SUPPORTING INFORMATION

Isocanthine Synthesis via Rh(III)-Catalyzed Intramolecular C─H Functionalization

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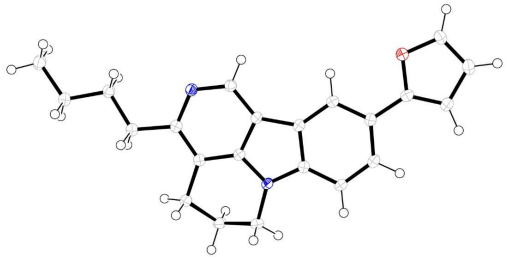
X-ray Crystal Structure data of 4b

A colorless plate 0.120 x 0.040 x 0.040 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 50 mm and exposure time was 10 seconds per frame using a scan width of 1.0°. Data collection was 100.0% complete to 25.000° in q. A total of 18904 reflections were collected covering the indices, -9<=*h*<=9, -10<=*k*<=10, -14<=*l*<=14. 3049 reflections were found to be symmetry independent, with an R_{int} of 0.0435. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be P -1 (No. 2). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.



ORTEP representation of **4b**: thermal elipsoids are shown at the 50% probability level

Table S1. Crystal data and structure refinement for gene334.

X-ray ID	gene334	
Sample/notebook ID	G02951040	
Empirical formula	C22 H22 N2 O	
Formula weight	330.41	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.9922(5) Å	α= 91.7530(10)°.
	b = 8.6781(5) Å	β= 97.9670(10)°.
	c = 12.2571(7) Å	γ = 98.9960(10)°.
Volume	830.37(9) $Å^3$	
Z	2	
Density (calculated)	1.322 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	352	
Crystal size	0.120 x 0.040 x 0.040 mm^3	
Theta range for data collection	1.680 to 25.352°.	
Index ranges	-9<=h<=9, -10<=k<=10, -14<=l<=14	
Reflections collected	18904	
Independent reflections	3049 [R(int) = 0.0435]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.928 and 0.850	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3049 / 0 / 227	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.0969	
R indices (all data)	R1 = 0.0542, wR2 = 0.1094	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.194 and -0.314 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for gene334. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3849(2)	5339(2)	6604(1)	18(1)
C(2)	4689(2)	6374(2)	5935(1)	16(1)
C(3)	4281(2)	7217(2)	4949(1)	16(1)
C(4)	2789(2)	7322(2)	4244(1)	17(1)
C(5)	2858(2)	8293(2)	3359(1)	17(1)
C(6)	4433(2)	9165(2)	3195(1)	19(1)
C(7)	5939(2)	9063(2)	3869(1)	18(1)
C(8)	5855(2)	8072(2)	4739(1)	16(1)
C(9)	8997(2)	8299(2)	5634(1)	20(1)
C(10)	9929(2)	7107(2)	6252(1)	20(1)
C(11)	9279(2)	6684(2)	7347(1)	20(1)
C(12)	7360(2)	6201(2)	7153(1)	17(1)
C(13)	6371(2)	5224(2)	7782(1)	17(1)
C(14)	6465(2)	6759(2)	6242(1)	16(1)
C(15)	1332(2)	8403(2)	2583(1)	18(1)
C(16)	1018(2)	9226(2)	1679(1)	24(1)
C(17)	-757(2)	8805(2)	1261(1)	26(1)
C(18)	-1427(2)	7760(2)	1937(1)	24(1)
C(19)	7206(2)	4653(2)	8839(1)	20(1)
C(20)	6116(2)	3424(2)	9415(1)	19(1)
C(21)	7091(2)	3051(2)	10504(1)	22(1)
C(22)	6071(2)	1838(2)	11128(1)	26(1)
N(1)	4652(2)	4795(1)	7505(1)	18(1)
N(2)	7165(2)	7753(1)	5515(1)	17(1)
O(1)	-170(1)	7491(1)	2761(1)	22(1)

Table S3. Bond lengths [Å] and angles [°] for gene334.

C(1)-N(1)	1.3361(19)	C(12)-C(14)	1.383(2)
C(1)-C(2)	1.392(2)	C(12)-C(13)	1.391(2)
C(1)-H(1)	0.9500	C(13)-N(1)	1.358(2)
C(2)-C(14)	1.401(2)	C(13)-C(19)	1.508(2)
C(2)-C(3)	1.457(2)	C(14)-N(2)	1.3733(19)
C(3)-C(4)	1.389(2)	C(15)-C(16)	1.352(2)
C(3)-C(8)	1.417(2)	C(15)-O(1)	1.3789(18)
C(4)-C(5)	1.396(2)	C(16)-C(17)	1.426(2)
C(4)-H(4)	0.9500	C(16)-H(16)	0.9500
C(5)-C(6)	1.406(2)	C(17)-C(18)	1.346(2)
C(5)-C(15)	1.457(2)	C(17)-H(17)	0.9500
C(6)-C(7)	1.378(2)	C(18)-O(1)	1.3745(19)
C(6)-H(6)	0.9500	C(18)-H(18)	0.9500
C(7)-C(8)	1.393(2)	C(19)-C(20)	1.523(2)
C(7)-H(7)	0.9500	C(19)-H(19A)	0.9900
C(8)-N(2)	1.3812(19)	C(19)-H(19B)	0.9900
C(9)-N(2)	1.4524(19)	C(20)-C(21)	1.520(2)
C(9)-C(10)	1.527(2)	C(20)-H(20A)	0.9900
C(9)-H(9A)	0.9900	C(20)-H(20B)	0.9900
C(9)-H(9B)	0.9900	C(21)-C(22)	1.520(2)
C(10)-C(11)	1.539(2)	C(21)-H(21A)	0.9900
C(10)-H(10A)	0.9900	C(21)-H(21B)	0.9900
C(10)-H(10B)	0.9900	C(22)-H(22A)	0.9800
C(11)-C(12)	1.509(2)	C(22)-H(22B)	0.9800
C(11)-H(11A)	0.9900	C(22)-H(22C)	0.9800
C(11)-H(11B)	0.9900		

N(1)-C(1)-C(2)	122.95(14)	C(4)-C(3)-C(8)	119.27(13)
N(1)-C(1)-H(1)	118.5	C(4)-C(3)-C(2)	134.75(14)
C(2)-C(1)-H(1)	118.5	C(8)-C(3)-C(2)	105.99(13)
C(1)-C(2)-C(14)	115.31(13)	C(3)-C(4)-C(5)	119.57(14)
C(1)-C(2)-C(3)	138.76(14)	C(3)-C(4)-H(4)	120.2
C(14)-C(2)-C(3)	105.93(13)	C(5)-C(4)-H(4)	120.2

C(4)-C(5)-C(6)	119.70(14)	C(12)-C(13)-C(19)	119.57(14)
C(4)-C(5)-C(15)	121.30(14)	N(2)-C(14)-C(12)	125.71(14)
C(6)-C(5)-C(15)	118.99(13)	N(2)-C(14)-C(2)	110.41(13)
C(7)-C(6)-C(5)	122.01(14)	C(12)-C(14)-C(2)	123.88(14)
C(7)-C(6)-H(6)	119.0	C(16)-C(15)-O(1)	109.18(14)
C(5)-C(6)-H(6)	119.0	C(16)-C(15)-C(5)	134.10(15)
C(6)-C(7)-C(8)	117.65(14)	O(1)-C(15)-C(5)	116.71(13)
C(6)-C(7)-H(7)	121.2	C(15)-C(16)-C(17)	107.14(15)
C(8)-C(7)-H(7)	121.2	C(15)-C(16)-H(16)	126.4
N(2)-C(8)-C(7)	128.88(14)	C(17)-C(16)-H(16)	126.4
N(2)-C(8)-C(3)	109.37(13)	C(18)-C(17)-C(16)	106.79(15)
C(7)-C(8)-C(3)	121.75(14)	C(18)-C(17)-H(17)	126.6
N(2)-C(9)-C(10)	108.87(12)	C(16)-C(17)-H(17)	126.6
N(2)-C(9)-H(9A)	109.9	C(17)-C(18)-O(1)	109.83(14)
C(10)-C(9)-H(9A)	109.9	C(17)-C(18)-H(18)	125.1
N(2)-C(9)-H(9B)	109.9	O(1)-C(18)-H(18)	125.1
C(10)-C(9)-H(9B)	109.9	C(13)-C(19)-C(20)	117.20(13)
H(9A)-C(9)-H(9B)	108.3	C(13)-C(19)-H(19A)	108.0
C(9)-C(10)-C(11)	113.45(12)	C(20)-C(19)-H(19A)	108.0
C(9)-C(10)-H(10A)	108.9	C(13)-C(19)-H(19B)	108.0
C(11)-C(10)-H(10A)	108.9	C(20)-C(19)-H(19B)	108.0
C(9)-C(10)-H(10B)	108.9	H(19A)-C(19)-H(19B)	107.2
C(11)-C(10)-H(10B)	108.9	C(21)-C(20)-C(19)	110.99(13)
H(10A)-C(10)-H(10B)	107.7	C(21)-C(20)-H(20A)	109.4
C(12)-C(11)-C(10)	109.98(12)	C(19)-C(20)-H(20A)	109.4
C(12)-C(11)-H(11A)	109.7	C(21)-C(20)-H(20B)	109.4
C(10)-C(11)-H(11A)	109.7	C(19)-C(20)-H(20B)	109.4
C(12)-C(11)-H(11B)	109.7	H(20A)-C(20)-H(20B)	108.0
C(10)-C(11)-H(11B)	109.7	C(20)-C(21)-C(22)	113.81(13)
H(11A)-C(11)-H(11B)	108.2	C(20)-C(21)-H(21A)	108.8
C(14)-C(12)-C(13)	115.48(14)	C(22)-C(21)-H(21A)	108.8
C(14)-C(12)-C(11)	117.26(13)	C(20)-C(21)-H(21B)	108.8
C(13)-C(12)-C(11)	127.25(14)	C(22)-C(21)-H(21B)	108.8
N(1)-C(13)-C(12)	122.71(14)	H(21A)-C(21)-H(21B)	107.7
N(1)-C(13)-C(19)	117.68(13)	C(21)-C(22)-H(22A)	109.5

C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(1)-N(1)-C(13)	119.60(13)
C(14)-N(2)-C(8)	108.26(12)
C(14)-N(2)-C(9)	121.33(12)
C(8)-N(2)-C(9)	130.41(13)
C(18)-O(1)-C(15)	107.05(12)

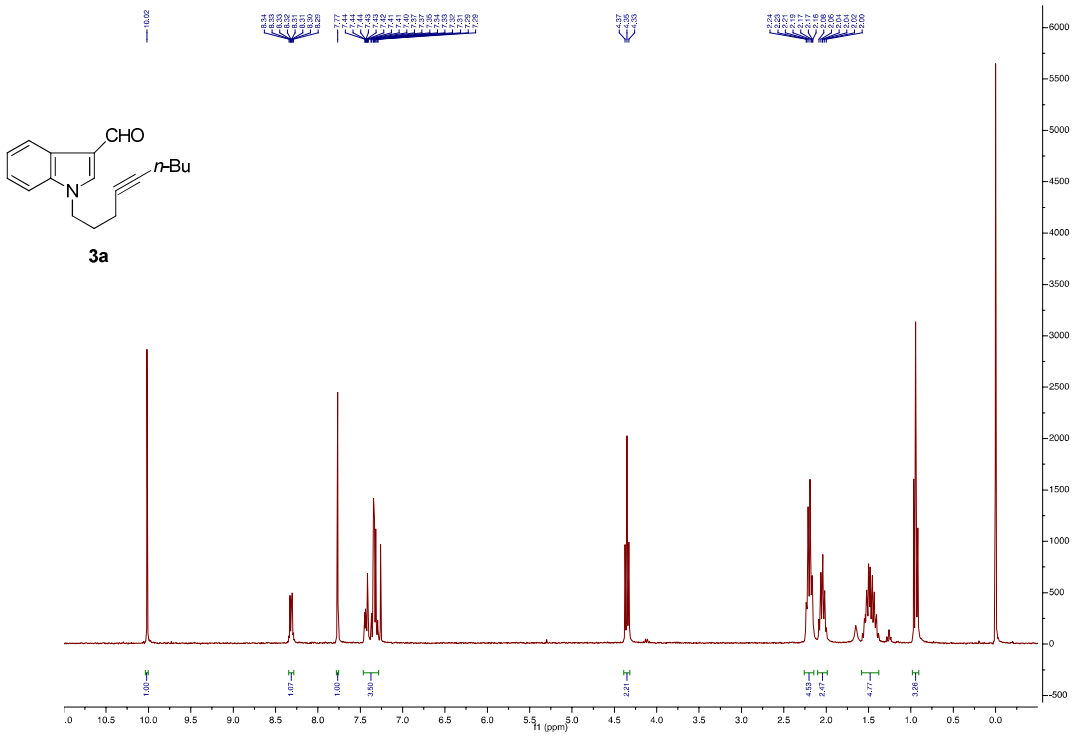
Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for gene334. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	17(1)	19(1)	18(1)	2(1)	3(1)	3(1)
C(2)	18(1)	14(1)	16(1)	1(1)	4(1)	3(1)
C(3)	19(1)	15(1)	15(1)	1(1)	5(1)	4(1)
C(4)	18(1)	15(1)	17(1)	0(1)	5(1)	2(1)
C(5)	21(1)	16(1)	14(1)	-1(1)	3(1)	4(1)
C(6)	24(1)	16(1)	17(1)	3(1)	5(1)	3(1)
C(7)	19(1)	16(1)	19(1)	3(1)	5(1)	1(1)
C(8)	19(1)	15(1)	16(1)	0(1)	3(1)	4(1)
C(9)	17(1)	20(1)	22(1)	2(1)	5(1)	0(1)
C(10)	17(1)	20(1)	24(1)	2(1)	5(1)	1(1)
C(11)	19(1)	20(1)	21(1)	5(1)	2(1)	2(1)
C(12)	19(1)	15(1)	17(1)	0(1)	2(1)	4(1)
C(13)	19(1)	16(1)	17(1)	-1(1)	4(1)	4(1)
C(14)	18(1)	15(1)	16(1)	1(1)	4(1)	2(1)
C(15)	20(1)	16(1)	18(1)	0(1)	6(1)	2(1)
C(16)	23(1)	26(1)	23(1)	8(1)	4(1)	3(1)
C(17)	25(1)	32(1)	22(1)	7(1)	-1(1)	7(1)
C(18)	20(1)	29(1)	21(1)	3(1)	-2(1)	4(1)
C(19)	20(1)	22(1)	18(1)	2(1)	2(1)	3(1)
C(20)	21(1)	18(1)	18(1)	1(1)	2(1)	3(1)
C(21)	22(1)	24(1)	18(1)	3(1)	2(1)	3(1)
C(22)	32(1)	24(1)	21(1)	4(1)	2(1)	1(1)
N(1)	18(1)	18(1)	18(1)	3(1)	3(1)	4(1)
N(2)	17(1)	18(1)	18(1)	5(1)	4(1)	2(1)
O(1)	19(1)	24(1)	21(1)	5(1)	1(1)	1(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for gene334.

