Supporting Information

Catalytic Direct α-Amination of Arylacetic Acid Synthons with Anilines

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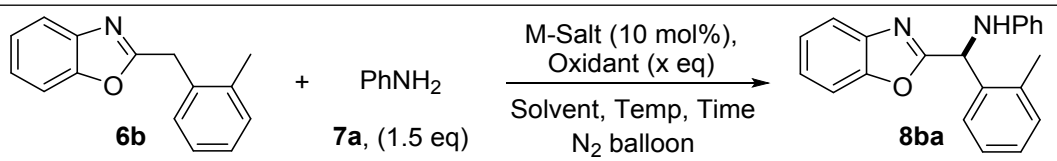
Table TS1: Optimization of the reaction conditions for direct α-amination



Sl. No.	M-Salt	Oxidant	Eq of oxidant	Solvent	Temp. (^{o}C)	8ba (%)
1	$FeCl_3$	DTBP	2.0	DCE	100	55
2	$FeCl_3$	DTBP	2.0	DMSO	100	ND
3	$FeCl_3$	DTBP	2.0	DMF	100	ND
4	$FeCl_3$	DTBP	2.0	Dioxane	100	35
5	$FeCl_3$	DTBP	2.0	Toluene	100	90
6	$FeCl_3$	DTBP	2.0	NMP	100	ND
7	$FeCl_3$	DTBP	2.0	DMAC	100	ND
8	$FeCl_3$	DTBP	2.0	Amyl alcohol	100	41
9	$FeCl_3$	DTBP	2.0	EtOAc	100	64
10	$FeCl_3$	DTBP	2.0	MeCN	100	10
11	$FeCl_3$	DTBP	2.0	Xylene	100	32
12	$FeCl_3$	DTBP	2.0	Mesitylene	100	63
13	$FeCl_2$	DTBP	2.0	Toluene	100	85
14	$Fe(OAc)_3$	DTBP	2.0	Toluene	100	ND
15	$Fe(acac)_3$	DTBP	2.0	Toluene	100	ND
16	$Fe_2(SO_4)_3.xH_2O$	DTBP	2.0	Toluene	100	ND
17	$Fe(NO_3).9H_2O$	DTBP	2.0	Toluene	100	ND
18	$Fe(ClO_4).xH_2O$	DTBP	2.0	Toluene	100	ND
19	Iron(III) phthalocyanine chloride	DTBP	2.0	Toluene	100	ND
20	CuCl	DTBP	2.0	Toluene	100	ND
21	$NiCl_2$	DTBP	2.0	Toluene	100	ND
22	$CoCl_2$	DTBP	2.0	Toluene	100	ND
23	$PdCl_2$	DTBP	2.0	Toluene	100	ND
24	$FeCl_3$	DDQ	2.0	Toluene	100	ND
25	$FeCl_3$	$K_2S_2O_8$	2.0	Toluene	100	25
26	$FeCl_3$	30% H_2O_2	2.0	Toluene	100	trace
27	$FeCl_3$	$(PhCOO)_2$	2.0	Toluene	100	trace
28	$FeCl_3$	Cumene Hydroperoxide	2.0	Toluene	100	ND
29	$FeCl_3$	NBS	2.0	Toluene	100	ND
30	$FeCl_3$	AIBN	2.0	Toluene	100	trace
31[b]	$FeCl_3$	DTBP	2.0	Toluene	100	68
32	–	DTBP	2.0	Toluene	100	ND
33	$FeCl_3$	–	2.0	Toluene	100	10
34	$FeCl_3$	DTBP	2.0	Toluene	80	46
35	$FeCl_3$	DTBP	2.0	Toluene	60	ND
36	$FeCl_3$	DTBP	1.5	Toluene	100	89
37	**$FeCl_3$**	**DTBP**	**1.2**	**Toluene**	**100**	**91**
38	$FeCl_3$	DTBP	1.0	Toluene	100	84

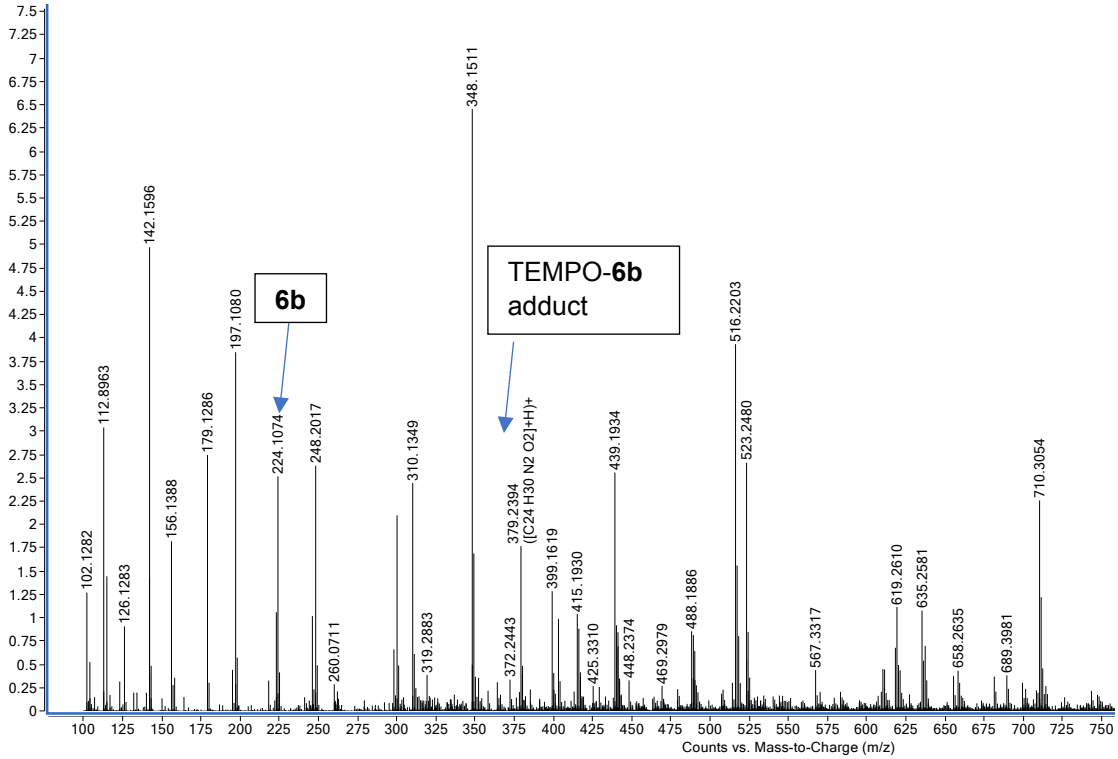
[a] *Reaction condition:* substrate (0.5 mmol), aniline (0.75 mmol, 1.5 eqv), M-cat (0.05 mmol, 10 mol%), in solvent (2.5 mL) under nitrogen at a given temp. for 3 hrs; Isolated yields of pure products. [b] using O_2 balloon. ND = Not Detected. DTBP = Di-*tert*-butyl peroxide, TBHP = *tert*-butyl hydroperoxide; DDQ = 2, 3-Dichloro-5, 6-Dicyno-1, 4-benzoquinone; NBS = N-bromosuccinimide; AIBN = Azobisisobutyronitrile.

Mechanistic Studies

Radical scavenging experiment in the presence of TEMPO

A 15 mL reaction tube was charged with 2-(2-methylbenzyl)benzo[*d*]oxazole **6b** (112 mg, 0.5 mmol, 1.0 equiv), $FeCl_3$ (8 mg, 0.1 mmol, 0.05 equiv) and TEMPO (156 mg, 1.0 mmol, 2.0 equiv). The vessel was evacuated and back-filled with nitrogen (x 3) and to it, anhydrous toluene (2.5 mL), DTBP (88 mg, 1.2 mmol, 0.6 equiv) and aniline **7a** (0.75 mmol, 1.5 equiv) were added. Subsequently, the reaction mixture was stirred at 100 ^oC for 3 h. After cooling, the solvent was evaporated and the residue was directly subjected to column chromatography on silica-gel to recover the starting material **6b** (100 mg, 90%). Furthermore, an aliquot (0.2 mL) from the crude reaction mixture was withdrawn and diluted with EtOAc (2.0 mL) and filtered through a pad of silica-gel. The organic layer was submitted to HRMS analysis, which indicated the formation of TEMPO-(**6b**) adduct along with the unreacted substrate **6b**.

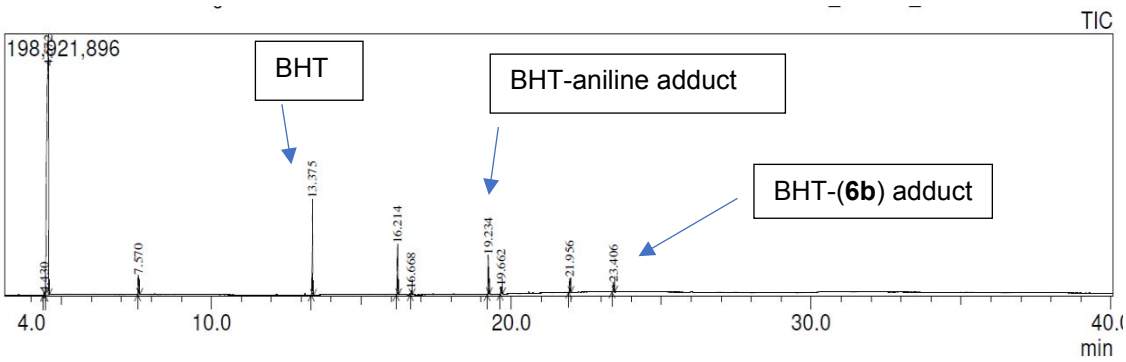
HRMS (ESI) analysis: *m/z* calcd. for (TEMPO-**6b** adduct) $C_{24}H_{31}N_2O_2$ $[M + H]^+$, 379.2380, found, 379.2394. *m/z* calcd. for (**6b**) $C_{15}H_{14}NO$ $[M + H]^+$, 224.1070, found, 224.1074



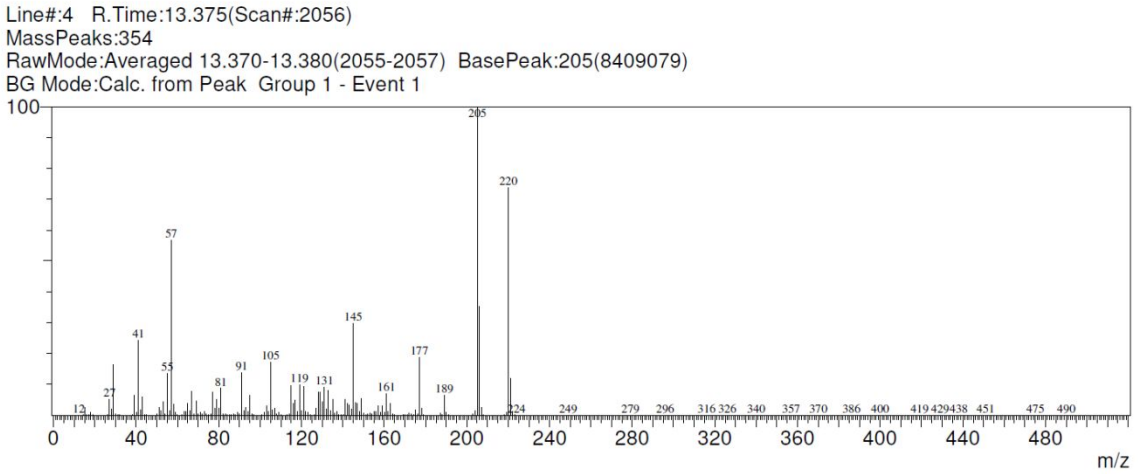
Radical scavenging experiment in the presence of BHT

A 15 mL reaction tube was charged with 2-(2-methylbenzyl)benzo[*d*]oxazole **6b** (112 mg, 0.5 mmol, 1.0 equiv), $FeCl_3$ (8.0 mg, 0.1 mmol, 0.05 equiv) and BHT (220 mg, 1.0 mmol, 2.0 equiv). The vessel was evacuated and back-filled with nitrogen (x 3) and to it, anhydrous toluene (2.5 mL), DTBP (88 mg, 1.2 mmol, 0.6 equiv) and aniline **7a** (0.75 mmol, 1.5 equiv) were added. Subsequently, the reaction mixture was stirred at 100 ^oC for 3 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 filtrate was submitted to GC-MS, which shows the formation of adducts such as BHT-aniline (*m/z* = 311) at R_t = 19.235 min and BHT(**6b**) (*m/z* = 441) at R_t = 23.405 min.

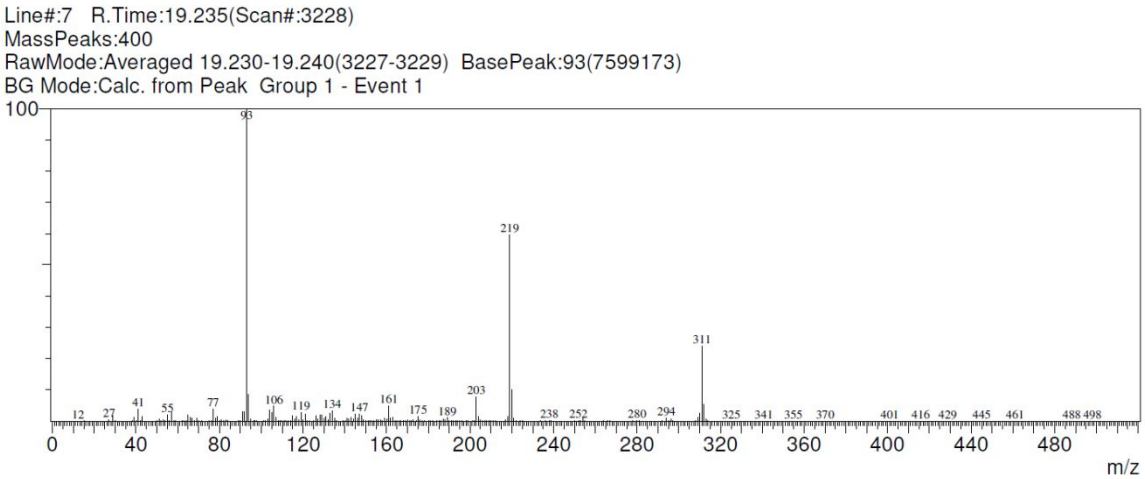
GC-MS spectra for the reaction between 6b and aniline (7a) in the presence of BHT



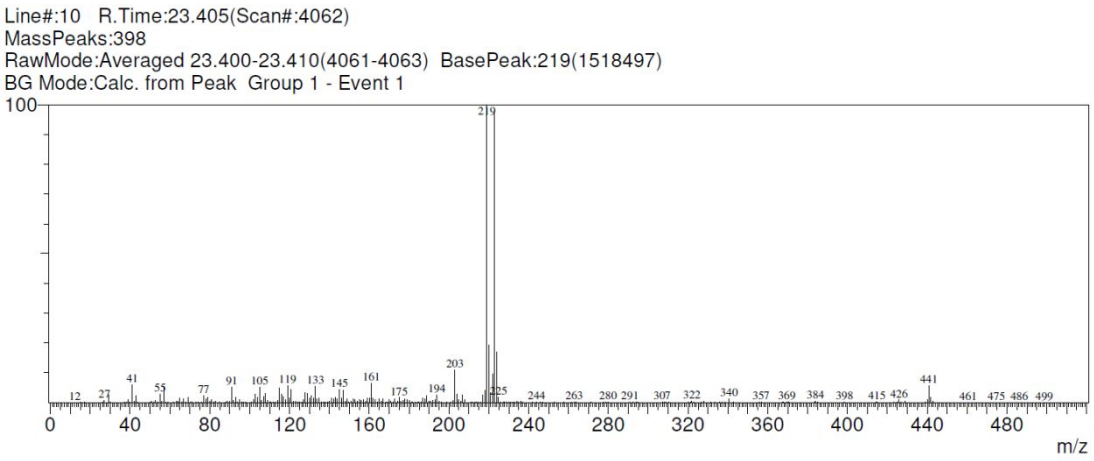
GCMS spectrum of BHT (*m/z* = 220, R_t = 13.375 min):



GCMS spectrum of BHT-aniline adduct (*m/z* = 311, R_t = 19.235 min):



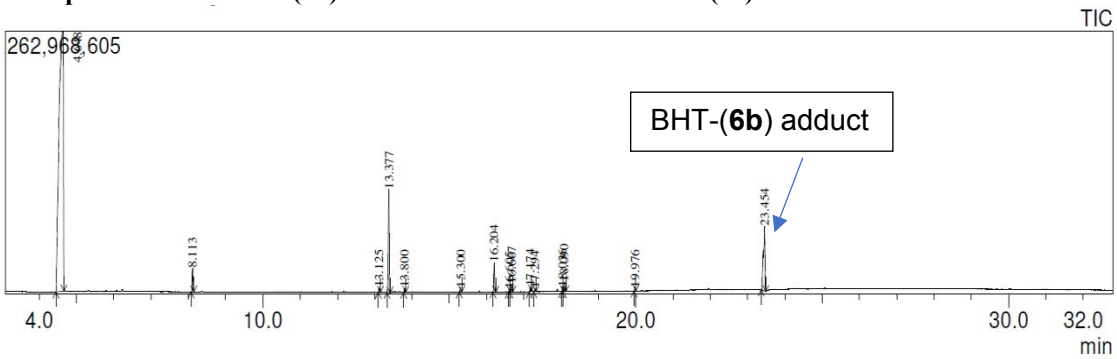
GCMS spectrum of BHT-(6b) adduct (*m/z* = 441, R_t = 23.405 min):



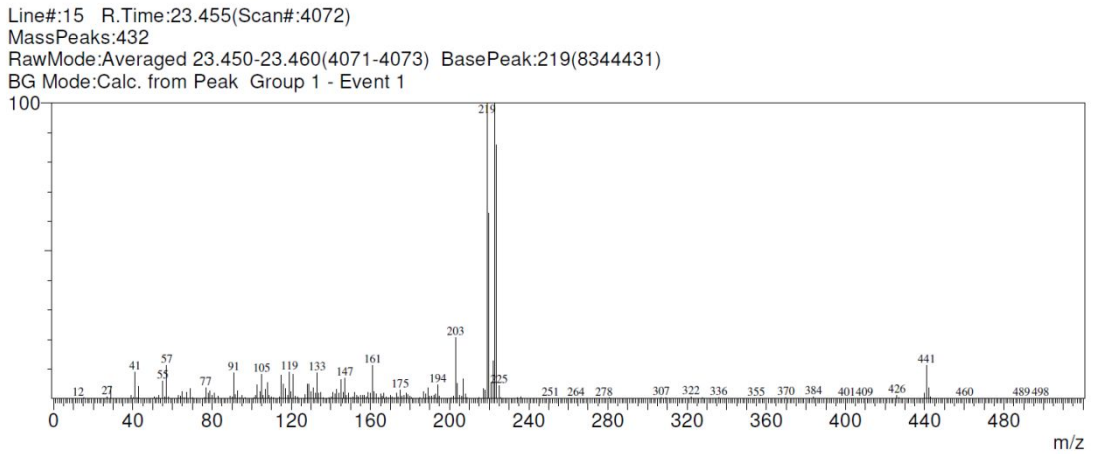
Radical scavenging experiment in the presence of BHT (In the absence of aniline)

Furthermore, the radical scavenging experiment with BHT was also performed in the absence of the aniline coupling partner **7a**. This experiment exhibited the formation of BHT-(**6b**) adduct in a greater extent as follows. A 15 mL reaction tube was charged with 2-(2-methylbenzyl)benzo[*d*]oxazole **6b** (112 mg, 0.5 mmol, 1.0 equiv), $FeCl_3$ (8 mg, 0.1 mmol, 0.05 equiv) and BHT (220 mg, 1.0 mmol, 2.0 equiv). Then vessel was evacuated and back-filled with nitrogen (x 3) and to it, anhydrous toluene (2.5 mL) and DTBP (88 mg, 1.2 mmol, 0.6 equiv) were added. The reaction mixture was stirred at 100 °C for 3 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 filtrate was submitted to GC-MS, which shows the formation of BHT-(**6b**) adduct (*m/z* = 441) at R_t = 23.454 min predominantly.

GC-MS spectra for the BHT-(6b) adduct in the absence of aniline (7a)

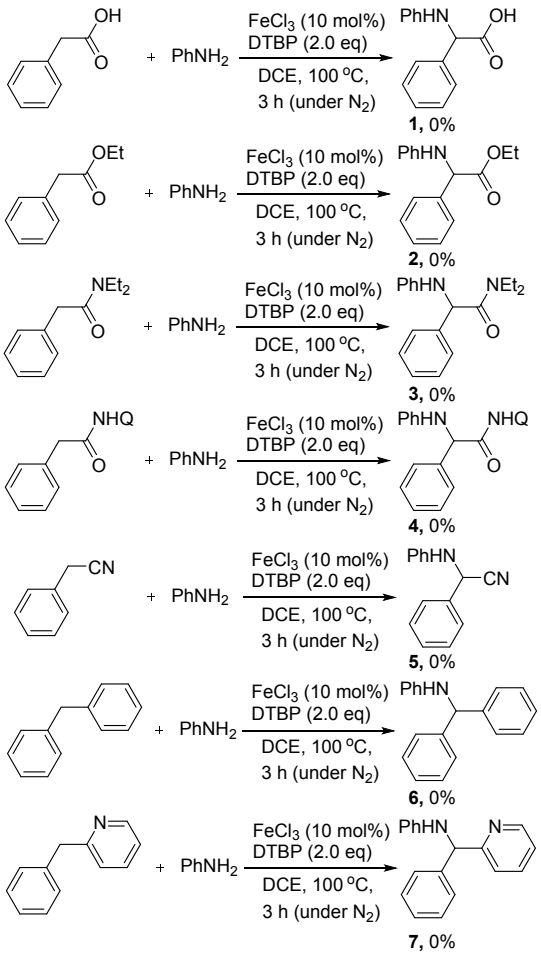


GCMS spectrum of BHT-(6b) adduct (*m/z* = 441, R_t = 23.455 min):



Reactions with various benzylic substrates:

Amination of benzylic substrates containing various functional groups with conjugation e.g., amides, ester, carboxylic acid, and phenyl under the optimized reaction condition:

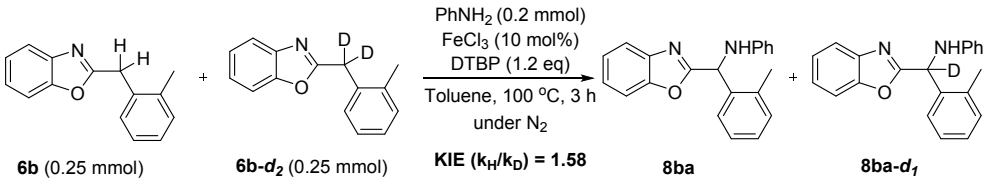


Scheme S1. Attempted Reactions between Aniline and Various Benzylic Substrates under Optimized Conditions

Kinetic Isotope Effect (KIE) Study

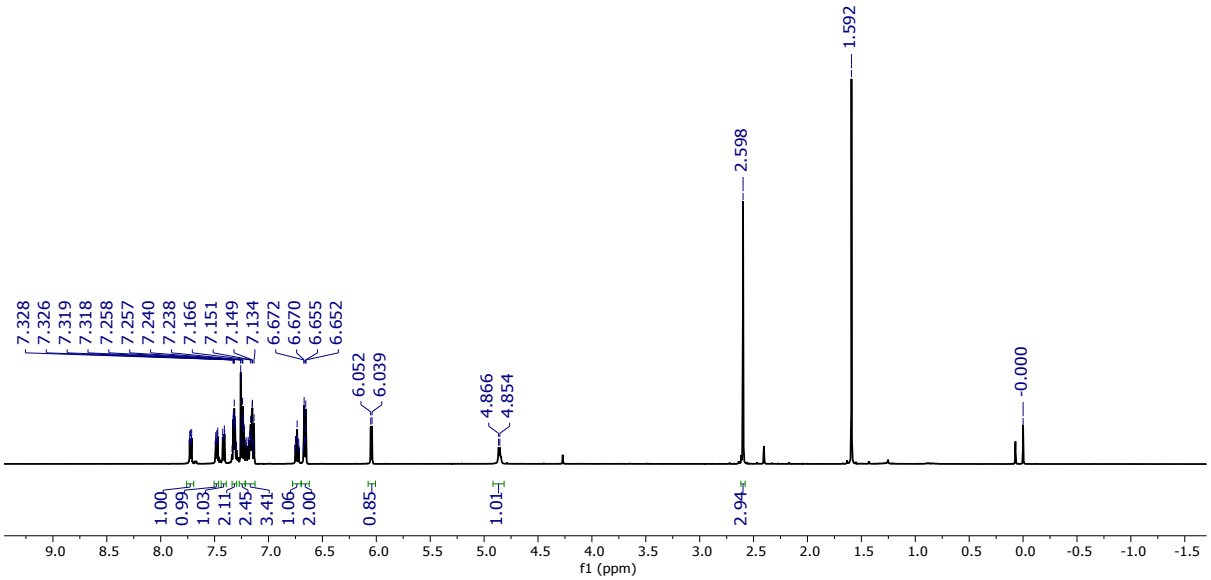
Intermolecular kinetic isotope effect study

For assessing the intermolecular kinetic isotope effect (KIE), a 1:1 mixture of **6b** (0.25 mmol) and the doubly deuterated substrate **6b-*d*$_2$** (0.25 mmol) was subjected to the amination using $PhNH_2$ (0.2 mmol) for 3 h and the product mixture was purified by column chromatography over silica-gel. The H/D ratio of the product mixture as found by ^1H NMR analysis indicated an intermolecular KIE, $k_H/k_D = 1.58$.



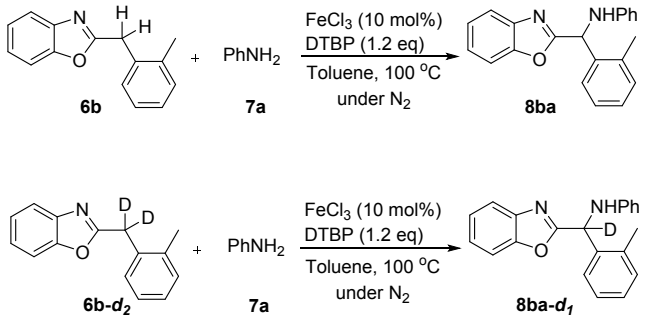
Scheme S2. Intermolecular KIE Study with the mixture of **6b** and **6b**-d_2

^{1}H NMR analysis for the determination of the intermolecular kinetic isotope effect:



Determination of KIE by independent parallel experiment

Two independent reactions with **6b** and **6b-*d*$_2$** under the optimal reaction conditions were conducted: Two 15 mL Schlenk tubes were charged with **6b** (112 mg, 0.5 mmol, 1.0 equiv) and **6b-*d*$_2$** (113 mg, 0.5 mmol, 1.0 equiv) separately. To each of them, $FeCl_3$ (8 mg, 0.1 mmol, 0.05 equiv) was added and the vessels were evacuated and back-filled with nitrogen (x 3). Subsequently, anhydrous toluene (2.5 mL), DTBP (88 mg, 1.2 mmol, 0.6 equiv) and aniline **7a** (0.75 mmol, 1.5 equiv) were added and the reaction mixtures were stirred at 100 °C for the required time as indicated in the following table. An aliquot of 0.1 mL was withdrawn periodically and passed through a small bed of silica-gel and monitored by GC analysis (Figure S1). Comparison of the two individual reactions showed a kinetic isotope effect of 1.63.



Scheme S3. KIE study by parallel independent experiments

Time (min)	5	10	15	20
6b (%)	9.1	20.3	25.9	33.2
6b-*d*$_2$ (%)	0	5.0	8.2	14.9

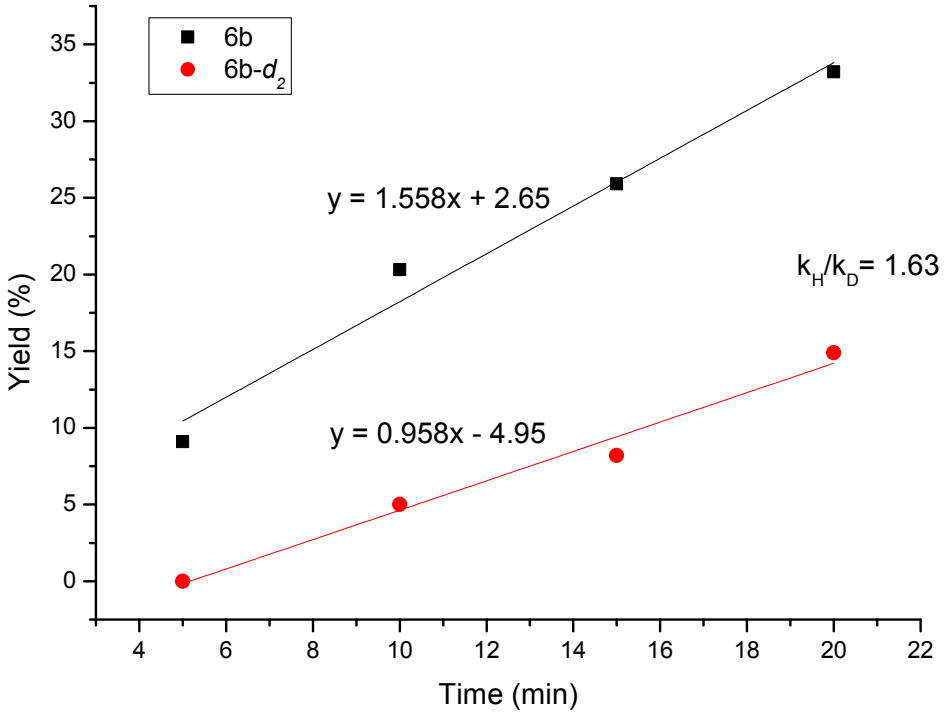
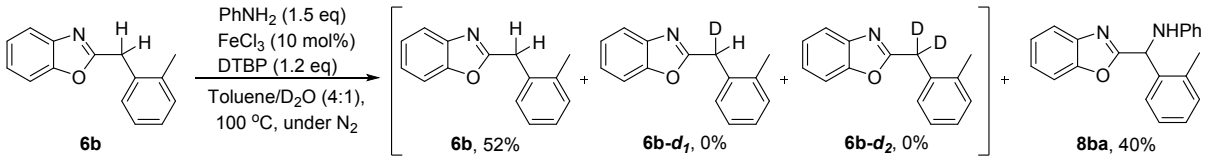


Figure S1. Determination of KIE by independent parallel experiments with **6b** and **6b**-d_2

H/D scrambling experiment in the presence of aniline:

A 15 mL reaction tube was charged with 2-(2-methylbenzyl)benzo[*d*]oxazole **6b** (112 mg, 0.5 mmol, 1.0 equiv), $FeCl_3$ (8 mg, 0.1 mmol, 0.05 equiv). The vessel was evacuated and back-filled with nitrogen (x 3) and to it, anhydrous toluene (2.0 mL), deuterium oxide (0.5 mL), DTBP (88 mg, 1.2 mmol, 0.6 equiv) and aniline **7a** (0.75 mmol, 1.5 equiv) were added. Subsequently, the reaction mixture was stirred at 100 °C for 3 h. After cooling, the solvent was evaporated and the residue was directly subjected to column chromatography on silica-gel to recover the starting material **6b**. The ^{1}H NMR analysis shows that there is no scrambling of H/D in the starting material (**6b**) during the amination with aniline in the presence of deuterium oxide, indicating the irreversibility of the C–H abstraction step.



Scheme S4. Study of H/D Scrambling in **6b** in the presence of Aniline

H/D scrambling experiment in the absence of aniline:

A 15 mL reaction tube was charged with 2-(2-methylbenzyl)benzo[*d*]oxazole **6b** (112 mg, 0.5 mmol, 1.0 equiv), $FeCl_3$ (8 mg, 0.1 mmol, 0.05 equiv). The vessel was evacuated and back-filled with nitrogen (x 3) and to it, anhydrous toluene (2.0 mL), deuterium oxide (0.5 mL), and DTBP (88 mg, 1.2 mmol, 0.6 equiv) were added. Subsequently, the reaction mixture was stirred at 100 °C for 3 h. After cooling, the solvent was evaporated and the residue was directly subjected to column chromatography on silica-gel to recover the starting material **6b**. The

X-ray Structure Report for 8md

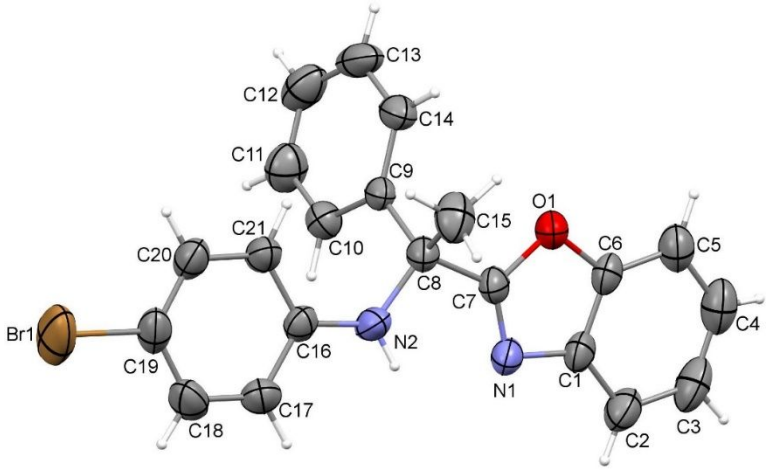


Figure S2. ORTEP diagram of **8md** (45% probability factor for the thermal ellipsoids)

Empirical formula	$C_{21}H_{17}BrN_2O$
Formula weight	393.27
Temperature/K	300
Crystal system	Monoclinic
Space group	P1 21/c1
a/Å	16.1173 (10)
b/Å	6.0319 (3)
c/Å	19.9118 (13)
α/o	90
β/o	110.983 (2)
γ/o	90
Volume/Å3	1807.42 (19)
Z	4
ρ_{calc} g/cm3	1.445
μ/mm-1	2.285
F(000)	800.0
Crystal size/mm3	0.920 x 0.320 x 0.201
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/o	2.707-27.8822
Index ranges	$-22 \leq h \leq 22$, $-8 \leq k \leq 8$, $-27 \leq l \leq 27$
Reflections collected	4864
Independent reflections	3005
Data/restraints/parameters	4864/0/294
Goodness-of-fit on F2	1.010
Final R indexes [I>= 2σ (I)]	R1 = 0.0424, wR2 = 0.0997
Final R indexes [all data]	R1 = 0.0799, wR2 = 0.1164
Largest diff. peak/hole/e Å-3	0.467/-0.666
CCDC	1990591

X-ray Structure Report for 8ua

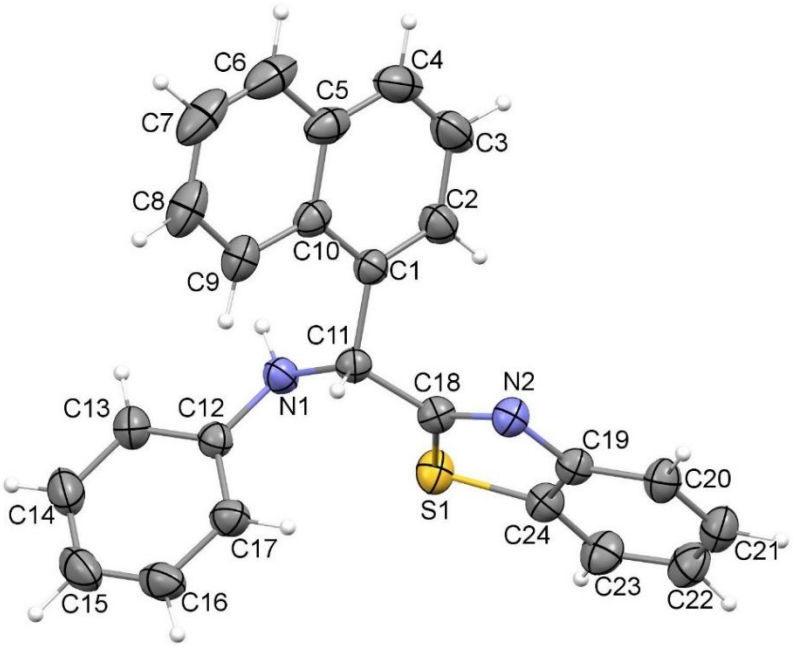
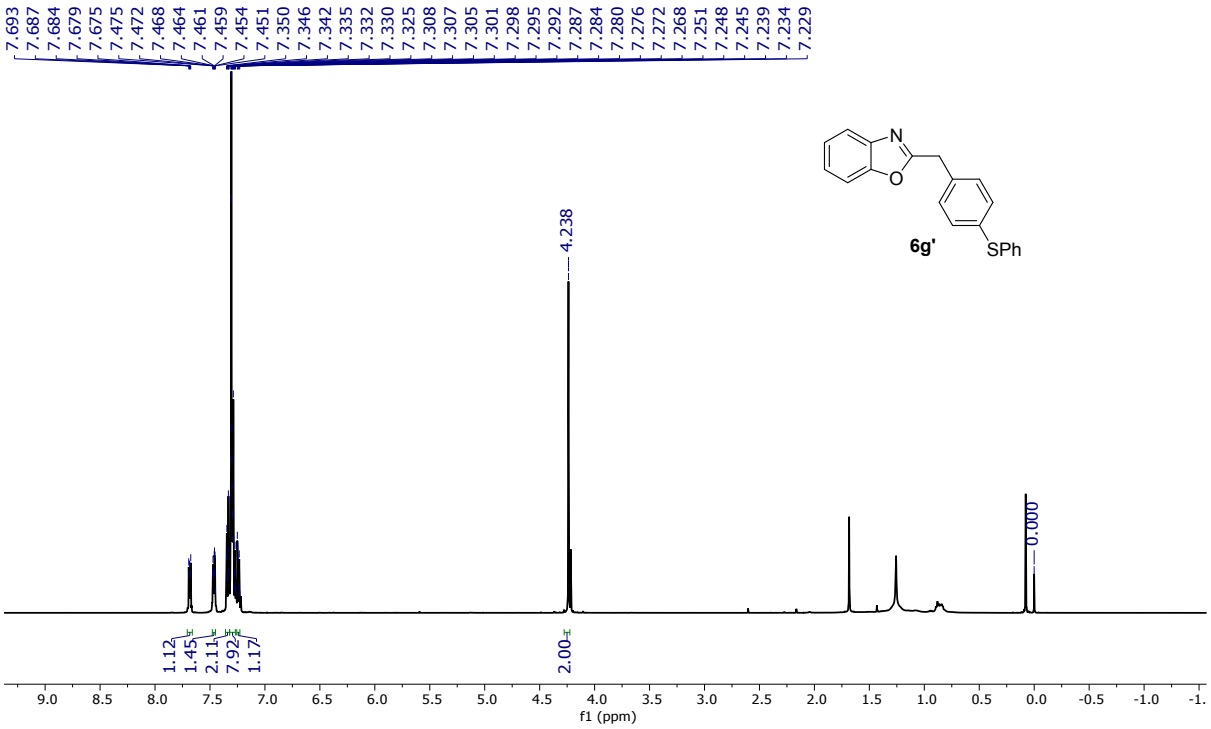


Figure S3. ORTEP diagram of **8ua** (50% probability factor for the thermal ellipsoids)

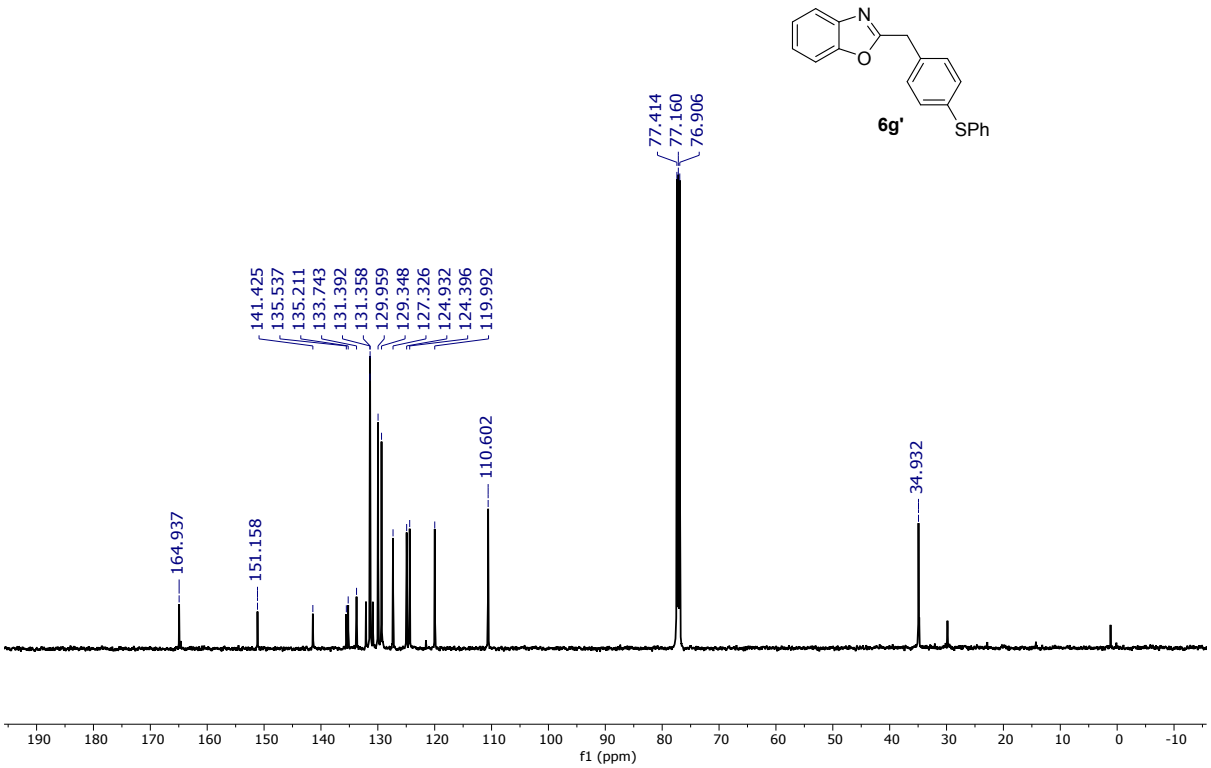
Empirical formula	$C_{24}H_{18}N_2S$
Formula weight	366.46
Temperature/K	264
Crystal system	Monoclinic
Space group	P1 21/c1
a/Å	10.0472 (10)
b/Å	9.0898 (8)
c/Å	20.6002 (19)
α/o	90
β/o	98.372 (3)
γ/o	90
Volume/Å3	1861.3 (3)
Z	4
ρ_{calc} g/cm3	1.308
μ/mm-1	0.184
F(000)	768.0
Crystal size/mm3	0.752 x 0.261 x 0.168
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/o	2.45-35.28
Index ranges	$-16 \leq h \leq 16$, $-14 \leq k \leq 14$, $-33 \leq l \leq 33$
Reflections collected	8279
Independent reflections	5836
Data/restraints/parameters	8279/0/316
Goodness-of-fit on F_2	1.081
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0484$, $wR_2 = 0.1274$
Final R indexes [all data]	$R_1 = 0.0769$, $wR_2 = 0.1500$
Largest diff. peak/hole/e Å-3	0.363/-0.349
CCDC	1990638

