

Supporting Information

Visible-Light Photoredox Catalysis with 9,10-Phenanthrene-9,10-dione as Catalyst: A Green Methodology for the Functionalisation of 3,4-dihydro-1,4-benzoxazin-2-ones through a Friedel-Crafts Reaction

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Table of Contents

1. General Experimental Methods.....	2
2. Characterization of the 3,4-dihydro-benzoxazin-2-ones derivatives 2d, 2e, 2f, 2g and 2h	2
3. UV-Vis absorption spectra of 9,10-phenanthrene-9,10-dione.....	4
4. Reaction Setup.....	4
5. Reaction Setup and Procedure for the Friedel-Crafts reaction with sunlight as visible-light radiation source.....	5
6. Specific Procedures for the Control Experiments.	5
7. References	6
8. NMR spectra	7

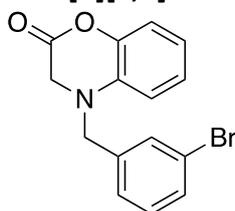
1. General Experimental Methods

Reactions were carried out in 5 mL vials under air unless otherwise indicated. Commercial reagents were used as purchased. Reactions were monitored by TLC analysis using Merck Silica Gel 60 F-254 thin layer plates and these are visualized using both an UV lamp (254 nm) and then a CAM solution (an aqueous solution of ceric ammonium molybdate). Flash column chromatography was performed on Merck Silica Gel 60, 0.040-0.063 mm. NMR spectra were run at 300 MHz for ^1H and 75 MHz for ^{13}C using residual nondeuterated solvent as internal standard (CHCl_3 : δ 7.26 and δ 77.00 ppm respectively, MeOH: δ 3.34 ppm and δ 49.87 ppm respectively, Acetone: δ 2.05 ppm and δ 29.84 ppm respectively). Chemical shifts are given in ppm. The carbon multiplicity was established by DEPT experiments. High resolution mass spectra (HRMS-ESI) were recorded on a AB SCIEX Triple TOFTM spectrometer equipped with an electrospray source with a capillary voltage of 4.5 kV (ESI).

All photocatalysts, indoles and related arenes were commercially available. 3,4-dihydro-benzoxazin-2-ones derivatives **2a**, **2b** and **2c** were synthesized according to a procedure published in the literature and the spectroscopic data (^1H -NMR and ^{13}C -NMR) match with those reported¹. 3,4-dihydro-benzoxazin-2-ones derivatives **2d**, **2e**, **2f**, **2g** and **2h** were synthesized according to the same procedure and were characterized by ^1H -NMR, ^{13}C -NMR and HRMS.

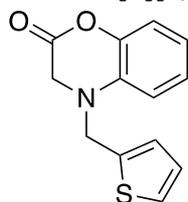
2. Characterization of the 3,4-dihydro-benzoxazin-2-ones derivatives **2d**, **2e**, **2f**, **2g** and **2h**

4-(3-bromobenzyl)-3,4-dihydro-2H-benzo[*b*][1,4]oxazin-2-one (**2d**)



Compound **2d** was obtained as a white oil (445 mg, 28% yield) after column chromatography; ^1H NMR (300 MHz, CDCl_3) δ 7.51 – 7.39 (m, 2H), 7.29 – 7.19 (m, 2H), 7.14 – 7.00 (m, 2H), 6.89 (td, J = 7.7, 1.4 Hz, 1H), 6.79 (dd, J = 8.0, 1.5 Hz, 1H), 4.34 (s, 2H), 3.81 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.60 (C), 141.77 (C), 138.15 (C), 134.41 (C), 131.11 (CH), 130.65 (CH), 130.53 (CH), 126.18 (CH), 125.32 (CH), 123.08 (C), 120.46 (CH), 117.18 (CH), 113.19 (CH), 53.10 (CH_2), 50.19 (CH_2); HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{13}\text{BrNO}_2$, 318,0130; found, 318.0127.

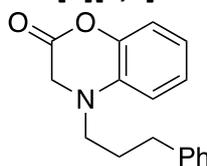
4-(thiophen-2-ylmethyl)-3,4-dihydro-2H-benzo[*b*][1,4]oxazin-2-one (**2e**)



Compound **2e** was obtained as a white solid (576 mg, 47% yield) after column chromatography; m.p. 73-74 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.27 (dd, J = 5.1, 1.3 Hz, 1H), 7.13 – 7.05 (m, 2H), 7.05 – 6.96 (m, 3H), 6.89 (ddd, J = 8.2, 7.2, 1.5 Hz, 1H), 4.58 (s, 2H), 3.80 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 164.75 (C), 141.85 (C), 137.64 (C), 133.88 (C), 127.15 (CH),

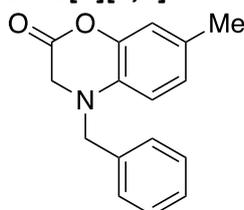
126.91 (CH), 125.91 (CH), 125.17 (CH), 120.37 (CH), 117.14 (CH), 113.21 (CH), 49.34 (CH₂), 48.16 (CH₂); HRMS (ESI) m/z : [M + H]⁺ calculated for C₁₅H₁₂NO₂S, 246.0589; found, 246.0586.

4-(3-phenylpropyl)-3,4-dihydro-2H-benzo[*b*][1,4]oxazin-2-one (2f)



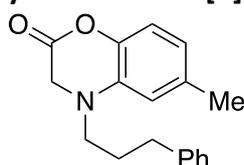
Compound **2f** was obtained as a greenish oil (734 mg, 58% yield) after column chromatography; ¹H NMR (300 MHz, CDCl₃) δ 7.21 – 7.13 (m, 2H), 7.11 – 7.02 (m, 3H), 6.93 – 6.85 (m, 2H), 6.70 – 6.62 (m, 1H), 6.51 (dd, *J* = 8.4, 1.5 Hz, 1H), 3.62 (s, 2H), 3.08 – 2.97 (m, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 1.78 (dq, *J* = 9.1, 7.5 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 164.60 (C), 141.46 (C), 140.76 (C), 134.18 (C), 128.32 (CH), 128.17 (CH), 125.98 (CH), 125.01 (CH), 119.14 (CH), 116.73 (CH), 112.35 (CH), 49.65 (CH₂), 48.24 (CH₂), 32.72 (CH₂), 26.35 (CH₂); HRMS (ESI) m/z : [M + H]⁺ calculated for C₁₇H₁₈NO₂, 268.1338; found, 268.1340.

4-benzyl-7-methyl-3,4-dihydro-2H-benzo[*b*][1,4]oxazin-2-one (2g)



Compound **2g** was obtained as a colourless oil (899 mg, 71% yield) after column chromatography; ¹H NMR (300 MHz, CDCl₃) δ 7.42 – 7.28 (m, 5H), 6.91 (d, *J* = 1.7 Hz, 1H), 6.86 (ddd, *J* = 8.2, 1.9, 0.7 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 4.33 (s, 2H), 3.74 (s, 2H), 2.29 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 165.21 (C), 141.78 (C), 135.77 (C), 132.48 (C), 130.16 (C), 128.91 (CH), 127.87 (CH), 127.85 (CH), 125.60 (CH), 117.54 (CH), 113.21 (C), 53.76 (CH₂), 50.08 (CH₂), 20.44 (CH₃); HRMS (ESI) m/z : [M + H]⁺ calculated for C₁₆H₁₆NO₂, 254.1181; found, 254.1183.

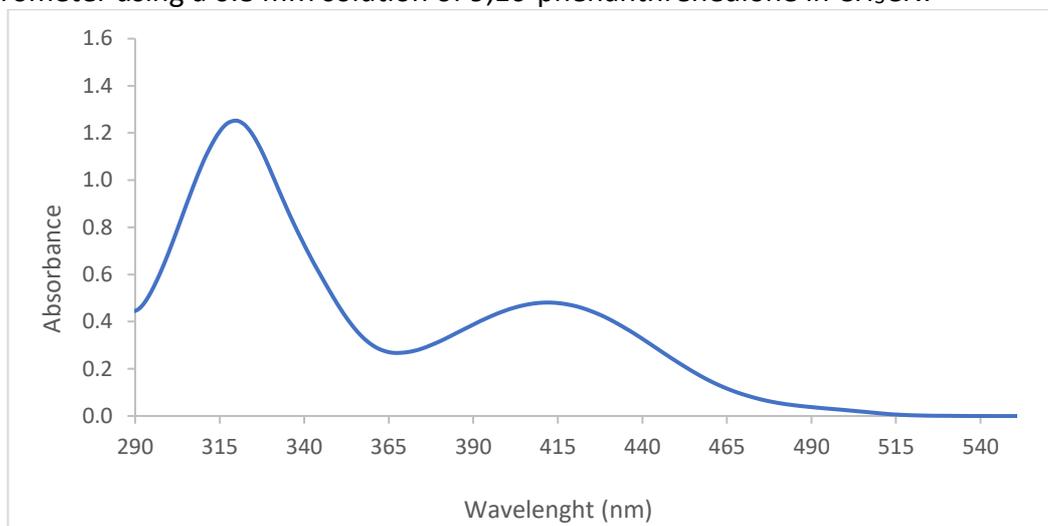
6-methyl-4-(3-phenylpropyl)-3,4-dihydro-2H-benzo[*b*][1,4]oxazin-2-one (2h)



Compound **2h** was obtained as a colourless oil (735 mg, 55% yield) after column chromatography; ¹H NMR (300 MHz, CDCl₃) δ 7.36 – 7.28 (m, 2H), 7.24 – 7.19 (m, 3H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.61 (ddd, *J* = 8.1, 1.9, 0.7 Hz, 1H), 6.40 (d, *J* = 1.5 Hz, 1H), 3.80 (s, 2H), 3.19 (dd, *J* = 8.3, 6.7 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.26 (s, 3H), 2.02 – 1.90 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 165.02 (C), 140.96 (C), 139.75 (C), 134.96 (C), 134.04 (C), 128.56 (CH), 128.44 (CH), 126.23 (CH), 119.91 (CH), 116.70 (CH), 113.15 (CH), 50.08 (CH₂), 48.35 (CH₂), 32.89 (CH₂), 26.59 (CH₂), 21.29 (CH₃). HRMS (ESI) m/z : [M + H]⁺ calculated for C₁₈H₂₀NO₂, 282.1494; found, 282.1493.

3. UV-Vis absorption spectra of 9,10-phenanthrenedione

The UV-Vis absorption spectra was recorded in a double beam UV-Visible absorption spectrometer using a 0.8 mM solution of 9,10-phenanthrenedione in CH₃CN.



The spectra shows two maximums of absorption:

- A strong absorption at 320 nm (Ultraviolet)
- A medium absorption at 412 nm (Visible)

4. Reaction Setup:

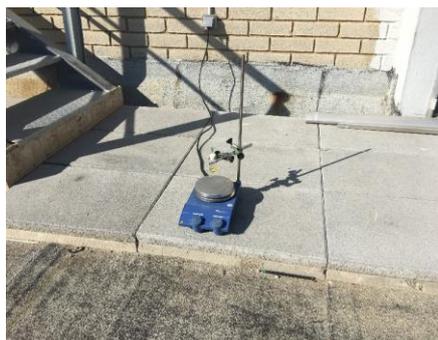
Reaction Setup:

In all cases, the reaction mixture was irradiated with Hidalgo's Group Adjustable LED light (5W, 350 lumen, REF: 64180) from 2 cm away. The temperature at this distance was 26-28 °C.



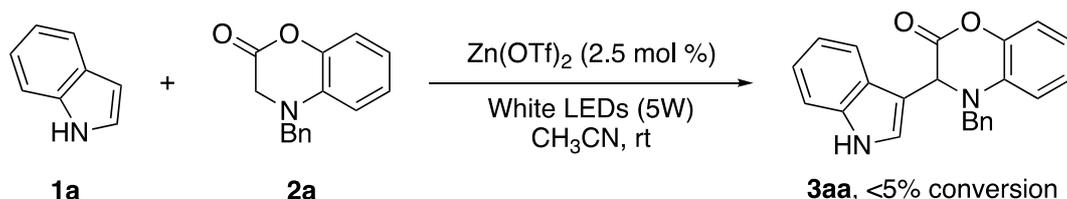
5. Reaction Setup and Procedure for the Friedel-Crafts reaction with sunlight as visible-light radiation source.

In a 10 mL round-bottomed flask were placed indole (**1a**, 11.7 mg, 0.10 mmol), 4-benzyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-2-one (**2a**, 35.8 mg, 0.15 mmol), Zn(OTf)₂ (0.0025 mmol, 2.5 mol %) and 9,10-phenanthrene-9,10-dione (0.005 mmol, 5 mol %). Then, the mixture was dissolved in non-dried acetonitrile (1 mL) and was placed in the upper part of the building in sunny hours (*vide infra*). The reaction was monitored by TLC and was stopped when indole was consumed (5 hours after). The resulted reaction mixture was purified by column chromatography using hexane:AcOEt mixtures (from 95:5 to 85:15) to afford the pure product (**3aa**, 30.8 mg, 0.087 mmol, 87% yield) as a colourless oil.



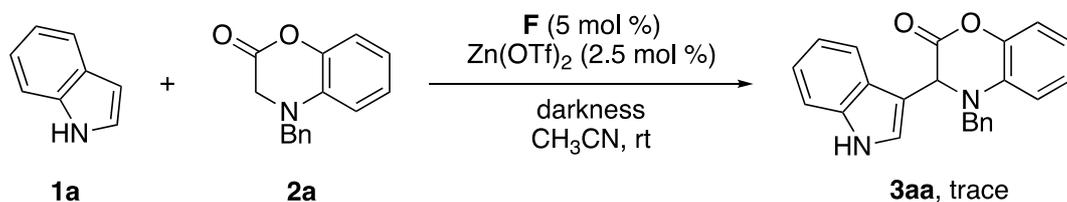
6. Specific Procedures for the Control Experiments.

Control A: Friedel-Crafts reaction between 4-benzyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-2-one and indole in the absence of 9,10-phenanthrene-9,10-dione.



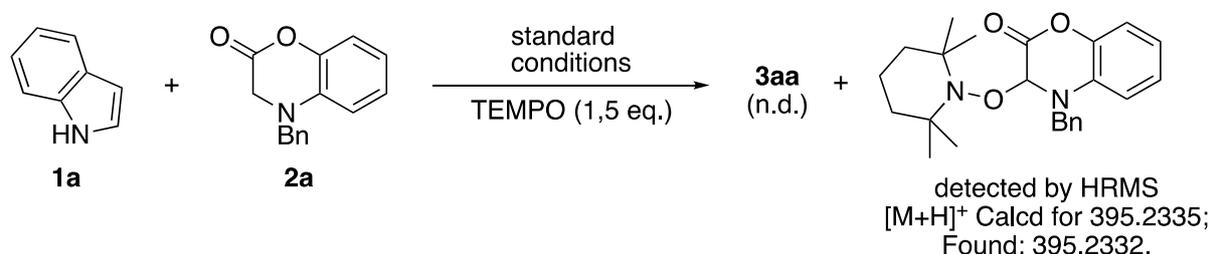
Following the General Procedure A without the addition of 9,10-phenanthrene-9,10-dione the reaction mixture was stirred for 72 h under the typical irradiation conditions. The crude reaction mixture was analysed by ¹H-NMR and <5% of conversion to **3aa** was observed.

Control B: Friedel-Crafts reaction between 4-benzyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-2-one and indole in the darkness.



Following the General Procedure A the reaction mixture was stirred for 72 h in the darkness. The crude reaction mixture was analysed by TLC only a trace amount of **3aa** was observed.

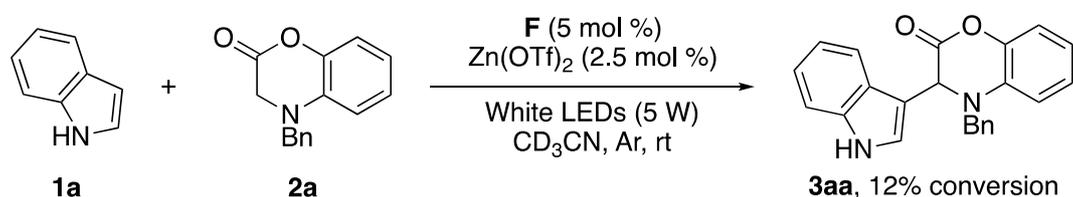
Control C: Friedel-Crafts reaction between 4-benzyl-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one and indole in the presence of TEMPO.



Following the General Procedure A with the addition of TEMPO (23.4 mg, 1.5 equivalents), the reaction mixture was stirred for 24 h under the typical irradiation conditions. The crude reaction mixture was analysed by HRMS and no conversion to **3aa** was observed, but the adduct of **2a** with TEMPO was detected.

Control D: Friedel-Crafts reaction between 4-benzyl-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one and indole under Ar.

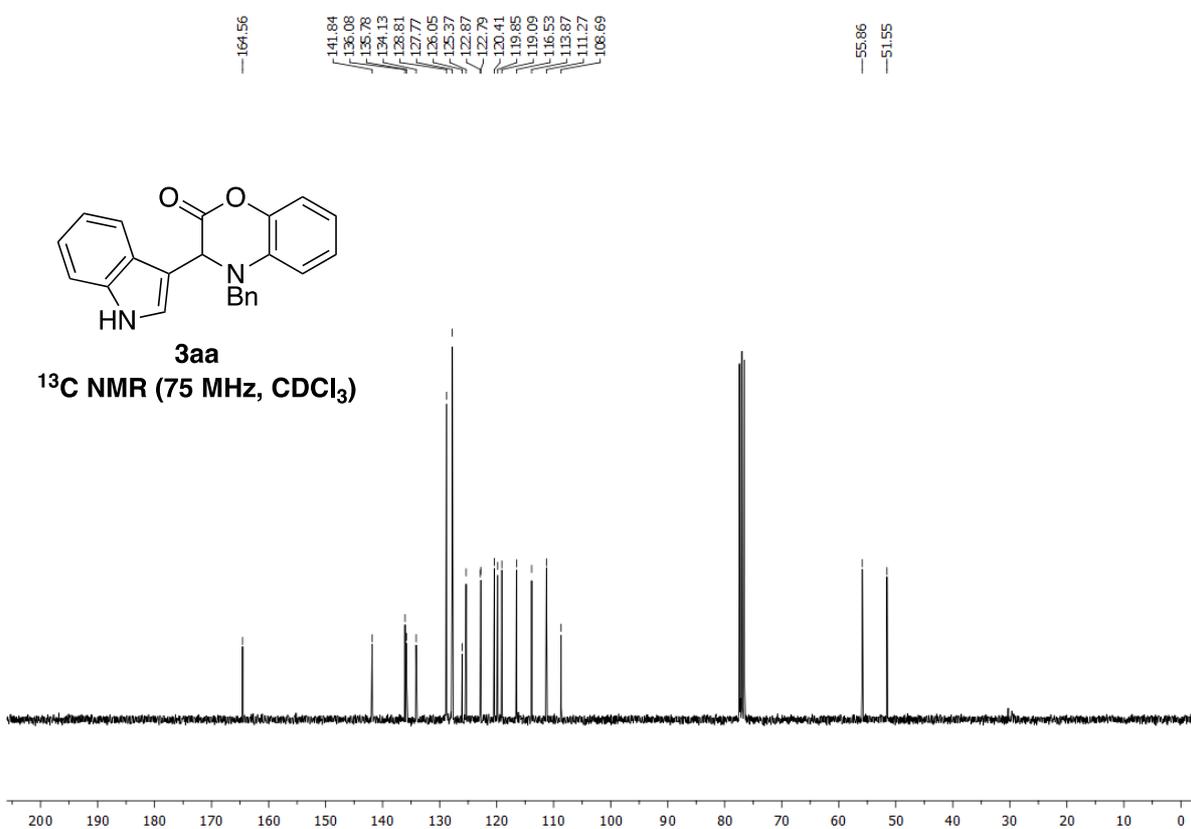
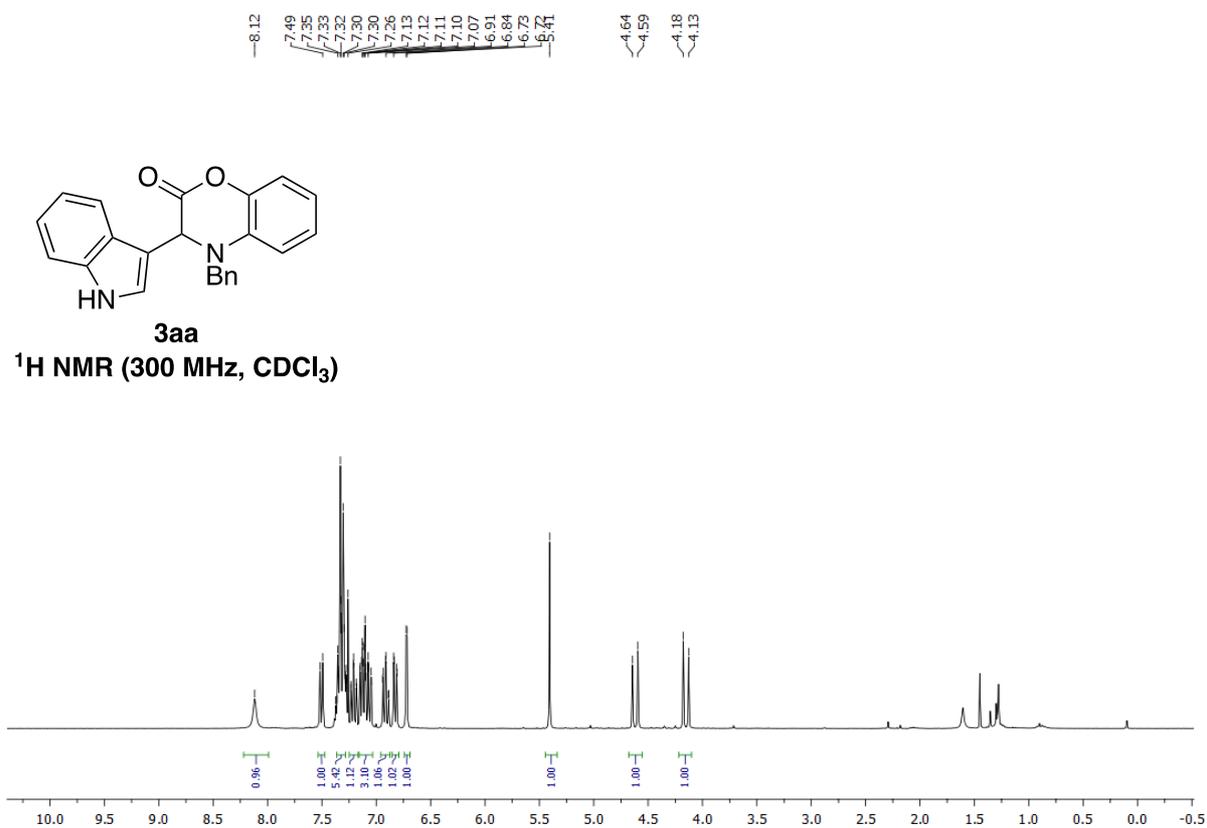
Following the General Procedure A but using CD₃CN instead of CH₃CN, the reaction mixture was stirred for 24 h under the typical irradiation conditions in argon atmosphere. The crude reaction mixture was analysed by ¹H-NMR (NOTE: it is important to fill the NMR tube with Ar prior to introduce the sample) and 12% of conversion to **3aa** was observed.

