

## *Supporting Information*

### **Synthesis of Benzo[4,5]imidazo[1,2-*c*]pyrimidin-1-amines and Their Analogs via Copper-Catalyzed C-N Coupling and Cyclization**

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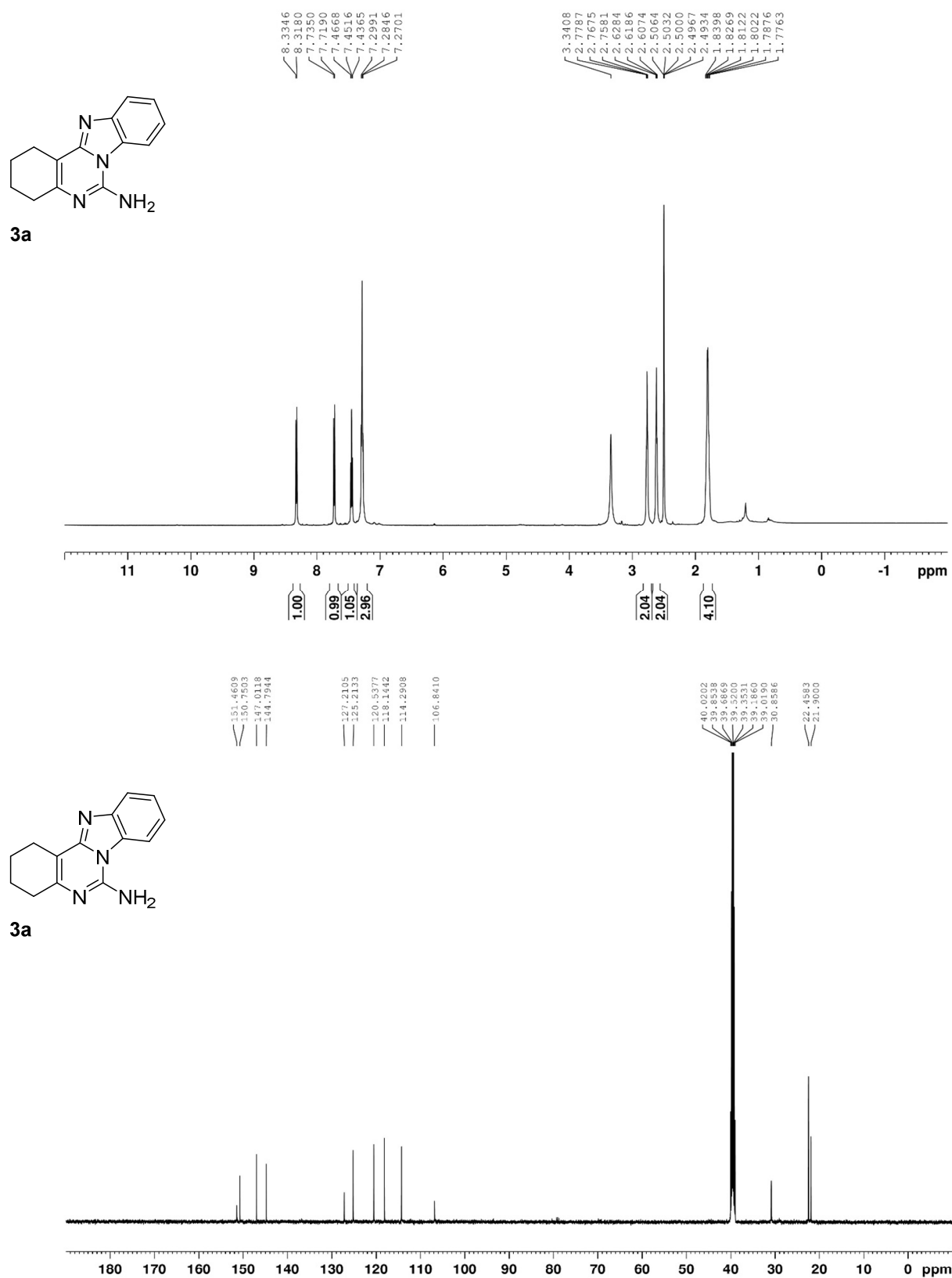
Copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds **3a-3k**, **3m-3o**, **5a-5d**: S2-S20

HRMS data of compounds **3a-3k**, **3m-3o**, **5a-5d**: S21-S30

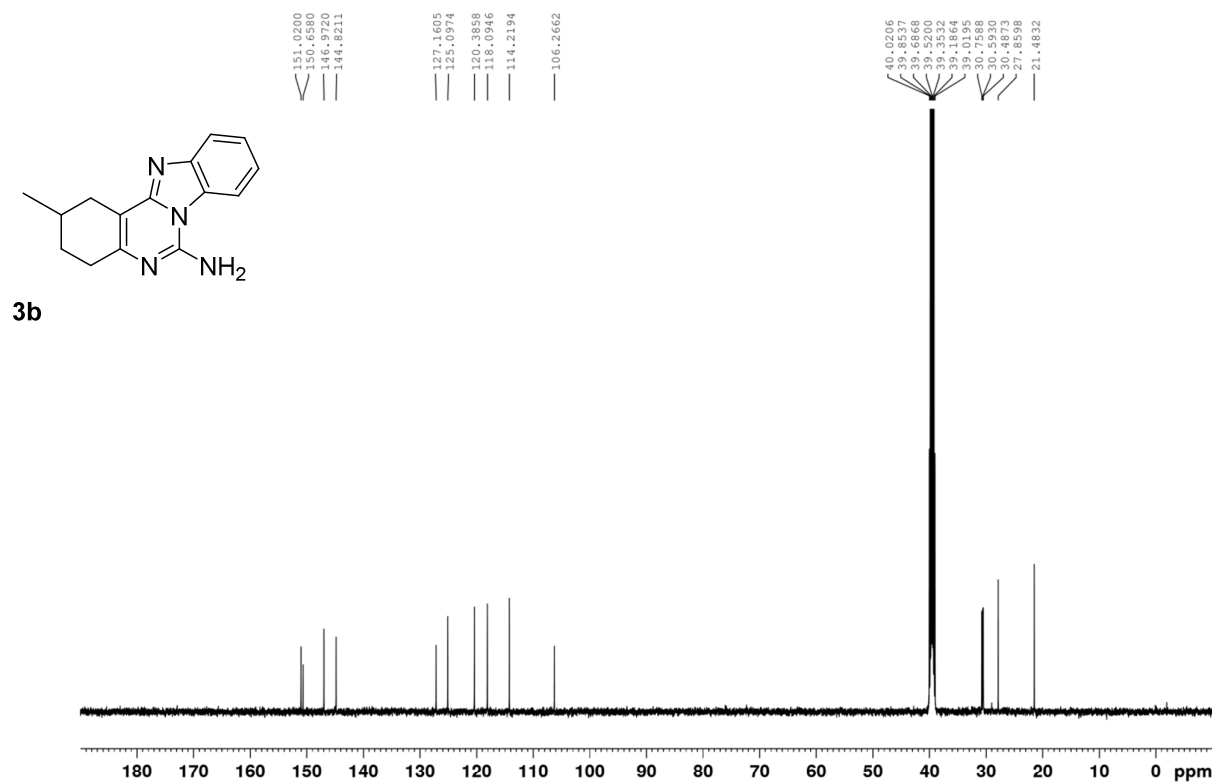
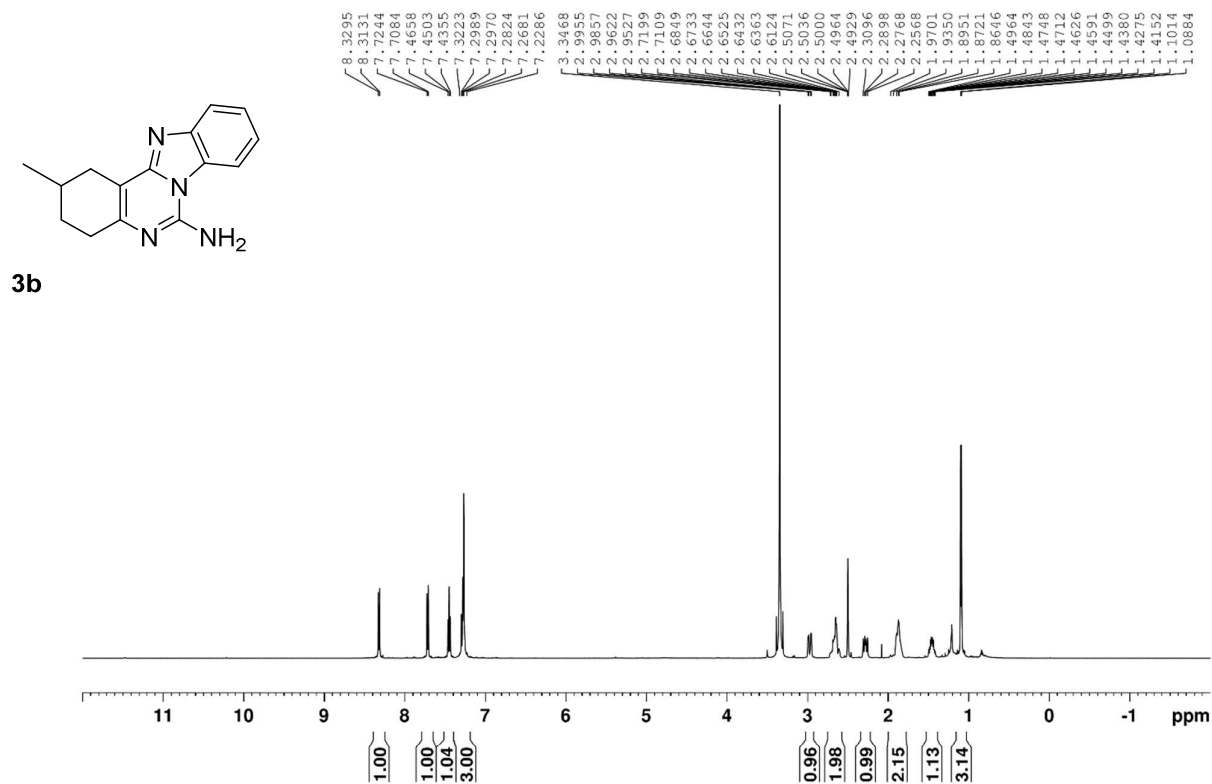
Experimental procedure for mechanism study and spectroscopic data of **9**: S31

Multiplet in the range ~2.49–2.51 is attributed to residual solvent H in DMSO- $d_6$ .

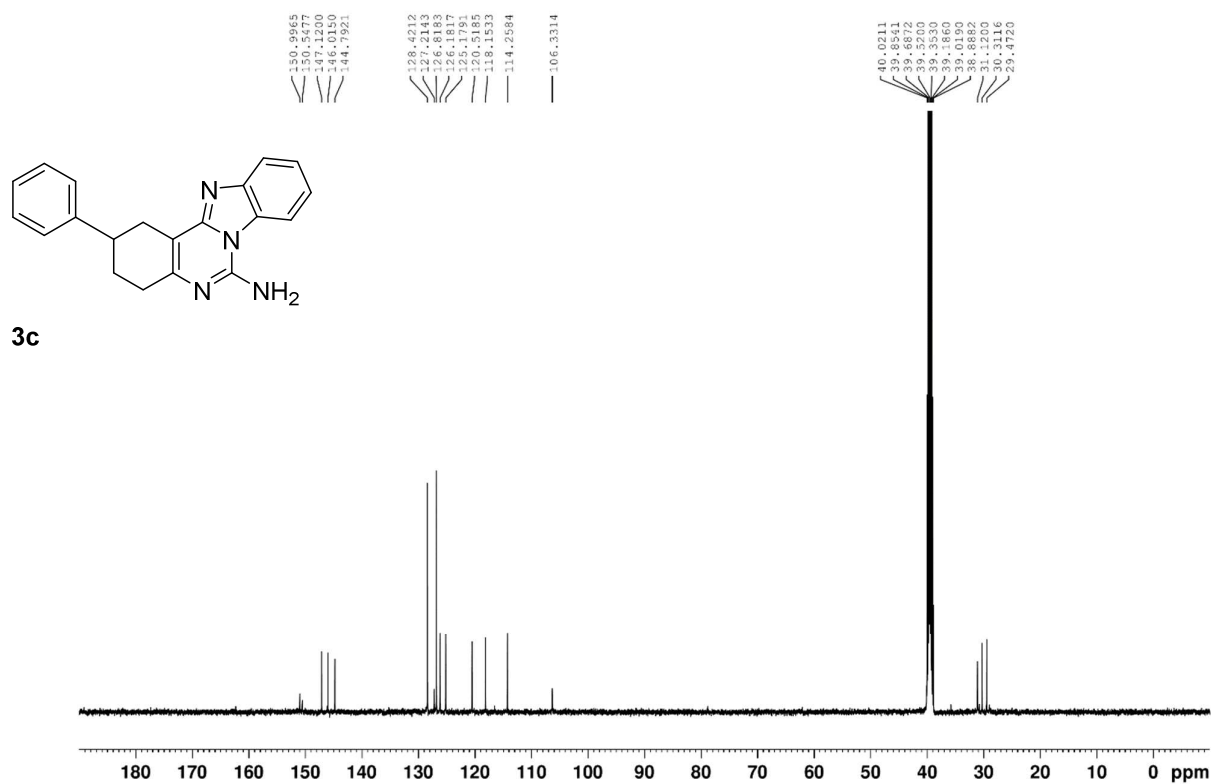
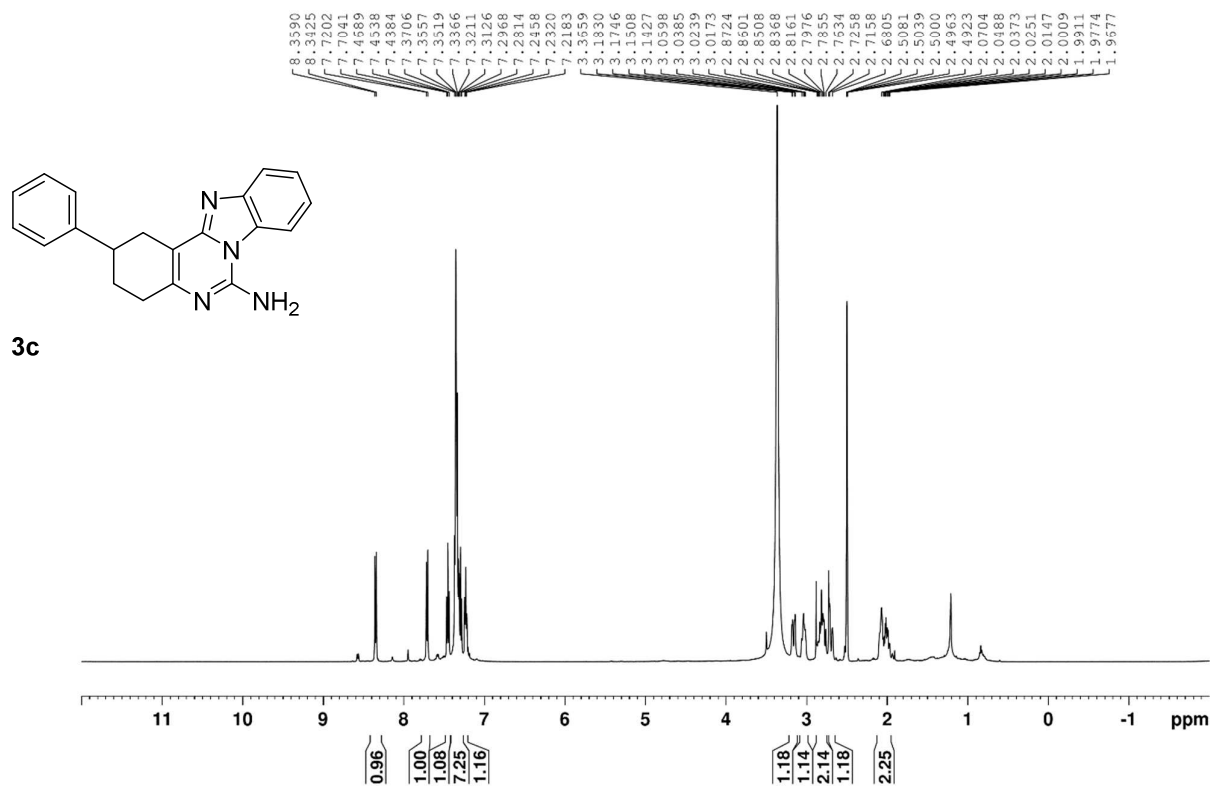
**Figure S1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3a**



**Figure S2.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3b**

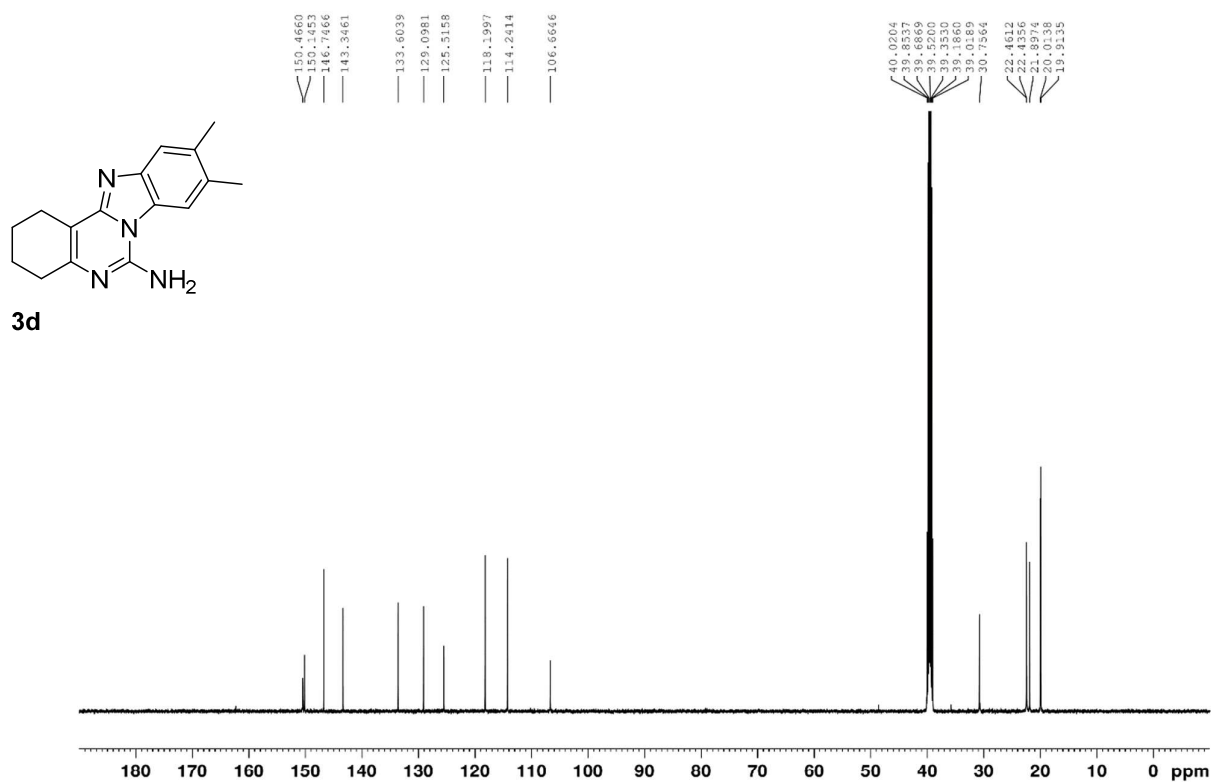
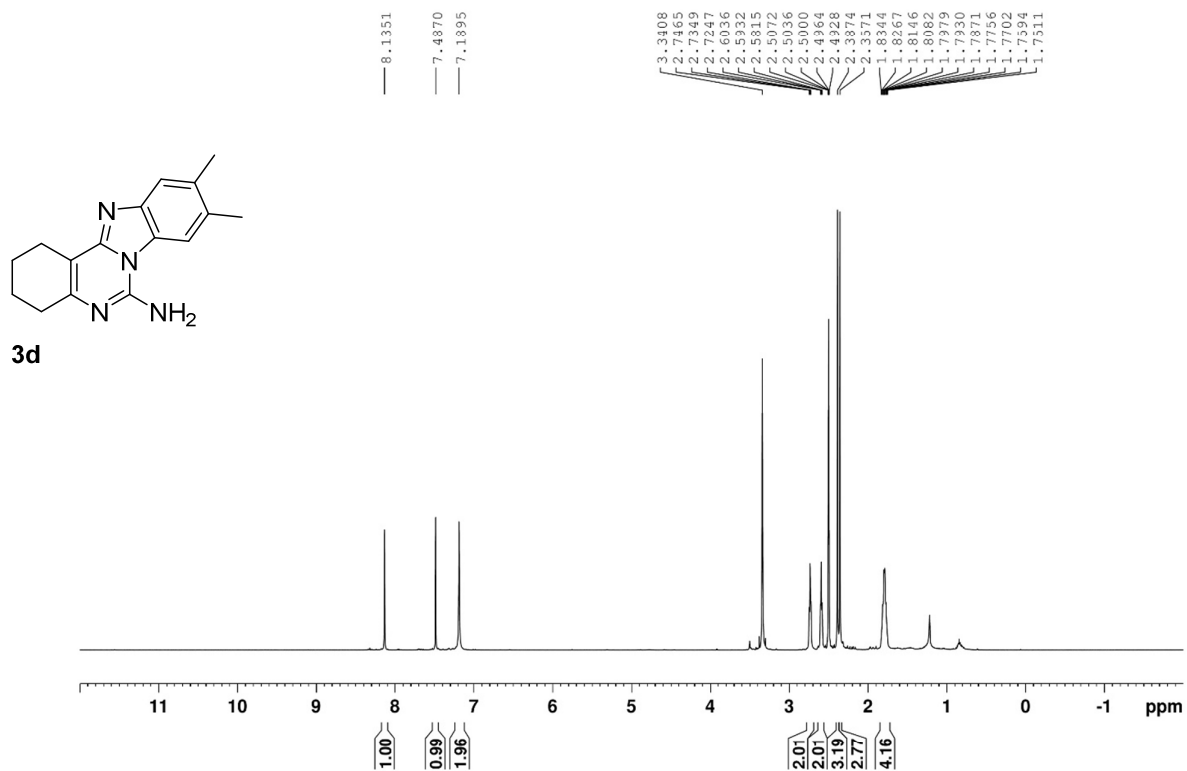


