Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Deproto-metallation using a mixed lithium-zinc base and computed CH acidity of 1-aryl 1*H*-benzotriazoles and 1-aryl 1*H*-indazoles

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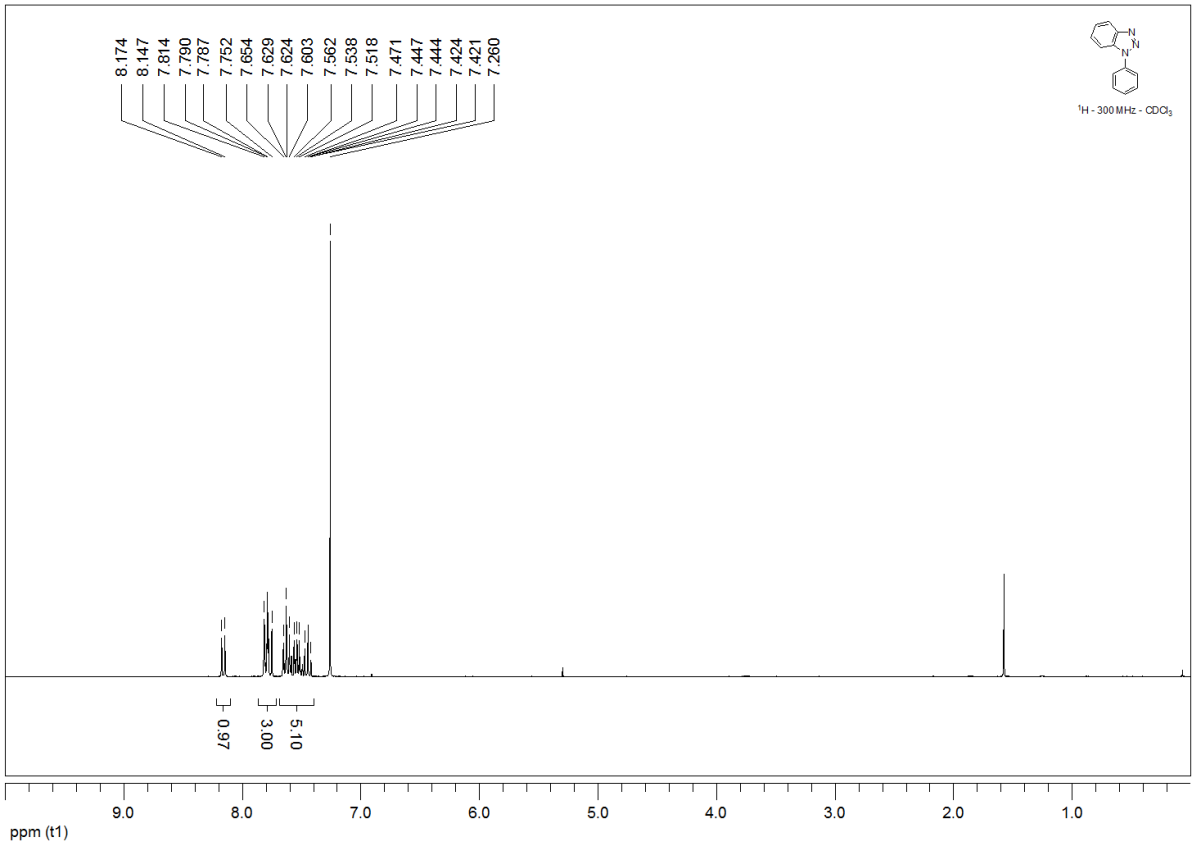
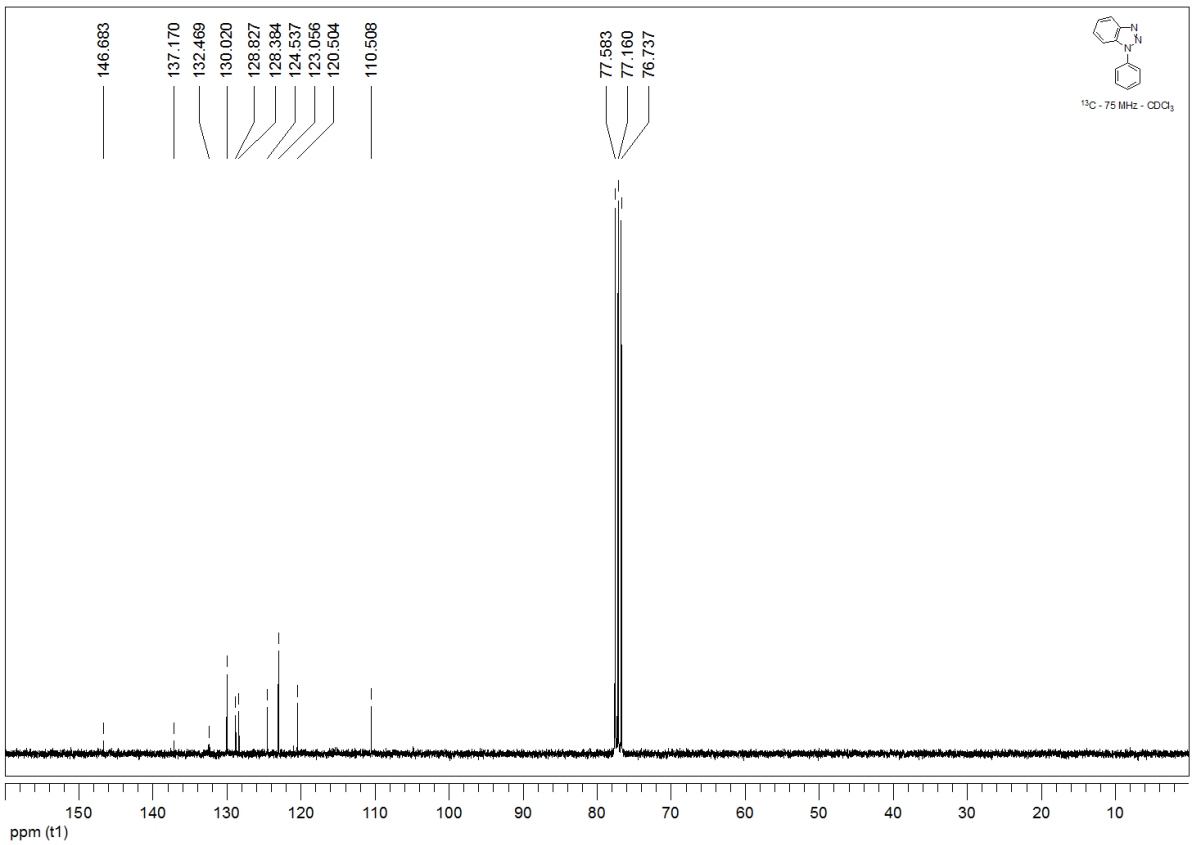
^{1}H, ^{13}C and ^{19}F NMR and spectra

1-Phenyl-1*H*-benzotriazole (1a).





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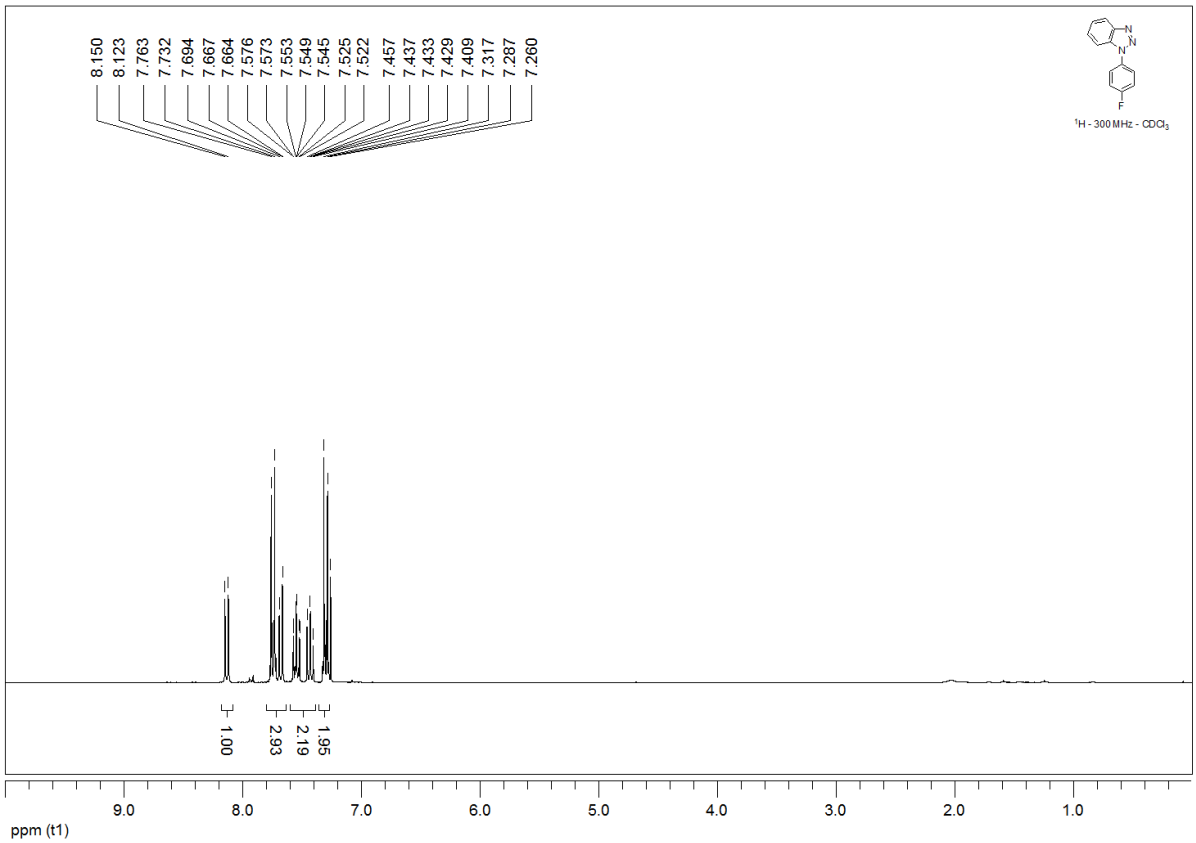

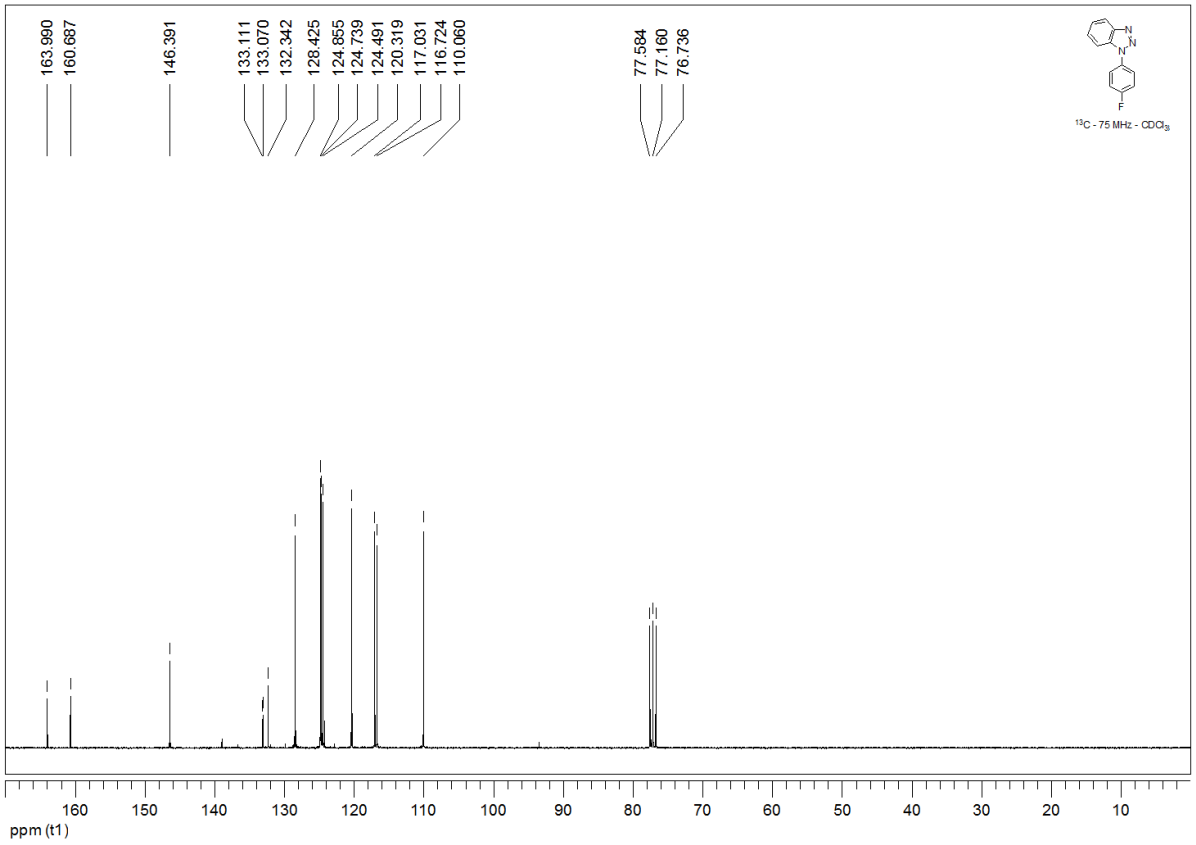

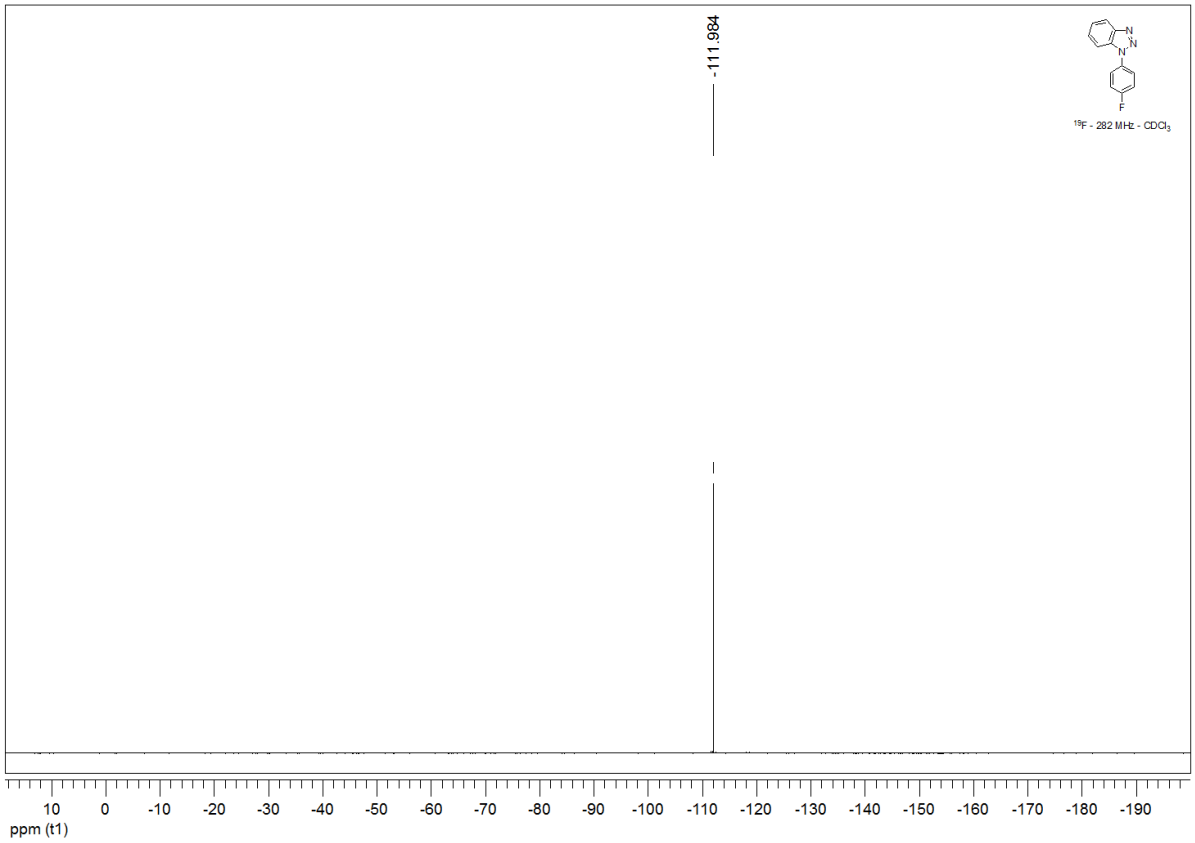

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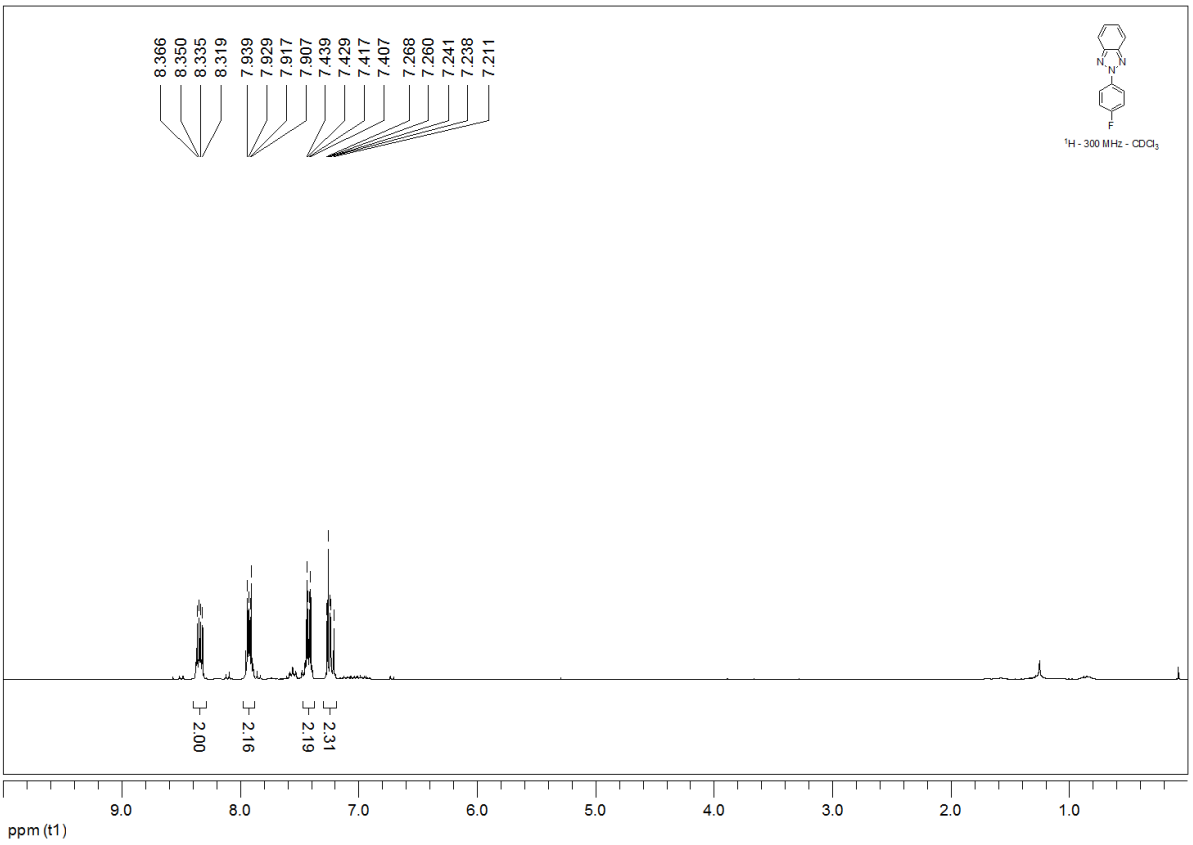

