Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Electronic Supplementary Information

Nickel catalysed SET-induced oxygenation of (aryl)(*N*-heteroaryl)methanes with molecular oxygen

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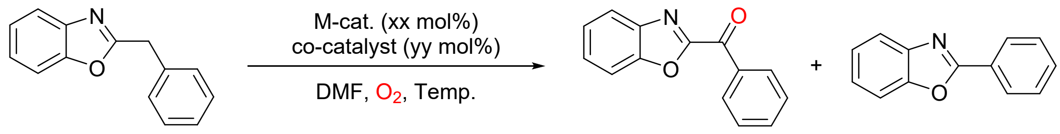
Table S1. Optimization of the reaction conditions for the oxygenation of 2-benzyl benzoxazole[a]



1a **2a** **3**

Sl. No.	M-Cat. (mol%)	Co-catalyst (eq)	Temp. (°C)	Time (h)	2a (%)	3 (%)
1	$NiBr_2$ (20)	DDQ (200)	120	0.25	60	32
2	$NiBr_2$ (20)	NFSI (200)	120	0.25	30	25
3	$NiBr_2$ (20)	$K_2S_2O_8$ (200)	120	0.25	32	10
4	$NiBr_2$ (20)	*p*-Benzoquinone (200)	120	0.25	25	10
5	$NiBr_2$ (20)	$(NH_4)_2S_2O_8$ (200)	120	0.25	28	0
6	$NiBr_2$ (20)	Oxone (200)	120	0.25	0	0
7	$NiBr_2$ (20)	Ag_2CO_3 (200)	120	0.25	34	0
8	$NiBr_2$ (20)	$CuCl_2$ (200)	120	0.25	0	0
9	$NiBr_2$ (20)	Chloranil (200)	120	0.25	0	0
10	$NiBr_2$ (20)	DTBP (200)	120	0.25	0	0
11	$NiBr_2$ (20)	AIBN (200)	120	0.25	0	0
12	$NiBr_2$ (20)	DDQ (100)	120	6	77	19
13	$NiBr_2$ (20)	DDQ (100)	120	12	80	10
14	$NiBr_2$ (20)	DDQ (50)	120	12	85	7
15	**$NiBr_2$ (20)**	**DDQ (25)**	**120**	**12**	**94**	**trace**
16	$NiCl_2.6H_2O$ (20)	DDQ (25)	120	12	60	<5
17	$Ni(OAc)_2.4H_2O$ (20)	DDQ (25)	120	12	64	<5
18	$NiCl_2$ glyme (20)	DDQ (25)	120	12	80	trace
19	$MnBr(CO)_5$(20)	DDQ (25)	120	12	56	<5
20	$FeCl_3$ (20)	DDQ (25)	120	12	58	trace
21	$FeBr_2$ (20)	DDQ (25)	120	12	61	trace
22	$CoCl_2$ (20)	DDQ (25)	120	12	48	<5
23	CuBr (20)	DDQ (25)	120	12	70	trace
24	$ZnCl_2$ (20)	DDQ (25)	120	12	45	<5
25	$Sc(OTf)_3$ (20)	DDQ (25)	120	12	55	<5
26	$BF_3.OEt_2$ (20)	DDQ (25)	120	12	58	<5
27	$NiBr_2$ (10)	DDQ (25)	120	12	82	trace
28	$NiBr_2$ (5)	DDQ (25)	120	12	22	0
29	$NiBr_2$ (10)	DDQ (10)	120	12	78	trace
30	$NiBr_2$ (20)	DDQ (25)	100	12	75	15
31	$NiBr_2$ (20)	DDQ (25)	80	12	70	16
32	$NiBr_2$ (20)	DDQ (25)	50	12	30	0
33	$NiBr_2$ (20)	DDQ (25)	RT	12	trace	0
34	-	DDQ (25)	120	12	0	0
35	$NiBr_2$ (20)	-	120	12	0	0
36[b]	$NiBr_2$ (20)	DDQ (25)	120	12	62	0
37[c]	$NiBr_2$ (20)	DDQ (25)	120	12	0	0

[a]***Reaction conditions**:* **1a** (0.5 mmol, 1.0 eq), Cat. (xx mol%), co-catalyst (yy mol%), oxygenated anhydrous DMF (2.0 mL), O_2 atm. [b] anhydrous and degassed DMF, O_2 atm. [c] anhydrous and degassed DMF, N_2 atm.

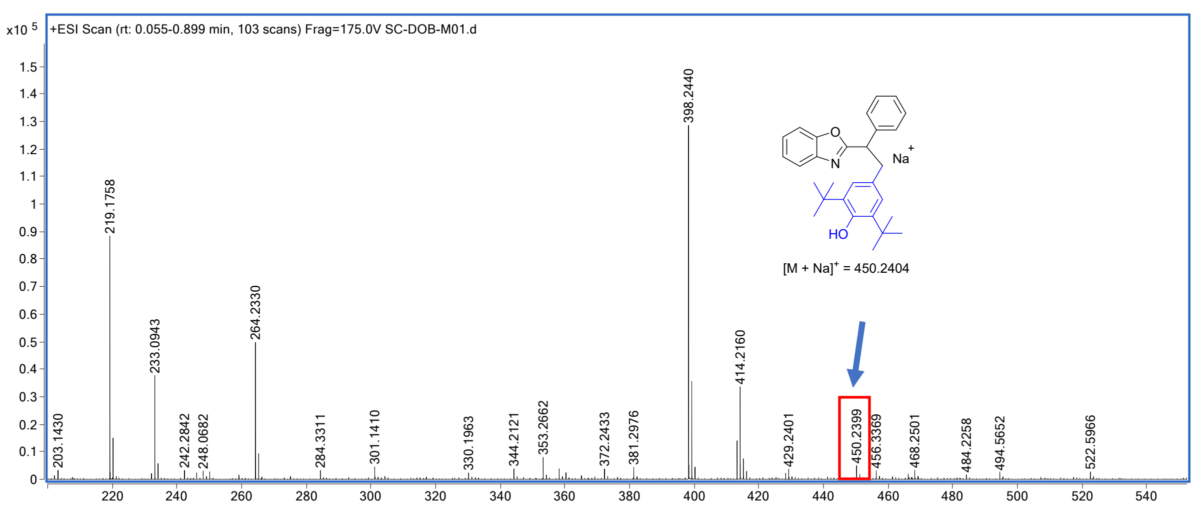
Mechanistic Study

The radical scavenging experiment using TEMPO for the oxygenation of 1a analyzed by HRMS

A 20 mL crimper cap vial, equipped with a magnetic stirring bar, was charged with **1a** (105 mg, 0.5 mmol, 1.0 eq), DDQ (28 mg, 0.125 mmol, 0.25 eq), $NiBr_2$ (21 mg, 0.1 mmol, 20 mol%) and TEMPO (156 mg, 1.0 mmol, 2.0 eq). The vial was then closed with a cap by a crimper tool. The vessel was evacuated and back-filled with oxygen (x 3). To it, anhydrous oxygenated DMF (2.0 mL) was added and the reaction mixture was stirred at 120 ^{o}C for 3.5 h. After cooling, an aliquot (0.2 mL) from the reaction mixture was withdrawn and diluted with EtOAc (2.0 mL) and filtered through a pad of silica gel. The reaction was completely shut down in presence of TEMPO.

The radical scavenging experiment using BHT for the oxygenation of 1a analyzed by HRMS

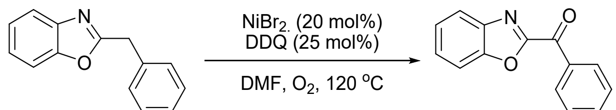
A 20 mL crimper cap vial, equipped with a magnetic stirring bar, was charged with **1a** (105 mg, 0.5 mmol, 1.0 eq), DDQ (28 mg, 0.125 mmol, 0.25 eq), $NiBr_2$ (21 mg, 0.1 mmol, 20 mol%) and BHT (221 mg, 1.0 mmol, 2.0 eq). The vial was then closed with a cap by a crimper tool. The vessel was evacuated and back-filled with oxygen (x 3). To it, anhydrous oxygenated DMF (2.0 mL) was added and the reaction mixture was stirred at 120 ^{o}C for 3.5 h. After cooling, an aliquot (0.2 mL) from the reaction mixture was withdrawn and diluted with EtOAc (2.0 mL) and filtered through a pad of silica gel. The reaction was completely shut down in presence of BHT. HRMS analysis of the filtrate suggests the formation of BHT-**1a** adduct. HRMS (ESI): *m/z* calcd. for $C_{29}H_{33}NNaO_2$ $[M + Na]^+$, 450.2404; found, 450.2399.



EPR studies

Ni-catalyzed oxygenation of 2-benzylbenzoxazole monitored by EPR

A 20 mL crimper cap vial, equipped with a magnetic stirring bar, was charged with **1a** (105 mg, 0.5 mmol, 1.0 eq), $NiBr_2$ (21 mg, 0.1 mmol, 20 mol%), and DDQ (28 mg, 1.0 mmol, 0.25 eq). The vial was then closed with a cap by a crimper tool. The vessel was evacuated and back-filled with oxygen (x 3). To it, anhydrous oxygenated DMF (2.0 mL) was added and the reaction mixture was stirred at 120 ^{o}C. An aliquot (0.1 mL) from the reaction mixture was withdrawn after 30 min and subjected to EPR analysis at 25 ^{o}C. A small peak at g = 2.005, B = 338.99 in the X-band EPR spectrum was observed, possibly due to the formation of a carbon-centered radical.



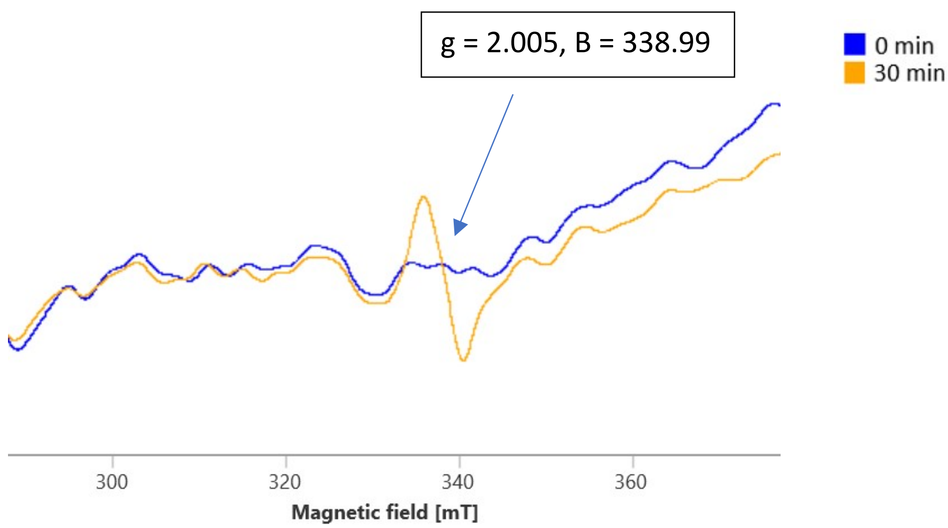
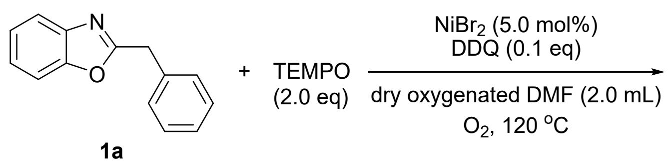


Figure S1. X-Band EPR spectra for the oxygenation of **1a**, in presence of $NiBr_2$, DDQ, and dry oxygenated DMF at 120 ^{o}C

Ni-catalyzed oxygenation of 2-benzylbenzoxazole in the presence of TEMPO monitored by EPR

A 20 mL crimper cap vial, equipped with a magnetic stirring bar, was charged with **1a** (105 mg, 0.5 mmol, 1.0 eq), $NiBr_2$ (21 mg, 0.1 mmol, 20 mol%), DDQ (28 mg, 1.0 mmol, 0.25 eq) and TEMPO (156 mg, 1.0 mmol, 2.0 eq). The vial was then closed with a cap by a crimper tool. The vessel was evacuated and back-filled with oxygen (x 3). Anhydrous oxygenated DMF (2.0 mL) was added, and the reaction mixture was stirred at 120 ^oC. An aliquot (0.1 mL) of the reaction mixture was withdrawn typically at 30 min intervals and subjected to EPR analysis at 25 ^oC. The intensity of the peak, appeared at the beginning (T = 0 min), possibly due to TEMPO, at g = 2.006, B = 338.0039, gradually decreased with time. The drop of the peak intensity is perhaps due to the reaction of TEMPO with the *in situ* formed organic radical from **1a** to give the TEMPO-(**1a-O$_2$**) adduct, which was also observed by HRMS analysis as above.



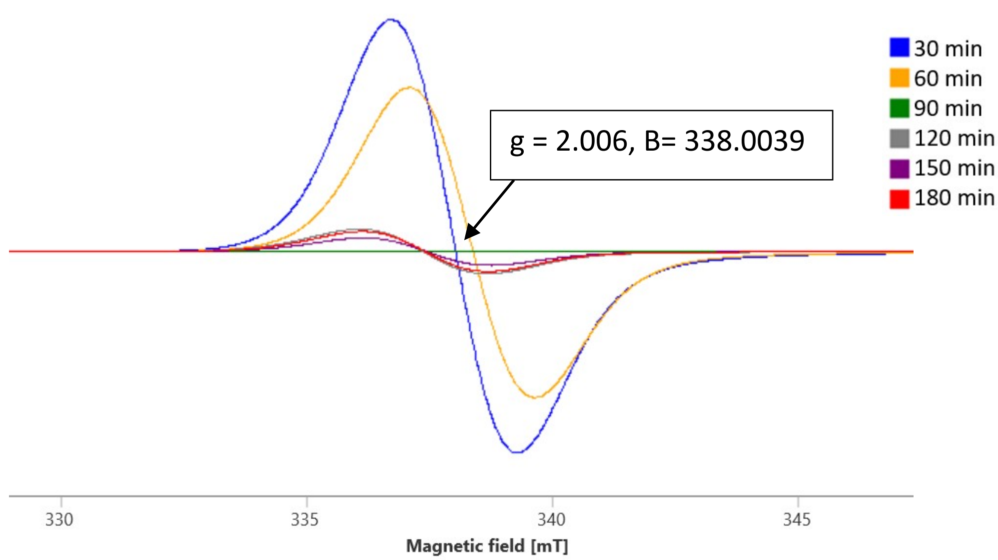
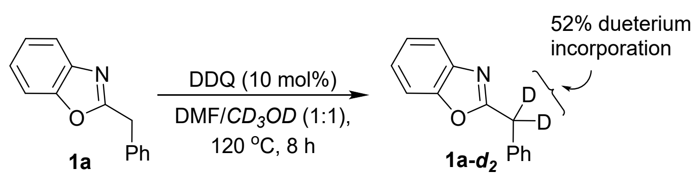


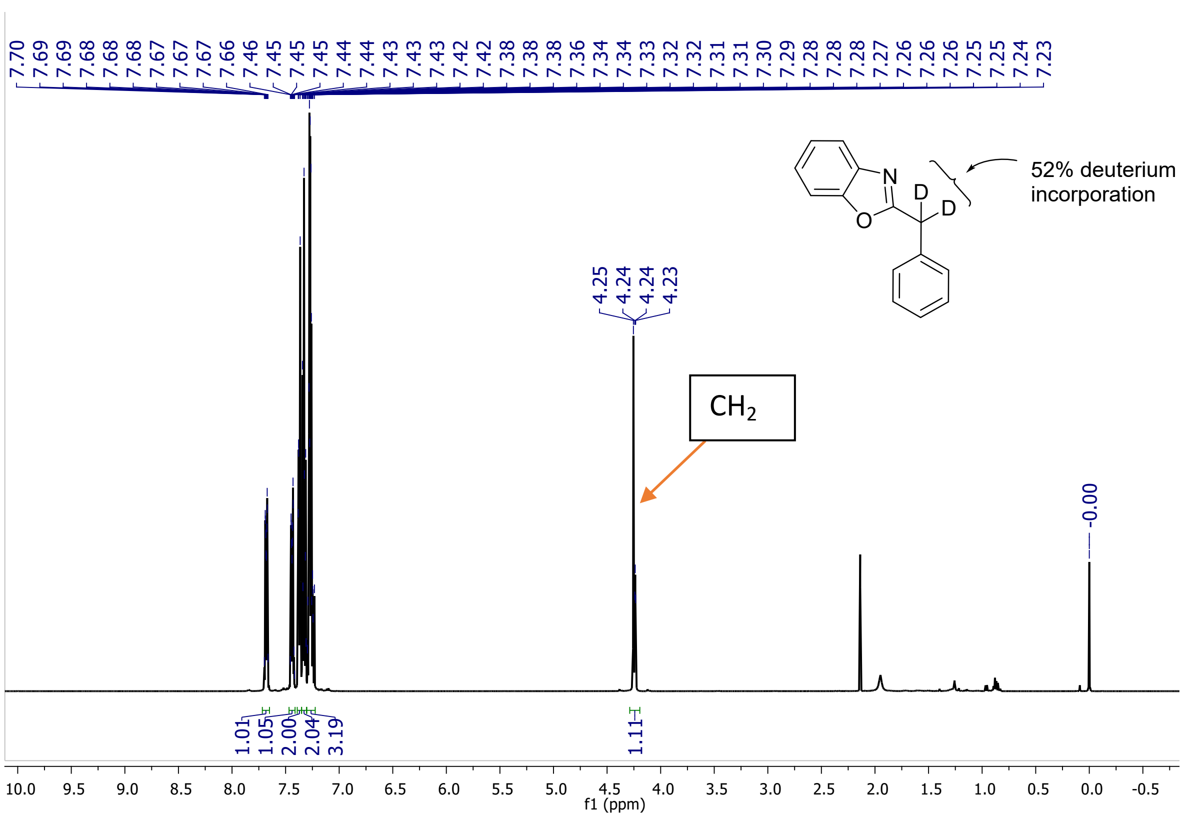
Figure S2. X-Band EPR spectra for the oxygenation of **1a**, in presence of $NiBr_2$, DDQ, and dry oxygenated DMF at 120 ^oC

H/D scrambling experiment in the absence of $NiBr_2$

A 20 mL crimper cap vial was charged with 2-benzylbenzoxazole **1a** (105 mg, 0.5 mmol, 1.0 eq), and DDQ (11 mg, 0.05 mmol, 0.1 eq). The vessel was evacuated and back-filled with oxygen (x 3), and to it, dry oxygenated DMF (1.0 mL), methanol-d_4 (1.0 mL) were added. Subsequently, the reaction mixture was stirred at 120 °C for 8 h. After cooling, the solvent was evaporated, and the residue was directly subjected to column chromatography on silica gel to obtain the unreacted starting material **1a**. ^{1}H NMR analysis confirms that ~52 % H/D scrambling occurs in the starting material (**1a**) using Methanol-d_4 in the absence of $NiBr_2$.

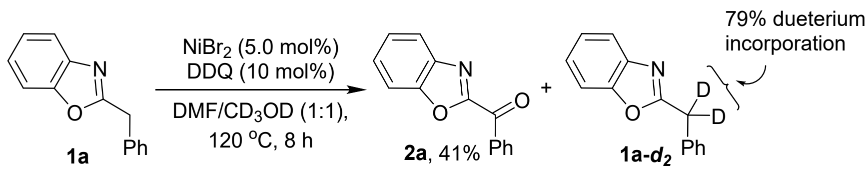


Scheme S1: H/D scrambling in **1a** by using MeOH-d_4 without $NiBr_2$



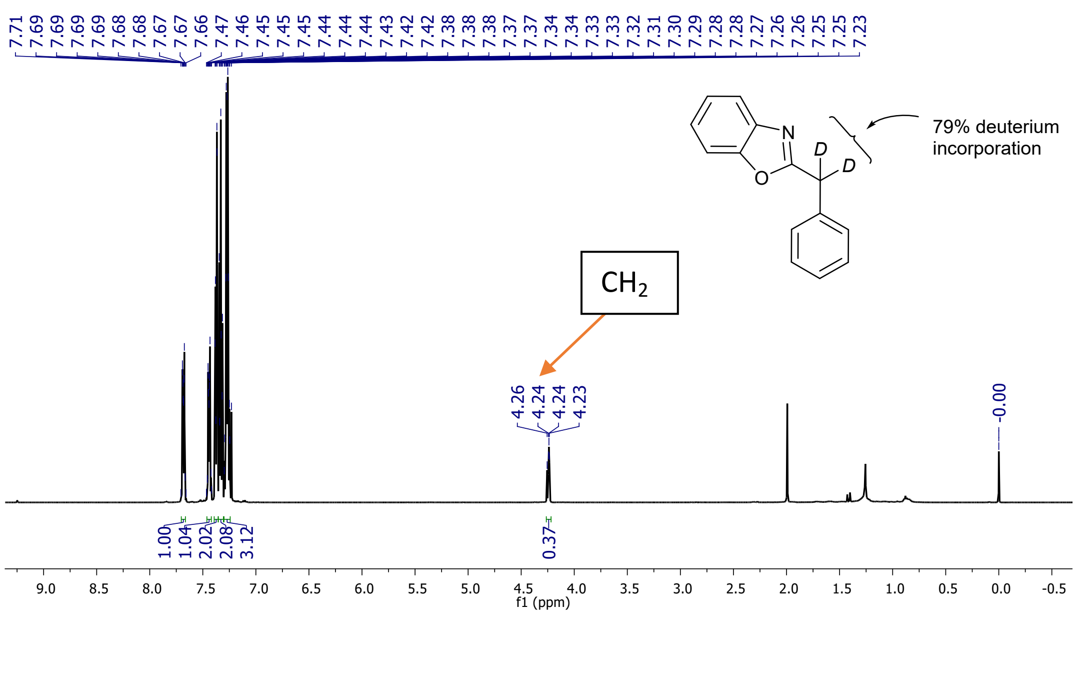
H/D scrambling experiment in the presence of $NiBr_2$:

A 20 mL crimper cap vial was charged with 2-benzylbenzoxazole **1a** (105 mg, 0.5 mmol, 1.0 eq), $NiBr_2$ (6 mg, 0.025 mmol, 0.05 eq), and DDQ (11 mg, 0.05 mmol, 0.1 eq). The vessel was evacuated and back-filled with oxygen (x 3), and to it, dry oxygenated DMF (1.0 mL), methanol-d_4 (1.0 mL) were added. Subsequently, the reaction mixture was stirred at 120 °C for 8 h. After cooling, the solvent was evaporated and the residue was directly subjected to column chromatography on silica-gel to obtain **2a** and the unreacted starting material **1a**. ^{1}H NMR analysis confirms that 79% H/D scrambling occurs in the starting material (**1a**) in the presence of $NiBr_2$ using Methanol-d_4, indicating the formation of an enamine intermediate is enhanced in the presence of $NiBr_2$.

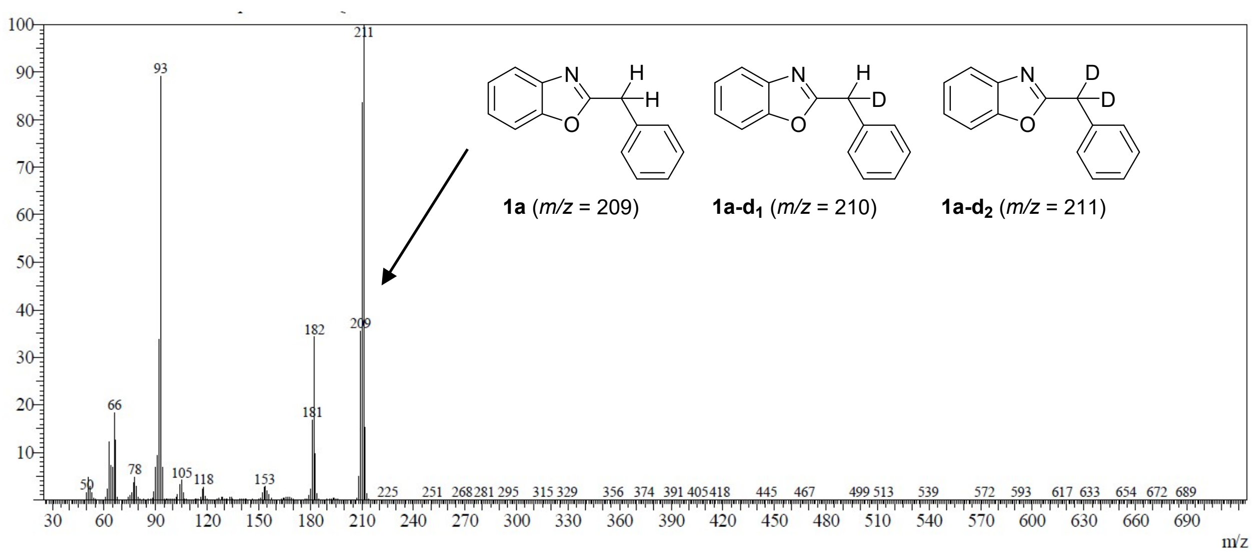


Scheme S2: H/D scrambling in **1a** by using MeOH-d_4 in presence of $NiBr_2$

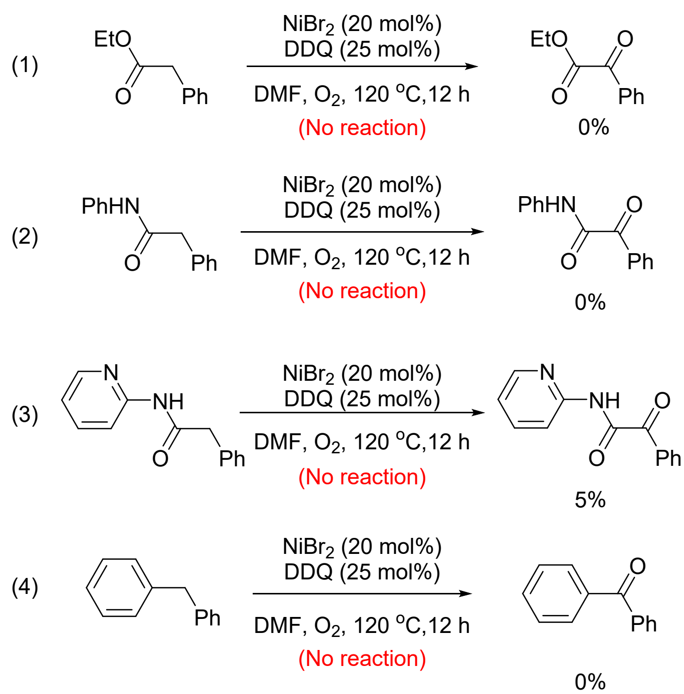
^{1}H NMR (500 MHz, $CDCl_3$)



Mass spectrum of the mixture of 1a (m/z = 209) 1a-d_1 (m/z = 210) and 1a-d_2 (m/z = 211) obtained in the H/D scrambling experiment



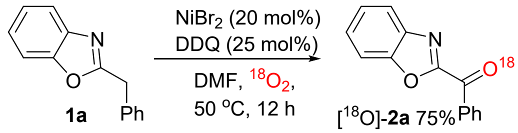
Oxygenation of various benzylic substrates bearing coordinating and non-coordinating functions under the optimized condition:



Scheme S3. Attempted oxygenation of various benzylic substrates under optimized conditions

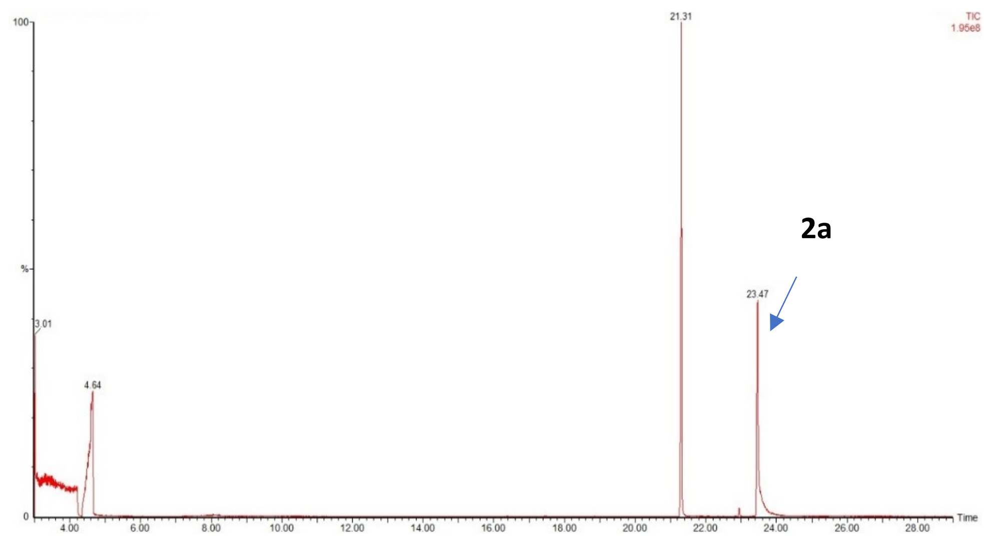
^{18}O Labeling experiment to determine the source of keto-oxygen in 2

A 30 mL clean, oven-dried Schlenk reaction tube, equipped with a magnetic stirring bar, was charged with **1a** (105 mg, 0.5 mmol, 1.0 eq), DDQ (170 mg, 0.75 mmol, 1.5 eq), $NiBr_2$ (21 mg, 0.1 mmol, 20 mol%) inside a glove box. The resulting mixture was degassed by the freeze-thaw method. Then the reaction tube was filled with $^{18}O_2$ gas. Anhydrous degassed DMF (2.0 mL) was added, and the reaction mixture was stirred at room temperature for 3-4 h. The mixture was then heated at 50 °C for 12h. After cooling, an aliquot (100 µl) was taken out by syringe and diluted with 3 mL of EtOAc and passed through a bed of silica gel. The ethyl acetate layer was submitted to GC-MS, which shows the formation of [^{18}O]-**2a** product with m/z = 225. After withdrawing the aliquot for GC-MS, water (10 mL) was added to the residue, and the resulting mixture was extracted with EtOAc (20 mL x 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude product mixture was purified by flash column chromatography on silica gel to provide the corresponding product as a colourless solid. Yield = 83 mg, 75 %.

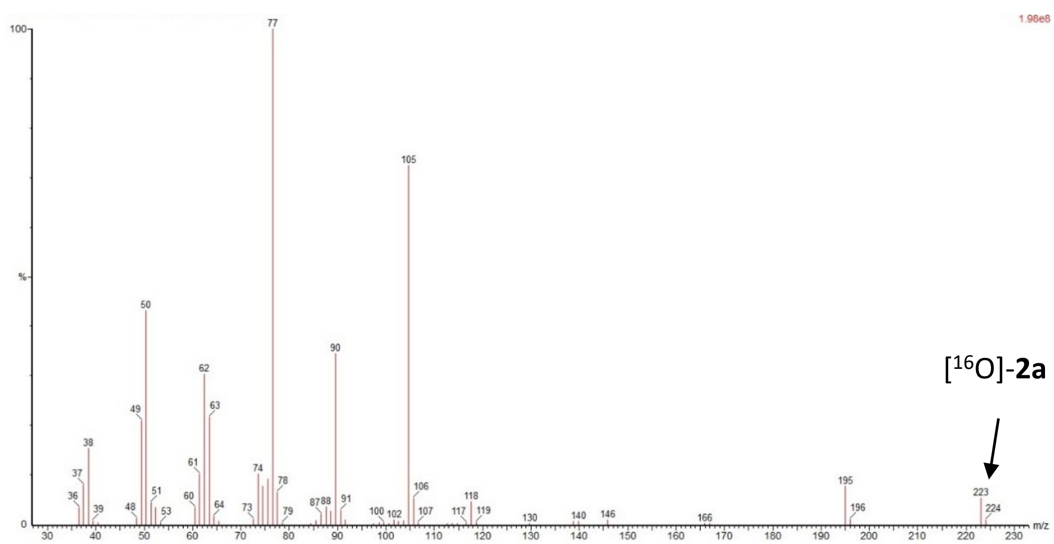


Scheme S4. Oxygenation of **1a** in the presence of $^{18}O_2$

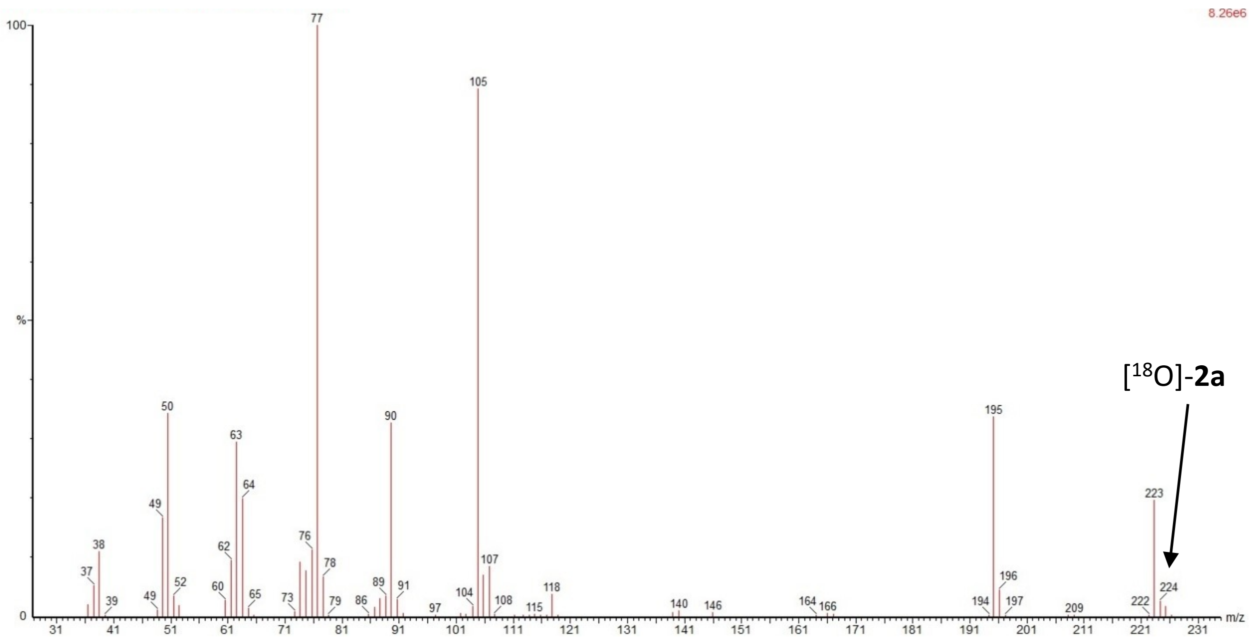
GCMS spectrum of the reaction in the presence of $^{18}O_2$



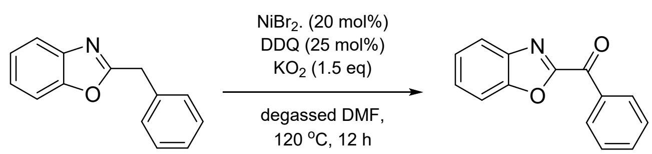
GCMS Spectrum of [^{16}O]-2a (*m/z* = 223, R_t = 23.47 min)



GCMS Spectrum of [^{18}O]-2a (*m/z* = 225, R_t = 23.47 min)



Attempted oxidation with potassium superoxide



Scheme S5: Attempted oxygenation of **1a** in presence potassium superoxide (KO_2)

A 20 mL crimper cap vial, equipped with a magnetic stirring bar, was charged with **1a** (105 mg, 0.5 mmol, 1.0 eq), $NiBr_2$ (21 mg, 0.1 mmol, 20 mol%), DDQ (28 mg, 1.0 mmol, 0.25 eq), and KO_2 (53 mg, 0.75 mmol, 1.5 eq). The vial was then closed with a cap by a crimper tool. The vessel was evacuated and back-filled with nitrogen (x 3). Then, degassed DMF (2.0 mL) was added, and the reaction mixture was stirred at 120 °C for 12 h. The reaction mixture was worked up with water and ethyl acetate, and purified over silica gel to recover unreacted starting materials. This suggests that a superoxide species may not be involved in the oxygenation of **1a** to give **2a**.

X-ray Structure Report for 2j

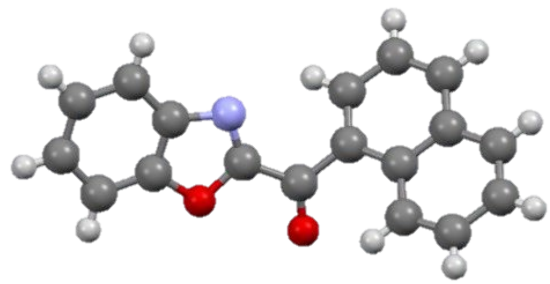


Figure **S3**. ORTEP diagram of **2j** (50% probability factor for the thermal ellipsoids)

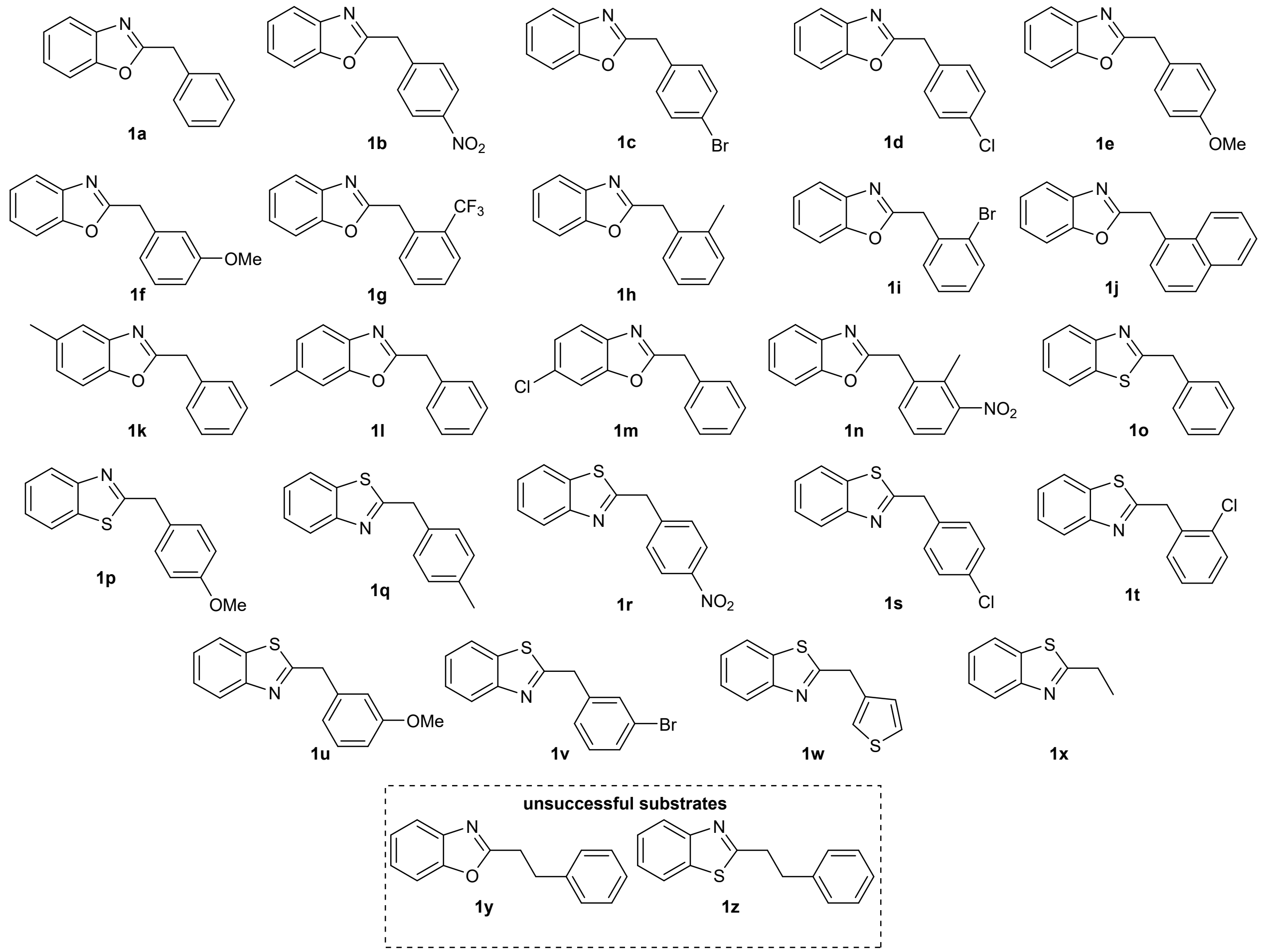
Empirical formula	$C_{18}H_{11}NO_2$
Formula weight	273.28
Temperature/K	298
Crystal system	monoclinic
Space group	P 1
a/Å	13.3789 (9)
b/Å	12.2013 (8)
c/Å	8.2874 (5)
a/o	90
b/o	105.751 (3)
g/o	90
Volume/Å^3	1302.04 (15)
Z	4
rcalc g/cm^3	1.394
m/mm^{-1}	0.092
F(000)	568.00
Crystal size/mm^3	0.24 X 0.15 X 0.07
Radiation	MoK\a (l = 0.71073)
2Q range for data collection/o	2.300-30.662
Index ranges	$-19 \leq h \leq 19$, $-17 \leq k \leq 17$, $-11 \leq l \leq 11$
Reflections collected	4013
Independent reflections	2329
Data/restrains/parameters	4013/0/190
Goodness-of-fit on F2	1.137
Final R indexes [I>= 2s (I)]	R1 = 0.1051, wR2 = 0.1797
Final R indexes [all data]	R1 = 0.0466, wR2 = 0.1217
Largest diff. peak/hole/e Å^{-3}	0.293/-0.294
CCDC	2449215

Preparative Procedures and Characterization of Unknown Substrates and All Products

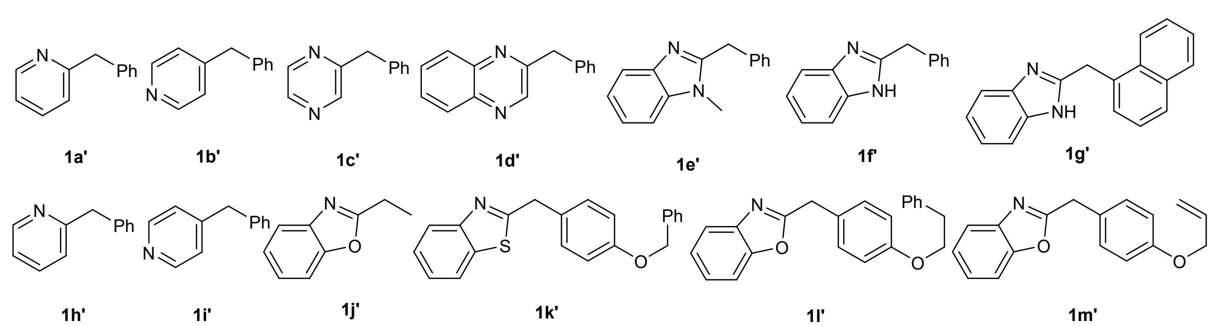
General methods: IR spectra were recorded on a Nicolet 6700, USA FTIR Spectrometer. NMR spectra were recorded on Jeol Resonance ECZ 600R spectrometer (600 MHz for ^{1}H NMR, 151 MHz for ^{13}C NMR, 565 MHz for ^{19}F) and/or Bruker AvanceII 500 spectrometer (500 MHz for ^{1}H NMR, 126 MHz for ^{13}C-NMR). Chemical shifts were reported in ppm on the δ scale relative to Me_4Si (δ = 0.00 for ^{1}H-NMR), $CDCl_3$ (δ = 77.160 for ^{13}C-NMR). Peaks at δ = 1.56–1.61 ppm in ^{1}H-NMR spectra of compounds recorded in $CDCl_3$ correspond to water present, if any. Additional peaks at δ = 0.86–0.88 ppm and δ = 1.25–1.28 ppm in ^{1}H-NMR spectra and δ = 29.7–29.8 ppm in ^{13}C-NMR spectra of compounds recorded in $CDCl_3$ correspond to grease present, if any. Multiplicities are indicated as: bs (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet). Coupling constants (*J*) are reported in Hertz (Hz). ^{19}F spectra were recorded in ppm on the δ scale relative to CF_3CO_2D as an external standard (δ = -76.55 in $CDCl_3$). HRMS (ESI) spectra were recorded on an Agilent AdvanceBio 6545XT LC/Q-TOF instrument and a Bruker Micro-TOF QII spectrometer. Melting Points (MP) of solid compounds were measured by an instrument manufactured by Patel Scientific Instruments Pvt. Ltd., India. GC spectral data were recorded on a Shimadzu GC-2014. Single crystal structures were determined using a Bruker D8 QUEST (CCD) diffractometer. All reactions that required heating were conducted in oil bath under continuous stirring by a magnetic stirrer equipped with a hot plate and temperature controller. All low temperature reactions were performed in a Siskin Profichill RFC-90 immersion cooler instrument. For Kugelrohr distillation, Buchi Glass-Oven B-585 was used. For thin-layer chromatography (TLC) analysis throughout this work, Macherey-Nagel pre-coated TLC plates (silica gel 60 F254 0.25 mm) were used. Solvents e.g. toluene, acetonitrile, methanol, THF, DMF, DMSO and DCM were dried by standard drying techniques.[1] All other solvents and commercially available compounds were used without further purification. The recrystallization of compound **2j** was performed by dissolving the compound in DCM and layered with hexane at -20 ^{o}C.

Preparation of starting materials

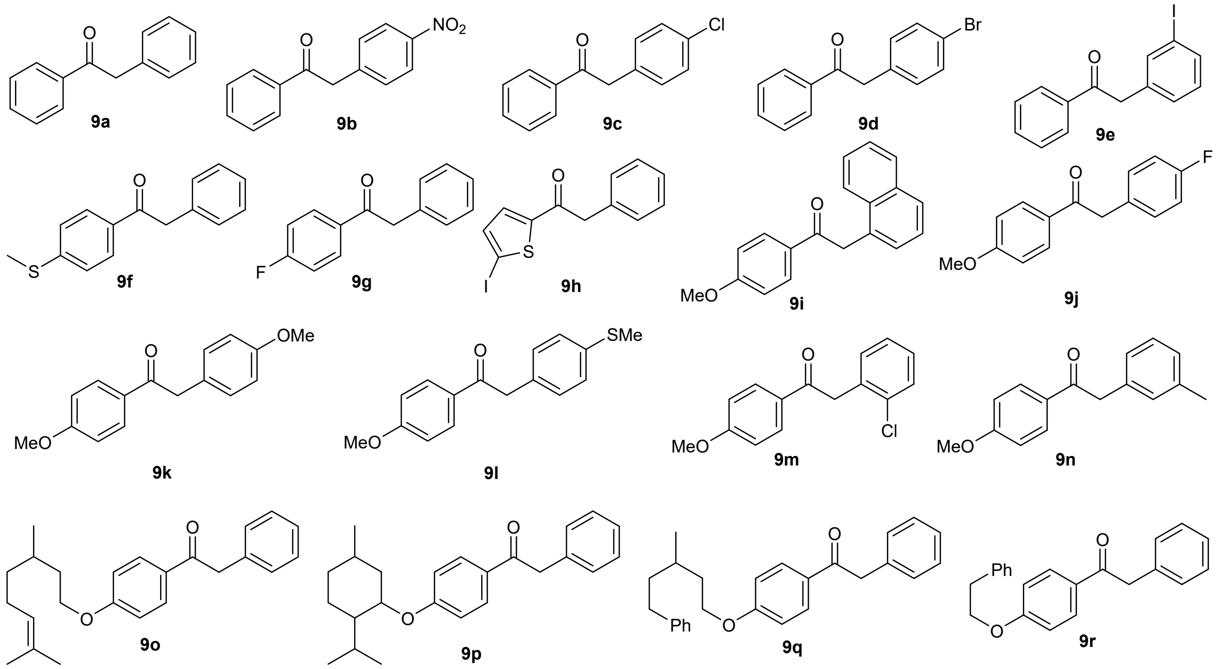
Substrates explored for the oxygenation of (Aryl)(Azolyl)Methanes



Substrates explored for the oxygenation of (Aryl)(Heteroaryl)Methanes

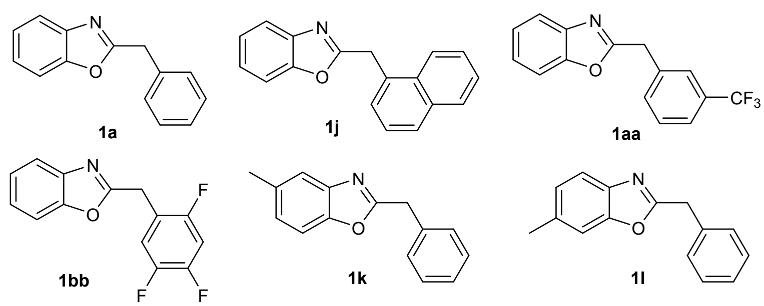


Substrates explored for the oxygenation of Arylbenzyl Ketones



9a, 9b, 9c, 9d, 9e, 9f, 9g, 9h, 9i, 9j, 9k, 9l, 9m, 9n, 9o, 9p, 9q, 9r

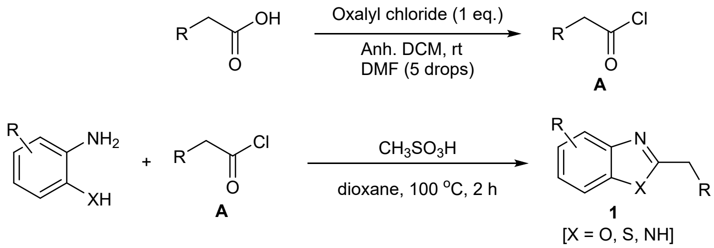
Substrates explored for the synthesis of Benzoxazinones



1a, 1j, 1aa, 1bb, 1k, 1l

Substrates **1a-1f**, **1h-1z**, **1c'-1d', 1j' and 1k'** are known compounds that were prepared by reported methods and characterized by matching their ^{1}H, ^{13}C and ^{19}F NMR spectral data with that of the reported compounds.[1] Substrates **1a'**, **1b'**, **1h'** and **1i'** were commercially available and used as received. Substrates **1g**, **1bb** and **1g'** were prepared by the modified reported procedures.[1a] Substrates **9a-9d** and **9f-9q**, are known compounds that were prepared by the reported procedures and characterized by matching their ^{1}H, ^{13}C and ^{19}F spectral data with reported compounds.[1a] Substrates **1l'**, **1m'**, **9e** and **9r** are new compounds, which were prepared by a modified reported procedure.[1a, 1k]

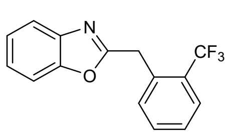
General procedure A: Synthesis of unknown benzoxazoles (1g, 1bb) and benzimidazole (1g')



To a solution of the acid (20 mmol, 1.0 eq) in dry DCM (76 mL) at 0 °C under N_2 atmosphere, oxalyl chloride (1.8 mL, 20 mmol, 1.0 eq) was added dropwise, followed by a catalytic amount of dry DMF (few drops). The mixture was stirred at room temperature until completion (typically 3 h). The volatiles were removed under reduced pressure and the resulting crude acid chloride **A** was used in the next step without further purification.

To the resulting residue, anhydrous 1,4-dioxane (40 mL), 2-aminophenol (2.18 g, 20 mmol, 1.0 eq) (for benzoxazoles, **1g**, **1bb**) or *o*-phenylenediamine (1.08 g, 10 mmol, 1.0 eq) (for benzimidazole, **1g'**) and CH_3SO_3H (4 mL) were added successively. The resultant mixture was stirred at 100 ºC for 2–4 h (TLC). After completion of the reaction, dioxane was removed under vacuo and the residue was diluted with EtOAc (30 mL), followed by saturated aq. $NaHCO_3$ (5 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3×20 mL). The combined EtOAc extracts were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure to afford the crude product, which was purified by column chromatography to furnish the pure compound **1**.

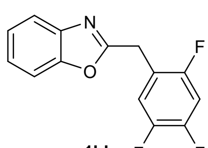
Characterization of compounds 1g, 1bb and 1g'



1g

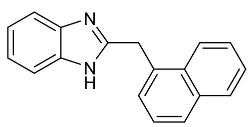
2-(2-(trifluoromethyl)benzyl)benzo[d]oxazole **(1g)** was prepared according to general procedure **A** starting from 2-(2-(trifluoromethyl)phenyl)acetic acid and 2-aminophenol. Yellow liquid (2.6 g, 9.5 mmol, 47%) R_f = 0.7 (Hexane:

Ether = 9:1). IR (neat): ν = 1608, 1455, 1240, 1102, 1060, 1036 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72−7.69 (m, 2H), 7.52 (t, *J* = 7.5, 1H), 7.48-7.44 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.32−7.28 (m, 2H), 4.48 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 151.1, 141.4, 133.3 (d, J_{C-F} = 1.3 Hz), 132.3, 131.8, 129.0 (q, J_{C-F} = 30.0 Hz), 127.7, 126.4 (q, J_{C-F} = 6.3 Hz), 125.0, 124.4 (q, J_{C-F} = 275.0 Hz), 124.4, 120.1, 110.6, 31.8 (q, J_{C-F} = 1.3 Hz) ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.76 ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{10}F_3NO$ [M + Na]$^+$ 300.0607, found 300.0619.



1bb

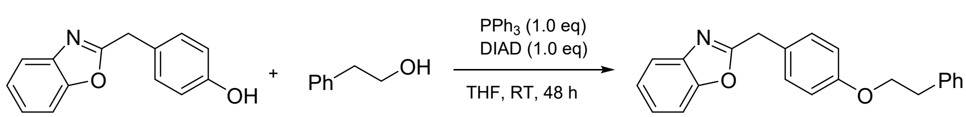
3-(2,4,5-Trifluorophenyl)-2H-benzo[b][1,4]oxazin-2-one **(1bb)** was prepared according to general procedure **A** starting from 2-(2,4,5-(trifluorophenyl)acetic acid and 2-aminophenol. Yellow solid (1.8 g, 7 mmol, 35%) R_f = 0.5 (Hexane:Ether = 9:1). MP = 62-68 °C. IR (neat): ν = 1509, 1211, 1158, 737, 704 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70−7.67 (m, 1H), 7.49−7.46 (m, 1H), 7.33−7.30 (m, 2H), 7.26−7.20 (m, 1H), 6.99−6.95 (m, 1H), 4.25 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3, 156.84−155.1 (m, 1C), 151.1, 150.6−148.7 (m, 1C), 147.8−146.1 (m, 1C), 141.3, 125.2, 124.6, 120.1, 119.0−118.8 (m, 1C), 118.3−118.2 (m, 1C), 110.6, 106.1−105.7 (m, 1C), 27.8 (d, J_{C-F} = 2.5 Hz, 1C) ppm. ^{19}F NMR (565 MHz, $CDCl_3$) δ -118.47−-118.49 (m, 1F), -134.05−-134.10 (m, 1F), -141.88−-141.97 (m, 1F) ppm. Anal. calcd. for $C_{14}H_8F_3NO$, C, 63.88; H, 3.06; N, 5.32; found C, 63.71; H, 2.93; N, 5.28.



1g'

2-(Naphthalen-1-ylmethyl)-1H-benzo[d]imidazole **(1g')** was prepared according to the general procedure **A** starting from 1-naphthaleneacetic acid and *o*-phenylenediamine. Compound **1g'** was a known compound and characterized by matching its ^{1}H, and ^{13}C spectral data with reported compounds.[1p]

Synthesis of 1l'

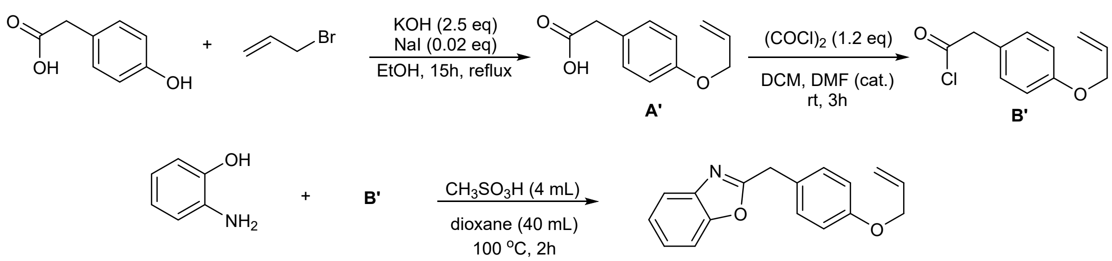


1l'

Compound **1l'** was prepared according a modified procedure as described in the literature.[1a] A 100 mL round bottom flask, equipped with a magnetic stirring bar, was charged with 4-(benzo*[d]*oxazol-2-ylmethyl)phenol (0.570g, 2.55 mmol, 1.0 eq) and the corresponding alcohol

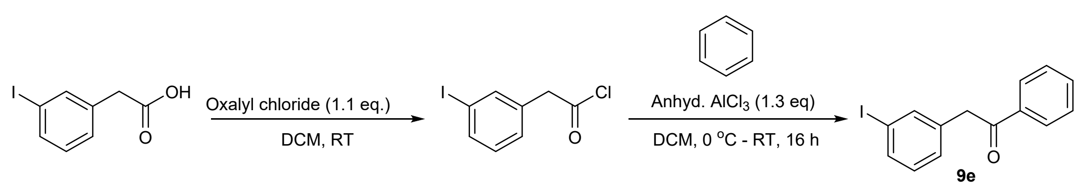
(1.0 eq). The flask was evacuated and back-filled with nitrogen (x 3) and then placed in an ice bath (0 °C), followed by the addition of anhydrous THF (0.1 M). Subsequently, PPh_3 (1.0 eq) and diisopropyl azodicarboxylate (DIAD, 1.0 eq) were added to it. The suspension was then stirred vigorously at room temperature for 48 h. The volatiles were evaporated under reduced pressure and purified by column chromatography on silica gel. colourless solid (570 mg, 1.73 mmol, 68%) $R_f = 0.5$ (Hexane:EtOAc = 9:1). MP = 56-58 °C. IR (neat): ν = 1515, 1252, 814, 741, 695 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ ^1H NMR (500 MHz, $CDCl_3$) δ 7.68–7.66 (m, 1H), 7.45–7.44 (m, 1H), 7.32–7.21 (m, 9H), 6.88–6.85 (m, 2H), 4.19 (s, 2H), 4.15 (t, J = 7 Hz, 2H), 3.07 (t, J = 7 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 158.2, 151.2, 141.5, 138.3, 130.2 (2C), 129.1 (2C), 128.6 (2C), 127.0, 126.6, 124.8, 124.3, 119.9, 115.0 (2C), 110.6, 68.8, 35.9, 34.6 ppm. HRMS (ESI): *m/z* calcd. for $C_{22}H_{20}O_2$ $[M + Na]^+$ 339.1356, found 339.1379.

Synthesis of 1m'



Compound **1m'** was prepared according a modified procedure as described in the literature.[1a] 4-Hydroxyphenylacetic acid (3.1 g, 20 mmol, 1 eq), allyl bromide (2.7 g, 22 mmol, 1.1 eq), KOH (2.8 g, 50 mmol, 2.5 eq), and NaI (60 mg, 0.4 mmol, 0.02 eq) were dissolved in absolute EtOH (50 mL) and refluxed for 15 h. The solution was allowed to stand at room temperature, concentrated in vacuo, diluted with EtOAc, and neutralized with 3 N aq. HCl. The organic layer was separated and the aqueous layer was extracted with EtOAc (3×30 mL). The combined EtOAc extracts were washed with H_2O (3×5 mL), dried (Na_2SO_4), and concentrated under reduced pressure to afford the crude product which was purified by column chromatography to give the compound **A'** as a colorless powder. Yield = 2.9 g, 75%. $R_f = 0.50$ (Hexane:EtOAc = 6:4). To a solution of **A'** (1.5 g, 8 mmol, 1 eq) in dry CH_2Cl_2 (32 mL) at 0 °C under N_2 was added dropwise oxalyl chloride (1.2 mmol, 1.2 eq) followed by a catalytic amount of dry DMF (3 drops). The reaction mixture was stirred at room temperature until the reaction was complete (typically 3 h). The volatiles were evaporated under reduced pressure and the resulting crude acid chloride was used directly for the next step without further purification. To the resulting residue (**B'**), anhydrous dioxane (16 mL), 2-amino phenol (1.0 g, 1.2 mmol, 1 eq) and CH_3SO_3H (0.5 mL) were added successively. The resultant mixture was stirred at 100 ºC for 2 h (TLC). After completion of the reaction, dioxane was removed and the residue was diluted with EtOAc (10 mL), followed by saturated aq. $NaHCO_3$ (5 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3×5 mL). The combined EtOAc extracts were washed with H_2O (3×5 mL), dried (Na_2SO_4), and concentrated under reduced pressure to afford the crude product which was purified by column chromatography to furnish the compound **1m'**. Yellow liquid. (838 mg, 39%). R_f = 0.5 (Hexane:EtOAc = 9:1). IR (neat): ν = 1511, 1456, 1238, 1223, 743 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.69–7.66 (m, 1H), 7.46–7.43 (m, 1H), 7.30–7.26 (m, 4H), 6.90–6.87 (m, 2H), 6.07–5.99 (m, 1H), 5.41–5.37 (m, 1H), 5.28–5.25 (m, 1H), 4.51–4.50 (m, 2H), 4.20 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 158.0, 151.2, 141.5, 133.3, 130.2 (2C), 127.1, 124.8, 124.3, 119.9, 117.8, 115.2 (2C), 110.6, 68.9, 34.5 ppm. Anal. calcd. for $C_{17}H_{15}NO_2$, C, 76.96; H, 5.70; N, 5.28; Found, C, 76.88; H, 5.75; N, 5.32.

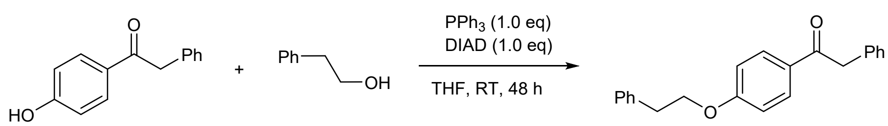
Synthesis of aryl benzyl ketone 9e



__**Step 1:**__ A 100 mL round bottom flask, equipped with a magnetic bead and septum, was charged with 2-(3-iodophenyl)acetic acid (2.62 g, 10 mmol, 1.0 eq). The flask was evacuated and backfilled with nitrogen (x 3). It was then placed in an ice bath followed by addition of dry DCM (38 mL) and 6-8 drops of DMF. To it, was added oxalyl chloride (1.4 g, 11 mmol, 1.1 eq). The reaction mixture was then stirred at room temperature for 3 h. The volatiles were evaporated under reduced pressure, and the resulting crude acid chloride was subjected to the next step without further purification.

Step 2: A 100 mL RB flask, equipped with a magnetic stirring bar, was charged with anhydrous $AlCl_3$ (1.73 g, 13.0 mmol, 1.3 eq). The flask was evacuated and backfilled with nitrogen (x 3) and then placed in an ice bath (0 °C), followed by the addition of dry DCM (10 mL). Benzene (1.01 g, 13.0 mmol, 1.3 eq) was then dissolved in DCM (5 mL) and added to the above flask. To the resulting mixture, 2-(3-iodophenyl)acetyl chloride (2.8 g, 10.0 mmol, 1.0 eq.), as obtained in step 1, in DCM (5 mL) was added dropwise. After 30 minutes, the ice bath was removed and the reaction was stirred further overnight at room temperature (monitored by TLC). After completion, the reaction mixture was poured into ice-cold water and stirred for 30 minutes. The aqueous part was then extracted with DCM (3 x 30 mL), the combined organic layers was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel to provide the desired aryl benzyl ketone **9e**. Yellow solid (1.4g, 4.3 mmol, 43%) R_f = 0.5 (Hexane:Ether = 9:1). MP = 66-70 °C. IR (neat): ν = 1674, 1342, 1216, 1205, 998 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.00–7.98 (m, 2H), 7.63 (s, 1H), 7.60–7.55 (m, 2H), 7.48–7.45 (m, 2H), 7.22 (d, J = 5 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 4.22 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 138.5, 136.9, 136.5, 136.1, 133.5, 130.4, 129.0, 128.9 (2C), 128.6 (2C), 94.6, 44.8 ppm. HRMS (ESI): *m/z* calcd. for $C_{14}H_{11}IO$ $[M + Na]^+$ 344.9747, found 344.9764.

