SUPPLEMENTARY INFORMATION FOR

Vinylazaarenes as Dienophiles in Lewis Acid-Promoted Diels-Alder Reactions

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CONTENTS

1. General Information

Materials and Methods: All reagents were obtained commercially in the highest available purity and used without further purification unless otherwise mentioned. Anhydrous solvents were obtained from a solvent purification system utilizing activated alumina columns under a positive pressure of argon. Reactions carried out at temperatures above room temperature (23 °C) were conducted in a pre-heated oil bath. Diels-Alder reactions were performed in 15 mL pressure tubes under magnetic stirring unless otherwise noted. Flash column chromatography was performed using silica or basic alumina gel (230 - 400 mesh) purchased from Silicycle (Siliaflash P60). Elution of compounds was monitored by UV and vanillin stain on TLC.

Instrumentation: ^{1}H and ^{13}C NMR spectra were measured on a Varian Inova 600 (600 MHz), Bruker Avance DRX 600 (600 MHz), or Bruker Avance III 800 (800 MHz) spectrometer and acquired at 300 K. Chemical shifts are reported in parts per million (ppm δ) referenced to the residual ^{1}H or ^{13}C resonance of the solvent. The following abbreviations are used singularly or in combination to indicate the multiplicity of signals: s - singlet, d - doublet, t - triplet, q - quartet, m – multiplet, br – broad, and ap – apparent. High-resolution mass spectrometry was obtained using an Agilent Q-TOF ESI spectrometer.

2. Screening and Reaction Optimization

Reaction conditions were screened with the Diels-Alder reaction of 4-vinylpyridine and isoprene using the following general procedure: To a 15 mL pressure tube equipped with a PTFE stir bar and charged with 4-vinylpyridine (213 µL, 2 mmol, 1 equiv) in the indicated solvent (4 mL) was added the specified Lewis acid (0 to 1.0 equiv) and isoprene (1-5 equiv). The vial was placed in an oil bath pre-heated to the specified temperature and allowed to stir for 24-72 hours. Upon reaction completion, the mixture was cooled to room temperature. Dodecane (0.25 mmol, 57 µL) was added as an internal standard and reaction was sampled and analyzed on GC-FID.

Mixtures of an authentic sample of **3** with dodecane were analyzed by GC to determine burn ratio of 1.29 for **3** for use in obtaining corrected GC yields. Authentic samples of starting material: 4-vinylpyridine were analyzed by GC to determine retention times. Regioselectivity is reported as a simple signal ratio between substituent peaks of **3.**

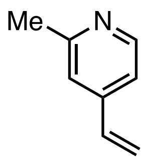
Table S1. Expanded Reaction Optimization Table

	temp (°C)	time (h)	equiv of **2**	Lewis acid (equiv)	solvent	GC Yield **3a** + **3b** (%) and ratio **3a**:**3b**
1	170	24	1	—	MeCN	9 (2:1)
2	170	72	1	—	MeCN	13 (2:1)
3	40	24	1	$Zn(NO_3)_2$ (0.025 equiv)	MeCN	<1
4	82	24	1	$Zn(NO_3)_2$ (1 equiv)	MeCN	<1
5	70	24	1	BF_3•OEt_2 (0.5 equiv)	MeCN	18 (5:1)
6	70	24	1	—	MeCN	<1
7	**70**	**72**	2	**BF_3•OEt_2 (0.5 equiv)**	**MeCN**	**54 (isolated) (5:1)**
8	70	24	2	BF_3•OEt_2 (0.5 equiv)	MeCN	35 (4:1)
9	70	48	2	BF_3•OEt_2 (0.5 equiv)	MeCN	47 (4:1)
10	70	24	5	BF_3•OEt_2 (0.5 equiv)	MeCN	36 (4:1)
11	50	24	2	BF_3•OEt_2 (0.5 equiv)	MeCN	3 (7:1)
12	60	24	2	BF_3•OEt_2 (0.5 equiv)	MeCN	16 (4:1)
13	82	24	2	BF_3•OEt_2 (0.5 equiv)	MeCN	18 (4:1)
14	70	24	2	BF_3•OEt_2 (1.0 equiv)	MeCN	37 (isolated) (5:1)
15	70	24	2	BF_3•OEt_2 (0.4 equiv)	MeCN	12 (4:1)
16	70	24	2	BF_3•OEt_2 (0.5 equiv)	DMF	21 (4:1)
17	70	24	2	BF_3•OEt_2 (0.5 equiv)	benzene	1 (4:1)
18	70	24	2	BF_3•OEt_2 (0.5 equiv)	CH2Cl2	5 (9:1)
19	70	24	2	BF_3•OEt_2 (0.5 equiv)	EtOH	6 (3:1)
20	70	24	2	Et_3Al (0.5 equiv)	MeCN	0
21	70	24	2	TMSOTf (0.5 equiv)	MeCN	0
22	70	24	2	*n*-Bu_3BOTf (0.5 equiv)	MeCN	0
23	70	24	2	$AlCl_3$ (0.5 equiv)	MeCN	12 (4:1)
24	70	24	2	$EtAlCl_2$ (0.5 equiv)	MeCN	12 (3:1)
25	70	24	2	$B(C_6F_5)_3$ (0.5 equiv)	MeCN	12 (3:1)
26	70	24	2	$B(C_6F_3(CF_3)_2)_3$ (0.5 equiv)	MeCN	2 (3:1)

3. Vinylazaarene Synthesis

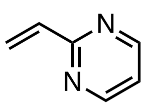
Vinylazaarenes **S1-S8** were prepared according to literature procedures.[1-6]

2-methyl-4-vinylpyridine (**S1**)



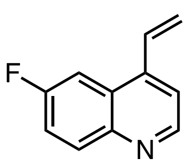
^{1}H NMR (800 MHz, $CDCl_3$): δ 8.38 (d, J = 5.3 Hz, 1H), 7.06 (s, 1H), 7.03 – 7.00 (m, 1H), 5.87 (d, J = 17.6 Hz, 1H), 5.38 (d, J = 10.9 Hz, 1H), 2.41 (s, 3H) ppm.
^{13}C NMR (201 MHz, $CDCl_3$): δ 158.8, 149.4, 145.0, 135.0, 120.4, 118.2, 117.8, 24.4 ppm.
NMR spectra are consistent with literature reports.[2]

2-vinylpyrimidine (**S2**)



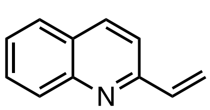
^{1}H NMR (800 MHz, $CDCl_3$): δ 7.10 (t, J = 4.9 Hz, 1H), 6.85 (dd, J = 17.3, 10.6 Hz, 1H), 6.60 (dd, J = 17.3, 1.6 Hz, 1H), 5.71 (dd, J = 10.6, 1.6 Hz, 1H) ppm.
^{13}C NMR (201 MHz, $CDCl_3$): δ 164.4, 157.0, 136.6, 123.9, 119.2 ppm.
NMR spectra are consistent with literature reports.[3]

6-fluoro-4-vinylquinoline (**S3**)



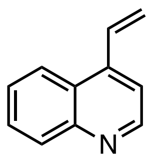
^{1}H NMR (800 MHz, $CDCl_3$): δ 8.84 (d, J = 4.5 Hz, 1H), 8.11 (dd, J = 9.2, 5.6 Hz, 1H), 7.68 (dd, J = 10.0, 2.7 Hz, 1H), 7.48 (dd, J = 9.7, 6.7 Hz, 2H), 7.28 (dd, J = 17.3, 11.0 Hz, 1H), 5.98 (d, J = 17.3 Hz, 1H), 5.68 (d, J = 11.0 Hz, 1H) ppm.
^{13}C NMR (201 MHz, $CDCl_3$): δ 161.3, 160.0, 149.6, 149.6, 145.8, 143.2, 143.1, 132.6, 132.6, 131.8, 127.1, 127.0, 121.3, 119.7, 119.6, 118.1, 107.4, 107.2 ppm.
NMR spectra are consistent with literature reports.[4]

2-vinylquinoline (**S4**)



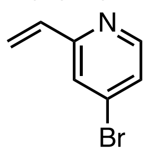
^{1}**H NMR** (600 MHz, $CDCl_3$): δ 8.07 – 8.00 (m, 2H), 7.74 – 7.70 (m, 1H), 7.66 (dddd, J = 8.4, 6.9, 2.7, 1.4 Hz, 1H), 7.54 (dd, J = 8.5, 3.8 Hz, 1H), 7.02 (dd, J = 17.7, 10.9 Hz, 1H), 6.25 (d, J = 17.6 Hz, 1H), 5.63 (d, J = 10.9 Hz, 1H) ppm.
^{13}**C NMR** (600 MHz, $CDCl_3$): δ 156.0, 148.0, 138.0, 136.3, 129.6, 129.4, 127.5, 126.3, 119.8, 118.3 ppm.
NMR spectra are consistent with literature reports.[5]

4-vinylquinoline (**S5**)



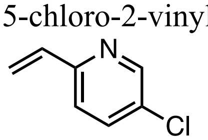
^{1}**H NMR** (800 MHz, $CDCl_3$): δ 8.84 (d, J = 4.6 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.41 (d, J = 4.6 Hz, 1H), 7.37 (dd, J = 17.4, 11.0 Hz, 1H), 5.93 (d, J = 17.4 Hz, 1H), 5.61 (d, J = 11.0 Hz, 1H) ppm.
^{13}**C NMR** (201 MHz, $CDCl_3$): δ 150.3, 148.5, 143.4, 132.0, 130.0, 129.3, 126.5, 126.2, 123.5, 120.7, 117.4 ppm.
NMR spectra are consistent with literature reports.[6]

4-bromo-2-vinylpyridine (**S6**)



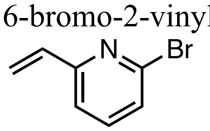
^{1}**H NMR** (800 MHz, $CDCl_3$): δ 8.38 – 8.32 (m, 1H), 7.46 (d, J = 2.0 Hz, 1H), 7.28 (dd, J = 5.3, 1.9 Hz, 1H), 6.71 (dd, J = 17.4, 10.8 Hz, 1H), 6.19 (dd, J = 17.4, 1.1 Hz, 1H), 5.50 (dd, J = 10.8, 1.1 Hz, 1H) ppm.
^{13}**C NMR** (201 MHz, $CDCl_3$): δ 157.1, 150.2, 135.8, 133.2, 125.6, 124.5, 119.9 ppm.
NMR spectra are consistent with literature reports.[1]

5-chloro-2-vinylpyridine (**S7**)



^{1}**H NMR** (600 MHz, $CDCl_3$): δ 8.48 (dd, J = 2.5, 0.7 Hz, 1H), 7.56 (dd, J = 8.4, 2.5 Hz, 1H), 7.23 (dd, J = 8.4, 0.7 Hz, 1H), 6.74 (dd, J = 17.4, 10.8 Hz, 1H), 6.15 (dd, J = 17.5, 1.1 Hz, 1H), 5.46 (dd, J = 10.8, 1.1 Hz, 1H) ppm.
^{13}**C NMR** (201 MHz, $CDCl_3$): δ 153.9, 148.4, 136.1, 135.8, 130.6, 121.8, 119.0 ppm.
NMR spectra are consistent with literature reports.[1]

6-bromo-2-vinylpyridine (**S8**)



^{1}**H NMR** (600 MHz, $CDCl_3$): δ 7.49 – 7.45 (t, J = 7.8 Hz, 1H), 7.31 (dd, J = 7.8, 0.8 Hz, 1H), 7.28

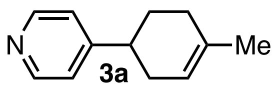
– 7.22 (dd, J = 7.8, 0.8 Hz, 1H), 6.71 (dd, J = 17.4, 10.8 Hz, 1H), 6.22 (dd, J = 17.4, 1.0 Hz, 1H), 5.50 (dd, J = 10.8, 1.0 Hz, 1H) ppm.
^{13}**C NMR** (201 MHz, $CDCl_3$): δ 157.0, 142.0, 138.8, 135.4, 127.1, 126.7, 120.0 ppm.
NMR spectra are consistent with literature reports.[1]

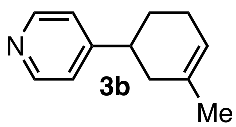
4. Diels-Alder Reactions

General Diels-Alder Procedure: To a 15 mL pressure tube equipped with a PTFE stir bar and charged with dienophile (2 mmol, 1 equiv) in acetonitrile (4 mL) was added boron trifluoride diethyl etherate (132 µL, 1 mmol, 0.5 equiv) and diene (4 mmol, 2 equiv). The vial was placed in a 70 °C oil bath and allowed to stir for 24-72 hours as noted. Upon reaction completion, the mixture was cooled to room temperature and quenched with brine (15 mL). The biphasic mixture was separated in a separatory funnel, and the aqueous layer was extracted 3 additional times with diethyl ether (20 mL). The combined organic layers were washed once more with brine and dried over $MgSO_4$, then concentrated in vacuo. The crude mixture was then purified by silica or alumina flash chromatography as noted.

4-(4-methylcyclohex-3-en-1-yl)pyridine (3a) and

4-(3-methylcyclohex-3-en-1-yl)pyridine (3b)

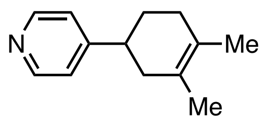




4-(4-methylcyclohex-3-en-1-yl) pyridine and 4-(3-methylcyclohex-3-en-1-yl) pyridine were prepared according to the general Diels-Alder procedure using 4-vinylpyridine (213 µL, 2 mmol, 1 equiv), $BF_3{\cdot}OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and isoprene (398 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 72 hr. After workup, the reaction mixture was purified on an alumina flash column (5% to 15% EtOAc/hexanes) to give an inseparable mixture of products **3a and 3b** as a yellow solid (93.5 mg, 1.08 mmol, 54% yield). Regioselectivity determined as 5:1 based on NMR integration of **3a:3b**.

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.40.
^{1}H NMR (**3a**) (600 MHz, $CDCl_3$): δ 8.72 (d, J = 5.3 Hz, 2H), 7.76 (d, J = 5.3 Hz, 2H), 5.48 (s, 1H), 3.04 (d, J = 11.6 Hz, 1H), 2.37 (d, J = 8.2 Hz, 1H), 2.16 (d, J = 8.2 Hz, 2H), 2.05 – 1.95 (m, 2H), 1.88 – 1.79 (m, 1H), 1.70 (s, 3H) ppm.
^{1}H NMR (**3b**) (600 MHz, $CDCl_3$): δ 8.72 (d, J = 5.3 Hz, 2H), 7.76 (d, J = 4.0 Hz, 2H), 5.51 (s, 1H), 3.13 (s, 1H), 2.26 (d, J = 13.5 Hz, 1H), 2.19 – 2.12 (m, 2H), 2.05 – 1.95 (m, 2H), 1.88 – 1.79 (m, 1H), 1.71 (s, 3H) ppm.
^{13}C NMR (**3a** and **3b**) δ 156.4, 156.3, 149.3, 134.2, 133.0, 122.6, 121.0, 120.0, 39.8, 39.3, 37.0, 32.4, 30.1, 29.1, 28.6, 25.2, 23.5, 23.4 ppm.
HRMS (EI/QTOF) m/z: $[M]^{\cdot+}$ Calcd for $C_{12}H_{15}N$ 174.1283, found 174.1278.

4-(3,4-dimethylcyclohex-3-en-1-yl)pyridine (4)



4-(3,4-dimethylcyclohex-3-en-1-yl)pyridine was prepared according to the general Diels-Alder procedure using 4-vinylpyridine (213 µL, 2 mmol, 1 equiv), $BF_3{\cdot}OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and 2,3-dimethylbutadiene (458 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on a silica flash column (5% to 15% EtOAc/hexanes) to give product **4** as a yellow oil (207.9 mg, 1.11 mmol, 56% yield).

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.34.

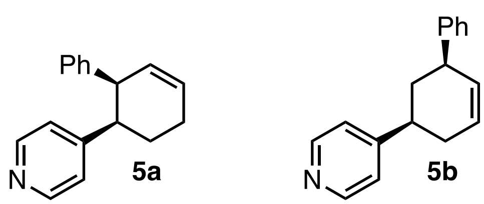
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.50 (s, 2H), 7.15 (s, 2H), 2.78 (ddd, J = 11.5, 5.4, 2.9 Hz, 1H), 2.19 – 2.08 (m, 3H), 1.99 – 2.02 (m, 1H), 1.94 – 1.87 (m, 1H), 1.73 – 1.66 (m, 1H), 1.65 (s, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 156.2, 149.5, 125.7, 124.7, 122.5, 40.2, 38.8, 31.7, 29.4, 19.0, 18.8 ppm.

HRMS (EI/QTOF) m/z: $[M]^{+}$ Calcd for $C_{13}H_{17}N$ 188.1440, found 188.1453.

4-((1S,2R)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2-yl)pyridine (5a) and

4-((1R,3R)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-3-yl)pyridine (5b)



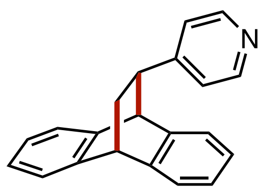
4-((1S,2R)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2-yl)pyridine and 4-((1R,3R)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-3-yl)pyridine were prepared according to the general Diels-Alder procedure using 4-vinylpyridine (213 µL, 2 mmol, 1 equiv), $BF_3{\cdot}OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and *trans*-1-phenyl-1,3-butadiene (559 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on an alumina flash column (5% to 15% EtOAc/hexanes) to give an inseparable mixture of products **5a** and **5b** as yellow oil (193.1 mg, 0.82 mmol, 41% yield). Regioselectivity determined as 4:1 based on NMR integration of **5a:5b**. Diastereoselectivity determined as >20:1 based on the absence of diastereomeric peaks in the crude NMR.

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.49.

^{1}H NMR (**5a**) (600 MHz, $CDCl_3$): δ 8.34 – 8.28 (m, 2H), 7.08 (dd, J = 7.0, 1.5 Hz, 3H), 6.77 – 6.71 (m, 2H), 6.68 – 6.62 (m, 2H), 6.03 – 6.05 (m, 1H), 5.86 (d, J = 10.0 Hz, 1H), 3.61 (d, J = 5.5 Hz, 1H), 3.23 (ddd, J = 13.1, 5.5, 2.1 Hz, 1H), 2.42 – 2.35 (m, 1H), 2.34 – 2.29 (m, 1H), 2.02 (dd, J = 13.1 6.7 Hz, 1H), 1.71 – 1.63 (m, 1H) ppm.

^{1}**H NMR** (**5b**) (600 MHz, $CDCl_3$): δ 8.40 – 8.35 (m, 2H), 7.19 – 7.11 (m, 3H), 6.94 – 6.91 (m, 2H), 6.90 – 6.86 (m, 2H), 5.98 – 5.91 (m, 1H), 5.74 (dd, J = 10.0, 2.3 Hz, 1H), 3.47 – 3.42 (m, 1H), 2.73 (ddd, J = 12.0, 9.5, 3.2 Hz, 1H), 2.40 – 2.38 (m, 1H), 2.25 – 2.18 (m, 1H), 1.99 – 1.96 (m, 1H), 1.95 – 1.90 (m, 1H) ppm.
^{13}**C NMR** (**5a** and **5b**) (151 MHz, $CDCl_3$): δ 153.3, 149.5, 149.0, 143.7, 139.2, 130.4, 130.1, 128.9, 128.2, 128.1, 128.0, 127.6, 127.4, 126.5, 126.4, 123.5, 123.1, 49.1, 48.8, 46.8, 44.5, 29, 25.8, 25.2, 21.4 ppm.
HRMS (EI/QTOF) m/z: $[M]^{\cdot+}$ Calcd for $C_{17}H_{17}N$ 236.1440, found 236.1435.

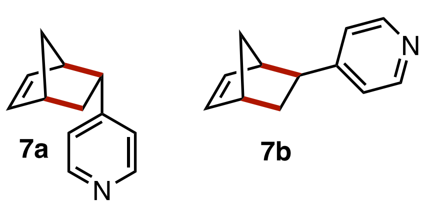
2-((9S,10S,12R)-9,10-dihydro-9,10-ethanoanthracen-12-yl)pyridine (6)



2-((9S,10S,12R)-9,10-dihydro-9,10-ethanoanthracen-12-yl)pyridine was prepared according to the general Diels-Alder procedure using 4 (213 µL, 2 mmol, 1 equiv), $BF_3 \cdot OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and anthracene (713 mg, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 72 hr. After workup, the reaction mixture was purified on a silica flash column (5% to 15% EtOAc/hexanes) to give product **6** as a colorless oil (218.9 mg, 0.78 mmol, 39% yield).
TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.60.
^{1}**H NMR** (600 MHz, $CDCl_3$): δ 8.33 (d, J = 5.1 Hz, 2H), 7.37 (d, J = 7.3 Hz, 1H), 7.32 (dd, J = 9.7, 4.3 Hz, 2H), 7.19 (dd, J = 7.3, 5.1 Hz, 1H), 7.15 (dd, J = 5.1, 1.4 Hz, 2H), 7.08 – 7.02 (m, 1H), 6.92 (d, J = 7.2 Hz, 1H), 6.51 (d, J = 7.2 Hz, 2H), 4.45 (s, 1H), 4.18 (s, 1H), 3.25 – 3.16 (m, 1H), 2.36 – 2.26 (m, 1H), 1.82 – 1.72 (m, 1H) ppm.
^{13}**C NMR** (151 MHz, $CDCl_3$): δ 154.6, 148.5, 144.1, 143.4, 143.1, 139.2, 126.5, 126.2, 126.1, 125.9, 125.7, 123.7, 123.5, 123.4, 123.1, 51.2, 44.6, 44.2, 35.6 ppm.
HRMS (EI/QTOF) m/z: $[M]^{\cdot+}$ Calcd for $C_{21}H_{17}N$ 284.1440, found 288.1437.

4-((1R,2R,4R)-bicyclo[2.2.1]hept-5-en-2-yl)pyridine (7a) and

4-((1R,2S,4R)-bicyclo[2.2.1]hept-5-en-2-yl)pyridine (7b)



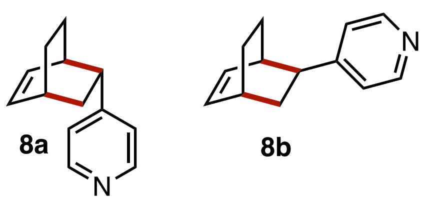
4-((1R,2R,4R)-bicyclo[2.2.1]hept-5-en-2-yl)pyridine and 4-((1R,2S,4R)-bicyclo[2.2.1]hept-5-en-

2-yl)pyridine were prepared according to the general Diels-Alder procedure using 4-vinylpyridine (213 µL, 2 mmol, 1 equiv), $BF_3{\cdot}OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and freshly distilled cyclopentadiene (264 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on an alumina flash column (5% to 15% EtOAc/hexanes) to give an inseparable mixture of products **7a** and **7b** as a brown oil (329.4 mg, 1.93 mmol, 97% yield). Diastereoselectivity determined as 4:1 based on NMR integration of **7a:7b**.

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.35.
^{1}H NMR (**7a**) (600 MHz, $CDCl_3$): δ 8.38 (d, J = 4.6 Hz, 2H), 7.01 (d, J = 4.6 Hz, 2H), 6.26 – 6.20 (m, 1H), 5.76 – 5.68 (m, 1H), 3.35 – 3.27 (m, 1H), 3.07 (s, 1H), 2.95 (s, 1H), 2.16 (ddd, J = 11.3, 3.9, 1.7 Hz, 1H), 1.51 – 1.41 (m, 2H), 1.27 (dt, J = 11.3, 1.7 Hz, 1H) ppm.
^{1}H NMR (**7b**) (600 MHz, $CDCl_3$): δ 8.45 (d, J = 4.5 Hz, 2H), 7.15 (d, J = 4.5 Hz, 2H), 6.21 (d, J = 3.1 Hz, 1H), 6.18 – 6.12 (m, 1H), 3.21 – 3.23 (m, 1H), 2.90 (s, 1H), 2.63 (dd, J = 8.9, 5.0 Hz, 1H), 1.71 – 1.60 (m, 2H), 1.41 – 1.43 (m, 1H) ppm.
^{13}C NMR (**7a**) (151 MHz, $CDCl_3$): δ 146.5, 135.1, 129.7, 121.0, 47.7, 45.8, 45.0, 40.7, 40.6 ppm.
^{13}C NMR (**7b**) (151 MHz, CDCl3): δ 151.6, 147.0, 134.3, 120.5, 43.2, 39.7, 30.8, 29.8, 29.7 ppm.
HRMS (EI/QTOF) m/z: $[M]^{+}$ Calcd for $C_{12}H_{13}N$ 172.1127, found 172.1135.

4-((1R,2R,4R)-bicyclo[2.2.2]oct-5-en-2-yl)pyridine (8a) and

4-((1R,2S,4R)-bicyclo[2.2.2]oct-5-en-2-yl)pyridine (8b)



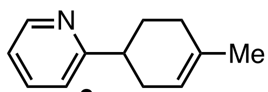
4-((1R,2R,4R)-bicyclo[2.2.2]oct-5-en-2-yl)pyridine and 4-((1R,2S,4R)-bicyclo[2.2.2]oct-5-en-2-yl)pyridine were prepared according to the general Diels-Alder procedure using 4-vinylpyridine (213 µL, 2 mmol, 1 equiv), $BF_3{\cdot}OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and 1,3-cyclohexadiene (380 µL 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 48 hr. After workup, the reaction mixture was purified on a silica flash column (5% to 15% EtOAc/hexanes) to give an inseparable mixture of products **8a** and **8b** as a white solid (131.2 mg, 0.70 mmol, 35% yield). Diastereoselectivity determined as 5:1 based on NMR integration of **8a:8b**.

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.35.
^{1}H NMR (**8a**) (600 MHz, $CDCl_3$): δ 8.44 – 8.37 (m, 2H), 7.09 – 7.04 (m, 2H), 6.41 (dd, J = 8.1, 6.5 Hz, 1H), 6.13 (dd, J = 8.1, 6.5 Hz, 1H), 2.92 (ddd, J = 10.1, 5.7, 1.9 Hz, 1H), 2.68 – 2.63 (m, 1H), 2.60 (td, J = 5.7, 1.9 Hz, 1H), 2.06 (td, J = 10.0, 2.8 Hz, 1H), 1.72 – 1.67 (m, 1H), 1.59 – 1.54 (m, 1H), 1.46 – 1.41 (m, 1H), 1.34 – 1.26 (m, 2H) ppm.

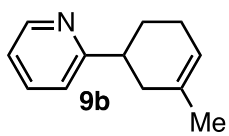
^{1}**H NMR** (**8b**) (600 MHz, $CDCl_3$): δ 8.50 (dd, J = 4.4, 1.9 Hz, 2H), 7.22 – 7.17 (m, 2H), 6.49 (t, J = 7.5 Hz, 1H), 6.33 (t, J = 7.5 Hz, 1H), 3.13 (dd, J = 10.1, 5.7 Hz, 1H), 2.84 – 2.76 (m, 1H), 2.75 – 2.69 (m, 1H), 2.48 (d, J = 3.3 Hz, 1H), 2.14 (ddd, J = 12.9, 10.1, 2.0 Hz, 1H), 1.74 – 1.72 (m, 1H), 1.63 – 1.59 (m, 1H), 1.38 (dt, J = 11.4, 3.3 Hz, 1H), 1.08 – 0.98 (m, 1H) ppm.
^{13}**C NMR** (**8a**) (151 MHz, $CDCl_3$): δ 157.5, 148.8, 135.6, 131.6, 43.2, 36.2, 35.4, 30.3, 30.0, 27.1, 24.0 ppm.
^{13}**C NMR** (**8b**) (151 MHz, $CDCl_3$): δ 149.1, 135.2, 134.4, 125.5, 42.5, 35.8, 30.5, 29.8, 26.0, 24.4, 8.9 ppm.
HRMS (EI/QTOF) m/z: $[M]^{+\cdot}$ Calcd for $C_{13}H_{15}N$ 186.1283, found 186.1279.

2-(4-methylcyclohex-3-en-1-yl)pyridine (9a) and

2-(3-methylcyclohex-3-en-1-yl)pyridine (9b)



9a

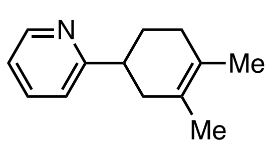


9b

2-(4-methylcyclohex-3-en-1-yl) pyridine and 2-(3-methylcyclohex-3-en-1-yl) pyridine were prepared according to the general Diels-Alder procedure using 2-vinylpyridine (215 µL, 2 mmol, 1 equiv), $BF_3 \cdot OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and isoprene (398 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on an alumina flash column (5% to 15% EtOAc/hexanes) to give an inseparable mixture of products **9a** and **9b** as a colorless oil (212.9 mg, 1.23 mmol, 61% yield). Regioselectivity determined as 10:1 based on NMR integration of **9a:9b**.

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.62.
^{1}**H NMR** (**9a**) (600 MHz, $CDCl_3$): δ 8.52 (s, 1H), 7.62 – 7.54 (m, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.09 – 7.04 (m, 1H), 5.57 – 5.38 (m, 1H), 2.90 (dd, J = 12.1, 5.7, Hz, 1H), 2.34 – 2.22 (m, 2H), 2.21 – 2.07 (m, 2H), 2.04 – 1.92 (m, 2H), 1.87 – 1.74 (m, 1H), 1.68 (s, 3H) ppm.
^{13}**C NMR** (**9a** and **9b**) (151 MHz, $CDCl_3$): δ 165.9, 149.1, 136.3, 133.9, 133.4, 121.2, 121.0, 120.7, 120.4, 42.6, 42.1, 36.3, 31.6, 30.4, 29.0, 28.4, 25.6, 23.6, 23.5 ppm.
HRMS (EI/QTOF) m/z: $[M]^{+\cdot}$ Calcd for $C_{12}H_{15}N$ 174.1283, found 174.1279

2-(3,4-dimethylcyclohex-3-en-1-yl)pyridine (10)



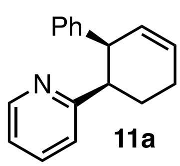
2-(3,4-dimethylcyclohex-3-en-1-yl)pyridine was prepared according to the general Diels-Alder procedure using 2-vinylpyridine (215 µL, 2 mmol, 1 equiv), BF_3·OEt_2 (132 µL, 1 mmol, 0.5 equiv), and 2,3-dimethylbutadiene (458 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on a silica flash column (5% to 15% EtOAc/hexanes) to give product **10** as a yellow oil (282.1 mg, 1.51 mmol, 75% yield).

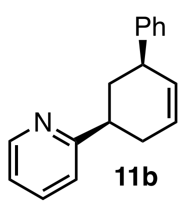
TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.66.
^{1}**H NMR** (600 MHz, $CDCl_3$): δ 8.52 (dt, J = 4.9, 1.4 Hz, 1H), 7.57 (td, J = 7.6, 1.4 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.05 – 7.07 (dd, J = 7.6, 4.9 Hz, 1H), 2.96 – 2.90 (m, 1H), 2.29 – 2.21 (m, 1H), 2.18 (m, 2H), 2.02 – 1.93 (m, 2H), 1.81 – 1.73 (m, 1H), 1.63 (s, 6H) ppm.
^{13}**C NMR** (151 MHz, $CDCl_3$): δ 165.9, 149.1, 136.3, 125.3, 125.0, 121.1, 121.0, 43.0, 38.0, 32.1, 29.3, 19.0 ppm.
HRMS (EI/QTOF) m/z: $[M]^{•+}$ Calcd for $C_{13}H_{17}N$ 188.1440, found 188.1450.

Product inhibition experiment: 2-vinylpyridine (215 µL, 2 mmol, 1 equiv), BF_3·OEt_2 (132 µL, 1 mmol, 0.5 equiv), 2,3-dimethylbutadiene (458 µL, 4 mmol, 2 equiv), and 2-(3,4-dimethylcyclohex-3-en-1-yl)pyridine (product **10**, 75.0mg, 0.4 mmol, 0.2 equiv) were dissolved in acetonitrile (4 mL). The resulting mixture was heated to 70 °C and allowed to stir for 24 hr. After workup, yield of the reaction was determined by crude ^{1}H NMR using methyl 3-nitrobenzoate as an internal standard. Using this method, the total amount of **10** present in the mixture was determined to be 1.46 mmol, indicating a yield of new product of 53% yield. Compared to the isolated yield of 75% in the above experiment, this observation is consistent with product inhibition.

2-((1S,2R)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2-yl)pyridine (11a) and

2-((1R,3R)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-3-yl)pyridine (11b)



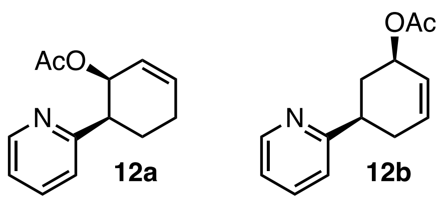


2-((1S,2R)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2-yl)pyridine and 2-((1R,3R)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-3-yl)pyridine were prepared according to the general Diels-Alder procedure using 2-vinylpyridine (215 µL, 2 mmol, 1 equiv), BF_3·OEt_2 (132 µL, 1 mmol, 0.5 equiv), and *trans*-1-phenyl-1,3-butadiene (559 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on an alumina flash column (5% to 15% EtOAc/hexanes) to give an inseparable mixture of products **11a** and **11b** as a yellow oil (296.8 mg, 1.26 mmol, 63% yield). Regioselectivity determined as >20:1 based on NMR integration of **11a:11b**. Diastereoselectivity determined as >20:1 based on the absence of diastereomeric peaks in crude NMR.

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.59.
^{1}H NMR (**11a**) (600 MHz, $CDCl_3$): δ 8.48 (dd, J = 4.9, 1.9 Hz, 1H), 7.27 (td, J = 7.7, 1.9 Hz, 1H), 7.04 – 6.94 (m, 4H), 6.74 – 6.68 (m, 2H), 6.39 (dt, J = 7.7, 1.0 Hz, 1H), 6.06 – 5.99 (m, 1H), 5.85 (dd, J = 9.7, 5.0, Hz, 1H), 3.94 – 3.89 (m, 1H), 3.47 (ddd, J = 13.3, 5.0, 2.5 Hz, 1H), 2.41 – 2.26 (m, 2H), 2.00 (ddd, J = 13.3, 11.0, 6.1 Hz, 1H), 1.79 – 1.70 (m, 1H) ppm.
^{1}H NMR (**11b**) (600 MHz, $CDCl_3$): δ 8.52 (dd, J = 4.9, 1.9 Hz, 1H), 7.35 (td, J = 7.6, 1.9 Hz, 1H), 7.13 – 7.07 (m, 2H), 6.98 – 6.92 (m, 5H), 5.89 – 5.93 (m, 1H), 5.75 (dd, J = 9.8, 2.9 Hz, 1H), 3.83 (ddd, J = 9.8, 4.3, 2.9 Hz, 1H), 2.88 (td, J = 12.6, 2.9 Hz, 1H), 2.26 – 2.18 (m, 2H), 2.11 – 2.13 (m, 1H), 1.96 – 1.90 (m, 1H) ppm.
^{13}C NMR (**11a**) (151 MHz, $CDCl_3$): δ 163.6, 148.5, 148.4, 140.2, 135.6, 129.8, 129.1, 128, 127.2, 126.1, 121.8, 121.0, 46.9, 46.1, 26.0, 26.0, 21.0 ppm.
HRMS (EI/QTOF) m/z: $[M]^{+}$ Calcd for $C_{17}H_{17}N$ 236.1440, found 236.1440.