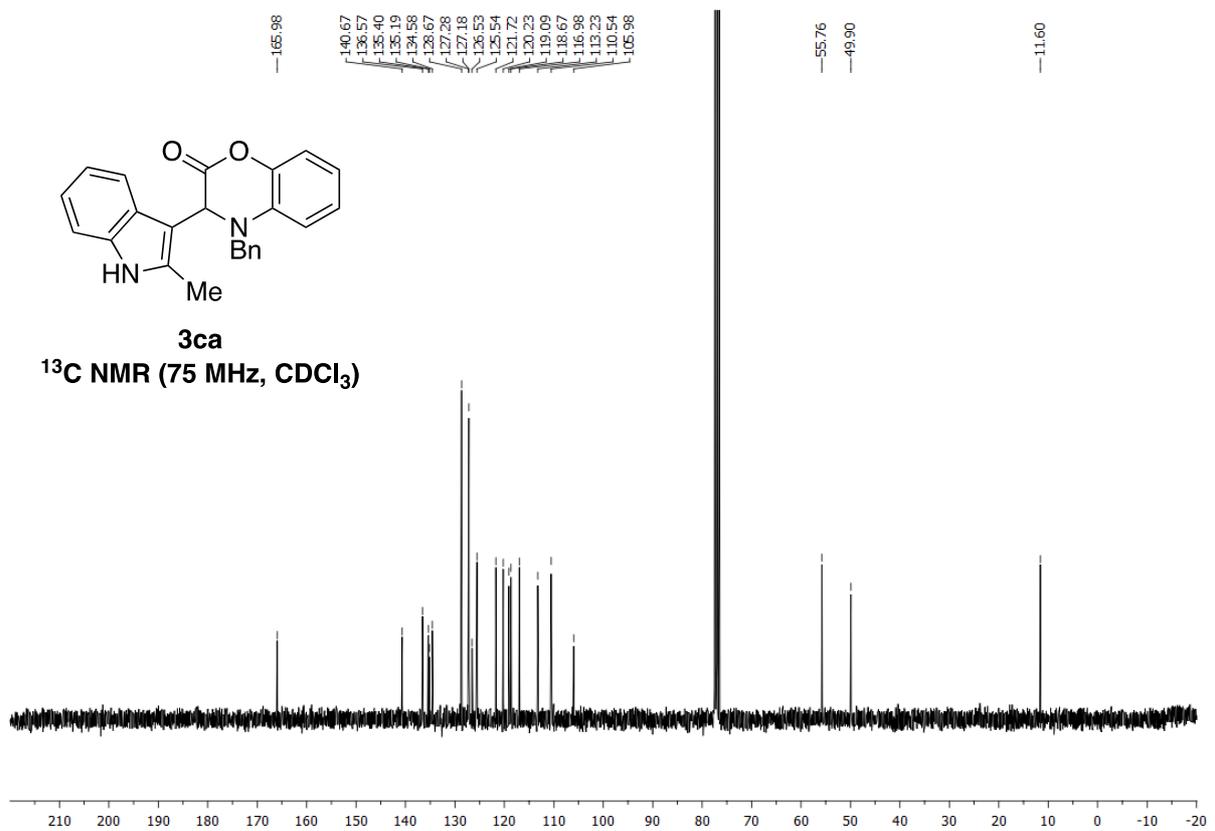
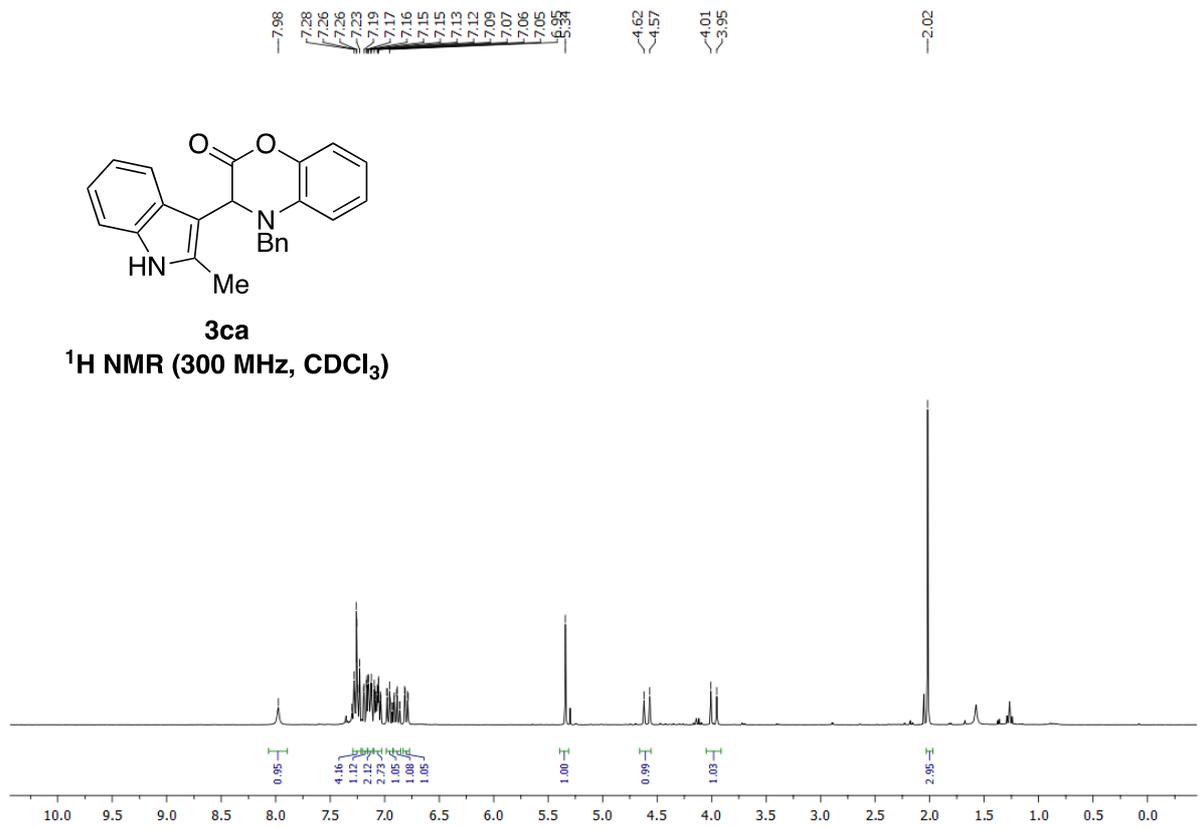


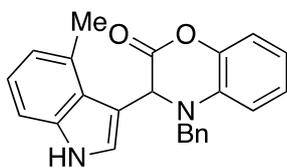
7. References

1. *Tetrahedron* **2008**, *64*, 5756 - 5761.
2. *RSC Adv.*, **2018**, *8*, 19580-19584.

8. NMR spectra

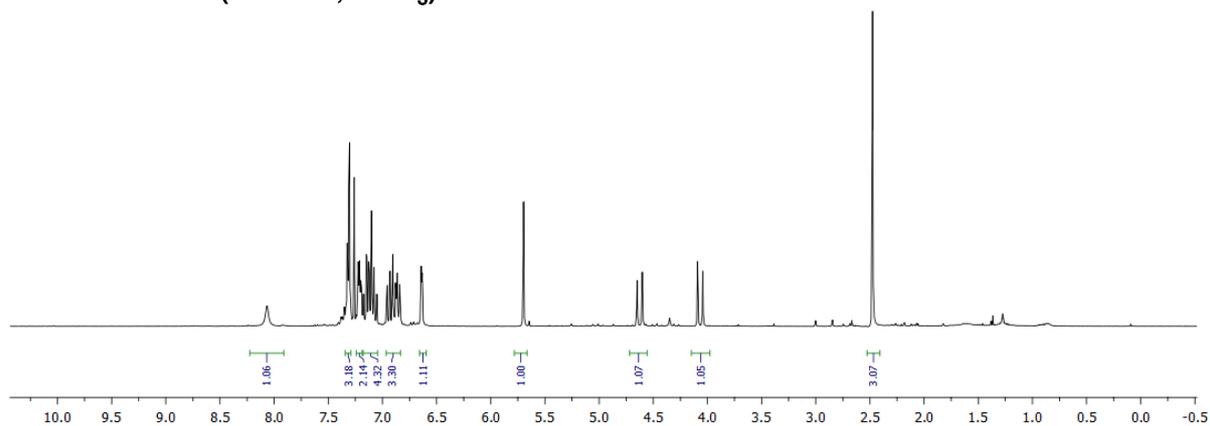




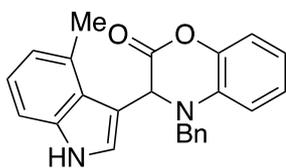


3da

¹H NMR (300 MHz, CDCl₃)

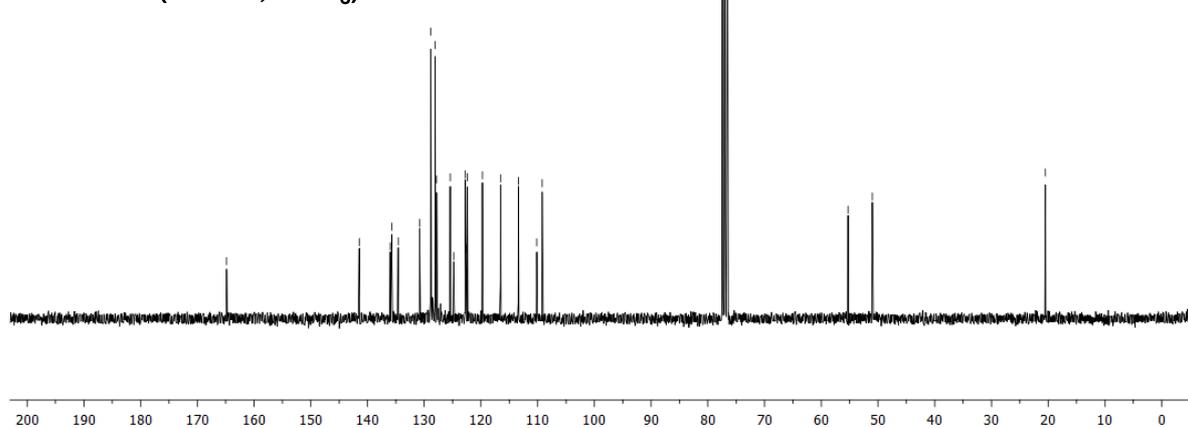


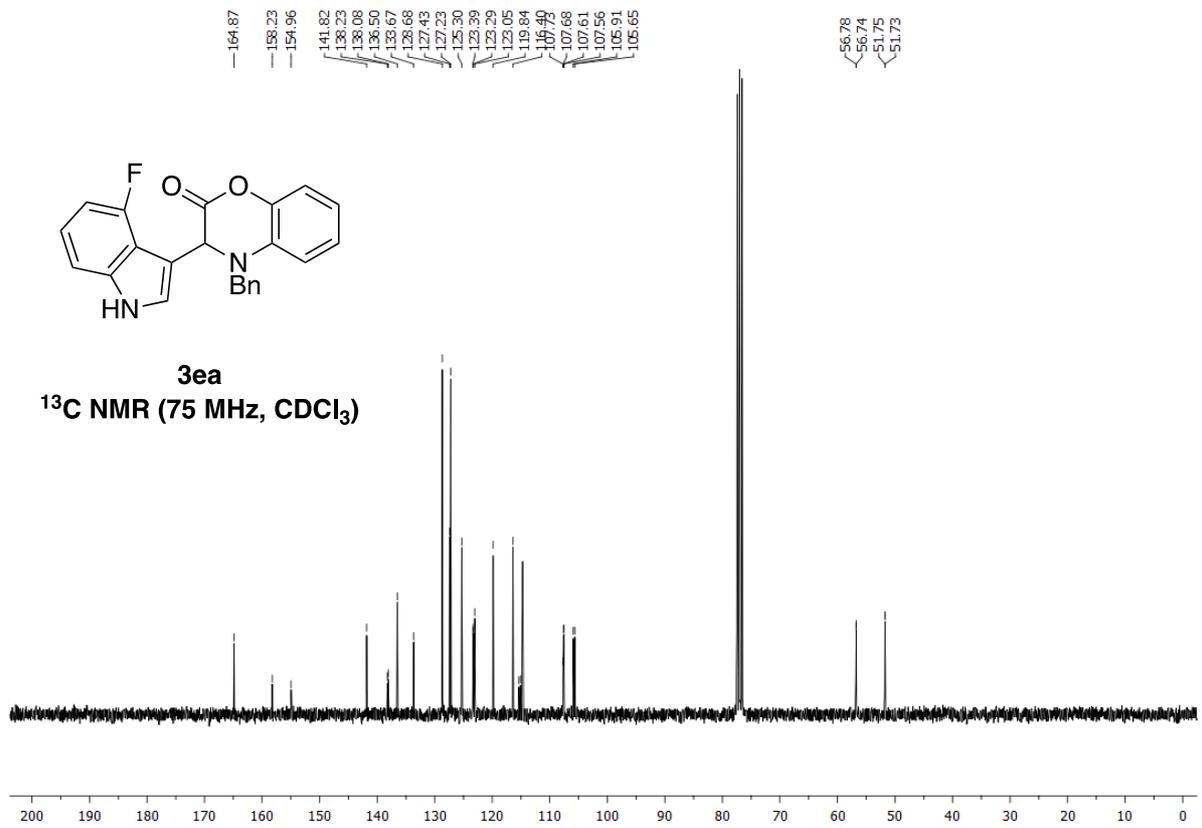
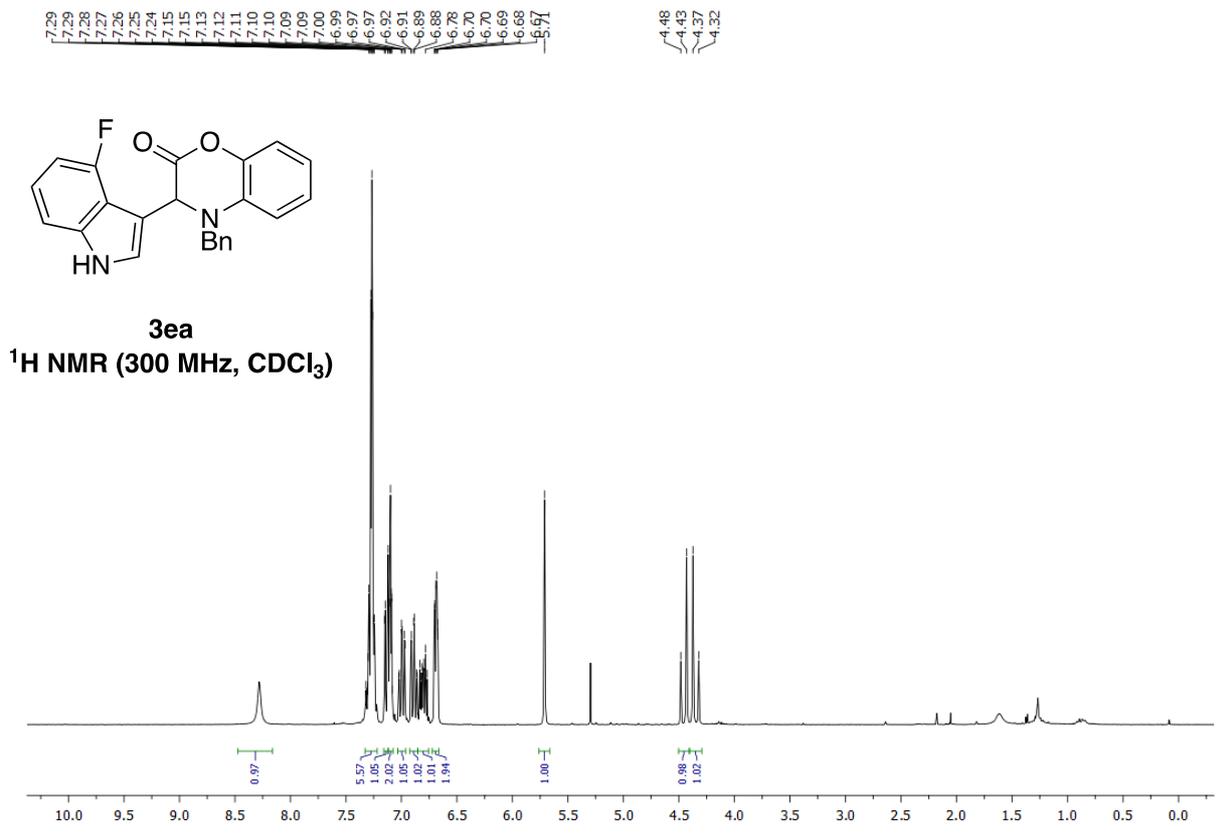
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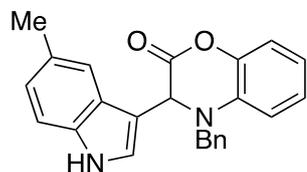


3da

¹³C NMR (75 MHz, CDCl₃)

