Light-Induced Metal-Free Transformations of Unactivated Pyridotriazoles

Ziyan Zhang†, Dongari Yadagiri† and Vladimir Gevorgyan*

Department of Chemistry, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607-7061, United States

Department of Chemistry and Biochemistry, University of Texas at Dallas, 800 W Campbell RD, Richardson, Texas 75080, United States, Email: vlad@utdallas.edu

Table of Contents

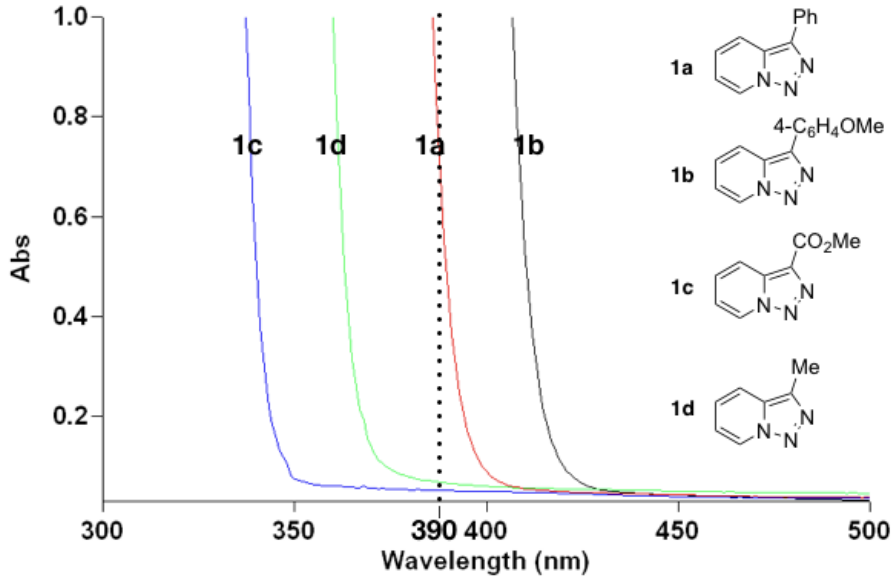
1. General Information

NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) or DPX-400 (400 MHz) instrument. ^{1}H signals are referenced to residual $CHCl_3$ at 7.26 ppm. ^{13}C signals are referenced to $CDCl_3$ at 77.16 ppm. GC/MS analysis was performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Silicycle Silica-P flash silica gel (40-63 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. LRMS and HRMS analyses were performed on Micromass 70 VSE mass spectrometer. Anhydrous solvents purchased from Aldrich were additionally purified on PureSolv PS-400-4 by Innovative Technology, Inc. purification system and/or stored over calcium hydride. All starting materials were purchased from Strem Chemicals, Aldrich, Gelest Inc., TCI America, Oakwood Chemical, AK Sci. or Alfa Aesar, or synthesized via known literature procedures. The 34 W Blue LED lamp (Kessil KSH150B LED Grow Light, 450nm), 23W Philips Household CFL, and Vornado 133 Small Air Circulator fan were purchased from amazon.com. 40 W Kessil LED PR160-390nm was purchased from kessil.com. All manipulations with transition metal catalysts were conducted in oven-dried glassware under inert atmosphere using a combination of glovebox and standard Schlenk techniques.

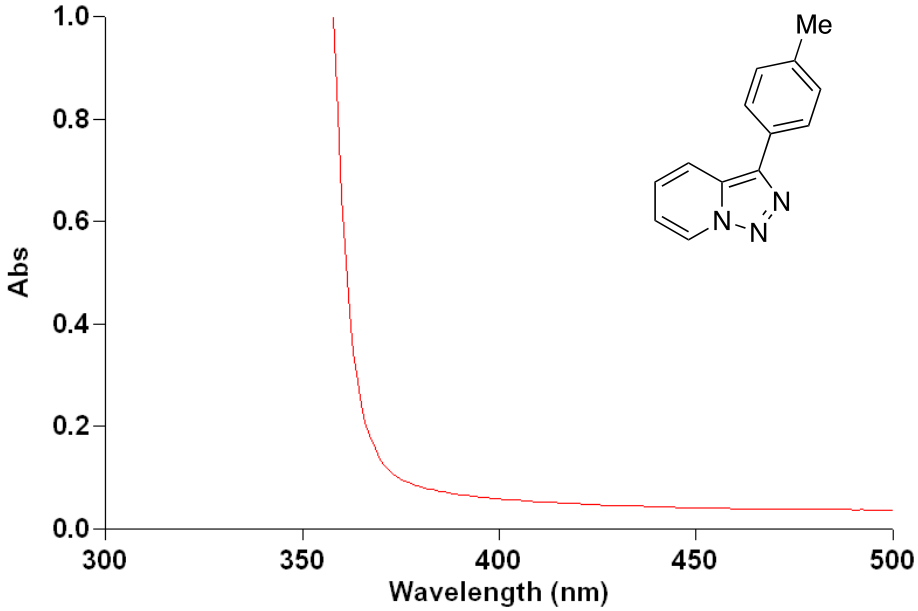
2. UV-vis absorption spectra of pyridotriazoles

Absorption spectra of various pyridotriazoles are employed in this study.

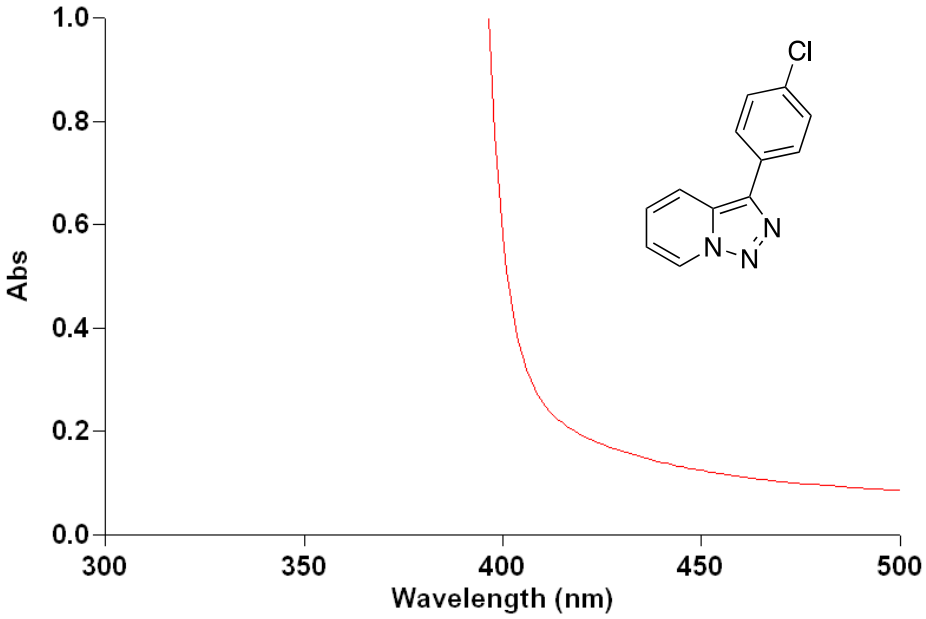
Concentration: 0.1 M in PhMe



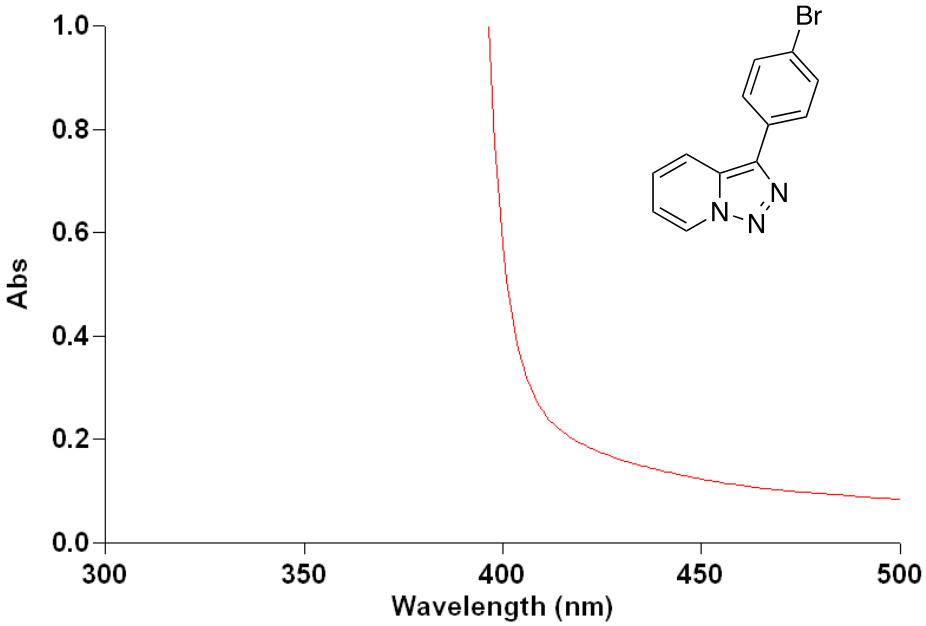
UV-vis absorption spectra of pyridotriazole **1e**



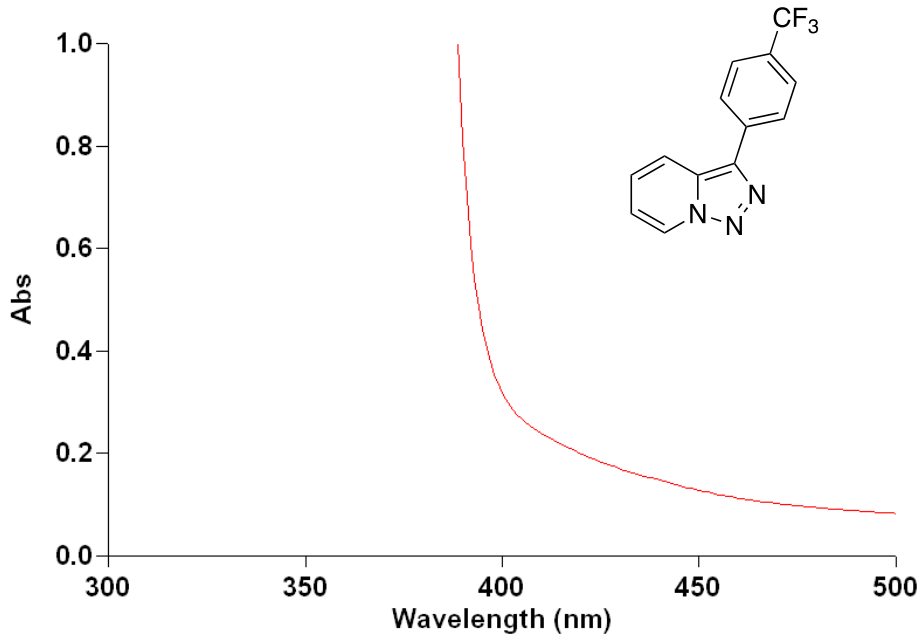
UV-vis absorption spectra of pyridotriazole **1f**



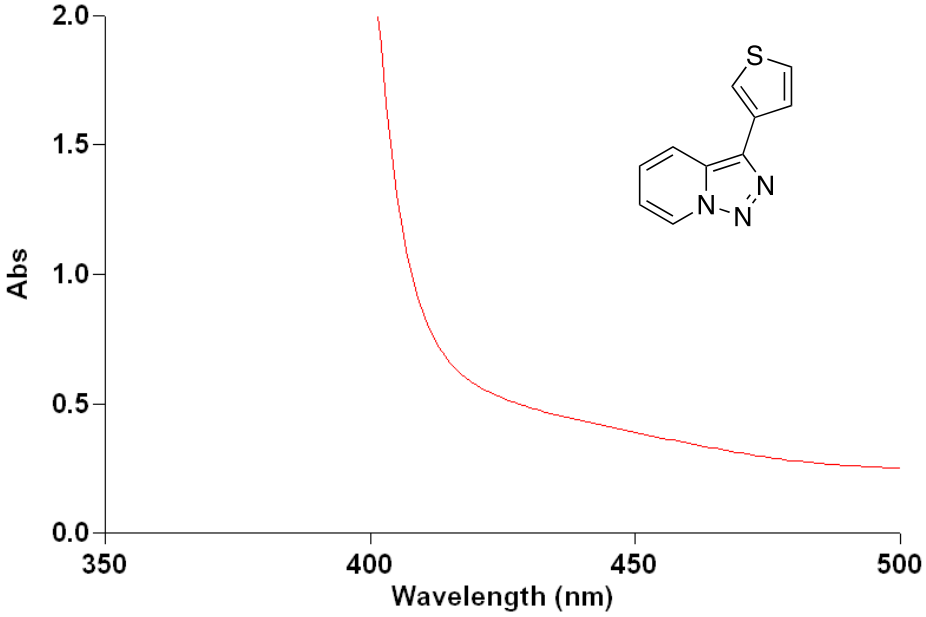
UV-vis absorption spectra of pyridotriazole **1g**



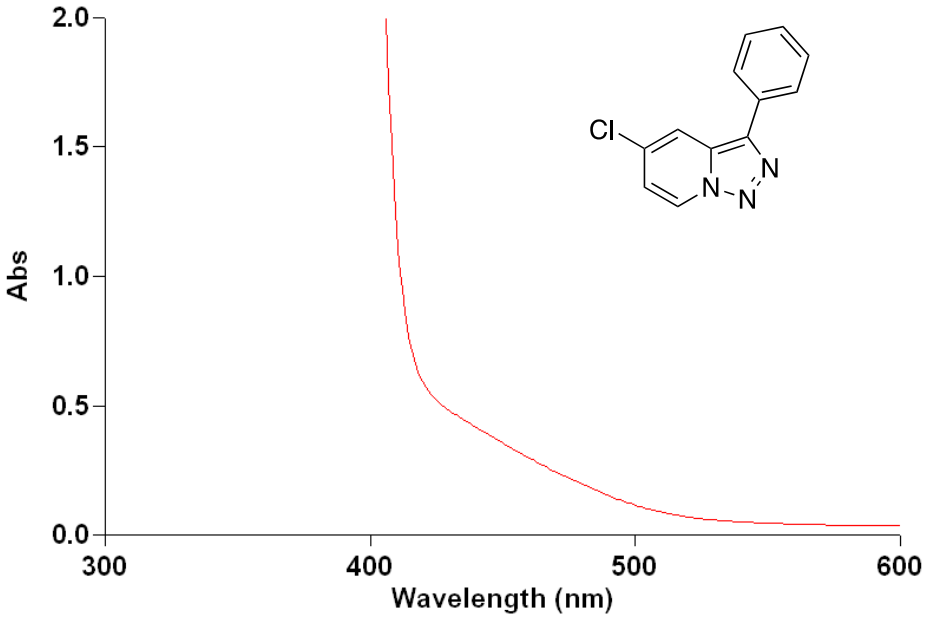
UV-vis absorption spectra of pyridotriazole **1h**



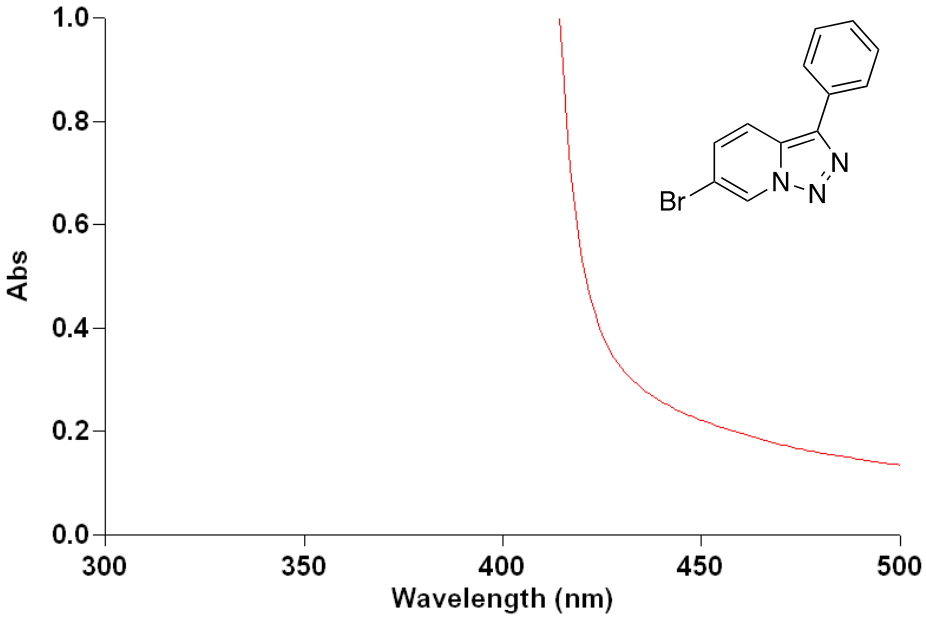
UV-vis absorption spectra of pyridotriazole **1i**



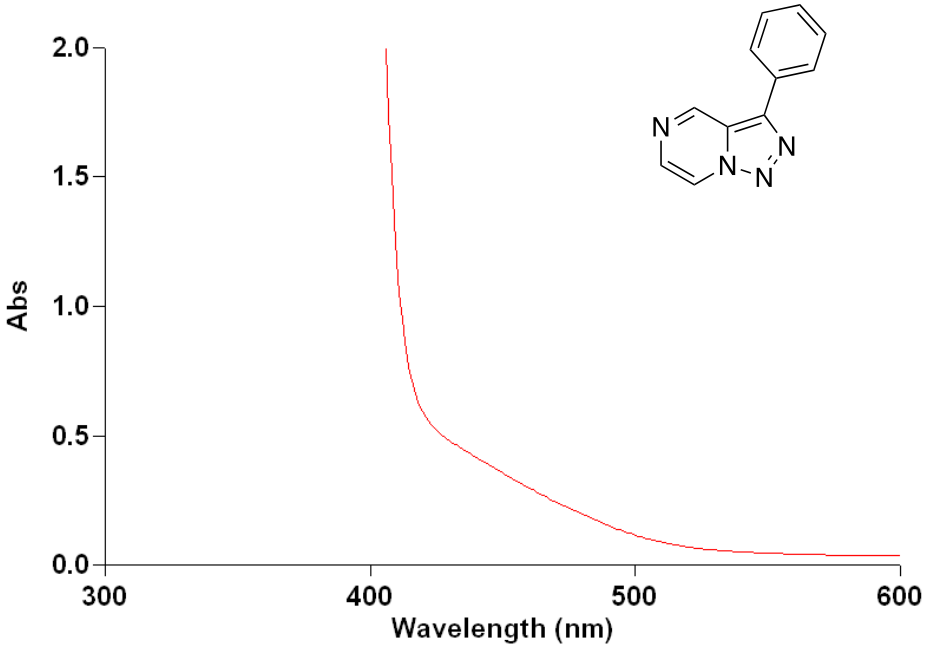
UV-vis absorption spectra of pyridotriazole **1j**



UV-vis absorption spectra of pyridotriazole **1k**

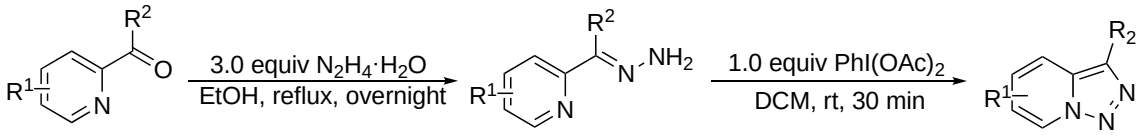


UV-vis absorption spectra of pyridotriazole **1l**



3. Preparation of Pyridoriazoles

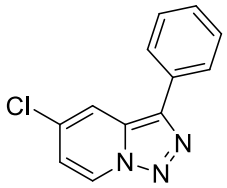
General Procedure: Pyridotriazoles[1,2] (**1a-1l**) were prepared from 2-pyridylketone.



To a solution of 2-pyridylketone in ethanol (1 mL/mmol), hydrazine monohydrate (3 equiv) was added. The reaction mixture was refluxed overnight, quenched with water, and extracted with EtOAc twice. The extract was washed with water and brine and dried over sodium sulfate. Removal of solvent afforded the crude hydrazone, which was dissolved in dichloromethane (1 mL/mmol), and $PhI(OAc)_2$ (1 equiv) was added to this solution in small portions. A rapid reaction occurred and the reaction mixture was stirred for 30 min at room temperature. The solvent was removed, and the residue was purified via flash Silica chromatography to afford corresponding pyridotriazoles as crystalline solid.

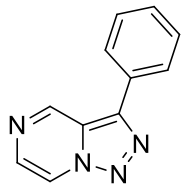
Pyridotriazoles **1a-1i** and **1k** were prepared according to general procedure. Spectral data are in accordance with the reported data.[3]

5-Chloro-3-phenyl-[1,2,3]triazolo[1,5-a]pyridine **1j**



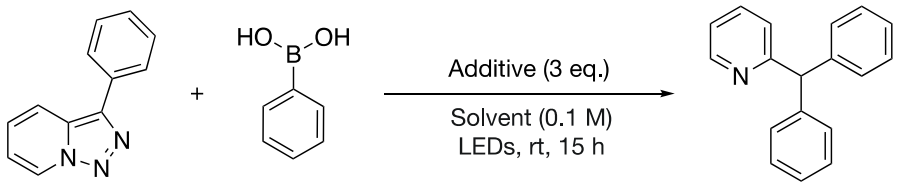
1j was prepared according to the general procedure. Yellow solid. R_f (hexanes/EtOAc = 2/1): 0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.67 (dd, *J* = 7.4, 0.9 Hz, 1H), 7.97 (d, *J* = 0.8 Hz, 1H), 7.91 (d, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.40 (dd, *J* = 10.8, 4.0 Hz, 1H), 6.96 (dd, *J* = 7.4, 1.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 138.2, 132.5, 131.2, 130.9, 129.5, 128.6, 127.0, 126.5, 117.5, 117.3. HRMS (EI+) calcd. for $C_{12}H_7N_3Cl$ $[M+H]^+$: 230.0485, found: 230.0482.

5-Chloro-3-phenyl-[1,2,3]triazolo[1,5-a]pyridine **1l**



1l was prepared according to the general procedure. Orange solid. R_f (hexanes/EtOAc = 2/1): 0.2. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.54 (s, 1H), 8.65 (dd, *J* = 4.8, 1.4 Hz, 1H), 8.08 – 7.98 (m, 3H), 7.57 (t, *J* = 6.9 Hz, 2H), 7.48 (dd, *J* = 11.1, 3.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 145.8, 140.5, 131.7, 129.8, 129.2, 129.1, 127.0, 118.3. HRMS (EI+) calcd. for $C_{11}H_8N_4$ $[M+H]^+$: 197.0827, found: 197.0823.

4. Reaction Optimization



1a **2a** **1aa**

An oven dried 3 mL Wheaton V-vial containing a stirring bar was charged with pyridotriazoles **1a** (0.05 mmol, 1 equiv), additive (0.15 mmol, 3 equiv), phenylboronic acid **2a** (0.075 mmol, 1.5 equiv) and internal standard pentadecane (5 μL) in dry solvents (0.5 mL) under argon atmosphere (outside glovebox). After the reaction vessel was capped with a pressure screw cap in the glove box. The vial was irradiated with 40 W Kessil LED PR160-390nm for 12-24 h (monitored by GC/MS), with cooling from a fan (vial temperature reached 37 °C). The vial distance from the lamp was about 2-3 cm. The reaction mixture was measured by GC/MS use pentadecane as an internal standard.

Table 1. Optimization studies of Arylation

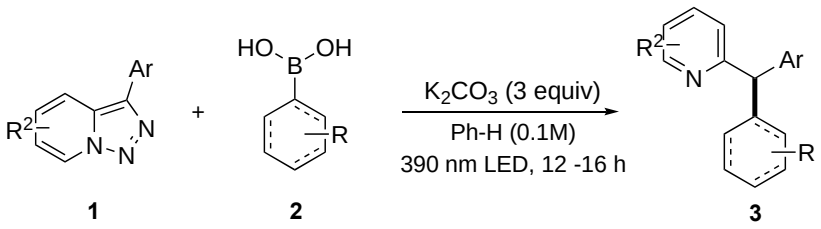
Entry	Additive	Solvent	LEDs	Yields (%)
1	**K_2CO_3**	**PhMe**	**390nm**	**84**
2	Cs_2CO_3	PhMe	390nm	73
3	Na_2CO_3	PhMe	390nm	73
4	KOH	PhMe	390nm	8
5	NaOH	PhMe	390nm	65
6	NaOAc	PhMe	390nm	33
7	K_3PO_4	PhMe	390nm	44
8	NaF	PhMe	390nm	56
9	CsF	PhMe	390nm	9
10	Li_2CO_3	PhMe	390nm	44
11	$NaHCO_3$	PhMe	390nm	53
12	NaO*t*Bu	PhMe	390nm	0
13	NEt_3	PhMe	390nm	40

14	KO*t*Bu	PhMe	390nm	0
15	*i*Pr$_2$NH	PhMe	390nm	90
16	-	PhMe	390nm	25
17	**K_2CO_3**	**PhH**	390nm	**89**
18	K_2CO_3	1,4-dioxane	390nm	68
19	K_2CO_3	THF	390nm	0
20	K_2CO_3	MeCN	390nm	0
21	K_2CO_3	$CHCl_3$	390nm	24
22	K_2CO_3	DCE	390nm	64
23	K_2CO_3	DMF	390nm	0
24	K_2CO_3	$PhCF_3$	390nm	60
25	K_2CO_3	PhH	427nm	0
26	K_2CO_3	PhH	455nm	0
27	K_2CO_3	PhH	Dark	0
28	K_2CO_3	PhH	-	0[a]

[a] Reaction temperatures are room temperature, 50°C, 100°C and 120°C.

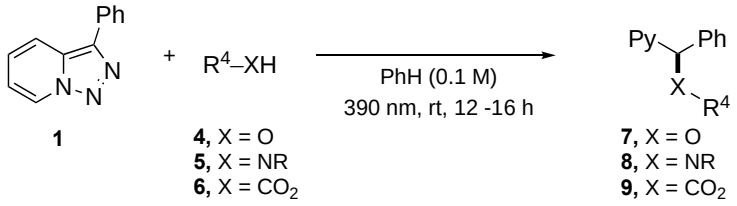
5. General Procedures for Arylation, X–H insertions, Cyclopropanation of Pyridotriazoles

General procedure A for arylation of pyridotriazoles



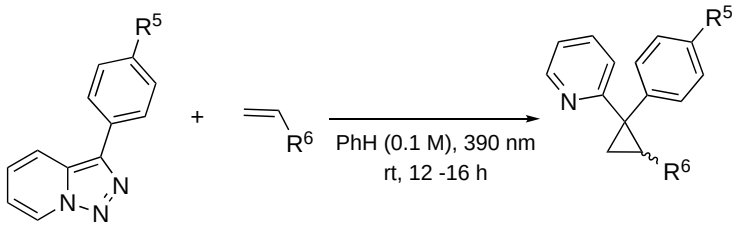
An oven dried 3 mL Wheaton V-vial containing a stirring bar was charged with Pyridotriazoles **1** (0.2 mmol, 1 equiv), K_2CO_3 (83 mg, 0.6 mmol, 3 equiv) and aryl or alkenylboronic acid **2** (0.3 mmol, 1.5 equiv) in dry and degassed benzene (2 mL) under argon atmosphere (outside glovebox). After the reaction vessel was capped with a pressure screw cap in the glove box. The vial was irradiated with 40 W Kessil LED PR160-390nm for 12-24 h (monitored by GC/MS), with cooling from a fan (vial temperature reached 37 °C). The vial distance from the lamp was about 2-3 cm. The resulting mixture was passed through a pad of Celite, and concentrated under a reduced pressure. The residue was purified by column chromatography in hexanes/EtOAc to afford the corresponding triarylmethanes.

General procedure B for X–H insertion of pyridotriazoles



An oven dried 3 mL Wheaton V-vial containing a stirring bar was charged with Pyridotriazoles **1** (0.2 mmol, 1 equiv), in dry and degassed benzene (2 mL) under argon atmosphere (outside glovebox) and compounds **4** or **5** or **6** (0.8 mmol, 4 equiv) were added. After the reaction vessel was capped with a pressure screw cap in the glove box. The vial was irradiated with 40 W Kessil LED PR160-390nm for 12-16 h (monitored by GC/MS), with cooling from a fan (vial temperature reached 37 °C). The vial distance from the lamp was about 2-3 cm. The solvent was removed under a reduced pressure. The residue was purified by column chromatography in hexanes/EtOAc to afford the corresponding compounds.

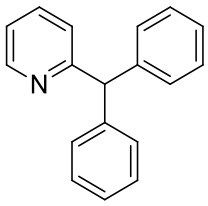
General procedure C for cyclopropanation of pyridotriazoles



1 **10** **11**

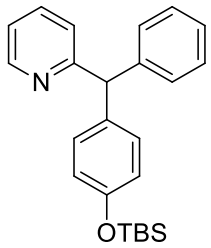
An oven dried 3 mL Wheaton V-vial containing a stirring bar was charged with Pyridotriazoles **1** (0.2 mmol, 1 equiv), in dry benzene (2 mL) under argon atmosphere (outside glovebox) and styrene **10** (0.6 mmol, 3 equiv) were added. After the reaction vessel was capped with a pressure screw cap in the glove box. The vial was irradiated with 40 W Kessil LED PR160-390nm for 12-16 h (monitored by GC/MS), with cooling from a fan (vial temperature reached 37 °C). The vial distance from the lamp was about 2-3 cm. The solvent was removed under a reduced pressure. The residue was purified by column chromatography in hexanes/EtOAc to afford the corresponding cyclopropanes **11**.

Diphenyl-2-pyridylmethane **3aa**



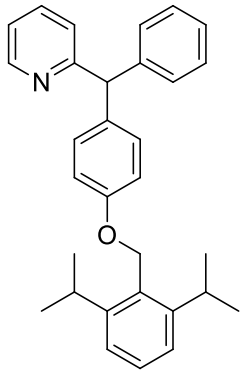
3aa was prepared according to the general procedure **A** in 89% yield (43.7 mg, 0.178 mmol) from 0.2 mmol of **1a**. White solid. R_f (hexanes/EtOAc = 4/1): 0.3. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.61 (d, *J* = 4.6 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.30 – 7.29 (m, 4H), 7.23 – 7.20 (m, 2H), 7.18 – 7.15 (m, 4H), 7.14 (d, 5.4 Hz, 1H), 7.09 – 7.04 (m, 1H), 5.71 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 163.3, 149.6, 142.8, 136.5, 129.5, 128.5, 126.6, 123.9, 121.5, 59.5. HRMS (EI+) calcd. for $C_{18}H_{15}N$ $[M+H]^+$: 246.1283, found: 246.1280.

2-((4-((Tert-butyldimethylsilyl)oxy)phenyl)(phenyl)methyl)pyridine **3ab**



3ab was prepared according to the general procedure **A** in 85% yield (64.0 mg, 0.17 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 3/1): 0.29. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.59 (d, *J* = 4.8 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.29 – 7.24 (m, 2H), 7.22 – 7.20 (m, 1H), 7.14 – 7.10 (m, 3H), 7.06 (d, *J* = 7.8 Hz, 1H), 7.01 – 7.00 (m, 2H), 6.77 – 6.75 (m, 2H), 5.64 (s, 1H), 0.97 (s, 9H), 0.18 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 163.7, 154.3, 149.6, 143.2, 136.5, 135.5, 130.4, 129.4, 128.5, 126.5, 123.8, 121.4, 120.0, 58.7, 25.8, 18.3, -4.2. HRMS (EI+) calcd. for $C_{24}H_{29}NOSi$ $[M+H]^+$: 376.2097, found: 376.2092.

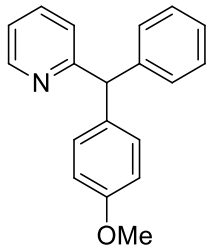
2-((4-((Tert-butyldimethylsilyl)oxy)phenyl)(phenyl)methyl)pyridine **3ac**



3ac was prepared according to the general procedure **A** in 87% yield (76.0 mg, 0.174 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 3/1): 0.29. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.62 (d, *J* = 4.3 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.46 – 7.43 (m, 2H), 7.33 – 7.30 (m, 2H), 7.25 – 7.23 (m, 3H), 7.21 – 7.19 (m, 2H), 7.17 – 7.13 (m, 5H), 5.74 (s, 1H), 4.78 (s, 2H), 3.42 – 3.37 (m, 2H), 1.24 (d, *J* = 1.6 Hz, 6H), 1.23 (d, *J* = 1.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 163.28, 153.1, 149.7, 142.7, 142.6, 142.07, 136.6, 136.0, 129.7, 129.5, 128.6, 127.7, 126.7, 124.8,

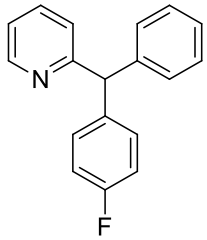
124.2, 123.9, 121.6, 76.3, 59.3, 26.6, 24.2. HRMS (EI+) calcd. for $C_{31}H_{33}NO$ $[M+H]^+$: 436.2640, found: 436.2634.

2-((4-Methoxyphenyl)(phenyl)methyl)pyridine **3ad**



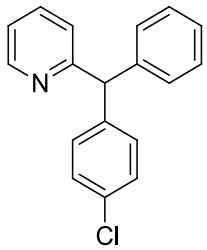
3ad was prepared according to the general procedure **A** in 45% yield (25.0 mg, 0.0908 mmol) from 0.2 mmol of **1a**. colorless liquid. R_f (hexanes/EtOAc = 3/1): 0.29. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.60 (d, *J* = 4.8 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.29 – 7.24 (m, 2H), 7.22 – 7.18 (m, 1H), 7.16 – 7.15 (m, 2H), 7.14 – 7.11 (m, 1H), 7.08 – 7.04 (m, 3H), 6.85 – 6.83 (m, 2H), 5.65 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 163.6, 158.3, 149.6, 143.2, 136.5, 135.0, 130.4, 129.4, 128.5, 126.5, 123.8, 121.4, 113.9, 58.7, 55.3. HRMS (EI+) calcd. for $C_{19}H_{17}NO$ $[M+H]^+$: 276.1388, found: 276.1385.

2-((4-Fluorophenyl)(phenyl)methyl)pyridine **3ae**



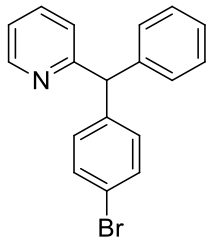
3ae was prepared according to the general procedure **A** in 84% yield (44.0 mg, 0.167 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 5/1): 0.30. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 – 8.58 (m, 1H), 7.61 – 7.58 (m, 1H), 7.31 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 7.15 – 7.11 (m, 5H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.99 – 6.95 (m, 2H), 5.69 (s, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 162.9, 162.5, 160.6, 149.6, 142.6, 138.5, 136.5, 130.8, 129.3, 128.5, 126.7, 123.7, 121.5, 115.3, 115.2, 58.5. HRMS (EI+) calcd. for $C_{18}H_{14}NF$ $[M+H]^+$: 264.1189, found: 264.1190.

2-((4-Chlorophenyl)(phenyl)methyl)pyridine **3af**



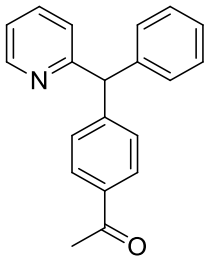
3af was prepared according to the general procedure **A** in 70% yield (39.0 mg, 0.139 mmol) from 0.2 mmol of **1a**. Light yelow liquid. R_f (hexanes/EtOAc = 5/1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.61 (d, *J* = 3.7 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.29 – 7.26 (m, 5H), 7.19 – 7.01 (m, 6H), 5.67 (s, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 162.9, 162.5, 160.5, 149.6, 142.6, 138.5, 136.5, 130.8, 130.8, 129.2, 128.5, 126.7, 123.7, 121.5, 115.3, 115.1, 58.5. HRMS (EI+) calcd. for $C_{18}H_{14}NCl$ $[M+H]^+$: 280.0893, found: 280.0887.

2-((4-Bromophenyl)(phenyl)methyl)pyridine **3ag**



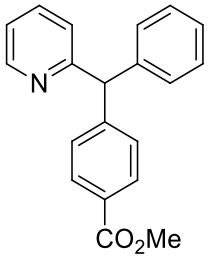
3ag was prepared according to the general procedure **A** in 50% yield (32.5 mg, 0.1 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 3/1): 0.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.59 – 8.58 (m, 1H), 7.65 – 7.60 (m, 1H), 7.42 – 7.40 (m, 2H), 7.30 – 7.28 (m, 1H), 7.26 – 7.23 (m, 1H), 7.20 – 7.16 (m, 1H), 7.14 – 7.12 (m, 2H), 7.09 – 7.06 (m, 1H), 7.04 – 7.03 (m, 2H), 6.63 – 6.60 (m, 1H), 5.67 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 163.3, 149.7, 137.2, 132.7, 131.9, 131.5, 129.6, 128.9, 127.2, 124.2, 122.2, 121.0, 117.7, 58.9. HRMS (EI+) calcd. for $C_{18}H_{14}NBr$ $[M+H]^+$: 324.0388, found: 324.0382.

1-(4-(Phenyl(pyridin-2-yl)methyl)phenyl)ethanone **3ah**



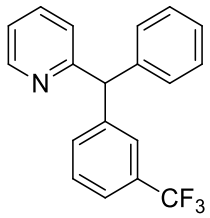
3ah was prepared according to the general procedure **A** in 75% yield (43.0 mg, 0.15 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 3/1): 0.34. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.64 – 8.58 (m, 1H), 7.90 – 7.88 (m, 2H), 7.64 – 7.60 (m, 1H), 7.33 – 7.23 (m, 5H), 7.21 – 7.13 (m, 3H), 7.10 (d, *J* = 7.9 Hz, 1H), 5.75 (s, 1H), 2.57 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 198.0, 162.4, 149.6, 148.3, 141.8, 136.9, 135.63, 130.9, 129.7, 129.4, 128.7, 127.0, 124.0, 121.9, 59.2, 26.7. HRMS (EI+) calcd. for $C_{20}H_{17}NO$ $[M+H]^+$: 288.1388, found: 288.1388.

Methyl 4-(phenyl(pyridin-2-yl)methyl)benzoate **3ai**



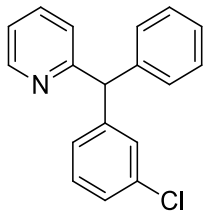
3ai was prepared according to the general procedure **A** in 60% yield (36.5 mg, 0.12 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 3/1): 0.32. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.60 (d, *J* = 4.0 Hz, 1H), 7.98 – 7.96 (m, 2H), 7.66 – 7.50 (m, 1H), 7.31– 7.28 (m, 2H), 7.26 – 7.23 (m, 3H), 7.17 – 7.15 (m, 3H), 7.08 (d, *J* = 7.8 Hz, 1H), 5.74 (s, 1H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 167.1, 162.5, 149.7, 148.1, 142.0, 136.7, 129.8, 129.5, 129.4, 128.7, 128.6 126.9, 123.9, 121.83, 59.3, 52.17. HRMS (EI+) calcd. for $C_{20}H_{17}NO_2$ $[M+H]^+$: 304.1338, found: 304.1337.

2-(Phenyl(3-(trifluoromethyl)phenyl)methyl)pyridine **3aj**



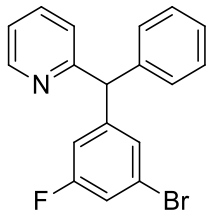
3aj was prepared according to the general procedure **A** in 72% yield (45.0 mg, 0.144 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 5/1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.62 (d, *J* = 2.8 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.52 – 7.45 (m, 2H), 7.45 – 7.36 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.23 (m, 1H), 7.18 – 7.13 (m, 3H), 7.10 (d, *J* = 7.8 Hz, 1H), 5.75 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 160.0, 147.5, 141.6, 139.7, 134.6, 130.7, 127.1, 126.7, 126.5, 124.8, 123.9, 121.6, 121.4, 119.6, 56.8. HRMS (EI+) calcd. for $C_{19}H_{14}NF_3$ $[M-H]^+$: 312.1000, found: 312.0993.

2-((3-Chlorophenyl)(phenyl)methyl)pyridine **3ak**



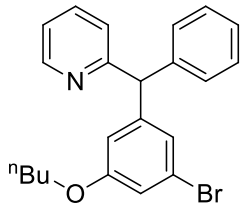
3ak was prepared according to the general procedure **A** in 68% yield (38.0 mg, 0.136 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 5/1): 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.61 (d, *J* = 3.9 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.35 – 7.28 (m, 2H), 7.28 – 7.19 (m, 3H), 7.16 – 7.11 (m, 4H), 7.08 – 7.05 (m, 2H), 5.67 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 162.8, 150.10 145.2, 142.4, 137.0, 134.7, 130.0, 129.9, 129.7, 129.0, 128.0, 127.2, 127.2, 124.1, 122.1, 59.4. HRMS (EI+) calcd. for $C_{18}H_{14}NCl$ $[M+H]^+$: 280.0893, found: 280.0884.

2-((3-Bromo-5-fluorophenyl)(phenyl)methyl)pyridine **3al**



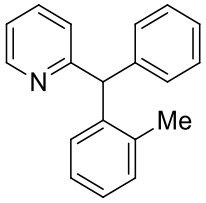
3al was prepared according to the general procedure **A** in 73% yield (50.0 mg, 0.146 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 3/1): 0.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.61 (d, *J* = 3.9 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.35 – 7.31 (m, 2H), 7.28 – 7.24 (m, 1H), 7.20 – 7.15 (m, 3H), 7.12 – 7.08 (m, 3H), 6.83 (d, *J* = 9.7 Hz, 1H), 5.62 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 163.9, 161.8, 161.5, 149.8, 146.9, 141.3, 136.9, 129.3, 128.8, 128.4, 127.2, 123.8, 122.6, 122.0, 117.5, 115.64, 58.7. HRMS (EI+) calcd. for $C_{18}H_{13}NBrF$ $[M+H]^+$: 342.0294, found: 342.0289.

2-((3-Bromo-5-butoxyphenyl)(phenyl)methyl)pyridine **3am**



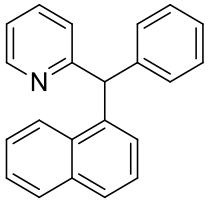
3am was prepared according to the general procedure **A** in 77% yield (61.0 mg, 0.154 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 3/1): 0.29. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.60 (d, *J* = 4.0 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.32 – 7.29 (m, 2H), 7.25 – 7.22 (m, 1H), 7.17–7.14 (m, 3H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.91 – 6.88 (m, 2H), 6.65 (s, 1H), 5.60 (s, 1H), 3.86 (t, *J* = 6.5 Hz, 2H), 1.71 – 1.68 (m, 2H), 1.43 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 162.5, 160.0, 149.7, 145.9, 141.9, 136.7, 129.4, 128.7, 126.9, 124.7, 123.8, 122.9, 121.8, 115.7, 115.3, 68.04, 59.1, 31.2, 19.2, 13.9. HRMS (EI+) calcd. for $C_{22}H_{22}NOBr$ $[M+H]^+$: 396.0963, 396.0959.

2-(Phenyl(o-tolyl)methyl)pyridine **3an**



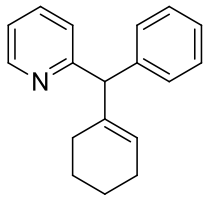
3an was prepared according to the general procedure **A** in 94% yield (49.0 mg, 0.189 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 5/1): 0.30. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.63 (d, *J* = 4.5 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.31 – 7.26 (m, 2H), 7.25 – 7.23 (m, 1H), 7.21 – 7.07 (m, 6H), 6.99 – 6.95 (m, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 5.89 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.2, 149.7, 142.3, 141.3, 136.9, 136.5, 130.7, 129.7, 129.3, 128.6, 126.7, 126.6, 125.9, 123.9, 121.4, 56.4, 20.1. HRMS (EI+) calcd. for $C_{19}H_{17}N$ $[M+H]^+$: 260.1439, found: 260.1434.

2-(Naphthalen-1-yl(phenyl)methyl)pyridine **3ao**



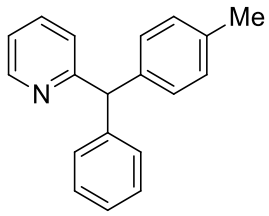
3ao was prepared according to the general procedure **A** in 63% yield (37.0 mg, 0.125 mmol) from 0.2 mmol of **1a**. colorless liquid. R_f (hexanes/EtOAc = 3/1): 0.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.64 – 8.63 (m, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.86 – 7.84 (m, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.56 (m, 1H), 7.46 – 7.41 (m, 2H), 7.39 – 7.37 (m, 2H), 7.32 – 7.26 (m, 2H), 7.16 – 7.13 (m, 3H), 6.99 (m, 2H), 6.47 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 163.4, 149.8, 142.5, 139.0, 136.6, 134.1, 129.8, 128.8, 128.7, 127.7, 127.4, 126.7, 126.3, 125.6, 125.4, 124.4, 124.1, 121.6, 108.7, 56.0. HRMS (EI+) calcd. for $C_{22}H_{17}N$ $[M+H]^+$: 296.1439, found: 296.1436.

2-(Cyclohex-1-en-1-yl(phenyl)methyl)pyridine **3ap**



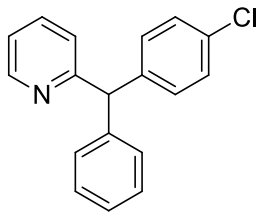
3ap was prepared according to the general procedure **A** in 70% yield (35.0 mg, 0.140 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.61 (s, 1H), 7.61 – 7.58 (m, 1H), 7.33 (m, 2H), 7.29 – 7.21 (m, 3H), 7.11 – 7.09 (m, 2H), 5.20 (s, 1H), 4.85 (s, 1H), 2.07 (s, 2H), 1.99 (s, 2H), 1.68 – 1.59 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 162.5, 149.2, 141.4, 139.0, 135.9, 129.1, 128.1, 126.2, 125.4, 123.4, 121.0, 61.1, 28.8, 25.3, 22.9, 22.2. HRMS (EI+) calcd. for $C_{18}H_{18}N$ $[M+H]^+$: 250.1596, found: 250.1588.

2-(Phenyl(p-tolyl)methyl)pyridine **3ea**



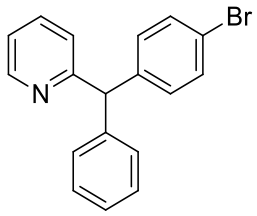
3ea was prepared according to the general procedure **A** in 83% yield (43.0 mg, 0.166 mmol) from 0.2 mmol of **1e**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.62 (s, 1H), 7.61 – 7.59 (m, 1H), 7.31 – 7.29 (m, 2H), 7.28 – 7.16 (m, 3H), 7.10 (m, 6H), 5.69 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.4, 149.5, 142.9, 139.7, 136.4, 136.1, 129.3, 129.2, 129.1, 128.4, 126.4, 123.7, 121.3, 59.0, 21.0. HRMS (EI+) calcd. for $C_{19}H_{17}N$ $[M+H]^+$: 260.1439, found: 260.1432.

2-((4-Chlorophenyl)(phenyl)methyl)pyridine **3fa**



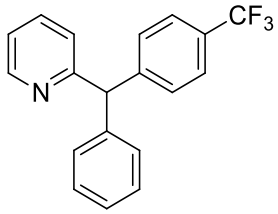
3fa was prepared according to the general procedure **A** in 72% yield (40.0 mg, 0.143 mmol) from 0.2 mmol of **1f**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.61 (s, 1H), 7.61 – 7.58 (m, 1H), 7.28 – 7.23 (m, 5H), 7.20 – 7.03 (m, 6H), 5.67 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.0, 150.0, 142.6, 141.6, 136.9, 132.7, 131.0, 129.6, 128.9, 127.1, 124.1, 121.9, 59.1. HRMS (EI+) calcd. for $C_{18}H_{14}NCl$ $[M+H]^+$: 280.0893, found: 280.0886.

2-((4-Bromophenyl)(phenyl)methyl)pyridine **3ga**



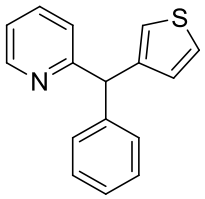
3ga was prepared according to the general procedure **A** in 90% yield (58.0 mg, 0.179 mmol) from 0.2 mmol of **1g**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.61 (d, *J* = 3.8 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.44 – 7.42 (m, 2H), 7.31 – 7.28 (m, 2H), 7.27 – 7.20 (m, 1H), 7.16 – 7.11 (m, 3H), 7.07 – 7.04 (m, 3H), 5.65 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 162.9, 150.0, 142.5, 142.2, 136.9, 131.8, 131.5, 129.7, 129.6, 128.9, 128.8, 127.1, 124.1, 121.9, 120.9, 59.1. HRMS (EI+) calcd. for $C_{18}H_{14}NBr$ $[M+H]^+$: 324.0388, found: 324.0382.

2-(Phenyl(4-(trifluoromethyl)phenyl)methyl)pyridine **3ha**



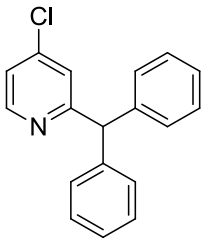
3ha was prepared according to the general procedure **A** in 56% yield (35.0 mg, 0.112 mmol) from 0.2 mmol of **1h**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.30. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.62 (d, J = 4.1 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.56 – 7.50 (m, 2H), 7.36 – 7.22 (m, 5H), 7.17 – 7.14 (m, 3H), 7.11 (d, J = 7.8 Hz, 1H), 5.74 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 162.4, 149.8, 147.0, 141.9, 136.8, 129.8, 129.4, 129.0, 128.7, 127.05, 125.5, 125.5, 123.9, 121.8, 59.2. HRMS (EI+) calcd. for $C_{19}H_{14}NF_3$ $[M+H]^+$: 314.1157, found: 314.1149.

2-(Phenyl(thiophen-3-yl)methyl)pyridine **3ia**



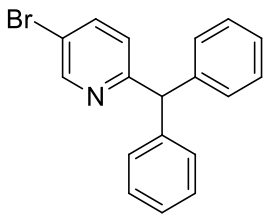
3ia was prepared according to the general procedure **A** in 30% yield (15.0 mg, 0.059 mmol) from 0.2 mmol of **1i**. Orange liquid. R_f (hexanes/EtOAc = 4/1): 0.30. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.63 – 8.57 (m, 1H), 7.61 – 7.57 (m, 1H), 7.34 – 7.27 (m, 3H), 7.24 – 7.20 (m, 4H), 7.14 – 7.10 (m, 2H), 6.96 – 6.88 (m, 1H), 6.84 (s, 1H), 5.67 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.1, 149.7, 143.6, 142.8, 136.7, 129.5, 129.1, 128.7, 128.6, 126.8, 125.7, 123.4, 122.9, 121.7, 55.3. HRMS (EI+) calcd. for $C_{16}H_{15}NS$ $[M+H]^+$: 252.0847, found: 252.0840.

2-Benzhydryl-4-chloropyridine **3ja**



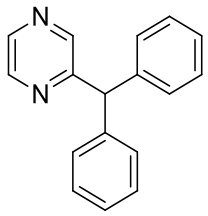
3ja was prepared according to the general procedure **A** in 90% yield (50.0 mg, 0.179 mmol) from 0.2 mmol of **1j**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.51 (d, J = 5.3 Hz, 1H), 7.33 – 7.29 (m, 4H), 7.26 – 7.20 (m, 2H), 7.18 – 7.14 (m, 5H), 7.13 (d, J = 1.7 Hz, 1H), 5.70 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 165.3, 150.8, 144.9, 142.4, 129.7, 128.9, 127.2, 124.4, 122.2, 59.5. HRMS (EI+) calcd. for $C_{18}H_{14}NCl$ $[M+H]^+$: 280.0893, found: 280.0888.

2-Benzhydryl-4-chloropyridine **3ka**



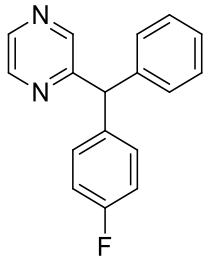
3ka was prepared according to the general procedure **A** in 77% yield (50.0 mg, 0.154 mmol) from 0.2 mmol of **1k**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.67 (d, *J* = 2.2 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.33 – 7.29 (m, 4H), 7.28 – 7.20 (m, 2H), 7.17 – 7.13 (m, 4H), 7.01 (d, *J* = 8.3 Hz, 1H), 5.67 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.9, 150.6, 142.3, 139.0, 129.3, 129.3, 128.6, 128.6, 128.6, 128.6, 126.8, 125.2, 118.6, 58.8. HRMS (EI+) calcd. for $C_{18}H_{14}NBr$ $[M+H]^+$: 324.0388, found: 324.0378.

2-Benzhydrylpyrazine **3la**



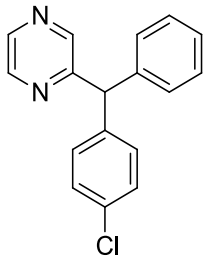
3la was prepared according to the general procedure **A** in 71% yield (35.0 mg, 0.142 mmol) from 0.2 mmol of **1l**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.30. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.62 – 8.55 (m, 1H), 8.51 – 8.41 (m, 2H), 7.33 – 7.29 (m, 4H), 7.27 – 7.23 (m, 2H), 7.24 – 7.18 (m, 4H), 5.69 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 158.5, 145.2, 144.1, 142.3, 141.4, 129.1, 128.5, 126.8, 56.7. HRMS (EI+) calcd. for $C_{17}H_{14}N_2$ $[M+H]^+$: 247.1235, found: 247.1231.

2-((4-Fluorophenyl)(phenyl)methyl)pyrazine **3le**



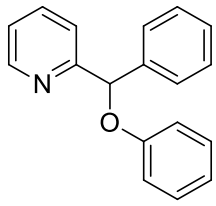
3le was prepared according to the general procedure **A** in 76% yield (41.0 mg, 0.155 mmol) from 0.2 mmol of **1l**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.57 (d, *J* = 1.4 Hz, 1H), 8.46 – 8.40 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 (d, *J* = 7.3 Hz, 1H), 7.22 – 7.09 (m, 4H), 7.01 – 6.97 (m, 2H), 5.66 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.2, 166.2, 163.8, 150.7, 149.7, 148.1, 146.8, 142.7, 136.2, 136.2, 134.7, 134.5, 134.1, 134.1, 132.5, 132.4, 120.9, 120.8, 61.5. HRMS (EI+) calcd. for $C_{17}H_{13}N_2F$ $[M+H]^+$: 265.1141, found: 265.1136.

2-((4-Chlorophenyl)(phenyl)methyl)pyrazine **3le**



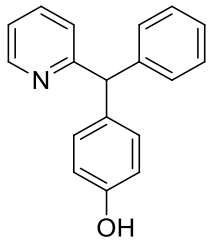
3lf was prepared according to the general procedure **A** in 75% yield (42.0 mg, 0.150 mmol) from 0.2 mmol of **1l**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.57 (s, 1H), 8.46 – 8.40 (m, 2H), 7.37 – 7.22 (m, 6H), 7.22 – 7.07 (m, 4H), 5.63 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 158.4, 145.5, 144.5, 143.0, 141.3, 140.3, 133.1, 130.8, 129.5, 129.3, 129.0, 128.9, 128.6, 127.4, 56.4. HRMS (EI+) calcd. for $C_{17}H_{13}N_2Cl$ $[M+H]^+$: 281.0846, found: 281.0840.

2-(Phenoxy(phenyl)methyl)pyridine **7aa**



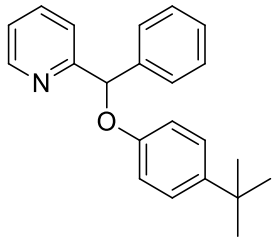
7aa was prepared according to the general procedure **B** in 50% yield (26.0 mg, 0.1 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.34. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.58 (d, J = 4.7 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.55 – 7.53 (m, 2H), 7.35 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 7.24 – 7.21 (m, 2H), 7.18 – 7.16 (m, 1H), 6.99 – 6.98 (m, 2H), 6.92 – 6.87 (m, 1H), 6.35 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 160.9, 157.8, 149.3, 140.3, 137.2, 129.5, 128.7, 128.0, 126.9, 122.7, 121.2, 120.9, 116.0, 82.6. HRMS (EI+) calcd. for $C_{18}H_{15}NO$ $[M+H]^+$: 262.1232, found: 262.1227.

4-(Phenyl(pyridin-2-yl)methyl)phenol **7aa'**



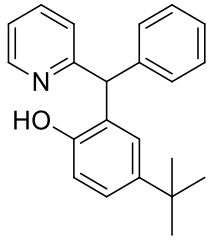
7aa' was prepared according to the general procedure **B** in 20% yield (10.5 mg, 0.04 mmol) from 0.2 mmol of **1a**. Colorless semi-solid. R_f (hexanes/EtOAc = 3/1): 0.28. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.55 (d, *J* = 4.1 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.25 – 7.21 (m, 3H), 7.19 – 7.17 (m, 1H), 7.00 – 6.98 (m, 1H), 6.98 – 6.96 (m, 2H), 6.89 – 6.86 (m, 1H), 5.32 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 162.6, 156.7, 148.2, 141.3, 138.6, 132.1, 129.5, 128.3, 127.7, 126.6, 124.7, 122.6, 119.8, 59.2. HRMS (EI+) calcd. for $C_{18}H_{15}NO$ $[M+H]^+$: 262.1232, found: 262.1230.

2-((4-(Tert-butyl)phenoxy)(phenyl)methyl)pyridine **7ab**



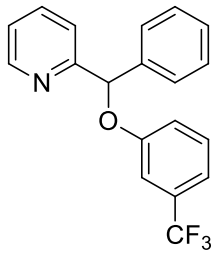
7ab was prepared according to the general procedure **B** in 50% yield (32.0 mg, 0.1 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.35. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.58 (d, *J* = 4.7 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.59 – 7.56 (m, 1H), 7.55 – 7.53 (m, 2H), 7.35 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 7.26 – 7.23 (m, 2H), 7.18 – 7.15 (m, 1H), 6.93 – 6.91 (m, 2H), 6.33 (s, 1H), 1.27 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 161.1, 155.6, 149.2, 143.8, 140.5, 137.1, 128.6, 127.9, 126.9, 126.3, 122.6, 120.9, 115.4, 82.6, 34.1, 31.6. HRMS (EI+) calcd. for $C_{22}H_{23}NO$ $[M+H]^+$: 318.1858, found: 318.1852.

4-(Tert-butyl)-2-(phenyl(pyridin-2-yl)methyl)phenol **7ab'**



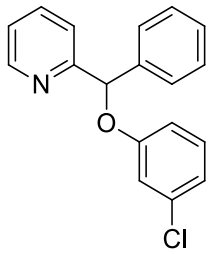
7ab' was prepared according to the general procedure **B** in 21% yield (13.5 mg, 0.042 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.28. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.54 (d, *J* = 4.9 Hz, 1H), 7.82 – 7.79 (m, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.29 – 7.21 (m, 6H), 7.20 – 7.17 (m, 1H), 7.00 – 6.96 (m, 2H), 6.95–6.92 (m, 1H), 5.32 (s, 1H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 162.8, 154.1, 148.2, 142.4, 141.5, 138.5, 128.9, 128.3, 127.8, 126.8, 126.5, 126.3, 124.8, 122.5, 119.1, 59.8, 34.1, 31.7. HRMS (EI+) calcd. for $C_{22}H_{23}NO$ $[M+H]^+$: 318.1858 found: 318.1857.

2-(Phenyl(3-(trifluoromethyl)phenoxy)methyl)pyridine **7ac**



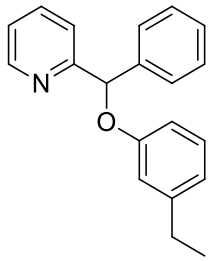
7ac was prepared according to the general procedure **B** in 52% yield (36.0 mg, 0.1 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.32. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.59 (d, *J* = 4.9 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.37 – 7.33 (m, 2H), 7.31 – 7.27 (m, 3H), 7.24 – 7.22 (m, 1H), 7.18 – 7.16 (m, 1H), 7.13 – 7.10 (m, 1H), 6.39 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 160.1, 157.8, 149.2, 139.4, 137.6, 130.2, 130.1, 128.9, 128.3, 126.8, 123.1, 121.1, 118.8, 118.0, 117.0, 113.6, 113.6, 82.8. HRMS (EI+) calcd. for $C_{19}H_{14}NOF_3$ $[M+H]^+$: 330.1106 , found: 330.1102.

2-((3-Chlorophenoxy)(phenyl)methyl)pyridine **7ad**



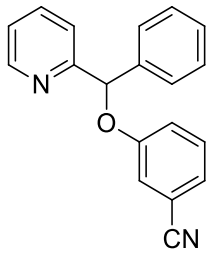
7ad was prepared according to the general procedure **B** in 59% yield (35.0 mg, 0.118 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.3. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.58 (d, *J* = 4.2 Hz, 1H), 7.69 – 7.67 (m, 1H), 7.54 – 7.50 (m, 3H), 7.36 – 7.33 (m, 2H), 7.29 – 7.28 (m, 1H), 7.20 – 7.18 (m, 1H), 7.14 – 7.11 (m, 1H), 7.02 – 7.01 (m, 1H), 6.91– 6.89 (m, 1H), 6.86 – 6.84 (m, 1H), 6.32 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 160.3, 158.5, 149.3, 139.7, 137.3, 134.9, 130.3, 128.8, 128.2, 126.8, 122.9, 121.5, 120.9, 116.8, 114.1, 82.9. HRMS (EI+) calcd. for $C_{18}H_{15}NOCl$ $[M+H]^+$: 296.0842, found: 296.0840.

2-((3-Ethylphenoxy)(phenyl)methyl)pyridine **7ae**



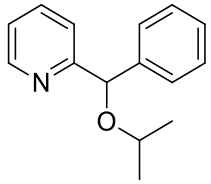
7ae was prepared according to the general procedure **B** in 54% yield (31.2 mg, 0.108 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.32. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.57 (d, *J* = 4.8 Hz, 1H), 7.66 – 7.65 (m, 1H), 7.58 – 7.56 (m, 1H), 7.54 – 7.52 (m, 2H), 7.35 – 7.32 (m, 2H), 7.27 – 7.26 (m, 1H), 7.17 – 7.15 (m, 1H), 7.13 – 7.10 (m, 1H), 6.87 – 6.85 (m, 1H), 6.77 – 6.75 (m, 2H), 6.34 (s, 1H), 2.57 (q, *J* = 7.6 Hz, 2H), 1.16 (t, J = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 160.1, 157.9, 149.2, 146.0, 139.3, 137.2, 129.3, 128.7, 127.9, 126.9, 122.6, 120.9, 115.9, 112.9, 110.3, 82.5, 28.9, 15.4. HRMS (EI+) calcd. for $C_{20}H_{20}NO$ $[M+H]^+$: 290.1545, found: 290.1548.

3-(Phenyl(pyridin-2-yl)methoxy)benzonitrile **7af**



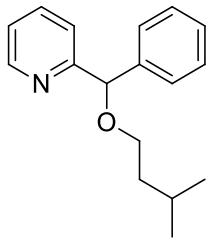
7af was prepared according to the general procedure **B** in 51% yield (29.0 mg, 0.101 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 7/3): 0.32. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.59 (d, *J* = 4.6 Hz, 1H), 7.69 – 7.59(m, 1H), 7.51 – 7.49 (m, 3H), 7.38 – 7.35 (m, 2H), 7.33 – 7.28 (m, 2H), 7.24 – 7.19 (m, 4H), 6.33 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 159.8, 157.9, 149.5, 139.2, 137.3, 130.5, 128.9, 128.4, 126.7, 125.1, 123.1, 120.9, 120.9, 119.4, 118.7, 113.4, 83.2. HRMS (EI+) calcd. for $C_{19}H_{15}N_2O$ $[M+H]^+$: 287.1184, found: 287.1184.

2-(Isopropoxy(phenyl)methyl)pyridine **7ag**



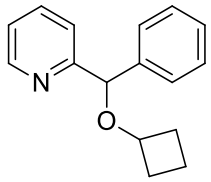
7ag was prepared according to the general Method A in 70% yield (32.0 mg, 0.141 mmol) from 0.2 mmol of **1a**. colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.4. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 – 8.47 (m, 1H), 7.67 –7.65 (m, 1H), 7.56 – 7.50 (m, 1H), 7.47 – 7.40 (m, 2H), 7.31 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 7.13 – 7.10 (m, 1H), 5.62 (s, 1H), 3.71 (dt, *J* = 12.2, 6.1 Hz, 1H), 1.25 (d, *J* = 6.1 Hz, 3H), 1.22 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 162.8, 148.9, 142.0, 136.8, 128.4, 127.5, 127.0, 122.3, 120.8, 81.9, 69.7, 22.4, 22.3. HRMS (EI+) calcd. for $C_{15}H_{17}NO$ $[M+H]^+$: 228.1388, found: 228.1385.

2-((Isopentyloxy)(phenyl)methyl)pyridine **7ah**



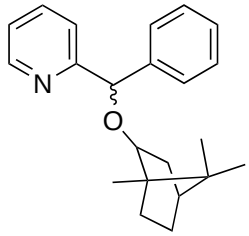
7ah was prepared according to the general procedure **B** in 60% yield (31.0 mg, 0.121 mmol) from 0.2 mmol of **1a**. colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.4. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 4.1, Hz, 1H), 7.68 – 7.66 (m, 1H), 7.53 – 7.49 (m, 1H), 7.50 – 7.38 (m, 2H), 7.36 – 7.29 (m, 2H), 7.24 – 7.20 (m, 1H), 7.14 – 7.11 (m, 1H), 5.46 (s, 1H), 3.62 – 3.45 (m, 2H), 1.83 – 1.74 (m, 1H), 1.56 (dt, *J* = 7.0, 4.0 Hz, 2H), 0.89 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 162.3, 149.0, 141.6, 136.9, 128.5, 127.6, 127.0, 122.3, 120.7, 85.0, 67.9, 38.8, 25.2, 22.8, 22.7. HRMS (EI+) calcd. for $C_{17}H_{21}NO$ $[M+H]^+$: 256.1701, found: 256.1699.

2-(Cyclobutoxy(phenyl)methyl)pyridine **7ai**



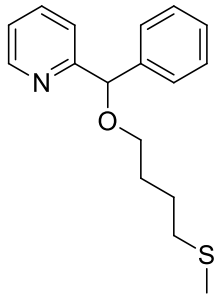
7ai was prepared according to the general procedure **B** in 67% yield (32.0 mg, 0.134 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.4. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.54 – 8.49 (m, 1H), 7.68 – 7.66 (m, 1H), 7.54 – 7.50 (m, 1H), 7.42 (m, 2H), 7.33 – 7.29 (m, 2H), 7.26 – 7.21 (m, 1H), 7.16 – 7.10 (m, 1H), 5.47 (s, 1H), 4.09 – 3.96 (m, 1H), 2.20 –2.11 (m, 2H), 2.02 (ddd, *J* = 9.4, 8.5, 4.6 Hz, 2H), 1.67 (dt, *J* = 19.3, 9.8 Hz, 1H), 1.49 – 1.37 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 162.2, 149.0, 141.5, 136.8, 128.4, 127.6, 127.1, 122.3, 121.0, 82.2, 71.9, 30.8, 30.7, 12.6. HRMS (EI+) calcd. for $C_{16}H_{17}NO$ $[M+H]^+$: 240.1388, found: 240.1385.

2-(Phenyl(((4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)pyridine **7aj**



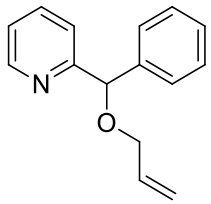
7aj was prepared according to the general procedure **B** in 65% yield (dr 1:1) (42.0 mg, 0.131 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.37. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.51 (d, *J* = 4.9 Hz, 1H), 8.47 (d, *J* = 4.8Hz, 1H), 7.67 – 7.64 (m, 2H), 7.63 – 7.61 (m, 2H), 7.54 – 7.52 (m, 2H), 7.43 – 7.41 (m, 4H), 7.32 – 7.26 (m, 4H), 7.24 – 7.19 (m, 2H), 7.16 – 7.09 (m, 2H), 5.52 (s, 1H), 5.49 (s, 1H), 3.76 – 3.69 (m, 2H). ^{1}H NMR contains small impurity of corresponding alcohol. ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm δ 163.4, 162.9, 148.7, 142.7, 141.9, 136.9, 128.3, 128.3, 127.5, 127.2, 126.7, 122.4, 122.1, 121.0, 121.8, 83.1, 82.9, 82.8, 82.5, 49.5, 48.1, 47.8, 45.2, 39.1, 36.2, 36.1, 29.8, 28.4, 27.1, 27.1, 26.0, 20.3, 19.9, 19.0, 18.8, 14.0, 13.4. HRMS (EI+) calcd. for $C_{22}H_{27}NO$ $[M+H]^+$: 322.2171, found: 322.2165.

2-((4-(Methylthio)butoxy)(phenyl)methyl)pyridine **7ak**



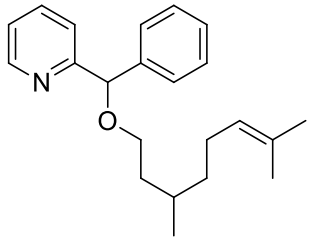
7ak was prepared according to the general procedure **B** in 47% yield (27.0 mg, 0.0939 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.39. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.51 (d, *J* = 4.8 Hz, 1H), 7.67 – 7.65 (m, 1H), 7.52 – 7.40 (m, 1H), 7.43 – 7.41 (m, 2H), 7.32 – 7.28 (m, 2H), 7.26 – 7.21 (m, 1H), 7.16 – 7.11 (m, 1H), 5.46 (s, 1H), 3.56 – 3.49 (m, 2H), 2.51 (t, *J* = 7.0 Hz, 2H), 2.08 (s, 3H), 1.75 (ddd, *J* = 9.9, 6.3, 2.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm δ 162.1, 149.0, 141.4, 136.9, 128.5, 127.7, 126.9, 122.4, 120.6, 84.9, 68.9, 34.1, 29.0, 26.0, 15.6. HRMS (EI+) calcd. for $C_{17}H_{21}NOS$ $[M+H]^+$: 288.1422, found: 288.1418.

2-((Allyloxy)(phenyl)methyl)pyridine **7al**



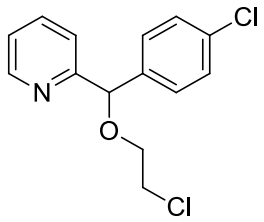
7al was prepared according to the general procedure **B** in 58% yield (26.0 mg, 0.115 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.4. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.53 (d, *J* = 4.9 Hz, 1H), 7.67 – 7.64 (m, 1H), 7.56 – 7.50 (m, 1H), 7.46 – 7.44 (m, 2H), 7.34 – 7.30 (m, 2H), 7.26 – 7.23 (m, 1H), 7.16 – 7.13 (m, 1H), 6.03 – 5.93 (m, 1H), 5.56 (s, 1H), 5.35 – 5.29 (m, 1H), 5.22 – 5.19 (m, 1H), 4.12 – 4.02 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 161.9, 149.1, 141.1, 136.9, 134.6, 128.5, 127.8, 127.1, 122.4, 120.7, 117.2, 84.0, 70.0. HRMS (EI+) calcd. for $C_{15}H_{15}NO$ $[M+H]^+$: 226.1232, found: 226.1229.

2-(((3,7-Dimethyloct-6-en-1-yl)oxy)(phenyl)methyl)pyridine **7am**



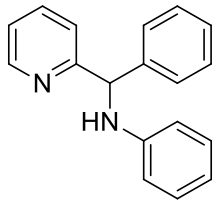
7am was prepared according to the general procedure **B** in 56% yield (36.0 mg, 0.111 mmol) from 0.2 mmol of **1a**. colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.38. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.52 (d, *J* = 4.5 Hz, 1H), 7.67 – 7.65 (m, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.31 – 7.27 (m, 2H), 7.23 – 7.20 (m, 1H), 7.13 (dd, *J* = 6.7, 5.5 Hz, 1H), 5.46 (s, 1H), 5.09 (d, *J* = 6.9 Hz, 1H), 3.59 – 3.47 (m, 2H), 2.02-1.93 (m, 2H), 1.74 – 1.71 (m, 1H), 1.68 (s, 3H), 1.59 (s, 3H), 1.51-1.43 (m, 1H), 1.38 – 1.31 (m, 2H), 1.18 – 1.14 (m, 1H), 0.87 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 162.3, 149.0, 141.6, 136.9, 131.2, 128.5, 127.6, 127.0, 124.9, 122.3, 120.6, 85.0, 67.8, 36.9, 29.7, 25.8, 25.6, 19.7, 17.7. HRMS (EI+) calcd. for $C_{22}H_{29}NO$ $[M+H]^+$: 324.2327, found: 324.2325.

2-((2-Chloroethoxy)(4-chlorophenyl)methyl)pyridine **7fn**



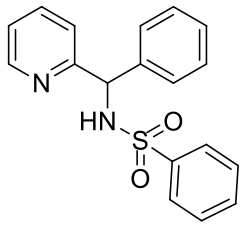
7fn was prepared according to the general procedure **B** in 80% yield (45.0 mg, 0.161 mmol) from 0.2 mmol of **1f**. Colorless liquid. R_f (hexanes/EtOAc = 3/1): 0.3. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.53 (d, *J* = 4.7 Hz, 1H), 7.70 – 7.67 (m, 1H), 7.55 – 7.53 (m, 1H), 7.39 – 7.37 (m, 2H), 7.30 – 7.29 (m, 2H), 7.19 – 7.14 (m, 1H), 5.52 (s, 1H), 3.78 (dd, *J* = 10.2, 5.1 Hz, 2H), 3.70 (t, *J* = 5.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 160.9, 149.2, 139.2, 137.1, 133.7, 128.8, 128.4, 122.8, 120.7, 84.4, 69.4, 43.0. LRMS (EI+) calcd. for $C_{14}H_{13}NOCl_2$ [M]: 282.0448.

N-(Phenyl(pyridin-2-yl)methyl)aniline **8aa**



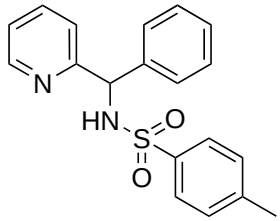
8aa was prepared according to the general procedure **B** in 10% yield (5.3 mg, 0.020 mmol) from 0.2 mmol of **1a**. colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.3. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.62 – 8.57 (m, 1H), 7.63 – 7.60 (m, 1H), 7.48 – 7.43 (m, 2H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.25 – 7.22 (m, 1H), 7.17 – 7.15 (m, 1H), 7.14 – 7.10 (m, 2H), 6.67 – 6.66 (m, 1H), 6.65 – 6.61 (m, 2H), 5.58 (d, *J* = 4.4 Hz, 1H), 5.46 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 161.0, 149.3, 147.1, 142.6, 136.9, 129.2, 128.9, 127.6, 127.5, 122.3, 122.0, 117.6, 113.7, 63.4. HRMS (EI+) calcd. for $C_{18}H_{16}N_2$ $[M+H]^+$: 261.1392, found: 261.1388.

N-(Phenyl(pyridin-2-yl)methyl)benzenesulfonamide **8ab**



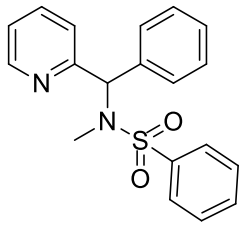
8ab was prepared according to the general procedure **B** in 50% yield (32.6 mg, 0.1 mmol) from 0.2 mmol of **1a**. White solid. R_f (hexanes/EtOAc = 2/1): 0.35. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.46 (d, *J* = 4.7 Hz, 1H), 7.64 – 7.63 (m, 2H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.27-7.24 (m, 2H), 7.18 – 7.14 (m, 5H), 7.13 – 7.10 (m, 1H), 7.01 – 6.98 (m, 2H), 5.57 (d, *J* = 6.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 157.6, 148.6, 140.1, 136.9, 132.1, 129.2, 128.6, 127.8, 127.7, 127.1, 126.5, 122.6, 122.5, 61.0. HRMS (EI+) calcd. for $C_{18}H_{16}N_2O_2S$ $[M+H]^+$: 325.1011, found: 325.1003.

4-Methyl-N-(phenyl(pyridin-2-yl)methyl)benzenesulfonamide **8ac**



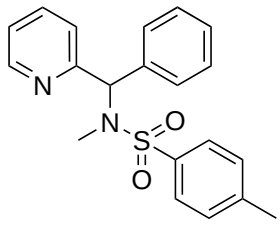
8ac was prepared according to the general procedure **B** in 40% yield (27.2 mg, 0.08 mmol) from 0.2 mmol of **1a**. White solid R_f (hexanes/EtOAc = 2/1): 0.35. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.47 (d, *J* = 4.6 Hz, 1H), 7.54 – 7.52 (m, 3H), 7.20 – 7.15 (m, 5H), 7.13 – 7.11 (m, 1H), 7.06 – 7.04 (m, 2H), 7.01 – 7.00 (m, 1H), 6.91 (d, *J* = 5.9 Hz, 1H), 5.53 (d, *J* = 6.1 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 157.8, 148.6, 142.9, 140.5, 136.8, 129.8, 129.2, 128.6, 127.8, 127.2, 126.6, 122.5, 122.5, 61.0, 21.5. HRMS (EI+) calcd. for $C_{19}H_{18}N_2O_2S$ $[M+H]^+$: 339.1167, found: 339.1162.

N-Methyl-N-(phenyl(pyridin-2-yl)methyl)benzenesulfonamide **8ad**



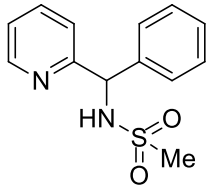
8ad was prepared according to the general procedure **B** in 74% yield (50 mg, 0.148 mmol) from 0.2 mmol of **1a**. Colorless liquid R_f (hexanes/EtOAc = 3/1): 0.28. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.47 – 8.39 (m, 1H), 7.72 – 7.70 (m, 2H), 7.62 – 7.58 (m, 1H), 7.49 – 7.47 (m, 1H), 7.40 – 7.36 (m, 2H), 7.25 – 7.24 (m, 4H), 7.16 – 7.13 (m, 1H), 7.05 – 6.98 (m, 2H), 6.45 (s, 1H), 2.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 158.4, 149.4, 139.7, 137.8, 136.5, 132.3, 129.2, 128.8, 128.5, 127.9, 127.3, 123.4, 122.5, 65.0, 32.0. HRMS (EI+) calcd. for $C_{15}H_{33}NO_2Si$ $[M+H]^+$: 339.1167, found: 339.1165.

N,4-dimethyl-*N*-(phenyl(pyridin-2-yl)methyl)benzenesulfonamide **8ae**



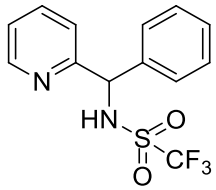
8ae was prepared according to the general procedure **B** in 64% yield (45 mg, 0.128 mmol) from 0.2 mmol of **1a**. White solid R_f (hexanes/EtOAc = 3/1): 0.3. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.45 (d, *J* = 4.1 Hz, 1H), 7.65 – 7.59 (m, 3H), 7.28 – 7.23 (m, 4H), 7.18 – 7.14 (m, 3H), 7.02 – 7.00 (m, 2H), 6.45 (s, 1H), 2.82 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 158.6, 149.4, 143.0, 137.9, 136.8, 136.5, 129.4, 129.2, 128.5, 127.8, 127.4, 123.4, 122.4, 65.0, 31.9, 21.6. HRMS (EI+) calcd. for $C_{20}H_{20}N_2O_2S$ $[M+H]^+$: 353.1324, found: 353.1322.

N-(phenyl(pyridin-2-yl)methyl)methanesulfonamide **8af**



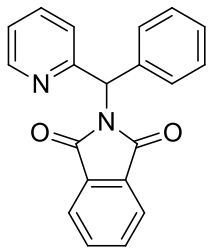
8af was prepared according to the general procedure **B** in 61% yield (32 mg, 0.122 mmol) from 0.2 mmol of **1a**. White solid R_f (hexanes/EtOAc = 1/1): 0.3. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.56 (d, *J* = 4.4 Hz, 1H), 7.64 – 7.62 (m, 1H), 7.39 – 7.29 (m, 5H), 7.23 – 7.19 (m, 1H), 7.14 – 7.12 (m, 1H), 6.92 (d, *J* = 5.1 Hz, 1H), 5.73 (d, *J* = 5.4 Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 157.6, 148.6, 140.7, 137.2, 129.1, 128.3, 128.0, 122.9, 122.6, 60.9, 42.0. HRMS (EI+) calcd. for $C_{13}H_{14}N_2O_2S$ $[M+H]^+$: 263.0854, found: 263.0850.

1,1,1-Trifluoro-*N*-(phenyl(pyridin-2-yl)methyl)methanesulfonamide **8ag**



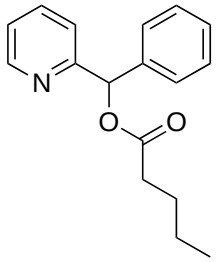
8ag was prepared according to the general procedure **B** in 90% yield (57 mg, 0.18 mmol) from 0.2 mmol of **1a**. White solid R_f (hexanes/EtOAc = 1/1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.58 (d, *J* = 4.3 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.39 – 7.28 (m, 6H), 7.28 – 7.25 (m, 1H), 7.18 – 7.16 (m, 1H), 5.80 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 156.4, 148.6, 140.1, 137.6, 129.0, 128.6, 127.4, 123.3, 122.4, 61.4. HRMS (EI+) calcd. for $C_{13}H_{11}N_2O_2SF_3$ $[M+H]^+$: 317.0572, found: 317.0571.

