Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Ni(II)-Catalyzed Oxidative Deamination of Benzyl Amines with Water

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General experimental details

All reactions were carried out under nitrogen atmosphere using standard Schlenk–line techniques unless stated otherwise. Glasswares were flame–dried under vacuum prior to use. ^{1}H, ^{13}C and ^{19}F NMR spectra were obtained on JEOL JNM–LA 500 MHz and JEOL JNM–LA 400 MHz spectrometers. Chemical shift values were referenced to the residual signals of the deuterated solvents. ESI–MS were recorded on a Waters Micro mass Quattro Micro triple–quadruple mass spectrometer. Elemental analyses were performed on a Thermoquest EA1110 CHNS/O analyzer. The crystallized compound was washed several times with dry diethyl ether, powdered and dried in vacuum for at least 48 h prior to elemental analyses. IR experiment was carried out using Mettler Toledo ReactIR instrument. UV−visible spectra were recorded using a JASCO V−670 UV−vis absorption spectrophotometer. GC–MS experiment was performed on an Agilent 7890A GC and 5975C MS system. ICP-MS analysis was performed using Agilent 8900 ICP-MS Triple Quad system.

Materials

Solvents were dried by conventional methods, distilled under nitrogen and deoxygenated prior to use. Anhydrous $NiCp_2$, primary amines, 2-aminothiophenol and $H_2{}^{18}O$ (97% ^{18}O-labeled) were purchased from Sigma-Aldrich. NMR solvents such as D_2O, $CDCl_3$, Methanol-D_4 were purchased from Cambridge Isotope Laboratories, and ultrapure water were purchased from SD Fine-Chemicals. $PhCD_2NH_2$ was synthesized according to the literature method. [1]

X-ray data collections and refinement

Single-crystal X-ray studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 100(2) K using graphite monochromatic Mo K_α radiation (λ_α = 0.71073 A). The frames were indexed, integrated, and scaled using the SMART and SAINT software packages,[2] and the data were corrected for absorption using the SADABS program.[3] The structures were solved and refined with the SHELX[4] and OLEX2[5] suites of programs, while additional crystallographic calculations were performed by the program PLATON.[6] All hydrogen atoms were included in the final stages of the refinement and were refined with a typical “riding model”. Disordered solvent molecules in the unit cell have been masked using Olex-2 mask program. The crystallographic figures have been generated using Diamond 3.1e[7] software. CCDC numbers 2209272-2209275 contains supplementary crystallographic data for all the

compounds. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data and refinement parameters for [**L^1.H**], **1**, **2** and **3**.

	[L^1.H]	1	2	3
Empirical formula	$C_{16}H_{17}N_3O_3S$	$C_{18}H_{20}N_3NiO_4S$	$C_{21}H_{20}BrCl_2N_3Ni$	$C_{31}H_{28}Br_2Cl_2N_6Ni$
Formula Weight	331.38	433.14	523.92	774.02
Crystal System	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space Group	$P2_1/c$	C2/c	$P2_1/c$	P-1
a (Å)	16.3160(12)	10.6620(4)	10.0731(2)	13.746(3)
b (Å)	5.3605(4)	22.8698(9)	20.1087(5)	16.148(4)
c (Å)	17.8044(15)	14.5817(5)	10.8313(3)	16.995(4)
α (deg)	90	90	90	65.764(7)
β (deg)	102.726(3)	95.6180(10)	105.3900(10)	69.468(6)
γ (deg)	90	90	90	74.868(5)
V (Å^3)	1519.0(2)	3538.5(2)	2115.28(9)	3191.2(13)
Z	4	8	4	4
ρ_{calcd} (g cm^{-3})	1.449	1.626	1.645	1.611
μ (mm–1)	0.233	1.246	3.071	3.311
F(000)	696.0	1800.0	1056.0	1552.0
Index ranges	-21 ≤ h ≤ 21, -7 ≤ k ≤ 7, -23 ≤ l ≤ 23	-14 ≤ h ≤ 14, -30 ≤ k ≤ 30, -19 ≤ l ≤ 19	-13 ≤ h ≤ 13, -26 ≤ k ≤ 26, -14 ≤ l ≤ 14	-18 ≤ h ≤ 18, -21 ≤ k ≤ 21, -22 ≤ l ≤ 22,
Reflections				
Collected	23297	26661	33907	47313
Independent	3765	4399	5250	15929
2Θ range for data collection/°	4.69 to 56.608	5.282 to 56.626	5.314 to 56.628	4.546 to 56.926
Data/restraints/parameters	3765/0/188	4399/0/233	5250/638/426	15929/814/796
GOF	1.092	1.068	1.044	1.034
R_{int}	0.0739	0.0320	0.0541	
Final R indices	R_1 = 0.0427	R_1 = 0.0318	R_1 = 0.0360	R_1 = 0.0655
[I > 2σ(I)][a]	wR_2 = 0.1237	wR_2 = 0.0871	wR_2 = 0.0719	wR_2 = 0.1726
R indices (all data)[a]	R_1 = 0.0724, wR_2 = 0.1652	R_1 = 0.0374 wR_2 = 0.0914	R_1 = 0.0558 wR_2 = 0.0832	R_1 = 0.1094 wR_2 = 0.2051
CCDC No.	2209272	2209273	2209274	2209275

[a] $R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma|F_o^2|^2]^{1/2}$

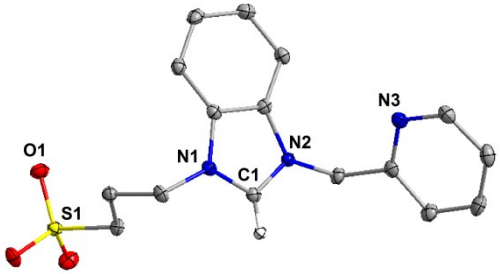


Figure S1. Molecular structure of **[L[1].H]** with important atoms labeled. Hydrogen atoms except the imidiazolium proton are omitted for the sake of clarity. Thermal ellipsoids are drawn at the 40% probability level.

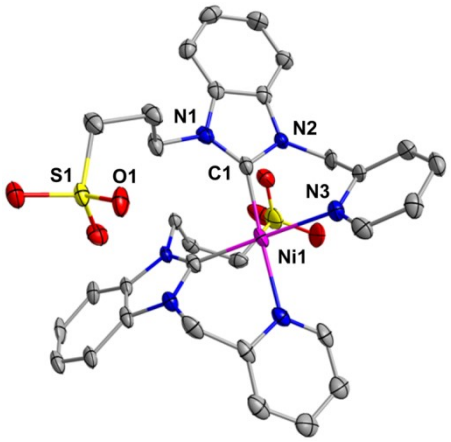


Figure S2. Molecular structure of **1** with important atoms labelled. All hydrogen atoms have been omitted for the sake of clarity. Thermal ellipsoids are drawn at the 40% probability level.

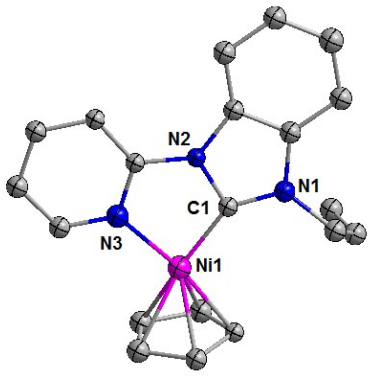


Figure S3. Molecular structure of [**2**-Br]$^{+}$ with important atoms labelled. All hydrogen atoms have been omitted for the sake of clarity. Thermal ellipsoids are drawn at the 40% probability level.

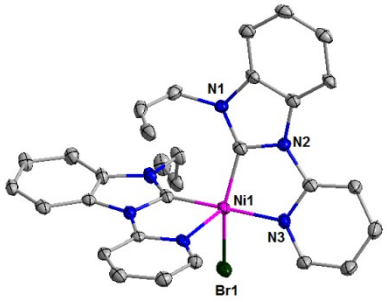
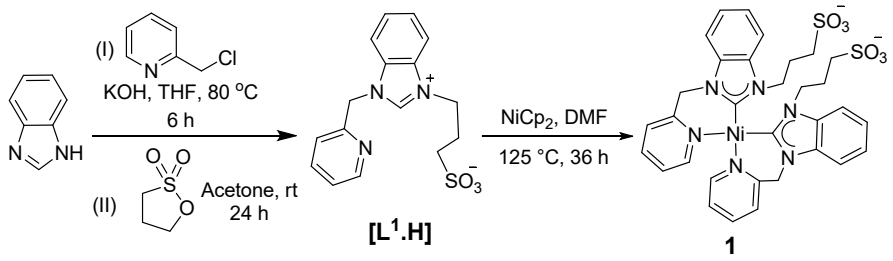


Figure S4. Molecular structure of [**3**-Br]$^{+}$ with important atoms labelled. All hydrogen atoms have been omitted for the sake of clarity. Thermal ellipsoids are drawn at the 40% probability level.



Scheme S1. Synthesis of **[L^{1}.H]** and **1**.

Synthesis of [L^{1}.H]

A round bottom flask charged with Benzimidazole (1.00 g, 8.46 mmol), picolyl chloride (1.19 g, 9.31 mmol), and KOH (1.04 g, 18.62 mmol, 2.2 equivalents) were dissolved in 15 mL THF and heated at 80 °C for 6 h. The reaction mixture was cooled to room temperature, and volatiles were evaporated under reduced pressure. In the resulting mixture water was added and extracted with dichloromethane (15 mL×3). After washing with water, the combined organic phases were dried over anhydrous $MgSO_4$, filtered, and solvents were removed under reduced pressure. Crude 1-(pyridin-2-ylmethyl)-1H-benzo[d]imidazole was obtained as yellow solid which was used in next step without further purification. In next step 1-(pyridin-2-ylmethyl)-1H-benzo[d]imidazole, 1,3-Propanesultone (1.09 mL, 12.69 mmol) and 15 mL dry acetone were taken in round bottom flask and stirred for 24h at room temperature. A light pink precipitate was formed, washes with acetone and finally dried in vacuum. Suitable crystals for X-ray diffraction were grown from concentrated methanolic solution of **[L^{1}.H]** layered by diethyl ether in 8 mm o.d. glass tube. Yield: 2.38 g (85%). ^{1}H NMR (400 MHz, CD_3OD): δ = 9.72 (s, 1H, CH-Im), 8.46 (d, *J* =8.2 Hz, 1H, ArH), 8.05 (d, *J* = 8.3 Hz, 1H, ArH), 7.87-7.83 (m, 1H, ArH), 7.80 (d, *J* = 8.0 Hz, 1H, ArH), 7.66-7.60 (m, 3H,

ArH), 7.34 (t, *J* = 7.4 Hz,1H, ArH), 5.87 (s, 2H, CH_2), 4.79 (t, *J* = 7.2 Hz, 2H, CH_2), 2.90 (t, *J* = 6.9 Hz, 2H, CH_2), 2.46 (q, *J* =7.0 Hz, 2H, CH_2); ^{13}C NMR (101 MHz, CD_3OD): δ = 155.98, 148.90, 137.69, 129.25, 128.98, 122.97, 122.90, 122.18, 121.77, 121.68, 121.43, 118.77, 45.55, 43.23, 39.79, 24.06; ESI–MS: *m/z* 332.1061 (*z* = 1) $[M+H]^+$. (CCDC No. 2209272)

Synthesis of 1

In a flame dried Schlenk flask **[L^1.H]** (100 mg, 0.302 mmol), and $NiCp_2$ (29 mg, 0.151 mmol) were dissolved in 10 mL dry DMF. The mixture was allowed to heat at 125 ºC for 36 h at N_2 atmosphere. The solvent was evaporated under reduced pressure. The crude compound was re-dissolved in 15 mL methanol and the greenish brown mixture was filtered through a small pad of celite. The solution was concentrated via vacuum, and 15 mL diethyl ether was added to induce precipitation. The supernatant was removed via cannula filtration, and the precipitate was further washed with diethyl ether (3x10 mL). The precipitate was dried under vacuum to afford **1** as a yellow solid. Yield: 156 mg (72%). Using similar volume of dry DMF (10 mL), 304 mg of **1** (70% yield) was synthesized from **[L^1.H]** (200 mg, 0.604 mmol) and $NiCp_2$ (59 mg, 0.301 mmol). Suitable crystals for X-ray diffraction were grown from concentrated methanolic solution of **1** layered by diethyl ether in 8 mm o.d. vacuum−sealed glass tube.^1H NMR (400 MHz, CD_3OD): δ = 8.43 (d, *J* = 8.26 Hz, 1H, ArH), 7.74-7.70 (m, 1H, ArH), 7.61 (t, *J* =7.8 Hz, 1H, ArH), 7.29-7.19 (m, 4H, ArH), 7.09-7.05 (m, 1H, ArH), 5.17 (s, 2H, CH_2), 4.09 (t, *J* =7.1 Hz, 2H, CH_2), 2.86 (t, *J* =7.2 Hz, 2H, CH_2), 2.21 (q, *J* = 7.0 Hz, 2H, CH_2); ^{13}C NMR (101 MHz, CD_3OD): δ = 163.50, 154.61, 149.48, 148.22, 143.48, 142.73, 136.88, 122.18, 121.77,121.43, 118.77, 110.25, 53.62, 45.68, 39.89, 25.50; ESI–MS: *m/z* 719.1349 (*z* = 1) [**1**+H]$^+$. (CCDC No. 2209273)

Synthesis of 2

In a flame dried Schlenk flask 3-allyl-1-(pyridin-2-yl)-1H-benzo[d]imidazol-3-ium bromide (100 mg, 0.316 mmol) was dissolved in 15 mL THF. Then $NiCp_2$ (60.44 mg, 0.320 mmol) was added to the mixture and the resulting mixture was allowed to heat at 80 ºC for 10 h. The solvent was evaporated under reduced pressure. The crude compound was re-dissolved in 15 mL DCM and the greenish mixture was filtered through a small pad of celite. The solution was concentrated via vacuum, and 15 mL n-hexane was added to induce precipitation. The supernatant was removed via cannula filtration, and the precipitate was further washed with petroleum ether (3x10 mL). The precipitate was dried under vacuum to afford **2** as a green solid. Yield: 103 mg (75%). Suitable crystals for X-ray diffraction were grown from concentrated DCM solution of **2** layered by petroleum ether in 8 mm o.d. vacuum−sealed glass. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.66-8.57 (m, 3H, Ar-H), 8.08-8.06

(m, 1H, Ar-H), 7.77-7.75 (m, 1H, Ar-H), 7.66-7.63 (2H, m, Ar-H), 7.48-7.46 (m, 1H, Ar-H), 6.20-6.14 (m, 1H, =CH-), 6.58-6.53 (m, 2H, CH_2) 5.44 (d, *J* = 10.3 Hz, 2H), 4.67 (s, 5H, Cp); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.25, 149.04, 148.09, 141.58, 140.78, 131.73, 130.21, 129.64, 128.25, 127.81, 124.91, 122.19, 117.74, 117.30, 113.54, 50.57; ESI–MS: *m/z* 358.0854 (*z* = 1) [**2**-Br]$^+$. (CCDC No. 2209274)

Synthesis of 3

In a flame dried Schlenk flask 3-allyl-1-(pyridin-2-yl)-1H-benzo[d]imidazol-3-ium bromide (100 mg, 0.316 mmol) was dissolved in 15 mL THF and cooled to -40°C. KO^{t}Bu(42 mg, 0.381 mmol) was added to this solution and the mixture was slowly taken at room temperature. Then $NiBr_2$ (34.5 mg, 0.158 mmol) was added to the mixture and the resulting mixture was allowed to reflux at 80 ºC for 14 h. The solvent was evaporated under reduced pressure. The crude compound was re-dissolved in 15 mL DCM and the brown mixture was filtered through a small pad of celite. The solution was concentrated via vacuum, and 15 mL n-hexane was added to induce precipitation. The supernatant was removed via cannula filtration, and the precipitate was further washed with petroleum ether (3x10 mL). The precipitate was dried under vacuum to afford **3** as a brown solid. Yield: 152 mg (70%). Suitable crystals for X-ray diffraction were grown from concentrated DCM solution of **3** layered by petroleum ether in 8 mm o.d. vacuum−sealed glass. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58-8.50 (m, 3H, ArH), 8.00(t, *J* = 8.5 Hz, 1H, ArH), 7.70-7.68 (m, 1H, ArH), 7.59-7.57 (m, 2H, ArH), 7.42-7.40 (m, 1H, ArH), 6.13-6.08(m, 1H, =CH-), 5.51-5.36 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.48, 146.81, 145.86, 139.35, 138.55, 129.50, 127.98, 127.41, 126.02, 125.58, 122.68, 119.96, 115.51, 111.31, 48.34; ESI–MS: *m/z* 607.0758 (*z* = 1) [**3**-Br]$^+$. (CCDC No. 2209275)

Synthesis of 4

Complex **4** was synthesized according to literature method.[8] In a flame dried Schlenk flask 3-(2-methoxyethyl)-1-(pyridin-2-ylmethyl)-1H-benzo[d]imidazol-3-ium bromide (242 mg, 0.70 mmol) was dissolved in 15 mL dry THF and cooled to 0°C. ^{n}BuLi (1.05 mmol, 1.6 M in hexane, 1.5 equivalents) was added to this solution followed by addition of anhydrous $NiCl_2$ (45 mg, 0.35 mmol, 0.5 equivalents). The mixture was allowed to attain room temperature and then refluxed for 36 h. The volatiles were evaporated and crude solid was re-dissolved in 15 mL dichloromethane and the yellow mixture was filtered through a small pad of celite. The filtrate was concentrated and 15 mL of n-hexane was added with stirring to induce precipitation. The supernatant solution was discarded by cannula filtration, and the precipitate was further washed with petroleum ether (3×10 mL). Finally, the precipitate was

dried under vacuum to afford **4** as a yellow solid. Yield: 429 mg (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.24 (m, 5H, ArH), 7.09-6.94 (m, 3H, ArH), 6.83 (d, *J* = 7.7 Hz, 1H, ArH), 5.04 (s, 2H, CH_2), 7.07 (t, *J* = 5.6 Hz, 2H, CH_2), 3.68 (t, *J* = 5.6 Hz, 2H, CH_2), 3.32 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.58, 136.42, 129.99, 129.27, 128.80, 127.72, 127.55, 121.42, 121.28, 108.48, 108.29, 59.05, 44.96, 41.41; Anal. Calcd for $C_{34}H_{38}Br_2N_4O_2Ni_1$: C, 54.39; H, 5.11; N, 7.47. Found: C, 54.09; H, 4.94; N, 7.25.

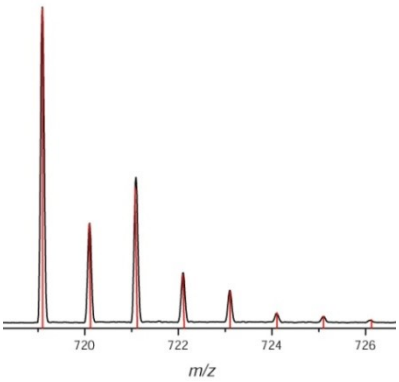


Figure S5. Experimental (black) and simulated (red) ESI-MS for molecular ion at *m/z* 719.1349 (*z* = 1) for [**1**+H]$^+$.

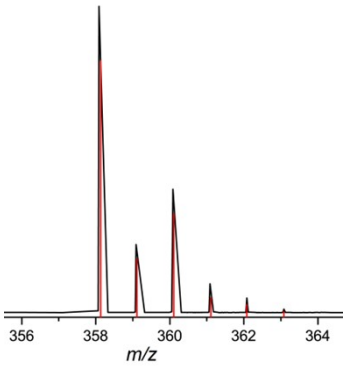


Figure S6. Experimental (black) and simulated (red) ESI-MS for molecular ion at *m/z* 358.0854 (*z* = 1) for [**2**-Br]$^+$.

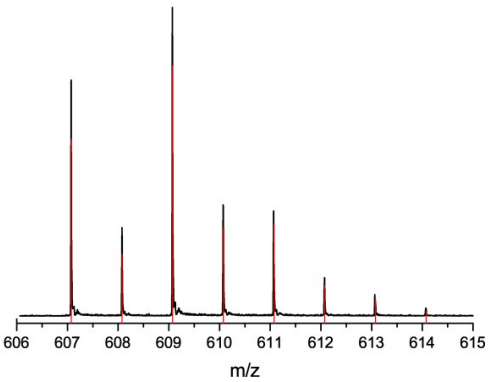


Figure S7. Experimental (black) and simulated (red) ESI-MS for molecular ion at *m/z* 607.0758 (*z* = 1) for [**3**-Br]$^+$.

Characterization of [L^1.H] and complexes 1- 4 by NMR spectroscopy

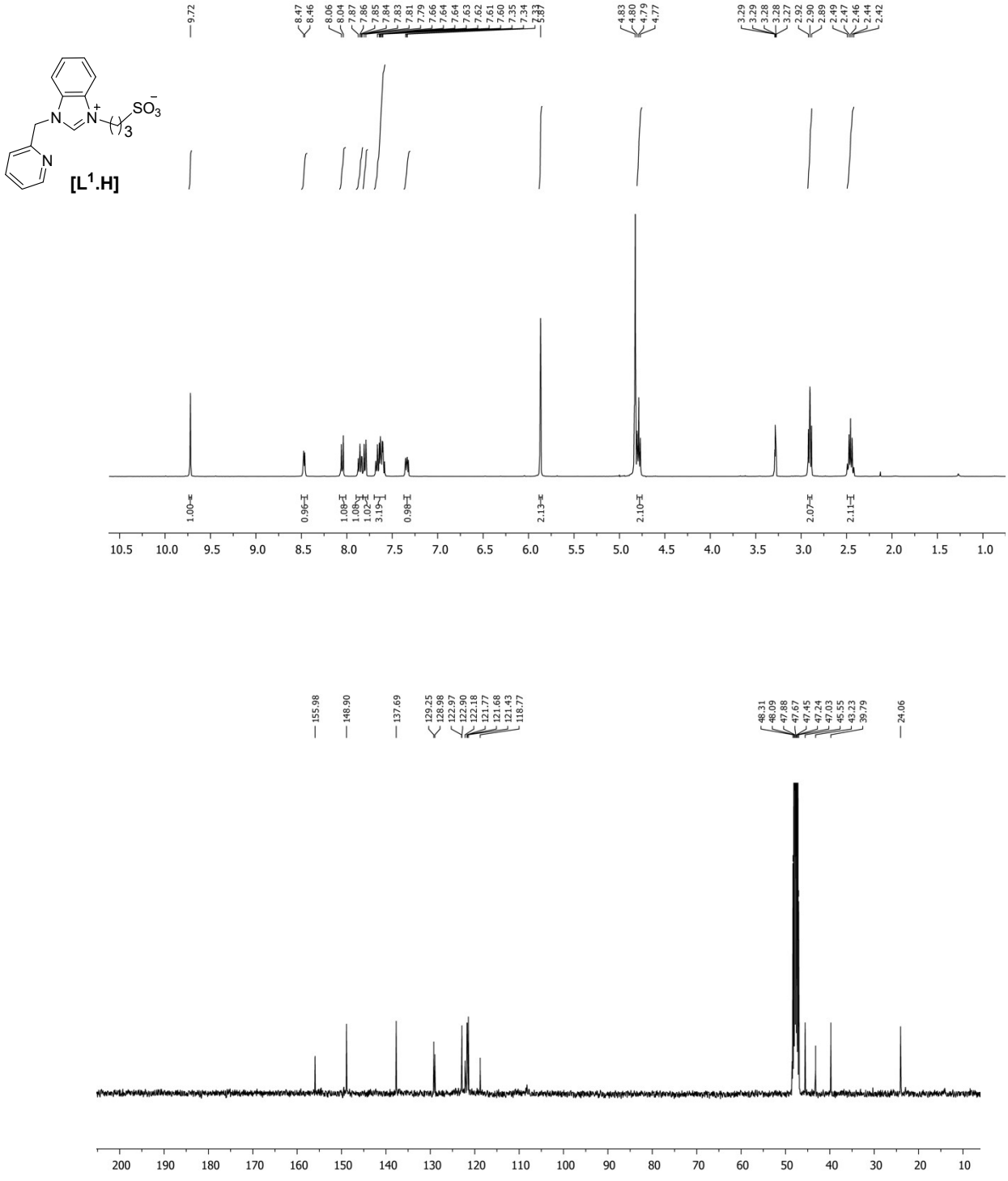


Figure S8. ^{1}H NMR and ^{13}C NMR spectrum for **[L^1.H]** in CD_3OD.

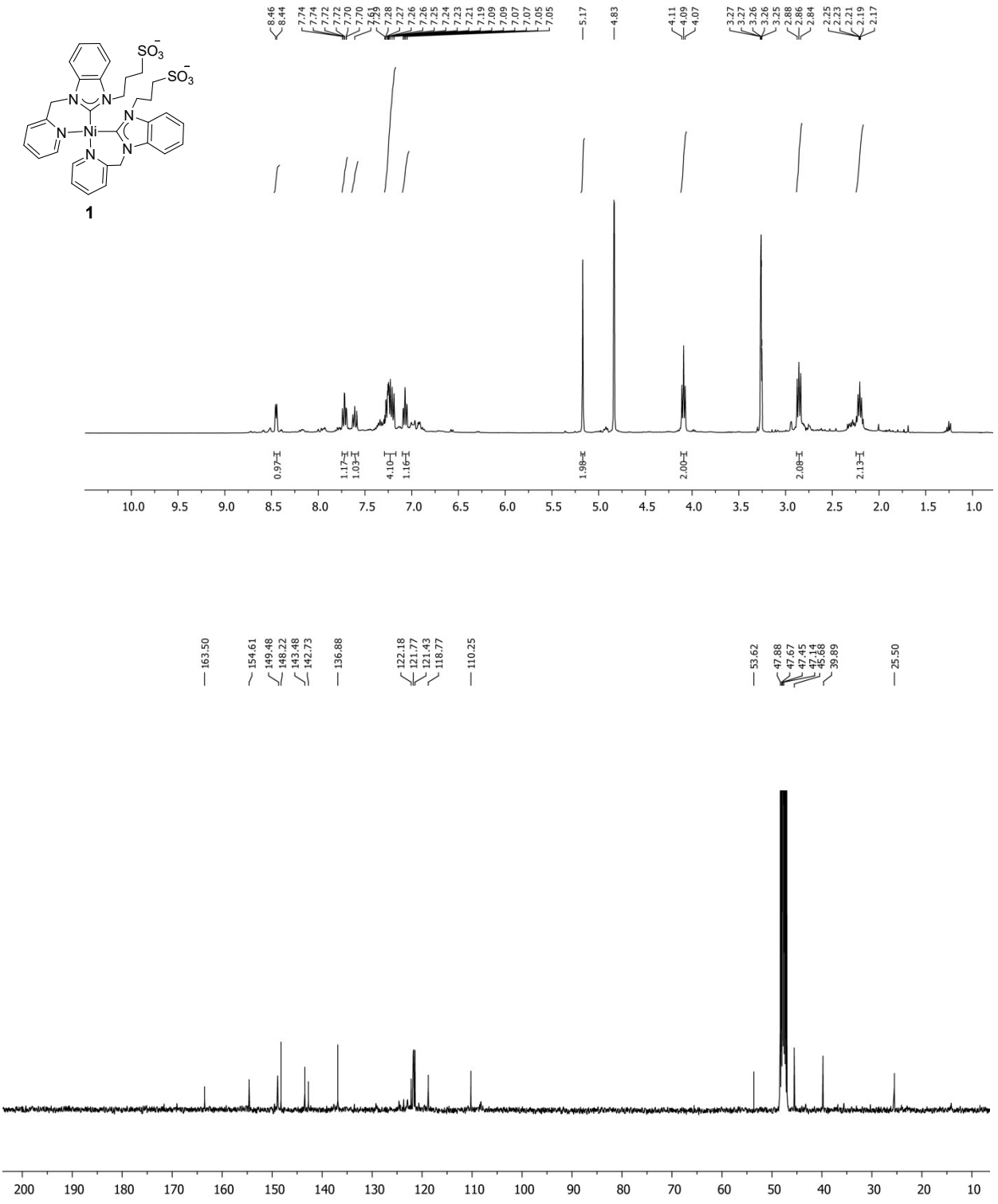


Figure S9. ^{1}H NMR and ^{13}C NMR spectrum for **1** in CD_3OD.

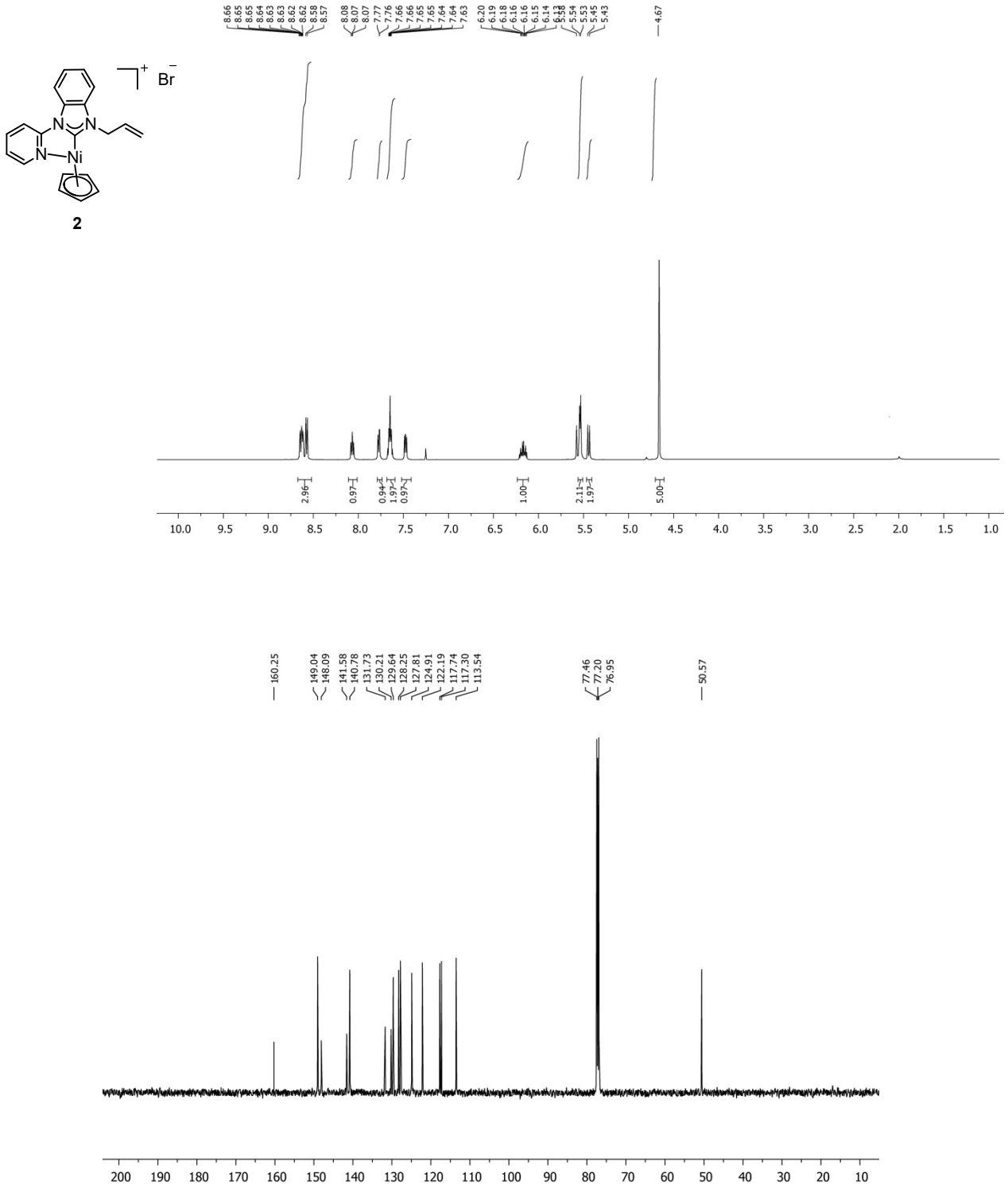


Figure S10. ^{1}H NMR and ^{13}C NMR spectrum for **2** in $CDCl_3$.

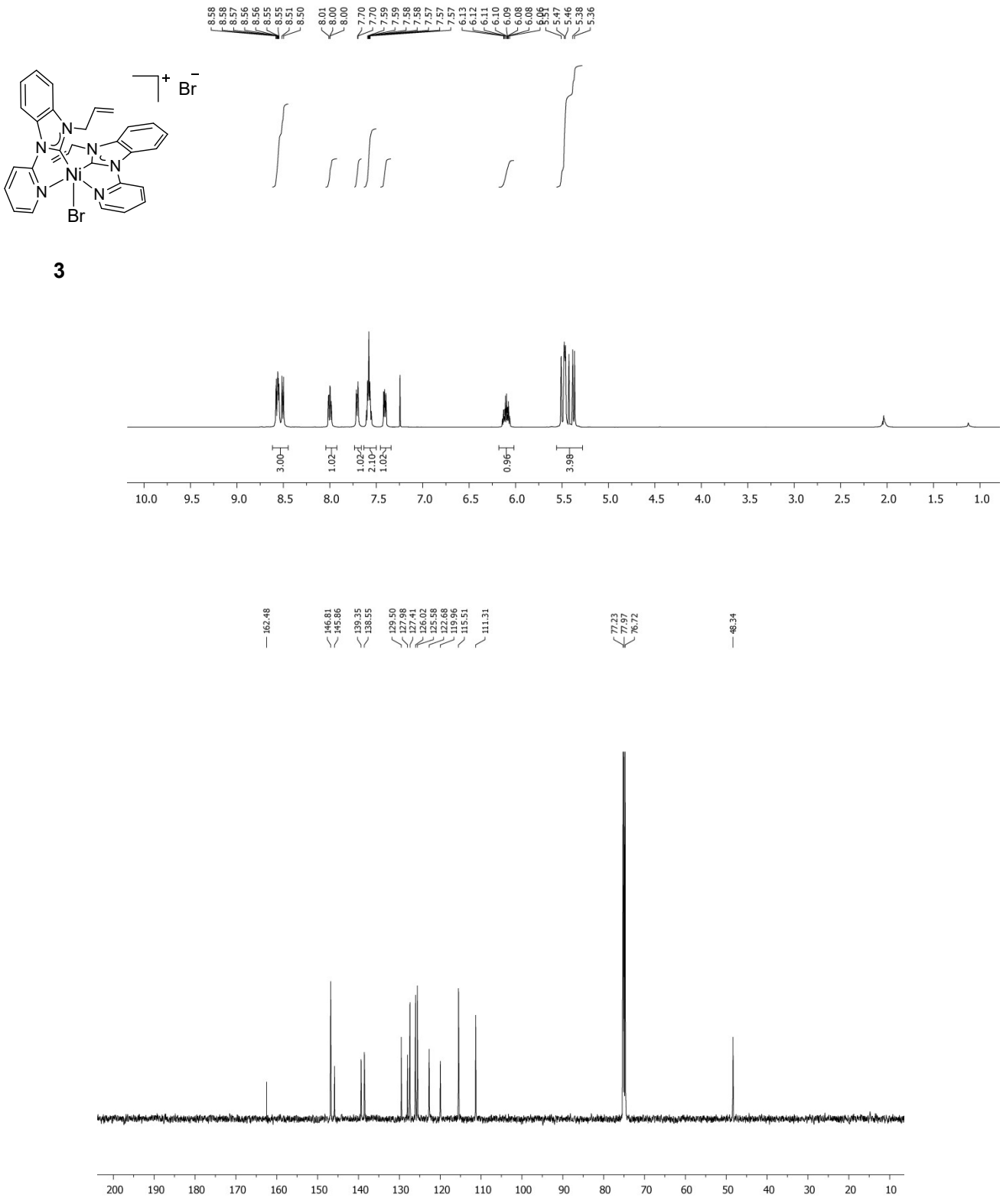


Figure S11. ^{1}H NMR and ^{13}C NMR spectrum for **3** in $CDCl_3$.

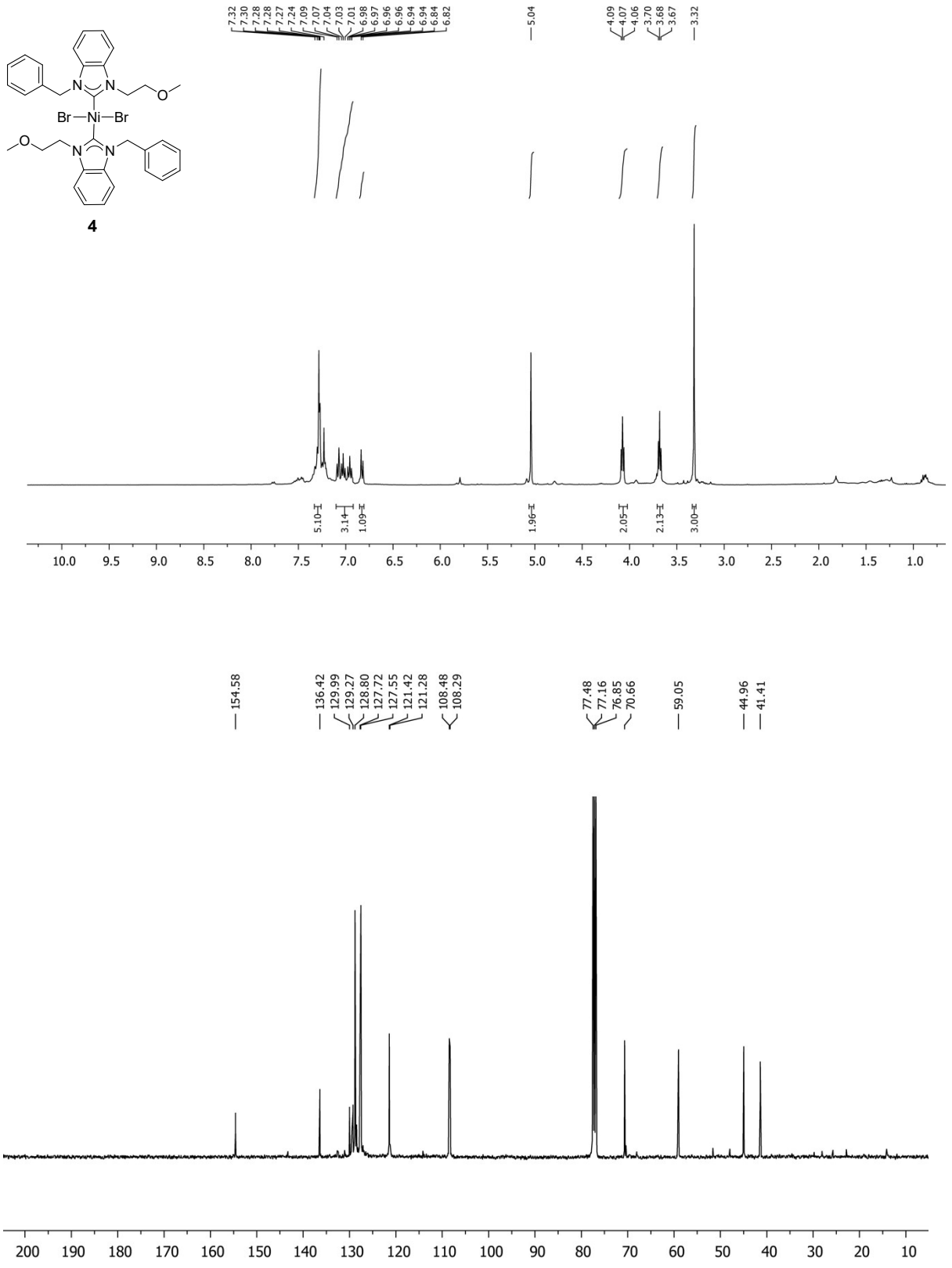
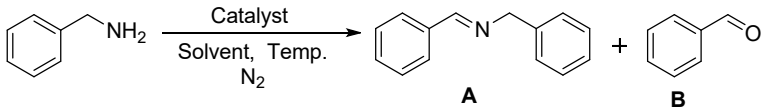


Figure S12. ^{1}H NMR and ^{13}C NMR spectrum for **4** in $CDCl_3$.

Table S2. Reaction optimization for imine formation

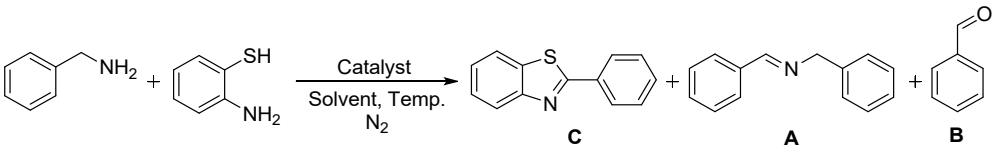


A B

Entry	Catalyst	Catalyst Loading (mol%)	Solvent (2 mL)	Temp.(°C)	Time (h)	Yield[a] (%) A	Yield[a] (%) B
1	1	5	^{i}PrOH/H_2O (1:1 v/v)	100	24	75	5
2	1	5	^{i}PrOH/H_2O (1:1 v/v)	100	12	68	7
3	1	5	H_2O	90	12	89	0
4	1	3	H_2O	90	24	87	0
5	1	3	H_2O	85	12	87	3
6	1	2	H_2O	100	24	89	0
7	1	2	H_2O	90	18	88	0
8	1	2	H_2O	85	12	86	0
9	1	2	H_2O	50	12	49	3
10	1	2	H_2O	rt	24	9	5
11	1	2	H_2O	rt	12	6	4
12	1	1	H_2O	85	12	70	0
13	1	0.5	H_2O	85	12	61	5
14[b]	-	-	H_2O	85	12	9	4
15	1	2	DMF	85	12	19	11
16	1	2	MeCN/H_2O (1:1 v/v)	80	12	27	2
17	1	2	MeCN	80	12	21	4
18	1	2	^{i}PrOH	85	12	26	6
19	1	2	DMSO	90	12	22	12
20	1	2	1,4- Dioxane	90	12	14	7
21	1	2	THF	75	12	18	3
22	1	2	DCM	40	12	5	2
23	2	2	H_2O	85	12	34	8
24	3	2	H_2O	85	12	38	4
25	4	2	H_2O	85	12	35	7
26	$NiCl_2$	2	H_2O	85	12	31	5
27	$Ni(acac)_2$	2	H_2O	85	12	28	6
28	$Ni(Cp)_2$	2	H_2O	85	12	24	3
29	$Ni(NO_3).6H_2O$	2	H_2O	85	12	40	7

[a]Yields are determined by GC–MS using mesitylene as an internal standard.
[b]Reaction was performed in the absence of catalyst.

Table S3. Reaction optimization for benzothiazole formation

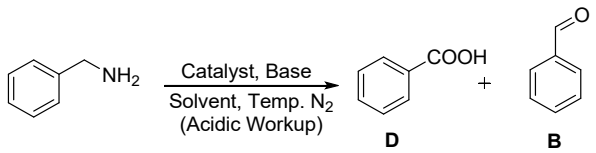


C A B

Entry	Catalyst	Catalyst Loading (mol%)	Solvent (2 mL)	Temp. (°C)	Time (h)	Yield[a] (%) C	Yield[a] (%) A	Yield[a] (%) B
1	1	5	^{i}PrOH/H_2O (1:1 v/v)	100	24	71	9	3
2	1	5	^{i}PrOH/H_2O (1:1 v/v)	100	18	67	10	6
3	1	5	H_2O	85	12	86	10	0
4	1	3	H_2O	100	24	84	7	0
5	1	3	H_2O	80	12	82	8	0
6	1	2	H_2O	100	24	83	10	0
7	1	2	H_2O	90	18	82	9	0
8	1	2	H_2O	100	12	82	8	0
9	1	2	H_2O	85	12	75	11	0
10	1	2	H_2O	50	12	46	13	7
11	1	2	H_2O	rt	24	9	6	4
12	1	2	H_2O	rt	12	6	4	5
13	1	1	H_2O	100	12	61	12	4
14	1	0.5	H_2O	100	12	54	15	3
15[b]	-	-	H_2O	100	12	8	6	3
16	1	2	DMF	100	12	45	11	2
17	1	2	MeCN/H_2O (1:1 v/v)	100	12	25	12	0
18	1	2	MeCN	80	12	18	14	2
19	1	2	^{i}PrOH	85	12	26	16	4
20	1	2	DMSO	90	12	43	12	6
21	1	2	1,4- Dioxane	90	12	21	17	0
22	1	2	THF	75	12	31	13	7
23	1	2	DCM	40	12	5	4	4
24	2	2	H_2O	100	12	32	7	3
25	3	2	H_2O	100	12	37	5	2
26	4	2	H_2O	100	12	38	8	4
27	$NiCl_2$	2	H_2O	100	12	34	15	0
28	$Ni(acac)_2$	2	H_2O	100	12	27	16	5
29	$Ni(cp)_2$	2	H_2O	100	12	24	13	3
30	$Ni(NO_3).6H_2O$	2	H_2O	100	12	36	17	0

[a]Yields are determined by GC–MS using mesitylene as an internal standard.
[b]Reaction was performed in the absence of catalyst.

