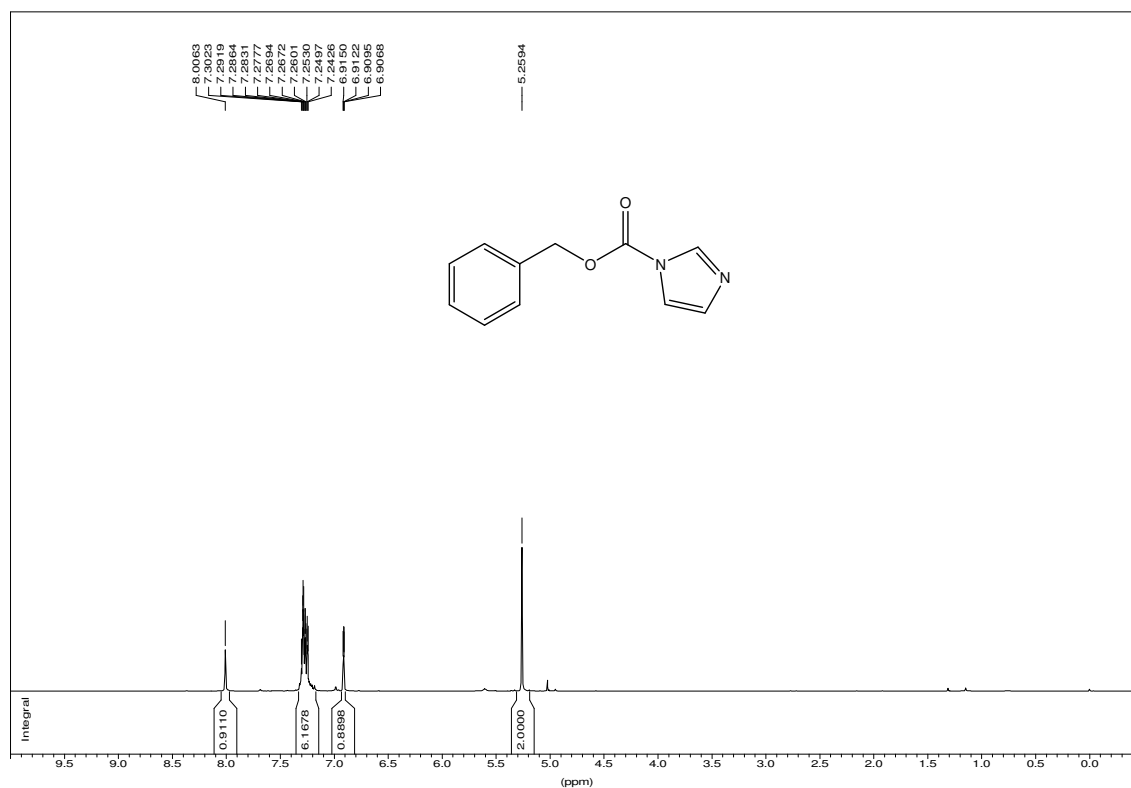


Synthesis of Pyrazolo[5,1-*d*][1,2,3,5]tetrazine-4(3*H*)-ones

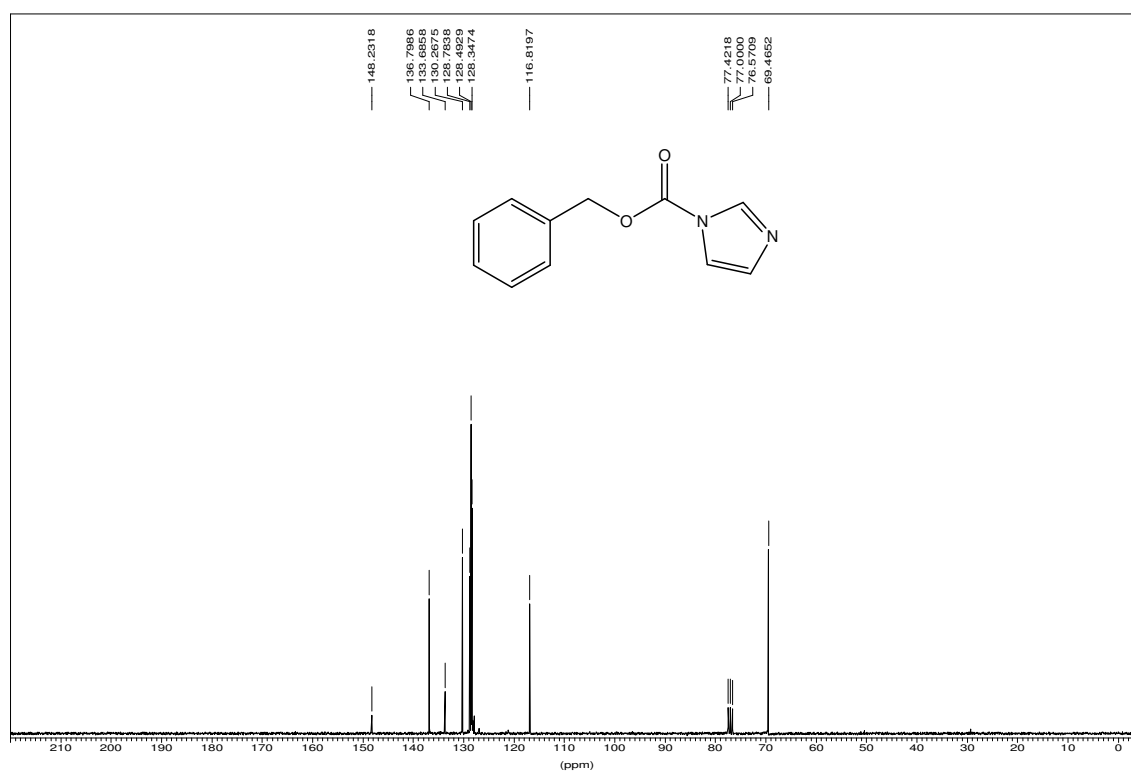
Yaojun Gao, and Yulin Lam*

Department of Chemistry, National University of Singapore, 3 Science Drive 3,
Singapore 117543

