**Supporting Information**

**Visible light-mediated photocatalytic bromination of 2-arylimidazo[1,2-*a*]pyridines using CBr4 as bromine source**

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1. **General information**

All commercial reagents and solvents were used without purification. TLC analyses were carried out on pre-coated silica gel plates with F254 indicator. Visualization was accomplished by UV light (254 nm), I2, *p*-anisaldehyde, ninhydrin, and phosphomolybdic acid solution as an indicator. Purification of reaction products was carried out by flash chromatography using E. Merck silica gel 60 (230-400 mesh). 1H NMR, 13C NMR, 31P NMR, and 19F NMR spectra were recorded at 400 MHz, 100 MHz, 376 MHz respectively, on a Jeol ECS 400 MHz NMR spectrometer. Chemical shift values () are reported in ppm relative to Me4Si as the internal references and PhCF3 as the external references. Mass spectra (MS-EI, 70 eV) were conducted on GC-MS Shimadzu QP2010. Mass spectra (MS-EI, 70 eV) were conducted on GC-MS Shimadzu QP2010. High resolution mass spectra were measured on Jeol HX110/110A using electrospray ionization technique.

1. **Preparation of starting materials**

Imidazopyridine derivatives **1** were prepared in accordance with literature methods.1

1. **General procedure for the photocatalytic bromination of 2-arylimidazopyridines (1) with CBr4 2:**

An oven-dried flask was equipped with a magnetic stir bar, 2-arylimidazo[1,2-a]pyridines **1** (0.1 mmol), carbon tetrabromide (**2**, 49.7 mg, 0.15 mmol), Ir(ppy)2(dtbbpy)PF6 (1.8 mg, 0.002 mmol), and DMSO (1 mL) under N2 atmosphere. The reaction mixture was then stirred for 7-21 h under irradiation using 5 W blue LEDs (max = 455 nm). Upon completion of the reaction, the mixture was concentrated in vacuum and purified by chromatography on silica gel (ethyl acetate:*n*-hexane = 1:5) to afford 3-bromo-2-arylimidazo[1,2-a]pyridines **3**.

1. **Characterization data of -bromoimidazopyridine derivatives2**

**3-Bromo-2-phenylimidazo[1,2-*a*]pyridine (3a)**



Yield: 84%; white solid; mp 63-65 oC; 1H NMR (400 MHz, CDCl3):  8.19 (d, *J* = 6.8 Hz, 1 H), 8.13 (d, *J* = 7.2 Hz, 2H), 7.66 (d, *J* = 9.2 Hz, 1 H), 7.49 (t, *J* = 7.6 Hz, 2 H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.32-7.26 (m, 1 H), 6.95 (td, *J* = 6.9 Hz, 1.1 Hz, 1 H); 13C NMR (100 MHz, CDCl3):  145.4, 142.6, 132.8, 128.5, 128.3, 127.9, 125.2, 124.0, 117.6, 113.1, 91.8; HRMS (ESI) calcd for C13H10BrN2 [M+H]+273.0027; found 273.0031.

**3-Bromo-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (3b)**



Yield: 78%; white solid; mp 126-129 oC; 1H NMR (400 MHz, CDCl3):  8.13-8.10 (m, 2 H), 7.95 (s, 1H), 7.53 (d, *J*= 9.2 Hz, 1 H), 7.49-7.45 (m, 2 H), 7.39-7.35 (m, 1H), 7.10 (dd, *J* = 9.2 Hz, 1.6 Hz, 1 H), 2.39 (s, 3 H); 13C NMR (100 MHz, CDCl3):  144.5, 142.4, 133.0, 128.4, 128.3, 128.1, 127.8, 122.9, 121.7, 117.0, 91.3, 18.4; HRMS (ESI) calcd for C14H12BrN2 [M+H]+287.0184; found 287.0186.

**3-Bromo-6-fluoro-2-phenylimidazo[1,2-a]pyridine (3c)**



Yield: 76%; yellow solid; mp 111-116 oC; 1H NMR (400 MHz, CDCl3):  8.15-8.13 (m, 1 H), 8.11-8.09 (m, 2 H), 7.63 (dd, *J* = 9.8 Hz, 5.0 Hz, 1 H), 7.49 (t, *J* = 7.6 Hz, 2 H), 7.41 (t, *J* = 7.4 Hz, 1 H), 7.21-7.16 (m, 1 H); 13C NMR (100 MHz, CDCl3):  154.9, 152.6, 144.1, 143.1, 132.6, 128.5, 127.8, 118.2 (d, *J*= 8.5 Hz), 117.2 (d, *J*= 25.7 Hz), 111.0 (d, *J*= 42 Hz), 93.0. 19F NMR (376 MHz, CDCl3) -138.2; HRMS (ESI) calcd for C13H9BrFN2 [M+H]+290.9933; found 290.9936.

**3,6-Dibromo-2-phenylimidazo[1,2-a]pyridine (3d)**



Yield: 68%; pale yellow solid; mp 141-144 oC; 1H NMR (400 MHz, CDCl3):  8.32-8.25 (m, 1 H), 8.11-8.09 (m, 2 H), 7.54−7.47 (m, 3 H), 7.42-7.39 (m, 1 H), 7.33-7.29 (m, 1 H); 13C NMR (100 MHz, CDCl3):  143.9, 143.5, 132.3, 128.6, 128.5, 127.8, 124.1, 118.2, 107.9, 92.0; HRMS (ESI) calcd for C13H9Br2N2 [M+H]+350.9132; found 350.9129.

**3-Bromo-7-methyl-2-phenylimidazo[1,2-a]pyridine (3e)**



Yield: 66%; white solid; mp 101-105 oC; 1H NMR (400 MHz, CDCl3):  8.12-8.10 (m, 2 H), 8.04 (d, *J* = 6.8 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.39−7.35 (m, 2 H), 6.76 (dd, *J* = 7.0 Hz, 1.0 Hz, 1 H), 2.43 (s, 3 H);13C NMR (100 MHz, CDCl3):  145.9, 142.4, 136.2, 133.1, 128,5, 128.2, 127.8, 123.2, 116.1, 115.7, 90.8, 21.4; HRMS (ESI) calcd for C14H12BrN2 [M+H]+287.0184; found 287.0187

**3-Bromo-8-methyl-2-phenylimidazo[1,2-a]pyridine (3f)**



Yield: 77%; yellow oil; 1H NMR (400 MHz, CDCl3)  8.13−8.11 (m, 2 H), 8.05 (d, *J* = 6.8 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.38 (t, *J* = 7.4 Hz, 1 H), 7.05 (d, *J* = 7.2 Hz, 1 H), 6.84 (t, *J* = 7.0 Hz, 1 H), 2.70 (s, 3 H);13C NMR (100 MHz, CDCl3):  = 145.8, 142.2, 133.2, 128.4, 128,1, 128.0, 127.7, 123.8, 121.8, 113.0, 92.0, 16.6; HRMS (ESI) calcd for C14H12BrN2 [M+H]+287.0184; found 287.0189.

**3,8-Dibromo-2-phenylimidazo[1,2-a]pyridine (3g)**



Yield: 64%; white solid; mp 137-139 oC; 1H NMR (400 MHz, CDCl3):  8.31-8.31 (m, 1H), 8.18 (d, *J* = 6.8 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.52 (dd, *J* = 7.8 Hz, 1.0 Hz, 1H), 7.34 (t, *J* = 7.8, 1H), 7.30-7.26 (m, 2H), 6.96 (t, J = 6.8, 1H); 13C NMR (100 MHz, CDCl3)  145.5, 141.1, 135.0, 131.3, 130.7, 130.0, 126.3, 125.5, 124.1, 122.7, 117.8, 113.4, 92.2; HRMS (ESI) calcd for C13H9Br2N2 [M+H]+350.9132; found 350.9135.

**3-Bromo-2-(p-tolyl)imidazo[1,2-a]pyridine (3h)**



Yield: 67%; yellow solid; mp 111-113 oC; 1H NMR (400 MHz, CDCl3)  8.18 (d, *J* = 7.2 Hz, 1 H), 8.02 (d, *J* = 8.4 Hz, 2 H), 7.64 (d, *J* = 9.2 Hz, 1 H), 7.30−7.24 (m, 3 H), 6.94 (t, *J* = 7.0 Hz, 1 H), 2.41 (s, 3 H); 13C NMR (100 MHz, CDCl3)  145.4, 142.8, 138.2, 130.0, 129.2, 127.8, 125.0, 123.9, 117.6, 113.0, 91.4, 21.4; HRMS (ESI) calcd for C14H12BrN2 [M+H]+287.0184; found 287.0186.

**3-Bromo-2-(4-methoxyphenyl)imidazo[1,2-a]pyridine (3i)**



Yield: 75%; yellow solid; mp 100-103 oC; 1H NMR (400 MHz, CDCl3)  8.16 (d, *J* = 7.2 Hz, 1 H), 8.10-8.07 (m, 2 H), 7.62 (d, *J* = 9.2 Hz, 1 H), 7.27−7.22 (m, 1 H), 7.02(d, *J* = 8.8 Hz, 2 H), 6.93 (t, *J* = 6.8 Hz, 1 H), 3.87 (s, 3 H); 13C NMR (100 MHz, CDCl3)  159.7, 145.4, 142.6, 129.2, 125.5, 124.9, 123.9, 117.4, 113.9, 112.9, 90.9, 55.3; HRMS (ESI) calcd for C14H12BrN2 O[M+H]+303.0133; found 303.0135.

**3-Bromo-2-(4-fluorophenyl)imidazo[1,2-a]pyridine (3j)**



Yield: 74%; yellow solid; mp 130-133 oC; 1H NMR (400 MHz, CDCl3)  8.18−8.15 (m, 1 H), 8.13-8.09 (m, 2 H), 7.62 (d, *J* = 8.8 Hz, 1 H), 7.29−7.25 (m, 1 H), 7.21-7.13 (m, 2 H), 6.94 (td, *J* = 6.8 Hz, 0.8 Hz, 1 H); 13C NMR (100 MHz, CDCl3) 13C NMR (100 MHz, CDCl3)  162.8 (d, *J* = 247.0 Hz), 145.5, 141.9, 129.7 (d, *J* = 7.6 Hz), 129.0 (d, *J* = 2.9 Hz), 125.2, 124.0, 117.6, 115.5 (d, *J* = 21.0 Hz), 113.1, 91.4; 19F NMR (376 MHz, CDCl3) -113.1; HRMS (ESI) calcd for C13H9BrFN2 [M+H]+290.9933; found 290.9937.

**3-Bromo-2-(4-bromophenyl)imidazo[1,2-a]pyridine (3k)**



Yield: 65%; white solid; mp 149-153 oC; 1H NMR (400 MHz, CDCl3)  8.18 (d, *J* = 6.8 Hz, 1 H), 8.04-8.00 (m, 2 H), 7.65-7.59 (m, 3 H), 7.30-7.26 (m, 1 H), 6.96 (td, *J* = 7.0 Hz, 0.9 Hz, 1 H); 13C NMR (100 MHz, CDCl3)  145.5, 141.6, 131.8, 131.6, 129.4, 129.0, 125.4, 124.0 , 122.7, 122.5, 117.7, 113.2, 91.8; HRMS (ESI) calcd for C13H9Br2N2 [M+H]+350.9132; found 350.9135.

**3-Bromo-2-(m-tolyl)imidazo[1,2-a]pyridine (3l)**



Yield: 83%; yellow solid; mp 129-133 oC; 1H NMR (400 MHz, CDCl3)  8.18 (d, *J* = 6.8 Hz, 1 H), 7.93 (d, *J* = 9.2 Hz, 2 H), 7.64 (d, *J* = 9.2 Hz, 1 H), 7.37 (t, *J* = 7.6 Hz, 1 H), 7.27-7.20 (m, 2 H), 6.93 (t, *J* = 6.8 Hz, 1 H), 2.45 (s, 3 H); 13C NMR (100 MHz, CDCl3)  145.5, 142.8, 138.2, 132.8, 129.1, 128.6, 128.4, 125.1, 124.9, 124.0, 117.6, 113.0, 91.7, 21.6; HRMS (ESI) calcd for C14H12BrN2 [M+H]+287.0184; found 287.0181.

**3-Bromo-2-(naphthalen-1-yl)imidazo[1,2-a]pyridine (3m)**



Yield: 58%; yellow solid; mp 155-156 oC; 1H NMR (400 MHz, CDCl3)  8.24-8.10 (m, 2 H), 7.96-7.91 (m, 2 H), 7.73-7.71 (m, 2 H), 7.57-7.53 (m, 1 H), 7.52-7.47 (m, 2 H), 7.34-7.31 (m, 1 H), 7.00 (td, *J* = 6.9 Hz, 1.0 Hz, 1 H); 13C NMR (100 MHz, CDCl3)  145.5, 143.6, 133.8, 131.8, 130.2, 129.2, 128.8, 128.3, 126.4, 126.3, 125.9, 125.1, 125.1, 124.1, 117.8, 113.2, 94.6; HRMS (ESI) calcd for C17H12BrN2 [M+H]+323.0184; found 323.0187.