Table S4. Reaction optimization for acid formation



Entry	Catalyst	Catalyst Loading (mol%)	Solvent (2 mL)	Base (equiv.)	Temp.(°C)	Time (h)	Yield[a] (%) D	Yield[a] (%) B
1	1	5	^{i}PrOH/H_2O (1:1 v/v)	NaOH (1)	120	24	79	1
2	1	5	^{i}PrOH/H_2O (1:1 v/v)	NaOH (1)	120	18	69	3
3	1	5	H_2O	K_2CO_3 (1)	85	24	71	0
4	1	3	H_2O	NEt_3 (1)	100	18	65	7
5	1	3	H_2O	NaOAC (1)	80	24	78	0
6	1	2	H_2O	NaOEt (1)	100	24	73	4
7	1	2	H_2O	Na_2CO_3 (1)	90	24	82	0
8	1	2	H_2O	NaOH (1)	100	24	87	0
9	1	2	H_2O	NaOH (1)	85	24	71	3
10	1	2	H_2O	NaOH (1)	50	24	46	4
11	1	2	H_2O	NaOH (1)	rt	24	19	6
12	1	2	H_2O	NaOH (1)	rt	24	6	4
13	1	1	H_2O	NaOH (1)	100	24	61	7
14	1	2	H_2O	NaOH (0.7)	80	24	64	5
15				NaOH (0.5)	80	24	47	6
16	1	0.5	H_2O	NaOH (1)	100	24	54	15
17[b]	-	-	H_2O	NaOH (1)	100	24	9	6
18	1	2	DMF	NaOH (1)	100	24	28	10
19	1	2	MeCN/H_2O (1:1 v/v)	NaOH (1)	100	12	25	12
20	1	2	MeCN	NaOH (1)	80	24	18	9
21	1	2	^{i}PrOH	NaOH (1)	85	12	26	16
22	1	2	DMSO	NaOH (1)	100	24	43	12
23	1	2	1,4- Dioxane	NaOH (1)	90	24	21	17
24	1	2	THF	KOH (1)	75	24	31	13
25	1	2	DCM	NEt_3 (1)	40	24	5	4
26	2	2	H_2O	NaOH (1)	100	24	38	7
27	3	2	H_2O	NaOH (1)	100	24	41	5
28	4	2	H_2O	NaOH (1)	100	24	39	4
29	$NiCl_2$	2	H_2O	NaOH (1)	100	24	32	12
30	$Ni(acac)_2$	2	H_2O	NaOH (1)	100	24	41	8
31	$Ni(cp)_2$	2	H_2O	NaOH (1)	100	24	17	13
32	$Ni(NO_3).6H_2O$	2	H_2O	NaOH (1)	100	24	39	17

[a]Yields are determined by GC–MS using mesitylene as an internal standard.
[b]Reaction was performed in the absence of catalyst.

Detection of NH_3 gas

A mixture of benzylamine (1 mmol) and catalyst **1** (2 mol%) in 2 mL H_2O was heated at 85 ^oC and the evolved gas was trapped under heating condition in Socklet apparatus containing Nessler's reagent attached to the catalytic vessel. Brown precipitate of $HgO.Hg(NH_2)I$ gradually developed which intensified with time. This observation indicates that the evolved gas is NH_3. Similar phenomenon happened for benzothiazole formation and acid formation.

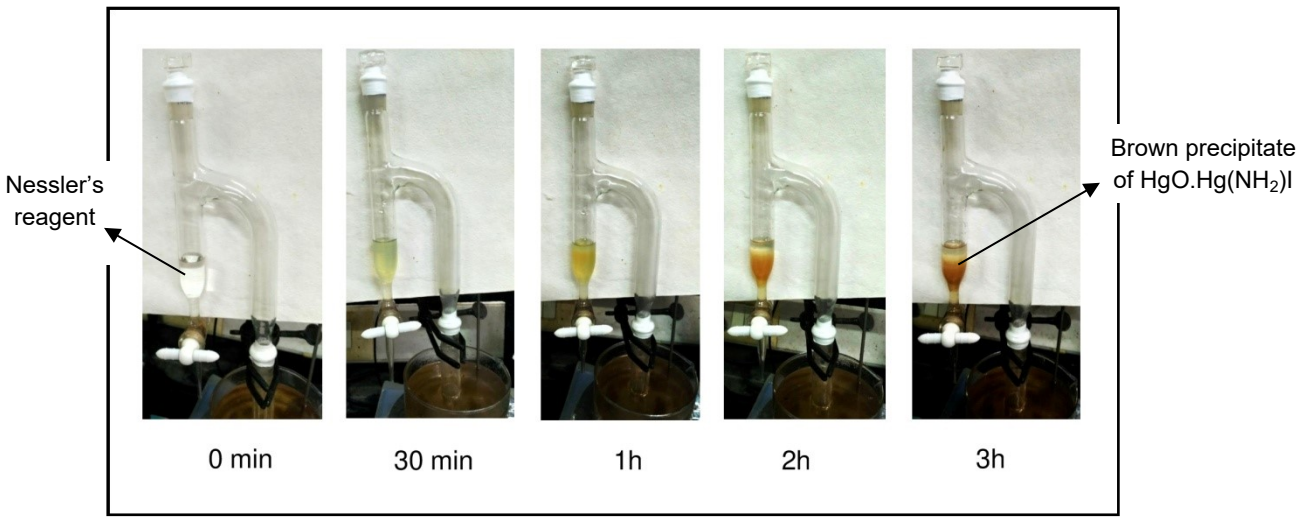


Figure S13. Ammonia trapping experiment.

Detection of H_2 gas

A mixture of benzylamine (1 mmol) and catalyst **1** (2 mol%) in 2 mL H_2O was heated at 85 ^oC in a Schlenk–tube with the headspace attached to a eudiometer. After 12 h of reaction it was cooled to room temperature and the gas collected in the eudiometer was subjected to GC analysis with a TCD detector, using N_2 as the carrier gas and the retention time matched with a sample collected from a hydrogen cylinder of 99.9% purity. Only H_2 was detected by GC while no other gases were present in detectable amounts as another gaseous by-product NH_3 remained dissolve in water under room temperature. In a parallel experiment, H_2 also identified by ^1H NMR spectroscopy. Characteristic peak at δ = 4.61 ppm in ^1H NMR spectrum closely resembles to spectrum of pure H_2 gas. Similar phenomenon observed for benzothiazole formation and acid formation.

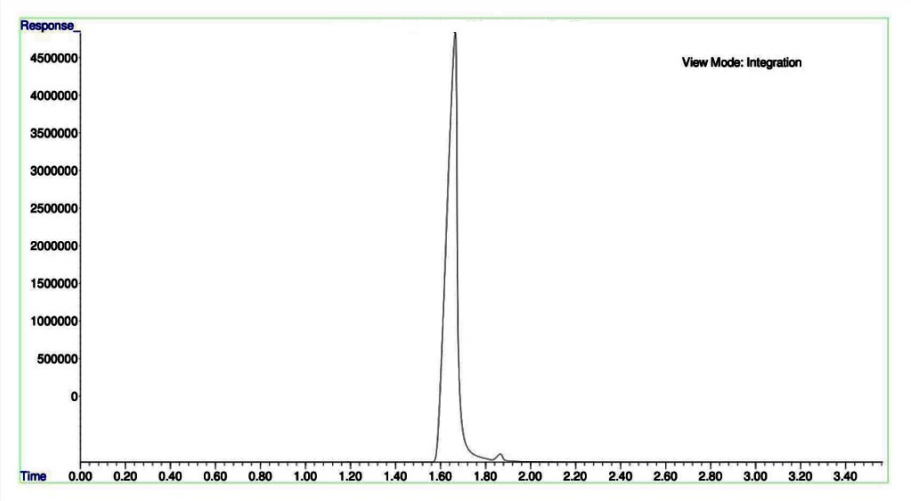


Figure S14. GC spectrum for evolved gas (TCD Mode).

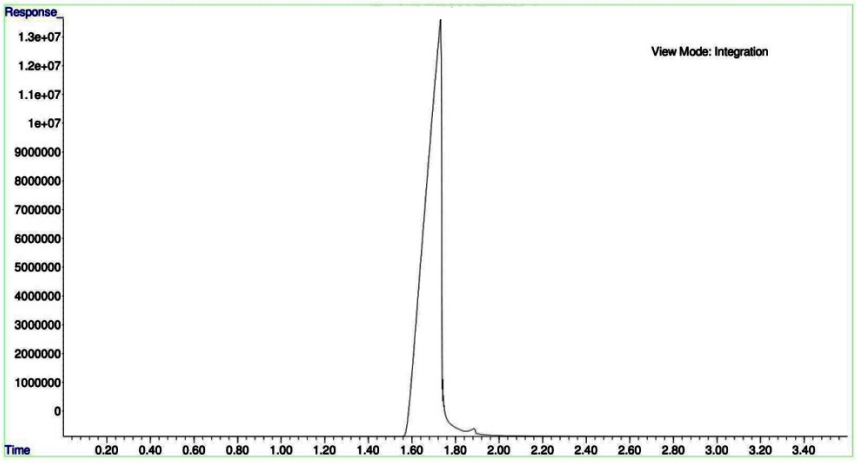


Figure S15. GC spectrum for pure H_2 (TCD mode).

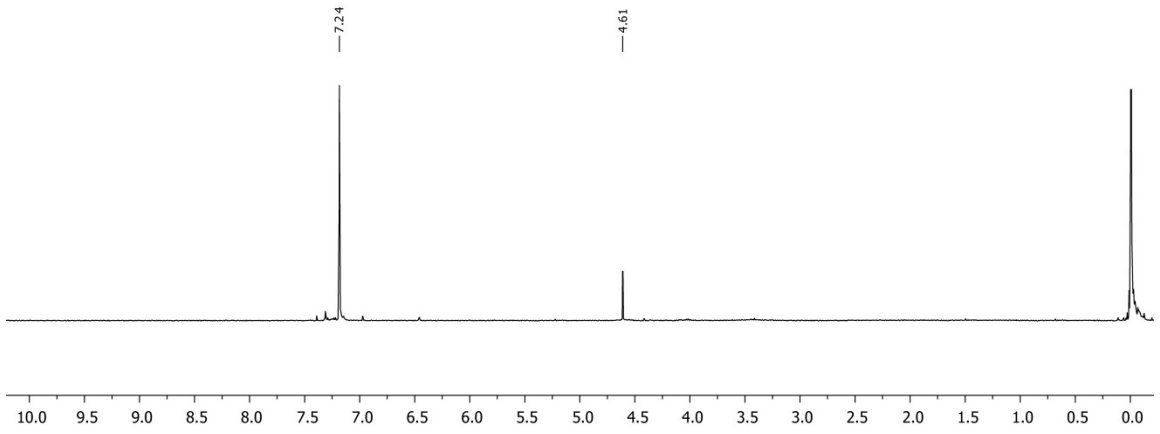


Figure S16. ^{1}H NMR (500 MHz) spectrum for evolved H_2 gas in $CDCl_3$.

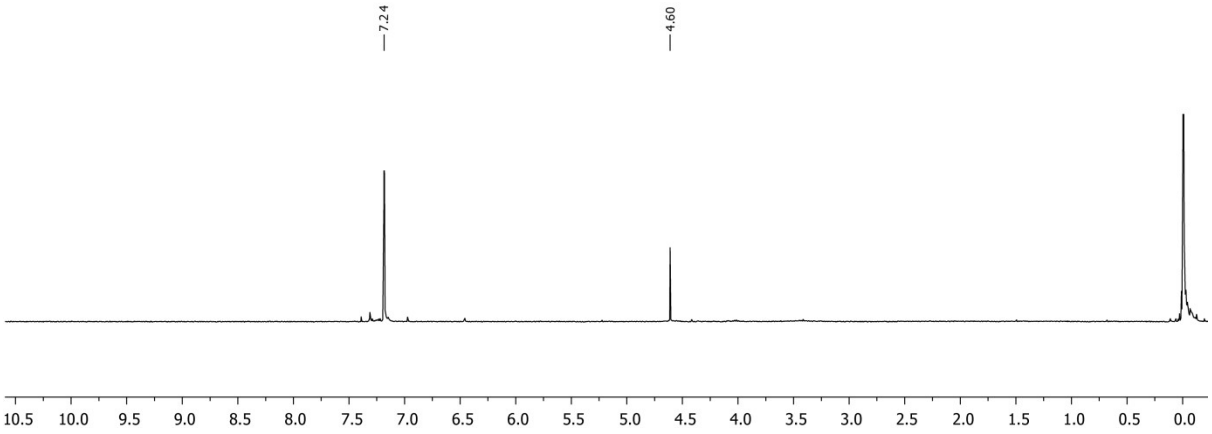


Figure S17. ^{1}H NMR (500 MHz) spectrum for pure H_2 gas in $CDCl_3$.

Quantitative estimation of evolved H_2 gas

For imine formation

A mixture of benzylamine (0.5 mmol) and catalyst **1** (2 mol%) in 2 mL water was heated at 85 ^oC with the headspace connected to a gas burette[9] via a cold trap to remove any other gaseous species. The reaction was continued till evolution of gas ceased. The experiment was repeated thrice to get concordant readings and the number of moles of hydrogen evolved was calculated taking into account the vapor pressure of water (P_{water}) at 298K = 0.0394 atm. Volume of water displaced = 5.2 mL, Atmospheric pressure = 1 atm, R = 0.0821 L atm K^{-1} mol^{-1}. $nH_2 = [(P_{atm} – P_{water}) \times V] / RT$ = 0.000204 mol or 0.204 mmol. Expected value = 0.25 mmol. Obtained H_2 is almost 0.41 equiv. with respect to substrate.

For benzothiazole formation

A mixture of benzylamine (0.5 mmol), 2-aminothiophenol (0.6 mmol) and catalyst **1** (2 mol%) in 2 mL water was heated at 100 ^oC with the headspace connected to a gas burette via a cold trap to remove any other gaseous species. The reaction was continued till evolution of gas ceased. The experiment was repeated thrice to get concordant readings and the number of moles of hydrogen evolved was calculated taking into account of the vapor pressure of water (P_{water}) at 298K = 0.0394 atm. Volume of water displaced = 23.6 mL, Atmospheric pressure = 1 atm, R = 0.0821 L atm K^{-1} mol^{-1}. $nH_2 = [(P_{atm} – P_{water}) \times V] / RT$ = 0.000927 mol or 0.927 mmol. Expected value = 1 mmol. Obtained H_2 is almost 1.85 equiv. with respect to substrate.

For acid formation

In another reaction, benzylamine (0.5 mmol), NaOH (0.5 mmol) and catalyst **1** (2 mol%) in 2 mL water was heated at 100 ^oC with the headspace connected to a gas burette via a cold trap to remove any other gaseous species. The reaction was continued till evolution of gas ceased. The experiment was repeated thrice to get concordant readings and the number of moles of hydrogen evolved was calculated taking into account of the vapor pressure of water (P_{water}) at 298K = 0.0394 atm. Volume of water displaced = 24.45 mL, Atmospheric pressure = 1 atm, R = 0.0821 L atm K^{-1} mol^{-1}. $nH_2 = [(P_{atm} – P_{water}) \times V] / RT$ = 0.000955 mol or 0.955 mmol. Expected value = 1 mmol. Obtained H_2 is almost 1.91 equiv. with respect to substrate.

General procedure for catalysis

For imine formation

Primary amine (0.5 mmol), catalyst **1** (2 mol%) and H_2O (2 mL) were taken in a Schlenk tube. It was allowed to stir for 12 hours at 85 ^oC in oil bath under N_2 atmosphere. Then the reaction mixture was transferred carefully into a small (20 mL) separating funnel using a dropper, and the organics were extracted with ethyl acetate (3 x 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by neutral Al_2O_3 column chromatography using petroleum ether/ethyl acetate as eluent to obtain the desired imine product. The isolated product was characterized by NMR spectroscopy.

For benzothiazole formation

Primary amine (0.5 mmol), 2-aminothiophenol (0.5 mmol), catalyst **1** (2 mol%) and H_2O (2 mL) were taken in a Schlenk tube. It was allowed to stir for 12 hours at 100 ^oC in oil bath under N_2 atmosphere. Then the reaction mixture was carefully transferred into a small (20 mL) separating funnel using a dropper, and the organics were extracted with ethyl acetate (3 x 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by neutral Al_2O_3 column chromatography using petroleum ether/ethyl acetate as eluent to obtain the desired benzothiazole product. The isolated product was characterized by NMR spectroscopy.

For acid formation

Primary amine (0.5 mmol), NaOH (0.5 mmol), catalyst **1** (2 mol%) and H_2O (2 mL) were taken in a Schlenk tube. It was allowed to stir for 24 hours at 100 ^oC in oil bath under N_2 atmosphere. Then the reaction mixture was carefully transferred into a small (20 mL) separating funnel using a dropper, and the organics were extracted with ethyl acetate (3 x 5 mL). Carboxylic acids were isolated after treatment of the aqueous layer with dilute HCl. The isolated product was characterized by NMR spectroscopy.

ICP-MS study of isolated imine product

Sample preparation and analysis method.

50 mg of sample was digested using HF:HNO_3 mixture at 130 °C for 24 h and then evaporated to dryness. The samples were further digested using aqua regia at 130 °C for next 24 h and the evaporation process was repeated. The sample was finally diluted to ~2400 times for the trace metal analysis. Three blanks and reference material was also prepared using the respective method to check the data quality. Seven point calibration curve was made from multi elemental standard solution appropriately diluted to 0.1, 1, 10, 20, 50, 75 and 100 ppb. Trace element concentrations were determined based on the calibration curve. We also monitored matrix effect using 100 ppb “Rh” solution using online spiking option to correct the matrix interferences. The instrument was run in both “no gas mode” and “He mode” as per the elemental reaction sensitivity to the respective mode. The final concentrations were measured by subtraction of corrected value from blank using the average procedural blank concentrations which was multiplied by dilution factor and the matrix effect was corrected by “Rh” normalization.

The Ni concentration of the imine product was measured to be 3.07 ppm.

Kinetic isotope effect

Kinetics of this reaction was performed using UV-Visible spectroscopy and its mathematical expression is as follows;

$$c \xrightarrow{k} \text{product}$$

$$\text{Rate} = k[c]^{\alpha} \quad (\alpha = \text{Order of reaction})$$

For a 1st order reaction $\alpha = 1$

$$-\frac{d[c]}{dt} = k[c]$$

$$\text{or, } -\int_{c_0}^{c} \frac{d[c]}{[c]} = k \int_{0}^{t} dt$$

$$\text{or, } -\ln(c/c_0) = kt$$

$$\text{or, } \ln(c_0/c) = kt$$

According to Lambert-Beer's law, Absorbance $A = \varepsilon cl$

$c_0 \propto A_0$ (Absorbance at t= 0 time)
$c \propto A_t$ (Absorbance at t time)

Hence, $\ln(A_0/A_t) = kt$ or $\log(A_0/A_t) = (k/2.303)t$

Therefore, for a 1st order reaction plot of $\log(A_0/A_t)$ *vs* time gives straight line of y = mx type. From this graph, rate constant is determined from its slope, i.e. k = slope × 2.303.

Relation is obtained for k_H/k_D: $k_H/k_D = (\text{slope})_H / (\text{slope})_D$

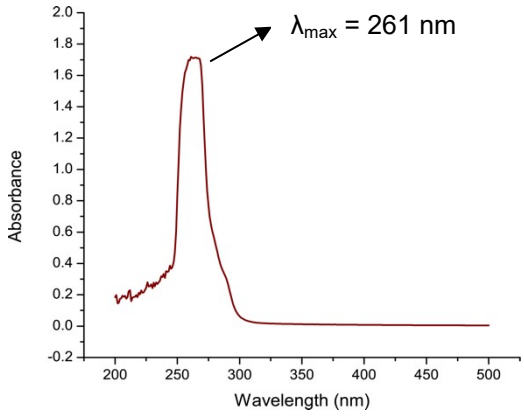


Figure S18. Determination of λ_{max} of benzylamine in UV-Visible spectrum. Concentration: 0.7 10^{-3} (M) in H_2O.

General procedures for the kinetic studies

A catalytic vessel was charged with benzylamine (0.3 mmol) and catalyst **1** (2 mol%) in 10 mL of water. 1mL of aliquot mixture was taken out and placed in 7 different catalytic vessels. Before heating 100 µL aliquot was taken out from one of these vessels and transferred to aquartz cuvette filled with 3 mL of same solvent used in this reaction. This cuvette was placed into the cell compartment of a UV-Visible spectrometer and absorption data of benzylamine was collected at 261 nm. This absorption is considered as A_0. Then the catalytic vessel was placed in pre-heated oil bath at 85 °C. With an interval of 1 h, 100 µL aliquot was taken out from each vessel and decay in absorption data of benzylamine (A_t) was collected at 261 nm. The experiment was repeated thrice to get consistent readings.

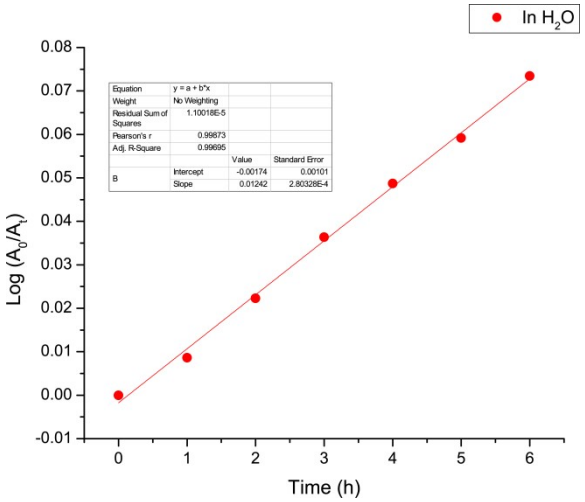


Figure S19. Log(A_0/A_t) *vs* time plot for $PhCH_2NH_2$ in H_2O.

Plot of Log(A_0/A_t) of *vs* time for benzylamine gives straight line of y = mx type. Hence, the reaction follows 1st order kinetics with respect to benzylamine with slope = 0.0124 h^{-1}.

Table S5. Absorbance data of $PhCH_2NH_2$ in H_2O

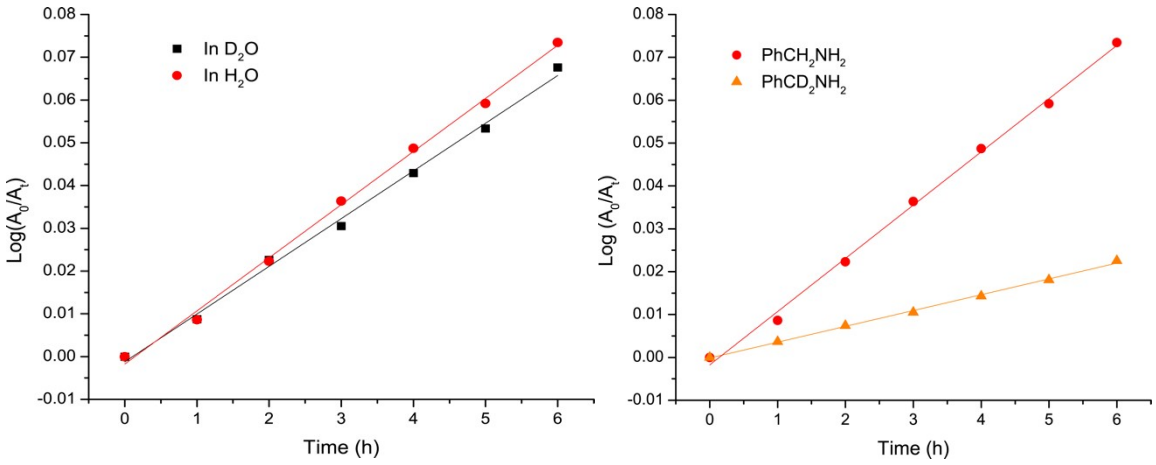
Time (h)	Absorbance (λ_{max} = 261nm)	A_0/A_t	log(A_0/A_t)
0	0.751013	1	0
1	0.736214	1.020101492	0.008643383
2	0.713421	1.05269259	0.022301566
3	0.690694	1.087331003	0.036361771
4	0.671286	1.11876756	0.048739865
5	0.655345	1.145981124	0.059177464
6	0.634165	1.184254886	0.073445185

Table S6. Absorbance data of $PhCH_2NH_2$ in D_2O

Time (h)	Absorbance (λ_{max} = 261nm)	A_0/A_t	$\log(A_0/A_t)$
0	0.741008	1	0
1	0.726212	1.020374216	0.008759476
2	0.703421	1.053434572	0.022607567
3	0.690694	1.072845573	0.030537213
4	0.671283	1.103868264	0.042917248
5	0.655348	1.13070918	0.053350918
6	0.634161	1.168485605	0.067623367

Table S7. Absorbance data of $PhCD_2NH_2$ in H_2O

Time (h)	Absorbance (λ_{max} = 261nm)	A_0/A_t	$\log(A_0/A_t)$
0	0.711241	1	0
1	0.705245	1.008507742	0.003679237
2	0.699243	1.01716149	0.007389909
3	0.694248	1.024487209	0.010506541
4	0.688246	1.033418575	0.014276263
5	0.682247	1.042507036	0.018078995
6	0.675241	1.053314377	0.022558012



(a) (b)

Figure S20. (a) Determination of k_H/k_D using H_2O *vs* D_2O. (b) Determination of k_H/k_D using $PhCH_2NH_2$ *vs* $PhCD_2NH_2$.

H_2O *vs* D_2O			$PhCH_2NH_2$ *vs* $PhCD_2NH_2$		
$(slope)_H$	$(slope)_D$	k_H/k_D	$(slope)_H$	$(slope)_D$	k_H/k_D
0.0124	0.0111	1.11	0.0124	0.0036	3.46

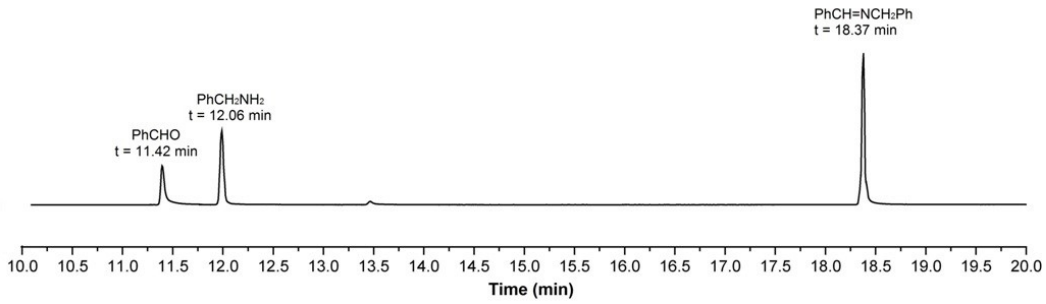


Figure S21. Gas chromatogram of reaction mixture after 8 h.

Isotope labeling experiment

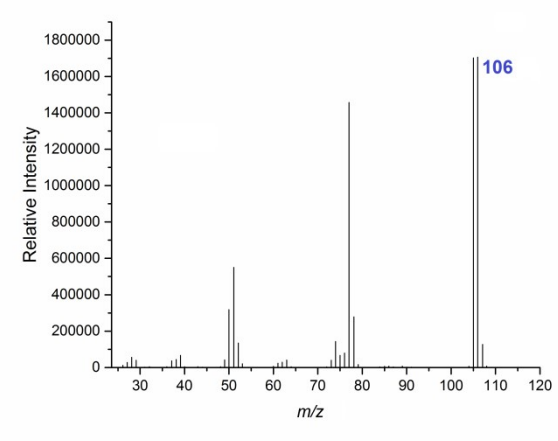


Figure S22. GC-MS of PhCHO, *m/z* (*z* = 1) 106 assigned as molecular ion.

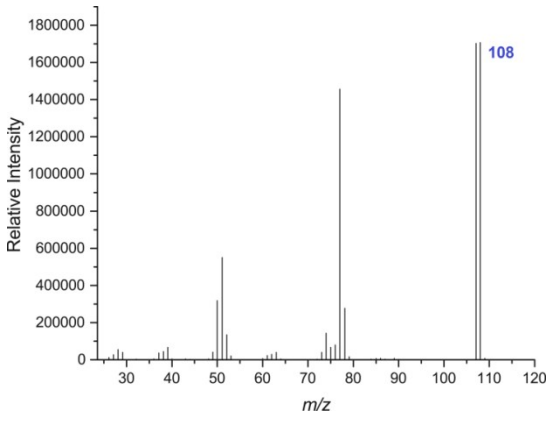
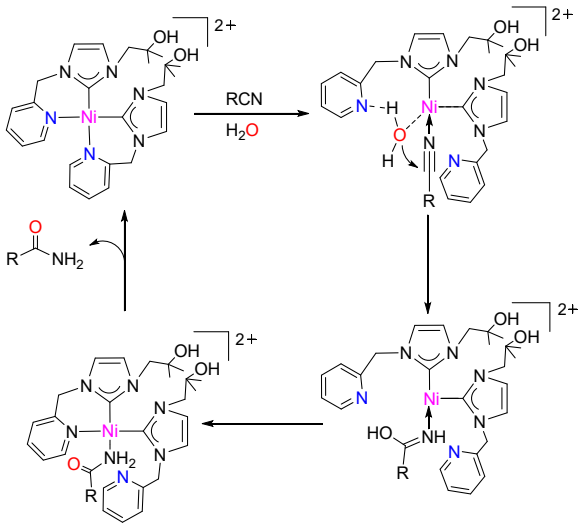


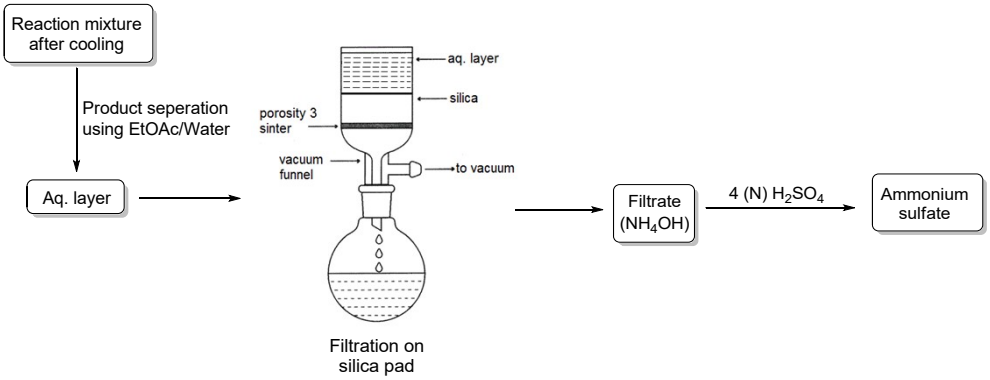
Figure S23. GC-MS of PhCH^{18}O, *m/z* (*z* = 1) 108 assigned as molecular ion.

Role of hemilabile side arm in nitrile hydration



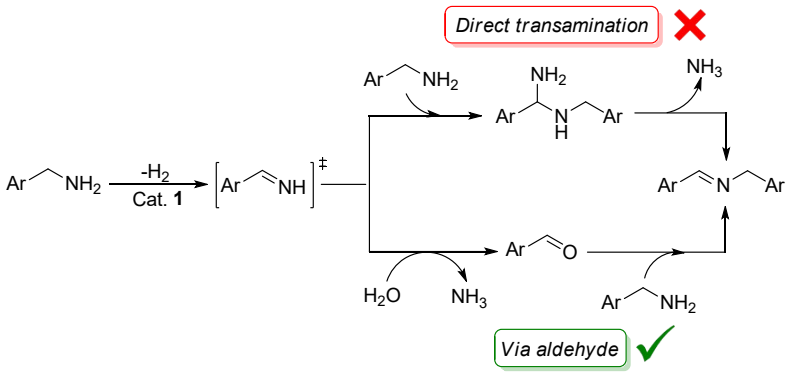
Scheme S2. Mechanism of nitrile hydration by a hemilabile Ni catalyst.[8]

Safe handling of NH_3 after the reaction

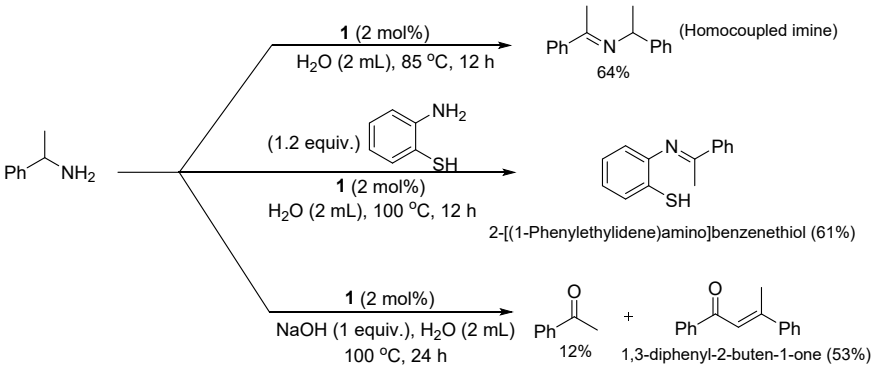


Scheme S3. Treatment of NH_3 at the end of reaction.

Pathways of oxidative deamination[10]



Scheme S4. Favoured pathway for the deamination catalyzed by **1**.



Scheme S5. Reactivity of 1-phenylethylamine under the standard reaction condition.

Recycling of water

Benzyl amine (0.5 mmol), catalyst **1** (2 mol%) and H_2O (2 mL) were taken in a Schlenk tube. It was allowed to stir for 12 hours at 85 °C in oil bath under N_2 atmosphere. Then the reaction mixture was transferred carefully to a small (20 mL) separating funnel using a dropper and the organics were extracted with ethyl acetate (3 x 5 mL) (Fig. S24-left). The water layer (2 mL) obtained after the extraction of organic product was further employed for another run of benzylamine deamination reaction. The catalyst retained a similar activity up to 3rd run, but the yield drops considerably on the 4th run and thereafter (Fig. S24-right). A fresh batch of catalyst was then added to the water and used for deamination of benzyl amine. An identical yield to the 1st cycle was regained.

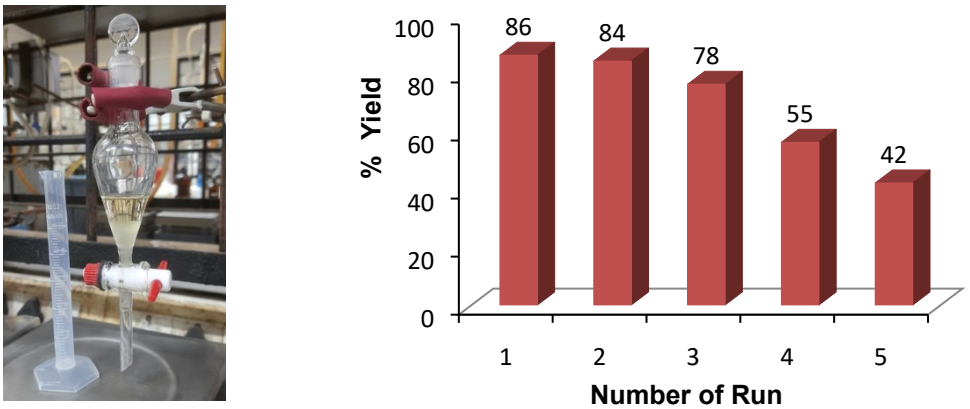


Figure S24. Recycling of water.

Calculation of E factor[11]

$$\text{E (Environmental) factor} = \frac{\text{Mass of total waste}}{\text{Mass of the product}}$$

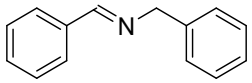
Table S8. Determination of E factor for oxidative deamination reactions with water

Type of the reaction	**Waste (mg)**	**Product (mg)**	**E factor**[a]
Imine formation	6.42	41.25	0.15
Benzothiazole formation	16.12	86.26	0.18
Acid formation	12.08	53.17	0.22

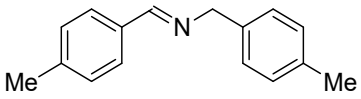
[a]As the water is recyclable, amount of water is excluded from waste generation. Calculation is based on 0.5 mmol scale reaction.

Characterization of products by NMR spectroscopy

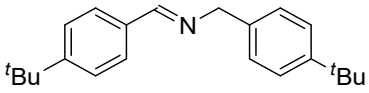
Imine products



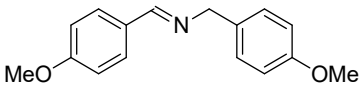
^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.41 (s, 1H, -N=CH-), 7.79 (m, 2H, ArH), 7.44-7.42 (m, 3H, ArH), 7.41-7.28 (m, 4H, ArH), 7.26 (d, *J*= 7.7 Hz, 1H, ArH), 4.84 (s, 2H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.38, 140.27, 136.24, 130.83, 128.67, 128.35, 128.56, 128.05, 127.06, 65.12.



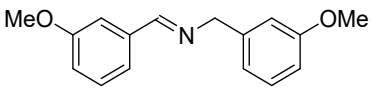
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.34 (s, 1H, -N=CH-), 7.66 (d, *J* = 8.0 Hz, 2H, ArH), 7.22-7.12 (m, 6H, ArH), 4.77 (s, 2H, CH_2), 2.38 (s, 3H, CH_3), 2.33 (s, 3H, CH_3) ; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.81, 141.11, 137.37, 136.45, 133.78, 129.37, 129.22, 128.31, 127.03, 64.70, 23.03, 21.11.



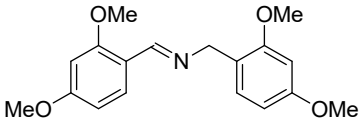
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.36 (s, 1H, -N=CH-), 7.70 (d, *J* = 8.3 Hz, 2H, ArH) 7.42 (d, *J* = 8.4 Hz, 2H, ArH), 7.35 (t, *J* = 8.2 Hz, 2H, ArH), 7.26 (d, *J* = 8.3 Hz, 2H, ArH), 4.77 (s, 2H, CH_2), 1.32 (s, 9H, ^{t}Bu), 1.30 (s, 9H, ^{t}Bu); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.80, 154.20, 149.89, 136.50, 133.65, 128.14, 127.74, 125.60, 125.45, 64.86, 34.97, 34.53, 31.45, 31.29.



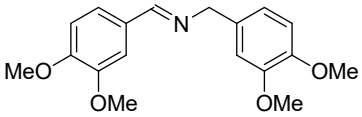
^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.22 (s, 1H, -N=CH-), 7.63 (t, *J* = 7.8 Hz, 2H, ArH), 7.17 (t, *J* = 7.7 Hz, 2H, ArH), 6.86-3.83 (m, 2H, ArH), 6.82-6.79 (m, 2H, ArH), 4.65 (s, 2H, CH_2), 3.76 (s, 3H, CH_3), 3.72 (s, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.59, 160.78, 158.79, 131.76, 129.88, 129.29, 114.05, 113.99, 64.26, 55.44, 54.94.



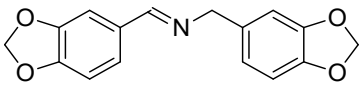
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.27 (s, 1H, -N=CH-), 7.25 (s, 1H, ArH), 7.01-6.90 (m, 3H, ArH), 6.53-6.52 (m, 1H, ArH), 6.49 (d, *J* = 2.5 Hz, 2H, ArH), 6.38-6.36 (m, 1H, ArH), 4.74 (s, 2H, CH_2), 3.81 (s, 3H, CH_3), 3.78 (s, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.02, 159.41, 158.38, 141.57, 138.25, 130.65, 129.87, 121.00, 120.34, 118.06, 113.35, 112.18, 111.59, 64.98, 55.59, 55.40.



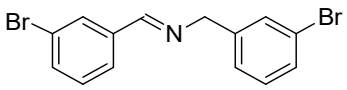
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.65 (s, 1H, -N=CH-), 7.80 (d, *J* = 8.4 Hz, 1H, ArH), 7.21 (d, *J* = 8.4 Hz, 1H, ArH), 6.47-6.39 (m, 4H, ArH), 4.73 (s, 2H, CH_2), 3.85 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 3.78 (s, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.69, 160.66, 160.26, 158.32, 158.07, 131.39, 130.86, 130.39, 119.14, 105.80, 104.20, 98.14, 98.03, 60.48, 55.71, 55.60, 55.47, 55.39.



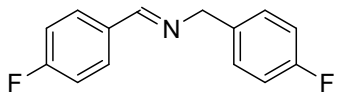
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.27 (s, 1H, -N=CH-), 7.41(s, 1H, ArH), 7.19-7.17 (m, 1H, ArH), 6.89-6.83 (m, 4H, ArH), 4.73 (s, 2H, CH_2), 3.92 (s, 3H, CH_3), 3.91 (s, 3H, CH_3), 3.87 (s, 3H, CH_3), 3.86 (s, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.38, 151.53, 149.76, 149.47, 148.82, 132.12, 129.46, 123.35, 120.32, 111.64, 111.44, 110.51, 109.04, 64.73, 56.25, 56.10, 56.05, 55.97.



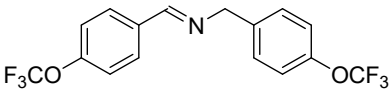
^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.26 (s, 1H, -N=CH-), 7.40 (d, *J* = 2.1 Hz, 1H, ArH), 7.18-7.16 (m, 1H, ArH), 6.86-6.82 (m, 4H, ArH), 6.01 (s, 2H, -O-CH_2-O-), 5.95 (s, 2H, -O-CH_2-O-), 4.72 (s, 2H, ArH); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.17, 150.17, 147.95, 147.55, 146.48, 133.29, 131.26, 125.57, 124.30, 121.14, 108.77, 108.21, 106.63, 100.72, 64.27.



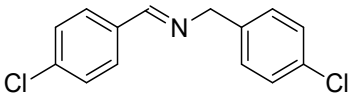
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.31 (s, 1H, -N=CH-), 7.96 (s, 1H, ArH), 7.66 (d, *J* = 7.6 Hz, 1H, ArH), 7.55 (d, *J* = 8.0 Hz, 1H, ArH), 7.40 (d, *J* = 7.8 Hz, 1H, ArH), 7.33-7.31 (m, 1H, ArH), 7.30-7.27 (m, 2H, ArH), 7.23-7.20 (m,1H, ArH), 4.77 (s, 2H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 160.89, 141.72, 137.12, 133.91, 131.01, 130.70, 130.29, 130.16, 127.18, 126.60, 124.43, 124.32, 123.18, 64.31.



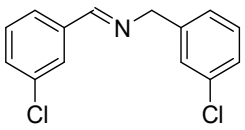
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.34 (s, 1H, -N=CH-), 7.78-7.75 (m, 2H, ArH), 7.30-7.27 (m, 2H, ArH), 7.12-7.00 (m, 4H, ArH), 4.76 (s, 2H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.47, 163.05, 160.60, 134.68, 132.72, 130.27, 130.20, 129.56, 129.50, 115.89, 115.72, 115.46, 115.29, 64.22. ^{19}F NMR (470 MHz, $CDCl_3$): δ = -108.95, -115.91.