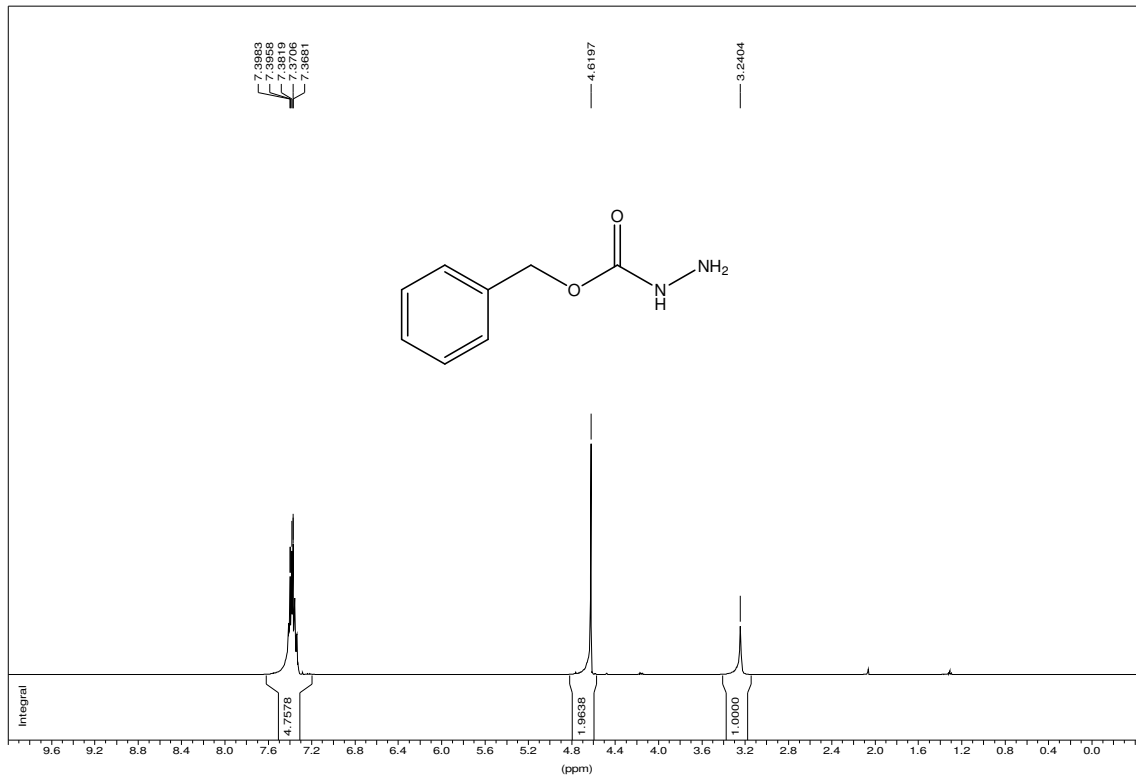
¹H NMR Spectrum of 4



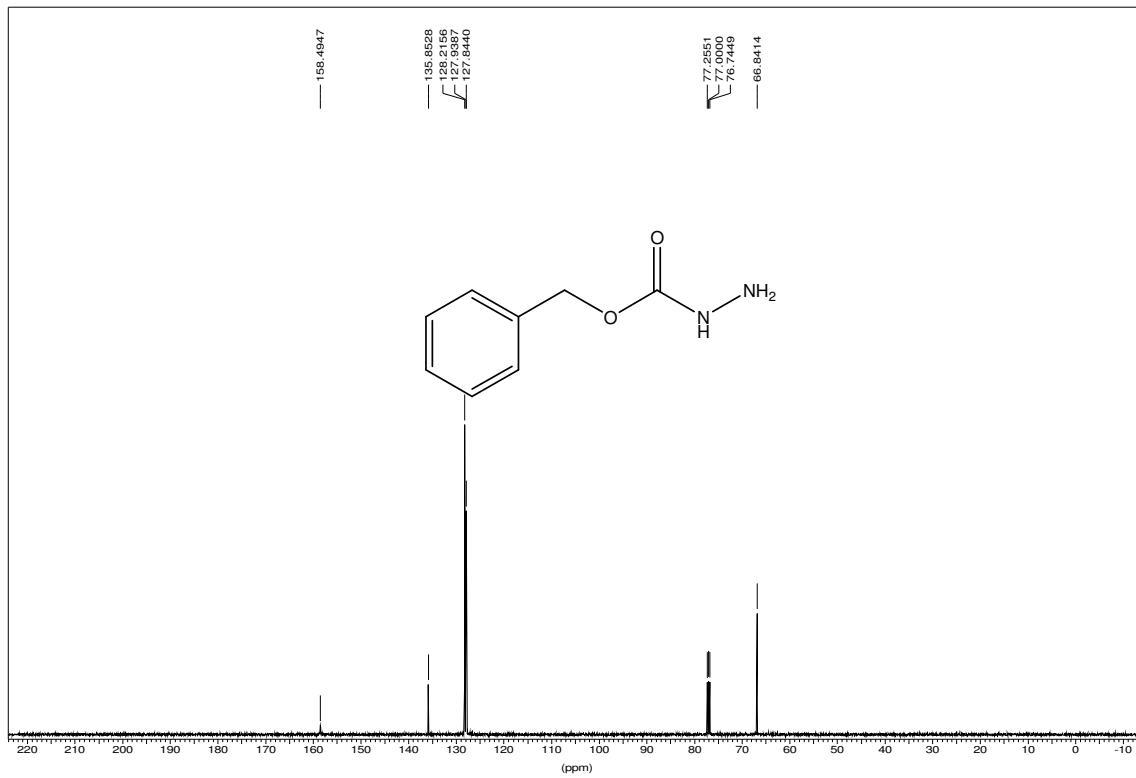
¹³C NMR Spectrum of 4



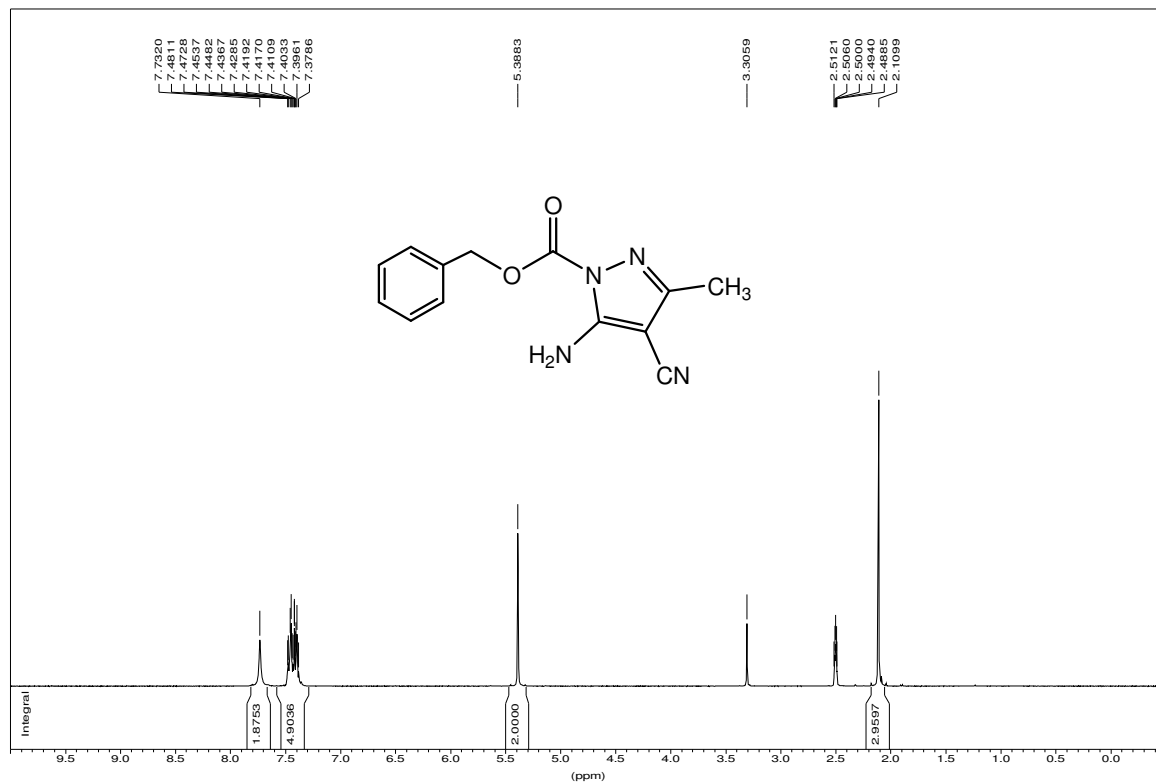
¹H NMR Spectrum of 5



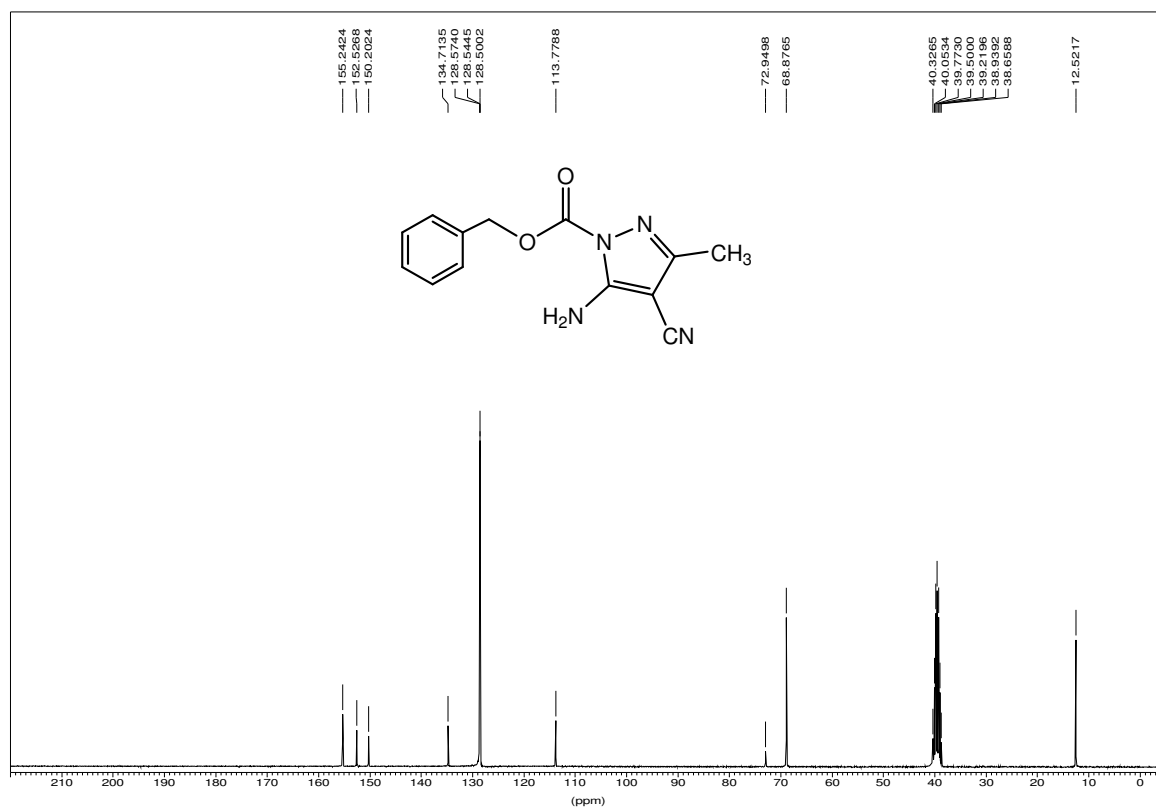
¹³C NMR Spectrum of 5



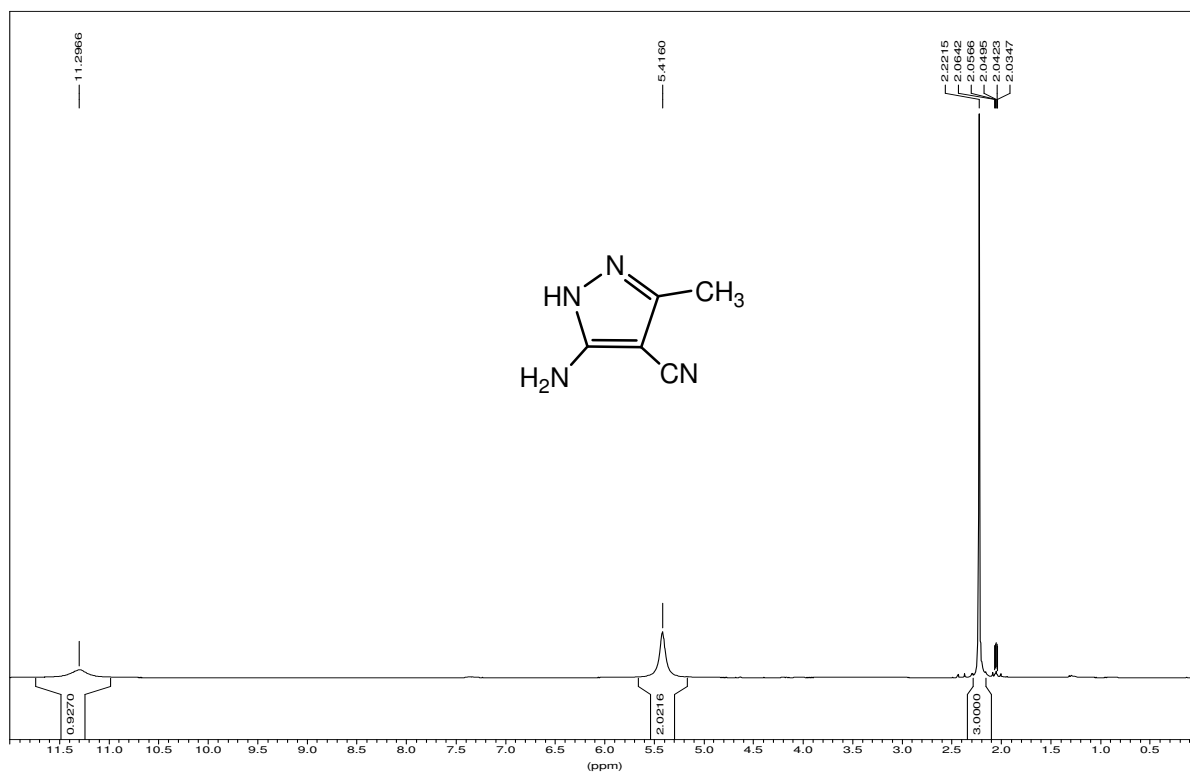
¹H NMR Spectrum of 6



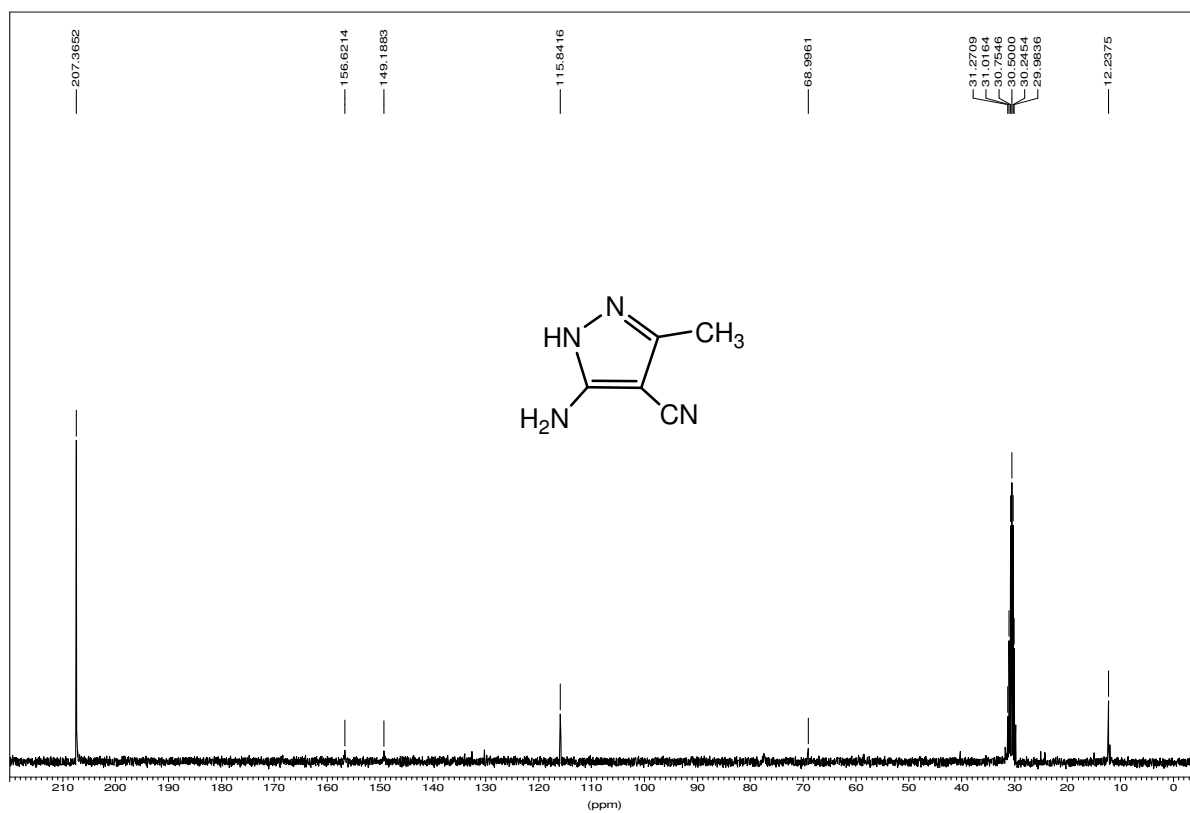
¹³C NMR Spectrum of 6



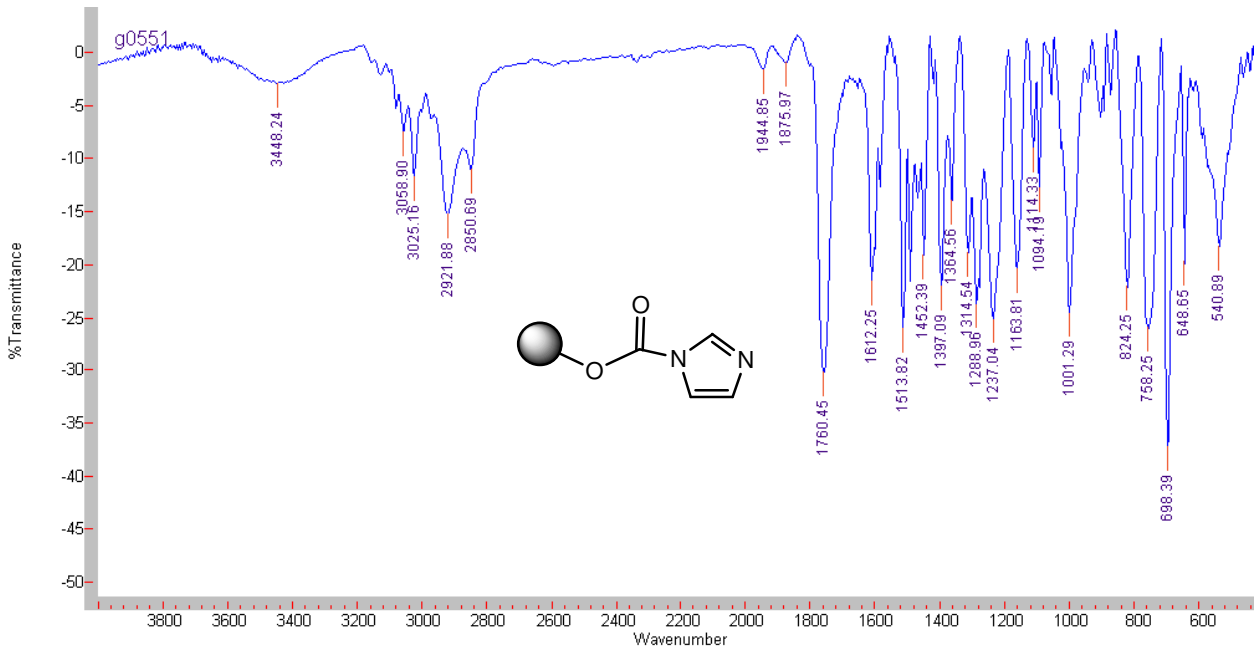
¹H NMR Spectrum of 2a



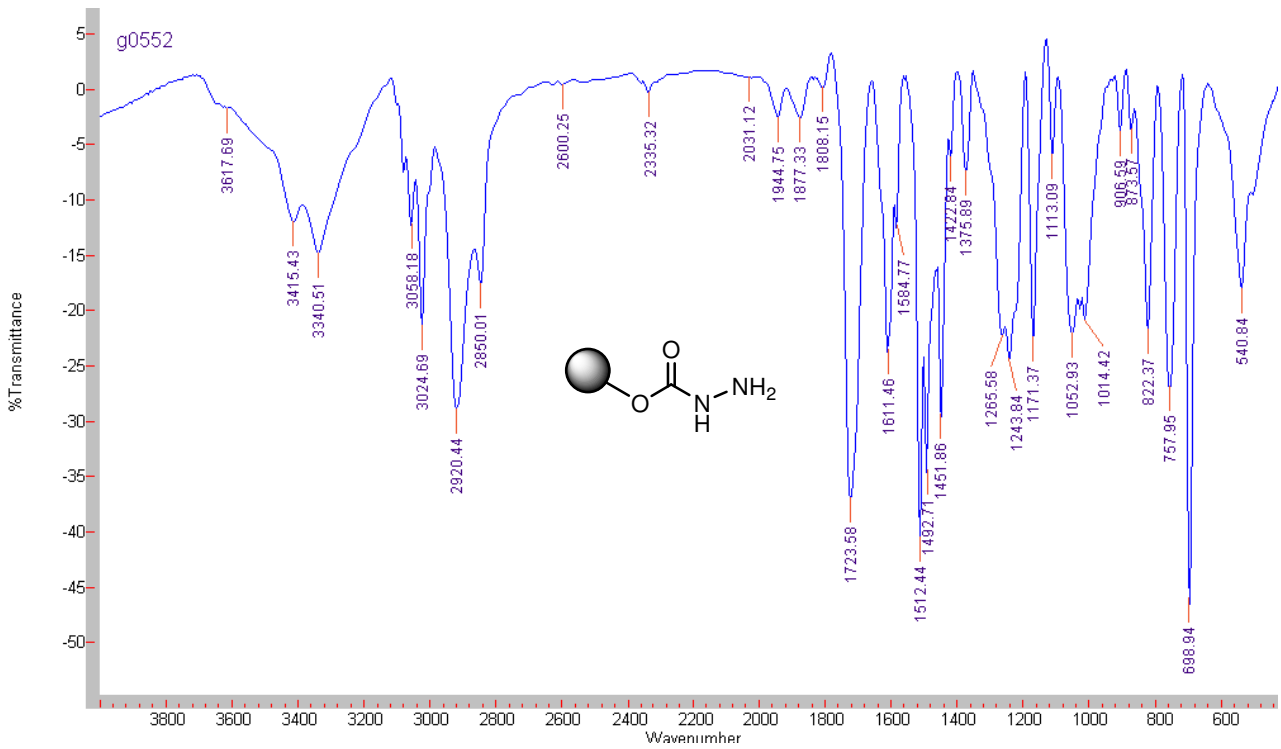
¹³C NMR Spectrum of 2a



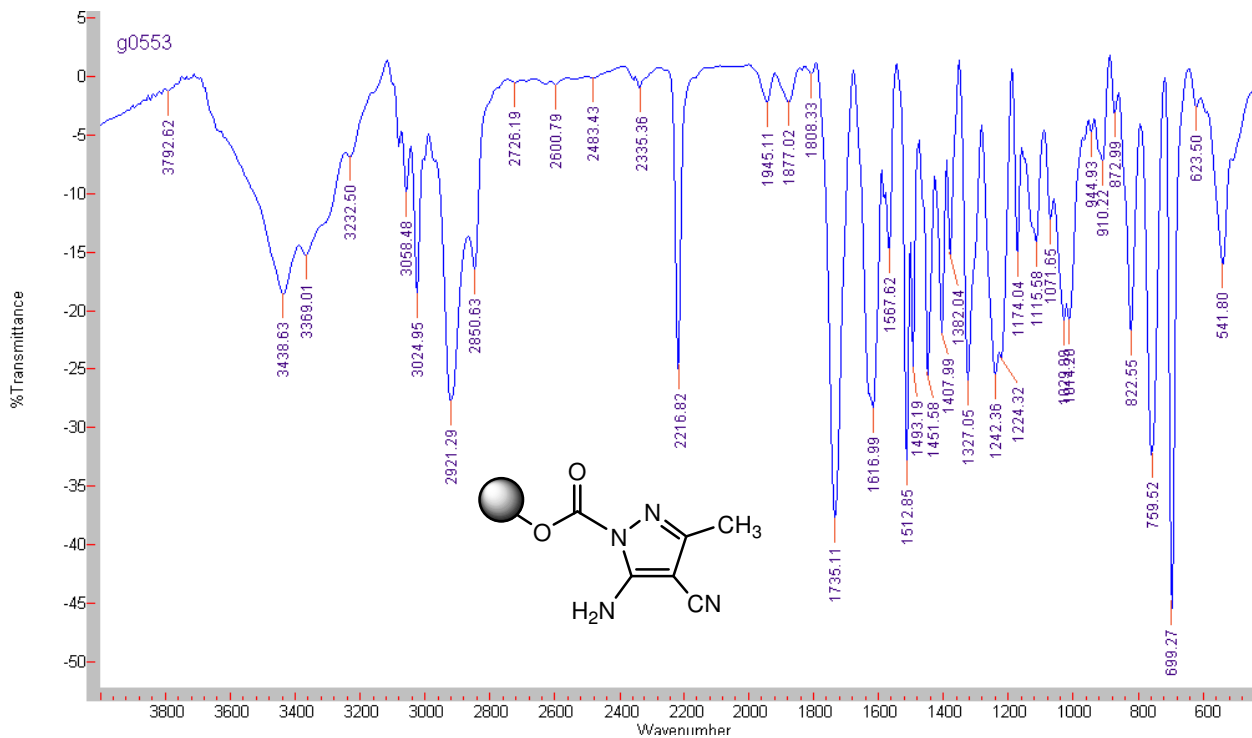
IR Spectrum of Resin 9



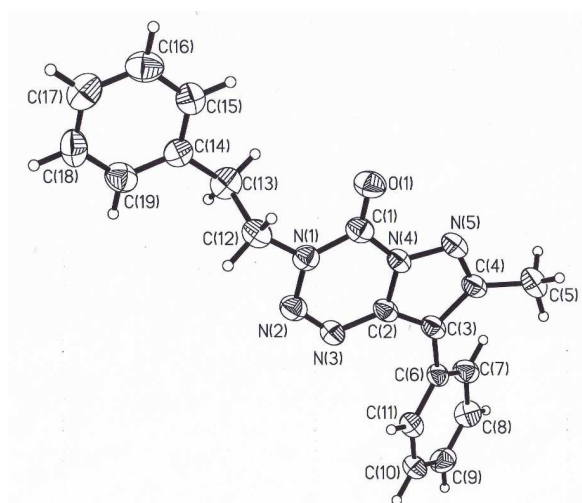
IR Spectrum of Resin 10



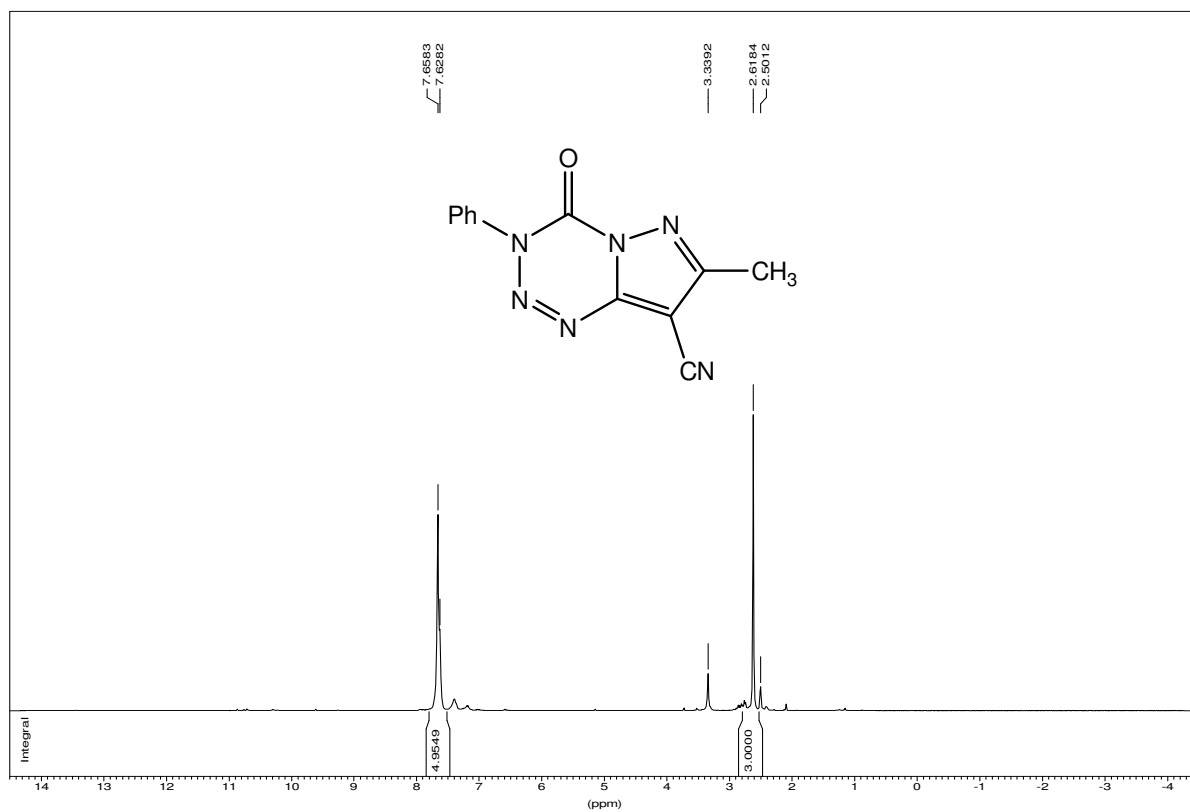
IR Spectrum of Resin 11



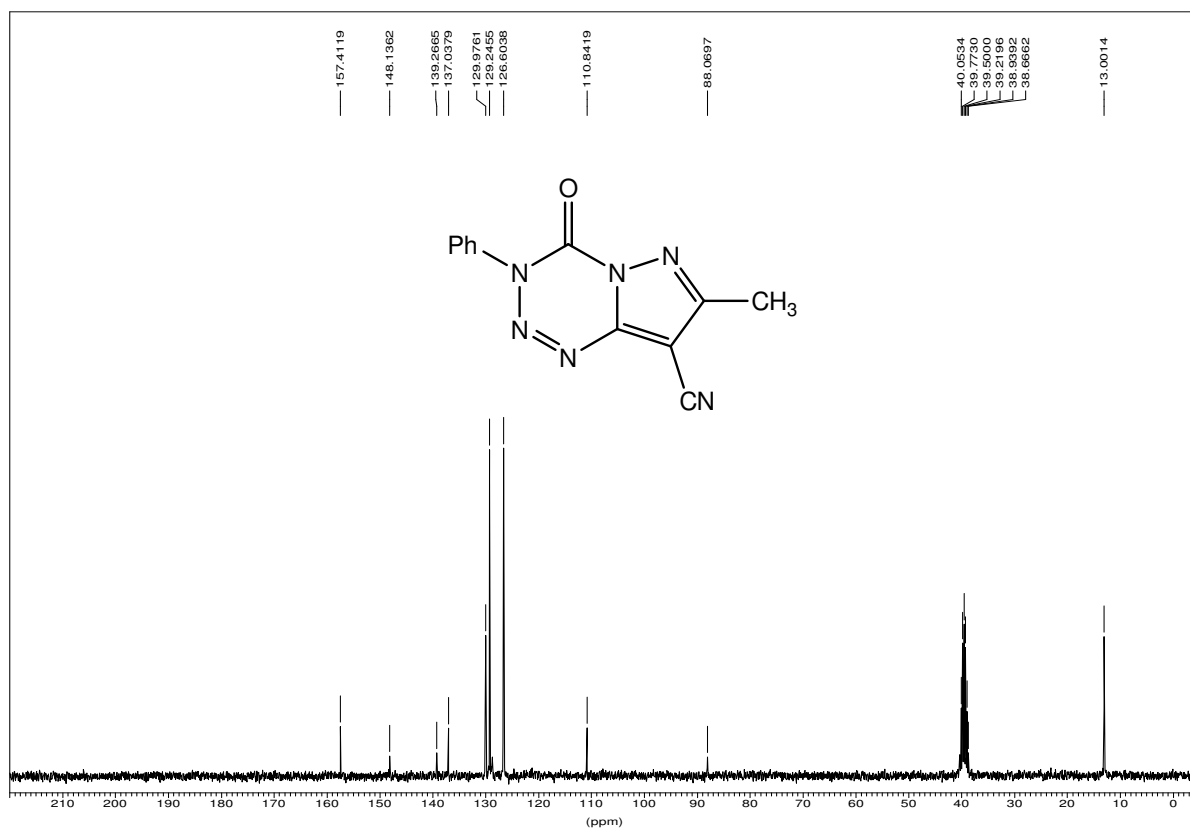
