Supporting Information for

Regioselective synthesis of 7-(trimethylsilylethynyl)pyrazolo[1,5-*a*]pyrimidines *via* reaction of pyrazolamines with enynones

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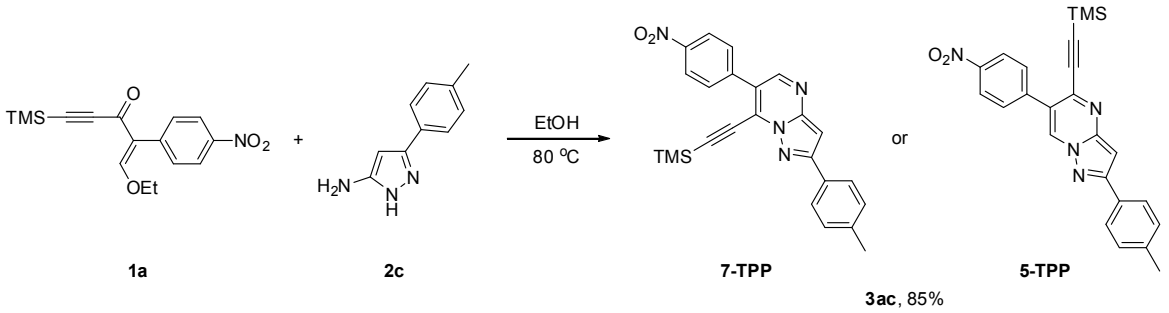
NMR structure evaluation for compound 3ac

Initially the reaction was tested using ketone **1a** and pyrazolamine **2c**, and a single product was isolated in 85% yield. According to its ^{1}H and ^{13}C NMR spectra and HRMS data, this product was identified as a (trimethylsilylethynyl)pyrazolo[1,5-*a*]pyrimidine. However, position of the alkynyl substituent could not be established unambiguously, and the product could either be a 7-(trimethylsilylethynyl)pyrazolopyrimidine (**7-TPP**) or a 5-(trimethylsilylethynyl)pyrazolo-pyrimidine (**5-TPP**). It is necessary to mention that signals of H^3 (δ = 7.08 ppm) and $H^{5(7)}$ (δ = 8.50 ppm) atoms are easy to distinguish in its ^{1}H NMR spectrum.



First, ^{1}H-^{15}N HMBC spectrum of the product was recorded (Figure 1). For both **5-TPP** and **7-TPP** one could expect to observe cross-peaks of H^3 proton with all three cyclic nitrogen atoms. But H^5 atom in **7-TPP** was expected to correlate with N^4 nitrogen atom (and probably with N^8), while H^7 proton in **5-TPP** would correlate with N^1 and N^8 nitrogen atoms (and probably with N^4).

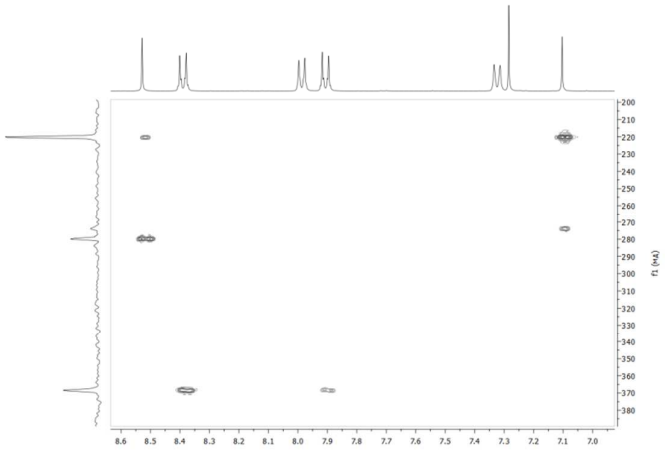


Figure 1. ^{1}H-^{15}N HMBC (400 MHz) spectrum of compound 3ac.

Projections of all four nitrogen atoms were visible in the spectrum at $\delta \approx 220$ (N^8), 270, 280 (N^1 and N^4) and 365 (NO_2) ppm. Unfortunately, not all cross-peaks were visible in the spectrum. Interaction between $\underline{N}O_2$ and protons of the adjacent aromatic ring was clearly seen. Nodal N^8 atom correlates

with both H^3 and $H^{5(7)}$. Each of this protons correlates with one of N^1 or N^4, but this is possible for **7-TPP** (H^3–$N^{1(4)}$, H^5–N^4), as well as for **5-TPP** (H^3–$N^{1(4)}$, H^7–N^1). We then proposed that choice between the two structures could be made on the basis of ^1H-^{15}N HSQMBC spectrum (Figure 2). Relying on the literature data[1] for ^1H-^{15}N spin-spin coupling constants in pyrrole and pyridine, we predicted ^1H-^{15}N constants sets for structures **7-TPP** and **5-TPP**. The key difference is a large N^4-H^5 constant ($^2J \approx 10$ Hz) in **7-TPP**, while all constants in **5-TPP** were expected to be lower.

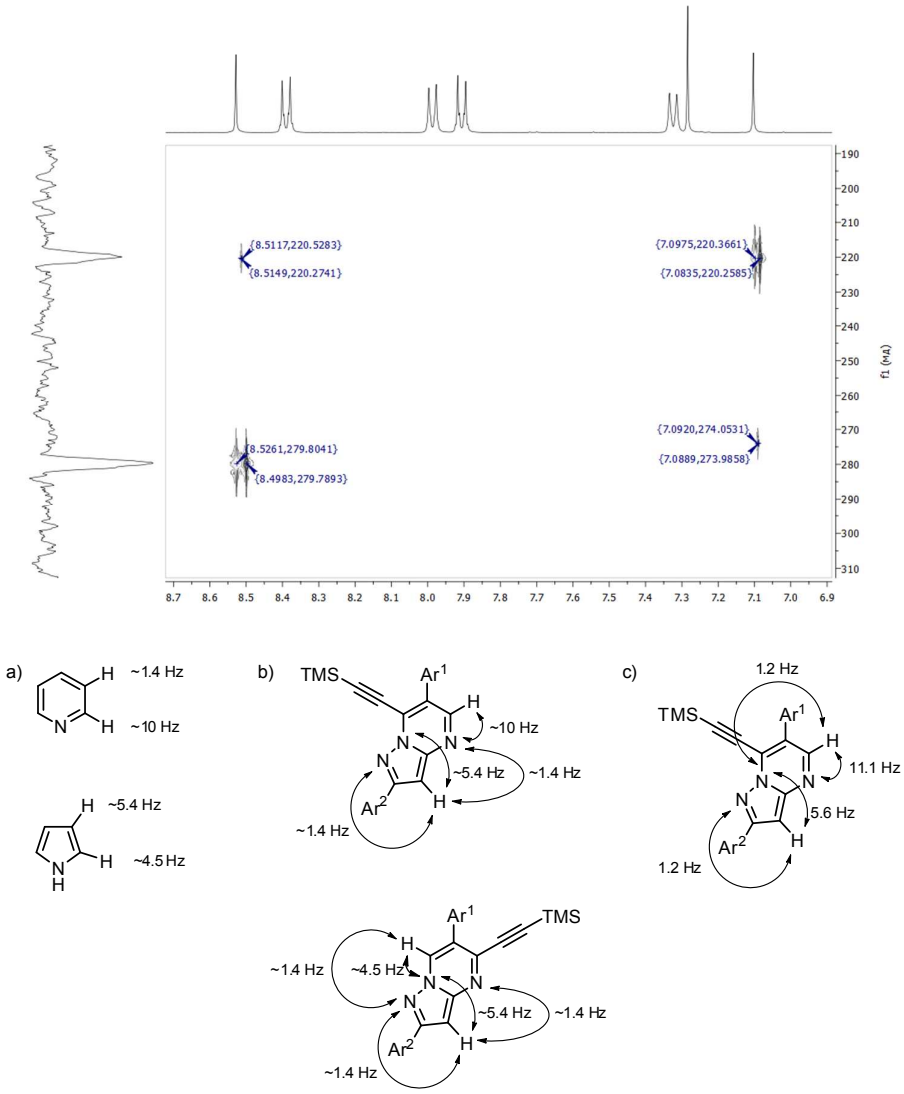


Figure 2. Top: ^1H-^{15}N HSQMBC (400 MHz) spectrum of compound 3ac. Bottom: N-H spin-spin coupling constants: a) literature data for pyridine and pyrrole;[1] b) predicted values for 7-TPP and 5-TPP; c) experimental data for the obtained product.

Experimental values of N-H spin-spin coupling constants were in agreement with those proposed for **7-TPP**, therefore the structure of 7-(trimethylsilylethynyl)pyrazolo[1,5-*a*]pyrimidine was ascribed to compound **3ac** and all obtained products.

X-Ray analysis data for compound 3aa

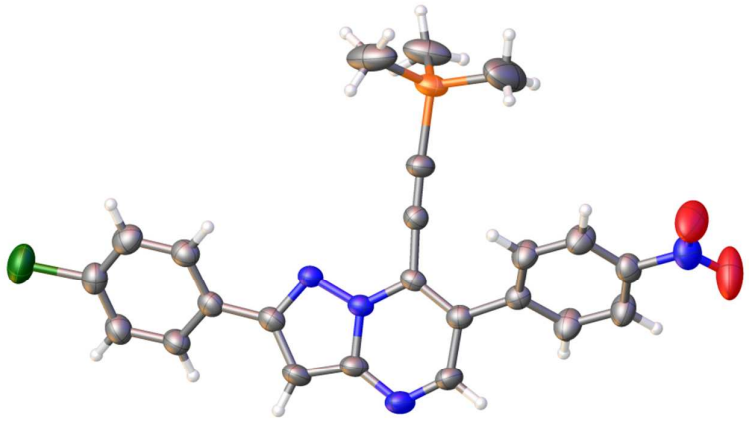


Figure 3. Olex2 representation of compound 3aa crystal structure.
Thermal ellipsoids are given at 50% probability level.

Single crystals of $C_{23}H_{19}ClN_4O_2Si$ were obtained from chloroform solution. A suitable crystal was selected and put on a diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2,[2] the structure was solved with the ShelXS[3] structure solution program using Direct Methods and refined with the XL[3] refinement package using CGLS minimization.

*Crystal structure determination of **3aa***

Crystal Data for $C_{23}H_{19}ClN_4O_2Si$ (M = 446.96 g/mol): monoclinic, space group Cc (no. 9), a = 6.9864(6) Å, b = 30.542(2) Å, c = 11.0261(8) Å, β = 106.329(8)°, V = 2257.8(3) Å^3, Z = 4, T = 100(2) K, μ(MoKα) = 0.249 mm^{-1}, *Dcalc* = 1.315 g/cm^3, 10094 reflections measured (6.222° ≤ 2Θ ≤ 52.99°), 4196 unique (R_{int} = 0.0175, R_{sigma} = 0.0223) which were used in all calculations. The final R_1 was 0.0339 (I > 2σ(I)) and wR_2 was 0.1095 (all data).

Refinement model description

Number of restraints - 2, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups

At 1.5 times of:

All C(H,H,H) groups

2.a Aromatic/amide H refined with riding coordinates:

C12(H12), C14(H14), C15(H15), C16(H16), C17(H17), C18(H18), C21(H21),

C22(H22), C24(H24), C27(H27)

2.b Idealised Me refined as rotating group:

C26(H26A,H26B,H26C), C29(H29A,H29B,H29C), C36(H36A,H36B,H36C)

Table 1. Crystal data and structure refinement for 3aa

Empirical formula	$C_{23}H_{19}ClN_4O_2Si$
Formula weight	446.96
Temperature/K	100(2)
Crystal system	monoclinic
Space group	Cc
a/Å	6.9864(6)
b/Å	30.542(2)
c/Å	11.0261(8)
α/°	90
β/°	106.329(8)
γ/°	90
Volume/Å^3	2257.8(3)
Z	4
ρ_{calc}g/cm^3	1.315
μ/mm^{-1}	0.249
F(000)	928.0
Crystal size/mm^3	0.22 × 0.20 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.222 to 52.99
Index ranges	-8 ≤ h ≤ 8, -35 ≤ k ≤ 38, -13 ≤ l ≤ 13
Reflections collected	10094
Independent reflections	4196 [R_{int} = 0.0175, R_{sigma} = 0.0223]
Data/restraints/parameters	4196/2/283
Goodness-of-fit on F^2	0.884
Final R indexes [I>=2σ (I)]	R_1 = 0.0339, wR_2 = 0.1052
Final R indexes [all data]	R_1 = 0.0362, wR_2 = 0.1095
Largest diff. peak/hole / e Å^{-3}	0.21/-0.18
Flack parameter	0.034(19)

Table 2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3aa. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Si1	519.0(13)	1198.7(3)	6402.9(8)	48.7(2)
Cl1	-10664.7(14)	2960.5(4)	-76.3(12)	77.4(3)
N2	-937(3)	1445.1(7)	1443.0(19)	33.6(4)
N3	-2422(3)	1681.9(7)	1687(2)	35.5(5)
C4	468(4)	1209.1(7)	2328(2)	32.1(5)

C5	1852(4)	982.9(8)	1899(3)	35.7(5)
C6	412(4)	1229.2(8)	3610(3)	36.1(6)
C7	-3393(4)	1852.8(9)	549(2)	37.9(6)
C8	3398(4)	697.2(8)	2696(2)	34.9(5)
C9	-5151(4)	2133.9(9)	432(3)	37.4(5)
C10	430(4)	1232.5(10)	4697(3)	43.5(7)
C11	-962(5)	1462.8(9)	179(3)	40.2(6)
C12	-6312(5)	2093(1)	1260(3)	44.0(6)
C13	-8516(5)	2646.5(10)	142(3)	49.6(7)
C14	2981(4)	407.1(9)	3566(3)	45.3(7)
C15	-5700(5)	2443.2(10)	-531(3)	43.8(6)
C16	1728(4)	1021.5(10)	586(3)	42.7(6)
C17	5306(5)	696.9(11)	2545(3)	50.5(7)
C18	-2540(5)	1729.1(10)	-395(3)	44.7(6)
N19	419(4)	1243.9(9)	-242(2)	48.1(6)
C20	6284(4)	125.7(9)	4045(3)	45.1(6)
C21	-7996(5)	2348.5(11)	1128(3)	51.3(7)
C22	4426(5)	118.8(10)	4248(3)	50.6(7)
N23	7822(5)	-177.7(10)	4767(3)	61.3(8)
C24	-7376(5)	2700.2(10)	-680(3)	49.4(7)
O25	9526(5)	-129.5(13)	4683(5)	102.6(13)
C26	1283(9)	1736.6(15)	7134(4)	78.0(13)
C27	6754(4)	409.8(11)	3215(3)	51.9(7)
O28	7336(5)	-467.6(12)	5361(4)	96.1(12)
C29	-2024(8)	1052(2)	6463(4)	94.8(18)
C36	2383(11)	776(2)	7099(5)	113(2)

Table 3. Anisotropic Displacement Parameters ($Å^2×10^3$) for 3aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	66.5(5)	52.2(5)	28.1(4)	3.5(3)	14.2(4)	0.5(4)
Cl1	53.5(5)	85.1(7)	94.9(8)	3.8(5)	23.0(5)	22.3(5)
N2	39.6(11)	35.4(10)	26.5(10)	0.5(8)	10.3(9)	-0.1(9)
N3	40.1(11)	38.9(10)	27.9(10)	2.1(8)	10.3(9)	4.6(9)
C4	37.6(12)	30.2(11)	27.1(12)	1.2(8)	6.7(10)	-4.4(9)
C5	38.8(12)	35.7(12)	34.3(13)	0.1(10)	12.9(11)	-3.4(11)
C6	37.4(12)	36.6(13)	34.0(14)	2.0(9)	9.6(11)	2.1(10)
C7	40.3(13)	39.1(12)	31.9(13)	0.2(10)	6.3(11)	-3.2(10)
C8	37.3(12)	32.8(11)	35.7(13)	-1.2(9)	12.4(11)	-1.6(10)
C9	36.2(12)	39.9(13)	33.2(13)	-1.1(10)	5.2(11)	-3.3(10)
C10	52.1(16)	48.6(15)	31.1(15)	1.8(10)	14.2(13)	5.4(12)
C11	50.7(15)	43.4(13)	27.9(12)	1.9(10)	13.2(12)	2.4(12)
C12	45.4(15)	45.9(14)	40.9(15)	4.9(11)	12.2(13)	-2.9(12)
C13	40.0(14)	49.0(15)	57.0(19)	-1.1(13)	9.1(14)	3.3(12)
C14	41.5(14)	45.0(15)	54.6(17)	9.9(12)	21.9(13)	2.3(11)
C15	43.1(14)	51.8(15)	35.9(14)	6.2(11)	10.1(12)	1.2(12)

C16	48.9(15)	47.4(15)	35.6(14)	0.2(11)	18.2(12)	7.7(12)
C17	45.5(15)	47.7(16)	64.4(19)	14.5(13)	25.4(15)	1.2(12)
C18	52.7(15)	53.2(15)	26.1(12)	3.0(11)	7.4(12)	5.5(13)
N19	60.6(16)	55.2(14)	31.5(13)	0.7(10)	17.7(12)	10.7(12)
C20	45.9(15)	38.3(14)	49.1(16)	2.6(12)	10.0(13)	7.5(11)
C21	45.6(16)	56.4(17)	56.0(19)	-2.6(14)	20.7(14)	-6.3(13)
C22	58.1(18)	41.8(15)	58.7(19)	13.8(13)	27.6(15)	7.4(13)
N23	60.5(18)	57.6(16)	64.0(18)	11.3(14)	14.3(15)	19.1(13)
C24	46.0(15)	51.8(16)	47.8(17)	9.1(13)	8.8(13)	4.9(13)
O25	49.9(16)	99(2)	155(4)	50(2)	22.6(19)	21.1(16)
C26	126(4)	70(2)	38.7(17)	-2.8(15)	25(2)	-21(2)
C27	38.5(14)	54.6(17)	66(2)	12.8(15)	20.2(14)	6.3(13)
O28	94(2)	100(2)	106(3)	60(2)	48(2)	46(2)
C29	106(4)	134(5)	56(3)	-24(3)	42(3)	-45(4)
C36	163(6)	116(4)	57(3)	28(3)	25(3)	65(4)

Table 4. Bond Lengths for 3aa

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si1	C10	1.867(3)	C8	C17	1.389(4)
Si1	C26	1.842(4)	C9	C12	1.386(4)
Si1	C29	1.852(5)	C9	C15	1.392(4)
Si1	C36	1.840(5)	C11	C18	1.373(4)
Cl1	C13	1.740(3)	C11	N19	1.358(4)
N2	N3	1.352(3)	C12	C21	1.385(5)
N2	C4	1.377(3)	C13	C21	1.386(5)
N2	C11	1.389(3)	C13	C24	1.374(5)
N3	C7	1.352(3)	C14	C22	1.391(4)
C4	C5	1.375(4)	C15	C24	1.380(5)
C4	C6	1.427(4)	C16	N19	1.289(4)
C5	C8	1.472(4)	C17	C27	1.385(4)
C5	C16	1.431(4)	C20	C22	1.378(5)
C6	C10	1.195(4)	C20	N23	1.472(4)
C7	C9	1.474(4)	C20	C27	1.367(4)
C7	C18	1.389(4)	N23	O25	1.229(5)
C8	C14	1.395(4)	N23	O28	1.205(4)

Table 5. Bond Angles for 3aa

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C26	Si1	C10	108.38(16)	C15	C9	C7	120.4(3)
C26	Si1	C29	111.2(3)	C6	C10	Si1	176.1(3)
C29	Si1	C10	106.80(17)	C18	C11	N2	105.5(2)
C36	Si1	C10	106.2(2)	N19	C11	N2	120.9(2)
C36	Si1	C26	111.0(3)	N19	C11	C18	133.6(2)
C36	Si1	C29	112.9(3)	C21	C12	C9	121.2(3)
N3	N2	C4	124.95(19)	C21	C13	Cl1	119.7(3)
N3	N2	C11	112.6(2)	C24	C13	Cl1	118.7(3)

C4	N2	C11	122.4(2)	C24	C13	C21	121.5(3)
C7	N3	N2	103.6(2)	C22	C14	C8	120.9(3)
N2	C4	C6	117.8(2)	C24	C15	C9	121.3(3)
C5	C4	N2	116.7(2)	N19	C16	C5	126.1(3)
C5	C4	C6	125.4(2)	C27	C17	C8	121.2(3)
C4	C5	C8	124.2(2)	C11	C18	C7	105.8(2)
C4	C5	C16	117.2(2)	C16	N19	C11	116.6(2)
C16	C5	C8	118.6(2)	C22	C20	N23	118.7(3)
C10	C6	C4	177.1(3)	C27	C20	C22	122.2(3)
N3	C7	C9	119.6(2)	C27	C20	N23	119.1(3)
N3	C7	C18	112.4(3)	C12	C21	C13	118.7(3)
C18	C7	C9	127.9(3)	C20	C22	C14	118.4(3)
C14	C8	C5	121.8(2)	O25	N23	C20	117.3(3)
C17	C8	C5	119.8(2)	O28	N23	C20	118.8(3)
C17	C8	C14	118.4(3)	O28	N23	O25	123.8(3)
C12	C9	C7	121.1(3)	C13	C24	C15	118.9(3)
C12	C9	C15	118.4(3)	C20	C27	C17	118.8(3)

Table 6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3aa

Atom	*x*	*y*	*z*	U(eq)
H12	-5954	1890	1914	53
H14	1719	407	3691	54
H15	-4923	2477	-1084	53
H16	2680	872	303	51
H17	5616	893	1984	61
H18	-2953	1810	-1242	54
H21	-8763	2321	1690	62
H22	4146	-74	4828	61
H24	-7727	2906	-1325	59
H26A	2695	1772	7283	117
H26B	957	1754	7923	117
H26C	594	1964	6579	117
H27	8024	410	3102	62
H29A	-2839	985	5627	142
H29B	-2595	1295	6794	142
H29C	-1957	802	7000	142
H36A	2147	522	6567	170
H36B	2278	699	7922	170
H36C	3695	888	7172	170

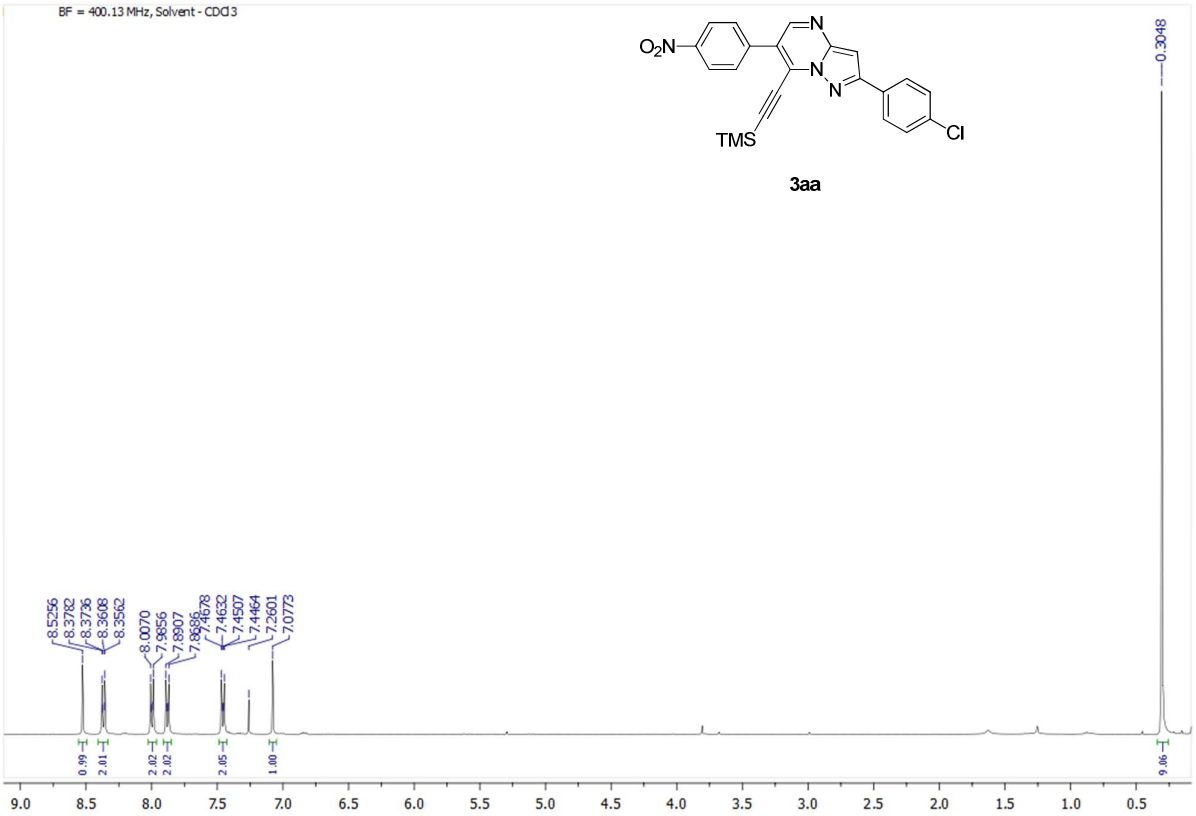
References

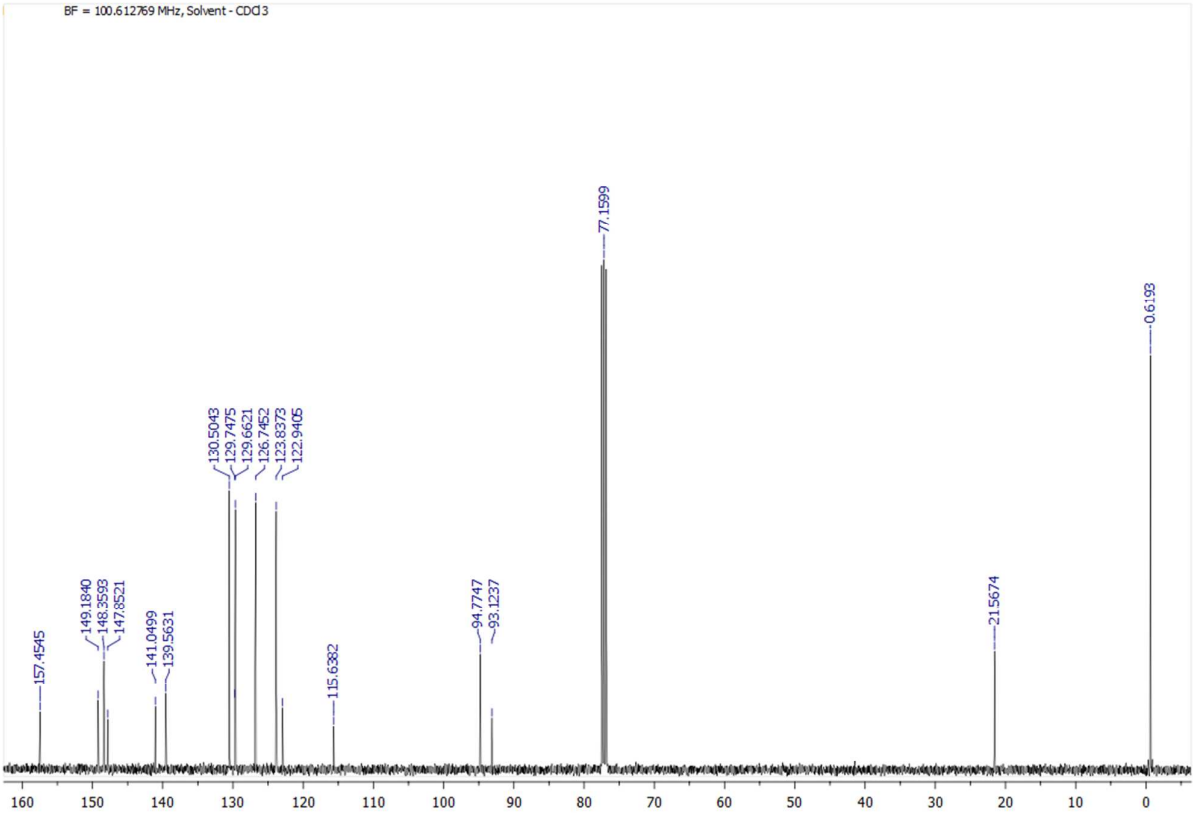
[1]. (a) Jakobsen, H.J.; Brey, W.S. *J. Chem. Soc., Chem. Commun.* **1979**, 478-479; (b) Bundgaard, T.; Jakobsen, H.J. *Tetrahedron Lett.* **1976**, *17*, 1621-1624; (c) Hawkes, G.E.; Randall, E.W.; Elguero, J.; Marzin, C.J. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1024-1027.

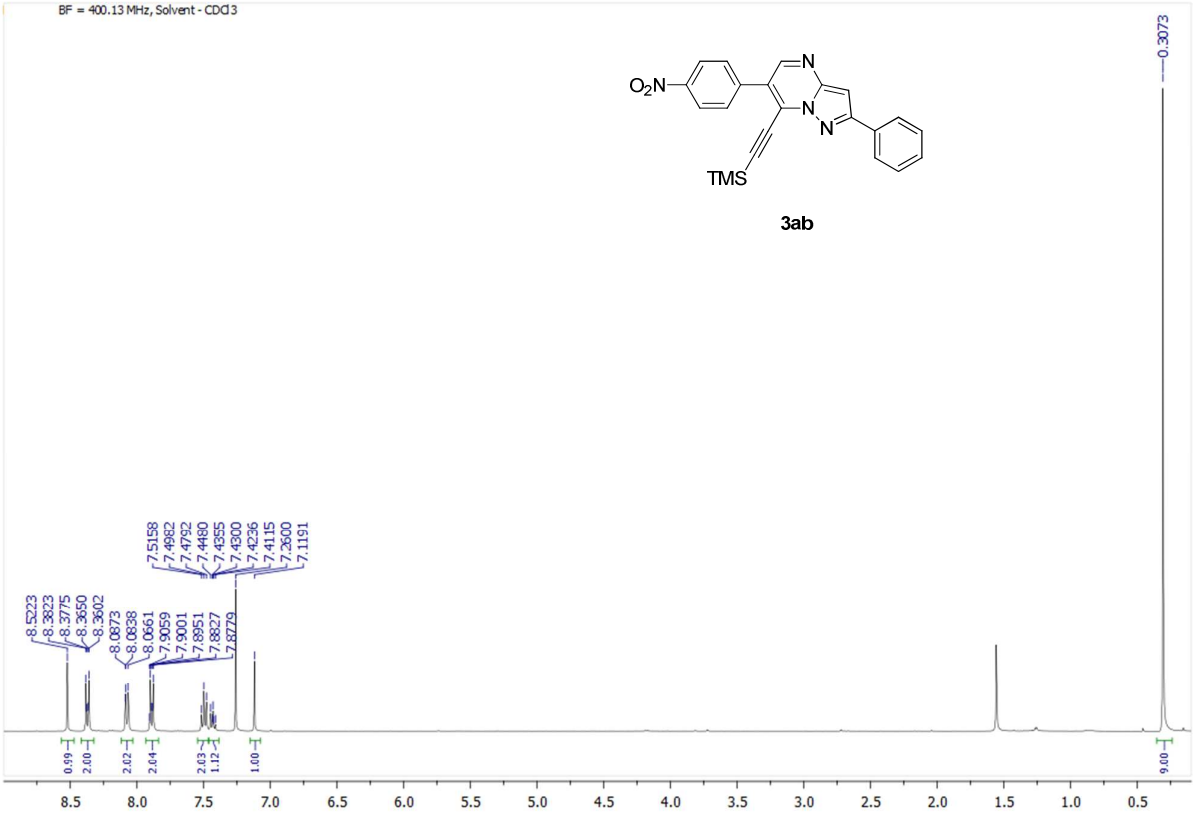
[2]. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

[3]. Sheldrick, G.M. *Acta Cryst.* **2008**, *A64*, 112-122.

