDCl_3$

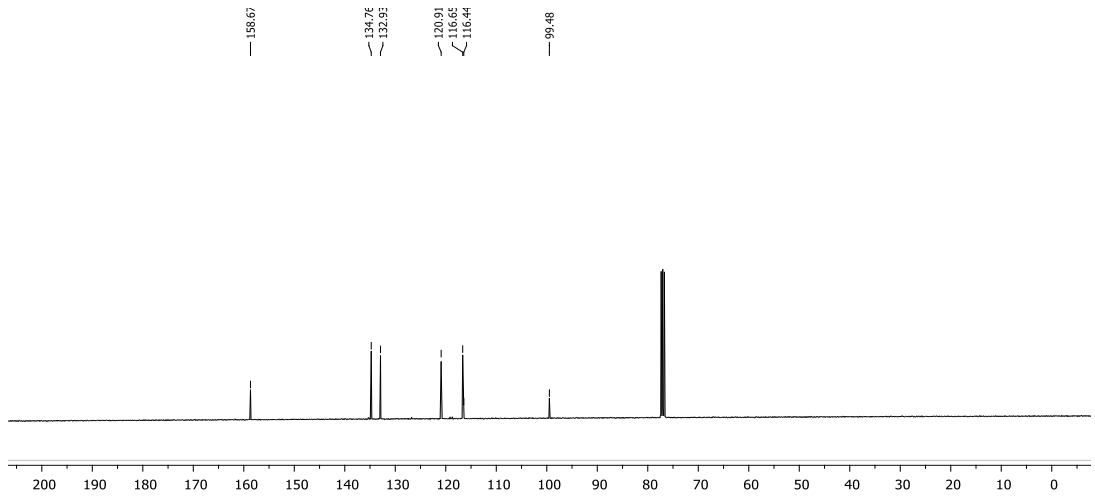


^{13}C-NMR (100 MHz) of compound **2o** in $CDCl_3$

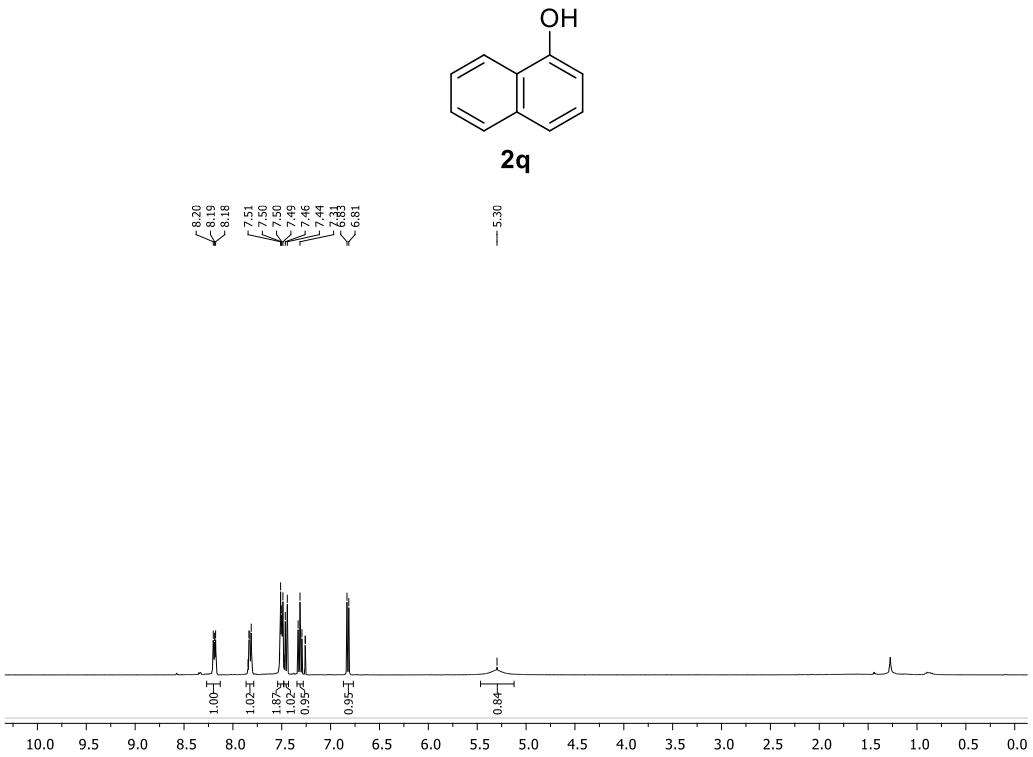
^{19}F-NMR (376 MHz) of compound **2o** in $CDCl_3$