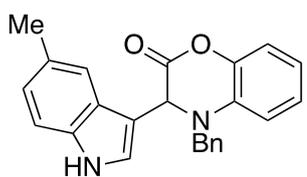
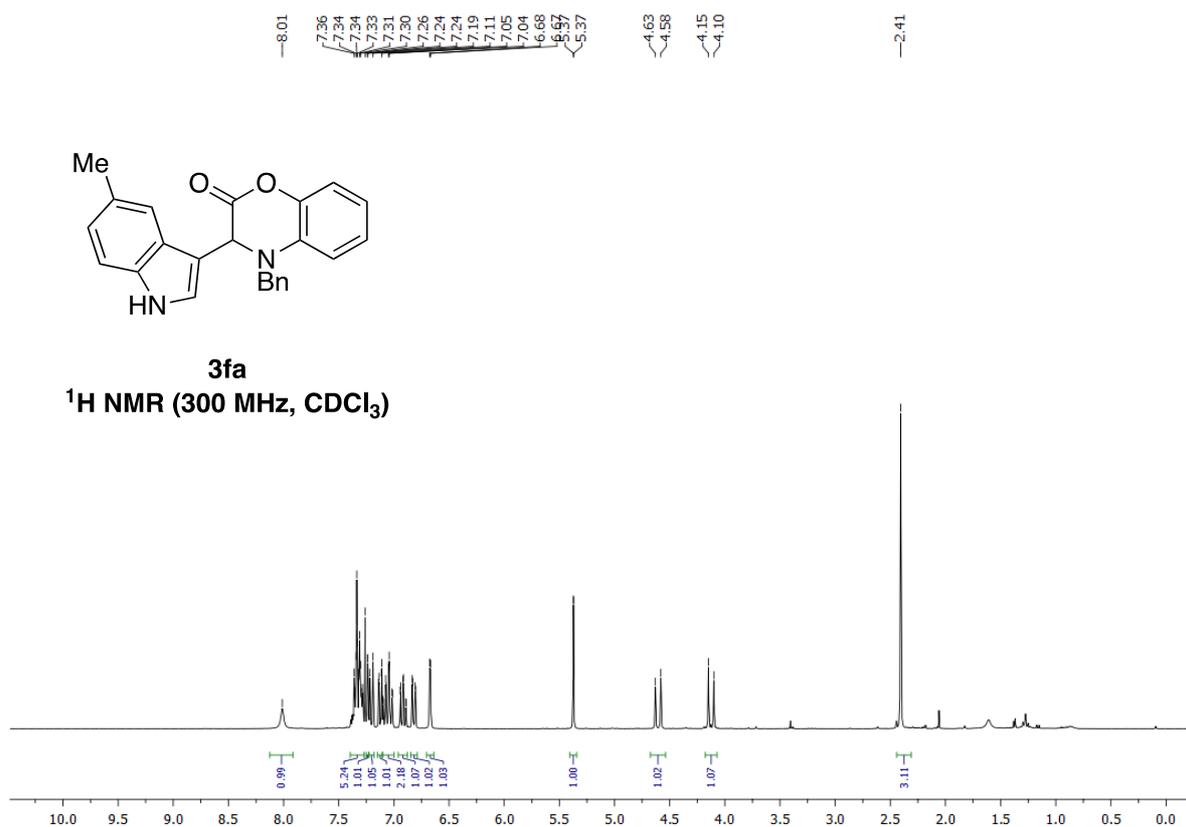






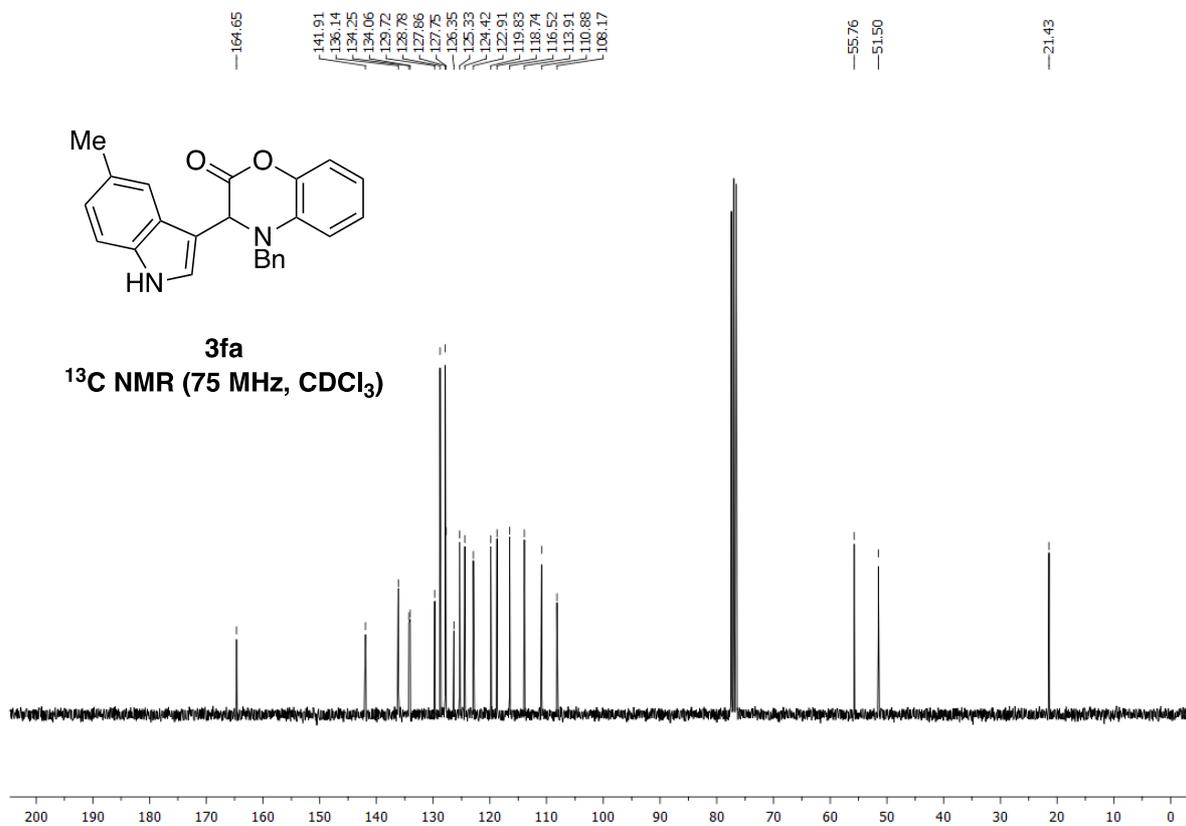
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¹H NMR (300 MHz, CDCl₃)

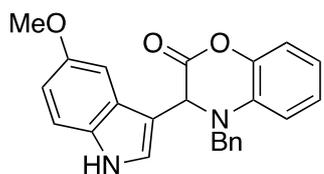


3fa

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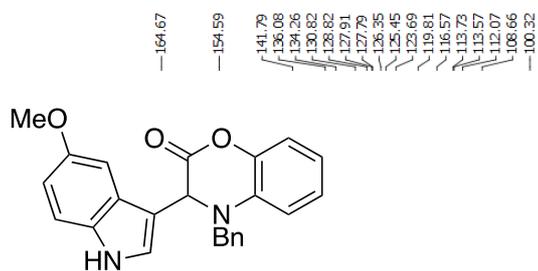
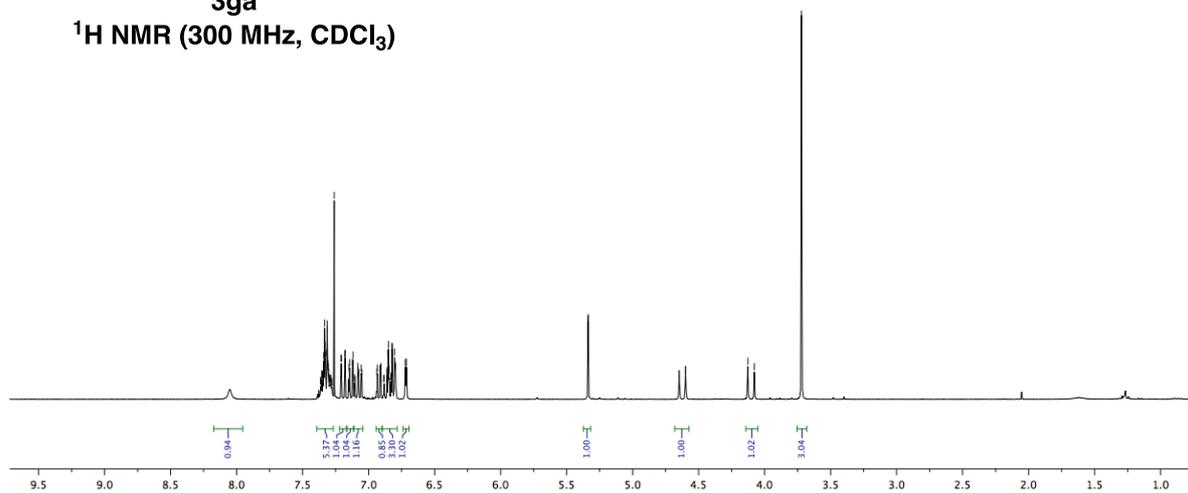


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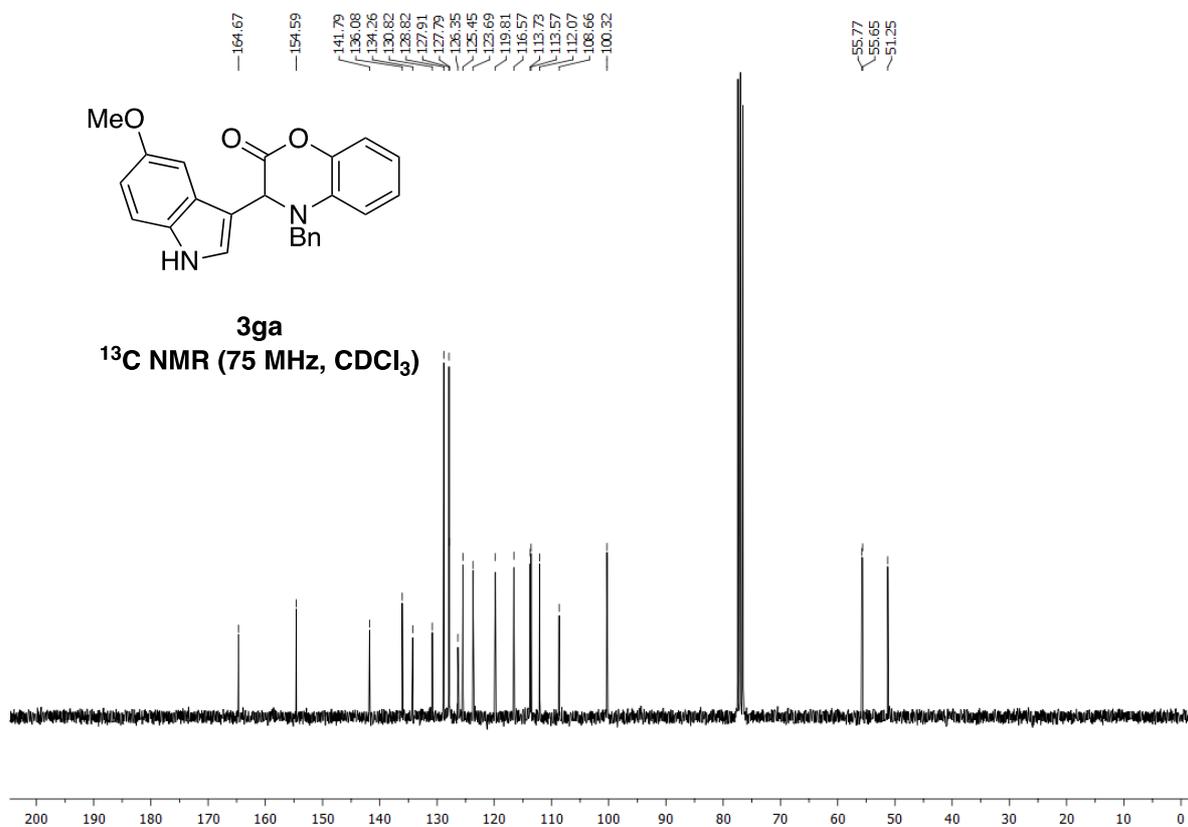
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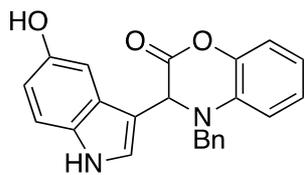
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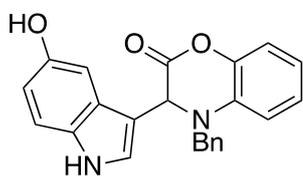
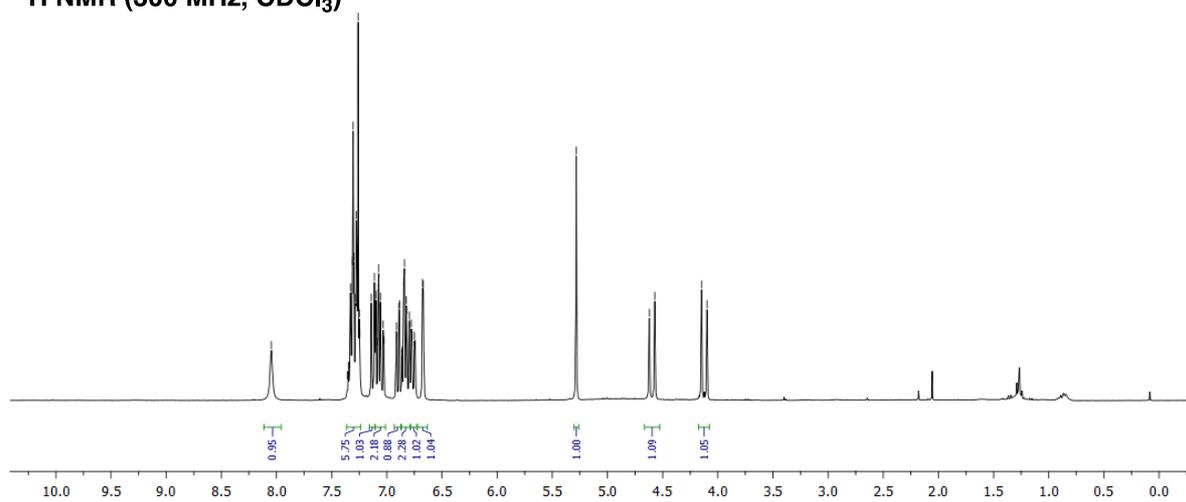
¹³C NMR (75 MHz, CDCl₃)





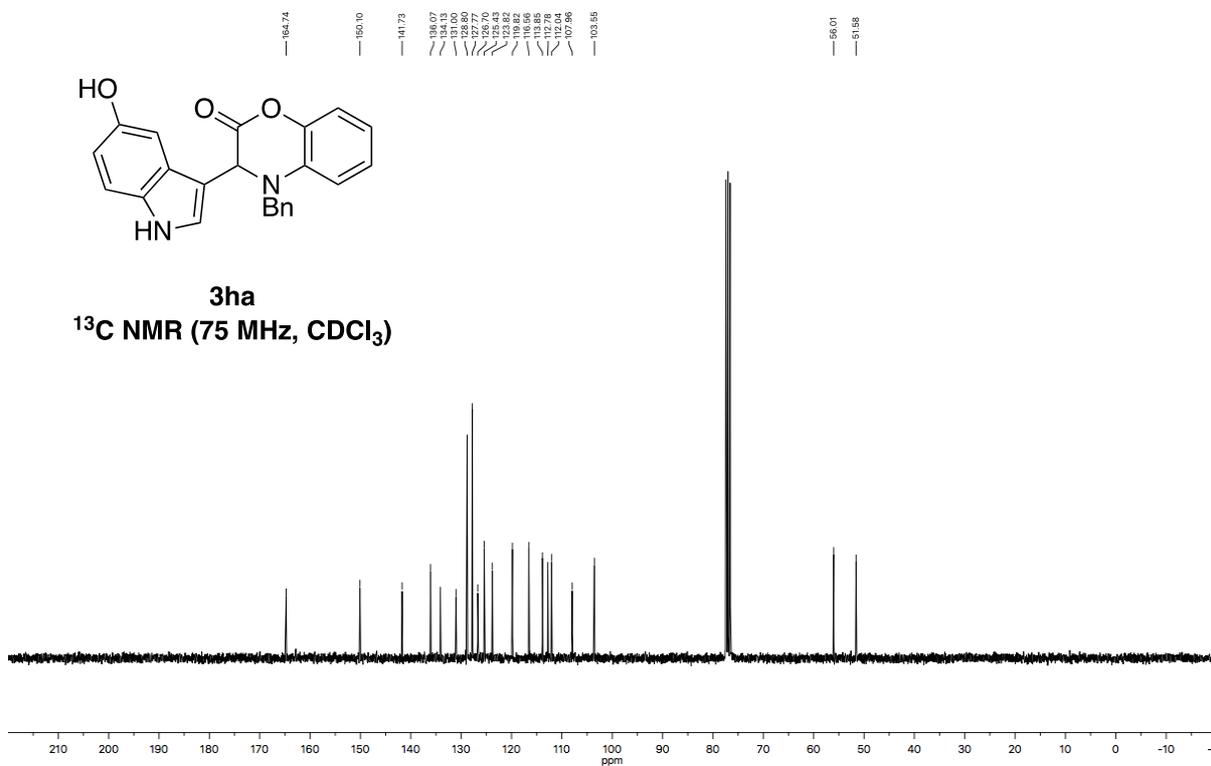
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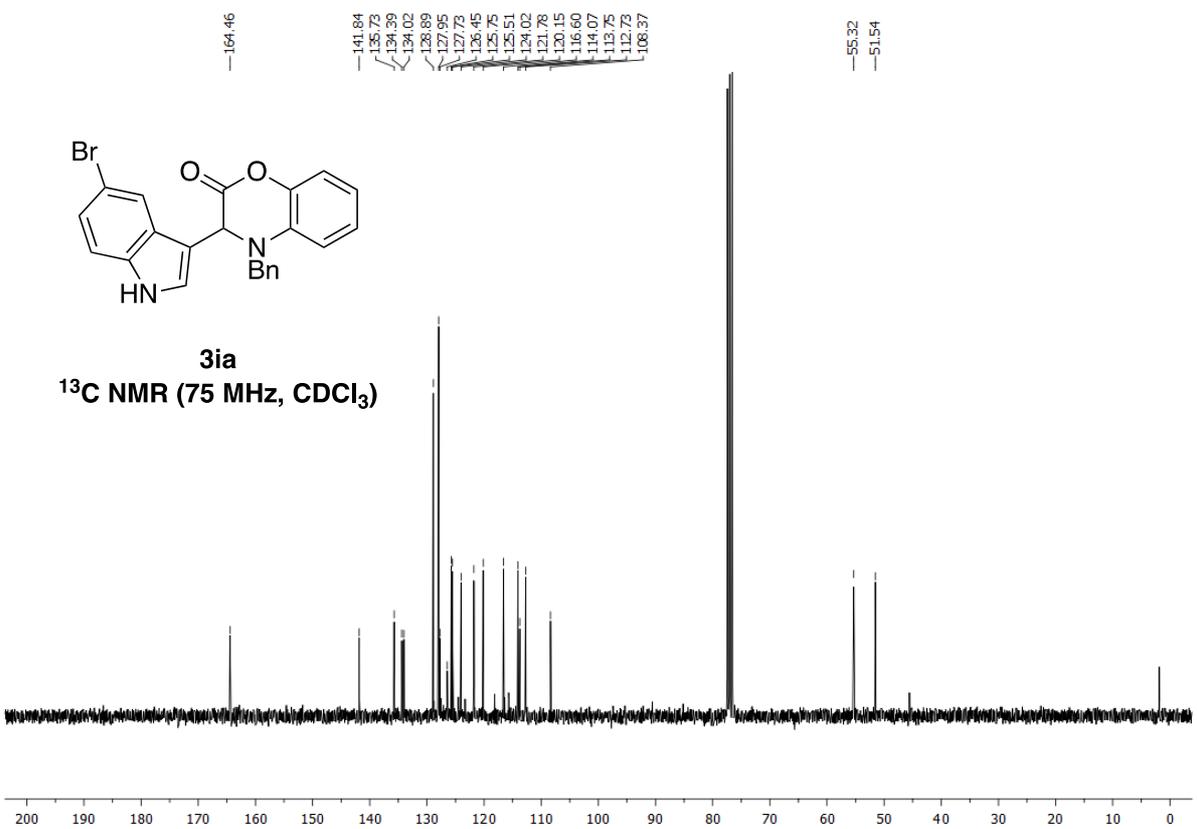
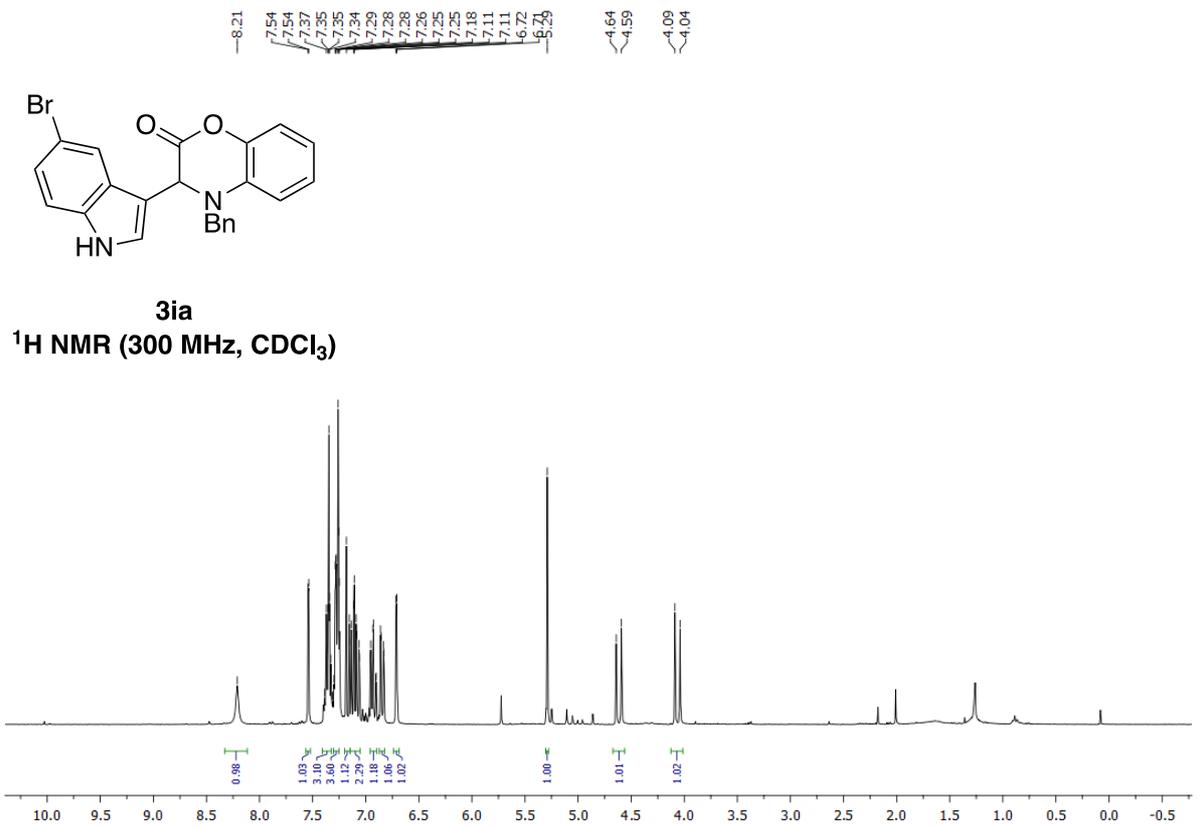
¹H NMR (300 MHz, CDCl₃)