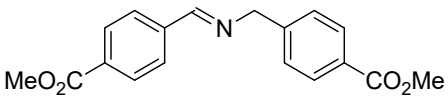
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.43 (s, 1H, -N=CH-), 7.86-7.83 (m, 2H, ArH), 7.65-7.62 (m, 2H, ArH), 7.57-7.54 (m, 2H, ArH), 7.43-7.40 (m, 2H, ArH), 4.84 (s, 2H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.17, 151.26, 148.39, 137.24, 134.14, 131.74, 130.77, 129.80, 128.59, 125.72, 124.45, 64.32.



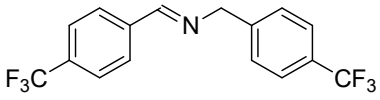
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.29 (s, 1H, -N=CH-), 7.68-7.65 (m, 2H, ArH), 7.37-7.33 (m, 2H, ArH), 7.28-7.26 (m, 2H, ArH), 7.21 (t, *J* = 8.3 Hz, 2H, ArH), 4.72 (s, 2H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 160.99, 138.07, 137.64, 134.49, 132.92, 129.54, 129.35, 129.03, 128.73, 64.26.



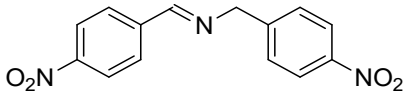
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.28 (s, 1H, -N=CH-), 7.63 (s, 1H, ArH), 7.44 (s, 1H, ArH),7.30-7.16 (m, 6H, ArH), 4.74 (s, 2H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.64, 141.05, 139.14, 137.87, 136.31, 134.66, 132.49, 131.78, 130.99, 128.76, 127.93, 127.35, 126.71, 65.06.



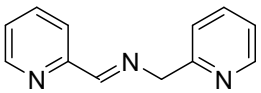
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.48 (s, 1H, -N=CH-), 8.15 (d, *J* = 7.9 Hz, 2H, ArH), 8.01-7.94 (m, 2H, ArH), 7.49-7.41 (m, 4H, ArH), 4.91 (s, 2H, CH_2), 4.02 (s, 3H, CH_3), 3.98 (s, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.85, 161.75, 144.29, 139.59, 132.56, 130.53, 129.88, 129.81, 129.24, 128.37, 127.64, 64.47, 52.53, 52.03.



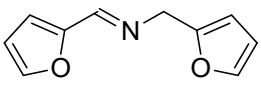
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.46 (s, 1H, -N=CH), 7.90 (d, *J*= 8.5 Hz, 2H, ArH), 7.68 (d, *J* = 8.4 Hz, 2H, ArH), 7.60 (d, *J* = 8.3 Hz, 2H, ArH), 7.46 (d, *J* = 8.2 Hz, 2H, ArH), 4.89 (s, 2H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.38, 143.16, 139.25, 134.33, 129.94, 129.62, 128.17, 127.38, 126.90, 124.91, 124.87, 124.80, 124.68, 64.73; ^{19}F NMR (470 MHz, $CDCl_3$): δ = -63.02, -63.58.



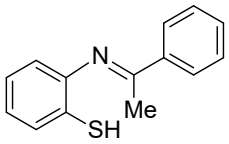
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.58 (s, 1H, -N=CH), 8.01 (d, *J* = 9.7 Hz, 2H, ArH), 7.80 (d, *J* = 8.1 Hz, 2H, ArH), 7.73 (d, *J* = 7.9 Hz, 2H, ArH), 7.58 (d, *J* = 8.3 Hz, 2H, ArH), 5.01 (s, 2H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.27, 154.72, 152.83, 143.71, 141.42, 135.69, 130.77, 128.59, 128.19, 65.91.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.66 (d, *J* = 4.5 Hz, 1H, ArH), 8.59-8.58 (m, 2H, ArH), 8.09 (d, *J* = 7.8 Hz, 1H, ArH), 7.75 (t, *J* = 7.7 Hz, 1H, ArH), 7.67 (t, *J* = 7.7 Hz, 1H, ArH), 7.43 (d, *J* = 7.8 Hz, 1H, ArH), 7.34-7.32 (m, 1H, ArH), 7.20-7.18 (m, 1H, ArH), 5.03 (s, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.97, 158.30, 157.11, 149.59, 149.34, 136.43, 136.38, 123.85, 122.21, 121.61, 121.21, 66.41.

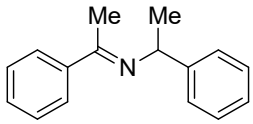


^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.04 (s, 1H, -N=CH), 7.44 (s, 1H, ArH), 7.31 (s, 1H, ArH), 6.71 (d, *J*= 3.3 Hz, 1H, ArH), 6.40 (s, 1H, ArH), 6.27 (t, *J* = 3.5 Hz, 1H, ArH), 6.21 (d, *J* = 3.5 Hz, 1H, ArH), 4.68 (s, 2H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.93, 151.52, 151.32, 144.96, 142.31, 114.57, 111.75, 110.45, 107.95, 56.89.



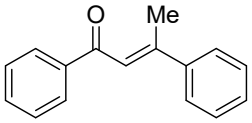
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30-8.22 (m, 3H, ArH), 7.92 (d, *J*= 7.8 Hz, 1H, ArH), 7.59-7.45 (m, 5H, ArH), 4.22 (br s, 1H, -SH), 1.49 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.66, 154.77, 146.69, 143.54, 132.45,

129.38, 128.29, 127.39, 126.34, 122.47, 121.75, 25.72.



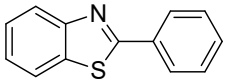
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.36 (m, 2H, ArH), 7.34-7.16 (m, 8H, ArH), 1.48 (s, 3H, CH_3), 1.40 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.82, 146.63, 141.82, 129.24, 128.74, 128.40, 126.99, 126.47, 125.52, 59.85, 25.27, 15.36.

α,β-Unsaturated carbonyl product

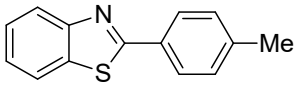


^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02-8.00 (m, 2H, ArH), 7.59-7.55 (m, 3H, ArH), 7.54-7.49 (m, 2H, ArH), 7.47-7.37 (m, 3H, ArH), 7.18 (d, *J*= 1.2 Hz, 1H, ArH), 2.62 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.83, 155.29, 142.79, 139.65, 131.76, 129.88, 129.29, 129.24, 128.40, 126.66, 122.23, 20.12.

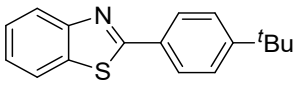
Benzothiazole products



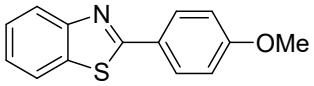
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 8.1 Hz, 1H, ArH), 8.07 (t, *J* = 7.7 Hz, 2H, ArH), 7.77 (d, *J* = 8.2 Hz, 1H, ArH), 7.44-7.39 (m, 4H, ArH), 7.32 (t, *J* = 7.6 Hz,1H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.55, 155.85, 135.03, 132.45, 132.38, 129.48, 128.26, 127.45, 126.30, 122.49, 121.84.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.2 Hz, 1H, ArH), 8.06 (d, *J* = 8.1 Hz, 2H, ArH), 7.89 (d, *J* = 8.0 Hz, 2H, ArH), 7.54-7.50 (m, 1H, ArH), 7.42-7.40 (m, 1H, ArH), 7.32 (d, *J* = 8.0 Hz, 1H, ArH) 2.43 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.76, 153.73, 140.67, 133.59, 129.01, 126.94, 125.88, 125.81, 124.64, 121.68, 120.72, 28.78.

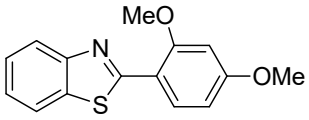


^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.4 Hz, 2H, ArH), 7.90 (d, *J* = 8.0 Hz, 1H, ArH), 7.57-7.53 (m, 3H, ArH), 7.47-7.43 (m, 2H, ArH), 1.36 (s, 9H, ^{t}Bu); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.04, 155.58, 155.13, 129.48, 127.79, 127.02, 126.86, 126.19, 125.78, 122.04, 121.50, 36.89, 30.86.

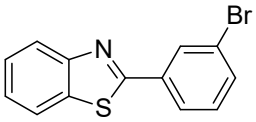


^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J*= 8.2 Hz, 1H, ArH), 7.92 (d, *J* = 8.3 Hz, 2H, ArH), 7.76 (d, *J* = 7.9 Hz, 1H, ArH), 7.40-7.37 (m, 1H, ArH), 7.29-7.26 (m, 1H, ArH), 7.19 (d, *J* = 8.4 Hz, 2H, ArH), 3.94 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 167.11, 161.31, 154.08, 130.00, 127.93, 126.80, 125.63, 122.67, 121.71,

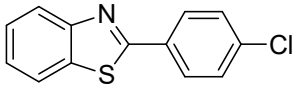
114.45, 54.97.



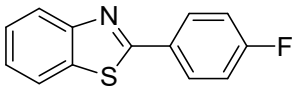
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.0 Hz, 1H, ArH), 7.89 (d, *J* = 8.1 Hz, 1H, ArH), 7.71 (s, 1H, ArH), 7.57 (t, *J* = 7.7 Hz, 1H, ArH), 7.45 (t, *J* = 7.6 Hz, 1H, ArH), 6.78 (d, *J* = 8.4 Hz, 1H, ArH), 6.59 (d, *J* = 7.4 Hz, 1H, ArH), 4.09 (s, 3H, CH_3), 3.92 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.21, 154.25, 149.49, 127.68, 126.27, 126.08, 125.05, 121.72, 121.37, 120.72, 120.63, 111.83, 109.59, 56.07, 55.95.



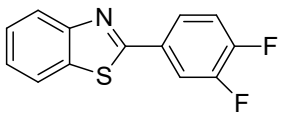
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (s, 1H, ArH), 8.09 (d, *J* = 8.1 Hz, 1H, ArH), 7.99 (d, *J* = 7.6 Hz, 1H, ArH), 7.91 (d, *J* = 7.9 Hz, 1H, ArH), 7.61 (d, *J* = 7.7 Hz, 1H, ArH), 7.51 (t, *J* = 7.5 Hz, 1H, ArH), 7.42-7.34 (m, 2H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.36, 153.72, 135.35, 134.99, 134.00, 130.62, 130.41, 126.74, 126.31, 125.76, 123.45, 123.29, 121.79.



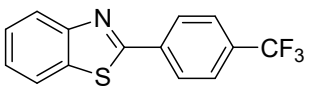
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.1 Hz, 1H, ArH), 8.07 (d, *J*= 8.3 Hz, 2H, ArH), 7.90 (d, *J* = 8.0 Hz, 1H, ArH), 7.55-7.51 (m, 1H, ArH), 7.44-7.41 (m, 1H, ArH), 7.33 (d, *J* = 7.9 Hz, 2H, ArH), ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.36, 154.60, 135.17, 132.29, 131.25, 129.18, 128.12, 128.05, 126.88, 123.92, 122.96.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 8.2 Hz, 2H, ArH), 8.10 (d, *J* = 8.1 Hz, 1H, ArH), 7.93 (d, *J* = 8.0 Hz, 1H, ArH), 7.75 (d, *J* = 8.1 Hz, 2H, ArH), 7.52 (t, *J* = 7.9 Hz, 1H, ArH), 7.42 (t, *J* = 7.8 Hz, 1H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.09, 165.96, 165.91, 163.49, 153.49, 134.77, 129.83, 129.74, 126.70, 125.53, 123.11, 121.72, 116.45, 116.23. ^{19}F NMR (376 MHz, $CDCl_3$): δ = - 108.30.



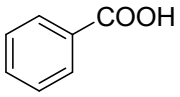
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 8.1 Hz, 1H, ArH), 8.14-8.09 (m, 1H, ArH), 8.05 (d, *J* = 8.0 Hz, 1H, ArH), 7.98-7.95 9 (m, 1H, ArH), 7.66 (t, *J* = 7.6 Hz, 1H, ArH), 7.56 (t, *J* = 7.5 Hz, 1H, ArH), 7.46-7.42 (m, 1H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.50, 153.91, 153.56, 153.48, 152.53, 151.74, 151.01, 150.89, 149.52, 149.44, 135.12, 130.92, 130.78, 130.75, 130.71, 130.19, 129.50, 126.73, 125.71, 124.08, 124.01, 123.46, 123.42, 121.77, 121.71, 118.17, 117.99, 116.72, 116.53; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -133.36, -136.03.



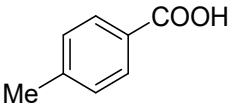
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.1 Hz, 2H, ArH), 8.11 (d, *J* = 8.1 Hz, 1H, ArH), 7.94 (d, *J* = 8.0 Hz, 1H, ArH), 7.76 (d, *J* = 8.0 Hz, 2H, ArH), 7.53 (t, *J* = 7.7 Hz, 1H, ArH), 7.43 (t, *J* = 7.6 Hz, 1H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.17, 154.09, 136.84, 135.28, 132.87, 132.73, 132.58, 132.30, 127.88, 126.75, 126.13, 126.09, 125.98, 125.89, 125.41, 123.71, 122.83,

121.84, 119.79; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.81.

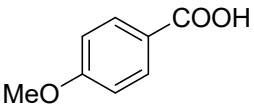
Acid products



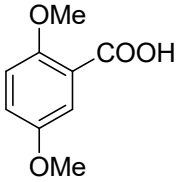
^{1}H NMR (500 MHz, $CDCl_3$): δ = 12.09 (br s, 1H, -COOH), 8.14-8.12 (m, 2H, ArH), 7.63-7.60 (m, 1H, ArH), 7.48 (t, *J* = 7.8 Hz, 2H, ArH); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 172.58, 133.92, 130.32, 129.42, 128.58.



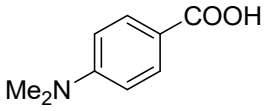
^{1}H NMR (500 MHz, $CDCl_3$): δ = 12.21 (br s, 1H, -COOH), 7.99 (d, *J* = 8.2 Hz, 2H, ArH), 7.26 (d, *J* = 8.1 Hz, 2H, ArH), 2.42 (s, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 172.24, 144.71, 130.33, 129.29, 126.65, 21.83.



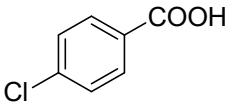
^{1}H NMR (500 MHz, $CDCl_3$): δ = 12.11 (br s, 1H, -COOH), 8.06 (d, *J* = 7.8 Hz, 2H, ArH), 6.94 (d, *J* = 7.8 Hz, 2H, ArH); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.62, 132.44, 129.39, 121.72, 113.83, 55.56.



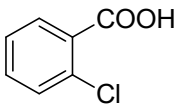
^{1}H NMR (500 MHz, DMSO-d_6): δ = 12.65 (s, 1H, -COOH), 7.16 (d, *J* = 2.9 Hz, 1H, ArH), 7.09-7.04 (m, 2H, ArH), 3.76 (s, 3H, CH_3), 3.73 (s, 3H, CH_3); ^{13}C NMR (126 MHz, DMSO-d_6): δ = 172.33, 157.82, 157.49, 127.23, 123.65, 120.51, 119.44, 61.64, 60.81.



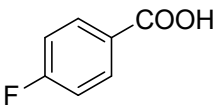
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.9 Hz,1H, ArH), 6.65 (d, *J* = 9.0 Hz, 1H, ArH), 3.05 (s, 6H, NMe_2); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 172.15,153.89, 132.10, 116.00, 110.76, 40.11.



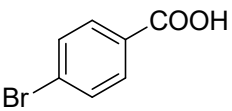
^{1}H NMR (500 MHz, $CDCl_3$): δ = 12.19 (br s, 1H, -COOH), 8.03 (d, *J* = 8.6 Hz, 2H, ArH), 7.44 (d, *J* = 8.4 Hz, 2H, ArH); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.88, 140.41, 131.66, 128.98, 128.22.



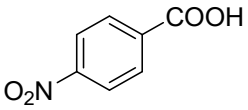
^{1}H NMR (500 MHz, $CDCl_3$): δ = 12.30 (br s, 1H, -COOH), 8.03-8.01 (m, 1H, ArH), 7.50-7.46 (m, 2H, ArH), 7.37-7.34 (m, 1H, ArH); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.89, 134.87, 133.66, 132.57, 131.59, 128.5, 126.78.



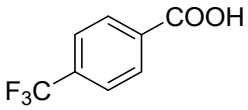
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15-8.12 (m, 2H, ArH), 7.16-7.13 (m, 2H, ArH);); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.21, 167.46, 165.43, 133.01, 132.93, 125.59, 125.58, 115.90, 115.73; ^{19}F NMR (470 MHz, $CDCl_3$): δ = -103.95.



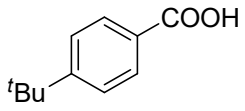
^{1}H NMR (500 MHz, DMSO-d_6): δ = 13.17 (s, 1H, -COOH), 7.84 (d, *J* = 8.4 Hz, 2H, ArH), 7.68 (d, *J* = 8.2 Hz, 2H, ArH); ^{13}C NMR (126 MHz, DMSO-d_6): δ = 167.12, 132.21, 131.80, 130.52, 127.40.



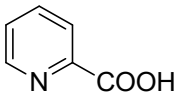
^{1}H NMR (500 MHz, DMSO-d_6): δ = 13.65 (s, 1H, -COOH), 8.30 (d, *J* = 8.2 Hz, 2H, ArH), 8.15 (d, *J* = 8.4 Hz, 2H, ArH); ^{13}C NMR (126 MHz, DMSO-d_6): δ = 166.30, 150.54, 136.89, 131.20, 124.22.



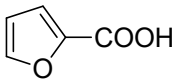
^{1}H NMR (500 MHz, DMSO-d_6): δ = 13.45 (s, 1H, -COOH), 8.12 (d, *J* = 8.1 Hz, 2H, ArH), 7.86 (d, *J* = 8.3 Hz, 2H, ArH); ^{13}C NMR (126 MHz, DMSO-d_6): 166.71, 135.12, 133.13, 132.87, 130.62, 126.67, 126.64, 126.14, 126.11, 125.42; ^{19}F NMR (470 MHz, $CDCl_3$): δ = -61.60.



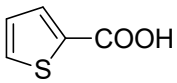
^{1}H NMR (500 MHz, DMSO-d_6): δ = 13.19 (s, 1H, -COOH), 7.86 (d, *J* = 8.2 Hz, 2H, ArH), 7.70 (d, J = 8.3 Hz, 2H, ArH), 1.32 (s, 9H, *t*Bu); ^{13}C NMR (126 MHz, DMSO-d_6): δ =167.20, 154.74, 130.60, 127.48, 124.33, 35.83.



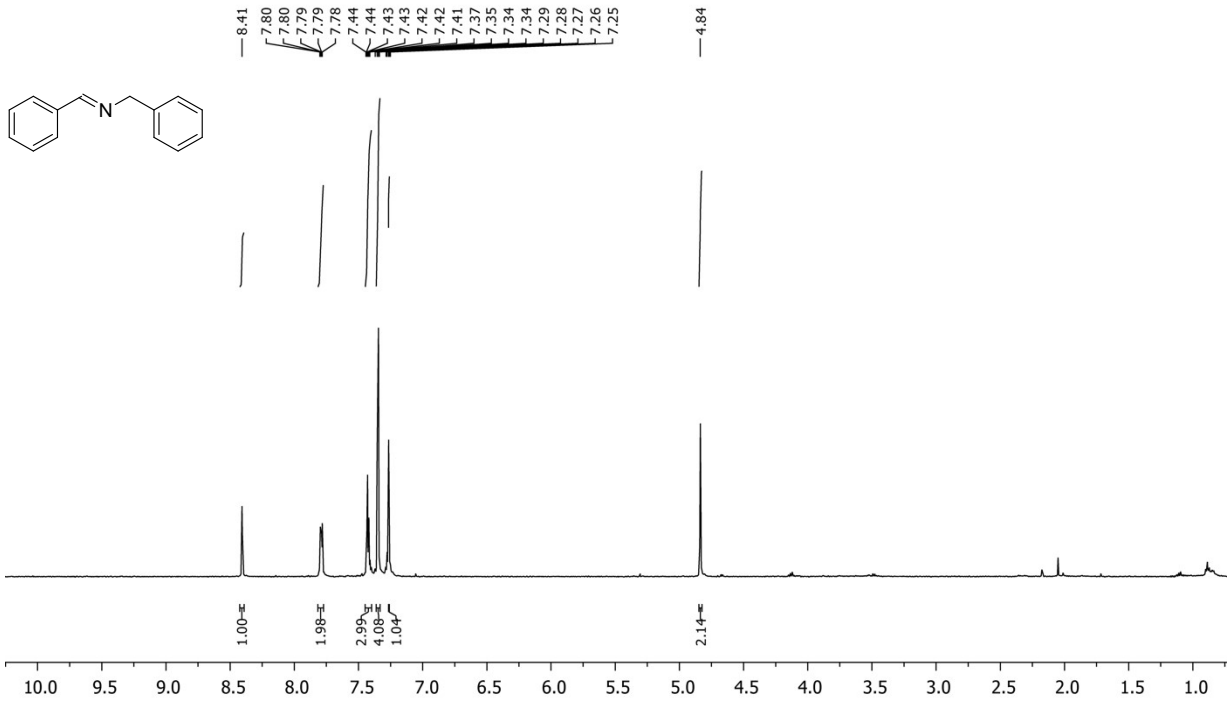
^{1}H NMR (500 MHz, DMSO-d_6): δ = 12.93 (br s, 1H, -COOH), 8.69 (d, *J* = 4.5 Hz, 1H, ArH), 8.02 (d, *J* = 7.7 Hz, 1H, ArH), 7.98-7.95 (m, 1H, ArH), 7.62-7.60 (m, 1H, ArH); ^{13}C NMR (126 MHz, DMSO-d_6): δ = 166.65, 149.90, 148.82, 138.08, 127.61, 125.18.



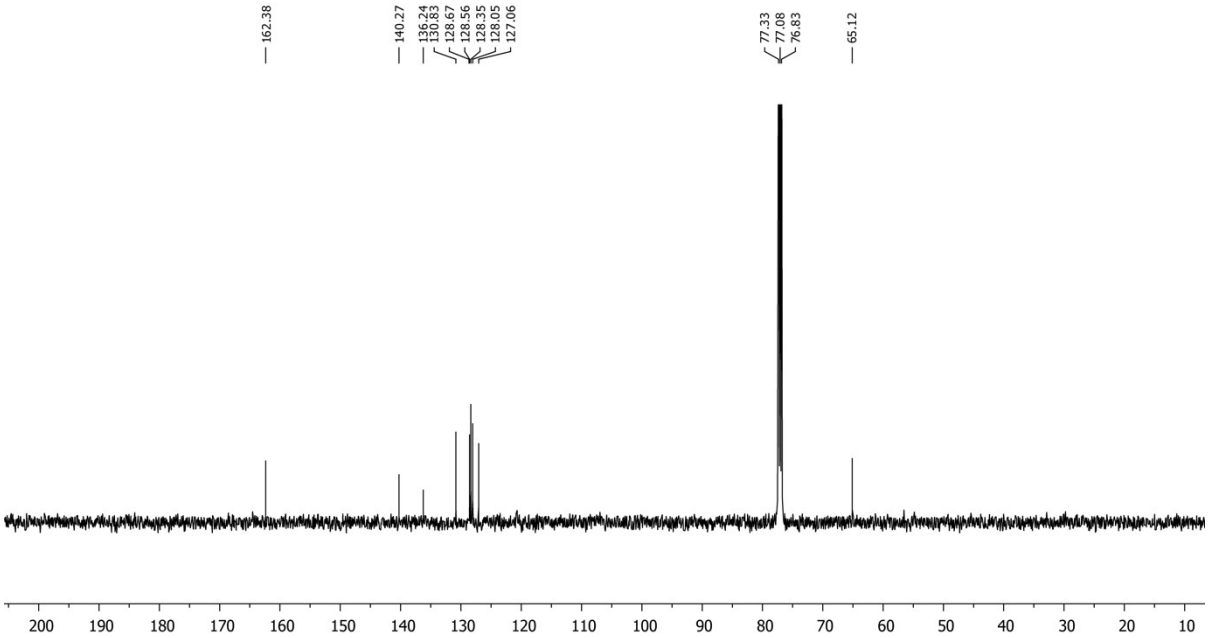
^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.44 (br s, 1H, -COOH), 7.64 (d, *J* = 3.1 Hz, 1H, ArH), 7.33-7.25 (m, 1H, ArH), 6.55 (dd, *J* = 3.5 Hz, 1.7 Hz, 1H, ArH); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.72, 147.52, 143.92, 120.24, 112.35.



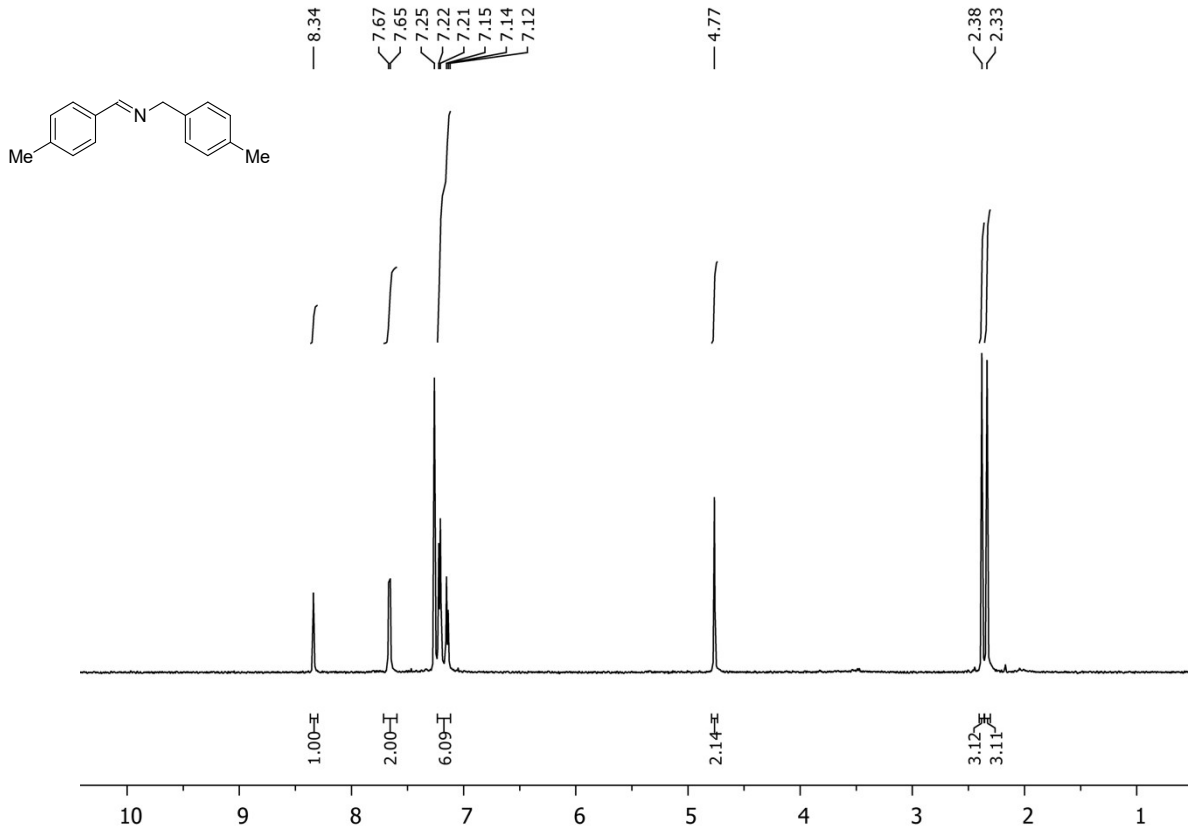
^{1}H NMR (500 MHz, $CDCl_3$): δ = 11.75 (br s, 1H, -COOH), 7.89 (d, 3.6 Hz, 1H, ArH), 7.65 (d, J = 4.8 Hz, 1H, ArH), 7.14 (dd, *J* = 3.5 Hz, 1.7 Hz, 1H, ArH), ^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.85, 135.12, 134.12, 132.96, 128.16.



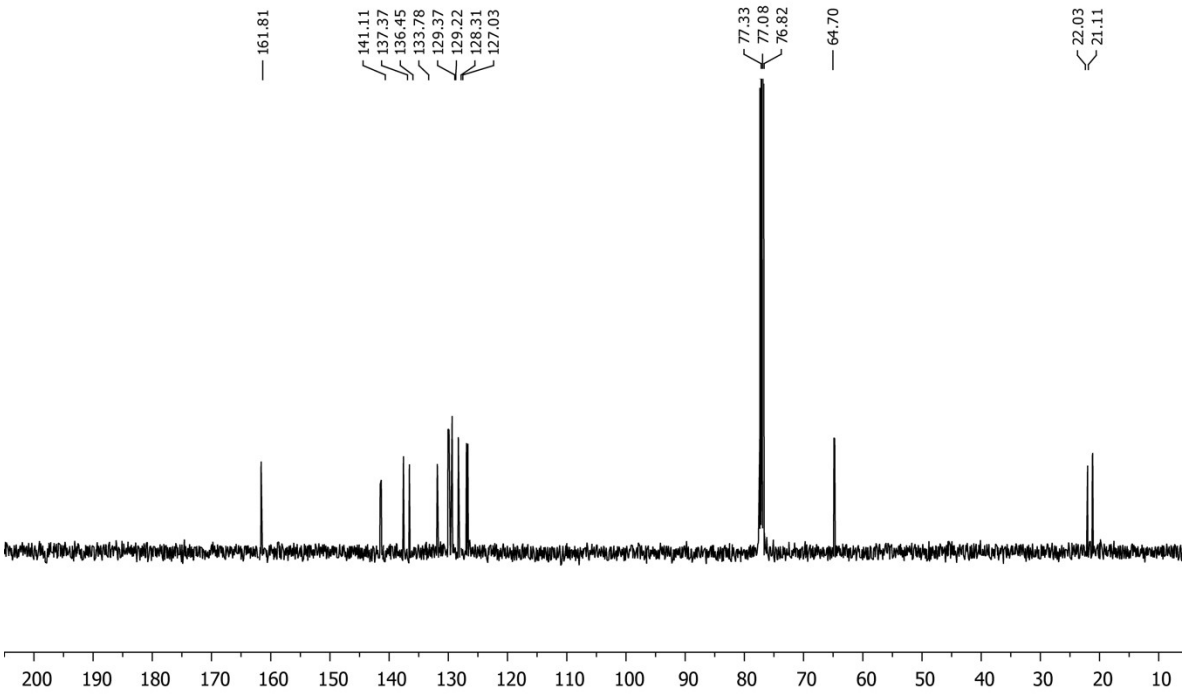
^{1}H NMR (500 MHz, $CDCl_3$)



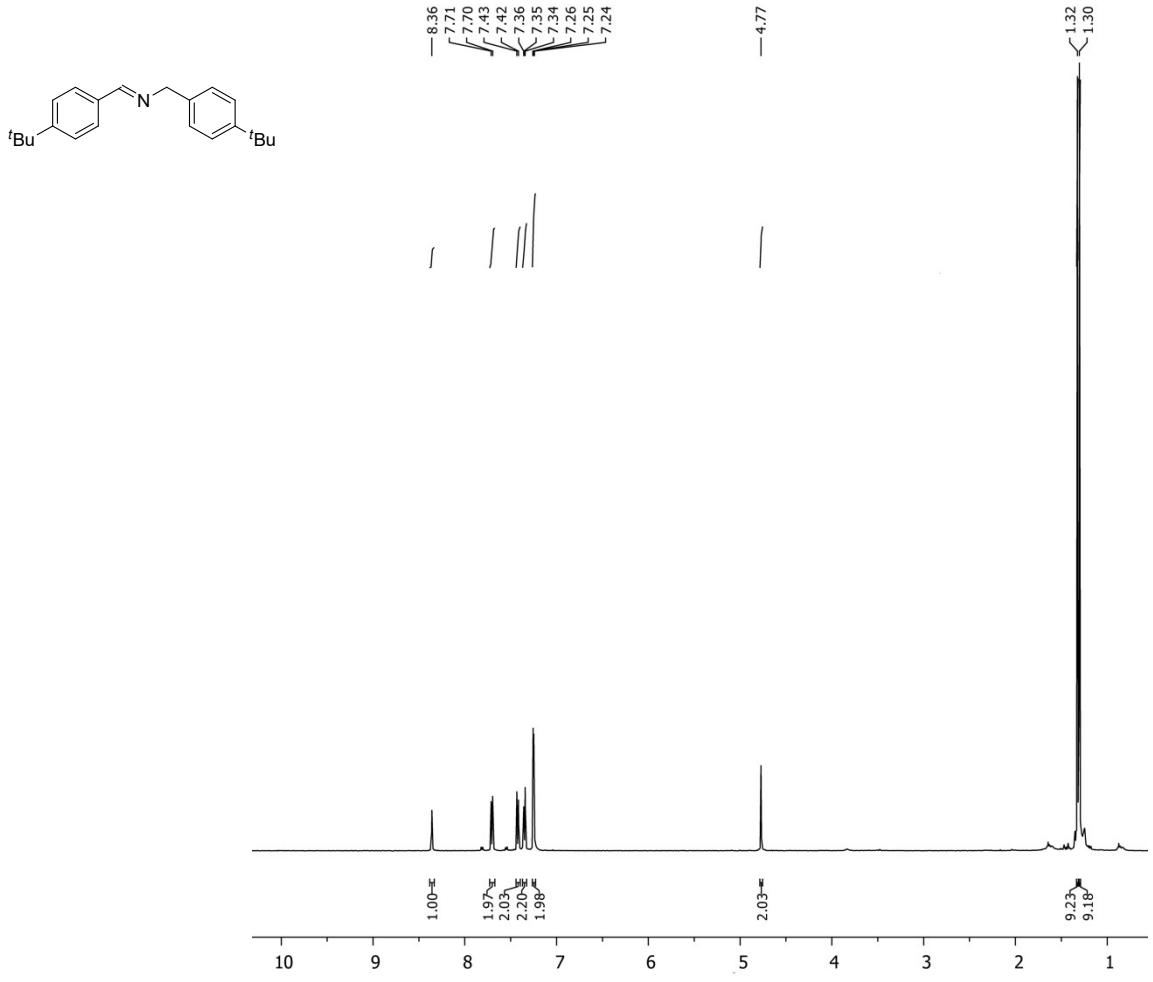
^{13}C NMR (126 MHz, $CDCl_3$)



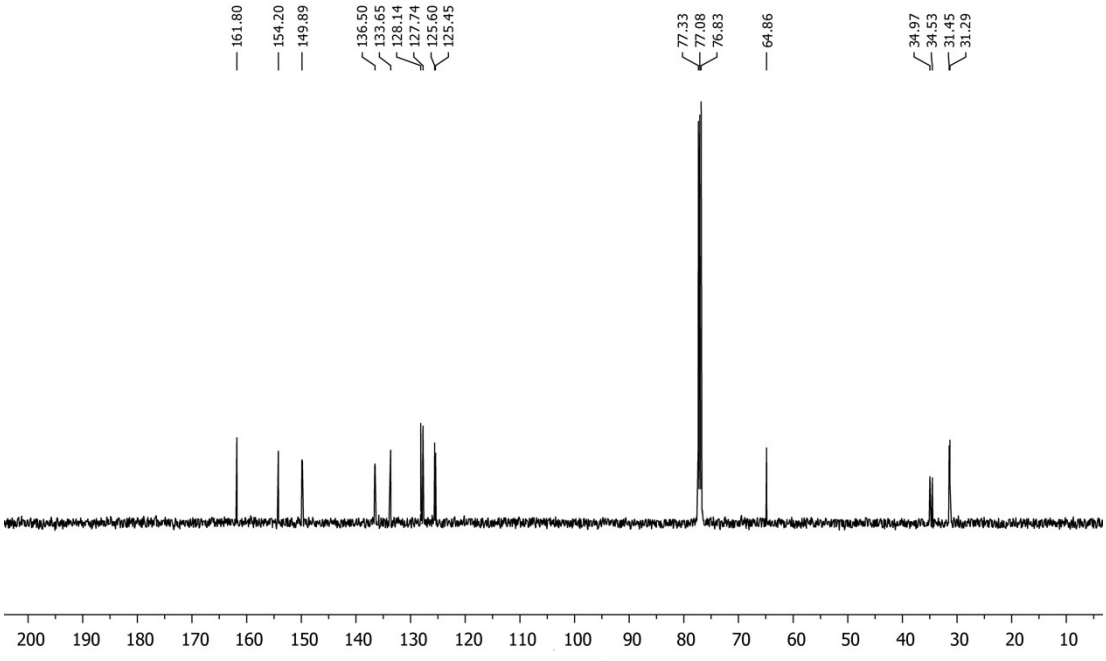
^{1}H NMR (500 MHz, $CDCl_3$)



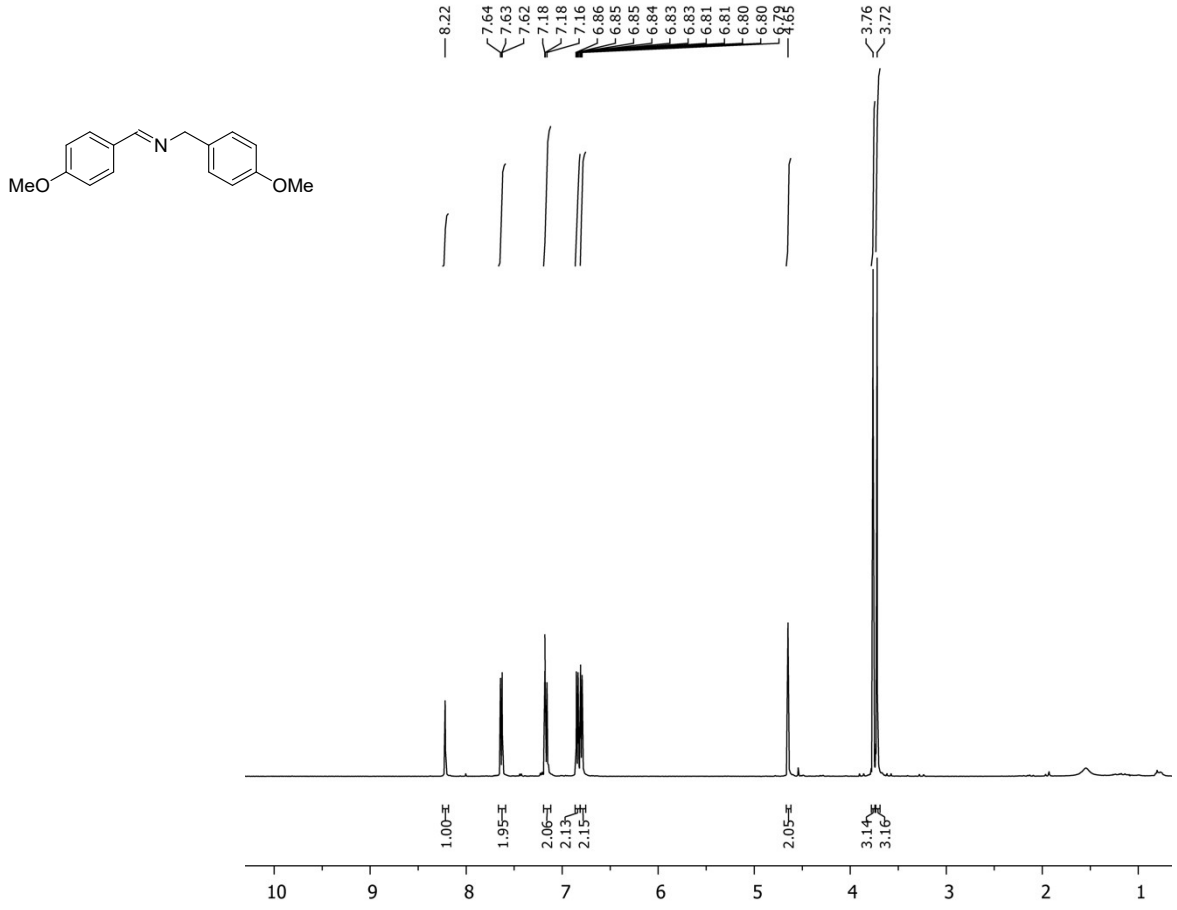
^{13}C NMR (126 MHz, $CDCl_3$)



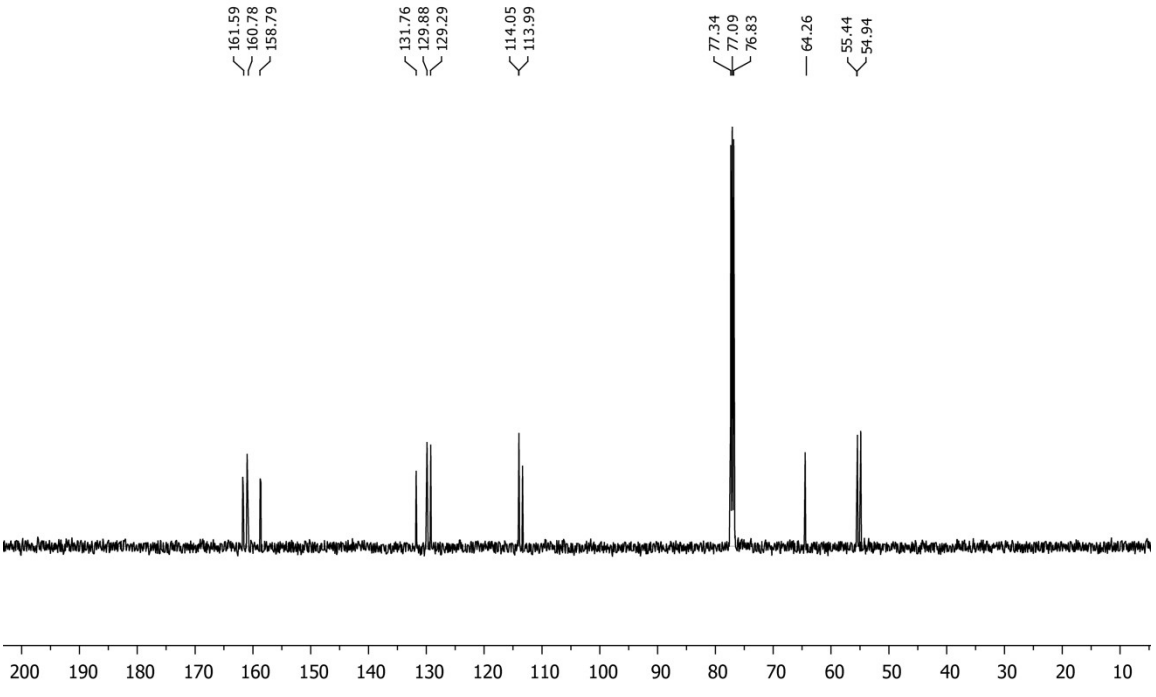
^{1}H NMR (500 MHz, $CDCl_3$)