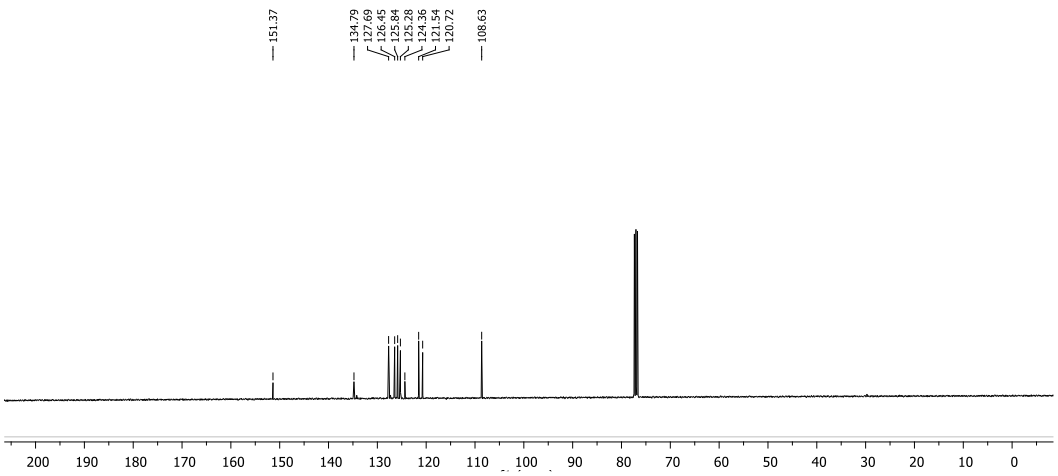
^{1}H-NMR (400 MHz) of compound **2p** in $CDCl_3$



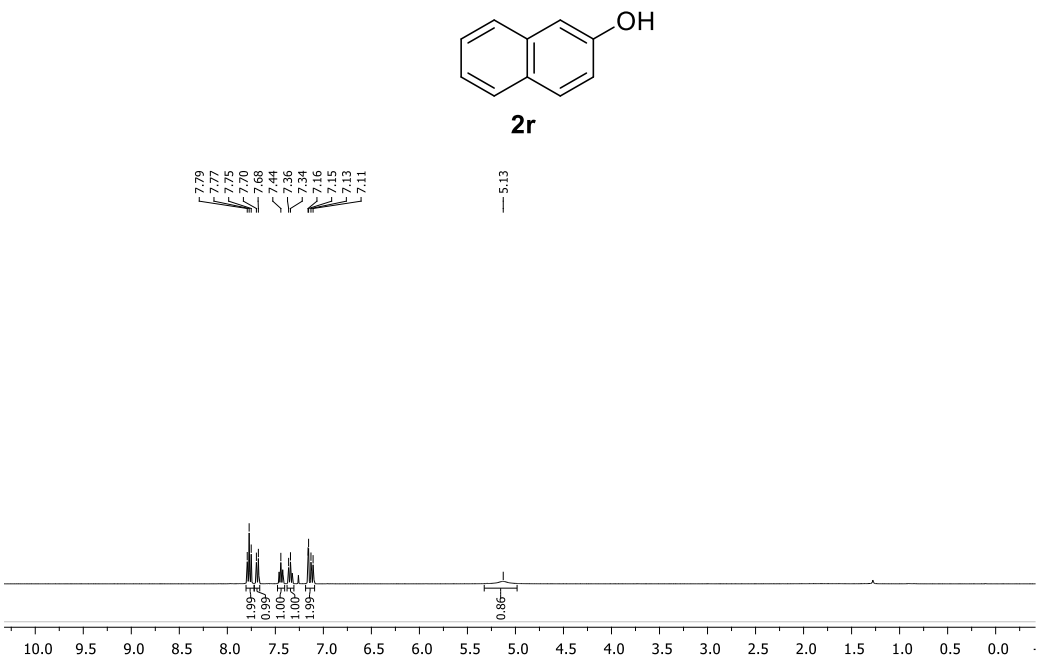
^{13}C-NMR (100 MHz) of compound **2p** in $CDCl_3$