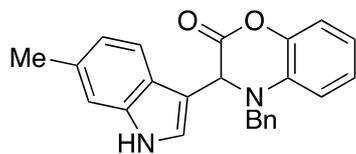


3ha

¹³C NMR (75 MHz, CDCl₃)

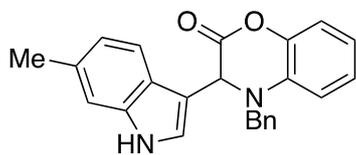
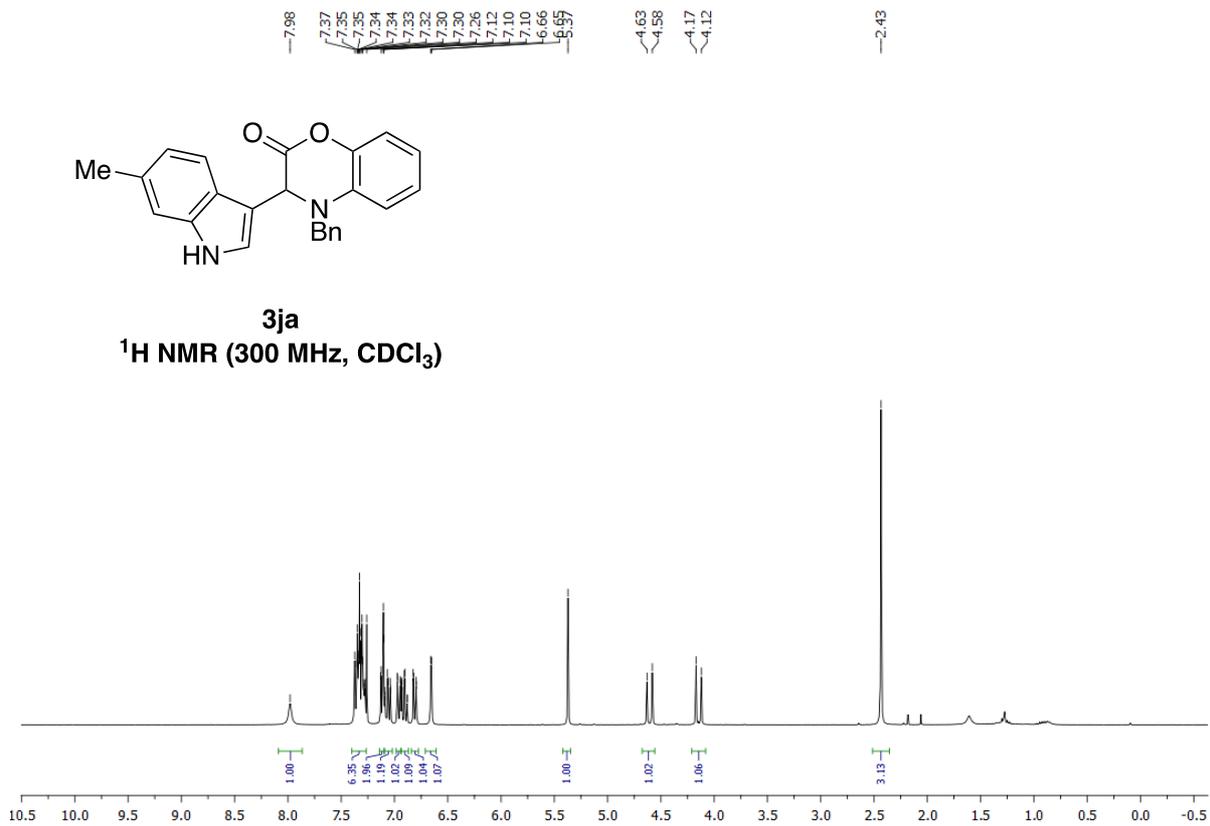






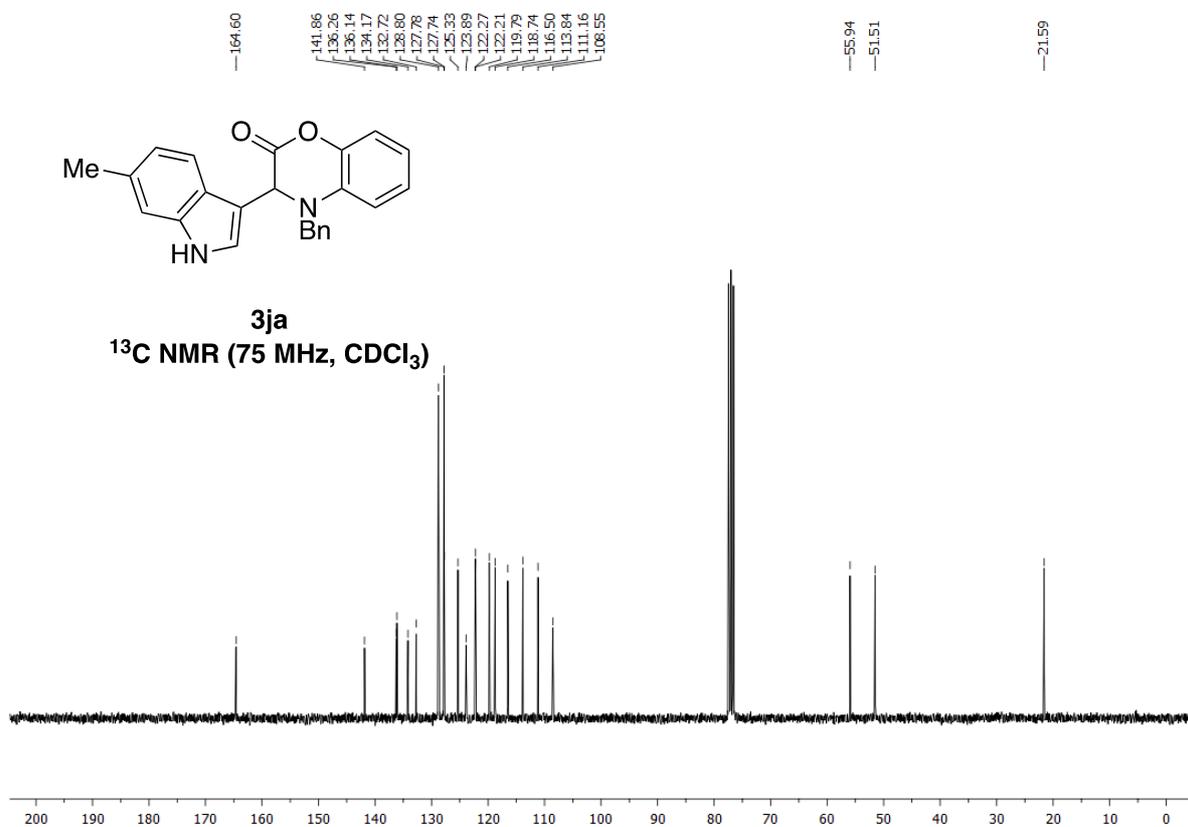
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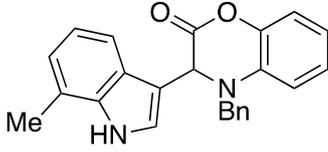


3ja

¹³C NMR (75 MHz, CDCl₃)

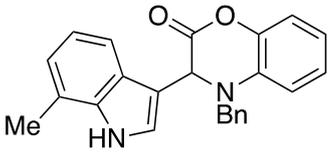
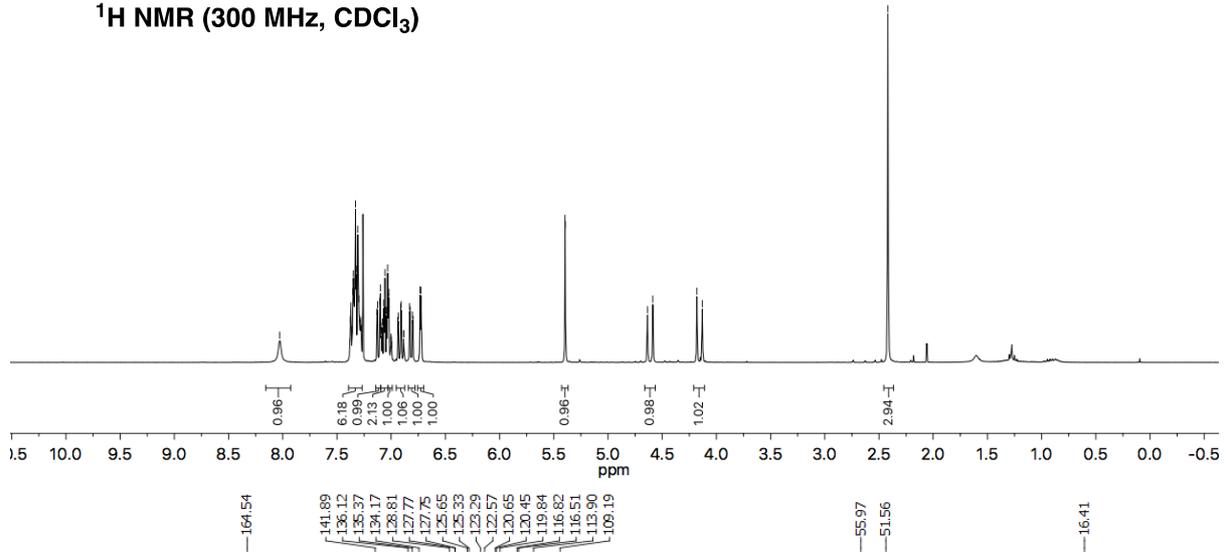


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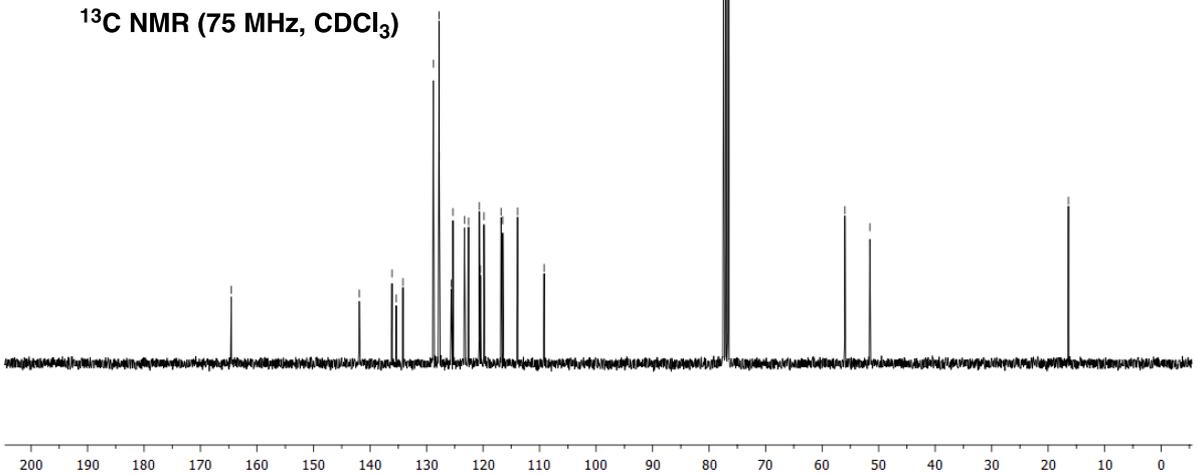
3ka

¹H NMR (300 MHz, CDCl₃)

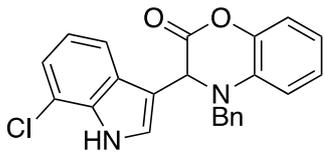


3ka

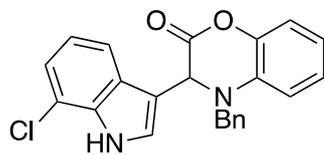
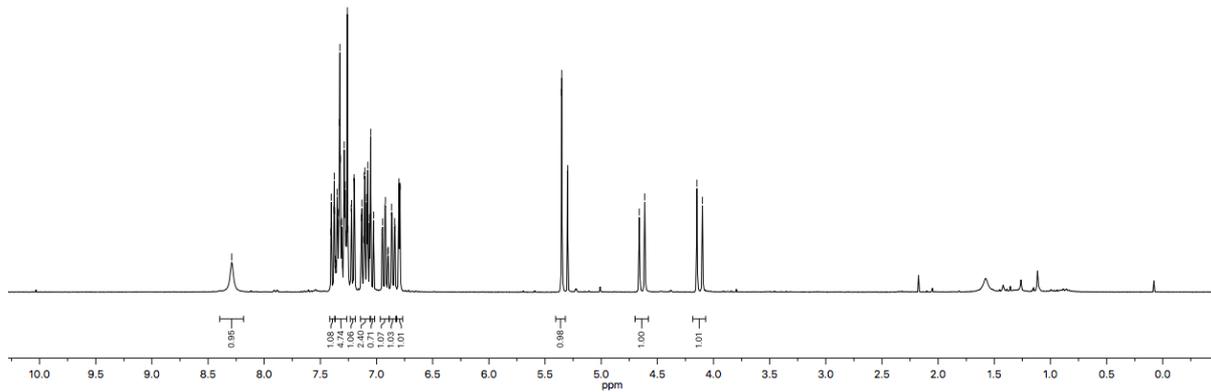
¹³C NMR (75 MHz, CDCl₃)



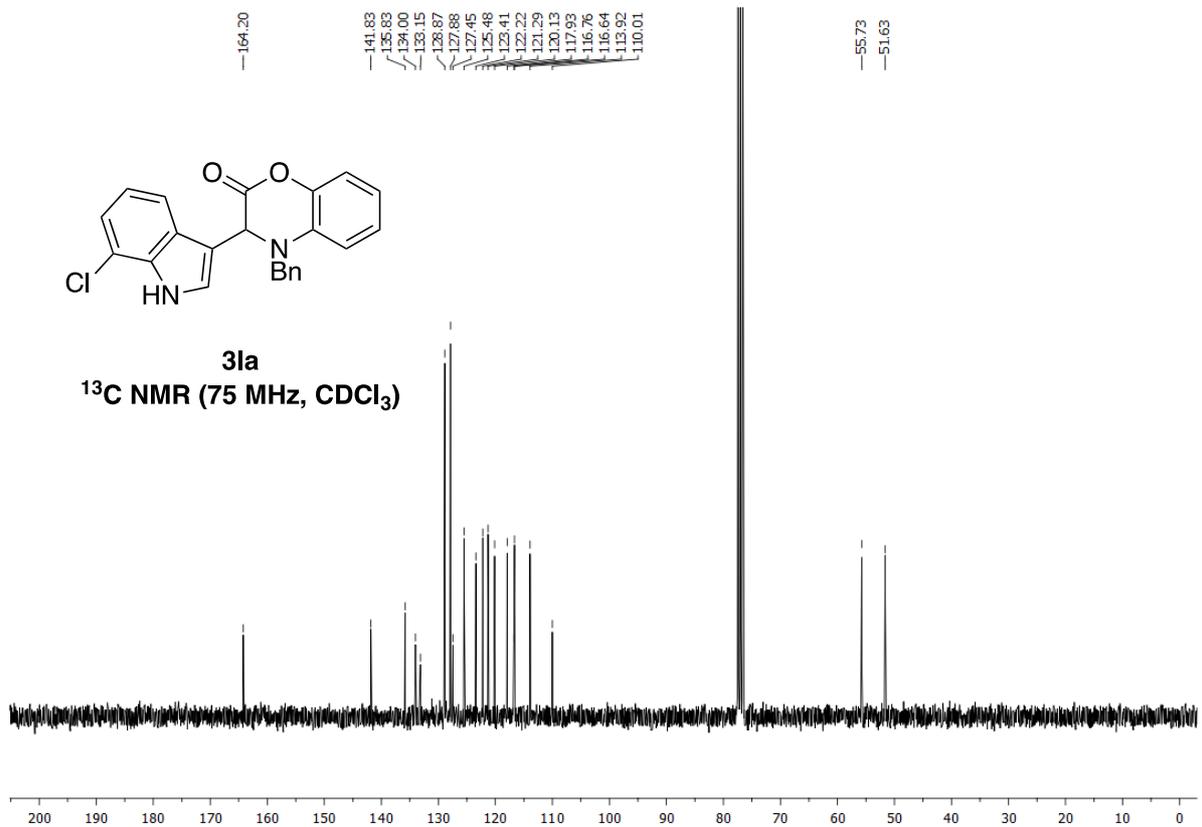
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7.37
7.36
7.35
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7.33
7.32
7.32
7.30
7.30
7.31
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.25
7.20
7.15
7.11
7.10
7.09
7.08
7.08
7.06
7.06
7.05
6.95
6.95
6.92
6.92
6.87
6.84
6.84
6.83
6.79
6.55
6.55
6.53
6.53
4.66
4.61
4.10



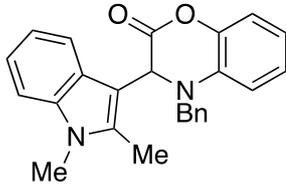
3la
¹H NMR (300 MHz, CDCl₃)



3la
¹³C NMR (75 MHz, CDCl₃)

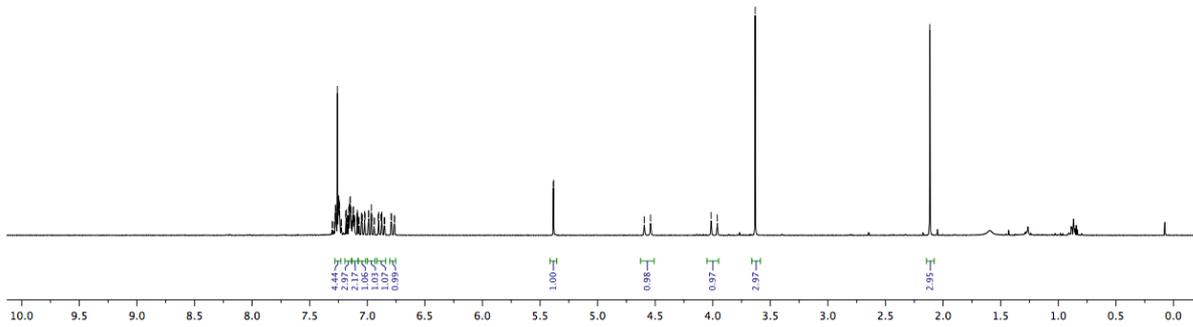


7.28
7.28
7.27
7.27
7.27
7.26
7.26
7.25
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7.24
7.19
7.18
7.16
7.15
7.14
7.14
7.13
7.12
7.11
7.11
7.09
7.09
7.05
7.05
7.02
7.02
6.99
6.99
6.97
6.96
6.96
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6.88
6.87
6.79
6.77
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3.96
3.63
2.12

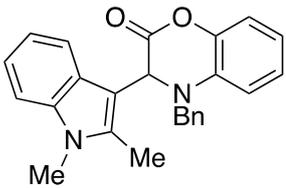


3na

¹H NMR (300 MHz, CDCl₃)