2-(Phenyl(pyridin-2-yl)methyl)isoindoline-1,3-dione **8ah**



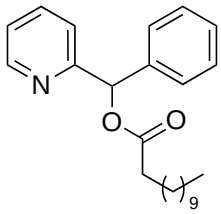
8ah was prepared according to the general procedure **B** in 50% yield (35 mg, 0.1 mmol) from 0.2 mmol of **1a**. White solid R_f (hexanes/EtOAc = 1/1): 0.3. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.55 (d, *J* = 4.4 Hz, 1H), 7.84 – 7.83 (m, 2H), 7.71 – 7.70 (m, 2H), 7.64 – 7.63 (m, 1H), 7.53 – 7.51 (m, 2H), 7.40 – 7.33 (m, 3H), 7.21 – 7.17 (m, 2H), 6.73 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 168.2, 157.5, 149.3, 137.6, 136.4, 134.1, 132.2, 129.7, 128.8, 128.3, 123.5, 123.0, 122.4, 59.5. HRMS (EI+) calcd. for $C_{20}H_{14}N_2O_2$ $[M+H]^+$: 315.1134, found: 315.1128.

Phenyl(pyridin-2-yl)methyl pentanoate **9aa**



9aa was prepared according to the general procedure **B** in 65% yield (35 mg, 0.13 mmol) from 0.2 mmol of **1a**. Colorless liquid R_f (hexanes/EtOAc = 4/1): 0.3. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.58 (d, *J* = 4.1 Hz, 1H), 7.69 – 7.67 (m, 1H), 7.44 – 7.40 (m, 3H), 7.35 – 7.32 (m, 2H), 7.29 – 7.26 (m, 1H), 7.19 – 7.16 (m, 1H), 6.89 (s, 1H), 2.47 (t, *J* = 7.6 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.39 – 1.31 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 172.8, 159.5, 149.6, 139.3, 136.8, 128.6, 128.2, 127.4, 122.7, 120.9, 77.8, 34.3, 27.0, 22.3, 13.8. HRMS (EI+) calcd. for $C_{17}H_{19}NO_2$ $[M+H]^+$: 270.1494, found: 270.1490.

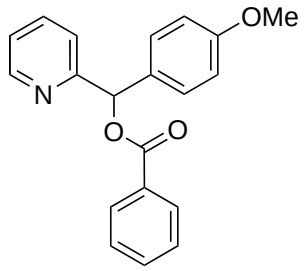
Phenyl(pyridin-2-yl)methyl dodecanoate **9ab**



9ab was prepared according to the general procedure **B** in 63% yield (46 mg, 0.125 mmol) from 0.2 mmol of **1a**. Colorless liquid R_f (hexanes/EtOAc = 4/1): 0.3. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.57 (d, *J* = 4.2 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.43 – 7.42 (m, 3H), 7.35 – 7.32 (m, 2H), 7.29 – 7.27 (m, 1H), 7.20 – 7.17 (m, 1H), 6.89 (s, 1H), 2.46 (t, *J* = 7.5 Hz, 2H), 1.69-1.65 (m, 2H), 1.28-

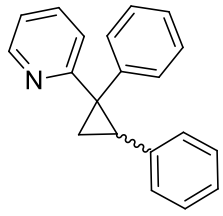
1.25 (m, 16H), 0.87 (d, J = 7.1 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 172.8, 159.5, 149.6, 139.3, 136.8, 128.6, 128.2, 127.4, 122.7, 120.9, 77.8, 34.6, 32.0, 30.0, 29.7, 29.5, 29.4, 29.3, 29.2, 25.0, 22.8, 14.2. HRMS (EI+) calcd. for $C_{24}H_{33}NO_2$ $[M+H]^+$: 368.2590, found: 368.2585.

(4-Methoxyphenyl)(pyridin-2-yl)methyl benzoate **9cc**



9cc was prepared according to the general procedure **B** in 60% yield (38.5 mg, 0.121 mmol) from 0.2 mmol of **1c**. Colorless solid R_f (hexanes/EtOAc = 2/3): 0.3. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.64 (d, J = 4.7 Hz, 1H), 8.17 – 8.16 (m, 2H), 7.71 – 7.72 (m, 1H), 7.59 – 7.54 (m, 2H), 7.50 – 7.43 (m, 4H), 7.22 – 7.20 (m, 1H), 7.11 (s, 1H), 6.90 – 6.88 (m, 2H), 3.78 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 165.6, 159.6, 159.5, 149.5, 137.1, 133.3, 130.1, 129.9, 129.0, 128.5, 128.4, 122.8, 120.7, 114.1, 78.1, 55.3. HRMS (EI+) calcd. for $C_{20}H_{17}NO_3$ $[M+H]^+$: 320.1287, found: 320.1278.

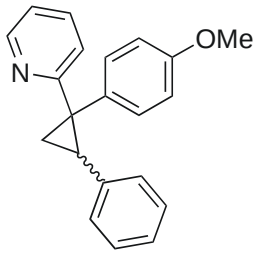
2-(1,2-Diphenylcyclopropyl)pyridine **11aa**



11aa was prepared according to the general procedure **C** in 77% yield, dr 1.33:1, (42 mg, 0.155 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, J = 4.1 Hz, 1H), 8.43 (d, J = 4.0 Hz, 1H), 7.49 – 7.47 (m, 1H), 7.43 – 7.24 (m, 4H), 7.24 – 7.15 (m, 3H), 7.15 – 7.01 (m, 7H), 6.98 – 6.96 (m, 2H), 6.94 – 6.92 (m, 1H), 6.85 – 6.83 (m, 2H), 6.77 (d, J = 7.9 Hz, 1H), 3.34 (t, J = 7.9 Hz, 1H), 3.02 (t, J = 7.8 Hz, 1H), 2.55 (t, J = 6.0 Hz, 1H), 2.25 (dd, J = 9.0, 4.5 Hz, 1H), 2.00 (dd, J = 6.7, 4.6 Hz, 1H), 1.75 (dd, J = 8.9, 5.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.9, 159.4, 149.0, 148.5, 145.3, 138.8, 138.4,

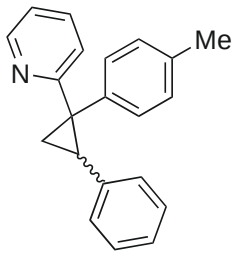
138.1, 135.6, 135.5, 132.5, 128.7, 128.5, 128.3, 128.1, 127.9, 127.6, 127.5, 126.8, 126.6, 126.5, 126.0, 125.9, 125.6, 125.5, 121.8, 120.9, 120.2, 77.3, 77.0, 76.8, 41.0, 40.2, 34.2, 32.1, 22.9, 18.9. HRMS (EI+) calcd. for $C_{20}H_{17}N$ $[M+H]^+$: 272.1439, found: 272.1427.

2-(1-(4-Methoxyphenyl)-2-phenylcyclopropyl)pyridine **11ba**



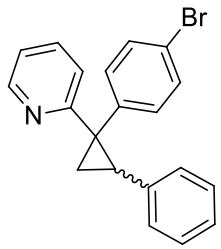
11ba was prepared according to the general procedure **C** in 72% yield, dr 1.25:1, (44 mg, 0.146 mmol) from 0.2 mmol of **1b**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.2. Minor diastereomer ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.57 (d, *J* = 4.2 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.13 – 6.97 (m, 6H), 6.84 – 6.82 (m, 2H), 6.75 – 6.70 (m, 3H), 3.76 (s, 3H), 3.27 (d, *J* = 7.0 Hz, 1H), 2.21 (dd, *J* = 8.9, 4.4 Hz, 1H), 1.92 (dd, *J* = 6.7, 4.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 164.7, 158.7, 149.4, 139.4, 136.0, 133.9, 130.7, 128.4, 127.9, 125.8, 122.2, 120.5, 113.9, 55.5, 34.7, 23.6. Major diastereomer ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.38 (d, *J* = 3.8 Hz, 1H), 7.42 – 7.40 (m, 2H), 7.31 – 7.24 (m, 1H), 7.07 – 7.00 (m, 2H), 7.02 (d, *J* = 6.0 Hz, 1H), 6.98 – 6.96 (m, 2H), 6.93 – 6.82 (m, 4H), 3.80 (s, 3H), 2.94 (s, 1H), 2.49 (t, *J* = 5.9 Hz, 1H), 1.68 (dd, *J* = 8.9, 5.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 160.2, 148.8, 138.7, 138.0, 135.9, 130.4, 128.5, 128.0, 126.0, 125.9, 121.2, 114.2, 55.7, 32.3, 19.1. HRMS (EI+) calcd. for $C_{21}H_{19}NO$ $[M+H]^+$: 302.1545, found: 302.1547.

2-(2-Phenyl-1-(p-tolyl)cyclopropyl)pyridine **11ea**



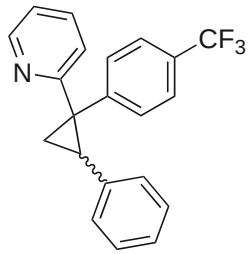
11ea was prepared according to the general procedure **C** in 86% yield, dr 1.2:1, (49mg, 0.172 mmol) from 0.2 mmol of **1e**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.2. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.57 (d, *J* = 2.3 Hz, 1H), 8.40 (d, *J* = 3.1 Hz, 1H), 7.43 – 7.33 (m, 3H), 7.32 – 7.21 (m, 2H), 7.17 – 7.13 (m, 2H), 7.12 – 7.05 (m, 5H), 7.05 – 6.95 (m, 10H), 6.93 – 6.90 (m, 2H), 6.87 – 6.81 (m, 3H), 6.77 (d, *J* = 8.0 Hz, 1H), 3.29 (t, *J* = 7.9 Hz, 1H), 2.98 (t, *J* = 7.8 Hz, 1H), 2.51 (t, *J* = 6.0 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H), 2.25 – 2.19 (m, 1H), 1.95 (dd, *J* = 6.7, 4.5 Hz, 1H), 1.70 (dd, *J* = 8.9, 5.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 164.2, 159.6, 148.9, 148.4, 142.4, 139.0, 138.3, 136.3, 136.1, 135.6, 135.5, 135.1, 132.3, 129.2, 128.9, 128.7, 128.1, 128.0, 127.6, 127.5, 125.8, 125.6, 125.4, 121.8, 120.8, 120.2, 40.7, 39.8, 34.2, 31.9, 23.0, 21.2, 21.0, 18.8. HRMS (EI+) calcd. for $C_{21}H_{19}N$ $[M+H]^+$: 286.1596, found: 286.1595.

2-(1-(4-bromophenyl)-2-phenylcyclopropyl)pyridine **11ga**



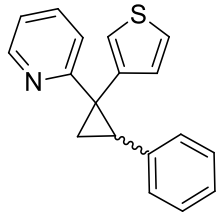
11ga was prepared according to the general procedure **C** in 71% yield, dr 1.2:1, (50mg, 0.143 mmol) from 0.2 mmol of **1g**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.2. Major diastereomer ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.60 – 8.53 (m, 1H), 7.44 – 7.37 (m, 1H), 7.35 – 7.29 (m, 2H), 7.08 – 7.03 (m, 4H), 7.01 – 6.94 (m, 2H), 6.84 – 6.80 (m, 2H), 6.75 – 6.96 (m, 1H), 3.33 (dd, *J* = 9.0, 6.9 Hz, 1H), 2.23 (dd, *J* = 9.0, 4.6 Hz, 1H), 1.95 (dd, *J* = 6.9, 4.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 163.2, 149.1, 138.3, 137.6, 135.7, 134.1, 131.3, 127.9, 127.7, 125.7, 121.6, 120.9, 120.4, 77.3, 77. 1, 76.7, 39.6, 34.1, 22.6. Minor diastereomer ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.44 – 8.32 (m, 1H), 7.47 – 7.40 (m, 2H), 7.35 – 7.27 (m, 3H), 7.07 – 7.00 (m, 3H), 6.98 – 6.90 (m, 3H), 6.88 – 6.83 (m, 1H), 2.95 (t, *J* = 7.9 Hz, 1H), 2.51 (t, *J* = 6.1 Hz, 1H), 1.70 (dd, *J* = 9.0, 5.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 158.8, 148.7, 144.3, 137.7, 135.6, 132.5, 131.5, 130.4, 128.1, 127.7, 125.8, 125.6, 121.1, 120.3, 77.3, 77.0, 76.6, 40.5, 32.1, 18.9. HRMS (EI+) calcd. for $C_{20}H_{16}BrN$ $[M+H]^+$: 350.0544, found: 350.0528.

2-(2-Phenyl-1-(4-(trifluoromethyl)phenyl)cyclopropyl)pyridine **11ha**



11ha was prepared according to the general procedure **C** in 80% yield, dr 1.1:1, (55 mg, 0.162 mmol) from 0.2 mmol of **1c**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.2. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.63 – 8.56 (m, 1H), 8.44 (d, *J* = 4.0 Hz, 1H), 7.56 – 7.50 (m, 4H), 7.44 – 7.40 (m, 4H), 7.35 – 7.33 (m, 1H), 7.25 – 7.20 (m, 3H), 7.09 – 7.00 (m, 8H), 6.98 – 6.94 (m, 3H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.84 – 6.82 (m, 2H), 6.71 – 6.64 (m, 1H), 3.38 (t, *J* = 7.9 Hz, 1H), 3.02 (t, *J* = 7.8 Hz, 1H), 2.56 (t, *J* = 6.0 Hz, 1H), 2.34 – 2.23 (m, 1H), 2.01 (t, J = 5.6 Hz, 1H), 1.81 – 1.73 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 162.8, 158.5, 149.2, 148.8, 142.8, 138.0, 137.5, 135.8, 135.7, 132.7, 128.7, 128.1, 127.8, 127.7, 125.9, 125.8, 125.8, 125.4, 125.1, 121.6, 121.3, 120.6, 40.6, 39.9, 34.1, 32.4, 22.4, 19.3. HRMS (EI+) calcd. for $C_{21}H_{16}NF_3$ $[M+H]^+$: 340.1313, found: 340.1306.

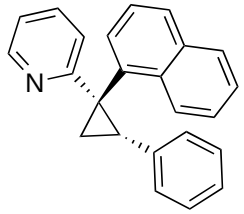
2-(2-Phenyl-1-(thiophen-3-yl)cyclopropyl)pyridine **11ia**



11ia was prepared according to the general procedure **C** in 38% yield, dr 2.5:1, (21.0 mg, 0.075 mmol) from 0.2 mmol of **1i**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.2. Major diastereomer ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.47 – 8.41 (m, 1H), 7.38 – 7.36 (m, 1H), 7.28 – 7.25 (m, 1H), 7.08 – 6.95 (m, 6H), 6.90 – 6.88 (m, 2H), 2.97 – 2.90 (m, 1H), 2.49 – 2.44 (m, 1H), 1.76 (dd, *J* = 8.8, 5.5 Hz, 1H). ^{13}C NMR δ ppm (126 MHz, $CDCl_3$) δ 158.9, 148.7, 146.7, 137.9, 135.6, 127.9, 127.6, 127.0, 126.1, 125.7, 121.3, 120.6, 77.2, 77.0, 76.7, 37.2, 33.2, 19.7. Minor diastereomer ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.60 – 8.53 (m, 1H), 7.46 – 7.44 (m, 1H), 7.09 – 7.00 (m, 5H),

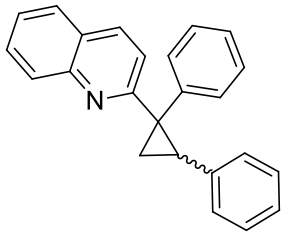
6.96 (s, 1H), 6.89 – 6.80 (m, 3H), 6.71 – 6.64 (m, 1H), 3.27 (t, *J* = 7.9 Hz, 1H), 2.21 – 2.19 (m, 1H), 1.98 –1.96 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.3, 149.0, 139.5, 138.6, 135.7, 130.5, 127.8, 127.5, 125.6, 125.0, 121.6, 120.4, 77.2, 77.0, 76.7, 35.2, 34.1, 23.0. HRMS (EI+) calcd. for $C_{18}H_{15}NS$ $[M+H]^+$: 278.1003, found: 278.0993.

2-(1-(Naphthalen-1-yl)-2-phenylcyclopropyl)pyridine **11na**



11na was prepared according to the general procedure **C** in 75% yield, dr >20:1, (48.0 mg, 0.149 mmol) from 0.2 mmol of **1n**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.3. Major diastereomer ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.48 (d, *J* = 7.5 Hz, 1H), 8.43 – 8.36 (m, 1H), 7.98 (d, *J* = 6.7 Hz, 1H), 7.86 – 7.79 (m, 2H), 7.59 – 7.57 (m, 1H), 7.51 – 7.45 (m, 2H), 7.23 – 7.21 (m, 2H), 7.19 – 7.10 (m, 3H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.86 – 6.71 (m, 2H), 3.24 (t, *J* = 7.7 Hz, 1H), 3.11 (d, *J* = 4.9 Hz, 1H), 1.69 (dd, *J* = 6.8, 5.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.3, 149.1, 148.1, 141.5, 137.9, 135.7, 135.4, 134.1, 132.8, 128.8, 128.5, 127.9, 127.9, 127.6, 126.1, 125.8, 125.7, 125.5, 125.1, 120.6, 120.3, 77.3, 77.0, 76.8, 39.3, 32.7, 18.1. HRMS (EI+) calcd. for $C_{24}H_{19}N$ $[M+H]^+$: 322.1596, found: 322.1582.

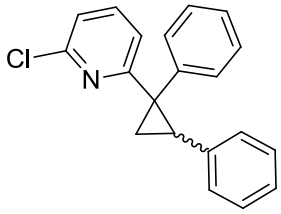
2-(1,2-Diphenylcyclopropyl)quinoline **11ma**



11ma was prepared according to the general procedure **C** in 31% yield, dr 1.7:1, (20.0 mg, 0.062 mmol) from 0.2 mmol of **1m**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.2. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.10 – 8.07 (m, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.68 – 7.60 (m, 3H), 7.46 – 7.40 (m, 3H), 7.35 – 7.31(m, 1H), 7.22 – 7.18 (m, 5H), 7.13 – 6.92 (m, 7H), 6.89 – 6.87 (m, 2H),

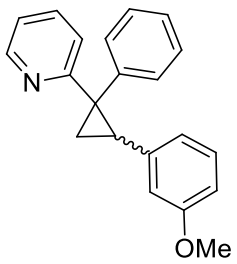
3.58 (t, J = 7.8 Hz, 1H), 3.13 (t, J = 7.8 Hz, 1H), 2.87 (t, J = 5.6 Hz, 1H), 2.43 (dd, J = 8.5, 3.8 Hz, 1H), 2.12 – 2.04 (m, 1H), 1.80 (dd, J = 8.1, 5.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.8, 159.5, 147.8, 138.9, 138.5, 137.8, 135.4, 135.4, 132.5, 129.3, 129.2, 129.1, 128.9, 128.6, 128.5, 128.2, 128.1, 127.6, 127.5, 127.4, 127.3, 126.8, 126.6, 126.4, 125.9, 125.7, 125.5, 125.5, 123.9, 120.5, 77.3, 77.0, 76.7, 41.9, 41.0, 34.7, 32.3, 23.3, 19.4. HRMS (EI+) calcd. for $C_{24}H_{19}N$ $[M+H]^+$: 322.1596, found: 322.1583.

2-Chloro-6-(1,2-diphenylcyclopropyl)pyridine **11oa**



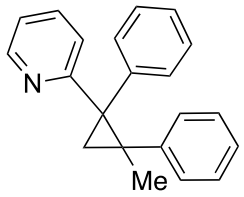
11oa was prepared according to the general procedure **C** in 95% yield, dr 1.2:1, (58.0 mg, 0.190 mmol) from 0.2 mmol of **1o**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.2. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.51 (d, J = 7.9 Hz, 2H), 7.42 – 7.25 (m, 5H), 7.23 – 7.20 (m, 4H), 7.18 – 7.13 (m, 2H), 7.13 – 6.99 (m, 9H), 6.93 (d, J = 7.8 Hz, 1H), 6.87 – 6.76 (m, 3H), 6.66 (d, J = 7.7 Hz, 1H), 3.34 (dd, J = 9.0, 7.0 Hz, 1H), 3.07 (t, J = 8.0 Hz, 1H), 2.69 (dd, J = 7.0, 5.3 Hz, 1H), 2.30 (dd, J = 9.1, 4.6 Hz, 1H), 2.03 (dd, J = 6.9, 4.6 Hz, 1H), 1.73 (dd, J = 9.0, 5.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 165.3, 160.7, 150.8, 149.8, 144.5, 138.4, 138.2, 138.0, 137.6, 137.3, 135.9, 135.7, 132.5, 129.3, 129.0, 128.9, 128.6, 128.6, 128.3, 128.1, 128.0, 127.7, 127.6, 127.3, 127.2, 127.0, 126.8, 126.7, 126.5, 125.9, 125.7, 125.5, 124.0, 121.1, 120.6, 120.2, 77.3, 77.1, 76.8, 40.4, 40.0, 34.9, 32.8, 23.3, 18.9. HRMS (EI+) calcd. for $C_{20}H_{16}ClN$ $[M+H]^+$: 306.1050, found: 306.1037.

2-(2-(3-Methoxyphenyl)-1-phenylcyclopropyl)pyridine **11ab**



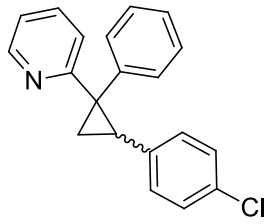
11ab was prepared according to the general procedure **C** in 96% yield, dr 1.1:1, (58.0 mg, 0.191 mmol) from 0.20 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 3/1): 0.3. Major diastereomer ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.58 (d, *J* = 3.9 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.27 – 7.11 (m, 5H), 7.06 – 6.95 (m, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.63 – 6.56 (m, 1H), 6.49 (d, *J* = 7.5 Hz, 1H), 3.57 (s, 3H), 3.30 (dd, *J* = 8.8, 7.0 Hz, 1H), 2.24 (dd, *J* = 9.0, 4.6 Hz, 1H), 1.96 (dd, *J* = 6.7, 4.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.8, 158.9, 149.1, 140.6, 138.3, 135.6, 132.4, 128.4, 128.3, 126.8, 121.9, 120.7, 120.3, 113.0, 111.7, 77.3, 77.0, 76.8, 54.9, 40.3, 34.2, 23.3. Minor diastereomer ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.46 – 8.41 (m, 1H), 7.51 – 7.42 (m, 2H), 7.33 – 7.28 (m, 3H), 7.24 – 7.20 (m, 1H), 7.02 – 7.00 (m, 1H), 6.97 – 6.92 (m, 2H), 6.65 – 6.54 (m, 2H), 6.46 (d, *J* = 1.7 Hz, 1H), 3.64 (s, 3H), 2.97 (dd, *J* = 8.8, 6.9 Hz, 1H), 2.50 (dd, *J* = 6.7, 5.4 Hz, 1H), 1.74 (dd, *J* = 8.9, 5.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.4, 159.1, 148.6, 145.3, 139.9, 135.6, 128.6, 128.5, 128.5, 126.5, 126.0, 121.0, 120.8, 113.2, 111.6, 77.2, 77.0, 76.8, 55.0, 41.1, 32.0, 19.2. HRMS (EI+) calcd. for $C_{21}H_{19}NO$ $[M+H]^+$: 302.1545, found: 302.1531.

2-(2-Methyl-1,2-diphenylcyclopropyl)pyridine **11ac**



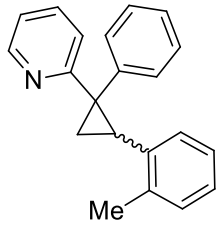
11ac was prepared according to the general procedure **C** in 96% yield, dr 1.6:1, (58.0 mg, 0.191 mmol) from 0.20 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.67 (d, *J* = 5.0 Hz, 1H), 8.22 (d, *J* = 5.0 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.60 – 7.55 (m, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.32 – 7.30 (m, 1H), 7.28 – 7.19 (m, 8H), 7.19 – 7.00 (m, 11H), 6.99 – 6.93 (m, 1H), 6.78 – 6.72 (m, 1H), 2.81 (d, *J* = 4.8 Hz, 1H), 2.27 (d, *J* = 5.4 Hz, 1H), 1.96 (d, *J* = 5.4 Hz, 1H), 1.56 (d, *J* = 4.9 Hz, 1H), 1.40 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 162.0, 160.8, 149.1, 148.1, 143.2, 142.8, 141.9, 141.5, 136.1, 135.2, 131.3, 130.4, 128.8, 128.3, 128.2, 127.6, 127.6, 127.5, 126.6, 125.8, 125.6, 125.4, 124.8, 123.9, 121.3, 120.1, 77.3, 77.1, 76.8, 44.4, 43.8, 34.7, 32.8, 26.7, 24.5, 24.2, 23.6. HRMS (EI+) calcd. for $C_{21}H_{19}N$ $[M+H]^+$: 286.1596, found: 286.1586.

2-(2-(4-Chlorophenyl)-1-phenylcyclopropyl)pyridine **11ad**



11ad was prepared according to the general procedure **C** in 99% yield, dr 1.5:1, (61.0 mg, 0.195 mmol) from 0.20 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.58 (d, *J* = 4.0 Hz, 1H), 8.41 (d, *J* = 4.2 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.36 – 7.30 (m, 4H), 7.29 – 7.18 (m, 5H), 7.16 – 7.09 (m, 3H), 7.05 – 7.00 (m, 5H), 6.93 – 6.89 (m, 4H), 6.75 – 6.70 (m, 3H), 3.36 – 3.30 (m, 1H), 3.01 – 2.94 (m, 1H), 2.54 (t, *J* = 5.9 Hz, 1H), 2.24 (dd, *J* = 8.8, 4.5 Hz, 1H), 1.97 – 1.91 (m, 1H), 1.74 (dd, *J* = 8.8, 5.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.5, 159.1, 149.0, 148.6, 145.0, 137.9, 137.6, 136.8, 135.7, 132.4, 131.4, 131.2, 129.6, 129.1, 128.9, 128.8, 128.7 128.6, 128.5, 128.7, 127.4, 127.7, 127.6, 127.2, 126.8, 126.6, 125.7, 121.8, 121.1, 120.4, 77.3, 77.0, 76.8, 41.0, 40.9, 33.4, 31.5, 23.1, 19.1. HRMS (EI+) calcd. for $C_{20}H_{16}ClN$ $[M+H]^+$: 306.1050, found: 306.1037.

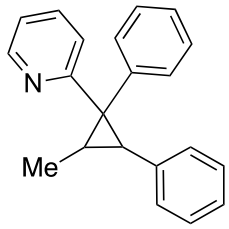
2-(1-Phenyl-2-(o-tolyl)cyclopropyl)pyridine **11ae**



11ae was prepared according to the general procedure **C** in 84% yield, dr 1.1:1, (48.0 mg, 0.168 mmol) from 0.20 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.64 – 8.57 (m, 1H), 8.37 – 8.31 (m, 1H), 7.57 – 7.49 (m, 2H), 7.42 – 7.38 (m, 1H), 7.37 – 7.33 (m, 2H), 7.28 – 7.24 (m, 2H), 7.18 – 7.10 (m, 4H), 7.07 – 7.02 (m, 4H), 7.01 – 6.95 (m, 2H), 6.95 – 6.78 (m, 6H), 6.52 (d, *J* = 7.7 Hz, 1H), 3.50 – 3.40 (m, 1H), 3.07 (dd, *J* = 8.6, 7.3 Hz, 1H), 2.73 (dd, *J* = 6.8, 5.1 Hz, 1H), 2.52 (s, 3H), 2.44 (s, 3H), 2.18 (dd, *J* = 7.1, 4.6 Hz, 1H), 2.14 (dd, *J* = 8.9, 4.5 Hz, 1H), 1.66 (dd, *J* = 8.9, 5.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$)

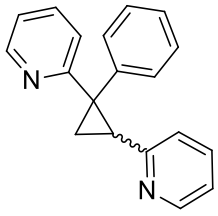
δ ppm 164.1, 159.7, 149.1, 148.3, 145.3, 138.8, 137.7, 136.8, 135.9, 135.6, 135.3, 131.7, 130.2, 129.4, 129.3, 128.6, 128.5, 128.0, 127.5, 126.6, 126.4, 125.9, 125.6, 125.1, 125.1, 124.8, 121.7, 120.7, 120.2, 77.3, 77.1, 76.8, 39.9, 39.4, 31.7, 30.0, 21.1, 20.7, 20.3, 18.6. HRMS (EI+) calcd. for $C_{21}H_{19}N$ $[M+H]^+$: 286.1572, found: 286.1582.

2-(1-Phenyl-2-(o-tolyl)cyclopropyl)pyridine **11af**



11af was prepared according to the general procedure **C** in 35% yield, dr 5:1, (20.0 mg, 0.070 mmol) from 0.20 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 4/1): 0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.64 – 8.57 (m, 1H), 8.37 – 8.31 (m, 1H), 7.57 – 7.49 (m, 2H), 7.42 – 7.38 (m, 1H), 7.37 – 7.34 (m, 2H), 7.29 – 7.25 (m, 2H), 7.18 – 7.10 (m, 4H), 7.06 – 7.02 (m, 4H), 7.01 – 6.95 (m, 2H), 6.95 – 6.78 (m, 6H), 6.52 (d, *J* = 7.7 Hz, 1H), 3.50 – 3.40 (m, 1H), 3.07 (dd, *J* = 8.6, 7.3 Hz, 1H), 2.73 (dd, *J* = 6.8, 5.1 Hz, 1H), 2.52 (s, 3H), 2.44 (s, 3H), 2.18 (dd, *J* = 7.1, 4.6 Hz, 1H), 2.14 (dd, *J* = 8.9, 4.5 Hz, 1H), 1.66 (dd, *J* = 8.9, 5.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 160.7, 148.4, 148.1, 141.8, 138.6, 135.8, 135.5, 131.2, 130.5, 128.4, 128.1, 128.0, 127.6, 127.5, 126.6, 126.3, 126.1, 126.1, 125.4, 125.3, 121.3, 120.8, 120.7, 77.3, 77.1, 76.8, 46.4, 37.6, 35.2, 26.1, 22.4, 15.4, 13.8. HRMS (EI+) calcd. for $C_{21}H_{19}N$ $[M+H]^+$: 286.1596, found: 286.1585.

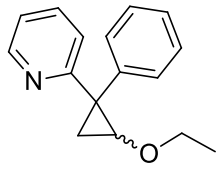
2,2'-(1-Phenylcyclopropane-1,2-diyl)dipyridine **11ag**



11ag was prepared according to the general procedure **C** in 97% yield, dr 1.8:1, (53.0 mg, 0.194 mmol) from 0.20 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 3/1): 0.2. Major diastereomer ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.59 – 8.51 (m, 1H), 8.27 – 8.23 (m, 1H), 7.41 – 7.32 (m, 2H),

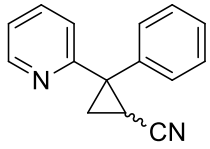
7.17 – 7.06 (m, 5H), 7.02 – 6.95 (m, 1H), 6.92 – 6.87 (m, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.78 – 6.73 (m, 1H), 3.54 (dd, *J* = 8.6, 6.8 Hz, 1H), 2.36 –2.34 (m, 1H), 2.24 – 2.21 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.4, 158.3, 148.9, 148.5, 138.4, 135.6, 135.2, 132.1, 128.5, 126.6, 122.7, 121.9, 120.4, 120.4, 77.3, 77.0, 76.7, 40.8, 35.6, 21.7. Minor diastereomer ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.36 (d, *J* = 3.4 Hz, 1H), 8.28 (d, *J* = 3.6 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.36 – 7.30 (m, 1H), 7.34 – 7.26 (m, 3H), 7.21 – 7.17 (m, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.96 – 6.90 (m, 1H), 6.91 – 6.87 (m, 2H), 3.20 – 3.12 (m, 1H), 2.72 – 2.66 (m, 1H), 1.80 (dd, *J* = 8.6, 5.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.4, 158.1, 148.5, 148.5, 144.8, 135.6, 135.6, 128.5, 128.3, 126.5, 125.8, 122.6, 120.9, 120.5, 77.2, 77.0, 76.7, 41.1, 33.6, 19.1. HRMS (EI+) calcd. for $C_{19}H_{16}N_2$ $[M+H]^+$: 273.1392, found: 273.1380.

2-(2-Ethoxy-1-phenylcyclopropyl)pyridine**11ah**



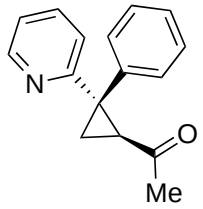
11ah was prepared according to the general procedure **C** in 42% yield, dr 1.1:1, (20.0 mg, 0.083 mmol) from 0.20 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 3/1): 0.2. Major diastereomer ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.52 – 8.45 (m, 1H), 7.39 – 7.34 (m, 5H), 7.31 – 7.26 (m, 1H), 7.04 – 6.97 (m, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 4.12 (dd, *J* = 6.7, 4.1 Hz, 1H), 3.63 (q, *J* = 7.0 Hz, 2H), 1.80 (dd, *J* = 6.6, 5.4 Hz, 1H), 1.65 – 1.62 (m, 1H), 1.08 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.5, 148.8, 138.4, 135.6, 131.6, 128.2, 126.8, 122.0, 120.2, 77.2, 77.0, 76.7, 66.2, 65.1, 37.0, 23.0, 15.0. Minor diastereomer ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.57 (d, *J* = 4.0, 1H), 7.52 – 7.47 (m, 1H), 7.37 – 7.33 (m, 2H), 7.32 – 7.28 (m, 2H), 7.25 – 7.19 (m, 2H), 7.08 – 7.00 (m, 1H), 3.89 (dd, *J* = 7.0, 4.2 Hz, 1H), 3.58 (dt, *J* = 14.1, 7.0 Hz, 1H), 3.47 – 3.40 (m, 1H), 2.29 (dd, *J* = 5.9, 4.2 Hz, 1H), 1.41 (dd, *J* = 6.9, 6.1 Hz, 1H), 0.98 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.3, 148.5, 143.4, 135.6, 129.6, 128.6, 126.6, 124.4, 120.8, 77.2, 77.0, 76.7, 66.3, 64.5, 38.5, 19.9, 14.8. HRMS (EI+) calcd. for $C_{16}H_{17}NO$ $[M+H]^+$: 240.1388, found: 240.1381.

2-Phenyl-2-(pyridin-2-yl)cyclopropanecarbonitrile **11ai**



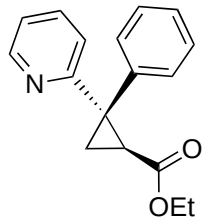
11ai was prepared according to the general procedure **C** in 68% yield, dr 1.5:1, (30.0 mg, 0.136 mmol) from 0.2 mmol of **1a**. Colorless semi-solid. R_f (hexanes/EtOAc = 4/1): 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) (NMR reported only for major diastereomer) δ ppm 8.48 (d, *J* = 3.9 Hz, 1H), 7.50 – 7.46 (m, 4H), 7.46 – 7.36 (m, 2H), 7.11 – 7.08 (m, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 2.89 – 2.85 (m, 1H), 2.10 (dd, *J* = 9.2, 4.3 Hz, 1H), 1.94 (dd, *J* = 6.0, 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 159.7, 149.2, 136.8, 136.3, 131.3, 129.2, 128.6, 122.5, 121.7, 119.8, 38.0, 23.4, 13.8. HRMS (EI+) calcd. for $C_{15}H_{13}N_2$ $[M+H]^+$: 221.1079, found: 221.1072.

1-(2-Phenyl-2-(pyridin-2-yl)cyclopropyl)ethanone **11aj**



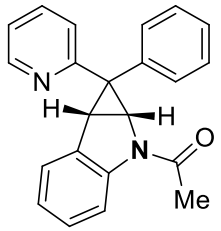
11aj was prepared according to the general procedure **C** in 70% yield, dr 4:1, (33.3 mg, 0.14 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 7/3): 0.32. ^{1}H NMR (500 MHz, $CDCl_3$) (NMR reported only for major diastereomer) δ ppm 8.52 (d, *J* = 4.6 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.37 – 7.35 (m, 2H), 7.31 – 7.30 (m, 1H), 7.28 – 7.26 (m, 2H), 7.08 – 7.06 (m, 1H), 6.77 – 6.76 (m, 1H), 3.40 – 3.37 (m, 1H), 2.26 – 2.24 (m, 1H), 2.18 (s, 3H), 1.89 (dd, *J* = 7.9, 3.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 204.3, 162.1, 149.1, 137.8, 136.0, 131.2, 128.7, 127.6, 122.7, 121.1, 43.0, 38.3, 31.8, 22.9. HRMS (EI+) calcd. for $C_{16}H_{16}NO$ $[M+H]^+$: 238.1232, found: 238.1227.

Ethyl 2-phenyl-2-(pyridin-2-yl)cyclopropanecarboxylate **11ak**



11ak was prepared according to the general procedure **C** in 90% yield, dr 9:1, (48.3 mg, 0.181 mmol) from 0.2 mmol of **1a**. Colorless semi-solid. R_f (hexanes/EtOAc = 7/3): 0.32. ^{1}H NMR (400 MHz, $CDCl_3$) (NMR reported only for major diastereomer) δ ppm 8.53 – 8.48 (m, 1H), 7.41 – 7.38(m, 1H), 7.36 – 7.34 (m, 4H), 7.33 – 7.29 (m, 1H), 7.06 – 7.02 (m, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 3.98 – 3.83 (m, 2H), 3.06 – 3.02 (dd, *J* = 8.1, 6.3 Hz, 1H), 2.15 (dd, *J* = 6.2, 4.0 Hz, 1H), 1.95 (dd, *J* = 8.2, 4.0 Hz, 1H), 1.00 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.7, 162.0, 149.1, 138.5, 135.9, 131.1, 128.6, 127.6, 122.5, 121.0, 60.4, 39.9, 31.0, 21.9, 14.1. HRMS (EI+) calcd. for $C_{17}H_{18}NO_2$ $[M+H]^+$: 268.1338, found: 268.1335.

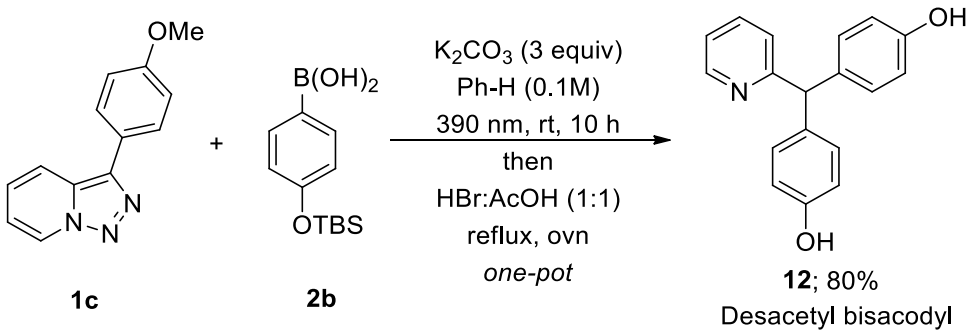
1-Phenyl-1-(pyridin-2-yl)-1,6b-dihydrocyclopropa[b]indol-2(1aH)-yl)ethanone **11al**



11al was prepared according to the general procedure **C** in 30% yield, dr 1:1, (19.6 mg, 0.06 mmol) from 0.2 mmol of **1a**. Colorless liquid. R_f (hexanes/EtOAc = 7/3): 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) (NMR reported only for major diastereomer) δ ppm 8.56 (d, *J* = 4.3 Hz, 1H), 7.80 (d, *J* = 7.4 Hz, 1H), 7.40 – 7.36 (m, 3H), 7.15 – 7.11 (m, 2H), 7.09 – 7.06 (m, 1H), 7.02 – 6.99 (m, 2H), 6.96 – 6.60 (m, 2H), 6.67 (d, J = 8.0 Hz, 1H), 4.95 (d, *J* = 6.9 Hz, 1H), 3.79 (d, *J* = 6.8 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 169.2, 162.4, 149.2, 143.3, 135.8, 133.1, 132.4, 131.6, 128.5, 127.4, 127.4, 125.0, 123.5, 122.3, 120.7, 116.9, 52.9, 37.8, 35.3, 24.7. HRMS (EI+) calcd. for HRMS (EI+) calcd. for $C_{22}H_{19}N_2O$ $[M+H]^+$: 327.1497, found: 327.1487.

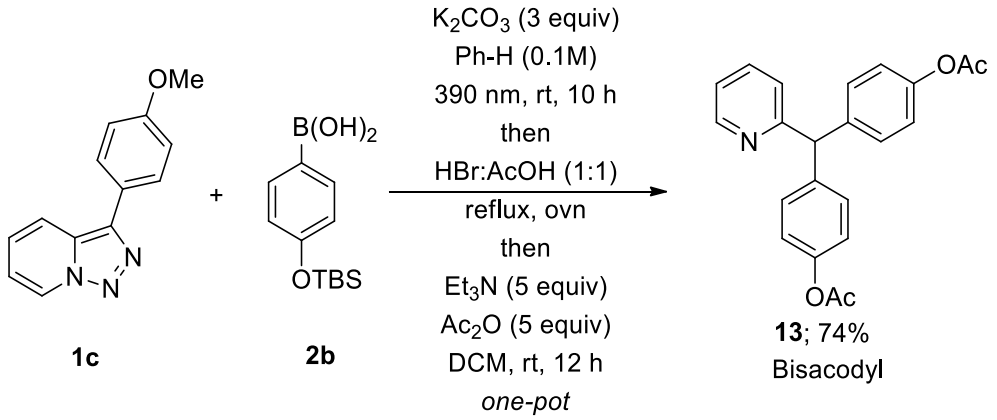
6. Synthesis of Biologically Active Molecules

Synthesis of 4,4'-(pyridin-2-ylmethylene)diphenol 12



An oven dried 3 mL Wheaton V-vial containing a stirring bar was charged with Pyridotriazoles **1c** (45 mg, 0.2 mmol, 1 equiv), K_2CO_3 (83 mg, 0.6 mmol, 3 equiv) and TBS protected aryl boronicacid **2b** (76 mg, 0.3 mmol, 1.5 equiv) in dry and degassed benzene (2 mL) under argon atmosphere (outside glovebox). After the reaction vessel was capped with a pressure screw cap in the glove box. The vial was irradiated with 40 W Kessil LED PR160-390 nm for 10 h (monitored by GC/MS), with cooling from a fan (vial temperature reached 37 °C). The vial distance from the lamp was about 2-3 cm. The resulting mixture was passed through a short pad of Celite, and concentrated under a reduced pressure. To the crude reaction mixture HBr (1.5 mL), AcOH (1.5 mL) were added and the reaction mixture was refluxed for overnight (monitored by TLC) complete conversation of the starting material. The cooled reaction mixture was diluted with H_2O (5 mL) and neutralized using a 10 M NaOH(aq) solution, extracted with EtOAc (5 mL) combined organic layers were dried over $MgSO_4$, filtered, and the solvent removed in vacuo and purified by column chromatography in hexanes/EtOAc to afford the *corresponding desacetyl biscodyl **12*** in 81% yield (50.0 mg, 0.162 mmol) browinsh solid. R_f (hexanes/EtOAc = 1/2): 0.3. ^{1}H NMR (500 MHz, $MeOD_4$): δ ppm 8.44 (d, J = 4.4 Hz, 1H), 7.75 –7.72 (m, 1H), 7.26 – 7.22 (m, 1H), 7.14 – 7.12 (m, 1H), 6.91 – 6.89 (m, 4H), 6.72 – 6.70 (m, 4H), 5.51 (s, 1H). ^{13}C NMR (126 MHz, $MeOD_4$): δ ppm 165.4, 157.1, 149.5, 138.6, 135.1, 131.3, 125.4, 122.9, 116.1, 58.6. HRMS (EI+) calcd. for $C_{18}H_{15}NO_2$ $[M+H]^+$: 278.1181, found: 278.1173.

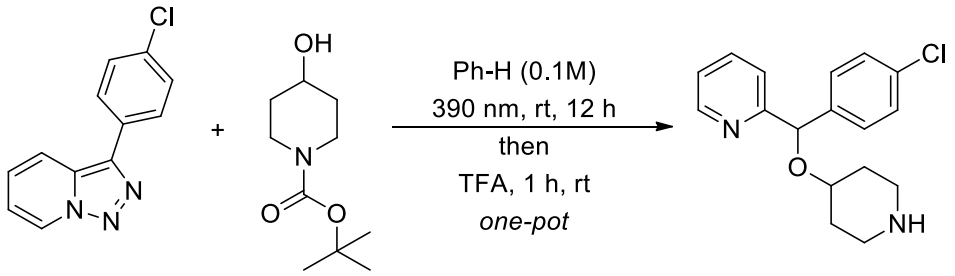
Synthesis of (pyridin-2-ylmethylene)bis(4,1-phenylene) diacetate 13



An oven dried 3 mL Wheaton V-vial containing a stirring bar was charged with Pyridotriazoles **1c** (45 mg, 0.2 mmol, 1 equiv), K_2CO_3 (83 mg, 0.6 mmol, 3 equiv) and TBS protected aryl boronic acid **2b** (76 mg, 0.3 mmol, 1.5 equiv) in dry and degassed benzene (2 mL) under argon atmosphere (outside glovebox). After the reaction vessel was capped with a pressure screw cap in the glove box. The vial was irradiated with 40 W Kessil LED PR160-390 nm for 10 h (monitored by GC/MS), with cooling from a fan (vial temperature reached 37 °C). The vial distance from the lamp was about 2-3 cm. The resulting mixture was passed through a short pad of Celite, and concentrated under a reduced pressure. To the crude reaction mixture HBr (1.5 mL), AcOH (1.5 mL) were added and the reaction mixture was refluxed for overnight (monitored by TLC) complete conversation of the starting material. The cooled reaction mixture was diluted with H_2O (5 mL) and neutralized using a 10 M NaOH(aq) solution, extracted with EtOAc (5 mL) combined organic layers were dried over Na_2SO_4, filtered, the solvent removed in vacuo. Crude compound was dissolved CH_2Cl_2 (4 mL). Et_3N (141 µL, 1 mmol, 5 equiv), Ac_2O (94.5 µL, 1 mmol, 5 equiv) were added to the reaction mixture and stirred at room temperature for 12 h monitored by TLC evaporated the solvent and purified by column chromatography in hexanes/EtOAc to afford the *corresponding Biscodyl* ***13*** in 74% yield (53.5 mg, 0.148 mmol). Colorless liquid. R_f (hexanes/EtOAc = 3/1): 0.32. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.59 (d, J = 4.2 Hz, 1H), 7.63 –7.59 (m, 1H), 7.18 – 7.16 (m, 4H), 7.15 – 7.14 (m, 1H), 7.11 – 7.09 (m, 1H), 7.02 – 7.00 (m, 4H), 5.65 (s, 1H), 2.28 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 169.5, 162.7, 149.7, 149.4, 140.1,

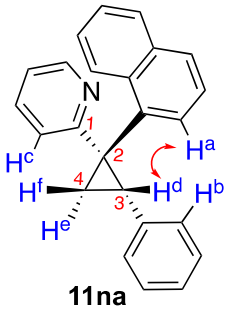
136.7, 130.4, 123.9, 121.7, 121.6, 58.2, 21.2. HRMS (EI+) calcd. for $C_{22}H_{19}NO_4$ $[M+H]^+$: 362.1392, found: 362.1386.

Synthesis of 2-((4-chlorophenyl)(piperidin-4-yloxy)methyl)pyridine 14



1d **4n** **14**; 71%

An oven dried 3 mL Wheaton V-vial containing a stirring bar was charged with Pyridotriazoles **1d** (46 mg, 0.2 mmol, 1 equiv), in dry and degassed benzene (2 mL) under argon atmosphere (outside glovebox) and 1-Boc-4-hydroxypiperidine **4n** were added (161 mg 0.8 mmol 4 equiv). After the reaction vessel was capped with a pressure screw cap in the glove box. The vial was irradiated with 40 W Kessil LED PR160-390nm for 12 h (monitored by GC/MS), with cooling from a fan (vial temperature reached 37 °C). The vial distance from the lamp was about 2-3 cm. To the reaction mixture TFA (0.5 mL) was added and stirred for 1 h reaction mixture was diluted with H_2O (5 mL) and neutralized using a 2 M NaOH(aq) solution, extracted with EtOAc (5 mL) combined organic layers were dried over Na_2SO_4, filtered, the solvent removed in vacuo. afford the *title compound **14*** without further purification in 71% yield (43.0 mg, 0.141 mmol). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.50 (d, *J* = 4.7 Hz, 1H), 7.69 –7.66 (m, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.37 – 7.36 (m, 2H), 7.28 – 7.26 (m, 2H), 7.18 – 7.13 (m, 1H), 5.63 (s, 1H), 3.54 – 3.47 (m, 1H), 3.08 (dd, *J* = 11.4, 6.1 Hz, 2H), 2.61 – 2.54 (m, 2H), 1.98 – 1.86 (m, 2H), 1.59 – 1.52 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 162.2, 149.0, 140.5, 137.0, 133.3, 128.6, 128.3, 122.5, 120.7, 80.8, 74.0, 44.4, 33.2. HRMS (EI+) calcd. for $C_{17}H_{19}N_2OCl$ $[M+H]^+$: 303.1264, found: 303.1260.

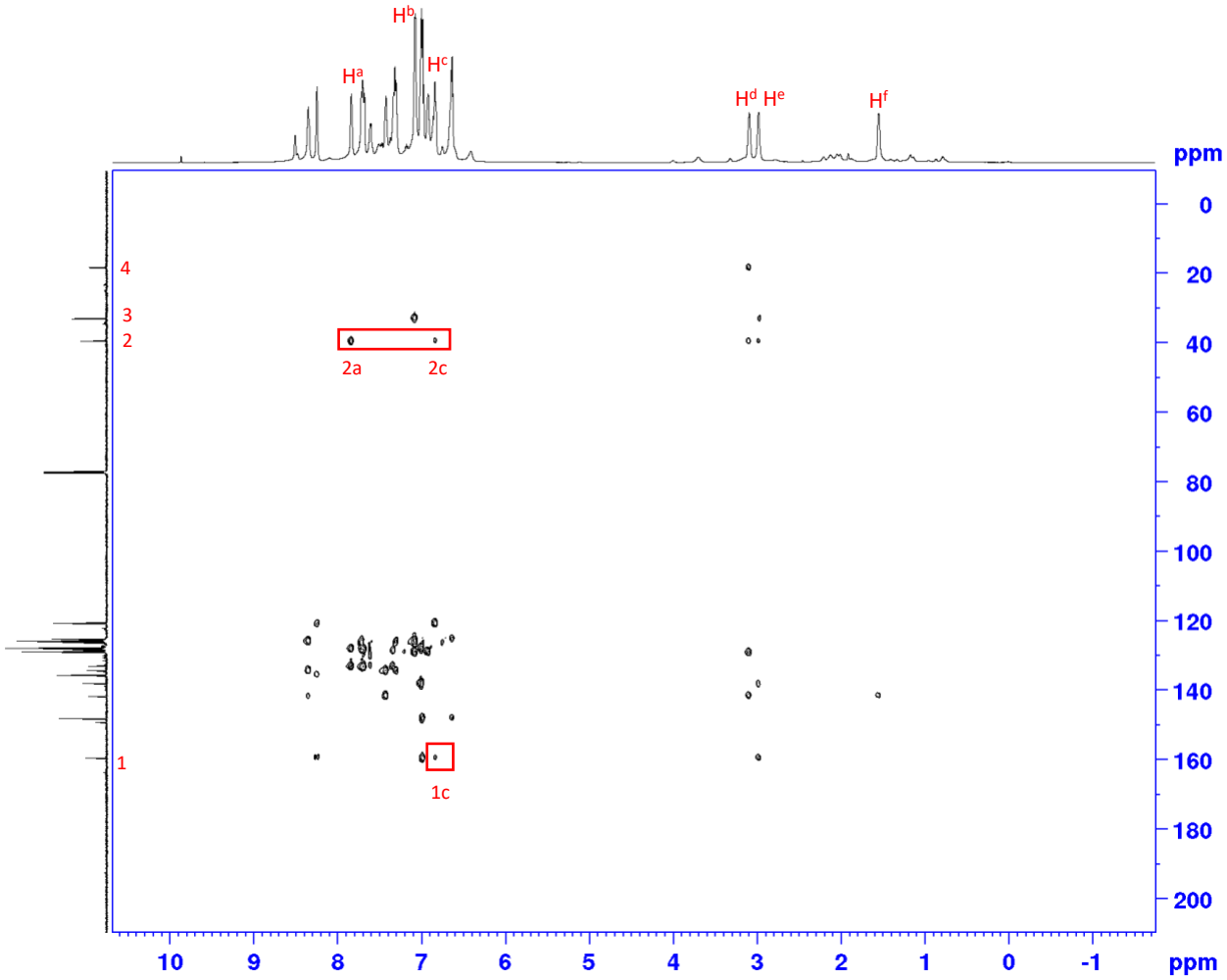


11na

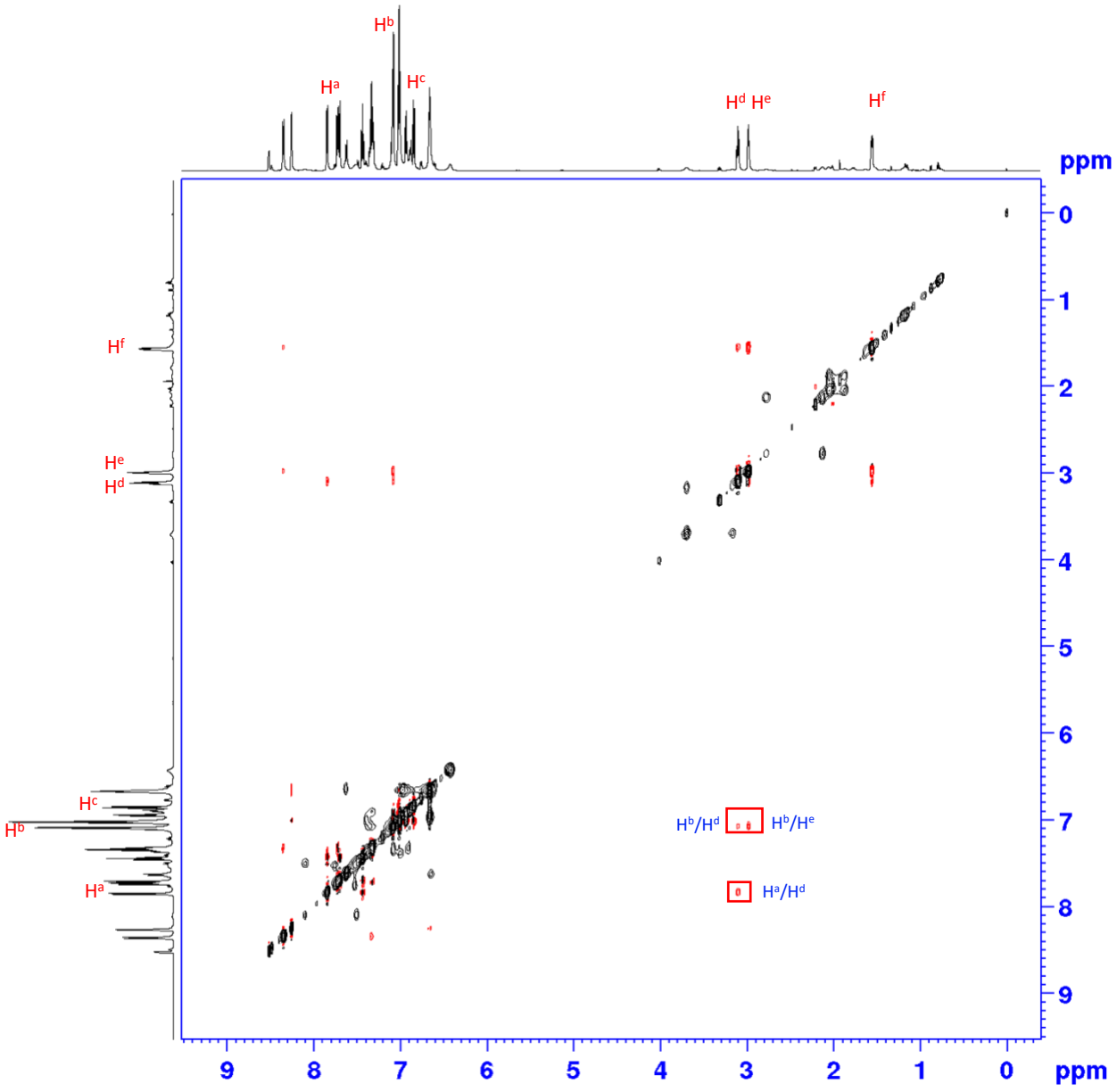
7. Determination of Stereochemistry of Cyclopropanes

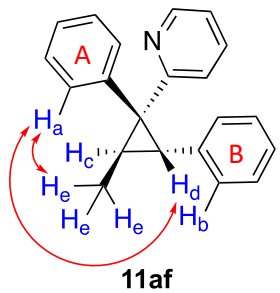
The geometry of cyclopropane **11na** was established on the basis of analysis of the chemical shifts and NOESY. From HMBC, cyclopropane quaternary carbon 2 has long range couplings with protons H^a and H^c, while pyridyl quaternary carbon 1 only has long range couplings signal with H^c. Thus, it indicates that H^c is on the pyridyl group and H^a is on the naphthyl group, respectively. Cyclopropane H^d proton showed NOESY correlations with naphthyl group H^a proton, which means that H^d is *cis* to the naphthyl group. Thus, pyridyl group is *cis* to phenyl group in cyclopropane **11na**.

HMBC of **11na**



NOESY of **11na**



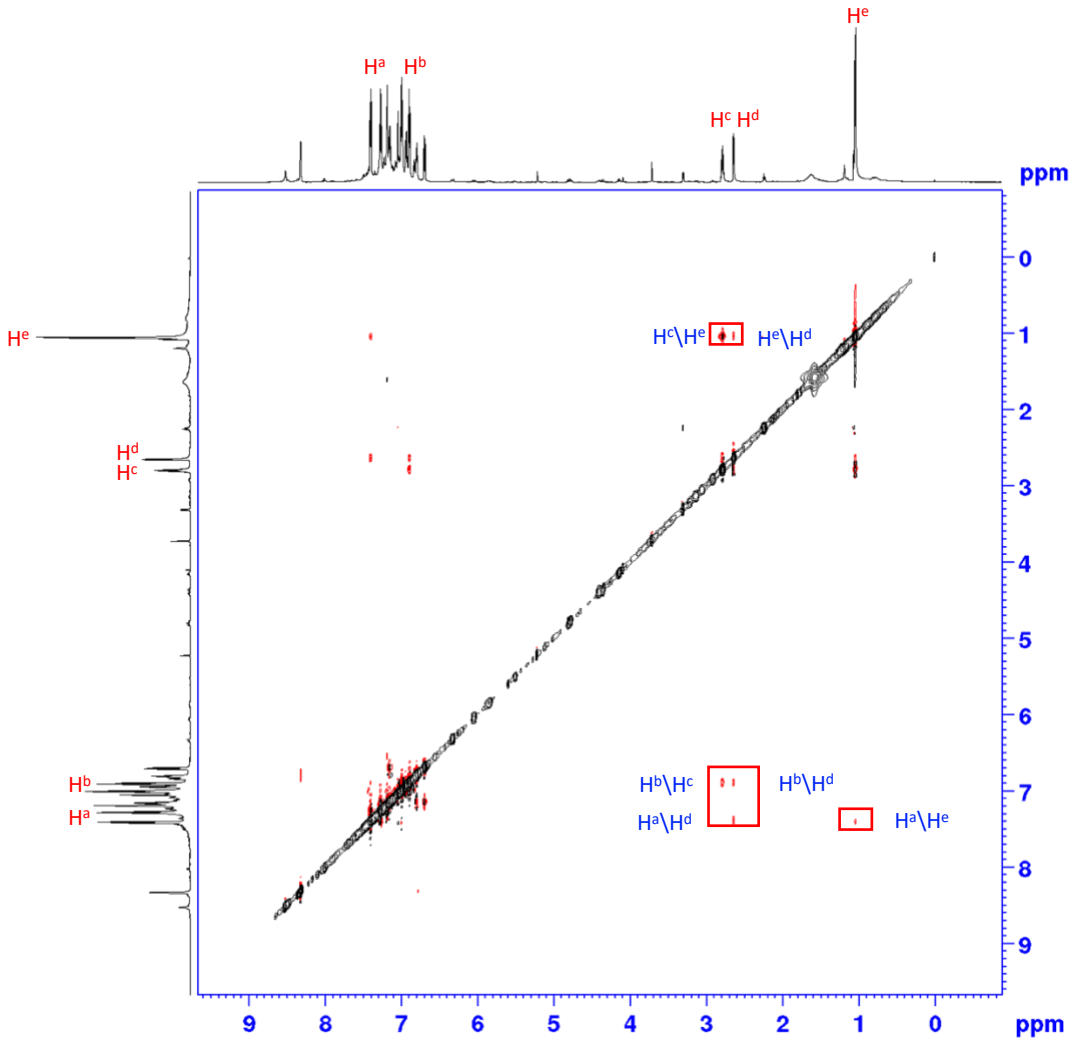


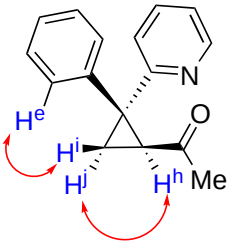
11af

The geometry of cyclopropane **11af** was established on the analysis of the chemical shifts, coupling constants of cyclopropane ring protons and NOESY. Based on NOESY correlations of benzylic proton H^d δ 2.72 ppm (J = 6.0 Hz) and H^e, the two protons are in relation *trans* to each other in the major diastereomer. H^d and methyl group proton H^e both has NOESY correlations with H^a, which means that α-phenyl group A is *cis* to both

methyl group and H^d. Thus, pyridyl group is *cis* to α-phenyl group B and *trans* to methyl group in cyclopropane **11af**.

NOSEY of **11af**

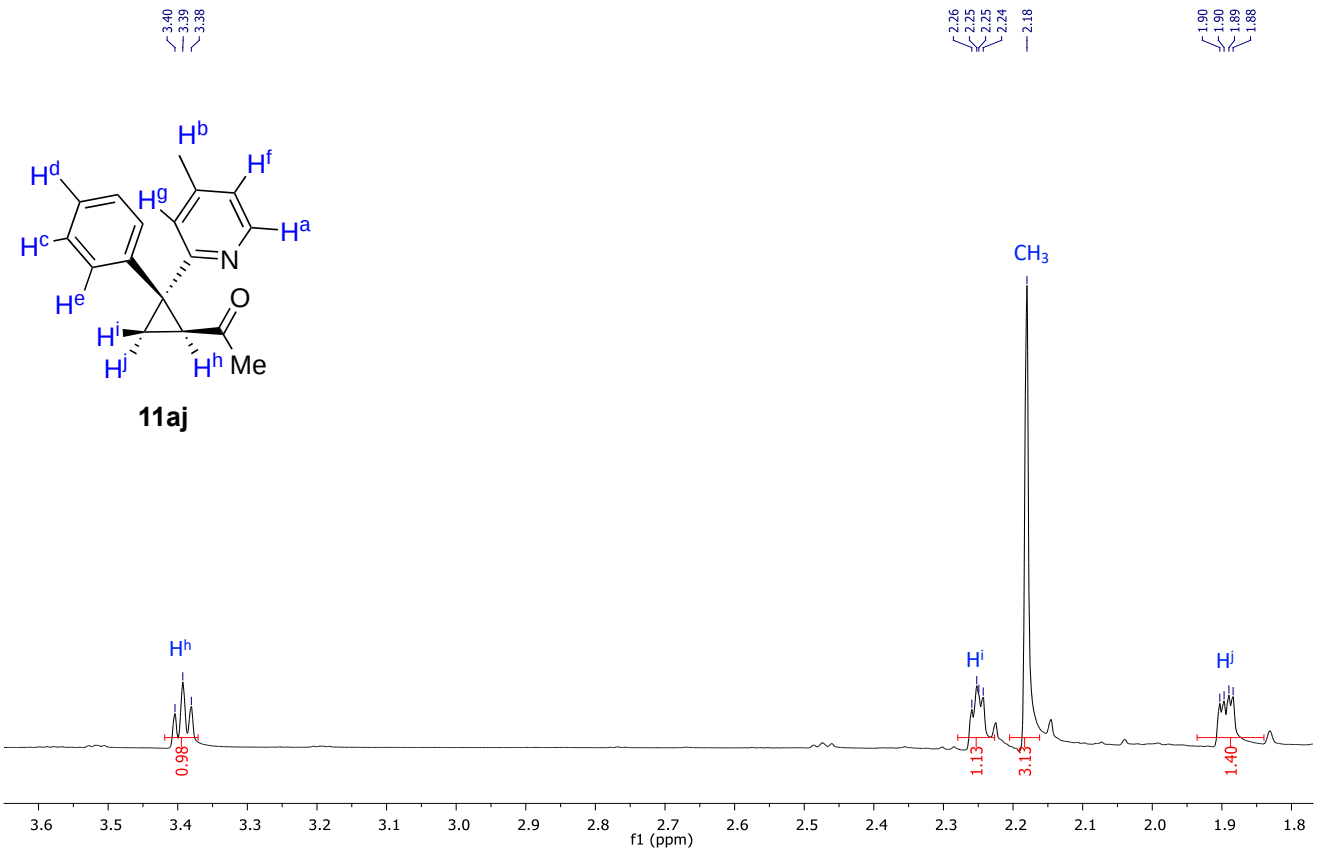


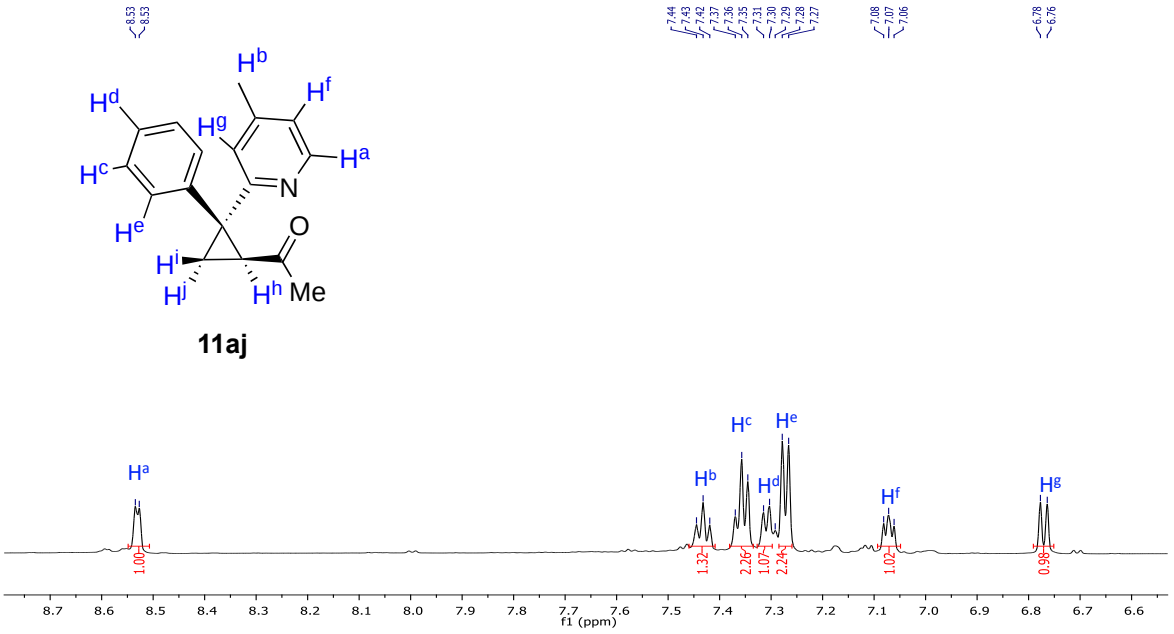


11aj

The geometry of cyclopropane **11aj** was established on the basis of analysis of the chemical shifts, COSY and NOESY. H^i has NOESY correlations with α-phenyl group proton H^e, which means that α-phenyl group is *cis* to H^i. Cyclopropane proton H^j has NOESY correlations with H^h, which means that they are *cis* to each other. Thus, pyridyl group is *trans* to acetyl group in cyclopropane **11aj**.

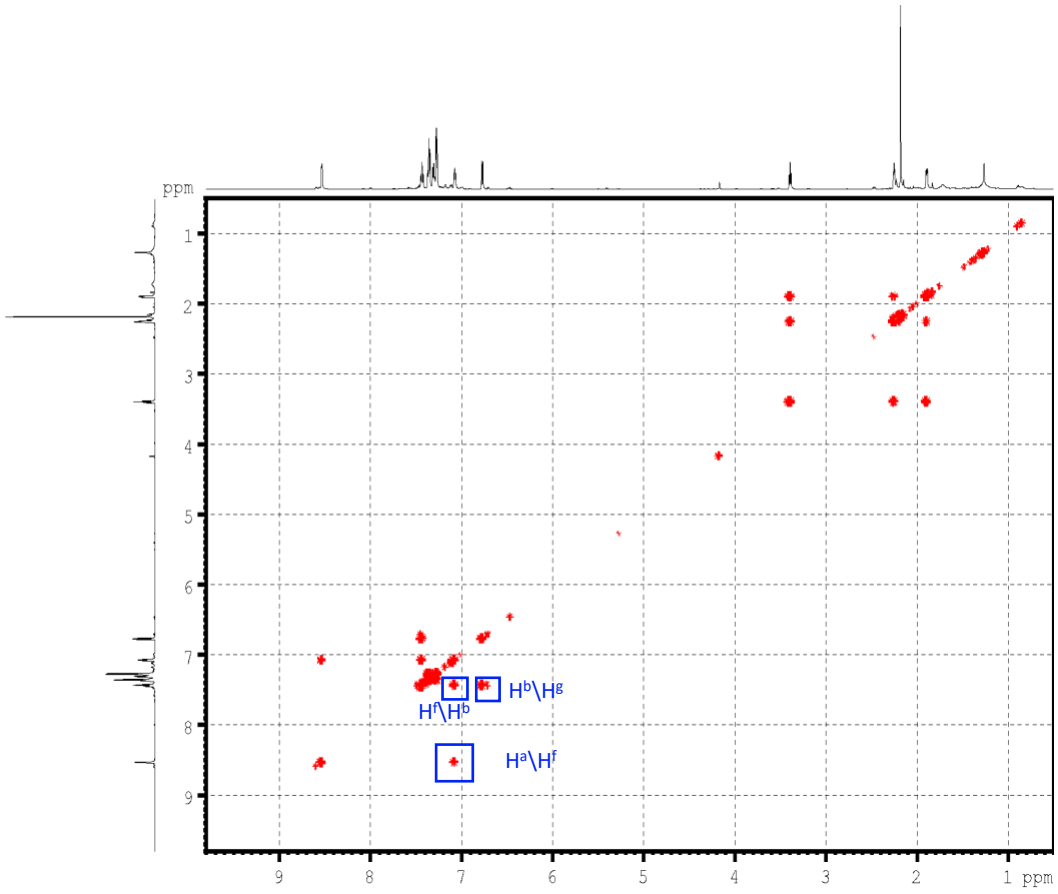
^{1}H NMR of **11aj** (expansion)



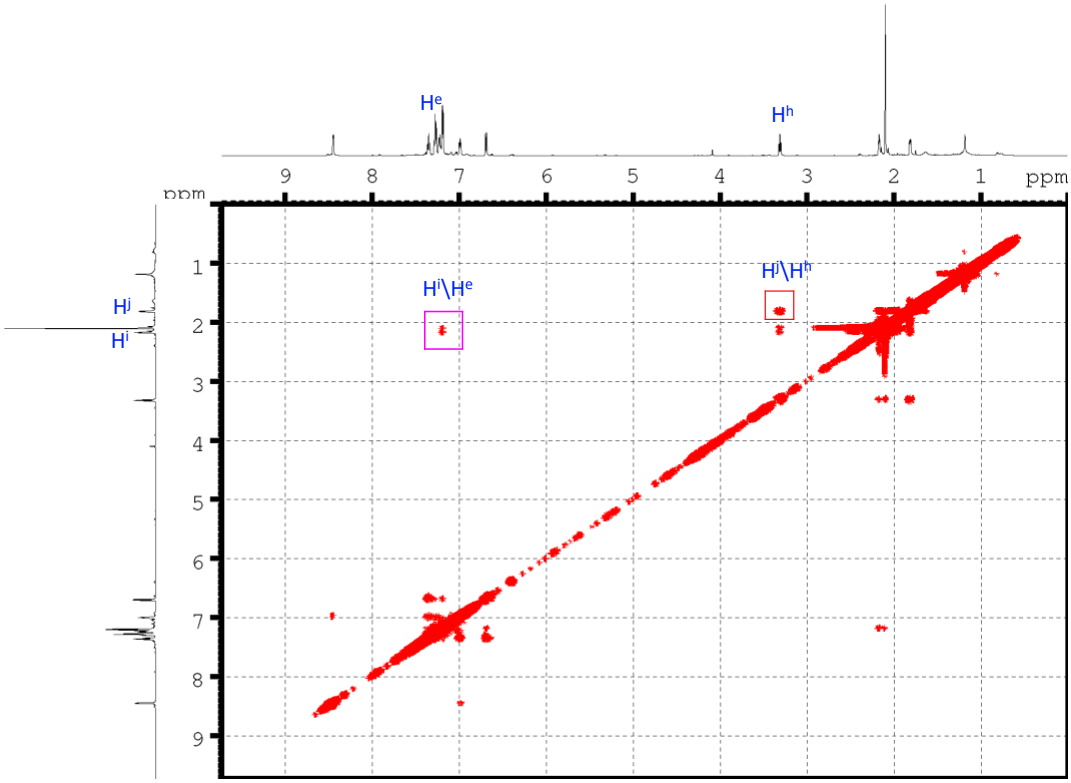


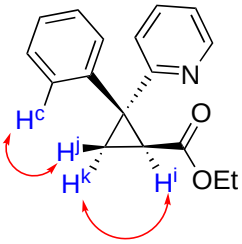
11aj

COSY of **11aj**



NOESY of **11aj**

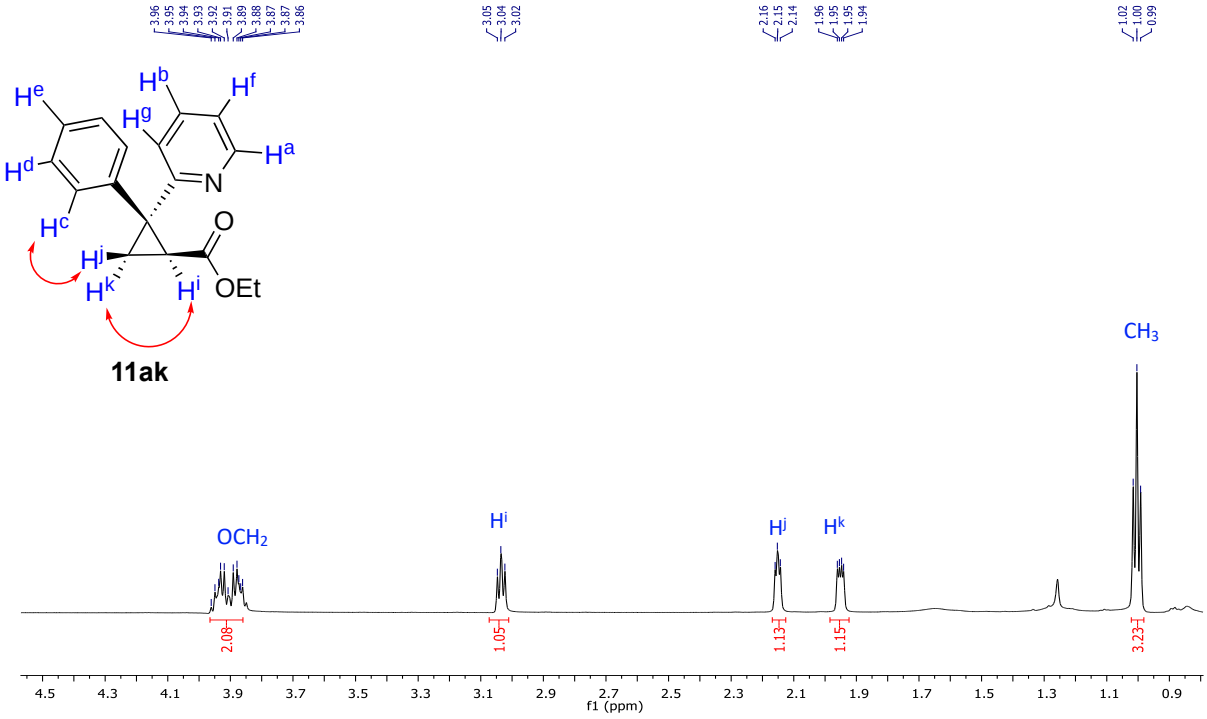


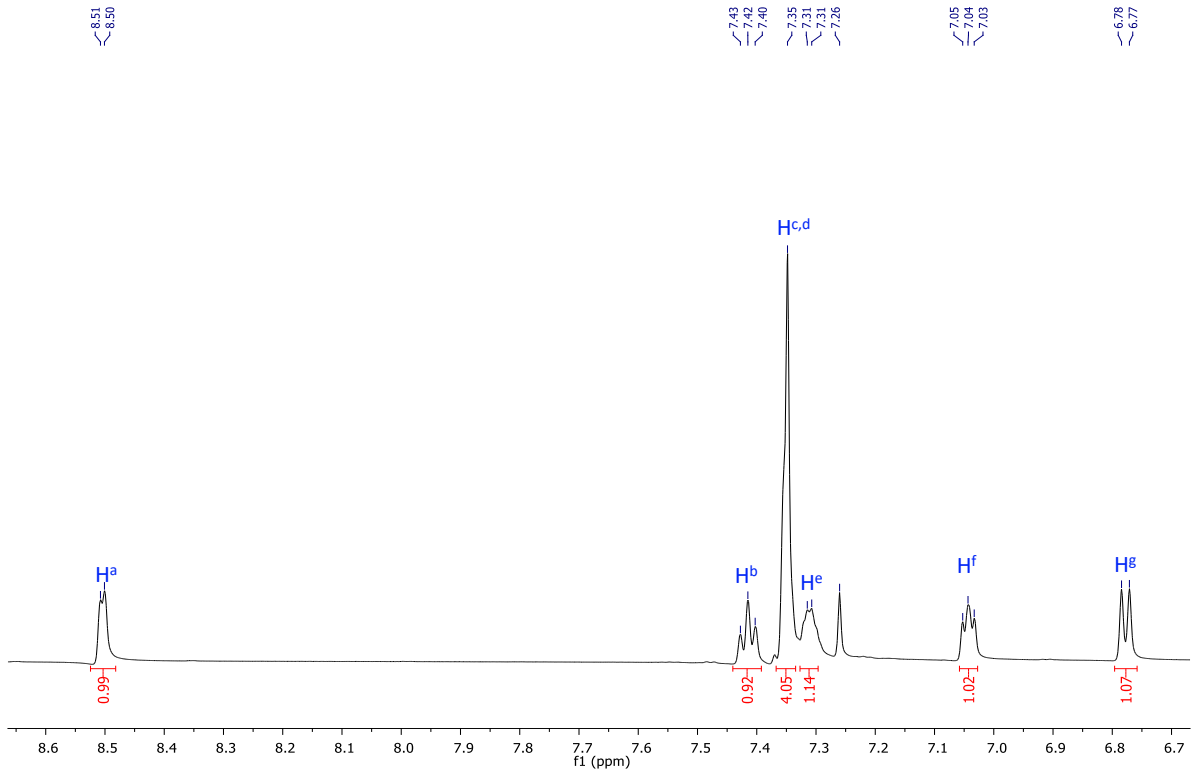


11ak

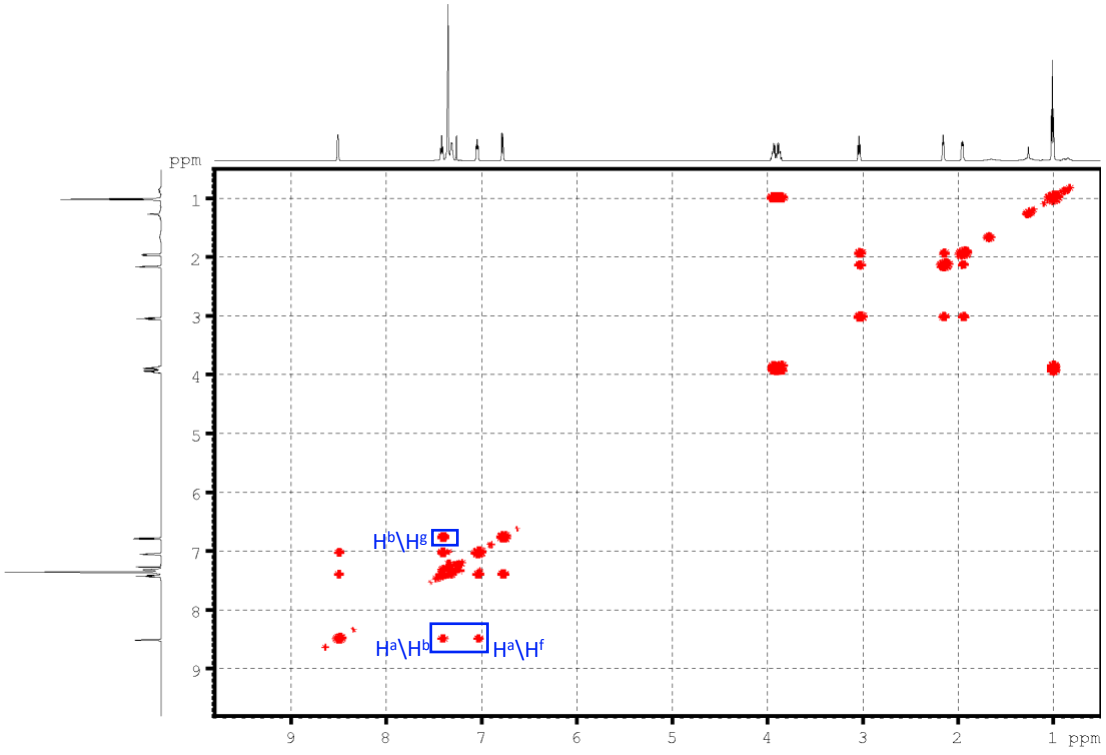
The geometry of cyclopropane **11ak** was established on the basis of analysis of the chemical shifts, COSY and NOESY. H^j has NOESY signals with α-phenyl group proton H^c, which means that α-phenyl group is *cis* to H^j. Cyclopropane proton H^k has NOESY correlations with H^i, which means that they are *cis* to each other. Thus, pyridyl group is *trans* to carbethoxy group in cyclopropane **11ak**.