(1S,6S)-6-(pyridin-2-yl)cyclohex-2-en-1-yl acetate (12a) and

(1R,5R)-5-(pyridin-2-yl)cyclohex-2-en-1-yl acetate (12b)



12a **12b**

(1S,6S)-6-(pyridin-2-yl)cyclohex-2-en-1-yl acetate and (1R,5R)-5-(pyridin-2-yl)cyclohex-2-en-1-yl acetate were prepared according to the general Diels-Alder procedure using 2-vinylpyridine (215 µL, 2 mmol, 1 equiv), BF_3·OEt_2 (132 µL, 1 mmol, 0.5 equiv), and *trans*-1-acetoxy-1,3-butadiene (474 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on an alumina flash column (5% to 15% EtOAc/hexanes) to give an inseparable mixture of products **12a** and **12b** as a yellow oil (307.9 mg, 1.42 mmol, 71% yield). Regioselectivity determined as 20:1 based on NMR integration of **12a:12b**. Diastereoselectivity determined as >20:1 based on the absence of diastereomeric peaks in crude NMR.

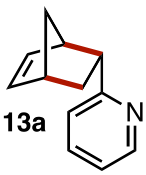
TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.63.
^{1}H NMR (**12a**) (600 MHz, $CDCl_3$): 8.51 (dd, J = 5.6, 1.7 Hz, 1H), 7.59 (td, J = 7.7, 1.7 Hz, 1H), 7.19 (d, J = 7.7 Hz, 1H), 7.13 – 7.08 (m, 1H), 6.03 – 6.06 (m, 1H), 5.96 – 5.89 (m, 1H), 5.53 (d, J = 4.5 Hz, 1H), 3.18 (dt, J = 12.8, 3.2 Hz, 1H), 2.36 – 2.27 (m, 1H), 2.24 – 2.11 (m, 2H), 1.98 – 1.93 (m, 1H), 1.74 (s, 3H) ppm.
^{13}C NMR (**12a**) (151 MHz, $CDCl_3$): δ 170.1, 161.4, 149.0, 135.9, 133.3, 124.8, 122.1, 121.5, 68.5, 45.9, 25.8, 21.3, 20.8 ppm.
HRMS (EI/QTOF) m/z: $[M]^{+}$ Calcd for $C_{13}H_{15}NO_2$ 218.1182, found 218.1178.

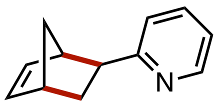
In a separate reaction, 2-vinylpyridine (4.80 mL, 44.6 mmol, 1 equiv), BF_3·OEt_2 (2.75 mL, 22.3 mmol, 0.5 equiv), and *trans*-1-acetoxy-1,3-butadiene (10.0 g, 89 mmol, 2 equiv) using the general Diels-Alder procedure above, with amounts of reagents adjusted to meet the larger scale.

Product **12a** was isolated as a yellow oil (4.95 g, 22.8 mmol, 51%); no **12b** was observable by NMR.

2-((1S,2R,4R)-bicyclo[2.2.1]heptan-2-yl)pyridine (13a) and

2-((1S,2S,4R)-bicyclo[2.2.1]heptan-2-yl)pyridine (13b)


13a

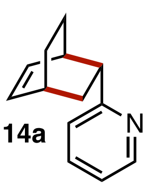

13b

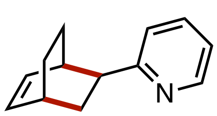
2-((1S,2R,4R)-bicyclo[2.2.1]heptan-2-yl)pyridine and 2-((1S,2S,4R)-bicyclo[2.2.1]heptan-2-yl)pyridine were prepared according to the general Diels-Alder procedure using 2-vinylpyridine (215 µL, 2 mmol, 1 equiv), $BF_3{\cdot}OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and freshly distilled cyclopentadiene (264 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on an alumina flash column (5% to 15% EtOAc/hexanes) to give an inseparable mixture of products **13a** and **13b** as a colorless oil (341.9 mg, 1.99 mmol, 99% yield). Diastereoselectivity determined as >20:1 based on NMR integration of **13a:13b**.

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.49.
^{1}**H NMR** (**13a**) (600 MHz, $CDCl_3$): δ 8.46 (dd, J = 4.8, 1.9 Hz, 1H), 7.49 (td, J = 7.7, 1.9 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.20 (dd, J = 5.7, 3.0 Hz, 1H), 5.73 (dd, J = 5.7, 3.0 Hz, 1H), 3.56 (ddd, J = 8.9, 4.1, 3.0 Hz, 1H), 3.25 (s, 1H), 2.93 (s, 1H), 2.19 (dd, J = 8.9, 4.1 Hz, 1H), 1.51 – 1.44 (m, 3H) ppm.
^{13}**C NMR** (**13a**) (151 MHz, $CDCl_3$): δ 146.1, 135.1, 129.7, 121.0, 47.7, 45.8, 45.0, 40.7, 40.6 ppm.
HRMS (EI/QTOF) m/z: $[M]^{\cdot+}$ Calcd for $C_{12}H_{13}N$ 172.1127, found 172.1125.

2-((1R,2R,4R)-bicyclo[2.2.2]oct-5-en-2-yl)pyridine (14a) and

2-((1R,2S,4R)-bicyclo[2.2.2]oct-5-en-2-yl)pyridine (14b)


14a

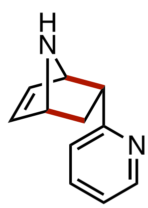

14b

2-((1R,2R,4R)-bicyclo[2.2.2]oct-5-en-2-yl)pyridine and 2-((1R,2S,4R)-bicyclo[2.2.2]oct-5-en-2-yl)pyridine were prepared according to the general Diels-Alder procedure using 2-vinylpyridine (215 µL, 2 mmol, 1 equiv), $BF_3{\cdot}OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and 1,3-cyclohexadiene (380 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on a silica flash column (5% to 15%

EtOAc/hexanes) to give an inseparable mixture of products **14a** and **14b** as a colorless oil (186.9 mg, 1.02 mmol, 51% yield). Diastereoselectivity determined as >20:1 based on NMR integration of **14a:14b**.

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.53.
^{1}H NMR (**14a**) (600 MHz, $CDCl_3$): δ 8.46 (dd, J = 4.9, 1.9 Hz, 1H), 7.52 (td, J = 7.7, 1.9 Hz, 1H), 7.11 (d, J = 7.7 Hz, 1H), 7.03 (dd, J = 7.7, 4.9 Hz, 1H), 6.37 – 6.41 (m, 1H), 6.17 – 6.09 (m, 1H), 3.19 (dd, J = 10.0, 5.9 Hz, 1H), 2.80 – 2.74 (m, 1H), 2.69 – 2.62 (m, 1H), 2.07 (dd, J = 12.8, 10.0 Hz, 1H), 1.78 – 1.72 (m, 1H), 1.69 – 1.62 (m, 1H), 1.62 – 1.54 (m, 1H), 1.36 – 1.26 (m, 2H) ppm.
^{13}C NMR (**14a**) (151 MHz, $CDCl_3$): δ 166.5, 148.6, 136.0, 135.1, 131.9, 121.5, 120.8, 45.7, 35.7, 34.2, 30.2, 27.1, 24.3 ppm.
HRMS (EI/QTOF) m/z: $[M]^{+}$ Calcd for $C_{13}H_{15}N$ 186.1283, found 186.1280.

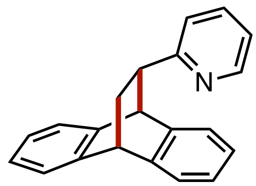
(1R,4R,5R)-5-(pyridin-2-yl)-7-azabicyclo[2.2.1]hept-2-ene (15)



(1R,4R,5R)-5-(pyridin-2-yl)-7-azabicyclo[2.2.1]hept-2-ene was prepared according to the general Diels-Alder procedure using 2-vinylpyridine (215 µL/mg, 2 mmol, 1 equiv), $BF_3{\cdot}OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and pyrrole (277 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on an alumina flash column (5% to 15% EtOAc/hexanes) to give product **15** as a brown solid (191.1 mg, 1.11 mmol, 55% yield) that was analytically pure. Diastereoselectivity determined as >20:1 based on the absence of diastereomeric peaks in crude NMR. Recrystallization from EtOAc/hexanes provided a light brown solid (170 mg, mp = 77.8-79.0 °C).

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.16.
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.92 (br s, 1H), 8.60 – 8.54 (m, 1H), 7.60 (td, J = 7.5, 1.9 Hz, 1H), 7.14 (dd, J = 7.5, 1.9 Hz, 2H), 6.68 – 6.62 (m, 1H), 6.10 (d, J = 3.0 Hz, 1H), 5.93 (d, J = 3.0 Hz, 1H), 3.13 (dd, J = 7.6, 5.6 Hz, 2H), 3.07 (dd, J = 7.6, 5.6 Hz, 2H) ppm.
^{13}C NMR (151 MHz, $CDCl_3$): δ 161.3, 149.0, 136.7, 132.0, 123.4, 121.3, 116.3, 107.9, 105.2, 38.0, 27.0 ppm.
HRMS (EI/QTOF) m/z: $[M]^{+}$ Calcd for $C_{11}H_{12}N_2$ 173.1079, found 173.1075.

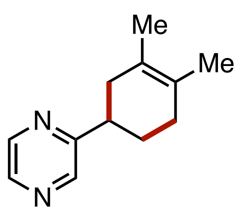
2-((9S,10S,12R)-9,10-dihydro-9,10-ethanoanthracen-12-yl)pyridine (16)



2-((9S,10S,12R)-9,10-dihydro-9,10-ethanoanthracen-12-yl)pyridine was prepared according to the general Diels-Alder procedure using 2-vinylpyridine (215 µL, 2 mmol, 1 equiv), $BF_3{\cdot}OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and anthracene (713 mg, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 72 hr. After workup, the reaction mixture was purified on a silica flash column (5% to 15% EtOAc/hexanes) to give product **16** as an analytically pure yellow solid (250.0 mg, 0.88 mmol, 44% yield). Recrystallization from EtOAc provided a yellow solid (200 mg, mp = 213.9-215.1 °C).

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.65.
^{1}**H NMR** (600 MHz, $CDCl_3$): δ 8.47 (d, J = 4.1 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.34 – 7.30 (m, 1H), 7.15 – 7.11 (m, 3H), 7.06 (dd, J = 7.4, 4.1 Hz, 1H), 6.98 (td, J = 7.4, 1.2 Hz, 1H), 6.88 (d, J = 6.7 Hz, 1H), 6.19 (d, J = 8.1 Hz, 1H), 4.47 – 4.43 (m, 2H), 3.59 (dd, J = 10.4, 2.6 Hz, 1H), 2.33 (ddd, J = 12.9, 10.4, 2.6 Hz, 1H), 2.00 (dd, J = 12.9, 2.6 Hz, 1H) ppm.
^{13}**C NMR** (151 MHz, $CDCl_3$): δ 163.2, 147.8, 144.1, 143.5, 143.5, 140.0, 136.6, 126.1, 125.9, 125.9, 125.8, 125.4, 123.7, 123.4, 123.0, 121.7, 121.5, 50.5, 46.5, 44.4, 34.3 ppm.
HRMS (EI/QTOF) m/z: $[M]^{+}$ Calcd for $C_{21}H_{17}N$ 284.1440, found 288.1434.

2-(3,4-dimethylcyclohex-3-en-1-yl)pyrazine (17)

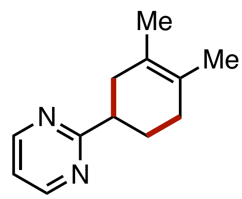


2-(3,4-dimethylcyclohex-3-en-1-yl)pyrazine was prepared according to the general Diels-Alder procedure using 2-vinylpyrazine (204 µL, 2 mmol, 1 equiv), $BF_3{\cdot}OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and 2,3-dimethylbutadiene (456 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on a silica flash column (5% to 15% EtOAc/hexanes) to give product **17** as an orange oil. (180.5 mg, 0.96 mmol, 48% yield).

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.62.
^{1}**H NMR** (600 MHz, $CDCl_3$): δ 8.51 – 8.44 (m, 2H), 8.37 (d, J = 2.5 Hz, 1H), 3.02 – 2.93 (m, 1H), 2.34 – 2.25 (m, 1H), 2.21 – 2.12 (m, 2H), 2.04 – 1.91 (m, 2H), 1.86 – 1.77 (m, 1H), 1.63 (s, 3H), 1.62 (s, 3H) ppm.
^{13}**C NMR** (151 MHz, $CDCl_3$): δ 161.2, 144.0, 143.6, 142.2, 125.5, 124.6, 40.5, 37.3, 31.7, 28.8, 19.0, 18.9 ppm.

HRMS (EI/QTOF) m/z: $[M]^{•+}$ Calcd for $C_{12}H_{26}N_2$ 189.1392, found 189.1389.

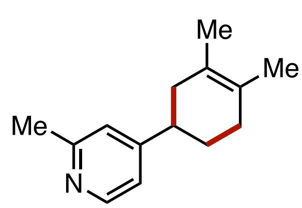
2-(3,4-dimethylcyclohex-3-en-1-yl)pyrimidine (18)



2-(3,4-dimethylcyclohex-3-en-1-yl)pyrimidine was prepared according to the general Diels-Alder procedure using 2-vinylpyrimidine (212 µL, 2 mmol, 1 equiv), $BF_3·OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and 2,3-dimethylbutadiene (456 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on a silica flash column (5% to 15% EtOAc/hexanes) to give product **18** as a yellow oil (248.5 mg, 1.32 mmol, 66% yield).

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.59.
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.62 (d, J = 4.9 Hz, 2H), 7.06 (t, J = 4.9 Hz, 1H), 3.06 (ddd, J = 12.3, 11.1, 5.3 Hz, 1H), 2.42 – 2.31 (m, 1H), 2.22 – 2.12 (m, 2H), 2.02 (dd, J = 12.3, 5.3 Hz, 1H), 1.95 – 1.99 (m, 1H), 1.76 – 1.73 (m, 1H), 1.59 (s, 6H) ppm.
^{13}C NMR (151 MHz, $CDCl_3$): δ 174.2, 156.9, 125.3, 124.7, 118.4, 44.1, 36.6, 32.0, 28.7, 19.0, 18.8 ppm.
HRMS (EI/QTOF) m/z: $[M]^{•+}$ Calcd for $C_{12}H_{26}N_2$ 189.1392, found 189.1387.

4-(3,4-dimethylcyclohex-3-en-1-yl)-2-methylpyridine (19)

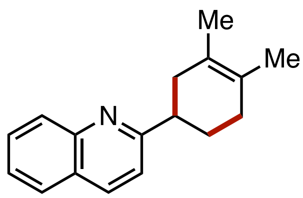


4-(3,4-dimethylcyclohex-3-en-1-yl)-2-methylpyridine was prepared according to the general Diels-Alder procedure using 2-methyl-4-vinylpyridine (238 µL, 2 mmol, 1 equiv), $BF_3·OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and 2,3-dimethylbutadiene (456 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on a silica flash column (5% to 15% EtOAc/hexanes) to give product **19** as a colorless oil (269.1 mg, 1.33 mmol, 67% yield).

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.30.
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.36 (d, J = 5.2 Hz, 1H), 6.99 (d, J = 1.7 Hz, 1H), 6.94 (dd, J = 5.2,

1.7 Hz, 1H), 2.76 – 2.67 (m, 1H), 2.52 (s, 3H), 2.17 – 2.03 (m, 3H), 2.02 – 1.95 (m, 1H), 1.85 – 1.88 (m, 1H), 1.70 – 1.64 (m, 1H), 1.63 (s, 6H) ppm.
^{13}C NMR (151 MHz, $CDCl_3$): δ 157.9, 156.8, 148.6, 125.7, 124.7, 122.0, 119.6, 40.2, 38.8, 31.8, 31.8, 29.5, 24.2, 19.0, 18.8 ppm.
HRMS (EI/QTOF) m/z: $[M]^{+\cdot}$ Calcd for $C_{14}H_{19}N$ 202.1596, found 202.1591.

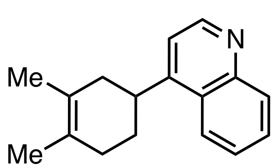
2-(3,4-dimethylcyclohex-3-en-1-yl)quinoline (20)



2-(3,4-dimethylcyclohex-3-en-1-yl)quinoline was prepared according to the general Diels-Alder procedure using 2-vinylquinoline (301 µL/mg, 2 mmol, 1 equiv), $BF_3{\cdot}OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and 2,3-dimethylbutadiene (456 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on a silica flash column (5% to 15% EtOAc/hexanes) to give product **20** as an orange oil (422.2 mg, 1.78 mmol, 89% yield).

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.80.
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12 (dt, J = 8.5, 0.9 Hz, 1H), 8.07 (dd, J = 8.5, 0.9 Hz, 1H), 7.72 (dd, J = 8.1, 1.4 Hz, 1H), 7.64 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.43 (ddd, J = 8.1, 6.8, 1.4 Hz, 1H), 7.29 (d, J = 8.5 Hz, 1H), 3.21 (ddd, J = 12.1, 10.9, 5.4 Hz, 1H), 2.38 – 2.31 (m, 1H), 2.29 – 2.16 (m, 2H), 2.08 – 1.94 (m, 2H), 1.91 – 1.81 (m, 1H), 1.63 (s, 6H) ppm.
^{13}C NMR (151 MHz, $CDCl_3$): δ 166.1, 146.7, 137.4, 130.5, 129.8, 128.1, 127.5, 127.0, 126.0, 125.5, 124.7, 119.7, 43.4, 37.7, 31.9, 29.2, 18.9 ppm.
HRMS (EI/QTOF) m/z: $[M]^{+\cdot}$ Calcd for $C_{17}H_{19}N$ 238.1596, found 238.1592.

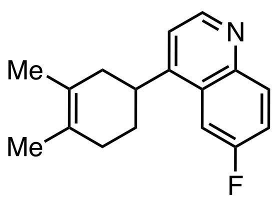
4-(3,4-dimethylcyclohex-3-en-1-yl)quinoline (21)



4-(3,4-dimethylcyclohex-3-en-1-yl)quinoline was prepared according to the general Diels-Alder procedure using 4-vinylquinoline (282 µL, 2 mmol, 1 equiv), $BF_3{\cdot}OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and 2,3-dimethylbutadiene (456 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on a silica flash column (5% to 15% EtOAc/hexanes) to give product **21** as a yellow oil (360.4 mg, 1.52 mmol, 76% yield).

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.58.
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.78 (d, J = 4.7 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 6.7 Hz, 1H), 7.62 (dd, J = 8.4, 6.7 Hz, 1H), 7.48 (dd, J = 8.4, 6.7Hz, 1H), 7.22 (s, 1H), 3.55 (ddd, J = 11.0, 8.0, 5.3 Hz, 1H), 2.13 – 2.20 (m, 2H), 2.14 – 2.05 (m, 1H), 1.93 – 1.96 (m, 1H), 1.91 (d, J = 12.5 Hz, 1H), 1.80 (ddd, J = 12.5, 11.0, 5.3 Hz, 1H), 1.63 (s, 3H), 1.60 (s, 3H) ppm.
^{13}C NMR (151 MHz, $CDCl_3$): δ 153.9, 149.6, 147.4, 129.6, 129.2, 127.1, 126.5, 125.7, 124.8, 123.1, 117.6, 38.9, 35.3, 31.9, 29.2, 19.0, 18.9 ppm.
HRMS (EI/QTOF) m/z: $[M]^{+}$ Calcd for $C_{17}H_{19}N$ 238.1596, found 238.1592.

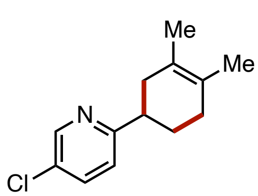
4-(3,4-dimethylcyclohex-3-en-1-yl)-6-fluoroquinoline (22)



4-(3,4-dimethylcyclohex-3-en-1-yl)-6-fluoroquinoline was prepared according to the general Diels-Alder procedure using 6-fluoro-4-vinylquinoline (346 mg, 2 mmol, 1 equiv), $BF_3·OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and 2,3-dimethylbutadiene (456 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on a silica flash column (5% to 15% EtOAc/hexanes) to give product **22** as an analytically pure yellow solid (390.3 mg, 1.62 mmol, 81% yield). Recrystallization from EtOAc provided a white solid (370.4 mg, mp = 68.0-69.5 °C).

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.57.
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.72 (d, J = 4.7 Hz, 1H), 8.08 (dd, J = 9.2, 5.6 Hz, 1H), 7.60 (dd, J = 10.4, 2.8 Hz, 1H), 7.36 (ddd, J = 9.2, 7.9, 2.8 Hz, 1H), 7.19 (d, J = 4.7 Hz, 1H), 3.36 (ddd, J = 10.7, 5.1, 2.8 Hz, 1H), 2.23 – 2.10 (m, 2H), 2.09 – 2.01 (m, 1H), 1.96 – 1.92 (m, 1H), 1.91 – 1.84 (m, 1H), 1.75 (ddd, J = 12.6, 11.0, 5.4 Hz, 1H), 1.59 (s, 3H), 1.57 (s, 3H) ppm.
^{13}C NMR (151 MHz, $CDCl_3$): δ 161.4, 159.7, 153.1, 149.0, 144.5, 132.2, 127.9, 125.7, 124.7, 119.3, 118.1, 106.9, 38.6, 35.5, 31.7, 29.1, 18.9, 18.8 ppm.
HRMS (EI/QTOF) m/z: $[M]^{+}$ Calcd for $C_{16}H_{16}NF$ 242.1346, found 242.1346.

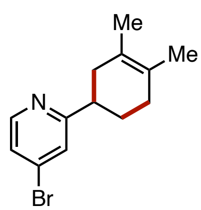
5-chloro-2-(3,4-dimethylcyclohex-3-en-1-yl)pyridine (23)



5-chloro-2-(3,4-dimethylcyclohex-3-en-1-yl)pyridine was prepared according to the general Diels-Alder procedure using 5-chloro-2-vinylpyridine (252 µL, 2 mmol, 1 equiv), $BF_3·OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and 2,3-dimethylbutadiene (456 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on a silica flash column (5% to 15% EtOAc/hexanes) to give product **23** as a colorless oil (380.0 mg, 1.72 mmol, 86% yield).

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.44.
^{1}H NMR (800 MHz, $CDCl_3$): δ 8.51 (d, J = 5.9 Hz, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.15 (dd, J = 7.2, 5.9 Hz, 1H), 2.97 (s, 1H), 2.19 – 2.25 (m, 3H), 2.01 (s, 2H), 1.78 (dd, J = 11.9, 5.9 Hz, 1H), 1.68 (s, 6H) ppm.
^{13}C NMR (201 MHz, $CDCl_3$): δ 164.2, 147.9, 136.1, 129.3, 125.5, 124.8, 122.0, 42.4, 37.9, 31.3, 29.3, 19.1, 18.9 ppm.
HRMS (EI/QTOF) m/z: $[M]^{+}$ Calcd for $C_{13}H_{16}NCl$ 222.1050, found 222.1051.

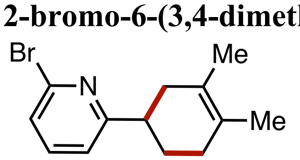
4-bromo-2-(3,4-dimethylcyclohex-3-en-1-yl)pyridine (24)



4-bromo-2-(3,4-dimethylcyclohex-3-en-1-yl)pyridine was prepared according to the general Diels-Alder procedure using 4-bromo-2-vinylpyridine (368 mg, 2 mmol, 1 equiv), $BF_3 \cdot OEt_2$ (132 µL, 1 mmol, 0.5 equiv), and 2,3-dimethylbutadiene (456 µL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on a silica flash column (5% to 15% EtOAc/hexanes) to give product **24** as a colorless oil (418.9 mg, 1.58 mmol, 79% yield).

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.45.
^{1}H NMR (800 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.36 (s, 1H), 7.28 (d, J = 2.6 Hz, 1H), 2.97 – 2.90 (m, 1H), 2.28 – 2.23 (m, 1H), 2.22 – 2.15 (m, 2H), 2.06 – 2.00 (m, 1H), 2.01 – 1.94 (m, 1H), 1.74 – 1.79 (m, 1H), 1.66 (s, 6H) ppm.
^{13}C NMR (201 MHz, $CDCl_3$): δ 167.6, 149.9, 133.1, 125.4, 124.7, 124.6, 124.5, 42.9, 38.0, 32.0, 29.1, 19.1, 18.9 ppm.
HRMS (EI/QTOF) m/z: $[M]^{+}$ Calcd for $C_{13}H_{16}NBr$ 266.0545, found 266.0547.

2-bromo-6-(3,4-dimethylcyclohex-3-en-1-yl)pyridine (25)

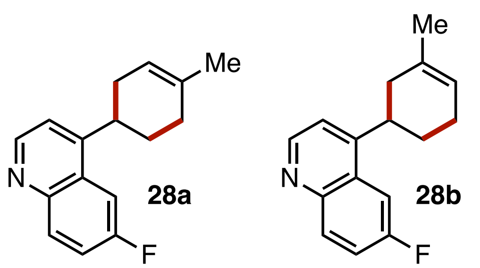


2-bromo-6-(3,4-dimethylcyclohex-3-en-1-yl)pyridine was prepared according to the general Diels-Alder procedure using 2-bromo-6-vinylpyridine (368 mg, 2 mmol, 1 equiv), $BF_3 \cdot OEt_2$ (132 μL, 1 mmol, 0.5 equiv), and 2,3-dimethylbutadiene (456 μL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 48 hr. After workup, the reaction mixture was purified on a silica flash column (2% to 5% EtOAc/hexanes) to give product **25** as a colorless oil (244.7 mg, 0.92 mmol, 46% yield).

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.88. ^{1}**H NMR** (600 MHz, $CDCl_3$):) δ 7.44 (t, J = 7.7 Hz, 1H), 7.28 (dd, J = 7.7, 0.9 Hz, 1H), 7.10 (dd, J = 7.7, 0.9 Hz, 1H), 2.92 (ddd, J = 12.2, 9.5, 6.2 Hz, 1H), 2.25 – 2.17 (m, 2H), 2.12 – 2.14 (m, 1H), 2.01 – 1.91 (m, 2H), 1.78 – 1.69 (m, 1H), 1.63 (s, 6H) ppm. ^{13}**C NMR** (151 MHz, $CDCl_3$): δ 167.8, 141.5, 138.6, 125.4, 125.3, 124.6, 119.7, 42.6, 37.7, 31.8, 29.1, 19.0, 18.9 ppm. **HRMS** (EI/QTOF) m/z: $[M]^{\cdot+}$ Calcd for $C_{13}H_{16}NBr$ 266.0545, found 266.0548.

6-fluoro-4-(4-methylcyclohex-3-en-1-yl)quinoline (28a) and

6-fluoro-4-(3-methylcyclohex-3-en-1-yl)quinoline (28b)



6-fluoro-4-(4-methylcyclohex-3-en-1-yl) quinoline and 6-fluoro-4-(3-methylcyclohex-3-en-1-yl) quinoline were prepared according to the general Diels-Alder procedure using 6-fluoro-4-vinylquinoline (346 mg, 2 mmol, 1 equiv), $BF_3{\cdot}OEt_2$ (132 μL, 1 mmol, 0.5 equiv), and isoprene (398 μL, 4 mmol, 2 equiv) in acetonitrile (4 mL). The resulting mixture was stirred at 70 °C for 24 hr. After workup, the reaction mixture was purified on a silica flash column (5% to 15% EtOAc/hexanes) to give an inseparable mixture of products **29a** and **29b** as a yellow oil (354.8 mg, 1.39 mmol, 70% yield). Regioselectivity determined as 3:1 based on NMR integration of **29a:29b**.

TLC (Vanillin, 25% EtOAc/Hexanes) R_f = 0.53.
^{1}**H NMR** (**28a** and **28b**) 1H NMR (600 MHz, cdcl3) δ 8.77 (dd, J = 5.8, 4.5 Hz, 1H), 8.12 – 8.05 (m, 1H), 7.66 (dd, J = 10.5, 3.0 Hz, 1H), 7.42 (ddd, J = 9.2, 7.9, 3.0 Hz, 1H), 7.25 (d, J = 7.9 Hz, H), 5.54 – 5.46 (m, 1H), 3.52 – 3.36 (m, 1H), 2.36 – 2.40 (m, 1H), 2.24 – 2.08 (m, 2H), 2.01 – 2.04, (m, 1H), 1.99 (s, 1H), 1.86 – 1.92 (m 1H), 1.71 (s, 3H) ppm.
^{13}**C NMR** (**28a** and **28b**) (151 MHz, $CDCl_3$): δ 161.3, 159.7, 152.2, 152.2, 149.6, 149.6, 149.6, 145.4, 134.2, 133.2, 132.8, 132.8, 132.7, 132.7, 127.9, 127.8, 121.1, 120.3, 120.2, 119.1, 119.0, 119.0, 118.9, 118.2, 118.1, 106.8, 106.8, 106.7, 106.6, 37.0, 35.0, 34.6, 32.4, 30.3, 28.9, 28.4, 25.4, 23.5, 23.4 ppm.

HRMS (EI/QTOF) m/z: $[M]^{\cdot+}$ Calcd for $C_{17}H_{16}NF$ 256.1502, found 256.1499.

5. References

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6 Computational details

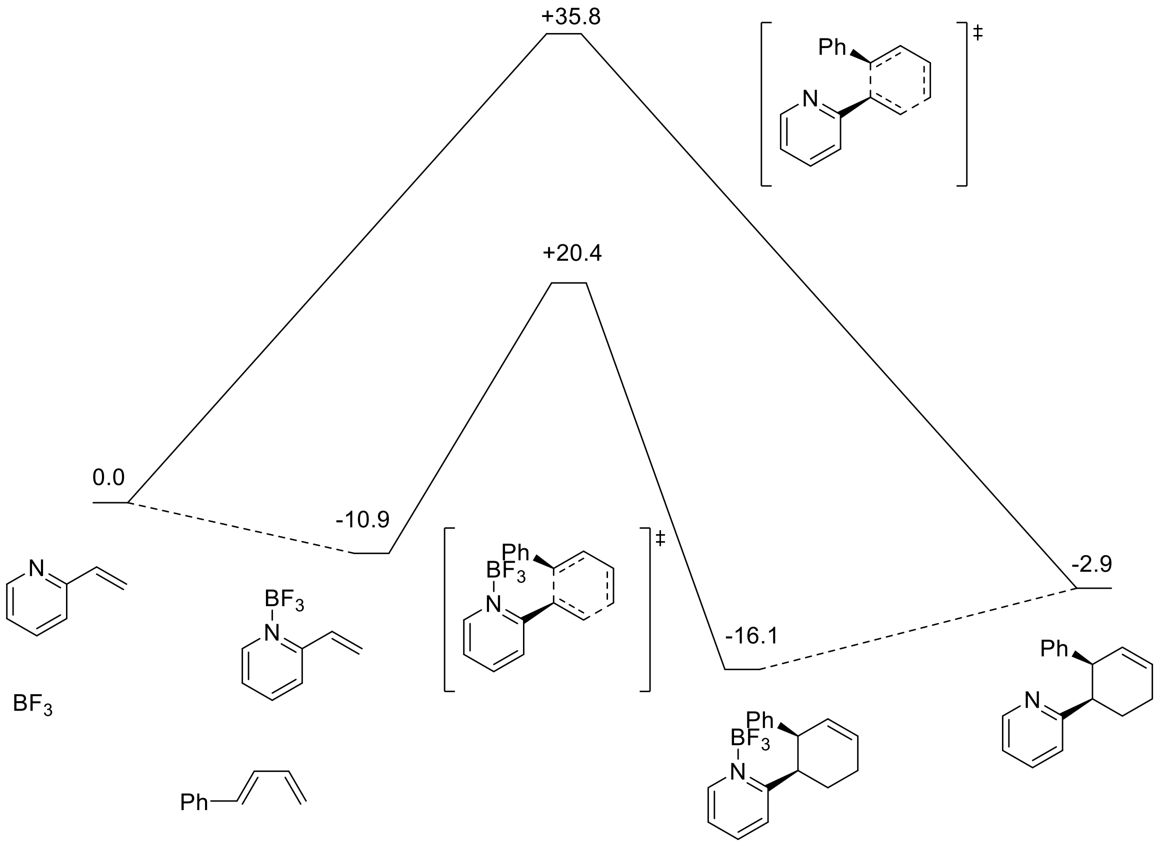


Figure S1: Free energy diagram of endo cycloadditions of 2-vinylpyridine and 1-phenylbutadiene with and without BF_3. Energies in kcal/mol. Solid lines show the transition state connects to reactant and product.