Synthesis of substrates 9r

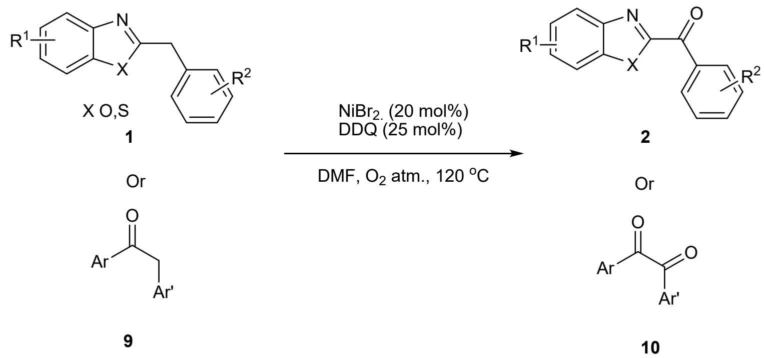


9r

Compound **4r** was prepared according a modified procedure as described in the literature.[1a] A 100 mL round bottom flask, equipped with a magnetic stirring bar, was charged with 1-(4-hydroxyphenyl)-2-phenylethan-1-one (0.637g, 3.0 mmol, 1.0 eq) and the corresponding alcohol (1.0 eq). The flask was evacuated and back-filled with nitrogen (x 3) and then placed in an ice bath (0 °C), followed by the addition of anhydrous THF (0.1 M). Subsequently, PPh_3 (1.0 eq) and diisopropyl azodicarboxylate (DIAD, 1.0 eq) were added to it. The suspension was then stirred vigorously at room temperature for 48 h. The volatiles were evaporated under reduced pressure and purified by column chromatography on silica gel. colourless solid (907 mg, 2.87 mmol, 57%) R_f = 0.5 (Hexane:Ether = 8:2). MP = 78-84 °C. IR (neat): ν = 1680, 1597, 1251, 1020, 991 cm^{-1}.

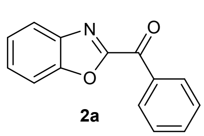
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.97–7.94 (m, 2H), 7.32–7.20 (m, 10H), 6.91–6.88 (m, 2H), 4.20 (t, *J* = 5.0 Hz, 4H), 3.09 (t, *J* = 5.0 Hz, 2H) ppm. ^{13}C NMR (126 MHz, CDCl$_3$) δ 196.3, 162.9, 137.9, 135.1, 131.0 (2C), 129.7, 129.5 (2C), 129.1 (2C), 128.7 (2C), 128.7 (2C), 126.9, 126.8, 114.4 (2C), 68.9, 45.3, 35.7 ppm. HRMS (ESI): *m/z* calcd. for $C_{22}H_{20}O_2$ [M + Na]$^+$ 339.1356, found 339.1379.

General Procedure B: Nickel catalyzed oxygenation of benzazoles and ketones



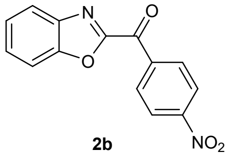
A 20 mL crimper cap vial, equipped with a magnetic stirring bar, was charged with **1** or **9** (0.5 mmol, 1.0 eq), DDQ (28 mg, 0.125 mmol, 25 mol%), $NiBr_2$ (22 mg, 0.1 mmol, 20 mol%). The vial was then closed with a cap by a crimper tool. The vessel was evacuated and back-filled with oxygen (x 3). Anhydrous oxygenated DMF (2.0 mL) was added, and the reaction mixture was stirred at 120 °C (monitored by TLC). After completion, water (10 mL) was added to the residue, and the resulting mixture was extracted with EtOAc (20 mL x 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude product mixture was purified by flash column chromatography on silica gel to provide the corresponding product **2** or **10**.

Characterization of Oxygenated products of (Aryl)(Azolyl)Methanes



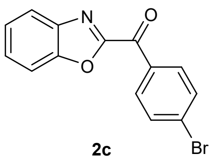
2a

Benzo[d]oxazol-2-yl(phenyl)methanone **(2a)** was prepared according to the general procedure **B** starting from 2-benzylbenzo[*d*]oxazole **1a** (105 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 105 mg, 0.47 mmol, 94%. colourless solid. R_f = 0.5 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[2] ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.57–8.54 (m, 2H), 7.96–7.94 (m, 1H), 7.72–7.67 (m, 2H), 7.59–7.54 (m, 3H), 7.49–7.46 (m, 1H) ppm. ^{13}C NMR (126 MHz, CDCl$_3$) δ 180.7, 157.2, 150.5, 140.9, 135.1, 134.4, 131.1 (2C), 128.8 (2C), 128.6, 125.9, 122.5, 112.0 ppm.



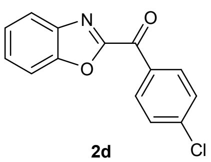
2b

Benzo[d]oxazol-2-yl(4-nitrophenyl)methanone **(2b)** was prepared according to the general procedure **B** starting from 2-(2-methylbenzyl)benzo[*d*]oxazole **1b** (127 mg, 0.5 mmol, 1.0 eq) in 24 h. Yield = 75 mg, 0.28 mmol, 56%. Yellow solid. R_f = 0.6 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[2] ^1H NMR (500 MHz, $CDCl_3$) δ 8.77−8.75 (m, 2H), 8.40−8.38 (m, 2H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.62−7.59 (m, 1H), 7.53−7.50 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.8, 156.6, 150.9, 150.6, 140.7, 139.6, 132.2 (2C), 129.3, 126.3, 123.7 (2C), 122.8, 112.1 ppm.



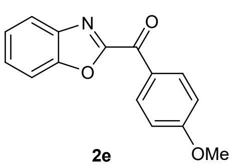
2c

Benzo[d]oxazol-2-yl(4-bromophenyl)methanone **(2c)** was prepared according to the general procedure **B** starting from 2-(4-bromobenzyl)benzo[*d*]oxazole **1c** (144 mg, 0.5 mmol, 1.0 eq) in 18 h. Yield = 103 mg, 0.34 mmol, 68%. colourless solid. R_f = 0.8 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[3] ^1H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J*= 5.0 Hz, 2H), 7.94 (d, *J*= 10.0 Hz, 1H), 7.70 (d, *J*= 10.0 Hz, 3H), 7.57−7.54 (m, 1H), 7.49−7.46 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.5, 157.0, 150.6, 140.8, 133.8, 132.6 (2C), 132.1 (2C), 130.1, 128.8, 126.0, 122.5, 112.0 ppm.



2d

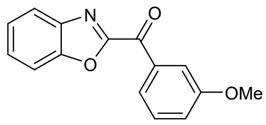
Benzo[d]oxazol-2-yl(4-chlorophenyl)methanone **(2d)** was prepared according to the general procedure **B** starting from 2-(4-chlorobenzyl)benzo[*d*]oxazole **1d** (121 mg, 0.5 mmol, 1.0 eq) in 18 h. Yield = 85 mg, 0.33 mmol, 66%. Dirty white solid. R_f = 0.7 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[2] ^1H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 10.0 Hz, 2H), 7.94 (d, *J* = 10.0 Hz, 1H), 7.70 (d, *J* = 5.0 Hz, 1H), 7.57−7.53 (m, 3H), 7.49−7.46 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.2, 157.0, 150.5, 141.2, 140.8, 133.4, 132.6 (2C), 129.1 (2C), 128.7, 126.0, 122.5, 112.0 ppm.



2e

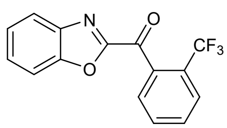
Benzo[d]oxazol-2-yl(4-methoxyphenyl)methanone **(2e)** was prepared according to the general procedure **B** starting from 2-(4-methoxybenzyl)benzo[*d*]oxazole **1e** (119 mg, 0.5 mmol, 1.0 eq) in 18 h. Yield = 65 mg, 0.25 mmol, 51%. colourless solid. R_f = 0.4 (Hexane:Ether = 8:2). All characterization data are in agreement with that as reported in the literature.[2] ^1H NMR (500 MHz, $CDCl_3$) δ

8.60−8.58 (m, 2H), 7.90 (d, J = 5.0 Hz, 1H), 7.67 (d, J = 10.0 Hz, 1H), 7.52−7.48 (m, 1H), 7.45−7.41 (m, 1H), 7.02−6.99 (m, 2H), 3.88 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.6, 164.7, 157.4, 150.3, 140.7, 133.6 (2C), 128.1, 127.9, 125.5, 122.2, 113.9 (2C), 111.7, 55.6 ppm.



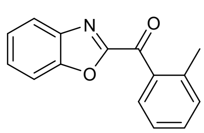
2f

Benzo[d]oxazol-2-yl(3-methoxyphenyl)methanone **(2f)** was prepared according to the general procedure **B** starting from 2-(3-methoxybenzyl)benzo[*d*]oxazole **1f** (119 mg, 0.5 mmol, 1.0 eq) in 18 h. Yield = 81 mg, 0.32 mmol, 64%. colourless solid. R_f = 0.4 (Hexane:Ether = 8:2). All characterization data are in agreement with that as reported in the literature.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, J = 10.0 Hz, 1H), 8.02−8.01 (m, 1H), 7.95 (d, J = 10.0 Hz, 1H), 7.71 (d, J = 5.0 Hz, 1H), 7.57−7.54 (m, 1H), 7.50−7.47 (m, 2H), 7.25−7.23 (m, 1H), 3.91 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.4, 159.8, 157.2, 150.5, 140.9, 136.3, 129.8, 128.6, 125.9, 124.1, 122.6, 121.2, 114.9, 112.0, 55.7 ppm.



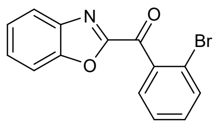
2g

Benzo[d]oxazol-2-yl(2-(trifluoromethyl)phenyl)methanone **(2g)** was prepared according to the general procedure **B** starting from 2-(2-(trifluoromethyl)benzyl)benzo[*d*]oxazole **1g** (138 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 127 mg, 0.43 mmol, 87%. Yellow oil. R_f = 0.5 (Hexane:Ether = 9:2). All characterization data are in agreement with that as reported in the literature.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 10.0 Hz, 1H), 7.85−7.83 (m, 1H), 7.80−7.78 (m, 1H), 7.75−7.70 (m, 3H), 7.59−7.56 (m, 1H), 7.48−7.45 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.8, 157.4, 151.1, 140.9, 135.6, 131.7, 131.6, 129.5, 129.2, 129.0 (q, J = 32.8 Hz, 1C), 127.2 (q, J = 5.0 Hz, 1C), 126.1, 123.6 (q, J = 274.7 Hz, 1C), 122.8, 112.1 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -57.70 ppm.



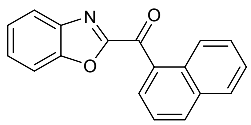
2h

Benzo[d]oxazol-2-yl(o-tolyl)methanone **(2h)** was prepared according to the general procedure **B** starting from 2-(2-methylbenzyl)benzo[*d*]oxazole **1h** (111 mg, 0.5 mmol, 1.0 eq) in 24 h. Yield = 78 mg, 0.33 mmol, 67%. colourless solid. R_f = 0.7 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[3] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, J = 6.0 Hz, 1H), 7.84 (d, J = 12.0 Hz, 1H), 7.63 (d, J = 6.0 Hz, 1H), 7.48 (t, J = 6.0 Hz, 1H), 7.43 (t, J = 12.0 Hz, 1H), 7.39 (t, J = 6.0 Hz, 1H), 7.29 (q, J = 6.0 Hz, 2H), 2.48 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 184.0, 158.0, 150.9, 141.0, 139.7, 135.1, 132.7, 131.9, 131.5, 128.6, 125.9, 125.7, 122.6, 112.0, 20.8 ppm.



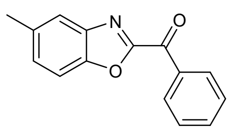
2i

Benzo[d]oxazol-2-yl(2-bromophenyl)methanone **(2i)** was prepared according to the general procedure **B** starting from 2-(2-bromobenzyl)benzo[*d*]oxazole **1i** (144 mg, 0.5 mmol, 1.0 eq) in 24 h. Yield = 105 mg, 0.35 mmol, 70%. colourless solid. R_f = 0.5 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91−7.89 (m, 1H), 7.79−7.70 (m, 3H), 7.58−7.55 (m, 1H), 7.52−7.43 (m, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.1, 157.1, 151.0, 141.0, 137.8, 133.9, 133.1, 130.8, 129.0, 127.4, 126.0, 122.8, 120.9, 112.1 ppm.



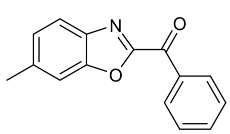
2j

Benzo[d]oxazol-2-yl(naphthalen-1-yl)methanone **(2j)** was prepared according to the general procedure **B** starting from 2-(naphthalen-1-ylmethyl)benzo[*d*]oxazole **1j** (129 mg, 0.5 mmol, 1.0 eq) in 24 h. Yield = 90 mg, 0.33 mmol, 65%. Yellow solid. R_f = 0.7 (Hexane: Ether = 9:1). All characterization data are in agreement with that as reported in the literature. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, J = 10.0 Hz, 1H), 8.41−8.40 (m, 1H), 8.13 (d, J = 10.0 Hz, 1H), 7.95−7.92 (m, 2H), 7.75−7.73 (m, 1H), 7.66−7.55 (m, 4H), 7.49−7.46 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.0, 158.3, 150.9, 140.9, 134.4, 133.9, 132.4, 132.2, 131.1, 128.8, 128.6, 128.6, 126.9, 125.9, 125.4, 124.4, 122.6, 112.0 ppm.



2k

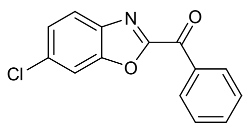
(5-Methylbenzo[d]oxazol-2-yl)(phenyl)methanone **(2k)** was prepared according to the general procedure **B** starting from 2-benzyl-5-methylbenzo[*d*]oxazole **1k** (111 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 73 mg, 0.31 mmol, 62%. Colourless solid. R_f = 0.5 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54−8.52 (m, 2H), 7.68−7.64 (m, 2H), 7.56−7.53 (m, 3H), 7.33-7.31 (m, 1H), 2.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.5, 157.2, 148.7, 141.0, 135.8, 135.0, 134.2, 131.0 (2C), 129.9, 128.6 (2C), 121.9, 111.2, 21.6 ppm.



2l

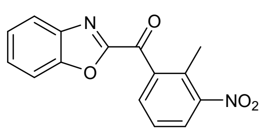
(6-Methylbenzo[d]oxazol-2-yl)(phenyl)methanone **(2l)** was prepared according to the general procedure **B** starting from 2-benzyl-6-methylbenzo[*d*]oxazole **1l** (111 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 71 mg, 0.3 mmol, 60%. Yellow oil. R_f = 0.5 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[2] ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, J = 6.0

Hz, 2H), 7.78 (d, J = 6.0 Hz, 1H), 7.66 (t, J = 6.0 Hz, 1H), 7.55 (t, J = 6.0 Hz, 2H), 7.47 (s, 1H), 7.26 (d, J = 6.0 Hz, 1H), 2.53 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.6, 156.9, 150.9, 139.6, 138.8, 135.2, 134.2, 131.0 (2C), 128.6 (2C), 127.4, 121.8, 111.8, 22.2 ppm.



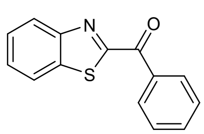
2m

(6-Chlorobenzo[d]oxazol-2-yl)(phenyl)methanone **(2m)** was prepared according to the general procedure **B** starting from 2-benzyl-6-chlorobenzo[*d*]oxazole **1m** (121 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 75 mg, 0.29 mmol, 58%. Yellow oil. R_f = 0.6 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[2] ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, J = 6.0 Hz, 2H), 7.87 (d, J = 12.0 Hz, 1H), 7.73 (d, J = 1.7 Hz, 1H), 7.70 (t, J = 6.0 Hz, 1H), 7.58 (t, J = 6.0 Hz, 2H), 7.48–7.46 (m, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.2, 157.7, 150.7, 139.6, 135.0, 134.6, 134.5, 131.1 (2C), 128.8 (2C), 126.9, 123.1, 112.5 ppm.



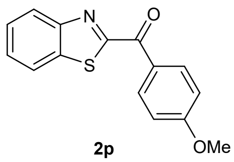
2n

Benzo[d]oxazol-2-yl(2-methyl-3-nitrophenyl)methanone **(2n)** was prepared according to the general procedure **B** starting from 2-(2-methyl-3-nitrobenzyl)benzo[*d*]oxazole **1n** (134 mg, 0.5 mmol, 1.0 eq) in 24 h. Yield = 82 mg, 0.29 mmol, 57%. colourless solid. MP = 140-145 °C. R_f = 0.5 (Hexane:Ether = 8:2). IR (neat): ν = 1677, 1516, 1356, 1310, 747, 715 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (t, J = 10.0 Hz, 2H), 7.90 (d, J = 10.0 Hz, 1H), 7.72 (d, J = 10.0 Hz, 1H), 7.62–7.59 (m, 1H), 7.54–7.48 (m, 2H), 2.56 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.9, 157.3, 151.4, 151.0, 140.8, 138.7, 133.8, 132.7, 129.4, 127.3, 126.6, 126.3, 122.8, 112.1, 16.4 ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{10}N_2O_4$ [M + Na]$^+$ 305.0533, found 305.0566.



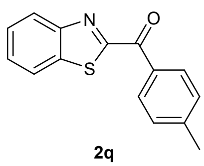
2o

Benzo[d]thiazol-2-yl(phenyl)methanone **(2o)** was prepared according to the general procedure **B** starting from 2-benzylbenzo[*d*]thiazole **1o** (112 mg, 0.5 mmol, 1.0 eq). Yield = 76 mg, 0.32 mmol, 63%. Yellow oil. R_f = 0.5 (Hexane:Ether = 9:1) in 12 h. All characterization data are in agreement with that as reported in the literature.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56–8.55 (m, 2H), 8.23 (d, J = 5.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.67–7.65 (m, 1H), 7.59–7.52 (m, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.5, 167.2, 154.0, 137.1, 135.1, 134.0, 131.4 (2C), 128.6 (2C), 127.7, 127.0, 125.8, 122.3 ppm.



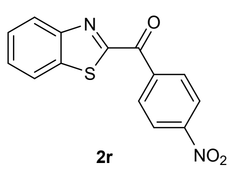
2p

Benzo[d]thiazol-2-yl(4-methoxyphenyl)methanone **(2p)** was prepared according to the general procedure **B** starting from 2-(4-methoxybenzyl)benzo[*d*]thiazole **1p** (127 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 75 mg, 0.28 mmol, 56%. Yellow oil. R_f = 0.6 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[3] ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 (d, *J* = 12.0 Hz, 2H), 8.23 (d, *J* = 12.0 Hz, 1H), 8.01 (d, *J* = 12.0 Hz, 1H), 7.59–7.52 (m, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 183.6, 168.1, 164.6, 154.1, 137.0, 134.0 (2C), 127.9, 127.5, 126.9, 125.7, 122.3, 114.0 (2C), 55.7 ppm.



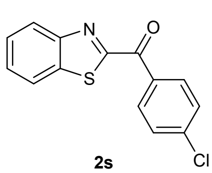
2q

Benzo[d]thiazol-2-yl(p-tolyl)methanone **(2q)** was prepared according to the general procedure **B** starting from 2-(4-methylbenzyl)benzo[*d*]thiazole **1q** (119 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 68 mg, 0.27 mmol, 54%. Yellow solid. R_f = 0.5 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 10.0 Hz, 2H), 8.22 (d, *J* = 5.0 Hz, 1H), 7.99 (d, *J* = 10.0 Hz, 1H), 7.58–7.51 (m, 2H), 7.34 (d, *J* = 5.0 Hz, 2H), 2.45 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.0, 167.5, 154.0, 145.1, 137.1, 132.5, 131.5 (2C), 129.3 (2C), 127.6, 126.9, 125.8, 122.2, 21.9 ppm.



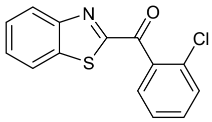
2r

Benzo[d]thiazol-2-yl(4-nitrophenyl)methanone **(2r)** was prepared according to the general procedure **B** starting from 2-(4-nitrobenzyl)benzo[*d*]thiazole **1r** (142.1 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 99 mg, 0.35 mmol, 80%. Yellow solid. R_f = 0.5 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 5.0 Hz, 2H), 8.39 (d, *J* = 10.0 Hz, 2H), 8.25 (d, *J* = 5.0 Hz, 1H), 8.04 (d, *J* = 5.0 Hz 1H), 7.64-7.58 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.0, 166.0, 153.9, 150.7, 139.9, 137.3, 132.4 (2C), 128.4, 127.5, 126.1, 123.6 (2C), 122.4 ppm.



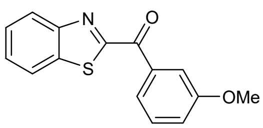
2s

Benzo[d]thiazol-2-yl(4-chlorophenyl)methanone **(2s)** was preparedaccording to the general procedure **B** starting from 2-(*4-chloro*benzyl)benzo[*d*]thiazole **1s** (127.5 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 90 mg, 0.33 mmol, 66%. colourless solid. R_f = 0.5 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[5] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57-8.54 (m, 2H), 8.24–8.22 (m, 1H), 8.02−8.00 (m, 1H), 7.61−7.55 (m, 2H), 7.54−7.52 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.1, 166.9, 153.9, 140.7, 137.2, 133.3, 132.8 (2C), 129.0 (2C), 127.9, 127.2, 125.9, 122.3 ppm.



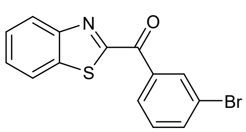
2t

Benzo[d]thiazol-2-yl(2-chlorophenyl)methanone **(2t)** was prepared according to the general procedure **B** starting from 2-(2-chlorobenzyl)benzo[*d*]thiazole **1t** (136.5 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 68 mg, 0.25 mmol, 51%. Light Yellow solid. R_f = 0.5 (Hexane:Ethyl acetate = 9.5:0.5). All characterization data are in agreement with that as reported in the literature.[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19−8.15 (m, 1H), 8.04−8.00 (m, 1H), 7.78−7.76 (m, 1H), 7.58−7.49 (m, 4H), 7.45−7.42 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.7, 166.1, 153.8, 137.5, 136.1, 132.7, 132.5, 130.9, 130.7, 128.1, 127.2, 126.6, 126.1, 122.5 ppm.



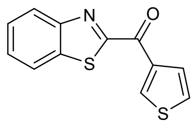
2u

Benzo[d]thiazol-2-yl(3-methoxyophenyl)methanone **(2u)** was prepared according to the general procedure **B** starting from 2-(3-methoxybenzyl)benzo[*d*]thiazole **1u** (134.5 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 88 mg, 0.33 mmol, 67%. Colourless solid. R_f = 0.5 (Hexane:Ethyl acetate = 9.5:0.5). All characterization data are in agreement with that as reported in the literature.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (t, *J* = 15.0 Hz, 2H), 8.04 (s, 1H), 7.95 (d, *J* = 10.0 Hz, 1H), 7.55−7.47 (m, 2H), 7.43 (t, *J* = 5.0 Hz, 1H), 7.19−7.17 (m, 1H), 3.87 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.8, 167.1, 159.5, 153.8, 136.9, 136.1, 129.5, 127.6, 126.9, 125.7, 124.1, 122.1, 120.5, 115.3, 55.4 ppm.



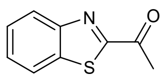
2v

Benzo[d]thiazol-2-yl(3-bromophenyl)methanone **(2v)** was prepared according to the general procedure **B** starting from 2-(3-bromo benzyl)benzo[*d*]thiazole **1v** (159.1mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 79 mg, 0.25 mmol, 49%. Colourless solid. R_f = 0.5 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[5] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.53 (d, *J* = 10.0 Hz, 1H), 8.25 (d, *J* = 5.0 Hz, 1H), 8.01 (d, *J* = 5.0 Hz, 1H), 7.78 (d, *J* = 5.0 Hz, 1H) 7.58 (t, *J* = 10.0 Hz, 2H), 7.44 (t, *J* = 6.5 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.0, 166.5, 153.9, 137.2, 136.8, 136.8, 134.1, 130.2, 130.0, 128.0, 127.2, 126.0, 122.8, 122.3 ppm.



2w

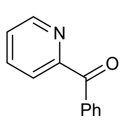
Benzo[d]thiazol-2-yl(thiophen-3-yl)methanone **(2w)** was prepared according to the general procedure **B** starting from 2-(thiophen-3-ylmethyl)benzo[*d*]thiazole **1w** (115 mg, 0.5 mmol, 1.0 eq) in 24 h. Yield = 59 mg, 0.24 mmol, 48%. Yellow oil. R_f = 0.5 (Hexane:Ether = 9.2:0.2). All characterization data are in agreement with that as reported in the literature.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.26 (s, 1H), 8.18 (d, *J* = 10.0 Hz, 1H), 7.97–7.94 (m, 2H), 7.55–7.47 (m, 2H), 7.36–7.35 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.2, 167.5, 153.8, 138.4, 138.1, 136.9, 128.8, 127.5, 126.9, 125.8, 125.6, 122.2 ppm.



2x

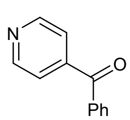
1-(benzo[d]thiazol-2-yl)ethan-1-one **(2x)** was prepared according to the general procedure **B** starting from 2-ethylbenzo[*d*]thiazole **2x** (82 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 28 mg, 0.16 mmol, 32%. Pink solid. R_f = 0.5 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[7] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20–8.19 (m, 1H), 7.99–7.98 (m, 1H), 7.60–7.52 (m, 2H), 2.83 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.3, 166.7, 153.7, 137.6, 127.9, 127.1, 125.6, 122.6, 26.3 ppm.

Characterization of oxygenated products of (Aryl)(Heteroaryl)Methanes



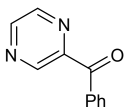
2a'

Phenyl(pyridine-2-yl)methanone **(2a')** was prepared according to the general procedure **B** starting from 2-benzylpyridine **1a'** (85 mg, 0.5 mmol, 1.0 eq) in 24 h. Yield = 28 mg, 0.15 mmol, 30%. Brown oil. R_f = 0.5 (Hexane:Ether = 7.5:2.5). All characterization data are in agreement with that as reported in the literature.[8] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73–8.71 (m, 1H), 8.08–8.02 (m, 3H), 7.91–7.87 (m, 1H), 7.60–7.57 (m, 1H), 7.50–7.46 (m, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.9, 155.2, 148.6, 137.1, 136.3, 133.0, 131.0 (2C), 128.2 (2C), 126.2, 124.7 ppm.



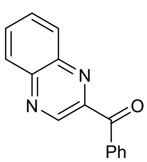
2b'

Phenyl(pyridine-2-yl)methanone **(2b')** was prepared according to the general procedure **B** starting from 4-benzylpyridine **1b'** (85 mg, 0.5 mmol, 1.0 eq) in 24 h. Yield = 84 mg, 0.46 mmol, 92%. Brown solid. R_f = 0.5 (Hexane:Ether = 7.5:2.5). All characterization data are in agreement with that as reported in the literature.[9] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73–8.71 (m, 1H), 8.08–8.02 (m, 3H), 7.91–7.87 (m, 1H), 7.60–7.57 (m, 1H), 7.50–7.46 (m, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.9, 155.2, 148.6, 137.1, 136.3, 133.0, 131.0 (2C), 128.2 (2C), 126.2, 124.7 ppm.



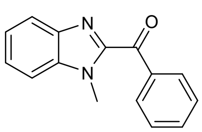
2c'

Phenyl(pyrazin-2-yl)methanone **(2c')** was prepared according to the general procedure **B** starting from 2-benzylpyrazine **1c'** (85 mg, 0.5 mmol, 1.0 eq) in 36 h. Yield = 30 mg, 0.16 mmol, 33%. Yellow liquid. R_f = 0.5 (Hexane:EtOAc = 8:2). All characterization data are in agreement with that as reported in the literature.[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.26 (d, *J* = 1.5 Hz, 1H), 8.79 (d, *J* = 2.5 Hz, 1H), 8.70–8.69 (m, 1H), 8.09–8.07 (m, 2H), 7.66–7.63 (m, 1H), 7.54–7.51 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.4, 150.1, 147.0, 146.3, 143.1, 135.7, 133.7, 131.0 (2C), 128.5 (2C).



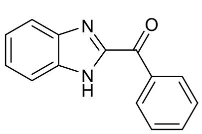
2d'

Phenyl(quinoxalin-2-yl)methanone **(2d')** was prepared according to the general procedure **B** starting from 2-benzylquinoxaline **1d'** (80 mg, 0.36 mmol, 1.0 eq) in 36 h. Yield = 48 mg, 0.2 mmol, 41%. Yellow solid. R_f = 0.5 (Hexane:EtOAc = 8:2). All characterization data are in agreement with that as reported in the literature.[11] ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.25–8.19 (m, 4H), 7.91–7.84 (m, 2H), 7.67–7.64 (m, 1H), 7.55–7.52 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.5, 148.8, 145.4, 143.3, 140.6, 135.6, 133.8, 132.2, 131.4 (2C), 130.9, 130.6, 129.5, 128.5 (2C) ppm.



2e'

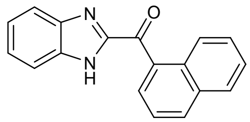
(1-Methyl-1H-benzo[d]imidazol-2-yl)(phenyl)methanone **(2e')** was prepared according to the general procedure **B** starting from 2-benzyl-1-methyl-1H-benzo[*d*]imidazole **1e'** (111 mg, 0.5 mmol, 1.0 eq) in 18 h. Yield = 87 mg, 0.37 mmol, 73%. Yellow oil. R_f = 0.6 (Hexane:EtOAc = 8:2). All characterization data are in agreement with that as reported in the literature.[12] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35–8.33 (m, 2H), 7.94–7.92 (m, 1H), 7.65–7.61 (m, 1H), 7.55–7.44 (m, 4H), 7.40–7.36 (m, 1H), 4.15 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.6, 146.8, 142.0, 137.0, 136.6, 133.6, 131.3 (2C), 128.5 (2C), 125.8, 123.7, 122.2, 110.5, 32.3 ppm.



2f'

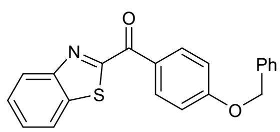
(1H-benzo[d]imidazol-2-yl)(phenyl)methanone **(2f')** was prepared according to the general procedure **B** starting from 2-benzyl-1*H*-benzo[*d*]imidazole **1f'** (104 mg, 0.5 mmol, 1.0 eq) in 36 h. Yield = 83 mg, 0.37 mmol, 75%. White solid. R_f = 0.6 (Hexane:EtOAc = 8:2). All characterization data are in agreement with that as reported in

the literature.[13] ^{1}H NMR (500 MHz, Acetone) δ 12.55 (bs, 1H), 8.76−8.74 (m, 2H), 7.91 (d, *J* = 8 Hz, 1H), 7.74−7.71 (m, 2H), 7.63−7.60 (m, 2H), 7.46-7.35 (m, 2H) ppm. ^{13}C NMR (126 MHz, Acetone) δ 183.2, 148.3, 143.9, 135.9, 134.7, 133.5, 131.1 (2C), 128.3, 128.3, 125.8, 123.2, 121.6, 112.6 ppm.



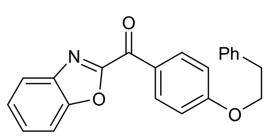
2g'

(1H-benzo[d]imidazol-2-yl)(naphthalen-1-yl)methanone **(2g')** was prepared according to the general procedure **B** starting from 2-(naphthalen-1-ylmethyl)-1*H*-benzo[*d*]imidazole **1g'** (129 mg, 0.5 mmol, 1.0 eq) in 36 h. Yield = 92 mg, 0.34 mmol, 68%. White solid. R_f = 0.6 (Hexane:EtOAc = 8:2). MP = 230-240 °C. All characterization data are in agreement with that as reported in the literature.[13] ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.68 (bs, 1H), 8.33−8.29 (m, 2H), 8.22 (d, *J* = 8 Hz, 1H), 8.08−8.07 (m, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.71−7.61 (m, 4H), 7.45, 7.43 (t, *J* = 7 Hz, 1H), 7.31 (t, *J* = 8 Hz, 1H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6) δ 186.9, 148.4, 142.9, 134.3, 133.1, 132.9, 132.1, 130.8, 130.1, 128.3, 127.4, 126.1, 125.6, 124.6, 124.2, 122.9, 121.1, 112.6 ppm.



2k'

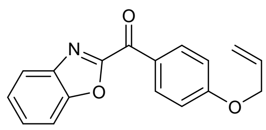
B*enzo[d]thiazol-2-yl(4-(benzyloxy)phenyl)methanone* **(2k')** was prepared according to the general procedure **B** starting from 2-(4-benzyloxy)benzyl)benzo[*d*]thiazole **1k'** (165 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 112 mg, 0.32 mmol, 65%. Light Yellow solid. R_f = 0.6 (Hexane:EtOAc = 9:1). All characterization data are in agreement with that as reported in the literature.[14] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66−8.63 (m, 2H), 8.24−8.22 (m, 1H), 8.02−8.00 (m, 1H), 7.59−7.51 (m, 2H), 7.46−7.39 (m, 4H), 7.37−7.34 (m, 1H), 7.13−7.10 (m, 2H), 5.19 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.5, 168.0, 163.7, 154.0, 137.0, 136.2, 134.0 (2C), 128.9 (2C), 128.4, 128.1, 127.6 (2C), 127.5, 126.9, 125.7, 122.3, 114.9 (2C), 70.4 ppm.



2l'

B*enzo[d]oxazol-2-yl(4-(phenethoxyphenyl)methanone* **(2l')** was prepared according to the general procedure **B** starting from 2-(4-phenethoxybenzyl)benzo[*d*]oxazole **1l'** (165 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 117 mg, 0.34 mmol, 68%. White solid. R_f = 0.5 (Hexane:EtOAc = 9:1). MP = 64-66 °C. IR (neat): ν = 1600, 1251, 1153, 750, 691 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60−8.57 (m, 2H), 7.94−7.92 (m, 1H), 7.70−7.68 (m, 1H), 7.54−7.51 (m, 1H), 7.47−7.44 (m, 1H), 7.35−7.24 (m, 5H), 7.03−7.00 (m, 2H), 4.29 (t, *J* = 7 Hz, 2H), 3.14 (t, *J* = 7 Hz, 2H) ppm. ^{13}C

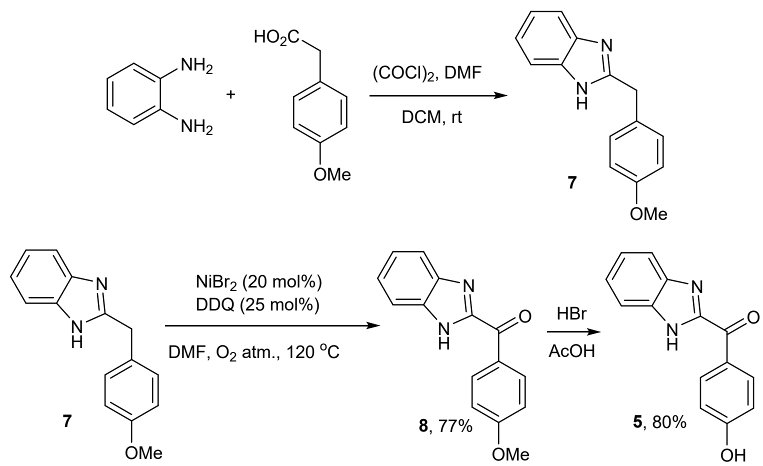
NMR (126 MHz, $CDCl_3$) δ 178.9, 164.1, 157.6, 150.4, 140.9, 137.8, 133.7 (2C), 129.1 (2C), 128.7 (2C), 128.2, 128.1, 126.8, 125.7, 122.3, 114.6 (2C), 111.9, 77.4, 77.2, 76.9, 69.1, 35.7 ppm. HRMS (ESI): *m/z* calcd. for $C_{22}H_{17}NO_3$ $[M + Na]^+$ 366.1101, found 366.1116.



2m'

(4-(allyloxy)phenyl)(benzo[d]oxazol-2-yl)methanone **(2m')** was prepared according to the general procedure **B** starting from 2-(4-phenethoxybenzyl)benzo[*d*]oxazole **1m'** (132 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 99 mg, 0.35 mmol, 71%. White solid. R_f = 0.5 (Hexane:EtOAc = 9:1). MP = 122 °C. IR (neat): ν = 1636, 1594, 992, 919, 835, 741 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.59 (t, *J* = 7 Hz, 2H), 7.93 (d, *J* = 8 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.09–6.03 (m, 1H), 5.43–5.43 (m, 1H), 5.35–5.32 (m, 1H), 4.65–4.64 (m, 2H) ppm. ^{13}C NMR (126 MHz, CDCl3) δ 178.8, 163.8, 157.5, 150.4, 140.8, 133.7, 132.4, 128.2, 128.1, 125.7, 122.3, 118.4, 114.7, 111.9, 69.1 ppm. Anal. calcd. for $C_{17}H_{13}NO_3$, C, 73.11; H, 4.69; N, 5.02; Found C, 73.08; H, 4.79; N, 5.12.

Synthesis of AMG 579 intermediate



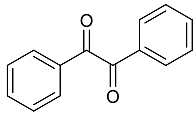
To a solution of the acid (20 mmol, 1.0 eq) in dry DCM (76 mL) at 0 °C under N_2 atmosphere, oxalyl chloride (1.8 mL, 20 mmol, 1.0 eq) was added dropwise, followed by a catalytic amount of dry DMF (few drops). The mixture was stirred at room temperature until completion (typically 3 h). The volatiles were removed under reduced pressure and the resulting crude acid chloride was used in the next step without further purification.

To the resulting residue, anhydrous 1,4-dioxane (40 mL), *o*-phenylene diamine (2.17 g, 20 mmol, 1.0 eq) and CH_3SO_3H (4 mL) were added successively. The resultant mixture was stirred at 100 ºC for 2 h (TLC). After completion of the reaction, dioxane was removed under vacuo and the residue was diluted with EtOAc (30 mL), followed by saturated aq. $NaHCO_3$ (5 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3×30 mL). The combined EtOAc extracts were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure to afford the crude product which was purified by column chromatography to furnish the pure compound **7**.

A 20 mL crimper cap vial, equipped with a magnetic stirring bar, was charged with **7** (1.19 g, 5 mmol, 1.0 eq), DDQ (284 mg, 1.25 mmol, 25 mol%), $NiBr_2$ (218 mg, 1 mmol, 20 mol%). The vial was then closed with a cap by a crimper tool. The vessel was evacuated and back-filled with oxygen (x 3). Anhydrous oxygenated DMF (10.0 mL) was added, and the reaction mixture was stirred at 120 ºC (monitored by TLC). After completion, water (10 mL) was added to the residue, and the resulting mixture was extracted with EtOAc (20 mL x 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude product mixture was purified by flash column chromatography on silica gel to provide the corresponding product **8** (971g, 3.8 mmol, 77%).

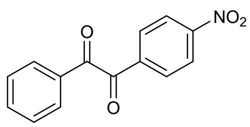
A 25 mL round bottom flask, equipped with magnetic bead was charged with **8** (126 mg, 0.5 mmol, 1eq), 48% HBr (1.1 mL), glacial acetic acid (1.2 mL). The flask was refluxed at 135 ºC for 5h. After completion, the obtained mixture was neutralized with saturated solution of aq. $NaHCO_3$ and the resulting mixture was extracted with EtOAc (20 mL x 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude product mixture was purified by flash column chromatography on silica gel to provide the corresponding product **5** (95 mg, 0.4 mmol, 80%). R_f = 0.5 (Hexane:EtOAc = 6.5:3.5). All characterization data are in agreement with that as reported in the literature.[15] ^1H NMR (500 MHz, DMSO) δ 13.37 (s, 1H), 10.60 (s, 1H), 8.63-8.61 (m, 2H), 7.87 (d, *J* = 10 Hz, 1 H), 7.61 (d, *J* = 5 Hz, 1H) 7.41–7.32 (m, 2H), 6.98–6.96 (m, 2H) ppm. ^{13}C NMR (126 MHz, DMSO) δ 181.75, 163.38, 148.95, 143.62, 134.38, 134.24 (2C), 127.36, 125.76, 123.42, 121.56, 115.75 (2C), 113.14 ppm.

Characterization of Oxygenated products of Arylbenzyl ketones



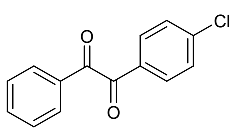
10a

1,2-Diphenylethane-1,2-dione **(10a)** was prepared according to the general procedure **B** starting from 1,2-diphenylethan-1-one **9a** (98 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 80 mg, 0.38 mmol, 75%. Yellow oil. R_f = 0.5 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[16] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 12.0 Hz, 4H), 7.58–7.56 (m, 2H), 7.43 (t, *J* = 7.9 Hz, 4H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.7 (2C), 135.0 (2C), 133.1 (2C), 130.0 (4C), 129.15 (4C) ppm.



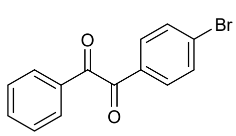
10b

1-(4-Nitrophenyl)-2-phenylethane-1,2-dione **(10b)** was prepared according to the general procedure **B** starting from 2-(4-nitrophenyl)-1-phenylethan-1-one **9b** (128 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 61 mg, 0.24 mmol, 48%. Yellow solid. R_f = 0.5 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[16] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 10.0 Hz, 2H), 8.17 (d, *J* = 10.0 Hz, 2H), 7.99 (d, *J* = 10.0 Hz, 2H), 7.71 (t, *J* = 15.0 Hz, 1H), 7.55 (t, *J* = 15.0 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 192.2, 151.2, 137.4, 135.5, 132.4, 131.1 (2C), 130.2 (2C), 129.3 (2C), 124.2 (2C) ppm.



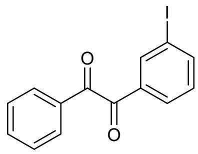
10c

1-(4-Chlorophenyl)-2-phenylethane-1,2-dione **(10c)** was prepared according to the general procedure **B** starting from 2-(4-chlorophenyl)-1-phenylethan-1-one **9c** (122 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 100 mg, 0.41 mmol, 83%. Yellow solid. R_f = 0.5 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[16] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97-7.96 (m, 2H), 7.94-7.91 (m, 2H), 7.69-7.65 (m, 1H), 7.54-7.48 (m, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.0, 193.2, 141.7, 135.2, 132.9, 131.4, 131.3 (2C), 130.0 (2C), 129.6 (2C), 129.2 (2C) ppm.



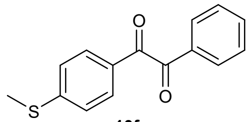
10d

1-(4-Bromophenyl)-2-phenylethane-1,2-dione **(10d)** was prepared according to the general procedure **B** starting from 2-(4-bromophenyl)-1-phenylethan-1-one **9d** (144.5 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 78 mg, 0.27 mmol, 55%. Yellow solid. R_f = 0.5 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[16] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98−7.96 (m, 2H), 7.86−7.83 (m, 2H), 7.69−7.65 (m, 3H), 7.54−7.51 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.0, 193.4, 135.2, 132.9, 132.6 (2C), 131.9, 131.4 (2C), 130.7, 130.1 (2C), 129.2 (2C) ppm.



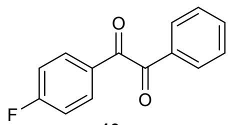
10e

1-(3-Iodophenyl)-2-phenylethane-1,2-dione **(10e)** was prepared according to the general procedure **B** starting from 2-(3-iodophenyl)-1-phenylethan-1-one **9e** (168.1 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 87 mg, 0.37 mmol, 73%. Yellow liquid. R_f = 0.5 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[17] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (t, J = 1.5 Hz, 1H), 7.98−7.95 (m, 3H), 7.92−7.90 (m, 1H), 7.69−7.65 (m, 1H), 7.54−7.50 (m, 2H), 7.24 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.6, 192.9, 143.6, 138.4, 135.2, 134.7, 132.7, 130.7, 130.0 (2C), 129.2, 129.2 (2C), 94.7 ppm.



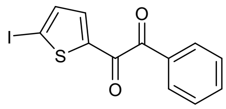
10f

1-(4-(Methylthio)phenyl)-2-phenylethane-1,2-dione **(10f)** was prepared according to general procedure **B** starting from 1-(4-(methylthio)phenyl)-2-phenylethan-1-one **9f** (122 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 90 mg, 0.35 mmol, 70%. Yellow solid. R_f = 0.7 (Hexane:Ether = 8:2). All characterization data are in agreement with that as reported in the literature.[16] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97−7.95 (m, 2H), 7.87−7.85 (m, 2H), 7.66−7.62 (m, 1H), 7.51−7.48 (m, 2H), 7.29−7.27 (m, 2H), 2.50 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.6, 193.6, 149.0, 134.9, 133.1, 130.2 (2C), 130.0 (2C), 129.2, 129.1 (2C), 125.1 (2C), 14.6 ppm.



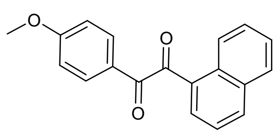
10g

1-(4-Fluorophenyl)-2-phenylethane-1,2-dione **(10g)** was prepared according to general procedure **B** starting from 1-(4-fluorophenyl)-2-phenylethan-1-one **9g** (107 mg, 0.5 mmol, 1.0 eq) in 36 h. Yield = 48 mg, 0.21 mmol, 41%. Colourless solid. R_f = 0.6 (Hexane:Ether = 8:2). All characterization data are in agreement with that as reported in the literature.[16] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04−8.00 (m, 2H), 7.98−7.96 (m, 2H), 7.69−7.65 (m, 1H), 7.54−7.51 (m, 2H), 7.21−7.17 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.2, 192.9, 166.9 (d, J = 258.3 Hz, 1C), 135.2, 133.0, 132.9, 132.8, 130.1 (2C), 129.6 (d, J = 2.5 Hz, 1C), 129.2 (2C), 116.6, 116.5 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -101.19−-101.21 (m, 1F) ppm.



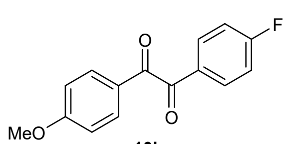
10h

1-(5-Iodothiophen-2-yl)-2-phenylethane-1,2-dione **(10h)** was prepared according to general procedure **B** starting from 1-(5-iodothiophen-2-yl)-2-phenylethan-1-one **9h** (164 mg, 0.5 mmol, 1.0 eq) in 24 h. Yield = 144 mg, 0.42 mmol, 84%. Yellow solid. MP = 58-62 ^{o}C. R_f = 0.5 (Hexane:Ether = 8:2). IR (neat): ν = 1667, 1637, 1399, 733, 680 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04–8.03 (d, *J* = 5.0 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 4.5 Hz, 1H), 7.35 (d, *J* = 4.0 Hz, 1H), ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.4, 183.4, 145.4, 138.8, 137.5, 135.1, 132.6, 130.4 (2C), 129.1 (2C), 90.0 ppm. HRMS (ESI): *m/z* calcd. for $C_{12}H_7IO_2S$ $[M + Na]^+$ 364.9104, found 364.9613.



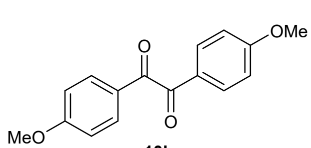
10i

1-(4-Methoxyphenyl)-2-(naphthalen-1-yl)ethane-1,2-dione **(10i)** was prepared according to the general procedure **B** starting from 1-(4-methoxyphenyl)-2-(naphthalen-1-yl)ethan-1-one **9i** (138 mg, 0.5 mmol, 1.0 eq) in 36 h. Yield = 67 mg, 0.23 mmol, 45%. Colourless solid. R_f = 0.5 (Hexane:Ether = 7:3). All characterization data are in agreement with that as reported in the literature.[18] ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.28 (d, *J* = 5.0 Hz,1H), 8.10 (d, *J* = 10.0 Hz, 1H), 8.01−7.98 (m, 2H), 7.93−7.91 (m, 2H), 7.74−7.71 (m, 1H), 7.63−7.60 (m, 1H), 7.49−7.46 (m, 1H), 6.99−6.96 (m, 2H), 3.87 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.6, 193.4, 165.0, 135.9, 135.0, 134.2, 132.6 (2C), 131.1, 129.4, 129.0, 128.9, 127.2, 126.6, 126.1, 124.6, 114.5 (2C), 55.8 ppm.



10j

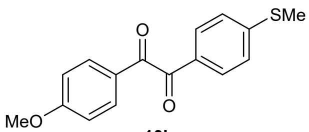
1-(4-Fluorophenyl)-2-(4-methoxyphenyl)ethane-1,2-dione **(10j)** was prepared according to the general procedure **B** starting from 2-(4-fluorophenyl)-1-(4-methoxyphenyl)ethan-1-one **9j** (122 mg, 0.5 mmol, 1.0 eq) in 36 h. Yield = 67 mg, 0.26 mmol, 52%. Yellow liquid. R_f = 0.5 (Hexane:Ether = 7:3). All characterization data are in agreement with that as reported in the literature.[19] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03−7.99 (m, 2H), 7.95−7.92 (m, 2H), 7.19−7.15 (m, 2H), 6.99−6.96 (m, 2H), 3.88 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.1, 192.7, 166.7 (d, *J* = 257.7 Hz, 1C), 165.2, 132.8, 132.7, 132.5 (2C), 129.8 (d, *J* = 2.5 Hz, 1C), 126.0, 116.5, 116.3, 114.5 (2C), 55.7 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -101.64 ppm.



10k

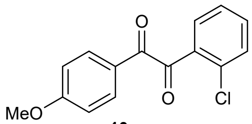
1,2-Bis(4-methoxyphenyl)ethane-1,2-dione **(10k)** was prepared according to the general procedure **B** starting from 1,2-bis(4-

methoxyphenyl)ethan-1-one **9k** (135.1 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 116 mg, 0.43 mmol, 85%. Yellow solid. R_f = 0.5 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[16] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96−7.93 (m, 4H), 6.98−6.95 (m, 4H), 3.88 (s, 6H), ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.6 (2C), 165.0 (2C), 132.5 (4C), 126.4 (2C), 114.4 (4C), 55.8 (2C) ppm.



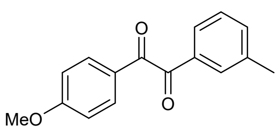
10l

1-(4-Methoxyphenyl)-2-(4-(methylthio)phenyl)ethane-1,2-dione **(10l)** was prepared according to the general procedure **B** starting from 1-(4-methoxyphenyl)-2-(4-(methylthio)phenyl)ethan-1-one **9l** (143.2 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 92 mg, 0.32 mmol, 64%. Yellow solid. R_f = 0.5 (Hexane:Ether = 9:1). MP = 114-122 °C. IR (neat): ν = 1653, 1586, 1007, 820, 742, 685 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95−7.92 (m, 2H), 7.88−7.85 (m, 2H), 7.29−7.27 (m, 2H), 6.98−6.95 (m, 2H), 3.88 (s, 3H), 2.52 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.8, 193.2, 164.9, 148.6, 132.4 (2C), 130.1 (2C), 129.4, 126.2, 125.0 (2C), 114.3 (2C), 55.6, 14.6 ppm. HRMS (ESI): *m/z* calcd. for $C_{16}H_{14}O_3S$ $[M + Na]^+$ 309.0556, found 309.0573.



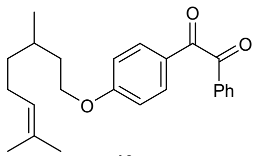
10m

1-(2-Chlorophenyl)-2-(4-methoxyphenyl)ethane-1,2-dione **(10m)** was prepared according to the general procedure **B** starting from 2-(2-chlorophenyl)-1-(4-methoxyphenyl)ethan-1-one **9m** (130 mg, 0.5 mmol, 1.0 eq) in 24 h. Yield = 63 mg, 0.23 mmol, 47%. Colourless solid. R_f = 0.6 (Hexane:Ether = 8:2). All characterization data are in agreement with that as reported in the literature.[20] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03−8.00 (m, 2H), 7.88 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.53−7.50 (m, 1H), 7.43−7.40 (m, 2H), 7.02−6.99 (m, 2H), 3.89 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.0, 190.9, 164.9, 134.5, 134.2, 134.0, 132.8 (2C), 132.3, 130.7, 127.4, 125.6, 114.4 (2C), 55.7 ppm.



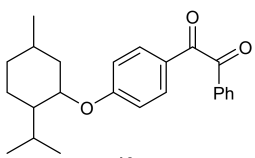
10n

1-(4-Methoxyphenyl)-2-(m-tolyl)ethane-1,2-dione **(10n)** was prepared according to the general procedure **B** starting from 1-(4-methoxyphenyl)-2-(*m*-tolyl)ethan-1-one **9n** (120 mg, 0.5 mmol, 1.0 eq) in 12 h. Yield = 84 mg, 0.33 mmol, 65%. Yellow oil. R_f = 0.6 (Hexane:Ether = 8:2). All characterization data are in agreement with that as reported in the literature.[22] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95−7.92 (m, 2H), 7.78−7.75 (m, 2H), 7.45−7.44 (m, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 6.98−6.95 (m, 2H), 3.87 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.2, 193.4, 165.0, 139.0, 135.7, 133.3, 132.4 (2C), 130.3, 128.9, 127.3, 126.2, 114.4 (2C), 55.7, 21.3 ppm.



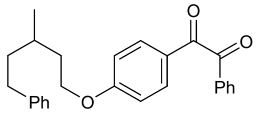
10o

1-(4-((3,7-Dimethyloct-6-en-1-yl)oxy)phenyl)-2-phenylethane-1,2-dione **(10o)** was prepared according to the general procedure **B** starting from 1-(4-((3,7-dimethyloct-6-en-1-yl)oxy)phenyl)-2-phenylethan-1-one **9o** (175 mg, 0.5 mmol, 1.0 eq) in 24 h. Yield = 117 mg, 0.32 mmol, 64%. Colourless oil. R_f = 0.5 (Hexane:Ether = 7:3). IR (neat): ν = 2924, 1593, 1258, 1213, 1163 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98−7.96 (m, 2H), 7.95−7.92 (m, 2H), 7.65−7.62 (m, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 6.97−6.95 (m, 2H), 5.11−5.08 (m, 1H), 4.11−4.04 (m, 2H), 2.05−1.95 (m, 2H), 1.89−1.82 (m, 1H), 1.72−1.58 (m, 8H), 1.42−1.36 (m, 1H), 1.27−1.19 (m, 1H), 0.96−0.95 (d, *J* = 6.5 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.1, 193.3, 164.8, 134.8, 133.4, 132.5 (2C), 131.6, 130.0 (2C), 129.1 (2C), 126.0, 124.6, 114.9 (2C), 66.9, 37.2, 35.9, 29.6, 25.8, 25.5, 19.6, 17.8 ppm. HRMS (ESI): *m/z* calcd. for $C_{24}H_{28}O_3$ [M + Na]$^+$ 387.1931, found 387.1956.



10p

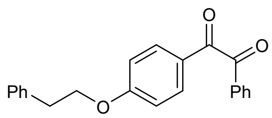
1-(4-((2-Isopropyl-5-methylcyclohexyl)oxy)phenyl)-2-phenylethane-1,2-dione **(10p)** was prepared according to general procedure **B** starting from 1-(4-((2-isopropyl-5-methylcyclohexyl)oxy)phenyl)-2-phenylethan-1-one **9p** (168.1 mg, 0.5 mmol, 1.0 eq) in 24 h. Yield = 120 mg, 0.33 mmol, 66%. Yellow solid. R_f = 0.5 (Hexane:Ether = 9:1). MP = 96-70 °C. IR (neat): ν = 2948, 1596, 1565, 1168, 644 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99−7.97 (m, 2H), 7.94−7.91 (m, 2H), 7.66−7.62 (m, 1H), 7.52−7.49 (m, 2H), 6.97−6.95 (m, 2H), 4.76 (s, 1H), 2.10−2.05 (m, 1H), 1.79−1.76 (m, 2H), 1.65−1.52 (m, 3H), 1.10−1.03 (m, 2H), 0.99−0.94 (m, 1H), 0.93 (d, *J* = 5.0 Hz, 3H), 0.82 (q, *J* = 10.0 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.1, 193.2, 164.1, 134.8, 133.4, 132.7 (2C), 130.1 (2C), 129.1 (2C), 125.6, 115.6 (2C), 74.2, 47.6, 37.6, 34.9, 29.4, 26.3, 24.9, 22.3, 21.1, 20.8 ppm. HRMS (ESI): *m/z* calcd. for $C_{24}H_{28}O_3$ [M + H]$^+$ 365.2112, found 365.2144.



10q

1-(4-((3-Methyl-5-phenylpentyl)oxy)phenyl)-2-phenylethane-1,2-dione **(10q)** was prepared according to the general procedure **B** starting from 2-(4-((3-methyl-5-phenylpentyl)oxy)phenyl)-1-phenylethan-1-one **9q** (164 mg, 0.5 mmol, 1.0 eq) in 24 h. Yield = 104 mg, 0.27 mmol, 55%. colourless solid. R_f = 0.5 (Hexane:Ether = 9:1). IR (neat): ν = 2924, 1594, 1258, 1213, 1163 cm^{-1}. ^{1}H NMR (500 MHz,

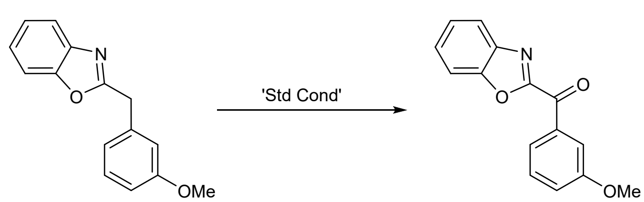
$CDCl_3$) δ 7.98−7.96 (m, 2H), 7.94−7.91 (m, 2H), 7.64−7.61 (m, 1H), 7.51−7.47 (m, 2H), 7.28−7.24 (m, 2H), 7.18−7.15 (m, 3H), 6.95−6.93 (m, 2H), 4.11−4.03 (m, 2H), 2.72−2.66 (m, 1H), 2.63−2.57 (m, 1H), 1.93−1.87 (m, 1H), 1.77−1.62 (m, 3H), 1.57−1.49 (m, 1H), 1.01 (d, J = 10.0 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.0, 193.3, 164.7, 142.7, 134.8, 133.4, 132.5 (2C), 130.0 (2C), 129.1 (2C), 128.5 (2C), 128.4 (2C), 126.0, 125.8, 114.9 (2C), 66.8, 38.9, 35.9, 33.4, 29.6, 19.6 ppm. HRMS (ESI): *m/z* calcd. for $C_{26}H_{26}O_3$ [M + Na] $^+$ 409.1775, found 409.1796.



10r

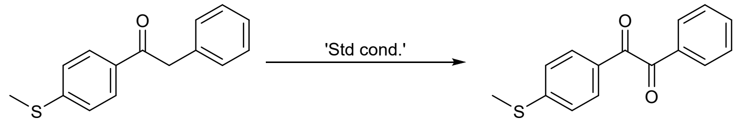
1-(4-((3,7-Dimethyloct-6-en-1-yl)oxy)phenyl)-2-phenylethane-1,2-dione **(10r)** was prepared according to the general procedure **B** starting from 2-(4-phenethoxyphenyl)-1-phenylethan-1-one **9r** (158 mg, 0.5 mmol, 1.0 eq) in 24 h. Yield = 96 mg, 0.29 mmol, 59%. colourless solid. MP = 72-76 ^{o}C. R_f = 0.5 (Hexane:Ether = 7:3). IR (neat): ν = 2930, 1584, 1456, 1193, 1188 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97−7.95 (m, 2H), 7.94−7.91 (m, 2H), 7.65−7.61 (m, 1H), 7.50−7.47 (m, 2H), 7.33−7.23 (m, 5H), 6.97−6.94 (m, 2H), 4.24 (t, J = 7.0 Hz, 2H), 3.11 (t, J = 7.0 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.0, 193.3, 164.4, 137.7, 134.8, 133.3, 132.5 (2C), 130.0 (2C), 129.1 (2C), 129.1 (2C), 128.7 (2C), 126.8, 126.2, 115.0 (2C), 69.2, 35.6 ppm. HRMS (ESI): *m/z* calcd. for $C_{22}H_{18}O_3$ [M + Na] $^+$ 353.1149, found 353.1666.

Representative procedure for the gram-scale synthesis of 2f



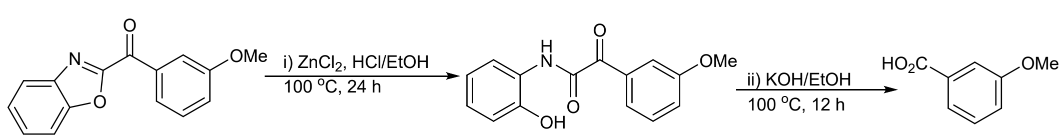
A 100 mL round bottom flask, equipped with a magnetic stirring bar, was charged with 2-(3-methoxybenzyl)benzo[*d*]oxazole **1f** (1.9 g, 7.9 mmol, 1.0 eq), DDQ (448 mg, 1.975 mmol, 25 mol%), $NiBr_2$ (345 mg, 1.58 mmol, 20 mol%). The RB was then attached with a condenser and then closed with a rubber septa. The vessel was evacuated and back-filled with oxygen (x 3). Anhydrous oxygenated DMF (32 mL) was added, and the reaction mixture was stirred at 120 ^{o}C (monitored by TLC). After completion, water (10 mL) was added to the residue and the resulting mixture was extracted with EtOAc (50 mL x 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude reaction mixture was purified by flash column chromatography on silica gel to provide the corresponding product **2f** (1.3 g, 5.1 mmol, 64%).

Representative procedure for the gram-scale synthesis of 10f



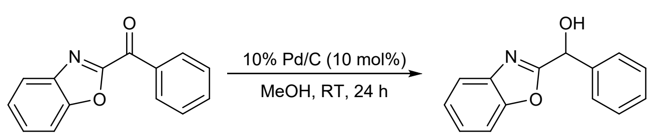
A 100 mL round bottom flask, equipped with a magnetic stirring bar, was charged with 1-(4-(methylthio)phenyl)-2-phenylethan-1-one **9f** (1.9 g, 7.8 mmol, 1.0 eq), DDQ (443 mg, 1.95 mmol, 25 mol%), $NiBr_2$ (341 mg, 1.56 mmol, 20 mol%). The RB was then attached with a condenser and then closed with a rubber septum. The vessel was evacuated and back-filled with oxygen (x 3). Anhydrous oxygenated DMF (31.0 mL) was added and the reaction mixture was stirred at 120 ^oC (monitored by TLC). After completion, water (10 mL) was added to the residue, and the resulting mixture was extracted with EtOAc (50 mL x 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude reaction mixture was purified by flash column chromatography on silica gel to provide the corresponding product **10f** (1.4 g, 5.49 mmol, 70%).