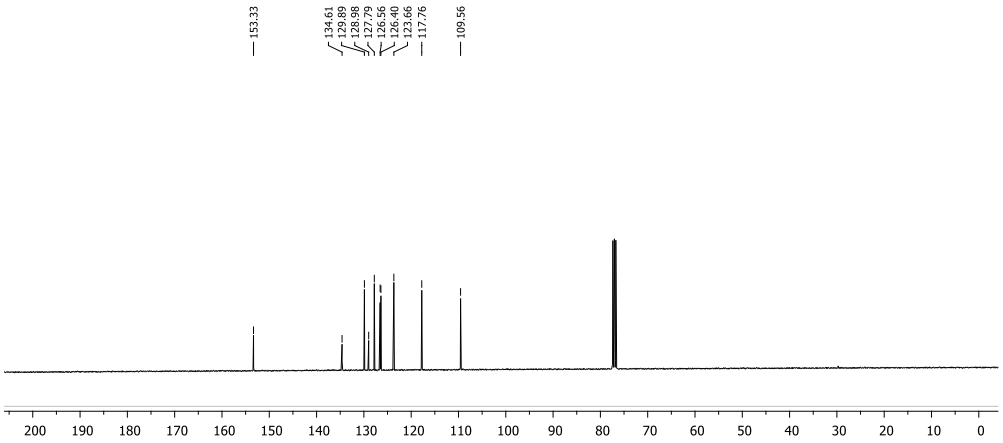
^{1}H-NMR (400 MHz) of compound **2q** in $CDCl_3$



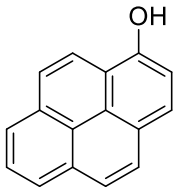
^{13}C-NMR (100 MHz) of compound **2q** in $CDCl_3$



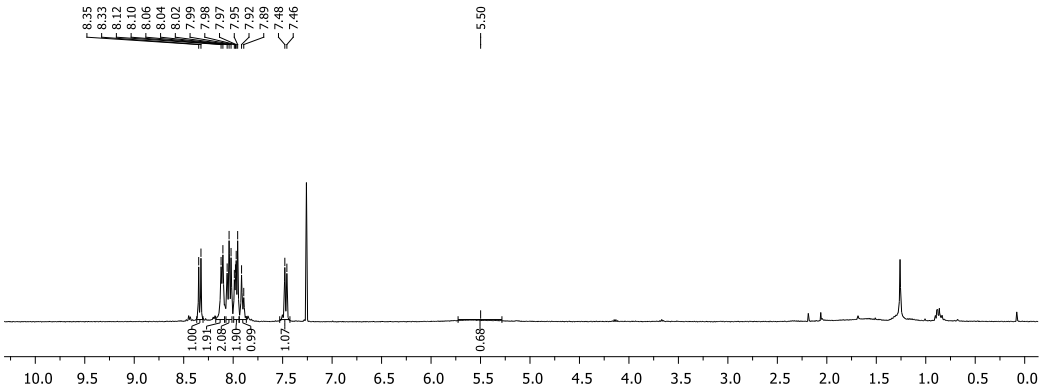
^{1}H-NMR (400 MHz) of compound **2r** in $CDCl_3$