^{1}H NMR of **11ak** (expansion)

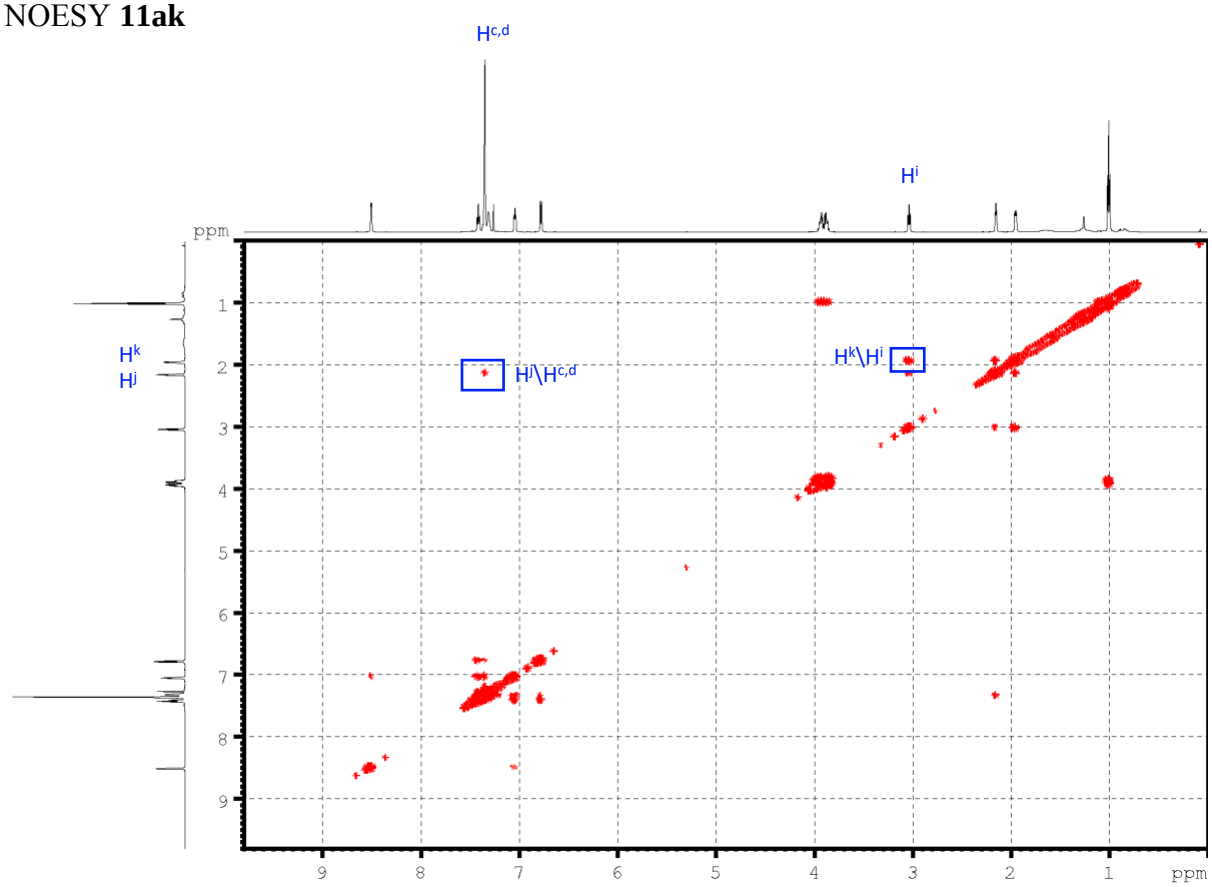



8.51
8.50
7.43
7.42
7.40
7.35
7.31
7.31
7.26
7.05
7.04
7.03
6.78
6.77
Hc,d
Ha
Hb
He
Hf
Hg
0.99
0.92
4.05
1.14
1.02
1.07
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)

COSY **11ak**

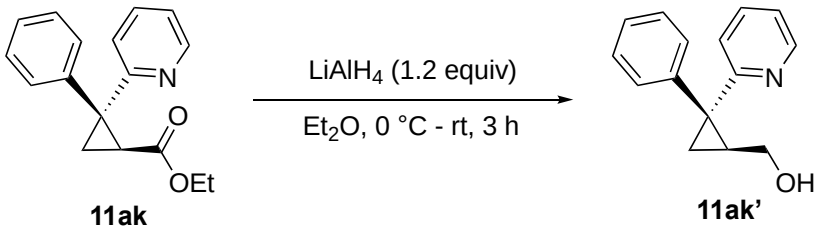

ppm
1
2
3
4
5
6
7
8
9
Hb\Hg
Ha\Hb
Ha\Hf
9
8
7
6
5
4
3
2
1 ppm

NOESY **11ak**



In order to get additional evidence for stereochemistry of **11ak**, it was reduced to alcohol **11ak'**.

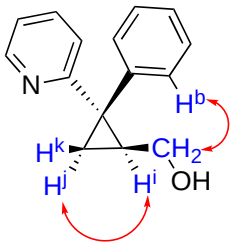
Preparation of **11ak'** from **11ak**



11ak **11ak'**

To a stirred solution of $LiAlH_4$ (9.0 mg, 0.24 mmol, 1.2 equiv) in Et_2O (4.0 mL) at 0 °C, compound **11ak** (53.0 mg, 0.2 mmol, 1.0 equiv) in Et_2O (2.0 mL) was added under Ar atmosphere. After being stirred for 3 h, the reaction mixture was quenched with saturated Na_2SO_4. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was dried over $MgSO_4$ and

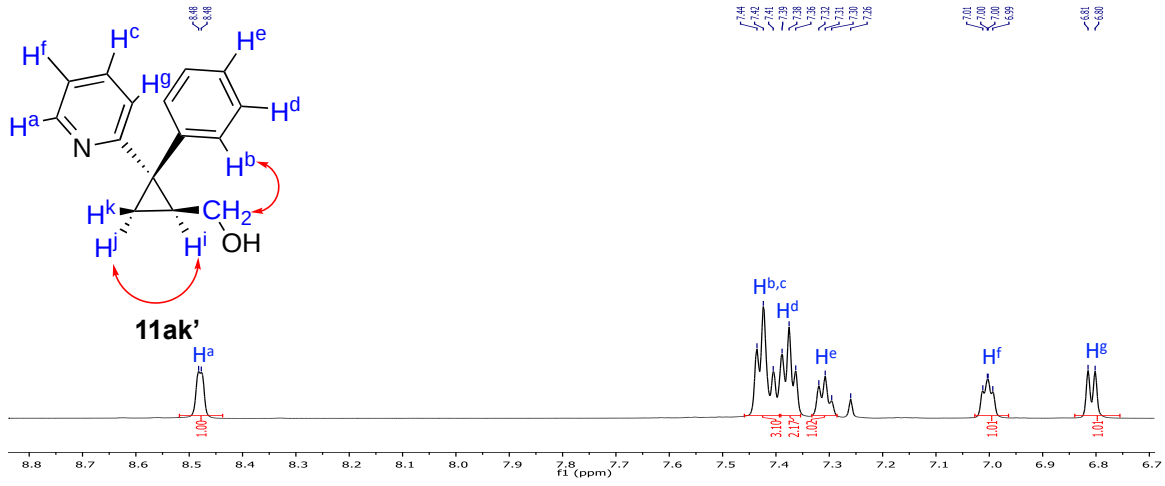
concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexanes : ethyl acetate = 70 : 30 to give reduced compound (**11ak'**) in 80% yield (36.0 mg, 0.16 mmol). Colorless oil. R_f (hexanes/EtOAc = 4/1): 0.27. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 8.48 (d, *J* = 3.0 Hz, 1H), 7.44 –7.41 (m, 3H), 7.39 –7.36 (m, 2H), 7.32 –7.30 (m, 1H), 7.01 – 6.99 (m, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.54 -3.36 (m, 2H), 2.46 - 2.39 (m, 1H), 1.84 (s, 1H), 1.64 (dd, *J* = 8.8, 4.1 Hz, 1H), 1.39-1.33 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ Ppm 164.0, 148.9, 139.4, 135.9, 131.4, 128.8, 127.3, 122.3, 120.5, 63.7, 36.6, 29.8, 20.3.

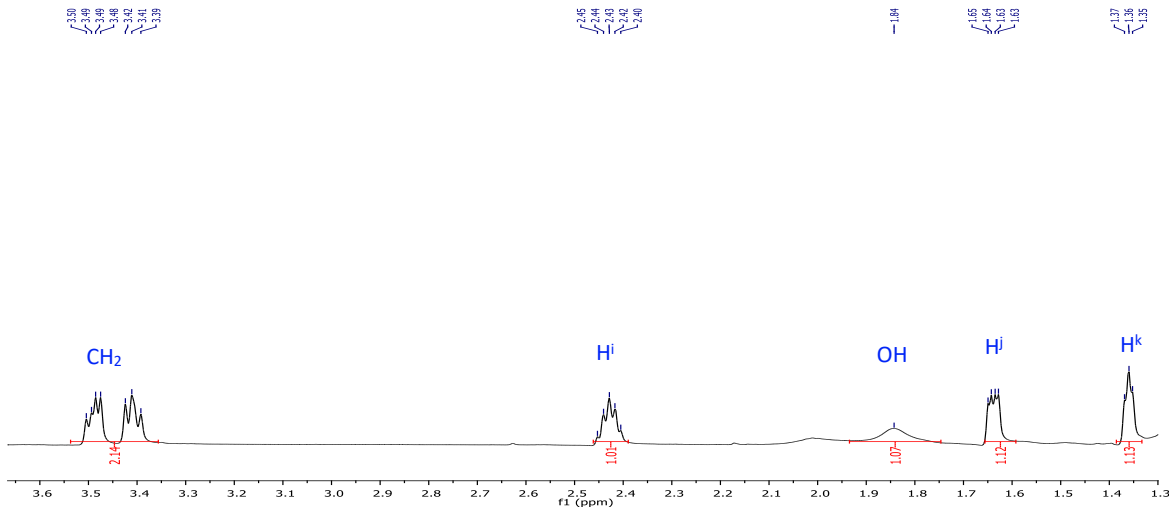


11ak'

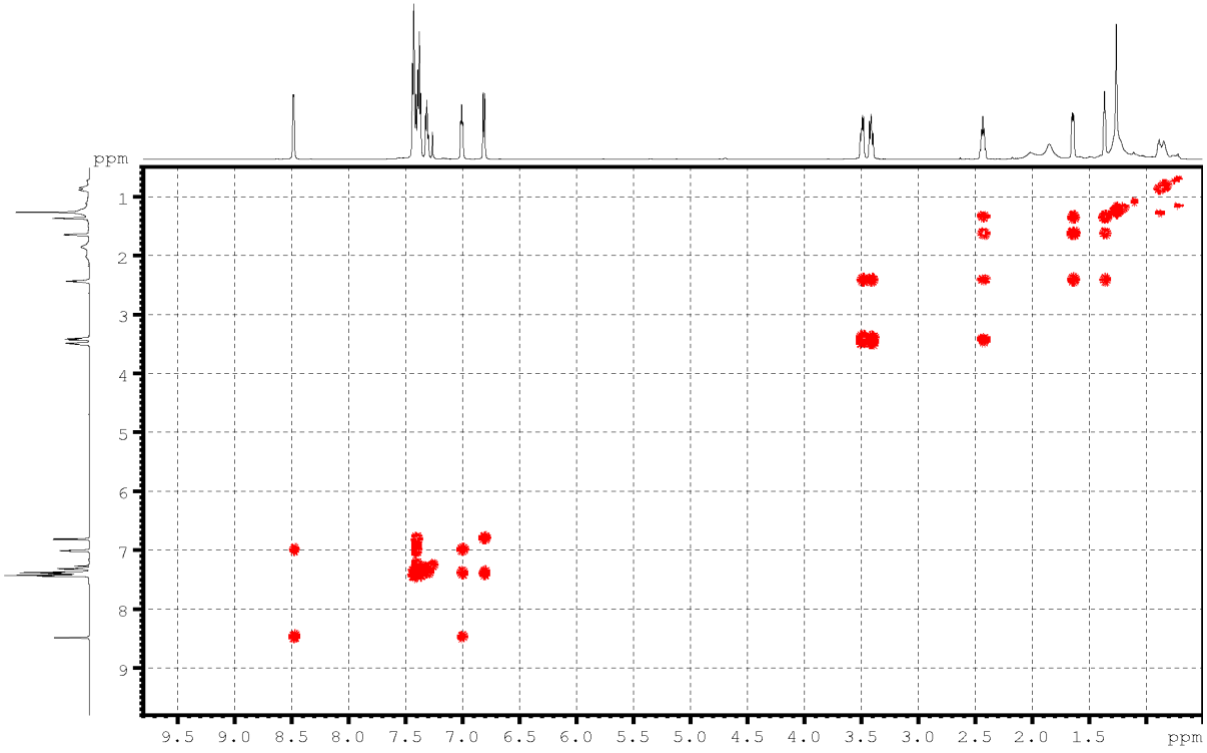
The geometry of cyclopropane **11ak'** was established on the basis of analysis of the chemical shifts, COSY and NOESY. H^j has NOESY correlations with cyclopropane proton H^i, which means that they are *cis* to each other. α-phenyl group proton H^b has NOESY correlations with CH_2, which means that they are *cis* to each other. Thus, pyridyl group is *trans* to hydroxymethyl group.

^{1}H NMR of **11ak**' (expansion)

