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## SUPPORTING INFORMATION

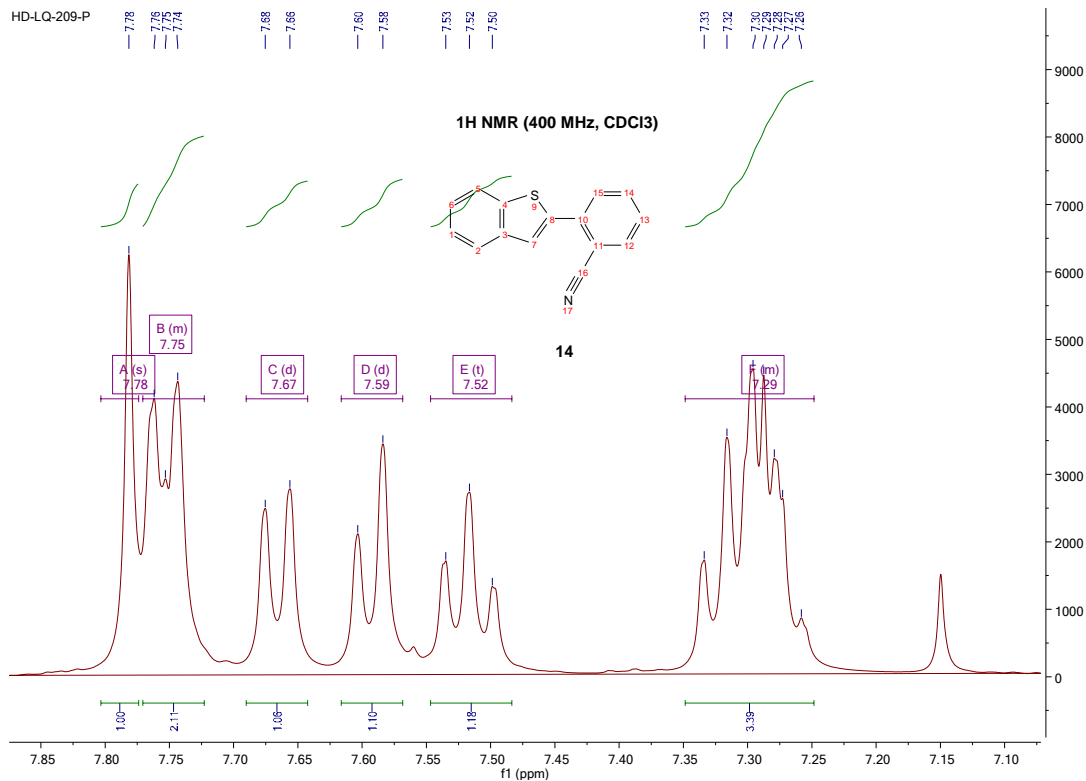
# Phosphine-free palladium-catalyzed direct C2-arylation of benzothiophenes with aryl bromides

**Liqin Zhao,<sup>[a]</sup> Christian Bruneau,<sup>[a]</sup> and Henri Doucet\*<sup>[a]</sup>**

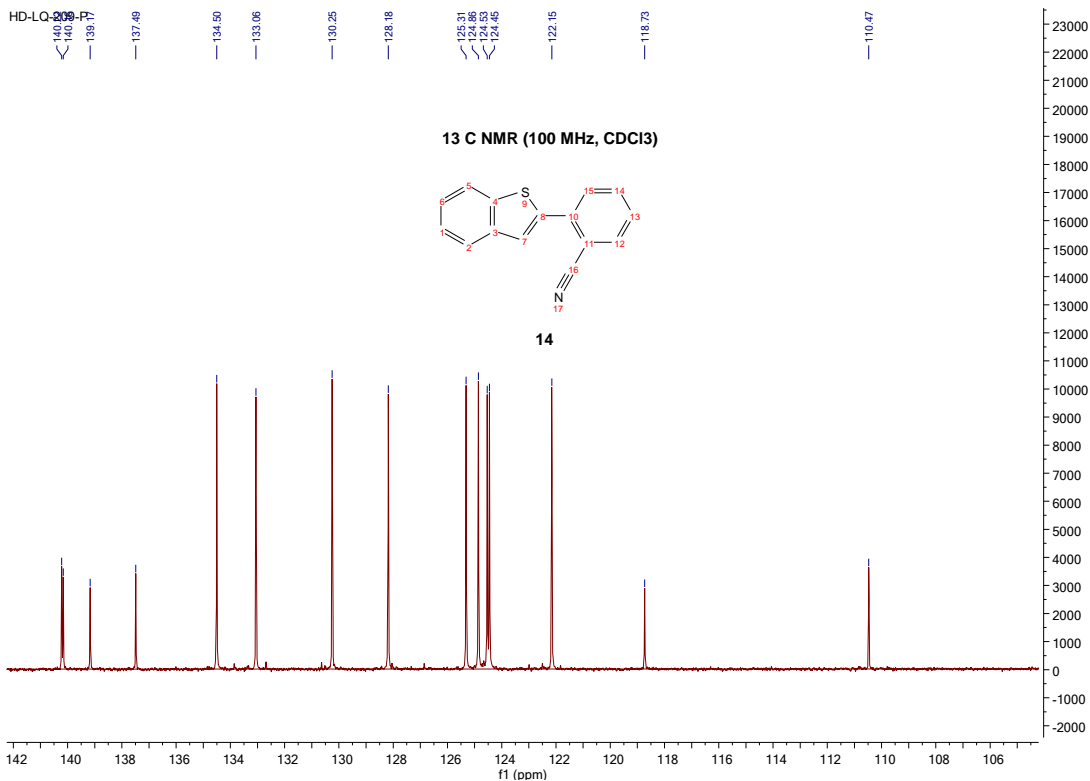
*Institut Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes1 "Organométalliques Matériaux et Catalyse e", 35042 Rennes, France. Tel: 33 (0)2 23 23 63 84; E-mail: henri.doucet@univ-rennes1.fr*

**<sup>1</sup>H and <sup>13</sup>C NMR spectra of all new compounds**

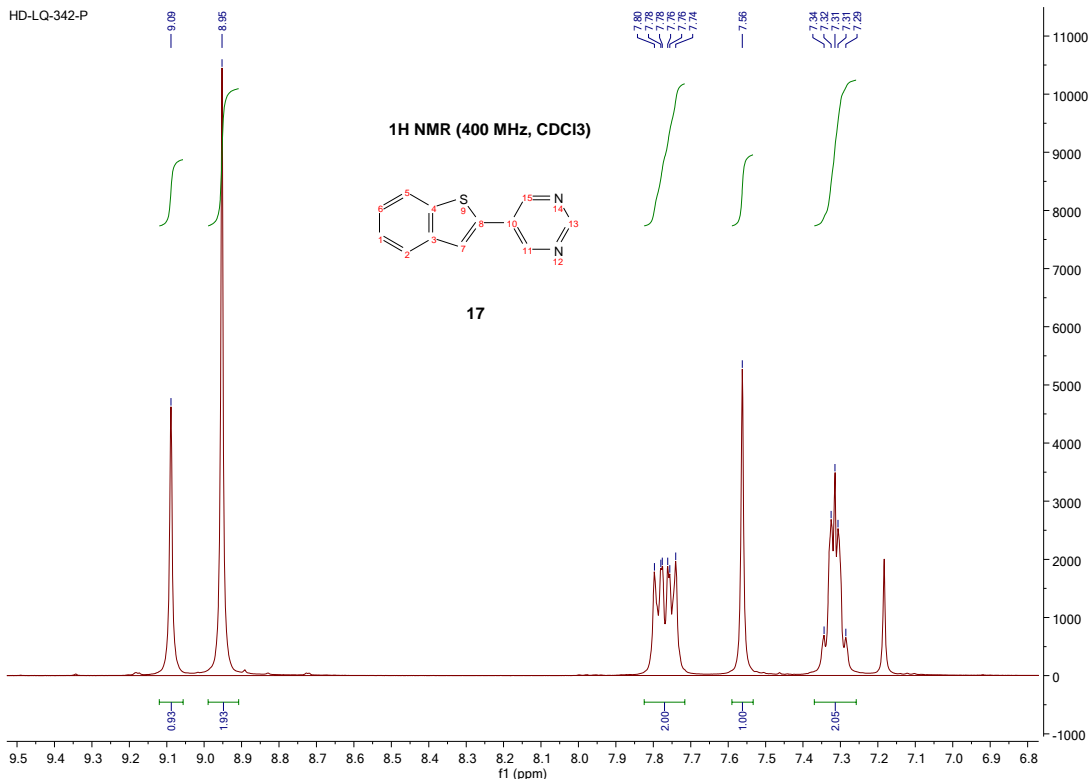
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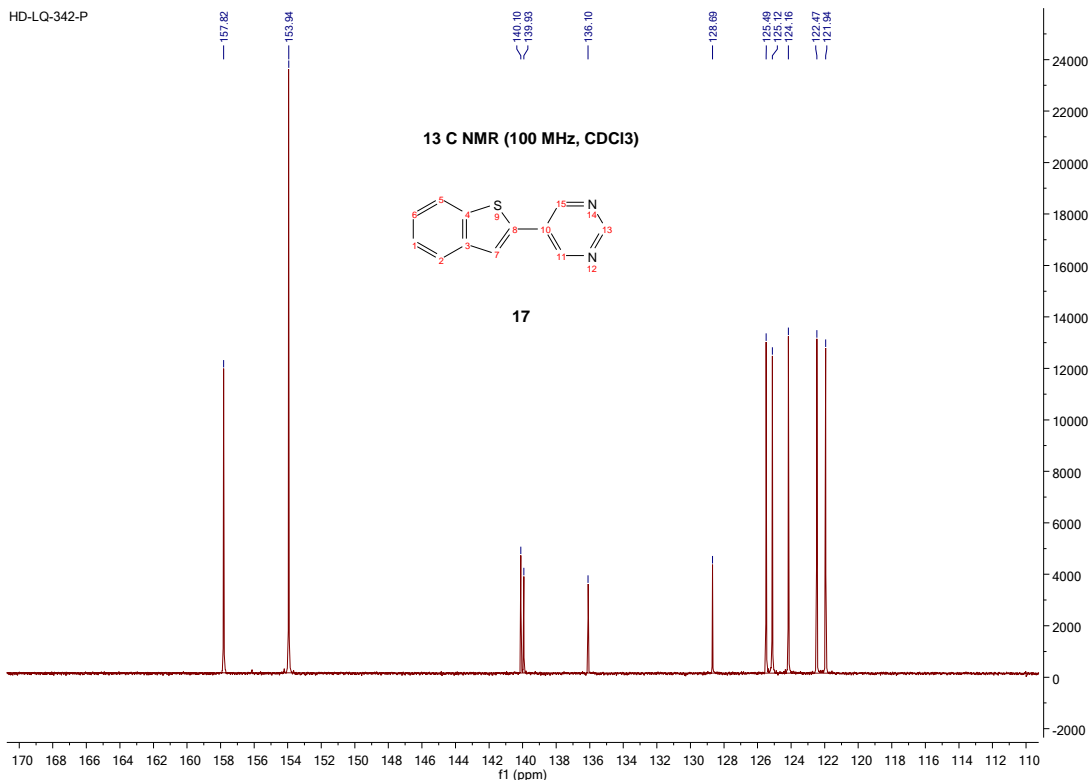
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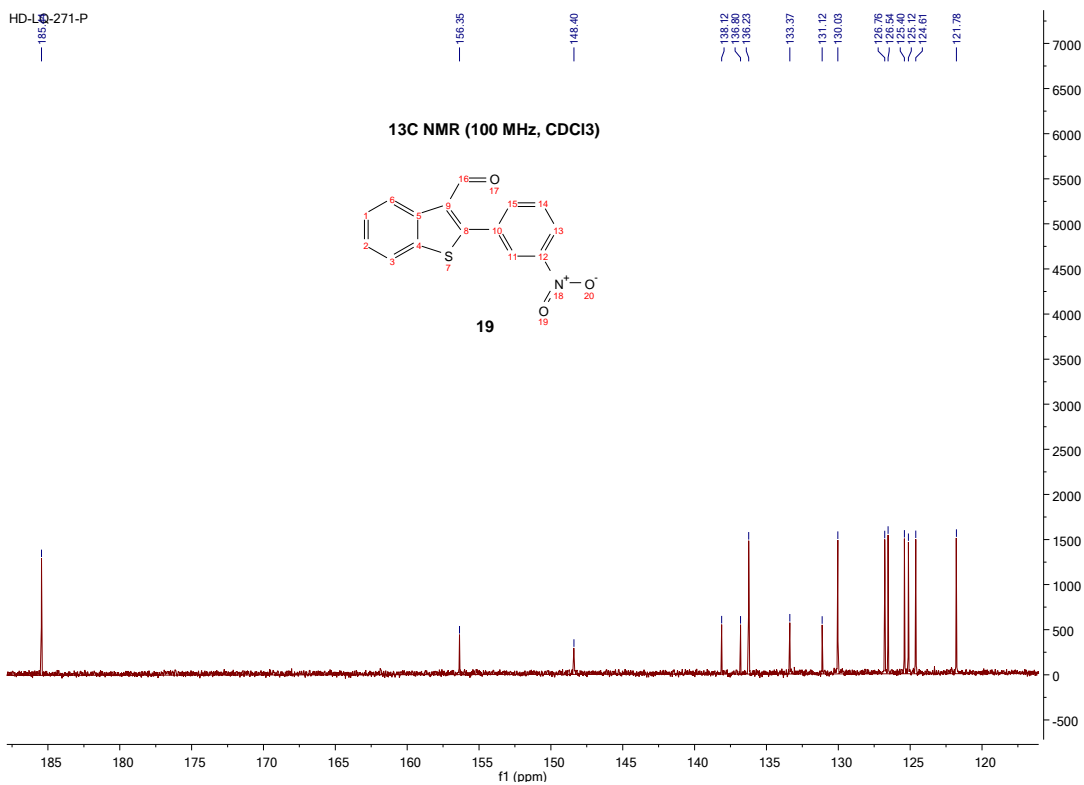
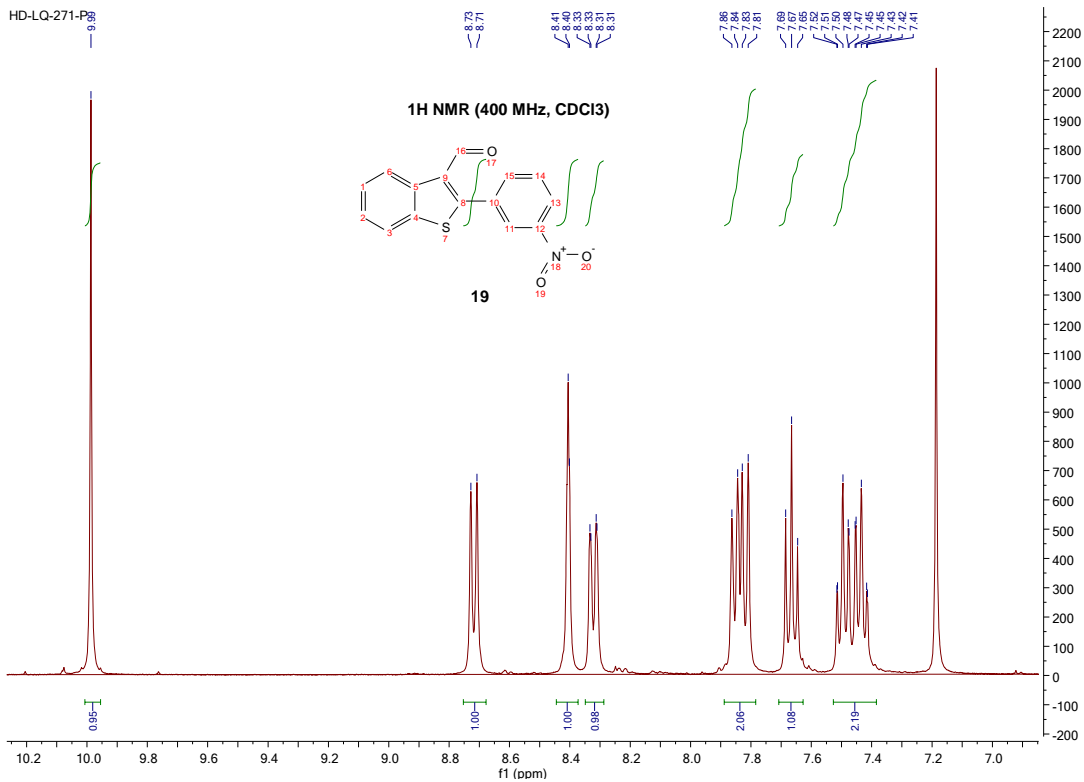