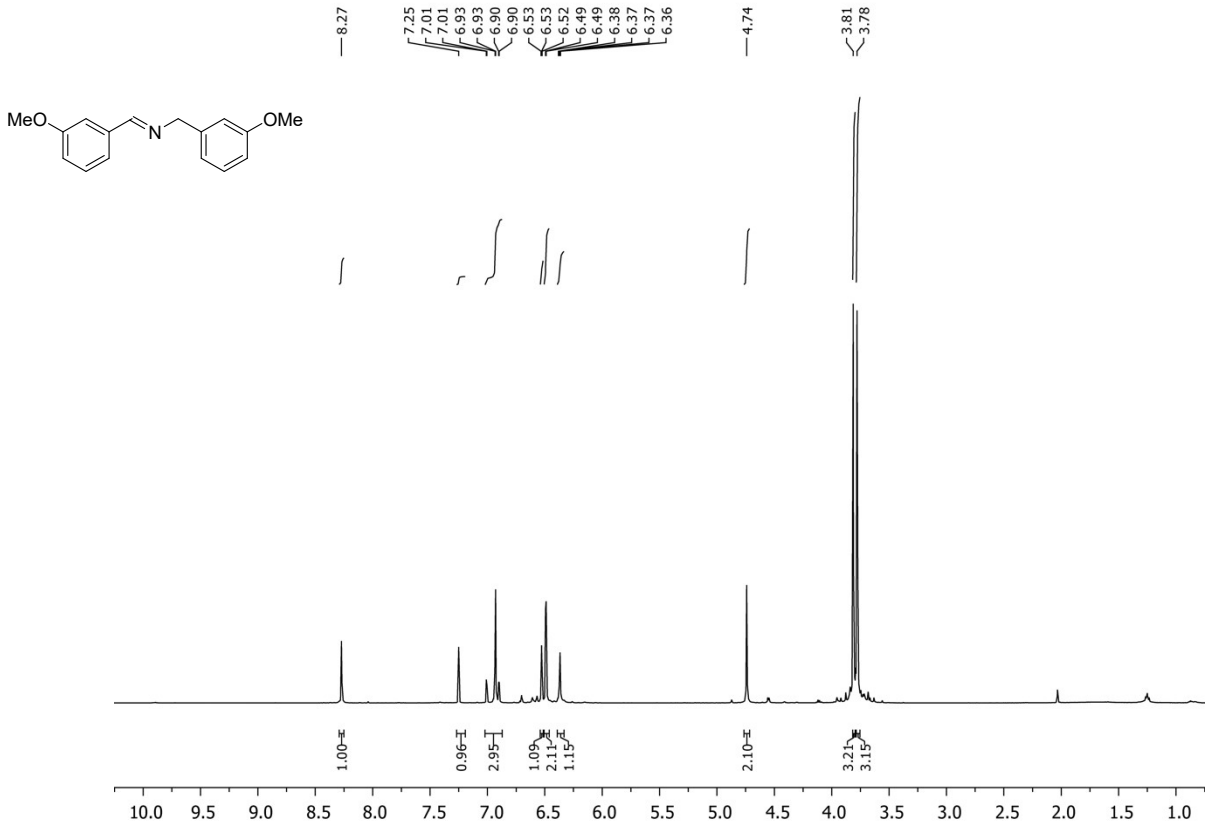
^{13}C NMR (126 MHz, $CDCl_3$)



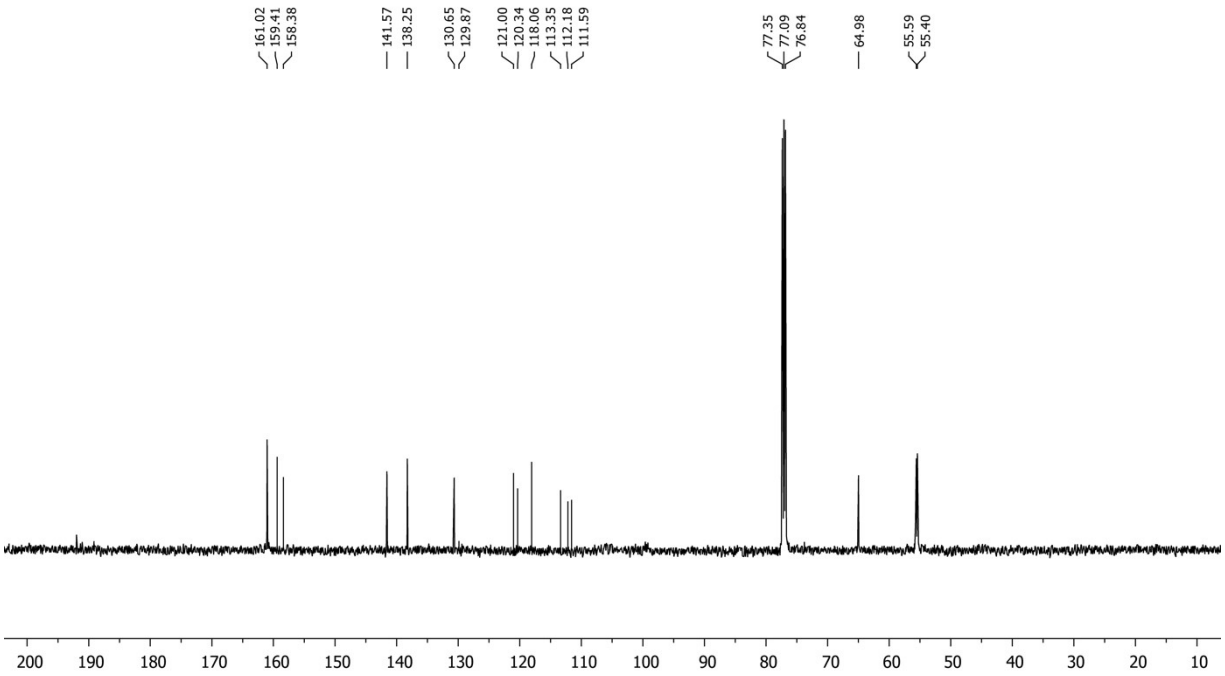
^{1}H NMR (500 MHz, $CDCl_3$)



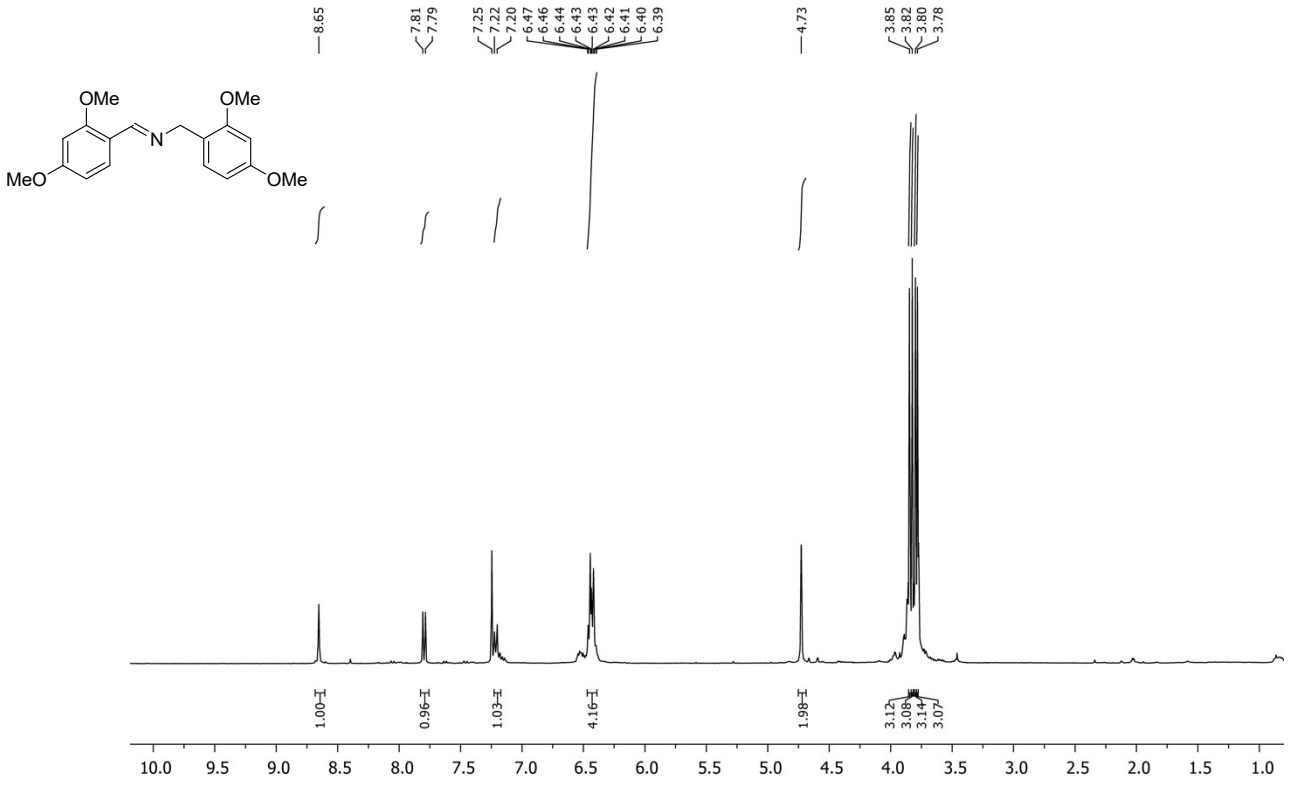
^{13}C NMR (126 MHz, $CDCl_3$)



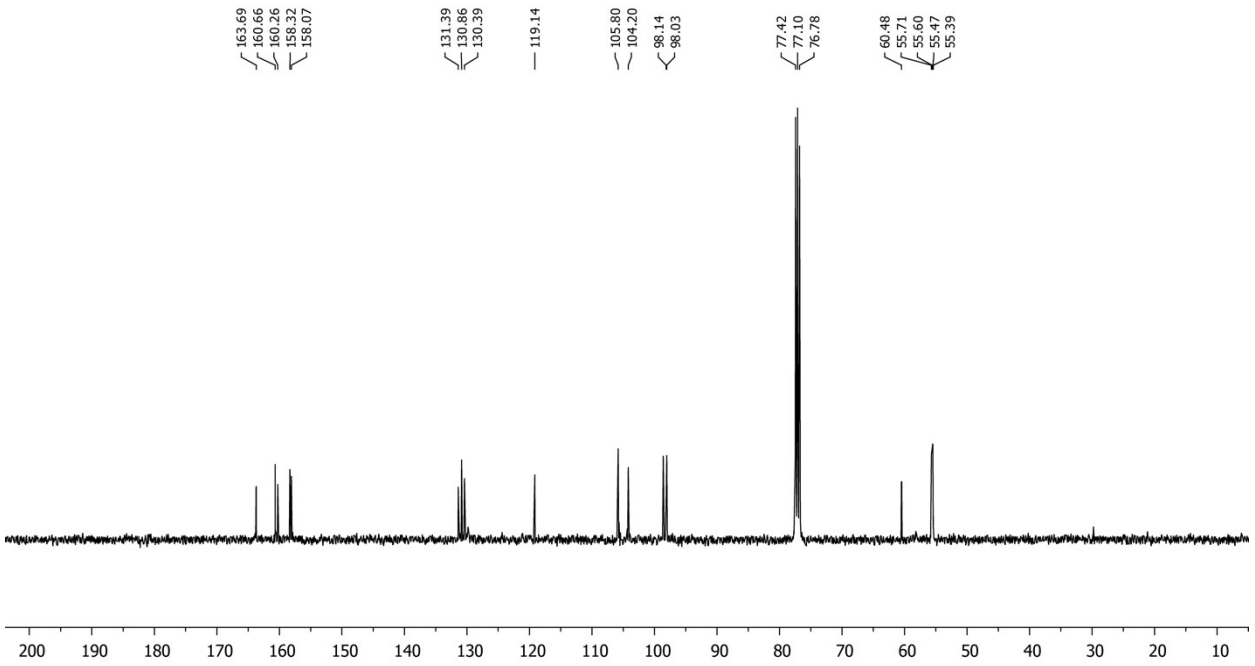
^{1}H NMR (500 MHz, $CDCl_3$)



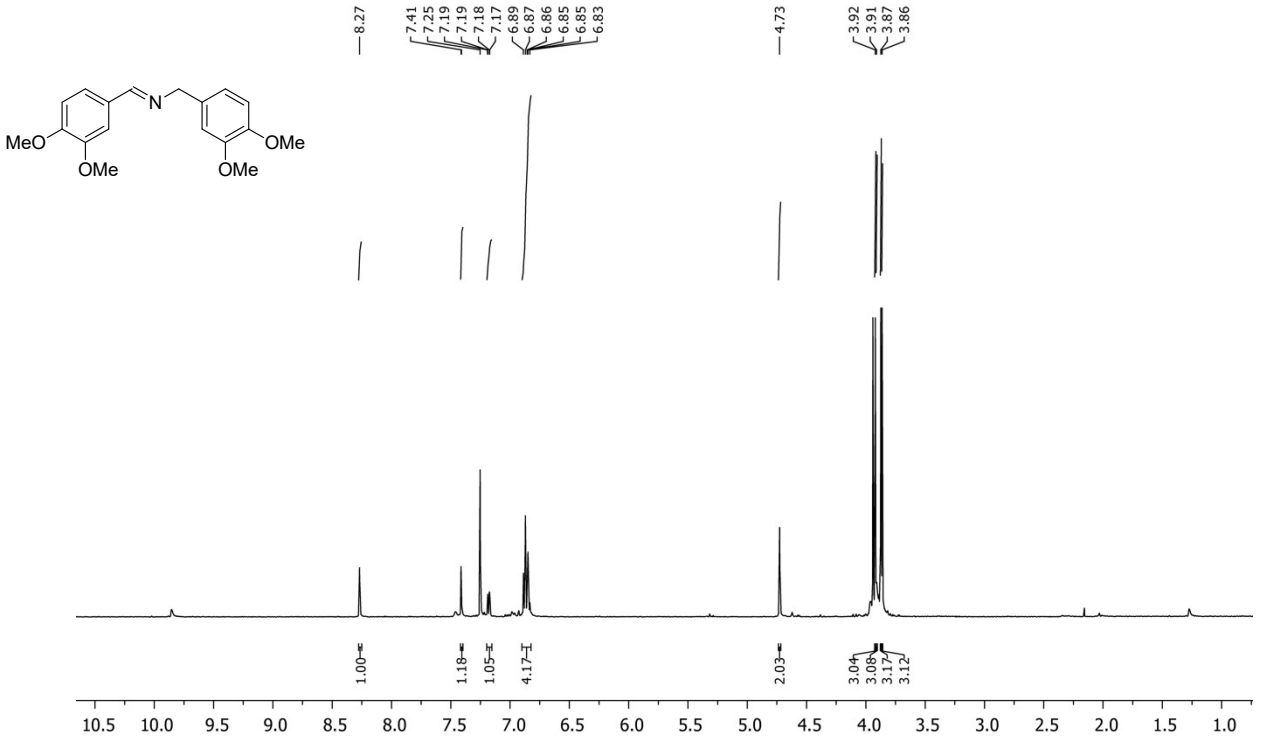
^{13}C NMR (126 MHz, $CDCl_3$)



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



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



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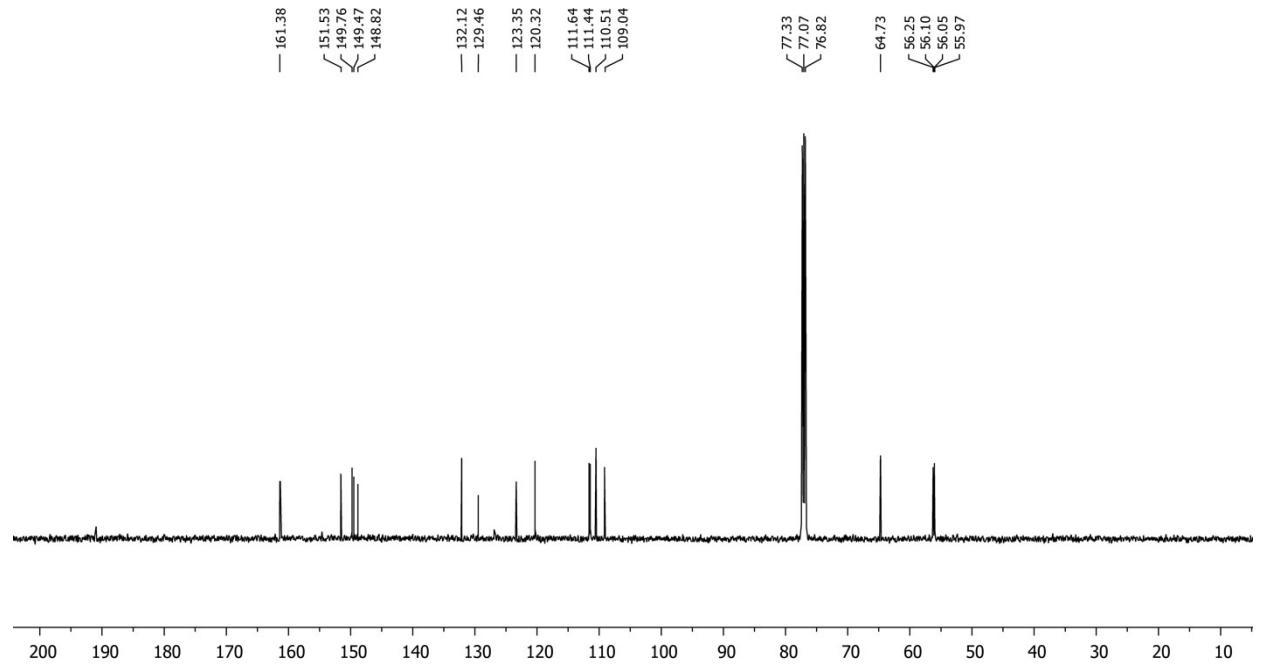
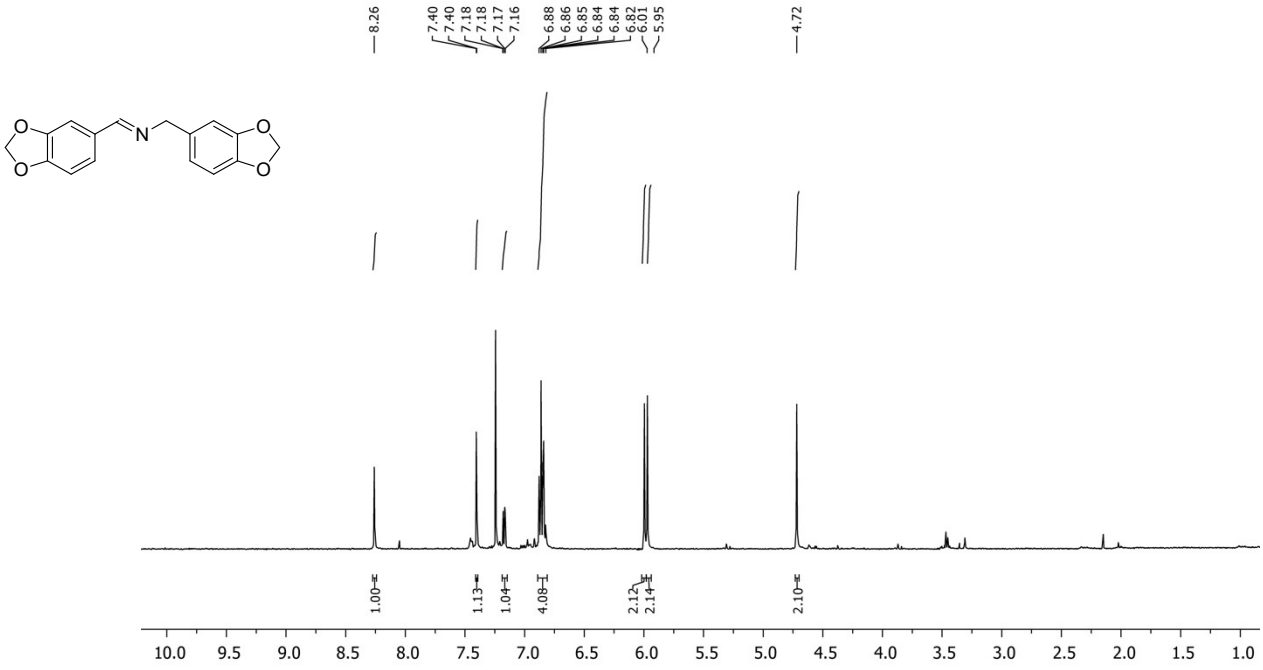
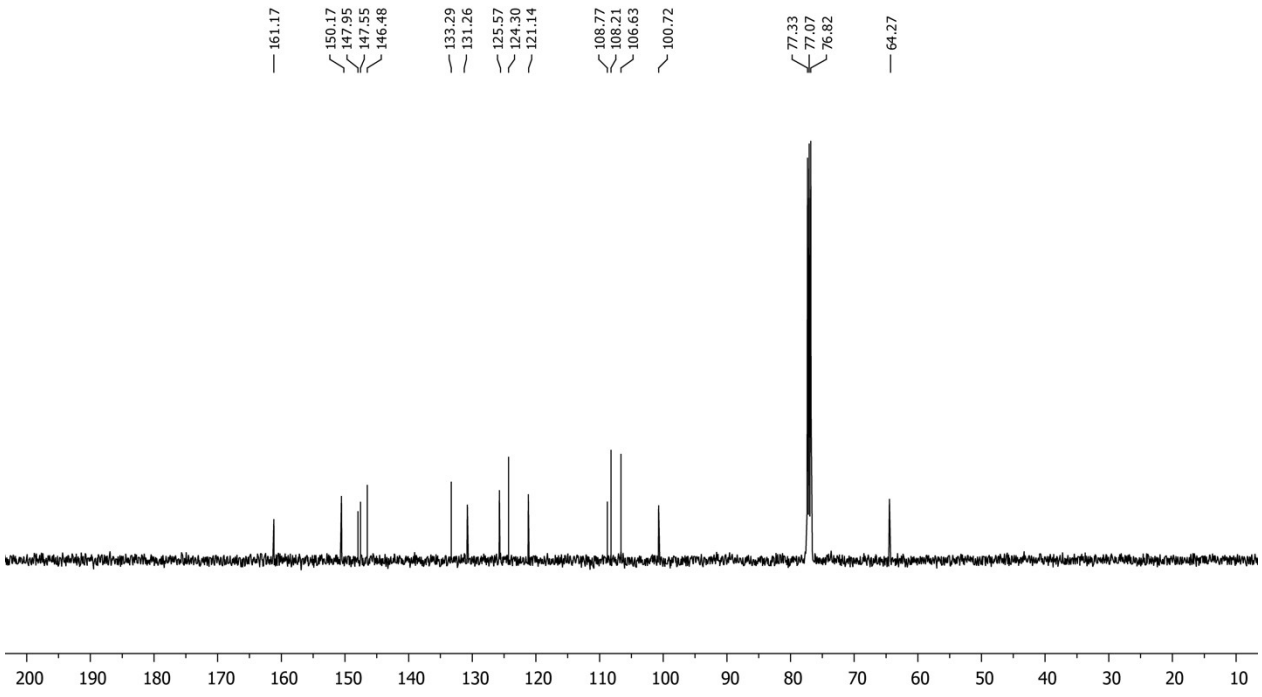


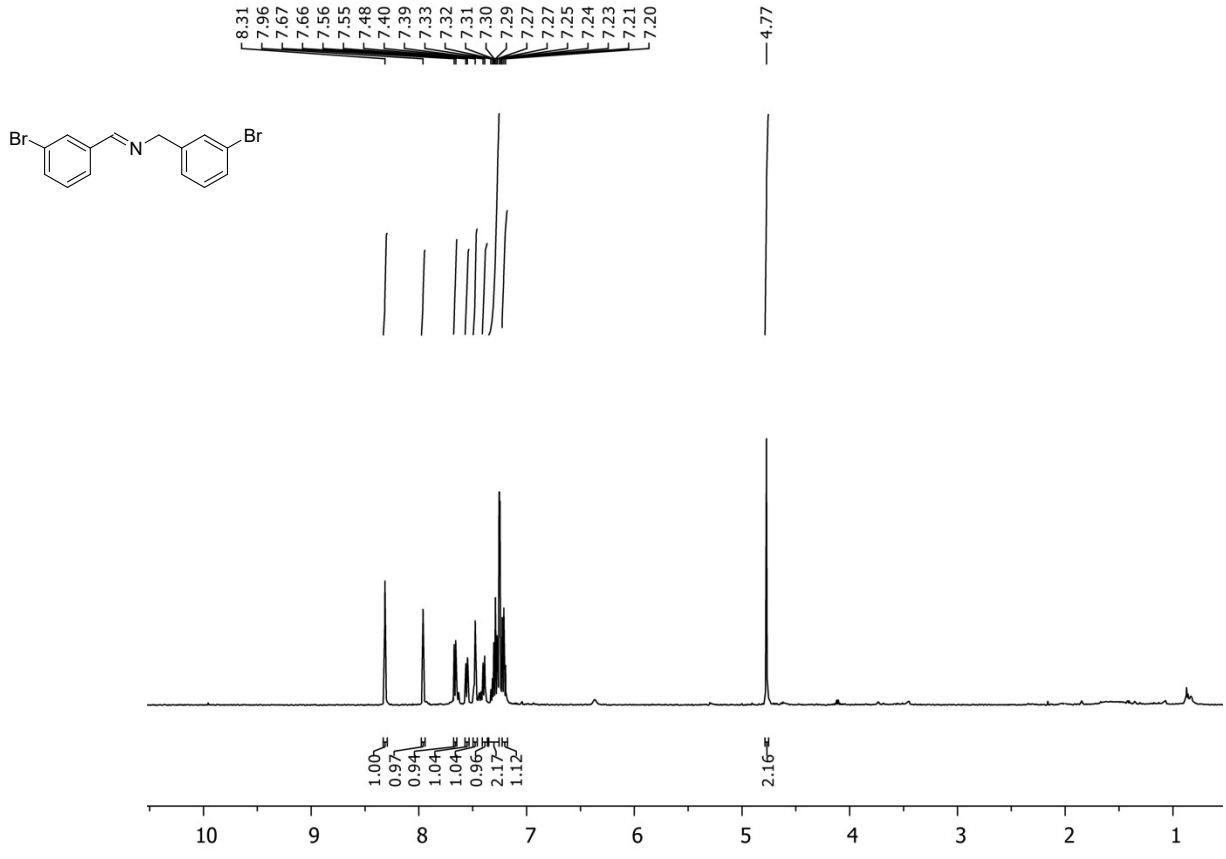
^{13}C NMR (126 MHz, $CDCl_3$)



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



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



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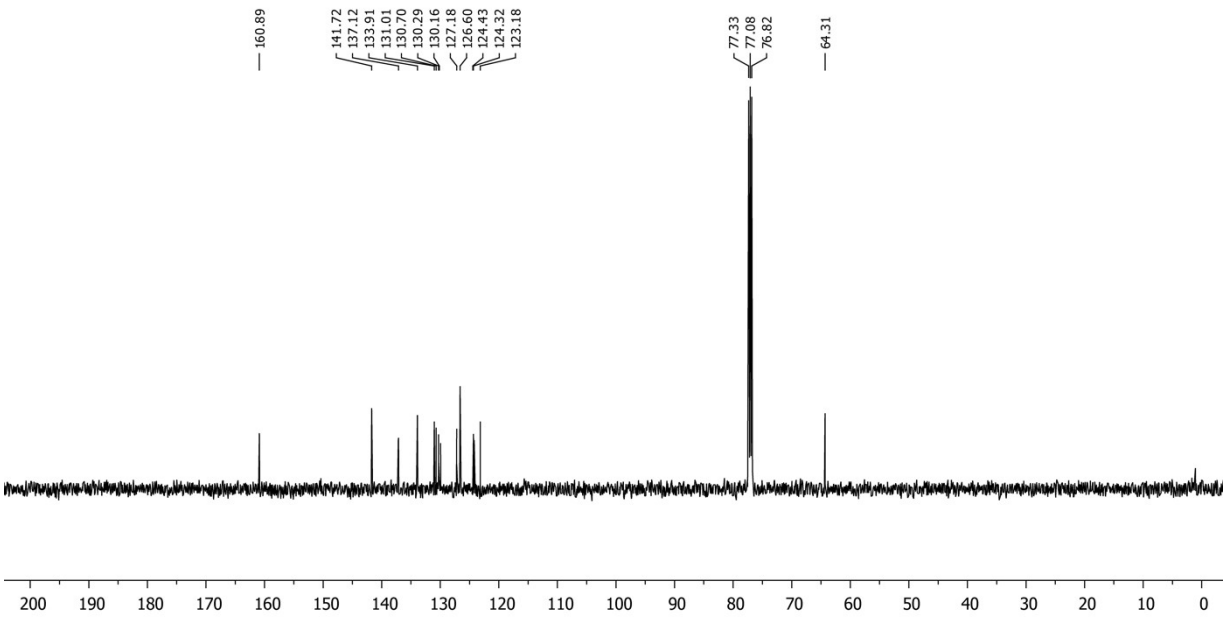
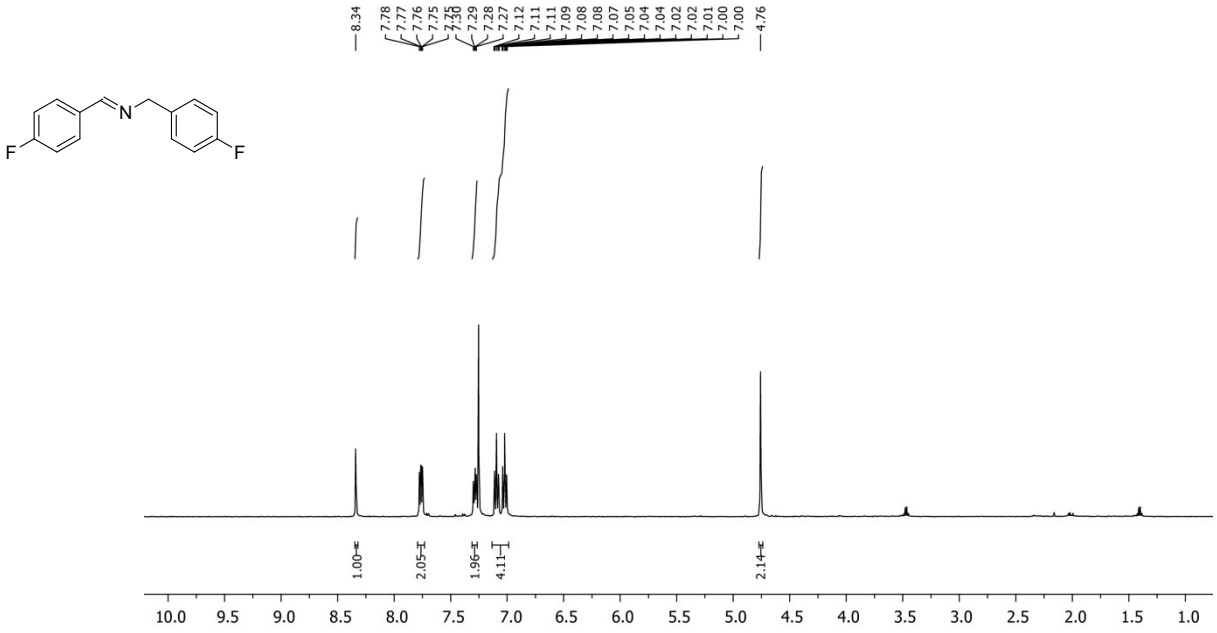


^{13}C NMR (126 MHz, $CDCl_3$)



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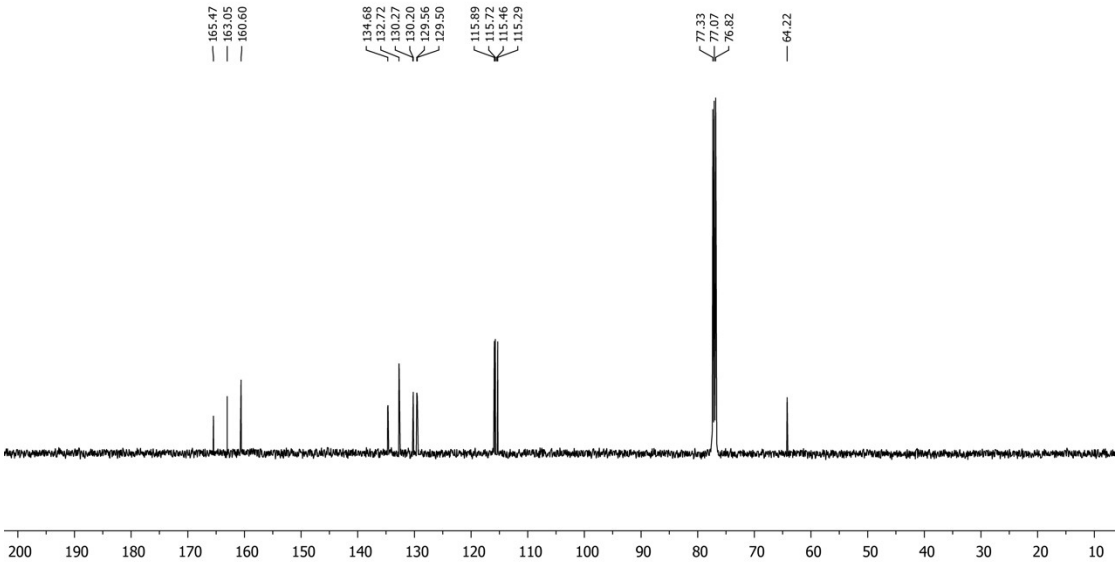
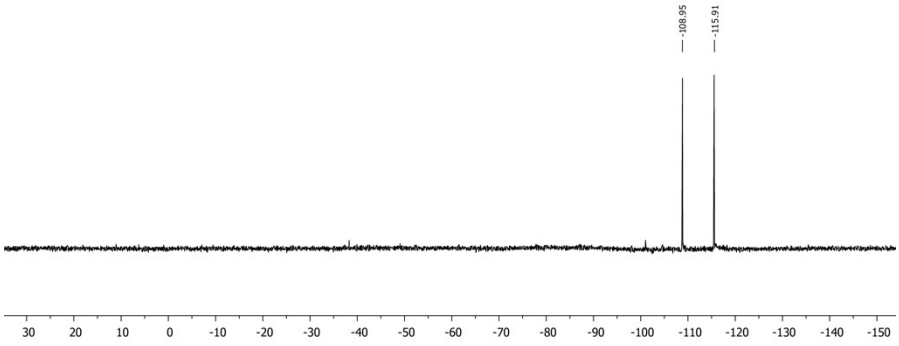
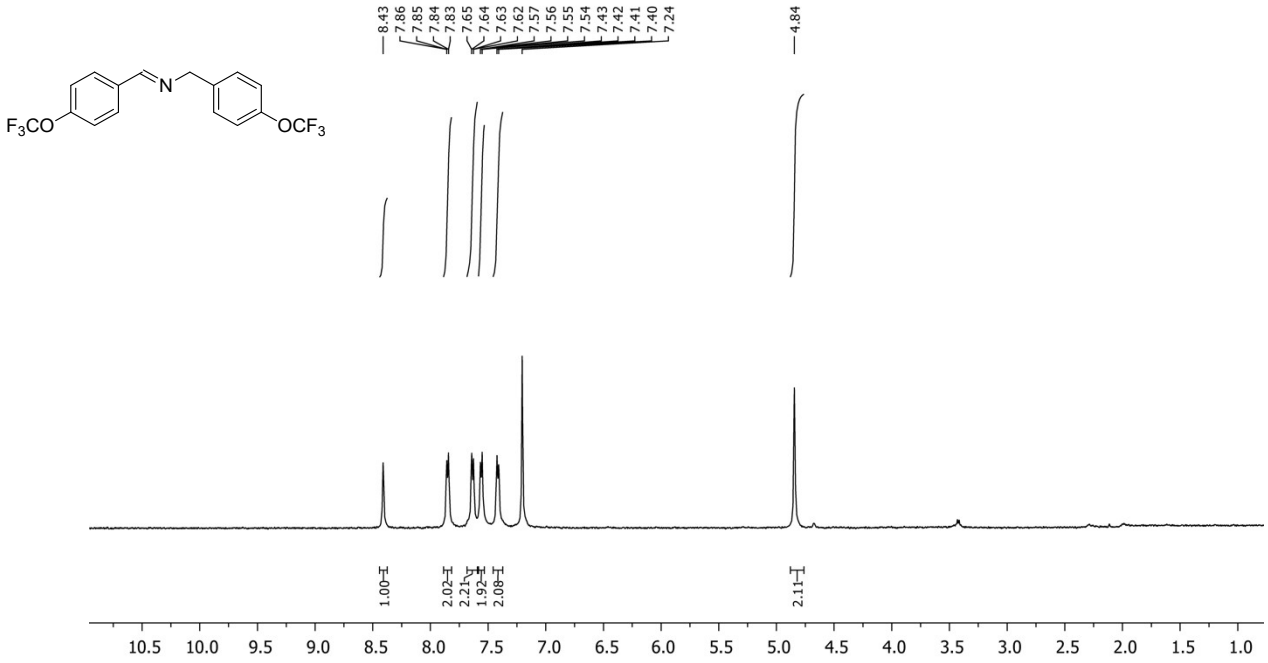


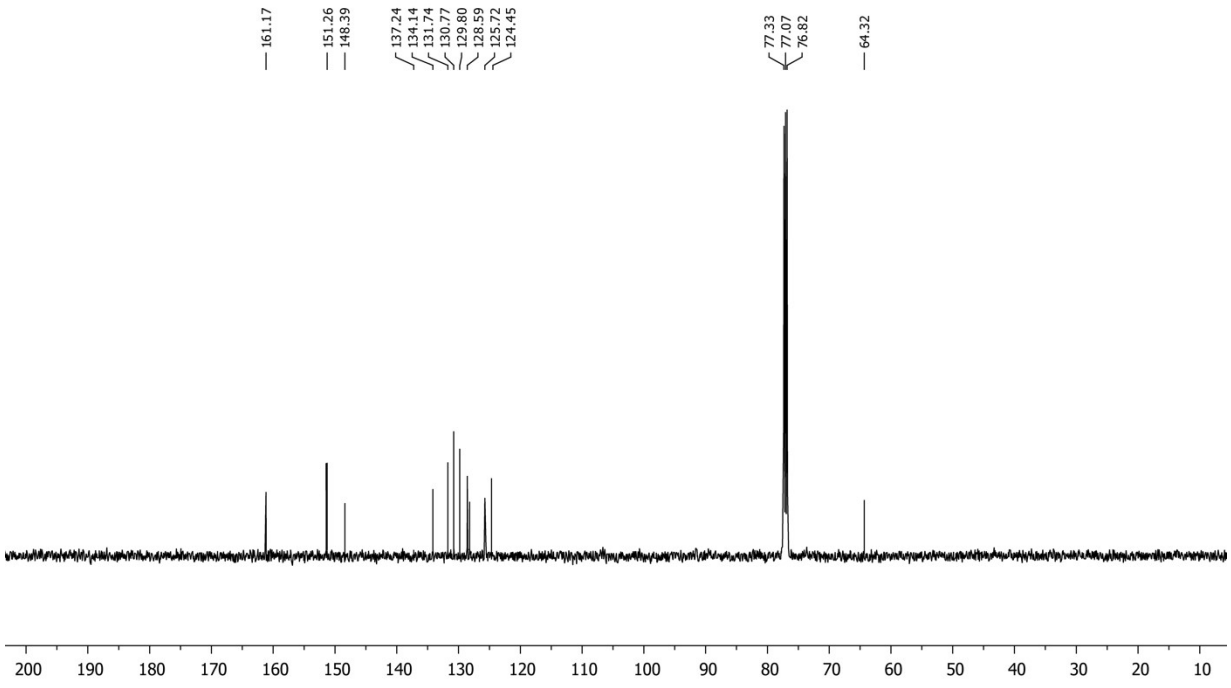
^{13}C NMR (126 MHz, $CDCl_3$)



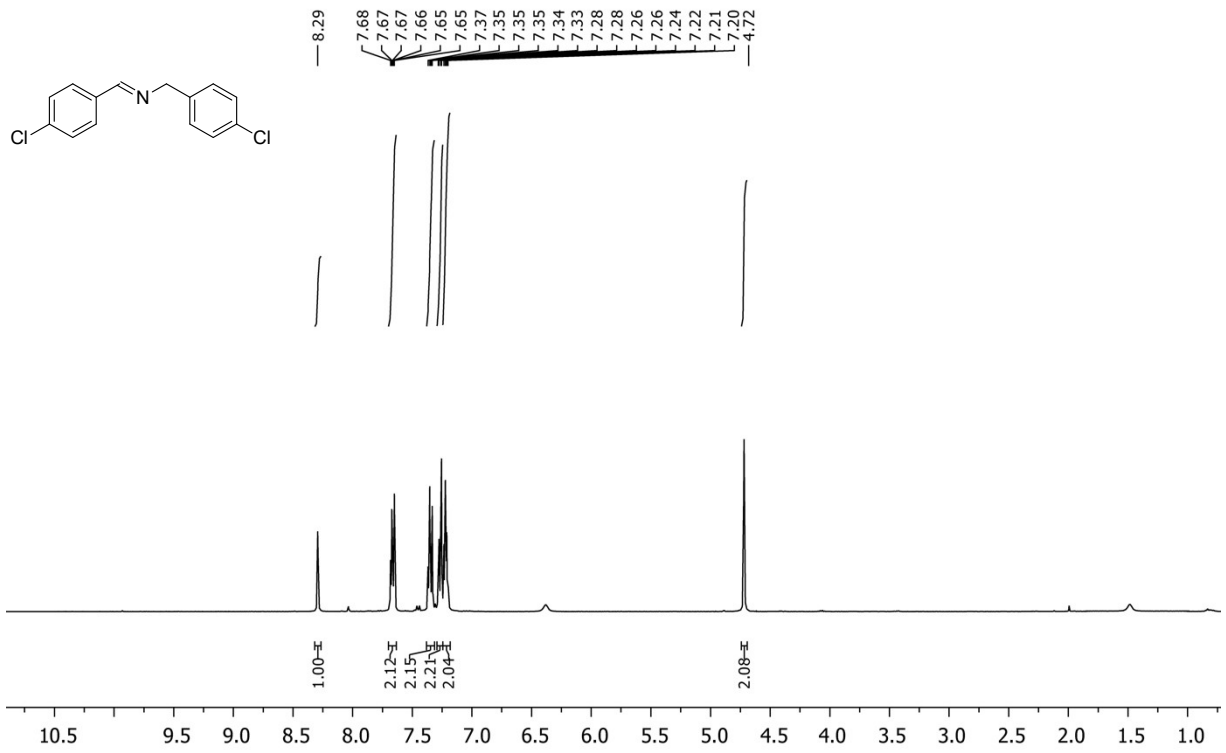
^{19}F NMR (470 MHz, $CDCl_3$)



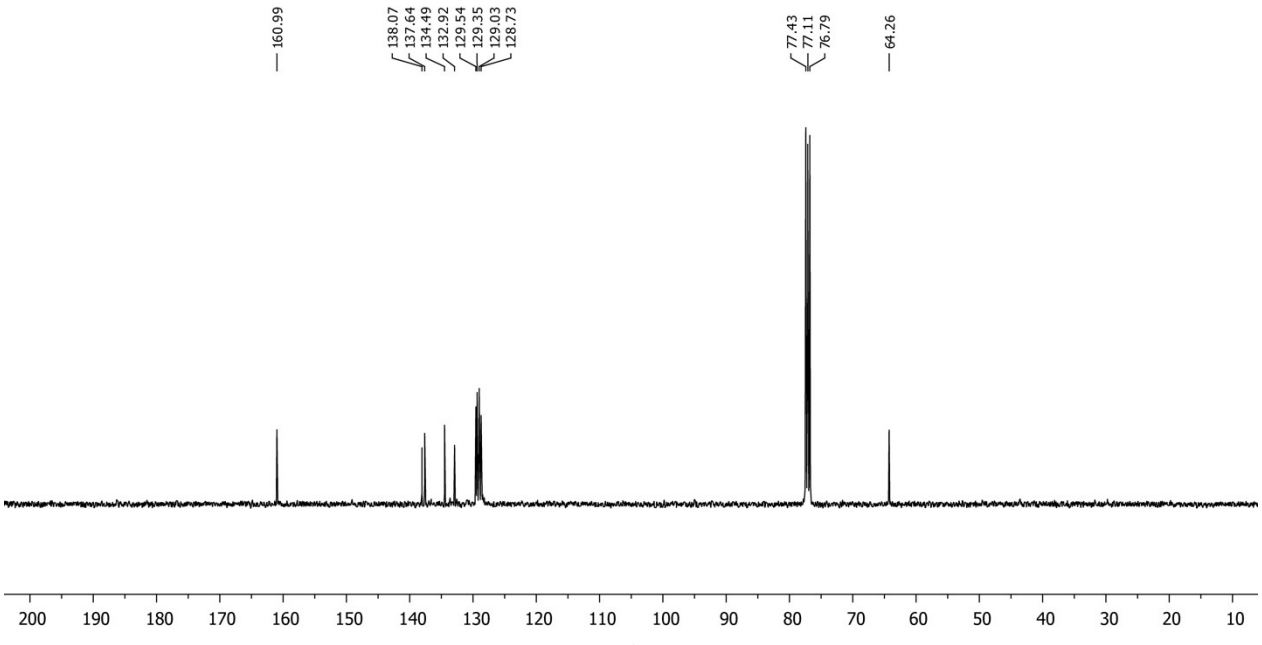
^{1}H NMR (500 MHz, $CDCl_3$)