**3-Bromo-2-(thiophen-2-yl)imidazo[1,2-a]pyridine (3n)**



Yield: 66%; yellow oil; 1H NMR (400 MHz, CDCl3)  8.11 (d, *J* = 6.8 Hz, 1 H), 7.86 (d, *J* = 3.6 Hz, 1 H), 7.63-7.61 (m, 1 H), 7.40 (d, *J* = 5.2 Hz, 1 H), 7.28-7.25 (m, 1 H),7.16-7.14 (m, 1 H), 6.92 (t, *J* = 6.8 Hz, 1 H); 13C NMR (100 MHz, CDCl3)  145.4, 138.5, 135.9, 127.7, 126.2, 125.5, 125.4, 123.8, 117.4, 113.2, 90.8; HRMS (ESI) calcd for C11H8BrN2S [M+H]+278.9592; found 278.9595.

**3-Bromo-2-methylimidazo[1,2-*a*]pyridine. (3o)**



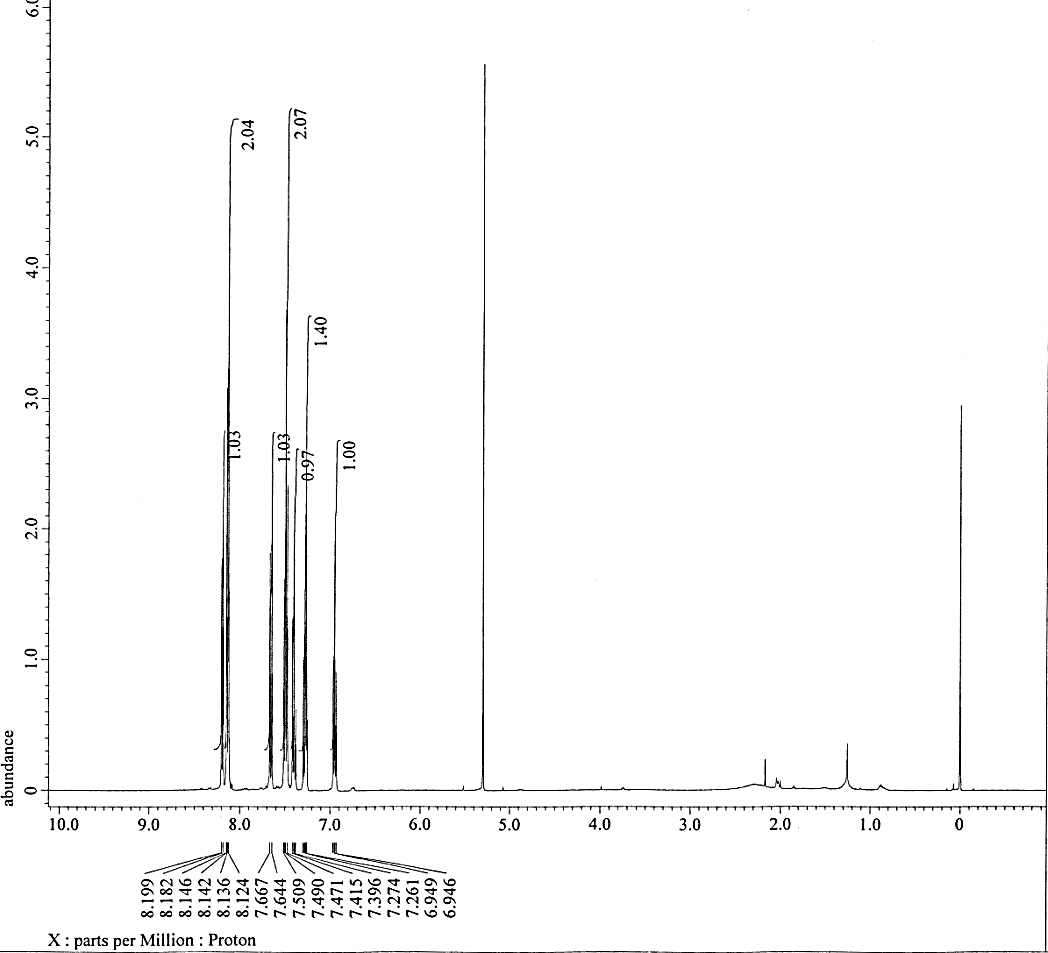
Yield: 8%; yellow solid; mp 50-53 oC; 1H NMR (400 MHz, CDCl3) 8.04 (d, *J* = 6.8 Hz, 1 H), 7.52 (d, *J* = 9.2 Hz, 1 H), 7.20 (td, *J* = 8.0 Hz, 2.0 Hz, 1 H), 6.881 (t, *J* = 6.6 Hz, 1 H), 2.47 (s, 3 H); 13C NMR (100 MHz, CDCl3) ; HRMS (ESI) calcd for C8H8BrN2 [M+H]+210.9871; found 210.9875.

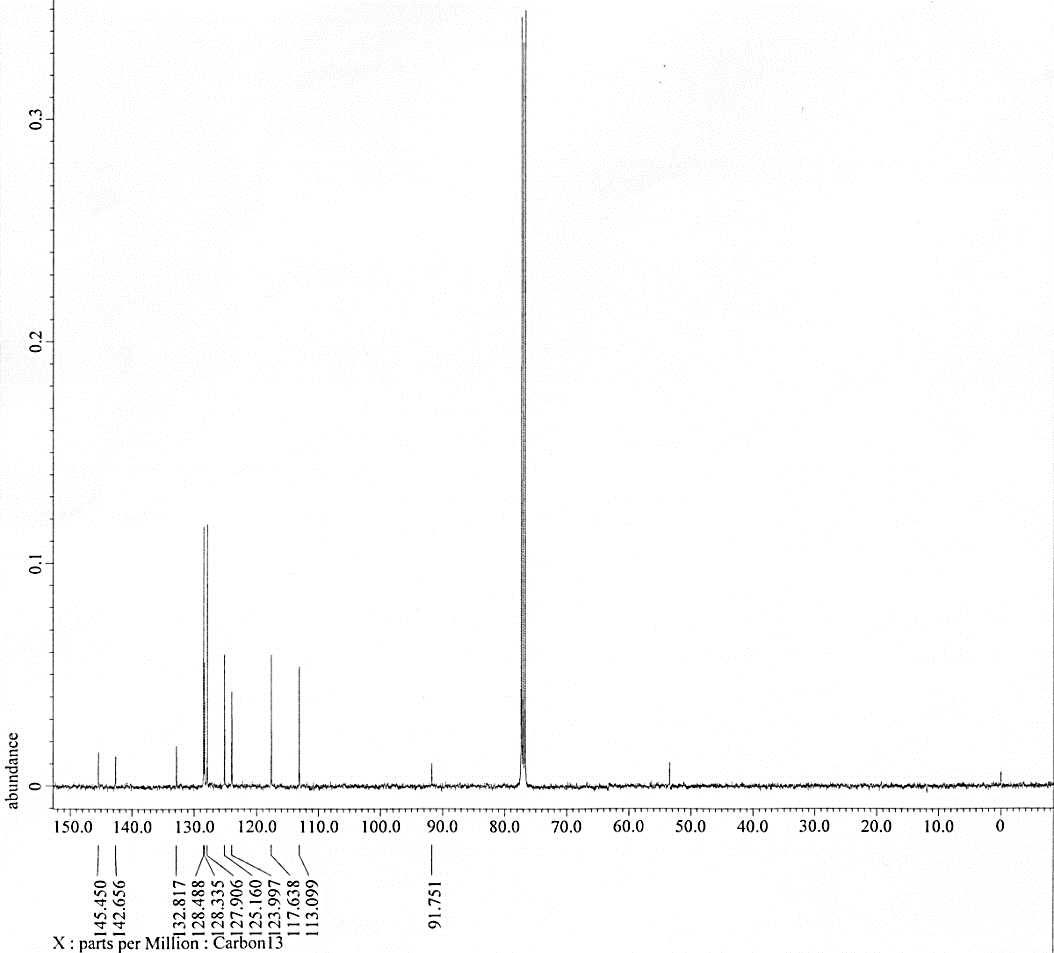
**5. References**

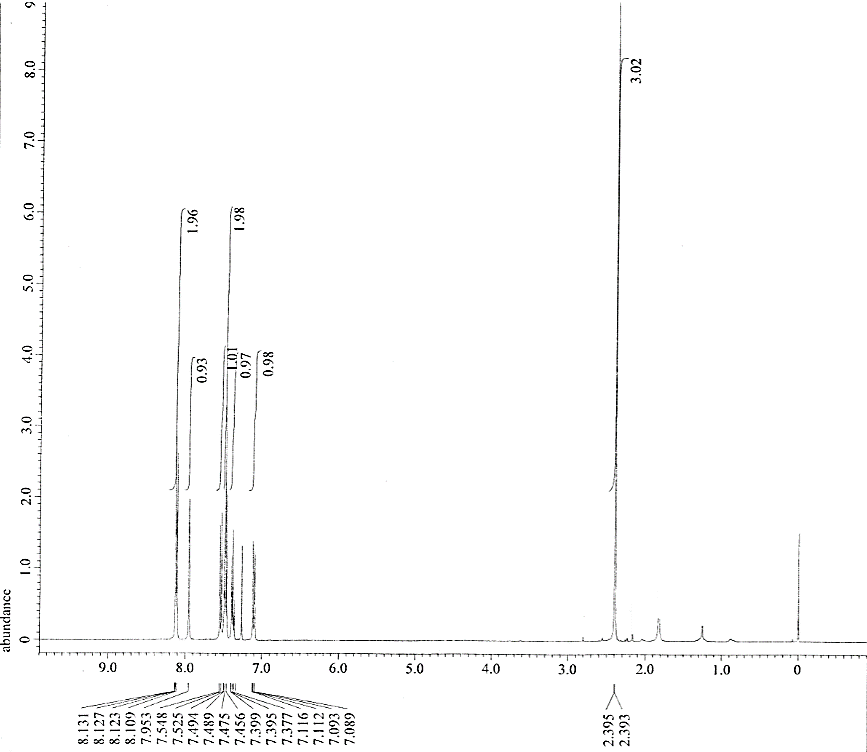
1. Cai, Q.; Liu, M.-C.; Mao, B.-M.; Xie, X.; Jia, F.-C.; Zhu, Y.-P.; Wu, A.-X. *Chin. Chem.Lett.* **2015**, *26*, 881.

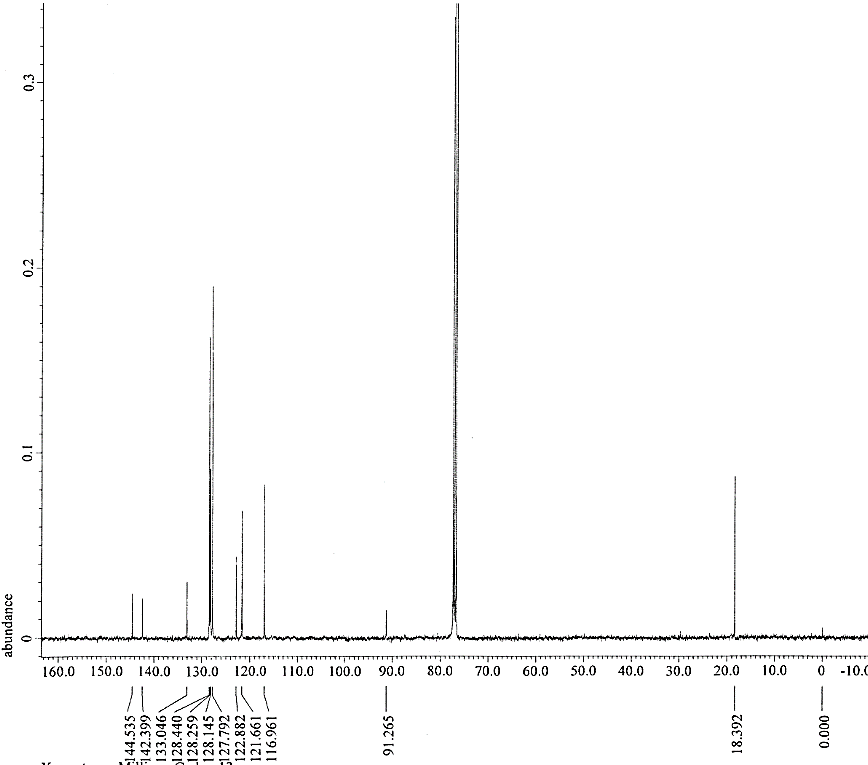
2. (a) Zhou, X.; Yan, H.; Ma, C.; He, Y.; Li, Y.; Cao, J.; Yan, R.; Huang, G. *J. Org. Chem*. **2016**, *81*, 25. (b) Jian, W.-Q.; Wang, H.-B.; Du, K.S.; Zhong, Q.-Q.; Hunag, J.-M. ChemElectroChem. **2019**, *6*, 2733. (c) Katrun, P.; Kuhakarn, C. *Tetrahedron Lett*. **2019**, *60*, 989. (d) Semwal, R.; Ravi, C.; Kumar, R.; Meena, R.; Adimurthy, S. *J. Org. Chem*. **2019**, *84*, 792. (e) Yuan, Y.; Yao, A.; Zheng, Y.; Gao, M.; Zhou, Z.; Qiao, J.; Hu, J.; Ye, B.; Zhao, J.; Wen, H.; Lei, A. *iScience* **2019**,*12*, 293. (f) Zhou, Z.; Yuan, Y.; Cao, Y.; Qiao, J.; Yao, A.; Zhao, J.; Zuo, W.; Chen, W.; Lei, A. *Chin. J. Chem.* **2019**, *37*, 611.