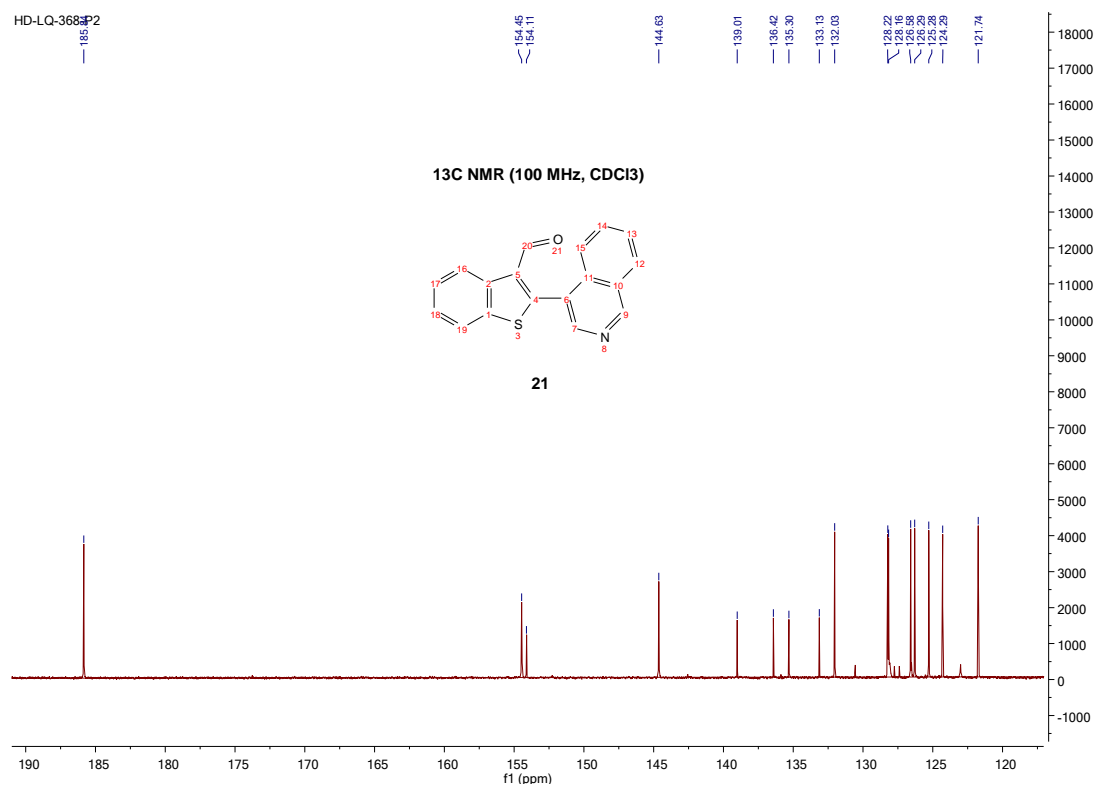
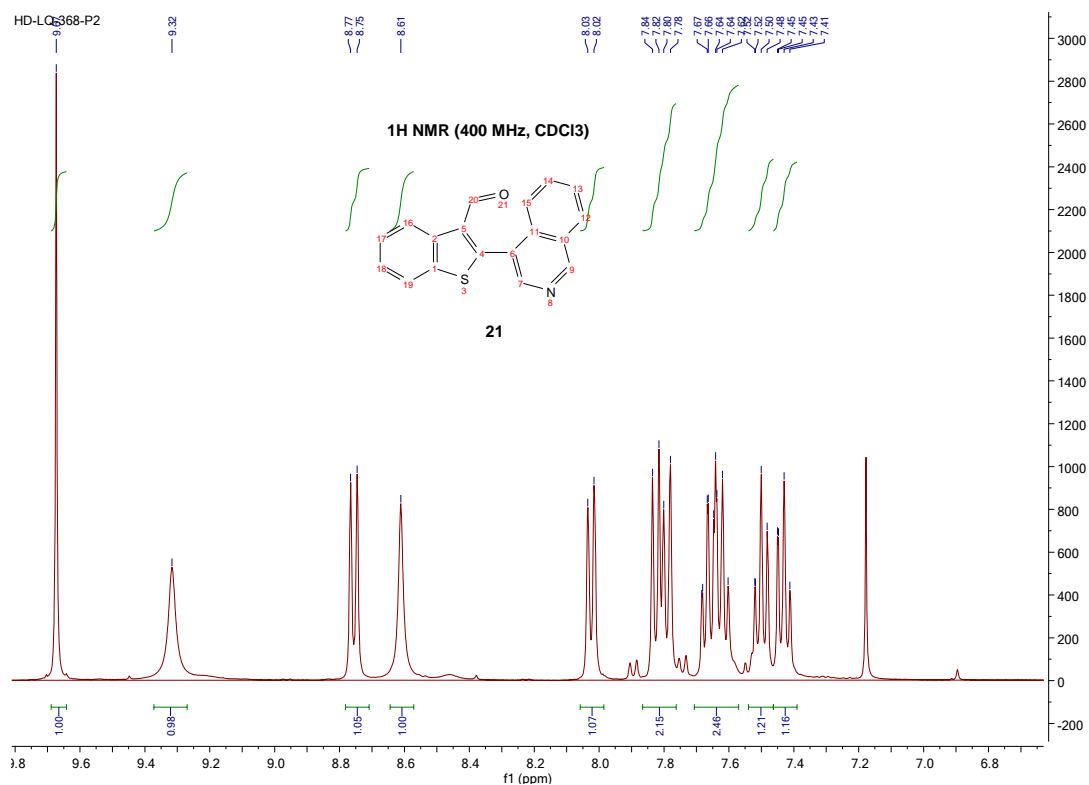
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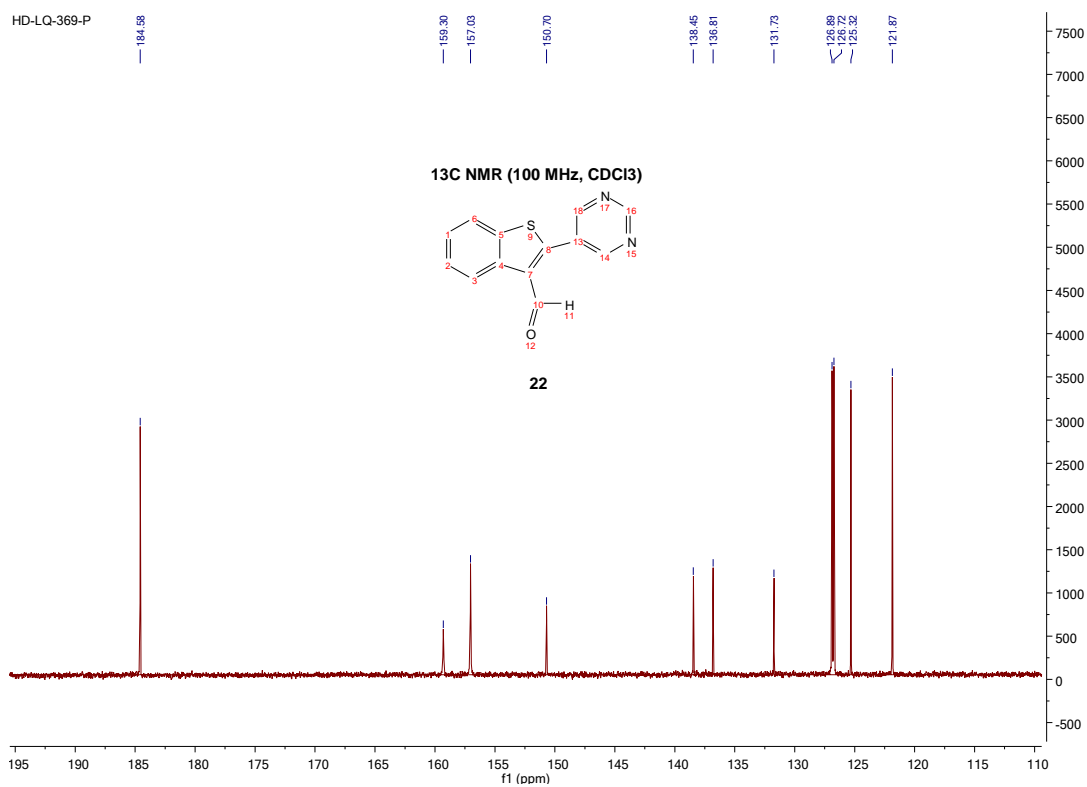
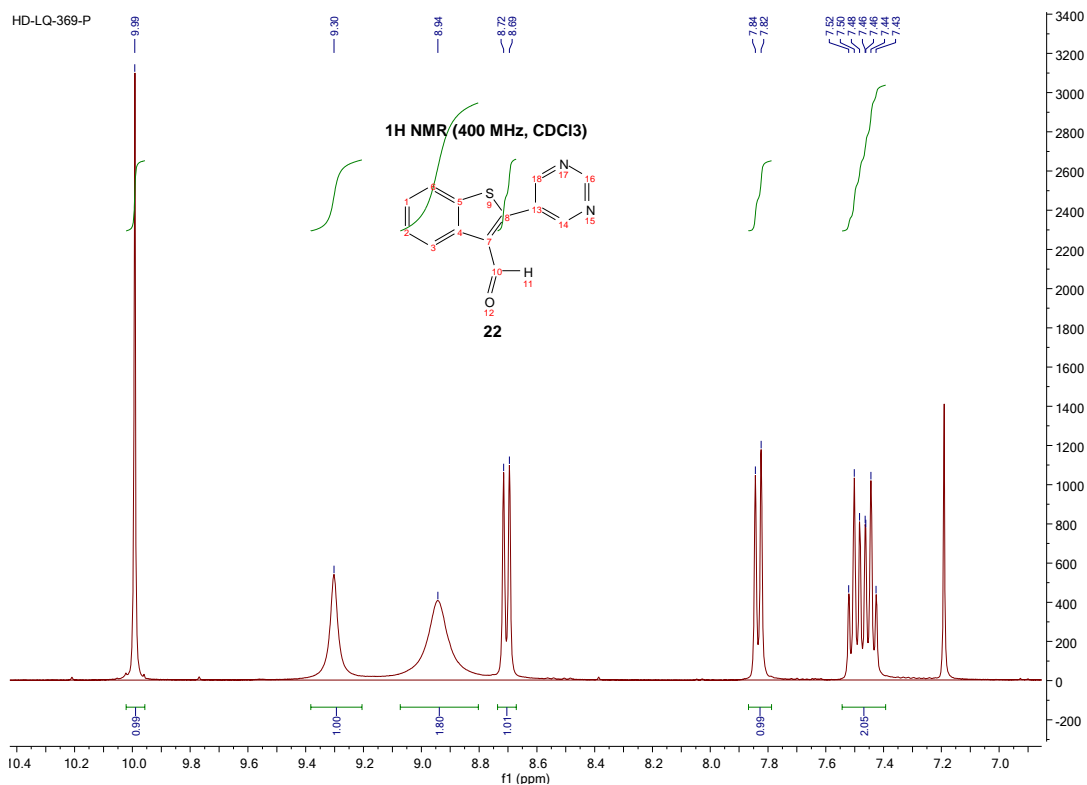


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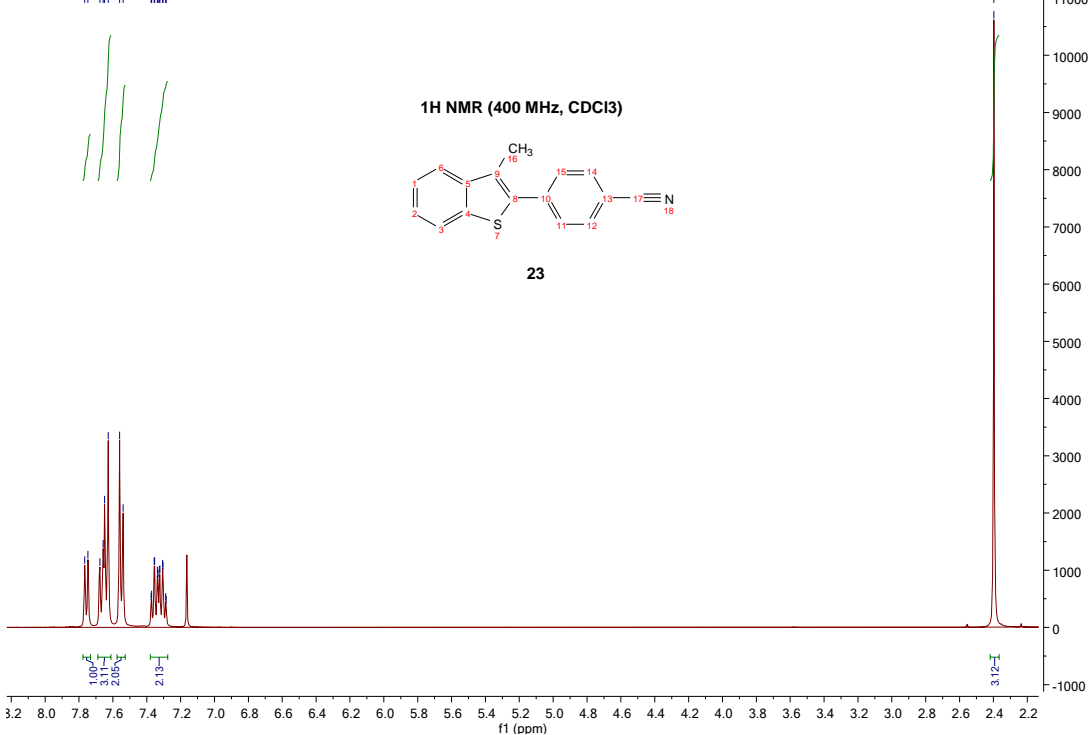




