Electronic Supplementary Information

Indium(III) catalyzed substrate selective hydrothiolation of terminal alkynes

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General information

All the commercially available regents were used as received. IR spectra were recorded on a SHIMADZU FTIR-8400. NMR spectra were recorded on Advance DPX 300 MHz FT-NMR spectrometer using tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on ESQUIRE 3000 Mass spectrometer. All experiments were monitored by thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates (Merck). After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining $KMnO_4$ and warming in a hot air oven. Column chromatography was performed on silica gel (100-200 mesh, Merck) using ethyl acetate: hexane as eluent.

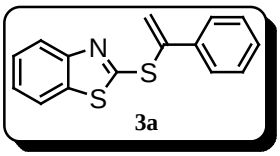
Experimental section

General procedure for hydrothiolation: Thiol (5 mmol), terminal alkyne (5.5 mmol) and $In(OTf)_3$ (0.5 mmol) were taken in a round bottom flask containing 10 ml toluene and refluxed for appropriate time. After completion of the reaction as indicated by TLC, the solvent was distilled off under reduced pressure and the crude product mixture is directly column chromatographed using ethylacetate:hexane (2:8) solvent mixture as the eluent to obtain the product **3** or **5**.

Table S1: Optimisation studies for Markovnikov hydrothiolation of phenylacetylene[a]

[a]Reaction Conditions: 2-marcaptobenzothiazole (5 mmol) and phenylacetylene were refluxed in 10 ml toluene. [b]Isolated Yield

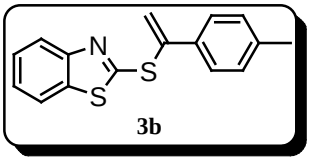
Characterization data of the Products



3a

2-(1-Phenylvinylthio)benzo[*d*]thiazole (3a)

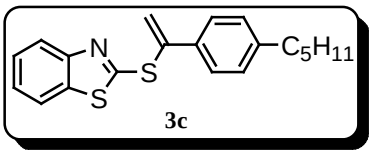
Yellow crystal; m.p. 83-85 ^{0}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.44-7.70 (m, 2H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.38-7.31 (m, 5H), 6.12 (s, 1H), 6.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.4, 153.4, 139.6, 137.6, 136.0, 129.1, 128.6, 127.4, 126.1, 125.4, 124.4, 122.1, 120.9; MS (GCMS, m/z) 195 $[M]^+$; Anal. calcd. for $C_{15}H_{11}NS_2$: C, 66.88; H, 4.12; N, 5.20. Found C, 66.92; H, 4.10; N, 5.12.



3b

2-(1-p-Tolylvinylthio)benzo[*d*]thiazole (3b)

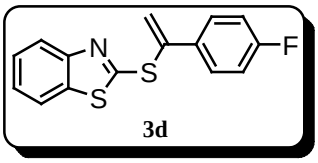
Yellow solid; m.p. 87-88 ^{0}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.92 (d, *J* = 13.74 Hz, 1H), 7.65-7.60 (m, 3H), 7.40-7.35 (m, 1H), 7.27-7.22 (m, 1H), 7.14 (d, *J* = 8.19, 2H), 6.08 (s, 1H), 6.03 (s, 1H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.8, 153.5, 139.4, 139.2, 136.0, 134.7, 129.4, 127.3, 126.1, 124.6, 124.4, 122.1, 120.9, 21.3; MS (GCMS, m/z) 283 $[M]^+$; Anal. calcd. for $C_{16}H_{13}NS_2$: C, 67.81; H, 4.62; N, 4.94. Found C, 67.88; H, 4.52; N, 4.90.



3c

2-(1-p-Pentylphenyl)vinylthio)benzo[*d*]thiazole (3c)

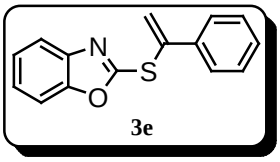
Yellow gum; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.86 (d, *J* = 8.16 Hz, 1H), 7.62-7.58 (m, 3H), 7.34-7.31 (m, 1H), 7.22-7.19 (m, 1H), 7.13 (d, *J* = 8.31 Hz, 2H), 6.06 (s, 1H), 6.0 (s, 1H), 2.62-2.51 (m, 2H), 1.60-1.50 (m, 2H), 1.32-1.22 (m, 4H), 0.85 (t, *J* = 6.75 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.9, 153.5, 144.3, 139.4, 136.0, 134.9, 128.6, 127.3, 126.1, 124.7, 124.4, 122.0, 120.9, 35.6, 31.5, 31.0, 22.6, 14.1; MS (GCMS, m/z) 339 $[M]^+$; Anal. calcd. for $C_{20}H_{21}NS_2$: C, 70.75; H, 6.23; N, 4.13. Found C, 70.79; H, 6.21; N, 4.10.



3d

2-(1-p-Fluorophenyl)vinylthio)benzo[*d*]thiazole (3d)

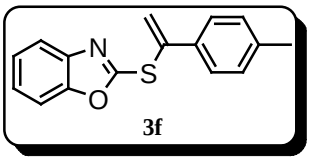
Brown gum; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.88 (d, *J* = 8.7 Hz, 1H), 7.69-7.63 (m, 3H), 7.37-7.34 (m, 1H), 7.27-7.24 (m, 1H), 7.02-6.96 (m, 2H), 6.03 (d, *J* = 3Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.9, 153.3, 138.5, 135.9, 135.5, 129.3, 129.2, 126.2, 126.1, 125.1, 124.6, 124.5, 122.1, 120.9, 116.1; MS (GCMS, m/z) 287 $[M]^+$; Anal. calcd. for $C_{15}H_{10}FNS_2$: C, 62.69; H, 3.51; N, 4.87. Found C, 62.75; H, 3.45; N, 4.82.



3e

2-(1-Phenylvinylthio)benzo[*d*]oxazole (3e)

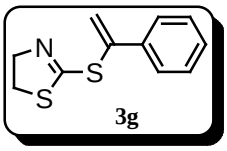
Brown gum; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69-7.66 (m, 2H), 7.56-7.34 (m, 1H), 7.33-7.18 (m, 10H), 6.07 (s, 1H), 6.03 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.9, 151.8, 141.9, 138.0, 137.3, 128.9, 128.7, 127.0, 124.4, 124.38, 124.30, 119.1, 110.0; MS (GCMS, m/z) 253 $[M]^+$; Anal. calcd. for $C_{15}H_{11}NOS$: C, 71.12; H, 4.38; N, 5.53. Found C, 71.20; H, 4.33; N, 5.48.



3f

2-(1-p-Tolylvinylthio)benzo[*d*]oxazole (3f)

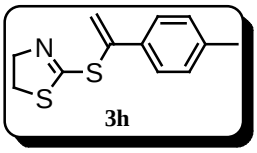
Yellow solid; m.p. 63-64 ^{0}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.58 (d, *J* = 8.13 Hz,2H), 7.37-7.34 (m, 1H), 7.25-7.19 (m, 3H), 7.12 (d, *J* = 8.04 Hz, 2H), 6.04 (s, 1H), 5.98 (s, 1H),2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.0, 151.9, 141.9, 139.0, 137.1, 135.1, 129.2, 126.9, 124.38, 124.34, 123.4, 119.2, 110.0, 21.2; MS (GCMS, m/z) 267 $[M]^+$; Anal. calcd. for $C_{16}H_{13}NOS$: C, 71.88; H, 4.90; N, 5.24. Found C, 71.83; H, 4.99; N, 5.21.



3g

2-(1-Phenylvinylthio)-4,5-dihydrothiazole (3g)

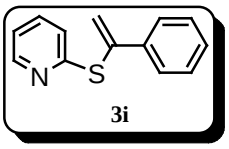
Brown gum; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.66-7.62 (m, 2H), 7.38-7.31 (m, 3H), 6.05 (s, 1H), 5.96 (s, 1H), 4.14 (t, *J* = 4.4 Hz, 2H), 3.23 (t, *J* = 4.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.9, 139.3, 138.4, 128.7, 128.3, 127.1, 125.0, 65.0, 35.1; MS (GCMS, m/z) 221 $[M]^+$; Anal. calcd. for $C_{11}H_{11}NS_2$: C, 59.69; H, 5.01; N, 6.33. Found C, 59.59; H, 4.88; N, 6.28.



3h

2-(1-p-Tolylvinylthio)-4,5-dihydrothiazole (3h)

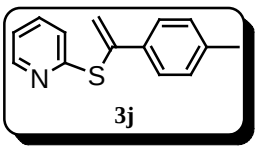
Brown gum; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.01 (s, 1H), 5.90 (s, 1H), 4.15 (t, *J* = 8.1 Hz, 2H), 3.23 (t, *J* = 8.1 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.3, 139.1, 138.7, 129.6, 129.4, 129.1, 126.9, 65.0, 35.1, 21.2; MS (GCMS, m/z) 235 $[M]^+$; Anal. calcd for $C_{12}H_{13}NS_2$: C, 61.24; H, 5.57; N, 5.95. Found C, 61.32; H, 5.55; N, 5.90.



3i

2-(1-Phenylvinylthio)pyridine (3i)

Brown gum; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.38-8.36 (m, 1H), 7.69-7.66 (m, 2H), 7.39-7.36 (m, 1H), 7.29-7.26 (m, 3H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.94 (m, 1H), 6.01 (s, 1H), 5.91 (S, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.1, 149.6, 140.6, 136.5, 128.6, 128.5, 128.4, 127.2, 123.2, 122.9, 120.1; MS (GCMS, m/z) 213 $[M]^+$; Anal. calcd for $C_{13}H_{11}NS$: C, 73.20; H, 5.20; N, 6.57. Found C, 73.31; H, 5.24; N, 6.48.