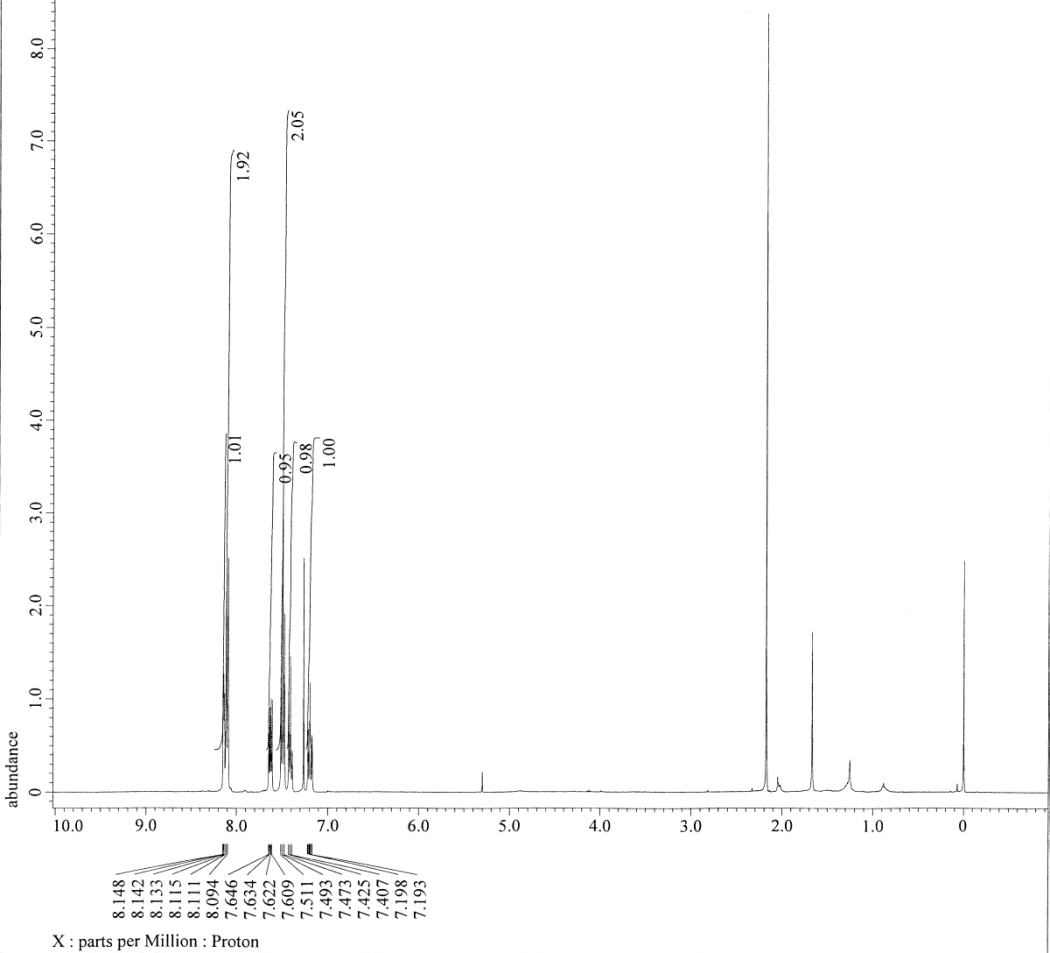
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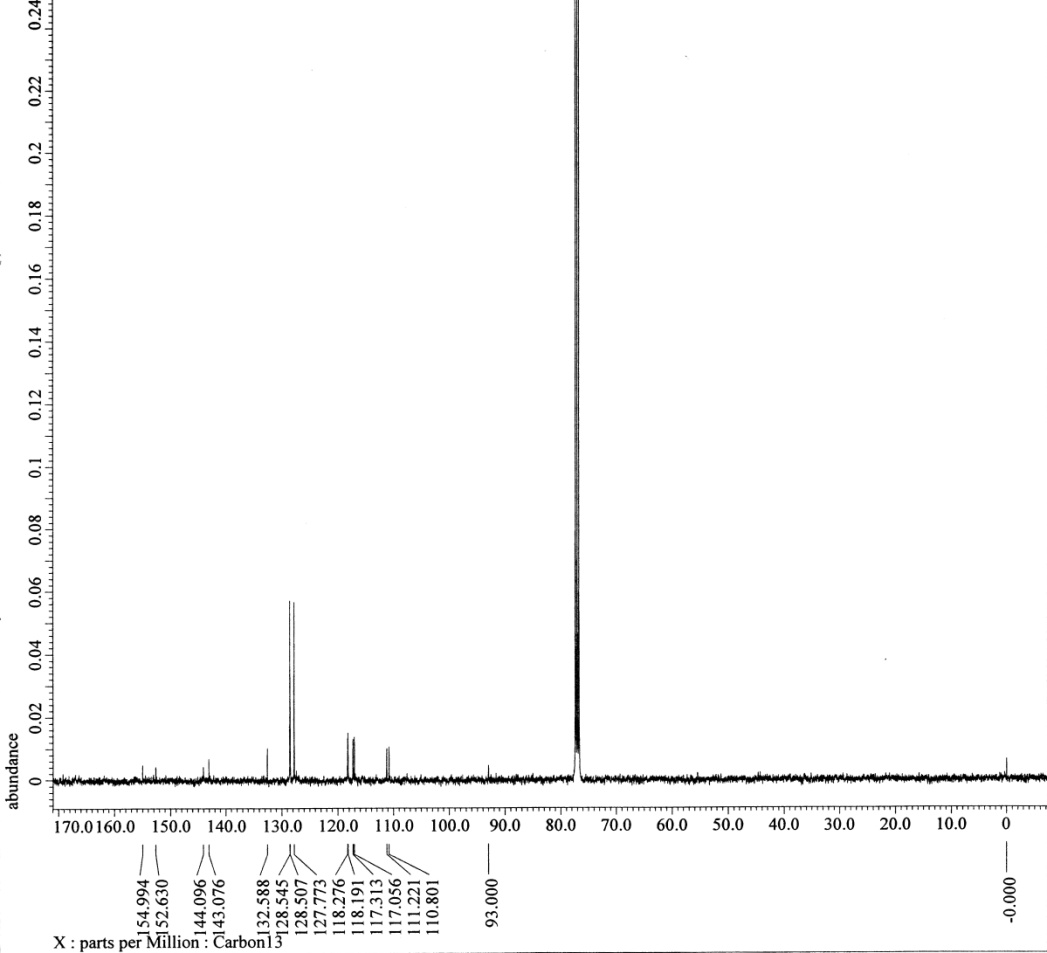
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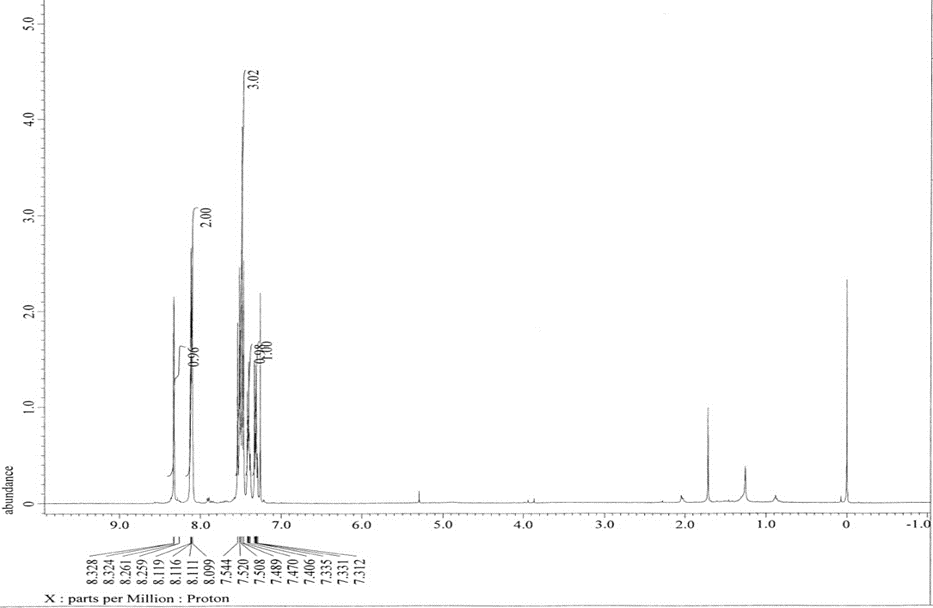
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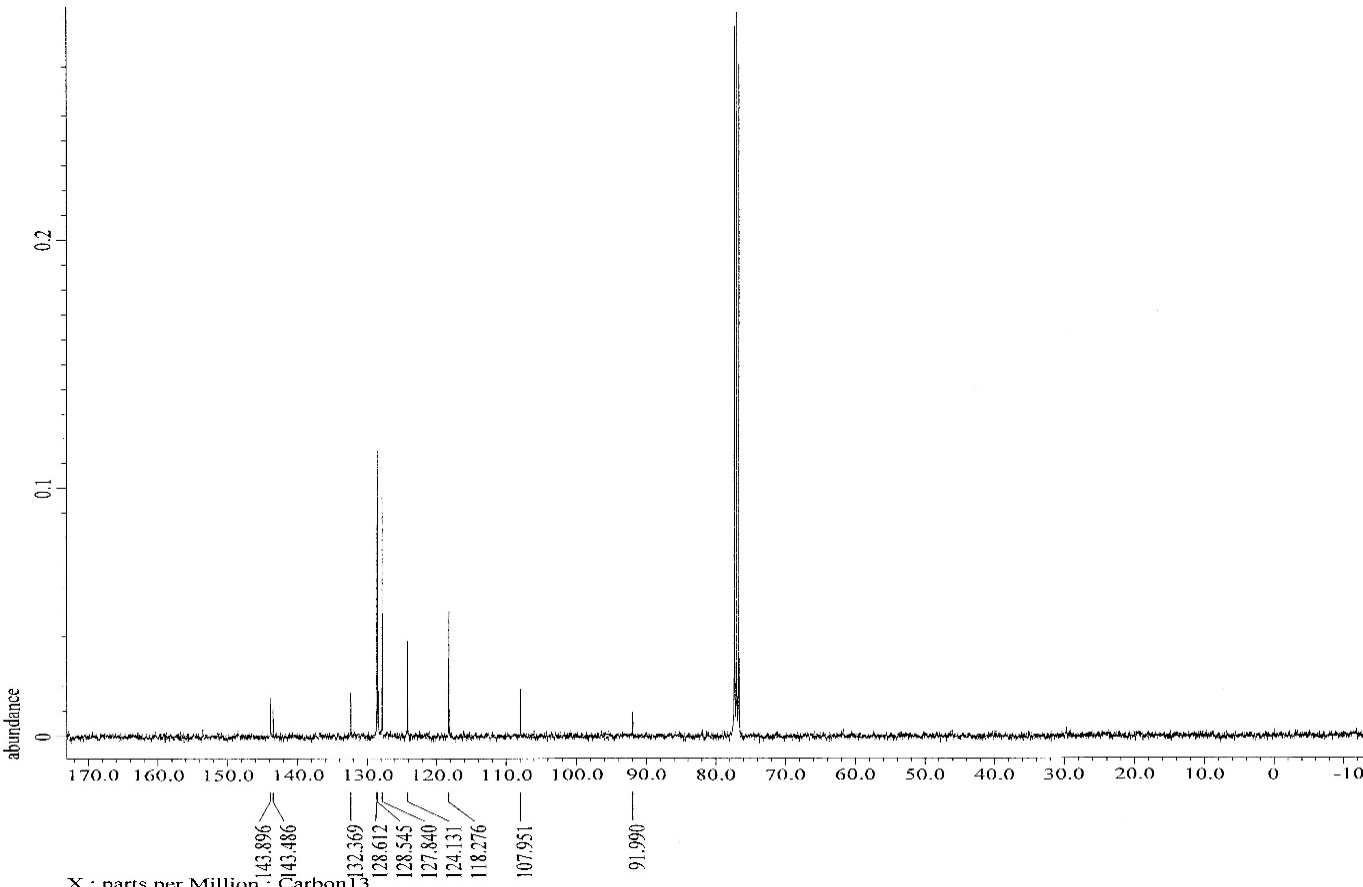