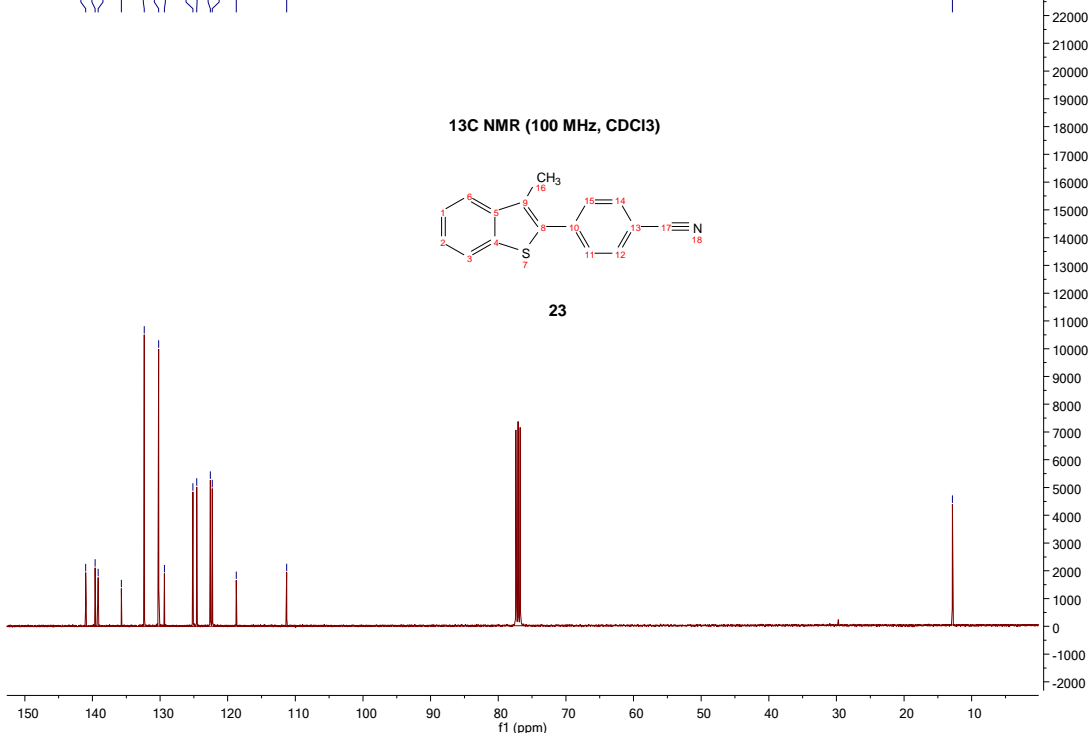




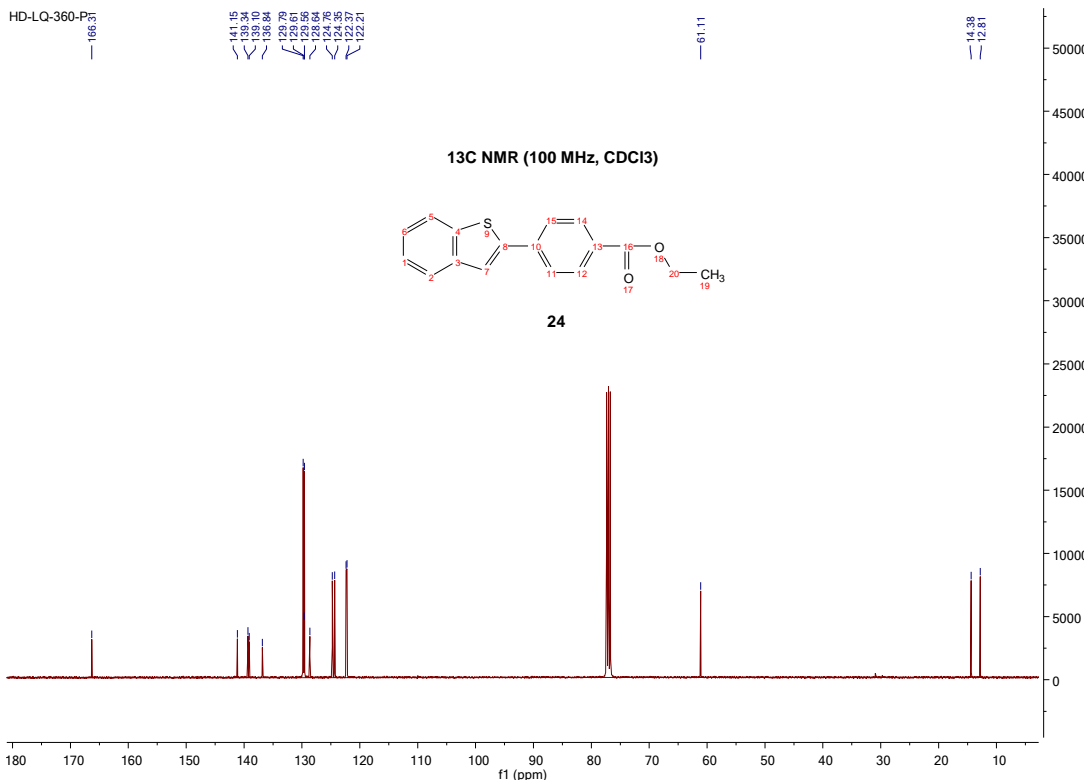
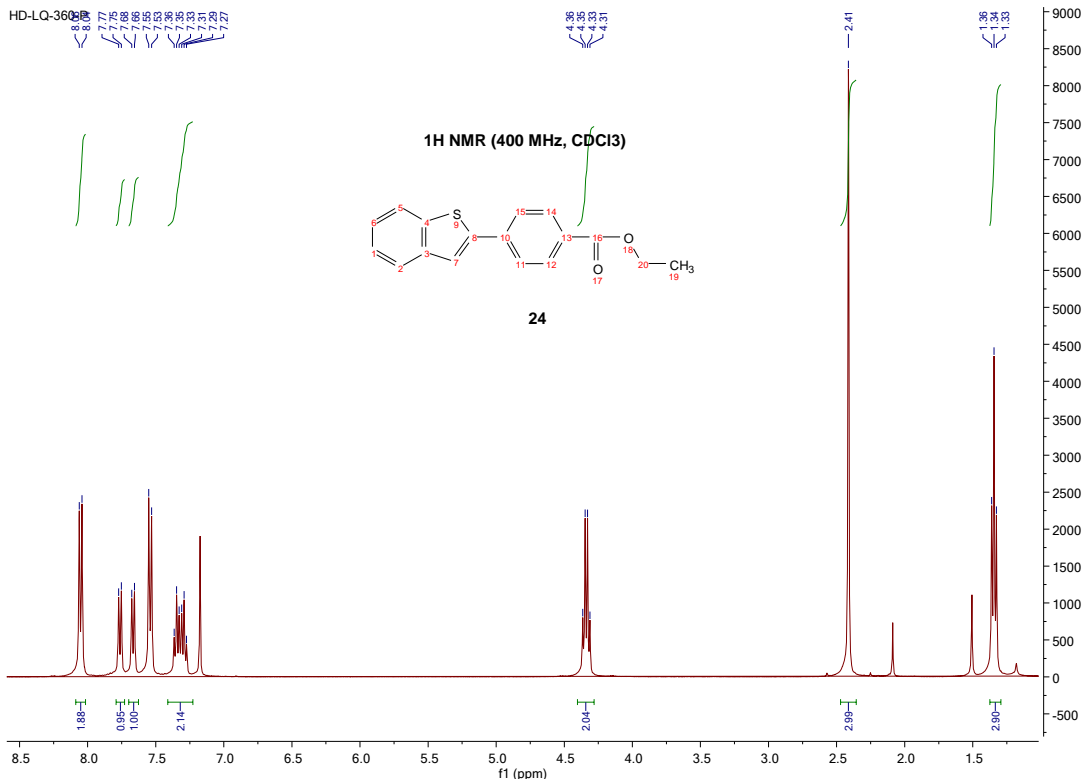
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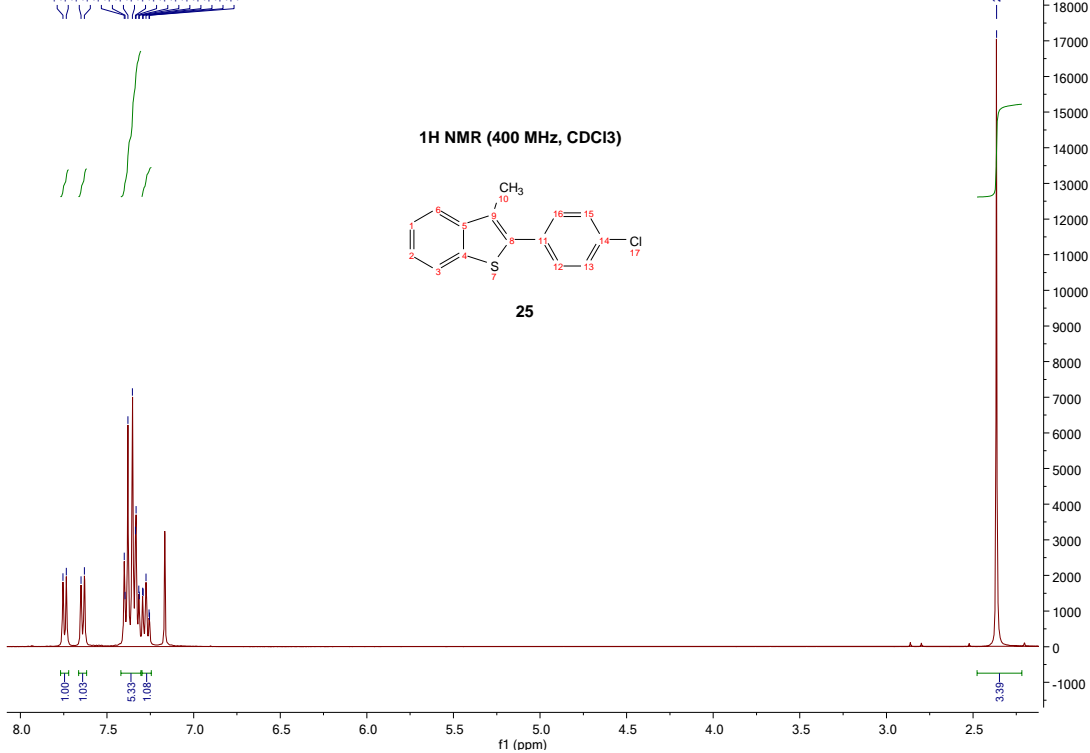
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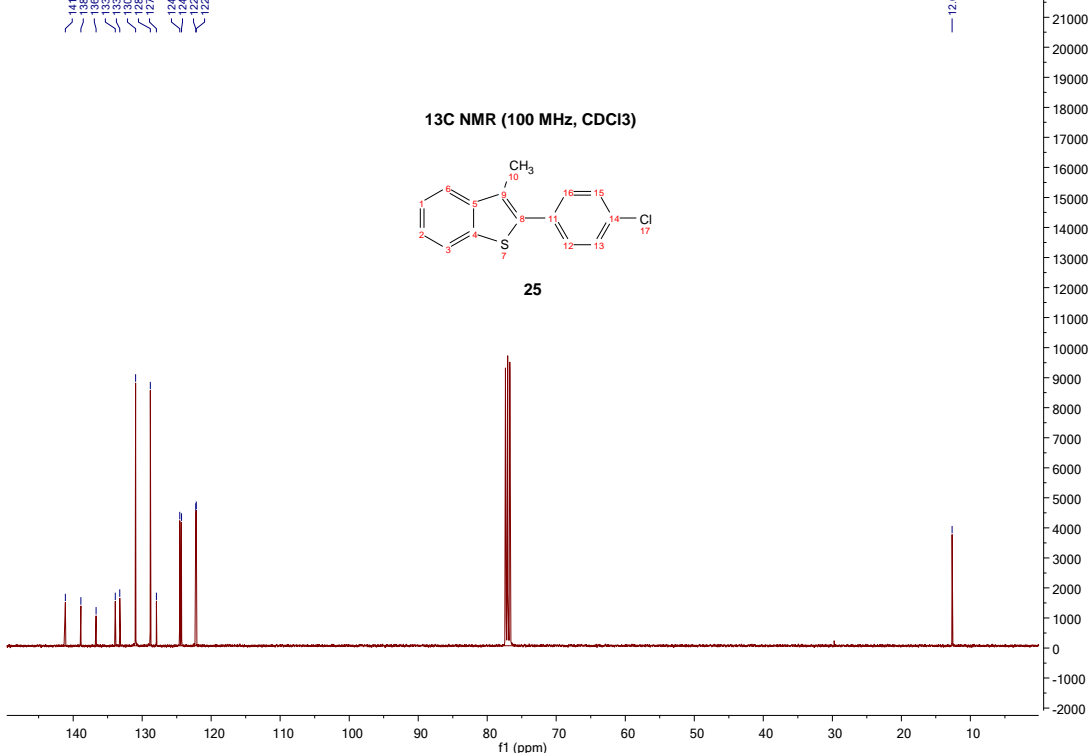


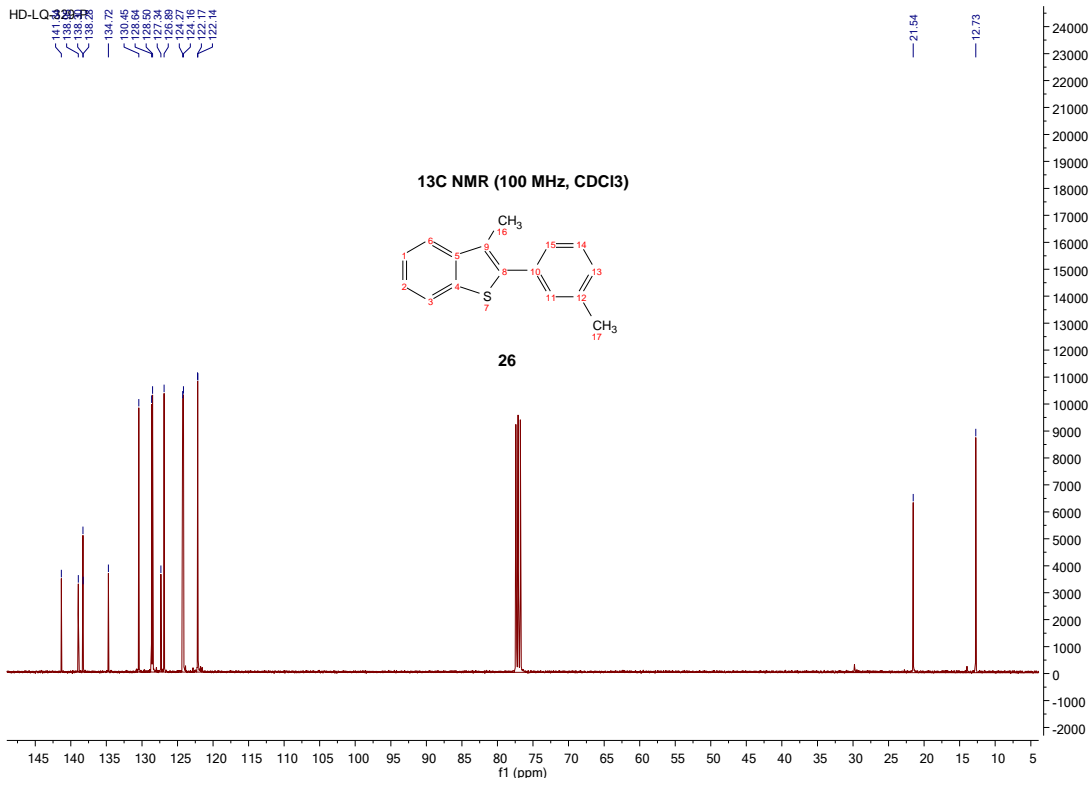
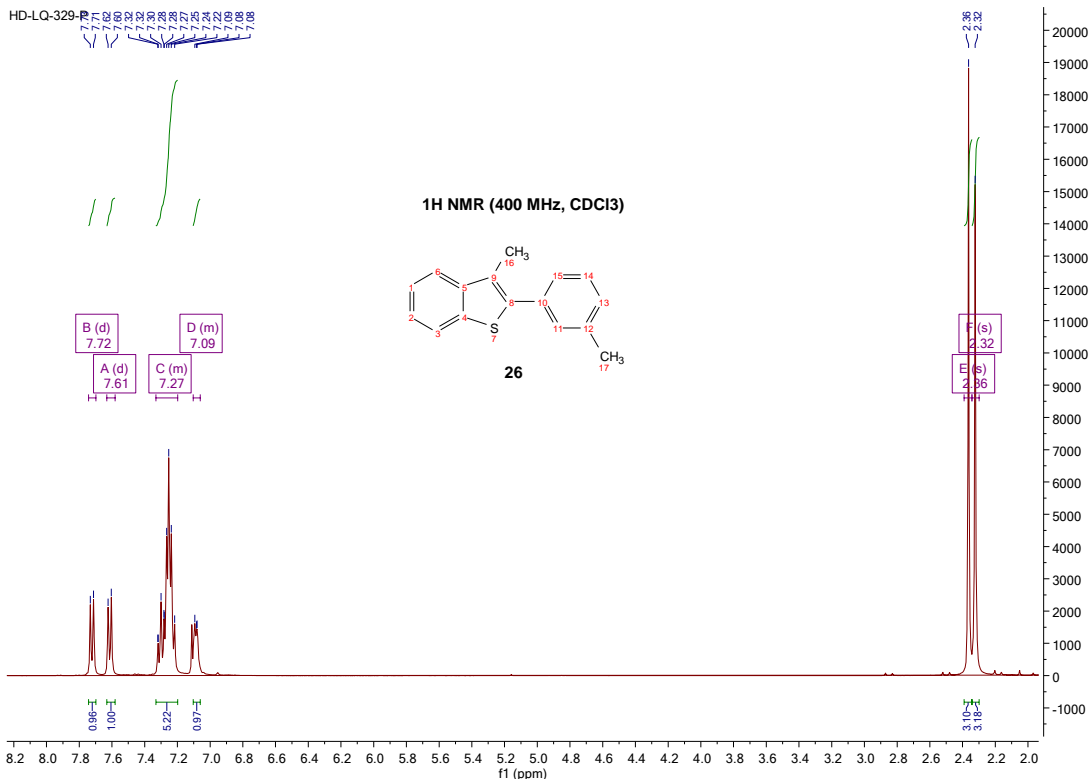