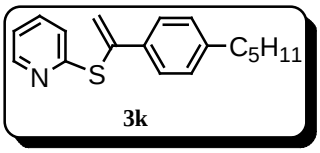


3j

2-(1-p-Tolylvinylthio)pyridine (3j)

Brown gum; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.31-8.30 (m, 1H), 7.51 (d, *J* = 8.1Hz, 2H), 7.32-7.29 (m, 1H), 7.03-6.95 (m. 3H), 6.89-6.85 (m, 1H), 5.91 (s, 1H), 5.80 (s, 1H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.4, 149.6, 140.4, 138.5, 136.5, 135.5, 129.1, 127.0, 122.8,

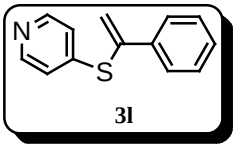
122.4, 120.0, 21.1; MS (GCMS, m/z) 227 $[M]^+$; Anal. calcd for $C_{14}H_{13}NS$: C, 73.97; H, 5.76; N, 6.16. Found C, 73.91; H, 5.73; N, 6.11.



3k

2-(1-p-Pentylphenyl)vinylthio)pyridine (3k)

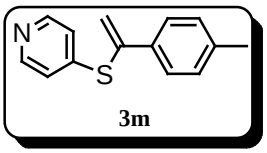
Brown gum; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.32-8.30 (m, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.32-7.28 (m, 1H), 7.03-6.95 (m, 3H), 6.89-6.86 (m, 1H), 5.92 (s, 1H), 5.79 (s, 1H), 2.48 (t, *J* = 7.6 Hz, 2H), 1.52-1.45 (m, 2H), 1.27-1.14 (m, 4H), 0.79 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.4, 149.6, 143.6, 140.4, 136.5, 135.6, 128.4, 127.0, 122.7, 122.4, 120.0, 35.5, 31.4, 30.9, 22.5, 14.0 ; MS (GCMS, m/z) 283 $[M]^+$; Anal. calcd for $C_{18}H_{21}NS$: C, 76.28; H, 7.47; N, 4.94. Found C, 76.35; H, 7.41; N, 4.88.



3l

4-(1-Phenylvinylthio)pyridine (3l)

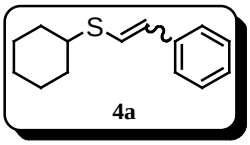
Brown gum; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.30 (d, *J* = 6.1 Hz, 2H), 7.64-7.60 (m, 2H), 7.34-7.29 (m, 3H), 7.05 (d, *J* = 6.1 Hz, 2H), 6.09 (s, 1H), 5.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.1, 147.9, 139.2, 137.5, 129.0, 128.6, 127.0, 124.5, 122.0 ; MS (GCMS, m/z) 213 $[M]^+$; Anal. calcd for $C_{13}H_{11}NS$: C, 73.20; H, 5.20; N, 6.57. Found C, 73.27; H, 5.14; N, 6.53.



3m

4-(1-p-Tolylvinylthio)pyridine (3m)

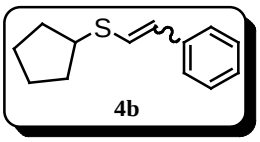
Brown gum; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.30-8.28 (m, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.05-7.03 (m, 2H), 6.06 (s, 1H), 5.87 (s, 1H), 2.32 (s, 3H); MS (GCMS, m/z) 227 $[M]^+$; Anal. calcd for $C_{14}H_{13}NS$: C, 73.97; H, 5.76; N, 6.16. Found C, 73.92; H, 5.81; N, 6.11.



4a

Cyclohexyl(styryl)sulfane (4a)

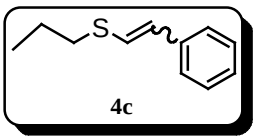
Yellow gum; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36-7.15 (m, 5H), 6.78 (d, *J* = 15.6 Hz, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 3.01-2.92 (m, 1H), 2.07-1.99 (m, 2H), 1.81-1.78 (m, 2H), 1.50-1.25 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.1, 128.6, 128.2, 126.9, 125.5, 124.0, 45.3, 33.6, 29.7, 26.0, 25.6; MS (GCMS, m/z) 218 $[M]^+$; Anal. calcd for $C_{14}H_{18}S$: C, 77.01; H, 8.31. Found C, 77.13; H, 8.25.



4b

Cyclopentyl(styryl)sulfane (4b)

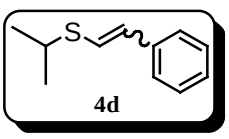
Yellow gum; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38-7.14 (m, 5H), 6.79 (d, *J* = 15.6 Hz, 1H), 6.52 (d, *J* = 15.6 Hz, 1H), 3.50-3.34 (m, 1H), 2.14-2.06 (m, 2H), 1.78-1.55 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.2, 128.6, 127.5, 126.8, 125.5, 125.1, 44.7, 33.6, 24.9; MS (GCMS, m/z) 204 $[M]^+$; Anal. calcd for $C_{13}H_{16}S$: C, 76.41; H, 7.89. Found C, 76.44; H, 7.80.



4c

Propyl(styryl)sulfane (4c)

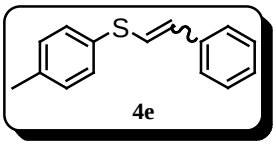
Yellow gum; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.61-7.15 (m, 5H), 6.74 (d, *J* = 15.6 Hz, 1H), 6.48 (d, *J* = 15.6 Hz, 1H), 2.77 (t, *J* = 7.3 Hz, 2H), 1.78-1.66 (m, 2H), 1.03 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.1, 128.4, 126.7, 126.6, 125.4, 125.3, 34.6, 22.8, 13.4; MS (GCMS, m/z) 178 $[M]^+$; Anal. calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.91. Found C, 74.17; H, 7.80.



4d

Isopropyl(styryl)sulfane (4d)

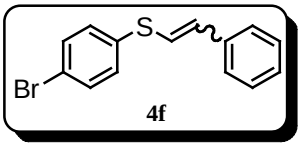
Yellow gum; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.46-7.18 (m, 5H), 6.78 (d, *J* = 15.6 Hz, 1H), 6.59 (d, *J* = 15.6 Hz, 1H), 3.28-3.09 (m,1H), 1.38-1.35 (m,6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.1, 128.8, 128.6, 126.9, 125.6, 124.1, 36.8, 23.4; MS (GCMS, m/z) 178 $[M]^+$; Anal. calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.91. Found C, 74.21; H, 7.88.



4e

Styryl(p-tolyl)sulfane (4e)

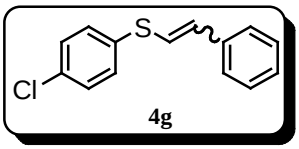
Yellow gum; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50 (d, *J* = 8.1 Hz, 1H), 7.36-7.20 (m, 7H), 7.13 (d, *J* = 7.9 Hz, 1H), 6.86 (d, *J* = 15.4 Hz, 1H), 6.65 (d, *J* = 15.4 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.4, 136.8, 130.7, 130.2, 128.9, 128.6, 127.6, 127.2, 126.1, 124.6, 21.6; MS (GCMS, m/z) 226 $[M]^+$; Anal. calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.23. Found C, 79.66; H, 6.27.



4f

(4-Bromophenyl)(styryl)sulfane (4f)

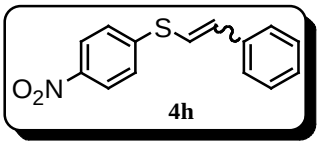
Colourless crystal; m.p 56-57 ^{0}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.49-7.24 (m, 9H), 6.84 (d, *J* = 15.4 Hz, 1H), 6.77 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 136.2, 135.4, 132.2, 131.4, 128.8, 128.4, 128.2, 127.9, 124.9, 122.2; MS (GCMS, m/z) 290 $[M]^+$; Anal. calcd for $C_{14}H_{11}$ BrS: C, 57.74; H, 3.81. Found C, 57.67; H, 3.93.



4g

(4-Chlorophenyl)(styryl)sulfane (4g)

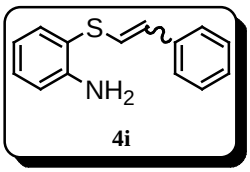
Colourless crystal m.p 41-42^{0}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.49 (d, *J* = 7.9 Hz, 1H), 7.38-7.25 (m, 8H), 6.83 (d, *J* = 15.4 Hz, 1H), 6.75 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 136.3, 133.9, 132.8, 130.9, 129.3, 128.8, 128.4, 127.4, 126.1, 125.2; MS (GCMS, m/z) 246 $[M]^+$; Anal. calcd for $C_{14}H_{11}$ ClS: C, 68.14; H, 4.49. Found C, 68.22; H, 4.41.