**Figure S3.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3c**

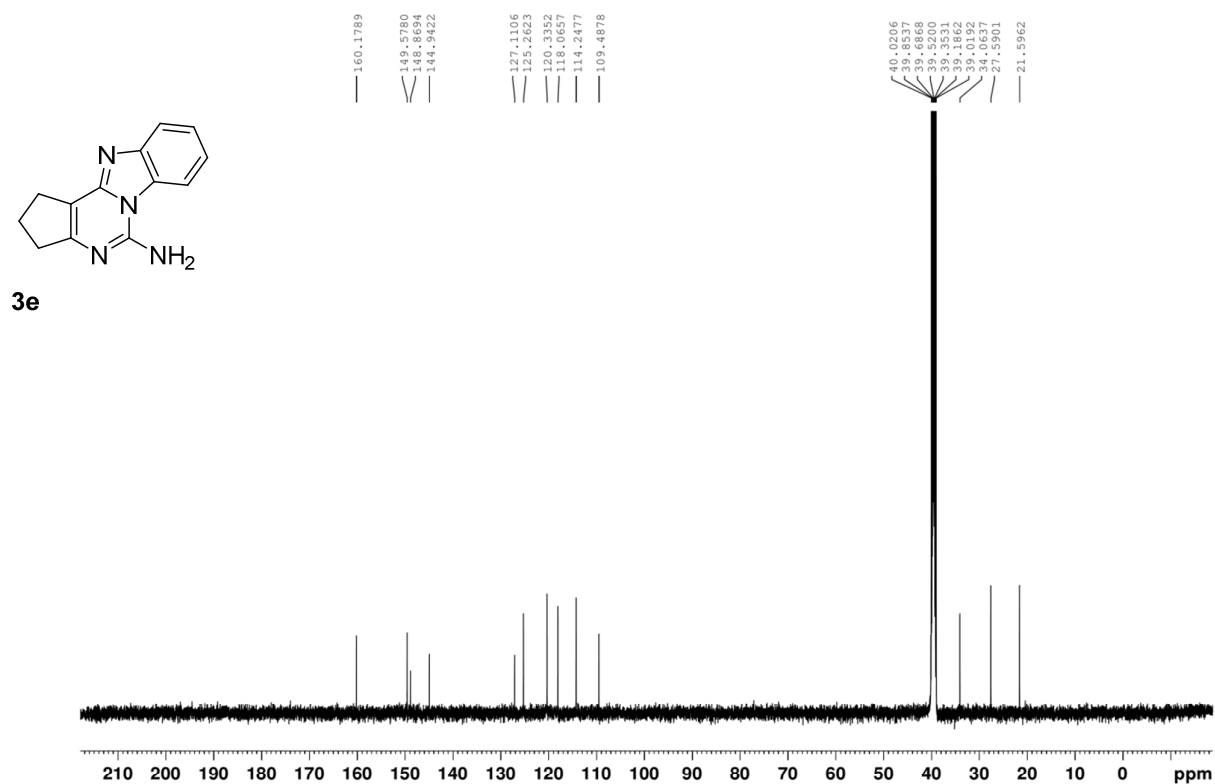
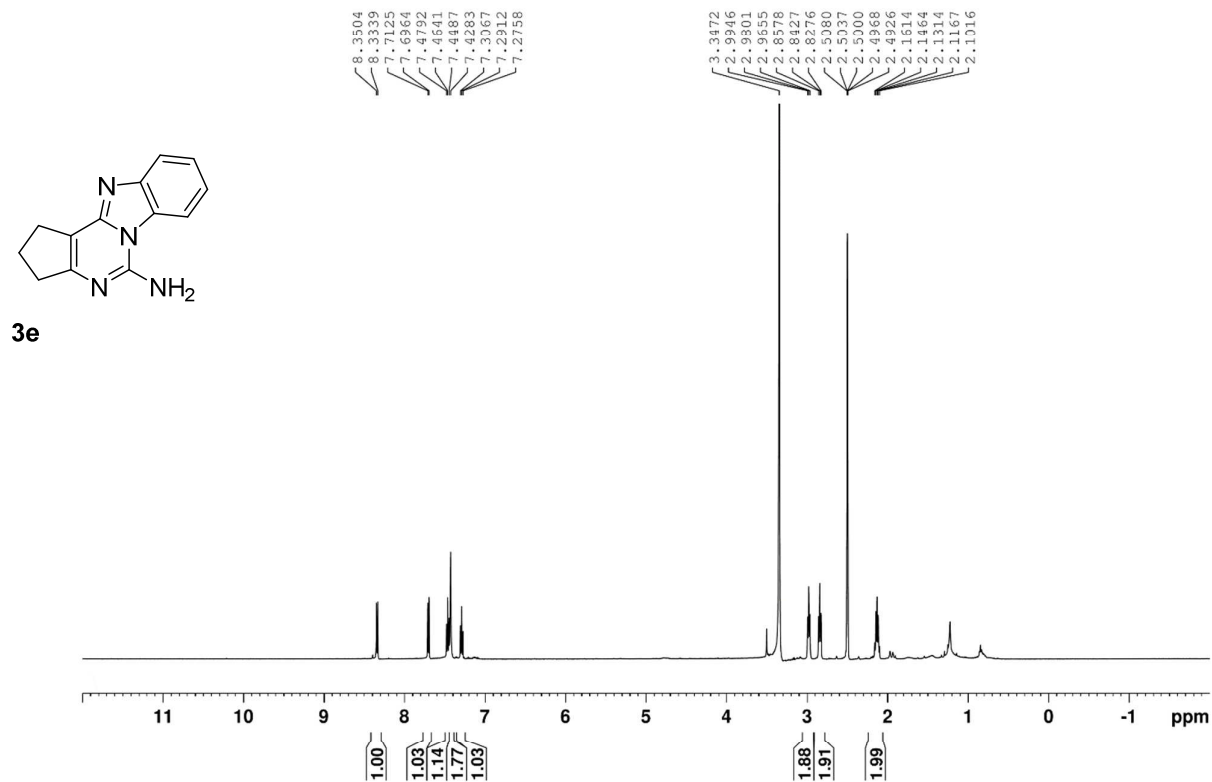




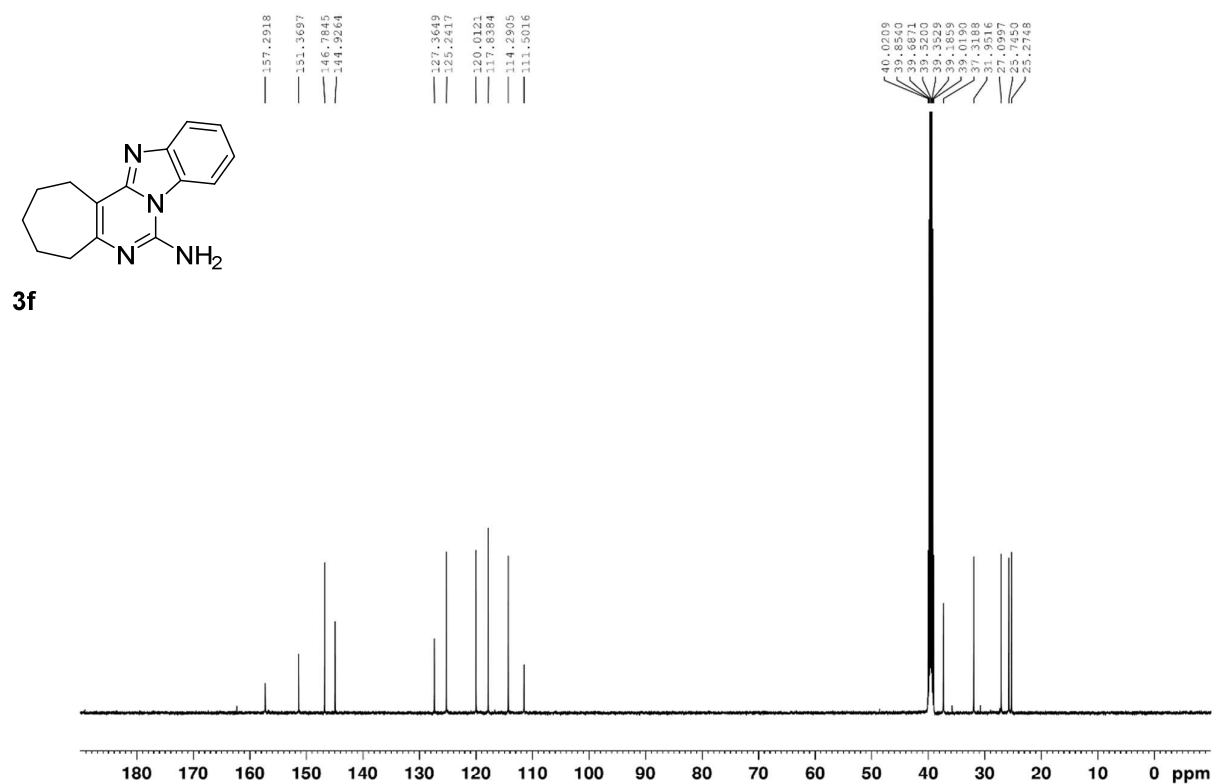
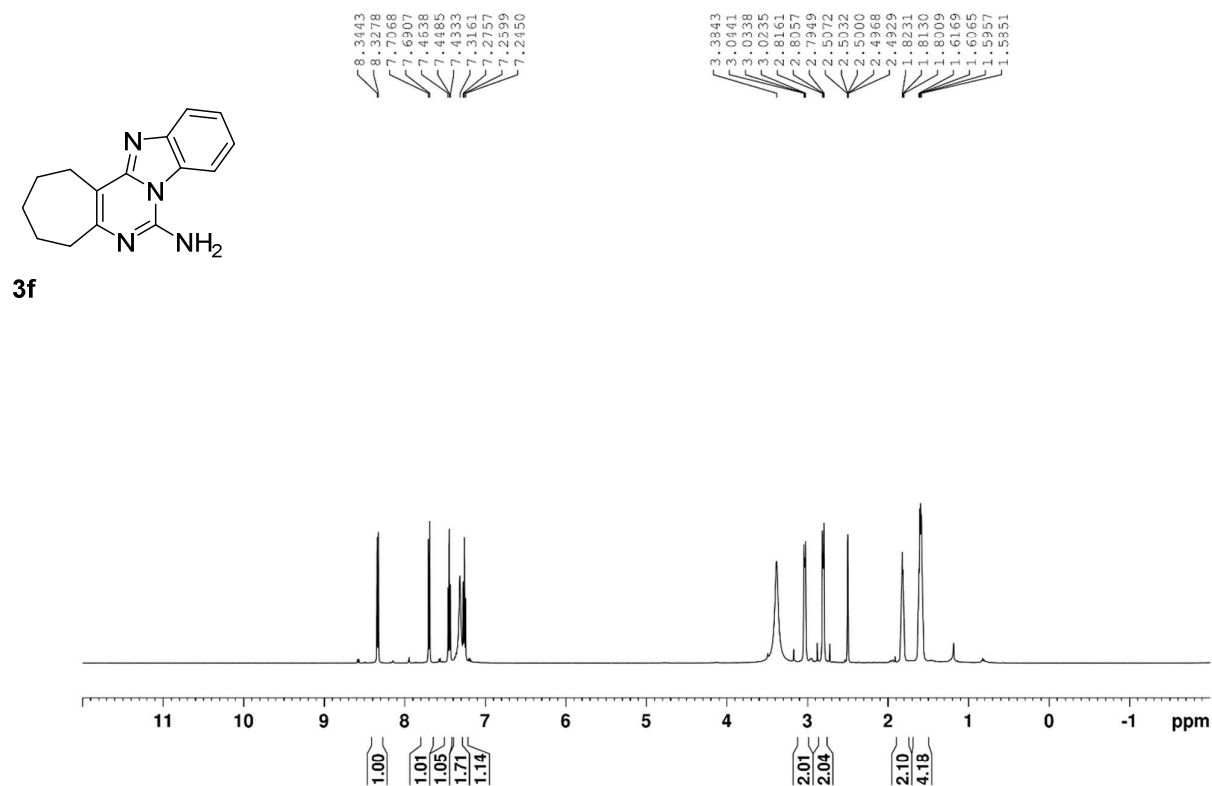
**Figure S4.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3d**



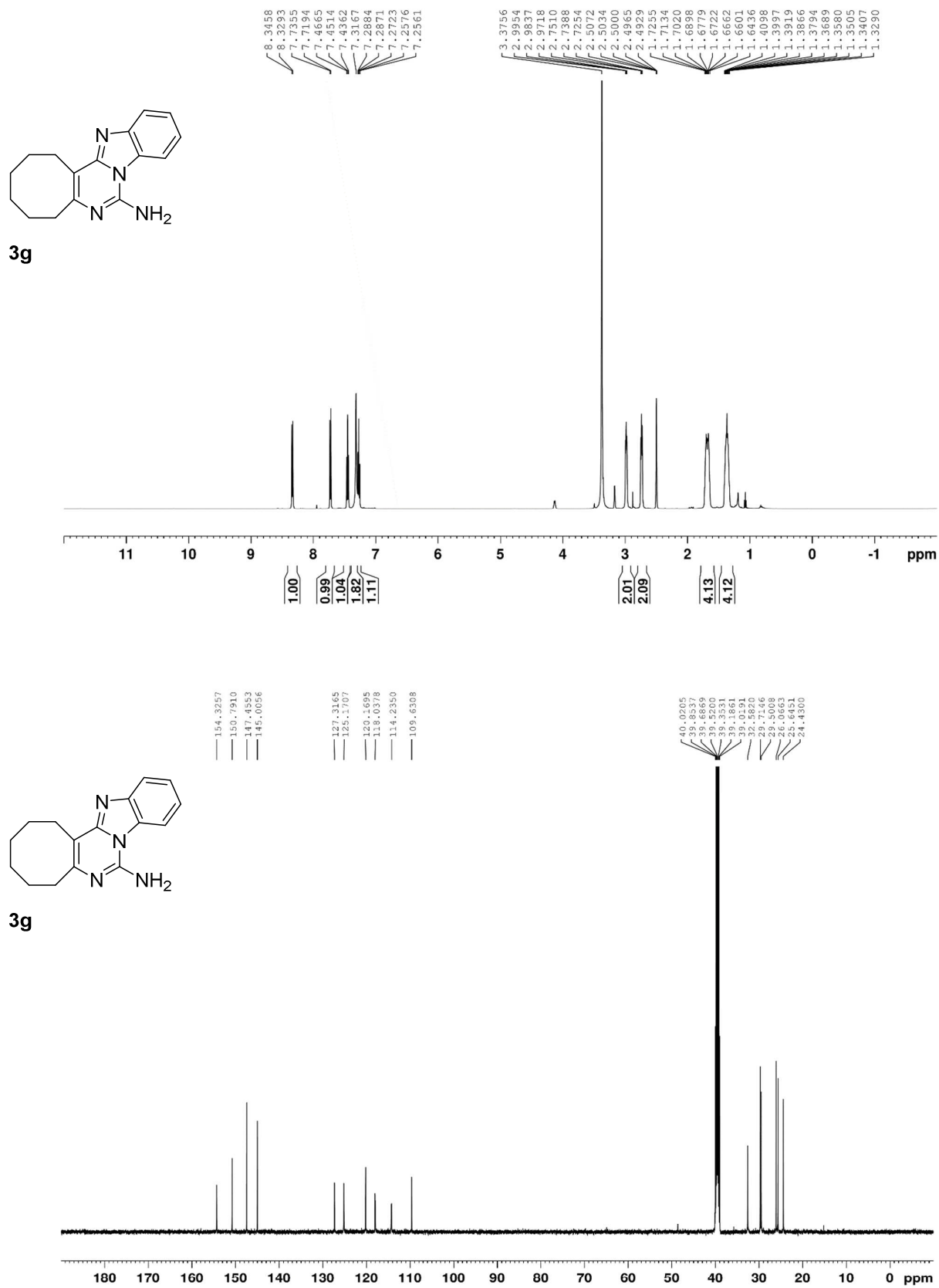
**Figure S5.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3e**