^{1}H and ^{13}C NMR spectra of unknown substrates

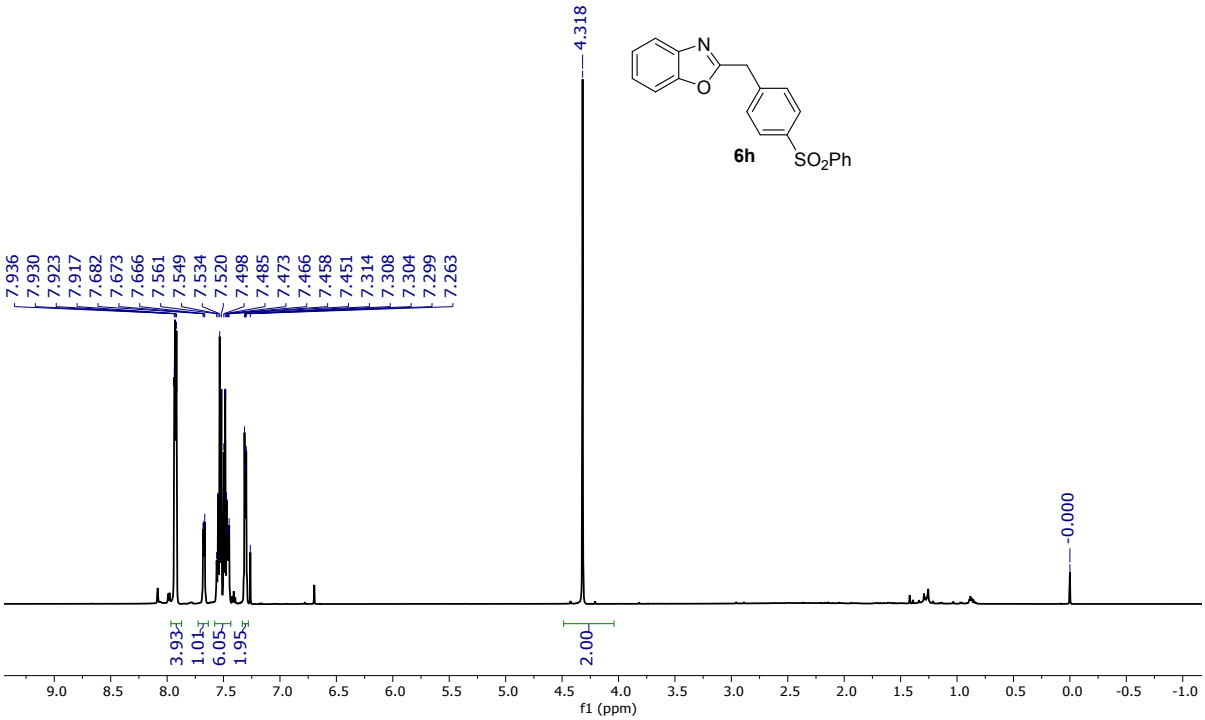
^{1}H NMR (500 MHz, $CDCl_3$):



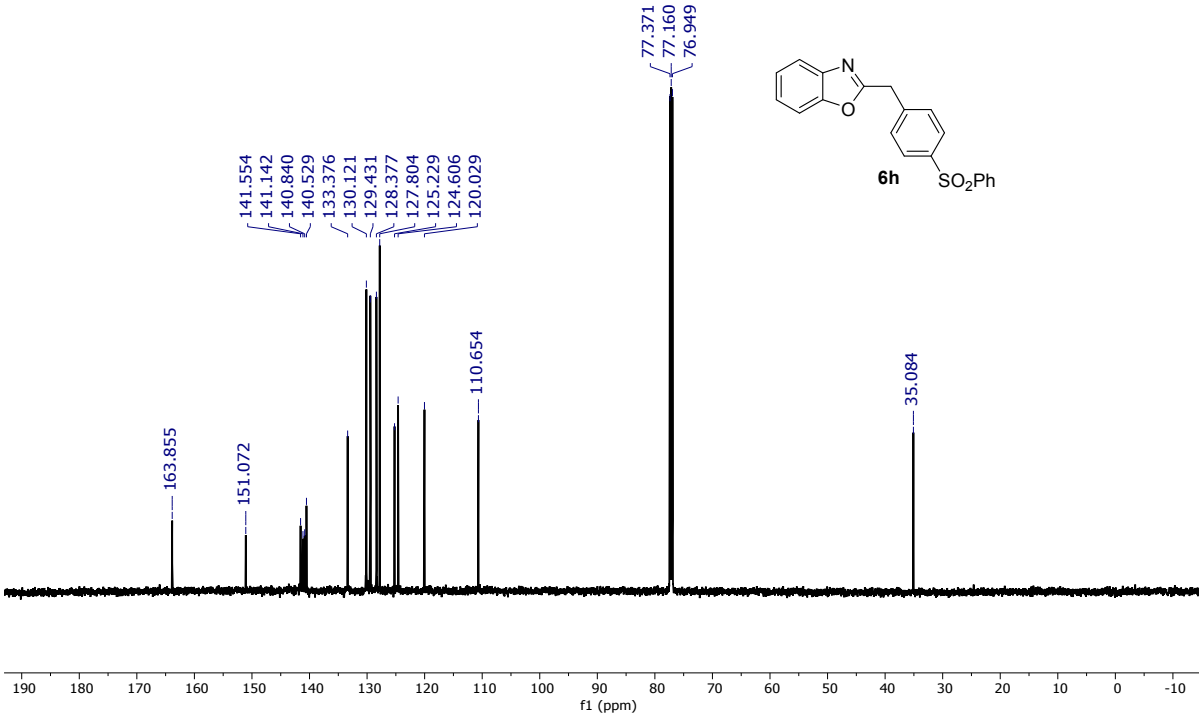
^{13}C NMR (126 MHz, $CDCl_3$):



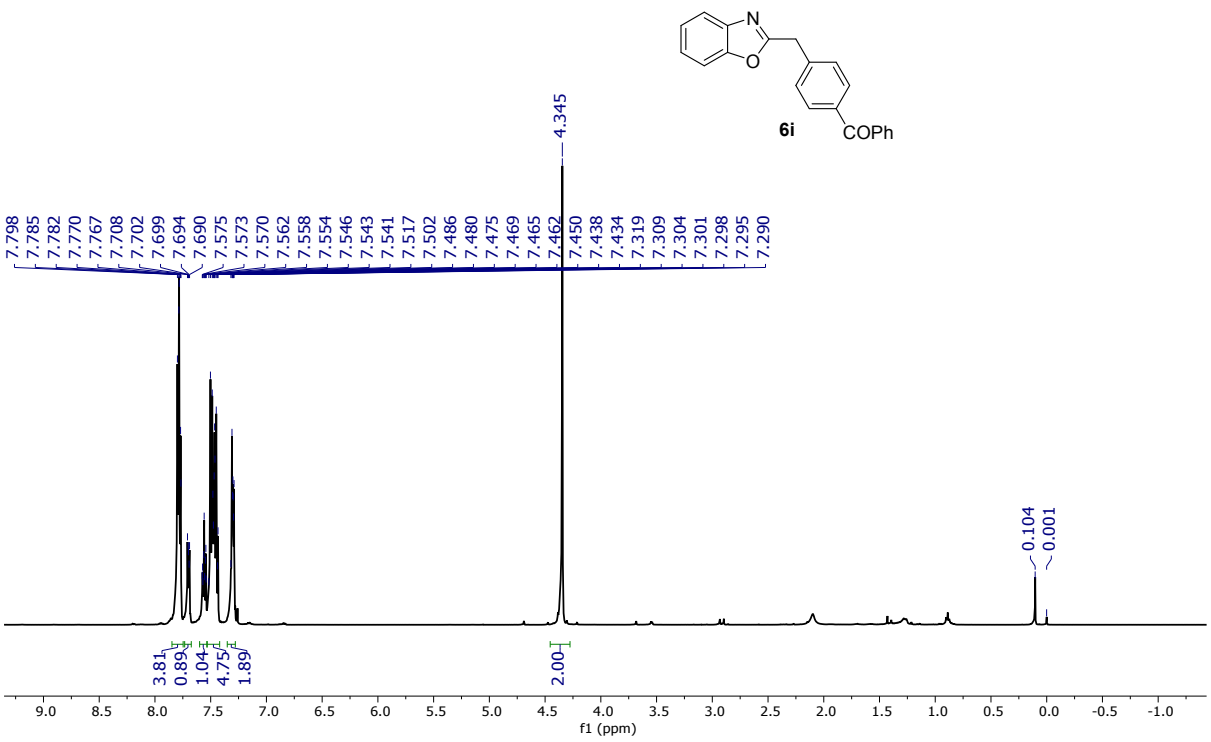
^{1}H NMR (600 MHz, $CDCl_3$):



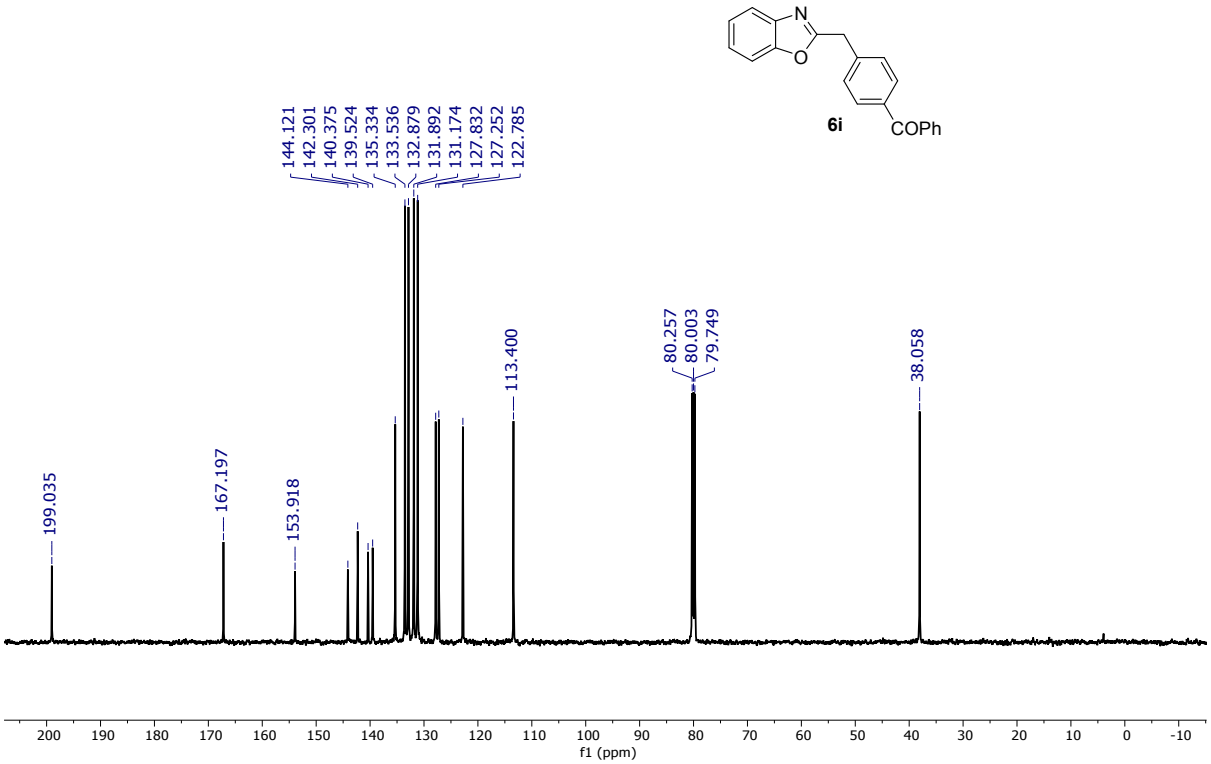
^{13}C NMR (151 MHz, $CDCl_3$):



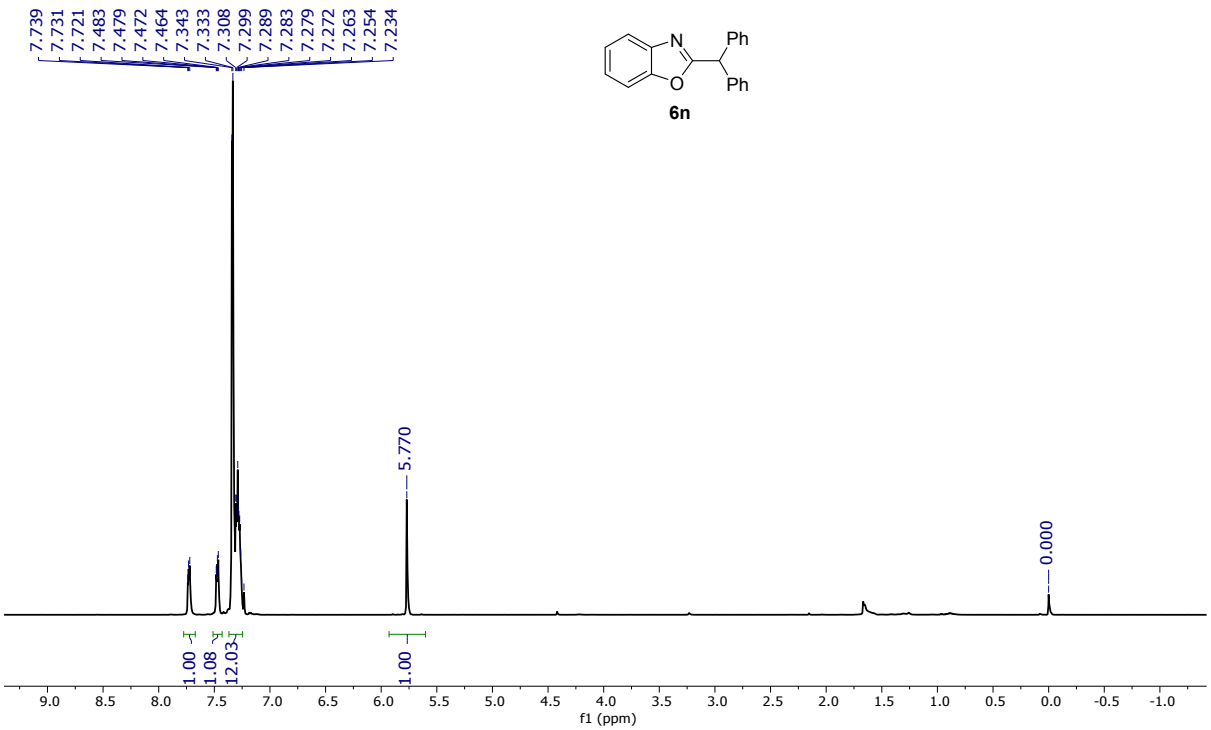
^{1}H NMR (500 MHz, $CDCl_3$):



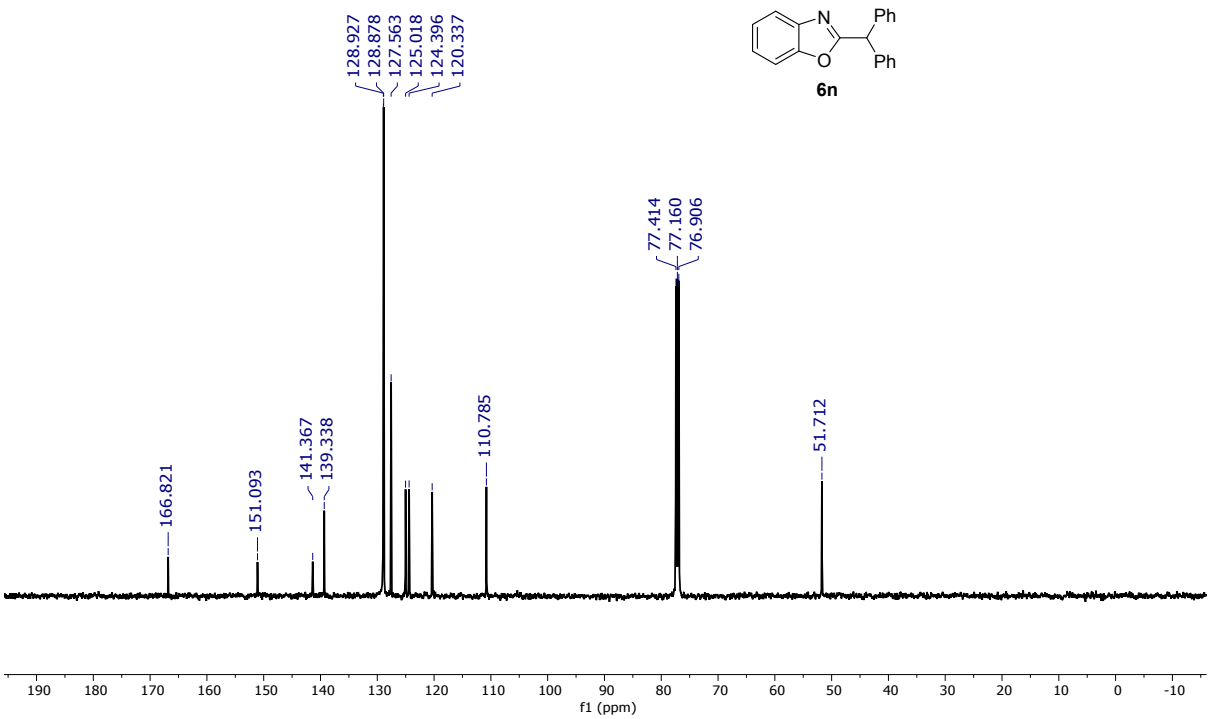
^{13}C NMR (126 MHz, $CDCl_3$):



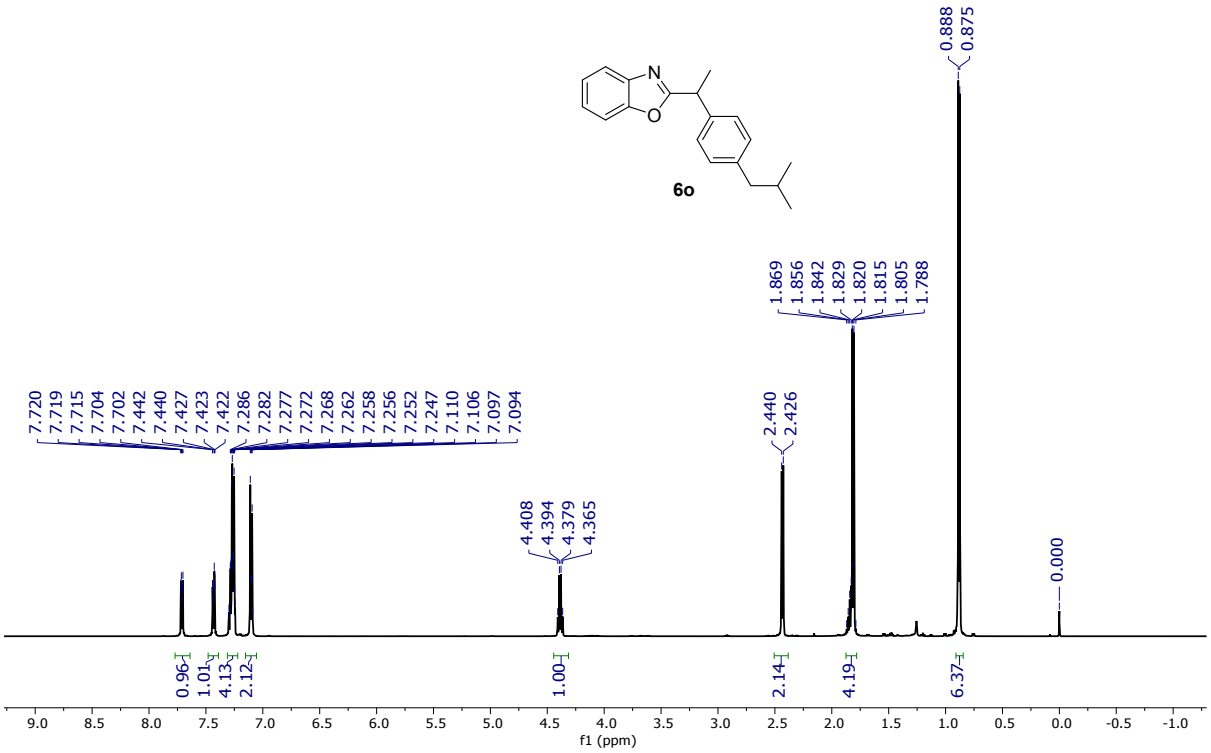
^{1}H NMR (500 MHz, $CDCl_3$):



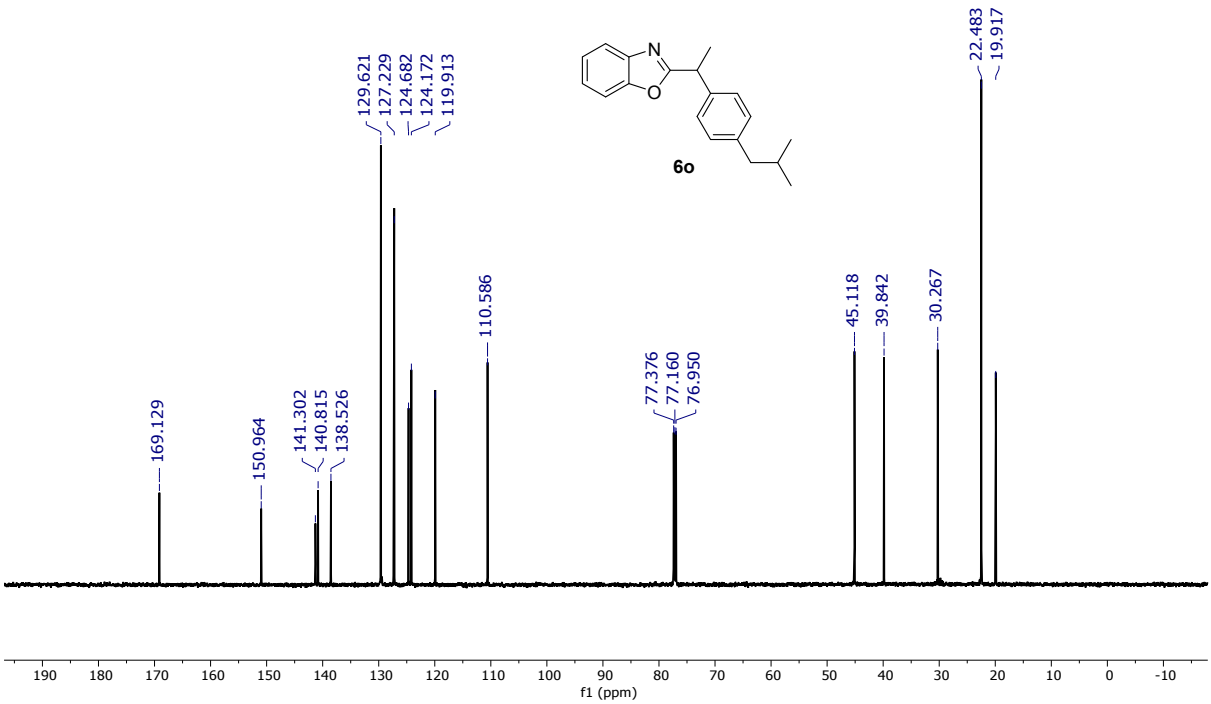
^{13}C NMR (126 MHz, $CDCl_3$):



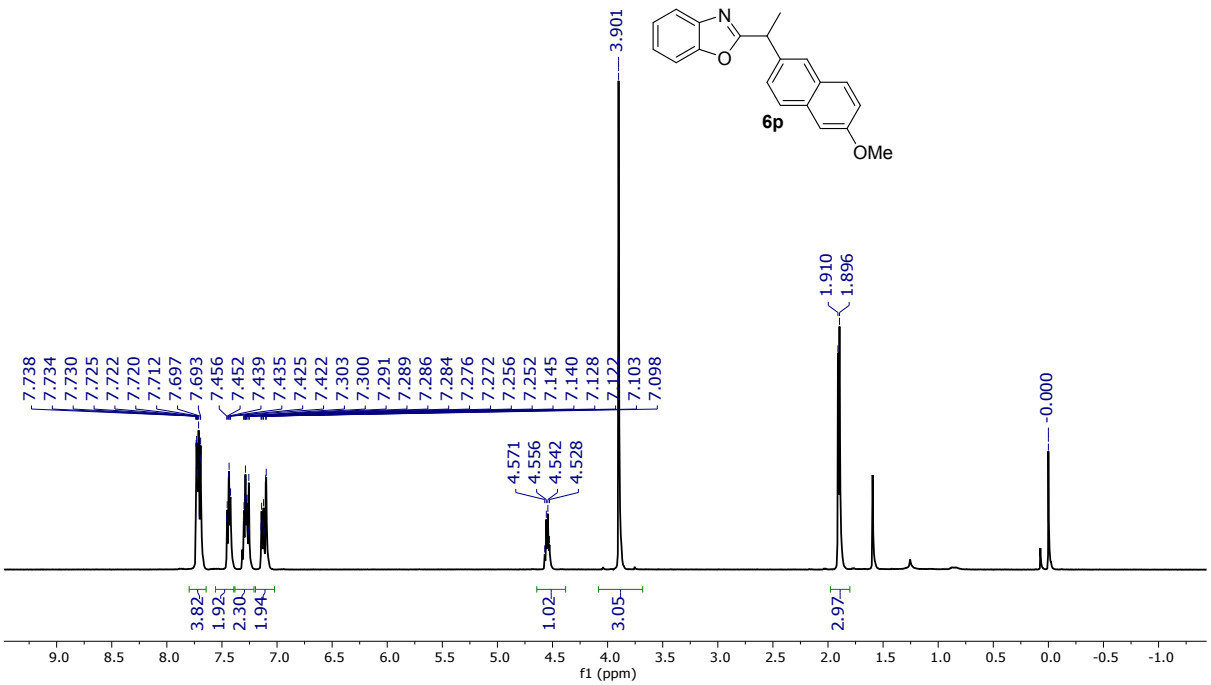
^{1}H NMR (500 MHz, $CDCl_3$):



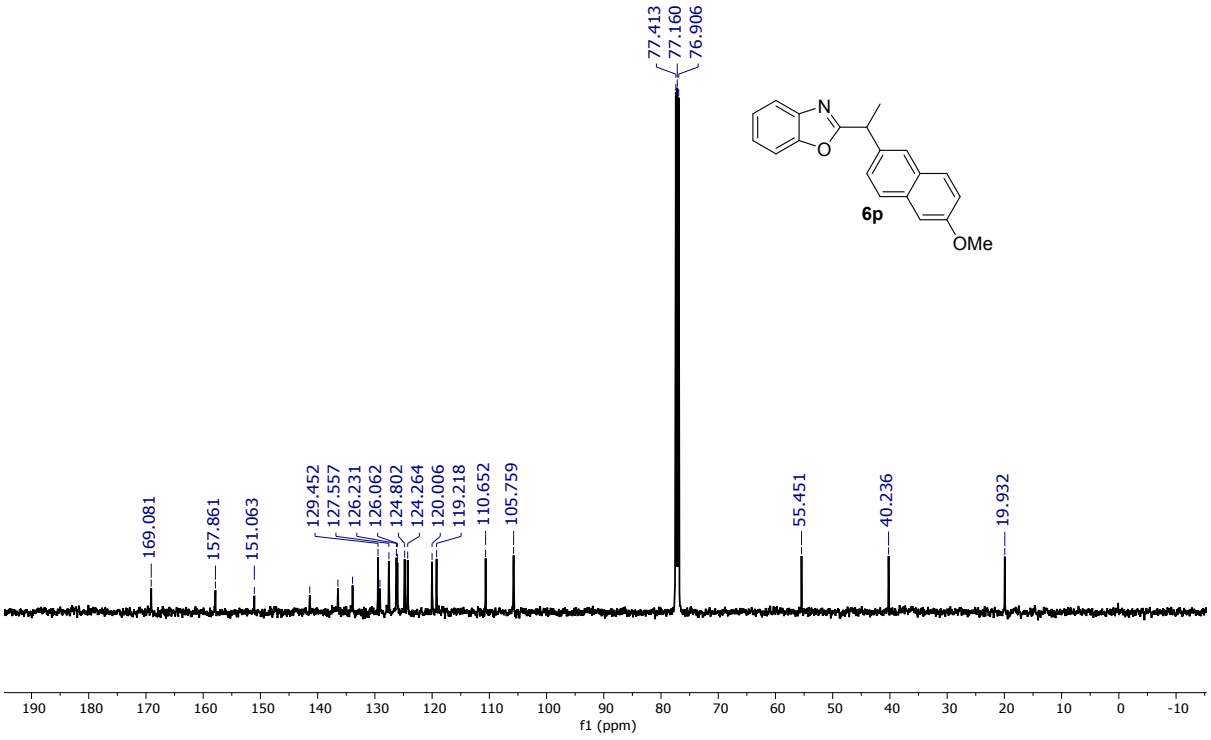
^{13}C NMR (151 MHz, $CDCl_3$):



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

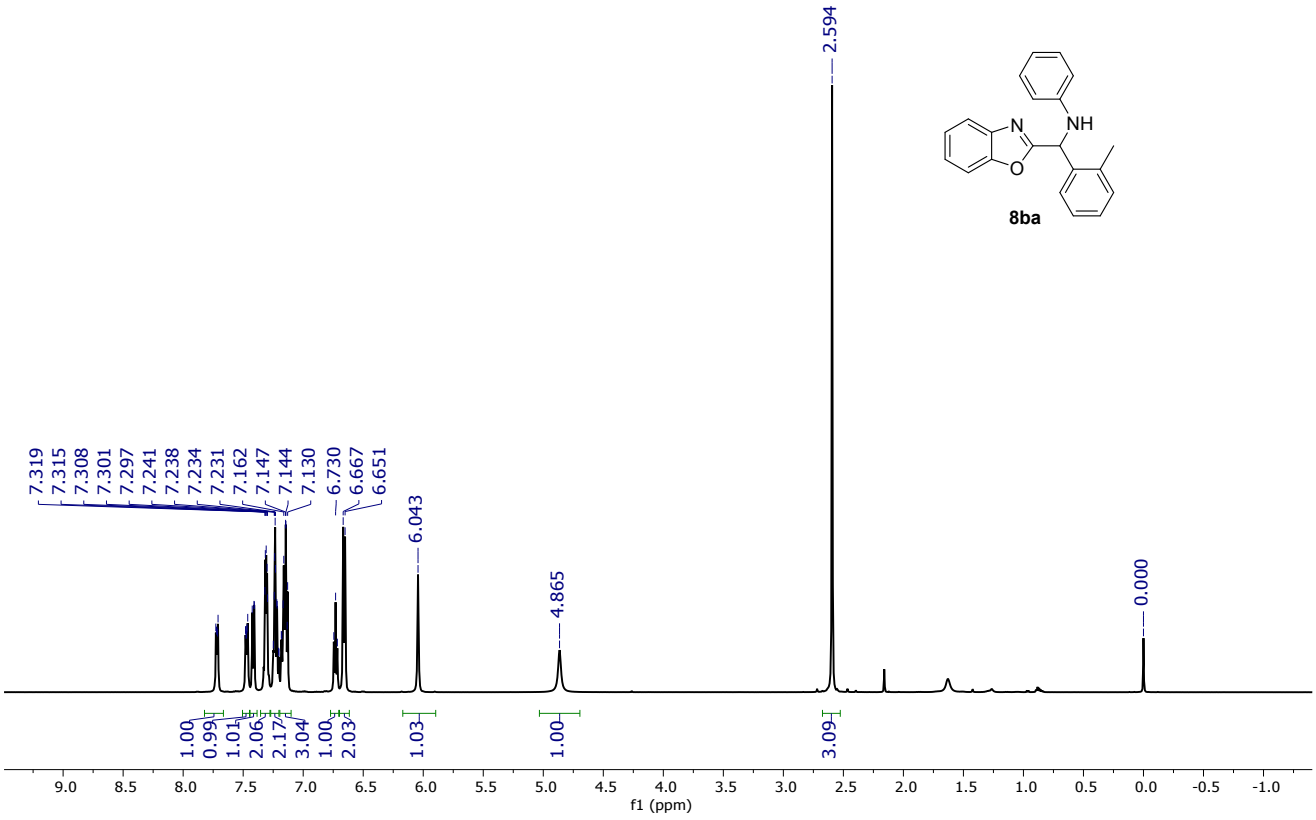


^{13}C NMR (126 MHz, $CDCl_3$):

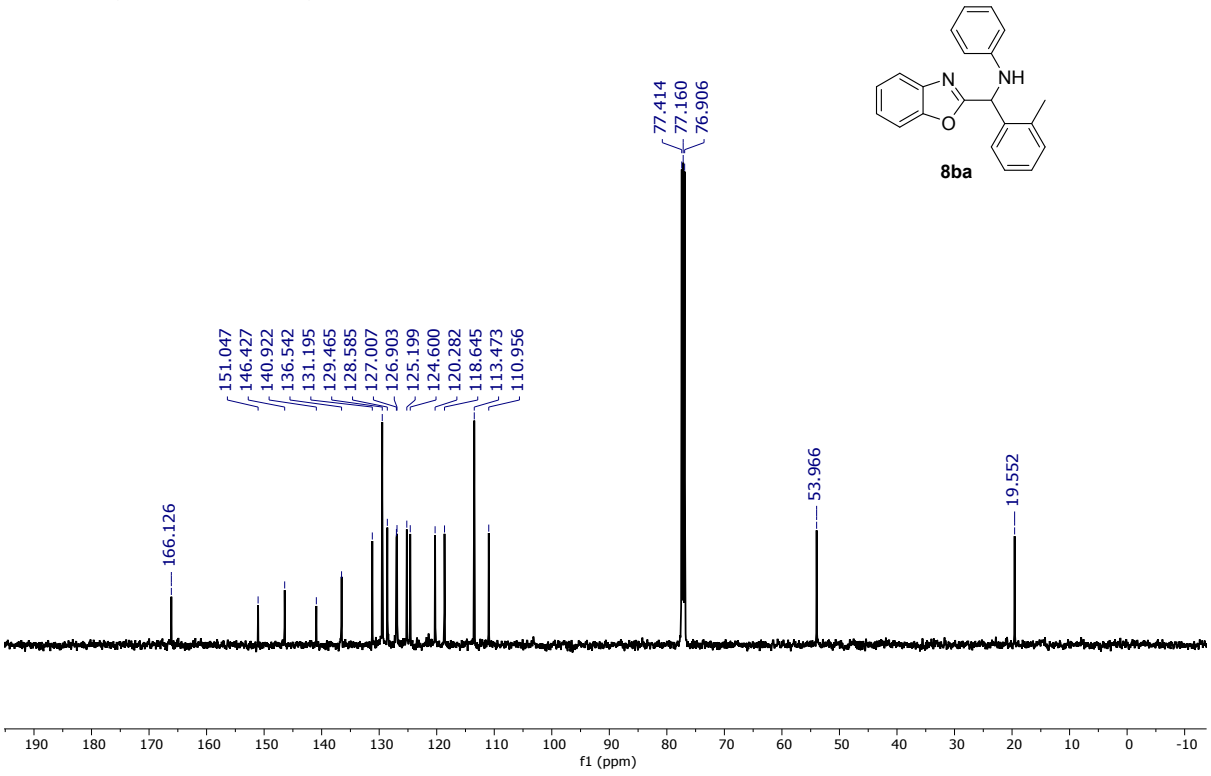


^{1}H and ^{13}C NMR spectra of all products

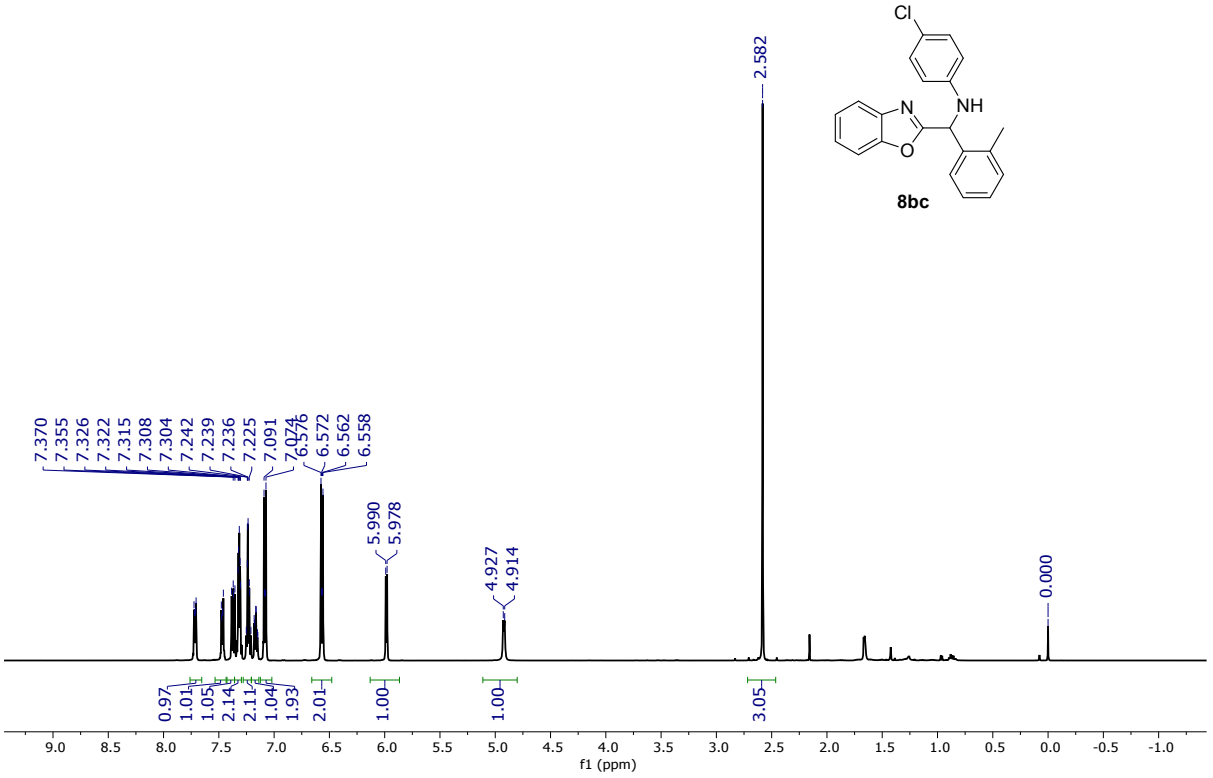
^{1}H NMR (500 MHz, $CDCl_3$):



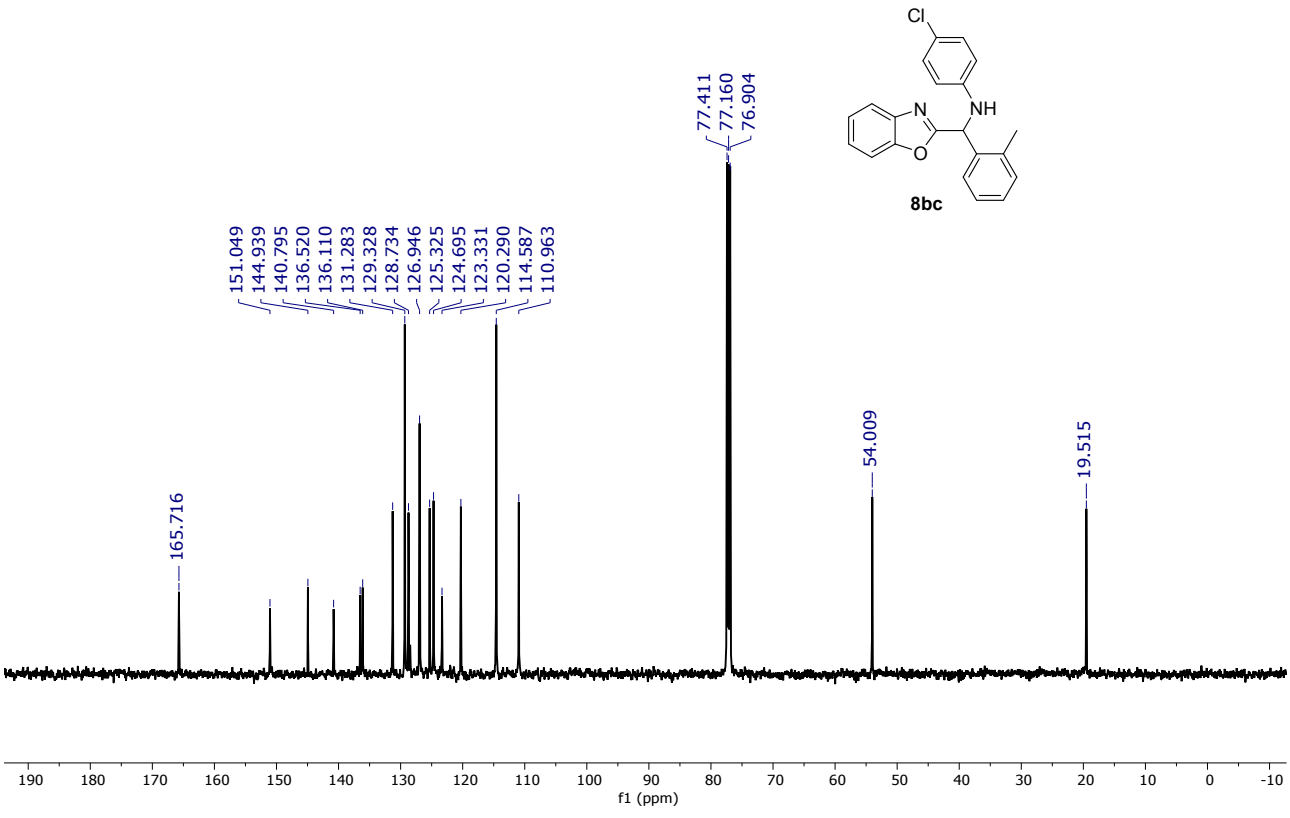
^{13}C NMR (126 MHz, $CDCl_3$):



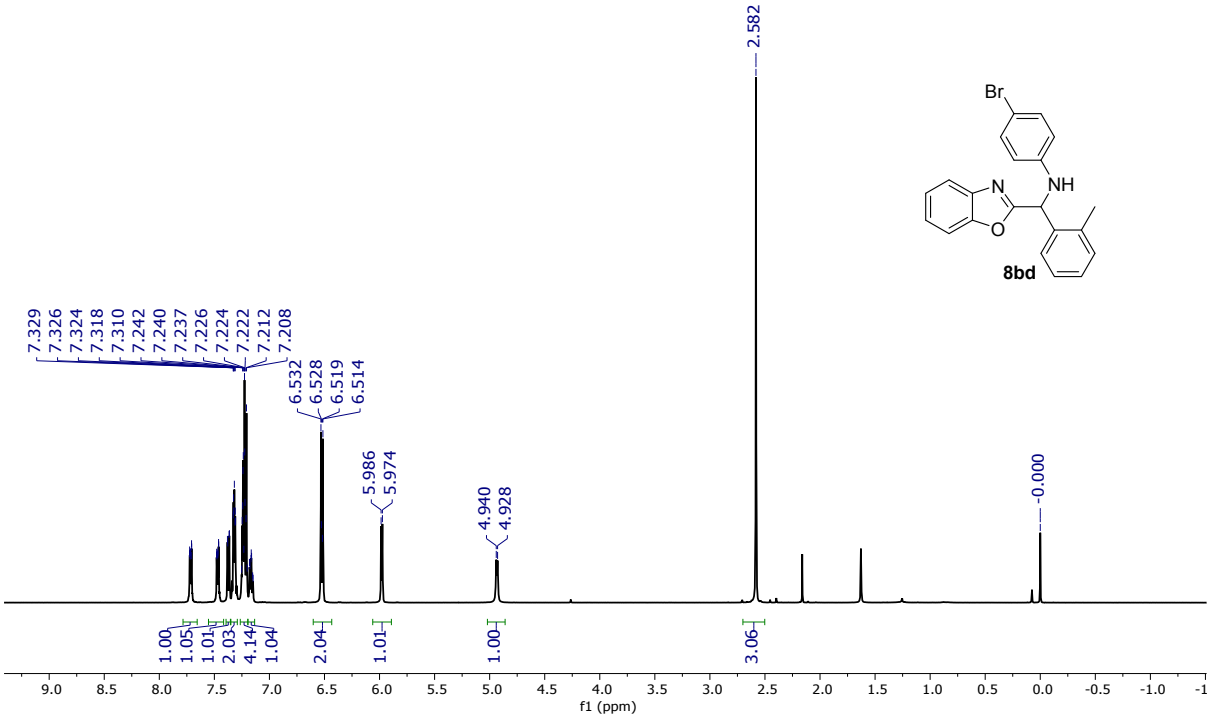
^{1}H NMR (500 MHz, $CDCl_3$):