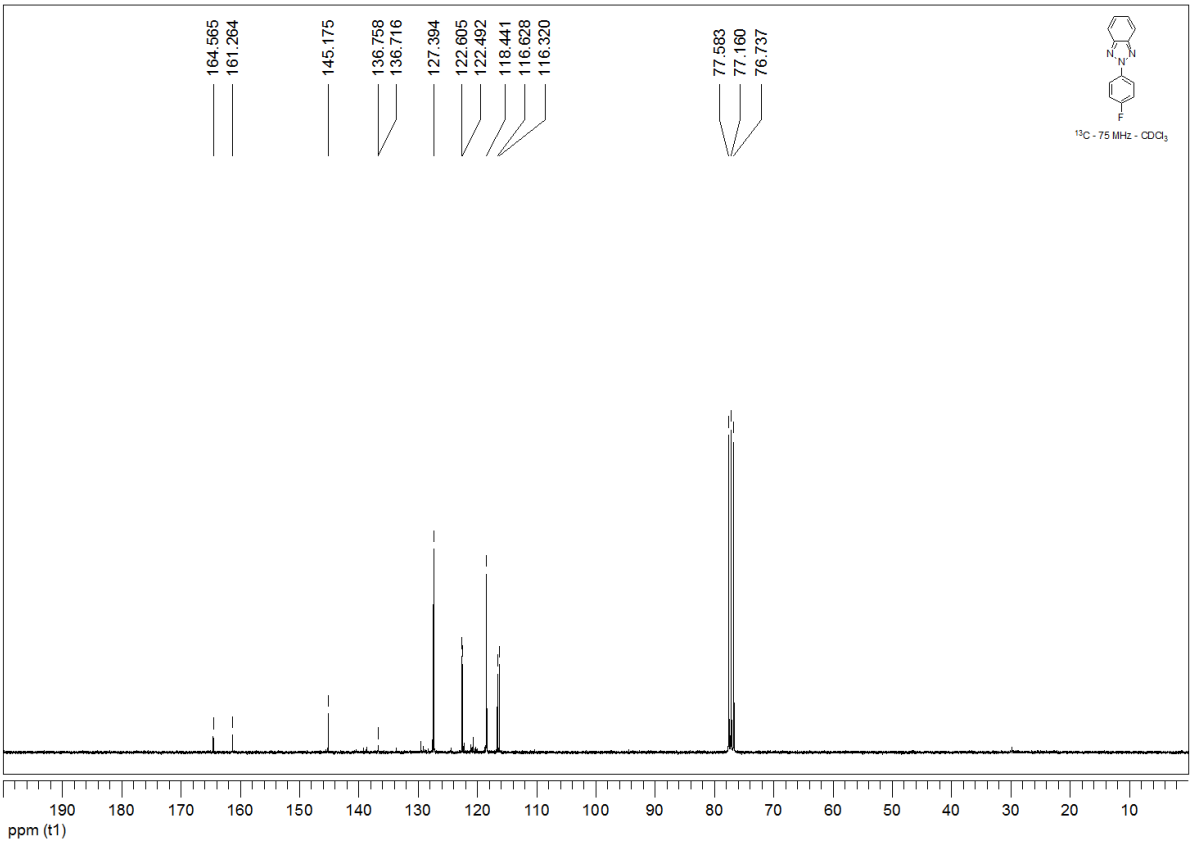

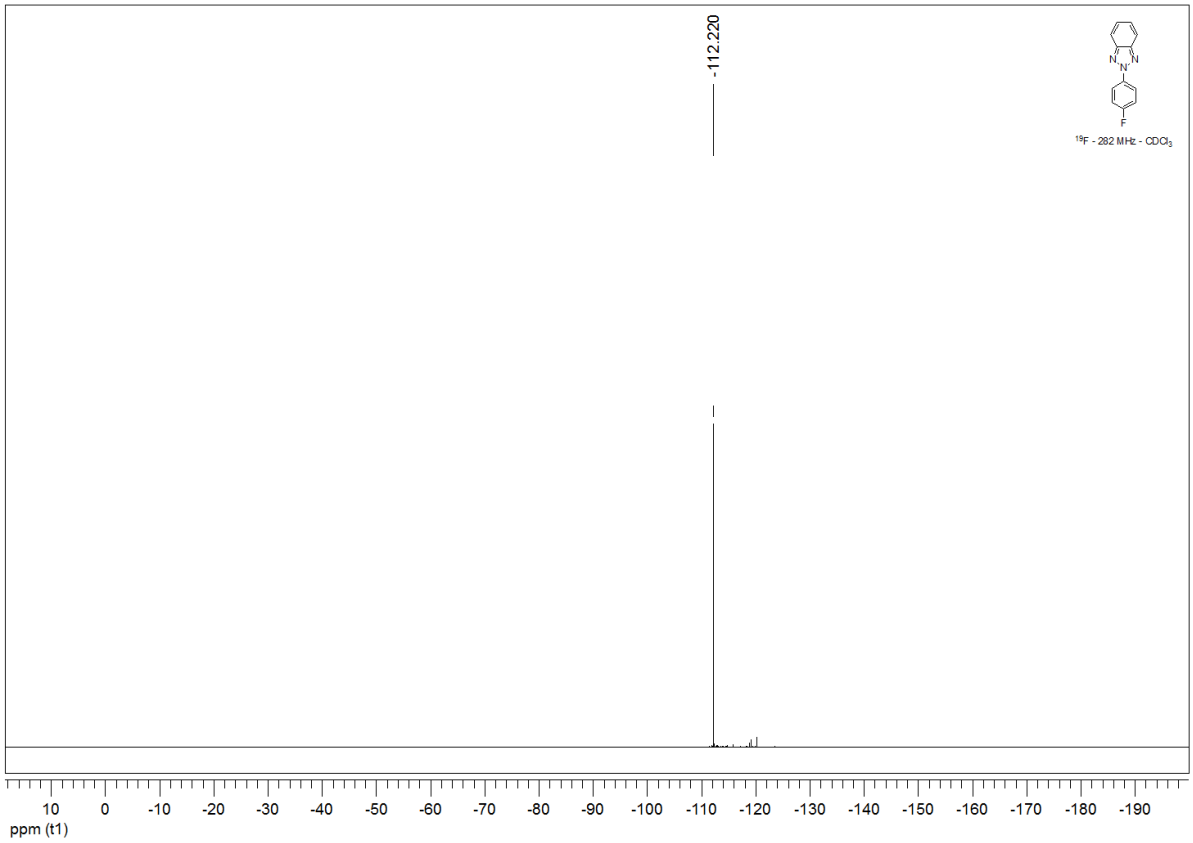

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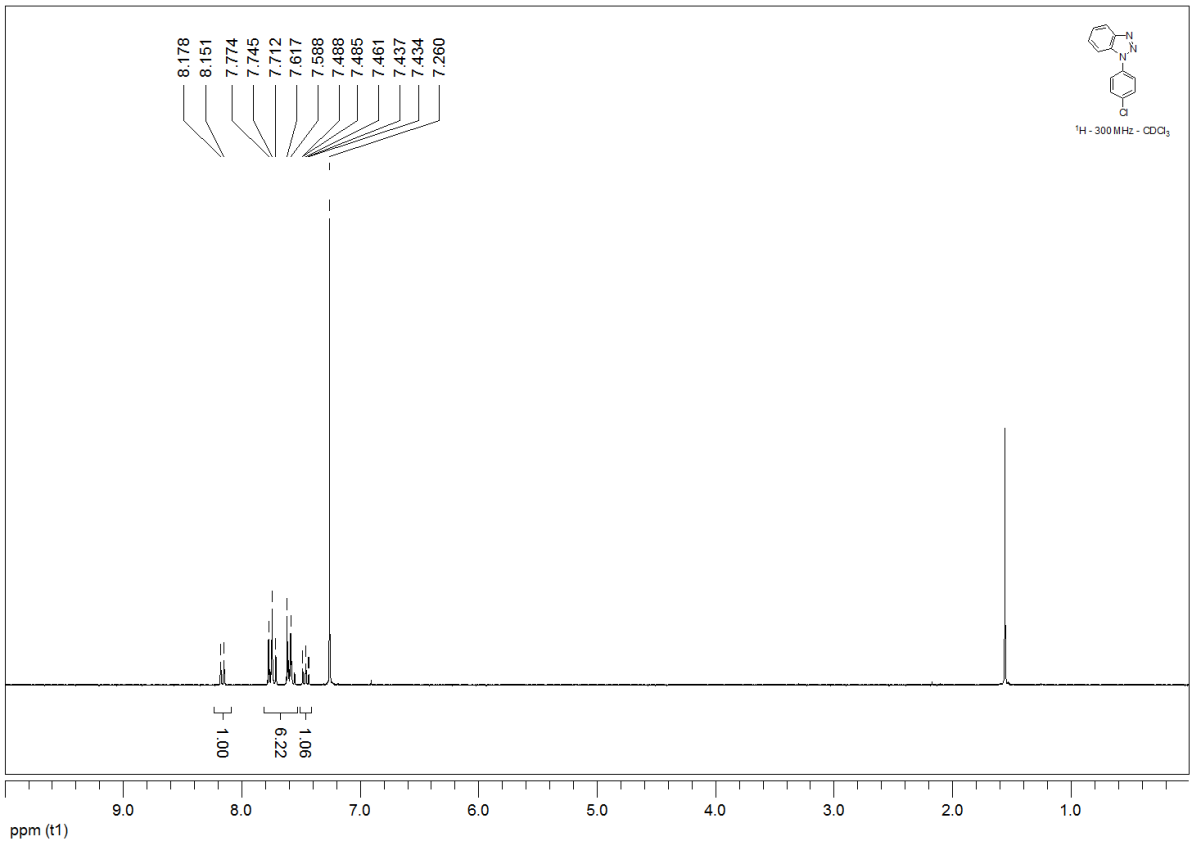

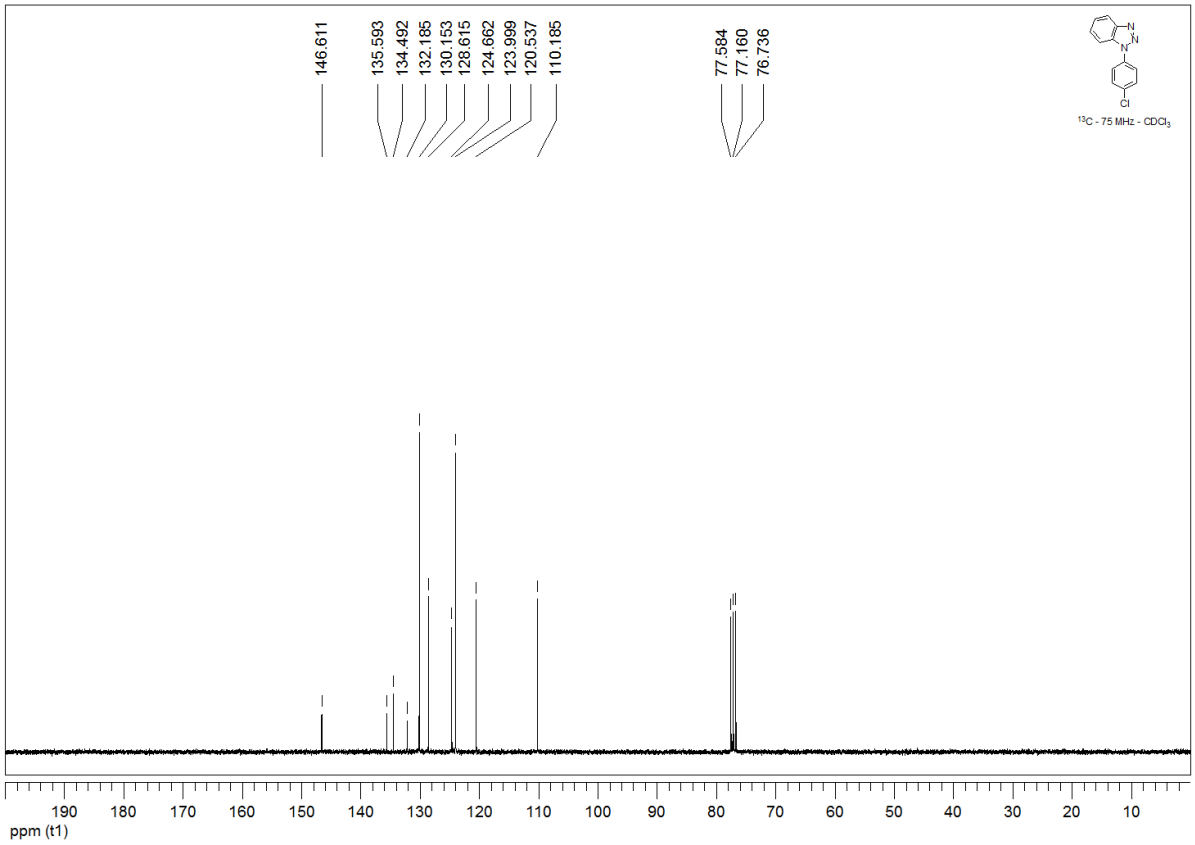

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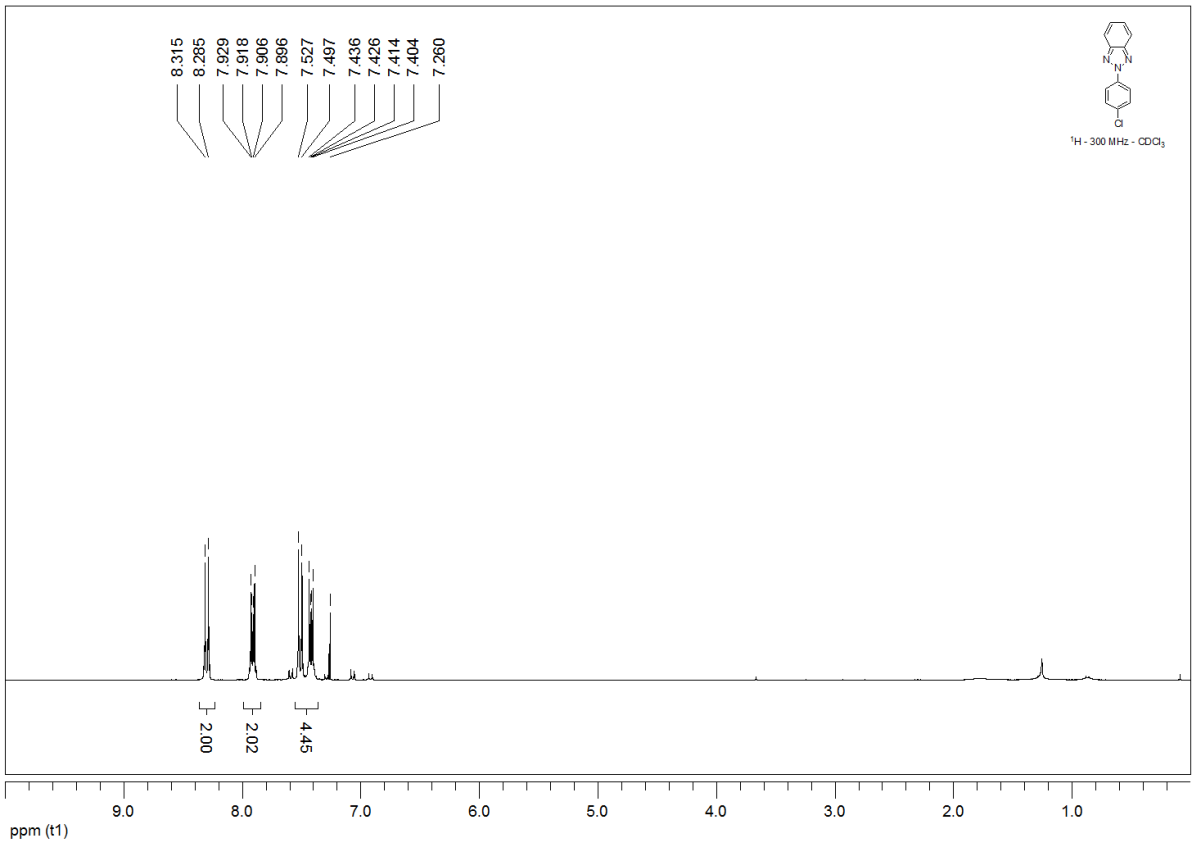

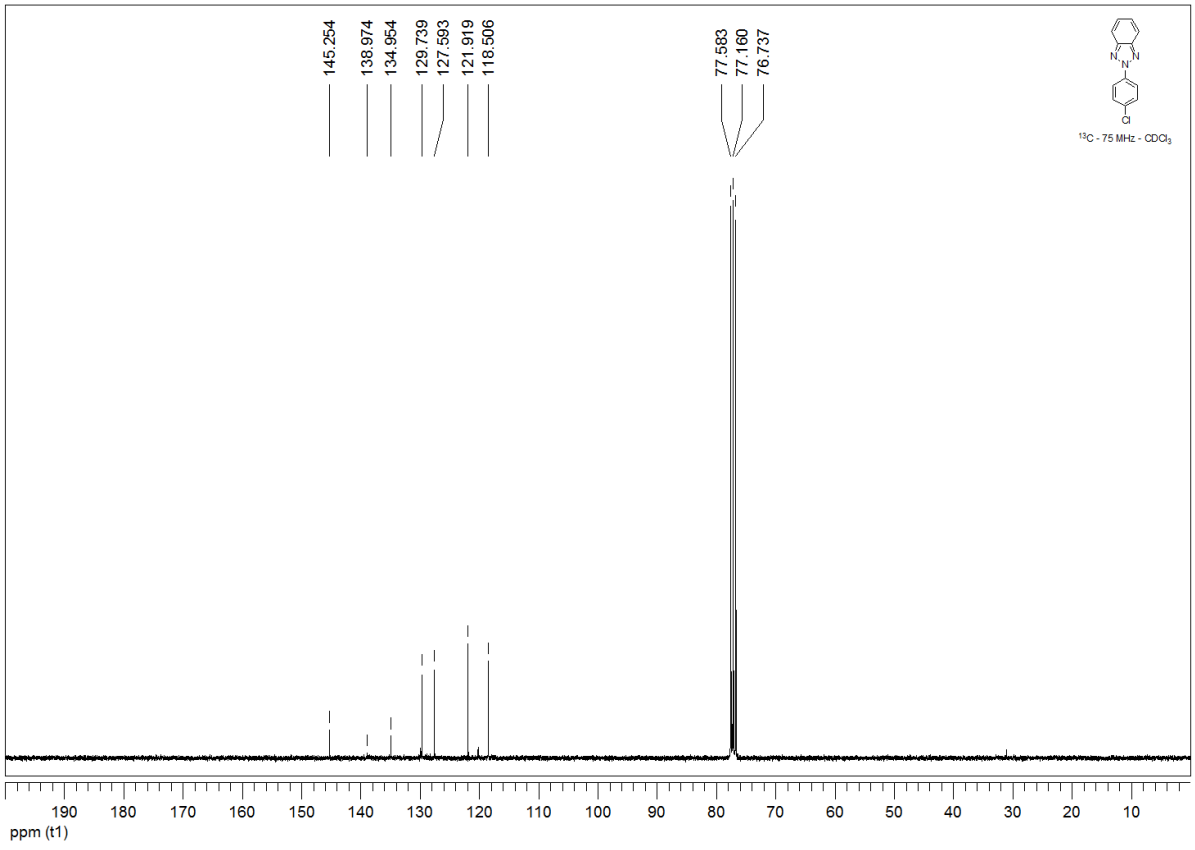

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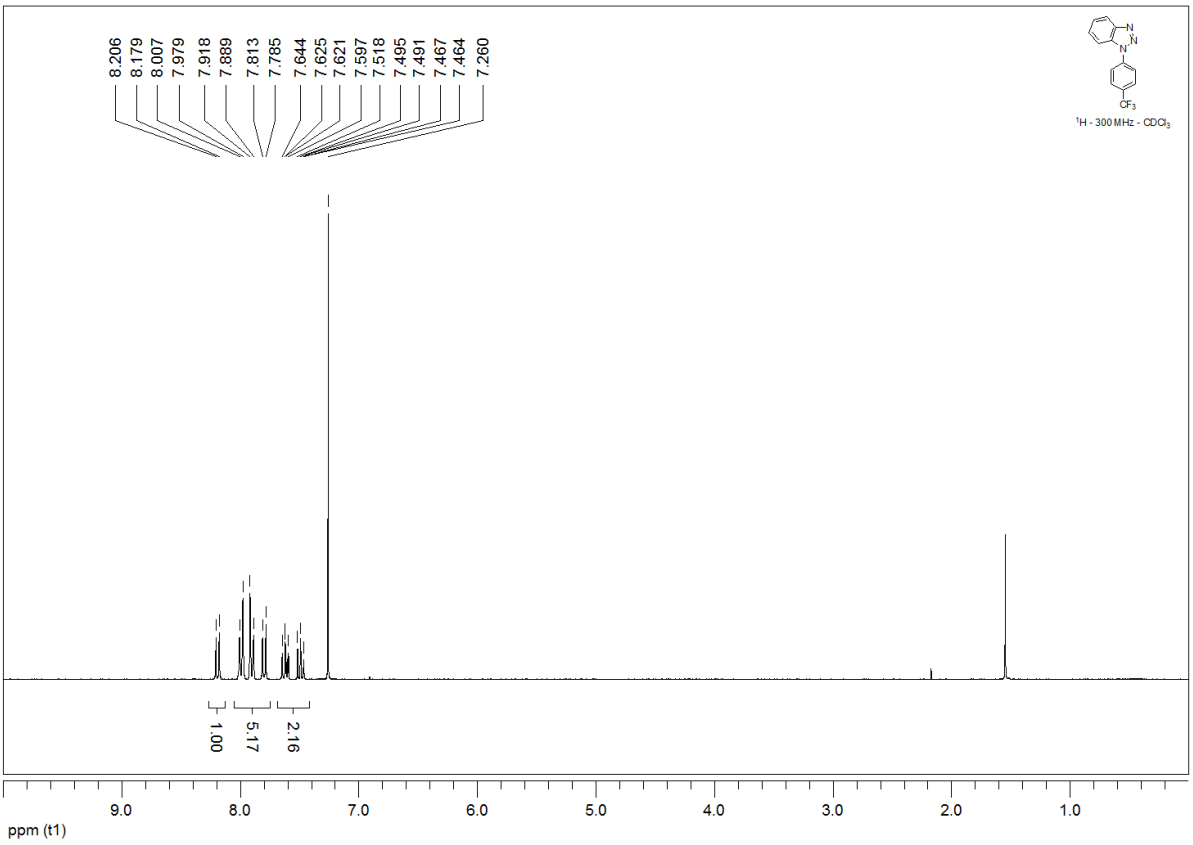

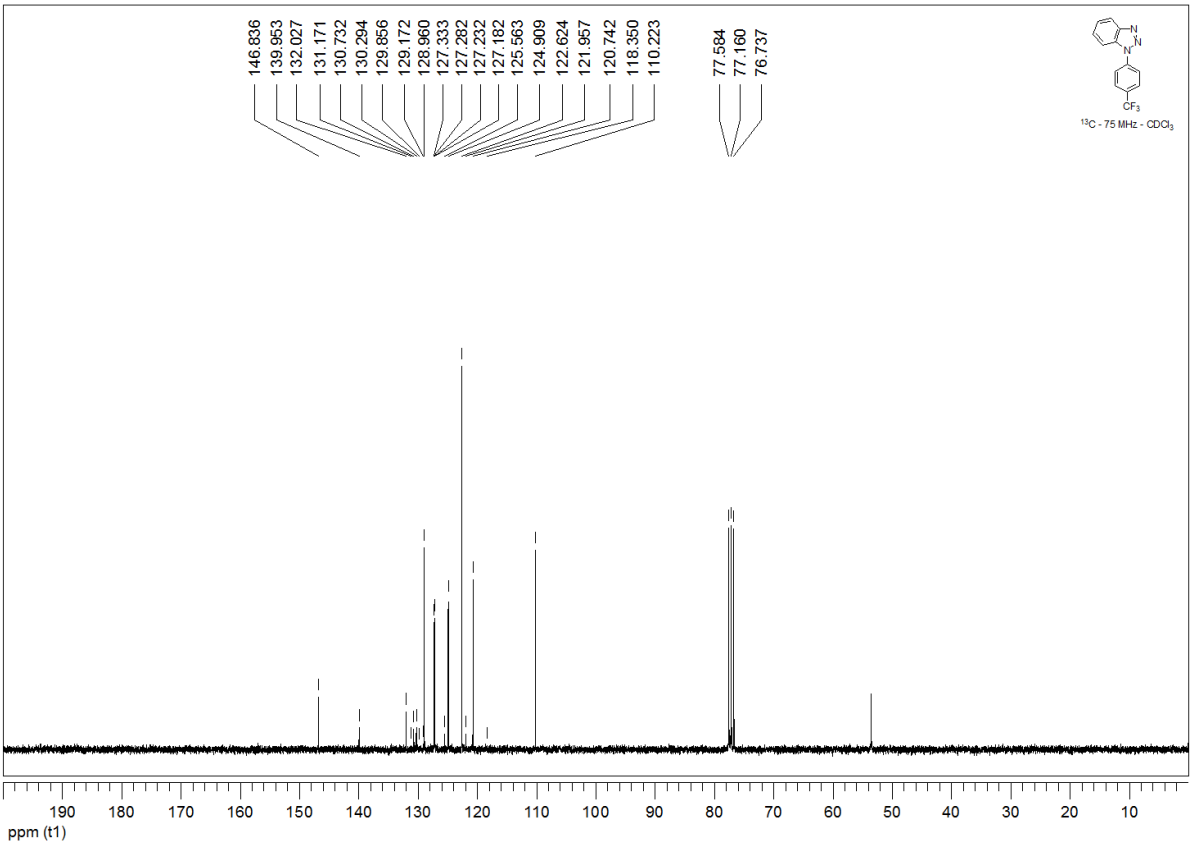

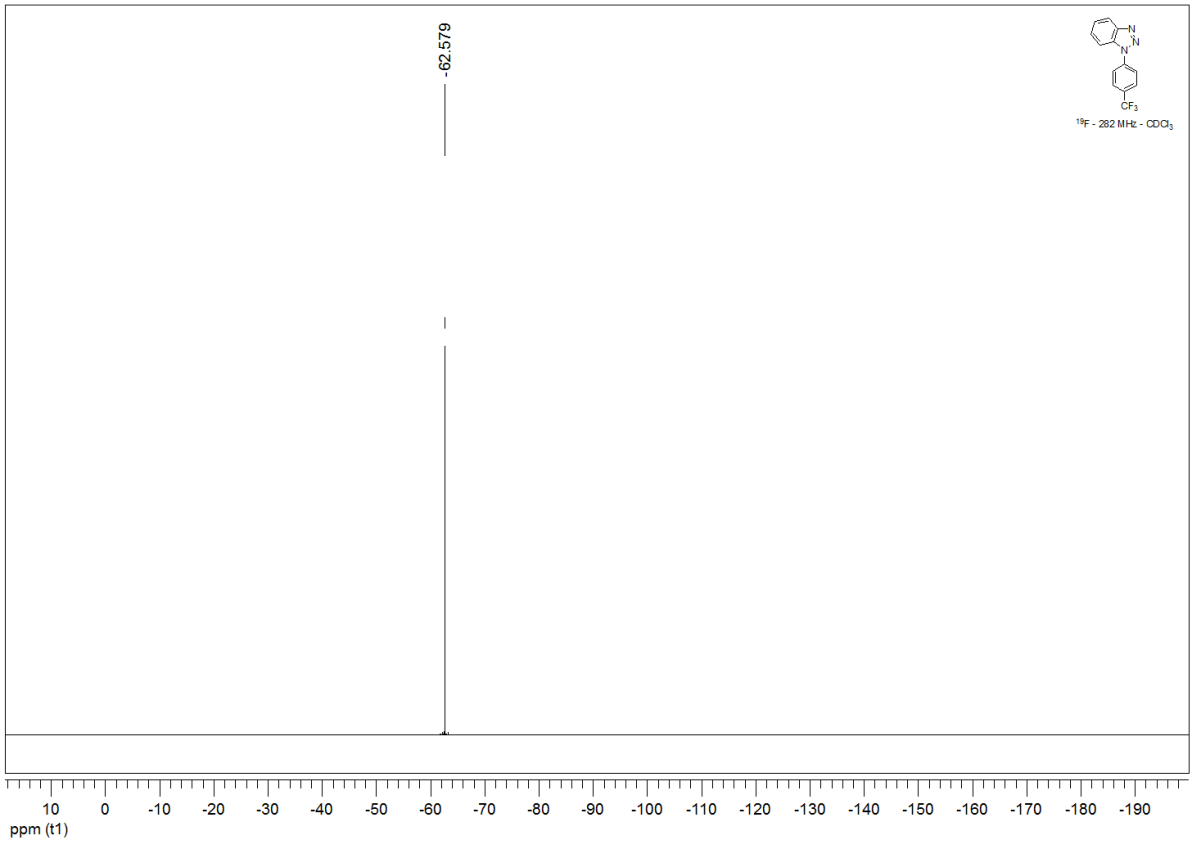

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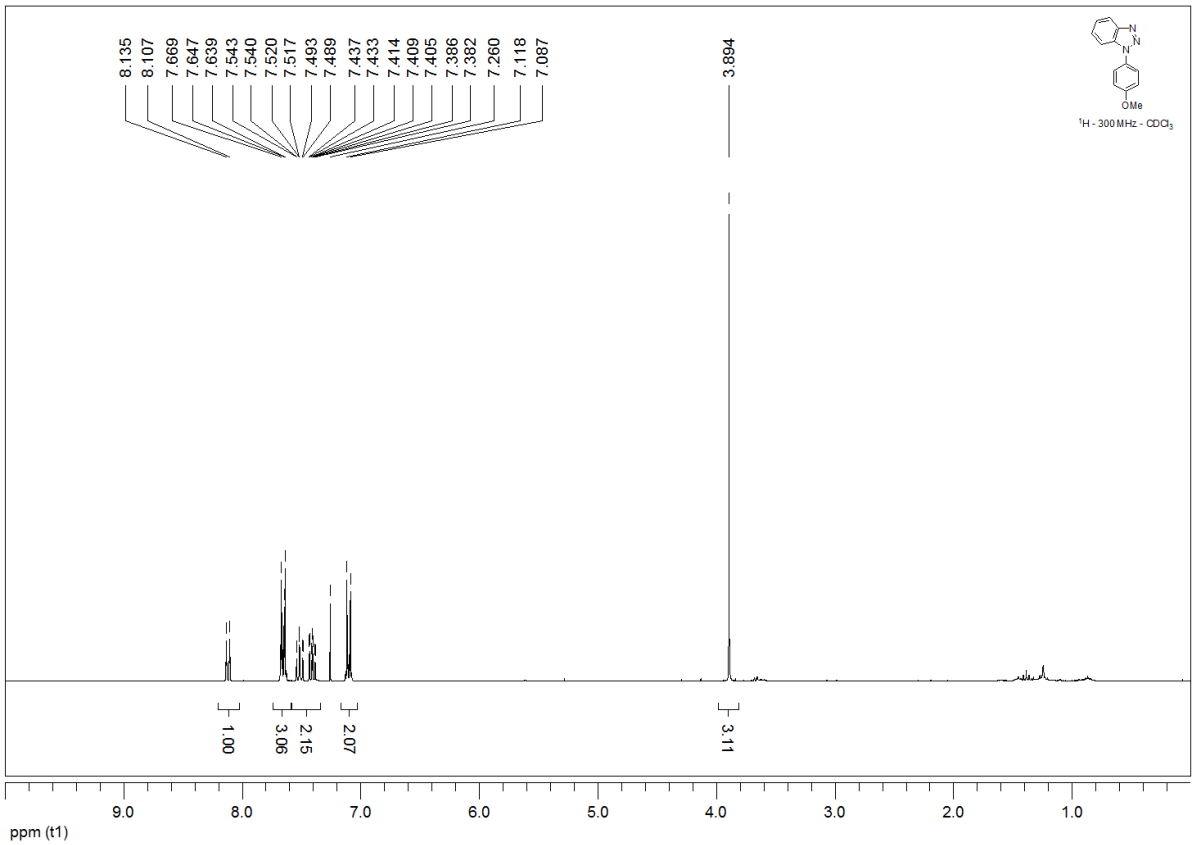