	x	y	z	U(eq)
H(1)	2652	5006	6412	21
H(4)	1729	6736	4364	20
H(6)	4460	9844	2603	22
H(7)	6997	9649	3744	22
H(9A)	9282	9326	6049	24
H(9B)	9362	8426	4898	24
H(10A)	11167	7533	6406	24
H(10B)	9791	6144	5772	24
H(11A)	9826	5817	7661	24
H(11B)	9592	7596	7881	24
H(16)	1829	9950	1378	28
H(17)	-1353	9188	628	31
H(18)	-2593	7281	1857	29
H(19A)	7616	5568	9364	24
H(19B)	8226	4220	8679	24
H(20A)	5059	3812	9552	23
H(20B)	5779	2460	8930	23
H(21A)	7439	4025	10977	26
H(21B)	8146	2668	10358	26
H(22A)	5017	2201	11270	39
H(22B)	6758	1683	11831	39
H(22C)	5782	848	10686	39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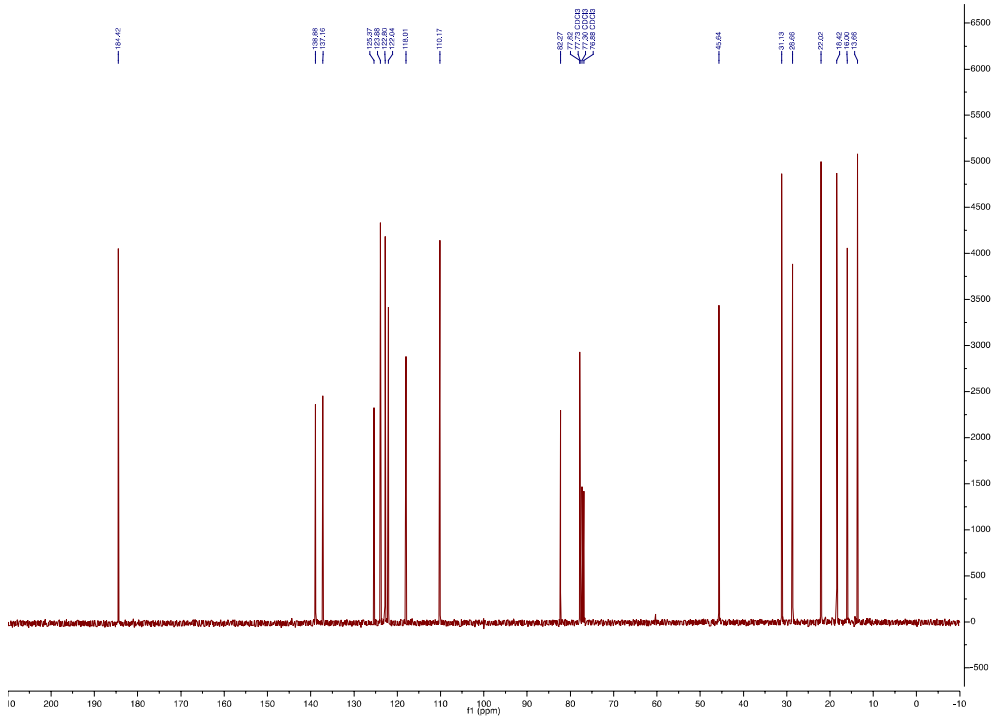
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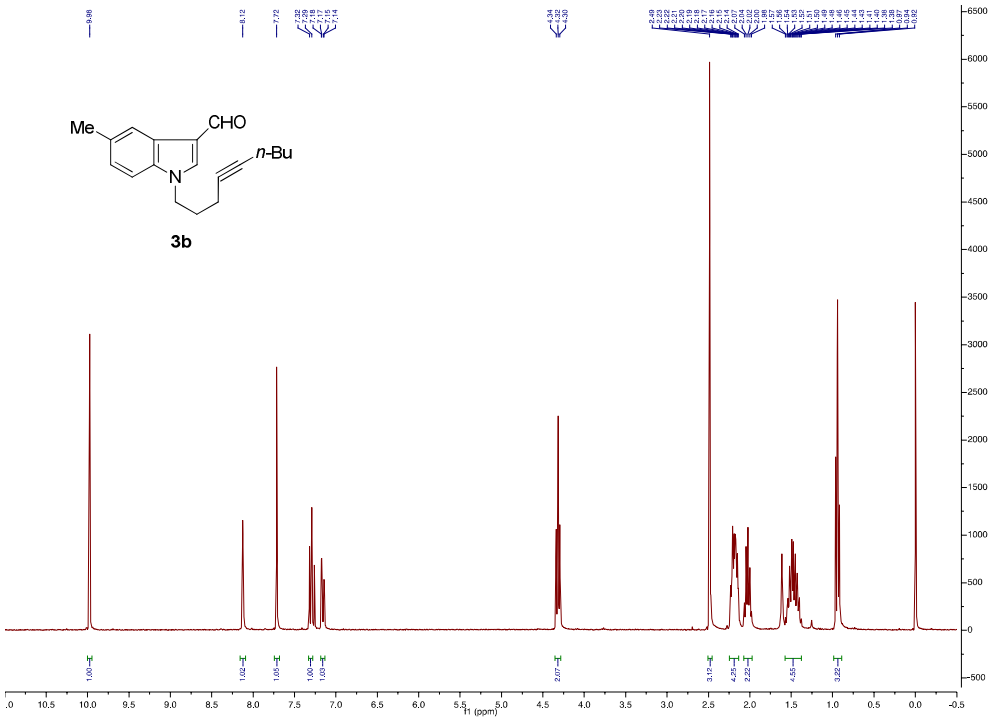
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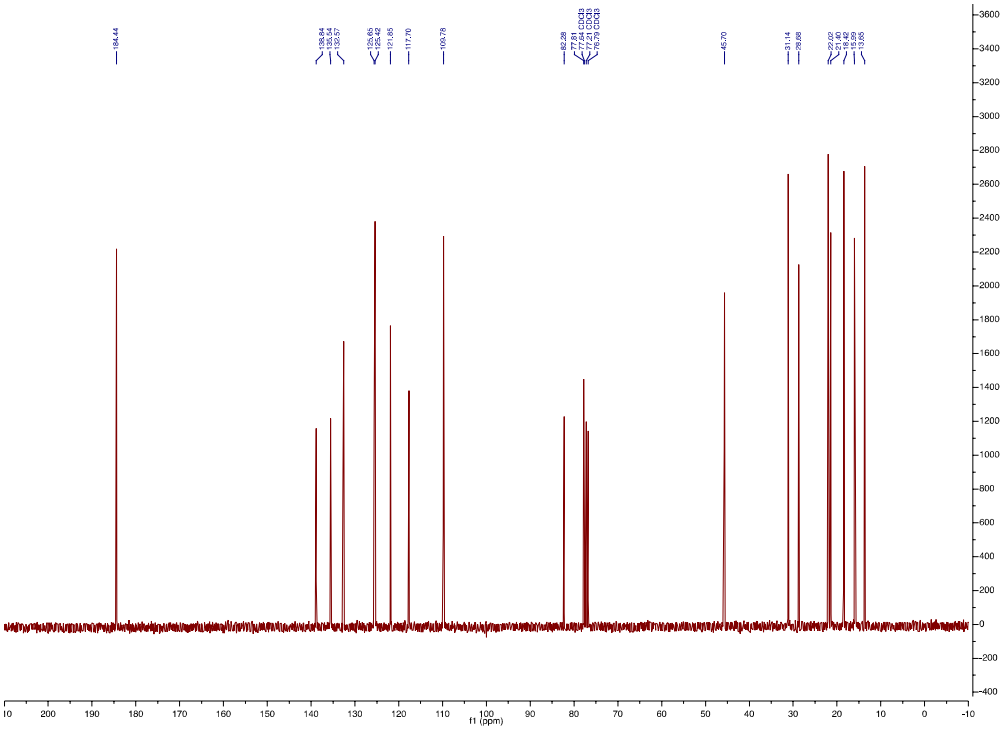
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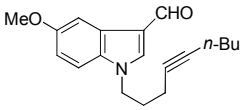

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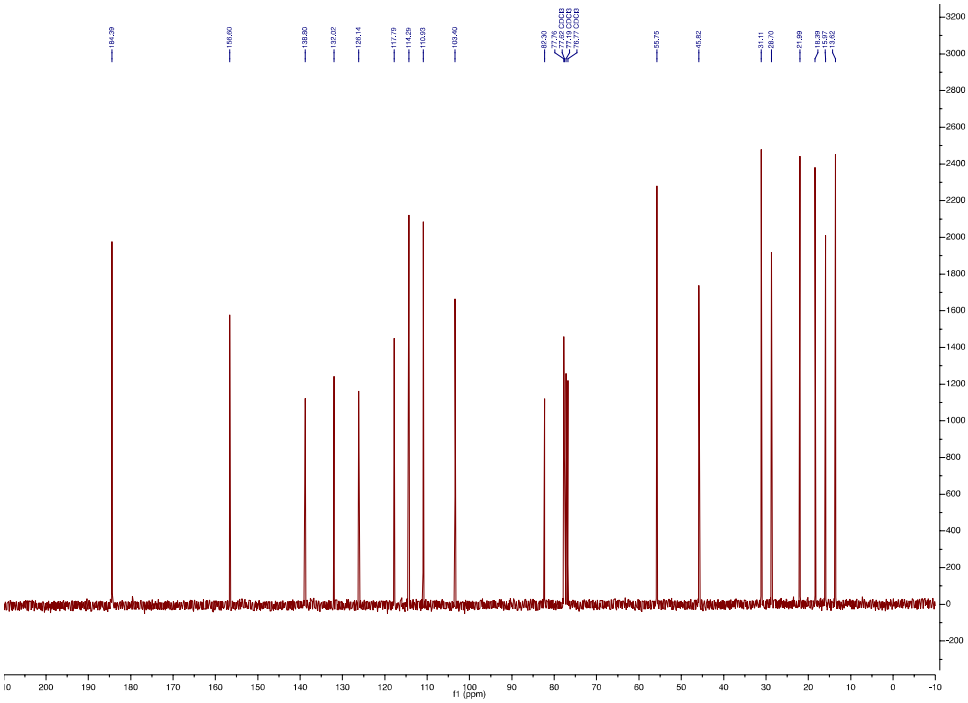

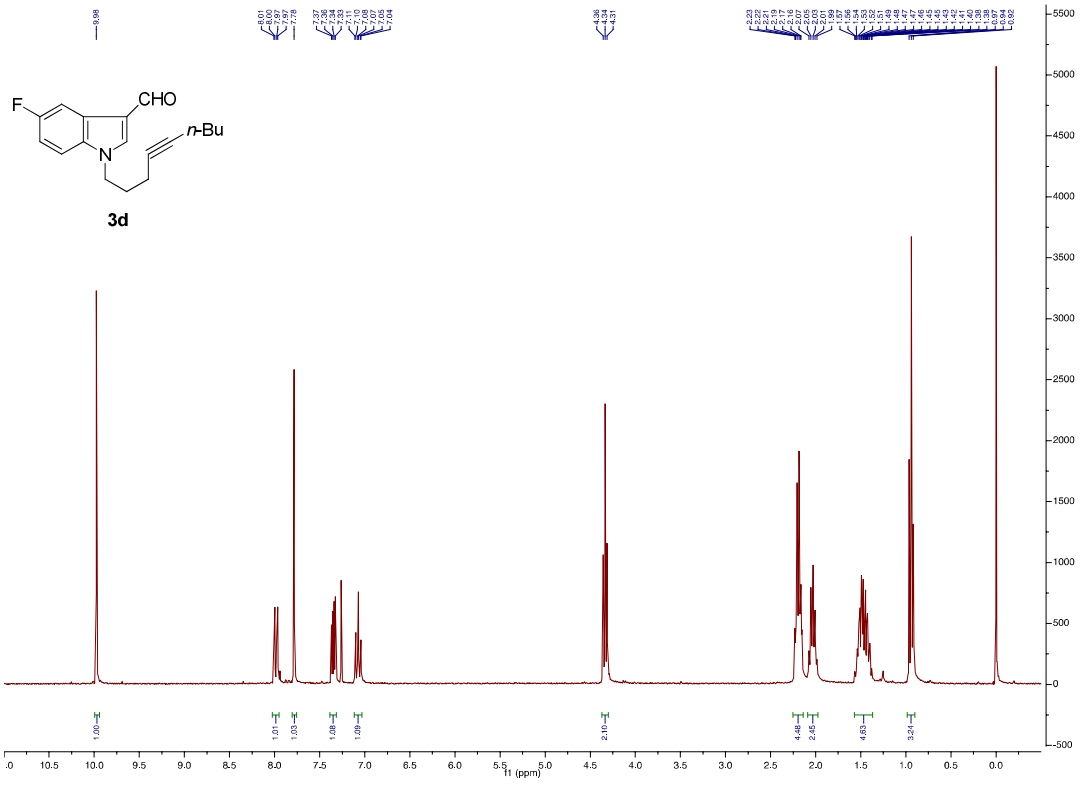
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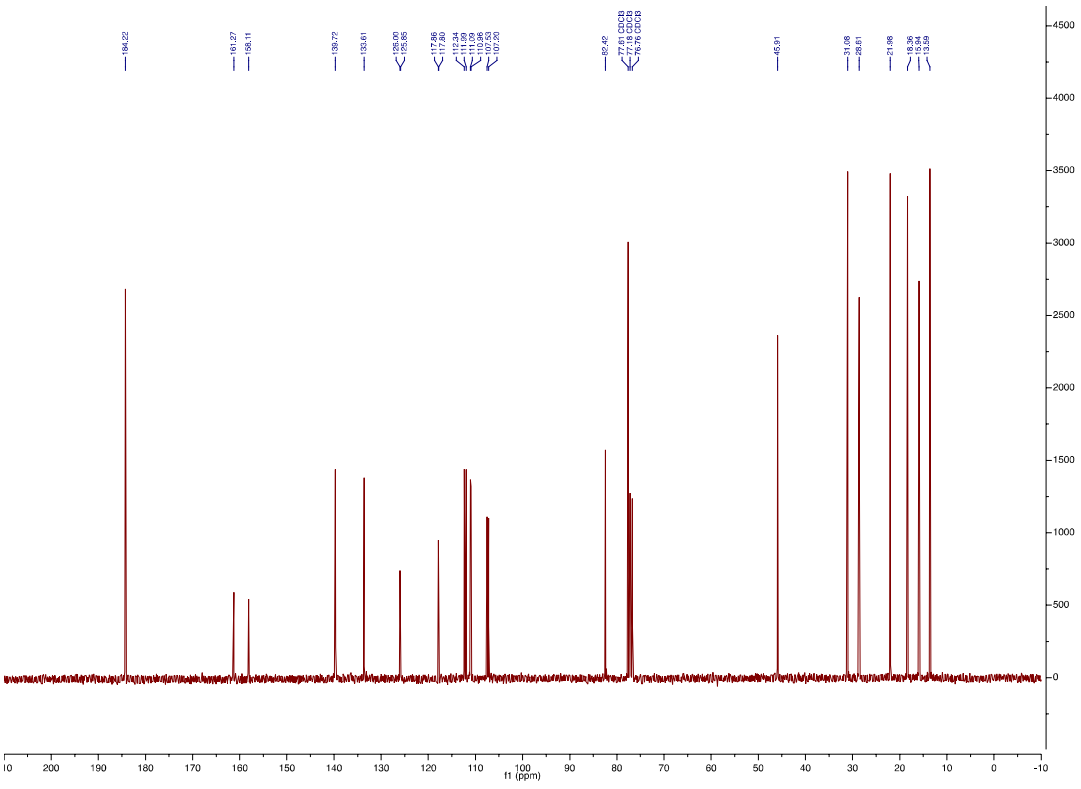
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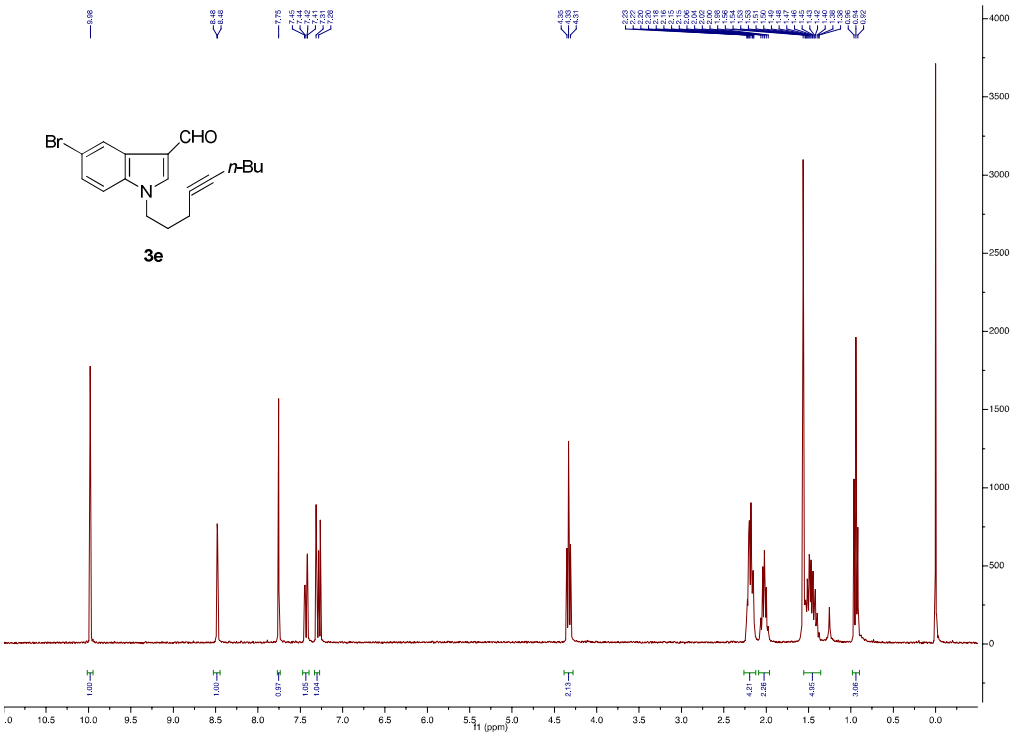
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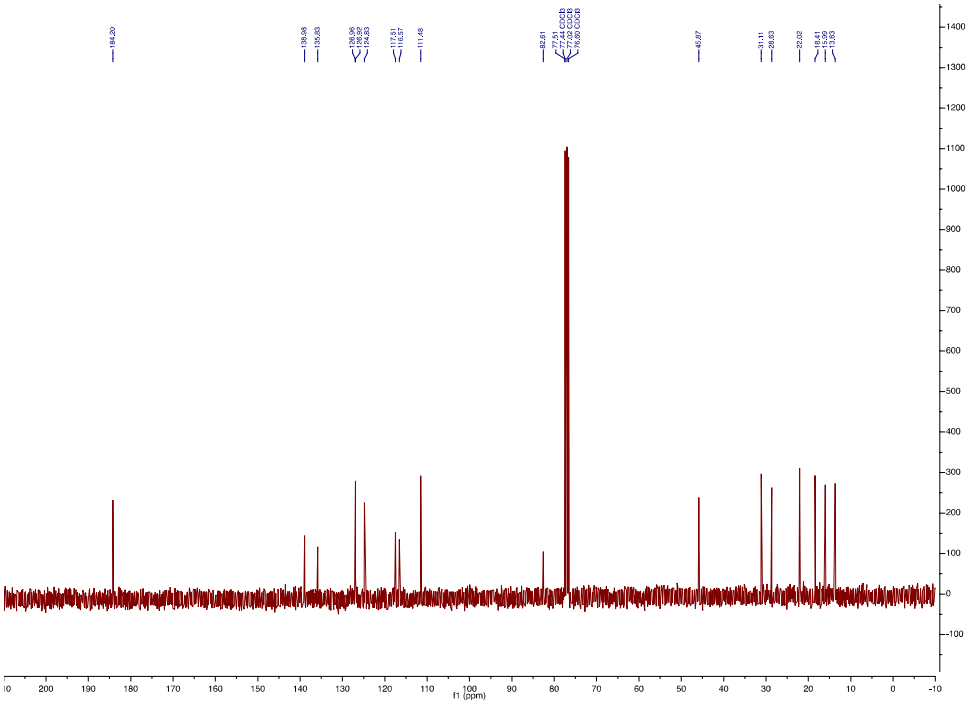
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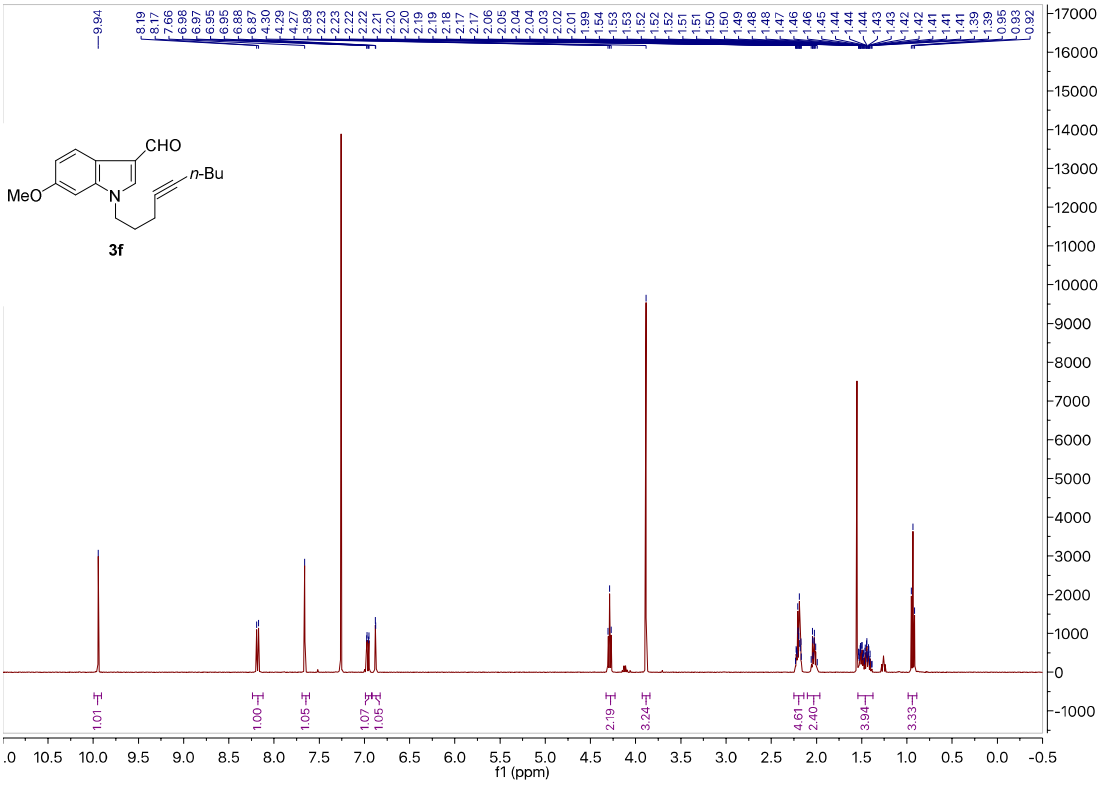
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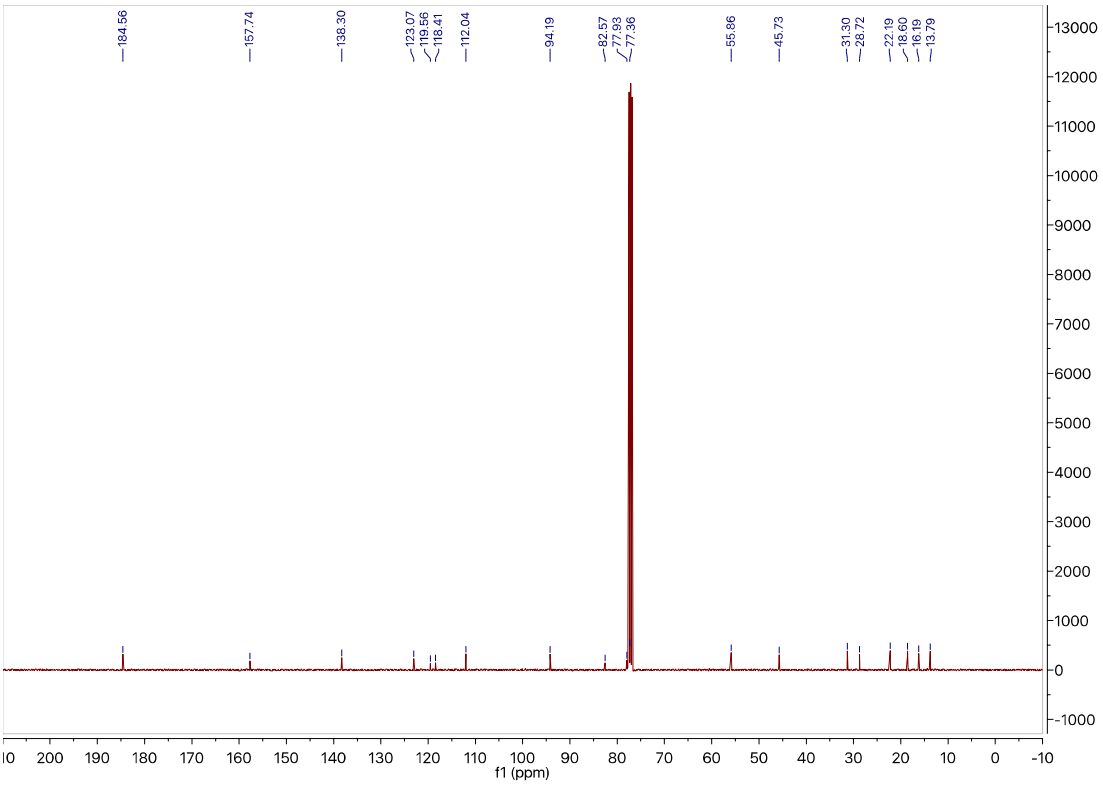
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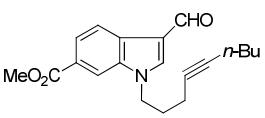