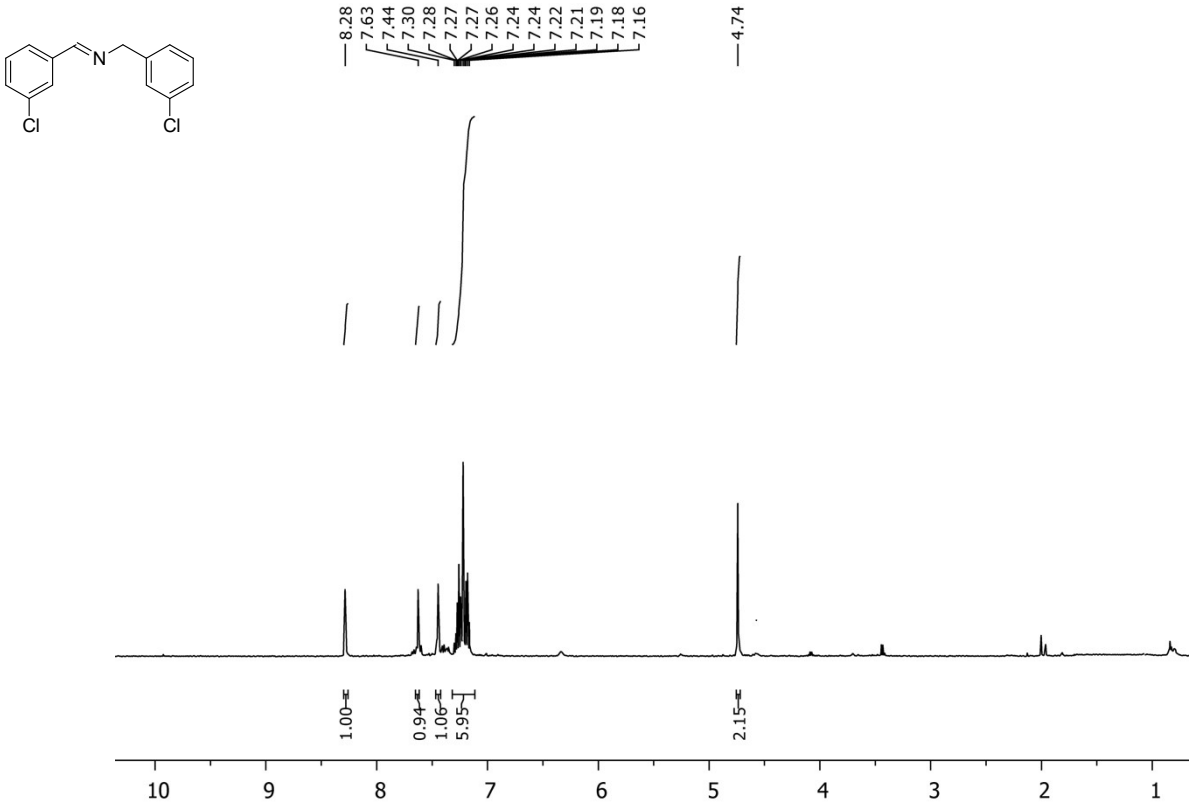
^{13}C NMR (126 MHz, $CDCl_3$)



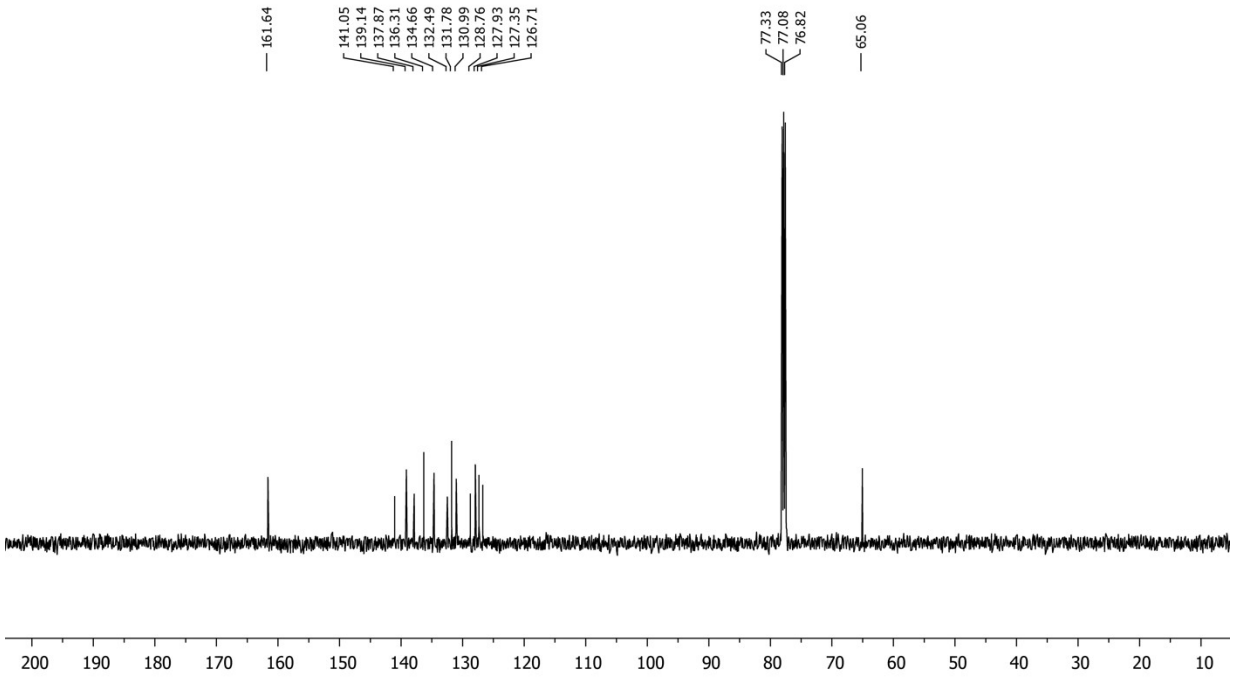
^{1}H NMR (500 MHz, $CDCl_3$)



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



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



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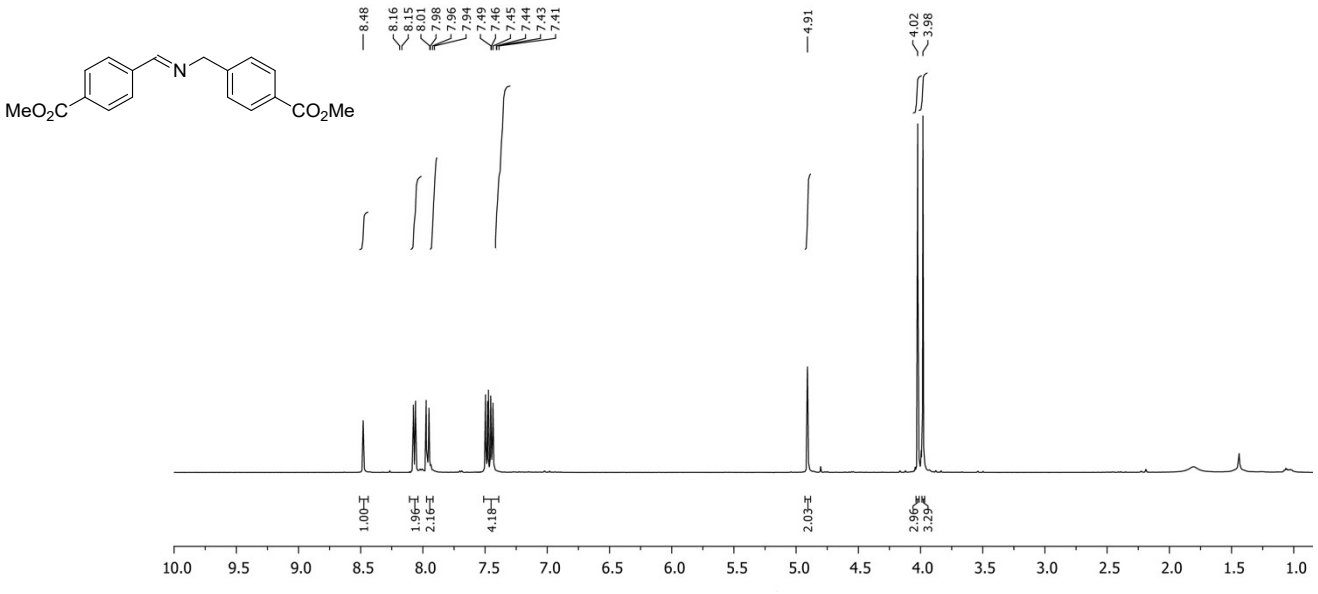
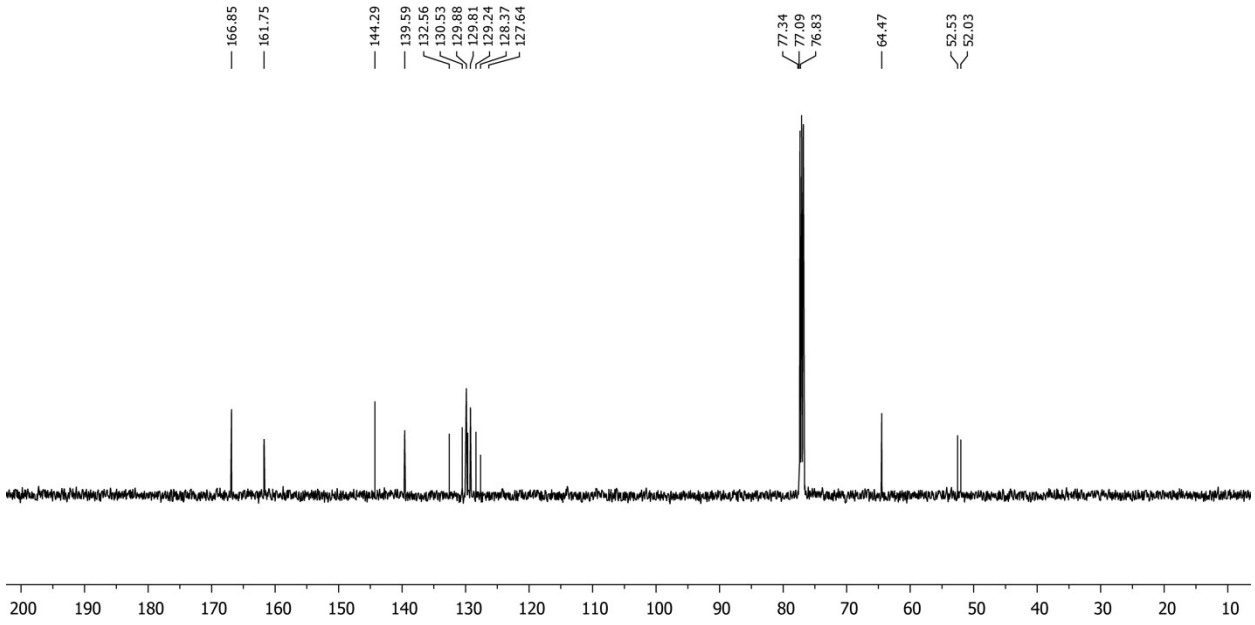


^{1}H NMR (500 MHz, $CDCl_3$)



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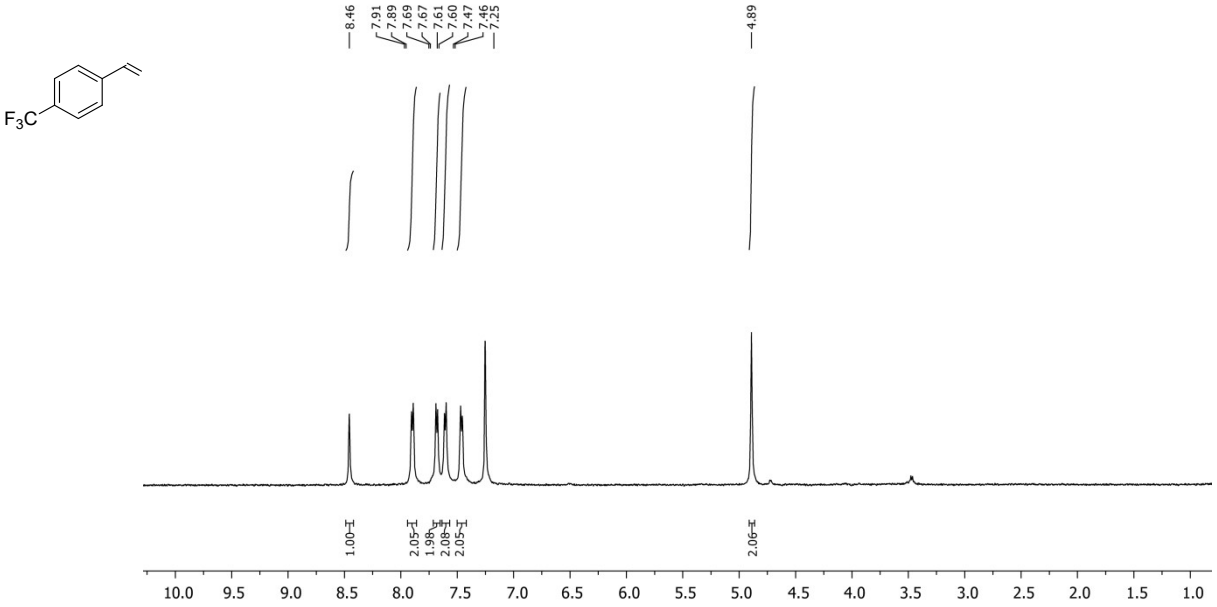

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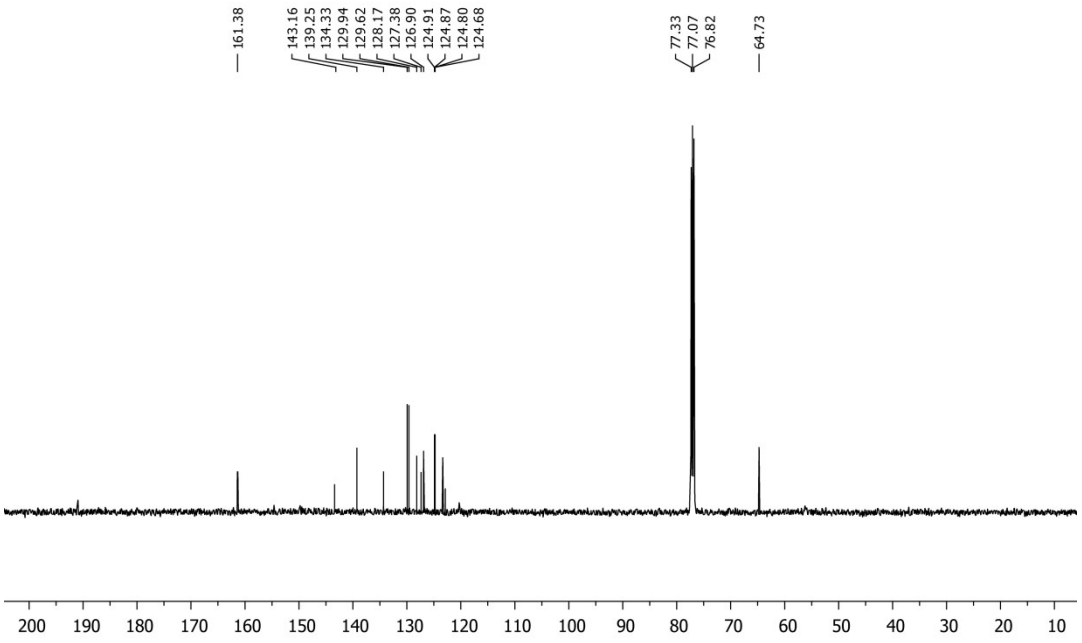
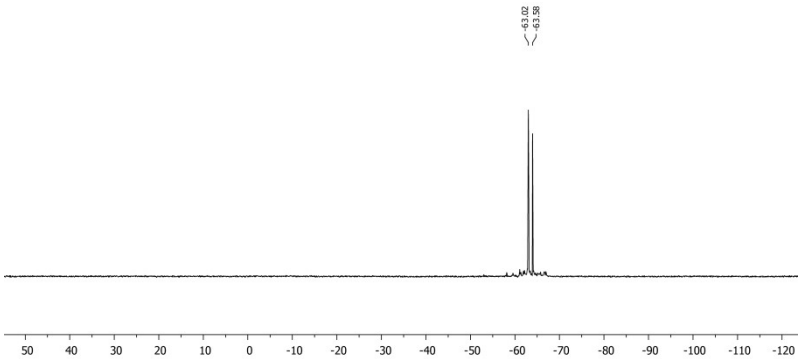
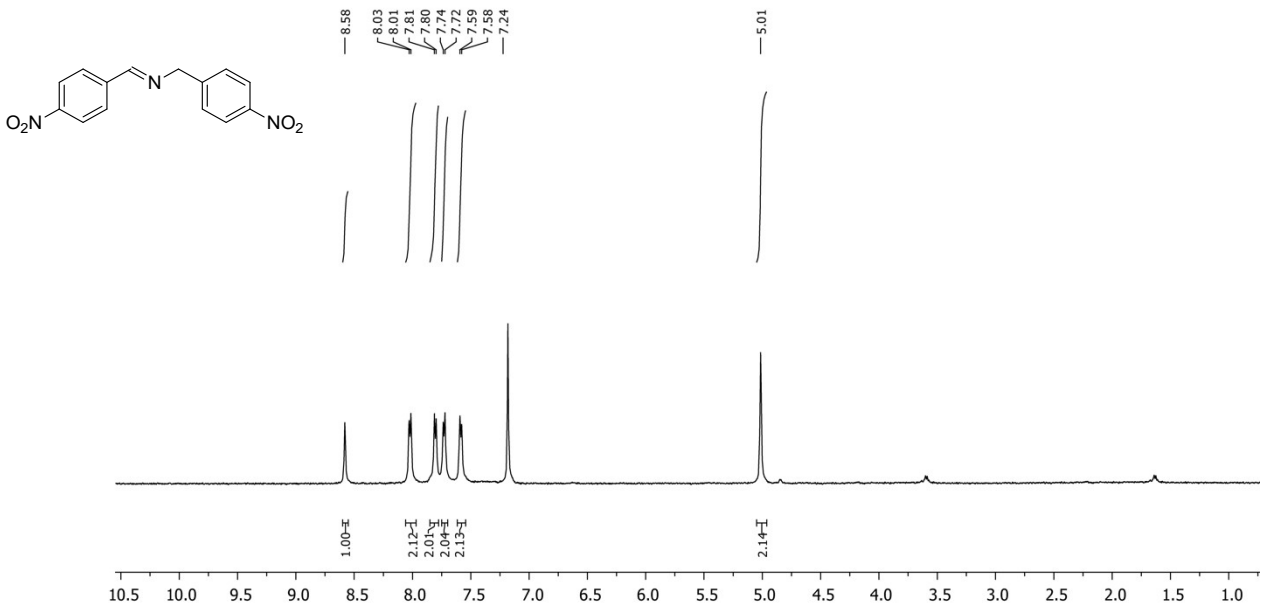


^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$)



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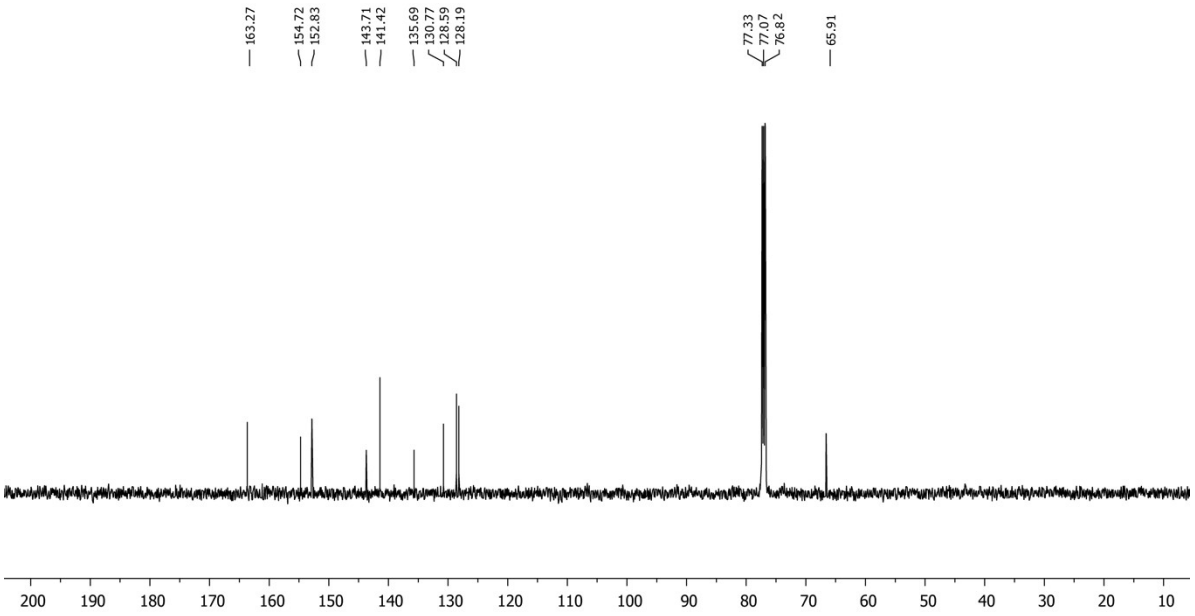
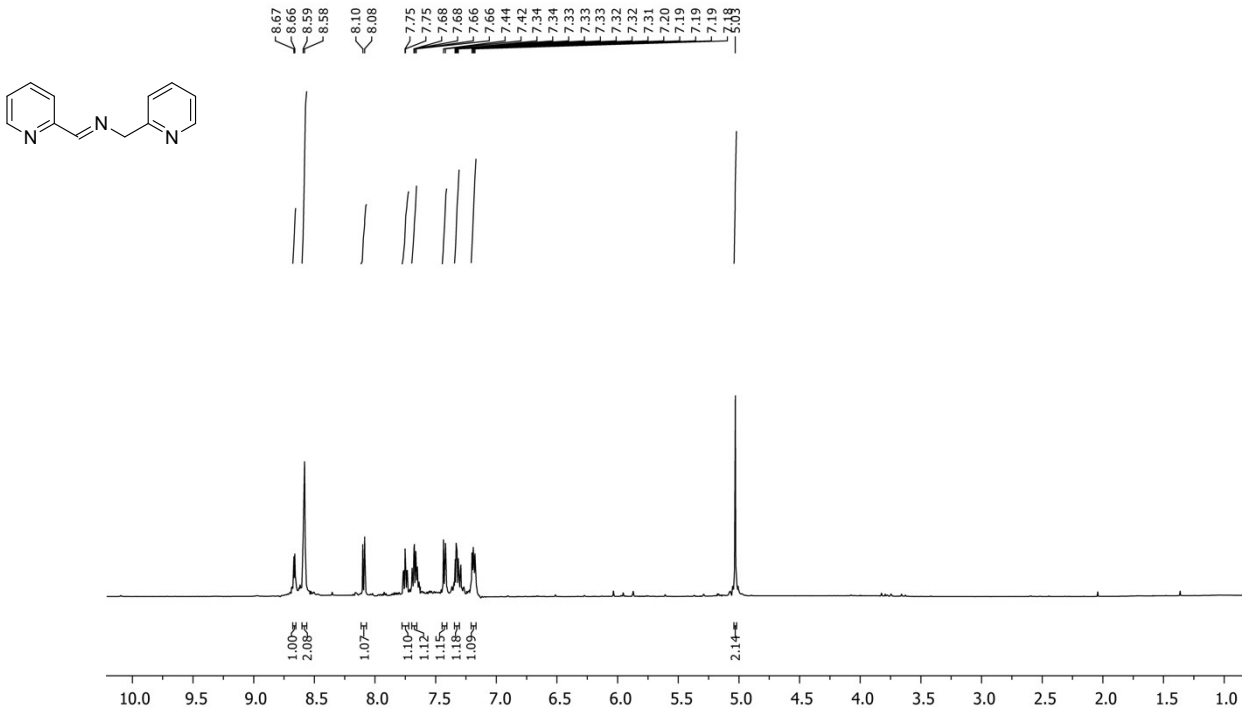
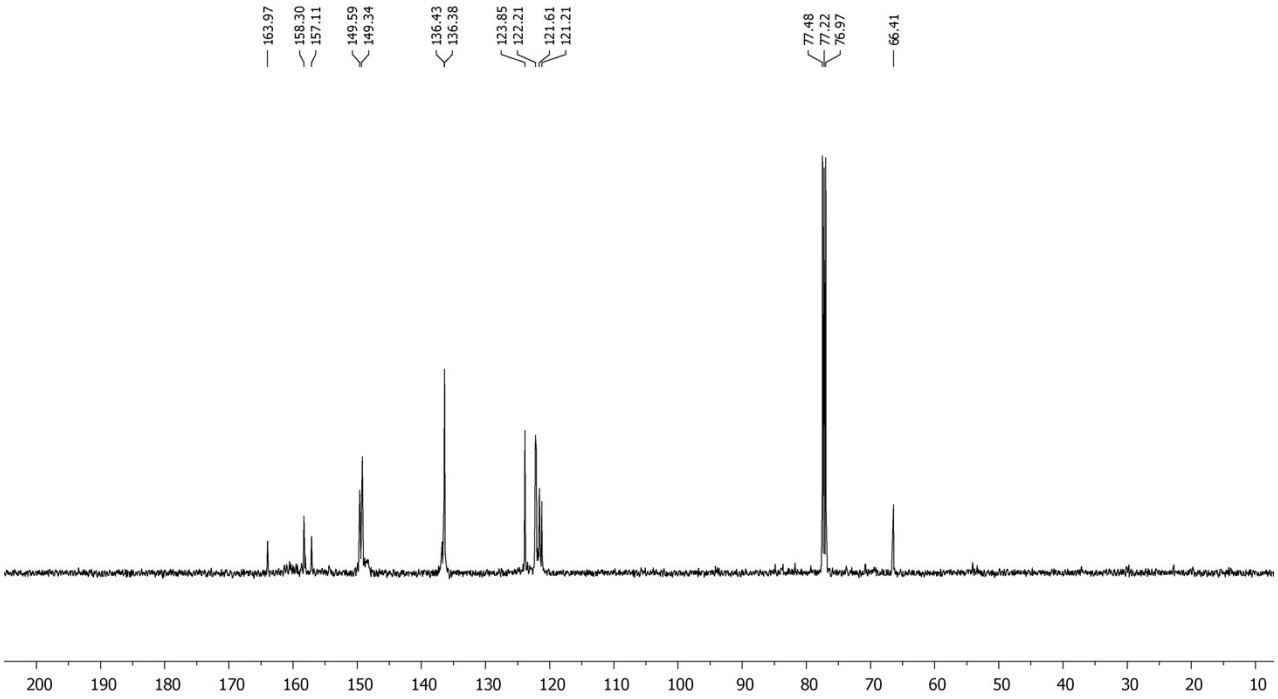


^{13}C NMR (126 MHz, $CDCl_3$)



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



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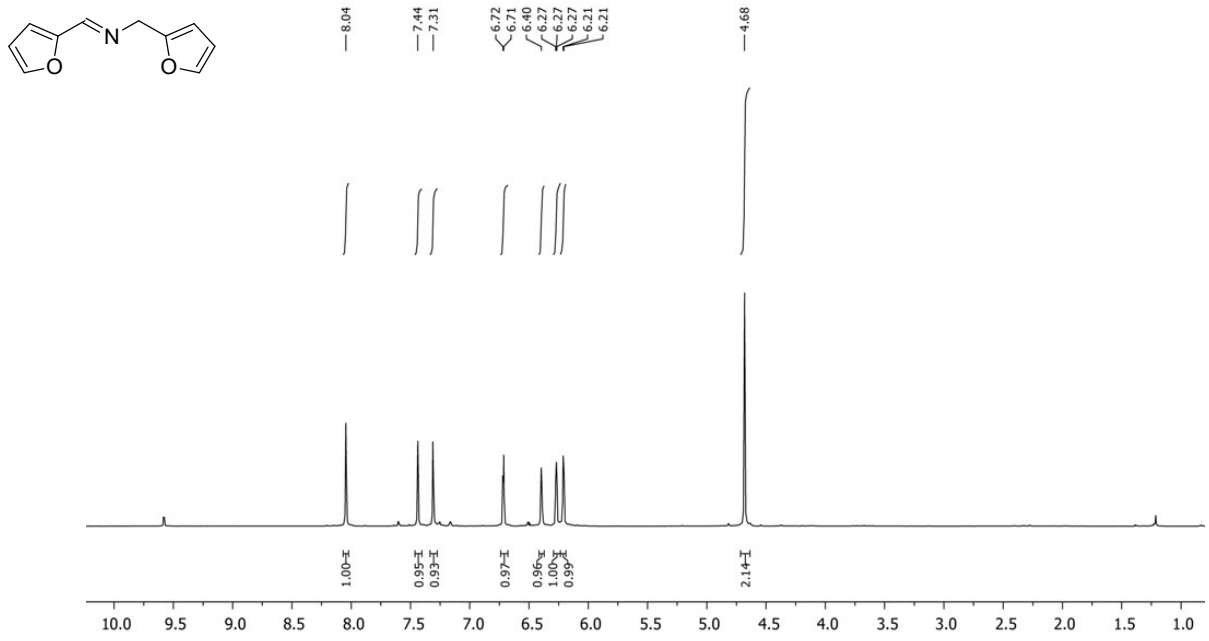
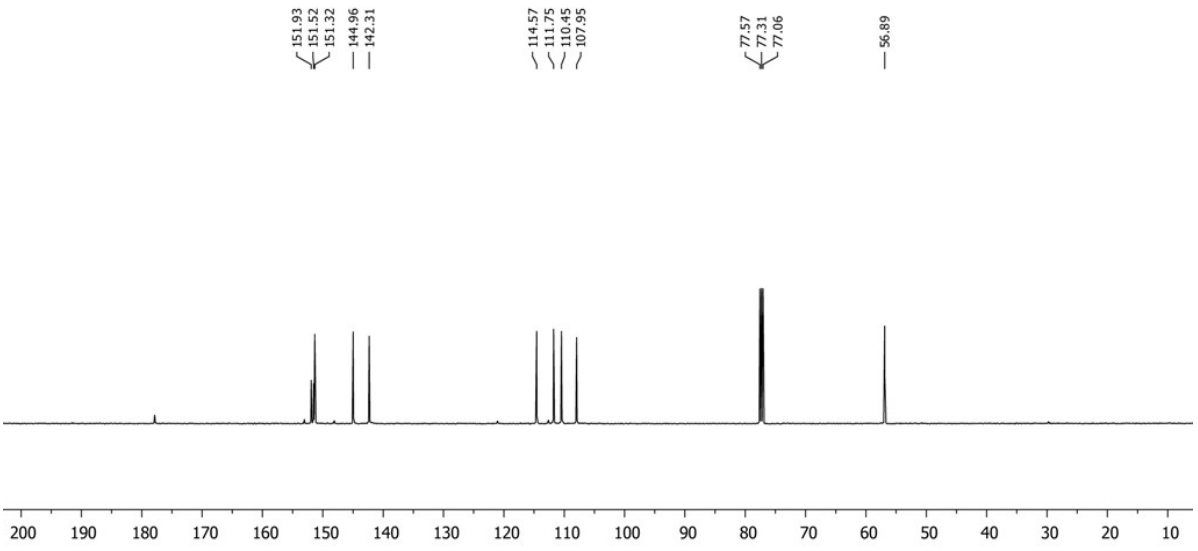
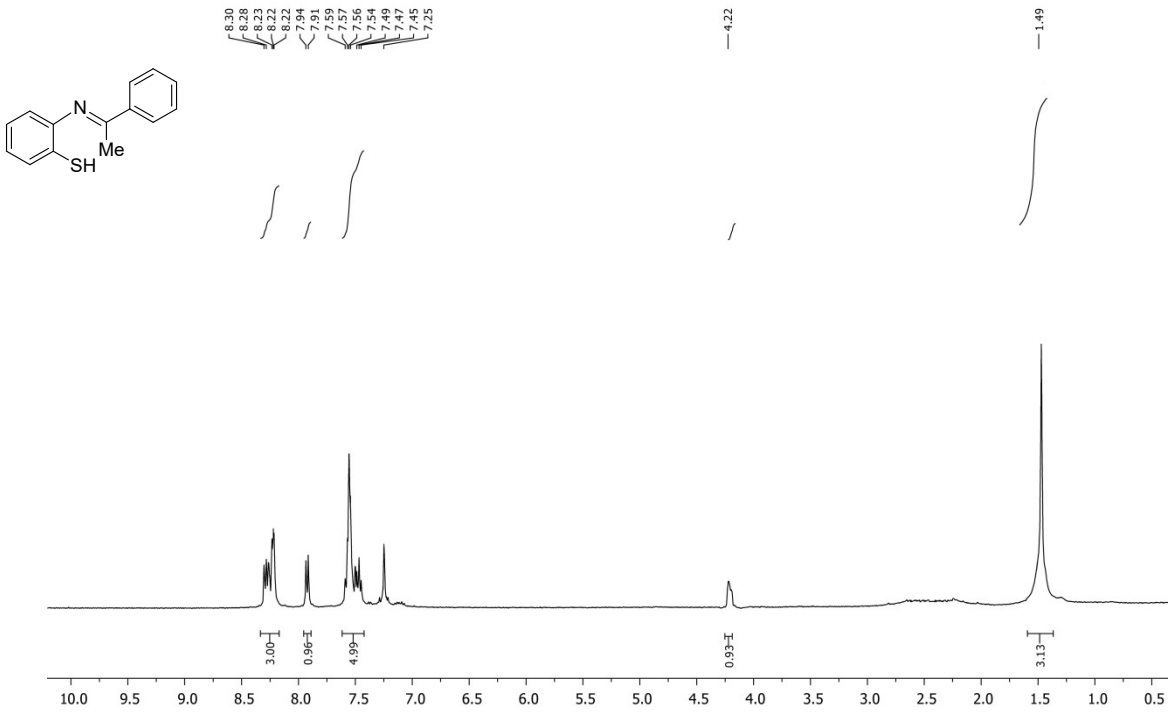


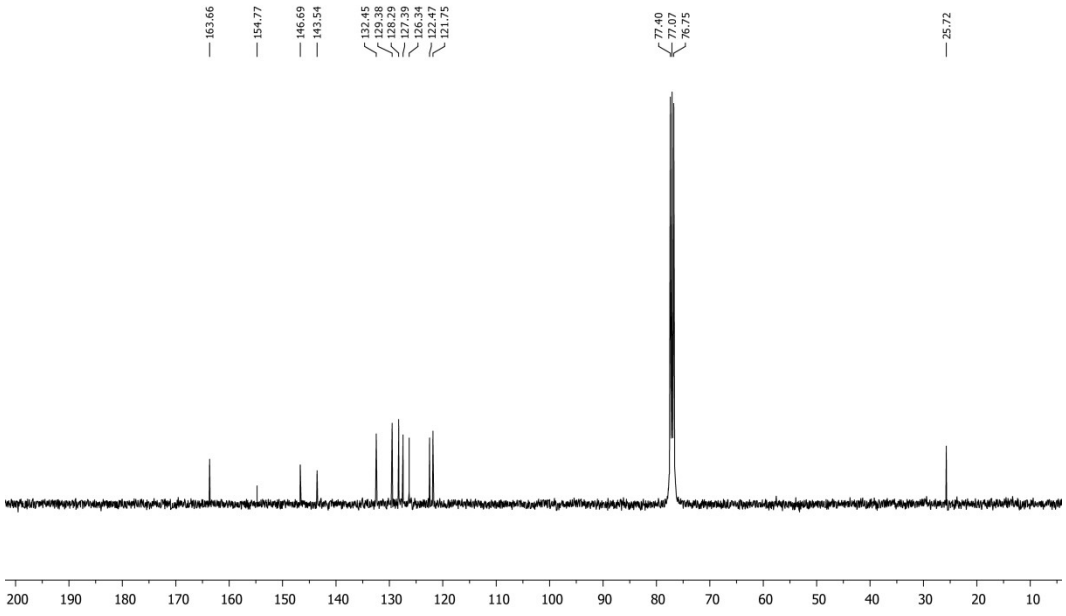
^{1}H NMR (500 MHz, $CDCl_3$)



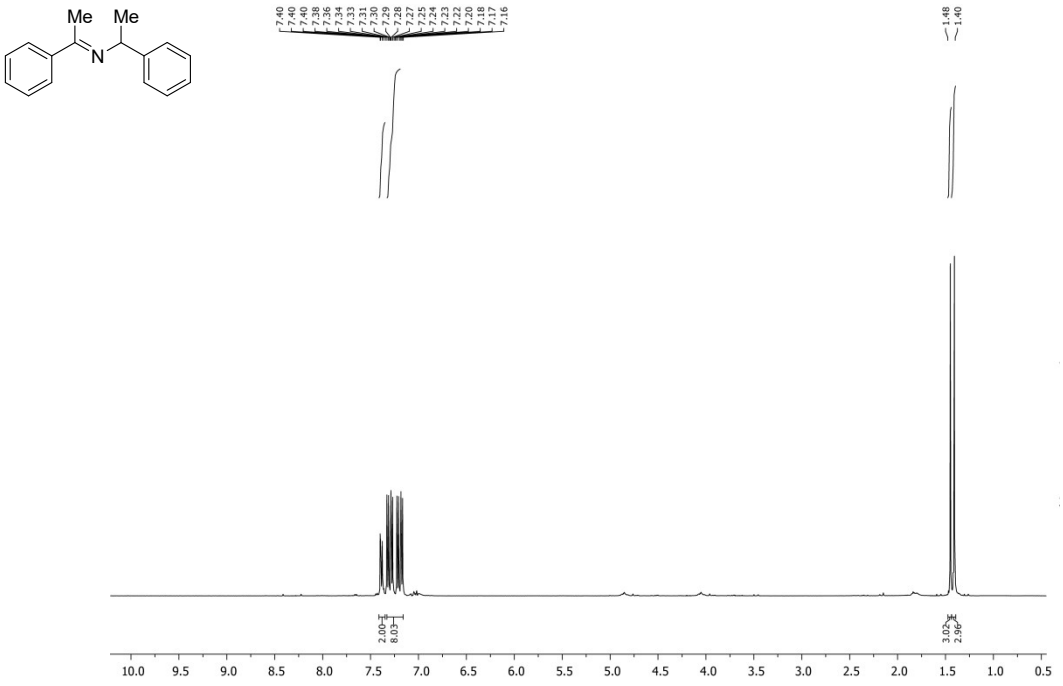
^{13}C NMR (126 MHz, $CDCl_3$)



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



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



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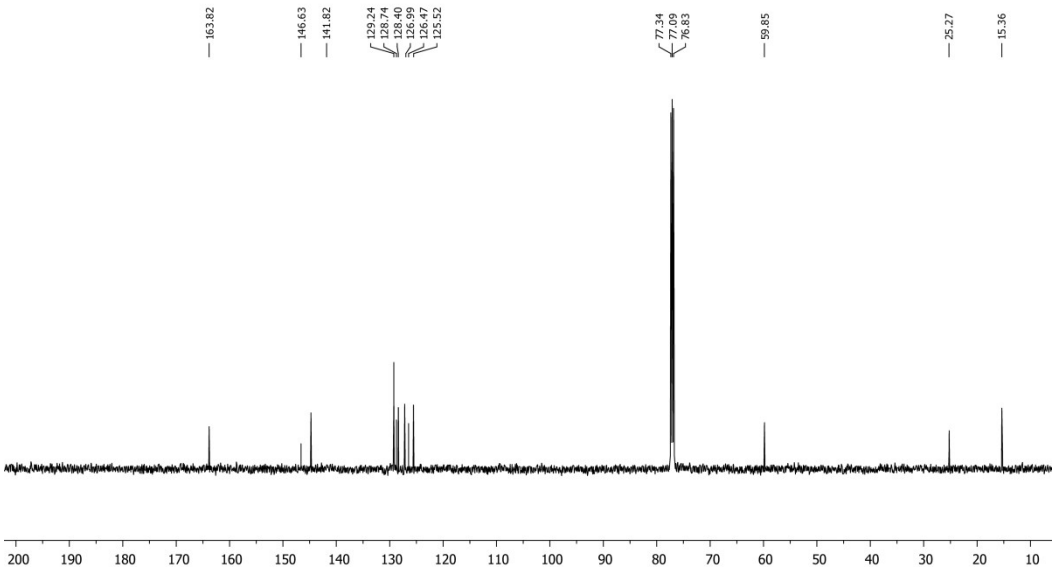
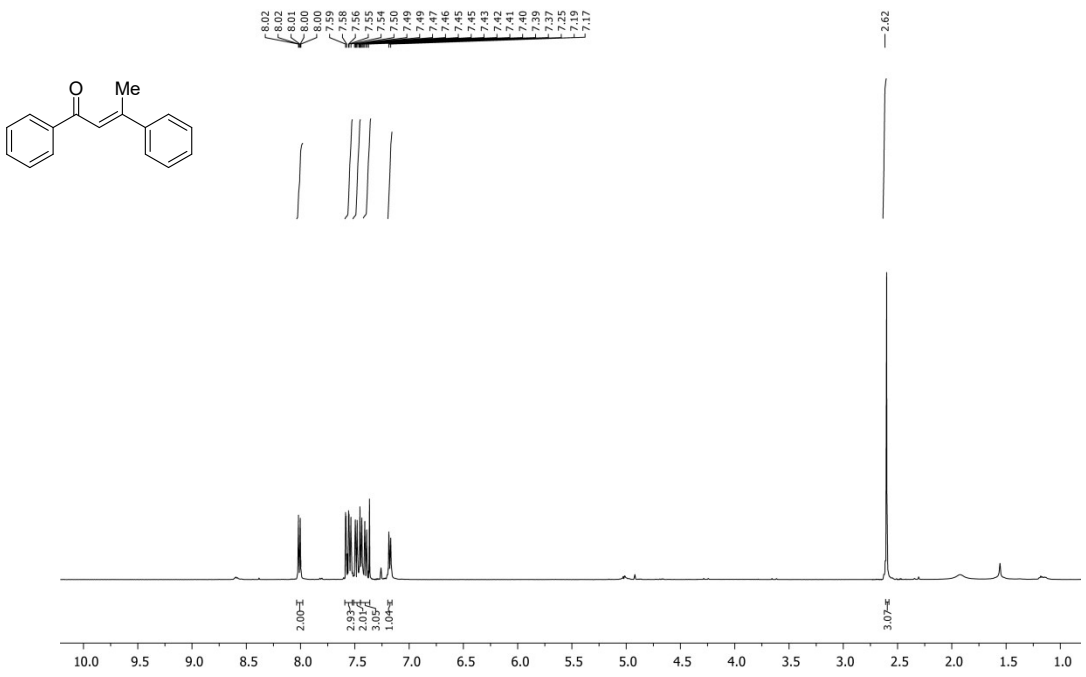
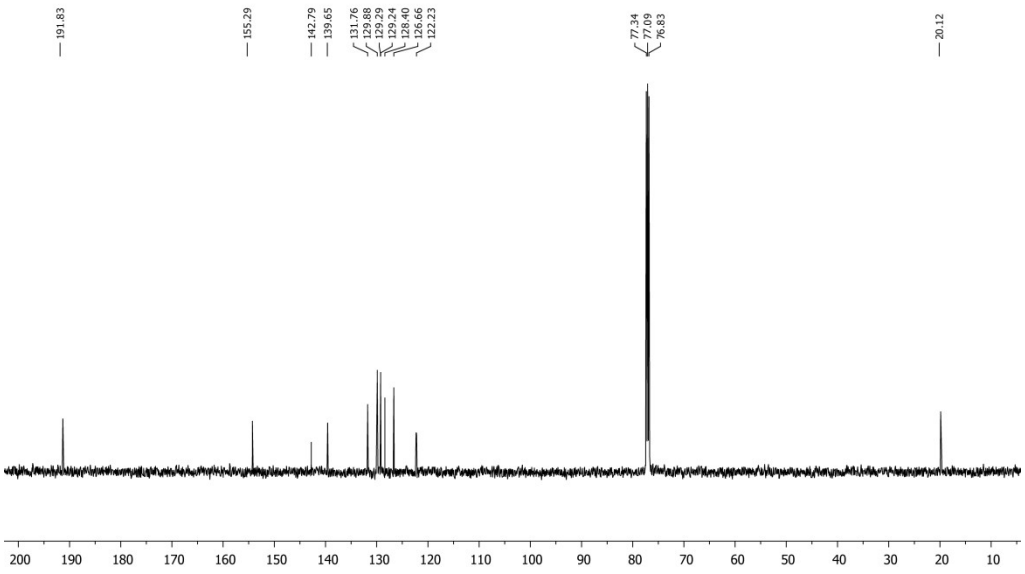