Copies of the NMR spectra



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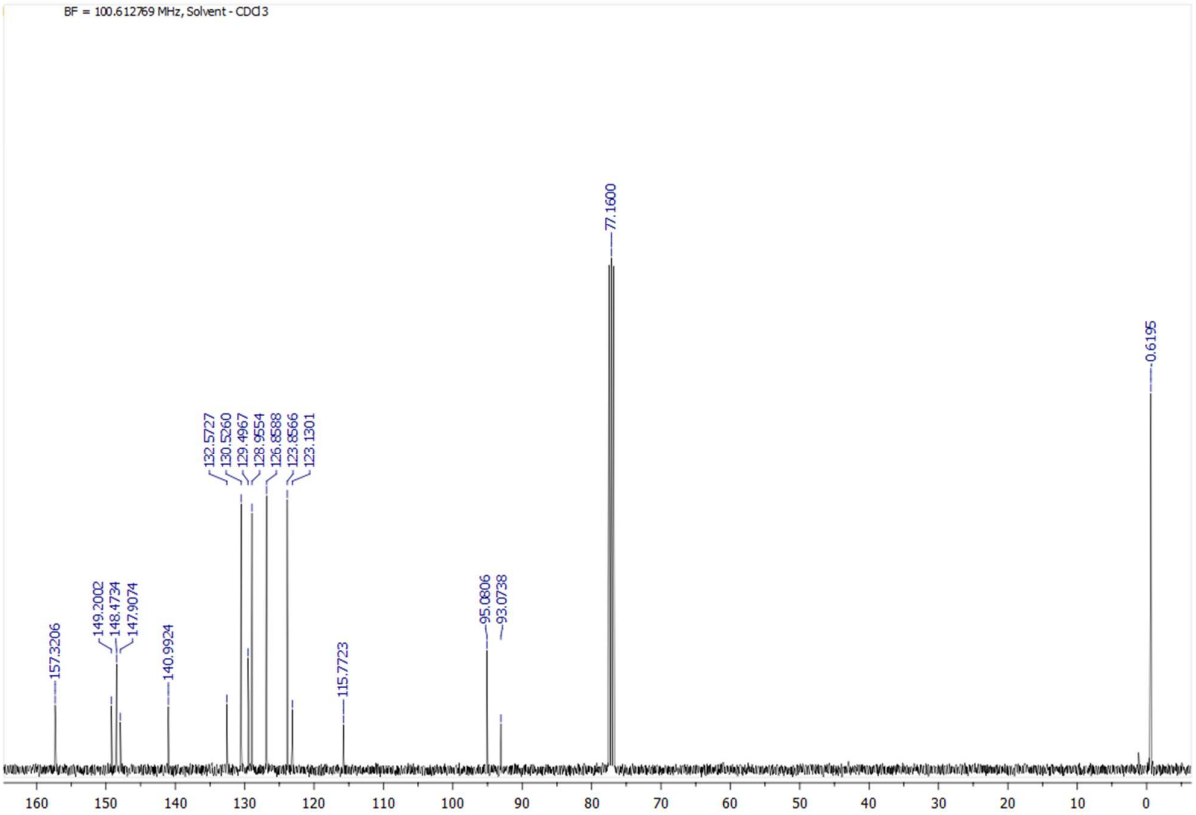
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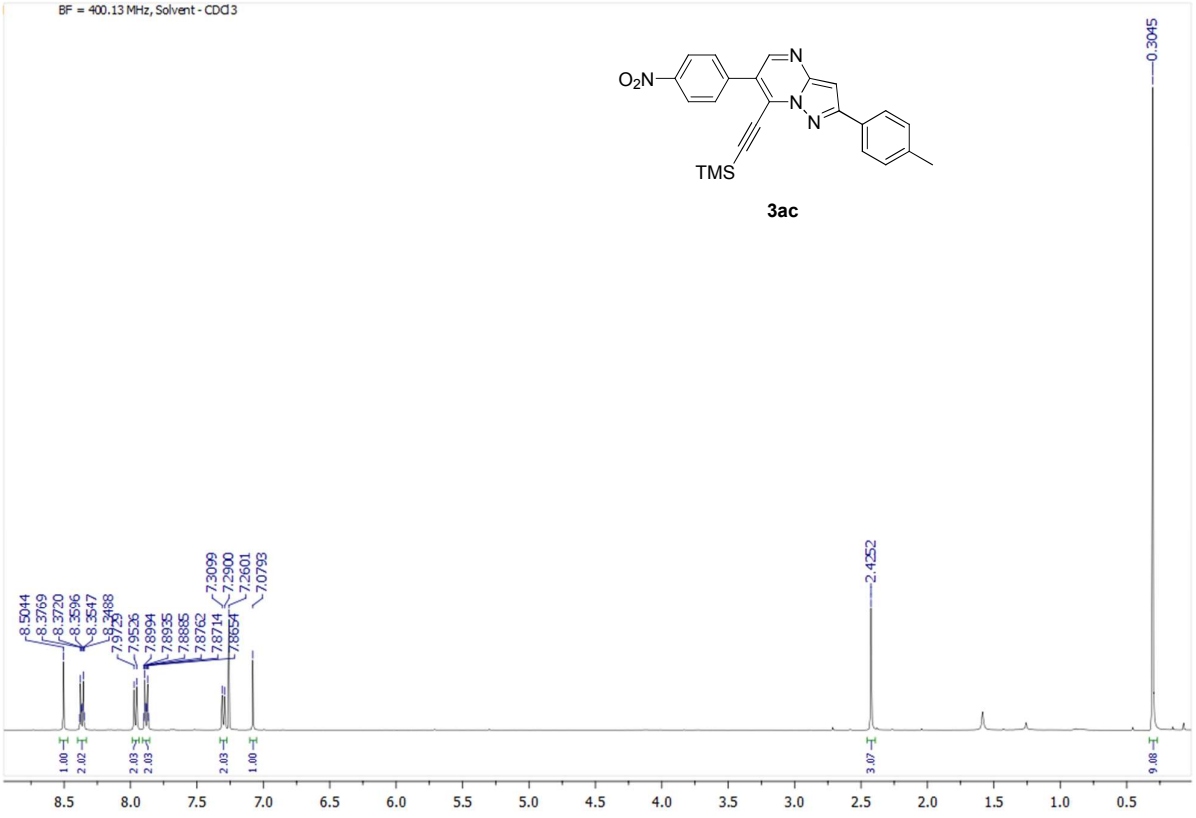
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7.9529
7.9526
7.8994
7.8935
7.8885
7.8762
7.8714
7.8654
7.3099
7.2900
7.2601
7.0793
1.00
2.02
2.03
2.03
2.03
1.00
3.07
9.88
8.5
8.0
7.5
7.0
6.5
6.0
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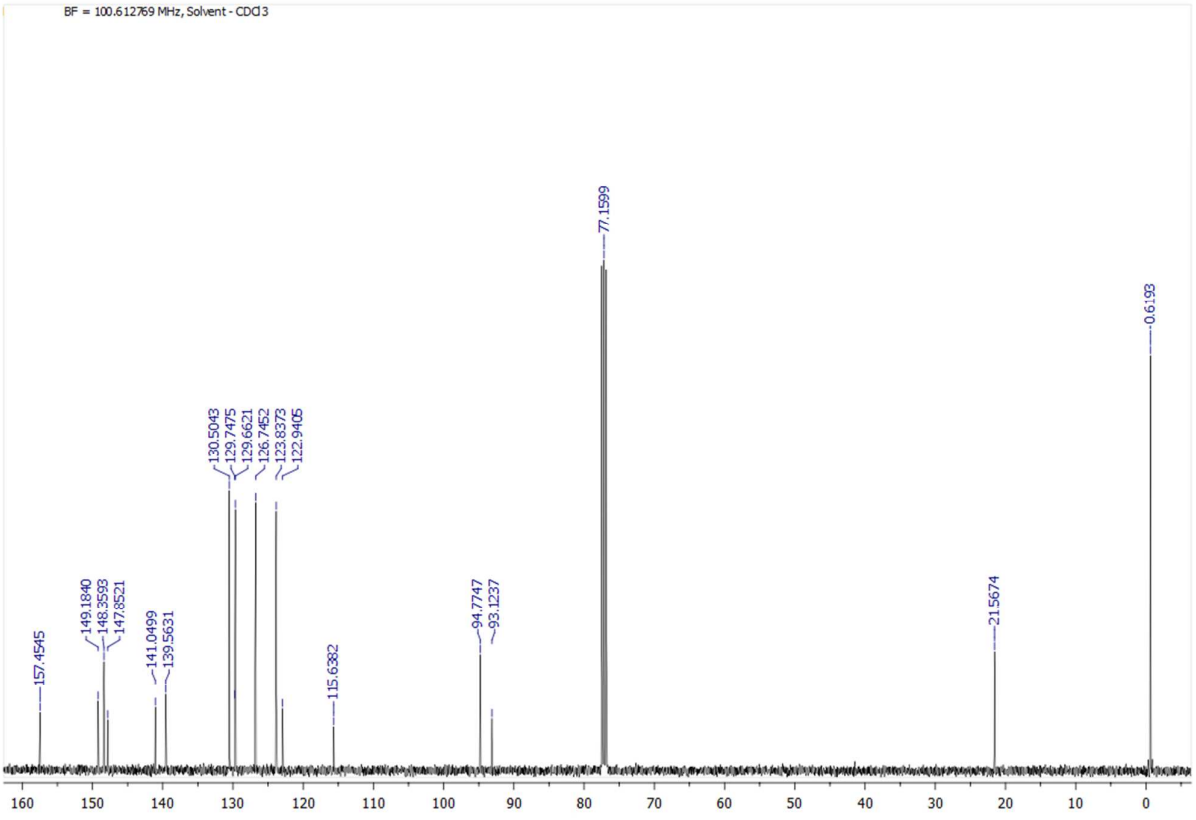
1.0
0.5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0.6193
130.5043
129.7475
129.6621
126.7452
123.8373
122.9405
157.4545
149.1840
148.3593
147.8521
141.0499
139.5631
115.6382
94.7747
93.1237
21.5674
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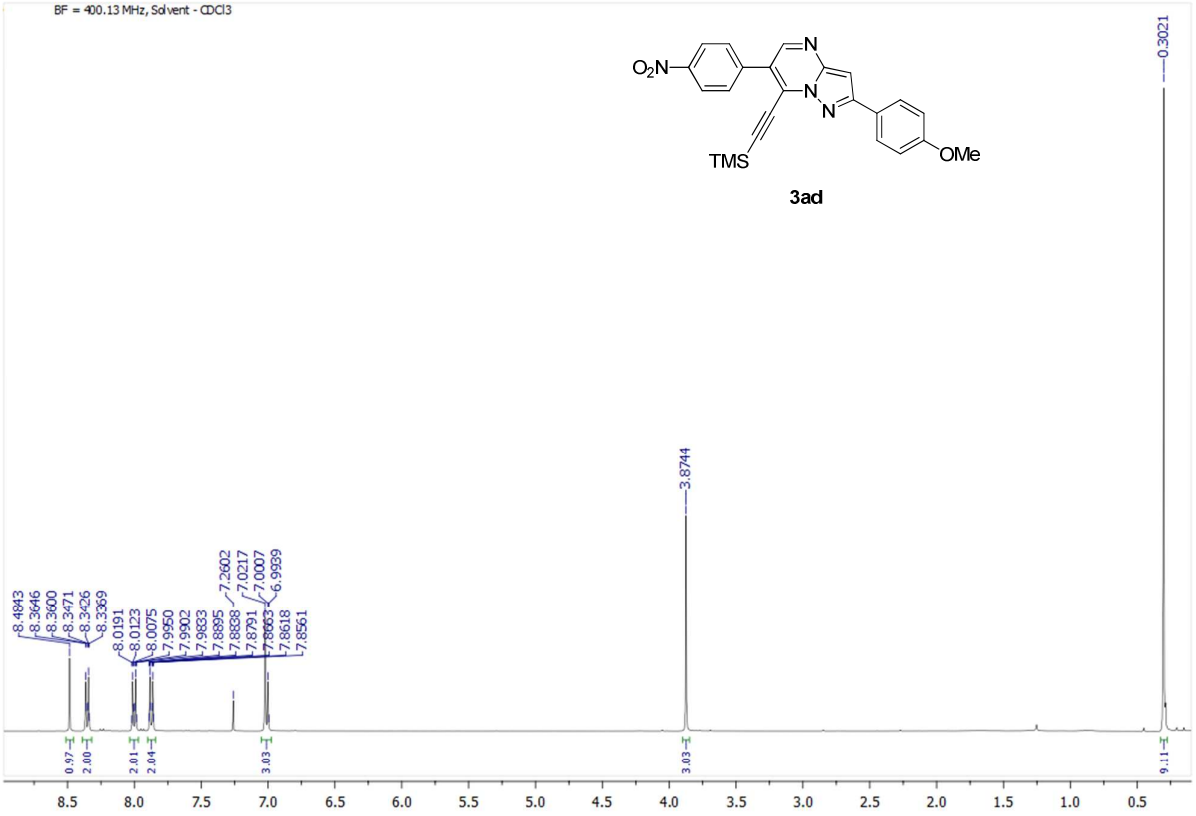
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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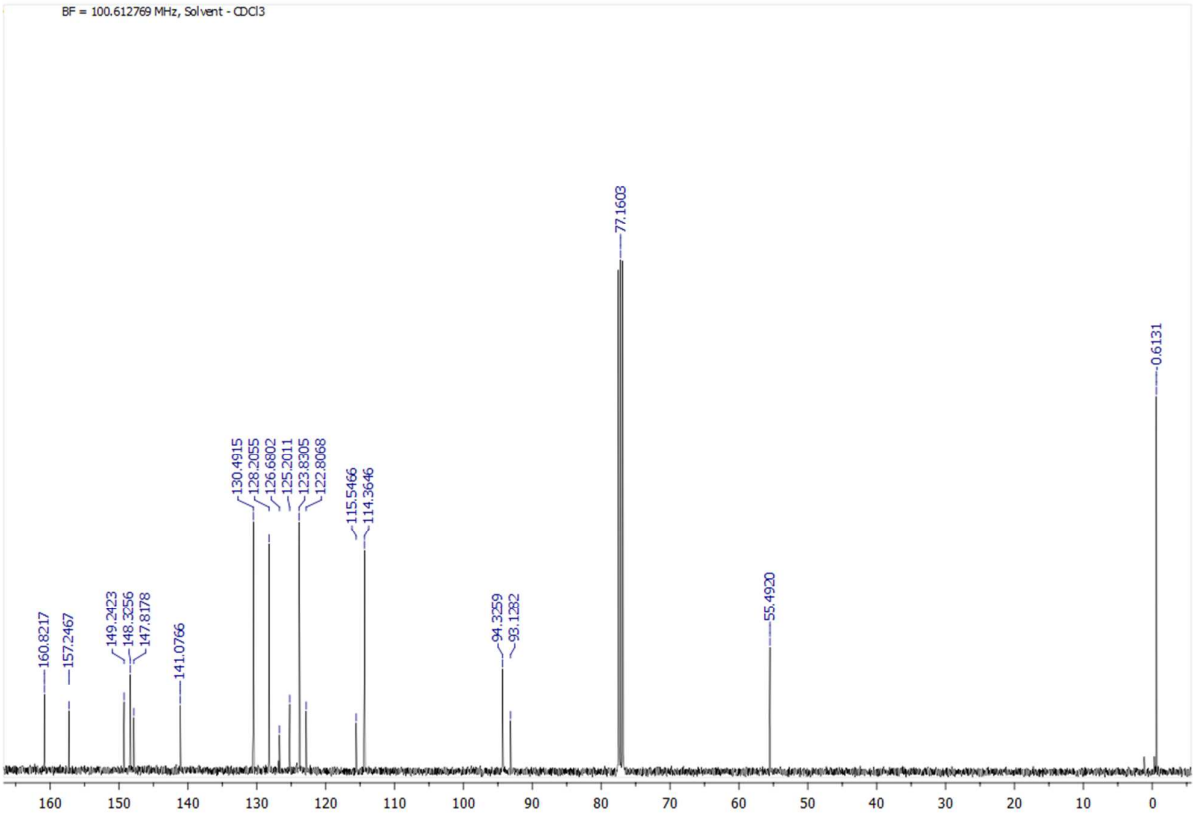
N
N
N
TMS
OMe
3ad
0.3021
3.8744
8.4843
8.3646
8.3600
8.3471
8.3426
8.3369
8.0191
8.0123
8.0075
7.9950
7.9902
7.9833
7.8895
7.8838
7.8791
7.8663
7.8618
7.8561
7.2602
7.0217
7.0007
6.9939
0.97
2.00
2.01
2.04
3.03
3.03
9.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


BF = 100.612769 MHz, Solvent - CDCl3
77.1603
0.6131
130.4915
128.2055
126.6802
125.2011
123.8305
122.8068
115.5466
114.3646
160.8217
157.2467
149.2423
148.3256
147.8178
141.0766
94.3259
93.1282
55.4920
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150
140
130
120
110
100
90
80
70
60
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30
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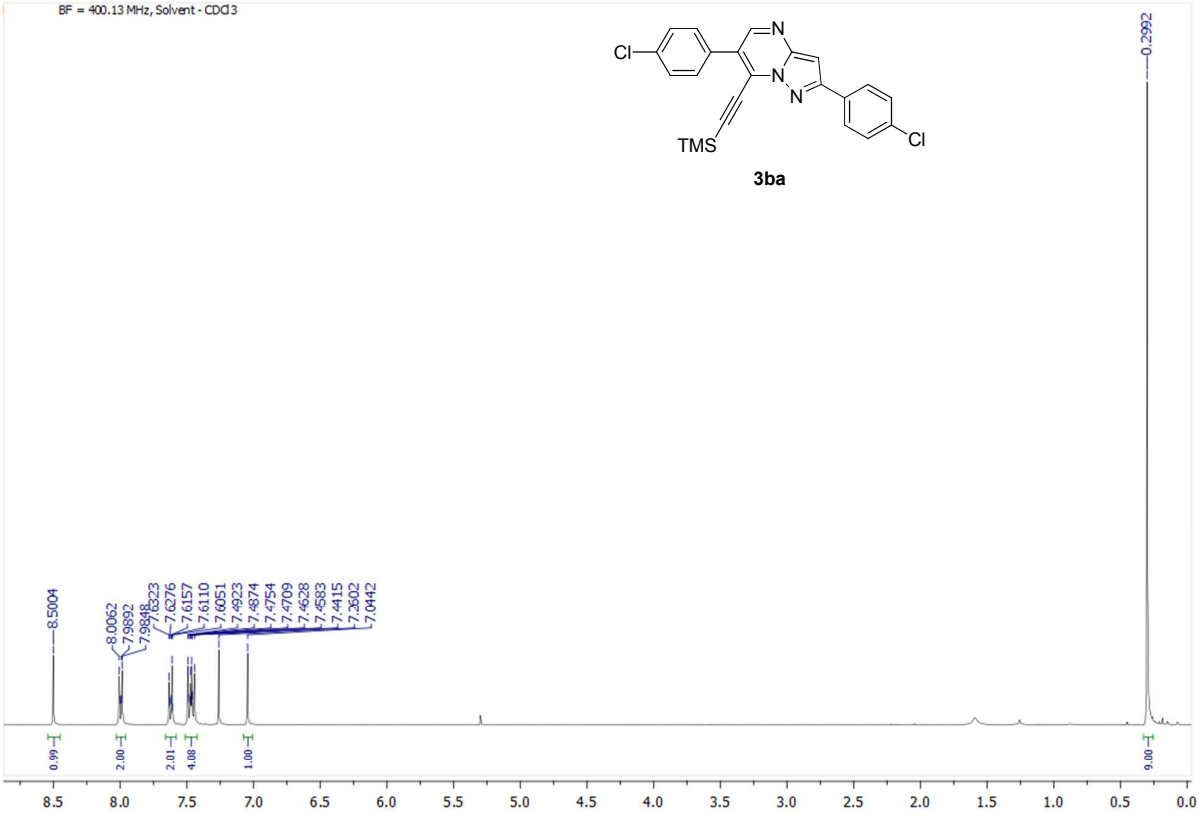
10
0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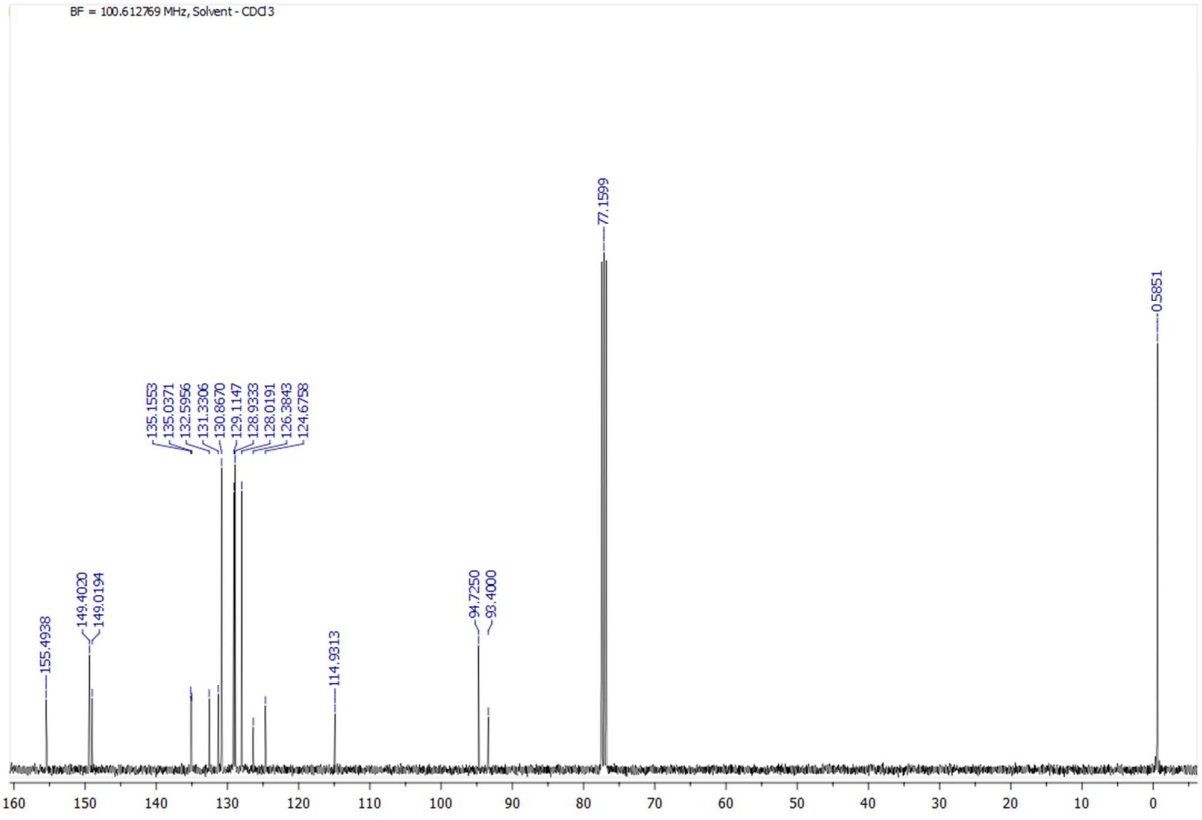
N
N
N
TMS
Cl
3ba
0.2992
8.5004
8.0062
7.9892
7.9848
7.6323
7.6276
7.6157
7.6110
7.6051
7.4923
7.4874
7.4754
7.4709
7.4628
7.4583
7.4415
7.3602
7.0442
0.99
2.00
2.01
4.08
1.00
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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0.5851
135.1553
135.0371
132.5956
131.3306
130.8670
129.1147
128.9333
128.0191
126.3843
124.6758
155.4938
149.4020
149.0194
114.9313
94.7250
93.4000
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150
140
130
120
110
100
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70
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30
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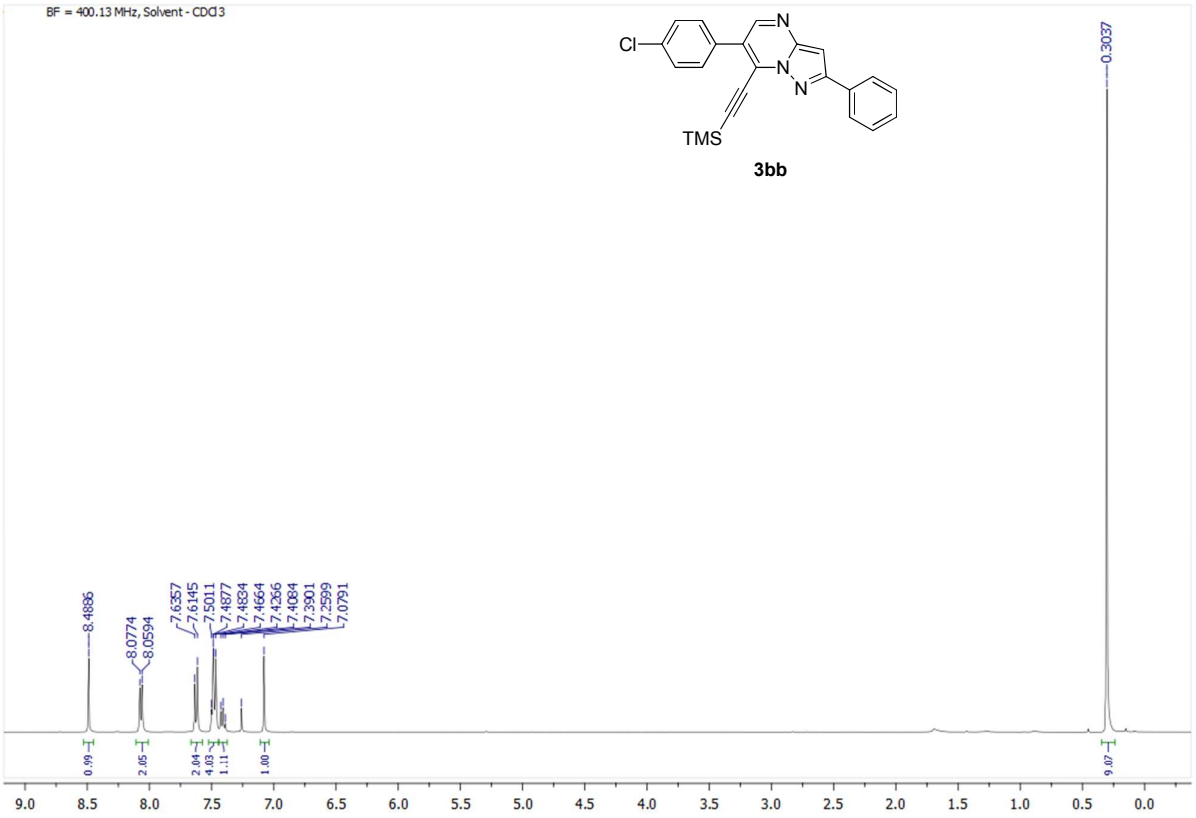
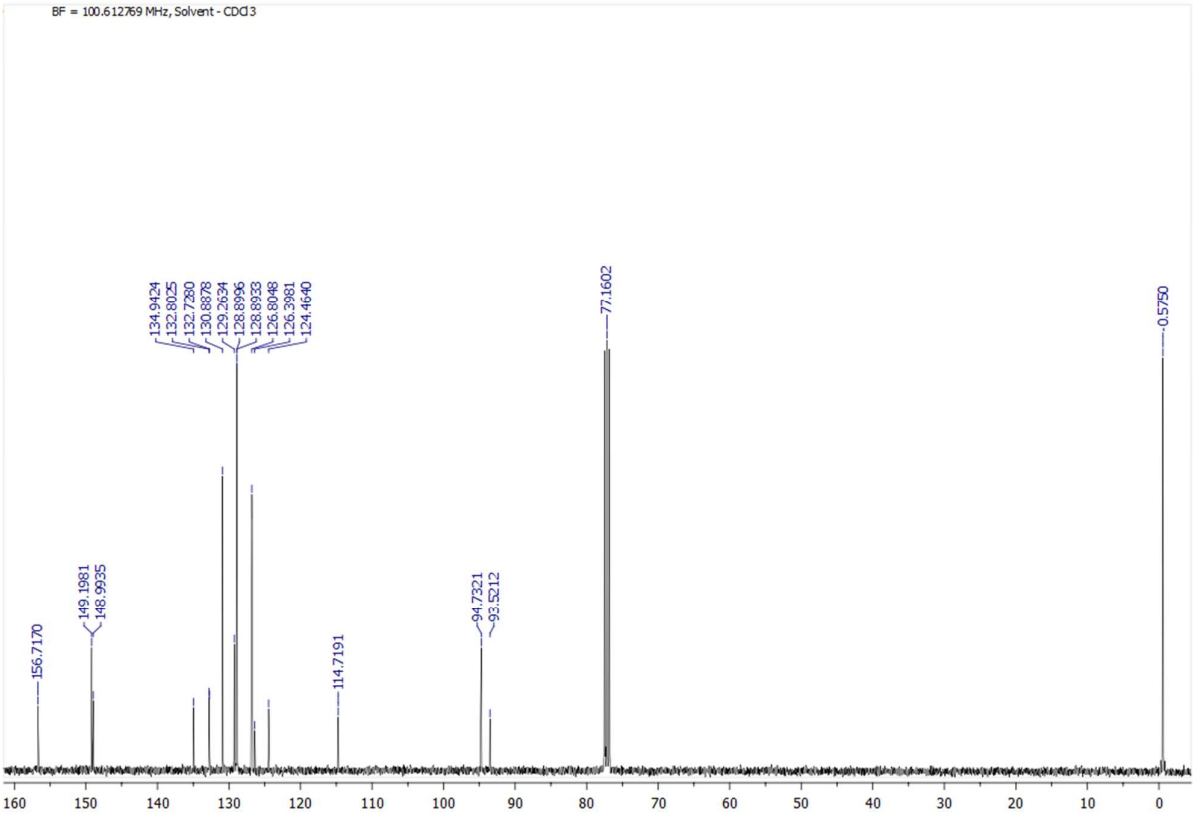