4h

(4-Nitrophenyl)(styryl)sulfane (4h)

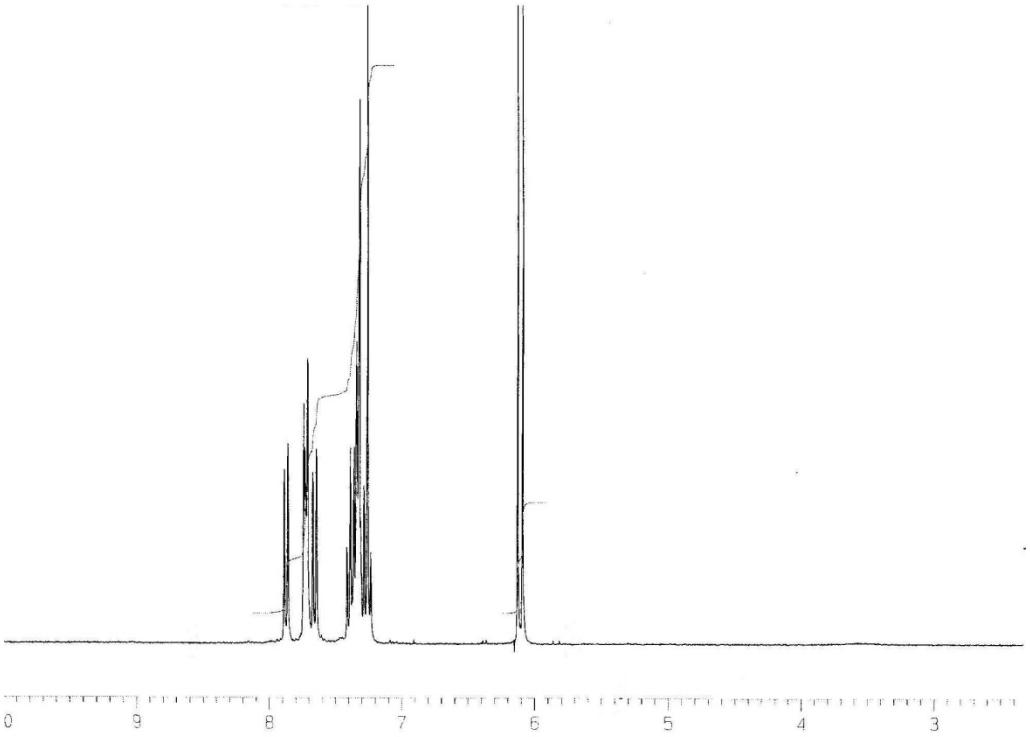
Yellow crystal; m.p 88-90 ^{0}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.20 (d, *J* = 7.0 Hz, 2H), 7.55-7.38 (m, 7H), 6.89 (d, *J* = 10.5 Hz, 1H), 6.54 (d, *J* = 10.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.7, 135.5, 132.0, 128.9, 128.4, 128.0, 127.8, 124.2, 124.1, 120.6; MS (GCMS, m/z) 257 $[M]^+$; Anal. calcd for $C_{14}H_{11}NO_2S$: C, 65.35; H, 4.31; N, 5.44. Found C, 65.30; H, 4.35; N, 5.36.



4i

2-(Styrylthio)aniline (4i)

Yellow solid m.p 51-52^{0}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55 (d, *J* = 7.55 Hz, 2H), 7.43-7.15 (m, 6H), 6.74-6.69 (m, 1H), 6.52 (d, *J* = 10.7 Hz, 1H), 6.18 (d, *J* = 10.7 Hz, 1H), 4.22 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ MS (GCMS, m/z) 227 $[M]^+$; Anal. calcd for $C_{14}H_3NS$: C, 73.97; H, 5.76; N, 6.16. Found C, 74.17; H, 5.61; N, 6.04.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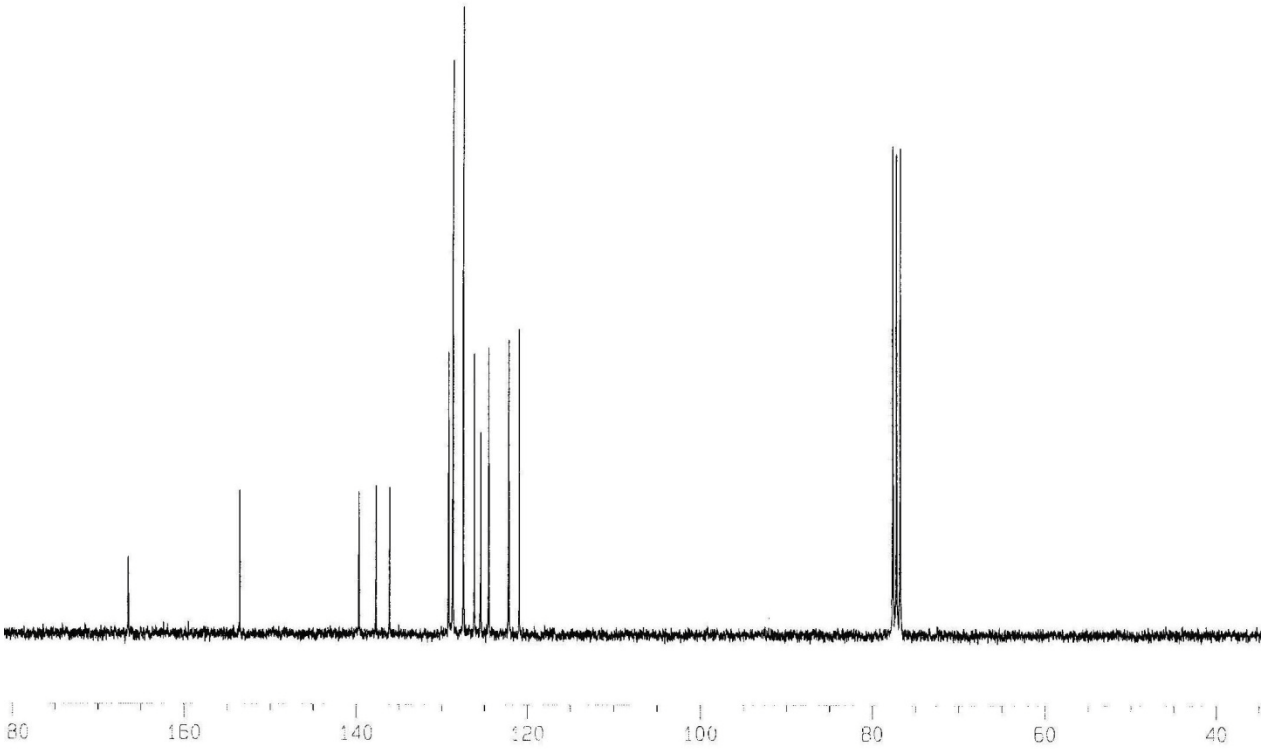
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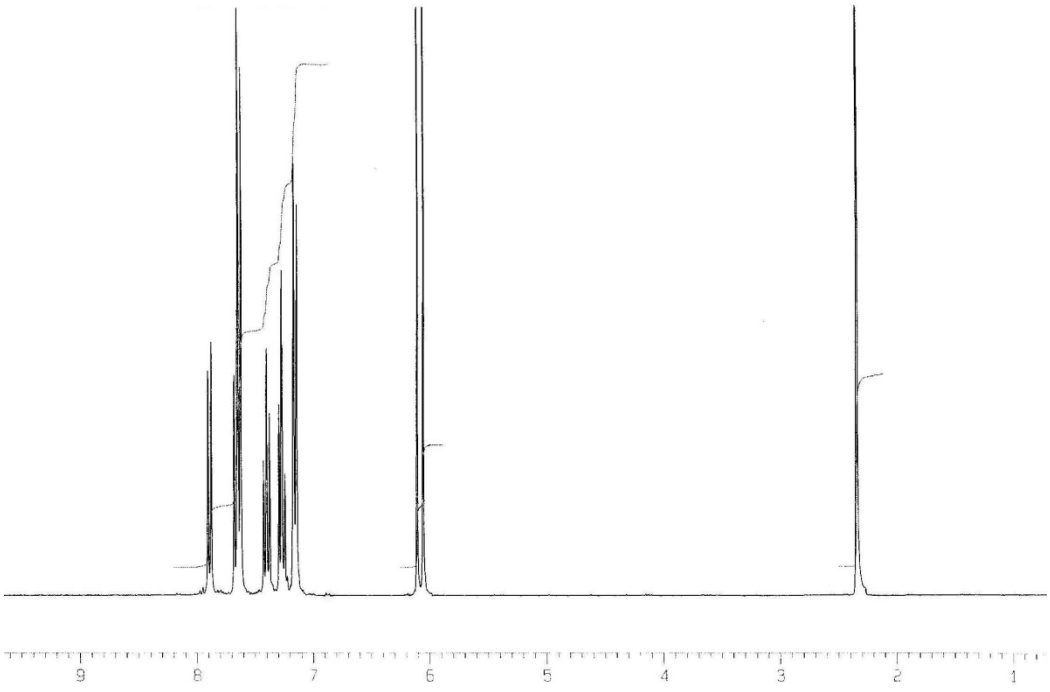