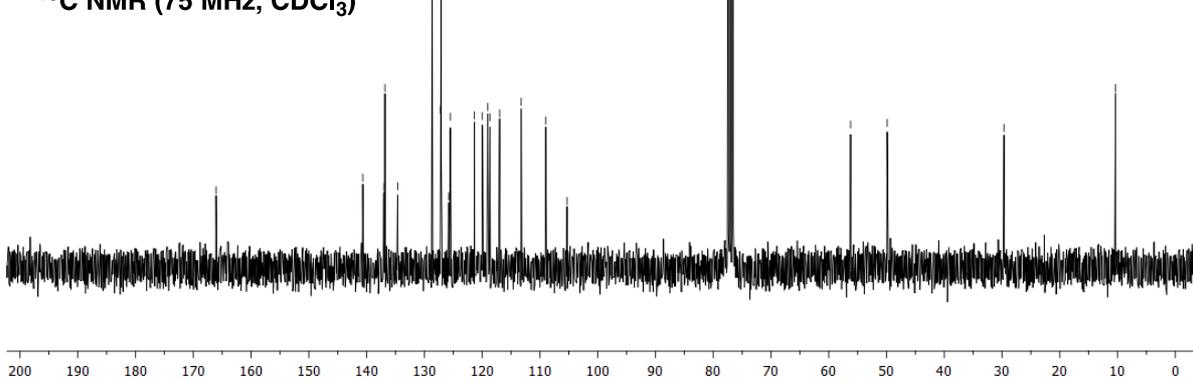


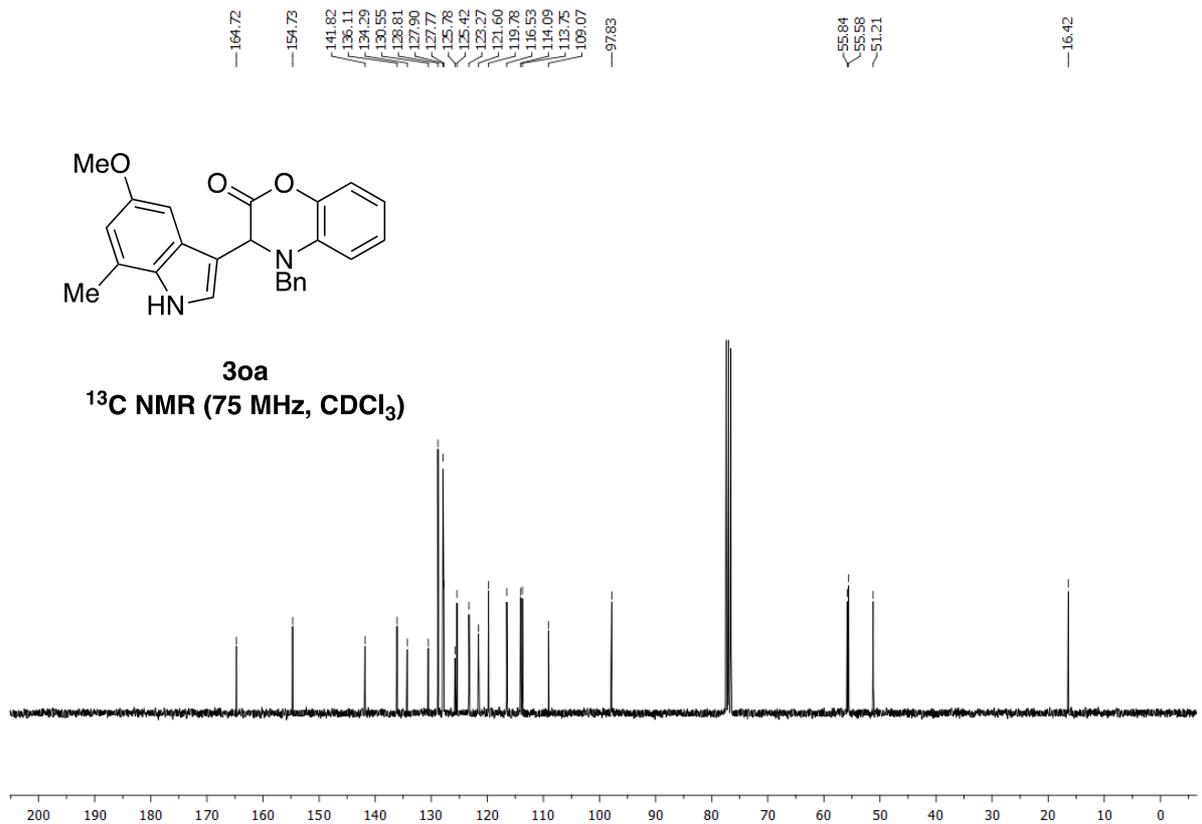
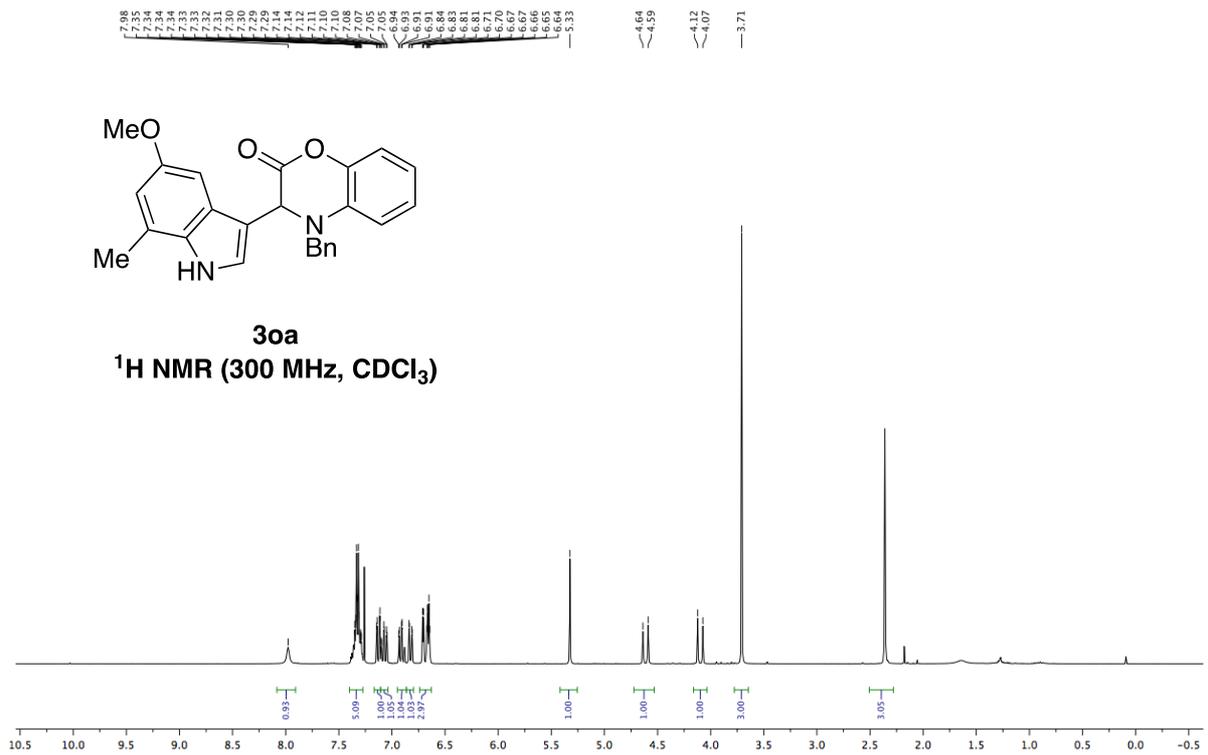
166.06
140.66
136.99
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134.63
128.65
127.21
127.09
125.81
125.49
121.32
119.95
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113.23
108.97
106.29
56.21
49.87
29.64
10.32



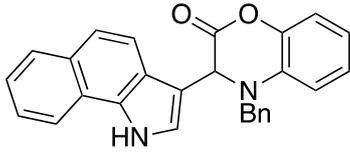
3na

¹³C NMR (75 MHz, CDCl₃)

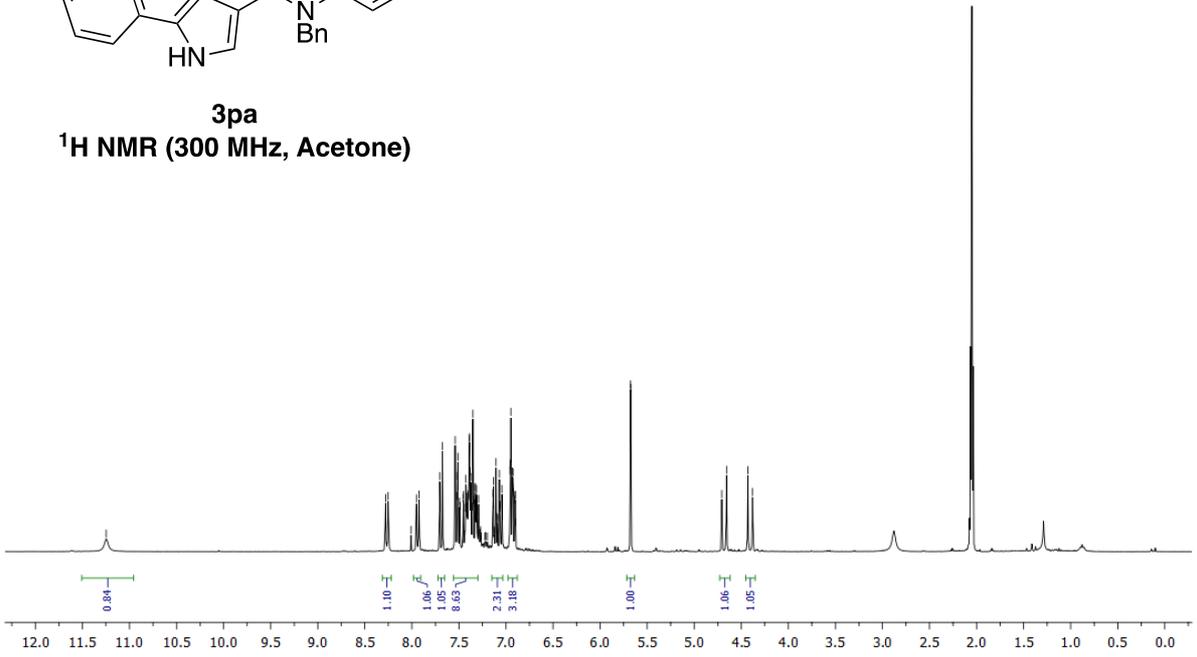




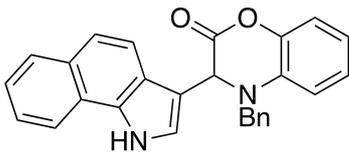
8.28
8.25
8.01
7.95
7.92
7.70
7.67
7.54
7.52
7.51
7.49
7.46
7.45
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.35
7.35
7.33
7.33
7.33
7.32
7.31
7.31
7.31
7.30
7.29
7.27
7.14
7.13
7.13
7.11
7.11
7.09
7.07
7.07
7.06
7.04
7.04
6.96
6.96
6.95
6.95
6.94
6.93
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6.90
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5.67
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4.66
4.43
4.38



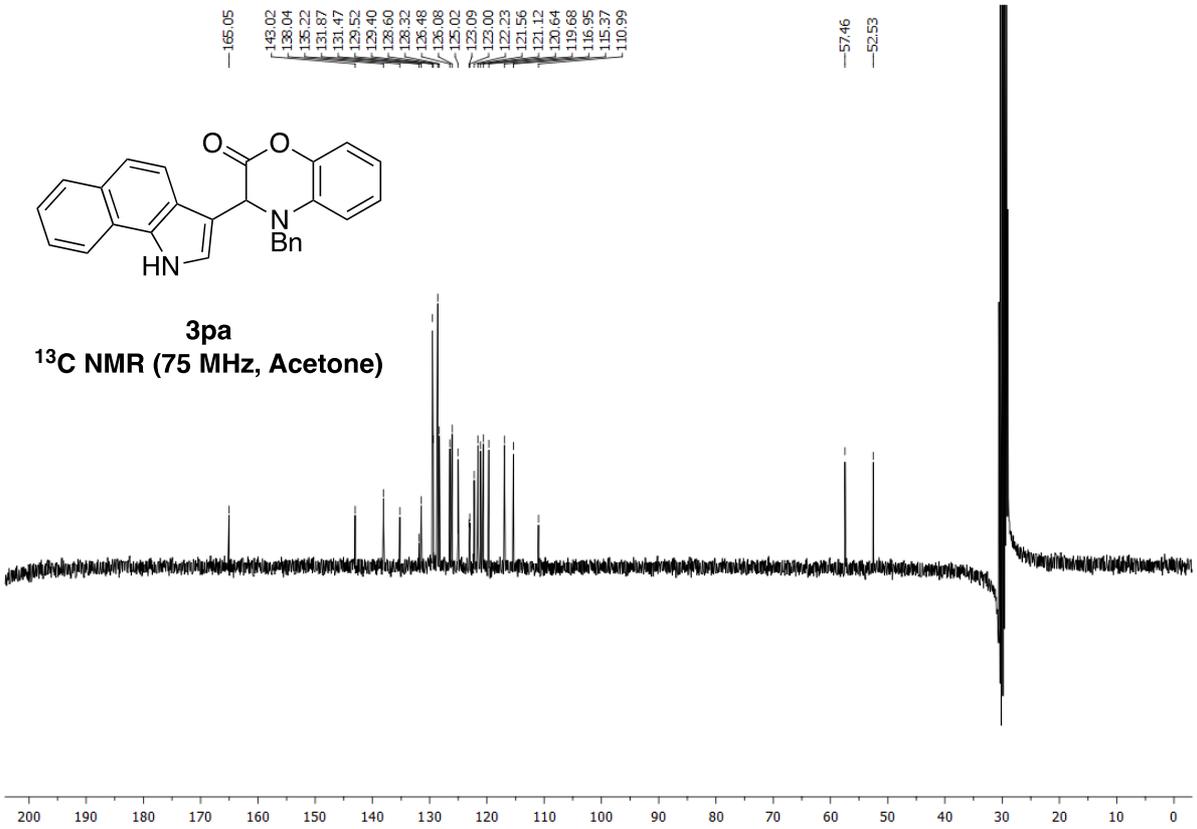
3pa
¹H NMR (300 MHz, Acetone)

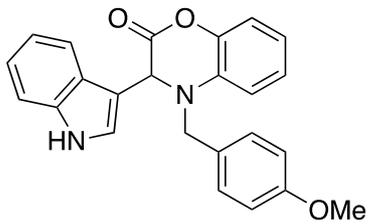


165.05
145.02
138.04
135.22
131.87
131.47
129.52
129.40
128.60
128.32
126.48
126.08
125.02
123.09
123.00
122.23
121.56
121.12
120.64
119.68
116.95
115.37
110.99
57.46
52.53



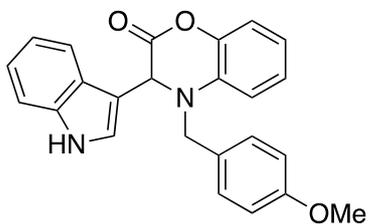
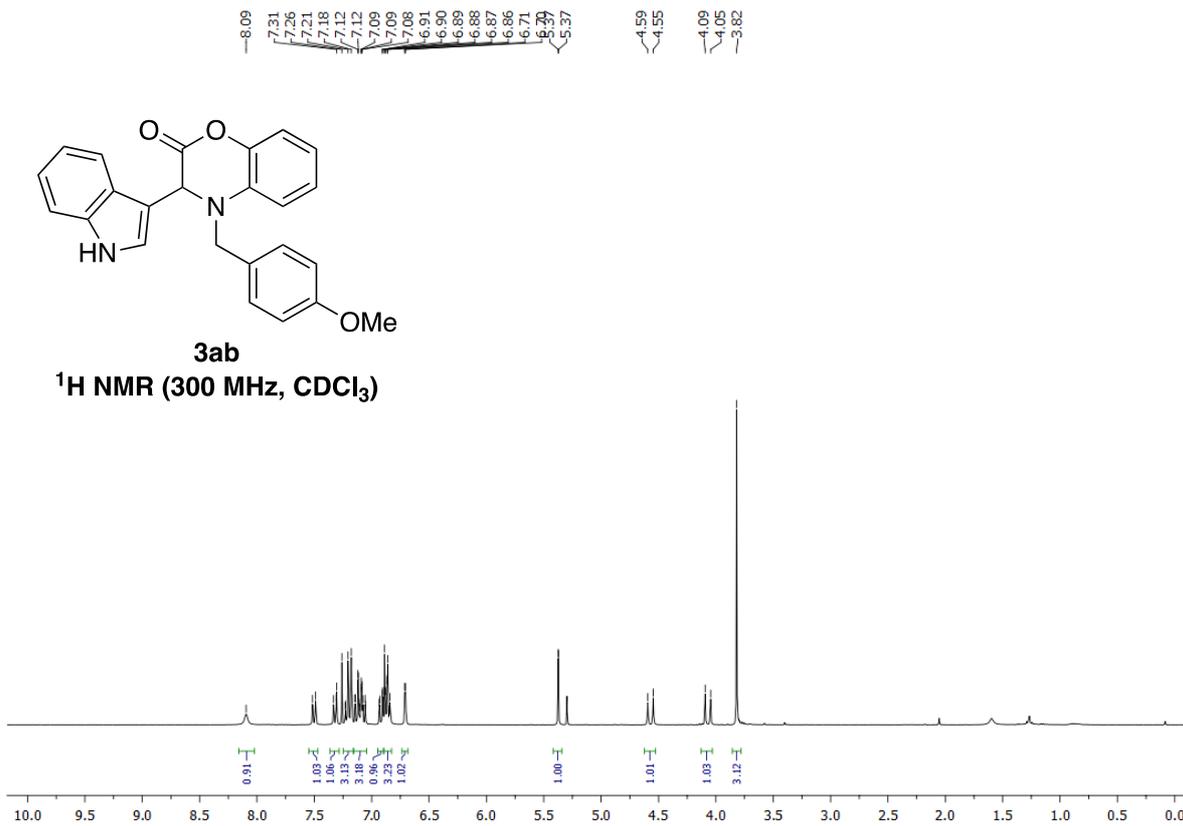
3pa
¹³C NMR (75 MHz, Acetone)





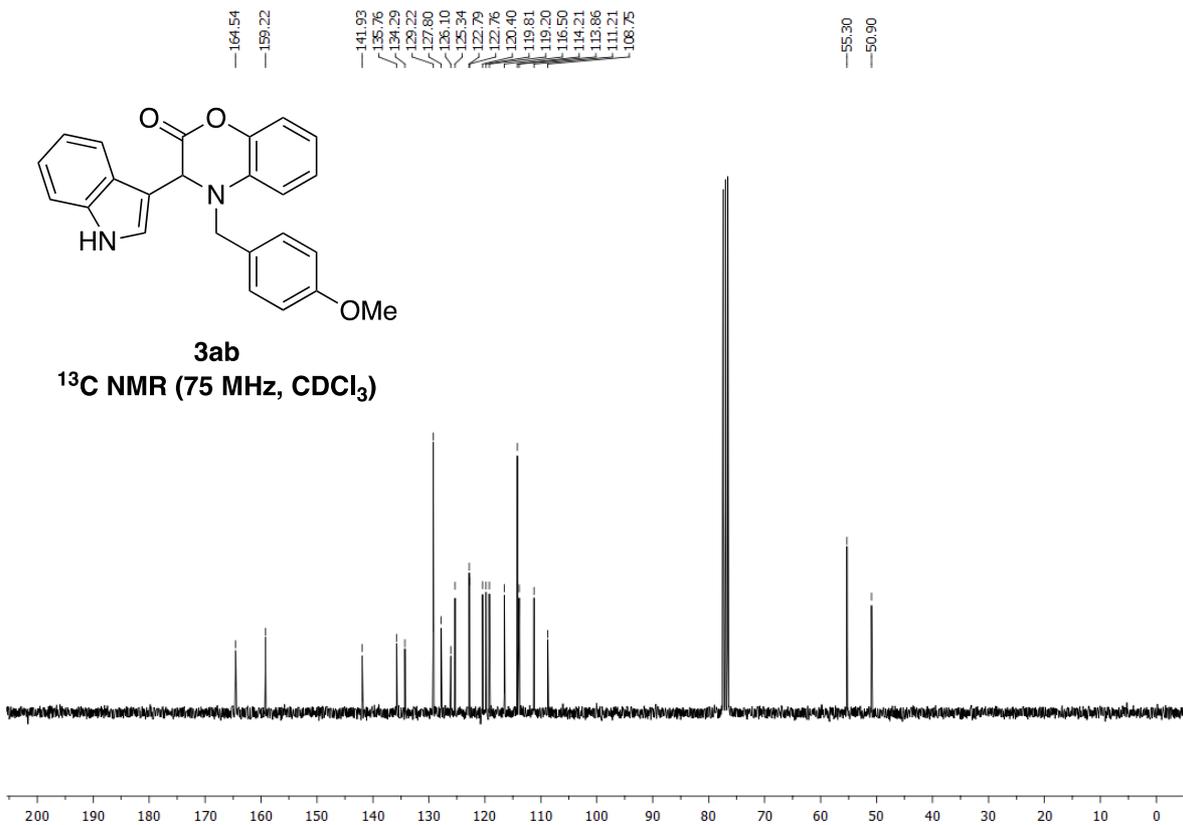
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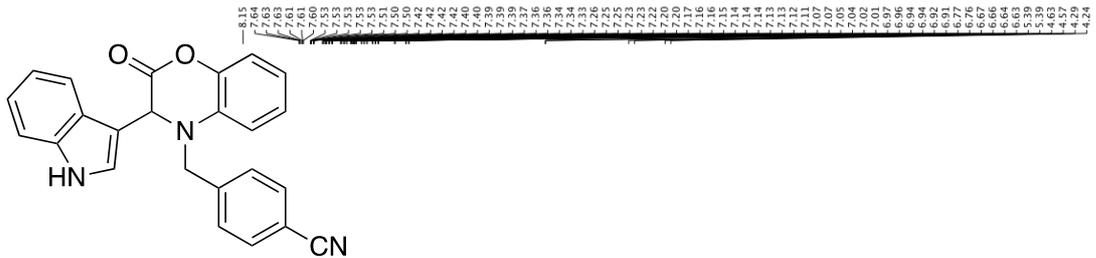
¹H NMR (300 MHz, CDCl₃)