X-ray Structure of 11



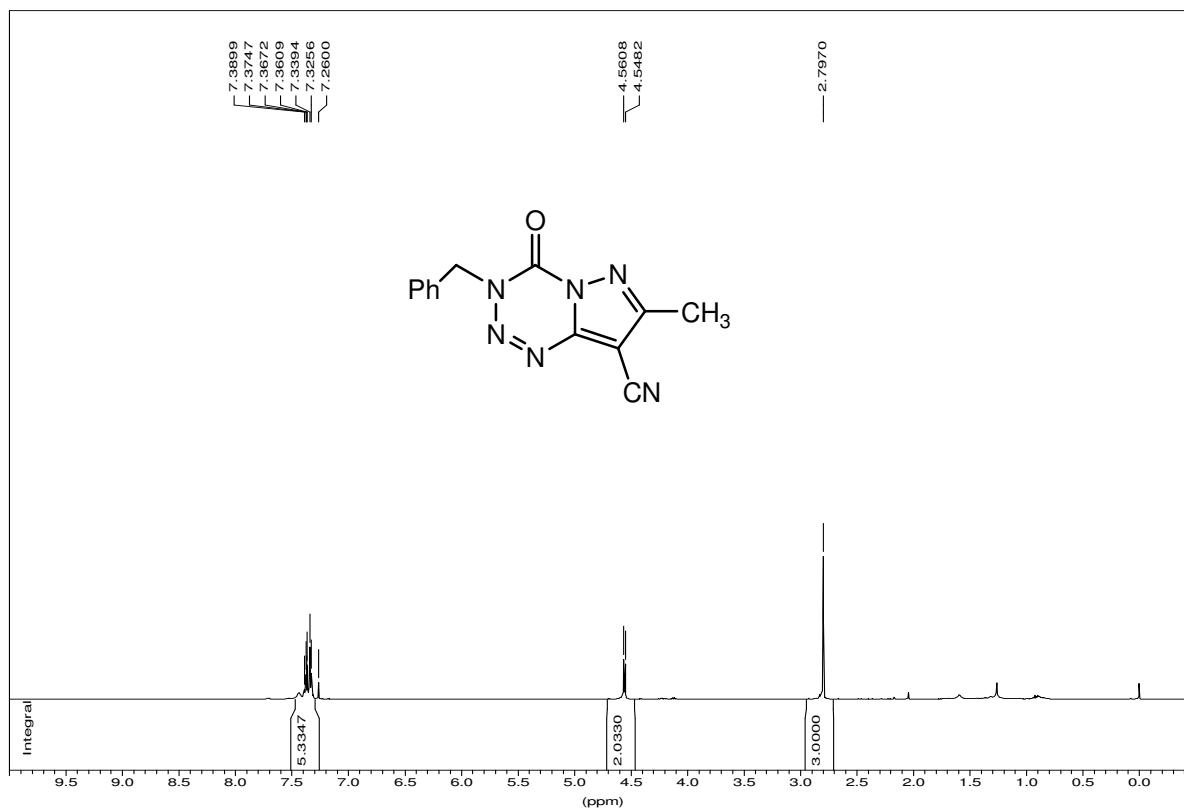
¹H NMR Spectrum of 1a



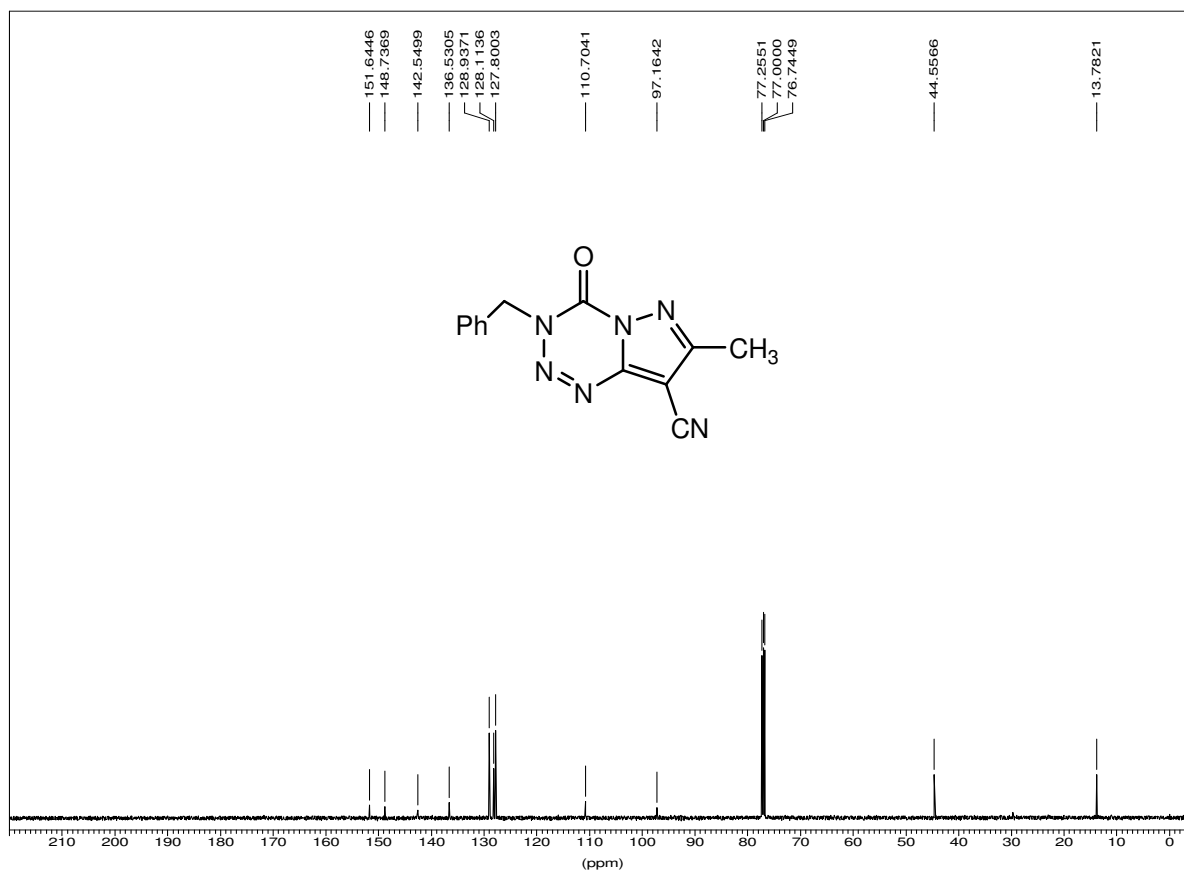
¹³C NMR Spectrum of 1a



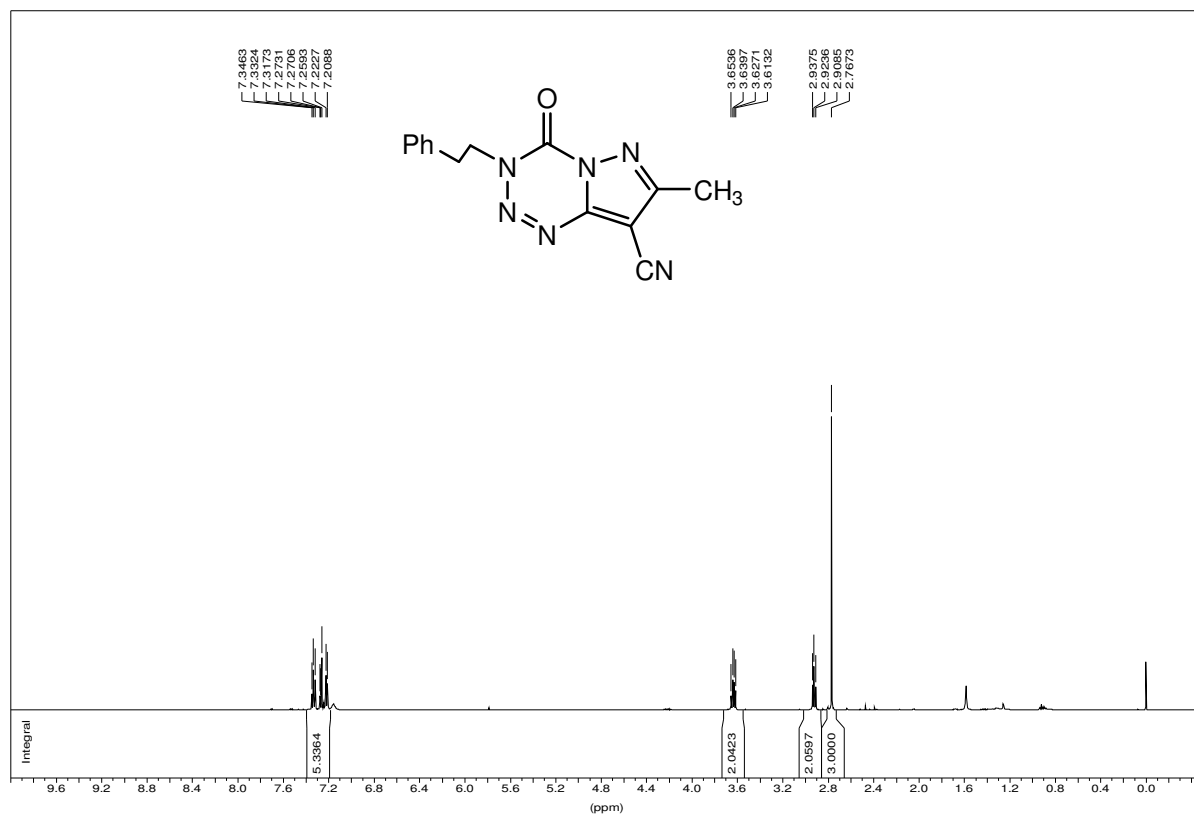
¹H NMR Spectrum of 1b



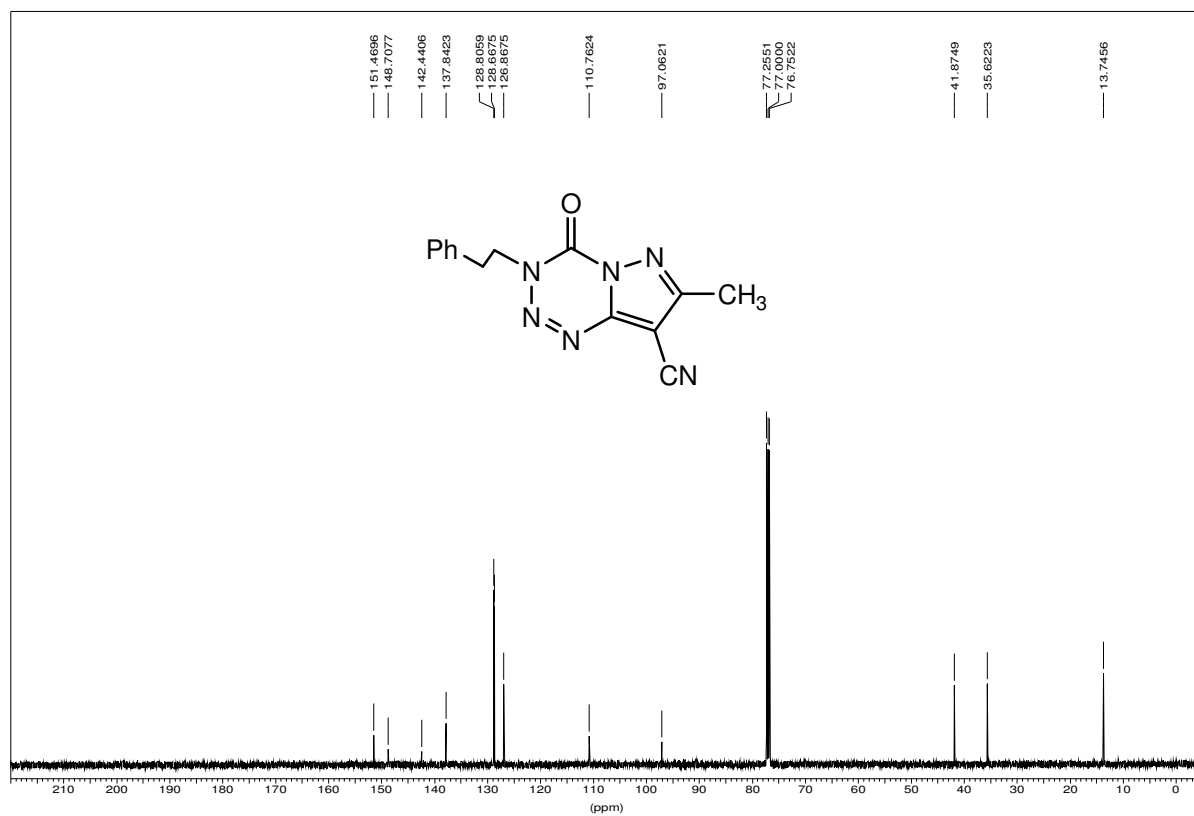
¹³C NMR Spectrum of 1b



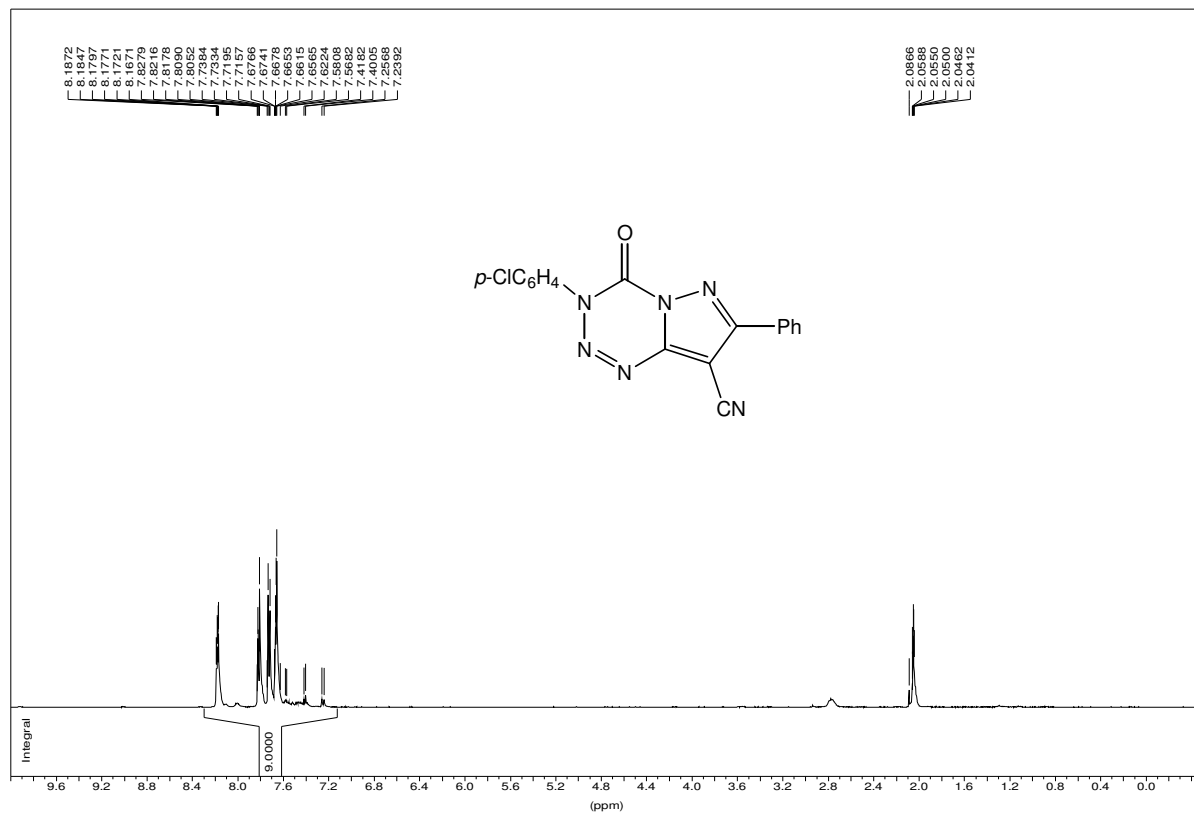
¹H NMR Spectrum of 1c



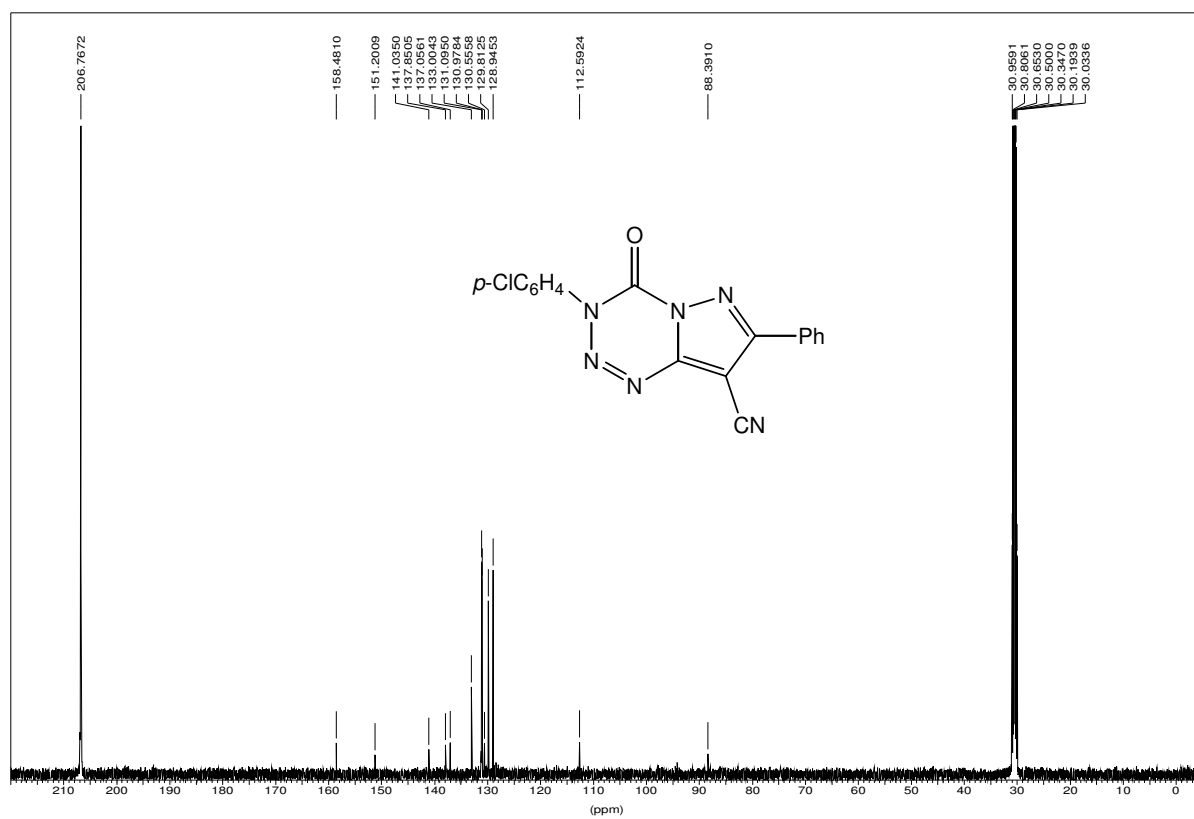
¹³C NMR Spectrum of 1c



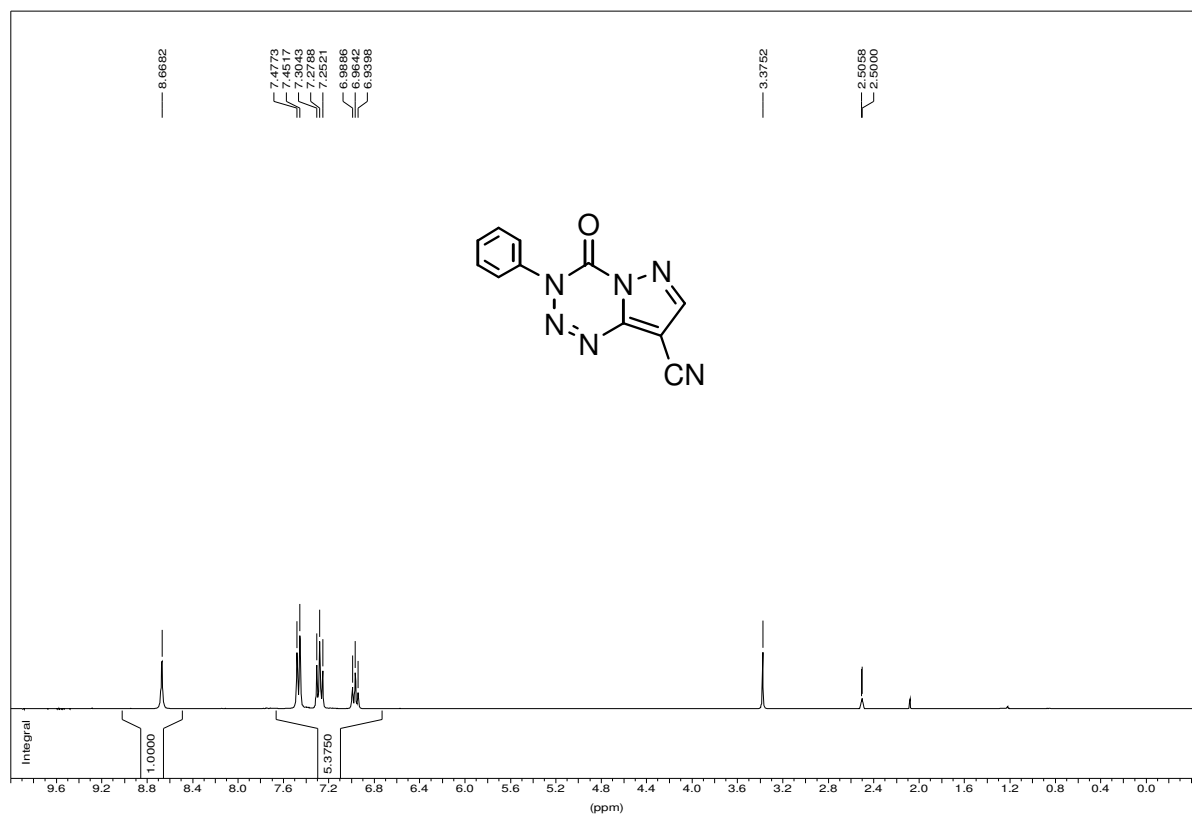
¹H NMR Spectrum of 1d



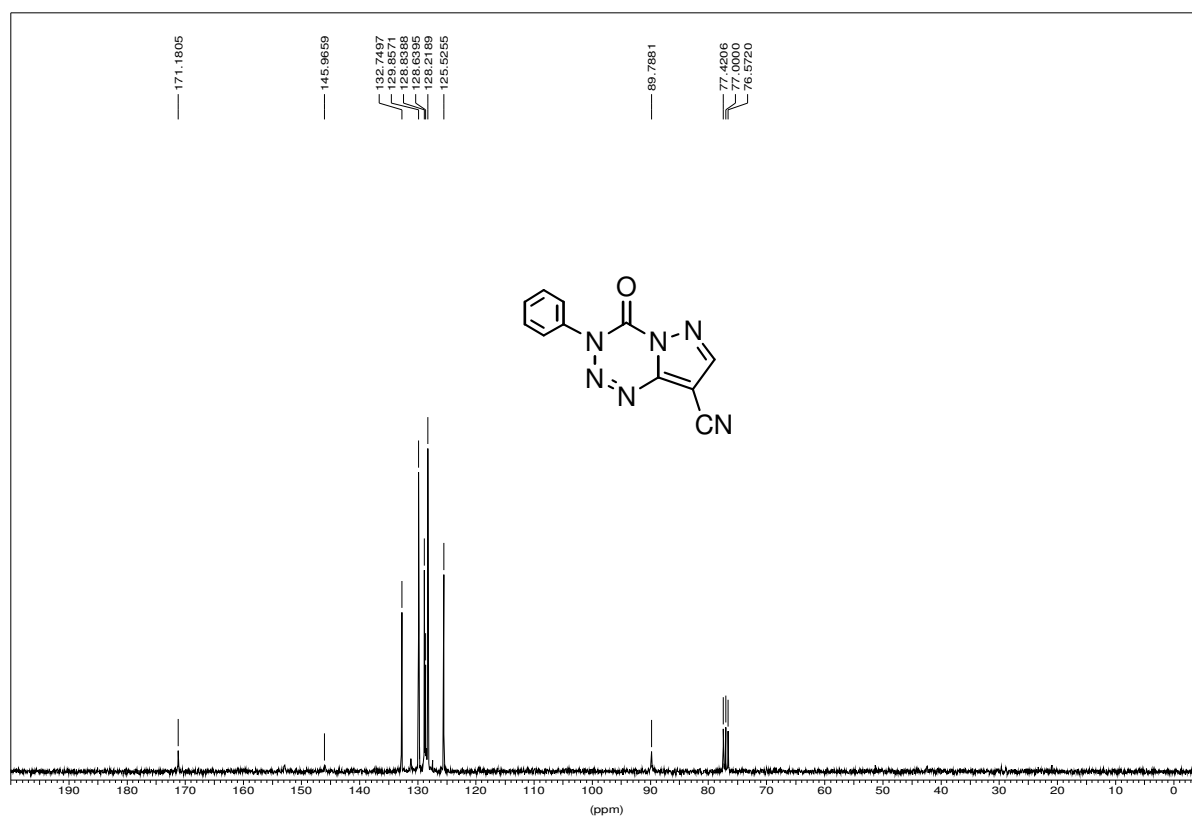
¹³C NMR Spectrum of 1d



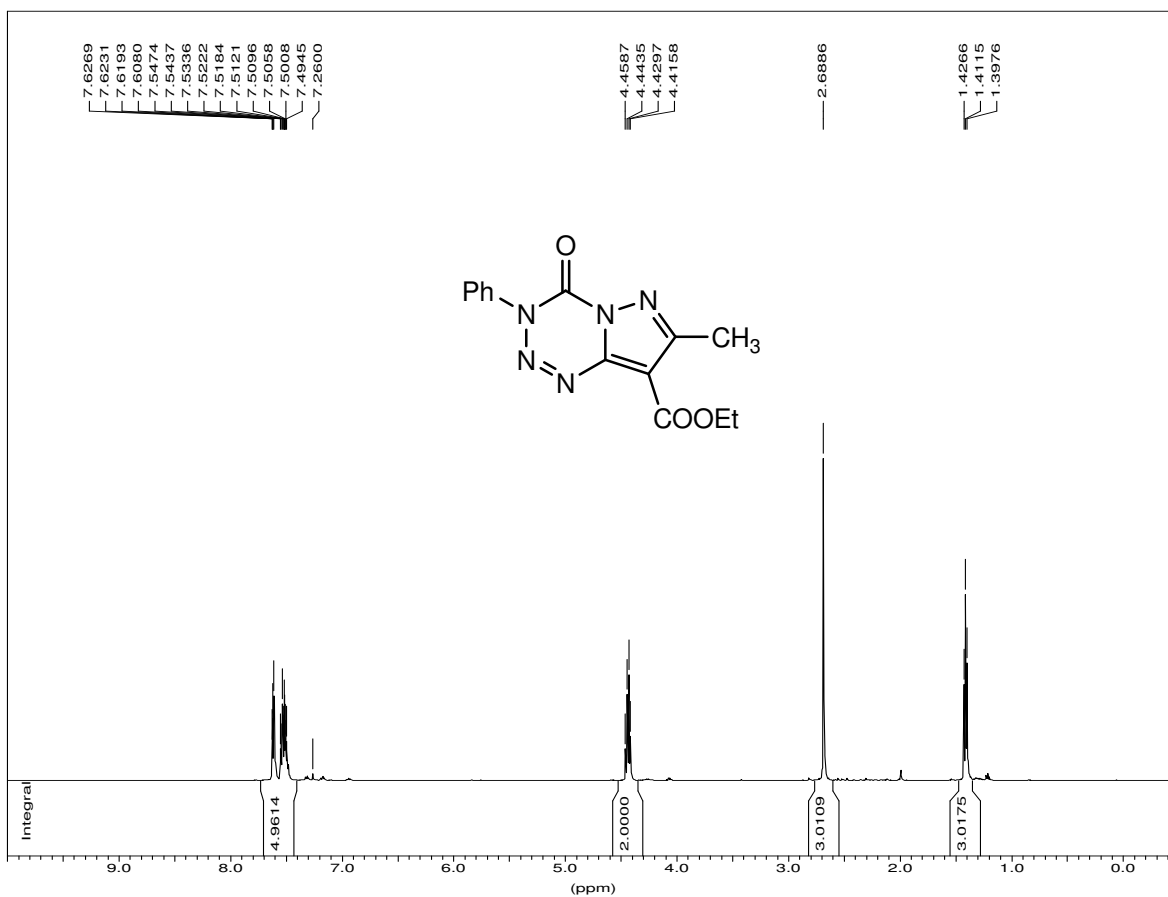
¹H NMR Spectrum of 1e



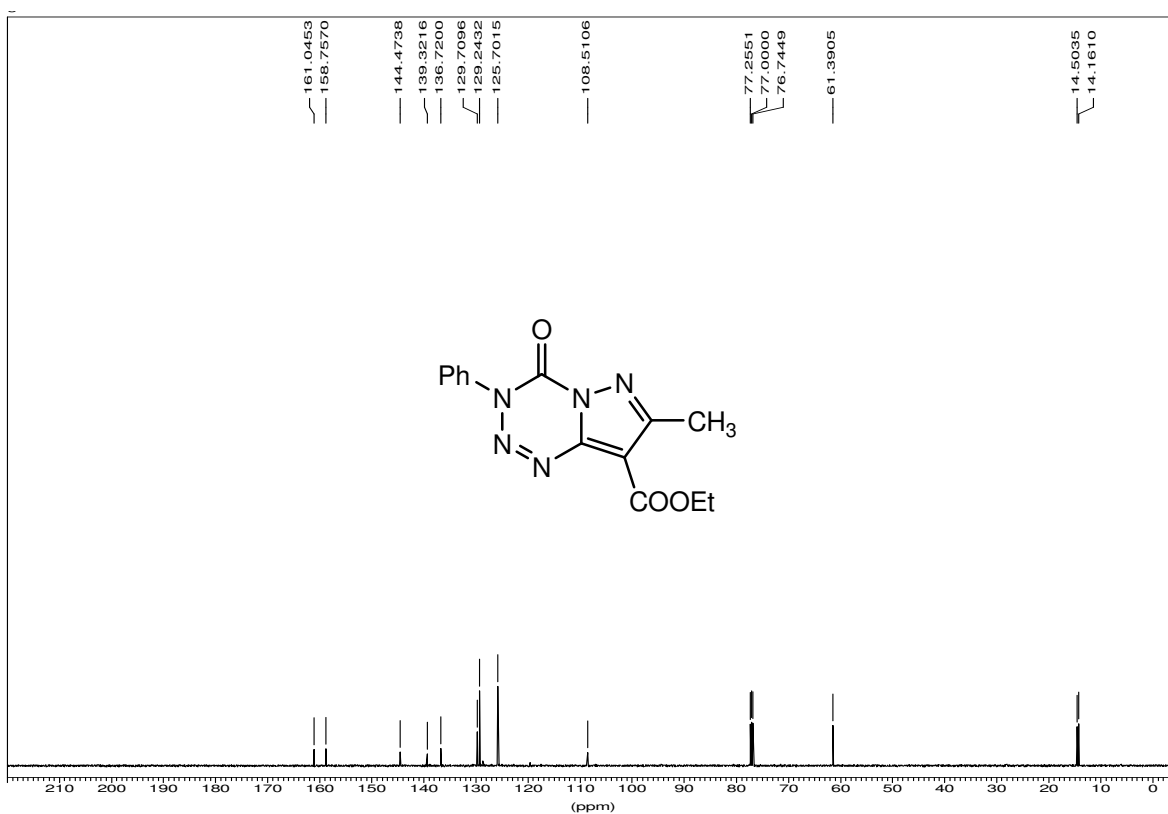
¹³C NMR Spectrum of 1e



¹H NMR Spectrum of 1f



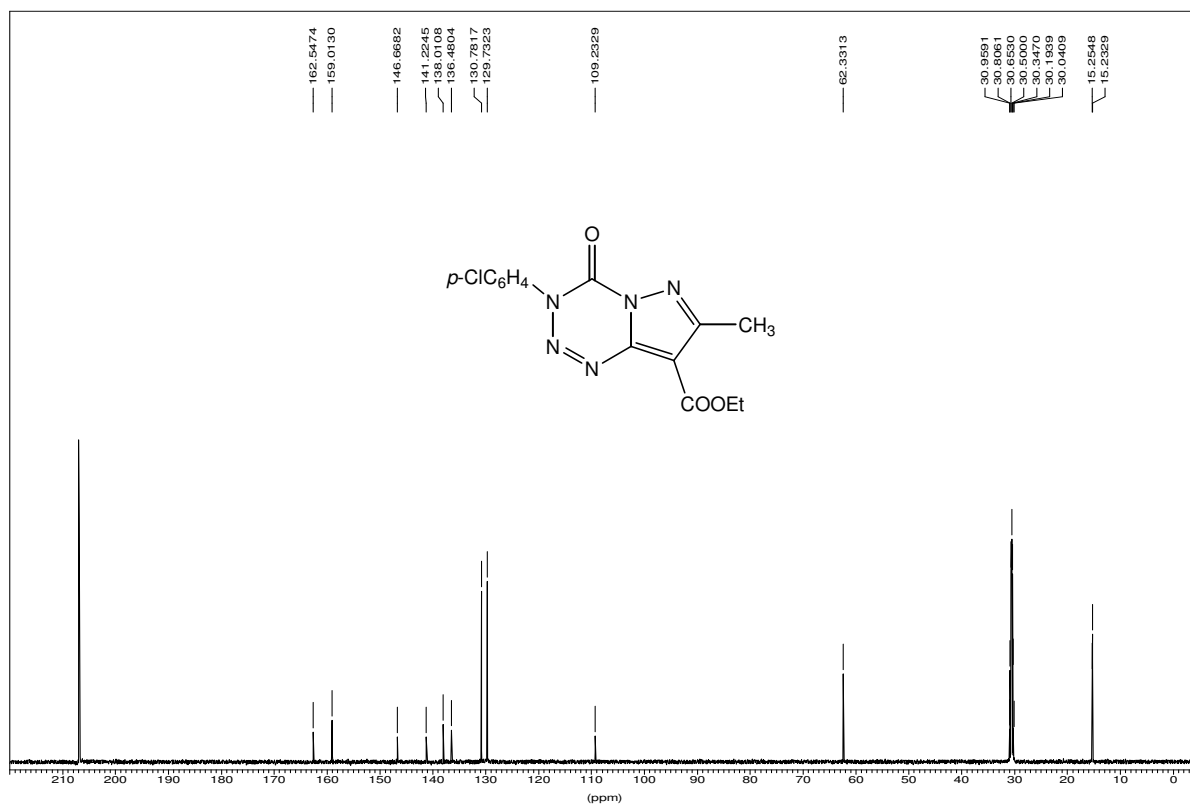
¹³C NMR Spectrum of 1f