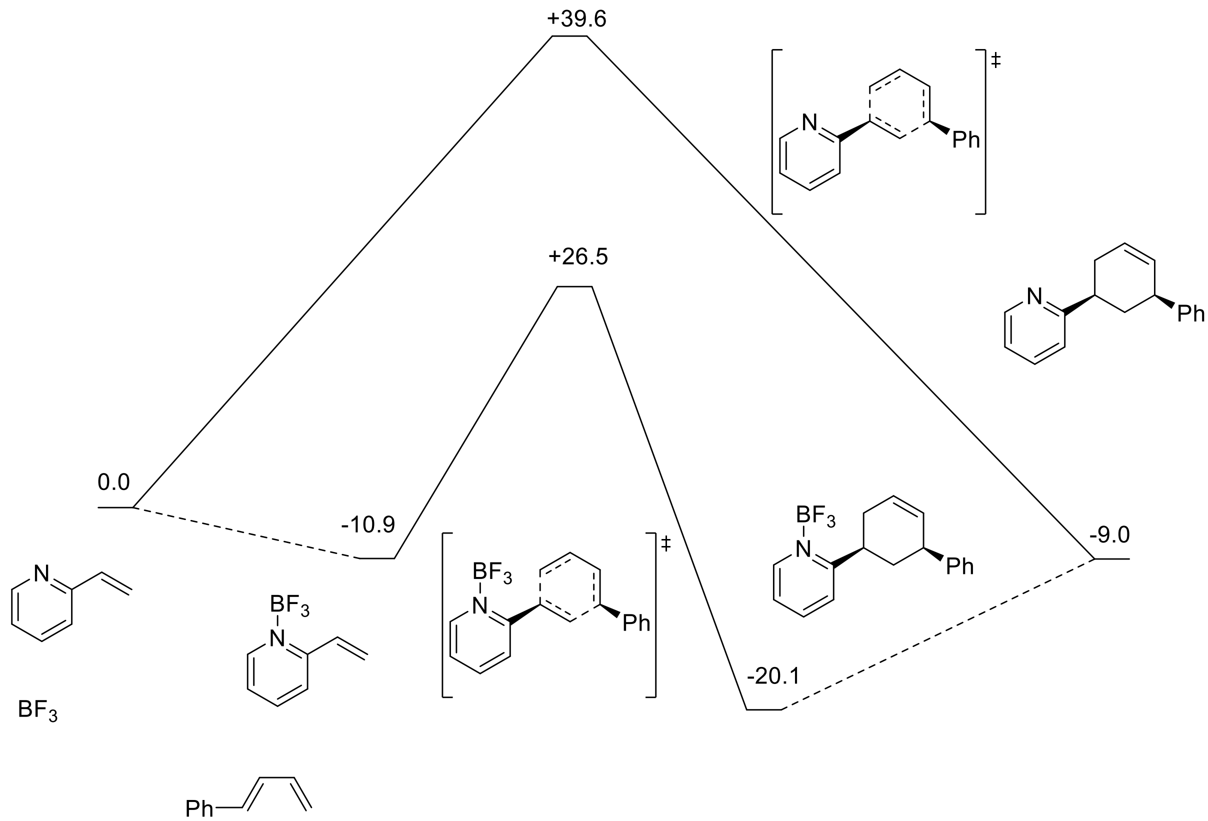


Figure S2: Free energy diagram of endo cycloadditions of 2-vinylpyridine and 1-phenylbutadiene with and without BF_3 to form the minor regioisomer Energies in kcal/mol. Solid lines show the transition state connects to reactant and product.

Table S2. Comparison of transition state values for the regioisomers for cycloaddition.

	Major (kcal/mol)	Minor (kcal/mol)	ΔΔG‡ (kcal/mol)
Thermal	35.8	39.6	3.8
Activated	20.4	26.6	6.2

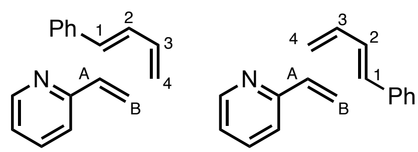
Table S3. Comparison of transition state values for the diastereomers for cycloaddition.

	Endo (kcal/mol)	Exo (kcal/mol)	ΔΔG‡ (kcal/mol)
Thermal - major	35.8	34.6	-1.2
Thermal - minor	39.6	39.1	-0.5
Activated – major	20.4	21.1	0.7
Activated - minor	26.6	26.9	0.3

Table S4. Frontier molecular orbital analysis of 2-vinylpyridine and 1-phenylbutadiene.

	HOMO (Diene)	LUMO (Dienophile)	Difference (eV)
Thermal - major	-6.06	-1.67	4.39
Activated - major		-2.48	3.59

Table S5. NBO-derived partial charges of the transition states of the cycloaddition of 2-vinylpyridine and 1-phenylbutadiene.



	Endo				Exo			
	C_1	C_4	C_A	C_B	C_1	C_4	C_A	C_B
Min	0.01544	0.06908	-0.02673	0.07552	0.01829	0.06934	-0.03087	0.07965
Maj	0.03901	0.05386	0.00629	0.05456	0.04005	0.05802	-0.00850	0.07134
Min-BF_3	0.01910	0.10703	-0.02031	0.09350	0.01584	0.10551	-0.02925	0.09642
Maj-BF_3	0.08334	0.05744	-0.02199	0.09894	0.09012	0.04979	-0.03094	0.09798

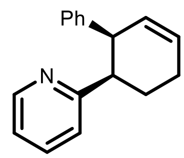
Table S6. Calculated versus experimental regioselectivities for 9 (2-vinylpyridine and isoprene), and 11 (2-vinylpyridine and 1-phenylbutadiene).

Product	ΔΔG(TS) (kcal/mol)	Calculated selectivity (rr)	Experimental selectivity (rr)
9	-1.5	13:1	10:1
11	-6.2	Major only	>20:1

Computational Method

Calculations were carried out with the Gaussian 16 program, Revision B.01. Geometry optimizations were performed with the B3LYP functional with the 6-311+G(d) basis set. The conductor-like polarizable continuum (CPCM) solvation model was used with solvent parameters for acetonitrile. Frequency calculations of the optimized structures were performed at the same level to verify the stationary points as real minima or transition states. Population analyses according to Mulliken and NBO (version 3.1) were performed to derive FMO information and partial charges.

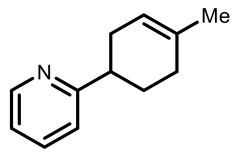
Table S7. Energies for optimized structures for the cycloaddition of 2-vinylpyridine and 1-phenylbutadiene to form **11**.



63%
rr= >20:1
dr= >20:1

Compound	Absolute E (a. u.)	Gibbs' free energy (a. u.)	# imaginary frequencies
2-vinylpyridine	-325.767175	-325.677502	0
BF3	-324.666704	-324.680423	0
1-phenylbutadiene	-387.139124	-387.008111	0
BF3-2-vinylpyridine	-650.474961	-650.375304	0
2-VP TS (endo)	-712.874223	-712.628597	1
BF3-2-VP TS (endo)	-1037.587920	-1037.333586	1
2-VP pdt (endo)	-712.942627	-712.690275	0
BF3-2-VP-pdt (endo)	-1037.655133	-1037.391707	0
2-VP TS (minor; endo)	-712.868485	-712.622459	1
BF3-2-VP TS (minor; endo)	-1037.580038	-1037.323731	1
2-VP pdt (minor; endo)	-712.951612	-712.699963	0
BF3-2-VP pdt (minor; endo)	-1037.659565	-1037.398035	0
2-VP TS (exo)	-712.875764	-712.630427	1
BF3-2-VP TS (exo)	-1037.586692	-1037.332484	1
2-VP pdt (exo)	-712.945533	-712.693183	0
BF3-pdt (exo)	-1037.656907	-1037.394291	0
2-VP TS (minor; exo)	-712.869060	-712.623251	1
BF3-2-VP TS (minor; exo)	-1037.578722	-1037.323084	1
2-VP pdt (minor; exo)	-712.943015	-712.692358	0
BF3-2-VP pdt (minor; exo)	-1037.650941	-1037.390164	0

Table S8. Energies for optimized structures for the cycloaddition of 2-vinylpyridine and isoprene to form **9**.



61%
rr=10:1

Compound	Absolute E (a. u.)	Gibbs' free energy (a. u.)	# imaginary frequencies
2-vinylpyridine	-325.767175	-325.677502	0
BF3	-324.666704	-324.680423	0
isoprene	-195.353371	-195.269670	0
BF3-2-vinylpyridine	-650.474961	-650.375304	0
major	-521.177535	-520.973199	0
minor	-521.177545	-520.973246	0
major TS	-521.085522	-520.889267	1
minor TS	-521.084394	-520.888015	1
major-act	-845.886001	-845.671690	0
minor-act	-845.885954	-845.671667	0
major-act-TS	-845.799251	-845.593249	1
minor-act-TS	-845.797098	-845.590797	1

Full Gaussian Reference

Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

Optimized Coordinates

2-vinylpyridine

C	-1.04971200	1.32396700	0.30113100
C	0.32160600	1.43143300	0.48746700
C	0.96305400	2.64548700	0.19356100
C	-1.04408200	3.59395900	-0.44027200
C	-1.75647500	2.42811700	-0.17432400
H	-1.56083700	0.39325200	0.52323900
H	0.88738000	0.58426700	0.85647400
H	-1.55622000	4.47769300	-0.81179800
H	-2.82769500	2.38942900	-0.33482700
N	0.27634400	3.71187900	-0.26559600
C	2.41293100	2.85624800	0.35771900
H	2.73975200	3.85738900	0.08825500
C	3.31534500	1.96787900	0.78630500
H	3.06035900	0.95219200	1.07077000
H	4.36234600	2.23808700	0.86669300

BF3

B	0.03229000	1.02505700	0.04027500
F	-0.62698000	2.16703200	0.04027500
F	-0.62698000	-0.11691800	0.04027500
F	1.35091000	1.02505700	0.04027500

1-phenylbutadiene

C	-2.87098400	-0.78445600	-0.38993200
H	-2.46560700	-1.54253400	-1.05342900
H	-3.94589600	-0.64240100	-0.41636700
C	-2.09880500	-0.06355100	0.43557400
H	-2.58711900	0.63999700	1.10787700
C	-0.64180300	-0.13403400	0.56258800
H	-0.24593000	0.22005900	1.51165500
C	0.20941900	-0.55897400	-0.39151500
H	-0.20417700	-0.84579400	-1.35667300
C	1.66937900	-0.66275100	-0.29841500
C	2.39496600	-1.02827400	-1.44679200
C	2.39254800	-0.41835500	0.88512900
C	3.78367500	-1.13933700	-1.42091100
H	1.85932900	-1.22591600	-2.37069900
C	3.77837600	-0.52754800	0.91096900
H	1.87060300	-0.14581400	1.79592800
C	4.48324000	-0.88802100	-0.24137400
H	4.31798600	-1.42254100	-2.32205600
H	4.31362100	-0.33471800	1.83524500
H	5.56447500	-0.97413200	-0.21605000

BF3-2-vinylpyridine

C	-0.98803400	1.31786900	0.19220500
C	0.39114000	1.39504600	0.30832500
C	1.05085800	2.62240500	0.19557000
C	-1.02452100	3.67223400	-0.17277000
C	-1.71254600	2.48091500	-0.05597400
H	-1.48924800	0.36094400	0.27994800
H	0.97528300	0.49855200	0.46434200
H	-1.53011100	4.60627000	-0.36489100
H	-2.78906500	2.47255800	-0.16462900
N	0.31892700	3.74971600	-0.05069800
C	2.51420700	2.72027800	0.30840900
H	2.98630500	3.55038000	-0.19993200
C	3.27139900	1.85935500	0.99463400
H	2.86339600	1.02886400	1.56048900
H	4.34804500	1.98029700	1.02458500
B	1.00808600	5.21599600	-0.17914400
F	-0.01118700	6.15477100	-0.32767700
F	1.73442000	5.45203600	0.98793700
F	1.83732800	5.20703400	-1.30474200

2-VP TS (endo)

C	-7.27942200	3.37605000	-2.04019500
C	-7.69703700	4.54614800	-2.67504500
C	-7.00179500	5.72167400	-2.39024900
C	-5.93285500	5.67917800	-1.50694000
C	-5.57509400	4.45220400	-0.90224800
N	-6.26348100	3.31254000	-1.17970300
H	-7.28690800	6.65934100	-2.85670600
H	-7.79433600	2.43811700	-2.23686600
H	-8.53234000	4.53061000	-3.36563300
H	-5.37765700	6.58211800	-1.28553200
C	-4.46670500	4.33196400	0.01775900
H	-4.32599700	3.34844600	0.45142700
C	-3.49259700	5.32260900	0.22361700
H	-3.40478700	6.10617500	-0.52139400
H	-2.52703600	4.97054000	0.57318200
C	-6.09050100	4.73329000	2.27326800
H	-5.12097900	4.35713600	2.57624200
C	-6.21819300	6.07744900	1.98690300
H	-7.20903900	6.49236300	1.82516800
C	-5.12605000	6.93019700	1.76268900
H	-5.33382900	7.93051800	1.39274300
C	-3.79644300	6.47872200	1.77191700
H	-3.51961800	5.72399900	2.50042600
H	-3.01680400	7.21945300	1.62135300
C	-7.17754400	3.76986400	2.38642800
C	-6.89981700	2.48301900	2.89131300
C	-8.50727800	4.05172400	2.01090000
C	-7.90142600	1.52721600	3.02877800
H	-5.88203200	2.23801600	3.18075600
C	-9.50838100	3.09674600	2.15101900
H	-8.76286700	5.02233200	1.60086600
C	-9.21373000	1.82931300	2.66064300
H	-7.65883300	0.54562500	3.42318000
H	-10.52451300	3.33906400	1.85630800
H	-9.99726300	1.08618600	2.76544100

BF3-2-VP TS (endo)

C	-2.10351300	1.71660800	0.05241100
C	-1.32685000	1.76397600	-1.08249000
C	-1.69135600	2.66208000	-2.09552700
C	-2.78957900	3.47300200	-1.91748000
C	-3.55021200	3.43257400	-0.72067700
N	-3.18634900	2.50787100	0.24389000
H	-1.11638300	2.72047000	-3.01313000
H	-1.89045700	1.02594700	0.85427300
H	-0.47282200	1.10649300	-1.17739400
H	-3.07408500	4.16717800	-2.69501300
C	-4.66092000	4.30056900	-0.51001400
H	-5.10967200	4.32389500	0.47153900
C	-5.24508400	5.08122000	-1.52439200
H	-6.27442400	5.37383800	-1.34264900
H	-5.07419800	4.80143900	-2.55765200
C	-2.62729000	6.45442000	0.55633700
C	-2.29855000	6.68793400	-0.75706300
H	-1.25627700	6.63758900	-1.05736400
C	-3.23525500	6.92923400	-1.78295300
H	-2.84824800	7.00357100	-2.79566100
C	-4.62611300	6.91672200	-1.61068300
H	-5.22631900	7.25450400	-2.44954100
H	-5.02837700	7.22305500	-0.65128800
B	-4.08087100	2.24489500	1.55125900
F	-5.36290500	1.85798500	1.13288500
F	-3.48682100	1.21363000	2.29069400
F	-4.14567600	3.40839200	2.32702700
H	-3.65751000	6.59003800	0.86736600
C	-1.70103000	6.13290200	1.63056700
C	-2.17369000	6.13871800	2.95861900
C	-0.34177300	5.82181700	1.41496500

C	-1.32651200	5.86201000	4.02612300
H	-3.21832700	6.36469400	3.14668300
C	0.50254300	5.54306400	2.48227300
H	0.05738000	5.78912200	0.40766200
C	0.01661600	5.56288400	3.79321900
H	-1.71354500	5.87640500	5.03962700
H	1.54425800	5.30459100	2.29427700
H	0.67945200	5.34290300	4.62342300

2-VP pdt (endo)

C	-1.11409100	2.97392700	2.16855200
C	-0.53122900	1.83746500	1.61469200
C	-1.18600000	1.22474600	0.54957900
C	-2.38156400	1.77174700	0.09524600
C	-2.90062400	2.91902000	0.71243700
N	-2.26317000	3.50743700	1.73851600
H	-0.77446200	0.33677100	0.08084900
H	-0.63450100	3.48343900	3.00115600
H	0.40276700	1.45090900	2.00673700
H	-2.91246200	1.31462400	-0.73267800
C	-4.19461500	3.52658300	0.19646900
H	-4.49733800	2.90039600	-0.64812000
C	-4.01347800	4.96182100	-0.35262100
H	-4.91557500	5.20686600	-0.92518700
H	-3.18213600	4.98142300	-1.06450500
C	-5.40015700	3.50506200	1.19982000
C	-5.41973500	4.70785300	2.11941700
H	-6.07590200	4.63964700	2.98479400
C	-4.73801100	5.83337200	1.89988300
H	-4.83413200	6.65868300	2.60302800
C	-3.81207200	6.02724600	0.73263200
H	-2.77736100	6.01606900	1.09442100
H	-3.96592700	7.02264700	0.29863200
H	-6.28922200	3.59231300	0.55930700
C	-5.54743700	2.17503800	1.92651300
C	-6.25994500	1.12991600	1.32368300
C	-4.97955200	1.94533500	3.18588400
C	-6.39577800	-0.10821200	1.95135500
H	-6.71930800	1.28832700	0.35155500
C	-5.11557800	0.71004200	3.82046600
H	-4.42305100	2.73811100	3.67380600
C	-5.82270100	-0.32319600	3.20521300
H	-6.95510700	-0.90115500	1.46461100
H	-4.66871900	0.55572300	4.79783600
H	-5.93056400	-1.28342700	3.69941500

BF3-2-VP-pdt (endo)

C	-3.57580200	0.83289300	0.65032400
C	-2.34134900	0.42420000	0.18881800
C	-1.56269200	1.33876900	-0.51207500
C	-2.05102500	2.62186200	-0.71295500
C	-3.30209700	3.00273600	-0.22658700
N	-4.05156100	2.08453100	0.45094200
H	-0.58895500	1.05883100	-0.89731200
H	-4.22873400	0.16639800	1.19218400
H	-2.01030600	-0.58932000	0.37438100
H	-1.45688100	3.34561700	-1.25216500
C	-3.82464800	4.40562000	-0.44909700
H	-4.90269200	4.38762400	-0.30272200
C	-3.58938100	4.90561900	-1.88955100
H	-3.89481300	4.13954300	-2.60764300
H	-2.52634000	5.09281300	-2.06435100
C	-3.29201100	5.44818400	0.60272800
C	-3.78020400	6.82899200	0.22049700
H	-3.71564000	7.58305900	1.00197400
C	-4.27124900	7.15748800	-0.97585800
H	-4.62407000	8.17285200	-1.14394100
C	-4.38064600	6.19689700	-2.12923300
H	-4.03384100	6.68129700	-3.04888900
H	-5.43928300	5.96219000	-2.30648400
B	-5.54760400	2.39785800	1.01067200
F	-6.37088300	2.66302800	-0.08780600
F	-5.99578500	1.26541700	1.69127700
F	-5.48048500	3.48987200	1.87641400
H	-3.77199600	5.18490800	1.54942400
C	-1.78735300	5.42413700	0.86372300
C	-1.28399000	4.70022100	1.95335100
C	-0.87627400	6.11493600	0.05409700
C	0.08386800	4.65254000	2.21897000
H	-1.97213100	4.16970800	2.60527400
C	0.49432700	6.06538900	0.31177200
H	-1.23866500	6.71189900	-0.77557600
C	0.98041900	5.33260500	1.39434200
H	0.44805100	4.08784000	3.07139800
H	1.18128200	6.60825600	-0.32984700
H	2.04564700	5.29942200	1.59893300

2-VP TS (minor; endo)

C	-4.62811200	5.68229600	-3.07952000
C	-5.04121800	4.60295100	-3.85446600
C	-5.02194700	3.33566300	-3.26833300
C	-4.60253600	3.21164200	-1.95244500
C	-4.20058200	4.35781600	-1.23992000
N	-4.21212800	5.57762000	-1.81193900
H	-5.32978500	2.46031400	-3.83112400
H	-4.62503400	6.68582500	-3.49886300
H	-5.36107200	4.75066300	-4.87960400
H	-4.58287100	2.24116100	-1.46762300
C	-3.74178800	4.23764900	0.15481900
H	-3.63556200	3.21980400	0.51353900
C	-2.97110200	5.23352000	0.76783900
H	-2.68478500	6.09609600	0.18116000
H	-2.26344300	4.93414800	1.53165000
C	-5.76178000	4.29168700	1.21225100
H	-6.34851800	3.52335500	0.71985200
H	-5.20543600	3.94944700	2.07493200
C	-6.10490000	5.62648000	1.06308300
H	-6.91558300	5.88445900	0.38680000
C	-5.29085500	6.66008100	1.53115700
H	-5.51736900	7.67263000	1.20920100
C	-4.08408000	6.40853100	2.19717900
H	-4.05709200	5.53665900	2.84201700
C	-3.15892300	7.48198500	2.61786800
C	-2.37517200	7.31153300	3.77098200
C	-3.00686900	8.67302100	1.88746200
C	-1.49001500	8.30126800	4.19435400
H	-2.46803700	6.39450300	4.34585900
C	-2.12376100	9.66365500	2.30983000
H	-3.57432100	8.82412300	0.97494700
C	-1.36195600	9.48451400	3.46652000
H	-0.90073500	8.14793700	5.09287900
H	-2.02384400	10.57593600	1.73018400
H	-0.67211400	10.25617000	3.79218700

BF3-2-VP TS (minor; endo)

C	-7.13925900	2.81881600	-2.04501100
C	-7.84917200	3.98578000	-2.21777400
C	-7.37335600	5.14542900	-1.59988000
C	-6.22510200	5.08137700	-0.83604500
C	-5.53356300	3.86713500	-0.66163000
N	-6.01139100	2.74735700	-1.29717800
H	-7.89827500	6.08716000	-1.71438500
H	-7.44543200	1.89403900	-2.50966700
H	-8.74382200	3.98503100	-2.82632900
H	-5.85411300	5.96993600	-0.34576900
C	-4.34870300	3.78738600	0.17546300
H	-3.89454600	2.81666700	0.28799000
C	-3.55234600	4.91475600	0.45031800
H	-3.73999600	5.84249800	-0.07540300
H	-2.49979100	4.72565900	0.62435000

C	-5.50074600	3.36807500	2.22799100
H	-6.16536000	2.53515700	2.03200500
H	-4.49852300	3.09138000	2.52474300
C	-6.00715000	4.63125000	2.46279600
H	-7.08216600	4.77966700	2.41142100
C	-5.19459600	5.76698800	2.52706600
H	-5.67902400	6.73895900	2.54337500
C	-3.80063700	5.70030200	2.35803300
B	-5.24820500	1.32575500	-1.23544700
F	-5.21654600	0.88327000	0.09155100
F	-3.95353200	1.50140400	-1.73784200
F	-5.95520000	0.41755800	-2.02874000
C	-2.94240100	6.90925000	2.39098500
C	-3.37000500	8.14640100	1.88245900
C	-1.64647100	6.82300900	2.92267400
C	-2.53780900	9.26235600	1.92749000
H	-4.35619100	8.24021400	1.43916300
C	-0.81241400	7.93877900	2.96822400
H	-1.29216700	5.87288700	3.31194300
C	-1.25587600	9.16471200	2.47223200
H	-2.88823900	10.20949800	1.53004800
H	0.18322800	7.84972500	3.39070900
H	-0.60803400	10.03449400	2.50383200
H	-3.31437800	4.81926900	2.76469900

2-VP pdt (minor; endo)

C	-3.58741600	0.39504800	-0.54003100
C	-2.57205100	0.26337800	-1.48457900
C	-1.92714800	1.41957300	-1.91520500
C	-2.32293000	2.64473000	-1.38589300
C	-3.35389600	2.68554000	-0.44013100
N	-3.97517900	1.56769900	-0.02680200
H	-1.13051000	1.36971000	-2.65025200
H	-4.11594400	-0.48339800	-0.17794000
H	-2.30088600	-0.71419000	-1.86678400
H	-1.83985800	3.56346000	-1.70077700
C	-3.80704100	3.99906600	0.16617600
H	-3.21496700	4.79648900	-0.29790200
C	-3.54785300	4.04644500	1.68484600
H	-2.50606800	3.78958400	1.90129500
H	-4.16960900	3.29112200	2.17563200
C	-5.29373900	4.28552300	-0.12292100
H	-5.43193400	4.49096600	-1.19107800
H	-5.88762800	3.38672800	0.08439300
C	-5.81752600	5.44256700	0.68653500
H	-6.76548200	5.87343500	0.37005900
C	-5.18605500	5.96015500	1.74250900
H	-5.61919600	6.81172600	2.26302500
C	-3.86549000	5.43972700	2.27180300
H	-3.07849400	6.13033500	1.93769200
C	-3.80969000	5.41853400	3.79308200
C	-2.69551600	5.92593200	4.47126700
C	-4.85128600	4.86573900	4.55058800
C	-2.61840100	5.88208300	5.86454900
H	-1.87852700	6.36267700	3.90349100
C	-4.78000700	4.81998800	5.94222500
H	-5.72894500	4.47087700	4.04734400
C	-3.66154600	5.32816200	6.60566300
H	-1.74501700	6.28364400	6.36892500
H	-5.59913600	4.38923600	6.50972800
H	-3.60617000	5.29482300	7.68900000

BF3-2-VP pdt (minor; endo)

C	-3.92439000	0.91005800	-1.28551700
C	-3.81131900	-0.21411200	-0.49432900
C	-3.86299400	-0.05888800	0.88794800
C	-4.02619500	1.21391300	1.41401900
C	-4.13697800	2.32871600	0.58145700
N	-4.08321400	2.15171700	-0.76837500
H	-3.77734400	-0.91591500	1.54594000
H	-3.89183300	0.85430700	-2.36263800
H	-3.68583000	-1.18381500	-0.95798200
H	-4.06742700	1.35349000	2.48619100
C	-4.30504400	3.70853800	1.18120600
H	-4.34751400	4.44061300	0.37953200
C	-3.10419800	4.08386900	2.07831200
H	-2.16511600	3.93650300	1.53788100
H	-3.07277800	3.43078900	2.95617100
C	-5.62435700	3.82850700	1.97605900
H	-6.47245500	3.79094300	1.28406100
H	-5.75728500	2.97305500	2.65025100
C	-5.67262400	5.10751700	2.77064600
H	-6.64739400	5.40781500	3.14850000
C	-4.60915700	5.87485100	3.01625100
H	-4.73310100	6.79765000	3.57836400
C	-3.20690900	5.55347600	2.54285900
B	-4.20296700	3.38556700	-1.82075600
F	-3.14167900	4.26290300	-1.58459400
F	-5.43845400	4.00659600	-1.62352700
F	-4.12201700	2.85820100	-3.10949000
H	-2.99419300	6.19264300	1.67506300
C	-2.14662800	5.86826600	3.58958400
C	-0.98627900	6.56663600	3.23718700
C	-2.28996800	5.44535900	4.91779000
C	0.00609400	6.83542700	4.18141100
H	-0.85760400	6.90689900	2.21347500
C	-1.30196400	5.71151700	5.86478800
H	-3.18482400	4.90729800	5.21638900
C	-0.14844300	6.40794500	5.49962200
H	0.89692000	7.38103700	3.88642400
H	-1.43362500	5.37713100	6.88912700
H	0.62001800	6.61760800	6.23664700

2-VP TS (exo)

C	-1.76236800	1.79917700	1.32277300
C	-2.11278200	0.73481000	0.49303300
C	-2.95966900	1.00105500	-0.58492000
C	-3.41075500	2.29680100	-0.78143200
C	-2.99602100	3.32303300	0.09723100
N	-2.17639600	3.05540800	1.14579400
H	-3.26373800	0.20673600	-1.25899100
H	-1.10929000	1.63021000	2.17630500
H	-1.73520600	-0.26235600	0.68786100
H	-4.07184000	2.53379900	-1.60771000
C	-3.43469200	4.68691800	-0.10816300
H	-4.12662800	4.85408500	-0.92508900
C	-2.91386100	5.78443700	0.59088100
H	-3.04562300	6.76179900	0.14157500
H	-1.94521600	5.64365900	1.05982900
C	-5.93762000	4.36285600	1.19440500
H	-5.13605600	3.84199600	1.70417100
C	-6.10077800	5.71187900	1.43425500
H	-7.00422600	6.20358300	1.08264400
C	-5.11601000	6.52963500	2.01180000
H	-5.31359900	7.59805000	2.04467000
C	-3.81449900	6.09228200	2.29920700
H	-3.65615500	5.07982300	2.65674500
H	-3.14555200	6.81175100	2.76265200
C	-6.85721000	3.50488500	0.45927600
C	-6.72753200	2.10541700	0.56993500
C	-7.88027400	4.00439800	-0.37494600
C	-7.59071100	1.24394200	-0.10258200
H	-5.94565000	1.69585000	1.20125500
C	-8.74102900	3.14331900	-1.04457600
H	-7.99547000	5.07421900	-0.51044900
C	-8.60399700	1.75762300	-0.91167000
H	-7.47182700	0.17058000	0.00556900
H	-9.51999700	3.55176600	-1.68057200
H	-9.27697800	1.08904000	-1.43825600

BF3-2-VP TS (exo)

C	-3.11307200	1.12157900	1.13826800
C	-1.76273900	1.07822300	0.88126300
C	-1.23084600	2.01709000	-0.01419500
C	-2.06265200	2.95501800	-0.58240300
C	-3.44614700	2.99934800	-0.27645500
N	-3.94533000	2.03697400	0.58359900
H	-0.17395300	2.01108900	-0.25653900
H	-3.58598700	0.40926600	1.79718900
H	-1.14779600	0.32583900	1.35701300
H	-1.65493000	3.68558400	-1.26732800
C	-4.30976200	3.99788000	-0.82014000
H	-5.30153300	4.08032300	-0.40378400
C	-3.97578600	4.82906900	-1.90611000
H	-4.81278400	5.27690500	-2.42807000
H	-3.19939300	4.49384800	-2.58746100
C	-3.73383000	6.03327200	1.44763700
H	-2.87879100	5.48262000	1.07219200
C	-4.26599700	7.02978100	0.66391800
H	-5.05138700	7.66008100	1.07029200
C	-3.90833800	7.25770500	-0.67952400
H	-4.47388800	8.01641400	-1.21413300
C	-3.03001000	6.45998700	-1.42334400
H	-2.20085000	5.98152900	-0.91204200
H	-2.76732900	6.81805700	-2.41374500
C	-4.11832000	5.70403800	2.81075300
C	-3.32122600	4.79708200	3.53795800
C	-5.24870400	6.25270700	3.45194100
C	-3.63011500	4.45970400	4.85159800
H	-2.44952900	4.35916700	3.06165600
C	-5.55570900	5.91447900	4.76358200
H	-5.89767500	6.93946600	2.92048400
C	-4.74879300	5.01788800	5.47121000
H	-2.99959900	3.76149400	5.39205200
H	-6.43066400	6.34626100	5.23828300
H	-4.99427400	4.75537000	6.49481200
B	-5.52138500	1.87334300	0.86032700
F	-6.16059000	1.66259900	-0.36959800
F	-5.70674500	0.76214700	1.69317800
F	-6.01702700	3.02274800	1.48588500

2-VP pdt (exo)

C	-1.98638900	1.87962900	2.34562300
C	-0.98391300	1.40323200	1.50912800
C	-1.11845100	1.62436400	0.13859800
C	-2.23484000	2.31011300	-0.32154200
C	-3.19705100	2.76355700	0.59488700
N	-3.06800300	2.54158200	1.90952400
H	-0.36889300	1.26321400	-0.55795200
H	-1.92596900	1.72281800	3.41973700
H	-0.13190300	0.87180500	1.91769200
H	-2.37008500	2.48904400	-1.38312900
C	-4.41209300	3.52431500	0.07362600
H	-4.74179300	2.98682200	-0.82144300
C	-4.02821500	4.95435600	-0.37639100
H	-4.88202800	5.38256500	-0.91217600
H	-3.20287700	4.91239000	-1.09289100
C	-5.60901800	3.56104700	1.07209600
H	-5.53434600	2.65890400	1.68824100
C	-5.54170200	4.73827000	2.01746600
H	-6.25606300	4.72598600	2.83870600
C	-4.67771700	5.74963800	1.91441400
H	-4.68426300	6.53653100	2.66617300
C	-3.66794900	5.85972800	0.80477200
H	-2.66959400	5.60984100	1.19044600
H	-3.59565200	6.89978800	0.46712500
C	-6.94669300	3.47257700	0.33795800
C	-7.48246800	2.21375400	0.02964900
C	-7.65661100	4.60800300	-0.06997300
C	-8.68211200	2.09101700	-0.66943300
H	-6.95340700	1.31818700	0.34429700
C	-8.85856600	4.49095200	-0.77136600
H	-7.27308300	5.59401500	0.17000300
C	-9.37594000	3.23251400	-1.07517700
H	-9.07793300	1.10507800	-0.89265800
H	-9.39180700	5.38605300	-1.07656700
H	-10.31183200	3.14077800	-1.61695200

BF3-2-VP-pdt (exo)

C	-3.68006300	0.74081700	0.31299800
C	-2.32666500	0.48908900	0.40114800
C	-1.44894100	1.56525900	0.32308800
C	-1.96702500	2.84446000	0.18333100
C	-3.34368500	3.06397200	0.12032100
N	-4.18313600	1.98979300	0.16888900
H	-0.37694900	1.41258100	0.37091000
H	-4.40899500	-0.05386500	0.34856800
H	-1.97842700	-0.52886400	0.51766500
H	-1.29466600	3.68876100	0.11781500
C	-3.89081800	4.46591200	-0.06191600
H	-4.96494000	4.44882300	0.10864200
C	-3.65311600	4.94182000	-1.51631300
H	-4.00394300	4.18037600	-2.21634400
H	-2.57717000	5.06116600	-1.68534200
C	-3.28932200	5.49548800	0.94516500
H	-2.19565300	5.43686100	0.89933000
C	-3.67511200	6.90685100	0.53923200
H	-3.53327700	7.67011700	1.30062500
C	-4.16154500	7.24899800	-0.65481600
H	-4.42368300	8.28789600	-0.84296400
C	-4.36652700	6.27087600	-1.77842000
H	-4.00454000	6.70492000	-2.71728200
H	-5.44137700	6.10280600	-1.93082900
C	-3.68485600	5.20528000	2.38911900
C	-2.74691200	4.70702400	3.30030400
C	-4.98941700	5.44137000	2.84185200
C	-3.10118500	4.44007400	4.62425100
H	-1.72533300	4.53062100	2.97689400
C	-5.34797800	5.17796900	4.16234100
H	-5.73263600	5.83805600	2.15726500
C	-4.40451600	4.67358600	5.05949900
H	-2.35655000	4.05482400	5.31365100
H	-6.36435600	5.36851600	4.49244600
H	-4.68279200	4.46976700	6.08845400
B	-5.80034100	2.11622400	0.01186400
F	-6.06573100	2.75807800	-1.19946500
F	-6.32835500	0.82411700	0.00311000
F	-6.29731900	2.83796300	1.09613800

2-VP TS (minor; exo)

C	-2.18950100	1.72442700	1.41181900
C	-2.42539100	0.69214500	0.50772100
C	-3.08151100	1.00662200	-0.68293900
C	-3.46467900	2.32074900	-0.91243900
C	-3.17634100	3.30470800	0.05083200
N	-2.54806200	2.99571300	1.20330100
H	-3.29019400	0.23792400	-1.41993100
H	-1.68647500	1.52087600	2.35425800
H	-2.10761600	-0.31959800	0.73196900
H	-3.97850700	2.59590400	-1.82745000
C	-3.56506300	4.70622500	-0.17920500
H	-4.05371800	4.89758800	-1.12676600
C	-2.90715500	5.76927800	0.45253300
H	-2.88053400	6.72950600	-0.04629000
H	-2.04390800	5.54315200	1.06574200
C	-5.64017100	4.56824500	0.81419200
H	-6.20081100	3.89263600	0.17657600
H	-5.08166700	4.08664700	1.60555400
C	-6.01062600	5.89929400	0.91084300

