Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Sulphur Promoted C(sp^3)-C(sp^2) Cross Dehydrogenative Cyclisation of Acetophenone Hydrazones with Aldehydes: An Efficient Synthesis of 3, 4, 5-Trisubstituted 1H-Pyrazoles

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1. General Information:

All the reagents were purchased from Sigma-Aldrich Corporation, Merck, Alfa Aesar, and Sd-Fine (India) and were used as received. The solvents employed in the reactions were distilled and dried prior to use. All the reactions were monitored by thin-layer chromatography (TLC) and visualized using UV light; products purification was done using silica gel column chromatography. ^{1}H and ^{13}C-NMR spectra were recorded on a JEOL FT-NMR spectrometer at 300 and 75.45 MHz respectively using $CDCl_3$ or DMSO-d_6 solution. Chemical shifts are given in ppm and are measured relative to tetramethylsilane (TMS) as an internal standard

2. Procedure[1] for Preparation of Hydrazones:

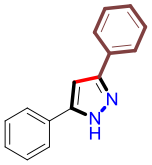
A 250 mL three necked flask was charged with acetophenone (10 mmol), and hydrazine monohydrate (80 mmol). The reaction mixture was then refluxed for 4 h. After cooling down to room temperature, the reaction mixture was extracted with DCM (50 mL x 5). The organic phase was dried over Na_2SO_4, concentrated under vacuum and the isolated product was used directly without further purification.

3. General Experimental Procedure:

To a solution of hydrazone **1** (0.5 mmol) and aldehydes **2** (1 mmol) in 1, 4-dioxane (0.75 mL) was added sulfur powder (1 mmol, mol. wt. 32). The reaction mixture was stirred for 24 h at 120 °C in an oil bath. After the completion of reaction; contents of the flask were cooled to room temperature. To this was added excess of water and then extracted with ethyl acetate (3 x 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to afford the crude product which was finally purified by column chromatography using ethyl acetate-n-hexane (10-15%) as eluent.

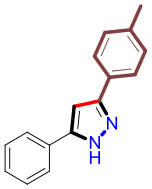
4. Characterisation Data of the Products (NMR & HRMS):

1. **3,5-Diphenyl-1H-pyrazole (3aa)**[2]



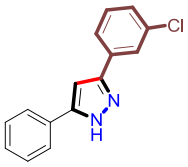
Yellow solid; **^{1}H-NMR ($CDCl_3$, 300 MHz):** δ 7.64-7.61 (m, 2H), 7.40-7.06 (m, 9H), 6.74 (s, 1H); **^{13}C-NMR ($CDCl_3$, 75 MHz)**: δ ^{13}C NMR (75 MHz, $CDCL_3$) δ 149.0, 131.5, 129.1, 128.5, 125.9, 100.3.

2. **5-Phenyl-3-(p-tolyl)-1H-pyrazole (3ab)**[2]



Yellow solid; **^{1}H-NMR ($CDCl_3$, 300 MHz)**: δ 8.80 (bs, 1H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.37-7.13 (m, 5H), 6.76 (s, 1H), 2.35 (s, 3H); δ **^{13}C-NMR ($CDCl_3$, 75 MHz)**: 149.4, 148.6, 138.4, 131.9, 129.8, 129.1, 128.6, 128.4, 125.9, 125.8, 100.0, 21.4.

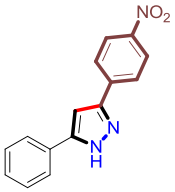
3. 3-(3-Chlorophenyl)-5-phenyl-1H-pyrazole (3ac)



Yellow solid; **^{1}H-NMR (DMSO, 300 MHz)**: δ 13.44 (bs, 1H), 7.88-7.79 (m, 3H), 7.69-7.33 (m, 6H), 7.26 (s, 1H); **^{13}C-NMR (DMSO, 75 MHz)**: δ 144.5, 130.9, 130.8, 130.0, 129.0, 127.6, 127.0, 126.0, 125.2, 124.8, 124.4, 123.8, 100.3.

HRMS (ESI +): ($M+H)^+$ calcd. For $C_{15}H_{11}ClN_2$: 255.0689; Found: 255.0681.

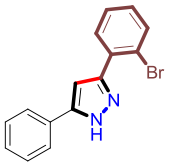
4. 3-(4-Nitrophenyl)-5-phenyl-1H-pyrazole (3ad)



Yellow solid; **^{1}H-NMR (DMSO, 300 MHz)**: δ 8.28-8.12 (m, 2H), 7.87-7.73 (m, 2H), 7.43-7.17 (m, 1H), 5.64 (bs, 1H); **^{13}C-NMR (DMSO, 75 MHz)**: δ 150.4, 146.6, 144.6, 135.6, 132.2, 129.3, 128.5, 127.6, 125.0, 123.8, 123.5, 105.0.

HRMS (ESI -): ($M-H)^+$ calcd. For $C_{15}H_{11}N_3O_2$: 264.0773; Found: 264.0775.

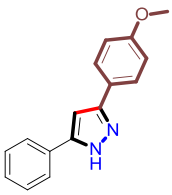
5. 3-(2-Bromophenyl)-5-phenyl-1H-pyrazole (3ae)



Yellow solid; **^{1}H-NMR ($CDCl_3$, 300 MHz)**: δ 9.85 (bs, 1H), 7.72-7.70 (m, 1H), 7.63-7.61(m, 1H), 7.54-7.52 (m, 1H), 7.35-7.12 (m, 6H), 6.94 (s, 1H); **^{13}C-NMR ($CDCl_3$, 75 MHz)**: δ 148.2, 146.6, 133.6, 132.1, 131.3, 130.8, 129.5, 128.7, 128.1, 127.5, 125.6, 121.7, 103.6.

HRMS (ESI +): ($M+H)^+$ calcd. For $C_{15}H_{11}BrN_2$: 299.0184, 301.0163; Found: 299.0178, 301.0154.

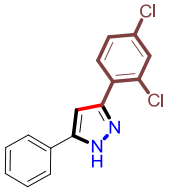
6. 3-(4-Methoxyphenyl)-5-phenyl-1H-pyrazole (3af)



Yellow solid; **^{1}H-NMR (DMSO, 300 MHz)**; δ 13.31 (bs, 1H), 7.88-7.85 (m, 2H), 7.81-7.78 (m, 2H), 7.47-7.42 (m, 2H), 7.34-7.30 (m, 1H), 7.07-7.00 (m, 3H), 3.77 (s, 3H); **^{13}C-NMR (DMSO, 75 MHz)**: δ ^{13}C NMR (75 MHz, DMSO) δ 159.2, 129.3, 128.9, 127.8, 126.7, 125.3, 122.3, 114.4, 98.9, 55.2.

HRMS (ESI +): (M+H)$^{+}$ calcd. For $C_{16}H_{15}N_2O$: 251.1184; Found: 251.1177.

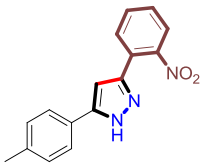
7. **3-(2,4-Dichlorophenyl)-5-phenyl-1H-pyrazole (3ag)**



Yellow solid; **^{1}H-NMR (DMSO, 300 MHz)**: δ 13.56 (bs, 1H), 7.80-7.77 (d, J = 7.2 Hz, 2H), 7.66 (s, 1H), 7.48-7.28 (m, 5H), 7.11 (s, 1H); **^{13}C-NMR (DMSO, 75 MHz)**: δ 133.2, 133.1, 132.0, 131.6, 130.9, 129.8, 129.0, 128.8, 128.1, 128.0, 127.9, 125.3, 103.3.

HRMS (ESI +): (M+H)$^{+}$ calcd. For $C_{15}H_{11}Cl_2N_2$: 289.0299; Found: 289.0299.

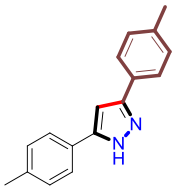
8. **3-(2-Nitrophenyl)-5-(p-tolyl)-1H-pyrazole (3ah)**



Yellow solid; **^{1}H-NMR (DMSO, 300 MHz)**: δ 13.50 (bs, 1H), 7.76-7.73 (d, J = 7.2 Hz, 2H), 7.65-7.48 (m, 5H), 7.20-7.17 (d, J = 7.8 Hz, 2H), 6.88 (s, 1H), 2.24 (s, 3H); **^{13}C-NMR (DMSO, 75 MHz)**: δ 148.8, 140.5, 138.0, 134.6, 132.1, 130.3, 129.7, 129.5, 128.9, 126.9, 125.2, 123.6, 101.1, 20.8.

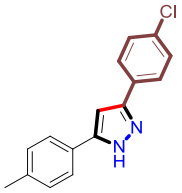
HRMS (ESI +): (M+H)$^{+}$ calcd. For $C_{16}H_{14}N_3O_2$: 280.1086; Found: 280.1095

9. **3, 5-Di-p-tolyl-1H-pyrazole (3ai)**[2]



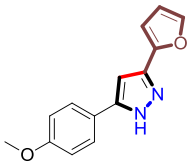
Yellow solid; **^{1}H-NMR (DMSO, 300 MHz):** δ 13.17 (bs, 1H), 7.70-7.68 (d, J = 7.8 Hz, 4H), 7.23-7.21 (d, J = 8.4), 7.04 (s, 1H), 2.30 (s, 6H); **^{13}C-NMR (DMSO, 75 MHz)**: δ 145.1, 137.5, 129.9, 129.7, 125.4, 99.3, 21.1.

10. 3-(4-Chlorophenyl)-5-(p-tolyl)-1H-pyrazole (3aj)[2]



Yellow solid; **^{1}H-NMR ($CDCl_3$, 300 MHz)**; δ 13.30 (bs, 1H), 7.79-7.76 (d, *J* = 7.5 Hz, 2H), 7.64-7.61 (d, *J* = 7.2 Hz, 2H), 7.41-7.39 (d, *J* = 7.5 Hz, 2H), 7.15-7.09 (d, J = 7.5 Hz, 2H), 7.05 (s, 1H), 2.23 (s, 3H); **^{13}C-NMR ($CDCl_3$, 75 MHz)**: δ 137.6, 137.5, 137.4, 132.2, 129.56, 128.9, 126.9, 126.9, 125.2, 125.1, 99.6, 20.8.

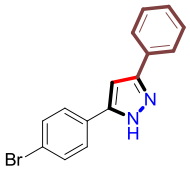
11. 3-(Furan-2-yl)-5-(4-methoxyphenyl)-1H-pyrazole (3ak)



Yellow solid; **^{1}H-NMR (DMSO, 300 MHz):** δ 13.17 (bs, 1H), 7.67-7.63 (m, 3H), 6.92-6.49 (m, 5H), 3.69 (s, 3H); **^{13}C-NMR (DMSO, 75 MHz)**: δ 159.1, 142.2, 126.5, 114.1, 111.4, 105.8, 105.7, 105.7, 105.6, 98.2, 98.2, 54.9.

HRMS (ESI +): ($M+H)^+$ calcd. $C_{14}H_{13}N_2O_2$: 241.0977; Found: 241.0973.

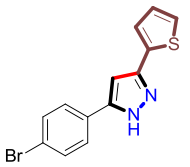
12. 5-(4-Bromophenyl)-3-phenyl-1H-pyrazole (3al)



Yellow solid; **^{1}H-NMR ($CDCl_3$+DMSO, 300 MHz):** δ 7.79-7.72 (m, 3H), 7.54-7.31 (7H), 6.90 (s, 1H); **^{13}C-NMR (DMSO, 75 MHz)**: δ 147.4, 146.7, 131.3, 128.7, 128.6, 128.4, 128.0, 127.7, 127.5, 126.7, 125.0, 120.8, 99.0.

HRMS (ESI +): ($M+H)^+$ calcd. $C_{15}H_{12}BrN_2$: 299.0184, 301.0163; Found: 299.0181, 301.0163.

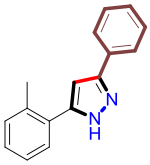
13. 5-(4-Bromophenyl)-3-(thiophen-2-yl)-1H-pyrazole (3am)



Yellow solid; **^{1}H-NMR ($CDCl_3$ + DMSO, 300 MHz):** δ 13.27 (bs, 1H), 7.72-7.69 (m, 2H), 7.55-7.52 (m, 2H), 7.46-7.31 (m, 2H), 7.18-7.04 (m, 1H), 6.83-6.81 (m, 1H); **^{13}C-NMR ($CDCl_3$ + DMSO, 75 MHz)**: δ 133.8, 130.4, 128.7, 127.8, 126.3, 126.1, 125.8, 123.4, 122.5, 120.0, 98.3.

HRMS (ESI +): $(M+H)^+$ calcd. For $C_{13}H_9BrN_2S$: 304.9748, 306.9728; found: 304.9748, 306.9730.

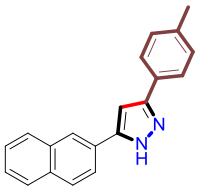
14. 3-Phenyl-5-(o-tolyl)-1H-pyrazole (3an)



Yellow solid; **^{1}H-NMR (DMSO, 300 MHz):** δ 7.68-7.65 (m, 2H), 7.36-7.33 (m, 1H), 7.25-7.20 (m, 2H), 7.13-7.05 (m, 4H), 6.73 (s, 1H), 2.26 (s, 3H) (-NH is missing); **^{13}C-NMR (DMSO, 75 MHz)**: δ 147.6, 146.6, 135.6, 131.4, 131.0, 129.0, 128.7, 128.7, 128.1, 127.9, 126.1, 125.4, 102.6, 20.9.

HRMS (ESI +): $(M+H)^+$ calcd. For $C_{16}H_{15}N_2$: 235.1235; Found: 235.1230.

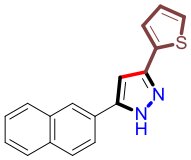
15. 5-(Naphthalen-2-yl)-3-(p-tolyl)-1H-pyrazole (3ao)



Yellow solid; **^{1}H-NMR (DMSO, 300 MHz)**; δ 13.34 (bs, 1H), 8.35-8.33 (m, 1H), 7.99-7.92 (m, 3H), 7.73 (s, 2H), 7.48-7.46 (m, 3H), 7.23 (s, 2H), 2.27 (s, 3H); **^{13}C-NMR (DMSO, 75 MHz)**: δ 137.3, 137.3, 133.3, 132.6, 129.5, 128.4, 128.0, 127.7, 126.6, 126.1, 125.1, 123.8, 123.5, 99.7, 20.73.

HRMS (ESI +): $(M+H)^+$ calcd. For $C_{20}H_{16}N_2$: 285.1392; Found: 285.1384.

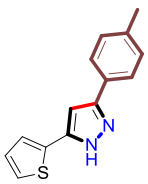
16. 5-(Naphthalen-2-yl)-3-(thiophen-2-yl)-1H-pyrazole (3ap)



Yellow solid; **^{1}H-NMR ($CDCl_3$, 300 MHz)**; δ 13.44 (bs, 1H), 8.32 (s, 1H), 7.94-7.89 (m, 4H), 7.48-7.46 (m, 4H), 7.13-7.09 (m, 1H); **^{13}C-NMR ($CDCl_3$, 75 MHz)**: δ 133.2, 132.7, 128.6, 128.1, 127.8, 126.9, 126.8, 126.5, 126.5, 126.4, 126.4, 124.0, 123.8, 123.7, 100.1.

HRMS (ESI +): $(M+H)^+$ calcd. For $C_{17}H_{12}N_2S$: 277.0799; Found: 277.0792.

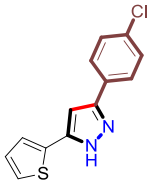
17. 5-(Thiophen-2-yl)-3-(p-tolyl)-1H-pyrazole (3aq)



Yellow solid; **^{1}H-NMR ($CDCl_3$, 300 MHz)**; δ 13.21 (bs, 1H), 7.77-7.68 (m, 2H), 7.49-7.43 (m, 1H), 7.28-7.11 (m, 1H), 6.98 (s, 1H), 2.33 (s, 3H); **^{13}C-NMR ($CDCl_3$, 75 MHz)**: δ 140.9, 137.6, 129.7, 129.6, 129.4, 128.4, 127.8, 125.6, 125.2, 123.9, 99.2, 20.8.

HRMS (ESI +): ($(M+H)^+$ calcd. For $C_{14}H_{12}N_2S$: 241.0799; Found: 241.0790.