BF = 400.13 MHz, Solvent - CDCl3
Cl
N
N
N
TMS
3bb
0.3037
8.4886
8.0774
8.0594
7.6357
7.6145
7.5011
7.4877
7.4834
7.4664
7.4256
7.4084
7.3901
7.2599
7.0791
0.99
2.05
2.04
4.03
1.11
1.00
9.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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134.9424
132.8025
132.7280
130.8878
129.2634
128.8996
128.8933
126.8048
126.3981
124.4640
77.1602
0.5750
156.7170
149.1981
148.9935
114.7191
94.7321
93.5212
160
150
140
130
120
110
100
90
80
70
60
50
40
30
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10
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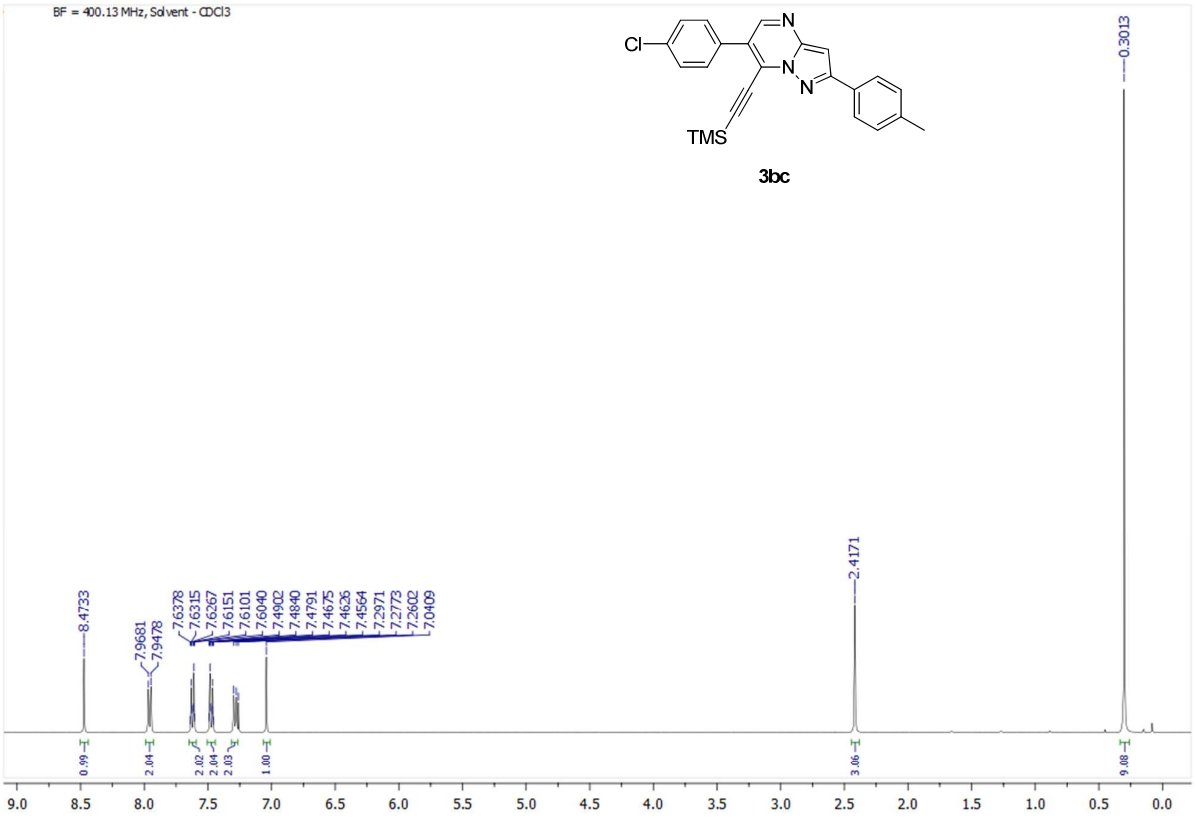
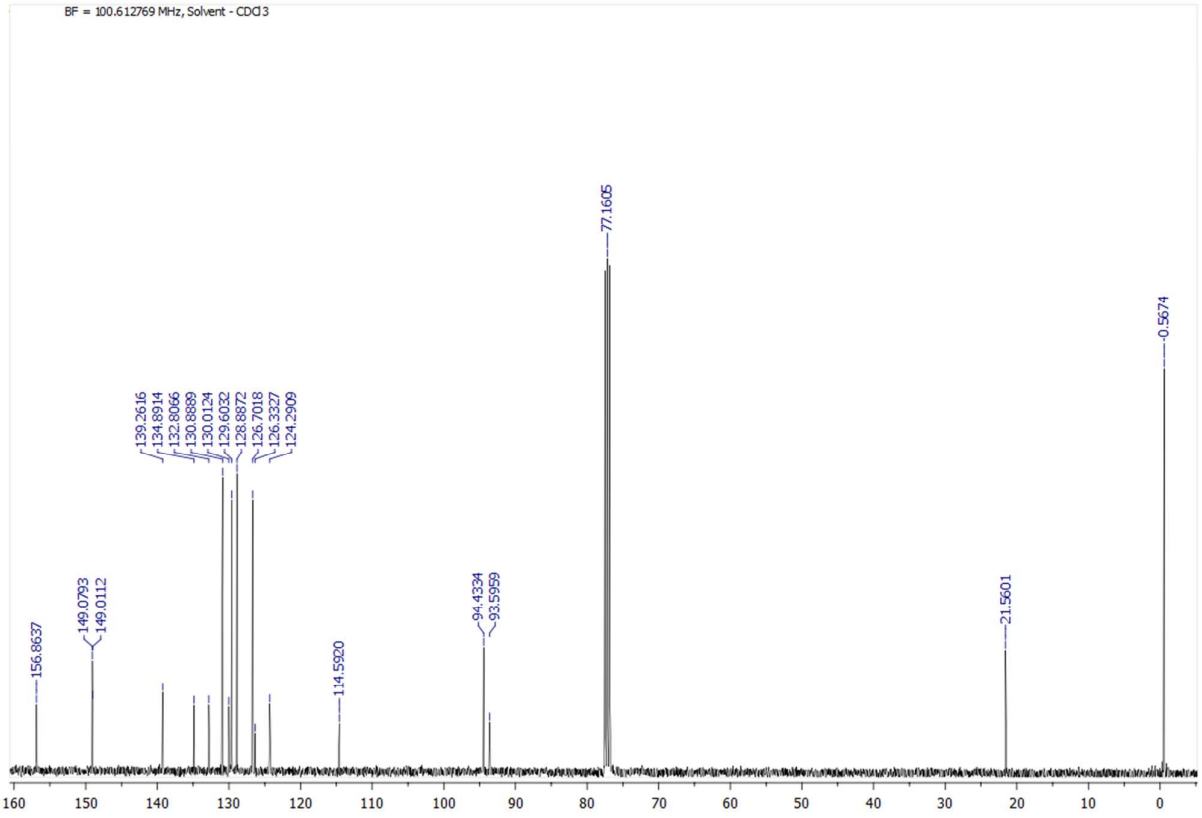

BF = 400.13 MHz, Solvent - CDCl3
Cl
N
N
N
TMS
3bc
0.3013
2.4171
8.4733
7.9681
7.9478
7.6378
7.6315
7.6267
7.6151
7.6101
7.6040
7.4902
7.4840
7.4791
7.4675
7.4636
7.4564
7.2971
7.2773
7.2602
7.0409
0.99
2.04
2.02
2.04
2.03
1.00
3.06
9.88
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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0.5674
139.2616
134.8914
132.8066
130.8889
130.0124
129.6032
128.8872
126.7018
126.3327
124.2909
149.0793
149.0112
156.8637
114.5920
94.4334
93.5959
21.5601
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150
140
130
120
110
100
90
80
70
60
50
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30
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10
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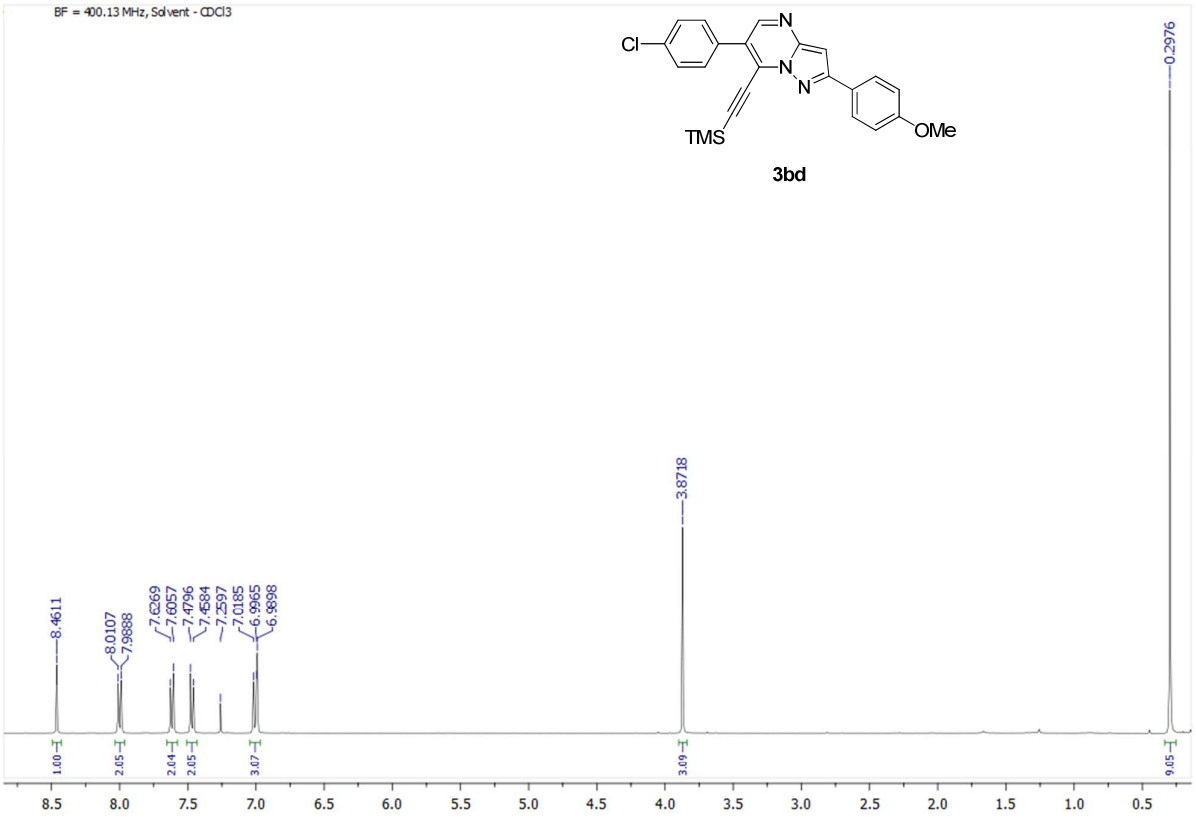
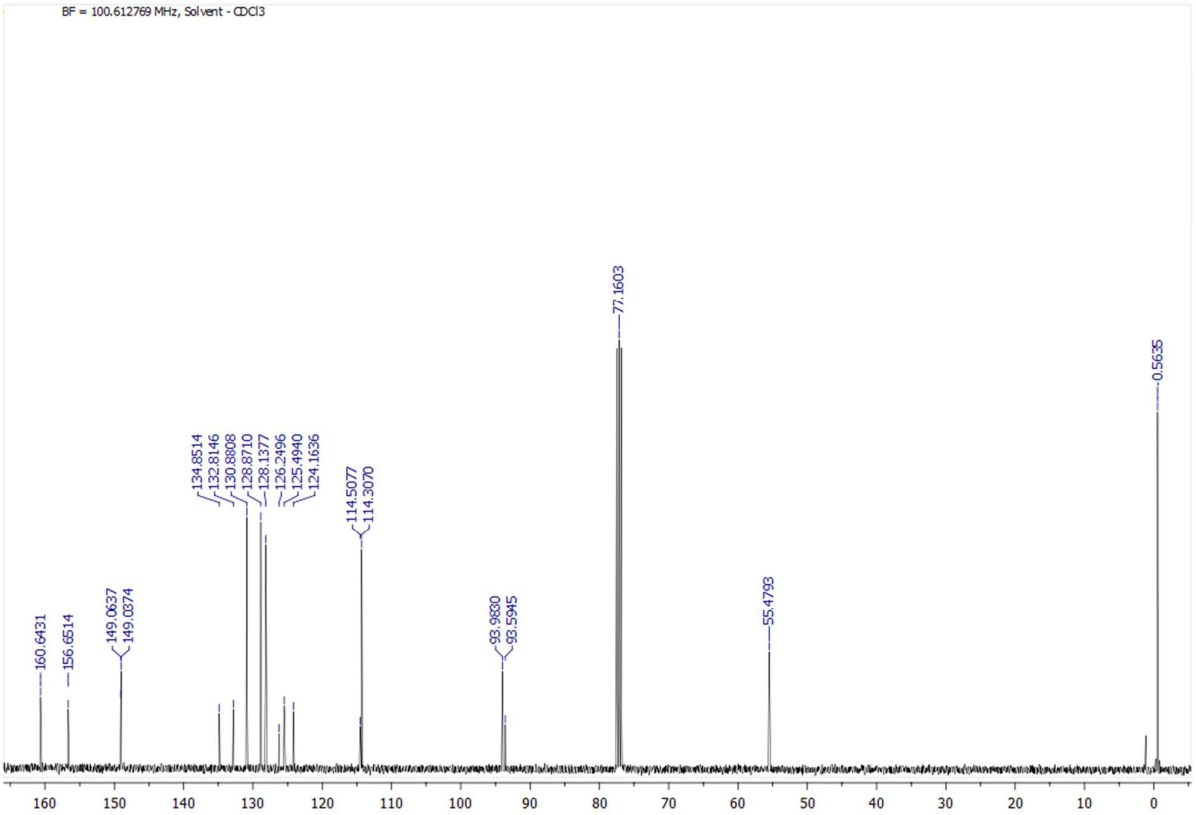

BF = 400.13 MHz, Solvent - CDCl3
Cl
N
N
N
TMS
OMe
3bd
8.4611
8.0107
7.9888
7.6269
7.6057
7.4796
7.4584
7.2597
7.0185
6.9965
6.9898
3.8718
0.2976
1.00
2.05
2.04
2.05
3.07
3.09
9.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


BF = 100.612769 MHz, Solvent - CDCl3
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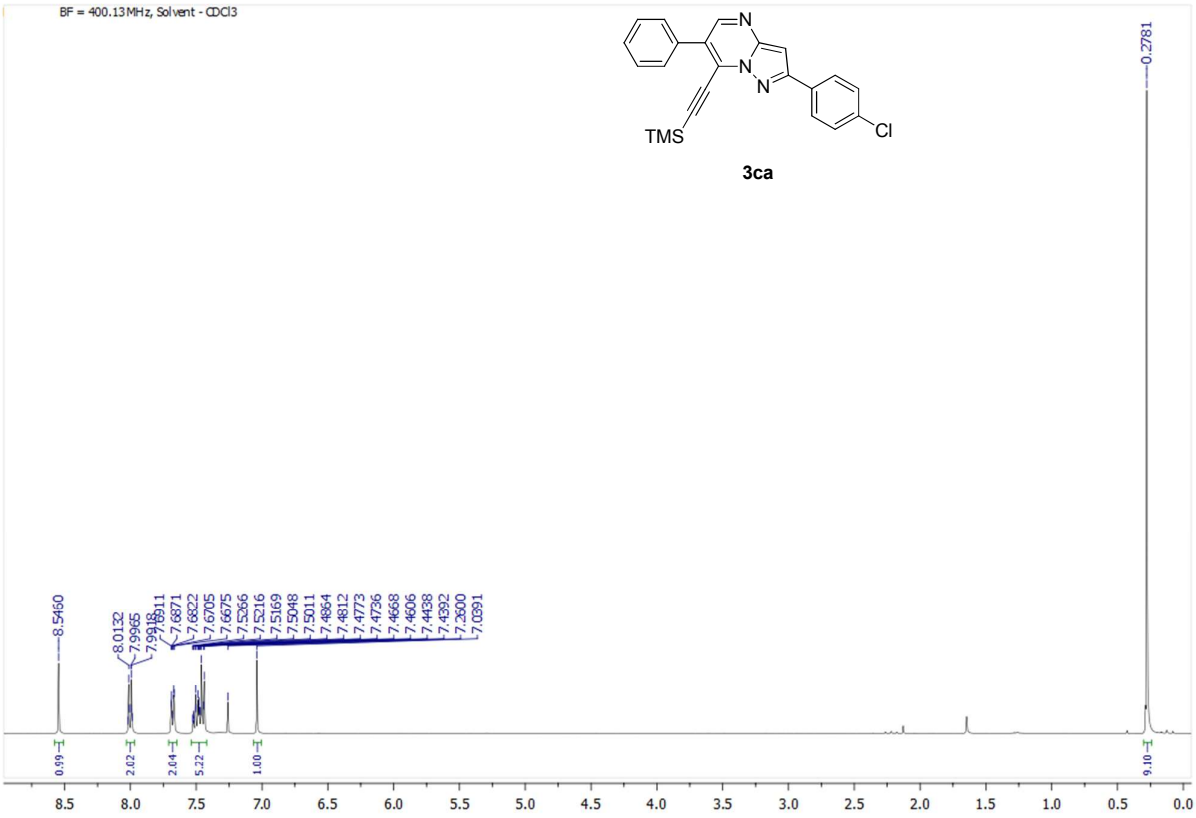
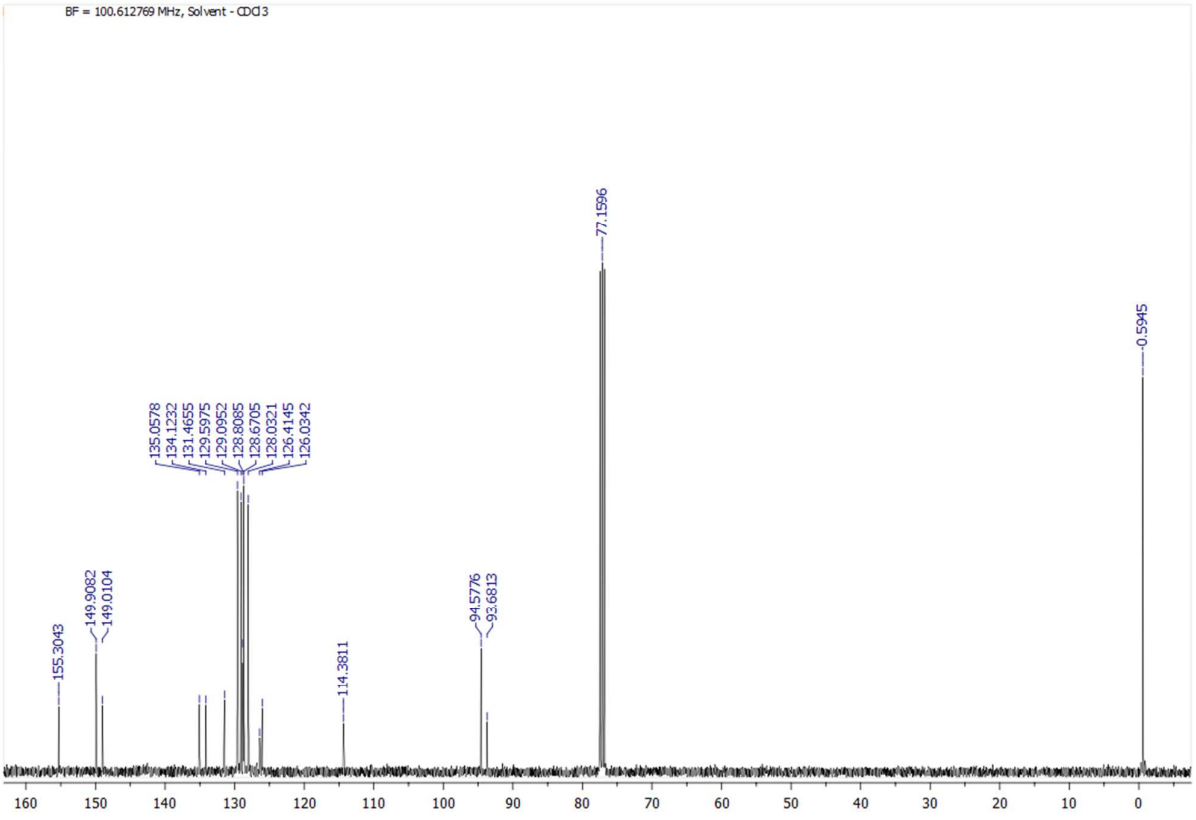
149.0637
149.0374
134.8514
132.8146
130.8808
128.8710
128.1377
126.2496
125.4940
124.1636
114.5077
114.3070
93.9830
93.5945
77.1603
55.4793
0.5635
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


BF = 400.13 MHz, Solvent - CDCl3
TMS
Cl
3ca
8.5460
8.0132
7.9965
7.8811
7.6871
7.6822
7.6705
7.6675
7.5266
7.5216
7.5169
7.5048
7.5011
7.4864
7.4812
7.4773
7.4736
7.4668
7.4606
7.4438
7.4392
7.2600
7.0391
0.2781
0.59
2.02
2.04
5.22
1.00
9.10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149.0104
135.0578
134.1232
131.4655
129.5975
129.0952
128.8085
128.6705
128.0321
126.4145
126.0342
114.3811
94.5776
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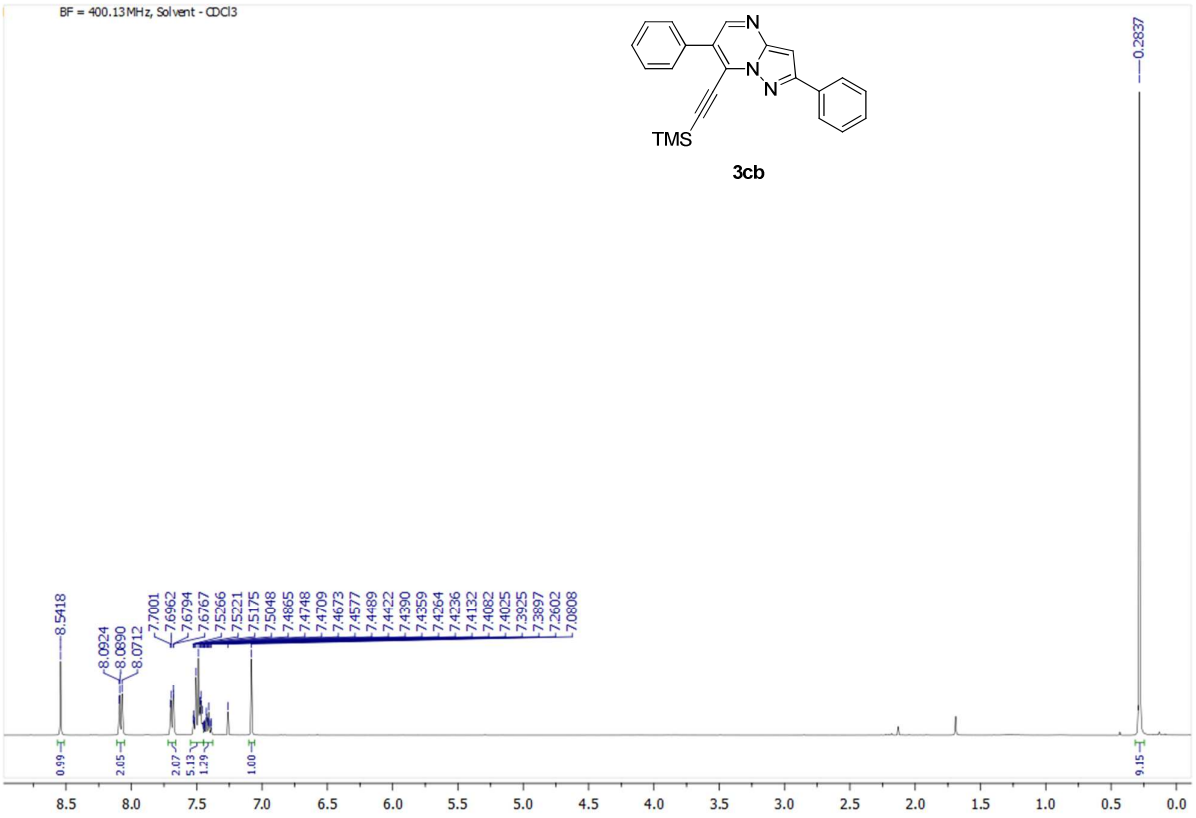
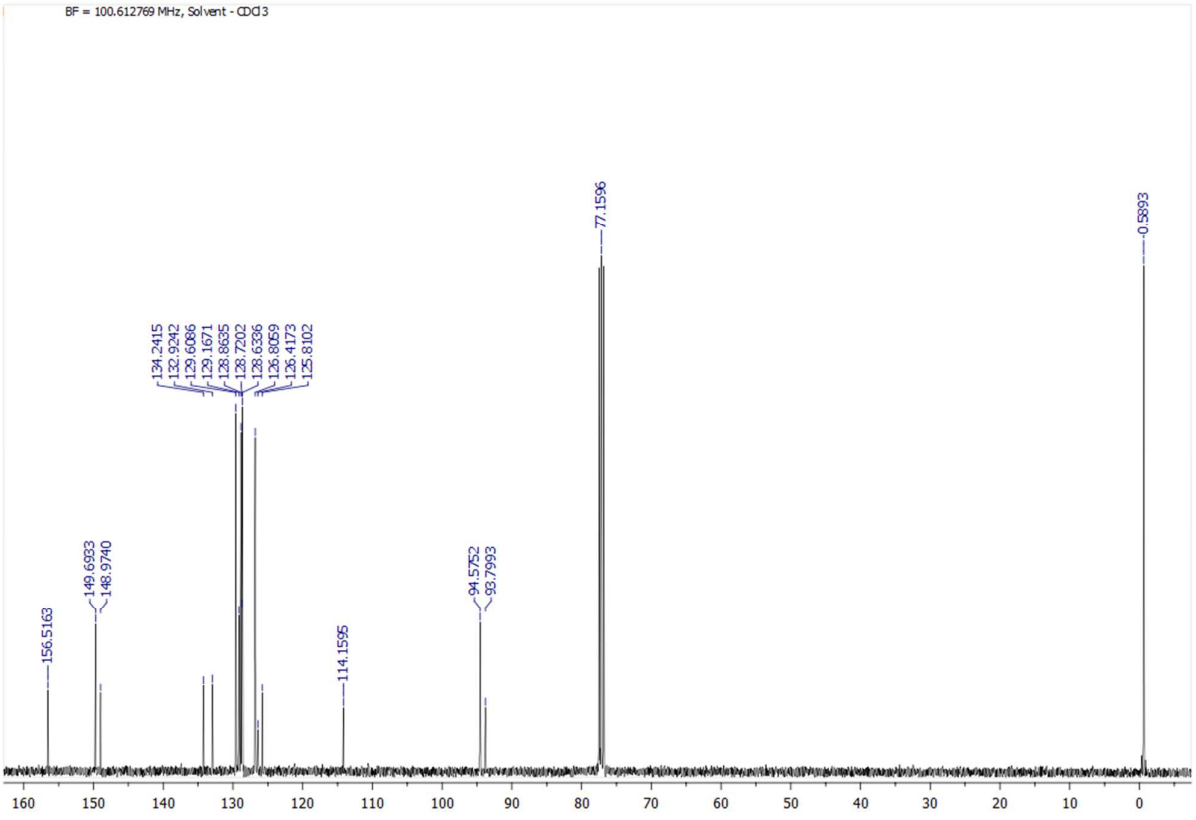
77.1596
0.5945


BF = 400.13 MHz, Solvent - CDCl3
TMS
3cb
8.5418
8.0924
8.0890
8.0712
7.7001
7.6962
7.6794
7.6767
7.5266
7.5221
7.5175
7.5048
7.4865
7.4748
7.4709
7.4673
7.4577
7.4489
7.4422
7.4390
7.4359
7.4264
7.4236
7.4132
7.4082
7.4025
7.3925
7.3897
7.2602
7.0808
0.2837
0.59
2.05
2.07
5.13
1.29
1.00
9.15


BF = 100.612769 MHz, Solvent - CDCl3
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148.9740
134.2415
132.9242
129.6086
129.1671
128.8635
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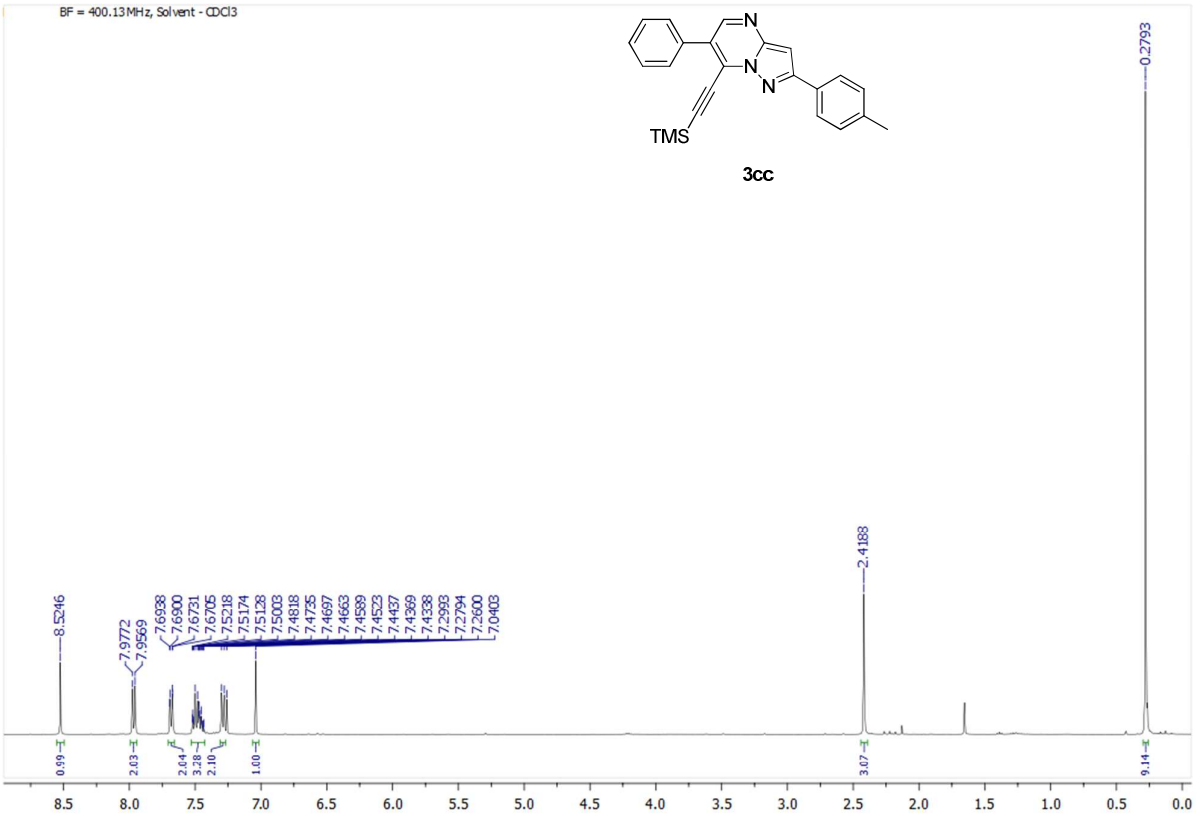
126.8059
126.4173
125.8102
114.1595
94.5752
93.7993
77.1596
0.5893