¹H NMR Spectrum of 1g



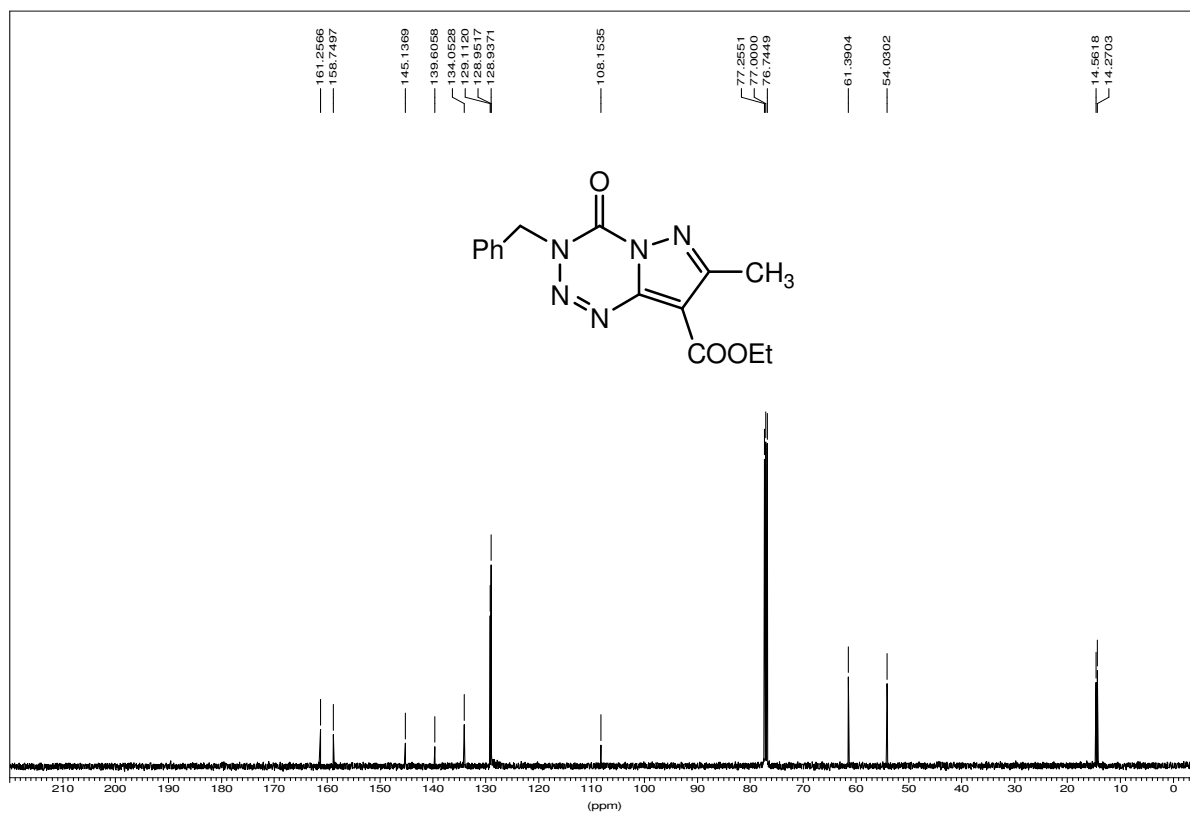
¹³C NMR Spectrum of 1g



¹H NMR Spectrum of 1h



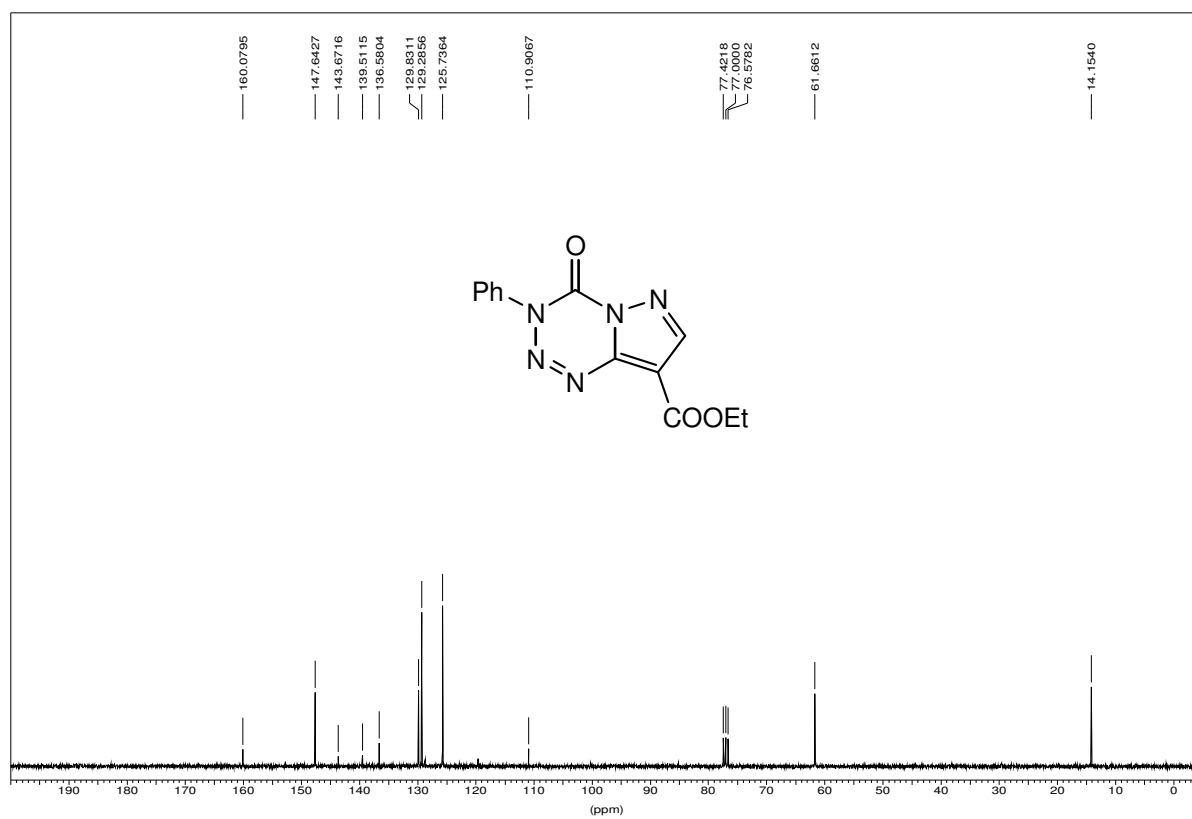
¹³C NMR Spectrum of 1h



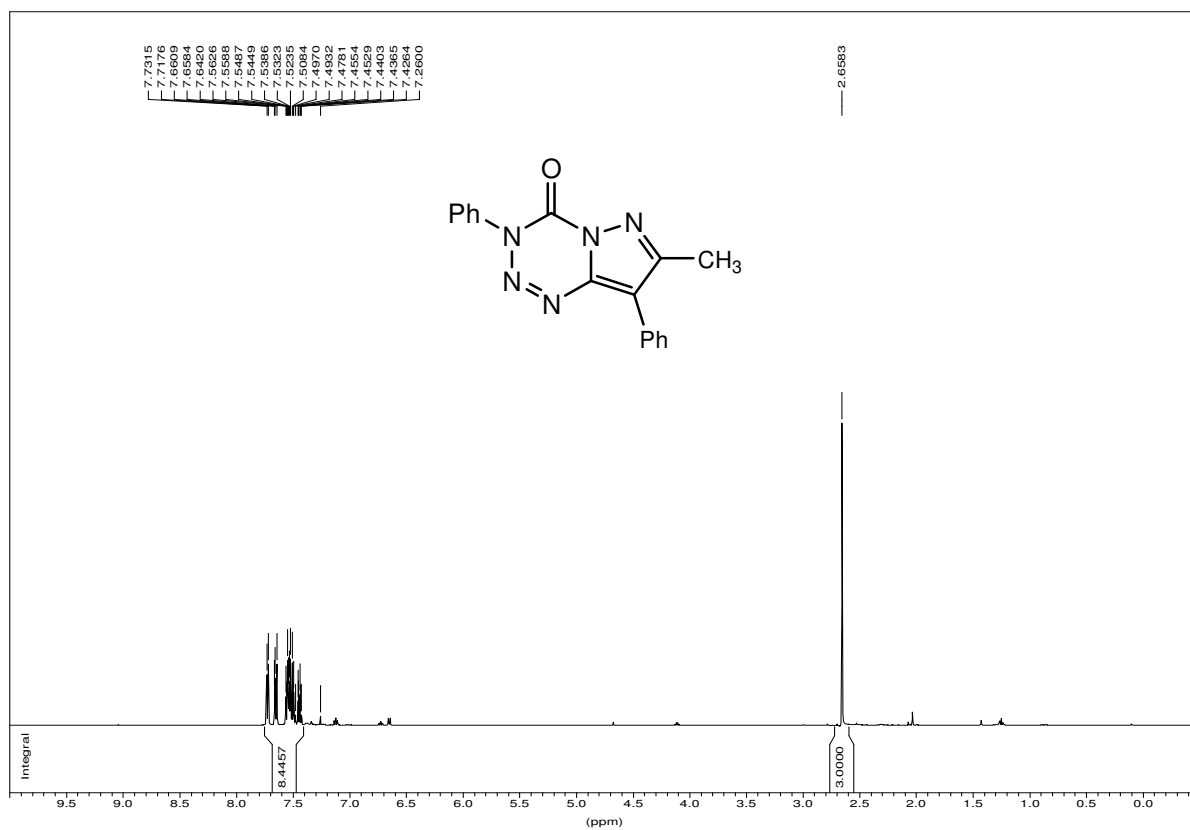
¹H NMR Spectrum of 1i



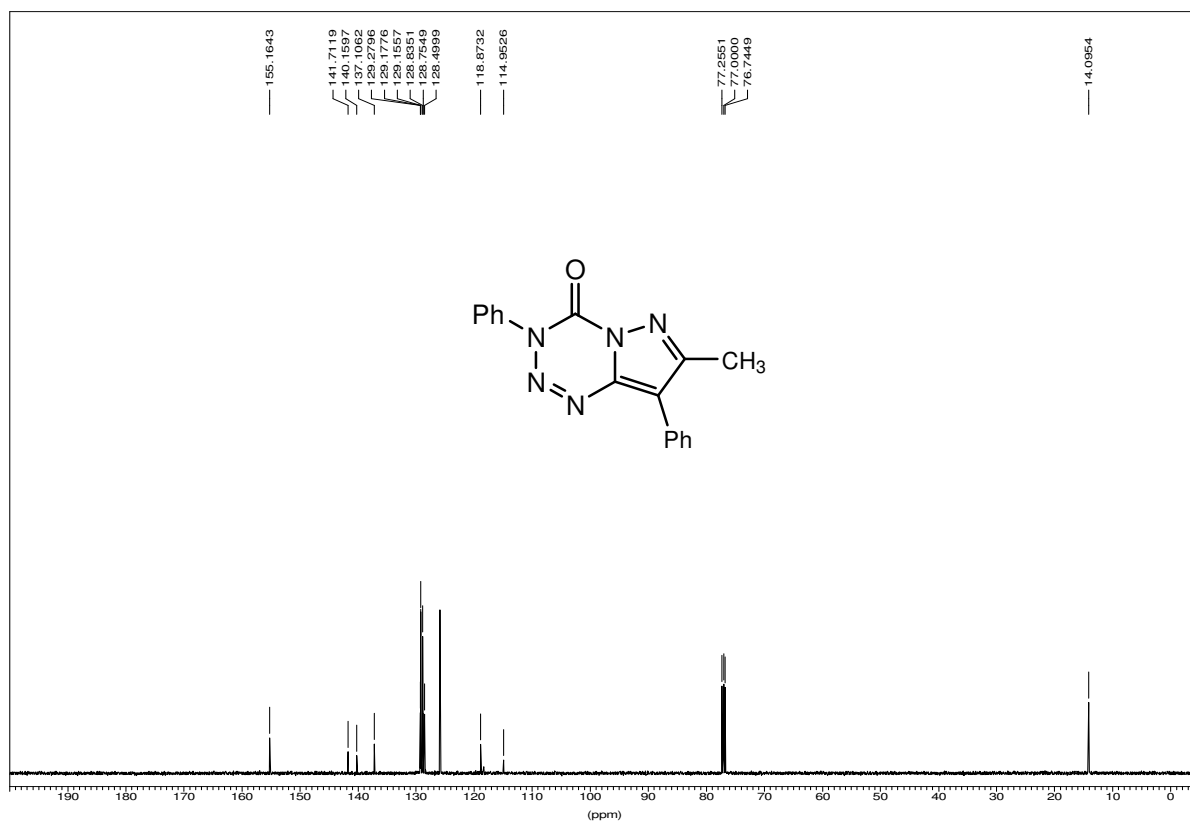
¹³C NMR Spectrum of 1i



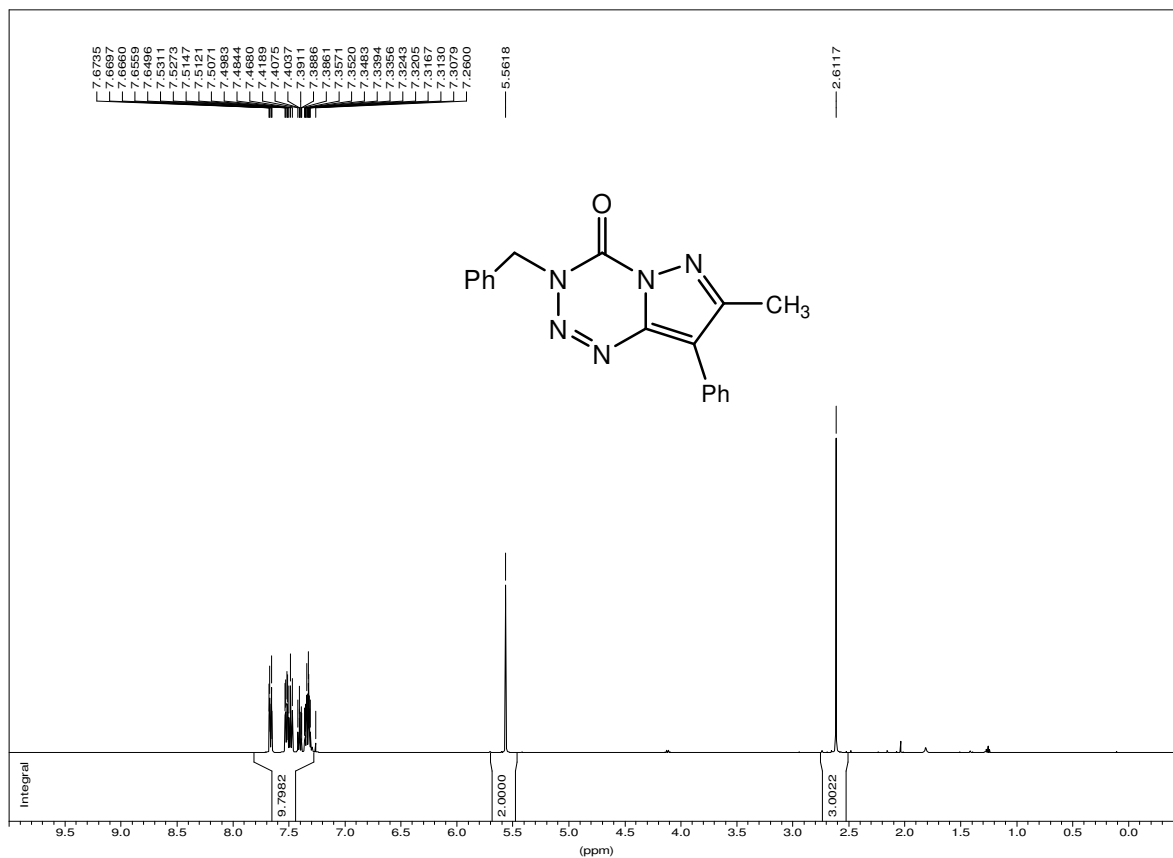
¹H NMR Spectrum of 1j



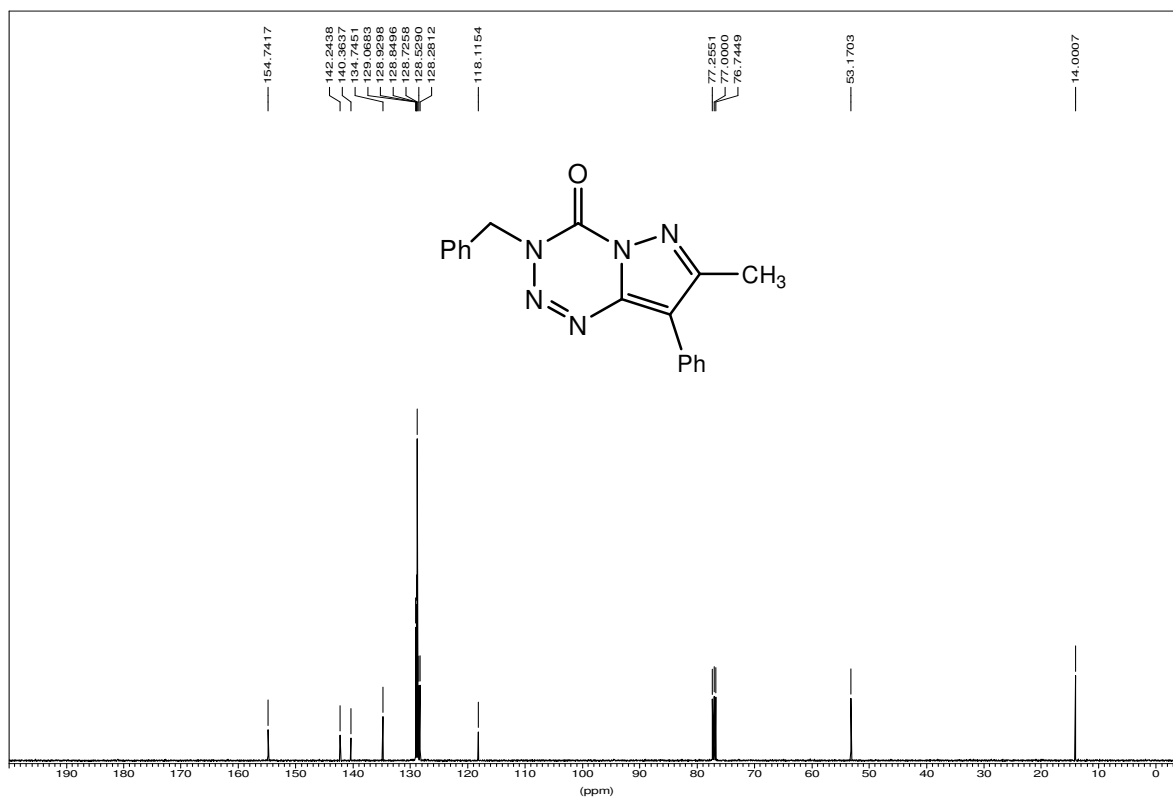
¹³C NMR Spectrum of 1j



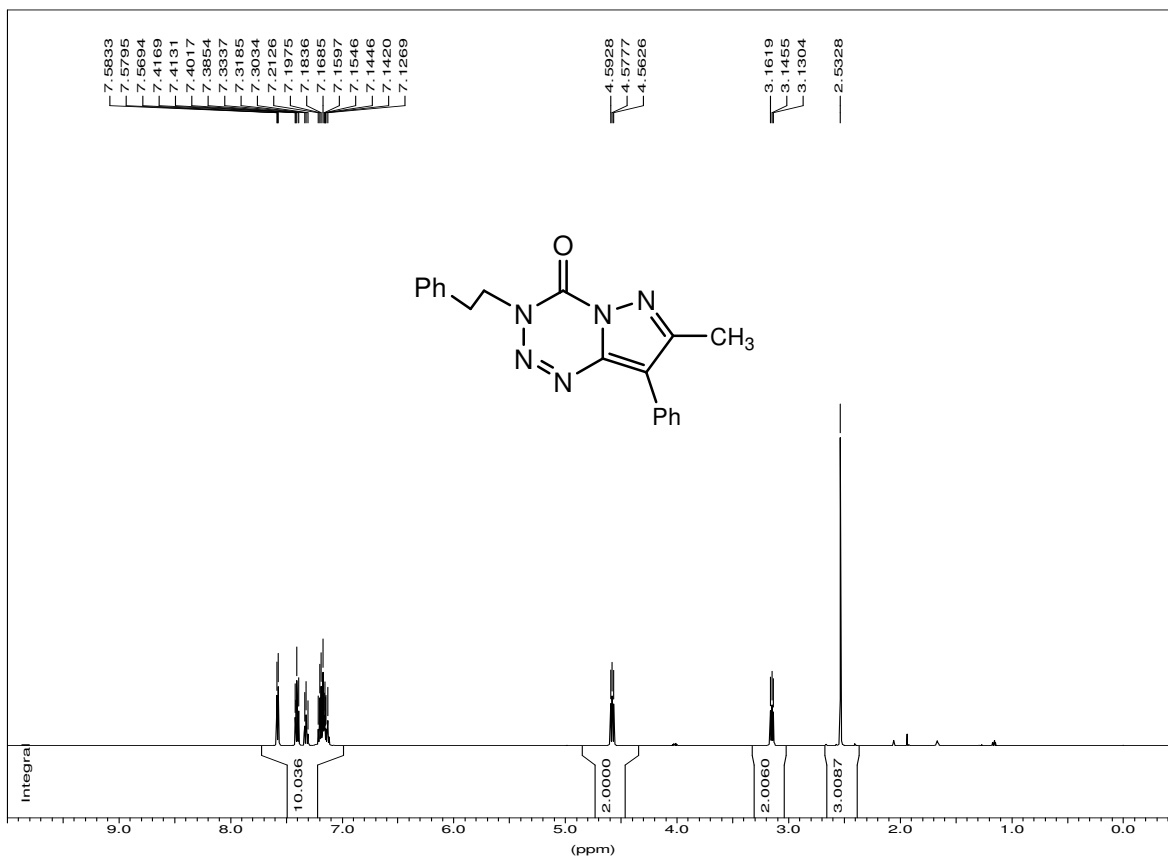
¹H NMR Spectrum of 1k



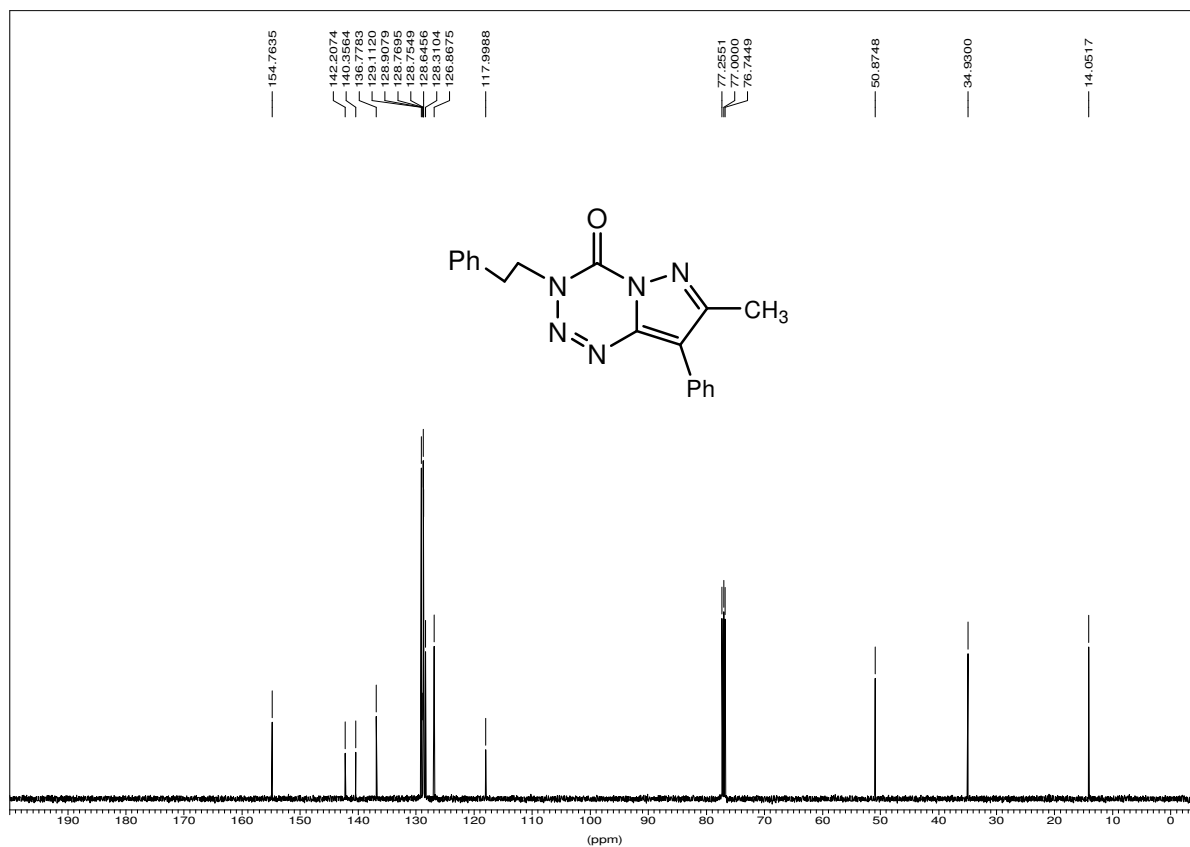
¹³C NMR Spectrum of 1k



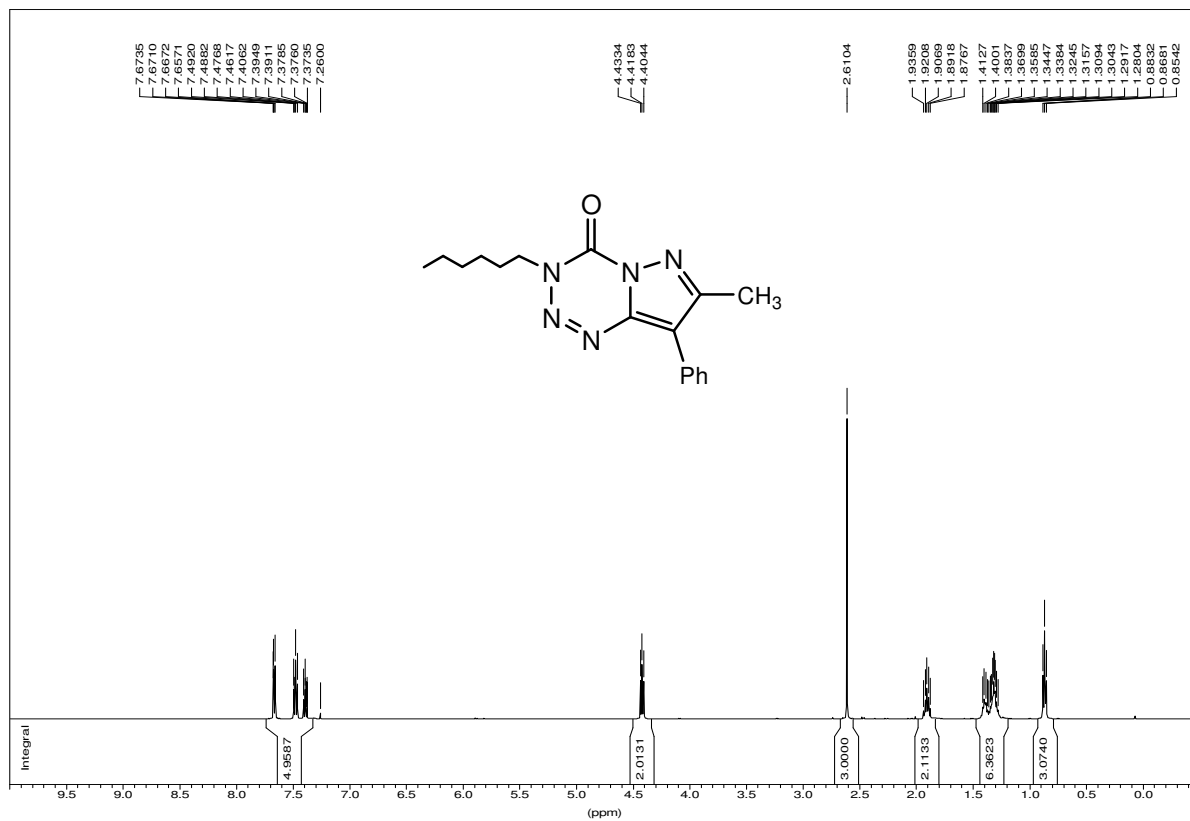
¹H NMR Spectrum of 11



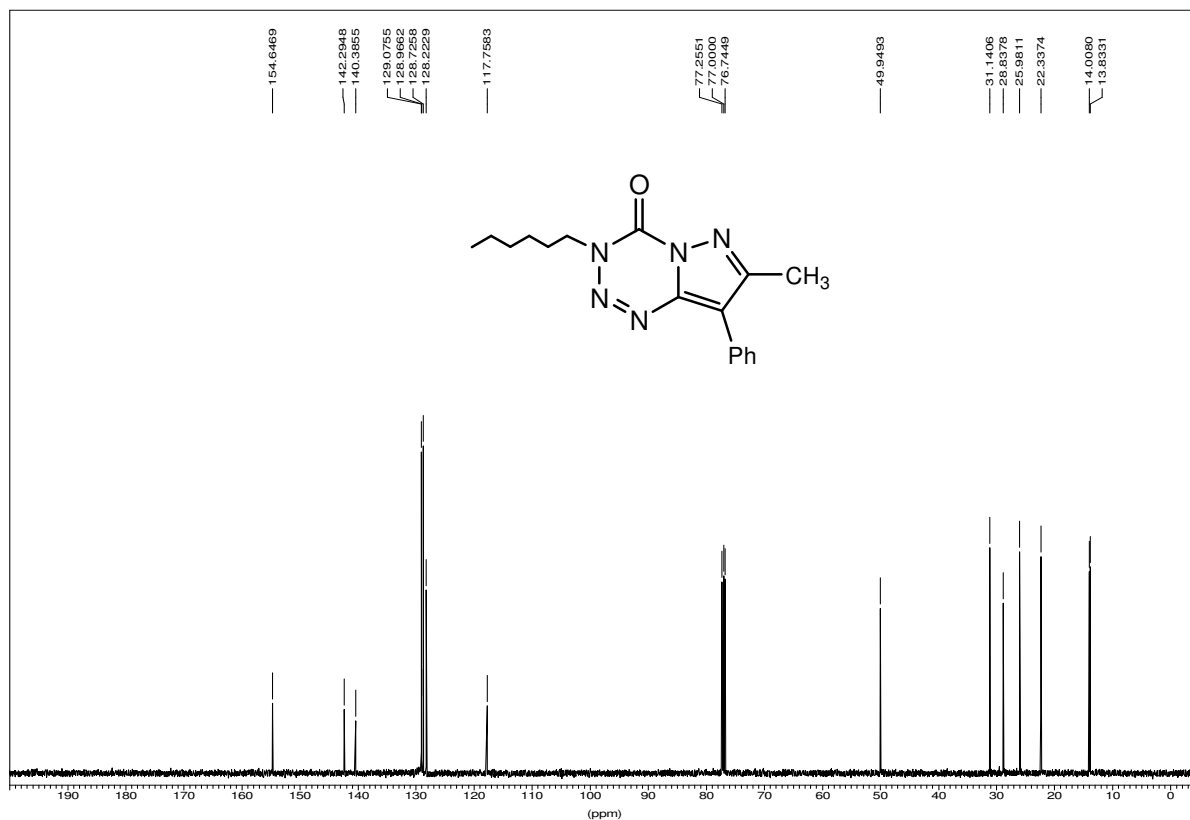
¹³C NMR Spectrum of 11



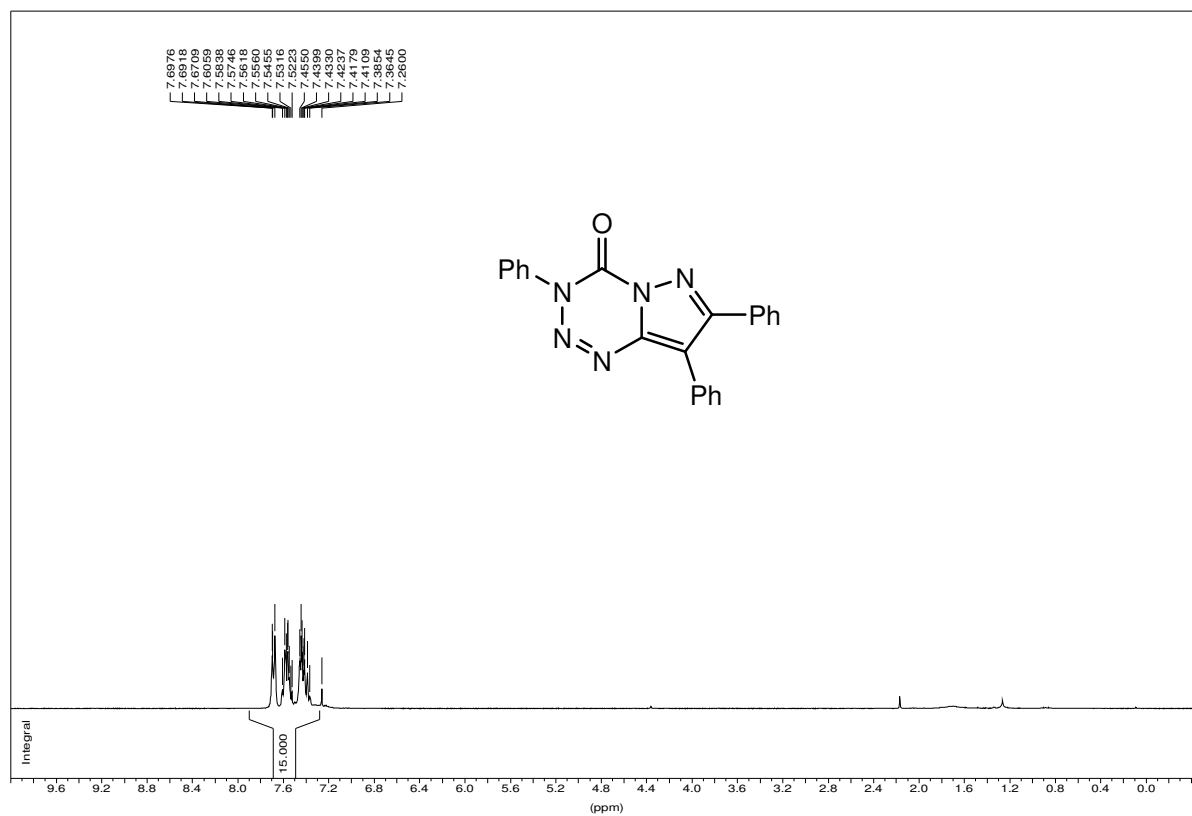