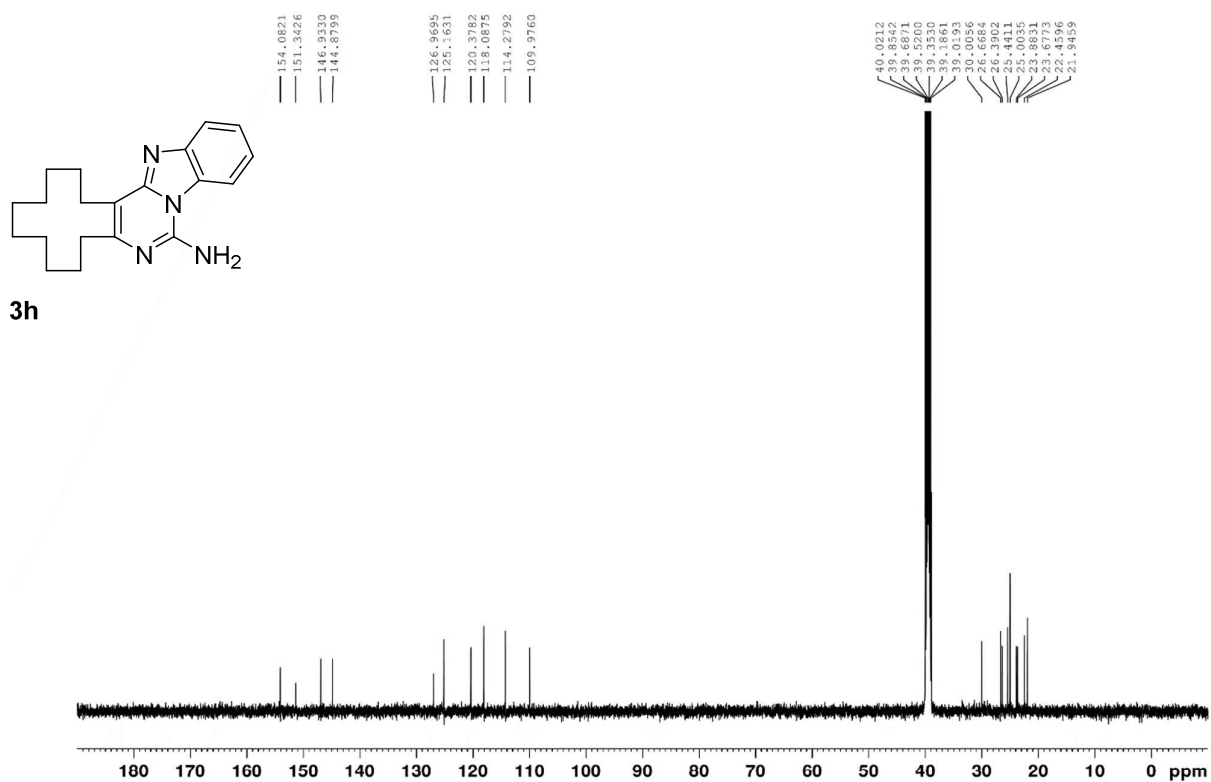
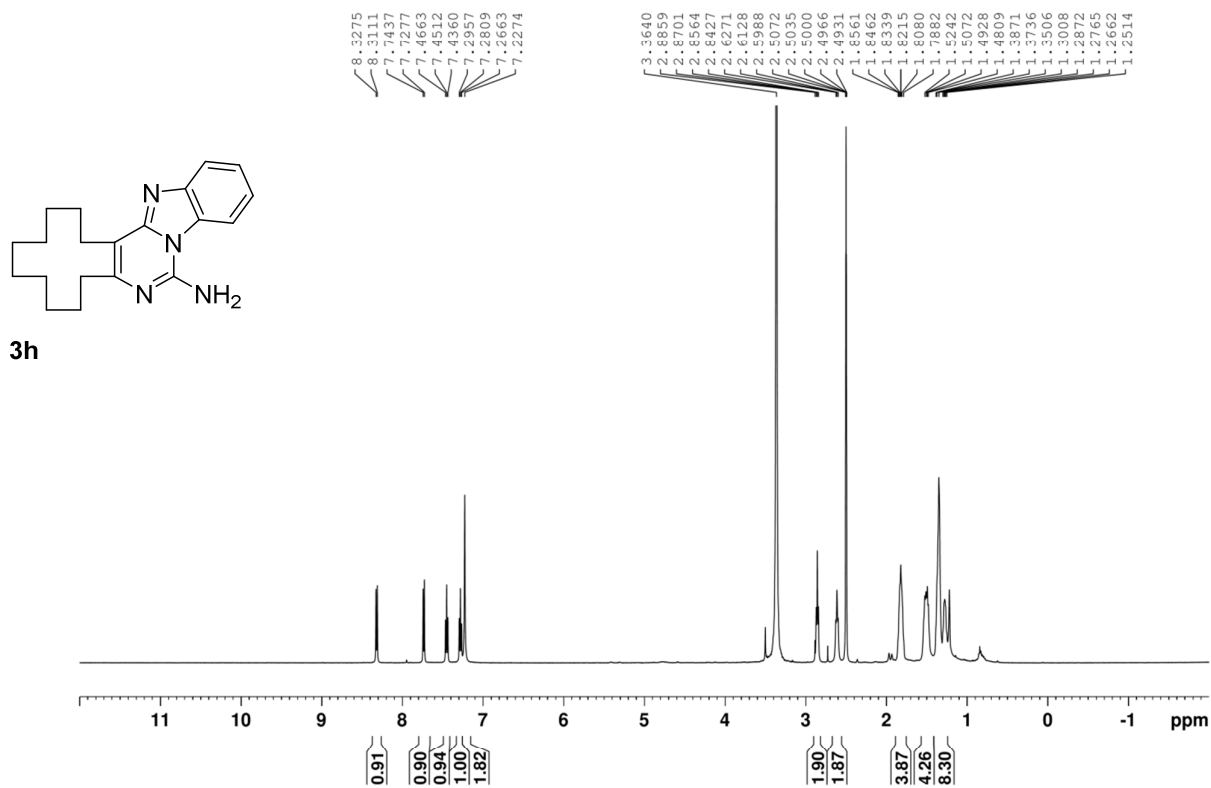
**Figure S6.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3f**



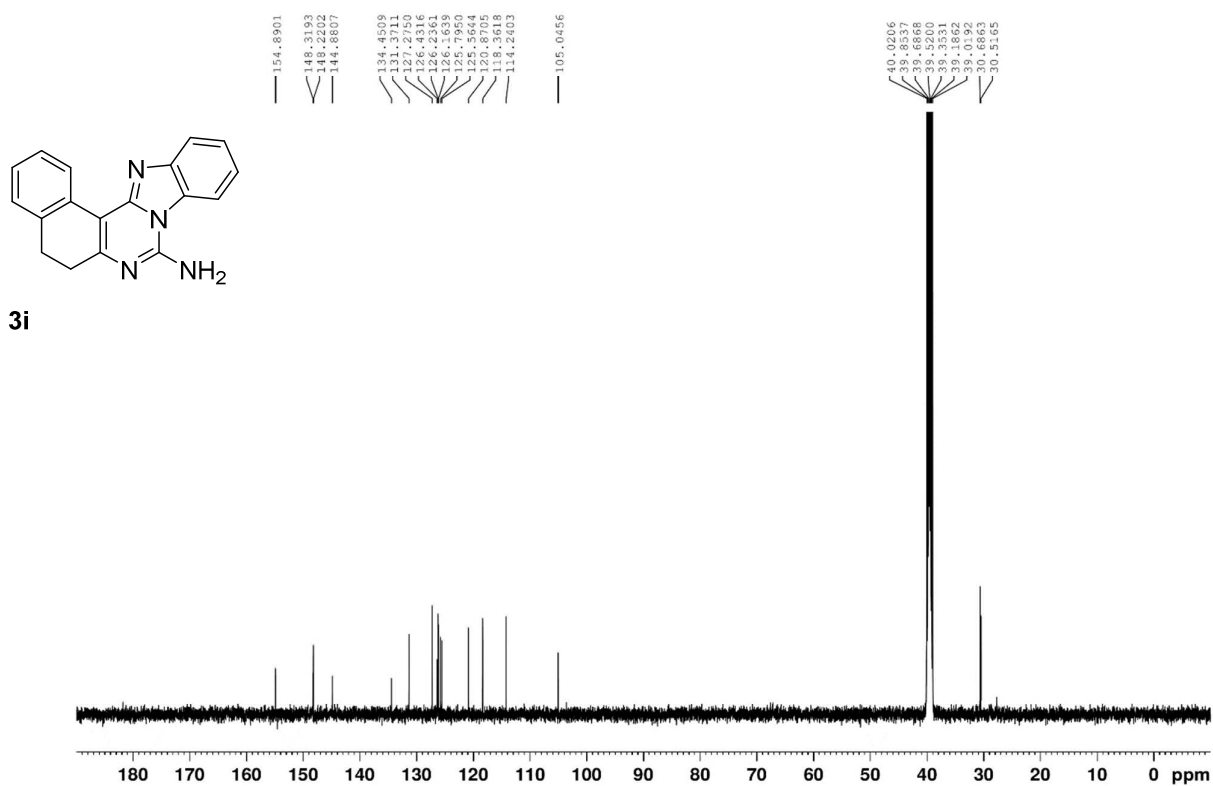
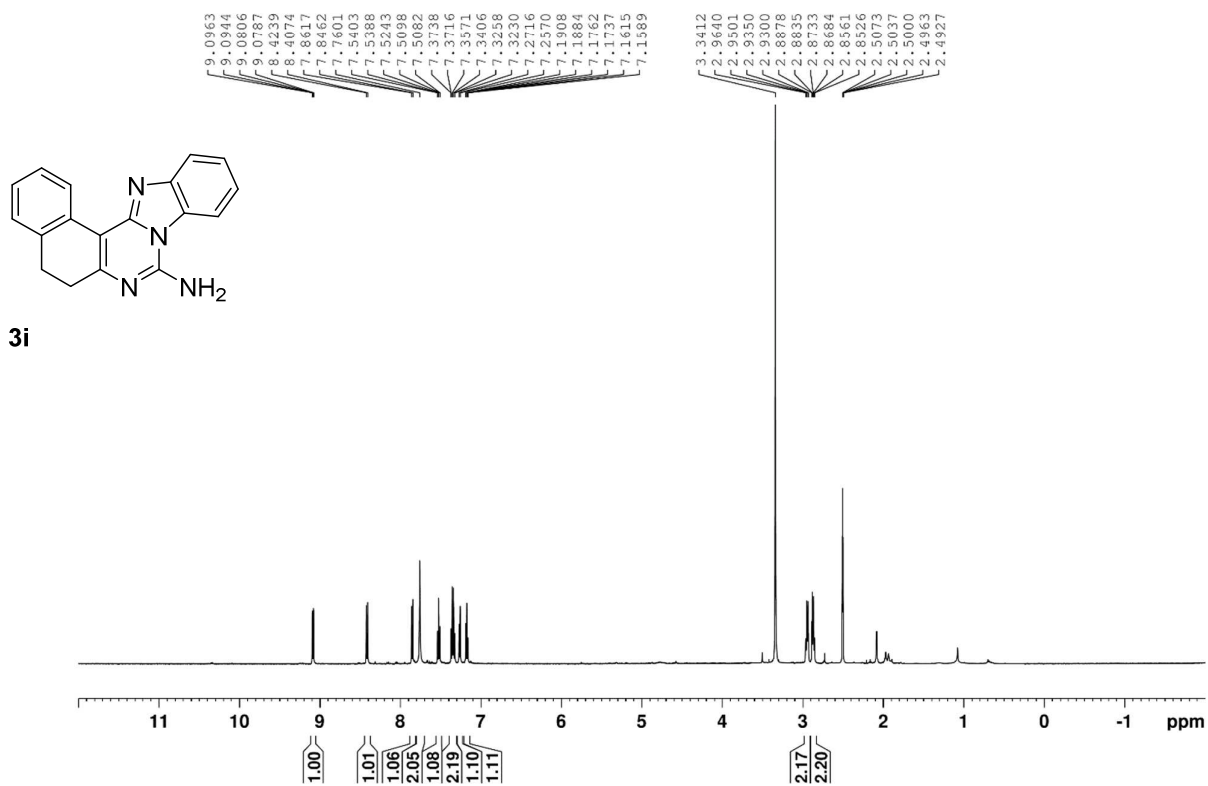
**Figure S7.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3g**



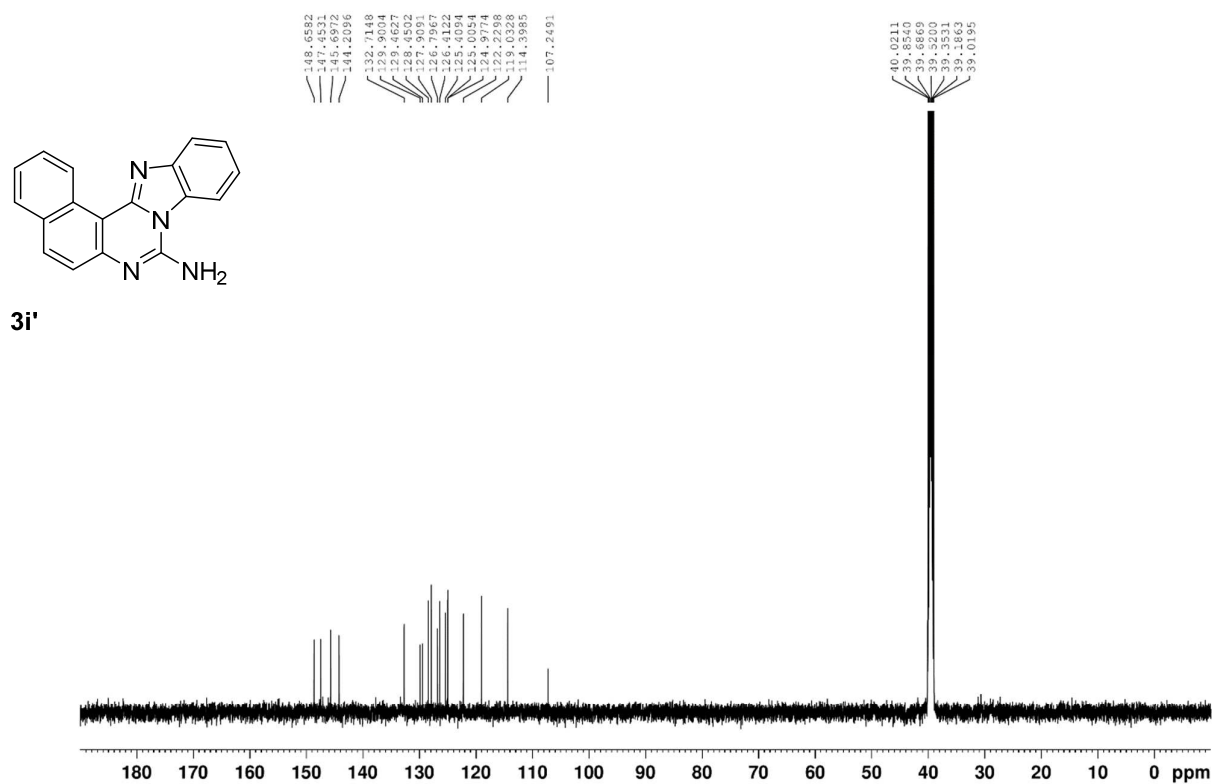
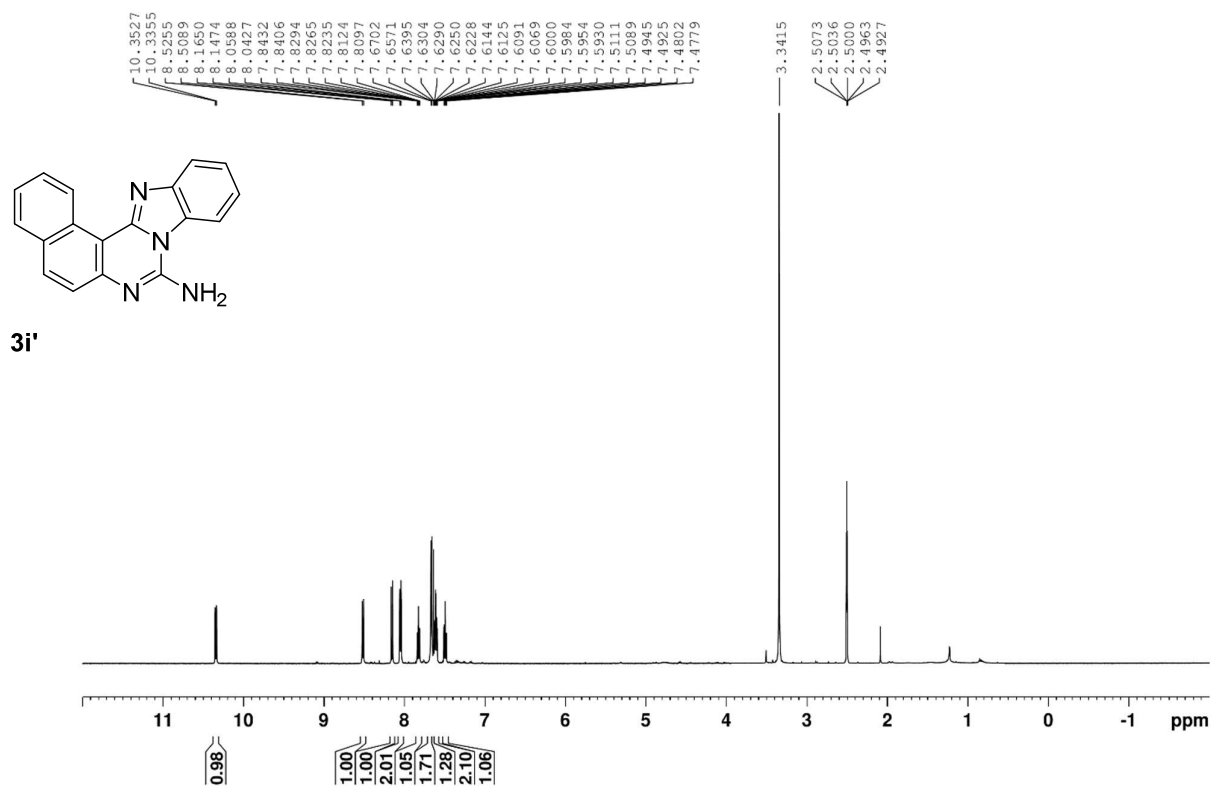
**Figure S8.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3h**



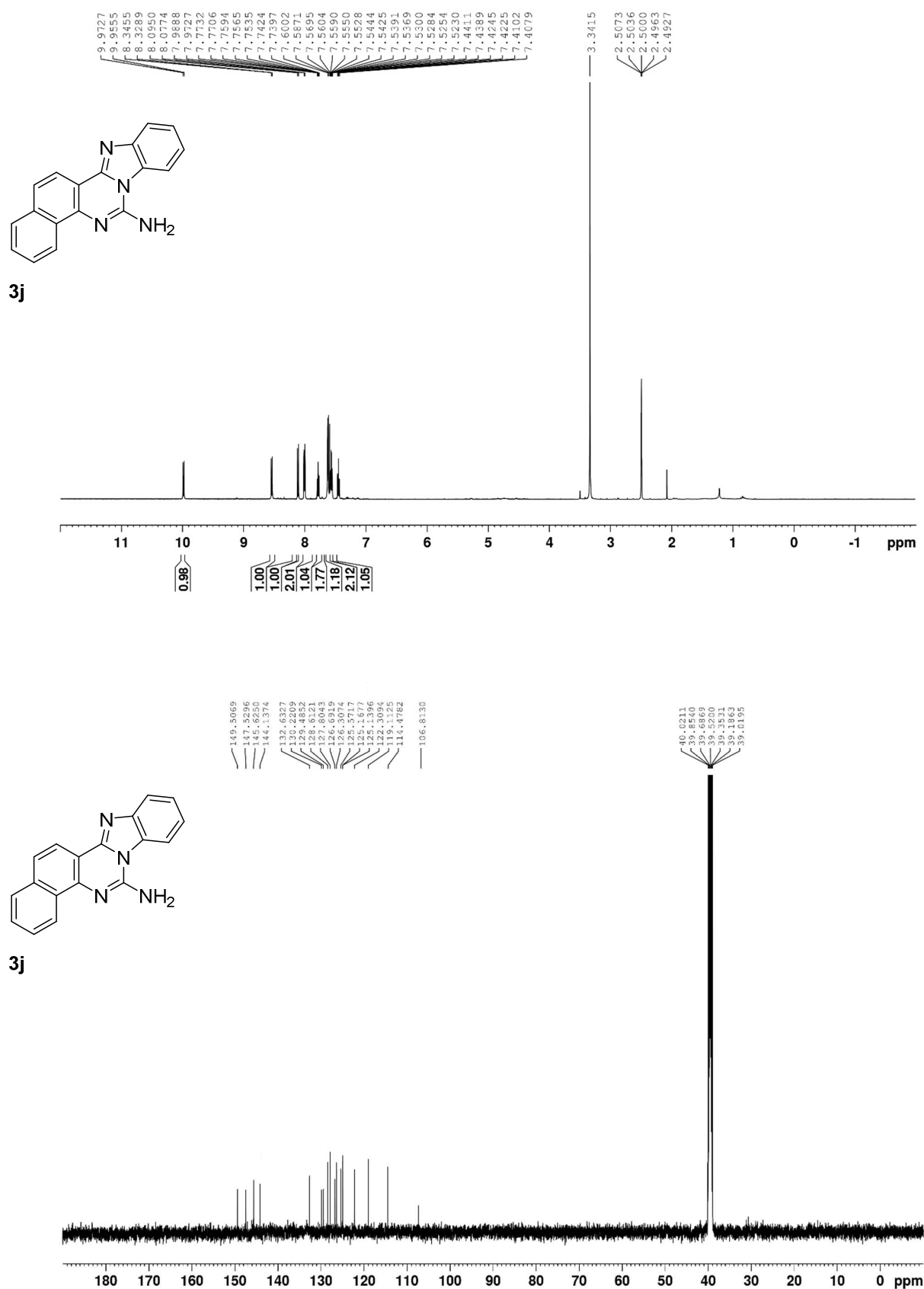
**Figure S9.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3i**