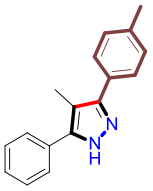
18. 3-(4-Chlorophenyl)-5-(thiophen-2-yl)-1H-pyrazole (3ar)



Yellow solid; **^{1}H-NMR (DMSO, 300 MHz):** δ 13.36 (bs, 1H), 7.83-7.80 (m, 2H), 7.46 (bs, 3H), 7.32-7.29 (m, 2H), 7.11-7.09 (m, 1H), 7.05 (s, 1H); **^{13}C-NMR (DMSO, 75 MHz)**: δ 130.8, 129.7, 129.1, 129.0, 128.9, 128.7, 128.0, 127.9, 127.0, 100.0.

HRMS (ESI +): ($(M+H)^+$ calcd. For $C_{13}H_{10}ClN_2S$: 261.0253; Found: 261.0259.

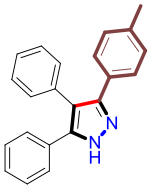
19. 4-Methyl-5-phenyl-3-(p-tolyl)-1H-pyrazole (3as)



Yellow solid; **^{1}H-NMR (DMSO, 300 MHz)**; δ 12.96 (bs, 1H), 7.59-7.56 (m, 2H), 7.48-7.40 (m, 4H), 7.33-7.28 (m, 1H), 7.24-7.22 (m, 2H), 2.29 (s, 3H), 2.20 (s, 3H); **^{13}C-NMR (DMSO, 75 MHz)**: δ 141.3, 136.9, 129.4, 129.3, 129.0, 128.7, 128.6, 128.5, 127.4, 127.3, 109.3, 20.7, 10.0.

HRMS (ESI +): ($(M+H^+)$ calcd. For $C_{17}H_{16}N_2$: 249.1392; Found: 249.1390.

20. 4,5-Diphenyl-3-(p-tolyl)-1H-pyrazole (3at)



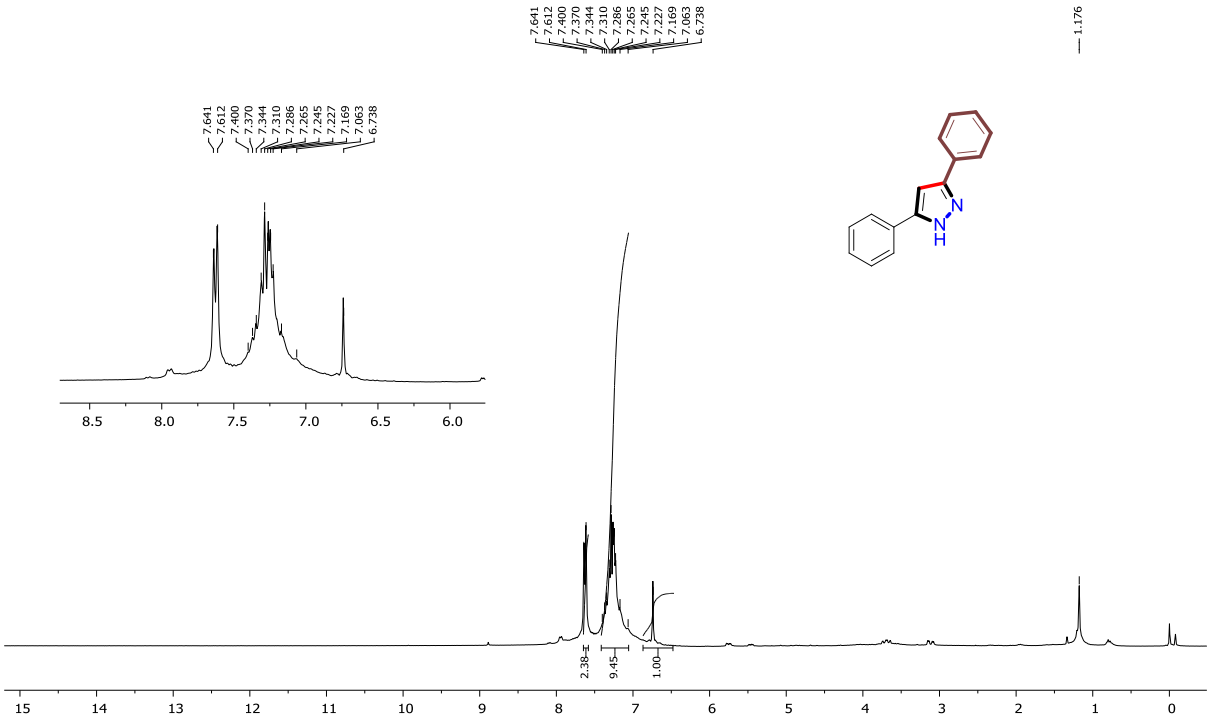
Yellow solid; **^{1}H-NMR (DMSO, 300 MHz):** δ 12.68 (s, 1H), 8.47-8.42 (m, 1H), 8.06-7.05 (m, 13H), 2.32 (s, 3H); **^{13}C-NMR (DMSO, 75 MHz)**: δ 161.8, 155.2, 136.0, 134.2, 131.5, 130.7, 130.4, 129.2, 128.8, 128.7, 127.5, 127.4, 126.3, 126.0, 116.7, 20.7.

HRMS (ESI +): ($(M+H^+)$ calcd. For $C_{22}H_{19}N_2$: 311.1548; Found: 311.1539.

5. References

1. Zhang, G.; Zhao, Y.; Ge, H. *Angew. Chem., Int. Ed*. **2013**, *52*, 2559. (b) Zhang, G.-W.; Miao, J.-M.; Zhao, Y.; Ge, H.-B. *Angew. Chem., Int. Ed*. **2012**, *51*, 8318.
2. (a) Harigae, R.; Moriyama, K.; Togo, H. *J. Org. Chem*. **2014**, *79*, 2049.