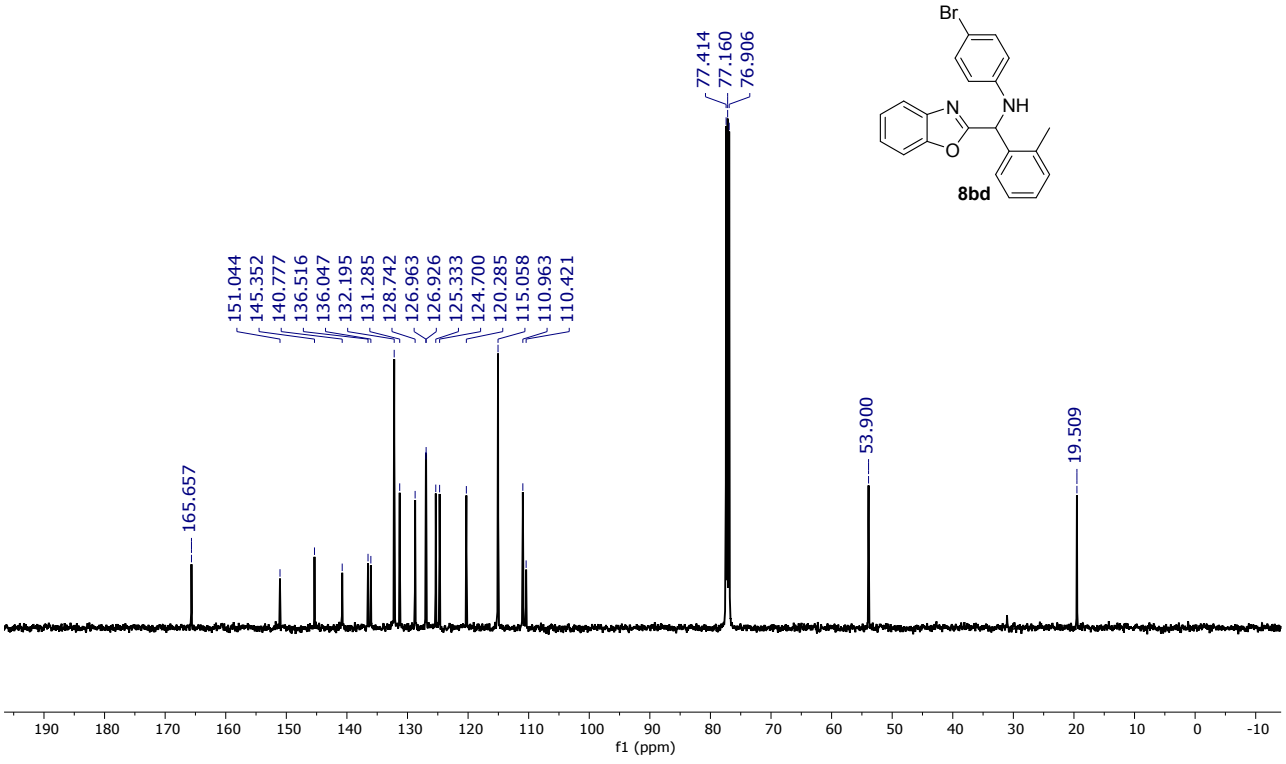
^{13}C NMR (126 MHz, $CDCl_3$):



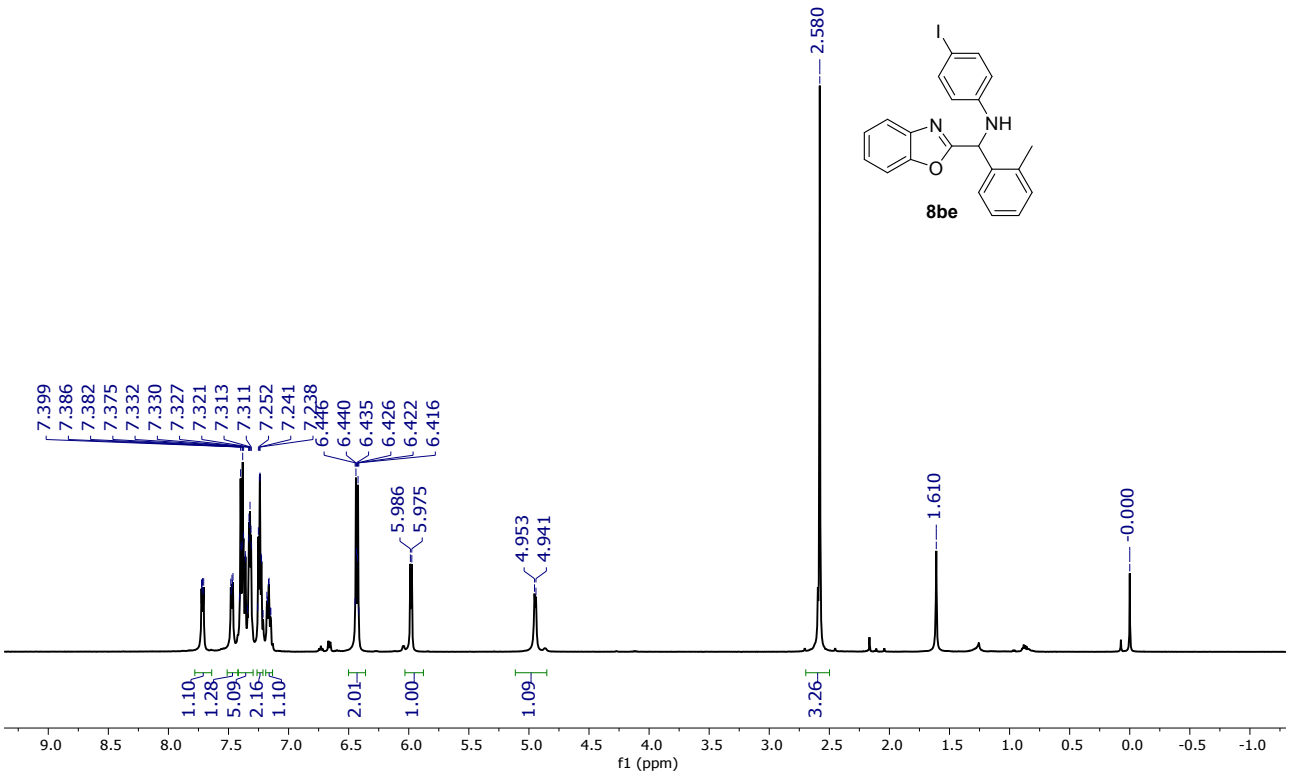
^{1}H NMR (500 MHz, $CDCl_3$):



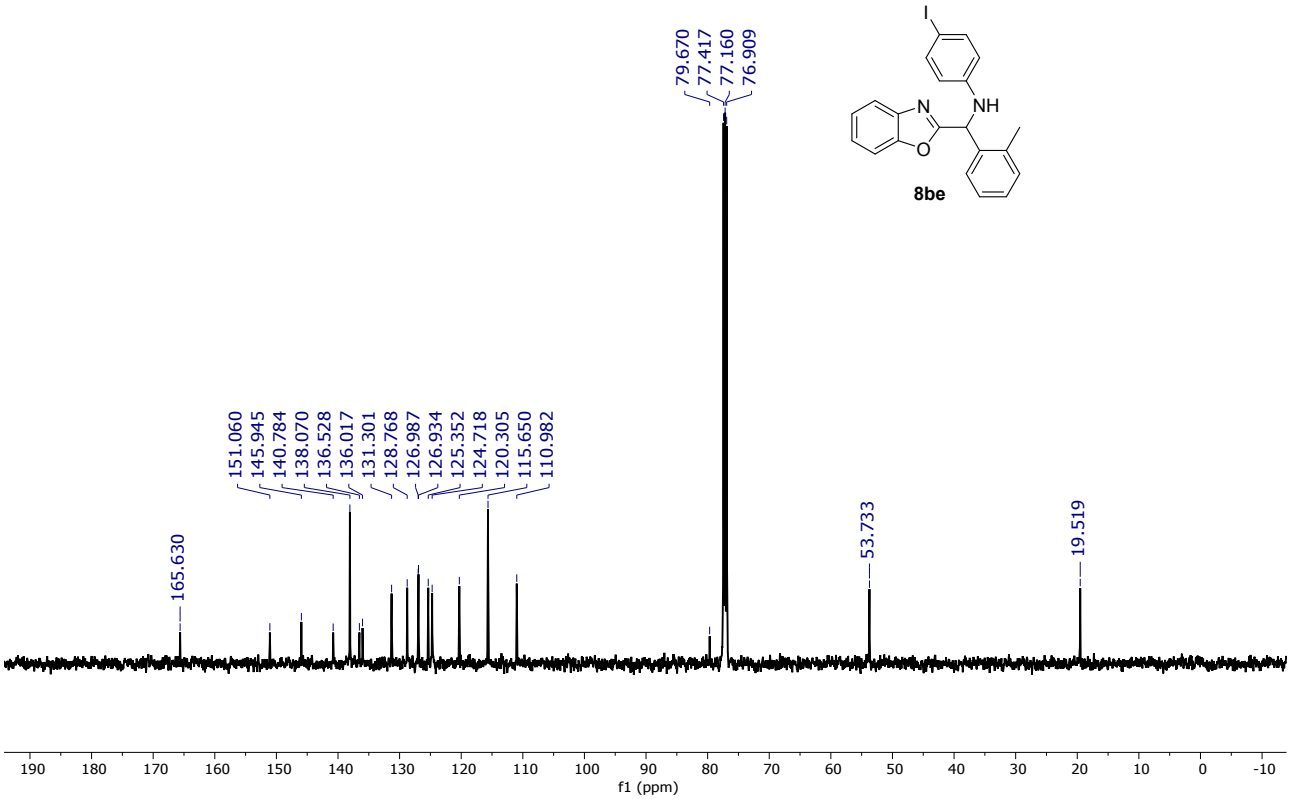
^{13}C NMR (126 MHz, $CDCl_3$):



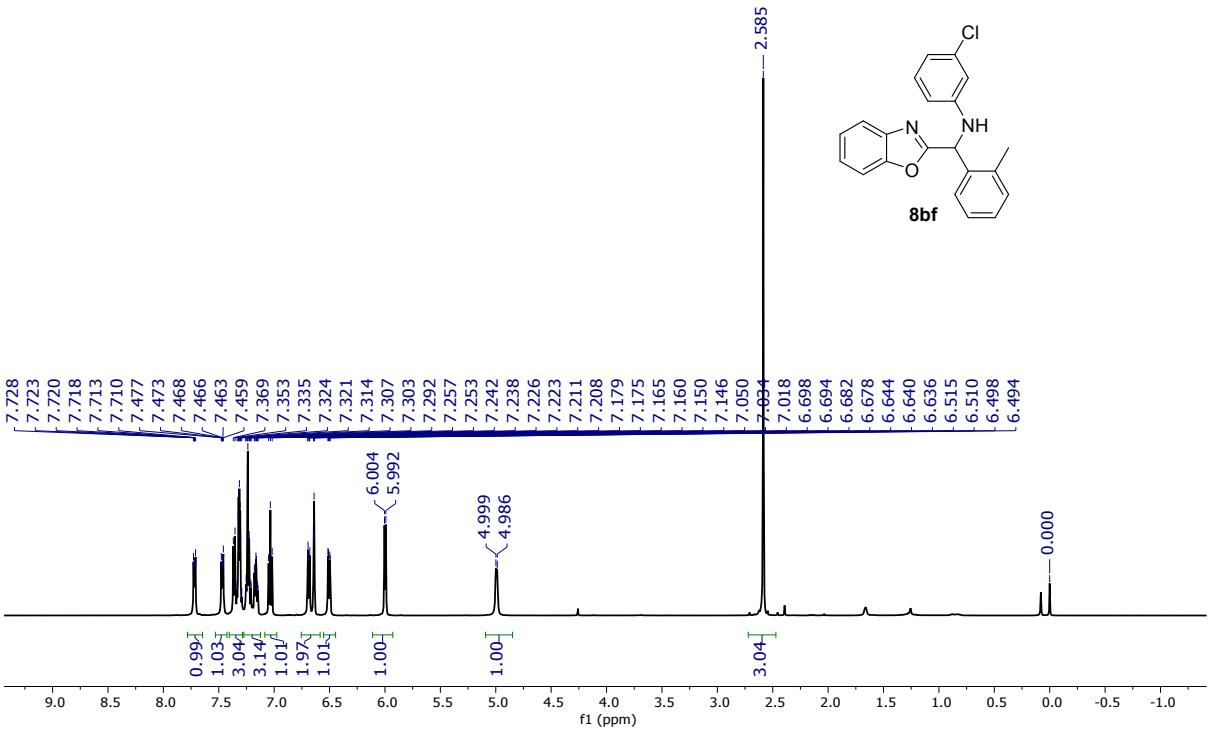
^{1}H NMR (500 MHz, $CDCl_3$):



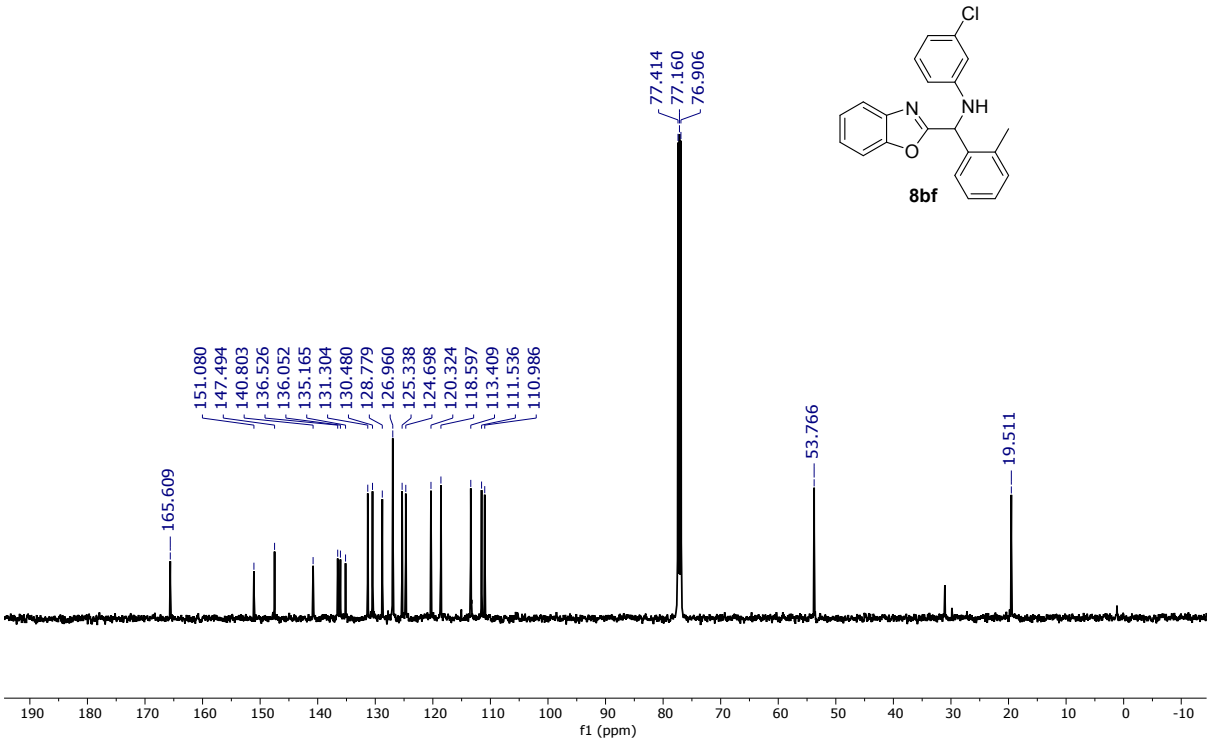
^{13}C NMR (126 MHz, $CDCl_3$):



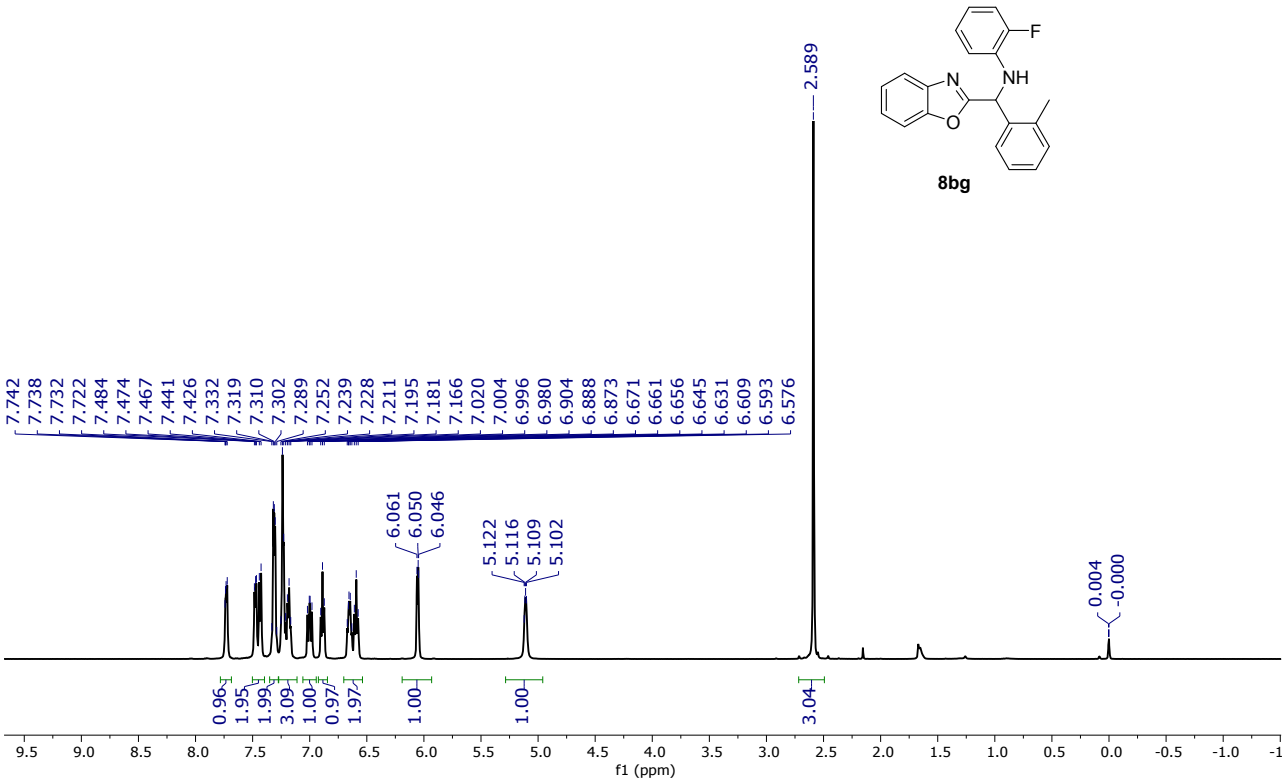
^{1}H NMR (500 MHz, $CDCl_3$):



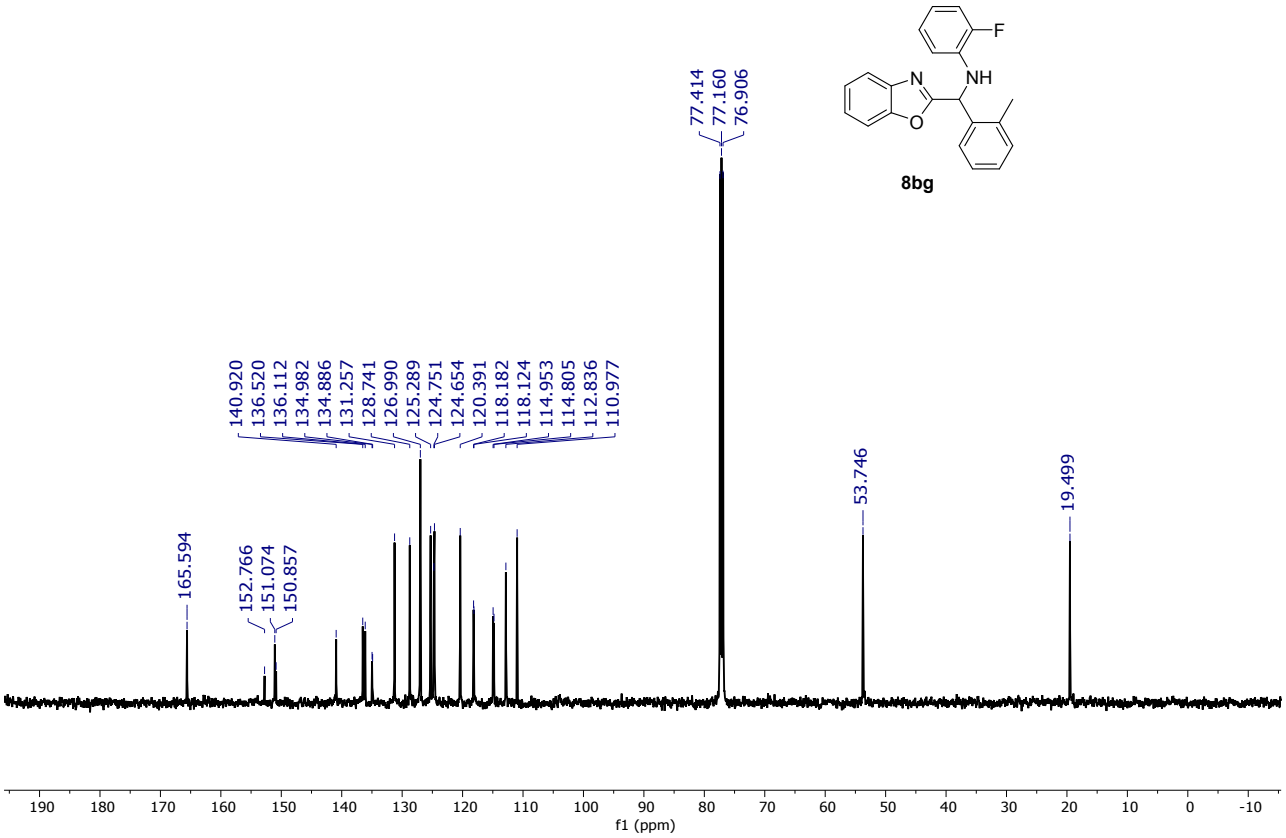
^{13}C NMR (126 MHz, $CDCl_3$):



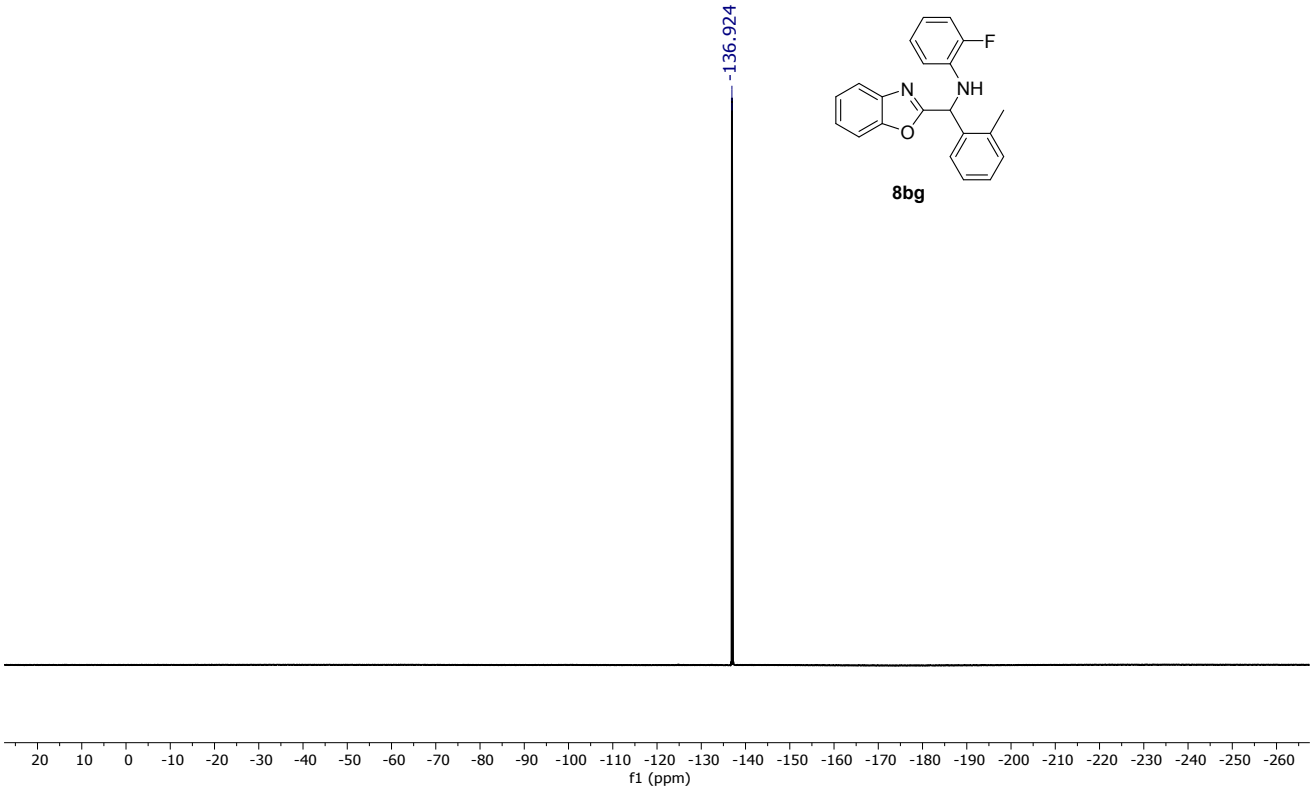
^{1}H NMR (500 MHz, $CDCl_3$):



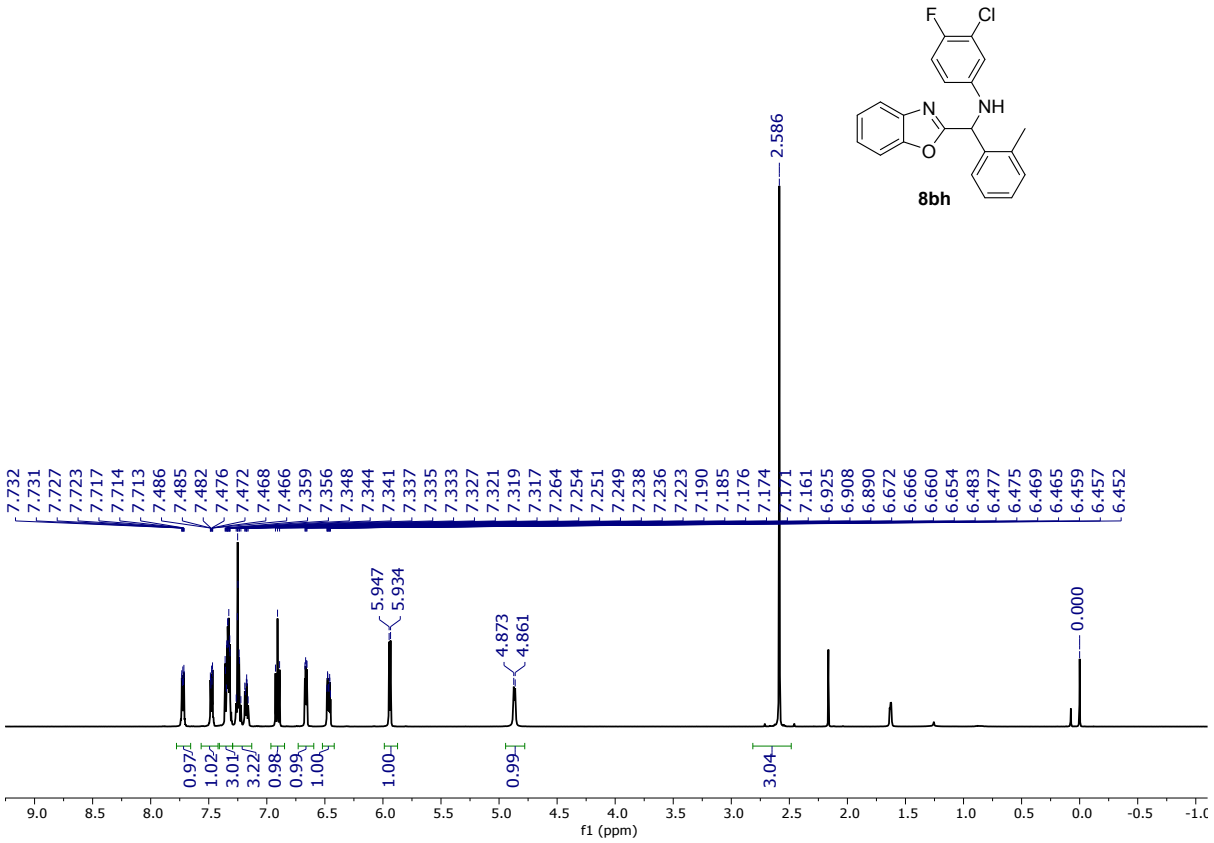
^{13}C NMR (126 MHz, $CDCl_3$):



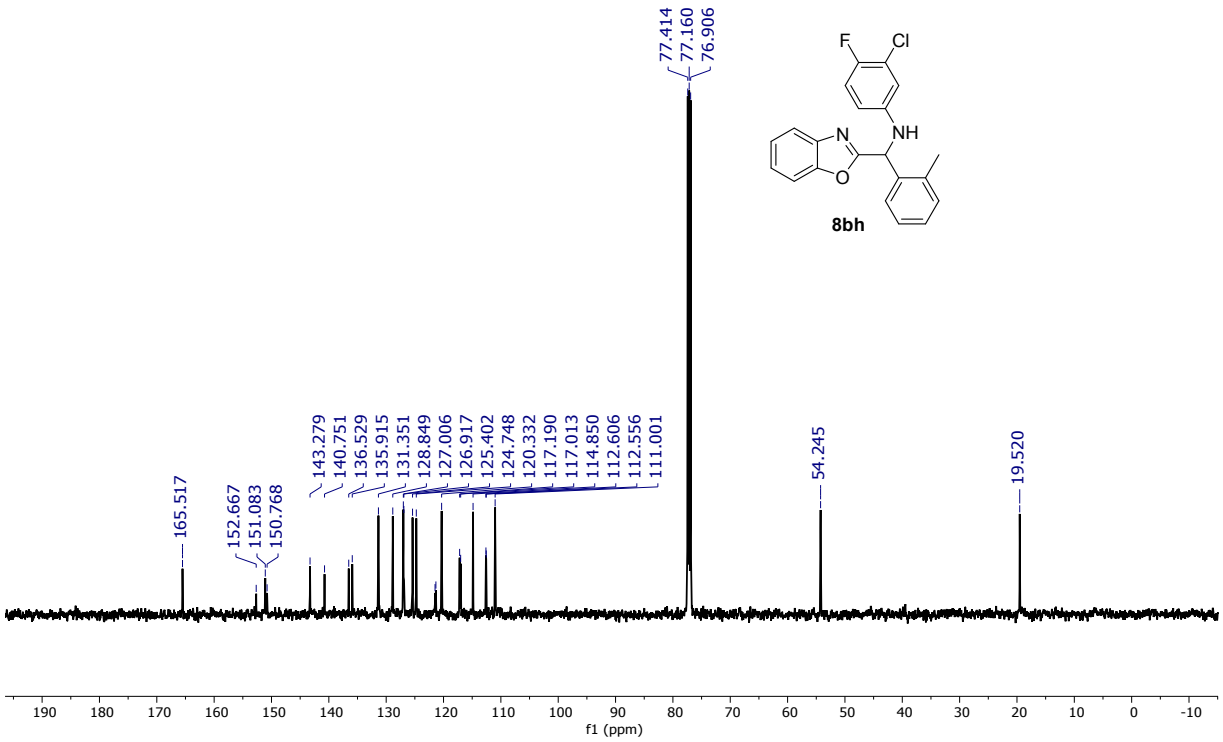
^{19}F NMR (565 MHz, $CDCl_3$):



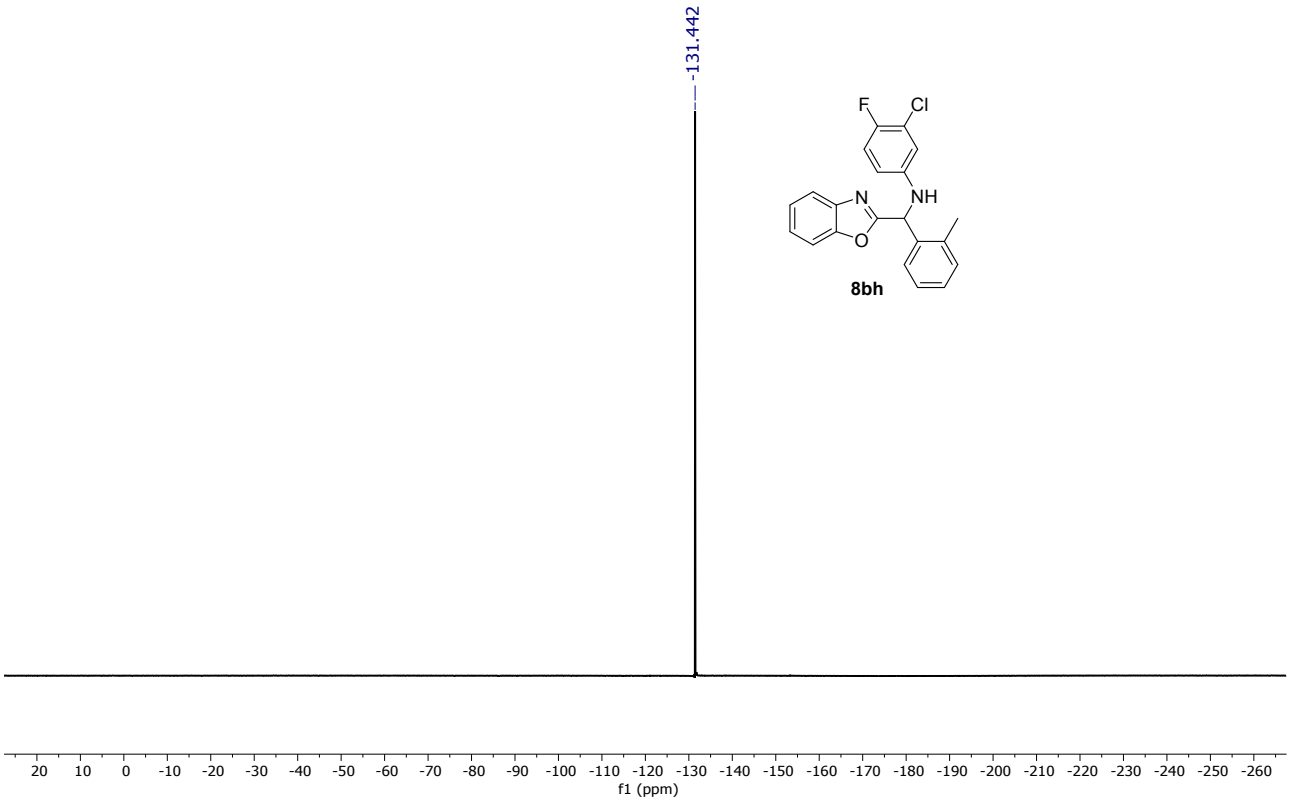
^{1}H NMR (500 MHz, $CDCl_3$):



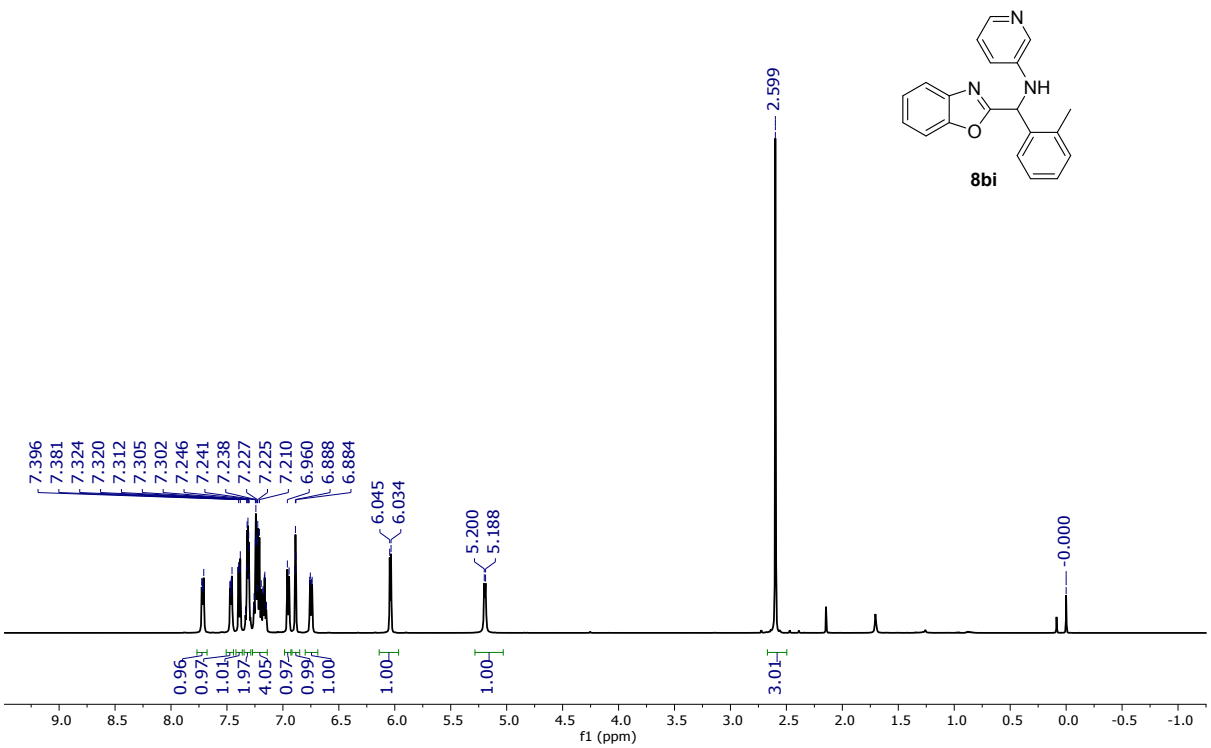
^{13}C NMR (126 MHz, $CDCl_3$):



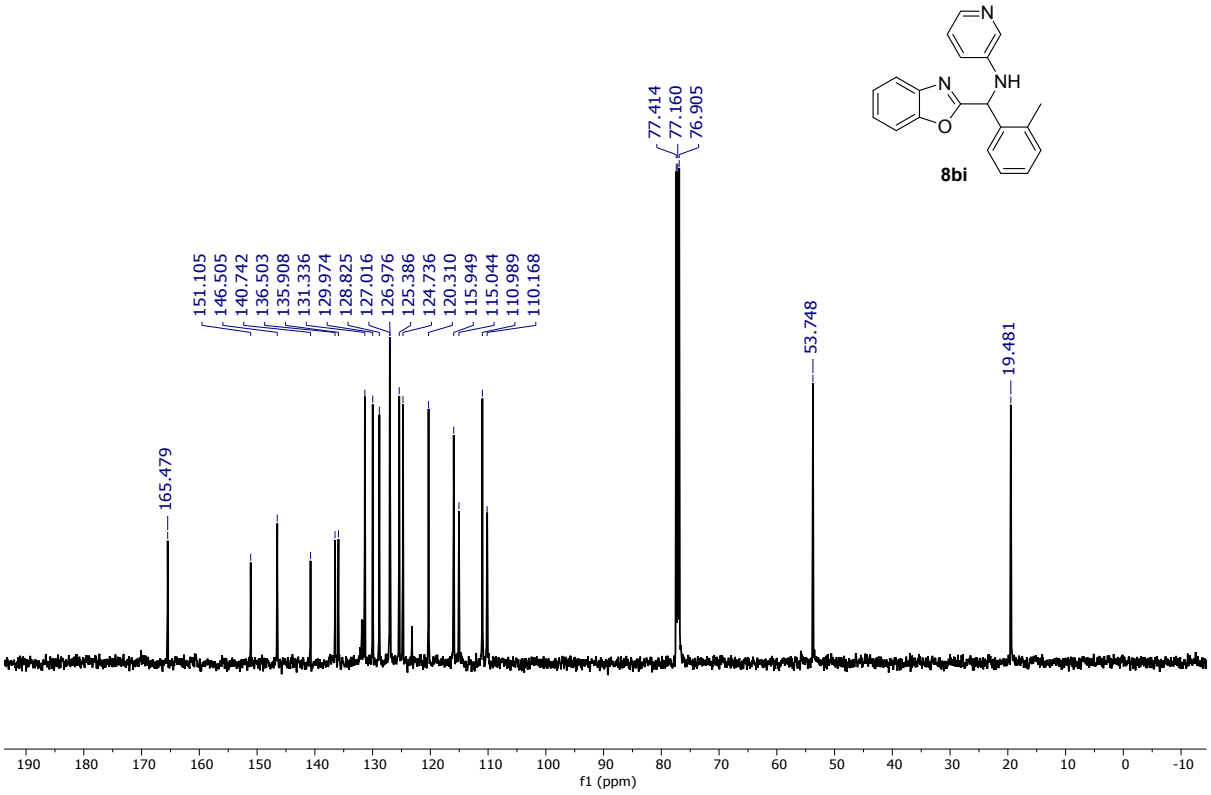
^{19}F NMR (565 MHz, $CDCl_3$):