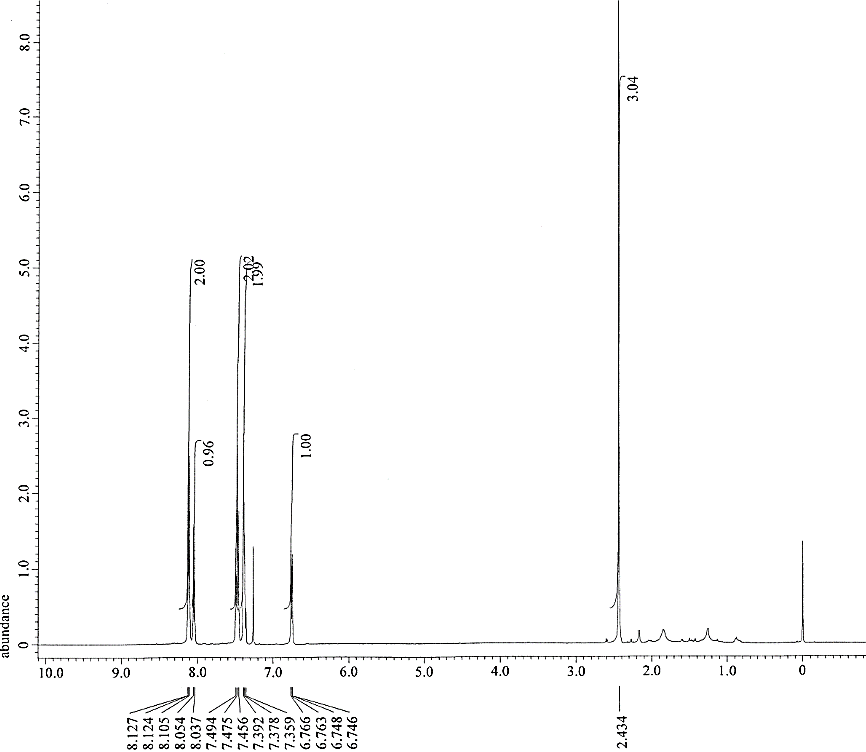


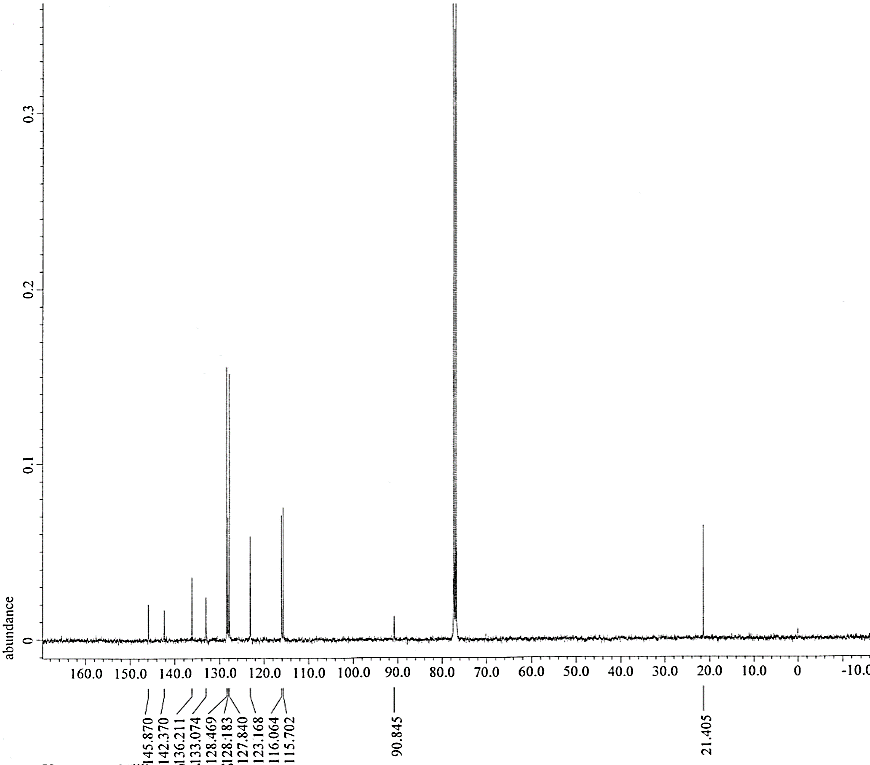


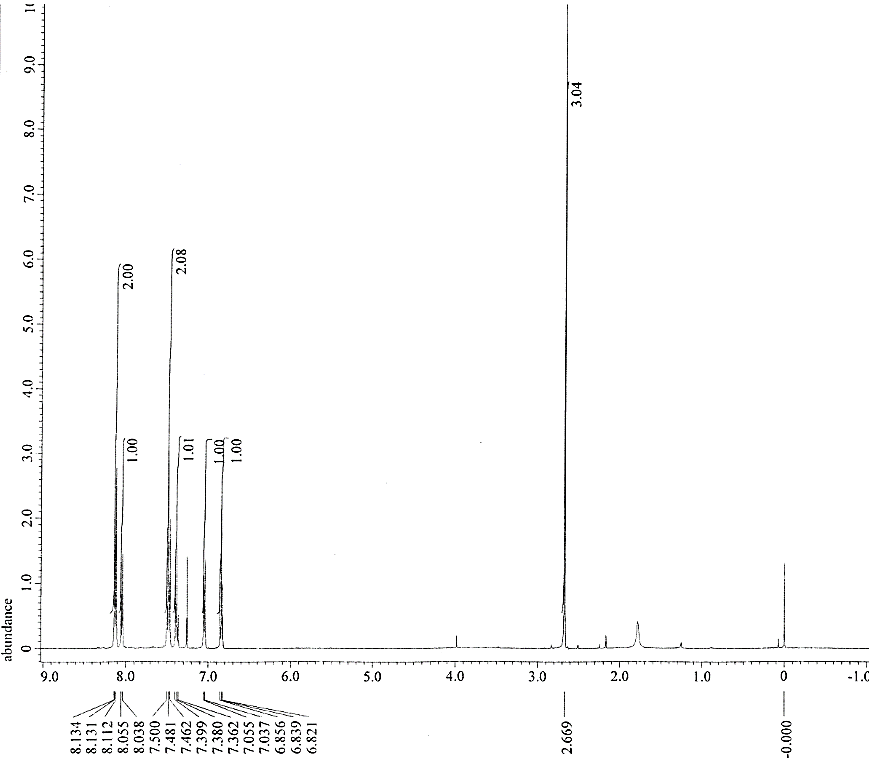
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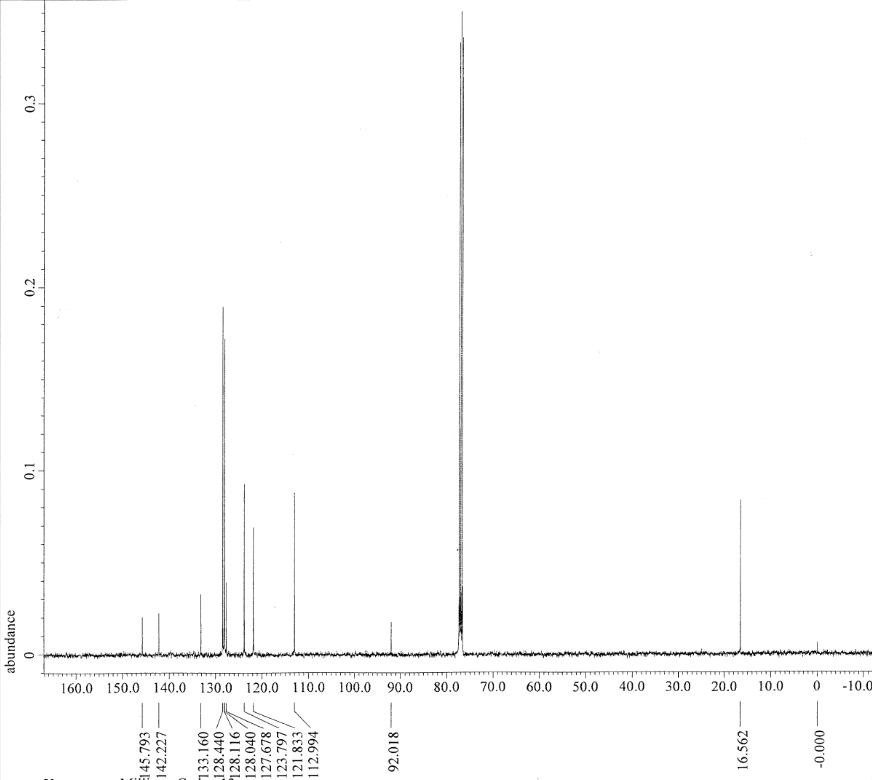


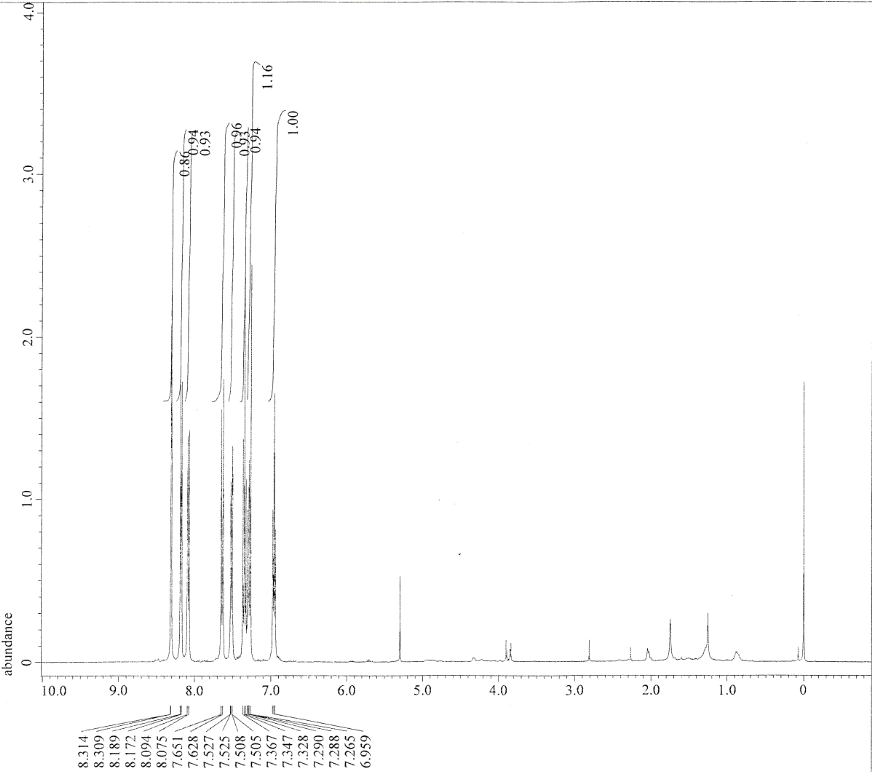
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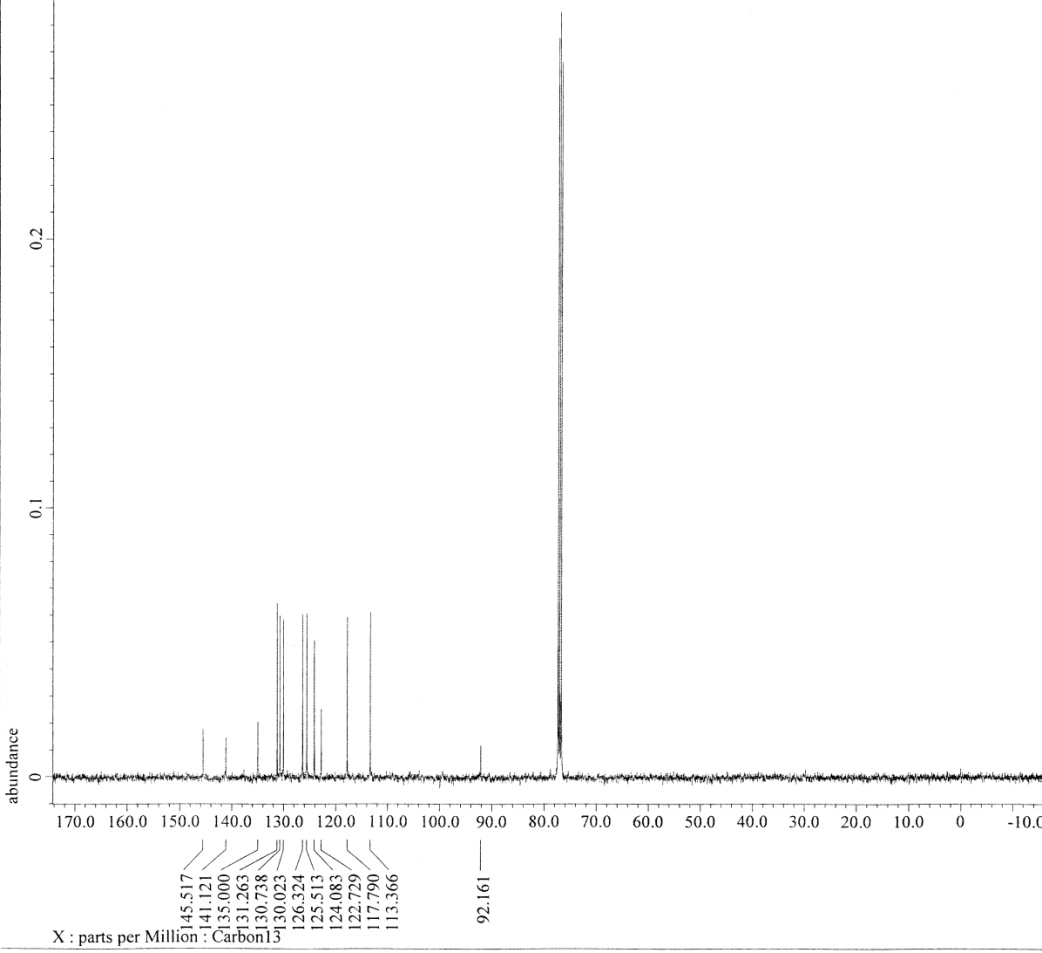