6. Copies of ^{1}H and ^{13}C NMR spectra


7.641
7.612
7.400
7.370
7.344
7.310
7.286
7.265
7.245
7.227
7.169
7.063
6.738
1.176
2.38
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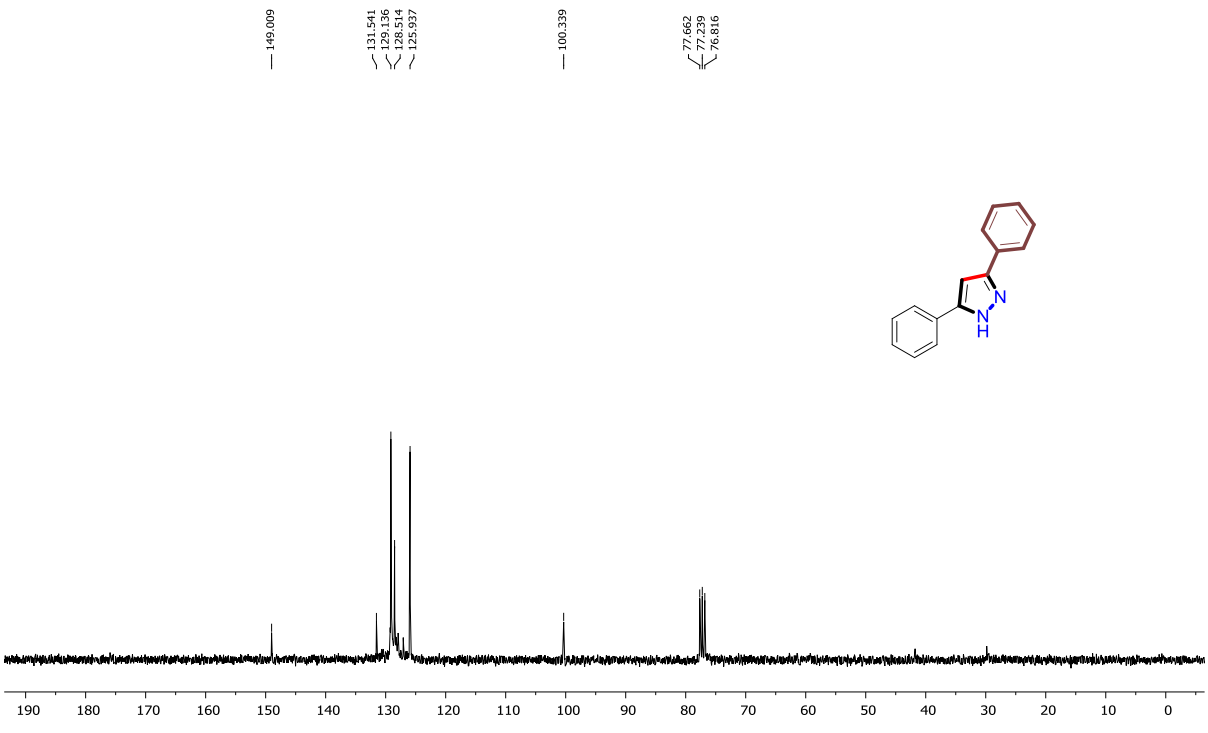
1.00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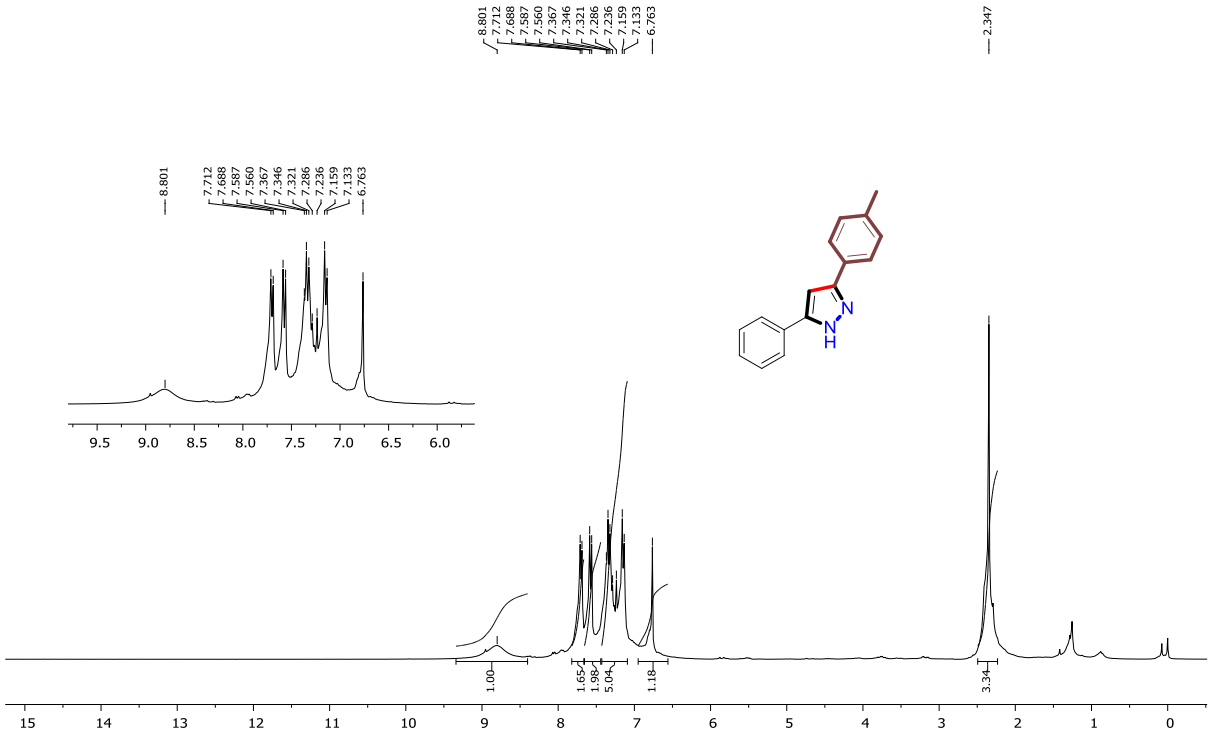
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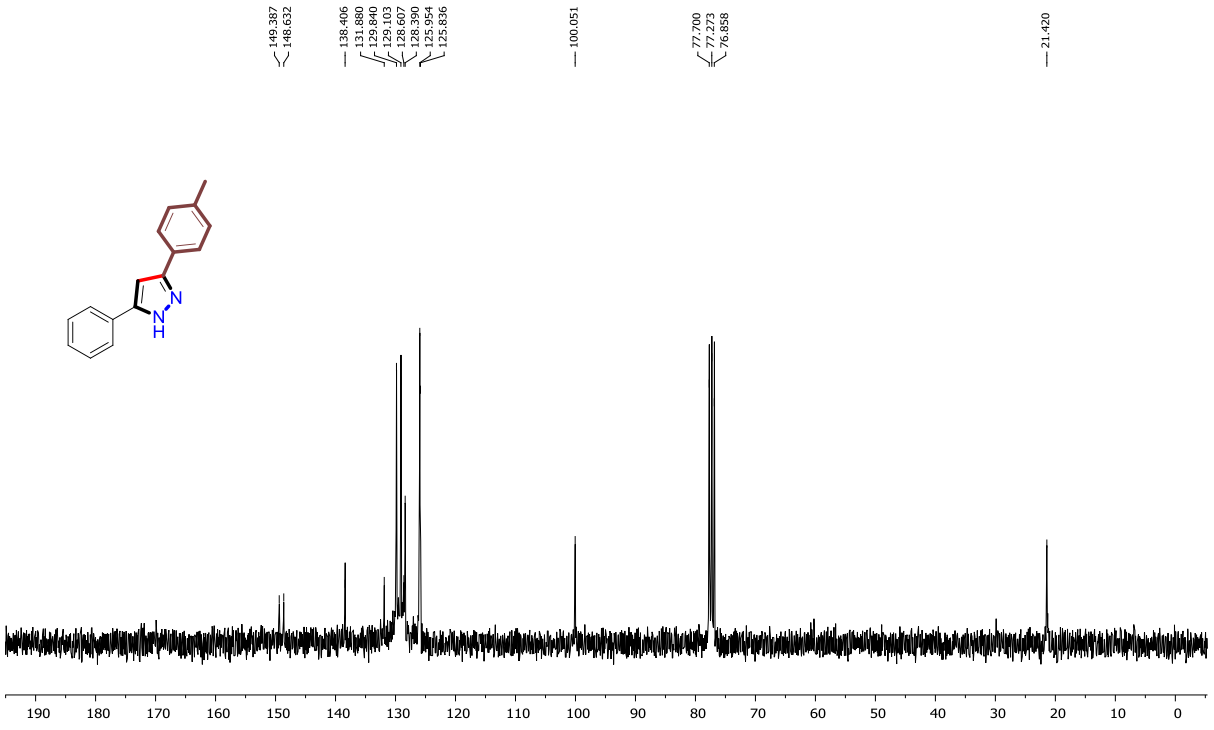
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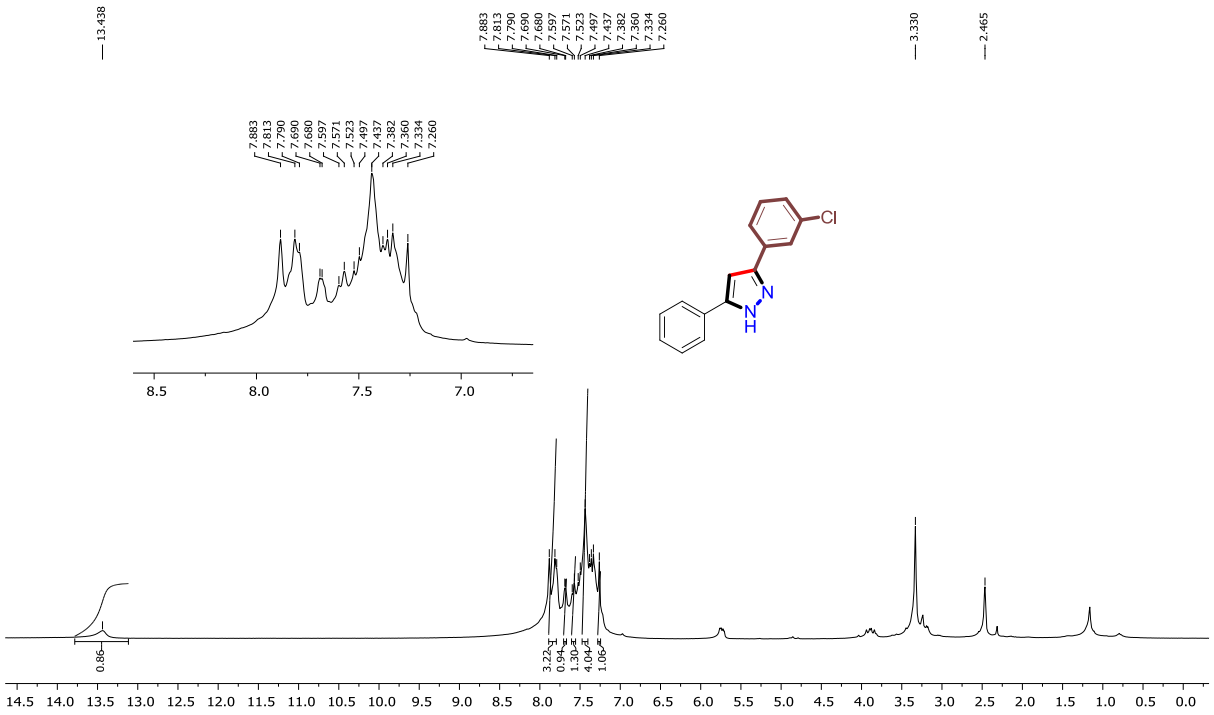
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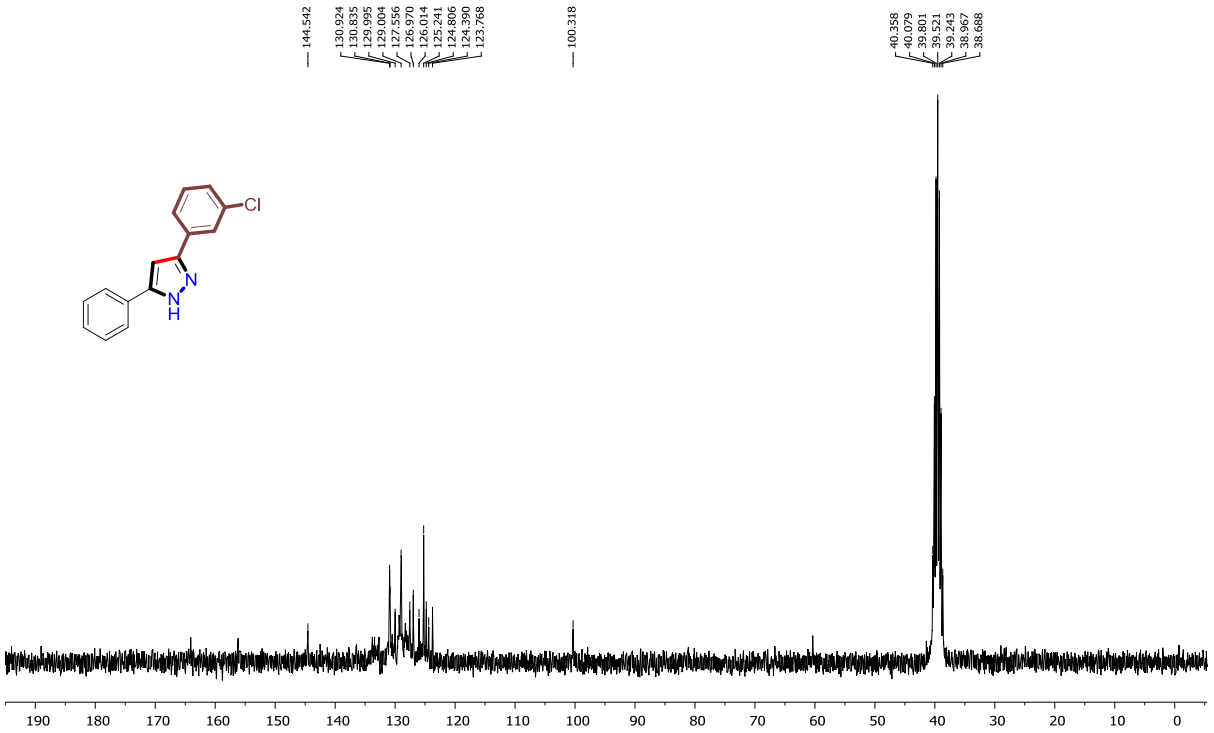