Synthesis of carboxylic acid 6 from 2f



A 50 mL R.B. flask was charged with benzo[*d*]oxazol-2-yl(3-methoxyphenyl)methanone (**2f**) (506 mg, 2.0 mmol, 1.0 eq), $ZnCl_2$ (545 mg, 4.0 mmol, 2.0 eq), 14% HCl (14 mL) and EtOH (14 mL). The reaction mixture was stirred at 100 ºC using a coil-condenser for 24 h. After completion, the resulting mixture was diluted with DCM (25 mL) and extracted with saturated aqueous $NaHCO_3$ solution (3 x 40 mL). The DCM layer was dried over Na_2SO_4 and concentrated in vacuum to give the crude amide **11'** (433.6 mg, 1.6 mmol, 80%), which was used for the next step without further purification. A 15 mL reaction tube charged with the crude amide (433.6 mg, 1.6 mmol, 1.0 eq) as obtained above and crushed KOH (538 mg, 9.6 mmol, 6.0 eq). Subsequently the mixture was heated in ethanol (13.0 mL) for 12 h at 100 °C. After completion, water was added to the reaction mixture followed by extraction with DCM (3 x 25 mL). These DCM extracts were discarded and the aqueous layer was acidified with 1 (N) $NaHSO_4$ until pH~2 followed by extraction with DCM (3 x 25 mL). DCM layers were combined and dried over Na_2SO_4 which was obtained from acidified aqueous layer. DCM was concentrated in vacuum to give the crude 3-methoxybenzoic acid (**11**), which was further purified by column chromatography over silica-gel. Brown solid (195 mg, 1.28 mmol, 80%, Overall yield of compound **11** starting from **1f** = 64%). R_f = 0.4 (Hexane:EtOAc = 7:3). ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 7.55−7.53 (m, 1H), 7.45−7.45 (m, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.20−7.18 (m, 1H), 3.81 (s, 1H) ppm. ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 167.2, 159.2, 132.2, 129.7, 121.6, 118.9, 113.9, 55.2 ppm.[23]

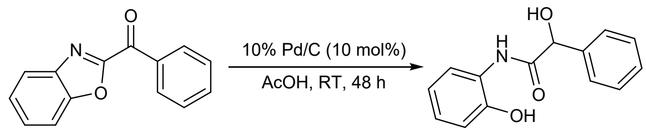
Reduction of the keto group in 2a to hydroxy 12



2a **12**

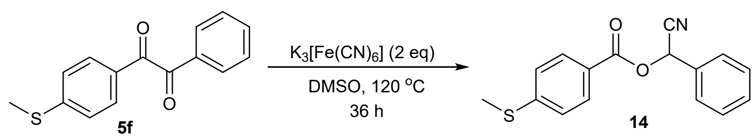
A 10 mL R.B. flask equipped with stirrer bar and septum was charged with benzo[*d*]oxazol-2-yl(phenyl)methanone (**2a**) (112 mg, 0.5 mmol, 1.0 eq) and 10% Pd/C (5.0 mg, 0.05 mmol, 0.1 eq). The RB flask was evacuated and back-filled with H_2 (x3). Methanol (5.0 mL) was added to the RB flask containing the reaction mixture, and the reaction was stirred at room temperature. The reaction progress was monitored via TLC. After completion of the reaction, it was filtered to remove the Pd/C using a celite filter, the filtrate was evaporated, and the residue was purified directly via column chromatography using hexane:ethyl acetate (9:1) as eluent to give the product **12** as a white solid (101 mg, 0.45 mmol, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 4 Hz, 1H), 7.53−7.51 (m, 2H), 7.45 (t, *J* = 4 Hz, 1H), 7.38−7.28(m, 5H), 6.05 (s, 1H), 5.19 (bs, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 151.1, 140.2, 138.91, 128.8, 128.7, 126.8, 125.3, 124.6, 120.1, 110.9, 70.5 ppm.

Reduction of the oxazole ring in 2a to an amide 13



A 10 mL R.B. flask equipped with stirrer bar and septum was charged with benzo[*d*]oxazol-2-yl(phenyl)methanone (**2a**) (112 mg, 0.5 mmol, 1.0 eq) and 10% Pd/C (5.0 mg, 0.05 mmol, 0.1 eq). The RB flask was evacuated and back-filled with H_2 (x3). Glacial acetic acid (1.2 mL) was added to the RB flask containing the reaction mixture, and the reaction was stirred at room temperature for 48h. The reaction progress was monitored via TLC. After completion of the reaction, it was filtered to remove the Pd/C using a celite filter, the filtrate was evaporated, and the residue was purified via column chromatography using hexane: ethyl acetate (9:1) as eluent to give the product **13** as a white solid (73 mg, 0.30 mmol, 60%). ^{1}H NMR (500 MHz, DMSO) δ 10.16 (s, 1H), 9.44 (s, 1H), 8.10 (d, J = 10 Hz, 1H), 7.46 (d, J = 7 Hz, 2H), 7.37–7.28 (m, 3H), 6.91–6.84 (m, 3H), 6.77–6.74 (m, 1H), 5.11 (d, J = 4.5 Hz, 1H) ppm. ^{13}C NMR (126 MHz, DMSO) δ 170.7, 146.7, 141.2, 128.6, 128.1, 127.1, 126.5, 124.3, 119.6, 119.4, 115.2, 74.1 ppm. HRMS (ESI): *m/z* calcd. for $C_{14}H_{13}NNaO_3$ [M + Na] $^+$ 266. 0788, found 266.0781.

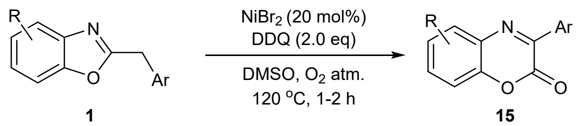
Synthesis of Cyanohydrin ester 14 from 5f



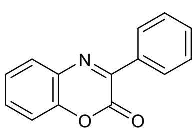
A 20 mL crimp cap vial was charged with 1-(4-(methylthio)phenyl)-2-phenylethane-1,2-dione **5f** (128 mg, 0.5 mmol, 1.0 eq), and potassium ferricyanide (329 mg, 1.0 mmol, 2.0 eq). The vial was then closed with the help of a crimper tool. To it, oxygenated DMSO (0.5 mL) was added and the reaction mixture was stirred at 120 ºC for 36 h (monitored by TLC). After cooling, the reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (10 mL). The aqueous layer was extracted with ethyl acetate (3 x 25 mL), and the organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel to provide the corresponding cyanohydrin ester **14**. Yield =

99 mg, 0.35 mmol, 70%. MP. = 118-120 °C. Yellow solid. R_f = 0.5, (Hexane: Ethyl acetate = 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96−7.96 (m, 2H), 7.62−7.59 (m, 2H), 7.49−7.47 (m, 3H), 7.27−7.25 (m, 2H), 6.66 (s, 1H), 2.52 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.5, 147.6, 132.1, 130.5, 130.5 (2C), 129.4 (2C), 128.0 (2C), 125.1 (2C), 124.1, 116.4, 63.4, 14.8 ppm.[1k]

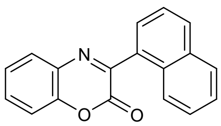
General procedure C: Synthesis of benzoxazinones 15



A 20 mL crimp cap vial, equipped with a magnetic stirring bar, was charged with **1** (0.5 mmol, 1.0 eq), DDQ (227 mg, 1.0 mmol, 2.0 eq) and $NiBr_2$ (21.8 mg, 0.05 mmol, 20 mol%). The vial was then closed with a cap by a crimper tool followed by evacuated and back-filled with oxygen (x 3). To it, dry DMSO (1.0 mL) was added and the reaction mixture was stirred at 120 ºC till completion (monitored by TLC). After cooling, the reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (10 mL). The aqueous layer was extracted with ethyl acetate (3 x 25 mL) The organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel to provide the corresponding benzoxazinone **15**. The characterization data including ^{1}H, ^{13}C and ^{19}F (if any) NMR products are given below:

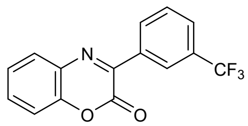

15a

3-Phenyl-2H-benzo[b][1,4]oxazin-2-one **(15a)** was prepared according to the general procedure **C** starting from 2-benzylbenzo[*d*]oxazole **1a** (105 mg, 0.5 mmol, 1.0 eq) in 15 minutes. Yield = 67 mg, 0.3 mmol, 60%. Colourless solid. R_f = 0.7 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[24] ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32−8.31 (m, 2H), 7.82−7.81 (m, 1H), 7.53−7.46 (m, 4H), 7.37−7.34 (m, 1H), 7.30−7.29 (1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.3, 150.8, 146.5, 134.2, 131.7, 131.5, 131.2, 129.5 (3C), 128.4 (2C), 125.6, 116.2 ppm.


15b

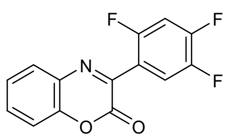
3-(Naphthalen-1-yl)-2H-benzo[b][1,4]oxazin-2-one **(15b)** was prepared according to the general procedure **C** starting from 2-(naphthalen-1-ylmethyl)benzo[*d*]oxazole **1j** (129 mg, 0.5 mmol, 1.0 eq) in 1-2 h (TLC). Yield

= 87 mg, 0.32 mmol, 64%. Brown solid. R_f = 0.7 (Hexane:Ether = 9:1). All characterization data are in agreement with that as reported in the literature.[24] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07−8.05 (m, 1H), 8.01 (d, *J* = 10.0 Hz, 1H), 7.94−7.92 (m, 1H), 7.91−7.89 (m, 1H), 7.86−7.84 (m, 1H), 7.61−7.57 (m, 2H), 7.55−7.51 (m, 2H), 7.45−7.41 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0, 153.0, 146.8, 134.0, 131.8, 131.6, 131.5, 131.3, 131.2, 129.8, 128.8, 128.6, 127.2, 126.4, 125.9, 125.0, 125.0, 116.6 ppm.



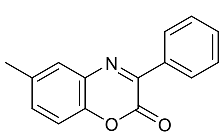
15c

3-(3-Trifluoromethyl)phenyl)-2H-benzo[b][1,4]oxazin-2-one **(15c)** was prepared according to the general procedure **C** starting from 2-(3-(trifluoromethyl)benzyl)benzo[*d*]oxazole **1aa** (138 mg, 0.5 mmol, 1.0 eq) in 1-2 h (TLC). Yield = 121 mg, 0.4 mmol, 83%. Yellow solid. R_f = 0.6 (Hexane:Ether = 8:2). All characterization data are in agreement with that as reported in the literature.[25] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.58-7.48 (m, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 149.3, 146.7, 134.9, 132.9, 132.0, 131.6, 131.3, 131.0, 129.9, 129.1, 128.0 (q, *J* = 4 Hz, 1C), 126.4 (q, *J* = 4 Hz, 1C), 126.0, 116.4 ppm. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.57 ppm.



15d

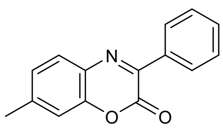
3-(2,4,5-Trifluorophenyl)-2H-benzo[b][1,4]oxazin-2-one **(15d)** was prepared according to general procedure **C** starting from 2-(2,4,5-trifluorophenyl)benzo[*d*]oxazole **1bb** (132 mg, 0.5 mmol, 1.0 eq) in 1-2 h (TLC). Yield = 97 mg, 0.35 mmol, 70%. Yellow solid. MP = 70-75 °C. R_f = 0.4 (Hexane:Ether = 7:3). IR (neat): ν = 1517, 1499, 1430, 1093, 742, cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73−7.70 (m, 1H), 7.37−7.33 (m, 2H), 7.31−7.28 (m, 1H), 7.09 (m, 1H), 6.94−6.90 (m, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.8, 150.8, 141.7, 130.1, 126.6 (2C), 125.1 (2C), 121.1 (2C), 119.5 (d, J_{C-F} = 21.0 Hz, 1C), 110.9 (2C), 106.6 (q, J_{C-F} = 6.0 Hz, 1C) ppm. ^{19}F NMR (565 MHz, $CDCl_3$) δ -112.25−-112.26 (m, 1F), -129.12−-129.17 (m, 1F), -140.75−-140.84 (m, 1F) ppm. HRMS (ESI): Anal. calcd. for $C_{14}H_6F_3NO_2$, C, 60.66; H, 2.18; N, 5.05; Found, C, 60.45; H, 2.50; N, 4.90.



15e

6-Methyl-3-phenyl-2H-benzo[b][1,4]oxazin-2-one **(15e)** was prepared according to the general procedure **C** starting from 2-benzyl-5-methylbenzo[*d*]oxazole **1k** (112 mg, 0.5 mmol, 1.0 eq) in 1-2 h (TLC). Yield

= 56 mg, 0.24 mmol, 47%. colourless solid. R_f = 0.7 (Hexane:Ether = 8:2). All characterization data are in agreement with that as reported in the literature.[25] ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33−8.31 (m, 2H), 7.65 (s, 1H), 7.54−7.48 (m, 3H), 7.32 (dd, *J* = 12.0 Hz, 1.8 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 2.46 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.7, 150.9, 144.6, 135.6, 134.4, 132.3, 131.6, 131.5, 129.6 (2C), 129.5, 128.5 (2C), 115.9, 21.0 ppm.


15f

7-Methyl-3-phenyl-2H-benzo[b][1,4]oxazin-2-one **(15f)** was prepared according to the general procedure **C** starting from 2-benzyl-6-methylbenzo[*d*]oxazole **1l** (112 mg, 0.5 mmol, 1.0 eq) in 1-2 h (TLC). Yield = 51 mg, 0.21 mmol, 43%. Colourless solid. R_f = 0.7 (Hexane:Ether = 8:2). All characterization data are in agreement with that as reported in the literature.[24] IR (neat): ν = 1732, 1443, 1101, 946, 797 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32−8.30 (m, 2H), 7.72−7.71 (m, 1H), 7.51−7.47 (m, 3H), 7.19 (d, *J* = 12.0 Hz, 1H), 7.12 (s, 1H), 2.48 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.7, 149.8, 146.5, 142.7, 134.4, 131.3, 129.9, 129.4 (2C), 129.2, 128.5 (2C), 126.9, 116.4, 21.9 ppm.

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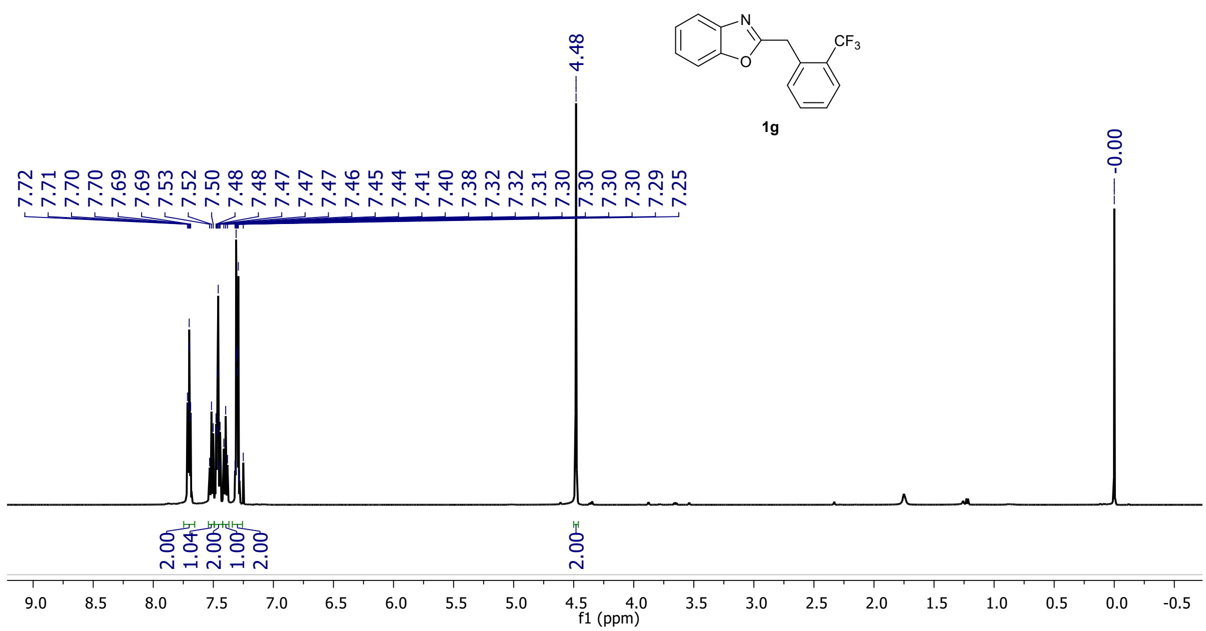
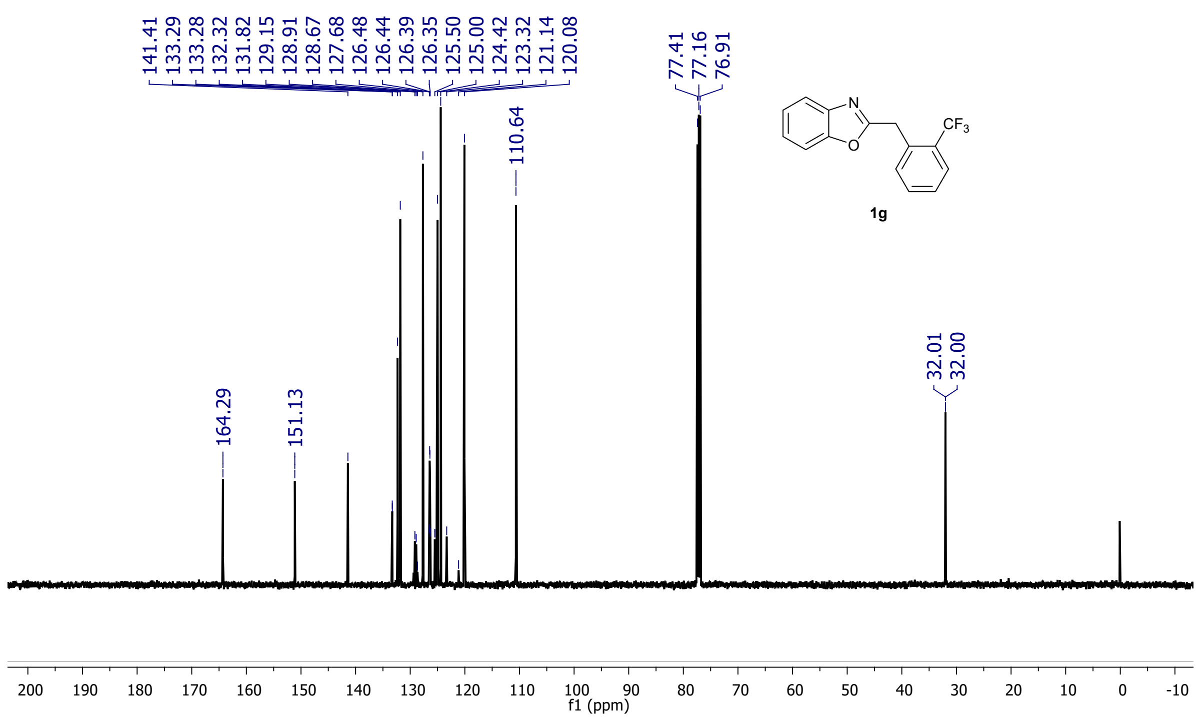
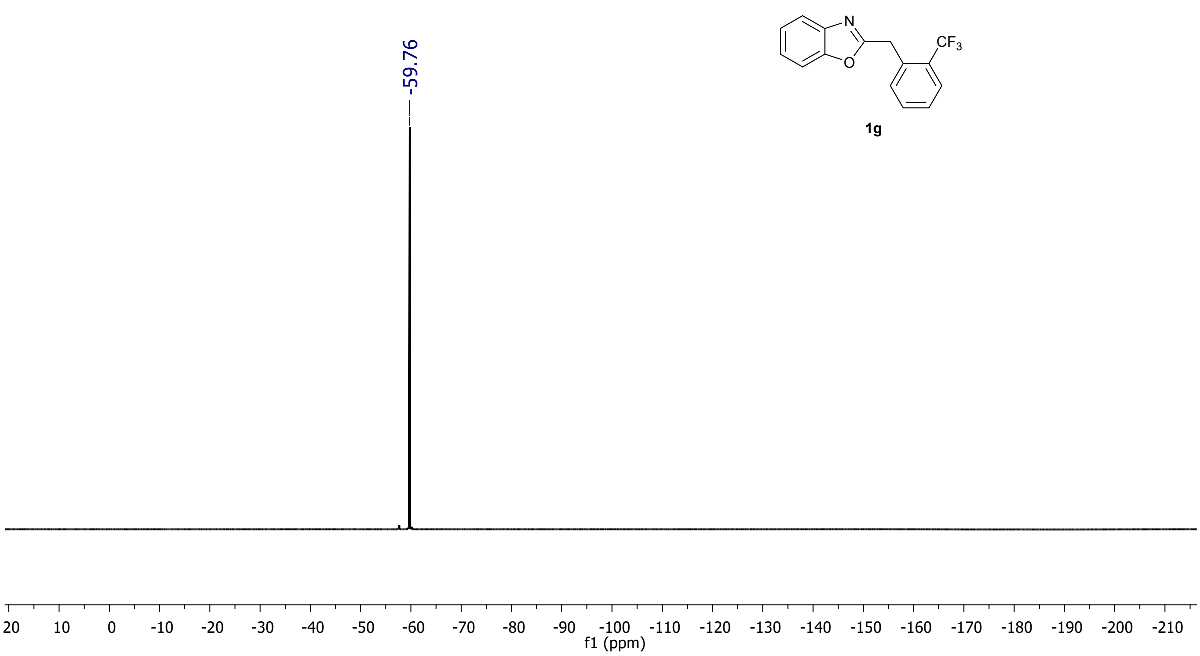
^{1}H NMR (500 MHz, $CDCl_3$)



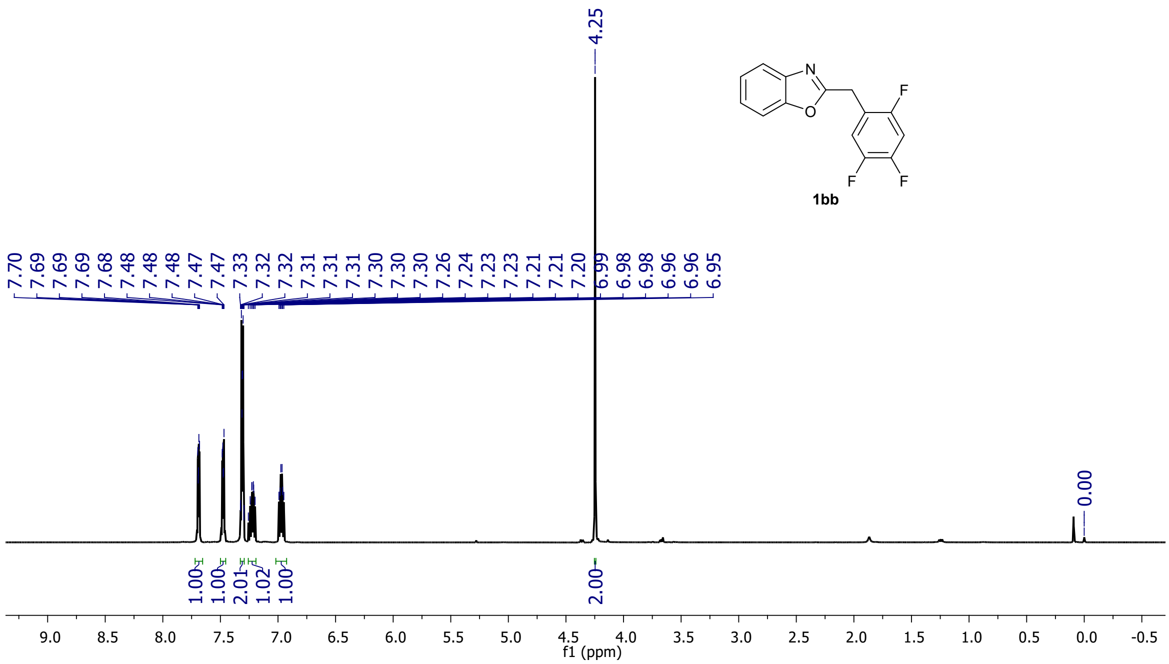
^{13}C NMR (126 MHz, $CDCl_3$):



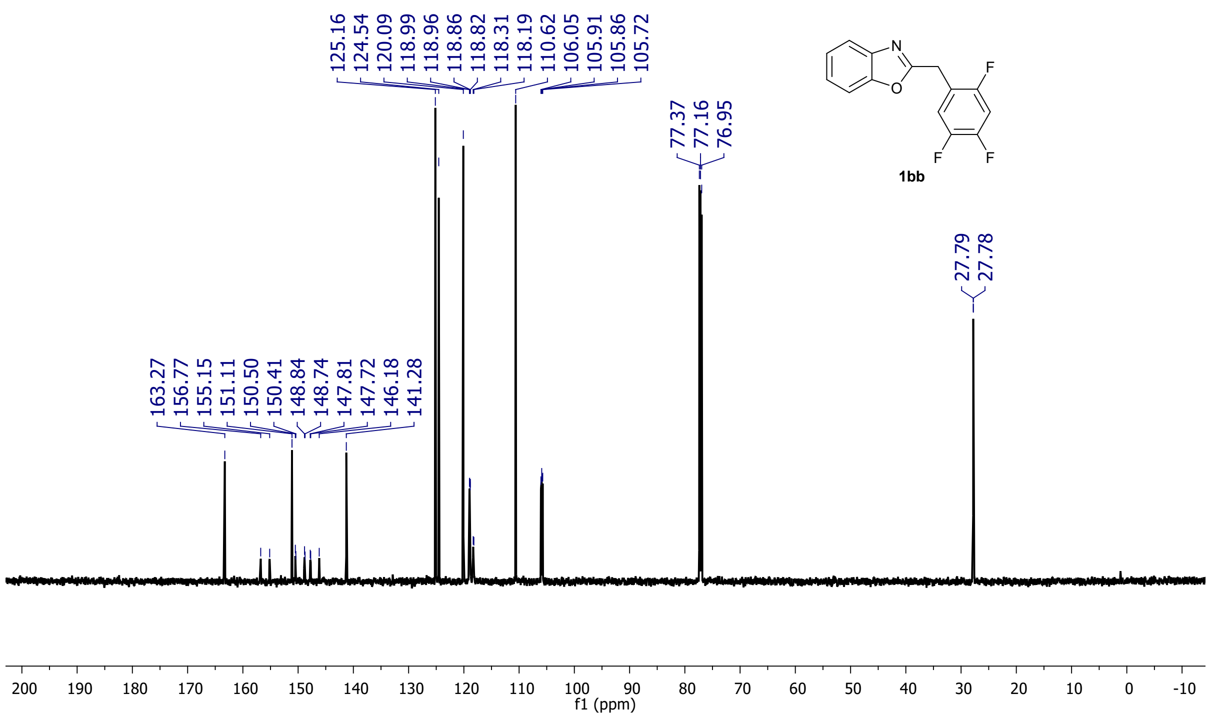
^{19}F NMR (471 MHz, $CDCl_3$)



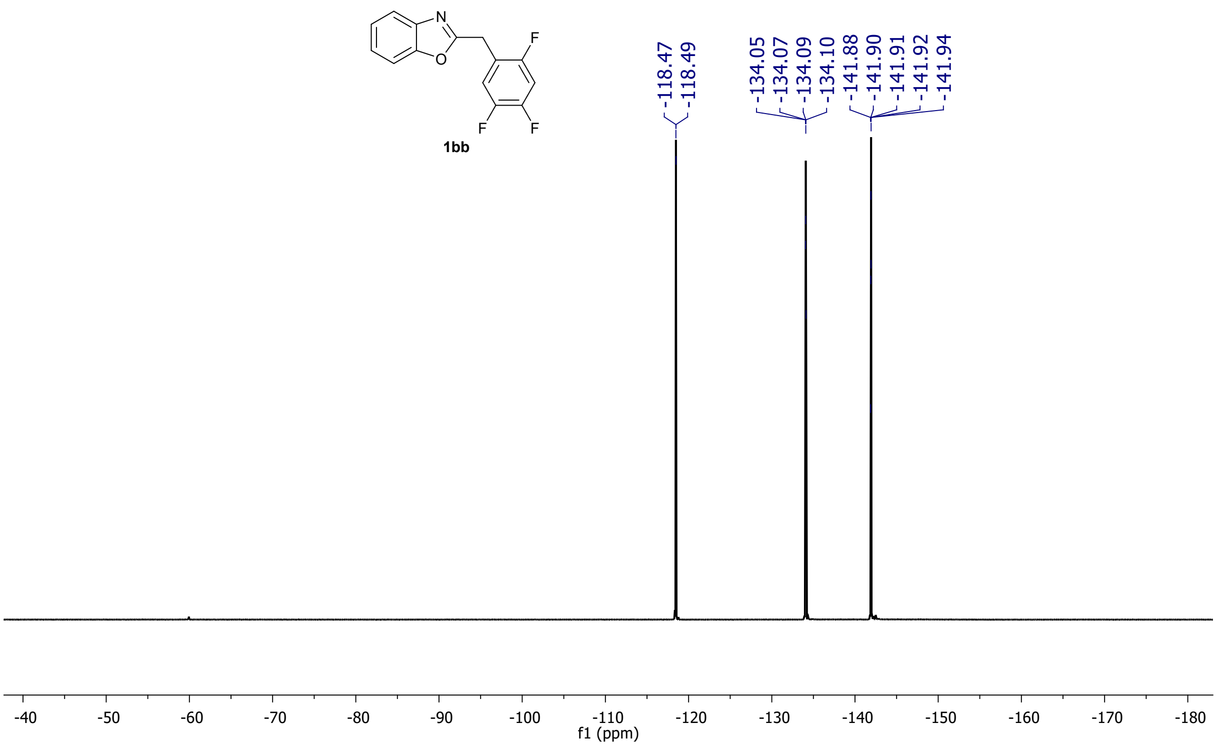
^{1}H NMR (500 MHz, $CDCl_3$)



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



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



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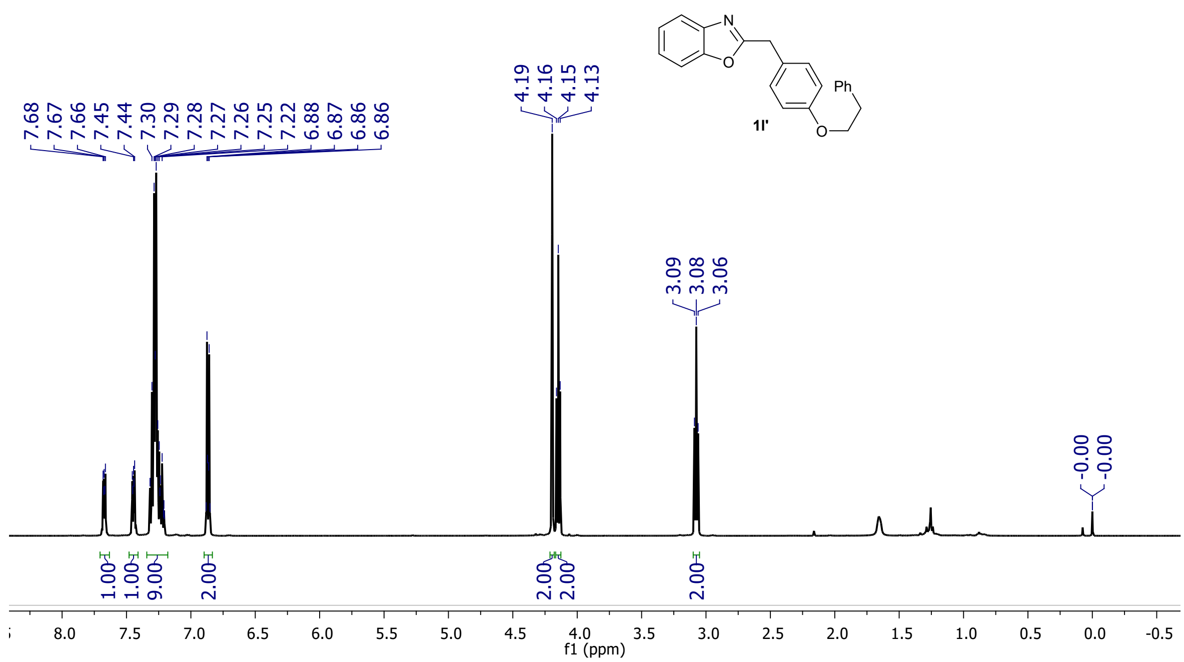

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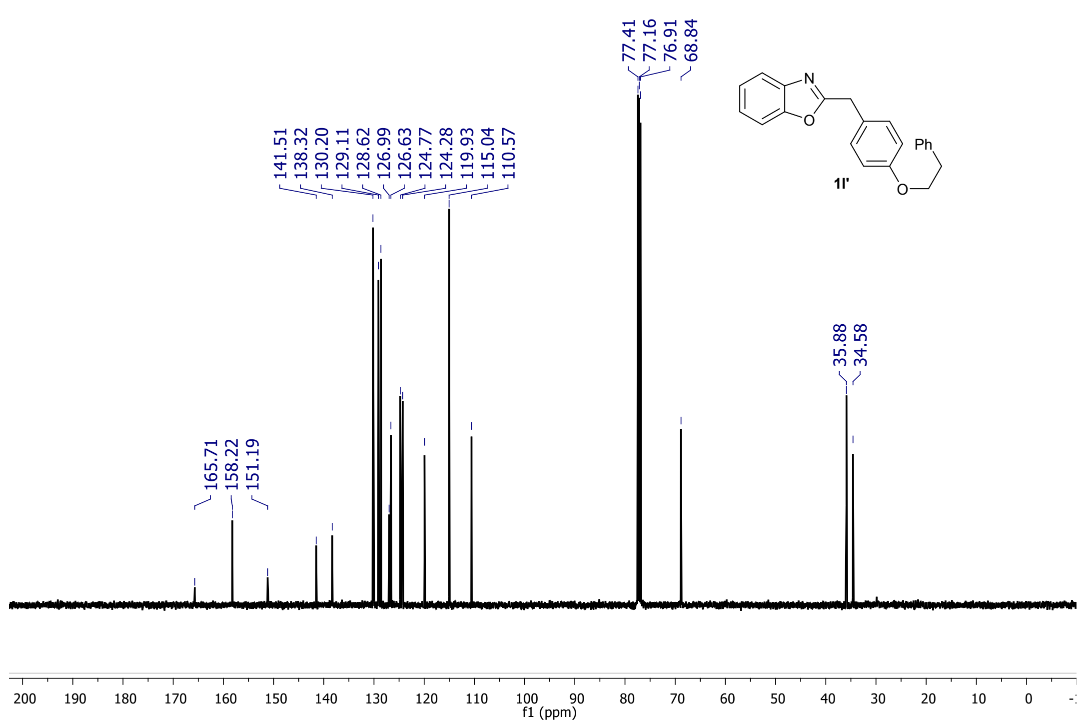

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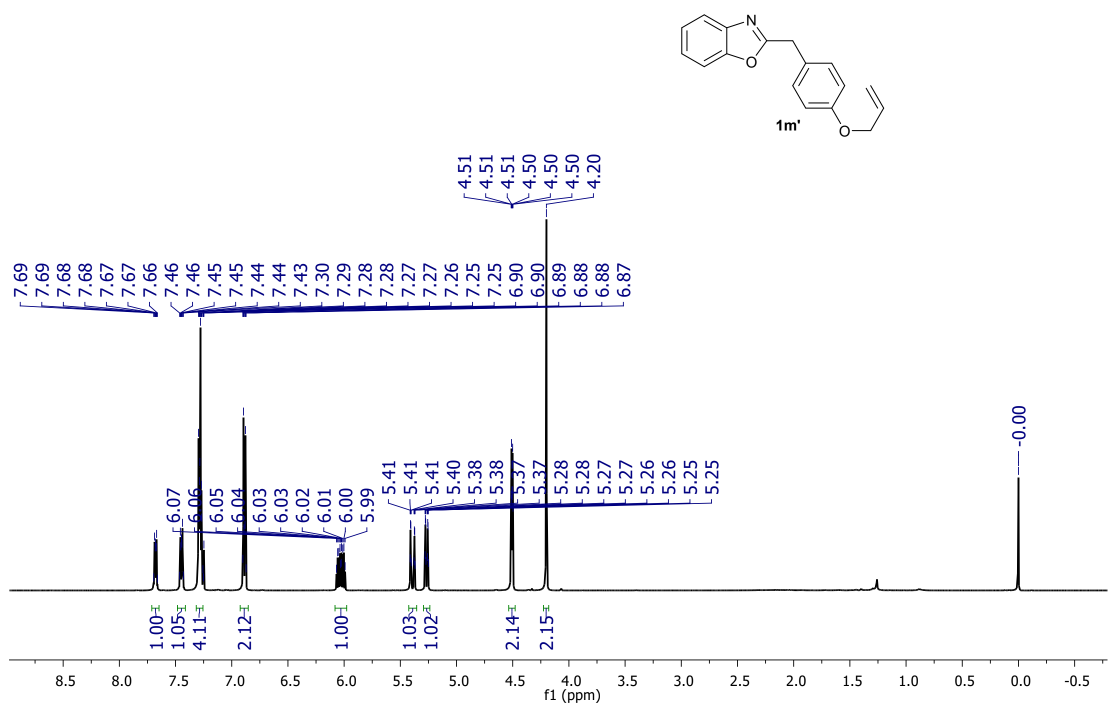

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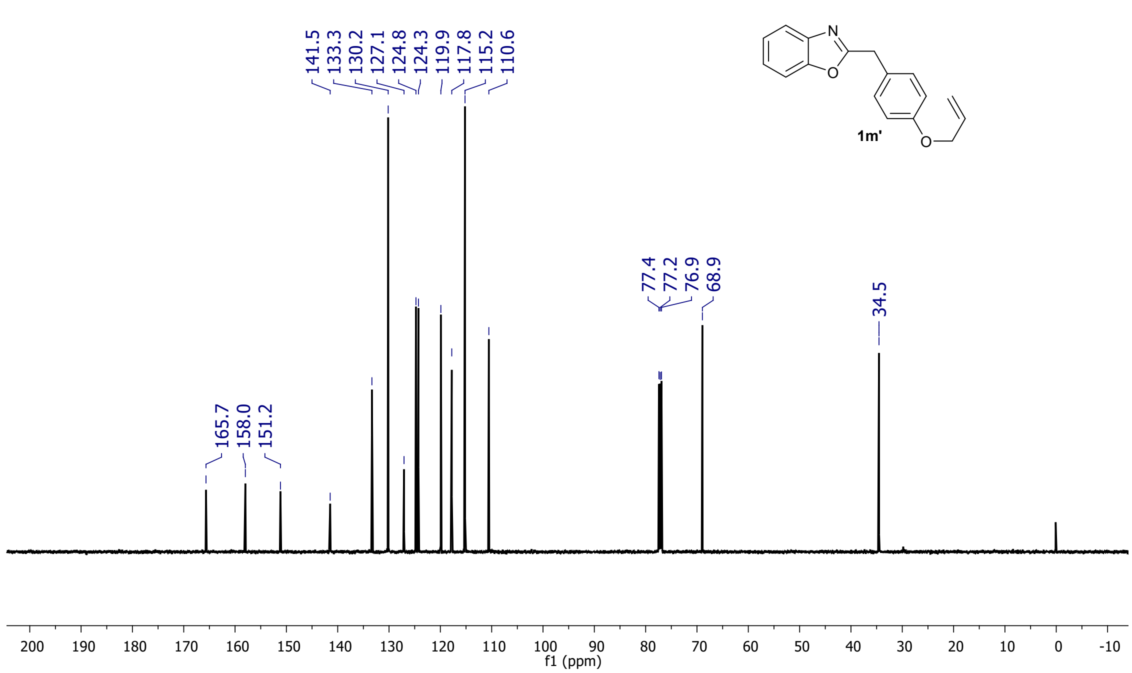

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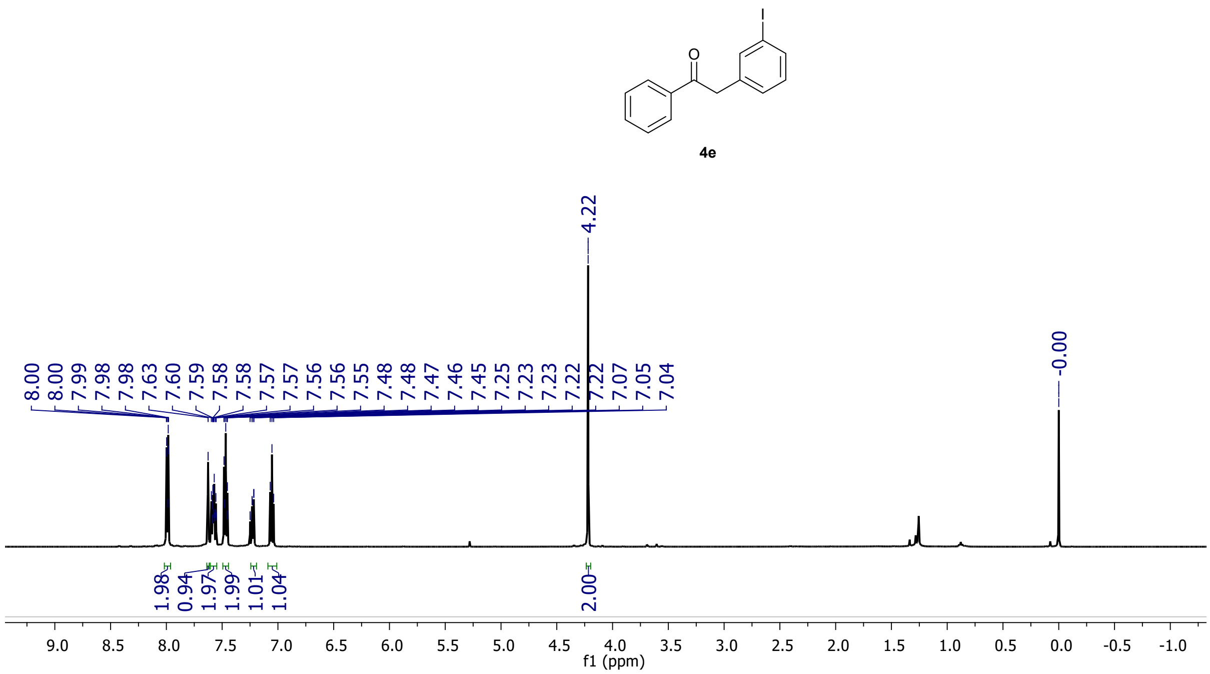

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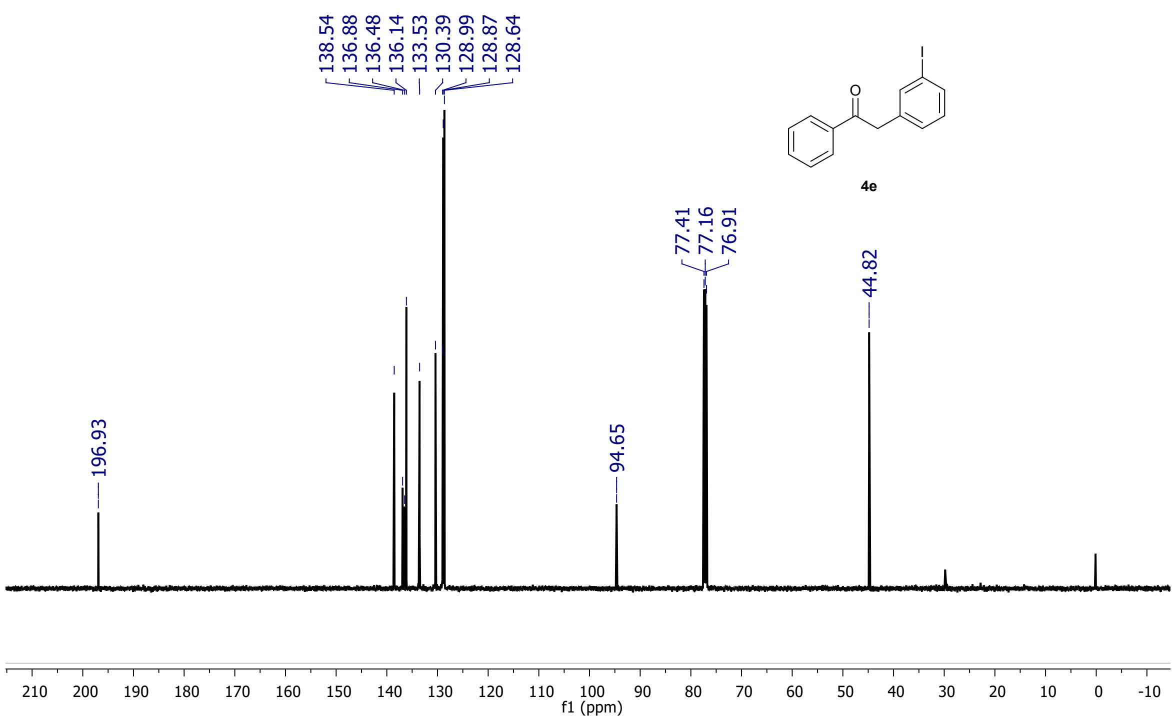

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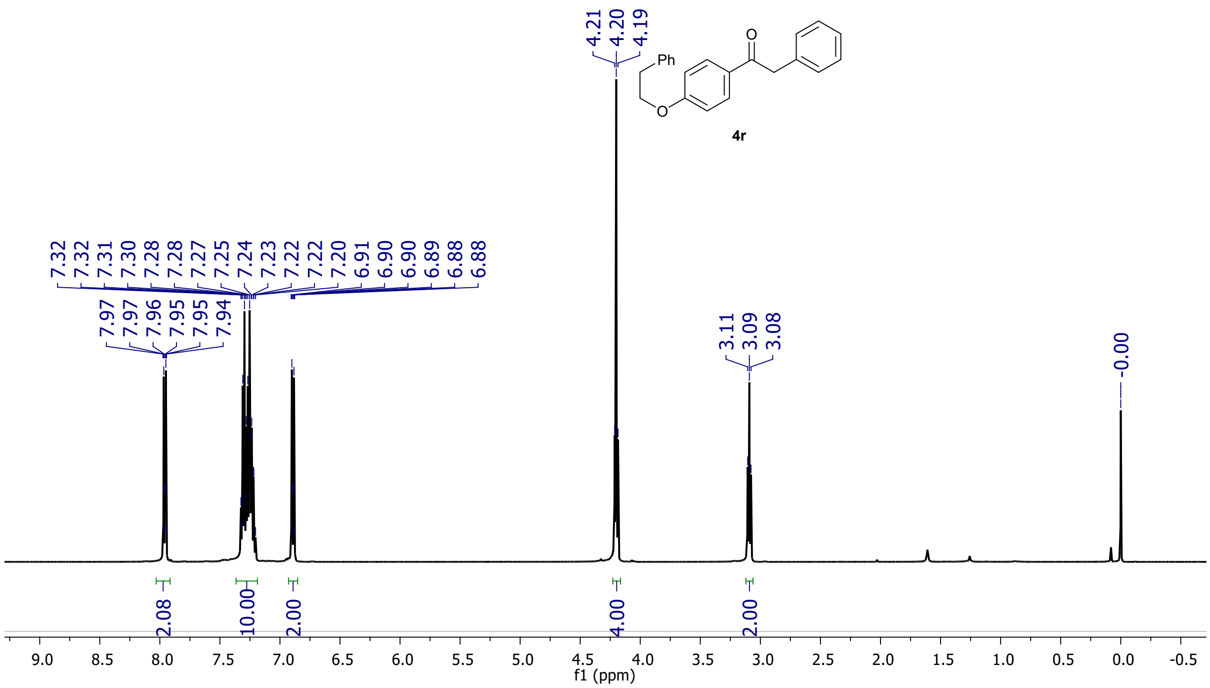

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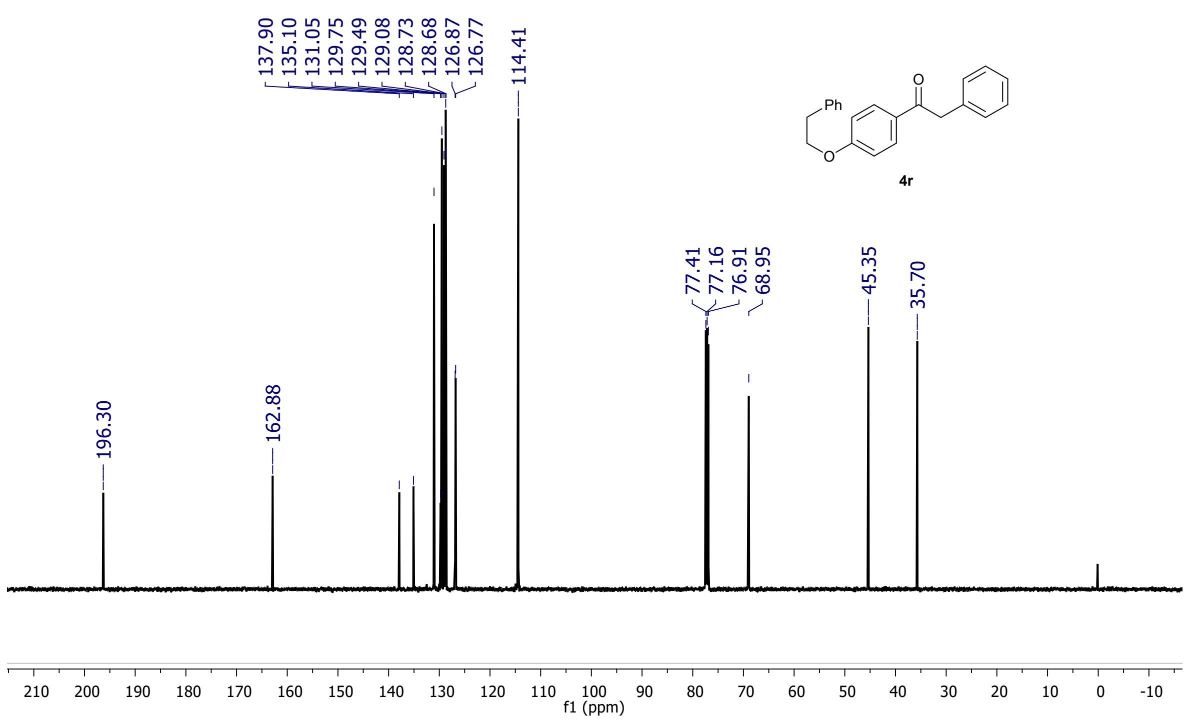

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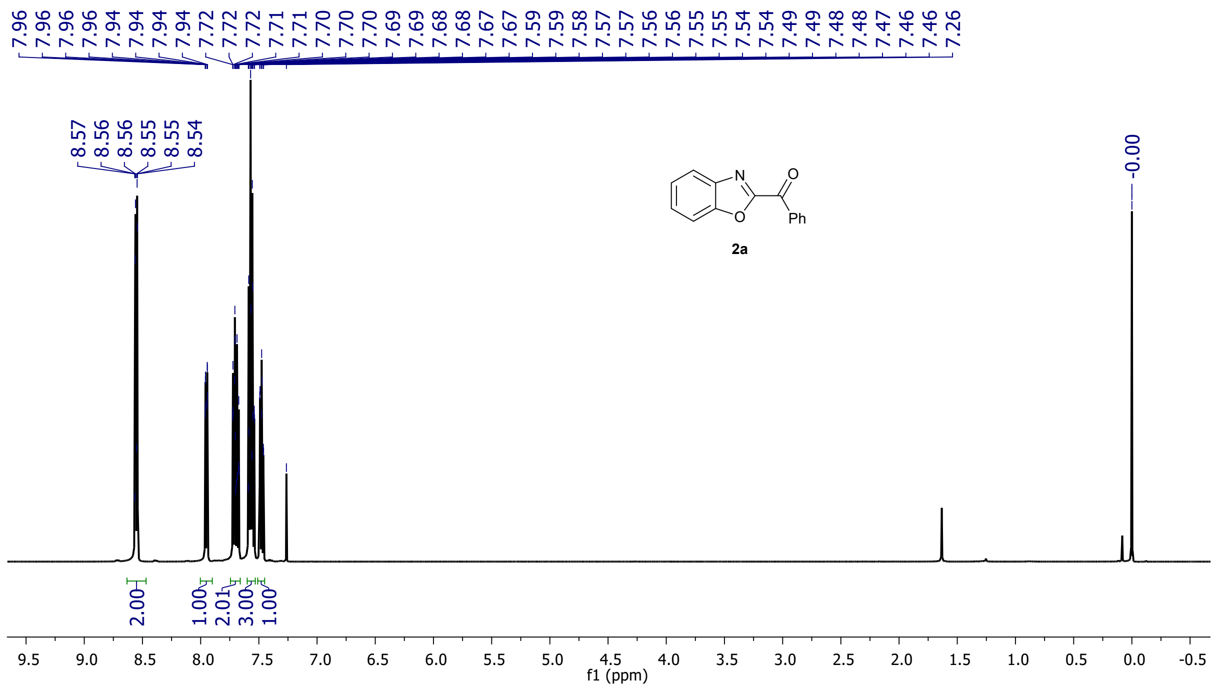

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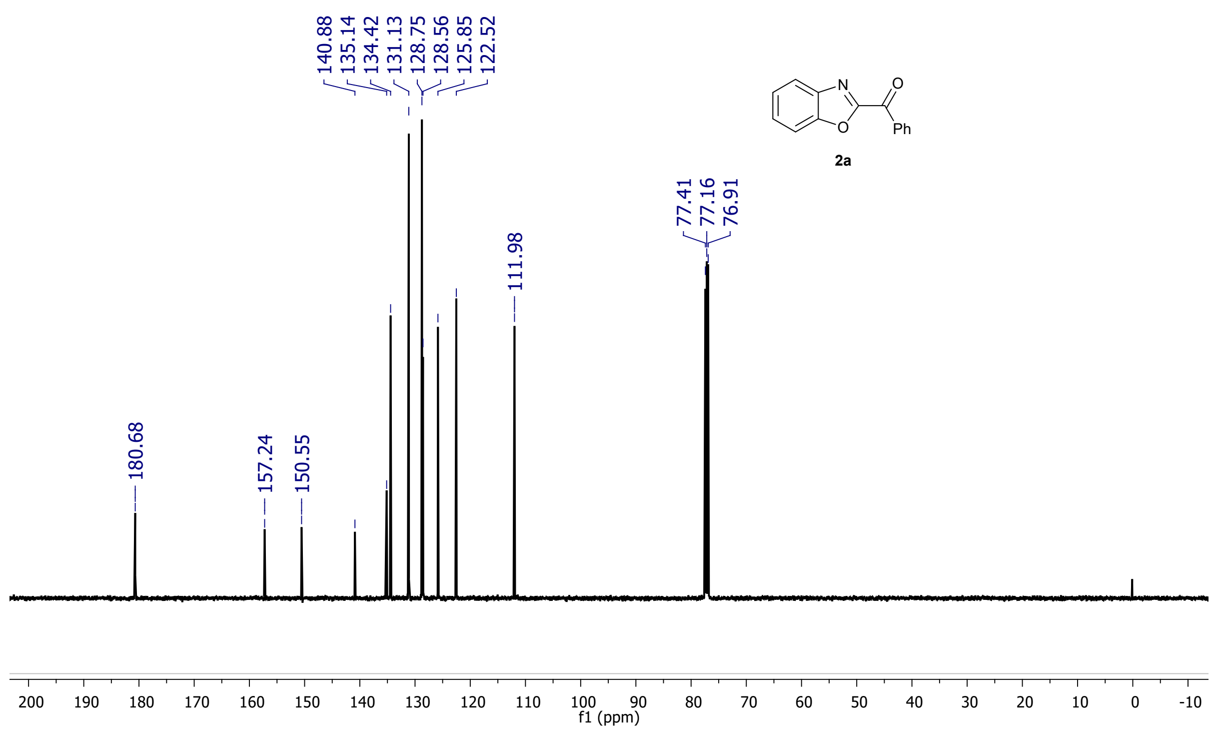

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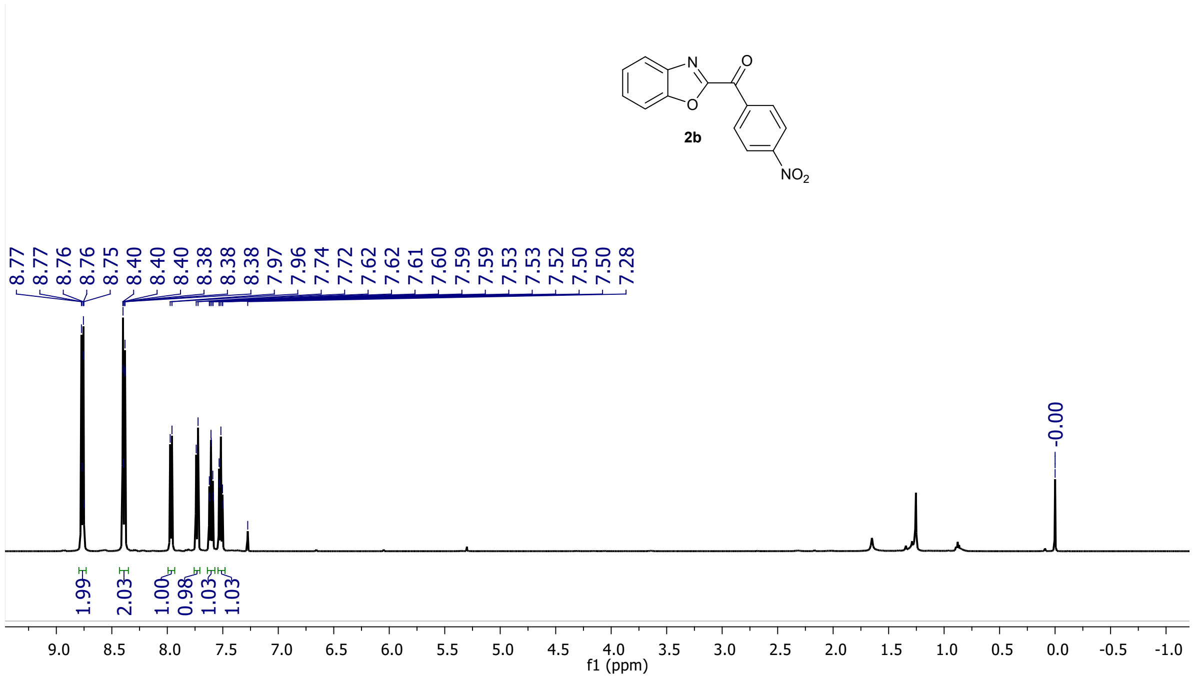

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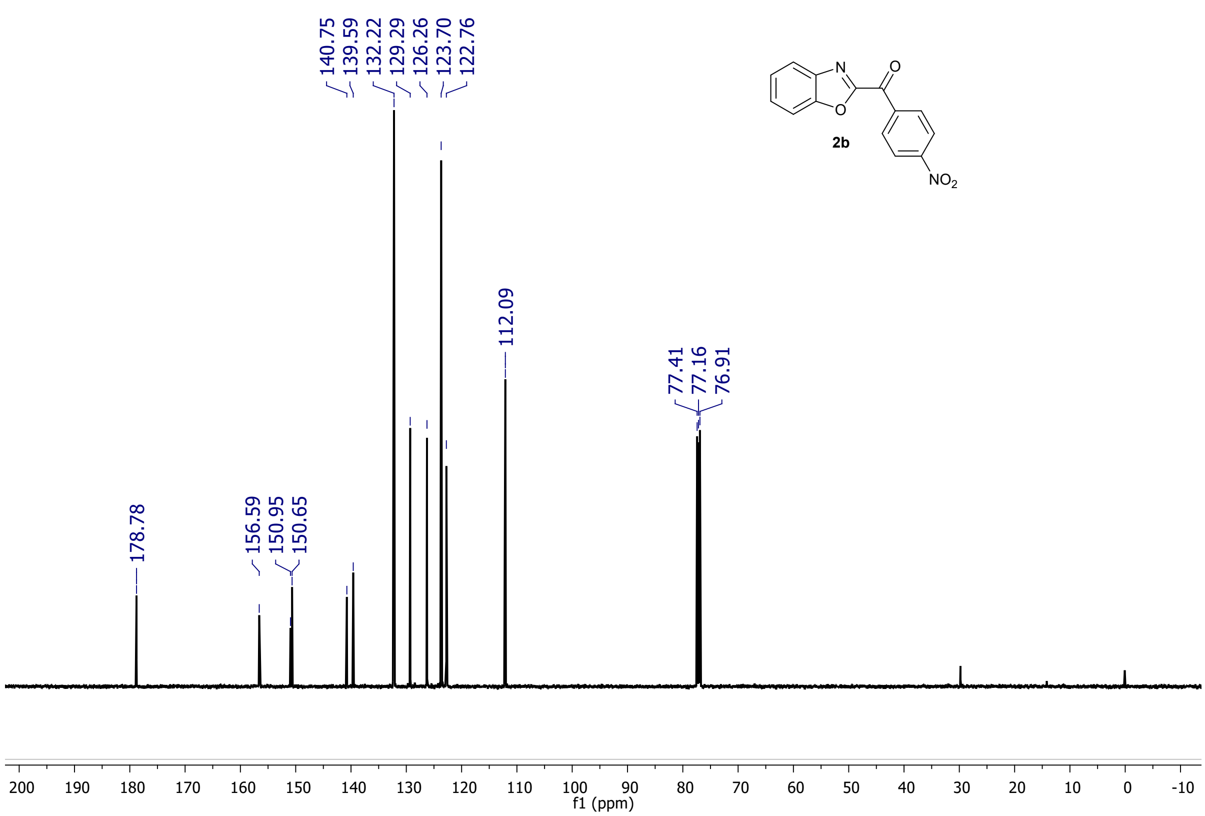
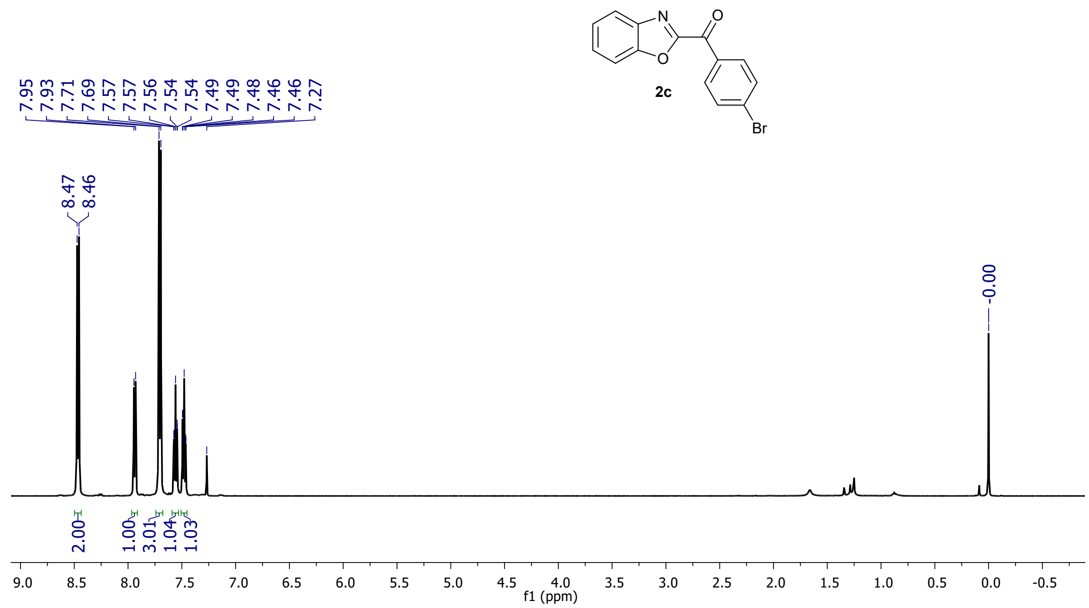


^{1}H NMR (500 MHz, $CDCl_3$)



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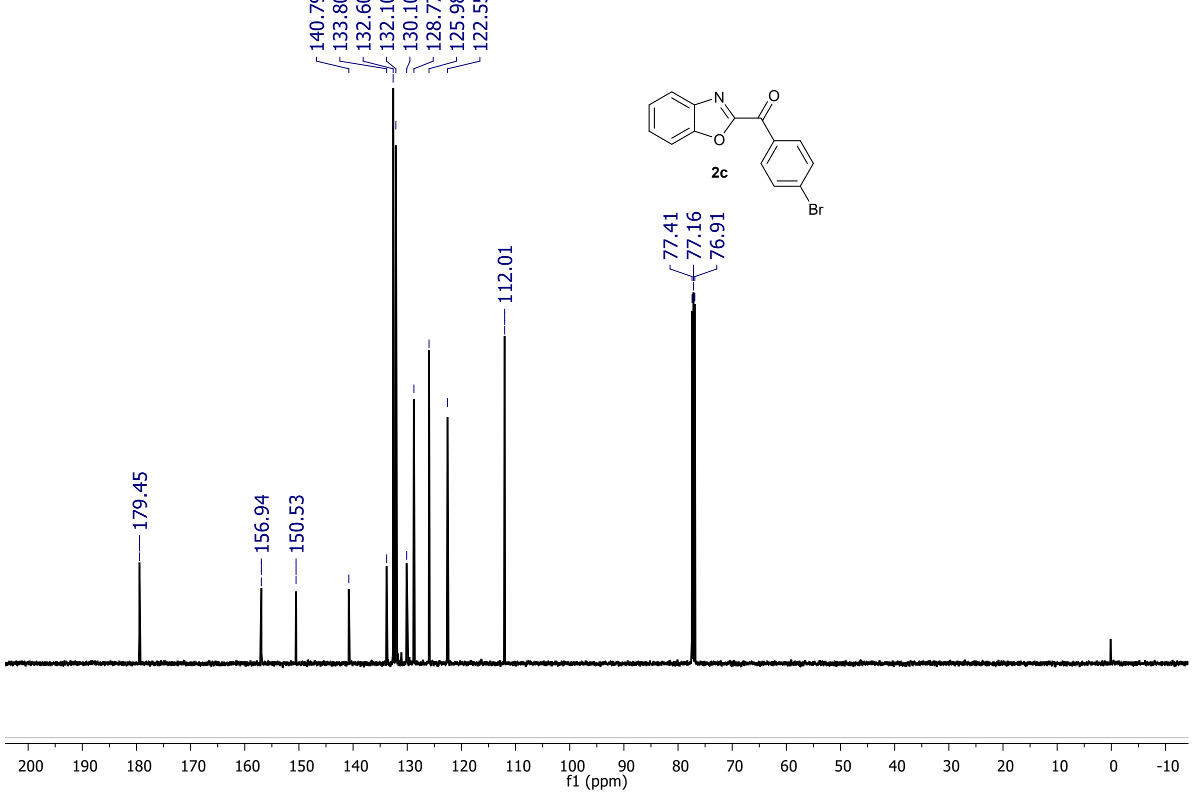