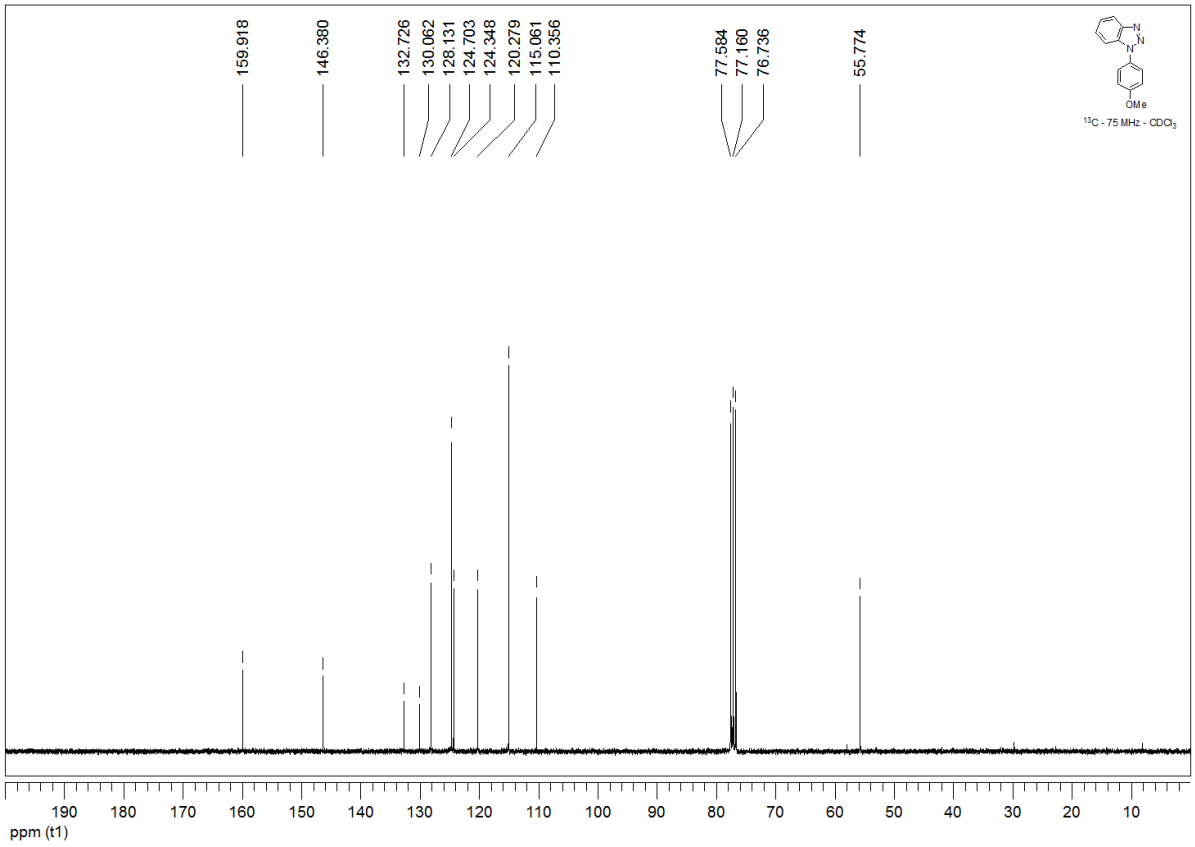

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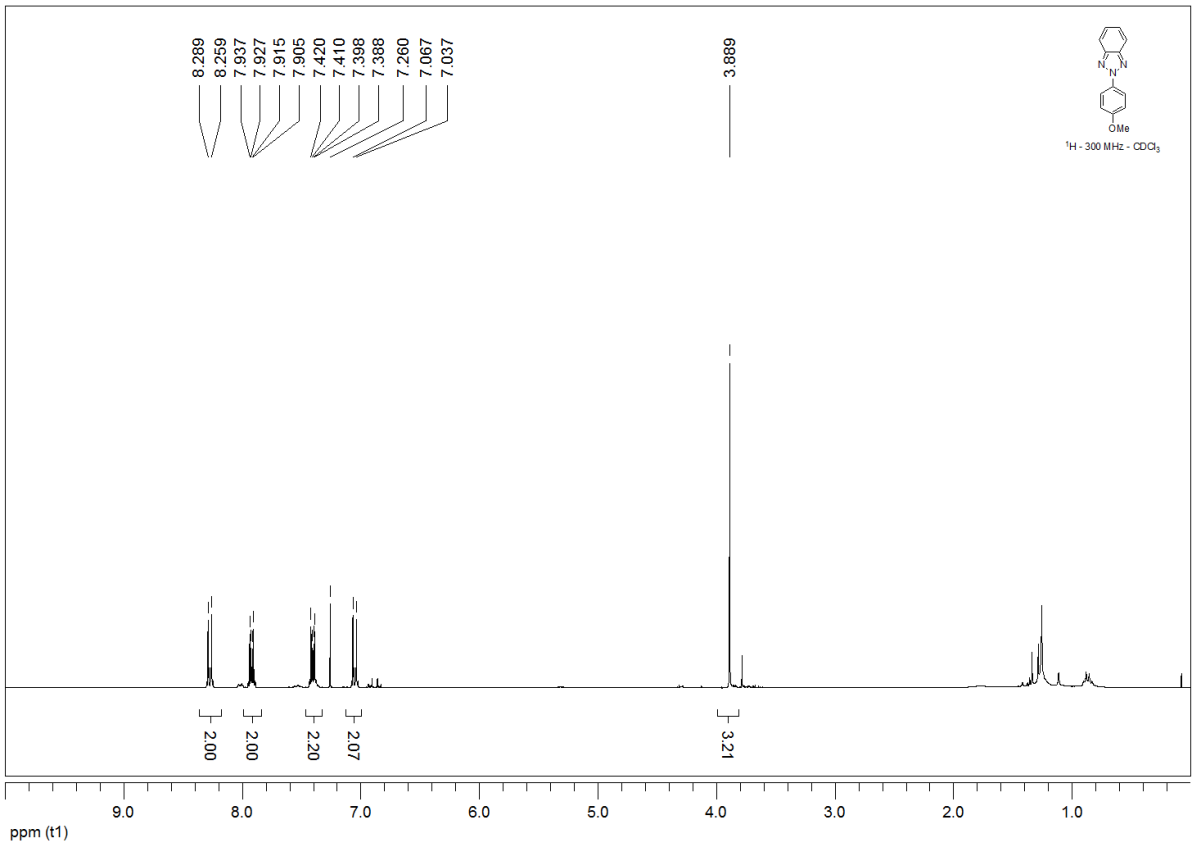

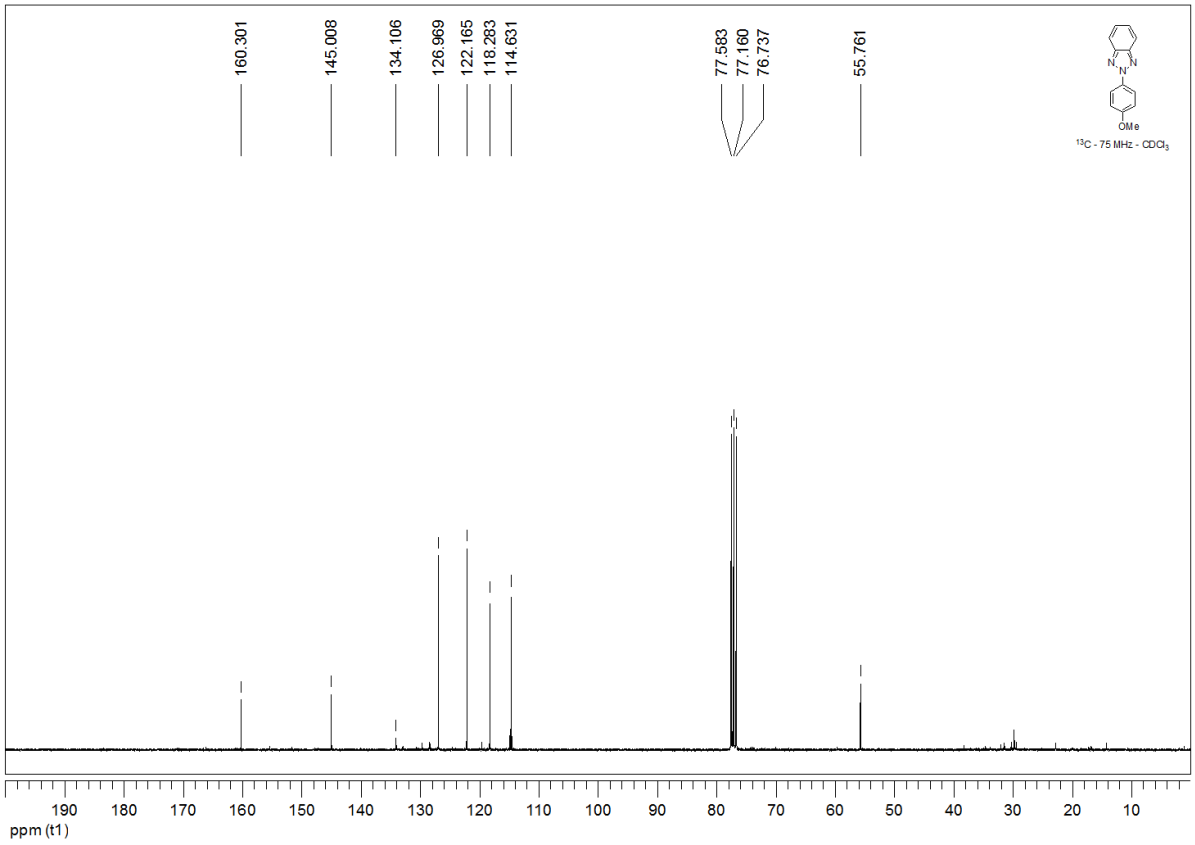

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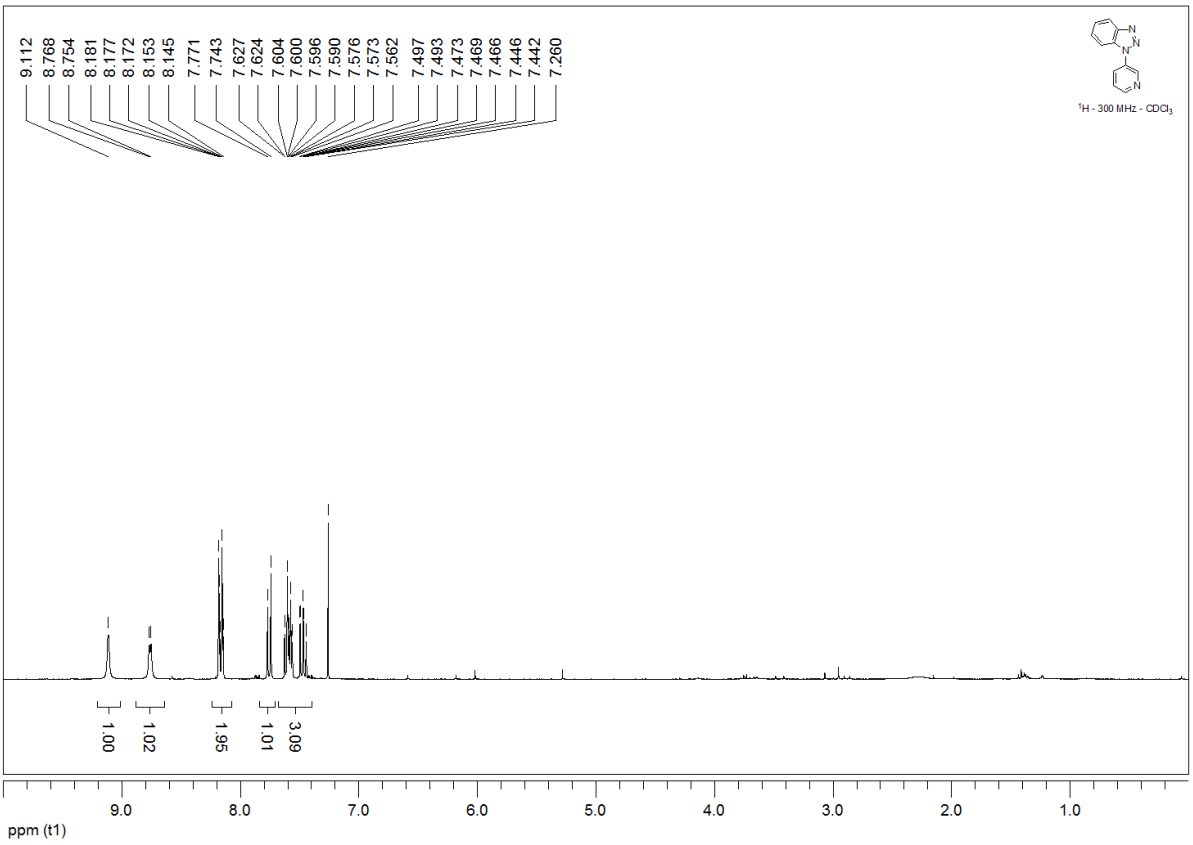