¹H NMR Spectrum of 1m



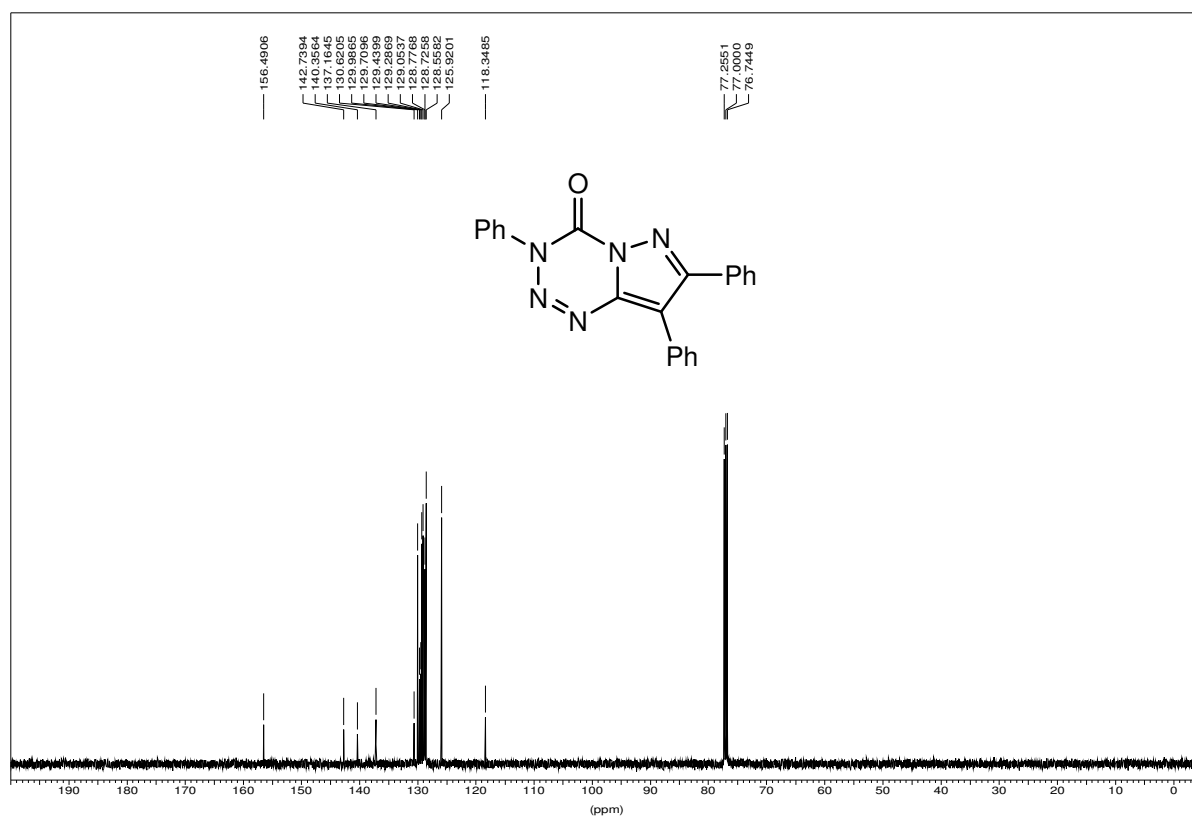
¹³C NMR Spectrum of 1m



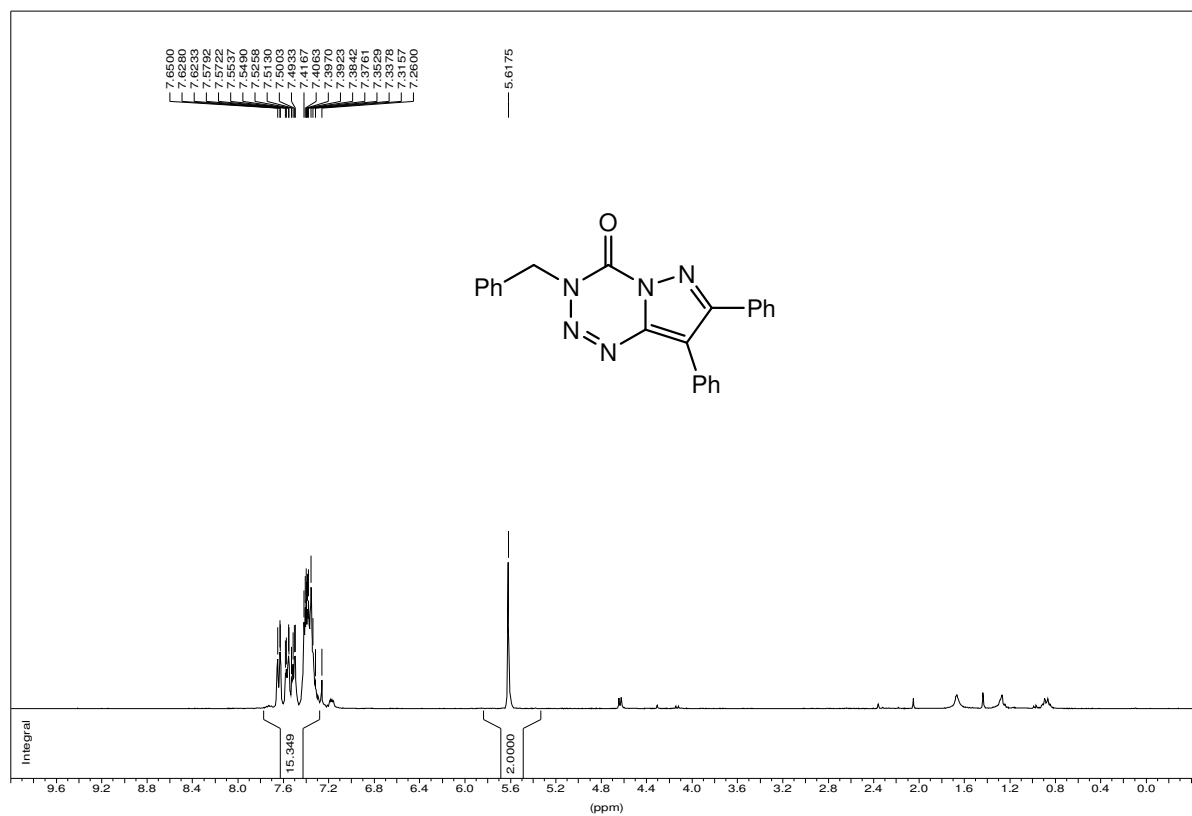
¹H NMR Spectrum of 1n



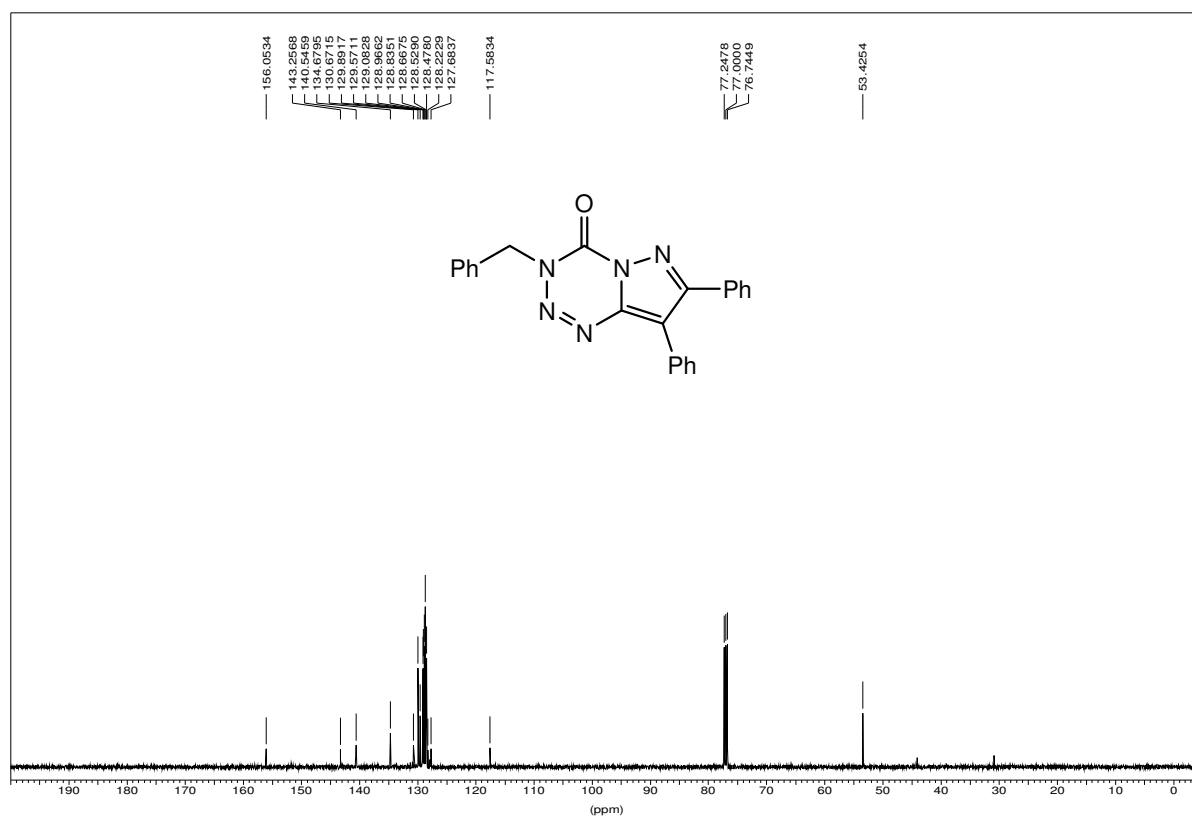
¹³C NMR Spectrum of 1n



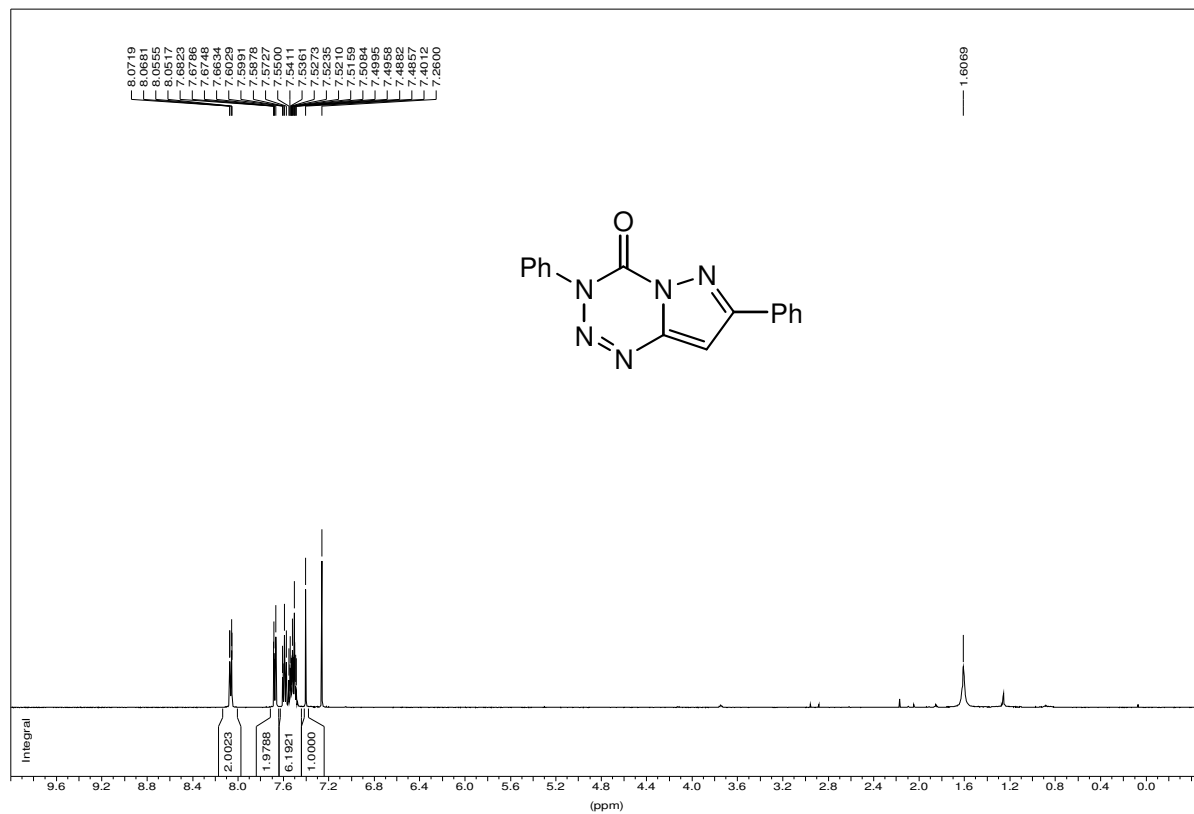
¹H NMR Spectrum of 1o



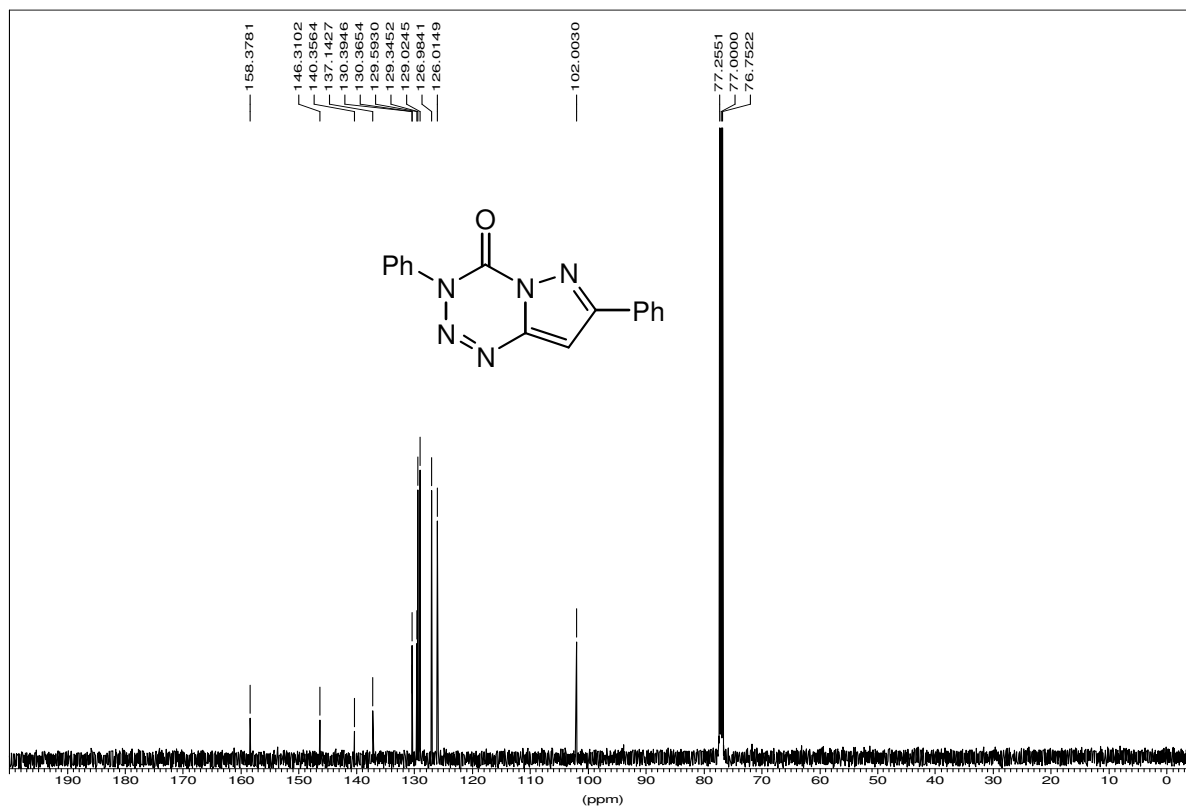
¹³C NMR Spectrum of 1o



¹H NMR Spectrum of 1p



¹³C NMR Spectrum of 1p



HPLC, MS and ¹H NMR Data of Unpurified Compound 2

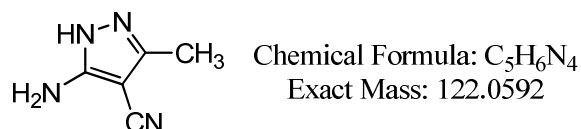
Analysis conditions:

The compounds were firstly dissolved in methanol, followed by LC-MS analysis

Column: Phenomenex C₁₈, 50 x 3 mm, 5micron

Buffer A: 0.1%TFA in Water; Buffer B: 0.1%TFA in ACN

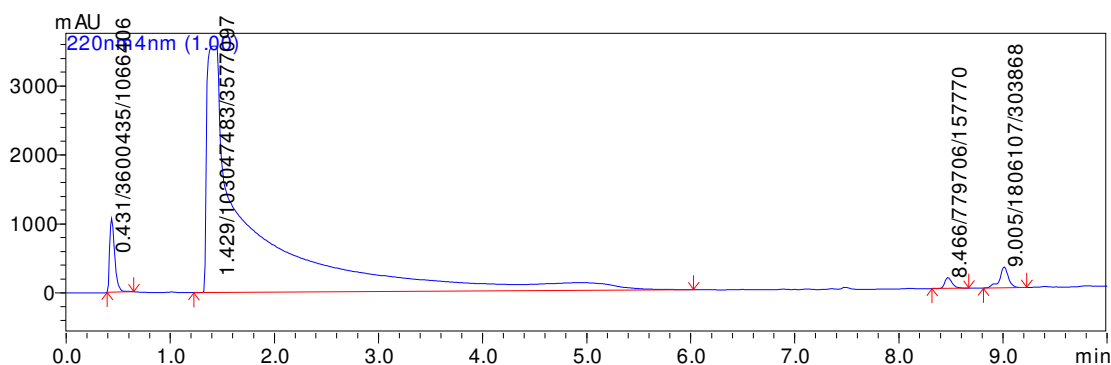