BF = 400.13 MHz, Solvent - CDCl3
TMS
3cc
8.5246
7.9772
7.9569
7.6938
7.6900
7.6731
7.6705
7.5218
7.5174
7.5128
7.5003
7.4818
7.4735
7.4697
7.4663
7.4589
7.4523
7.4437
7.4369
7.4338
7.2993
7.2794
7.2600
7.0403
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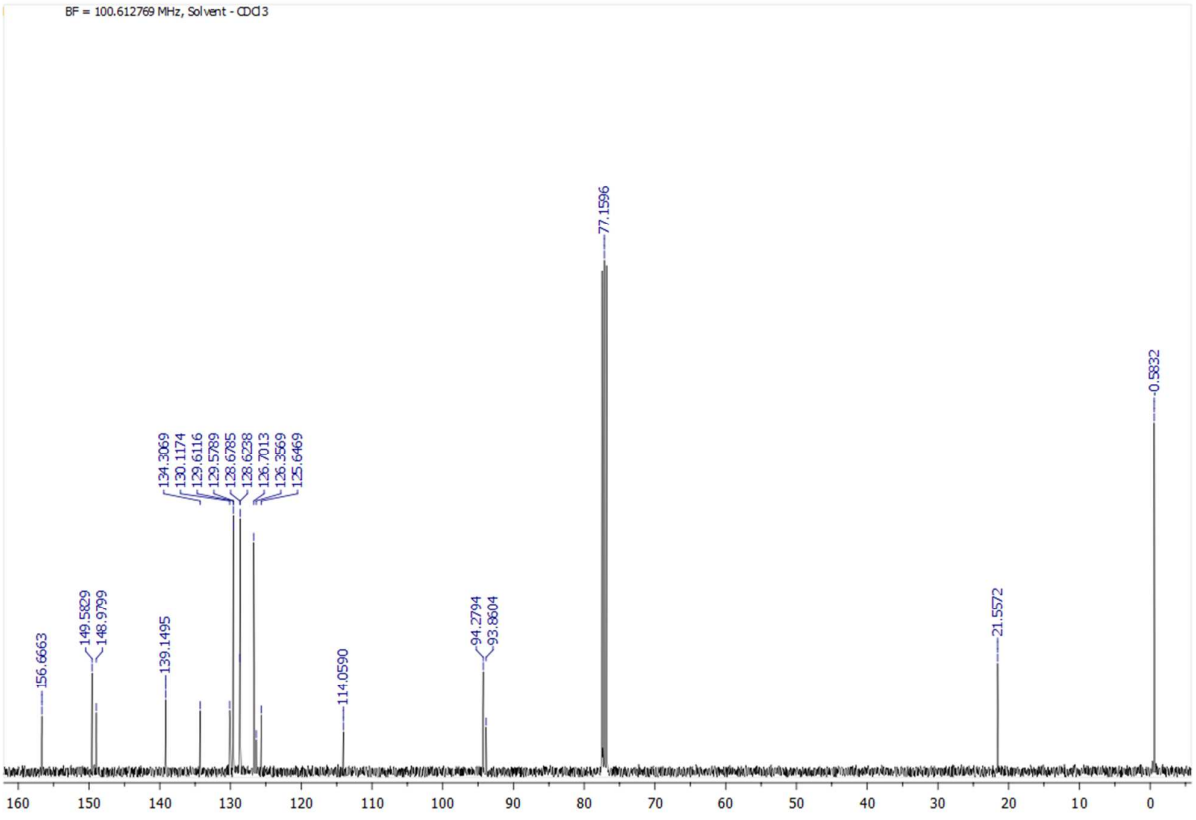
0.2793
0.59
2.03
2.04
3.28
2.10
1.00
3.07
9.14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139.1495
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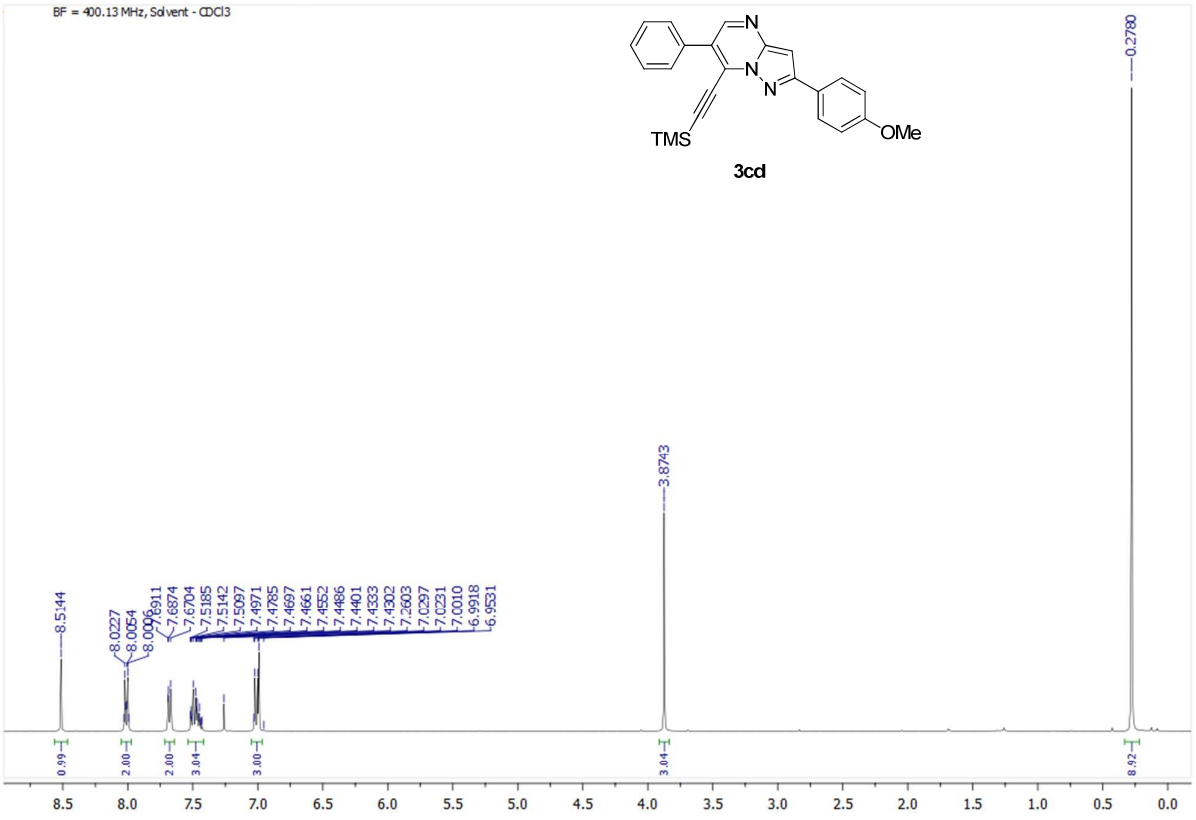
130.1174
129.6116
129.5789
128.6785
128.6238
126.7013
126.3569
125.6469
114.0590
94.2794
93.8604
77.1596
21.5572
0.5832


BF = 400.13 MHz, Solvent - CDCl3
TMS
OMe
3cd
0.2780
3.8743
8.5144
8.0227
8.0054
8.0006
7.6911
7.6874
7.6704
7.5185
7.5142
7.5097
7.4971
7.4785
7.4697
7.4661
7.4552
7.4486
7.4401
7.4333
7.4302
7.2603
7.0297
7.0231
7.0010
6.9918
6.9531
0.99
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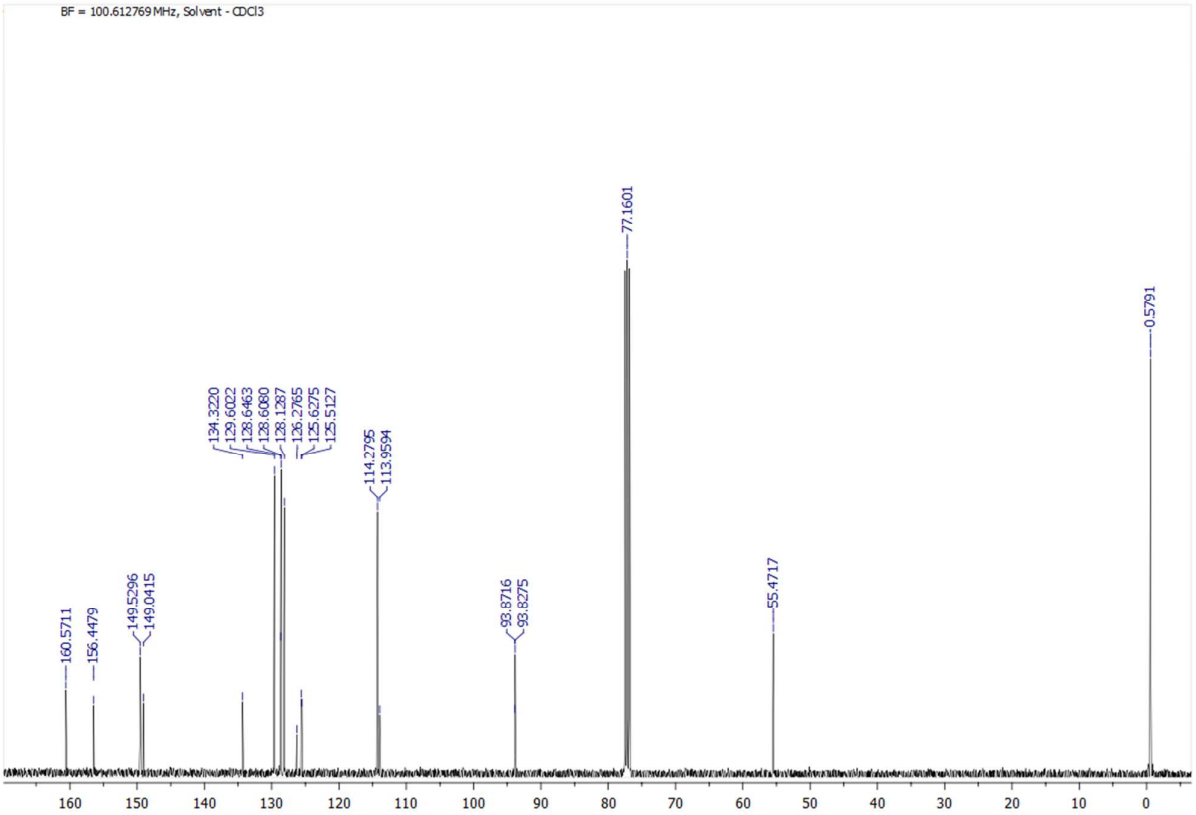
2.00
3.04
3.00
3.04
8.92


BF = 100.612769 MHz, Solvent - CDCl3
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0.5791
134.3220
129.6022
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128.6080
128.1287
126.2765
125.6275
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160.5711
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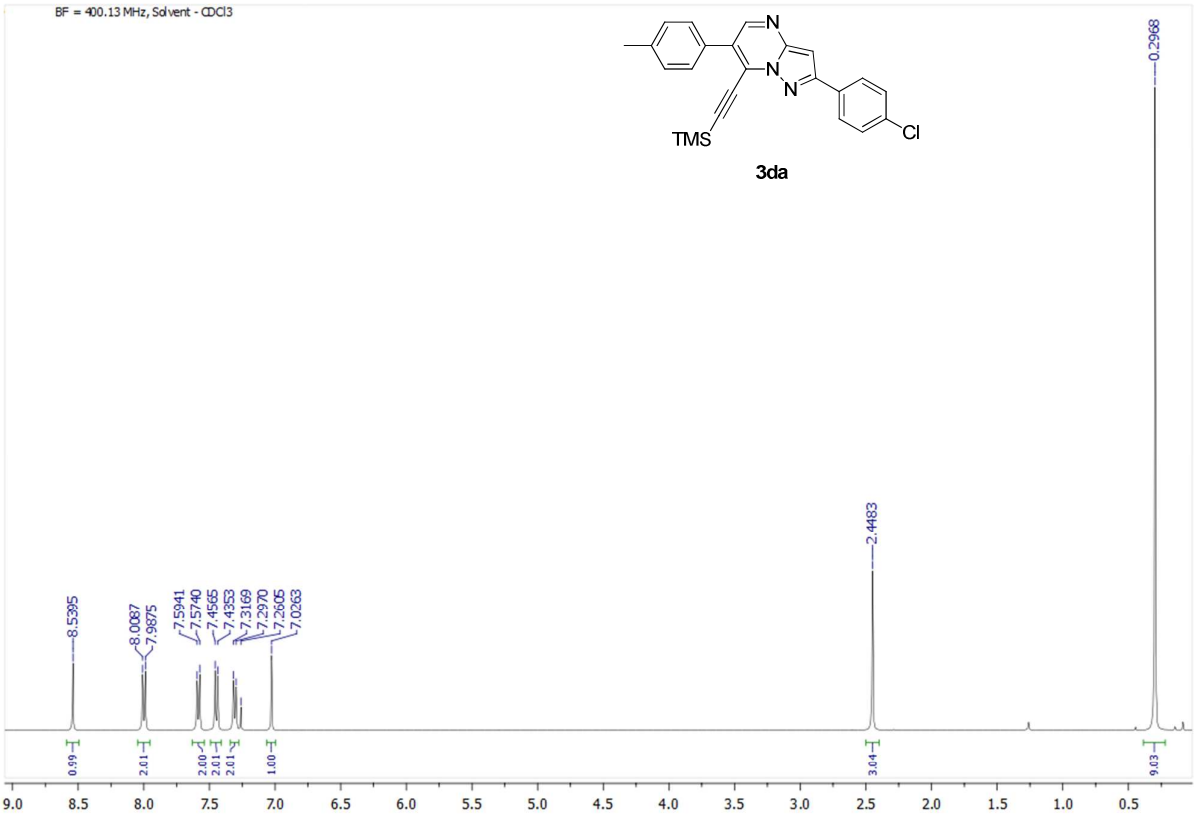
149.0415
93.8716
93.8275
55.4717


BF = 400.13 MHz, Solvent - CDCl3
N
N
N
TMS
Cl
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8.5395
8.0087
7.9875
7.5941
7.5740
7.4565
7.4353
7.3169
7.2970
7.2605
7.0263
0.99
2.01
2.00
2.01
2.01
1.00
3.04
9.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
3.0
2.5
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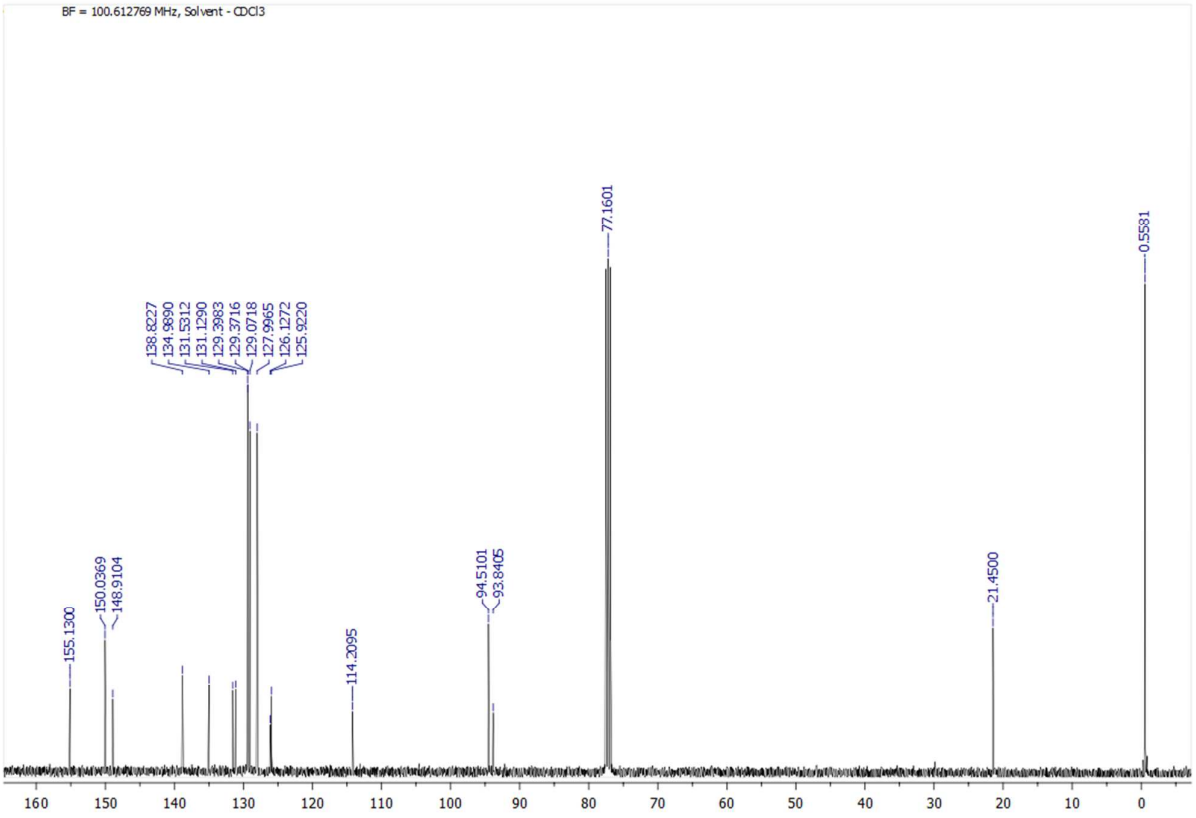
1.5
1.0
0.5


BF = 100.612769 MHz, Solvent - CDCl3
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138.8227
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131.1290
129.3983
129.3716
129.0718
127.9965
126.1272
125.9220
155.1300
150.0369
148.9104
114.2095
94.5101
93.8405
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150
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130
120
110
100
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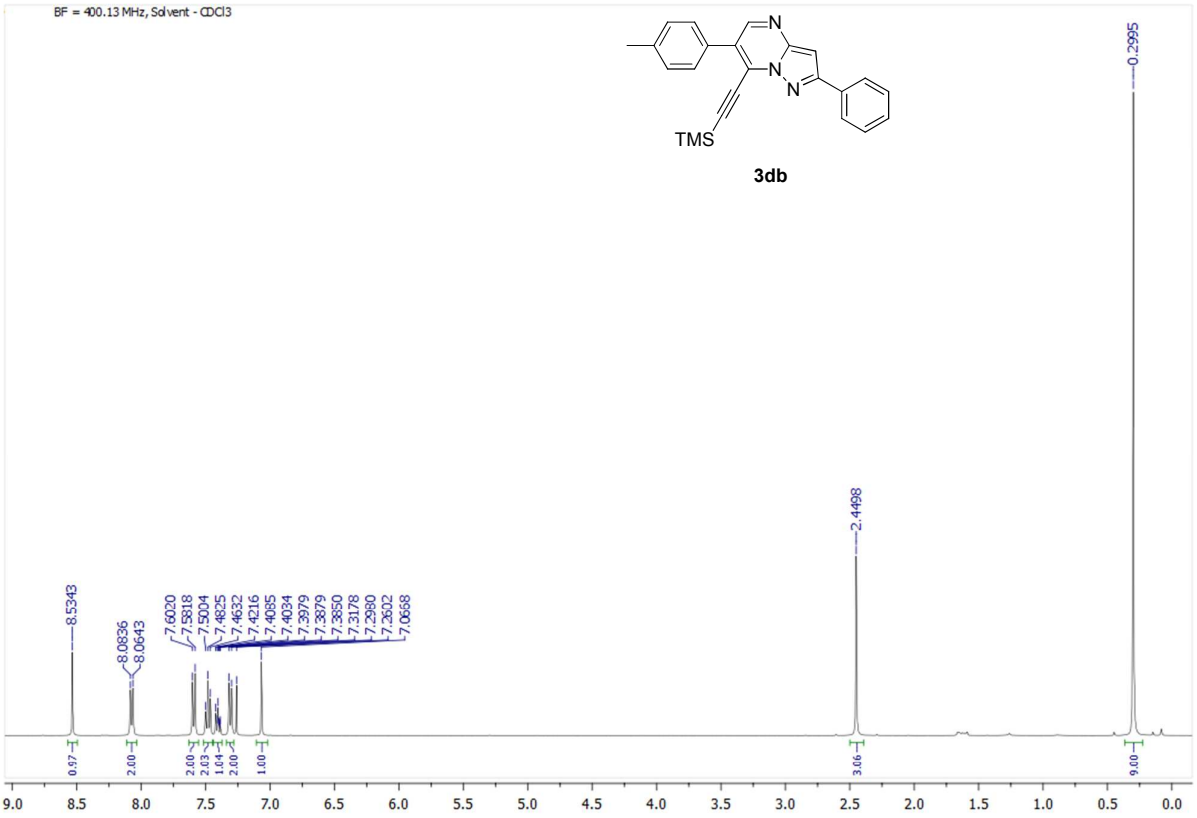
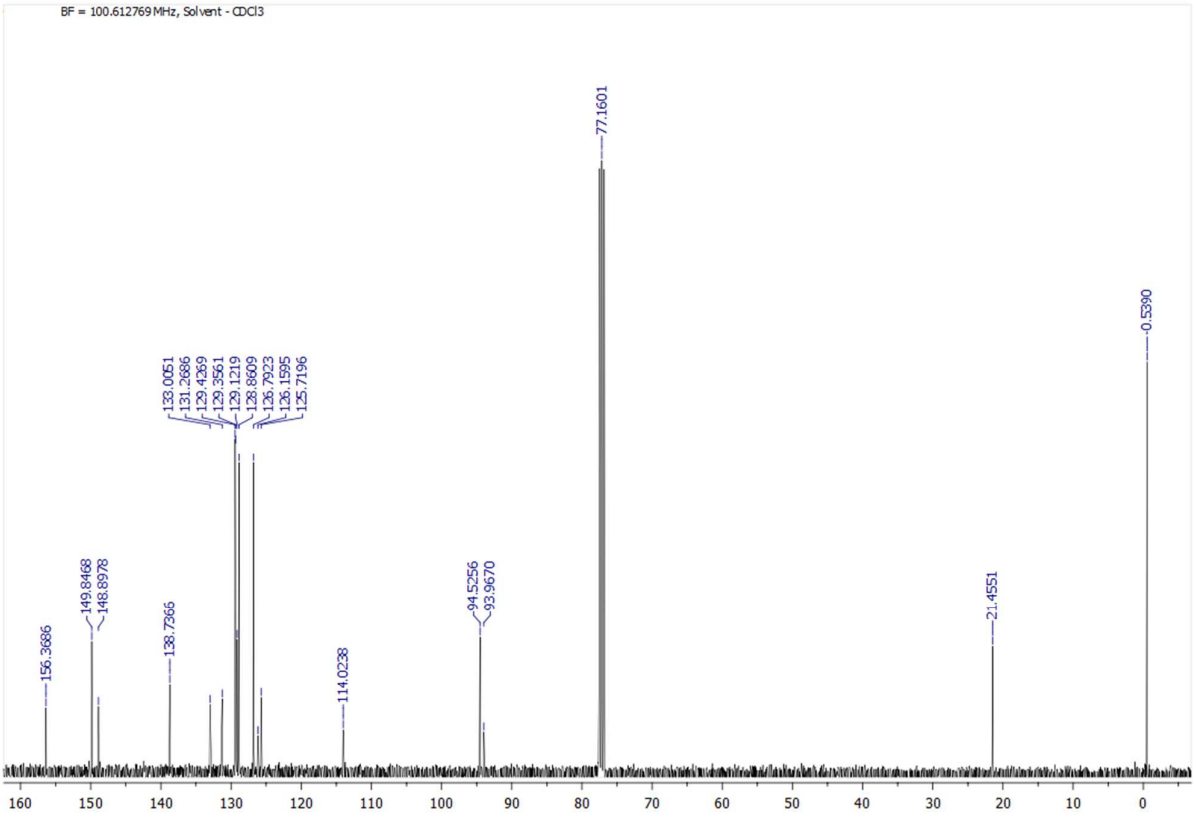
70
60
50
40
30
20
10
0


BF = 400.13 MHz, Solvent - CDCl3
TMS
3db
8.5343
8.0836
8.0643
7.6020
7.5818
7.5004
7.4825
7.4632
7.4216
7.4085
7.4034
7.3979
7.3879
7.3850
7.3178
7.2980
7.2602
7.0668
2.4498
0.2995
0.97
2.00
2.00
2.03
1.64
2.00
1.00
3.06
9.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


BF = 100.612769 MHz, Solvent - CDCl3
156.3686
149.8468
148.8978
138.7366
133.0051
131.2686
129.4269
129.3561
129.1219
128.8609
126.7923
126.1595
125.7196
114.0238
94.5256
93.9670
77.1601
21.4551
0.5390
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150
140
130
120
110
100
90
80
70
60
50
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10
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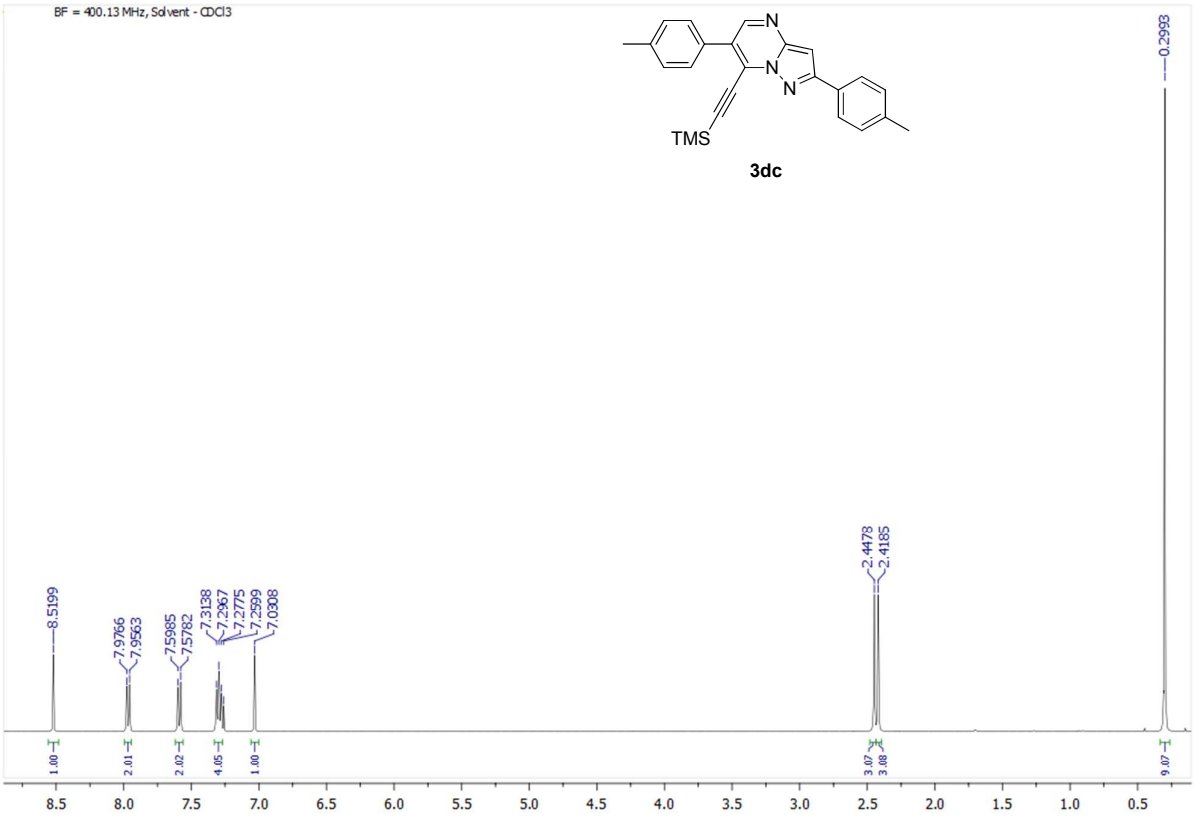
BF = 400.13 MHz, Solvent - CDCl3
TMS
8.5199
7.9766
7.9563
7.5985
7.5782
7.3138
7.2967
7.2775
7.2599
7.0308
2.4478
2.4185
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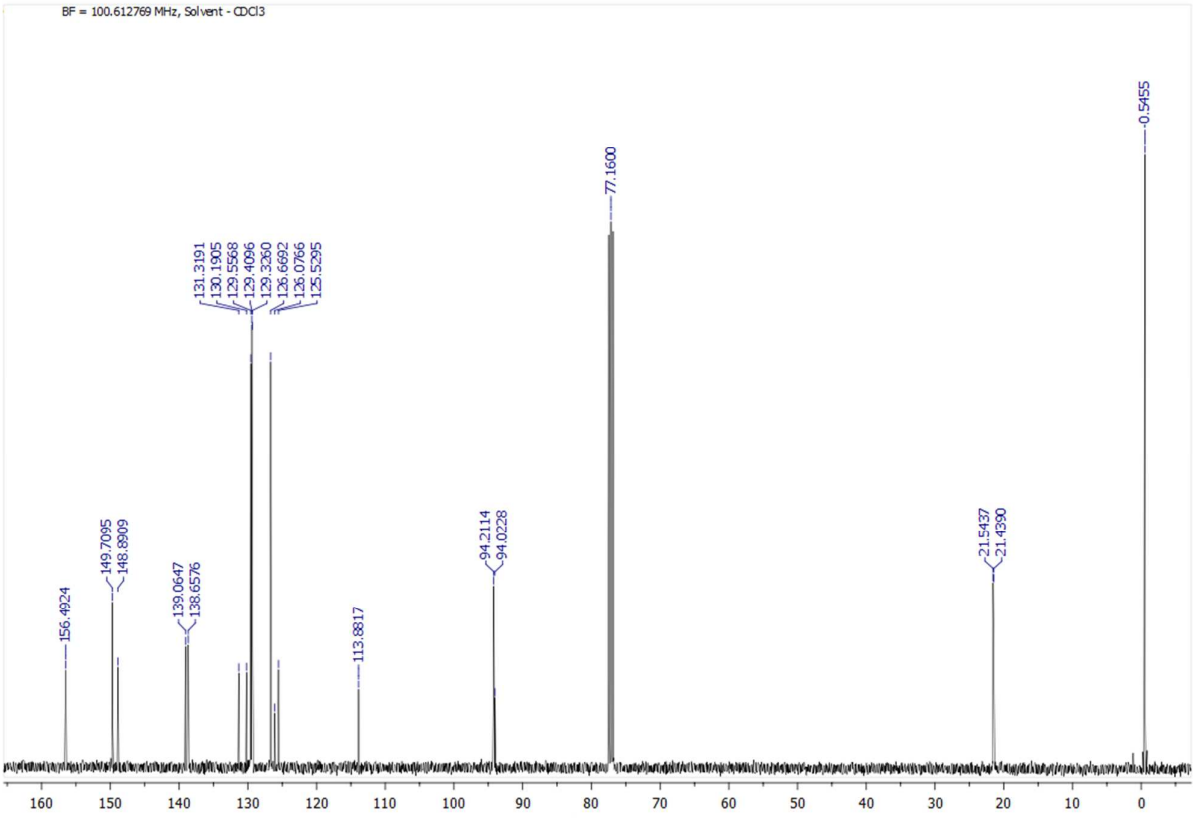
1.00
2.01
2.02
4.05
1.00
3.07
3.08
9.07