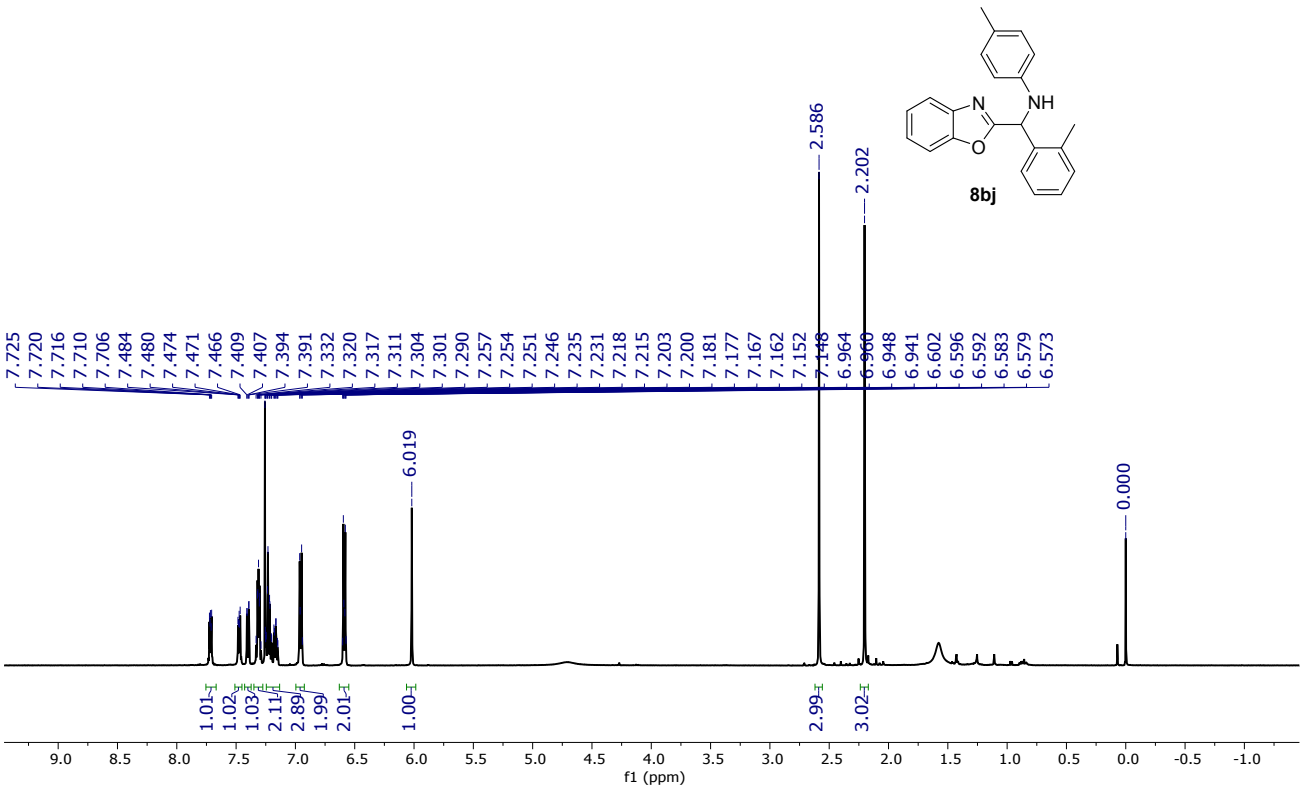
^{1}H NMR (500 MHz, $CDCl_3$):



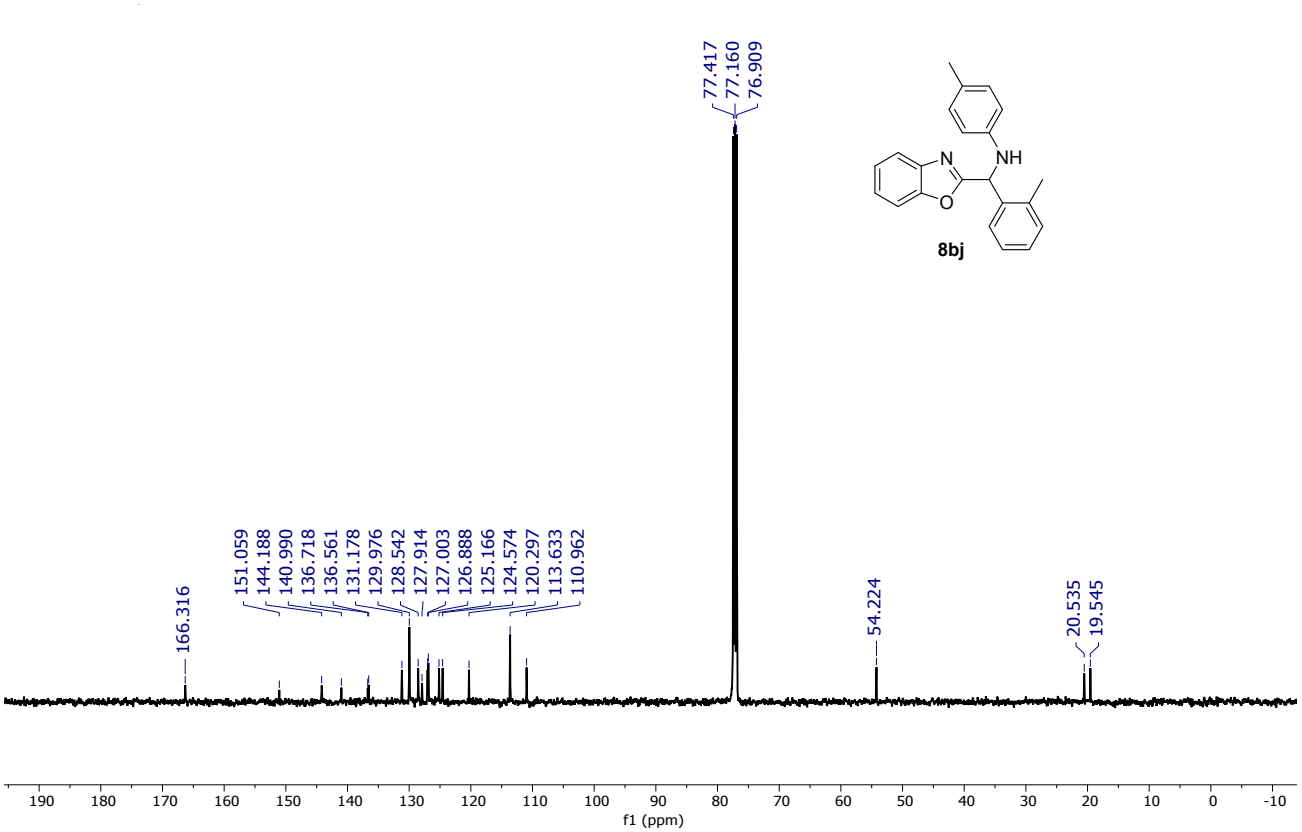
^{13}C NMR (126 MHz, $CDCl_3$):



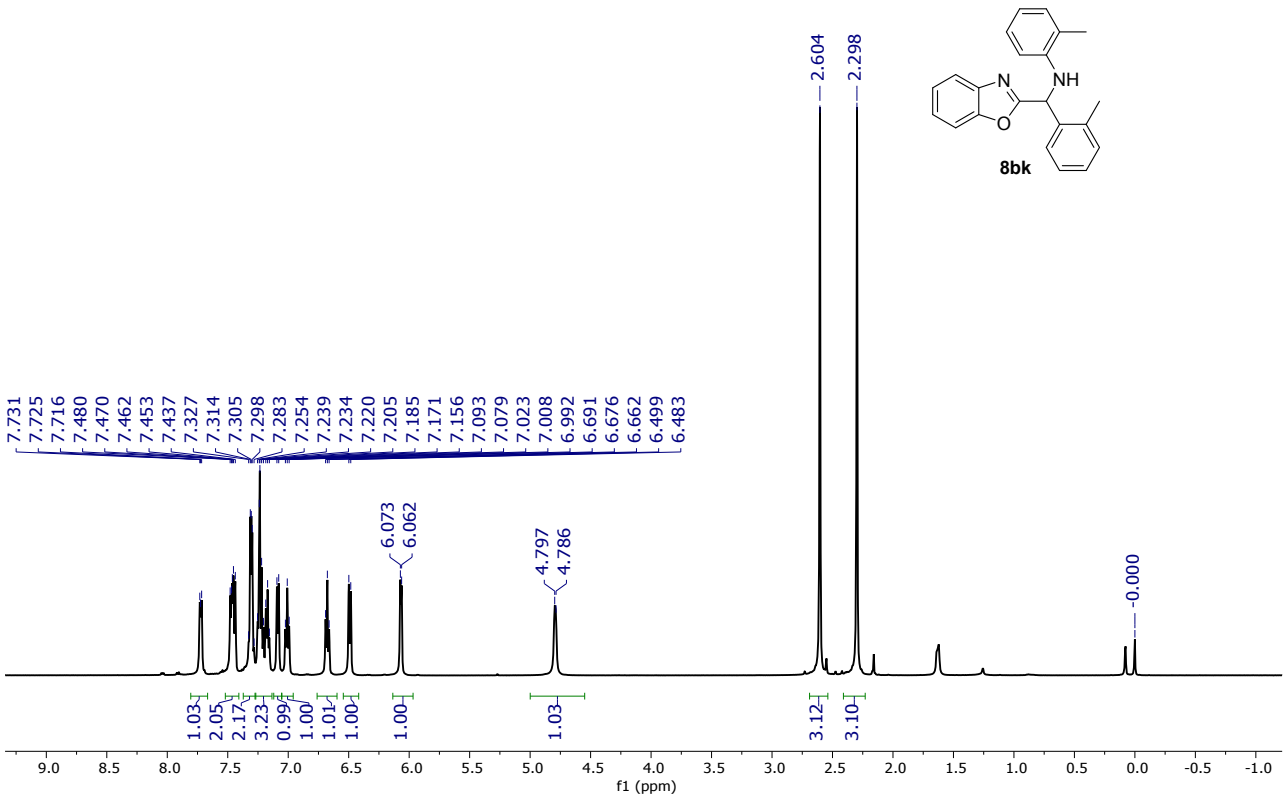
^{1}H NMR (500 MHz, $CDCl_3$):



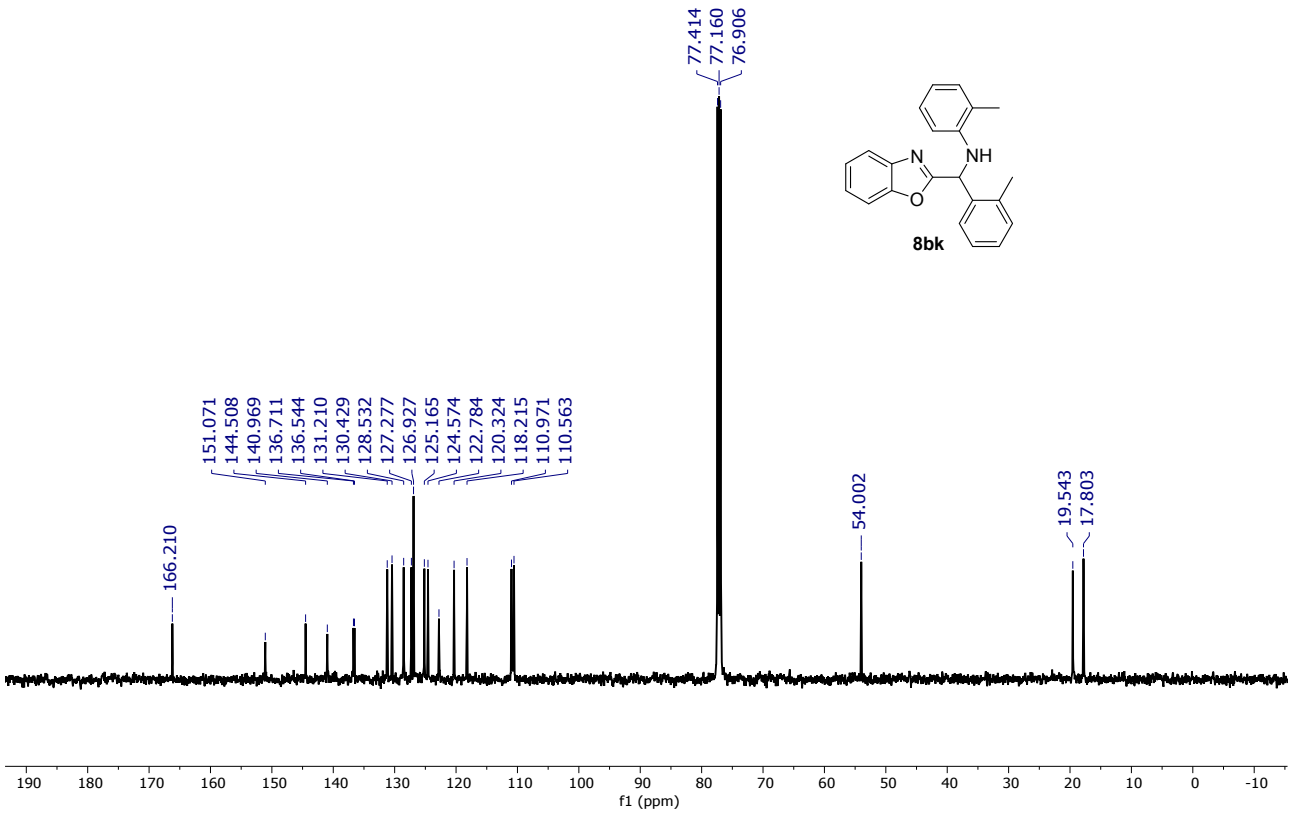
^{13}C NMR (126 MHz, $CDCl_3$):



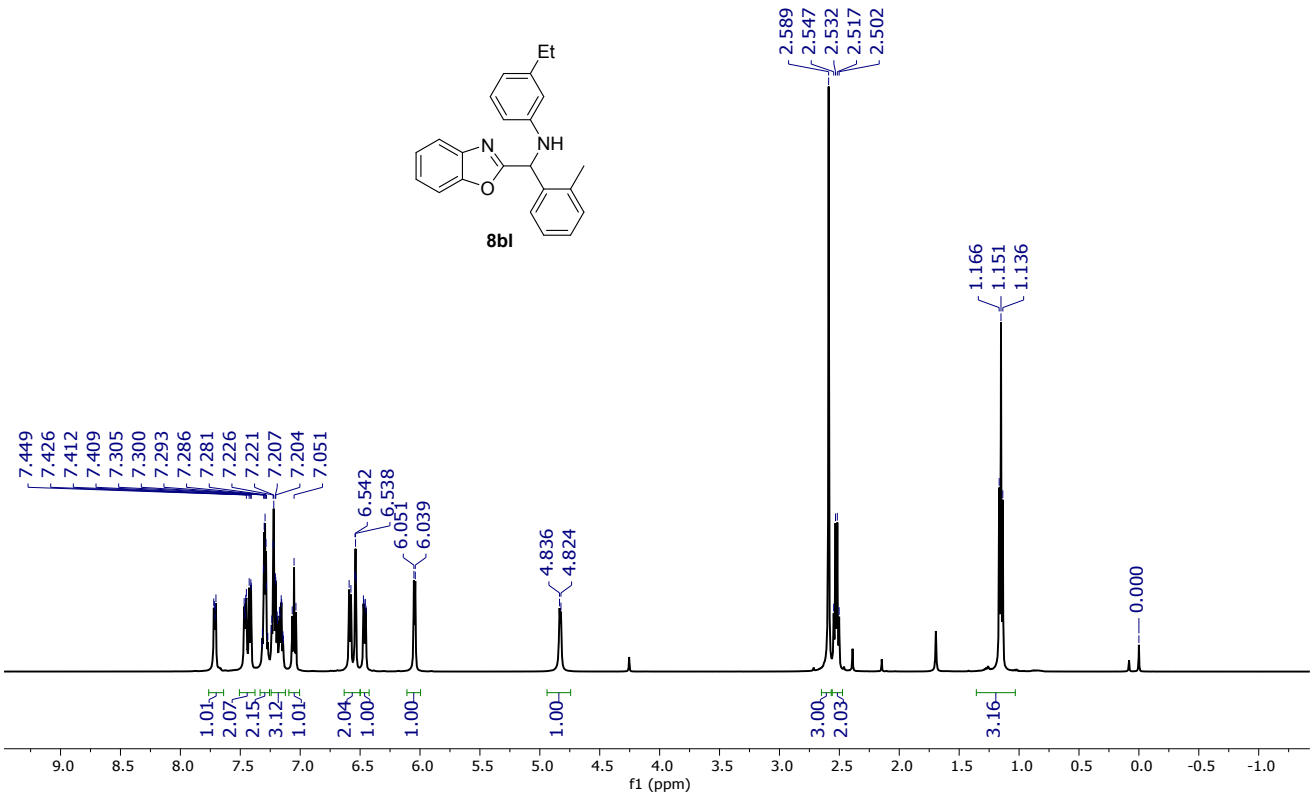
^{1}H NMR (500 MHz, $CDCl_3$):



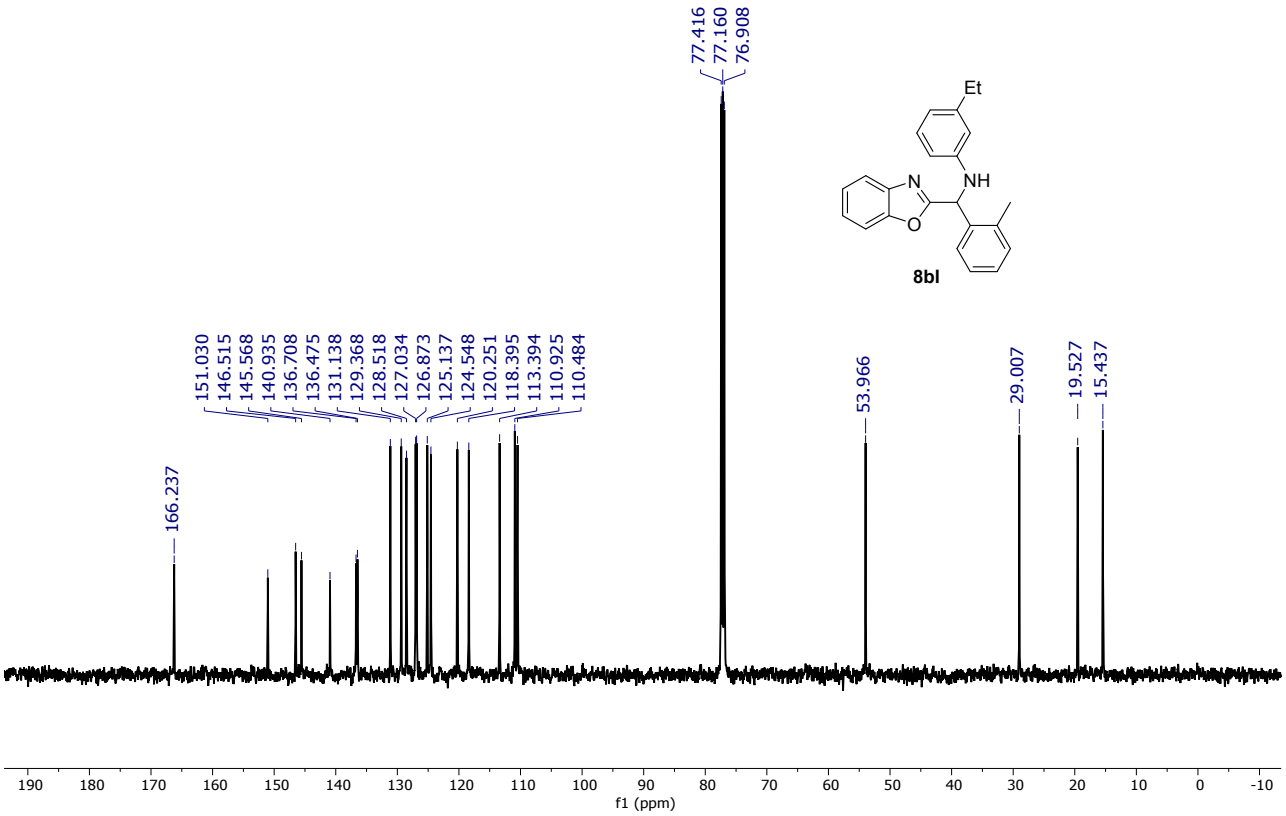
^{13}C NMR (126 MHz, $CDCl_3$):



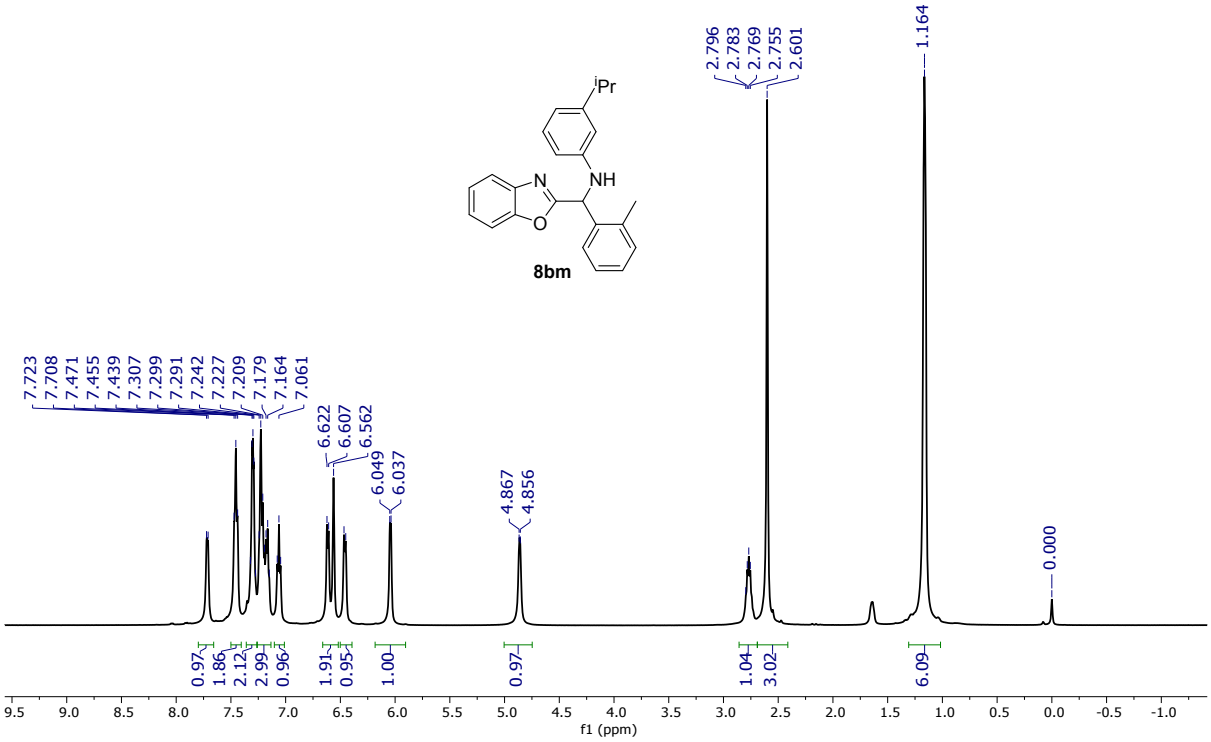
^{1}H NMR (500 MHz, $CDCl_3$):



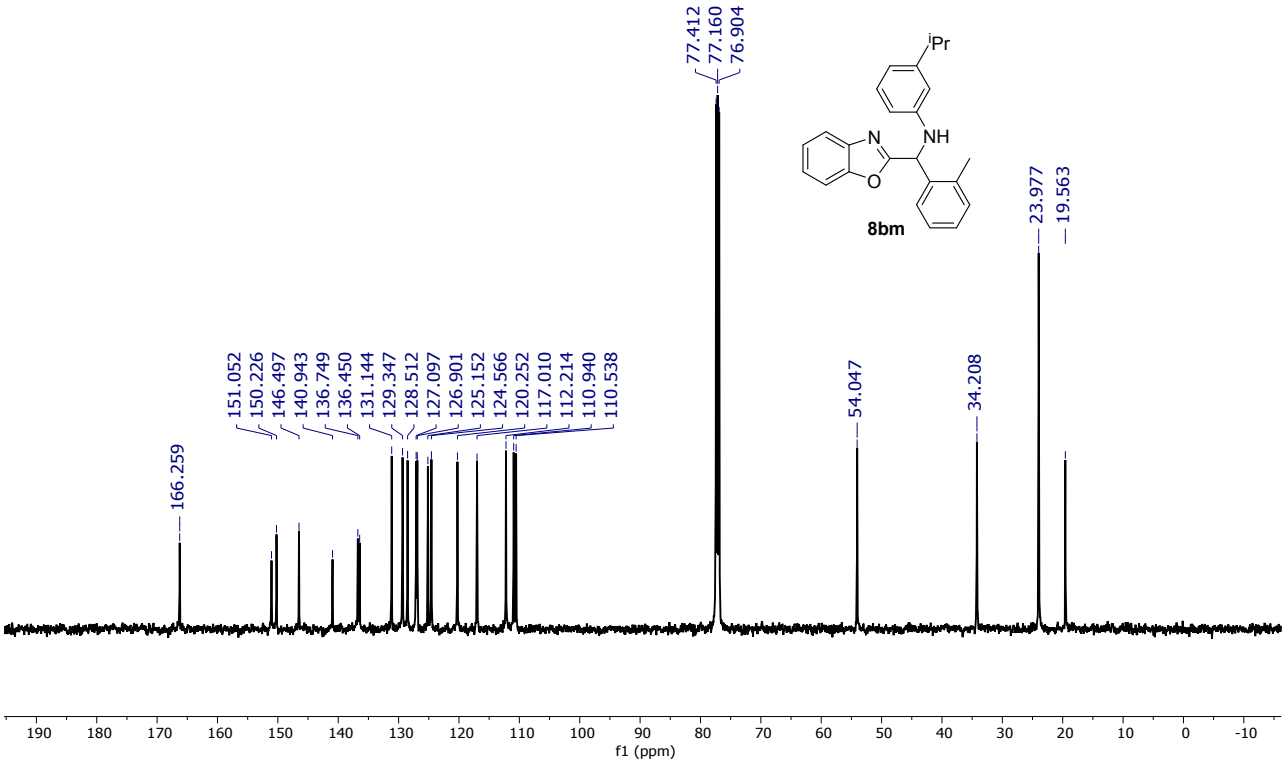
^{13}C NMR (126 MHz, $CDCl_3$):



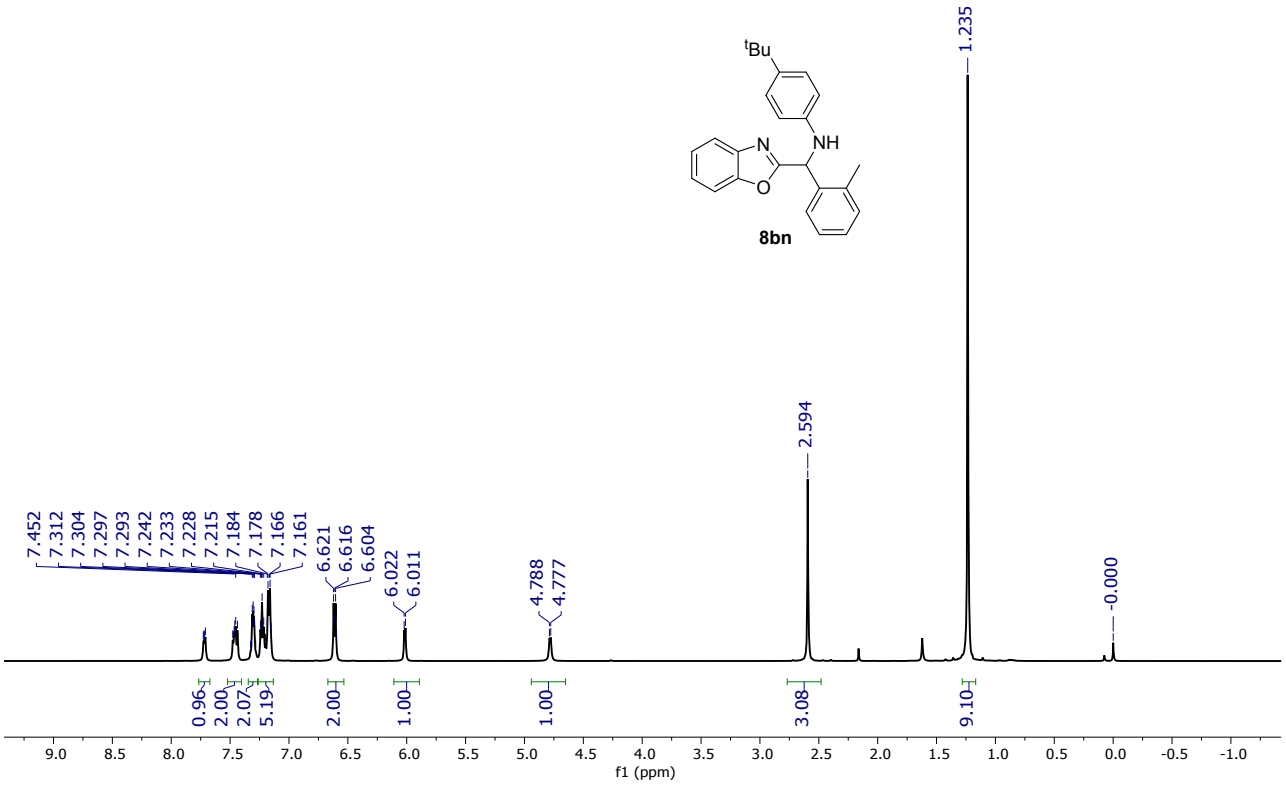
^{1}H NMR (500 MHz, $CDCl_3$):



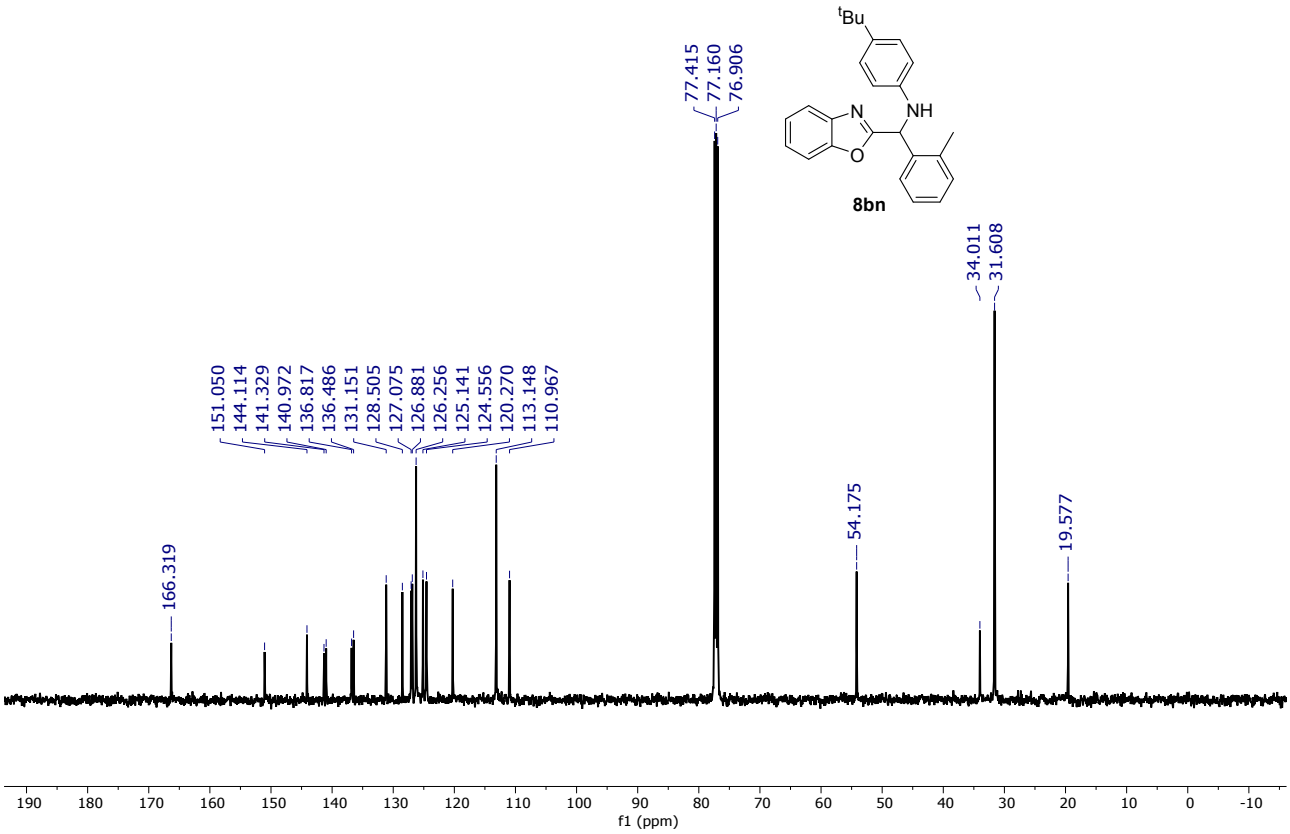
^{13}C NMR (126 MHz, $CDCl_3$):



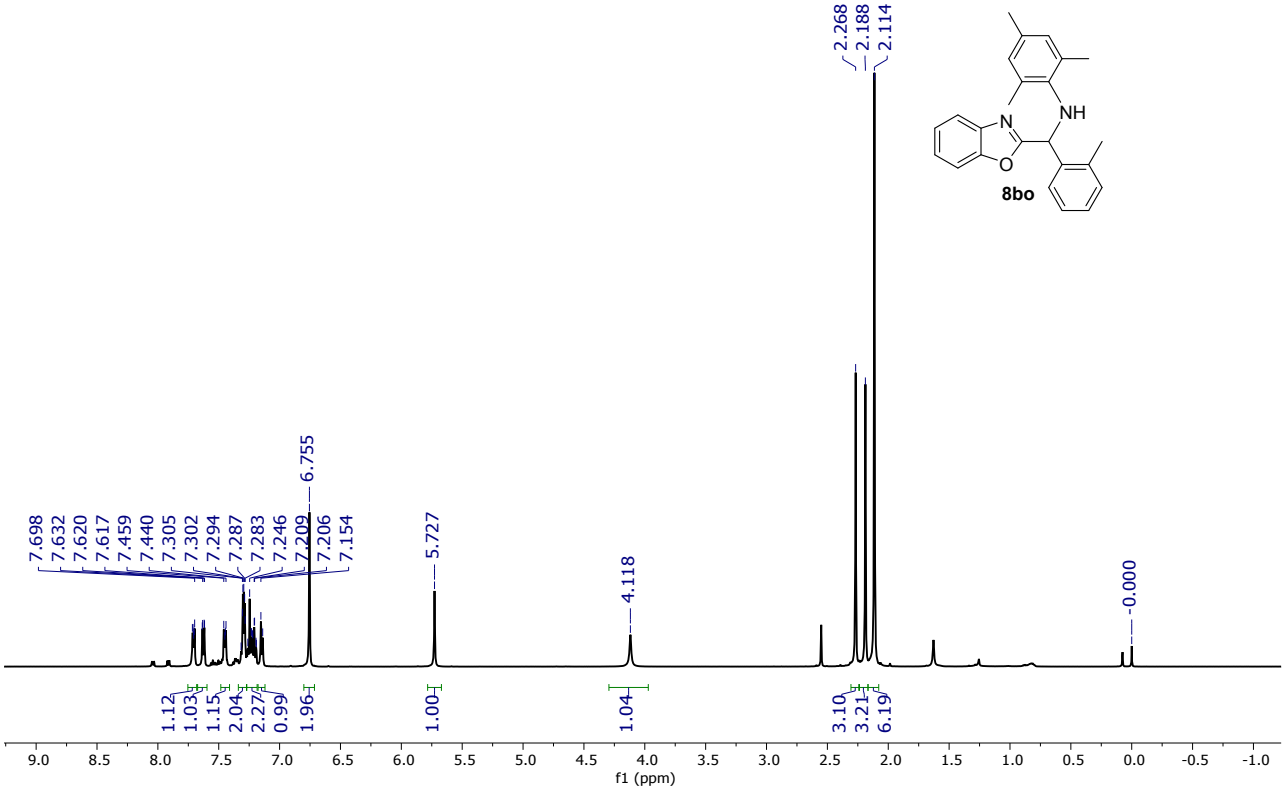
^{1}H NMR (500 MHz, $CDCl_3$):



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



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



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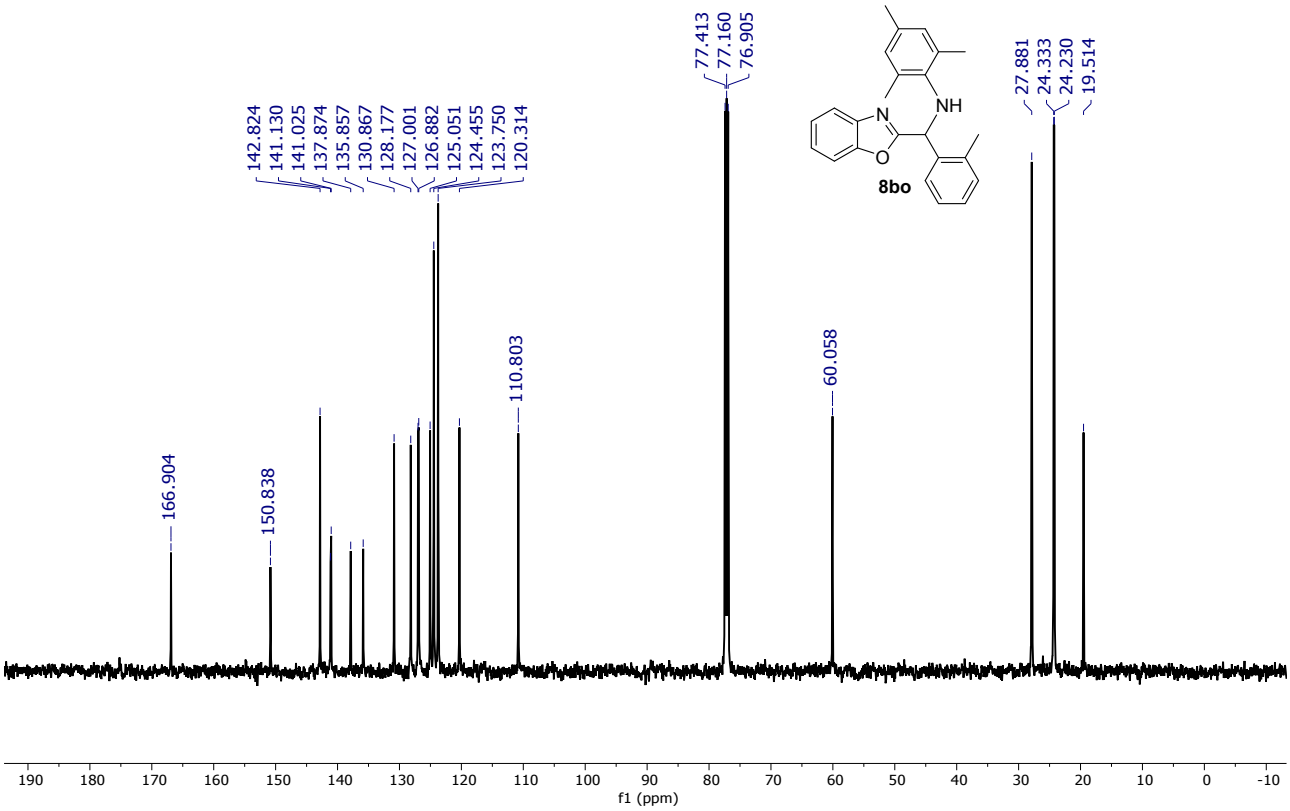

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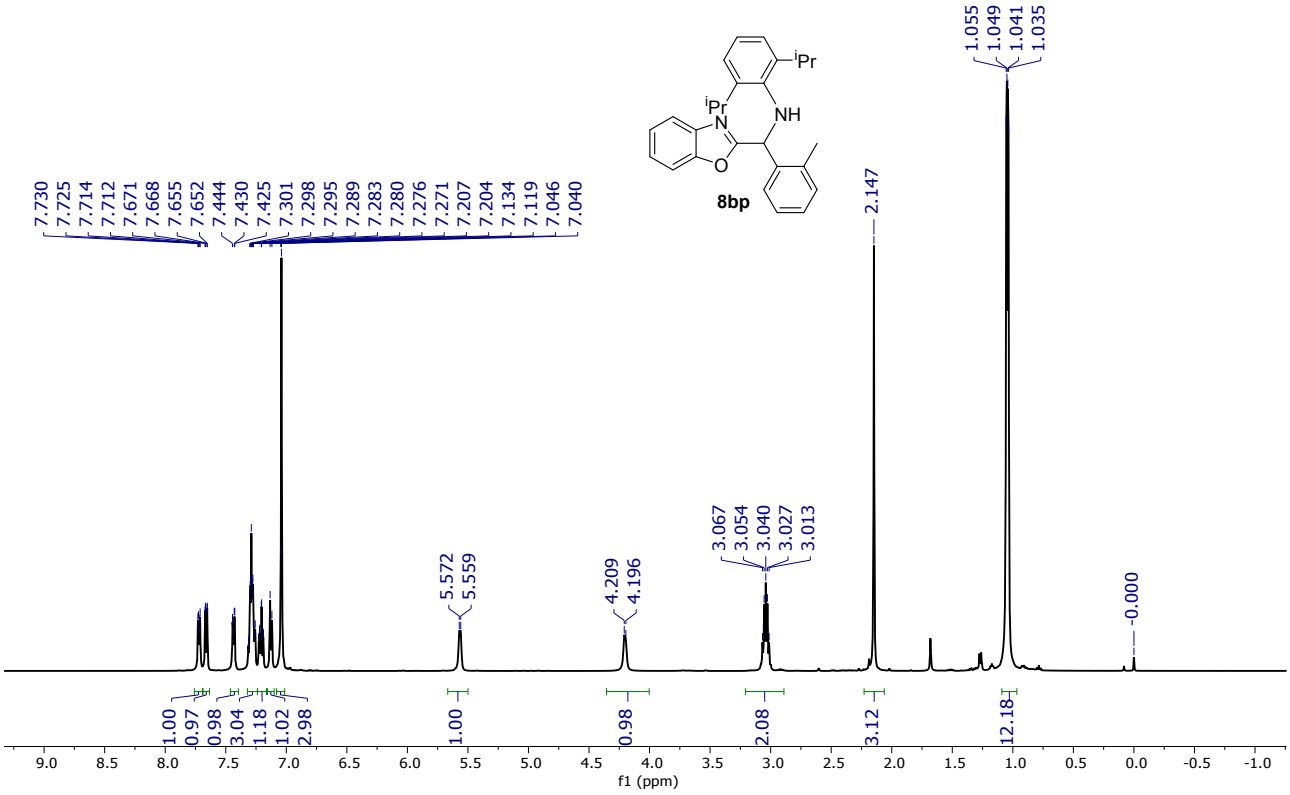
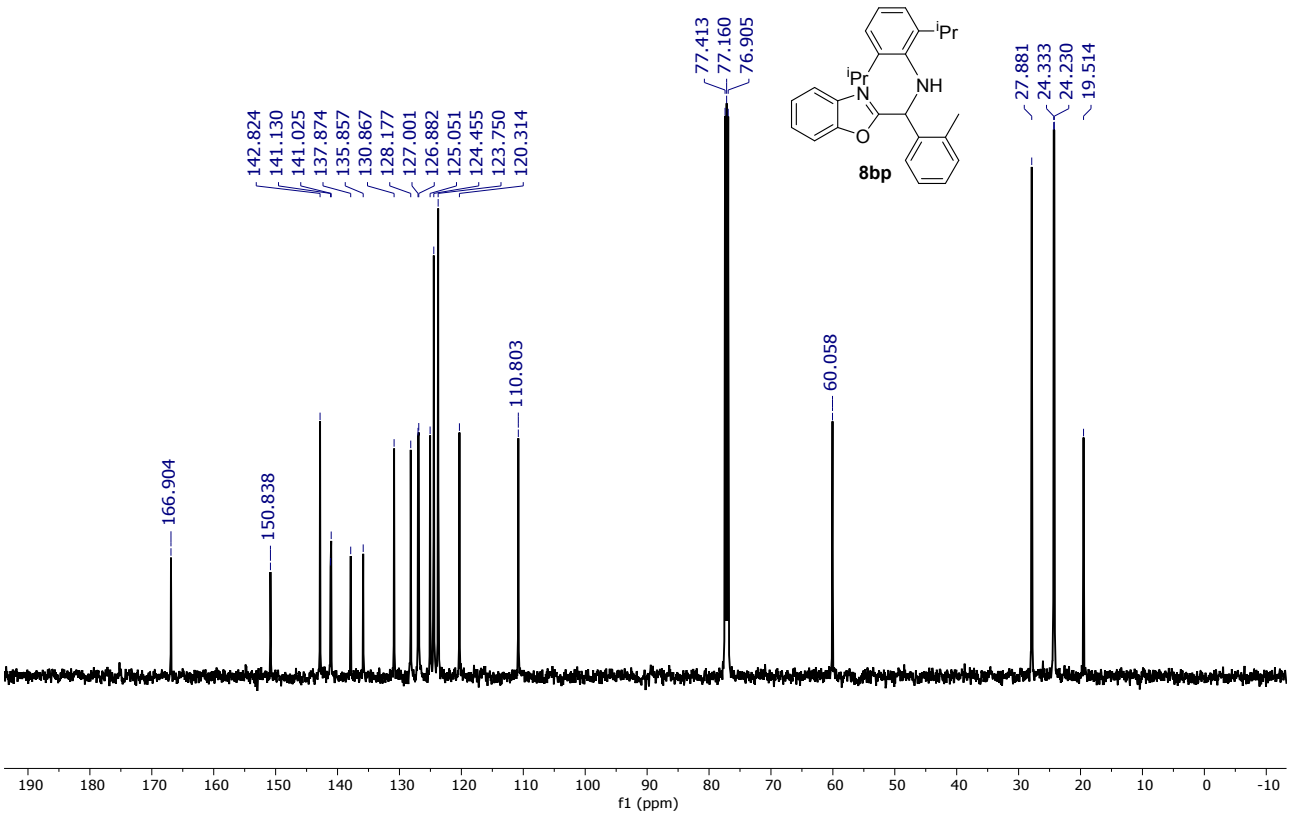