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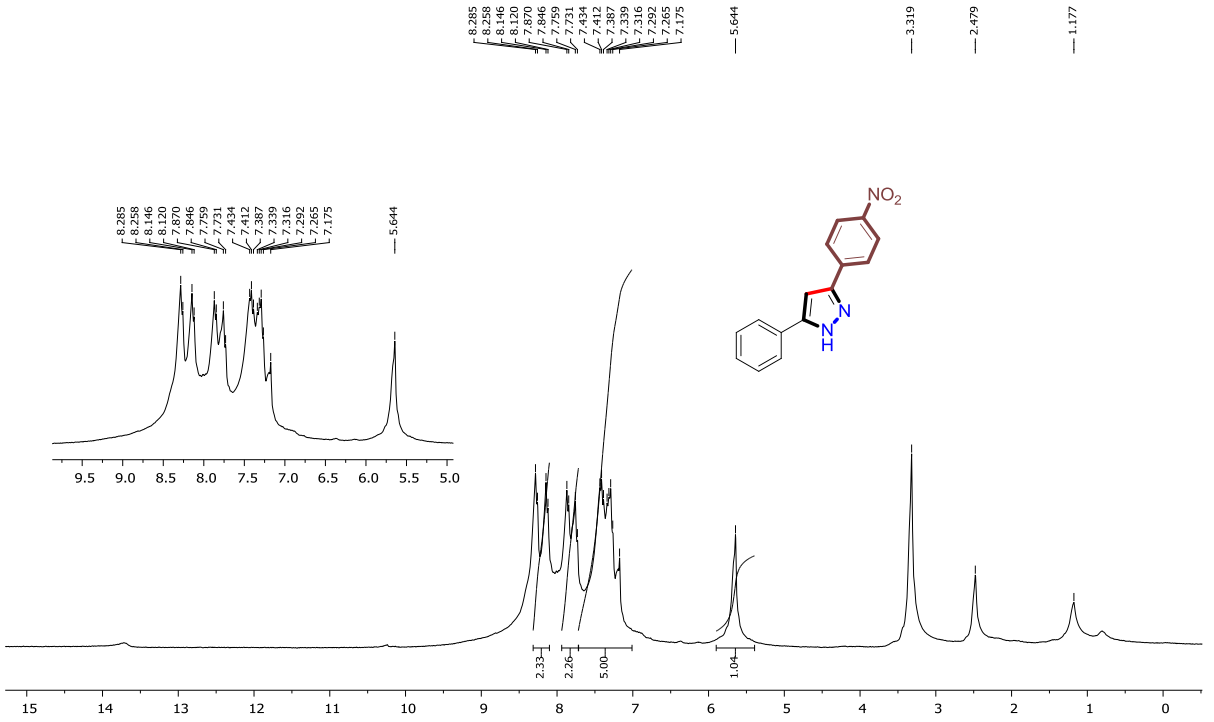
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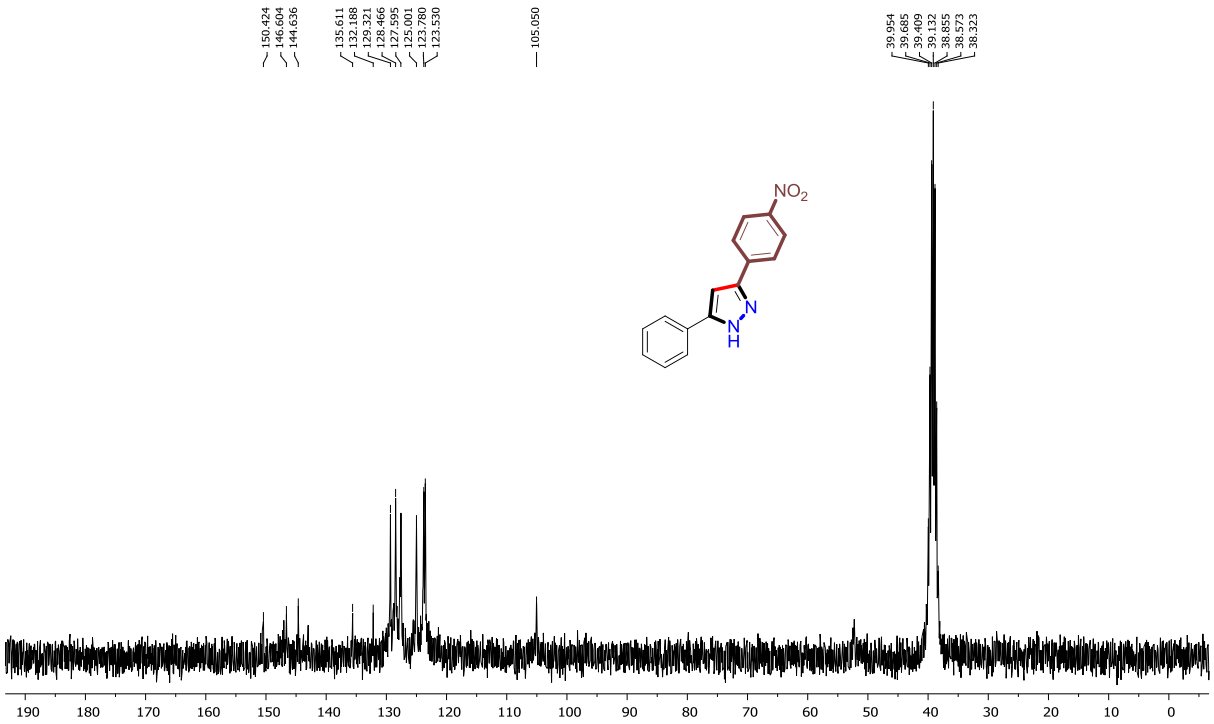
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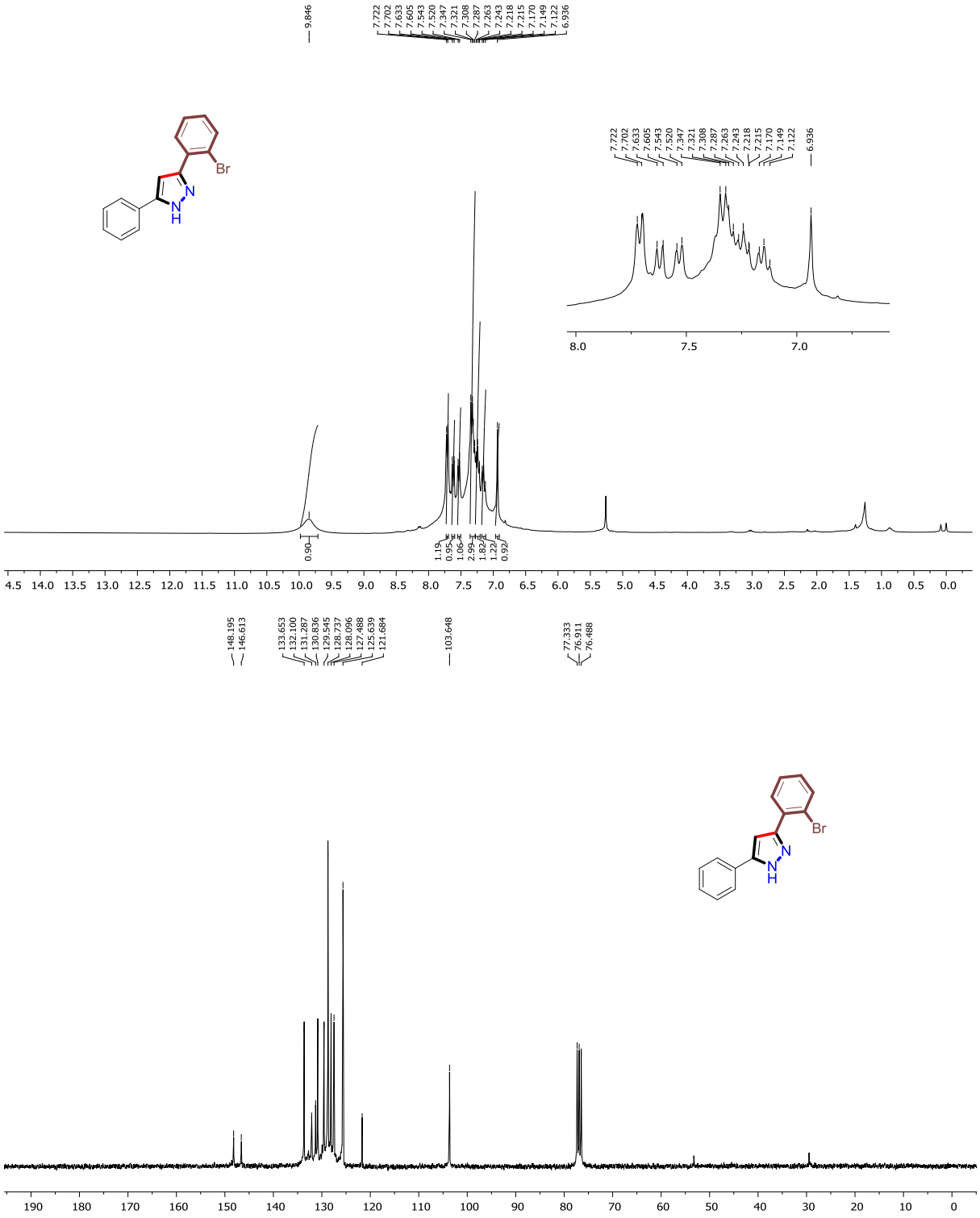
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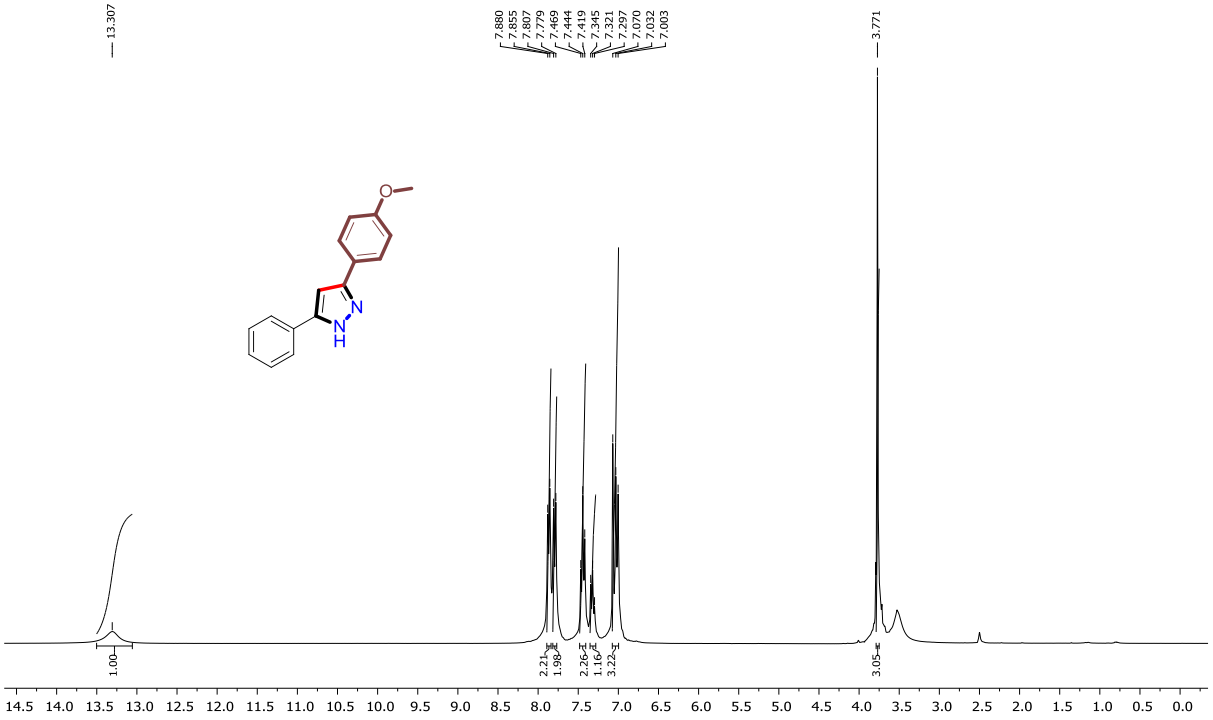
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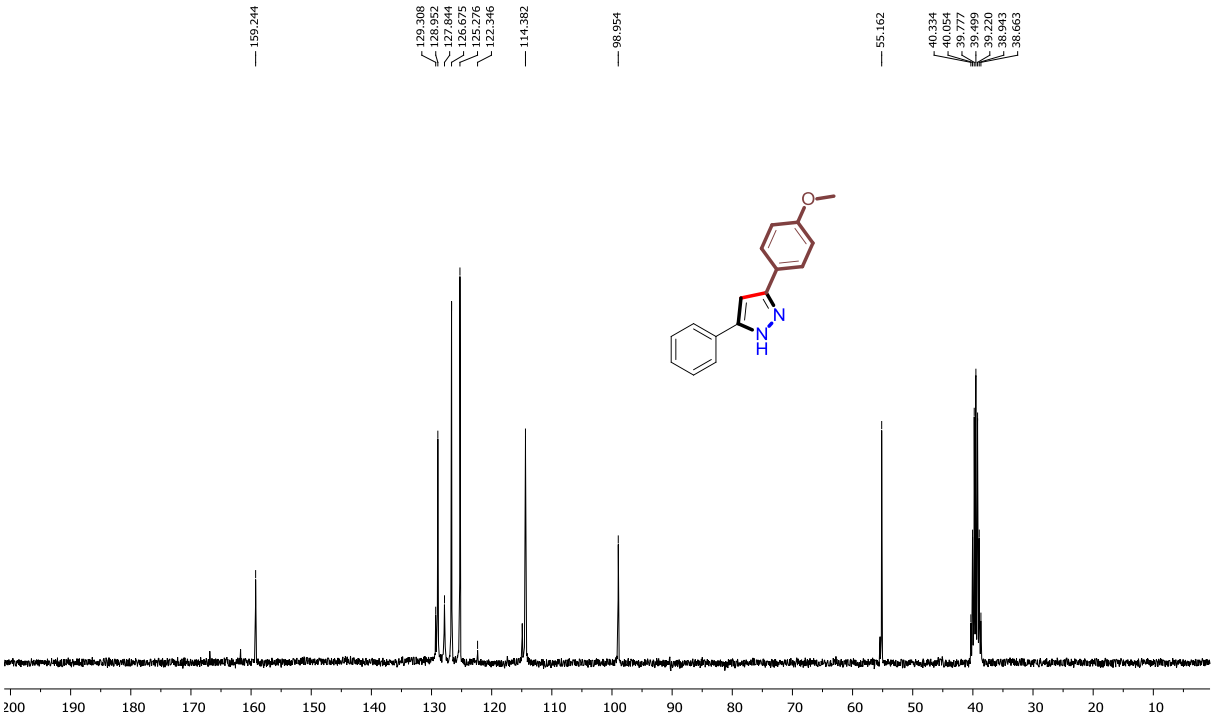
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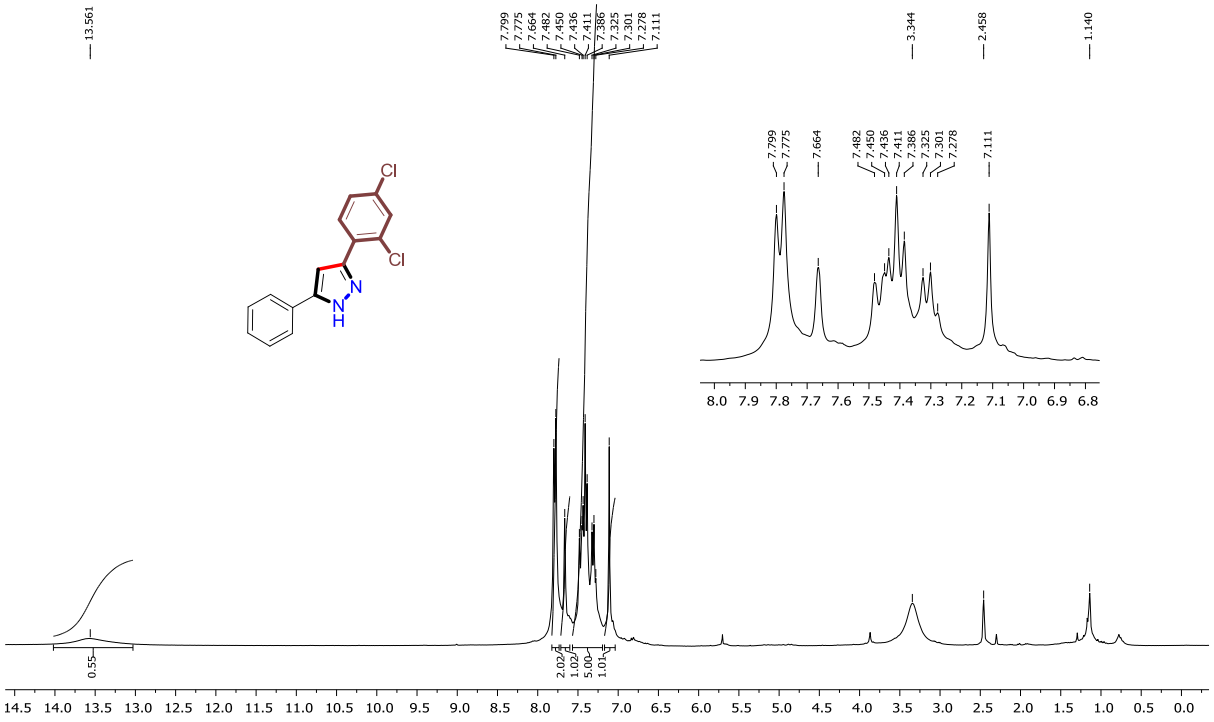
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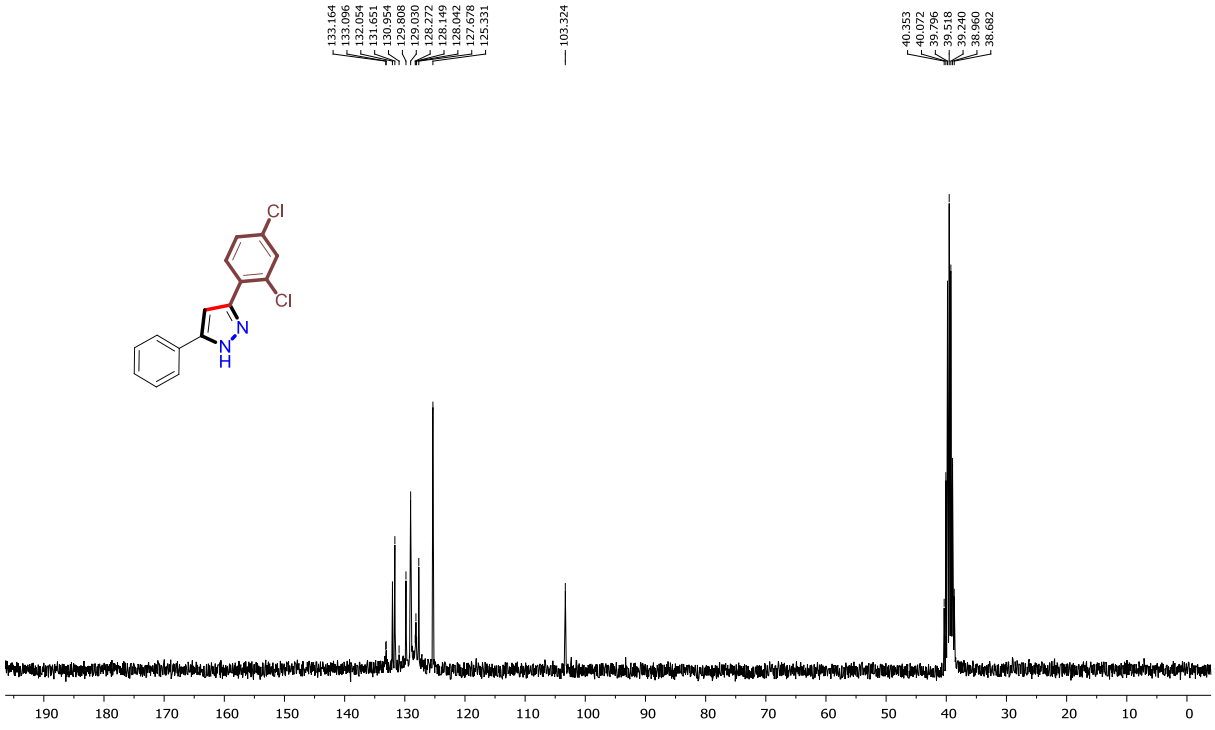