3dc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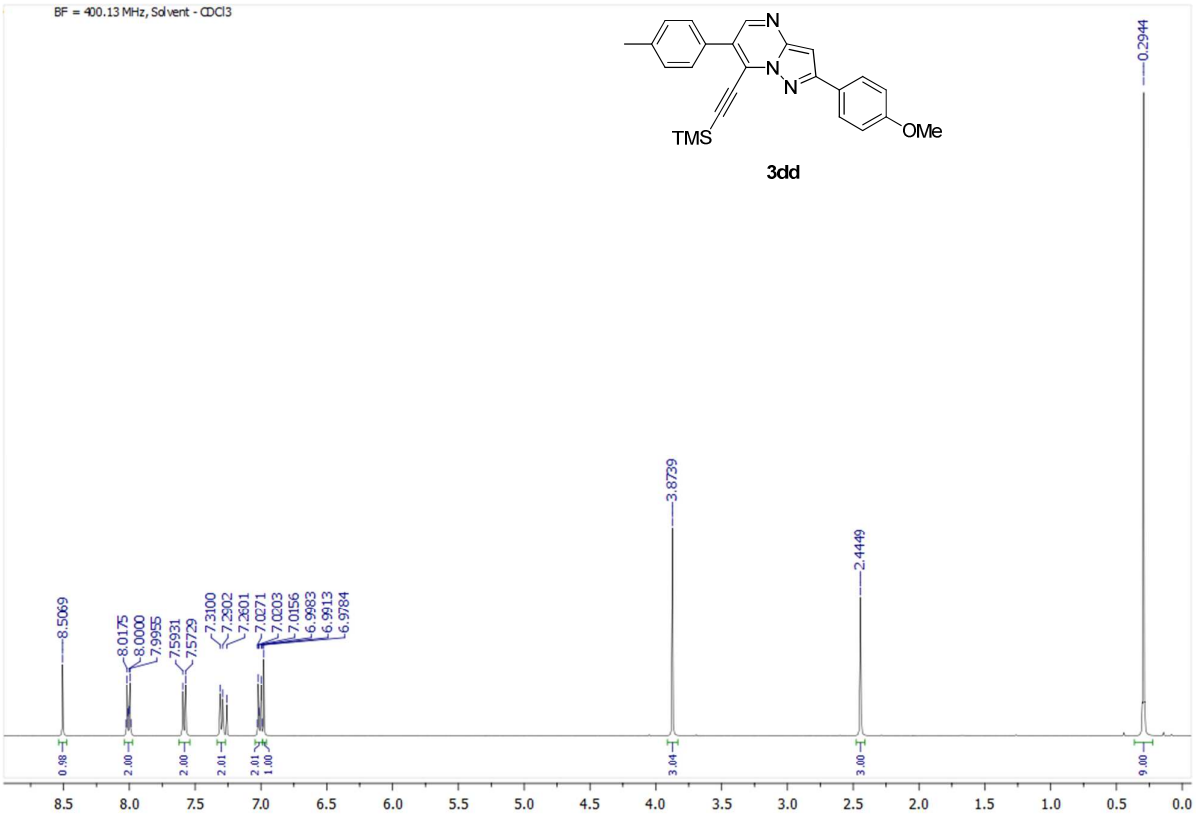
148.8909
139.0647
138.6576
131.3191
130.1905
129.5568
129.4096
129.3260
126.6692
126.0766
125.5295
113.8817
94.2114
94.0228
77.1600
21.5437
21.4390
0.5455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TMS
OMe
3dd
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8.0000
7.9955
7.5931
7.5729
7.3100
7.2902
7.2601
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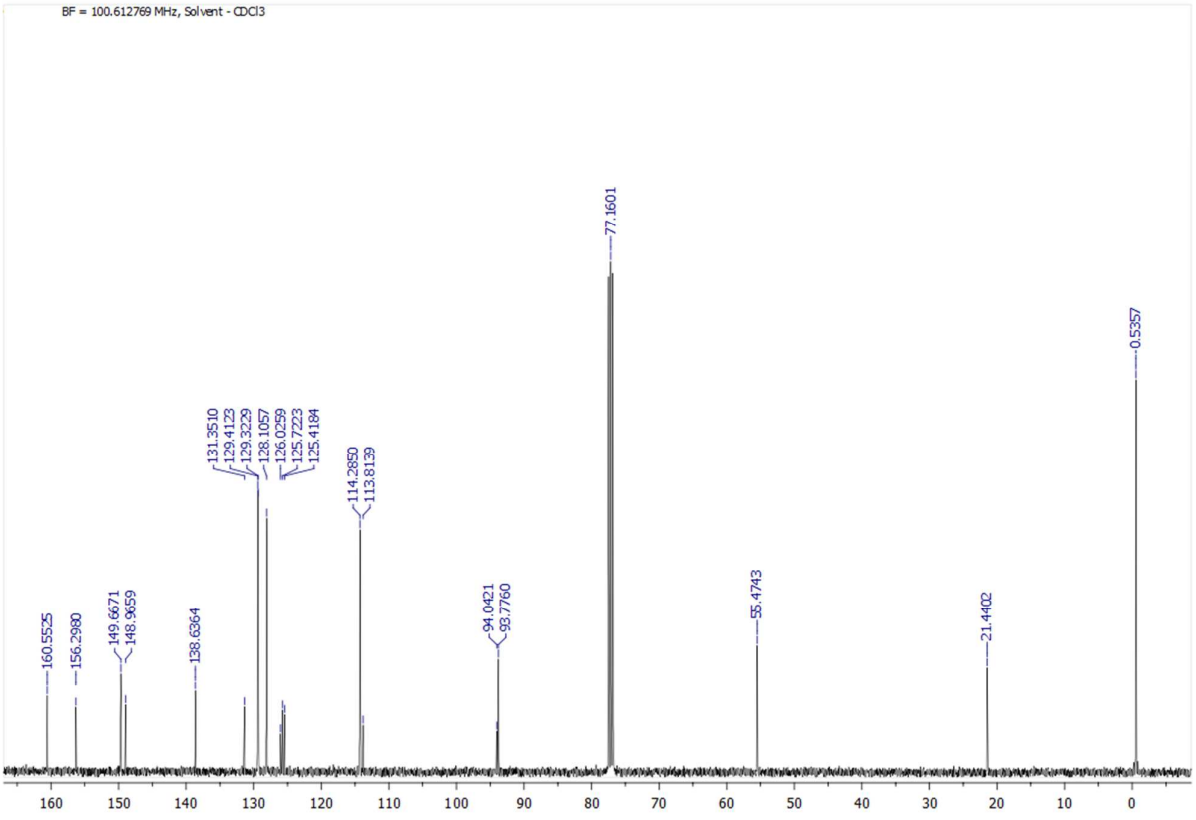
7.0203
7.0156
6.9983
6.9913
6.9784
3.8739
2.4449
0.2944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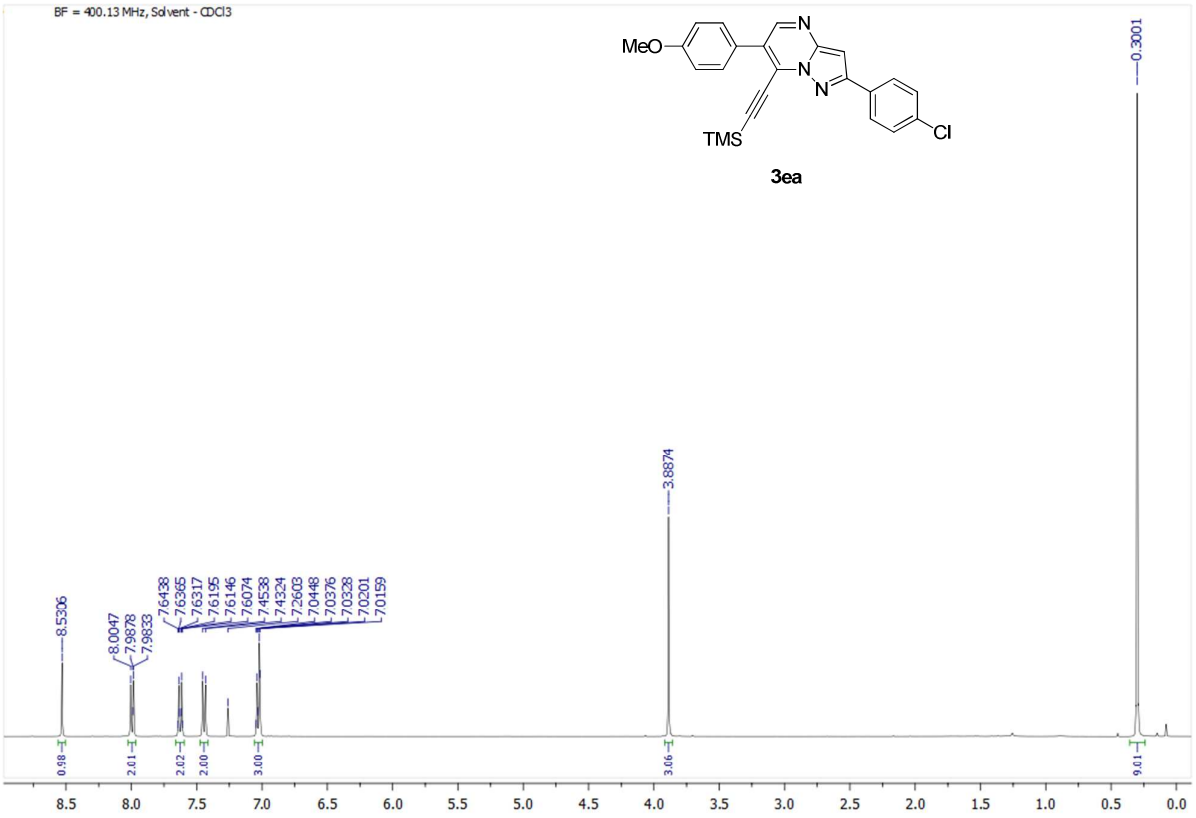
156.2980
149.6671
148.9659
138.6364
131.3510
129.4123
129.3229
128.1057
126.0259
125.7223
125.4184
114.2850
113.8139
94.0421
93.7760
77.1601
55.4743
21.4402
0.5357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N
N
TMS
Cl
3ea
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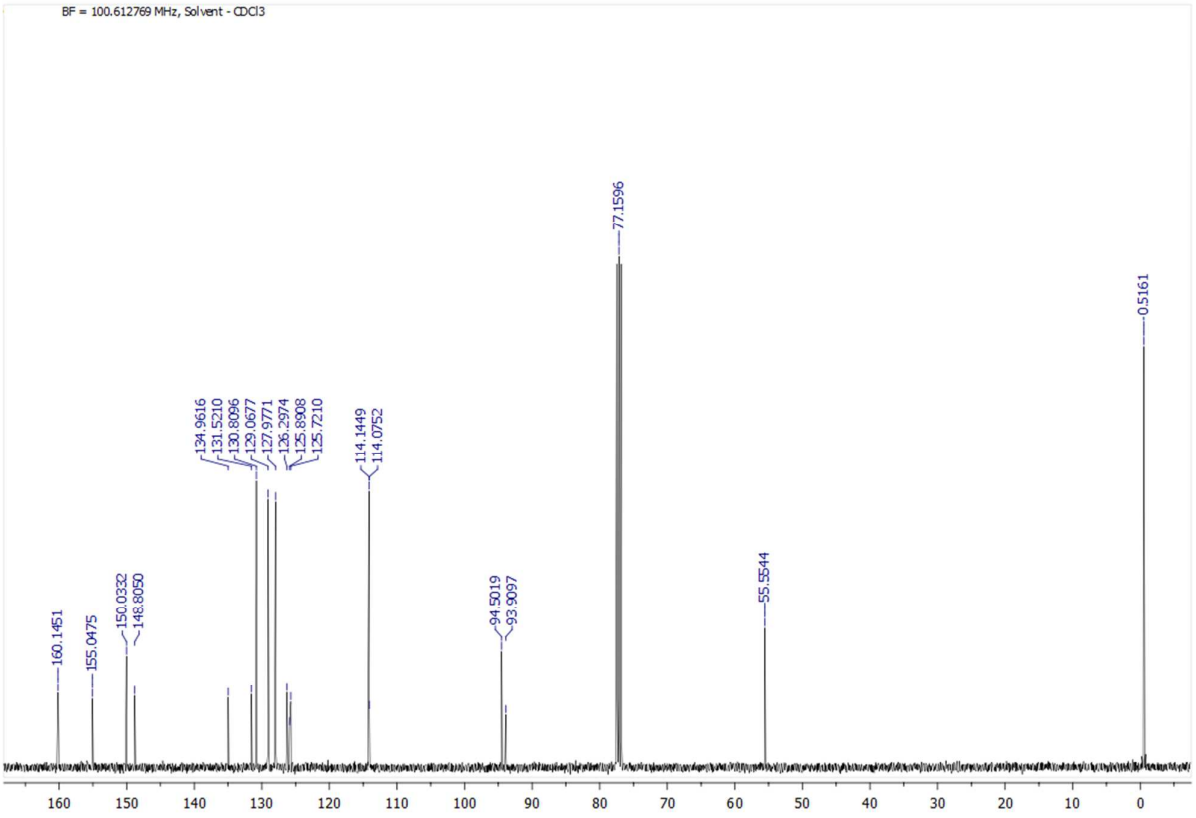
3.8874
8.5306
8.0047
7.9878
7.9833
7.6438
7.6365
7.6317
7.6195
7.6146
7.6074
7.4538
7.4324
7.2603
7.0448
7.0376
7.0328
7.0201
7.0159
0.58
2.01
2.02
2.00
3.00
3.06
9.01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0.5161
134.9616
131.5210
130.8096
129.0677
127.9771
126.2974
125.8908
125.7210
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114.0752
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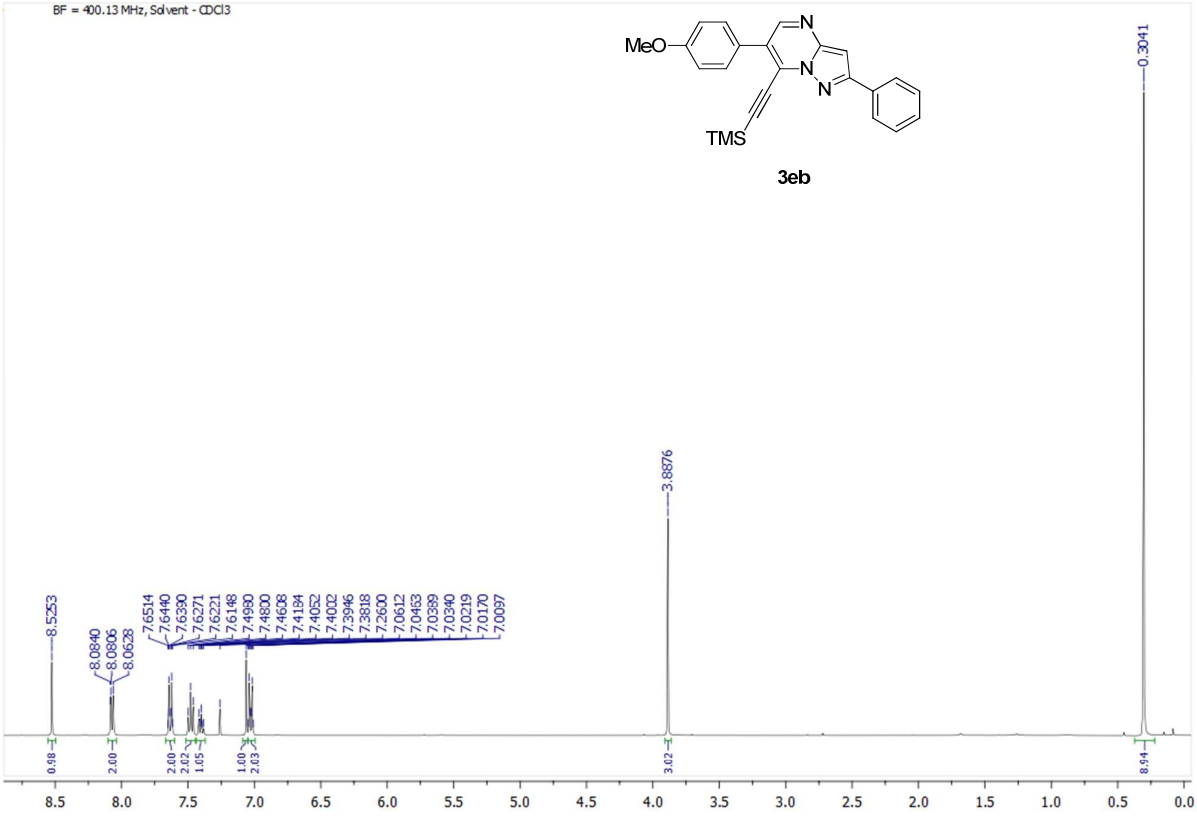
150.0332
148.8050
94.5019
93.9097
55.5544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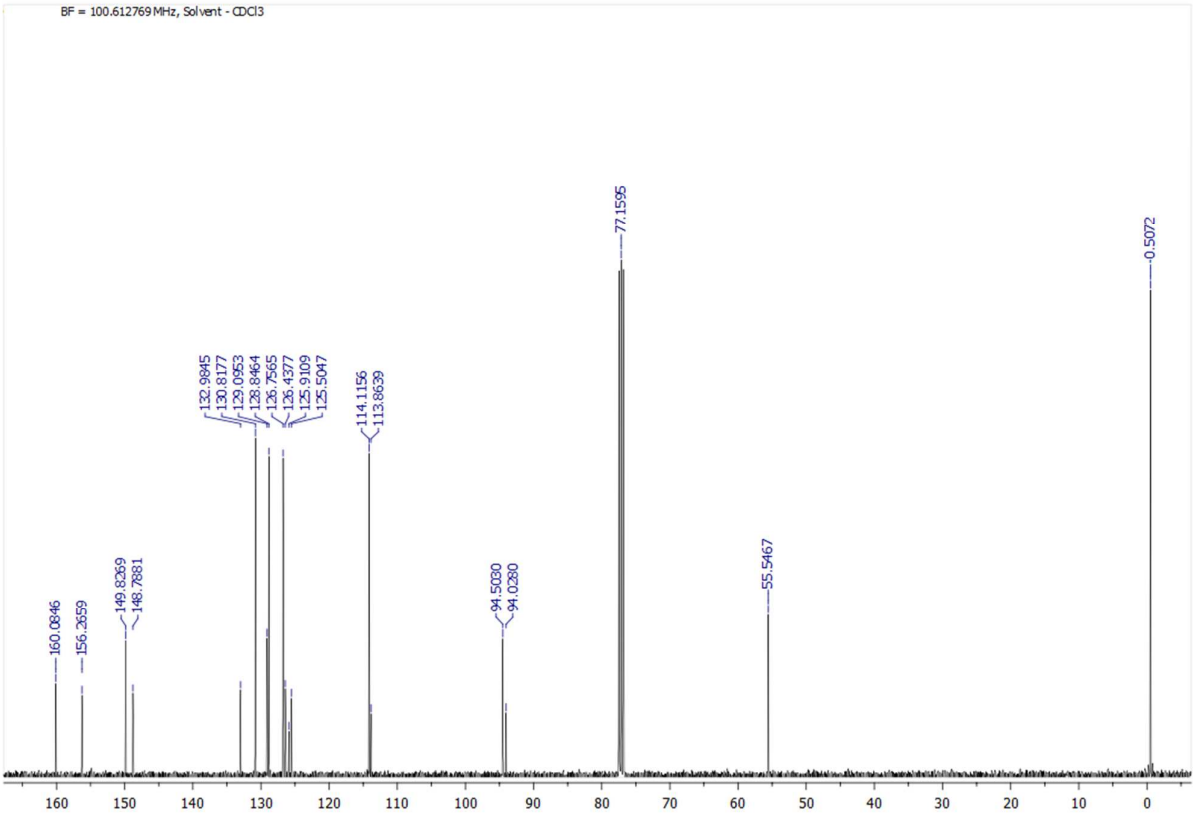
MeO
N
N
N
TMS
3eb
0.3041
3.8876
8.5253
8.0840
8.0806
8.0628
7.6514
7.6440
7.6390
7.6271
7.6221
7.6148
7.4980
7.4800
7.4608
7.4194
7.4052
7.4002
7.3946
7.3818
7.2600
7.0612
7.0463
7.0389
7.0340
7.0219
7.0170
7.0097
0.98
2.00
2.00
2.02
1.05
1.00
2.03
3.02
8.14
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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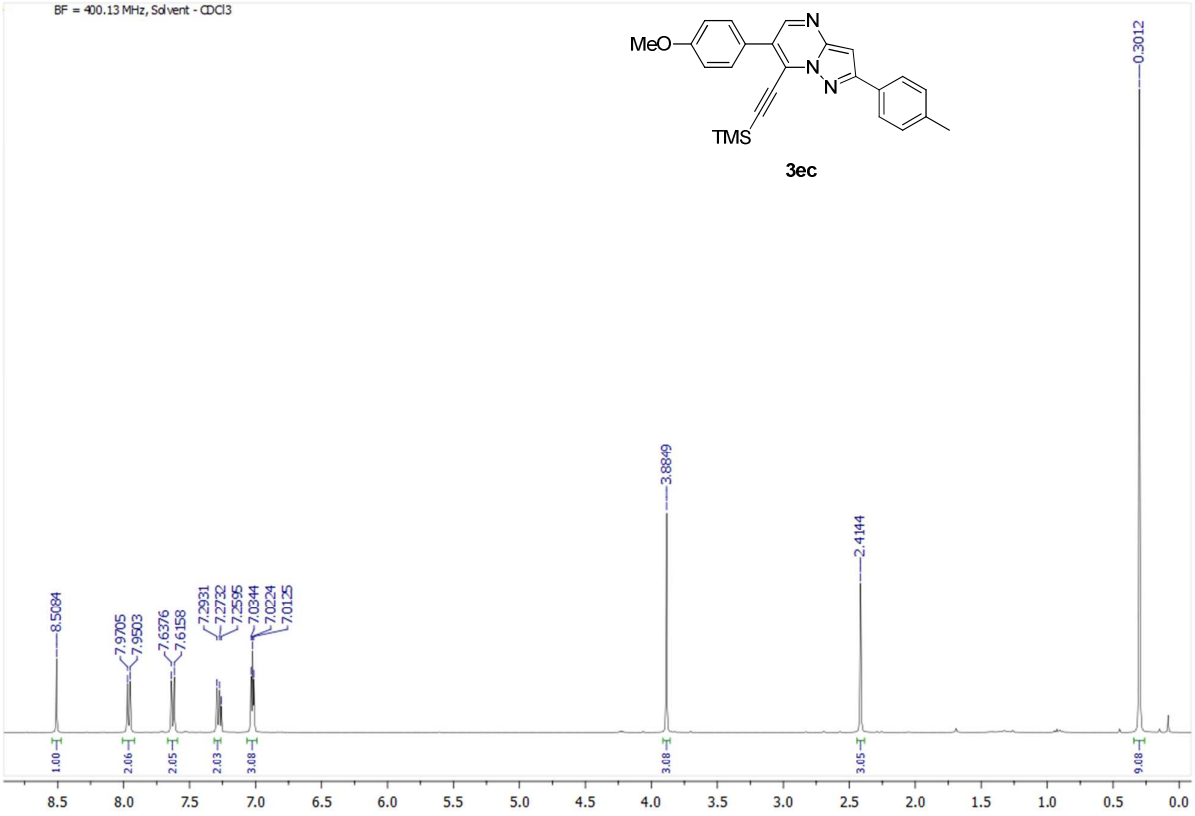
129.0953
128.8464
126.7565
126.4377
125.9109
125.5047
114.1156
113.8639
160.0846
156.2659
149.8269
148.7881
94.5080
94.0280
55.5467
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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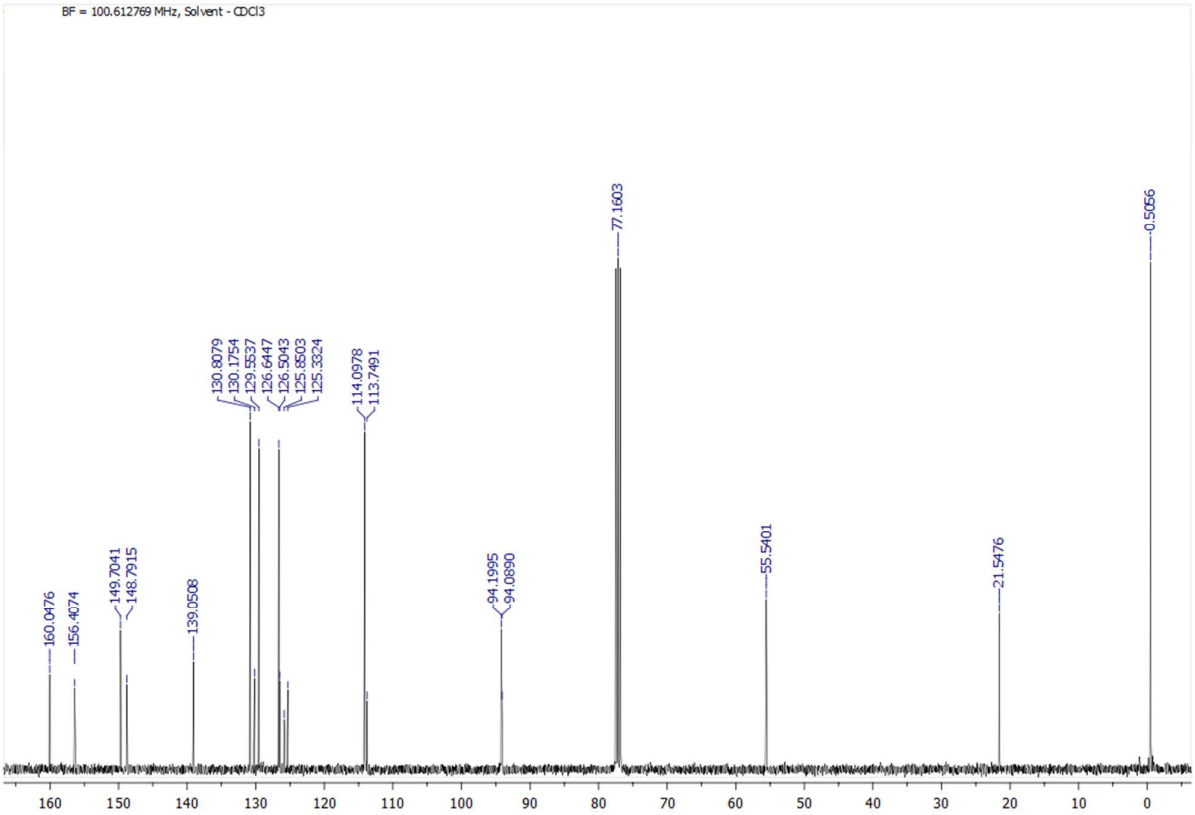
N
N
TMS
3ec
0.3012
3.8849
2.4144
8.5084
7.9705
7.9503
7.6376
7.6158
7.2931
7.2732
7.2595
7.0344
7.0224
7.0125
1.00
2.06
2.05
2.03
3.08
3.08
3.05
9.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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130.8079
130.1754
129.5537
126.6447
126.5043
125.8503
125.3324
114.0978
113.7491
160.0476
156.4074
149.7041
148.7915
139.0508
94.1995
94.0890
55.5401
21.5476
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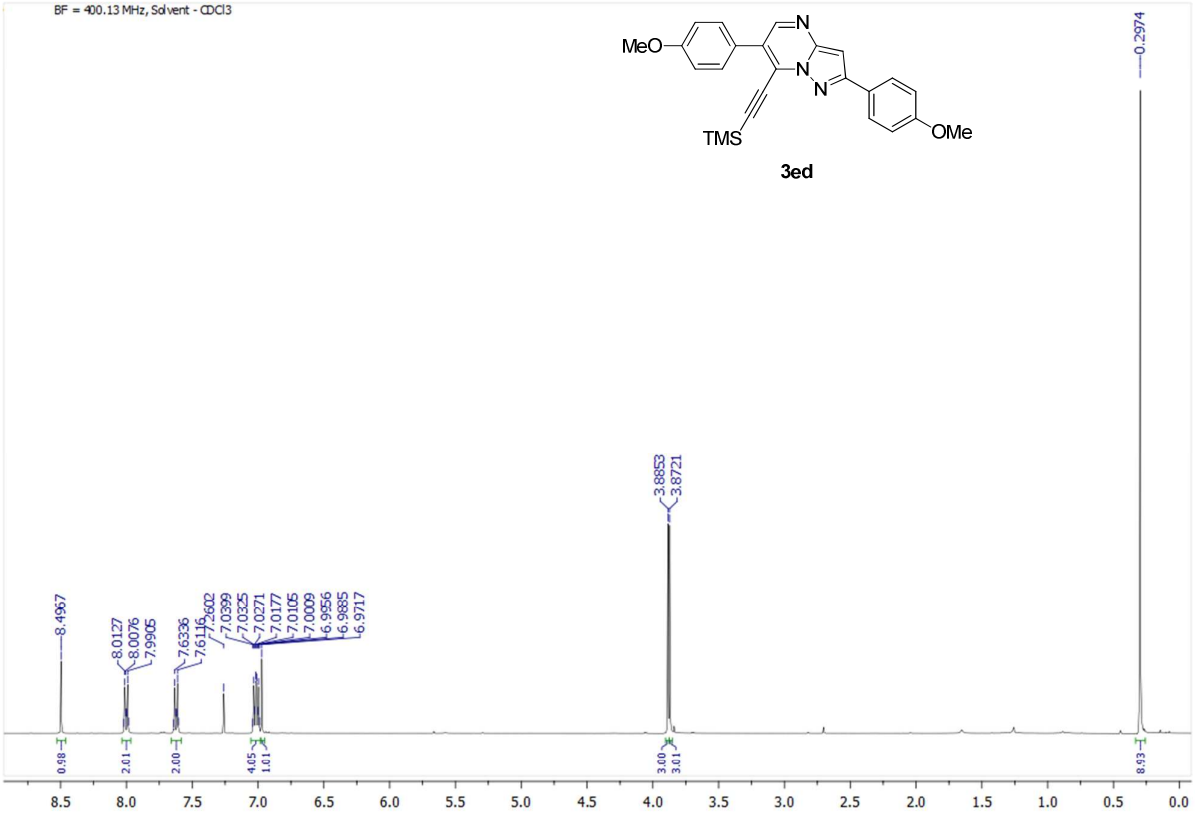
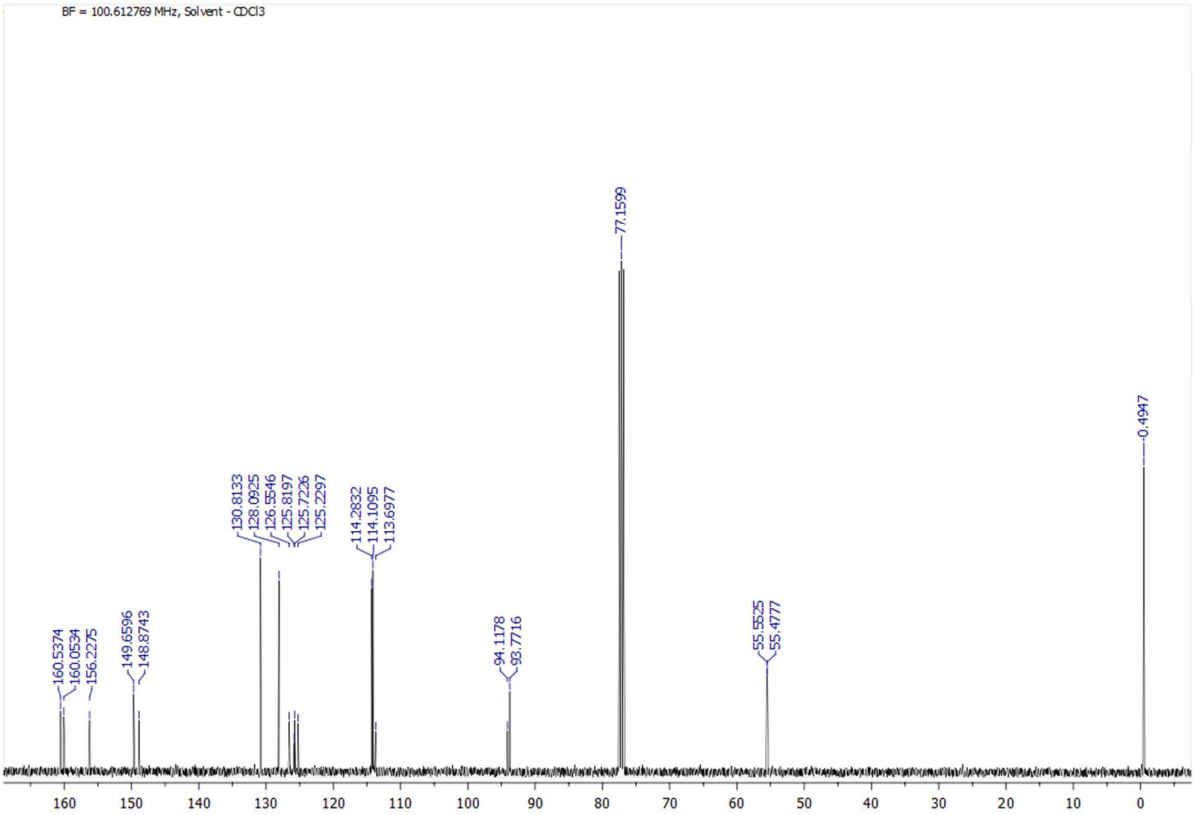
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