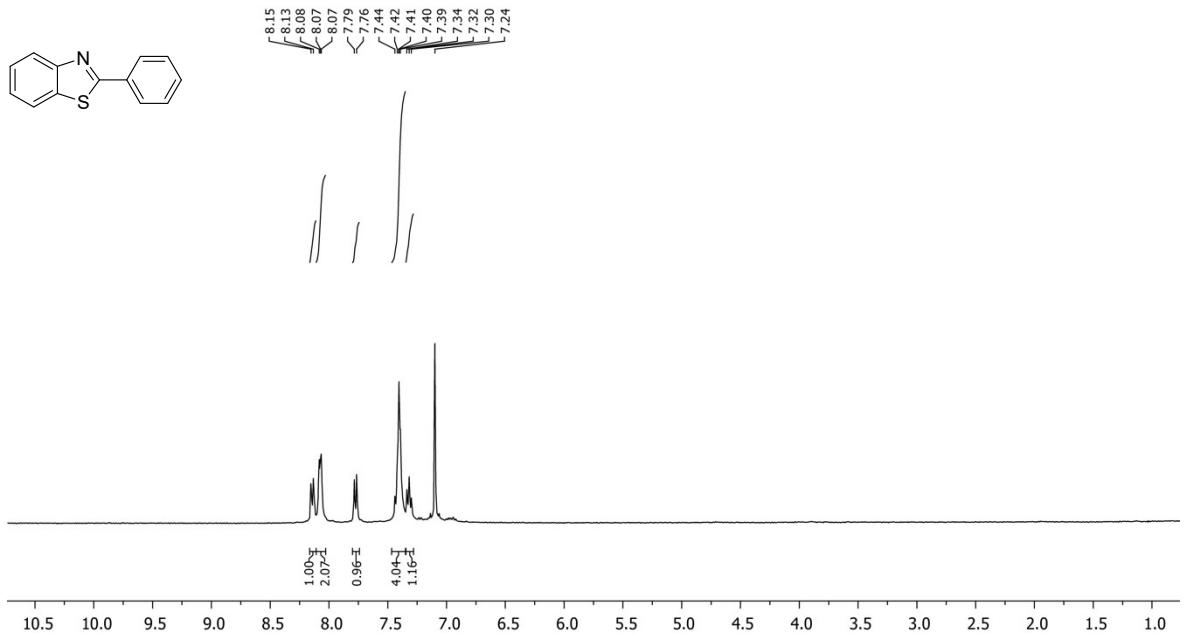
^{13}C NMR (101 MHz, $CDCl_3$)



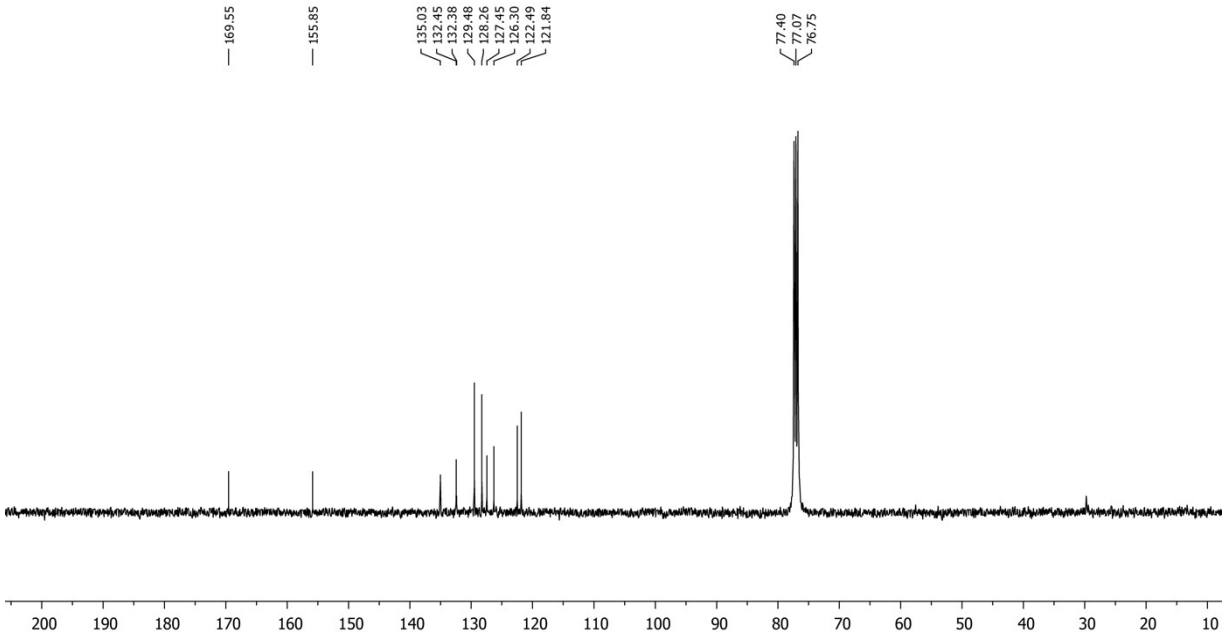
^{1}H NMR (400 MHz, $CDCl_3$)



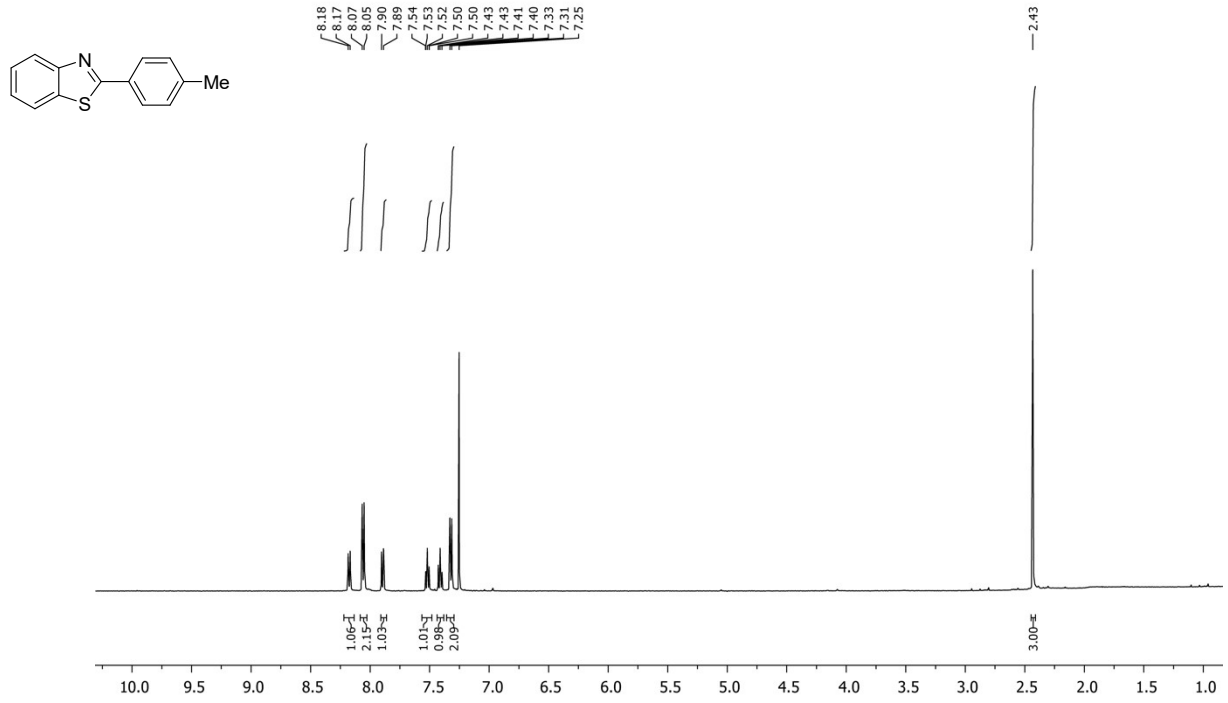
^{13}C NMR (101 MHz, $CDCl_3$)



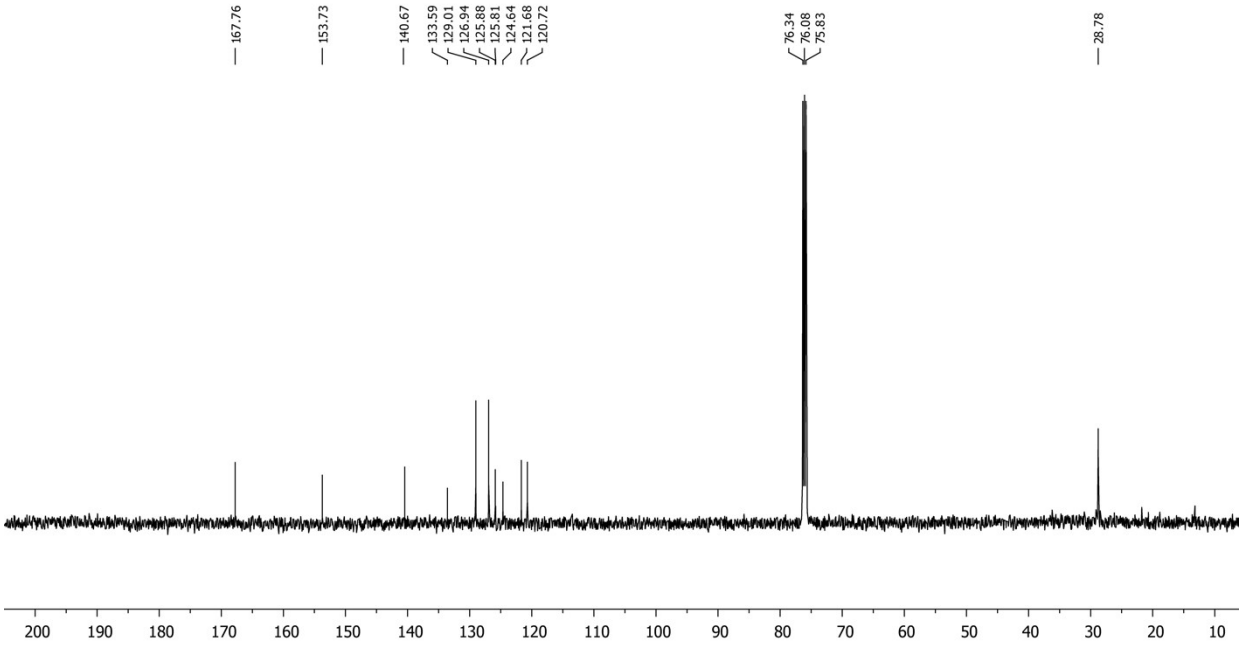
^{1}H NMR (400 MHz, $CDCl_3$)



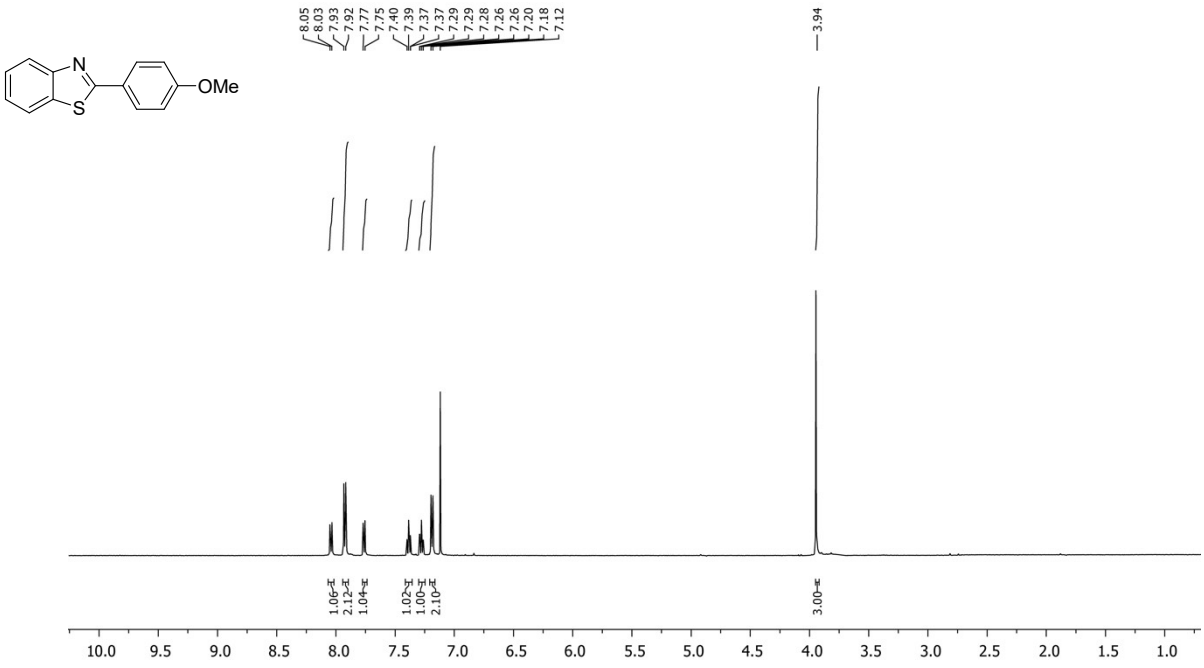
^{13}C NMR (101 MHz, $CDCl_3$)



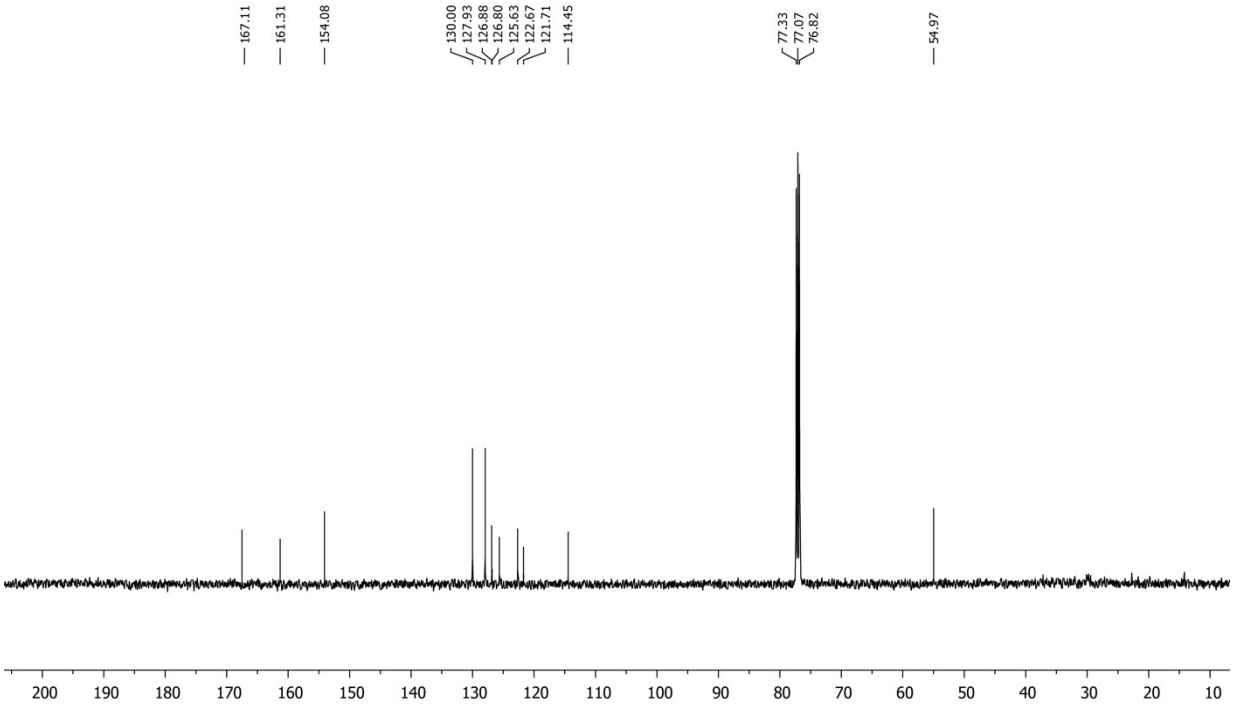
^{1}H NMR (400 MHz, $CDCl_3$)



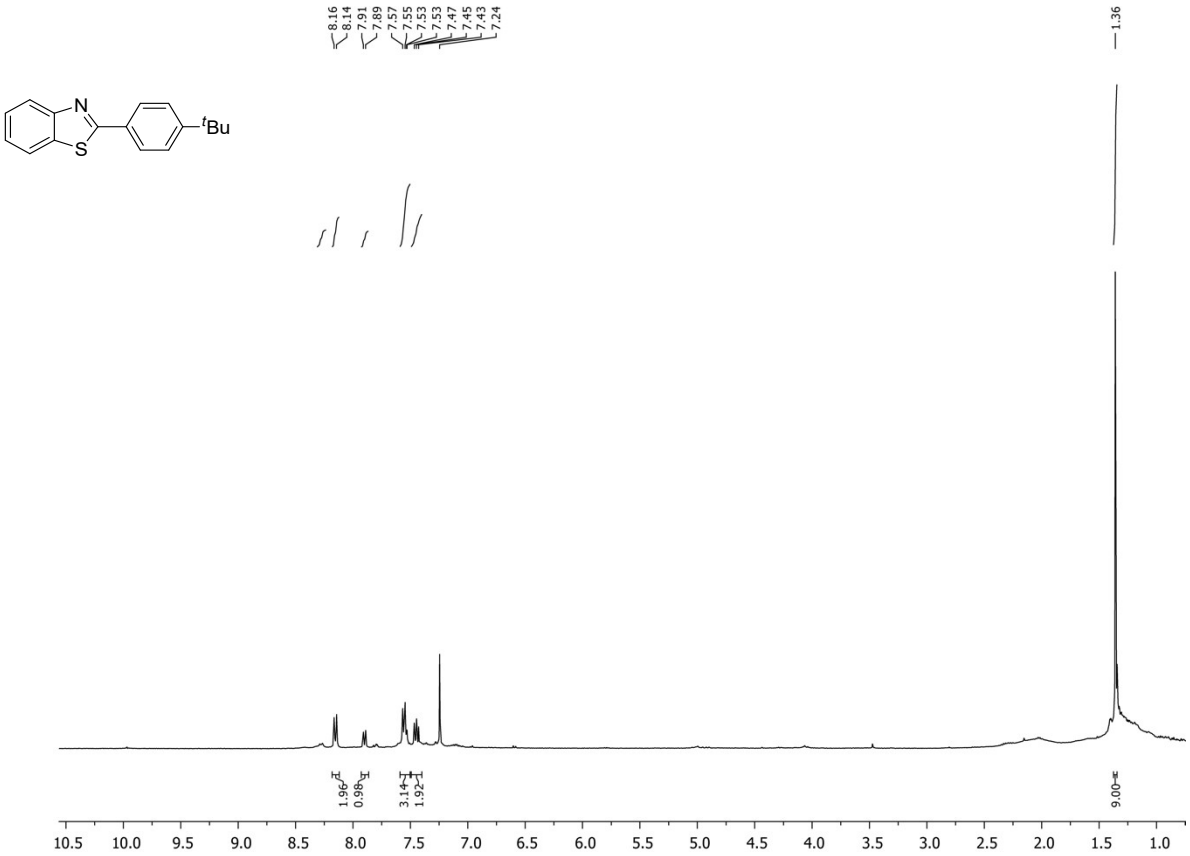
^{13}C NMR (101 MHz, $CDCl_3$)



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



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



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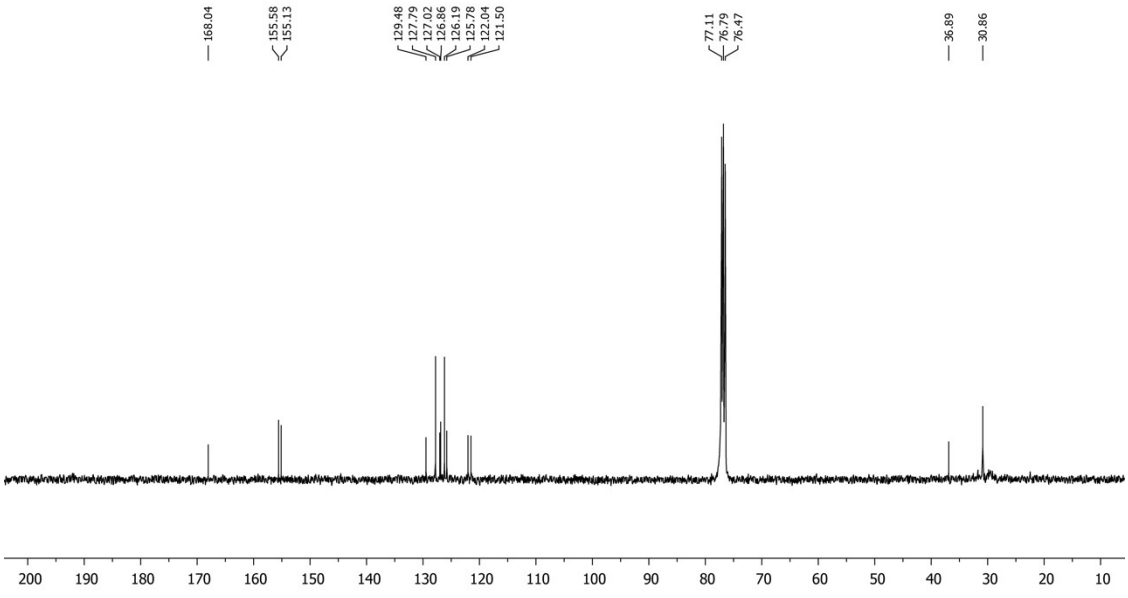
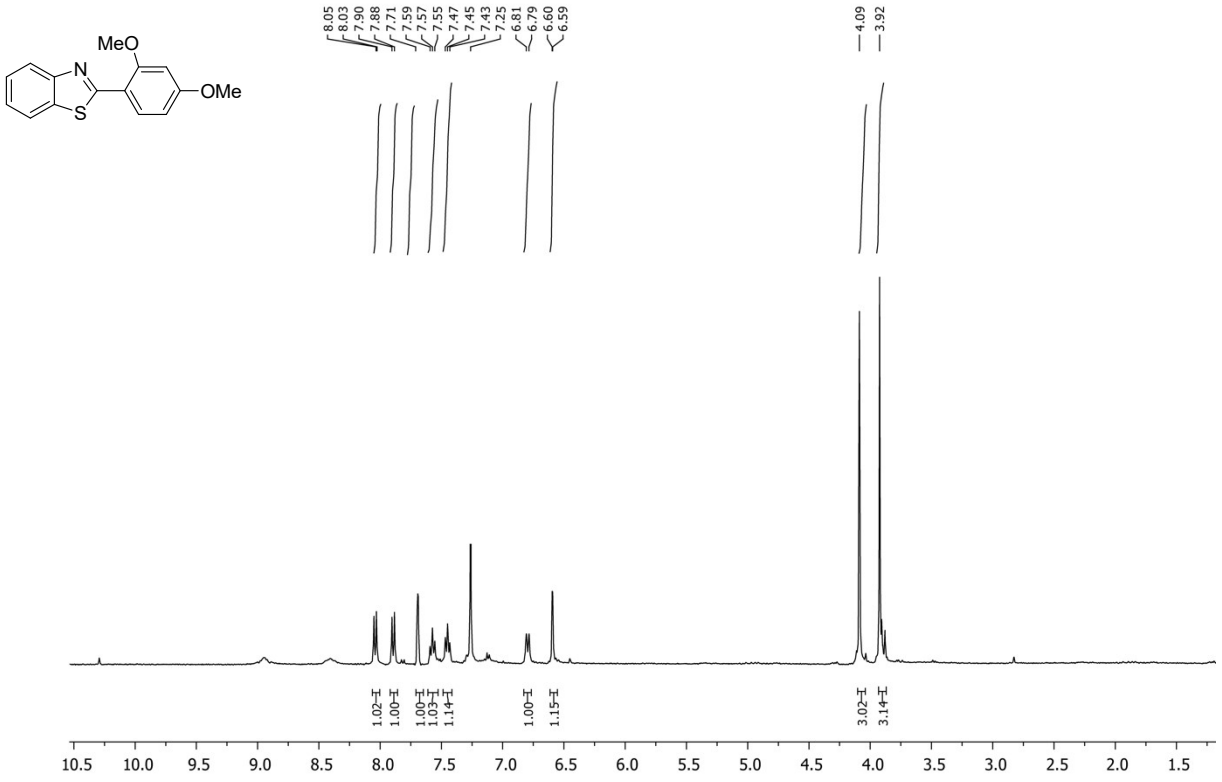
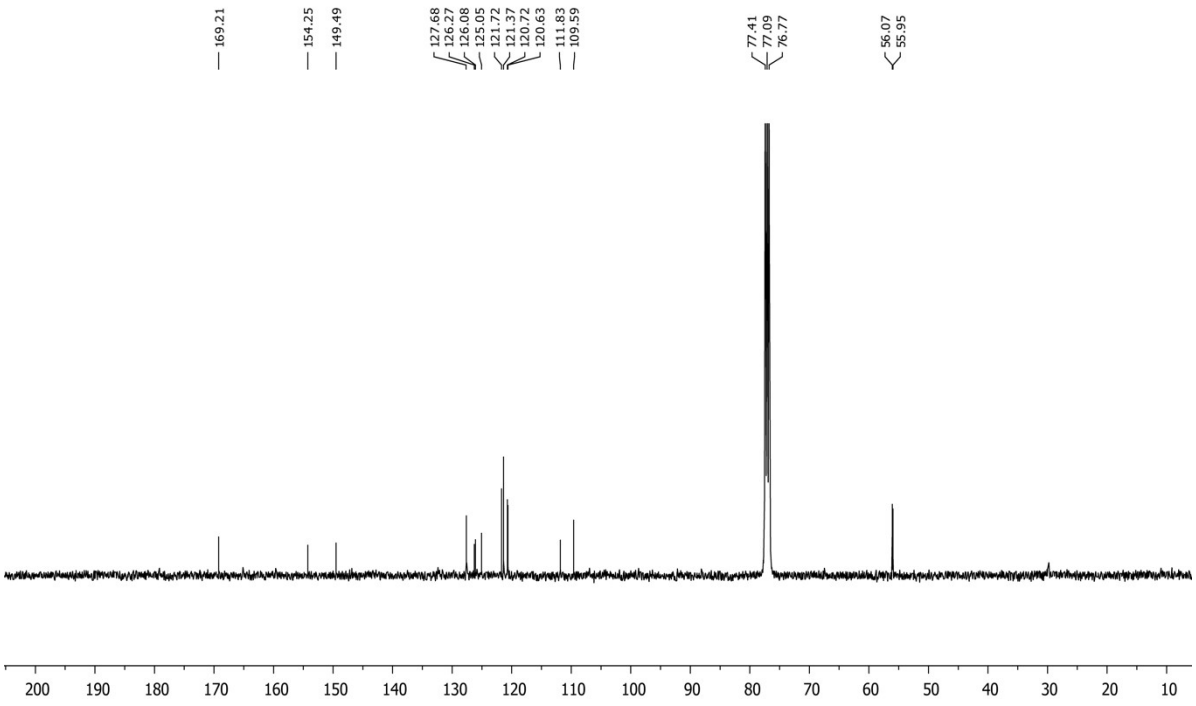


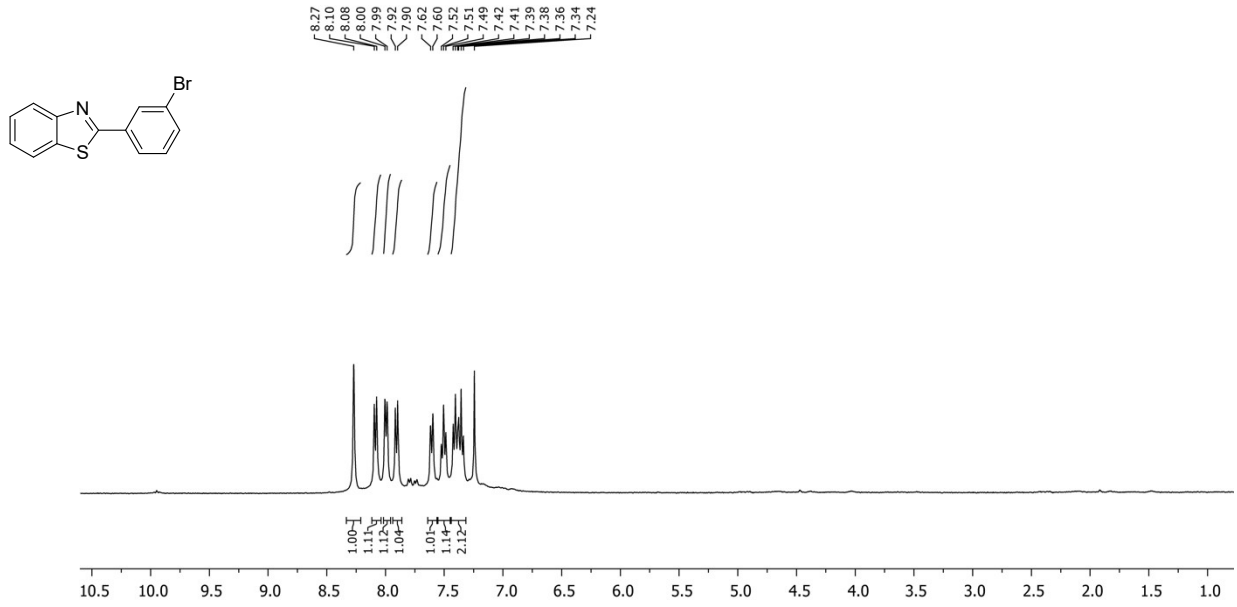
^{13}C NMR (101 MHz, $CDCl_3$)



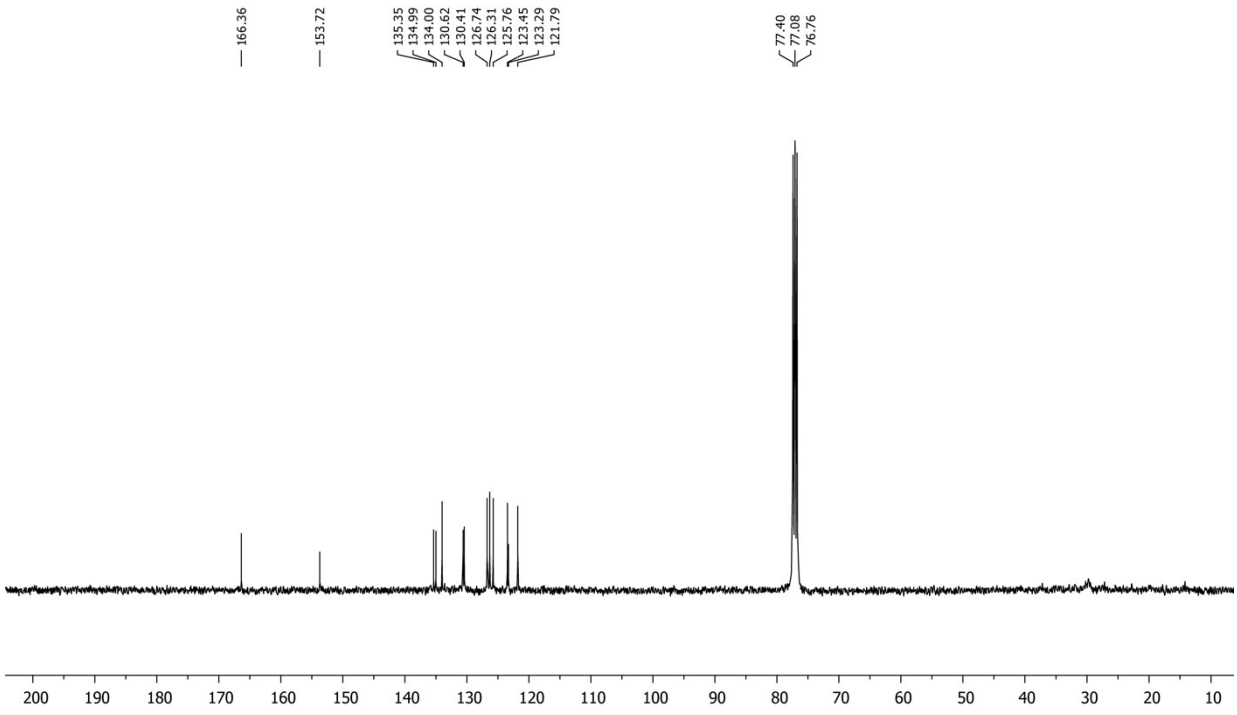
^{1}H NMR (400 MHz, $CDCl_3$)



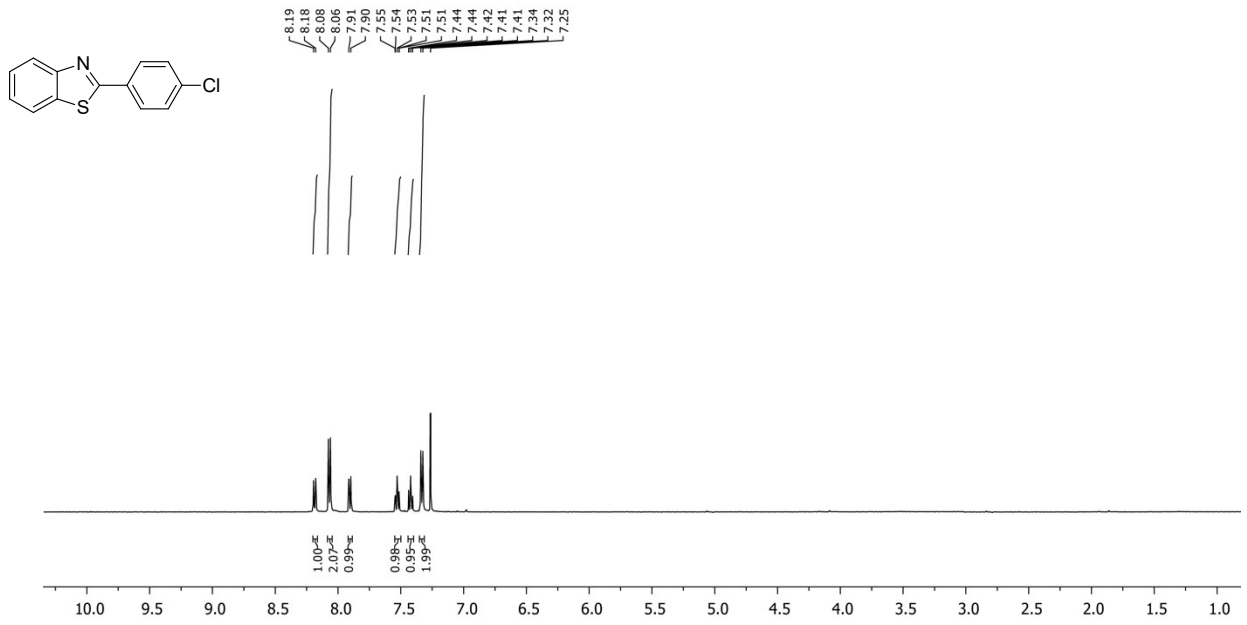
^{13}C NMR (101 MHz, $CDCl_3$)



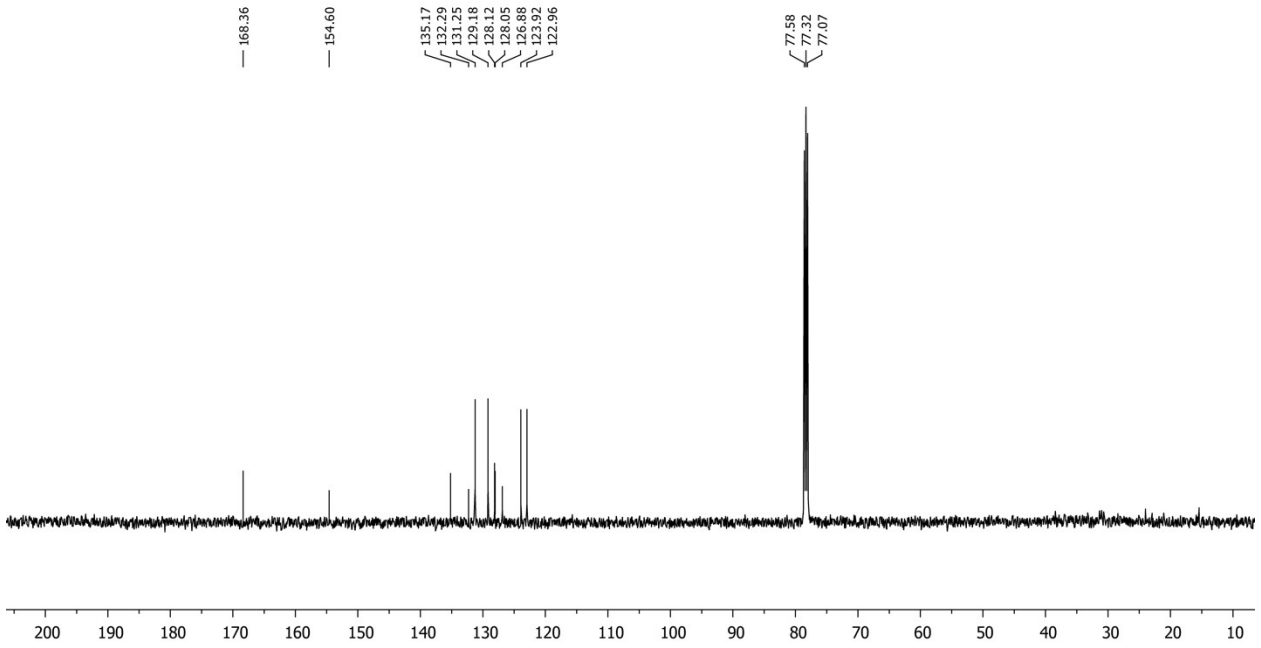
^{1}H NMR (400 MHz, $CDCl_3$)



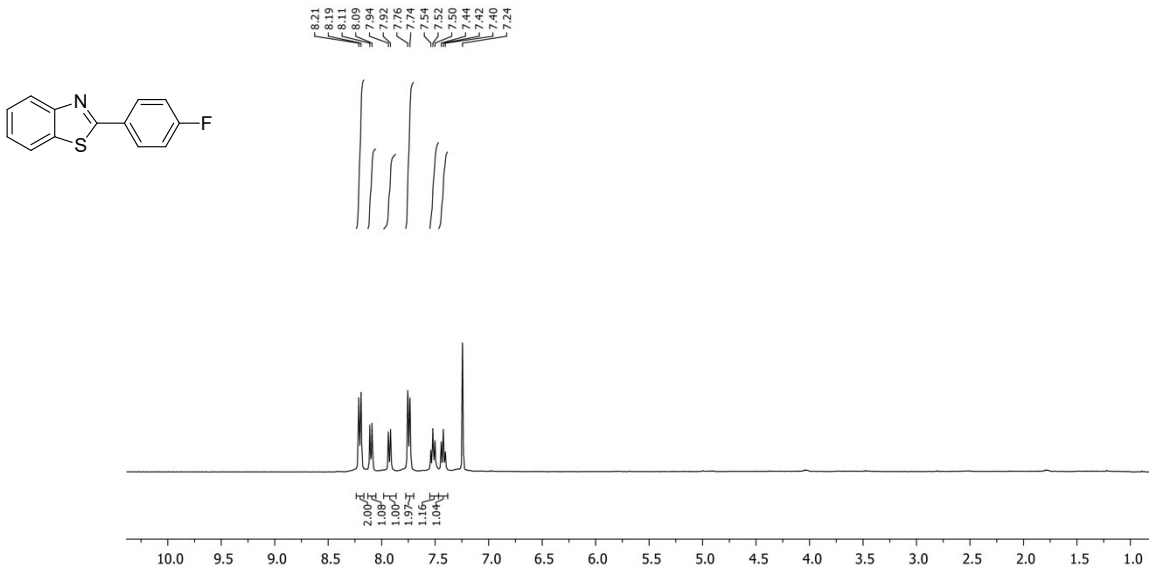
^{13}C NMR (101 MHz, $CDCl_3$)



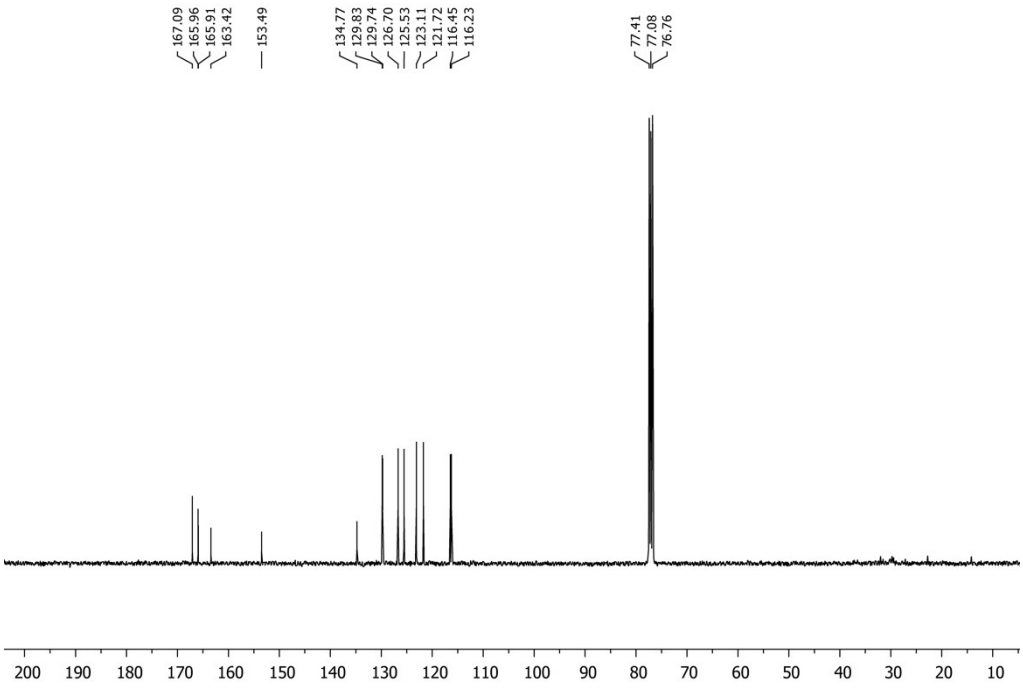
^{1}H NMR (400 MHz, $CDCl_3$)