^{13}C NMR (126 MHz, $CDCl_3$):



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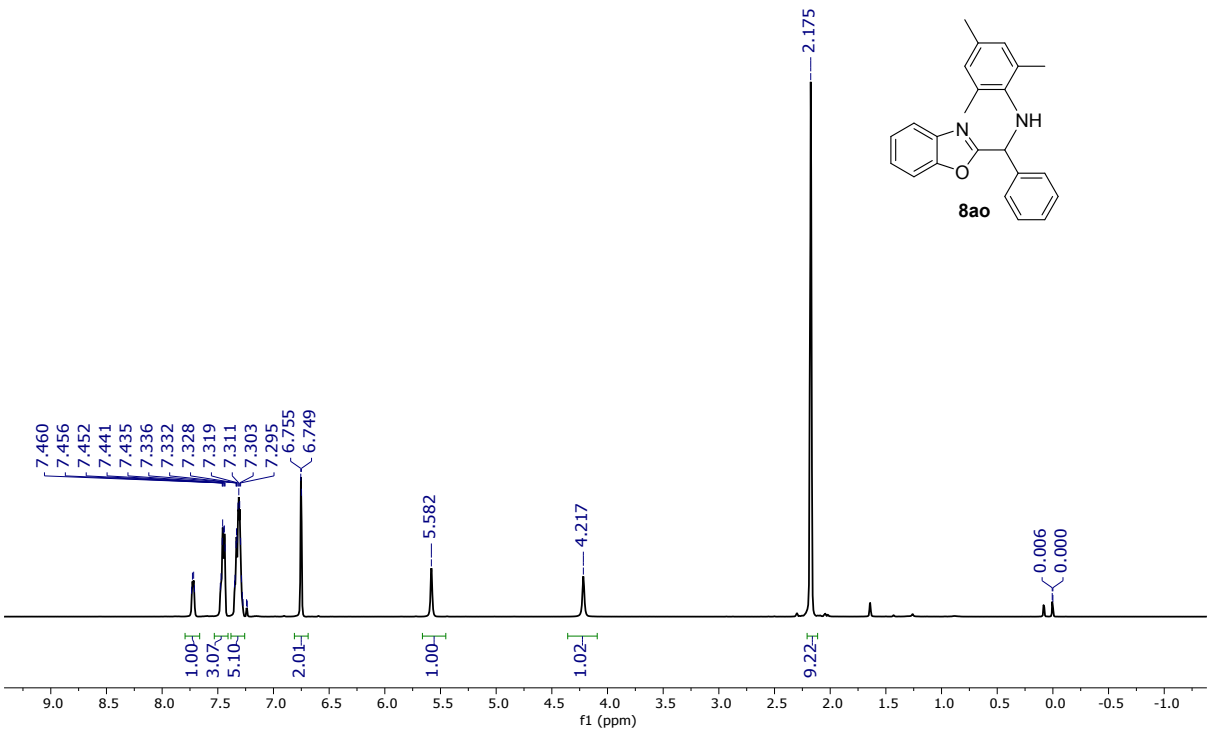
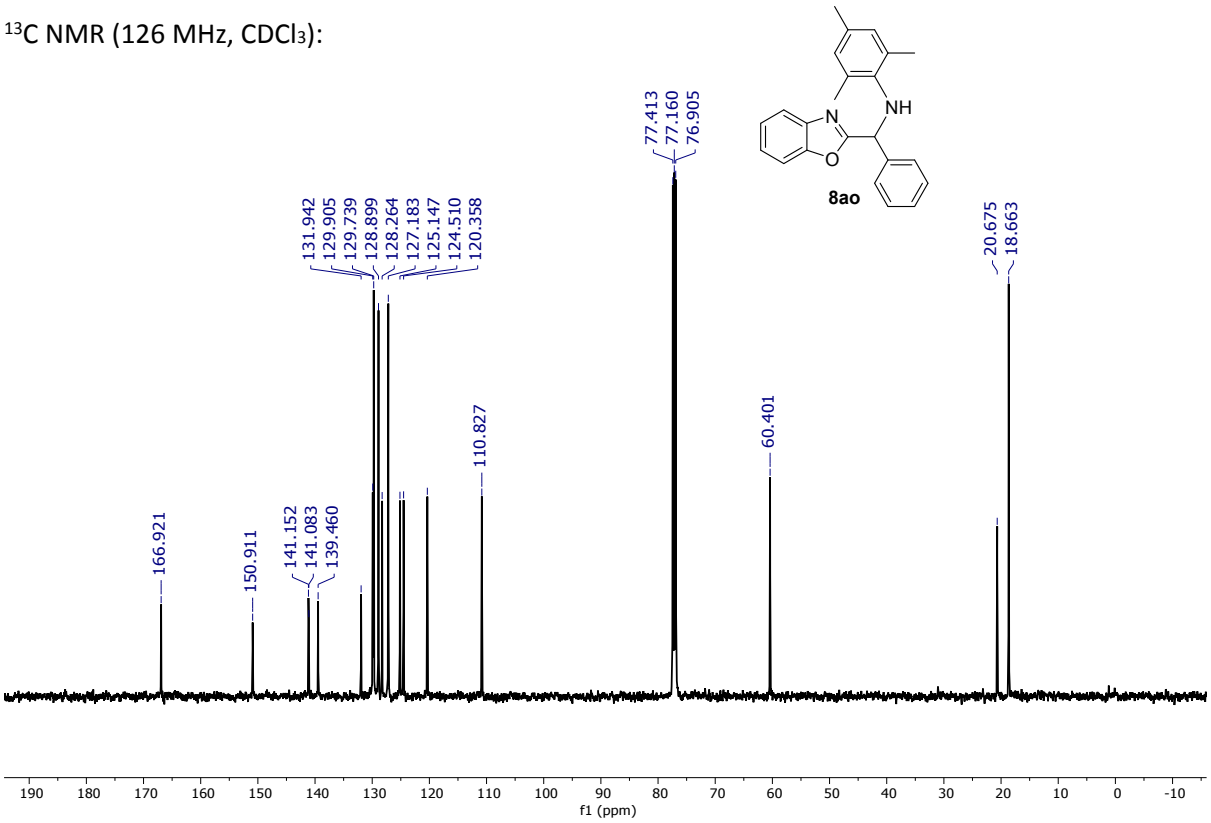
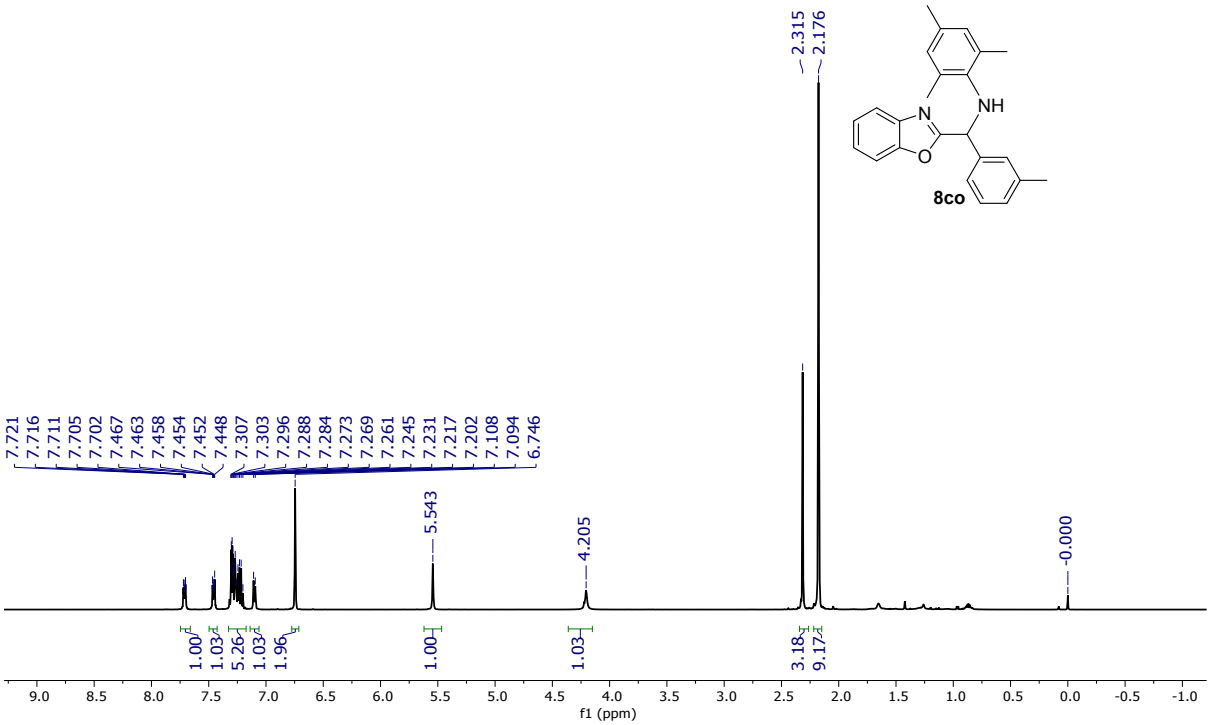


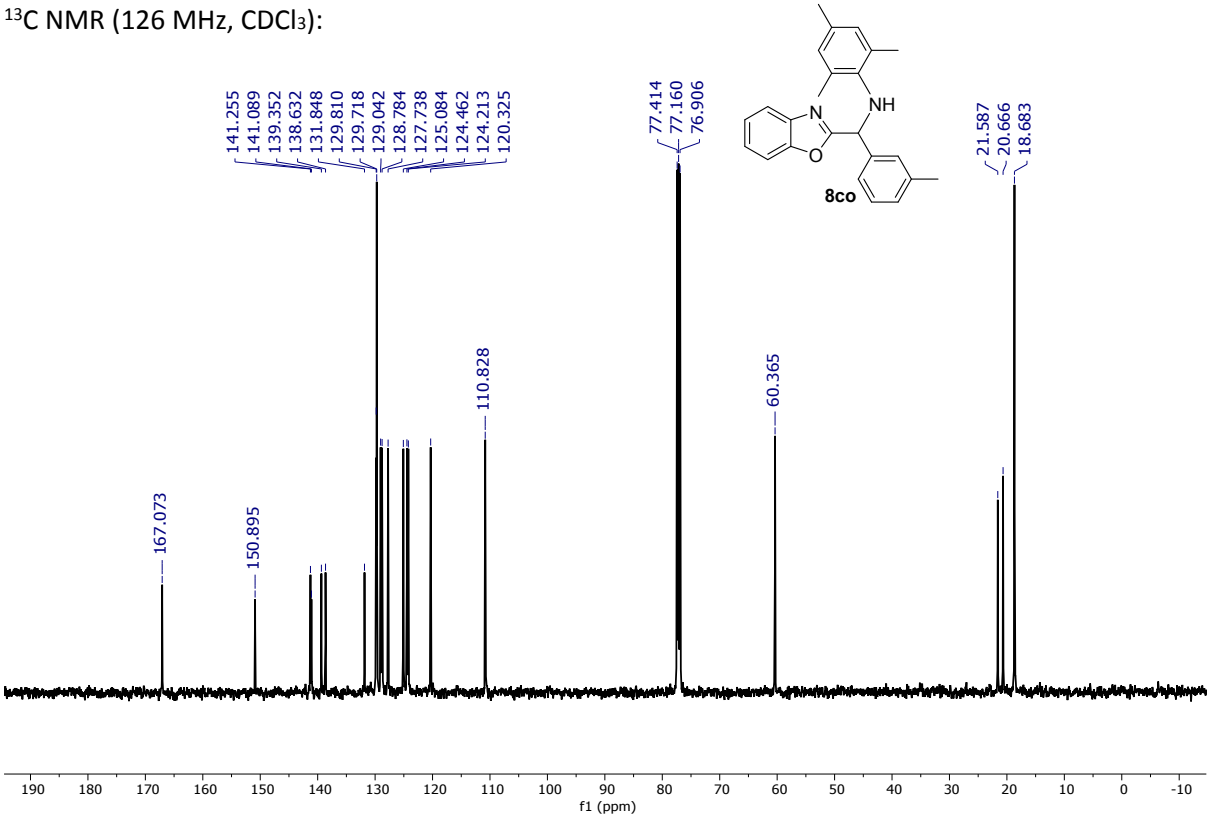
^{13}C NMR (126 MHz, $CDCl_3$):



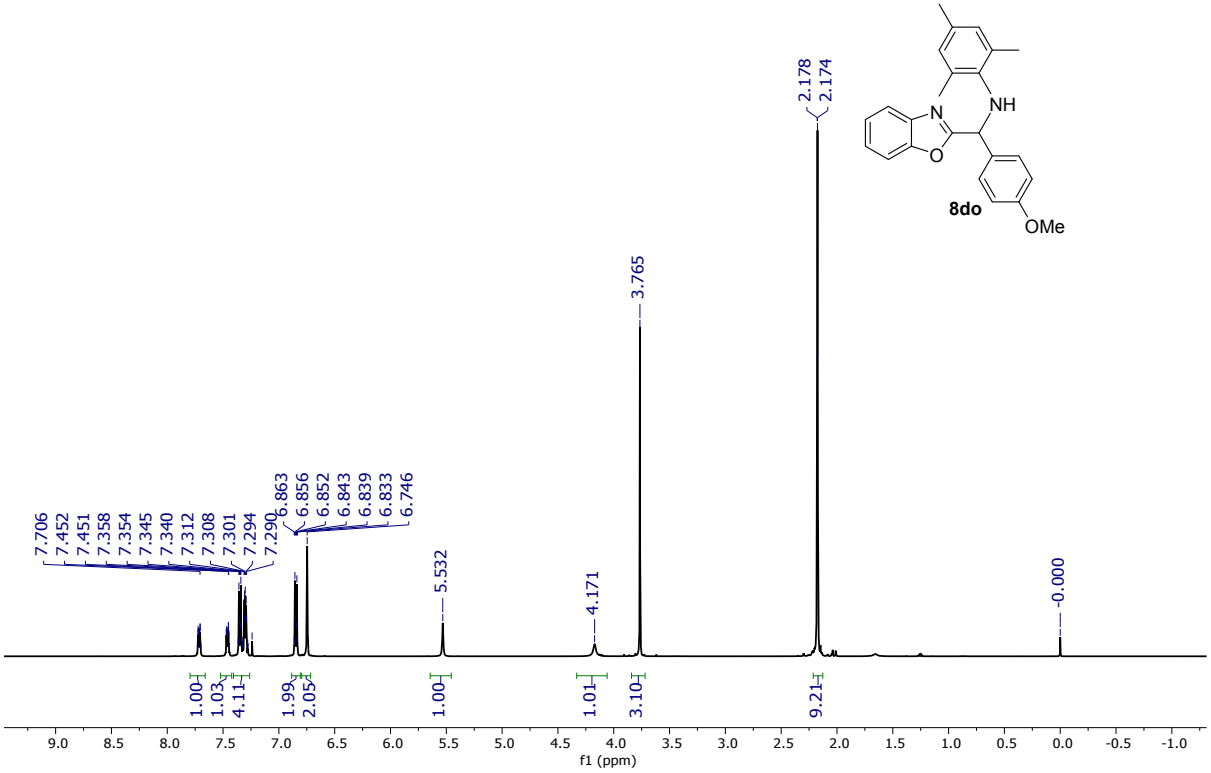
^{1}H NMR (500 MHz, $CDCl_3$):



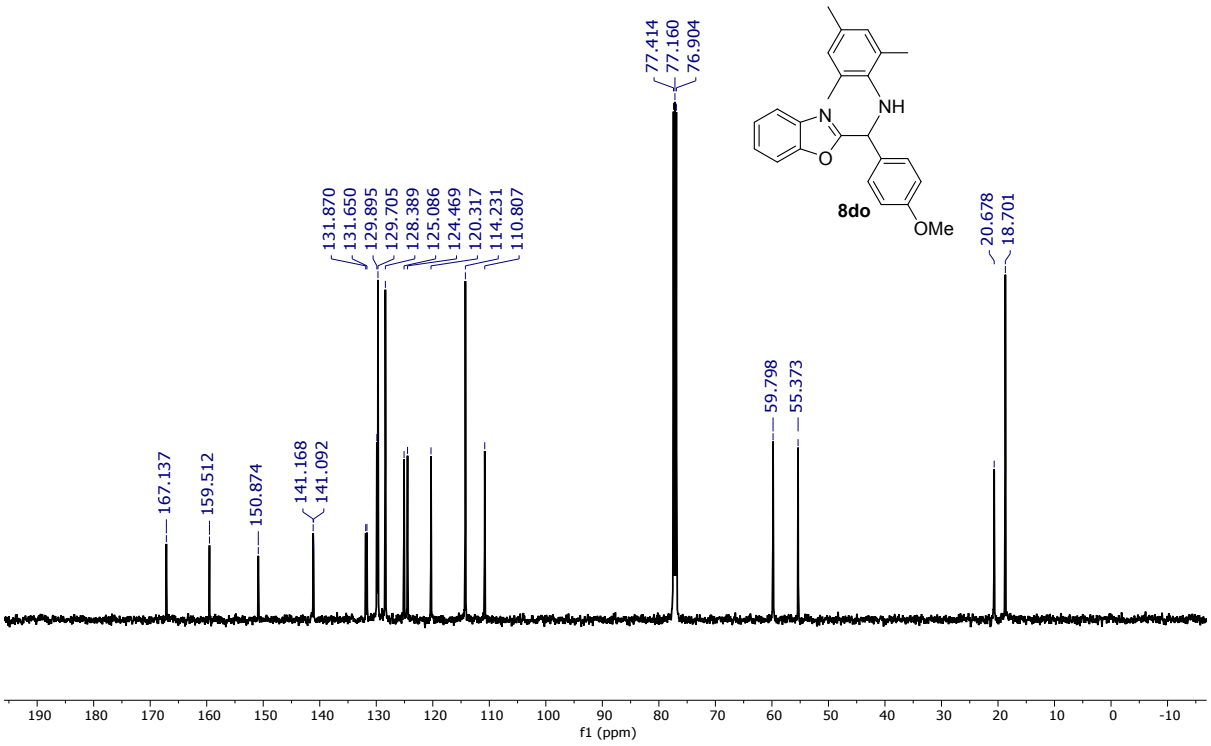
^{13}C NMR (126 MHz, $CDCl_3$):



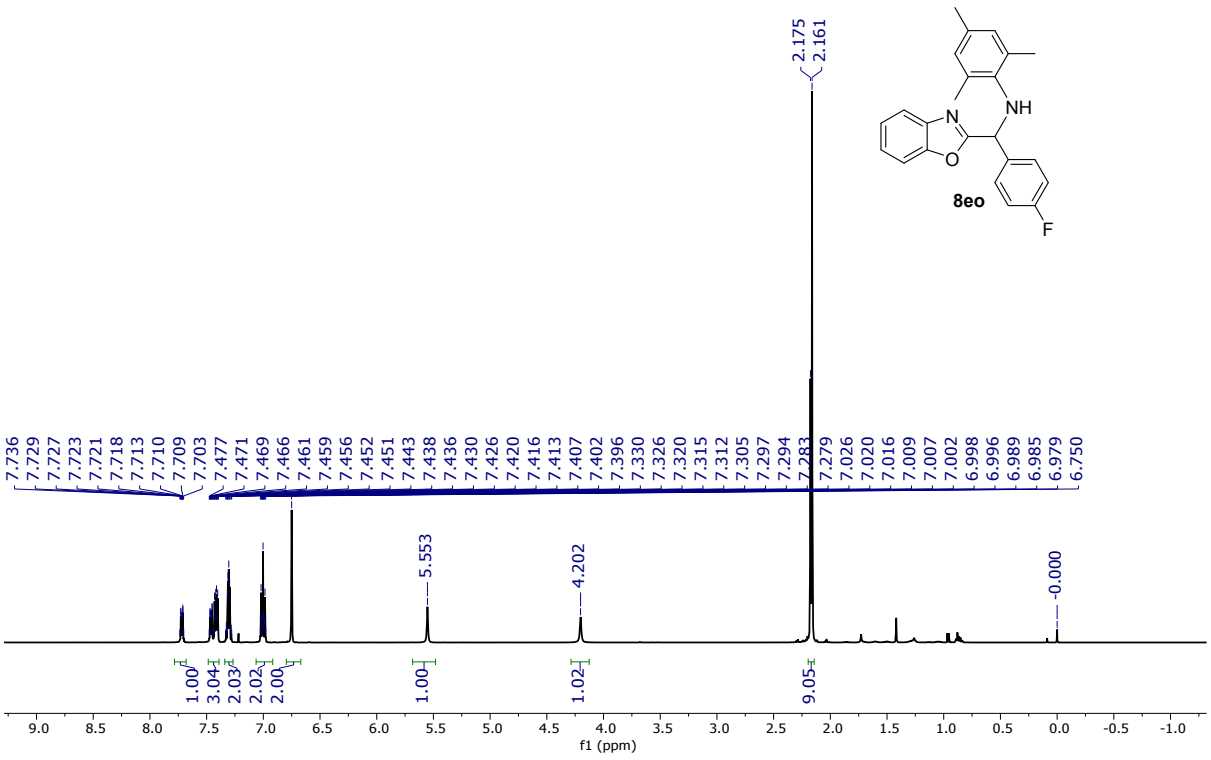
^{1}H NMR (500 MHz, $CDCl_3$):



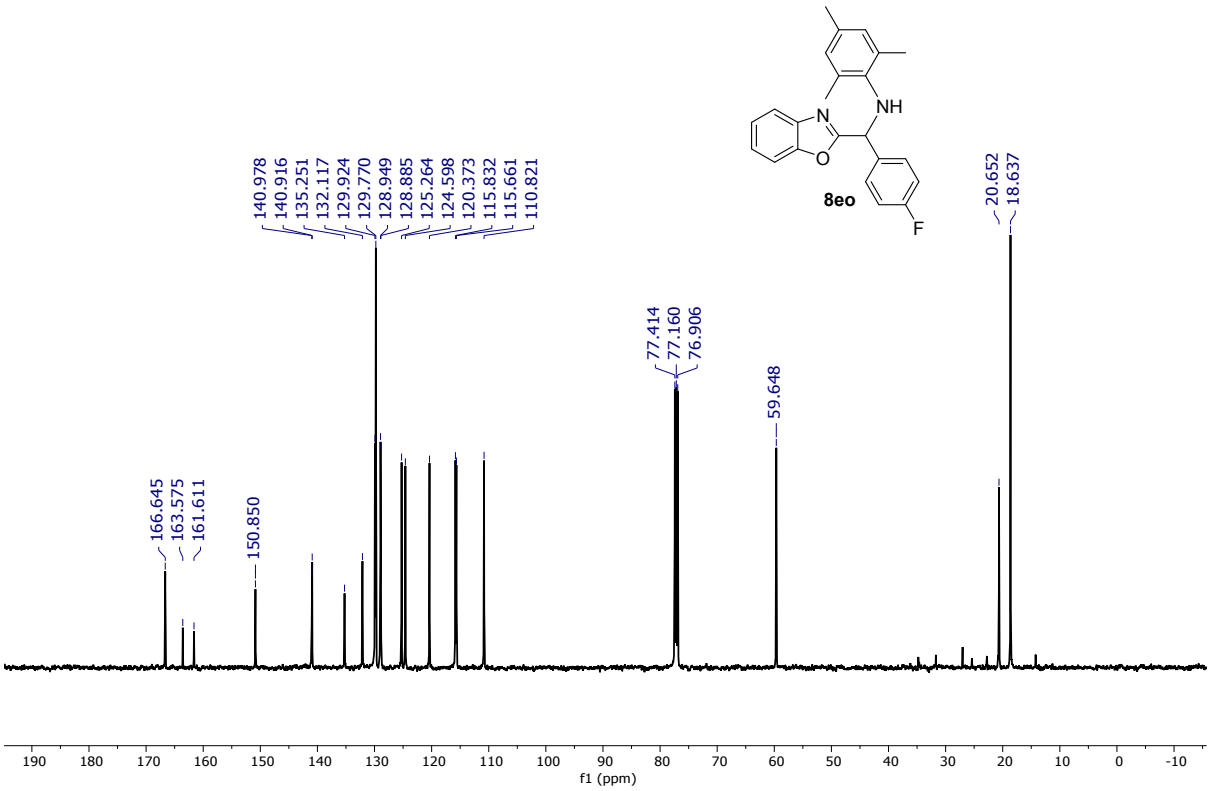
^{13}C NMR (126 MHz, $CDCl_3$):



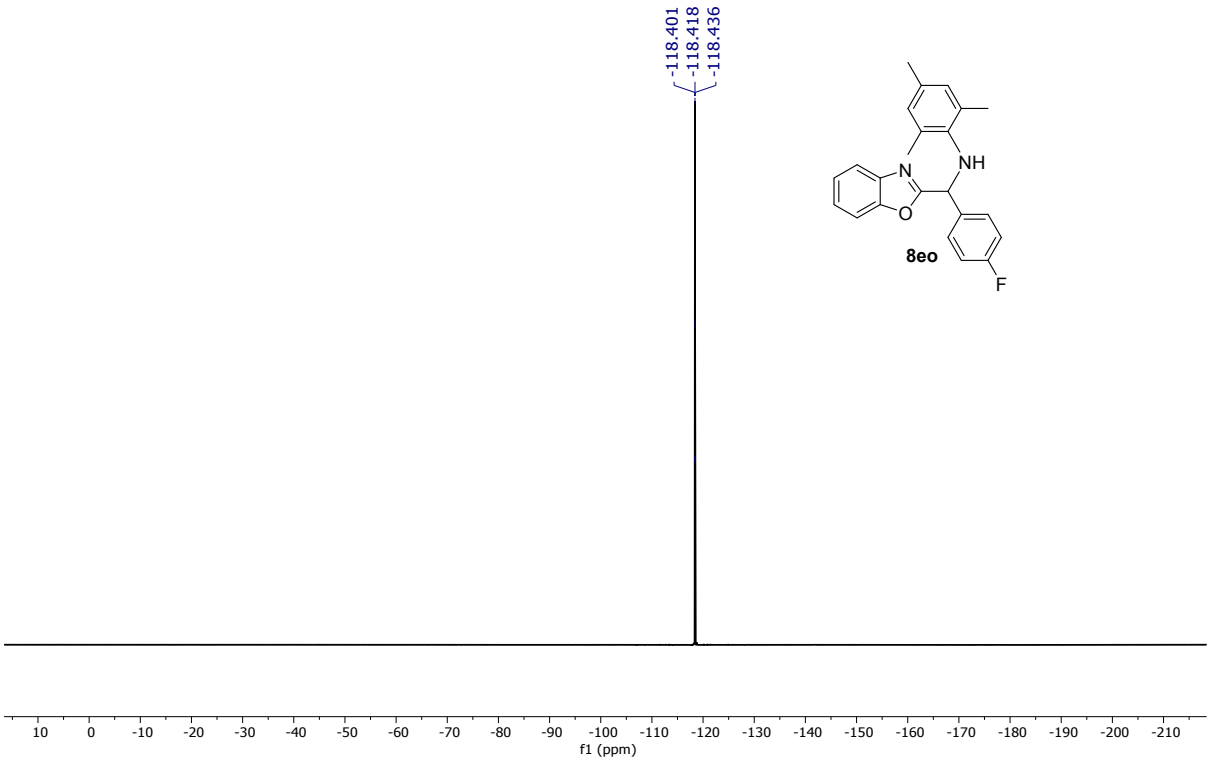
^{1}H NMR (500 MHz, $CDCl_3$):



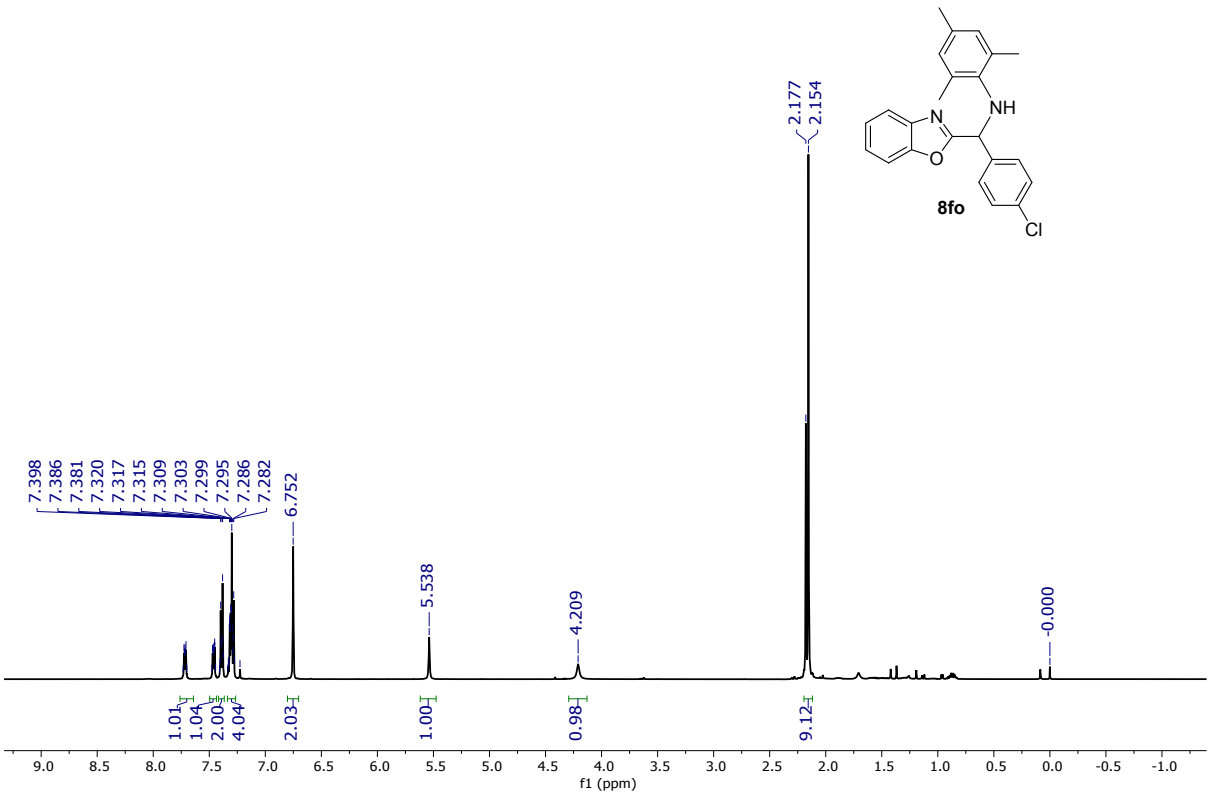
^{13}C NMR (126 MHz, $CDCl_3$):



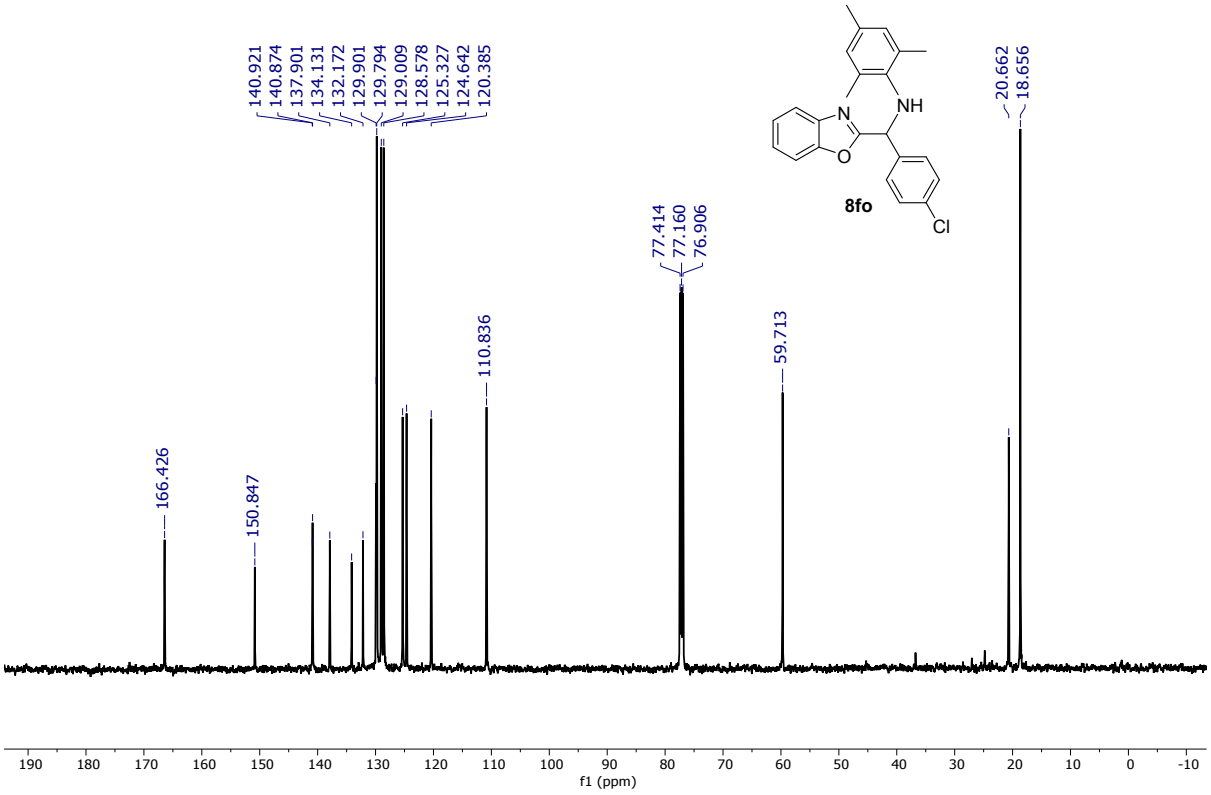
^{19}F NMR (565 MHz, $CDCl_3$):



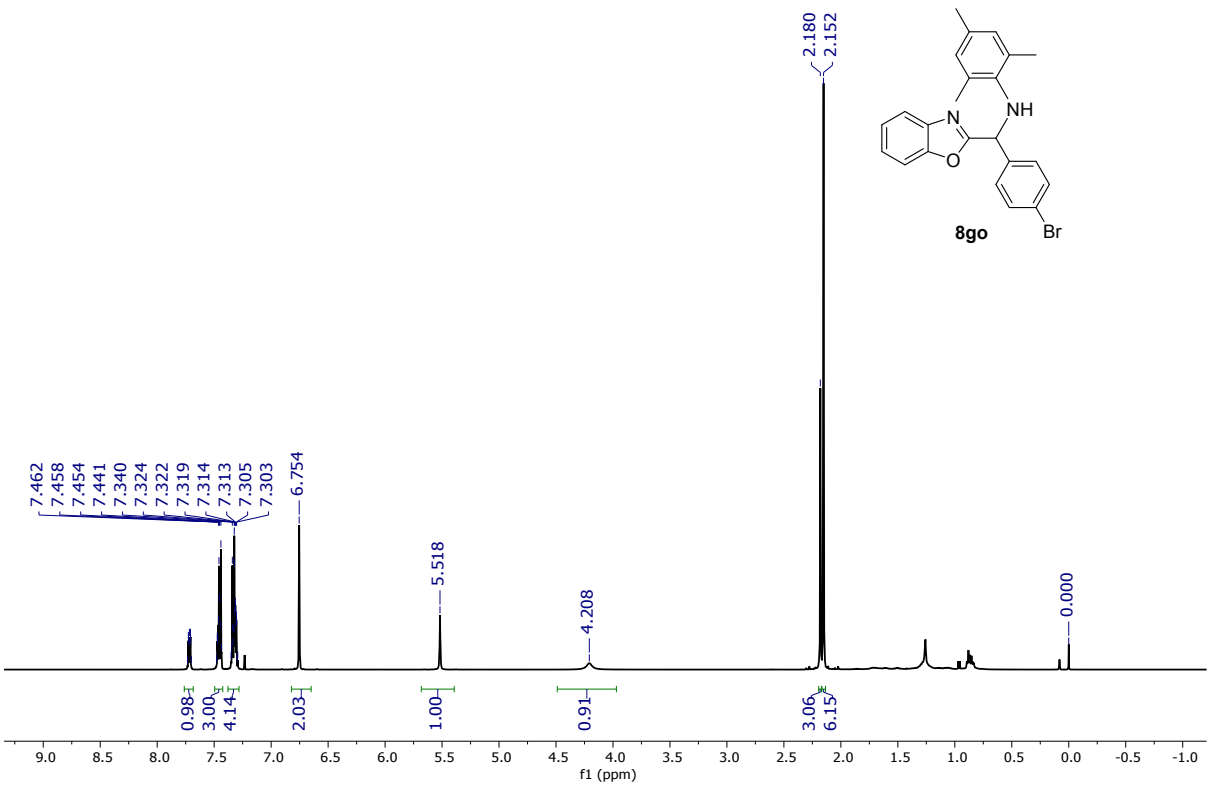
^{1}H NMR (500 MHz, $CDCl_3$):



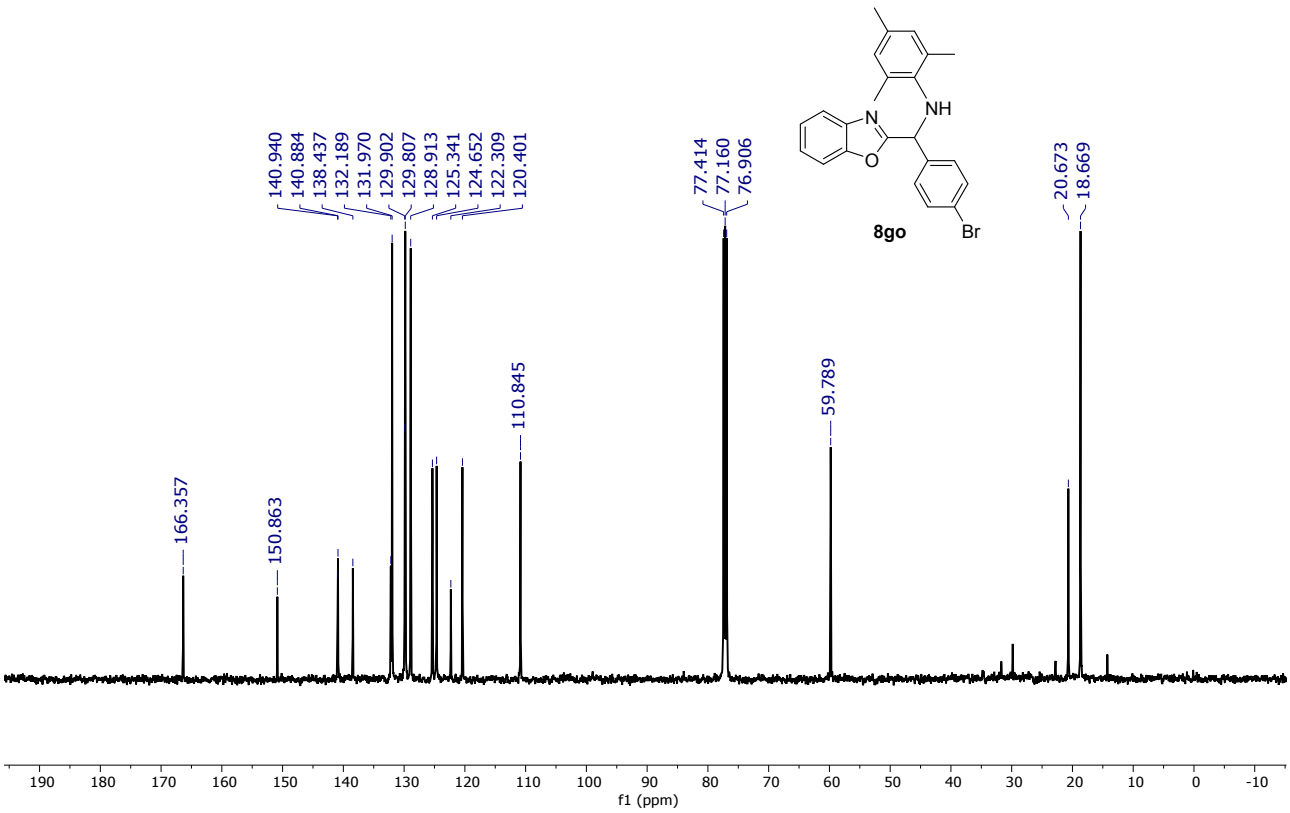
^{13}C NMR (126 MHz, $CDCl_3$):



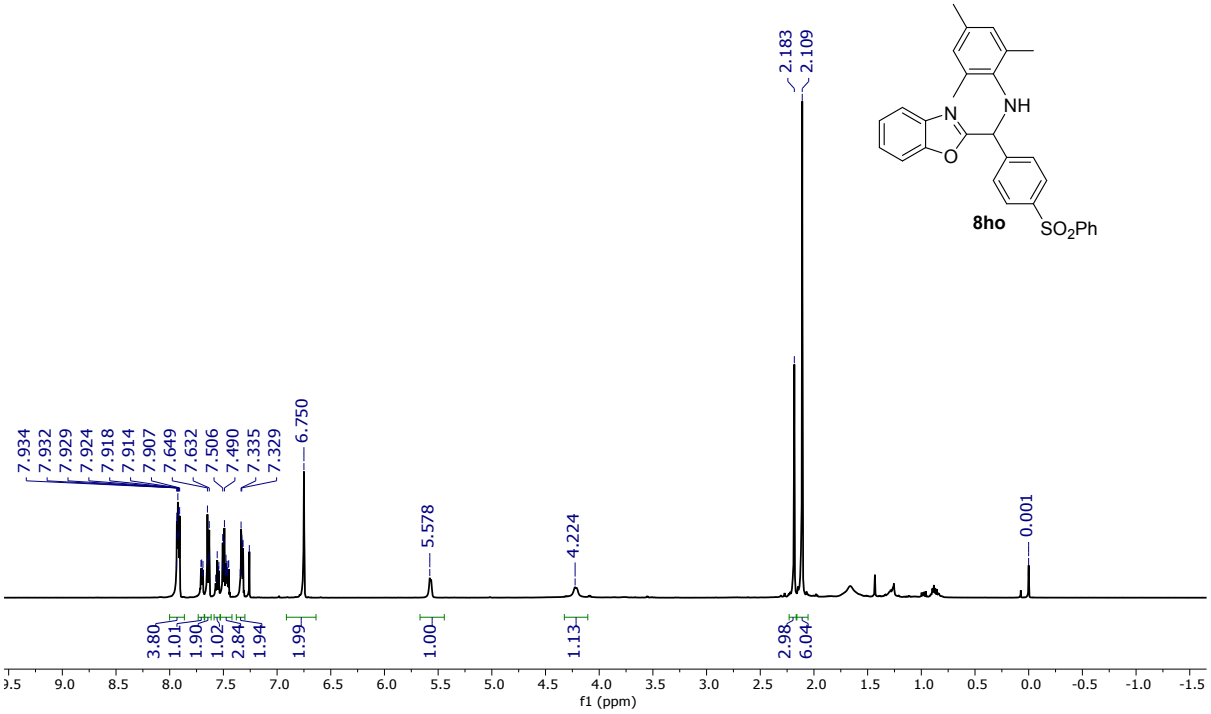
^{1}H NMR (500 MHz, $CDCl_3$):