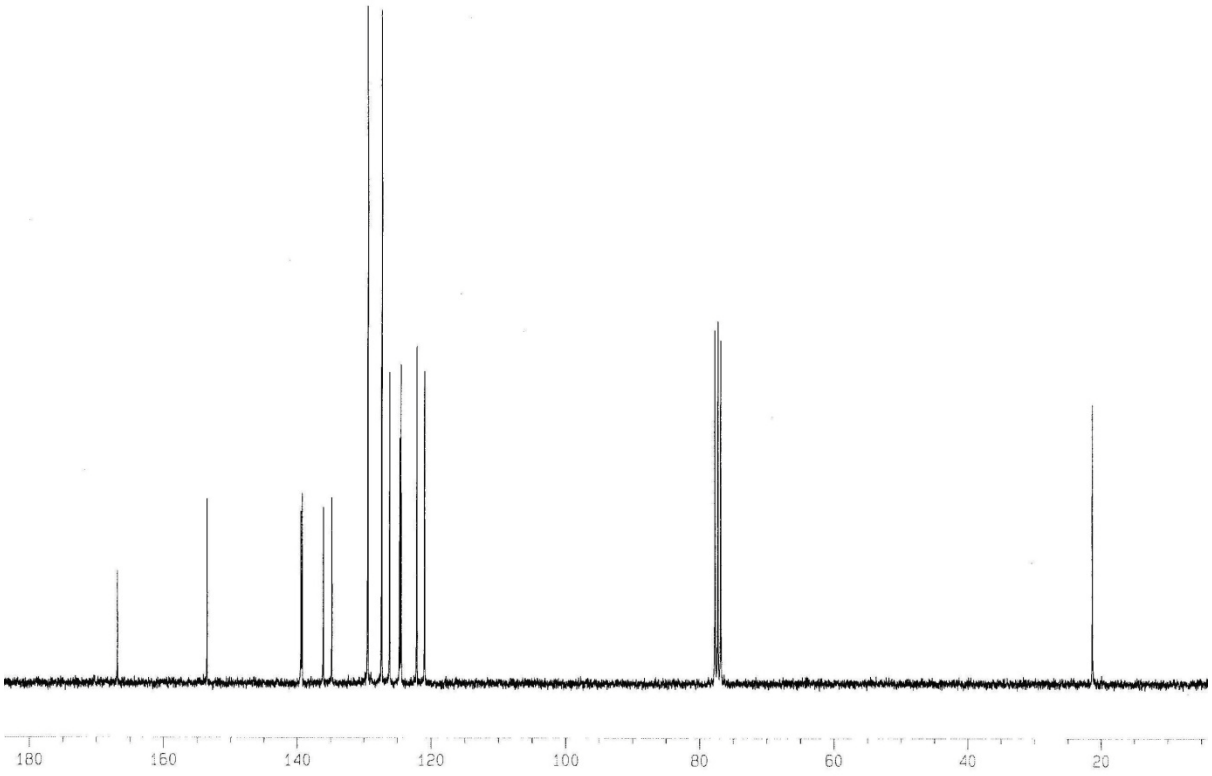

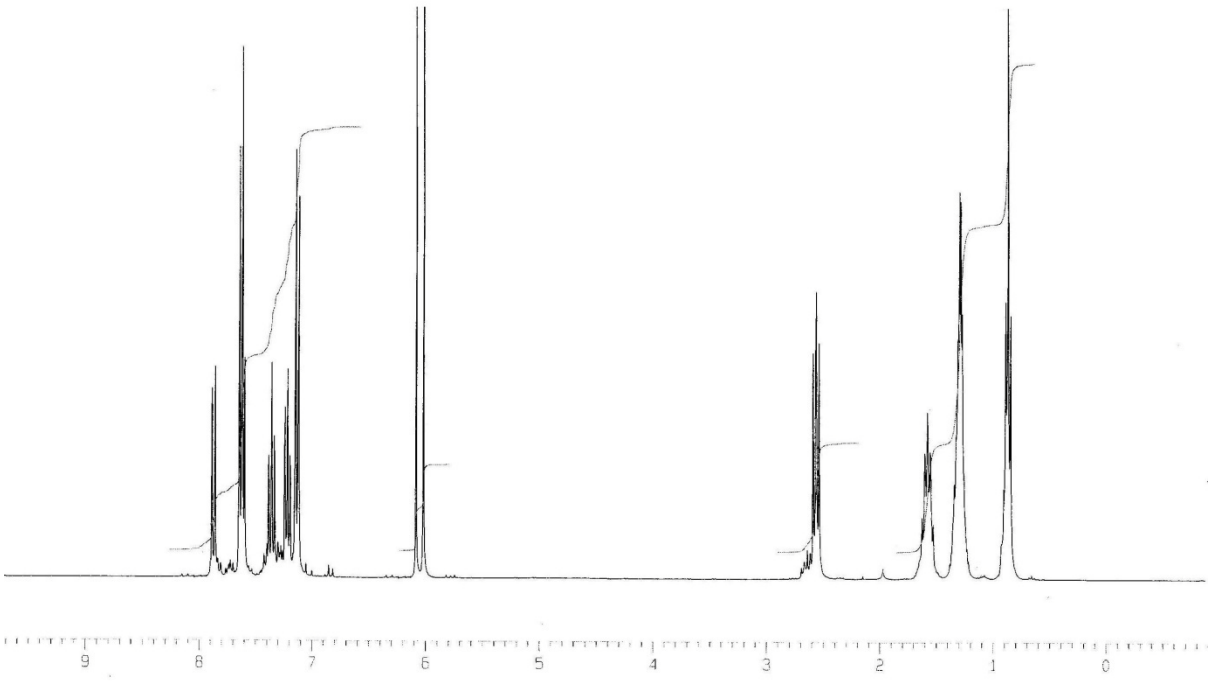
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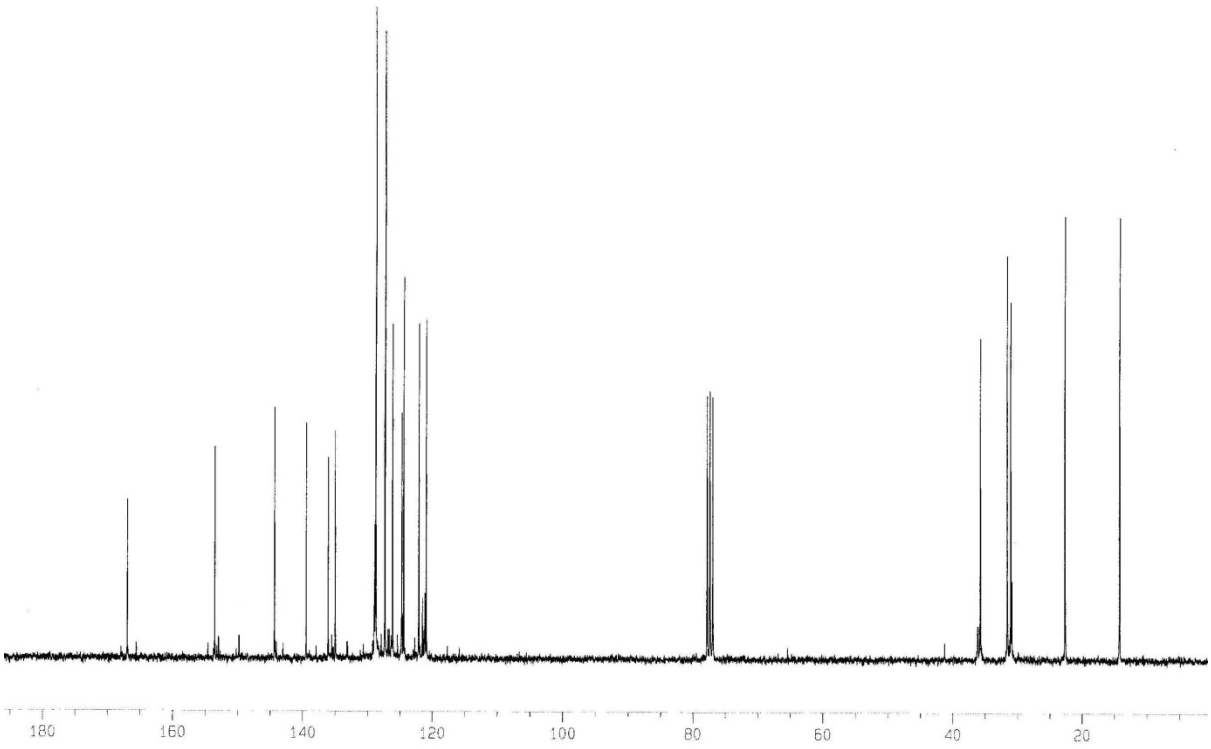
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