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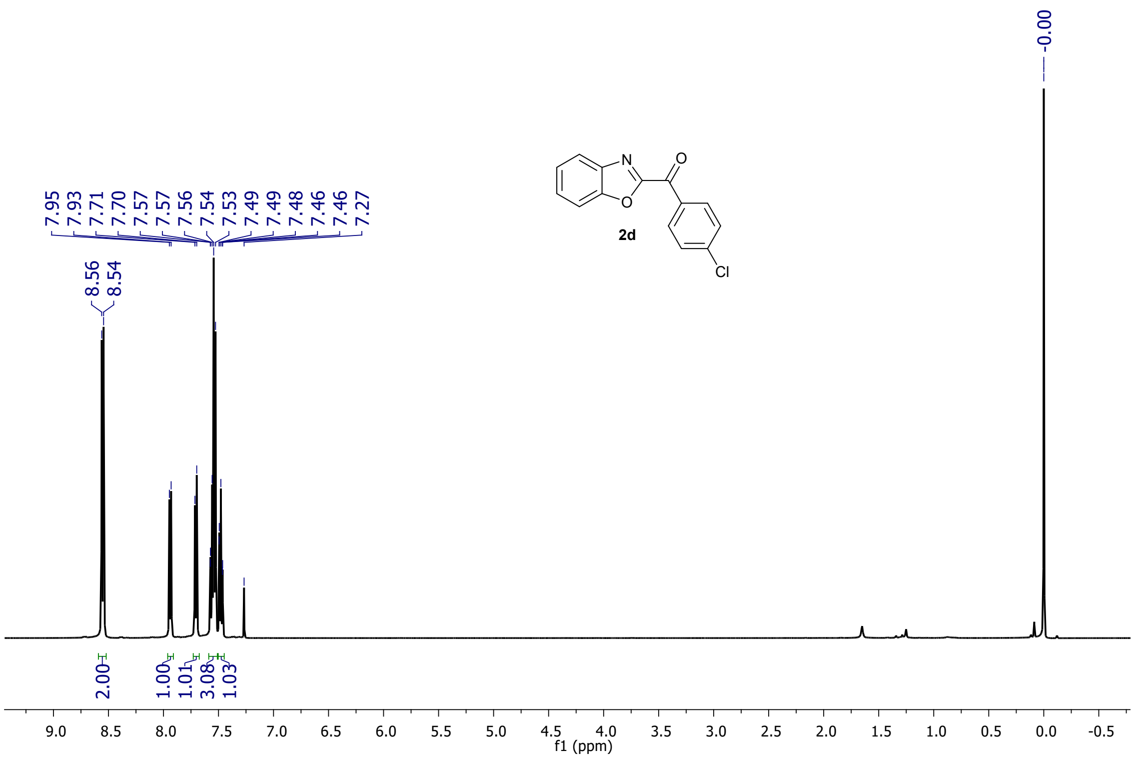
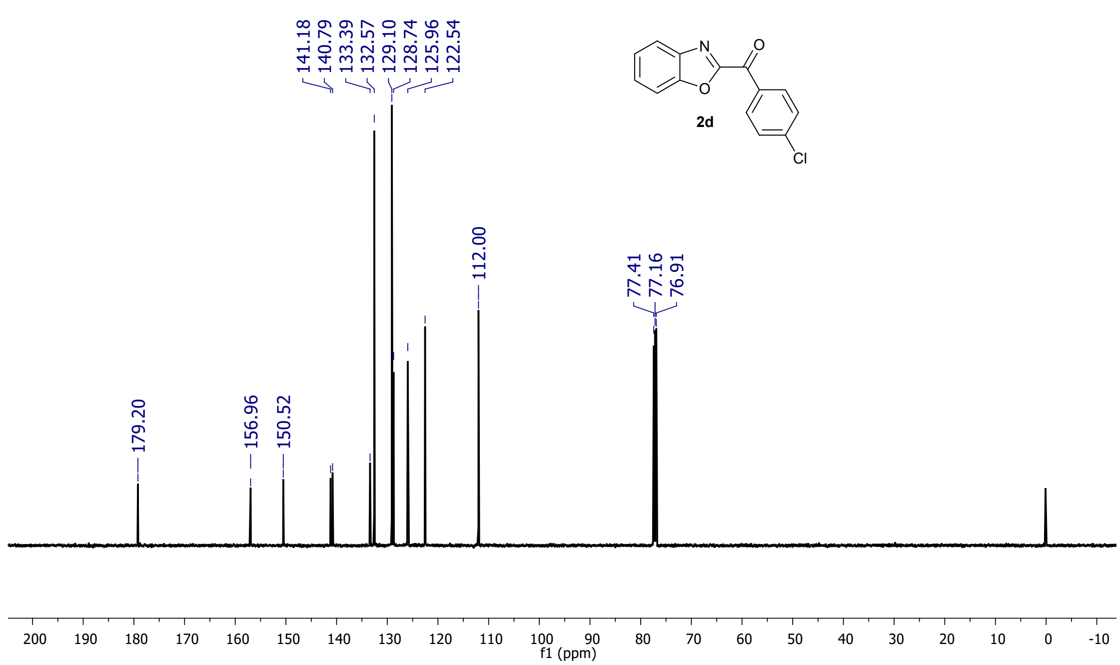


^{13}C NMR (126 MHz, $CDCl_3$)



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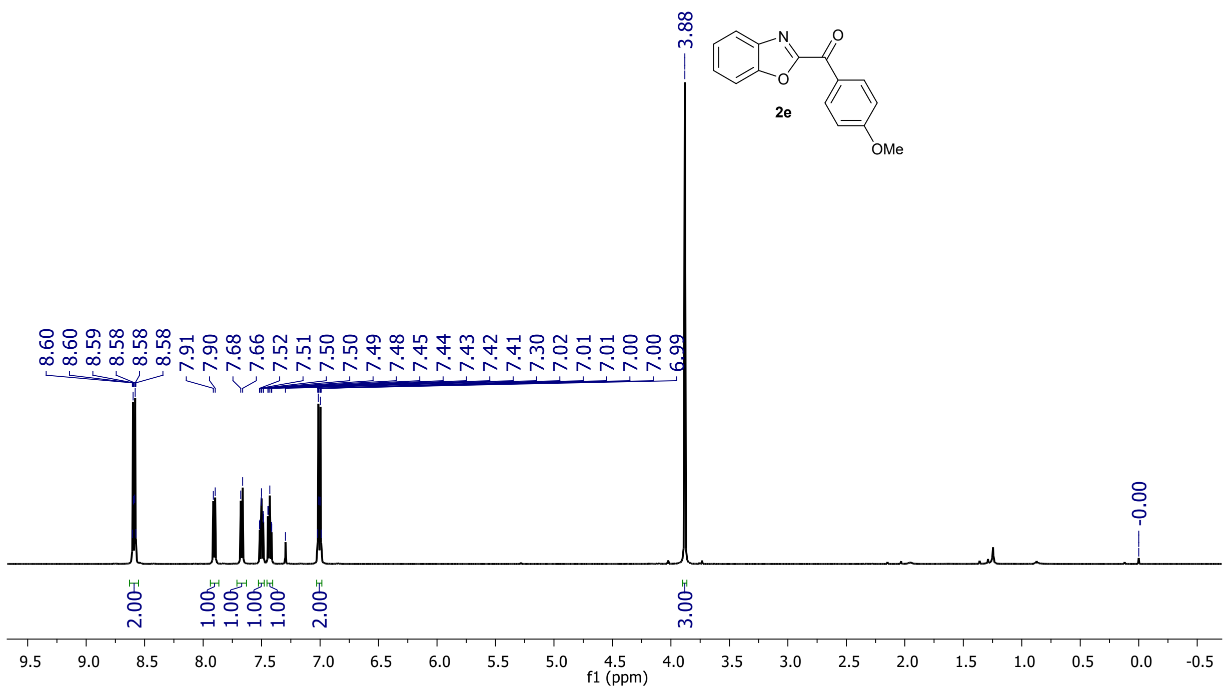
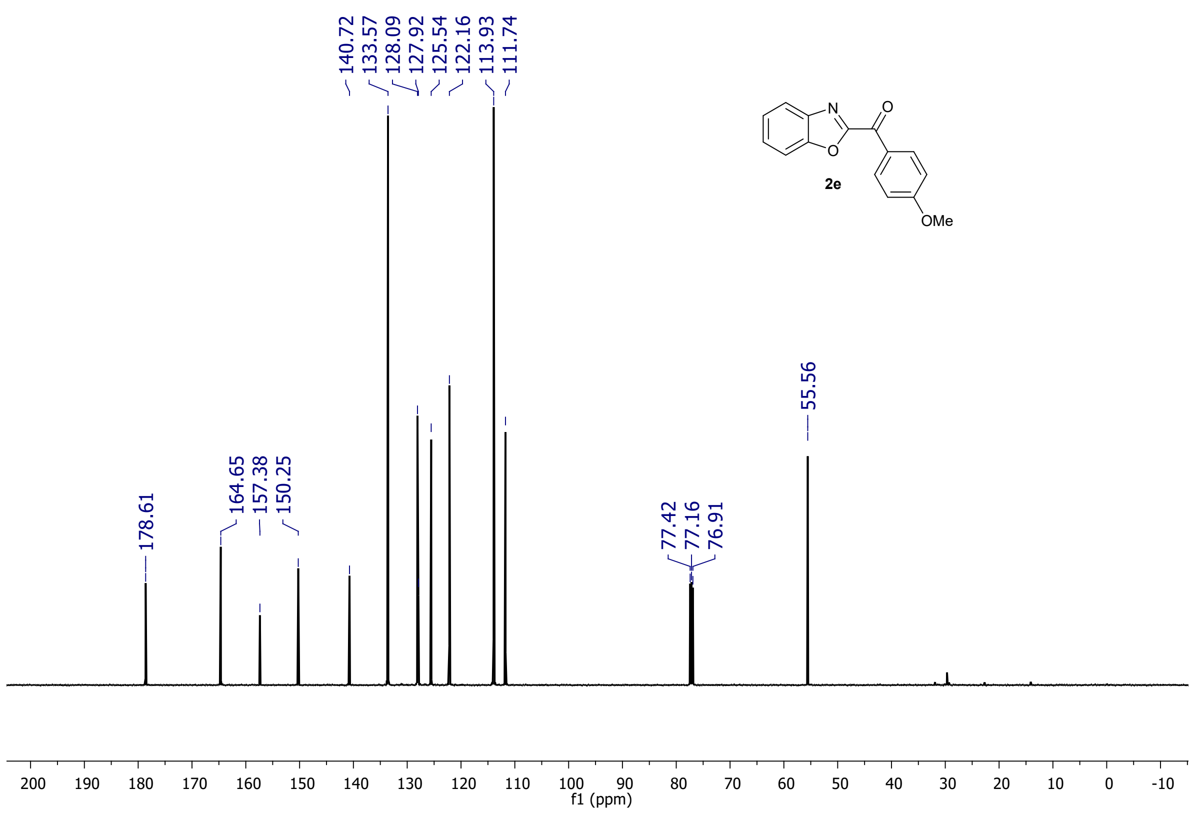
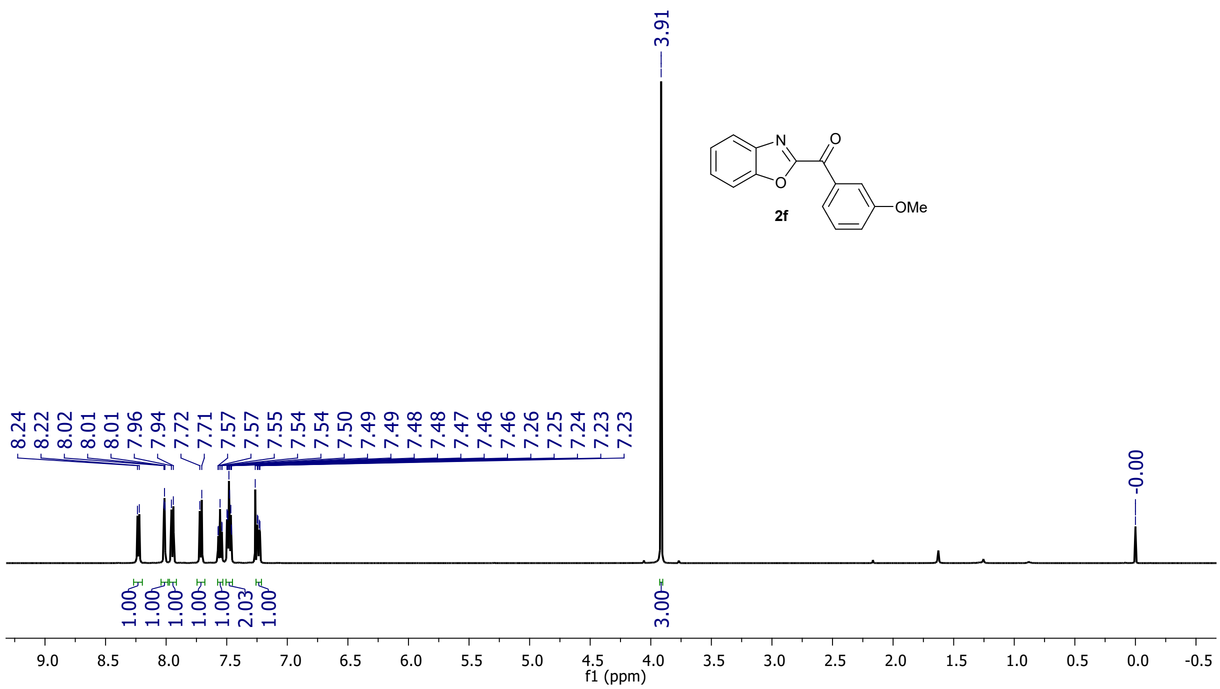


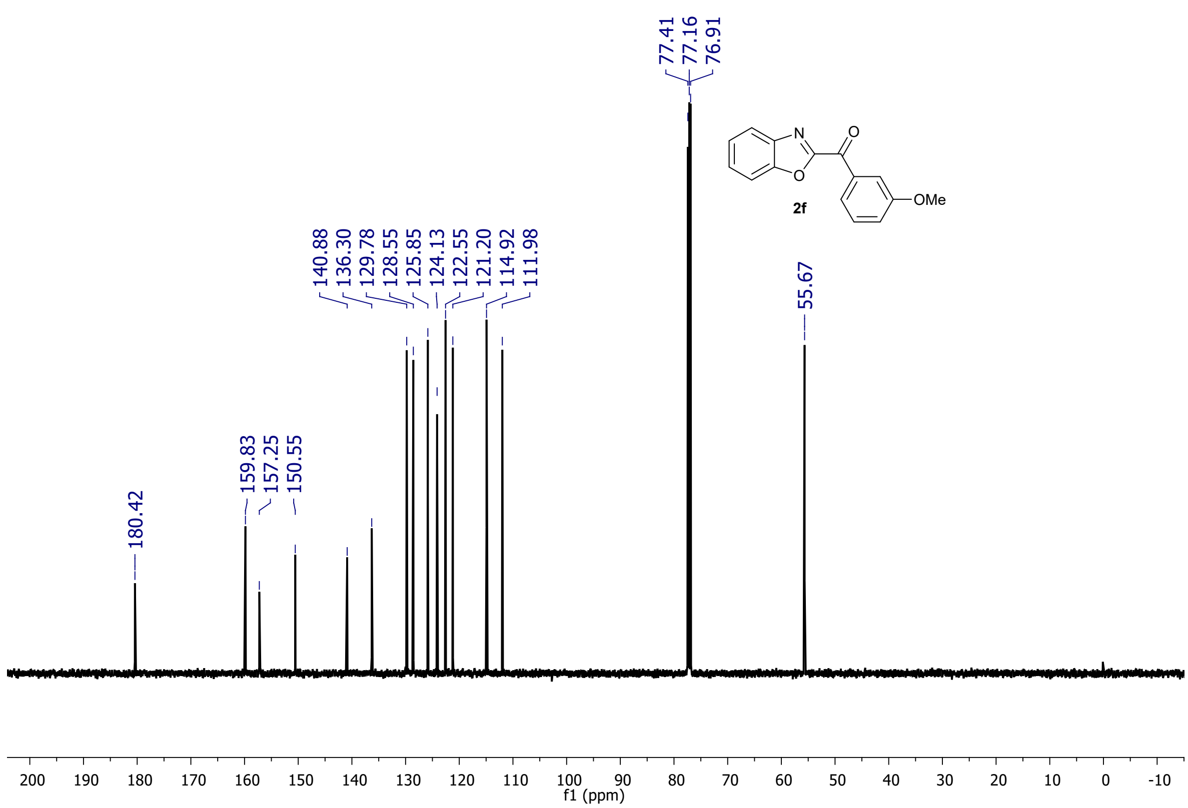
^{13}C NMR (126 MHz, $CDCl_3$)



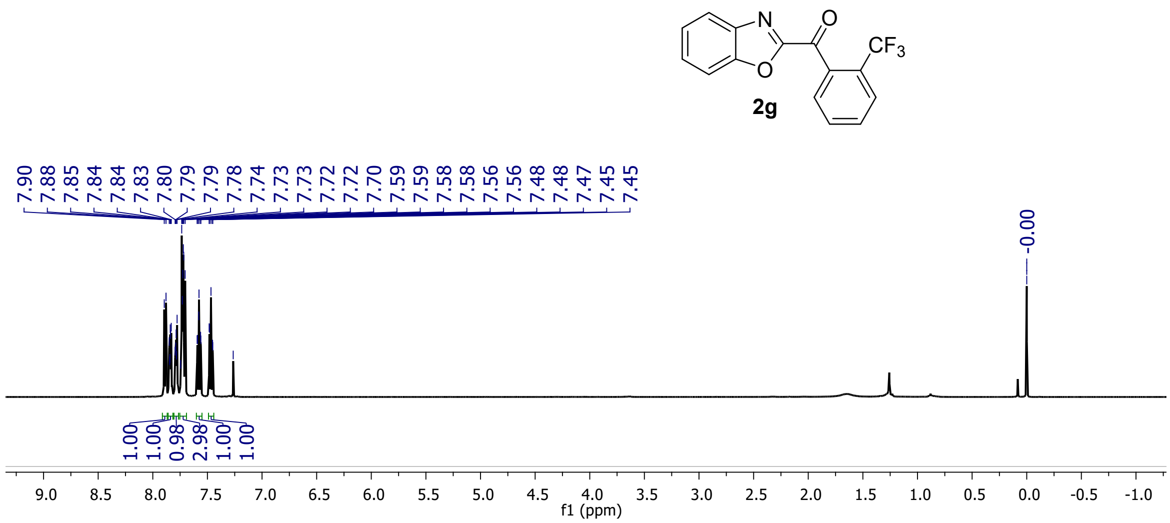
^{1}H NMR (500 MHz, $CDCl_3$)



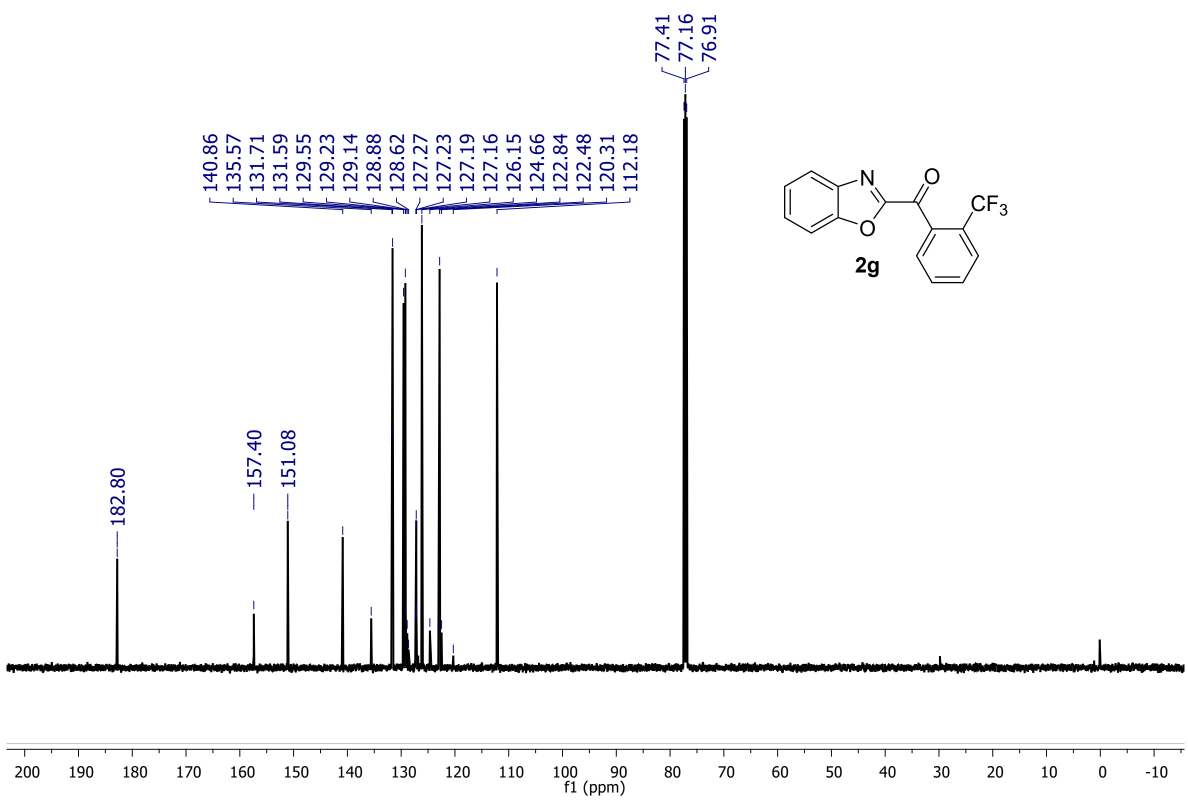
^{13}C NMR (126 MHz, $CDCl_3$)



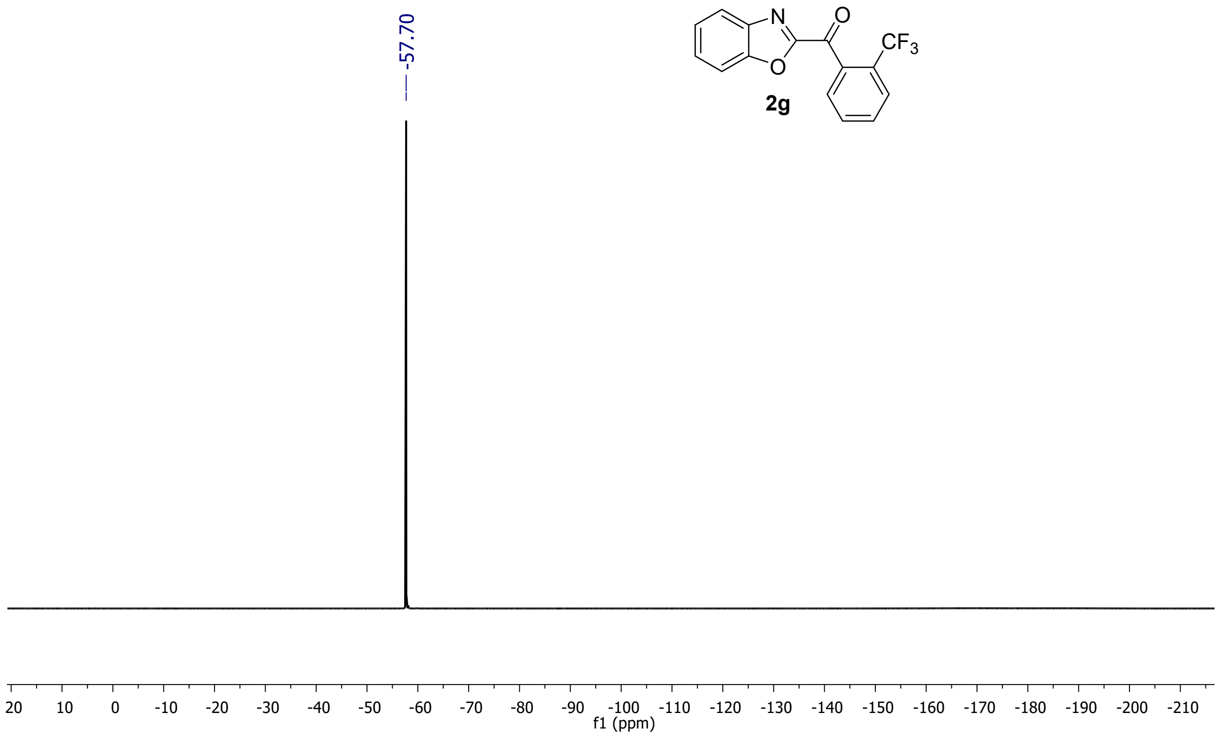
^{1}H NMR (500 MHz, $CDCl_3$)



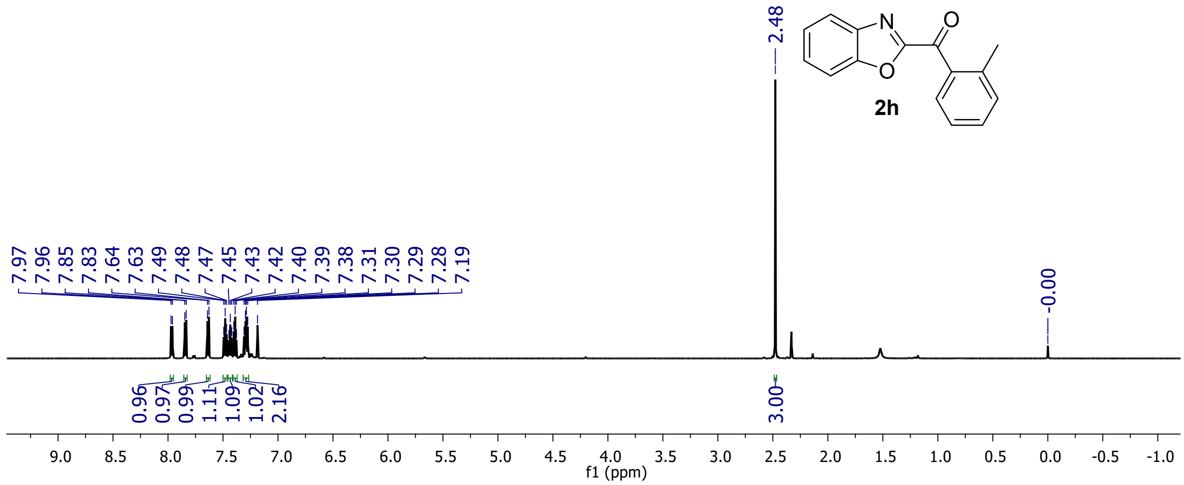
^{13}C NMR (126 MHz, $CDCl_3$)



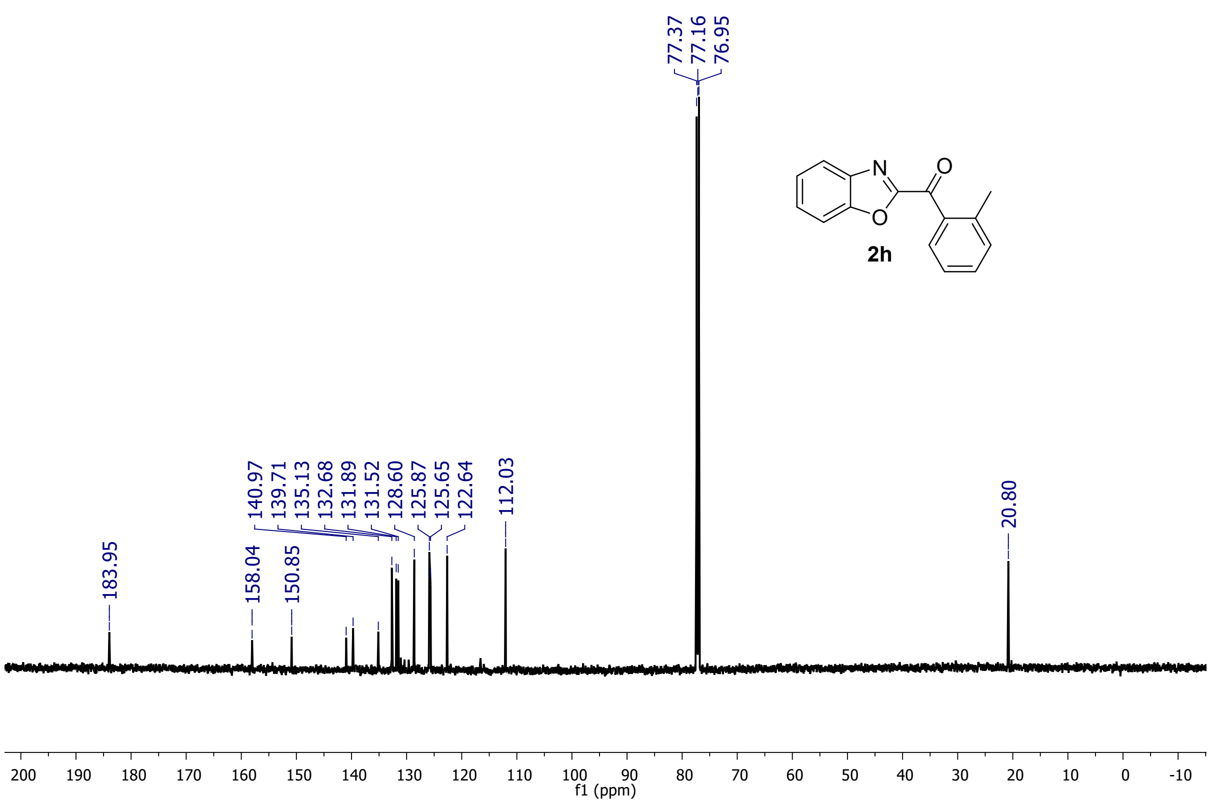
^{19}F NMR (471 MHz, $CDCl_3$)



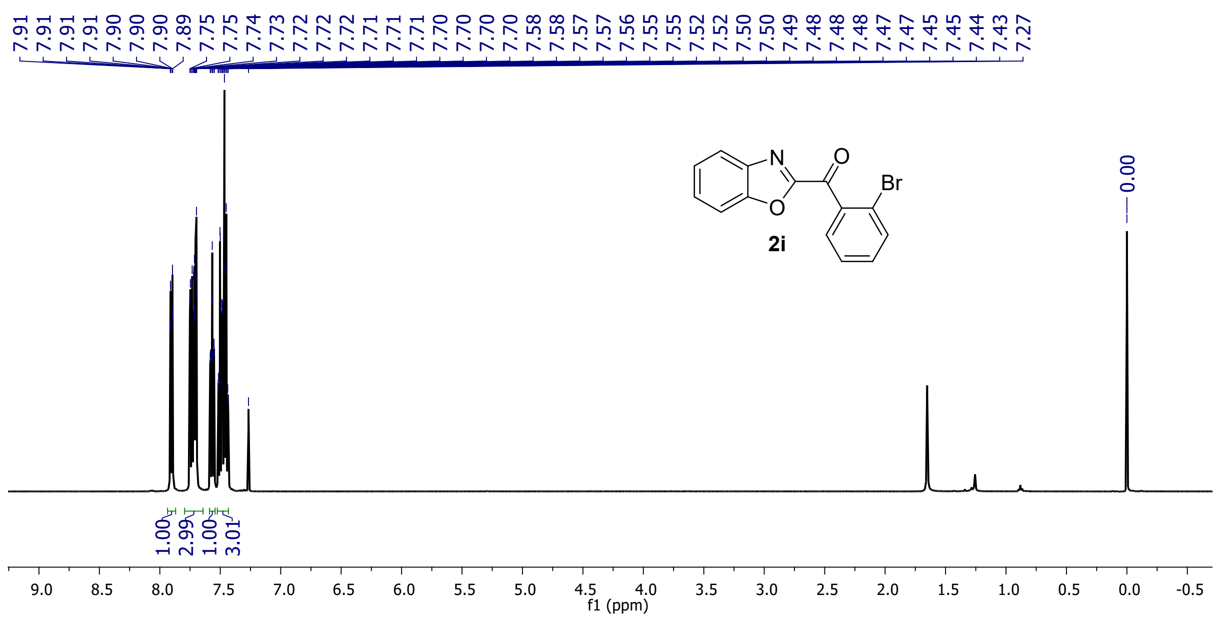
^{1}H NMR (600 MHz, $CDCl_3$)



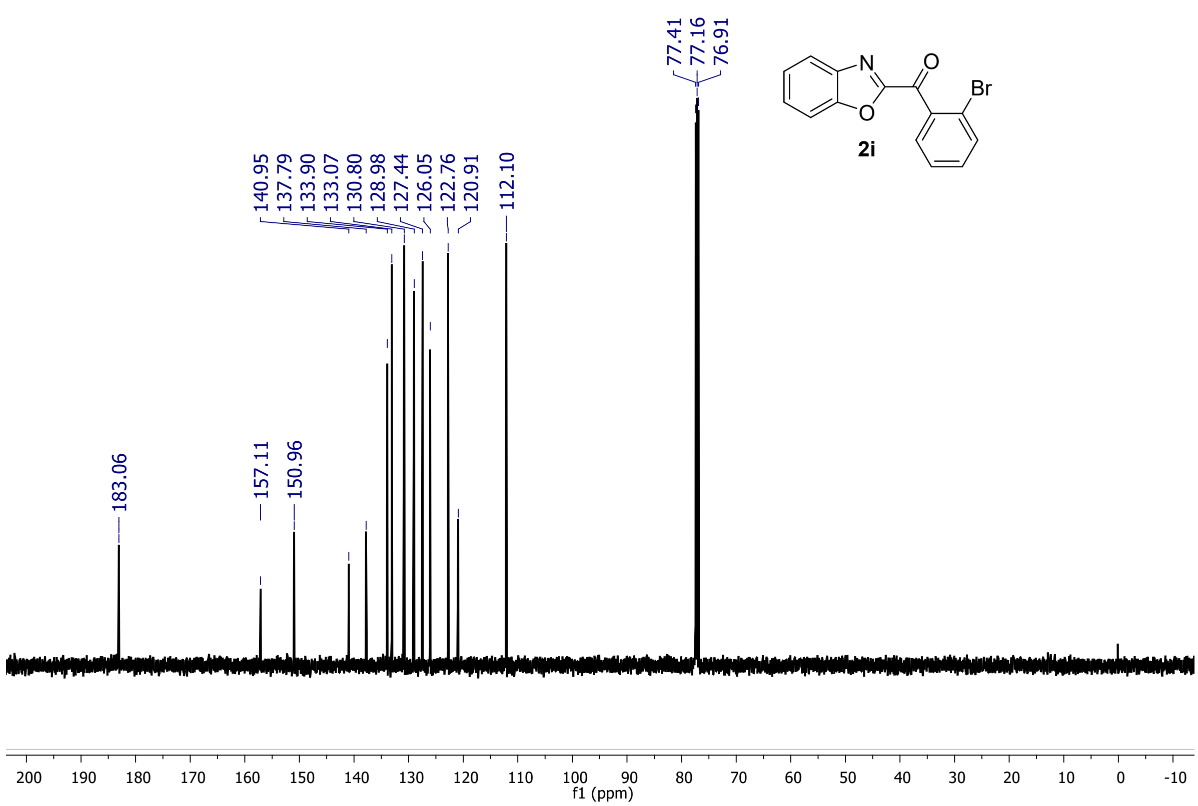
^{13}C NMR (151 MHz, $CDCl_3$)



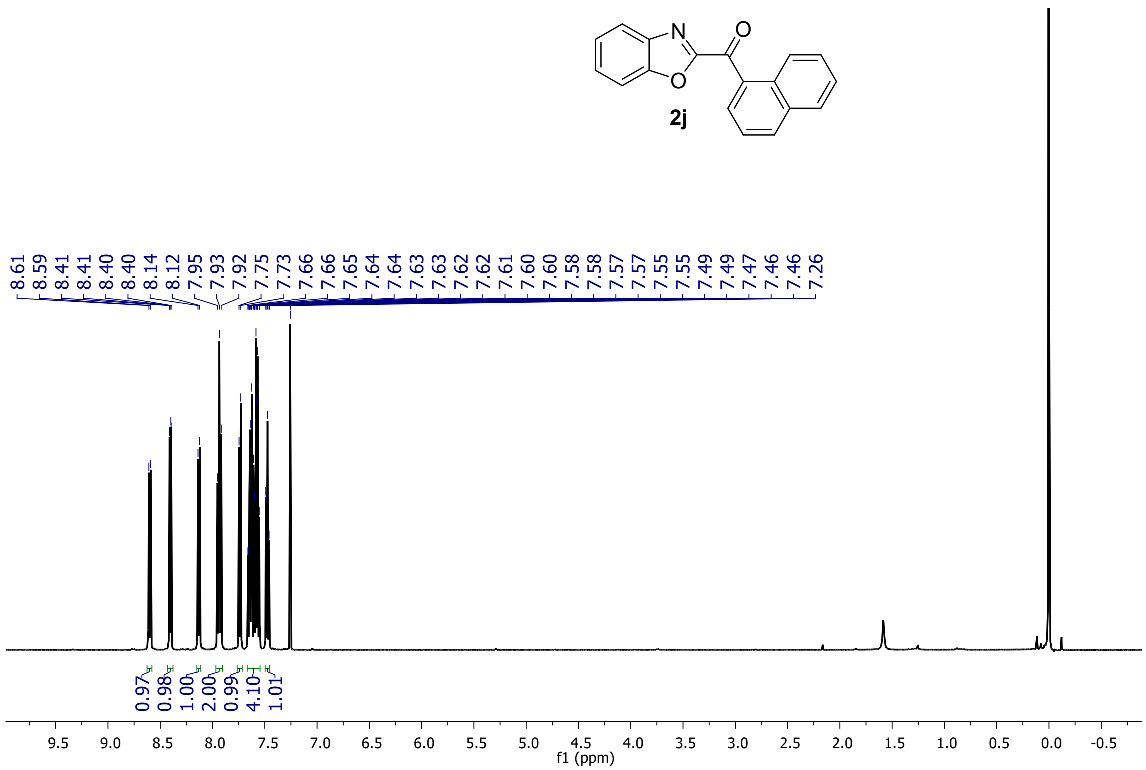
^{1}H NMR (500 MHz, $CDCl_3$)



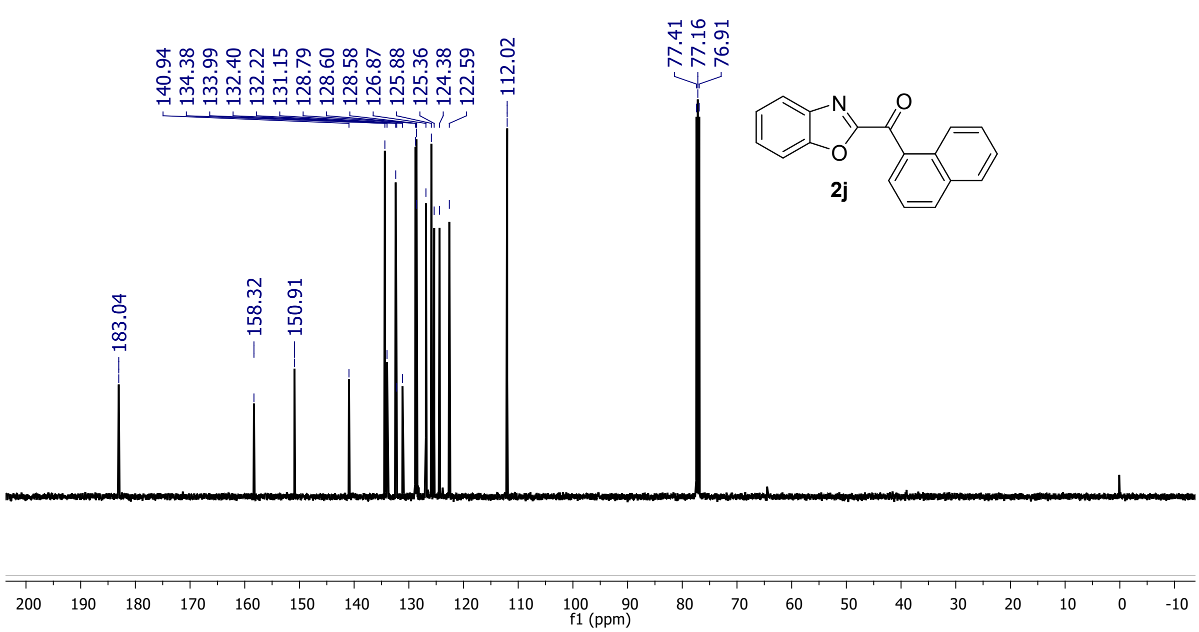
^{13}C NMR (126 MHz, $CDCl_3$)



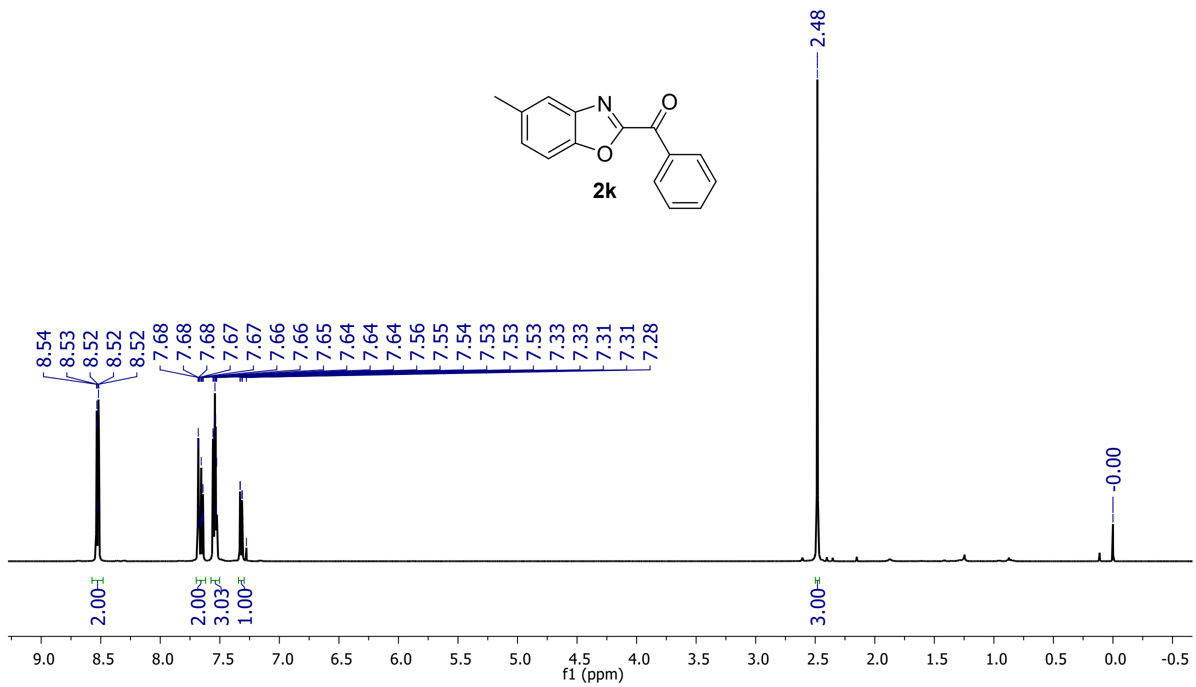
^{1}H NMR (500 MHz, $CDCl_3$)



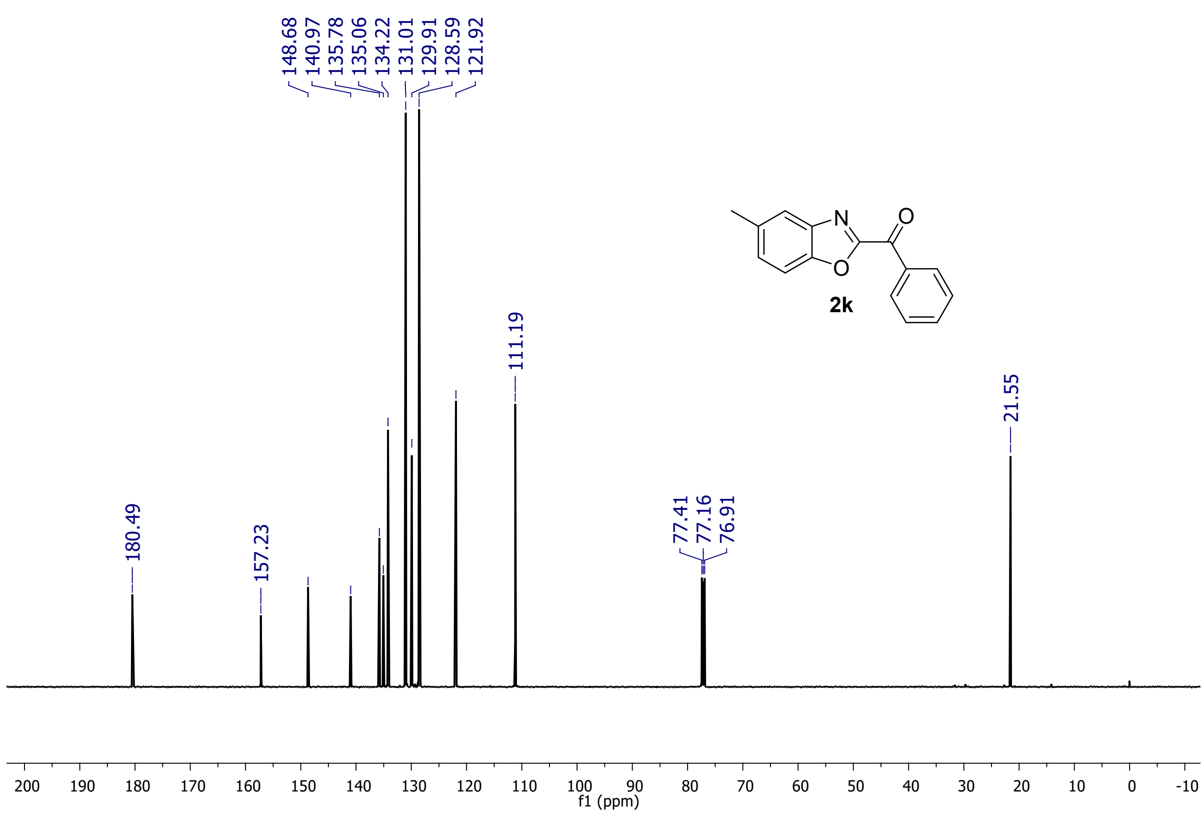
^{13}C NMR (126 MHz, $CDCl_3$)



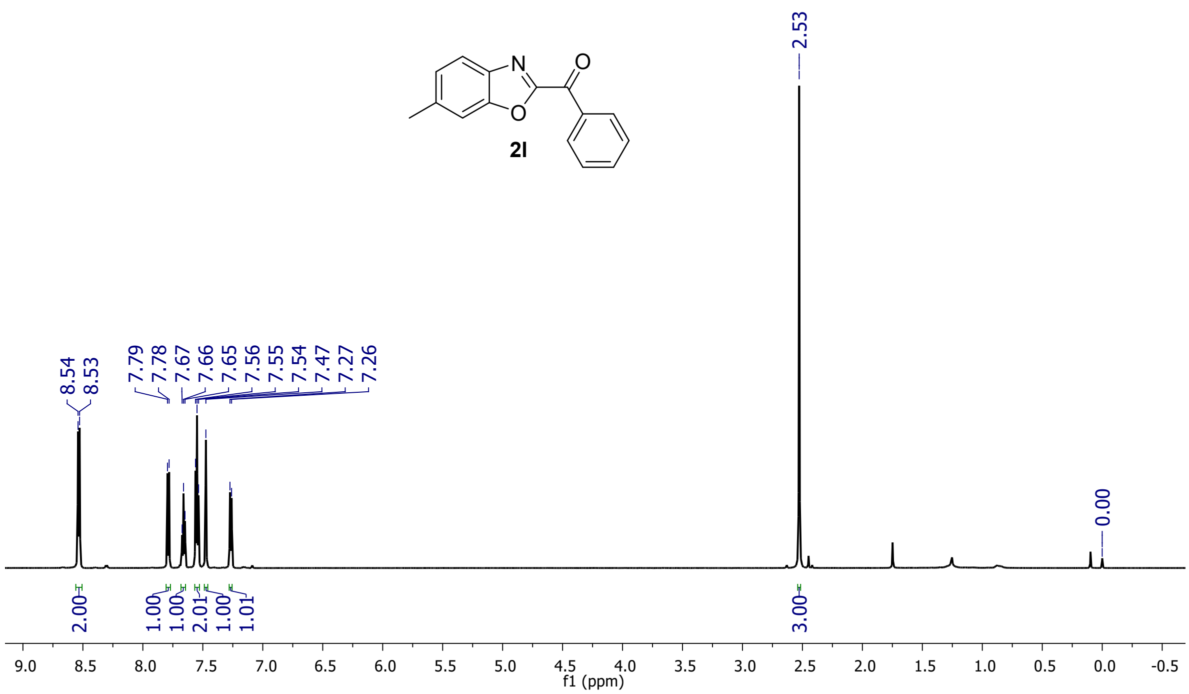
^{1}H NMR (500 MHz, $CDCl_3$)



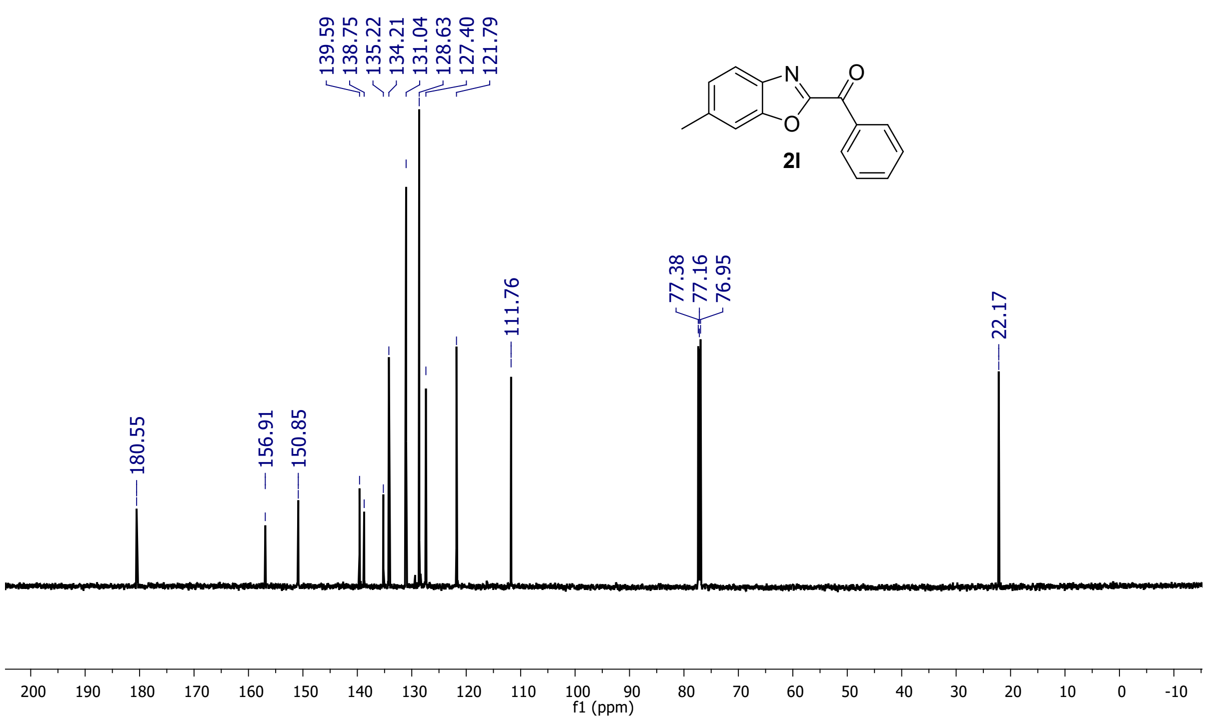
^{13}C NMR (126 MHz, $CDCl_3$)



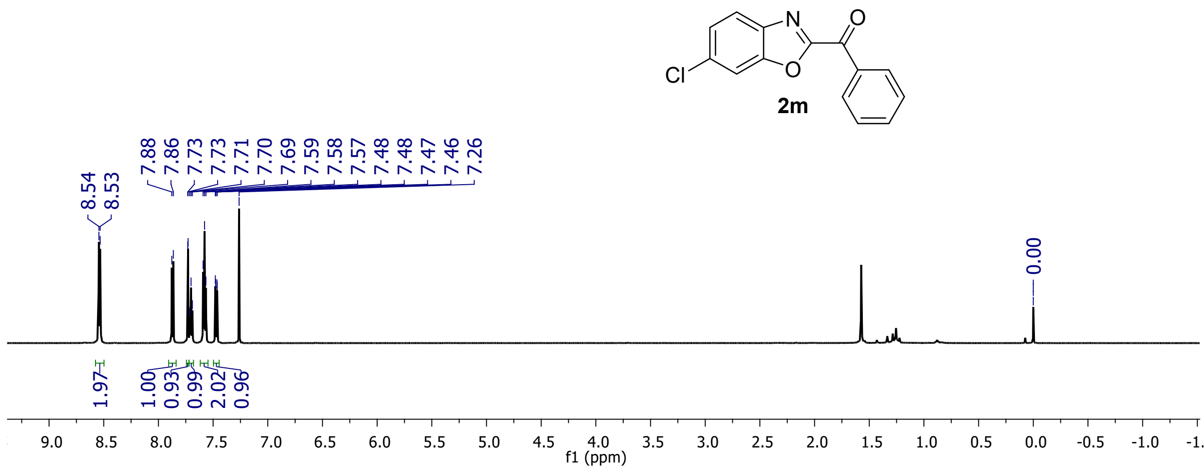
^{1}H NMR (600 MHz, $CDCl_3$)



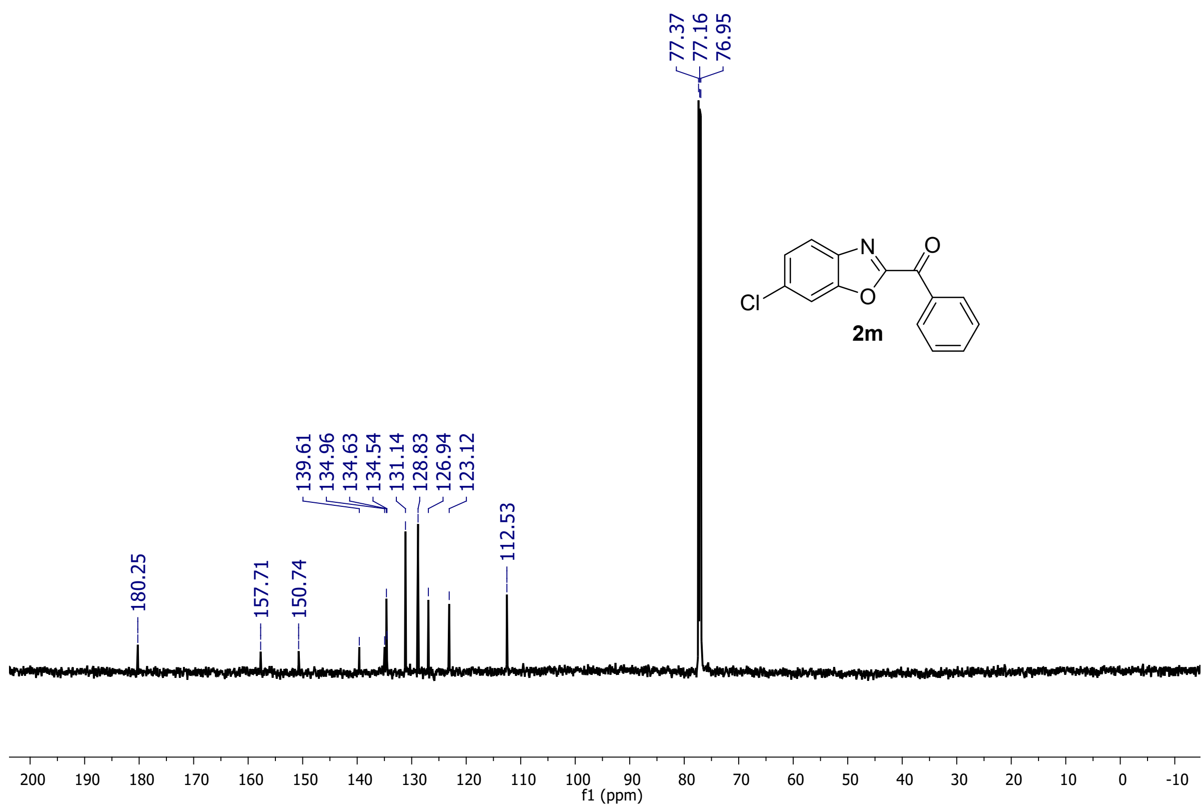
^{13}C NMR (151 MHz, $CDCl_3$)



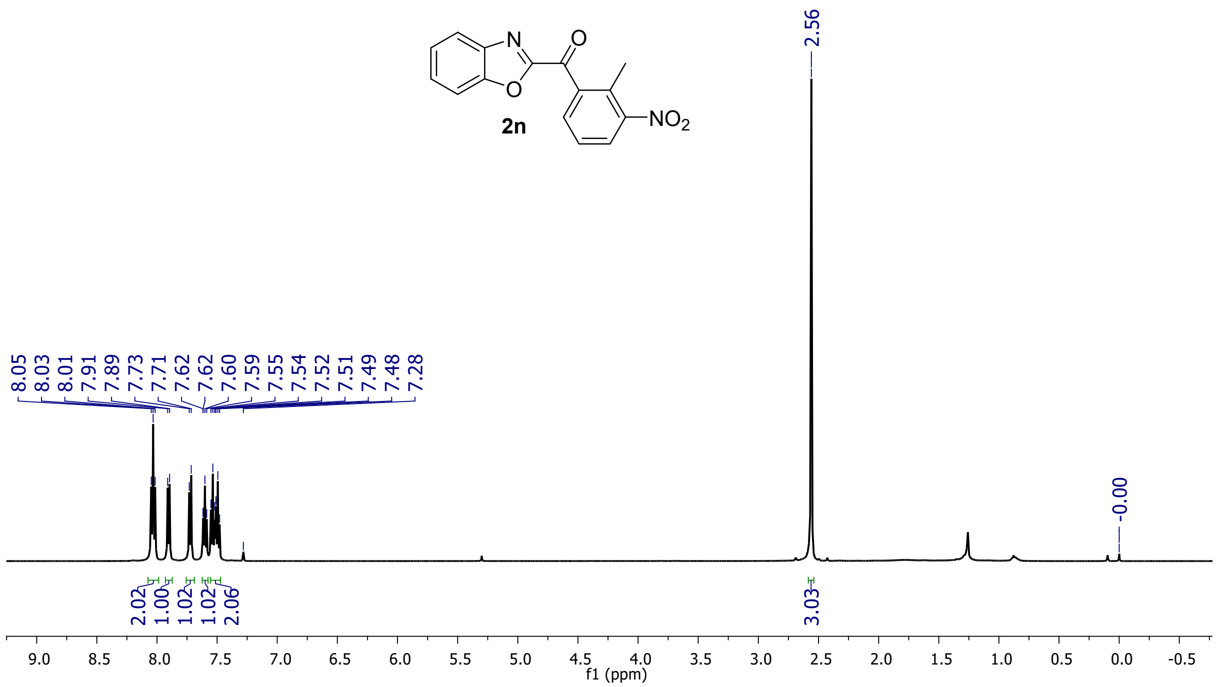
^{1}H NMR (600 MHz, $CDCl_3$)



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



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



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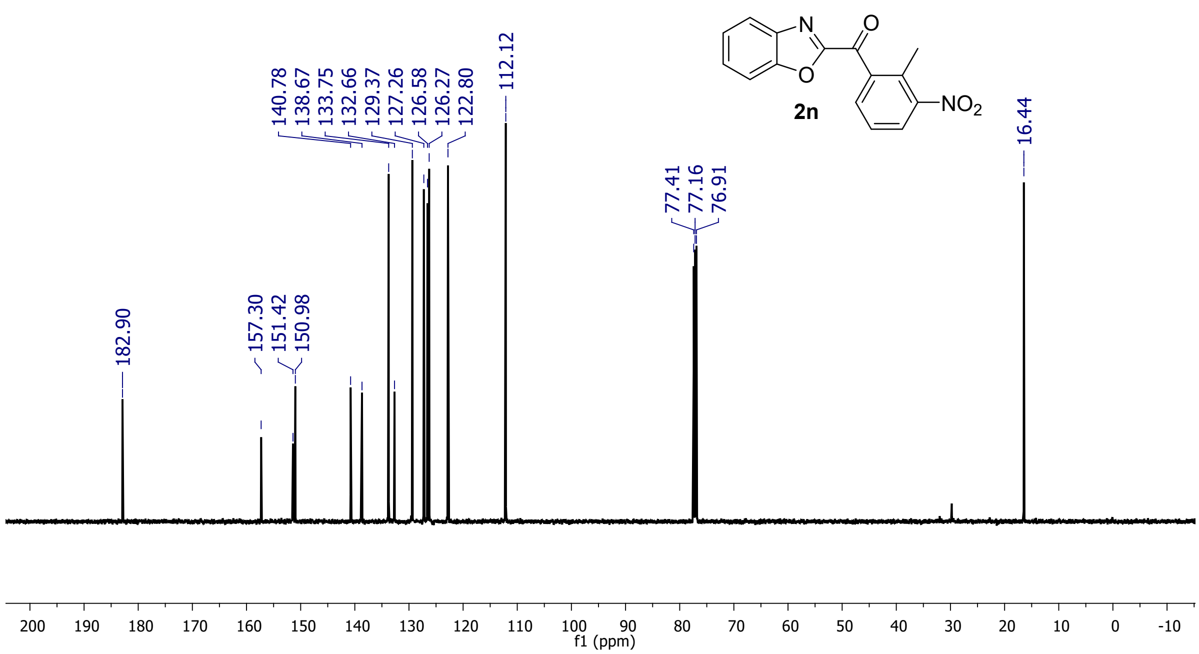

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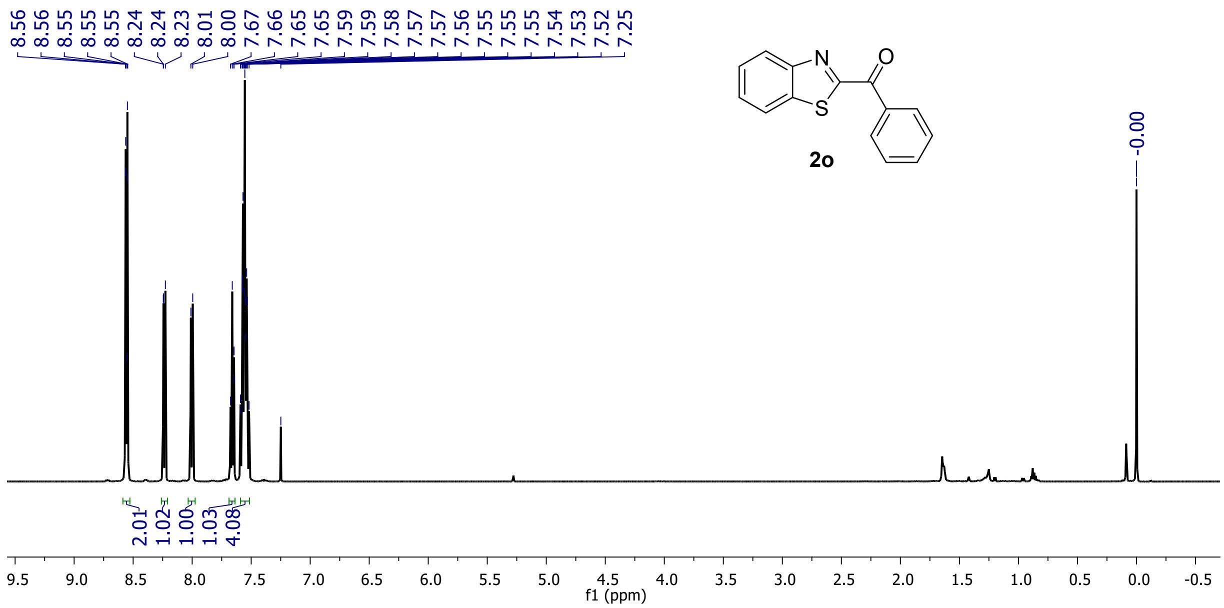