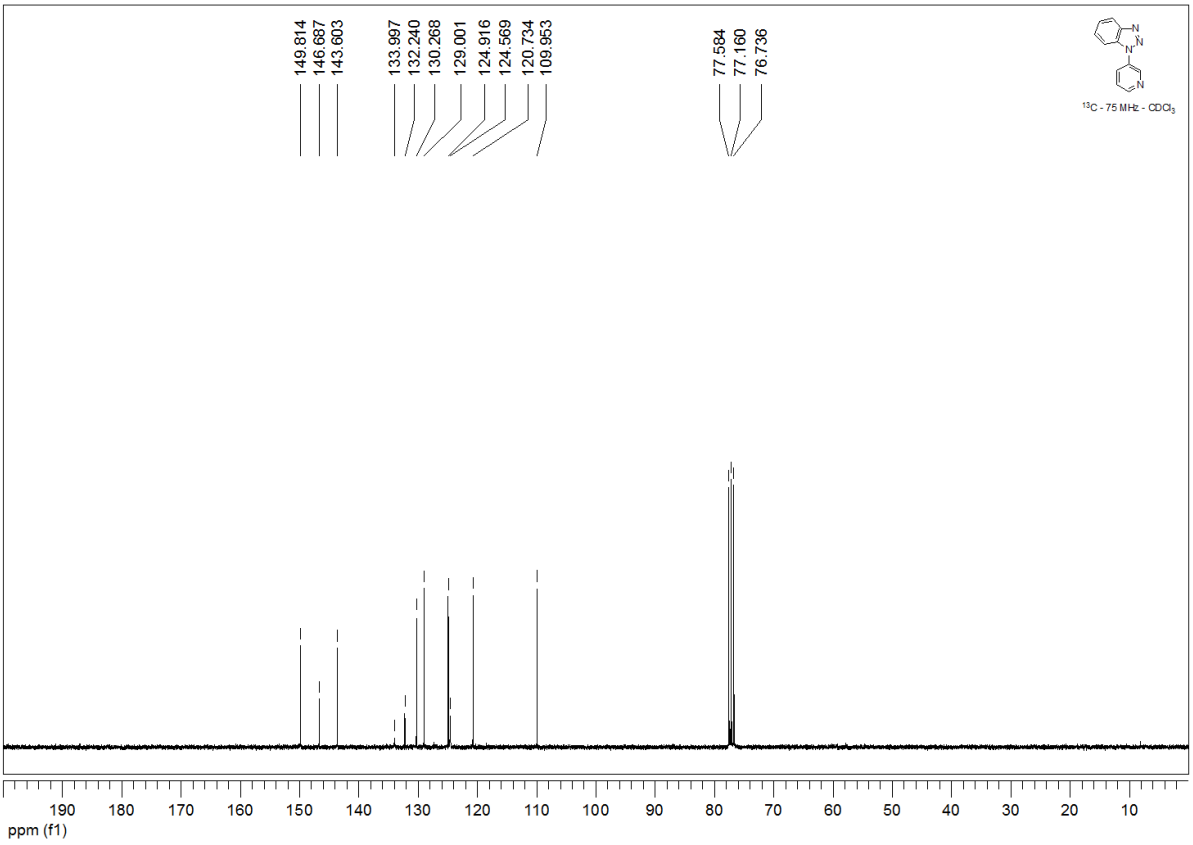

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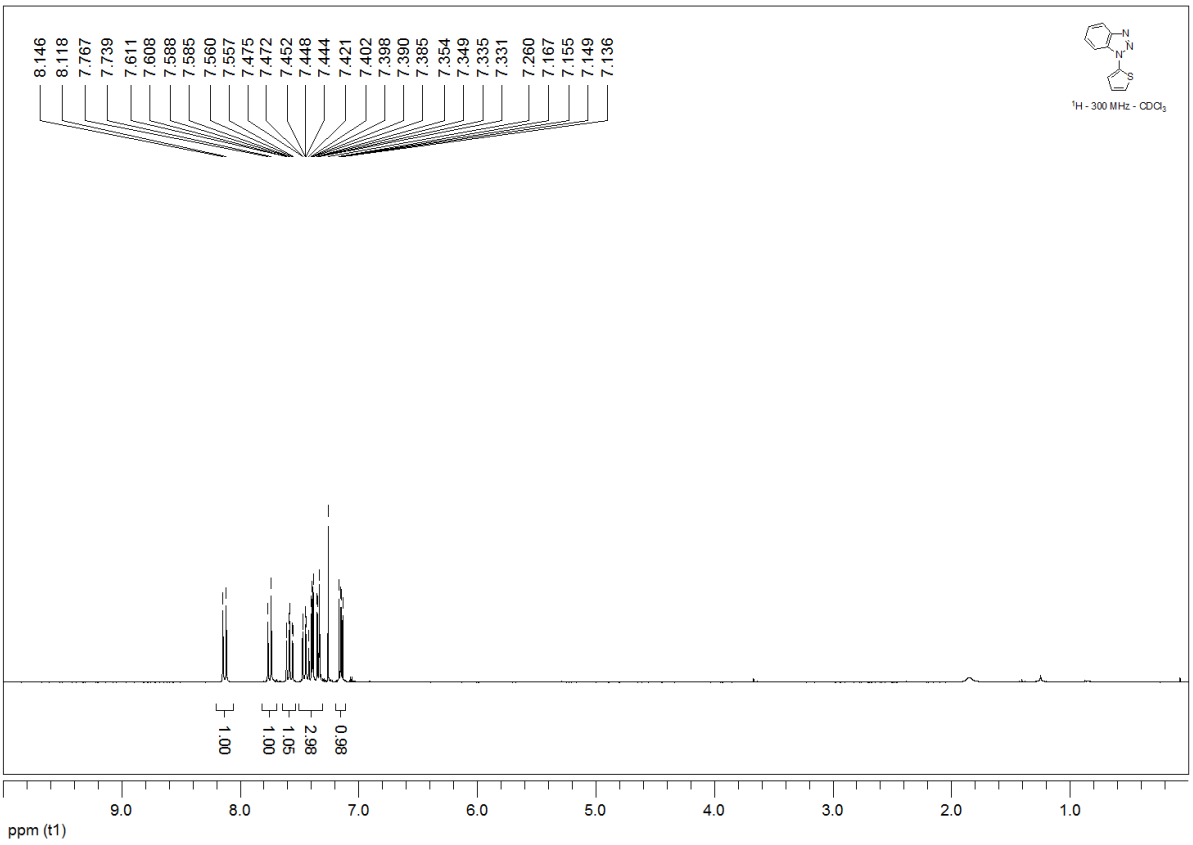
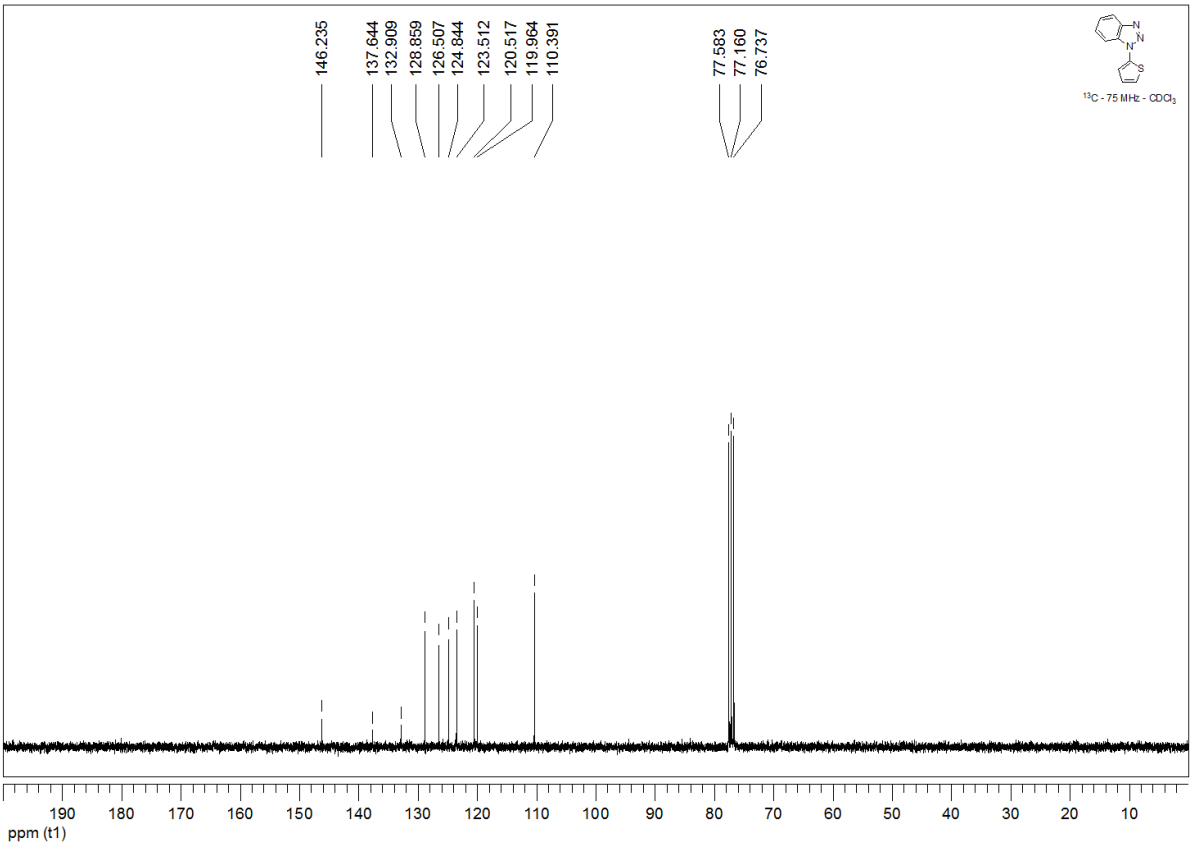
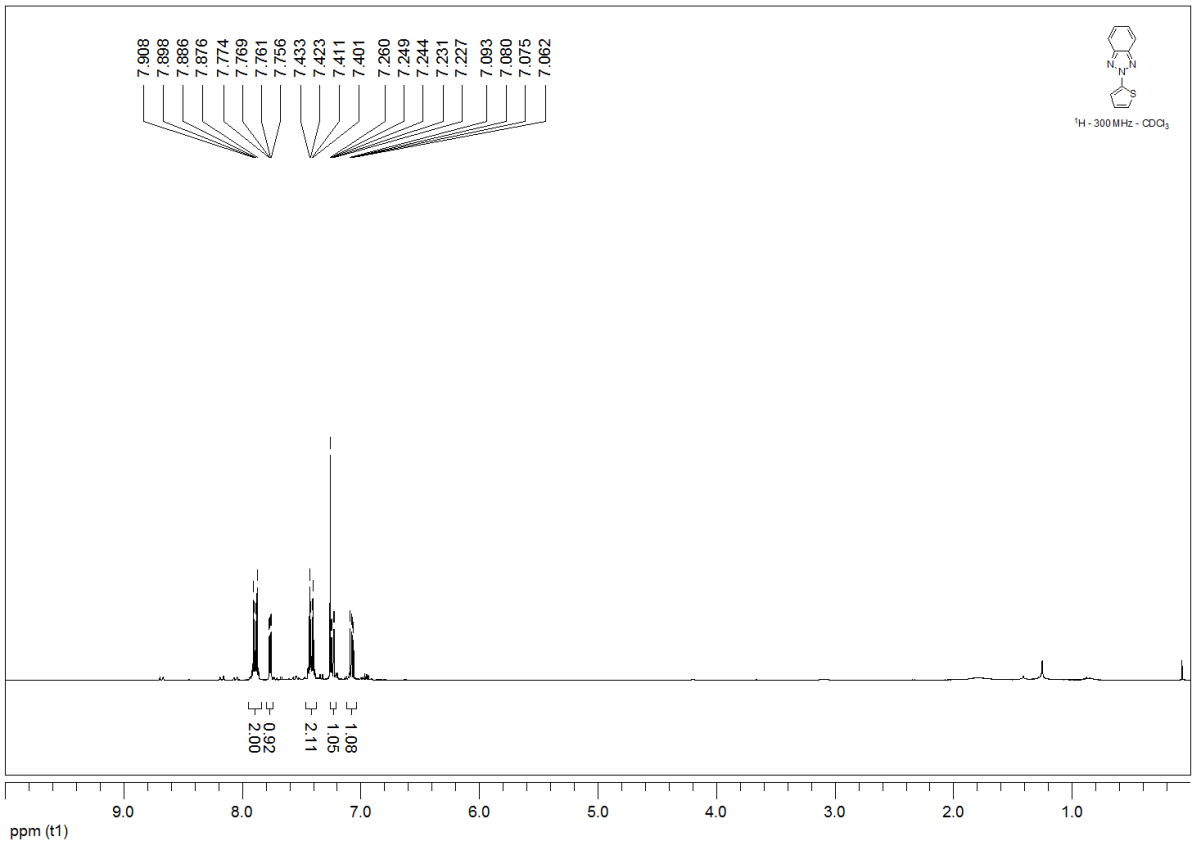
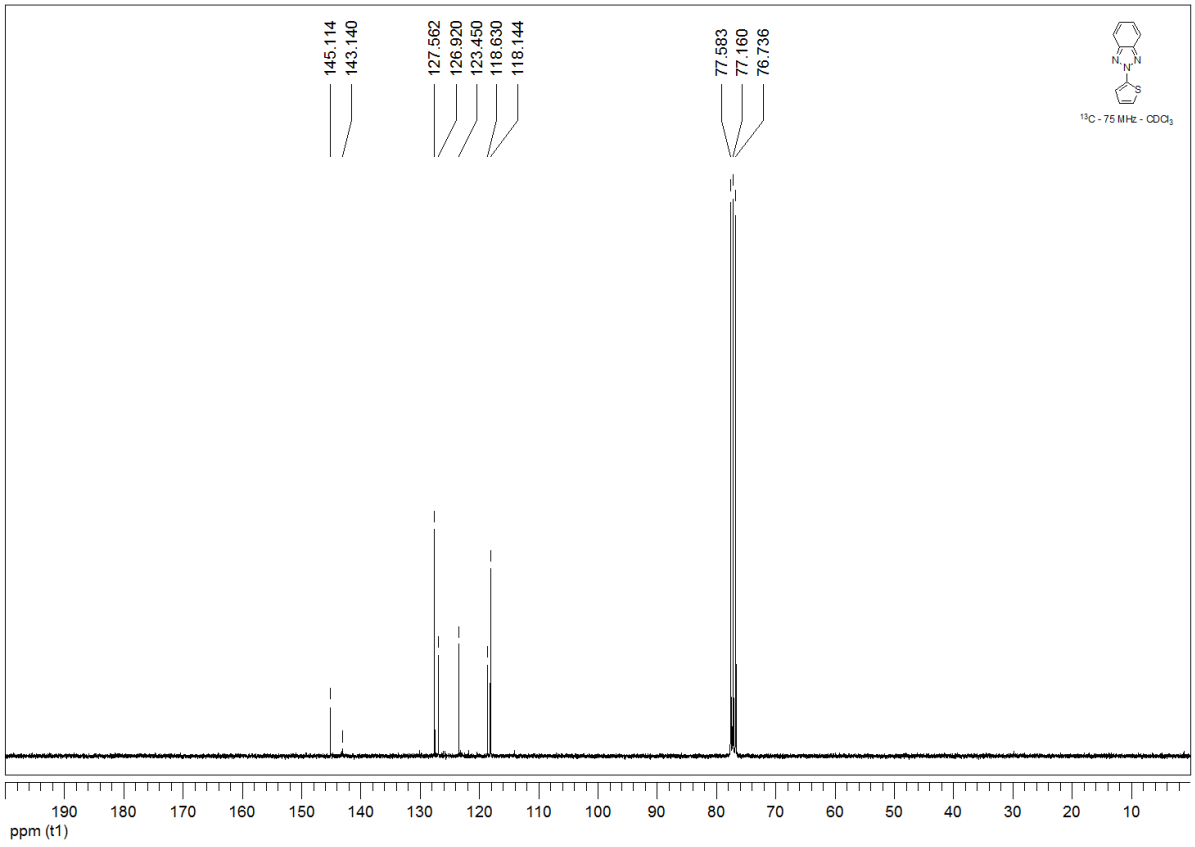




2-(2-Thienyl)-2*H*-benzotriazole (1g').





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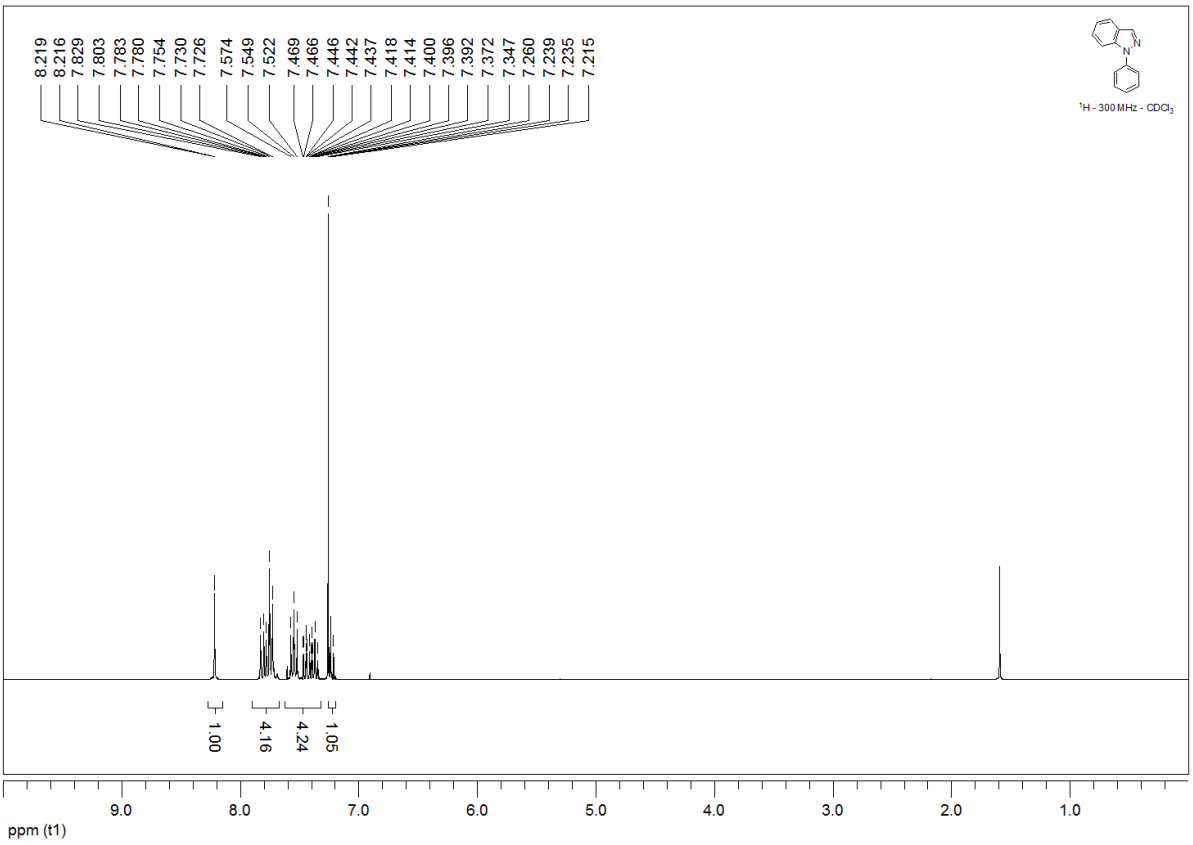

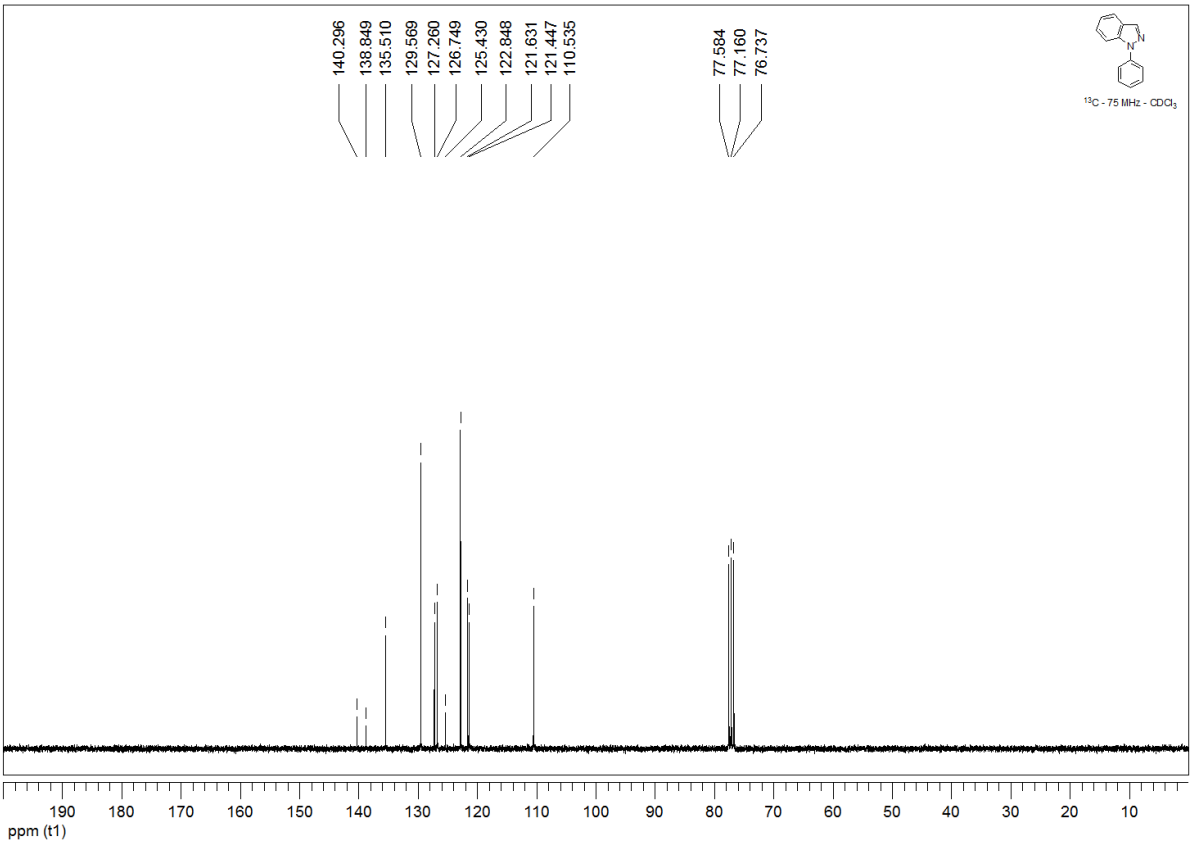

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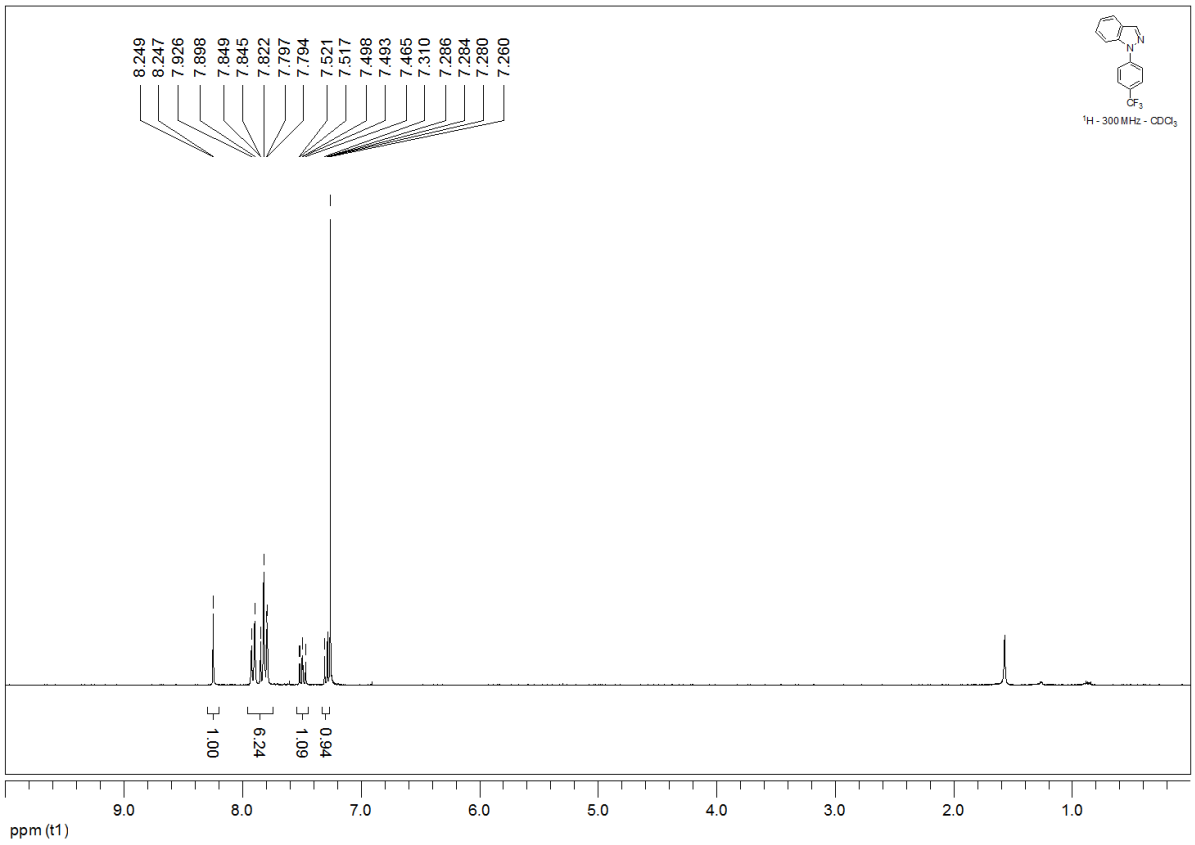

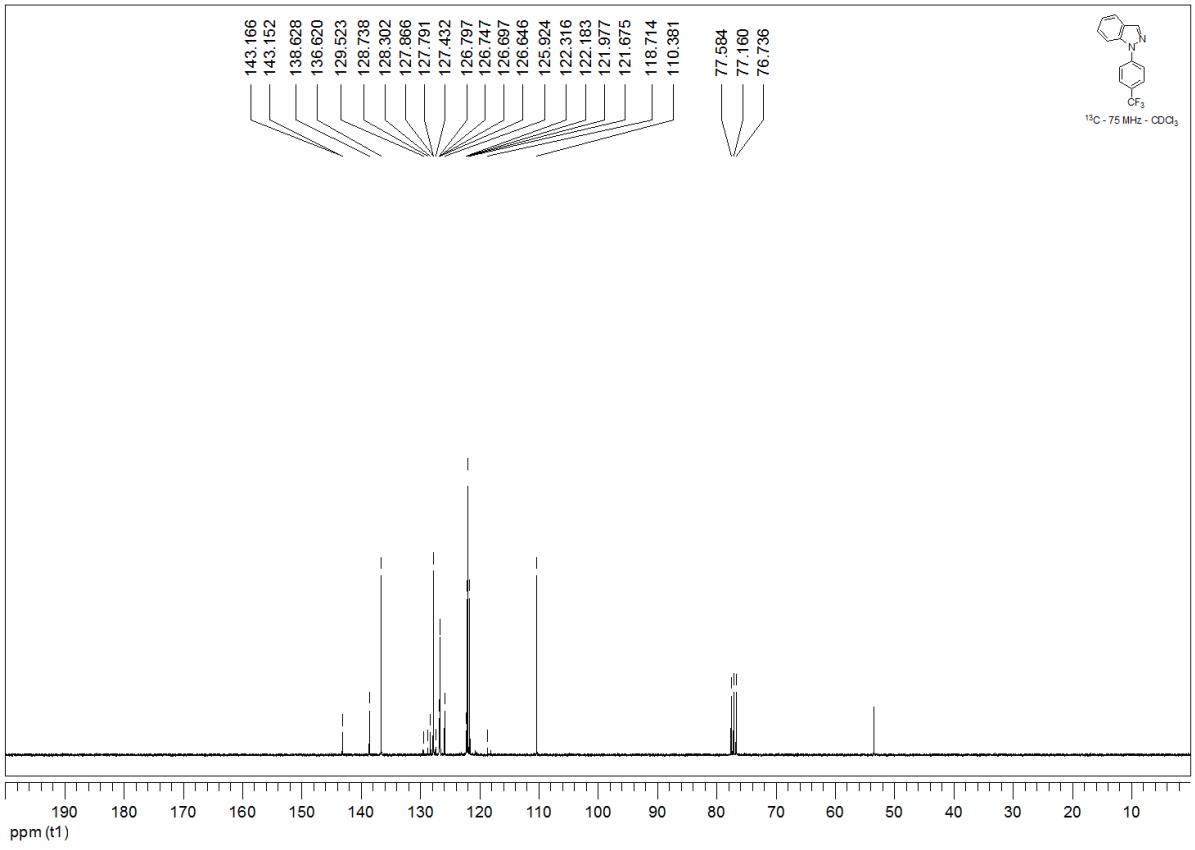

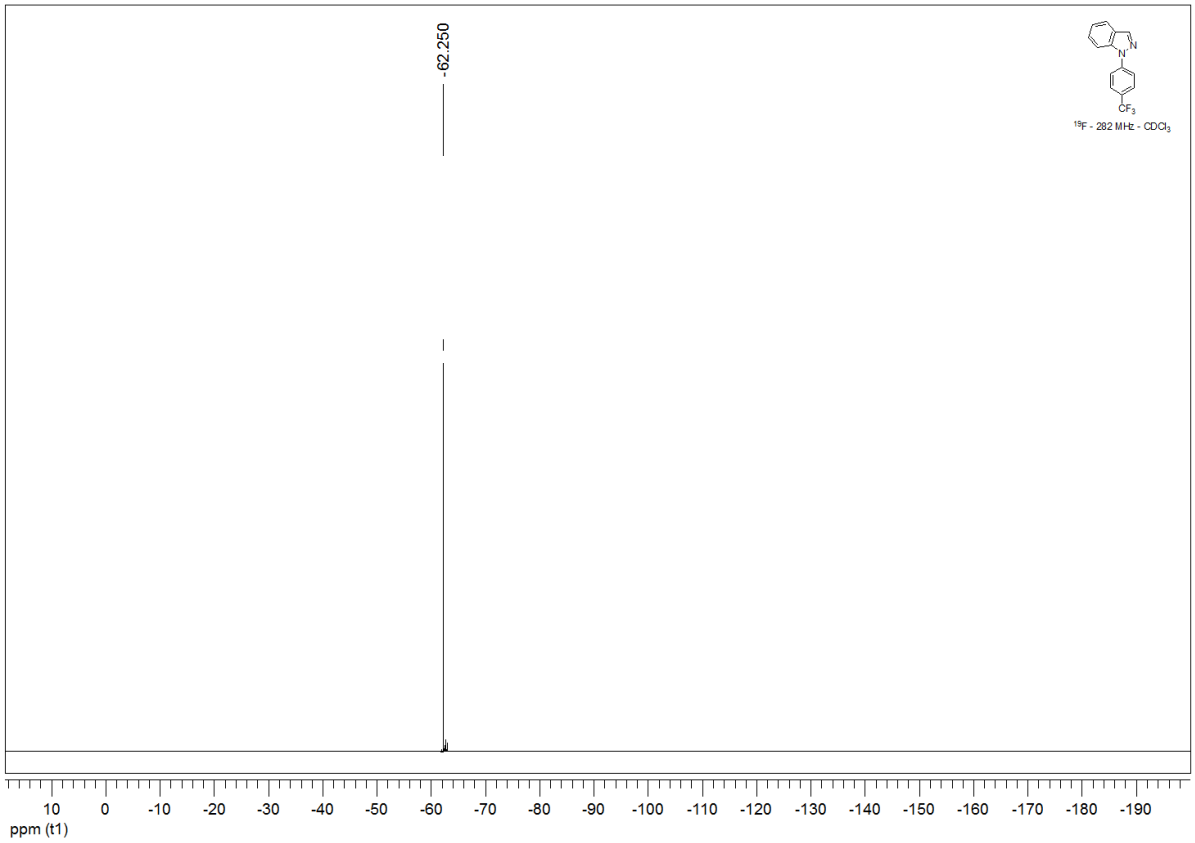

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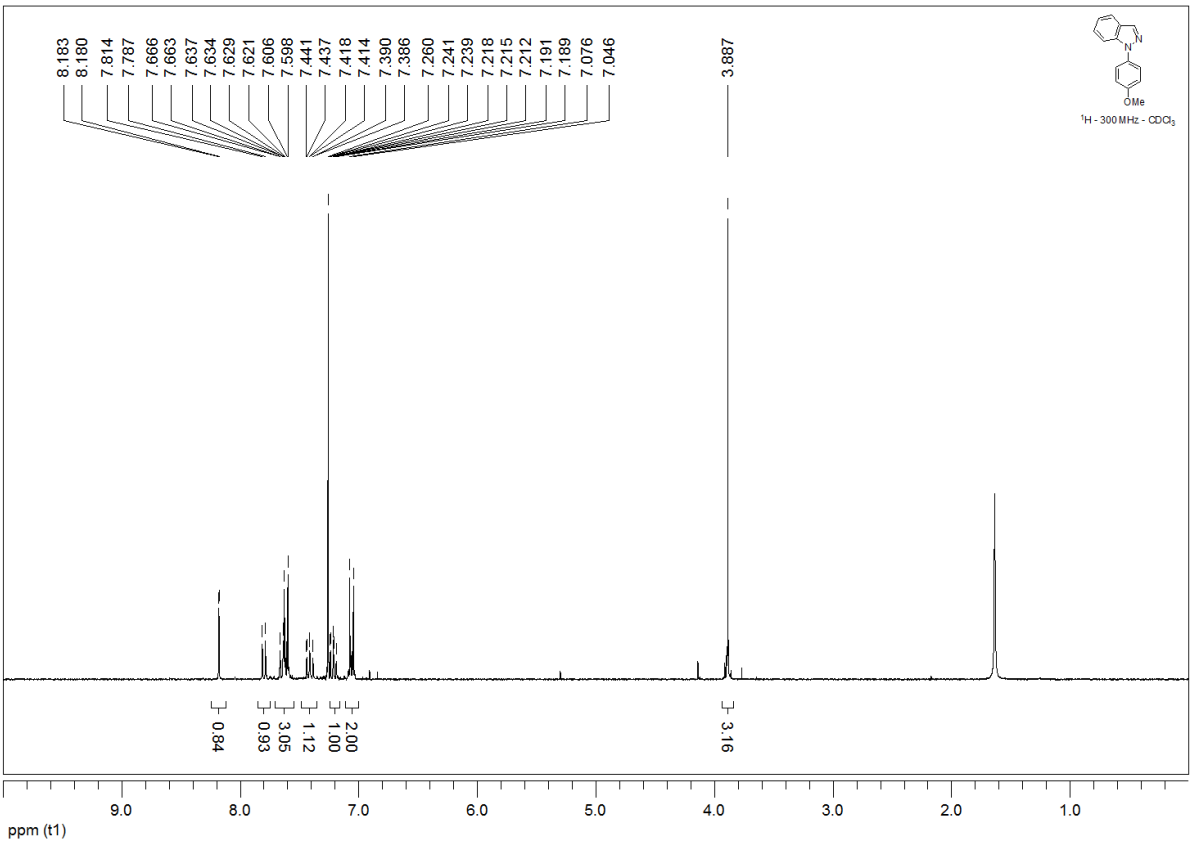