**Figure S10.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3i'**

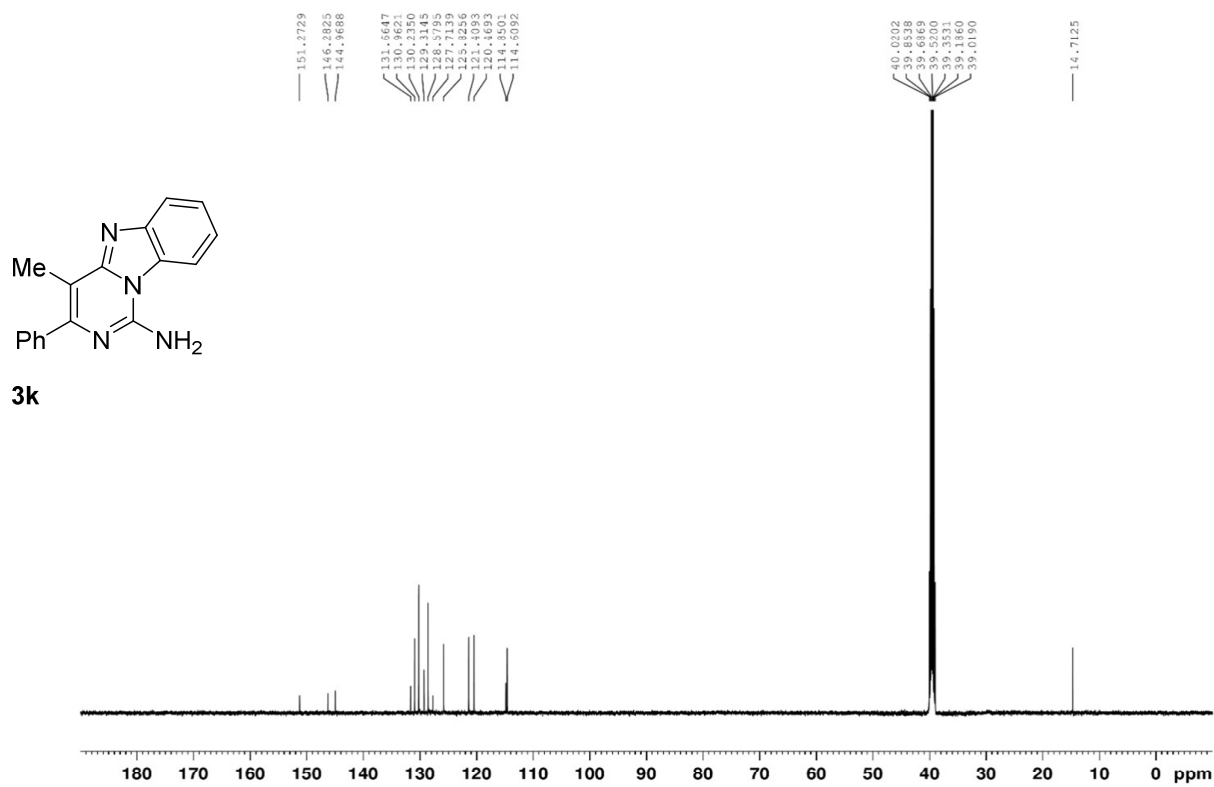
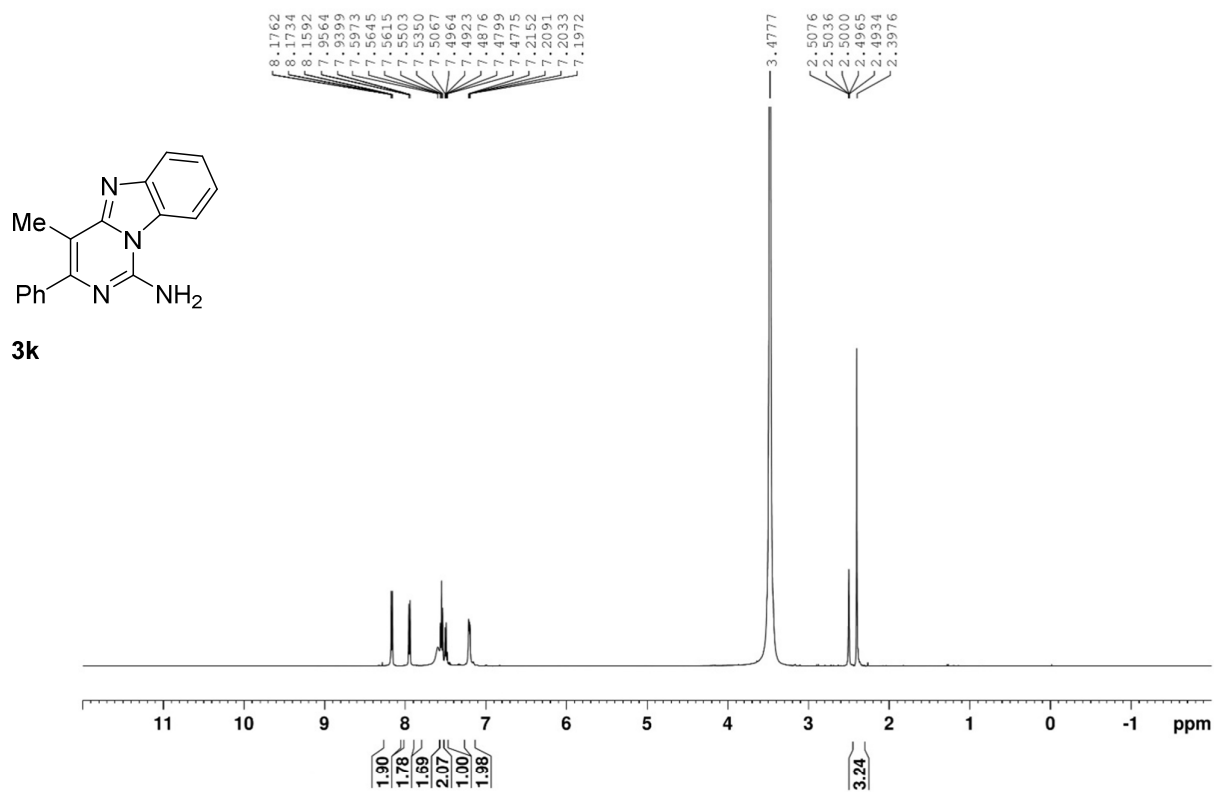


**Figure S11.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3j**

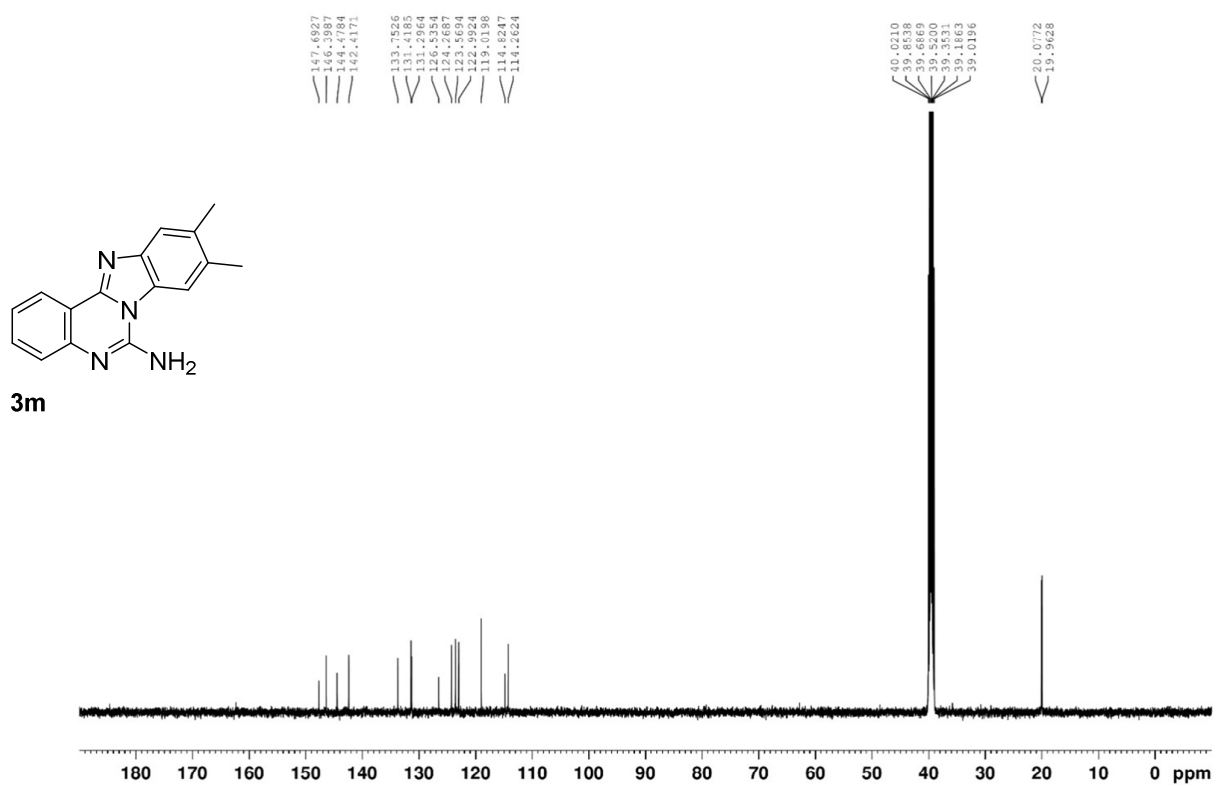
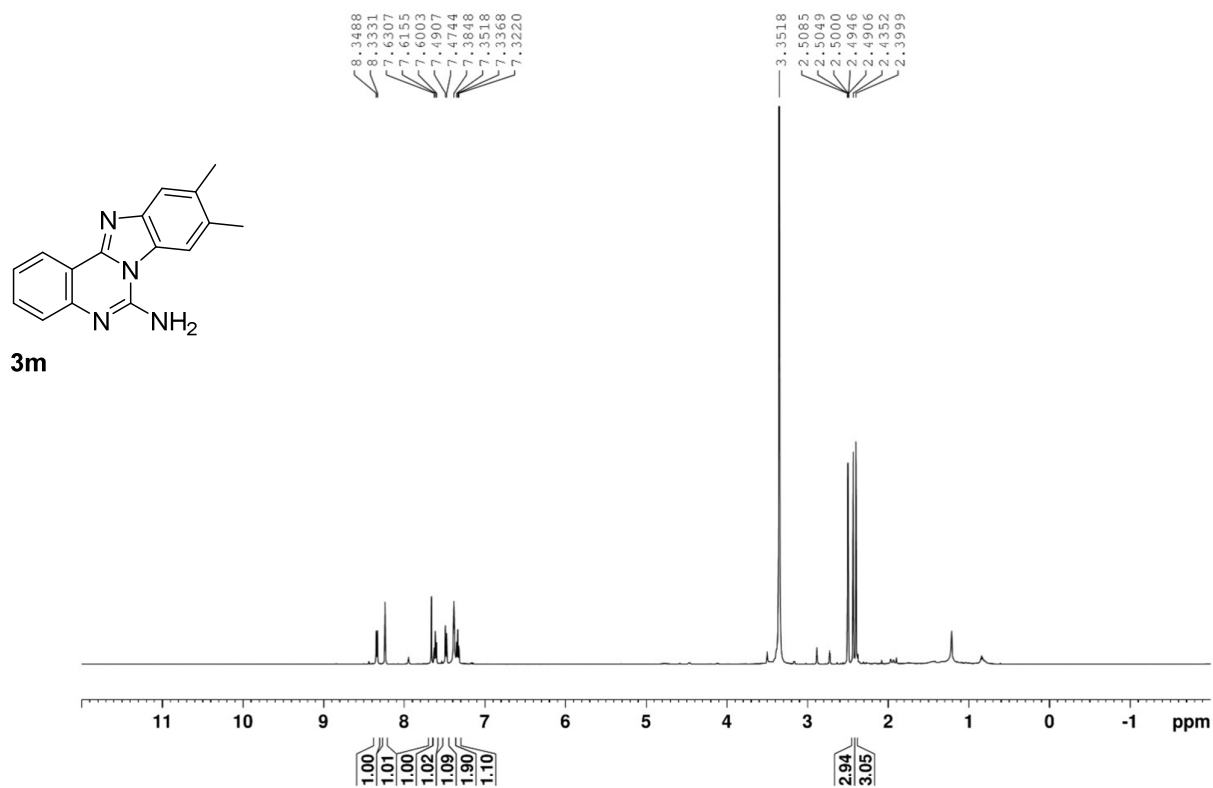




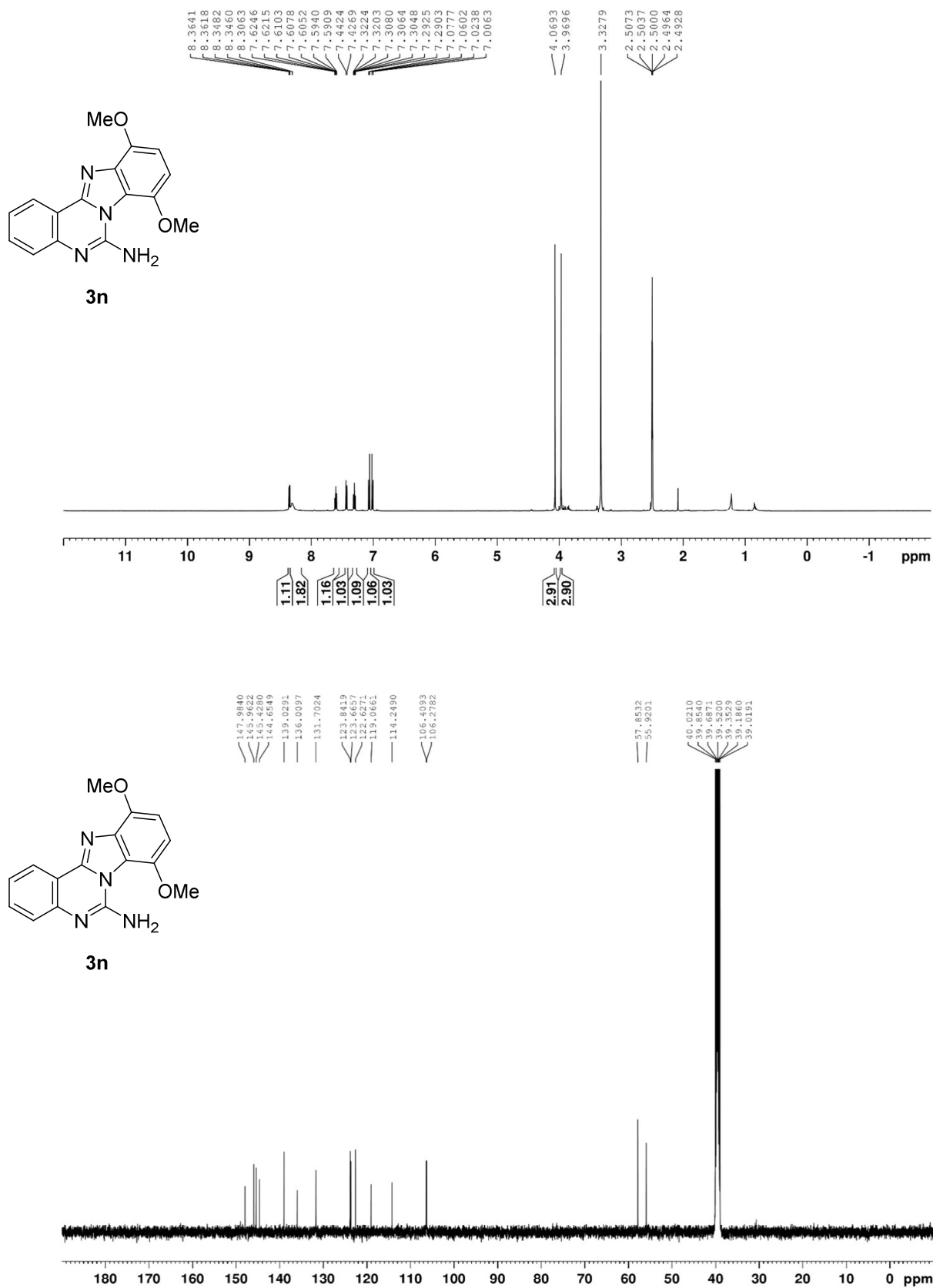
**Figure S12.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3k**



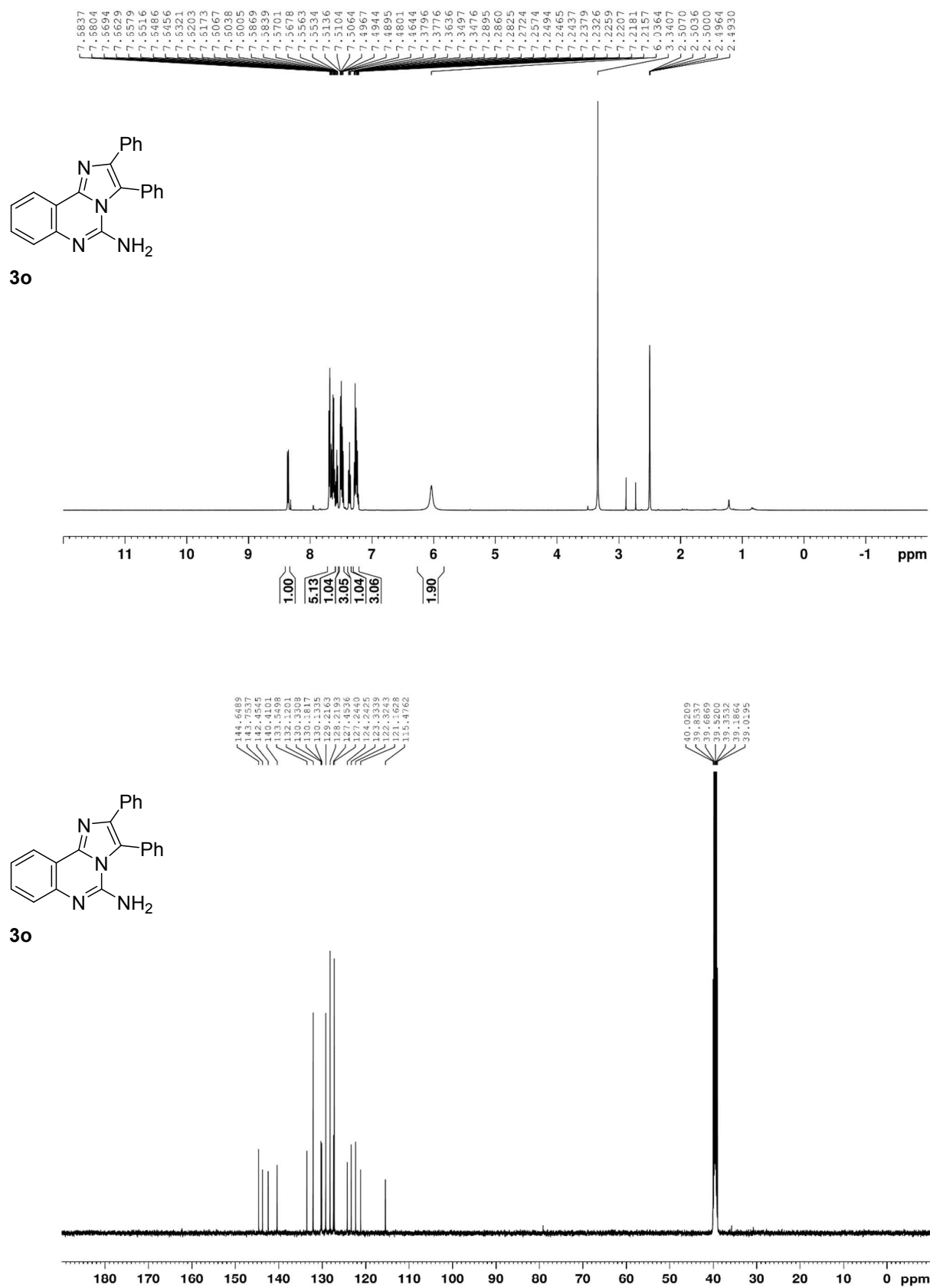
**Figure S13.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3m**