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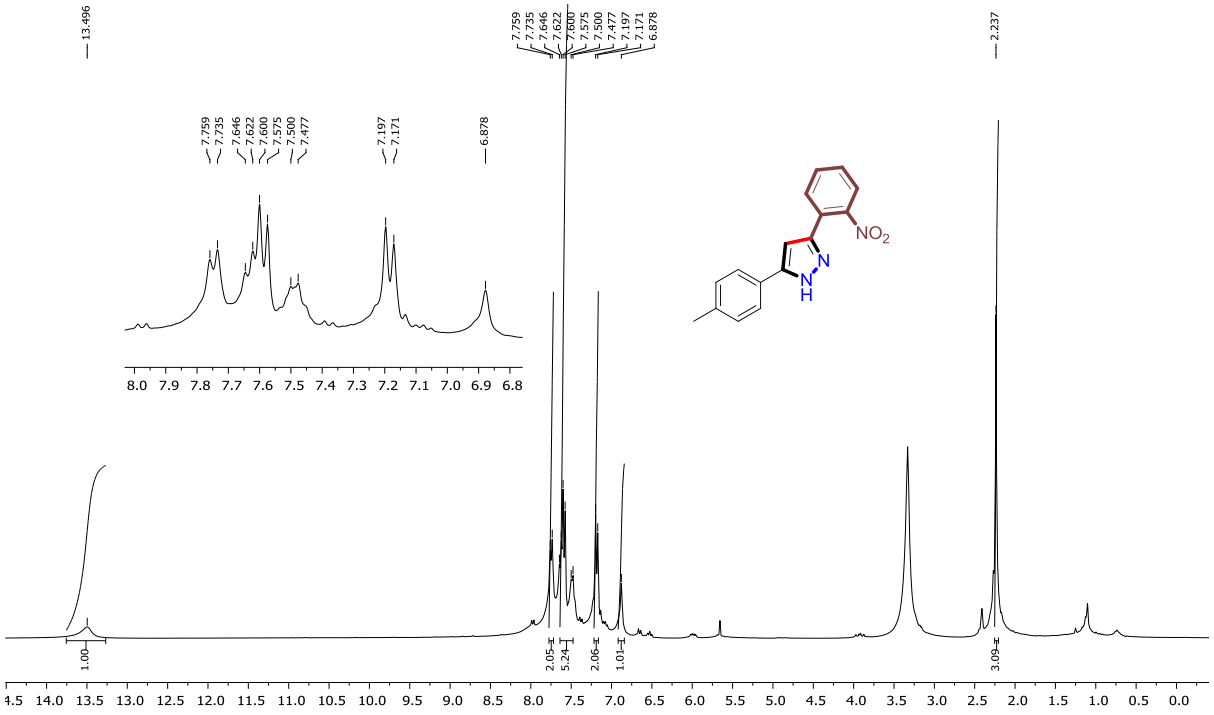
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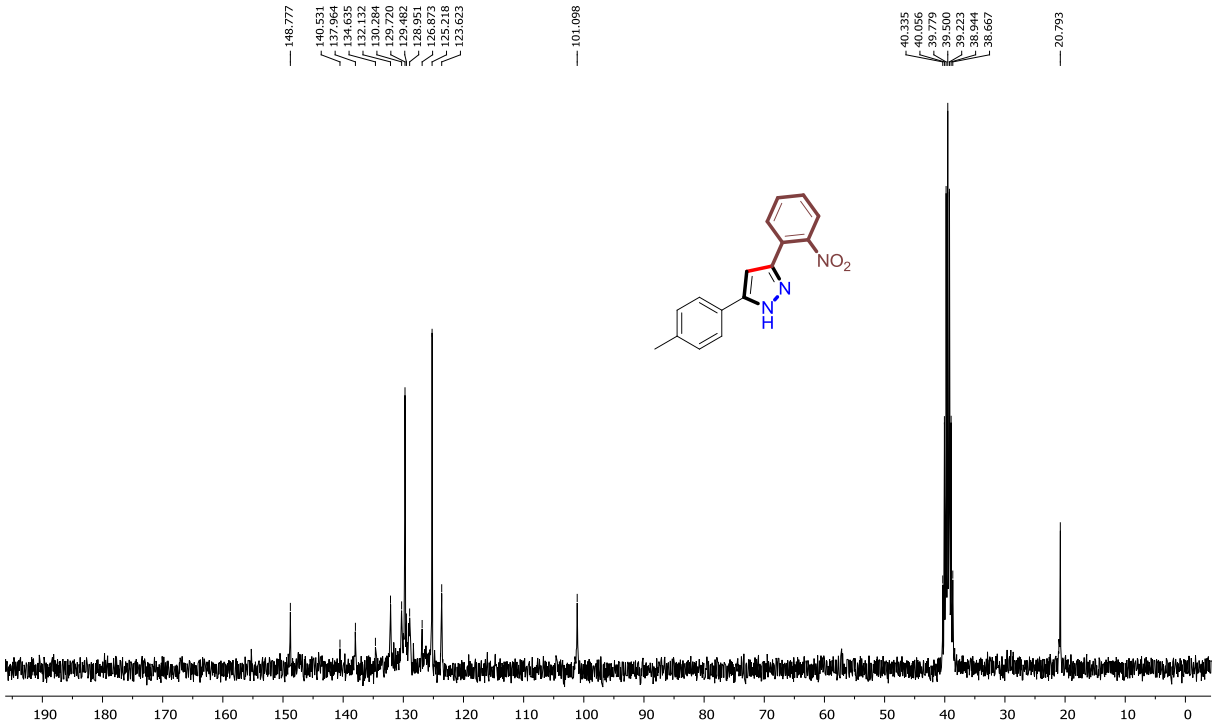
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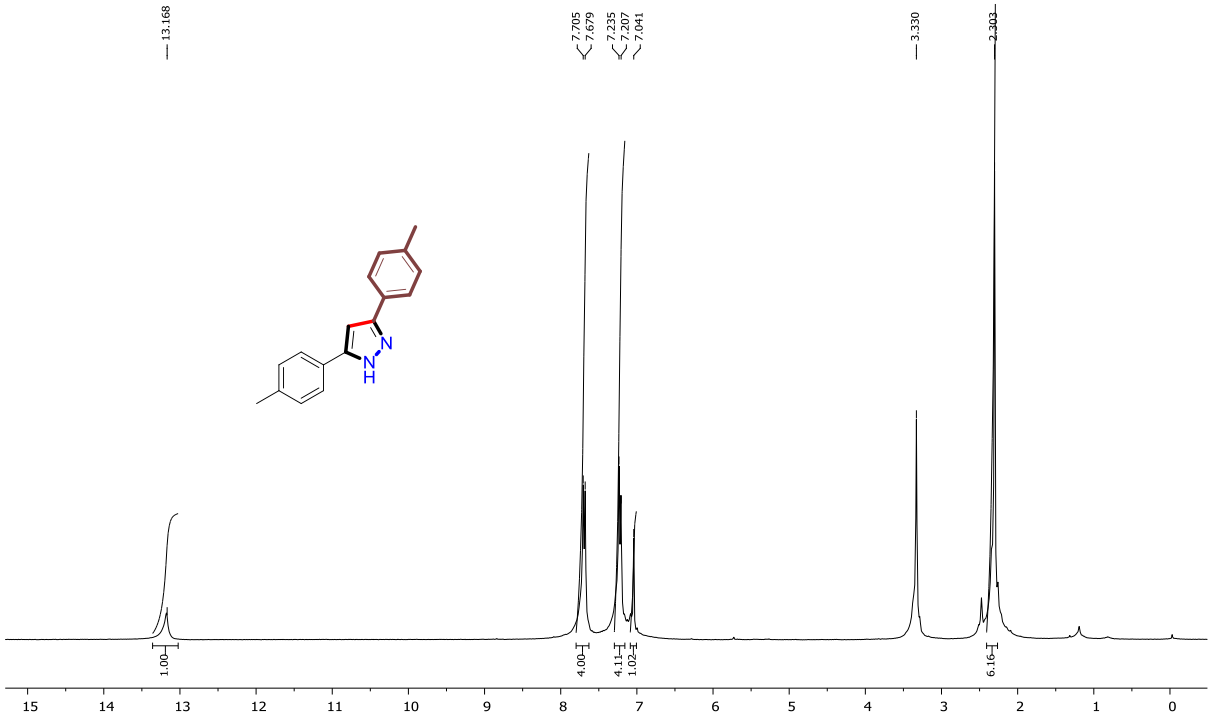
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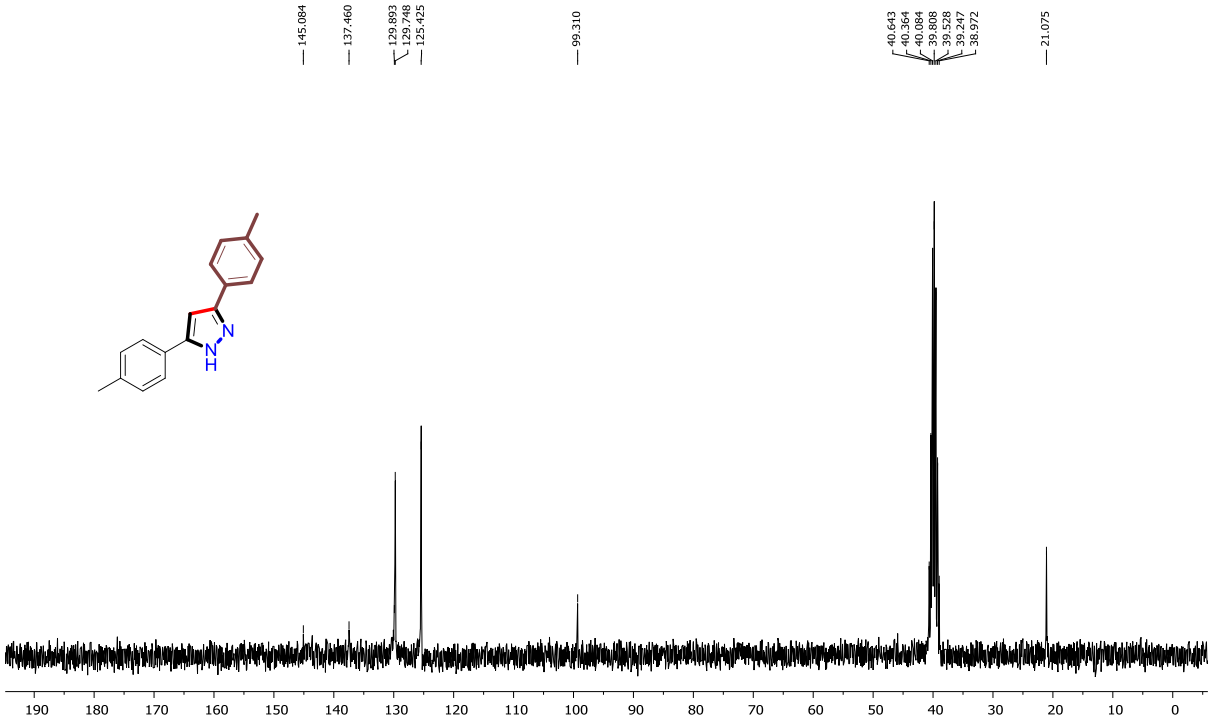
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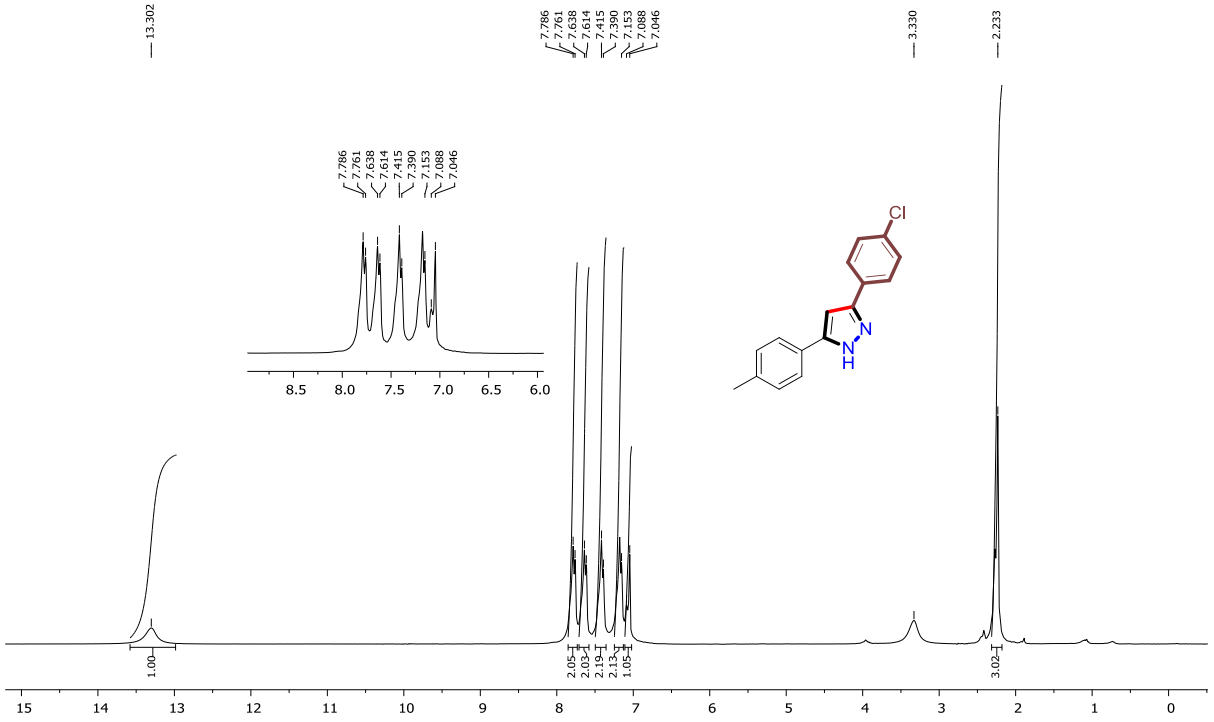
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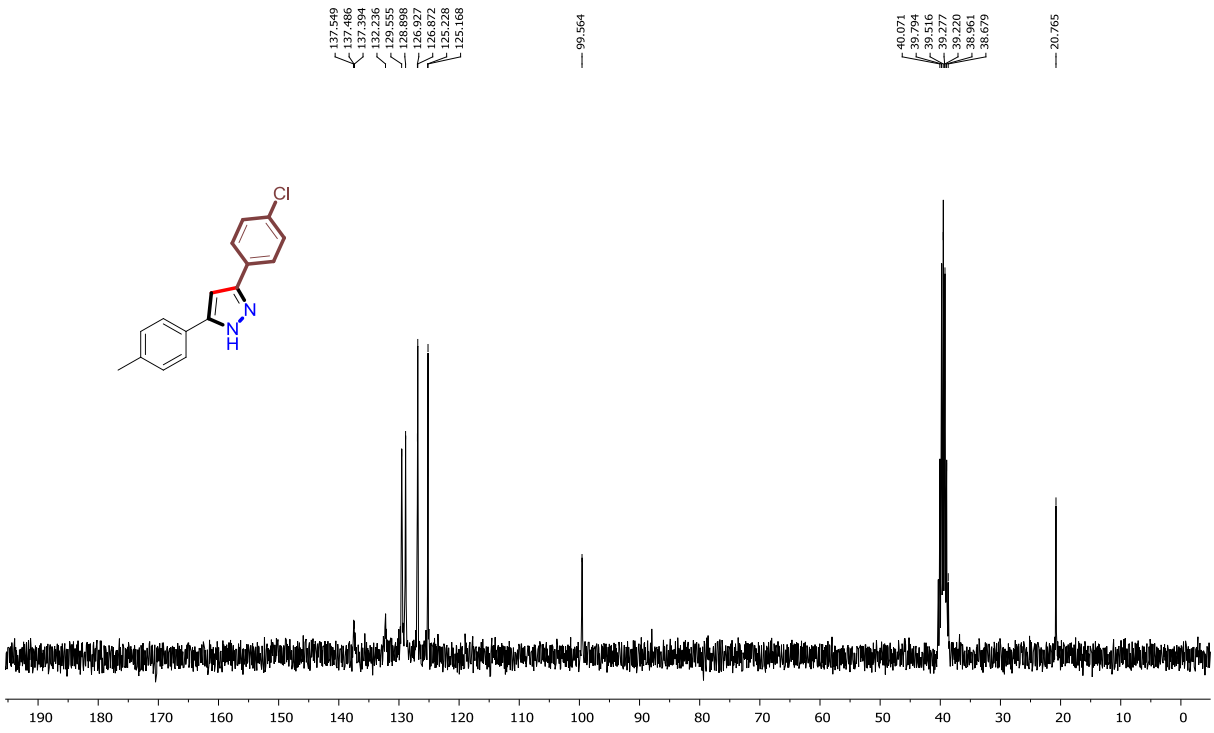
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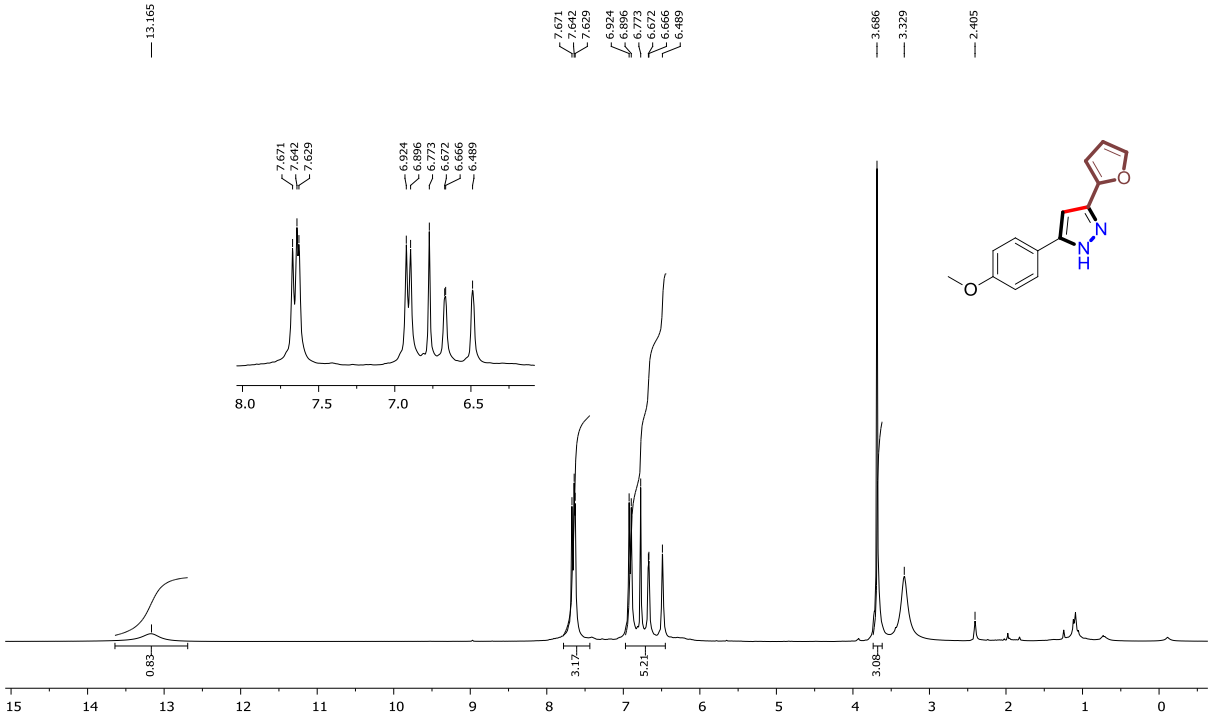