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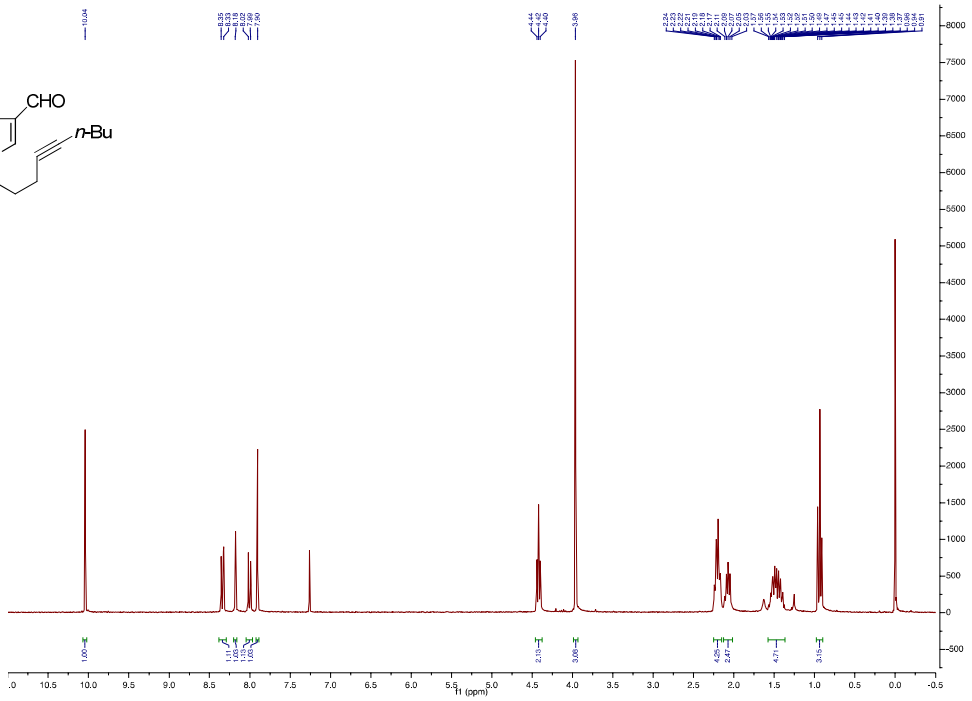

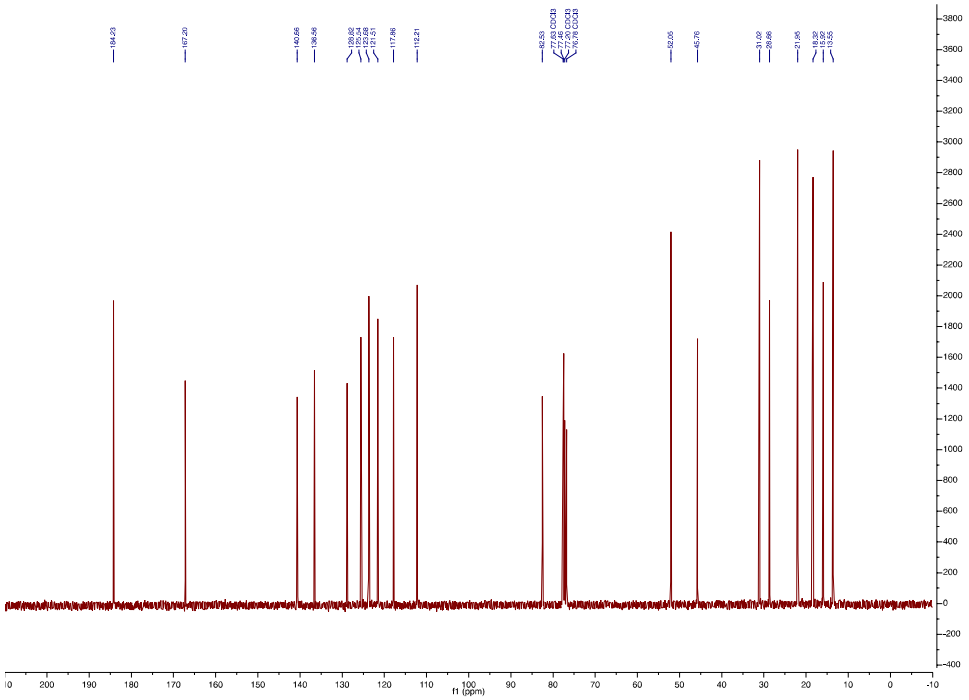

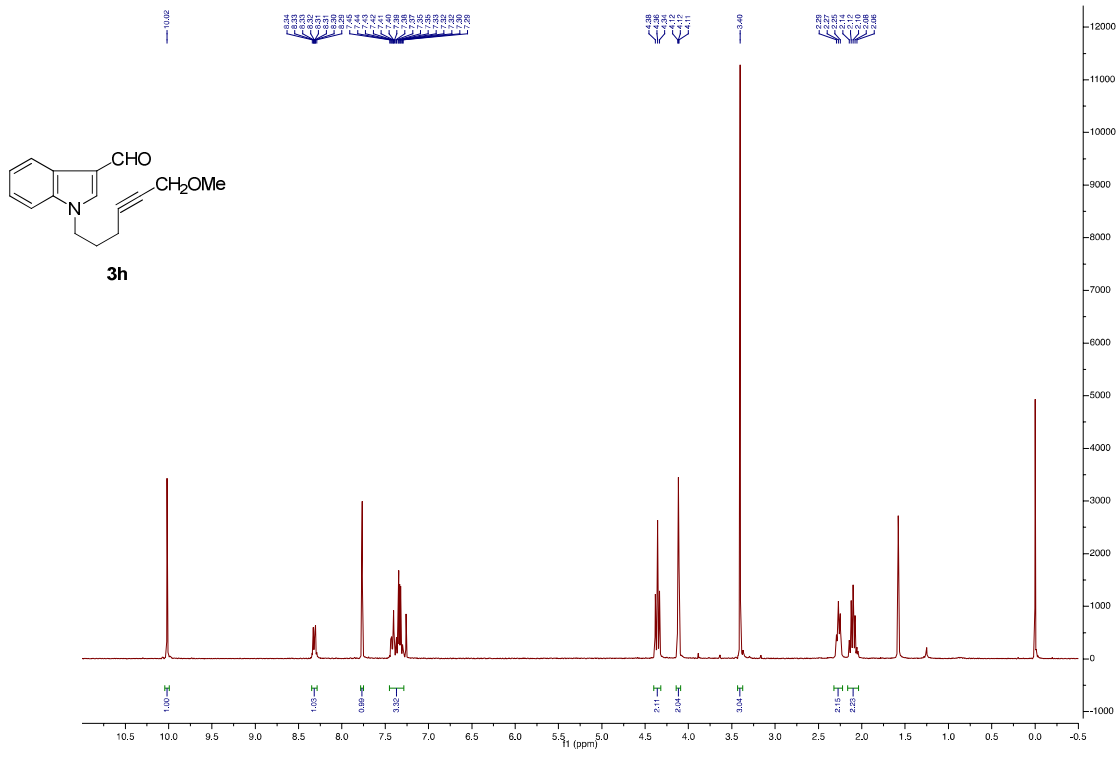
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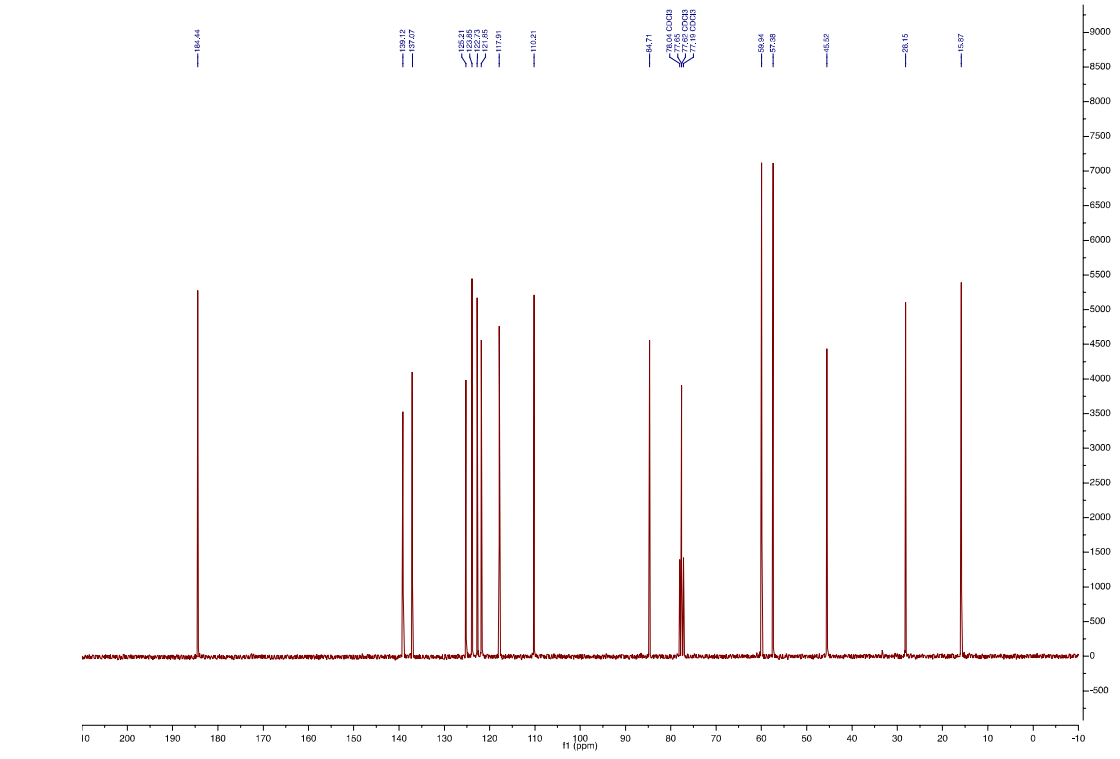
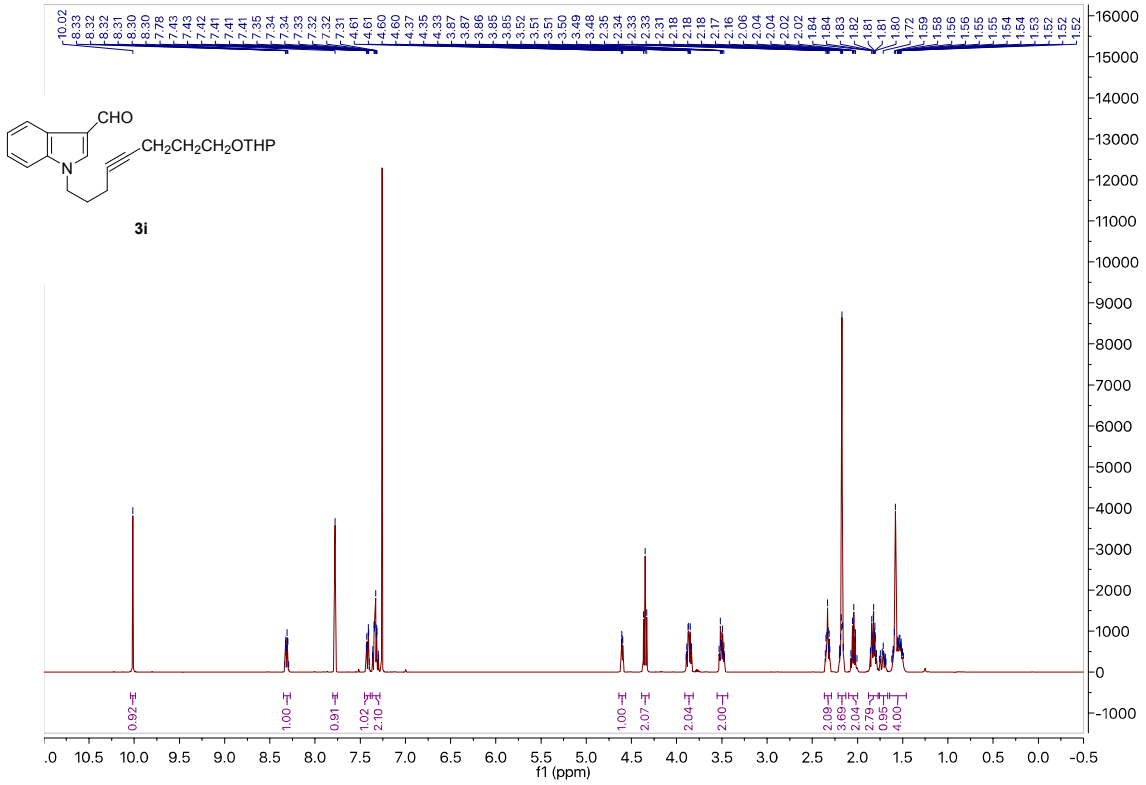
N
3h
f1 (ppm)