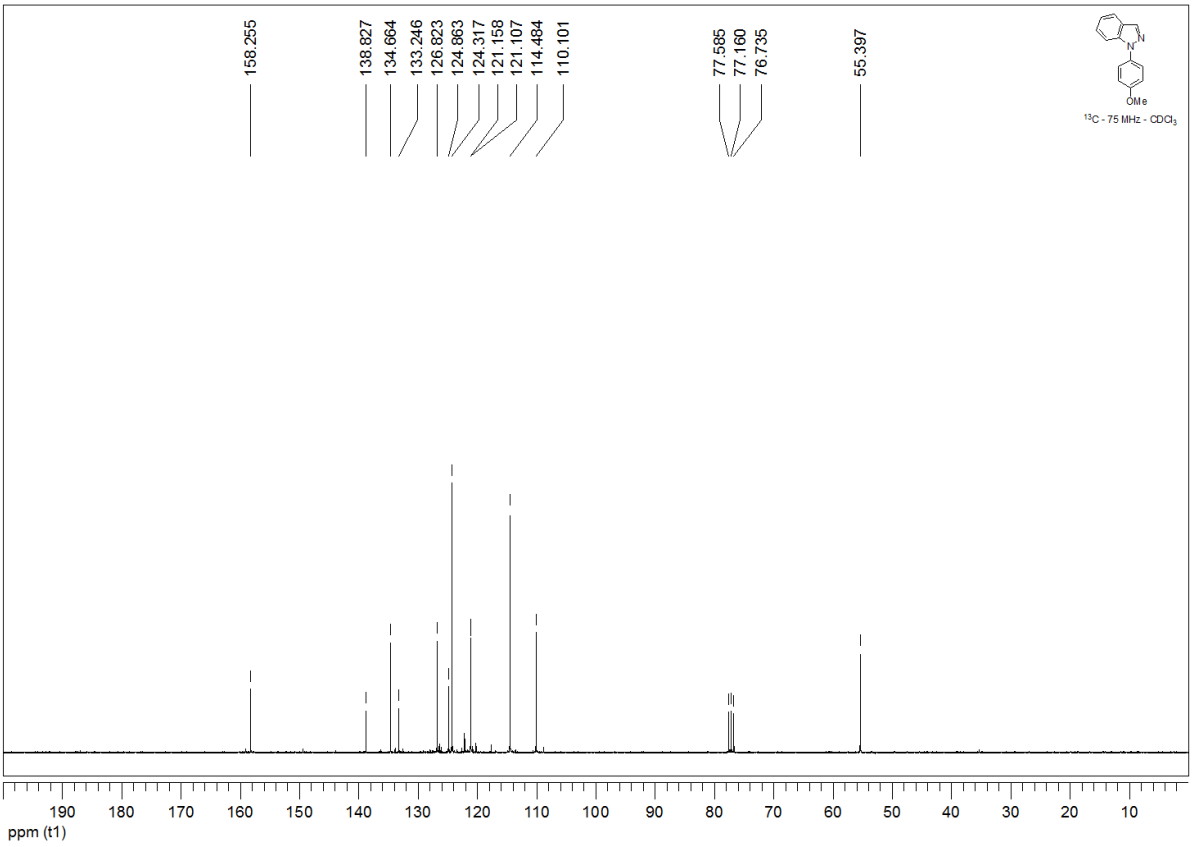

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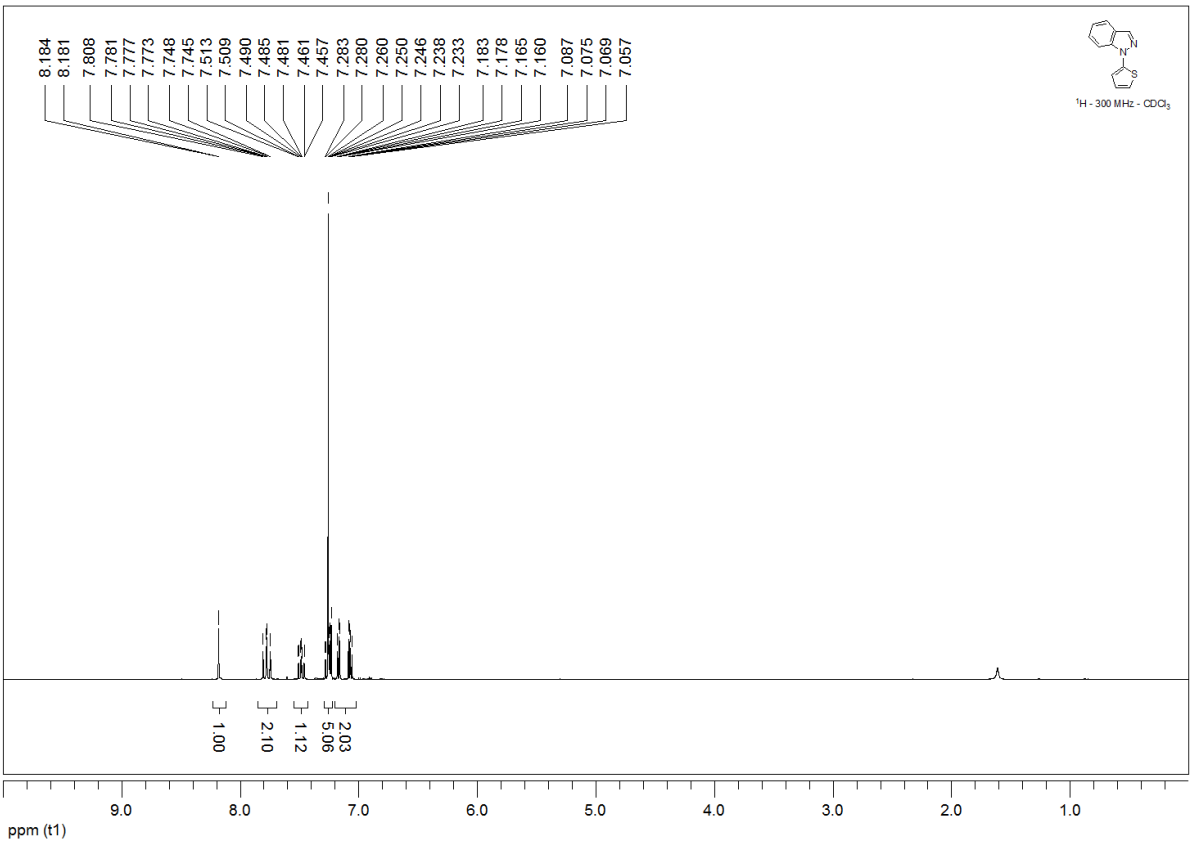

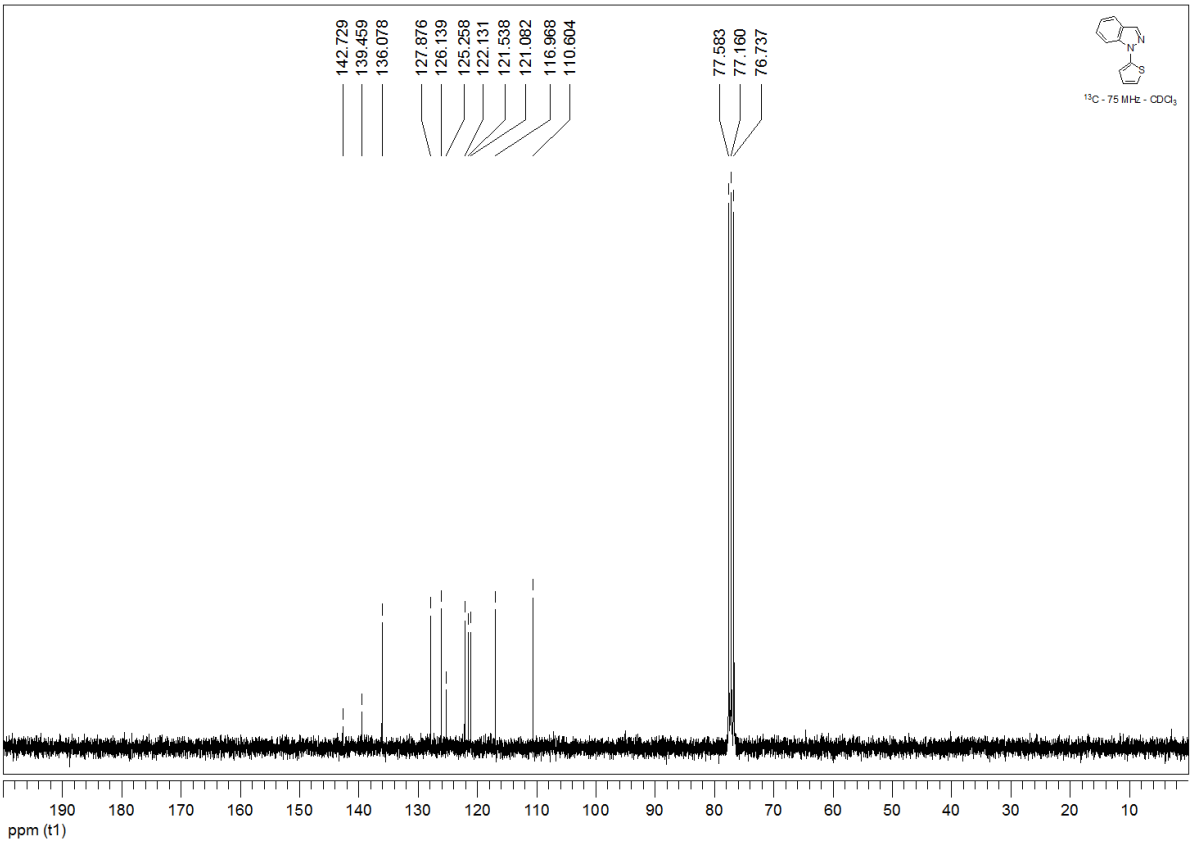

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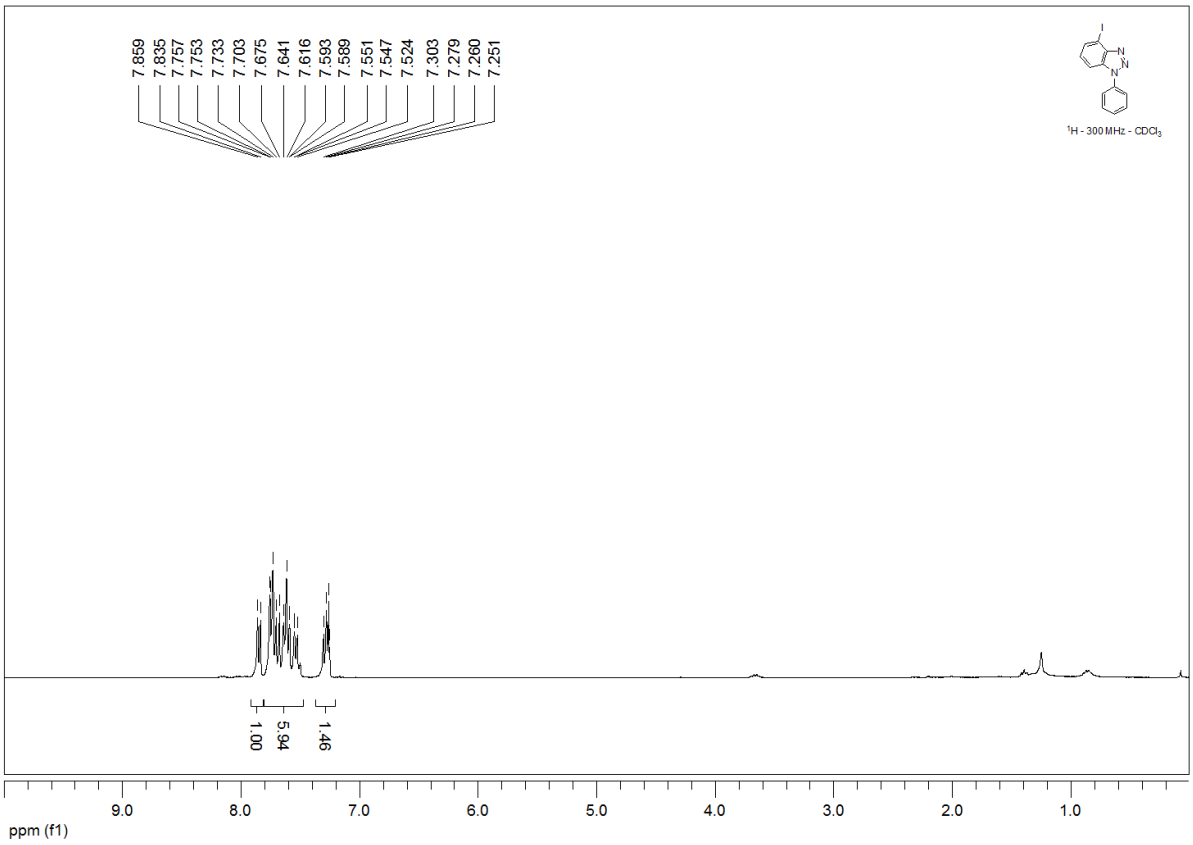

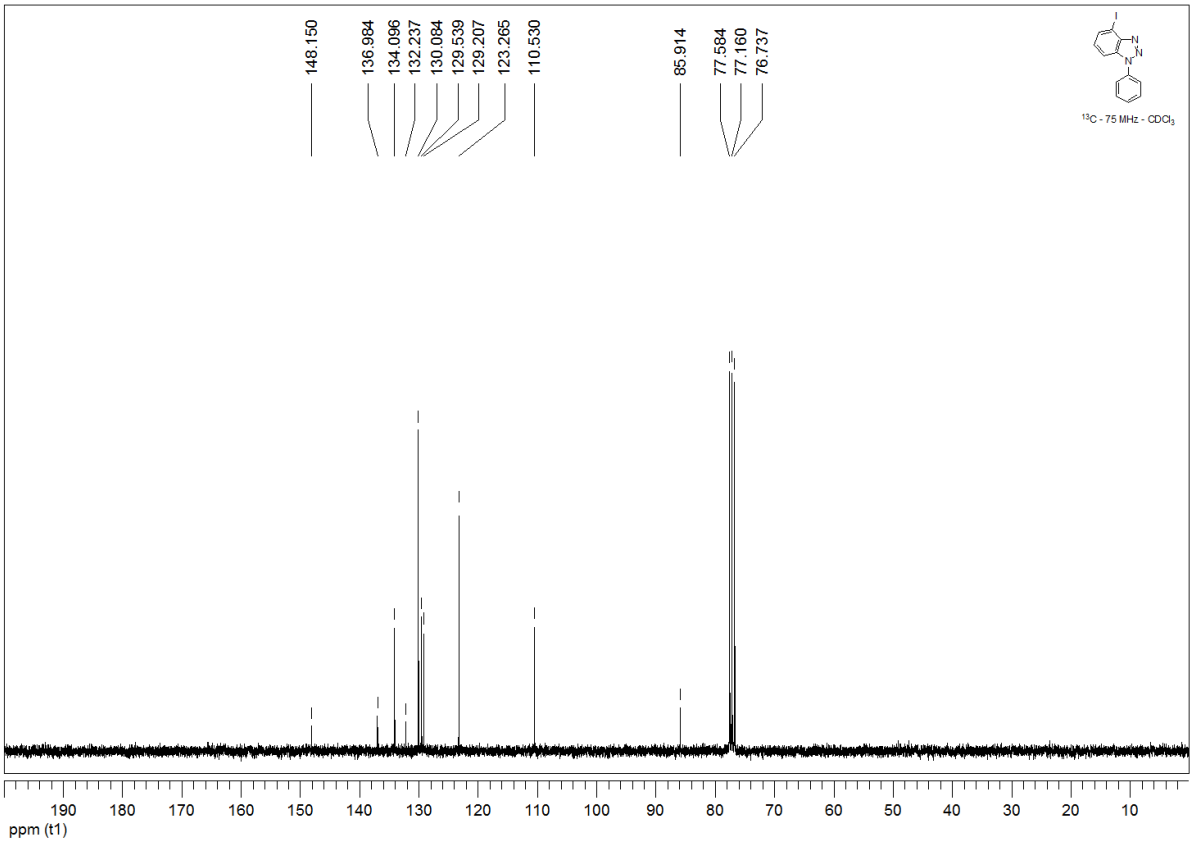

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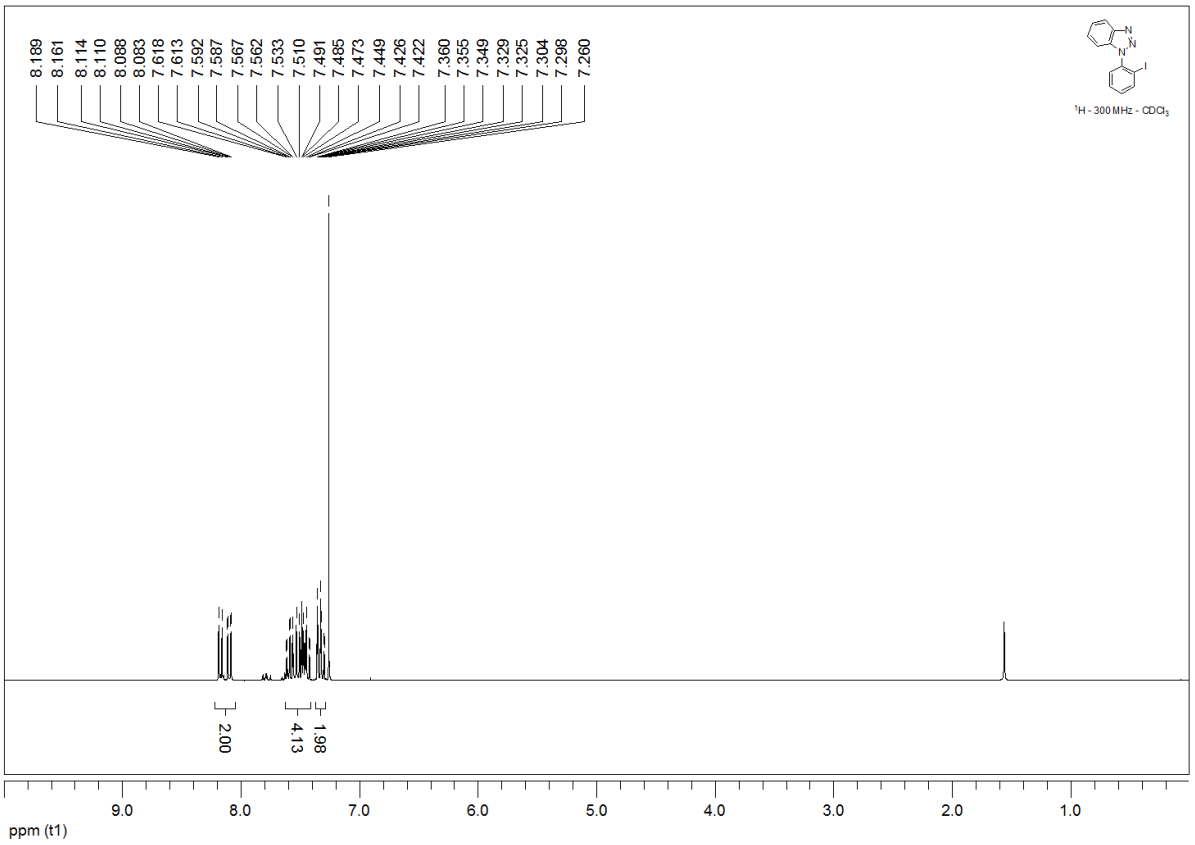

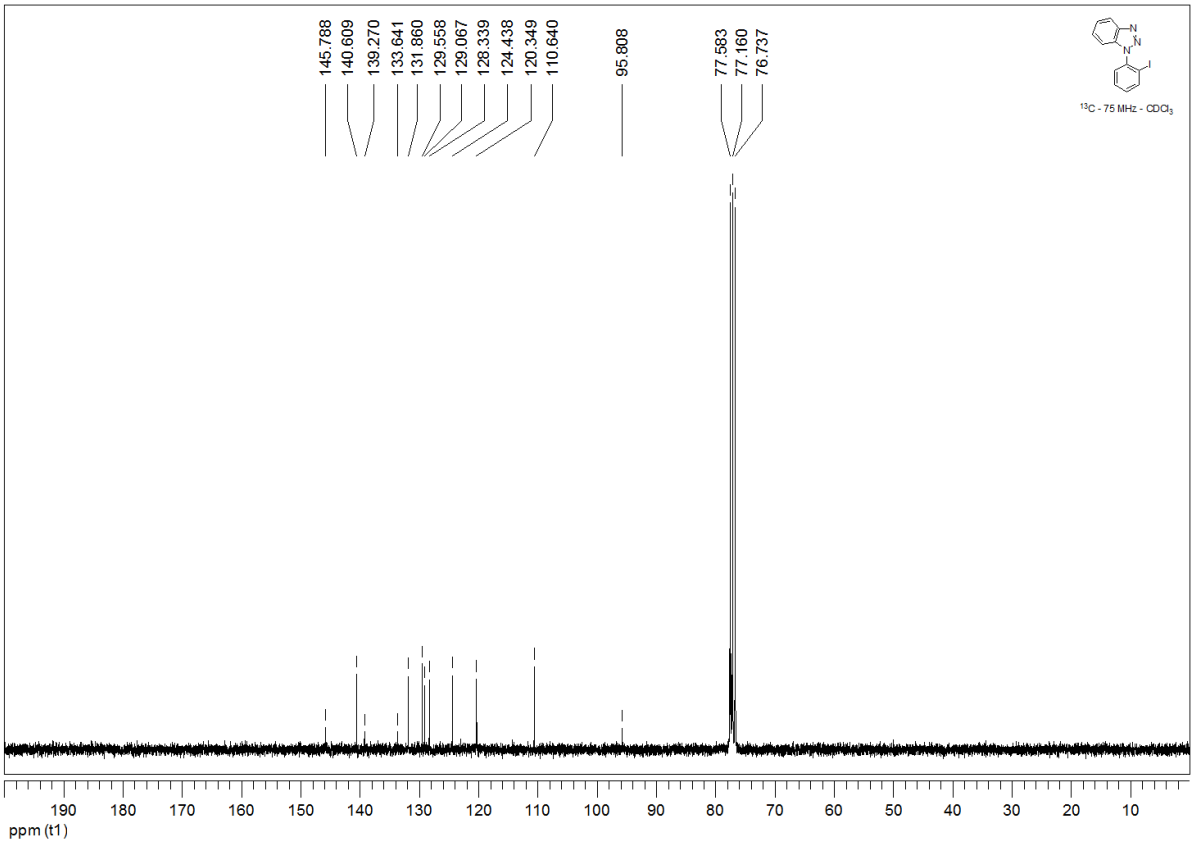

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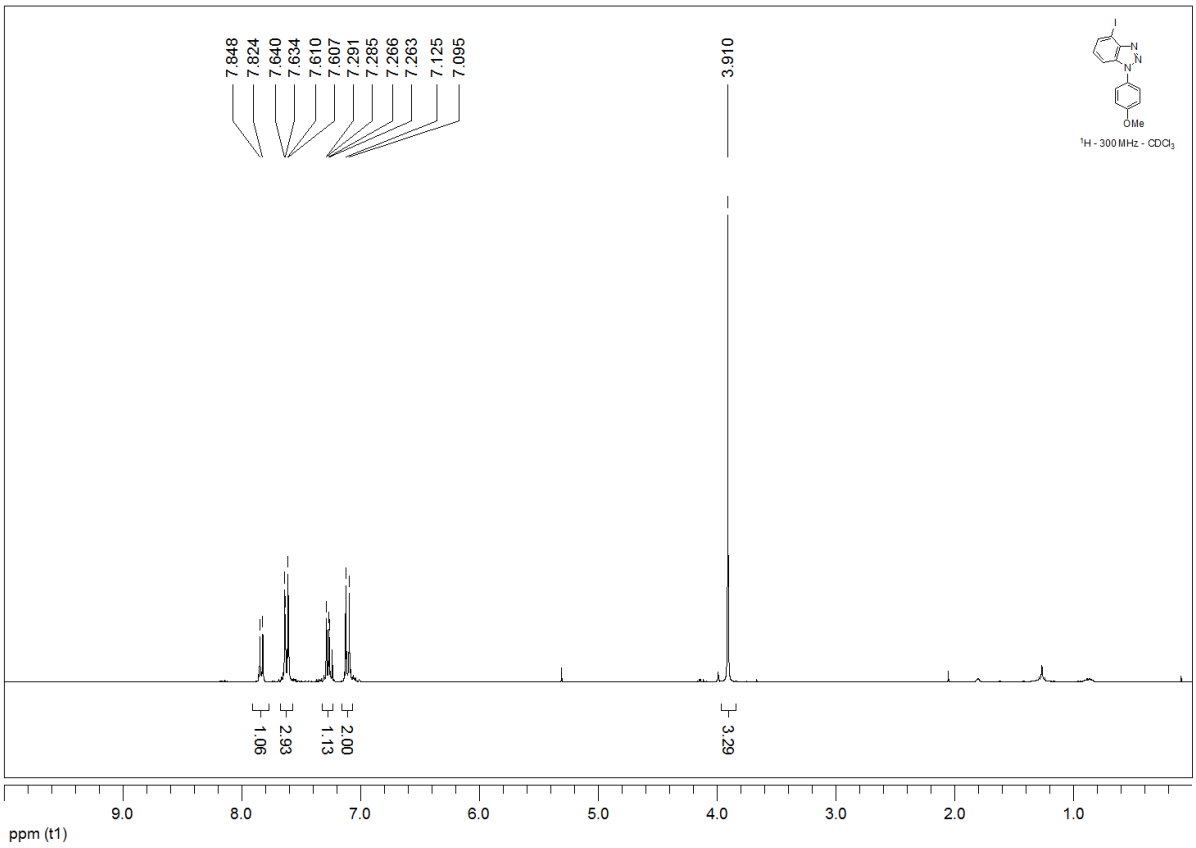