H	-6.83189900	6.26098400	0.29667400
C	-5.22282700	6.84501600	1.57205900
H	-5.49180600	7.89265200	1.46925500
C	-3.98773800	6.51327500	2.14614500
H	-3.89223800	5.52276000	2.57877600
C	-3.10124200	7.51940700	2.77006700
C	-2.28299200	7.14897300	3.85011000
C	-3.02045700	8.84312000	2.30540000
C	-1.43364200	8.06986800	4.46033400
H	-2.32057100	6.12813800	4.21932700
C	-2.17211500	9.76495200	2.91425500
H	-3.61652200	9.15557900	1.45420400
C	-1.37588700	9.38443400	3.99638500
H	-0.81693000	7.76047300	5.29820000
H	-2.12701100	10.78227000	2.53846600
H	-0.71371000	10.10322300	4.46780300

BF3-2-VP TS (minor; exo)

C	-4.17295200	0.67074400	0.30069900
C	-3.01563000	0.38078600	0.98685800
C	-2.26698600	1.44500300	1.49690300
C	-2.71496500	2.73673700	1.30681400
C	-3.91026200	3.00082800	0.61099400
N	-4.61731000	1.93702100	0.10729300
H	-1.34686200	1.26330500	2.04068200
H	-4.78766900	-0.10536400	-0.12877500
H	-2.70910500	-0.64918100	1.11279200
H	-2.14677300	3.56508800	1.70741100
C	-4.40726500	4.35708600	0.44128500
H	-5.36596500	4.46419600	-0.03651200
C	-3.55517200	5.47733600	0.45188100
H	-3.87102200	6.33591700	-0.12626400
H	-2.48182200	5.32797600	0.44653600
C	-5.56568700	4.45676400	2.54241600
H	-6.35464700	3.71906400	2.45761800
H	-4.62431800	4.08521000	2.92339500
C	-5.86530600	5.80414300	2.55721700
H	-6.90432700	6.10914600	2.46246100
C	-4.88394900	6.79486300	2.45750000
H	-5.21285400	7.82261200	2.33446400
C	-3.52522600	6.49130300	2.26983000
H	-3.15553000	5.60069100	2.76907200
C	-2.49426800	7.54499600	2.11416800
C	-1.20126400	7.32751500	2.61537000
C	-2.75439700	8.75624500	1.45296000
C	-0.20716700	8.29524600	2.48366400
H	-0.97555300	6.39324900	3.12139400
C	-1.76141900	9.72396600	1.31977000
H	-3.73566800	8.94492700	1.02977000
C	-0.48385400	9.49944800	1.83611200
H	0.78307900	8.10805800	2.88631200
H	-1.98387700	10.65350800	0.80567600
H	0.28893300	10.25353000	1.72941900
B	-5.95771800	2.12626400	-0.77681100
F	-5.64257600	2.92006700	-1.88484400
F	-6.94164100	2.72928100	0.01348700
F	-6.38390500	0.86192500	-1.19333200

2-VP pdt (minor; exo)

C	-2.60831500	1.03826400	1.05295300
C	-2.35493300	0.40126500	-0.15992300
C	-2.59014100	1.11345400	-1.33271400
C	-3.06528700	2.41891100	-1.24090700
C	-3.29188300	2.98172400	0.02020000
N	-3.06236300	2.29227200	1.15058300
H	-2.40626600	0.66229500	-2.30228000
H	-2.43702400	0.51720600	1.99172400
H	-1.98460200	-0.61741600	-0.17839600
H	-3.25887500	2.99959700	-2.13639900
C	-3.82802800	4.39348100	0.16270100
H	-3.90719700	4.81169700	-0.84447700
C	-2.87226000	5.31022400	0.98032800
H	-2.31401400	5.93820800	0.28115300
H	-2.13494600	4.70513900	1.51221900
C	-5.27260100	4.38186300	0.73205300
H	-5.93358300	3.84803900	0.04406100
H	-5.27773300	3.81439900	1.67176300
C	-5.75221400	5.78851200	0.96674500
H	-6.75317700	6.06934000	0.65013900
C	-4.94122300	6.67403100	1.54940000
H	-5.25908000	7.69699800	1.73140600
C	-3.57425400	6.23344700	2.02793300
H	-3.73730600	5.61505400	2.92081400
C	-2.66532400	7.37741500	2.43863600
C	-1.99469700	7.35313300	3.66666900
C	-2.45441900	8.47375200	1.59081200
C	-1.13831000	8.39037000	4.04101600
H	-2.14563800	6.51433300	4.34055400
C	-1.60235500	9.51344500	1.96020900
H	-2.96227500	8.51702400	0.63146100
C	-0.93948000	9.47550600	3.18847500
H	-0.63050300	8.35051400	4.99962900
H	-1.45601700	10.35430500	1.28936300
H	-0.27657900	10.28475700	3.47732900

BF3-2-VP pdt (minor; exo)

C	-3.74542200	0.84350900	-0.63191400
C	-2.82647900	0.20296400	0.17221100
C	-2.32759100	0.88307100	1.28018000
C	-2.77208600	2.17189600	1.53119100
C	-3.70715200	2.78719600	0.69634800
N	-4.17991900	2.10225400	-0.38184600
H	-1.60306000	0.41653100	1.93762100
H	-4.16566500	0.37051900	-1.50598800
H	-2.51304600	-0.80380800	-0.07125400
H	-2.39219600	2.71896100	2.38436000
C	-4.19329600	4.18704100	1.00691900
H	-4.91174100	4.48249800	0.25107200
C	-3.03116500	5.22581300	0.96363100
H	-3.05563700	5.71200900	-0.01405400
H	-2.05813000	4.73391500	1.03129500
C	-4.97806500	4.21684500	2.34968500
H	-5.84695400	3.55910500	2.27680300
H	-4.35601200	3.82205200	3.16314600
C	-5.39024400	5.63266400	2.65140800
H	-6.40497900	5.82642000	2.98704700
C	-4.51518700	6.62656600	2.48960900
H	-4.78931000	7.65698200	2.69724200
C	-3.09068700	6.31930600	2.07904900
H	-2.59883100	5.88655100	2.96021300
C	-2.28621200	7.54284100	1.67815700
C	-1.02165300	7.77789800	2.22878800
C	-2.77819800	8.45279900	0.73234700
C	-0.26625300	8.88874200	1.84844100
H	-0.62296800	7.08635200	2.96580100
C	-2.02917200	9.56475500	0.35069600
H	-3.75738000	8.29300000	0.28986900
C	-0.76819400	9.78677600	0.90756900
H	0.71170100	9.05216400	2.29017700
H	-2.42998500	10.25885300	-0.38134300
H	-0.18457800	10.65245200	0.61146900
B	-5.26323100	2.73445100	-1.41620800
F	-4.70791400	3.88764900	-1.97581300
F	-6.43134500	3.01821400	-0.70438600
F	-5.51454900	1.78443400	-2.40638500

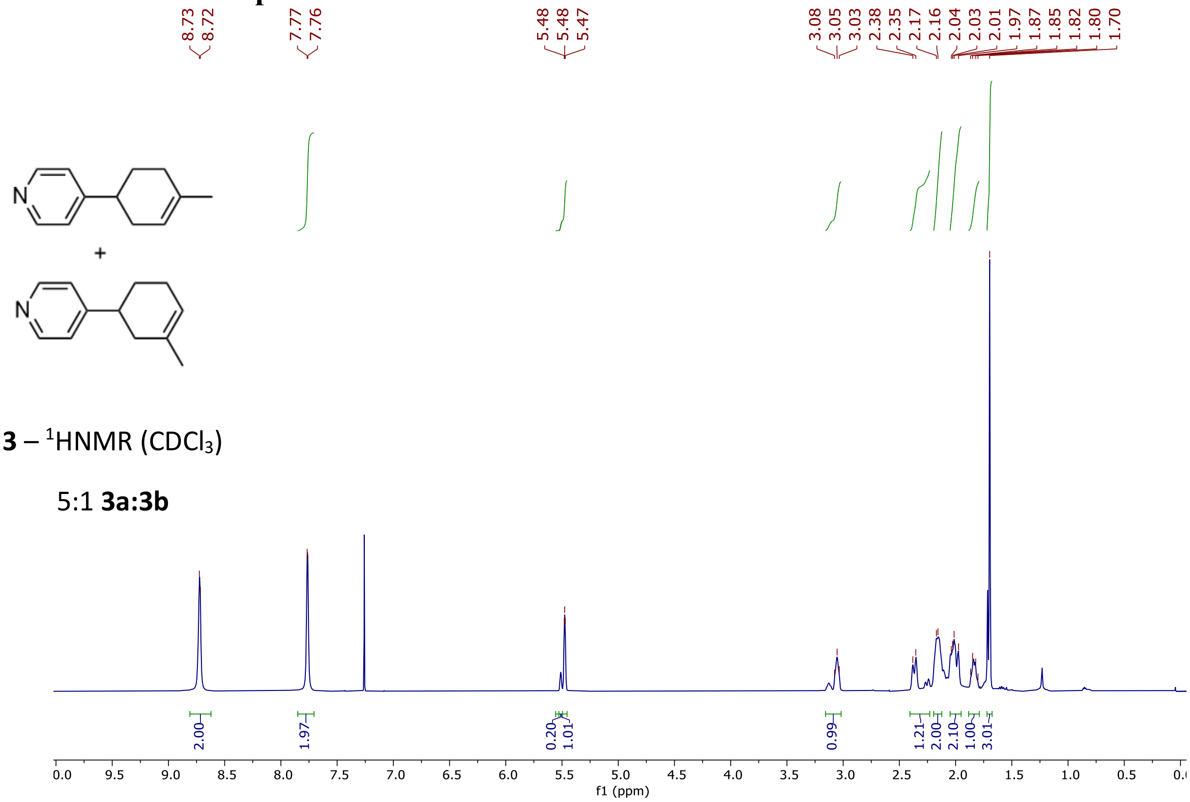
9-major-act-TS

C	-0.50716900	0.38856300	0.63451200
C	0.84591900	0.59477000	0.50174400
C	1.28105400	1.85333900	0.06625200
C	0.35199500	2.83564400	-0.19600600
C	-1.03457600	2.60404800	-0.03159800
N	-1.43206300	1.34605100	0.37515500
H	2.33828600	2.05865300	-0.05979300
H	-0.90617300	-0.56378700	0.94906300
H	1.53748300	-0.20664000	0.72542500
H	0.68409600	3.81116100	-0.52341900
C	-2.00530500	3.63657700	-0.26000100
H	-3.03045600	3.41914200	-0.01105100
C	-1.73393900	4.81689500	-0.98508400
H	-0.86350100	4.83363500	-1.63339300
H	-2.59297000	5.29868100	-1.43821800
C	-1.92445800	4.58589500	2.26540200
H	-2.34777600	3.85954300	2.94898300
H	-0.89851900	4.41380200	1.97349300
C	-2.58752400	5.74550000	1.98175000
C	-2.20145200	6.64787200	0.95952800
C	-1.11897400	6.33461600	0.12270100
H	-0.84461600	7.06083900	-0.63670400
H	-0.26294700	5.82047800	0.54598100
B	-2.98207000	0.93355600	0.50105600
F	-3.59935400	1.14199900	-0.73942900
F	-3.58828900	1.70750800	1.49803600
F	-3.04826100	-0.42228700	0.84549100
H	-3.54831500	5.91887900	2.46192500
C	-3.13295100	7.77080300	0.59031000
H	-2.59541700	8.62996700	0.18429400
H	-3.84741200	7.44453800	-0.17777800
H	-3.71953200	8.10237200	1.44967200

9-minor-act-TS

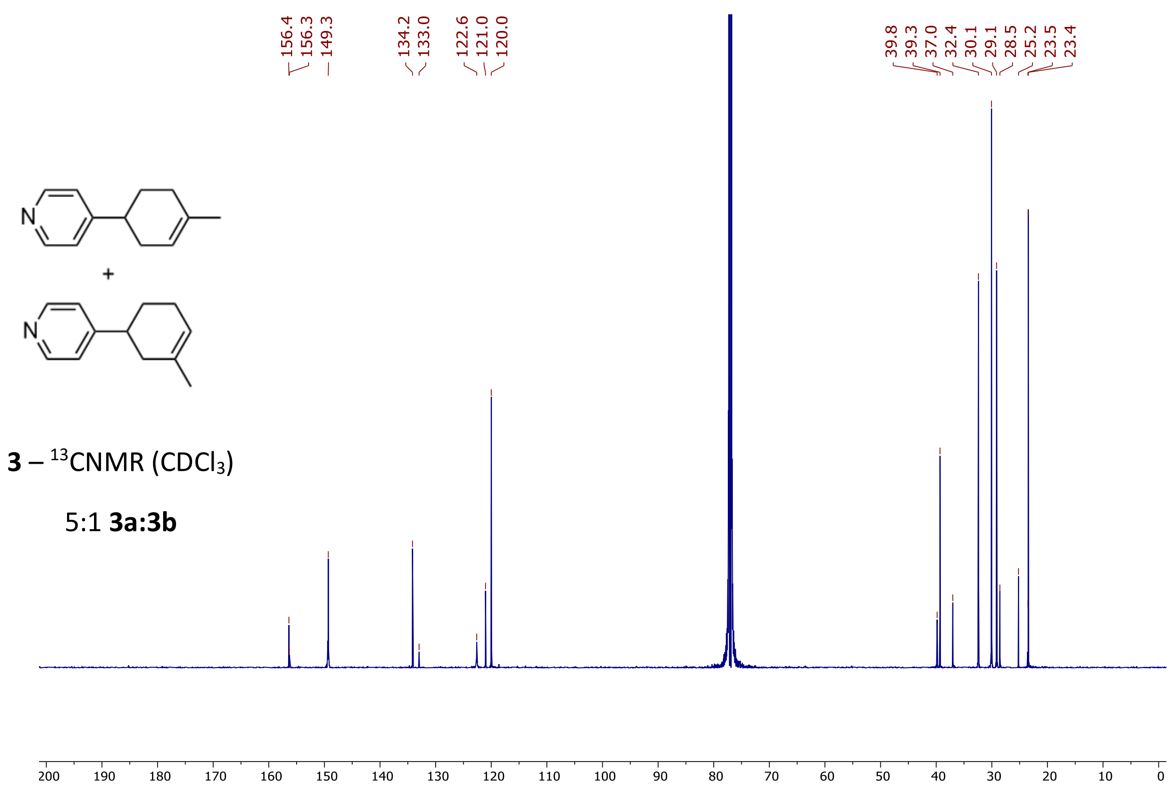
C	-0.50528400	0.40064700	0.64510500
C	0.84842600	0.61372500	0.52300800
C	1.28084600	1.87090700	0.08440100
C	0.34808900	2.84733200	-0.19120500
C	-1.03640700	2.60895600	-0.03446300
N	-1.43177400	1.35232500	0.37381700
H	2.33788200	2.08074200	-0.03503200
H	-0.90205400	-0.55258200	0.95970900
H	1.54197100	-0.18320100	0.75635400
H	0.67775500	3.82188500	-0.52370900
C	-2.01392500	3.63610000	-0.27681600
H	-3.03745000	3.41641800	-0.02256100
C	-1.74809900	4.81026900	-1.00526300
H	-0.87461200	4.83572100	-1.64900900
H	-2.60665500	5.29448800	-1.45346200
C	-1.93702000	4.58234300	2.26700600
H	-2.33485500	3.83386200	2.94259500
H	-0.91031600	4.44176500	1.96267700
C	-2.62889800	5.73353000	2.00047400
C	-2.18878900	6.61010500	0.97642200
C	-1.13120600	6.31960700	0.11285500
H	-0.88512000	7.05918300	-0.64261900
H	-0.26119400	5.79695400	0.49674500
B	-2.98303800	0.93077600	0.48406000
F	-3.58521500	1.13462700	-0.76394900
F	-3.60308800	1.70323500	1.47250200
F	-3.04344900	-0.42437300	0.82963100
H	-2.84714300	7.43425400	0.70960400
C	-3.96291300	6.01208600	2.65954300
H	-4.77395900	6.04578000	1.92555000
H	-4.21023700	5.25269200	3.40301200
H	-3.94996600	6.98213900	3.16580900

7. NMR Spectra



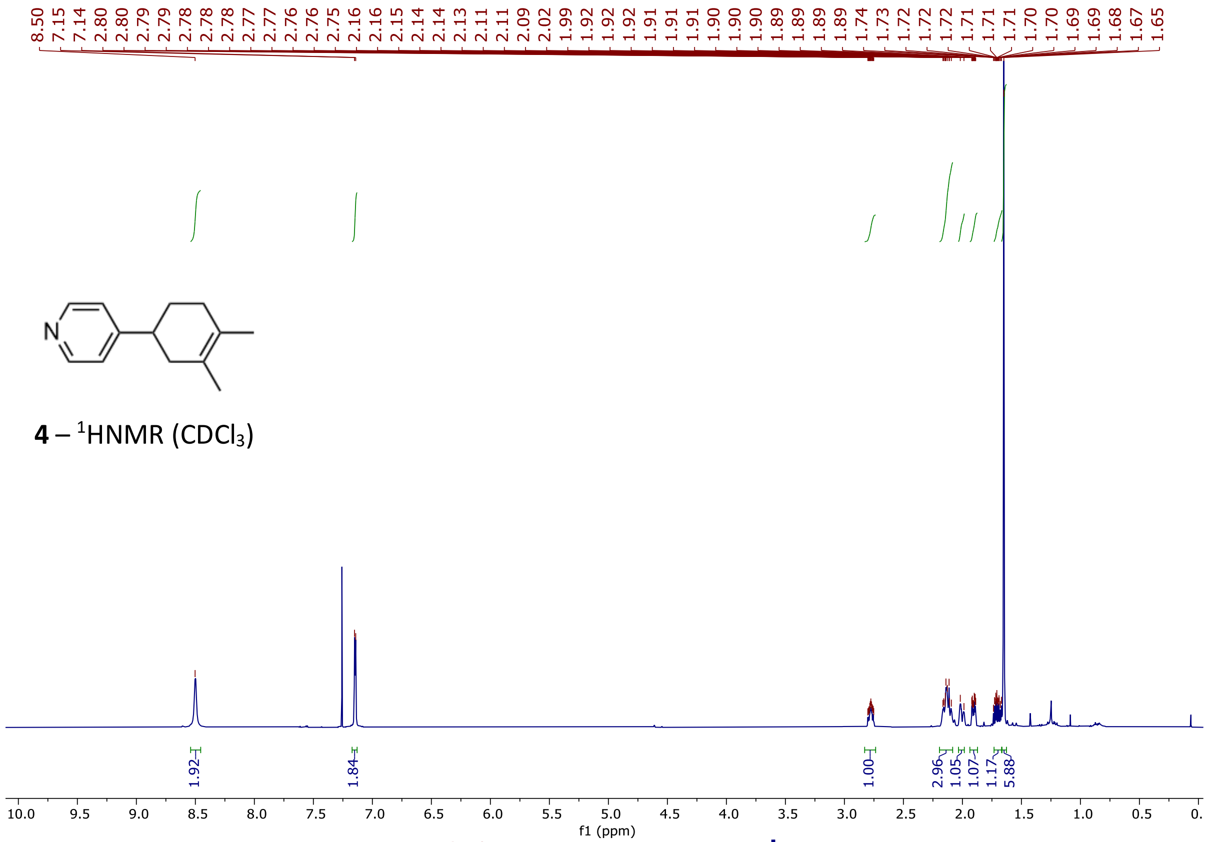
3 – [1]HNMR ($CDCl_3$)

5:1 **3a:3b**

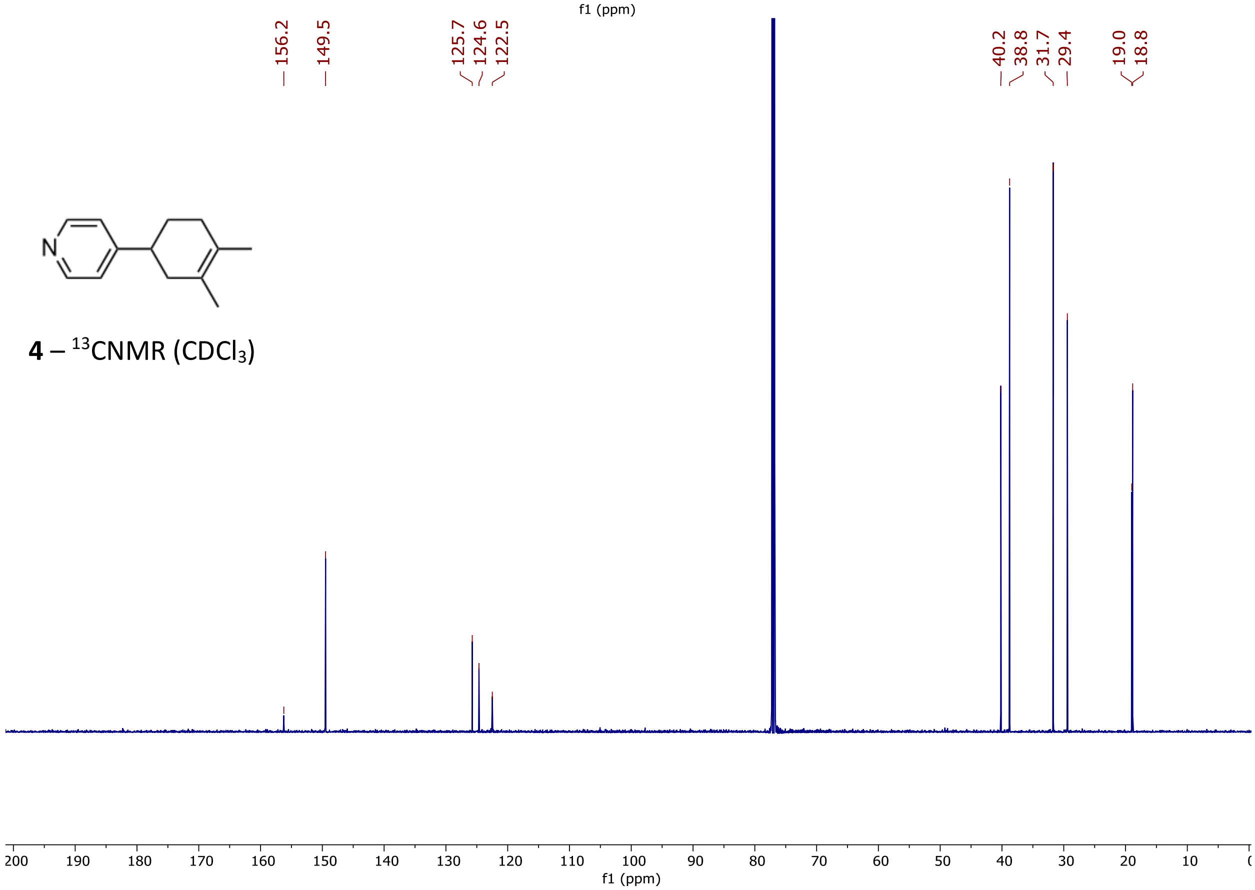


3 – [13]CNMR ($CDCl_3$)

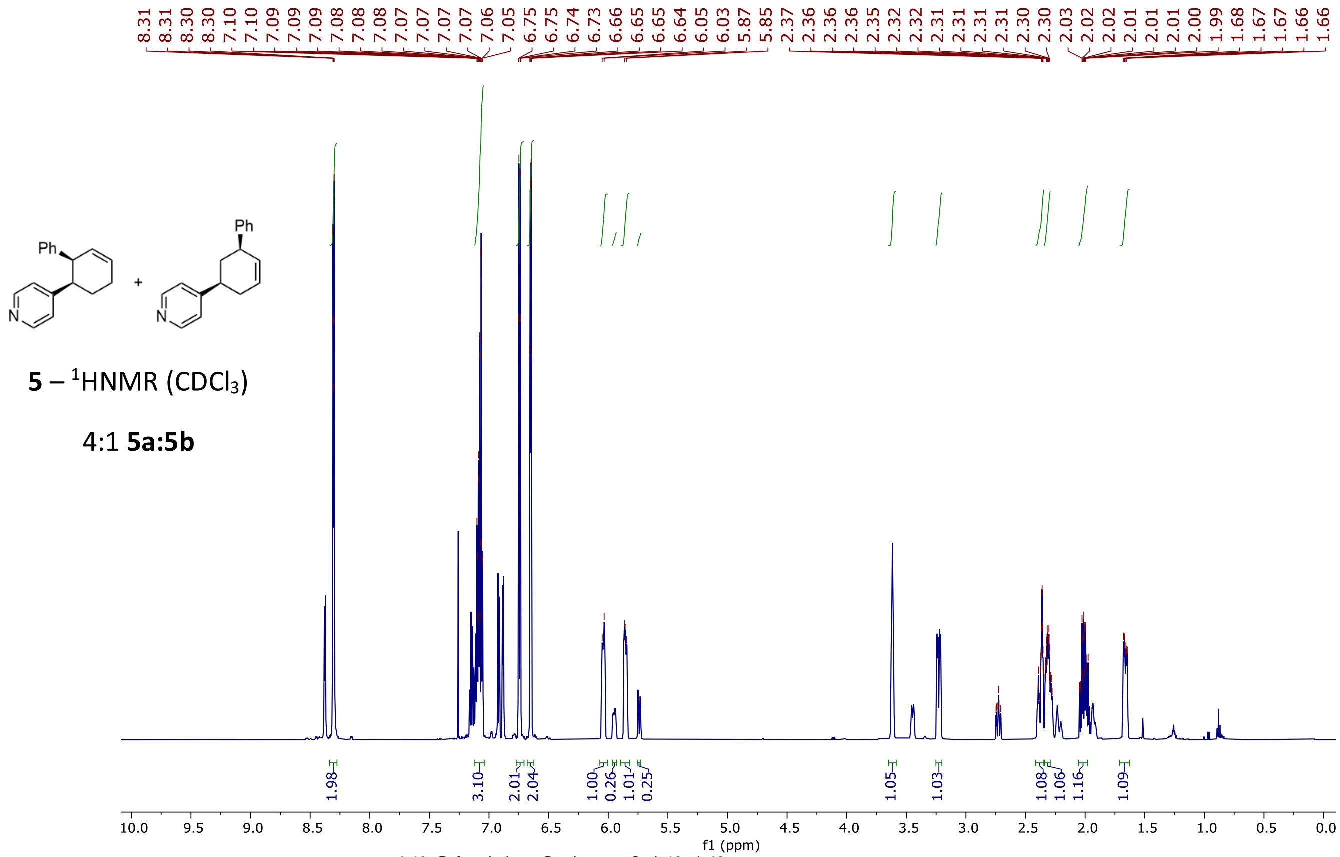
5:1 **3a:3b**



4 – ^{1}HNMR ($CDCl_3$)

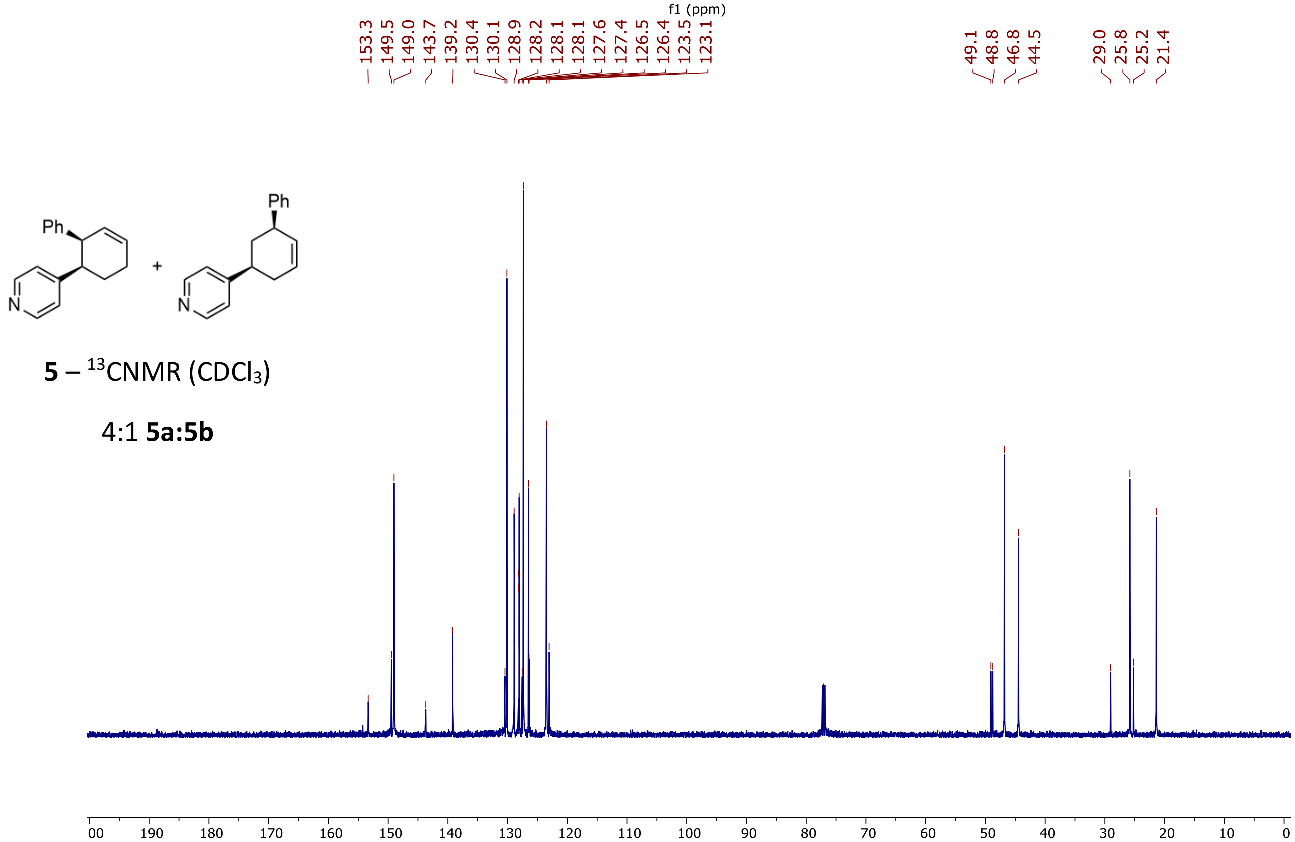


4 – ^{13}CNMR ($CDCl_3$)



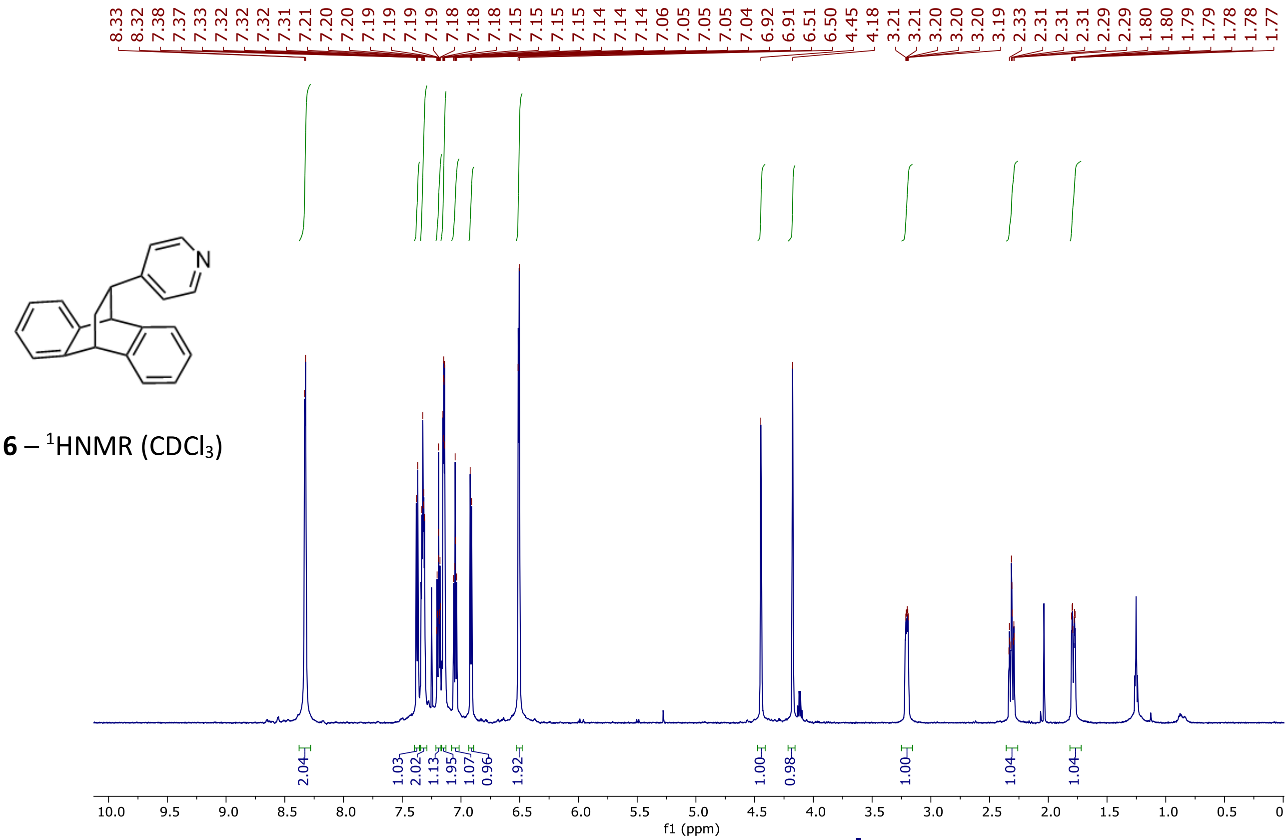
5 – ¹HNMR ($CDCl_3$)