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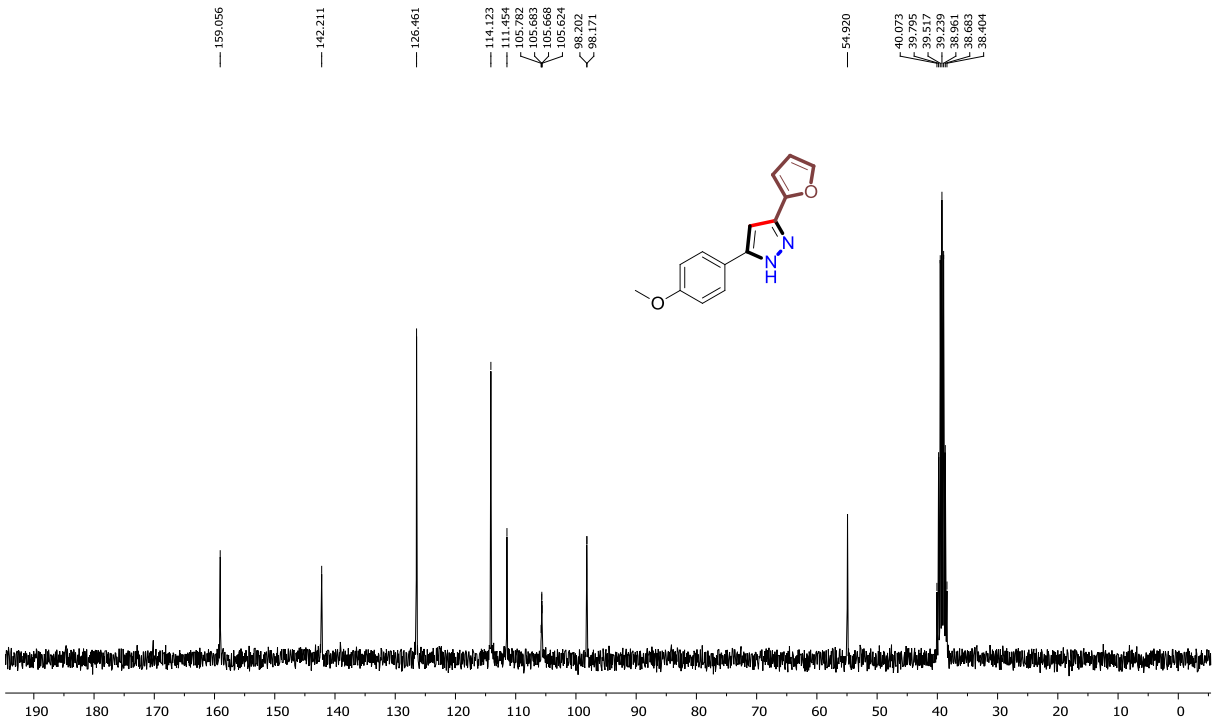
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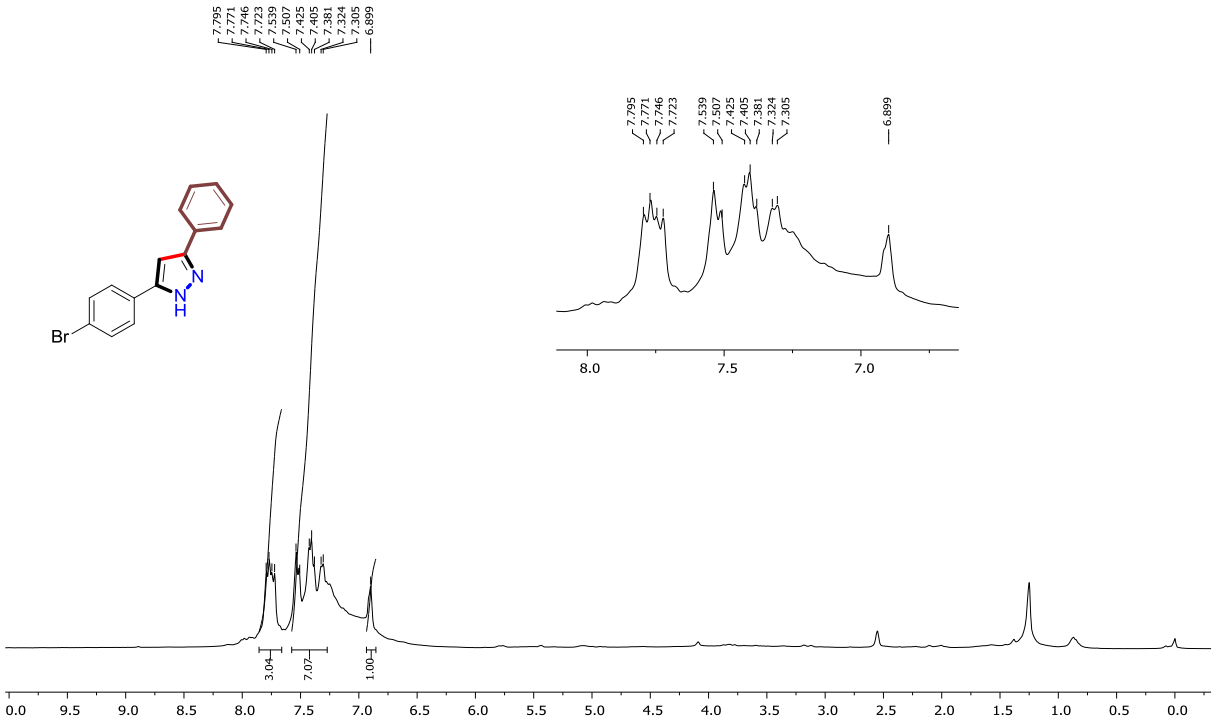
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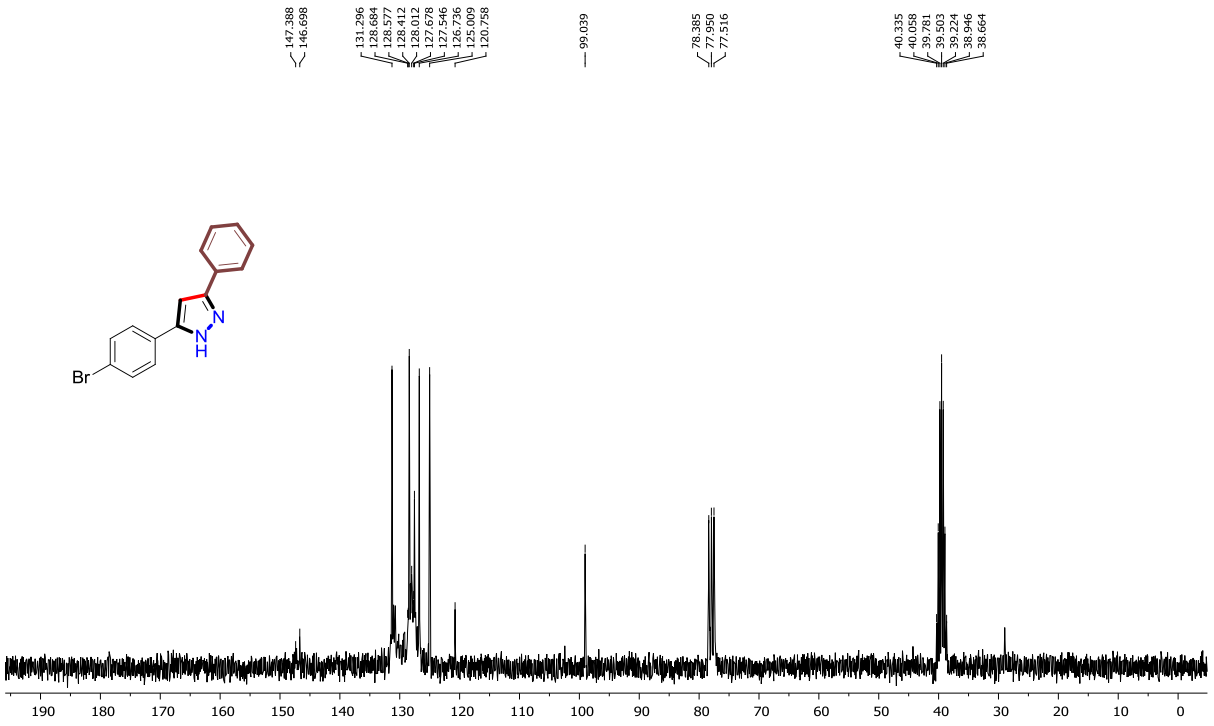
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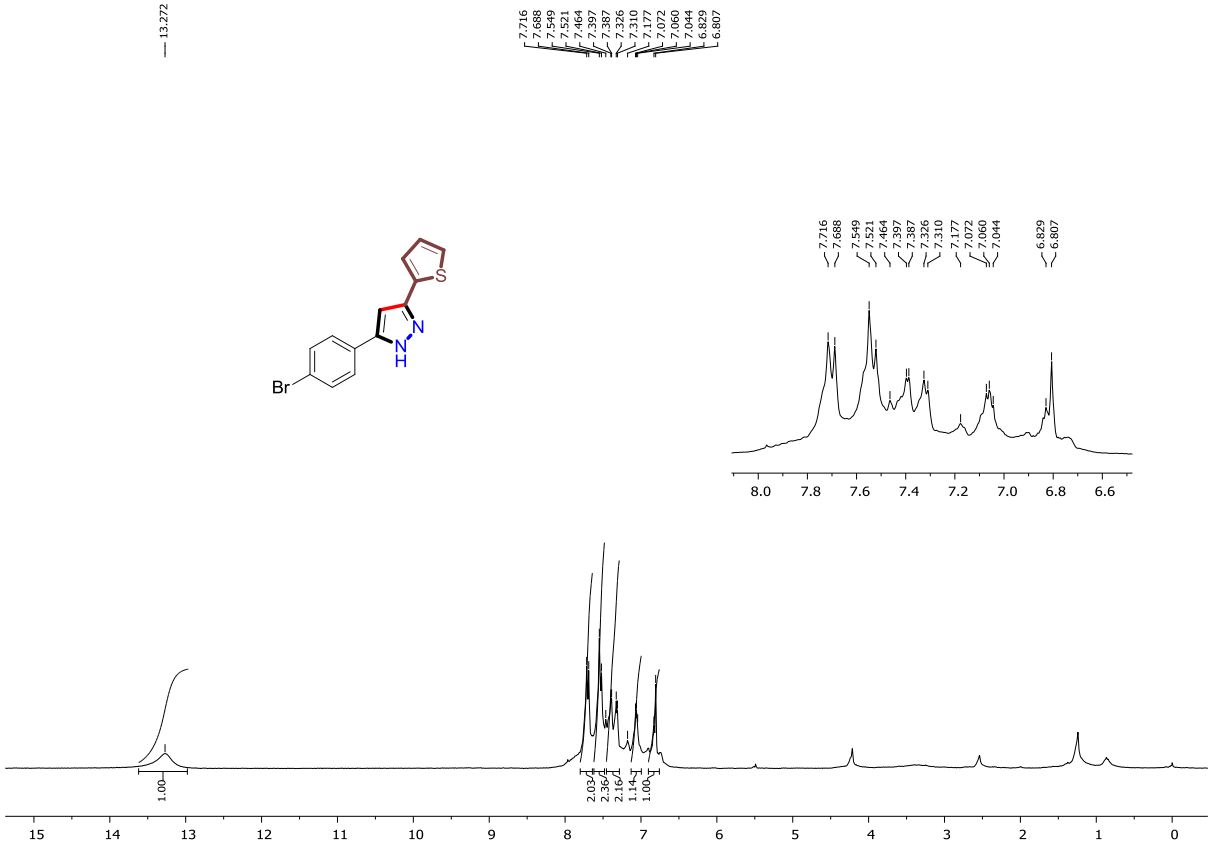
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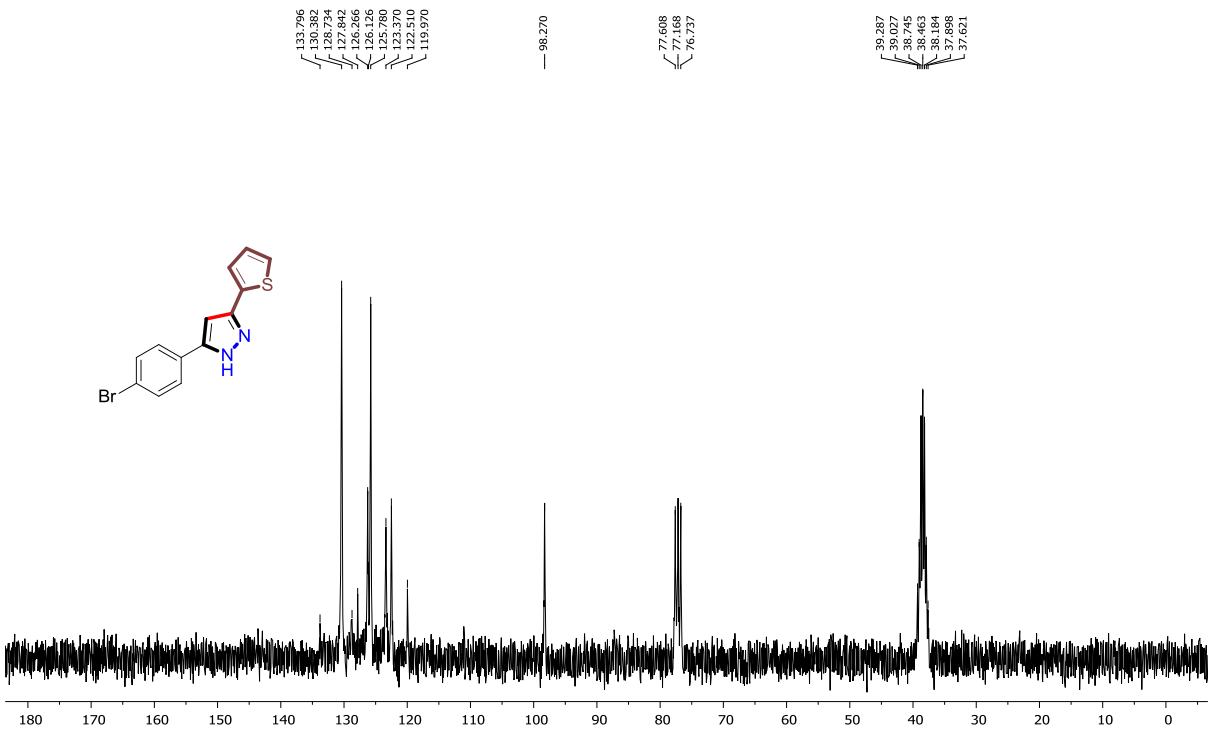
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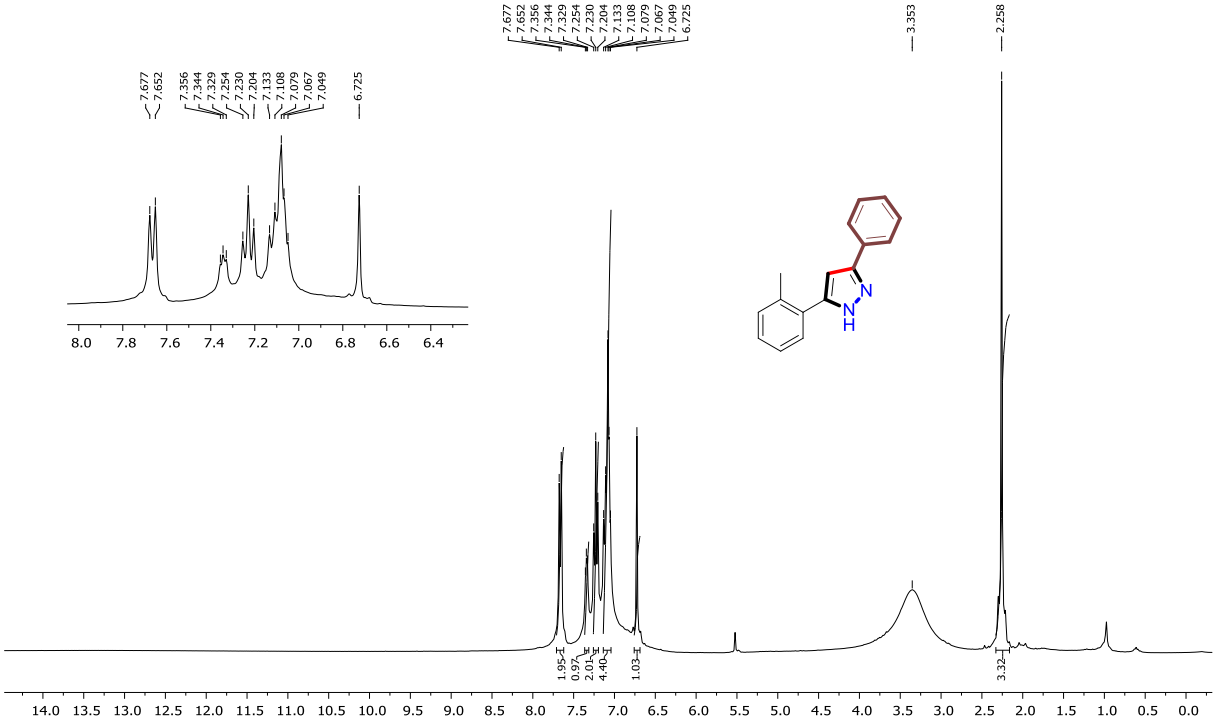
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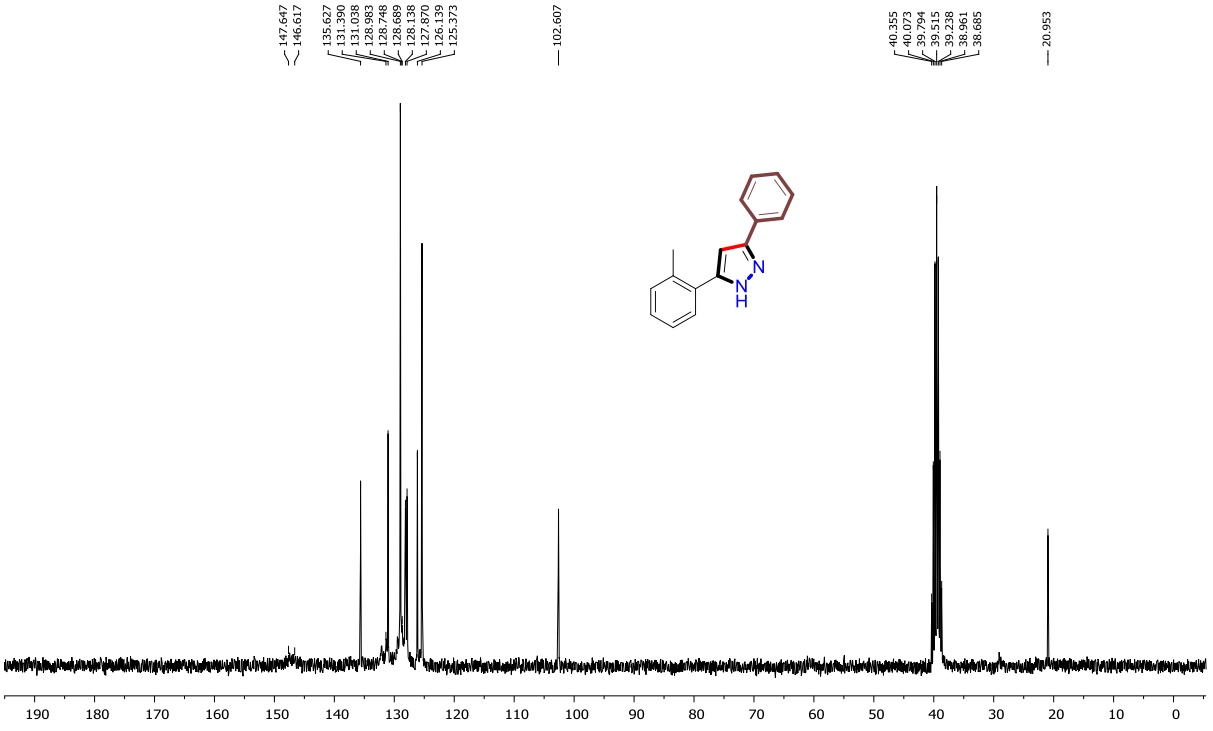