f1 (ppm)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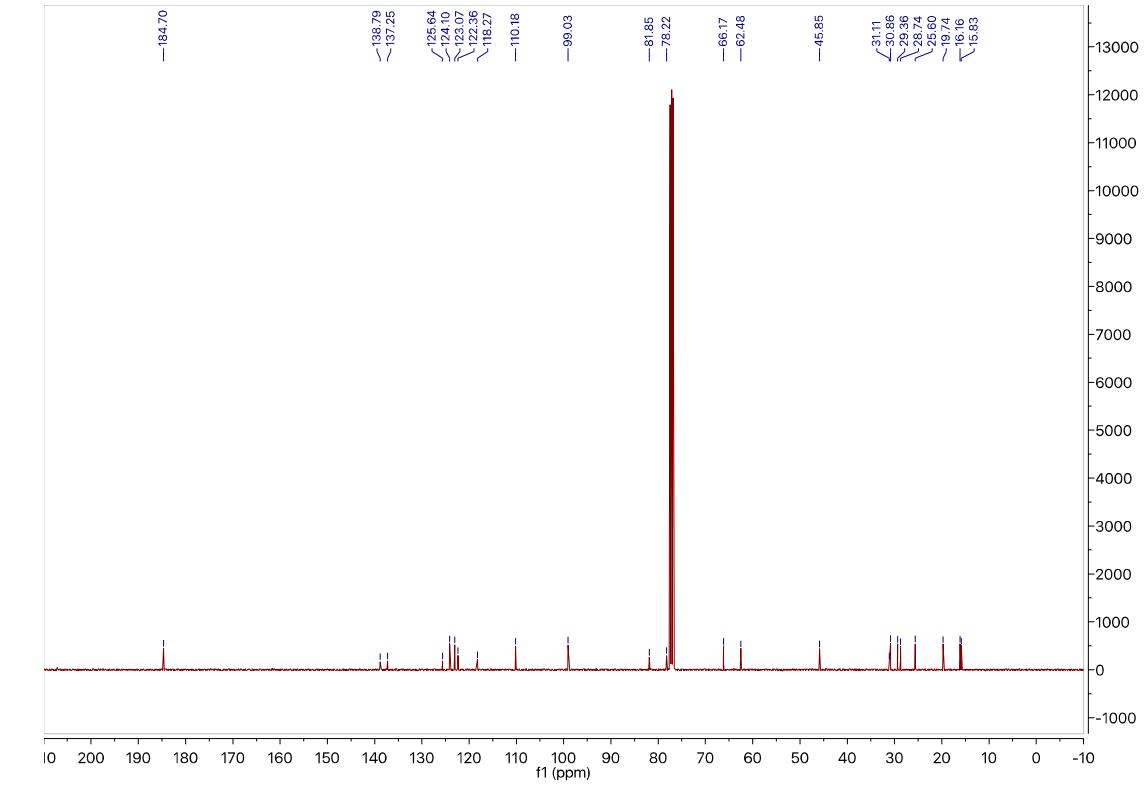
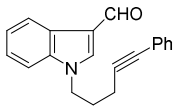
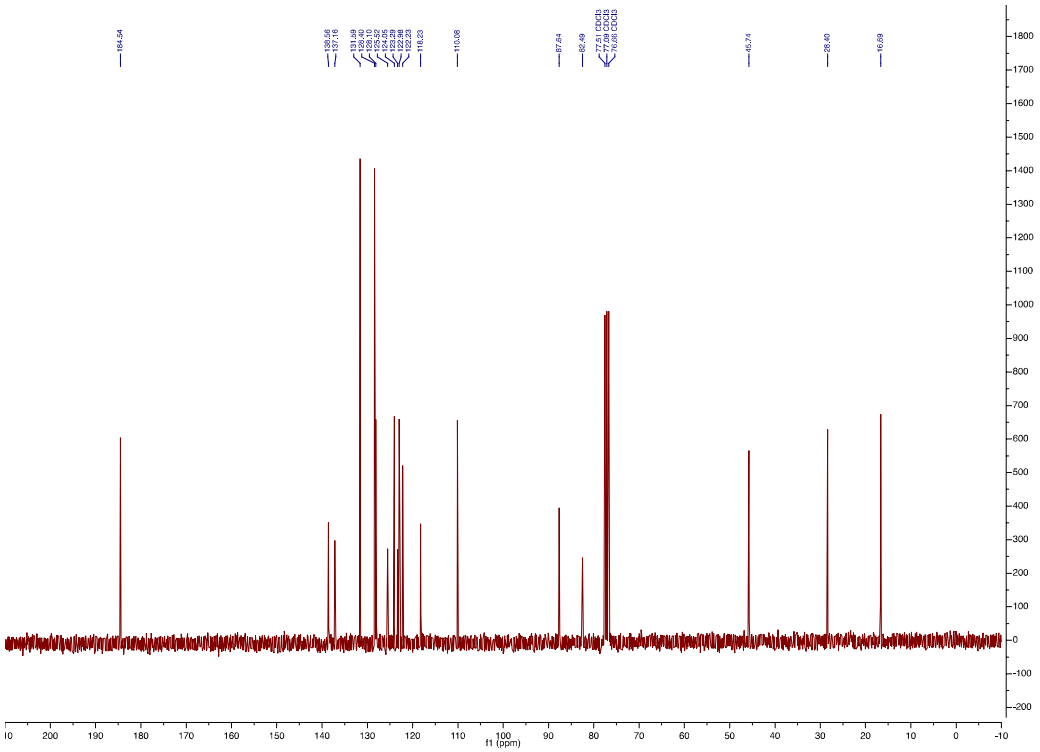
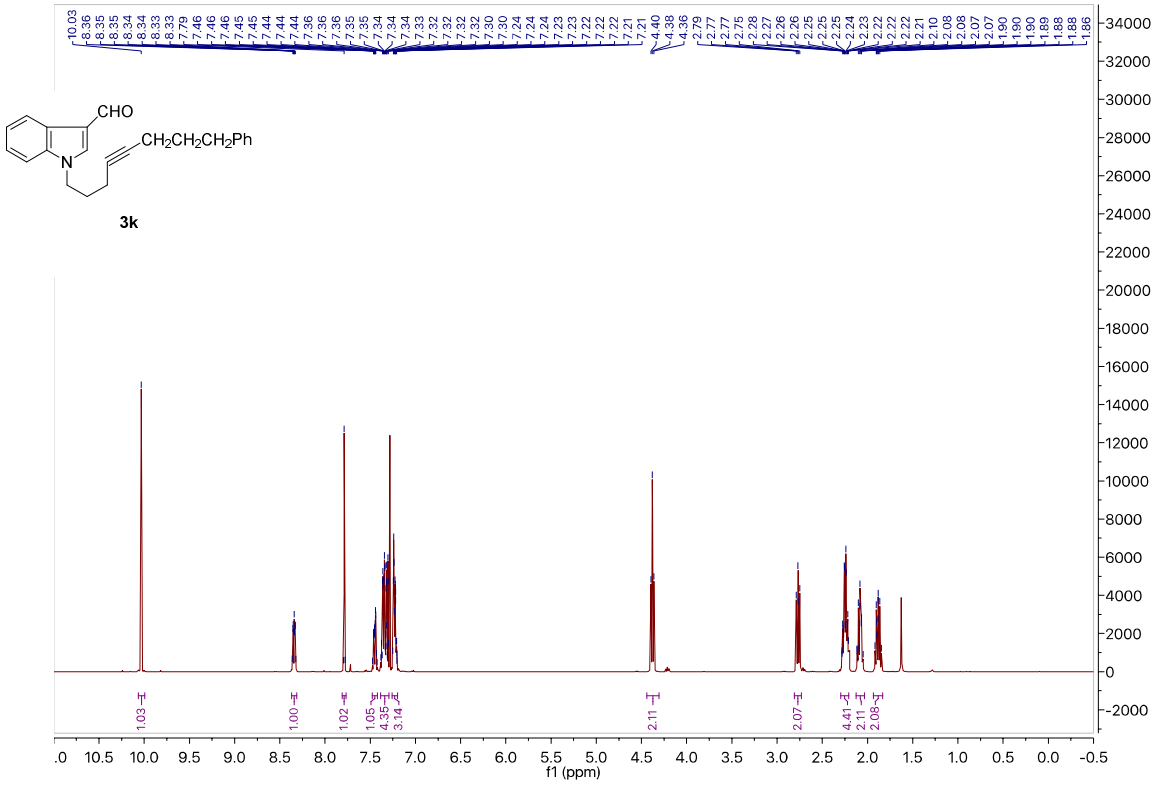
N
3i
f1 (ppm)


f1 (ppm)



3j




CHO
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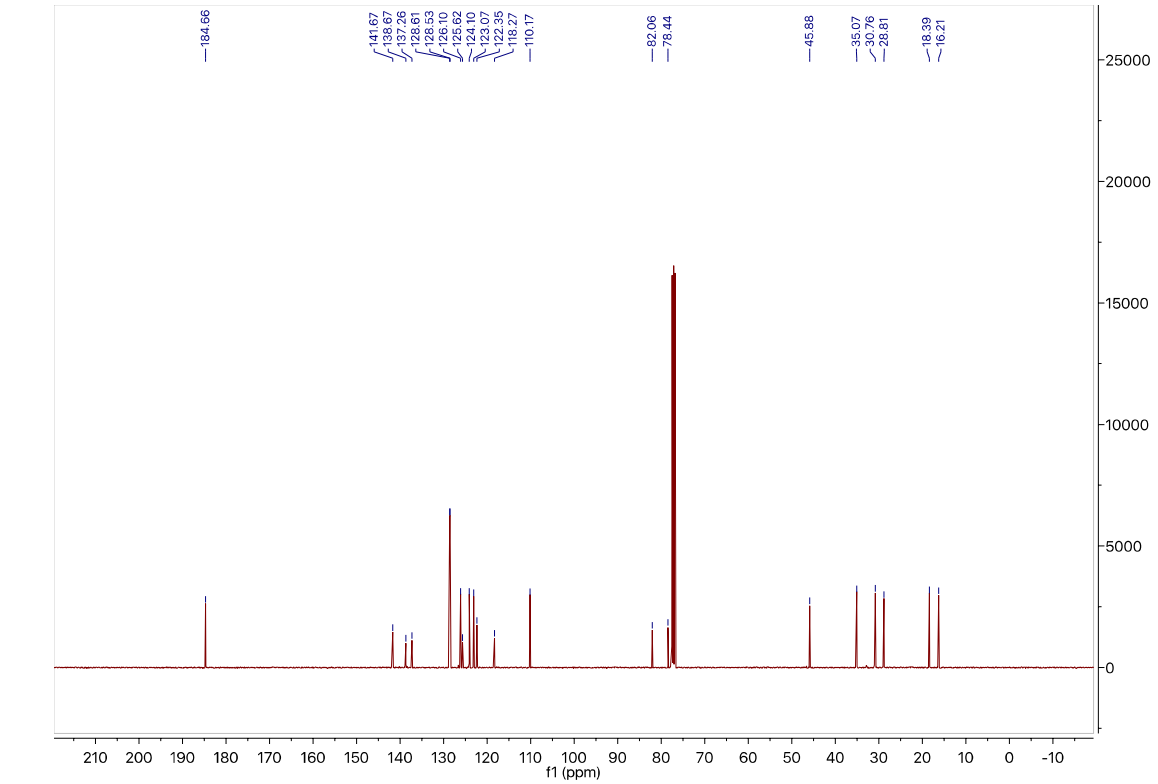
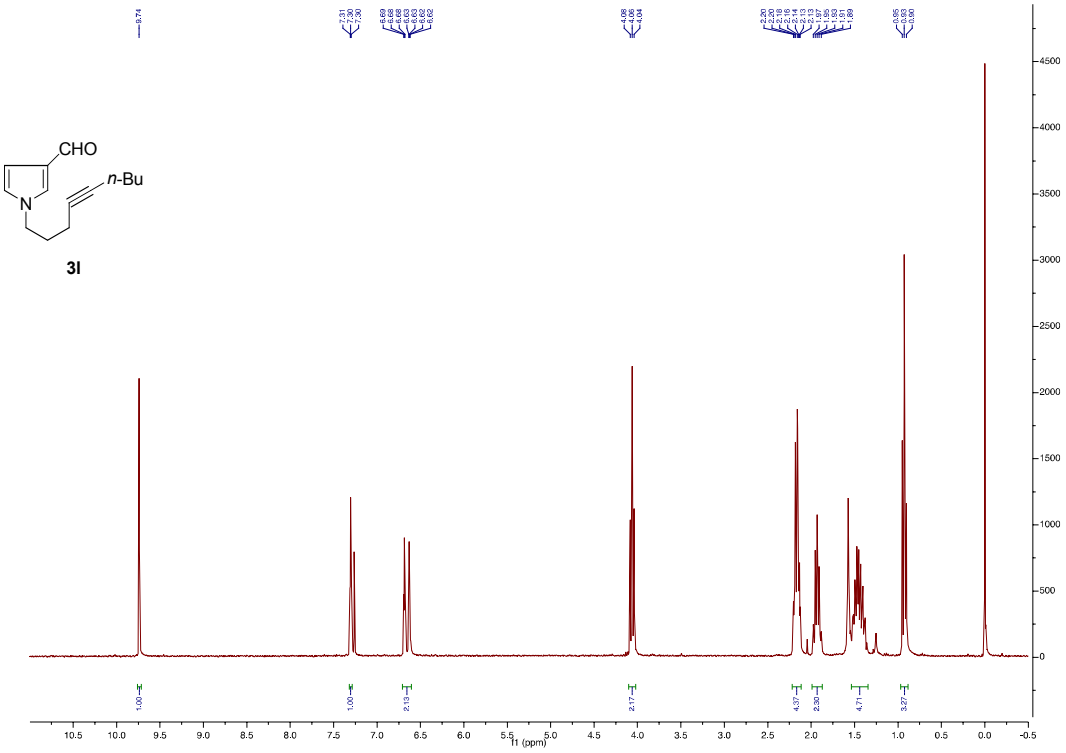
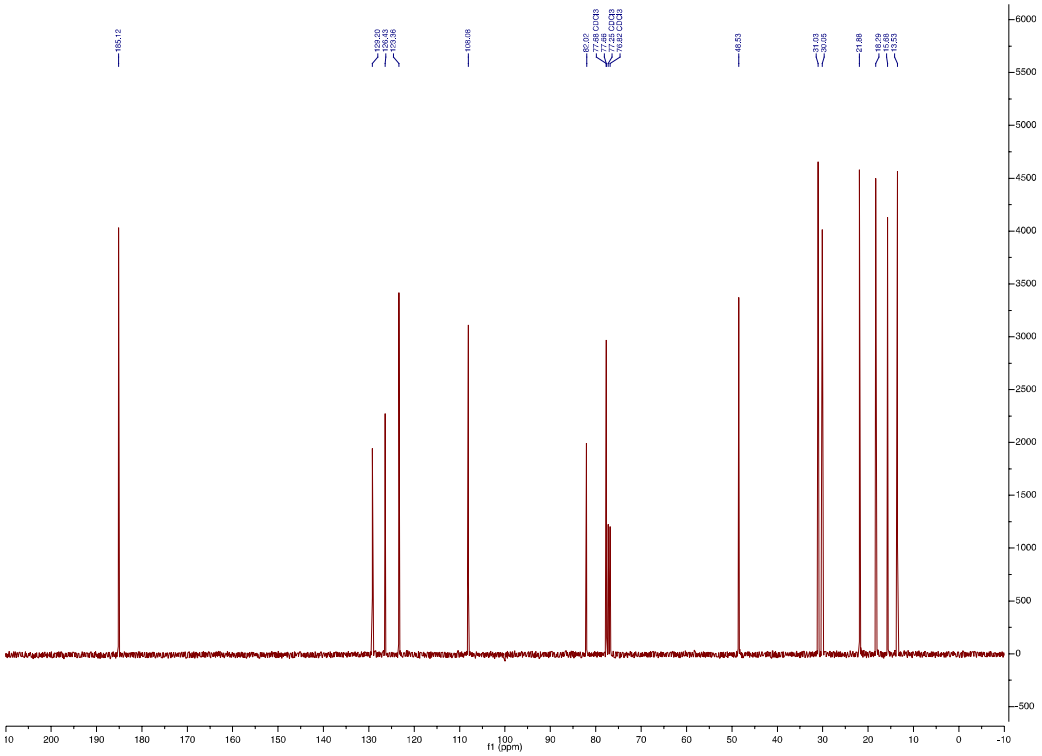
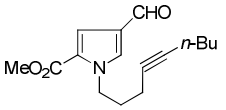
N
3k
f1 (ppm)