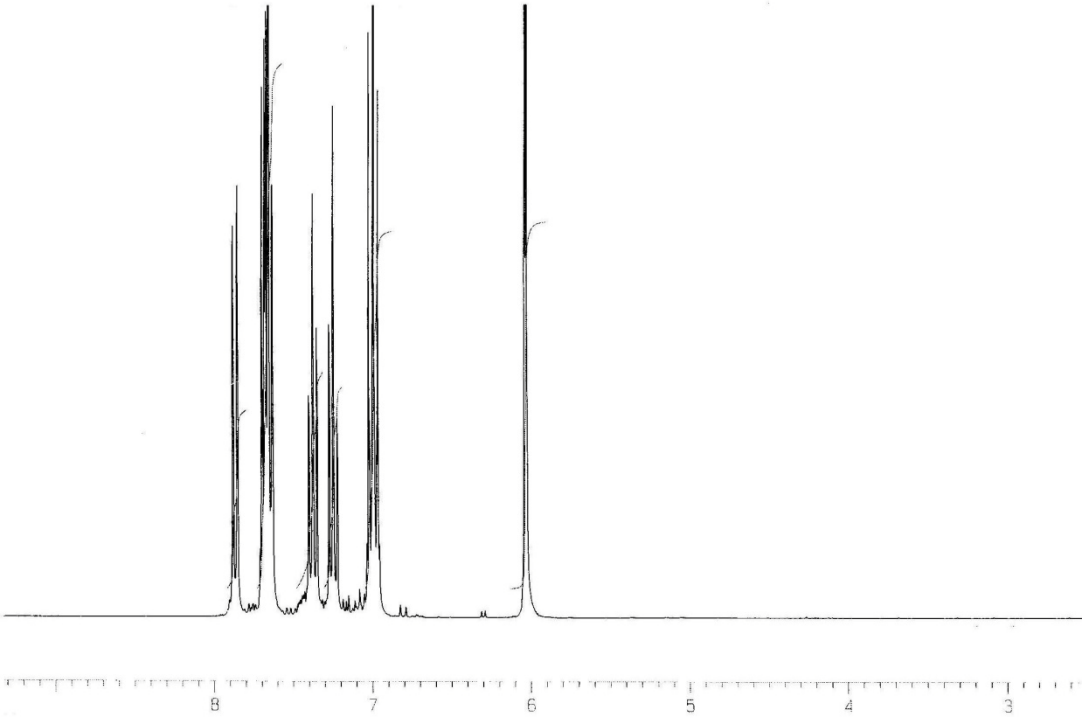
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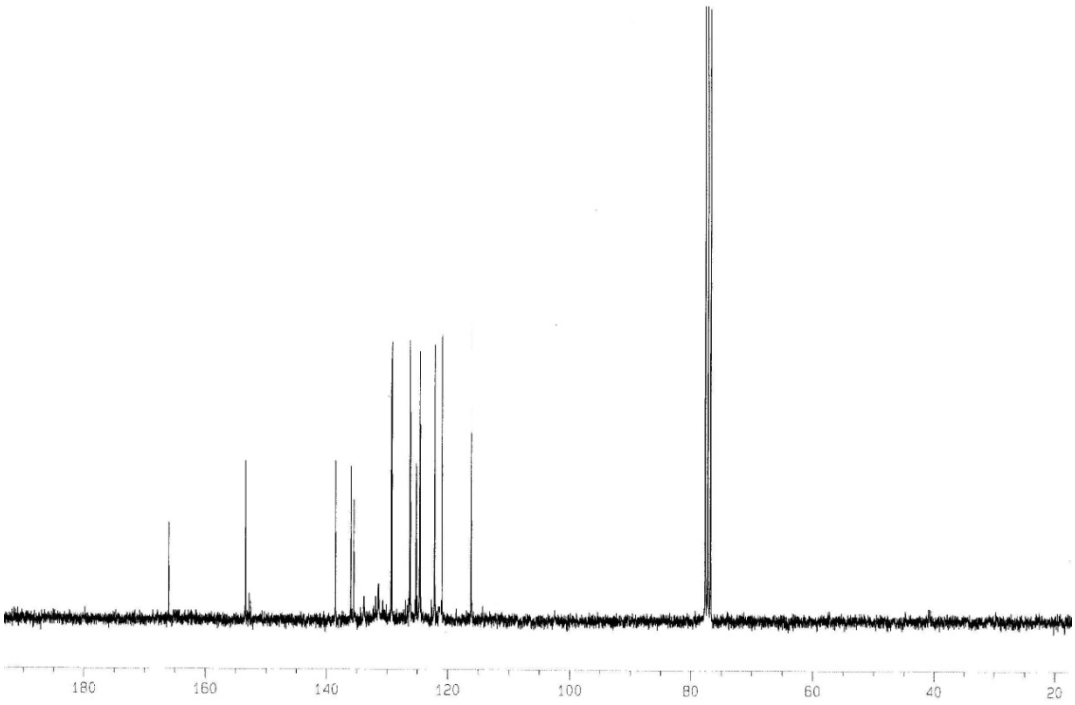
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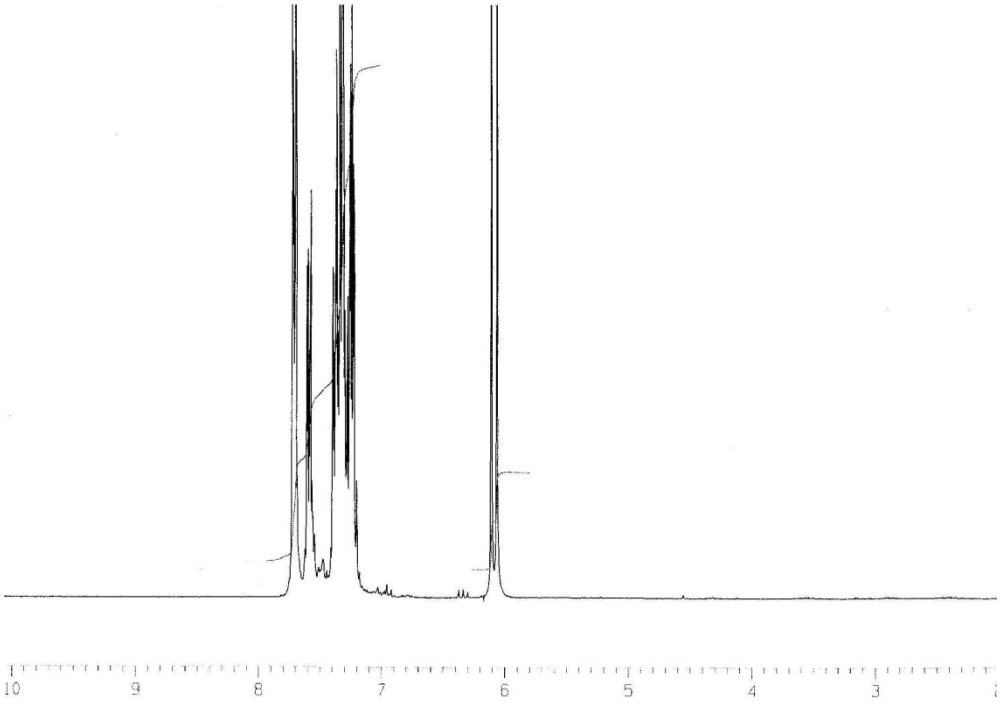