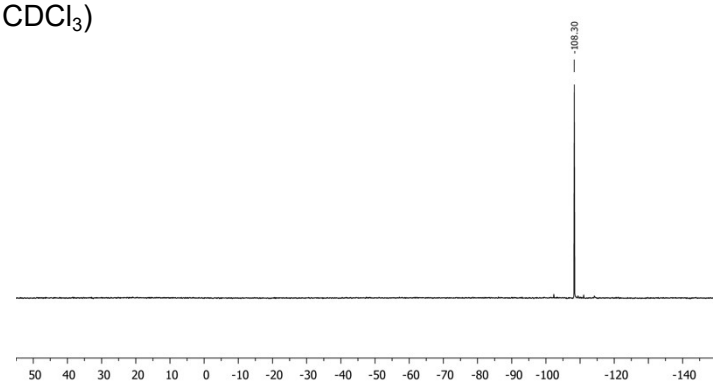
^{13}C NMR (101 MHz, $CDCl_3$)



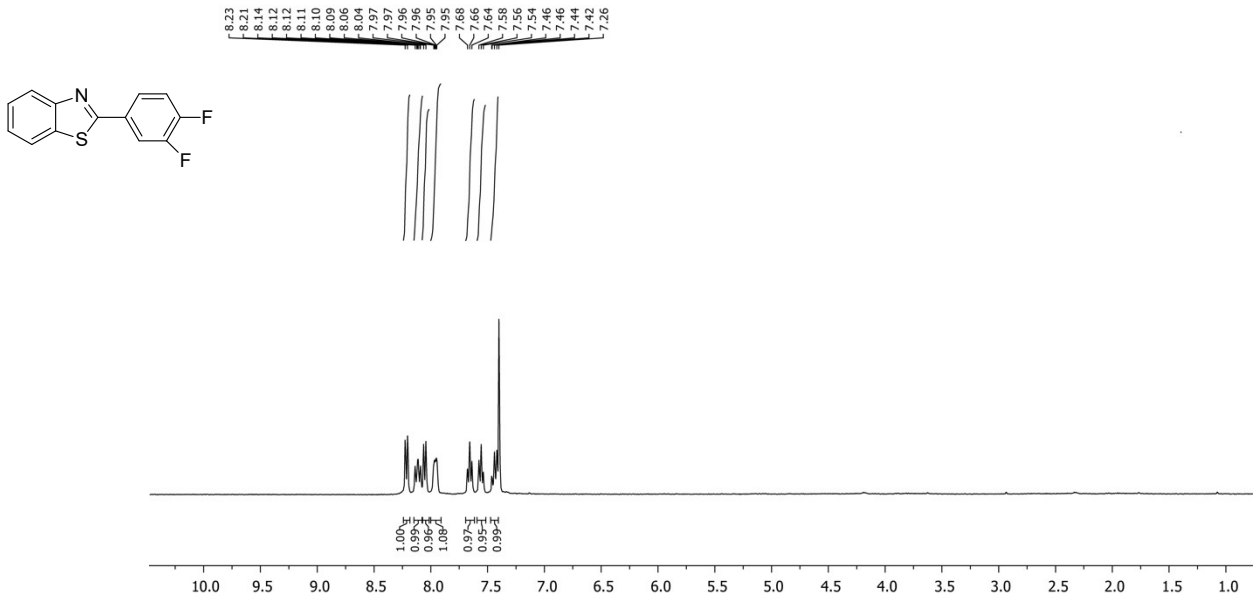
^{1}H NMR (400 MHz, $CDCl_3$)



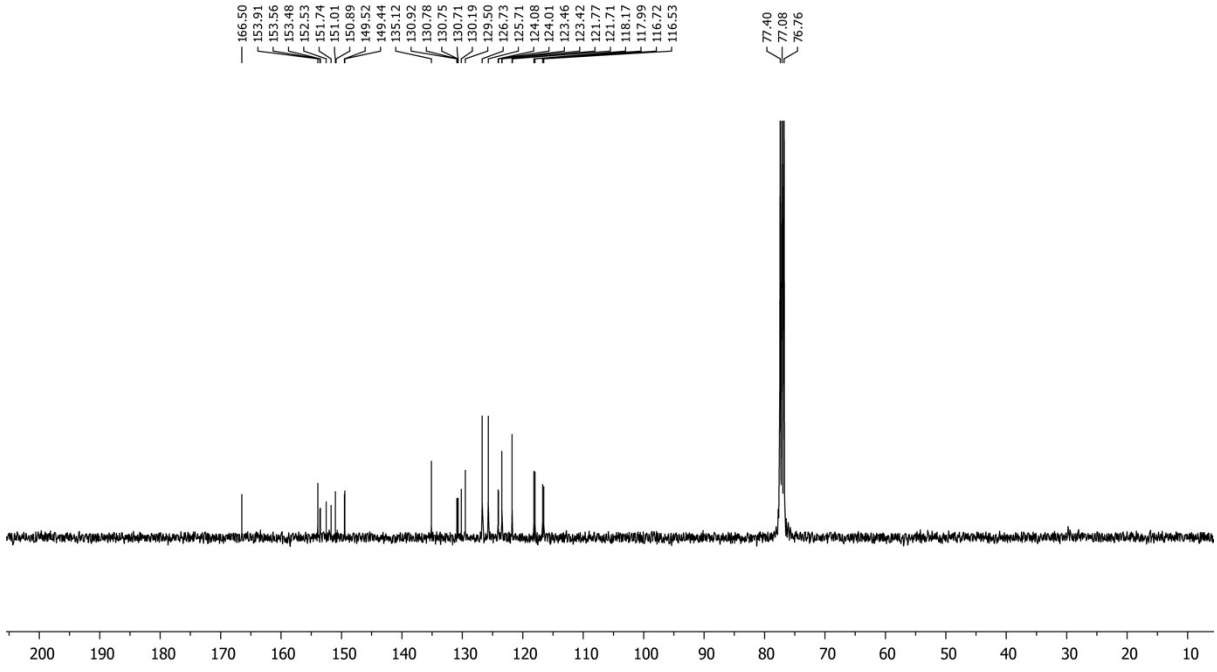
^{13}C NMR (101 MHz, $CDCl_3$)



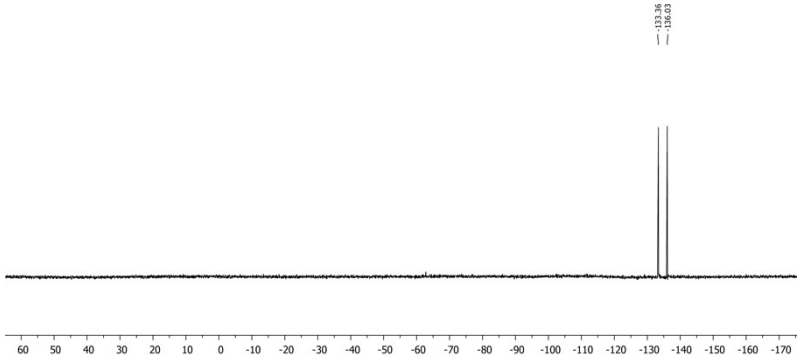
^{19}F NMR (376 MHz, $CDCl_3$)



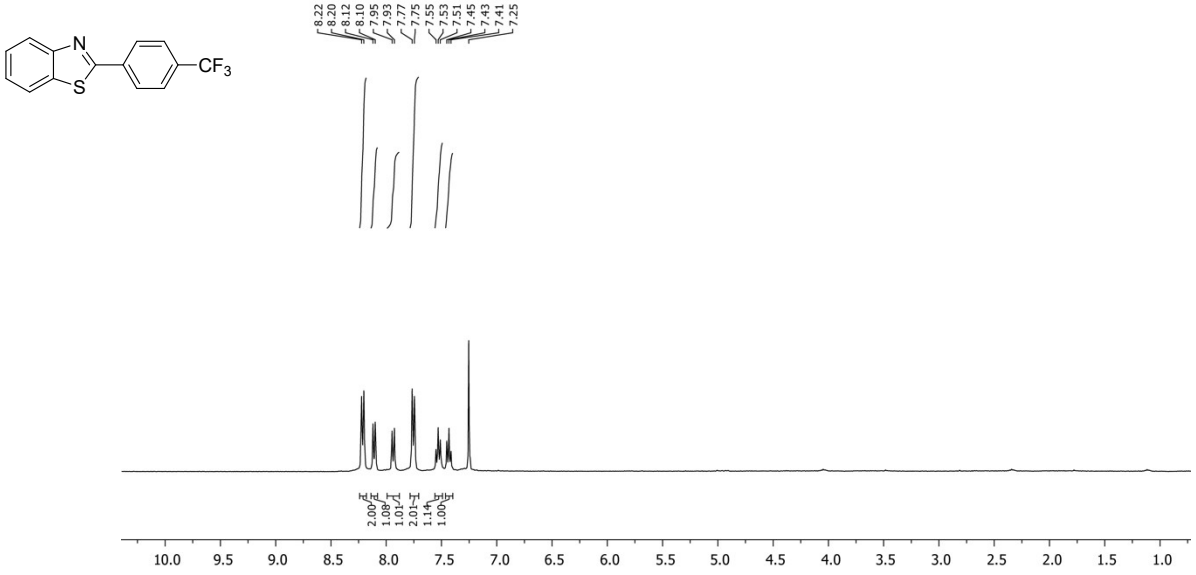
^{1}H NMR (400 MHz, $CDCl_3$)



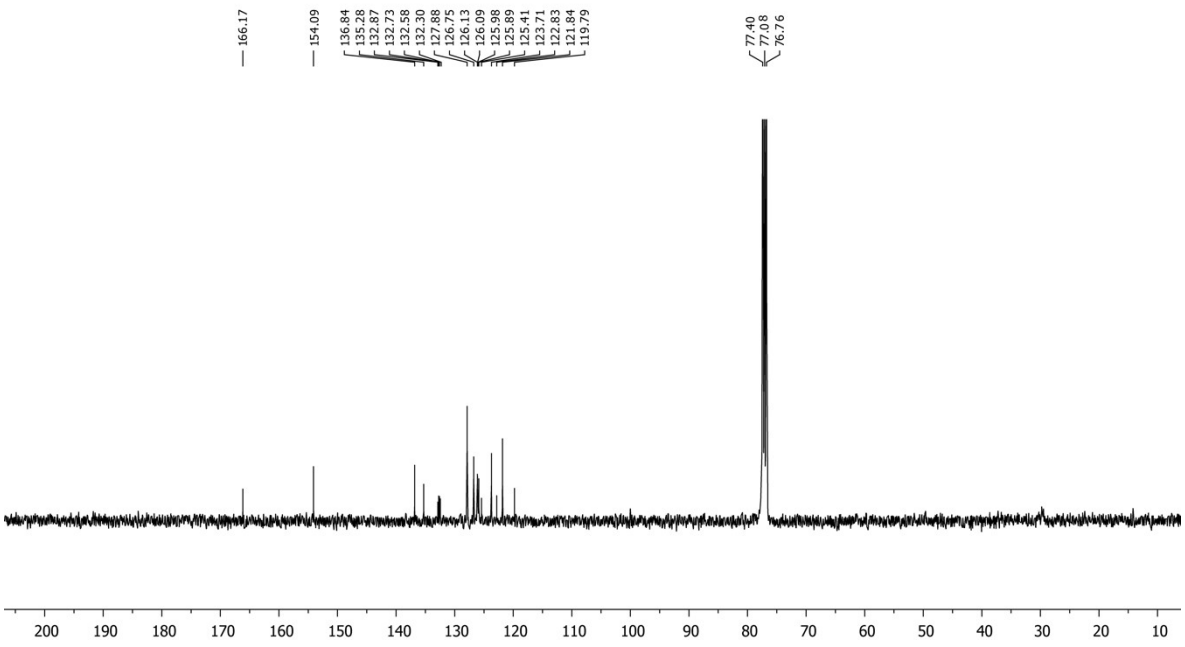
^{13}C NMR (101 MHz, $CDCl_3$)



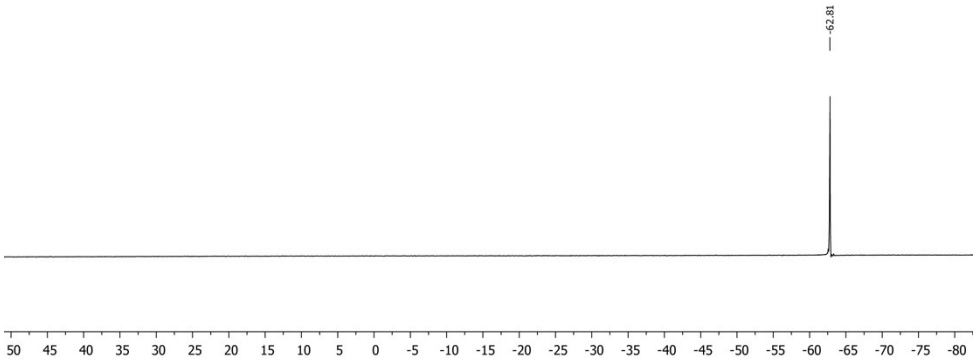
^{19}F NMR (376 MHz, $CDCl_3$)



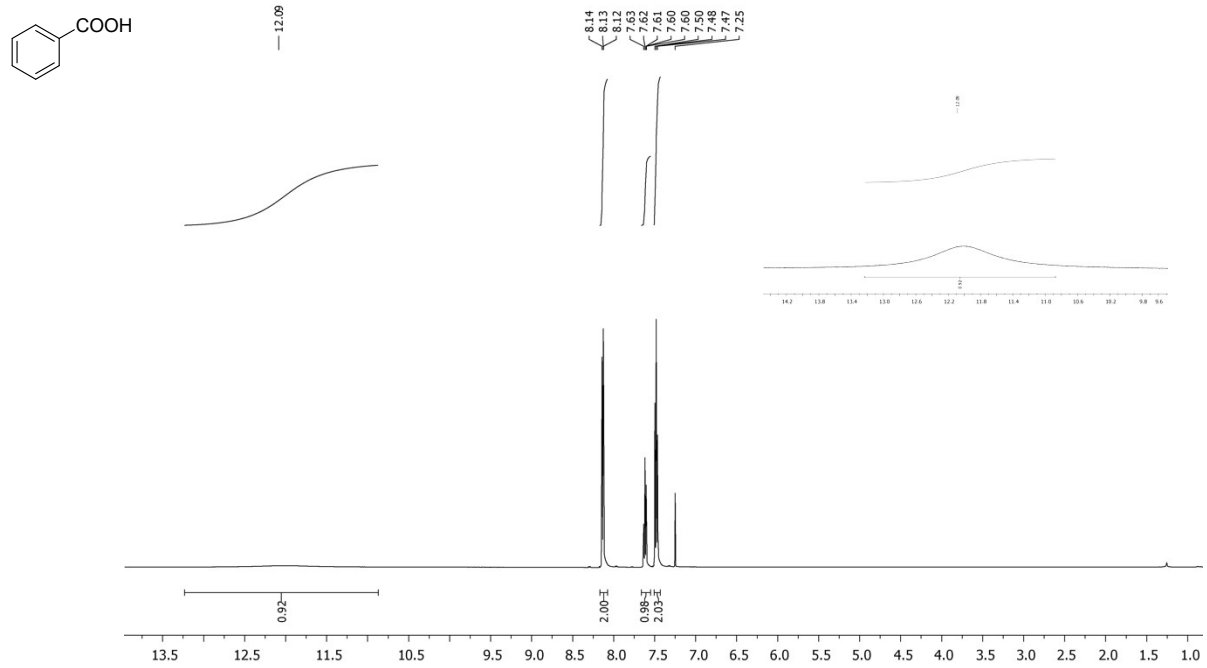
^{1}H NMR (400 MHz, $CDCl_3$)



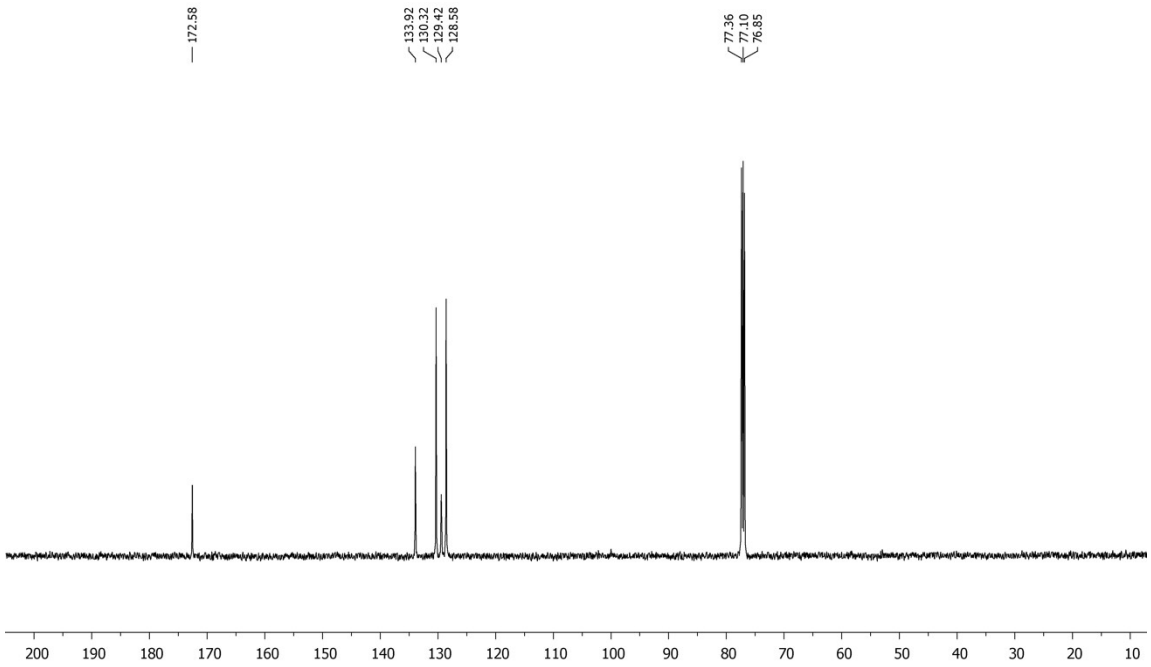
^{13}C NMR (101 MHz, $CDCl_3$)



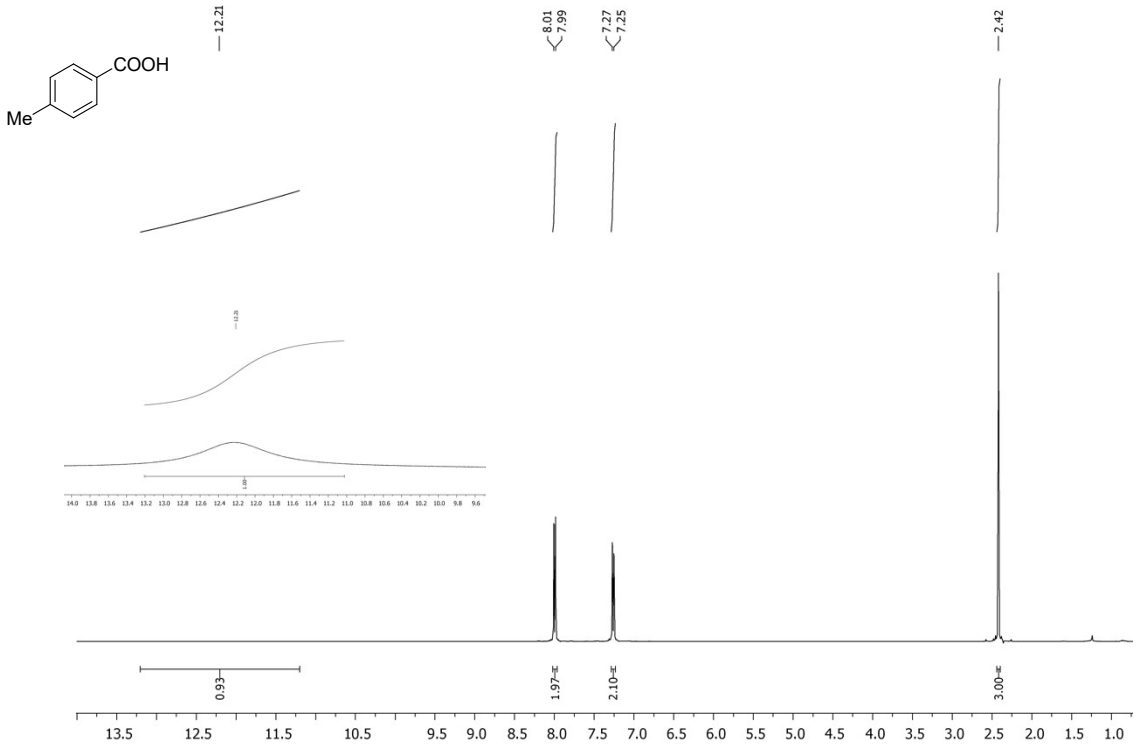
^{19}F NMR (376 MHz, $CDCl_3$)



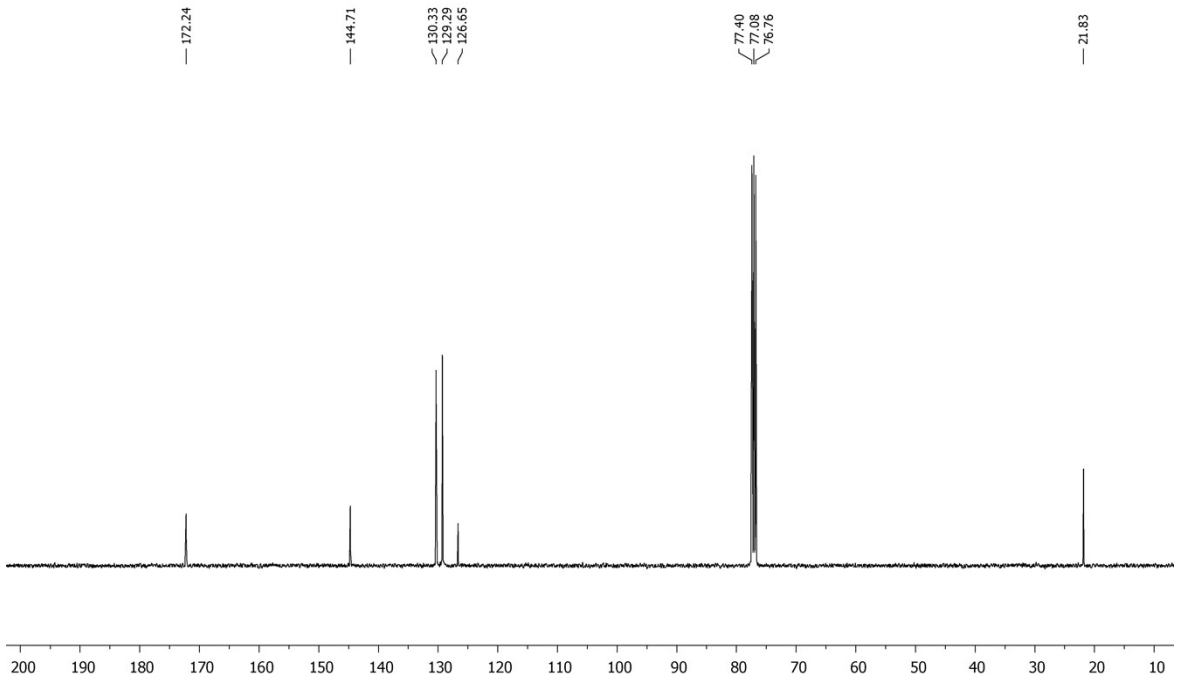
^{1}H NMR (500 MHz, $CDCl_3$)



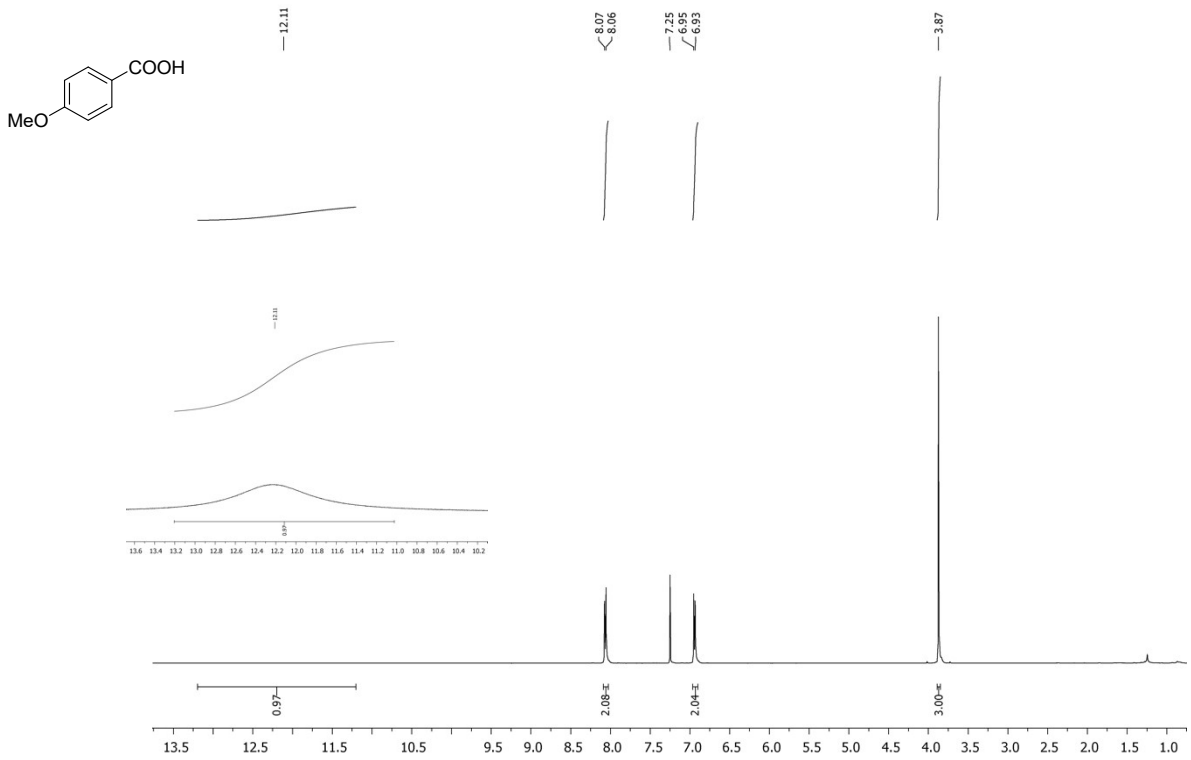
^{13}C NMR (126 MHz, $CDCl_3$)



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



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



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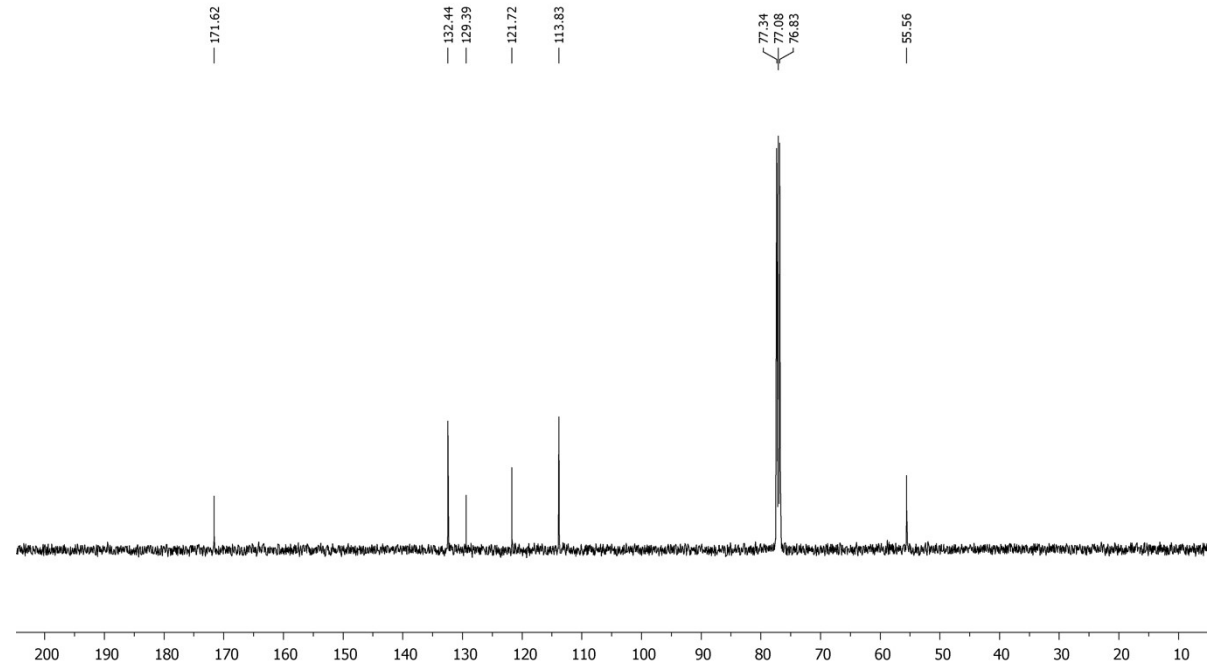
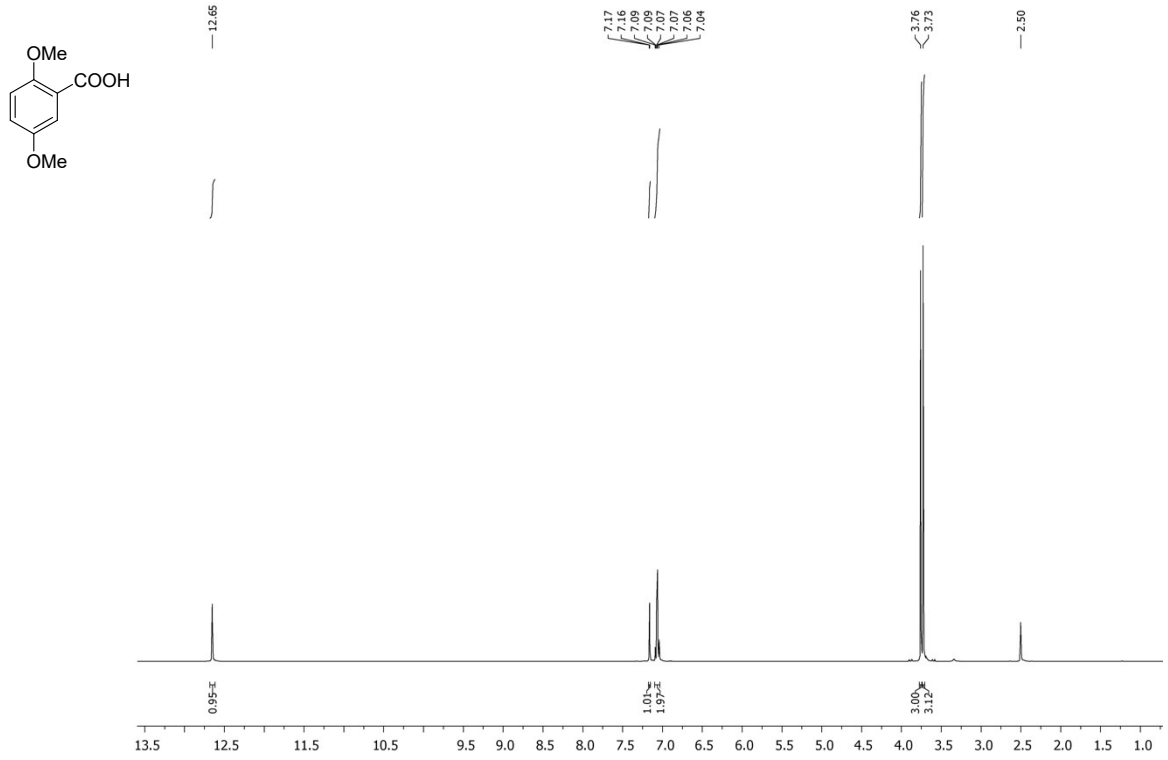


^{13}C NMR (126 MHz, $CDCl_3$)



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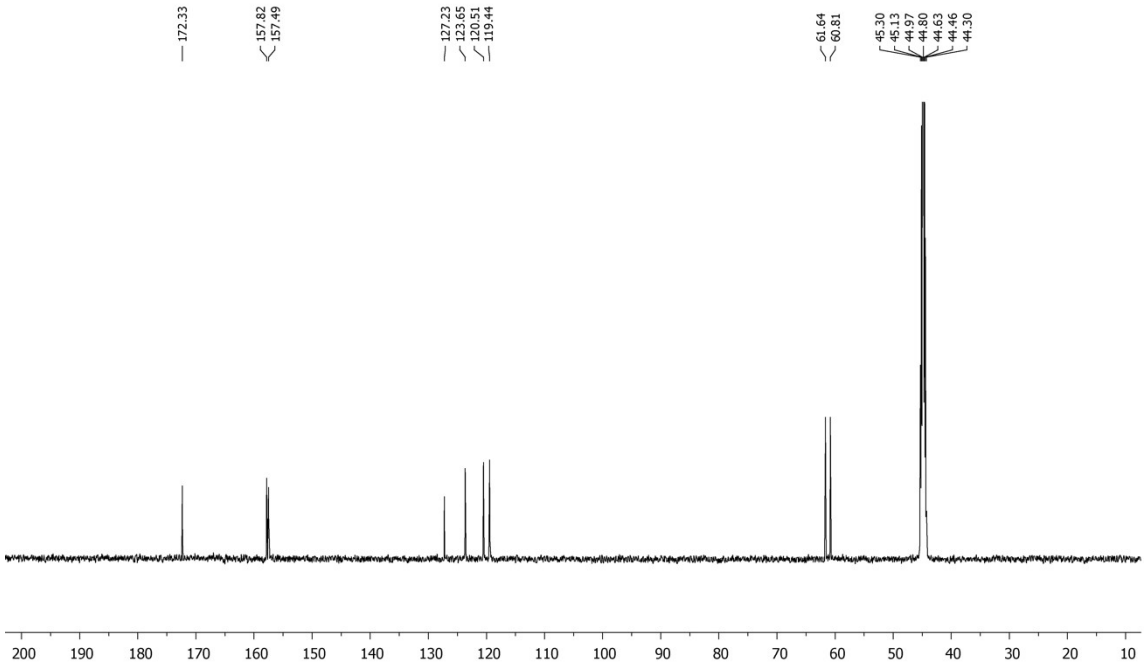

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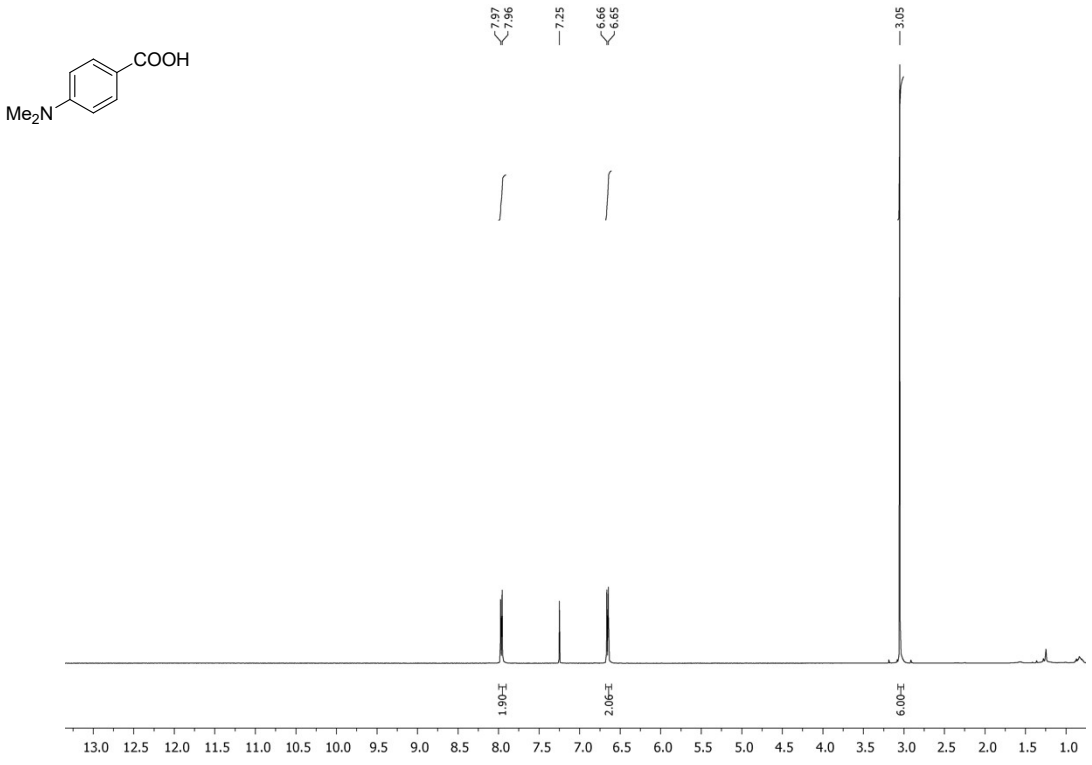

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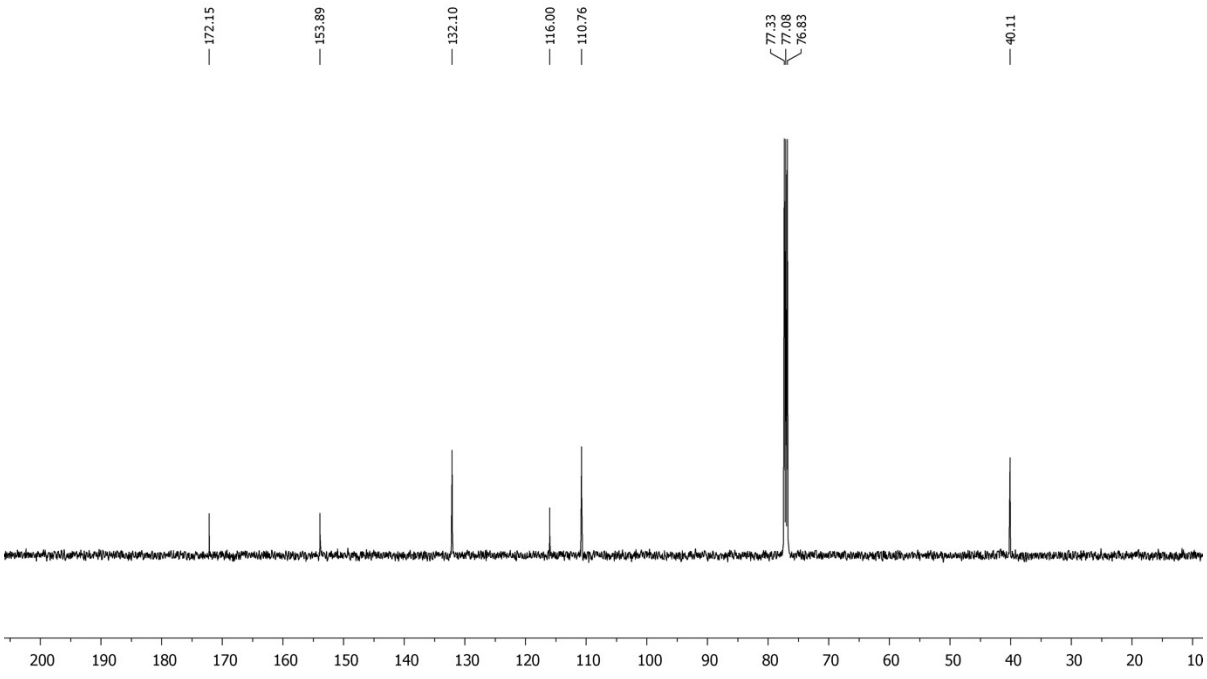

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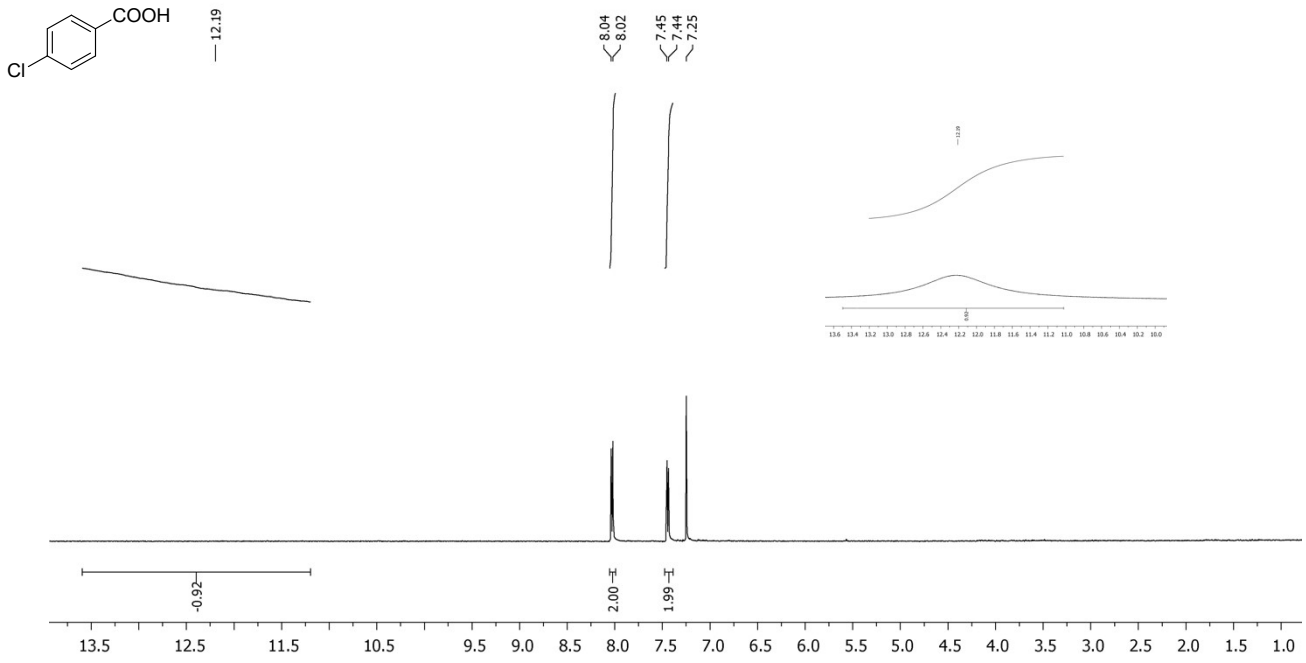

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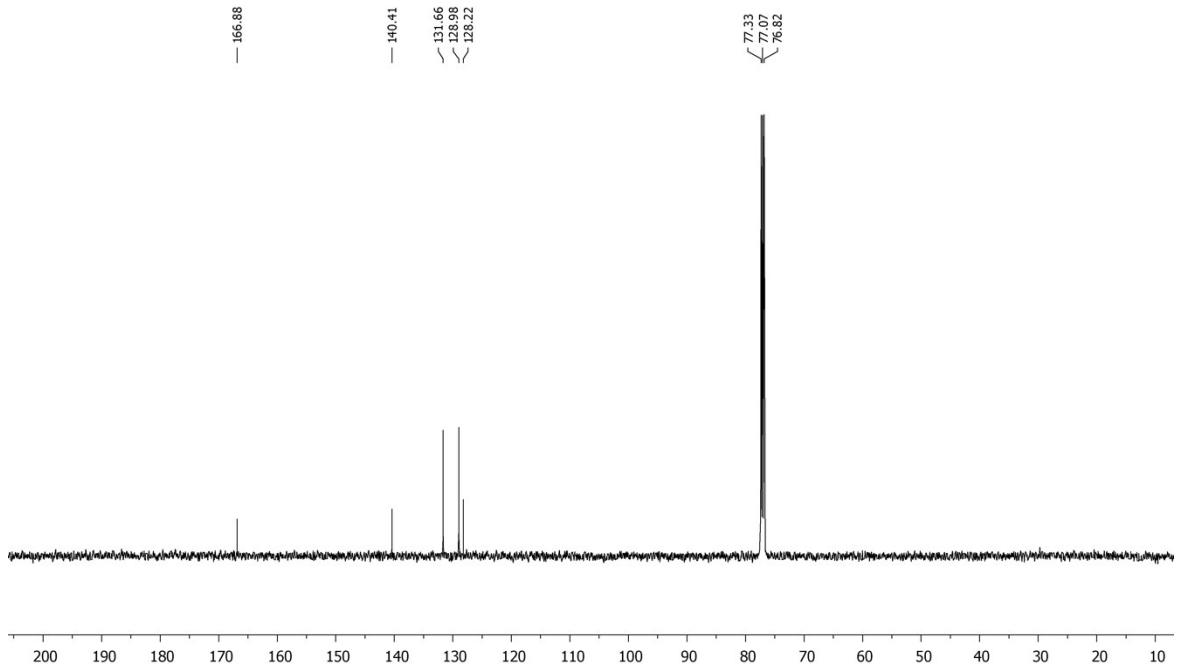