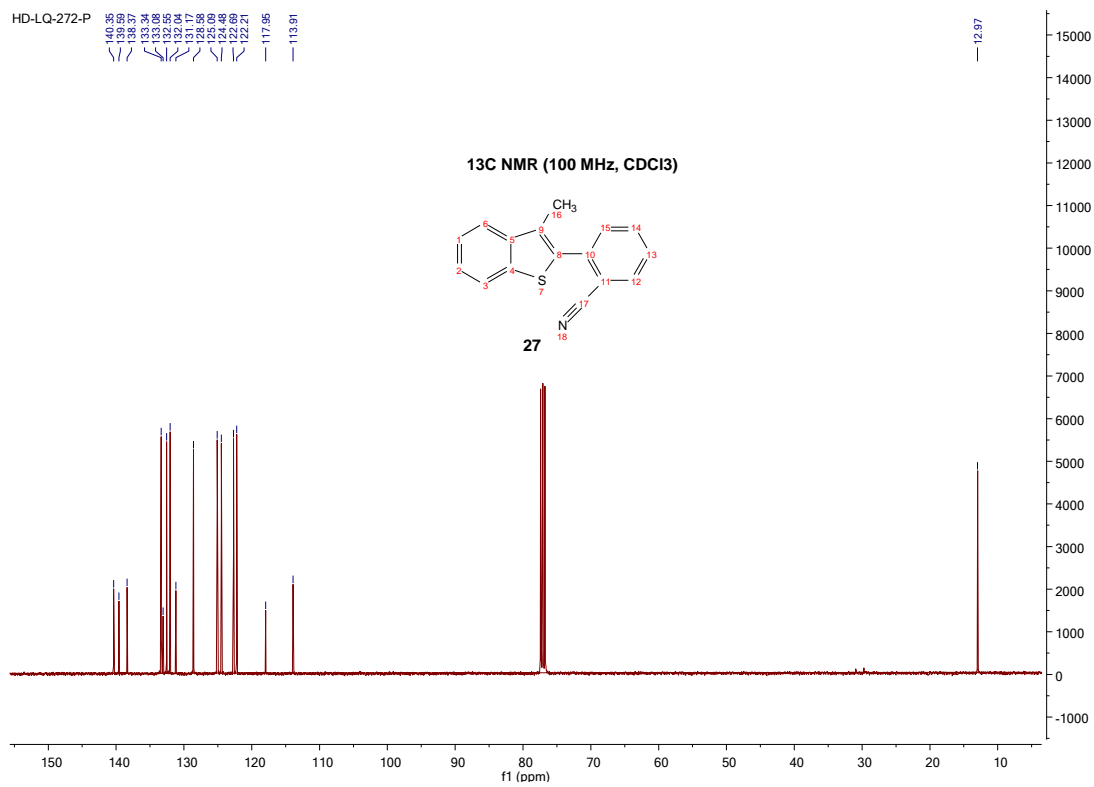
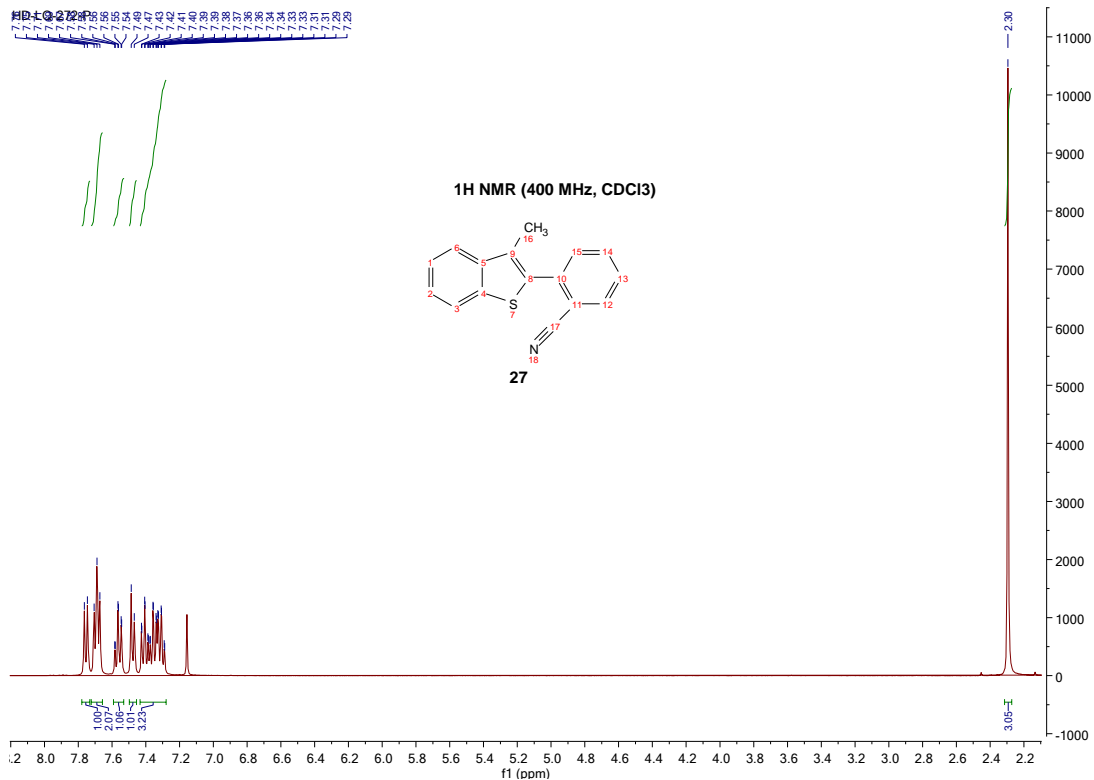
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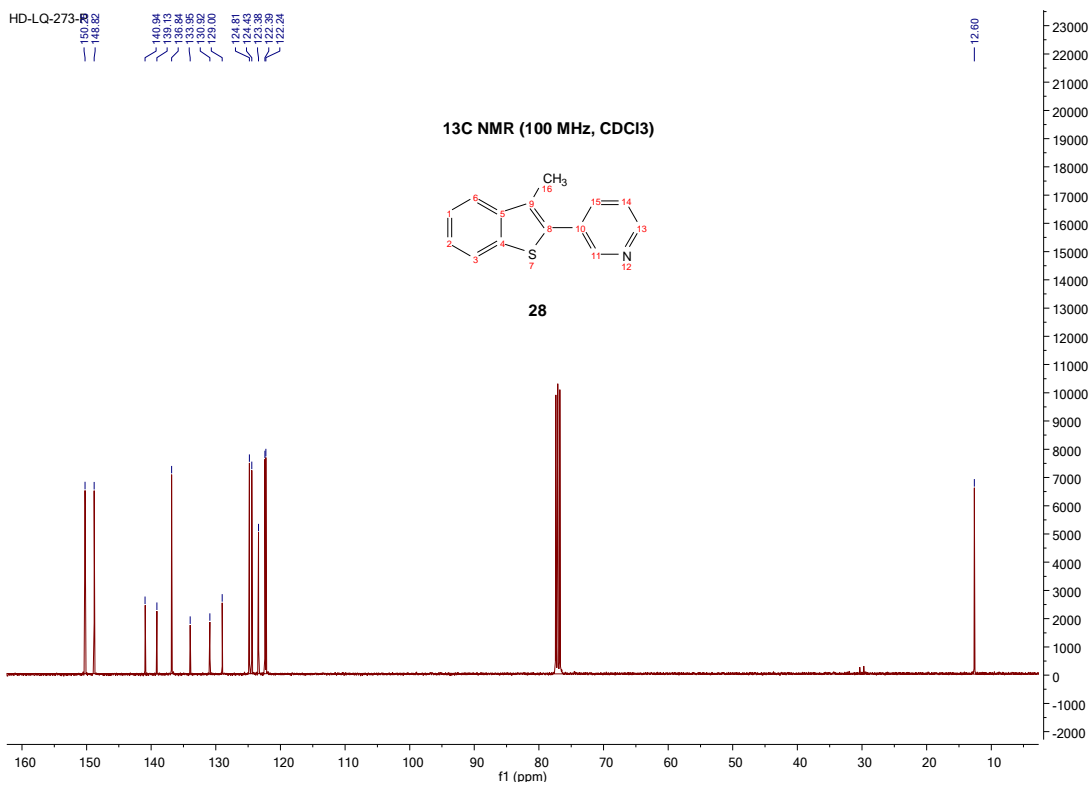
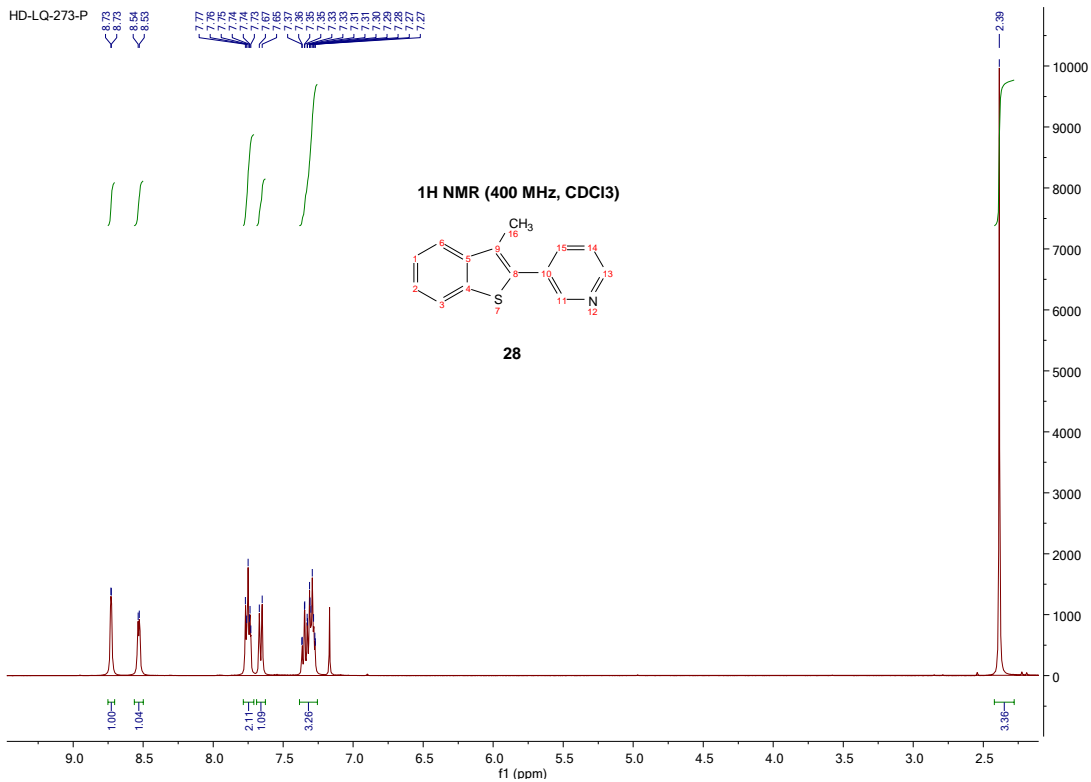