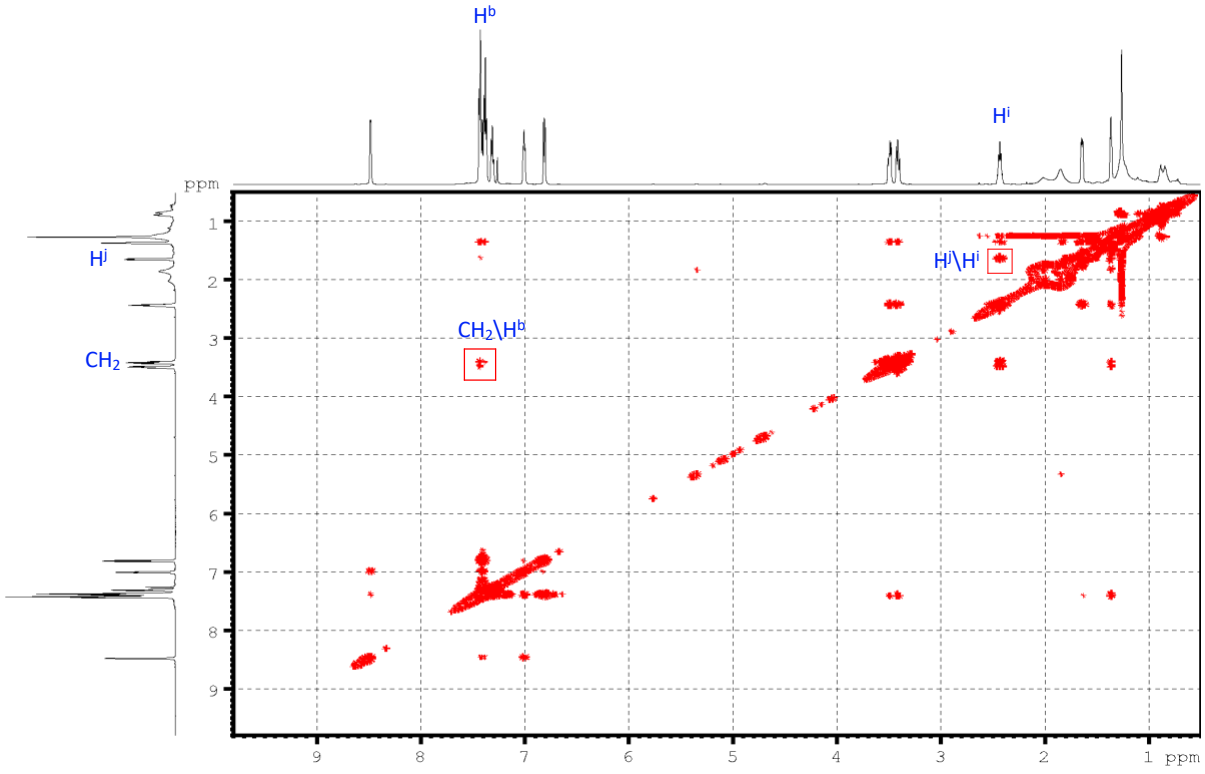




COSY **11ak'**

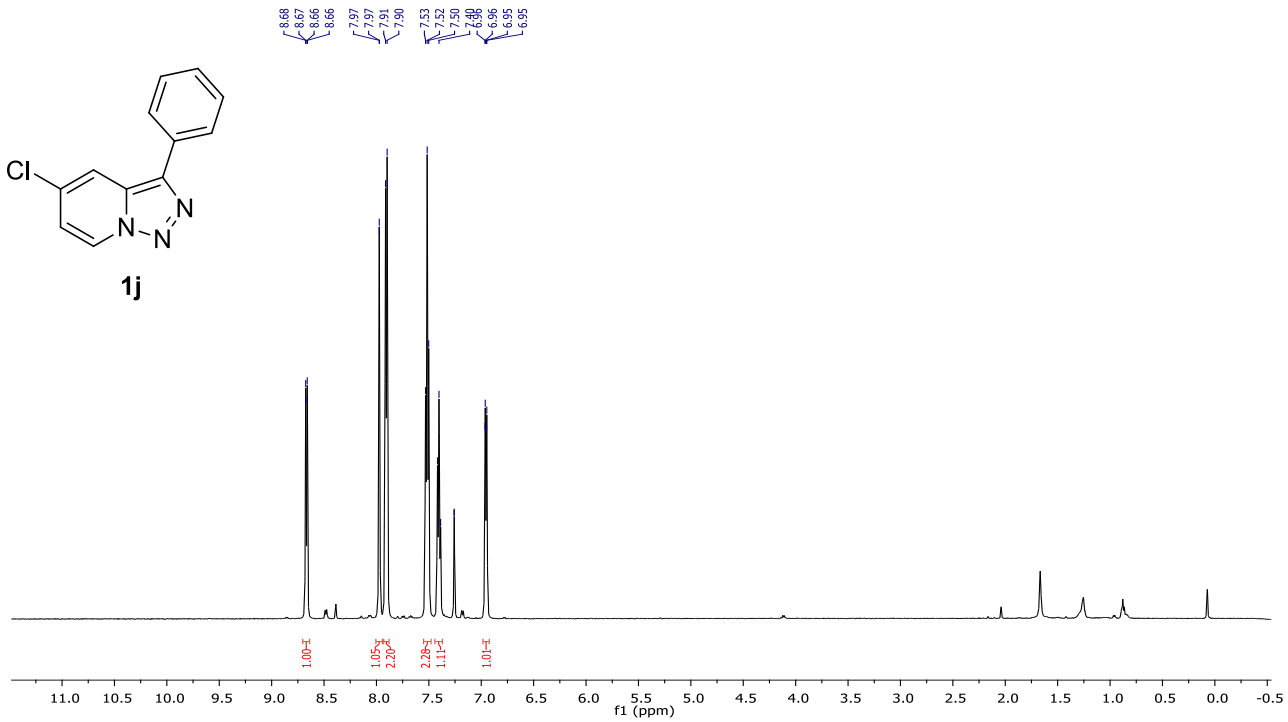


NOESY **11ak'**

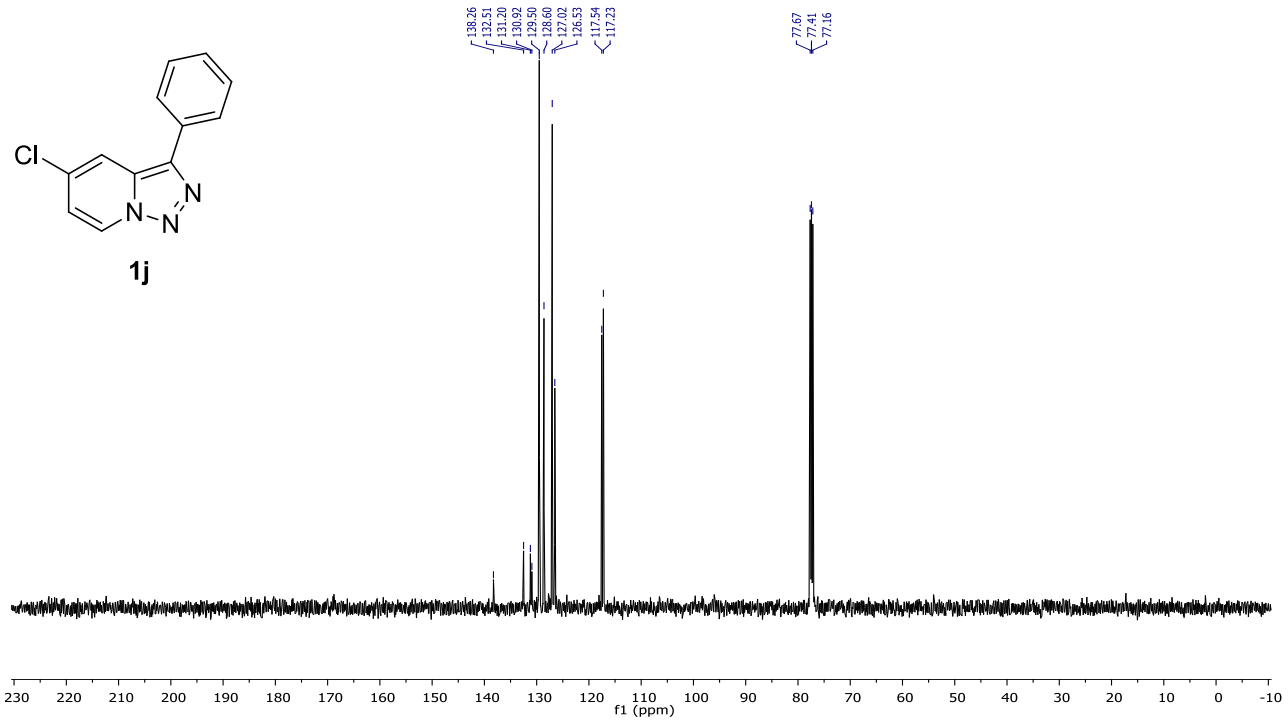


7. NMR Spectral Data

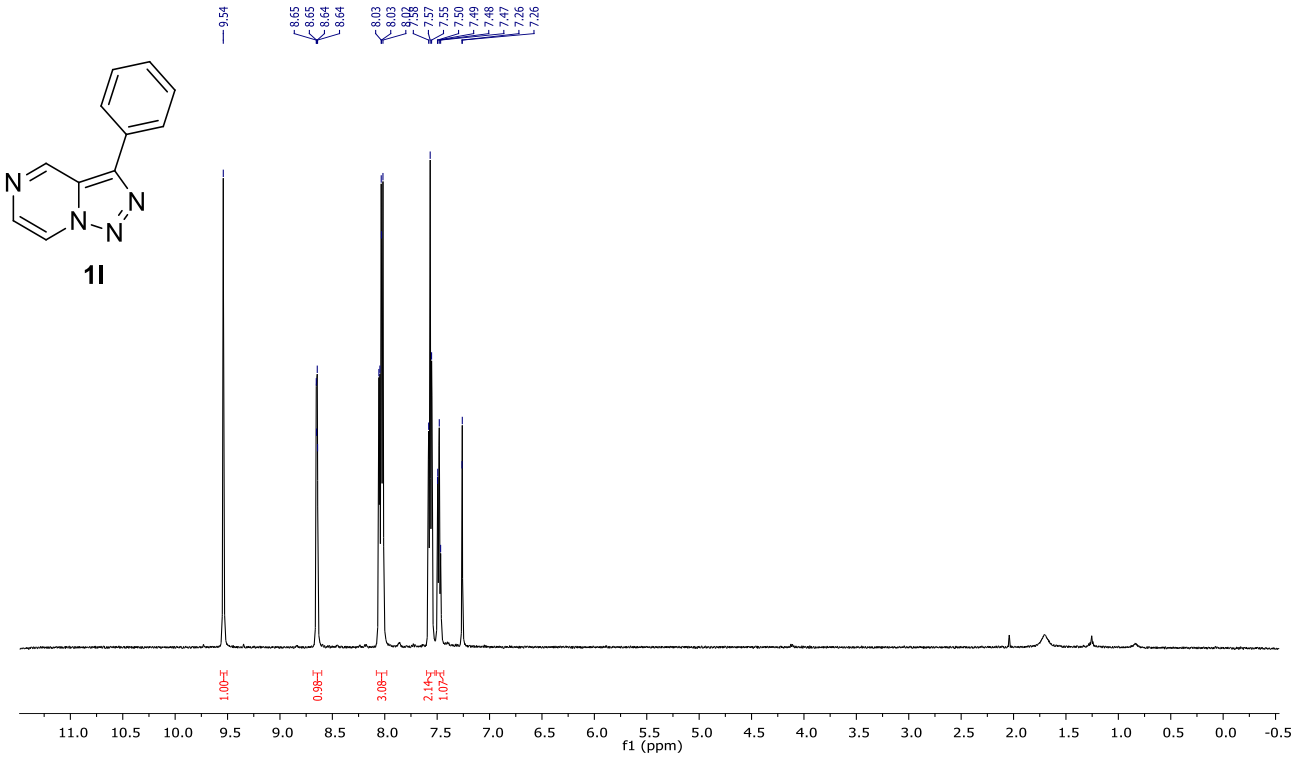
1H NMR of **1j**



^{13}C NMR of **1j**

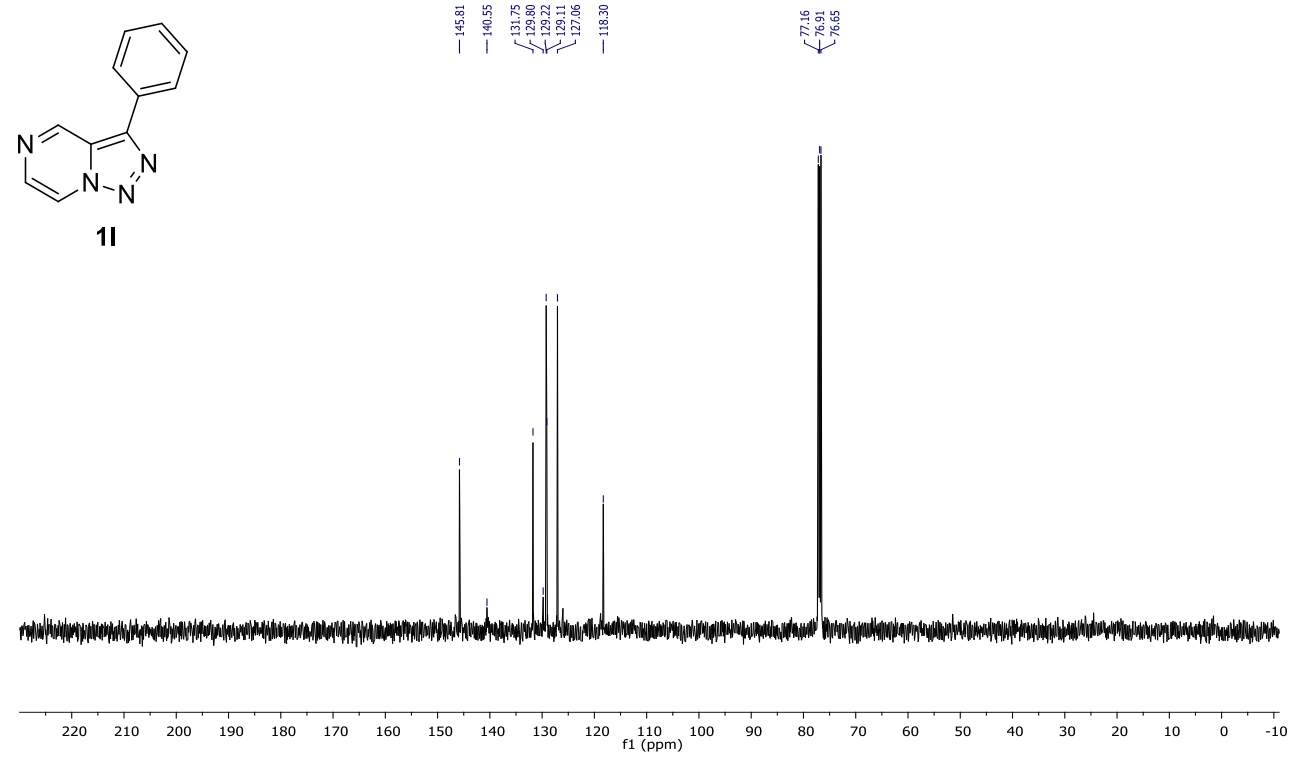


^{1}H NMR of **1l**



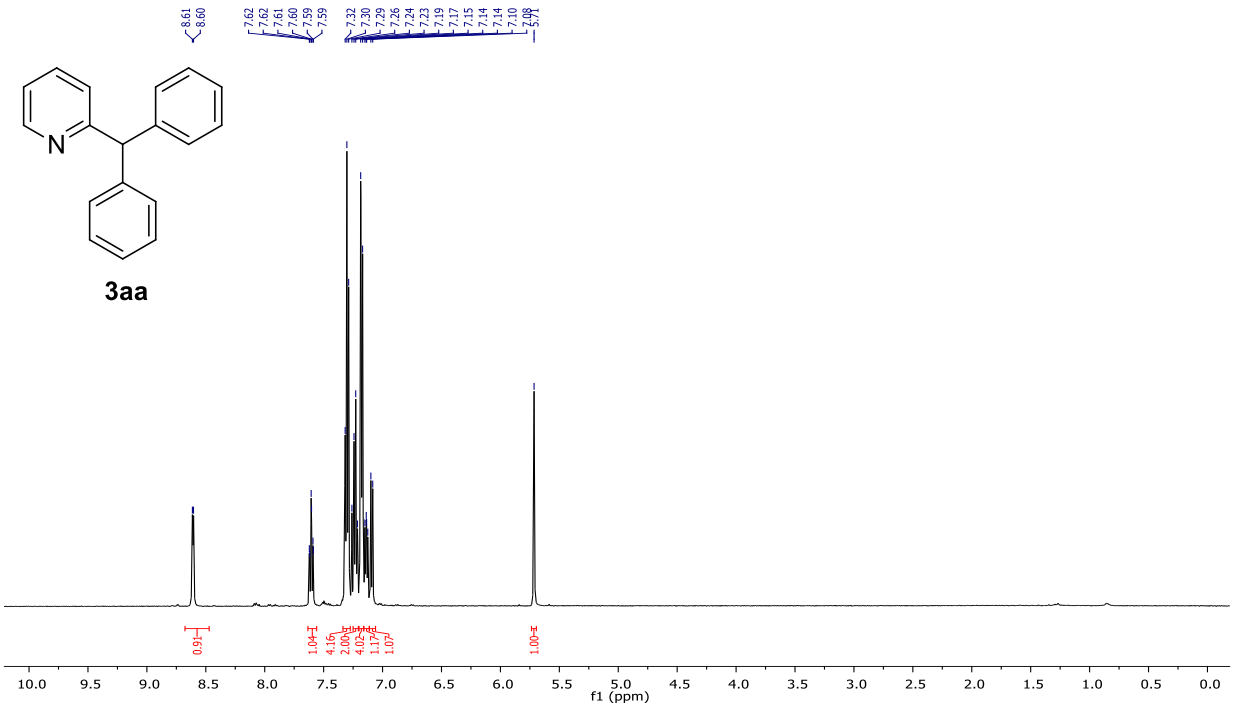
1l

^{13}C NMR of **1l**

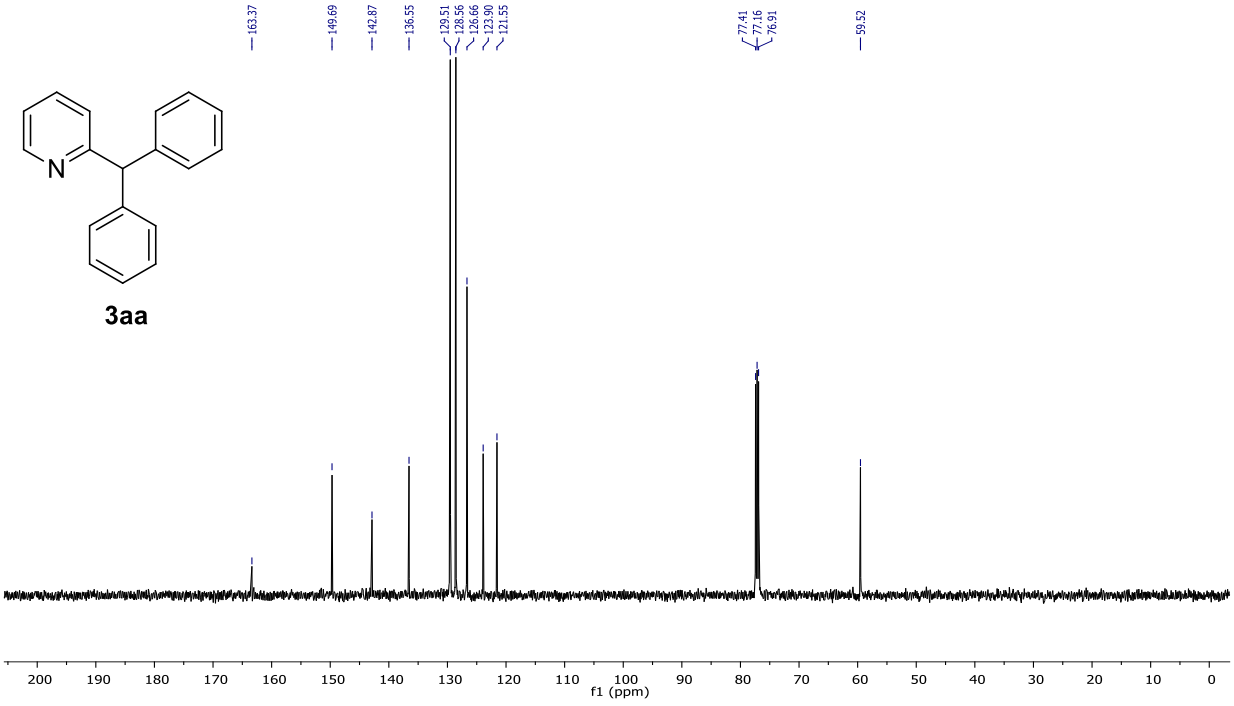


1l

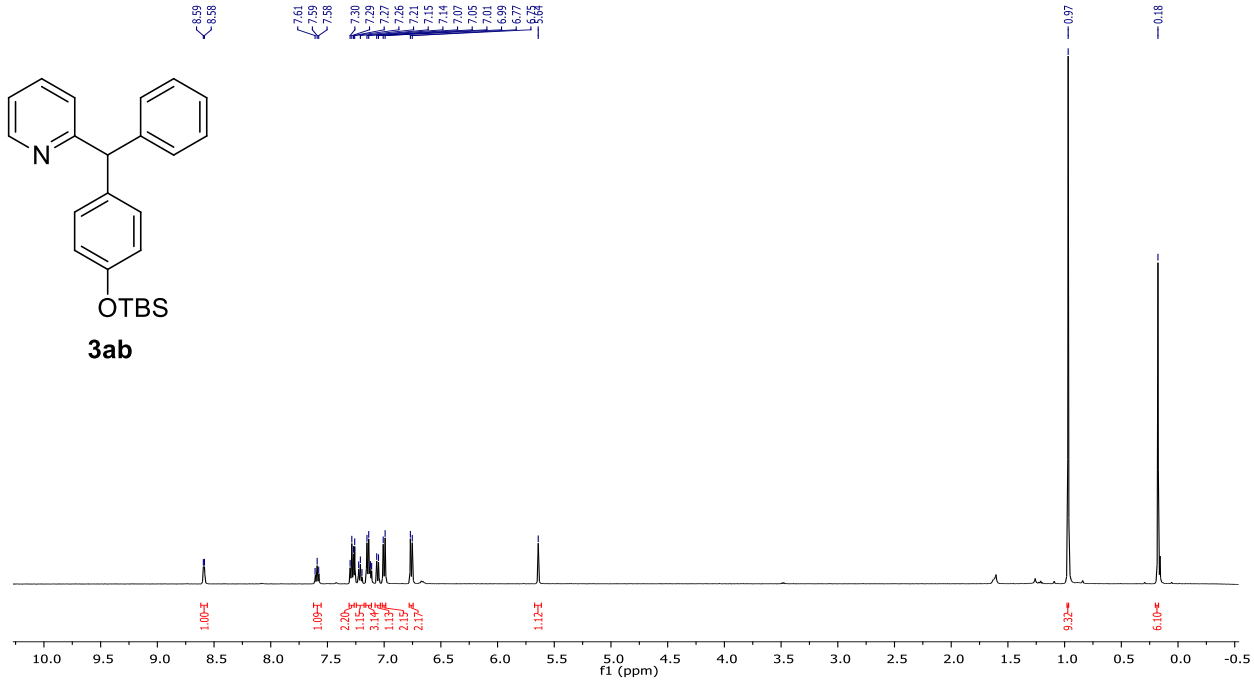
^{1}H NMR of **3aa**



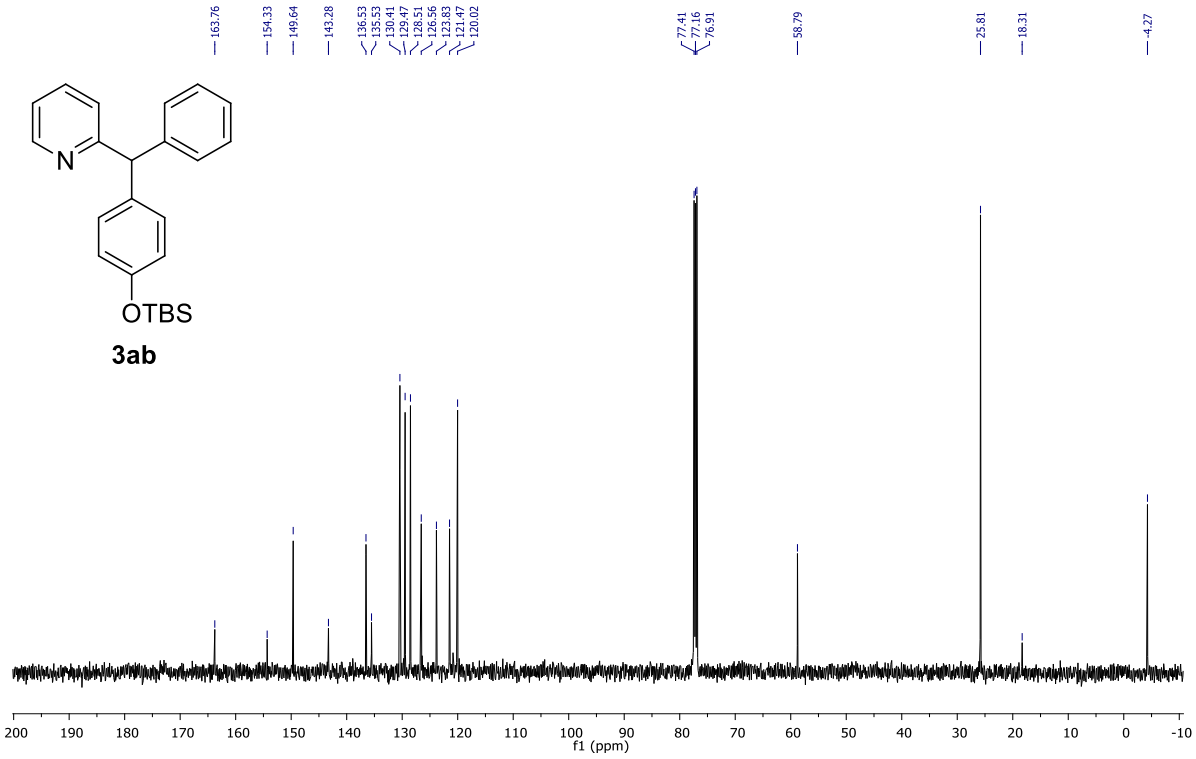
^{13}C NMR of **3aa**



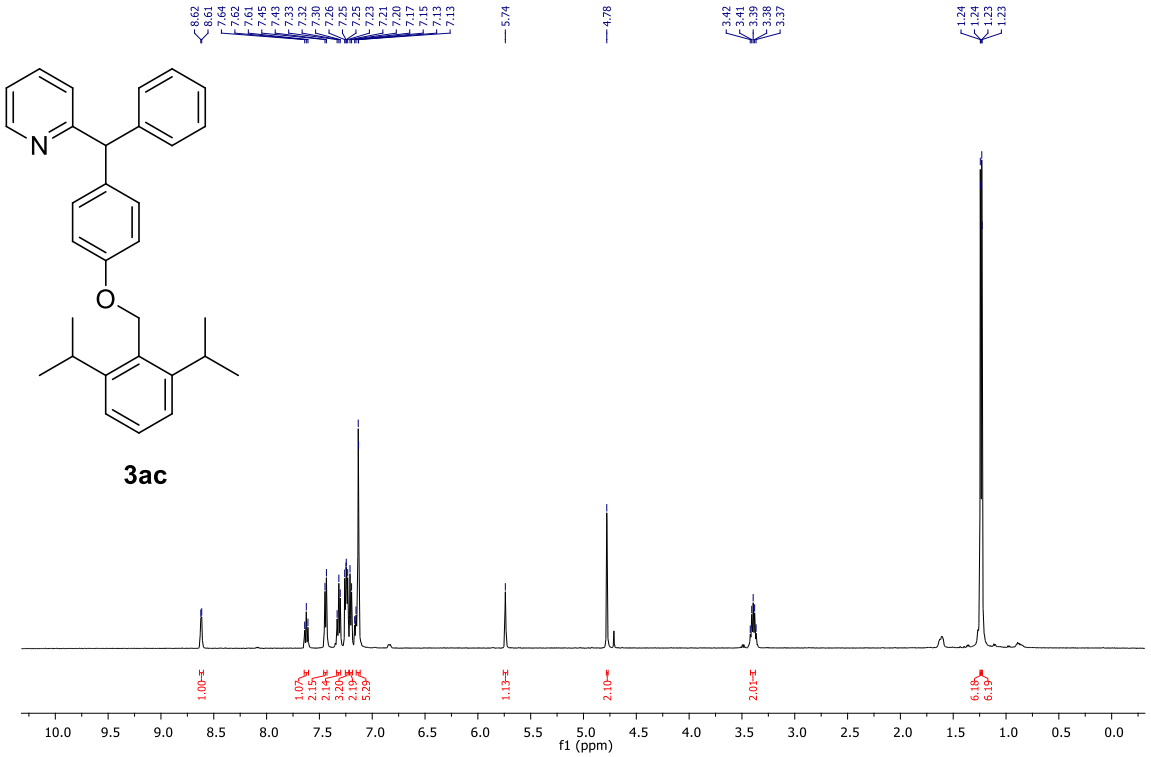
^{1}H NMR of **3ab**



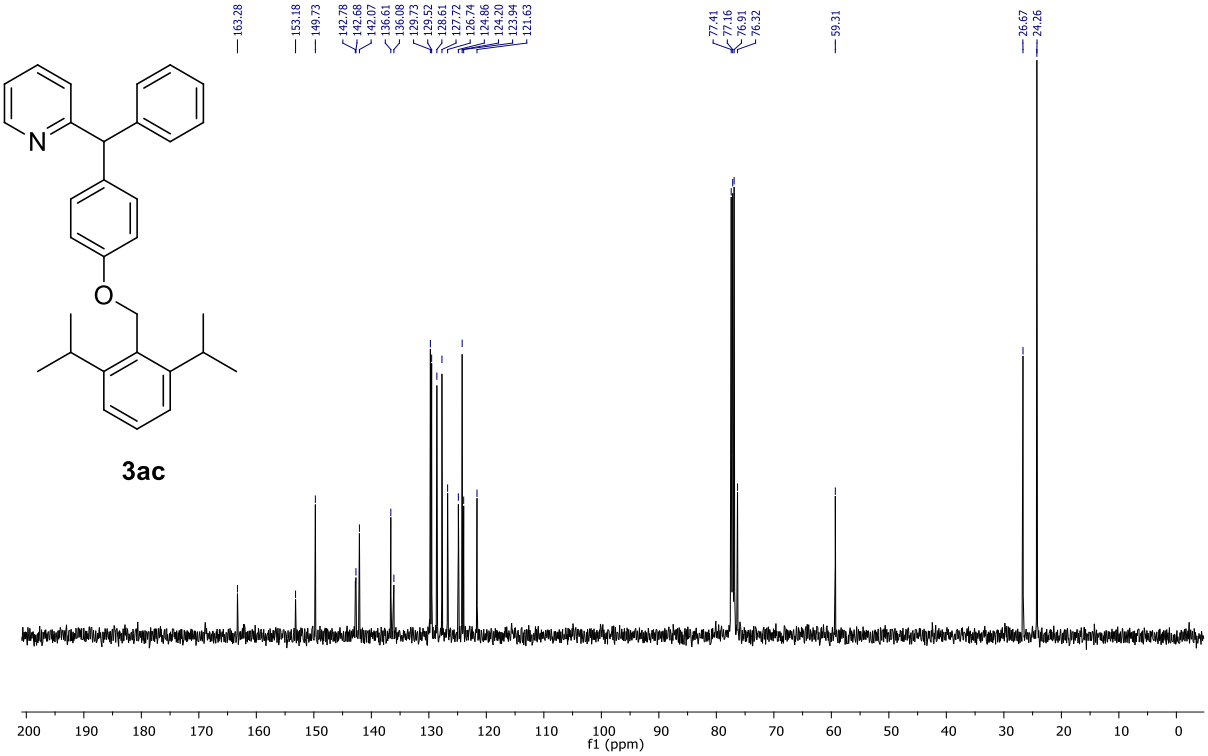
^{13}C NMR of **3ab**



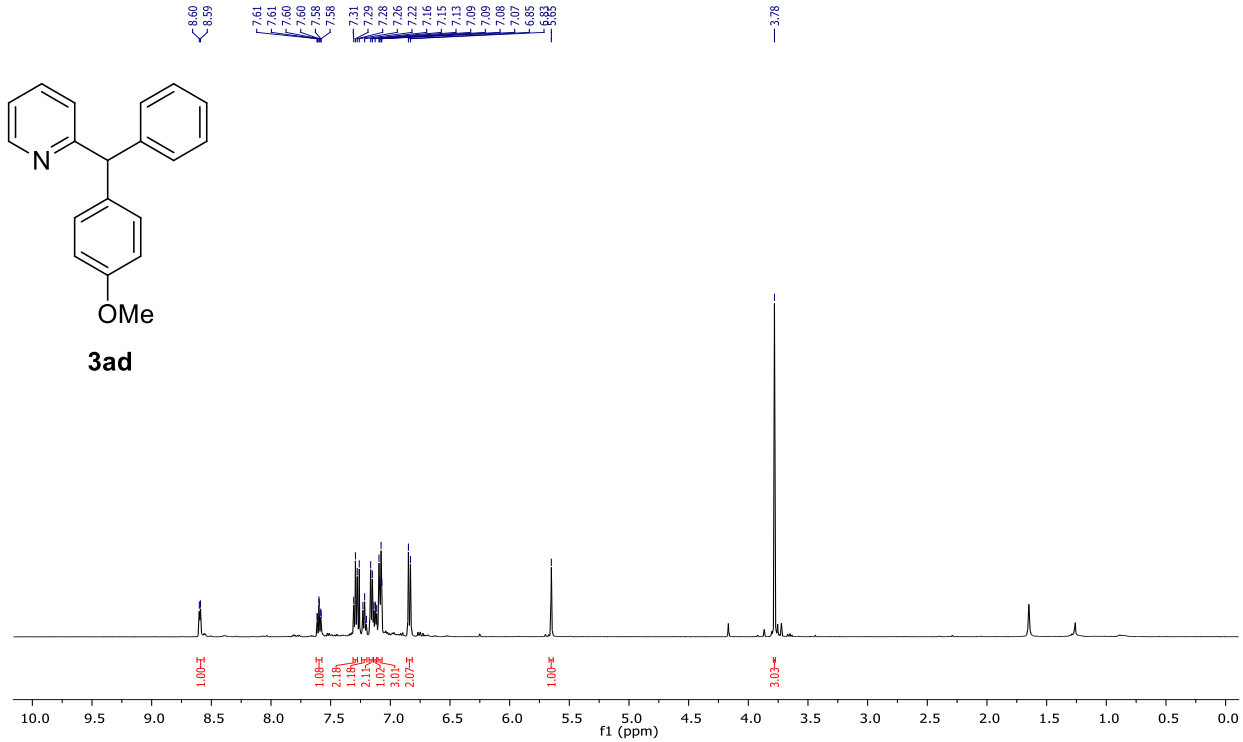
^{1}H NMR of **3ac**



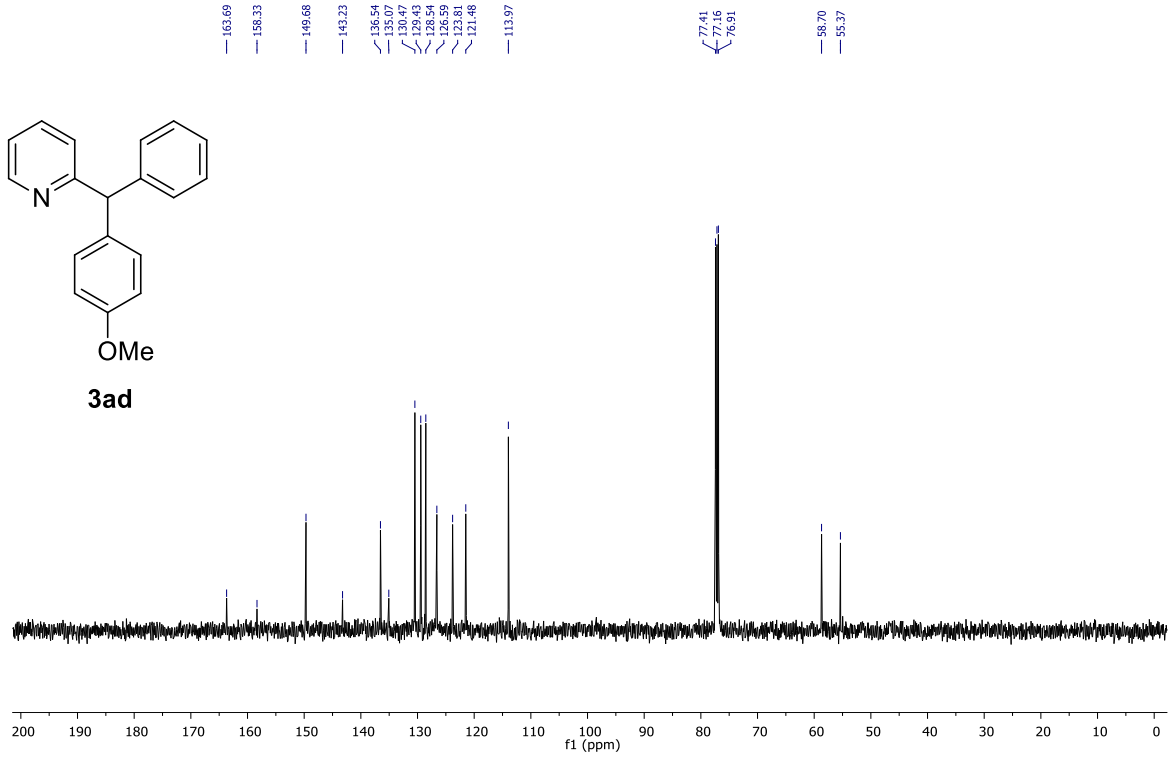
^{13}C NMR of **3ac**



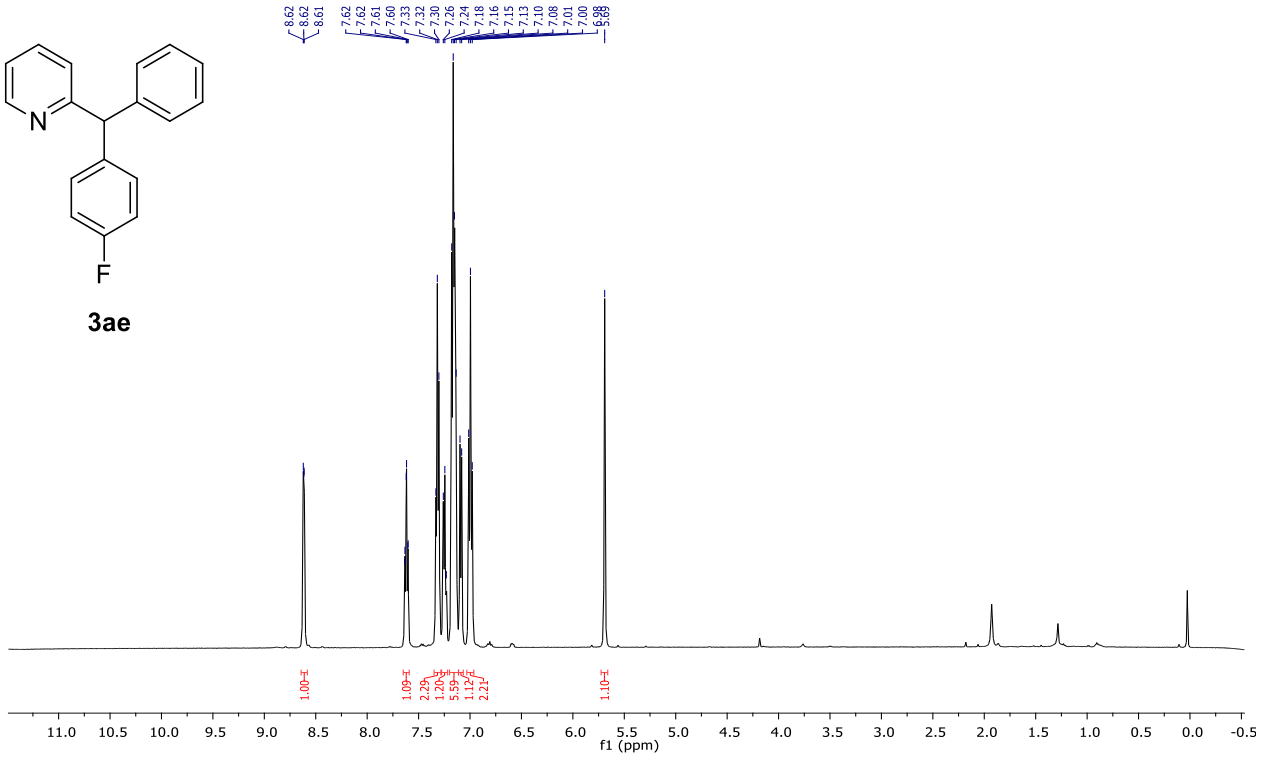
^{1}H NMR of **3ad**



^{13}C NMR of **3ad**

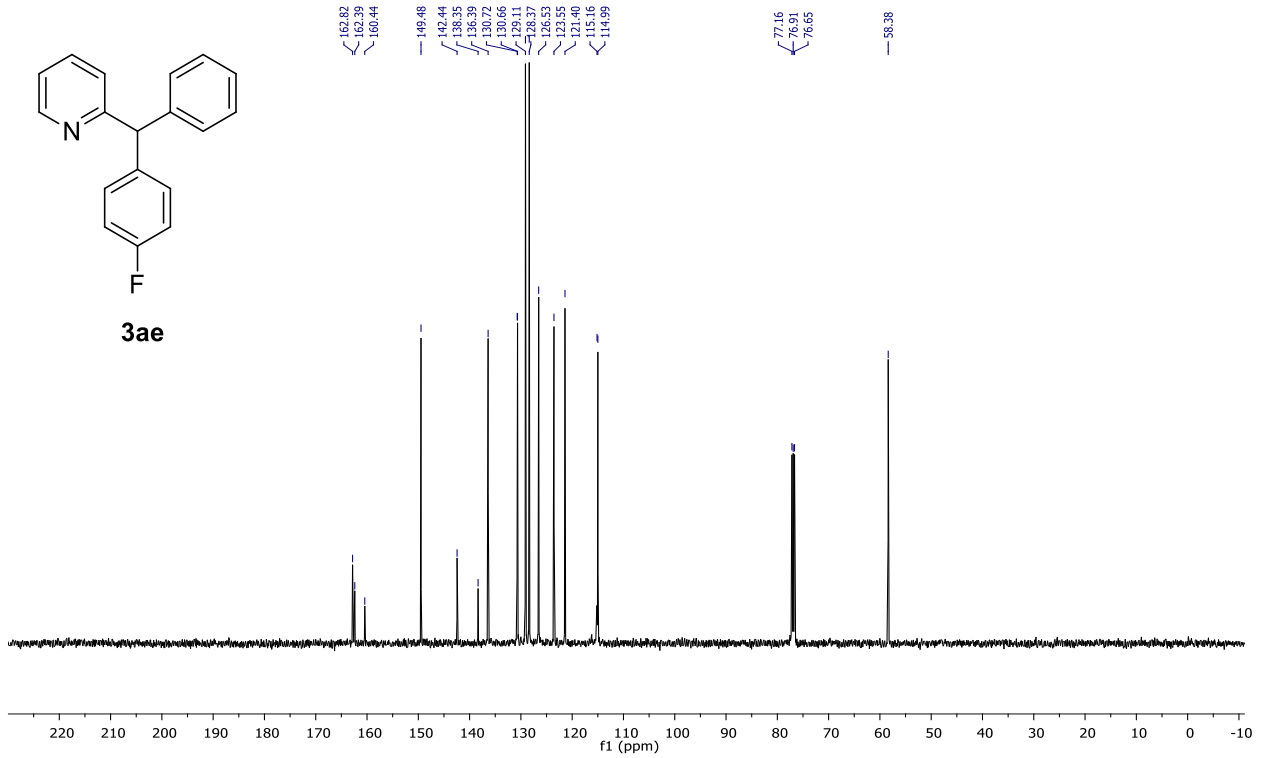


^{1}H NMR of **3ae**



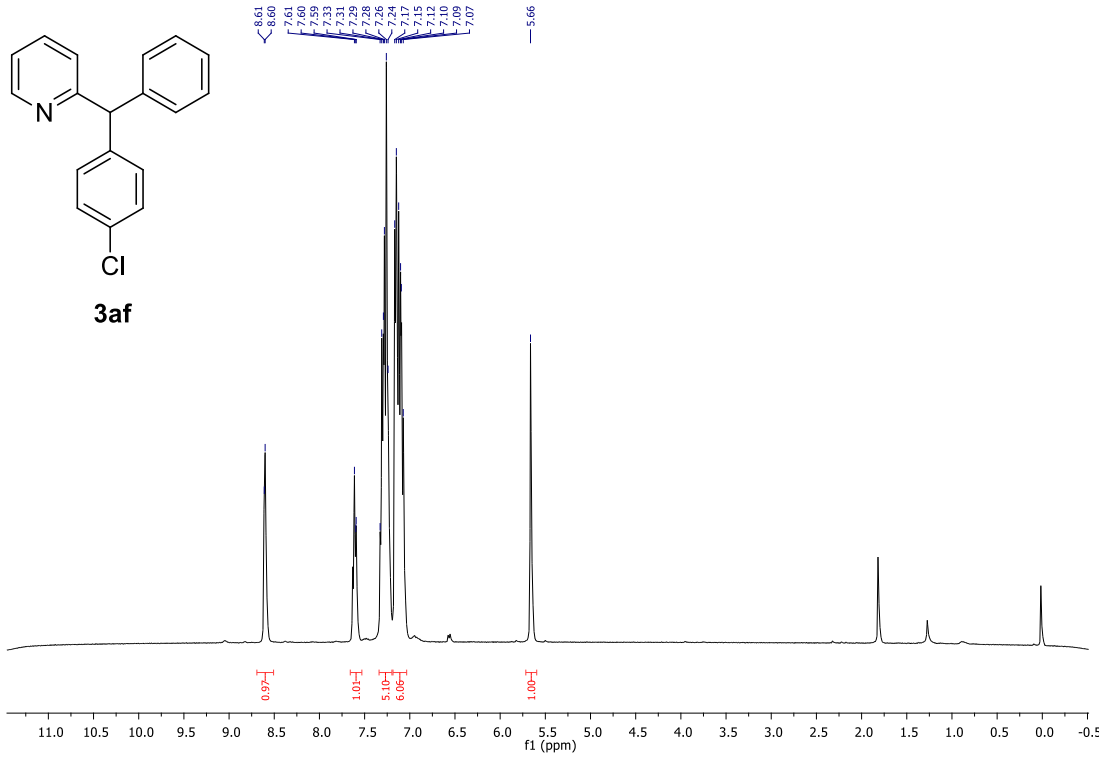
3ae

^{13}C NMR of **3ae**

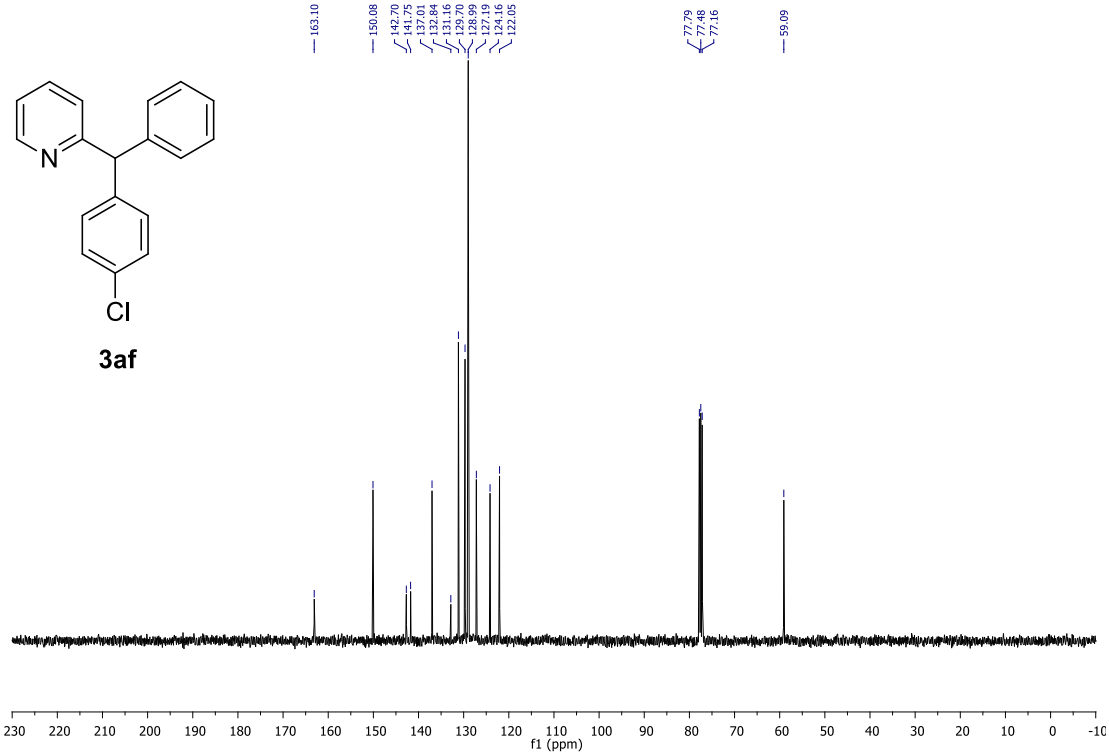


3ae

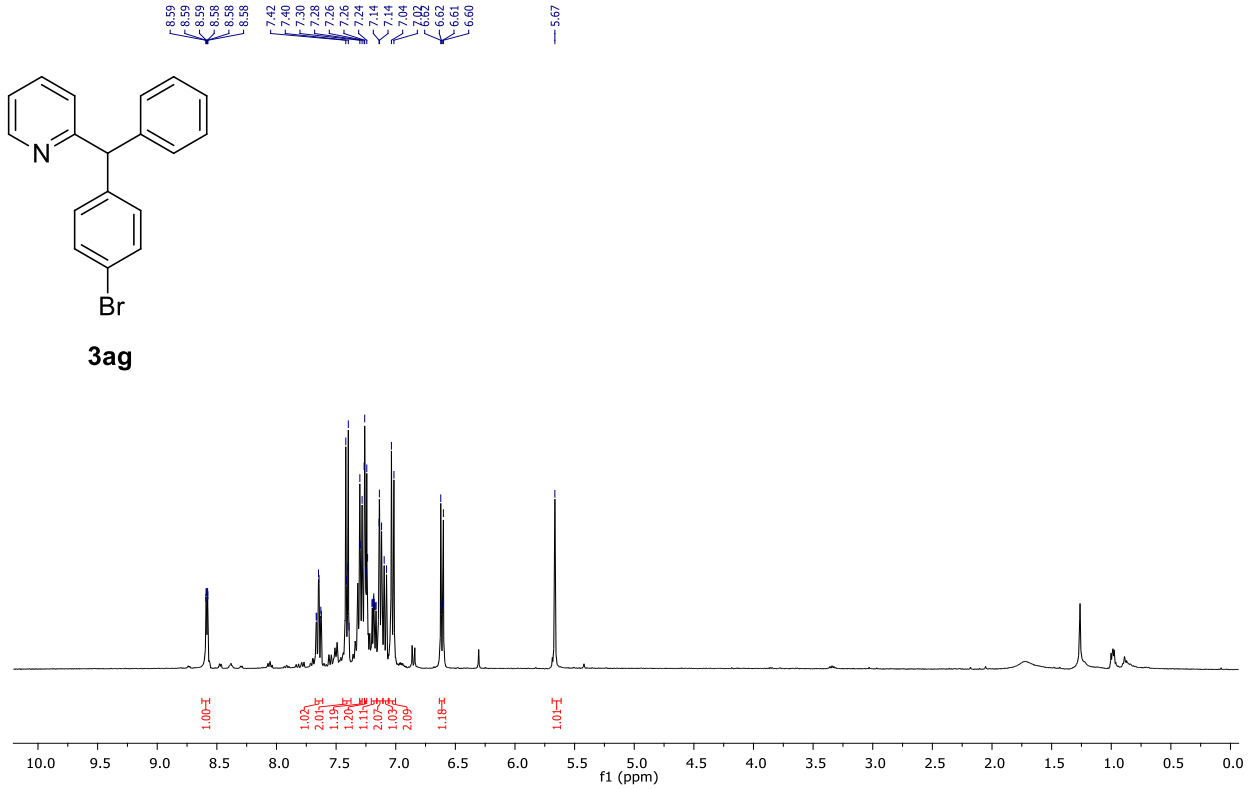
^{1}H NMR of **3af**



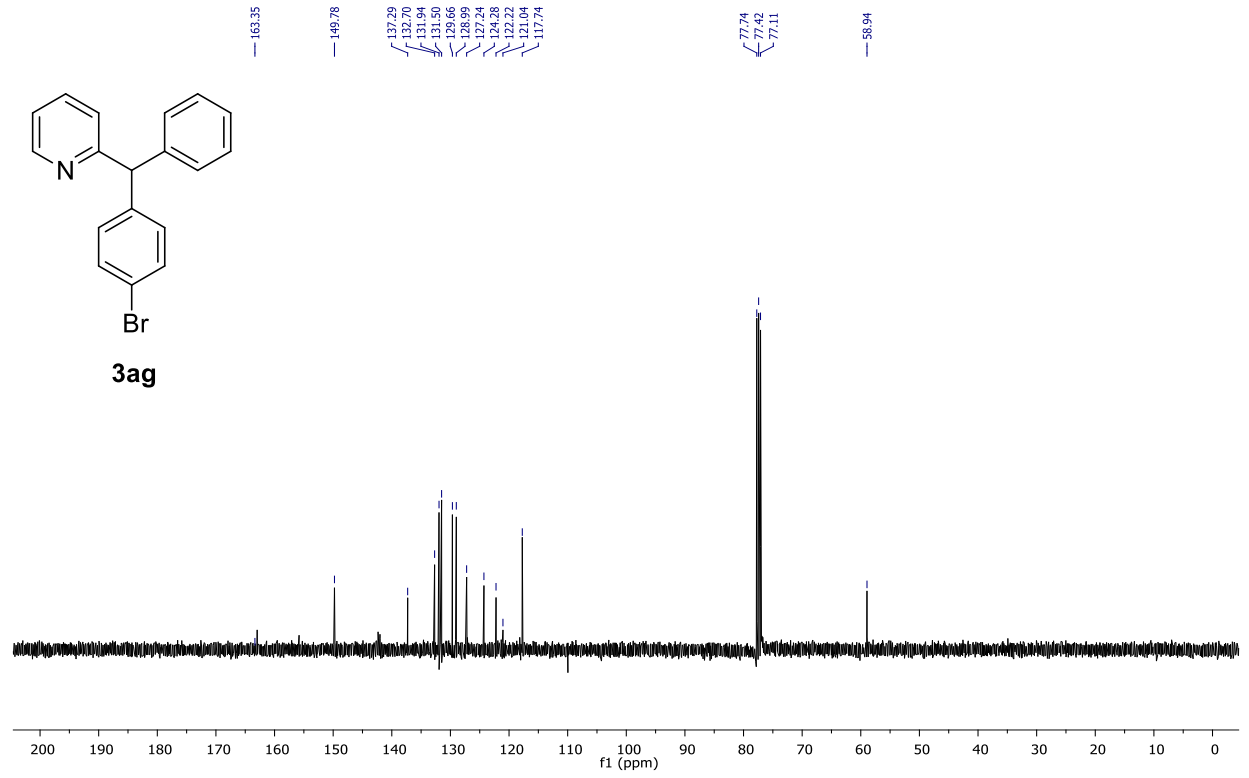
^{13}C NMR of **3af**



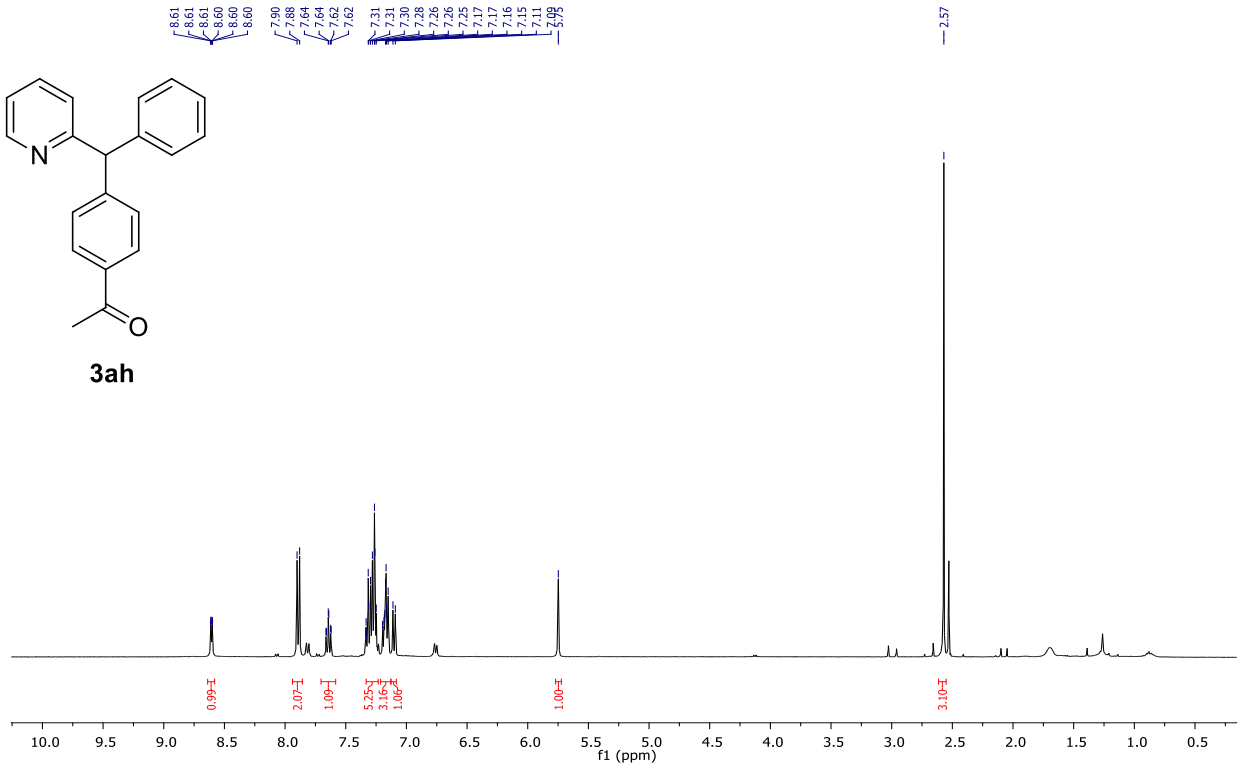
^{1}H NMR of **3ag**



^{13}C NMR of **3ag**

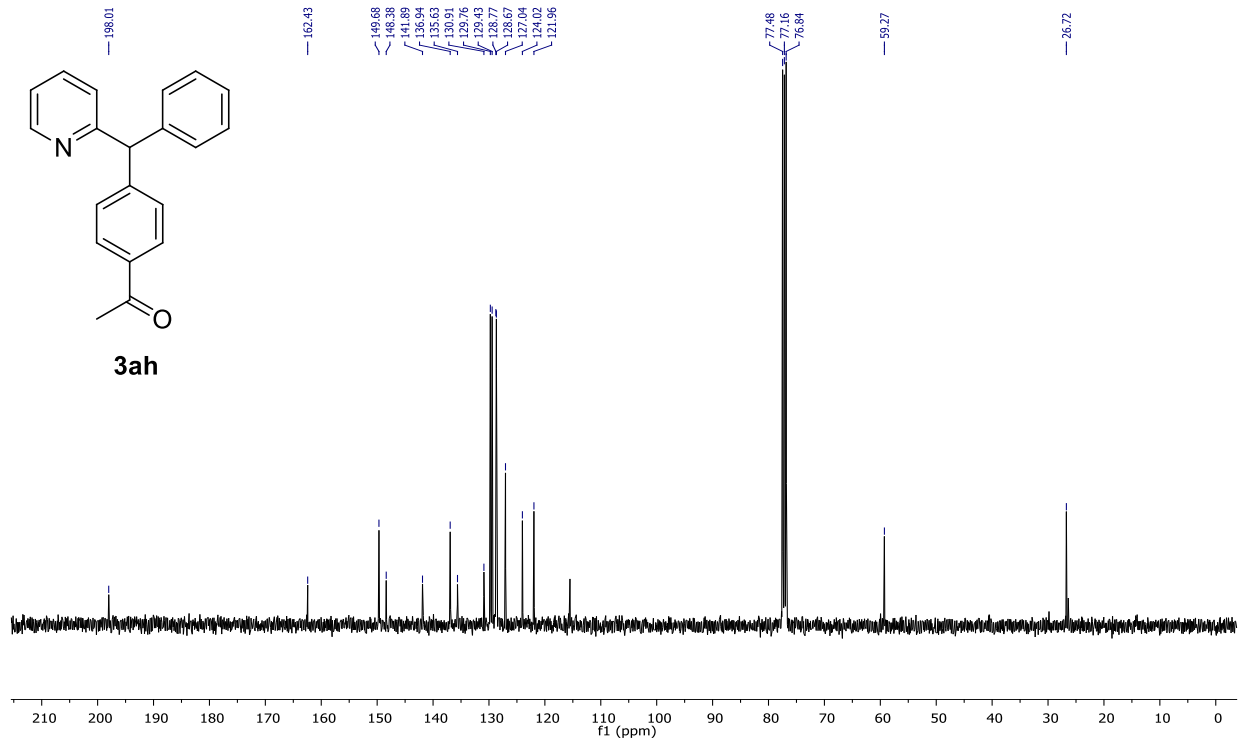


^{1}H NMR of **3ah**



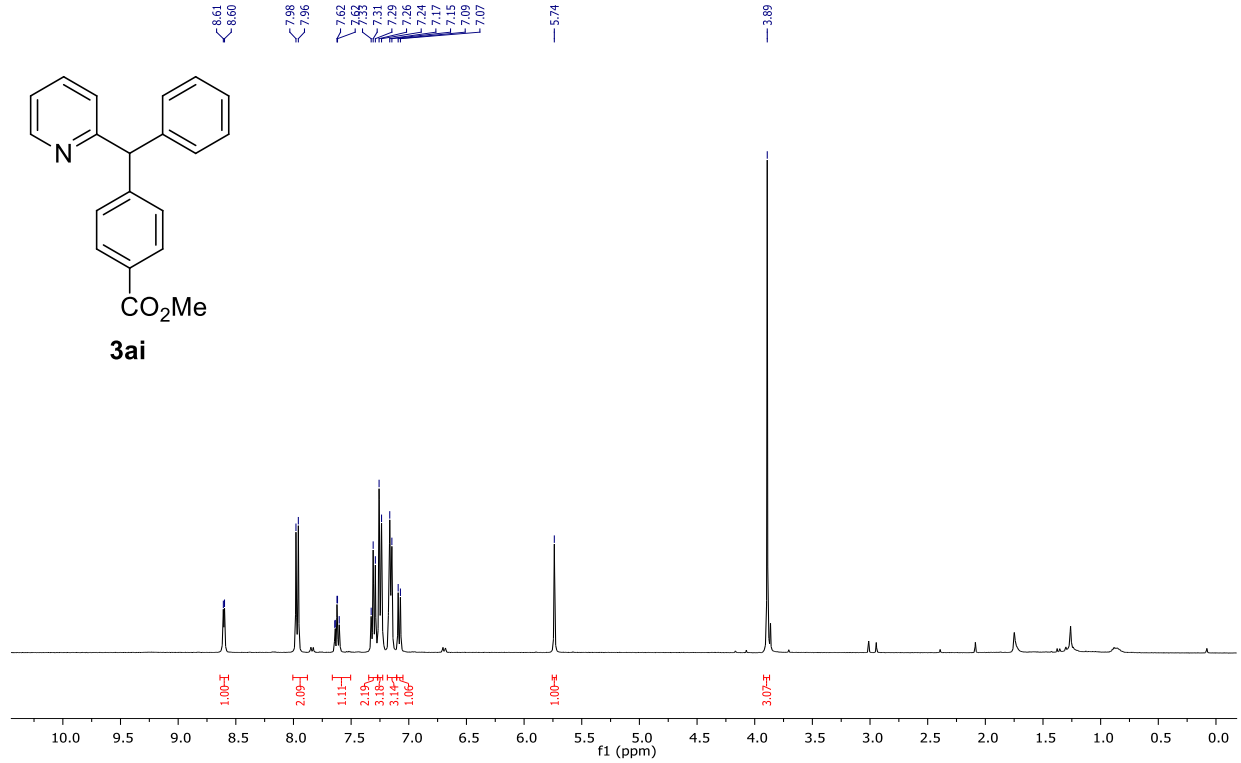
3ah

^{13}C NMR of **3ah**

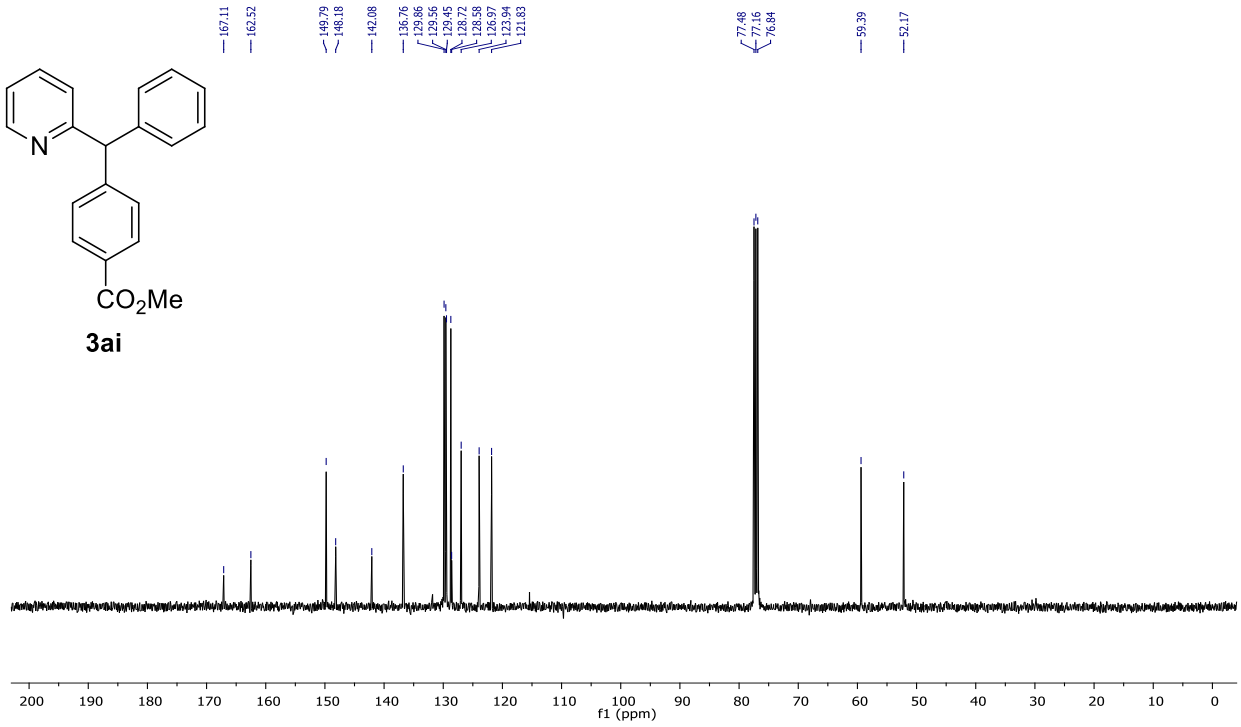


3ah

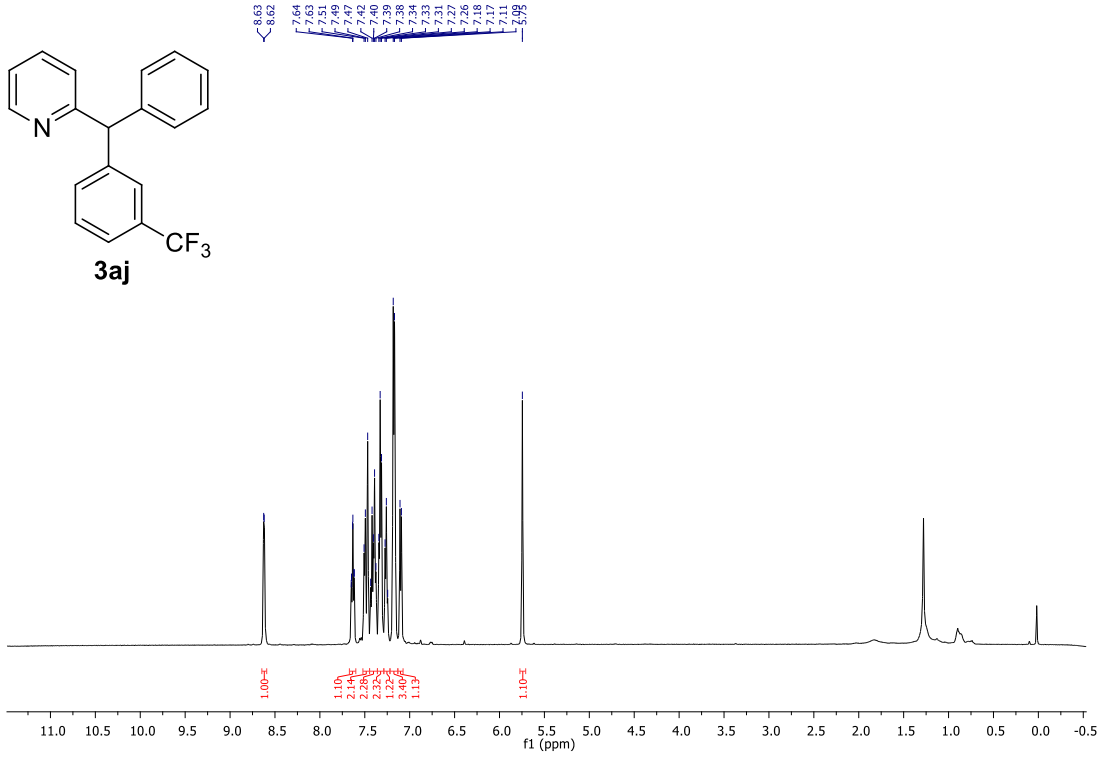
^{1}H NMR of **3ai**



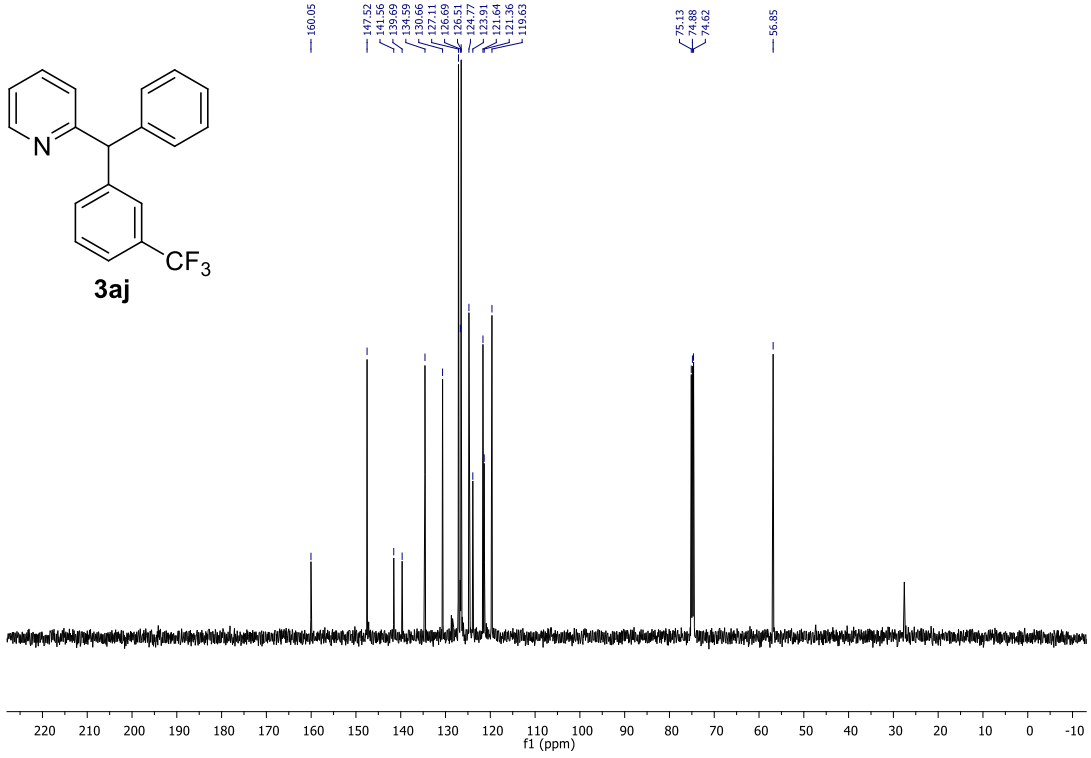
^{13}C NMR of **3ai**



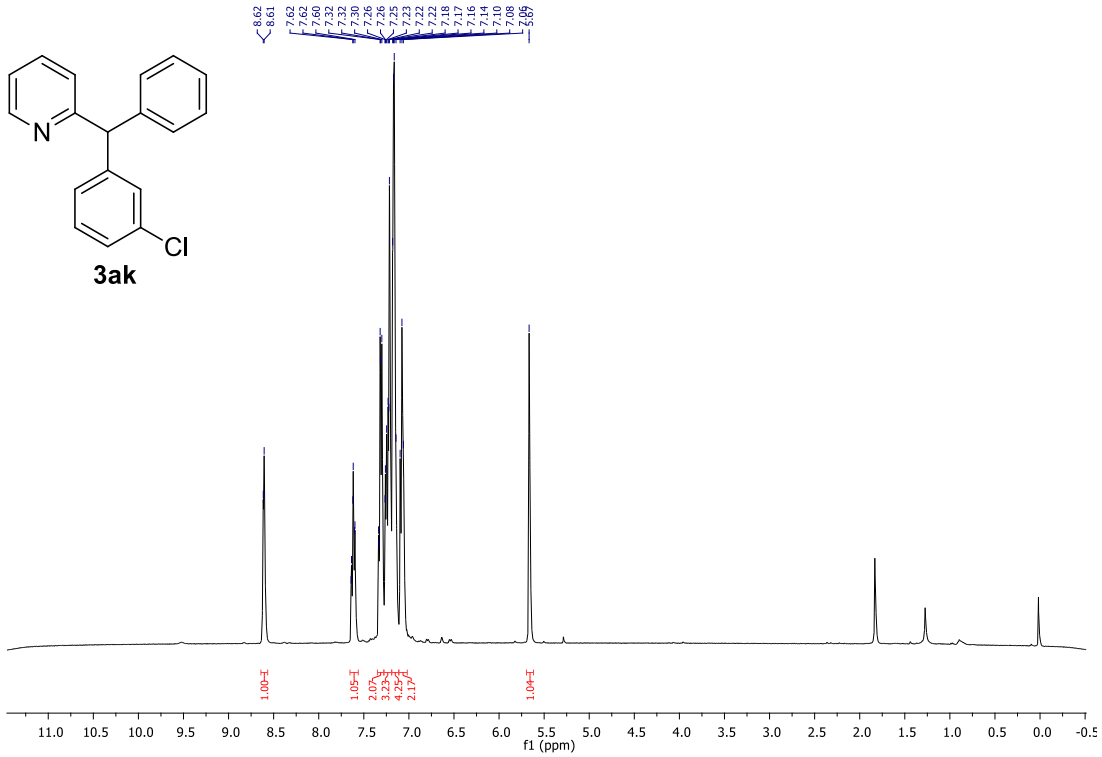
^{1}H NMR of **3aj**



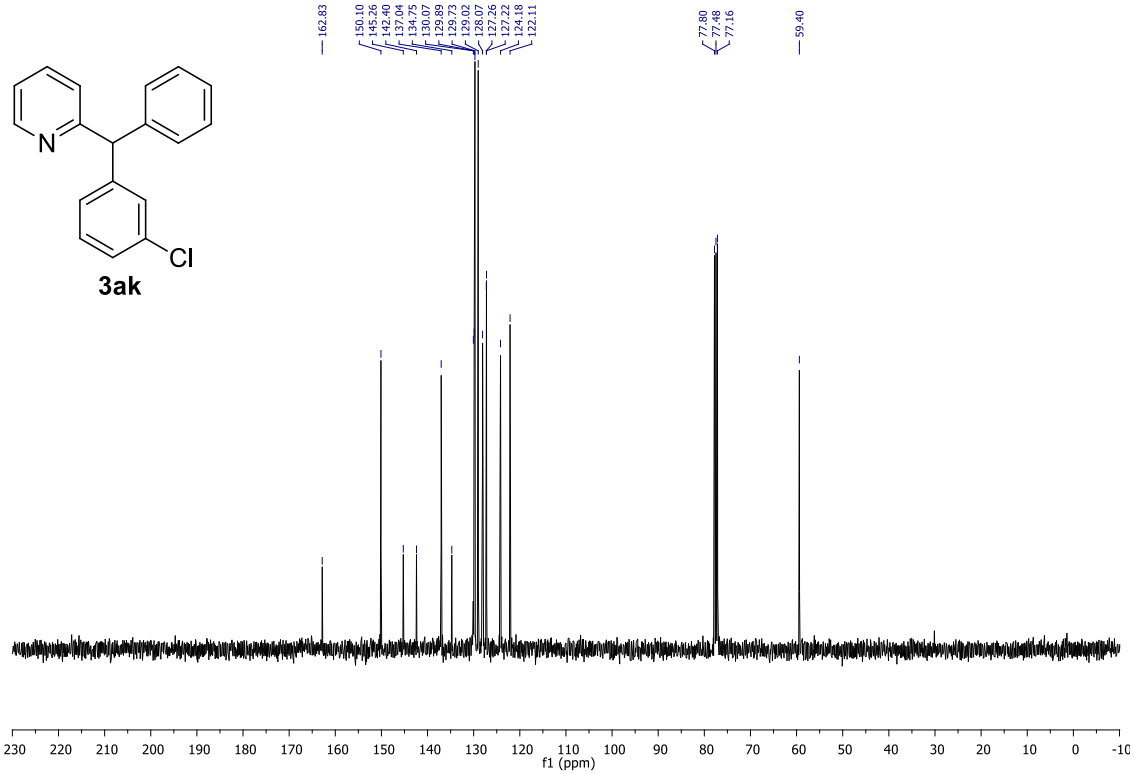
^{13}C NMR of **3aj**



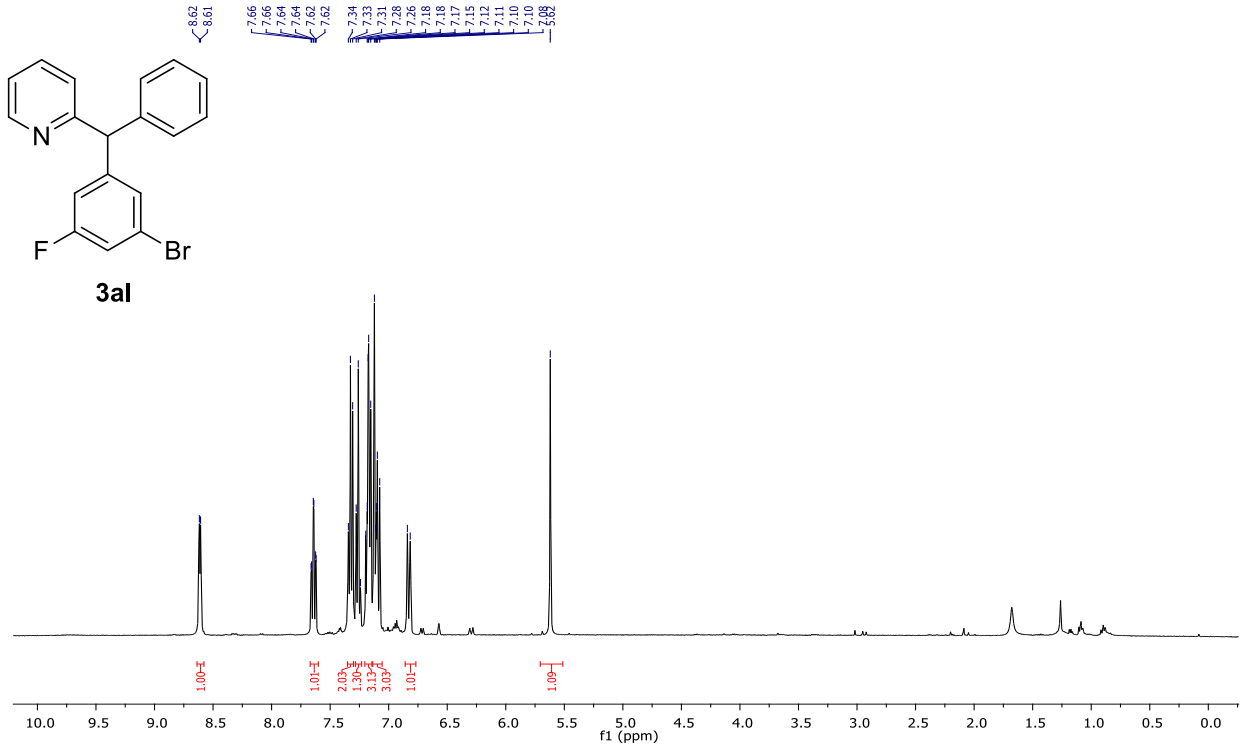
^{1}H NMR of **3ak**



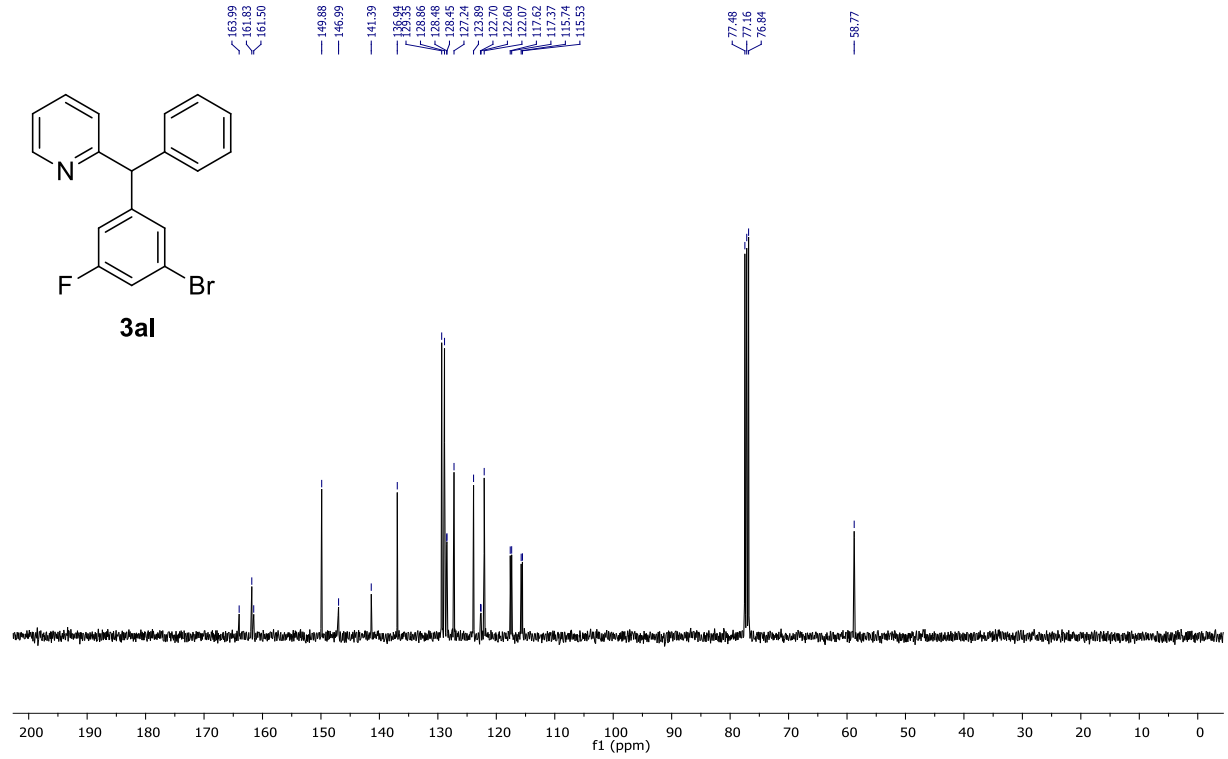
^{13}C NMR of **3ak**



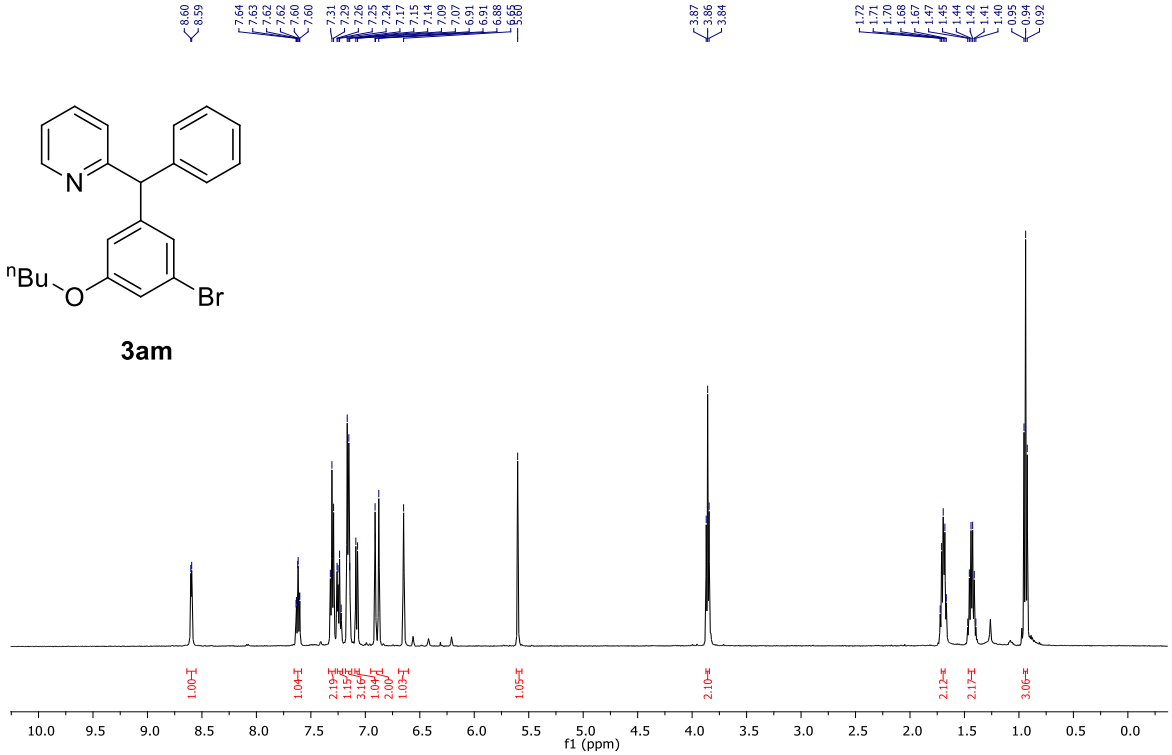
^{1}H NMR of **3al**



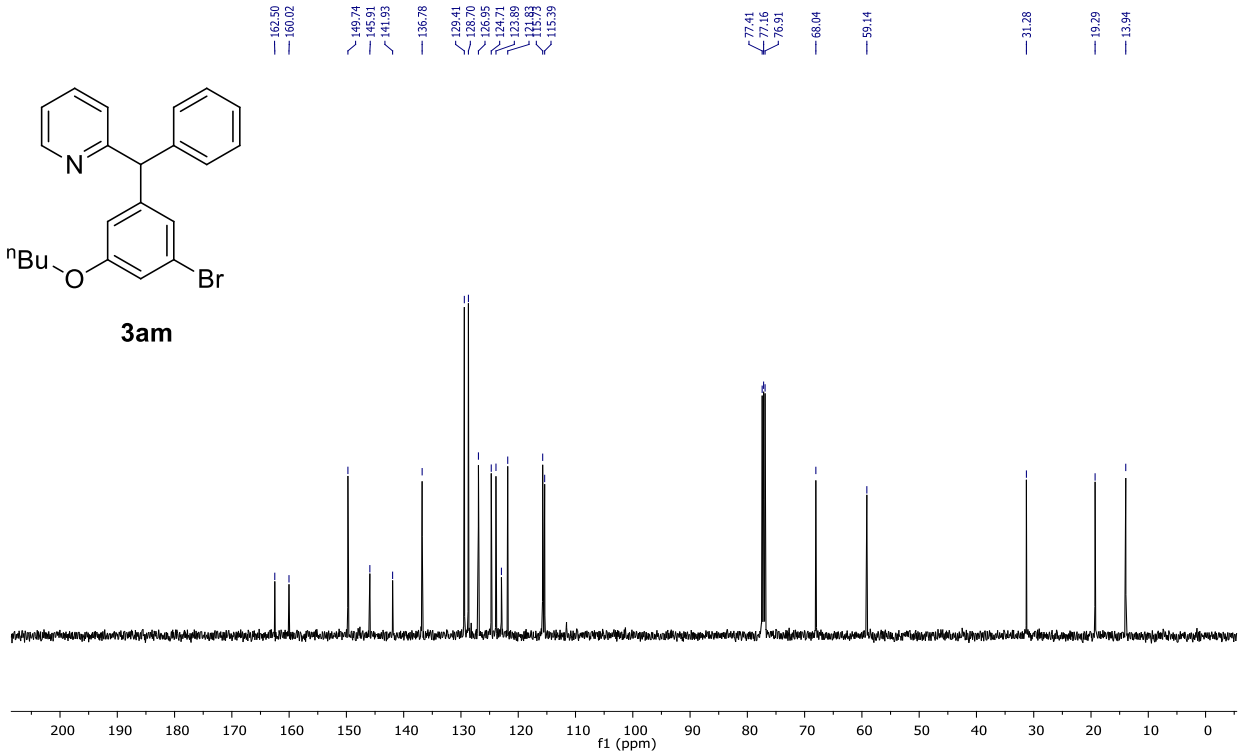
^{13}C NMR of **3al**



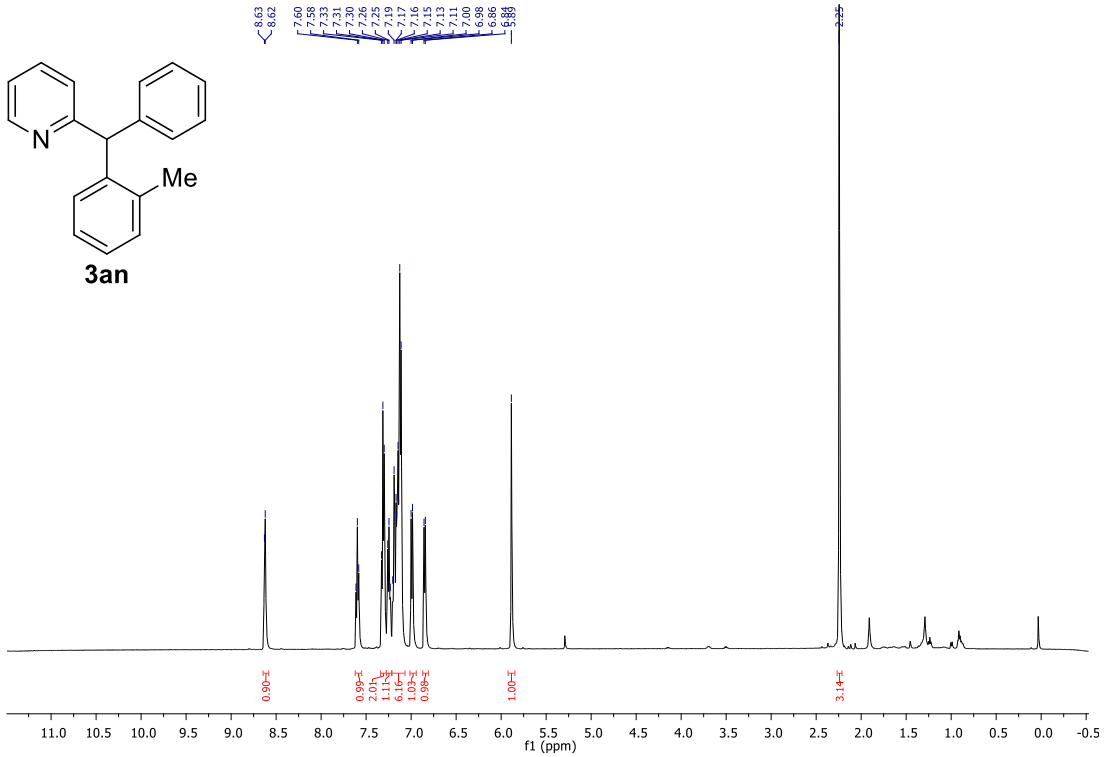
^{1}H NMR of **3am**



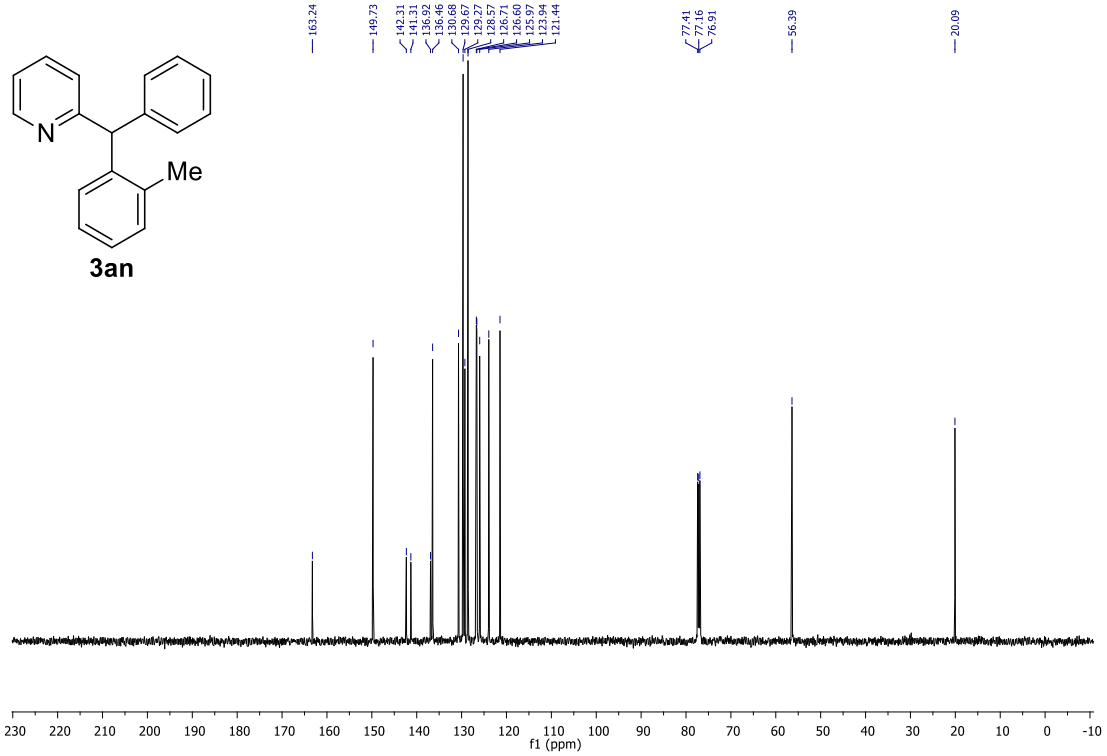
^{13}C NMR of **3am**



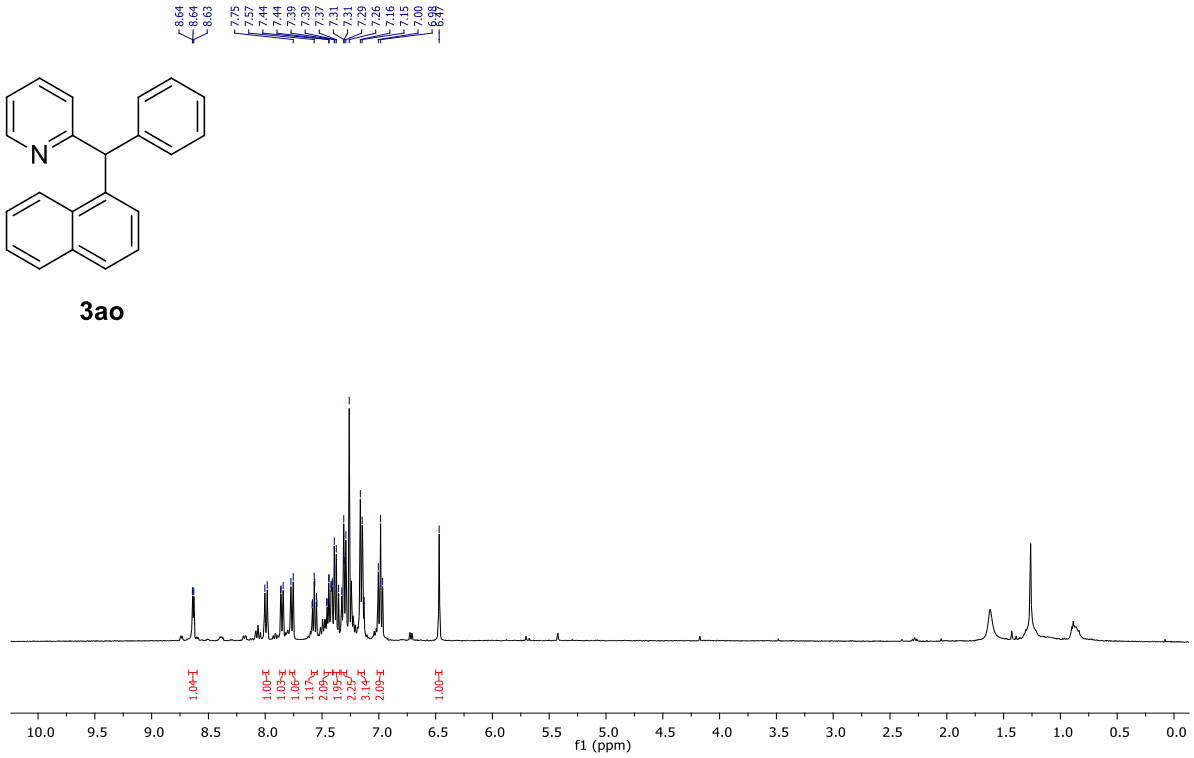
^{1}H NMR of **3an**



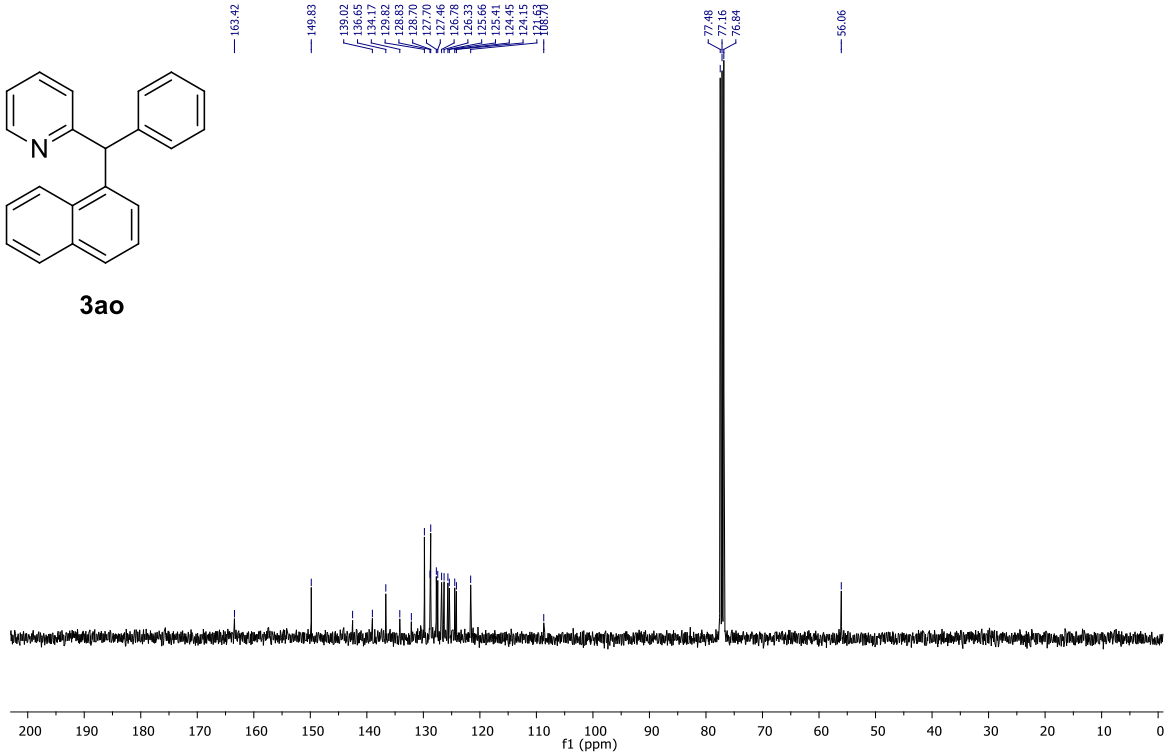
^{13}C NMR of **3an**



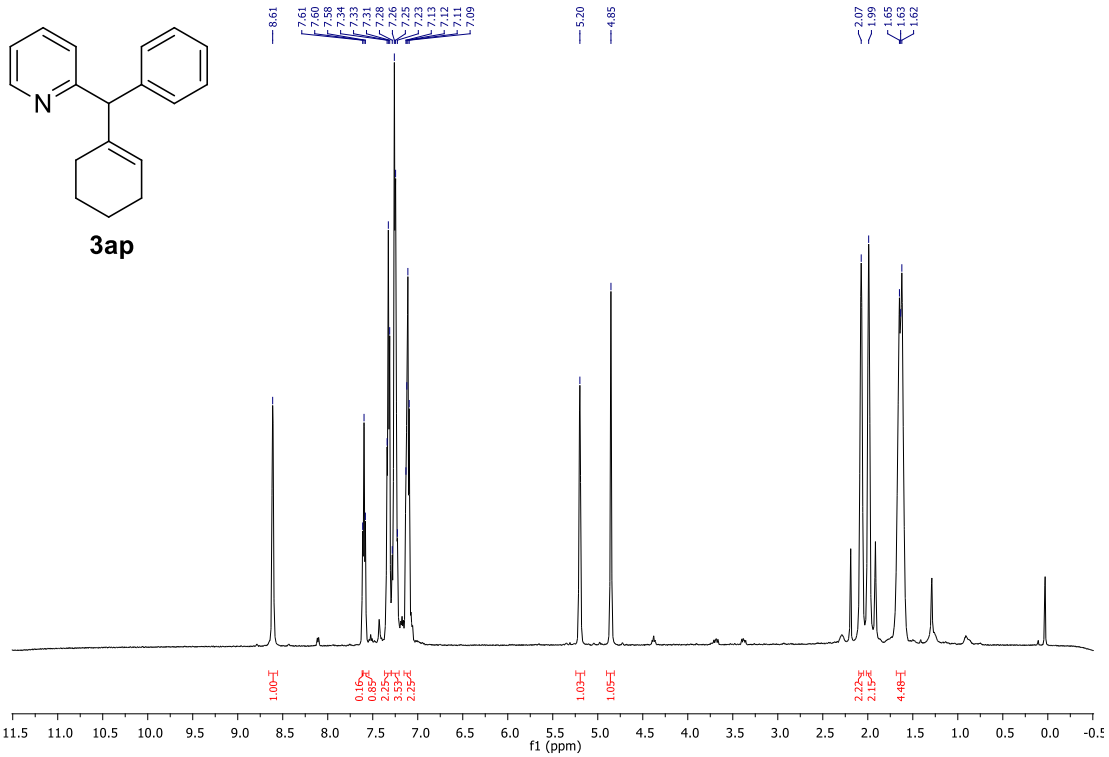
^{1}H NMR of **3ao**



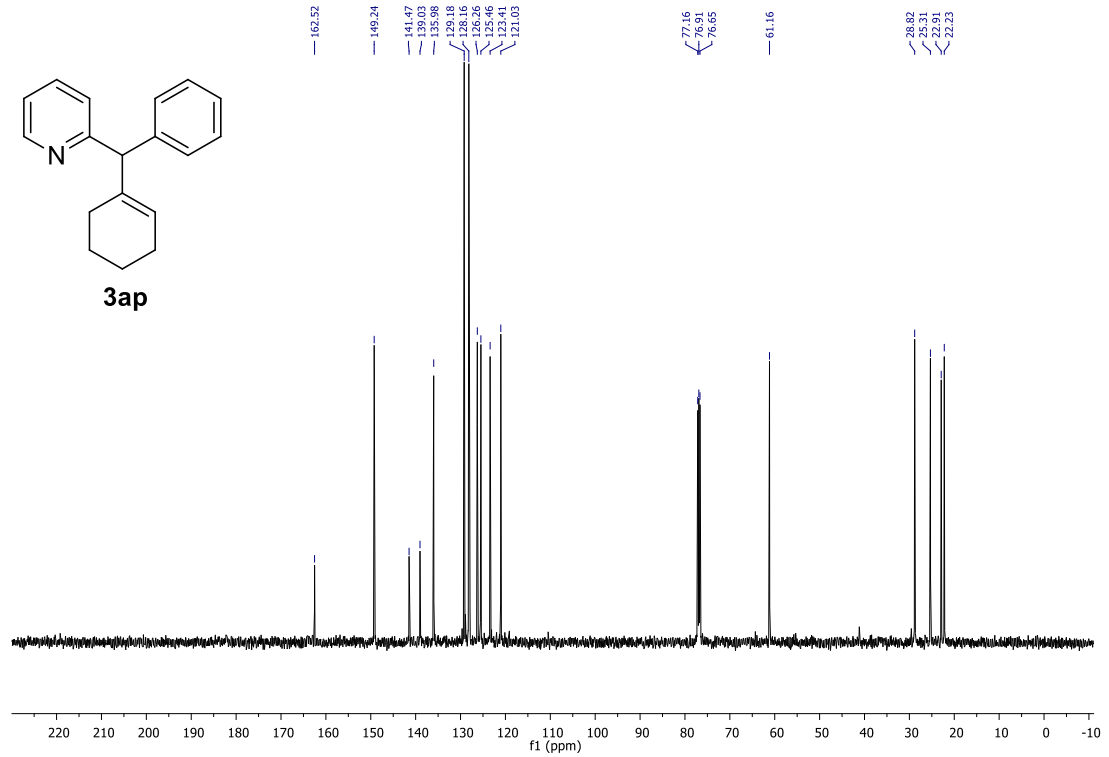