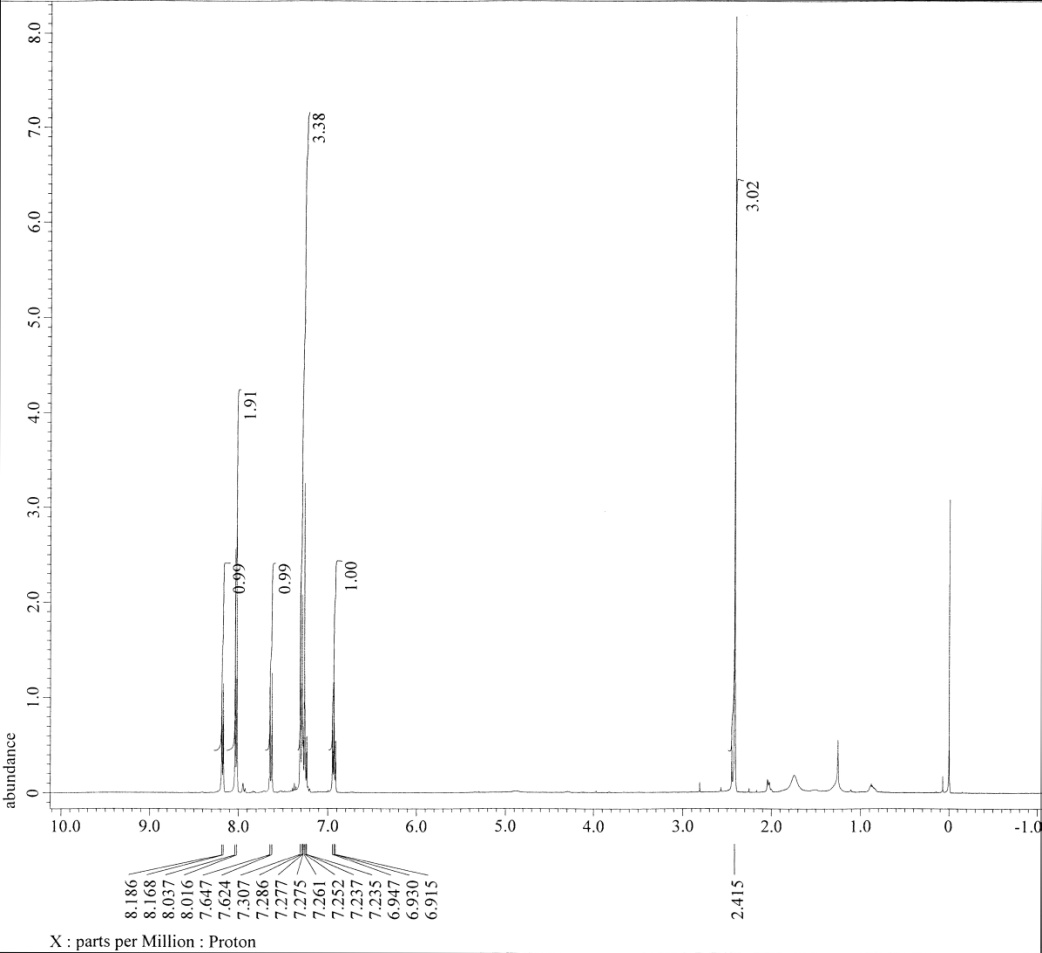


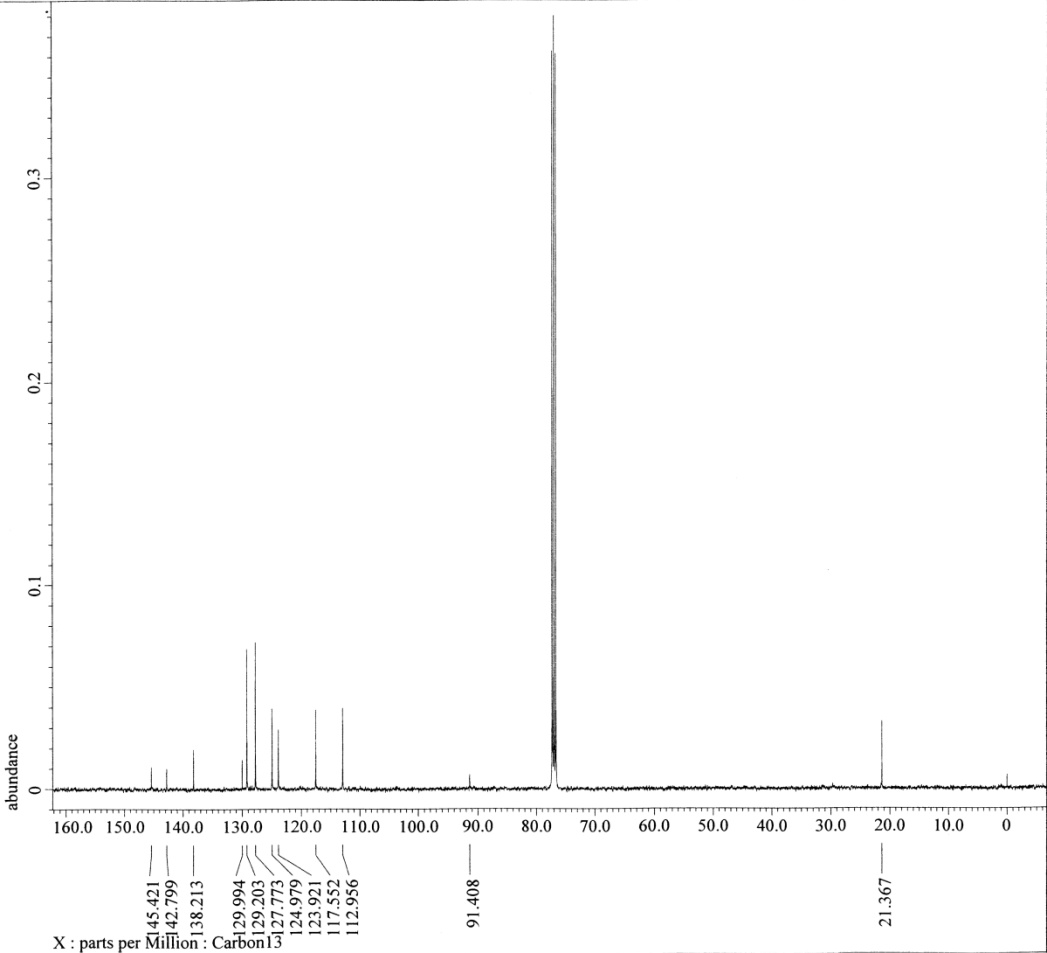


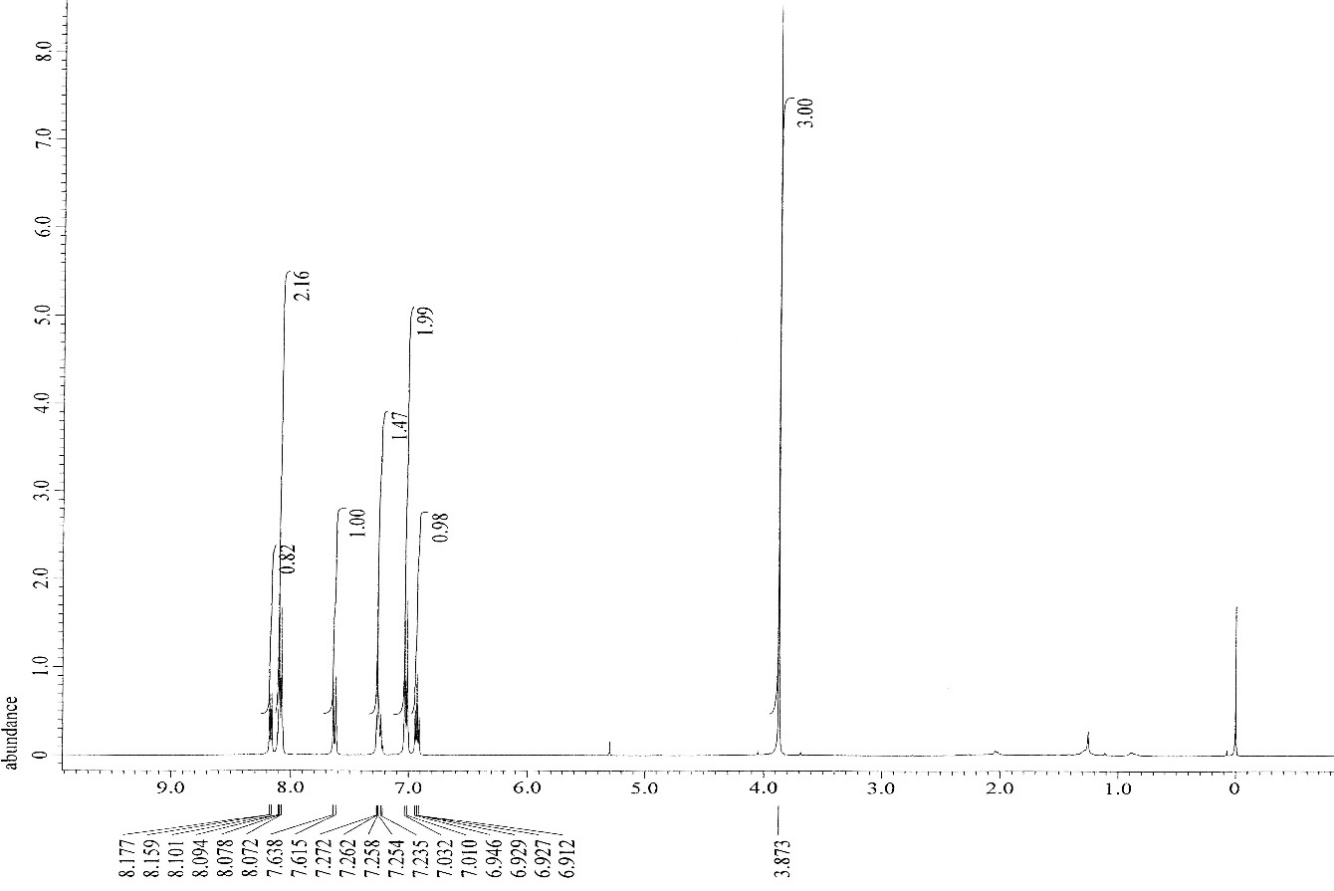


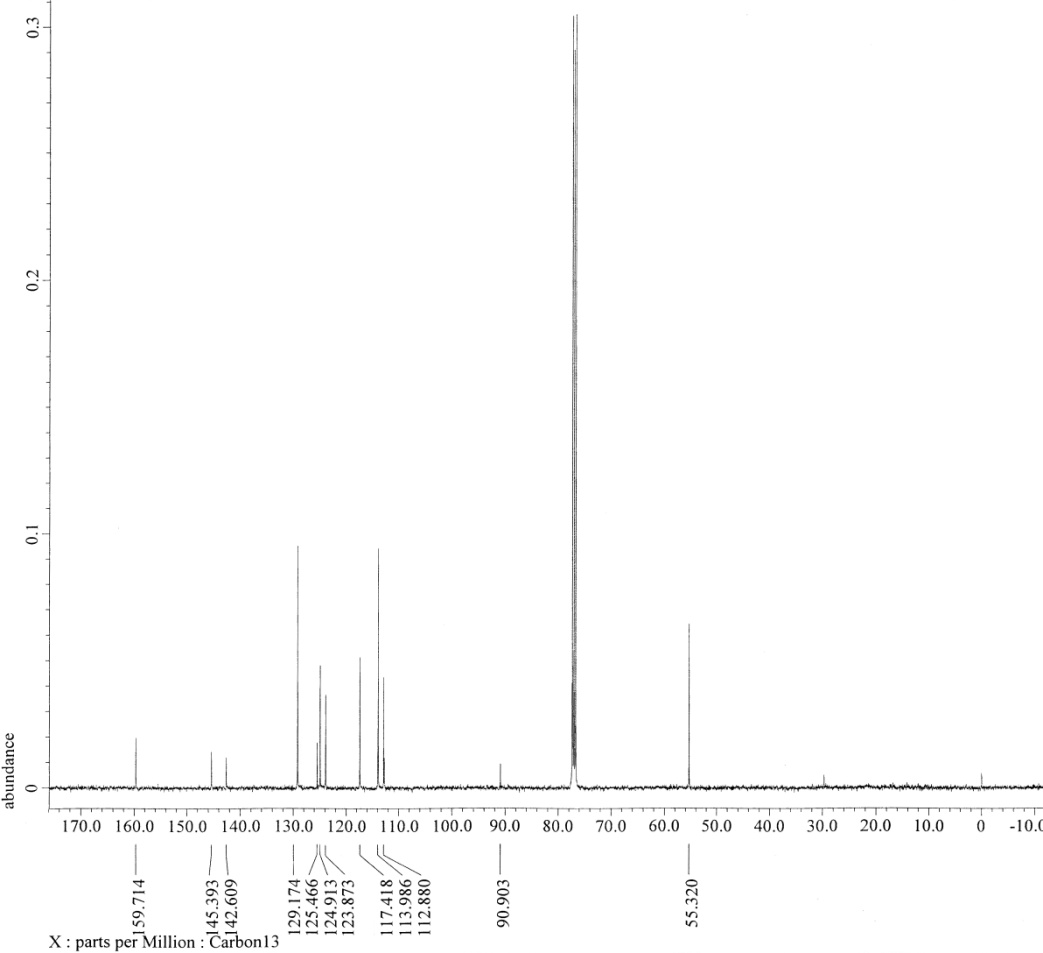


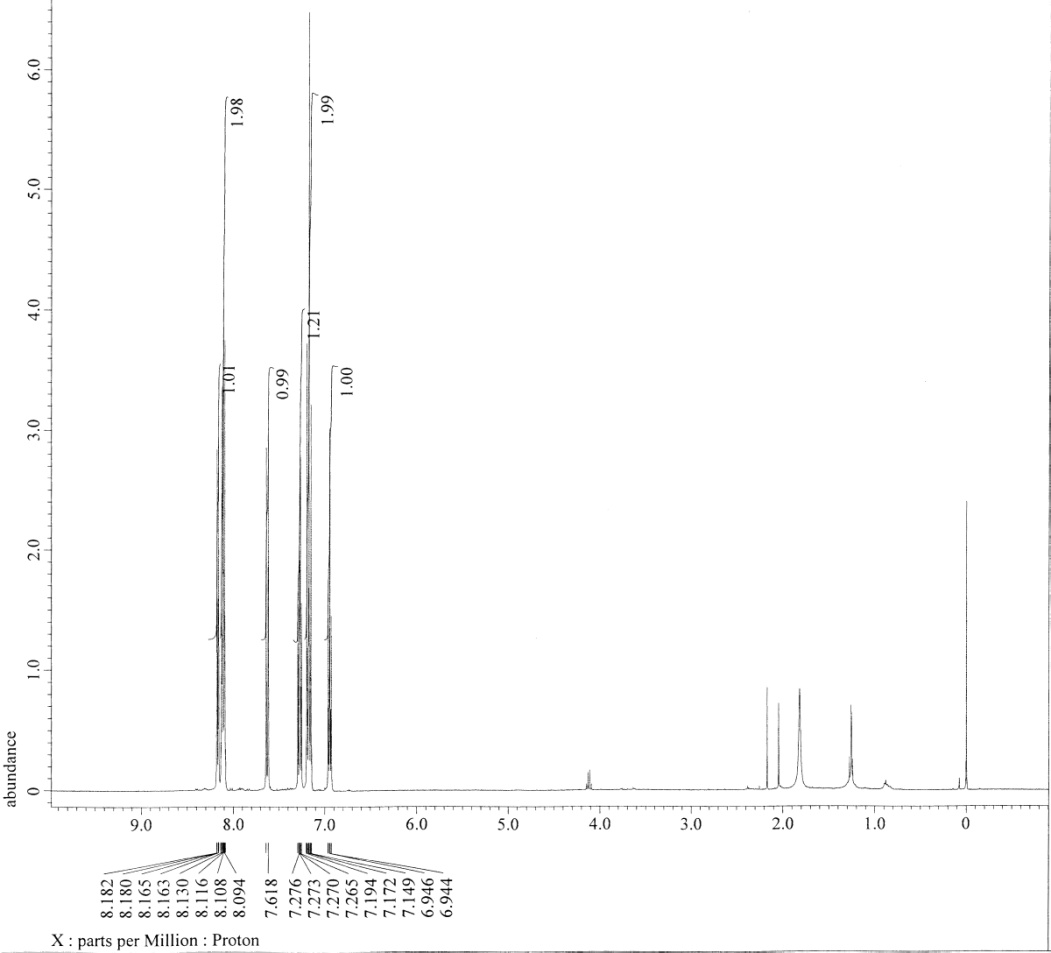