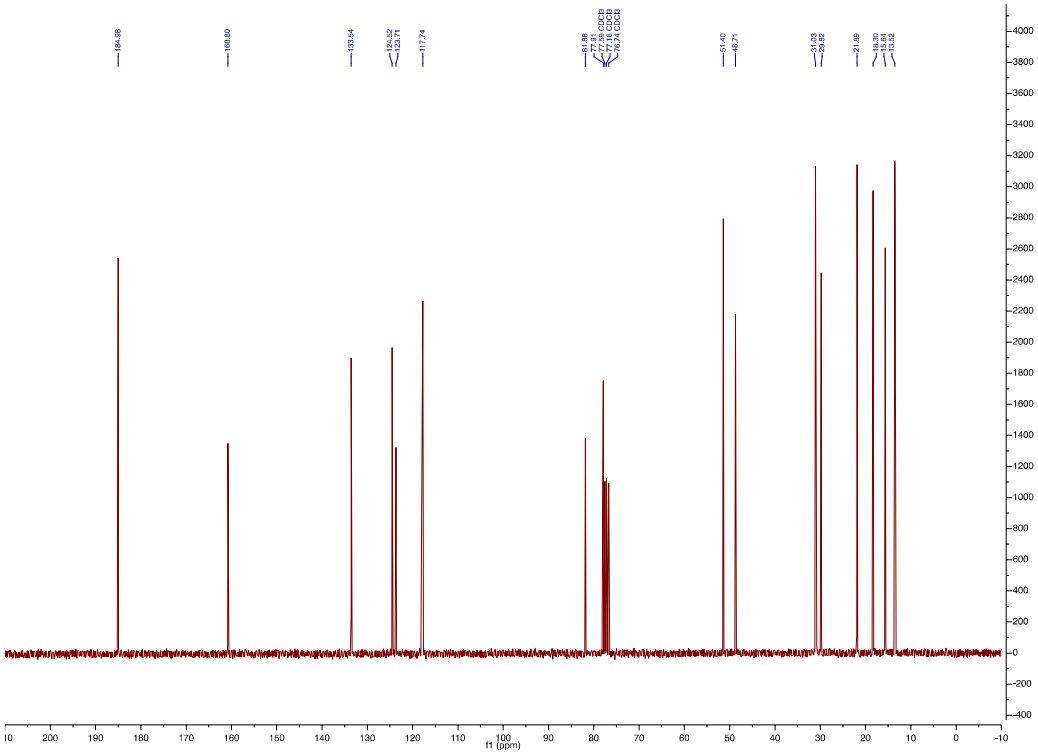

f1 (ppm)

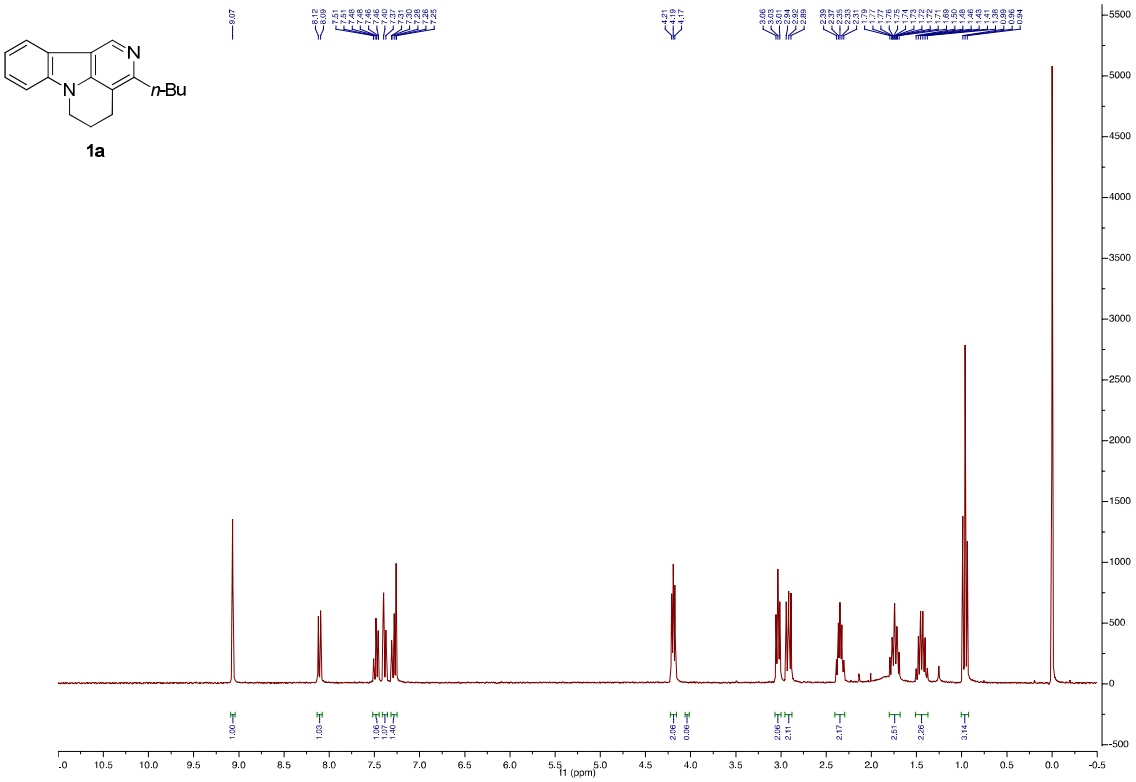

CHO
n-Bu
N
3l
f1 (ppm)

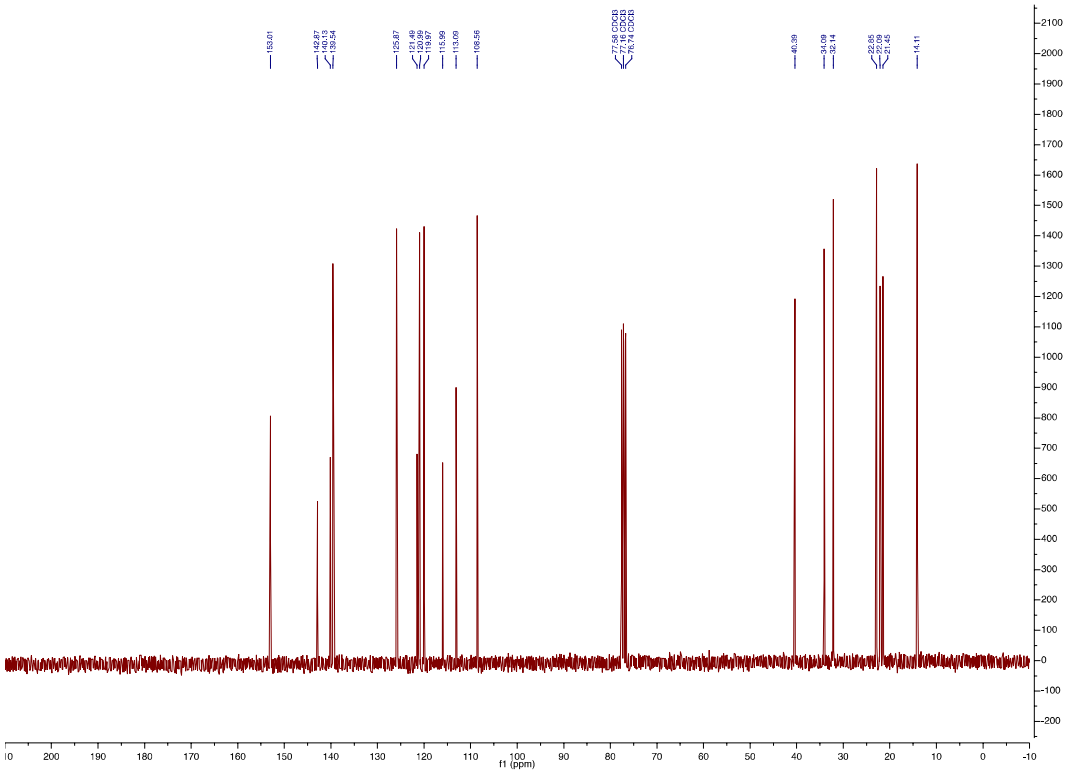

f1 (ppm)

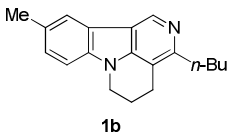


3m

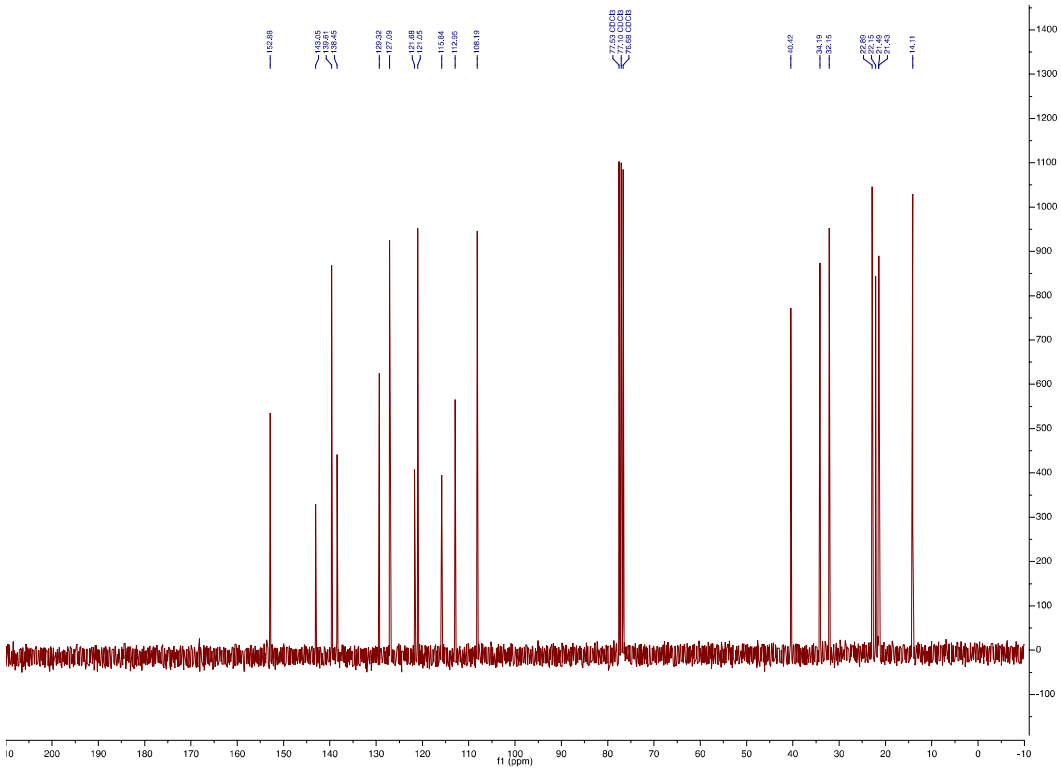


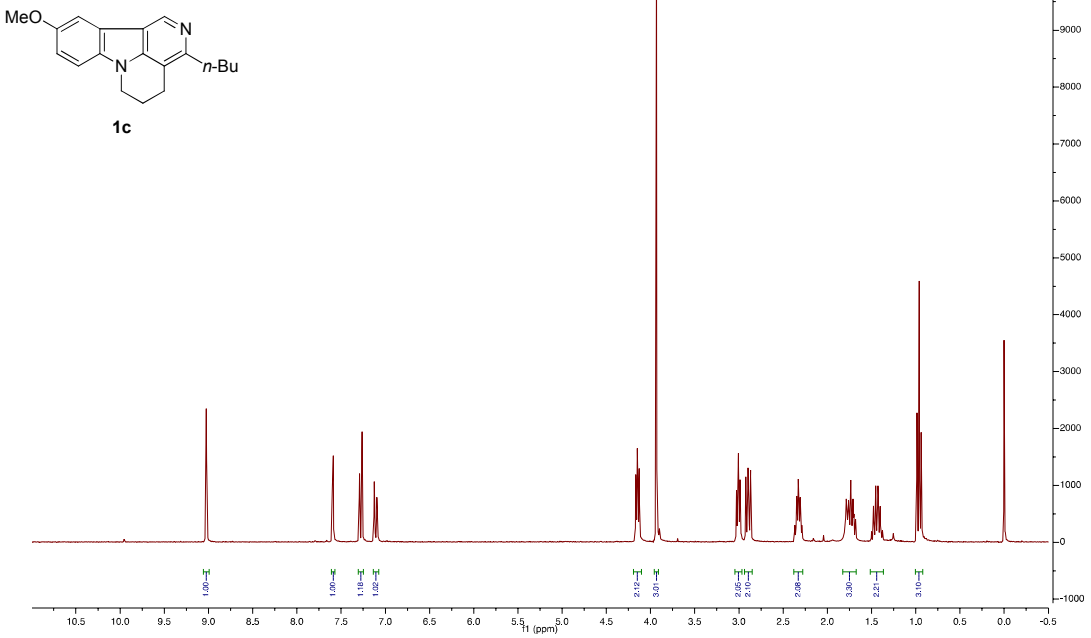

n-Bu
1a
f1 (ppm)


f1 (ppm)