^{13}C NMR of **3ao**



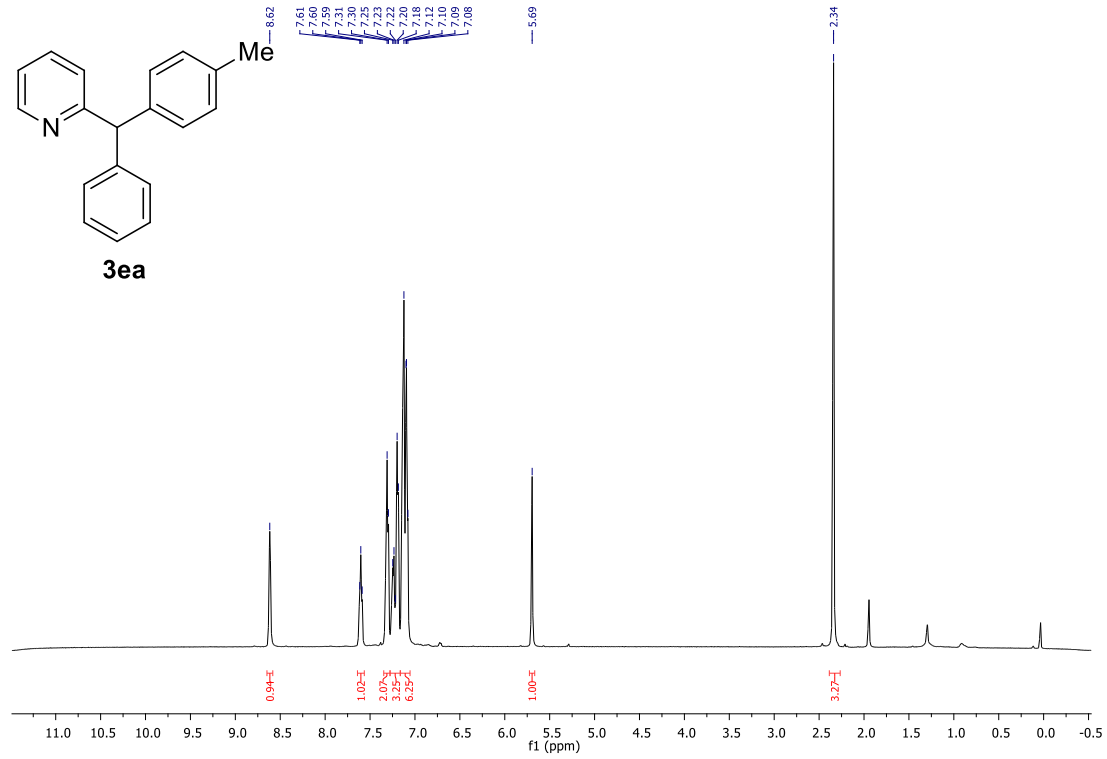
^{1}H NMR of **3ap**



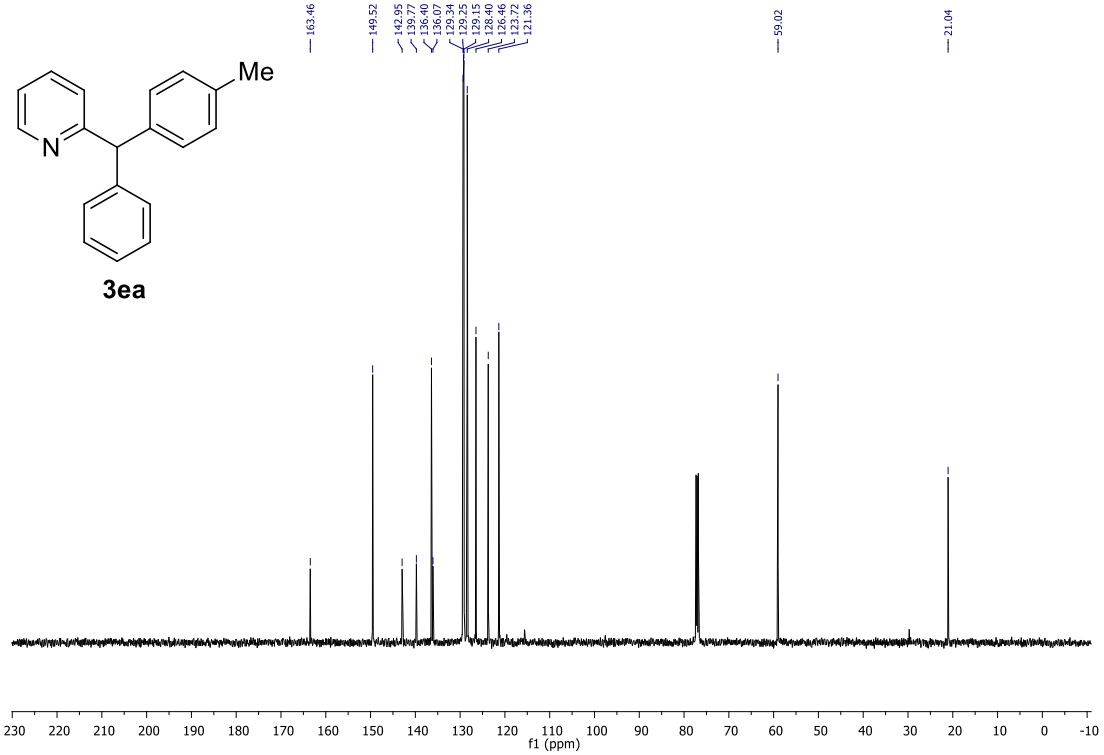
^{13}C NMR of **3ap**



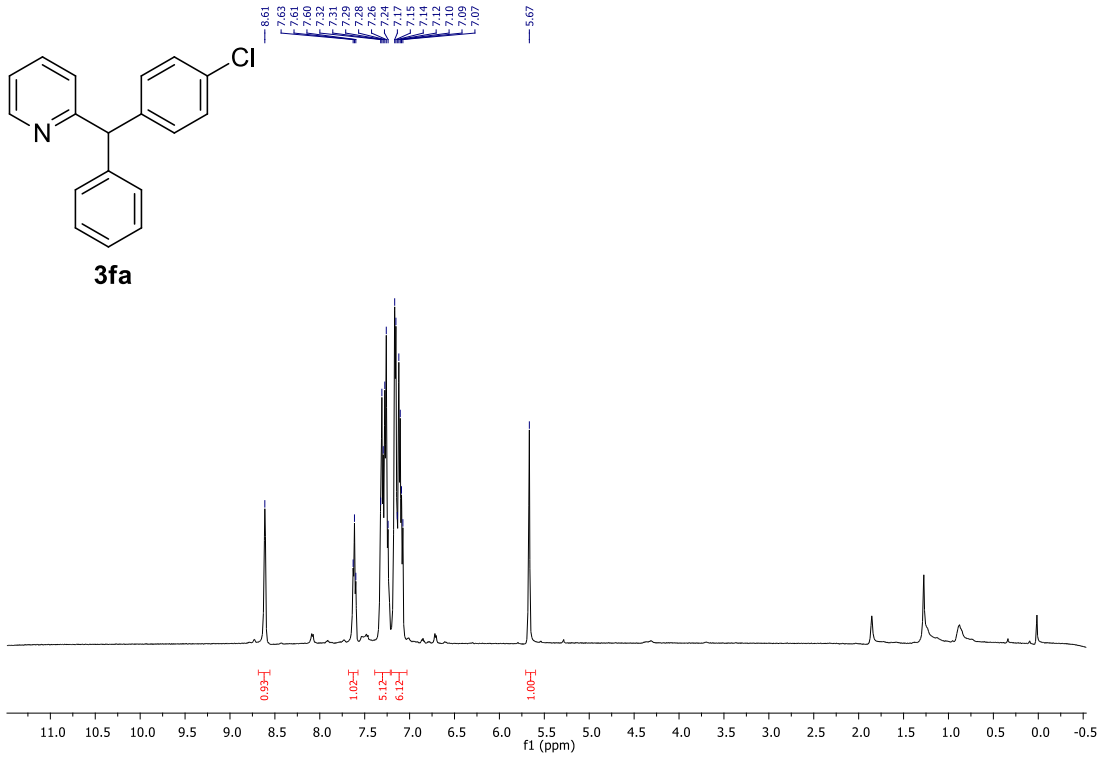
^{1}H NMR of **3ea**



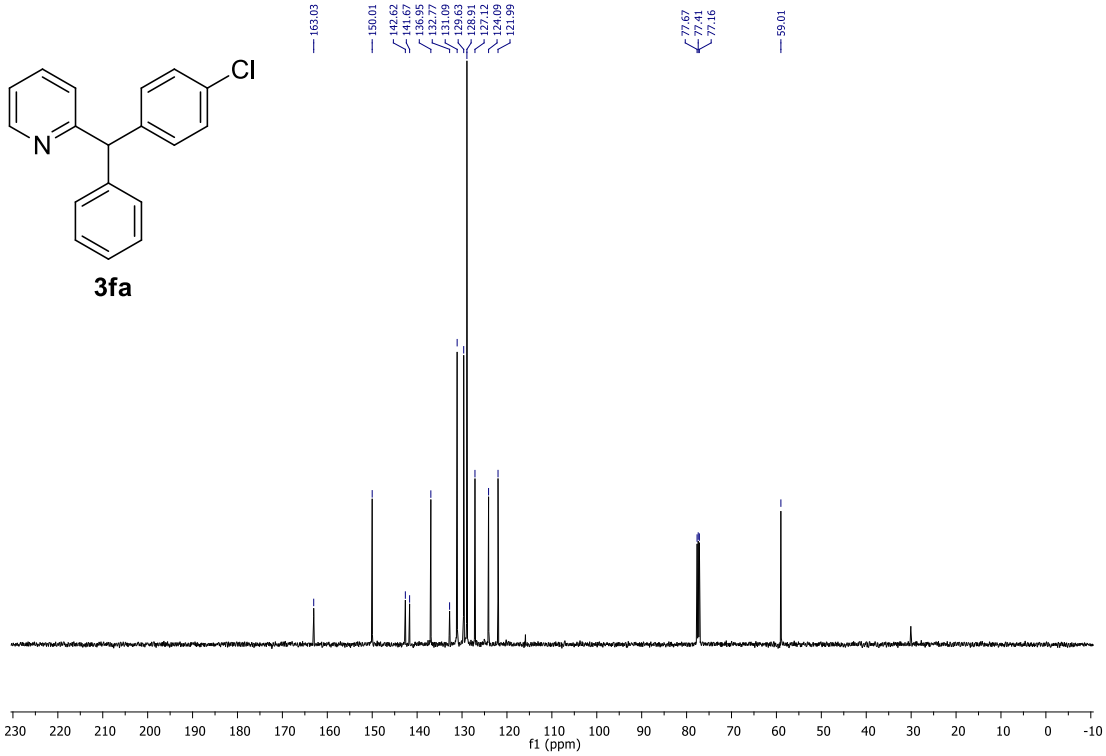
^{13}C NMR of **3ea**



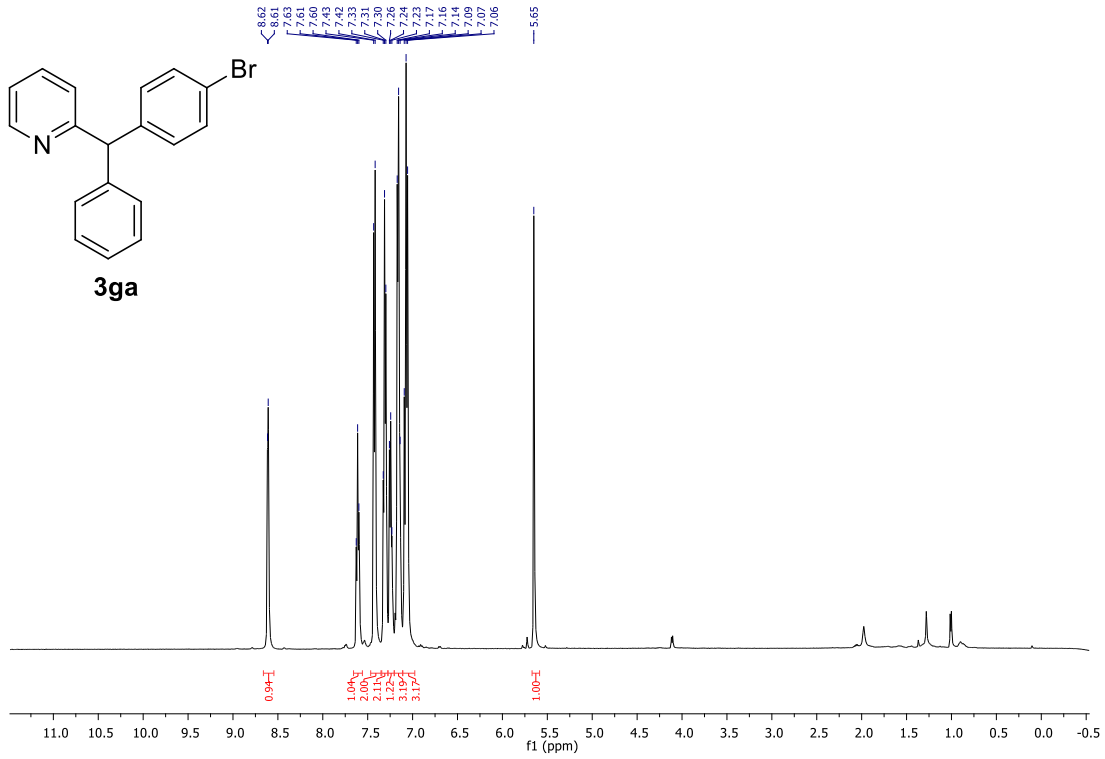
^{1}H NMR of **3fa**



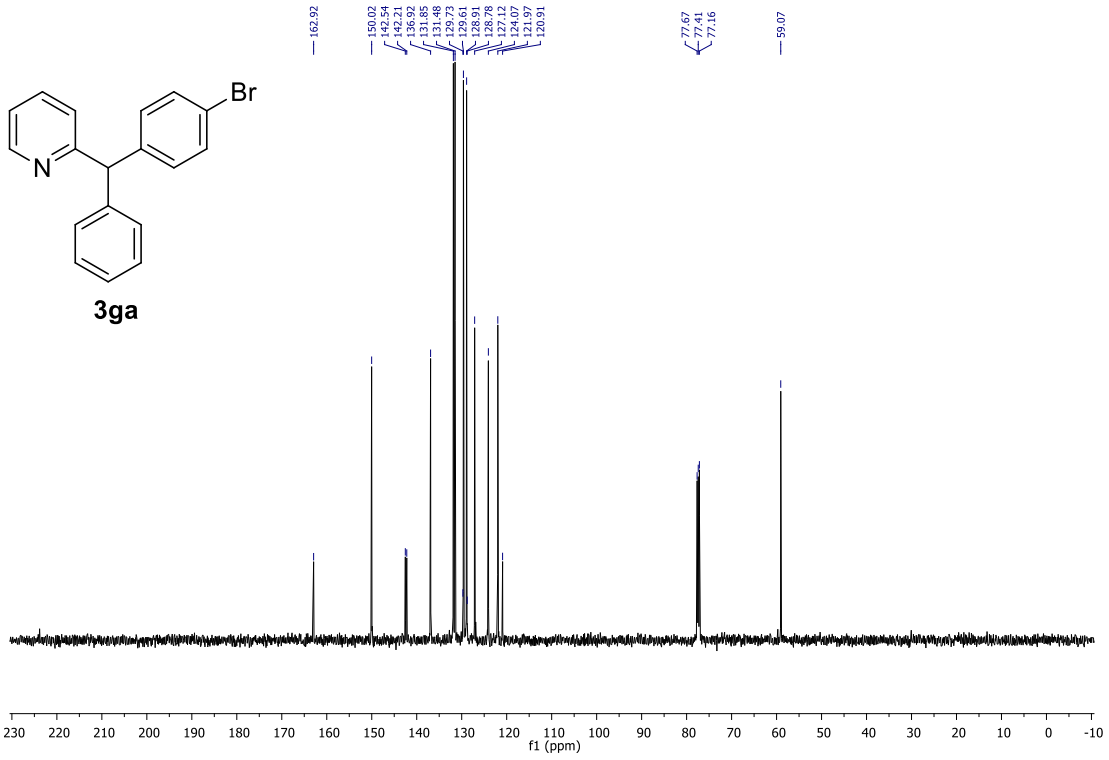
^{13}C NMR of **3fa**



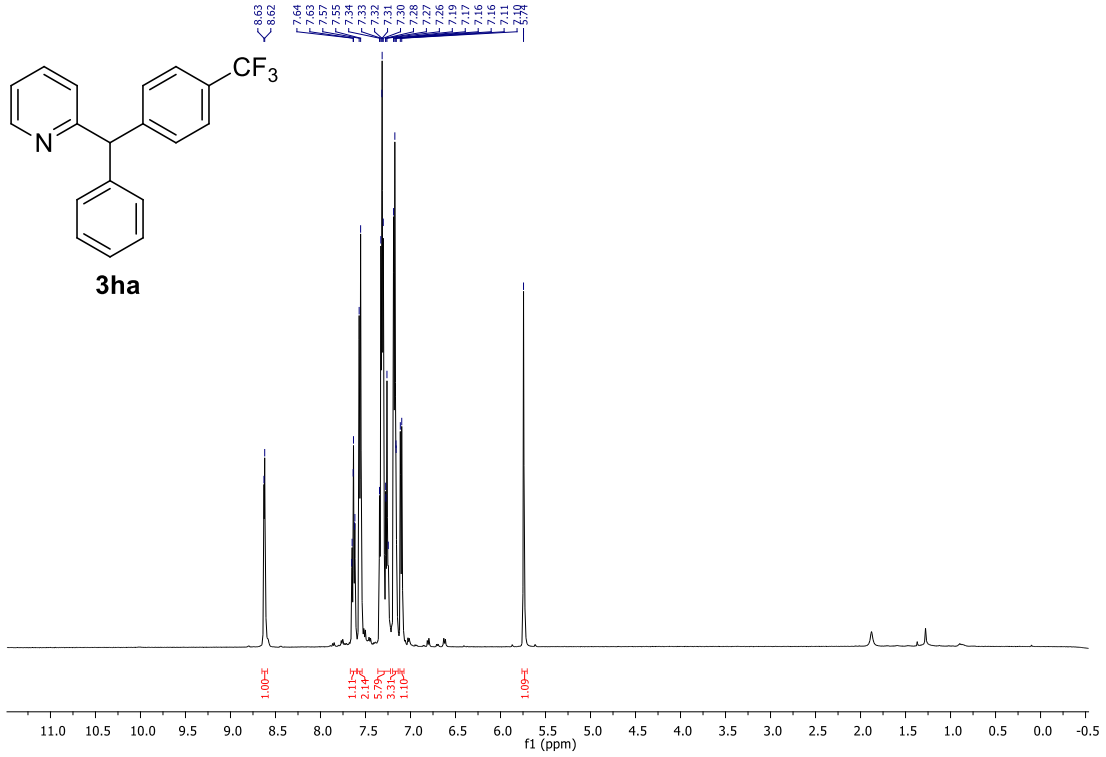
^{1}H NMR of **3ga**



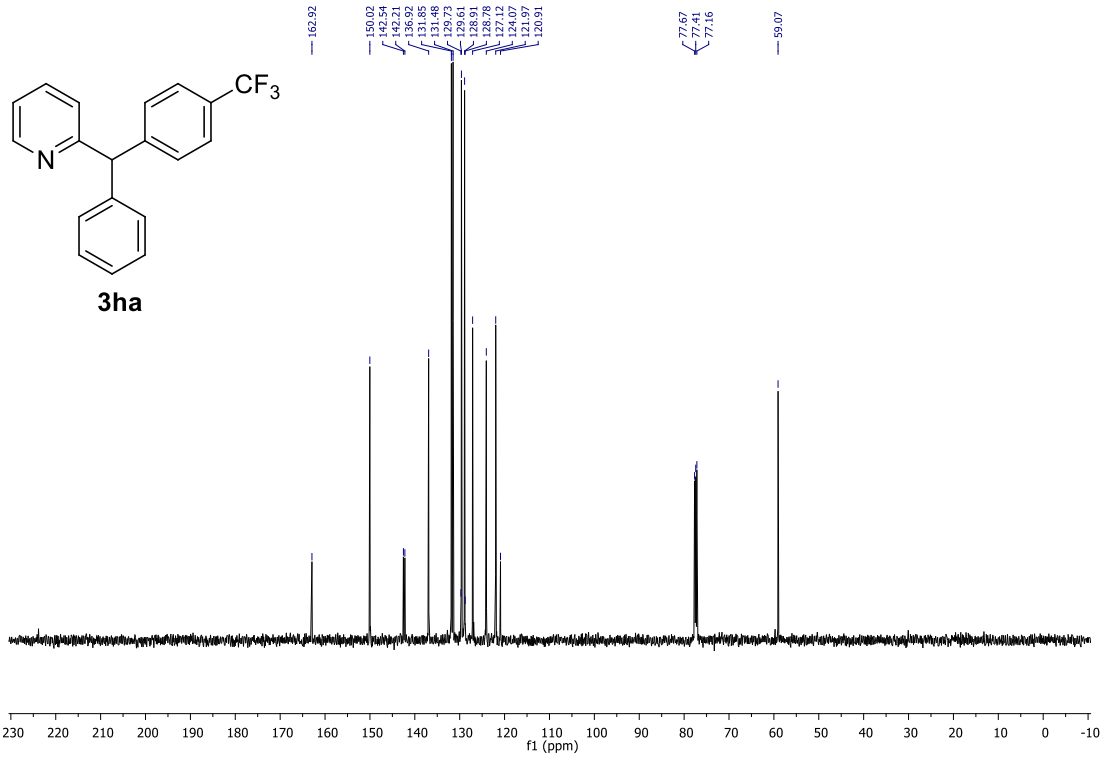
^{13}C NMR of **3ga**



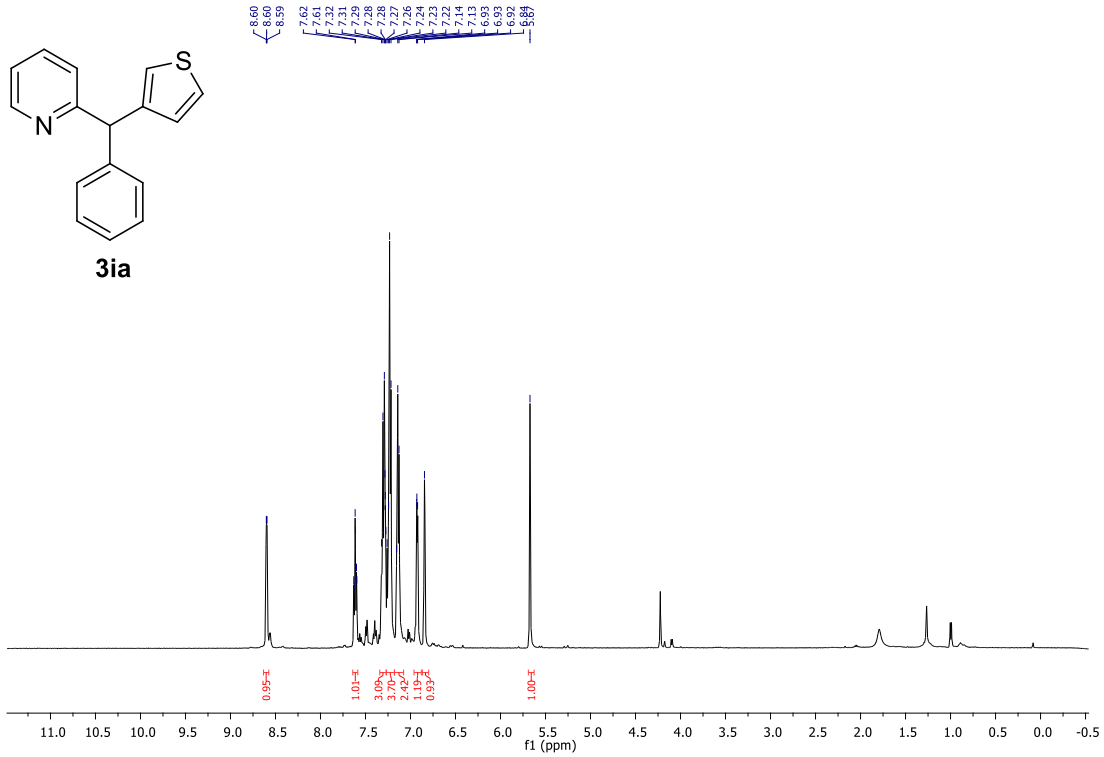
^{1}H NMR of **3ha**



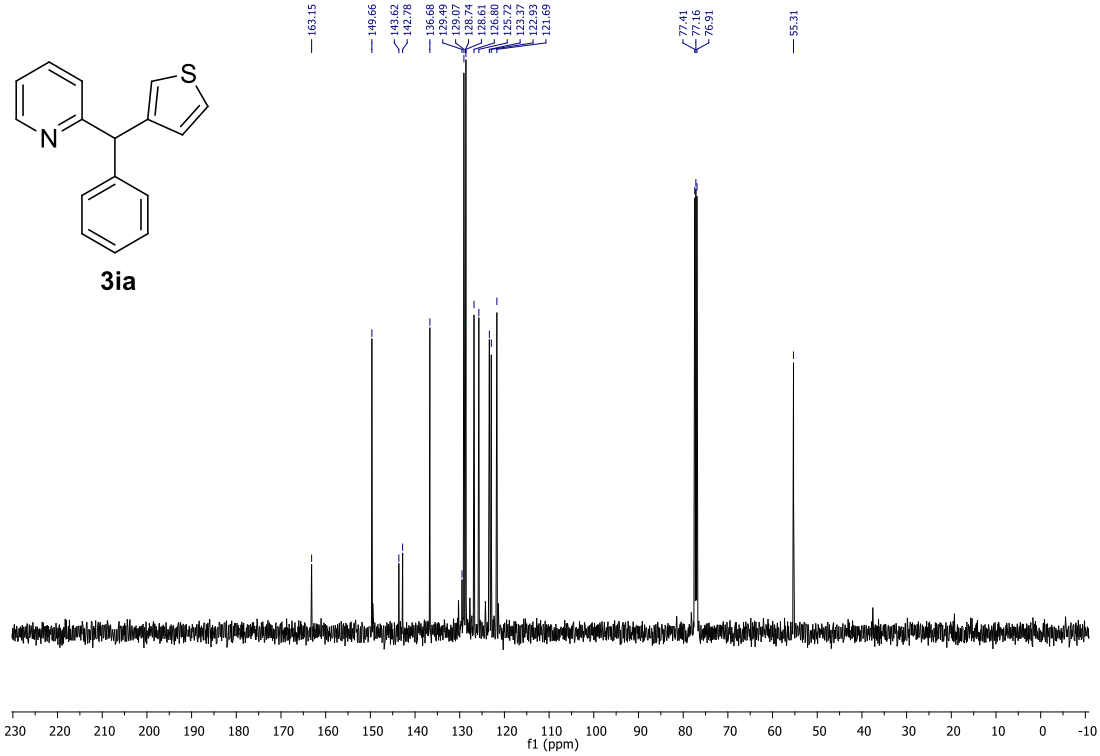
^{13}C NMR of **3ha**



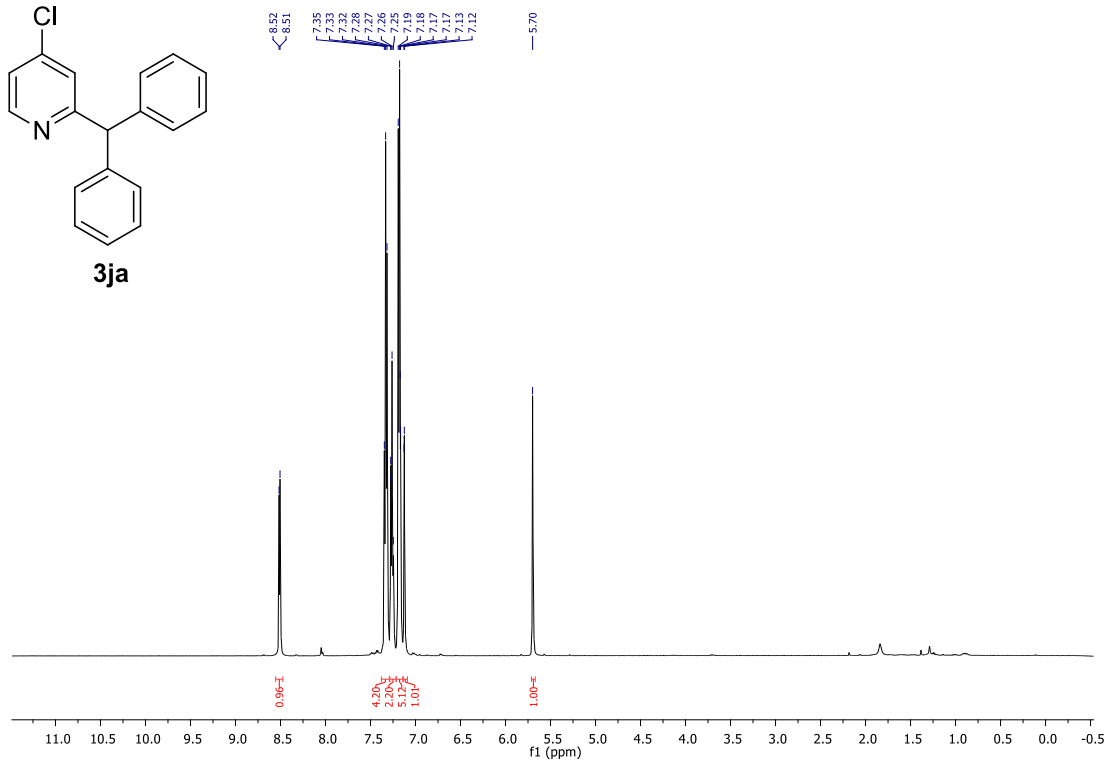
^{1}H NMR of **3ia**



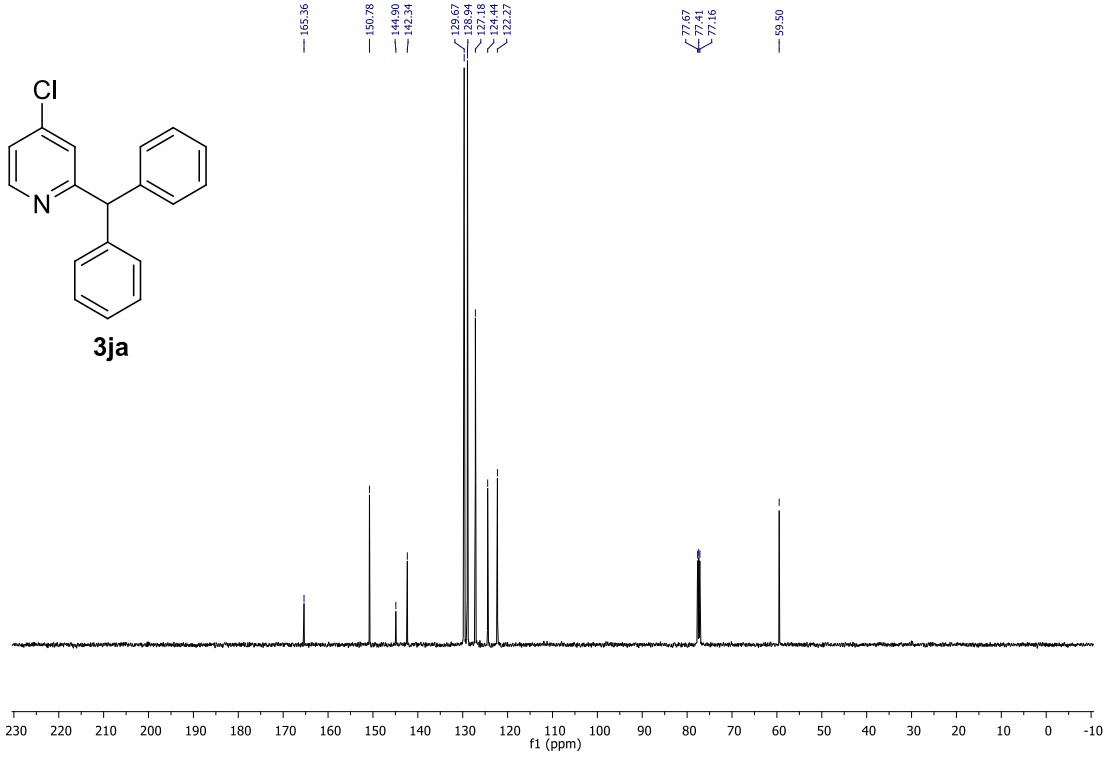
^{13}C NMR of **3ia**



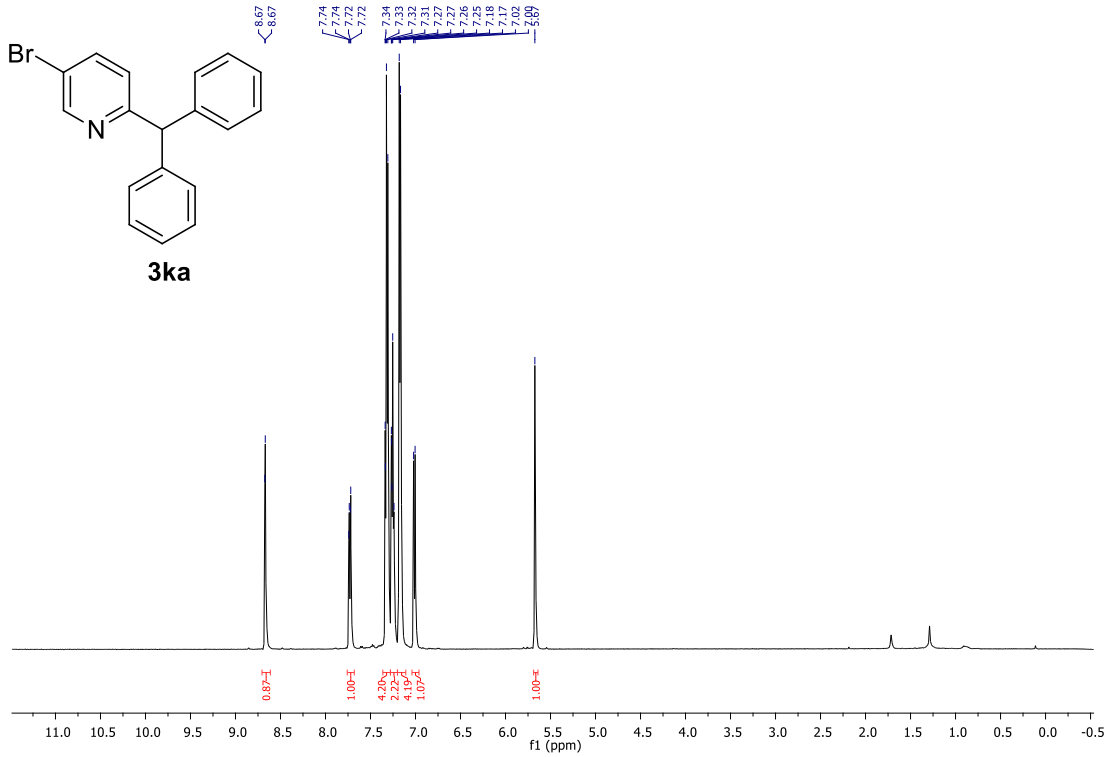
^{1}H NMR of **3ja**



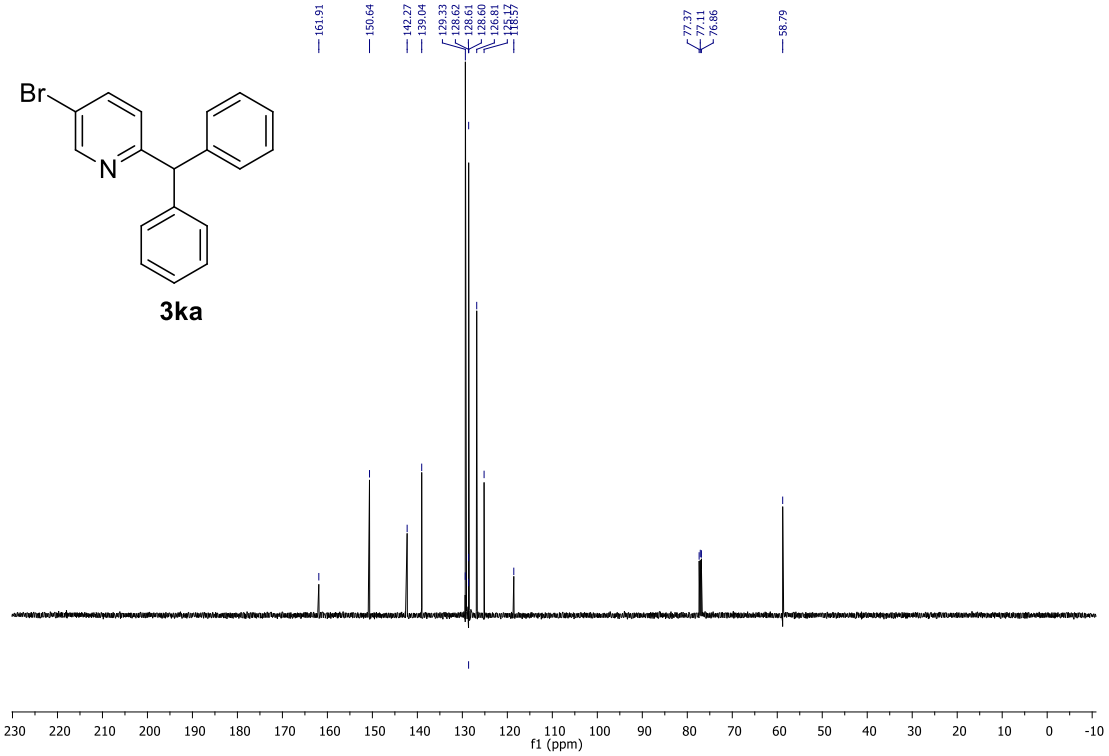
^{13}C NMR of **3ja**



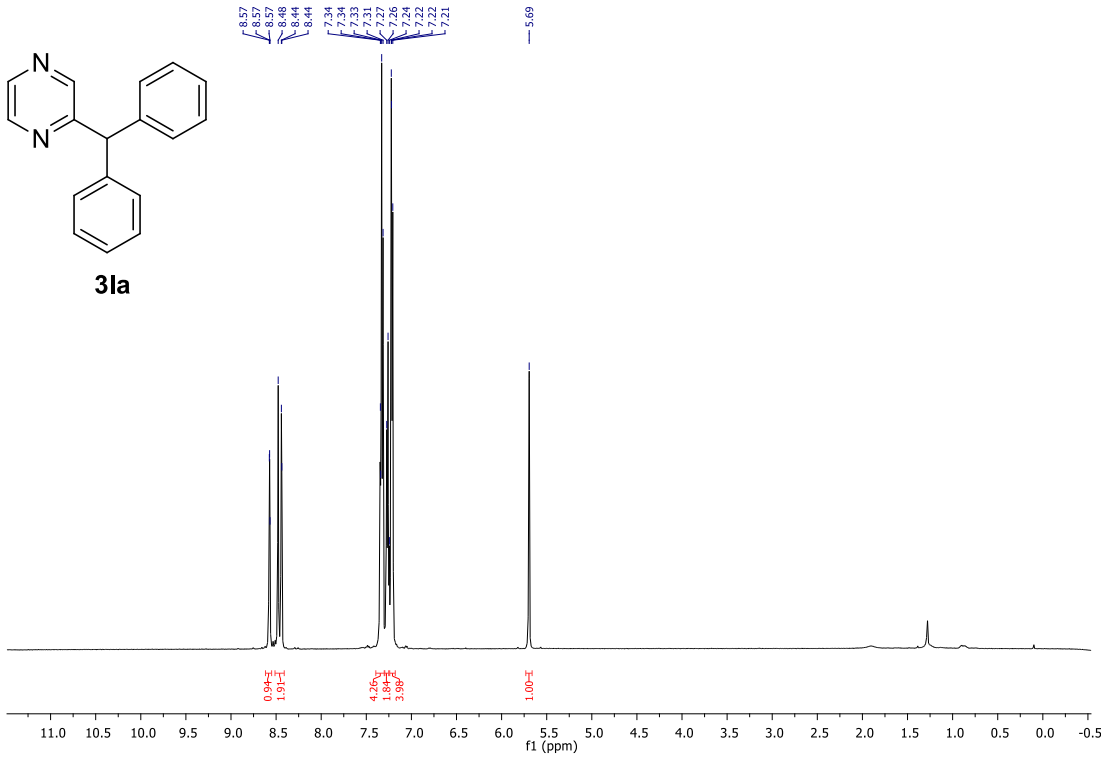
^{1}H NMR of **3ka**



^{13}C NMR of **3ka**

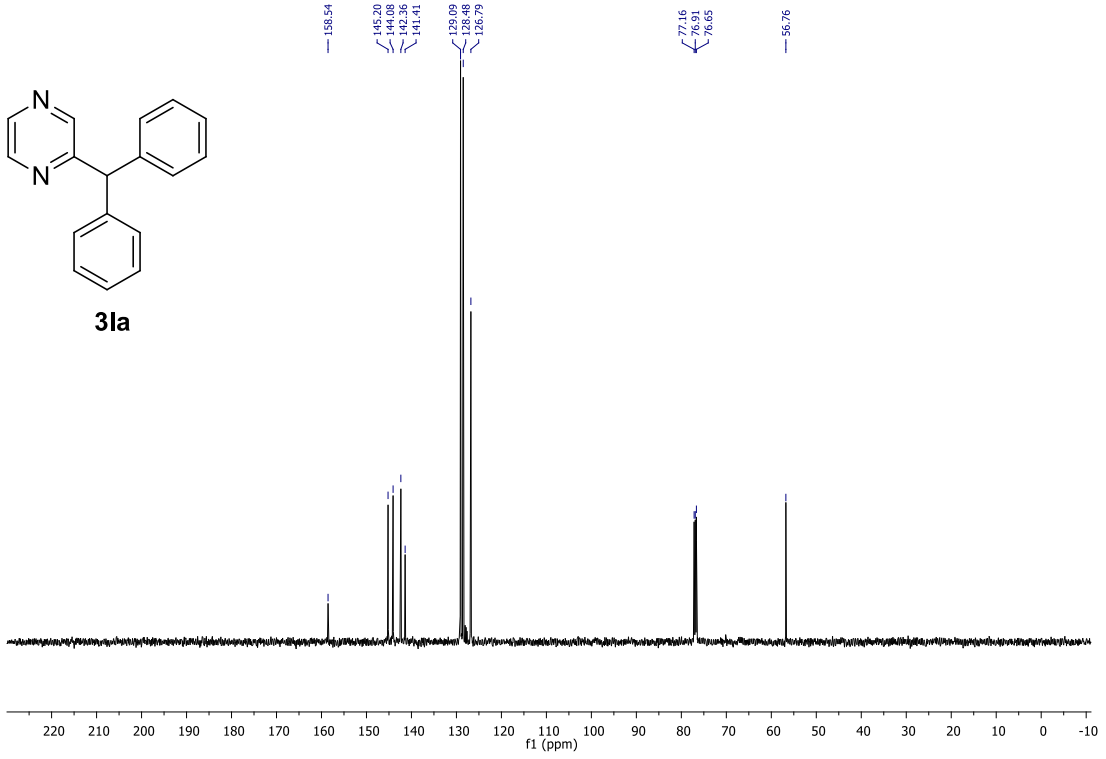


^{1}H NMR of **3la**



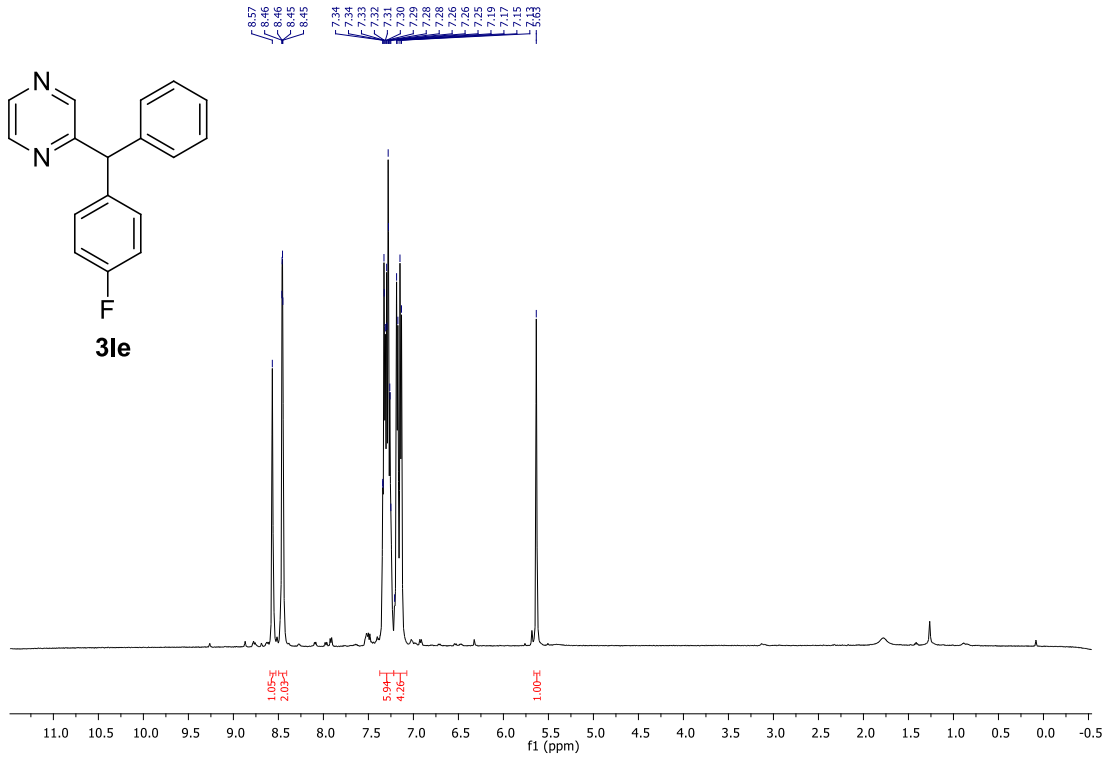
3la

^{13}C NMR of **3la**

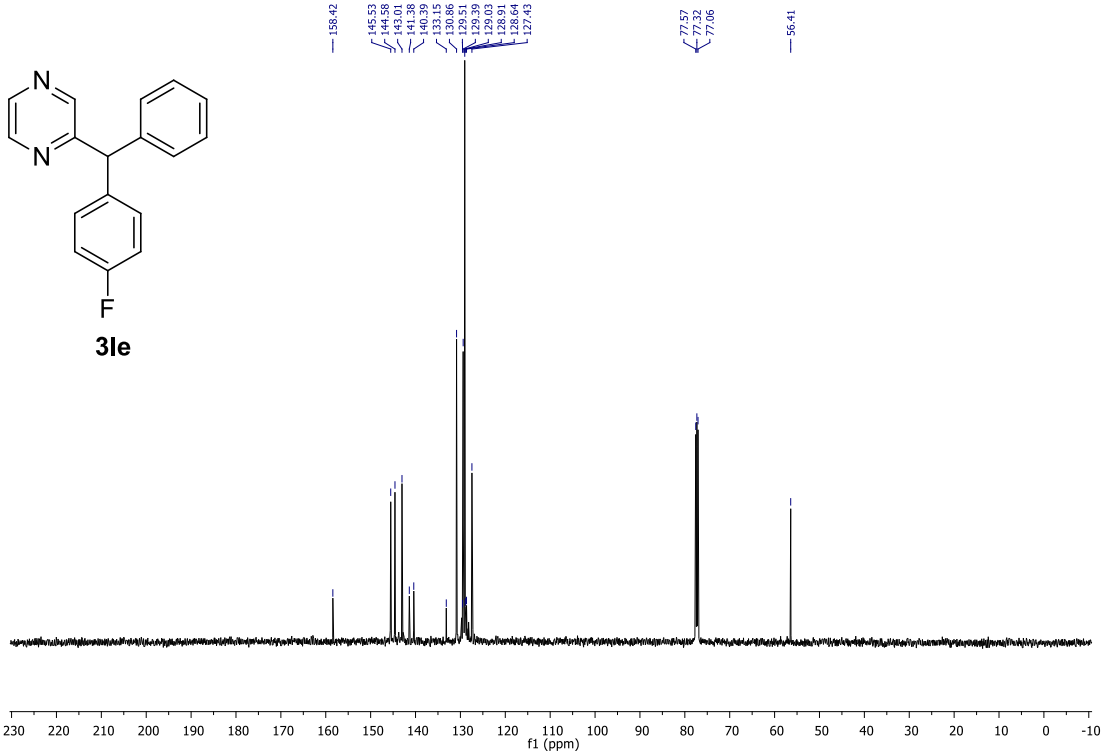


3la

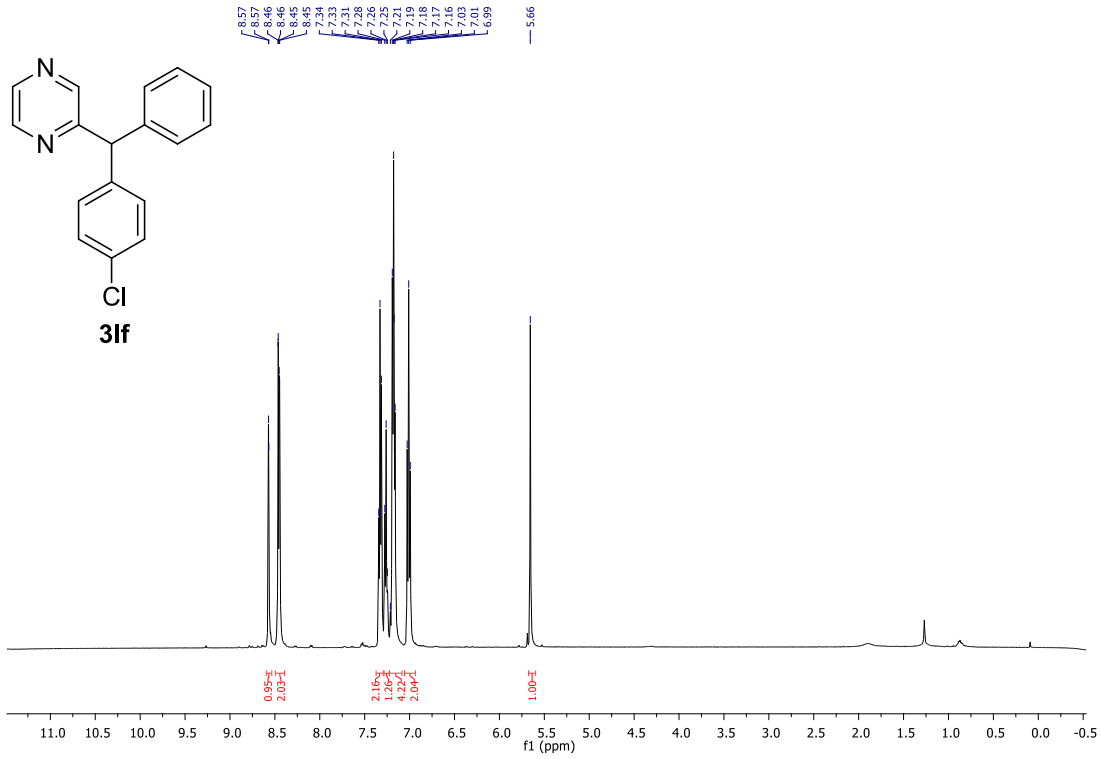
^{1}H NMR of **3le**



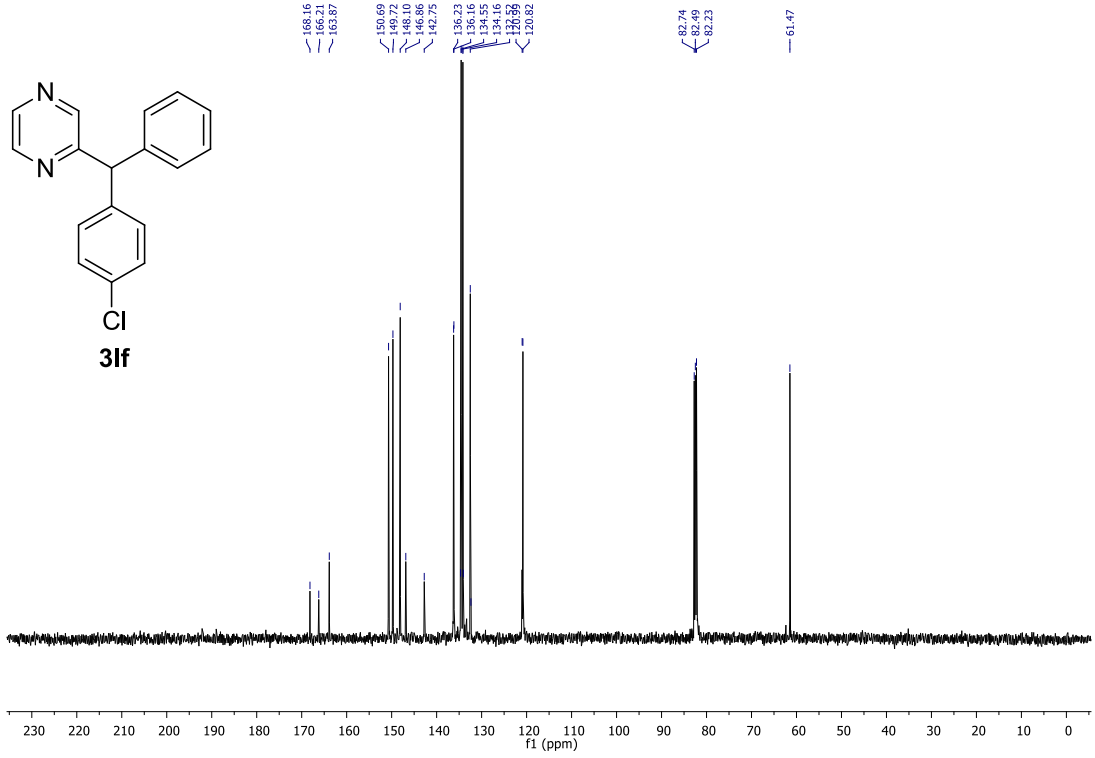
^{13}C NMR of **3le**



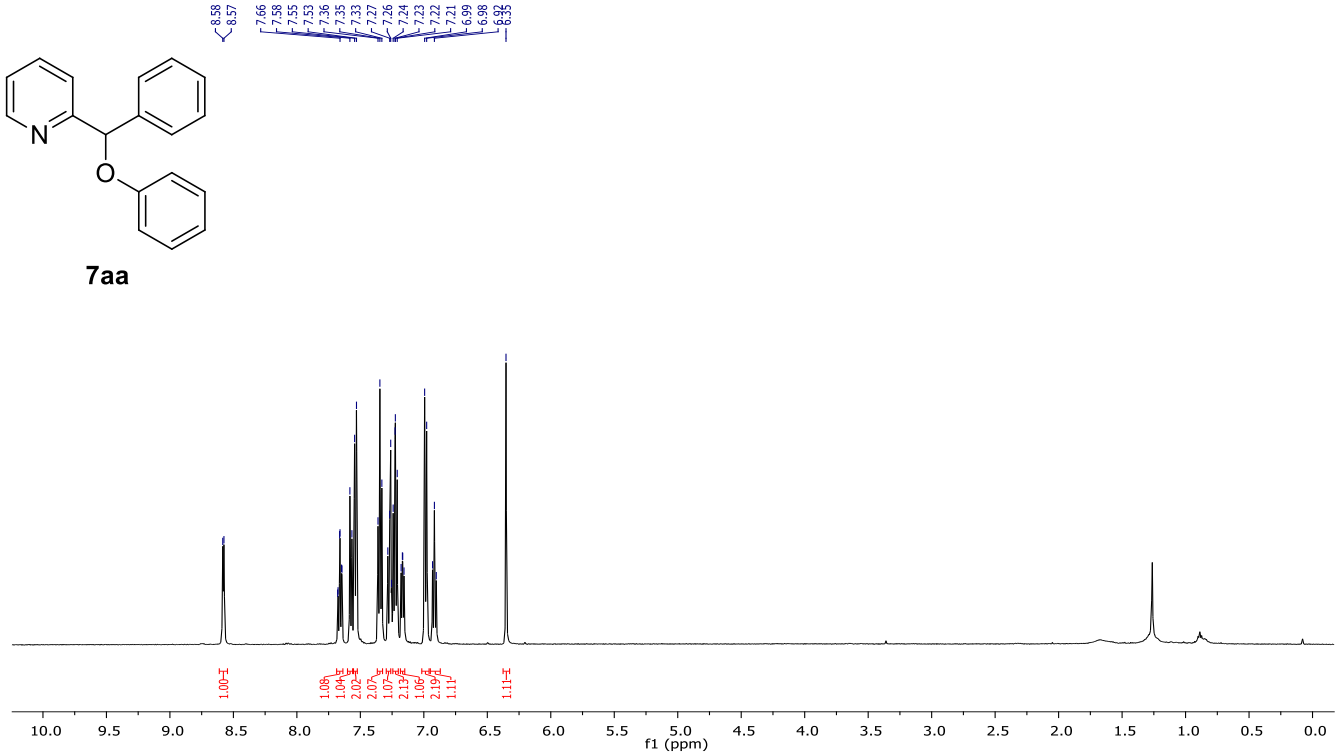
^{1}H NMR of **3lf**



^{13}C NMR of **3lf**

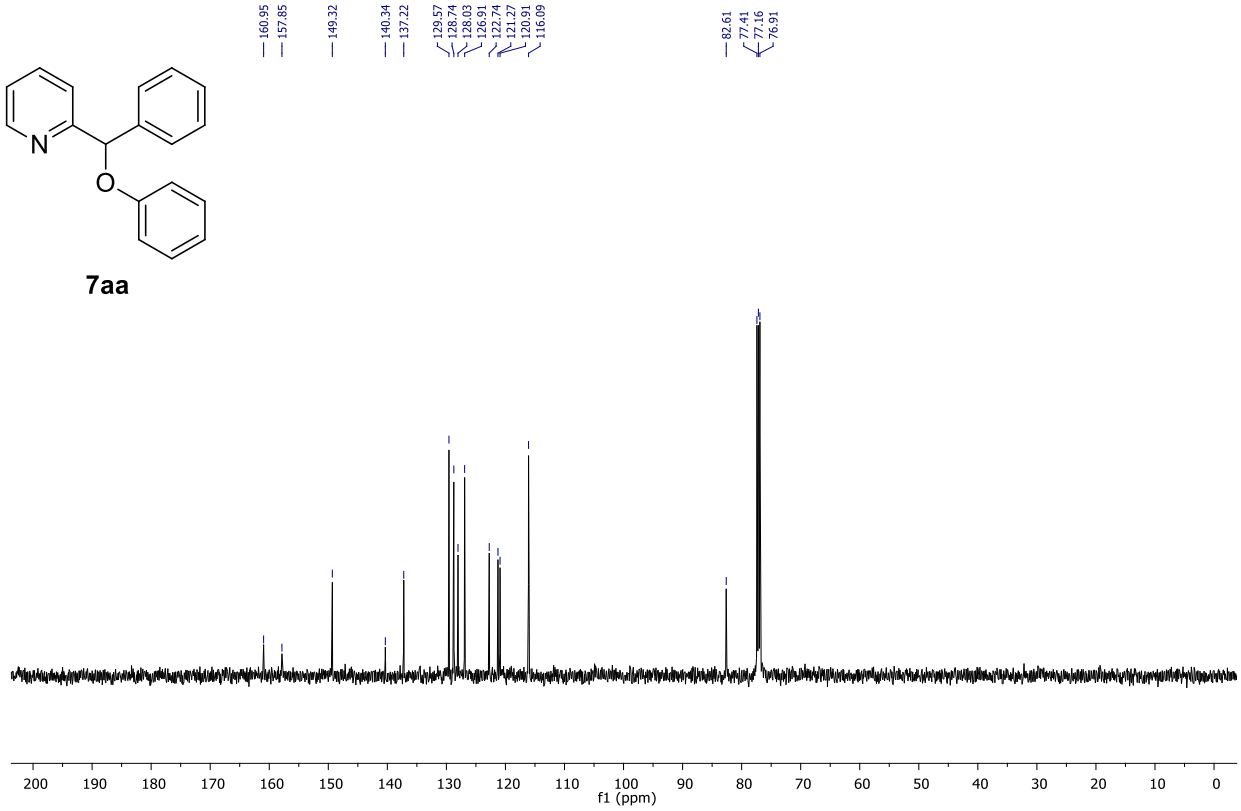


^{1}H NMR of **7aa**



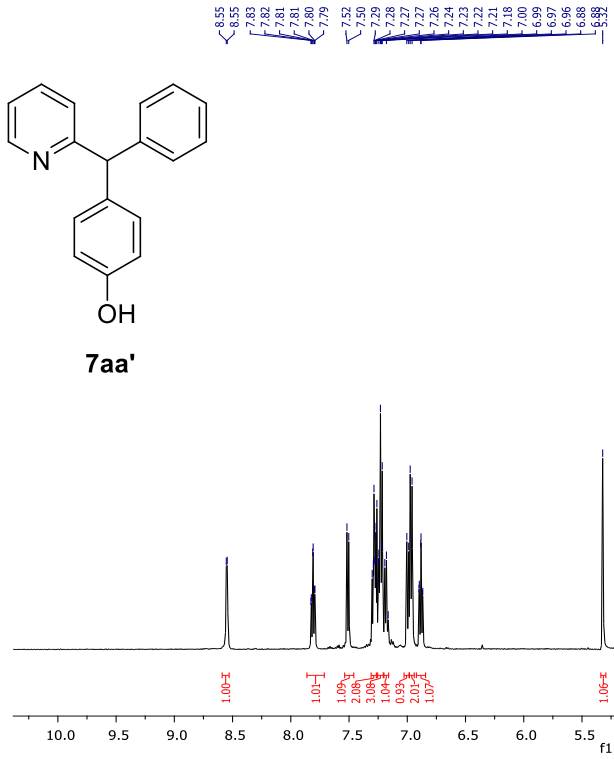
7aa

^{13}C NMR of **7aa**

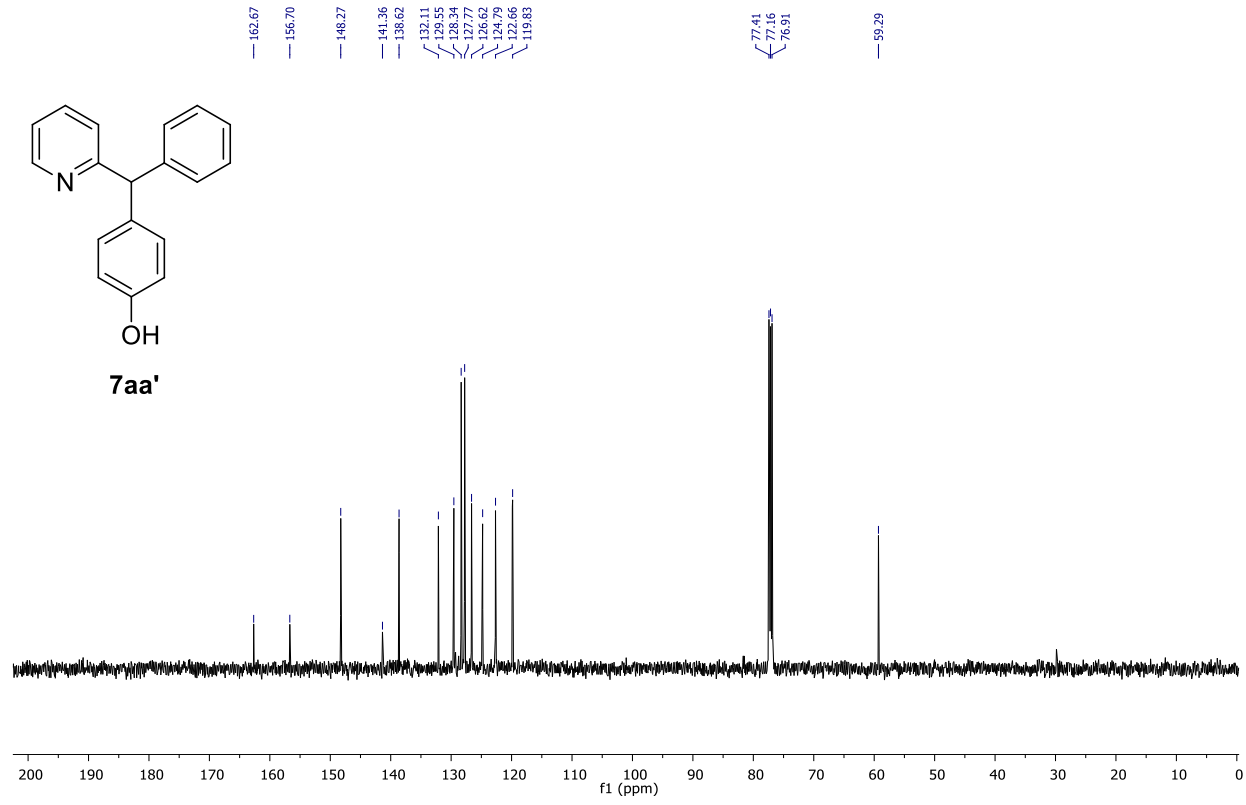


7aa

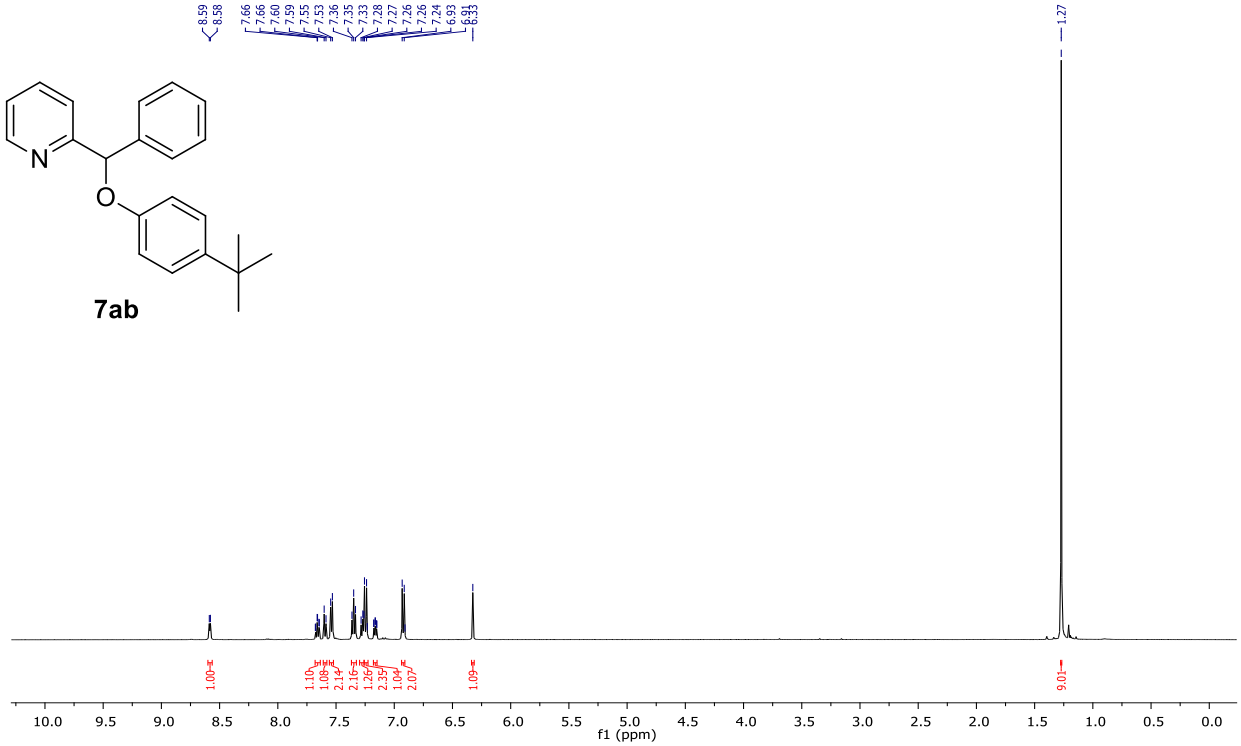
^{1}H NMR of **7aa'**



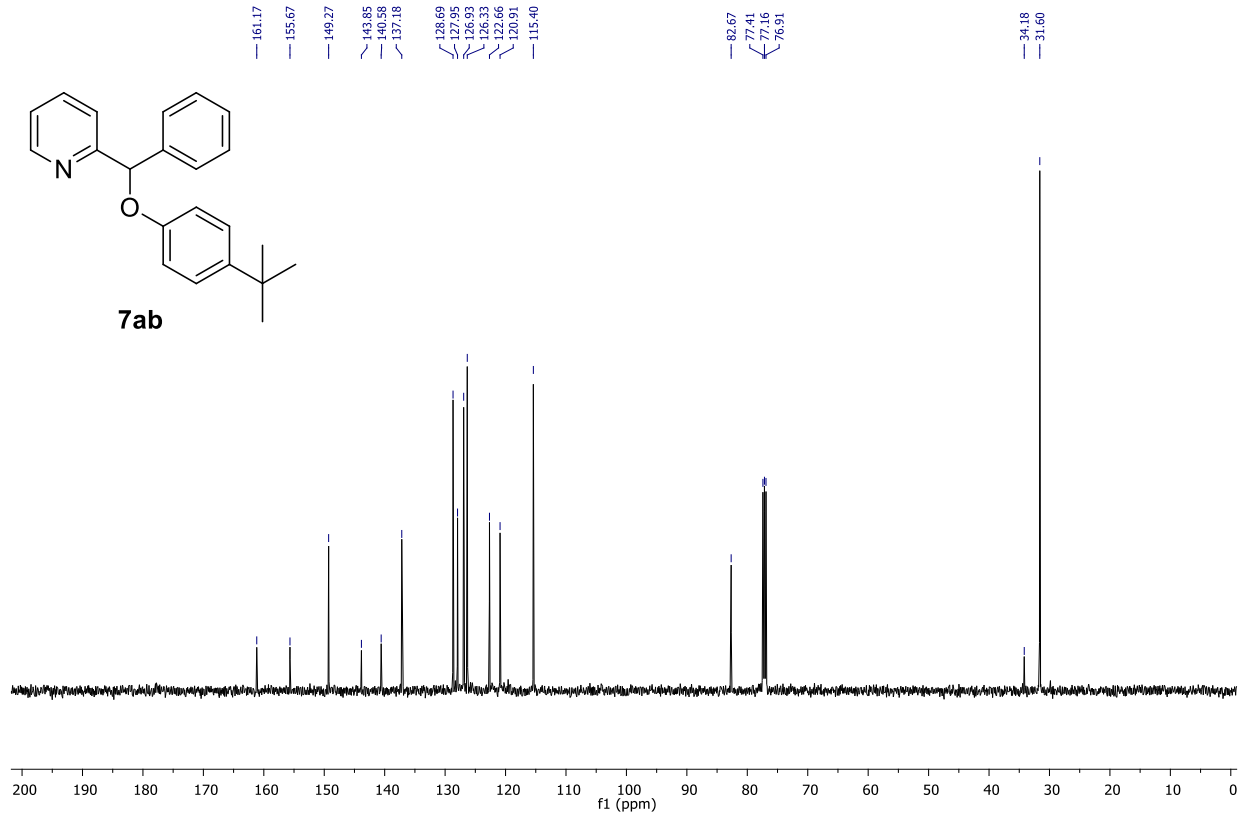
^{13}C NMR of **7aa'**



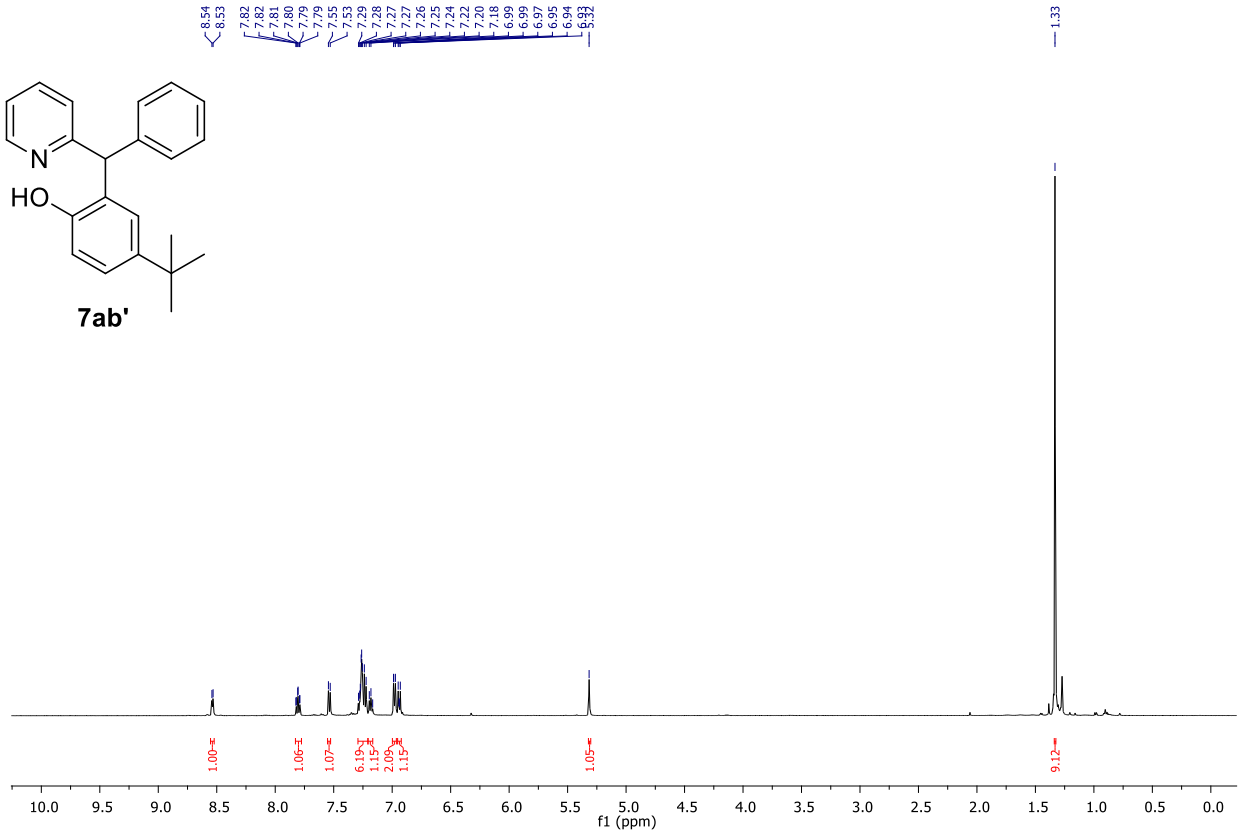
^{1}H NMR of **7ab**



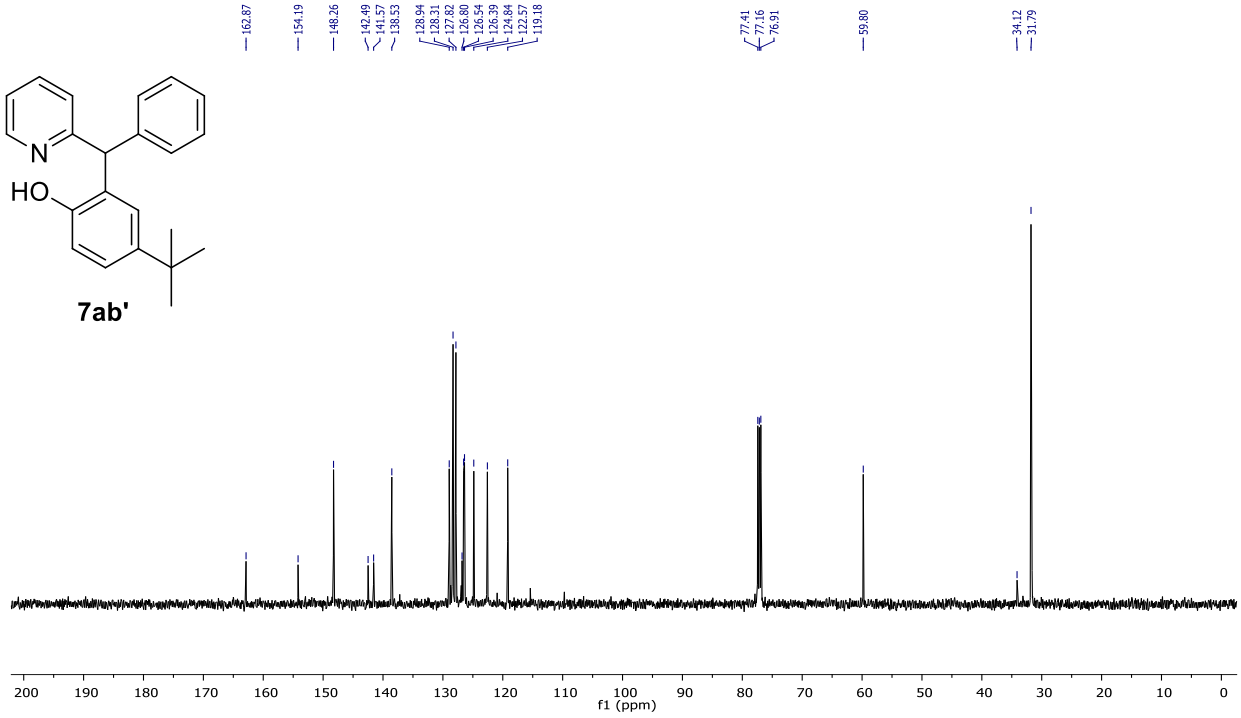
^{13}C NMR of **7ab**



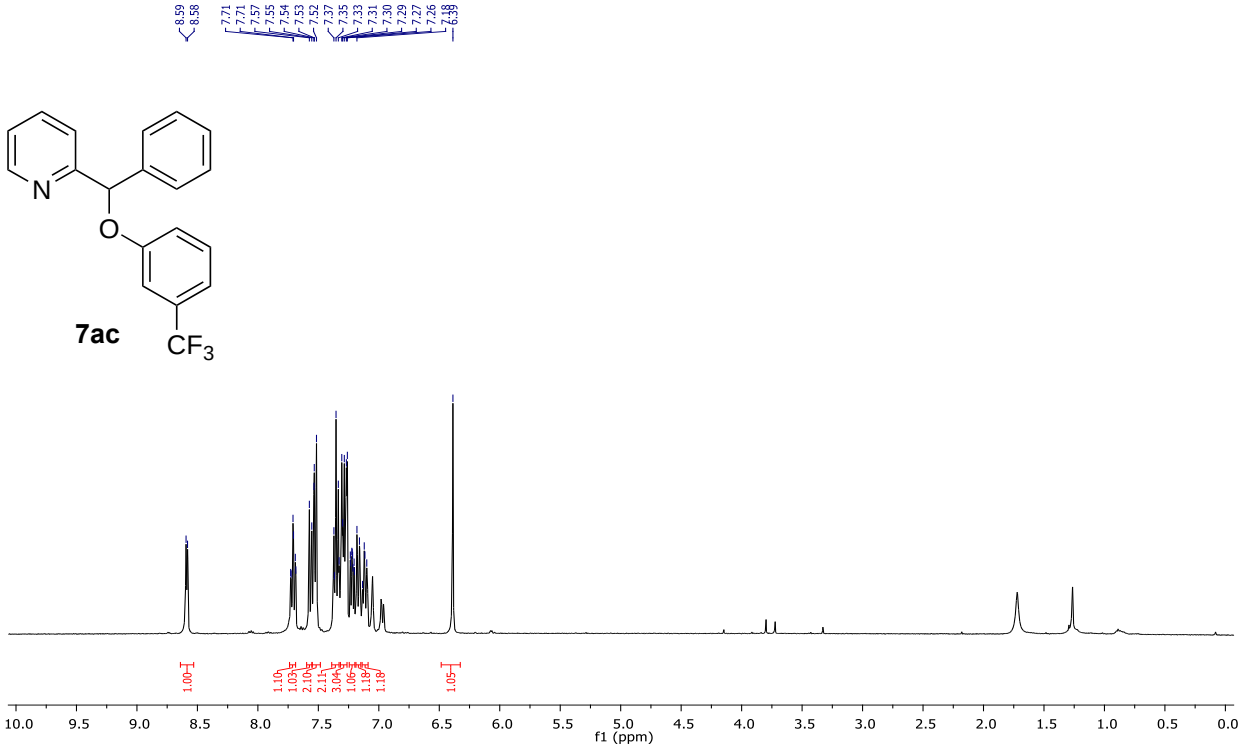
^{1}H NMR of **7ab'**



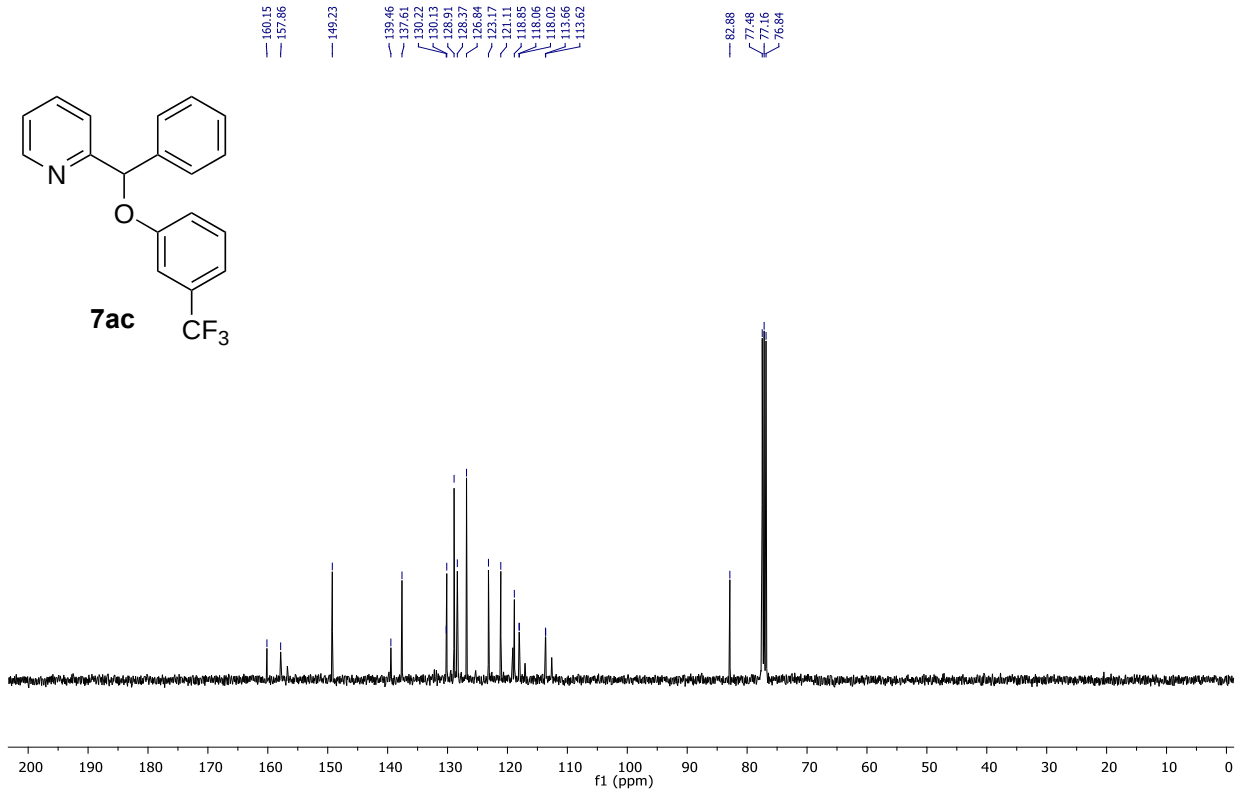
^{13}C NMR of **7ab'**



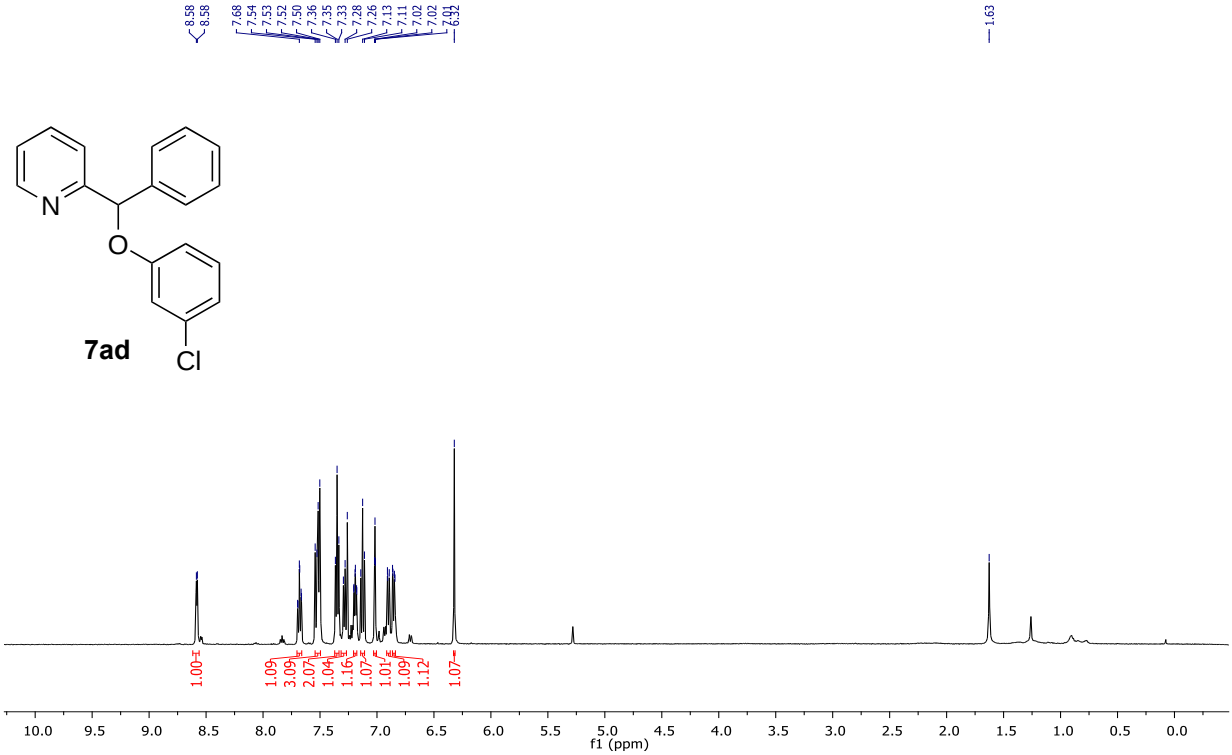
^{1}H NMR of **7ac**



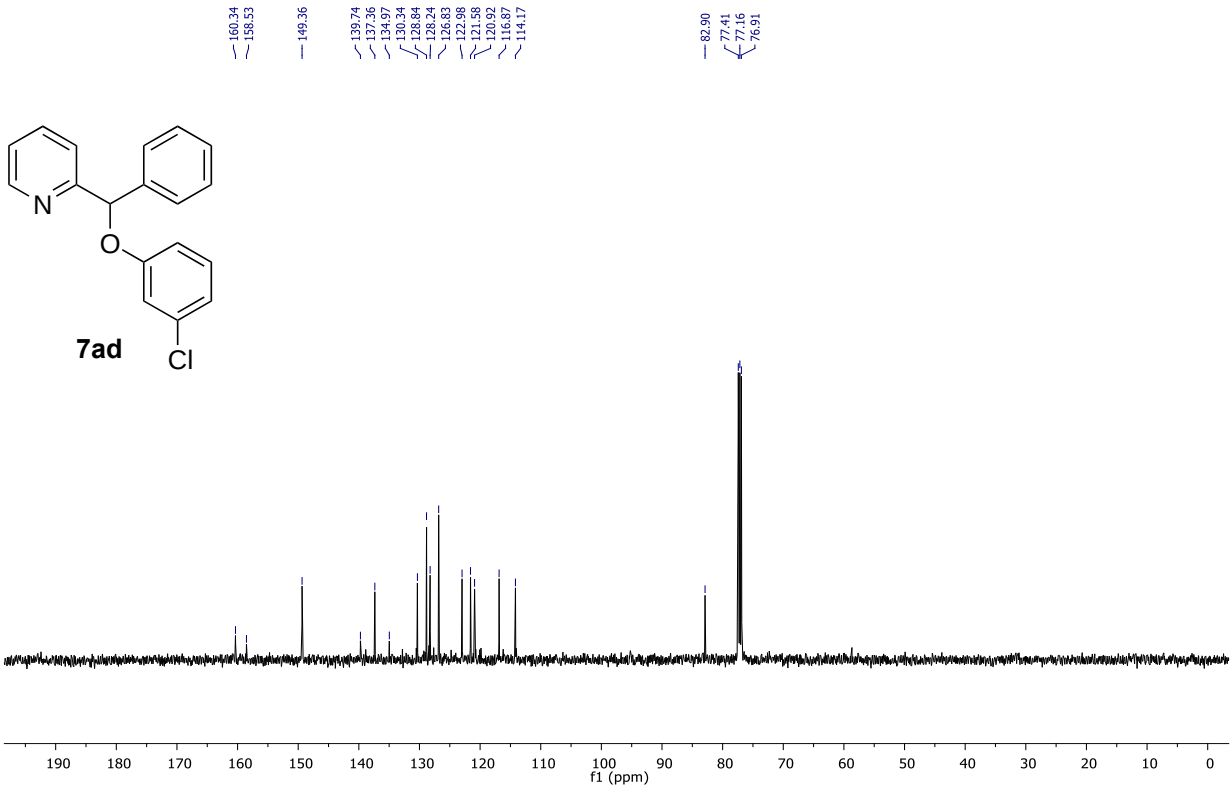
^{13}C NMR of **7ac**



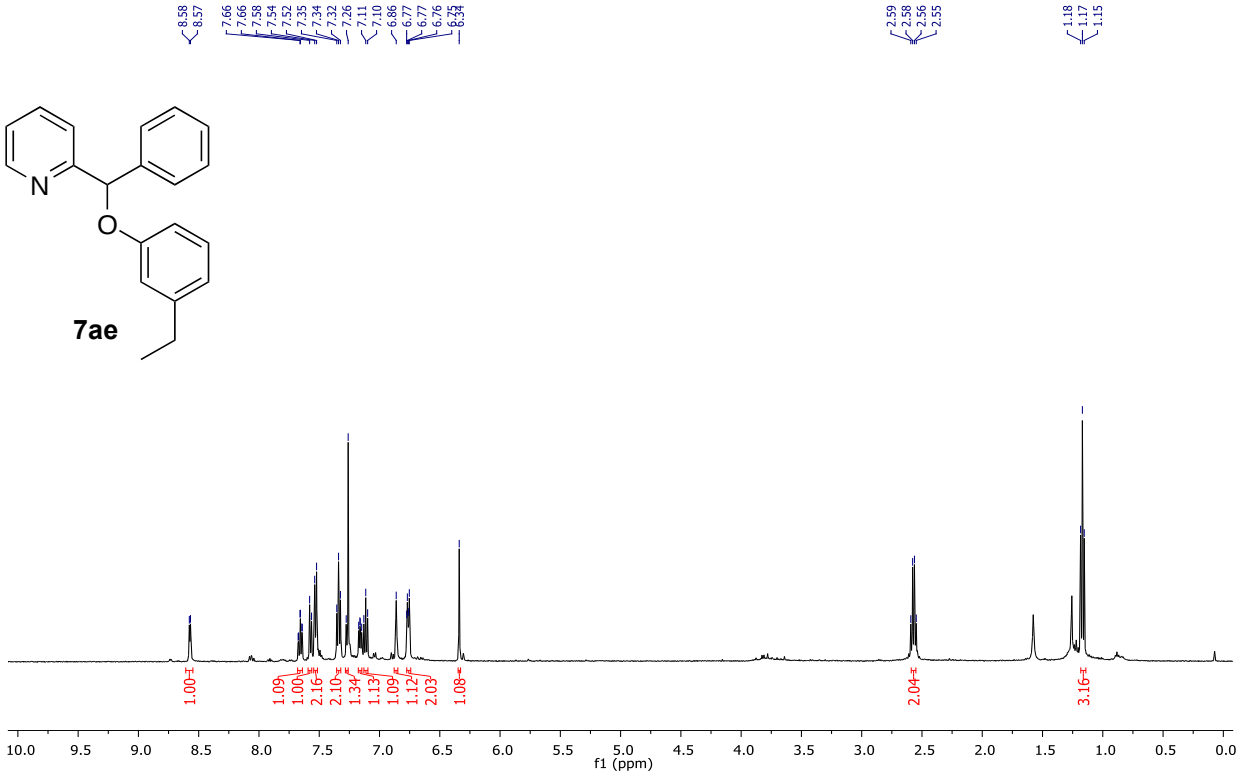
^{1}H NMR of **7ad**



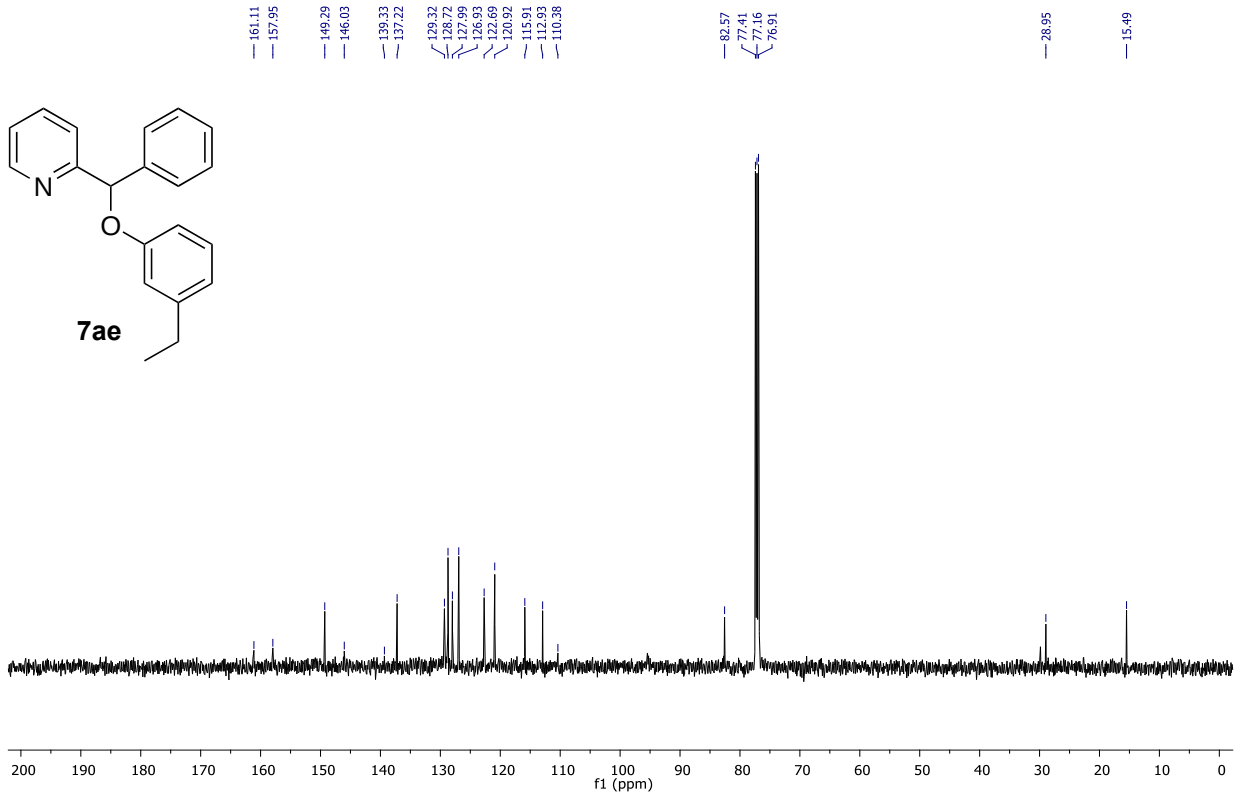
^{13}C NMR of **7ad**



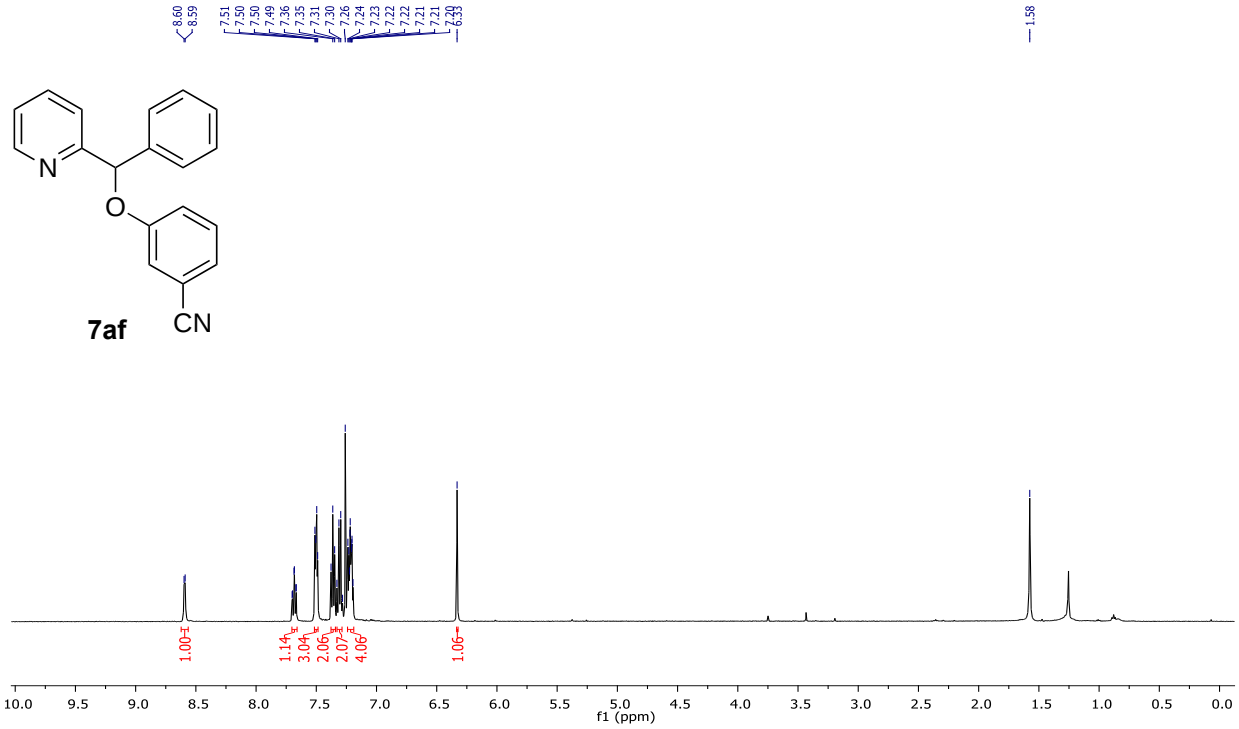
^{1}H NMR of **7ae**



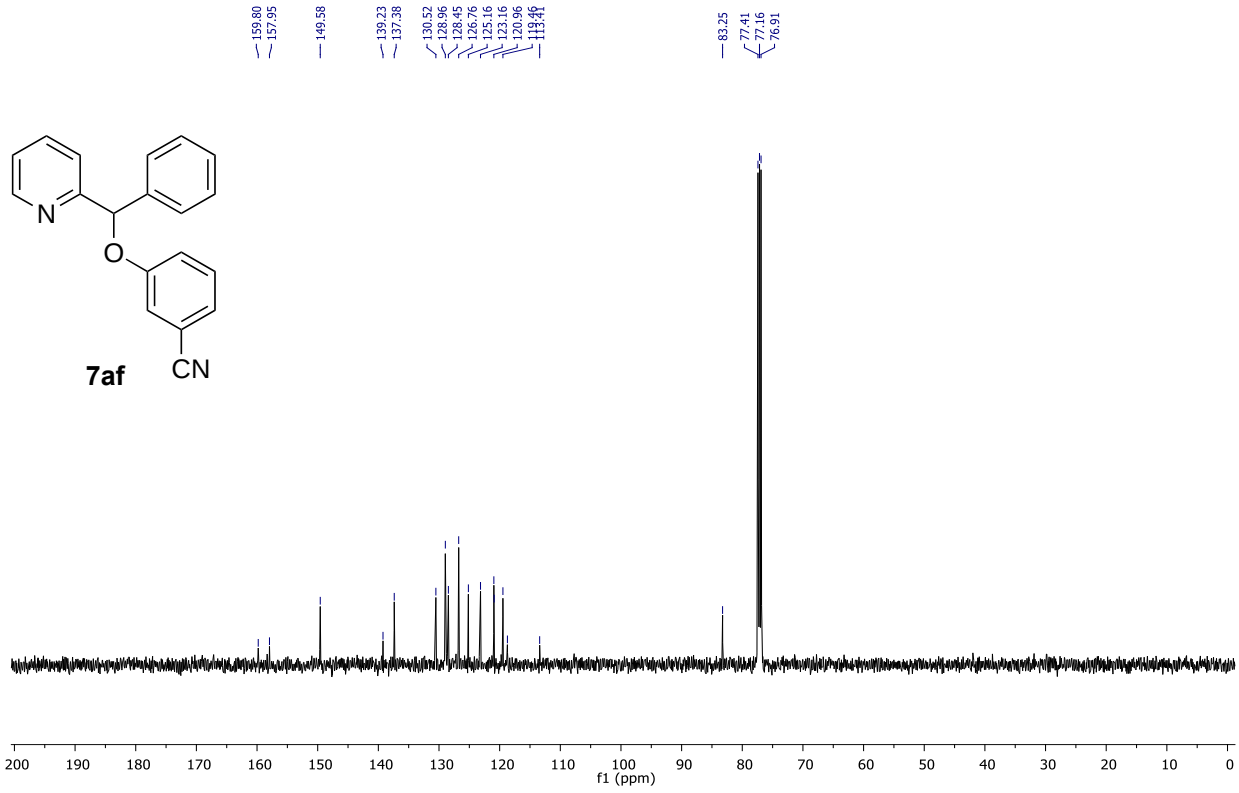
^{13}C NMR of **7ae**



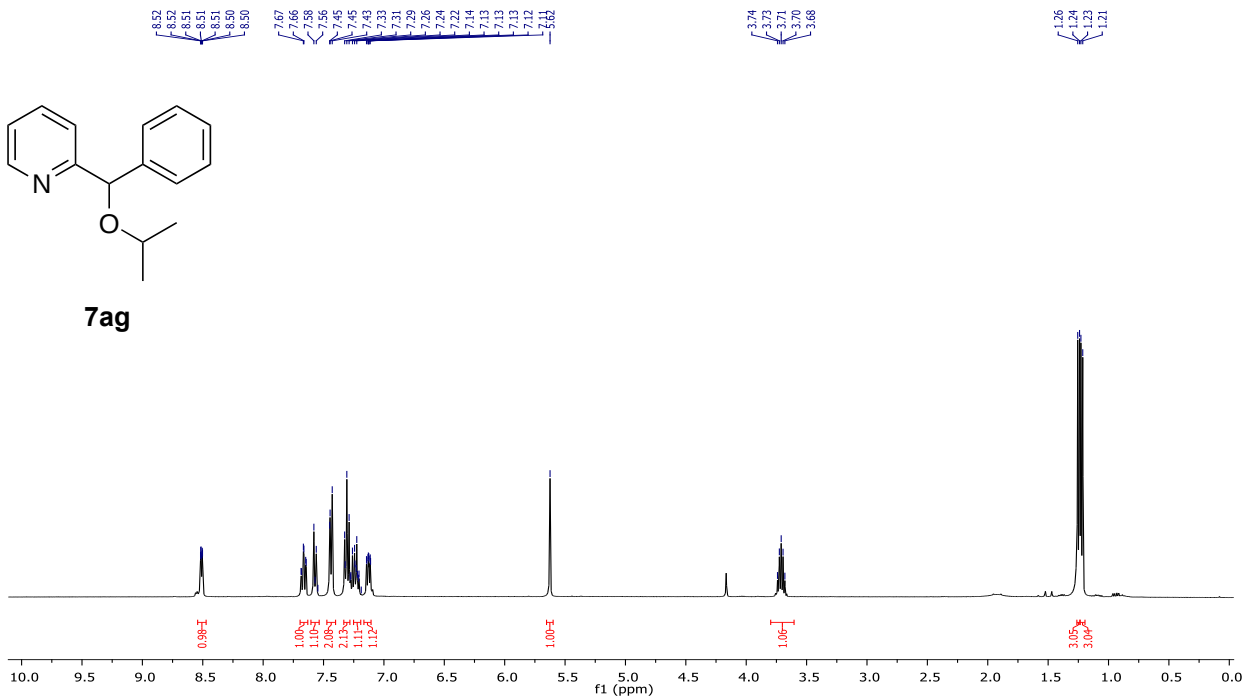