4:1 **5a:5b**

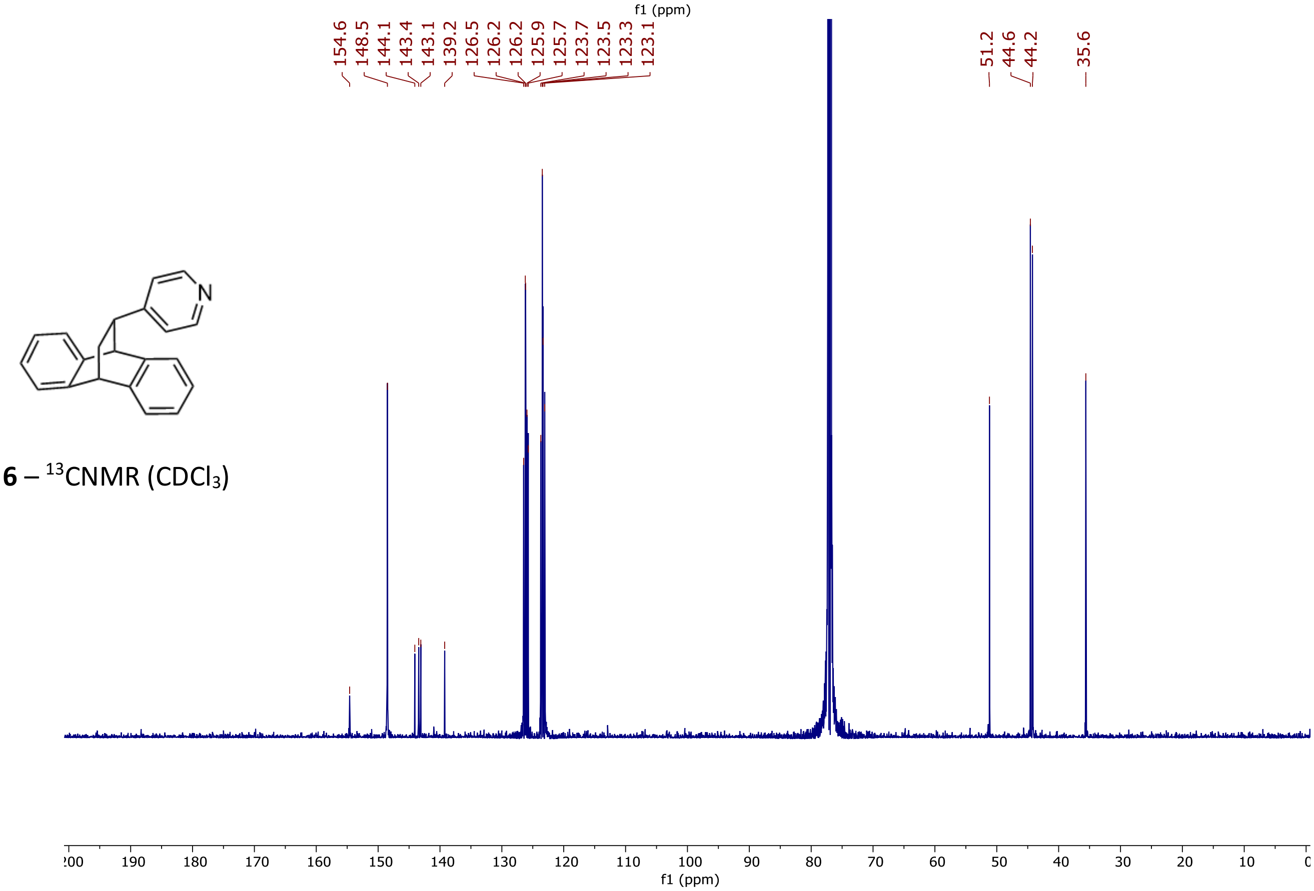


5 – ¹³CNMR ($CDCl_3$)

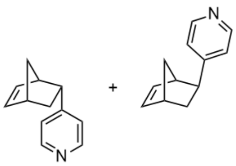
4:1 **5a:5b**



6 – [1]HNMR ($CDCl_3$)

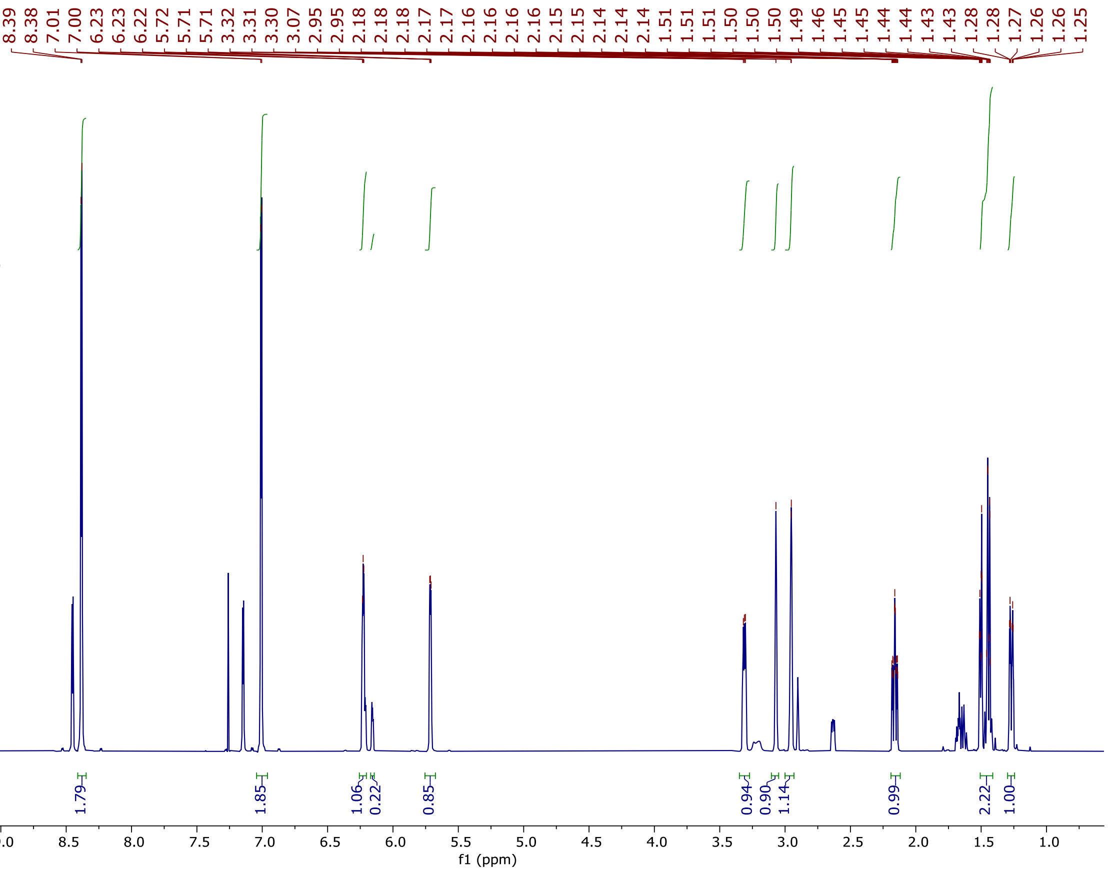


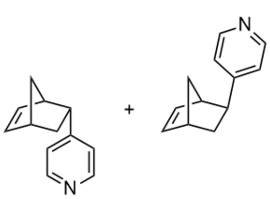
6 – [13]CNMR ($CDCl_3$)



7 – [1]HNMR ($CDCl_3$)

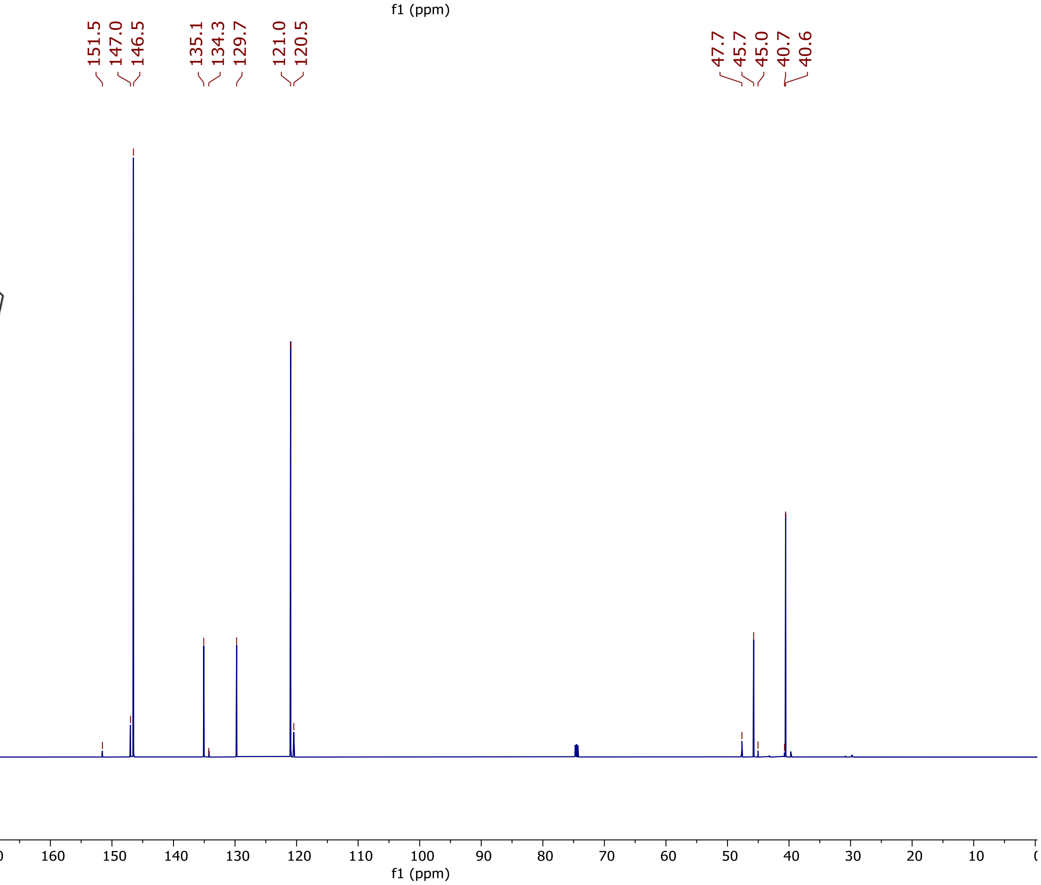
4:1 **7a:7b**

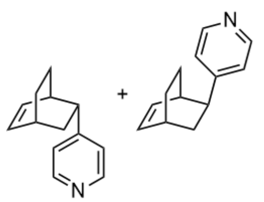




7 – [13]CNMR ($CDCl_3$)

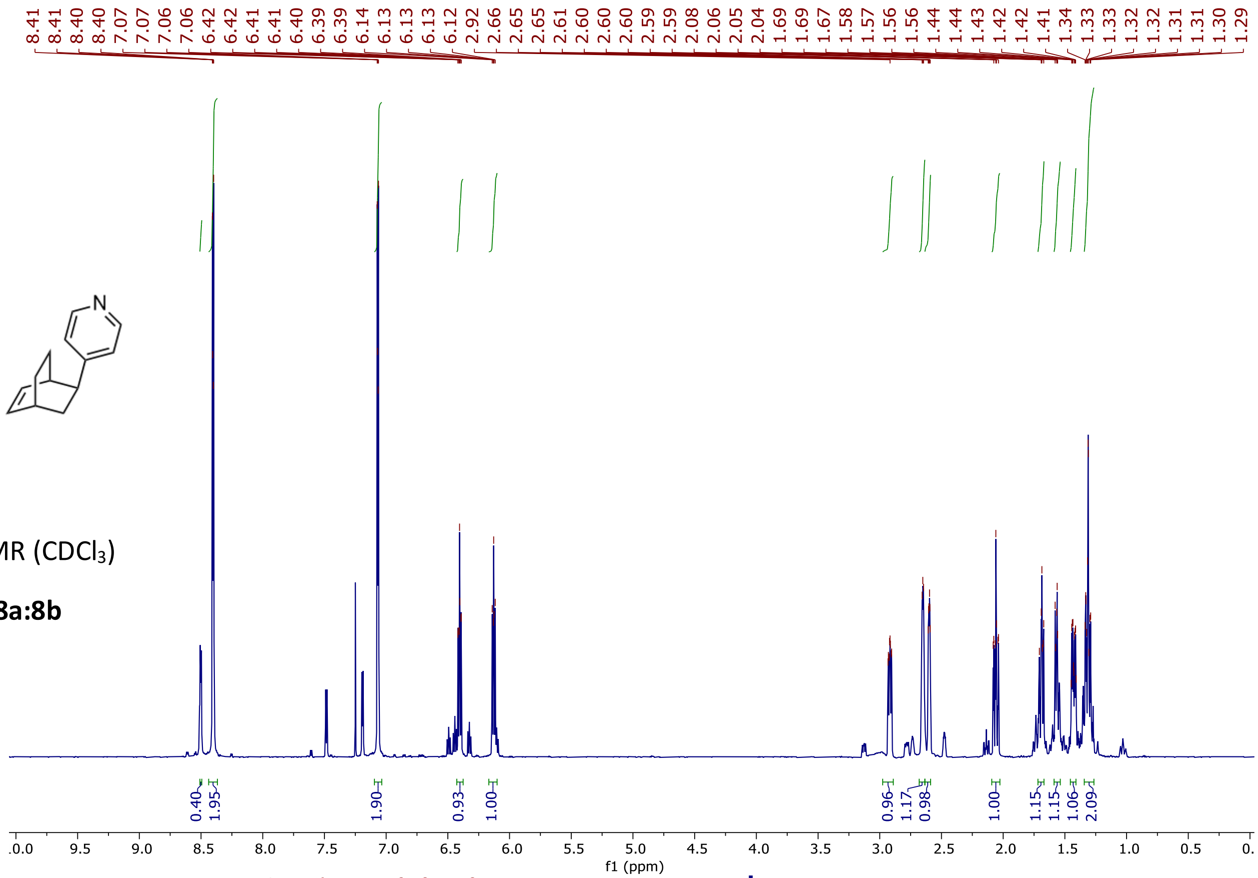
4:1 **7a:7b**

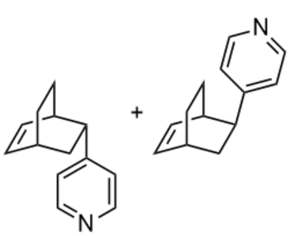




8 – ^{1}HNMR ($CDCl_3$)

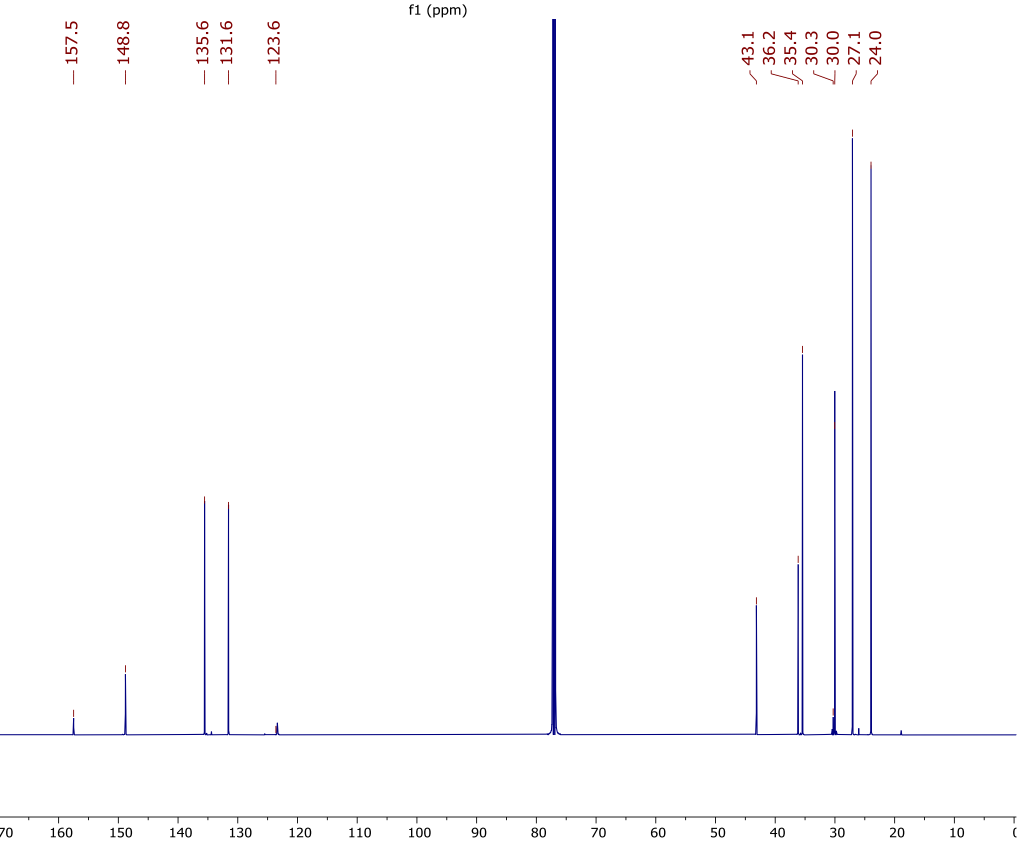
5:1 **8a:8b**

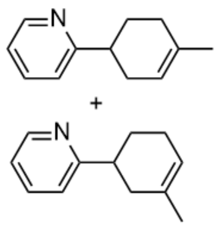




8 – ^{13}CNMR ($CDCl_3$)

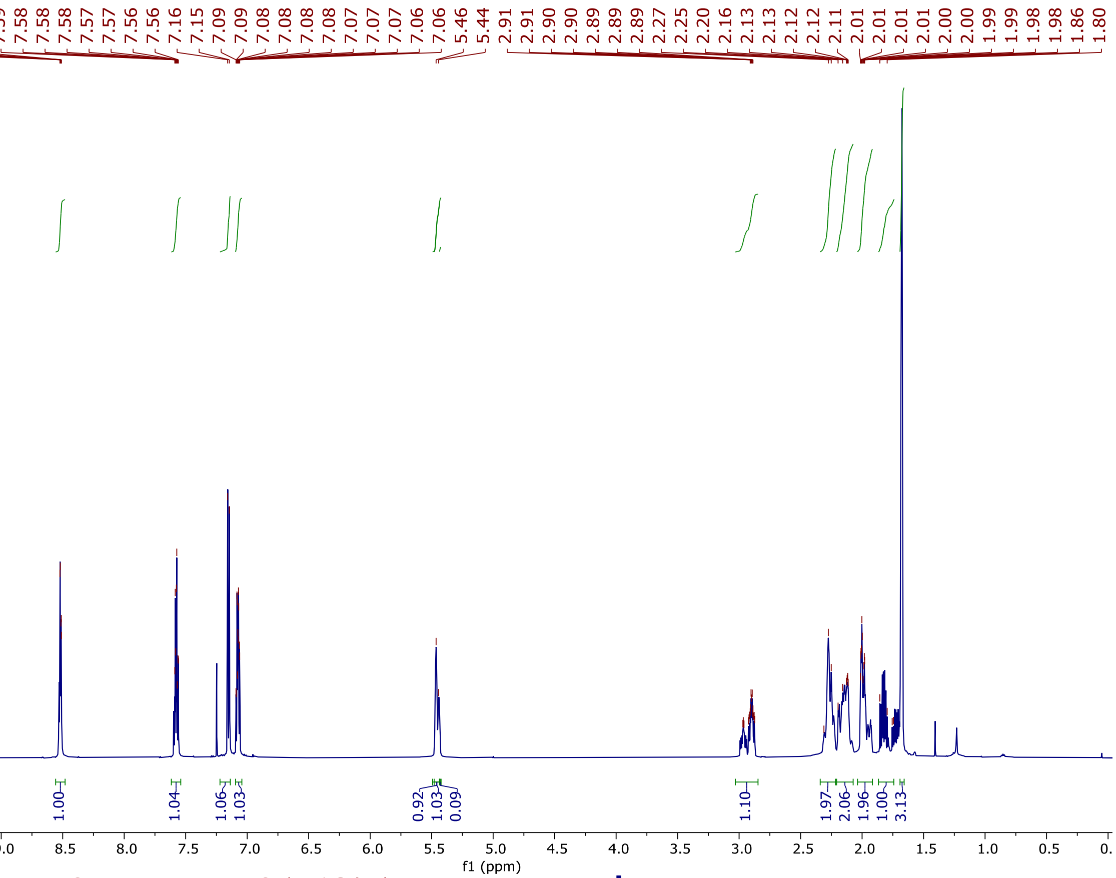
5:1 **8a:8b**

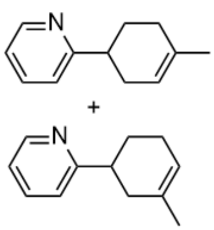




9 – ¹HNMR ($CDCl_3$)

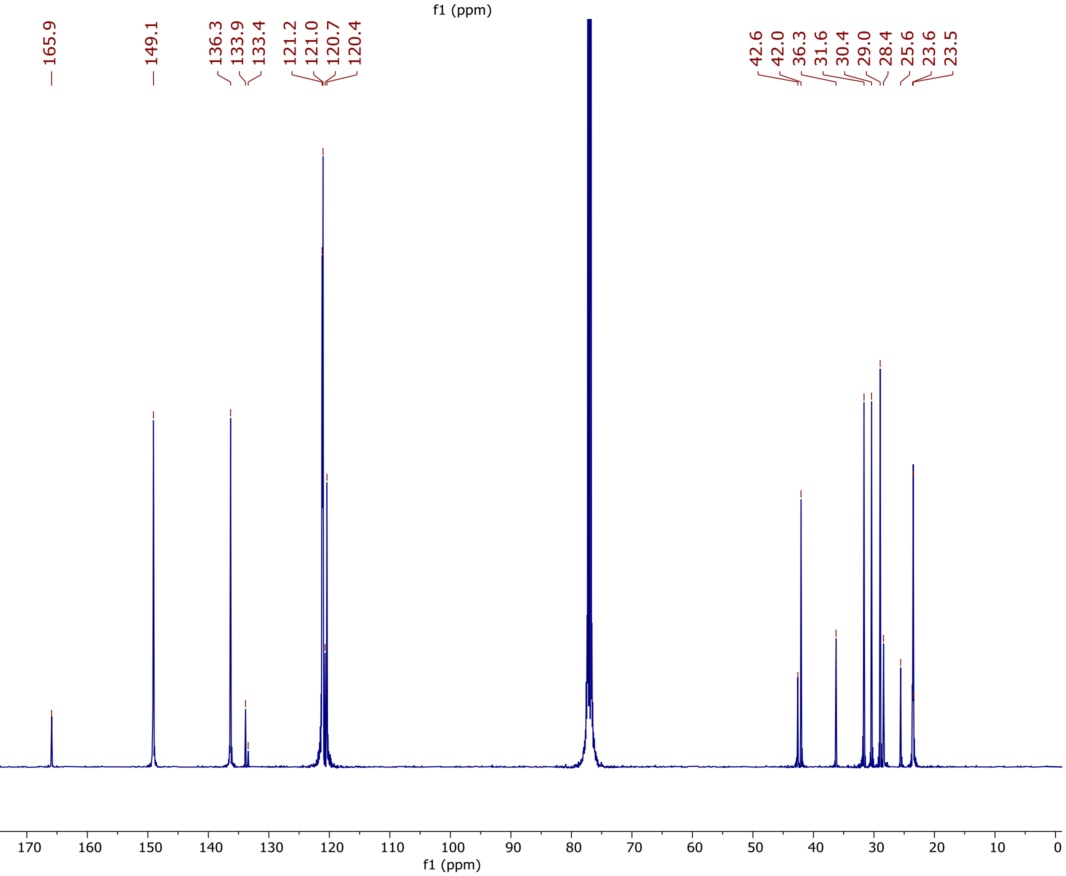
10:1 **9a:9b**

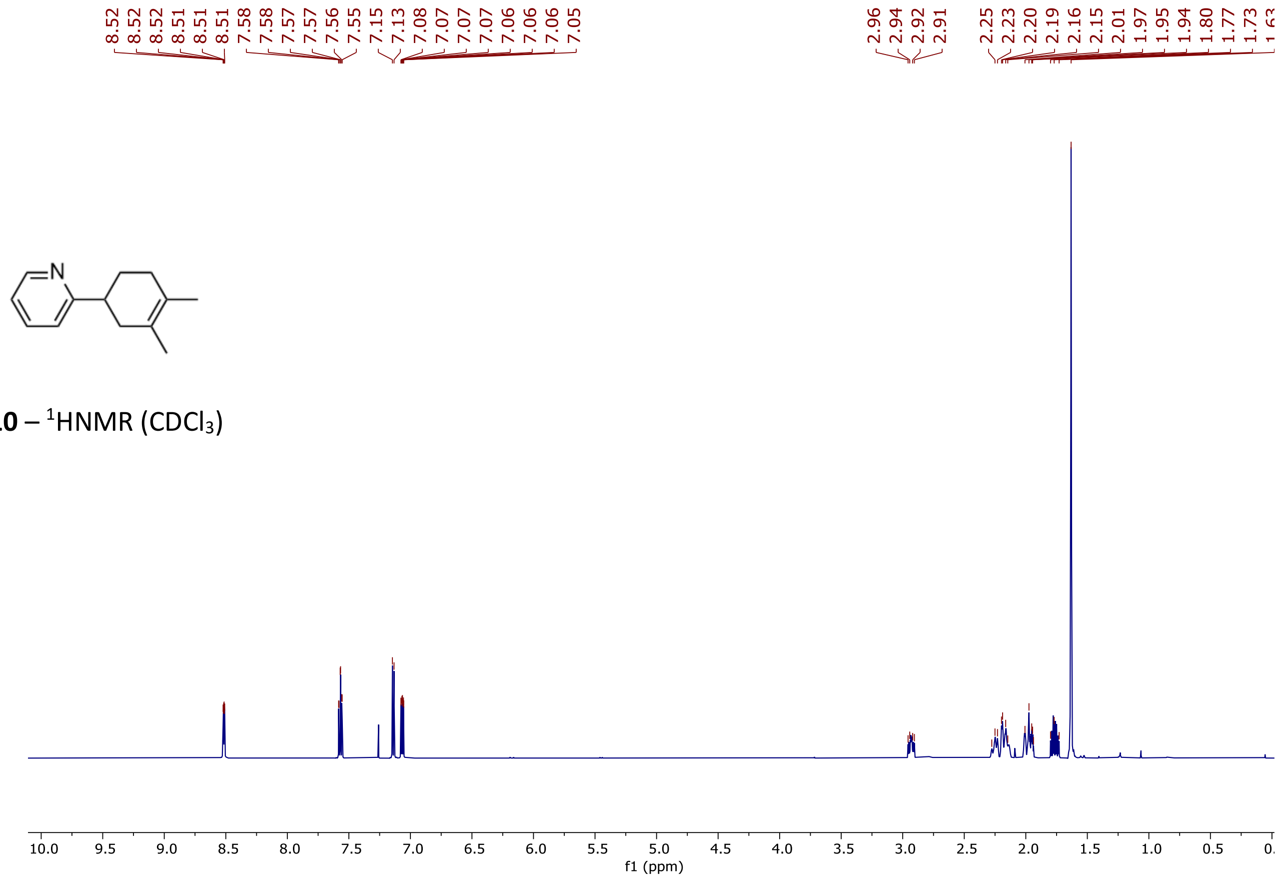




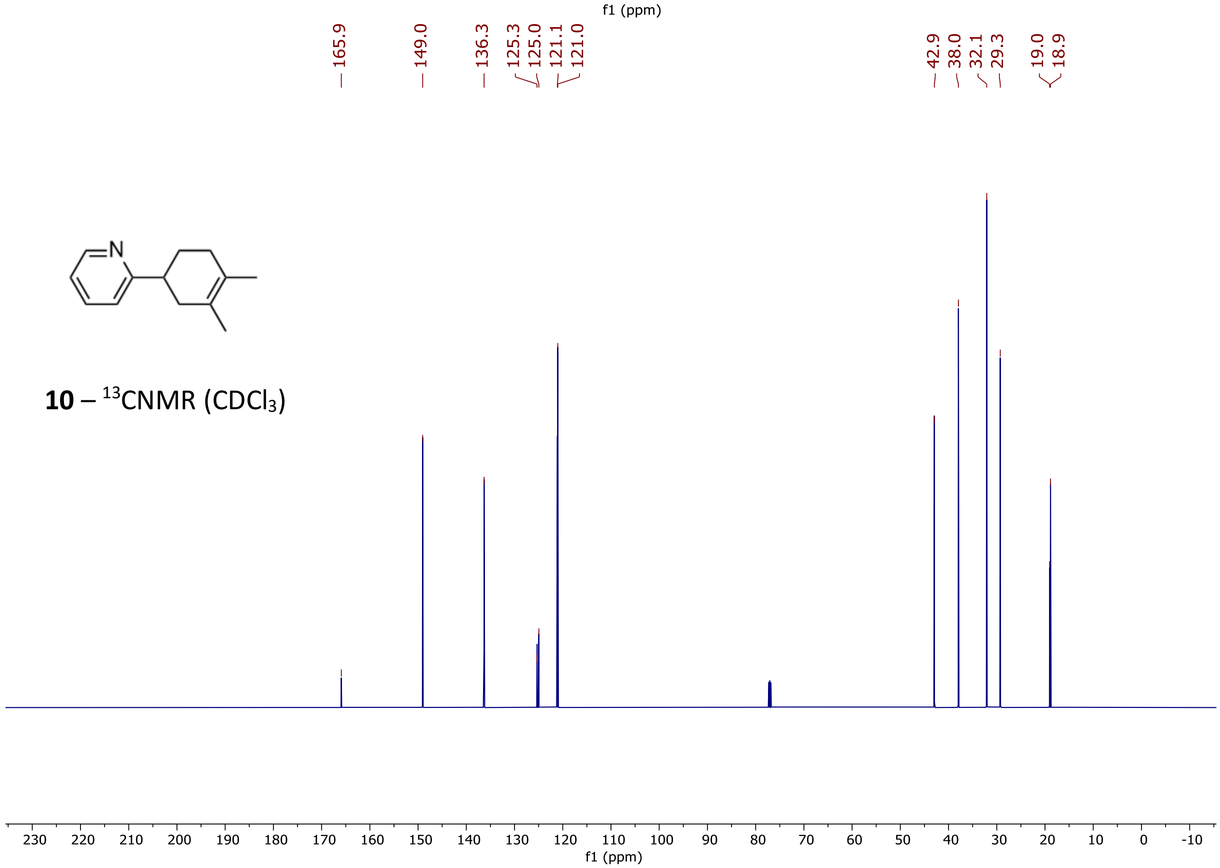
9 – ¹³CNMR ($CDCl_3$)