Running method: Gradient, Buffer B, 0%-100% from 1-7min, 100% from 7-10min, flow rate: 0.6ml/min



5-Amino-3-methyl-1H-pyrazole-4-carbonitrile, 2a

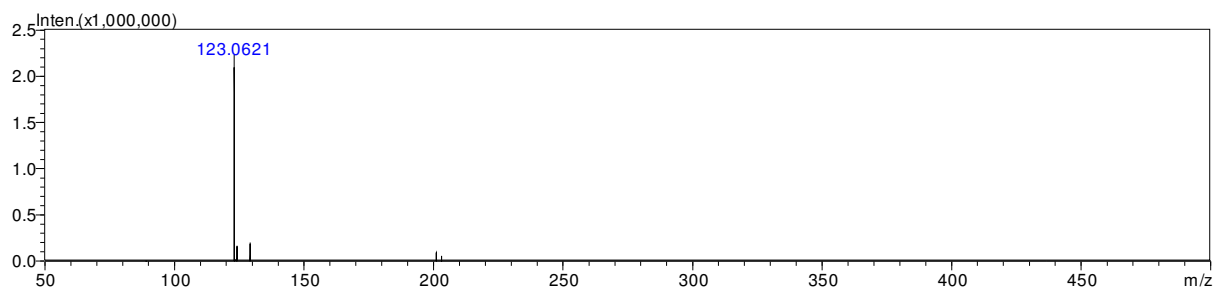
Crude overall yield (from Wang resin **8**) = 73%

LC data-220nm

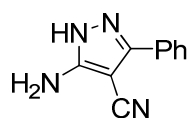
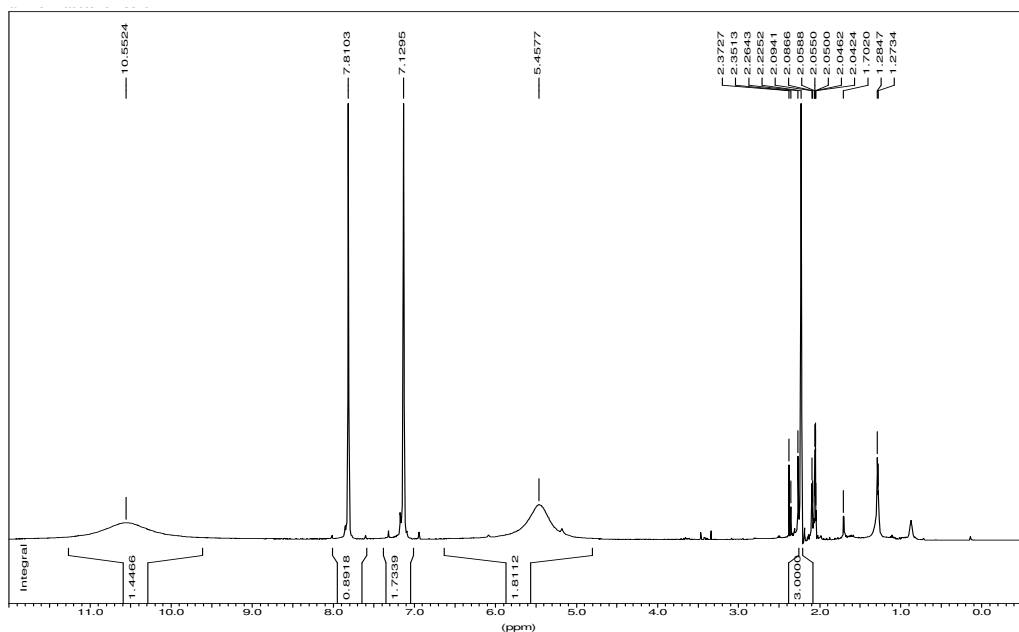


Peak	RT/min	Area	height	Area%	Height%
1	0.431	3600435	1066406		
2	1.429	103047483	3577097	94.33669	70.06853
3	8.466	779706	157770		
4	9.005	1806107	303868		
total		109233731	5105141		

MS-data, Positive



¹H NMR

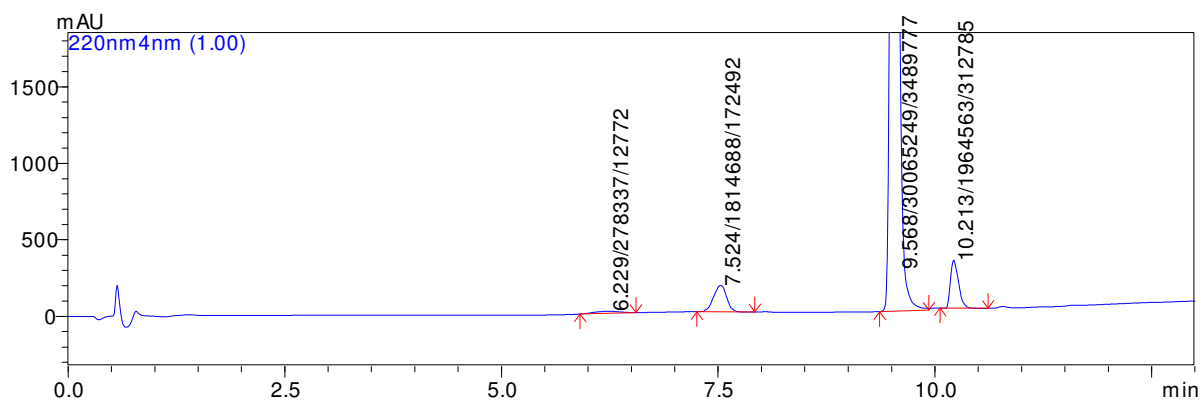


Chemical Formula: C₁₀H₈N₄
Exact Mass: 184.07

5-Amino-3-phenyl-1H-pyrazole-4-carbonitrile, 2d

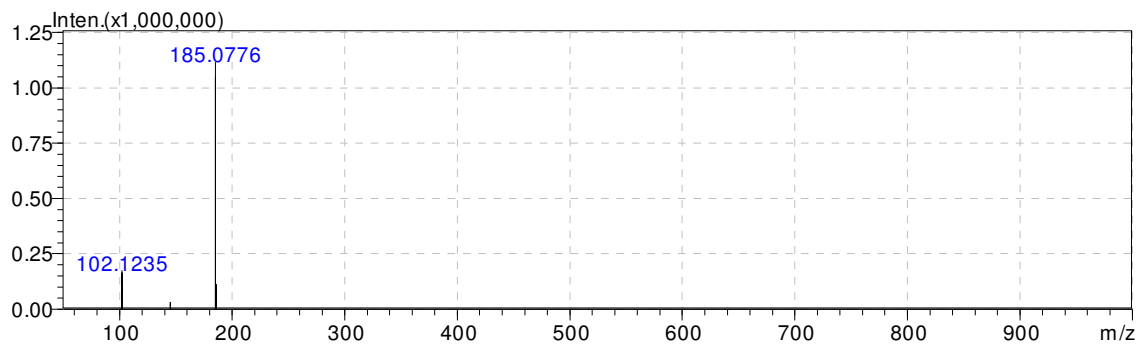
Crude overall yield (from Wang resin **8**) = 48%

LC data-220nm