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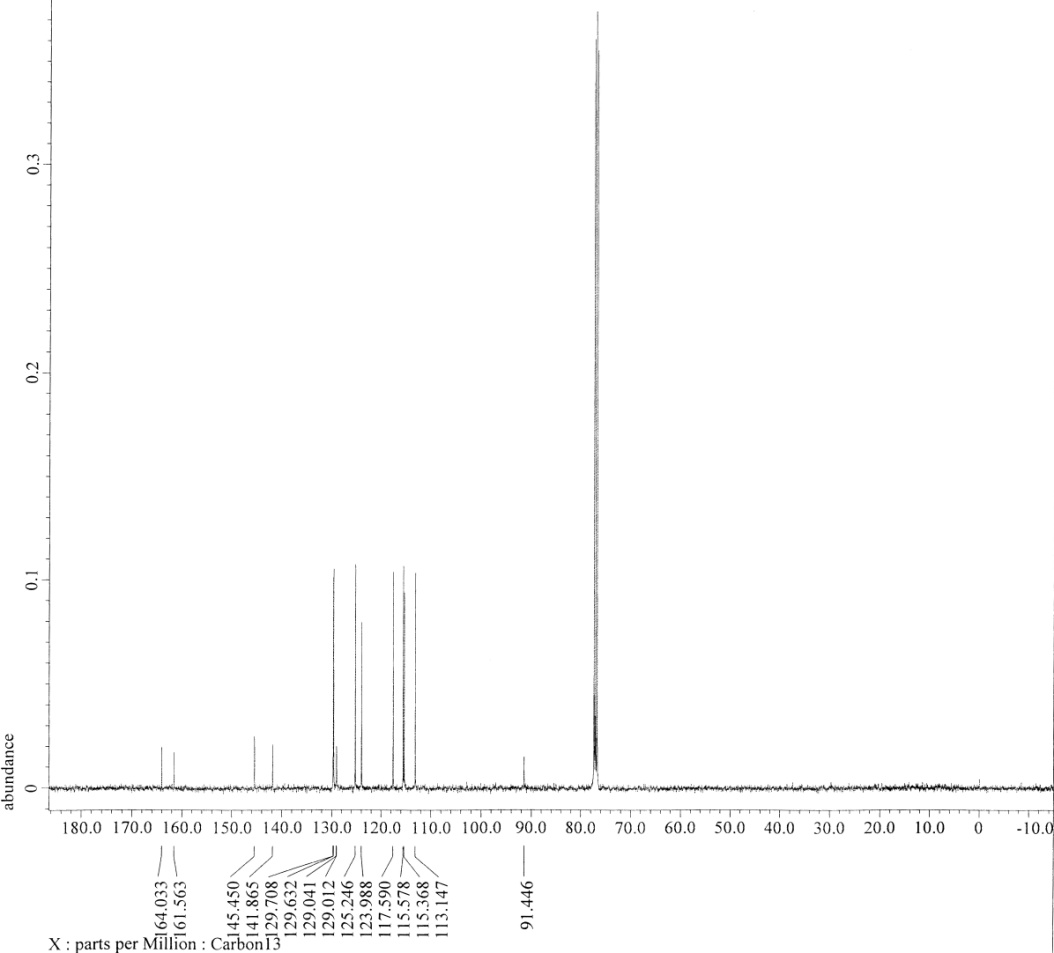


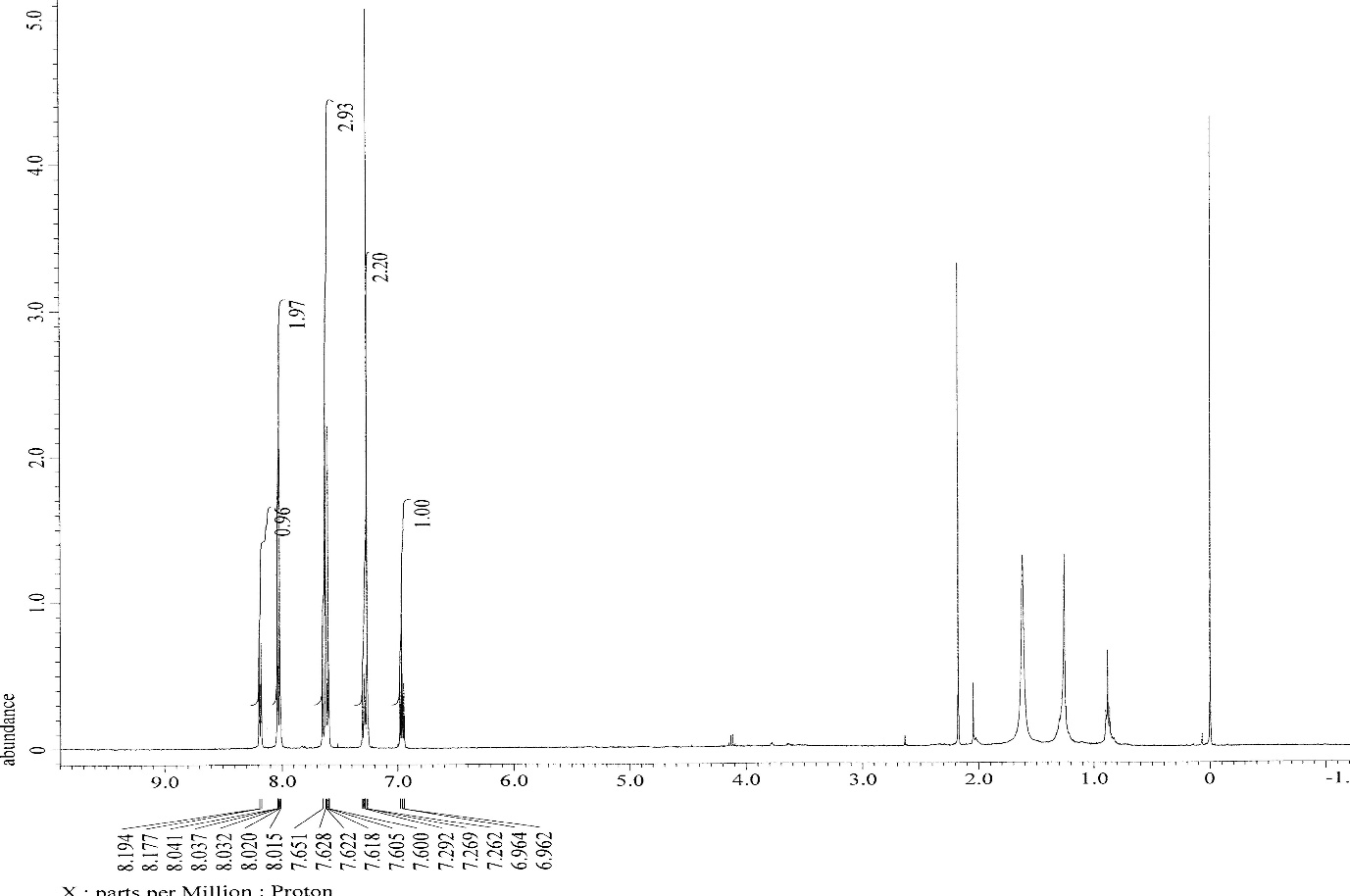
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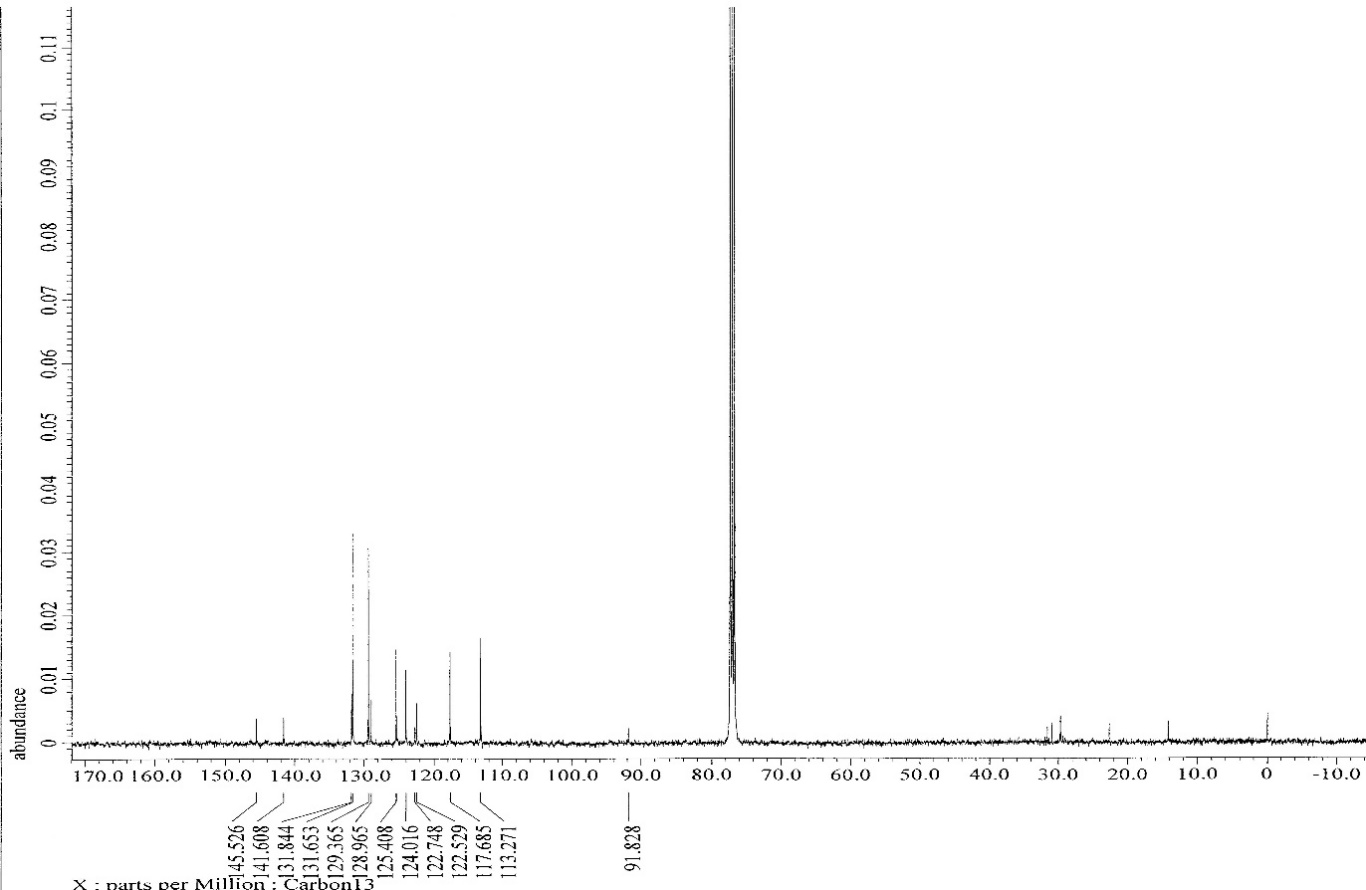