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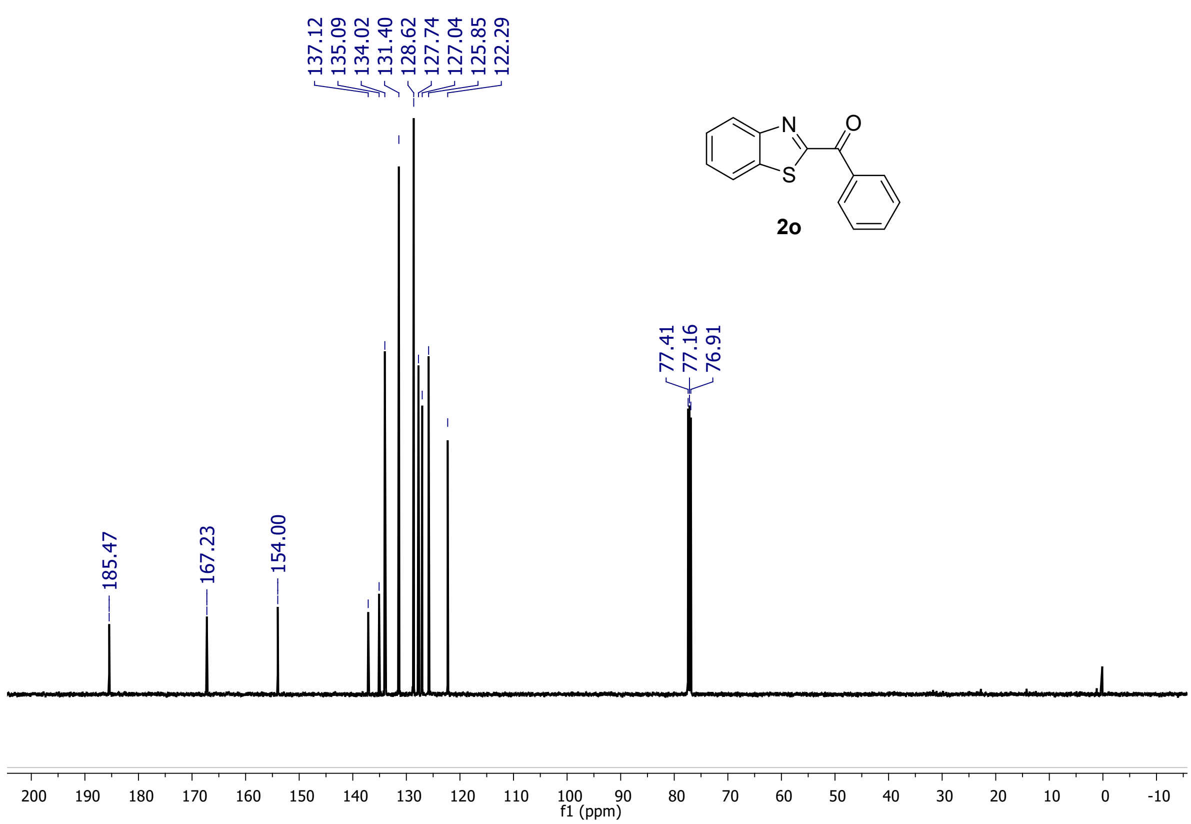

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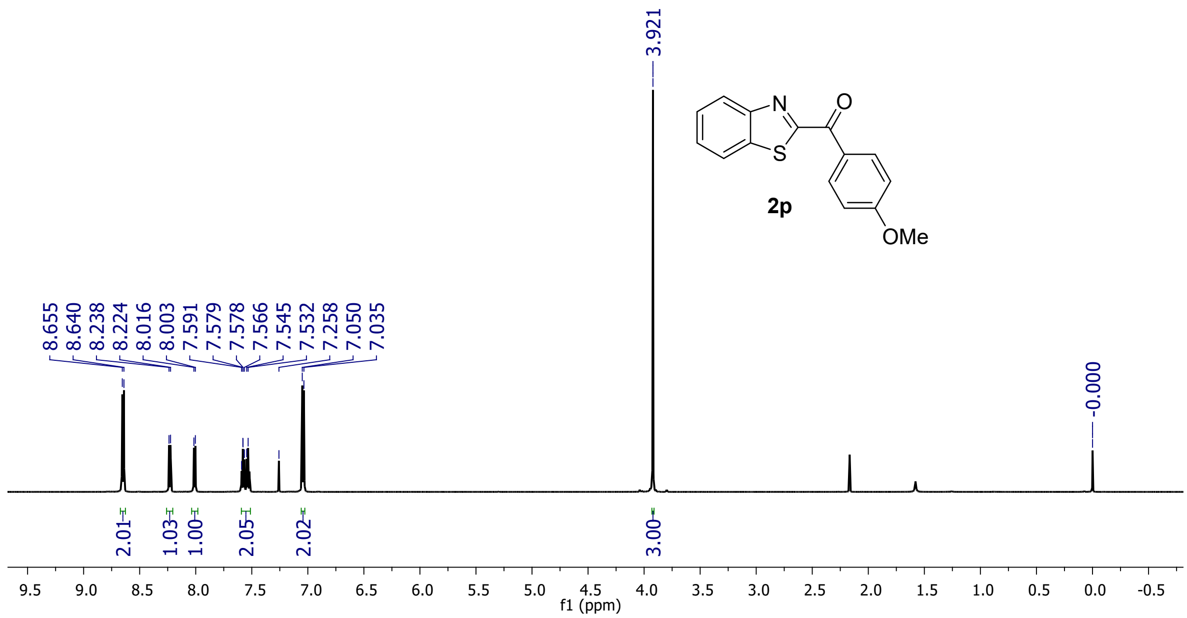
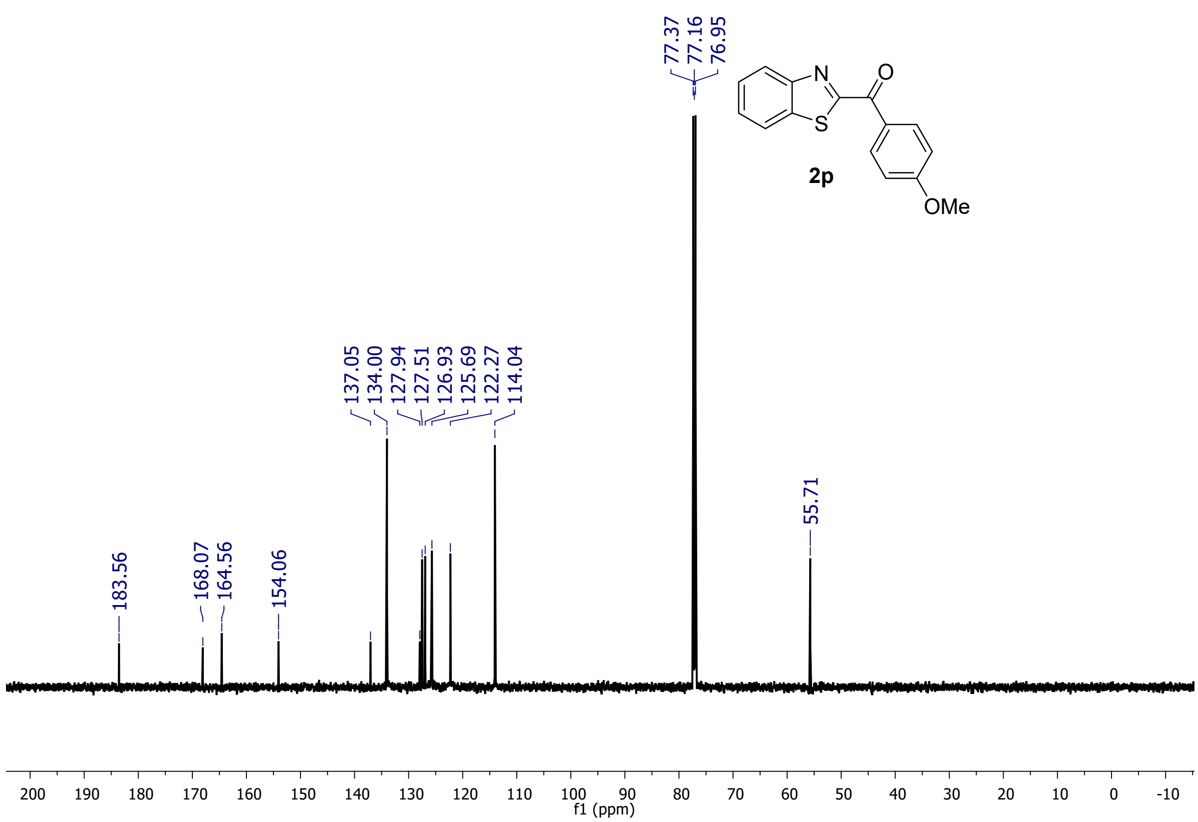


^{13}C NMR (151 MHz, $CDCl_3$)



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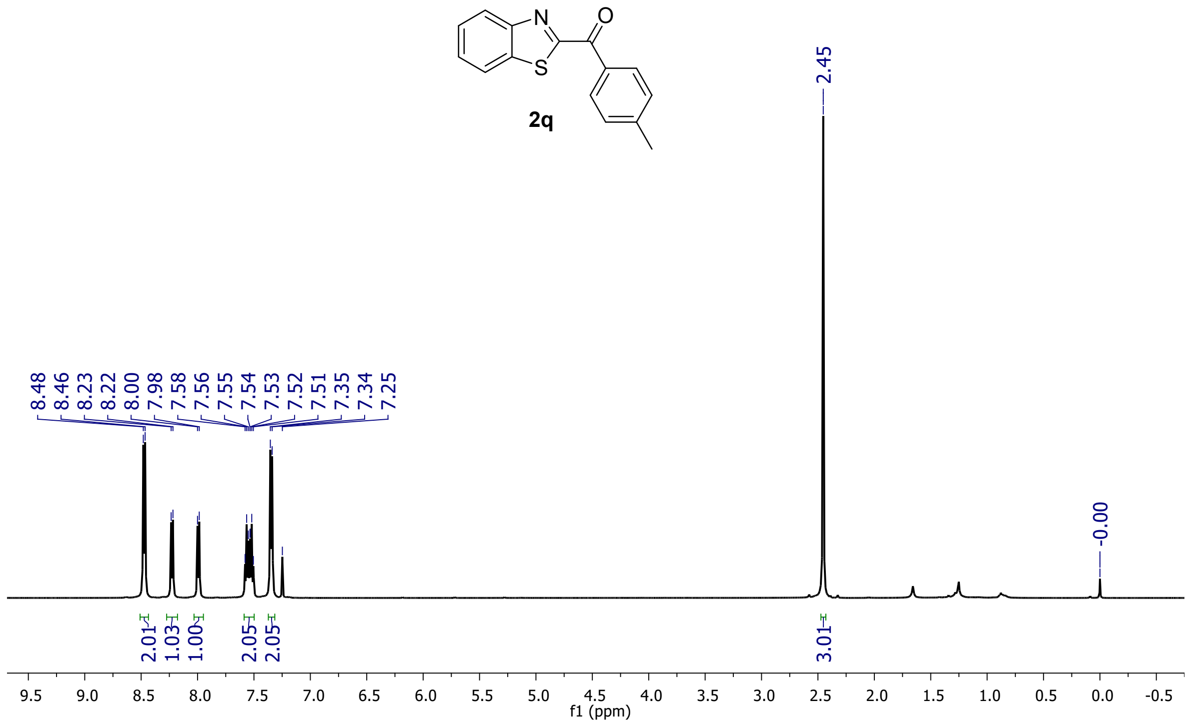

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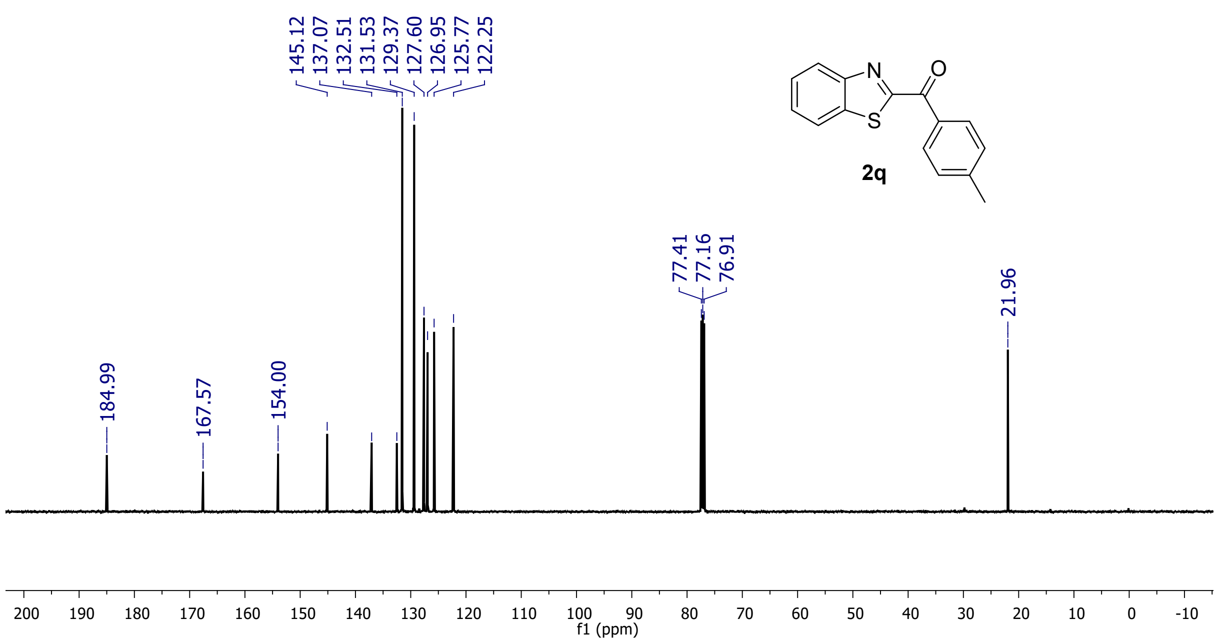

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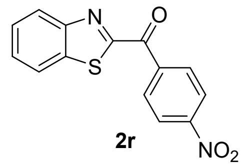

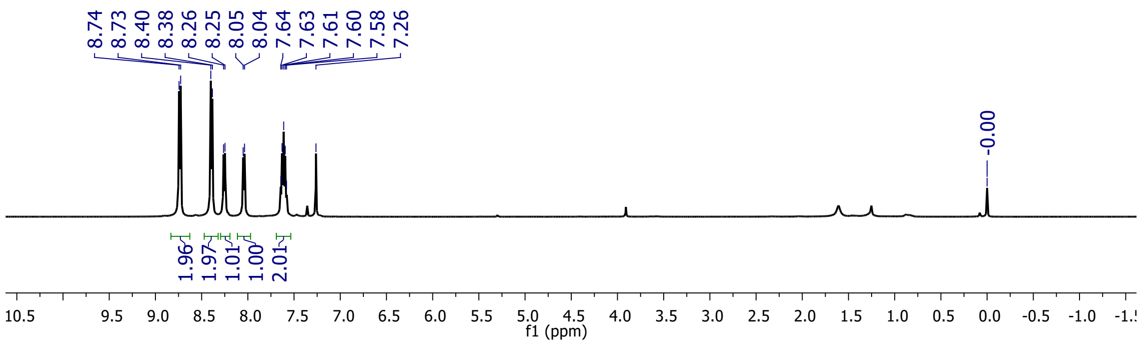

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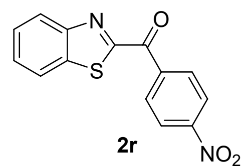
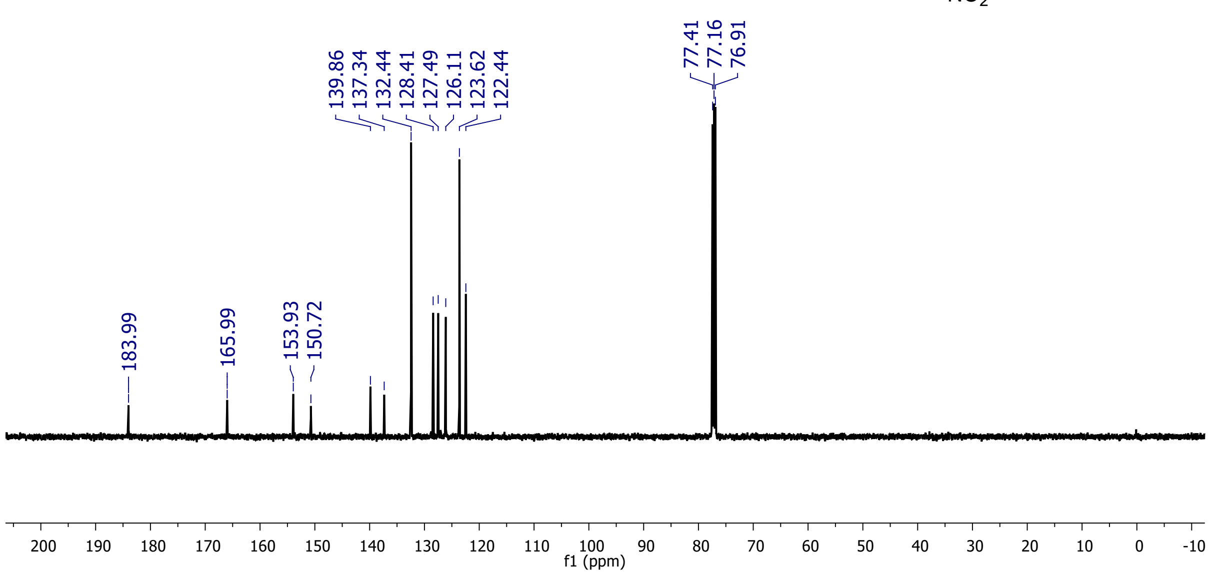
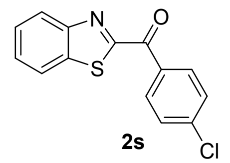




[1]H NMR (500 MHz, $CDCl_3$)



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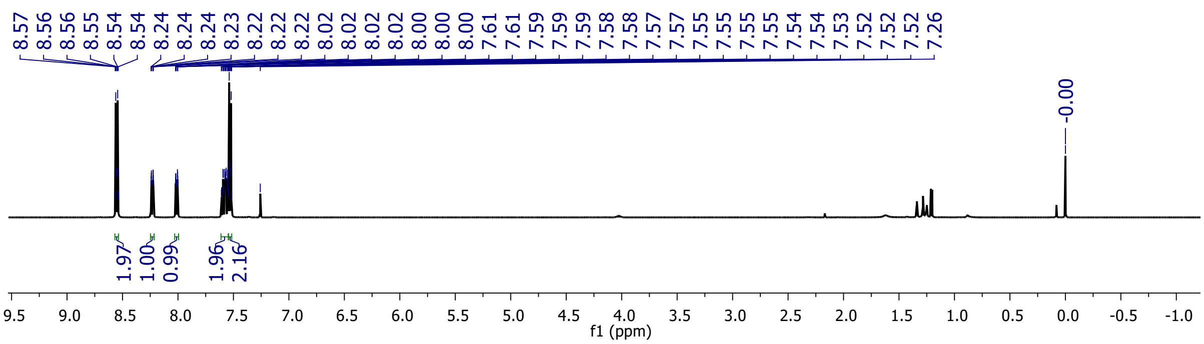

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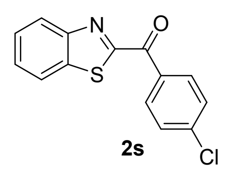

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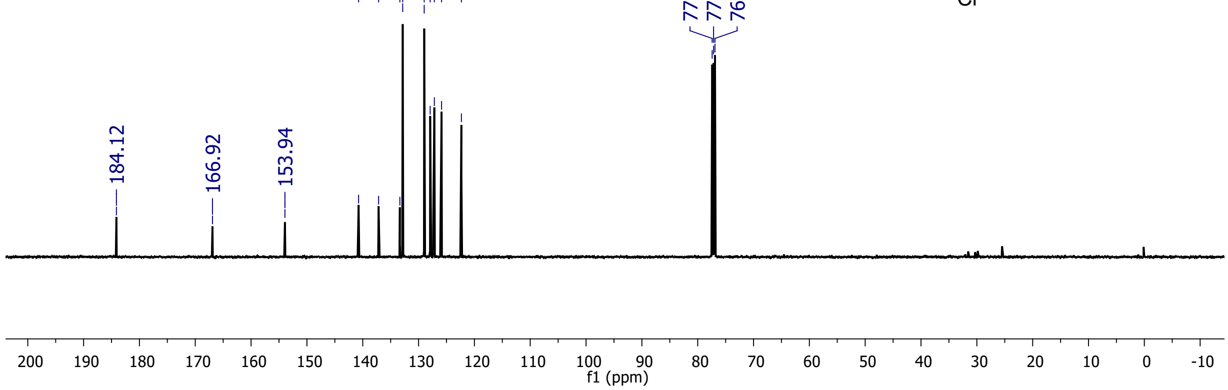

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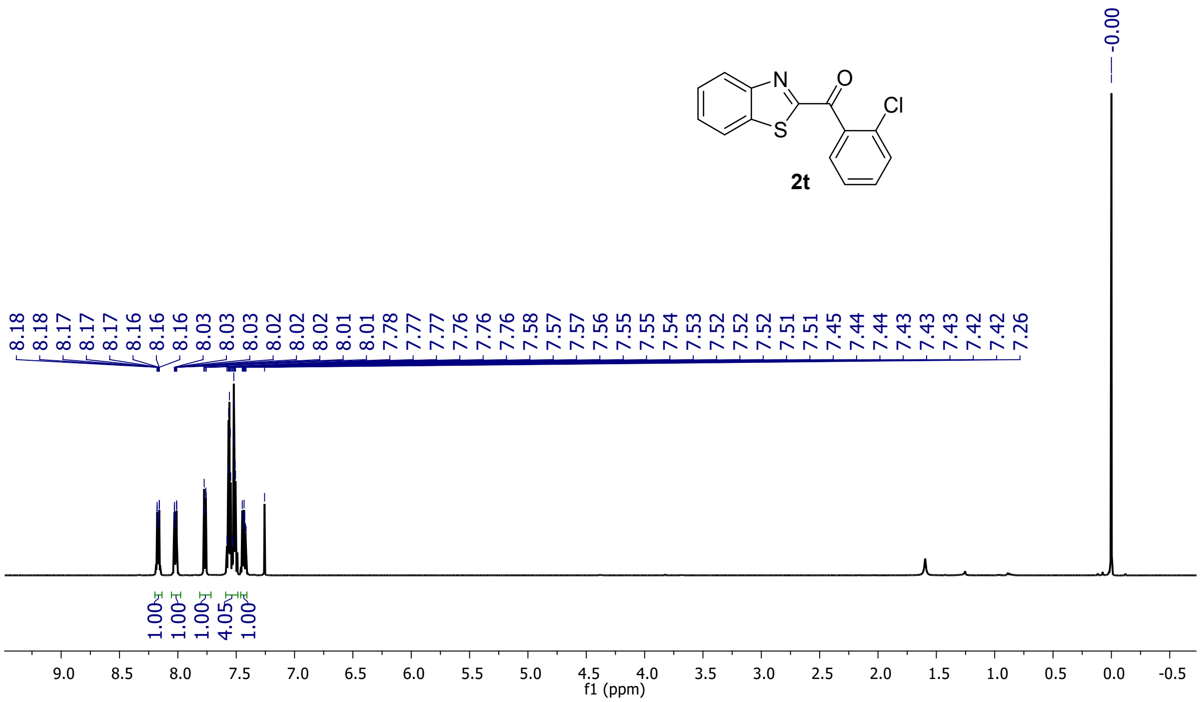

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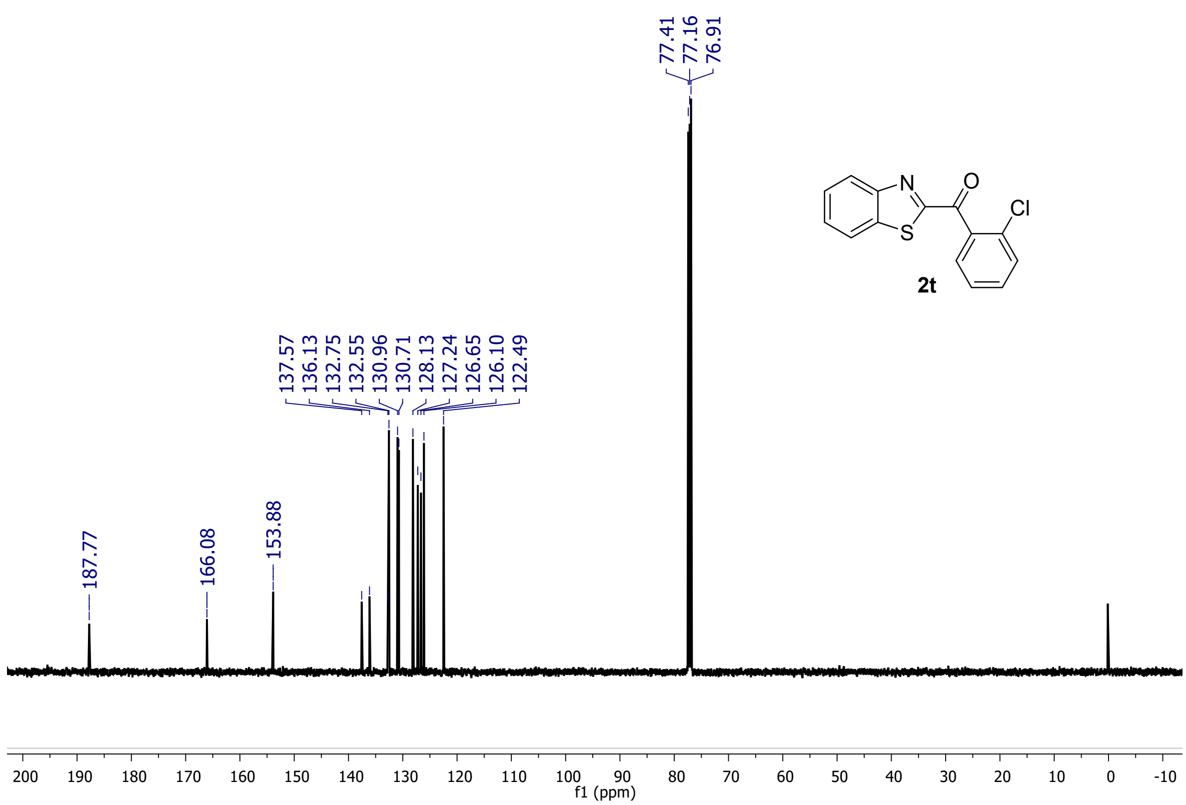

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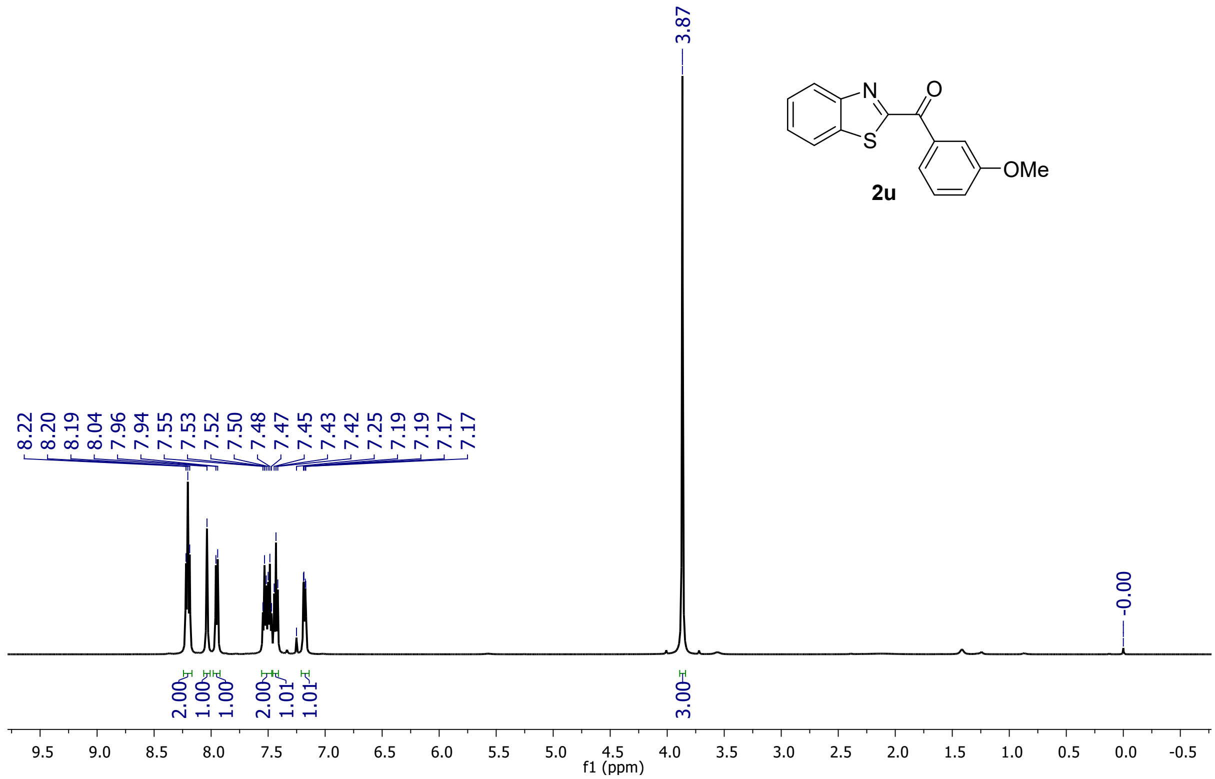

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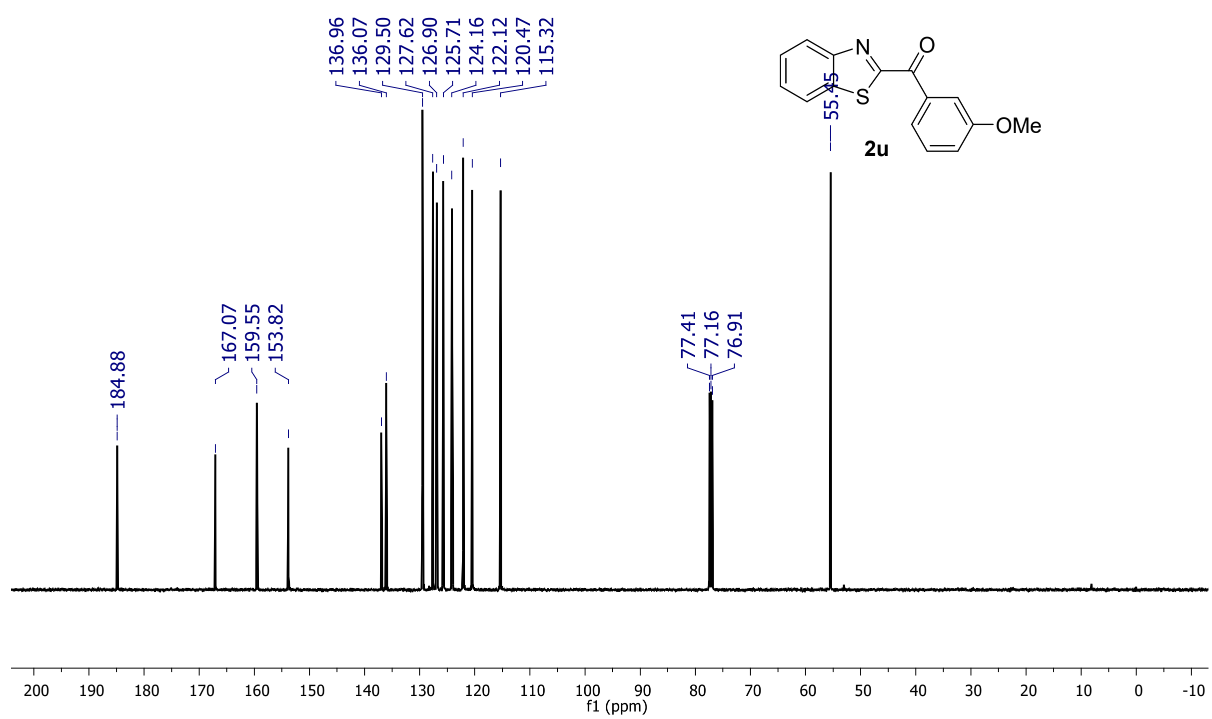

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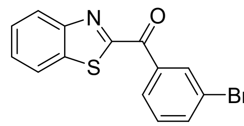

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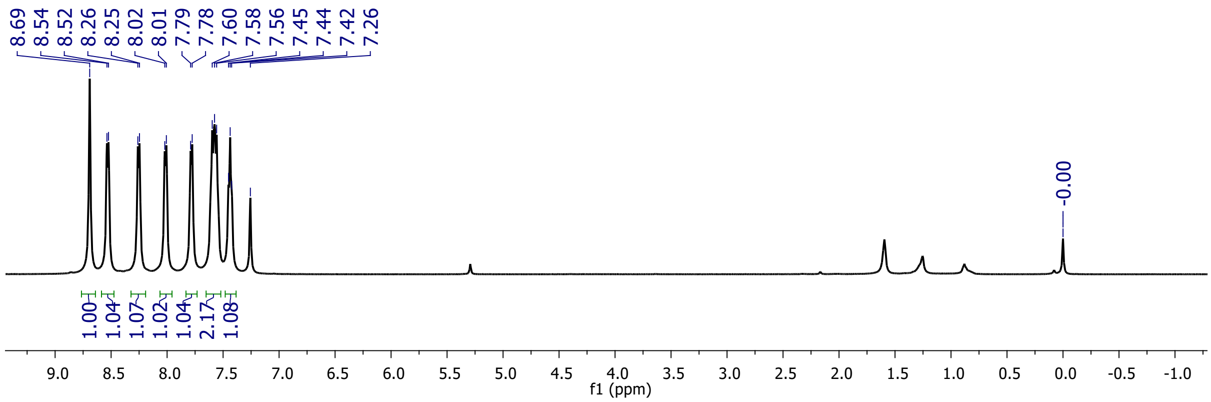

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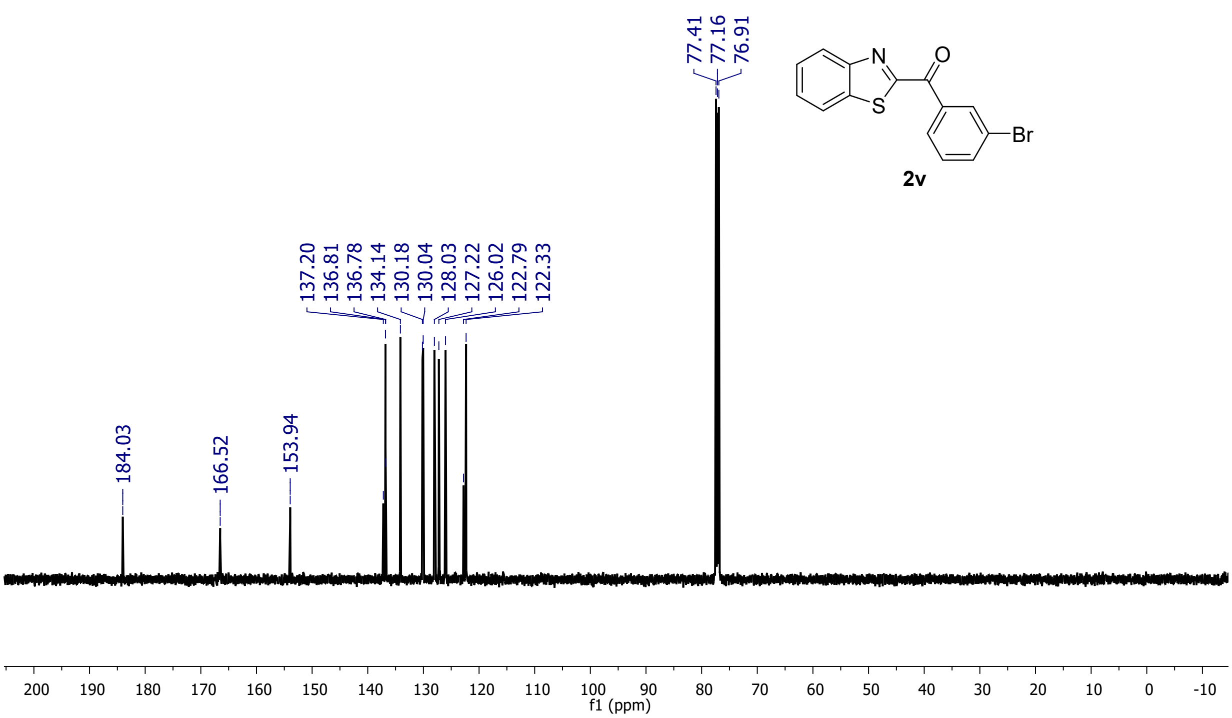
2v



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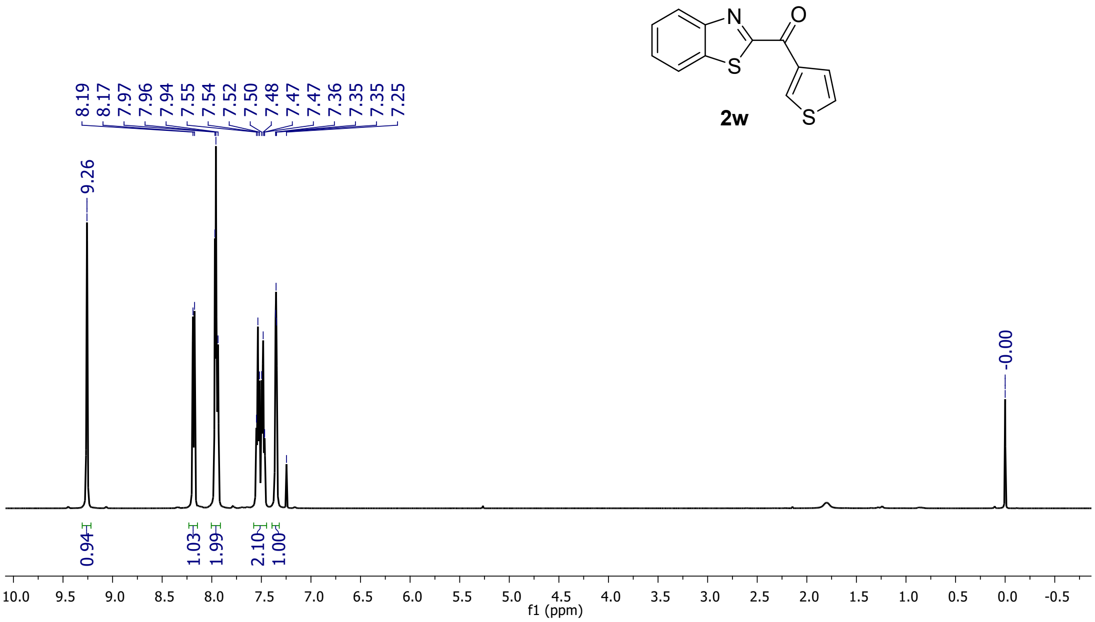

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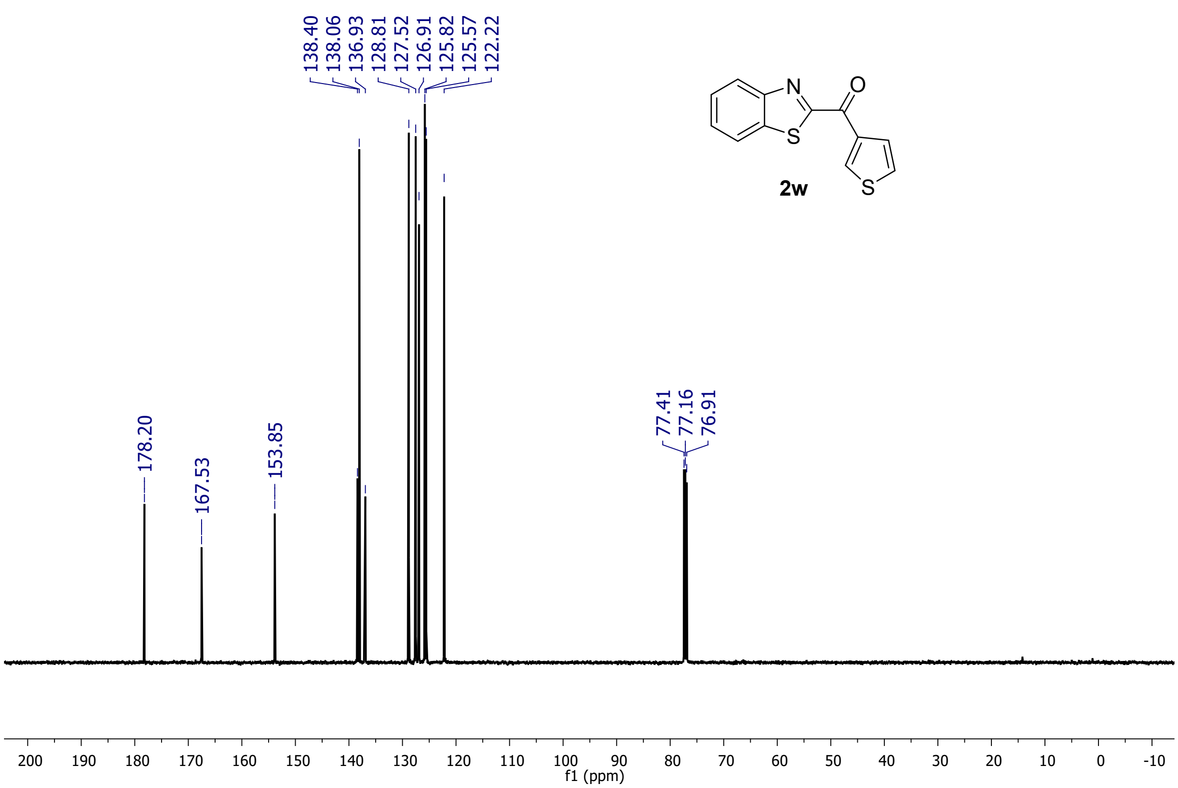

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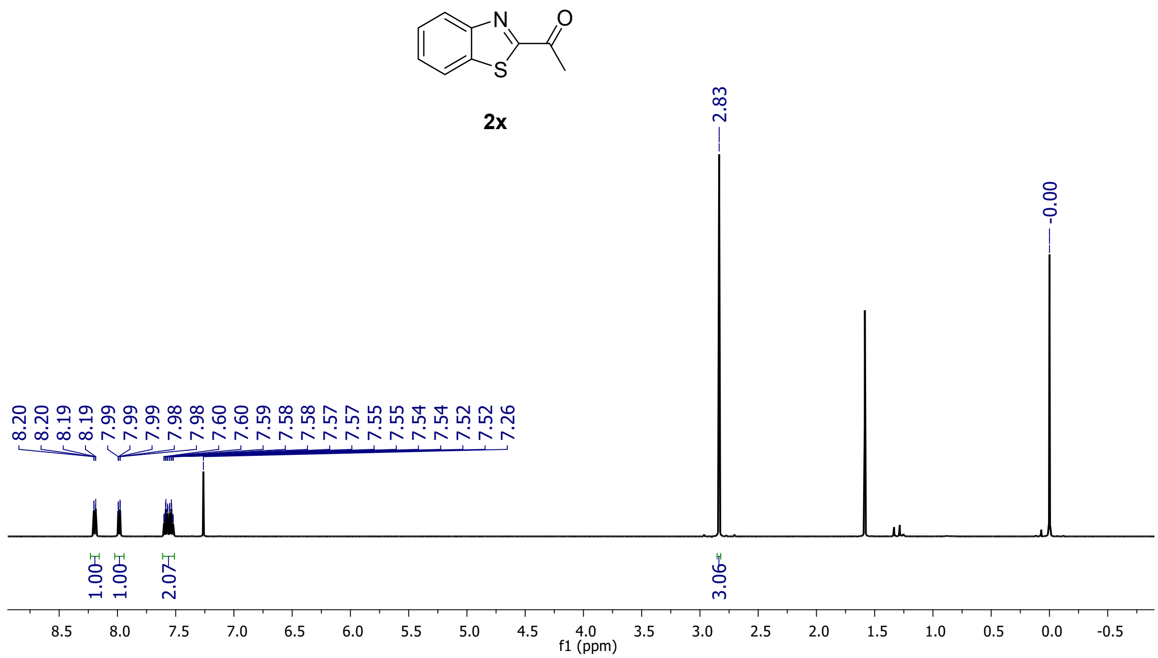

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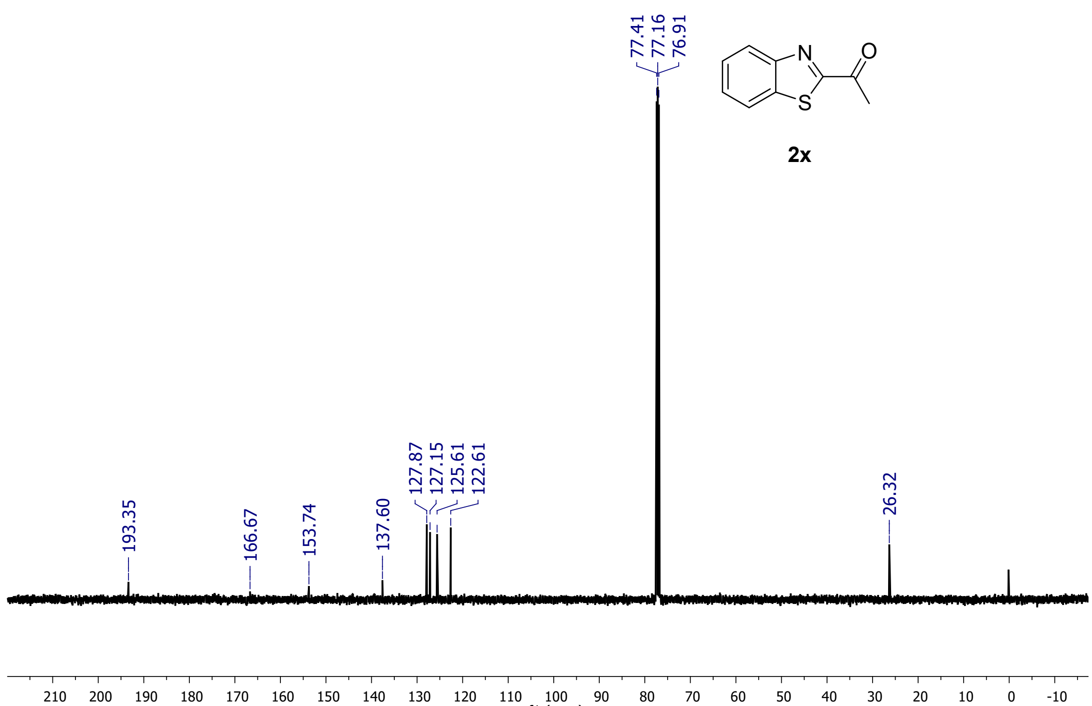

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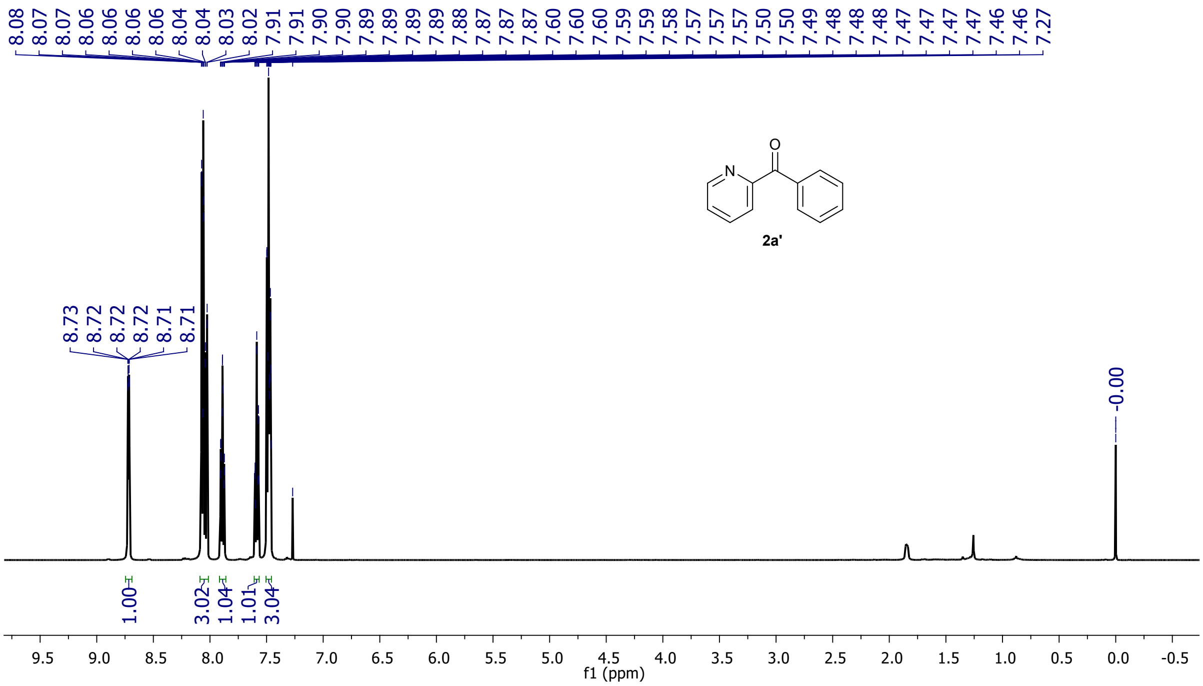

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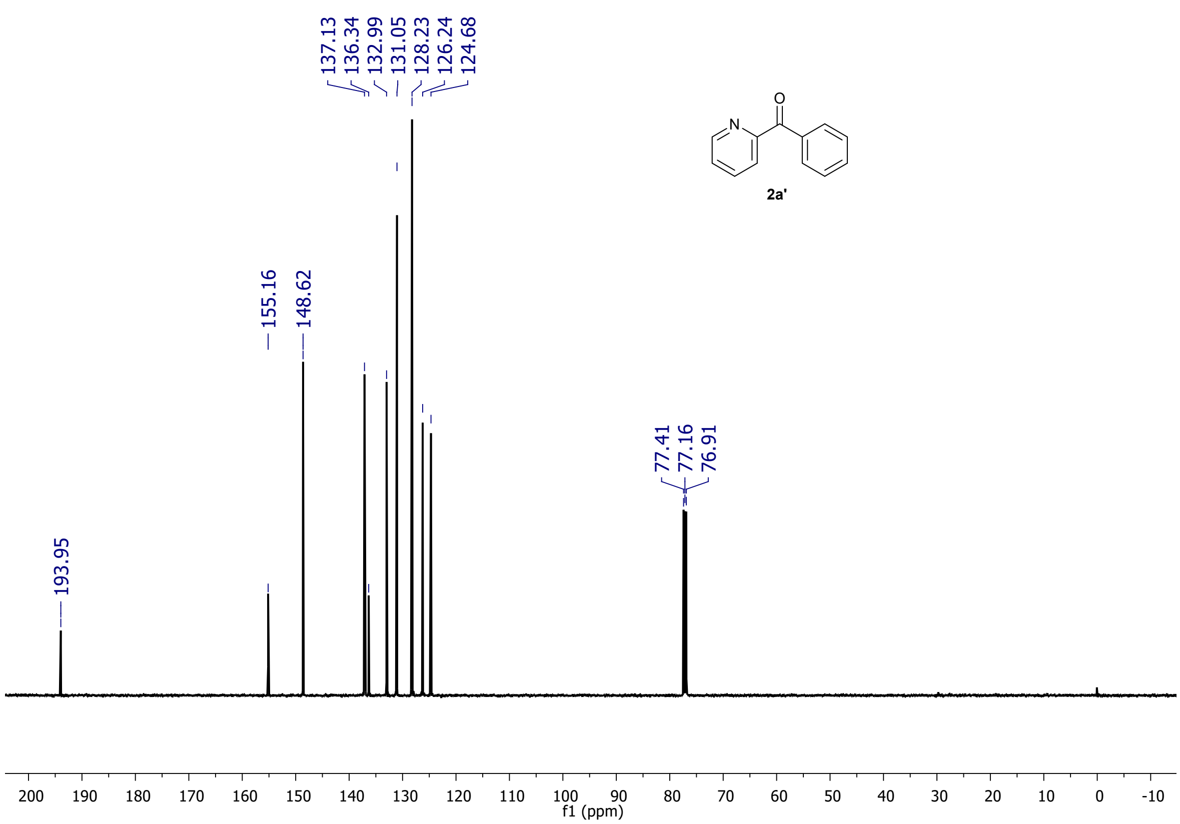
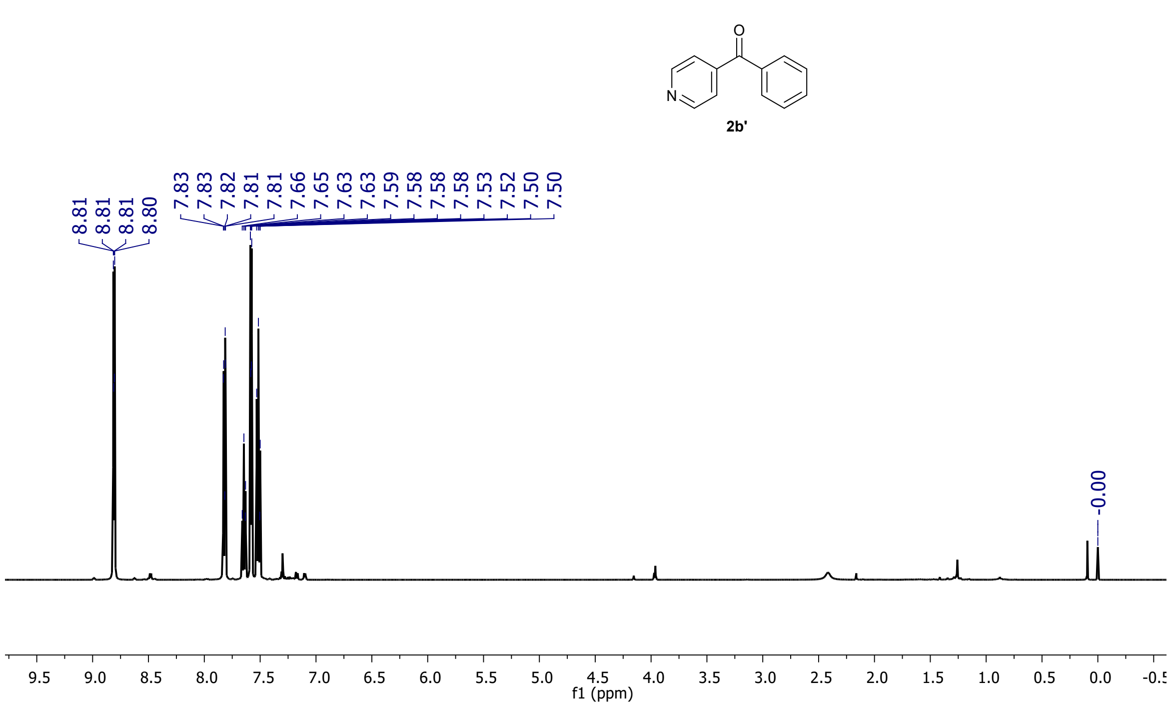
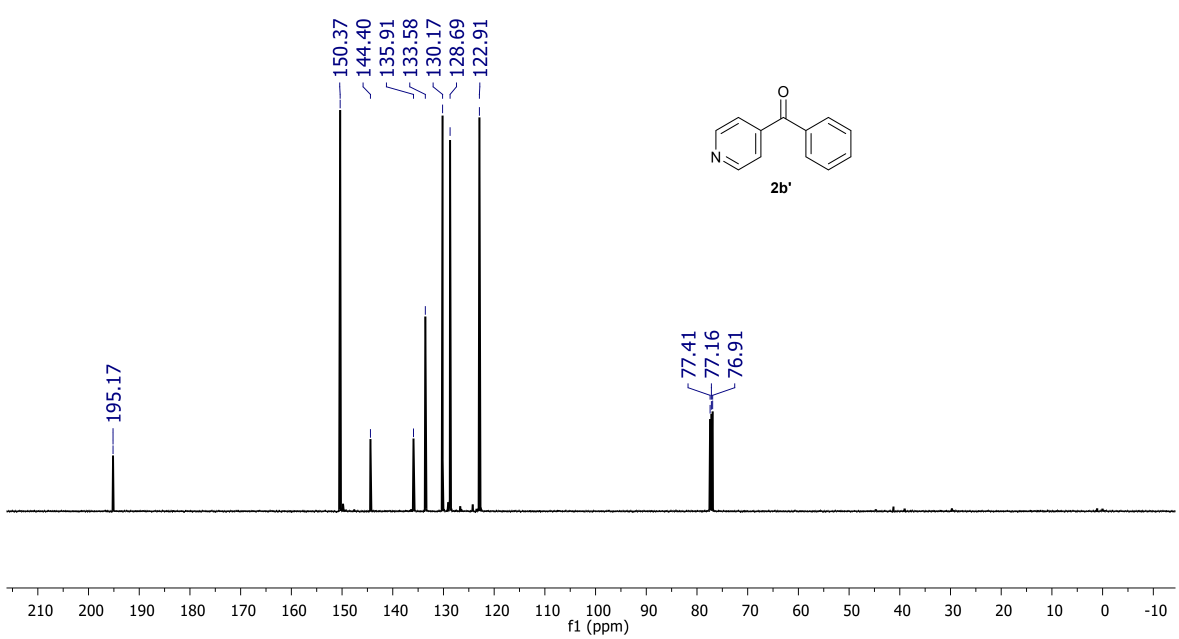


^{1}H NMR (500 MHz, $CDCl_3$)



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



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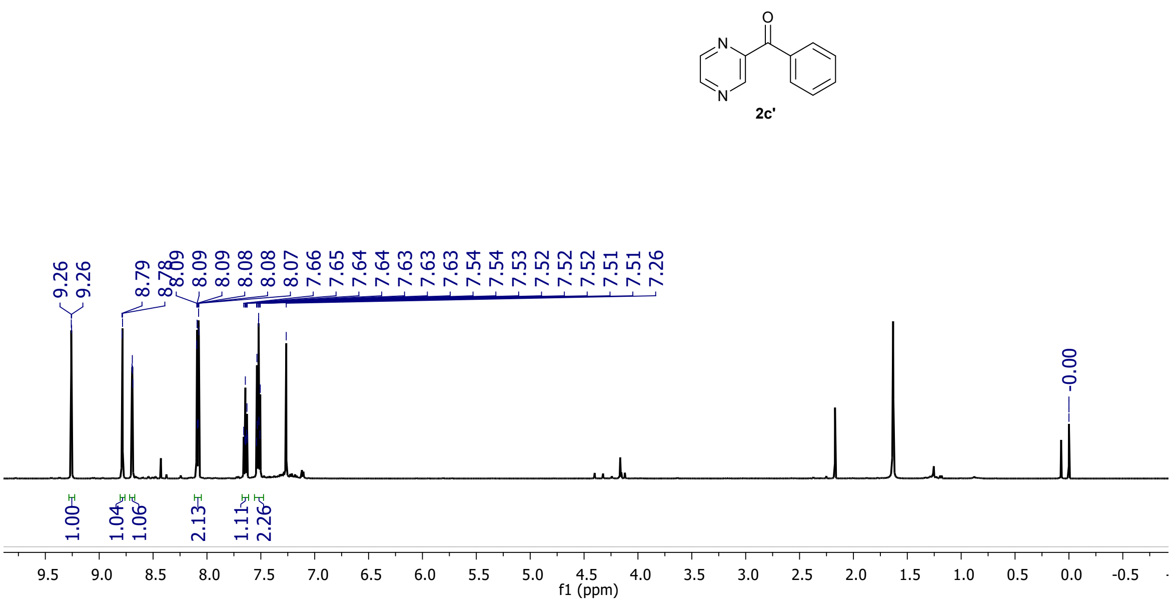
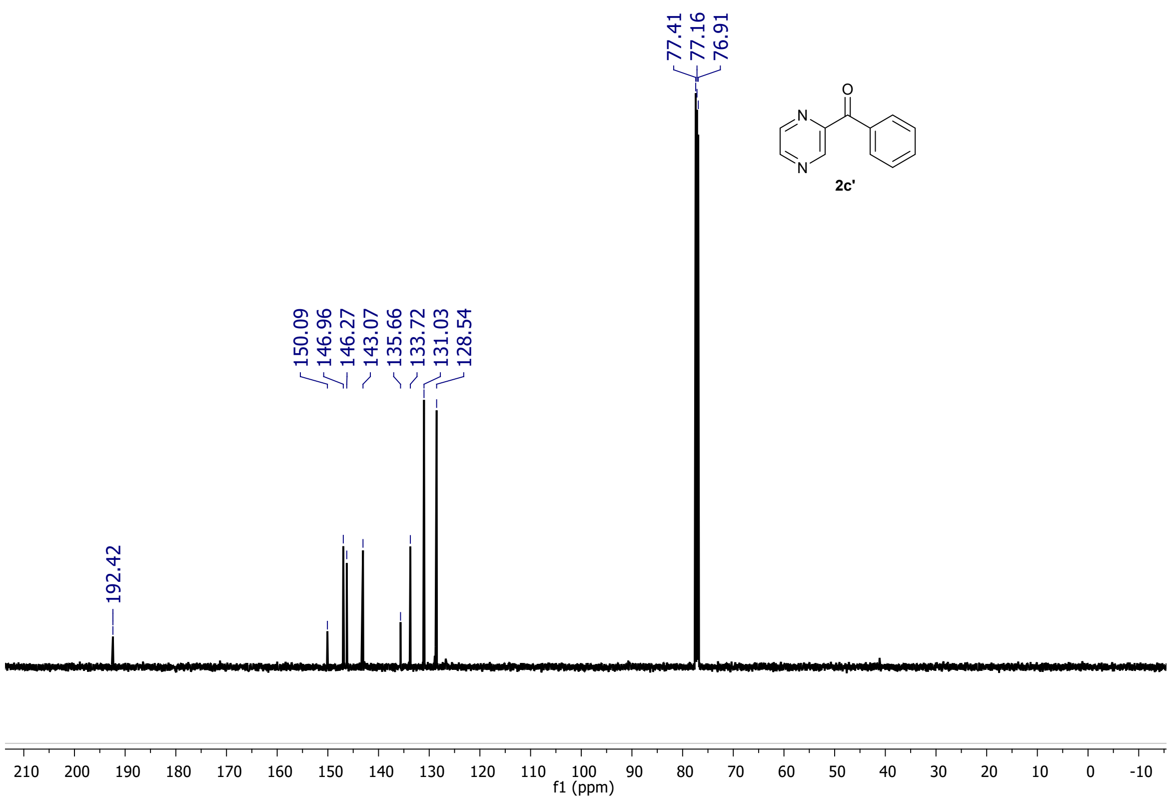
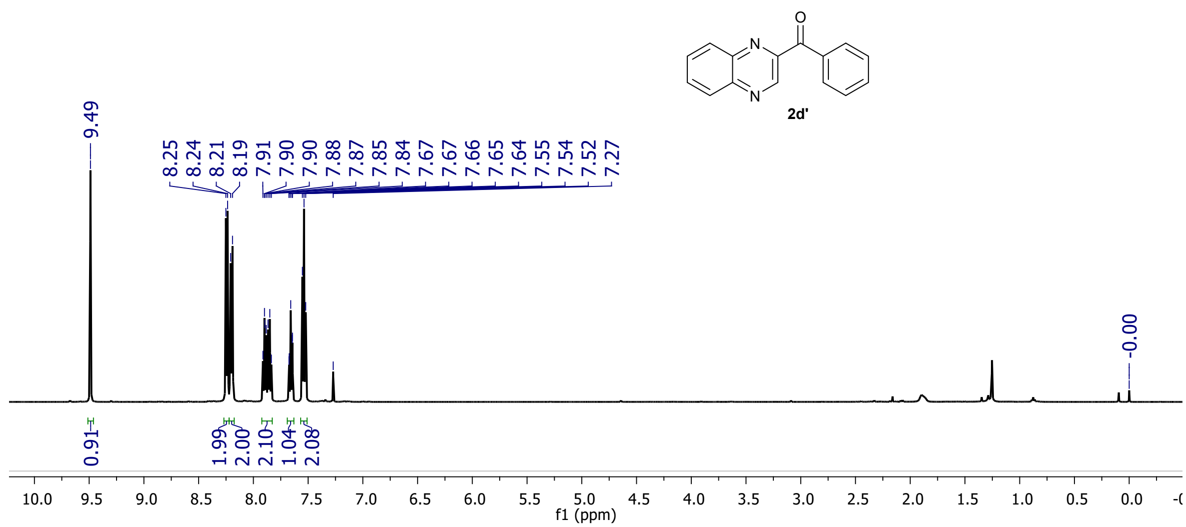