10:1 **9a:9b**

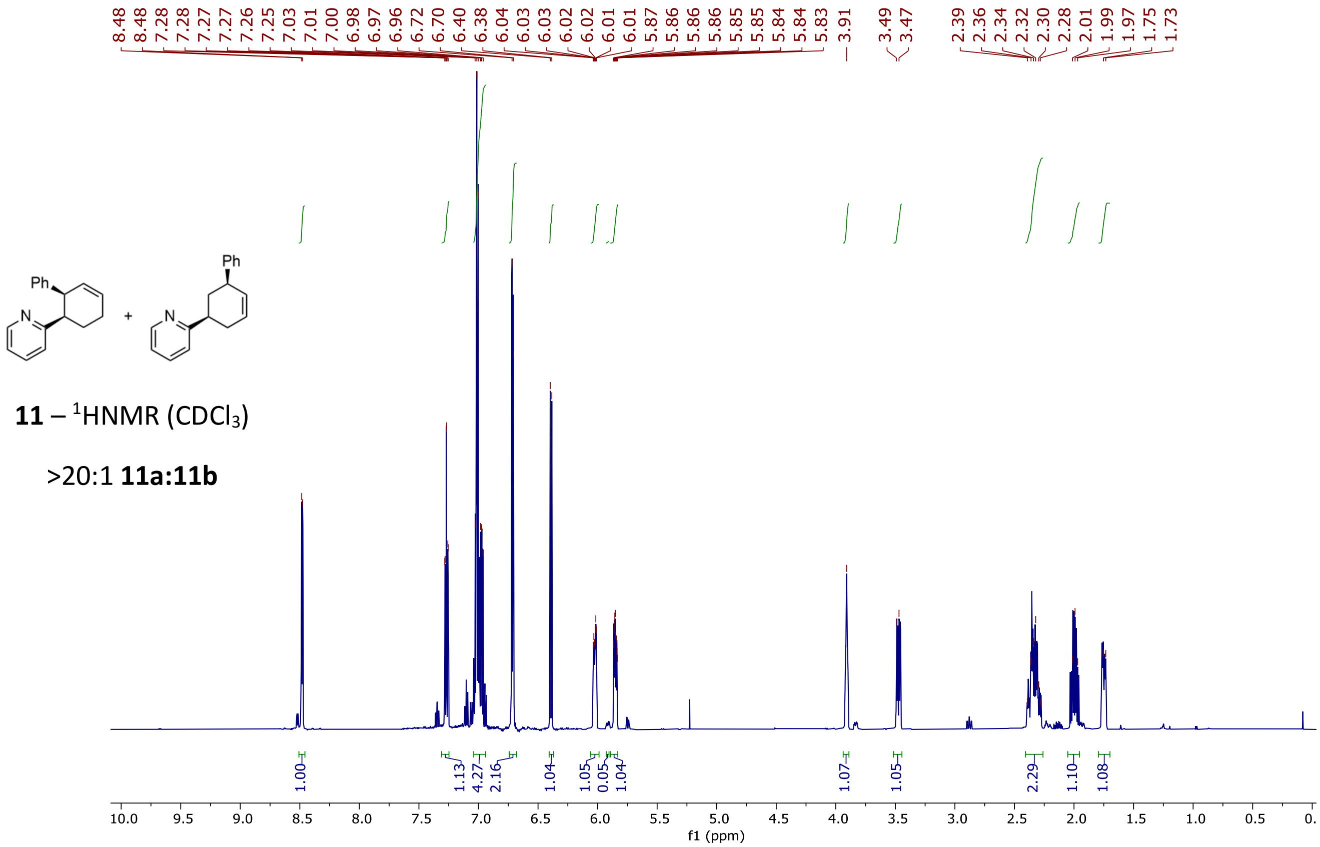


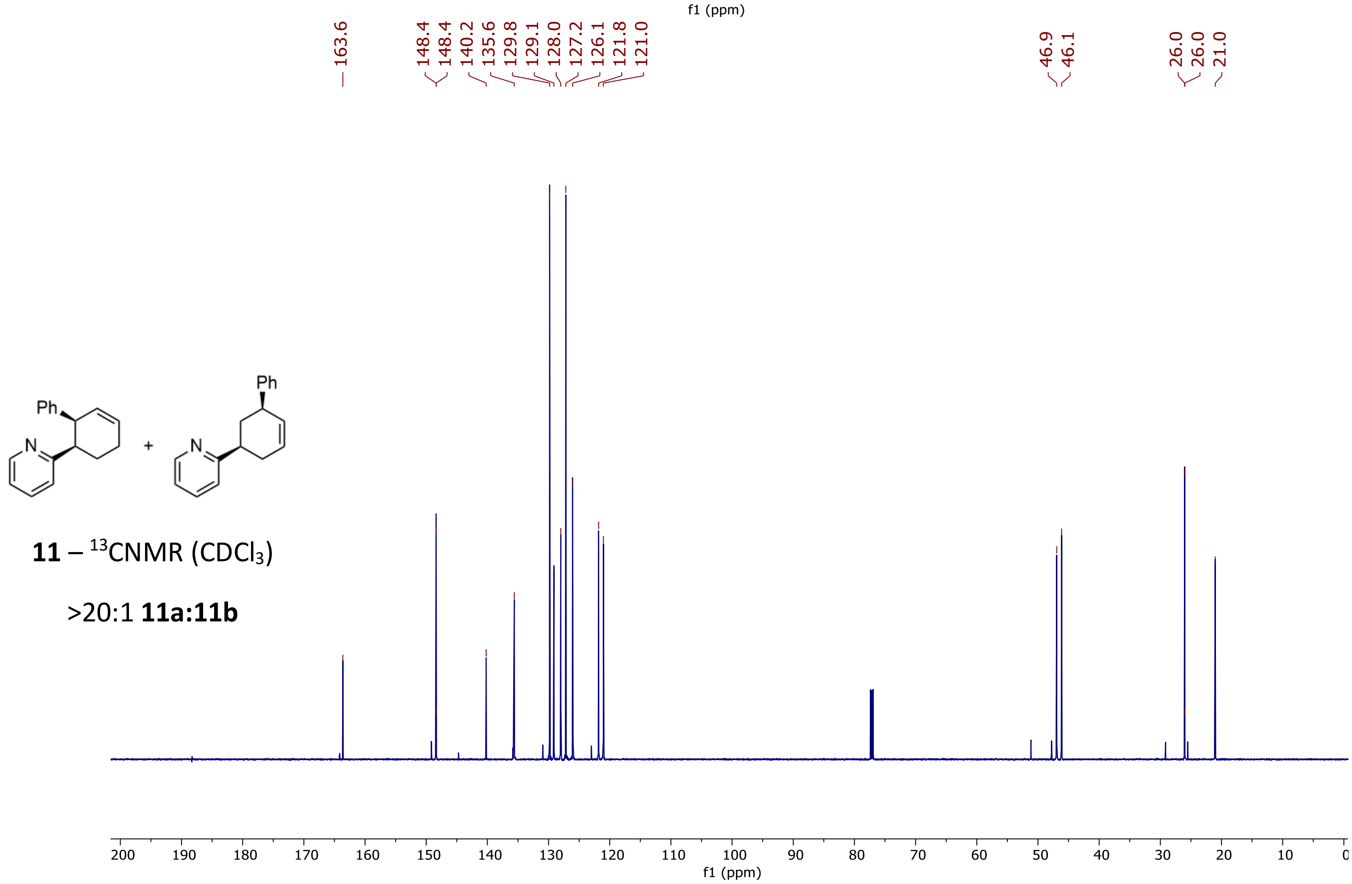


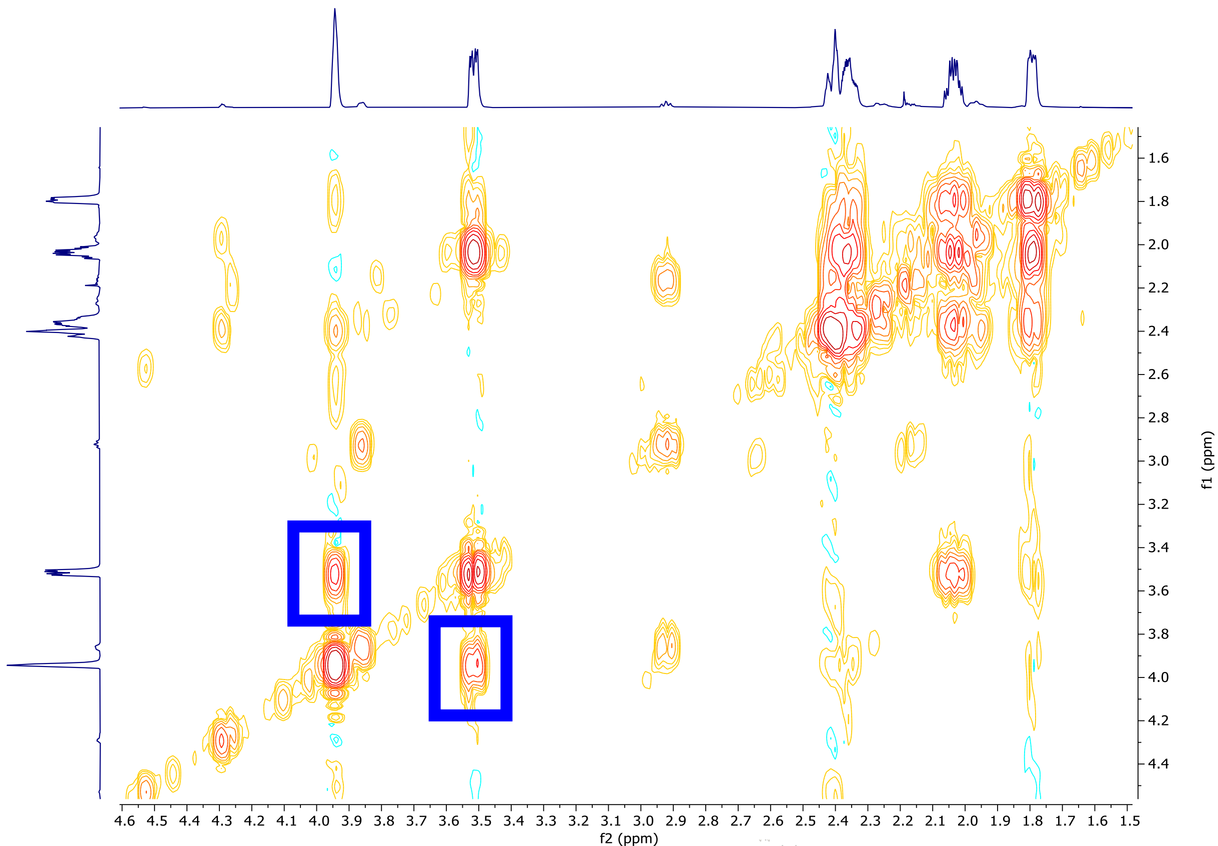
10 – [1]HNMR (CDCl$_3$)

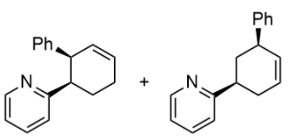


10 – [13]CNMR (CDCl$_3$)

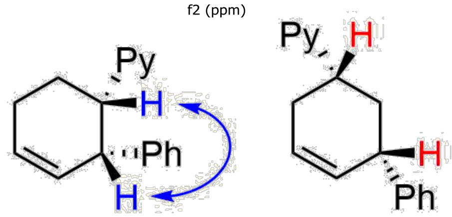

8.48 8.48 7.28 7.28 7.27 7.27 7.26 7.25 7.03 7.01 7.00 6.98 6.97 6.96 6.72 6.70 6.40 6.38 6.04 6.03 6.03 6.02 6.02 6.01 6.01 5.87 5.86 5.86 5.86 5.85 5.85 5.84 5.84 5.83 3.91 3.49 3.47 2.39 2.36 2.34 2.32 2.30 2.28 2.01 1.99 1.97 1.75 1.73
Ph
N
+
Ph
N
11 – 1HNMR (CDCl3)
>20:1 11a:11b
1.00 1.13 4.27 2.16 1.04 1.05 0.05 1.04 1.07 1.05 2.29 1.10 1.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


163.6 148.4 148.4 140.2 135.6 129.8 129.1 128.0 127.2 126.1 121.8 121.0 46.9 46.1 26.0 26.0 21.0
Ph
N
+
Ph
N
11 – 13CNMR (CDCl3)
>20:1 11a:11b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

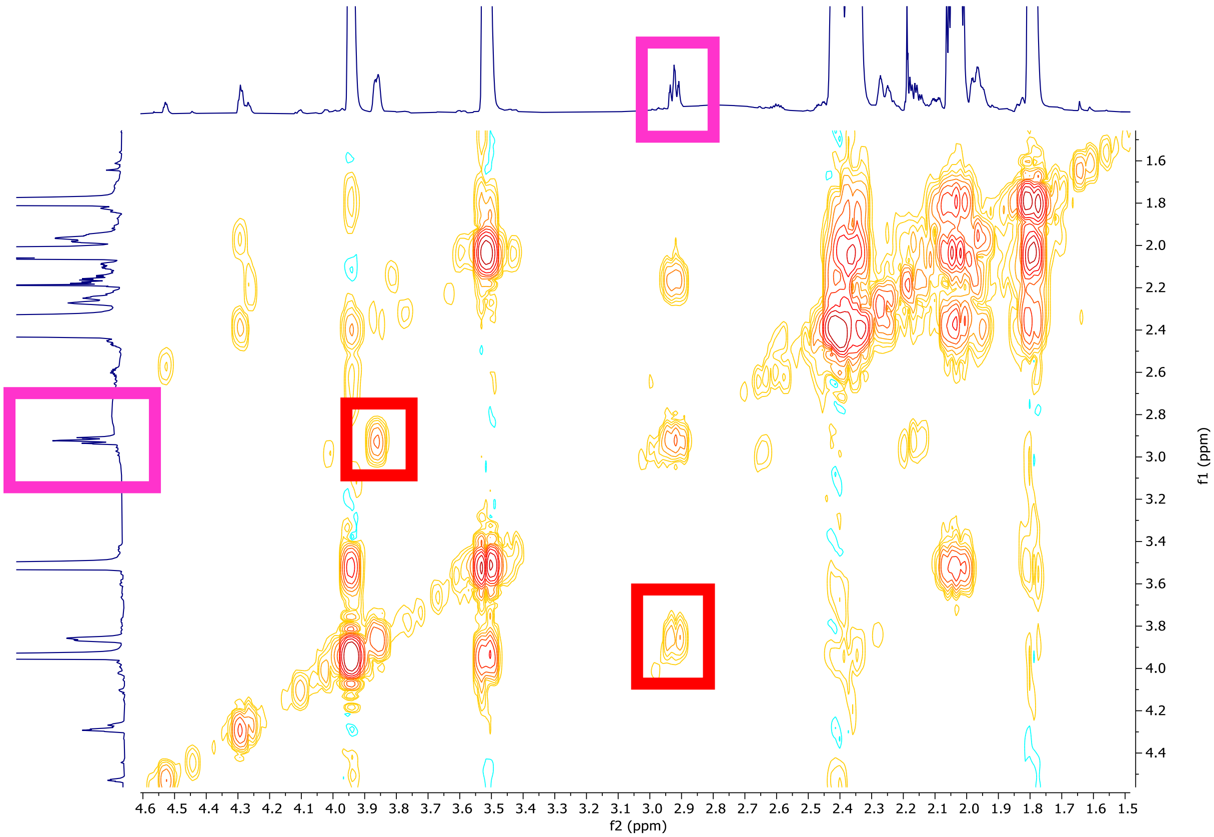


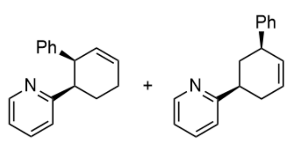


11 – 13H-COSY NMR in aliphatic region ($CDCl_3$)

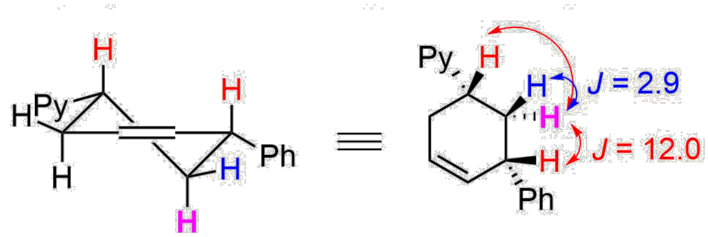


^3J coupling between methine protons on major isomer

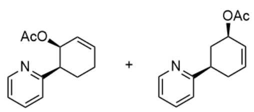




11 – ^{13}H-COSY NMR in aliphatic region ($CDCl_3$)

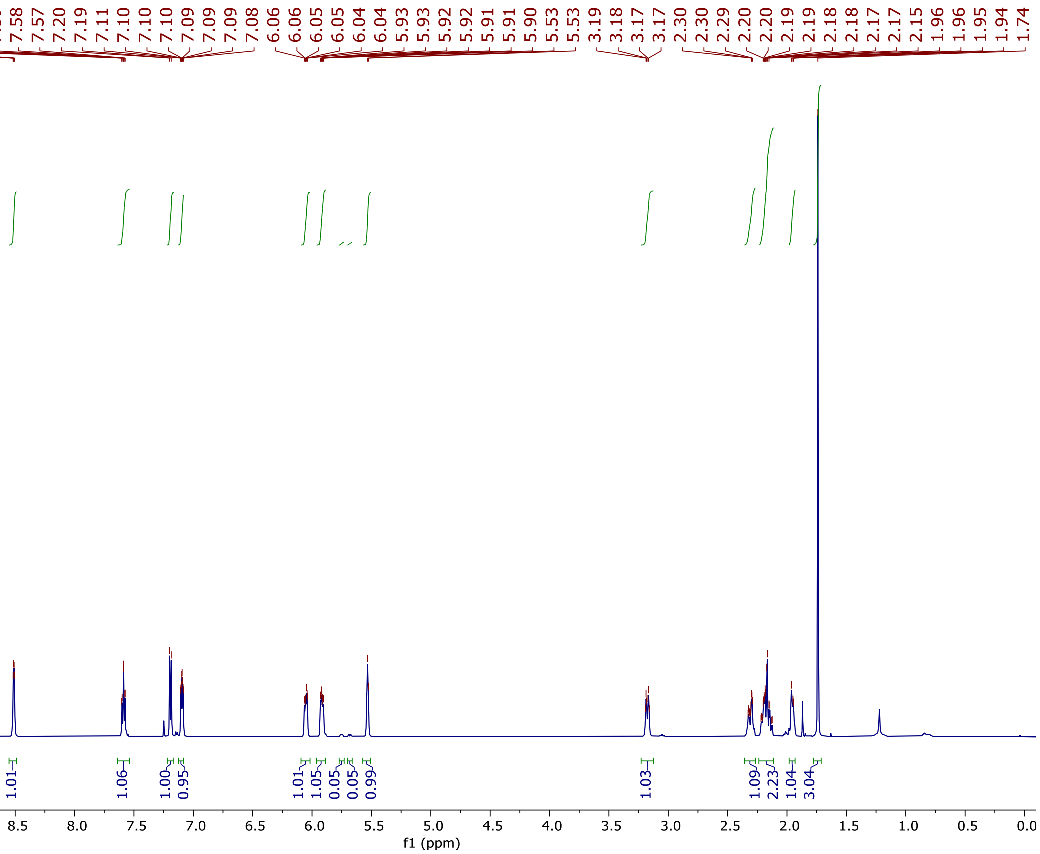


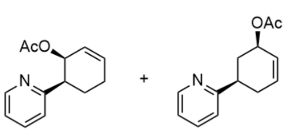
minor isomer td, *J* = 12.0, 2.9
coupling to visible minor methine peak



12 – [1]HNMR ($CDCl_3$)

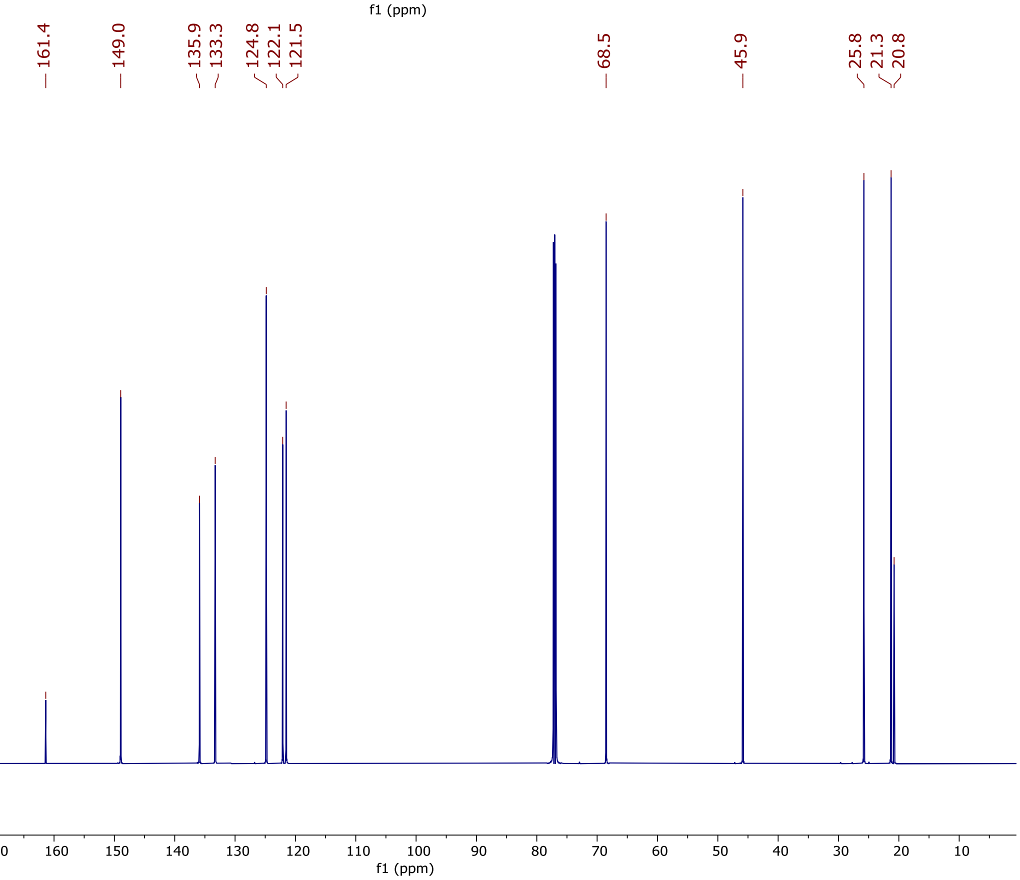
20:1 **12a:12b**





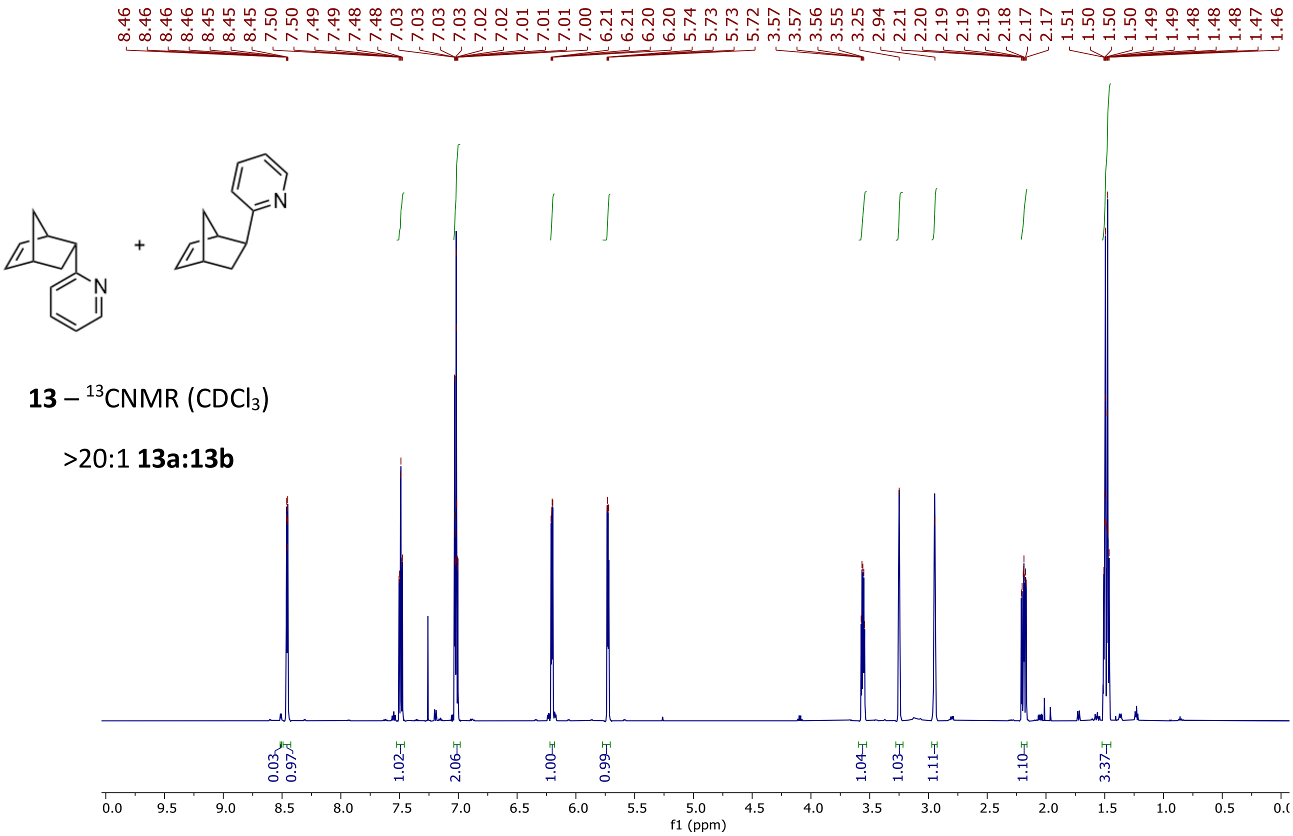
12 – [13]CNMR ($CDCl_3$)

20:1 **12a:12b**



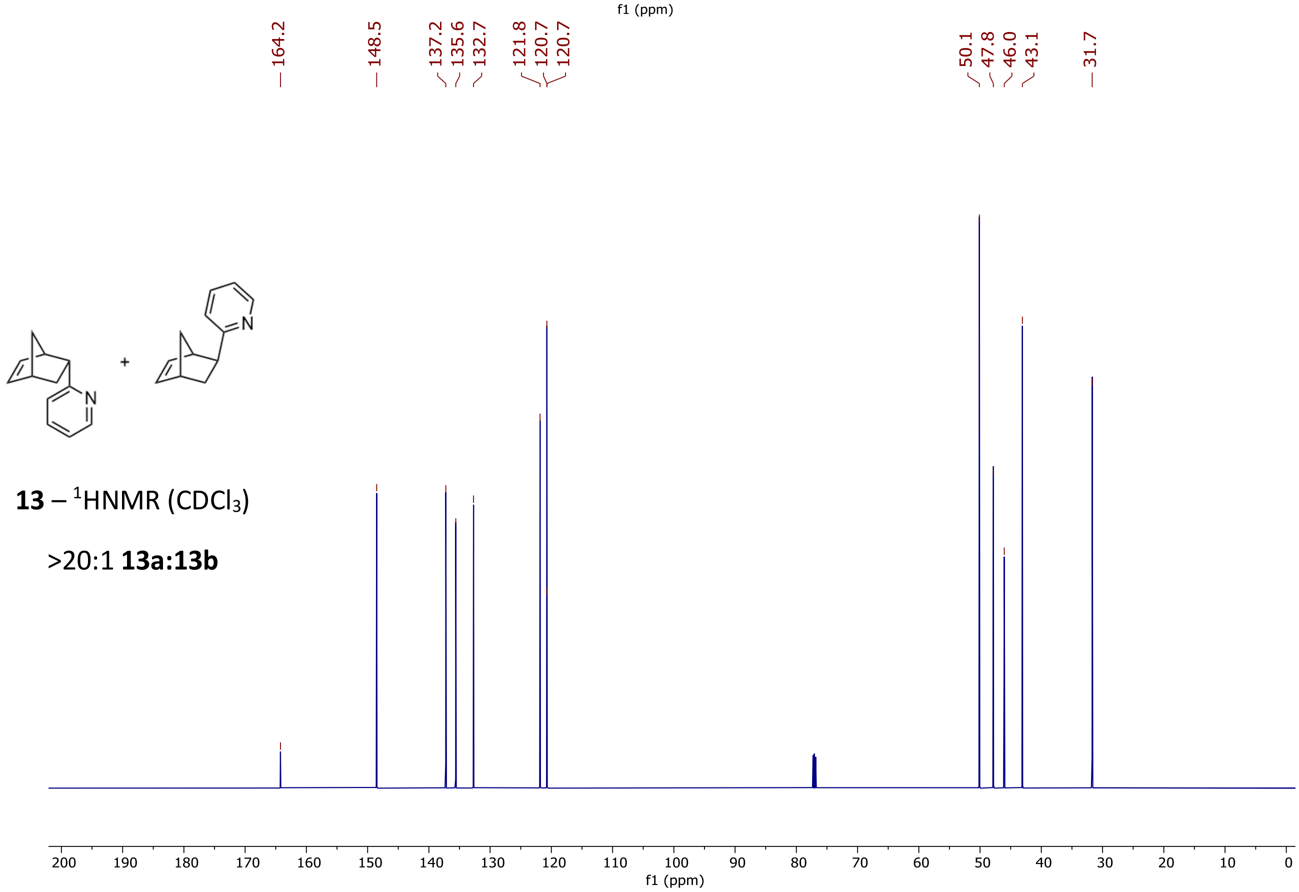
13 – ^{13}CNMR ($CDCl_3$)

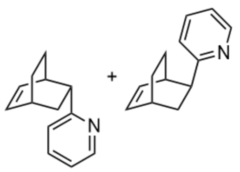
>20:1 **13a:13b**



13 – ^{1}HNMR ($CDCl_3$)

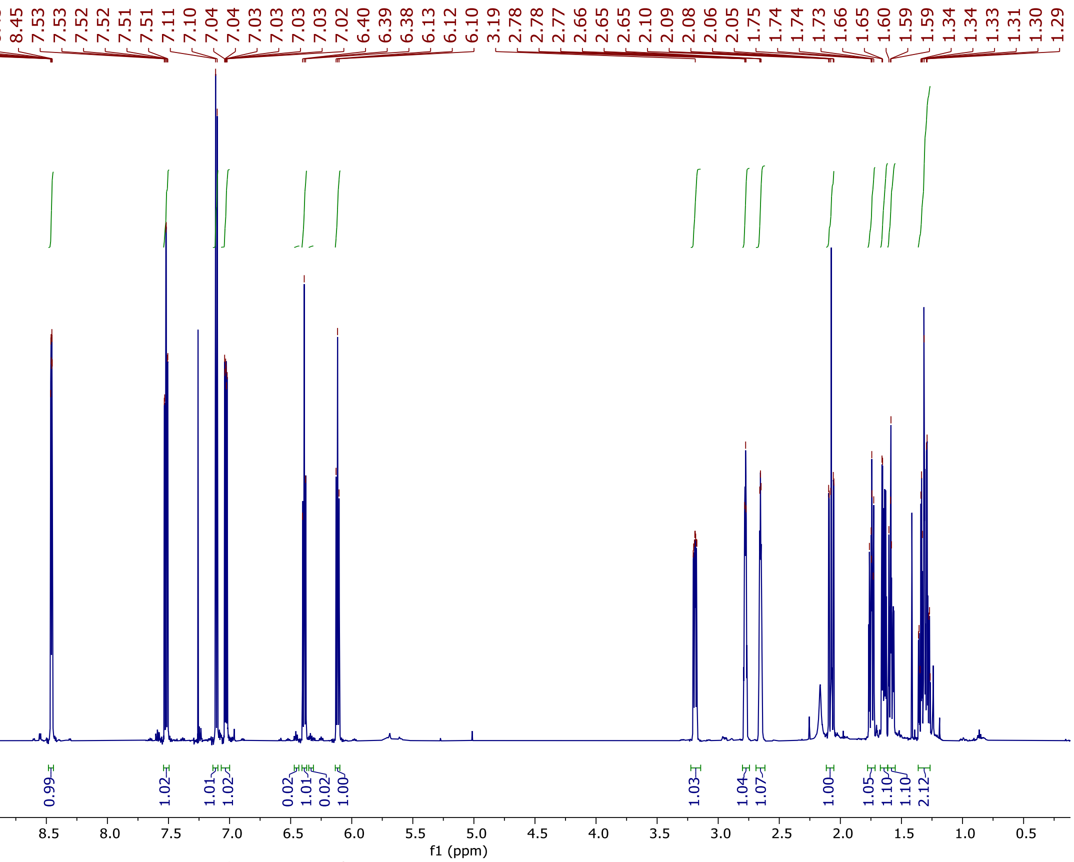
>20:1 **13a:13b**

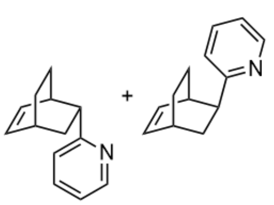




14 – ¹HNMR ($CDCl_3$)

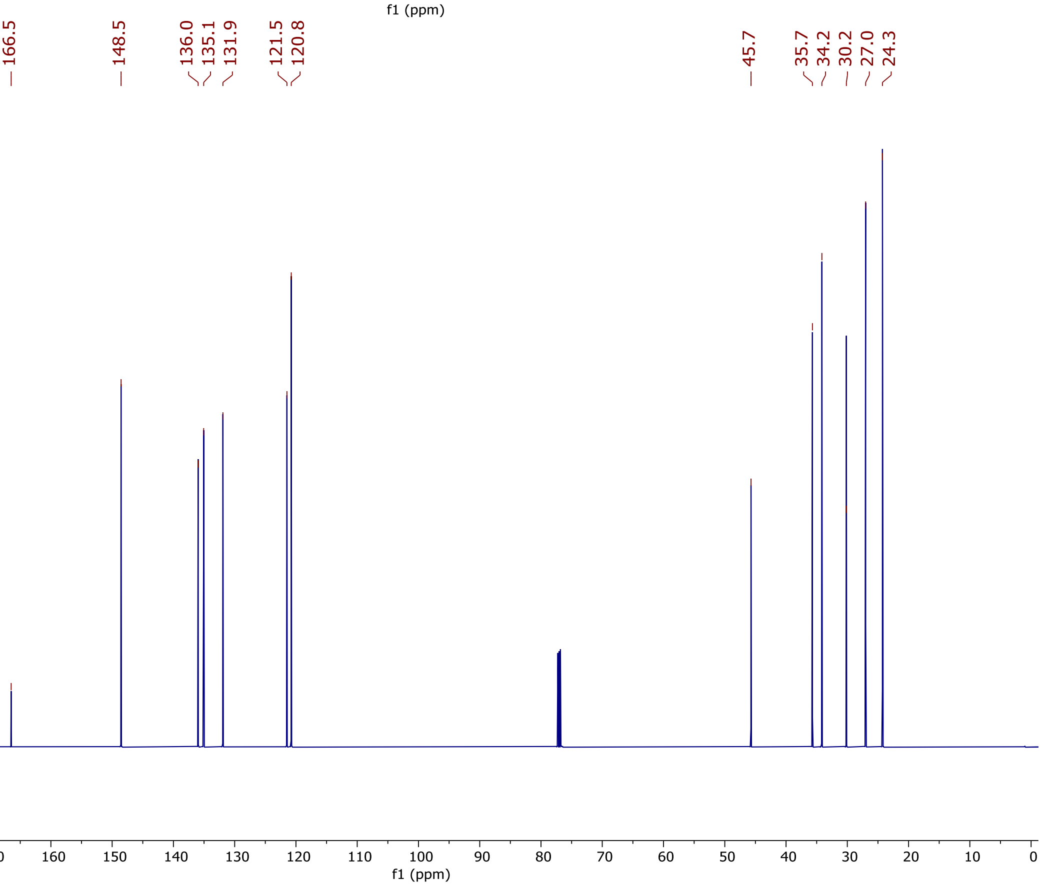
>20:1 **14a:14b**



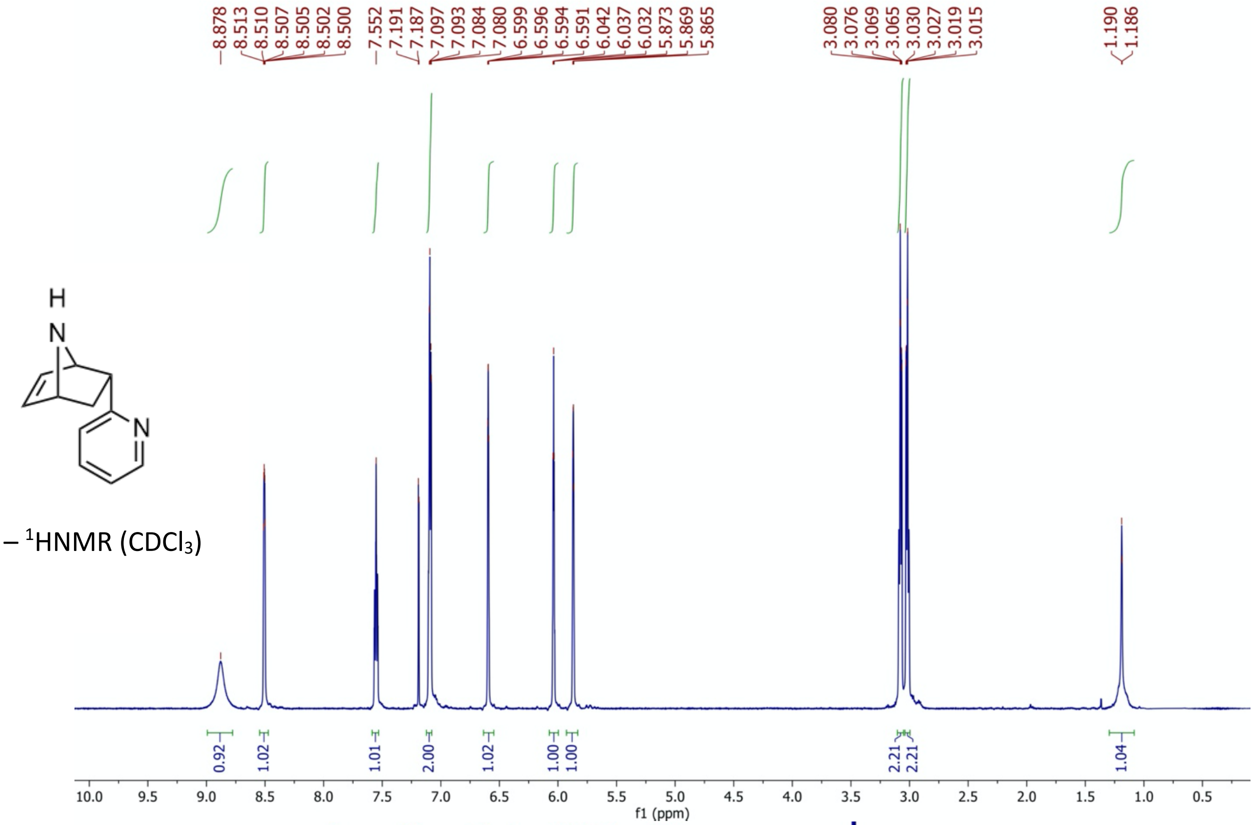


14 – ¹³CNMR ($CDCl_3$)