3ab

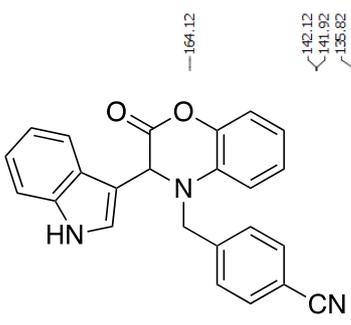
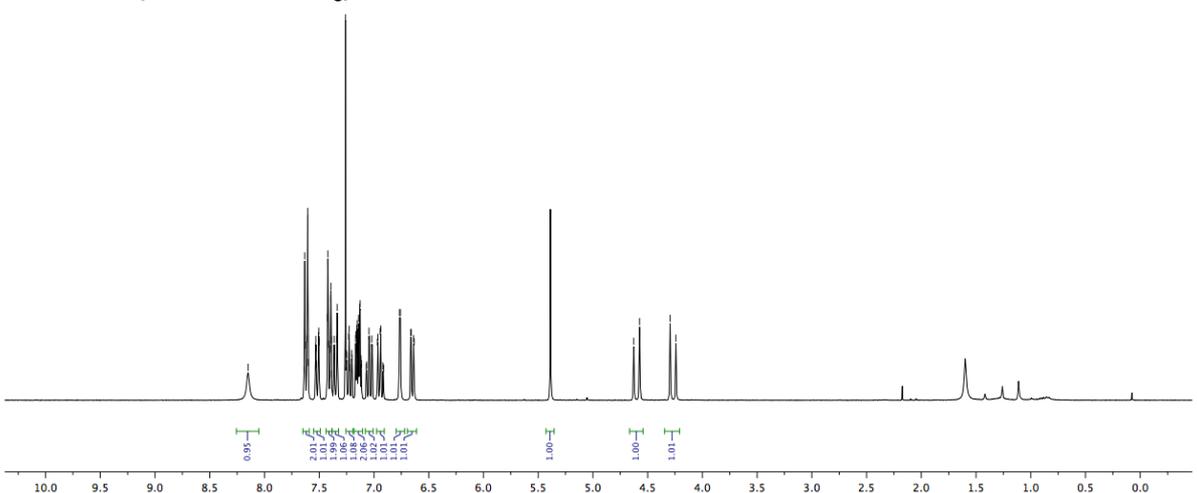
¹³C NMR (75 MHz, CDCl₃)





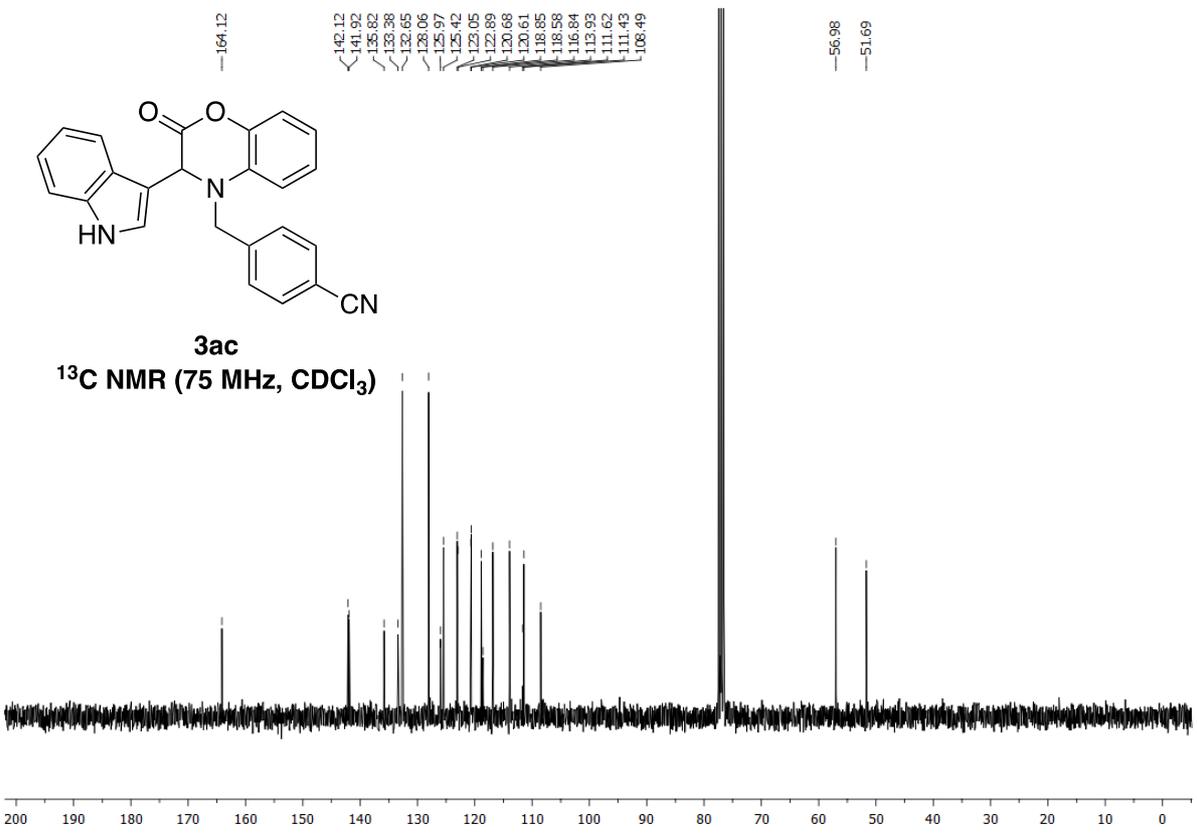
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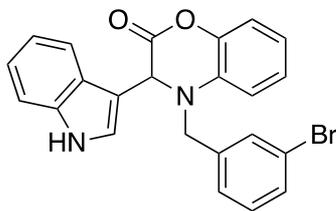
¹H NMR (300 MHz, CDCl₃)



3ac

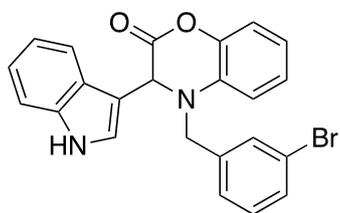
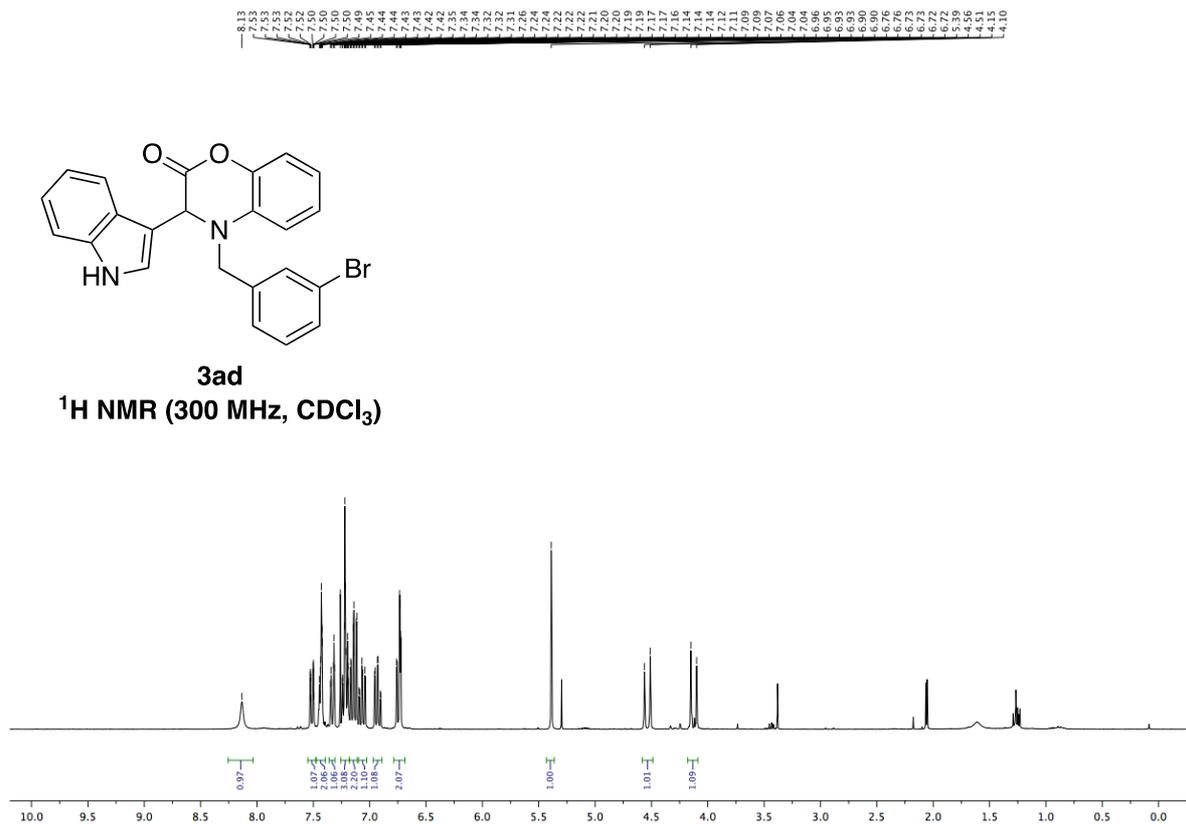
¹³C NMR (75 MHz, CDCl₃)





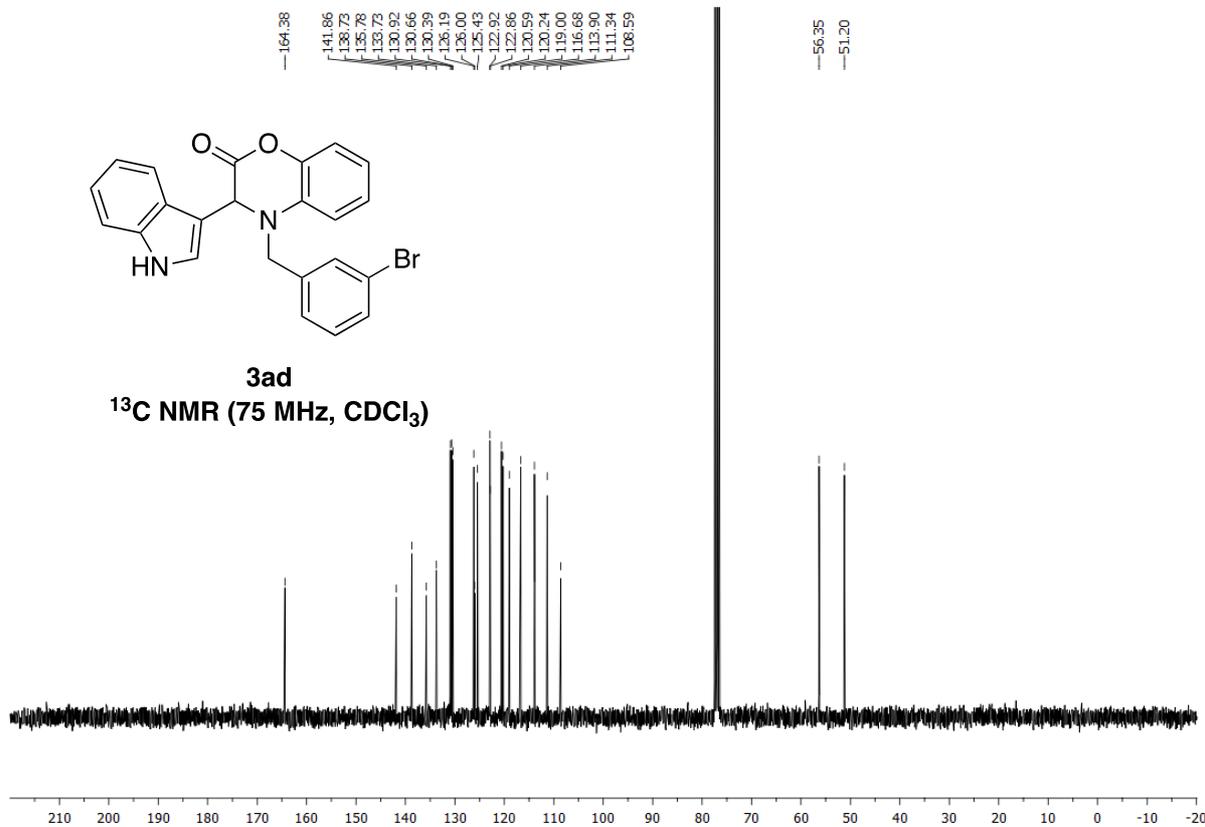
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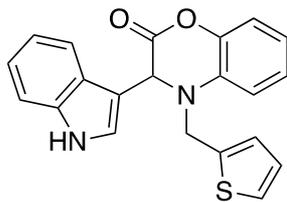
¹H NMR (300 MHz, CDCl₃)



3ad

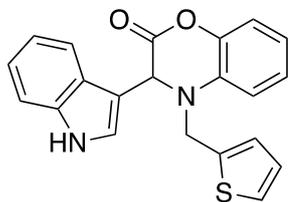
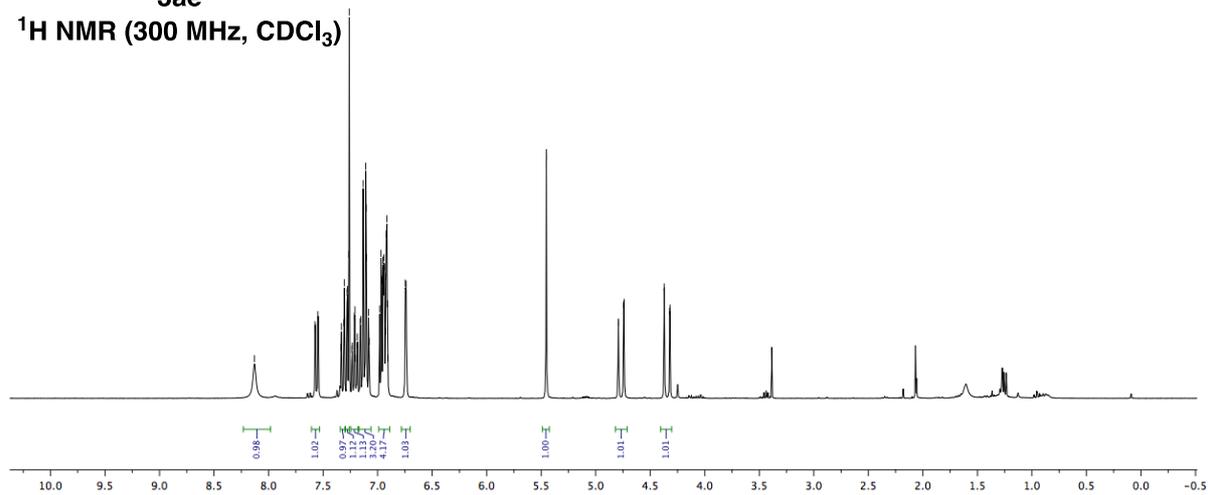
¹³C NMR (75 MHz, CDCl₃)





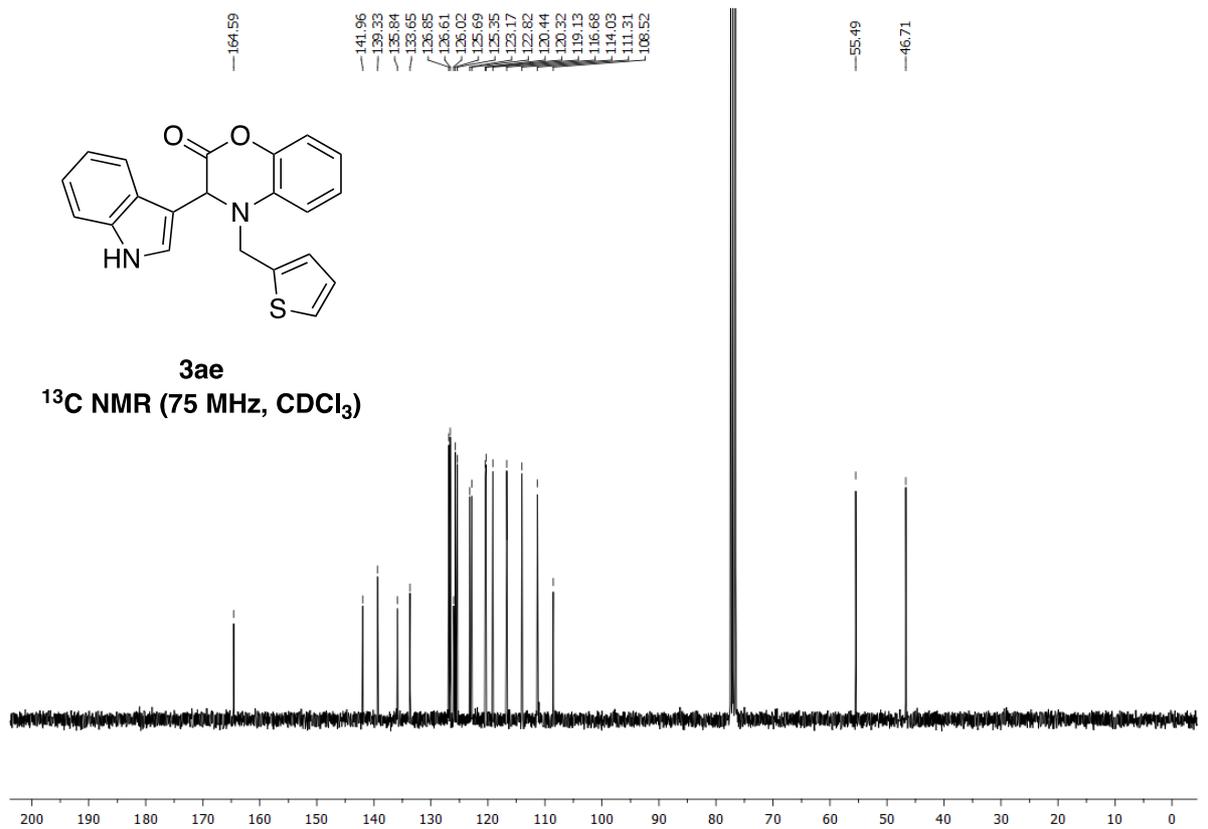
3ae

¹H NMR (300 MHz, CDCl₃)

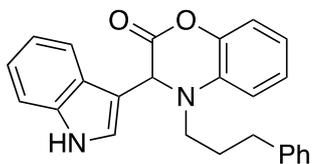


3ae

¹³C NMR (75 MHz, CDCl₃)