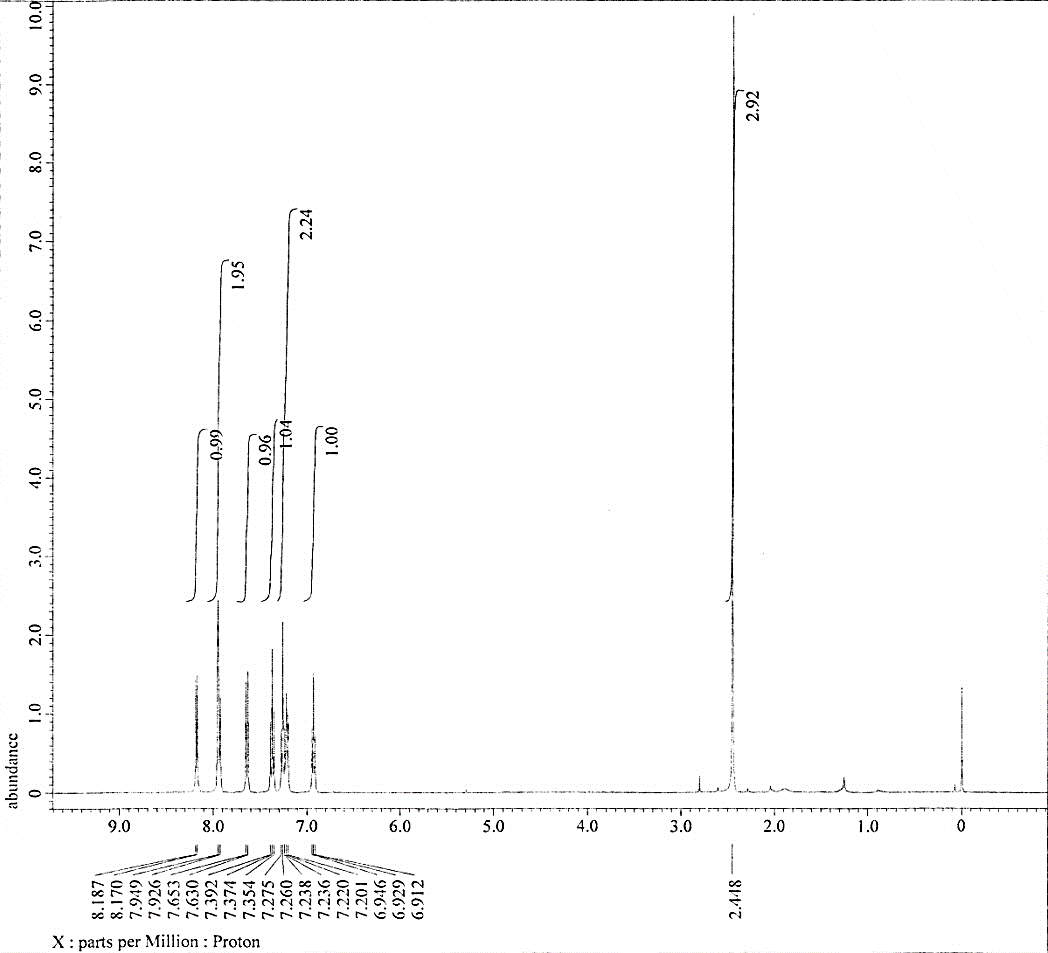


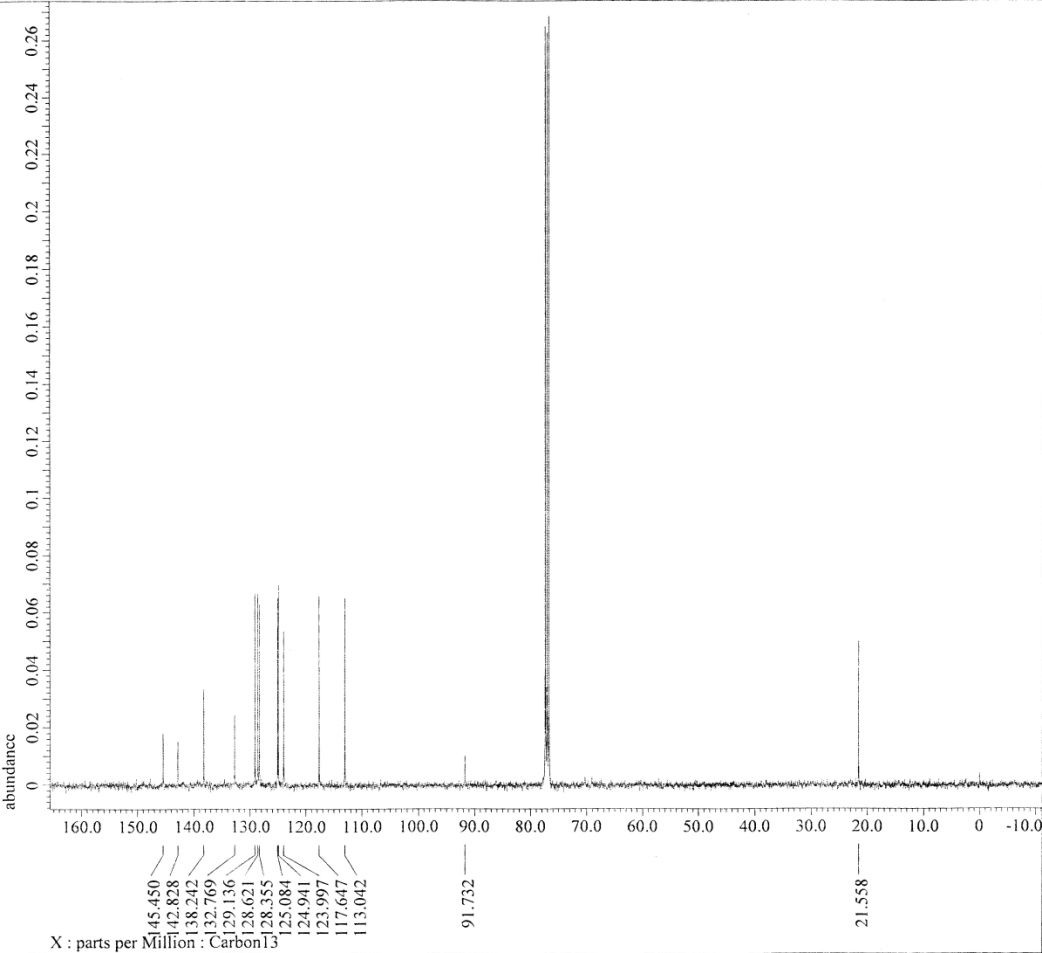


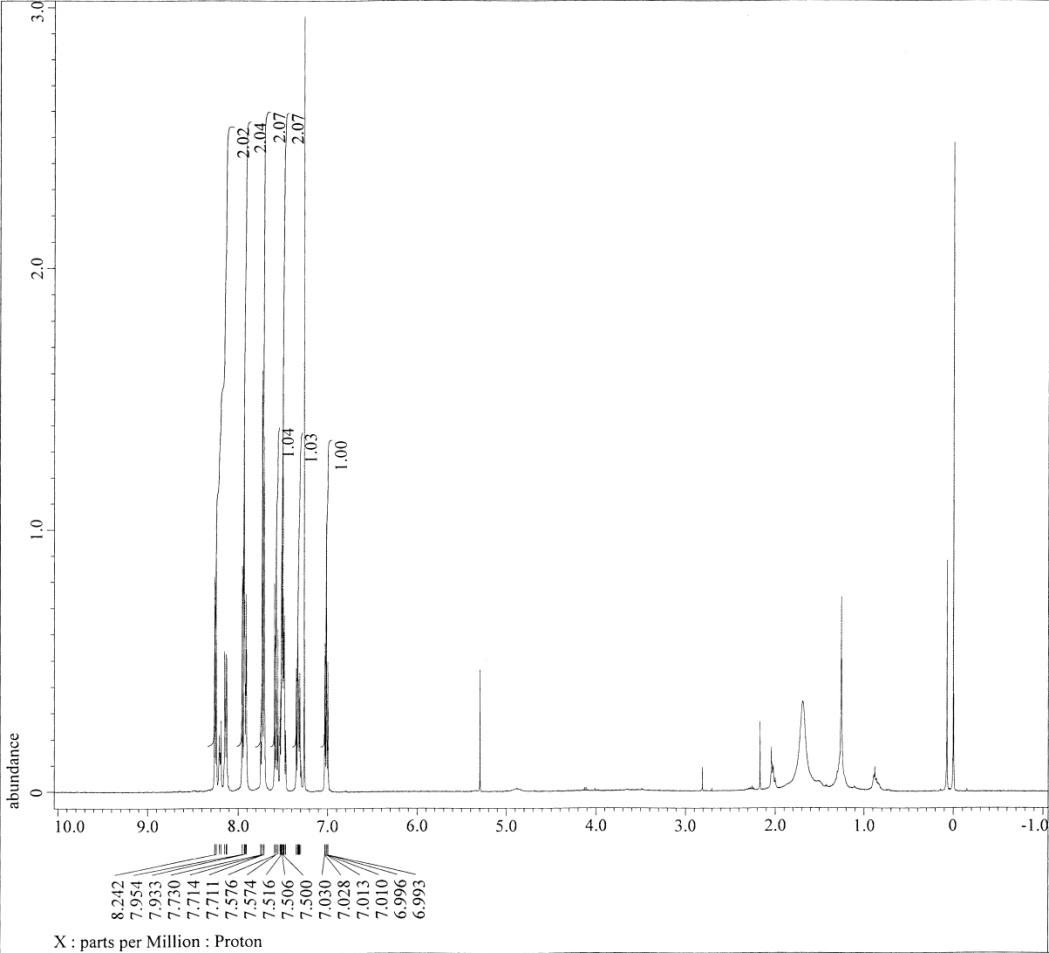
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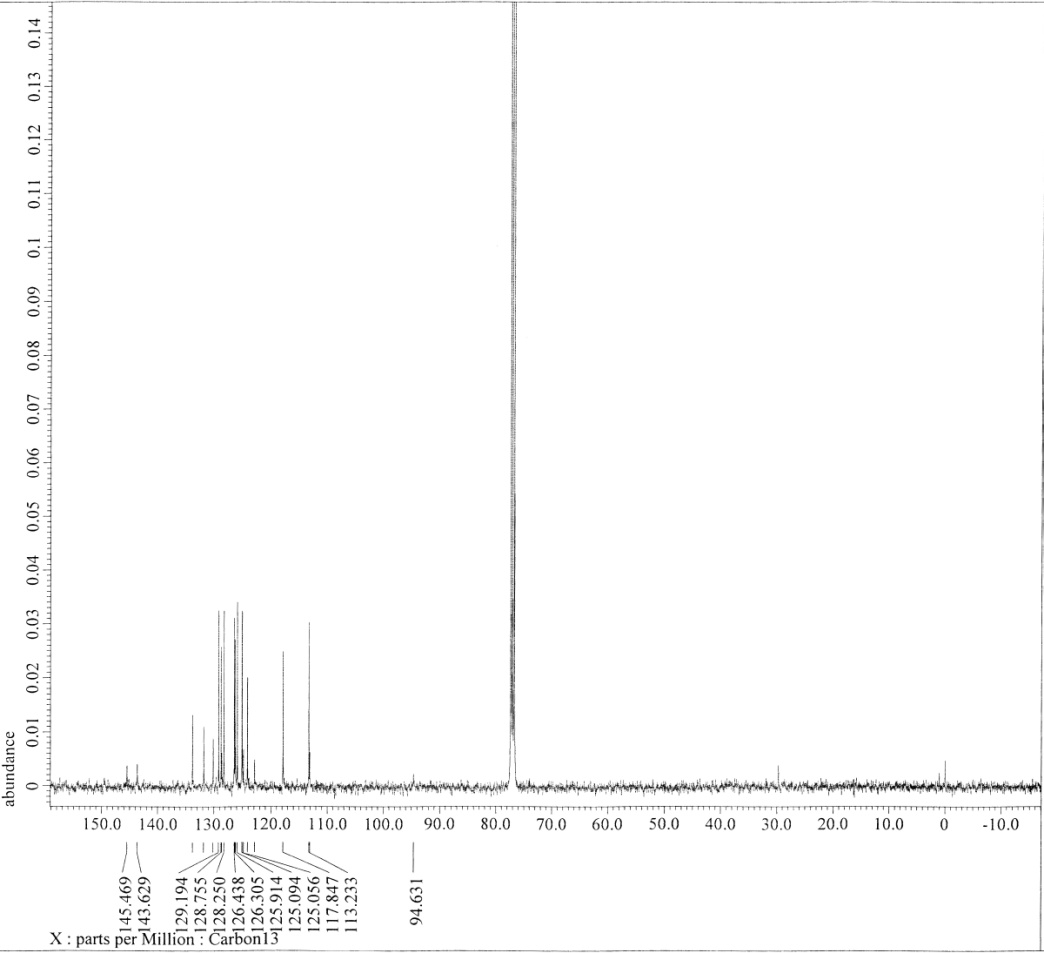