BF = 400.13 MHz, Solvent - CDCl3
MeO
N
N
N
TMS
OMe
3ed
8.4957
8.0127
8.0076
7.9905
7.6336
7.6116
7.2602
7.0399
7.0325
7.0271
7.0177
7.0105
7.0009
6.9956
6.9885
6.9717
3.8853
3.8721
0.2974
0.58
2.01
2.00
4.65
1.01
3.00
3.01
8.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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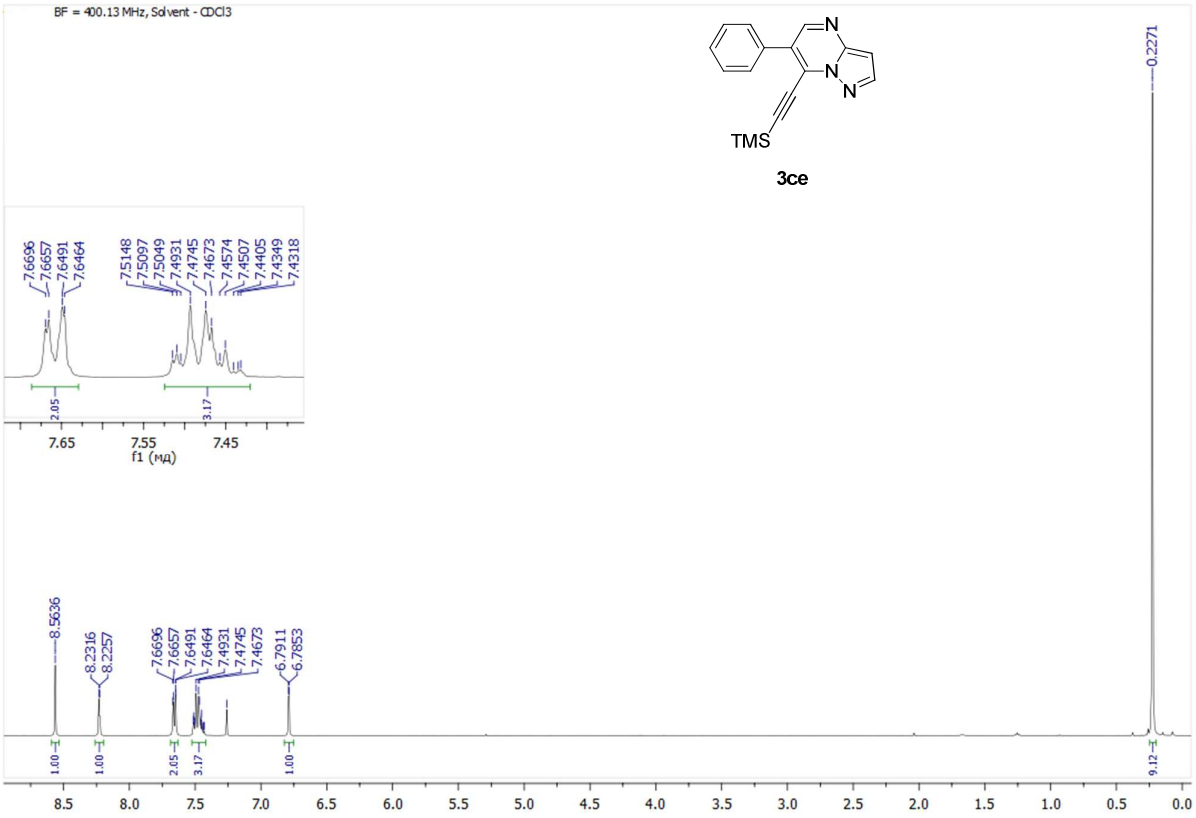
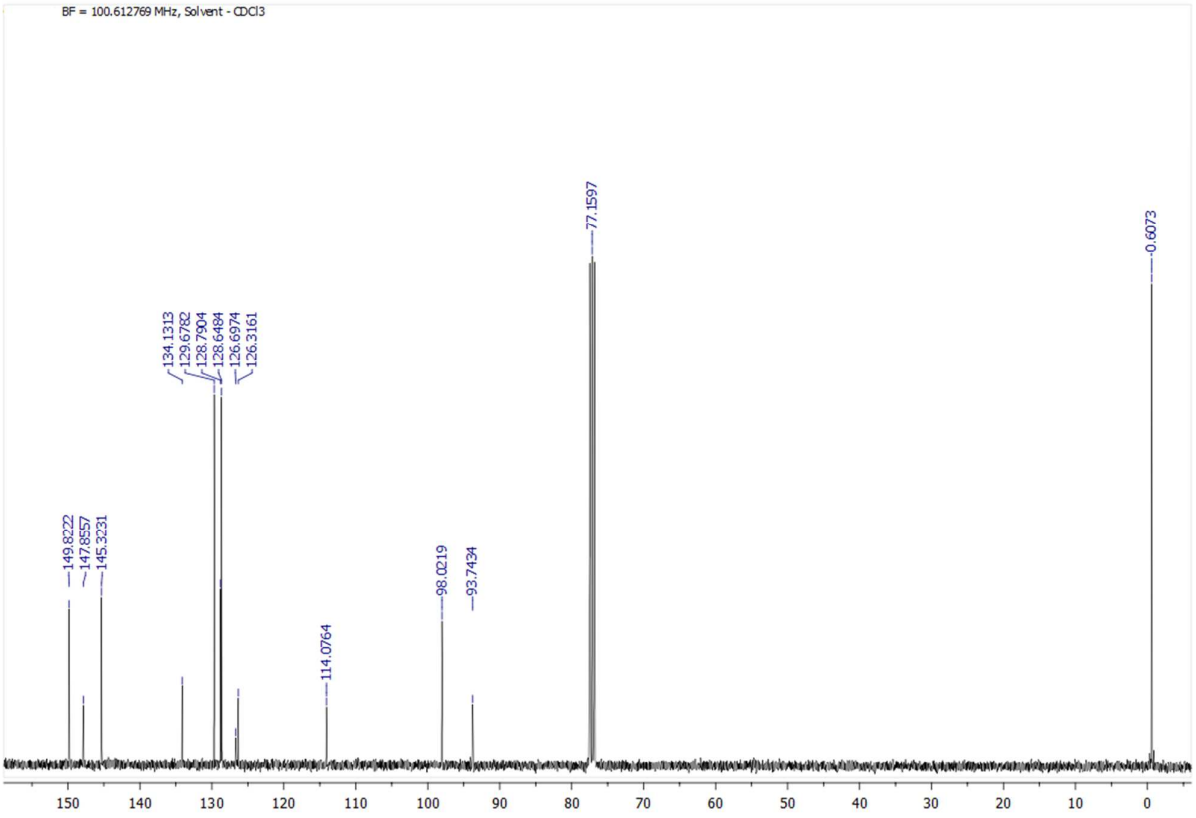
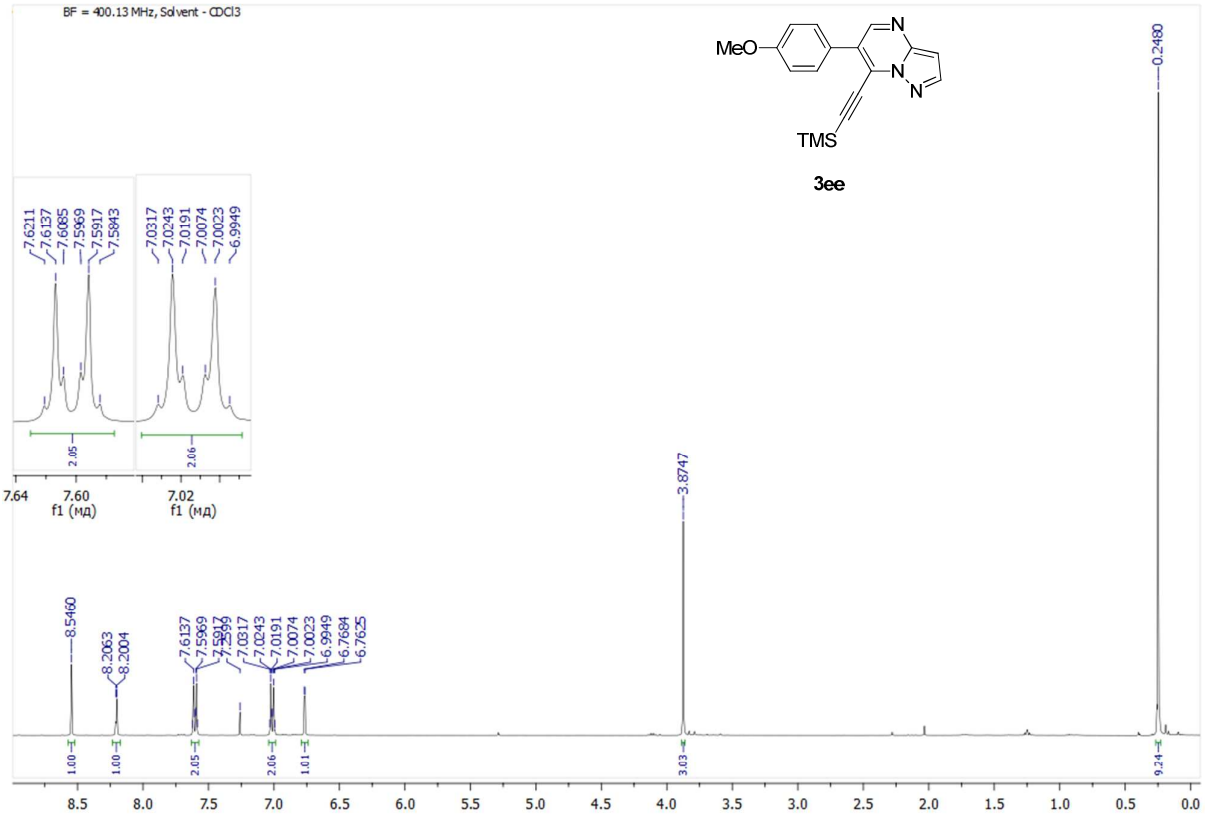
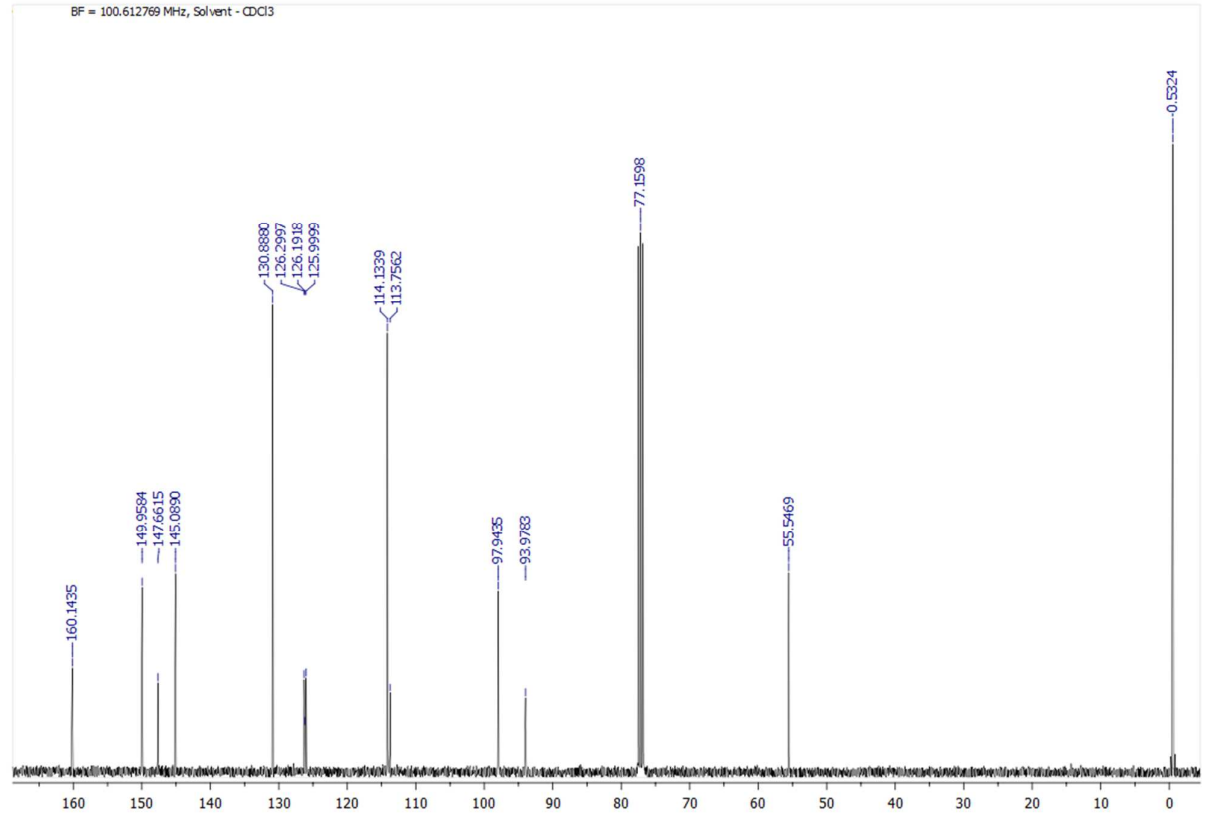
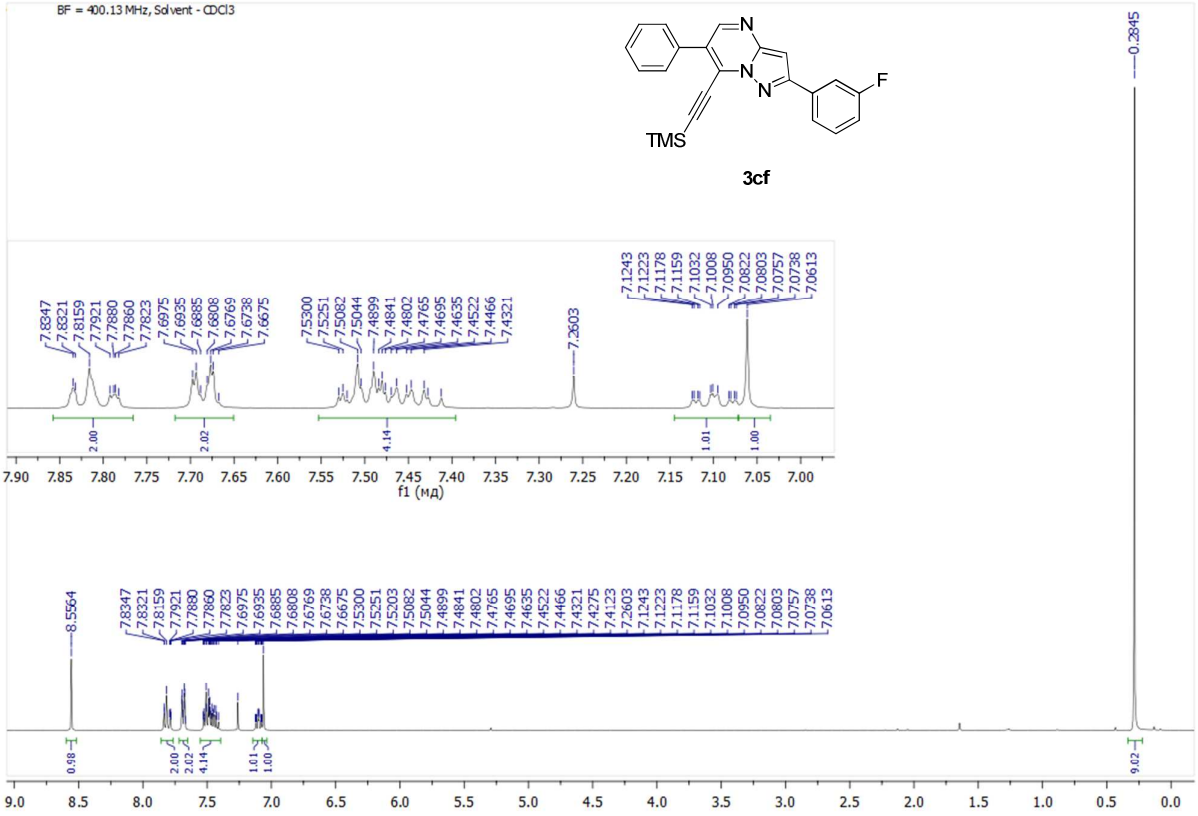
160.0534
156.2275
149.6596
148.8743
130.8133
128.0925
126.5546
125.8197
125.7226
125.2297
114.2832
114.1095
113.6977
94.1178
93.7716
77.1599
55.5525
55.4777
0.4947
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


BF = 400.13 MHz, Solvent - CDCl3
TMS
3ce
7.6696
7.6657
7.6491
7.6464
7.5148
7.5097
7.5049
7.4931
7.4745
7.4673
7.4574
7.4507
7.4405
7.4349
7.4318
2.05
3.17
7.65
7.55
7.45
f1 (мд)
8.5636
8.2316
8.2257
6.7911
6.7853
0.2271
1.00
1.00
2.05
3.17
1.00
9.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


BF = 100.612769 MHz, Solvent - CDCl3
149.8222
147.8557
145.3331
134.1313
129.6782
128.7904
128.6484
126.6974
126.3161
114.0764
98.0219
93.7434
77.1597
0.6073
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


BF = 400.13 MHz, Solvent - CDCl3
MeO
N
N
N
TMS
3ee
0.2480
3.8747
8.5460
8.2063
8.2004
7.6137
7.5969
7.5917
7.5843
7.0317
7.0243
7.0191
7.0074
7.0023
6.9949
6.7684
6.7625
1.00
1.00
2.05
2.06
1.01
3.03
9.24
f1 (мд)
f1 (мд)


BF = 100.612769 MHz, Solvent - CDCl3
0.5324
77.1598
130.8880
126.2997
126.1918
125.9999
114.1339
113.7562
160.1435
149.9584
147.6615
145.0890
97.9435
93.9783
55.5469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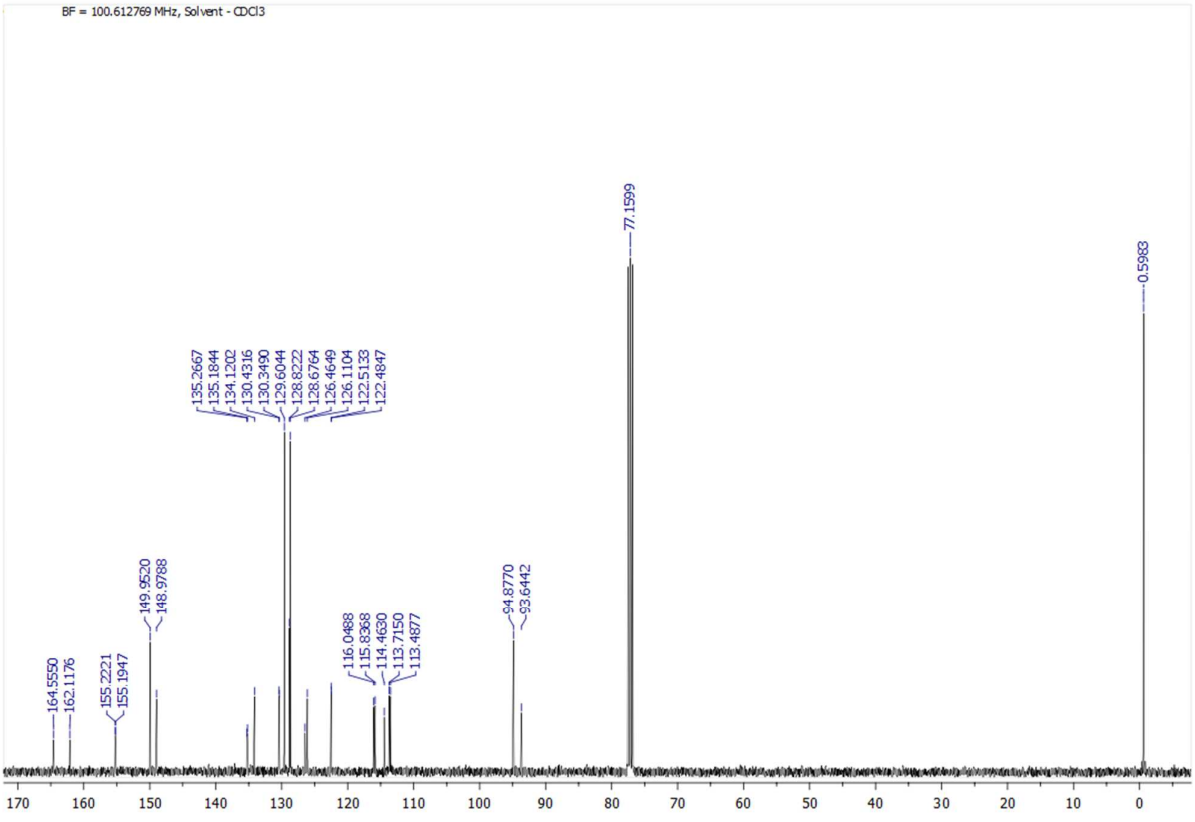
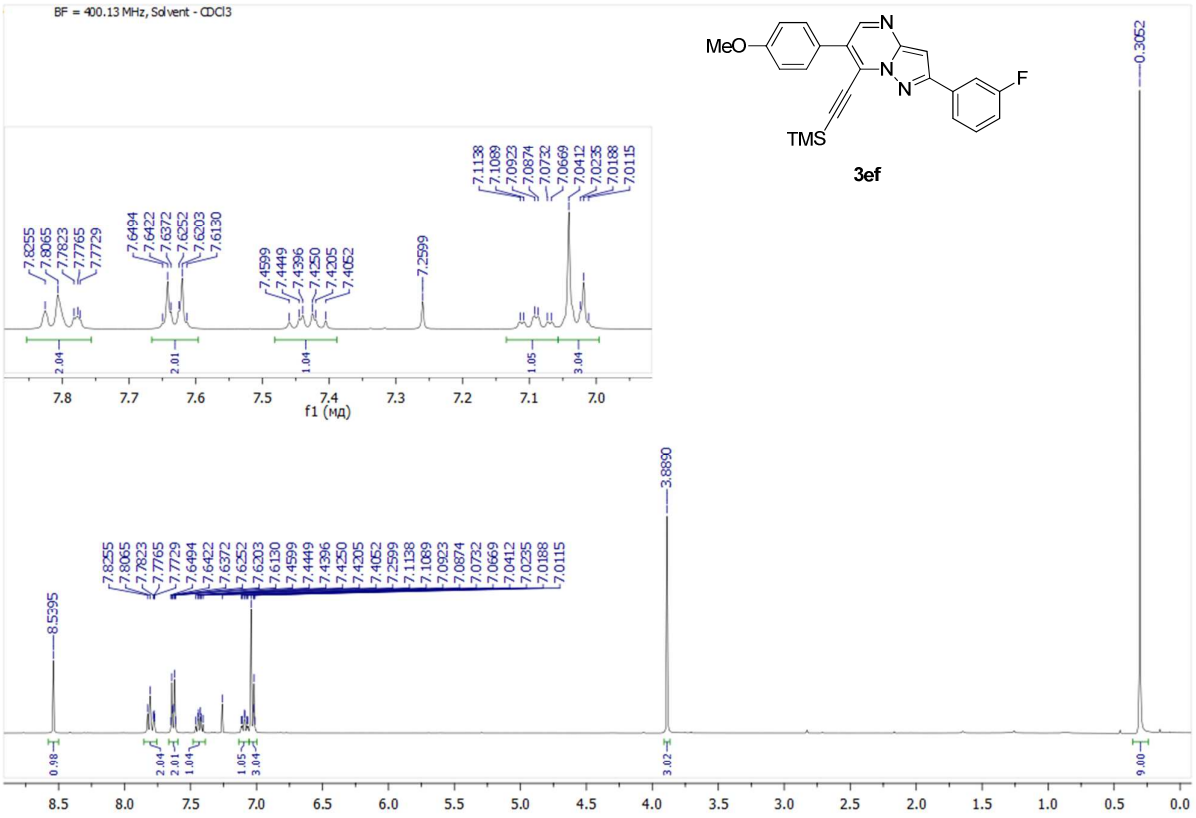
TMS
F
N
N
N
3cf
f1 (мд)