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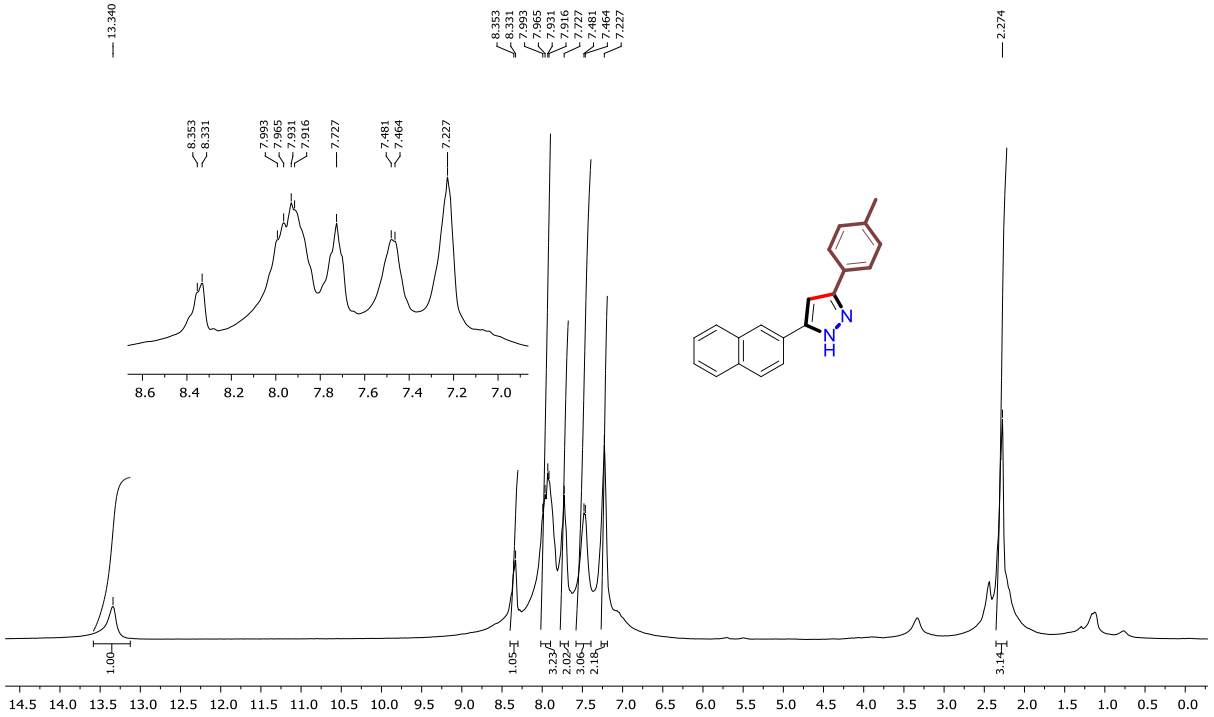
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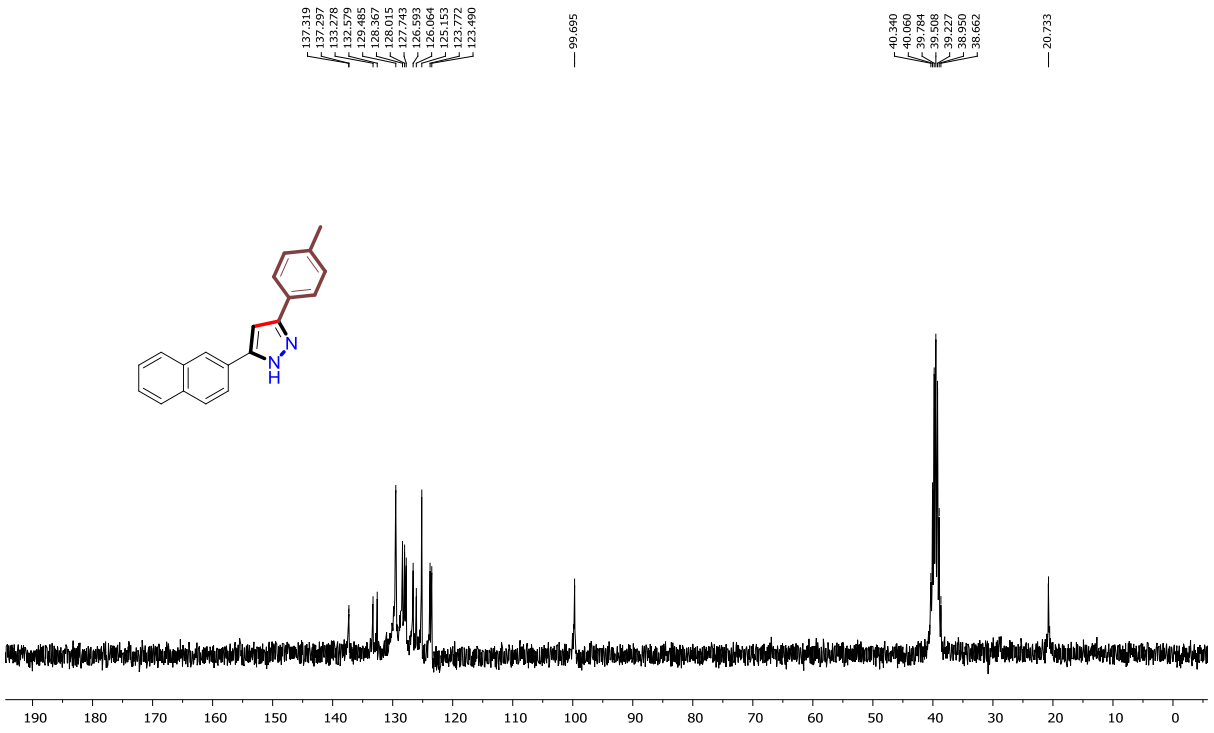
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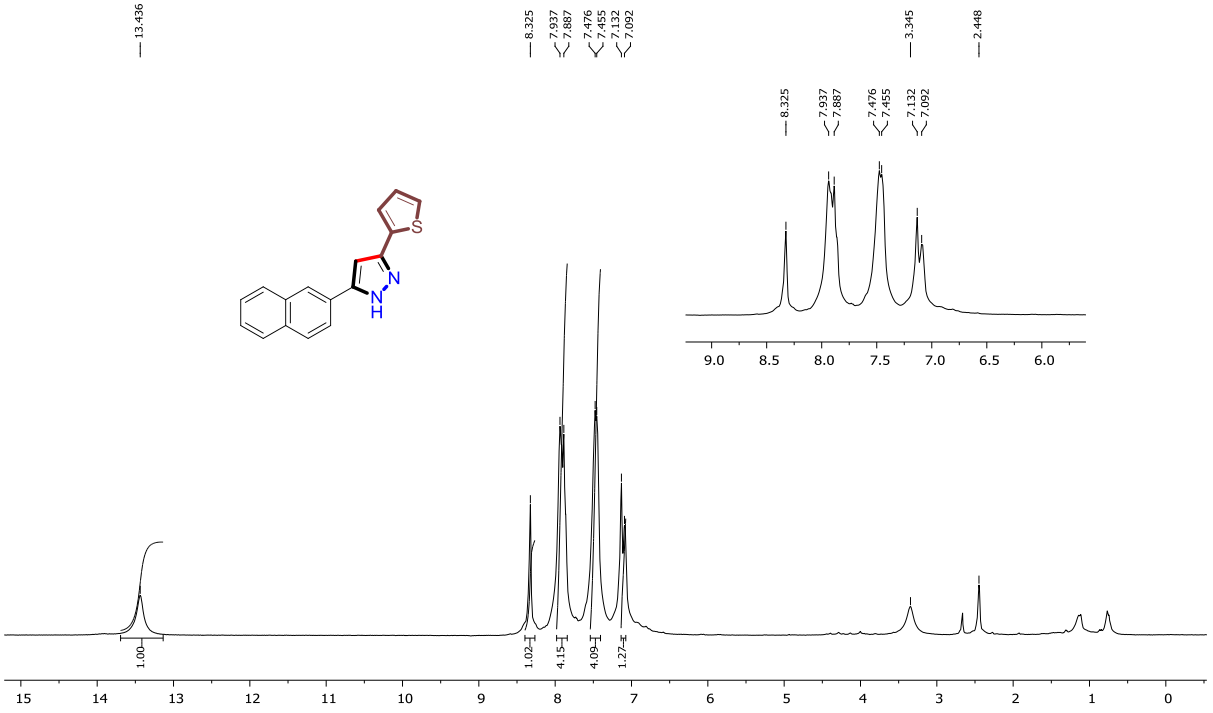
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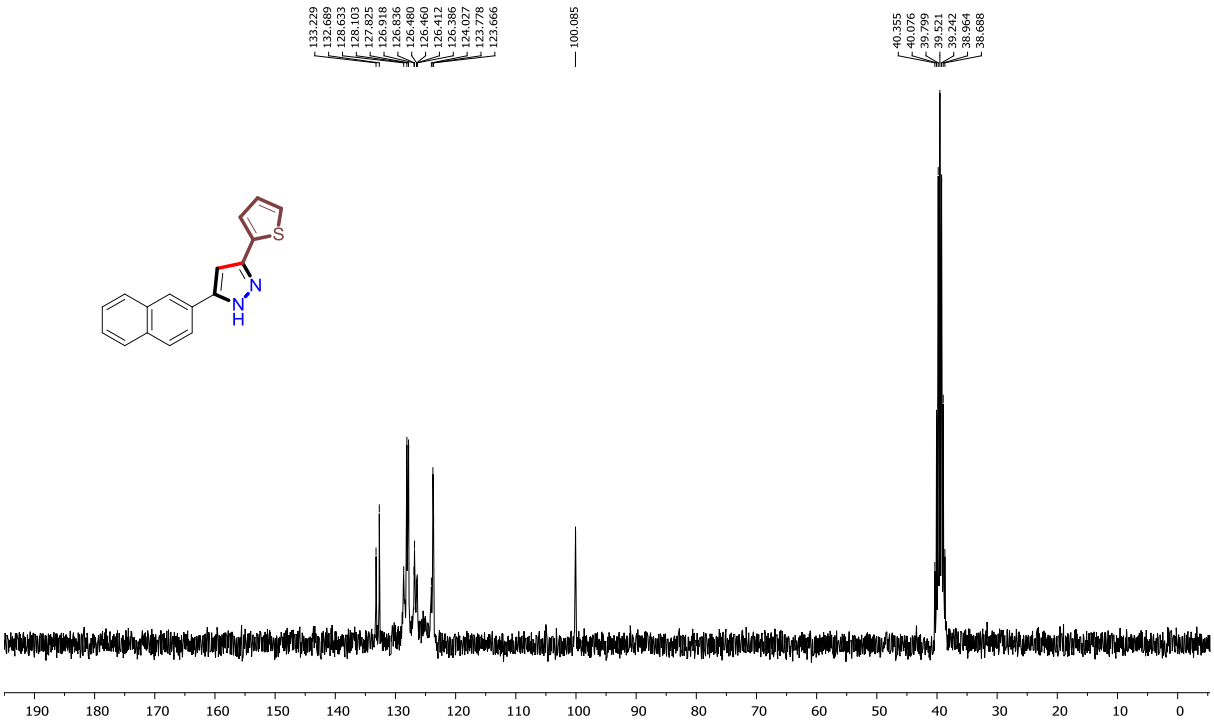
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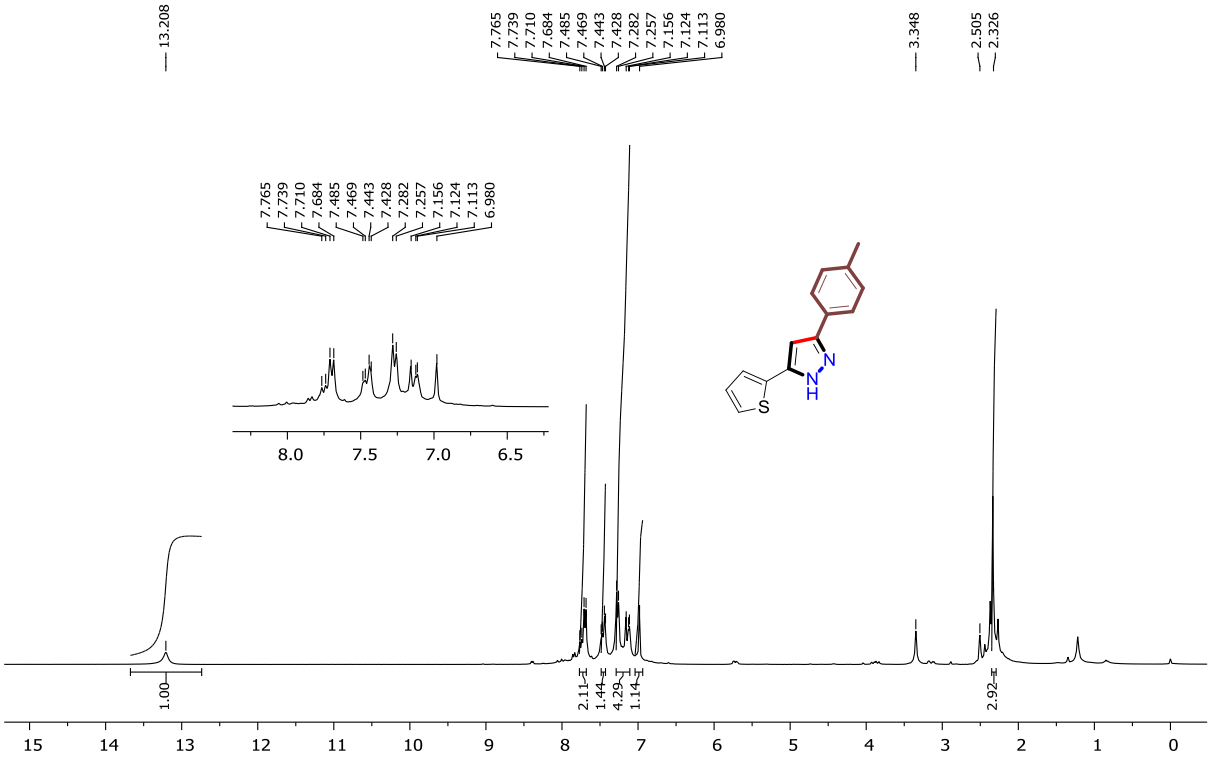
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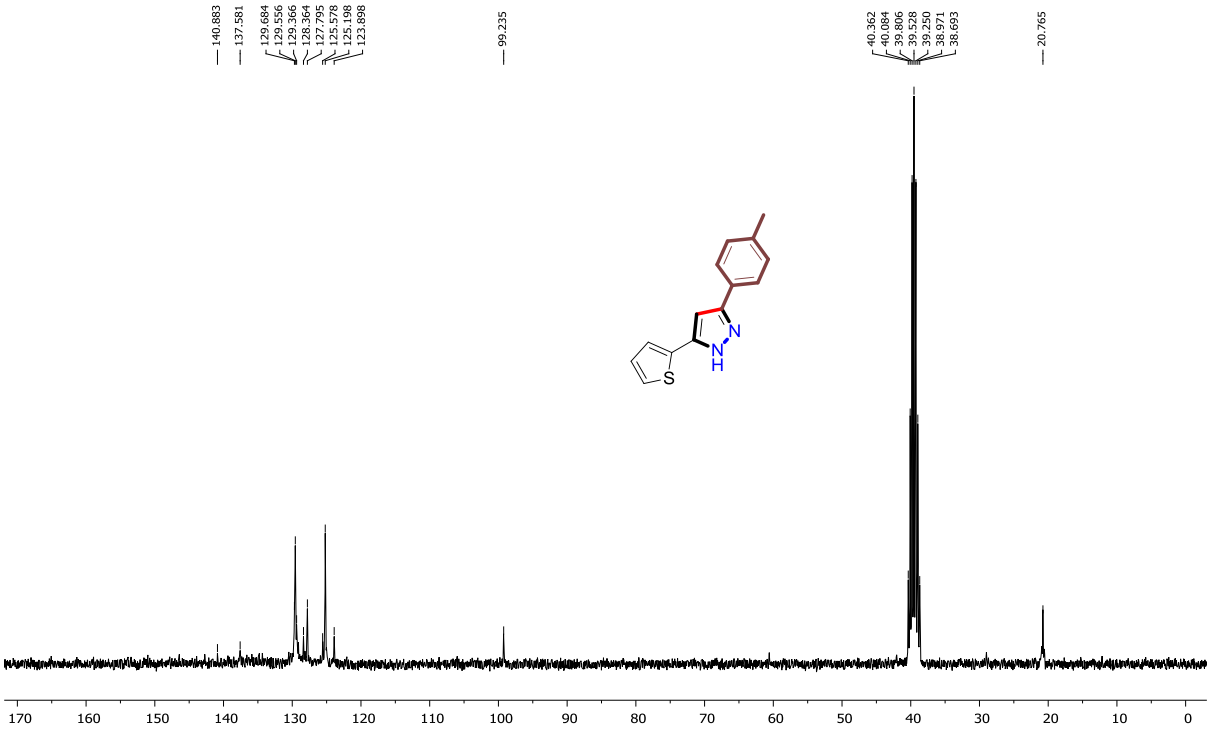
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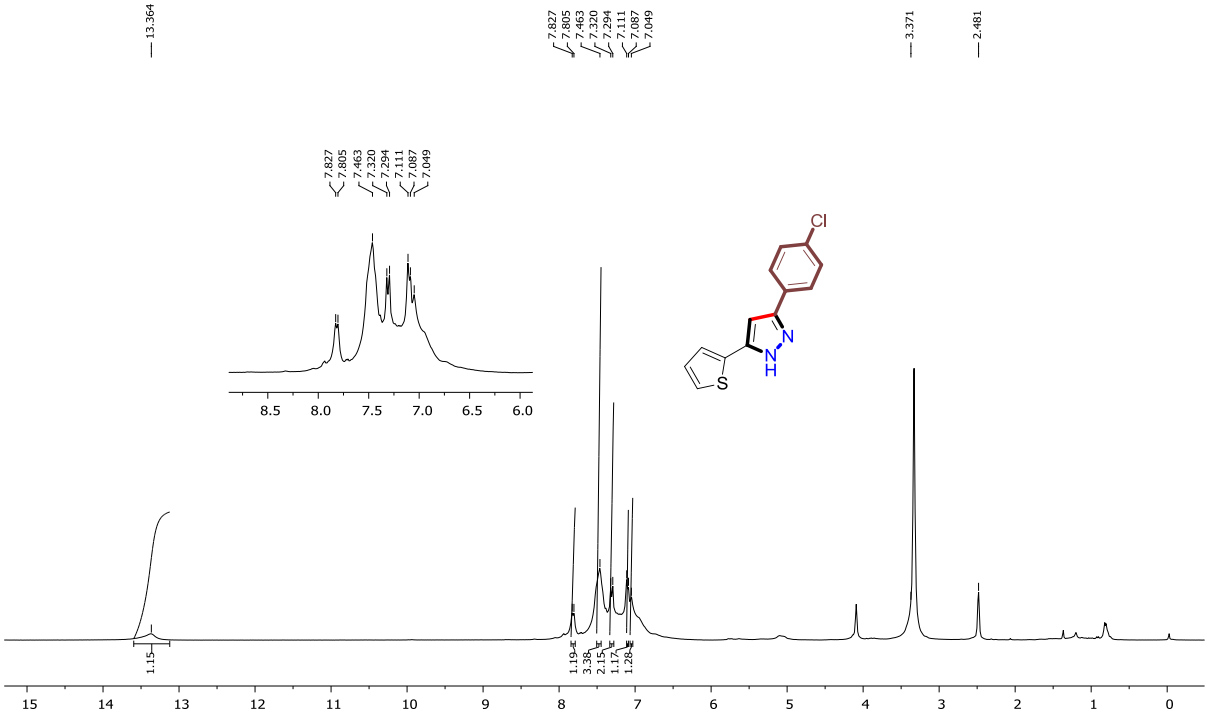