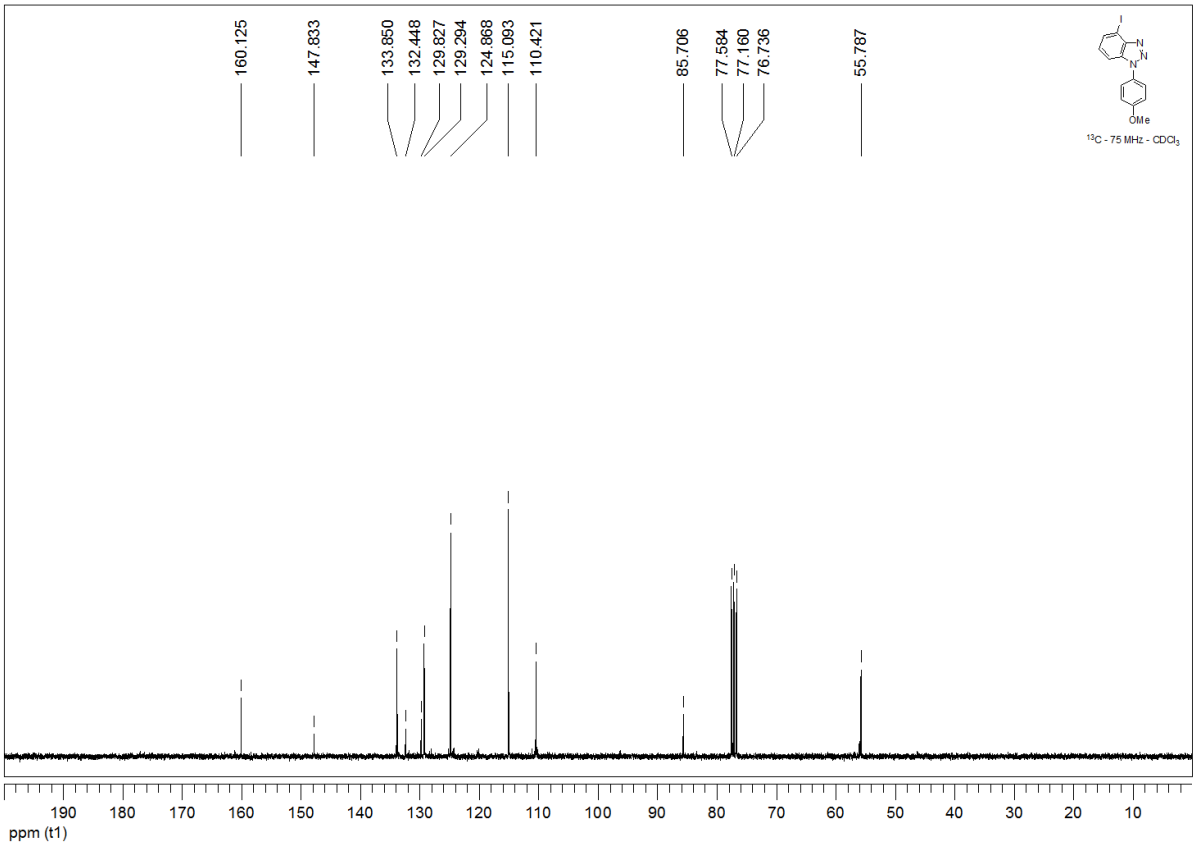

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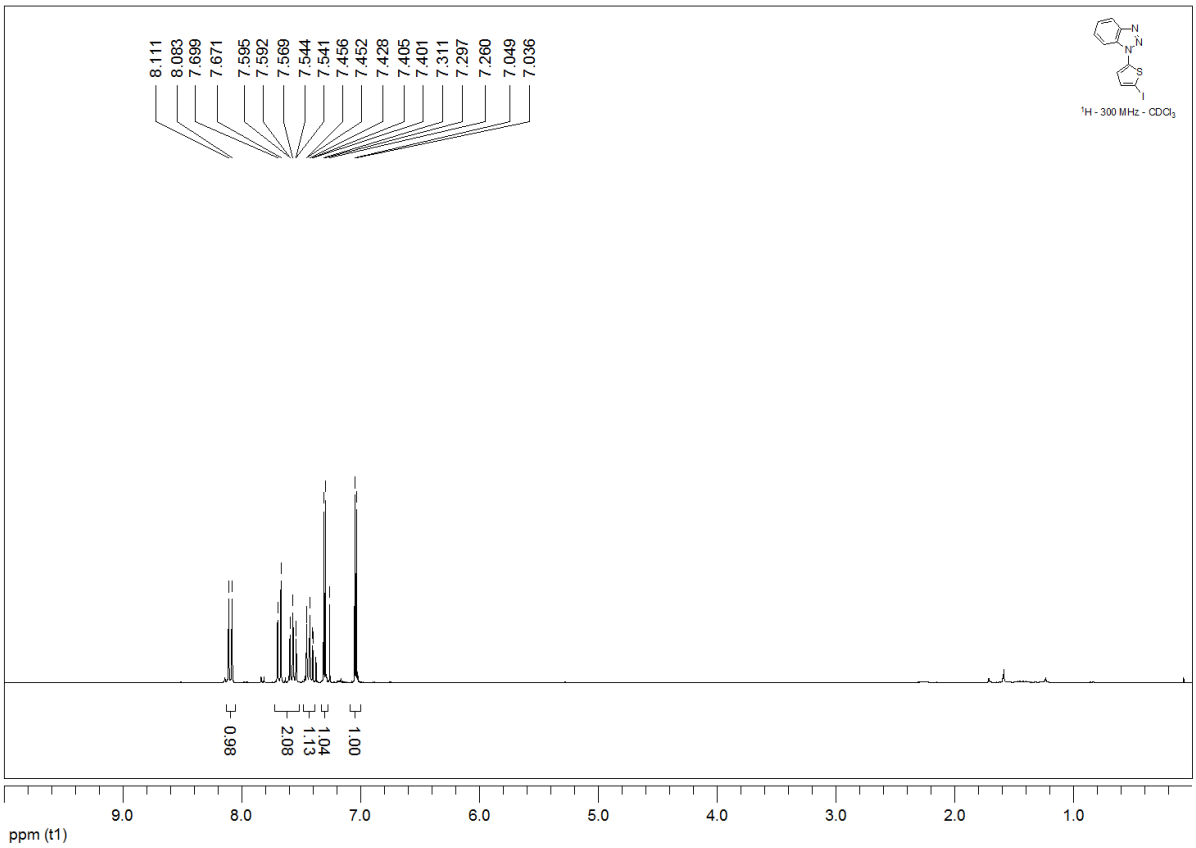

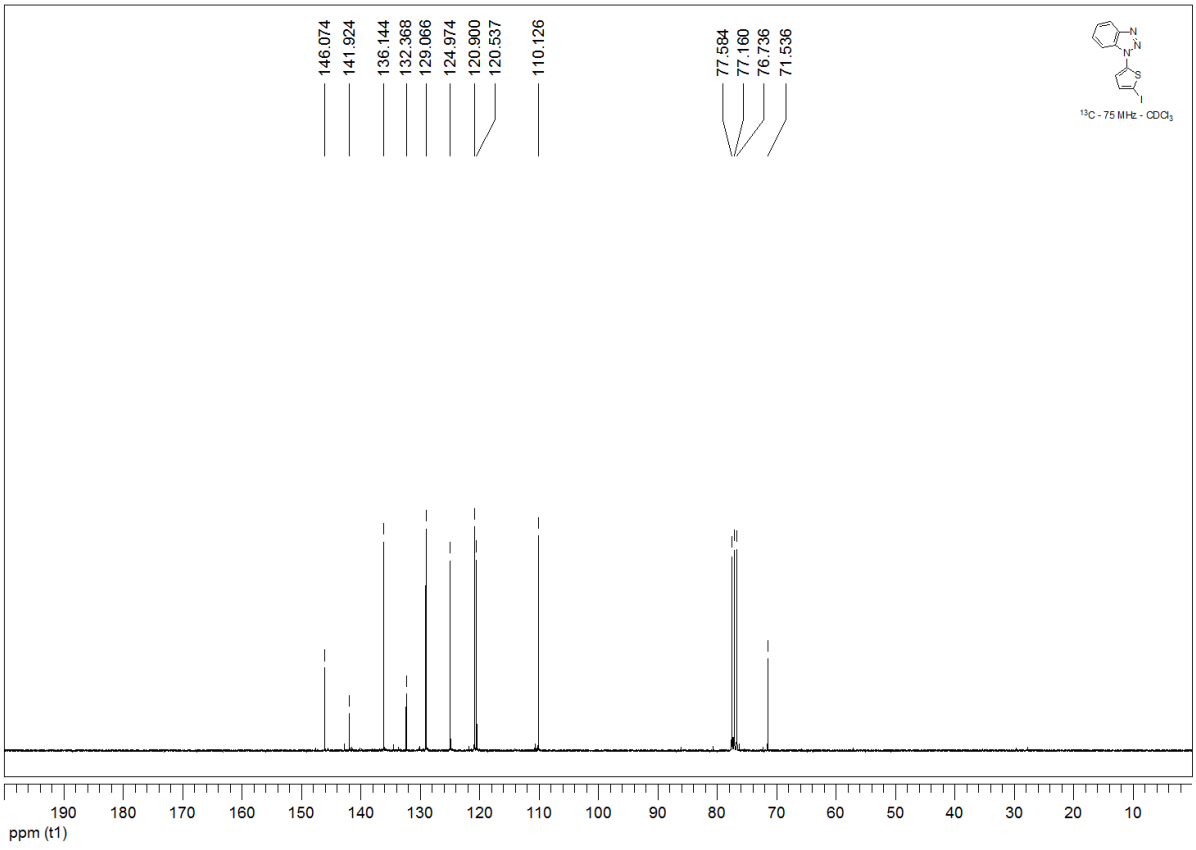

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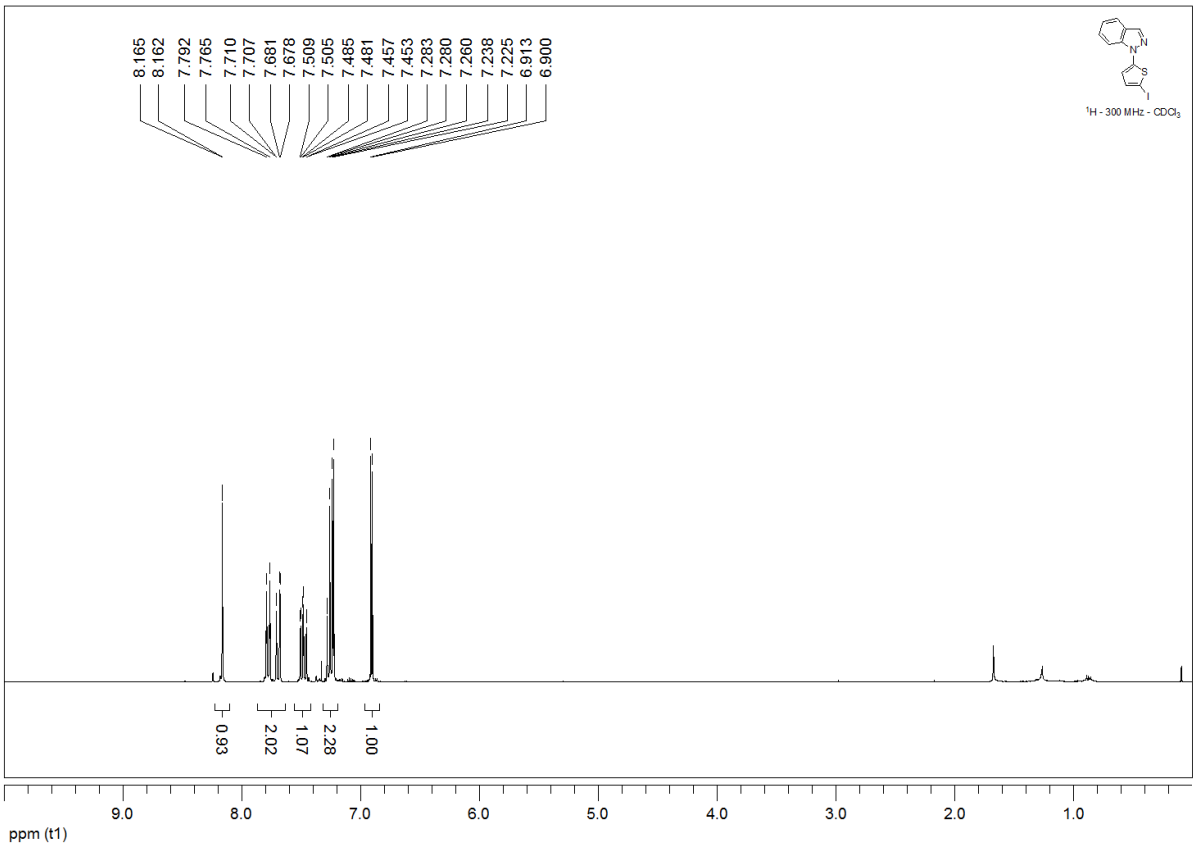

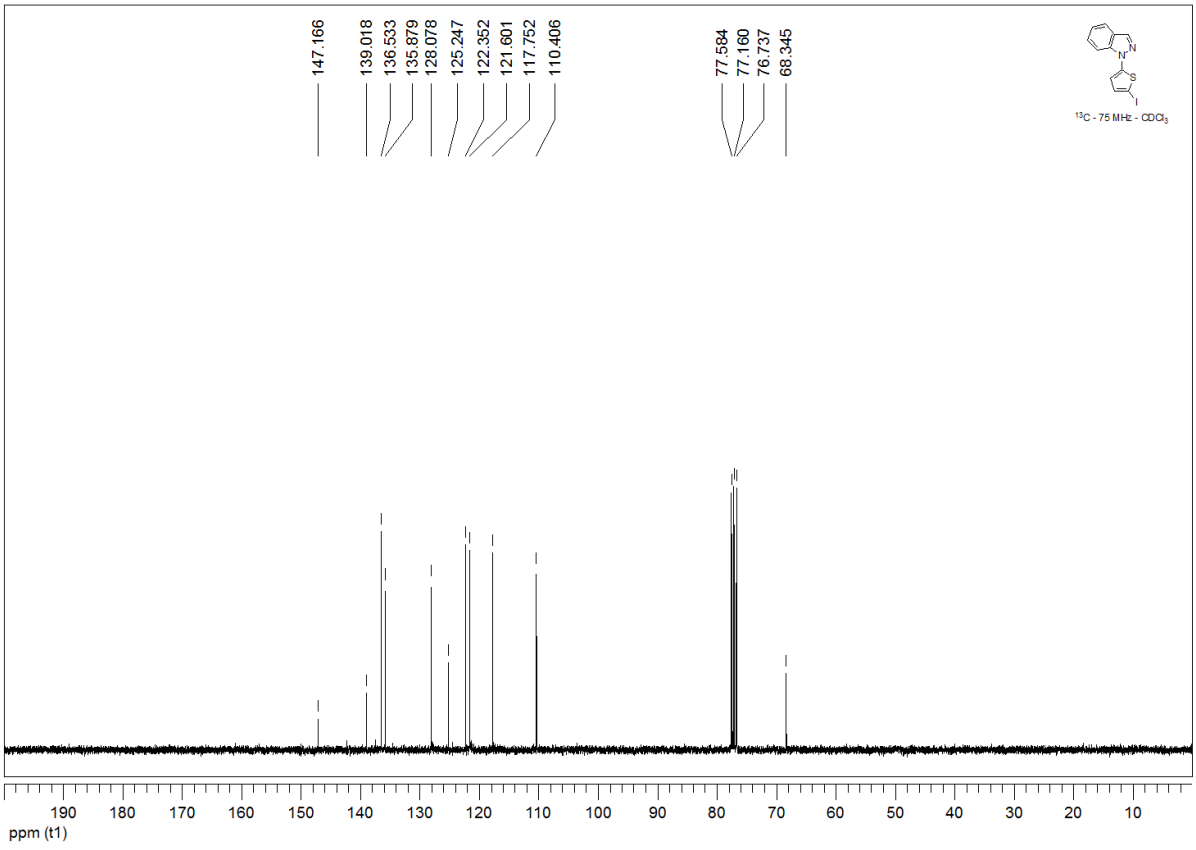

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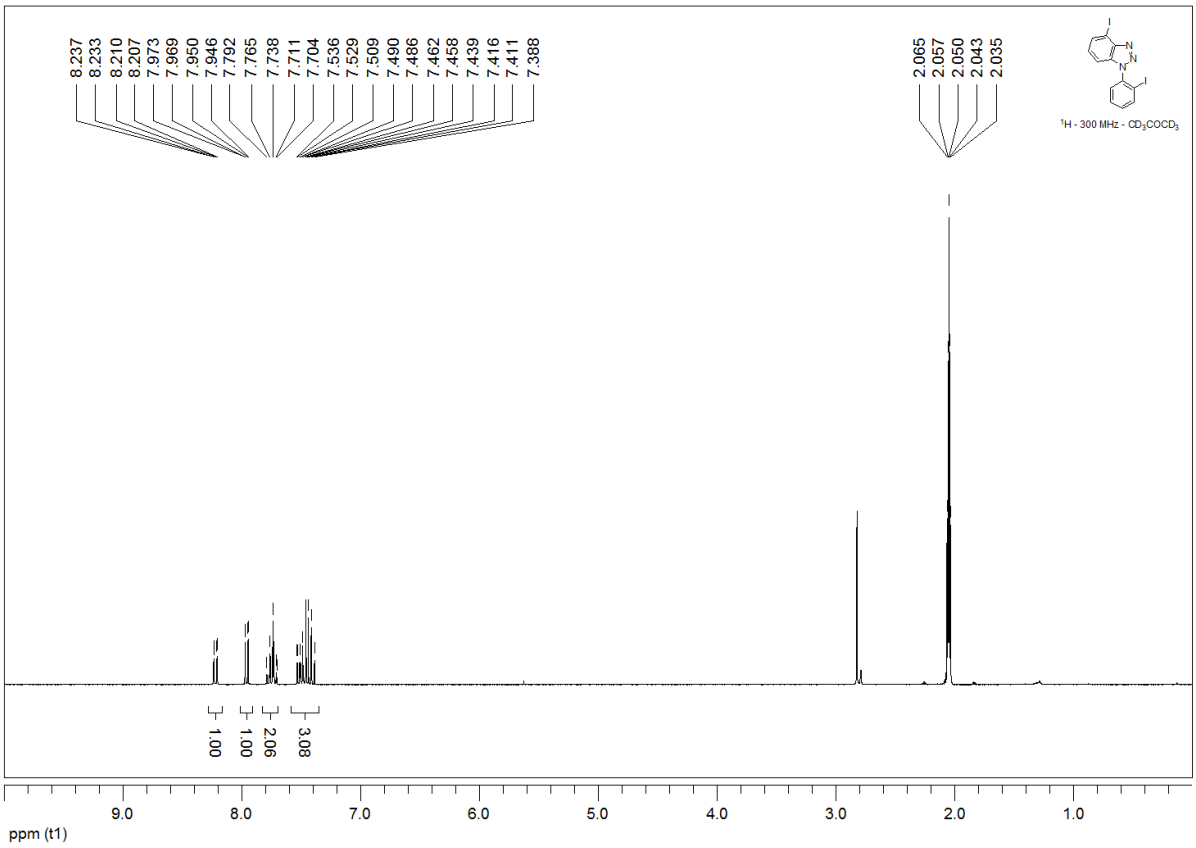

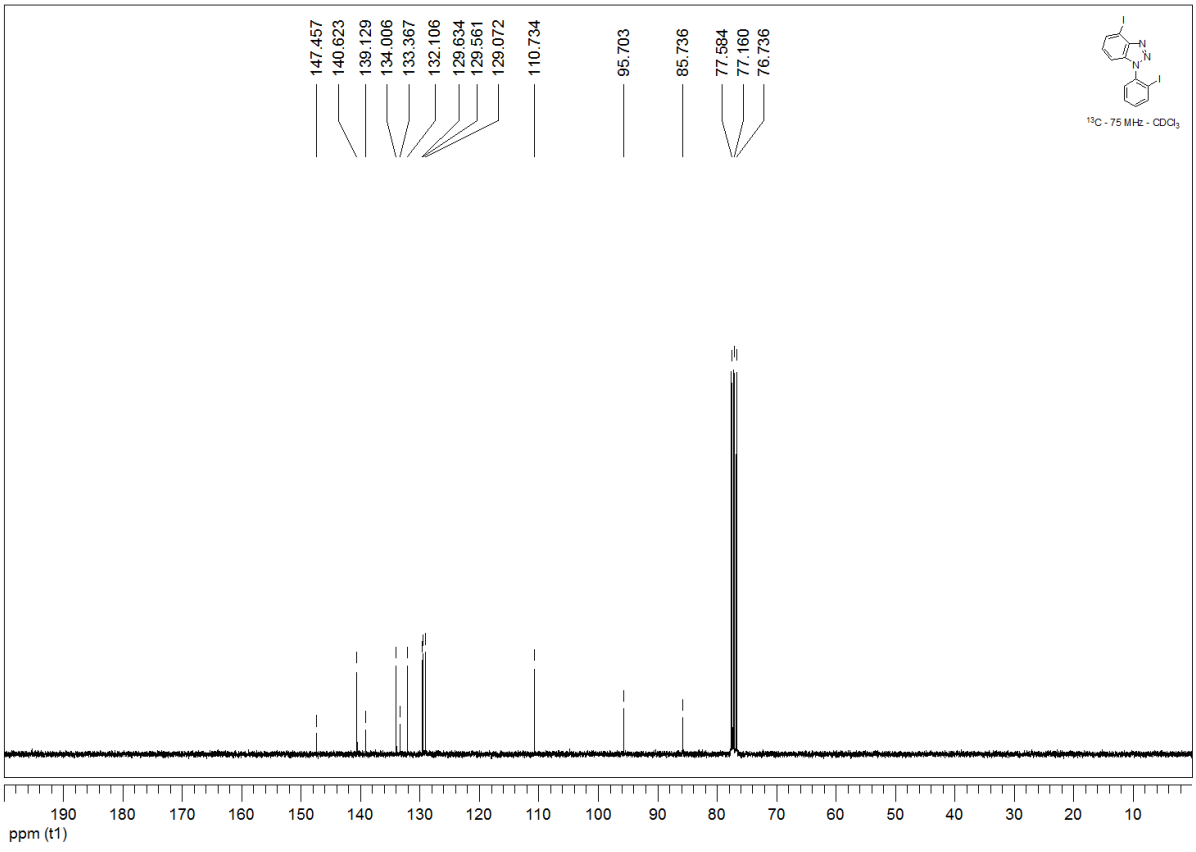

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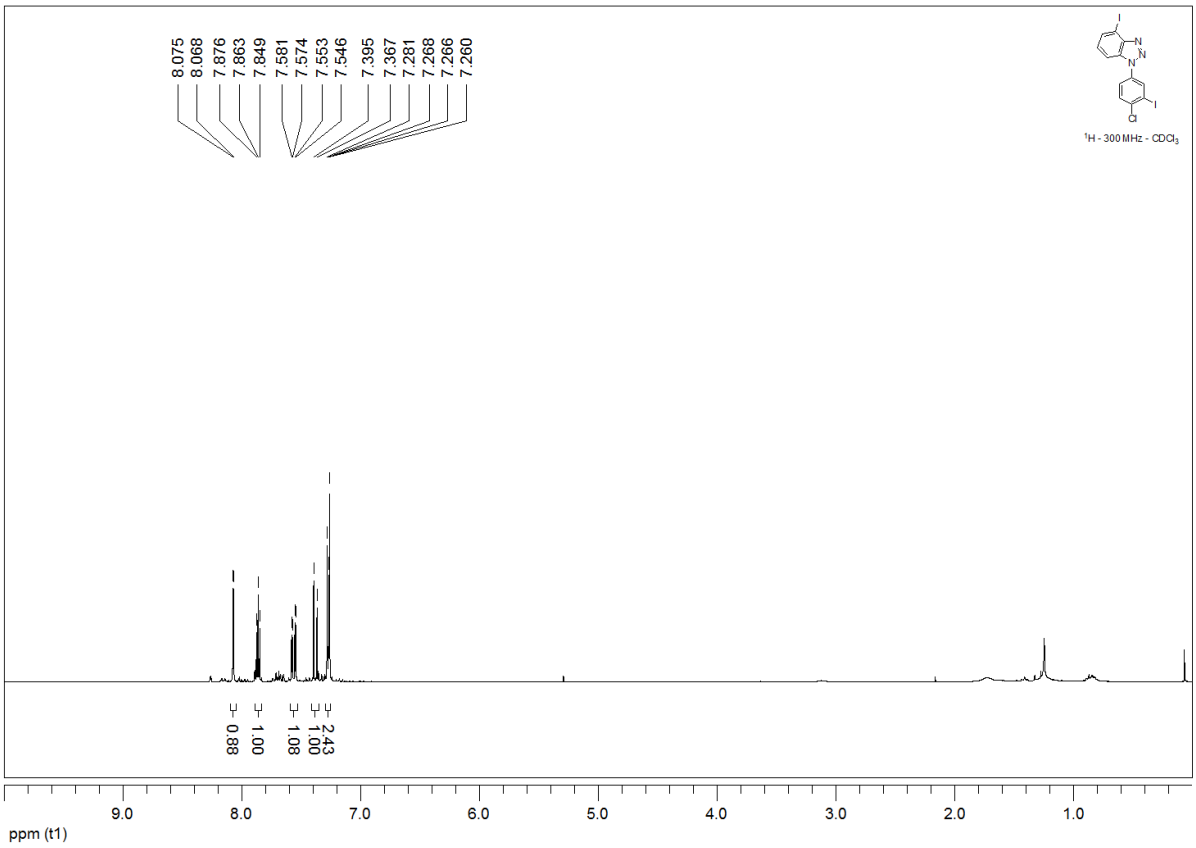