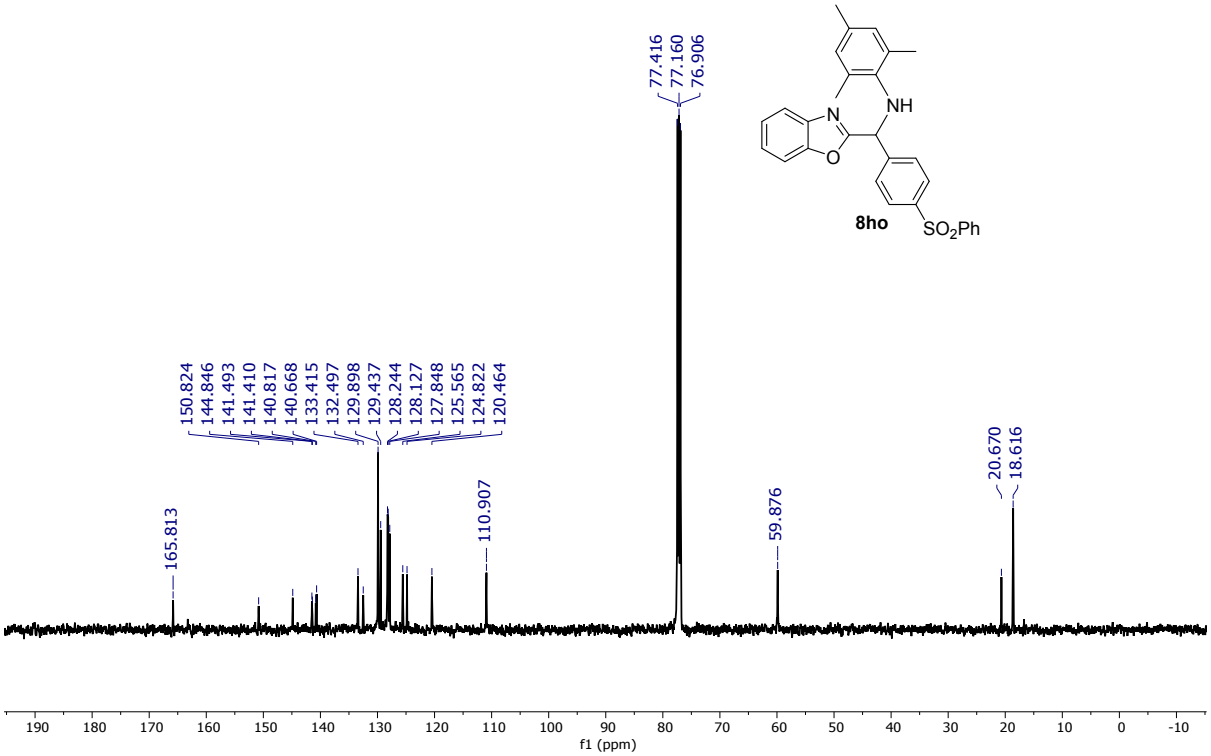
^{13}C NMR (126 MHz, $CDCl_3$):



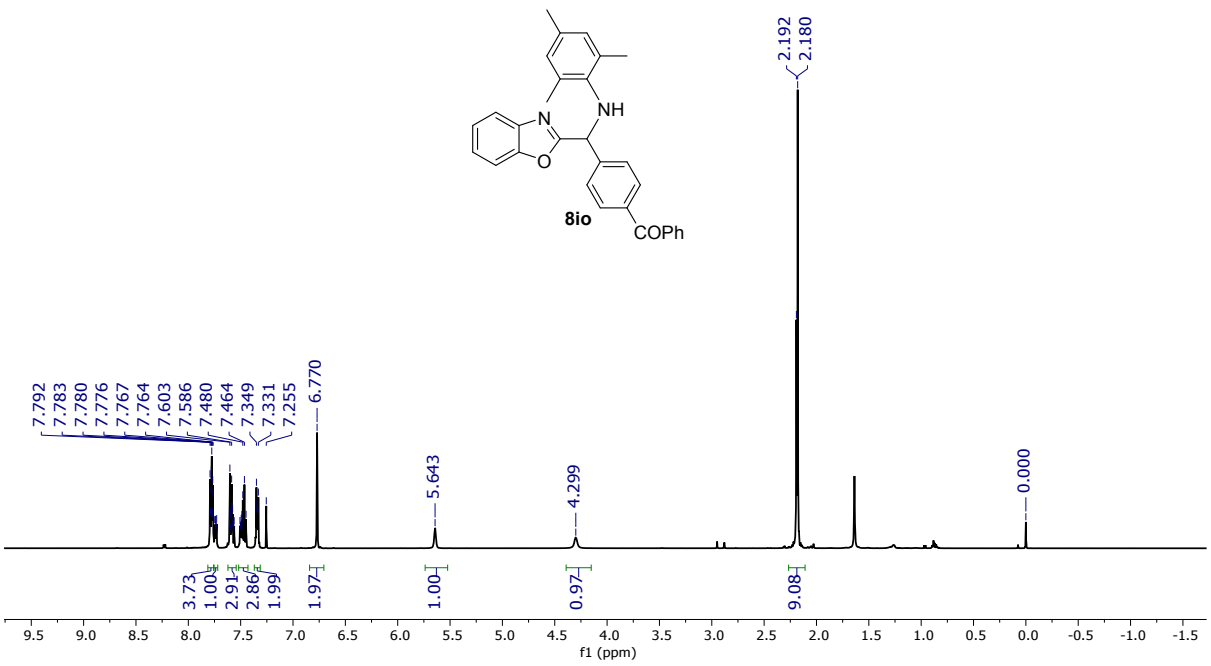
^{1}H NMR (500 MHz, $CDCl_3$):



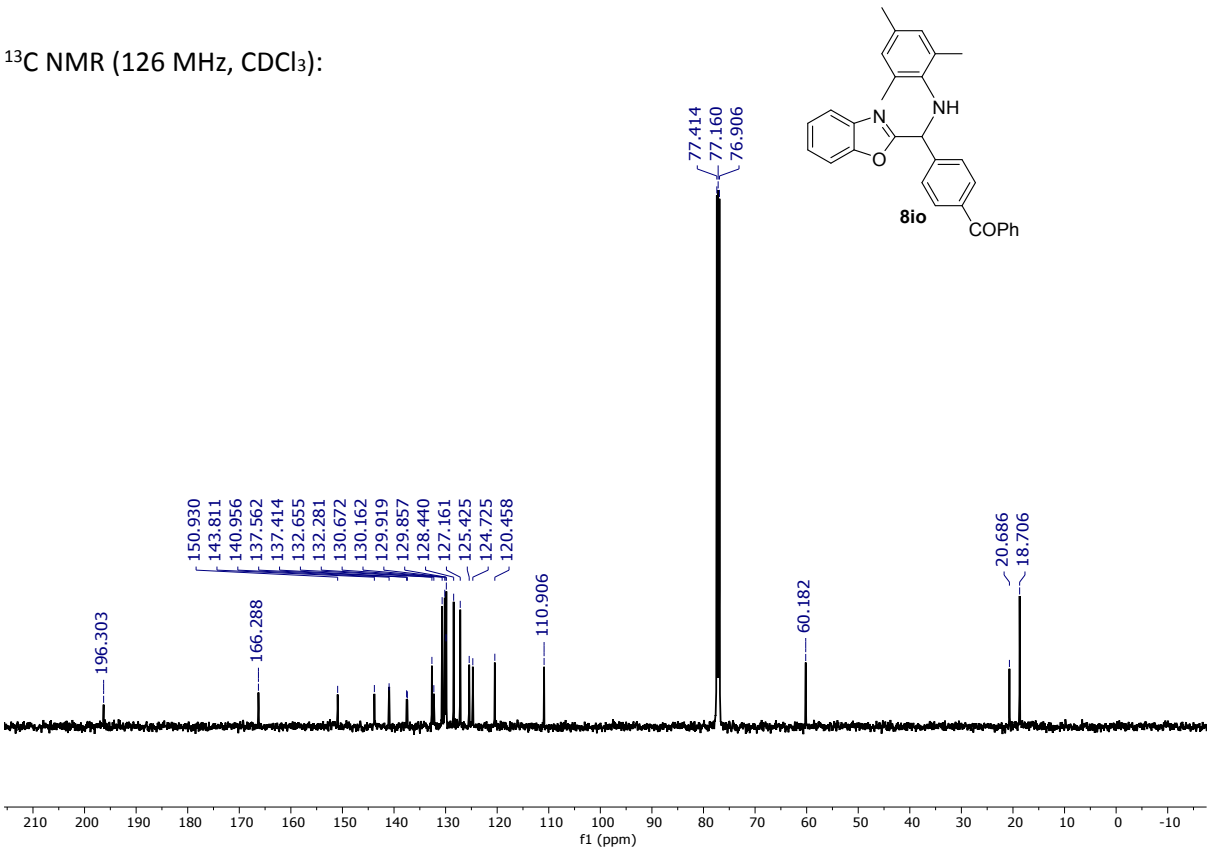
^{13}C NMR (126 MHz, $CDCl_3$):



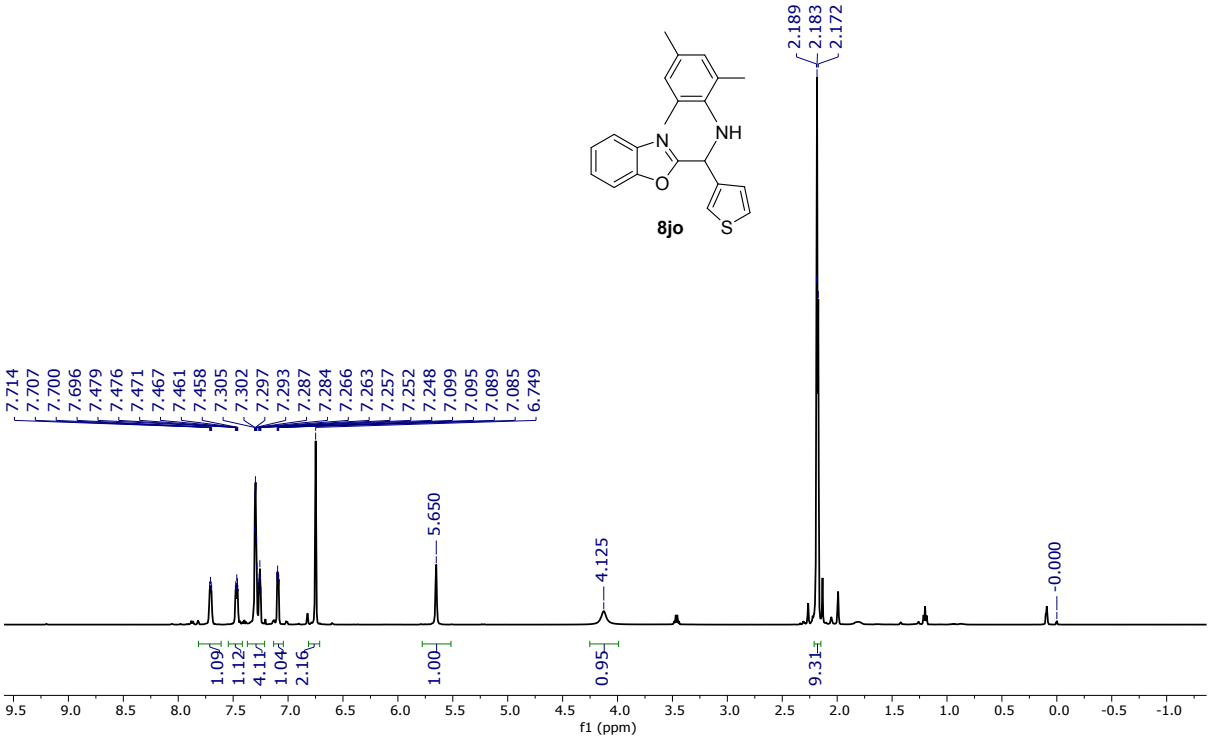
^{1}H NMR (500 MHz, $CDCl_3$):



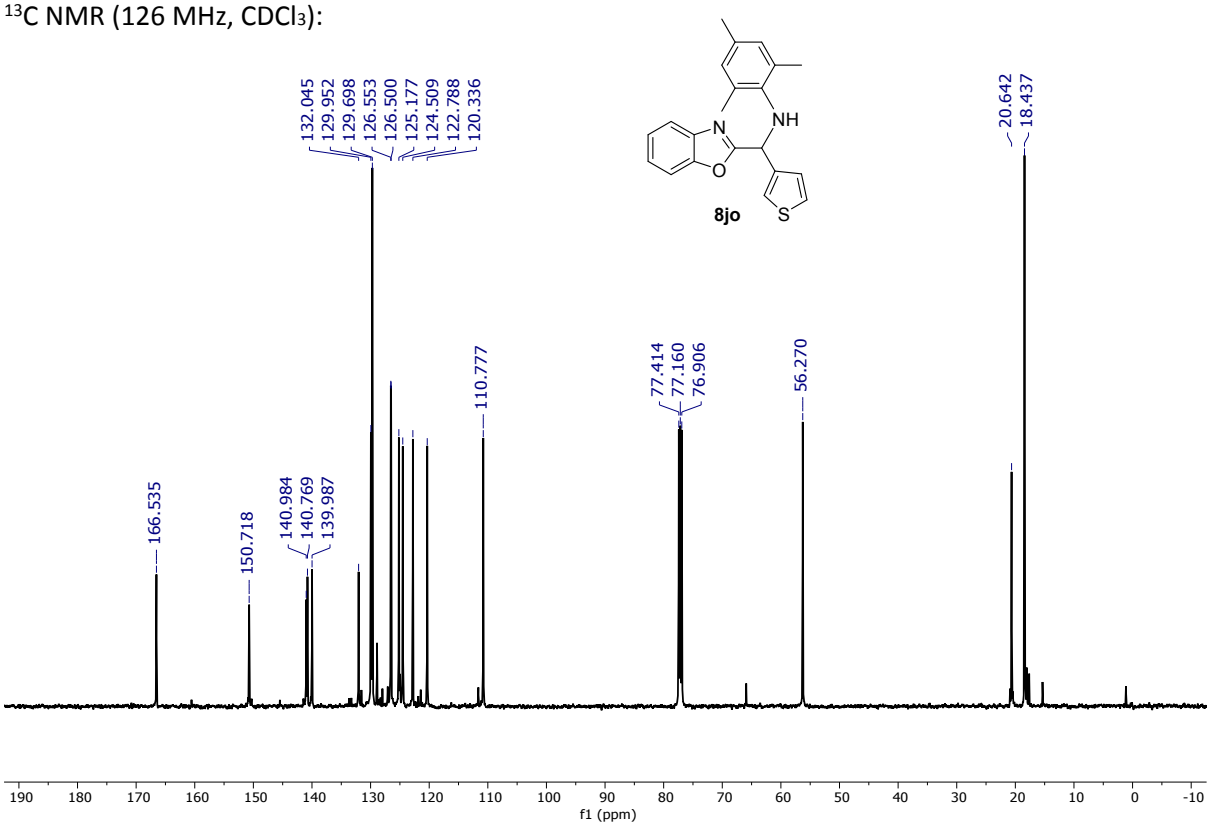
^{13}C NMR (126 MHz, $CDCl_3$):



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



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



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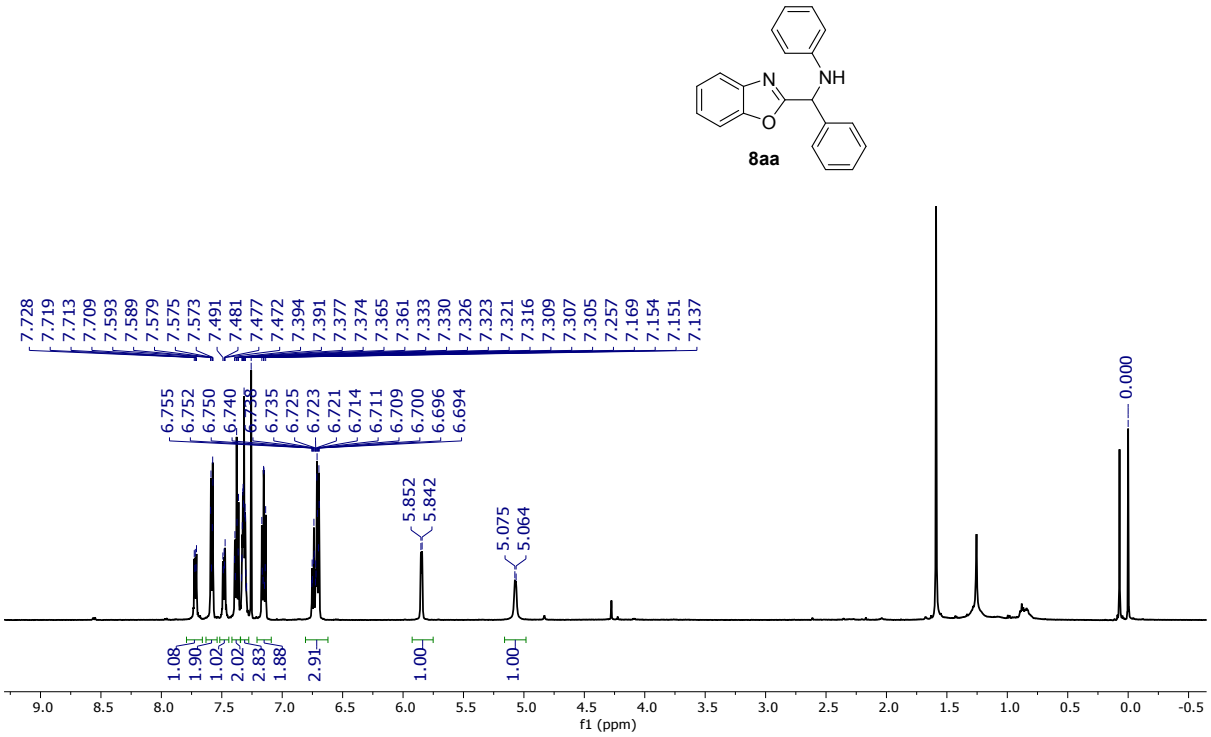
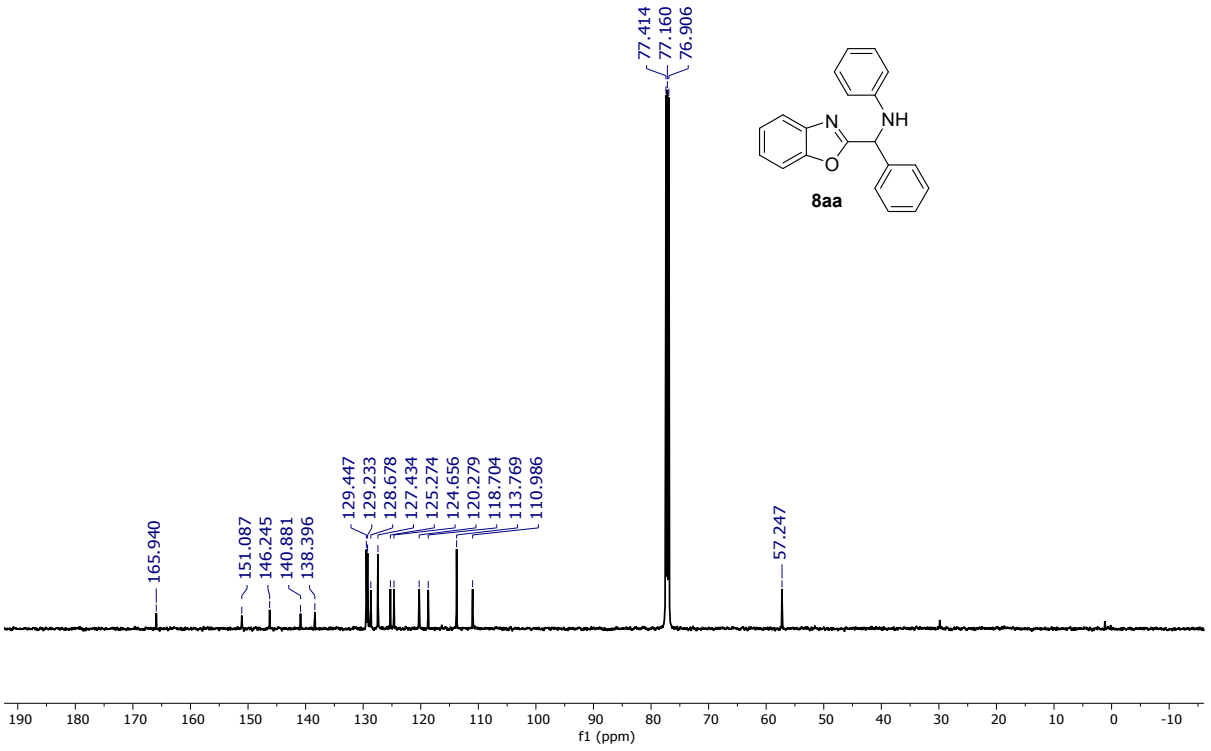
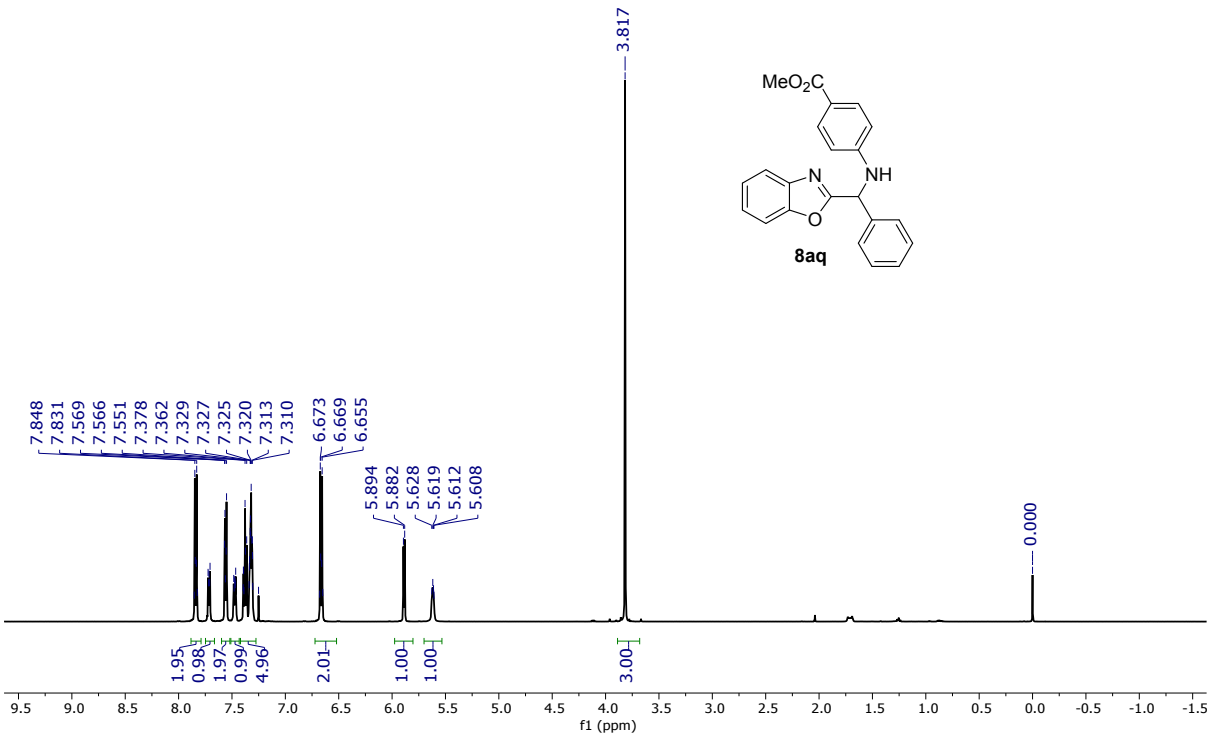


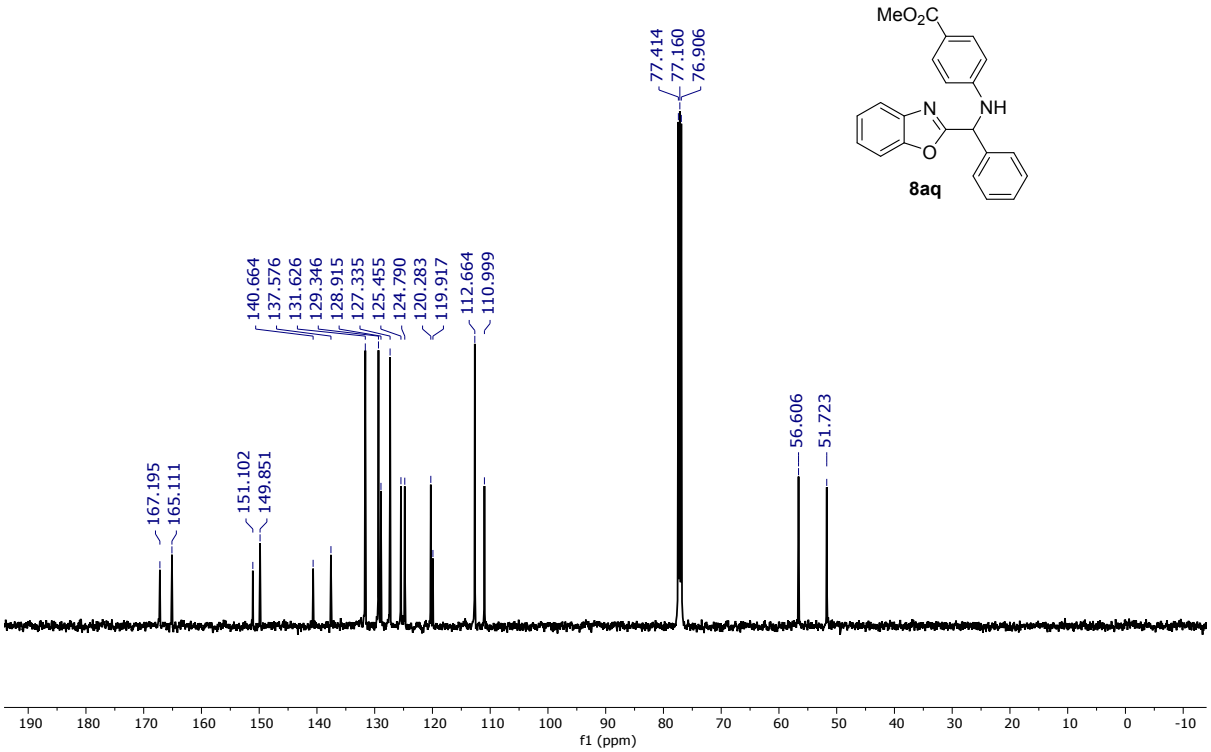
^{13}C NMR (126 MHz, $CDCl_3$):



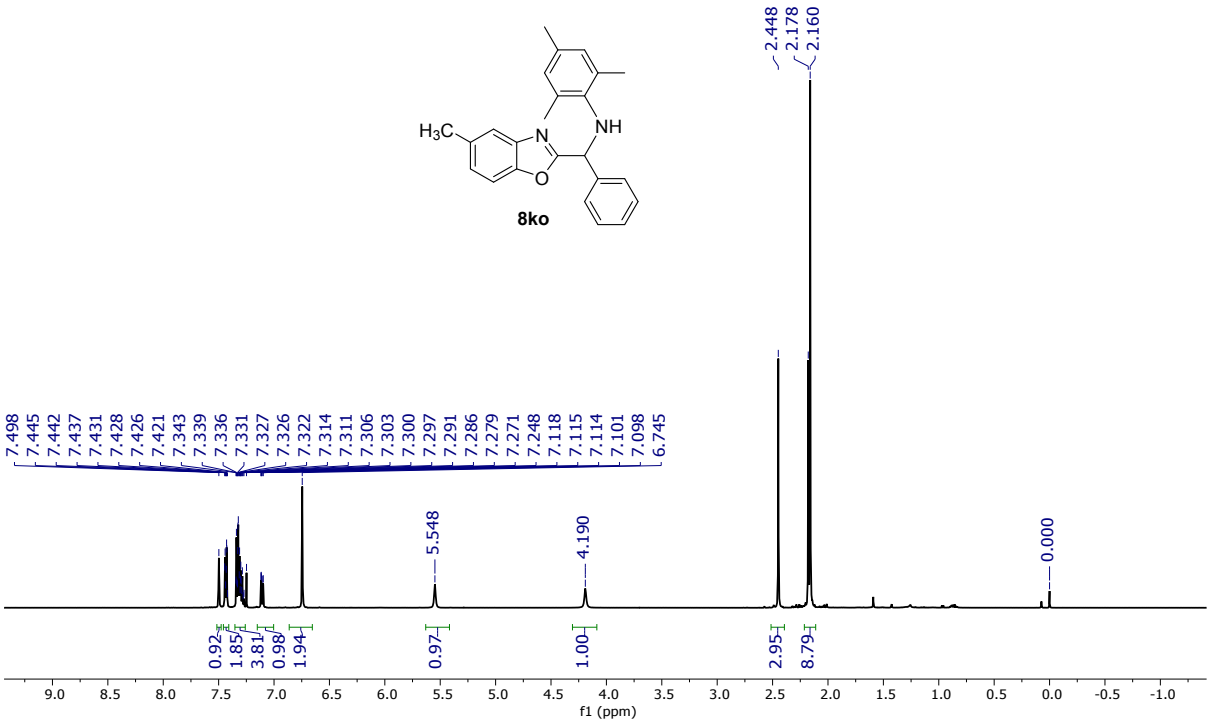
^{1}H NMR (500 MHz, $CDCl_3$):



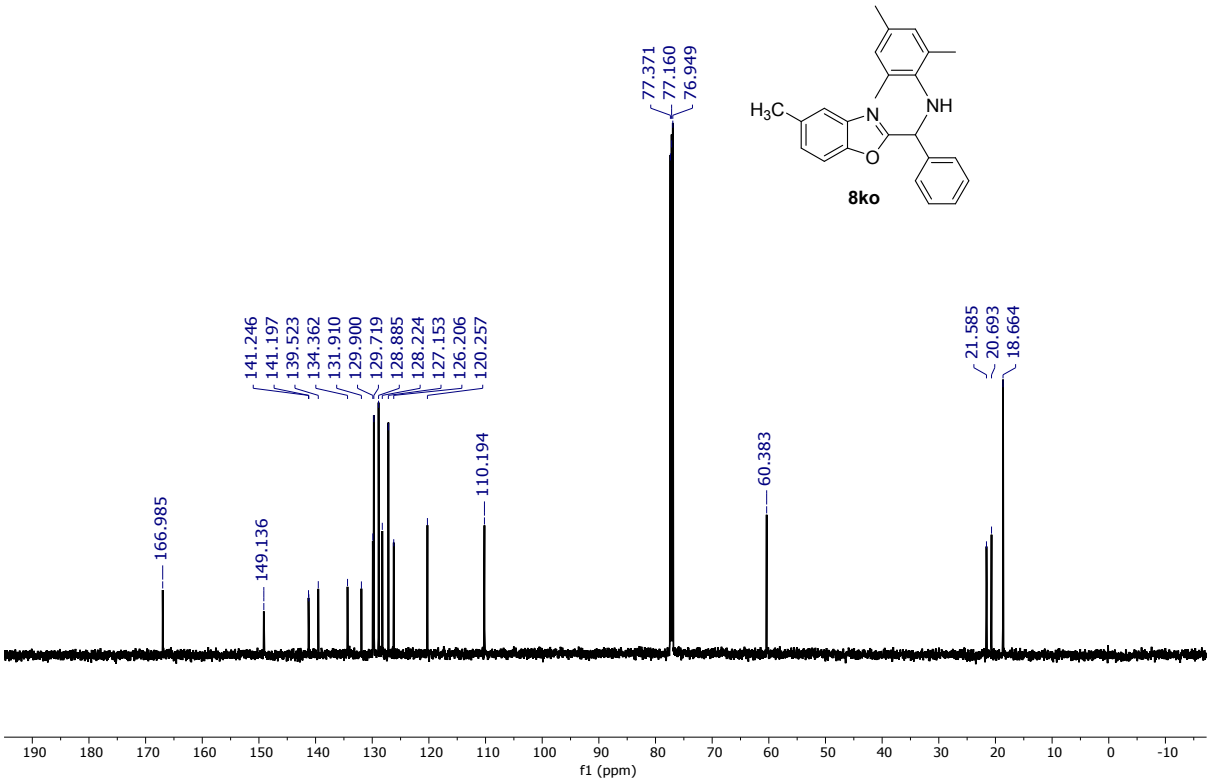
^{13}C NMR (126 MHz, $CDCl_3$):



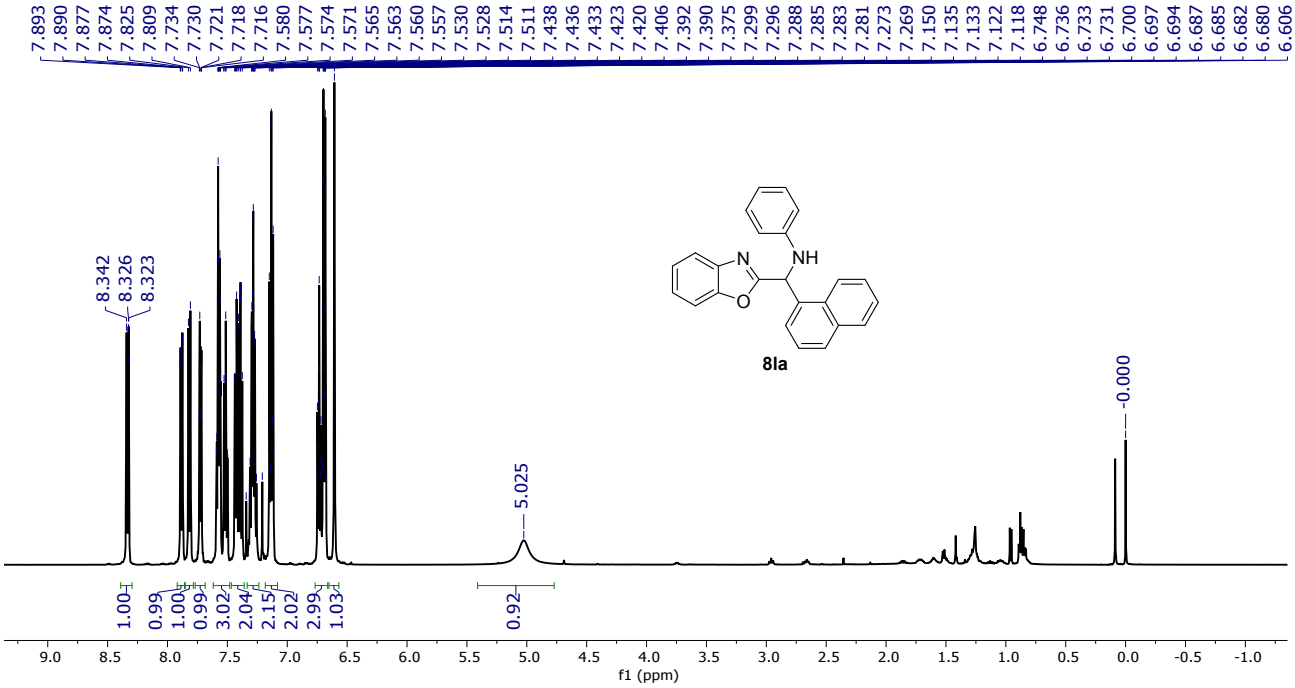
^{1}H NMR (500 MHz, $CDCl_3$):



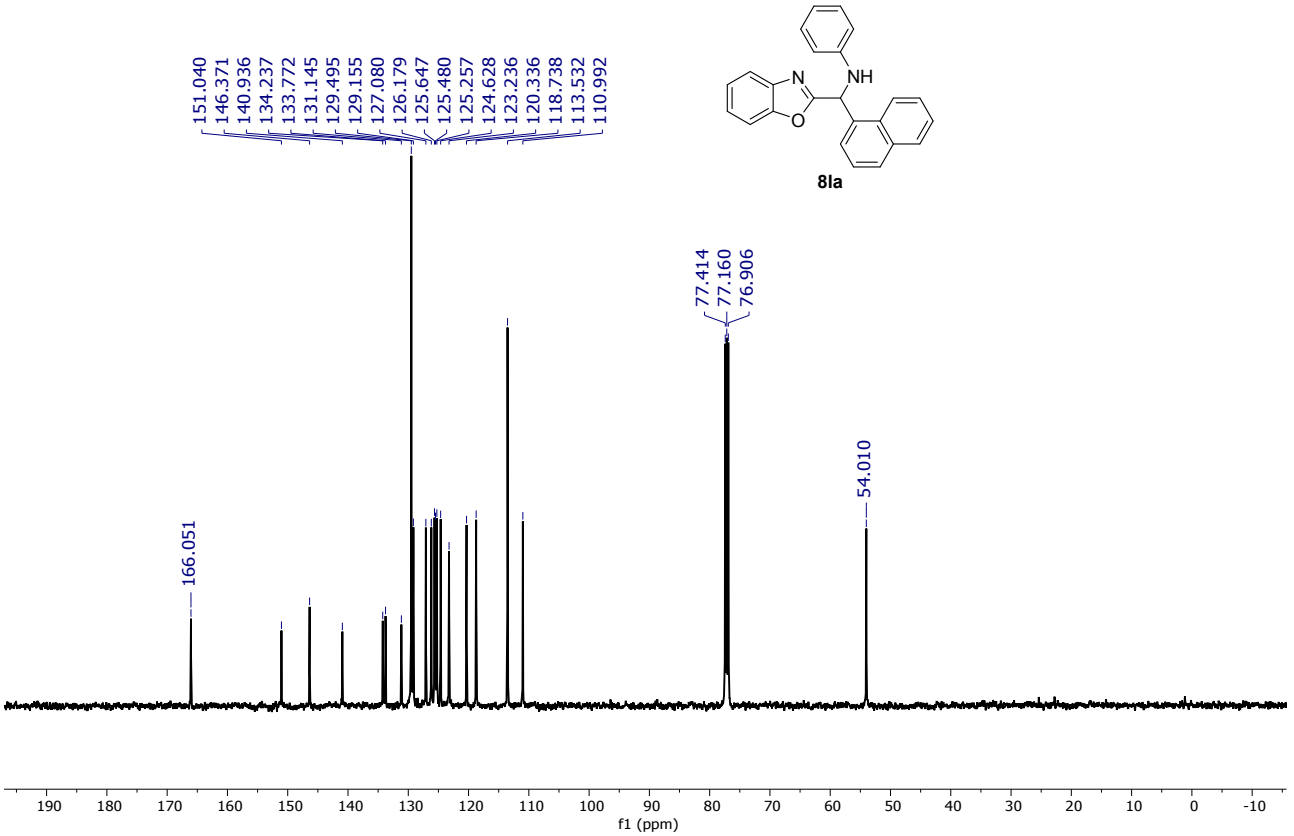
^{13}C NMR (151 MHz, $CDCl_3$):



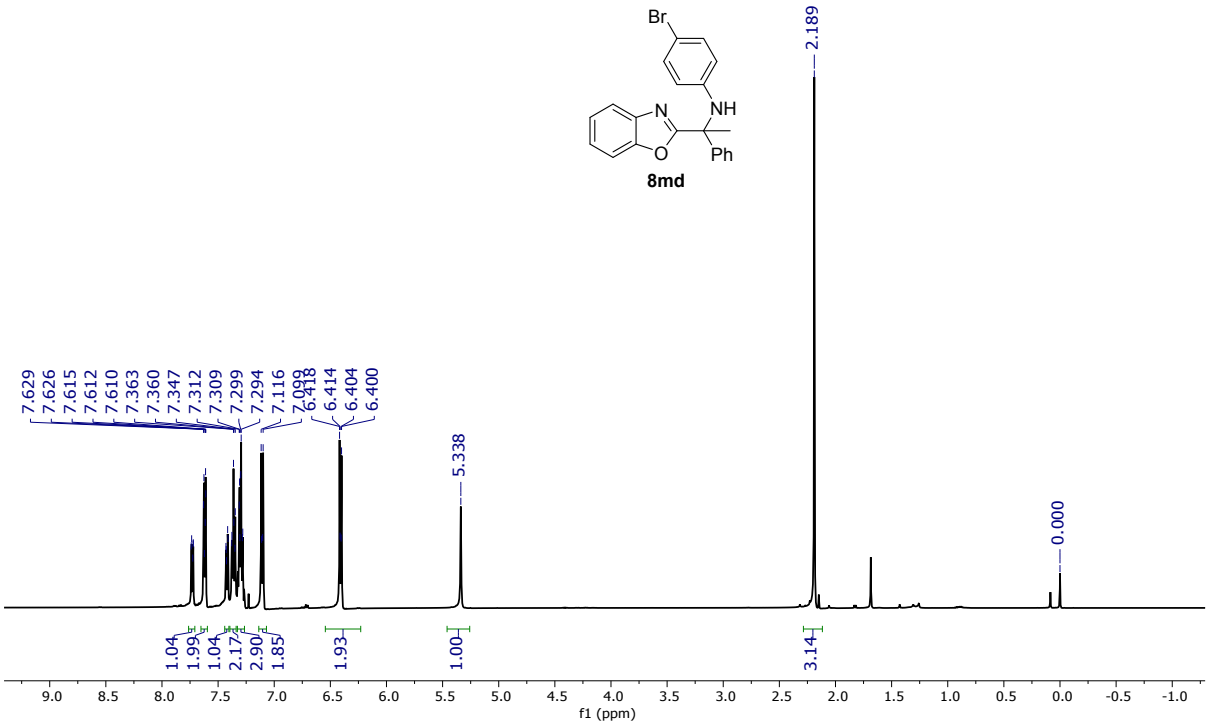
^{1}H NMR (500 MHz, $CDCl_3$):