^{13}C NMR (126 MHz, $CDCl_3$)



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



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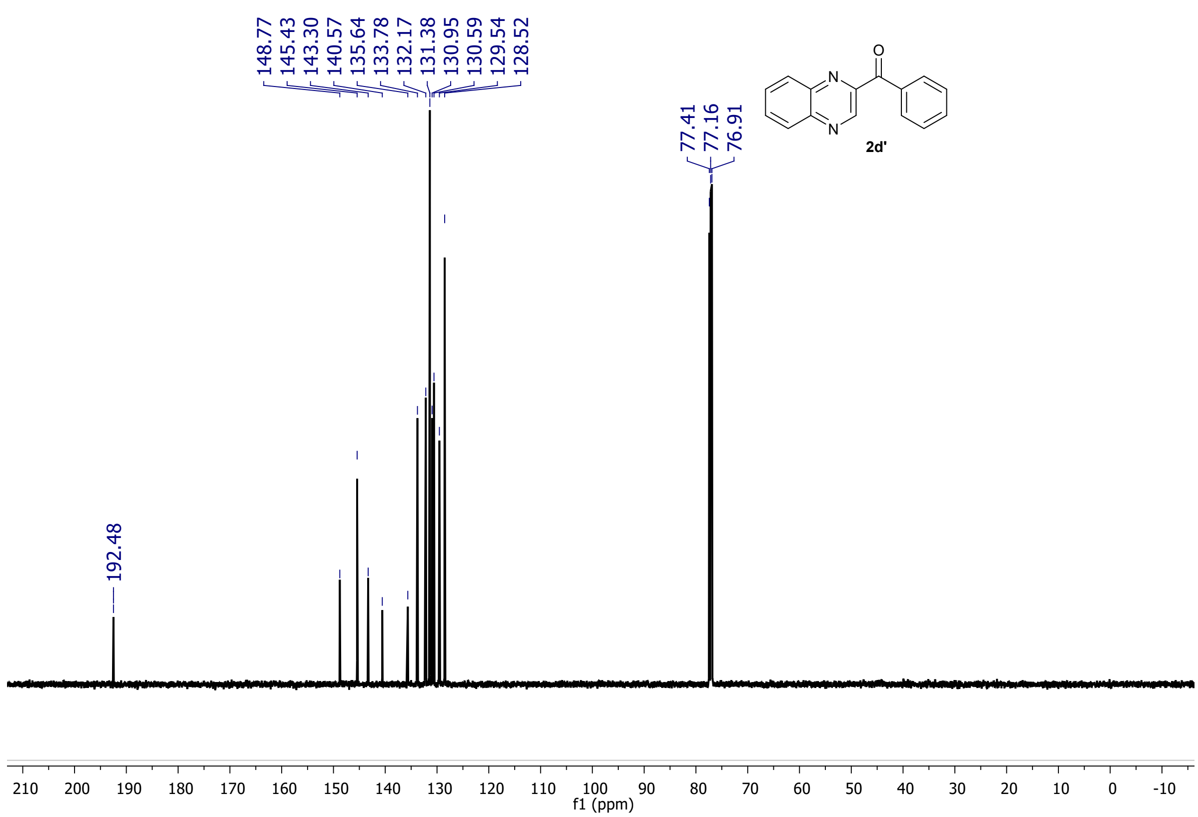

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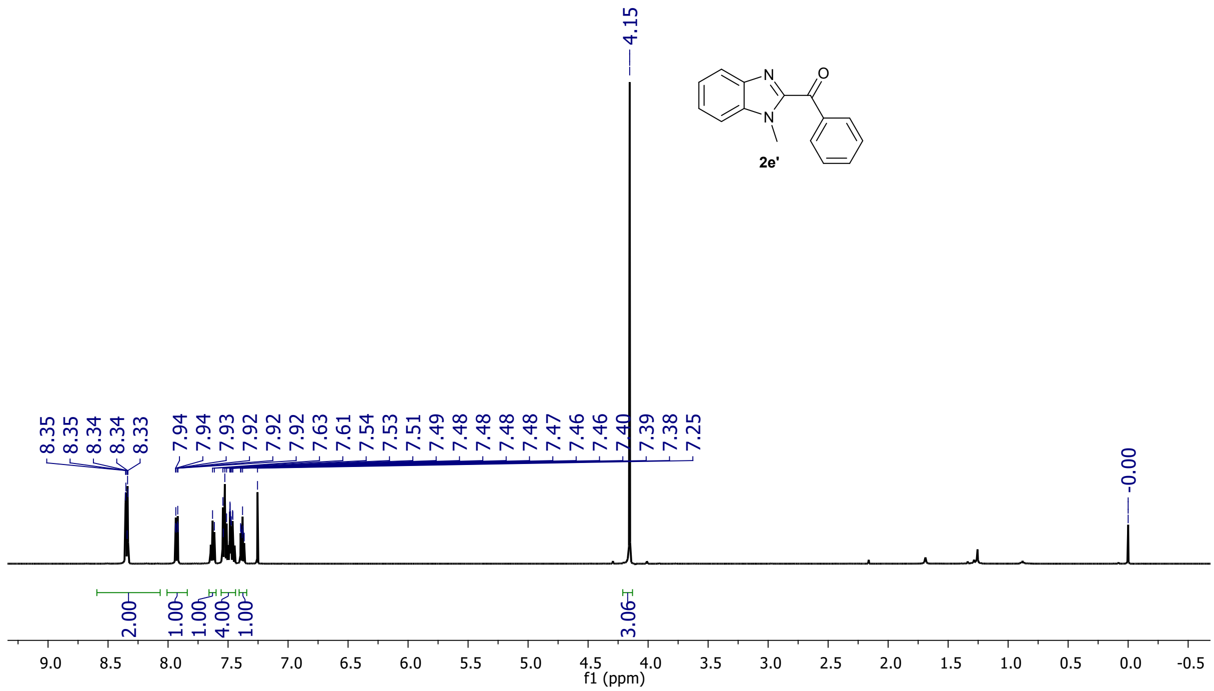
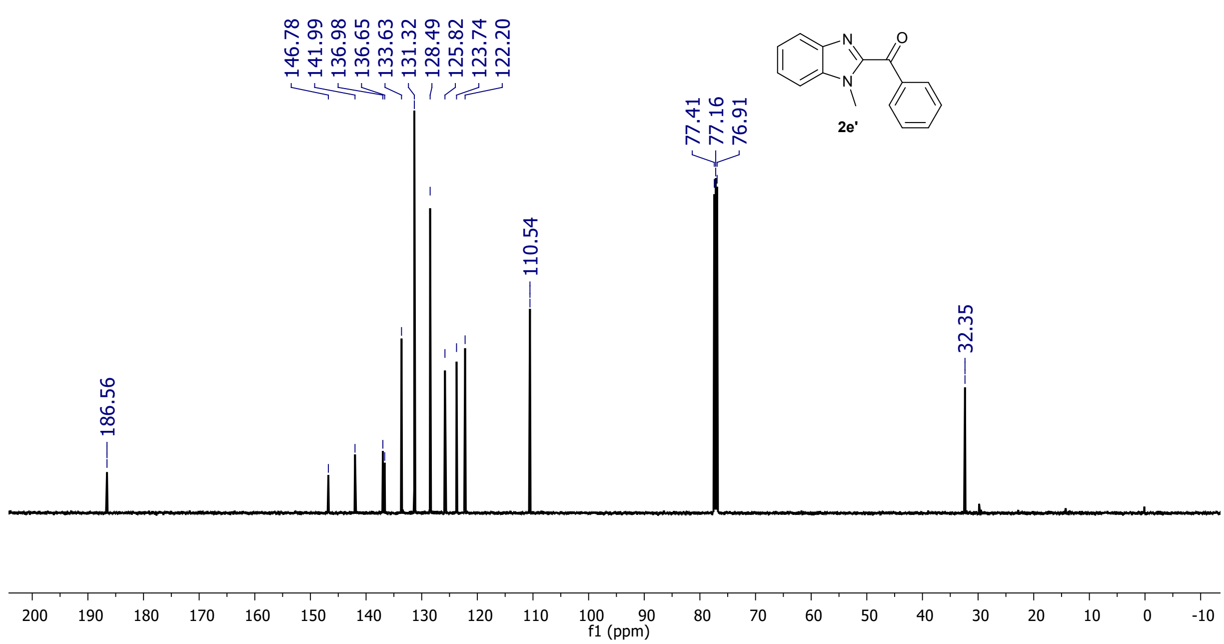
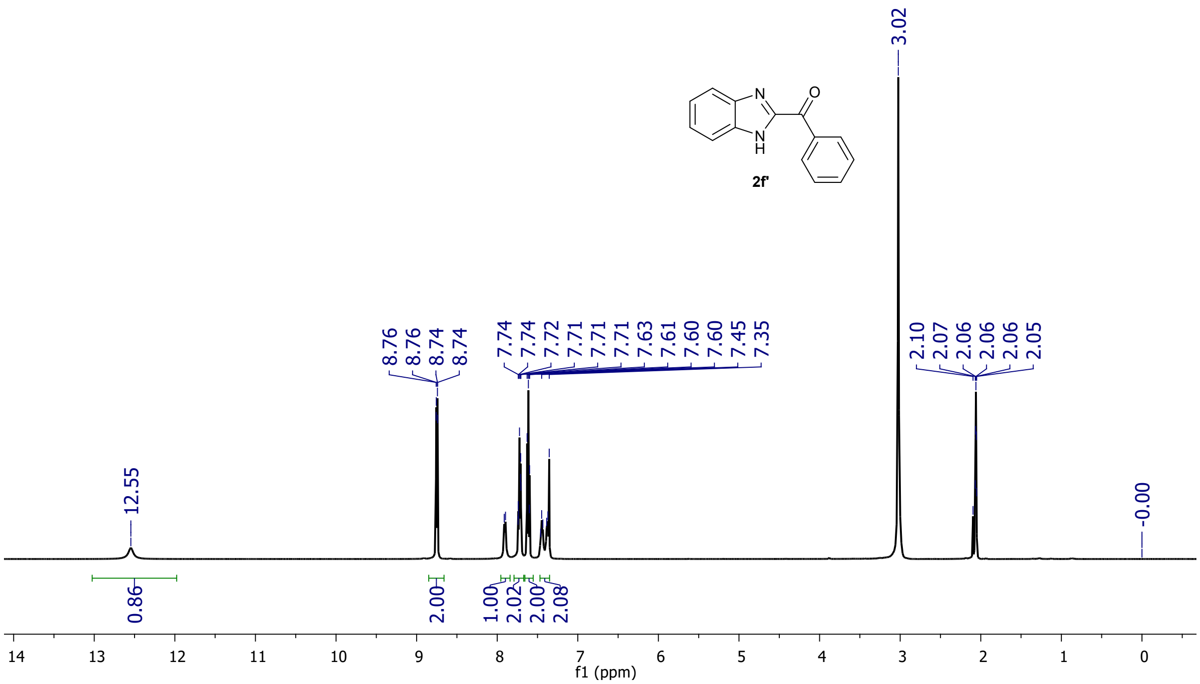


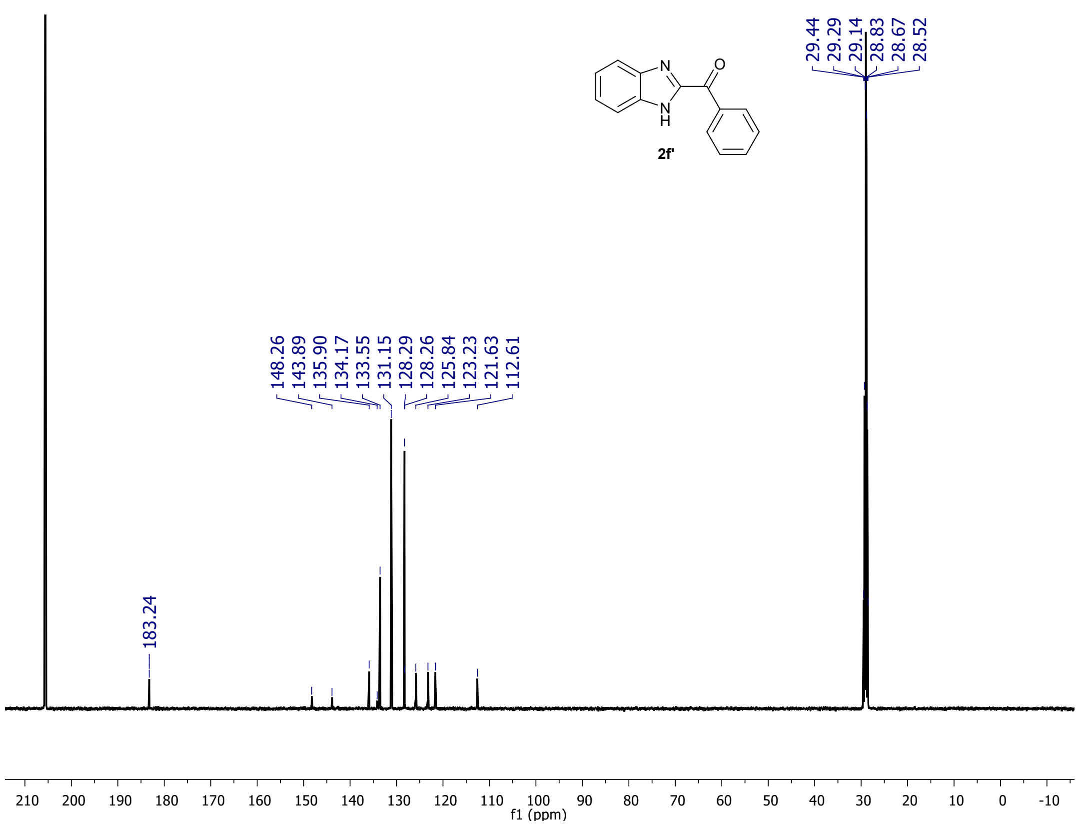
^{13}C NMR (126 MHz, $CDCl_3$)



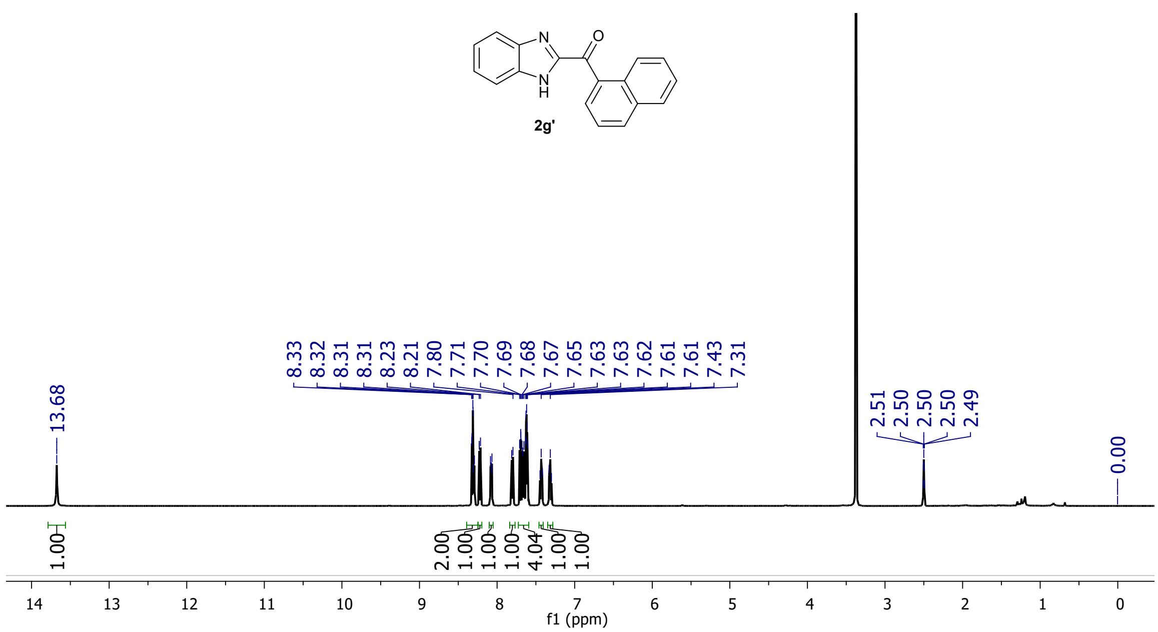
^{1}H NMR (500 MHz, Acetone-d_6)



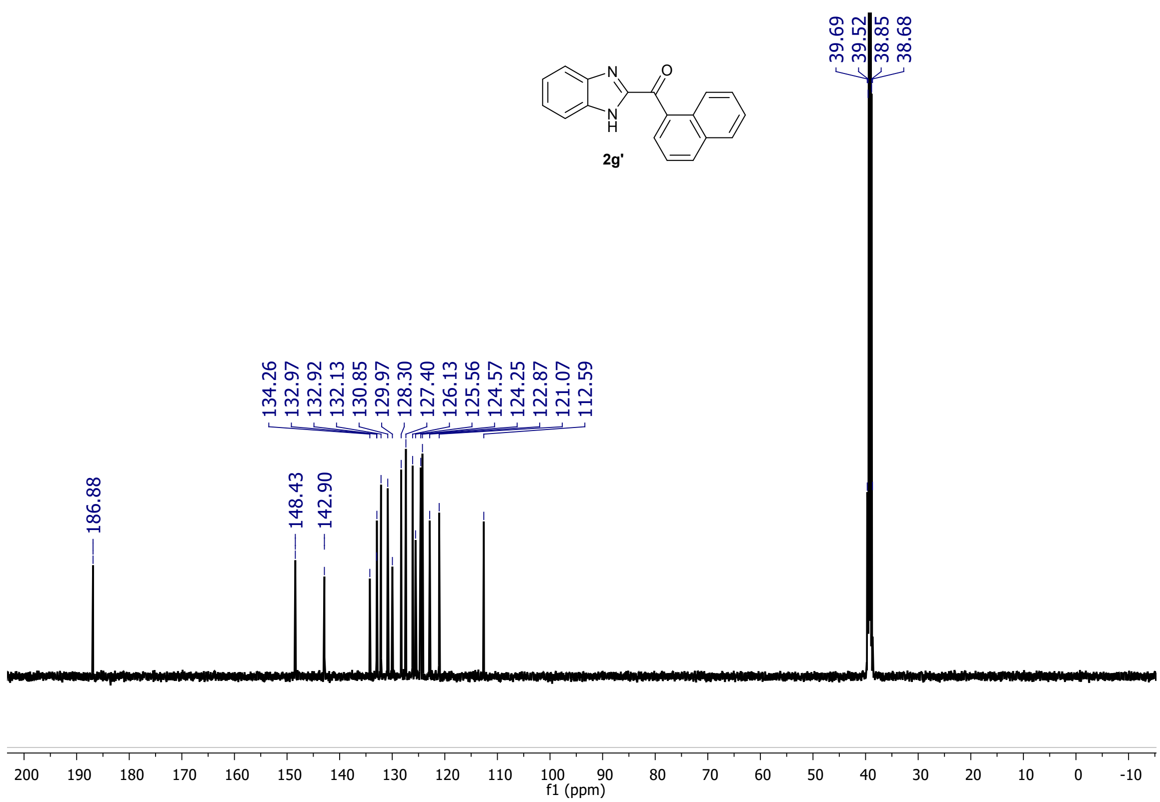
^{13}C NMR (126 MHz, Acetone-d_6)



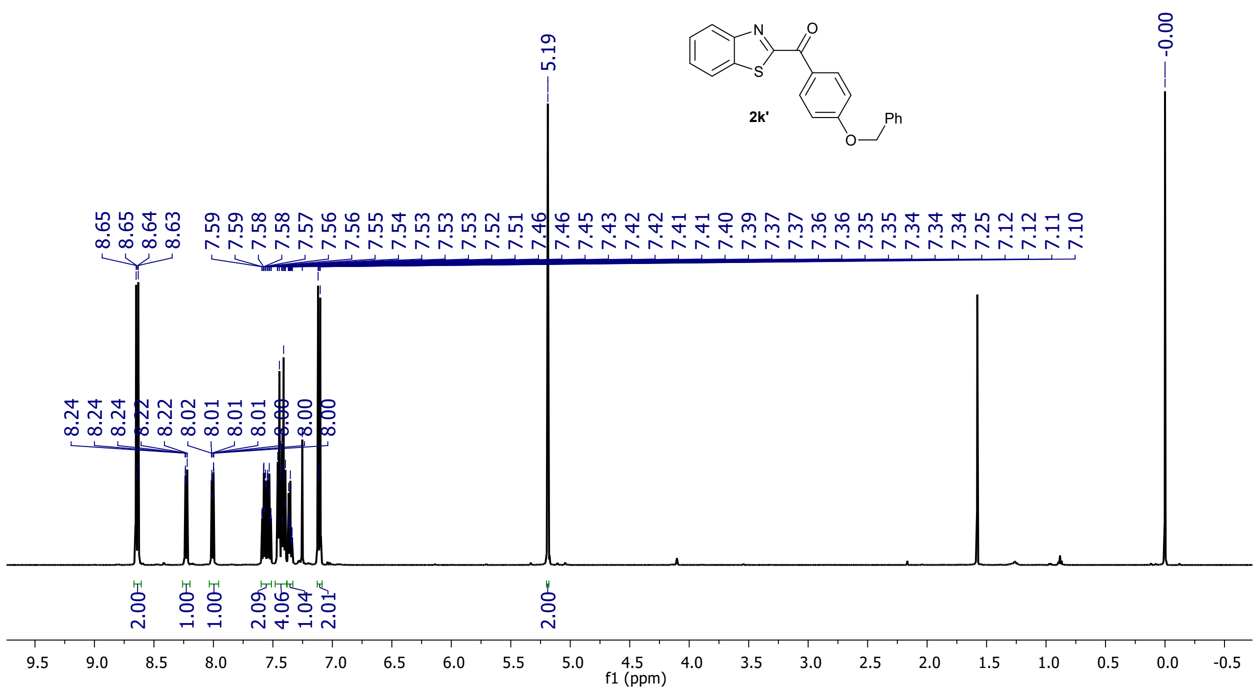
^1H NMR (500 MHz, DMSO-d_6)



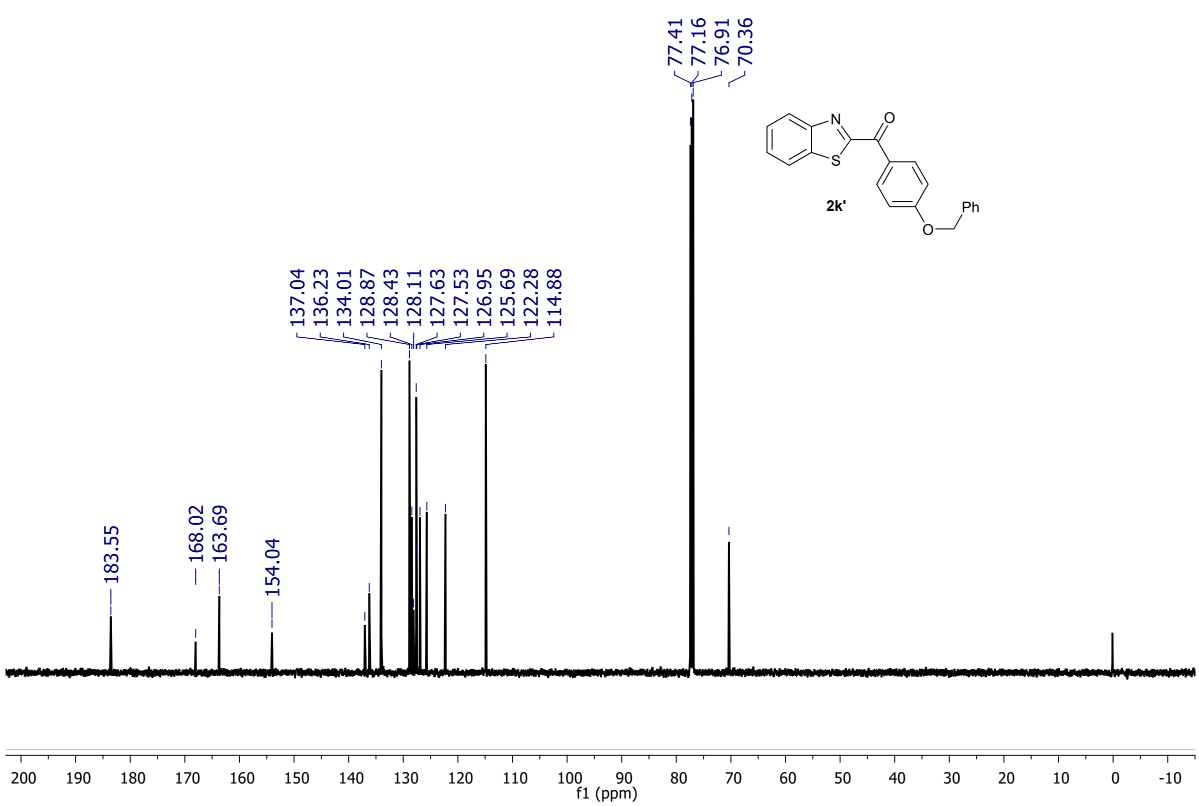
^{13}C NMR (126 MHz, DMSO-d_6)



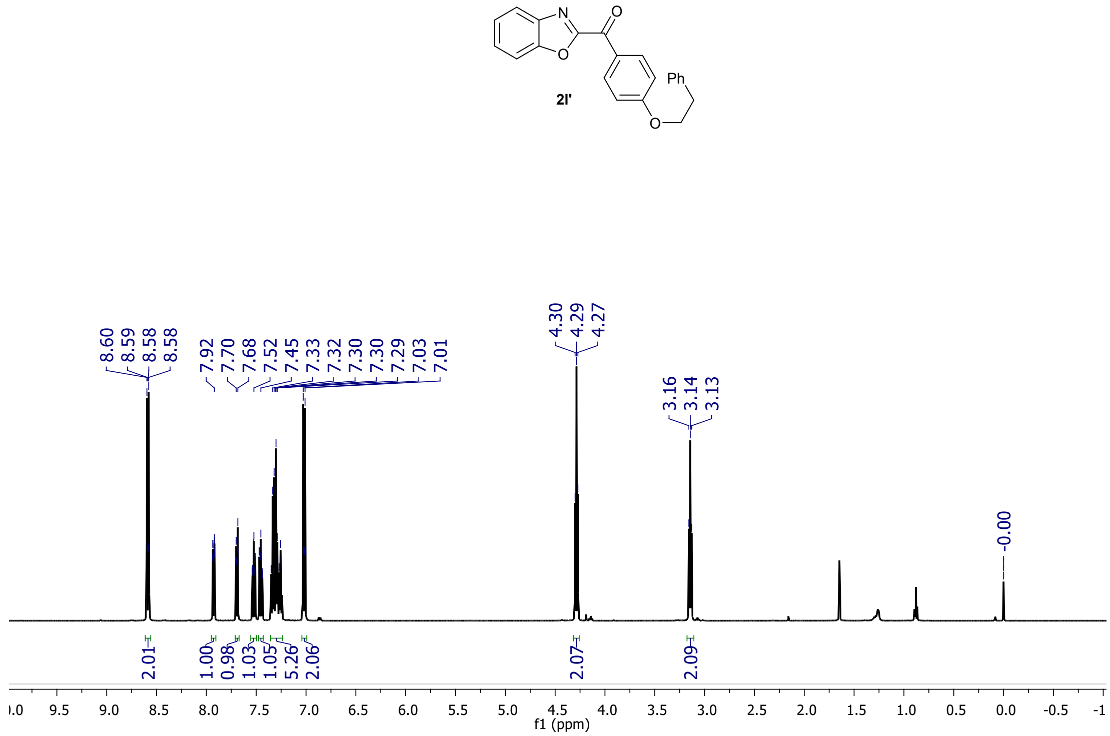
[1]H NMR (500 MHz, $CDCl_3$)



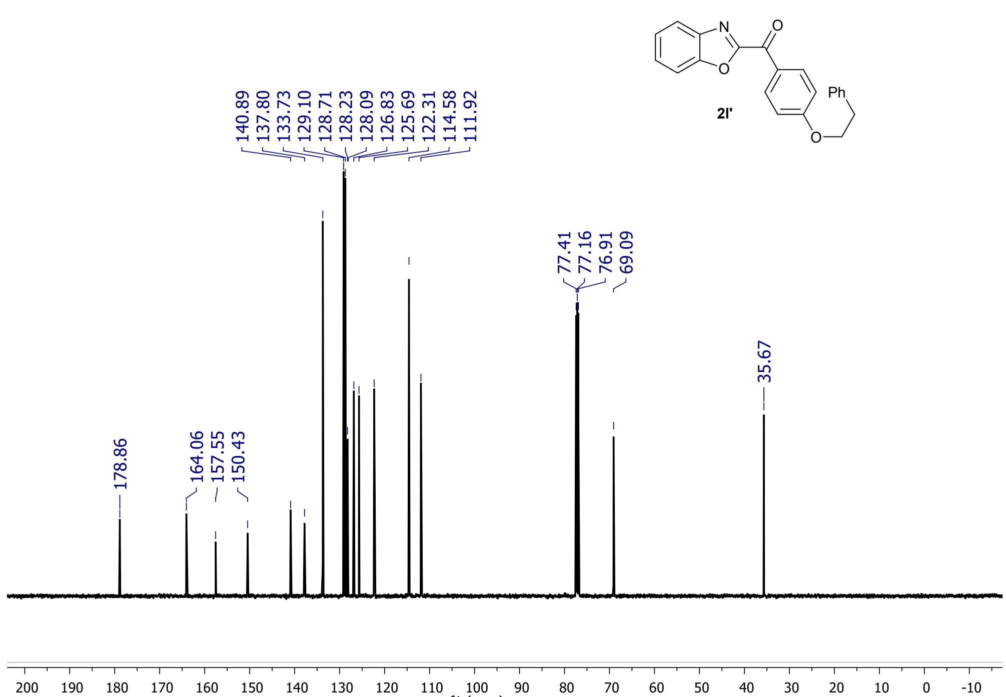
[13]C NMR (126 MHz, $CDCl_3$)



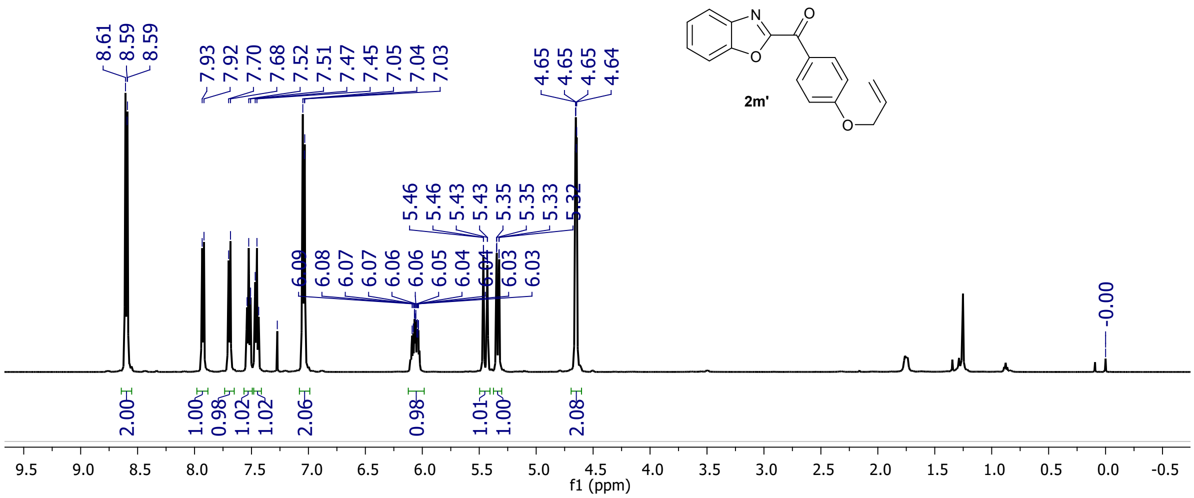
^{1}H NMR (500 MHz, $CDCl_3$)



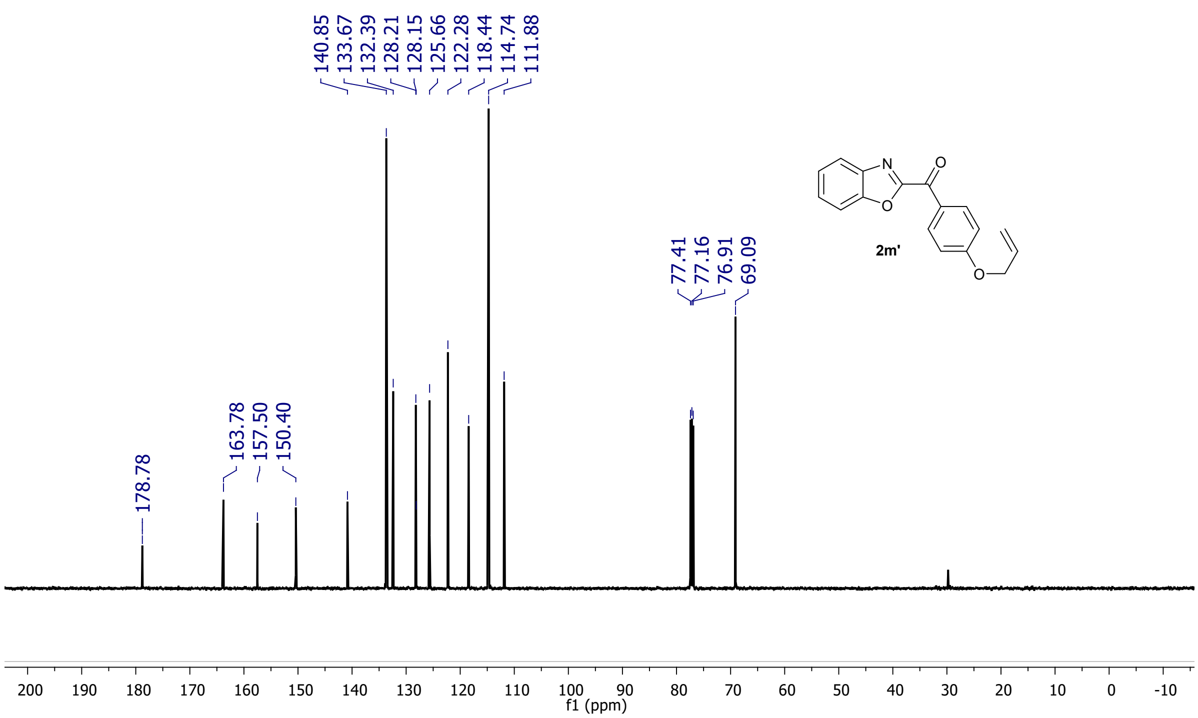
^{13}C NMR (126 MHz, $CDCl_3$)



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



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



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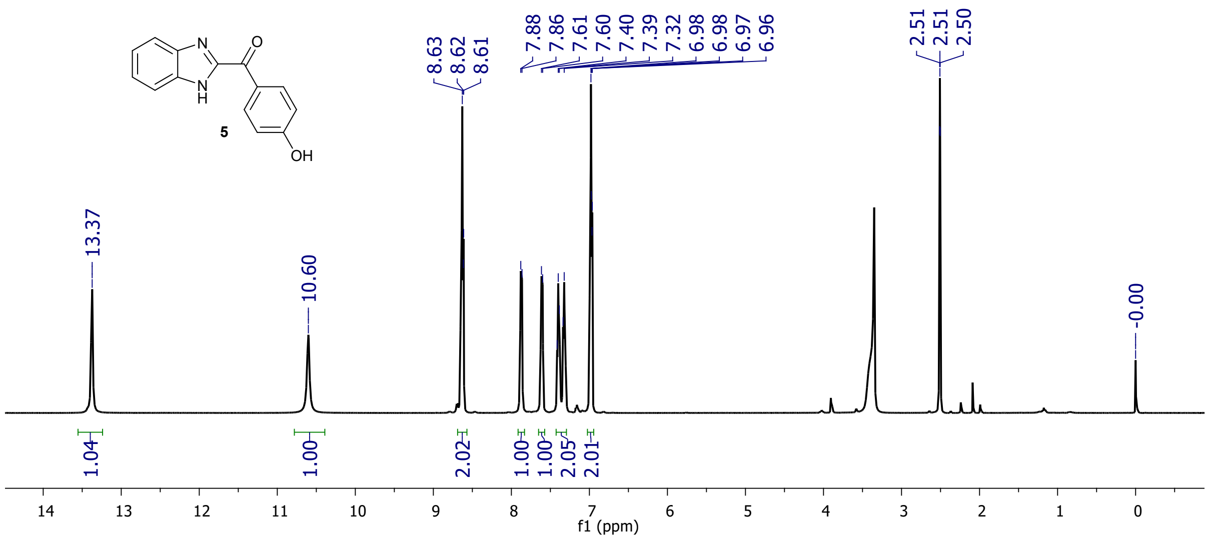

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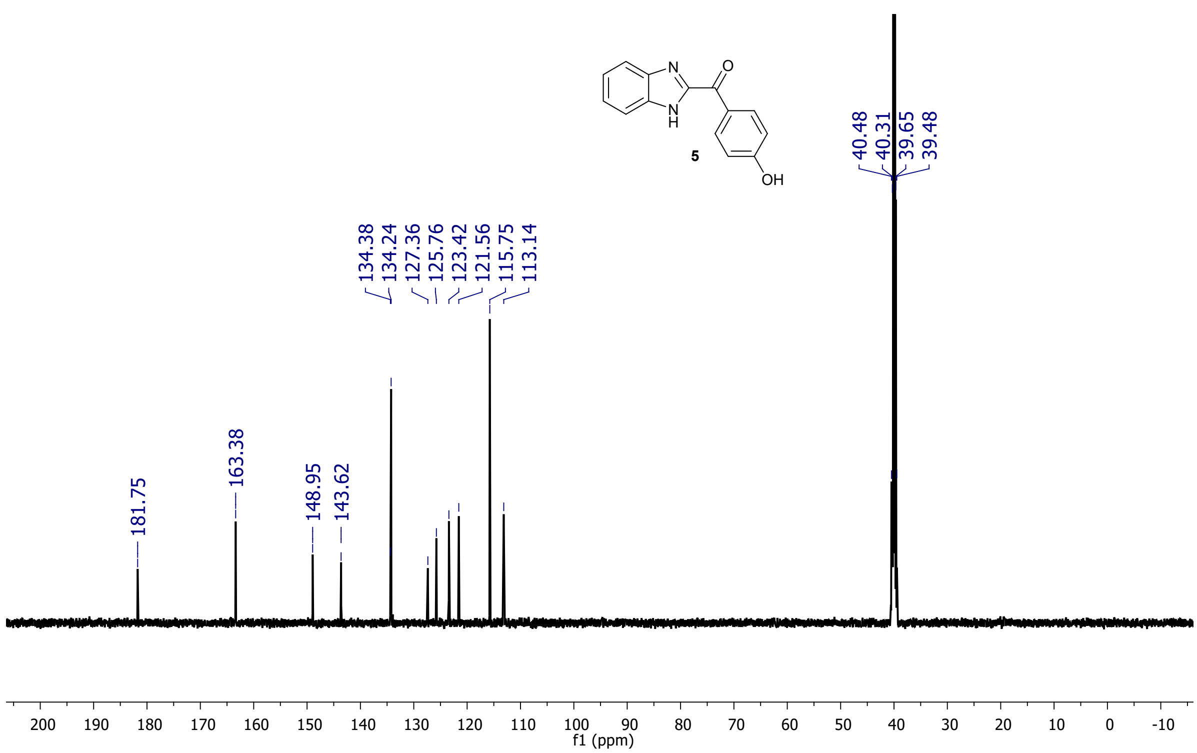
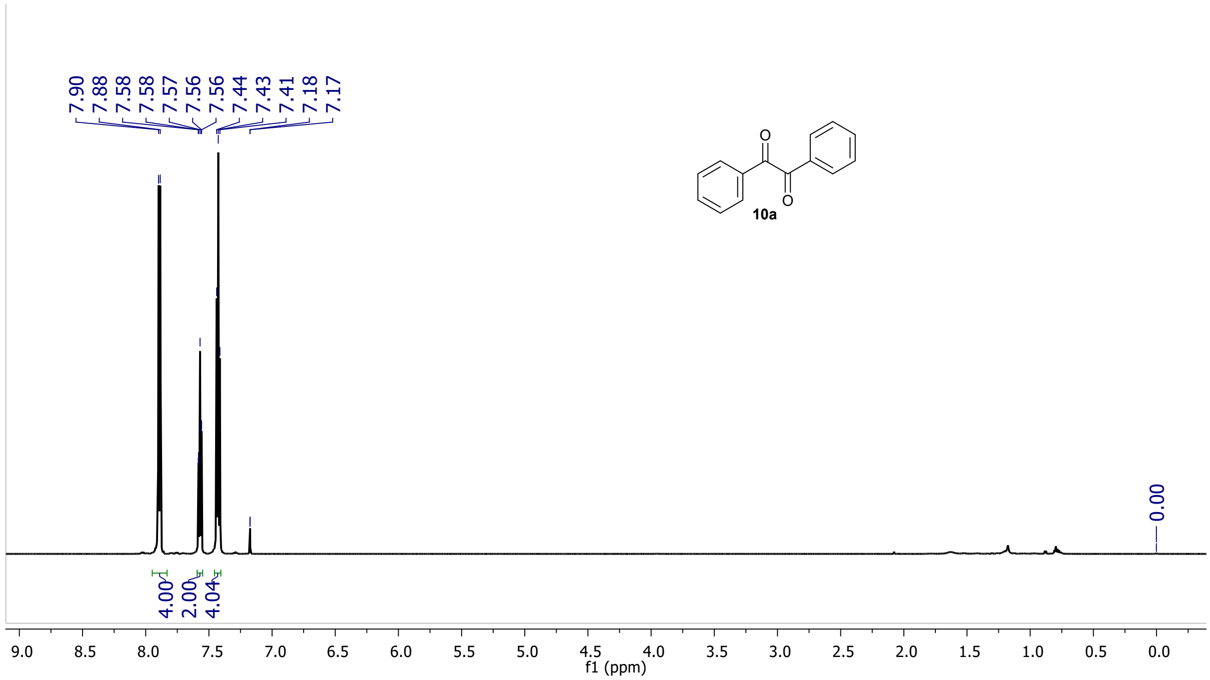
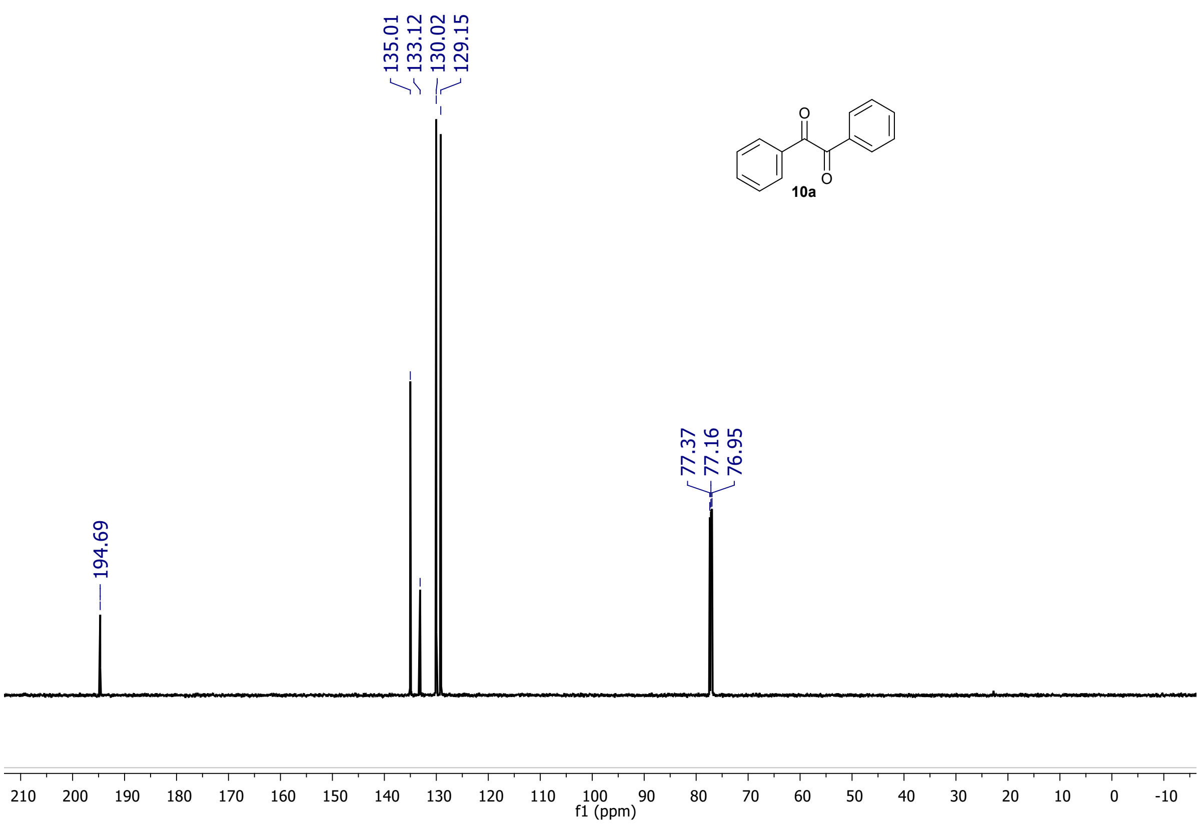


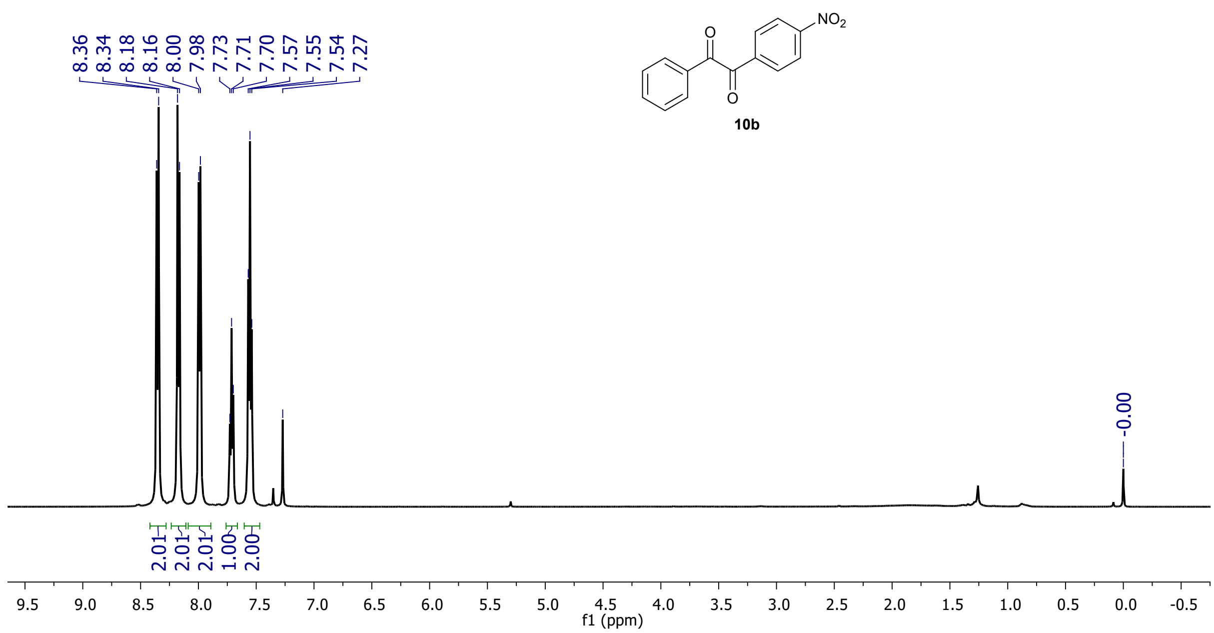
^{1}H NMR (600 MHz, $CDCl_3$)



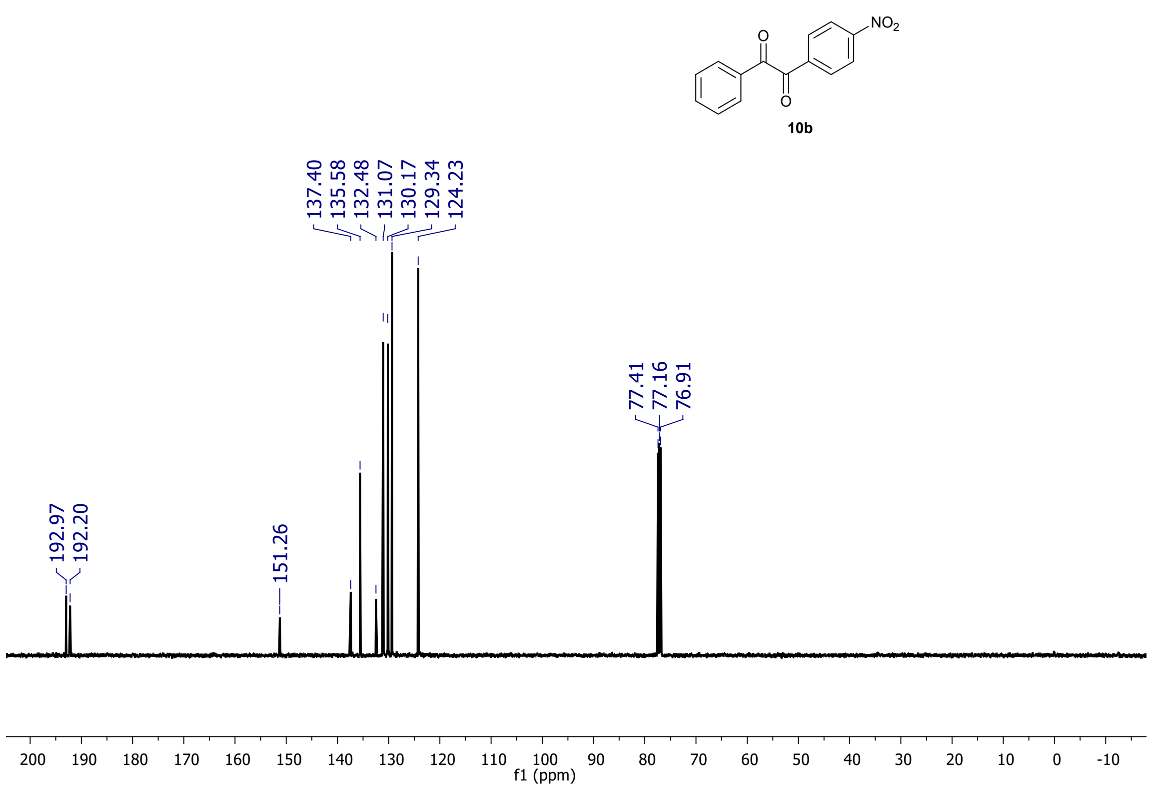
^{13}C NMR (151 MHz, $CDCl_3$)



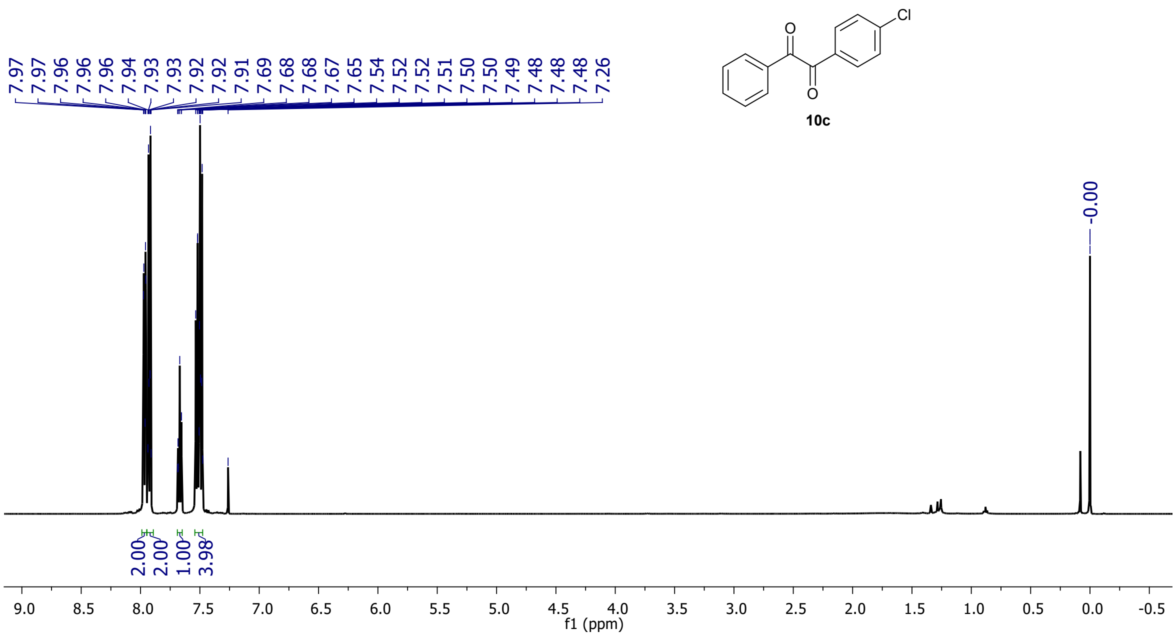
^{1}H NMR (500 MHz, $CDCl_3$)



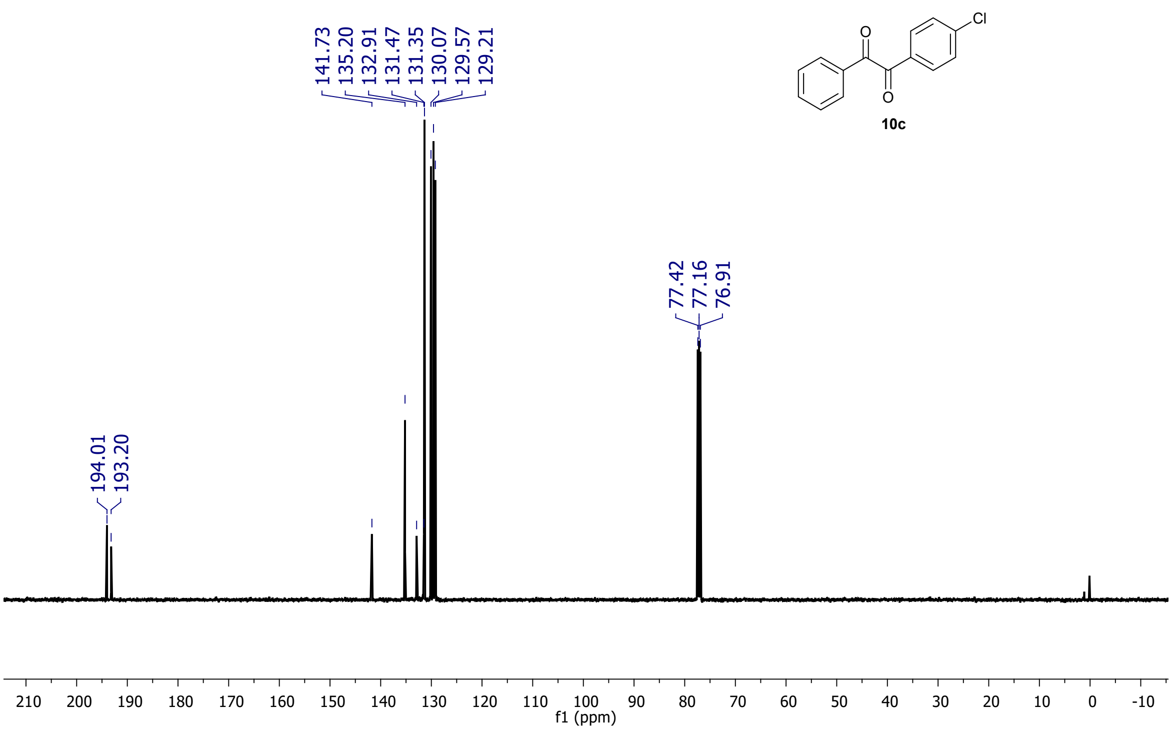
^{13}C NMR (126 MHz, $CDCl_3$)



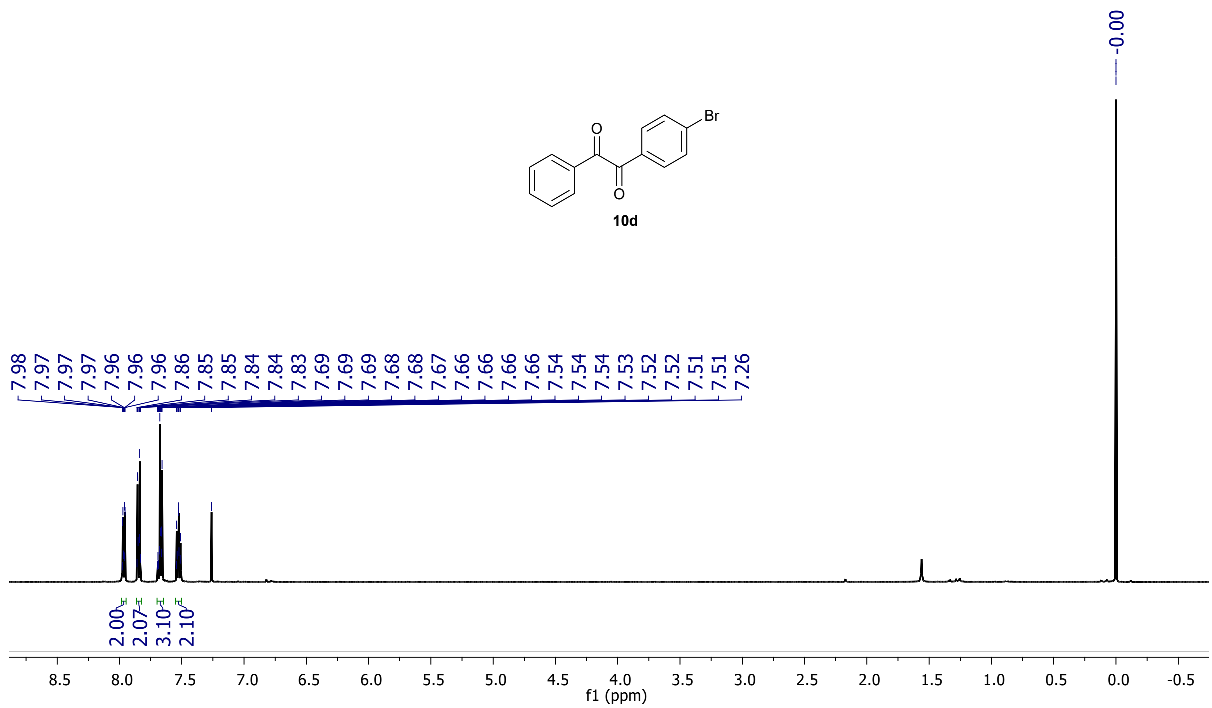
^{11}H NMR (500 MHz, $CDCl_3$)



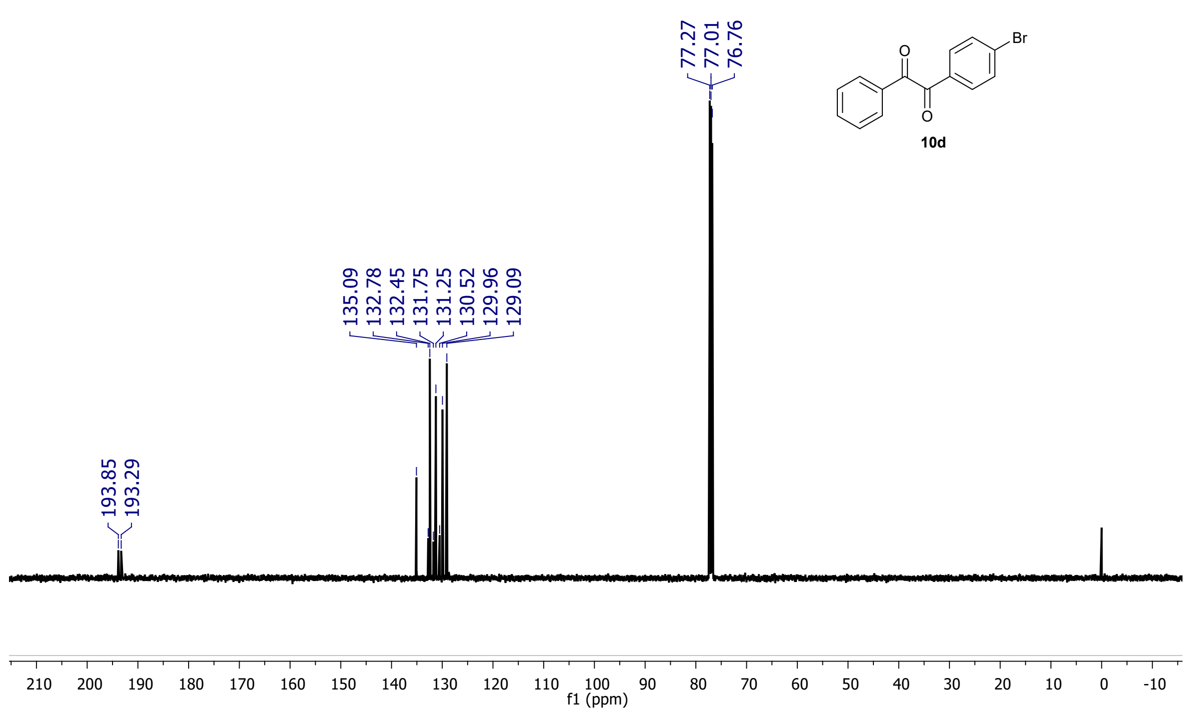
^{13}C NMR (126 MHz, $CDCl_3$)



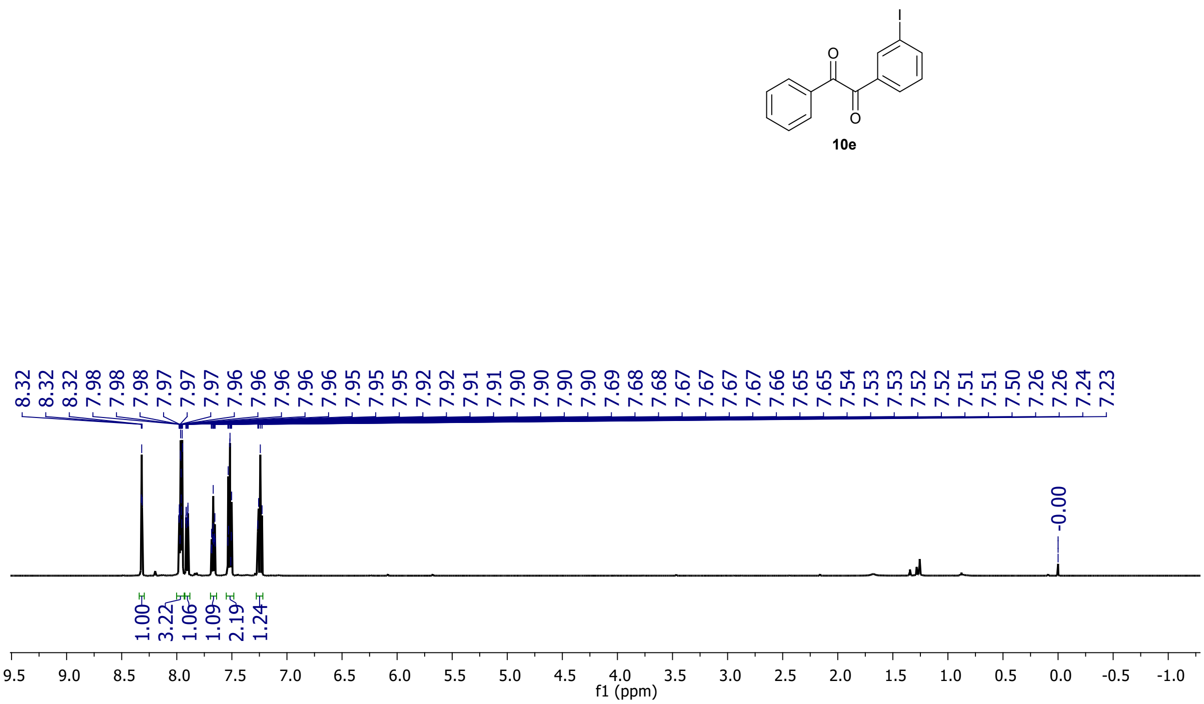
^{1}H NMR (500 MHz, $CDCl_3$)