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H
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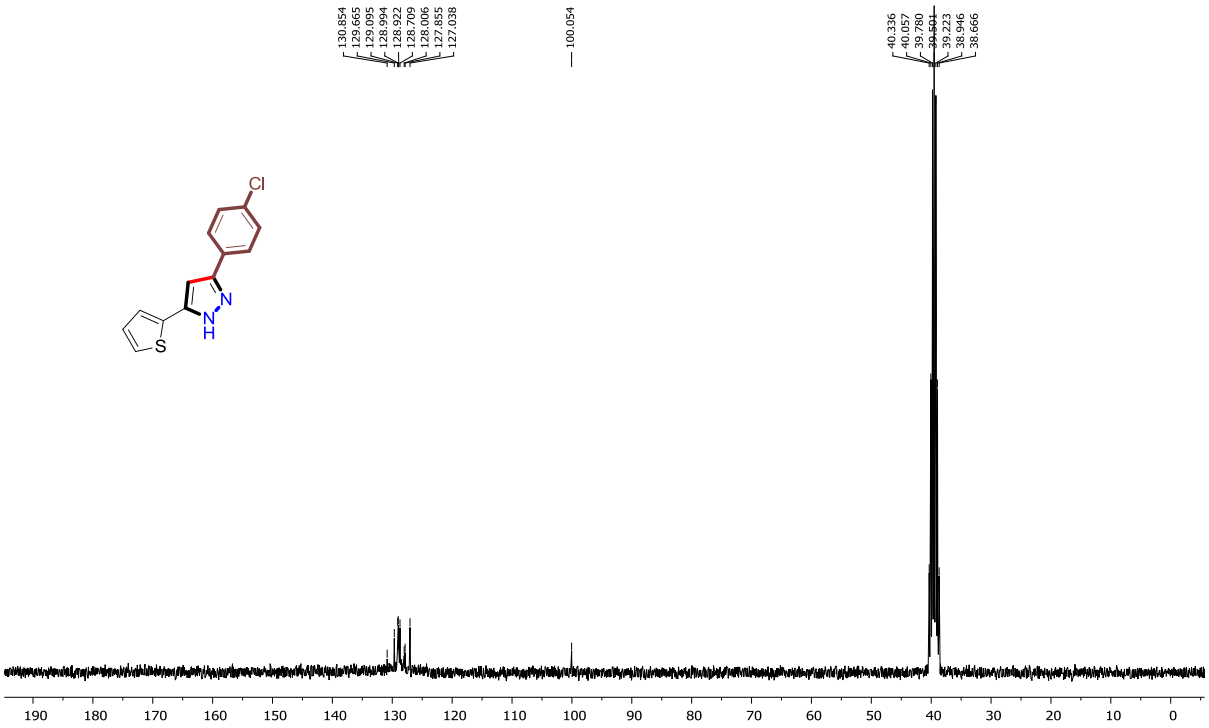
2.15
1.17
1.28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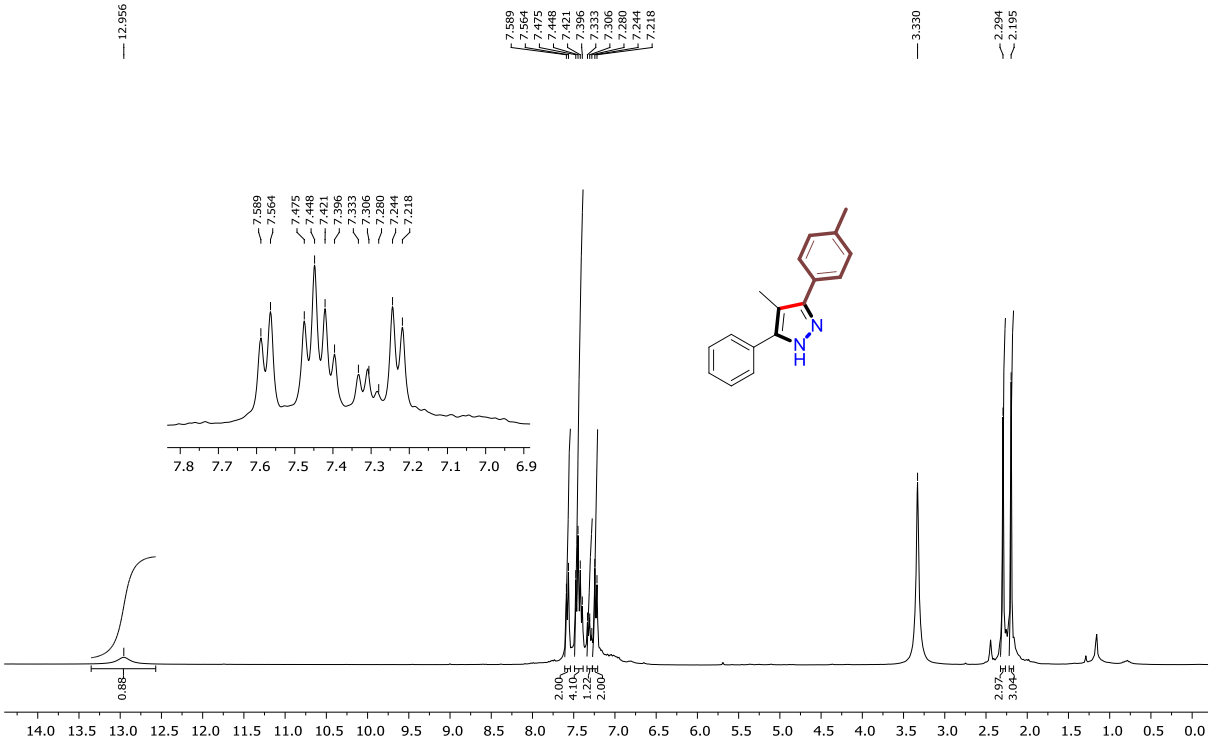
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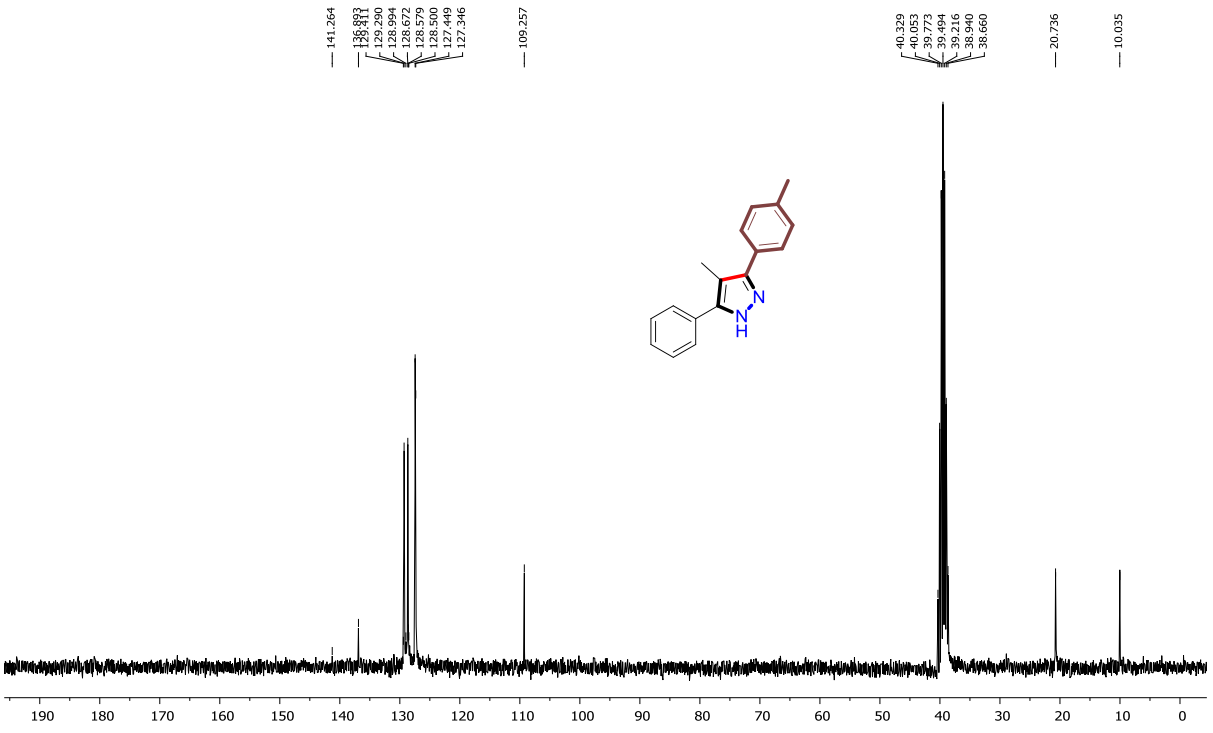
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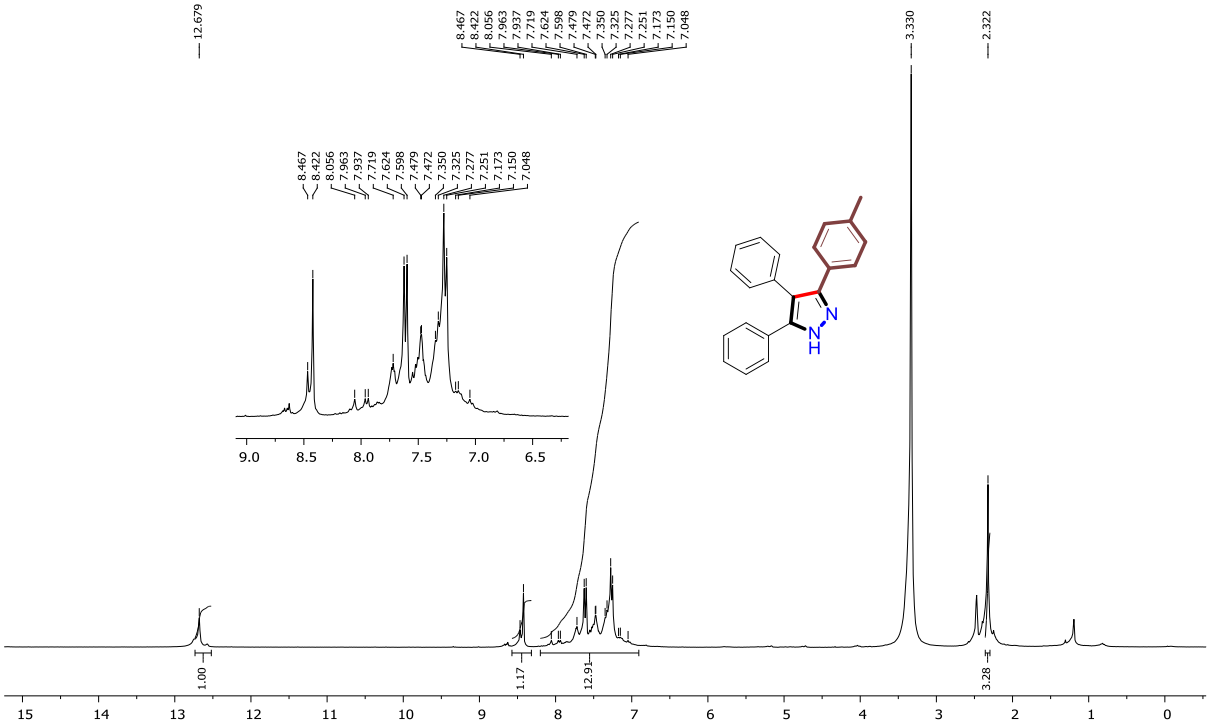
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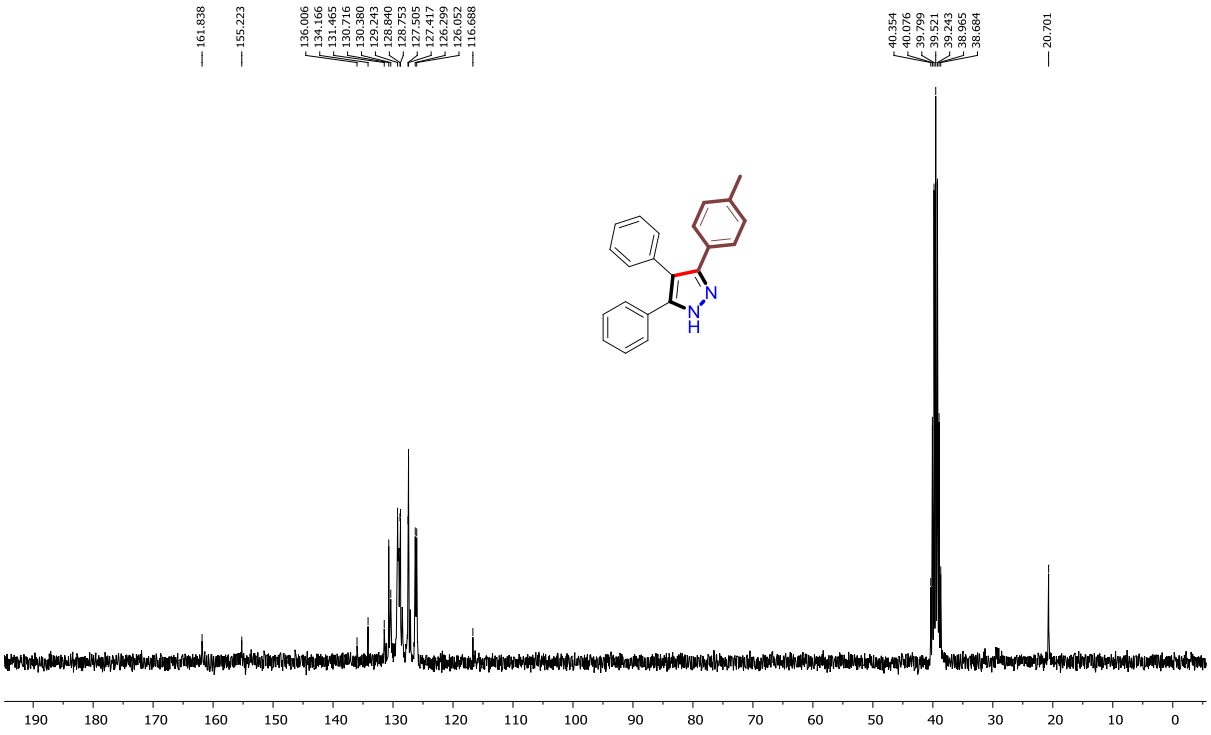
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H