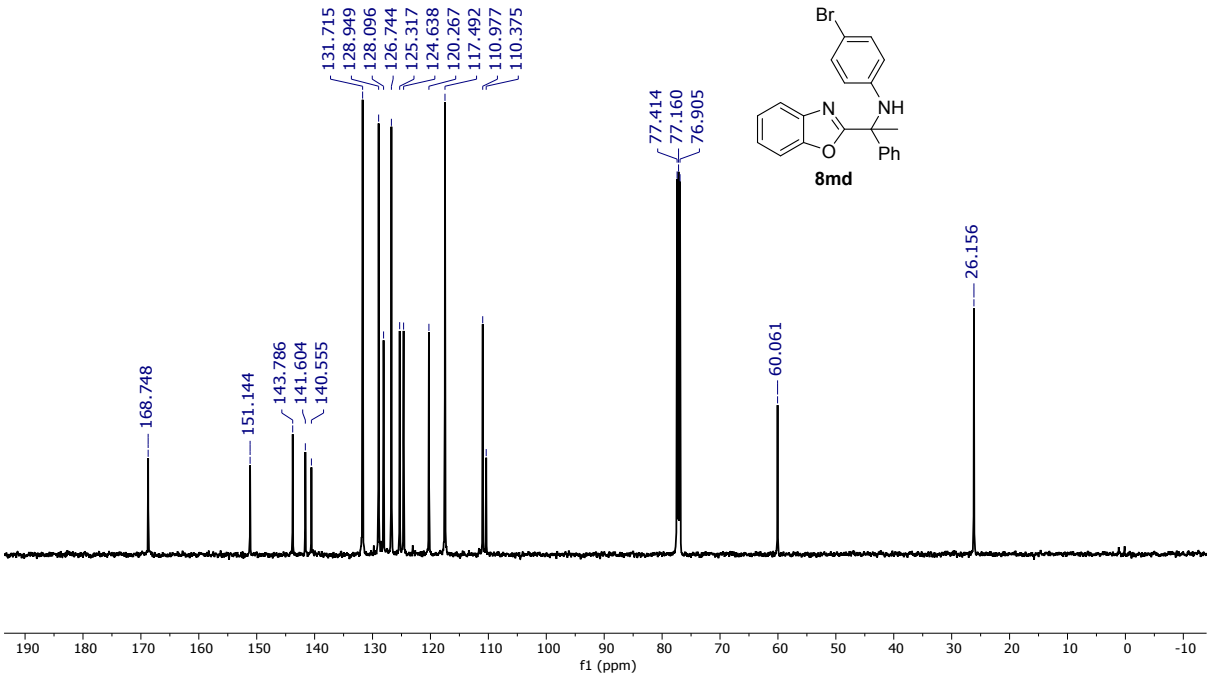
^{13}C NMR (126 MHz, $CDCl_3$):



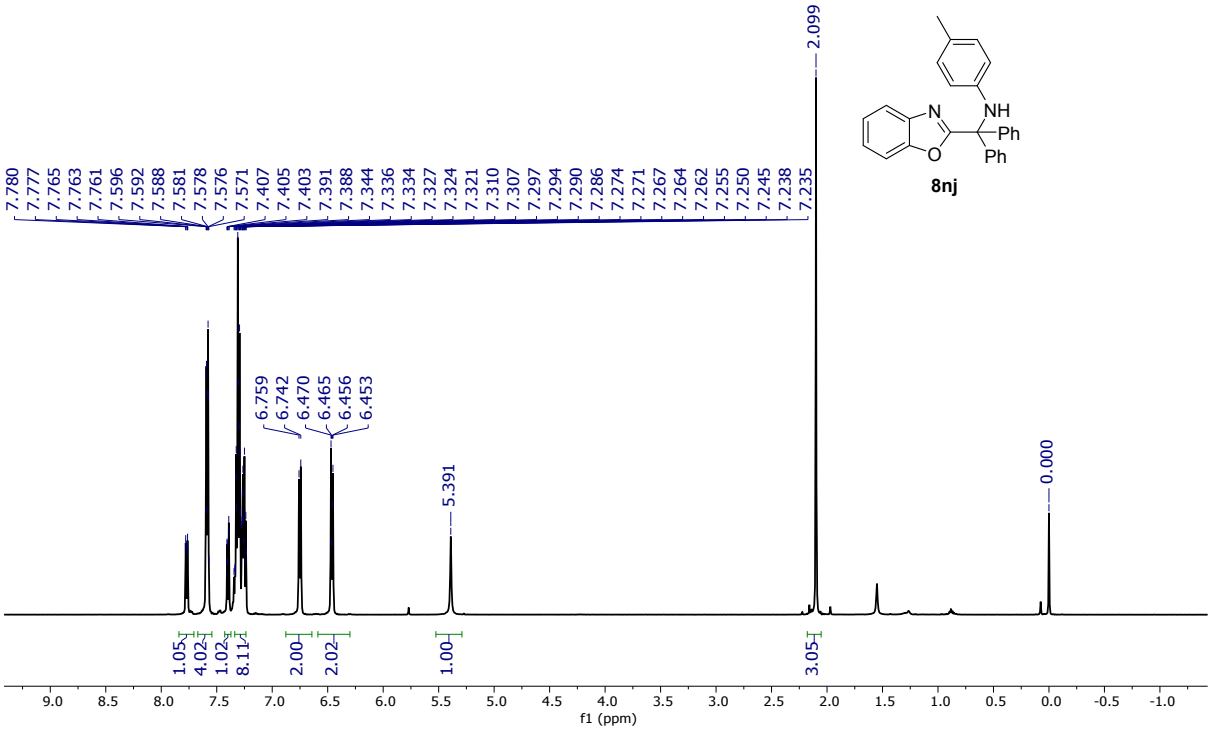
^{1}H NMR (500 MHz, $CDCl_3$):



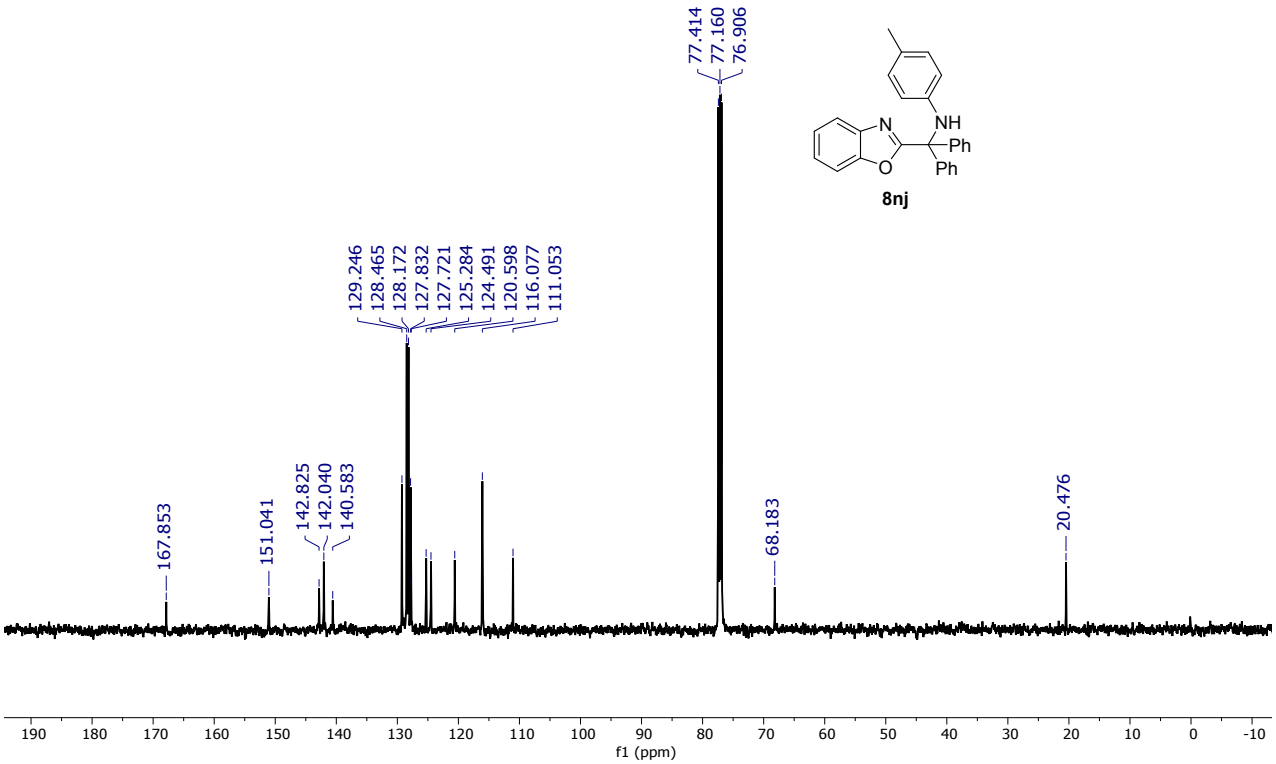
^{13}C NMR (126 MHz, $CDCl_3$):



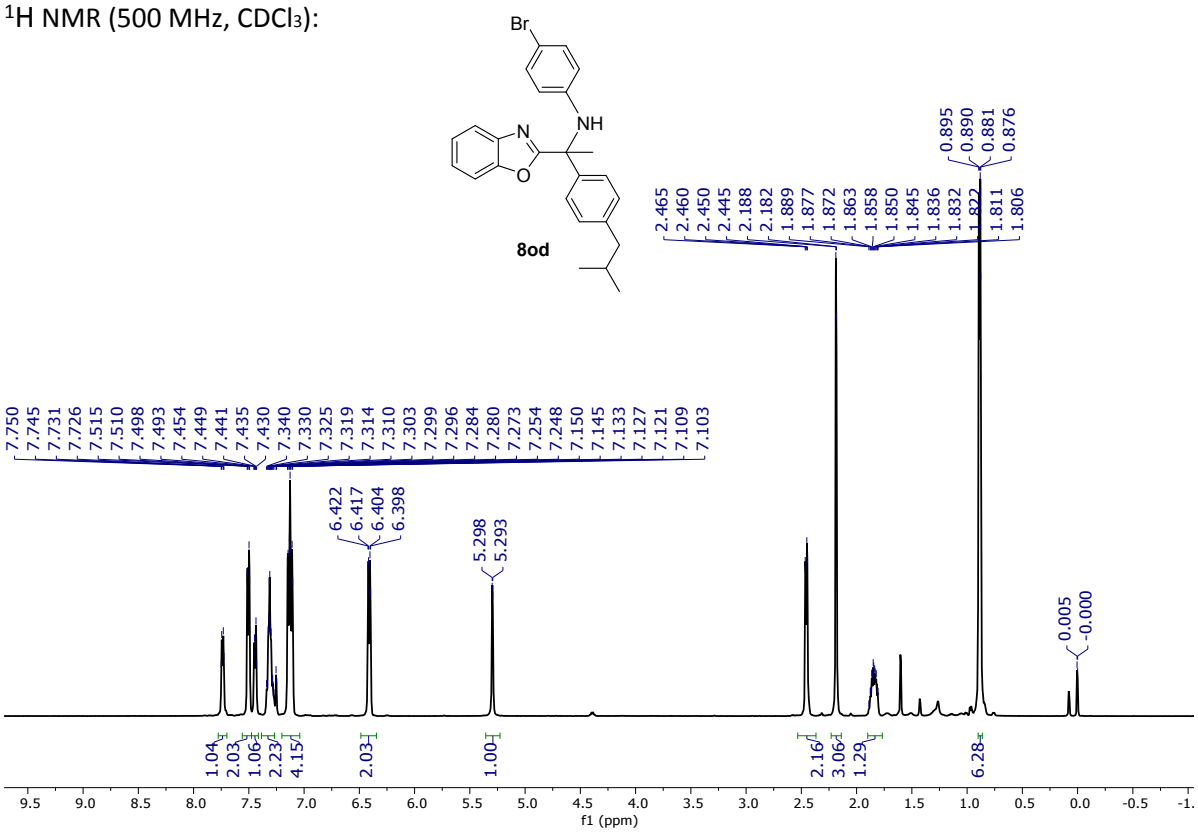
^{1}H NMR (500 MHz, $CDCl_3$):



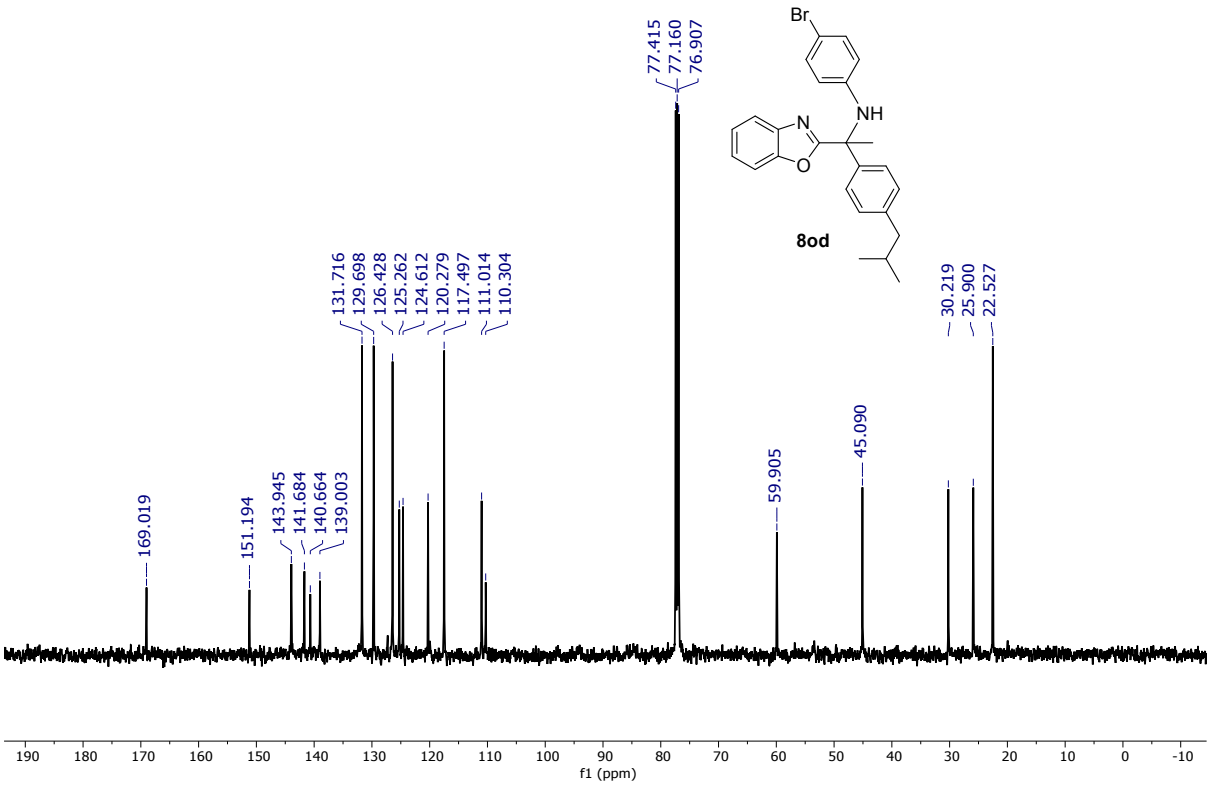
^{13}C NMR (126 MHz, $CDCl_3$):



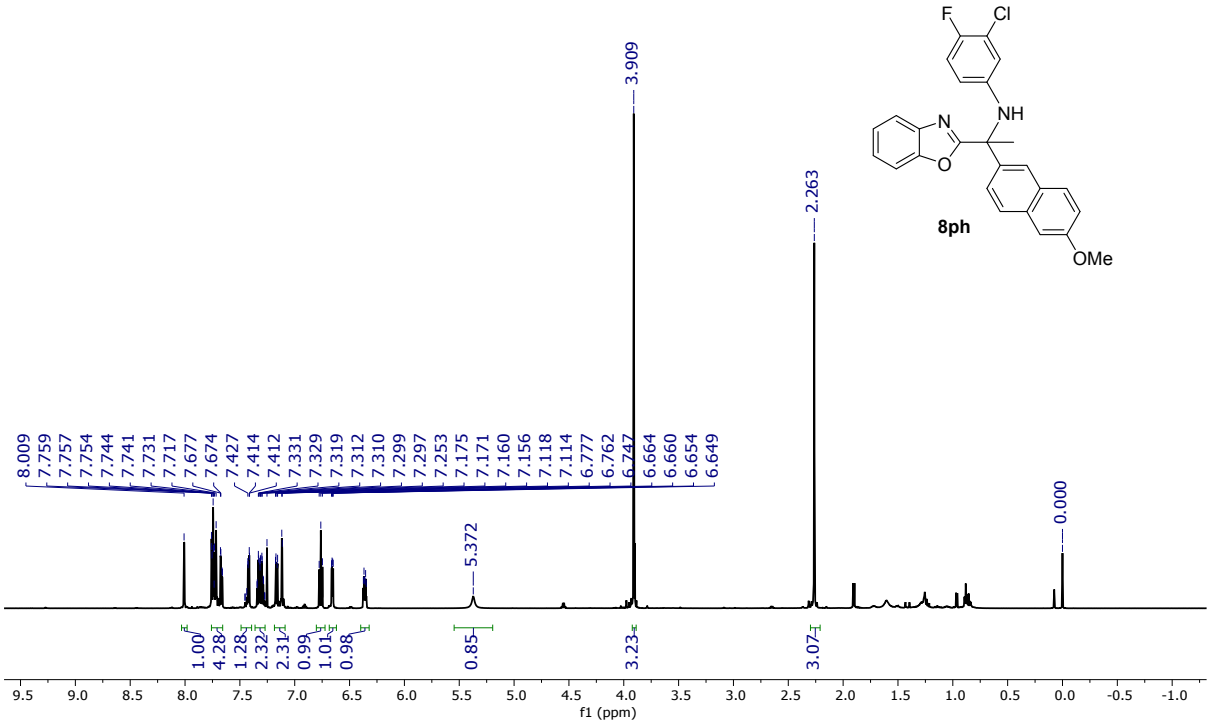
^{1}H NMR (500 MHz, $CDCl_3$):



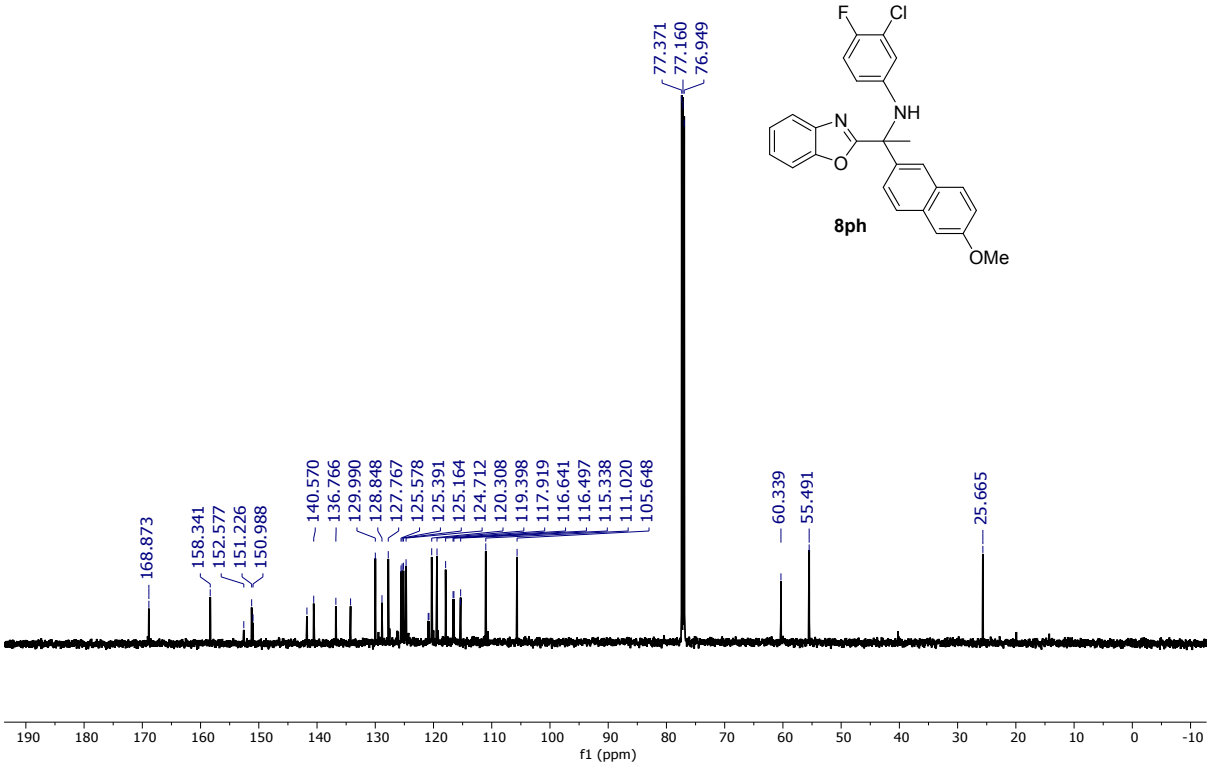
^{13}C NMR (126 MHz, $CDCl_3$):



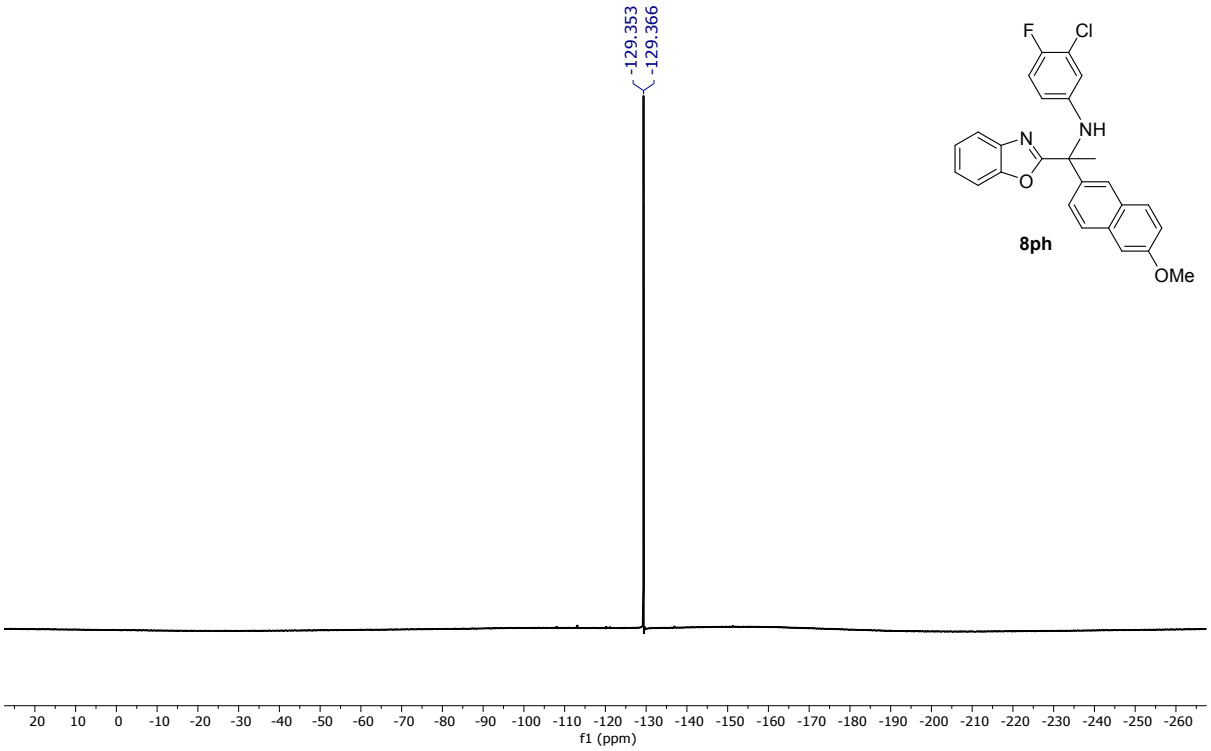
^{1}H NMR (500 MHz, $CDCl_3$):



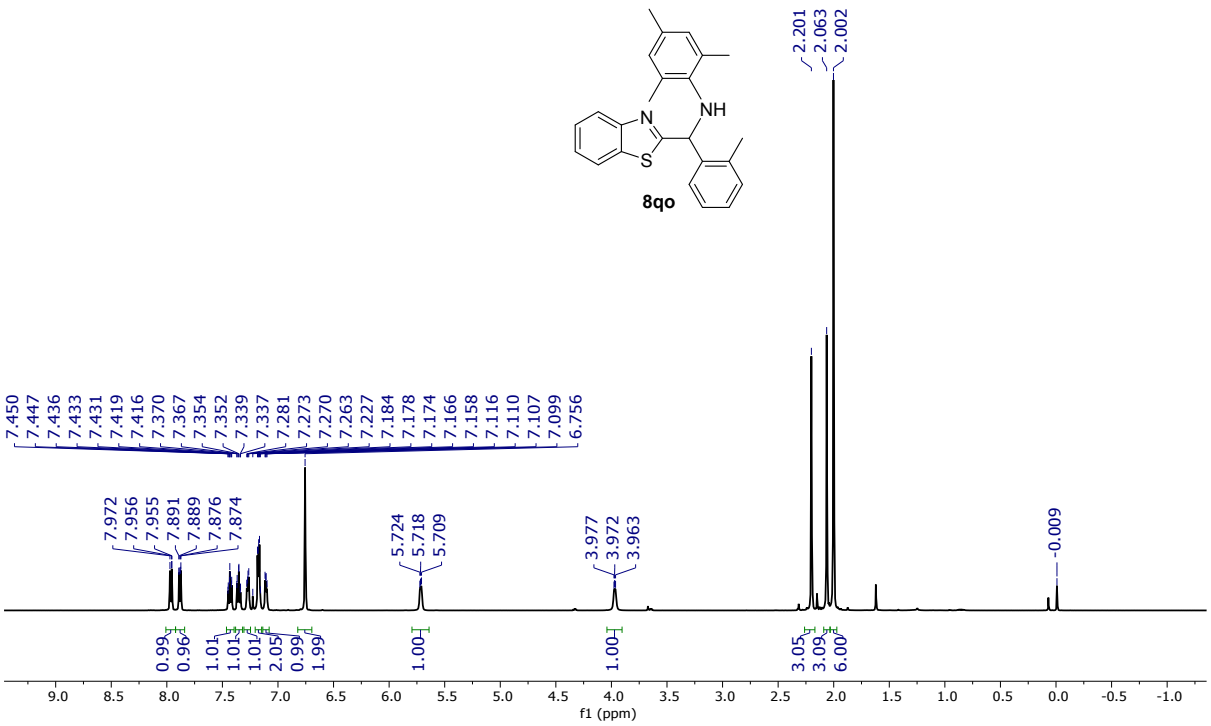
^{13}C NMR (151 MHz, $CDCl_3$):



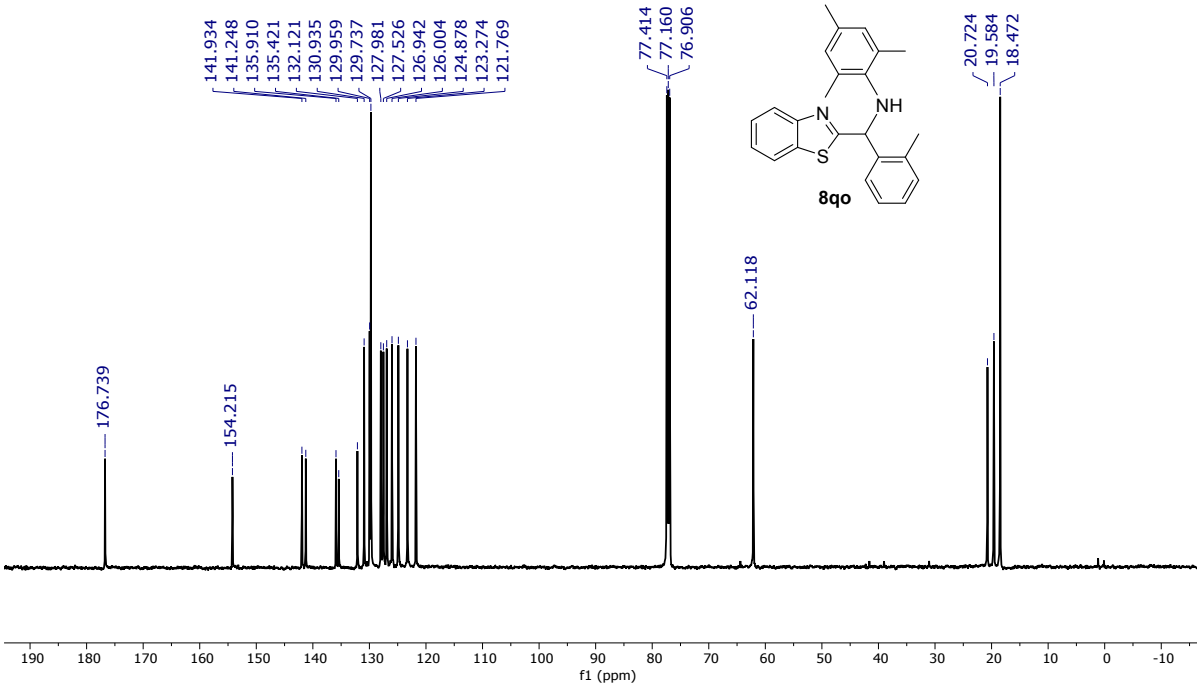
^{19}F NMR (565 MHz, $CDCl_3$):



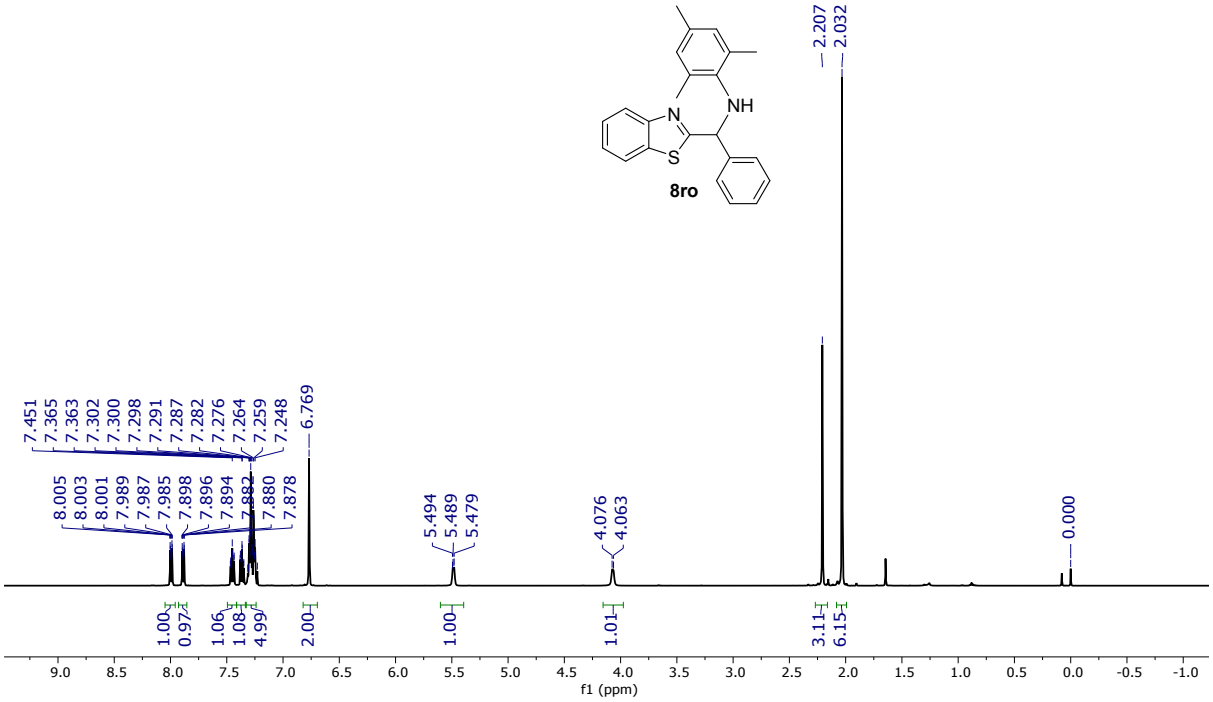
^{1}H NMR (500 MHz, $CDCl_3$):



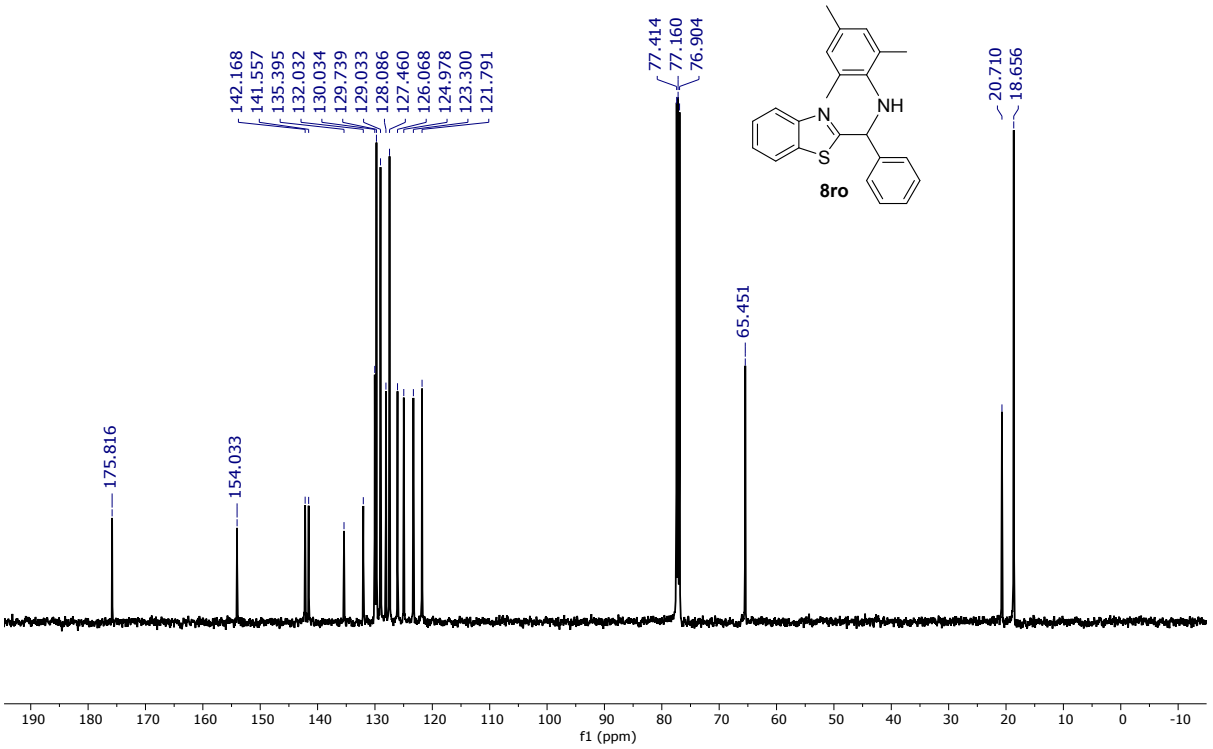
^{13}C NMR (126 MHz, $CDCl_3$):



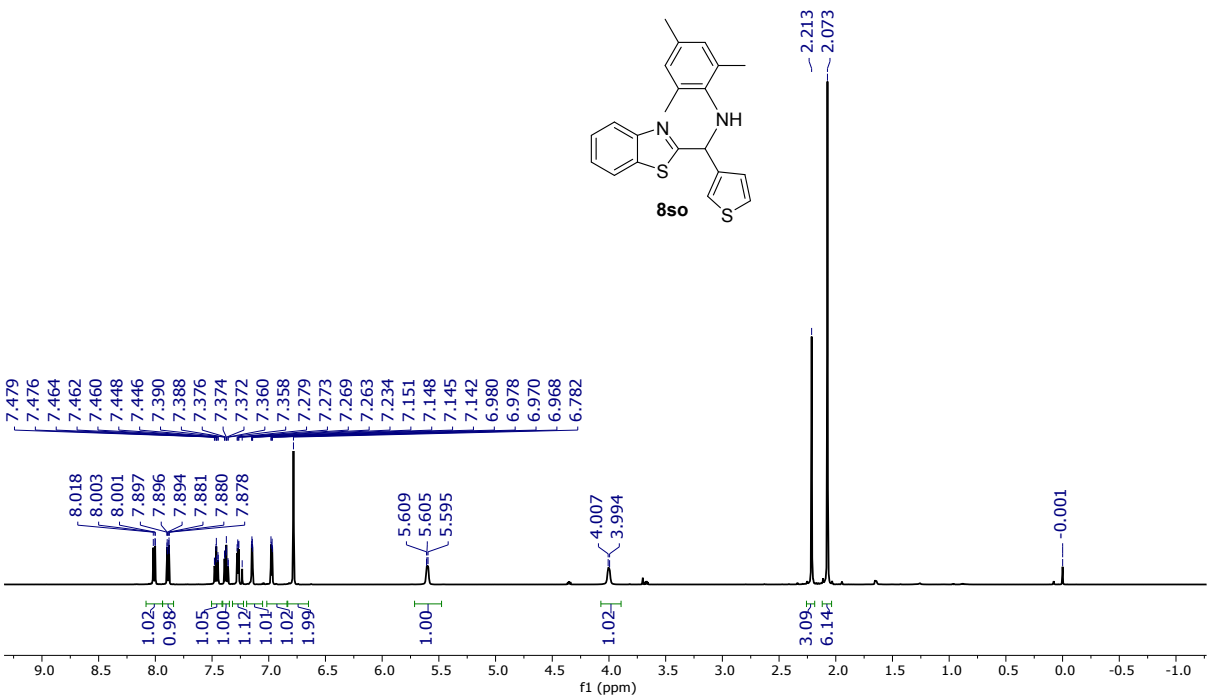
^{1}H NMR (500 MHz, $CDCl_3$):



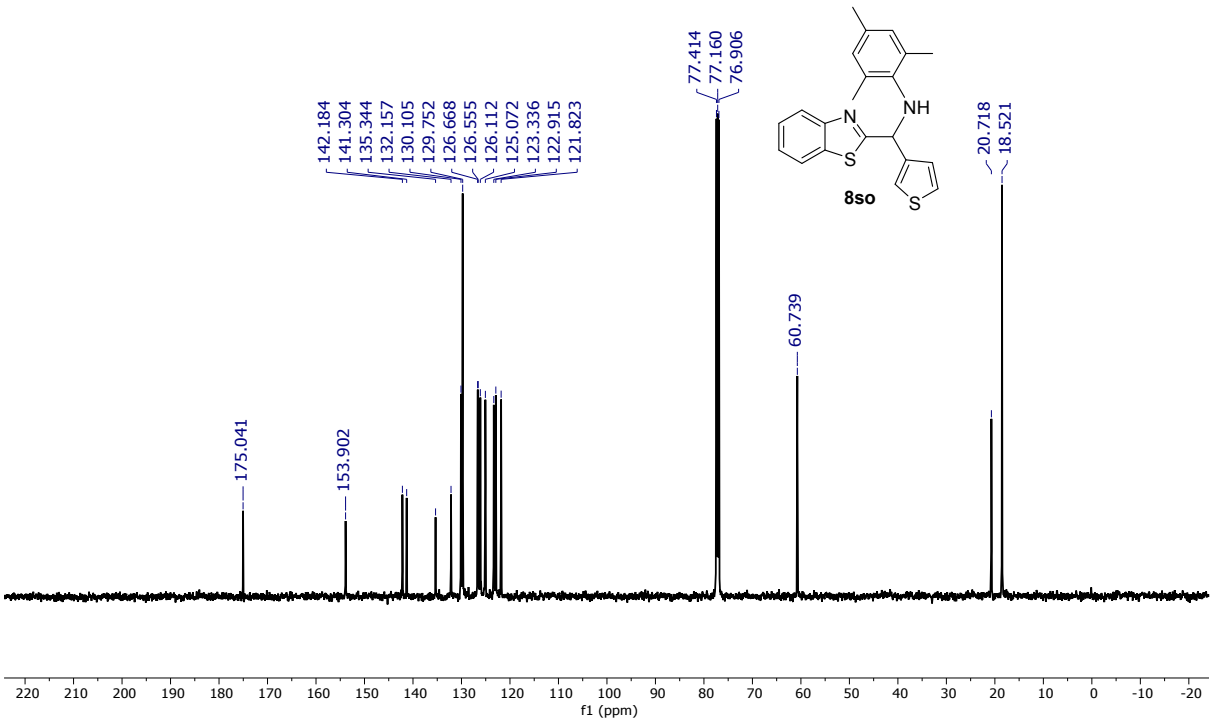
^{13}C NMR (126 MHz, $CDCl_3$):



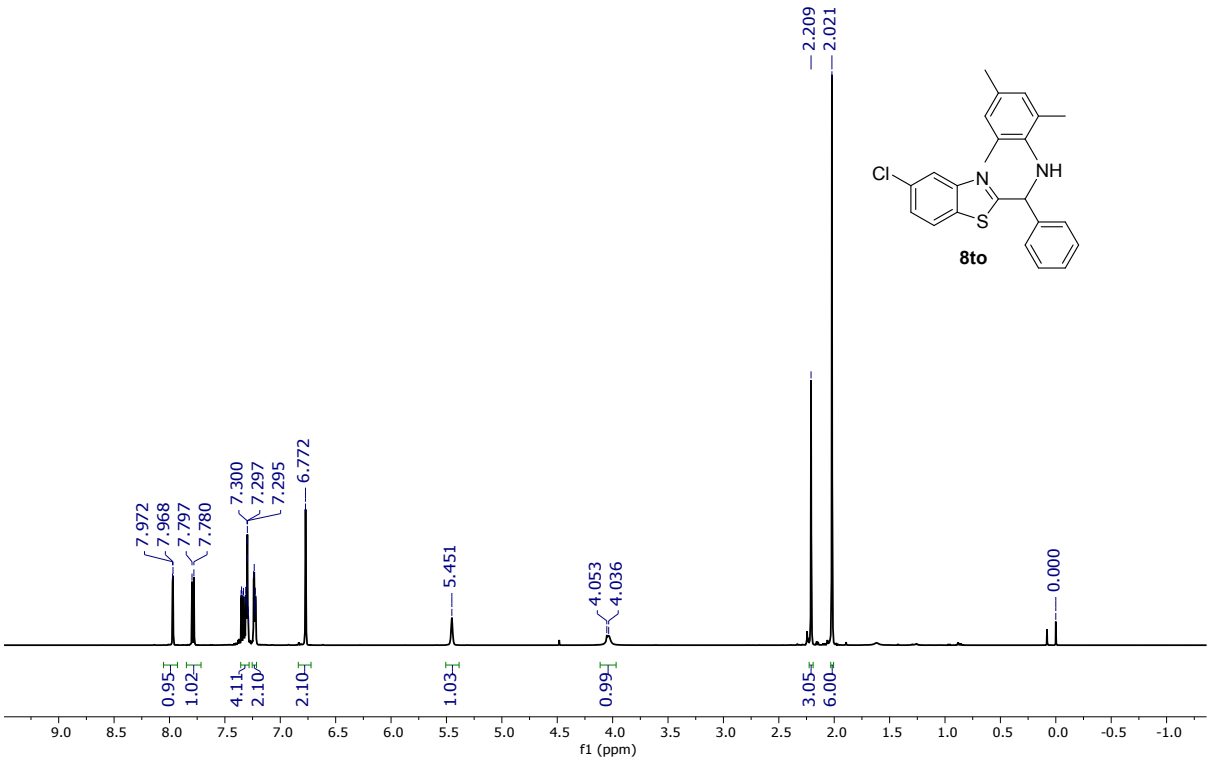
^{1}H NMR (500 MHz, $CDCl_3$):