^{1}H NMR of **7af**



^{13}C NMR of **7af**

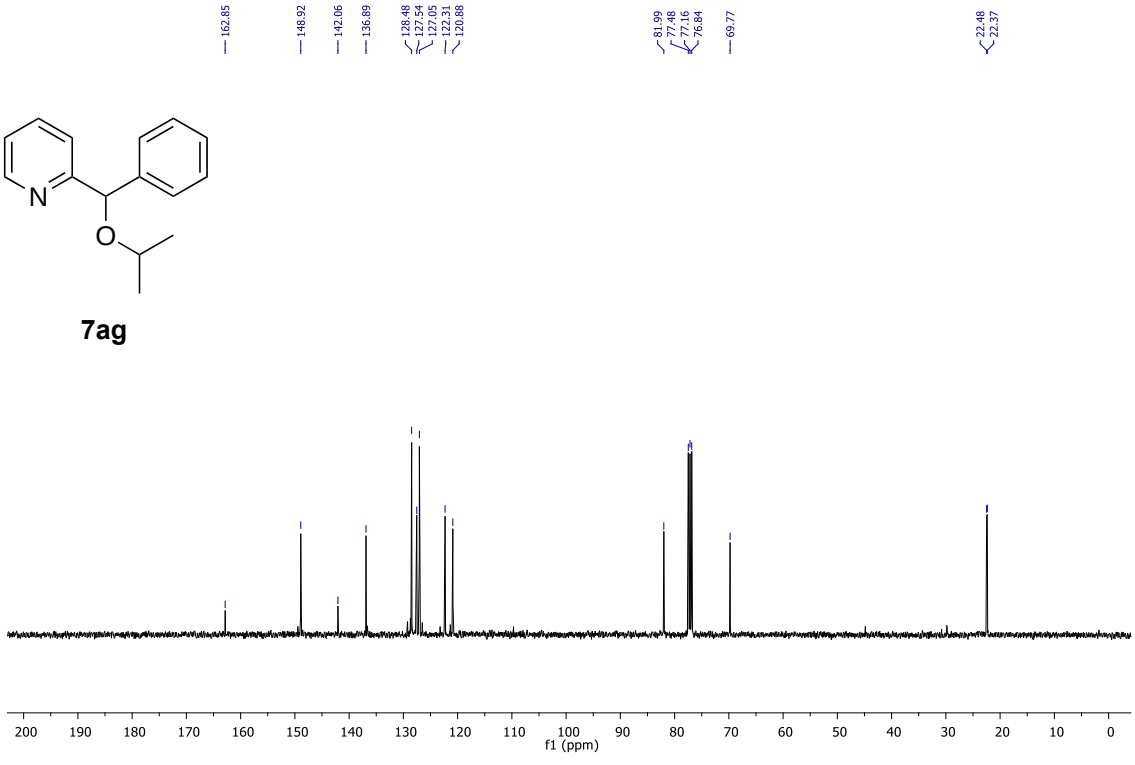


^{1}H NMR of **7ag**



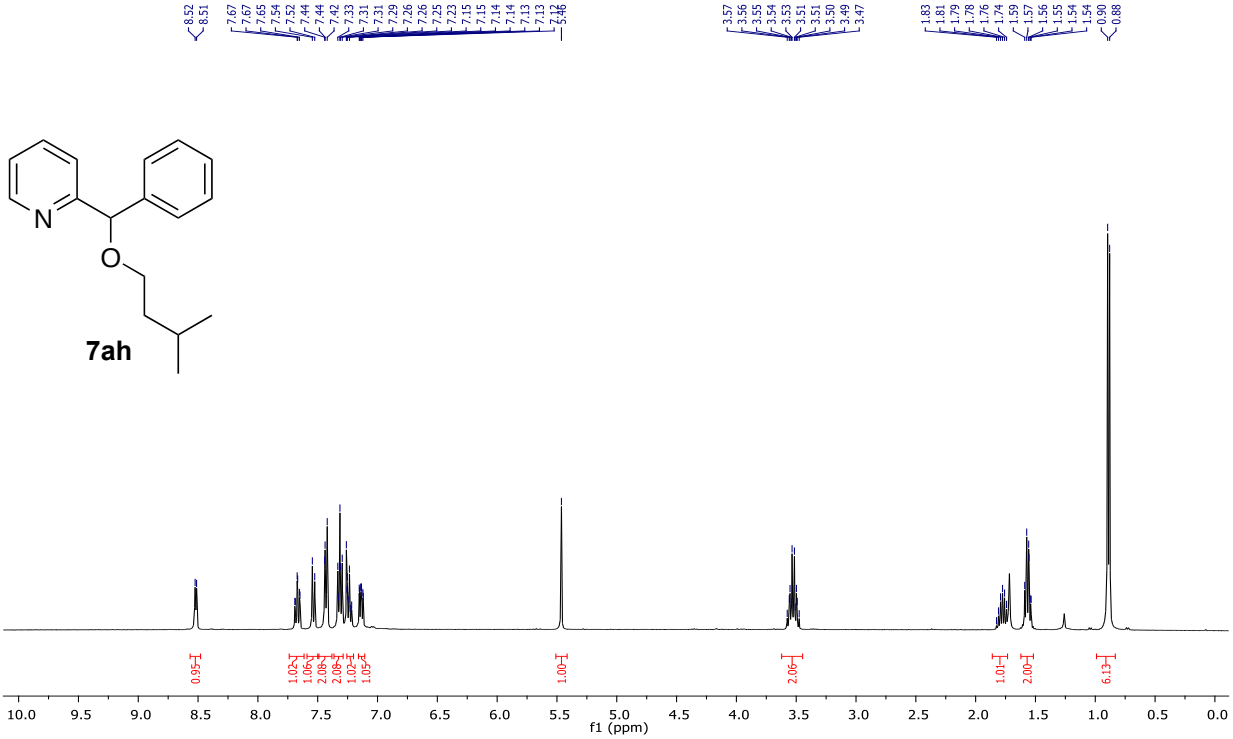
7ag

^{13}C NMR of **7ag**

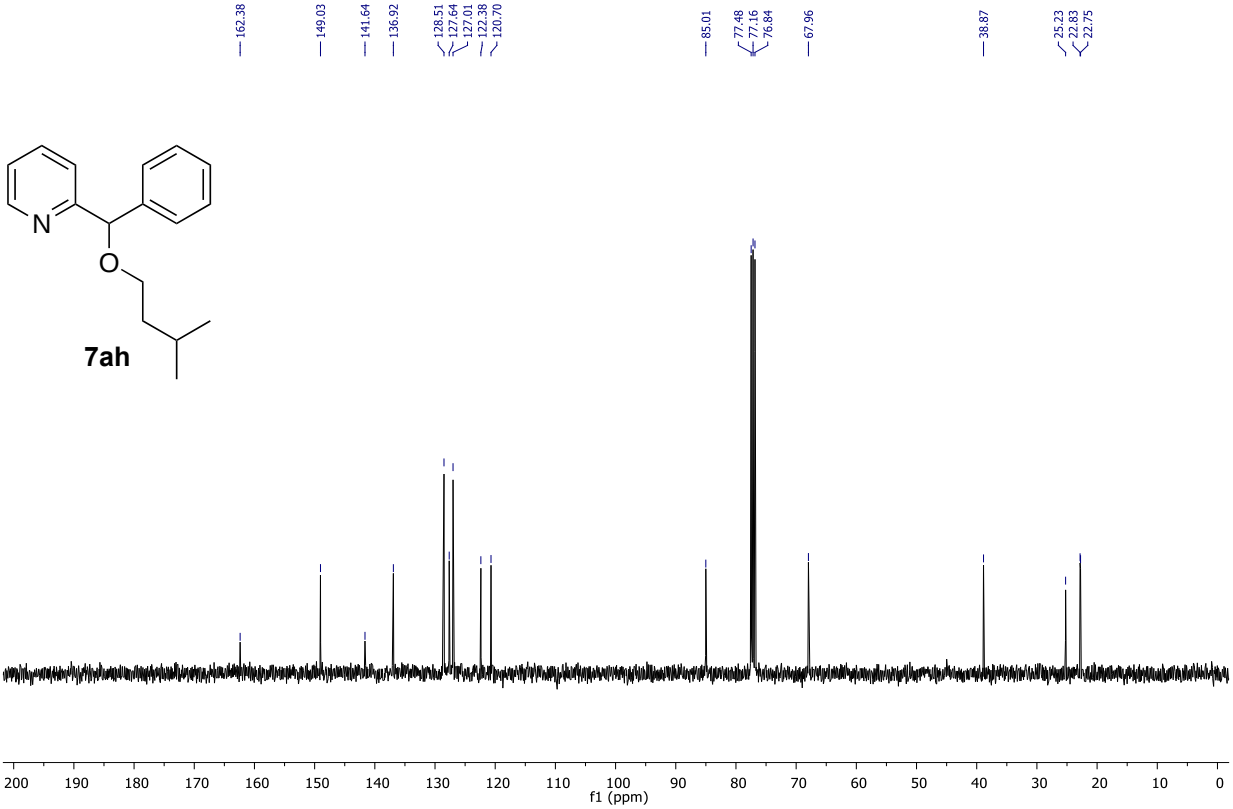


7ag

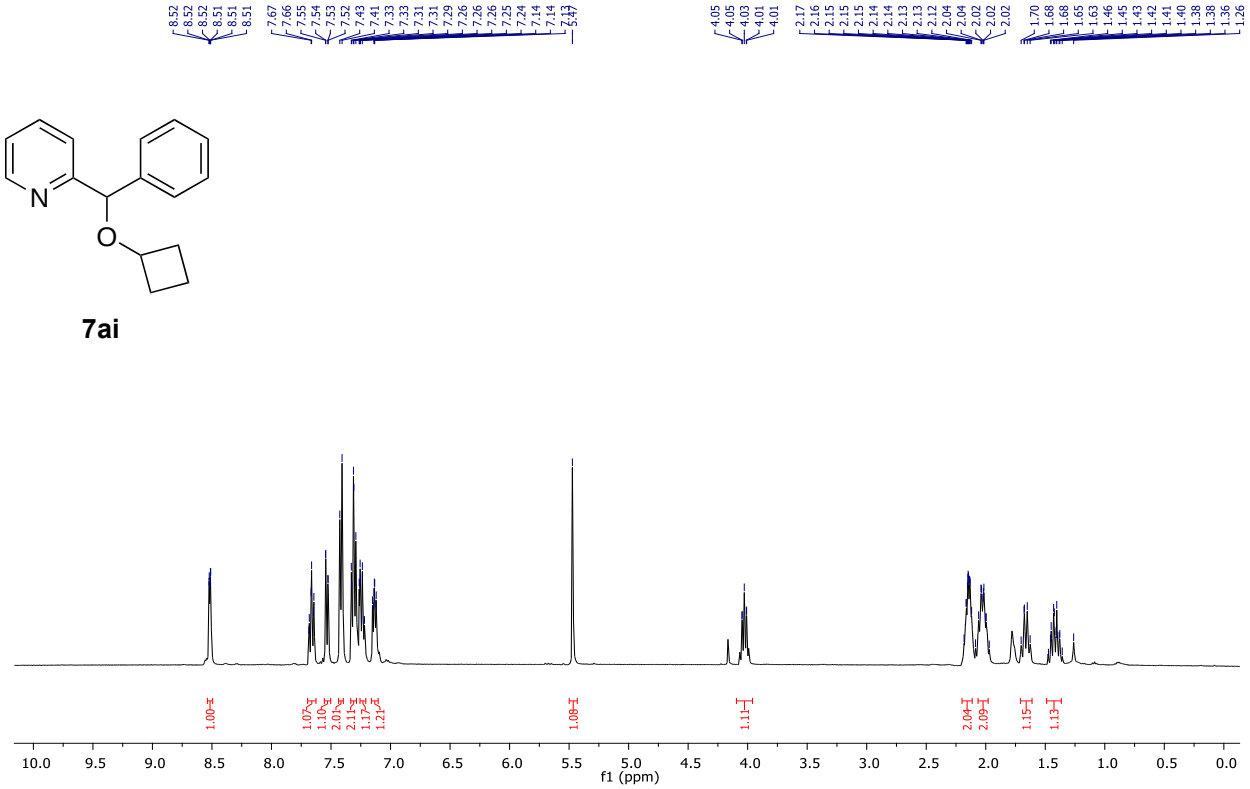
^{1}H NMR of **7ah**



^{13}C NMR of **7ah**

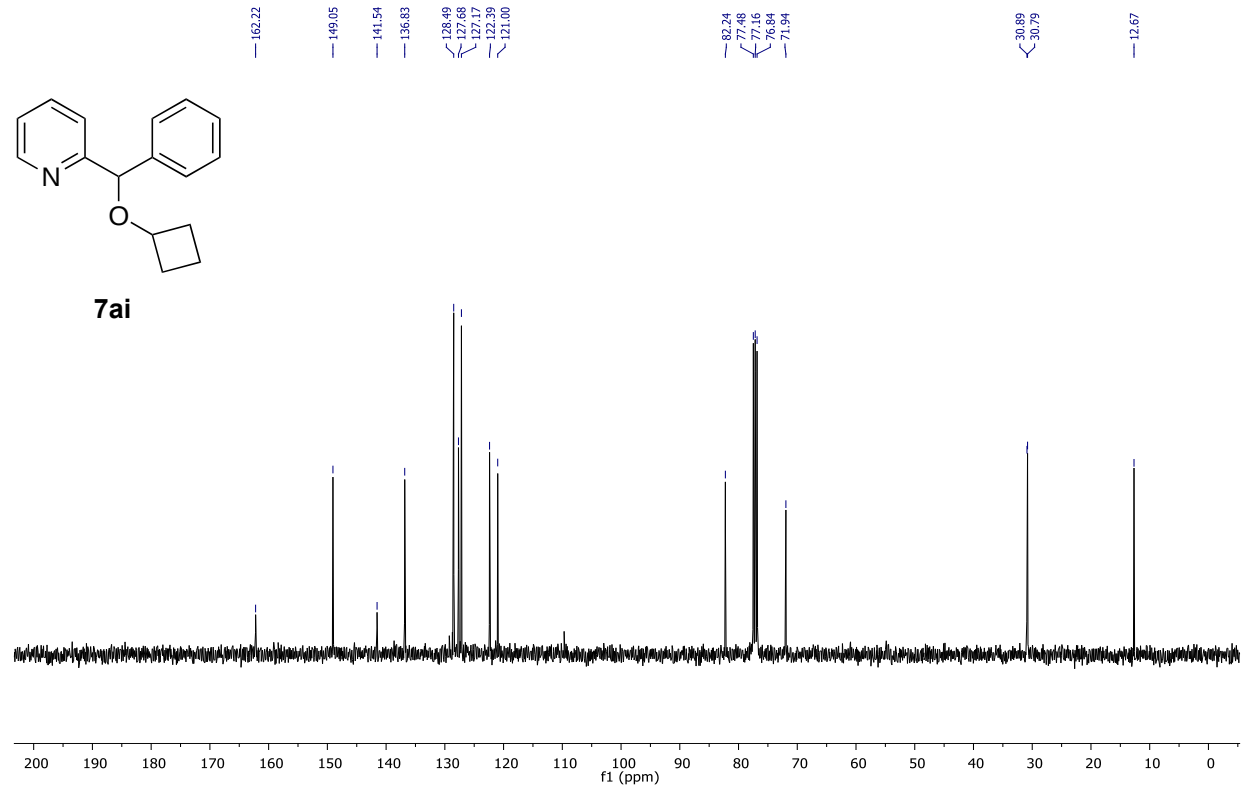


^{1}H NMR of **7ai**



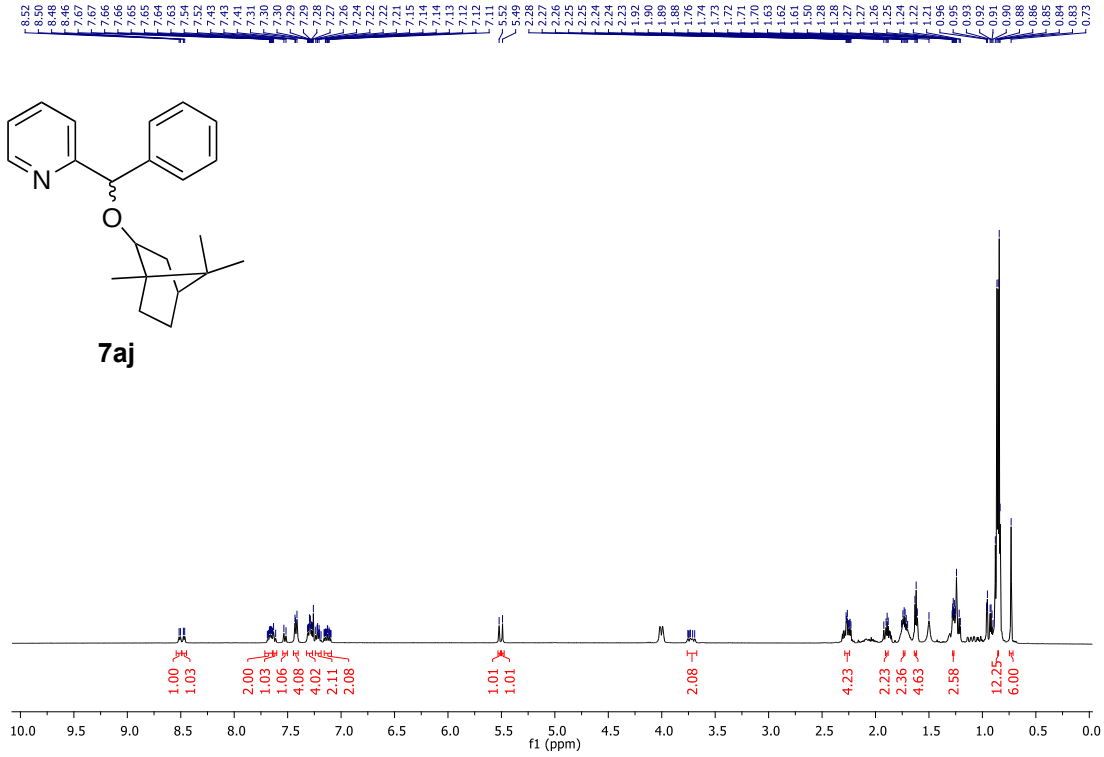
7ai

^{13}C NMR of **7ai**

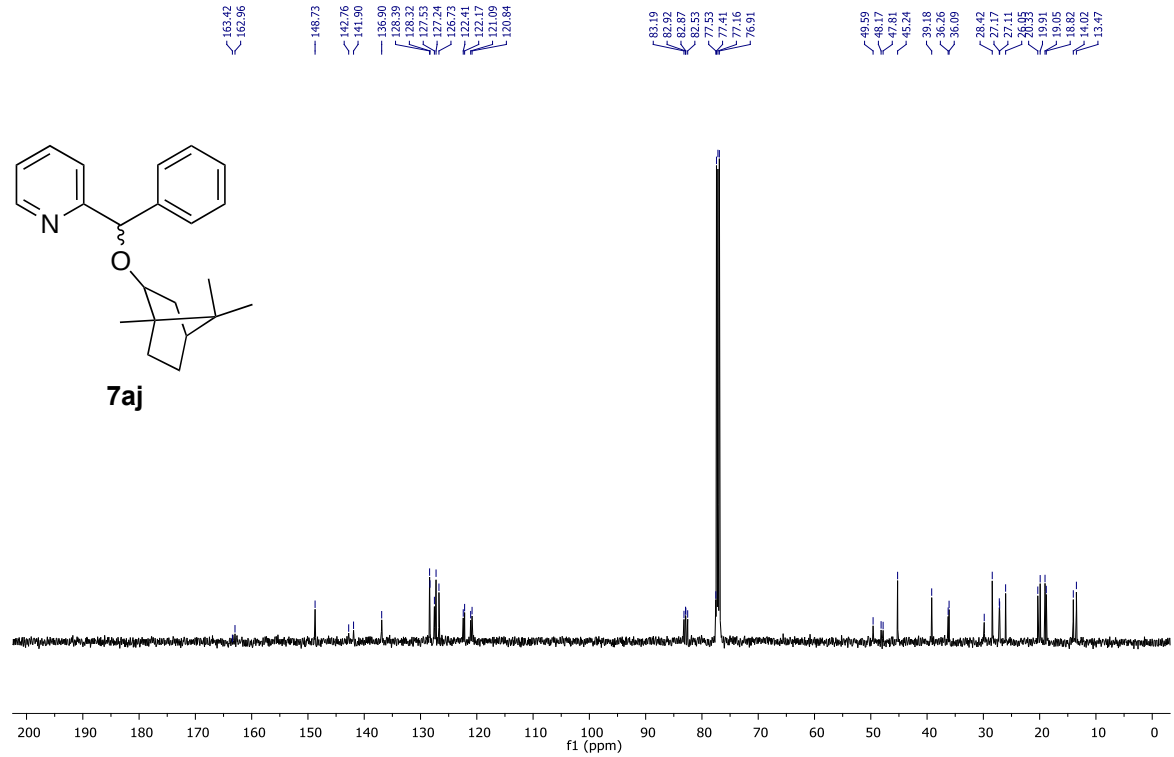


7ai

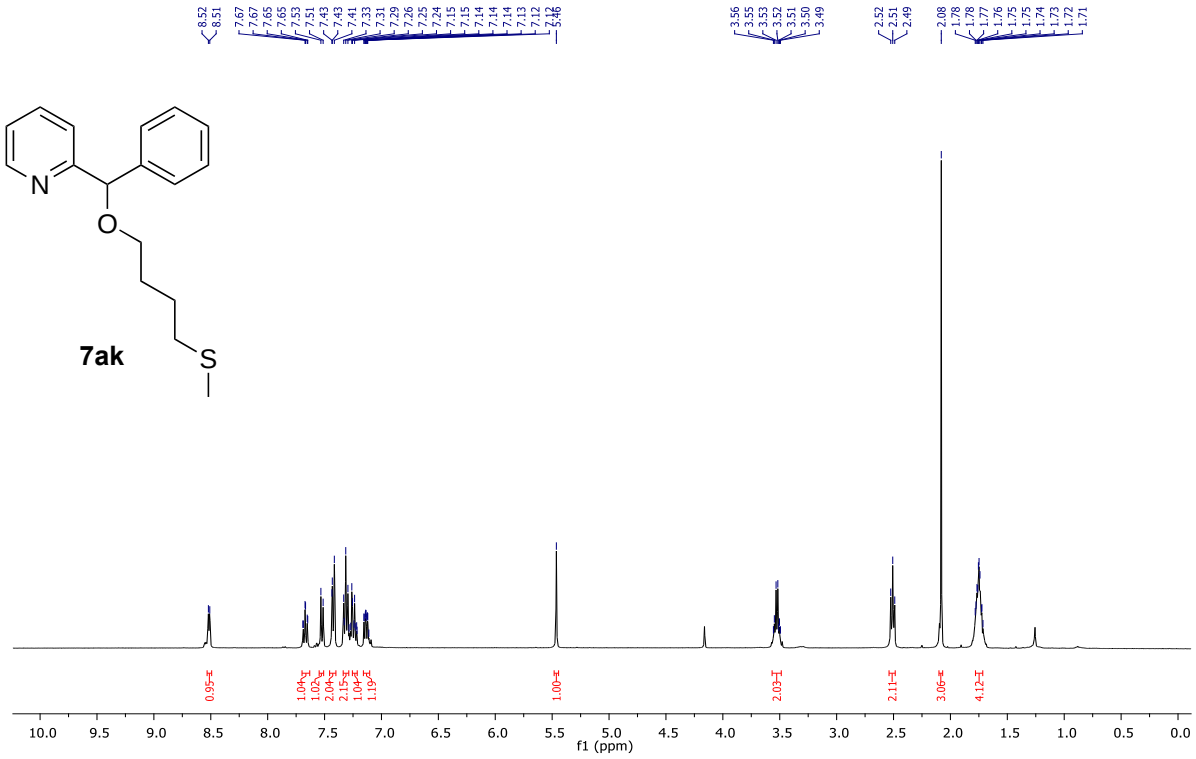
^{1}H NMR of **7aj**



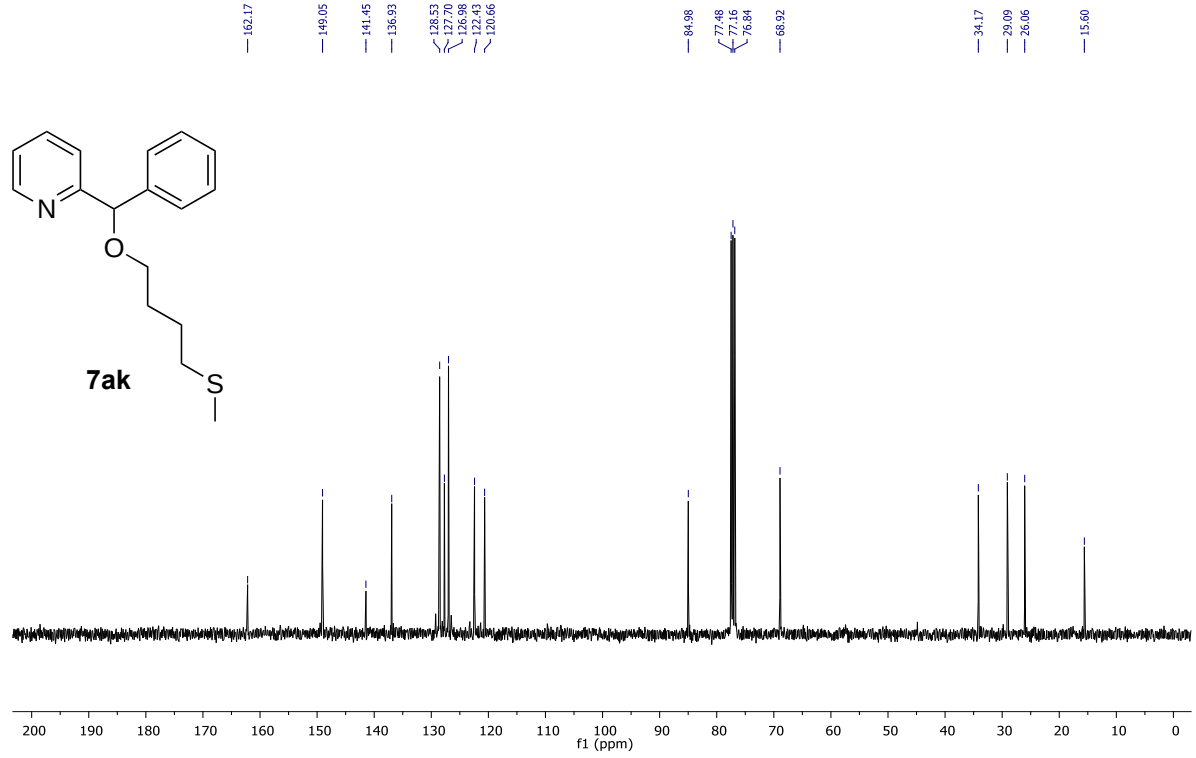
^{13}C NMR of **7aj**



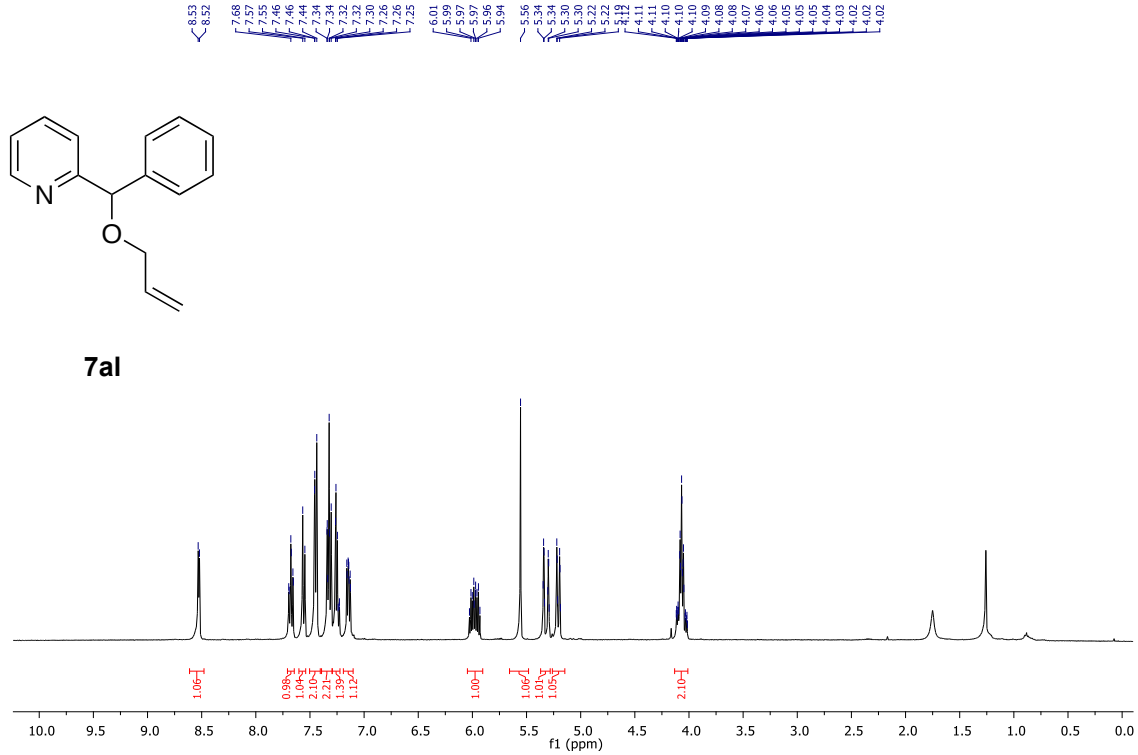
^{1}H NMR of **7ak**



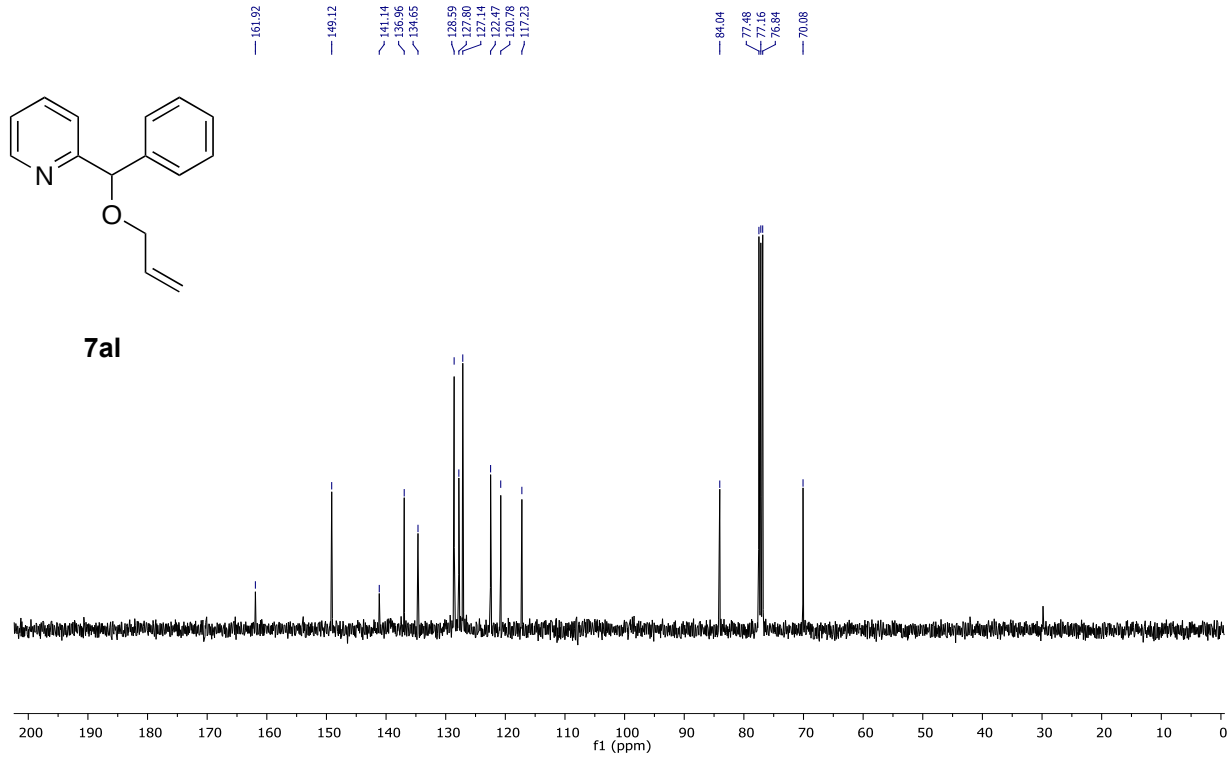
^{13}C NMR of **7ak**



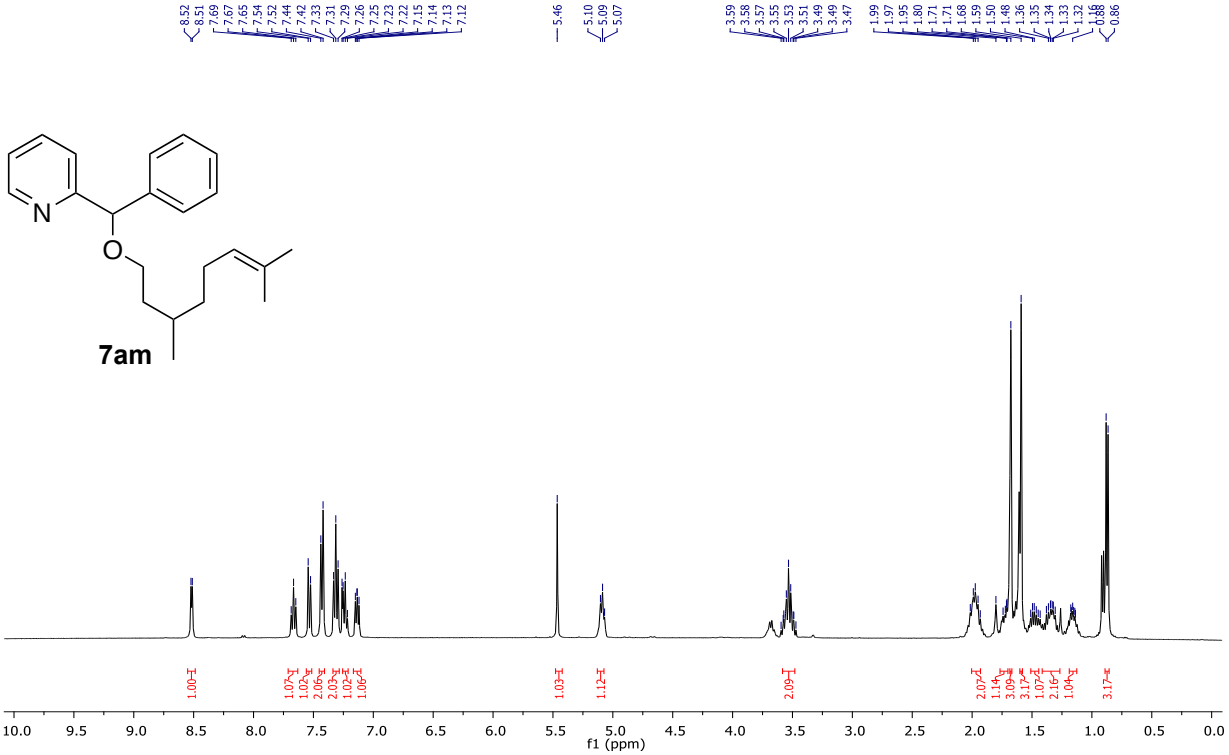
^{1}H NMR of **7al**



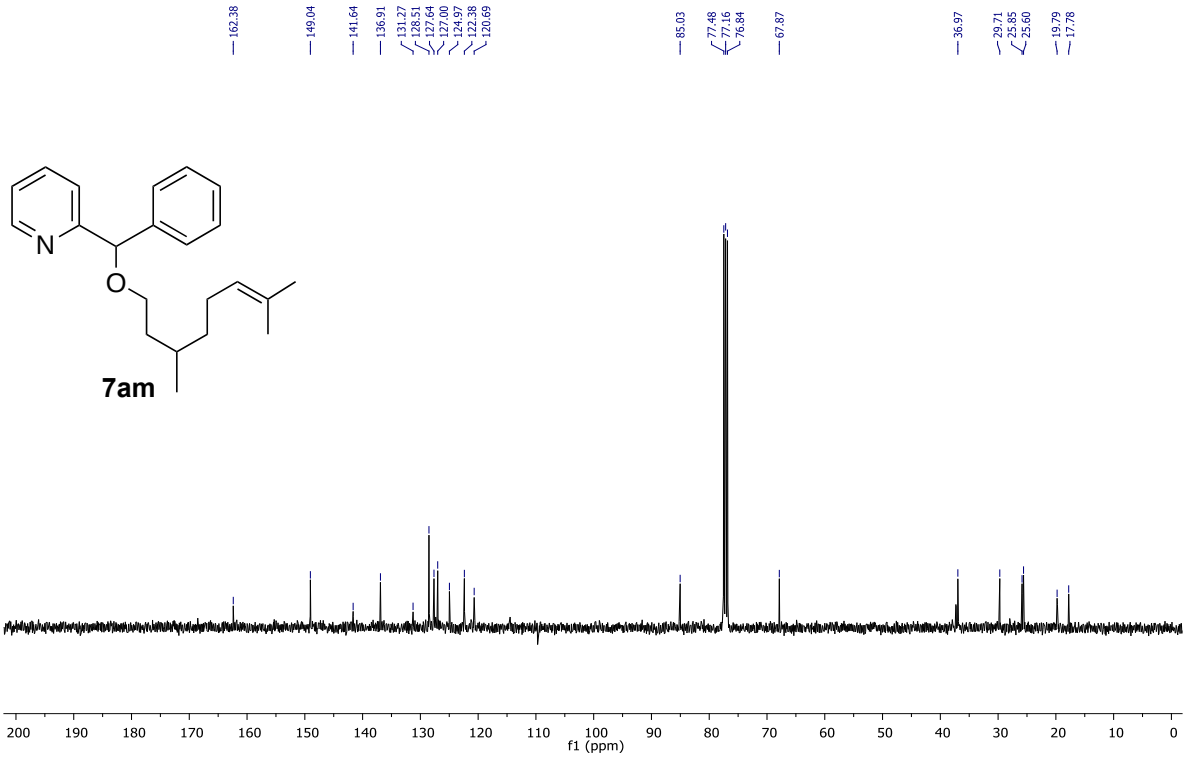
^{13}C NMR of **7al**



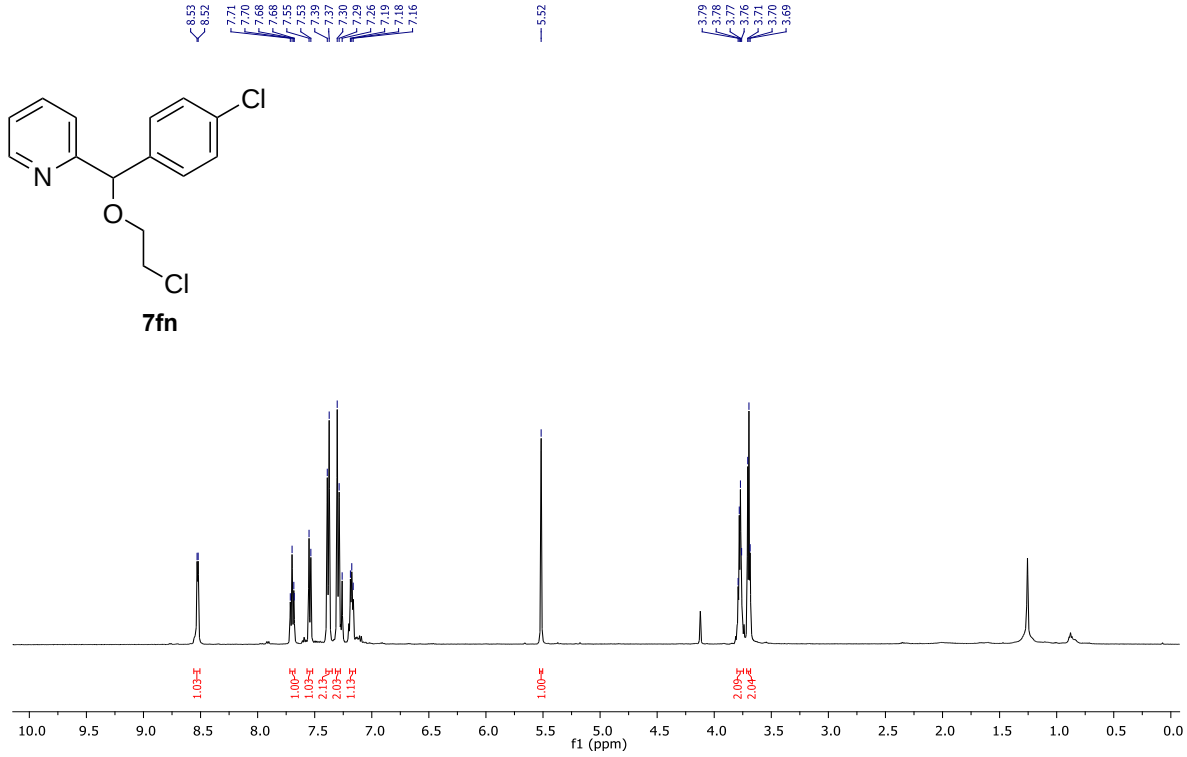
^{1}H NMR of **7am**



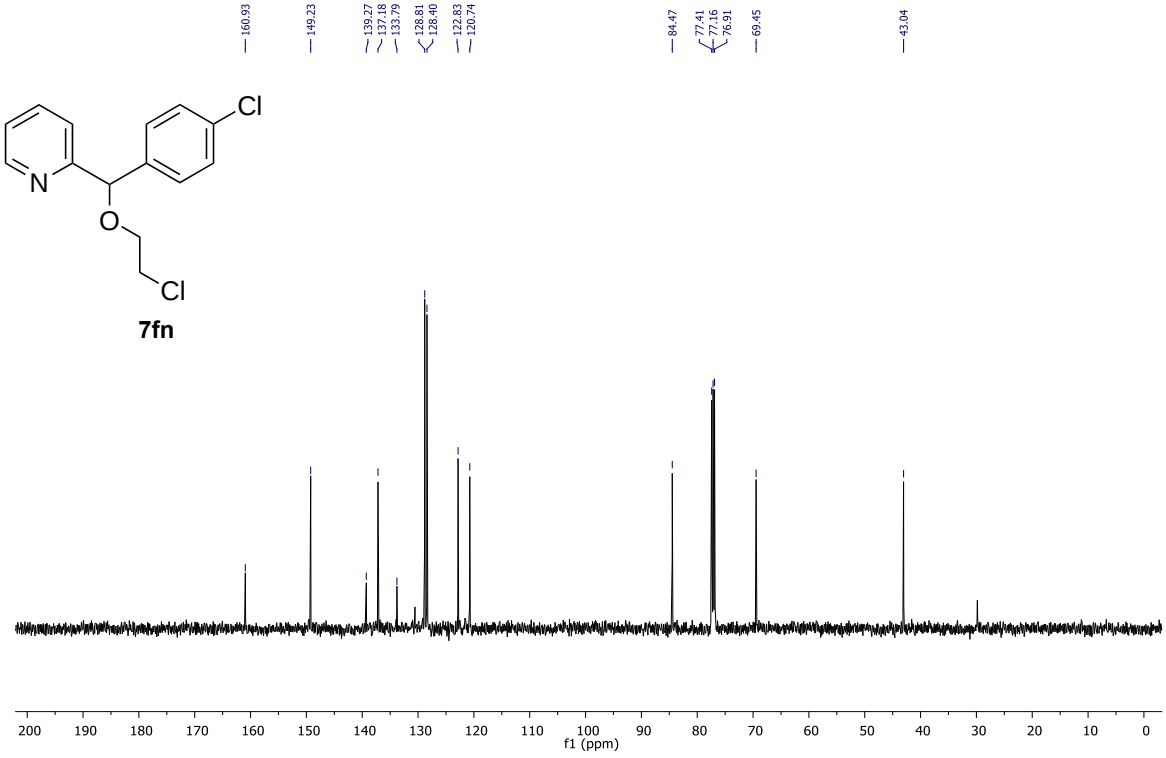
^{13}C NMR of **7am**



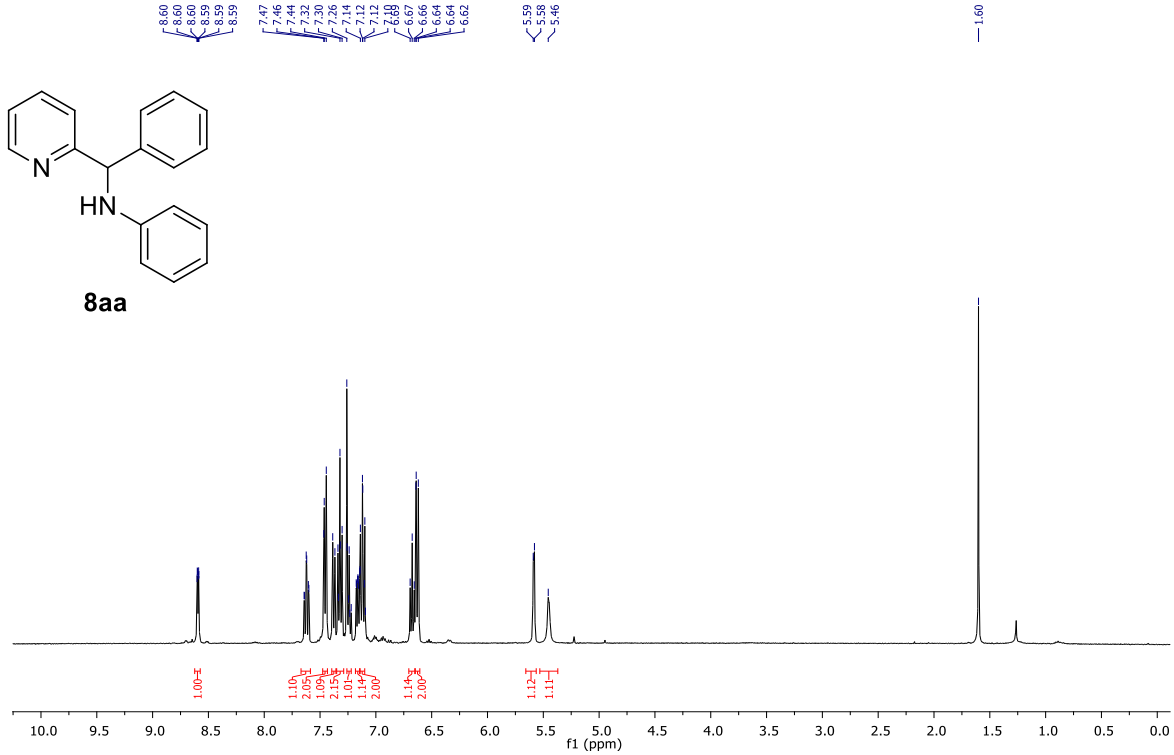
^{1}H NMR of **7fn**



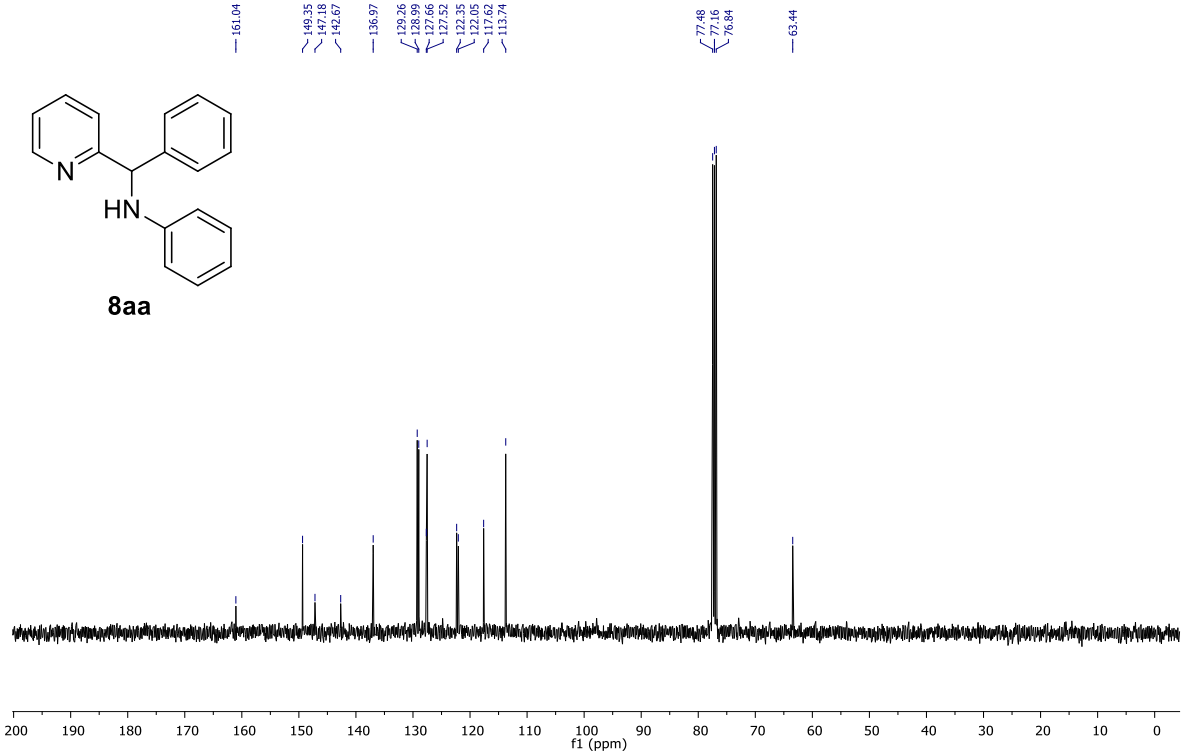
^{13}C NMR of **7fn**



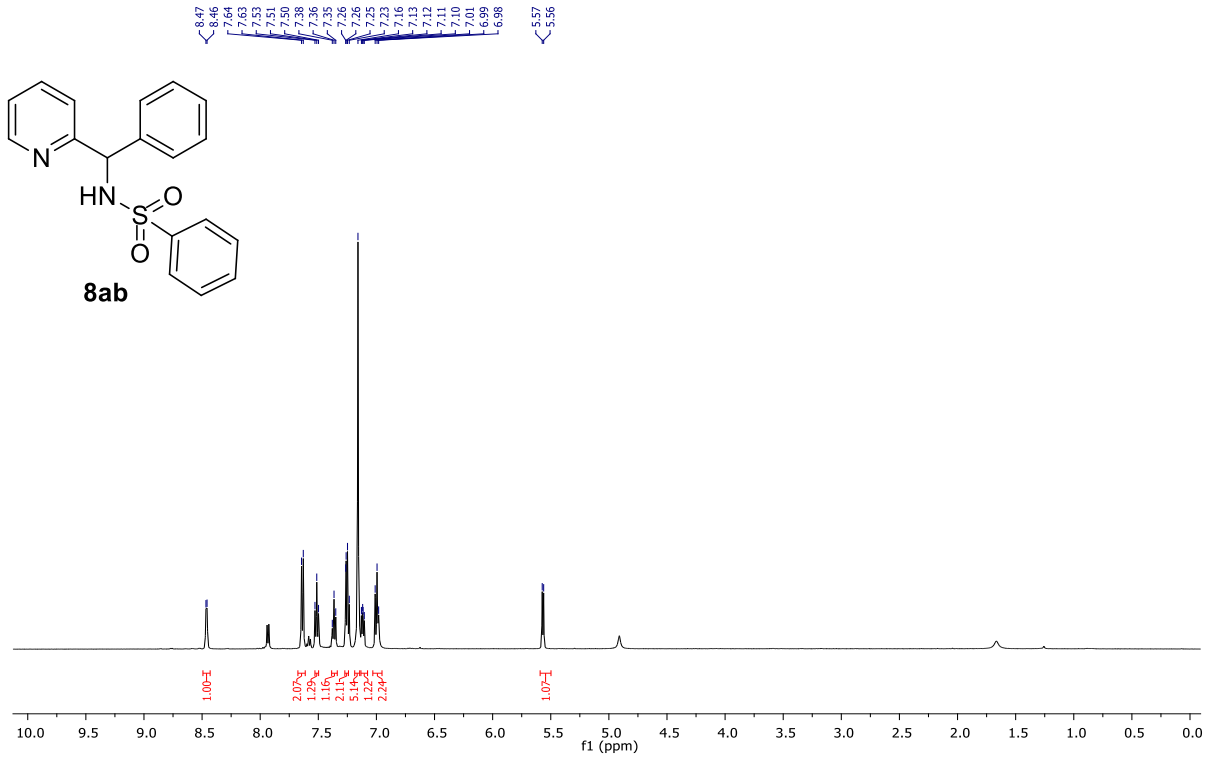
^{1}H NMR of **8aa**



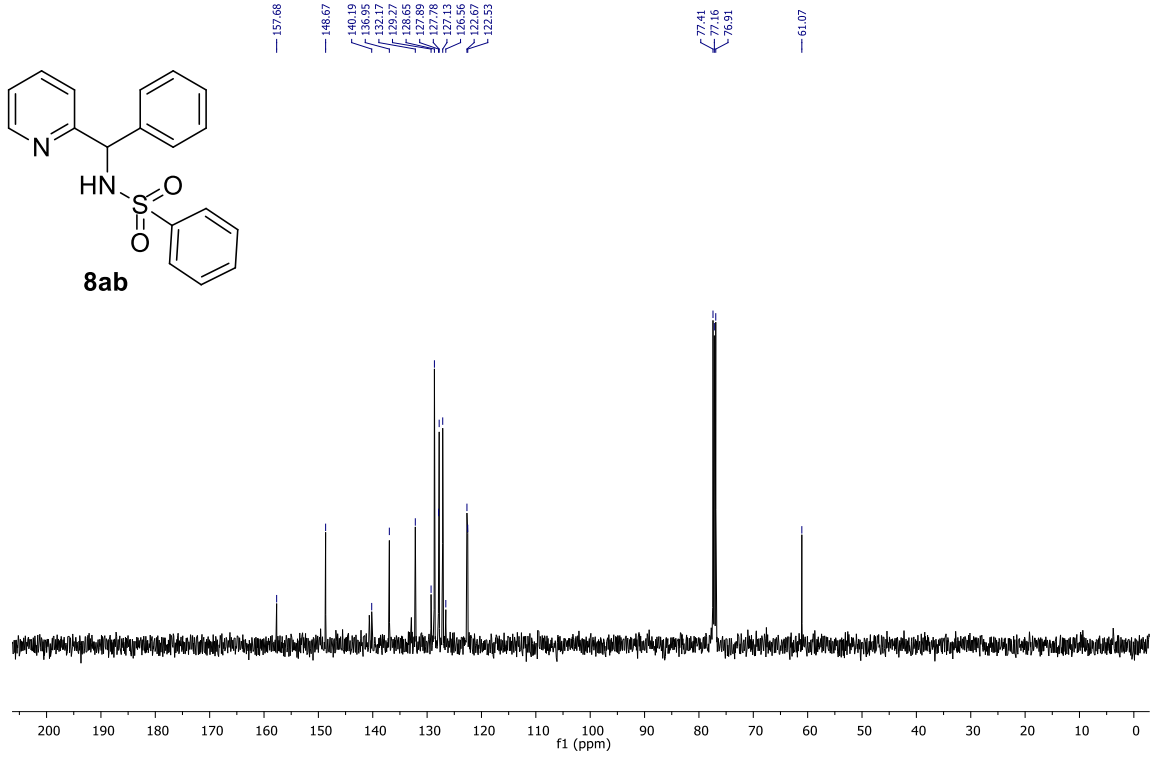
^{13}C NMR of **8aa**



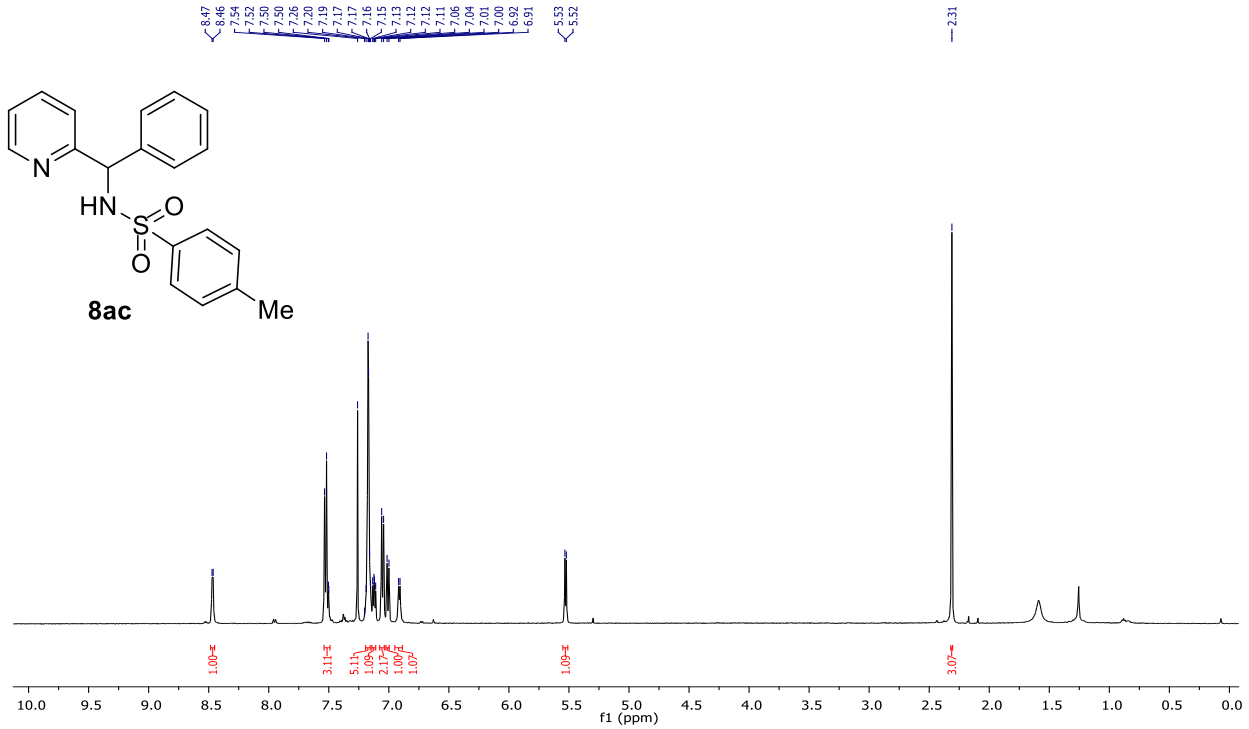
^{1}H NMR of **8ab**



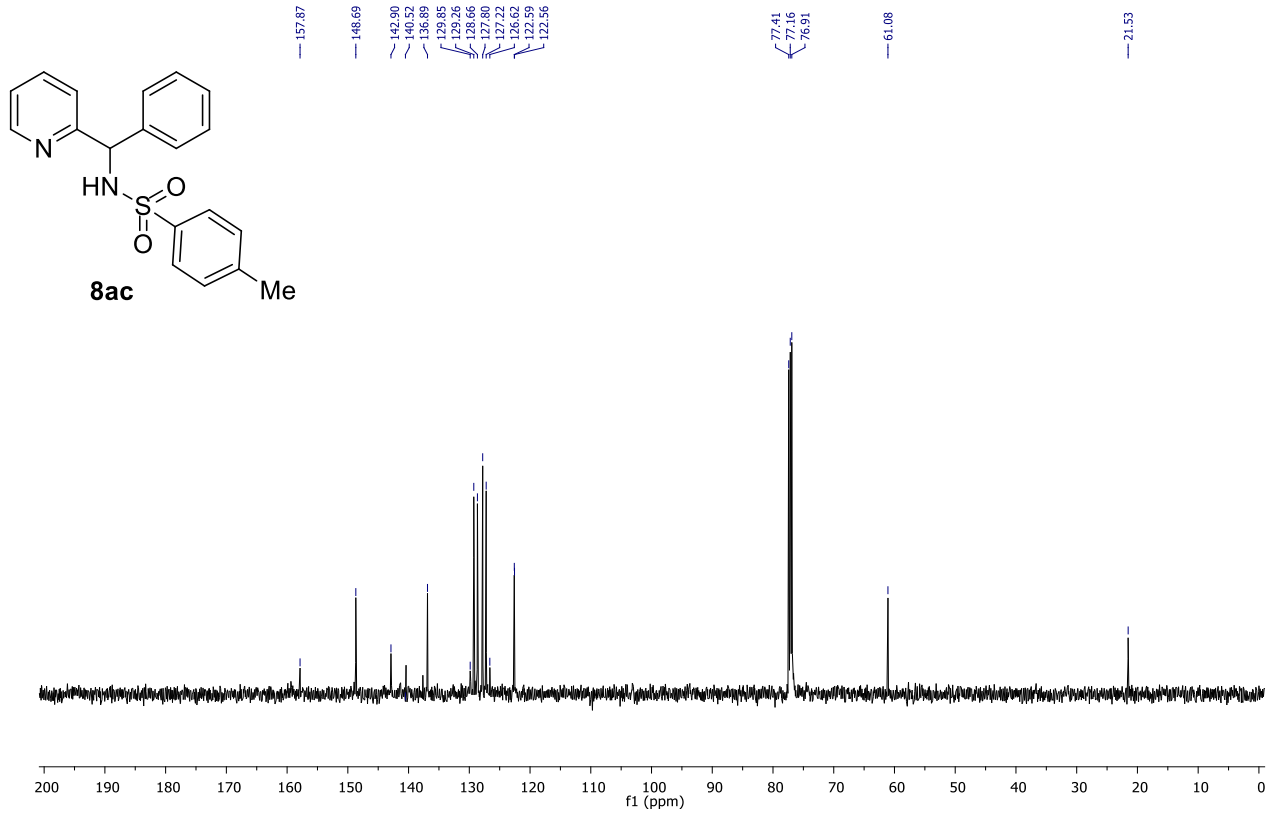
^{13}C NMR of **8ab**



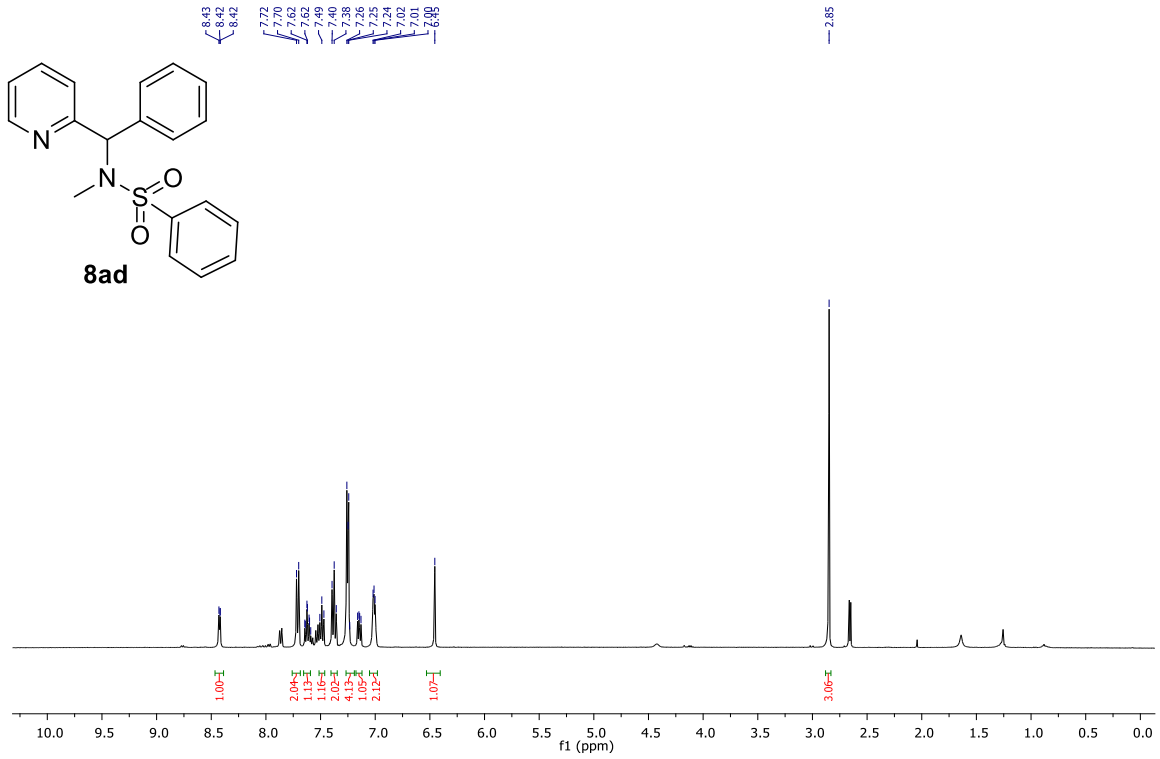
^{1}H NMR of **8ac**



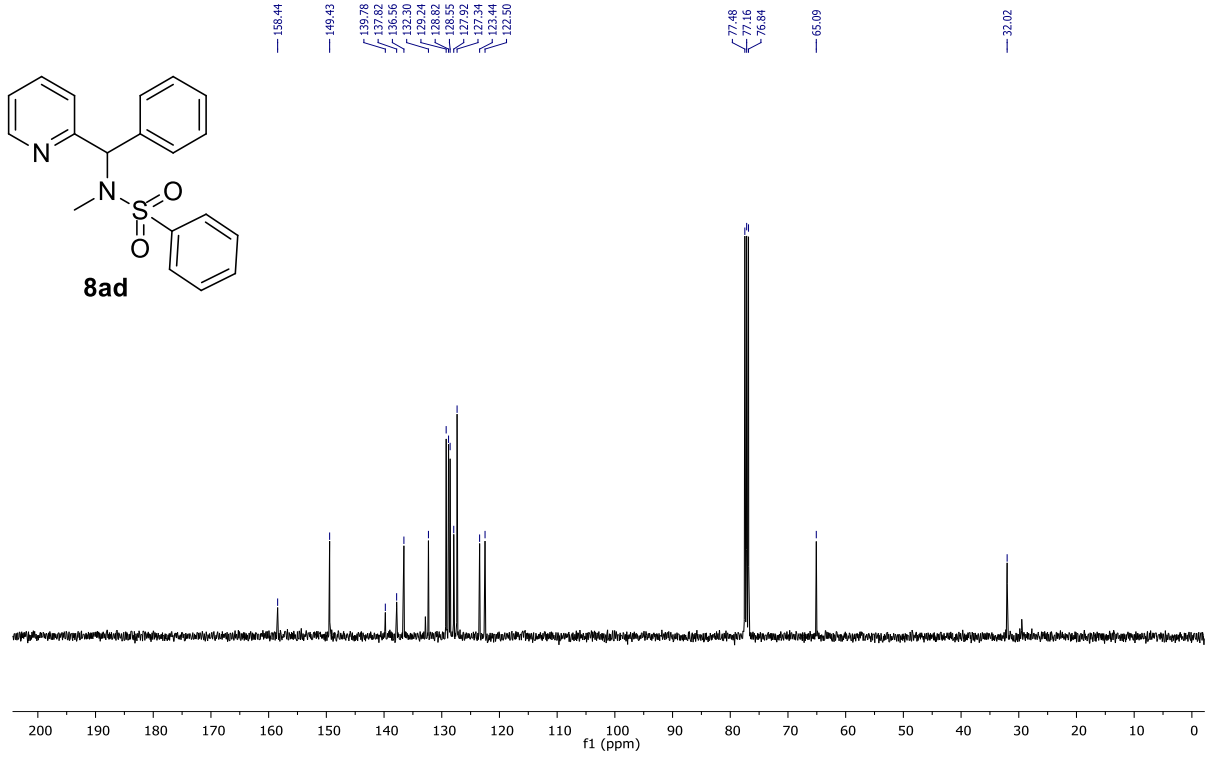
^{13}C NMR of **8ac**



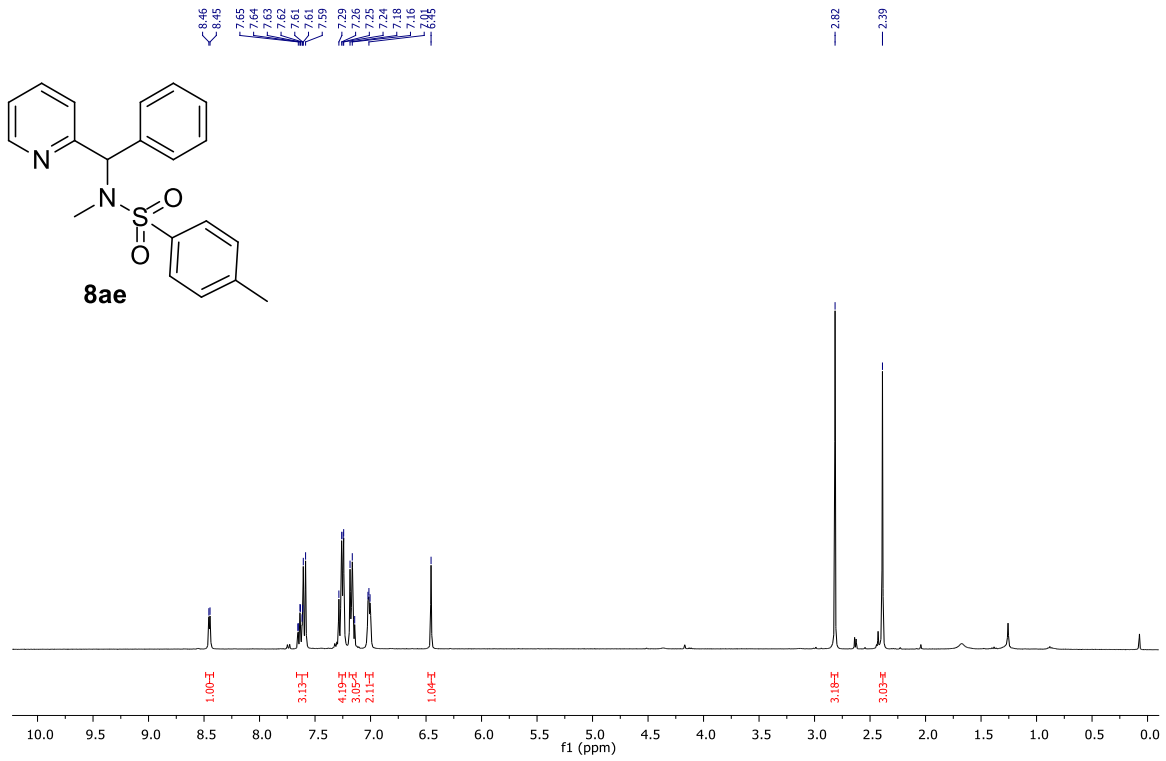
^{1}H NMR of **8ad**



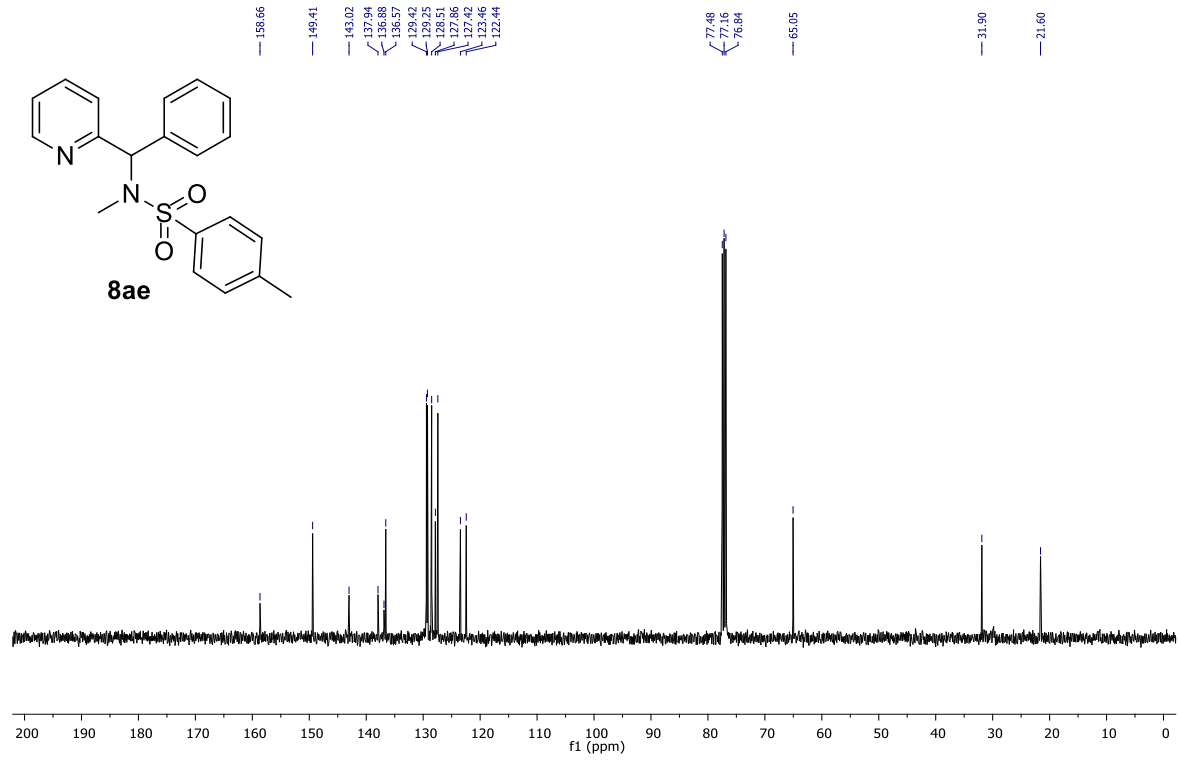
^{13}C NMR of **8ad**



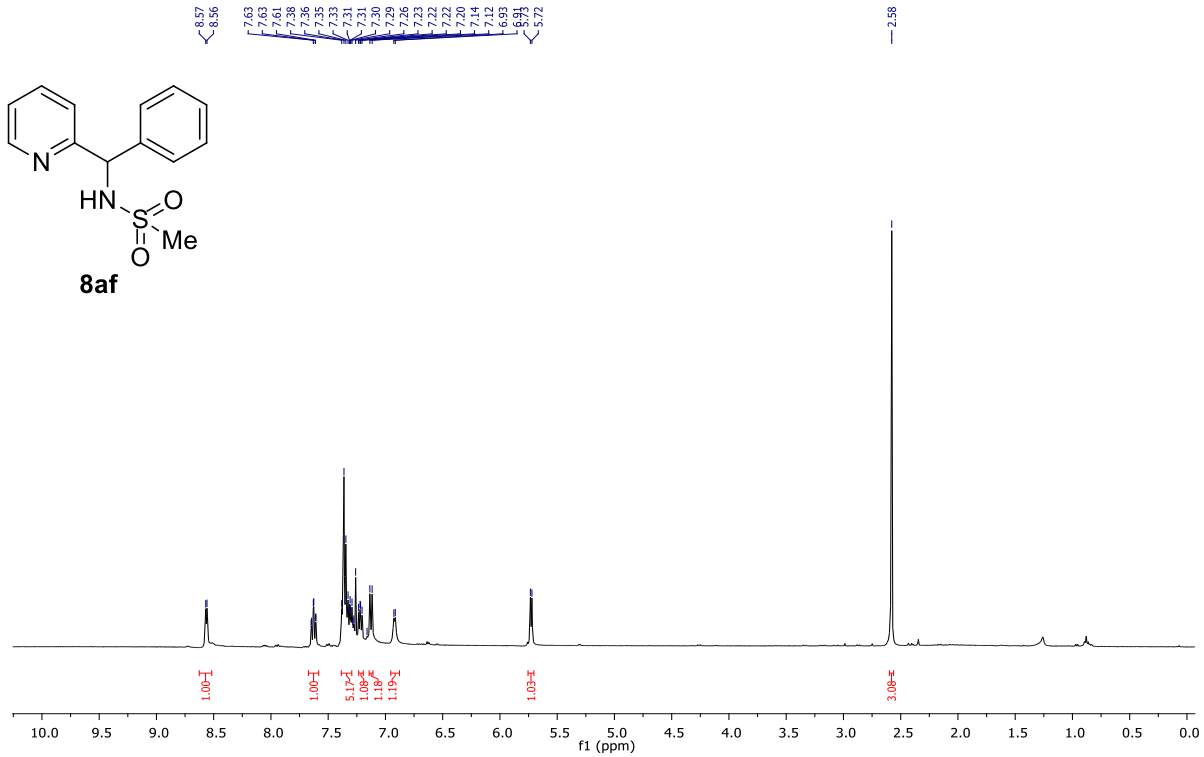
^{1}H NMR of **8ae**



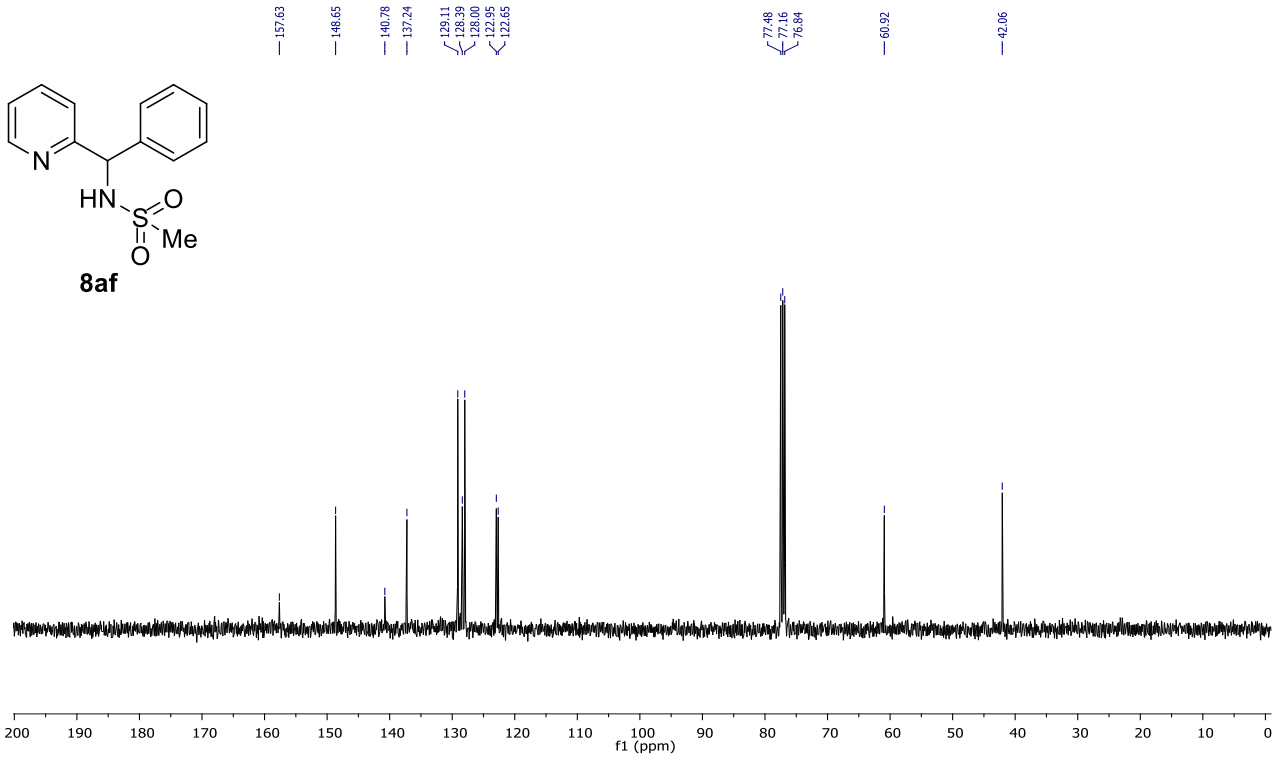
^{13}C NMR of **8ae**



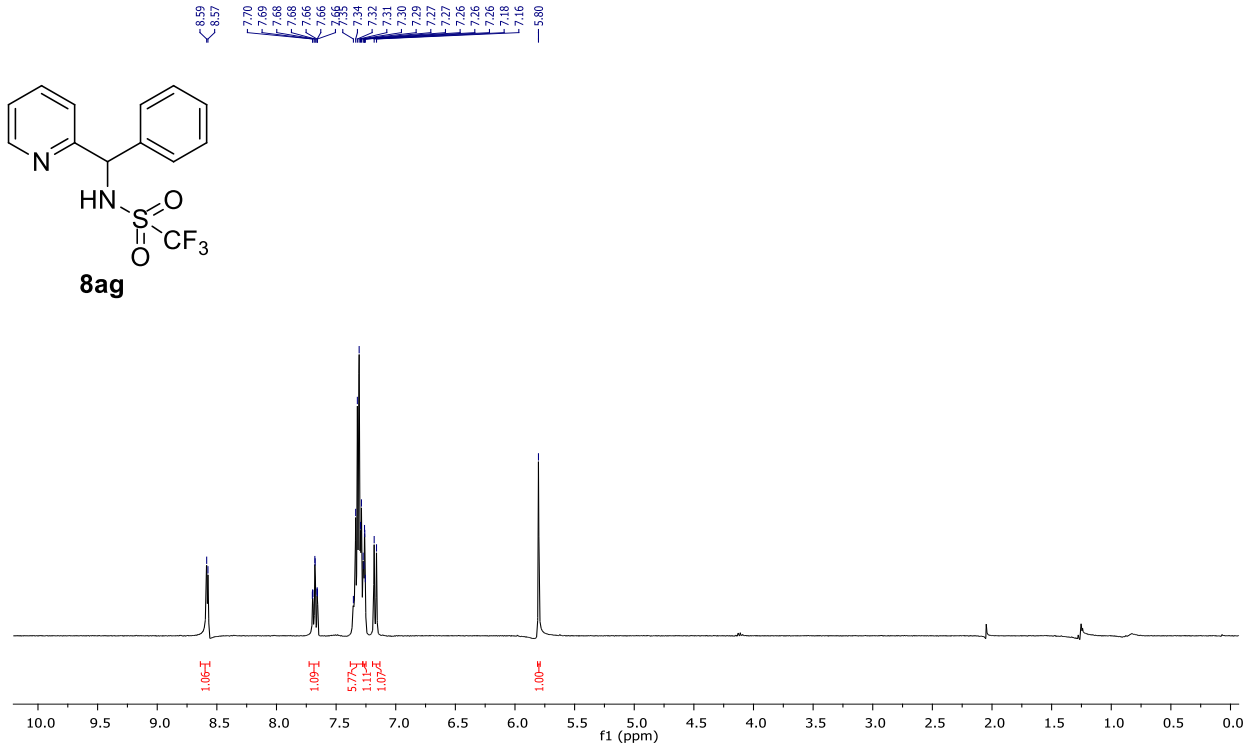
^{1}H NMR of **8af**



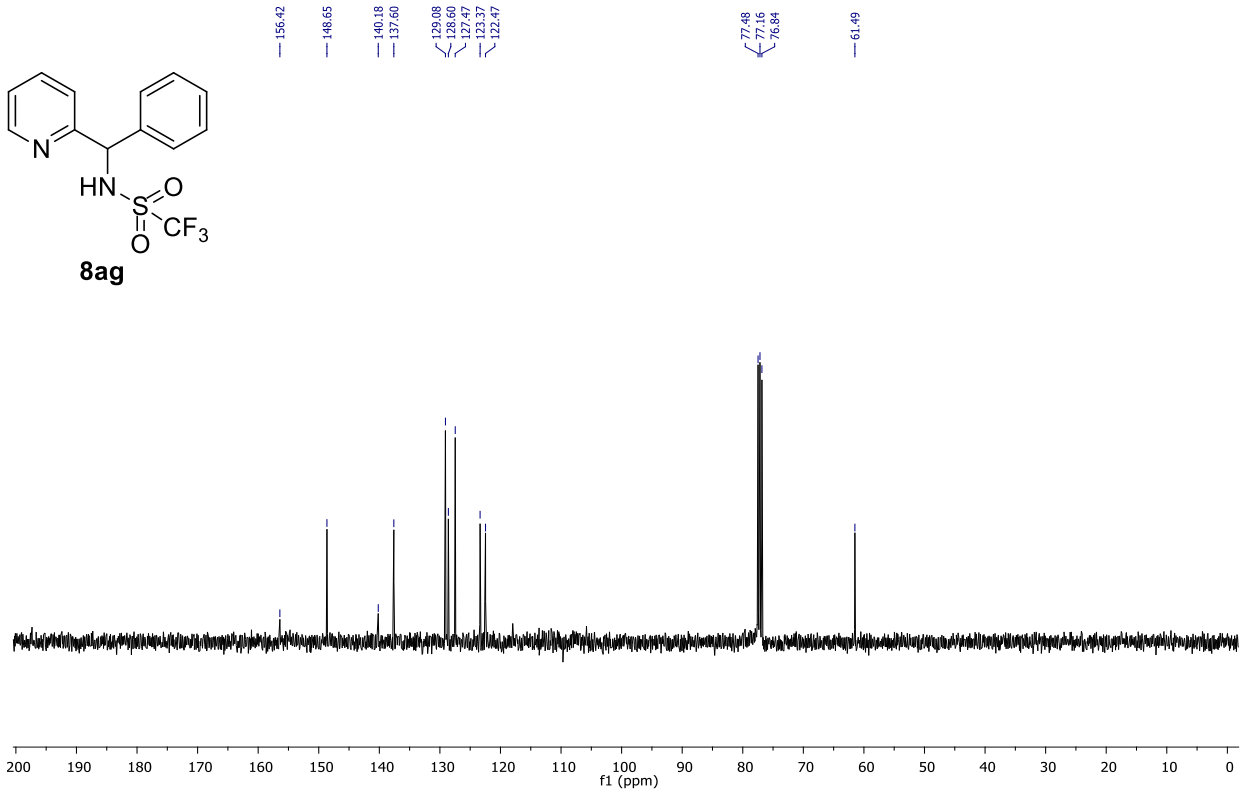
^{13}C NMR of **8af**



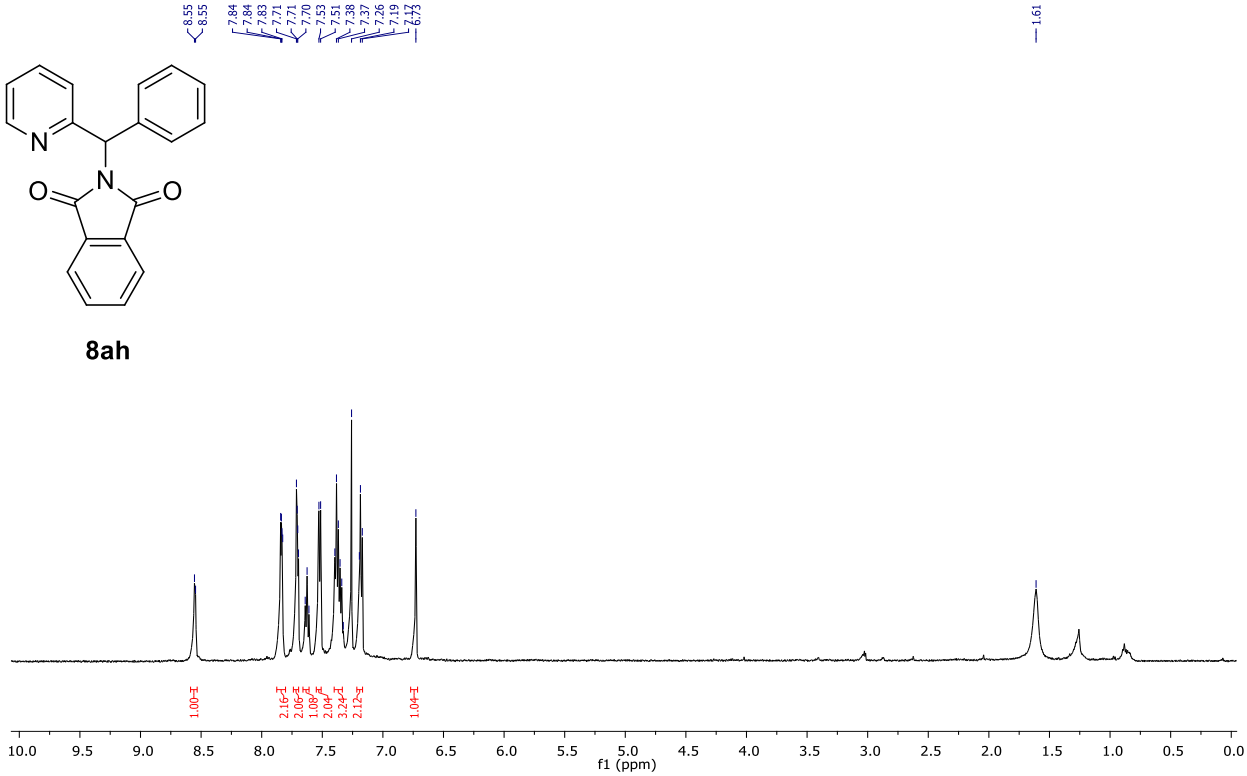
^{1}H NMR of **8ag**



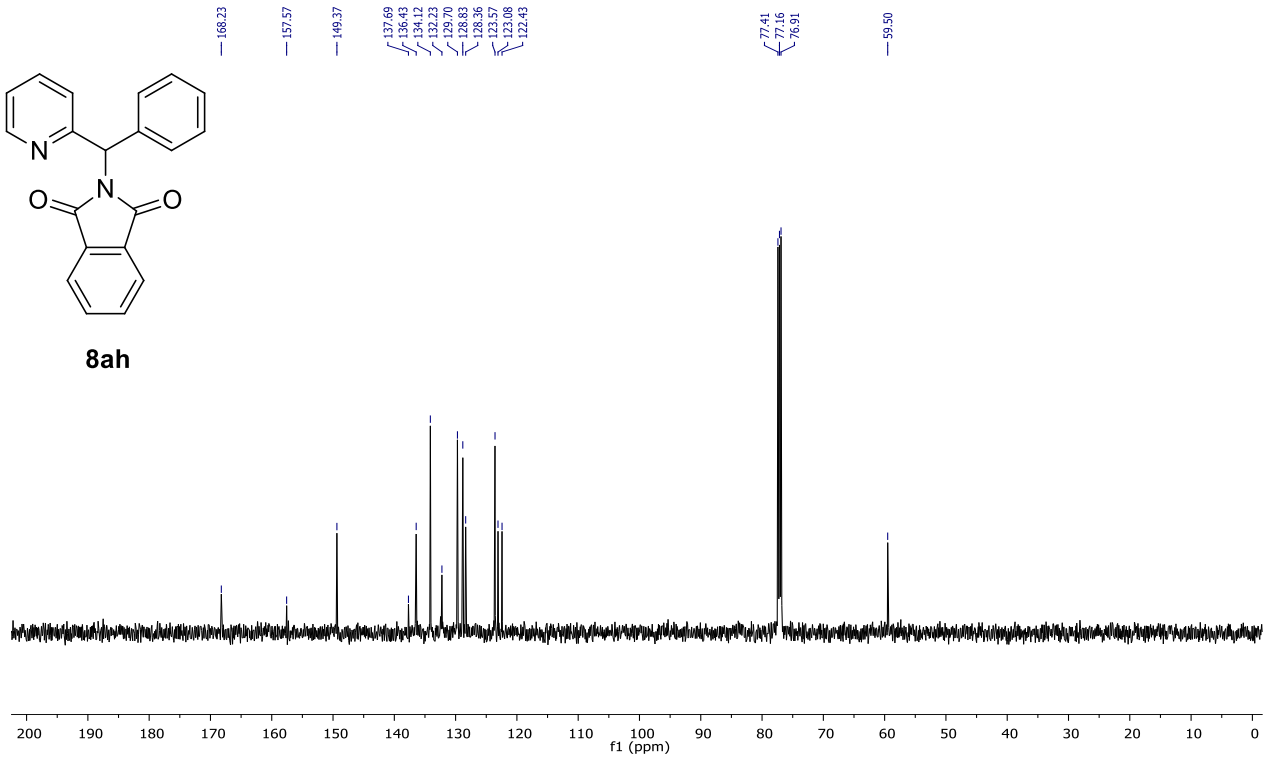
^{13}C NMR of **8ag**



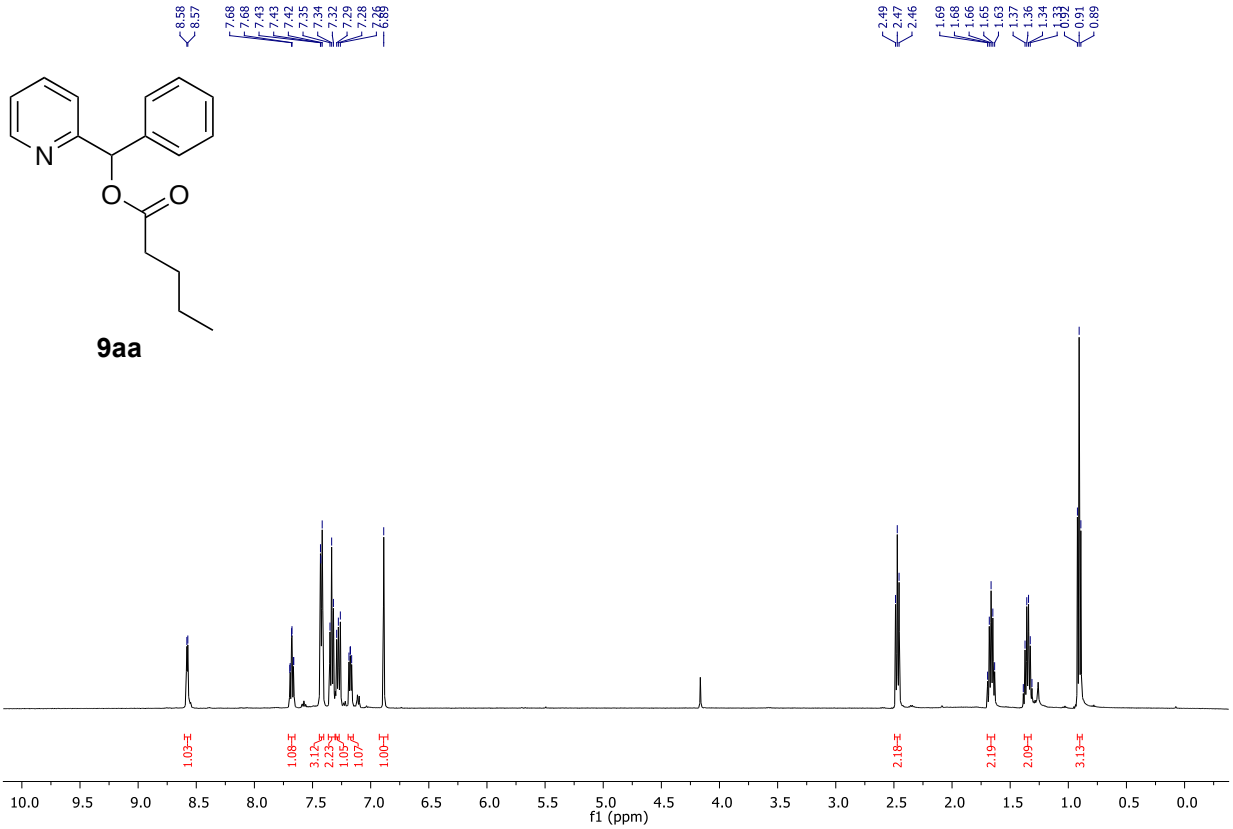
^{1}H NMR of **8ah**



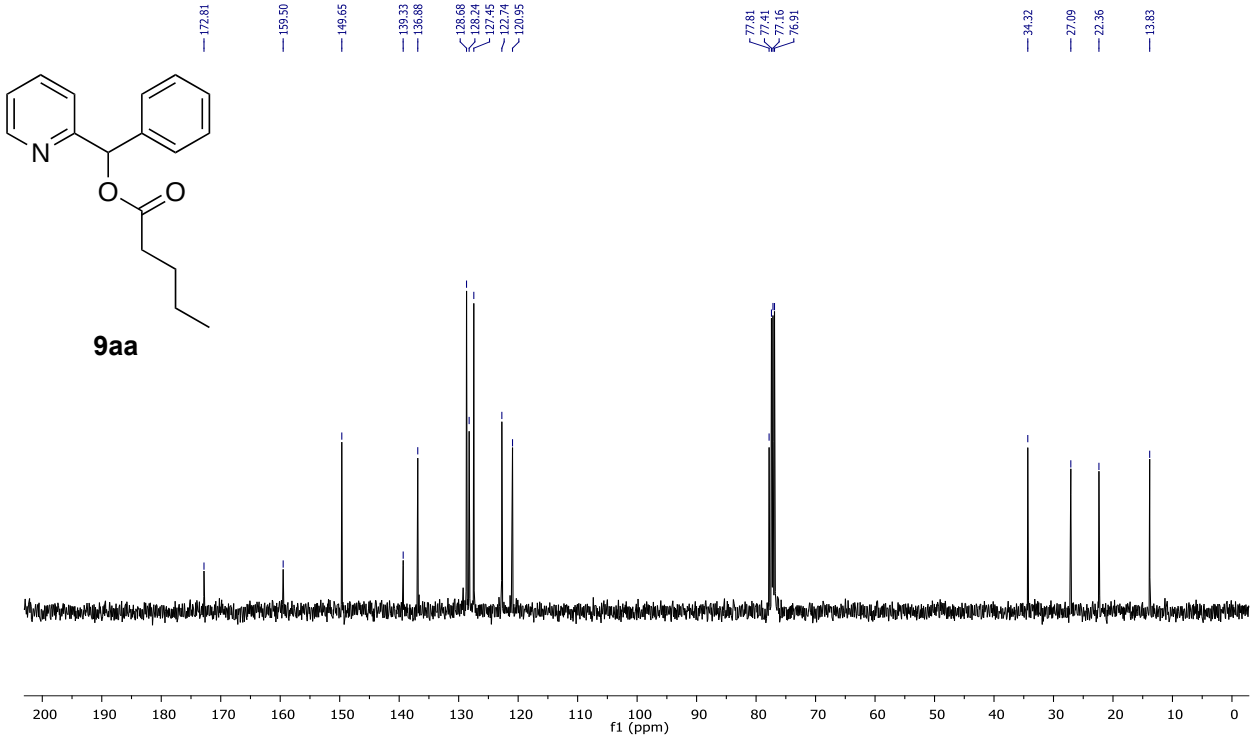
^{13}C NMR of **8ah**



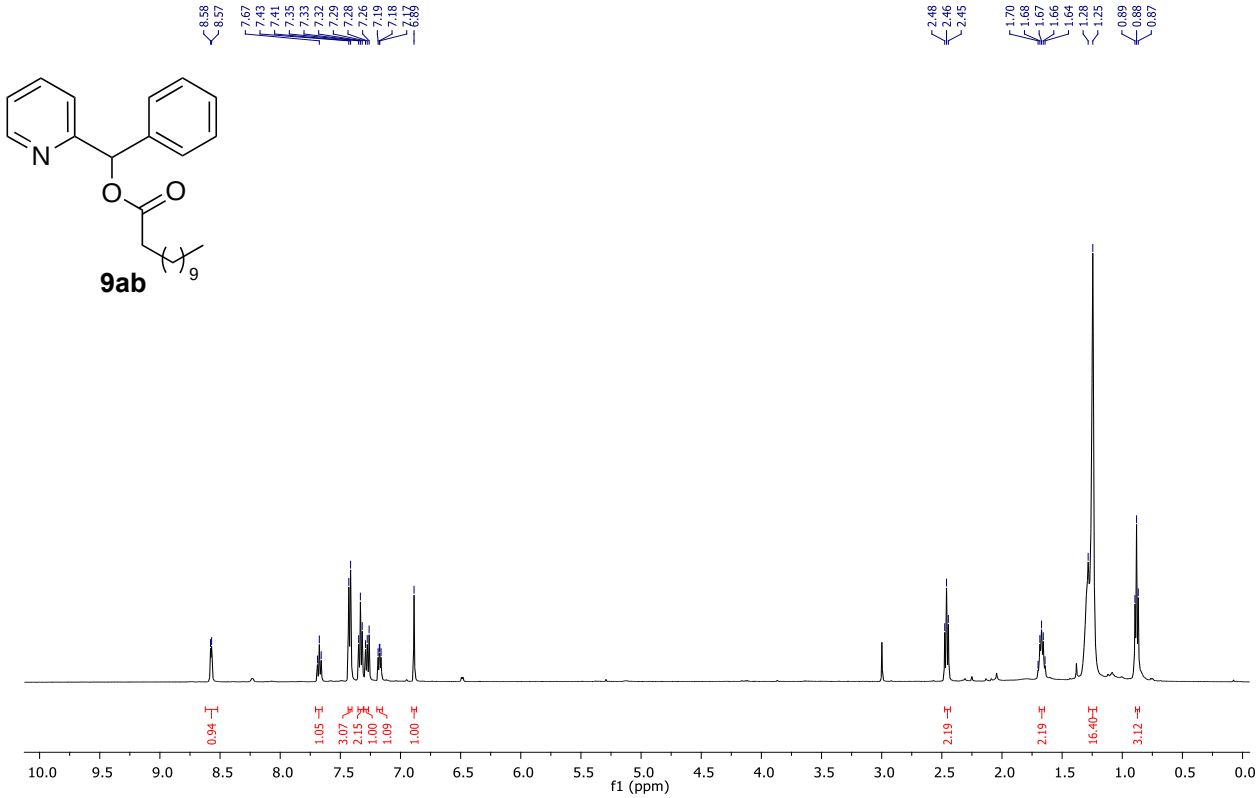
^{1}H NMR of **9aa**



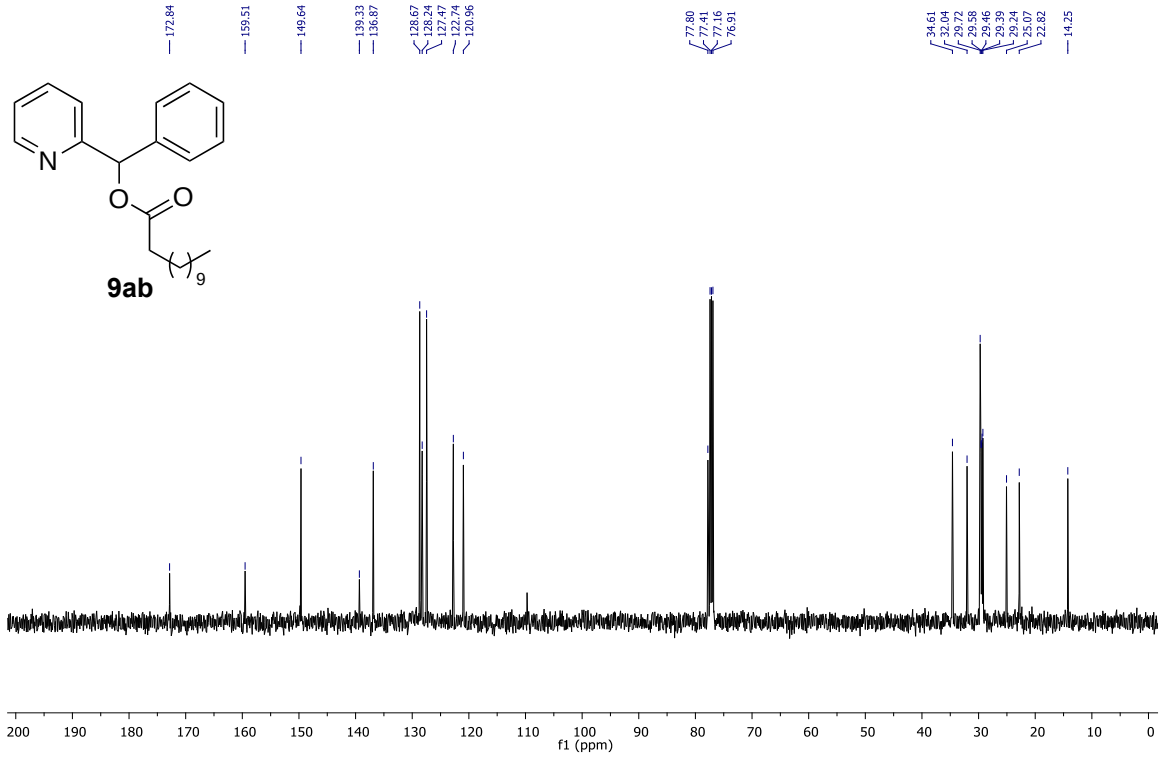
^{13}C NMR of **9aa**



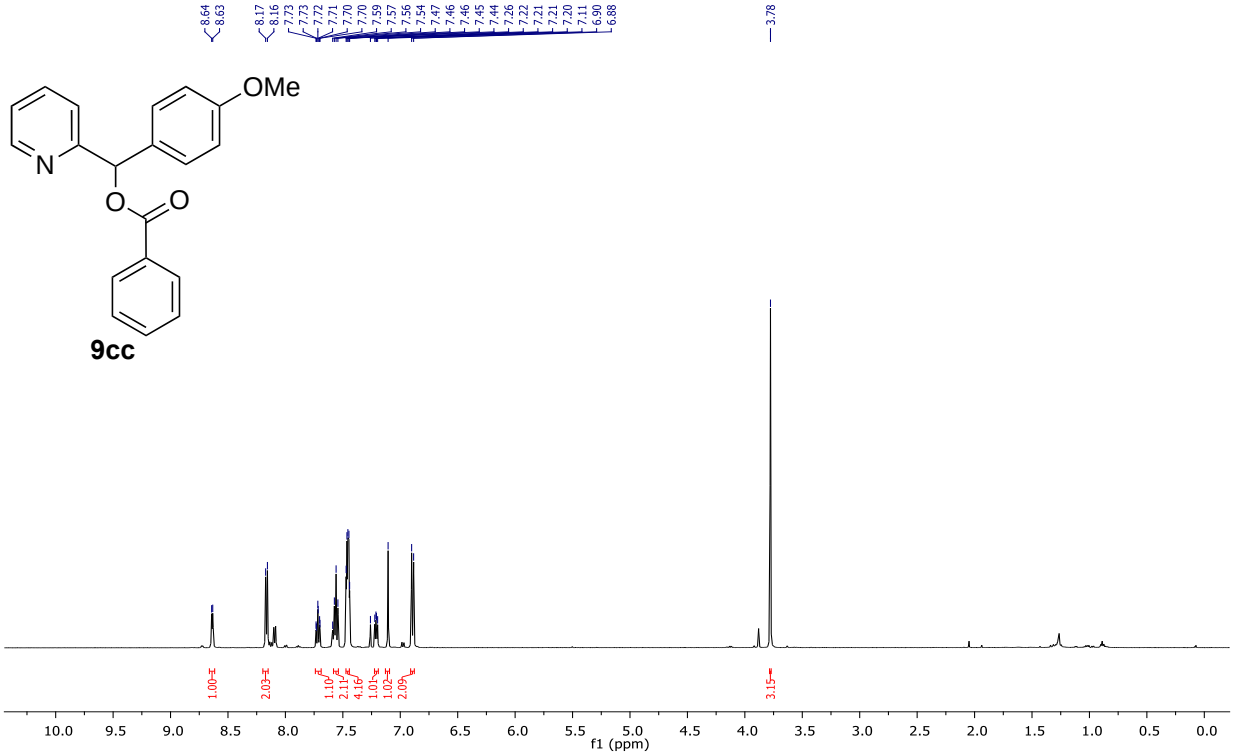
^{1}H NMR of **9ab**