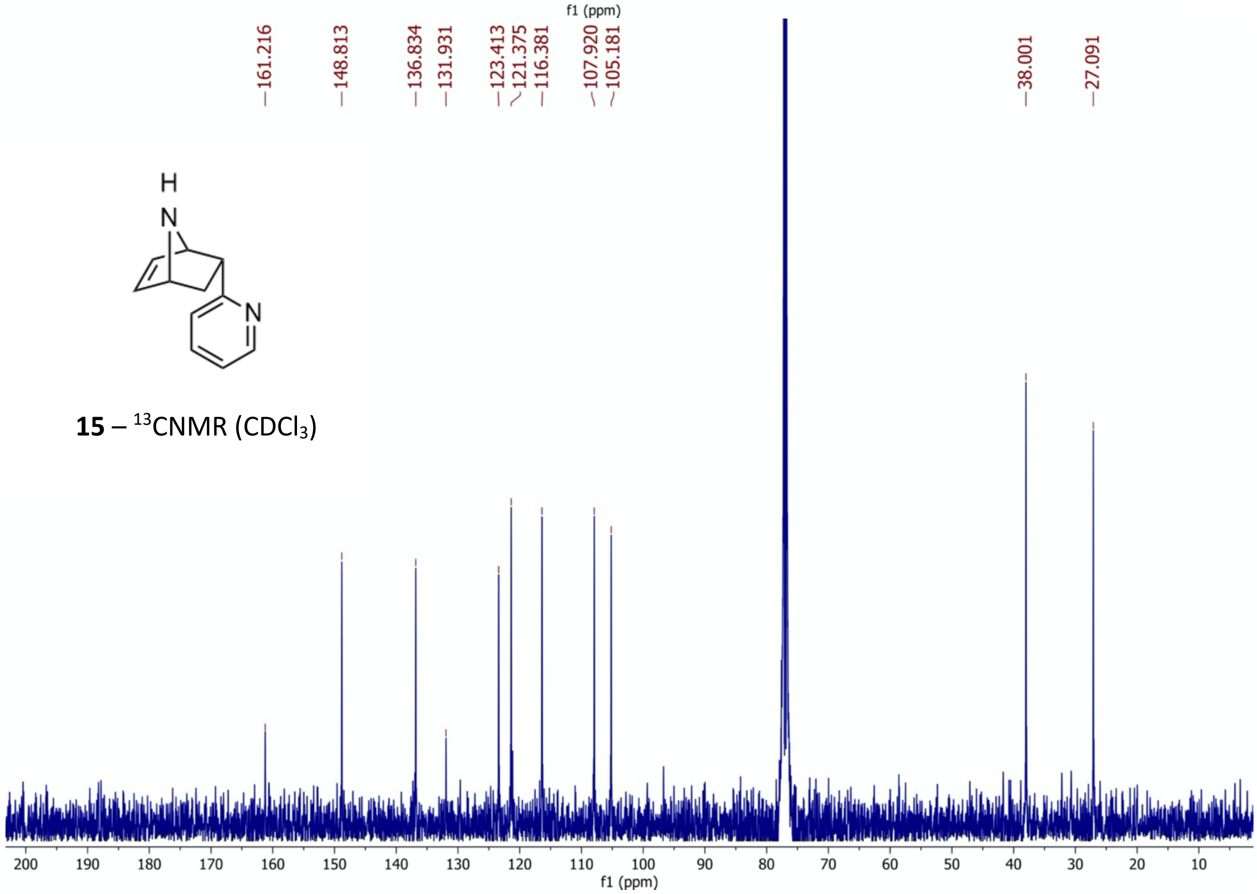
>20:1 **14a:14b**

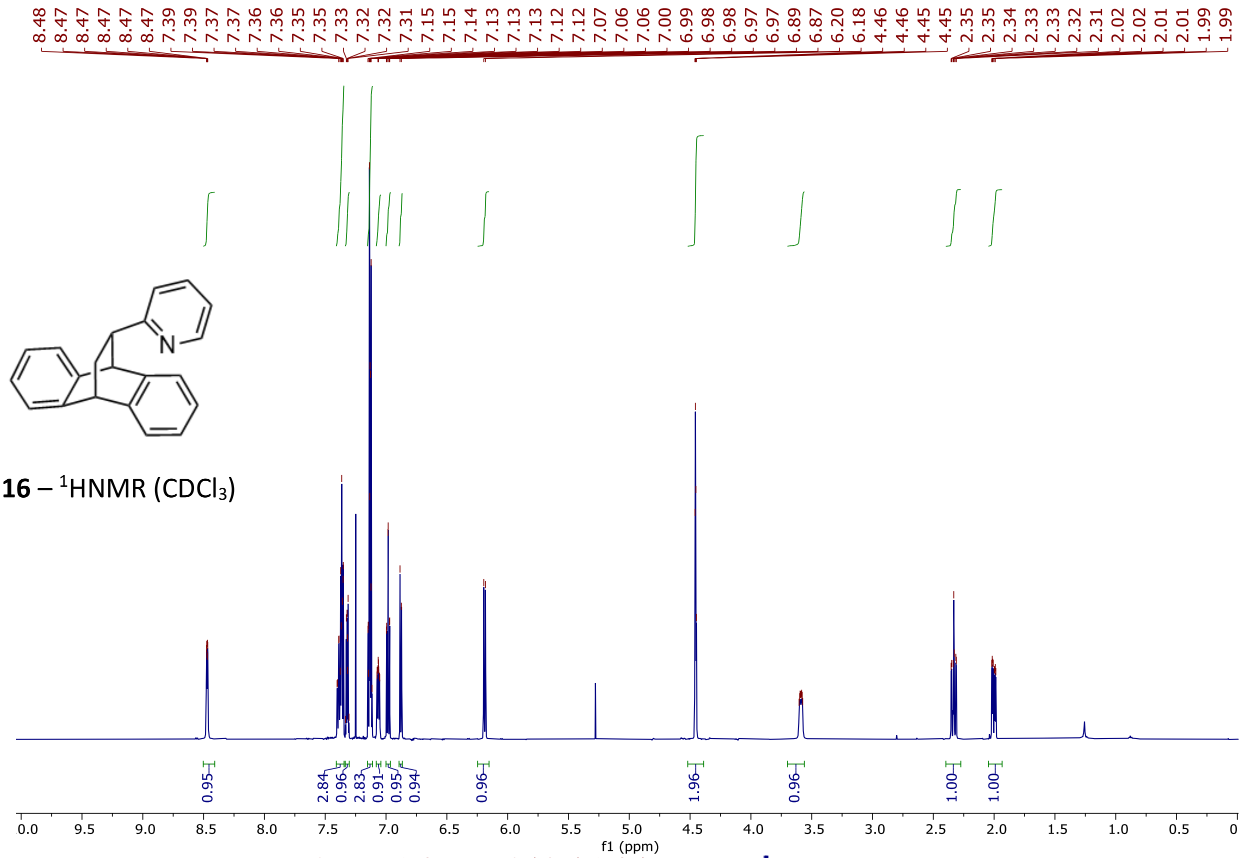


15 – [1]HNMR ($CDCl_3$)

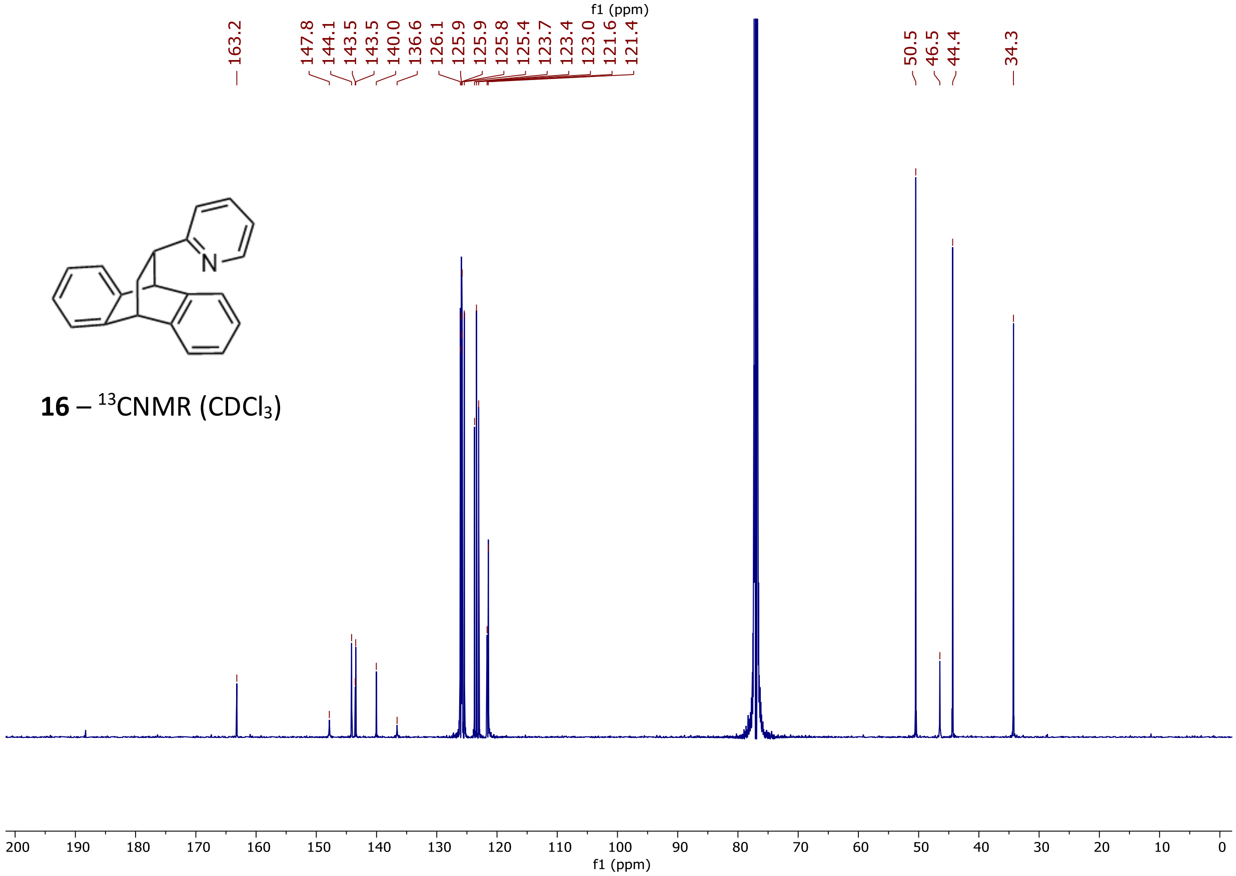


15 – [13]CNMR ($CDCl_3$)

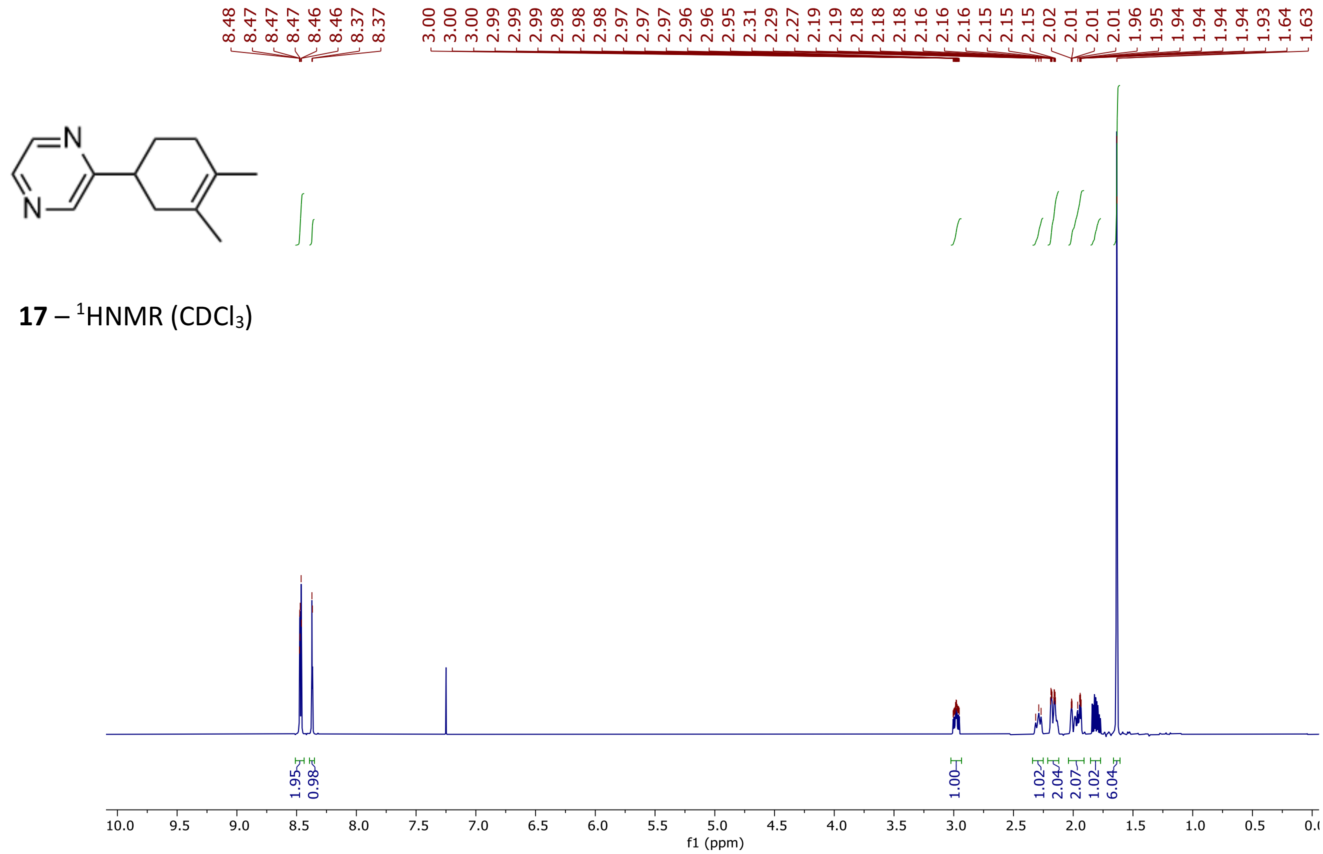




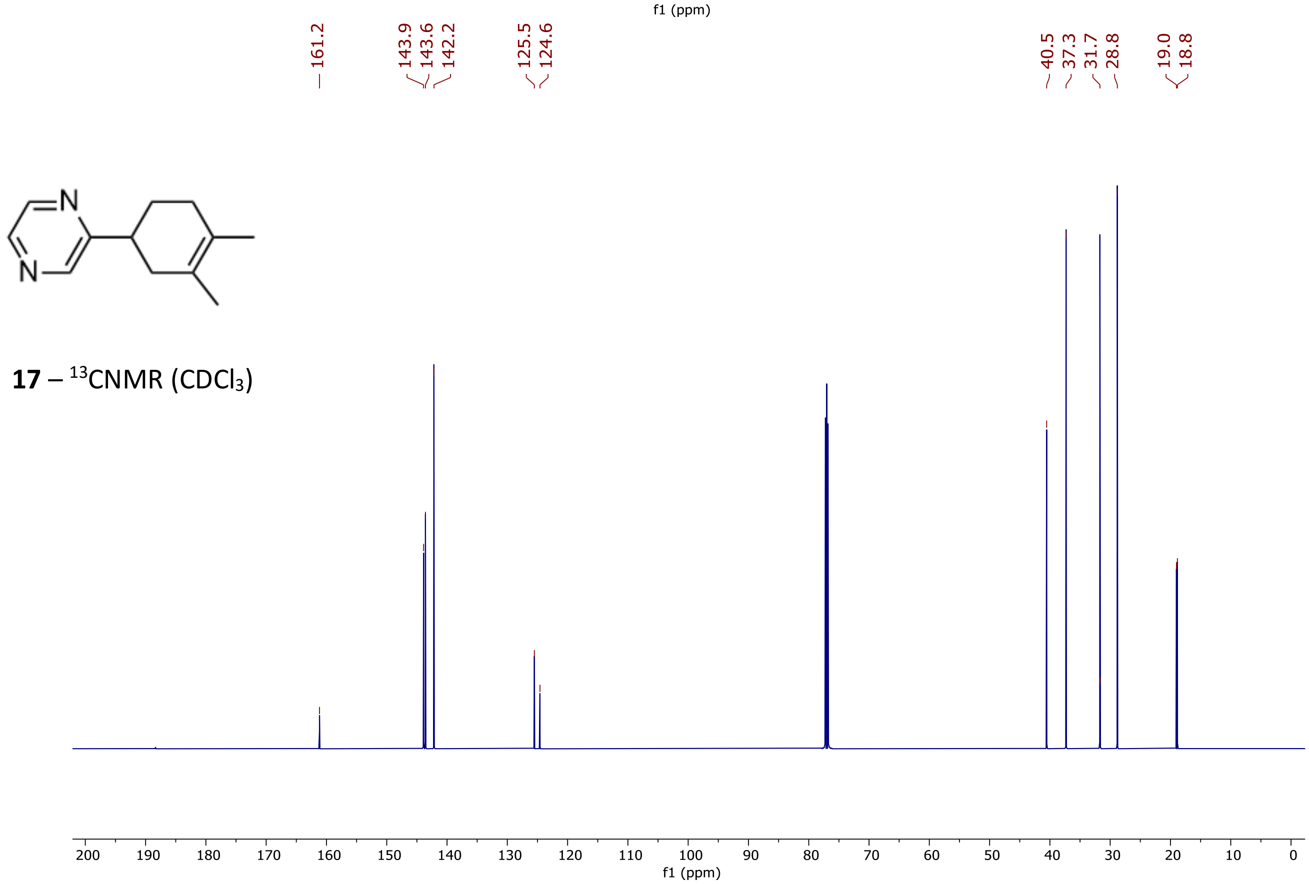
16 – ¹HNMR ($CDCl_3$)



16 – ¹³CNMR ($CDCl_3$)

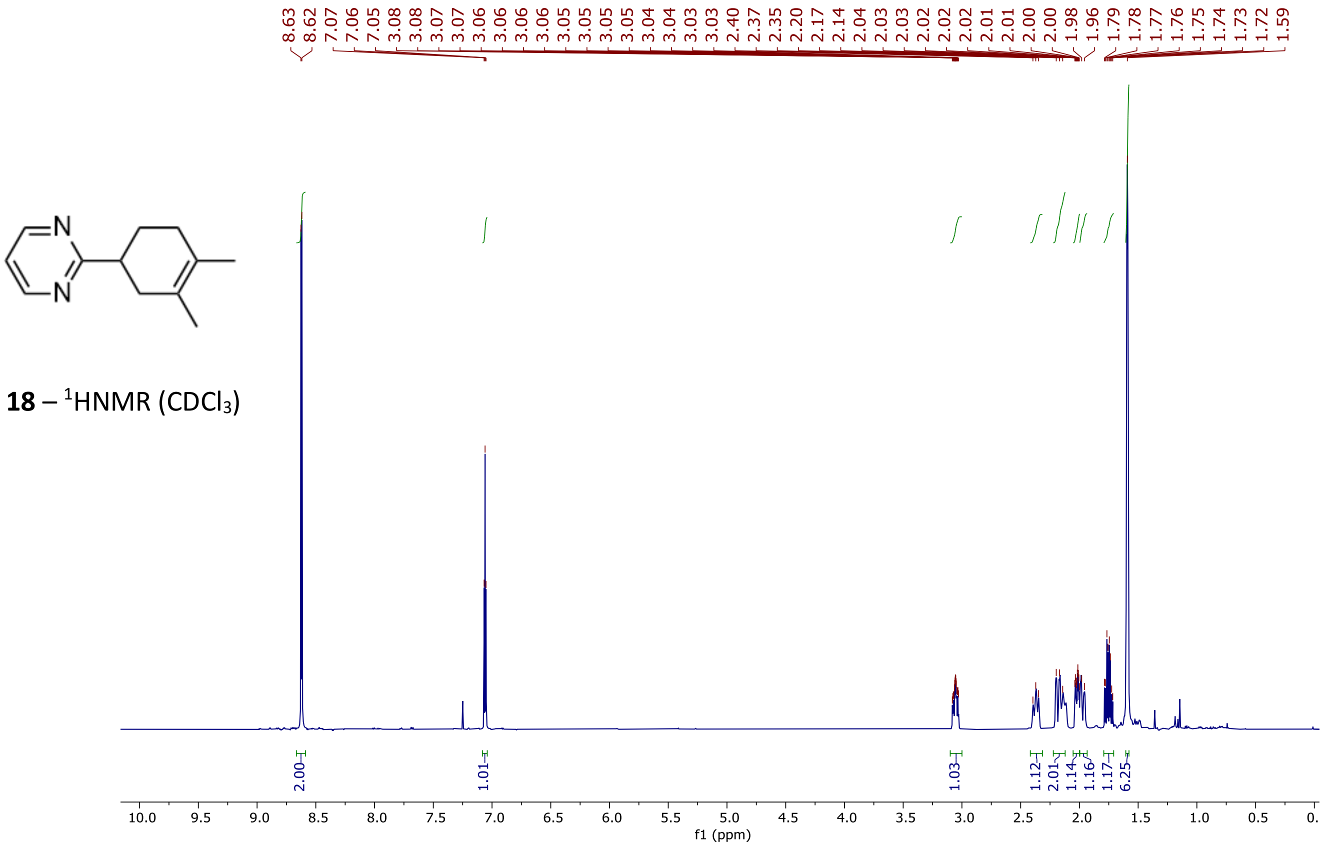


17 – ^{1}HNMR ($CDCl_3$)

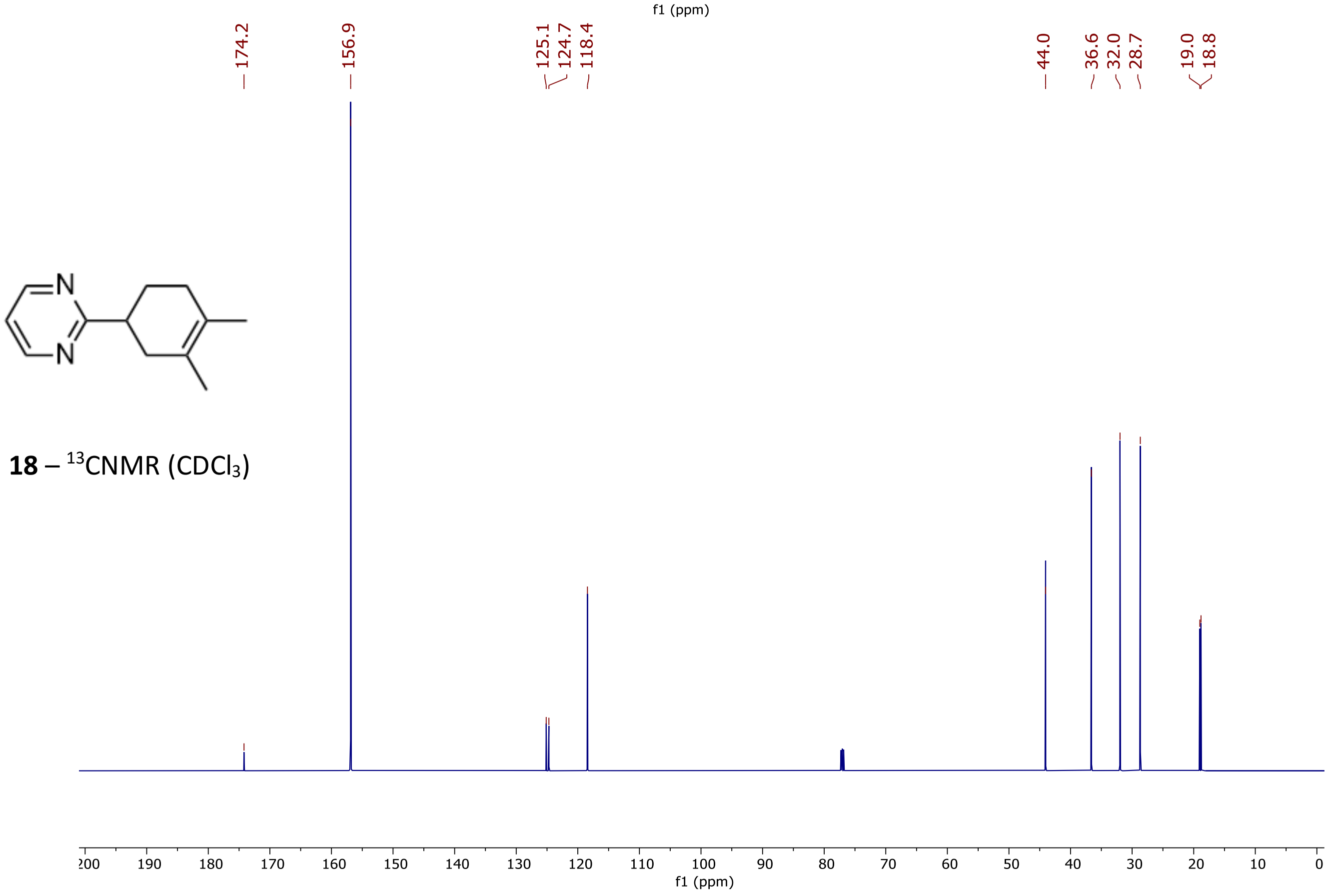


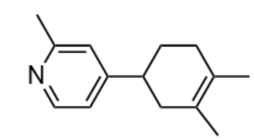
17 – ^{13}CNMR ($CDCl_3$)

18 – ^{1}HNMR ($CDCl_3$)

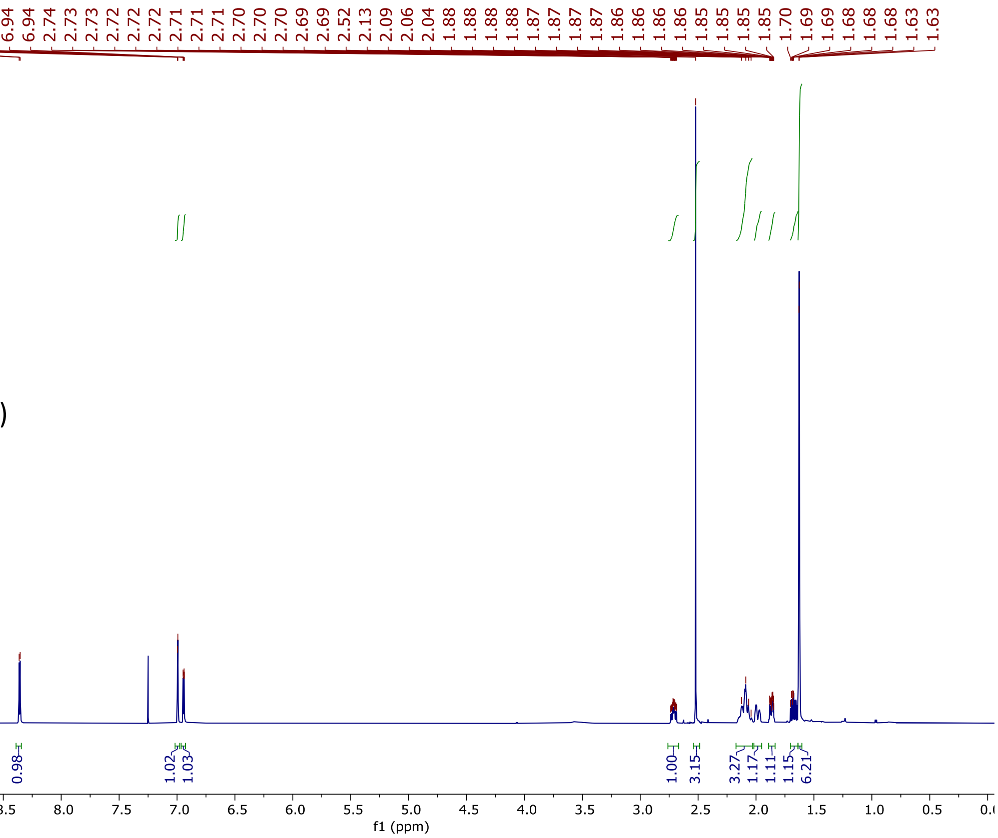


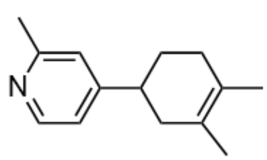
18 – ^{13}CNMR ($CDCl_3$)



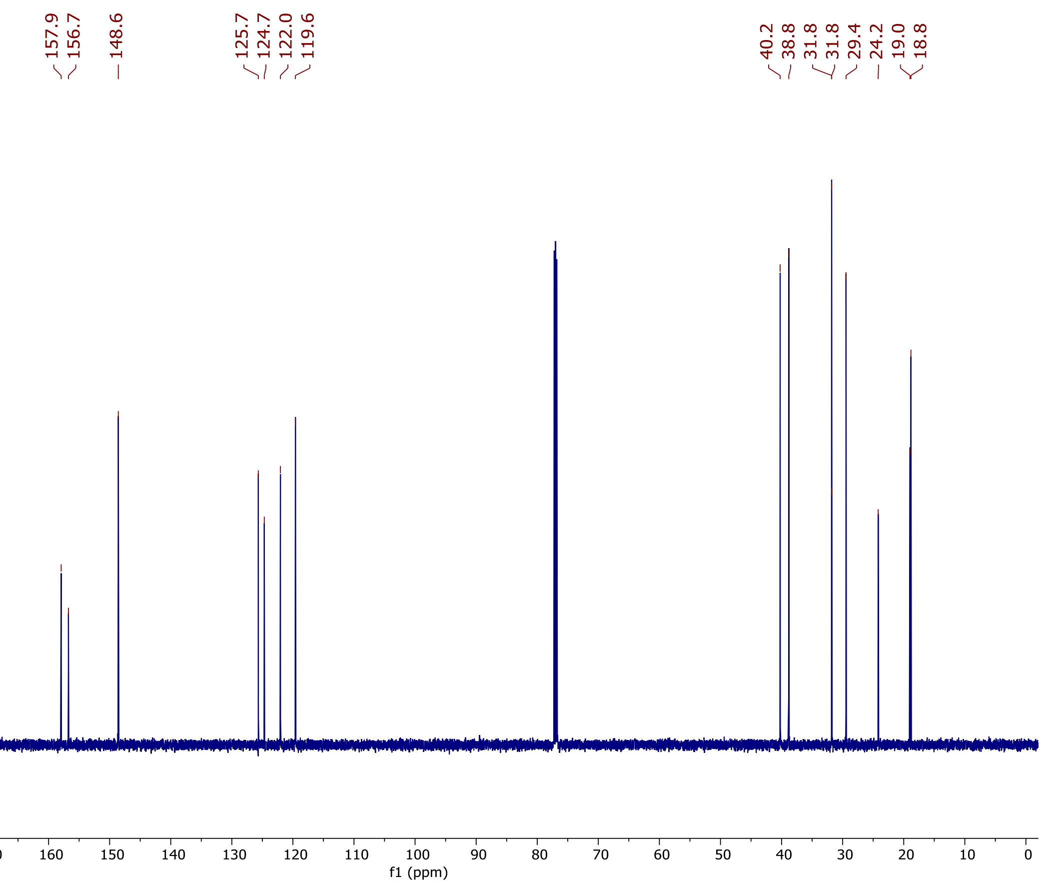


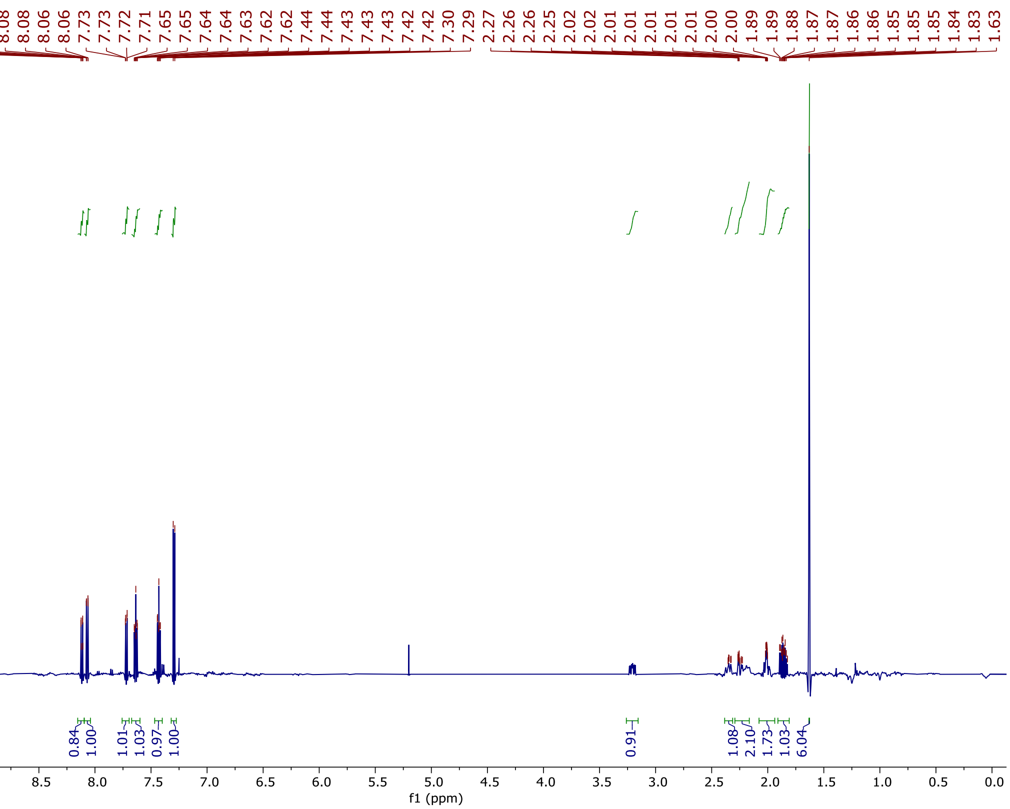
19 – [1]HNMR ($CDCl_3$)