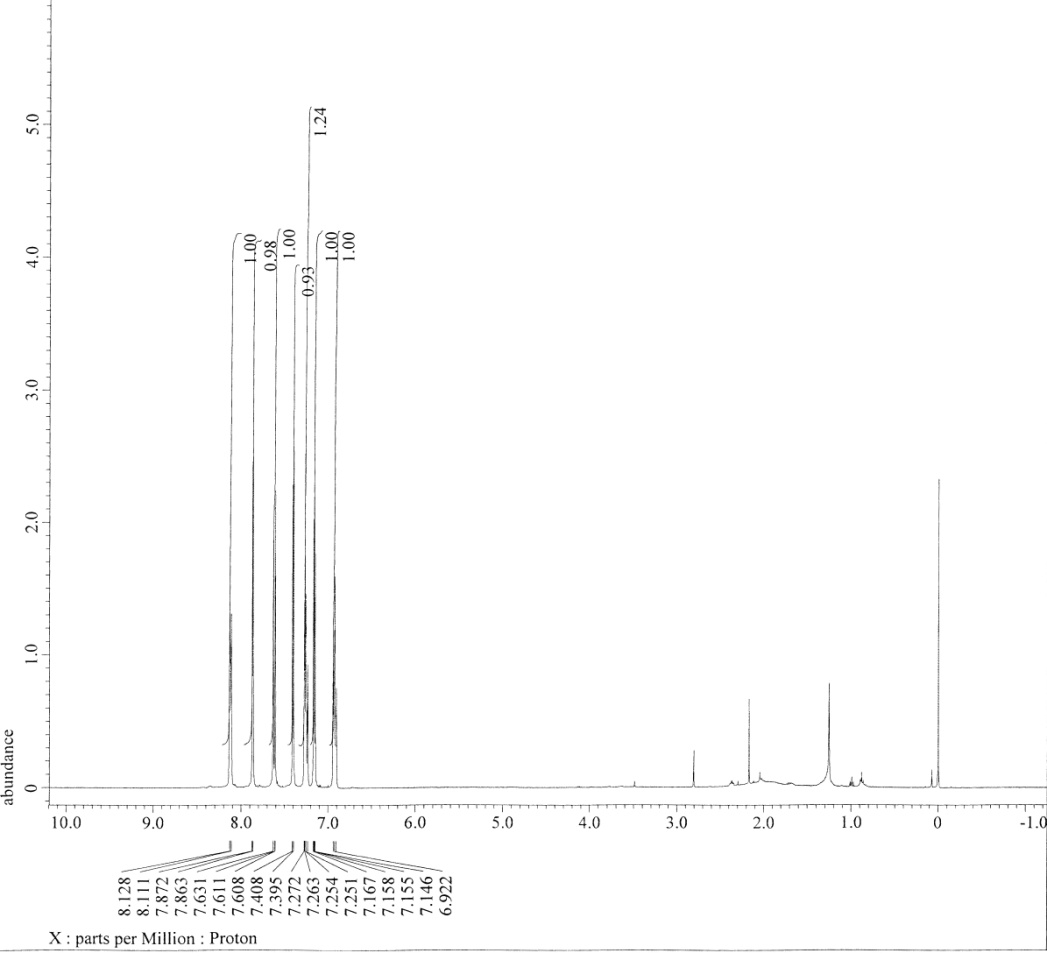




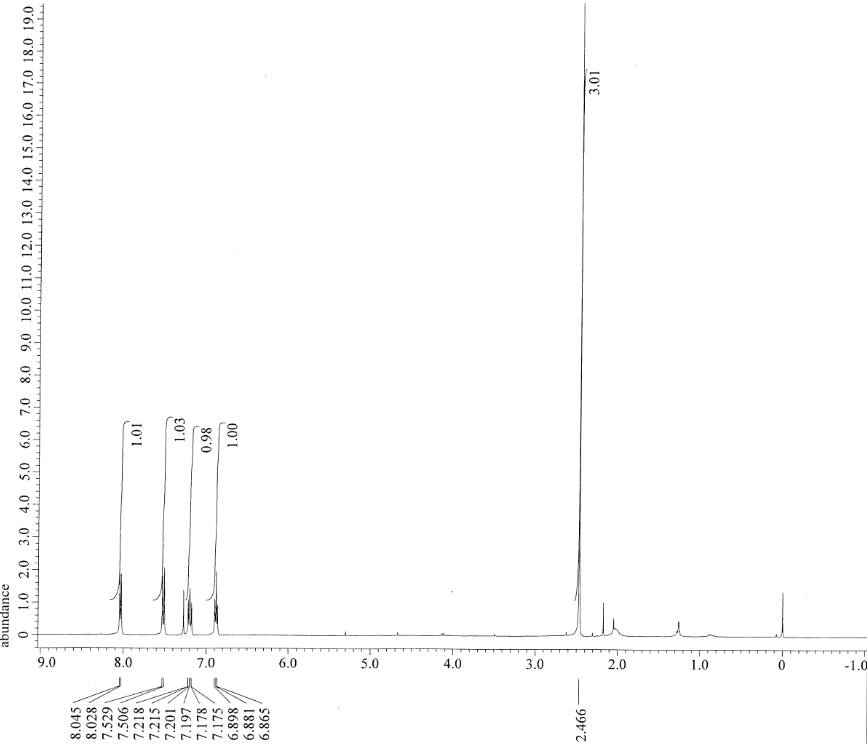
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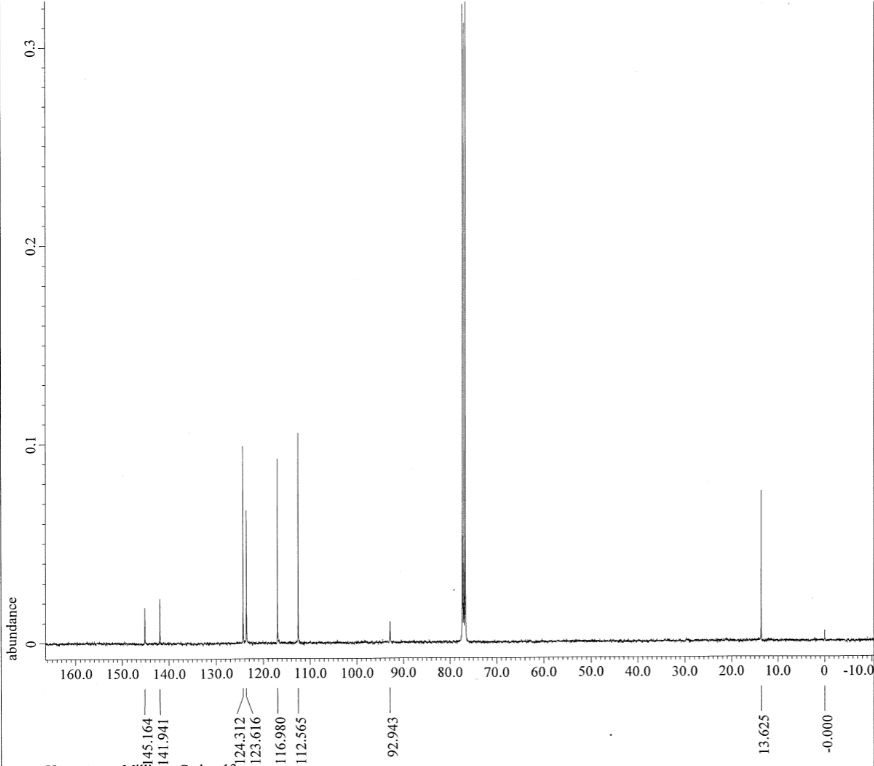


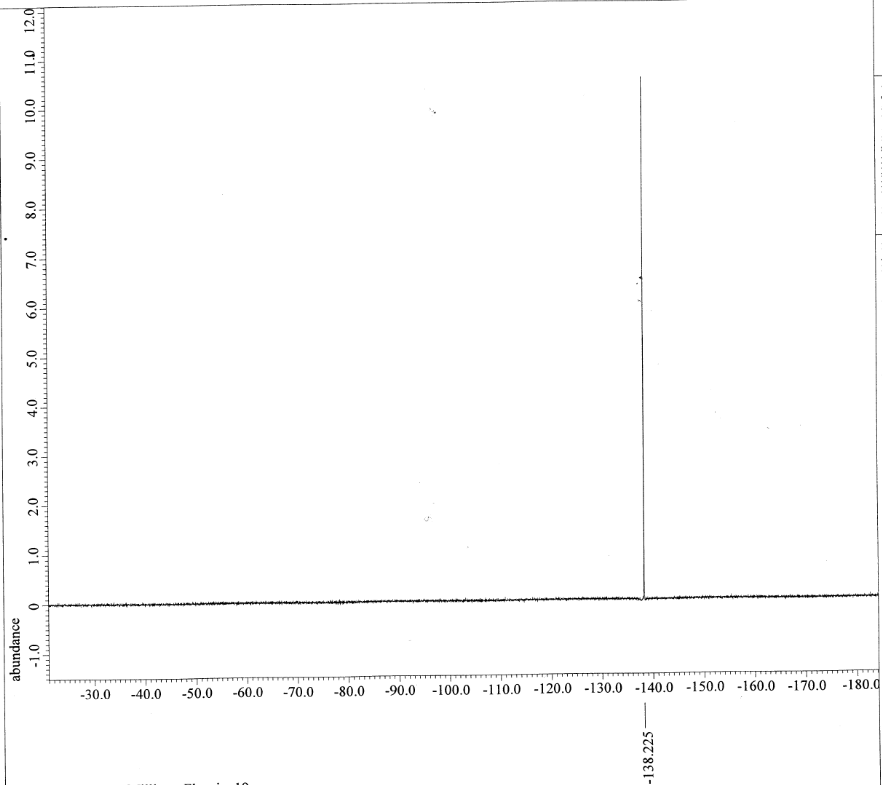
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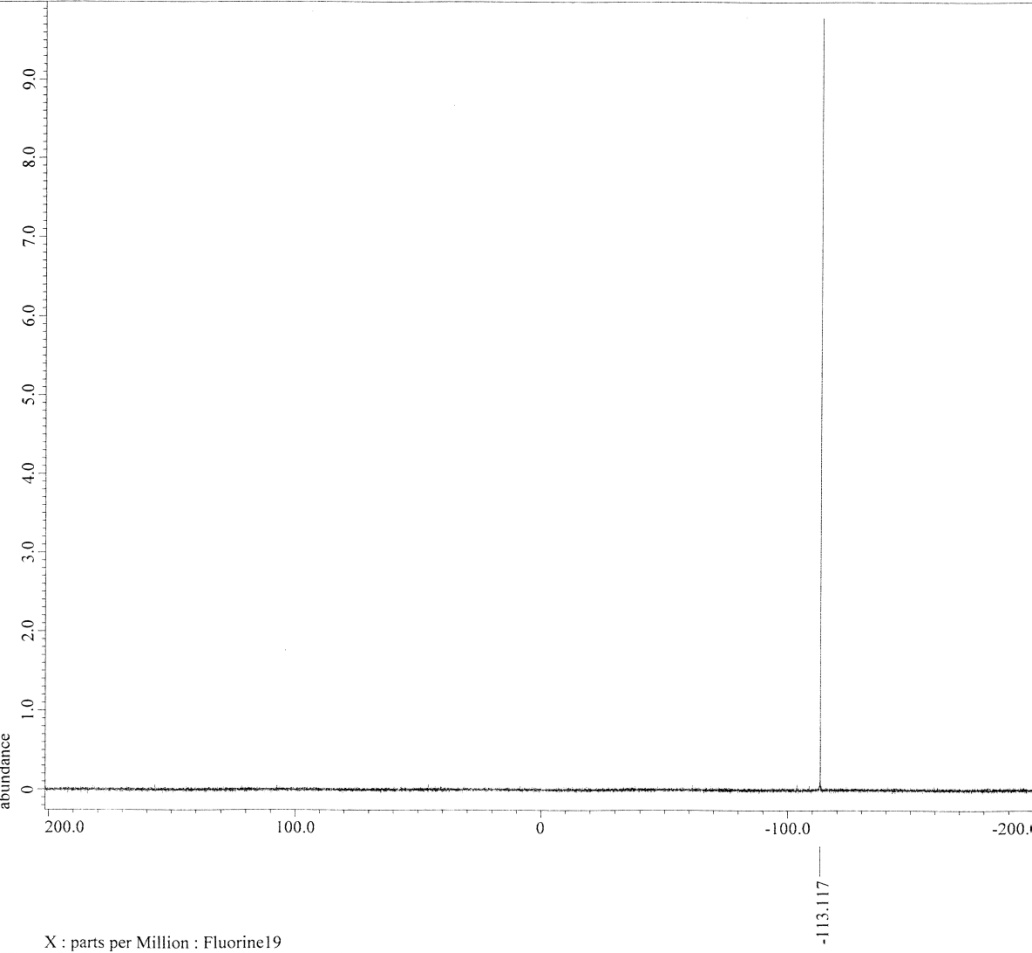


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