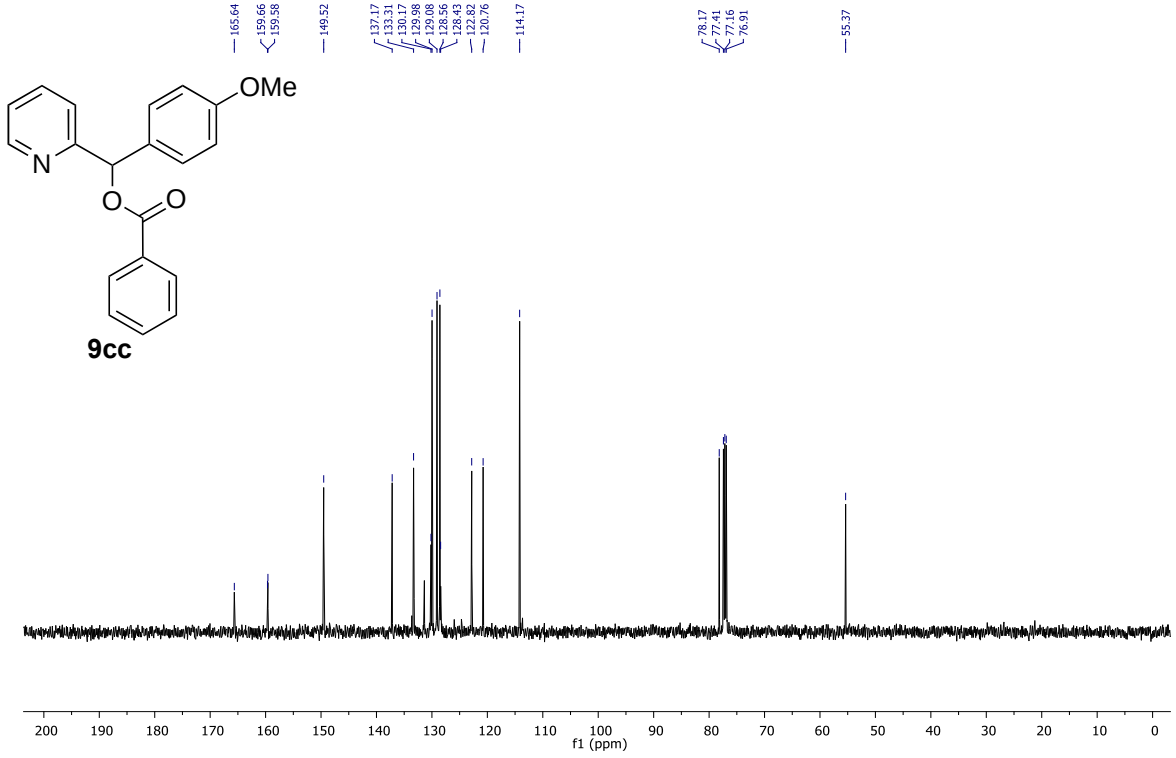
^{13}C NMR of **9ab**



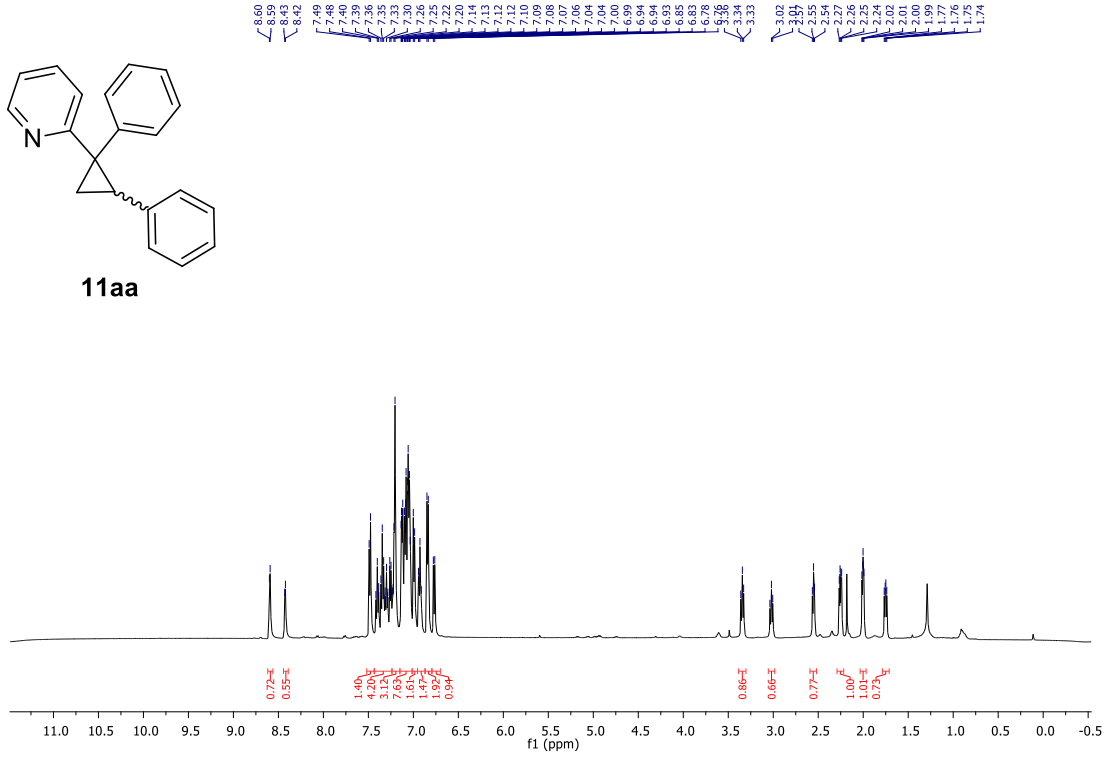
^{1}H NMR of **9cc**



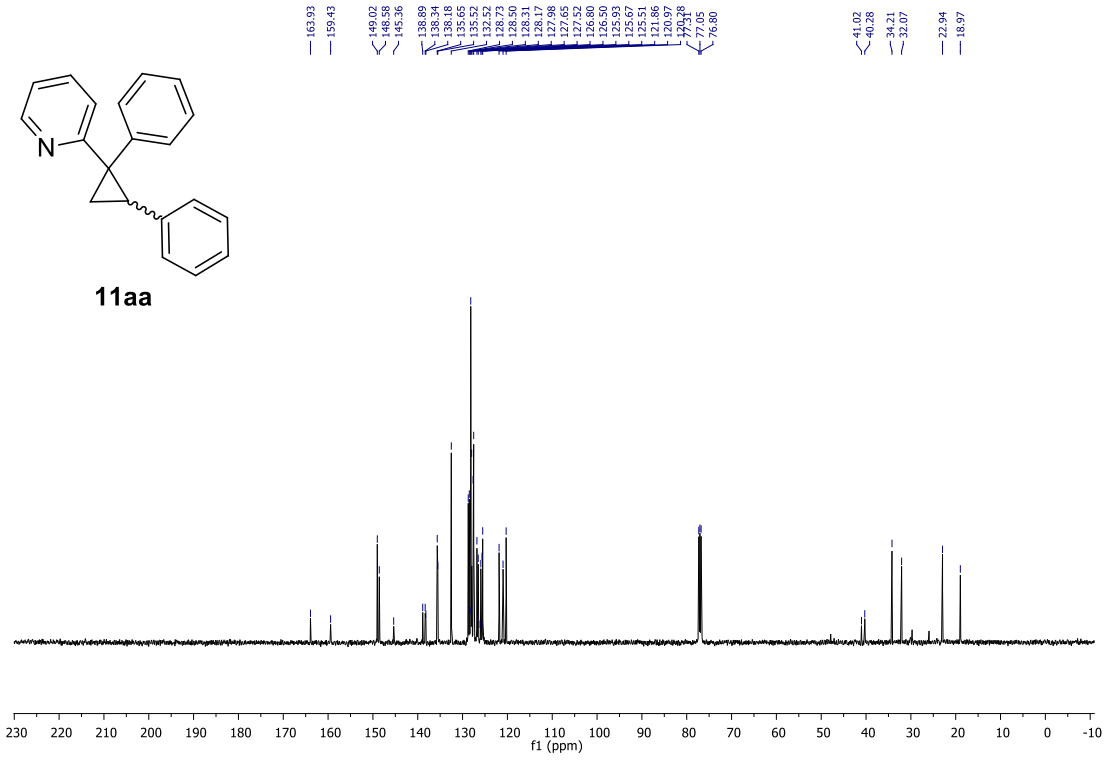
^{13}C NMR of **9cc**



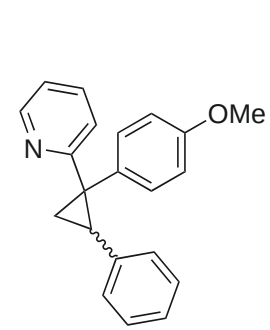
^{1}H NMR of **11aa**



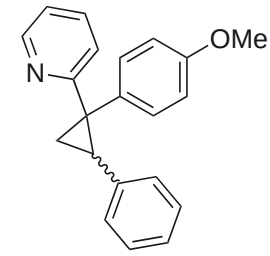
^{13}C NMR of **11aa**



^{1}H NMR of **11ba**

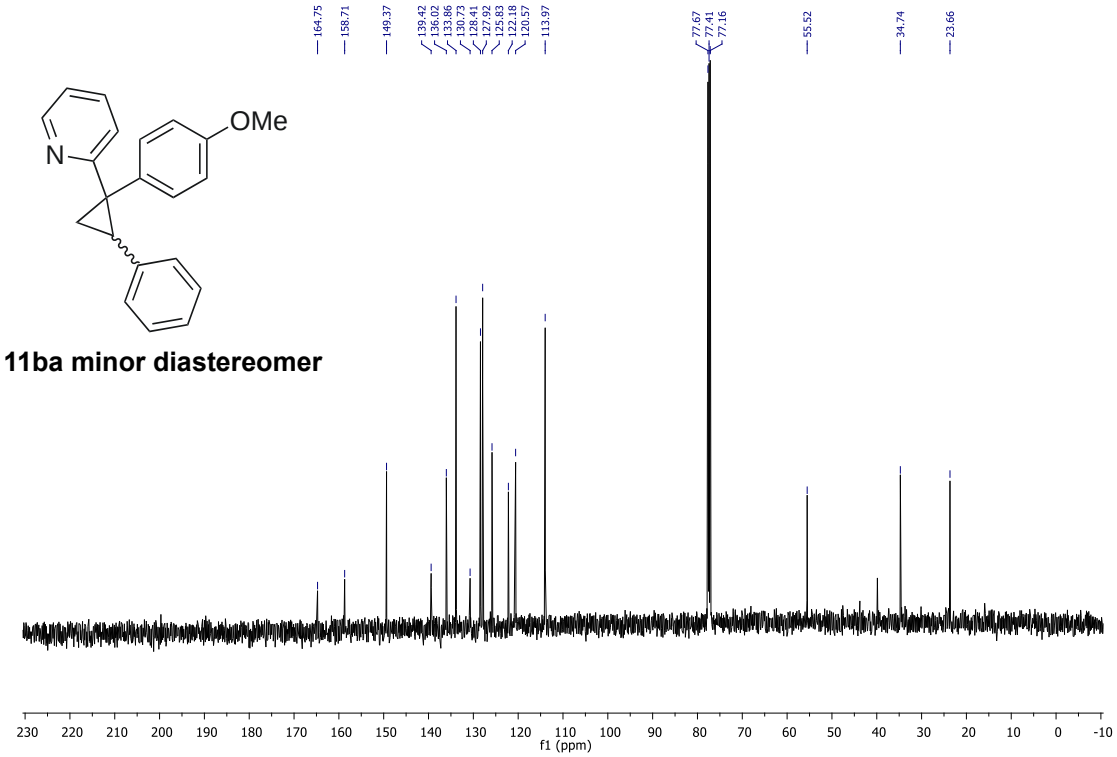


11ba minor diastereomer

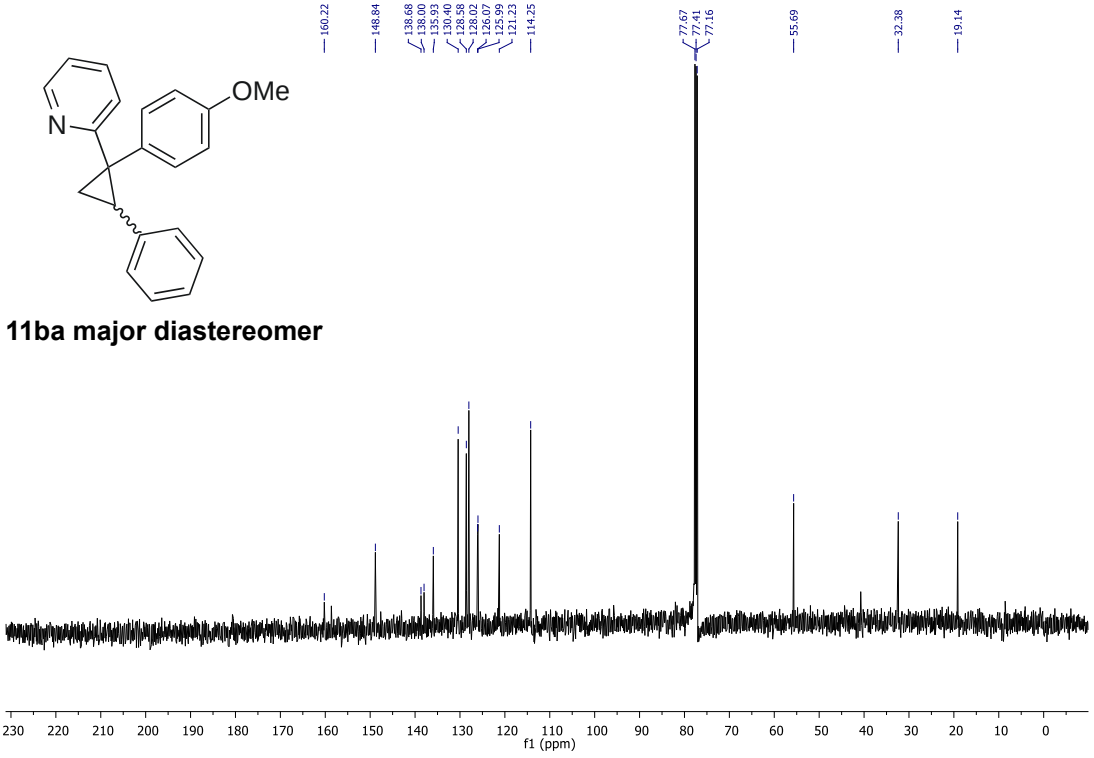


11ba major diastereomer

^{13}C NMR of **11ba**

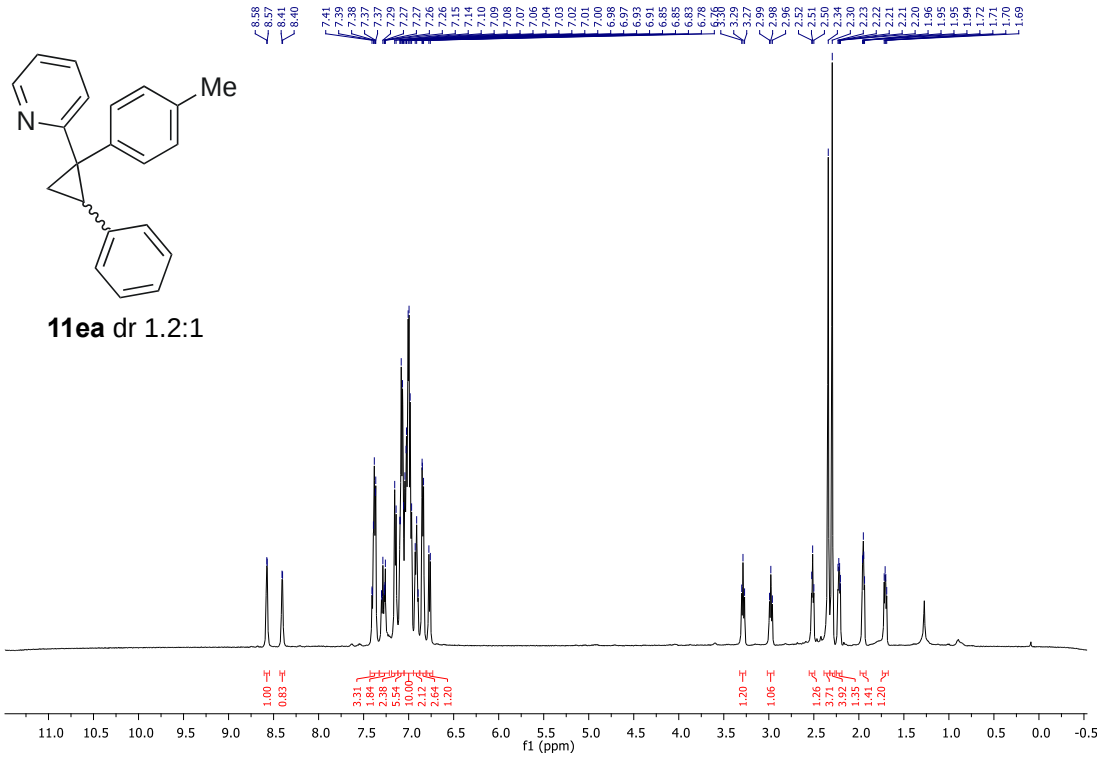


11ba minor diastereomer

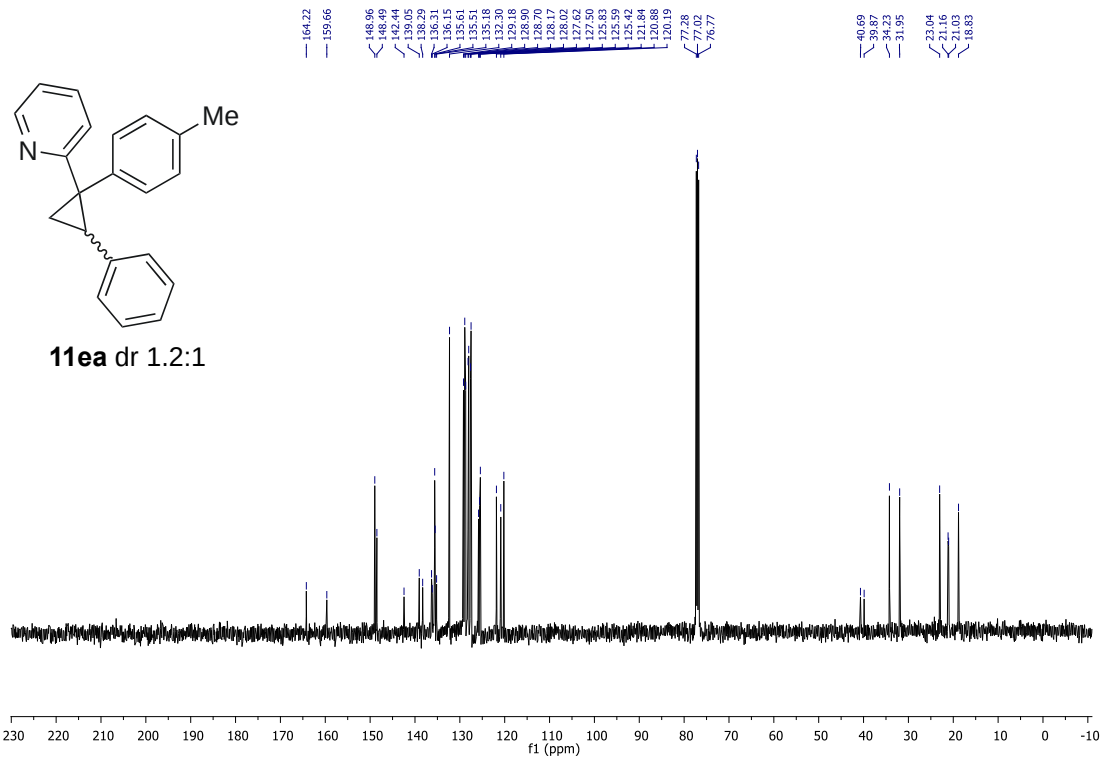


11ba major diastereomer

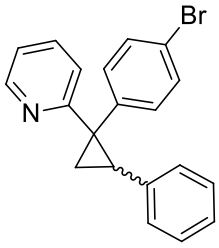
^{1}H NMR of **11ea**



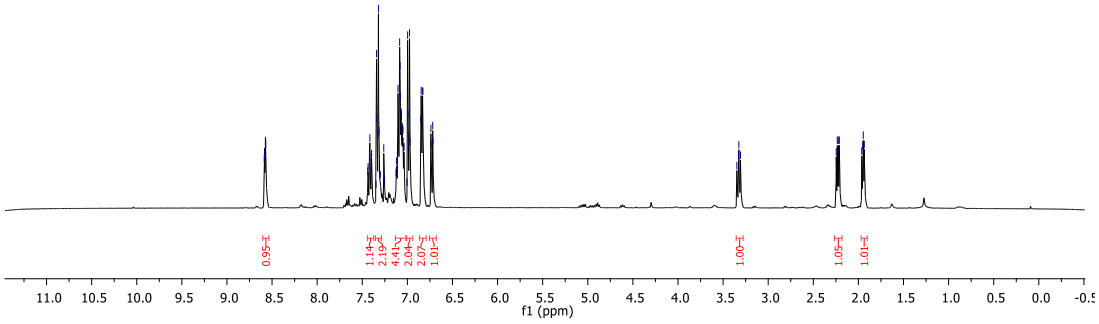
^{13}C NMR of **11ea**

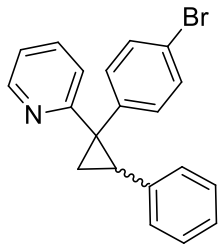


^{1}H NMR of **11ga**

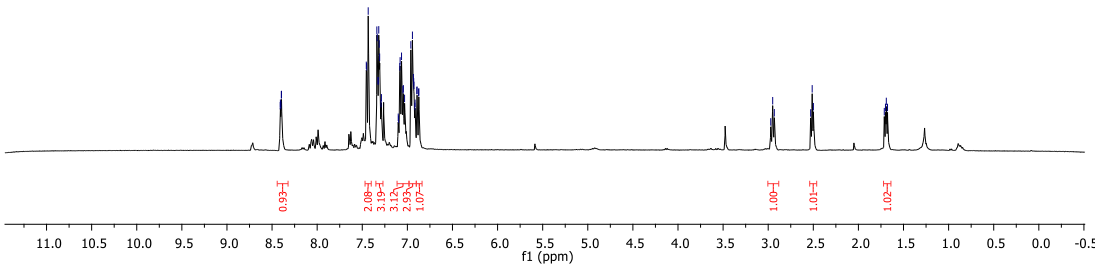


11ga, major diastereomer

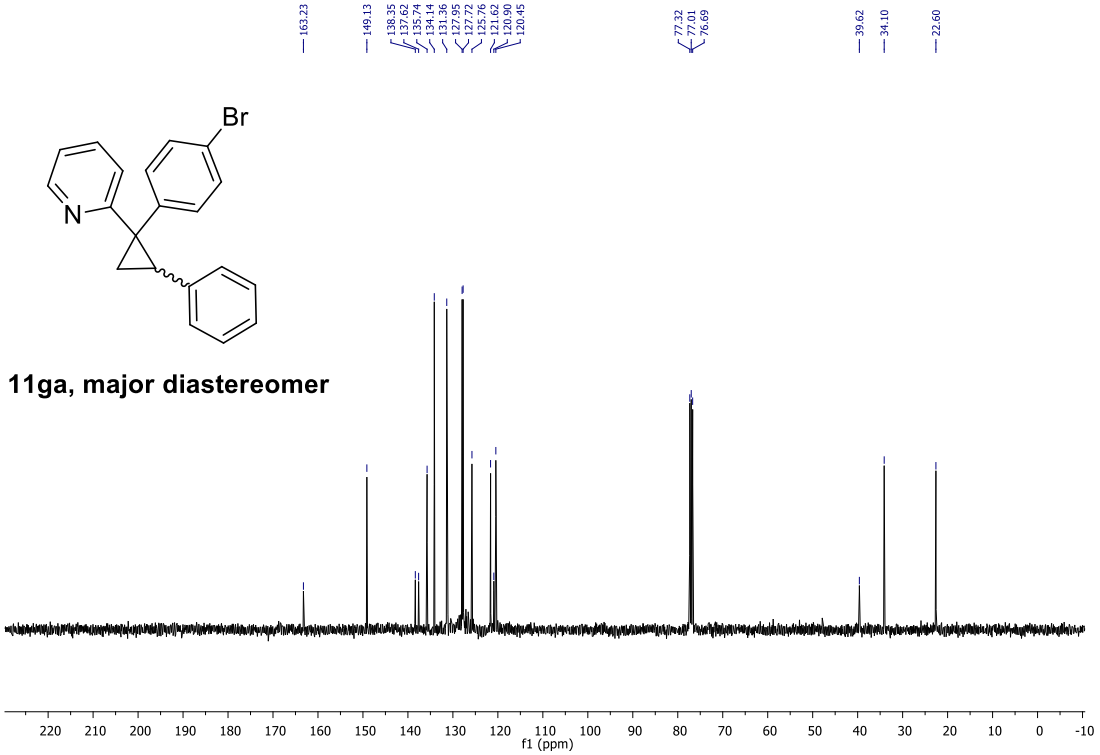


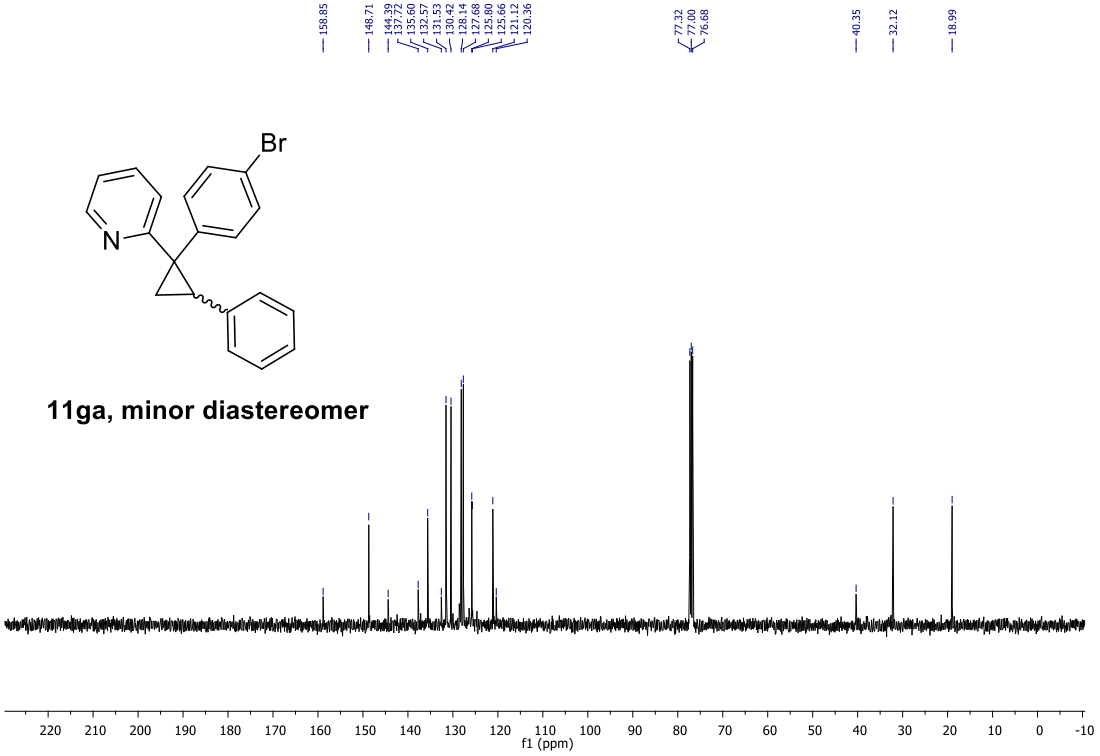


11ga, minor diastereomer

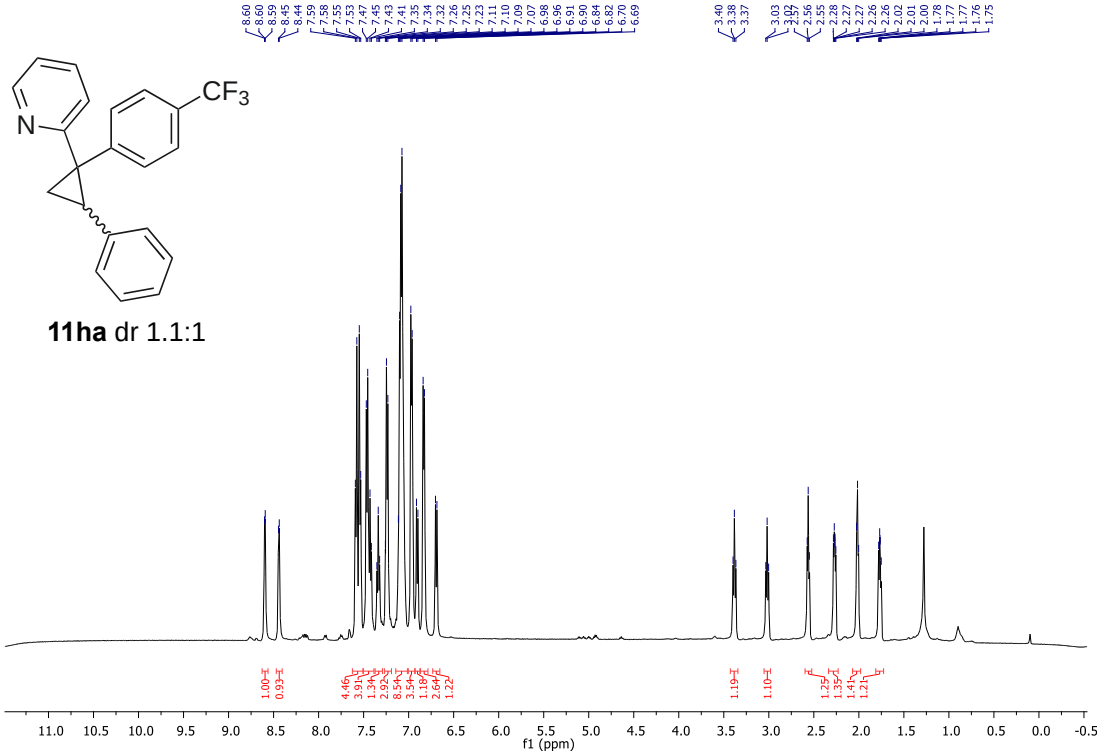


^{13}C NMR of **11ga**

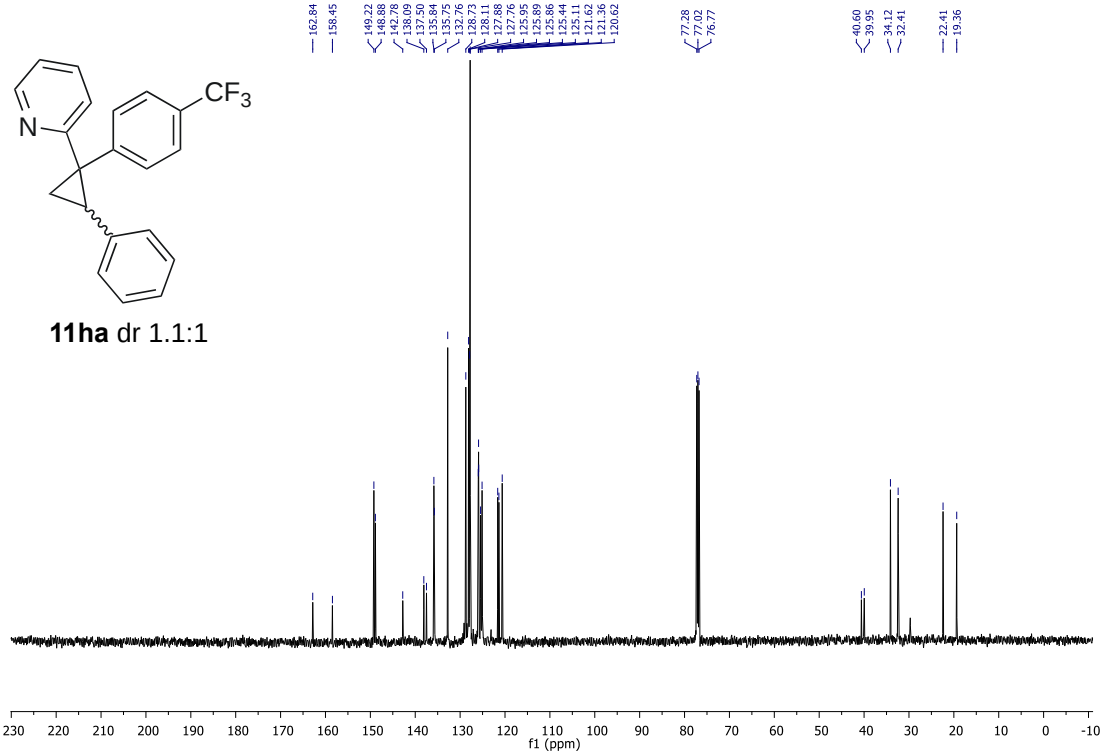




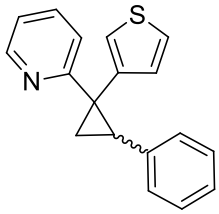
^{1}H NMR of **11ha**



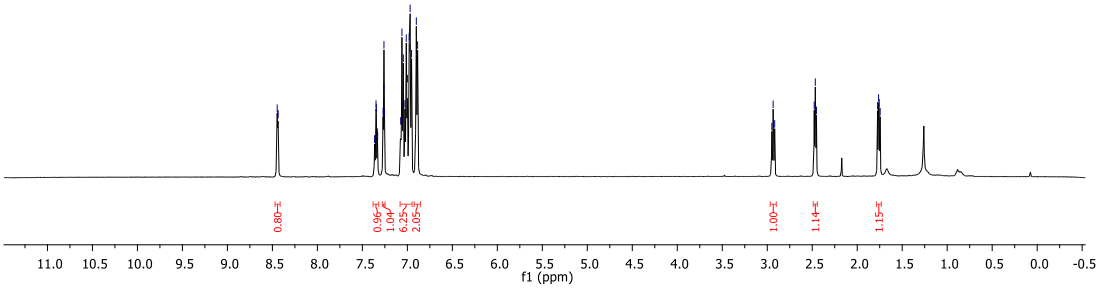
^{13}C NMR of **11ha**

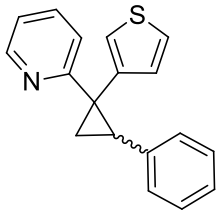


^{1}H NMR of **11ia**

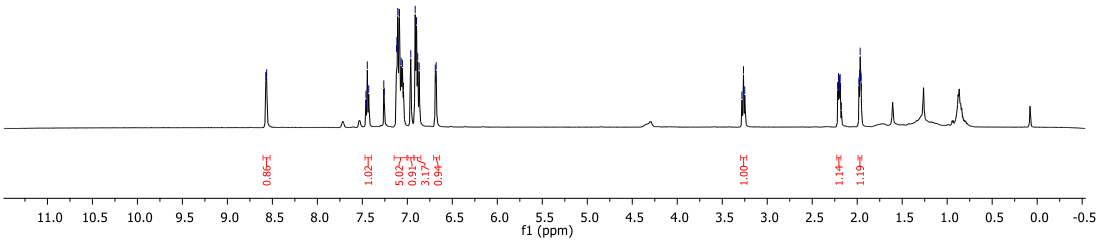


11ia, major diastereomer

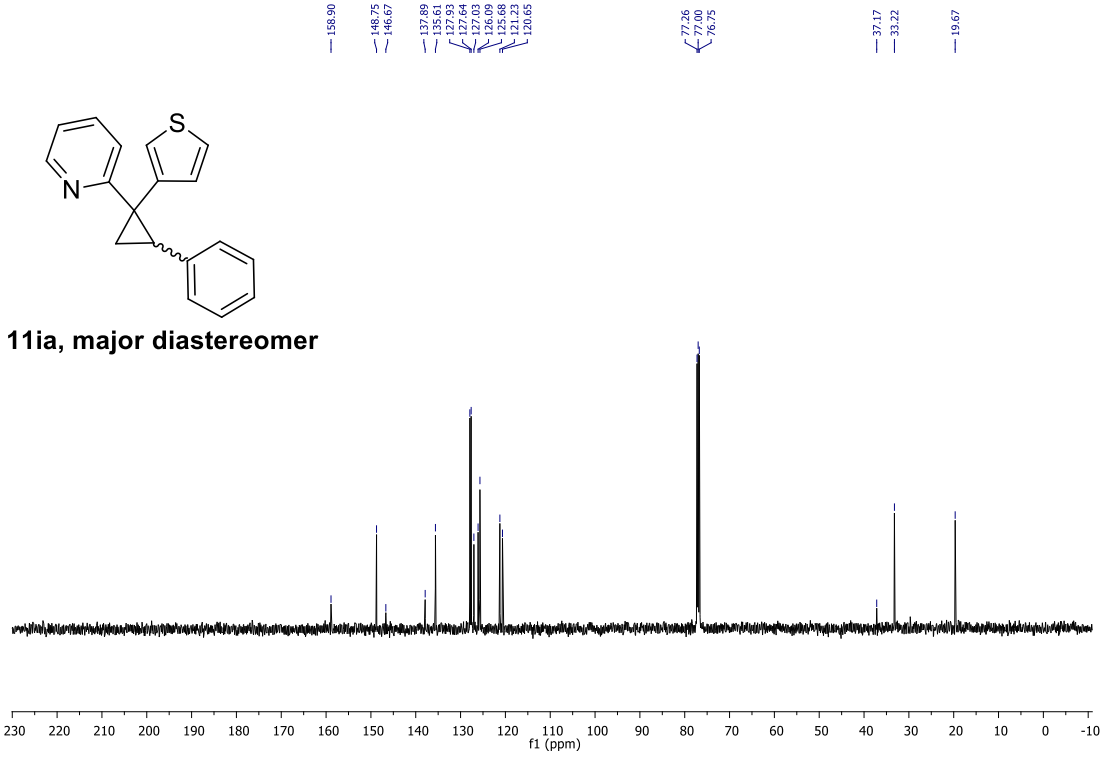


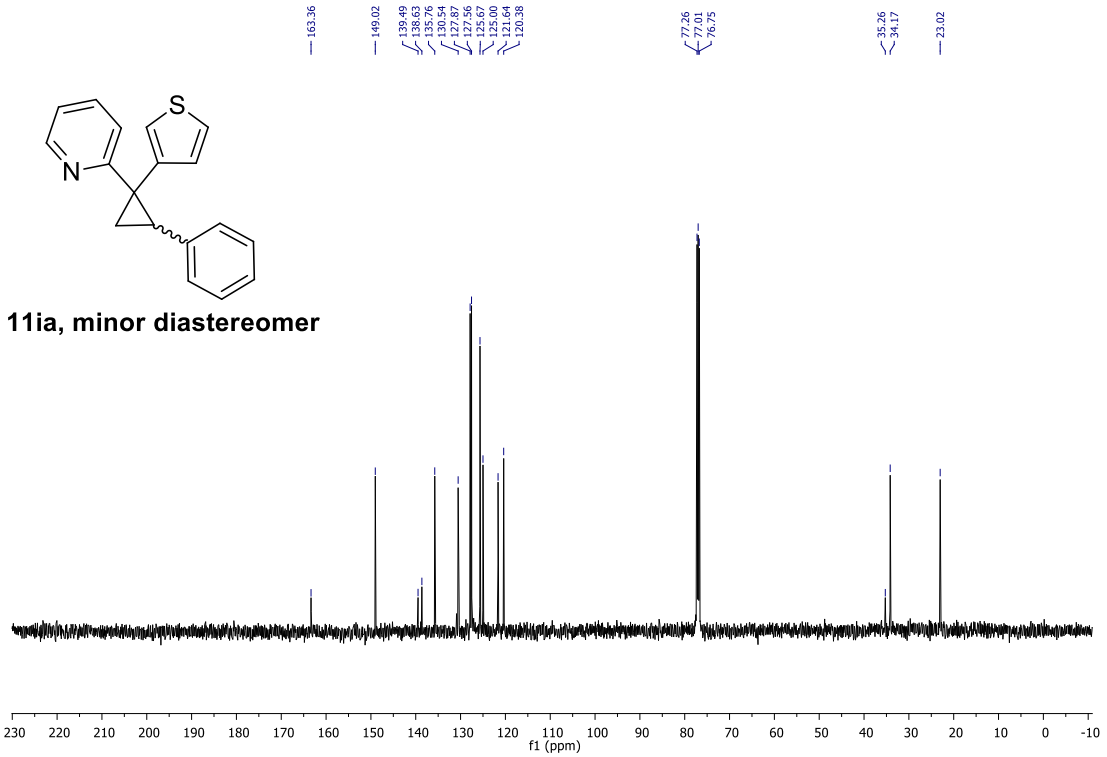


11ia, minor diastereomer

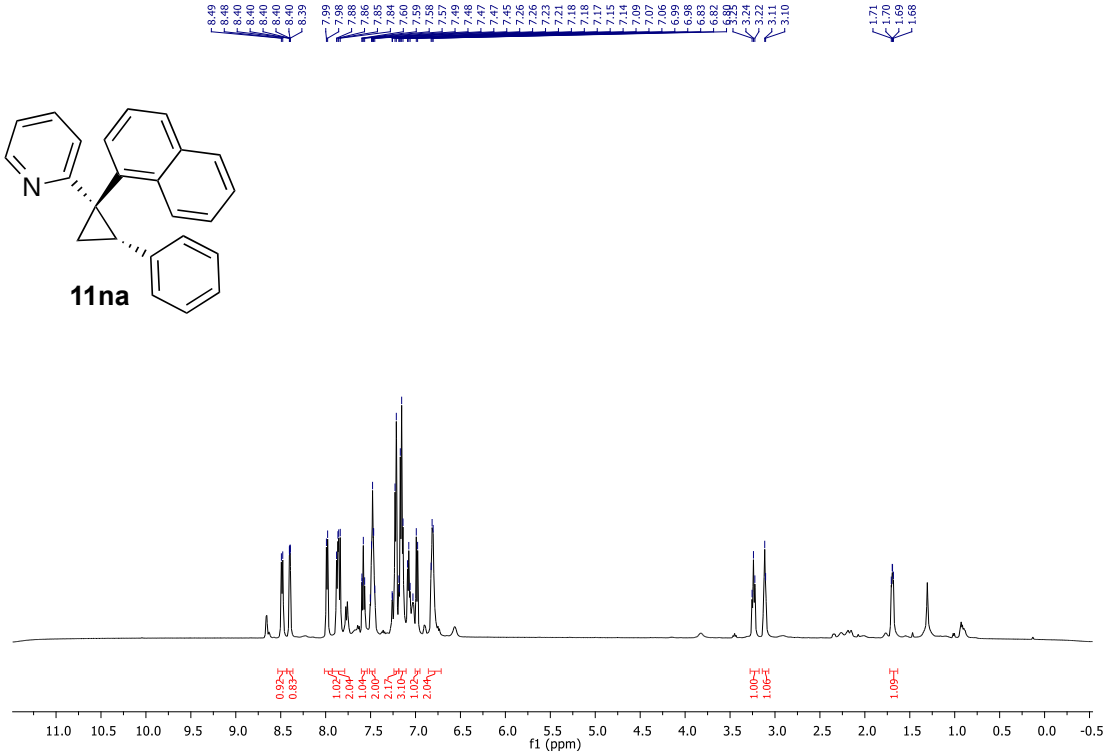


^{13}C NMR of **11ia**

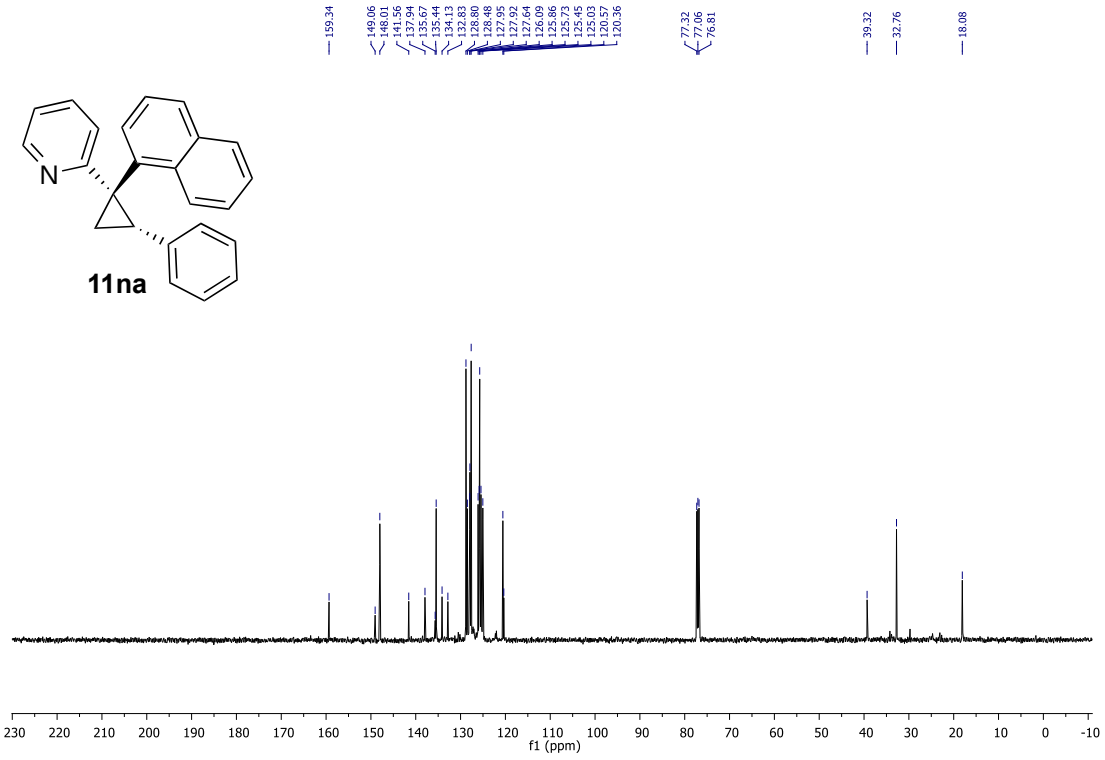




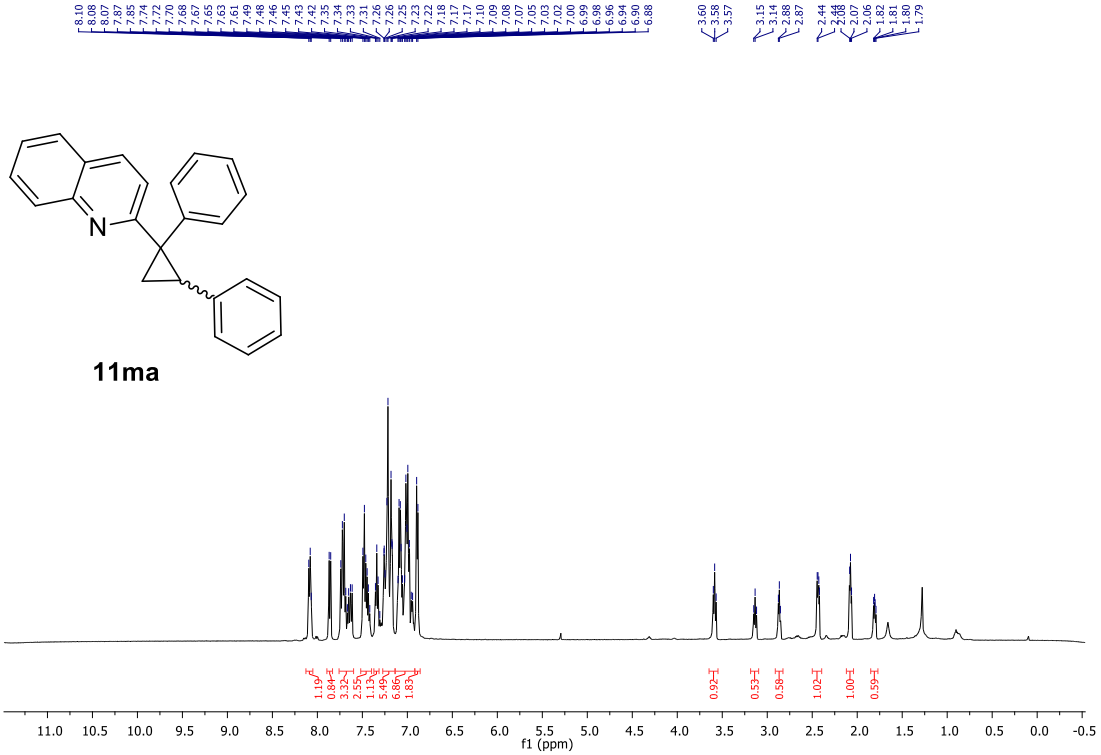
^{1}H NMR of **11na**



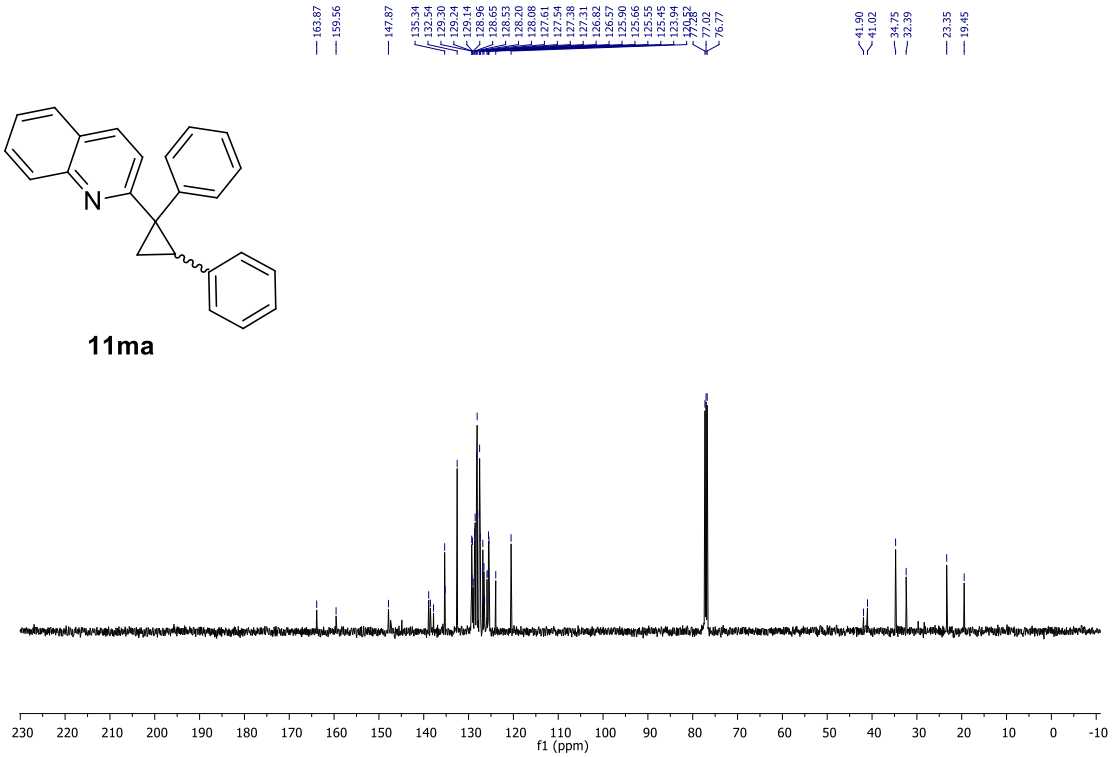
^{13}C NMR of **11na**



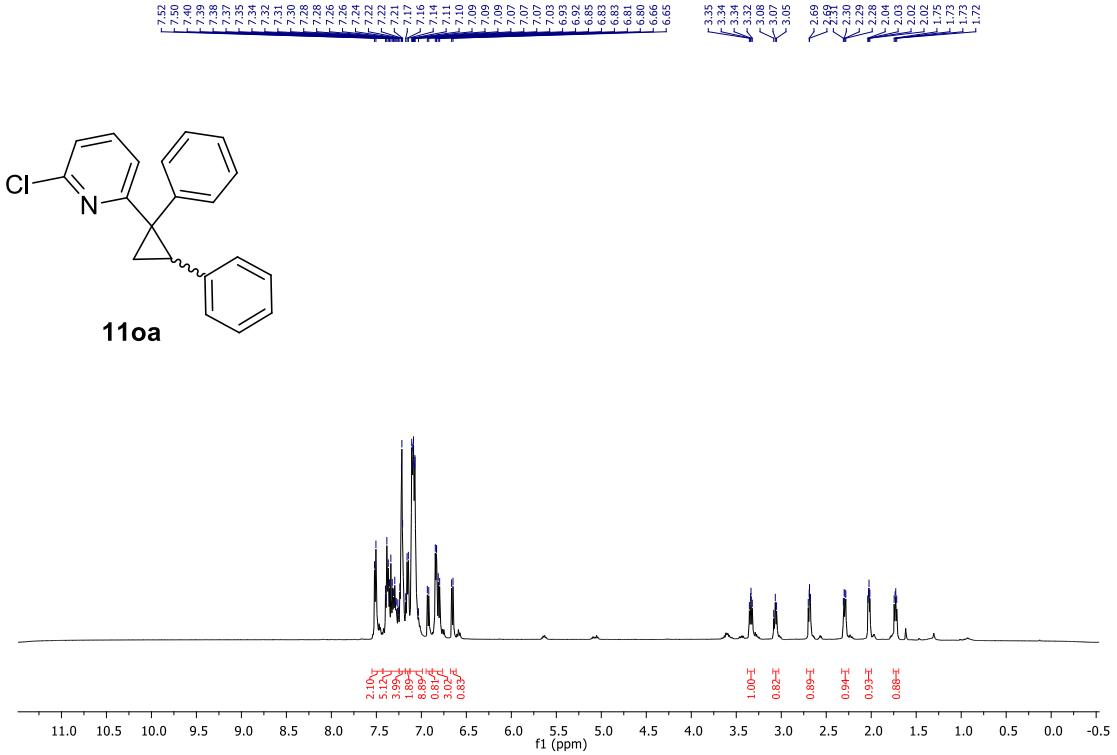
^{1}H NMR of **11ma**



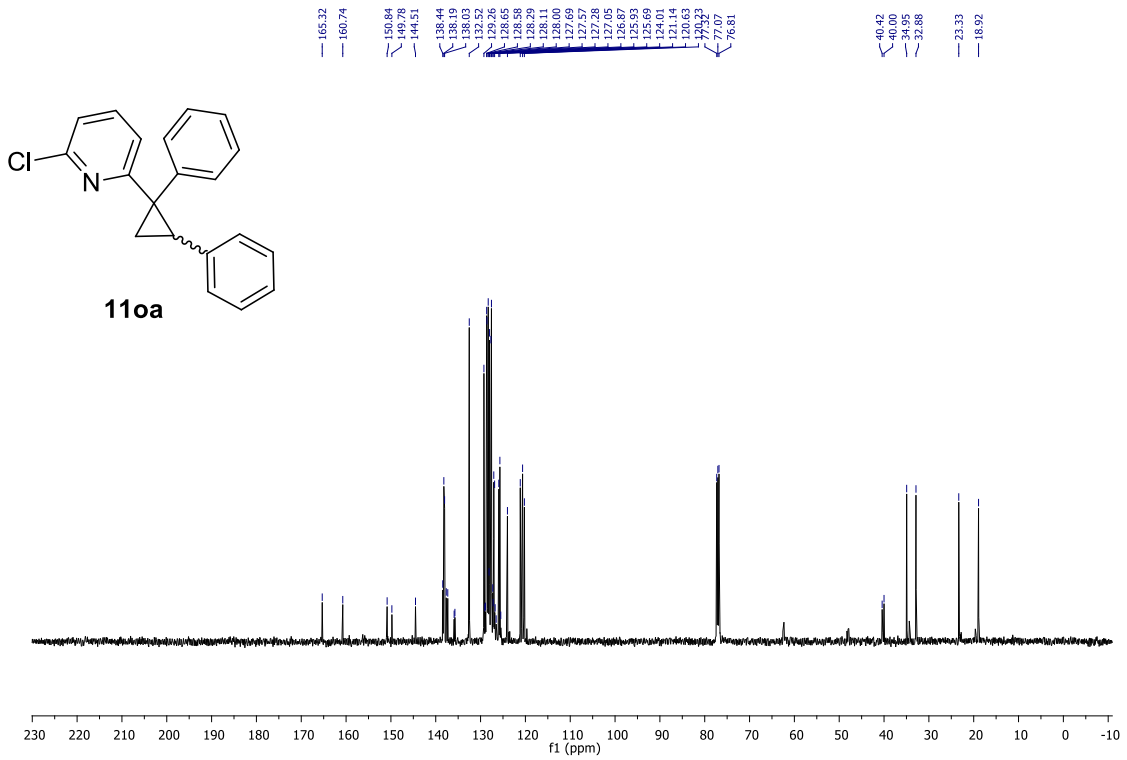
^{13}C NMR of **11ma**



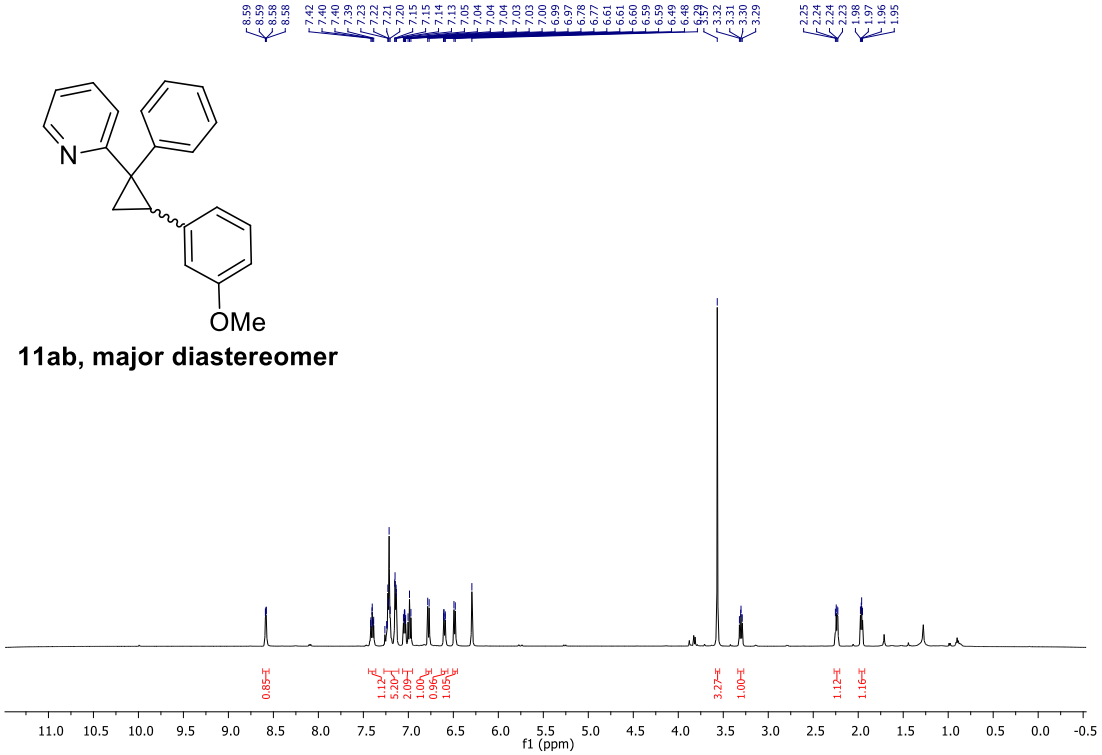
^{1}H NMR of **11oa**



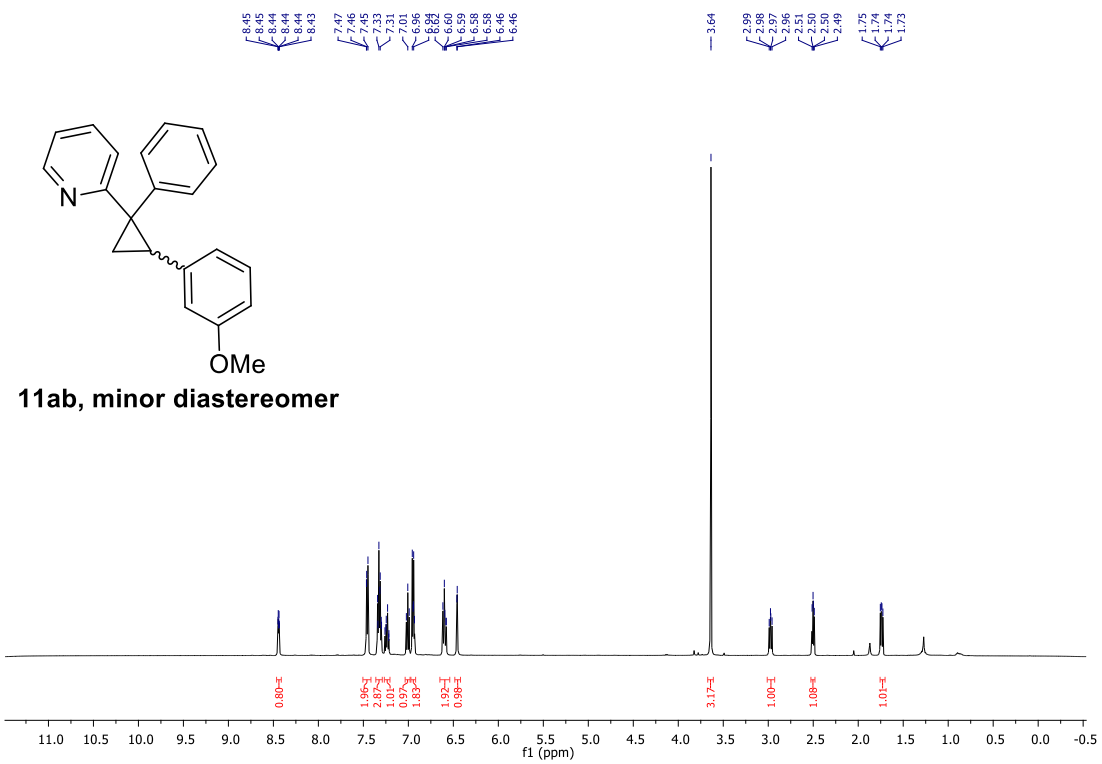
^{13}C NMR of **11oa**



^{1}H NMR of **11ab**

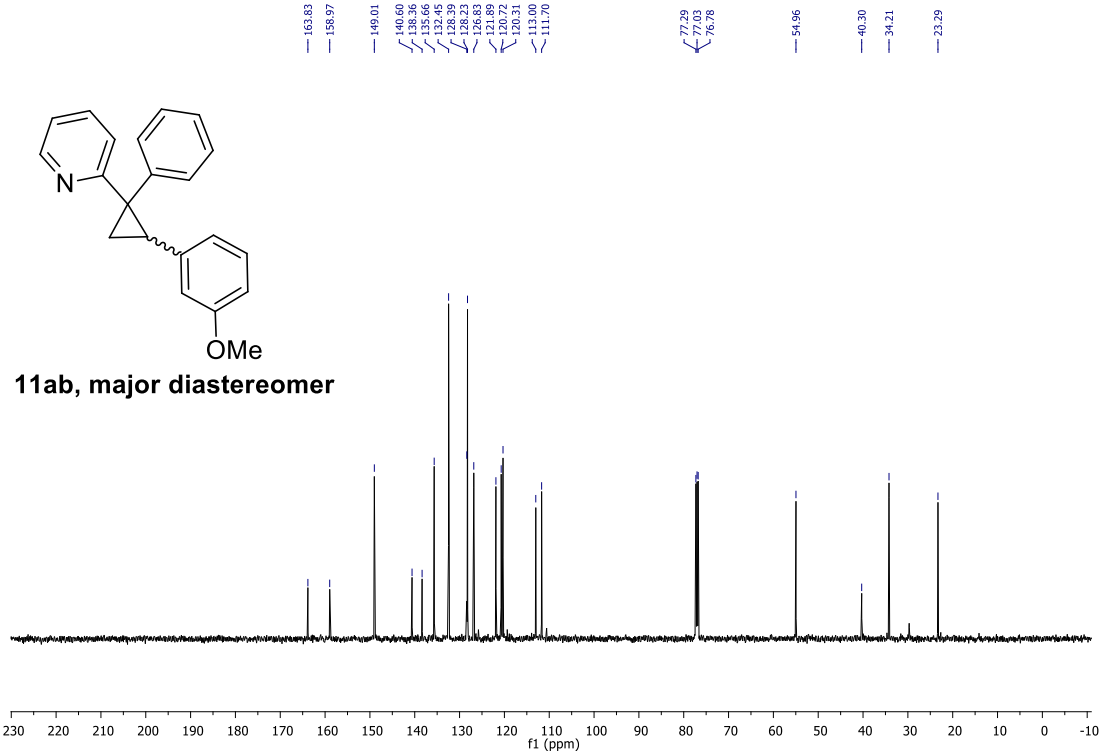


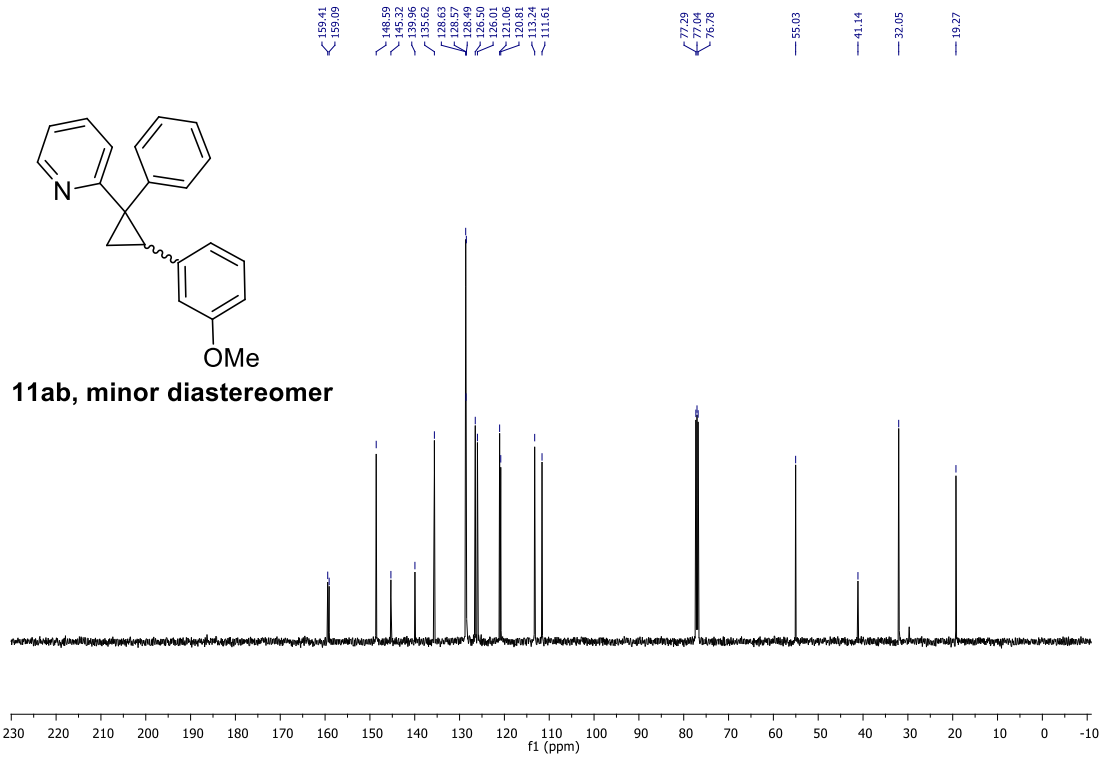
11ab, major diastereomer



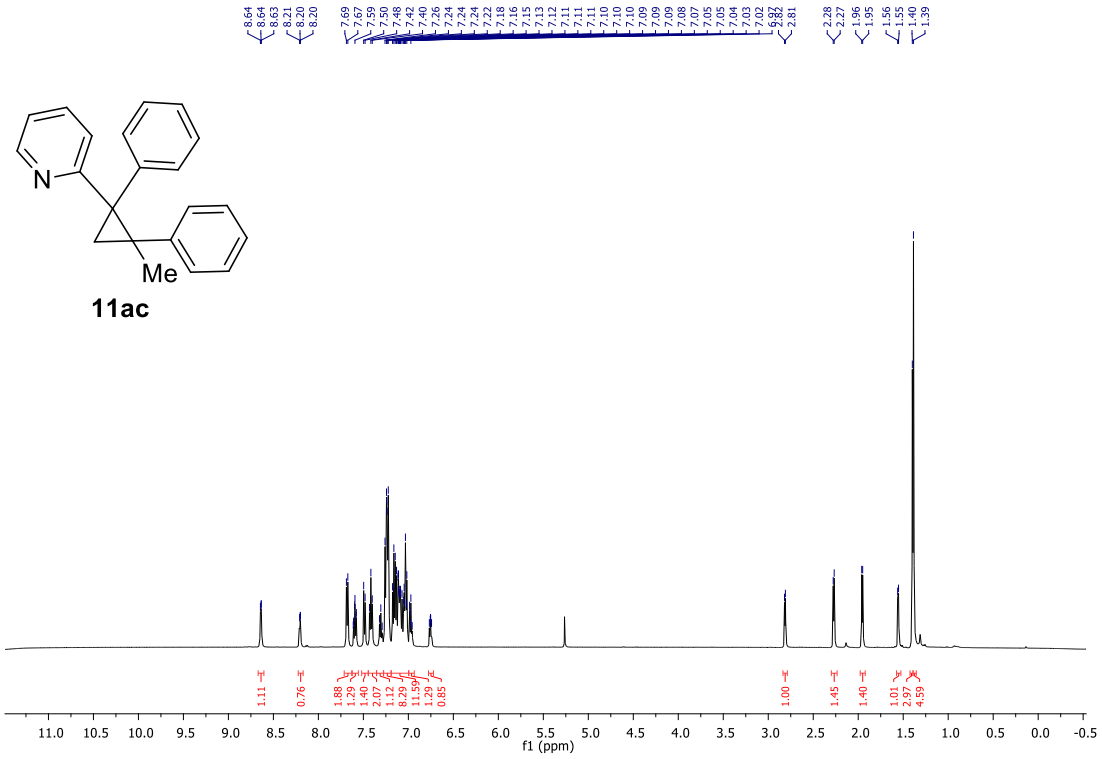
11ab, minor diastereomer

^{13}C NMR of **11ab**

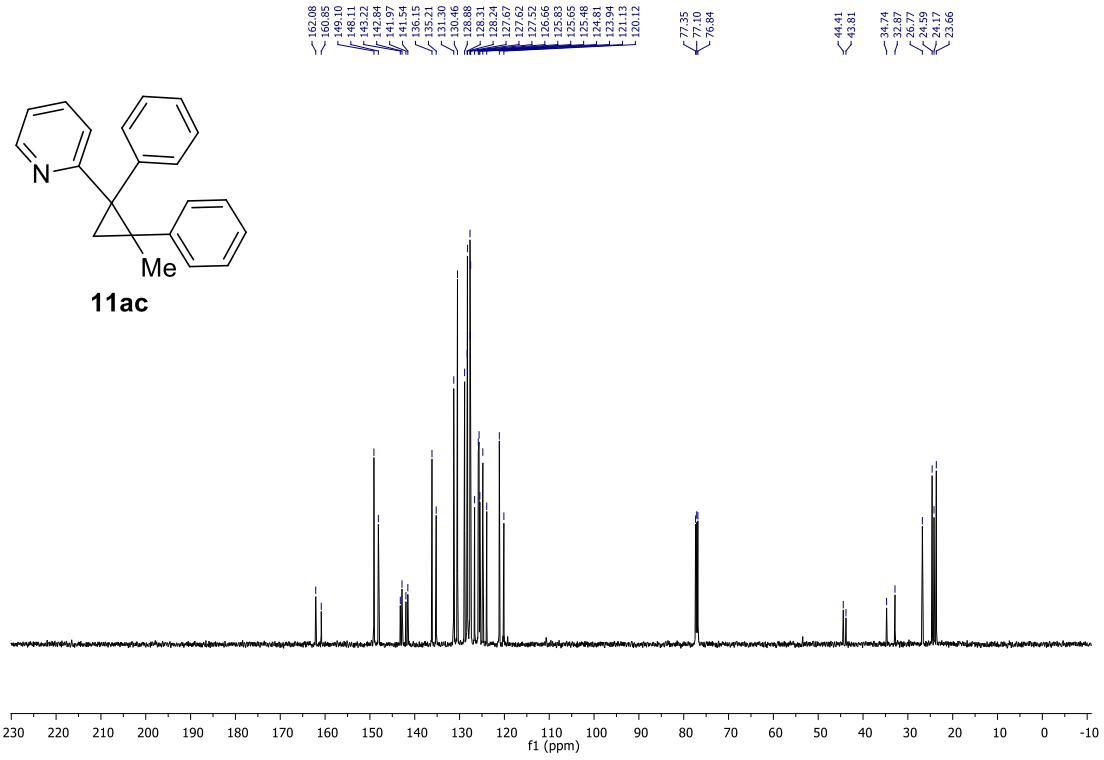




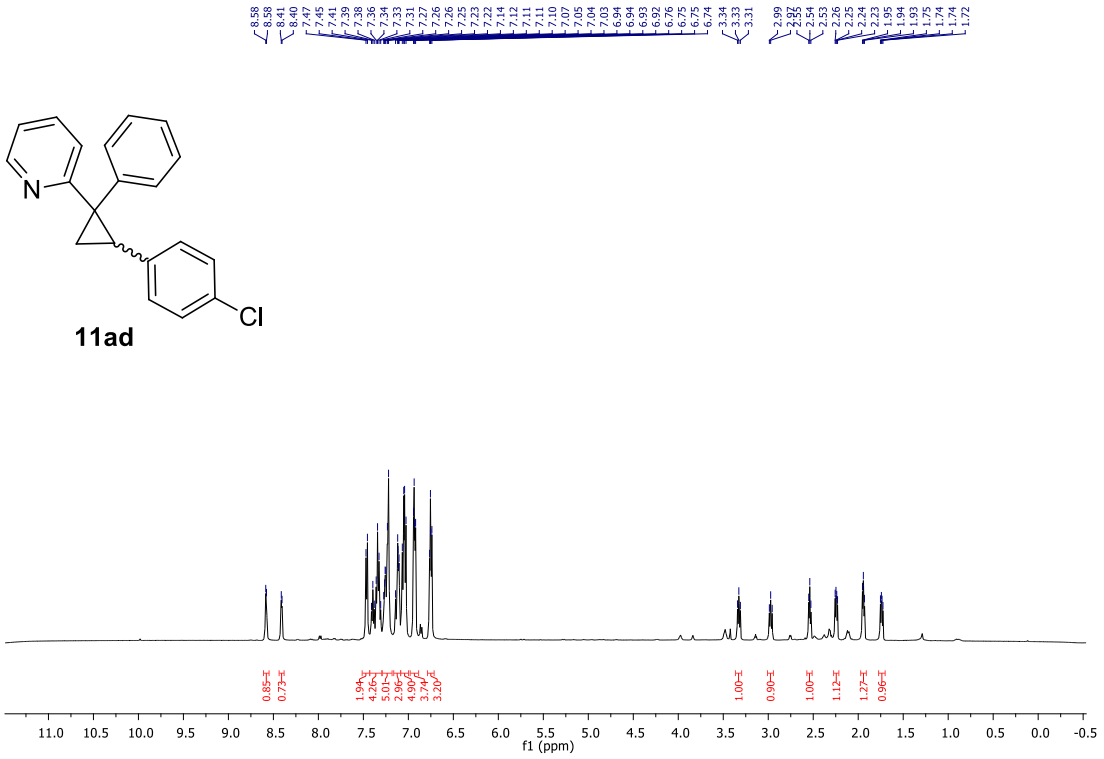
^{1}H NMR of **11ac**



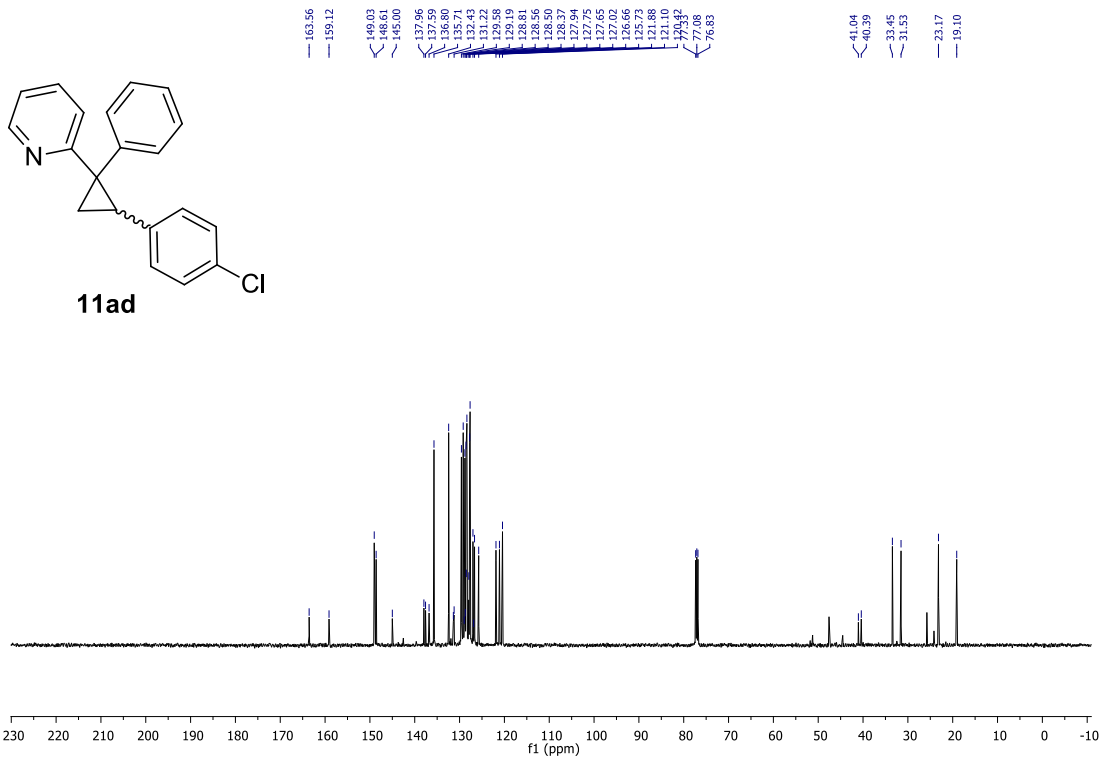
^{13}C NMR of **11ac**