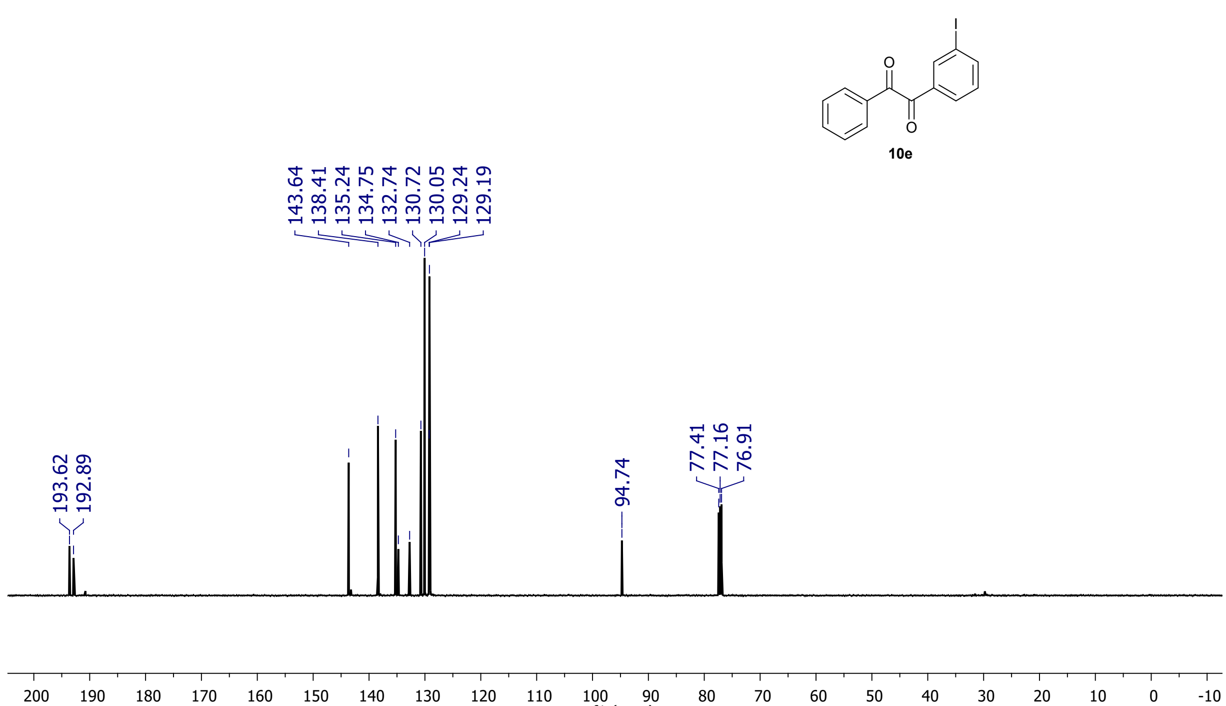
^{13}C NMR (126 MHz, $CDCl_3$)



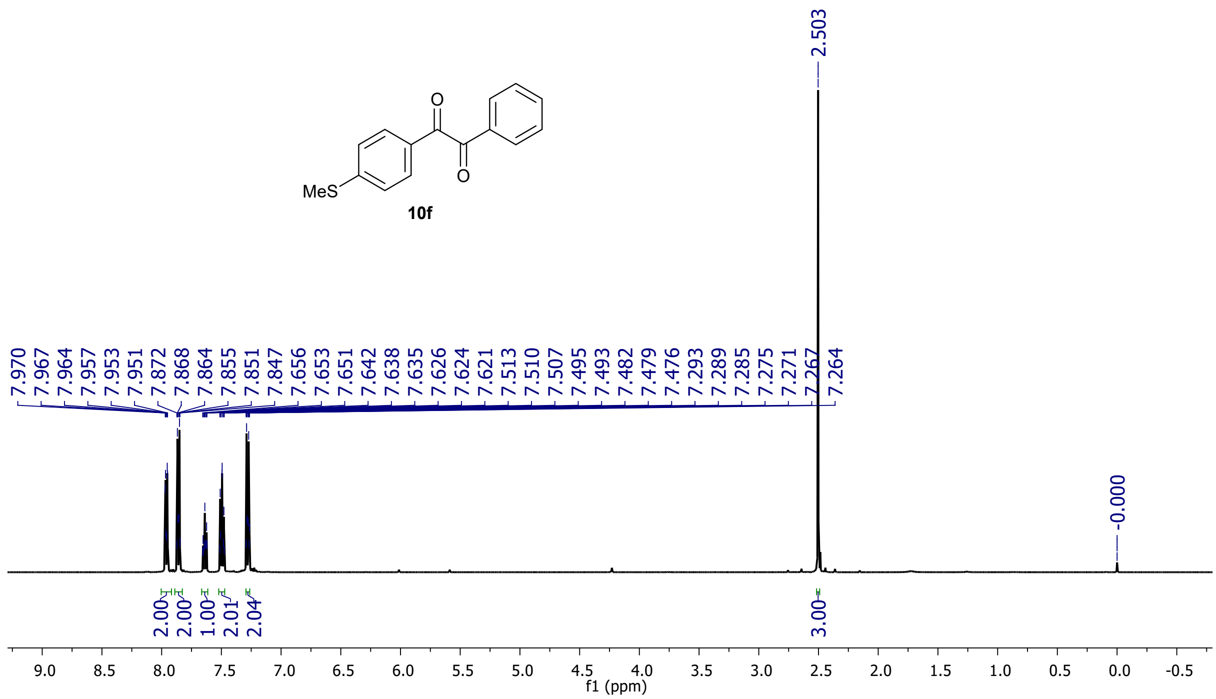
^{1}H NMR (500 MHz, $CDCl_3$)



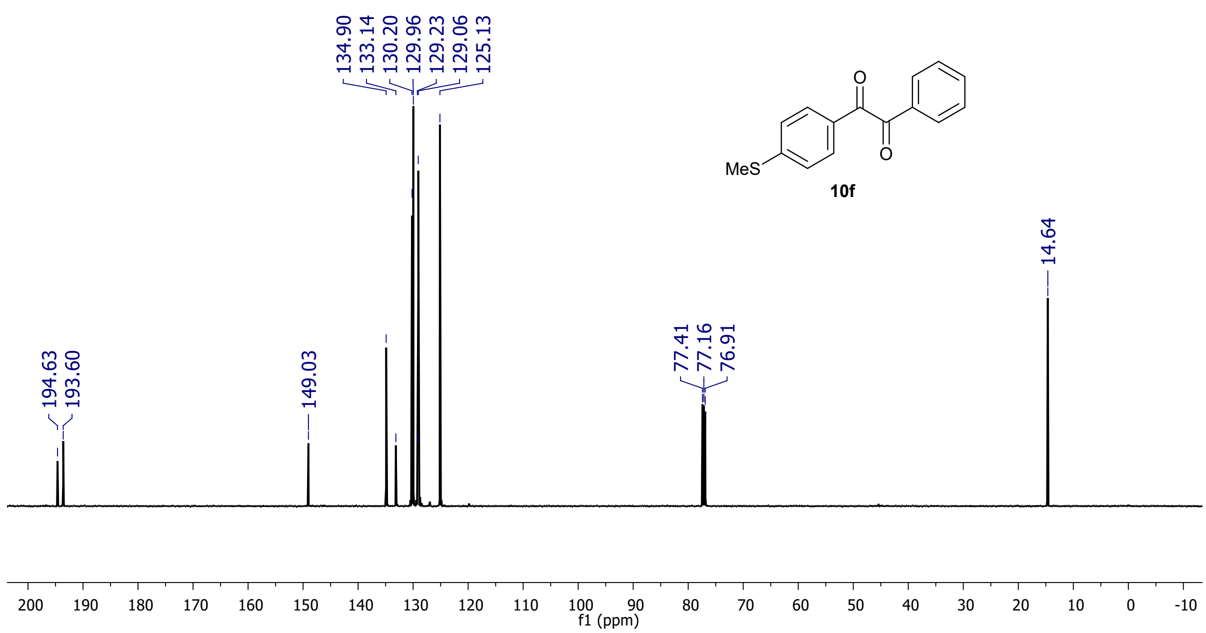
^{13}C NMR (126 MHz, $CDCl_3$)



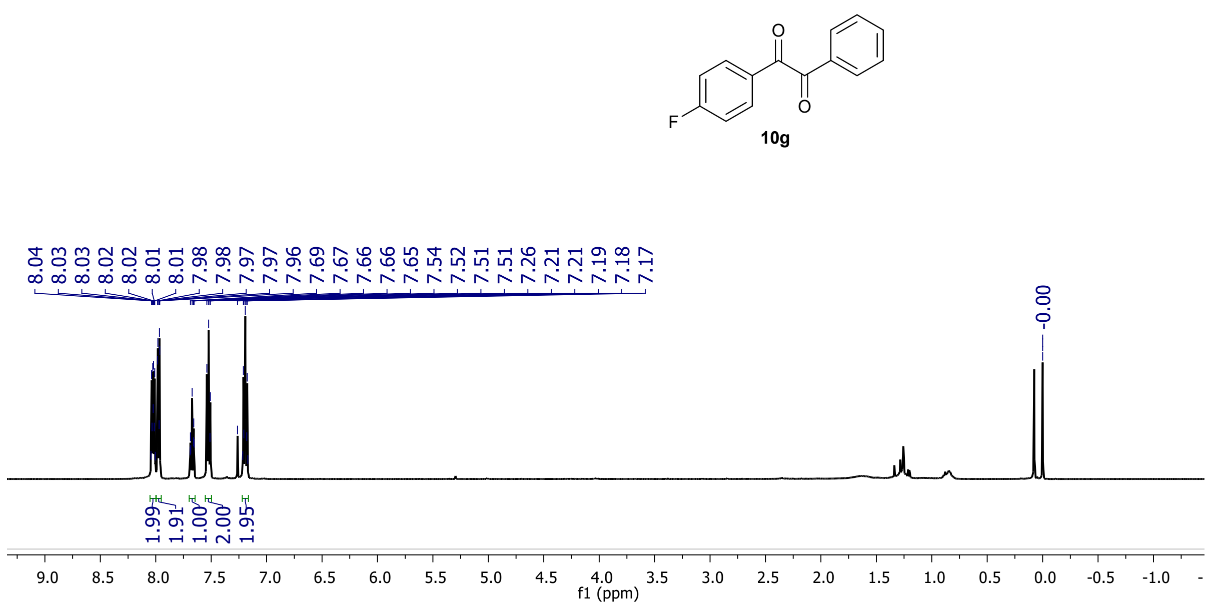
^{1}H NMR (500 MHz, $CDCl_3$)



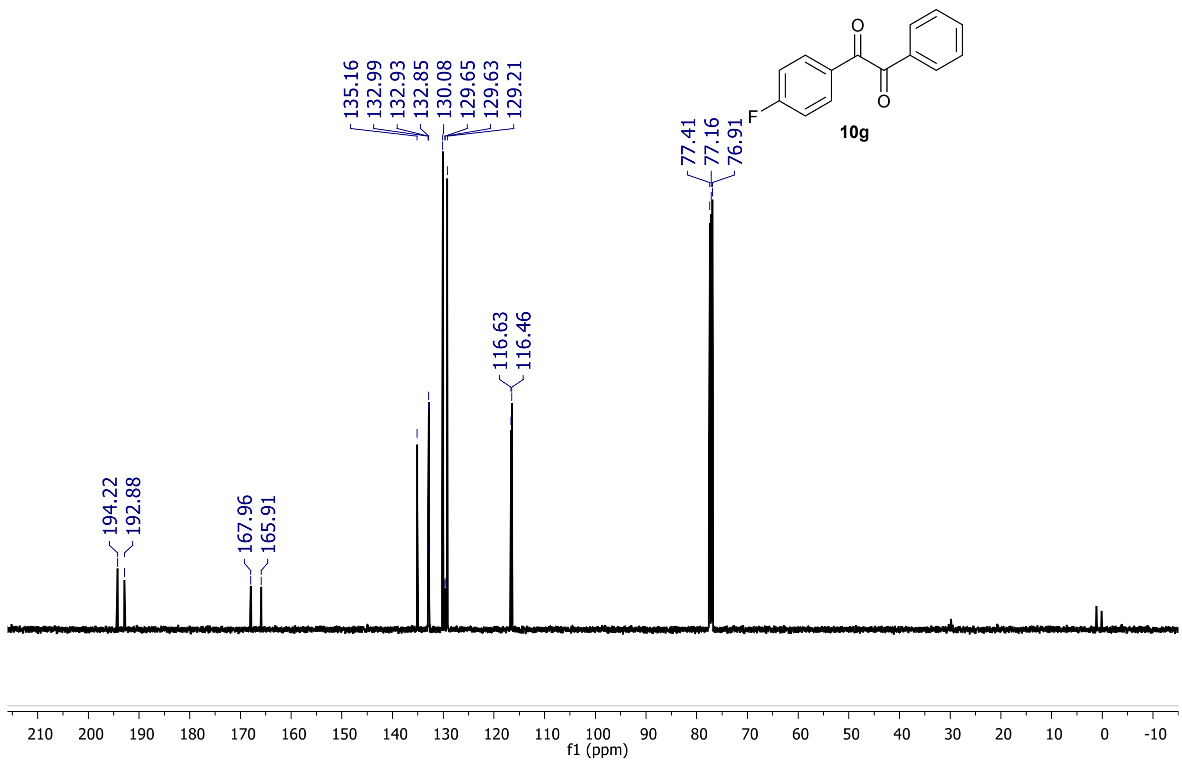
^{13}C NMR (126 MHz, $CDCl_3$)



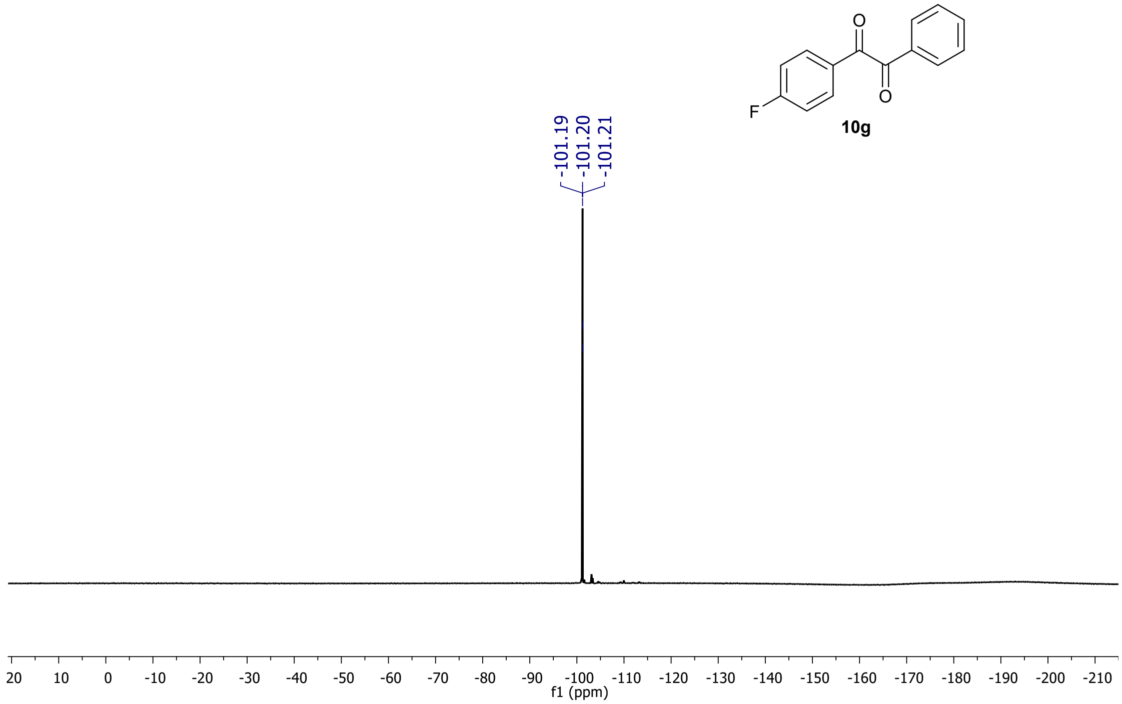
^{1}H NMR (500 MHz, $CDCl_3$)



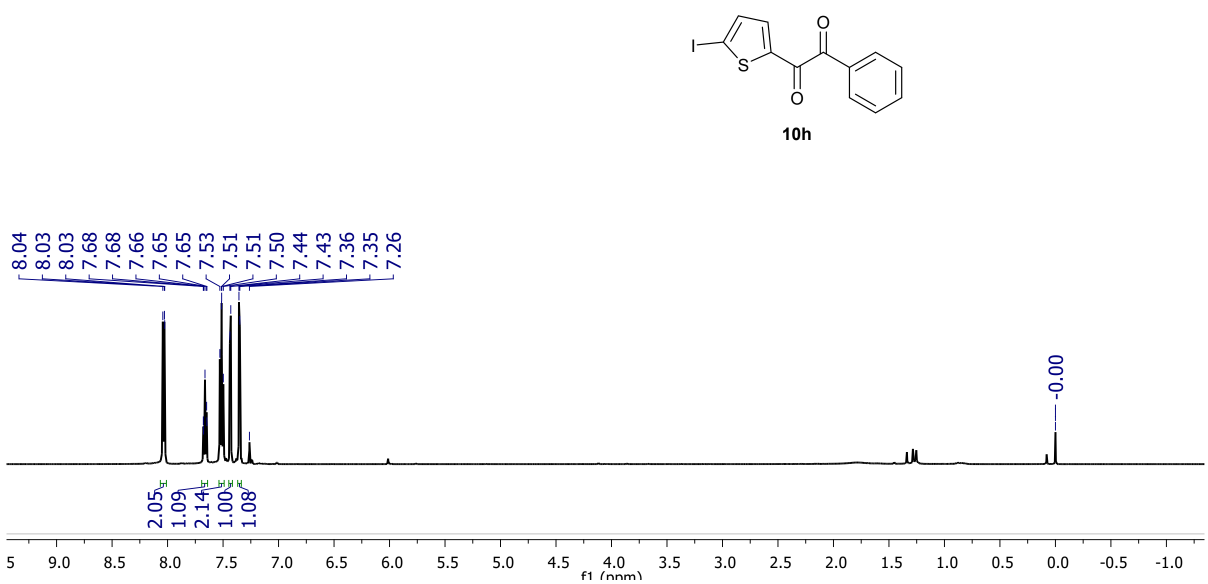
^{13}C NMR (126 MHz, $CDCl_3$)



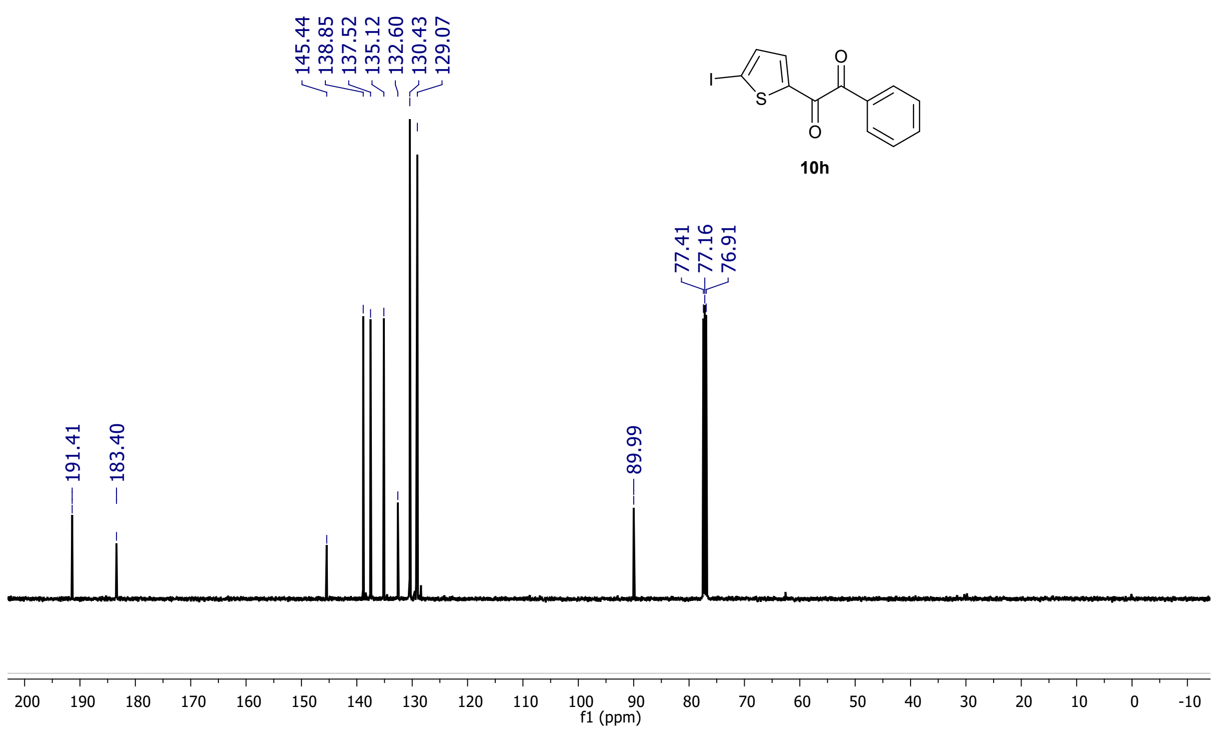
^{19}F NMR (471 MHz, $CDCl_3$)



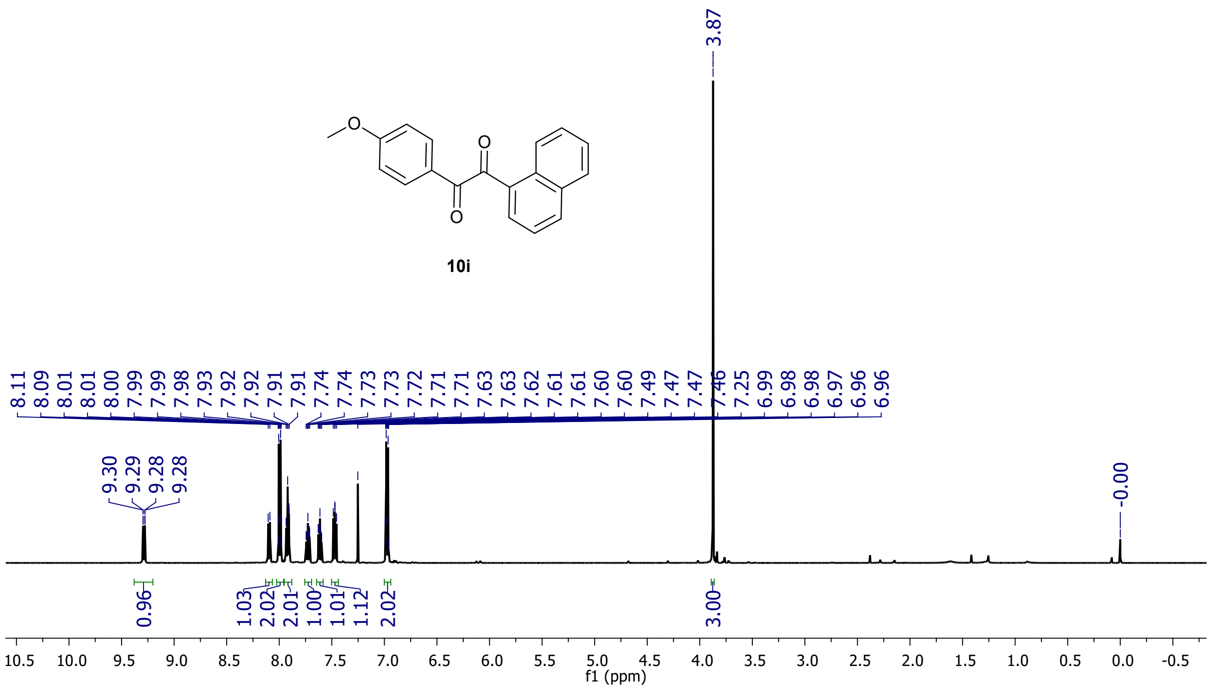
^{1}H NMR (500 MHz, $CDCl_3$)



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

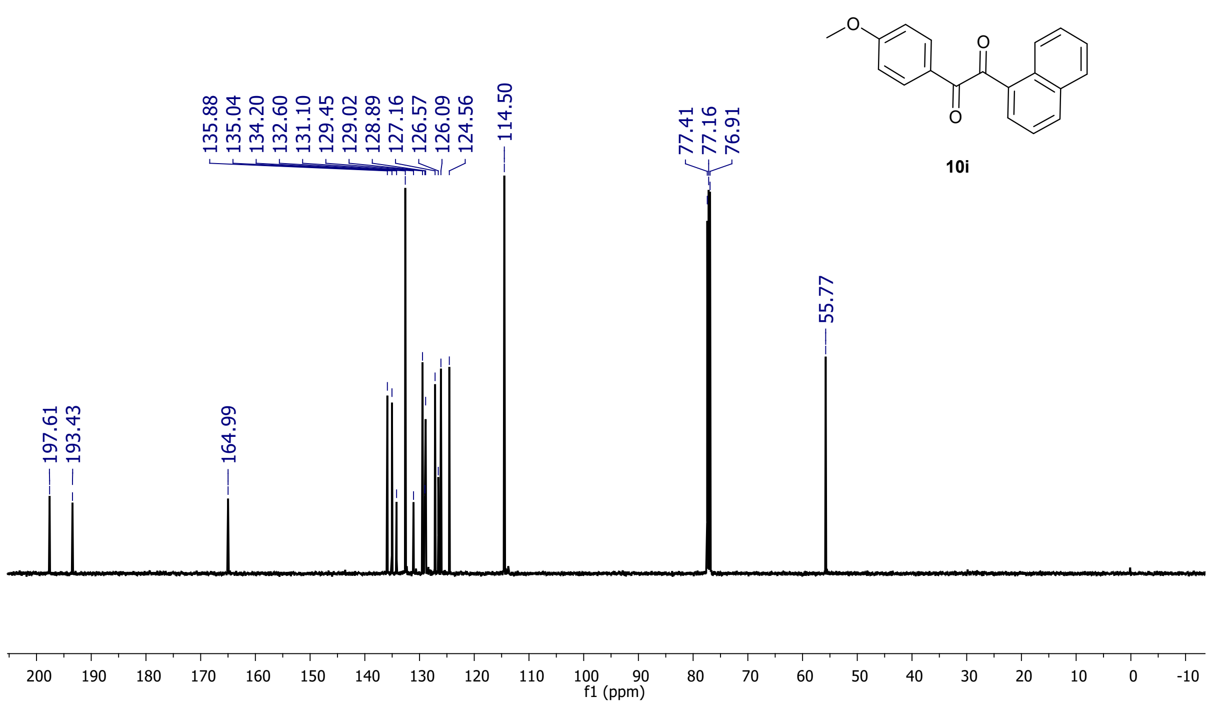


^{1}H NMR (500 MHz, $CDCl_3$)



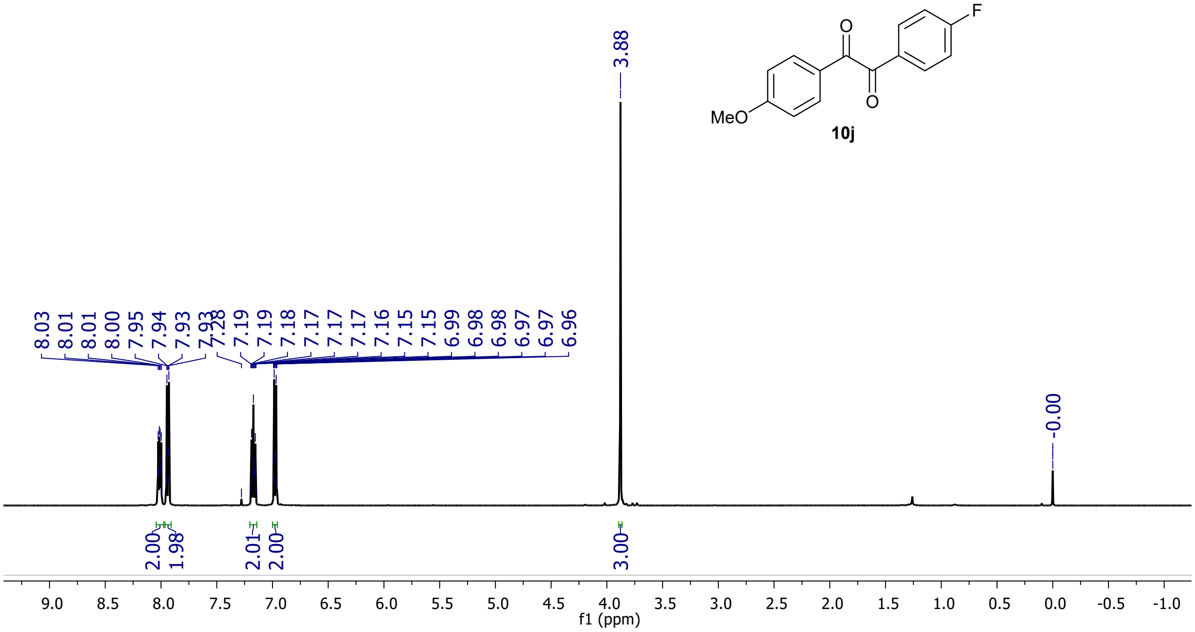
10i

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

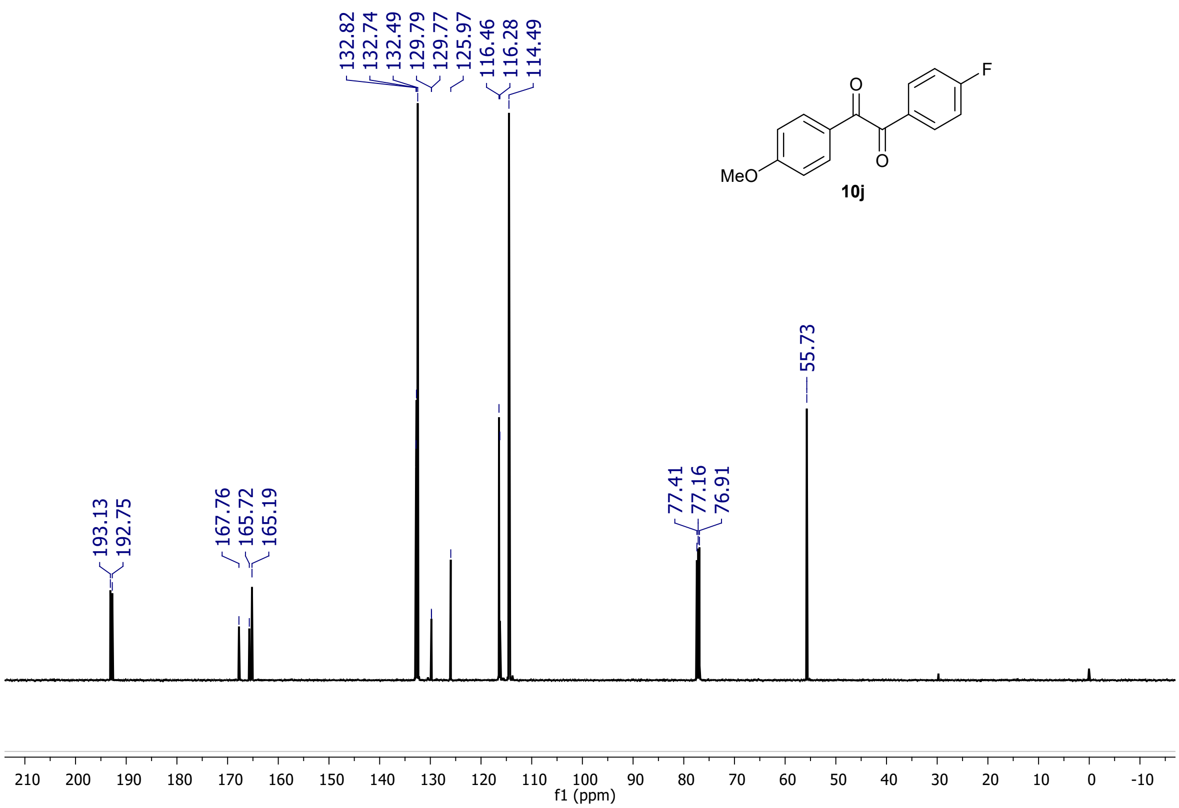


10i

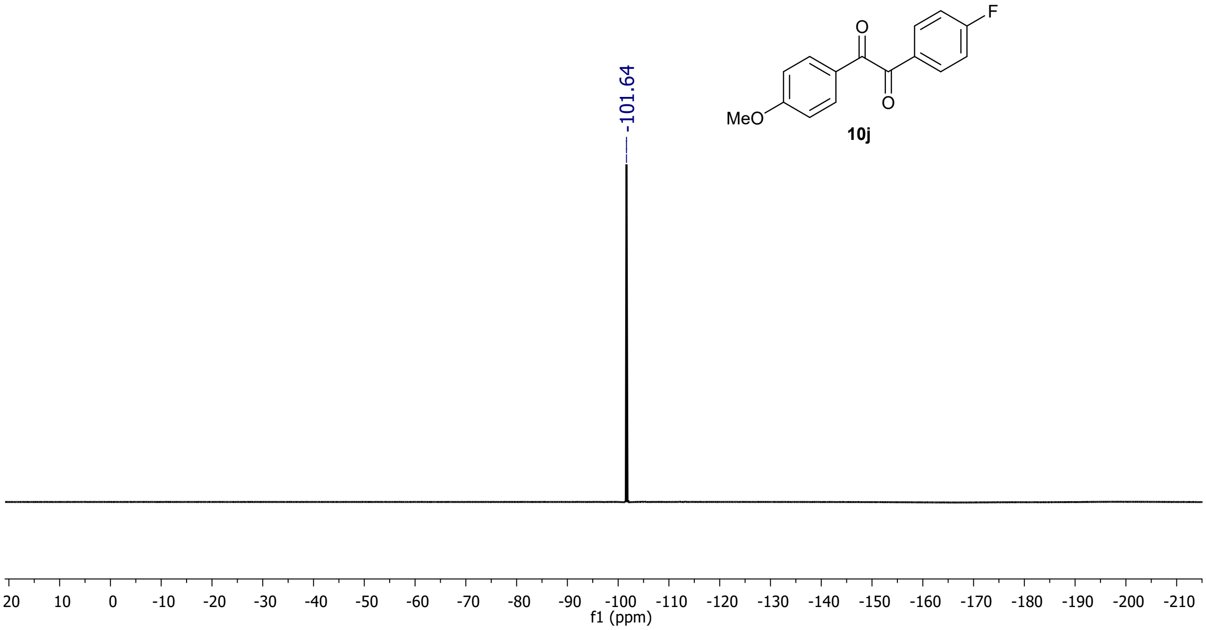
^{1}H NMR (500 MHz, $CDCl_3$)



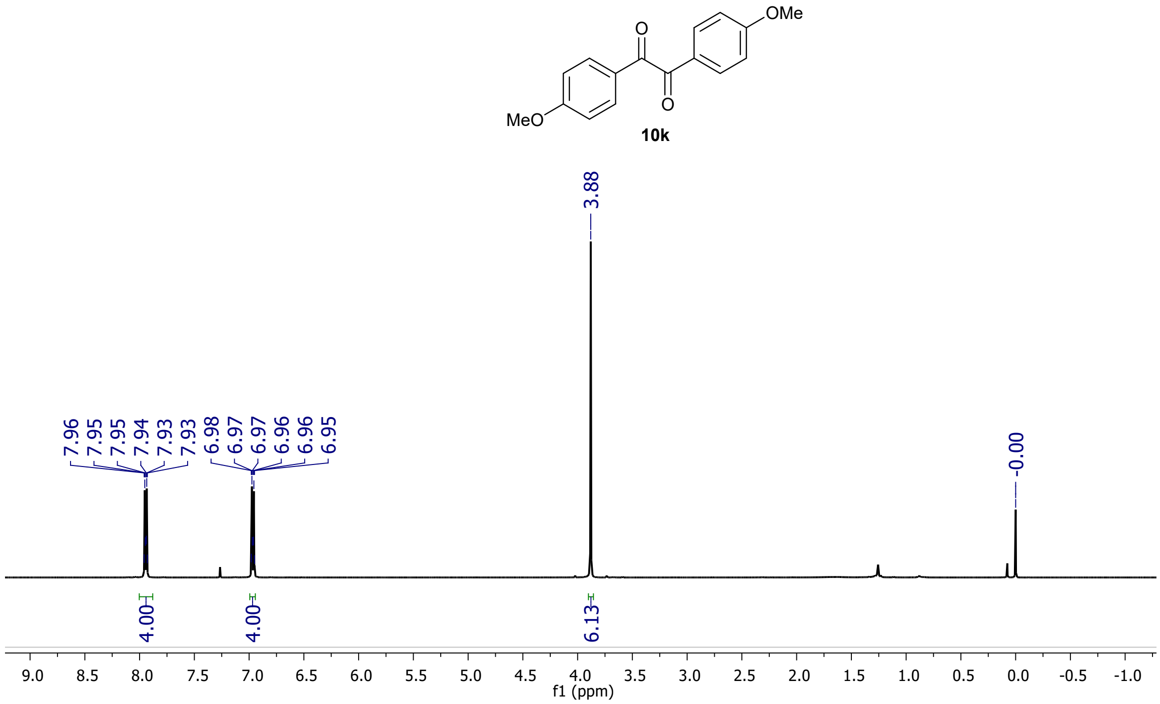
^{13}C NMR (126 MHz, $CDCl_3$)



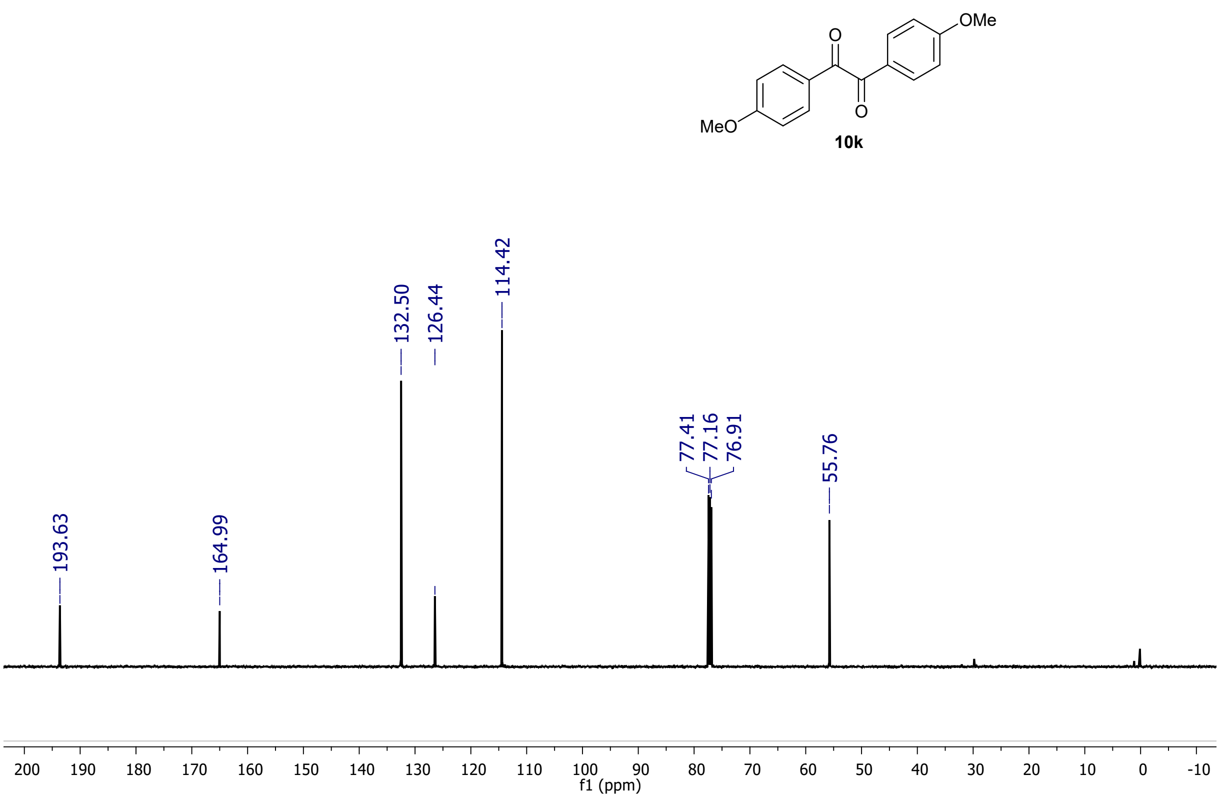
^{19}F NMR (471 MHz, $CDCl_3$)



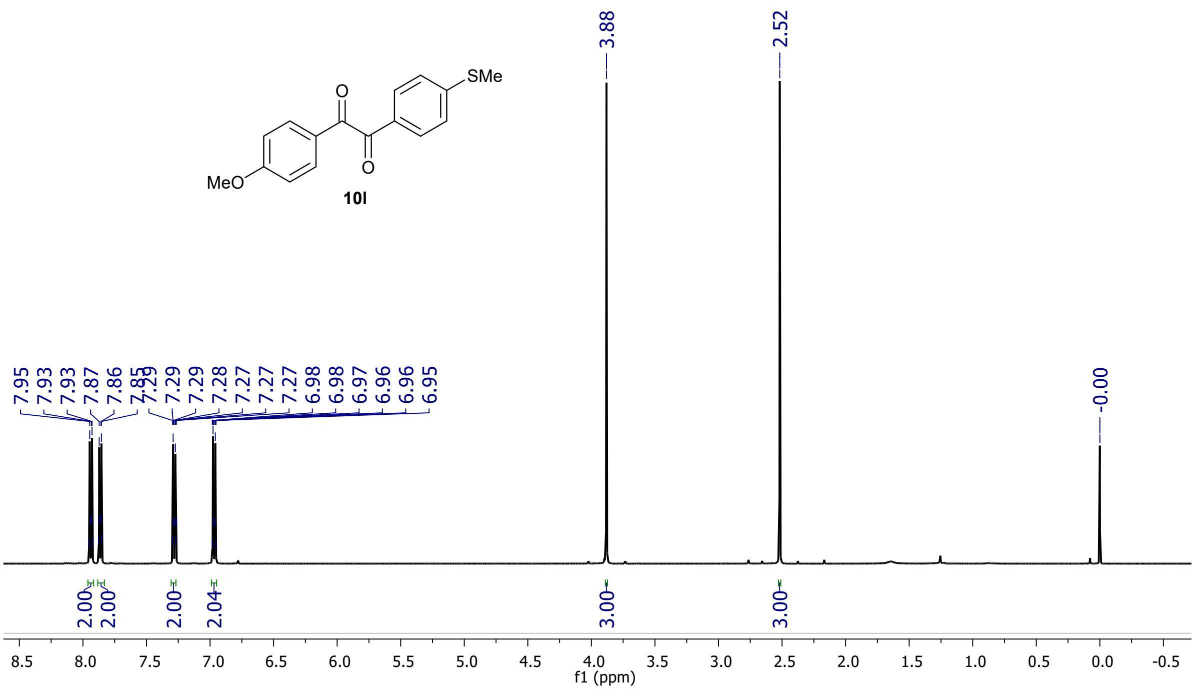
^{1}H NMR (500 MHz, $CDCl_3$)



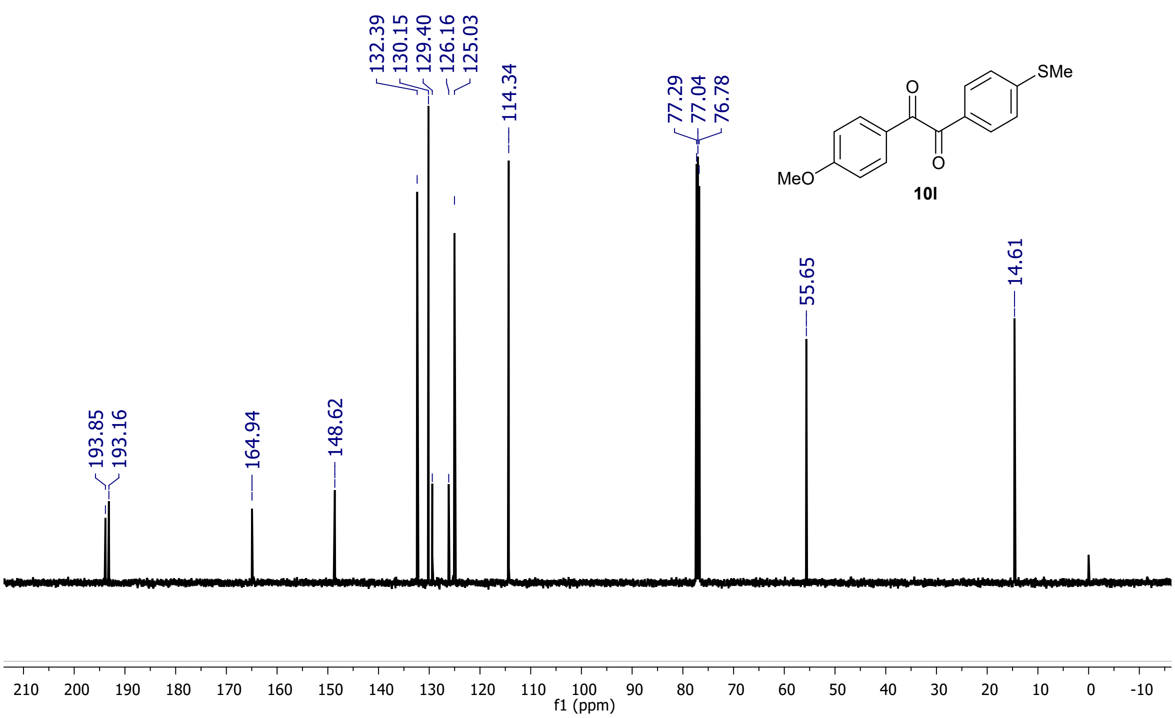
^{13}C NMR (126 MHz, $CDCl_3$)



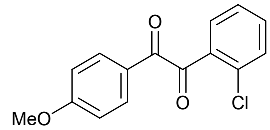
^{1}H NMR (500 MHz, $CDCl_3$)



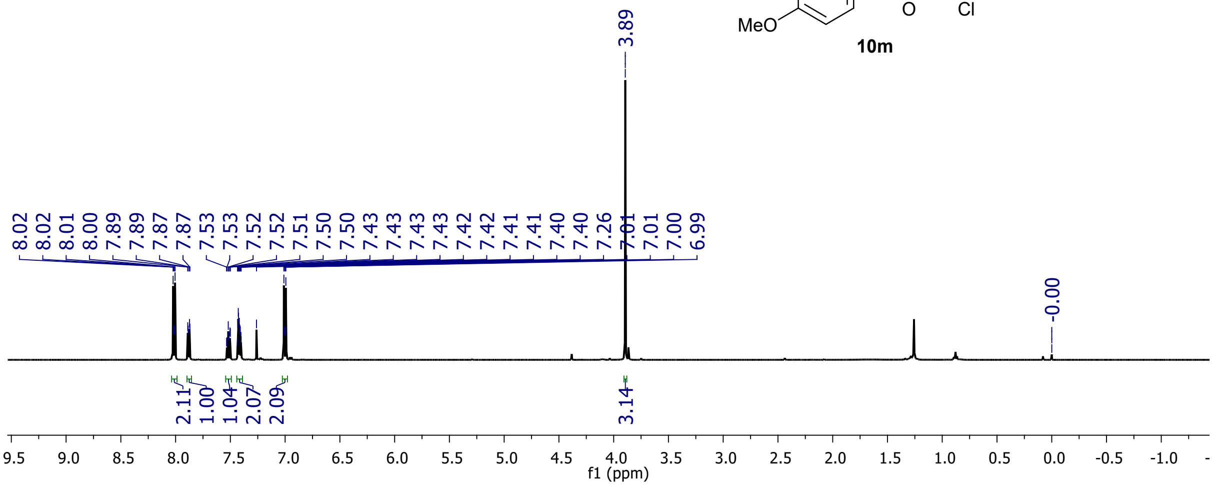
^{13}C NMR (126 MHz, $CDCl_3$)



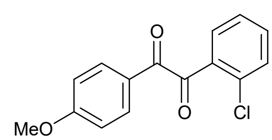
[1]H NMR (500 MHz, $CDCl_3$)



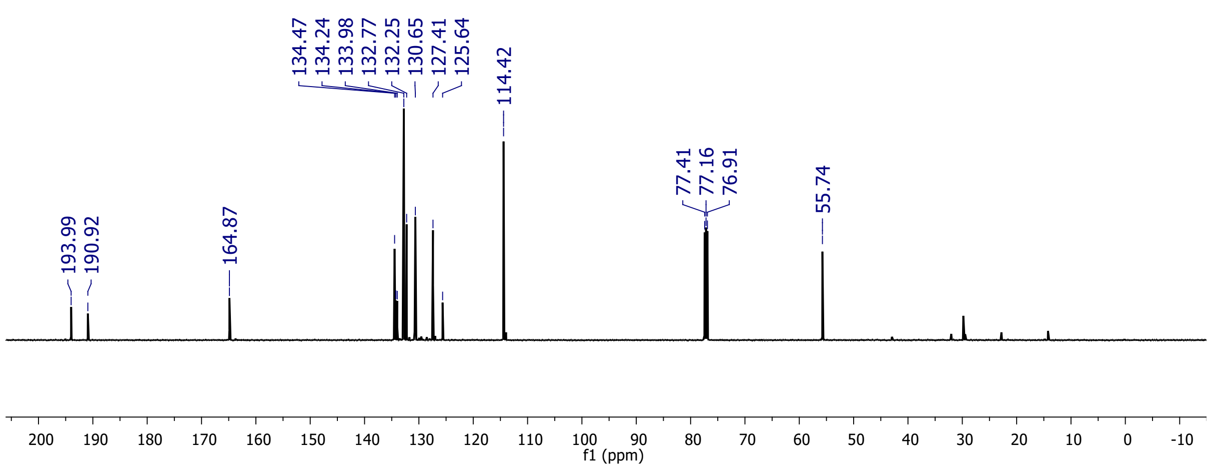
10m



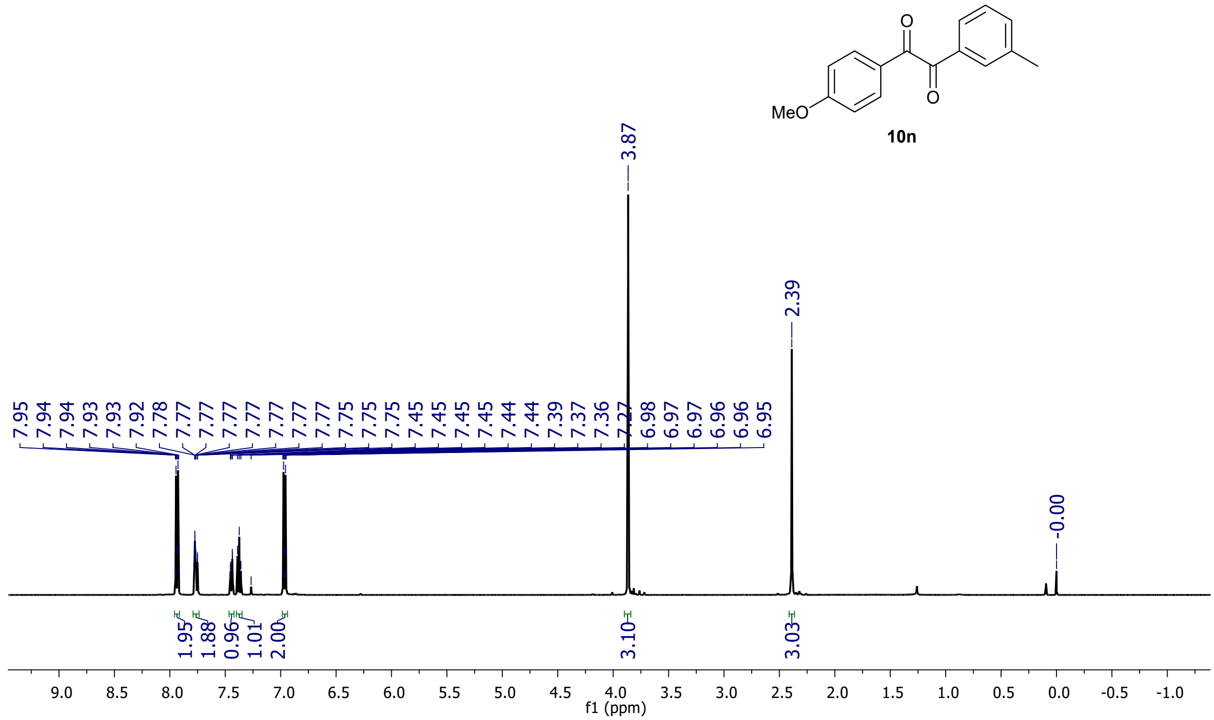
[13]C NMR (126 MHz, $CDCl_3$)



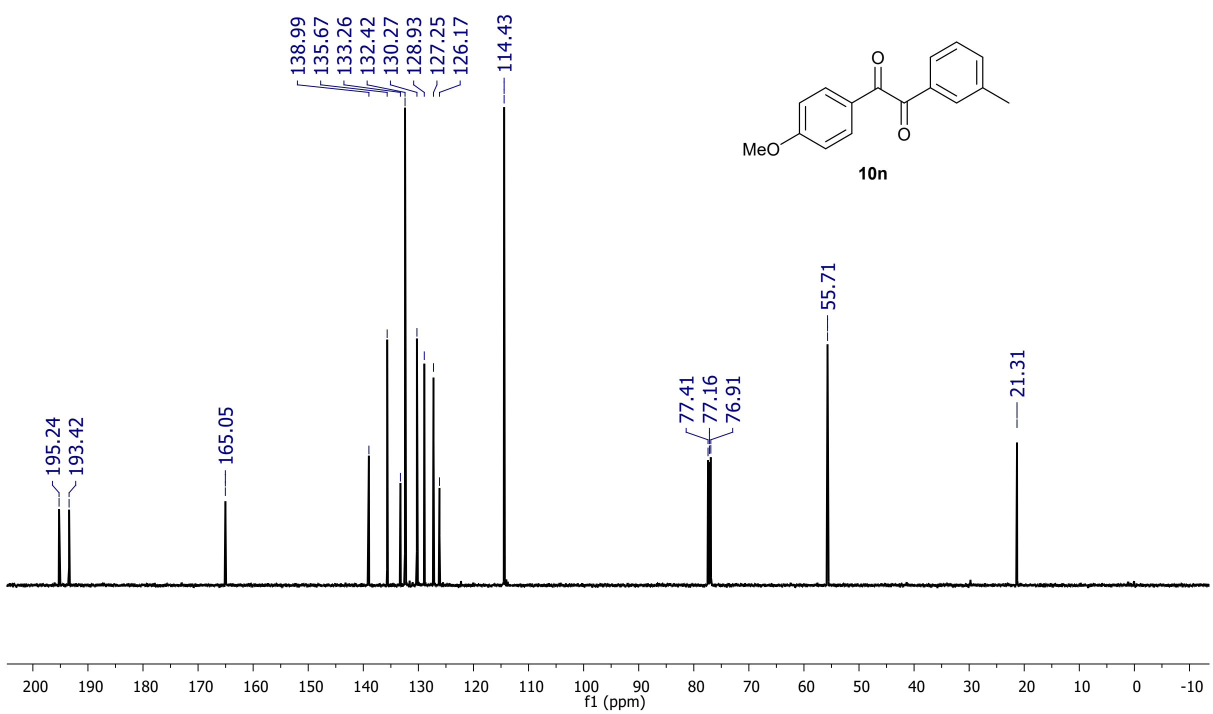
10m



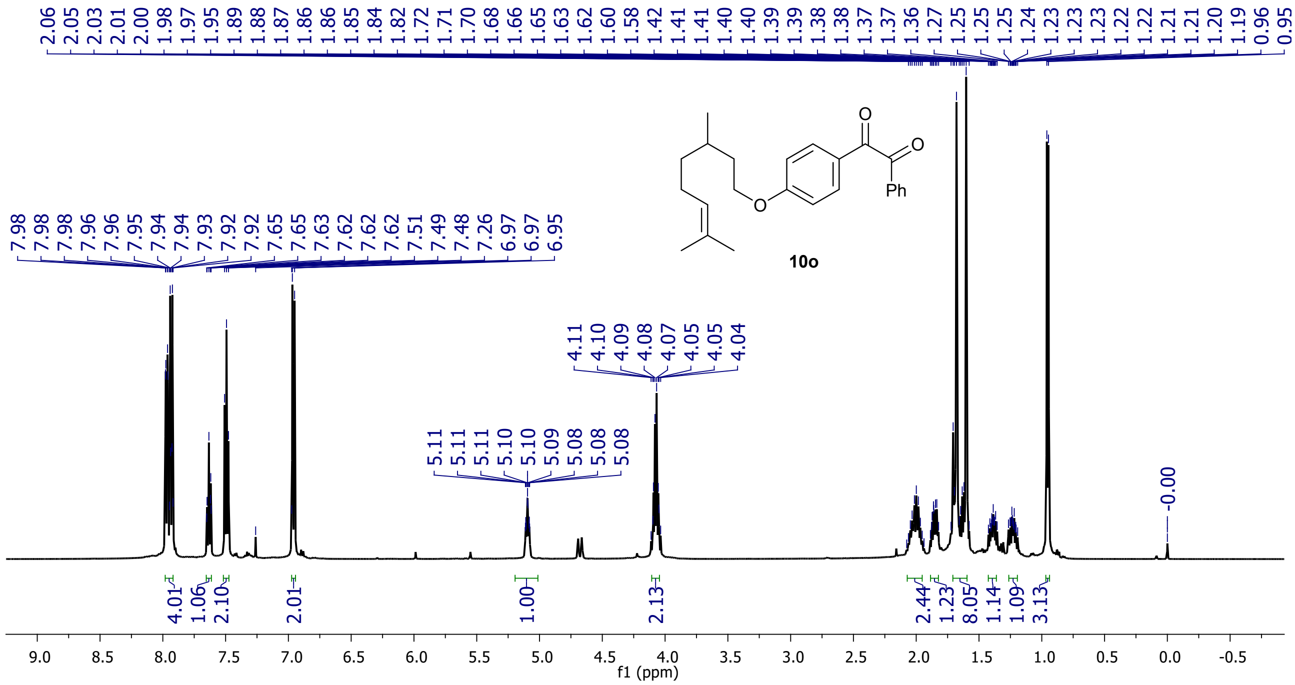
^{1}H NMR (500 MHz, $CDCl_3$)



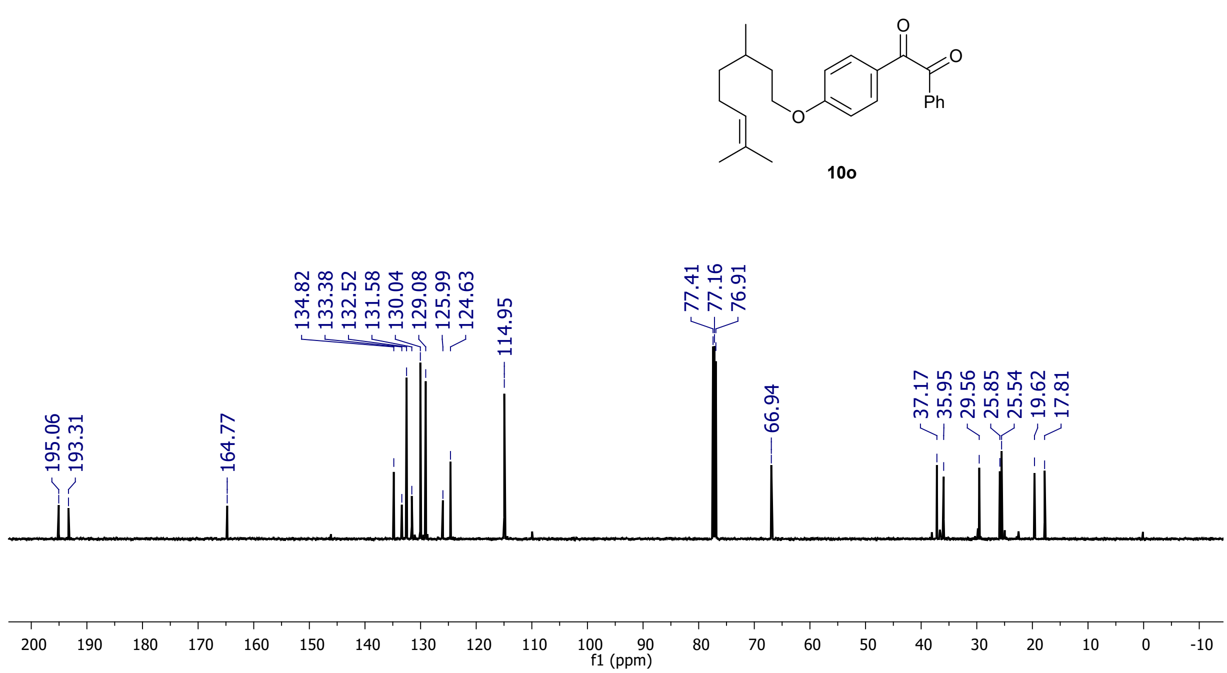
^{13}C NMR (126 MHz, $CDCl_3$)



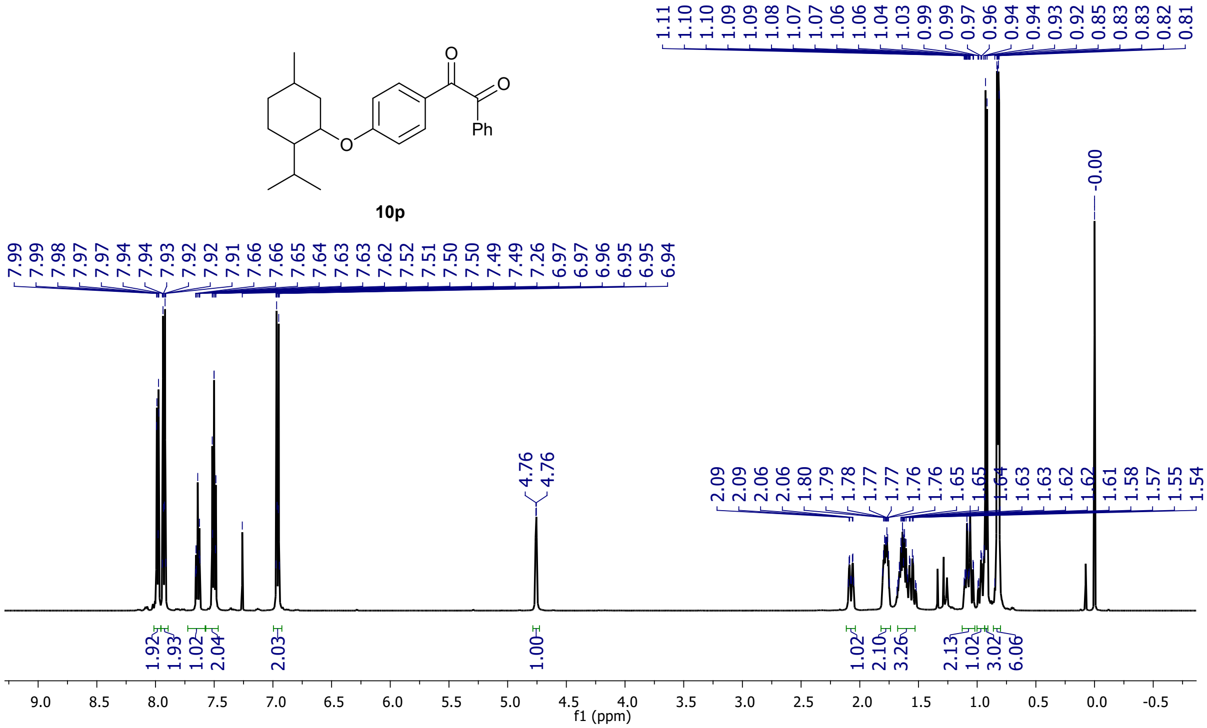
^{1}H NMR (500 MHz, $CDCl_3$)