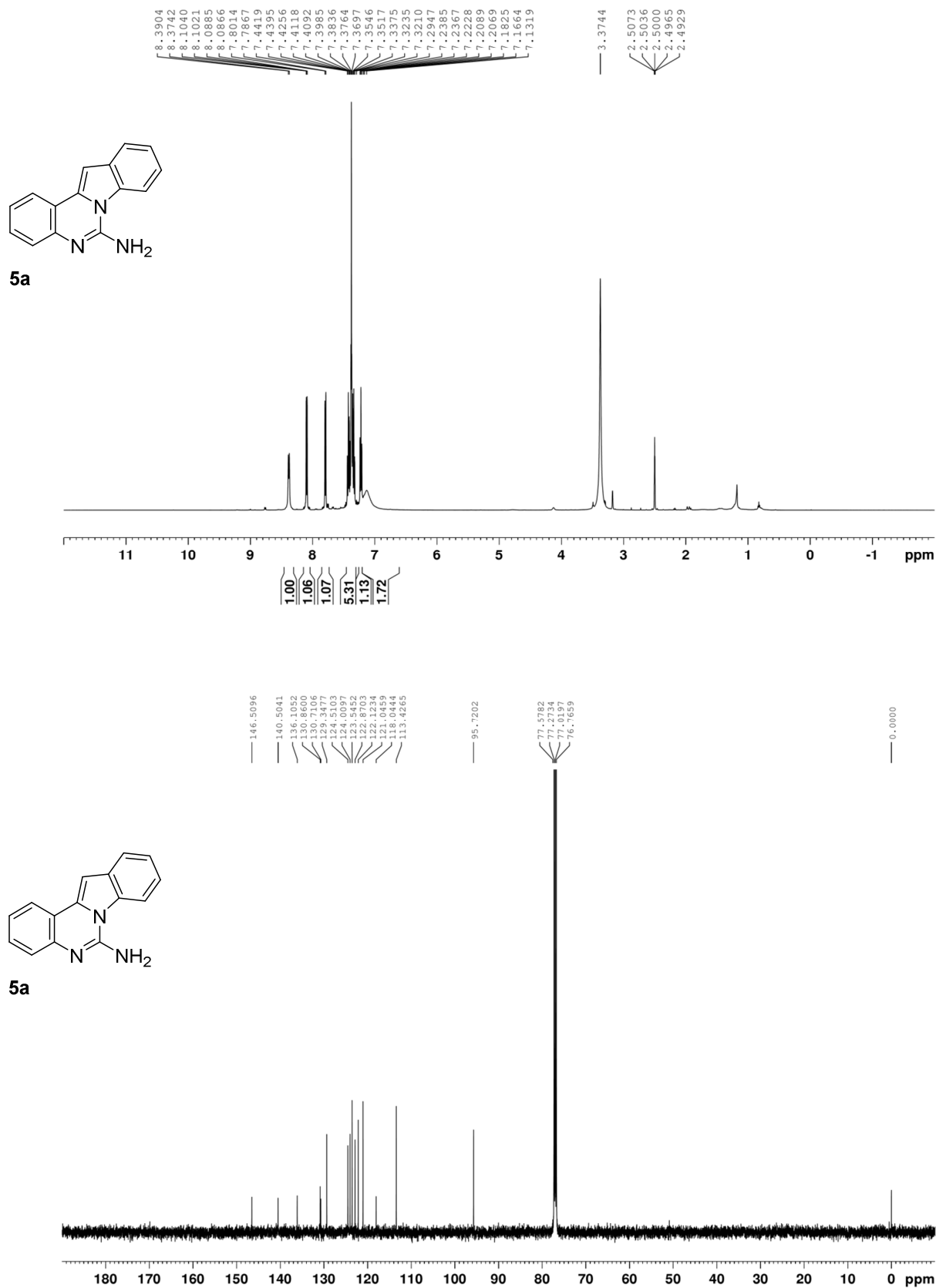
**Figure S14.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3n**



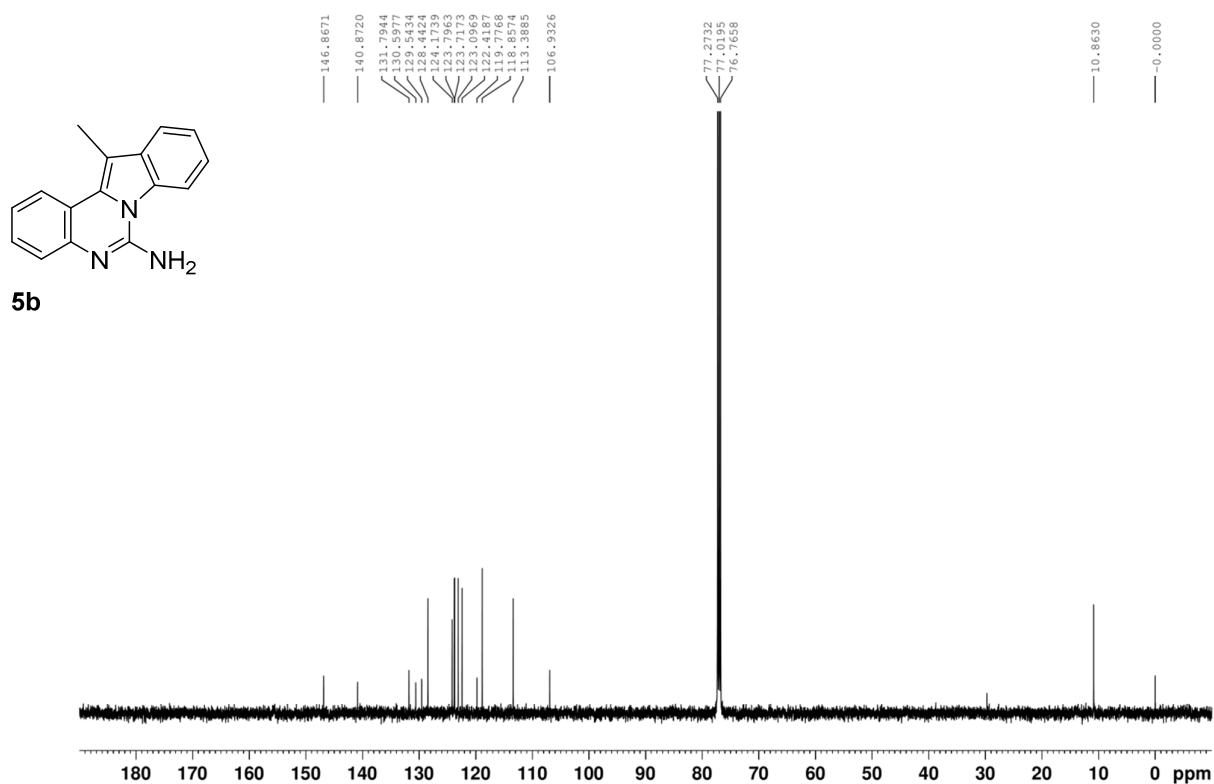
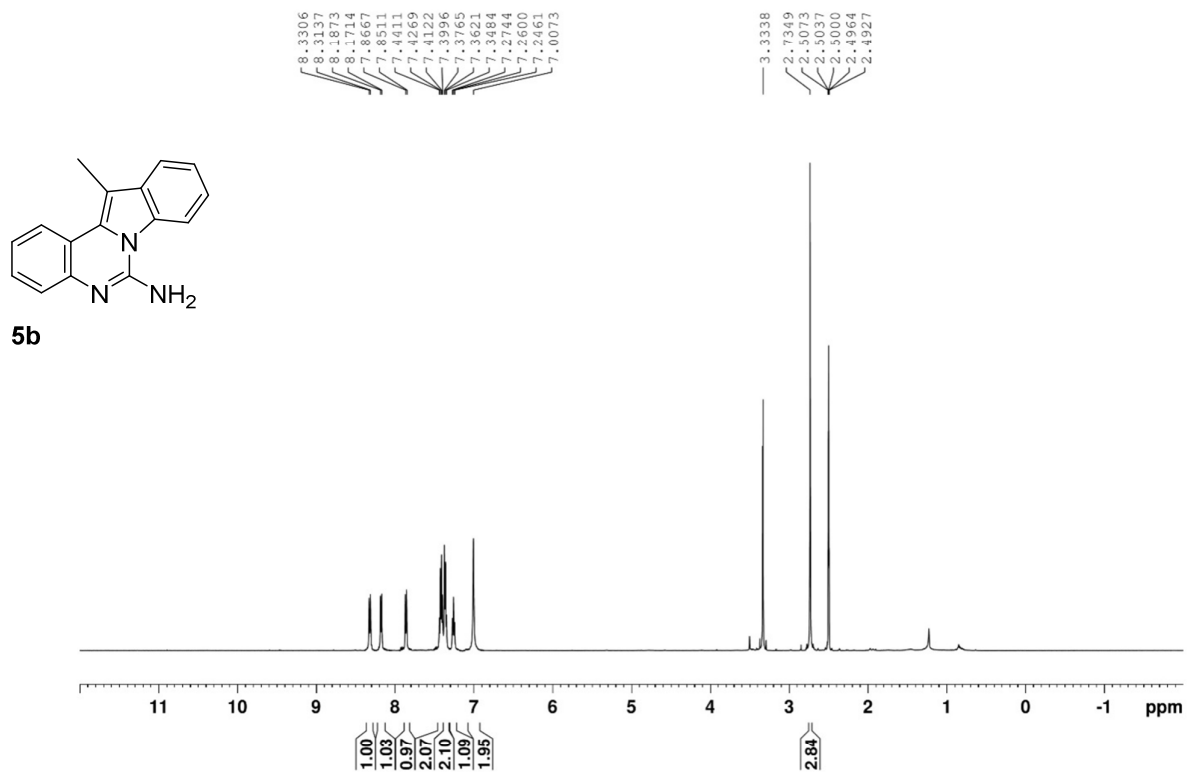
**Figure S15.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3o**



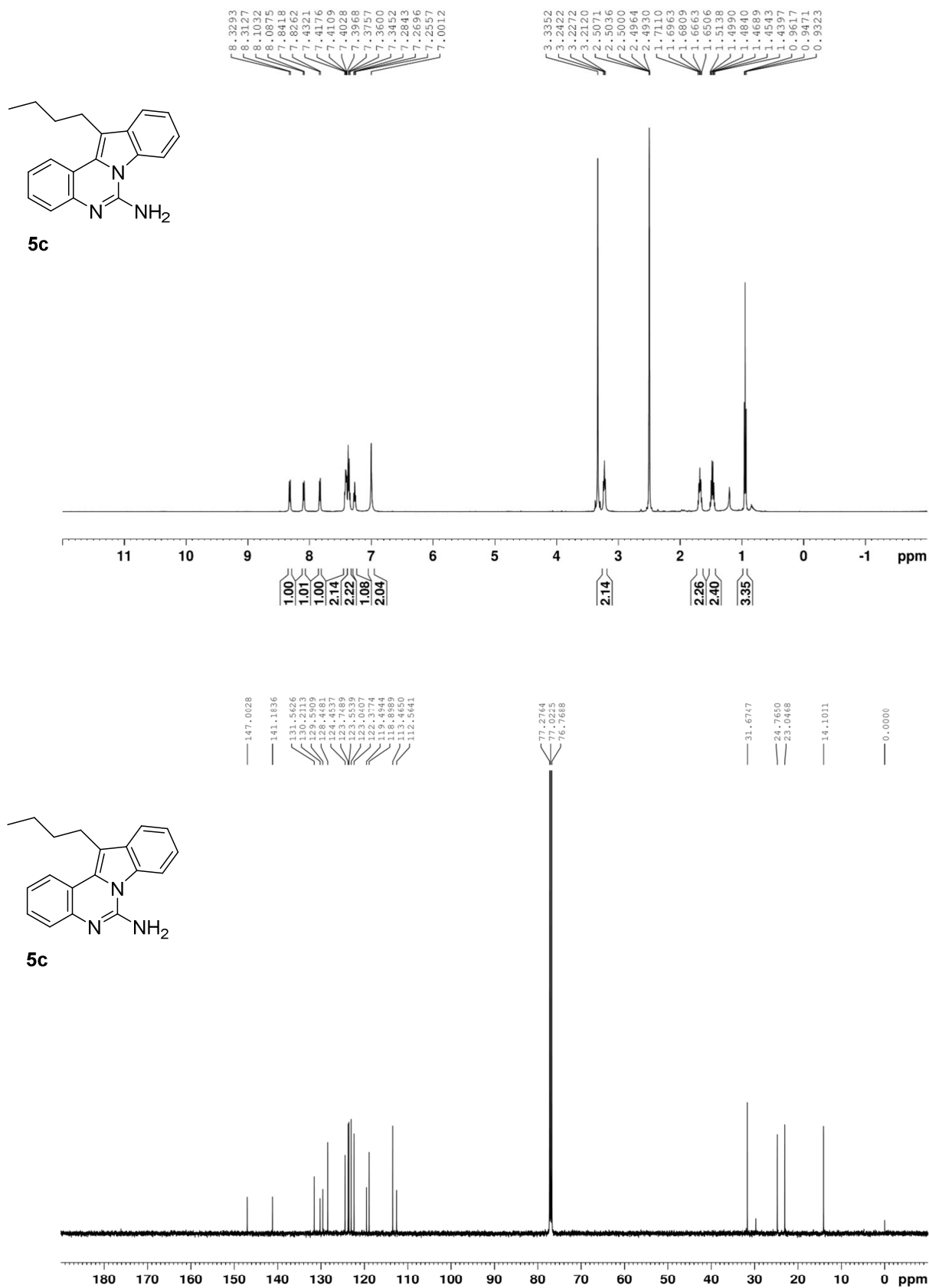
**Figure S16.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **5a**



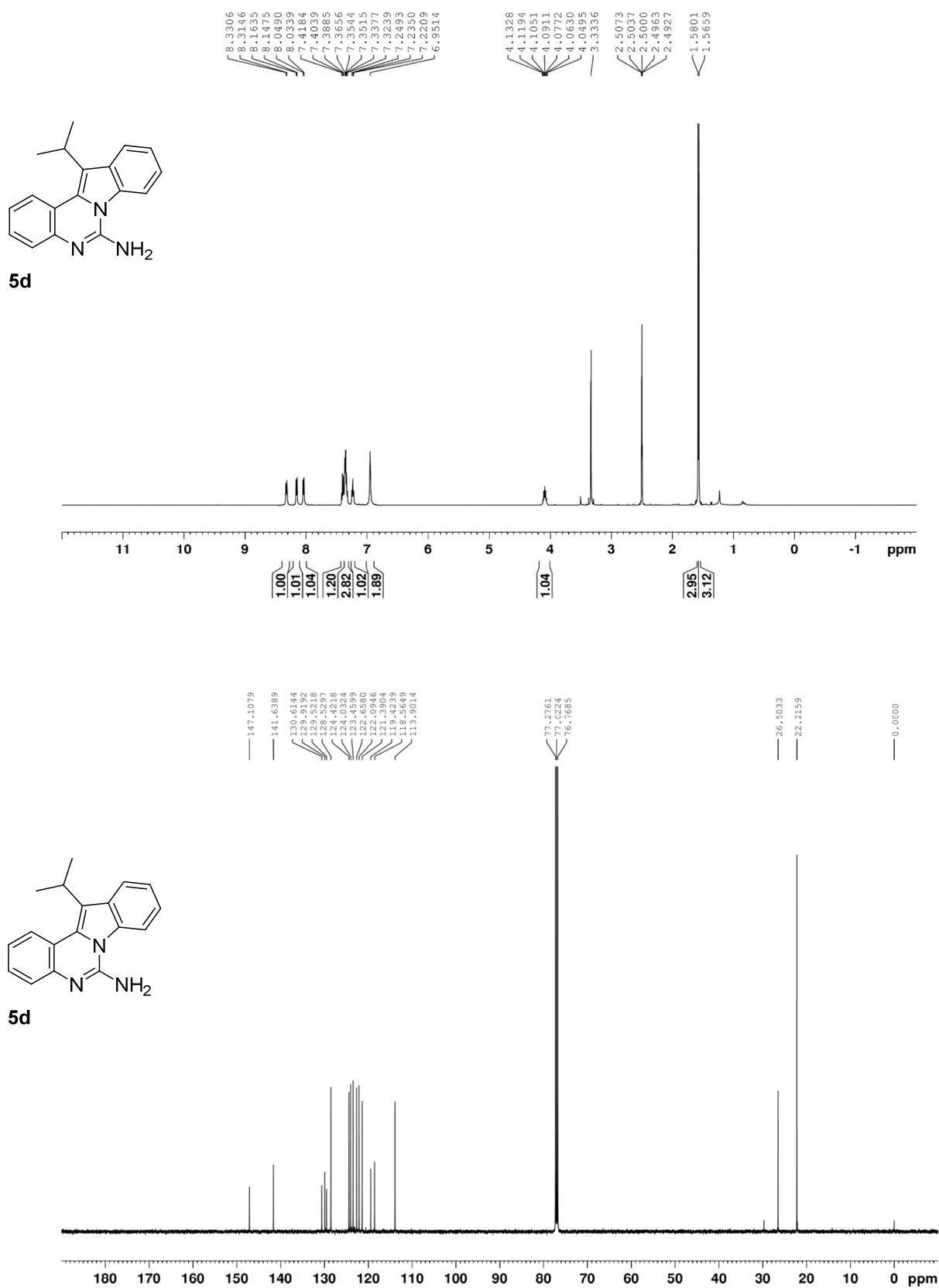
**Figure S17.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **5b**