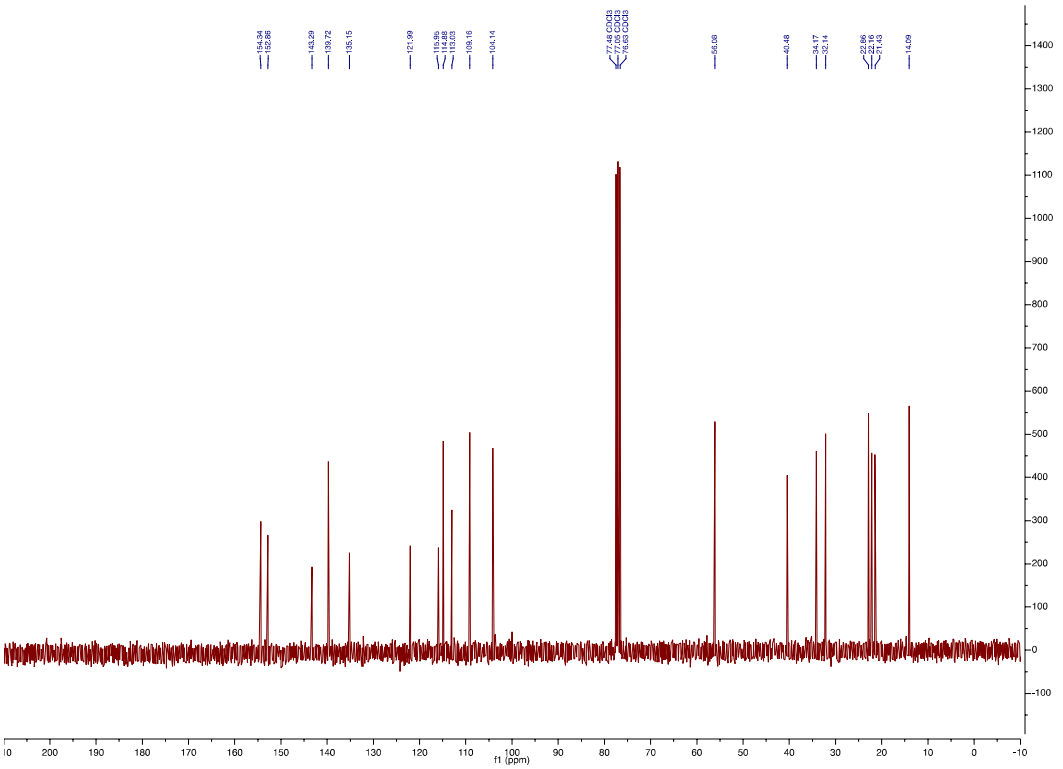


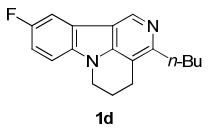
1b



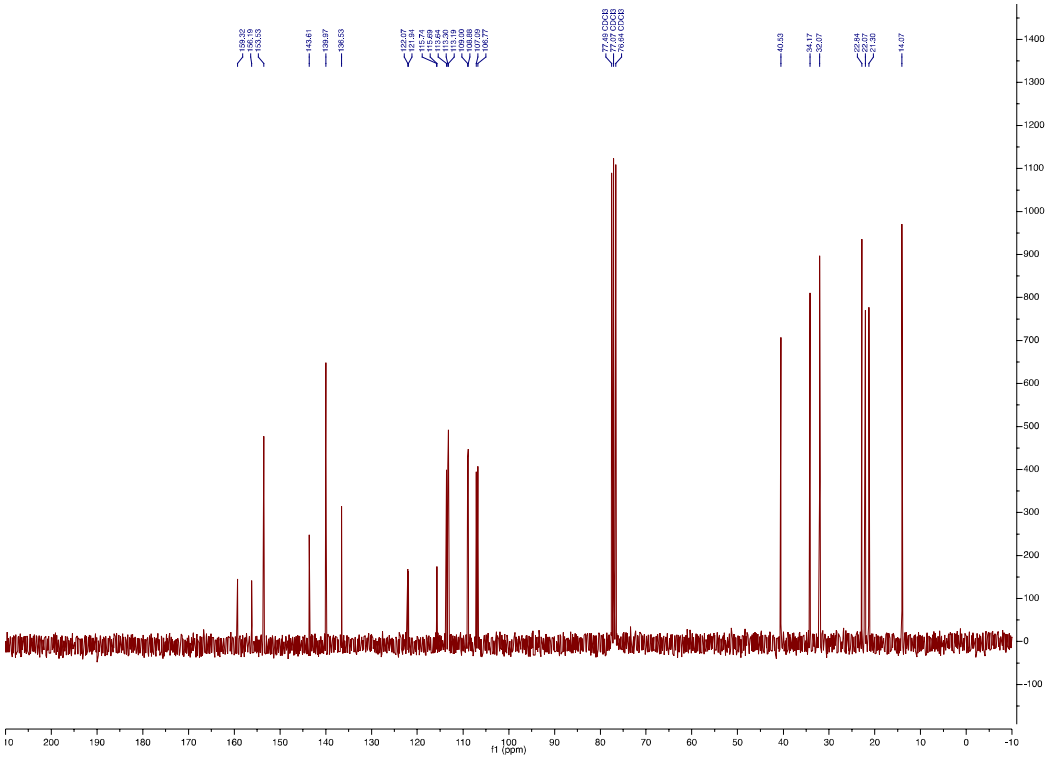


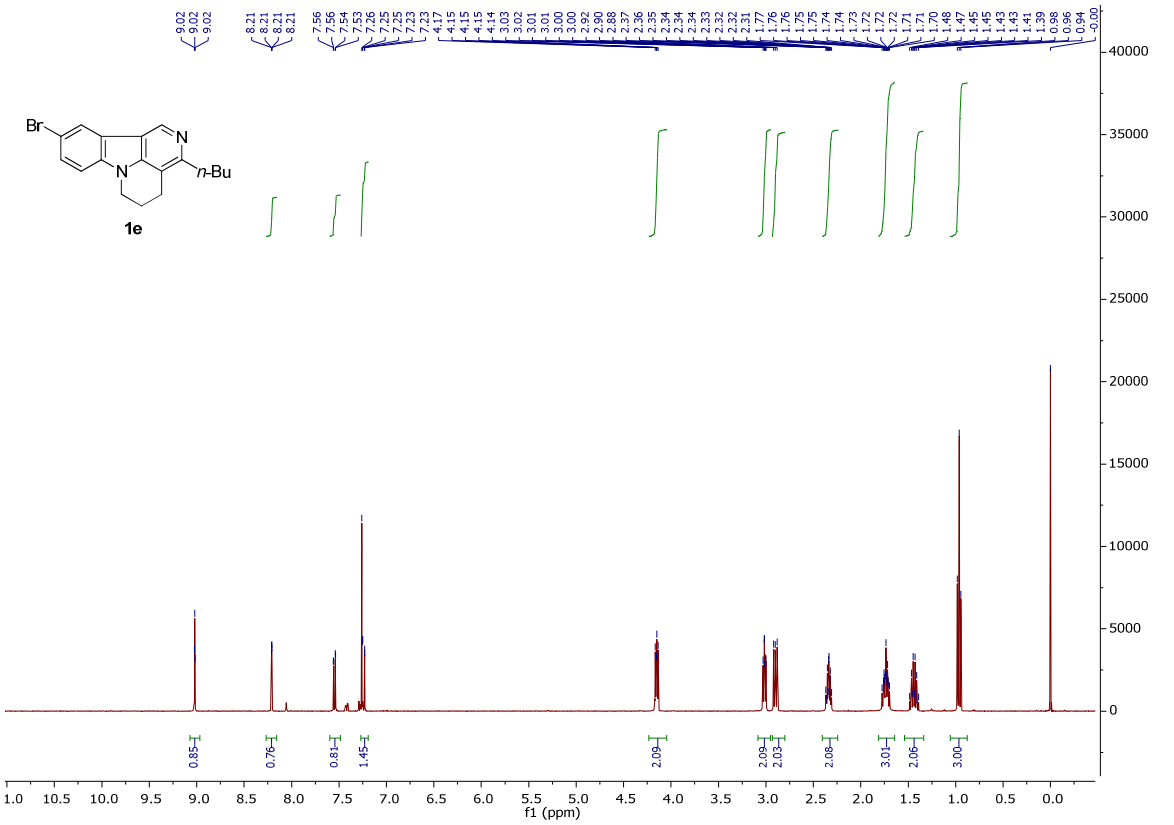
1c

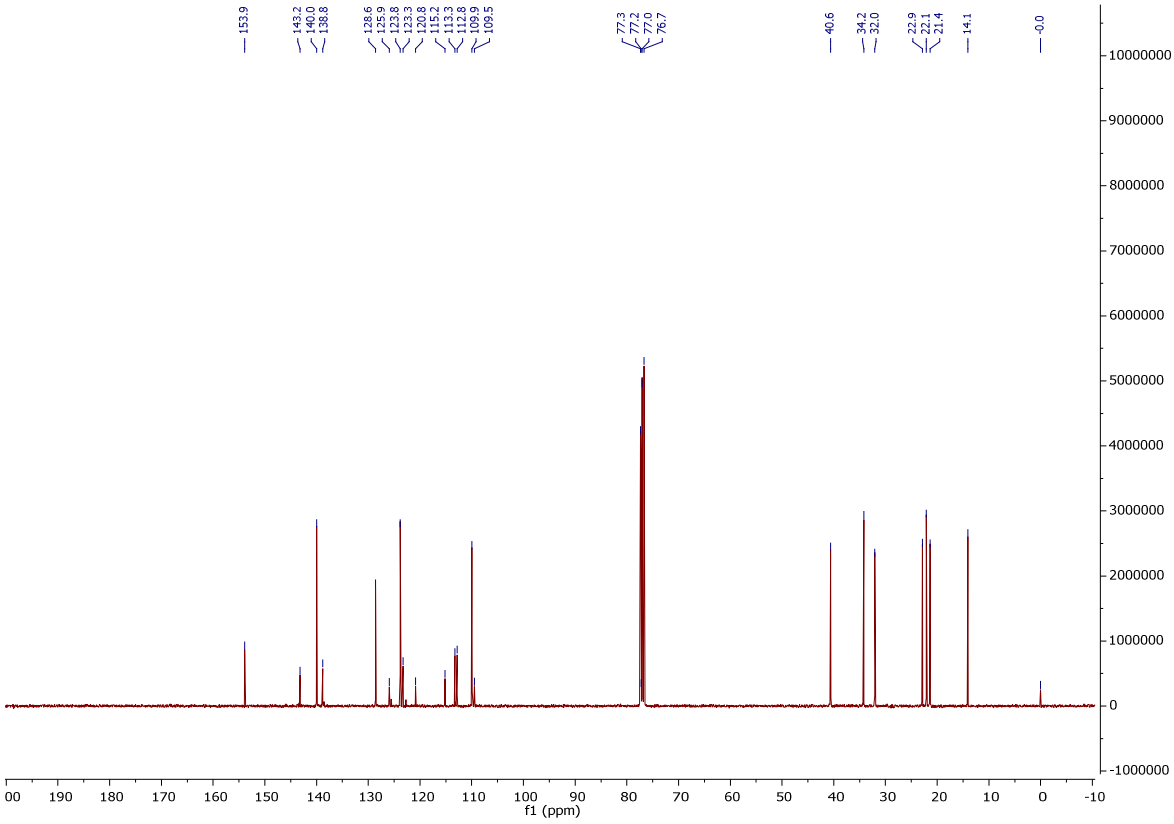


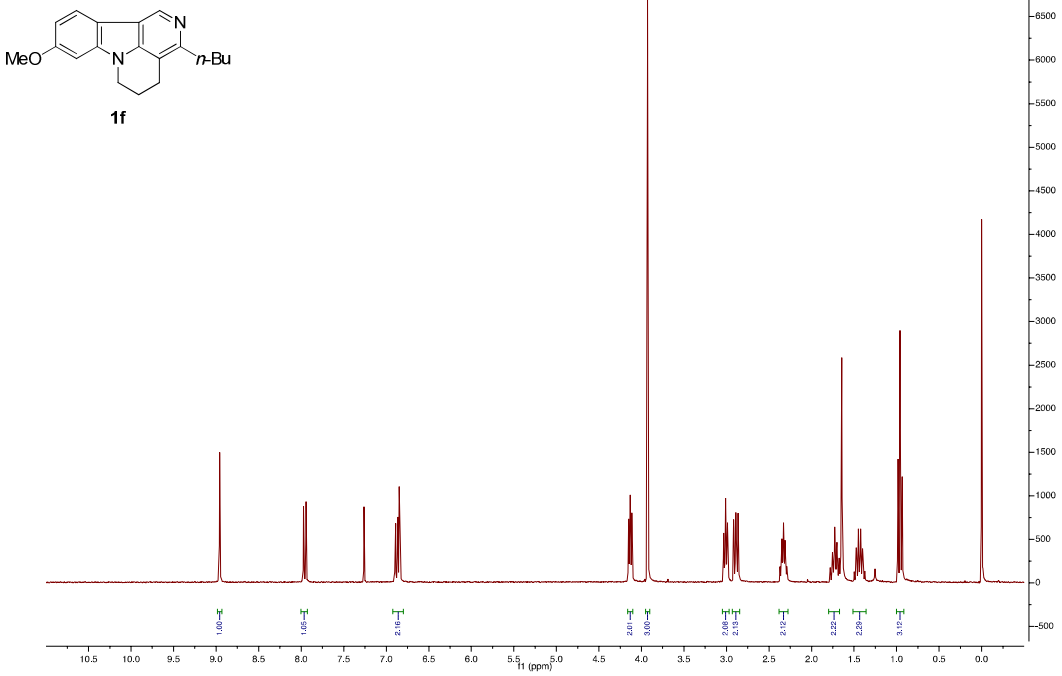


1d

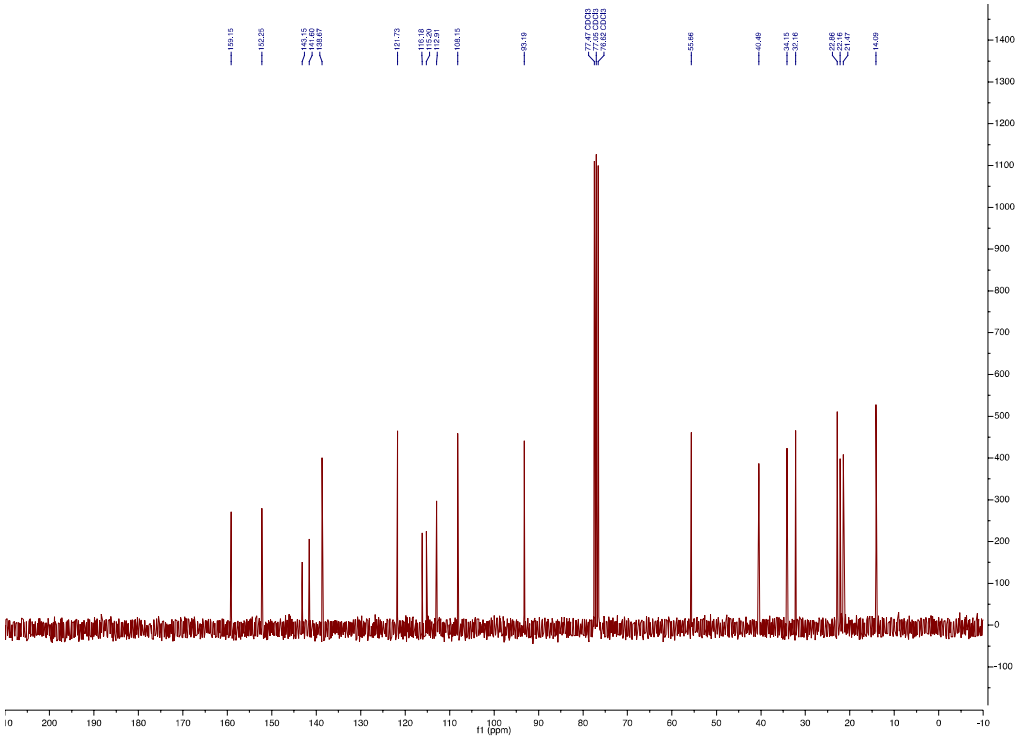


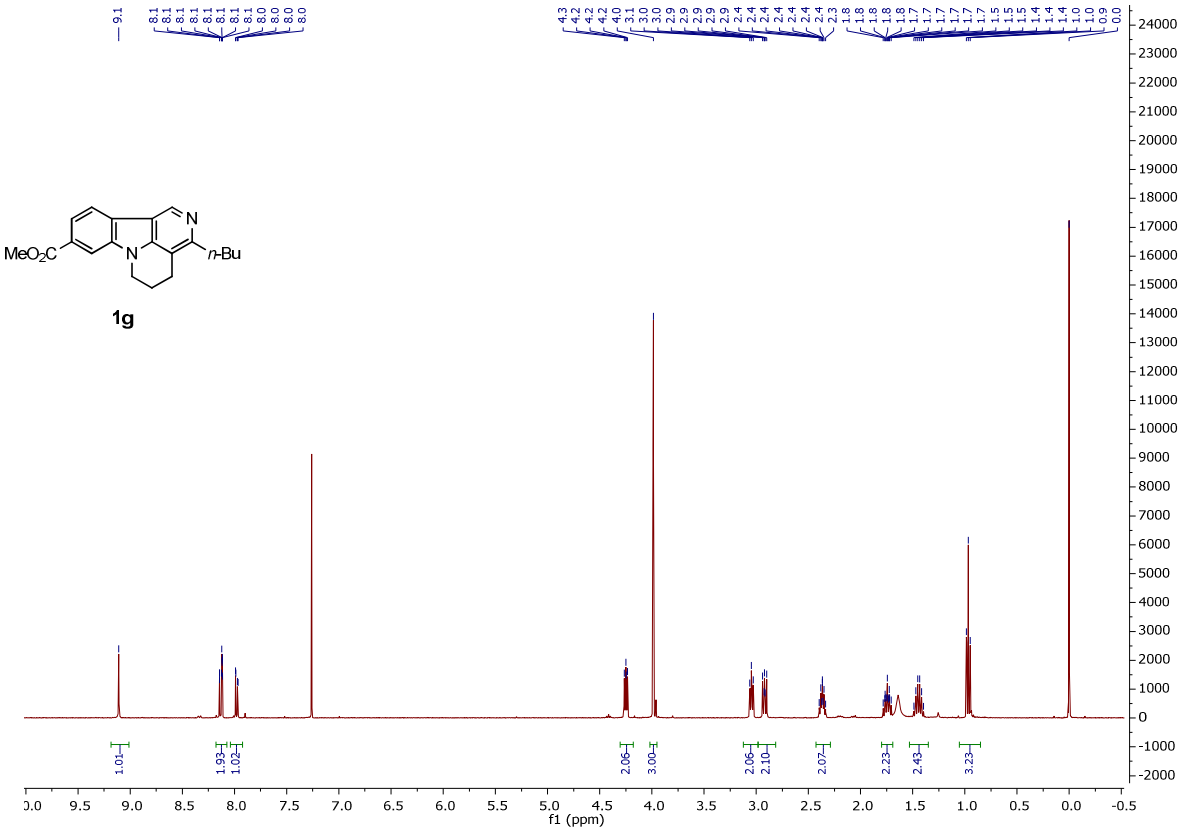

Br
N
N
n-Bu
1e
f1 (ppm)