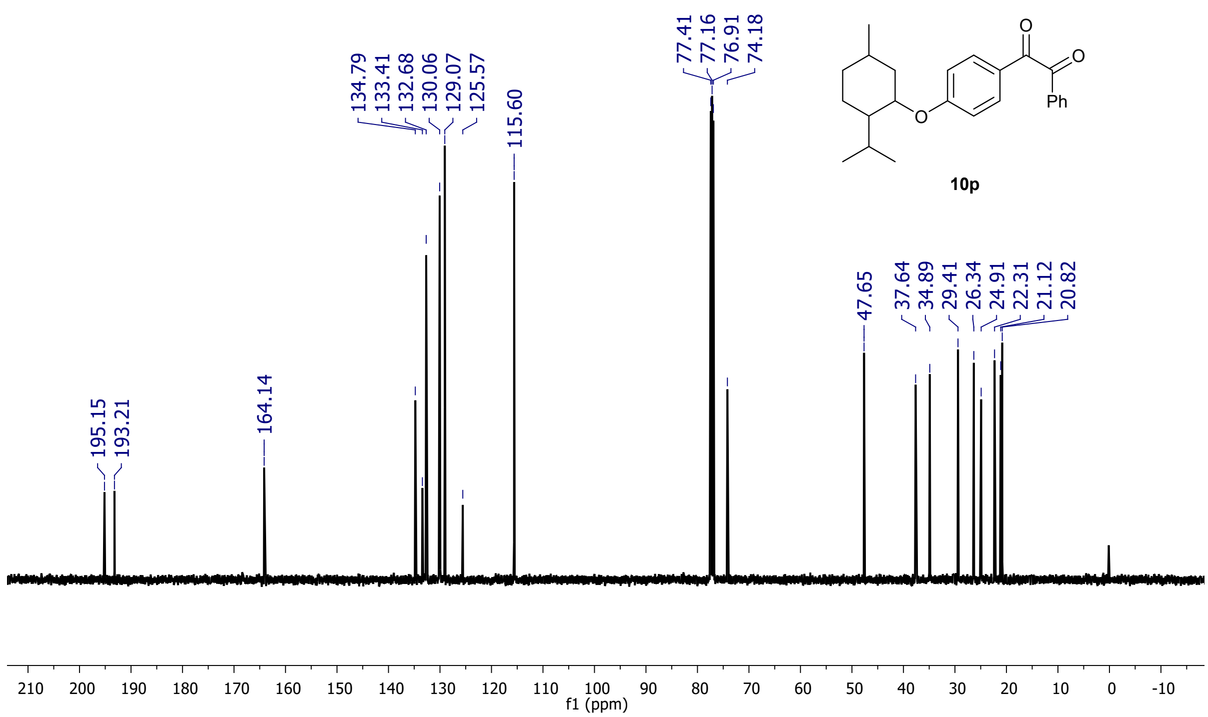
^{13}C NMR (126 MHz, $CDCl_3$)



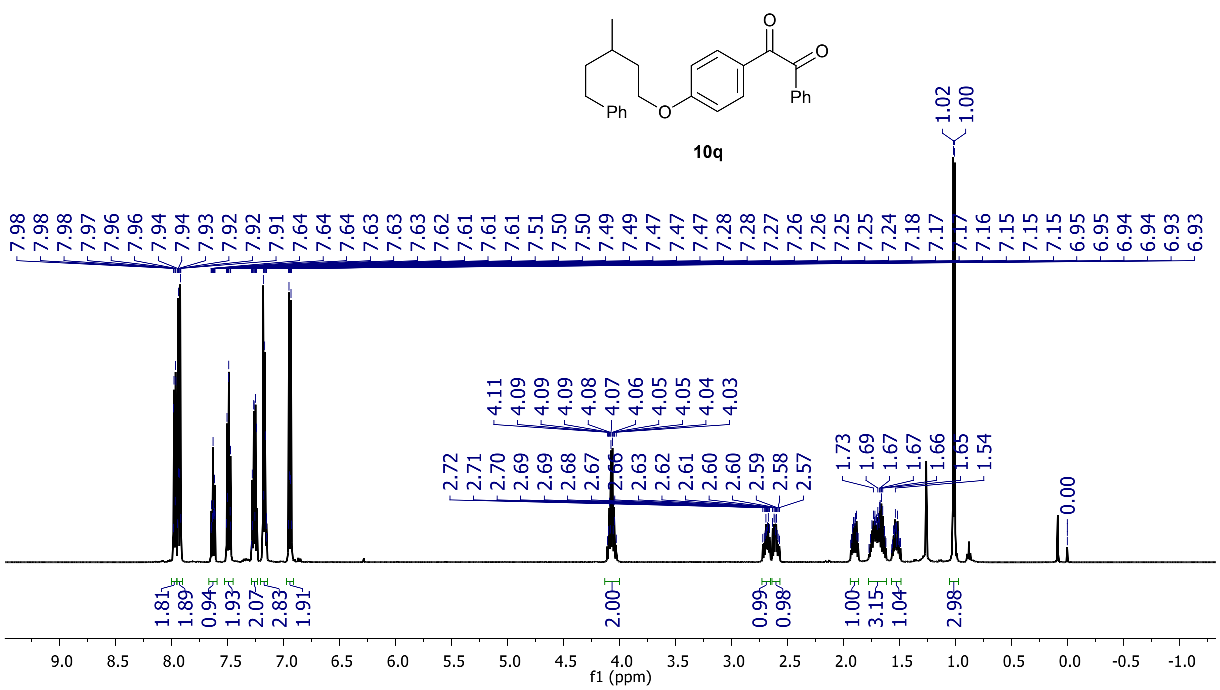
^{1}H NMR (500 MHz, $CDCl_3$)



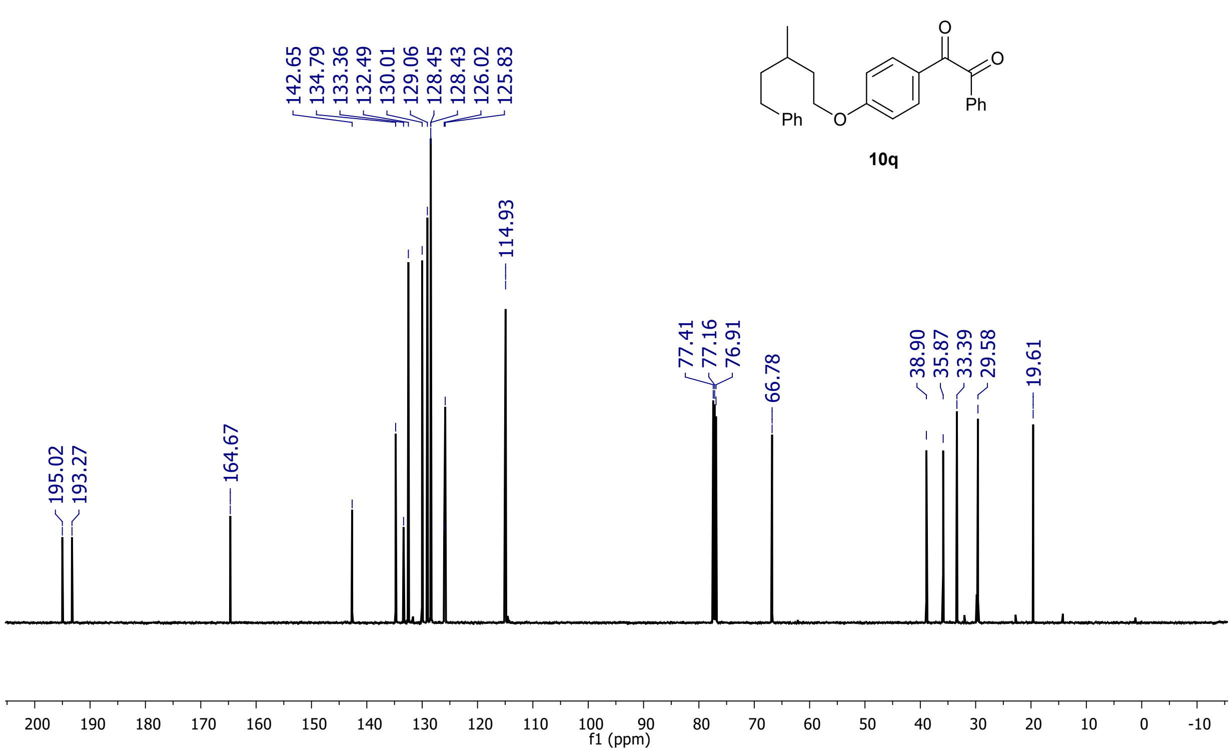
^{13}C NMR (126 MHz, $CDCl_3$)



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



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



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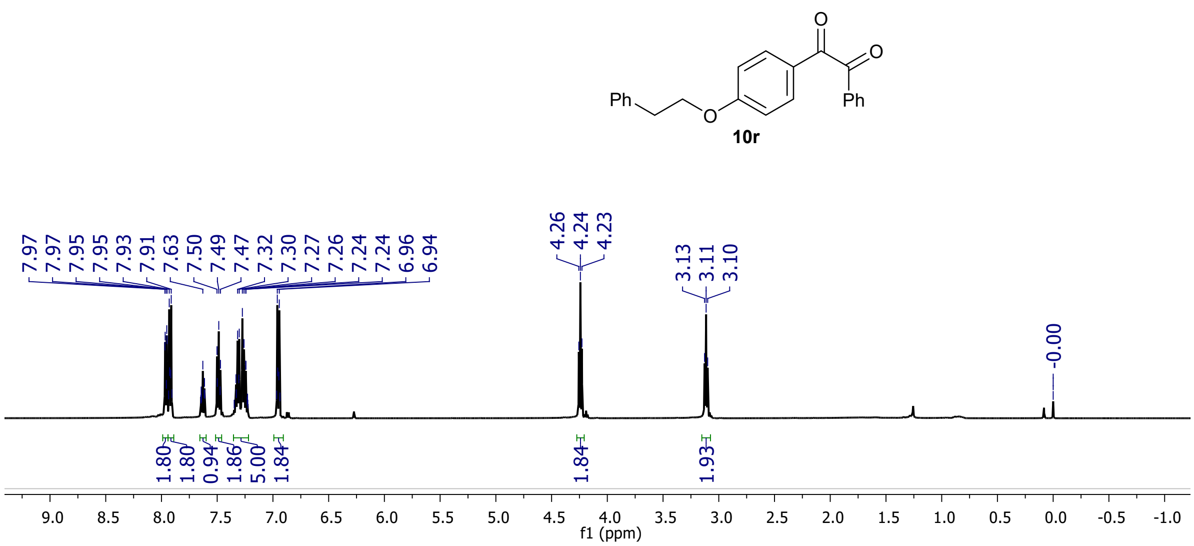
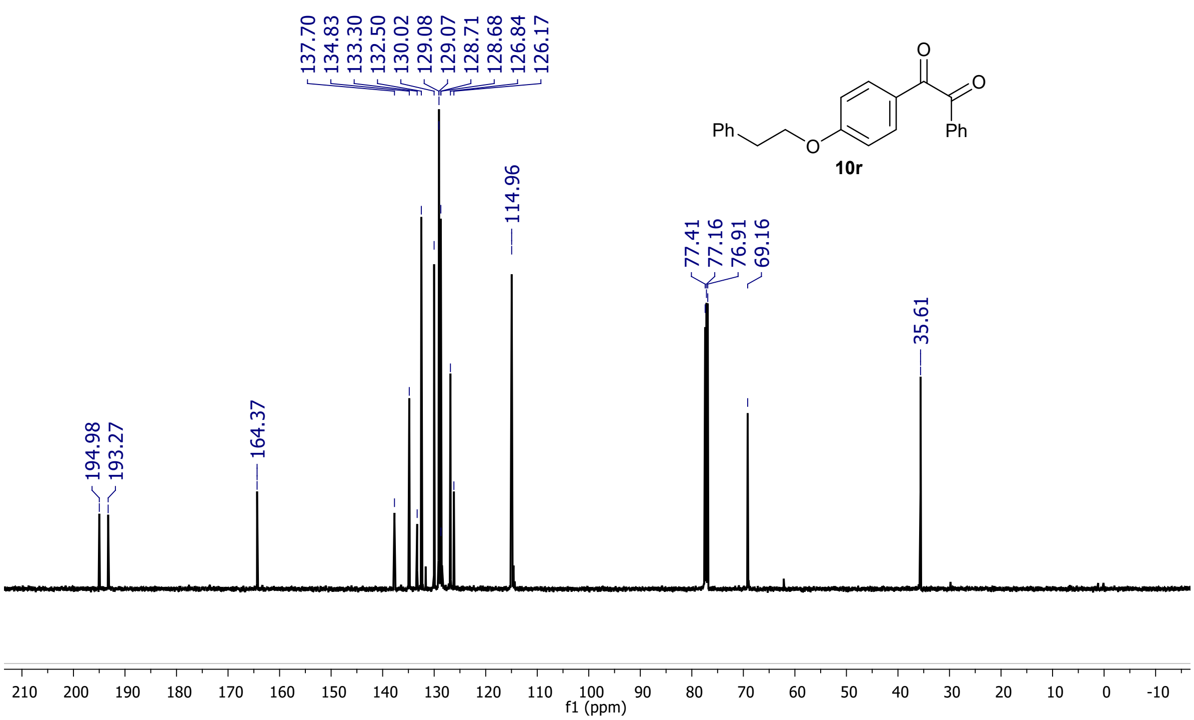
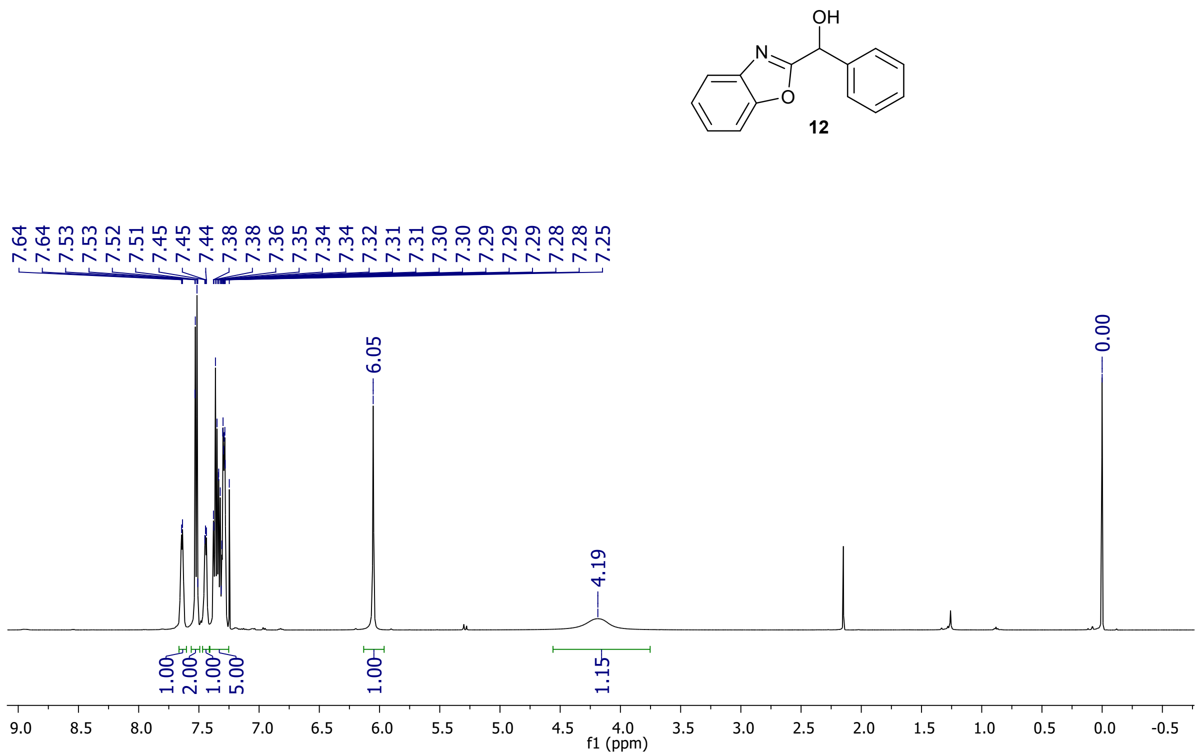
^{1}H NMR (500 MHz, $CDCl_3$)



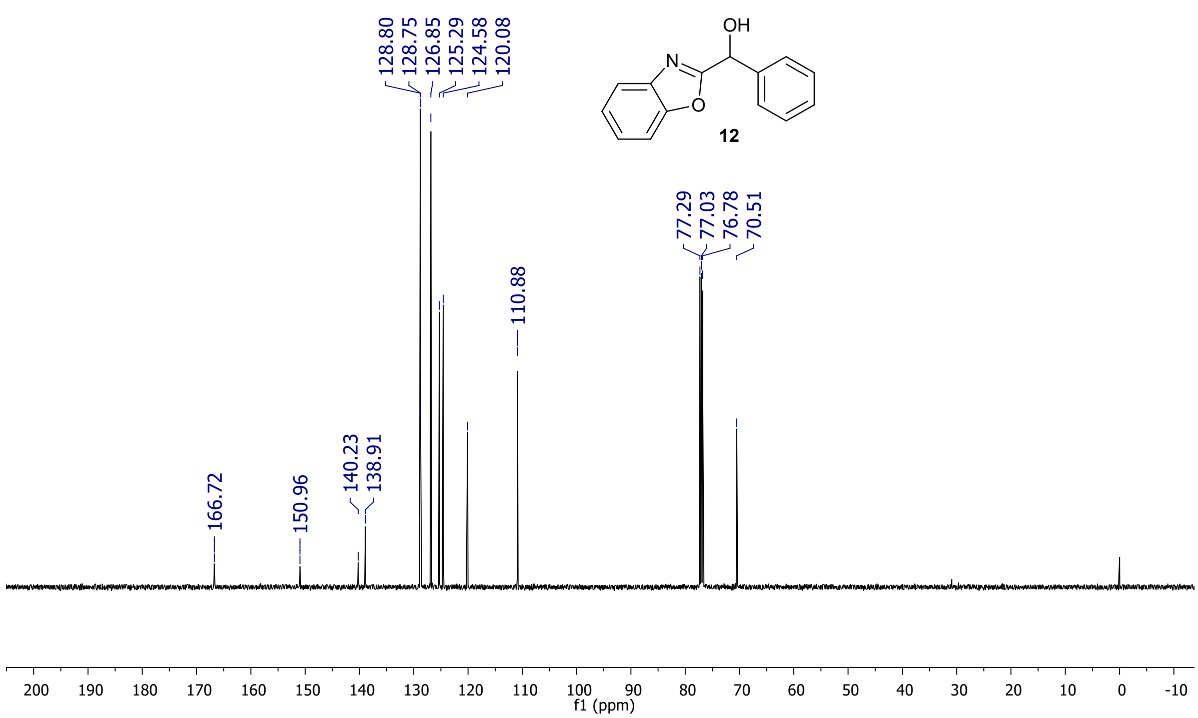
^{13}C NMR (126 MHz, $CDCl_3$)



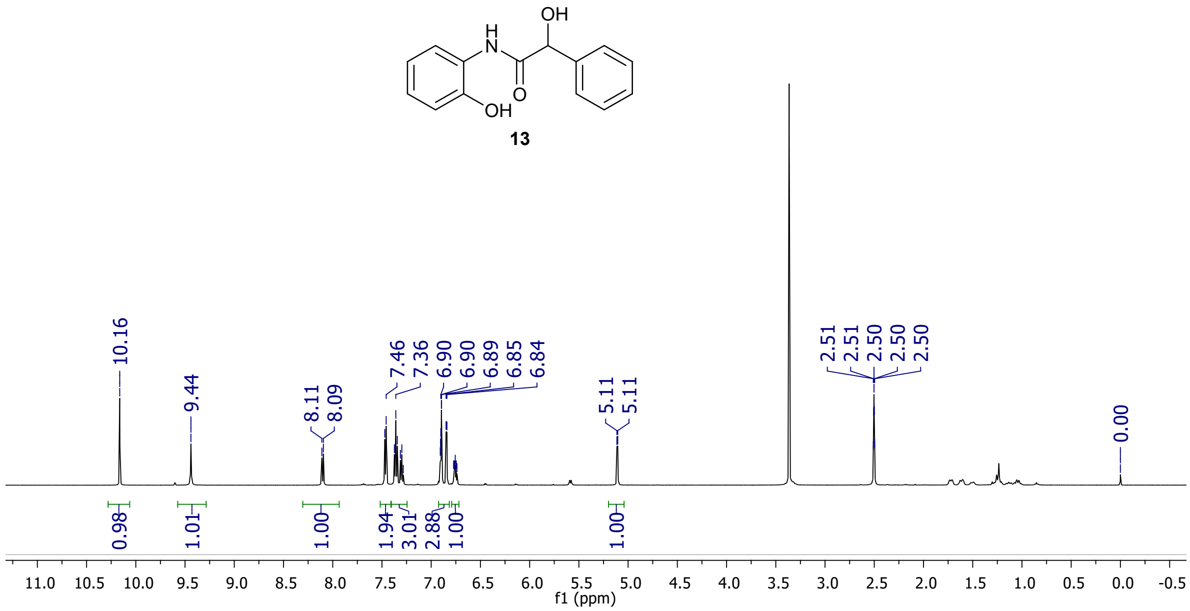
^{1}H NMR (500 MHz, $CDCl_3$):



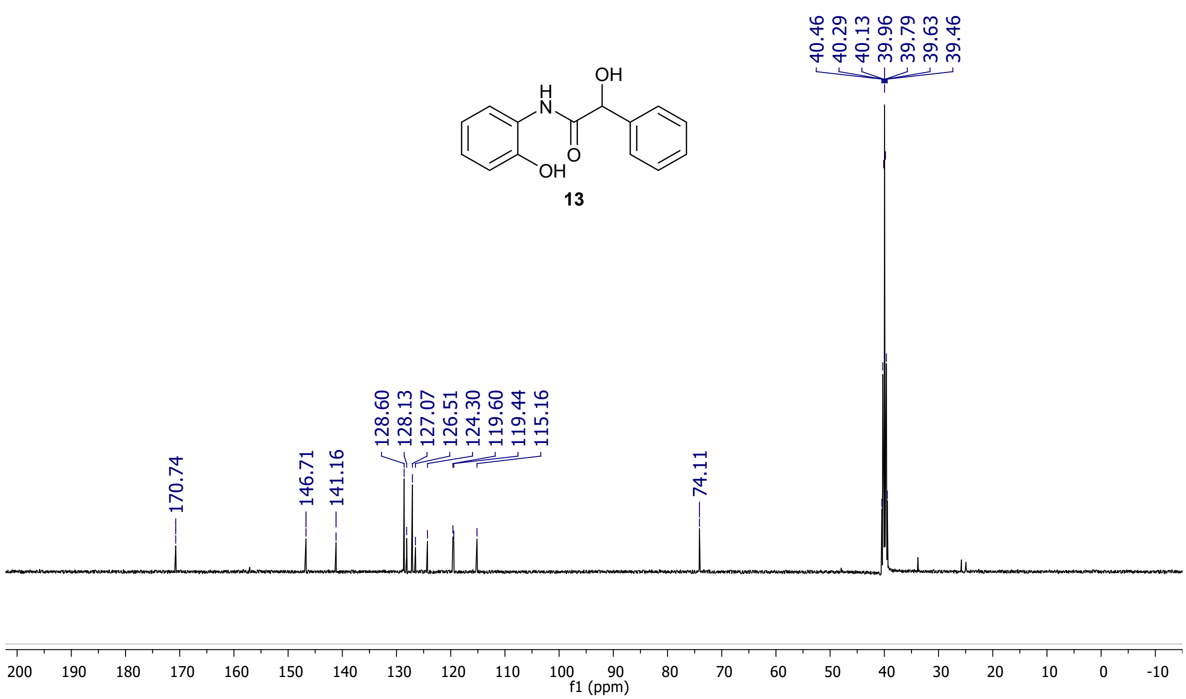
^{13}C NMR (126 MHz, $CDCl_3$)



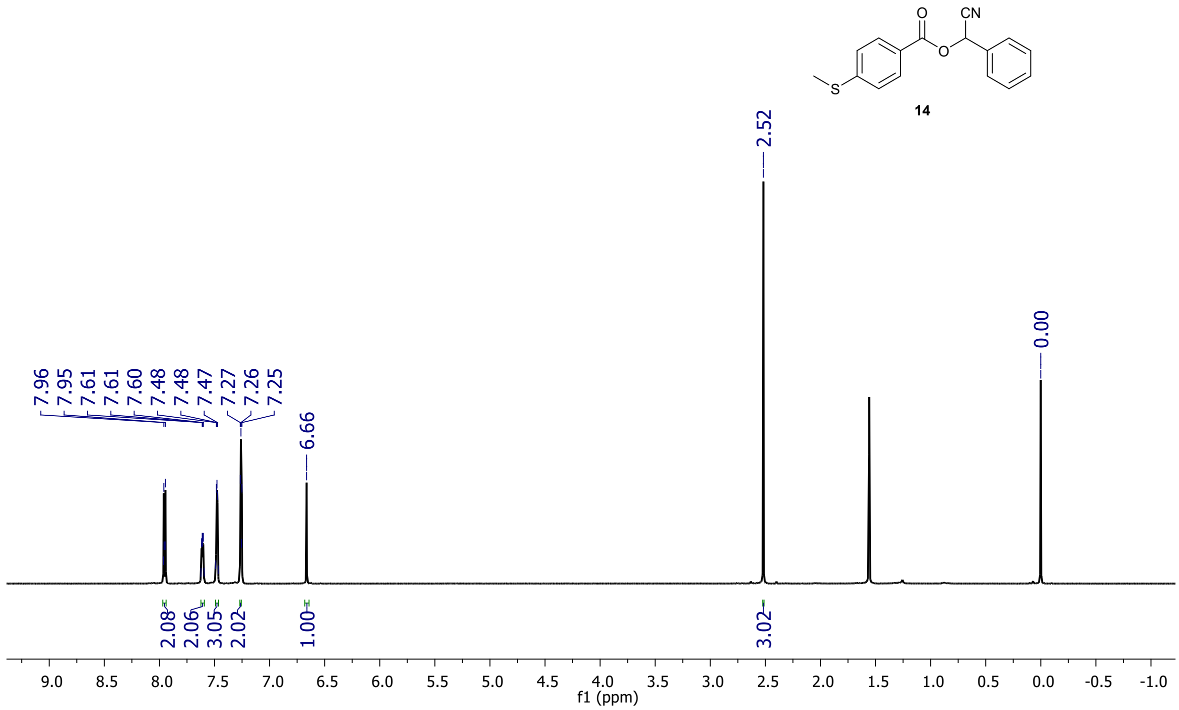
^{1}H NMR (500 MHz, DMSO-d_6):



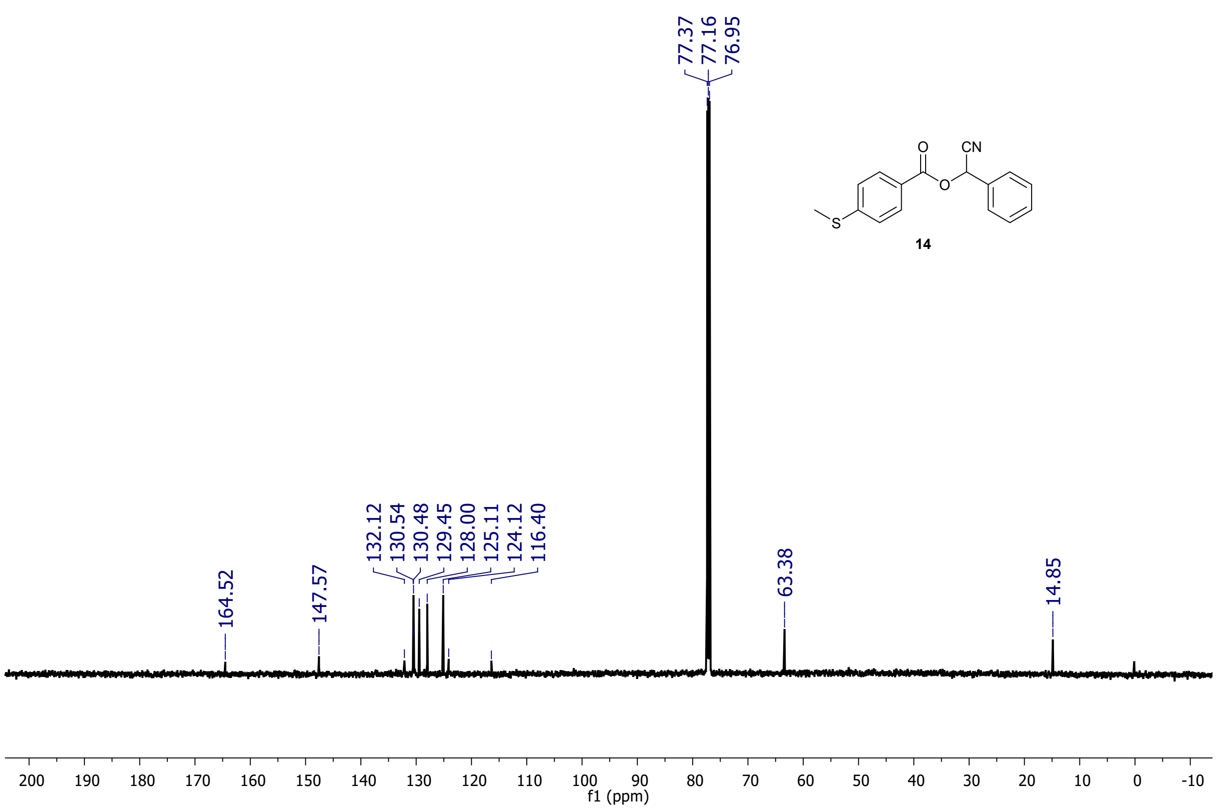
^{13}C NMR (126 MHz, DMSO-d_6)



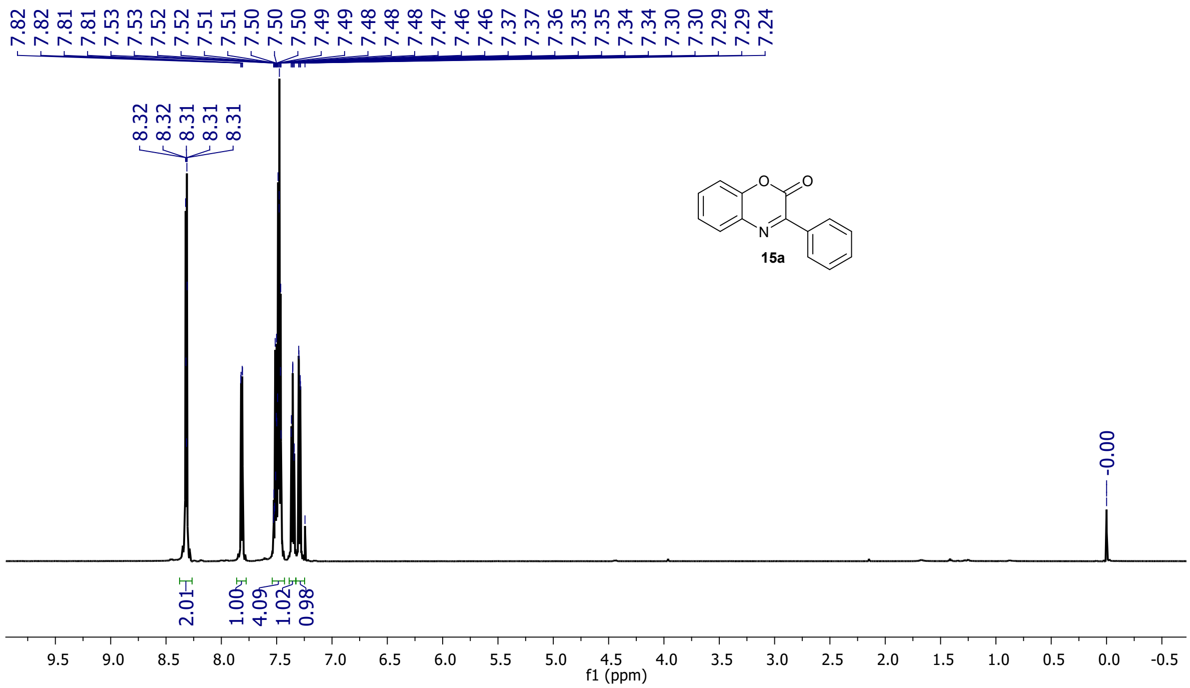
^{1}H NMR (600 MHz, $CDCl_3$):



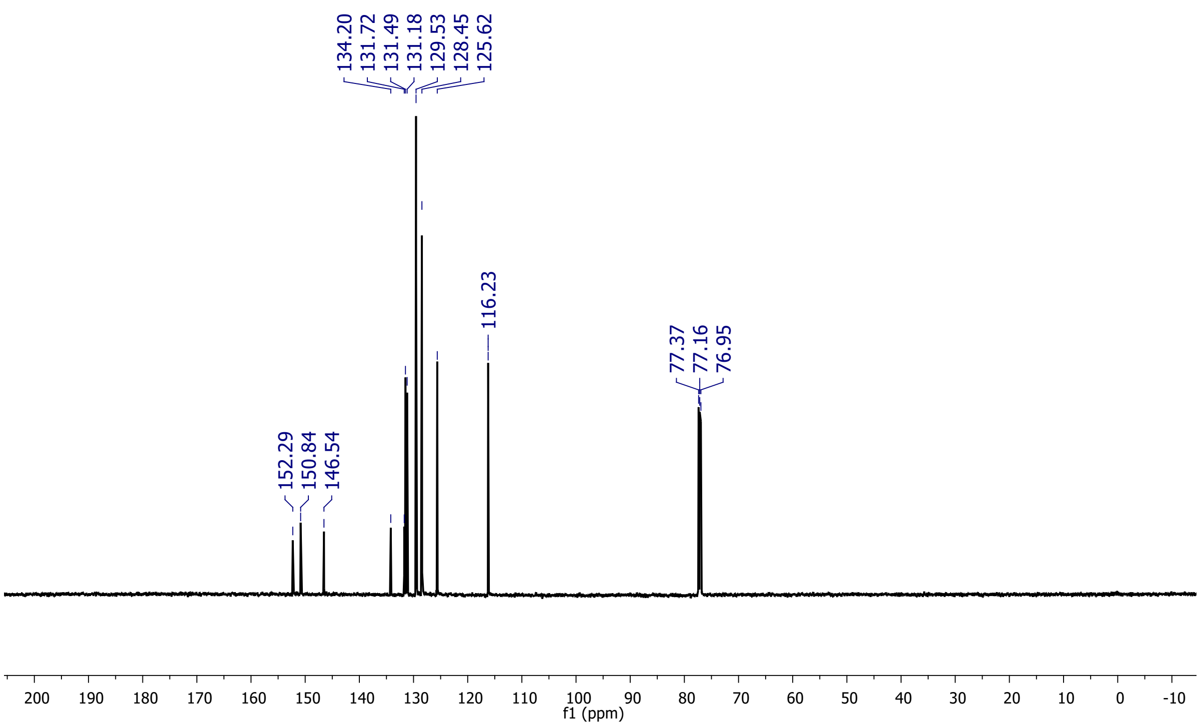
^{13}C NMR (151 MHz, $CDCl_3$)



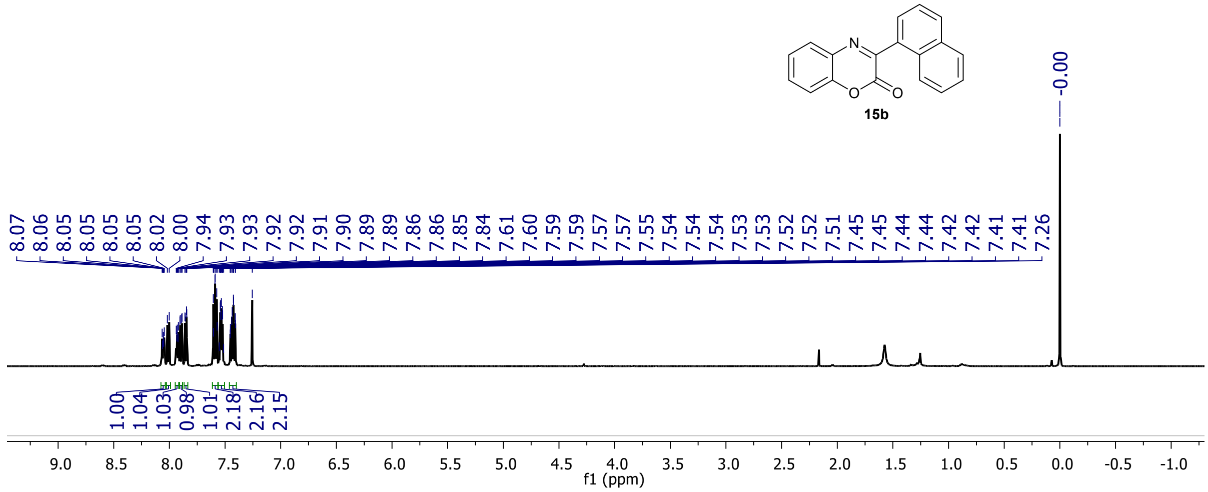
^{1}H NMR (500 MHz, $CDCl_3$)



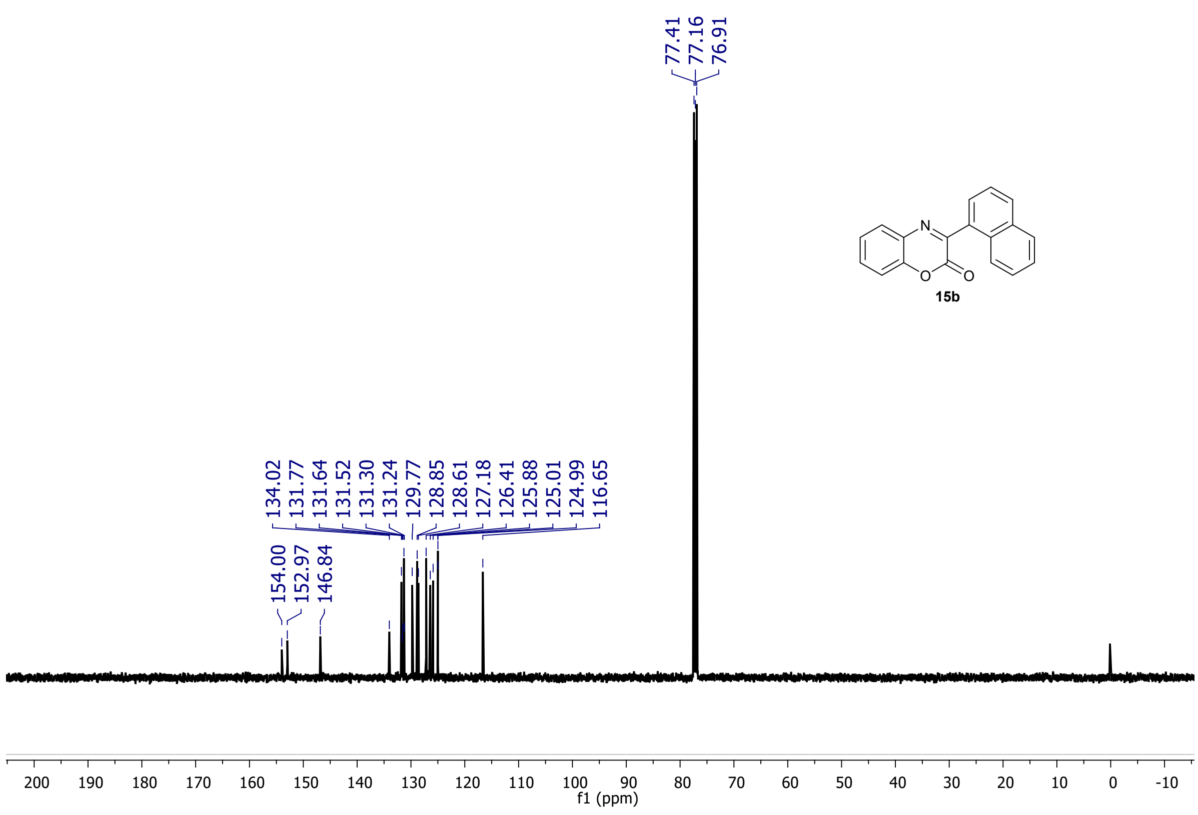
^{13}C NMR (126 MHz, $CDCl_3$)



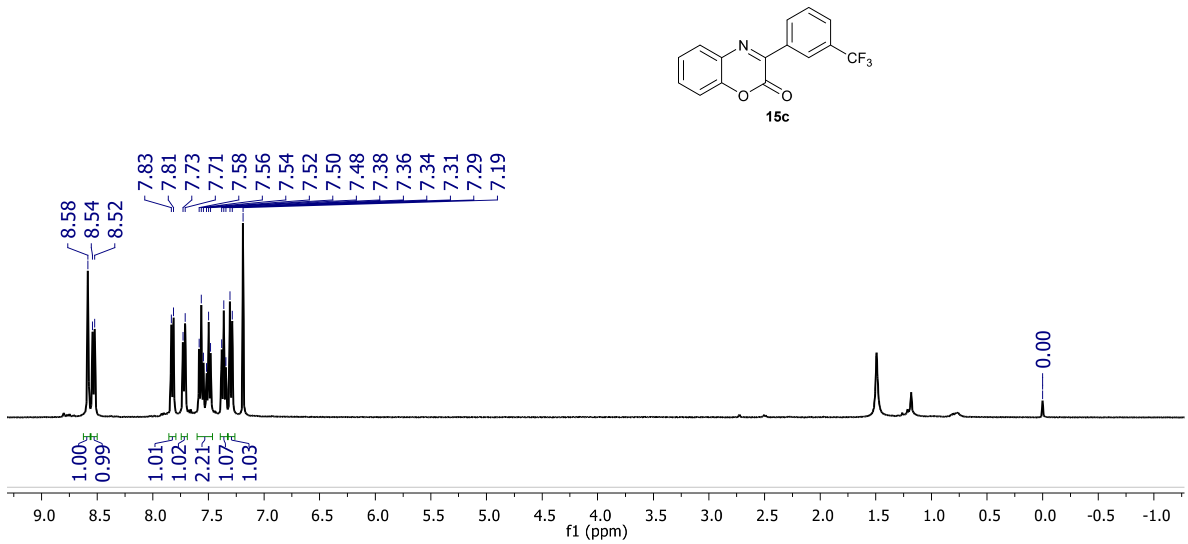
^{1}H NMR (500 MHz, $CDCl_3$)



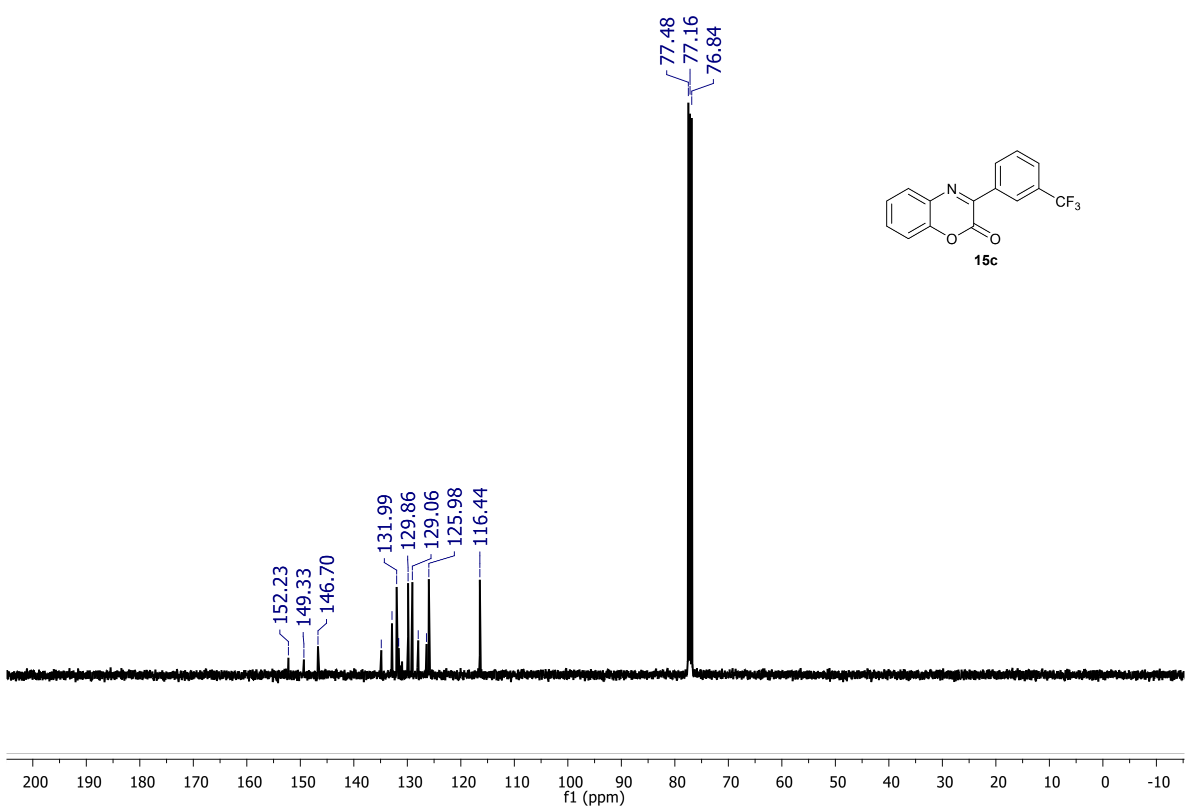
^{13}C NMR (126 MHz, $CDCl_3$):



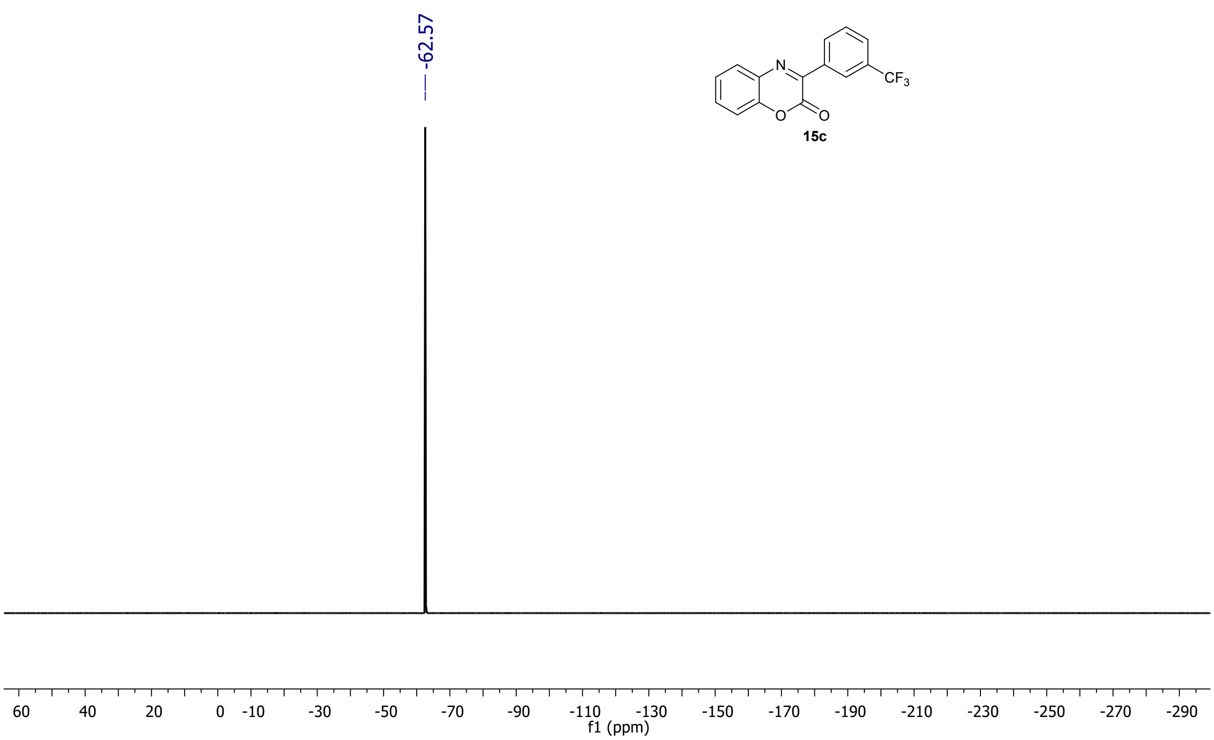
^{1}H NMR (400 MHz, $CDCl_3$)



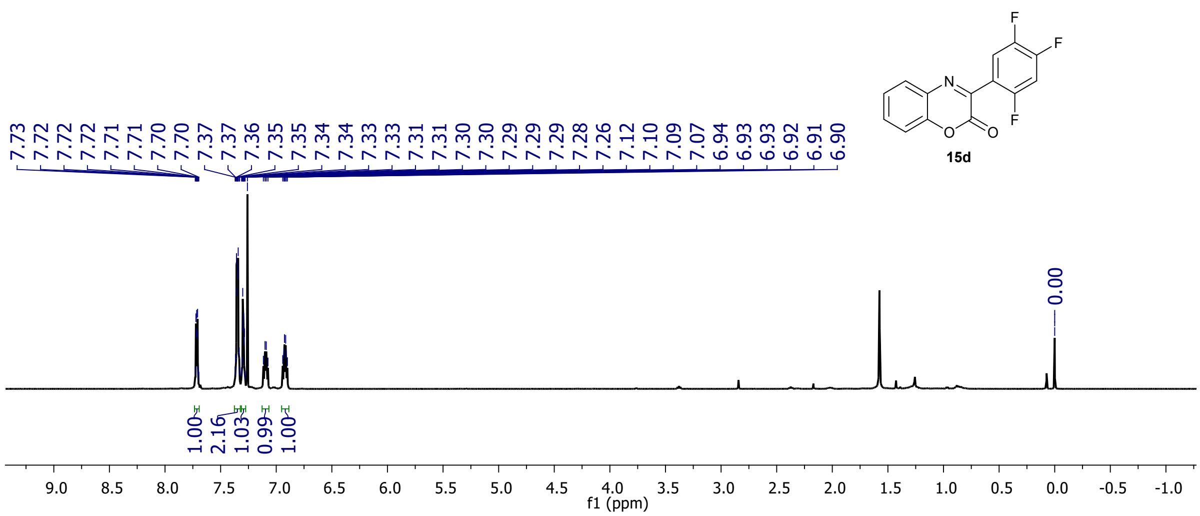
^{13}C NMR (101 MHz, $CDCl_3$):



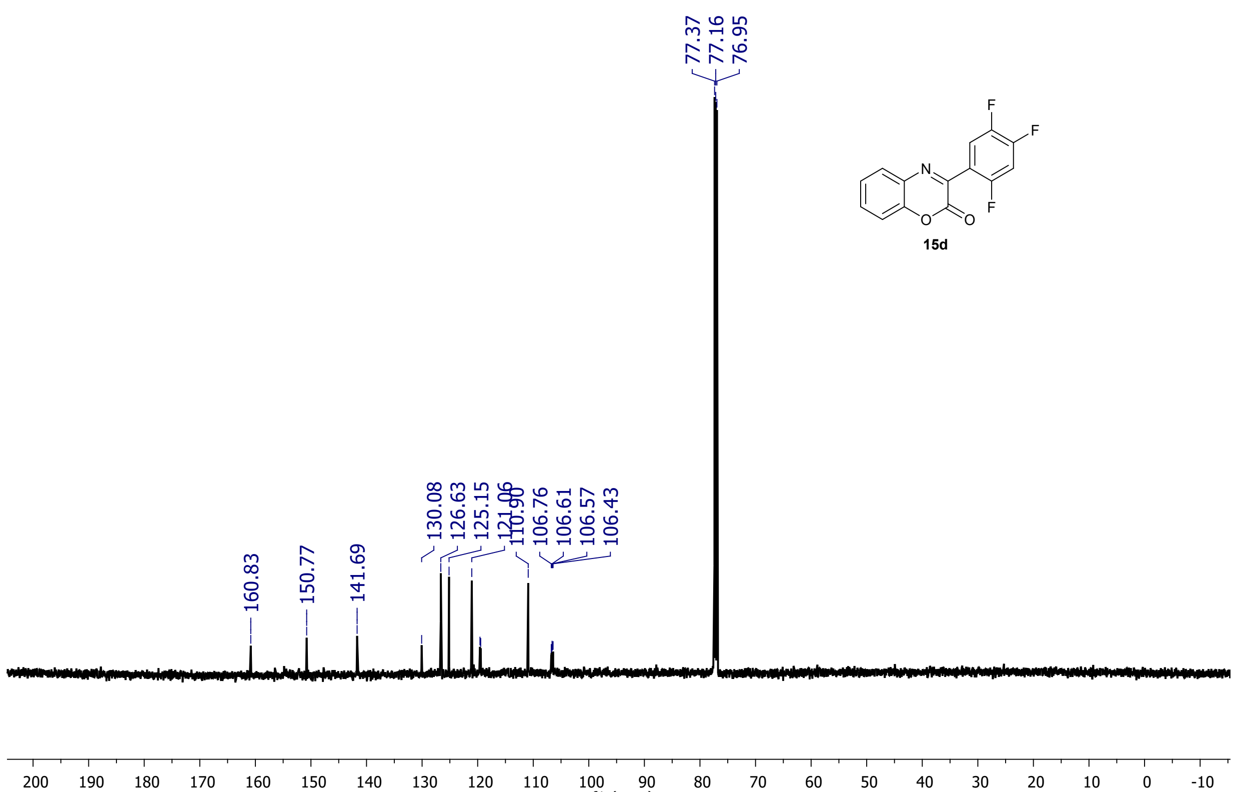
^{19}F NMR (565 MHz, $CDCl_3$):



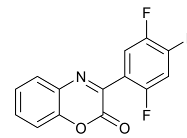
^1H NMR (600 MHz, $CDCl_3$)



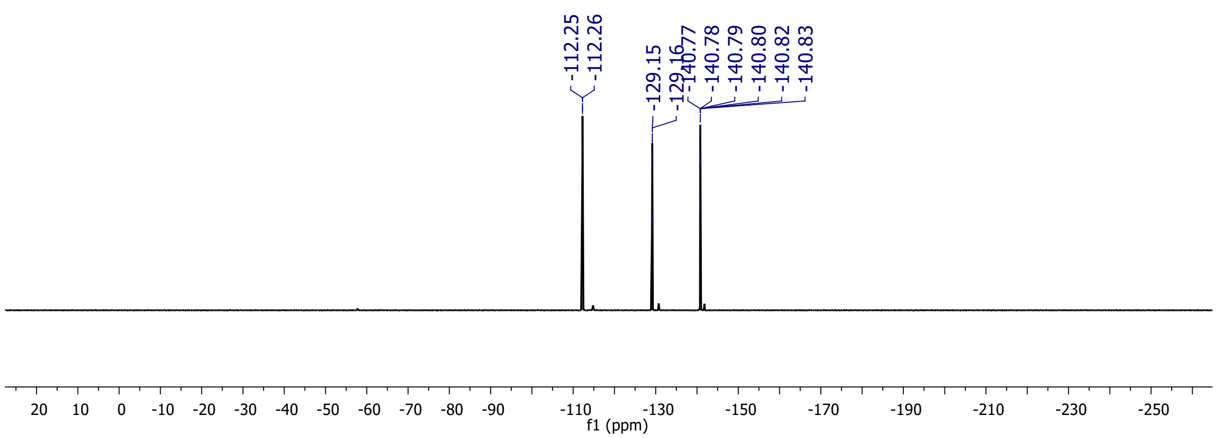
^{13}C NMR (151 MHz, $CDCl_3$)



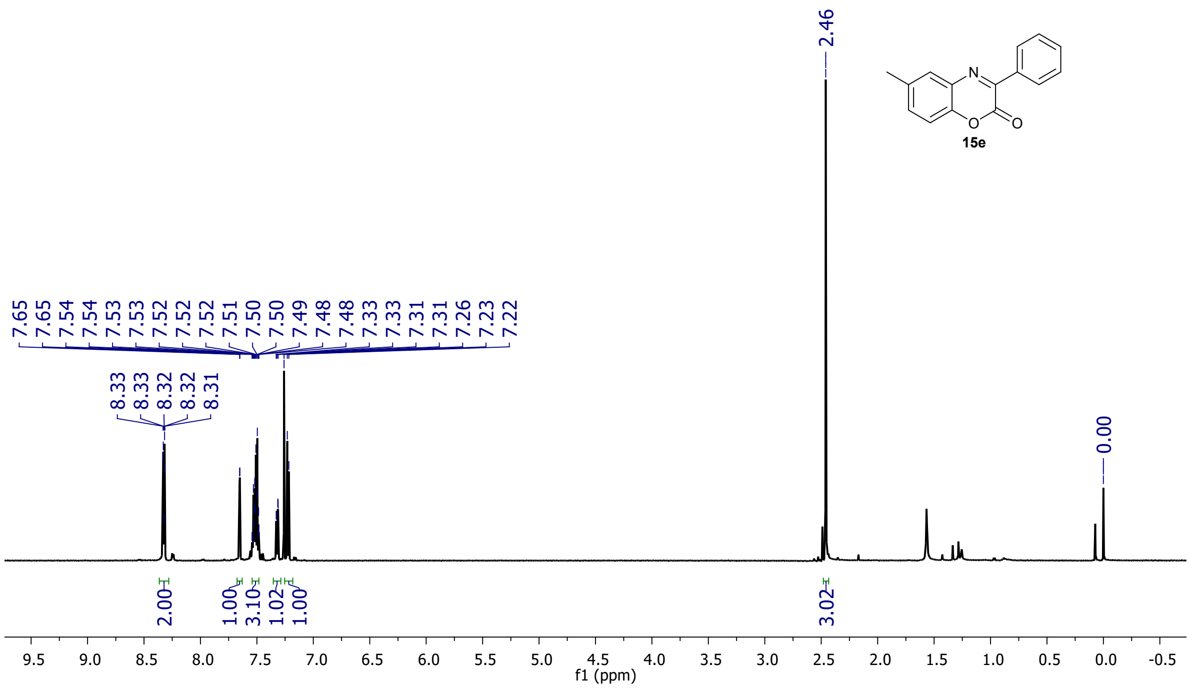
^{19}F NMR (565 MHz, $CDCl_3$)



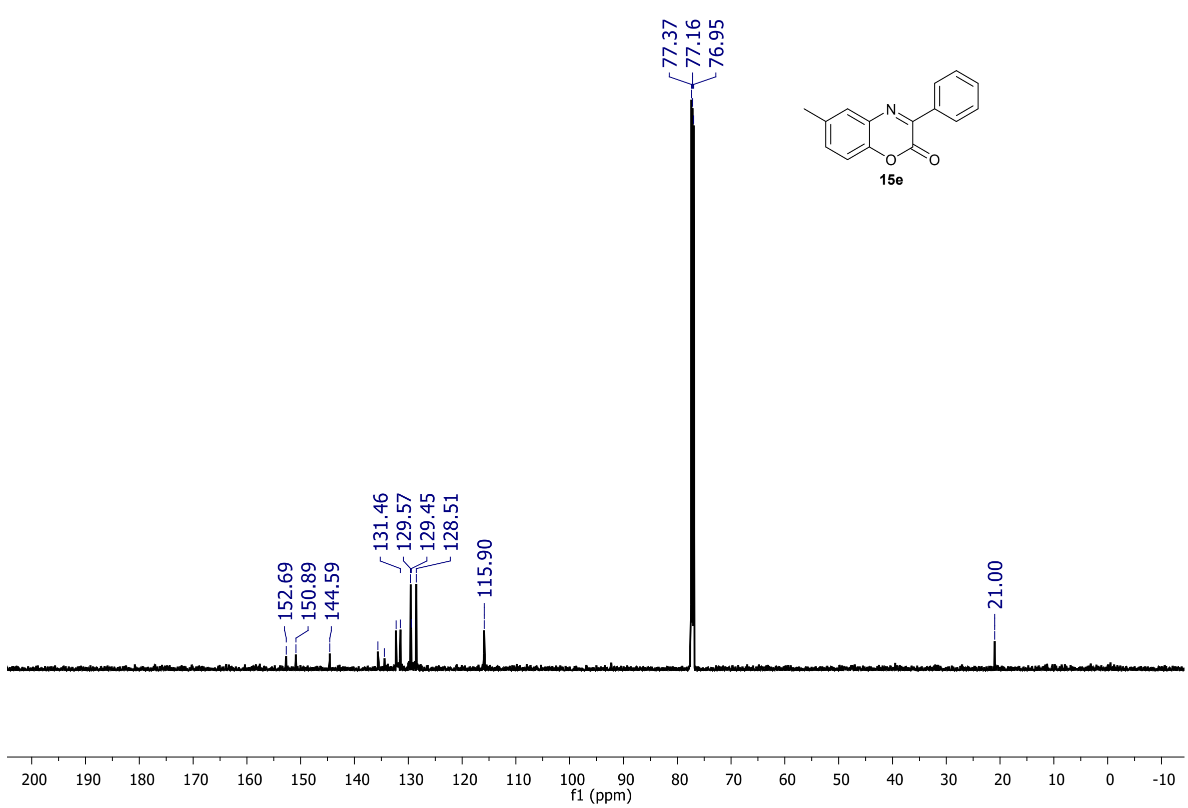
15d



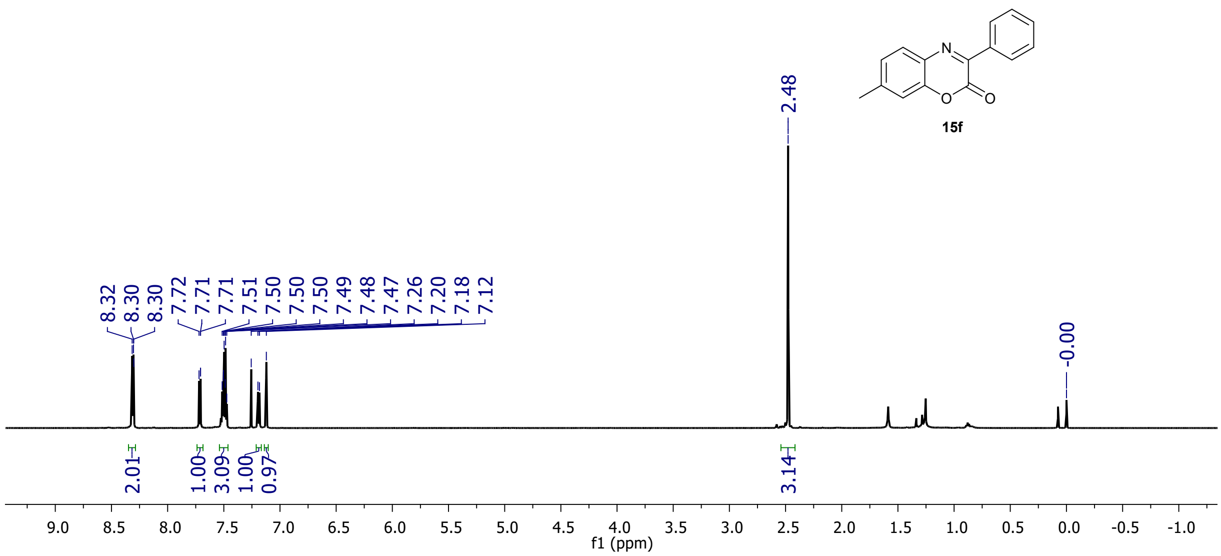
^{1}H NMR (600 MHz, $CDCl_3$)



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



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



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