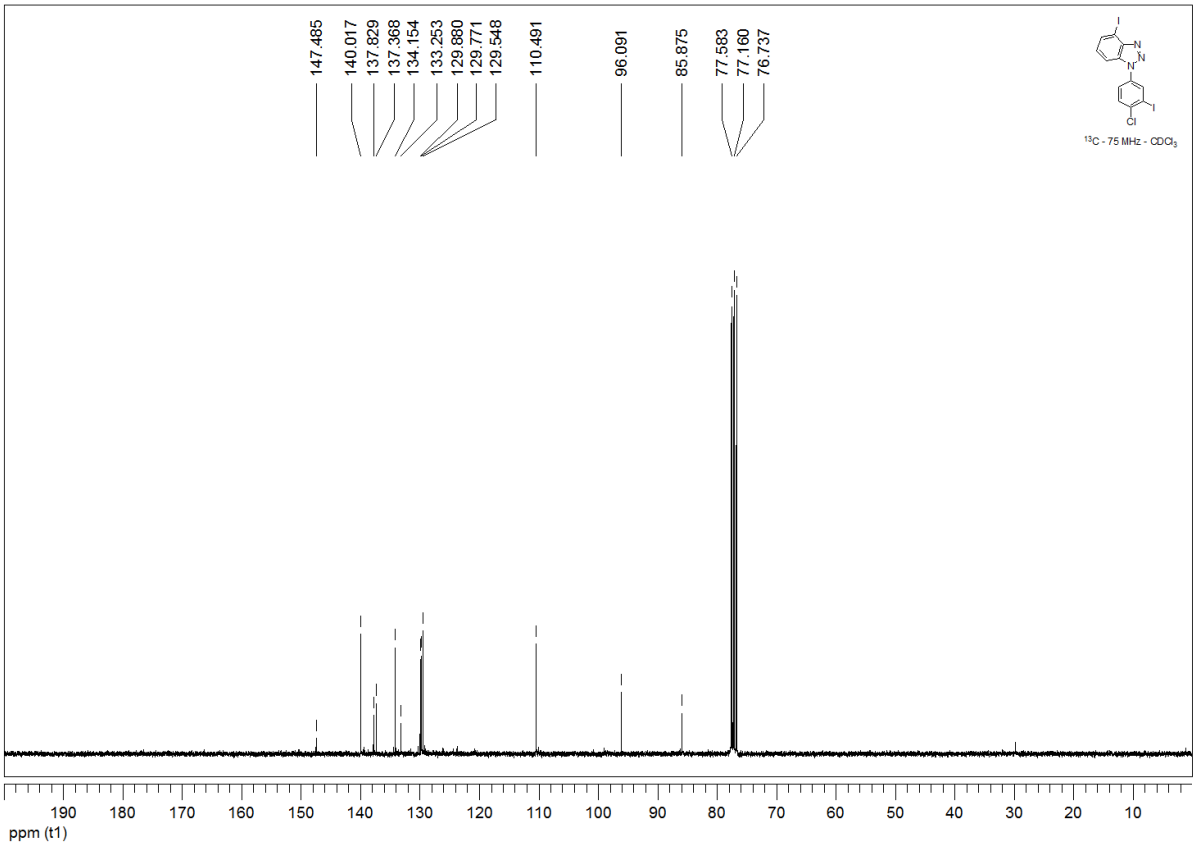

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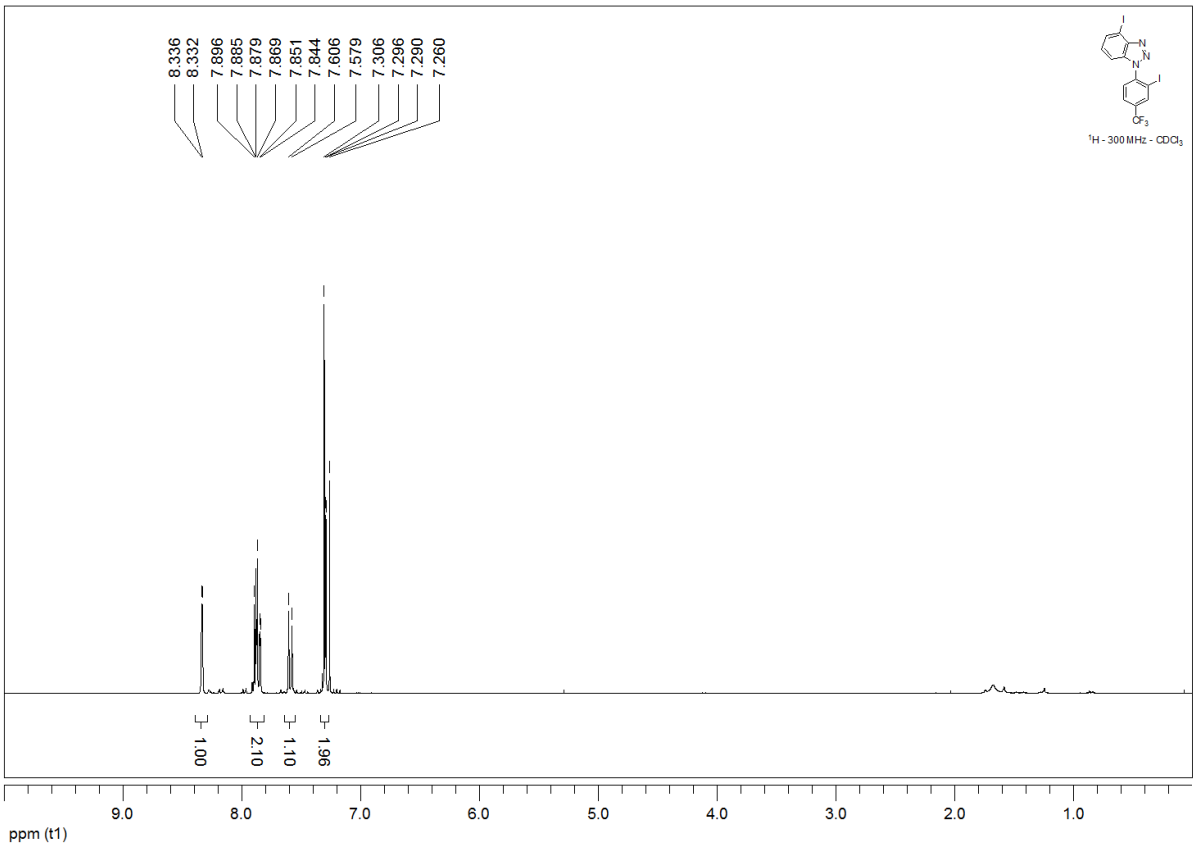

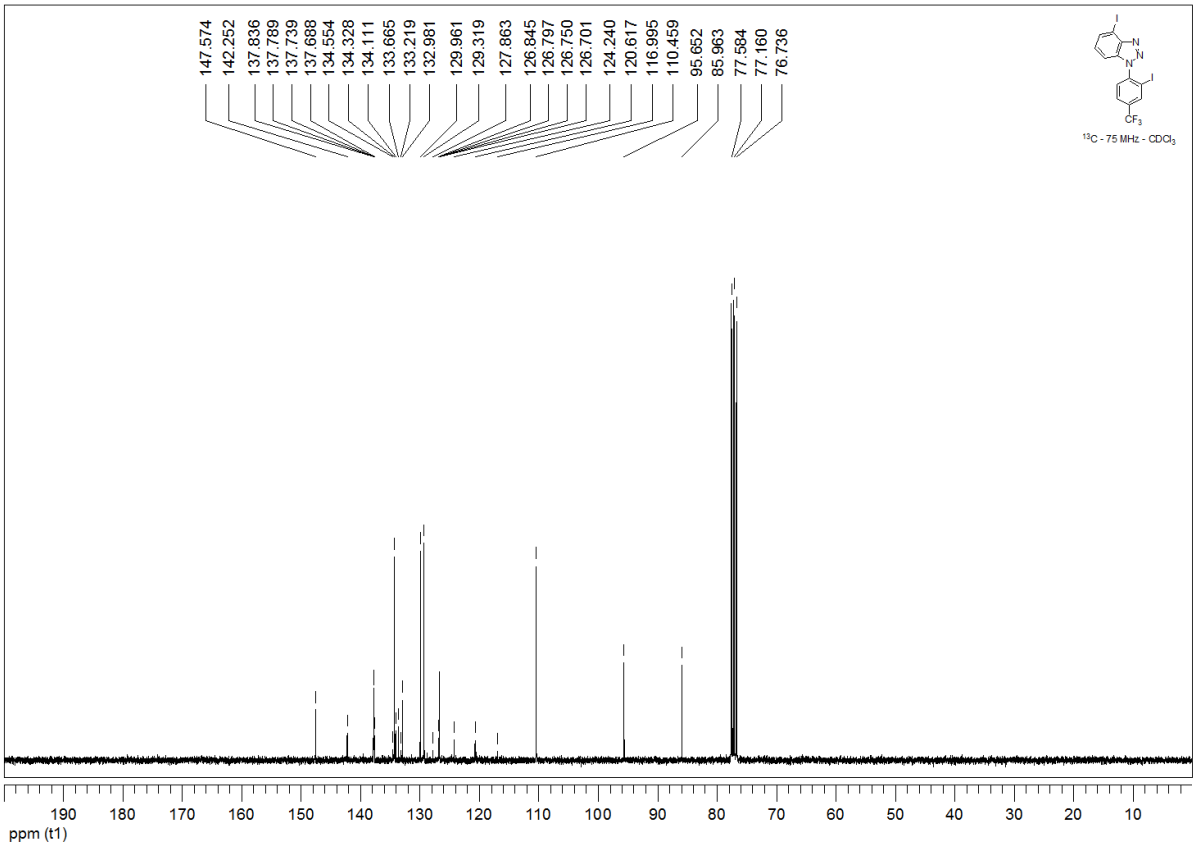

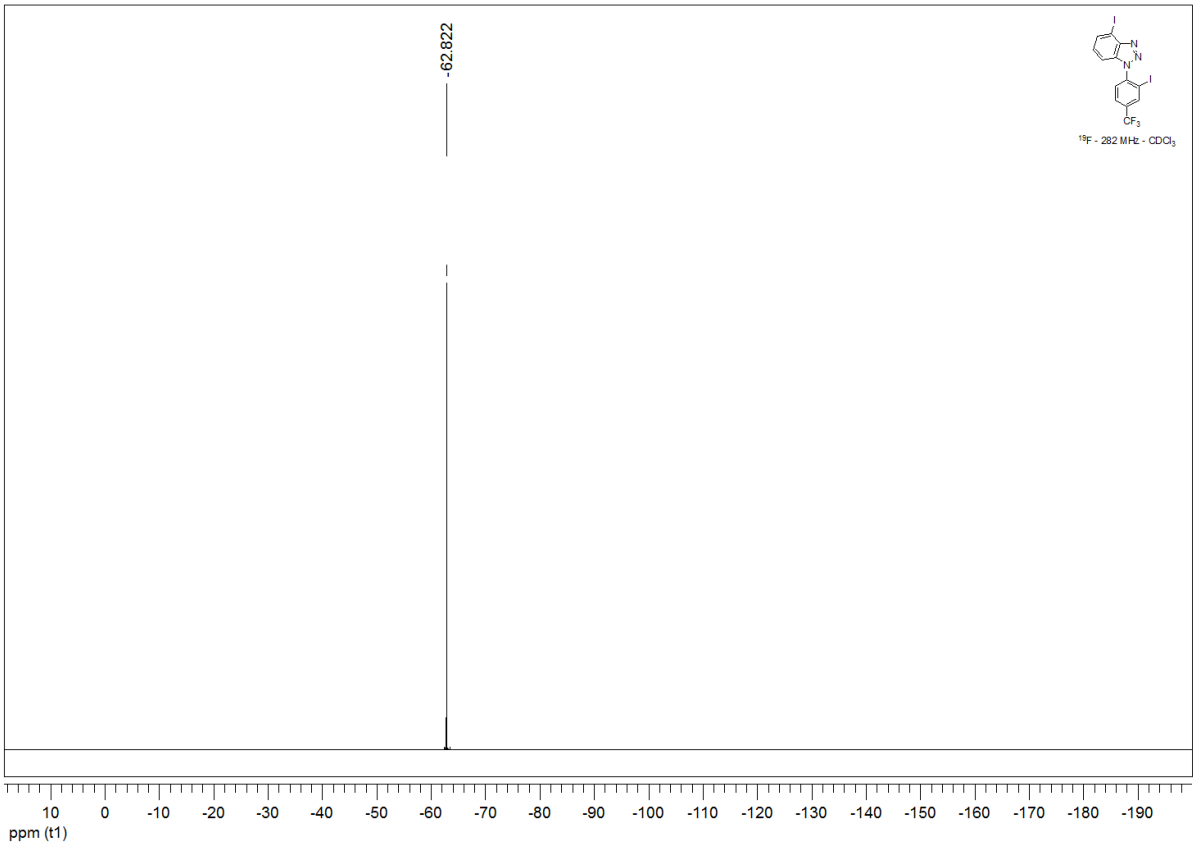

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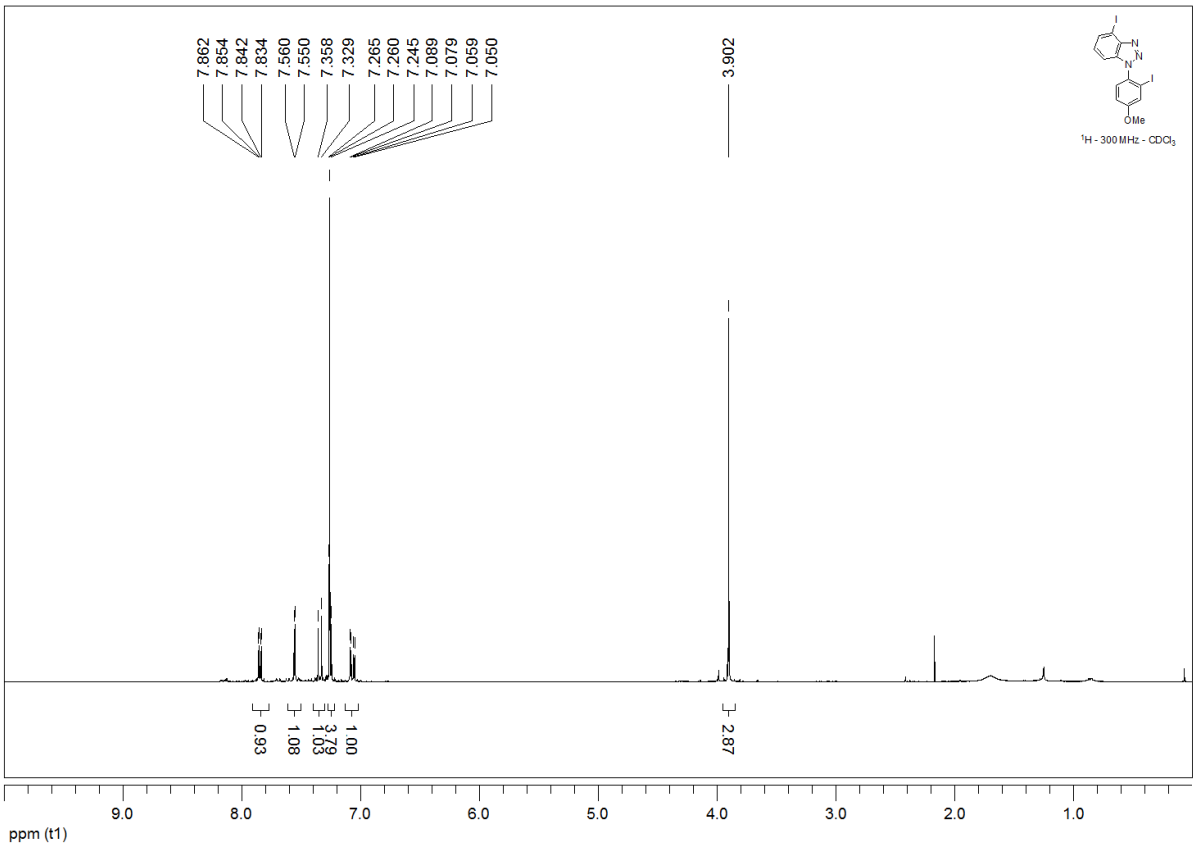
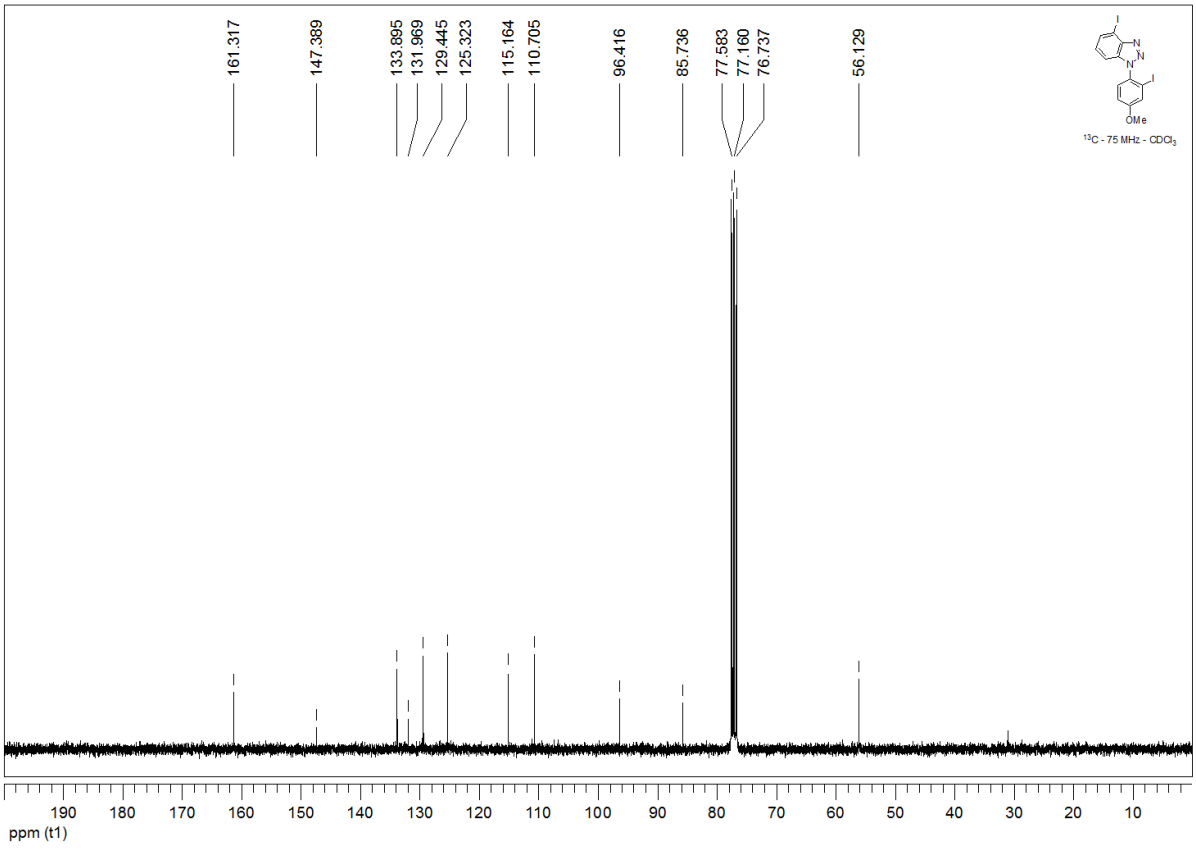
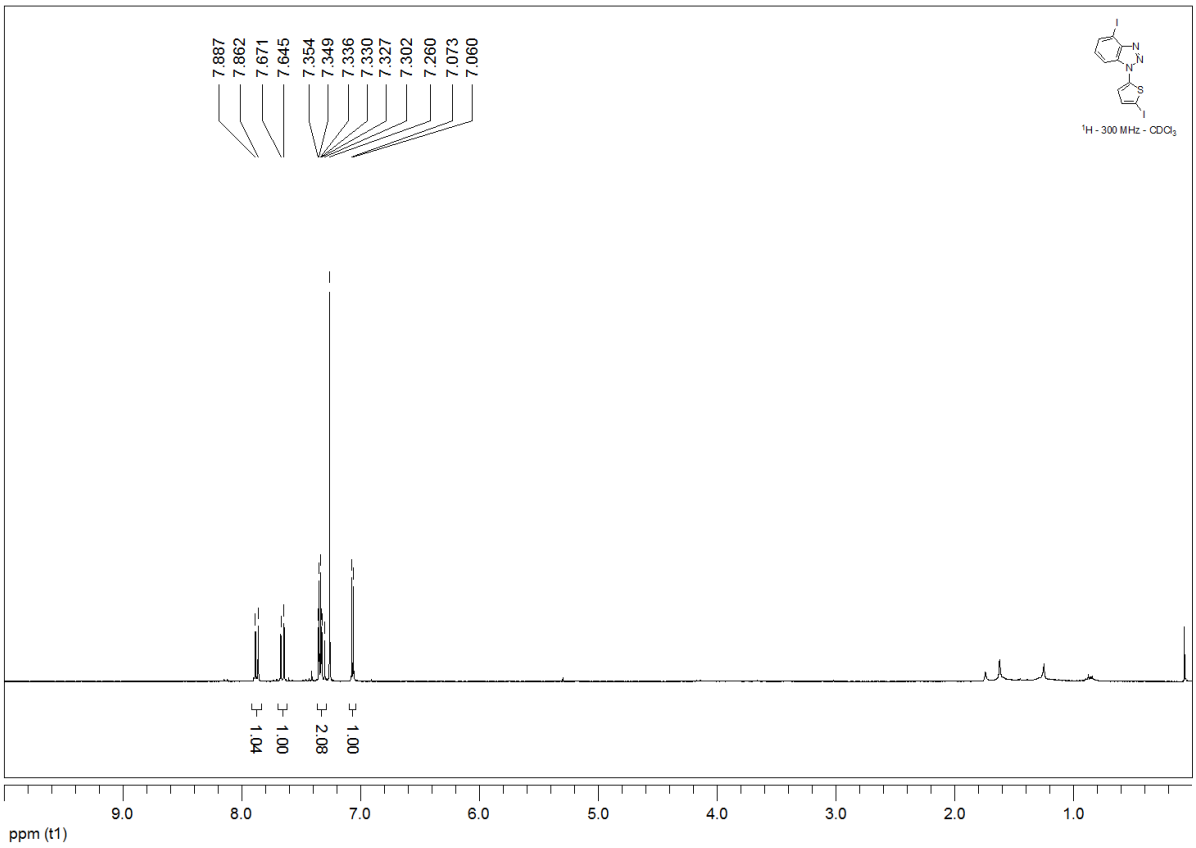
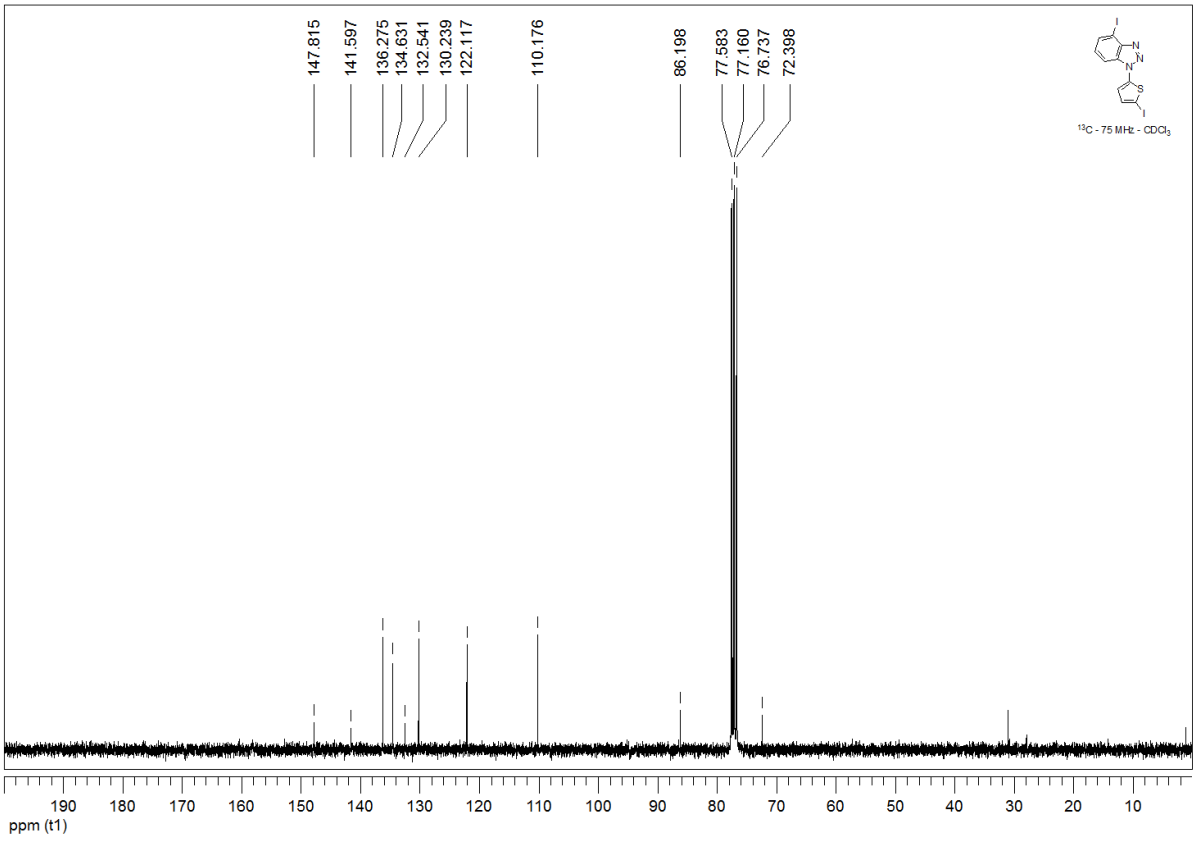