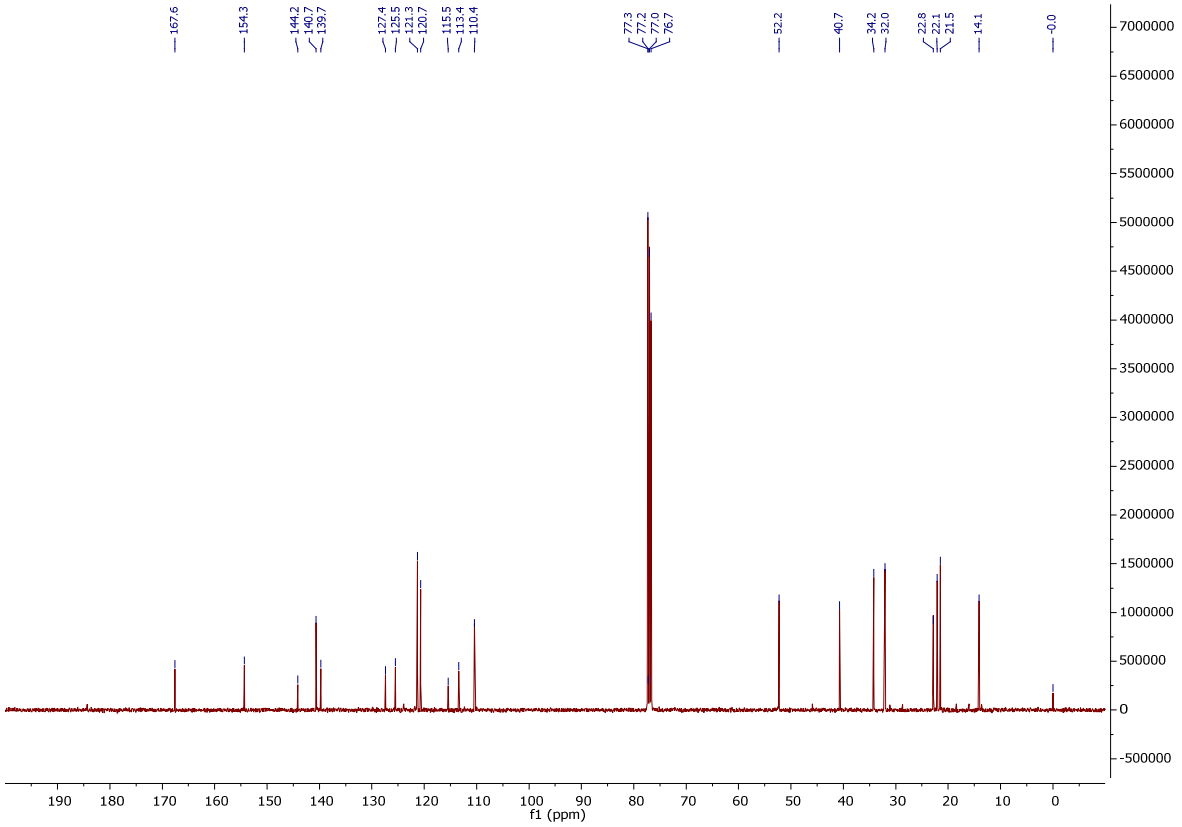

f1 (ppm)

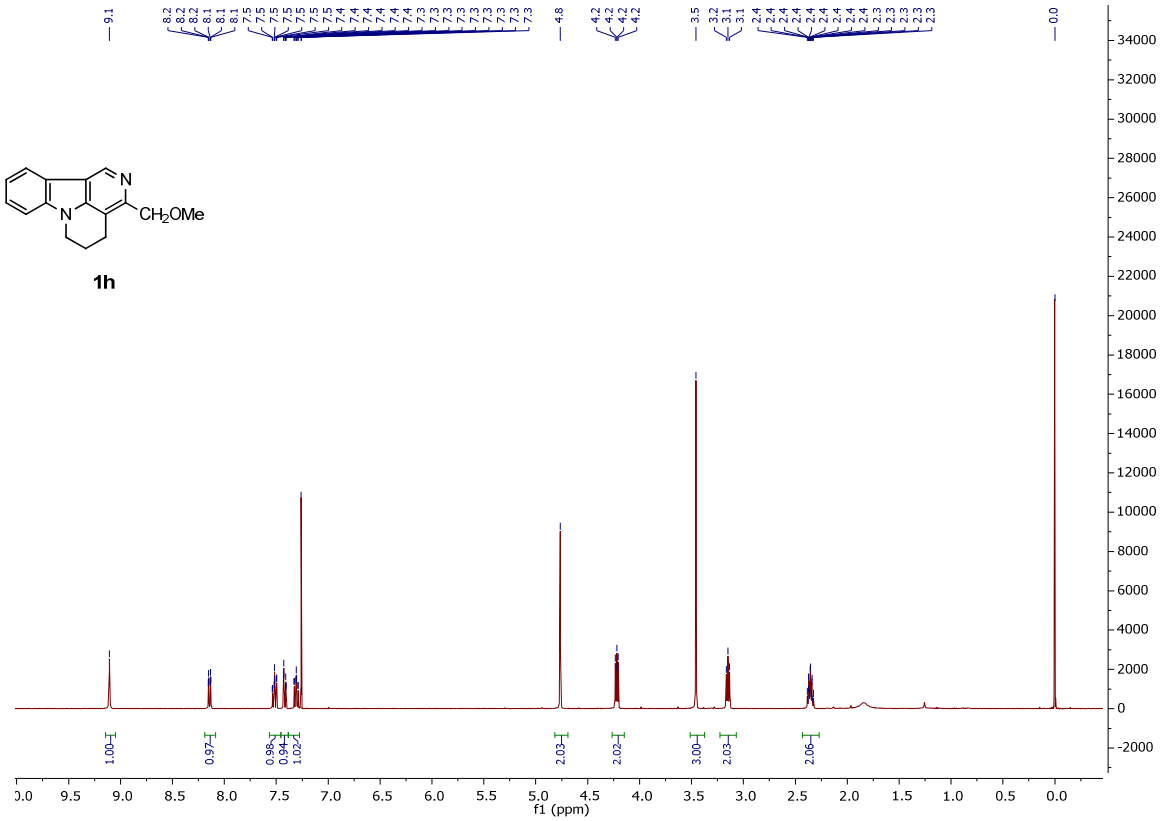


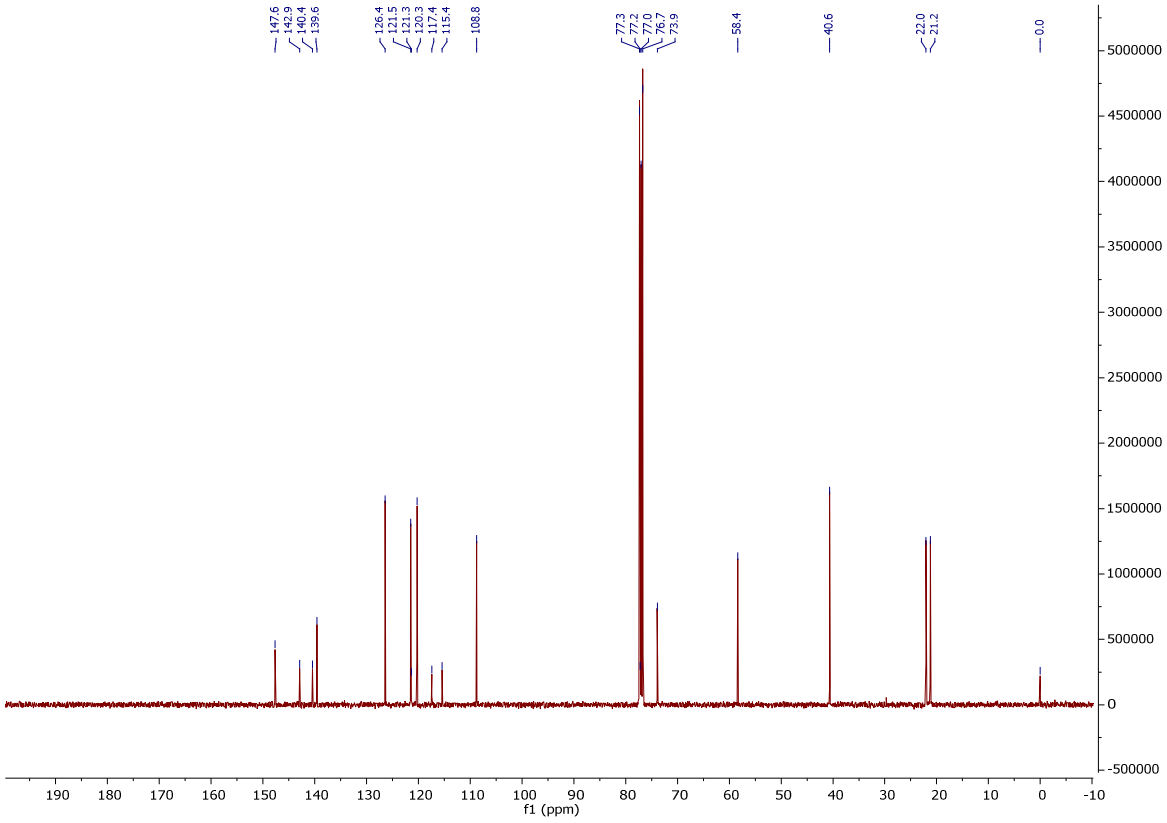
1f

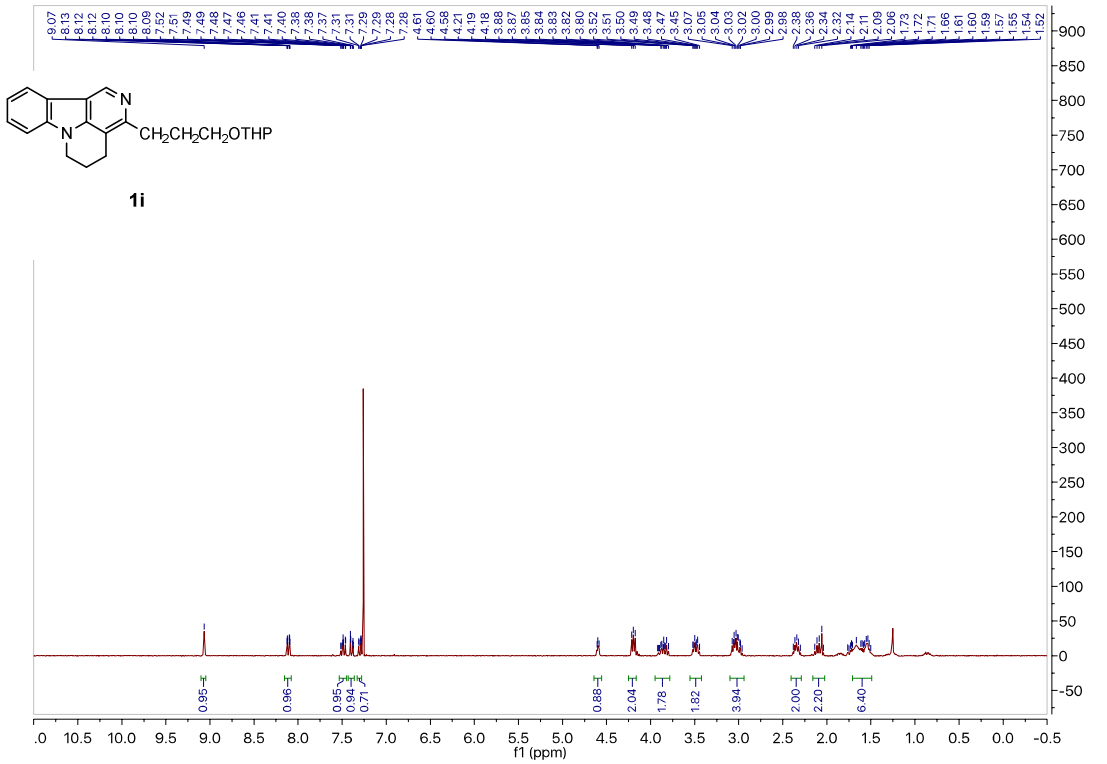


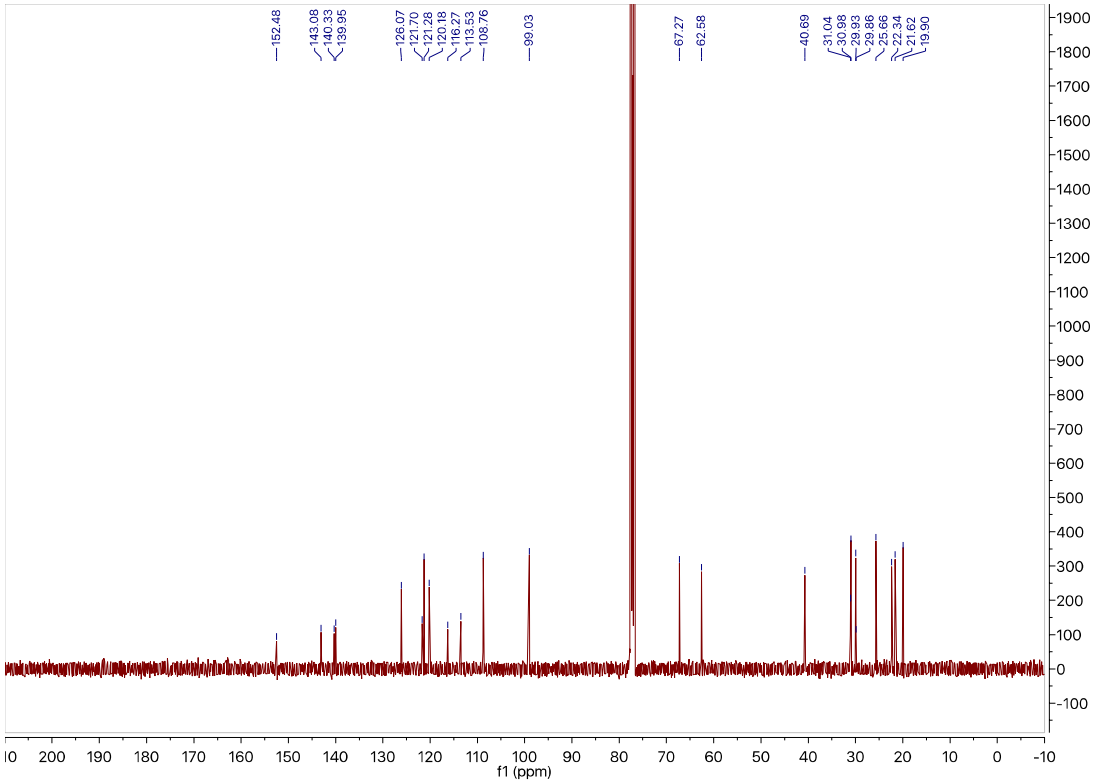

MeO2C
N
n-Bu
1g
f1 (ppm)

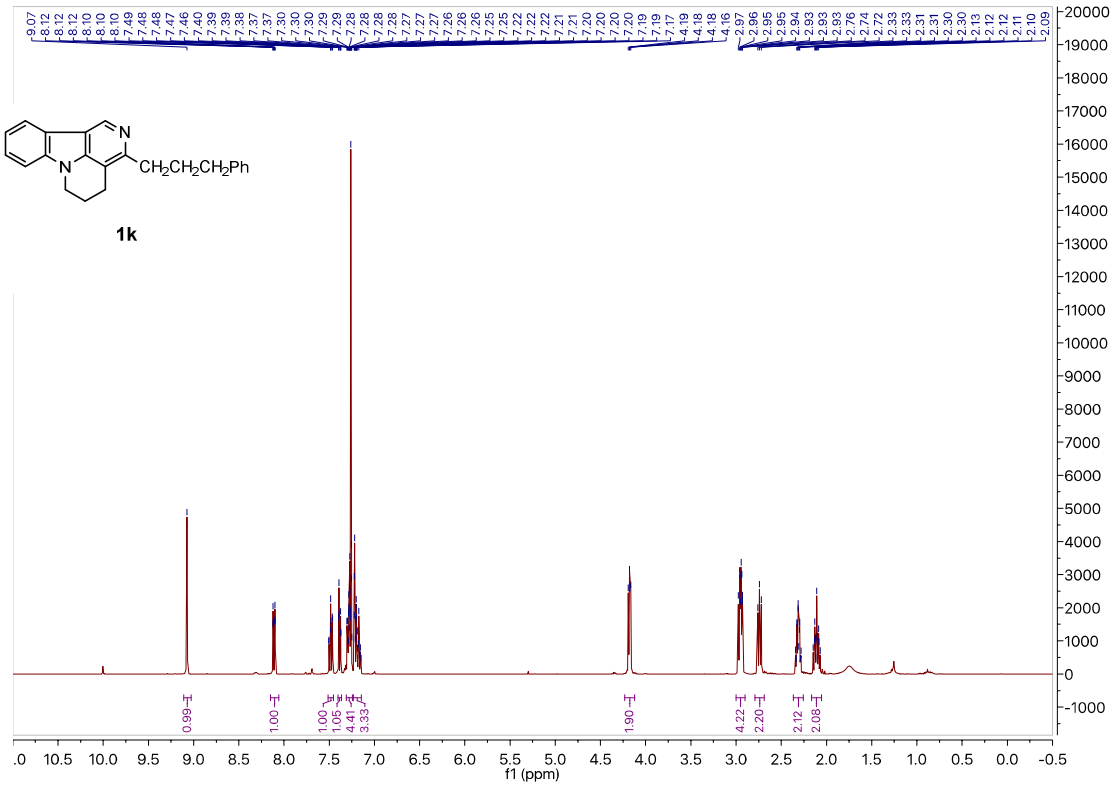

f1 (ppm)