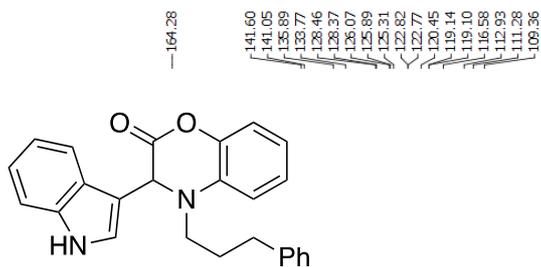
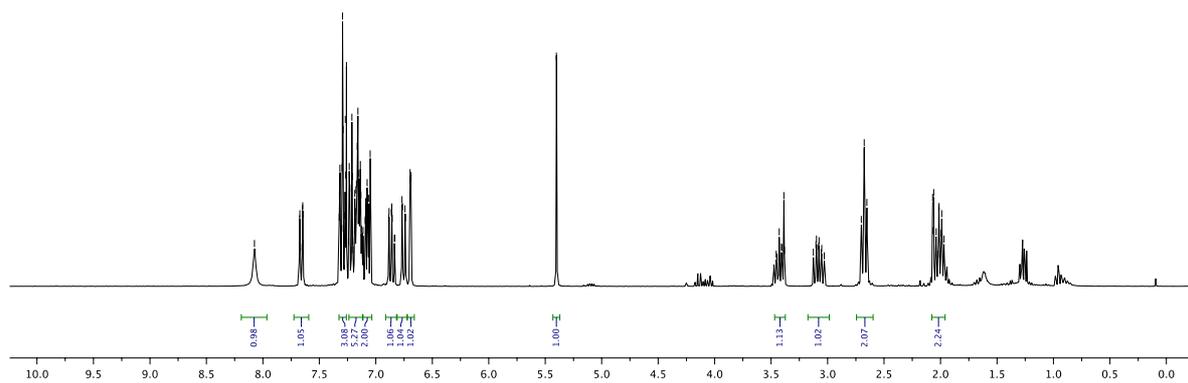


8.07
7.68
7.67
7.67
7.65
7.65
7.64
7.32
7.32
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7.13
7.12
7.12
7.03
7.09
7.08
7.08
7.07
7.07
7.05
7.05
6.89
6.88
6.86
6.86
6.86
6.84
6.83
6.76
6.74
6.74
6.70
6.69
6.69
5.40
5.40
3.46
3.43
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3.39
3.18
3.18
3.10
3.10
3.08
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2.07
2.06
2.04
2.02
2.00
2.00
1.97



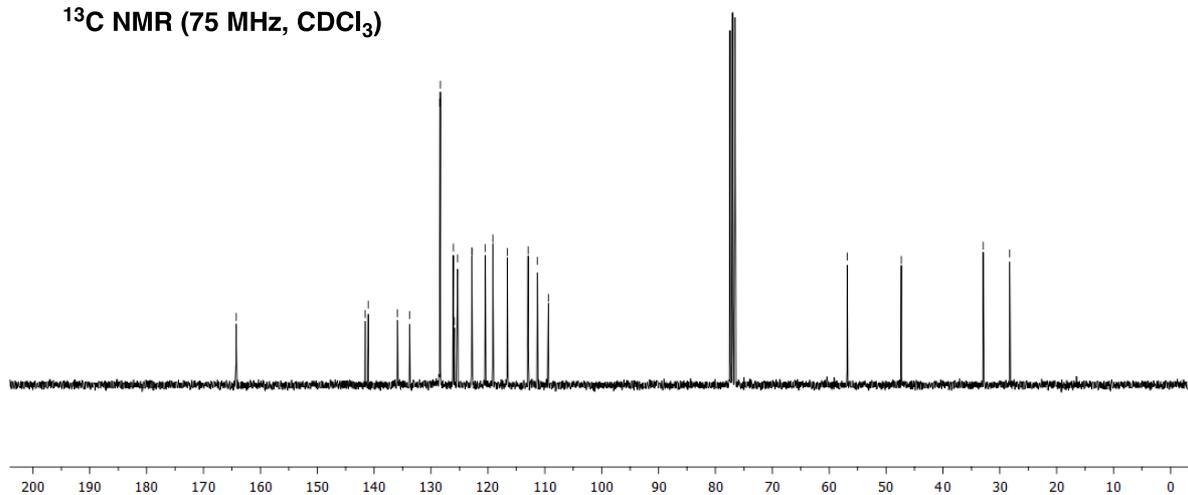
3af

¹H NMR (300 MHz, CDCl₃)

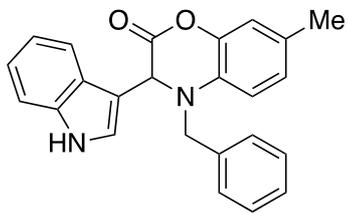


3af

¹³C NMR (75 MHz, CDCl₃)

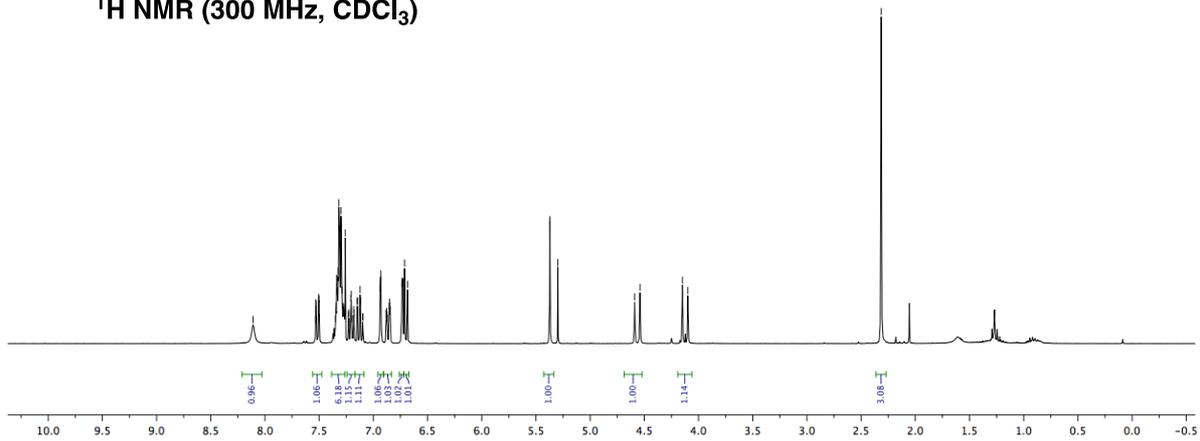


8.11
7.53
7.52
7.52
7.50
7.50
7.50
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.31
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7.26
7.23
7.23
7.21
7.20
7.20
7.18
7.18
7.15
7.13
7.12
7.12
7.10
7.10
6.94
6.94
6.93
6.93
6.88
6.88
6.87
6.87
6.85
6.85
6.84
6.84
6.73
6.73
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5.37
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4.54
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4.15
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4.10
4.10
2.31

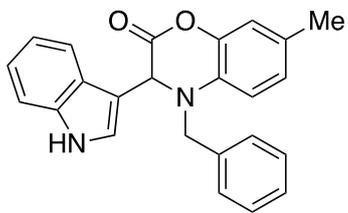


3ag

¹H NMR (300 MHz, CDCl₃)

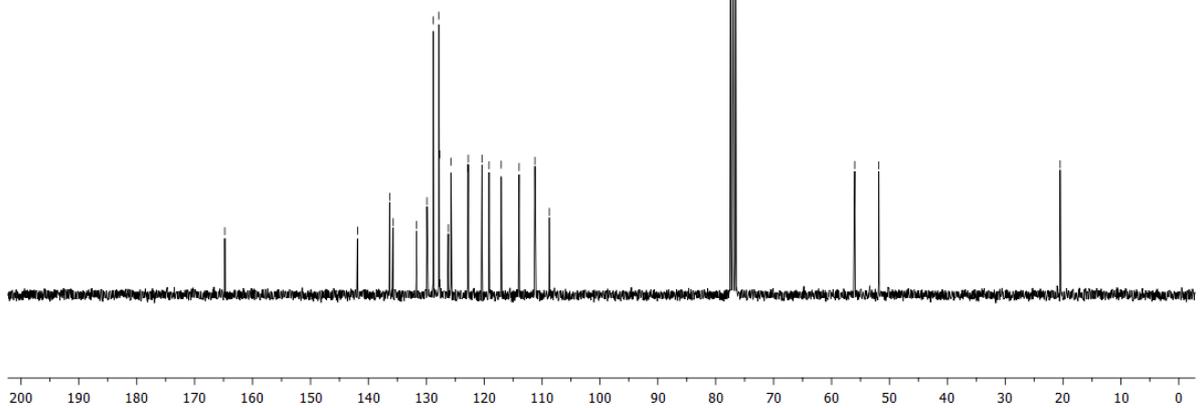


164.79
141.88
136.33
135.75
131.69
129.87
128.77
127.81
126.20
125.72
122.83
122.75
120.38
119.15
117.06
113.96
111.23
108.75
55.98
51.83
20.51



3ag

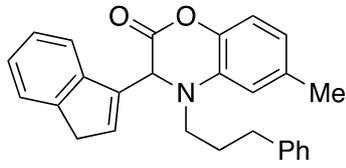
¹³C NMR (75 MHz, CDCl₃)



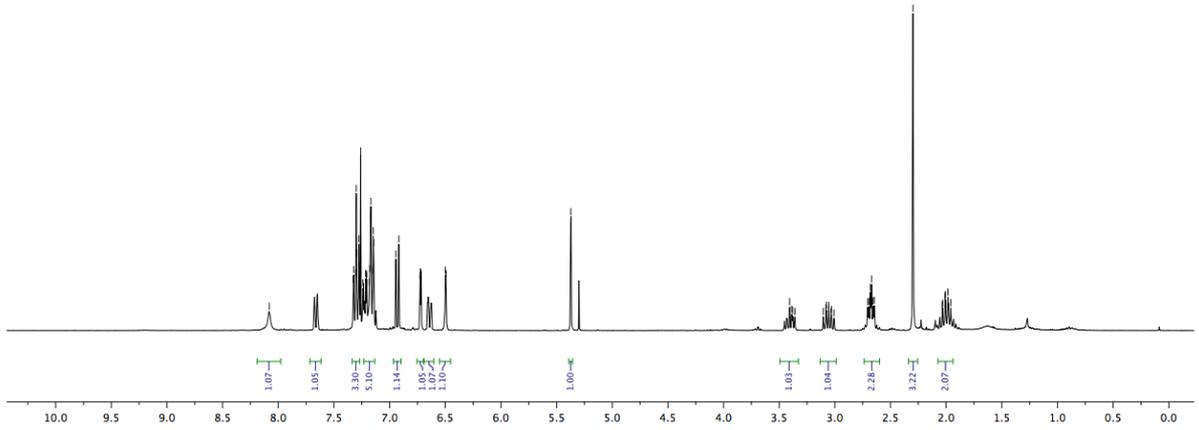
8.08
7.33
7.32
7.30
7.29
7.27
7.26
7.24
7.23
7.22
7.20
7.18
7.17
7.15
7.14
6.94
6.92
6.72
6.72
6.60
6.49

— 5.37

3.41
3.39
3.38
3.36
3.10
3.08
3.06
3.05
3.03
3.01
2.71
2.68
2.67
2.66
2.66
2.30
2.01
2.00
1.98
1.96



3ah
¹H NMR (300 MHz, CDCl₃)



— 164.43
141.13
138.63
135.90
135.00
133.39
132.47
132.44
132.07
125.95
122.87
122.74
100.43
119.59
119.14
116.22
113.53
111.27
109.52

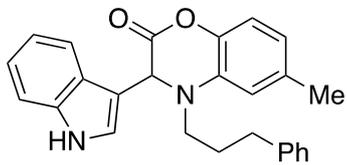
— 56.85

— 47.20

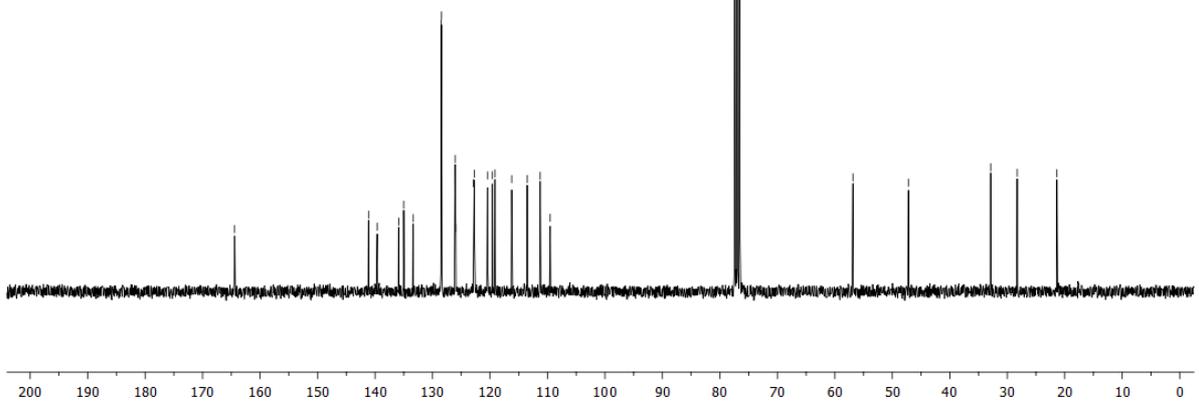
— 32.89

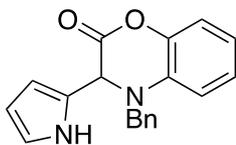
— 28.28

— 21.37



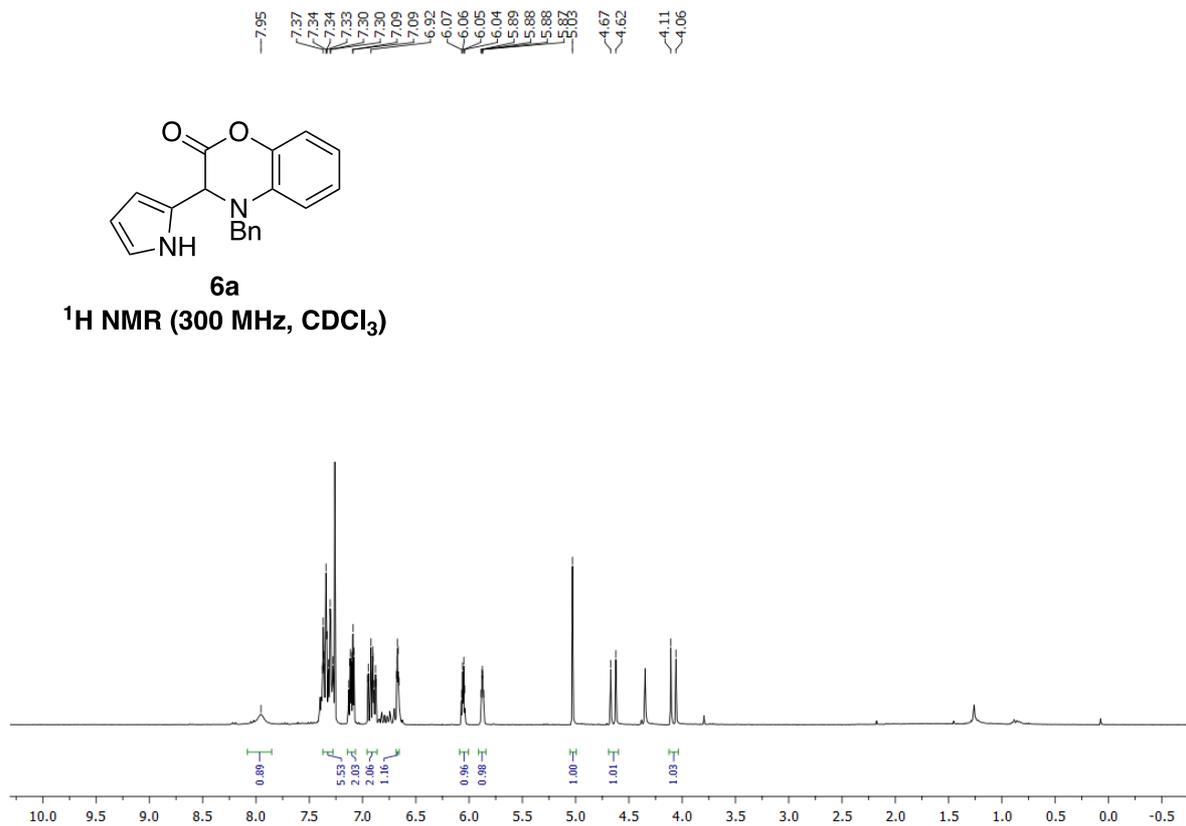
3ah
¹³C NMR (75 MHz, CDCl₃)





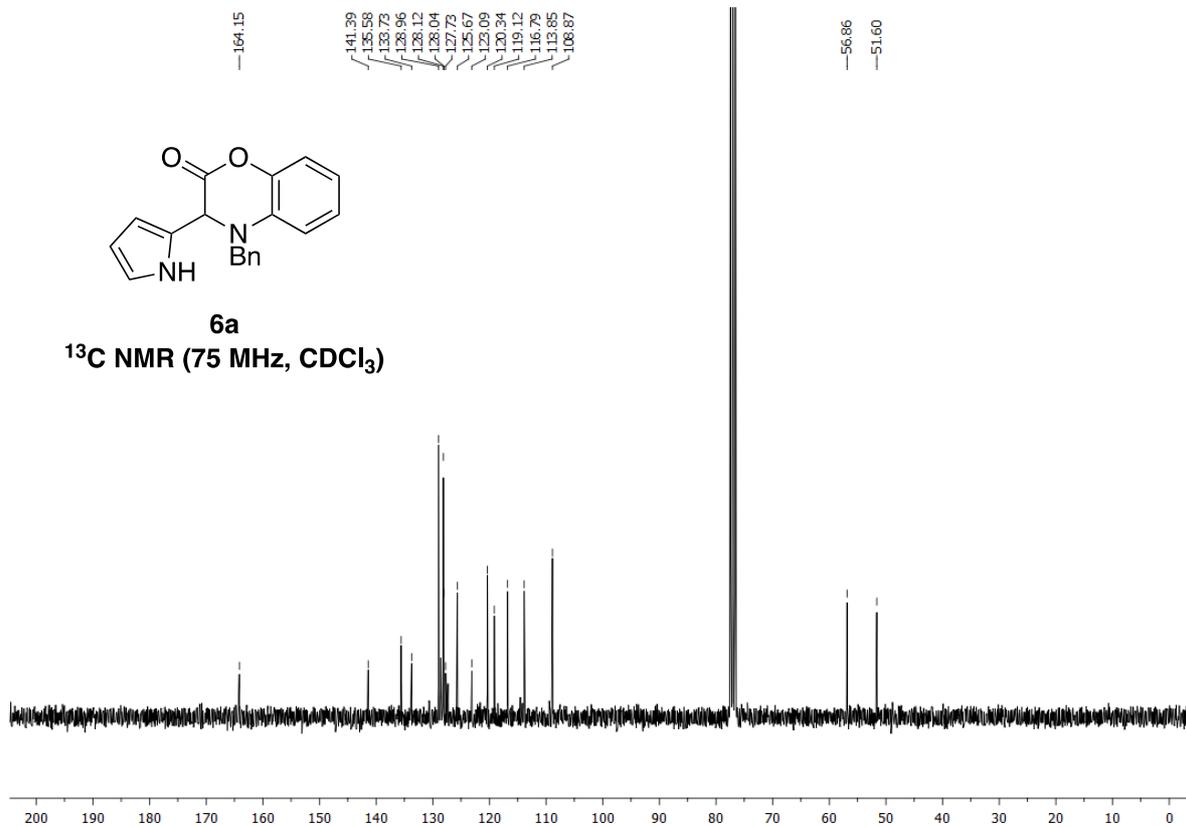
6a

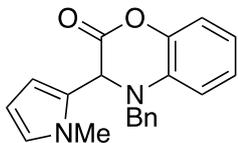
¹H NMR (300 MHz, CDCl₃)