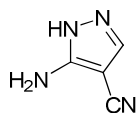
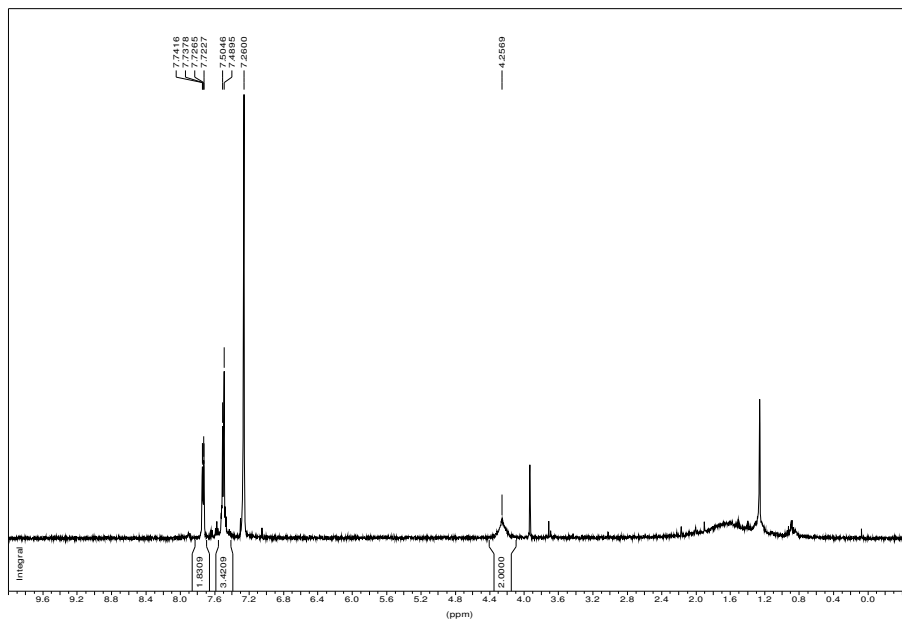


Peak	RT/min	Area	height	Area%	Height%
1	6.229	278337	12772		
2	7.524	1814688	172492		
3	9.568	30065249	3489777	92.92925	87.5112
4	10.213	194563	312765		
total		32352837	3987806		

MS-data, Positive



¹H NMR

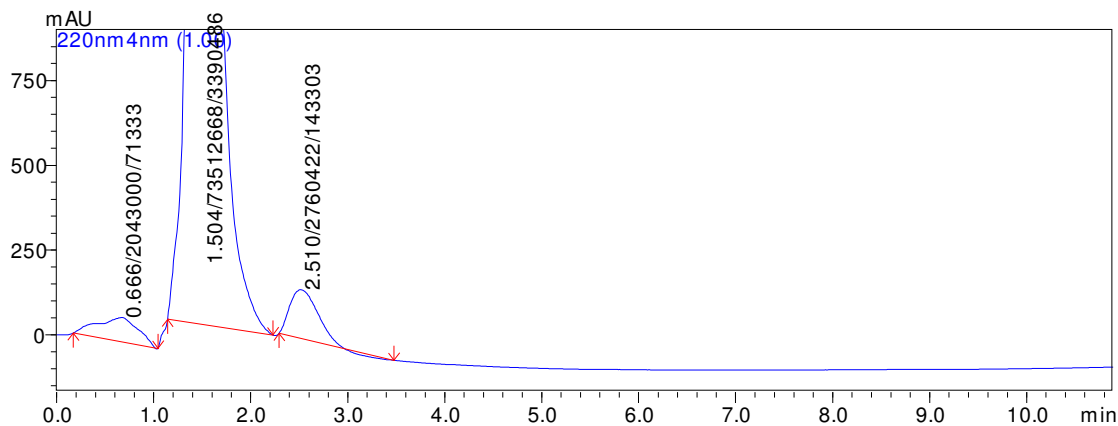


Chemical Formula: C₄H₄N₄
Exact Mass: 108.0436

5-Amino-1H-pyrazole-4-carbonitrile, 2e

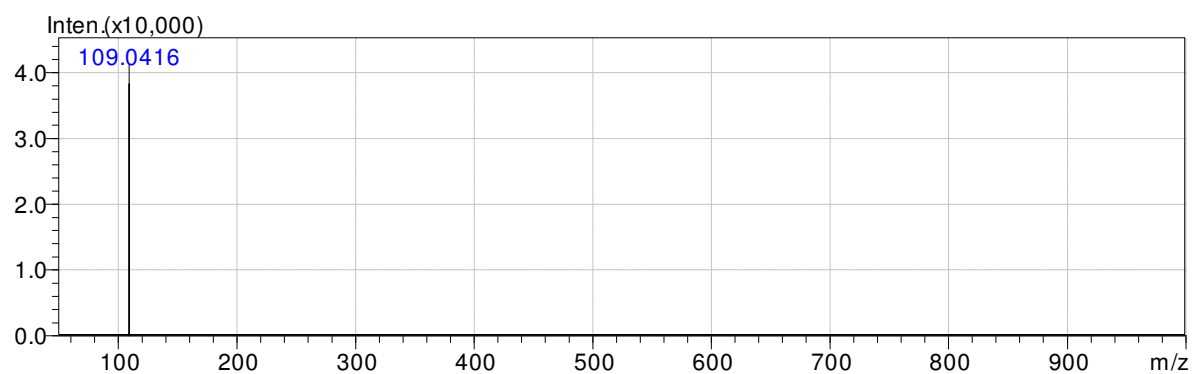
Crude overall yield (from Wang resin **8**) = 52%

LC data-220nm

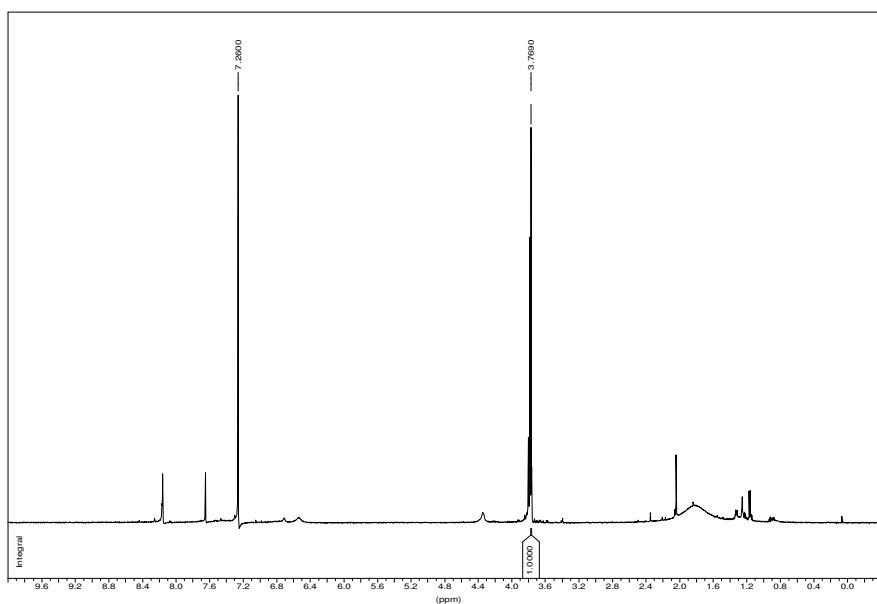


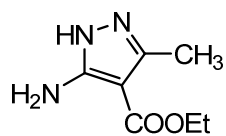
Peak	RT/min	Area	height	Area%	Height%
1	0.666	2043000	71333		
2	1.504	73512668	3390486	93.86662	94.04636
3	2.510	2760422	143303		
total		78316090	3605122		