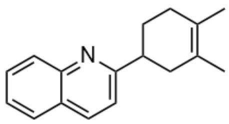




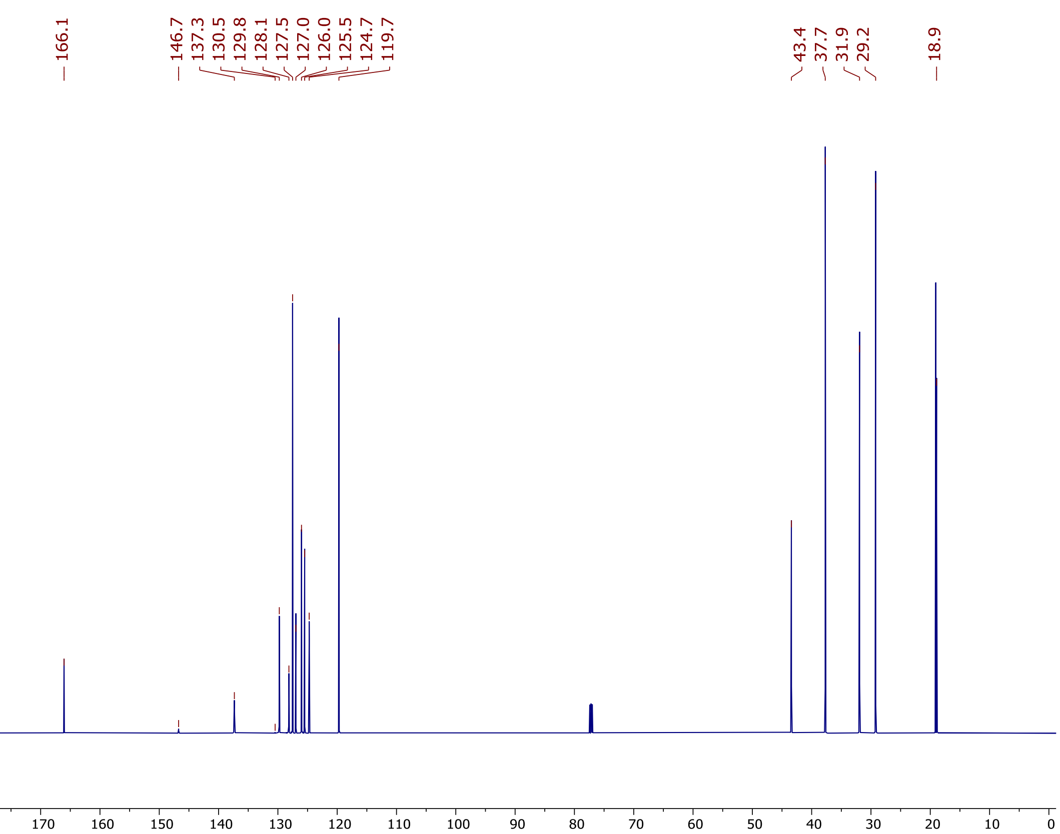
19 – [13]CNMR ($CDCl_3$)

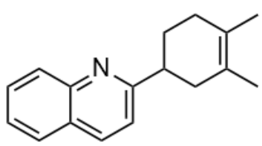




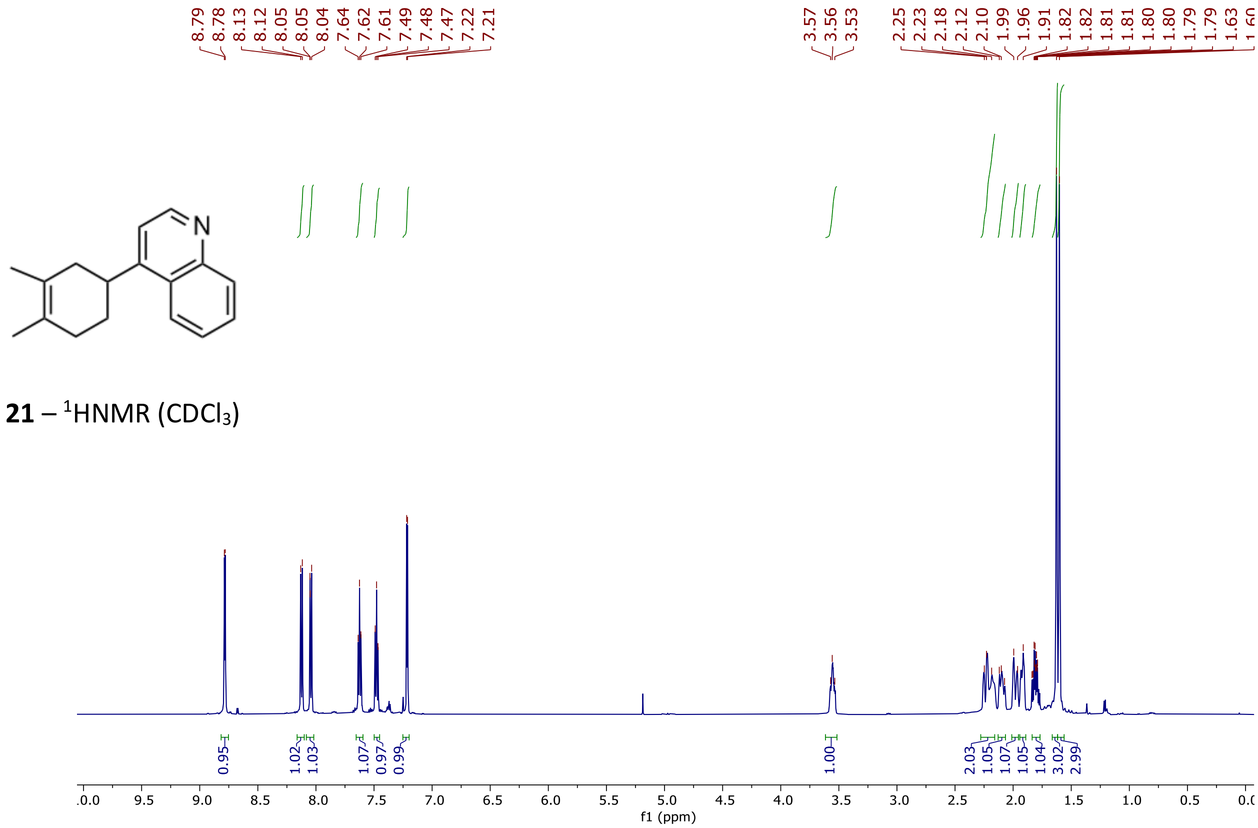


20 – [1]HNMR ($CDCl_3$)

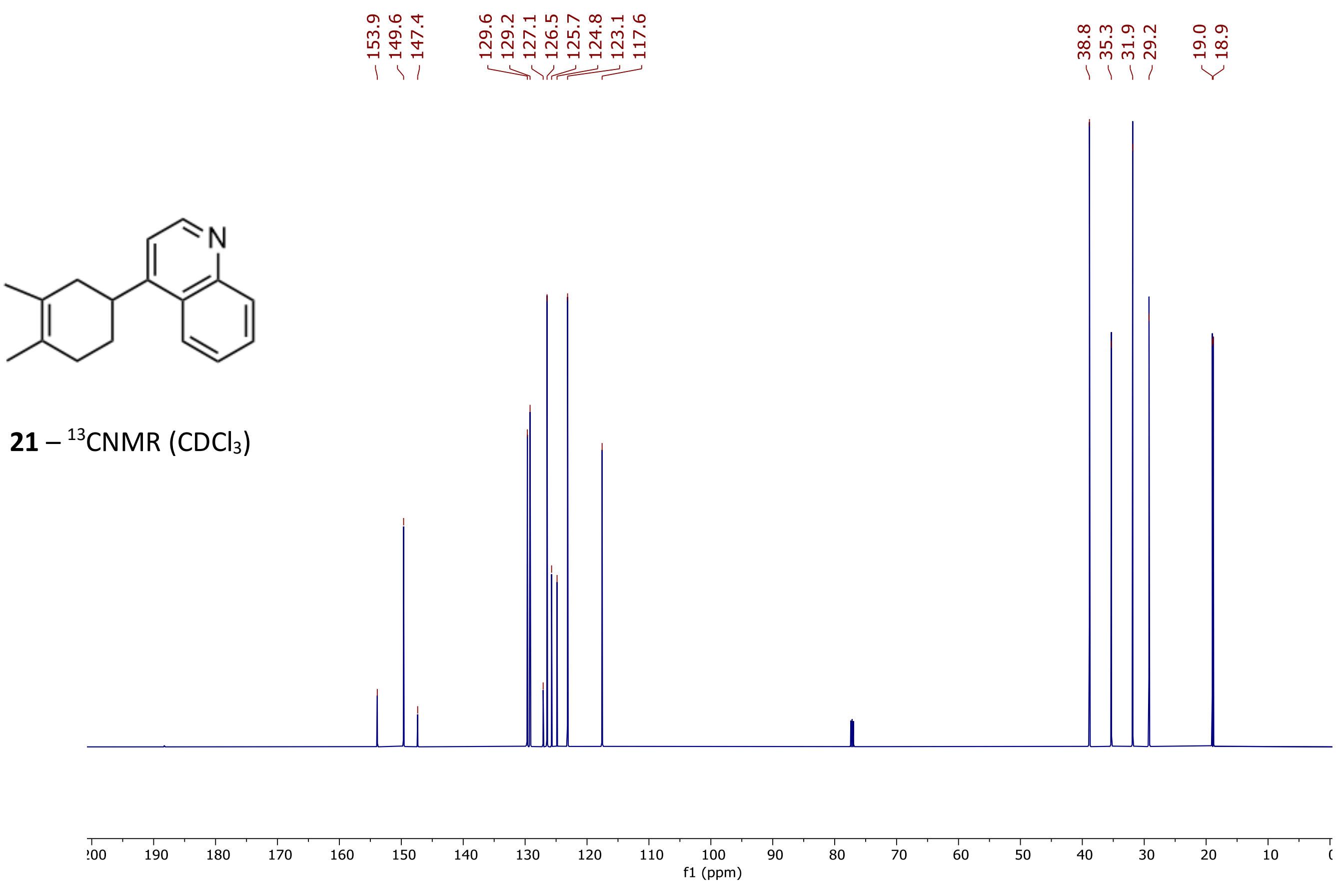




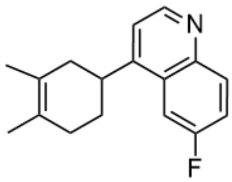
20 – [13]CNMR ($CDCl_3$)



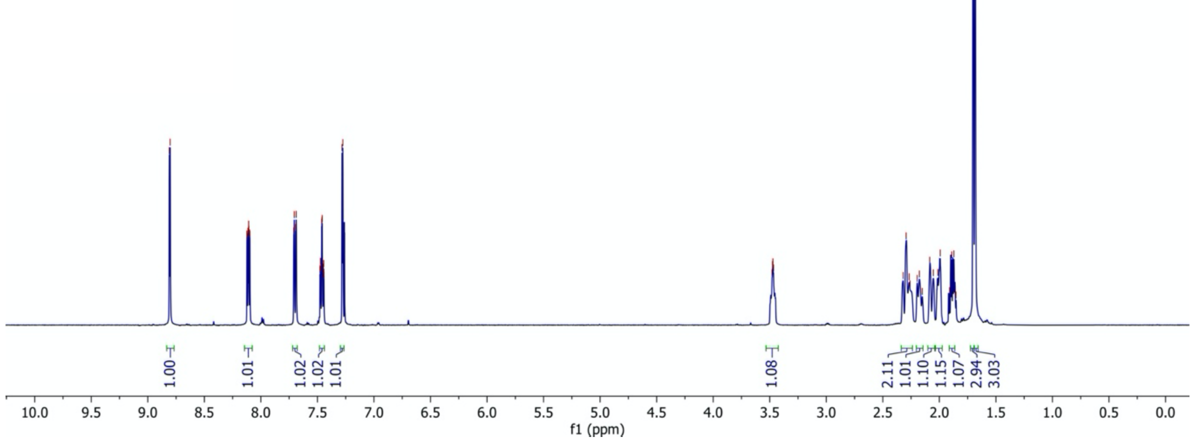
21 – [1]HNMR ($CDCl_3$)

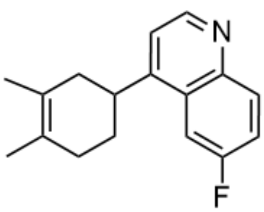


21 – [13]CNMR ($CDCl_3$)

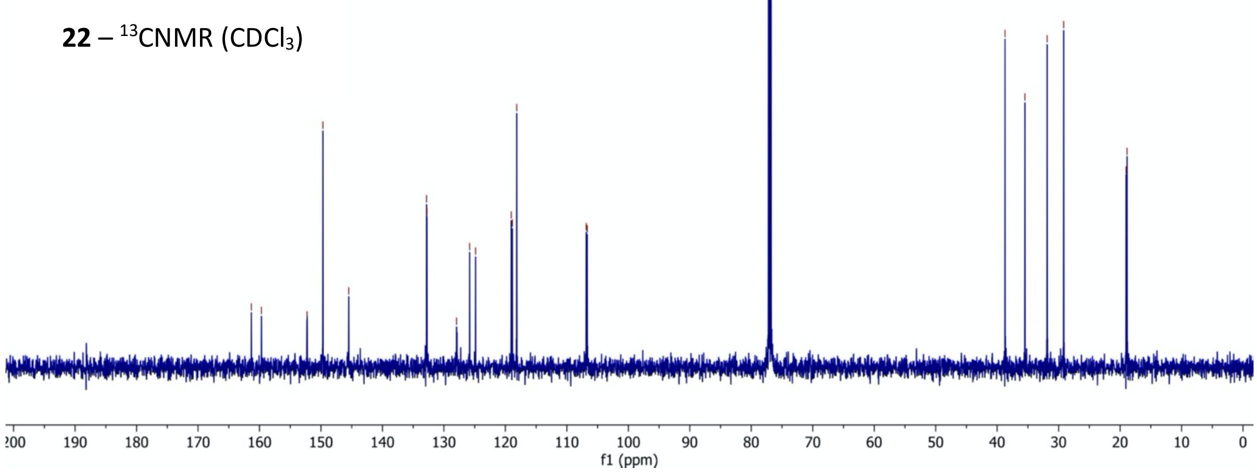


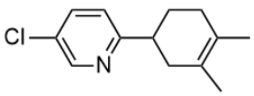
22 – [1]HNMR ($CDCl_3$)



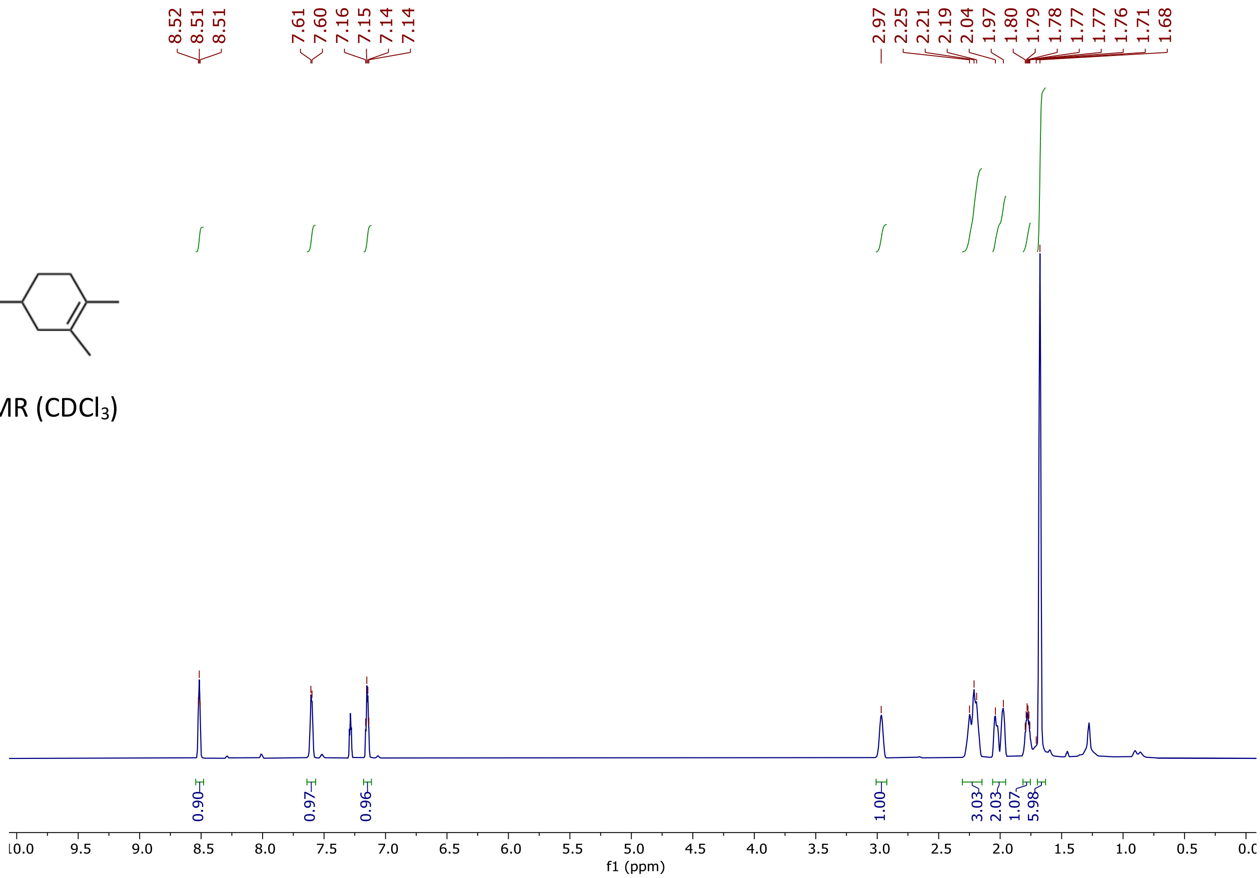


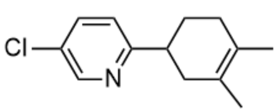
22 – [13]CNMR ($CDCl_3$)



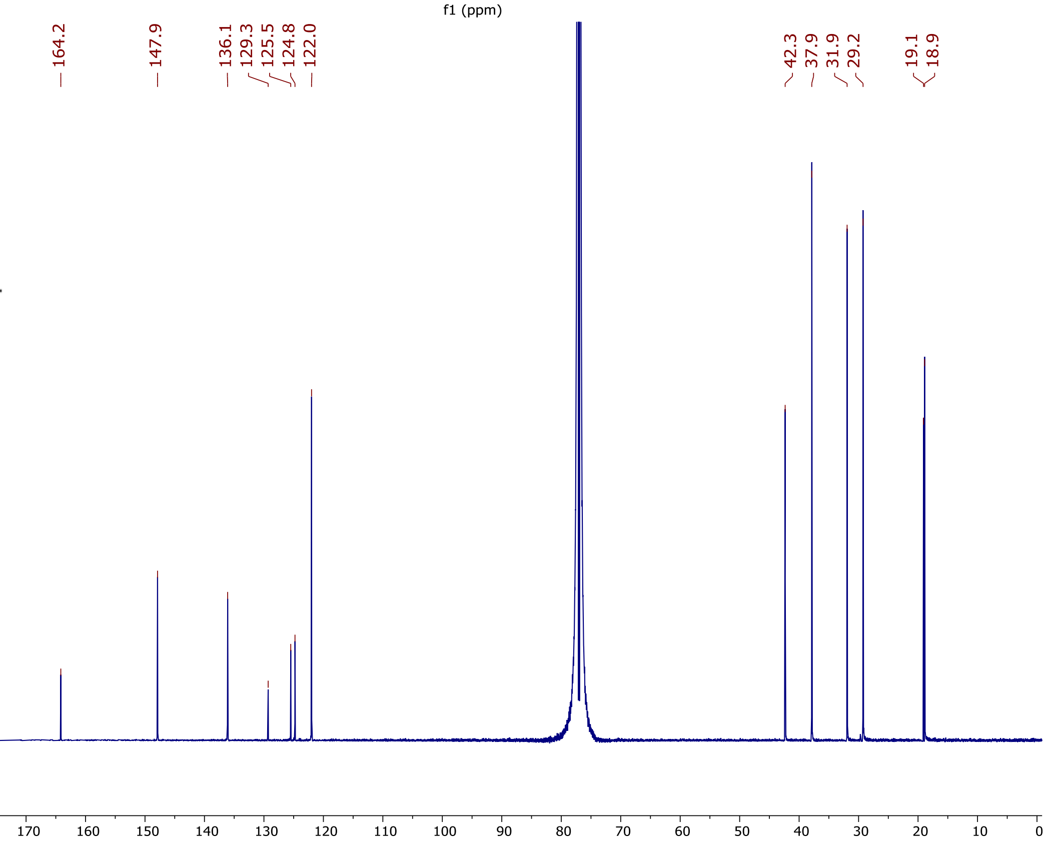


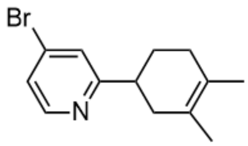
23 – [1]HNMR ($CDCl_3$)



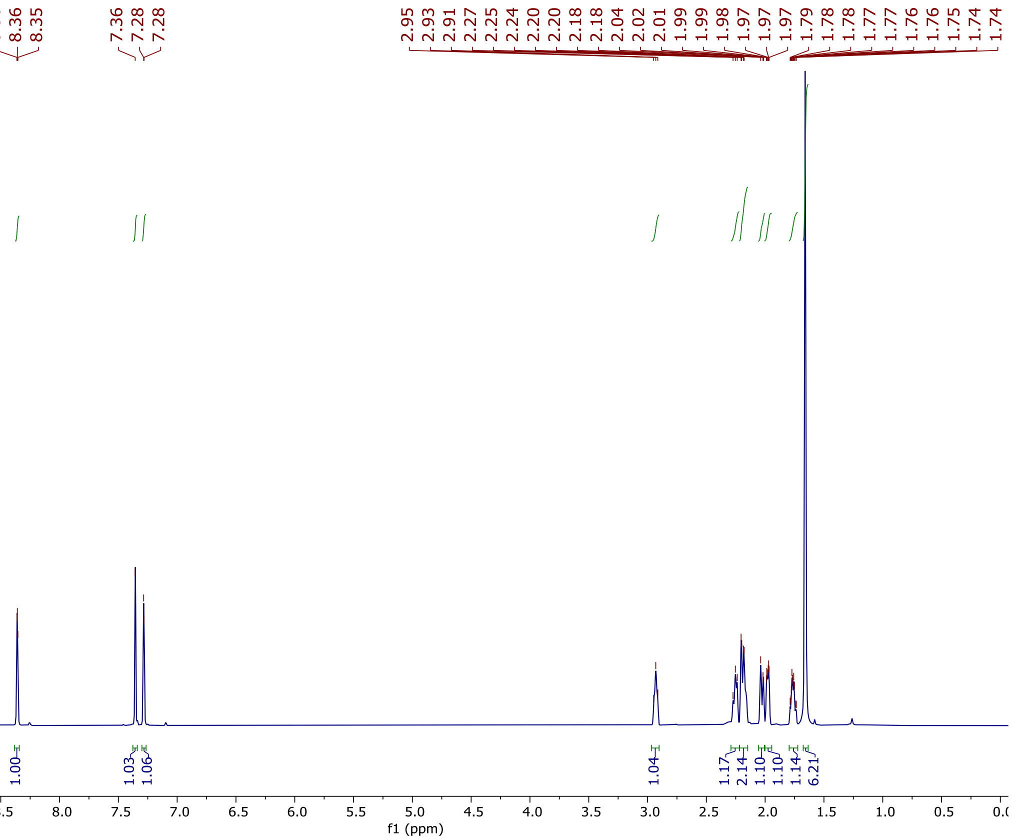


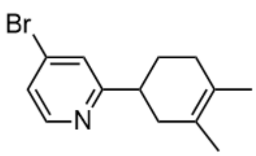
23 – [13]CNMR ($CDCl_3$)



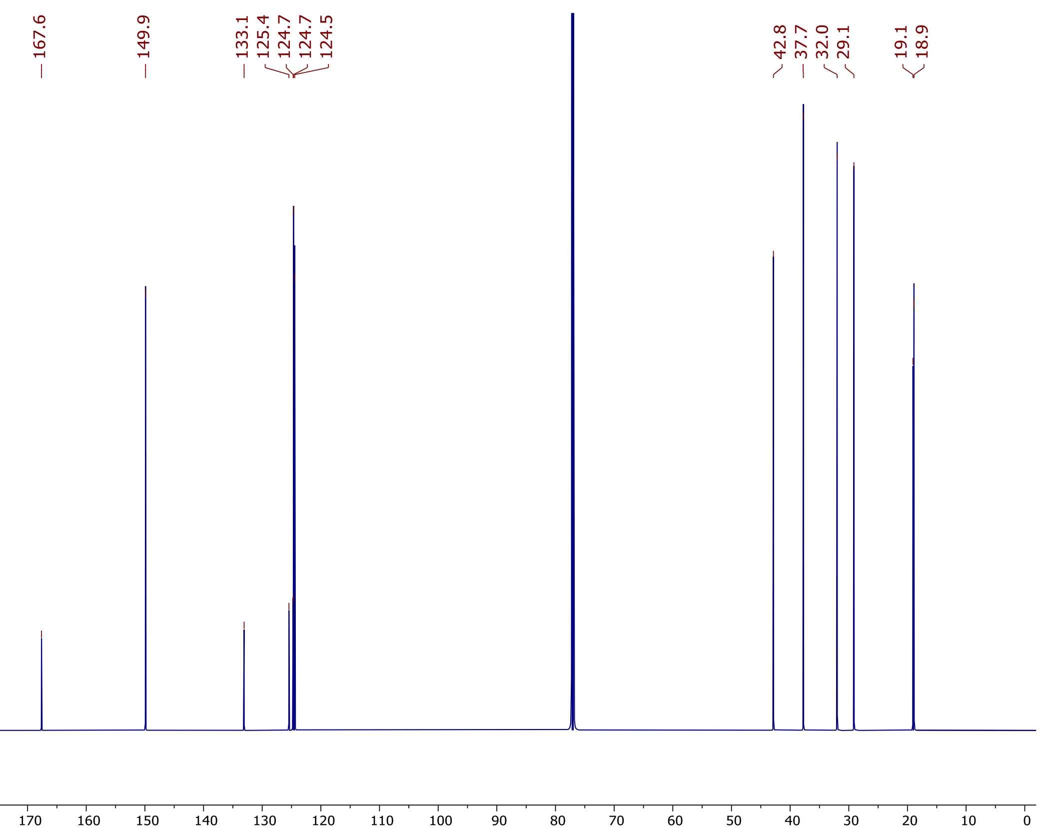


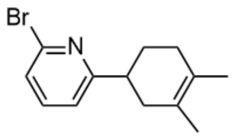
24 – ^{1}HNMR ($CDCl_3$)

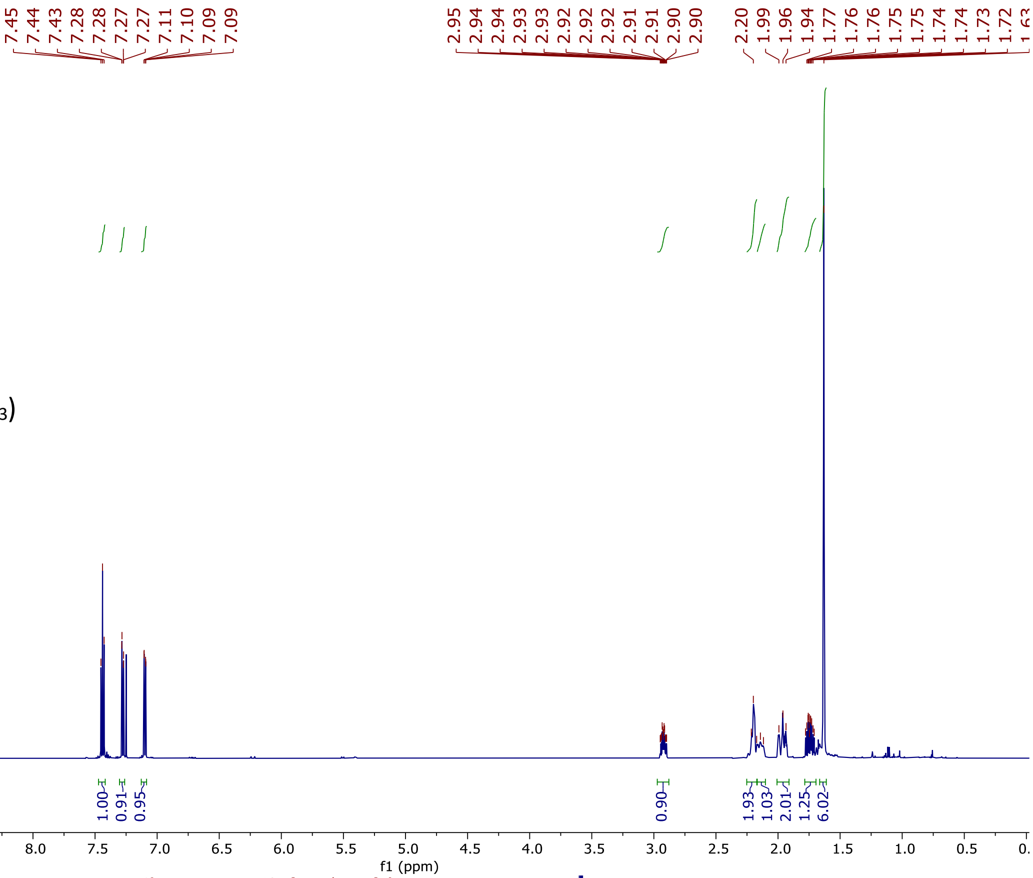




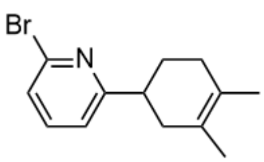
24 – ^{13}CNMR ($CDCl_3$)

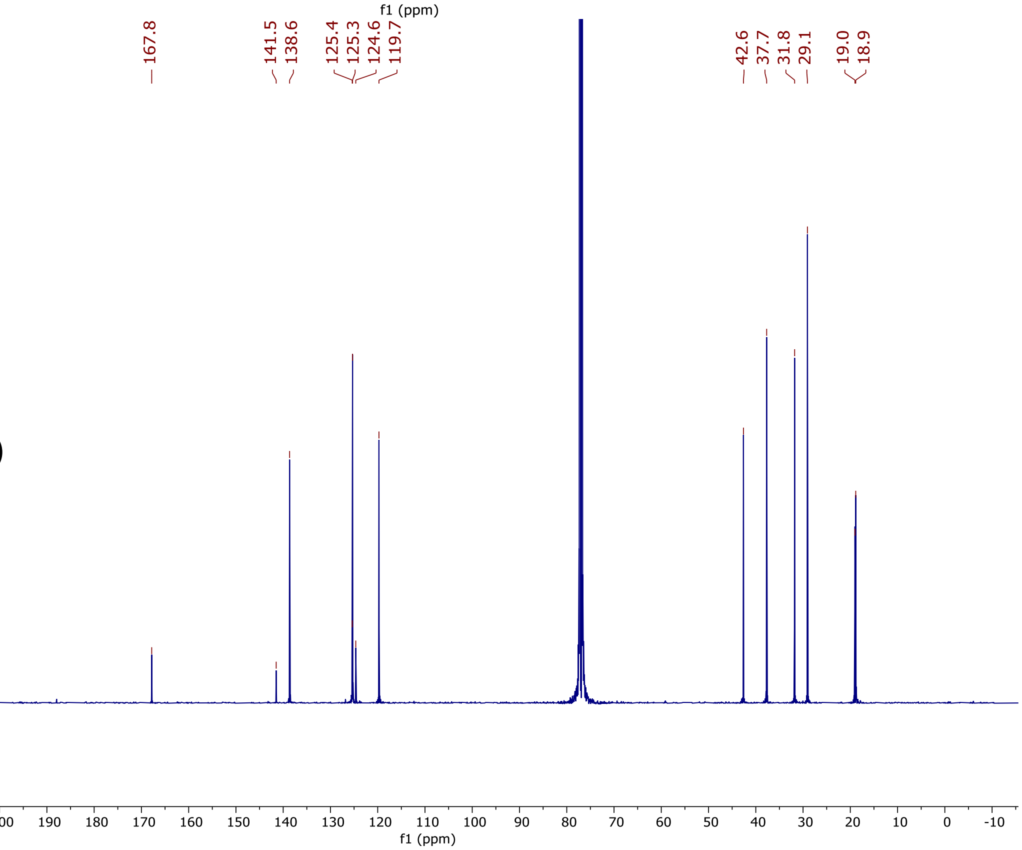




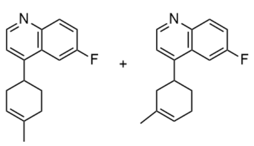


25 – ^{1}HNMR ($CDCl_3$)

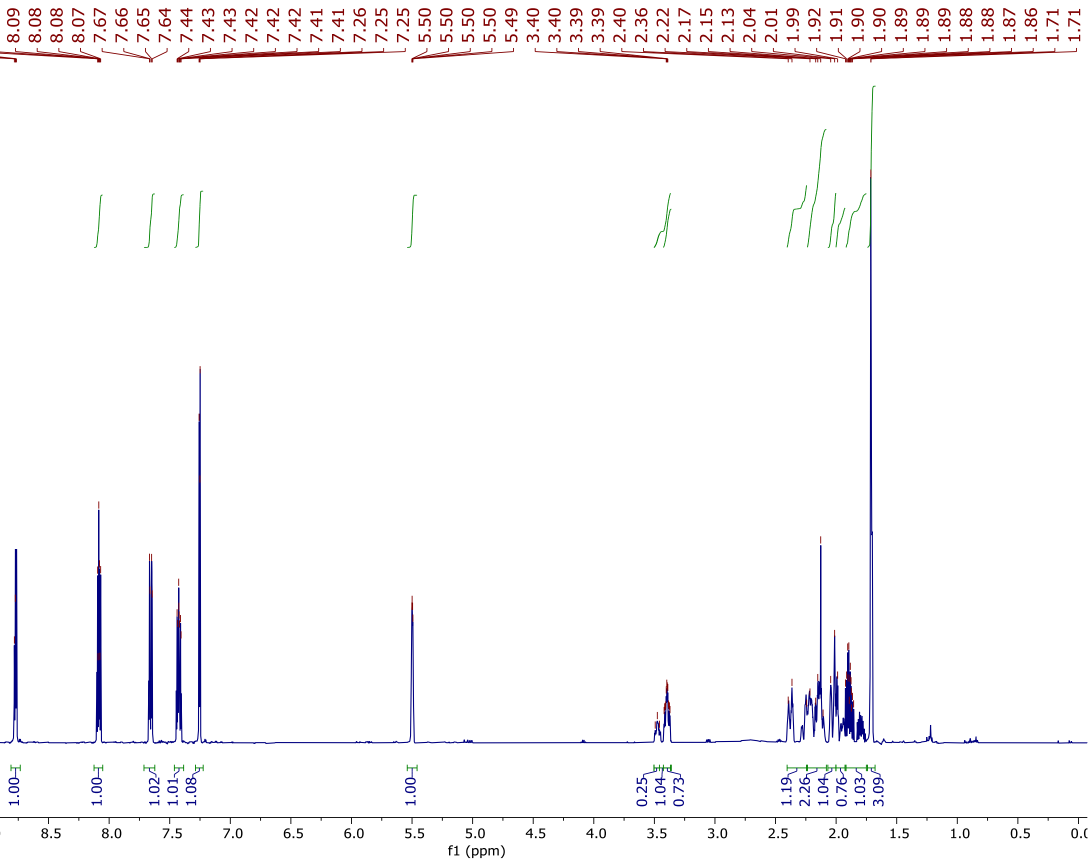


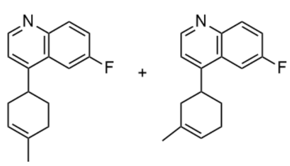


25 – ^{13}CNMR ($CDCl_3$)



28 – [1]HNMR ($CDCl_3$)





28 – [13]CNMR ($CDCl_3$)