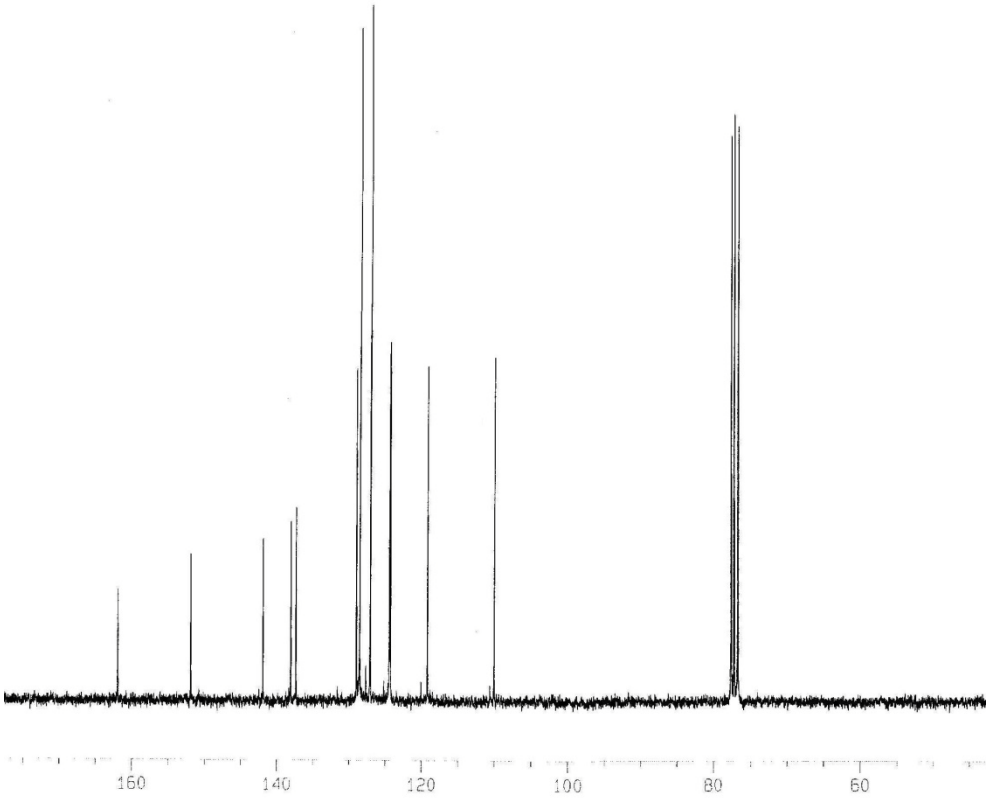

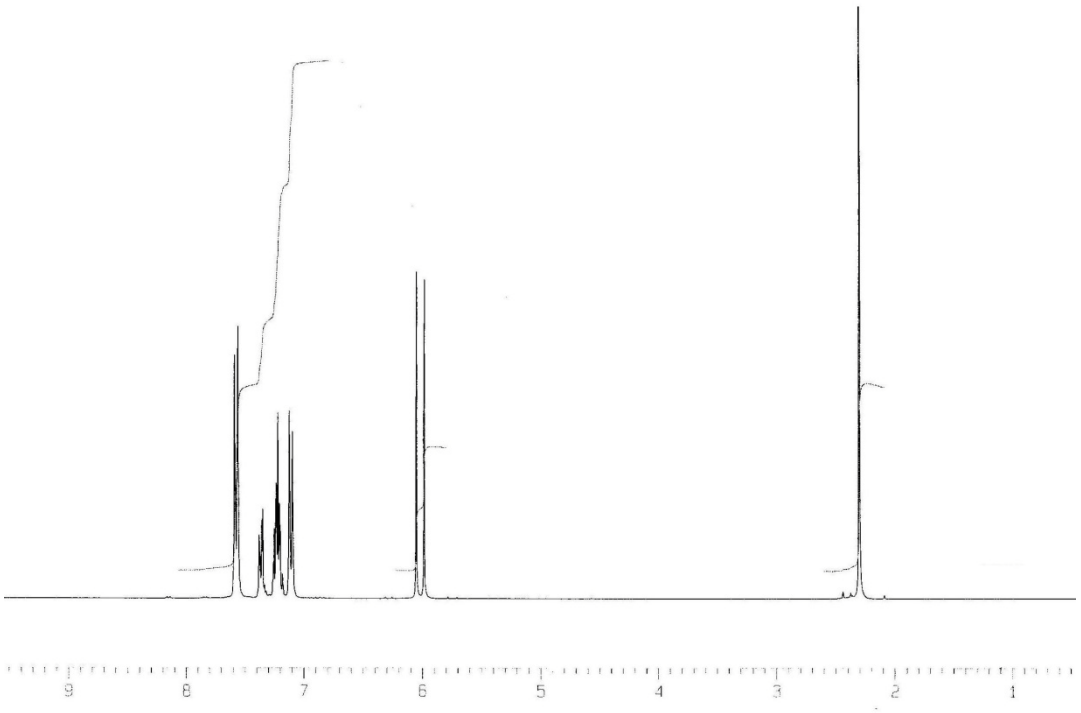
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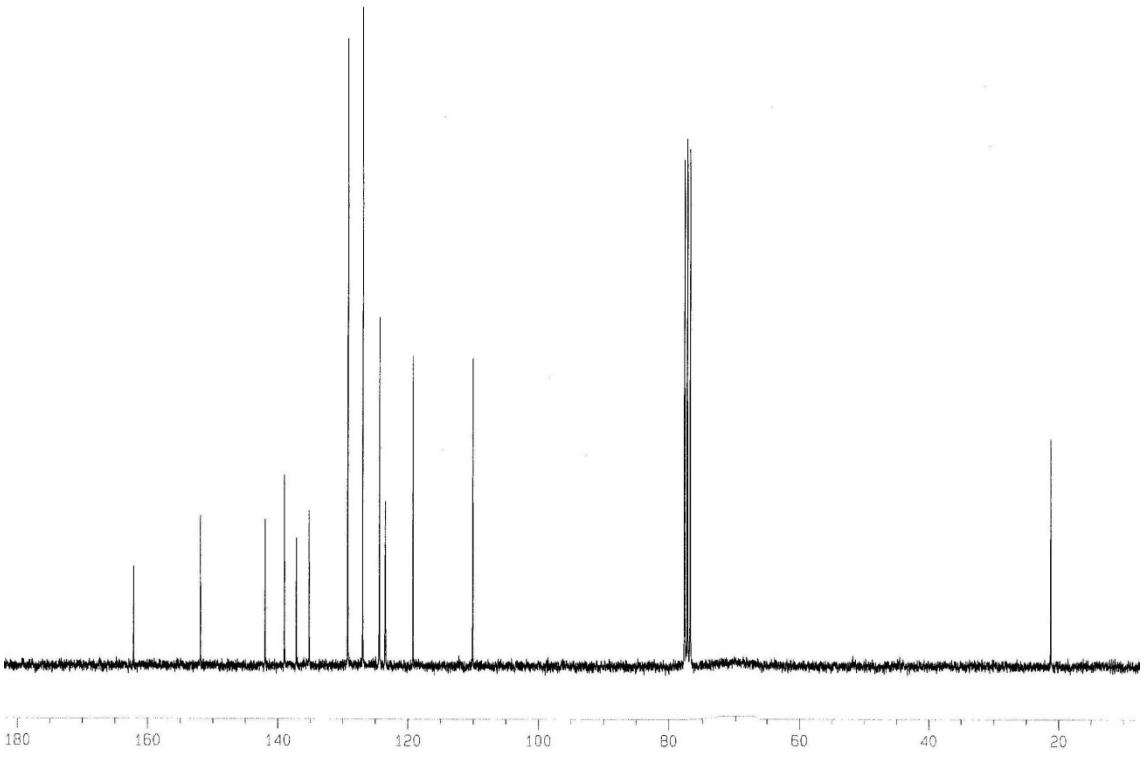
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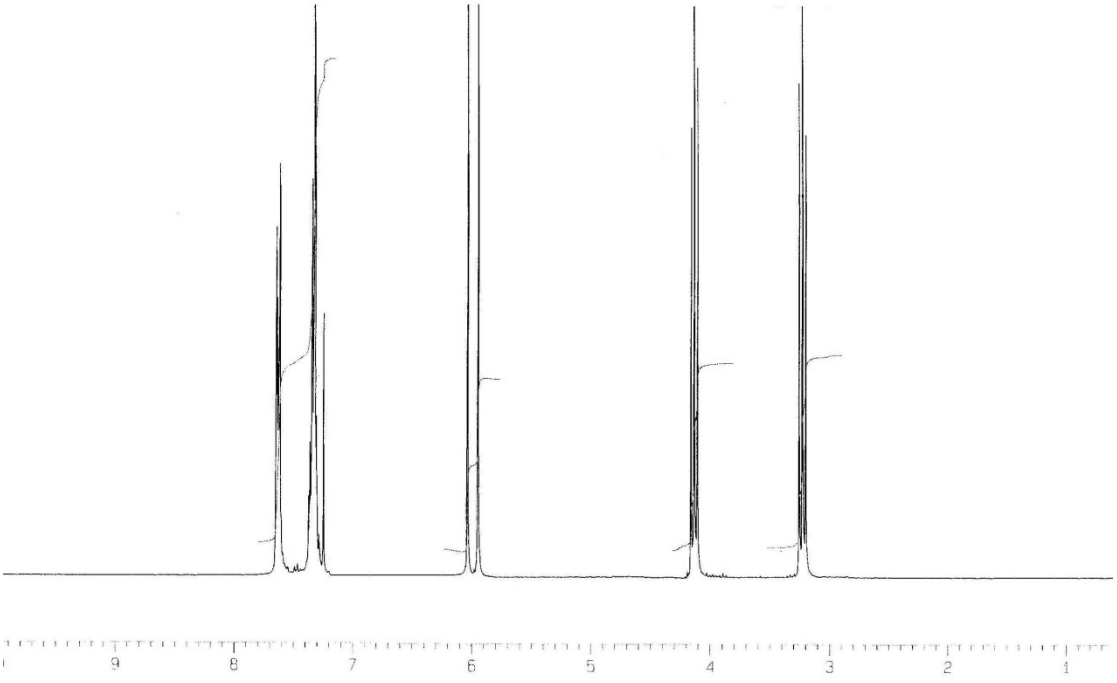
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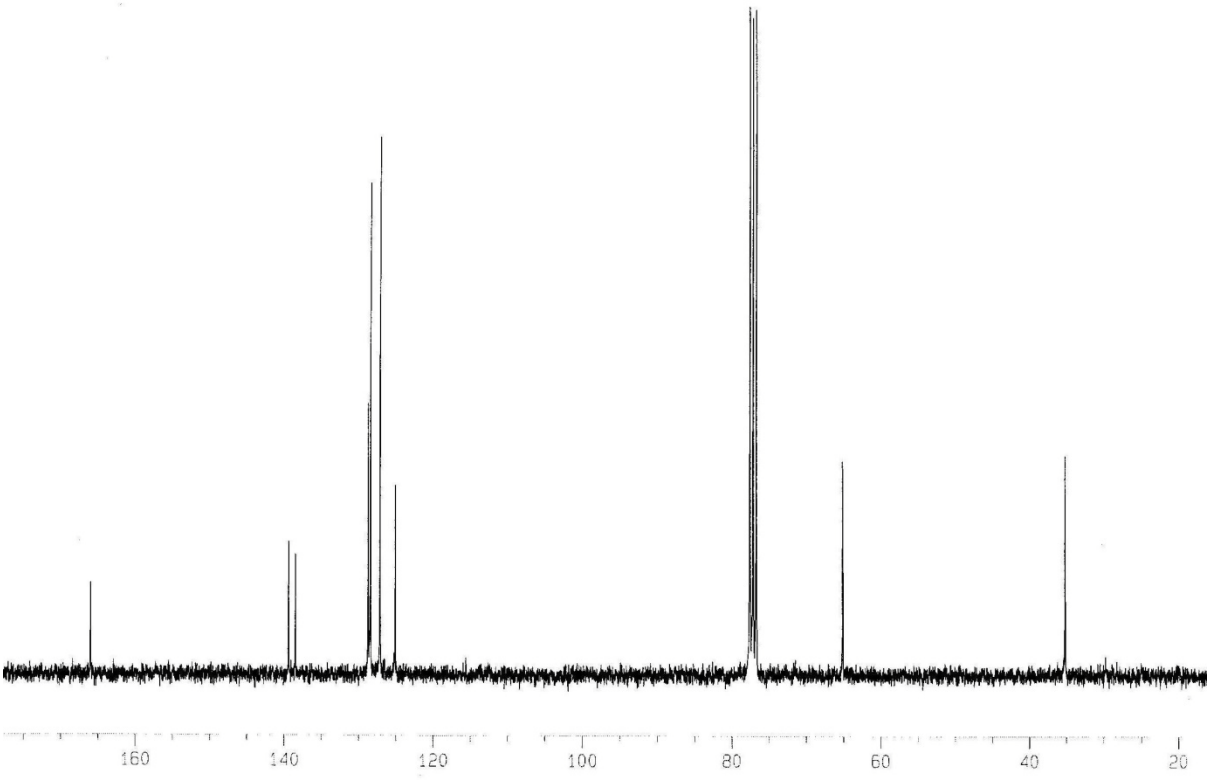