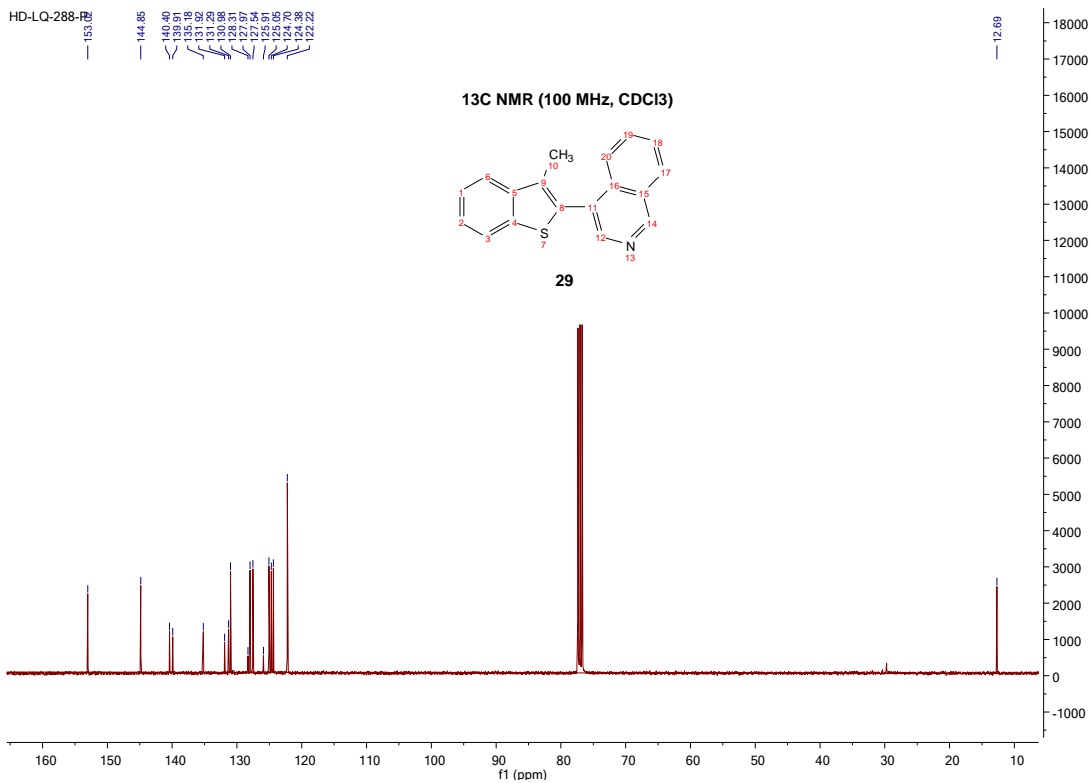
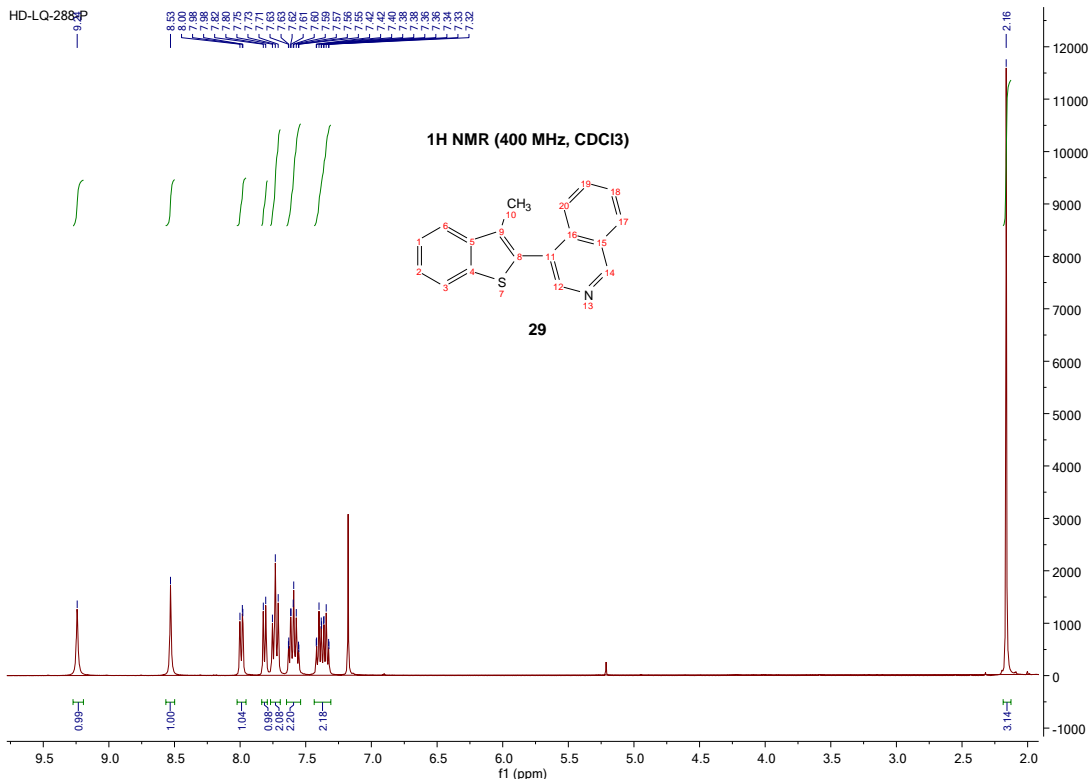
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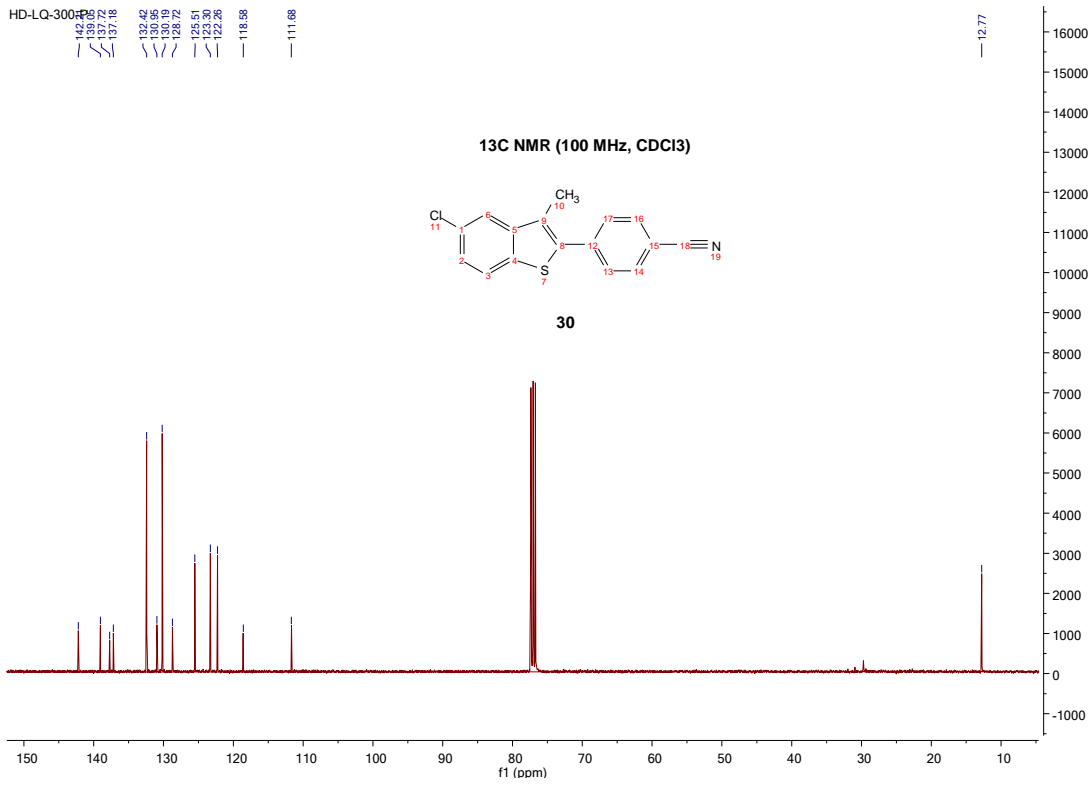
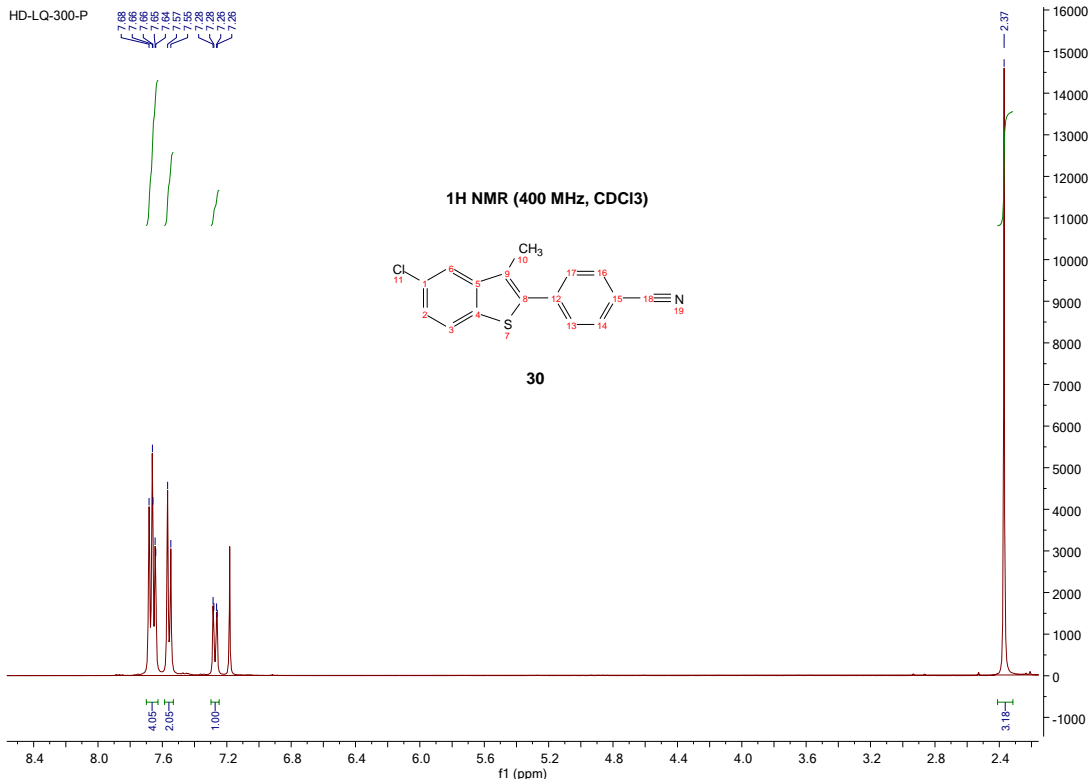












HD-LQ-328-P

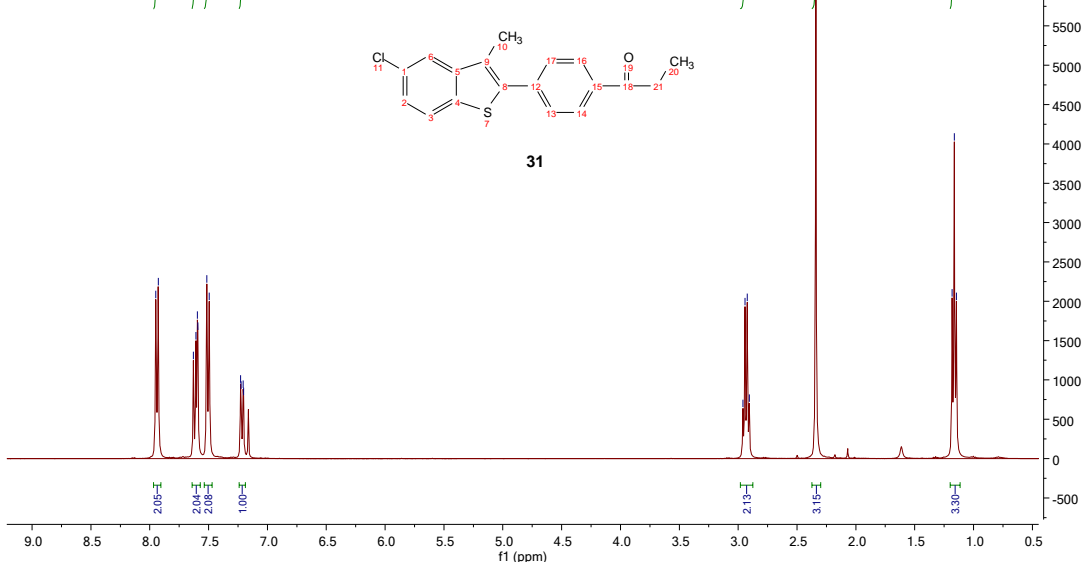
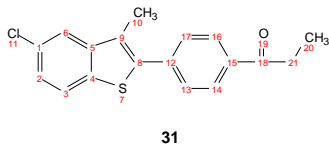
7.95  
7.93  
7.61  
7.59  
7.57  
7.55  
7.21  
7.20

2.98  
2.95  
2.91

2.34

1.18  
1.15

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



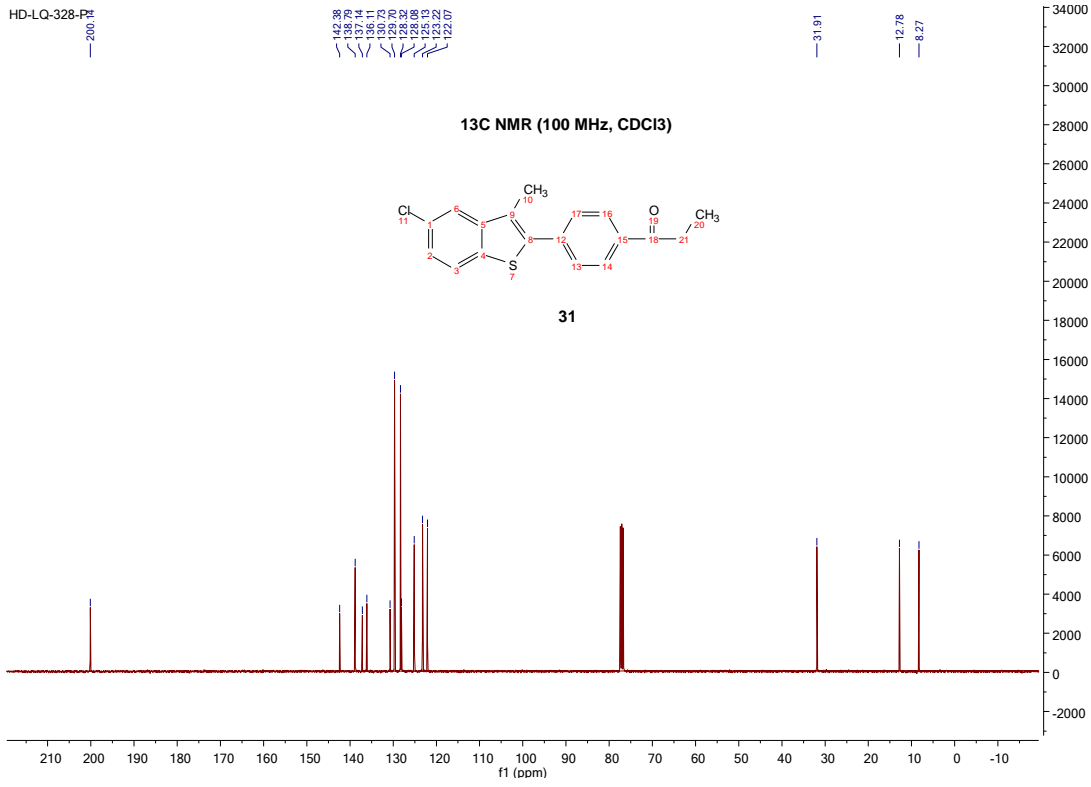
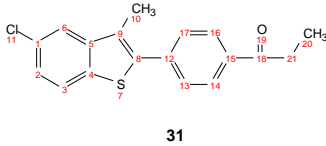
HD-LQ-328-P