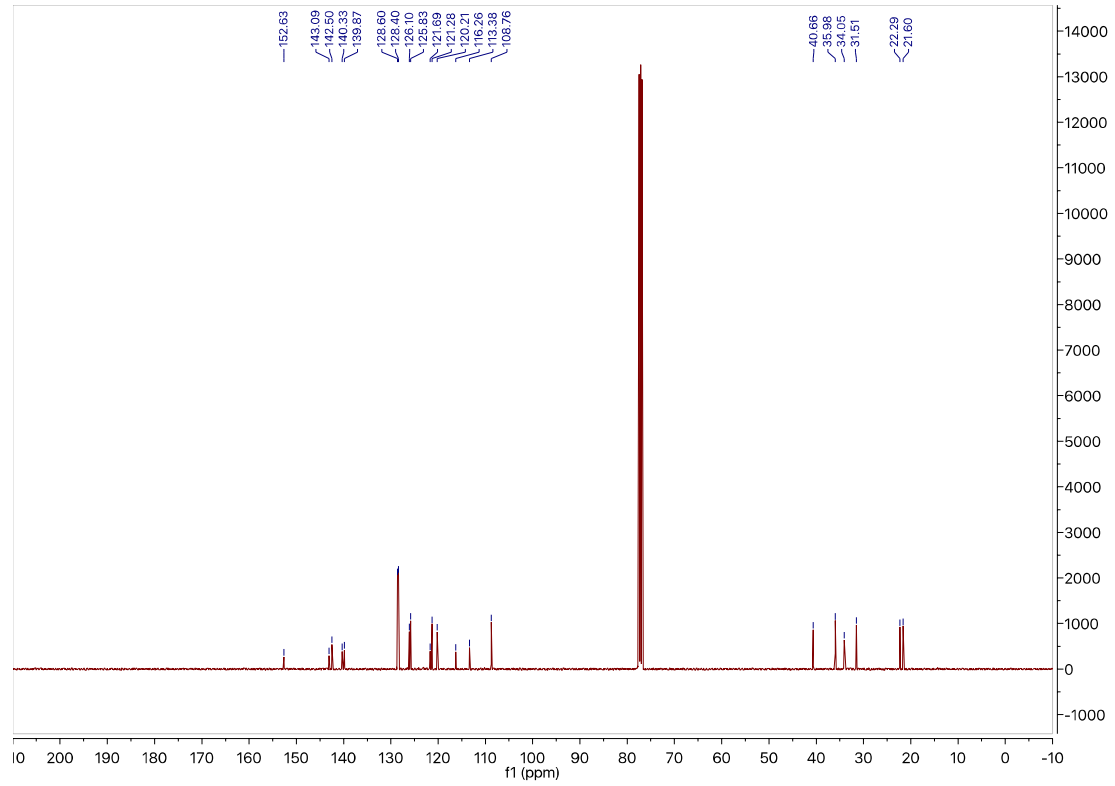

CH2OMe
1h
f1 (ppm)

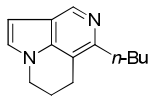

f1 (ppm)


CH2CH2CH2OTHP
1i
f1 (ppm)

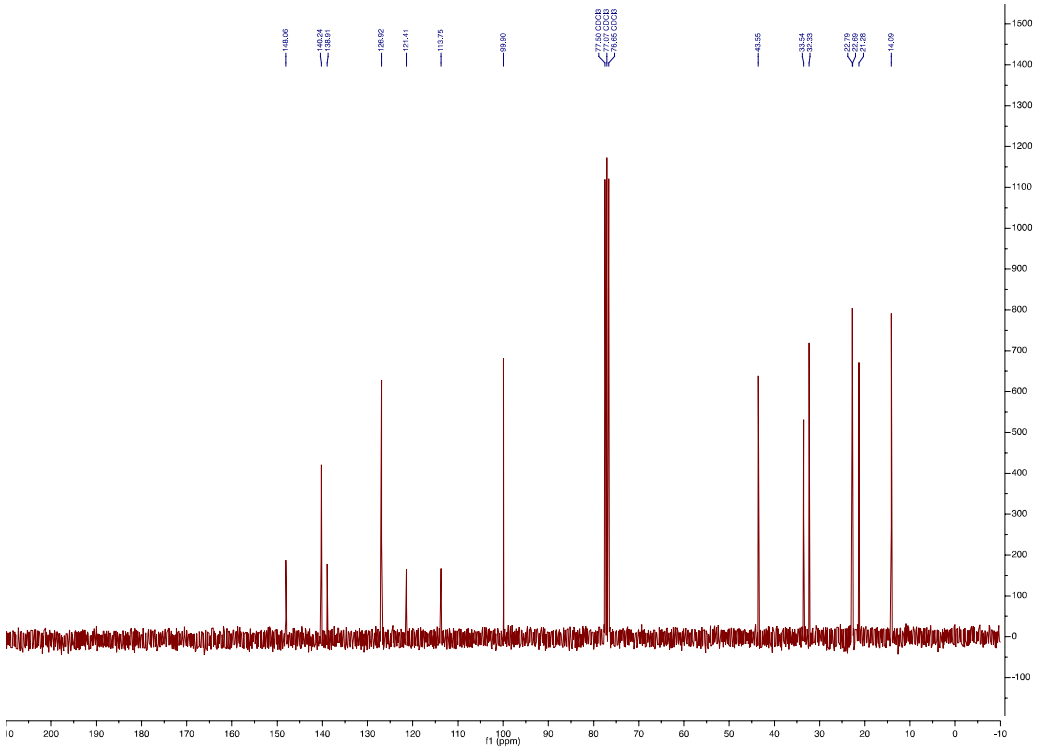

f1 (ppm)

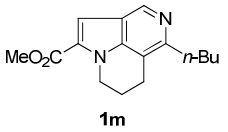

CH2CH2CH2Ph
1k
f1 (ppm)


f1 (ppm)



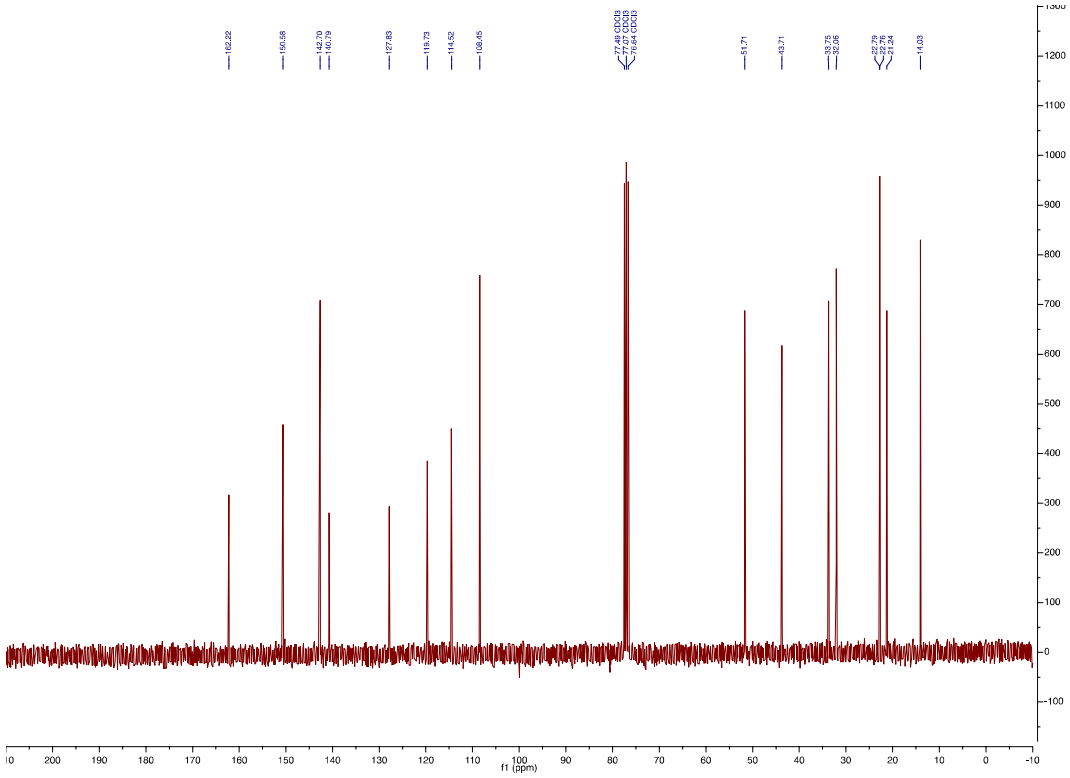
1l




MeO2C
N
N
n-Bu

1m

8.80
7.23
4.52
4.50
4.48
3.92
2.96
2.94
2.89
2.87
2.85
2.82
2.30
2.28
2.26
2.24
2.22
2.20
1.73
1.72
1.71
1.70
1.69
1.68
1.67
1.65
1.48
1.45
1.43
1.40
1.38
1.35
0.97
0.95
0.92
1.00
0.91
2.07
2.07
2.12
2.05
2.17
2.39
2.46
3.14
f1 (ppm)


162.22
150.58
142.70
140.79
127.83
116.73
114.52
108.45
77.49 CDCl3
77.07 CDCl3
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51.71
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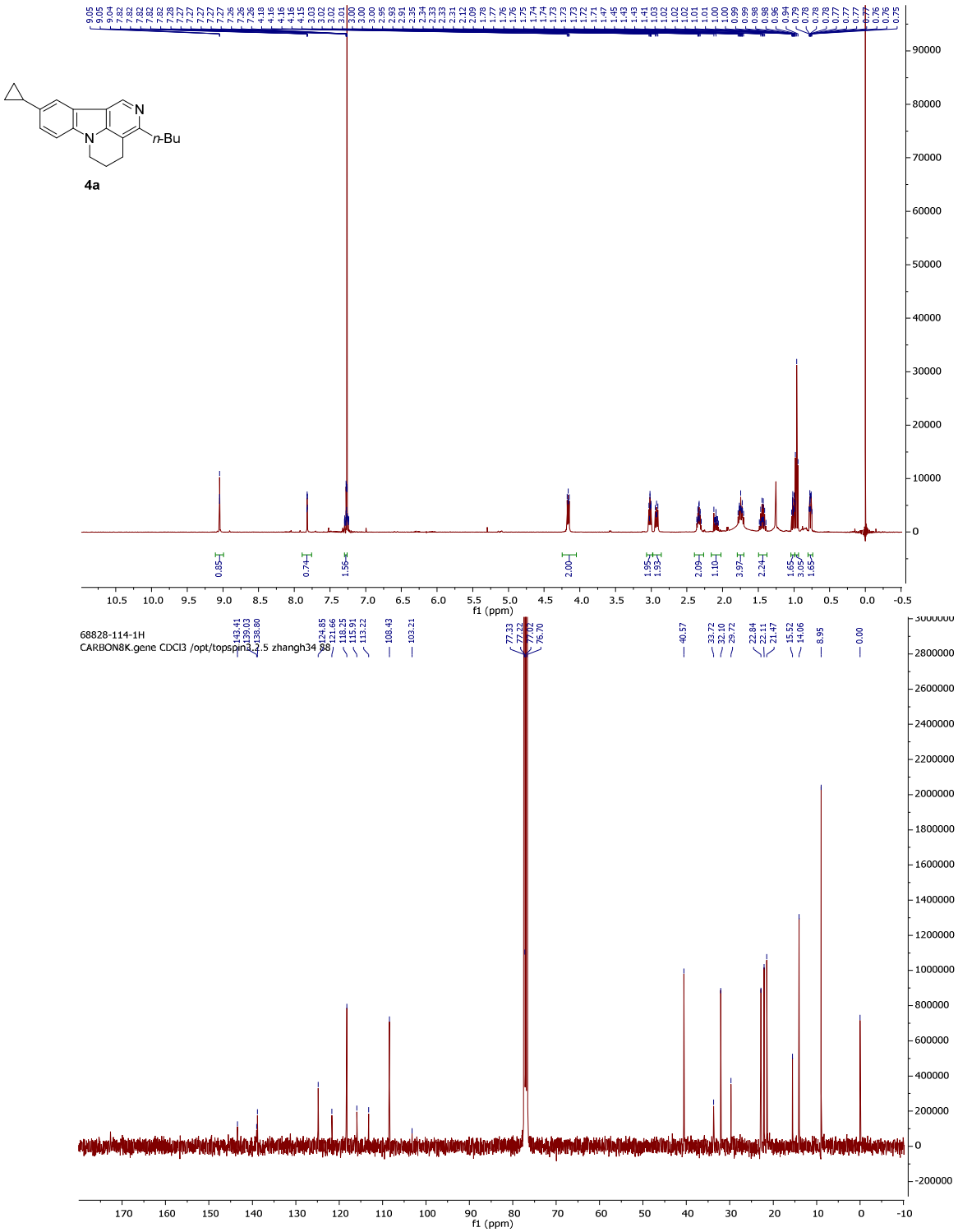
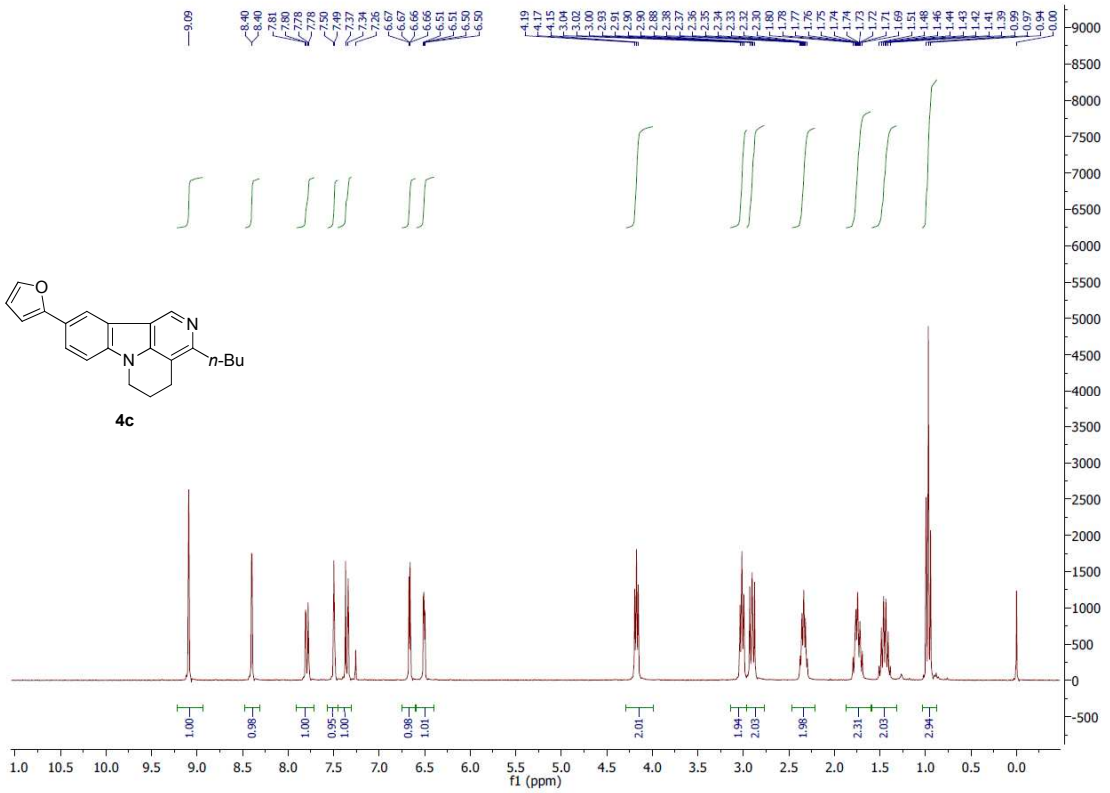
22.79
22.76
21.24
14.03
f1 (ppm)


n-Bu
4a
f1 (ppm)
68828-114-1H
CARBON8K.gene CDCl3 /opt/topspin3.2-5 zhangh34 88
f1 (ppm)



4c