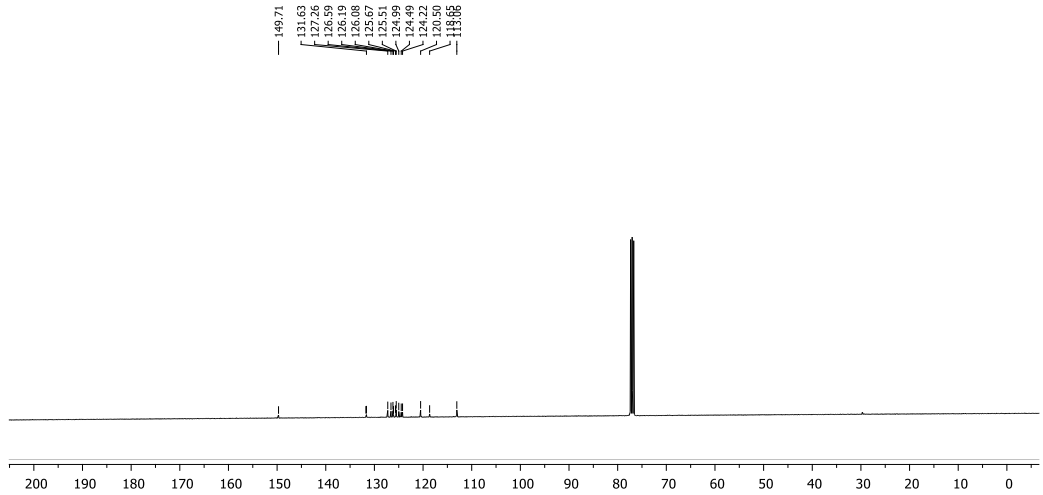
^{13}C-NMR (100 MHz) of compound **2r** in $CDCl_3$



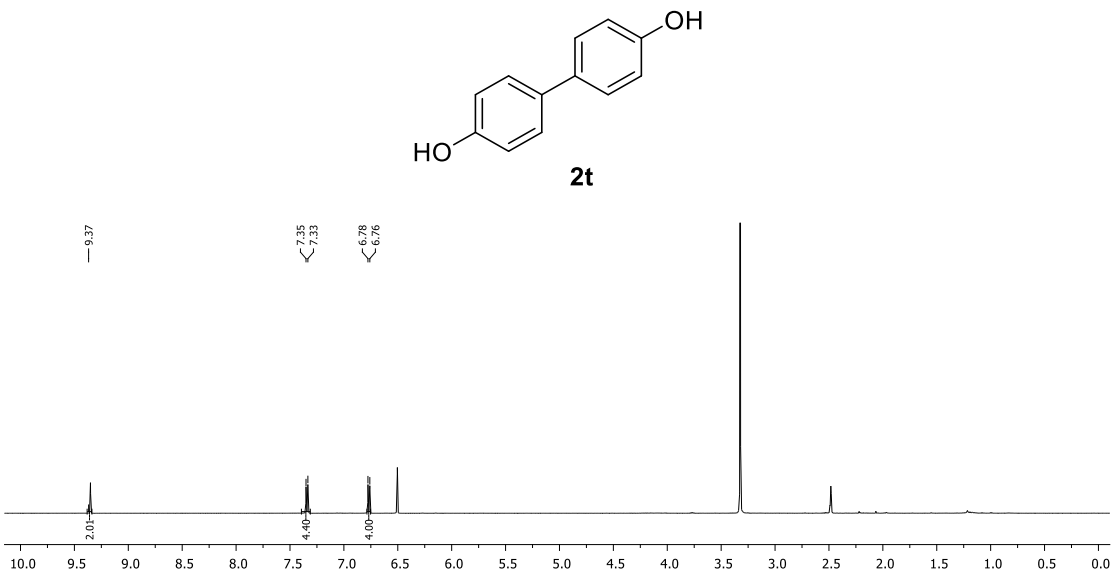
2s



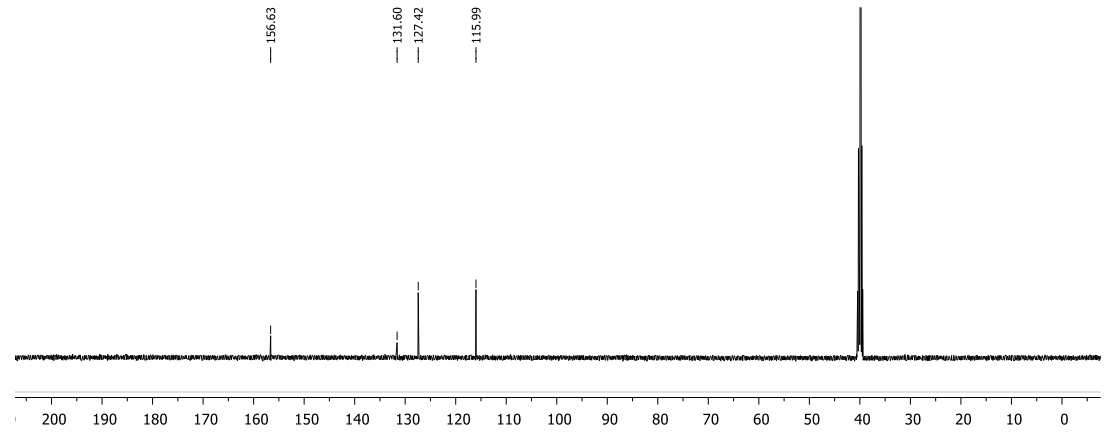
^{1}H-NMR (400 MHz) of compound **2s** in $CDCl_3$