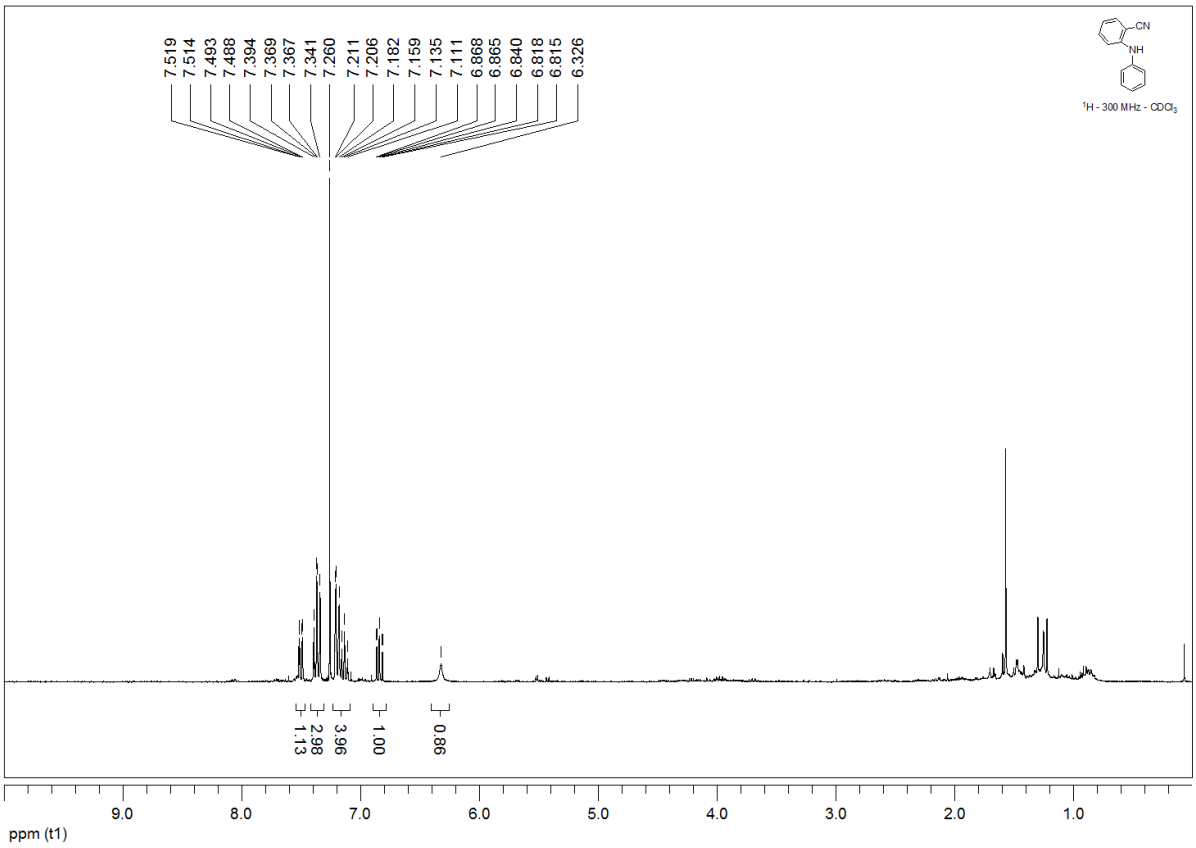


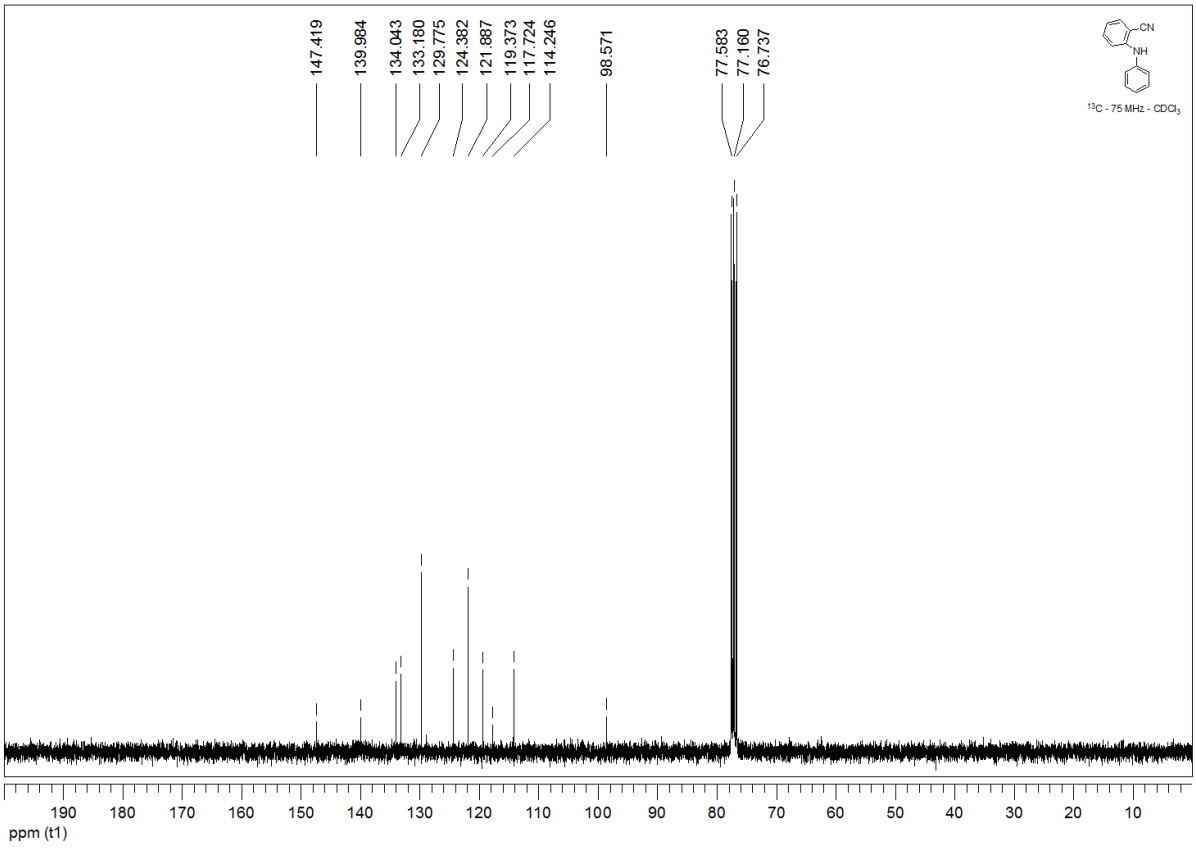
4-Iodo-1-(5-iodo-2-thienyl)-1*H*-benzotriazole (4g).





2-(Phenylamino)benzonitrile (6a).





Crystal data

The samples were studied with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). X-ray diffraction data were collected at T = 150(2) K using APEXII Bruker-AXS diffractometer. The structure was solved by direct methods using the SIR97 program,[1] and then refined with full-matrix least-square methods based on F^2 (SHELX-97)[2] with the aid of the WINGX program.[3] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. Molecular diagrams were generated by ORTEP-3 (version 2.02).

Crystal data for 1f. $C_{11}H_8N_4$, M = 196.21, monoclinic, $P\ 2_1/c$, a = 11.2914(14), b = 3.7335(4), c = 21.924(3) Å, β = 96.597(7) °, V = 918.1(2) Å^3, Z = 4, d = 1.42 g cm^{-3}, μ = 0.091 mm^{-1}. A final refinement on F^2 with 2081 unique intensities and 137 parameters converged at ωR(F^2) = 0.1134 (R(F) = 0.0533) for 1241 observed reflections with $I > 2\sigma(I)$.

Crystal data for 2g. $C_{11}H_8N_2S$, M = 200.25, monoclinic, $P\ 2_1$, a = 6.4535(5), b = 7.2728(5), c = 10.4085(6) Å, β = 105.814(3) °, V = 470.03(6) Å^3, Z = 2, d = 1.415 g cm^{-3}, μ = 0.299 mm^{-1}. A final refinement on F^2 with 1885 unique intensities and 127 parameters converged at ωR(F^2) = 0.0857 (R(F) = 0.0414) for 1683 observed reflections with $I > 2\sigma(I)$.

Crystal data for 3b. $C_{12}H_8IN_3$, M = 321.11, monoclinic, $P2_1/c$, a = 8.00450(10), b = 15.6507(3), c = 9.0232(2) Å, β = 100.4390(10) °, V = 1111.68(4) Å^3, Z = 4, d = 1.919 g cm^{-3}, μ = 2.854 mm^{-1}. A final refinement on F^2 with 2544 unique intensities and 145 parameters converged at ωR(F^2) = 0.0507 (R(F) = 0.0215) for 2303 observed reflections with $I > 2\sigma(I)$.

Crystal data for 3b'. $C_{12}H_8IN_3$, M = 321.11, monoclinic, $P2_1/n$, a = 9.9051(6), b = 7.5720(5), c = 14.9735(9) Å, β = 100.491(3) °, V = 1104.26(12) Å^3, Z = 4, d = 1.932 g cm^{-3}, μ = 2.873 mm^{-1}. A final refinement on F^2 with 2504 unique intensities and 145 parameters converged at ωR(F^2) = 0.0627 (R(F) = 0.0257) for 2241 observed reflections with $I > 2\sigma(I)$.

Crystal data for 3e. $C_{13}H_{10}IN_3O$, M = 351.14, monoclinic, $P\ 2_1/a$, a = 12.1661(7), b = 7.2750(4), c = 14.9877(8) Å, β = 111.5170(17) °, V = 1234.09(12) Å^3, Z = 4, d = 1.89 g cm^{-3}, μ = 2.586 mm^{-1}. A final refinement on F^2 with 2827 unique intensities and 164 parameters converged at ωR(F^2) = 0.0629 (R(F) = 0.0281) for 2515 observed reflections with $I > 2\sigma(I)$.

Crystal data for 3g. $C_{10}H_6IN_3S$, M = 327.14, monoclinic, $P2_1/c$, a = 6.6989(10), b = 8.5117(12), c = 19.409(3) Å, β = 96.629(5) °, V = 1099.3(3) Å^3, Z = 4, d = 1.977 g cm^{-3}, μ = 3.071 mm^{-1}. A final refinement on F^2 with 2509 unique intensities and 136 parameters converged at ωR(F^2) = 0.1004 (R(F) = 0.0392) for 1970 observed reflections with $I > 2\sigma(I)$.

[1] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115-119.
[2] G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **A64**, 112-122.
[3] L. J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849-854.

Crystal data for 4b. $C_{12}H_7I_2N_3$, M = 447.01, orthorhombic, $P2_12_12_1$, a = 4.4884(2), b = 12.4932(5), c = 22.1910(10) Å, V = 1244.35(9) Å^3, Z = 4, d = 2.386 g cm^{-3}, μ = 5.034 mm^{-1}. A final refinement on F^2 with 2732 unique intensities and 154 parameters converged at $\omega R(F^2)$ = 0.0747 ($R(F)$ = 0.0314) for 2611 observed reflections with $I > 2\sigma(I)$.

Crystal data for 4c. $C_{12}H_6ClI_2N_3$, M = 481.45, orthorhombic, $P\ b\ c\ 2_1$, a = 4.0838(4), b = 14.2493(13), c = 23.294(2) Å, V = 1355.5(2) Å^3, Z = 4, d = 2.359 g cm^{-3}, μ = 4.821 mm^{-1}. A final refinement on F^2 with 2941 unique intensities and 163 parameters converged at $\omega R(F^2)$ = 0.0796 ($R(F)$ = 0.0429) for 2555 observed reflections with $I > 2\sigma(I)$.

Crystal data for 4c'. $C_{12}H_6ClI_2N_3$, M = 481.45, triclinic, $P\ -1$, a = 7.1169(3), b = 8.2892(3), c = 12.3378(5) Å, α = 77.399(2), β = 74.075(2), γ = 73.384(2) °, V = 662.94(5) Å^3, Z = 2, d = 2.412 g cm^{-3}, μ = 4.929 mm^{-1}. A final refinement on F^2 with 2987 unique intensities and 163 parameters converged at $\omega R(F^2)$ = 0.0789 ($R(F)$ = 0.0416) for 2162 observed reflections with $I > 2\sigma(I)$.

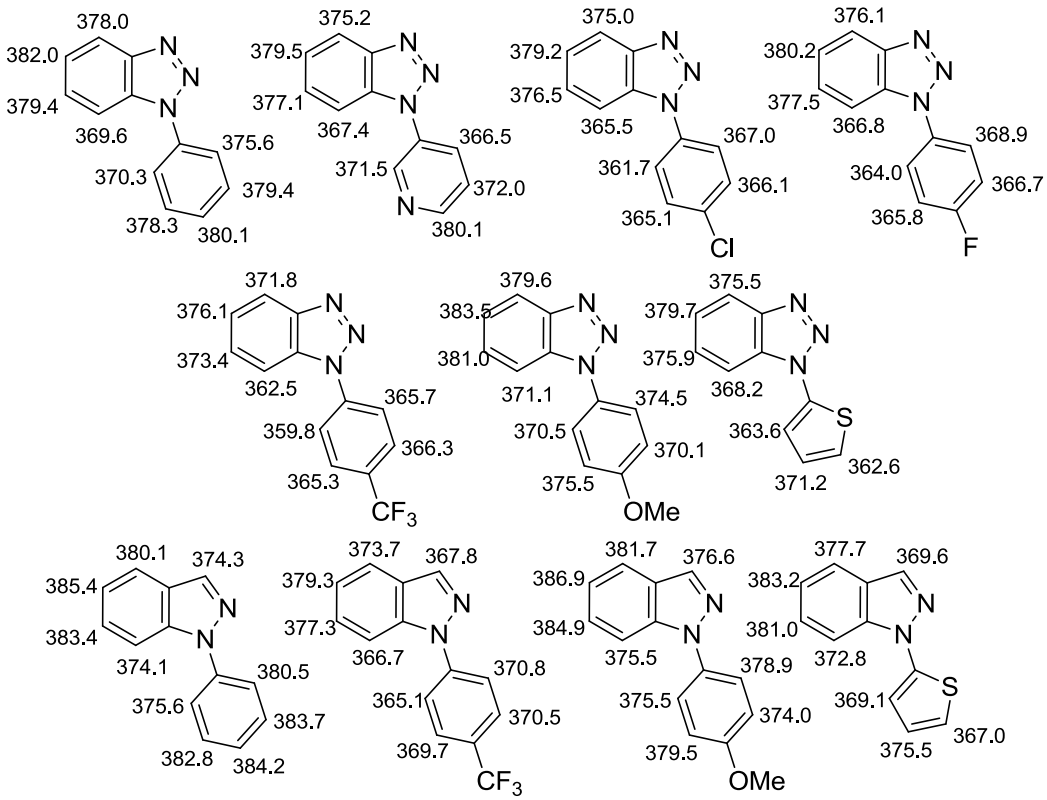
Crystal data for 4d. $C_{13}H_6F_3I_2N_3$, M = 515.01, monoclinic, $P2_1/a$, a = 13.300(3), b = 5.2093(11), c = 21.672(6) Å, β = 95.208(8) °, V = 1495.3(6) Å^3, Z = 4, d = 2.288 g cm^{-3}, μ = 4.234 mm^{-1}. A final refinement on F^2 with 3424 unique intensities and 209 parameters converged at $\omega R(F^2)$ = 0.0706 ($R(F)$ = 0.0327) for 2806 observed reflections with $I > 2\sigma(I)$.

Crystal data for 4e. $C_{13}H_9I_2N_3O$, M = 477.03, monoclinic, $P\ 2_1/c$, a = 8.2536(4), b = 15.6664(7), c = 11.6615(5) Å, β = 108.822(2) °, V = 1427.25(11) Å^3, Z = 4, d = 2.22 g cm^{-3}, μ = 4.402 mm^{-1}. A final refinement on F^2 with 3270 unique intensities and 173 parameters converged at $\omega R(F^2)$ = 0.0783 ($R(F)$ = 0.0348) for 2889 observed reflections with $I > 2\sigma(I)$.

Crystal data for 4e'. $C_{13}H_9I_2N_3O$, M = 477.03, monoclinic, $P2_1/n$, a = 4.2004(2), b = 20.7217(14), c = 15.9102(11) Å, β = 97.125(3) °, V = 1374.12(15) Å^3, Z = 4, d = 2.306 g cm^{-3}, μ = 4.572 mm^{-1}. A final refinement on F^2 with 3121 unique intensities and 173 parameters converged at $\omega R(F^2)$ = 0.108 ($R(F)$ = 0.0356) for 2789 observed reflections with $I > 2\sigma(I)$.

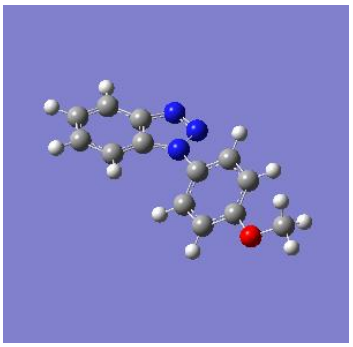
Crystal data for 4g. $C_{10}H_5I_2N_3S$, M = 453.04, orthorhombic, $P\ b\ c\ 2_1$, a = 4.10400(10), b = 22.5488(7), c = 25.9538(10) Å, V = 2401.77(13) Å^3, Z = 8, d = 2.506 g cm^{-3}, μ = 5.386 mm^{-1}. A final refinement on F^2 with 5344 unique intensities and 217 parameters converged at $\omega R(F^2)$ = 0.1001 ($R(F)$ = 0.0441) for 5098 observed reflections with $I > 2\sigma(I)$.

Calculated values of the Gibbs energies $\Delta_{acid}G$ [kcal mo1^{-1}] for deprotonation at the corresponding positions of the investigated heteroaromatic compounds

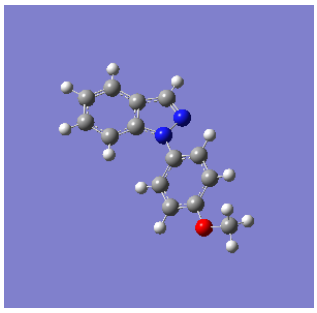


Cartesian coordinates of molecular geometries for most stable rotamer forms of selected heteroaromatics (on example of 1e, 2e) (neutral molecule, gas phase) optimized at B3LYP/6-31G(d) level of theory

1e



C	-1.90121	0.39199	0.055327
C	-2.10959	1.769358	-0.11828
C	-3.42905	2.189511	-0.2042
C	-4.51372	1.282504	-0.12501
C	-4.30318	-0.07773	0.03184
C	-2.97369	-0.52082	0.117184
H	-1.28552	2.470358	-0.19359
H	-3.63731	3.247217	-0.33989
H	-5.52711	1.666795	-0.19554
H	-5.12339	-0.78655	0.082583
N	-0.78939	-0.40676	0.160562
N	-1.17504	-1.72359	0.272634
N	-2.46279	-1.79565	0.245949
C	0.588611	-0.06427	0.155427
C	1.042616	1.062851	0.85348
C	1.497841	-0.86671	-0.5338
C	2.391018	1.391342	0.83835
H	0.34398	1.667135	1.422901
C	2.856425	-0.55028	-0.53418
H	1.138684	-1.74241	-1.0628
C	3.309394	0.587742	0.145765
H	2.76092	2.260273	1.372846
H	3.544979	-1.18992	-1.07358
O	4.608253	0.996049	0.198123
C	5.587198	0.217552	-0.47426
H	5.39461	0.173519	-1.55421
H	6.53992	0.719682	-0.29803
H	5.635212	-0.8033	-0.07336



2e

C	-1.93096	0.279145	0.045031
C	-2.06485	1.670827	-0.10288
C	-3.35258	2.177784	-0.18975
C	-4.49064	1.339481	-0.13657
C	-4.35681	-0.03325	-0.01085
C	-3.06194	-0.57622	0.073875
H	-1.20078	2.323069	-0.1625
H	-3.49085	3.249312	-0.30637
H	-5.47976	1.783361	-0.20442
H	-5.23001	-0.67953	0.014633
N	-0.8261	-0.54224	0.138575
N	-1.19002	-1.86076	0.204347
C	0.549868	-0.19596	0.142705
C	1.005771	0.923024	0.853621
C	1.465789	-0.9906	-0.54817
C	2.354399	1.25415	0.84328
H	0.308831	1.518647	1.433549
C	2.824112	-0.67274	-0.54408
H	1.108953	-1.86524	-1.08028
C	3.275133	0.460192	0.14485
H	2.721639	2.117065	1.38952
H	3.514353	-1.30849	-1.08633
O	4.575813	0.869921	0.203312
C	5.553668	0.097932	-0.47546
H	5.361625	0.062418	-1.55609
H	6.507123	0.597818	-0.2955
H	5.602349	-0.92702	-0.08438
C	-2.50795	-1.88771	0.170132
H	-3.0249	-2.83764	0.218757