**Figure S18.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **5c**

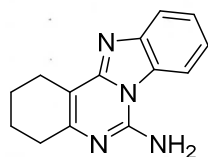


**Figure S19.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **5d**





**Figure S20. HRMS spectrum of 3a**

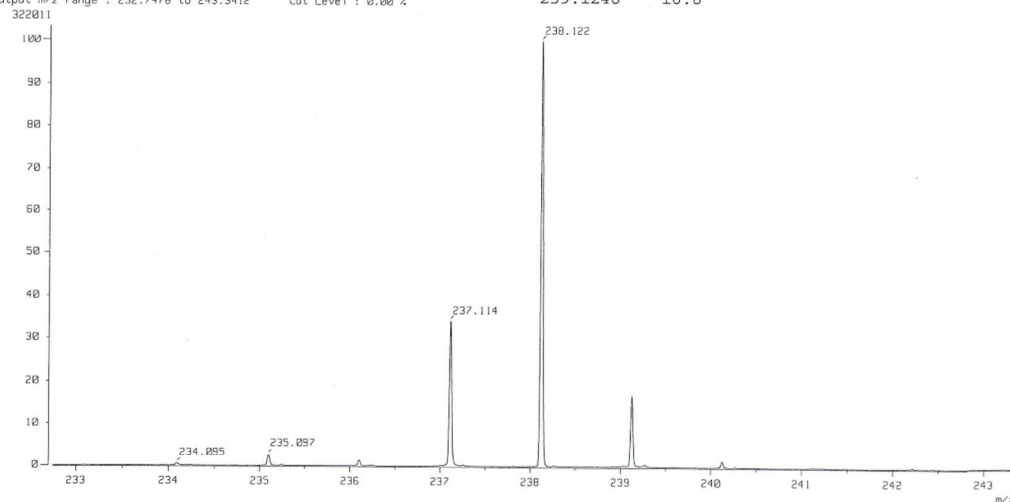


**3a**

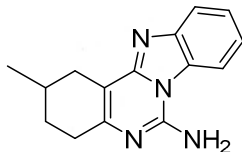
[ Mass Spectrum ]  
Data : QD-310-C14H14N4 Date : 07-Sep-2016 13:45  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
Spectrum Type : Normal Ion (EF-Linear)  
RT : 0.93 min Scan# : (19,20)  
BP : m/z 238.1218 Int. : 14.65  
Output m/z range : 232.7478 to 243.3412 Cut Level : 0.00 %

[ Elemental Composition ]  
Data : QD-310-C14H14N4 Date : 07-Sep-2016 13:45  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
RT : 0.93 min Scan# : (19,20)  
Elements : C 14/0, H 14/0, N 4/0  
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
210.0902	21.1	-1.6 / -0.3	10.0	C 12 H 10 N 4
237.1143	34.1	+1.1 / +0.3	10.5	C 14 H 13 N 4
238.1218	100.0	-0.3 / -0.1	10.0	C 14 H 14 N 4
239.1248	16.8			



**Figure S21. HRMS spectrum of 3b**

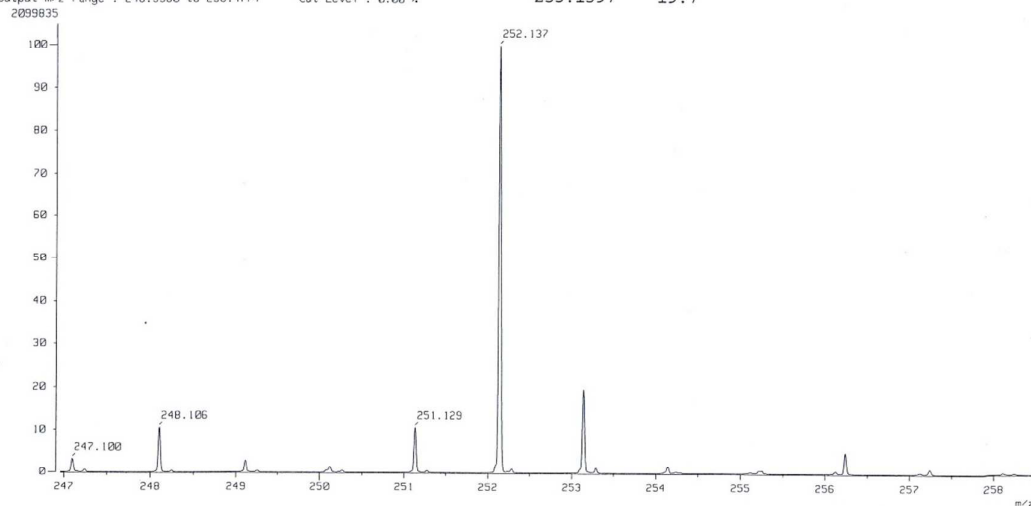


**3b**

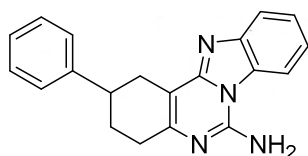
[ Mass Spectrum ]  
Data : QD-316-HREI Date : 26-Jan-2017 13:53  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
Spectrum Type : Normal Ion (EF-Linear)  
RT : 0.83 min Scan# : (17,18)  
BP : m/z 252.1372 Int. : 95.54  
Output m/z range : 246.9588 to 258.4774 Cut Level : 0.00 %

[ Elemental Composition ]  
Data : QD-316-HREI Date : 26-Jan-2017 13:53  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
RT : 0.83 min Scan# : (17,18)  
Elements : C 15/0, H 16/0, N 4/0  
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
251.1295	10.6	-0.7 / -0.2	10.5	C 15 H 15 N 4
252.1372	100.0	-1.0 / -0.3	10.0	C 15 H 16 N 4
253.1397	19.7			



**Figure S22. HRMS spectrum of 3c**

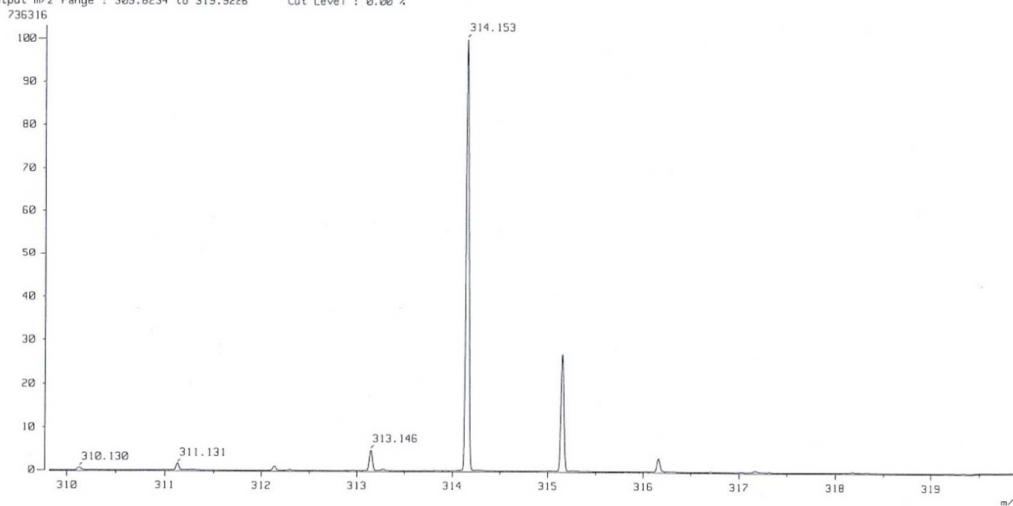


**3c**

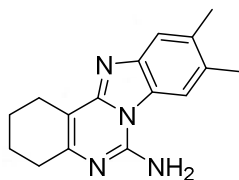
[ Mass Spectrum ]  
Data : QD-326-HREI Date : 26-Jan-2017 14:14  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
Spectrum Type : Normal Ion (EF-Linear)  
RT : 0.63 min Scan# : (13,14)  
BP : m/z 314.1528 Int. : 34.12  
Output m/z range : 309.8234 to 319.9226 Cut Level : 0.00 %

[ Elemental Composition ]  
Data : QD-326-HREI Date : 26-Jan-2017 14:14  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
RT : 0.63 min Scan# : (13,14)  
Elements : C 20/0, H 18/0, N 4/0  
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
314.1528	100.0	-1.1 / -0.3	14.0	C 20 H 18 N 4
315.1559	26.9			



**Figure S23. HRMS spectrum of 3d**

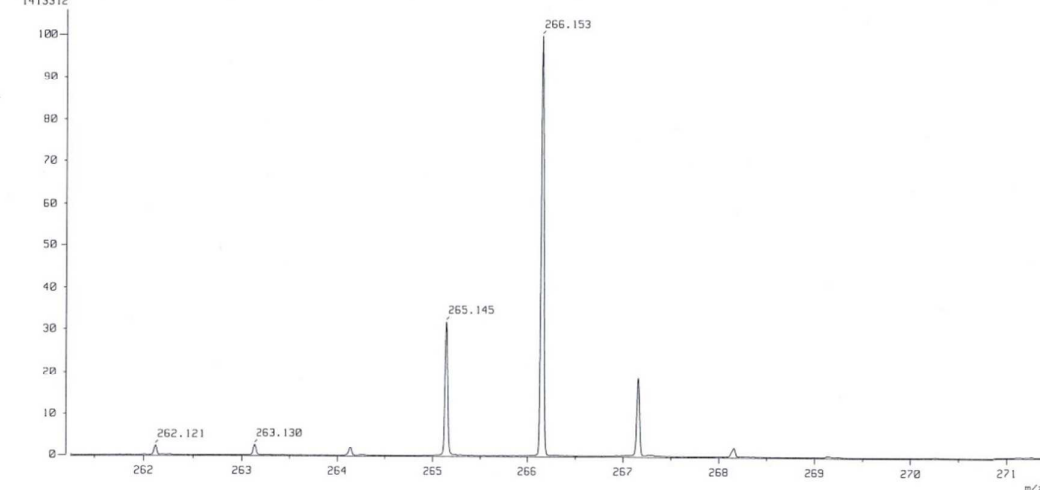


**3d**

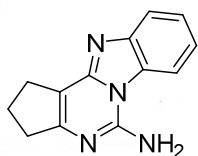
[ Mass Spectrum ]  
Data : QD-323-HREI Date : 26-Jan-2017 14:06  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
Spectrum Type : Normal Ion (EF-Linear)  
RT : 0.98 min Scan# : (20,21)  
BP : m/z 266.1531 Int. : 63.72  
Output m/z range : 261.2500 to 271.3854 Cut Level : 0.00 %

[ Elemental Composition ]  
Data : QD-323-HREI Date : 26-Jan-2017 14:06  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
RT : 0.98 min Scan# : (20,21)  
Elements : C 16/0, H 18/0, N 4/0  
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
251.1295	11.1	-0.7 / -0.2	10.5	C 15 H 15 N 4
252.1372	37.9	-1.3 / -0.3	10.0	C 15 H 16 N 4
265.1454	31.8	+0.5 / +0.1	10.5	C 16 H 17 N 4
266.1531	100.0	-0.3 / -0.1	10.0	C 16 H 18 N 4
267.1555	18.7			



**Figure S24. HRMS spectrum of 3e**

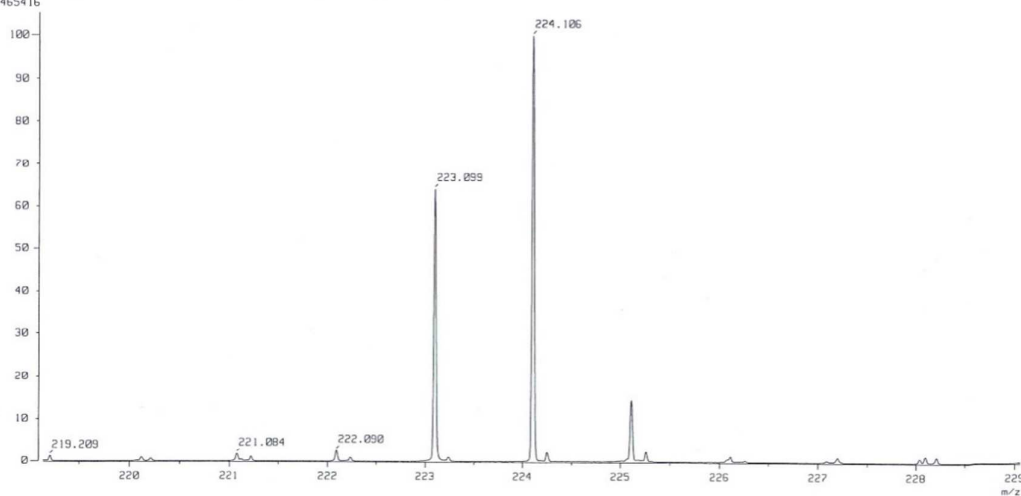


**3e**

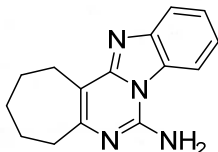
[ Mass Spectrum ]  
Data : QD-317-HREI Date : 26-Jan-2017 13:58  
Sample: -  
Note: -  
Inlet : Direct Ion Mode: EI+  
Spectrum Type: Normal Ion (EF-Linear)  
RT : 0.48 min Scan#: (10,11)  
BP : m/z 224.1060 Int. : 66.30  
Output m/z range : 219.1406 to 229.0592 Cut Level : 0.00 %  
1465416

[ Elemental Composition ]  
Data : QD-317-HREI Date : 26-Jan-2017 13:58  
Sample: -  
Note: -  
Inlet : Direct Ion Mode: EI+  
RT : 0.48 min Scan#: (10,11)  
Elements : C 13/0, H 12/0, N 4/0  
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
223.0987	64.1	+1.4 / +0.3	10.5 C 13 H 11 N 4
224.1060	100.0	-0.9 / -0.2	10.0 C 13 H 12 N 4
225.1082	14.5		



**Figure S25. HRMS spectrum of 3f**

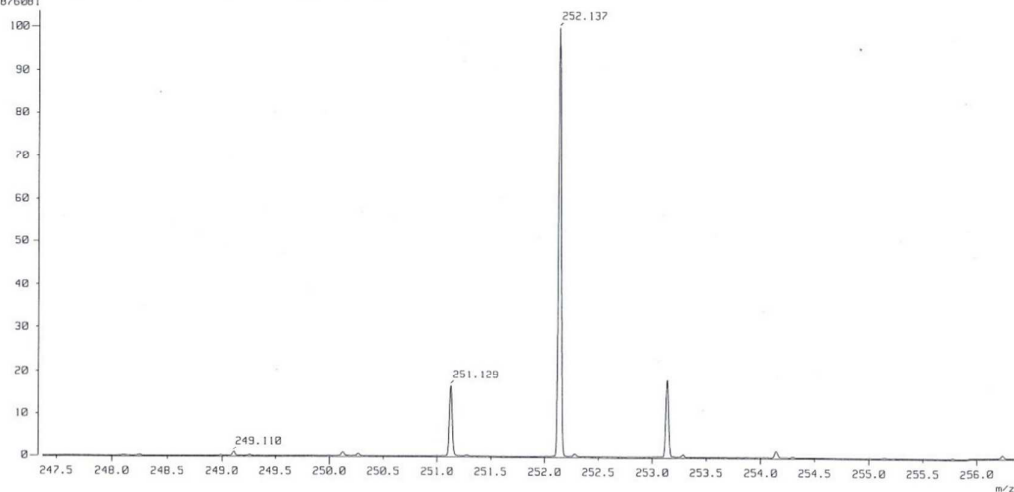


**3f**

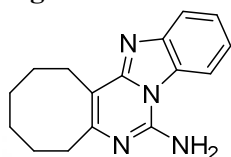
[ Mass Spectrum ]  
Data : QD-311-HREI Date : 26-Jan-2017 13:46  
Sample: -  
Note: -  
Inlet : Direct Ion Mode: EI+  
Spectrum Type: Normal Ion (EF-Linear)  
RT : 0.48 min Scan#: (10,11)  
BP : m/z 252.1373 Int. : 40.34  
Output m/z range : 247.3744 to 256.3468 Cut Level : 0.00 %  
876081

[ Elemental Composition ]  
Data : QD-311-HREI Date : 26-Jan-2017 13:46  
Sample: -  
Note: -  
Inlet : Direct Ion Mode: EI+  
RT : 0.48 min Scan#: (10,11)  
Elements : C 15/0, H 16/0, N 4/0  
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
237.1137	12.0	-1.4 / -0.3	10.5 C 14 H 13 N 4
251.1294	16.5	-1.2 / -0.3	10.5 C 15 H 15 N 4
252.1373	100.0	-0.8 / -0.2	10.0 C 15 H 16 N 4
253.1408	18.1		

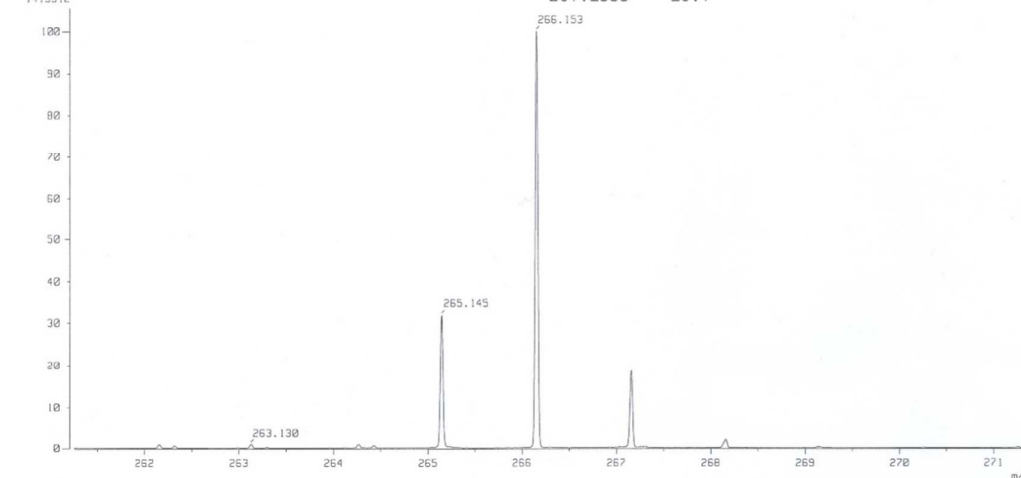


**Figure S26. HRMS spectrum of 3g**



**3g**

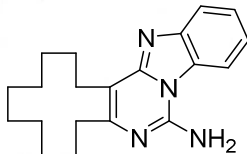
[ Mass Spectrum ]  
Data : QD-328-HREI Date : 26-Jan-2017 14:18  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
Spectrum Type : Normal Ion [EF-Linear]  
RT : 0.98 min Scan# : (20,21)  
BP : m/z 266.1531 Int. : 53.72  
Output m/z range : 261.2500 to 271.3854 Cut Level : 0.00 %  
1413312



[ Elemental Composition ]  
Data : QD-328-HREI Date : 26-Jan-2017 14:18  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
RT : 0.98 min Scan# : (20,21)  
Elements : C 16/0, H 18/0, N 4/0  
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.) : -0.5 - 100.0

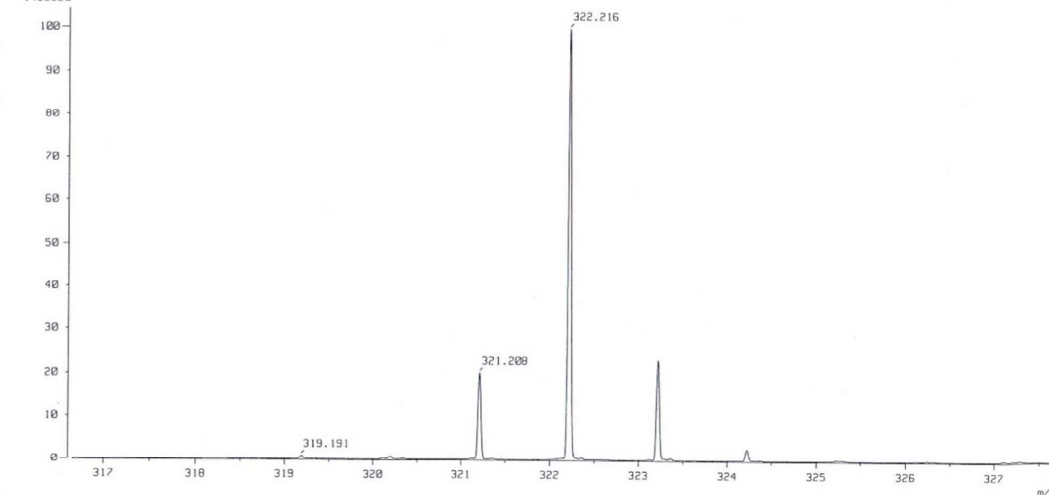
Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
251.1295	11.1	-0.7 / -0.2	10.5	C 15 H 15 N 4
252.1372	37.9	-1.3 / -0.3	10.0	C 15 H 16 N 4
265.1454	31.8	+0.5 / +0.1	10.5	C 16 H 17 N 4
266.1531	100.0	-0.3 / -0.1	10.0	C 16 H 18 N 4
267.1555	18.7			