143.28  
138.79  
137.14  
130.71  
129.70  
128.82  
125.13  
122.22

31.91

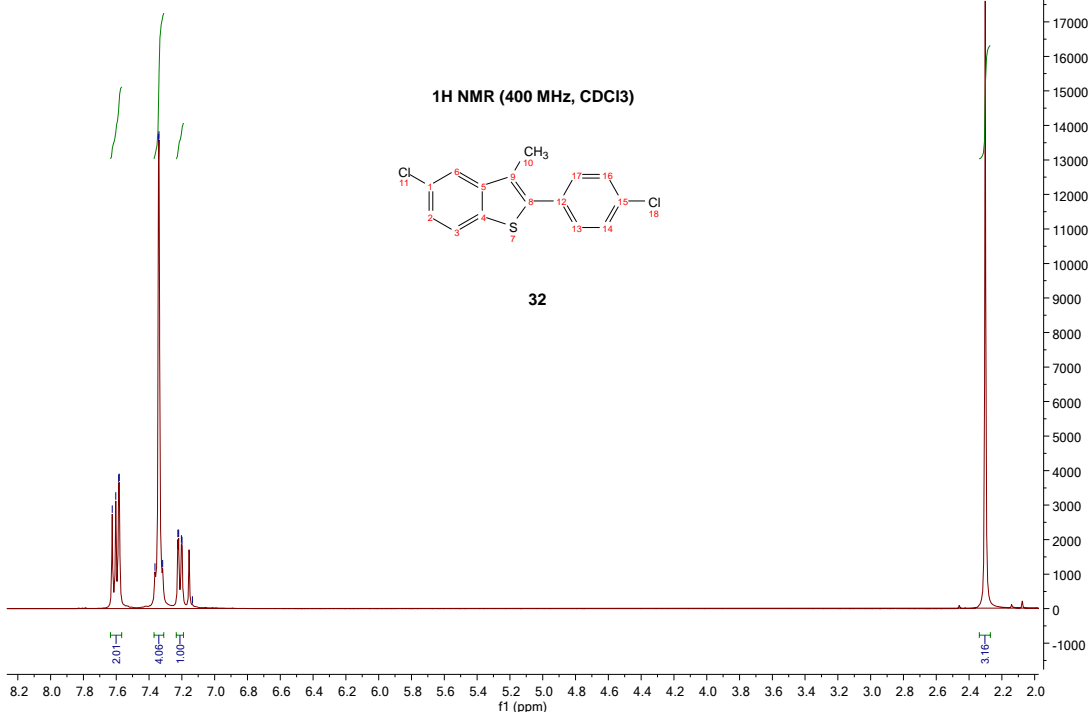
12.78  
8.27

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



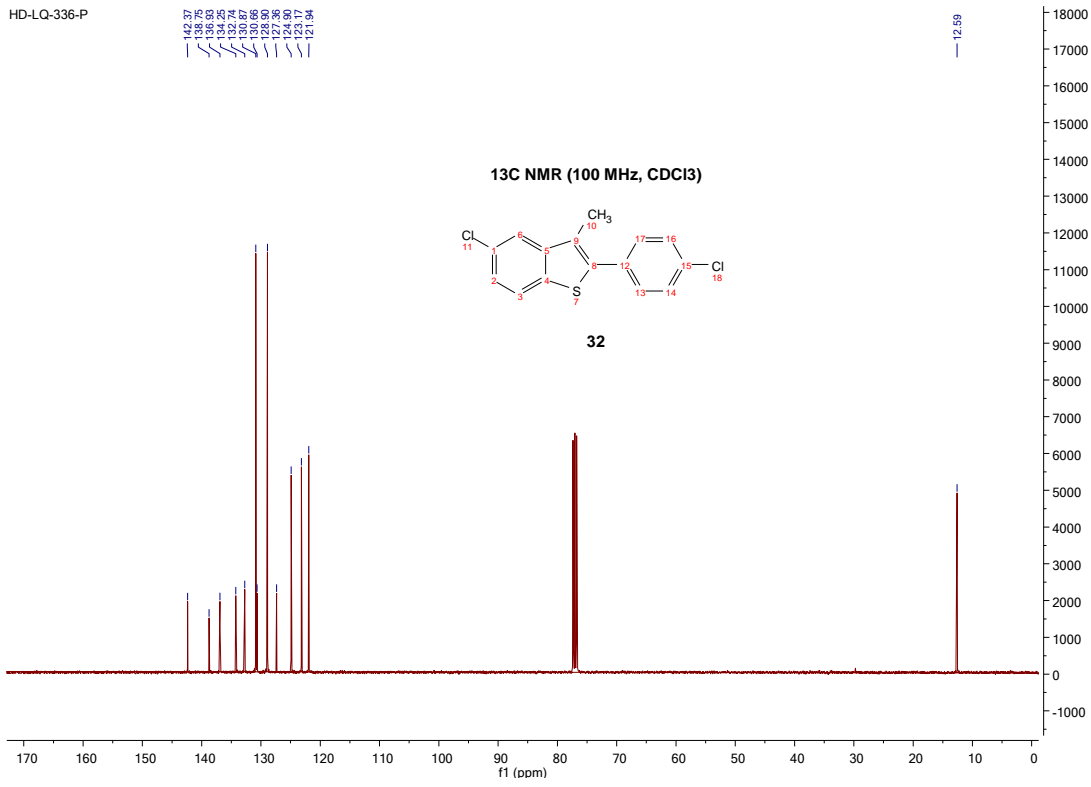


HD-LQ-336-P  
7.60  
7.59  
7.58  
7.57  
7.56  
7.55  
7.54  
7.53  
7.52  
7.51  
7.50  
7.49  
7.48



HD-LQ-336-P

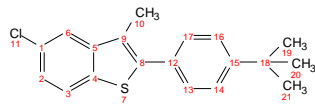
142.37  
138.75  
138.42  
137.74  
136.86  
128.90  
127.46  
123.17  
121.94



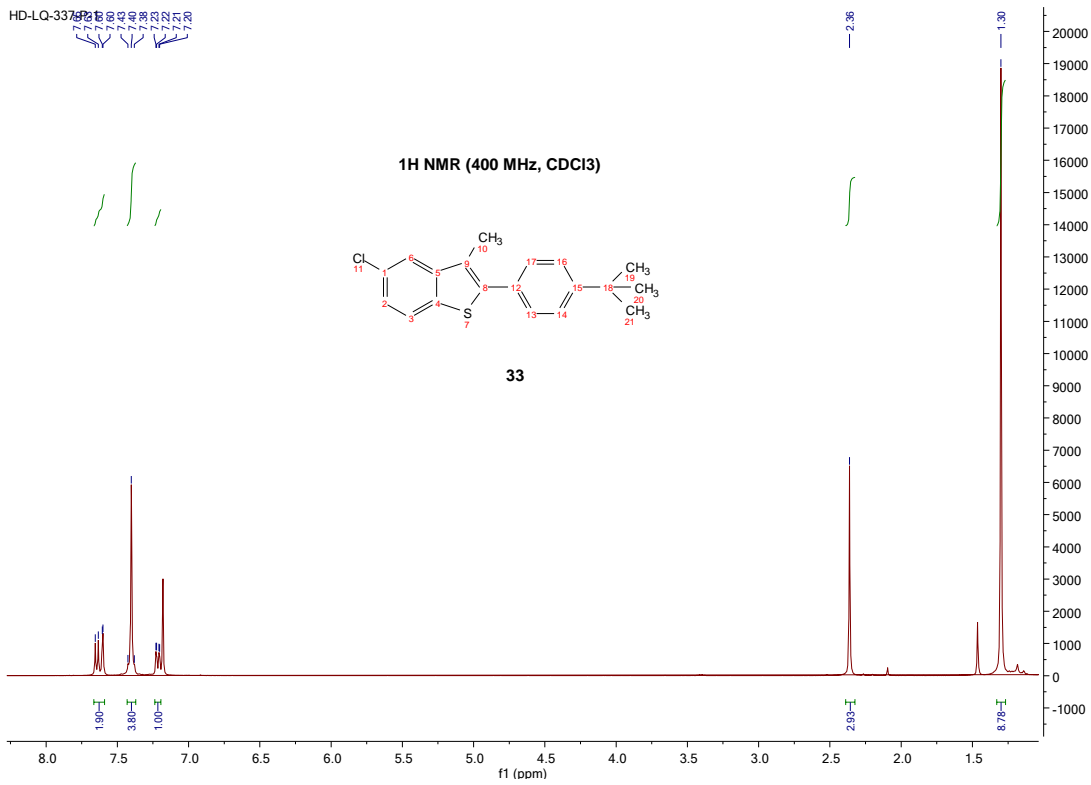
HD-LQ-337-P-12

7.762  
7.752  
7.742  
7.732  
7.722  
7.712  
7.702  
7.692  
7.682  
7.672  
7.662  
7.652  
7.642  
7.632  
7.622  
7.612  
7.602  
7.592  
7.582  
7.572  
7.562  
7.552  
7.542  
7.532  
7.522  
7.512  
7.502  
7.492  
7.482  
7.472  
7.462  
7.452  
7.442  
7.432  
7.422  
7.412  
7.402  
7.392  
7.382  
7.372  
7.362  
7.352  
7.342  
7.332  
7.322  
7.312  
7.302  
7.292  
7.282  
7.272  
7.262  
7.252  
7.242  
7.232  
7.222  
7.212  
7.202

1H NMR (400 MHz, CDCl3)



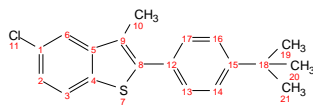
33



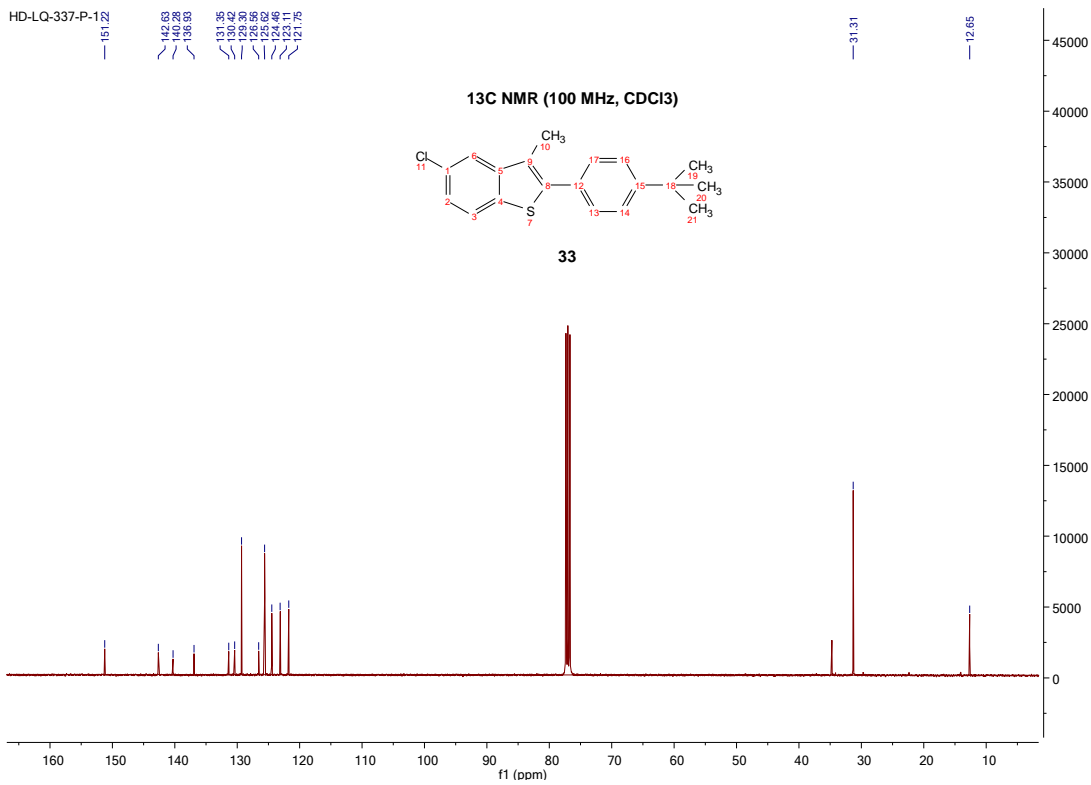
HD-LQ-337-P-12

151.22  
145.03  
144.26  
143.26  
138.93  
131.35  
130.42  
129.59  
128.92  
128.62  
127.19  
125.11  
121.75

13C NMR (100 MHz, CDCl3)



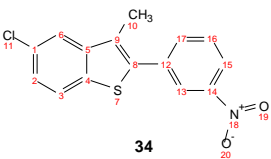
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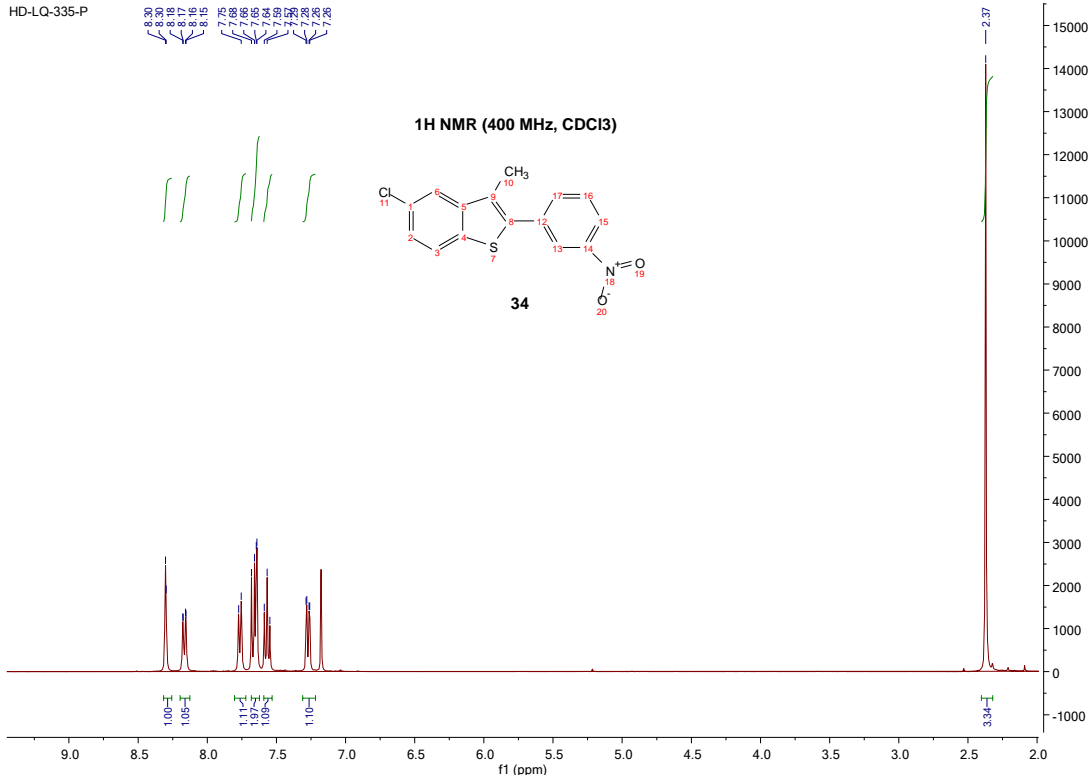
HD-LQ-335-P

8.30  
8.30  
8.18  
8.16  
8.15  
7.75  
7.68  
7.65  
7.64  
7.59  
7.58  
7.29

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



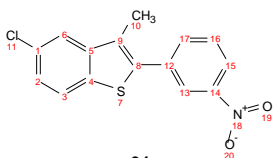
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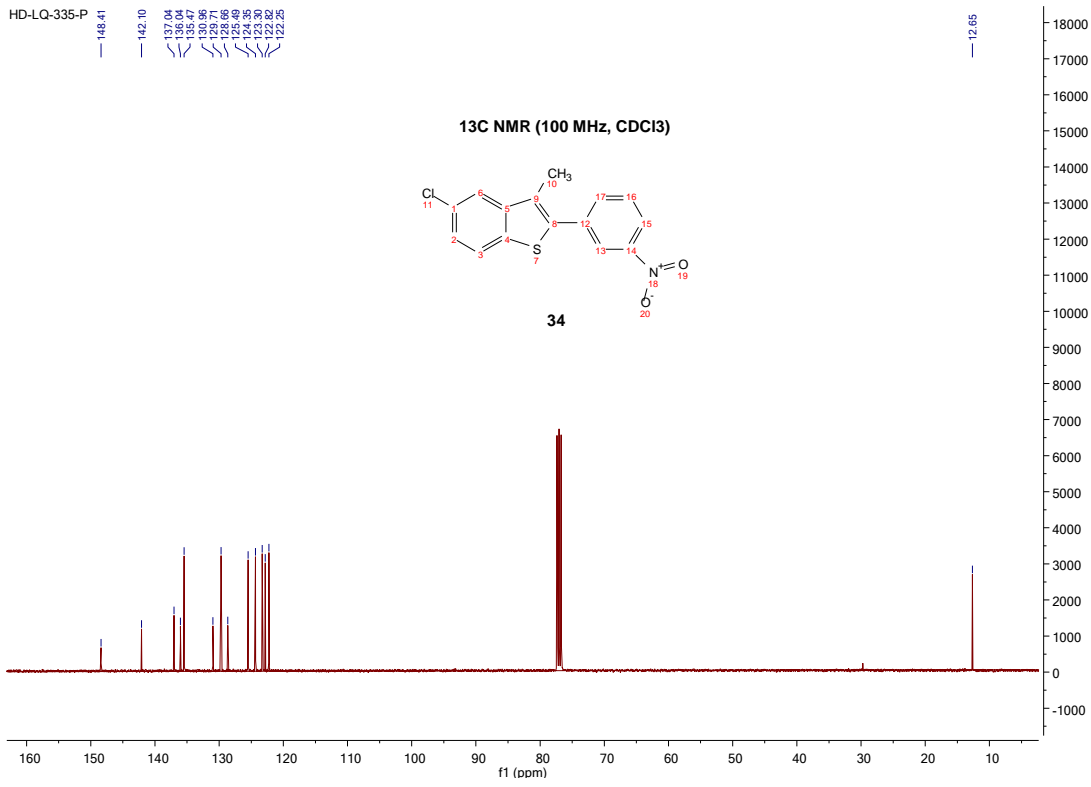
HD-LQ-335-P

148.41  
142.10  
137.04  
135.97  
130.96  
129.71  
128.49  
124.35  
122.82  
122.25