BF = 100.612769 MHz, Solvent - CDCl3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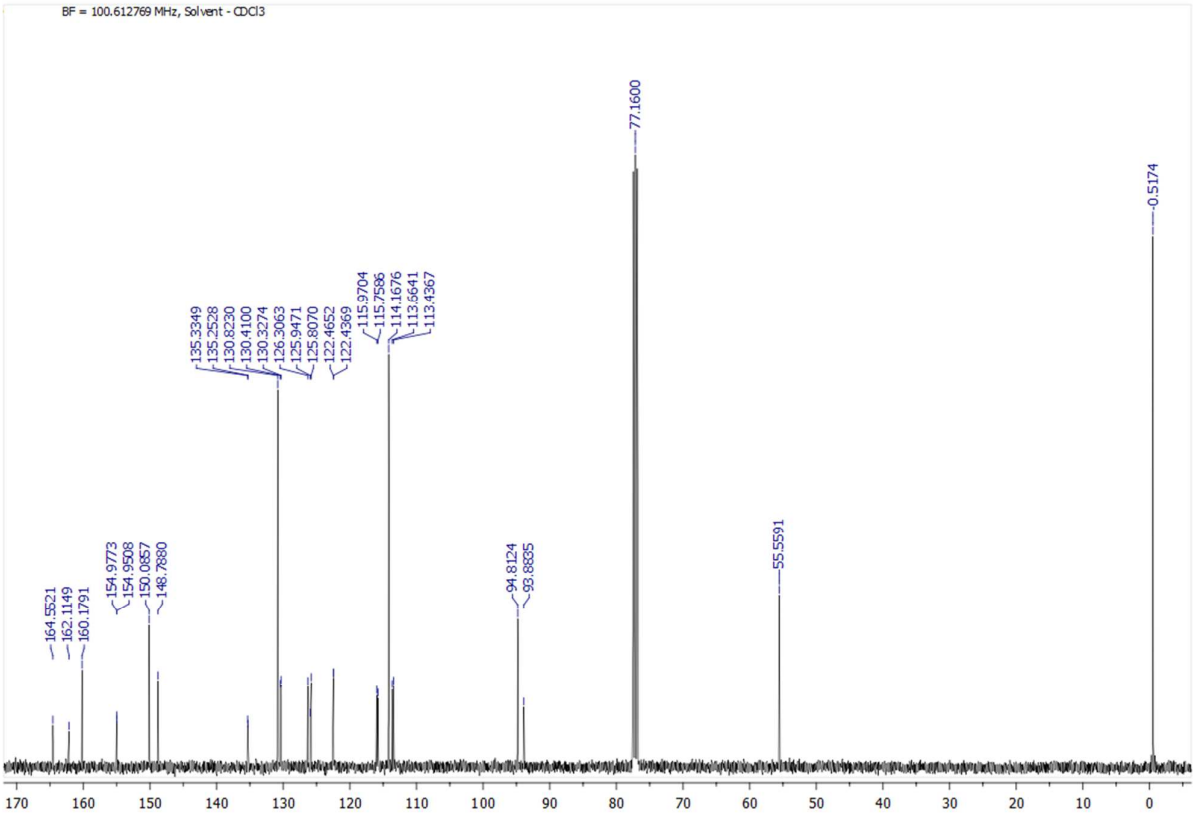
MeO
N
N
N
F
TMS
3ef
f1 (мд)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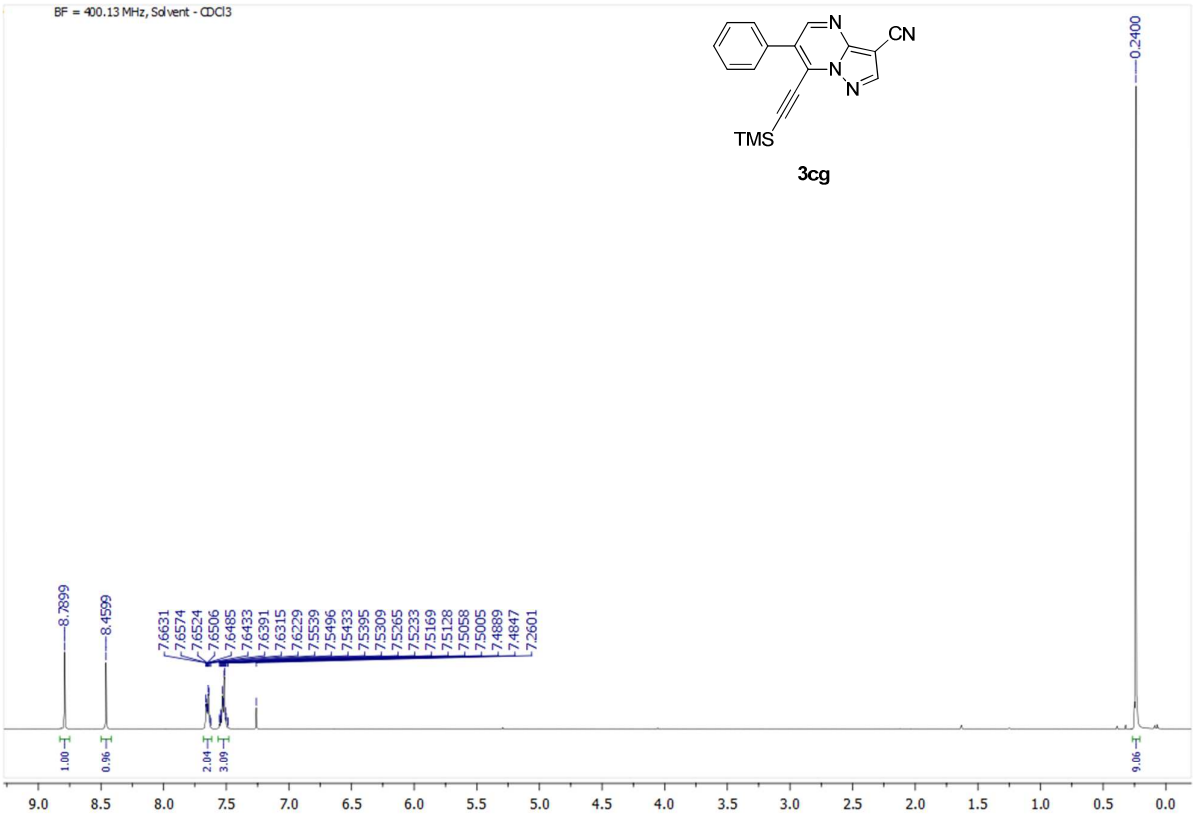
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CN
N
N
TMS
3cg
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8.4599
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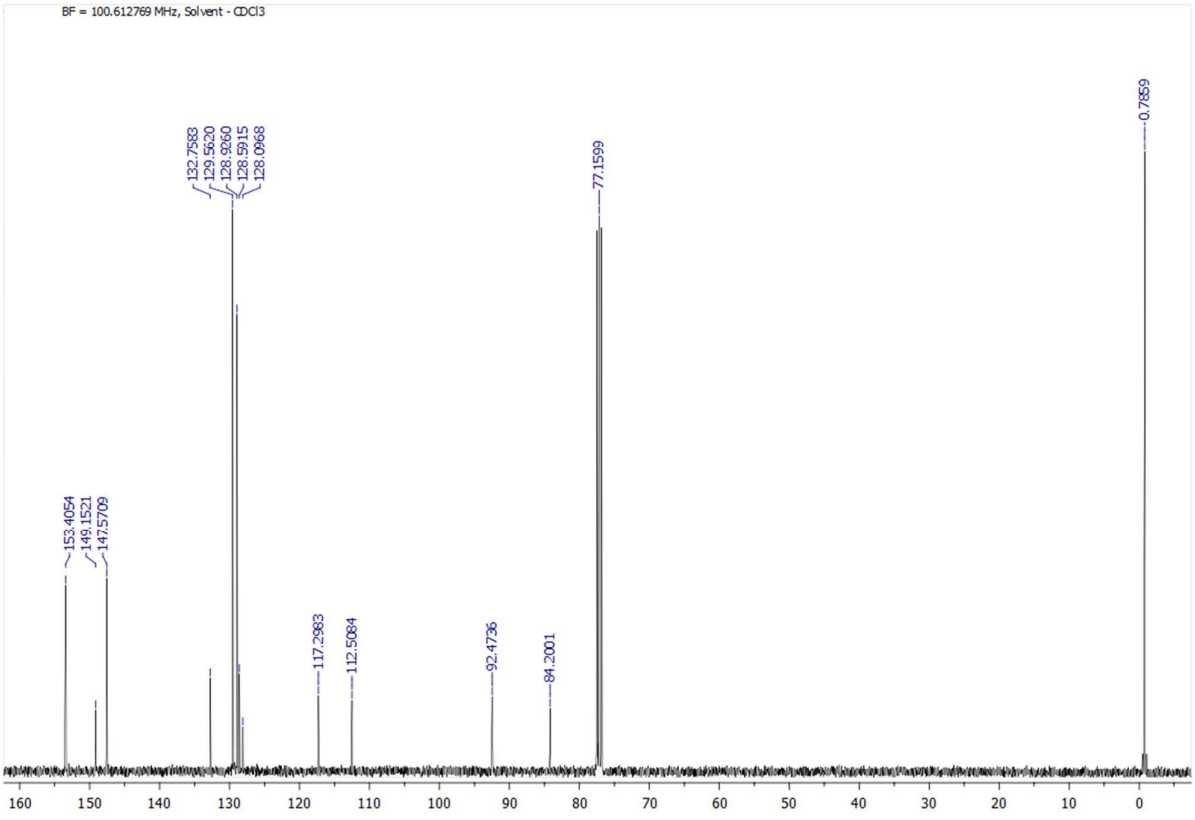
7.6574
7.6524
7.6506
7.6485
7.6433
7.6391
7.6315
7.6229
7.5539
7.5496
7.5433
7.5395
7.5309
7.5265
7.5233
7.5169
7.5128
7.5058
7.5005
7.4889
7.4847
7.2601
1.00
0.96
2.04
3.09
9.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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132.7583
129.5620
128.9260
128.5915
128.0868
77.1599
153.4054
149.1521
147.5709
117.2983
112.5084
92.4736
84.2001
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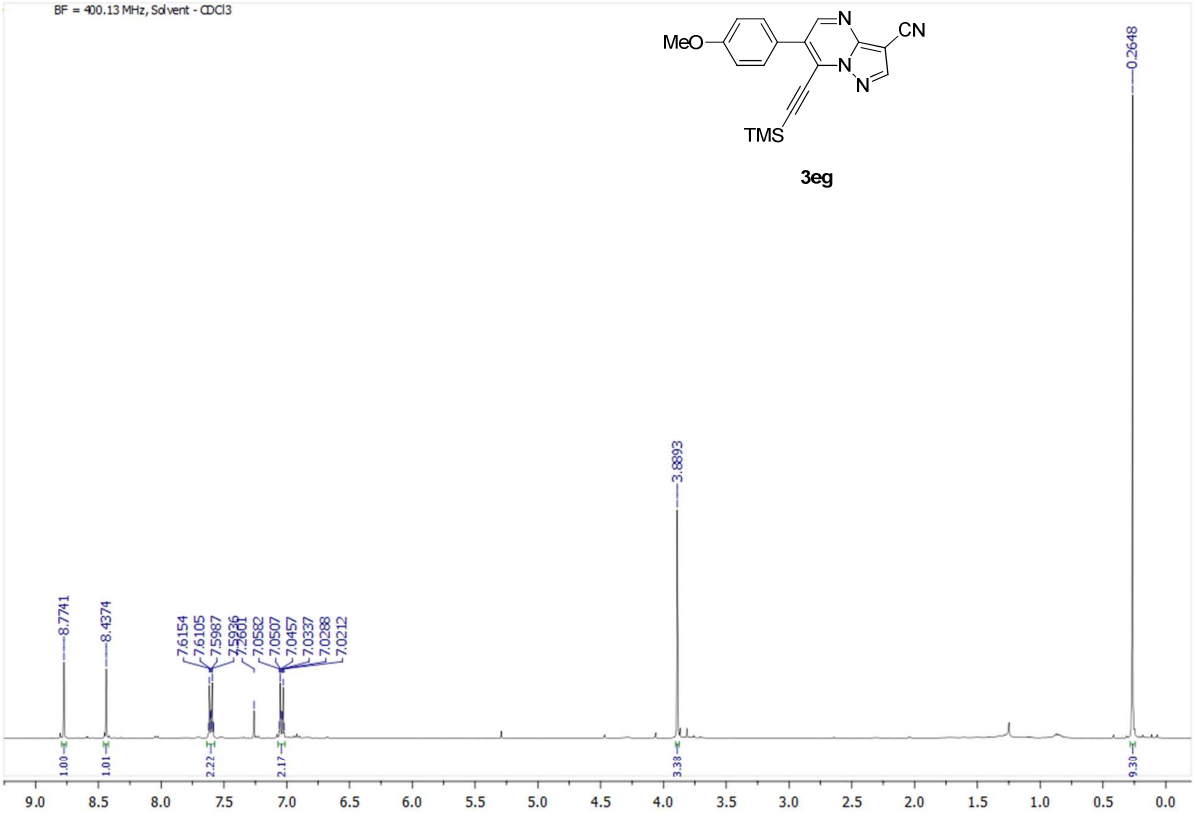
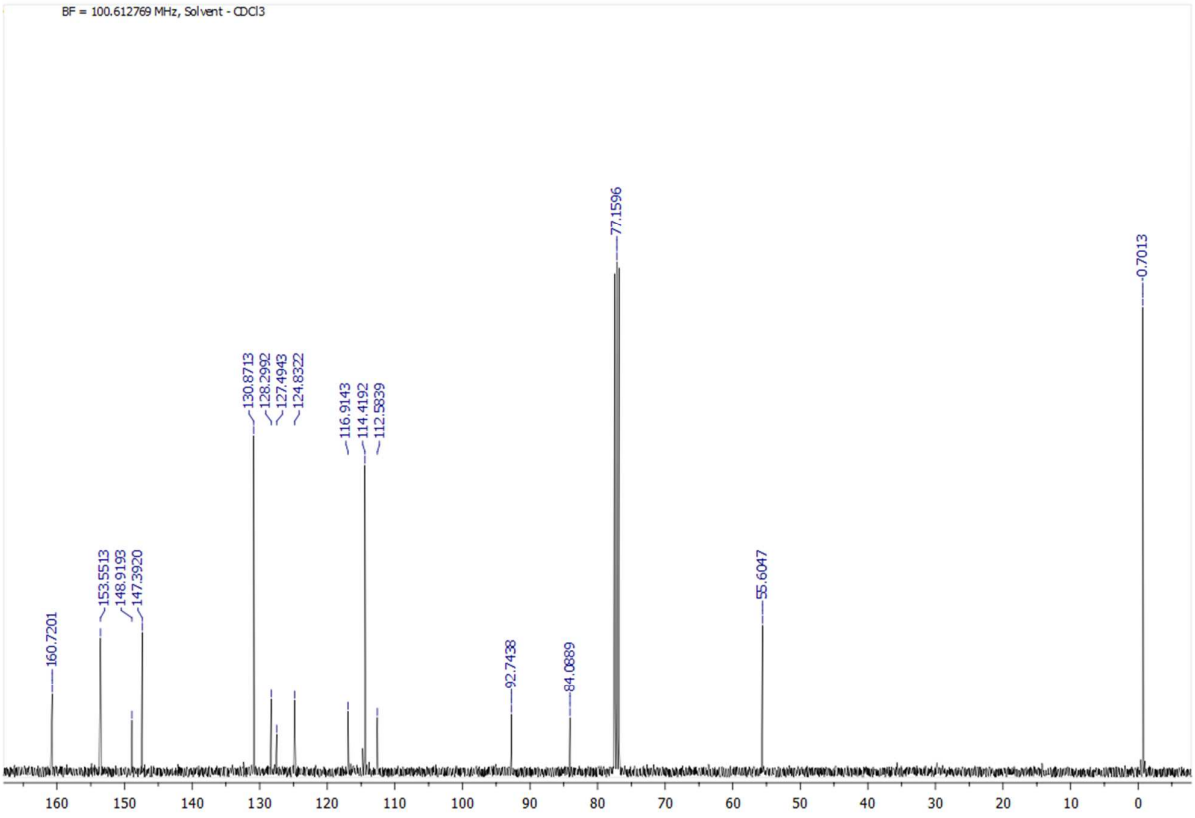
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


BF = 400.13 MHz, Solvent - CDCl3
MeO
N
CN
N
N
TMS
3eg
0.2648
3.8893
8.7741
8.4374
7.6154
7.6105
7.5987
7.0582
7.0507
7.0457
7.0337
7.0288
7.0212
1.03
1.01
2.22
2.17
3.38
9.30
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


BF = 100.612769 MHz, Solvent - CDCl3
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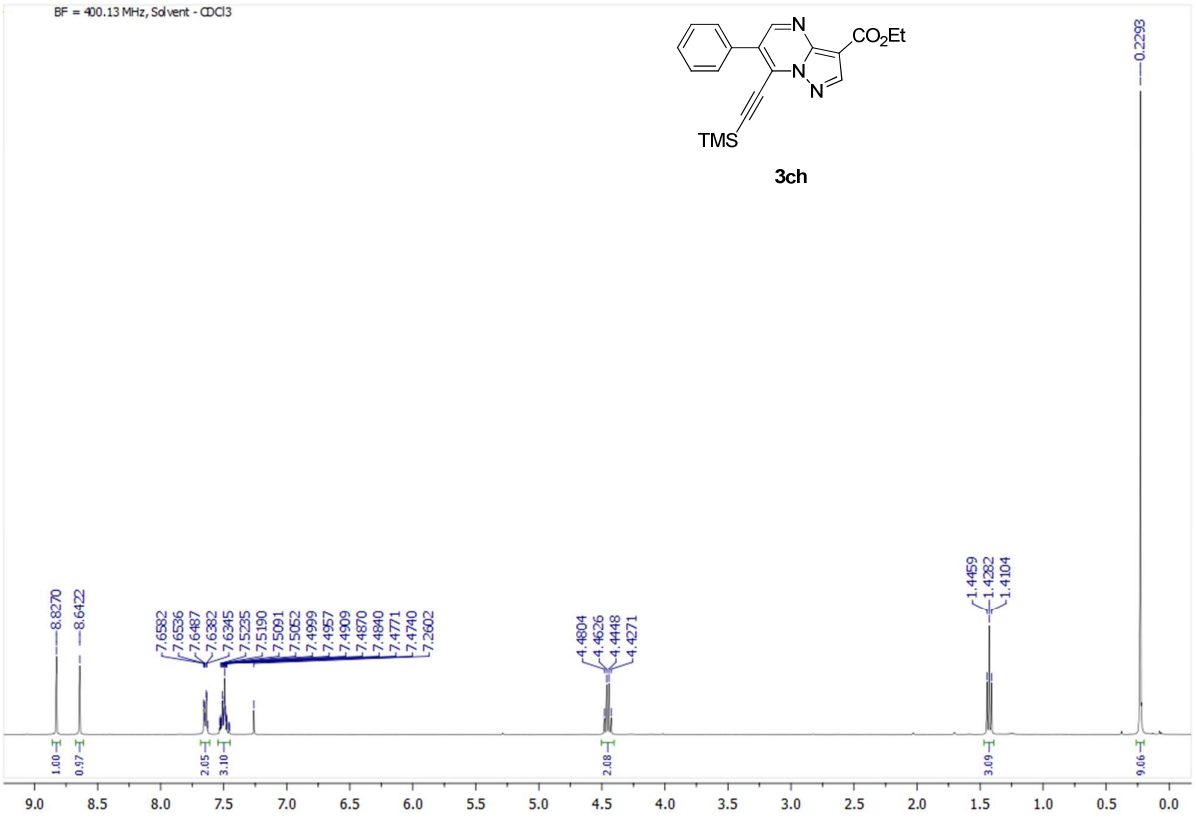
148.9193
147.3920
130.8713
128.2992
127.4943
124.8322
116.9143
114.4192
112.5839
92.7438
84.0889
77.1596
55.6047
0.7013
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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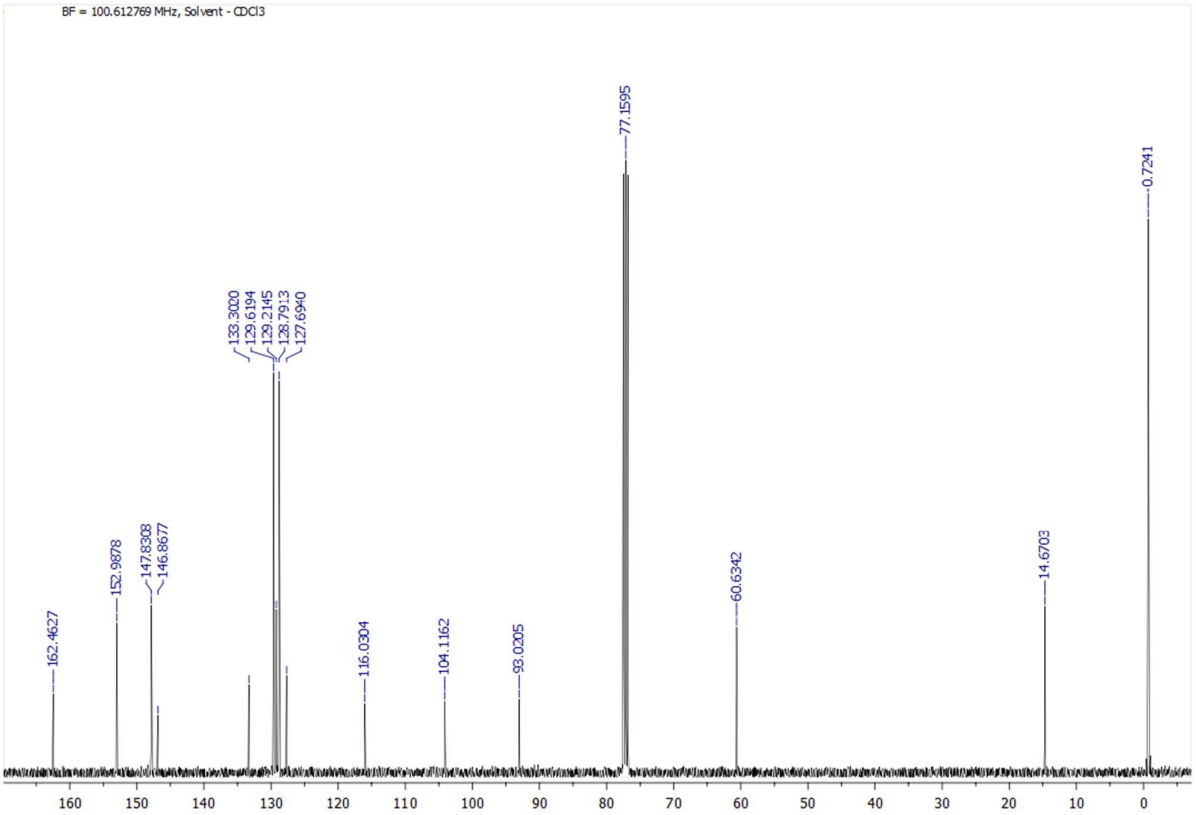
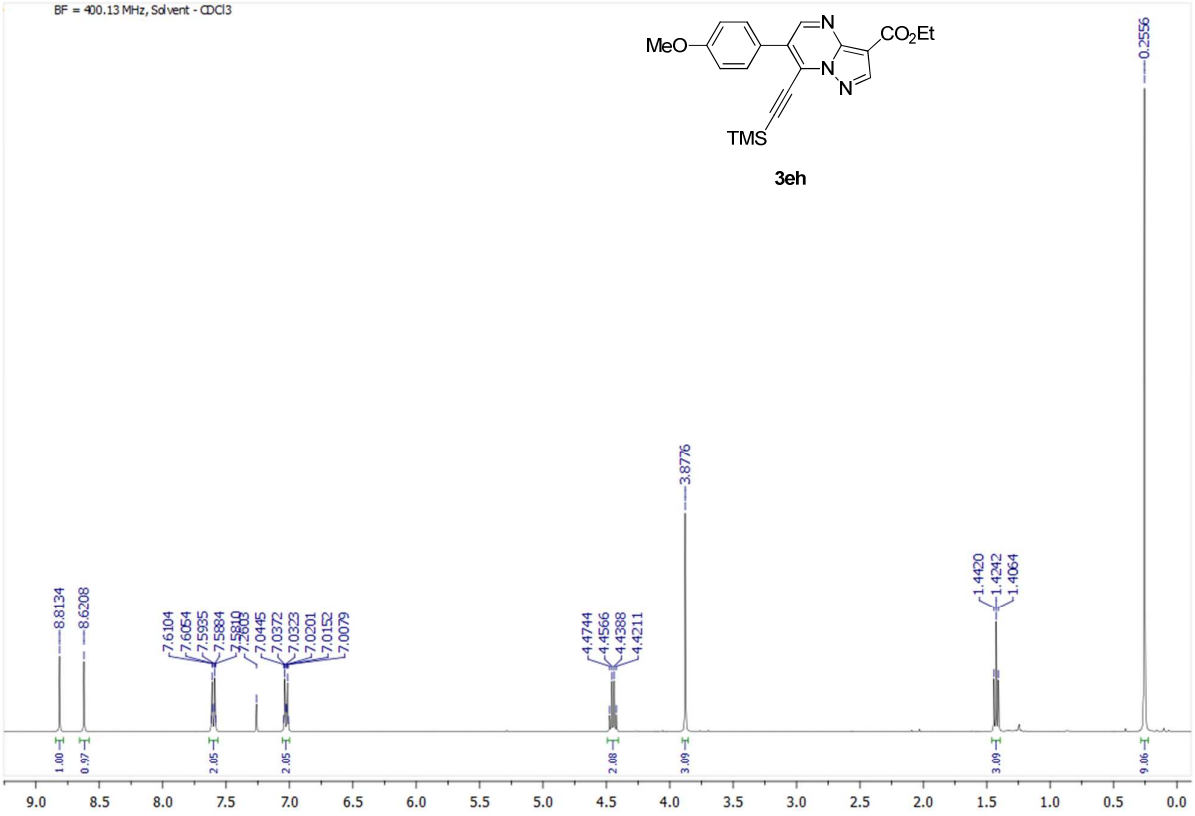
CO2Et
N
N
N
TMS
3ch
0.2293
8.8270
8.6422
7.6582
7.6536
7.6487
7.6382
7.6345
7.5225
7.5190
7.5091
7.5052
7.4999
7.4957
7.4909
7.4870
7.4840
7.4771
7.4740
7.2602
4.4804
4.4626
4.4448
4.4271
1.4459
1.4282
1.4104
1.00
0.97
2.05
3.10
2.08
3.09
9.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


BF = 100.612769 MHz, Solvent - CDCl3
77.1595
0.7241
133.3020
129.6194
129.2145
128.7913
127.6940
162.4627
152.9878
147.8308
146.8677
116.0304
104.1162
93.0205
60.6342
14.6703
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