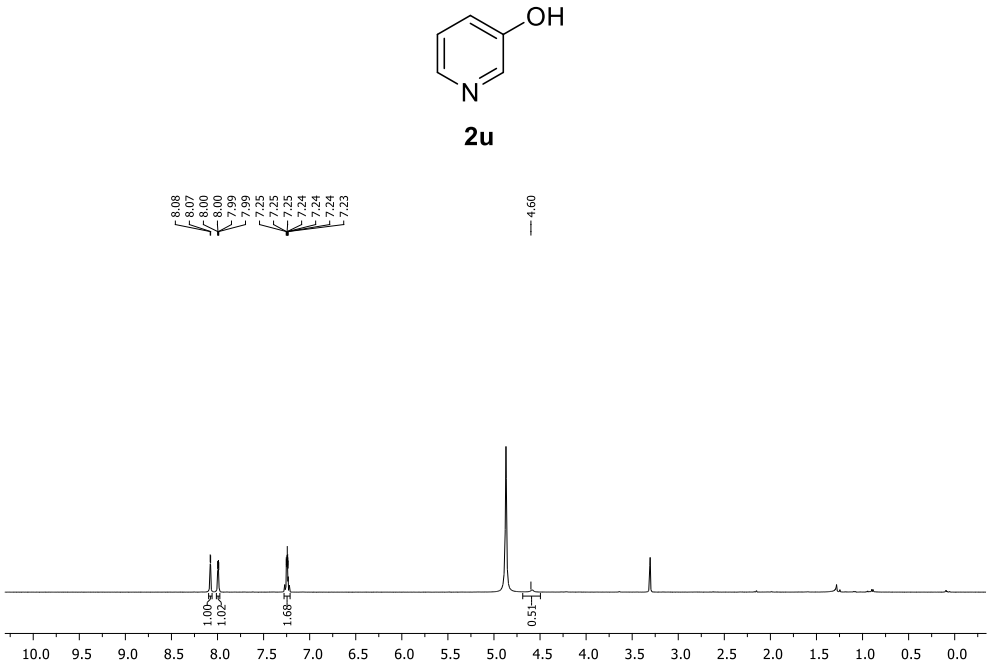
^{13}C-NMR (100 MHz) of compound **2s** in $CDCl_3$



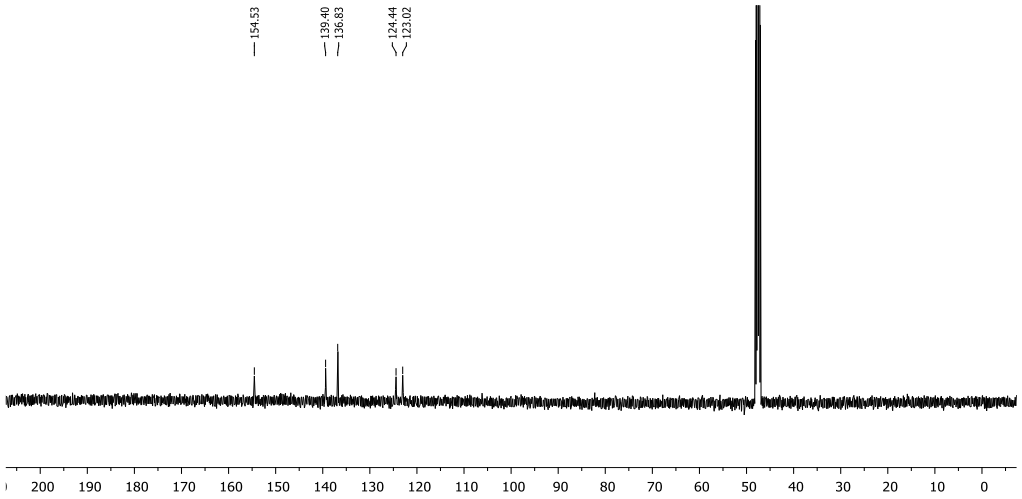
^{1}H-NMR (400 MHz) of compound **2t** in CD_3OD