**Figure S27. HRMS spectrum of 3h**



**3h**

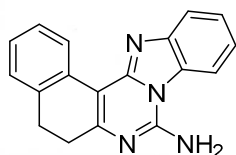
[ Mass Spectrum ]  
Data : QD-329-C20H26N4 Date : 12-Dec-2016 16:11  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
Spectrum Type : Normal Ion [EF-Linear]  
RT : 1.73 min Scan# : (35,36)  
BP : m/z 322.2159 Int. : 66.07  
Output m/z range : 316.6588 to 327.6973 Cut Level : 0.00 %  
1463620



[ Elemental Composition ]  
Data : QD-329-C20H26N4 Date : 12-Dec-2016 16:11  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
RT : 1.73 min Scan# : (35,36)  
Elements : C 20/0, H 26/0, N 4/0  
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.) : -0.5 - 100.0

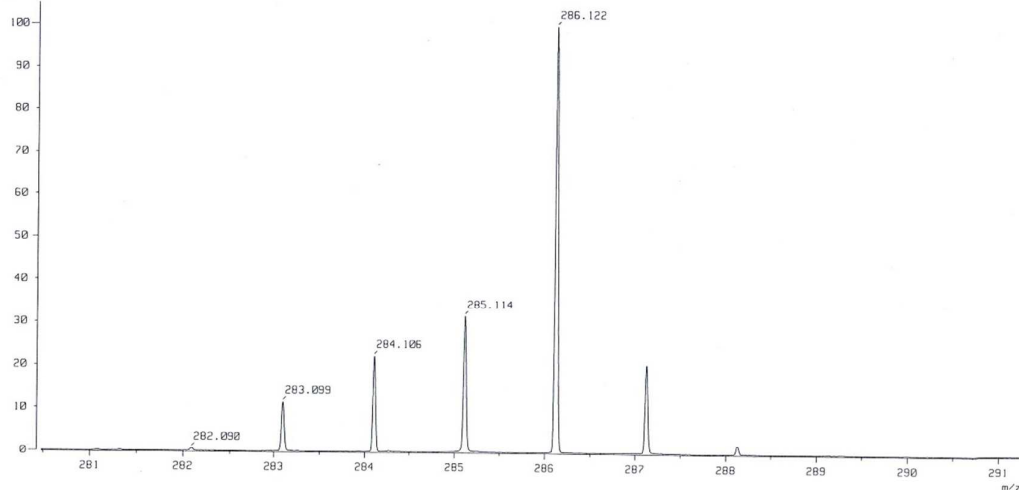
Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
293.1767	13.4	+0.2 / +0.0	10.5	C 18 H 21 N 4
321.2083	20.2	+1.1 / +0.4	10.5	C 20 H 25 N 4
322.2159	100.0	+0.6 / +0.2	10.0	C 20 H 26 N 4
323.2198	23.3			

**Figure S28. HRMS spectrum of 3i**



**3i**

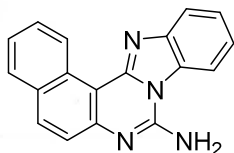
[ Mass Spectrum ]  
Data : QD-330U-C18H14N4 Date : 12-Dec-2016 16:24  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
Spectrum Type : Normal Ion (EF-Linear)  
RT : 1.28 min Scan# : (26,27)  
BP : m/z 286.1219 Int. : 34.19  
Output m/z range : 280.4807 to 291.2522 Cut Level : 0.00 %  
751887



[ Elemental Composition ]  
Data : QD-330U-C18H14N4 Date : 12-Dec-2016 16:24  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
RT : 1.28 min Scan# : (26,27)  
Elements : C 18/0, H 14/0, N 4/0  
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.) : -0.5 - 100.0

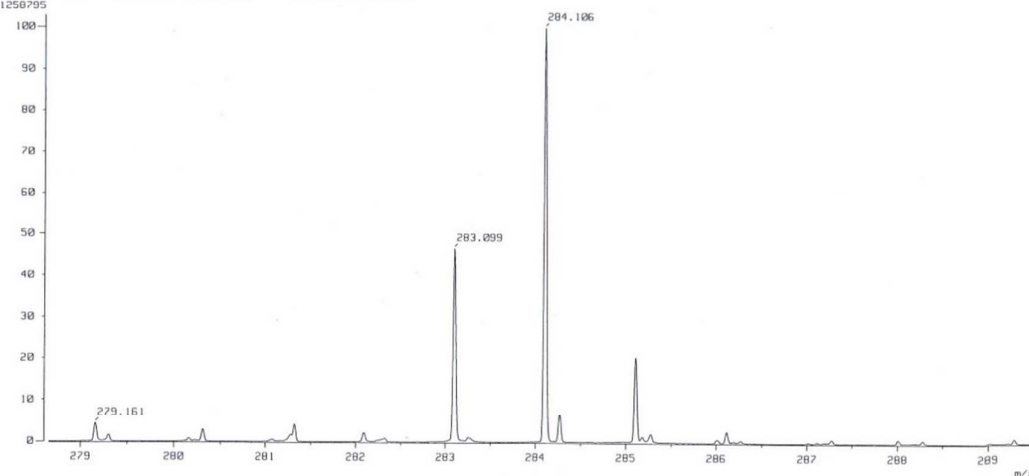
Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
283.0986	11.5	+0.8 / +0.2	15.5 C 18 H 11 N 4
284.1060	22.3	-0.8 / -0.2	15.0 C 18 H 12 N 4
285.1140	31.6	-0.1 / +0.0	14.5 C 18 H 13 N 4
286.1219	100.0	+0.4 / +0.1	14.0 C 18 H 14 N 4
287.1255	20.7		

**Figure S29. HRMS spectrum of 3i'**



**3i'**

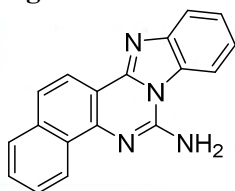
[ Mass Spectrum ]  
Data : QD-330-HREI Date : 26-Jan-2017 14:23  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
Spectrum Type : Normal Ion (EF-Linear)  
RT : 0.53 min Scan# : (11,12)  
BP : m/z 284.1060 Int. : 58.36  
Output m/z range : 278.6598 to 289.4983 Cut Level : 0.00 %  
1250795



[ Elemental Composition ]  
Data : QD-330-HREI Date : 26-Jan-2017 14:23  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
RT : 0.53 min Scan# : (11,12)  
Elements : C 18/0, H 12/0, N 4/0  
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
283.0986	46.5	+0.7 / +0.2	15.5 C 18 H 11 N 4
284.1060	100.0	-0.7 / -0.2	15.0 C 18 H 12 N 4
285.1089	20.4		

**Figure S30. HRMS spectrum of 3j**

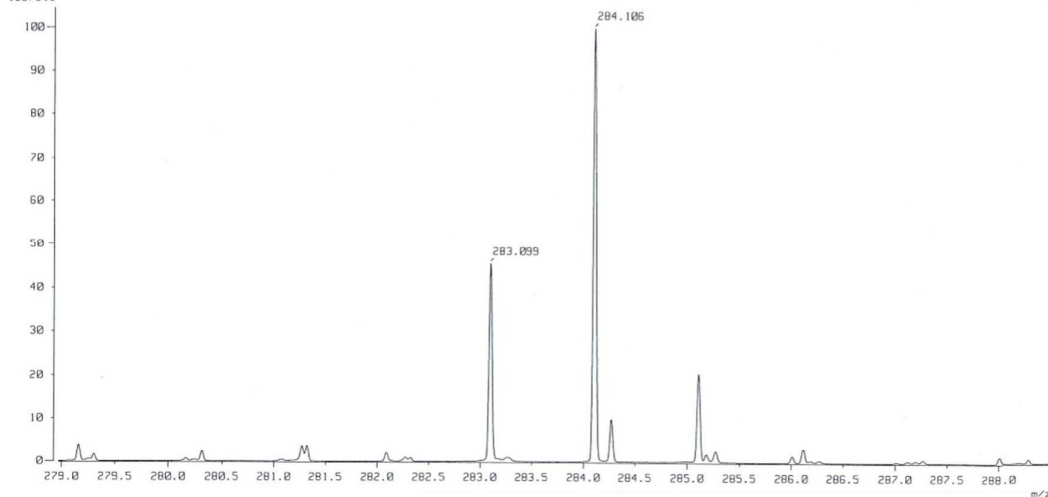


**3j**

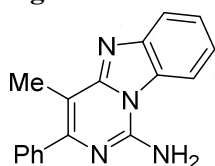
[ Mass Spectrum ]  
Data : QD-333-C18H12N4 Date : 12-Dec-2016 16:19  
Sample: -  
Note : -  
Inlet : Direct Ion Mode : EI+  
Spectrum Type : Normal Ion (EF-Linear)  
RT : 0.88 min Scan# : (18,19)  
BP : m/z 284.1060 Int. : 72.53  
Output m/z range : 278.9674 to 288.4926 Cut Level : 0.00 %  
1587515

[ Elemental Composition ]  
Data : QD-333-C18H12N4 Date : 12-Dec-2016 16:19  
Sample: -  
Note : -  
Inlet : Direct Ion Mode : EI+  
RT : 0.88 min Scan# : (18,19)  
Elements : C 18/0, H 12/0, N 4/0  
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
283.0986	45.5	+0.9 / +0.3	15.5	C 18 H 11 N 4
284.1060	100.0	-0.7 / -0.2	15.0	C 18 H 12 N 4
285.1091	20.7			



**Figure S31. HRMS spectrum of 3k**

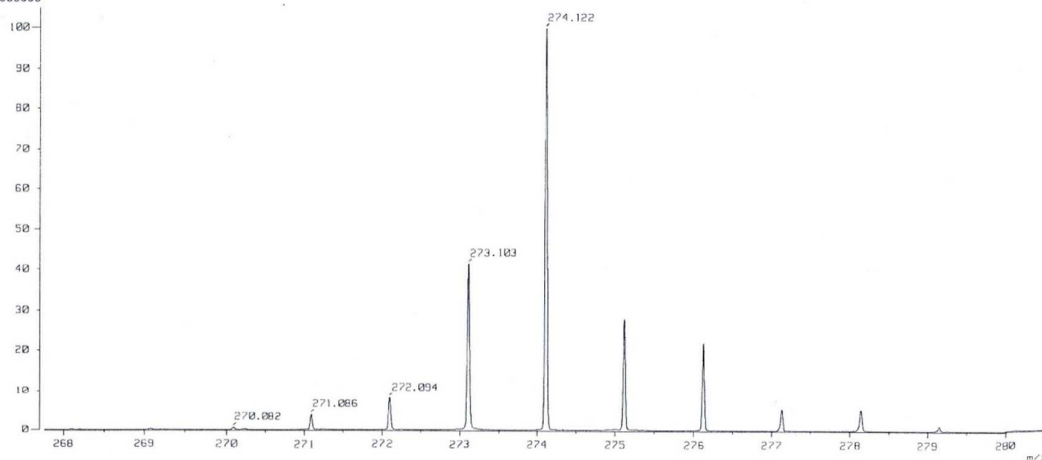


**3k**

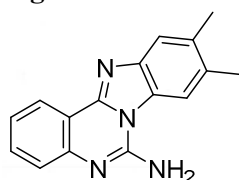
[ Mass Spectrum ]  
Data : QD-380-HREI Date : 29-Mar-2017 09:34  
Sample: -  
Note : -  
Inlet : Direct Ion Mode : EI+  
Spectrum Type : Normal Ion (EF-Linear)  
RT : 1.00 min Scan# : 21  
BP : m/z 274.1220 Int. : 60.90  
Output m/z range : 268.7685 to 280.4985 Cut Level : 0.00 %  
669555

[ Elemental Composition ]  
Data : QD-380-HREI Date : 29-Mar-2017 09:34  
Sample: -  
Note : -  
Inlet : Direct Ion Mode : EI+  
RT : 1.00 min Scan# : 21  
Elements : C 17/0, H 14/0, N 4/0  
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
261.1030	18.6	-0.6 / -0.1	12.5	C 16 H 13 N 4
273.1033	41.3	+0.7 / +0.2	13.5	C 17 H 13 N 4
274.1220	100.0	+0.3 / +0.1	13.0	C 17 H 14 N 4
275.1150	27.8			
276.1244	21.9			



**Figure S32. HRMS spectrum of 3m**

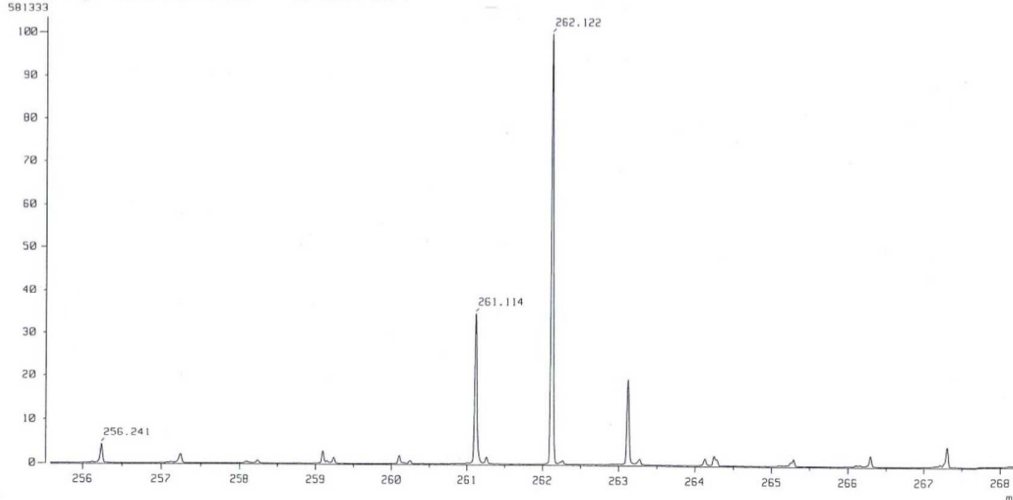


**3m**

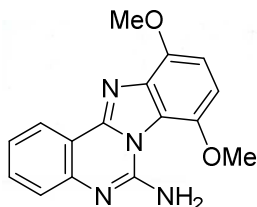
[ Mass Spectrum ]  
Data : QD-324-C16H14N4 Date : 12-Dec-2016 15:57  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
Spectrum Type : Normal Ion [EF-Linear]  
RT : 1.13 min Scan#: (23,24)  
BP : m/z 262.1215 Int. : 26.81  
Output m/z range : 255.5905 to 269.3205 Cut Level : 0.00 %

[ Elemental Composition ]  
Data : QD-324-C16H14N4 Date : 12-Dec-2016 15:57  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
RT : 1.13 min Scan#: (23,24)  
Elements : C 16/0, H 14/0, N 4/0  
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
247.0986	16.8	+0.9 / +0.2	12.5	C 15 H 11 N 4
261.1142	34.6	+0.7 / +0.2	12.5	C 16 H 13 N 4
262.1215	100.0	-1.2 / -0.3	12.0	C 16 H 14 N 4
263.1243	19.4			



**Figure S33. HRMS spectrum of 3n**

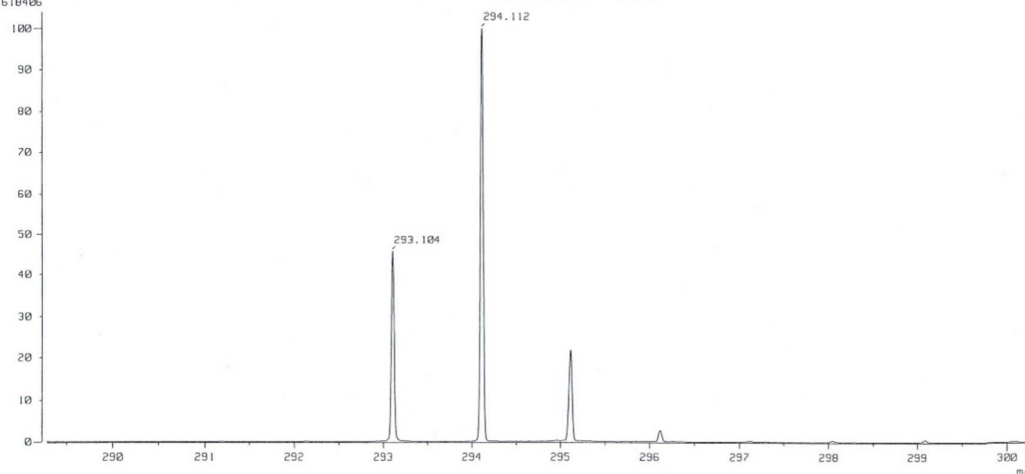


**3n**

[ Mass Spectrum ]  
Data : QD-376-HREI Date : 29-Mar-2017 09:30  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
Spectrum Type : Normal Ion [EF-Linear]  
RT : 1.00 min Scan#: 21  
BP : m/z 294.1120 Int. : 56.77  
Output m/z range : 289.2619 to 300.3205 Cut Level : 0.00 %

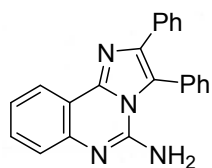
Data : QD-376-HREI Date : 29-Mar-2017 09:30  
Sample: -  
Note: -  
Inlet : Direct Ion Mode : EI+  
RT : 1.00 min Scan#: 21  
Elements : C 16/0, H 14/0, N 4/0, O 2/0  
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
265.1085	18.7	-1.7 / -0.4	11.5	C 15 H 13 N 4 O
279.6880	44.3			
280.6420	12.5			
293.1041	45.9	+0.8 / +0.2	12.5	C 16 H 13 N 4 O 2
294.1120	100.0	+1.1 / +0.3	12.0	C 16 H 14 N 4 O 2
295.1132	21.8			





**Figure S34. HRMS spectrum of 3o**

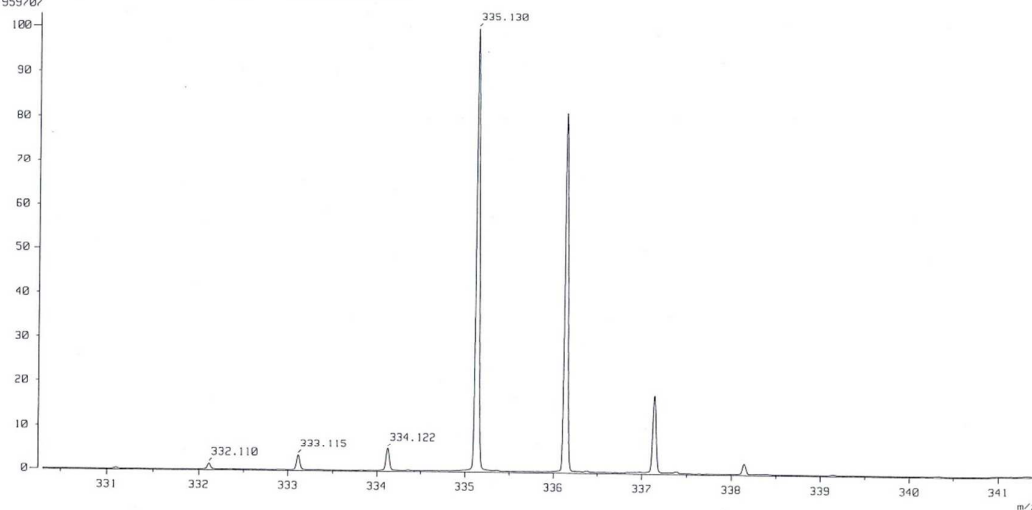


**3o**

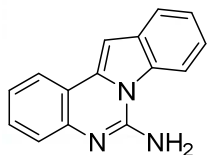
[ Mass Spectrum ]  
Data : OD-325-C22H16N4 Date : 12-Dec-2016 16:07  
Sample: -  
Note: -  
Inlet: Direct Ion Mode: EI+  
Spectrum Type: Normal Ion (EF-Linear)  
RT: 0.73 min Scan#: (15,16)  
BP: m/z 335.1299 Int.: 44.47  
Output m/z range: 330.3027 to 341.4303 Cut Level: 0.00 %  
959707