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



34

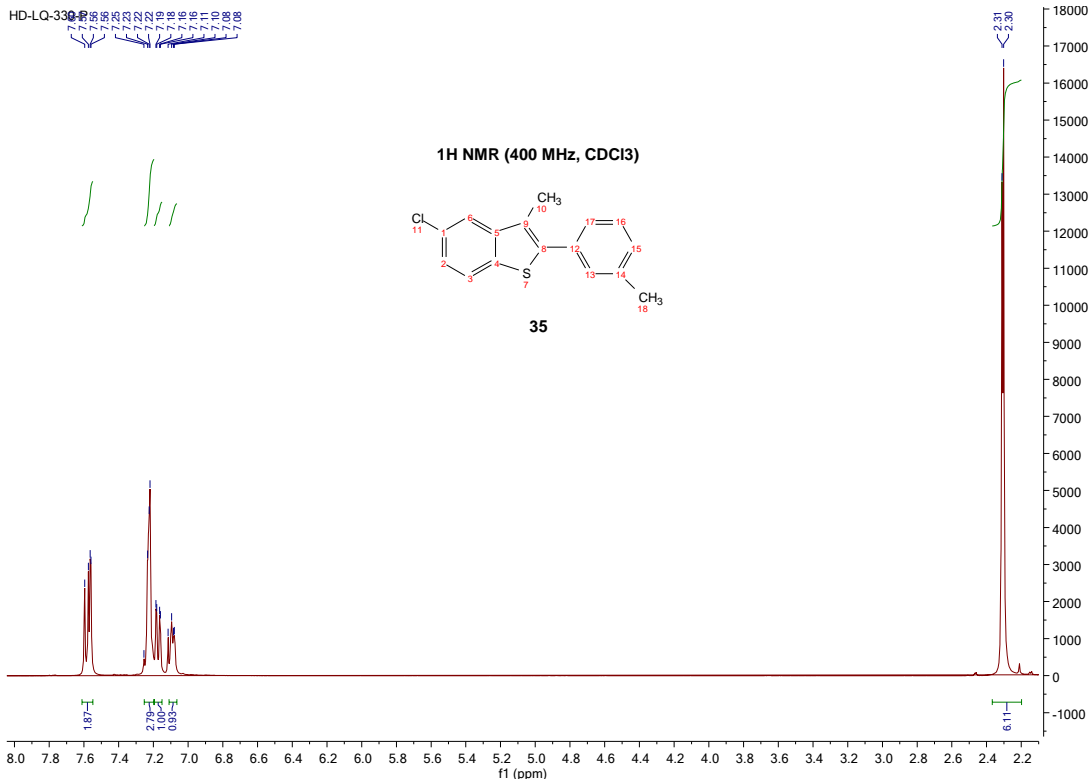
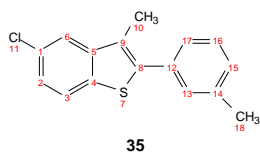


HD-LQ-330-P

7.59  
7.58  
7.57  
7.56  
7.55  
7.54  
7.53  
7.52  
7.51  
7.50  
7.49  
7.48  
7.47  
7.46  
7.45  
7.44  
7.43  
7.42  
7.41  
7.40  
7.39  
7.38  
7.37  
7.36  
7.35  
7.34  
7.33  
7.32  
7.31  
7.30  
7.29  
7.28  
7.27  
7.26  
7.25  
7.24  
7.23  
7.22  
7.21  
7.20  
7.19  
7.18  
7.17  
7.16  
7.15  
7.14  
7.13  
7.12  
7.11  
7.10  
7.09  
7.08



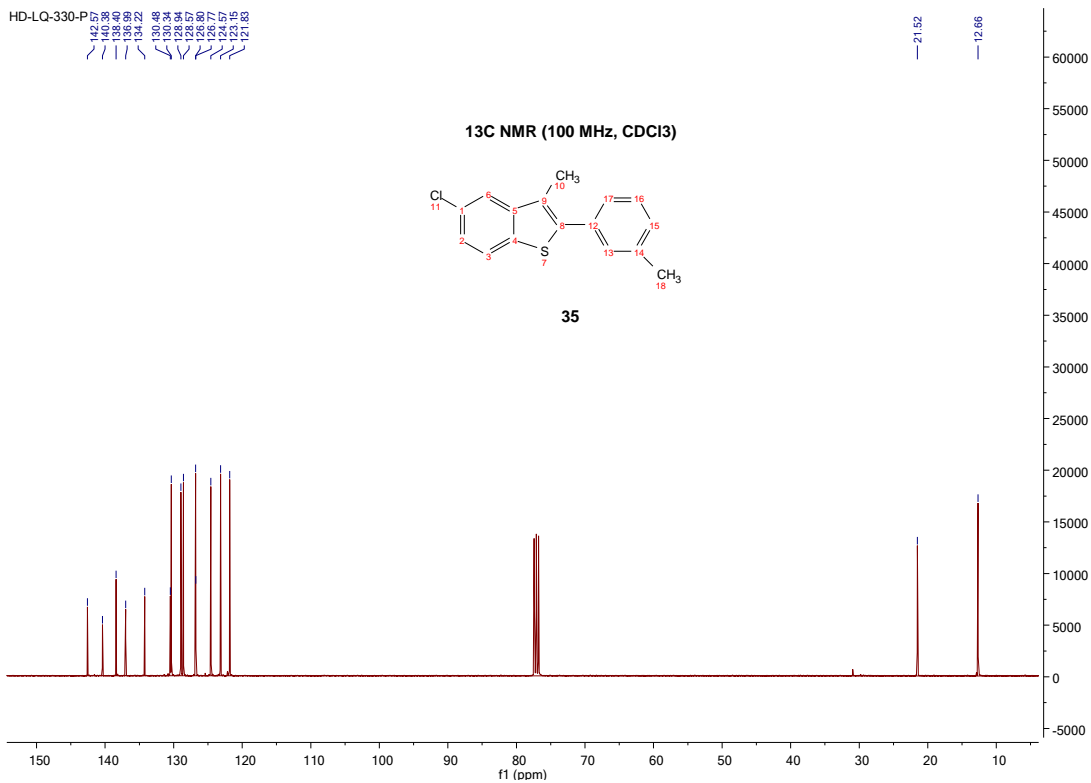
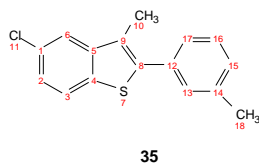
1H NMR (400 MHz, CDCl3)

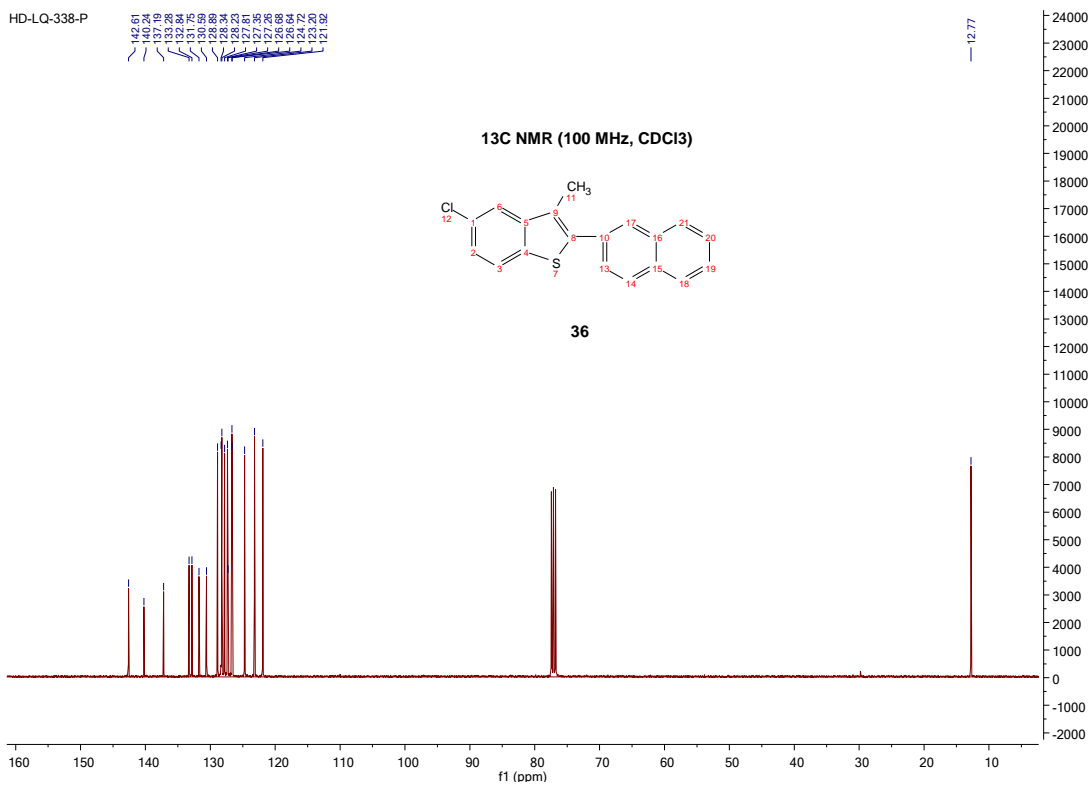
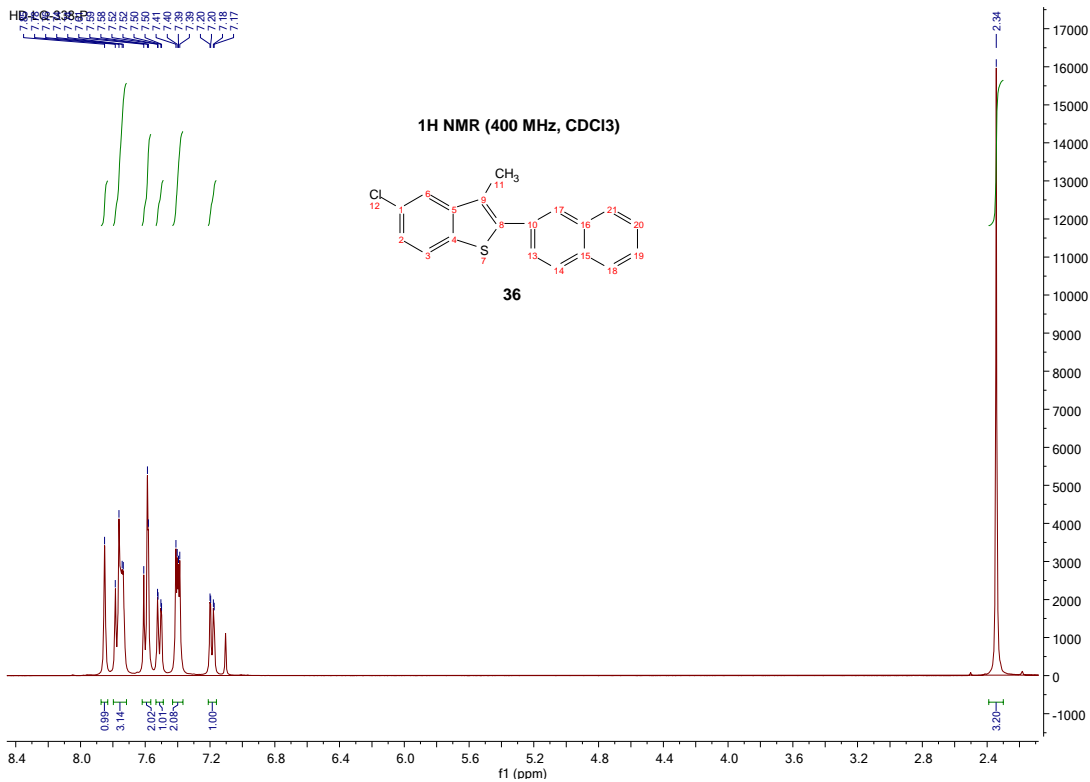


HD-LQ-330-P

142.57  
140.38  
139.96  
138.99  
134.22  
130.48  
130.34  
129.87  
128.80  
128.57  
127.47  
123.15  
121.83

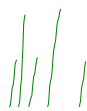
13C NMR (100 MHz, CDCl3)



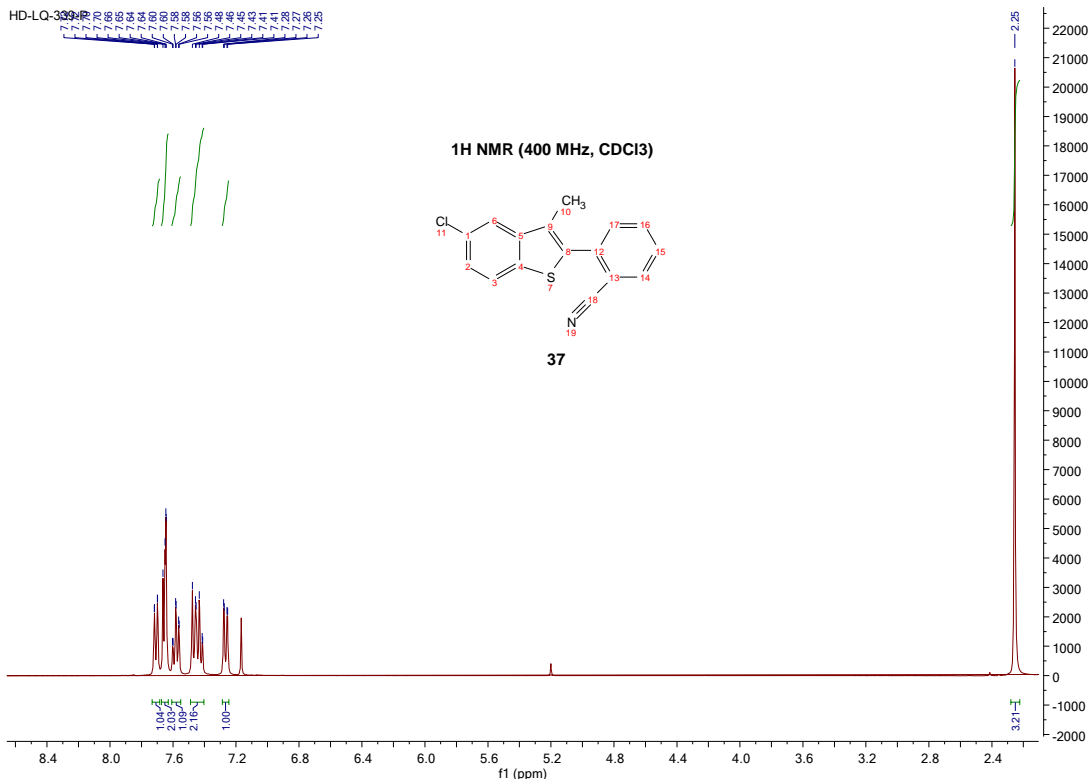
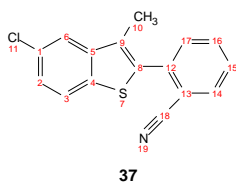


HD-LQ-339-P

7.77, 7.76, 7.66, 7.65, 7.64, 7.63, 7.62, 7.61, 7.59, 7.58, 7.56, 7.55, 7.48, 7.47, 7.46, 7.45, 7.44, 7.41, 7.39, 7.37, 7.27, 7.25



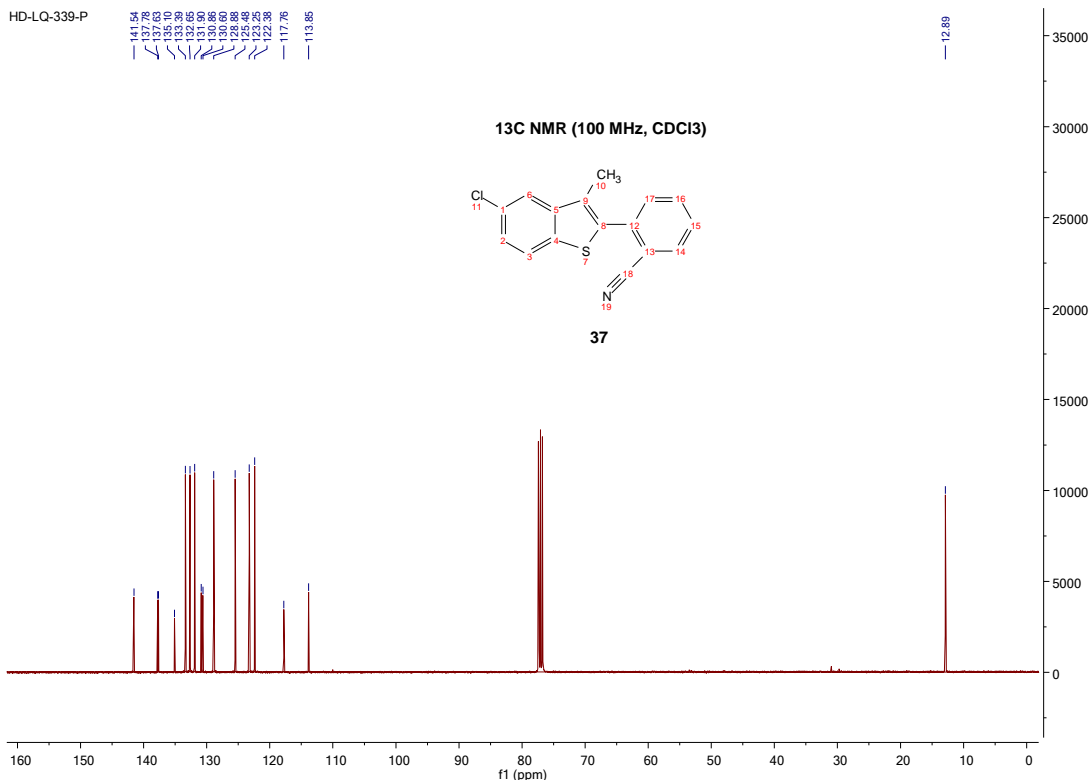
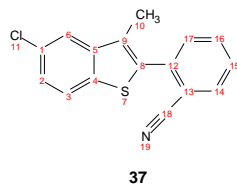
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