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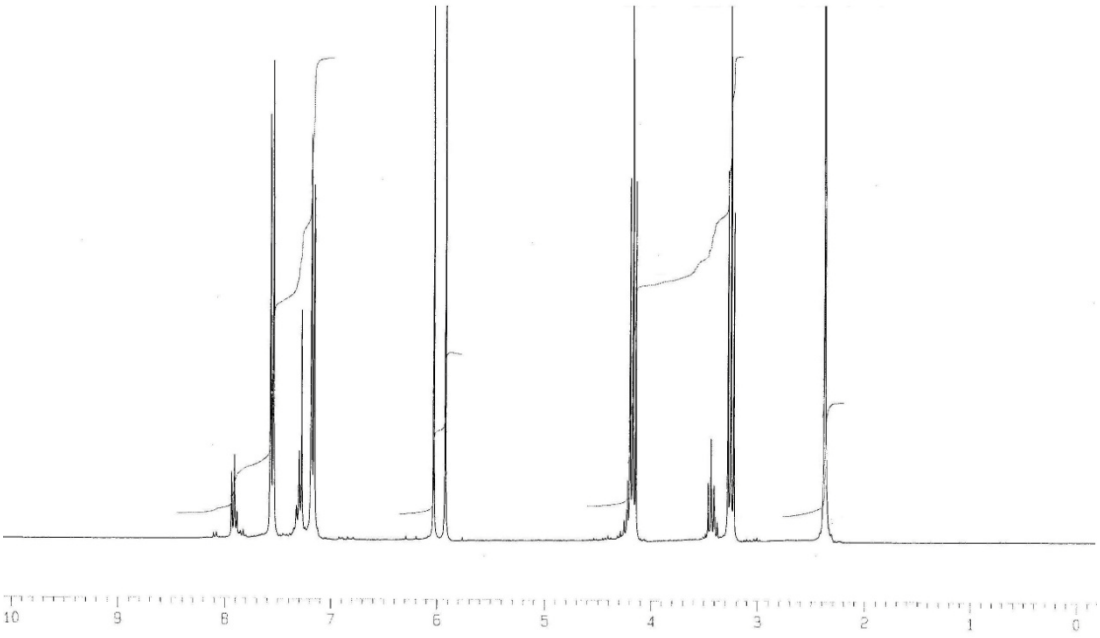
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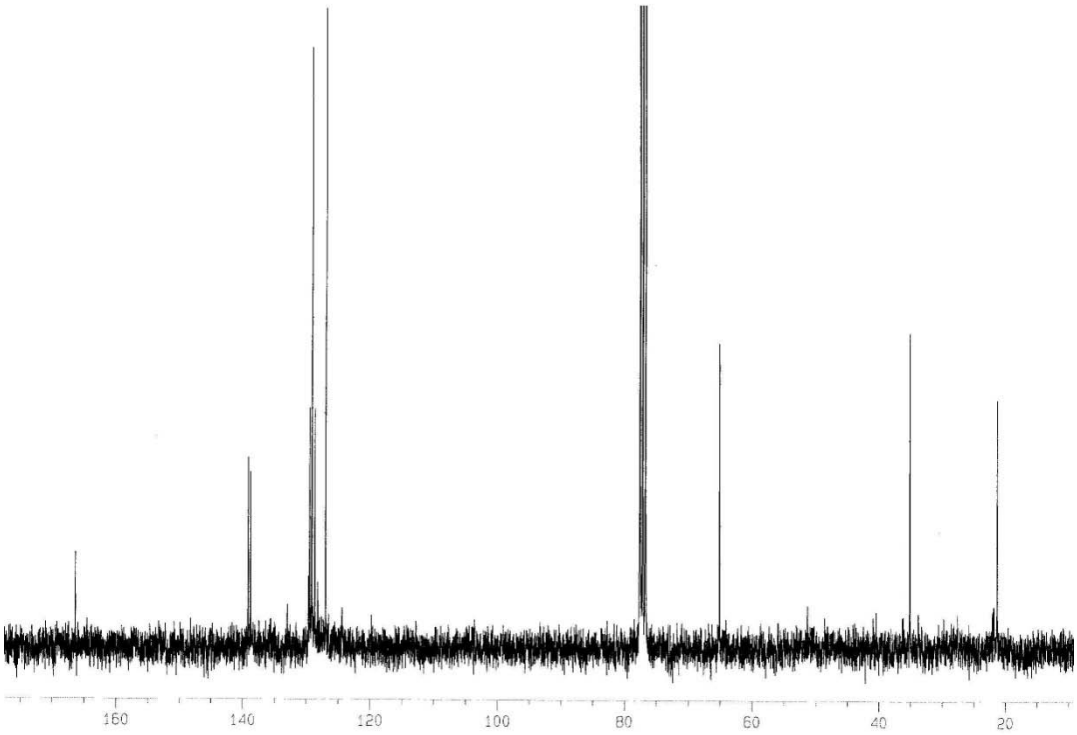
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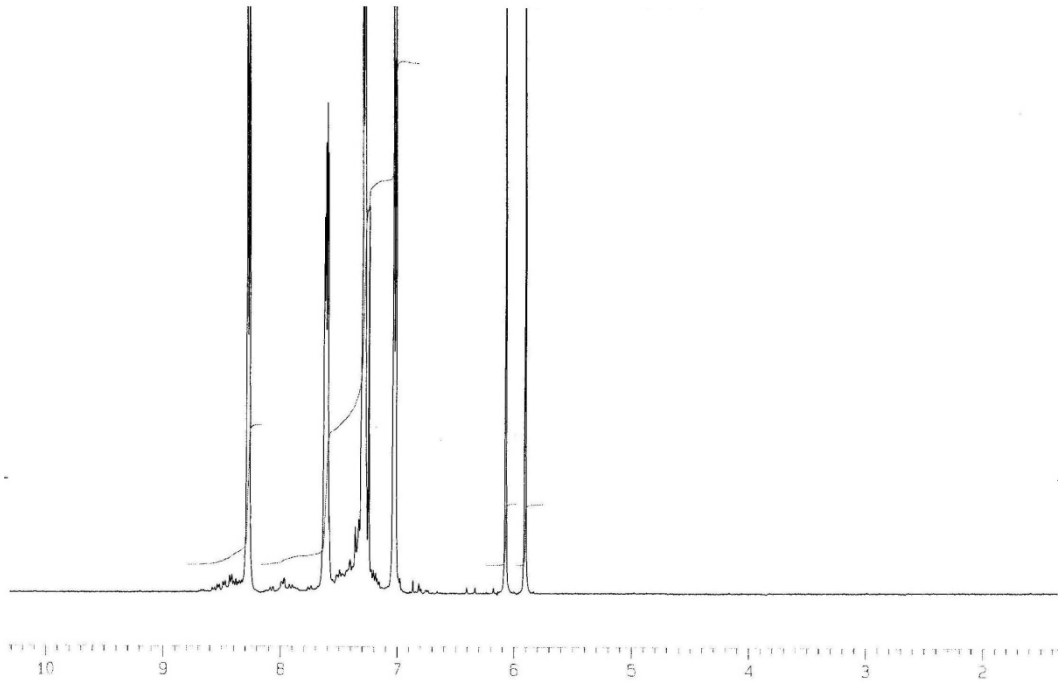