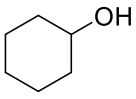
^{13}C-NMR (100 MHz) of compound **2t** in CD_3OD



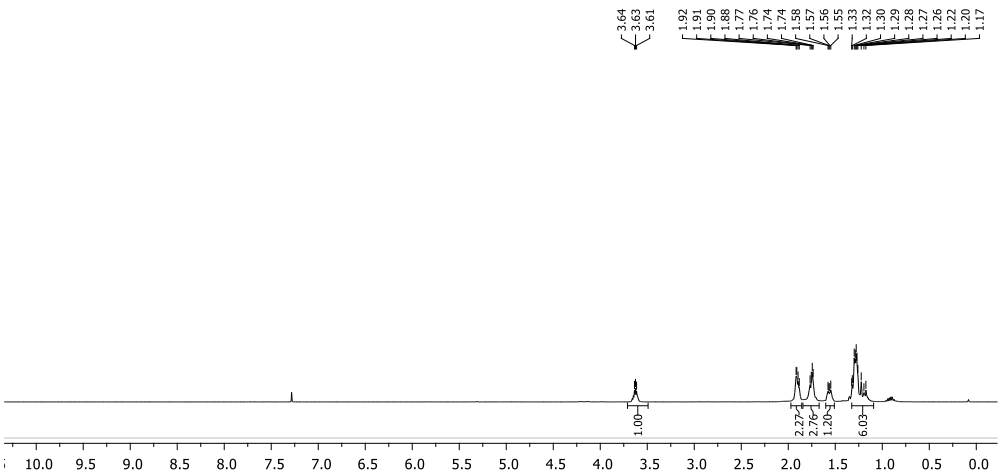
^{1}H-NMR (400 MHz) of compound **2u** in CD_3OD



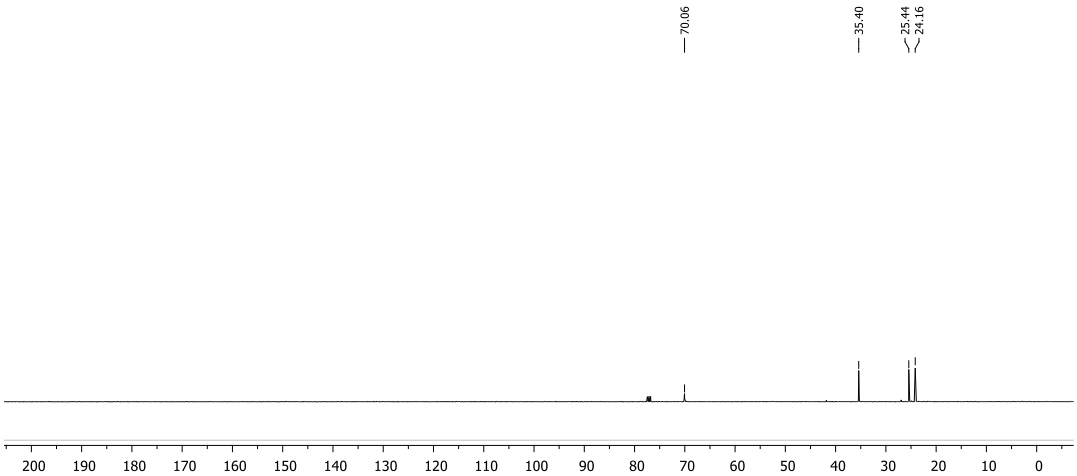
^{13}C-NMR (100 MHz) of compound **2u** in CD_3OD



2v



^{1}H-NMR (400 MHz) of compound **2v** in $CDCl_3$



^{13}C-NMR (100 MHz) of compound **2v** in $CDCl_3$