MS-data, Positive



¹H NMR



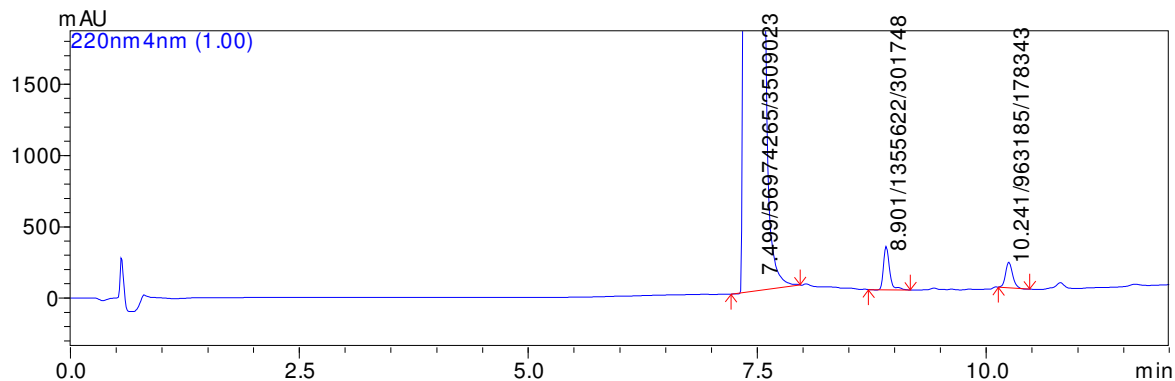


Chemical Formula: C₇H₁₁N₃O₂
Exact Mass: 169.0851

Ethyl 5-amino-3-methyl-1H-pyrazole-4-carboxylate, 2f

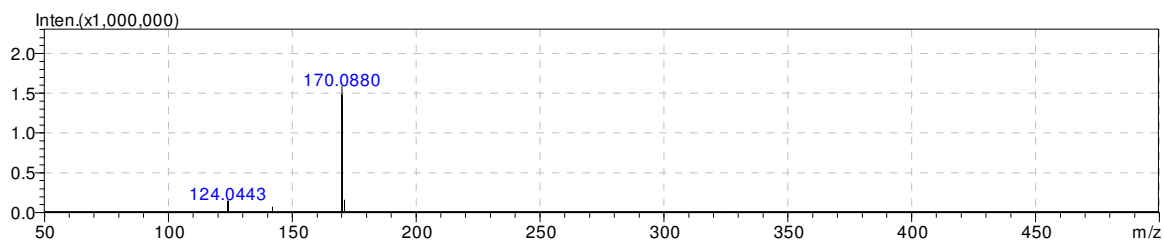
Crude overall yield (from Wang resin **8**) = 62%

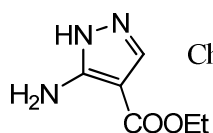
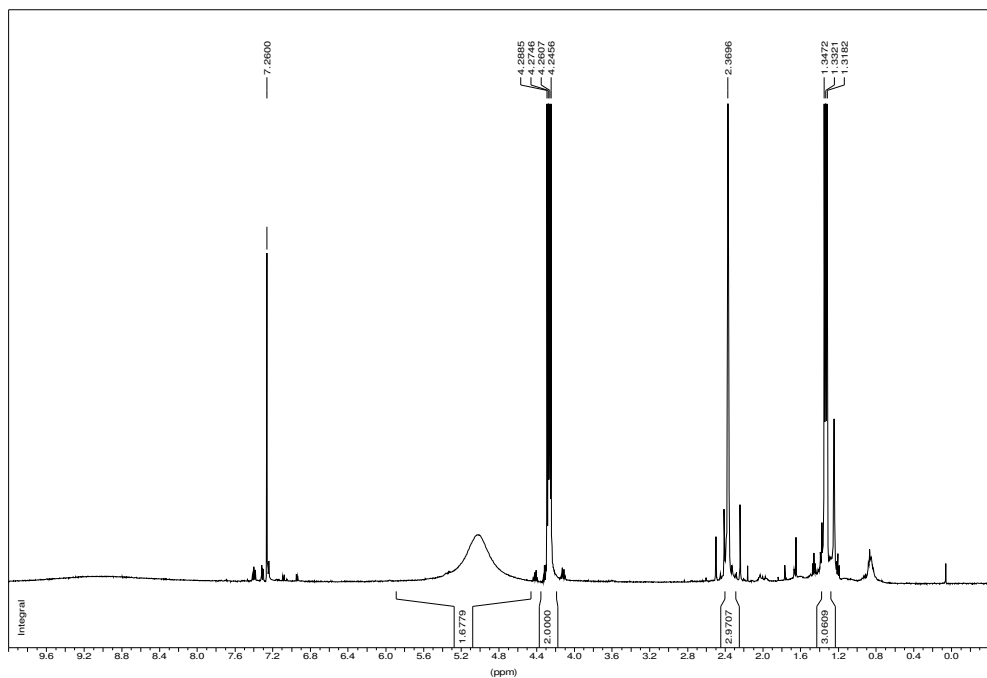
LC data-220nm



Peak	RT/min	Area	height	Area%	Height%
1	7.499	56974265	3509023	96.089245	87.964972
2	8.901	1355622	301748		
3	10.241	963185	178343		
total		59293072	3989114		

MS-data, Positive



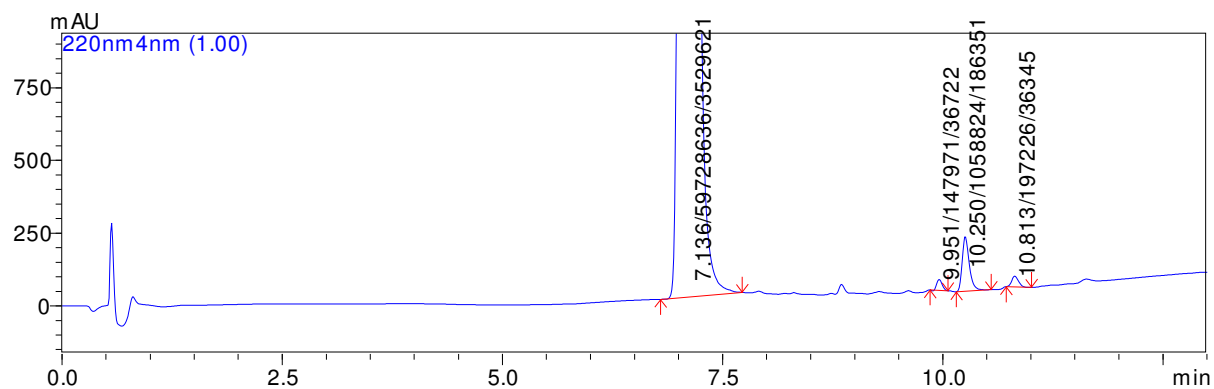


Chemical Formula: C₆H₉N₃O₂
Exact Mass: 155.0695

Ethyl 5-amino-1H-pyrazole-4-carboxylate, 2i

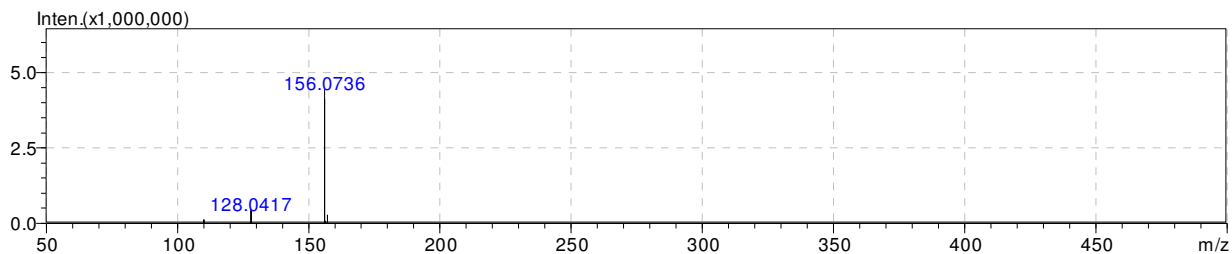
Crude overall yield (from Wang resin **8**) = 60%

LC data-220nm

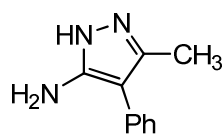
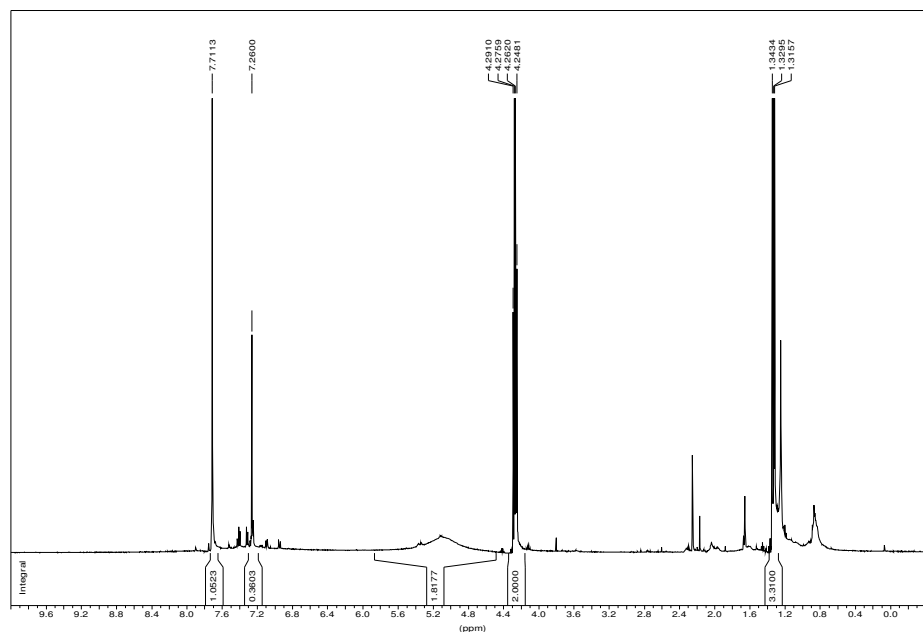


Peak	RT/min	Area	height	Area%	Height%
1	7.136	59728636	3529621	97.703321	93.15346
2	9.951	147971	36722		
3	10.250	1058824	186351		
4	10.813	197226	36345		
total		61132657	3789039		

MS-data, Positive



¹H NMR

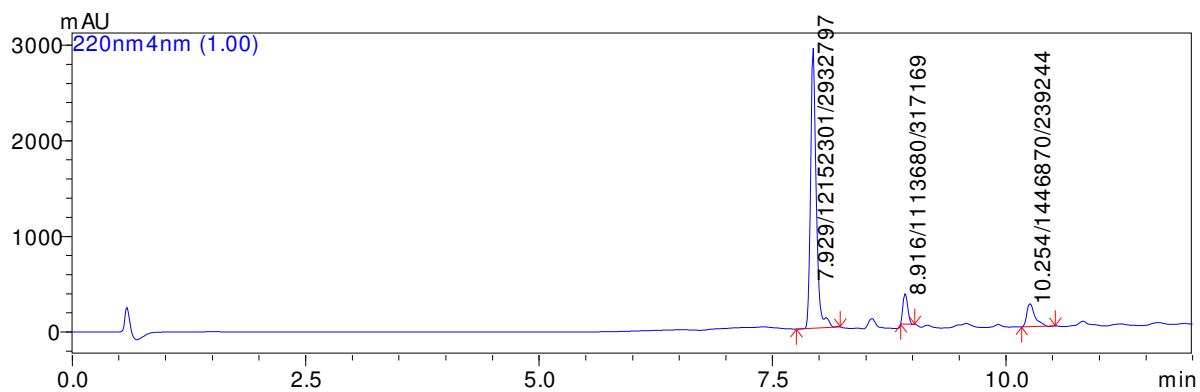


Chemical Formula: C₁₀H₁₁N₃
Exact Mass: 173.0953

3-Methyl-4-phenyl-1H-pyrazol-5-amine, **2j**

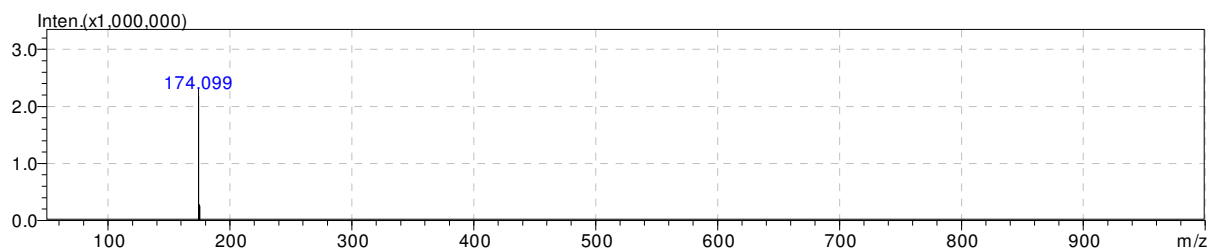
Crude overall yield (from Wang resin **8**) = 56%

LC data-220nm

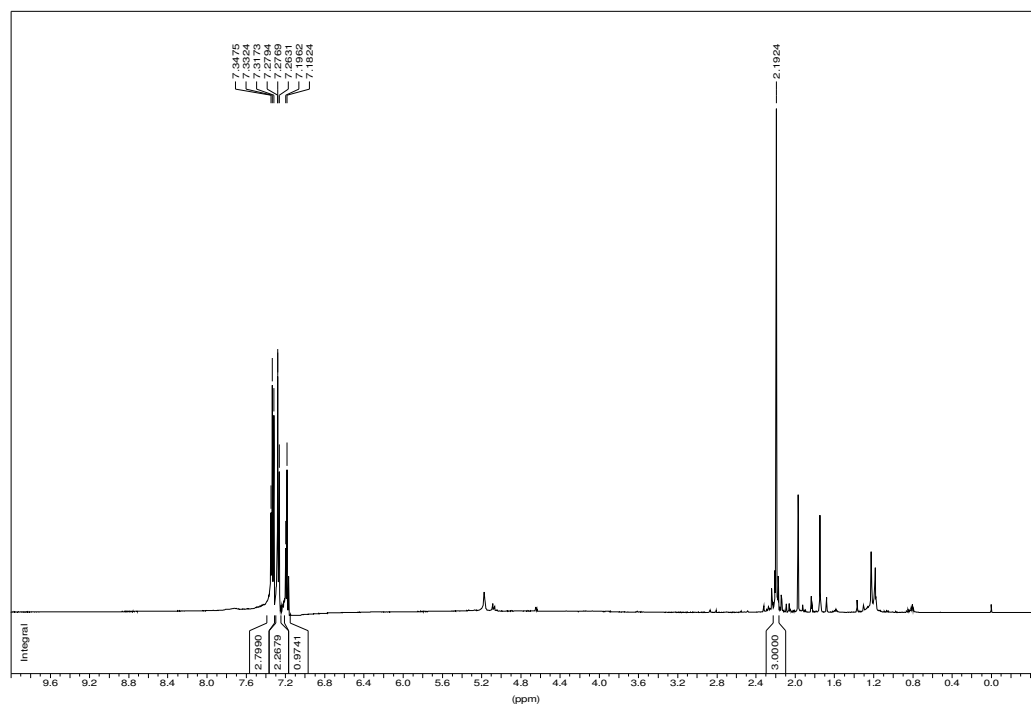


Peak	RT/min	Area	height	Area%	Height%
1	7.929	12152301	2932797	82.596507	84.053324
2	8.916	1113680	317169		
3	10.254	1446870	239244		
total		14712851	3489210		

MS-data, Positive



¹H NMR

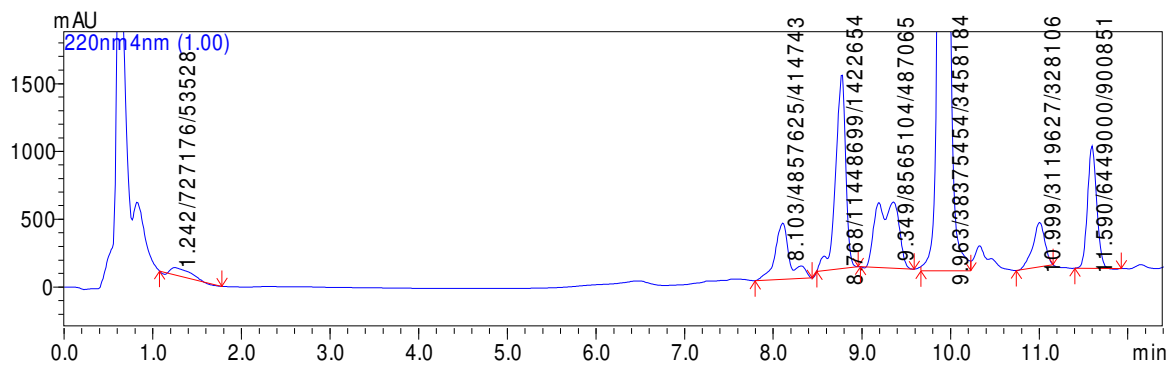




3,4-Diphenyl-1H-pyrazol-5-amine, 2n

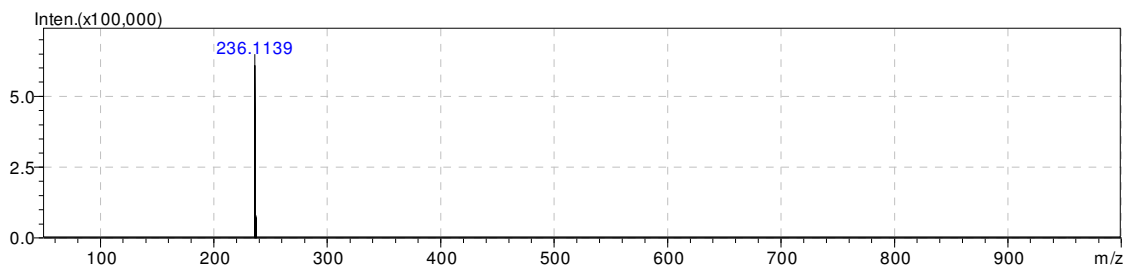
Crude overall yield (from Wang resin **8**) = 45%

LC data-220nm

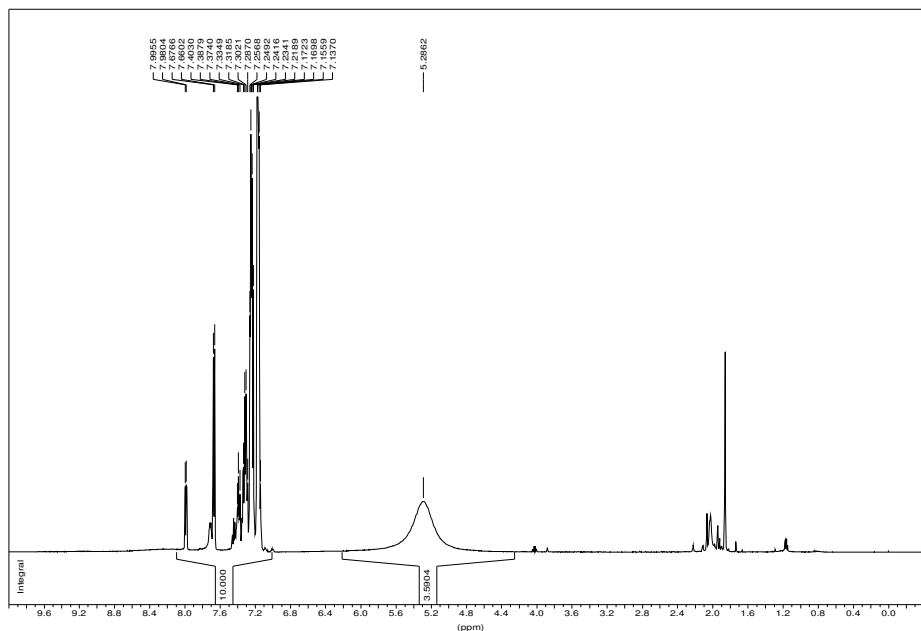


Peak	RT/min	Area	height	Area%	Height%
1	1.242	727176	53528		
2	8.103	4857625	414743		
3	8.768	1148699	1422654		
4	9.349	8565104	487065		
5	9.963	38375454	3458184	67.56993	51.33103
6	10.999	3119627	900851		
total		56793685	6737025		

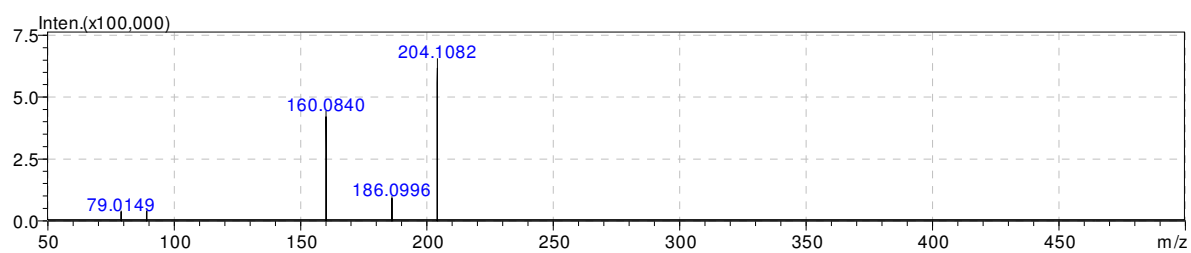
MS-data, Positive



¹H NMR



MS-data, Positive



¹H NMR