[ Elemental Composition ]  
Data : QD-325-C22H16N4 Date : 12-Dec-2016 16:07  
Sample: -  
Note: -  
Inlet: Direct Ion Mode: EI+  
RT: 0.73 min Scan#: (15,16)  
Elements: C 22/0, H 16/0, N 4/0  
Mass Tolerance: 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.): -0.5 - 100.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
335.1299	100.0	+0.7 / +0.2	17.5	C 22 H 15 N 4
336.1373	81.4	-0.6 / -0.2	17.0	C 22 H 16 N 4
337.1398	17.6			



**Figure S35. HRMS spectrum of 5a**

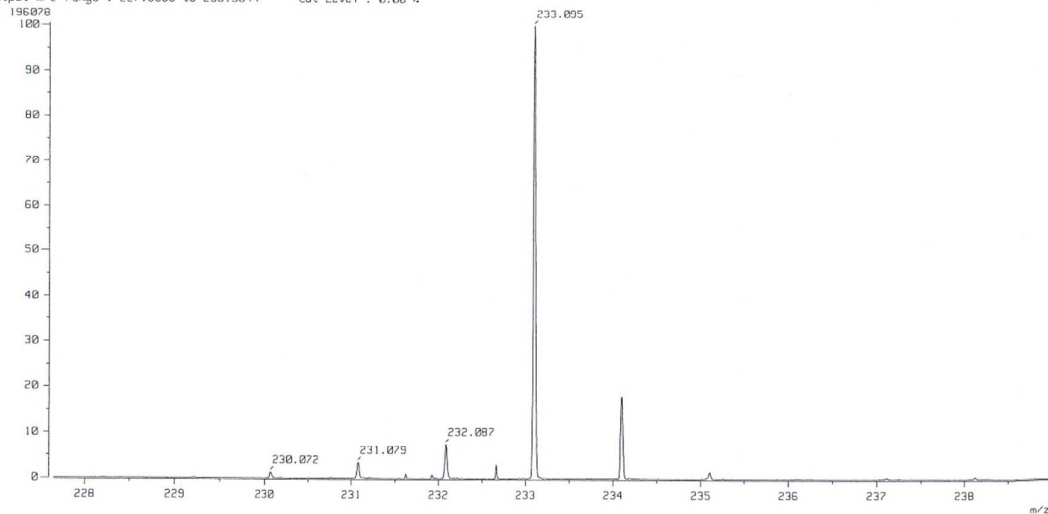


**5a**

[ Mass Spectrum ]  
Data : HK-211-C15H11N3 Date : 07-Sep-2016 13:50  
Sample: -  
Note: -  
Inlet: Direct Ion Mode: EI+  
Spectrum Type: Normal Ion (EF-Linear)  
RT: 1.33 min Scan#: (27,28)  
BP: m/z 233.0951 Int.: 9.30  
Output m/z range: 227.6588 to 238.9644 Cut Level: 0.00 %  
196070

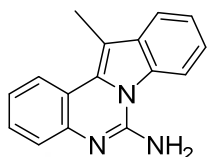
[ Elemental Composition ]  
Data : HK-211-C15H11N3 Date : 07-Sep-2016 13:50  
Sample: -  
Note: -  
Inlet: Direct Ion Mode: EI+  
RT: 1.33 min Scan#: (27,28)  
Elements: C 15/0, H 11/0, N 3/0  
Mass Tolerance: 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.): -0.5 - 100.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
205.0770	10.3	+2.1 / +0.4	11.5	C 14 H 9 N 2
233.0951	100.0	-0.8 / -0.2	12.0	C 15 H 11 N 3
234.0966	18.1			





**Figure S36. HRMS spectrum of 5b**

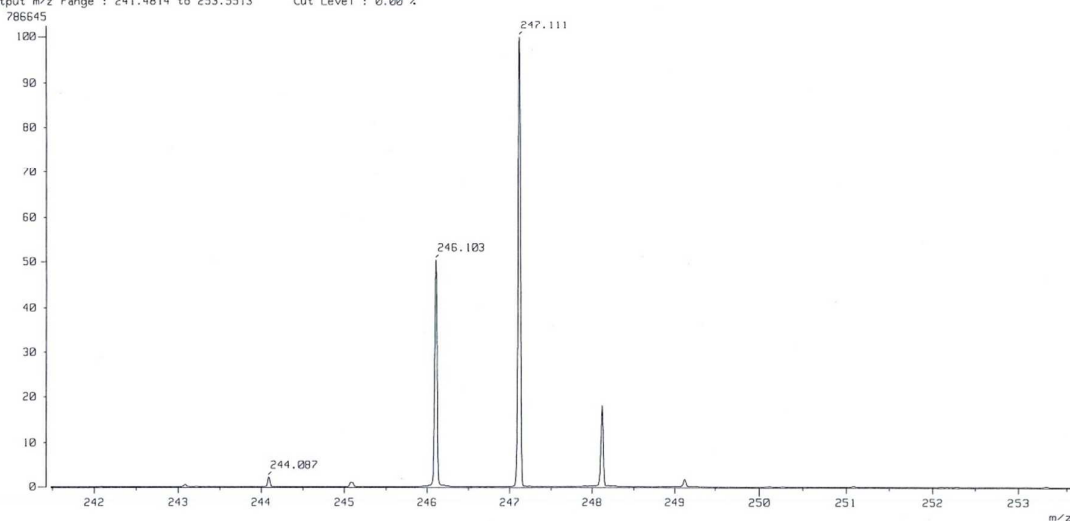


**5b**

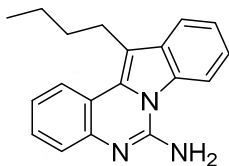
[ Mass Spectrum ]  
Data : HK-210-C16H13N3 Date : 07-Mar-2017 15:35  
Sample: -  
Note: -  
Inlet: Direct Ion Mode: EI+  
Spectrum Type: Normal Ion (EF-Linear)  
RT: 1.05 min Scan#: 22  
BP: m/z 247.1108 Int.: 73.28  
Output m/z range: 241.4814 to 253.5513 Cut Level: 0.00 %

[ Elemental Composition ]  
Data : HK-210-C16H13N3 Date : 07-Mar-2017 15:35  
Sample: -  
Note: -  
Inlet: Direct Ion Mode: EI+  
RT: 1.05 min Scan#: 22  
Elements: C 16/0, H 13/0, N 3/0  
Mass Tolerance: 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.): -0.5 - 100.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
246.1033	50.4	+0.9 / +0.2	12.5	C 16 H 12 N 3
247.1108	100.0	-0.5 / -0.1	12.0	C 16 H 13 N 3
248.1142	18.1			



**Figure S37. HRMS spectrum of 5c**

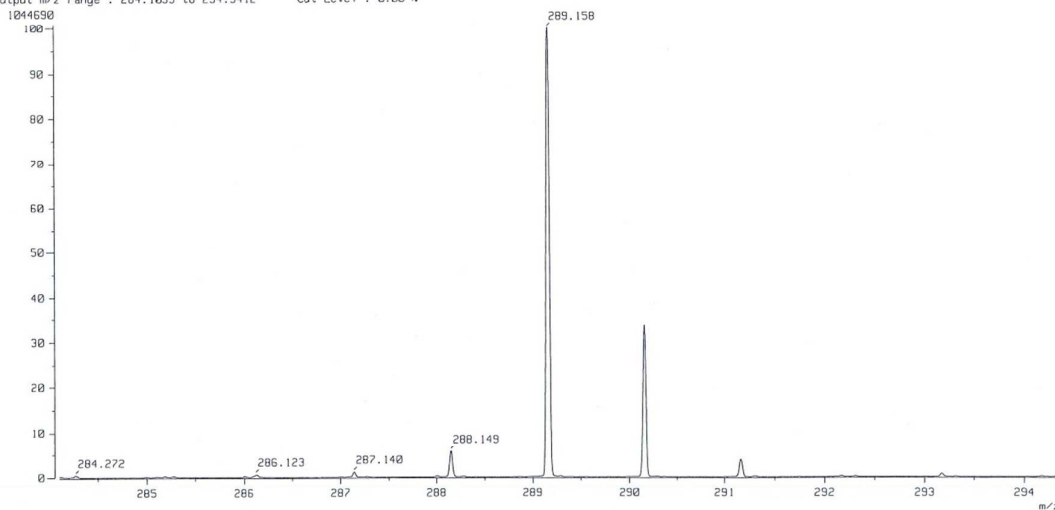


**5c**

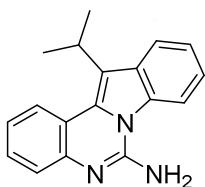
[ Mass Spectrum ]  
Data : HK-217-HREI Date : 28-Feb-2017 09:38  
Sample: -  
Note: -  
Inlet: Direct Ion Mode: EI+  
Spectrum Type: Normal Ion (EF-Linear)  
RT: 0.75 min Scan#: 16  
BP: m/z 289.1580 Int.: 98.67  
Output m/z range: 284.1039 to 294.3412 Cut Level: 0.00 %

[ Elemental Composition ]  
Data : HK-217-HREI Date : 28-Feb-2017 09:38  
Sample: -  
Note: -  
Inlet: Direct Ion Mode: EI+  
RT: 0.75 min Scan#: 16  
Elements: C 19/0, H 19/0, N 3/0  
Mass Tolerance: 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
Unsaturation (U.S.): -0.5 - 100.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
289.1580	100.0	+0.2 / +0.1	12.0	C 19 H 19 N 3
290.1593	33.6			



**Figure S38. HRMS spectrum of 5d**

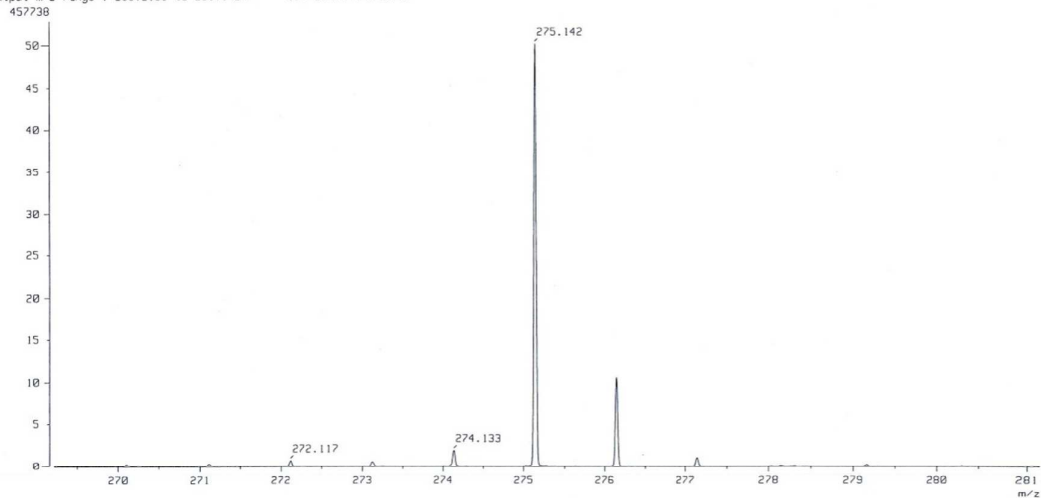


**5d**

[ Mass Spectrum ]  
 Data : HK-228-HREI Date : 28-Feb-2017 09:42  
 Sample: -  
 Note : -  
 Inlet : Direct Ion Mode : EI+  
 Spectrum Type : Normal Ion (EF-Linear)  
 RT : 1.00 min Scan# : 21  
 BP : m/z 260.1187 Int. : 92.50  
 Output m/z range : 269.2136 to 281.1424 Cut Level : 0.00 %

[ Elemental Composition ]  
 Data : HK-228-HREI Date : 28-Feb-2017 09:42  
 Sample: -  
 Note : -  
 Inlet : Direct Ion Mode : EI+  
 RT : 1.00 min Scan# : 21  
 Elements : C 18/0, H 17/0, N 3/0  
 Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3  
 Unsaturation (U.S.) : -0.5 - 100.0

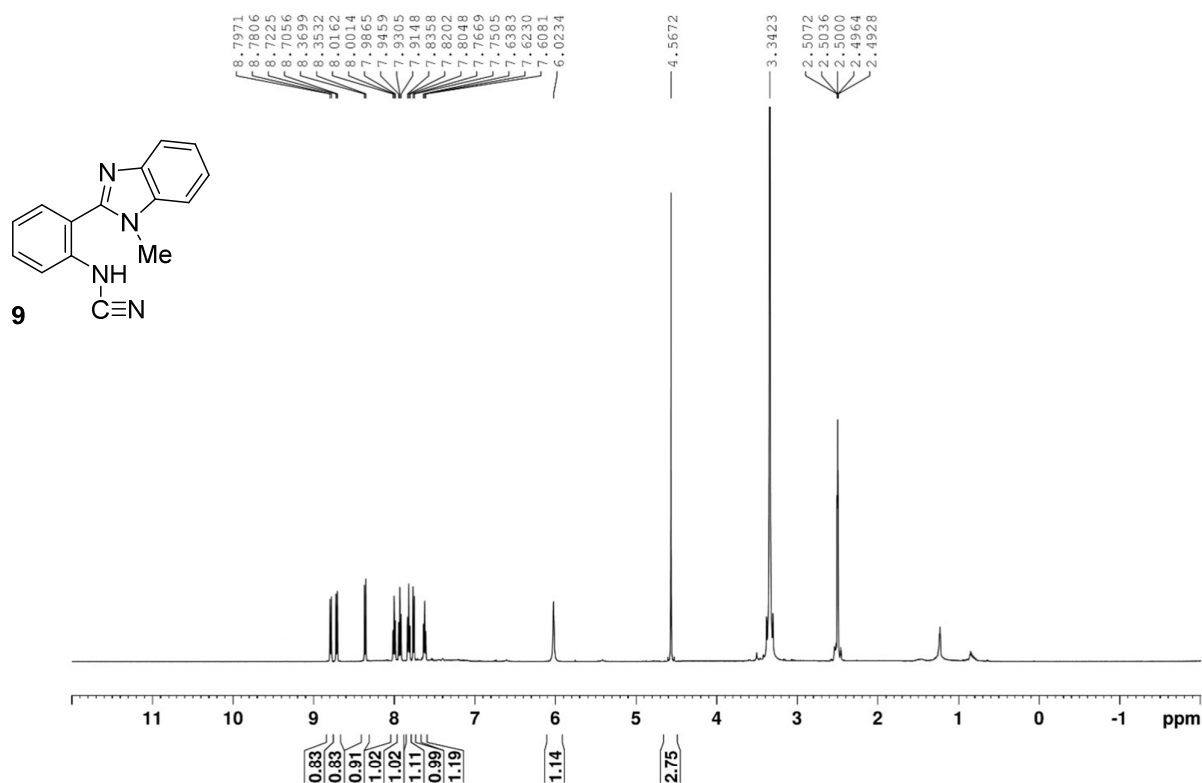
Observed m/z	Int%	Err[ppm / mmu]	U.S. Composition
260.1187	100.0	-0.3 / -0.1	12.5 C 17 H 14 N 3
261.1220	20.5		
275.1420	50.1	-0.9 / -0.2	12.0 C 18 H 17 N 3
276.1458	10.5		

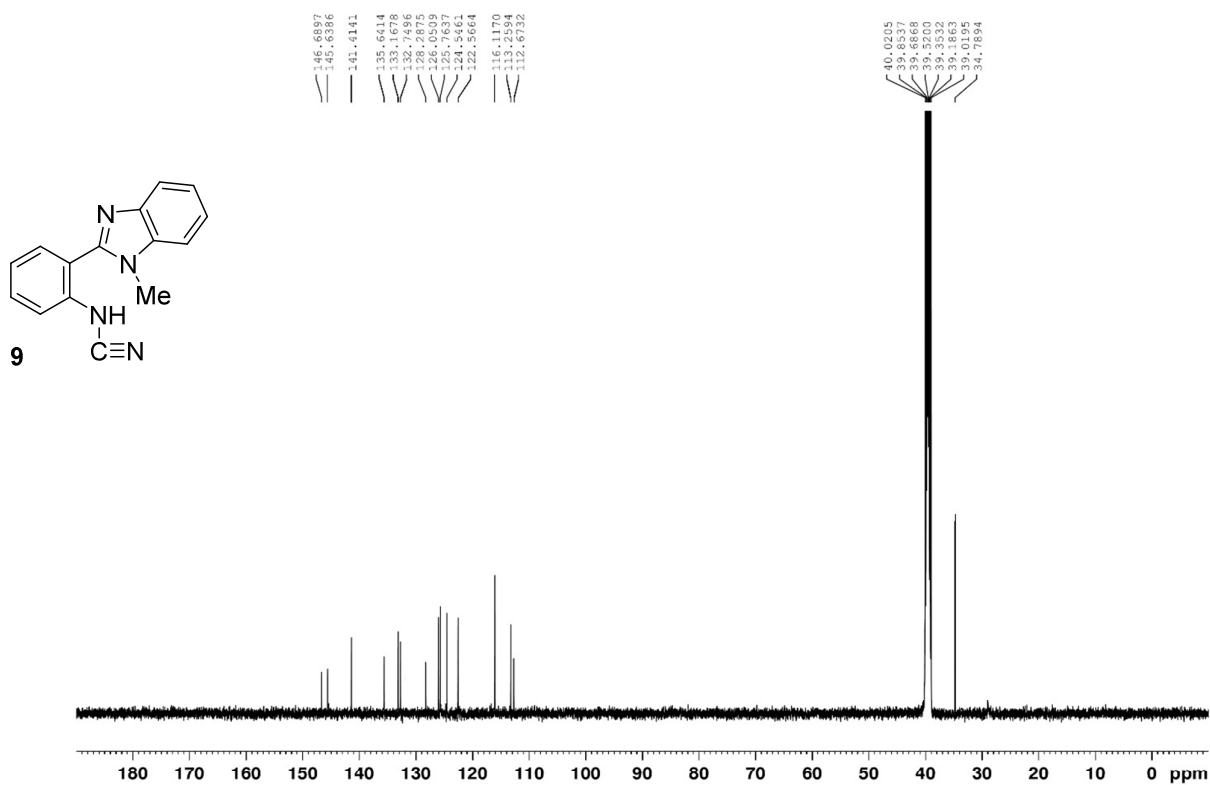


**Experimental Procedure for Mechanism Study.** A 10 mL microwave reaction tube was charged with **8** (0.086 g, 0.3 mmol) and **2** (0.025 g, 0.6 mmol) together with CuI (0.006 g, 0.03 mmol), K<sub>3</sub>PO<sub>4</sub> (0.127 g, 0.6 mmol), and DMF (3 mL). The reaction mixture was heated to 100 °C for 1 h by microwave irradiation at 100 W initial power. The mixture was then cooled to room temperature and filtered through a short silica gel column (ethyl acetate) to remove inorganic components. Removal of the solvent left a crude mixture, which was separated by TLC (dichloromethane/MeOH = 9/1) to give **9**.

*N*-(2-(1-Methyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)cyanamide (**9**). Pale yellow solid (58 mg, 78%). mp 125-127 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 4.57 (s, 3H), 6.02 (s, 1H), 7.61-7.64 (m, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.80-7.84 (m, 1H), 7.91-7.95 (m, 1H), 7.99-8.02 (m, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 8.71 (d, *J* = 8.5 Hz, 1H), 8.79 (d, *J* = 8.3 Hz, 1H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 34.8, 112.7, 113.3, 116.1, 122.6, 124.5, 125.8, 126.1, 128.3, 132.7, 133.2, 135.6, 141.4, 145.6, 146.7. HRMS (EI) calcd for C<sub>15</sub>H<sub>12</sub>N<sub>4</sub> (M<sup>+</sup>): 248.1062. Found 248.1059.

**Figure S39.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **9**





**Figure S40.** HRMS spectrum of **9**