HD-LQ-339-P

143.54, 137.76, 137.63, 135.10, 133.65, 133.65, 133.60, 133.60, 128.88, 127.48, 122.38, 117.76, 113.85

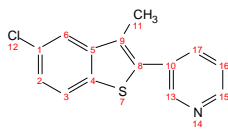
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



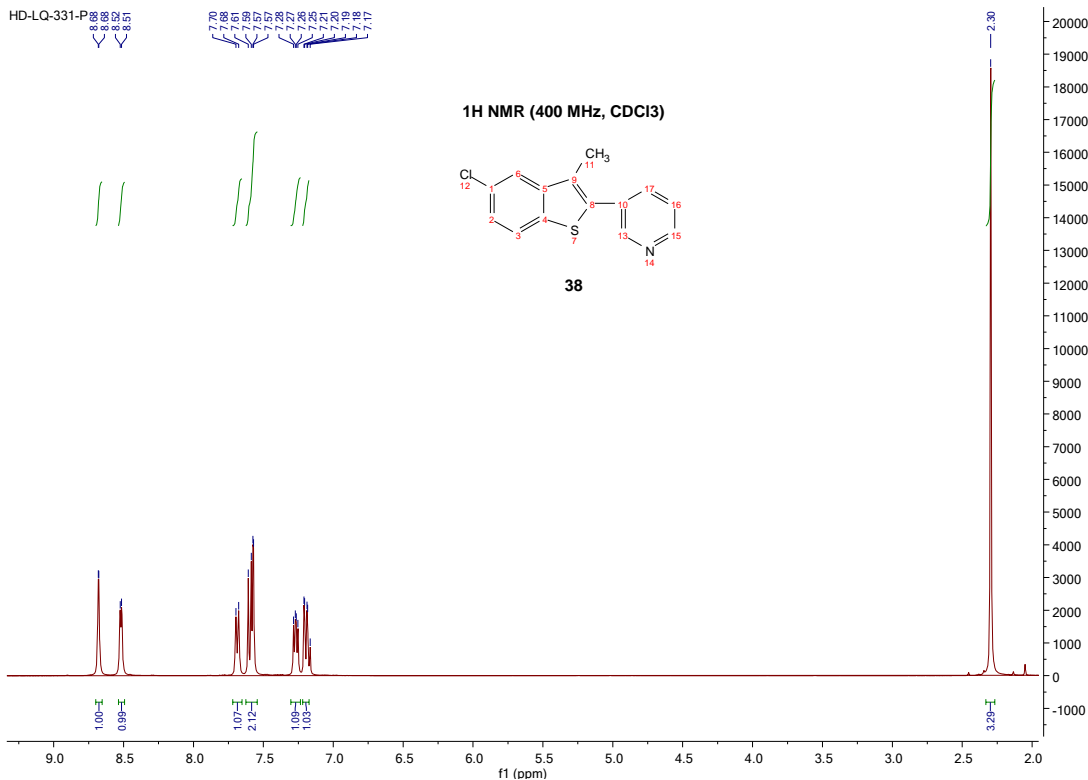
HD-LQ-331-P  
8.88  
8.85  
8.51

7.78  
7.61  
7.57  
7.57  
7.29  
7.26  
7.25  
7.21  
7.19  
7.11

### 1H NMR (400 MHz, CDCl3)



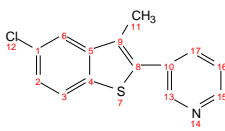
38



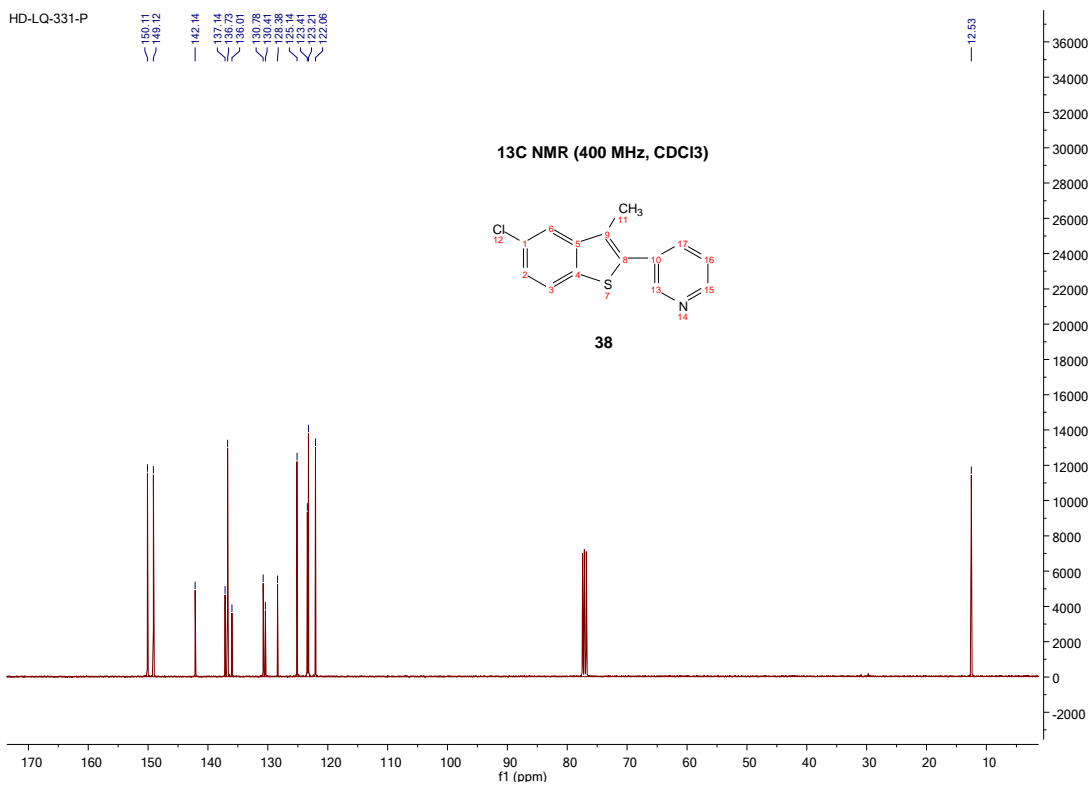
HD-LQ-331-P

150.11  
149.12  
142.14  
137.14  
136.03  
136.03  
130.78  
130.41  
128.38  
123.41  
123.21  
122.06

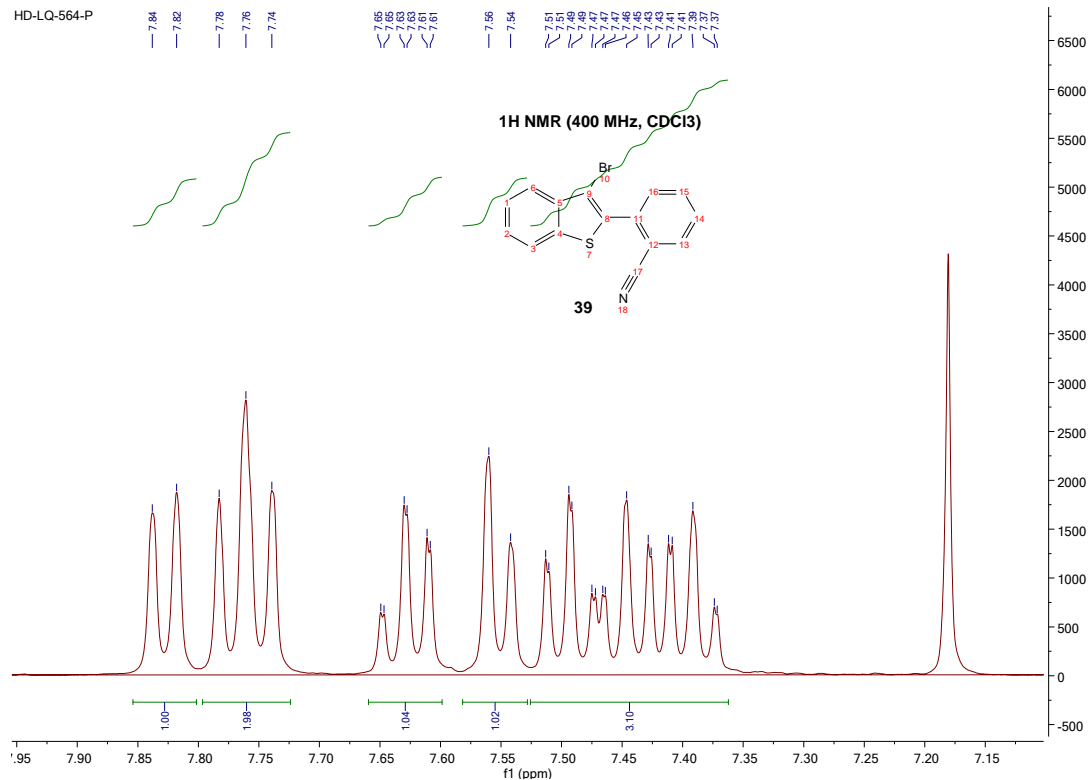
### 13C NMR (400 MHz, CDCl3)



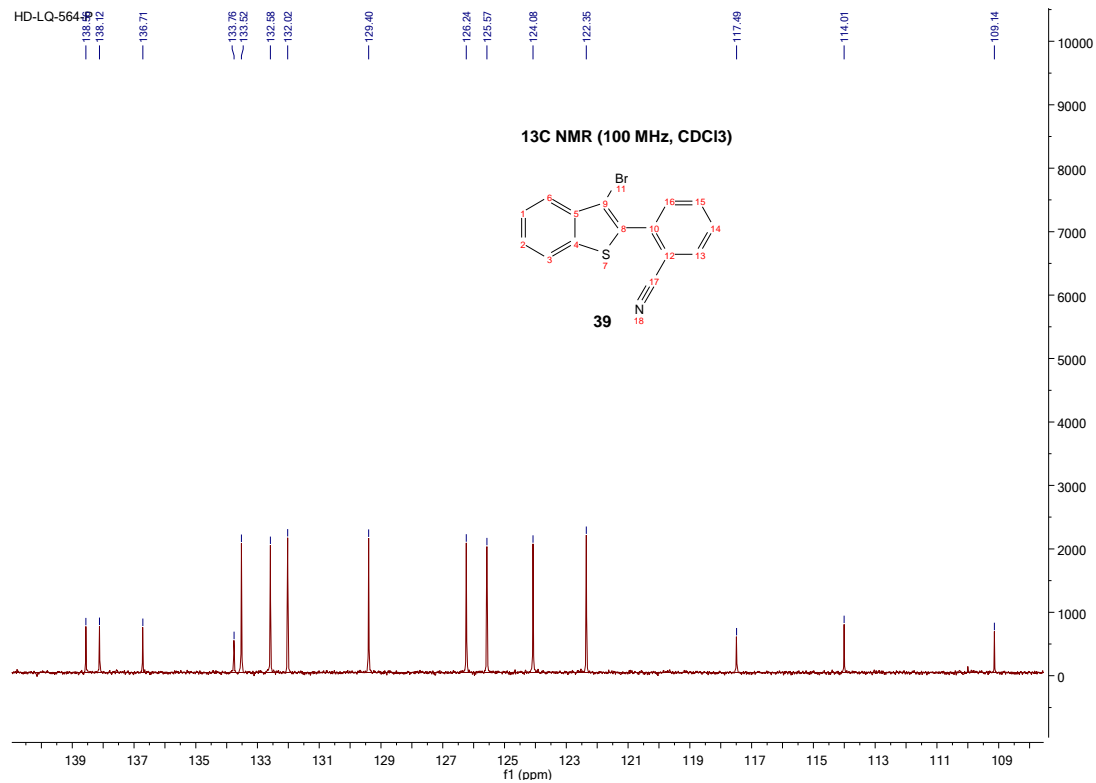
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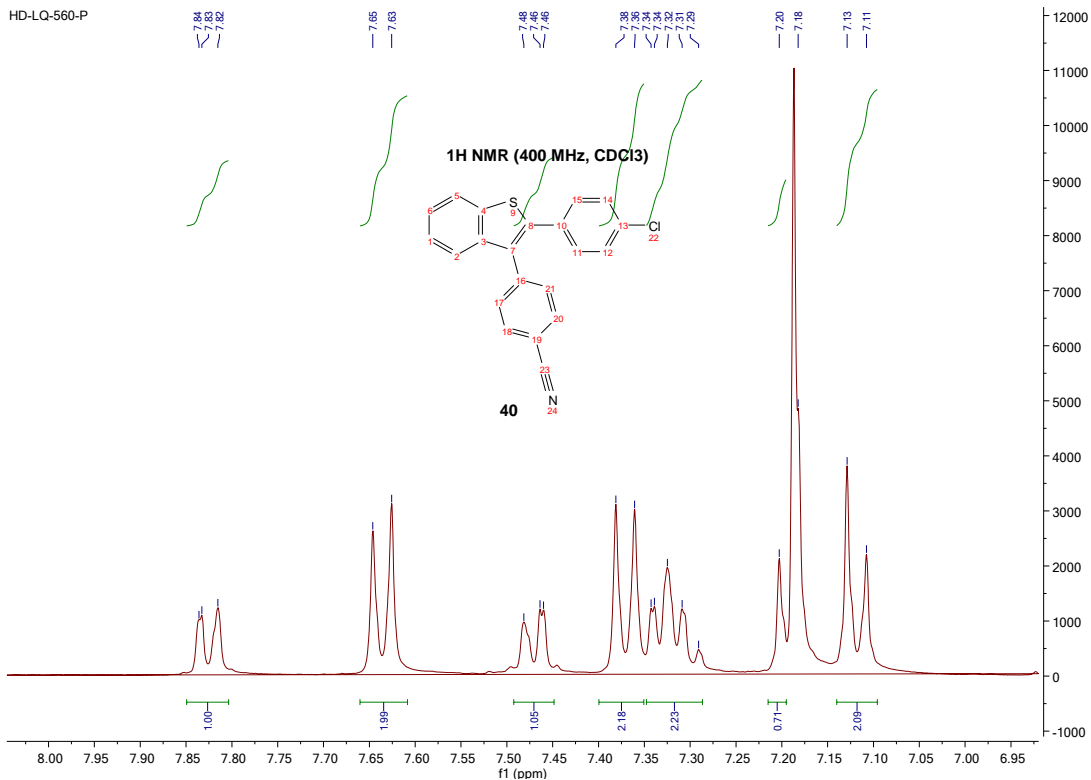


HD-LQ-564-P





HD-LQ-560-P



HD-LQ-560-P