BF = 400.13 MHz, Solvent - CDCl3
MeO
CO2Et
N
N
N
TMS
3eh
0.2556
3.8776
1.4420
1.4242
1.4064
8.8134
8.6208
7.6104
7.6054
7.5995
7.5884
7.5810
7.5803
7.0445
7.0372
7.0323
7.0201
7.0152
7.0079
4.4744
4.4566
4.4388
4.4211
1.00
0.97
2.05
2.05
2.08
3.09
3.09
9.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
3.0
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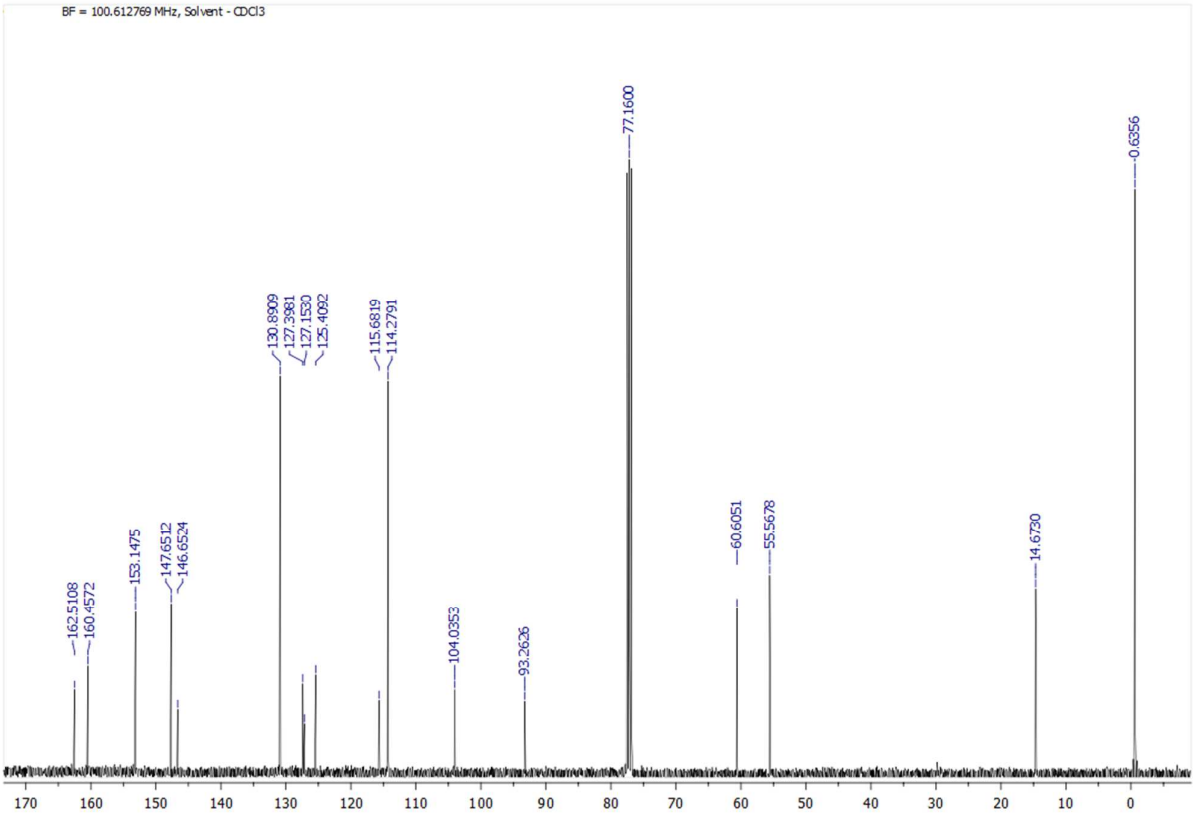
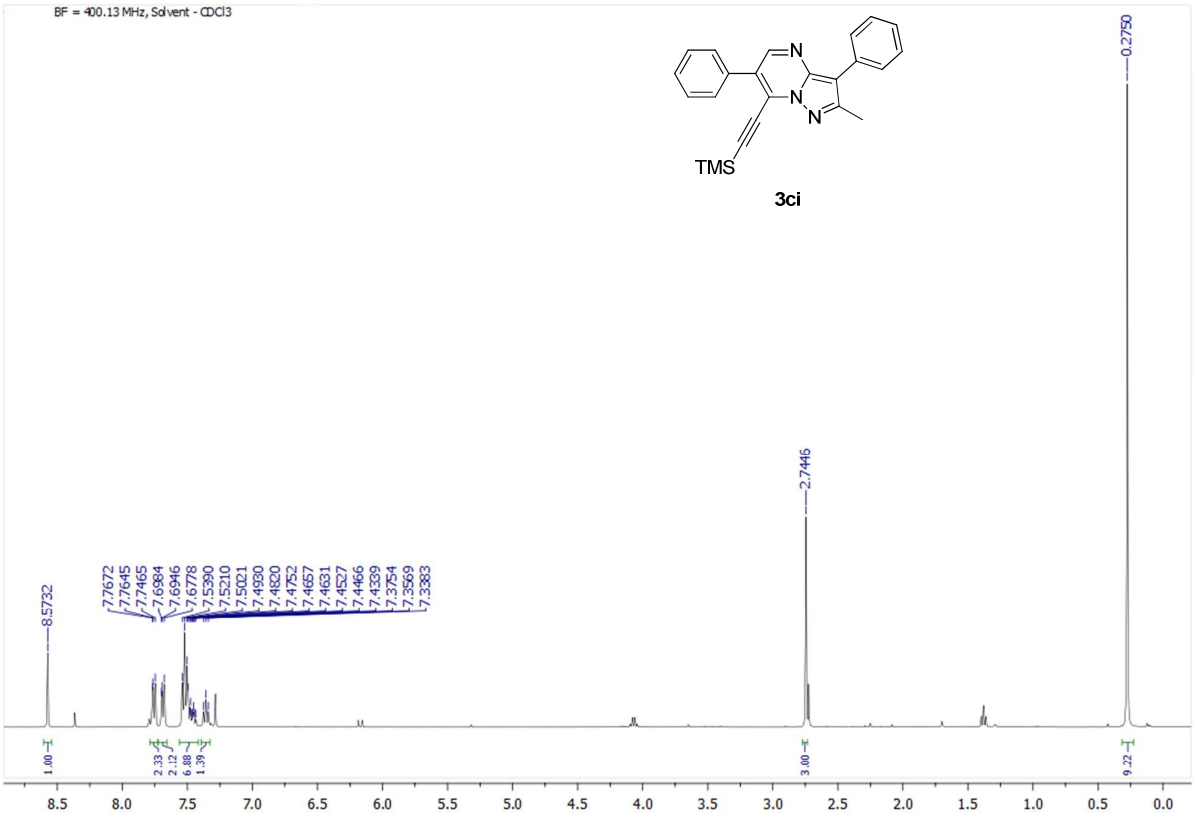
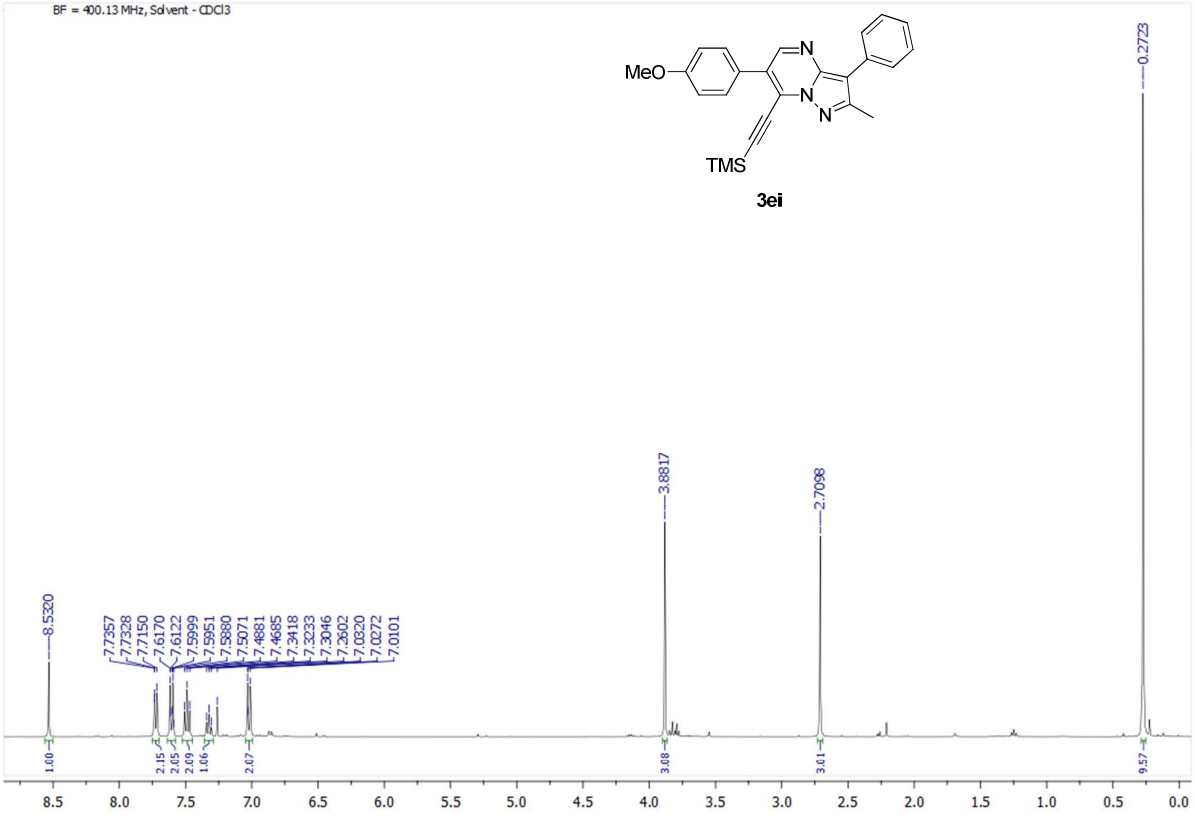
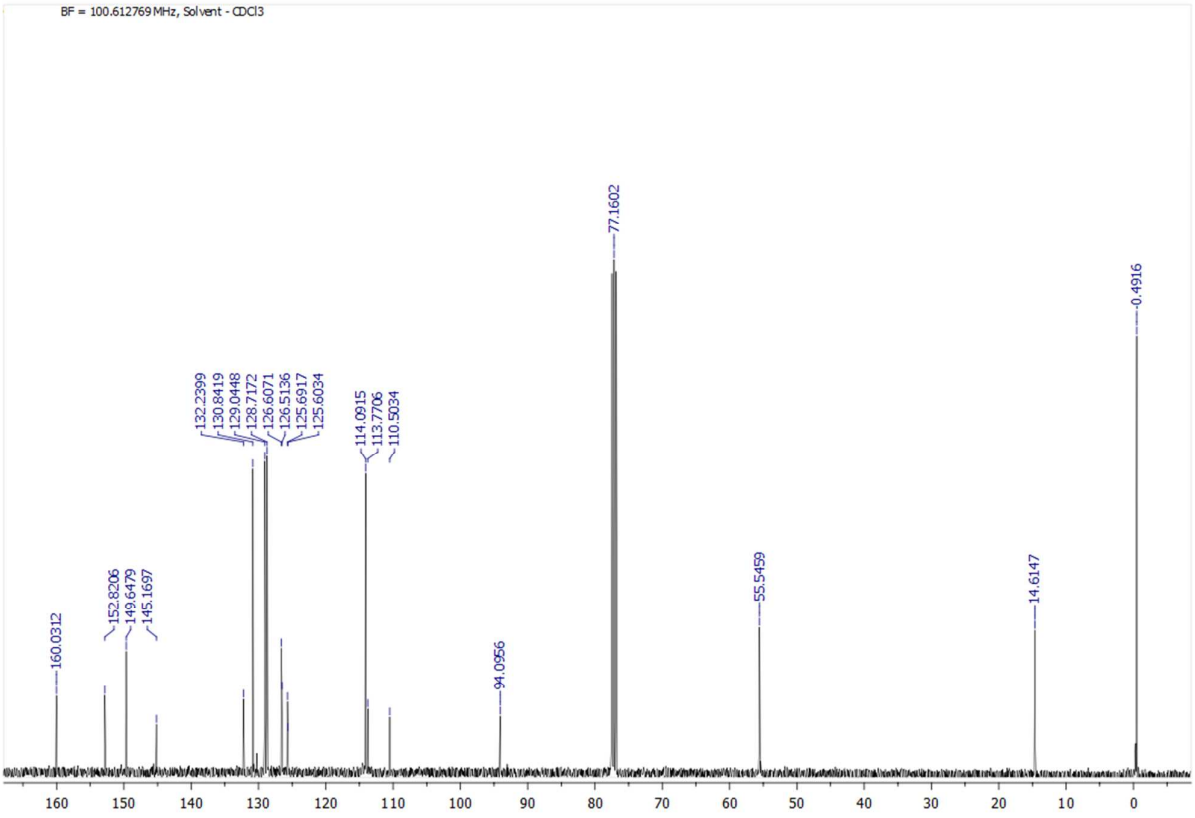
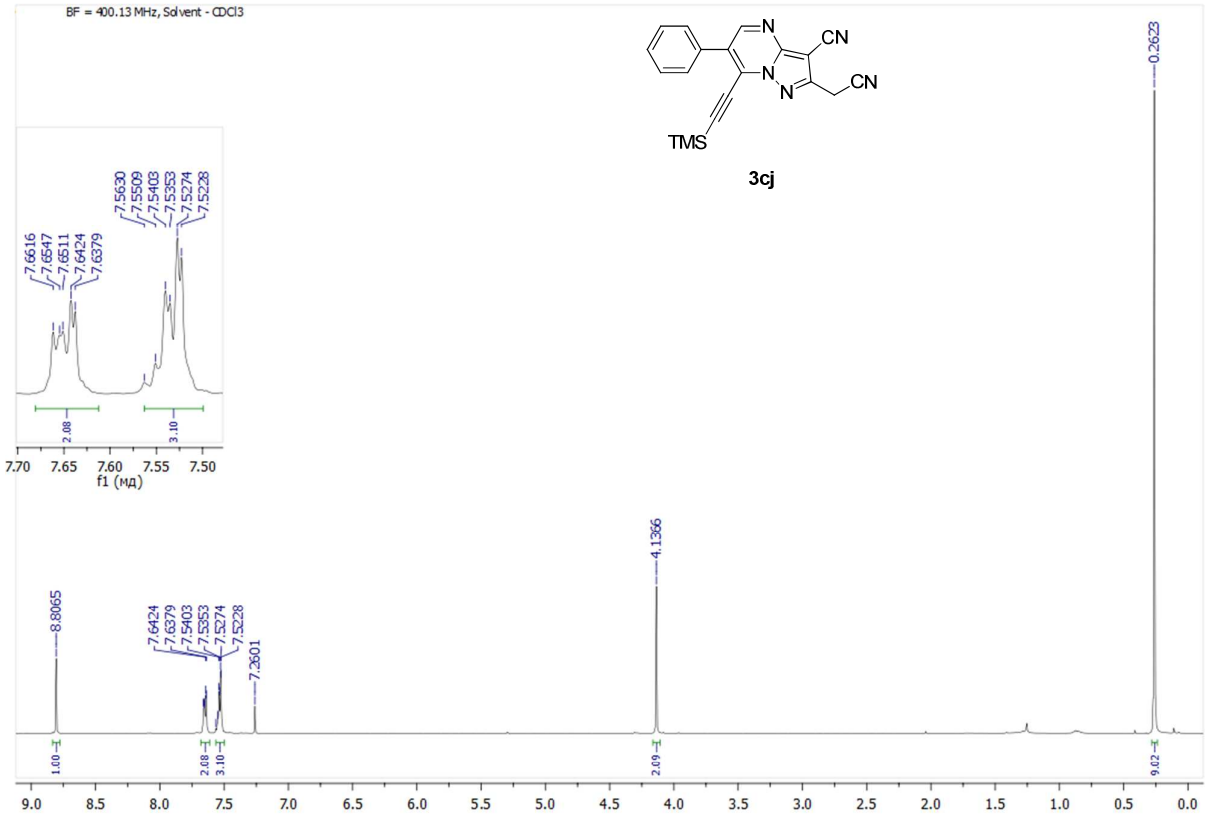
2.0
1.5
1.0
0.5
0.0

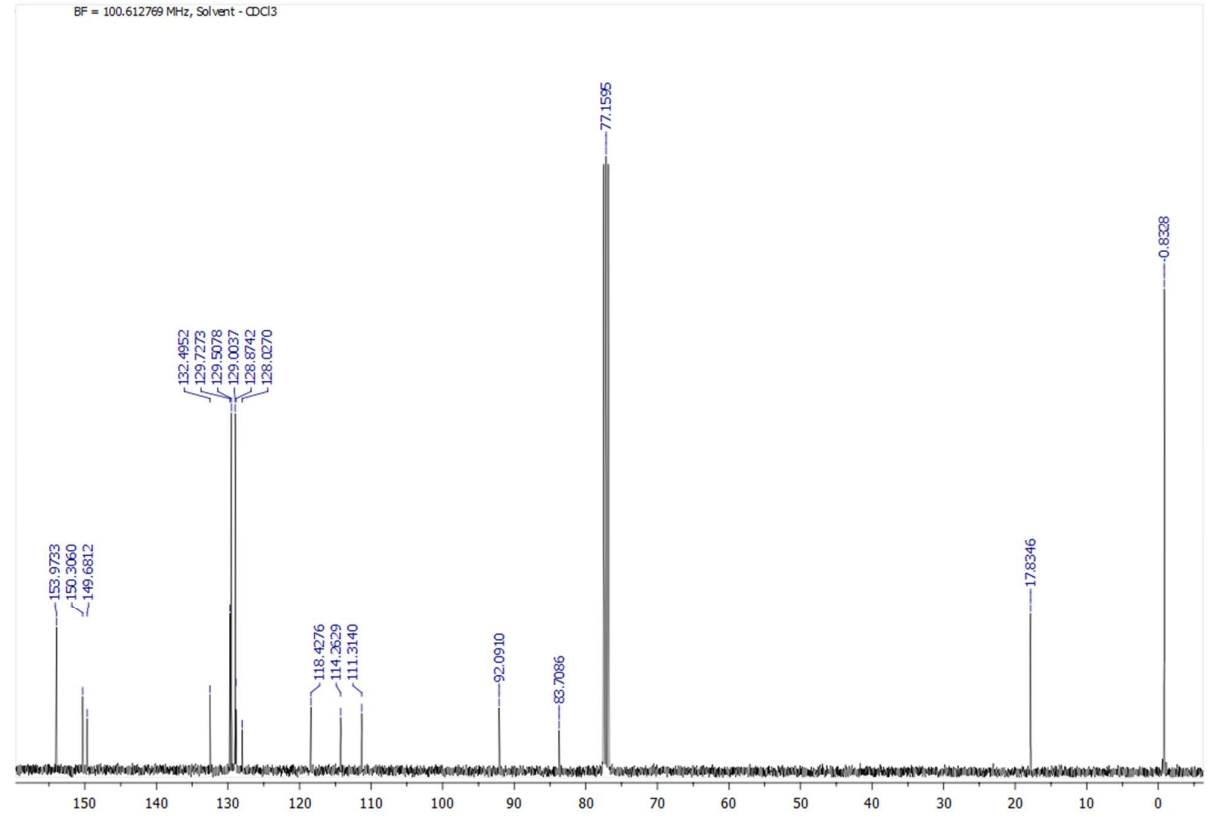

BF = 100.612769 MHz, Solvent - CDCl3
77.1600
0.6356
130.8909
127.3981
127.1530
125.4092
115.6819
114.2791
162.5108
160.4572
153.1475
147.6512
146.6524
104.0353
93.2626
60.6051
55.5678
14.6730
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

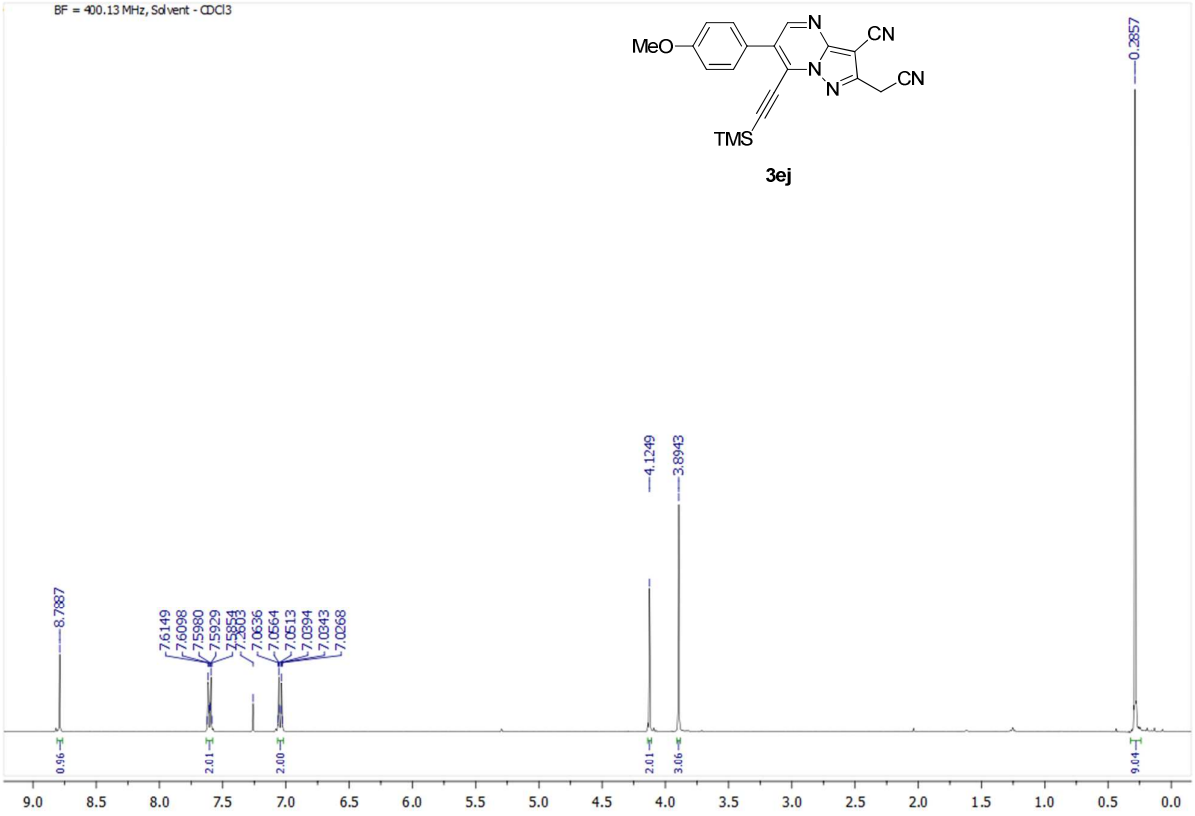

BF = 400.13 MHz, Solvent - CDCl3
TMS
3ci
8.5732
7.7672
7.7645
7.7465
7.6984
7.6946
7.6778
7.5390
7.5210
7.5021
7.4930
7.4820
7.4752
7.4657
7.4631
7.4527
7.4466
7.4339
7.3754
7.3569
7.3383
2.7446
0.2750
1.00
2.33
2.12
6.88
1.39
3.00
9.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

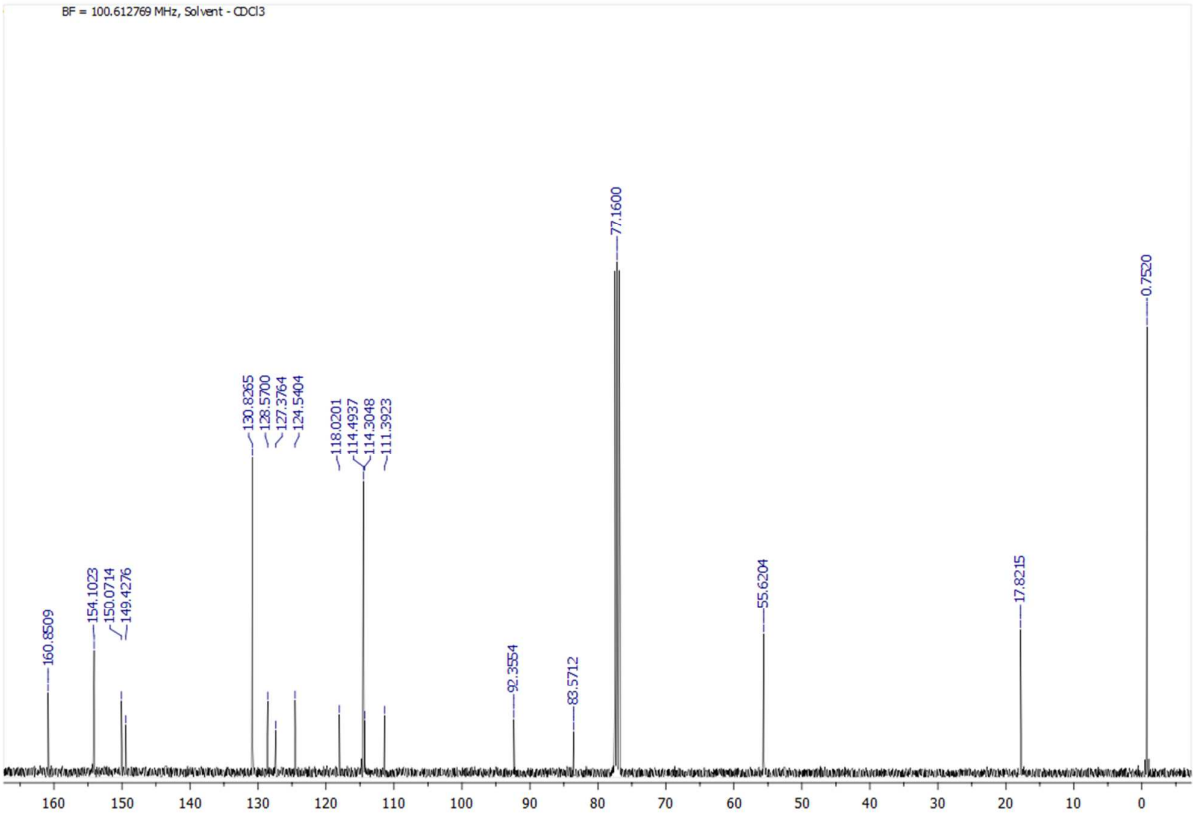

BF = 400.13 MHz, Solvent - CDCl3
MeO
N
N
N
TMS
3ei
0.2723
3.8817
2.7098
8.5320
7.7357
7.7328
7.7150
7.6170
7.6122
7.5999
7.5951
7.5880
7.5071
7.4881
7.4685
7.3418
7.3233
7.3046
7.2602
7.0320
7.0272
7.0101
1.00
2.15
2.05
2.09
1.06
2.07
3.08
3.01
9.57
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

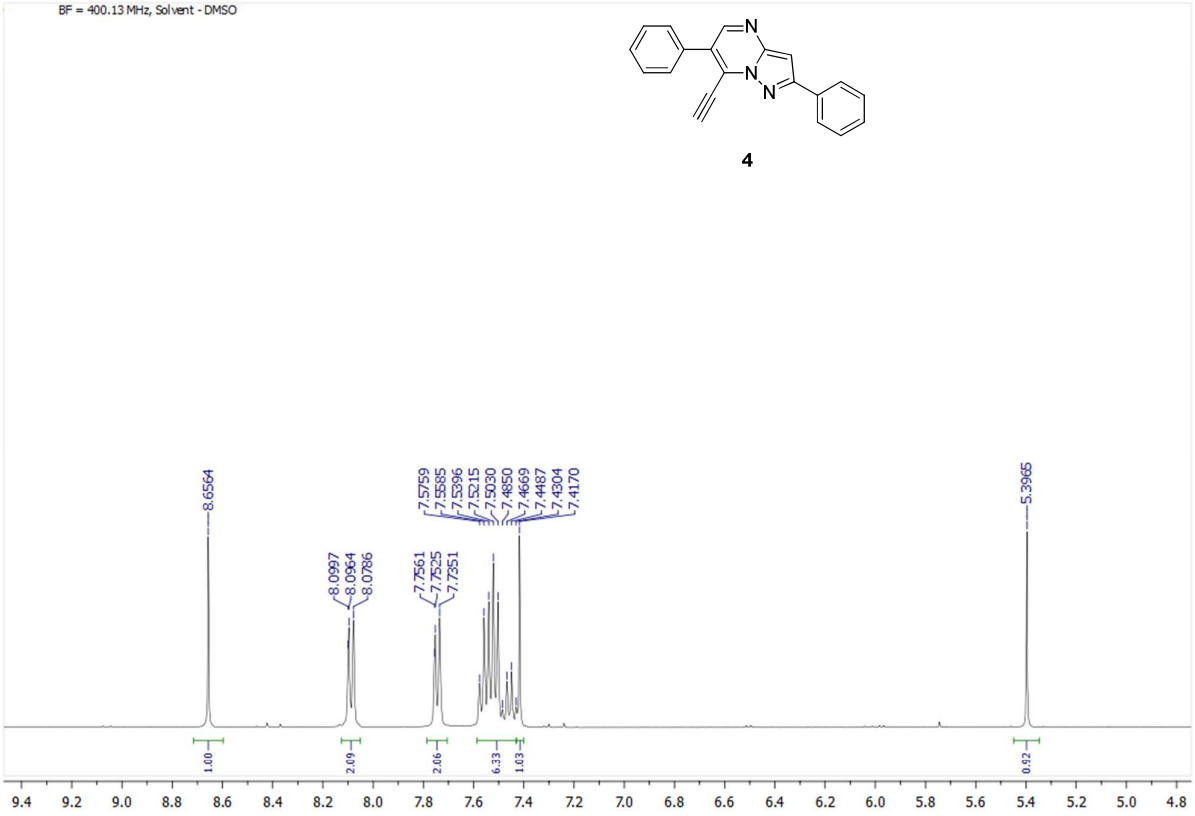

BF = 100.612769 MHz, Solvent - CDCl3
77.1602
-0.4916
132.2399
130.8419
129.0448
128.7172
126.6071
126.5136
125.6917
125.6034
114.0915
113.7706
110.5034
152.8206
149.6479
145.1697
160.0312
94.0956
55.5459
14.6147
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

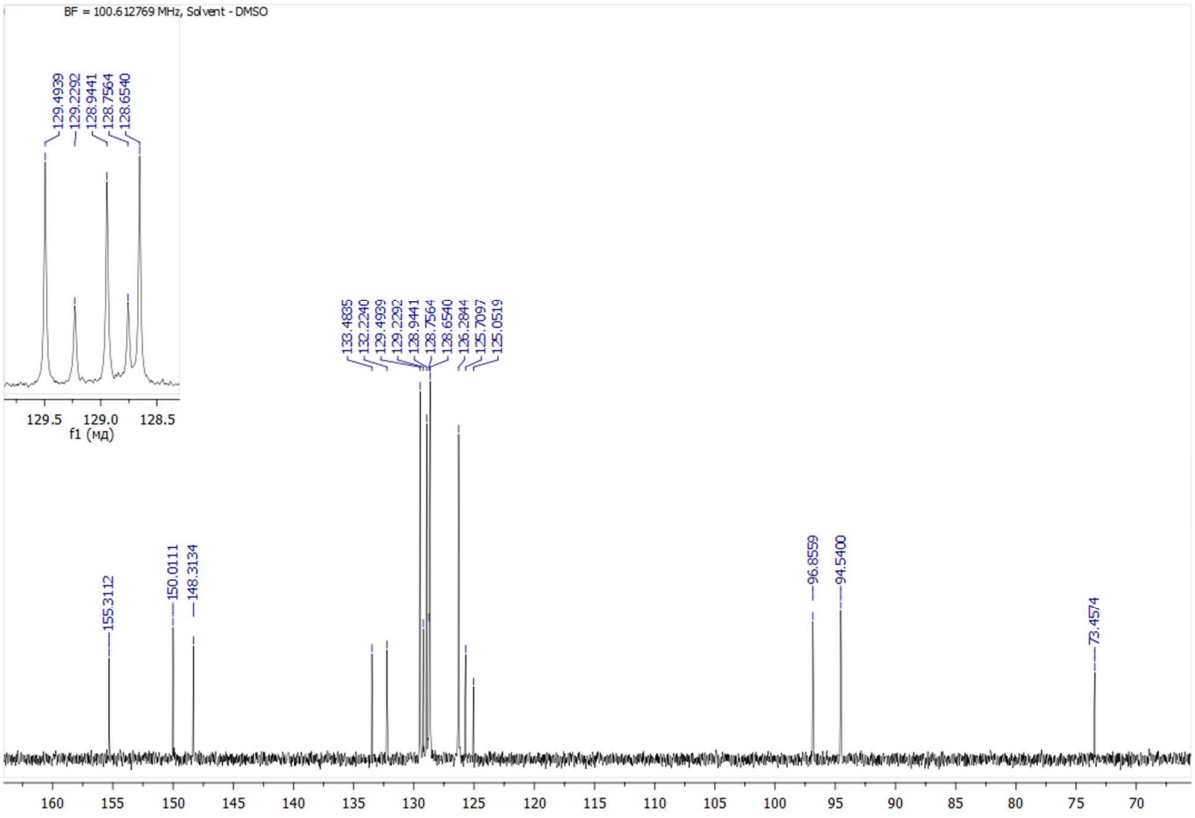

BF = 400.13 MHz, Solvent - CDCl3
N
CN
N
N
CN
TMS
3cj
7.6616
7.6547
7.6511
7.6424
7.6379
7.5630
7.5509
7.5403
7.5353
7.5274
7.5228
2.08
3.10
7.70 7.65 7.60 7.55 7.50
f1 (мд)
8.8065
7.6424
7.6379
7.5403
7.5353
7.5274
7.5228
7.3601
4.1366
0.2623
1.00
2.08
3.10
2.09
9.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


BF = 100.612769 MHz, Solvent - CDCl3
153.9733
150.3060
149.6812
132.4952
129.7273
129.5078
129.0037
128.8742
128.0270
118.4276
114.2629
111.3140
92.0910
83.7086
77.1595
17.8346
0.8328
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


BF = 400.13 MHz, Solvent - CDCl3
MeO
N
CN
N
N
CN
TMS
3ej
0.2857
4.1249
3.8943
8.7887
7.6149
7.6098
7.5980
7.5929
7.0636
7.0564
7.0513
7.0394
7.0343
7.0268
0.86
2.01
2.00
2.01
3.06
9.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


BF = 100.612769 MHz, Solvent - CDCl3
77.1600
0.7520
130.8365
128.5700
127.3764
124.5404
118.0201
114.4937
114.3048
111.3923
160.8509
154.1023
150.0714
149.4276
92.3554
83.5712
55.6204
17.8215
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


BF = 400.13 MHz, Solvent - DMSO
8.6564
8.0997
8.0964
8.0786
7.7561
7.7525
7.7351
7.5759
7.5585
7.5396
7.5215
7.5030
7.4850
7.4669
7.4487
7.4304
7.4170
5.3965
1.00
2.09
2.06
6.33
1.03
0.82
9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8


BF = 100.612769 MHz, Solvent - DMSO
129.4939
129.2292
128.9441
128.7564
128.6540
129.5 129.0 128.5
f1 (мд)
133.4835
132.2240
129.4939
129.2292
128.9441
128.7564
128.6540
126.2844
125.7097
125.0519
155.3112
150.0111
148.3134
96.8559
94.5400
73.4574
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70