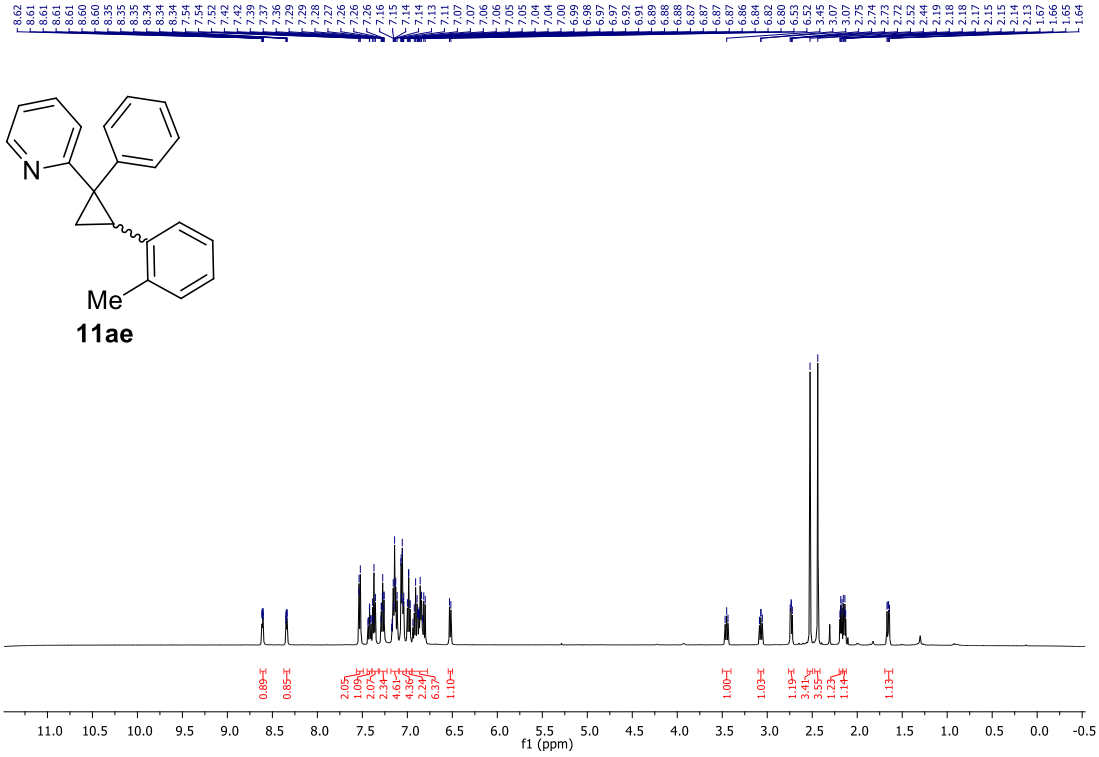
^{1}H NMR of **11ad**



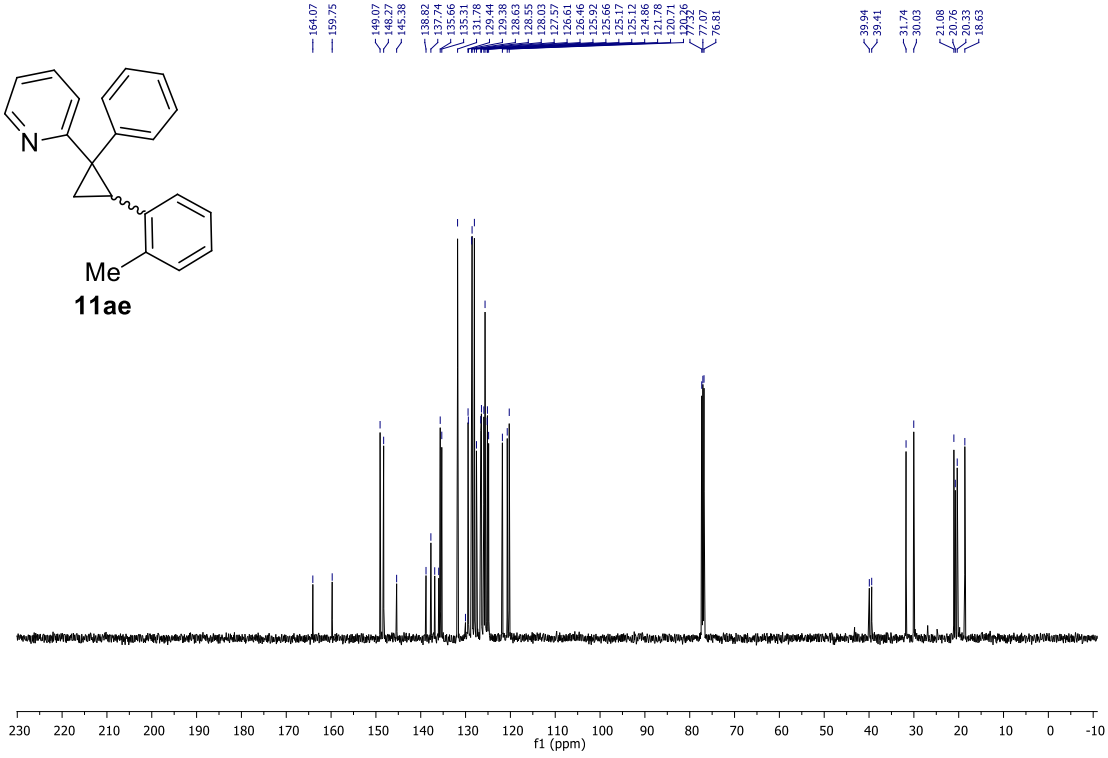
^{13}C NMR of **11ad**



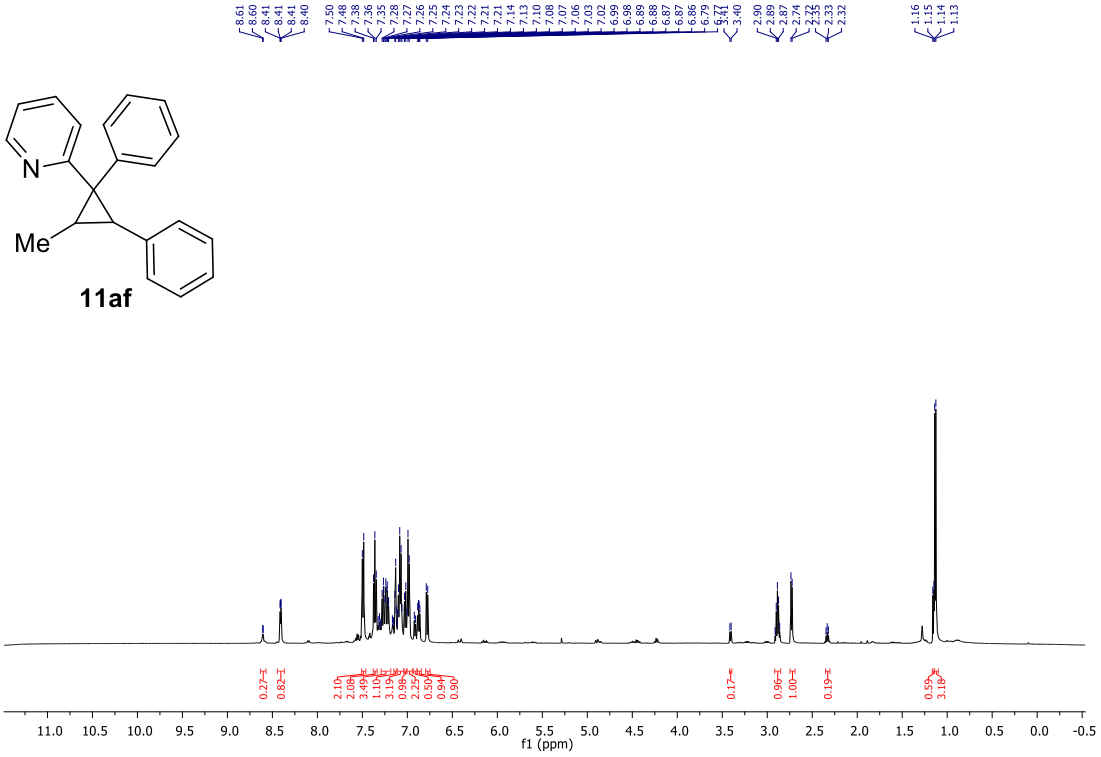
^{1}H NMR of **11ae**



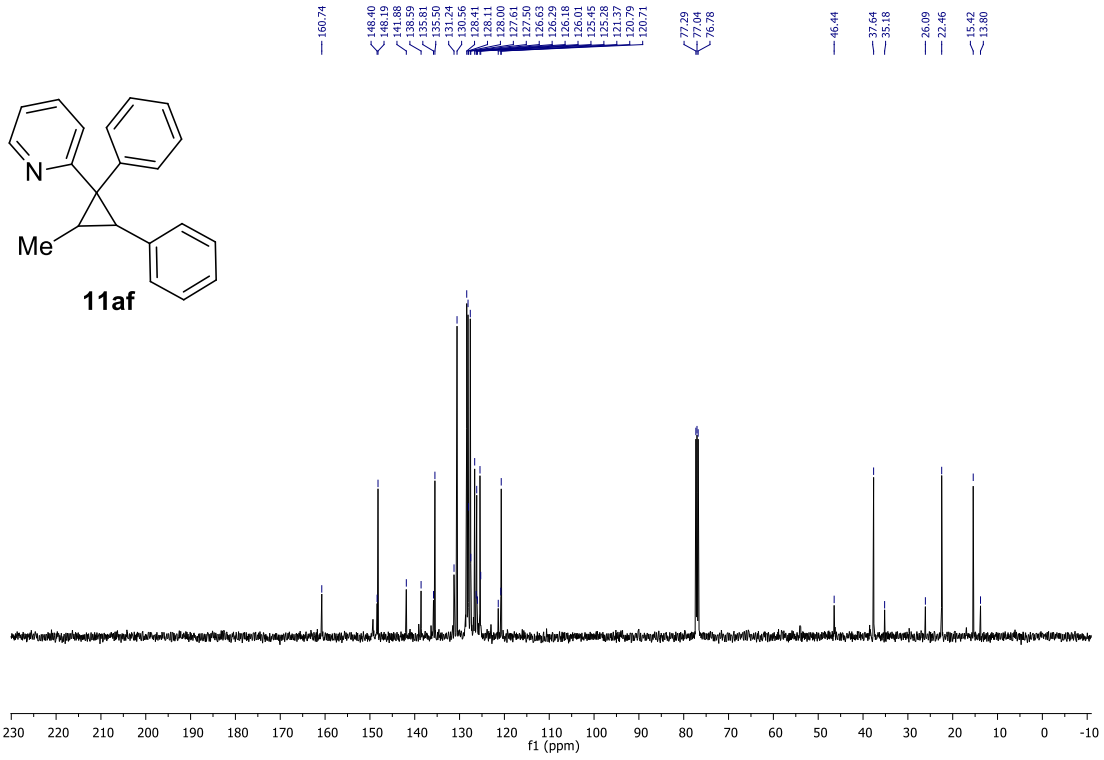
^{13}C NMR of **11ae**



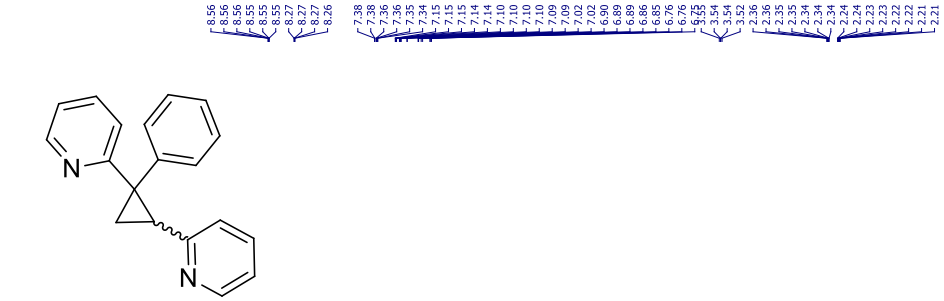
^{1}H NMR of **11af**



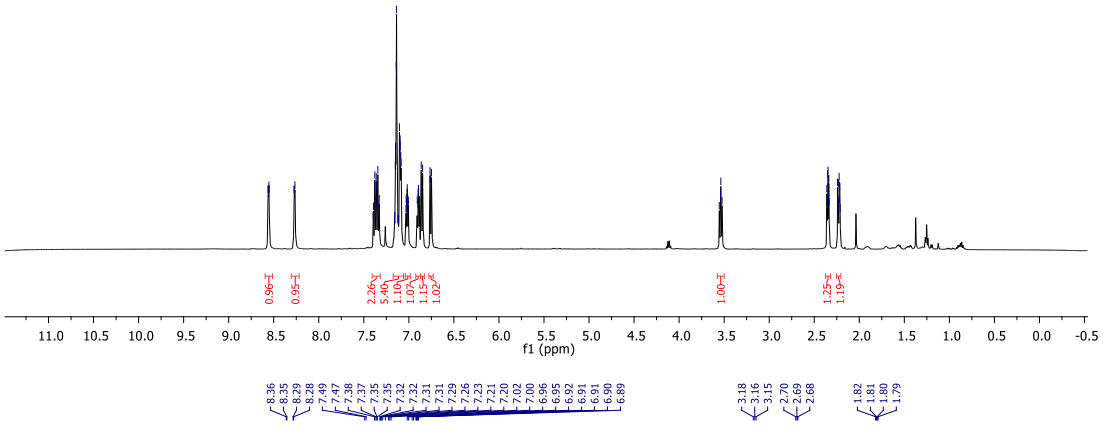
^{13}C NMR of **11af**

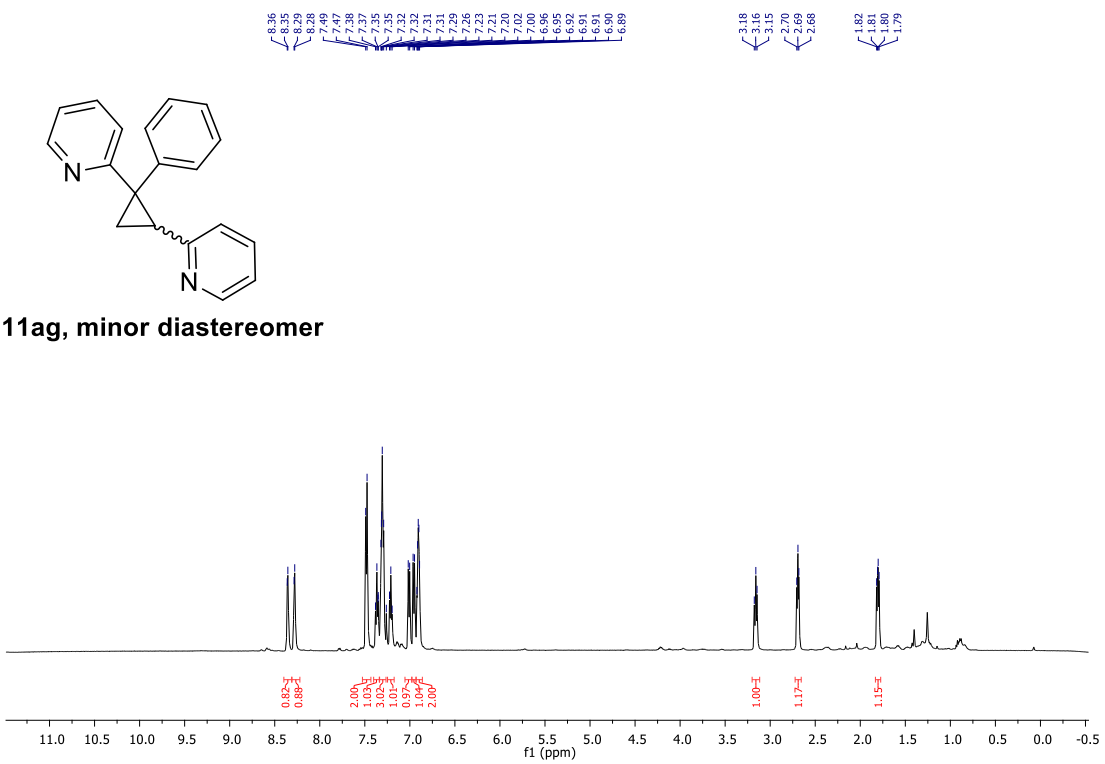


^{1}H NMR of **11ag**



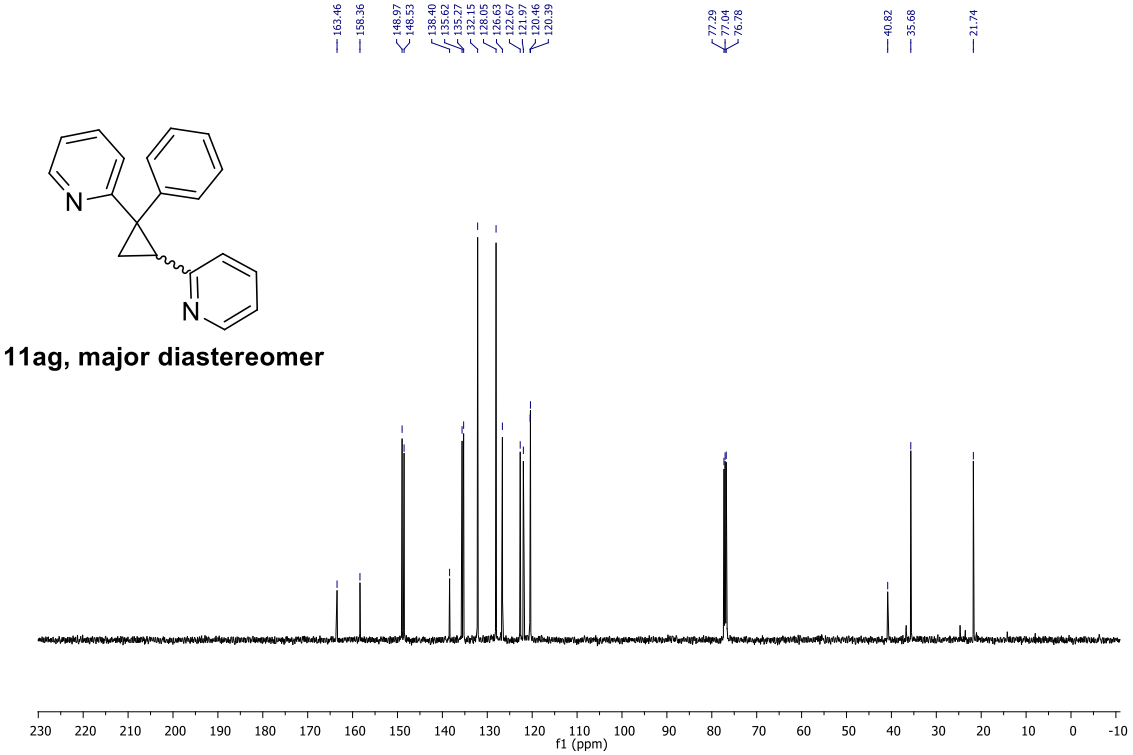
11ag, major diastereomer

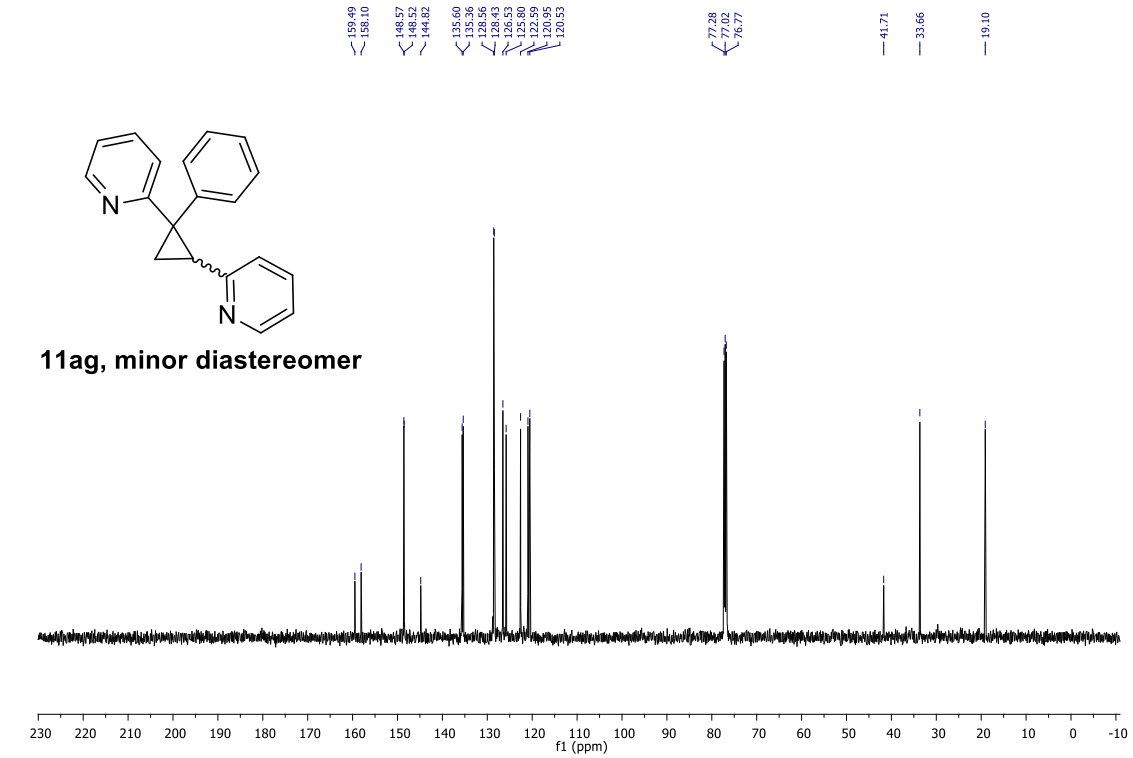




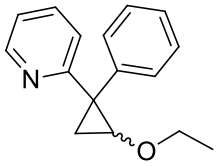
11ag, minor diastereomer

^{13}C NMR of **11ag**

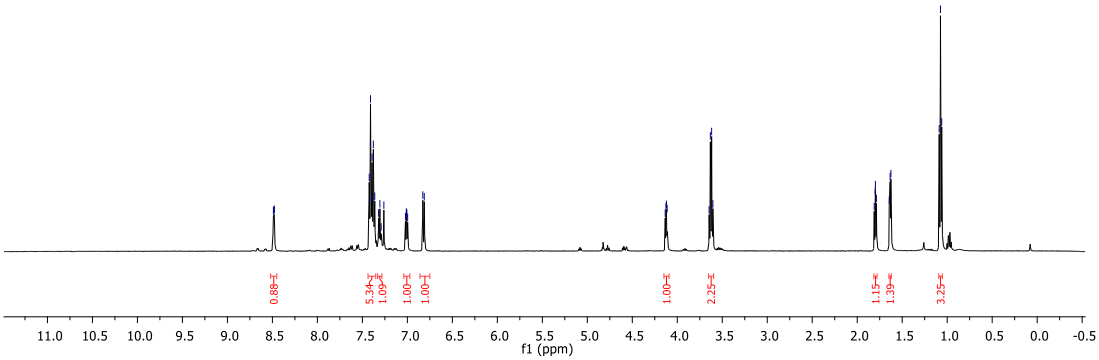


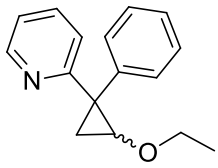


^{1}H NMR of **11ah**

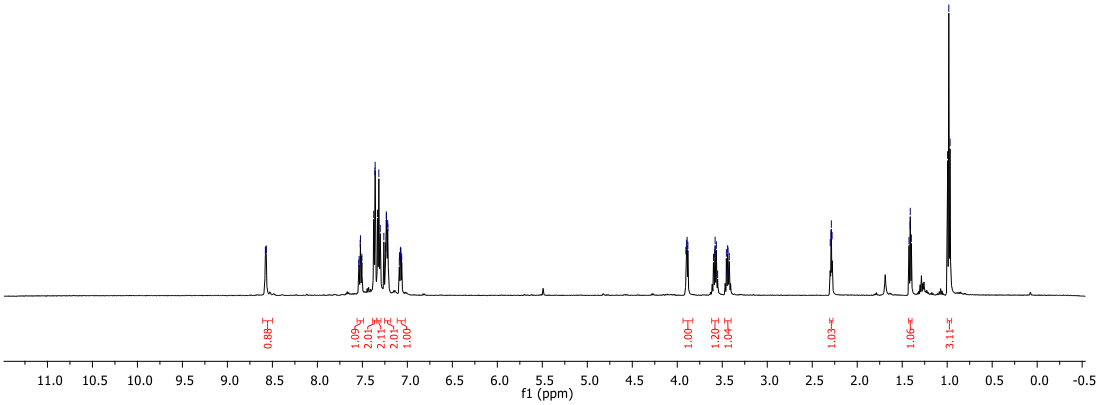


11ah, major diastereomer

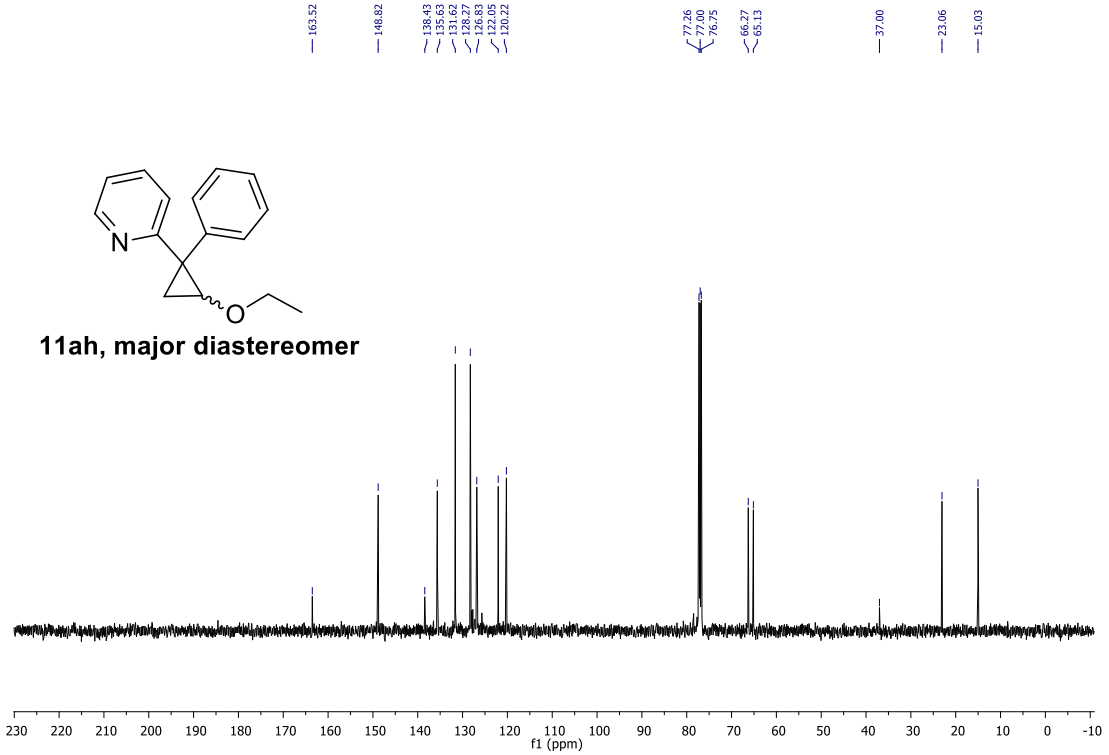


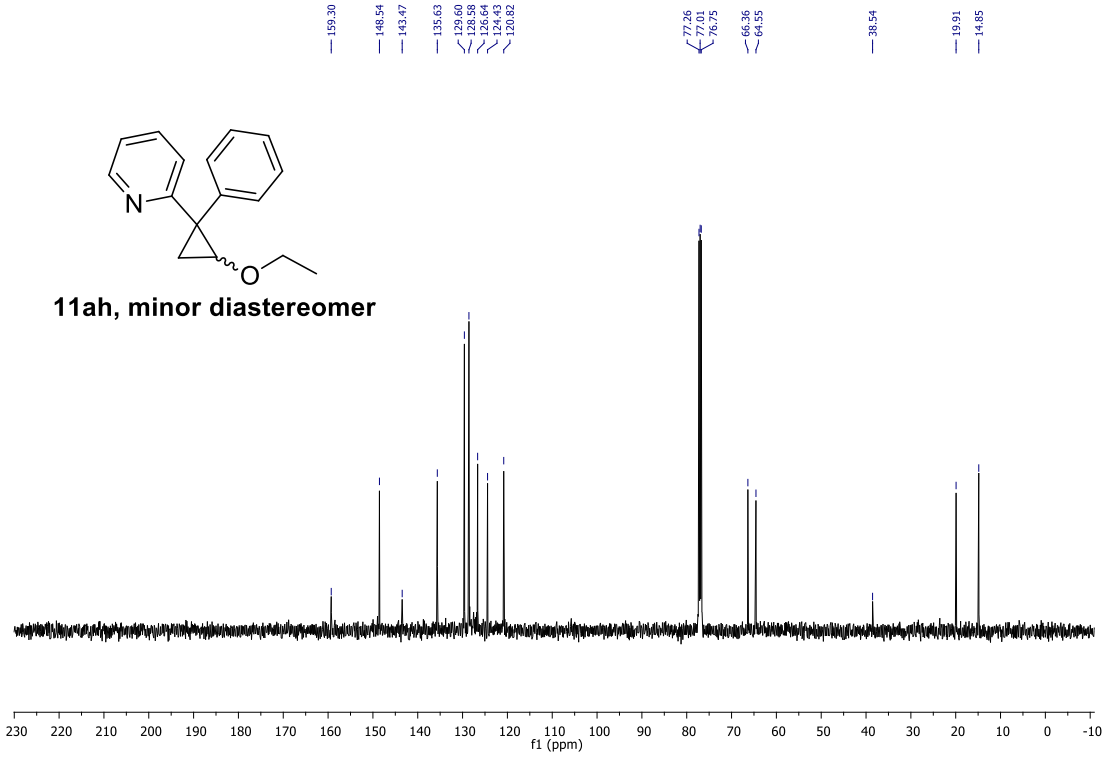


11ah, minor diastereomer

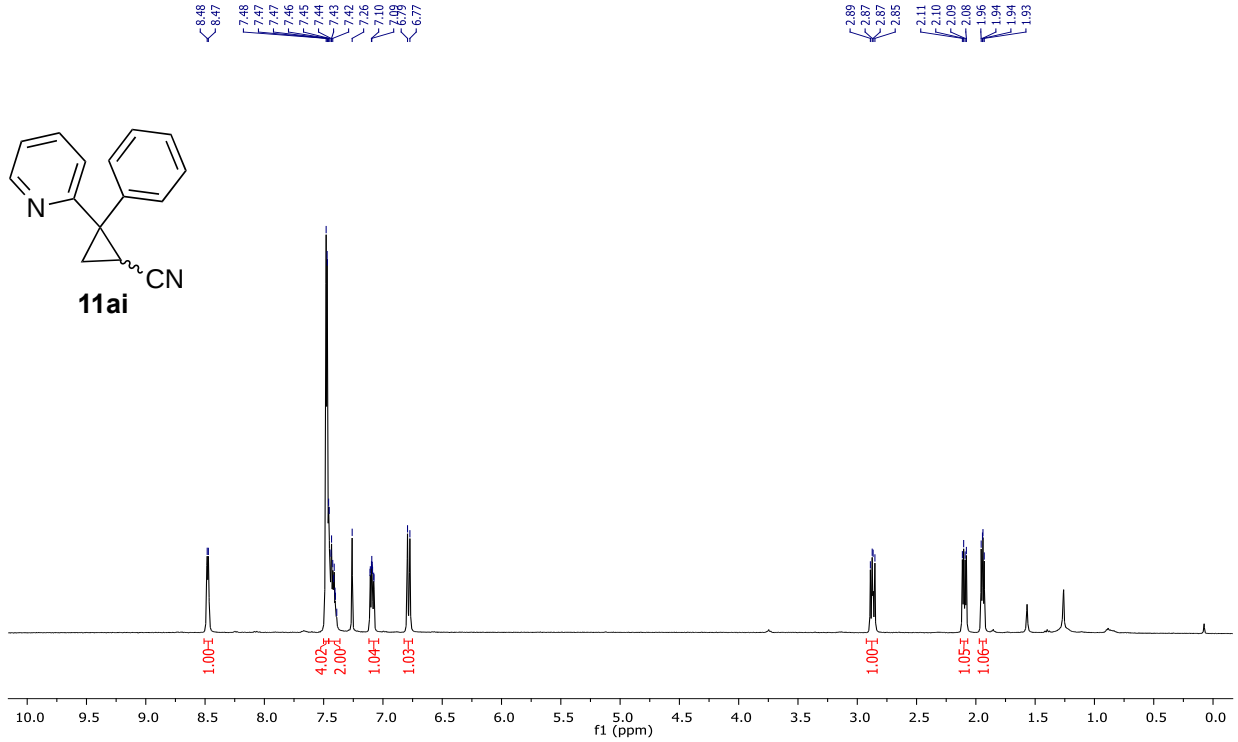


^{13}C NMR of **11ah**

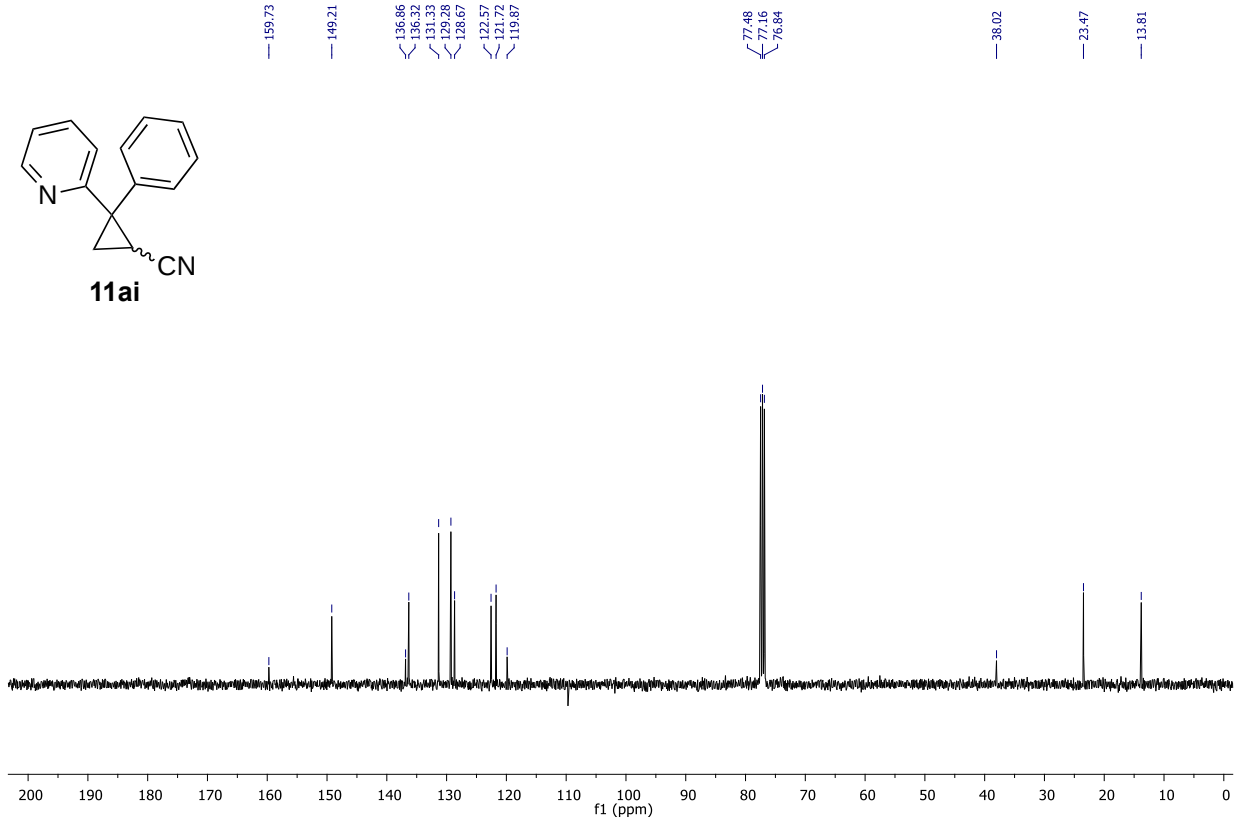




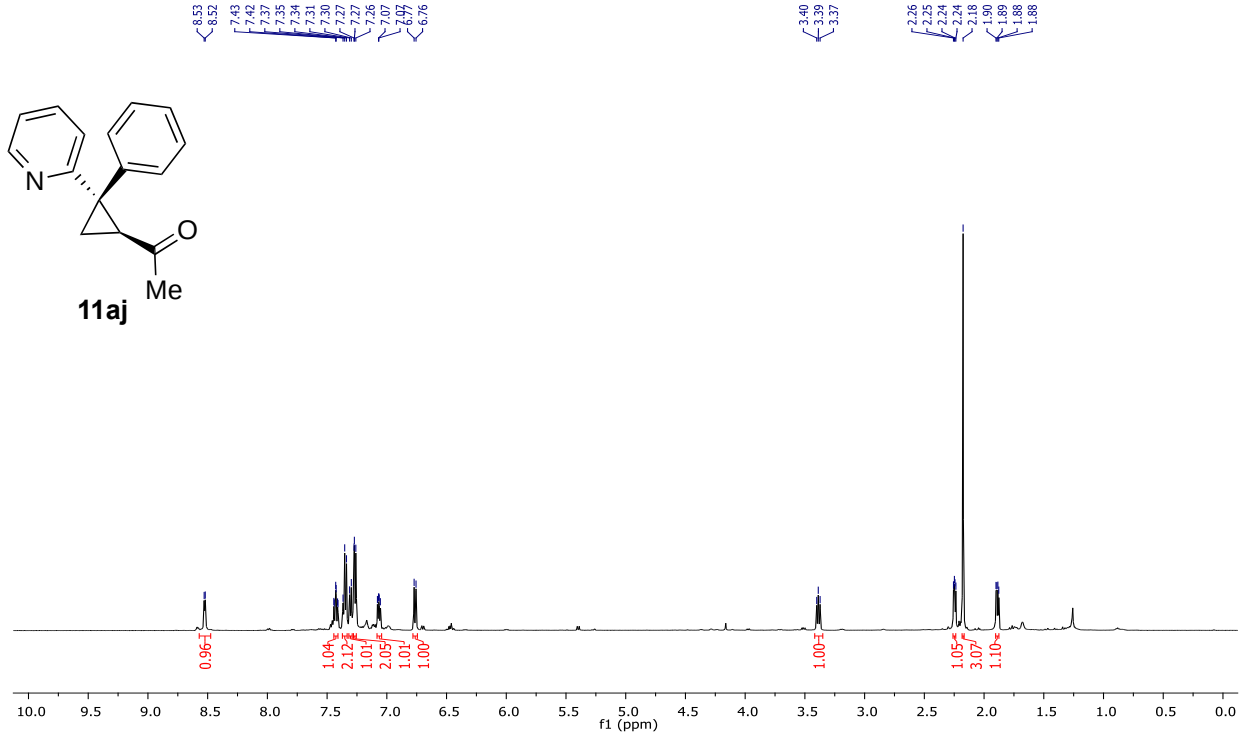
^{1}H NMR of **11ai**



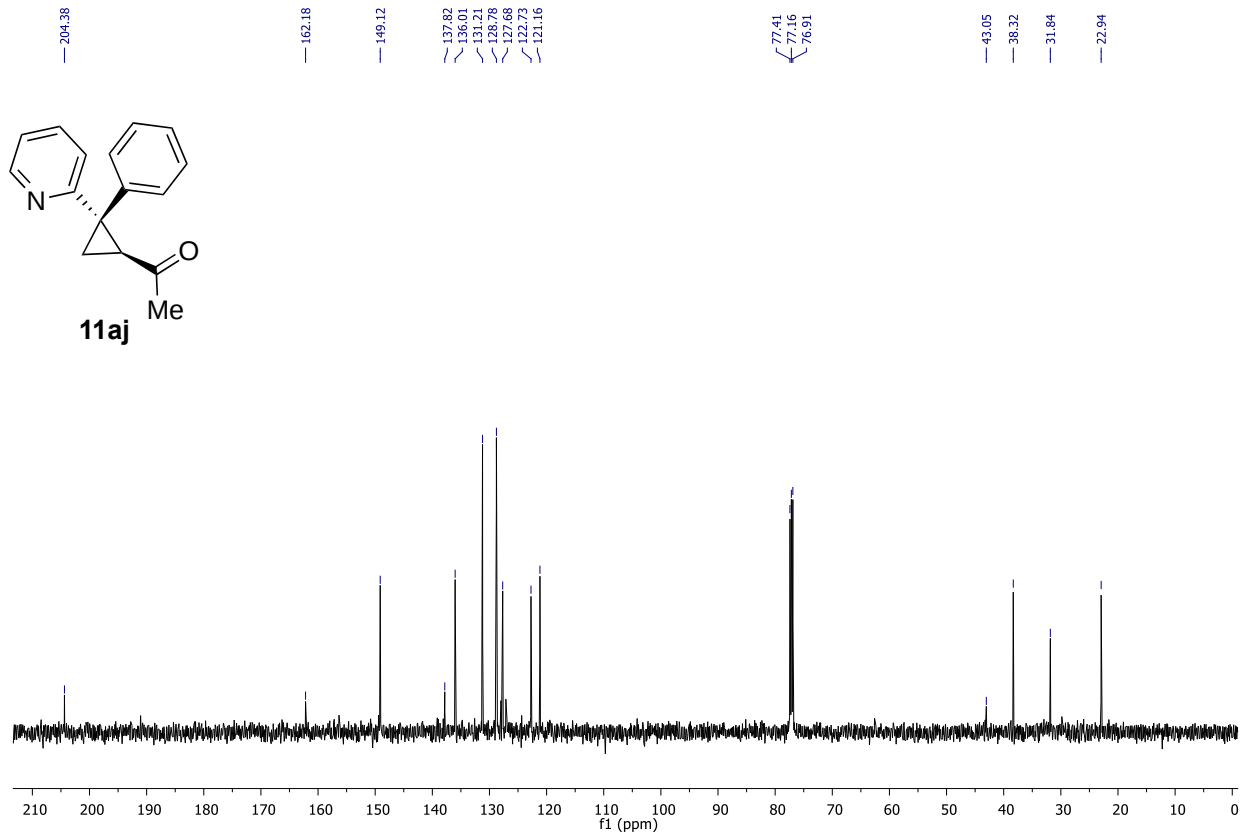
^{13}C NMR of **11ai**



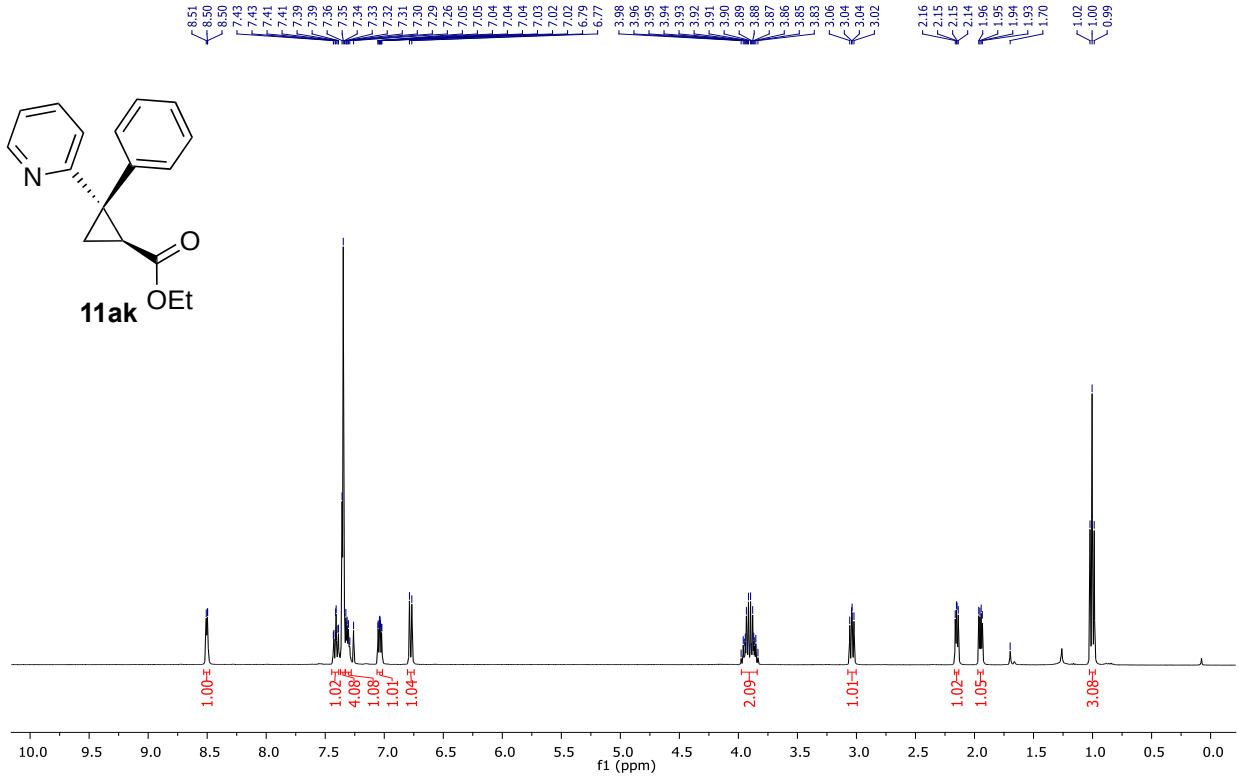
^{1}H NMR of **11aj**



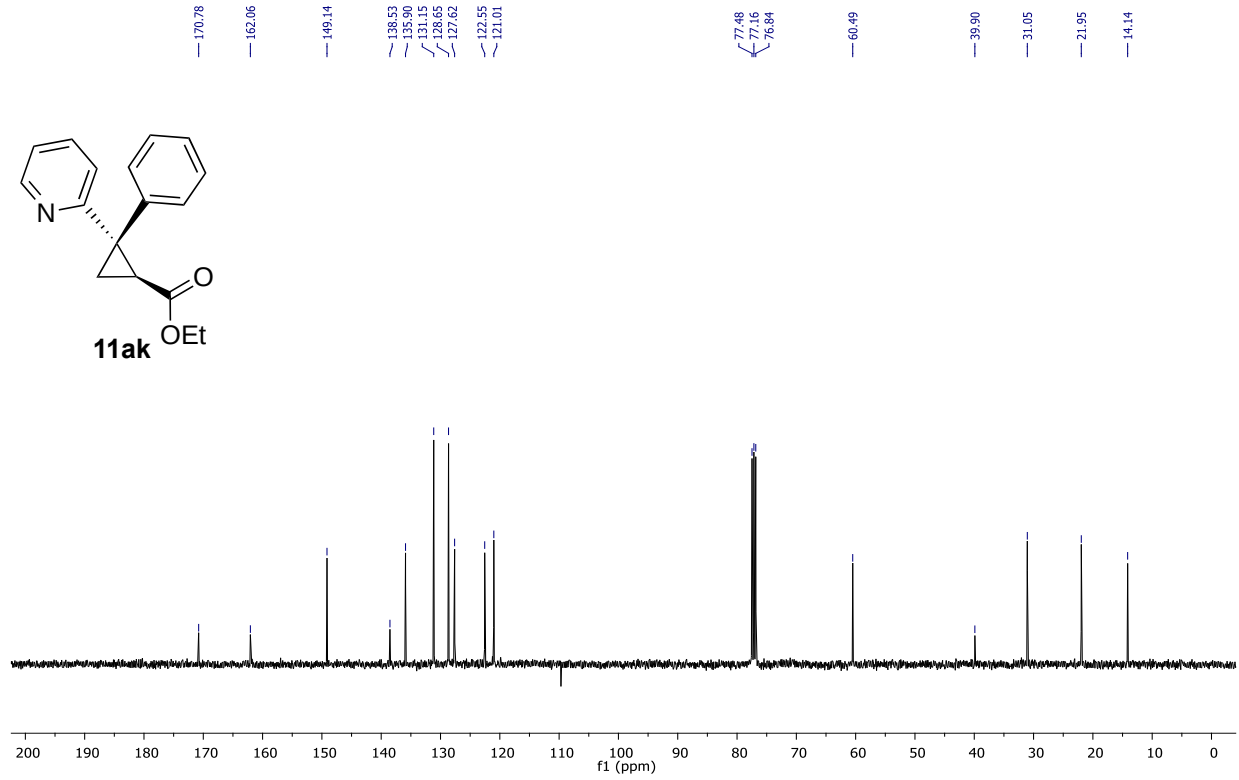
^{13}C NMR of **11aj**



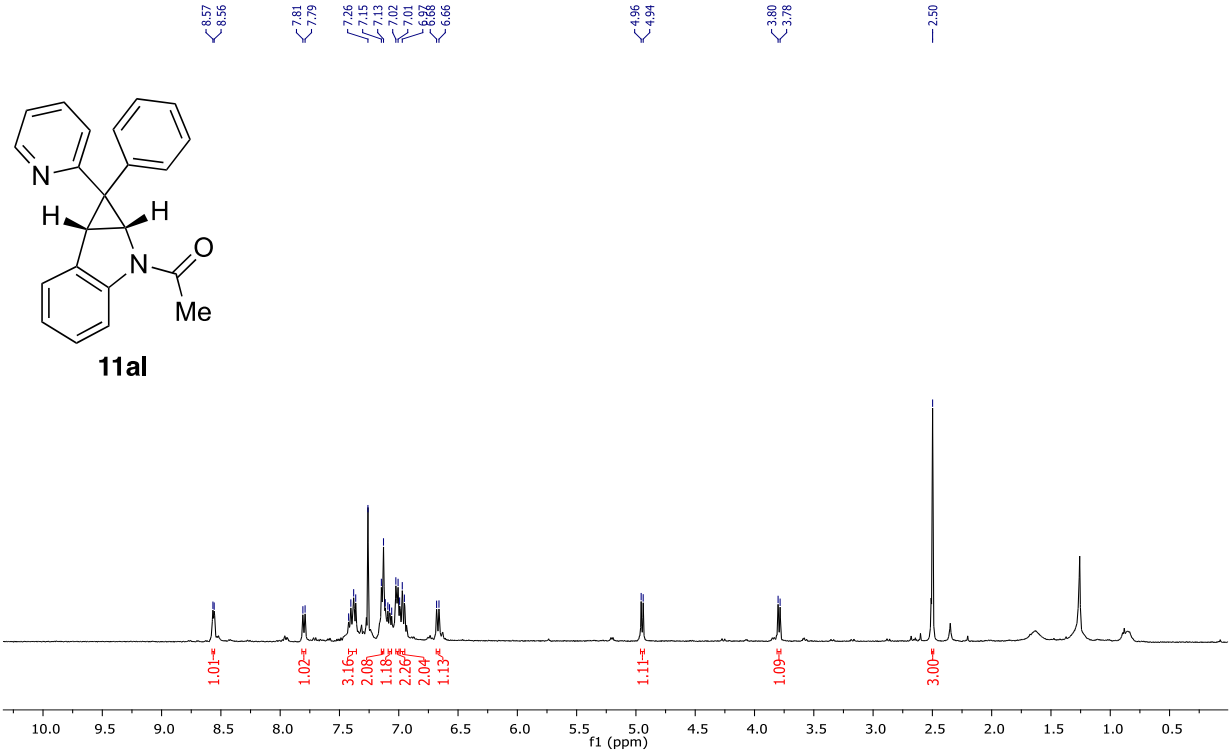
^{1}H NMR of **11ak**



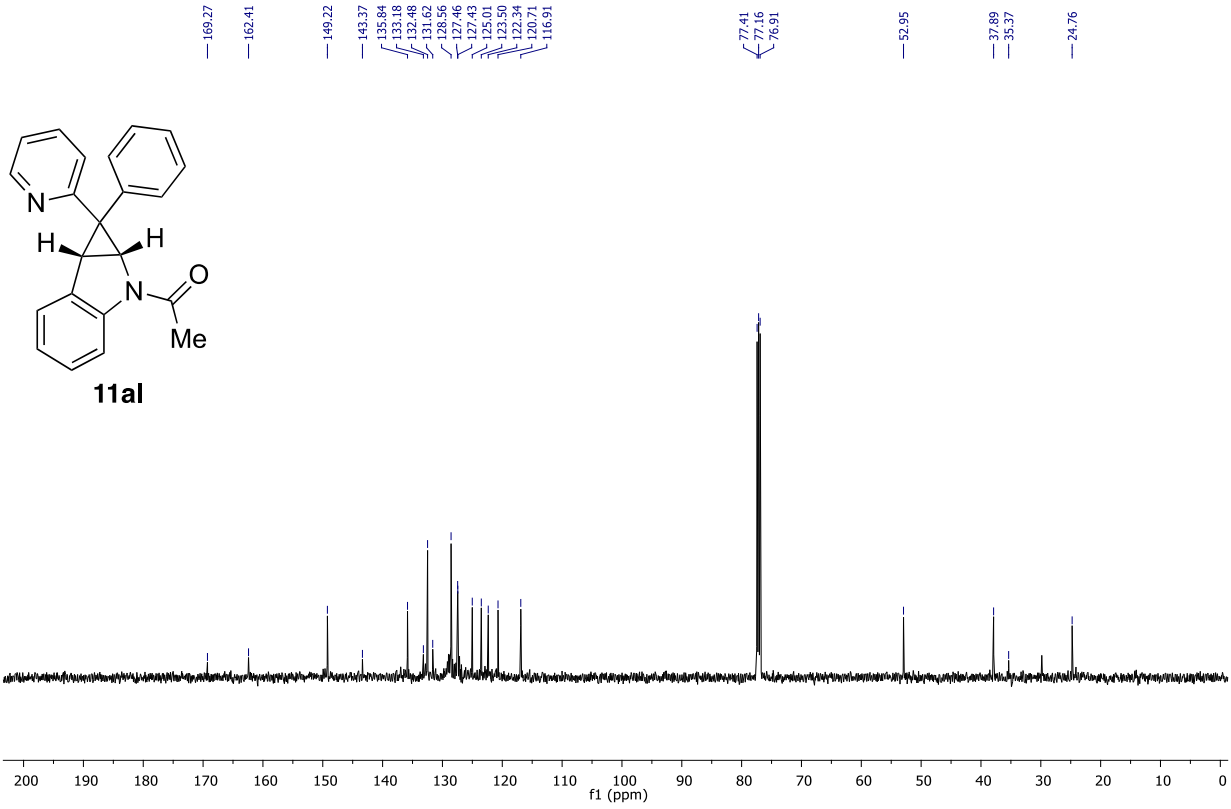
^{13}C NMR of **11ak**



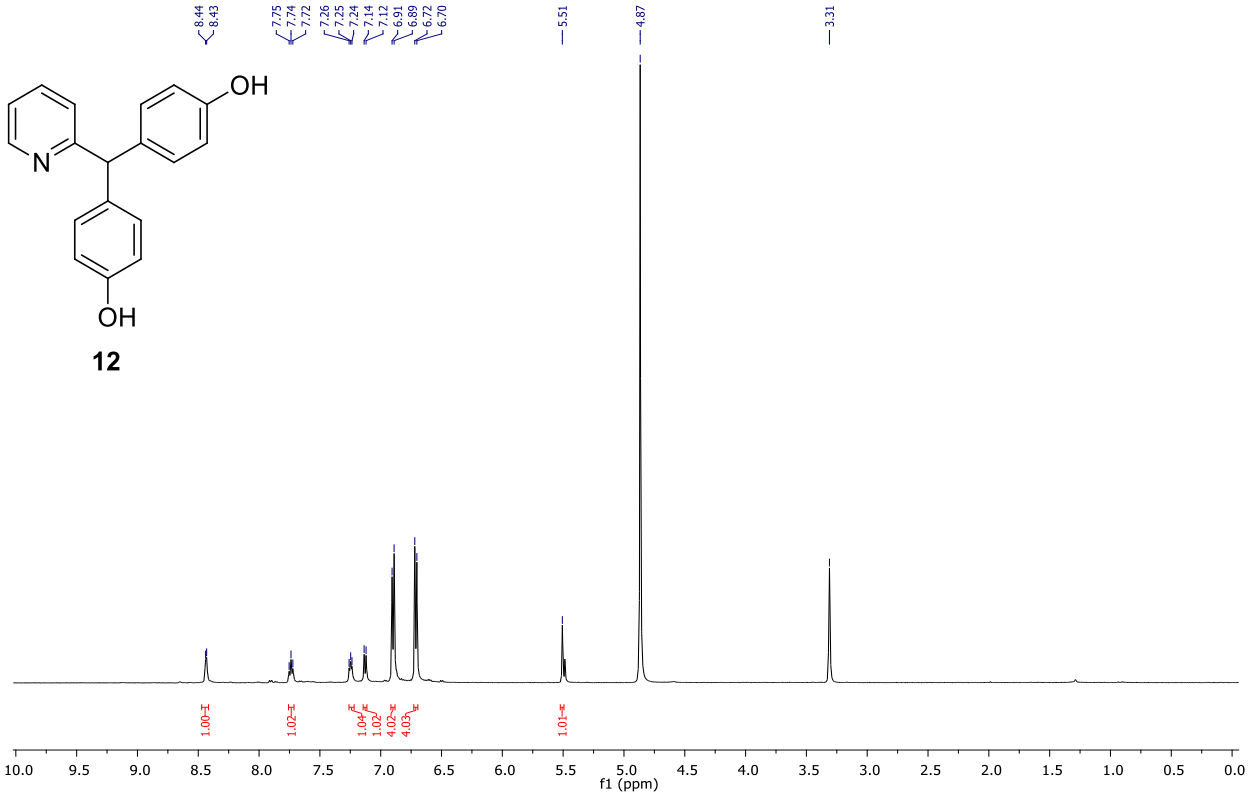
^{1}H NMR of **11al**



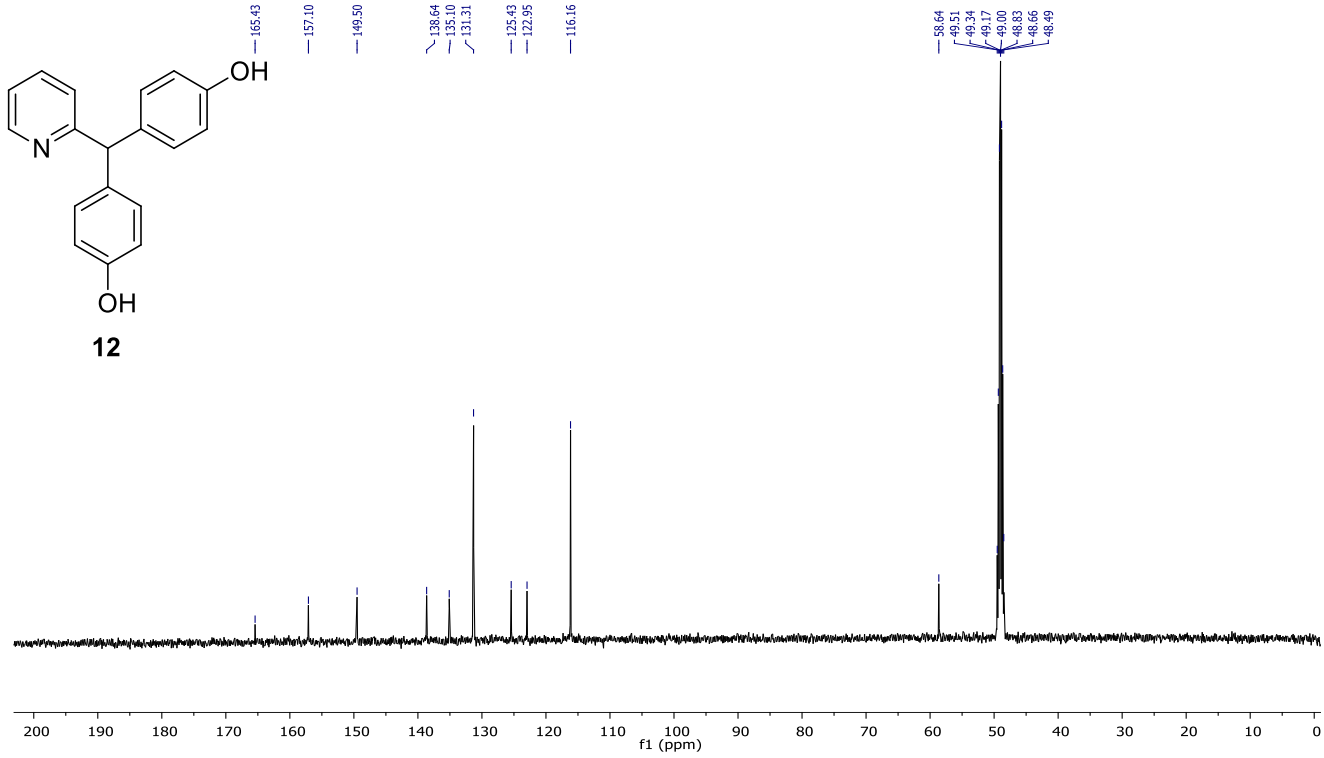
^{13}C NMR of **11al**



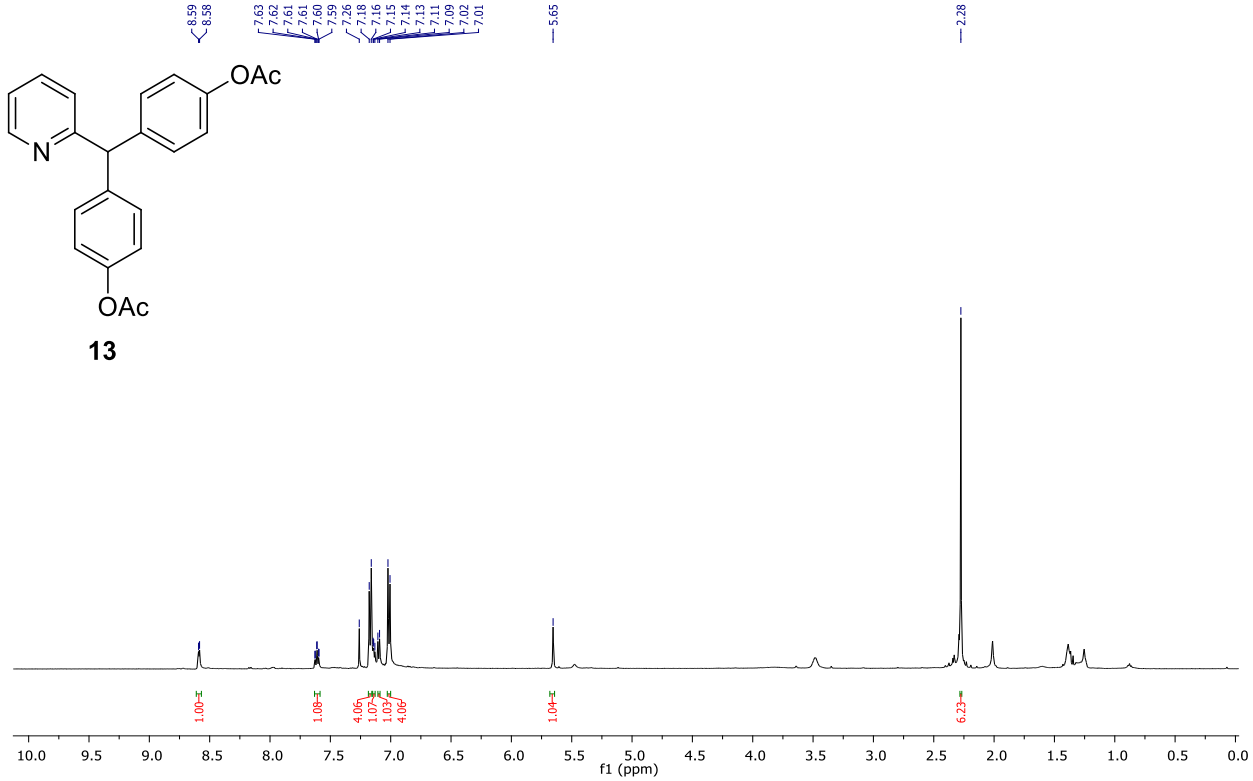
^{1}H NMR of **12 (**Solvent-MeOD$_4$)



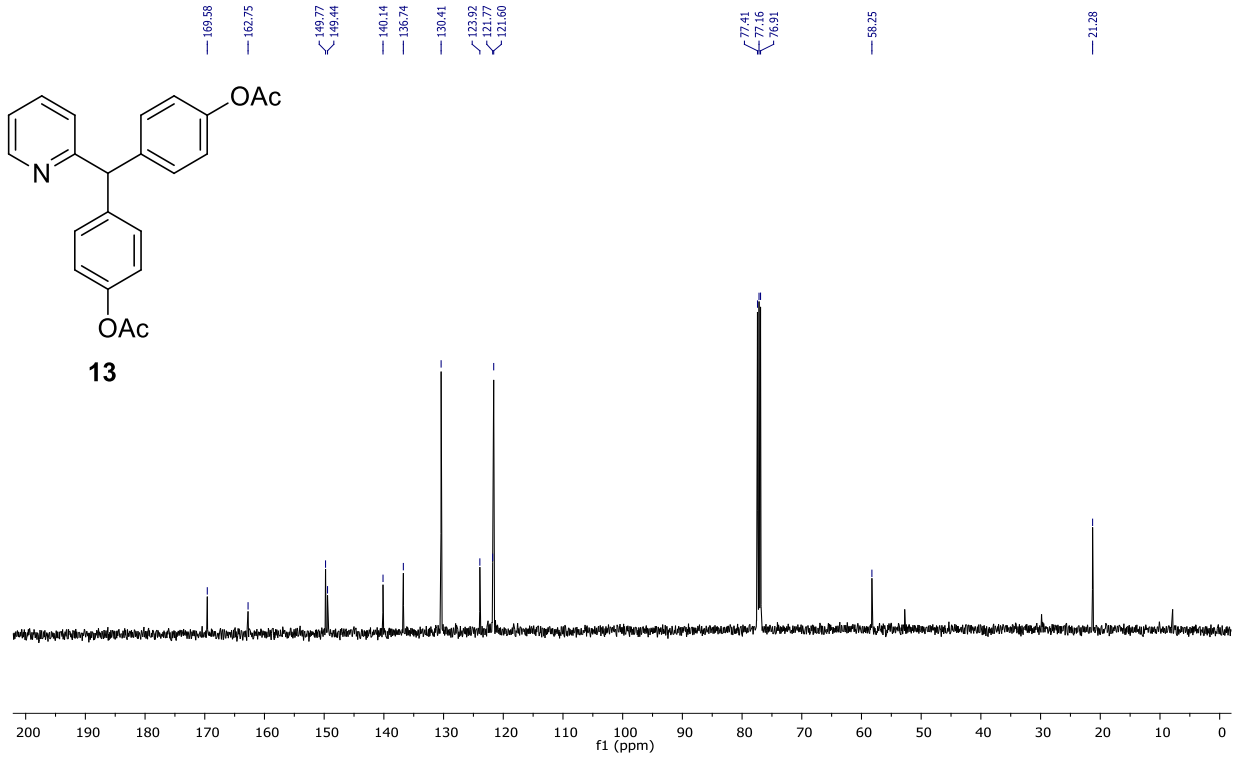
^{13}C NMR of **12 (**Solvent-MeOD$_4$)



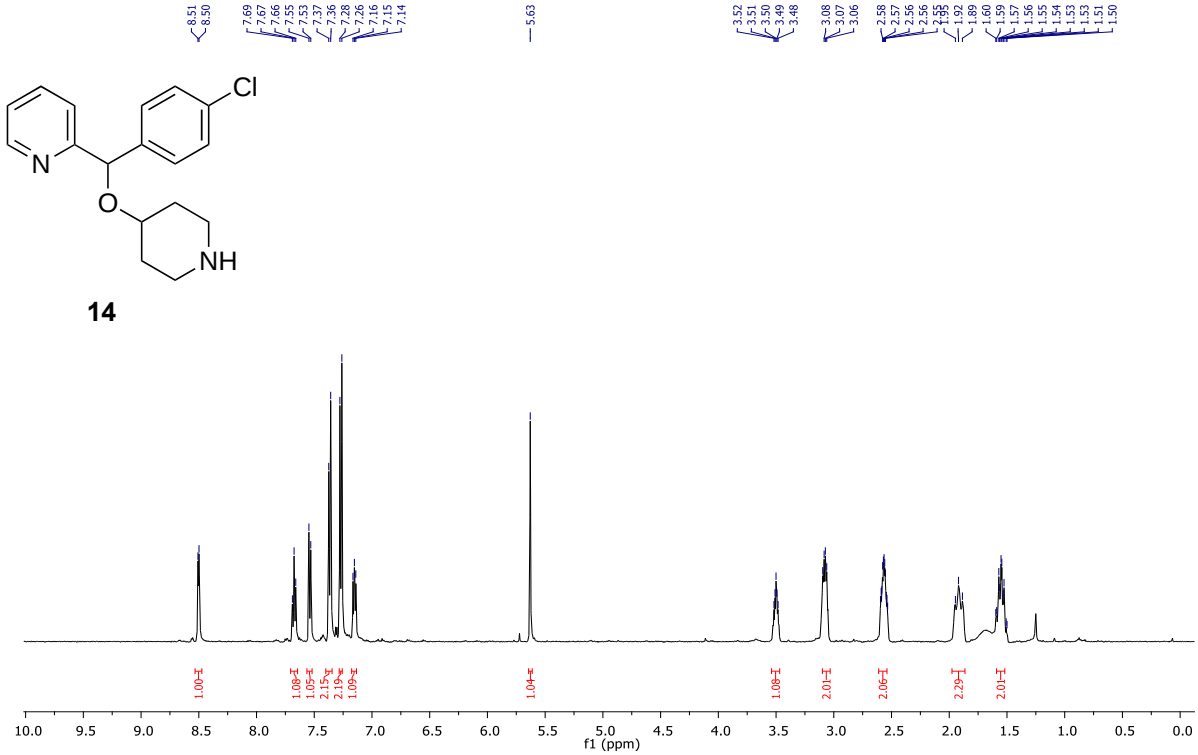
^{1}H NMR of **13**



^{13}C NMR of **13**

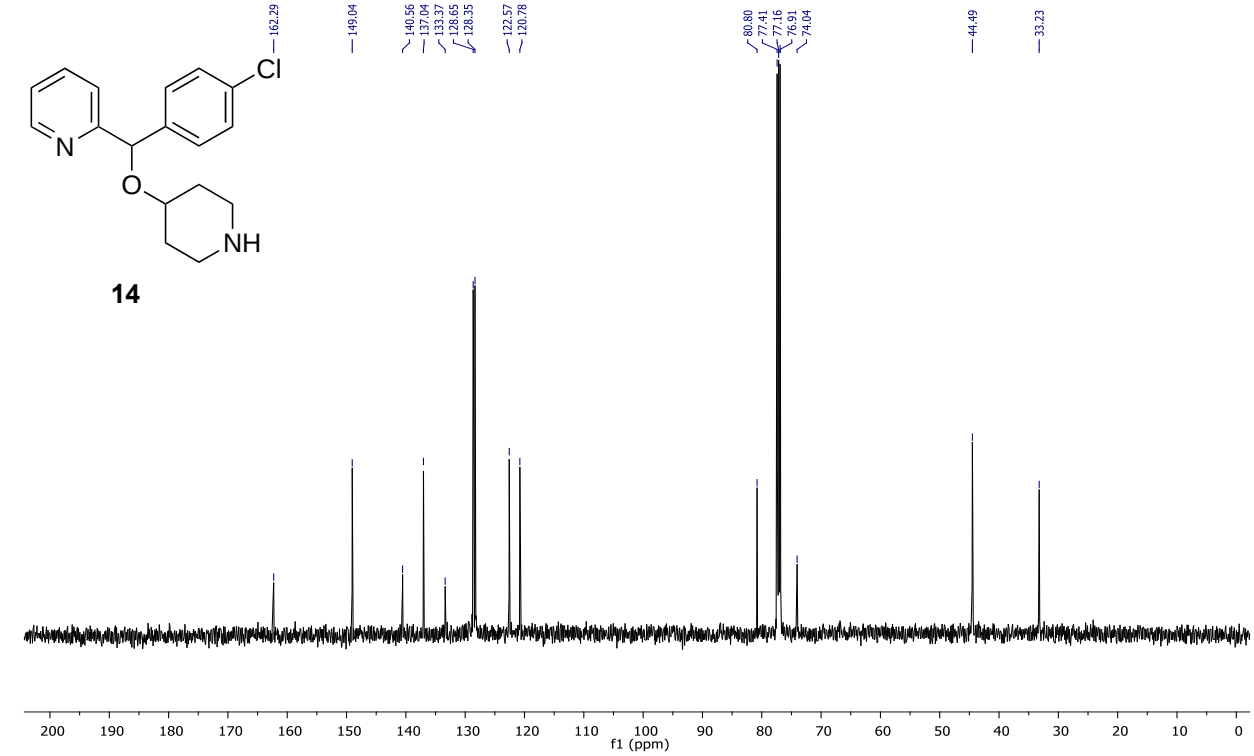


^{1}H NMR of **14**



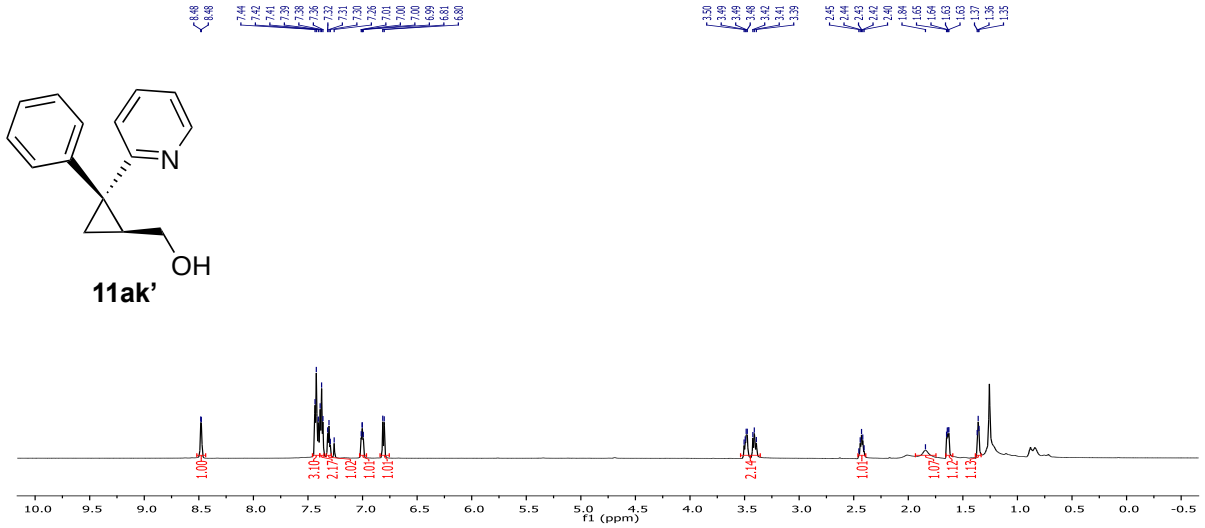
14

^{13}C NMR of **14**

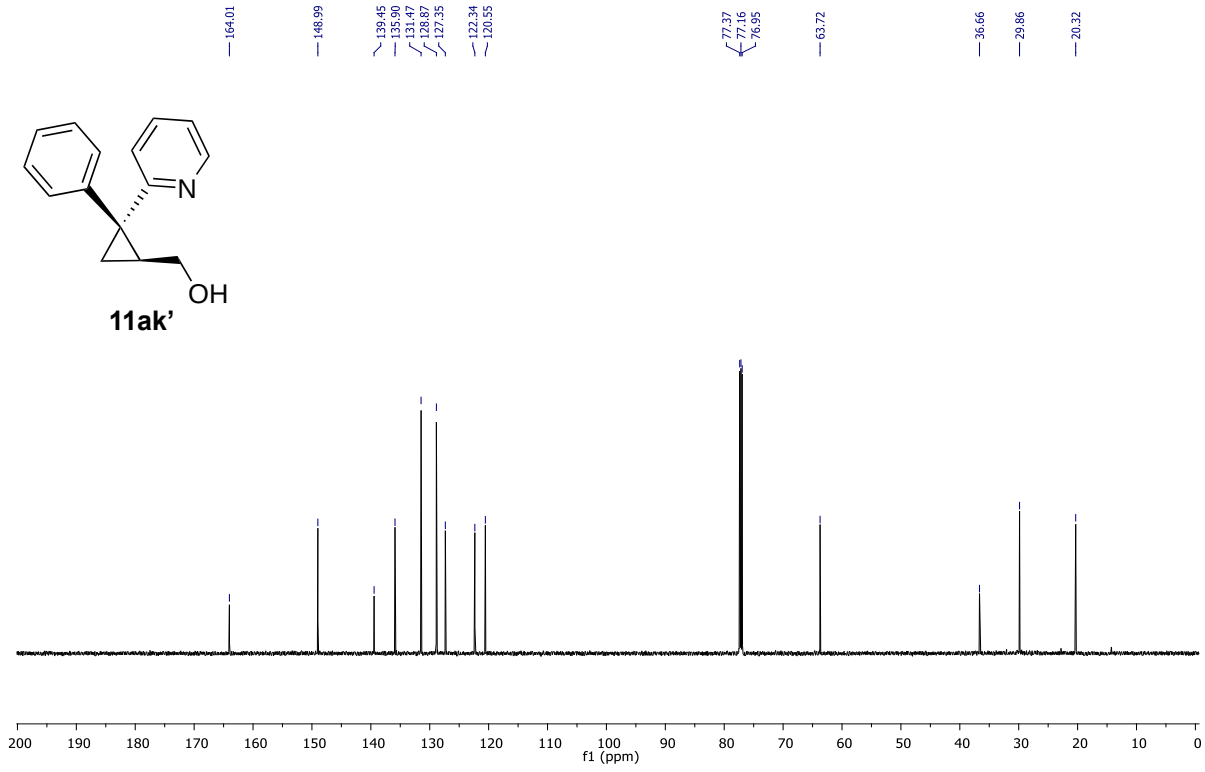


14

^{1}H NMR of **11ak'**



^{13}C NMR of **11ak'**



8. References

[1] S. Chuprakov, F. W. Hwang, V. Gevorgyan, *Angew. Chem., Int. Ed.* **2007**, *46*, 4757-4759.

[2] H. K. Gujral, N. Rani, S. P. Singh, O. Prakash, *Synth. Commun*, **2000**, *30*, 417-425.

[3] T. Hirayama, S. Ueda, T. Okada, N. Tsurue, K. Okuda, H. Nagasawa, *Chem. Eur. J.* **2014**, *20*, 4156-4162.