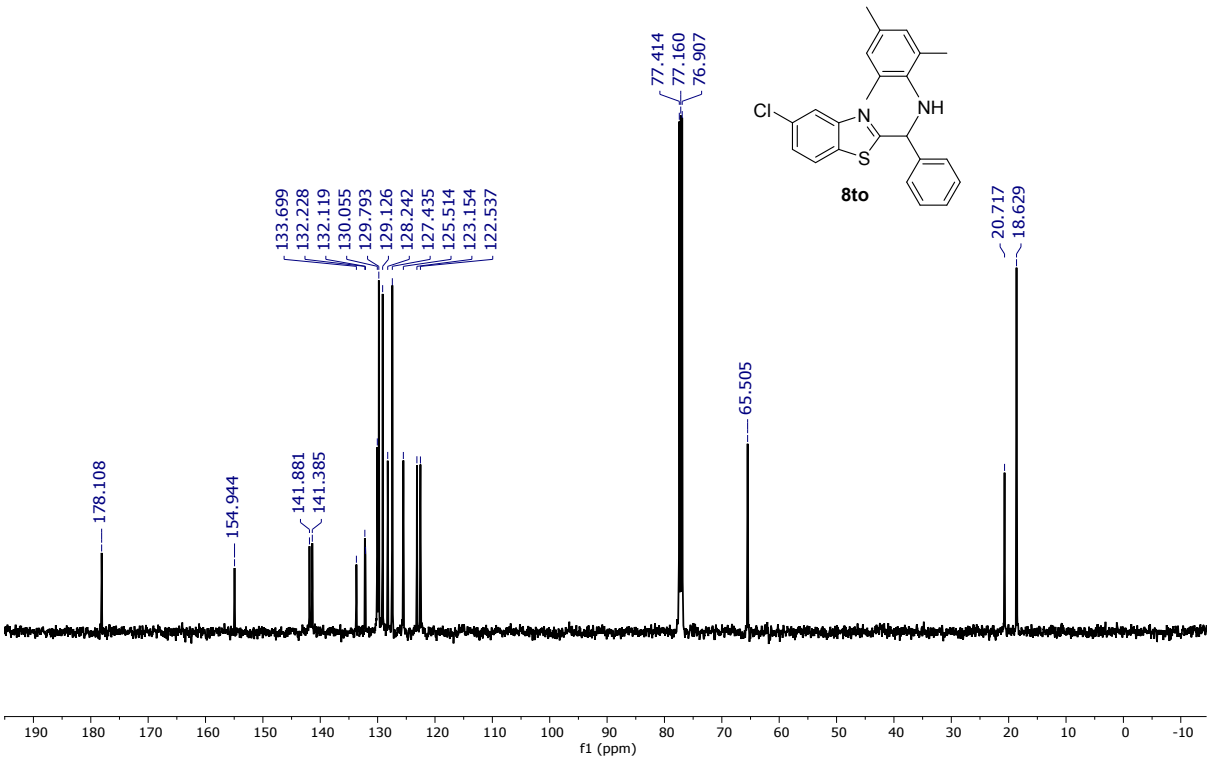
^{13}C NMR (126 MHz, $CDCl_3$):



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



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



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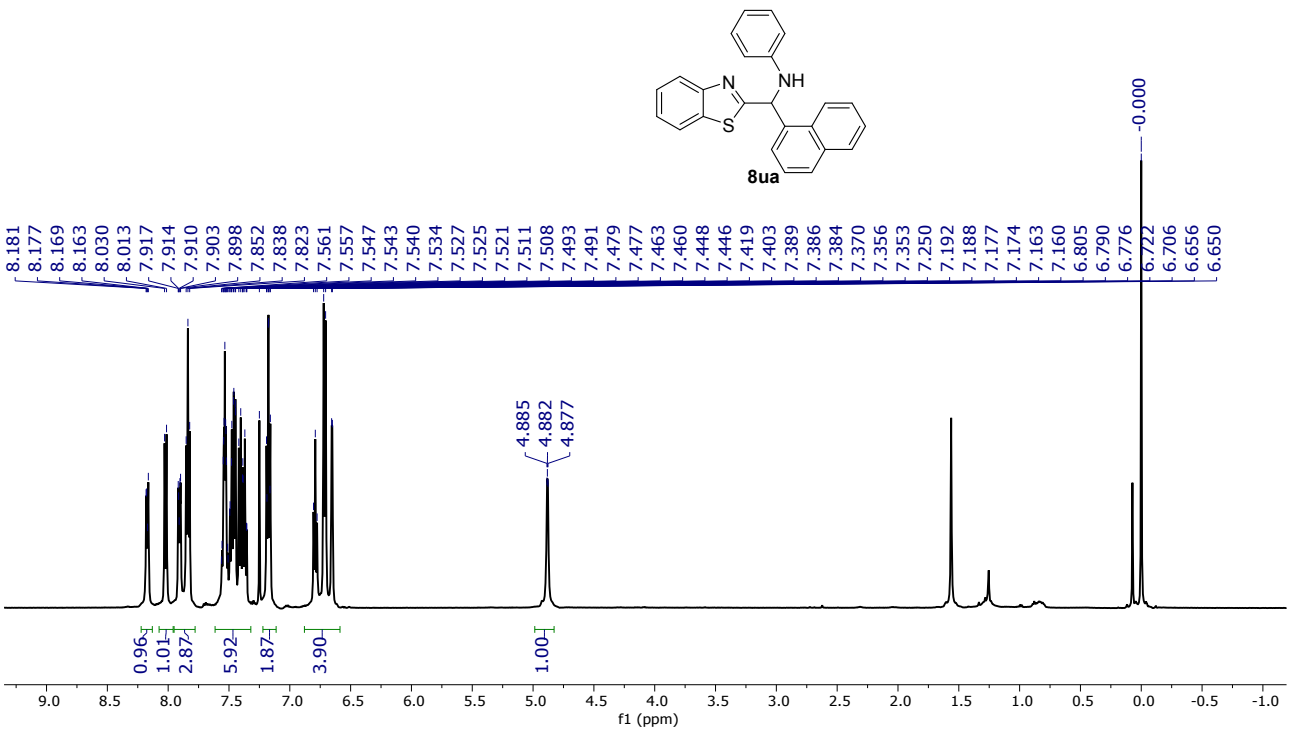
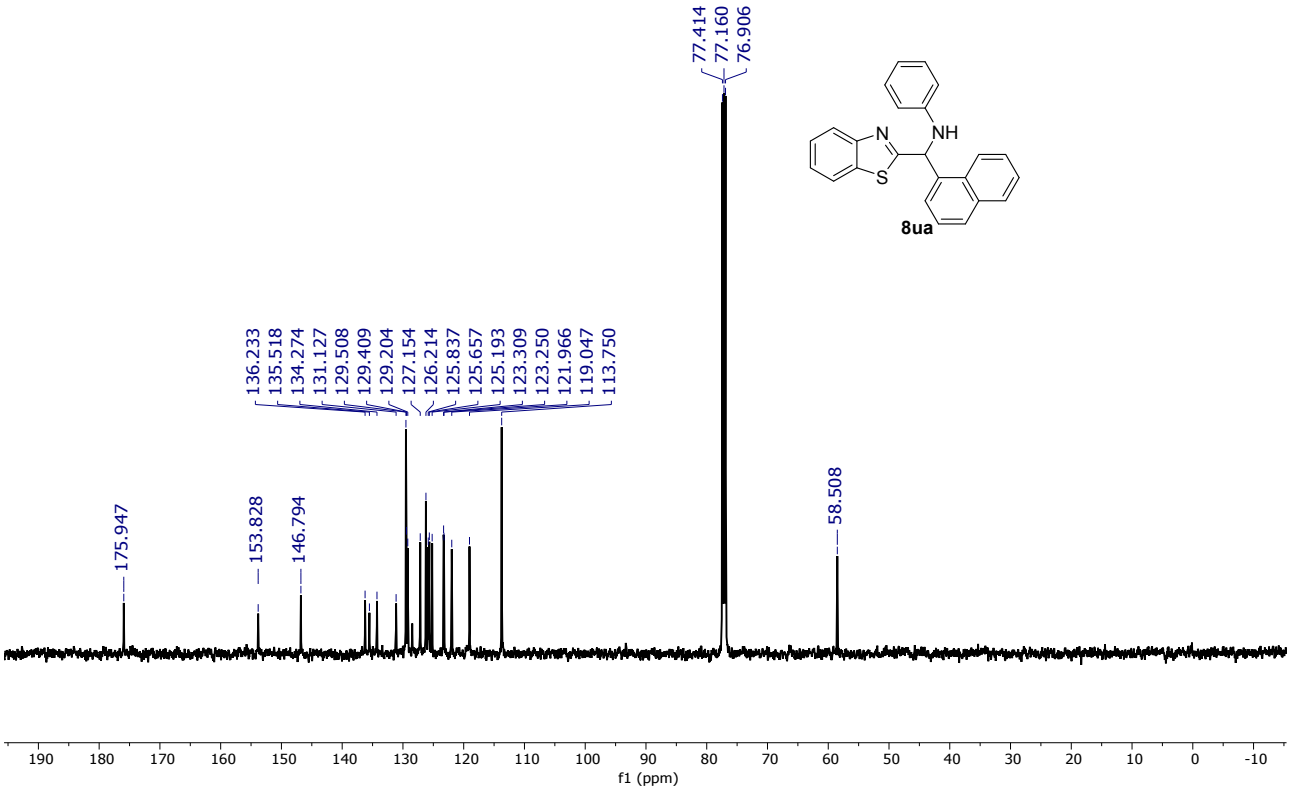
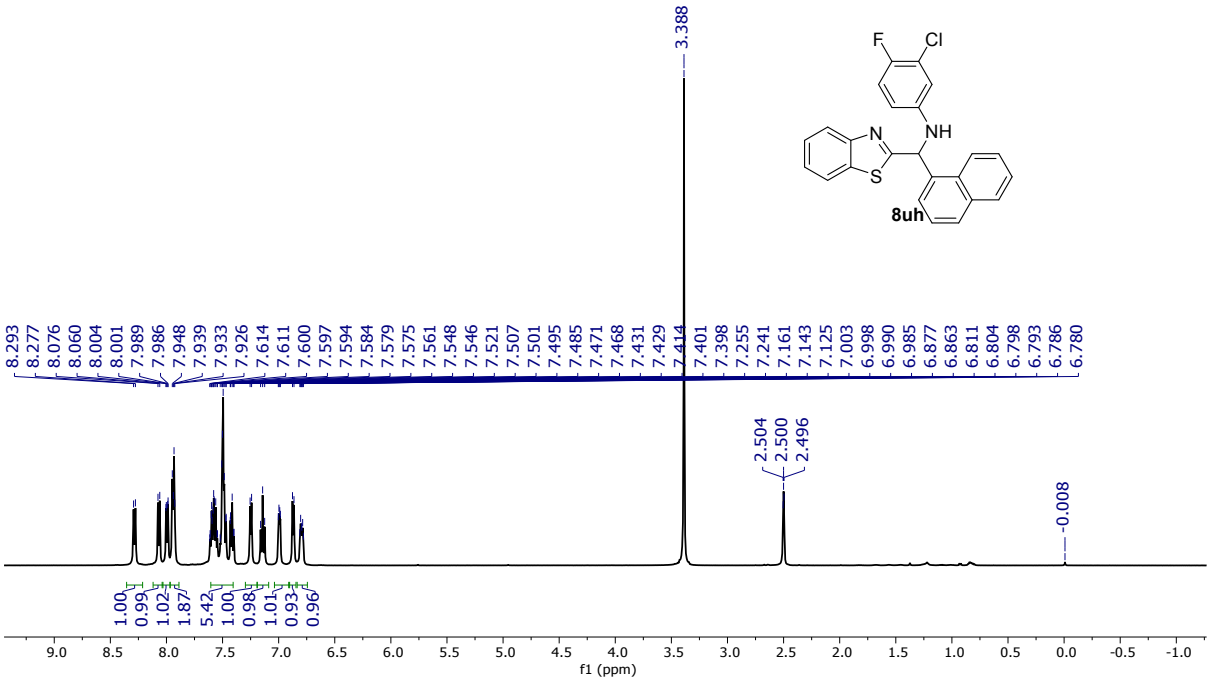


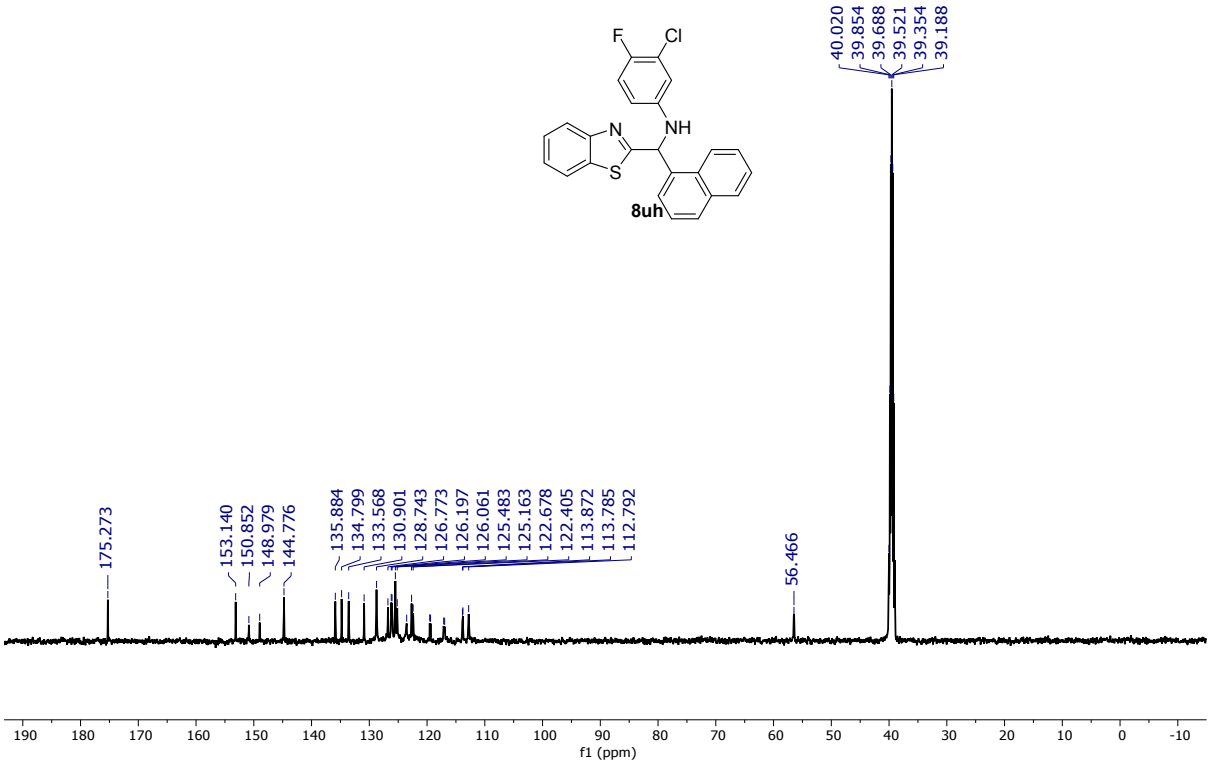
^{13}C NMR (500 MHz, $CDCl_3$):



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

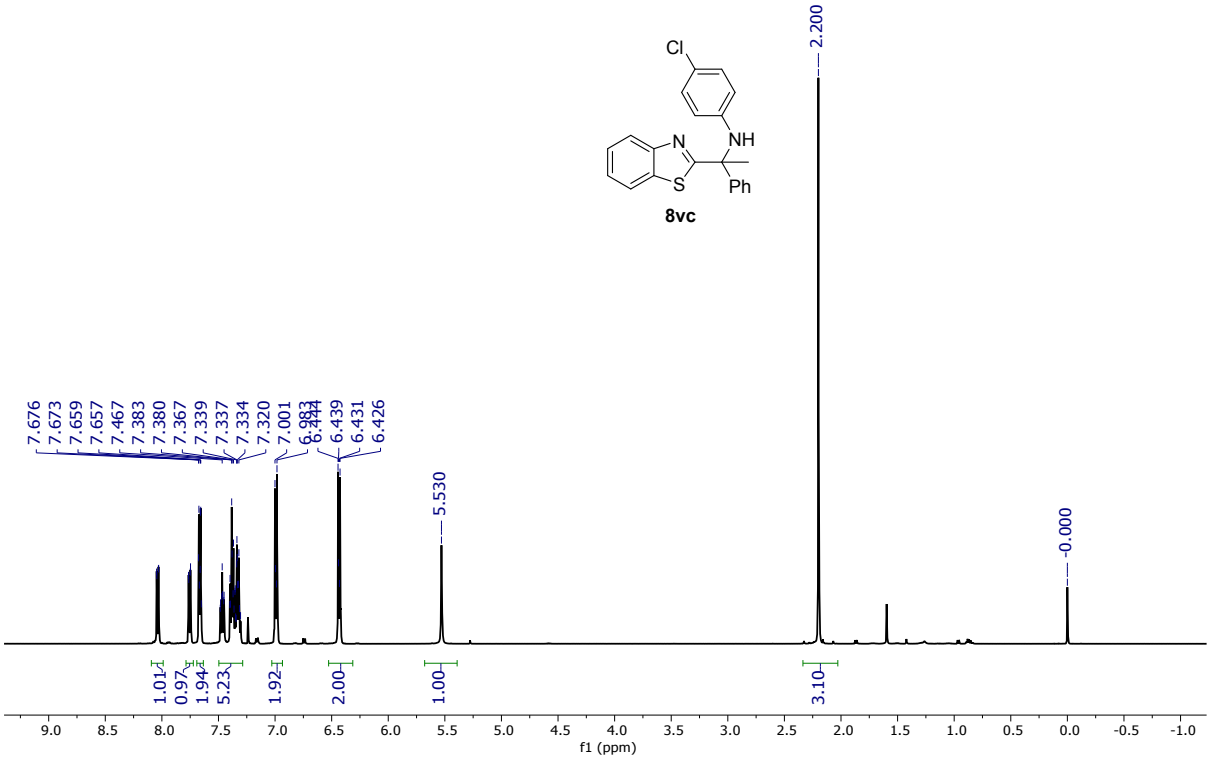


^{13}C NMR (126 MHz, DMSO-d_6):

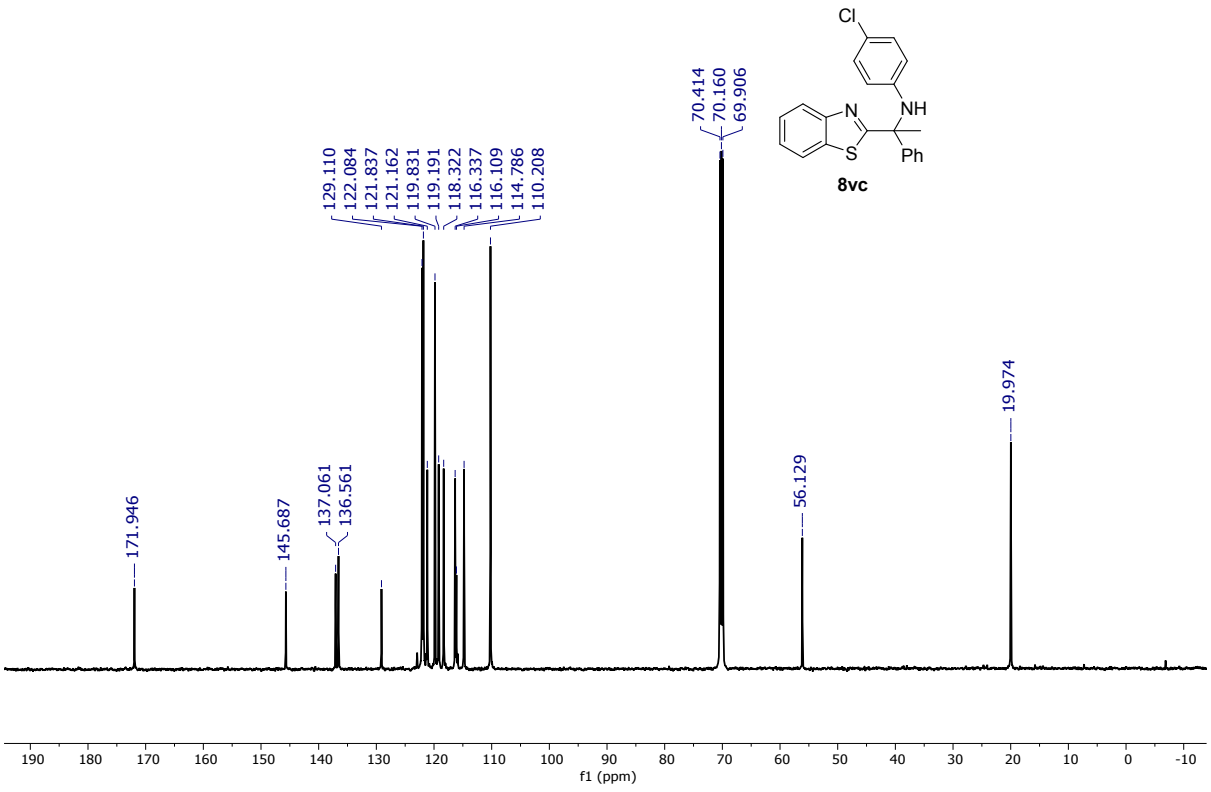


^{19}F NMR (565 MHz, DMSO-d_6):

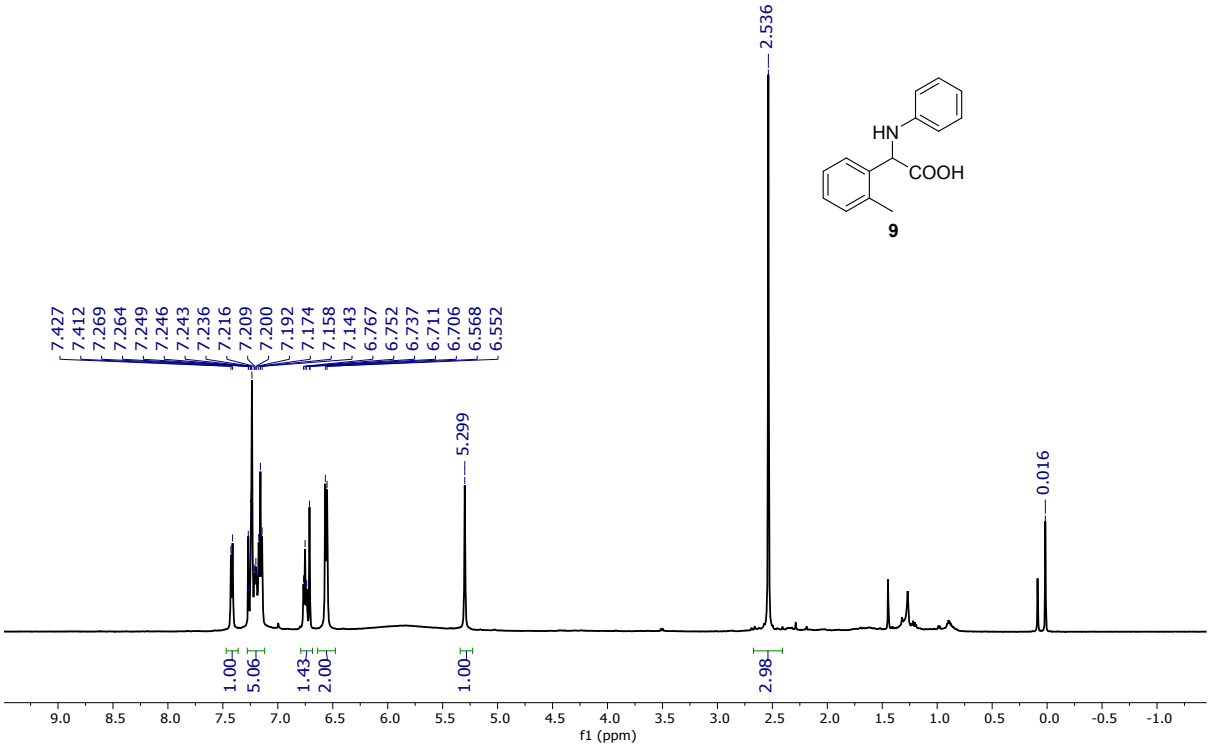
^{1}H NMR (500 MHz, $CDCl_3$):



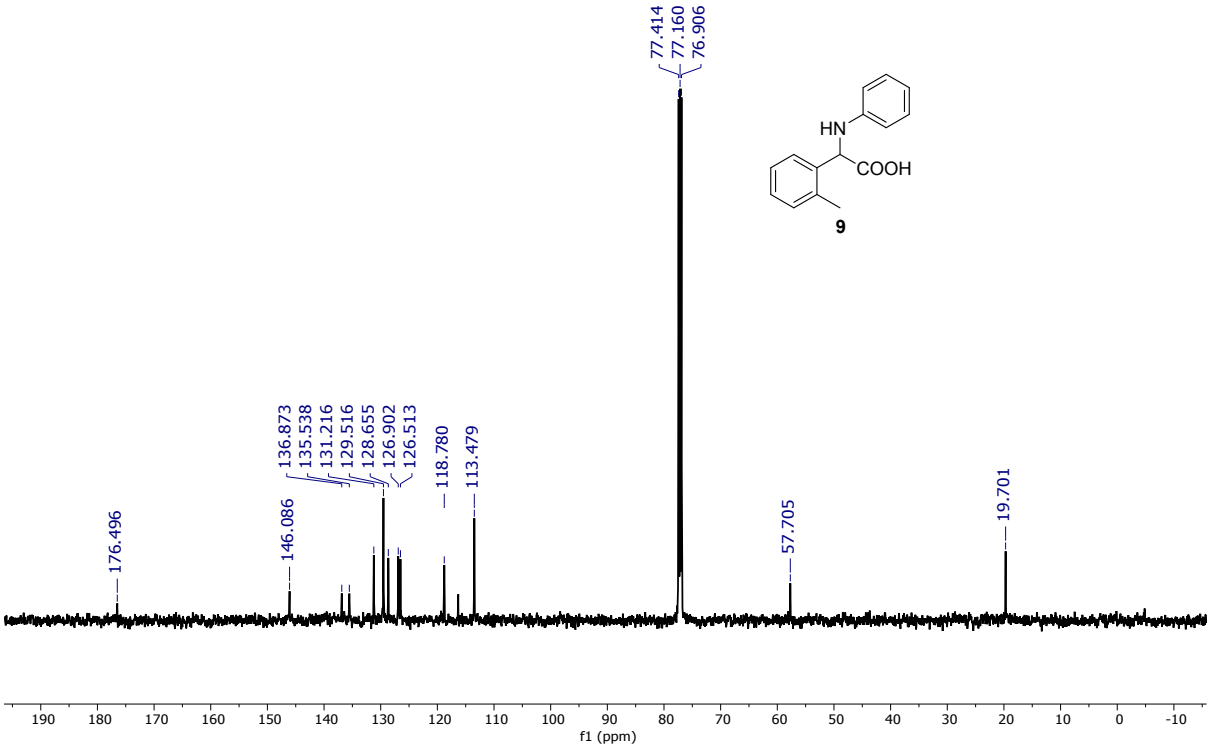
^{13}C NMR (126 MHz, $CDCl_3$):



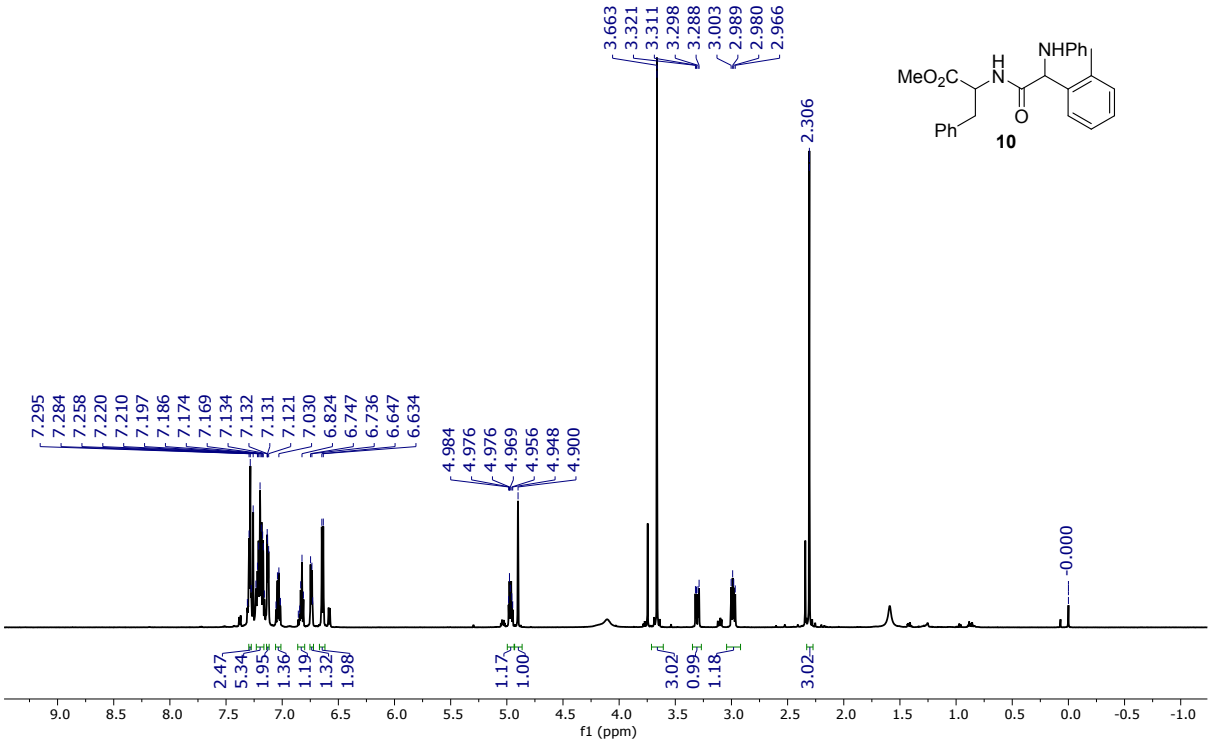
^{1}H NMR (500 MHz, $CDCl_3$):



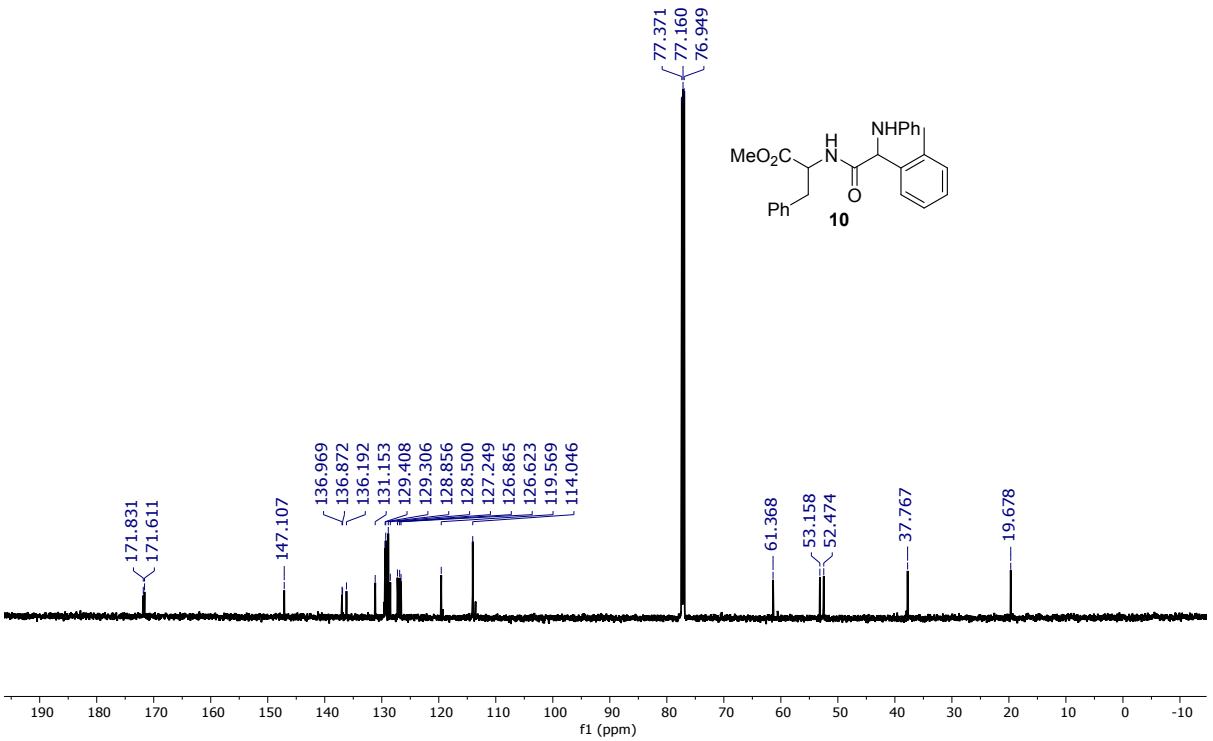
^{13}C NMR (126 MHz, $CDCl_3$):



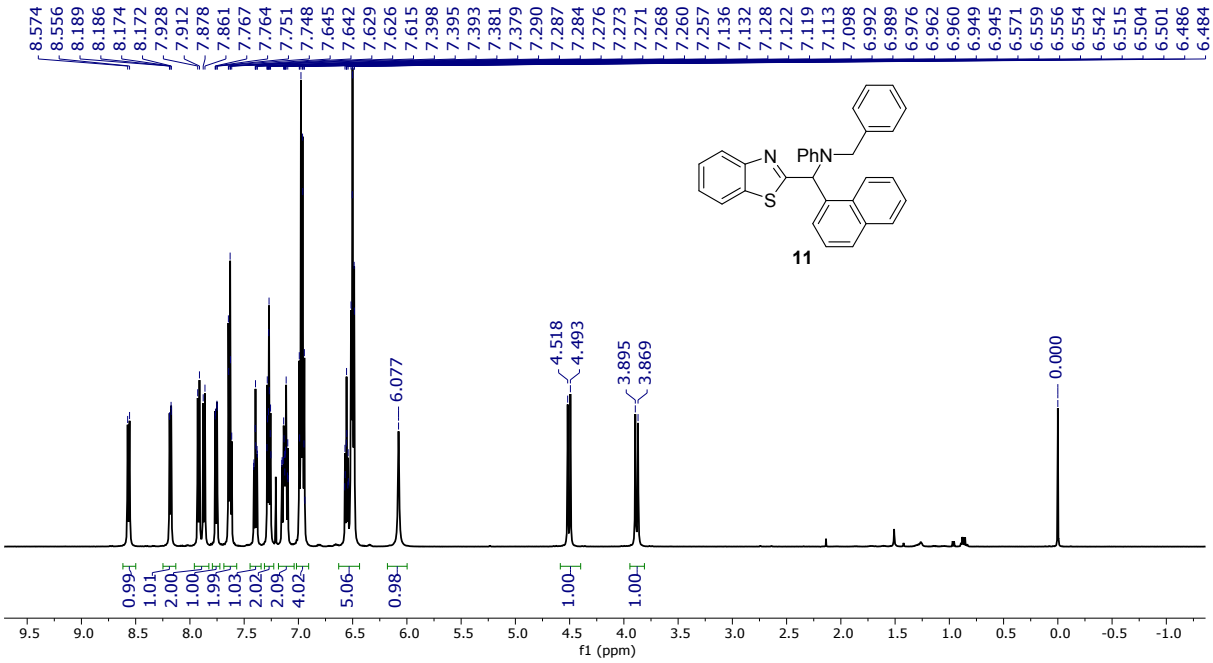
^{1}H NMR (600 MHz, $CDCl_3$):



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



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



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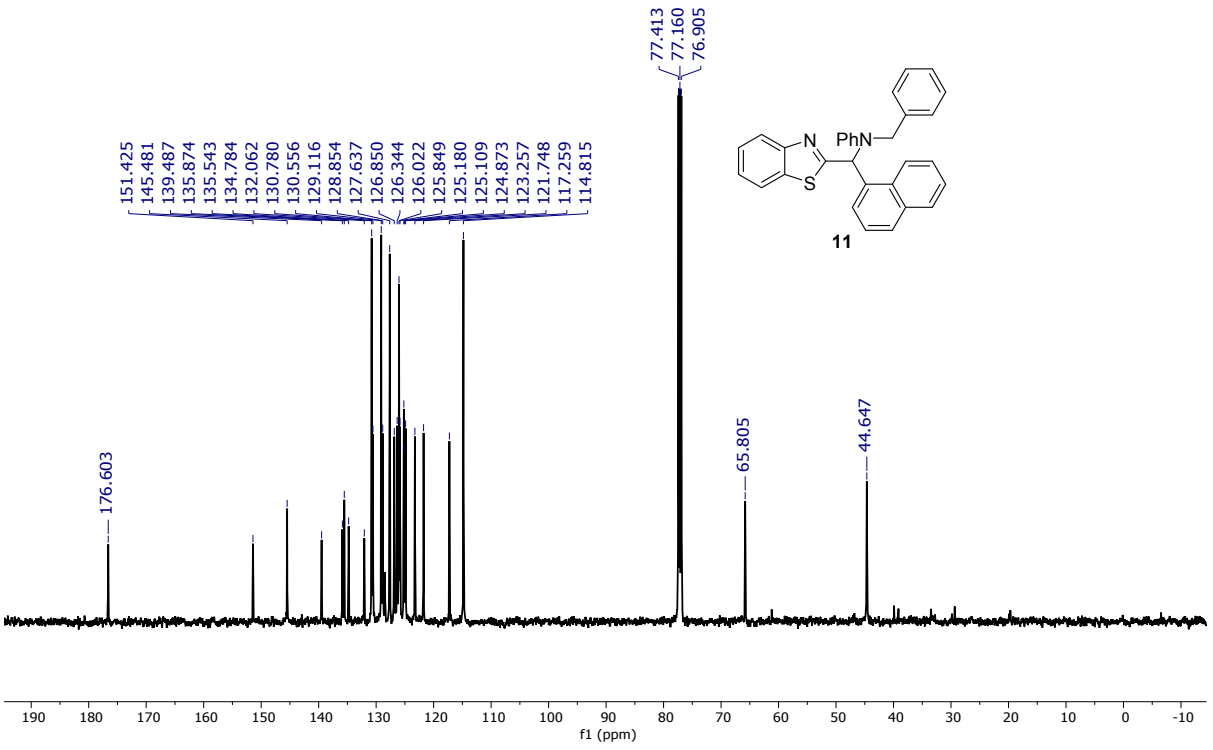

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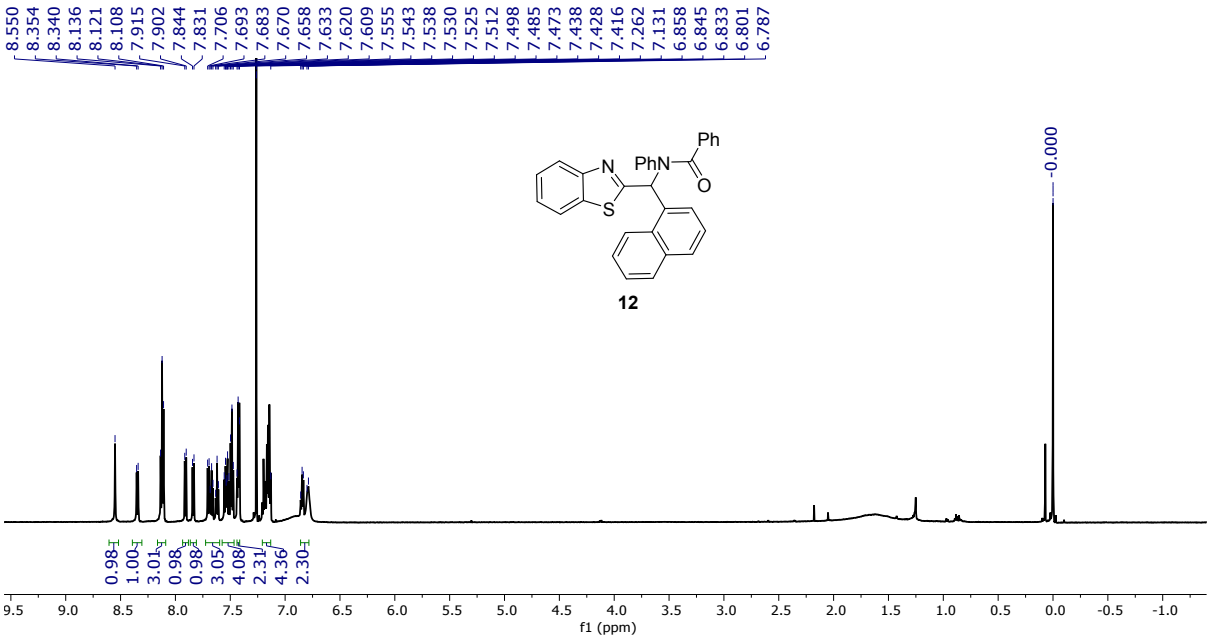

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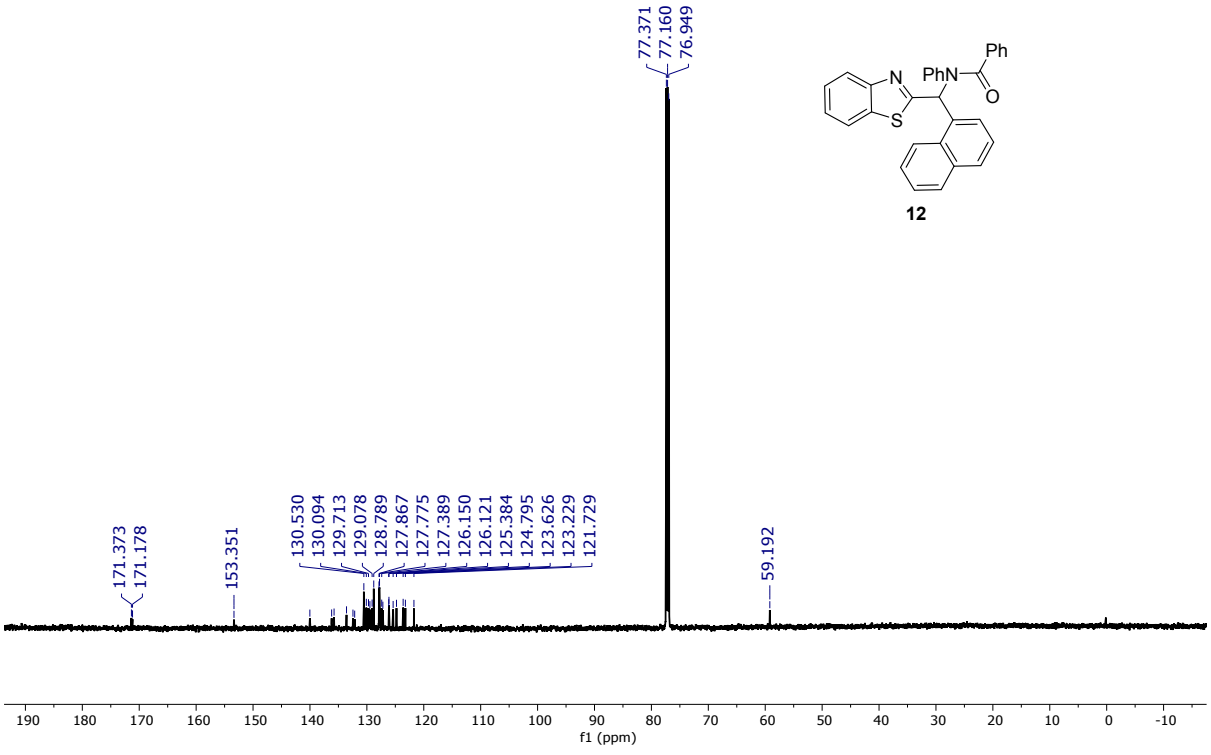

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