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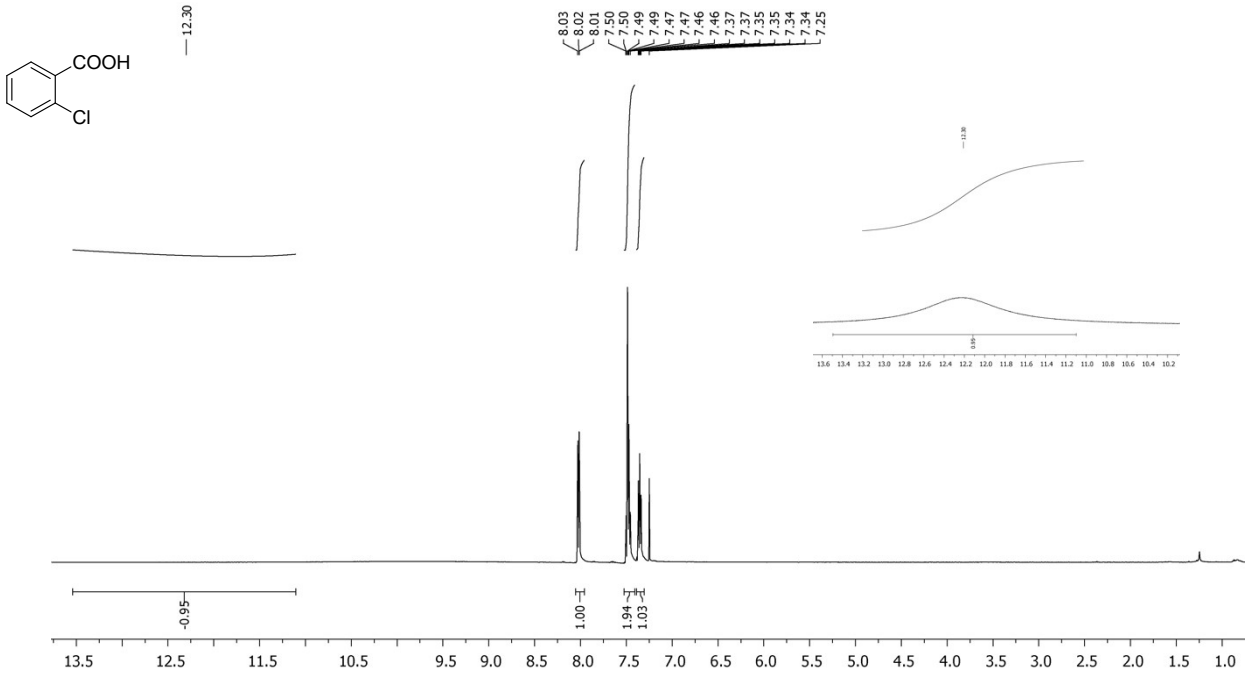

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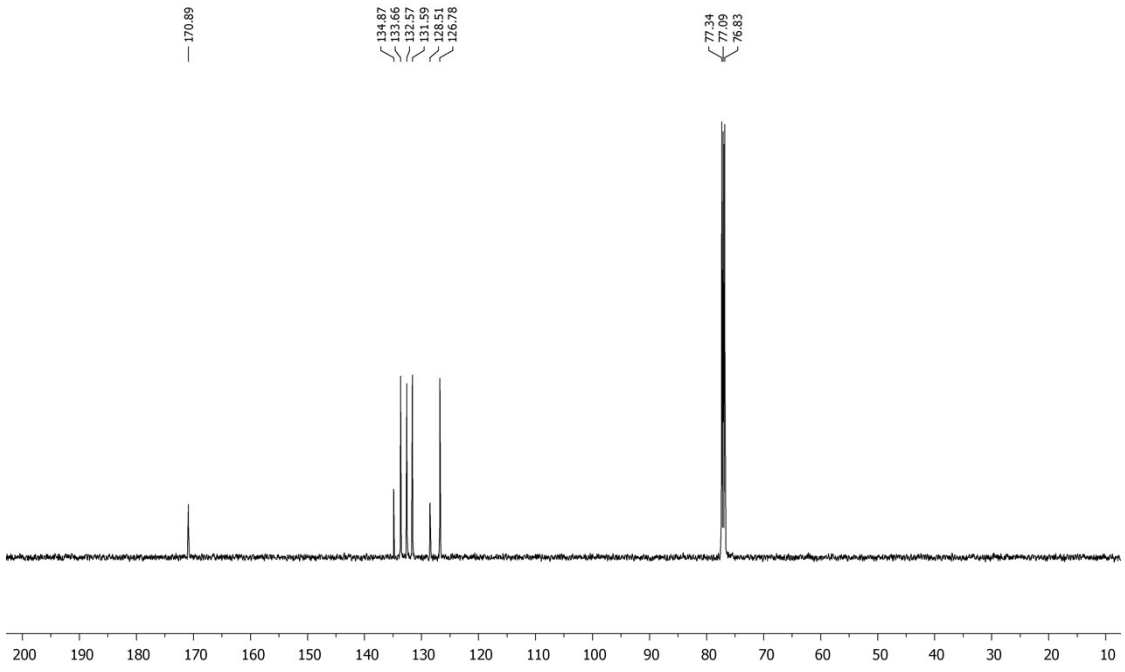

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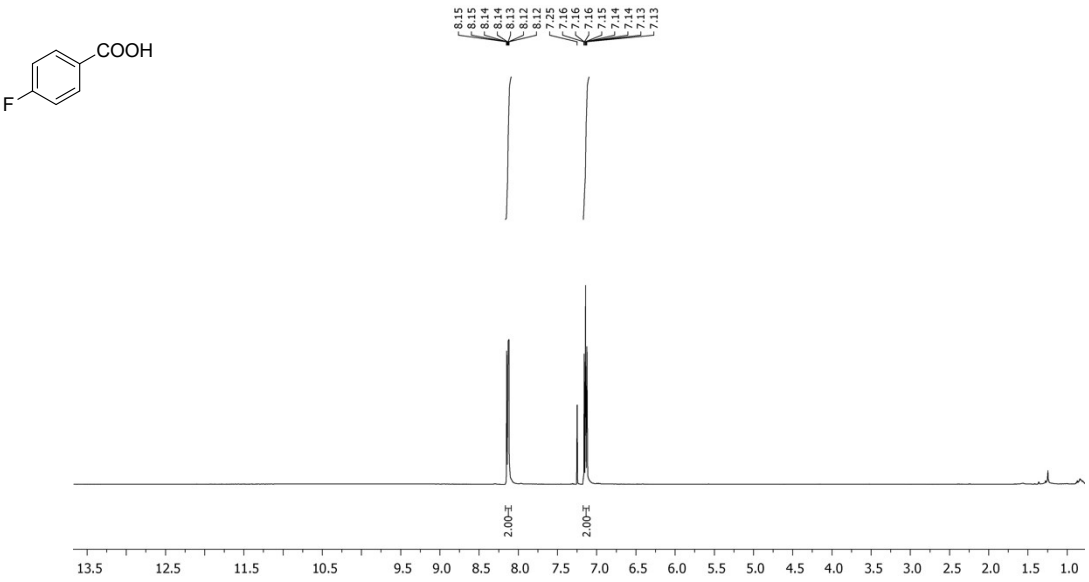

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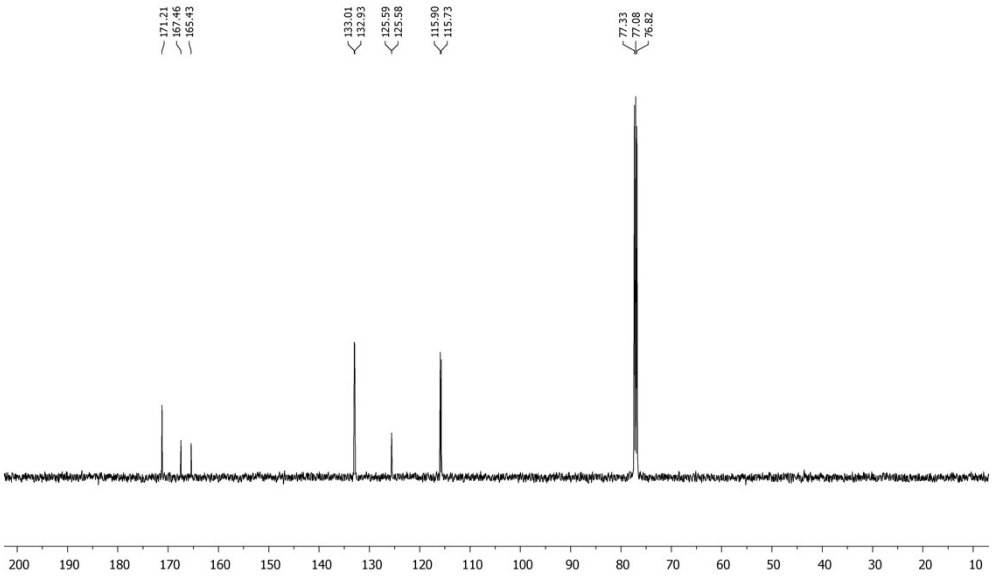
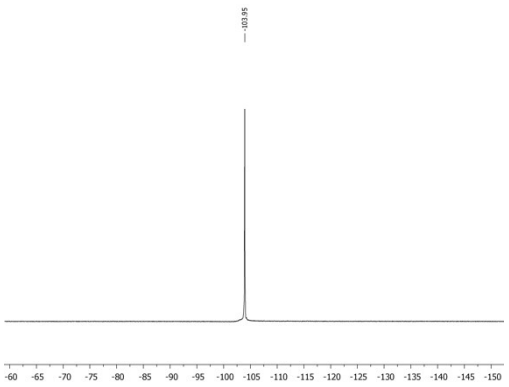
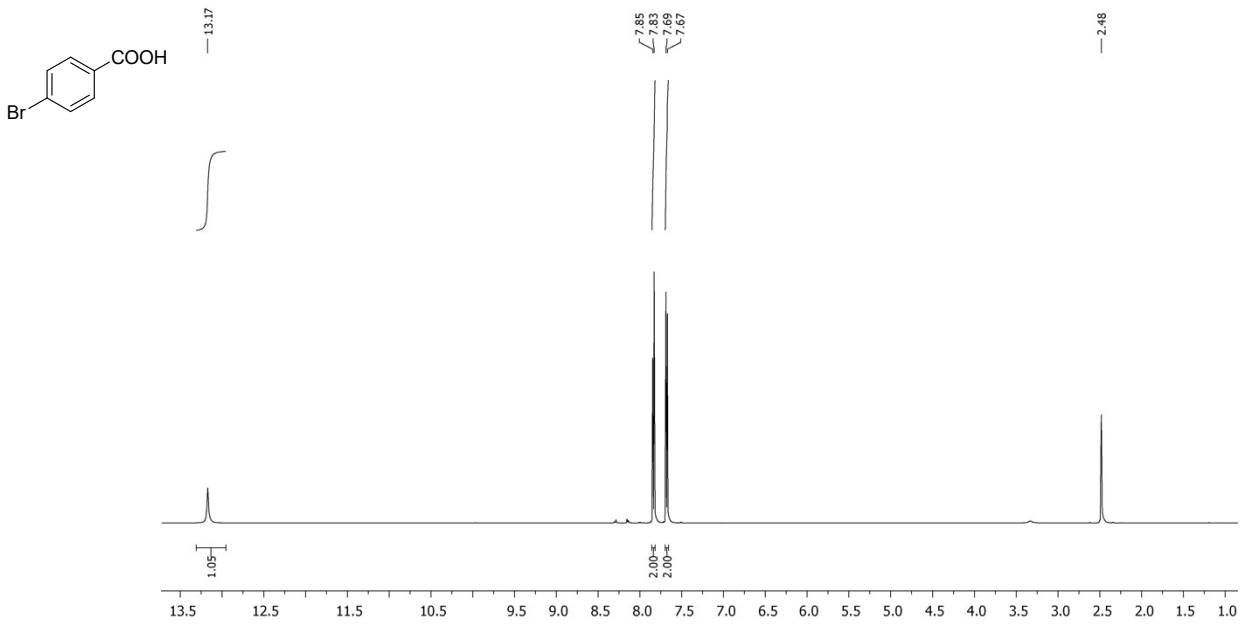


^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$)



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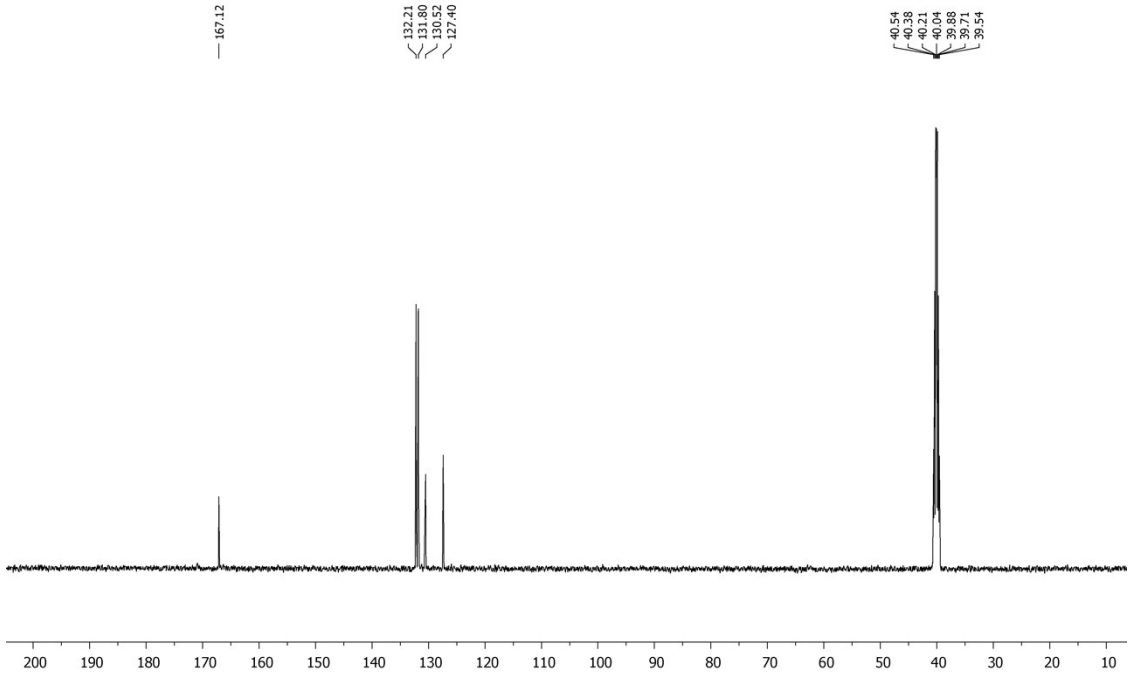

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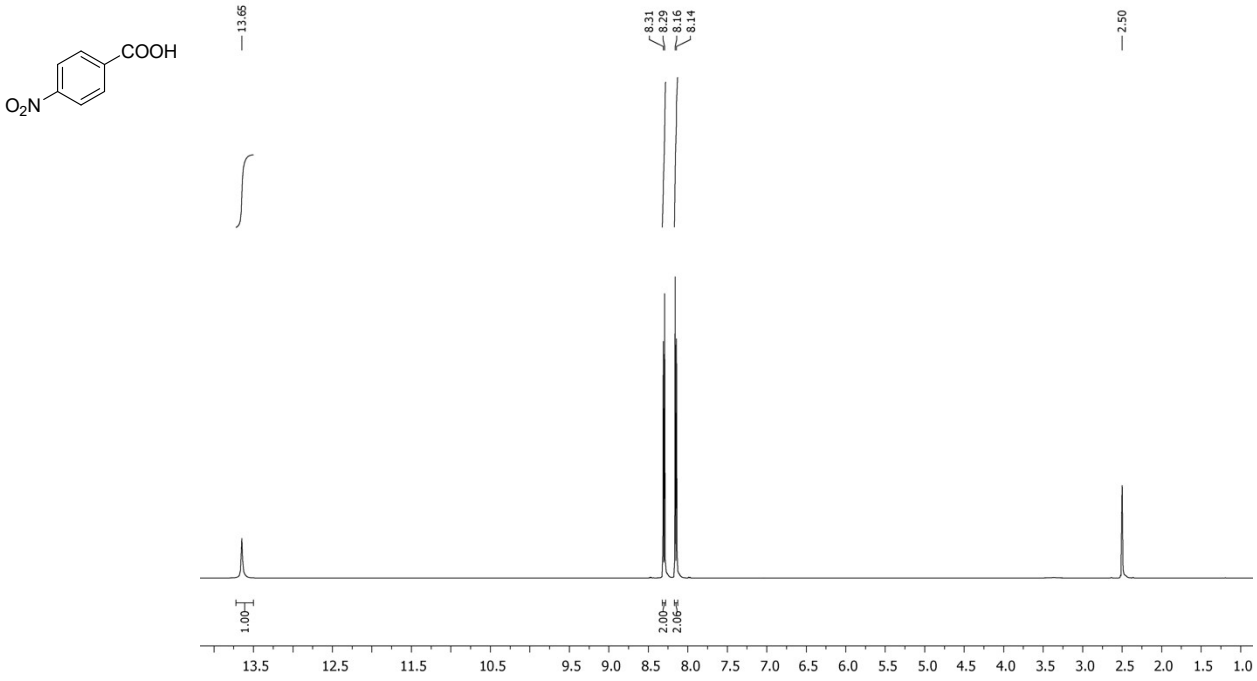
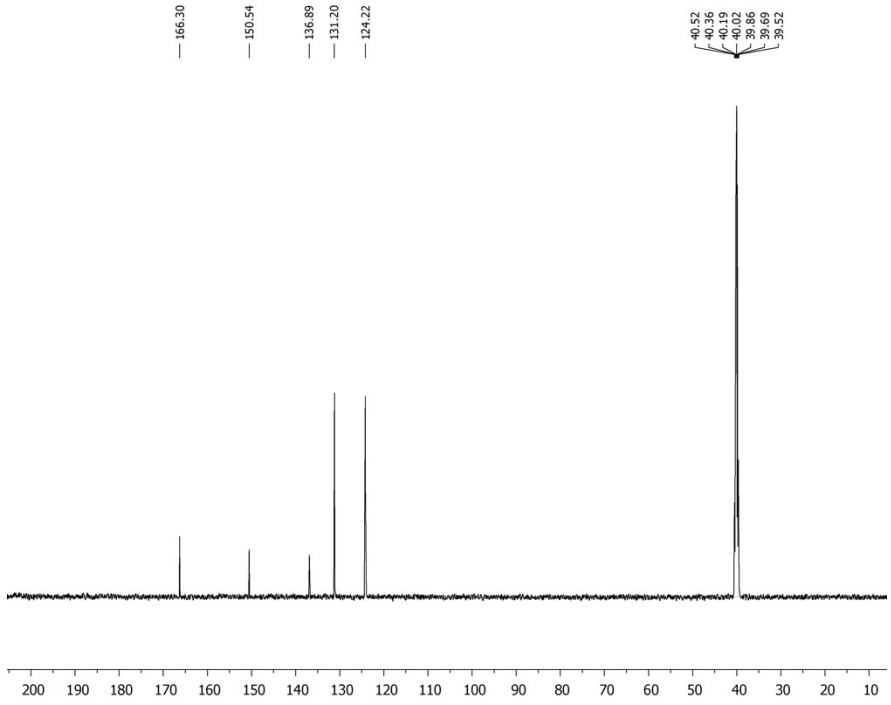


^{1}H NMR (500 MHz, DMSO-d_6)



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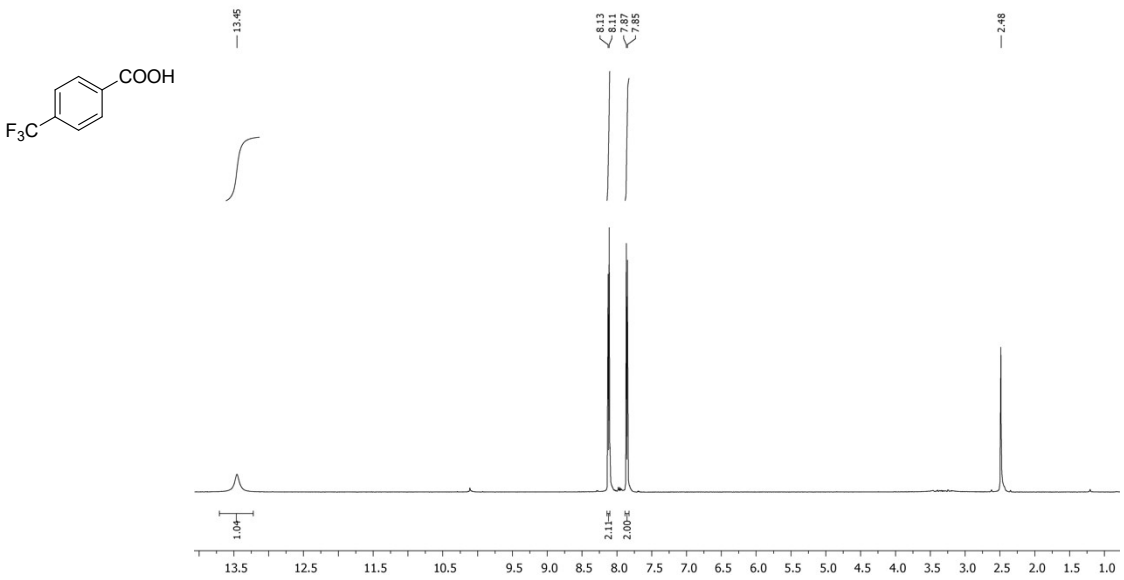

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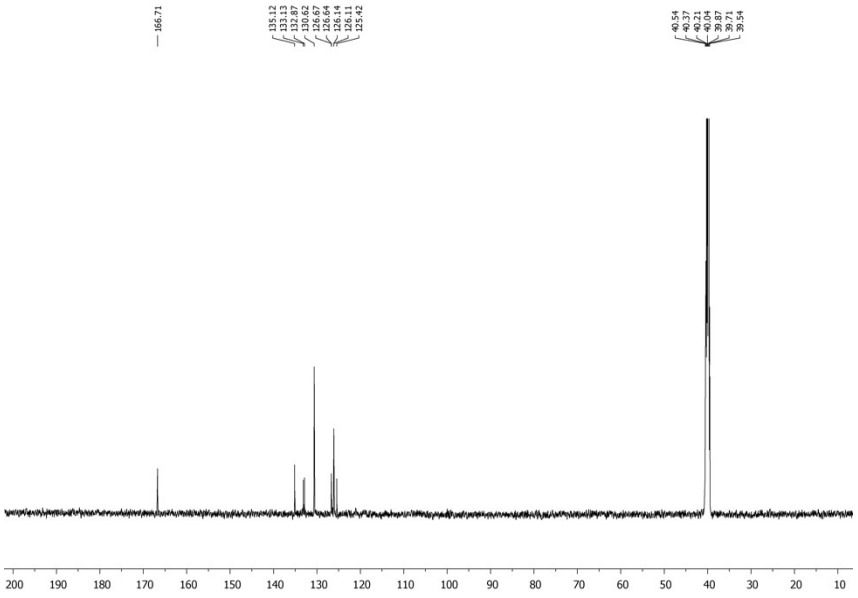

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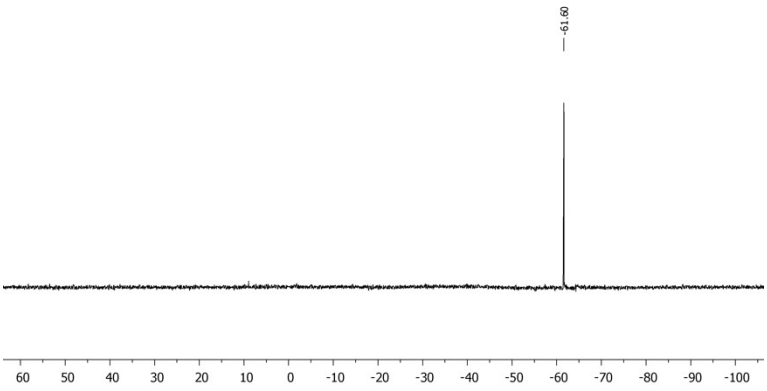
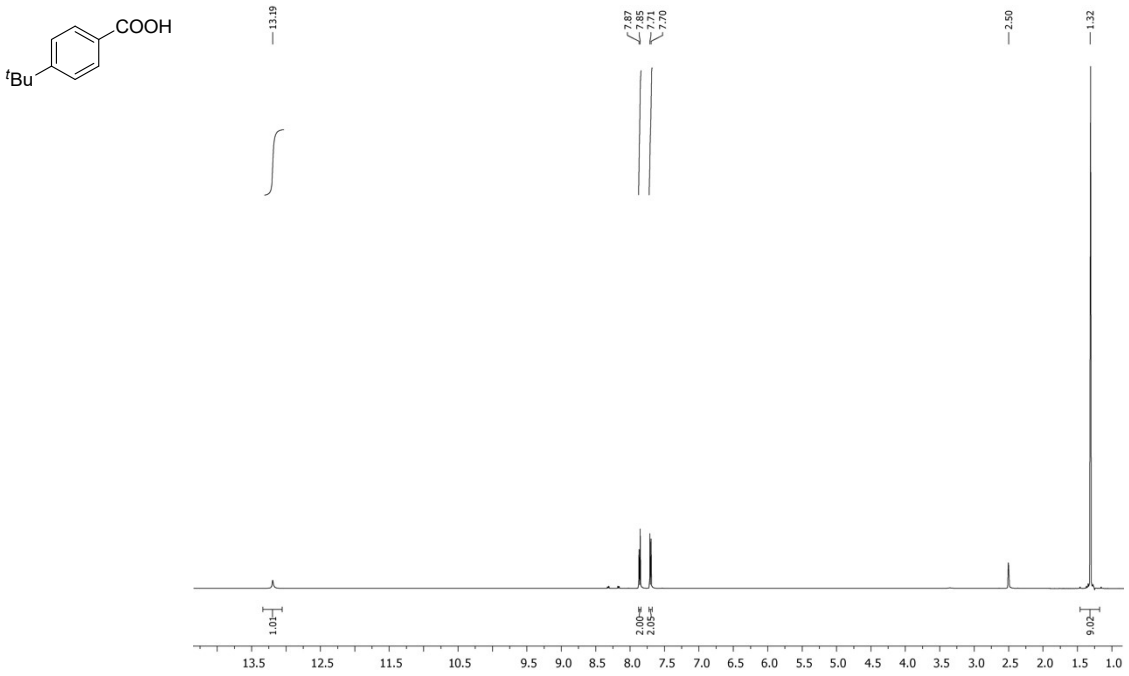


^{19}F NMR (470 MHz, DMSO-d_6)



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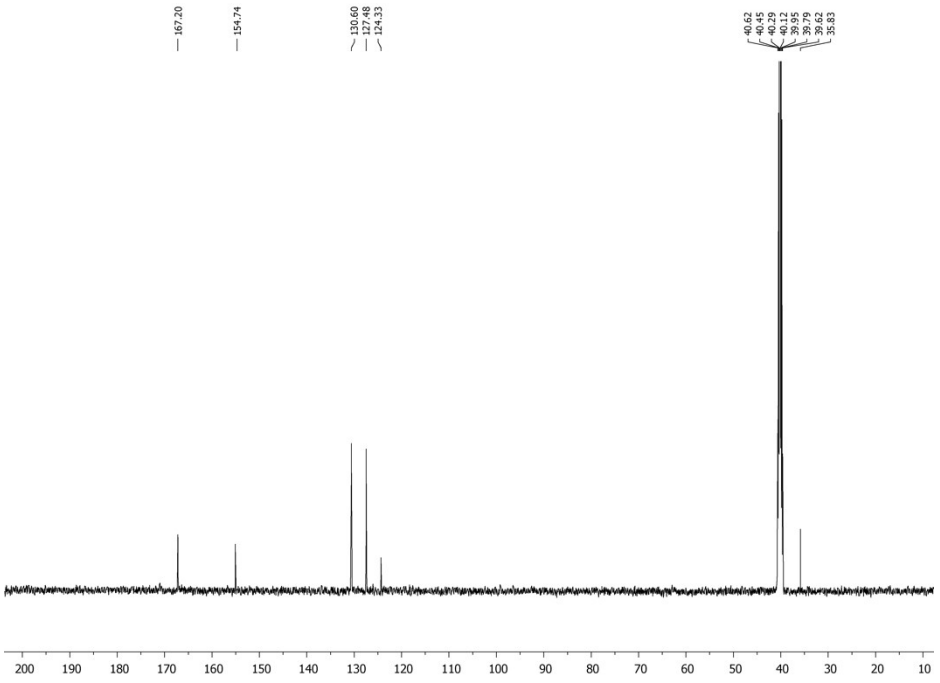

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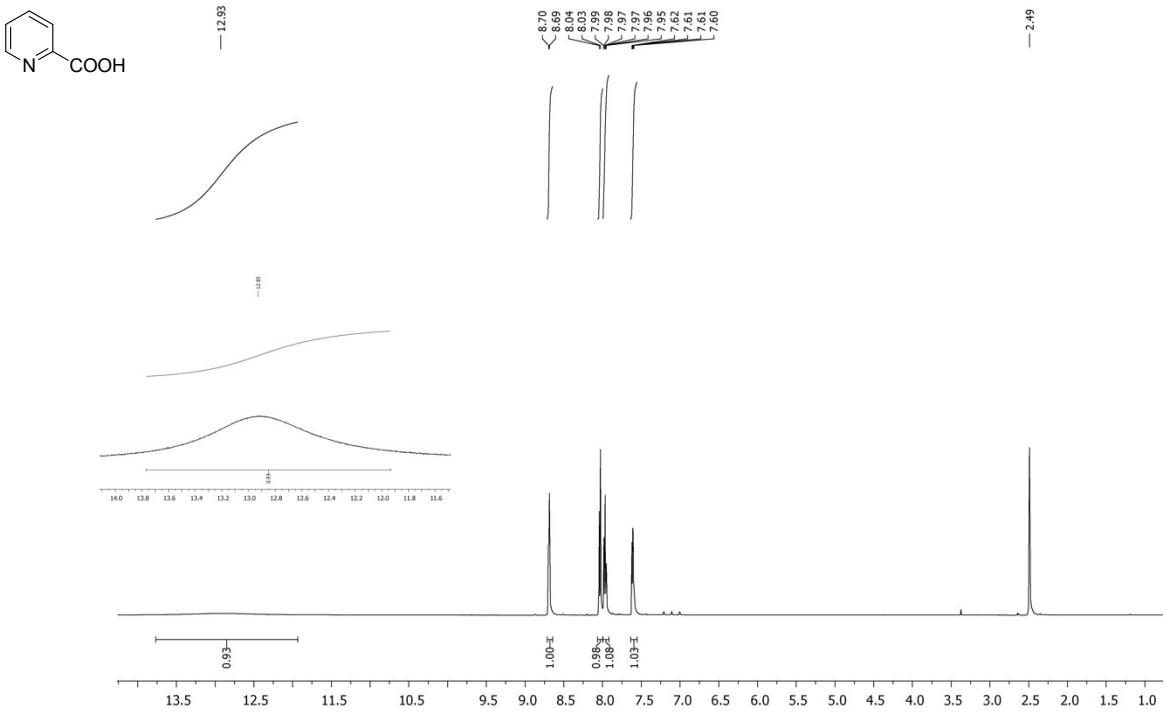

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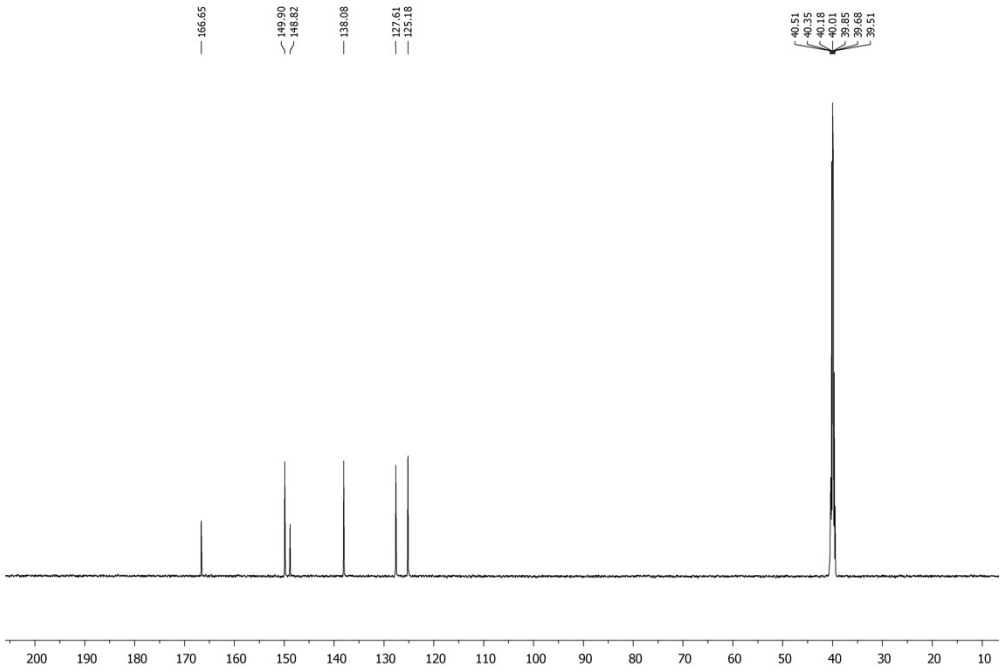

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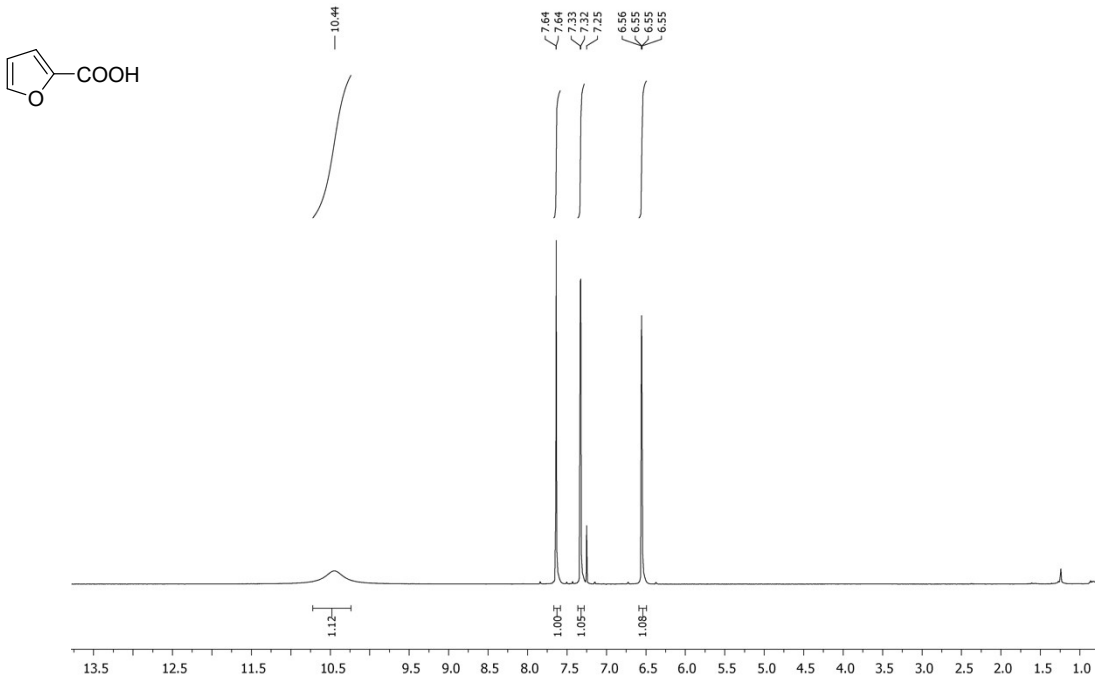
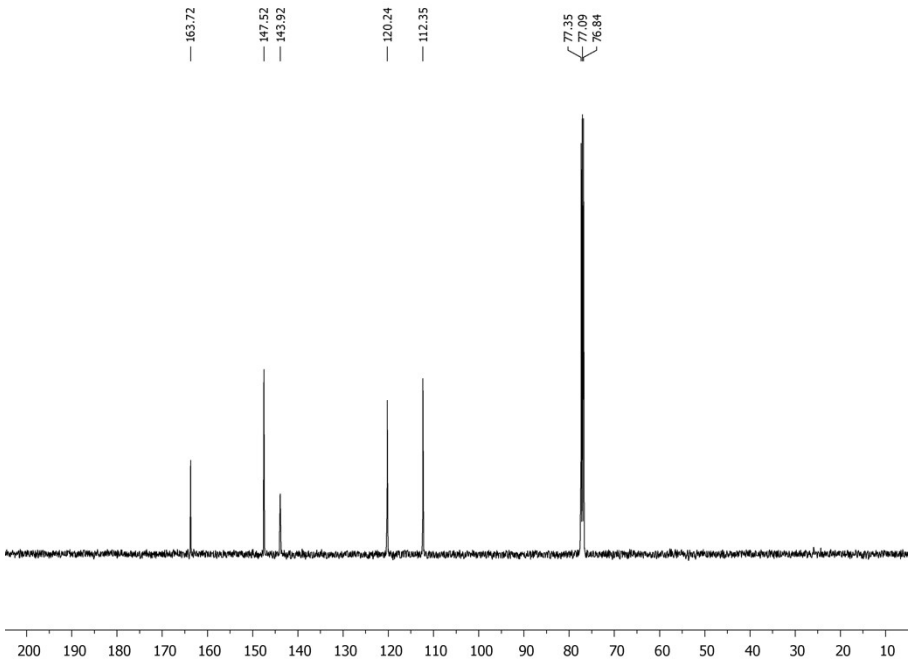


^{1}H NMR (500 MHz, $CDCl_3$)



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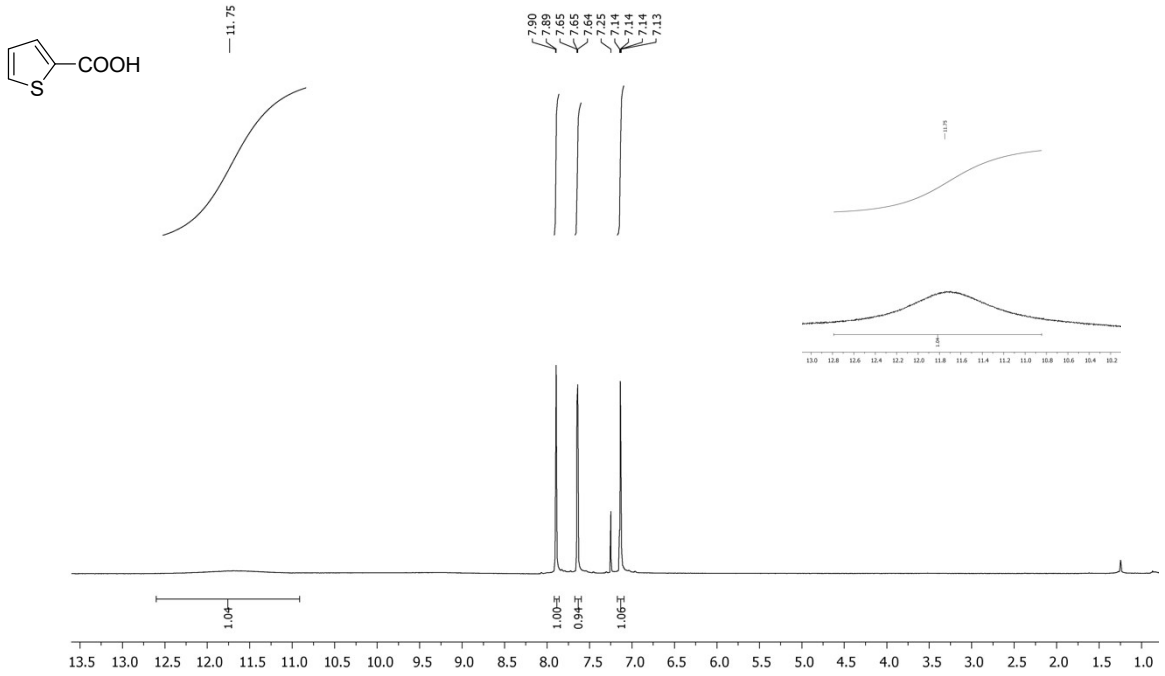
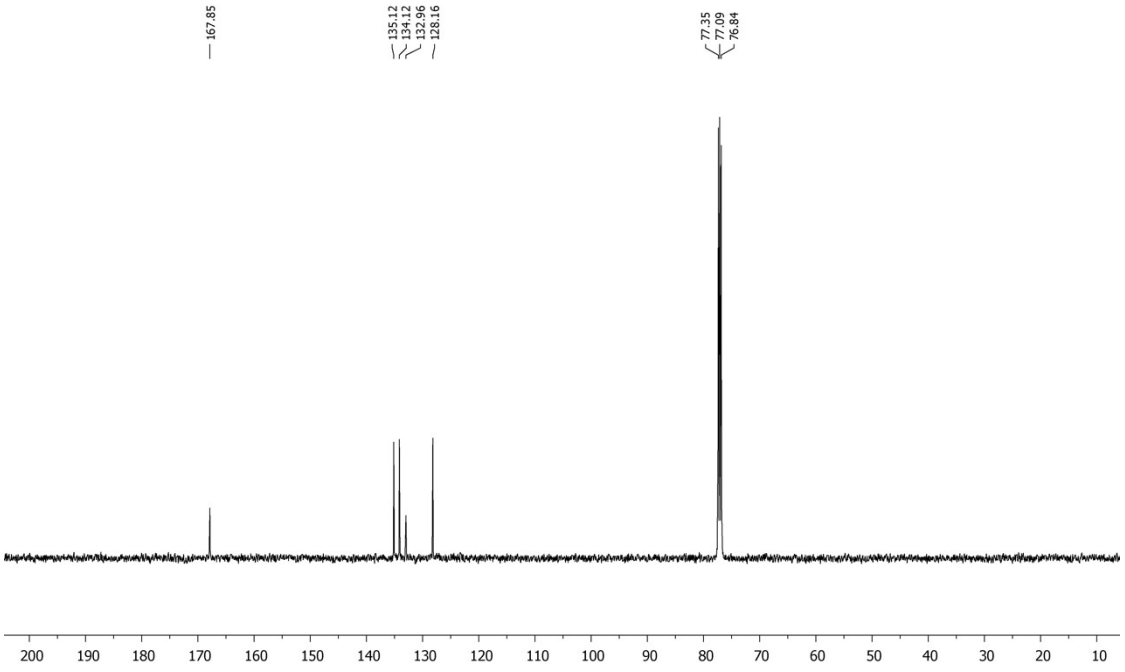


^{1}H NMR (500 MHz, $CDCl_3$)



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

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