6a

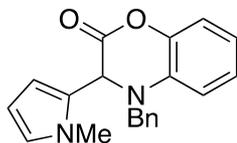
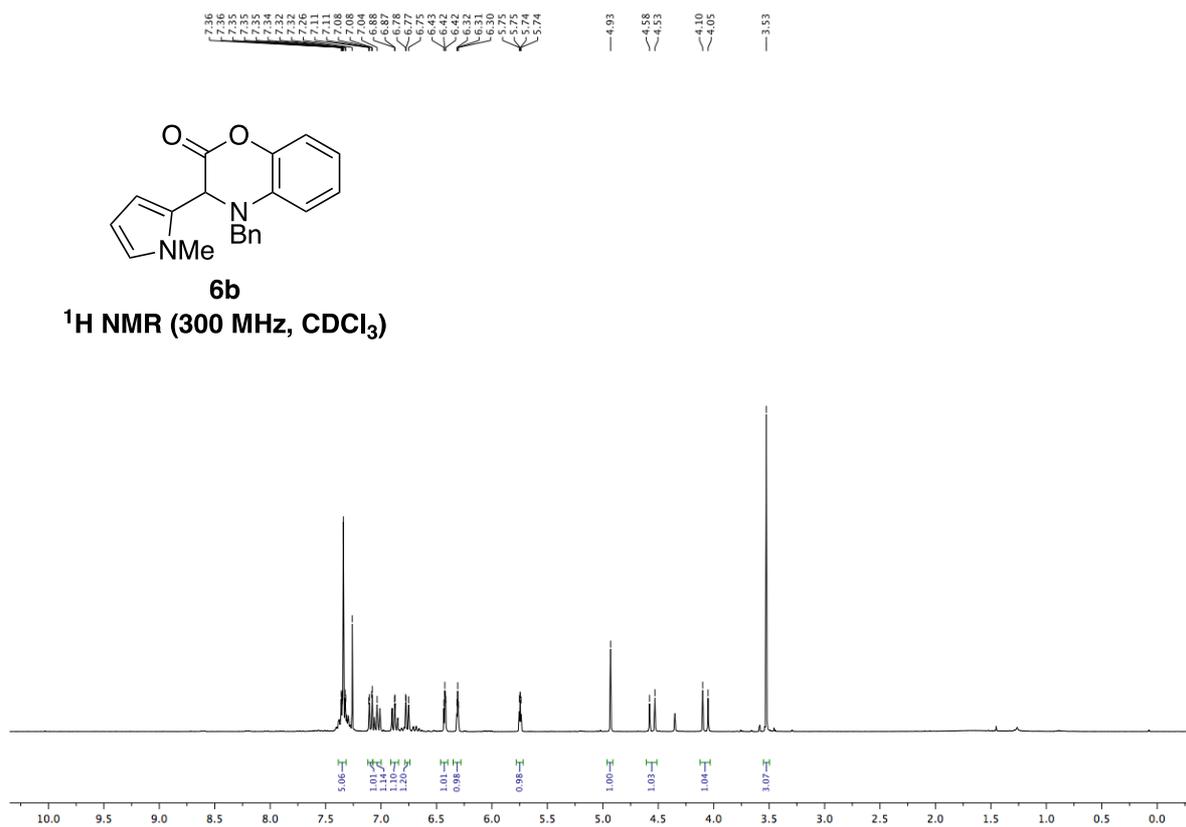
¹³C NMR (75 MHz, CDCl₃)





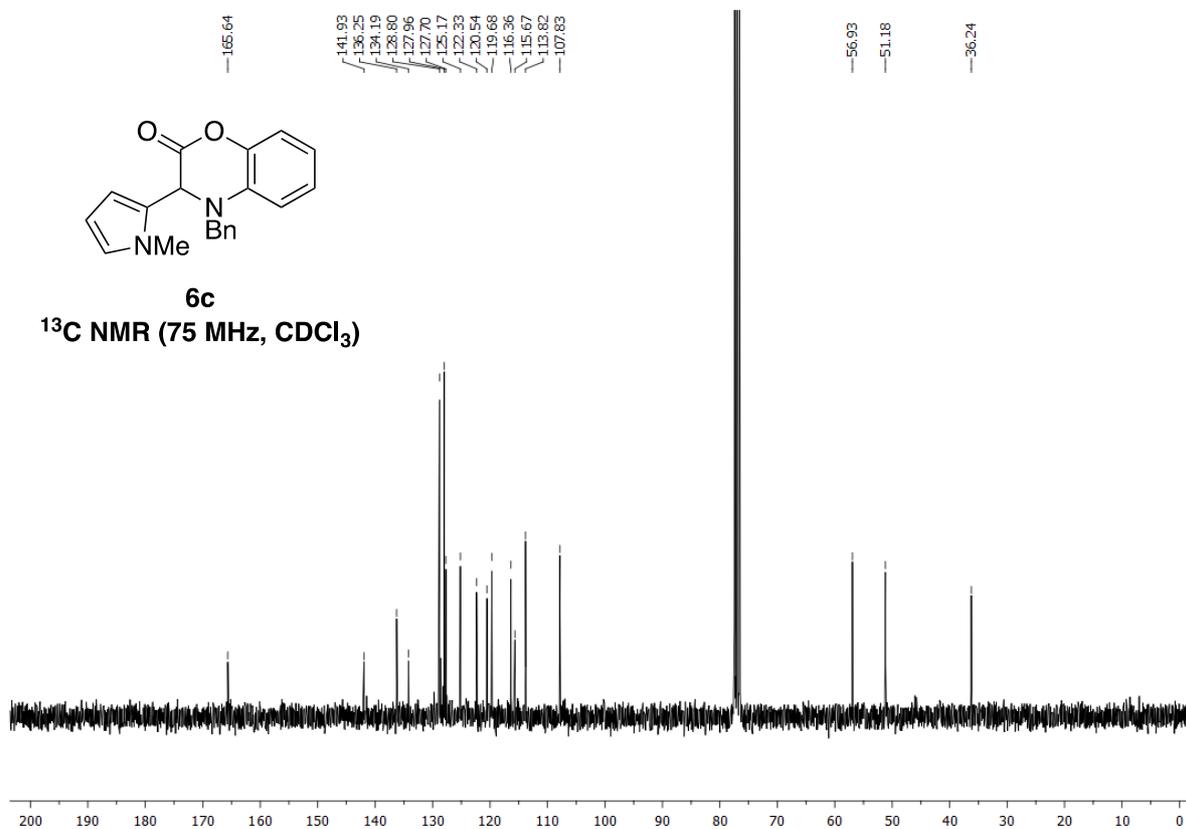
6b

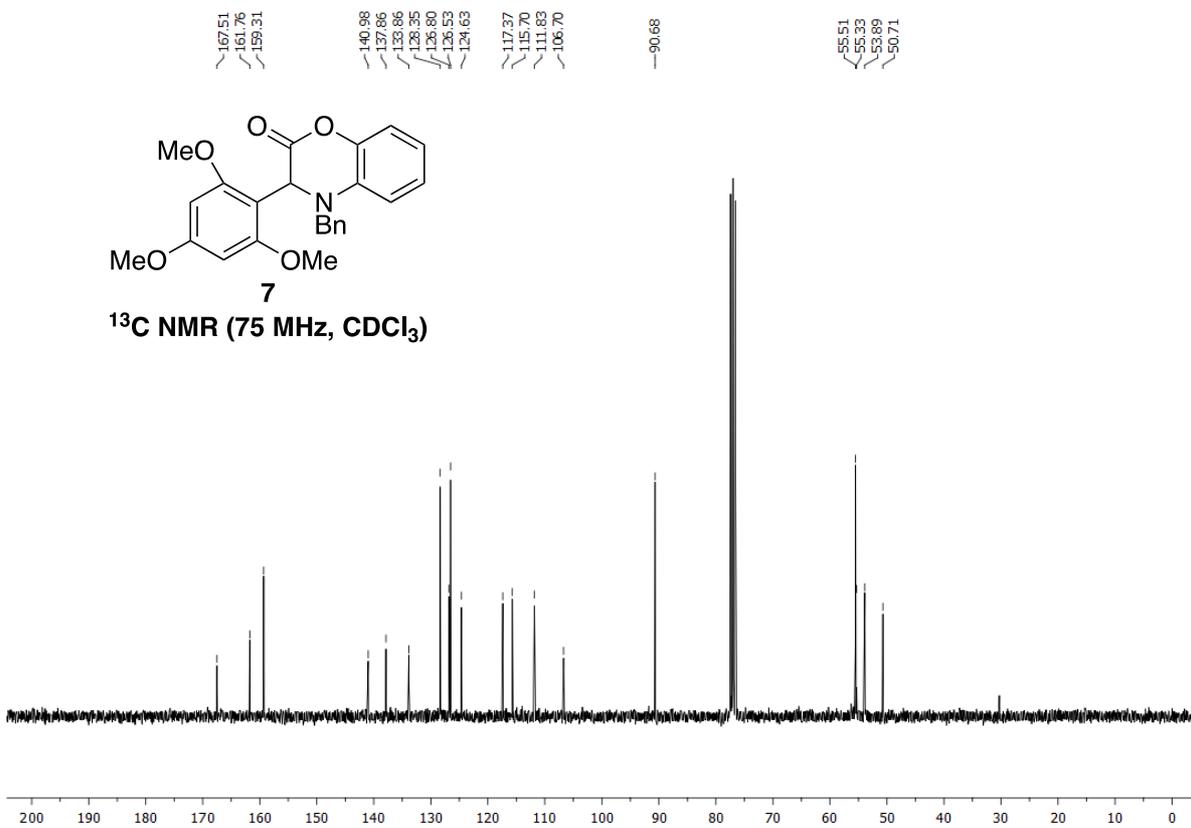
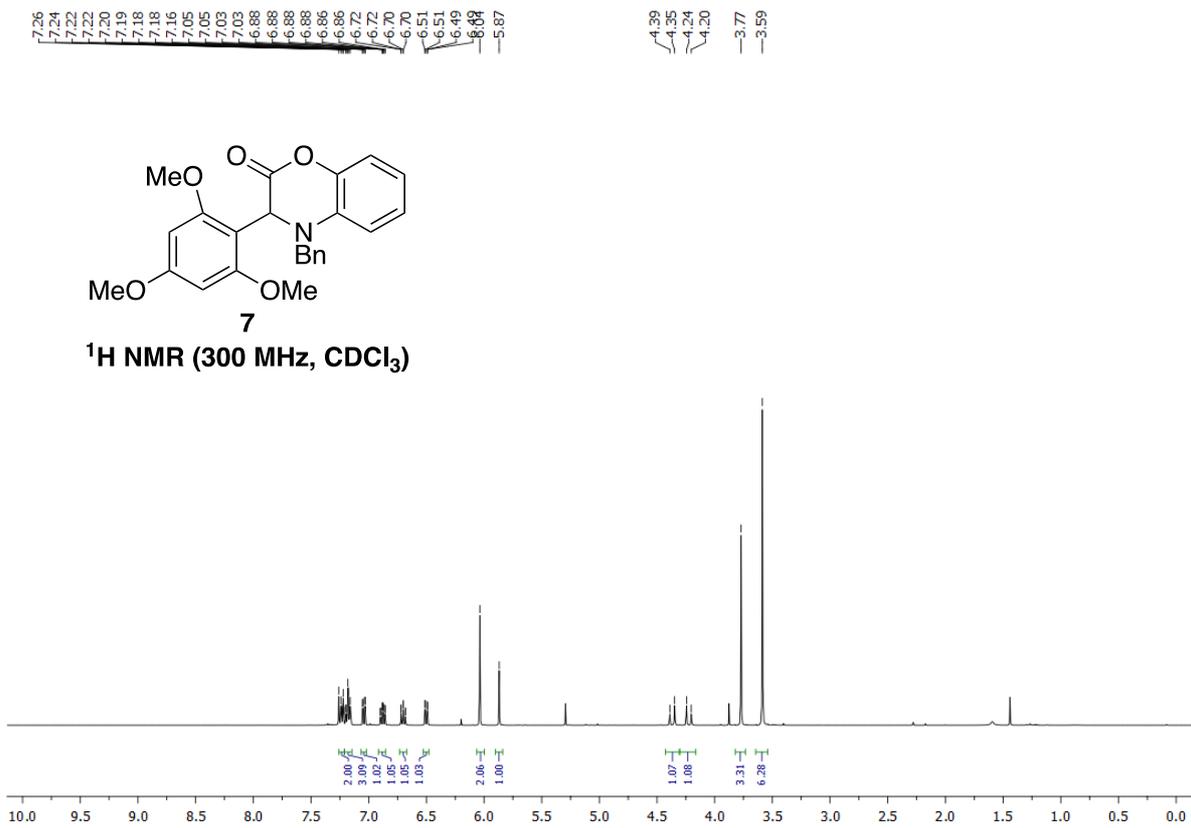
¹H NMR (300 MHz, CDCl₃)

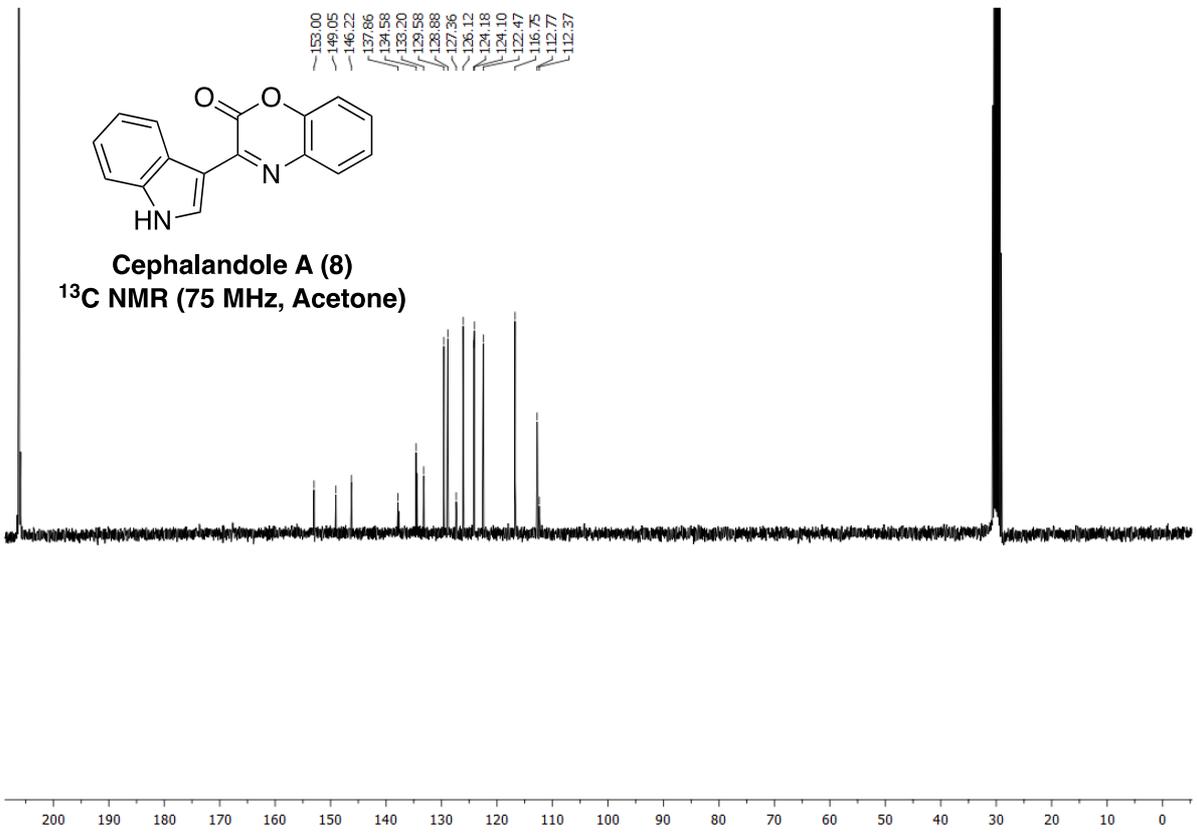
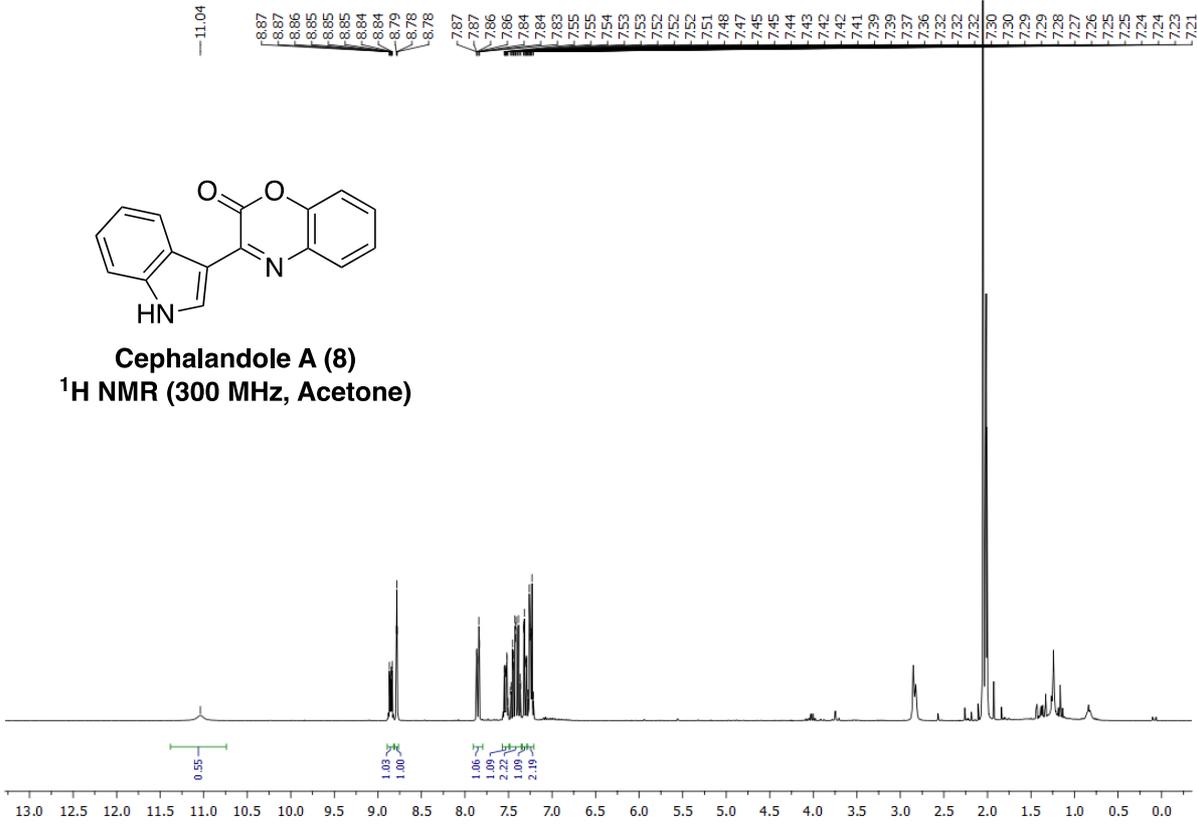


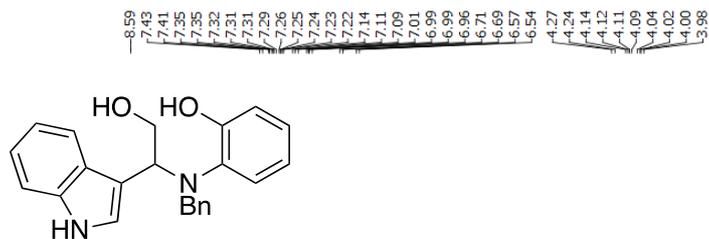
6c

¹³C NMR (75 MHz, CDCl₃)



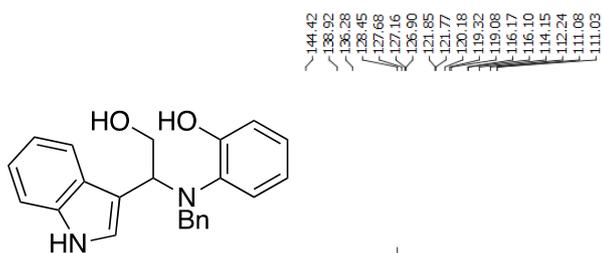
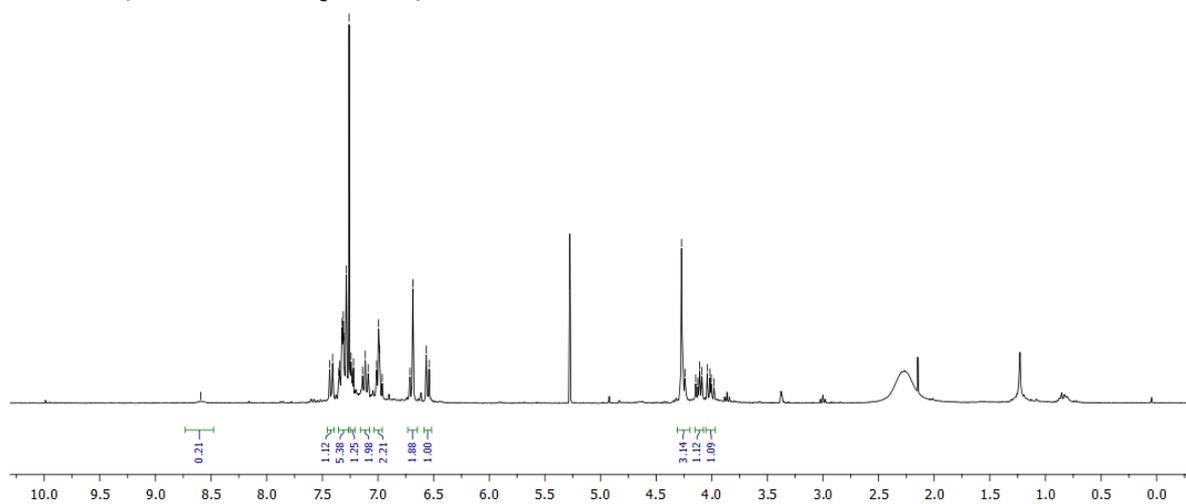






9

¹H NMR (300 MHz, CDCl₃:MeOD)



9

¹³C NMR (75 MHz, CDCl₃:MeOD)