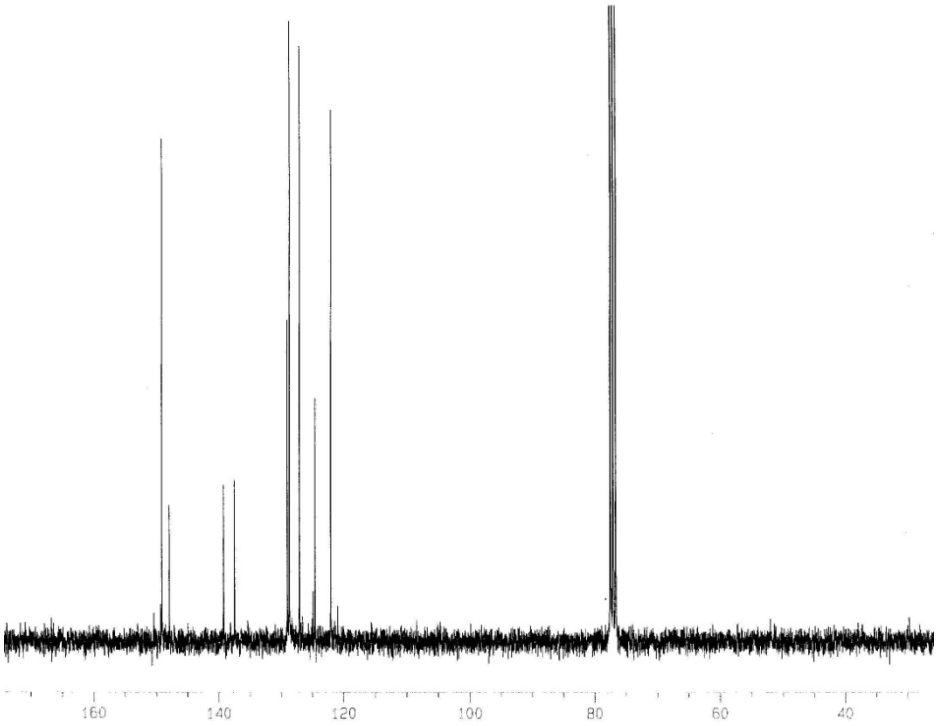

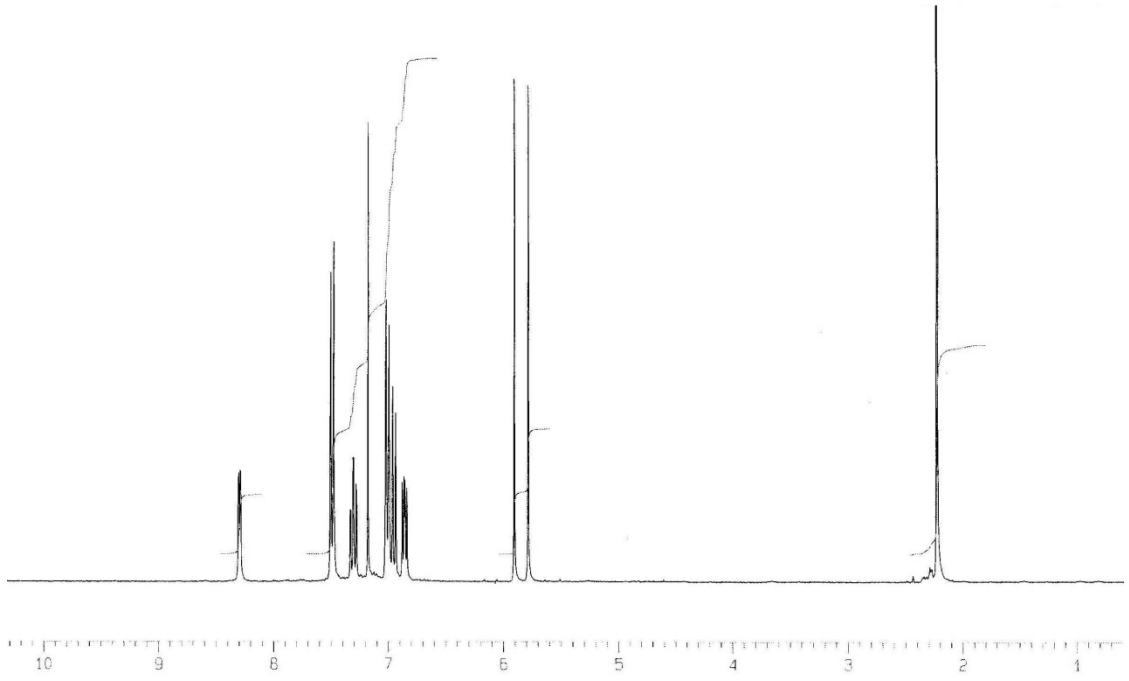

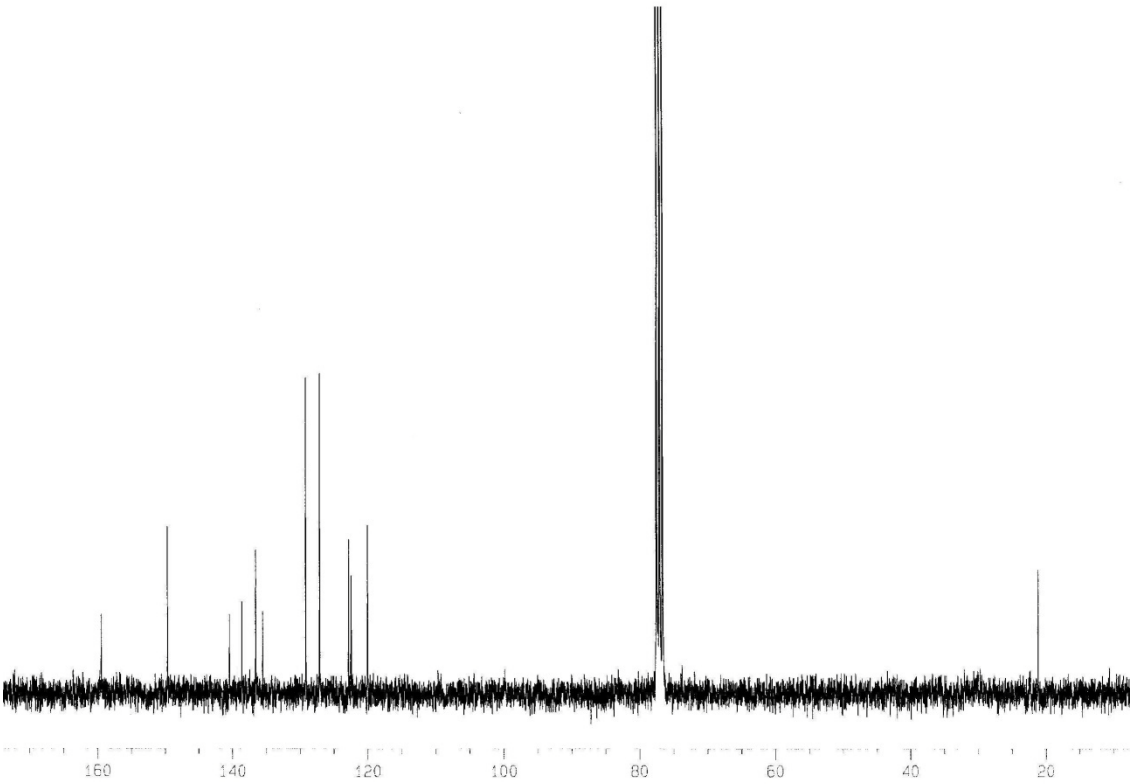

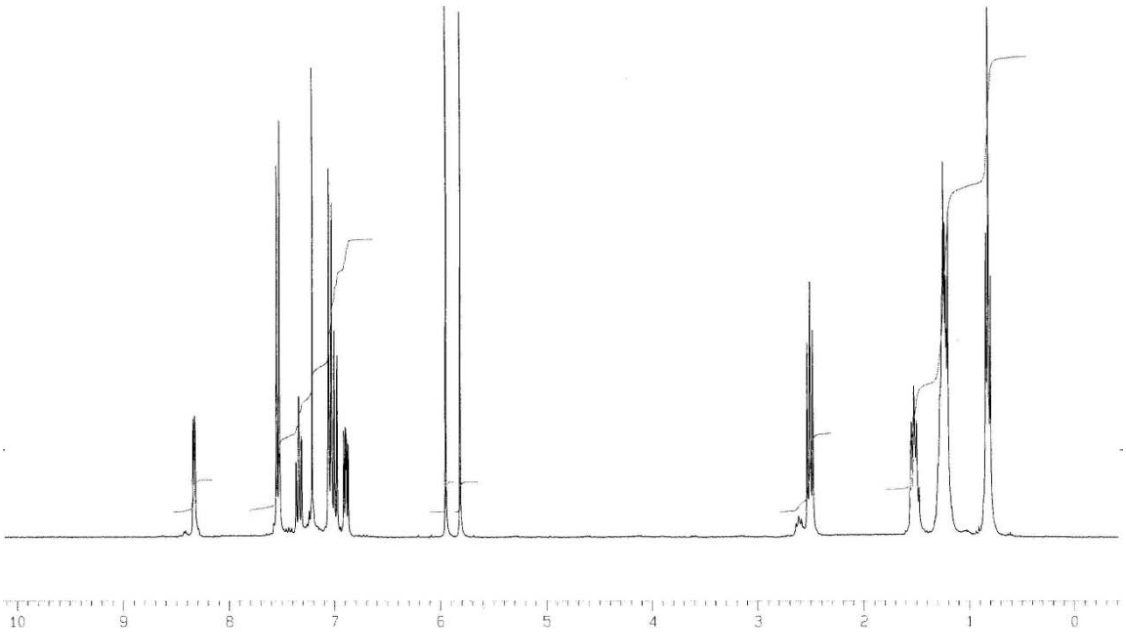

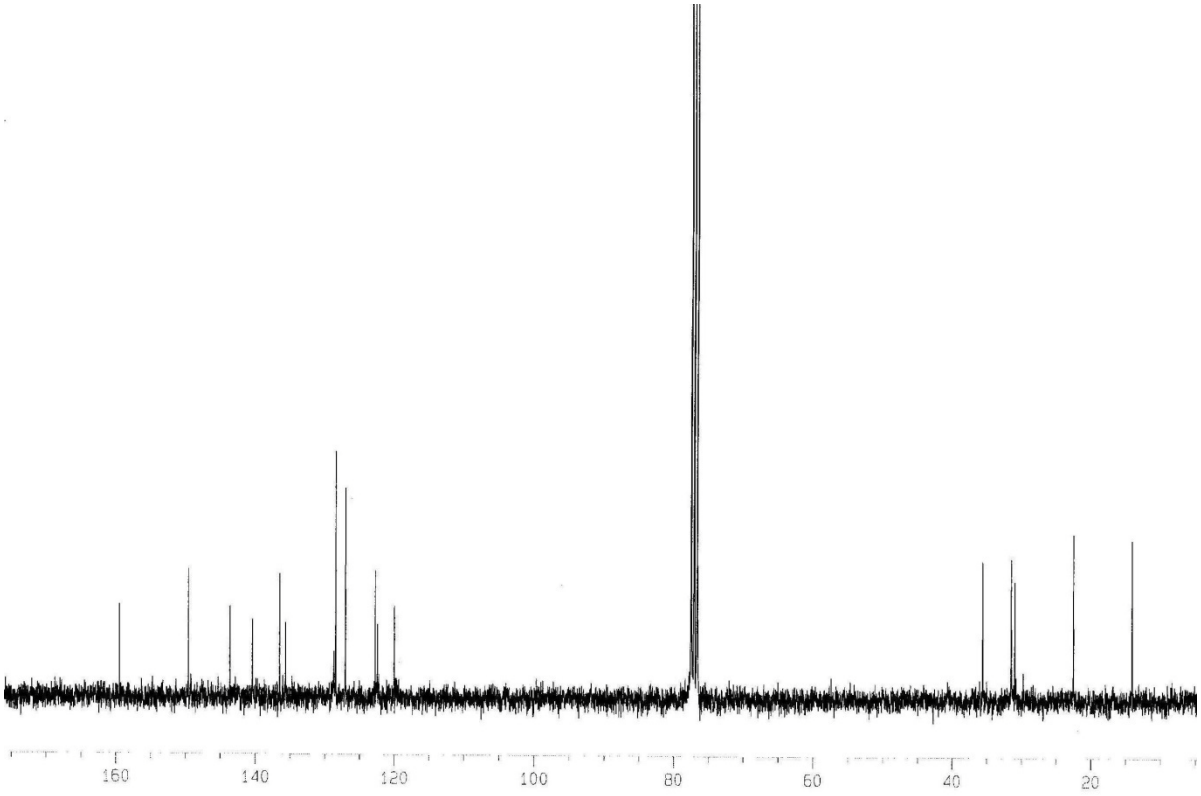

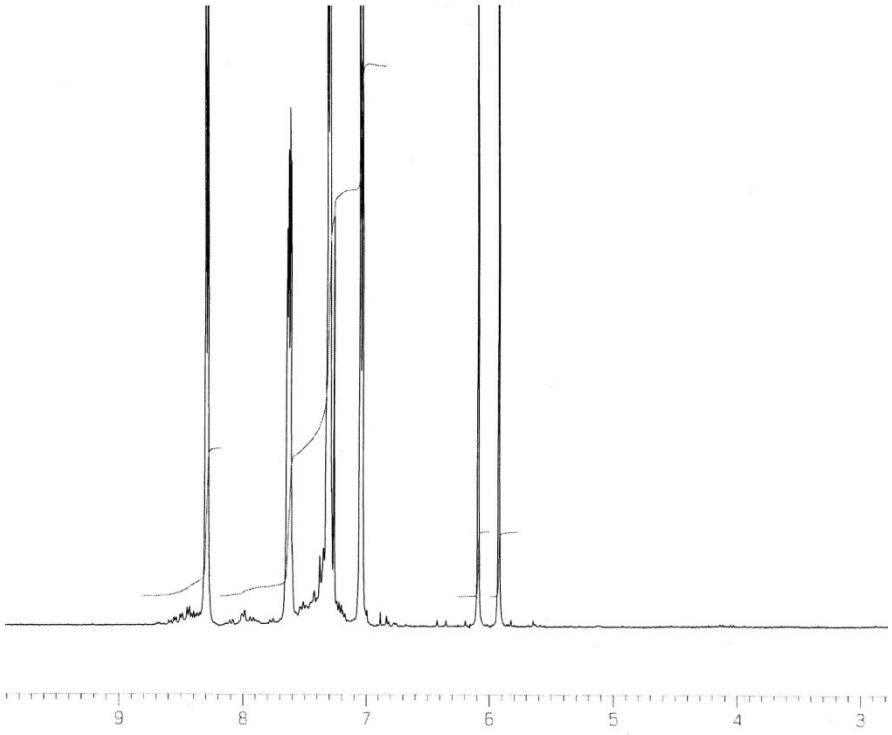

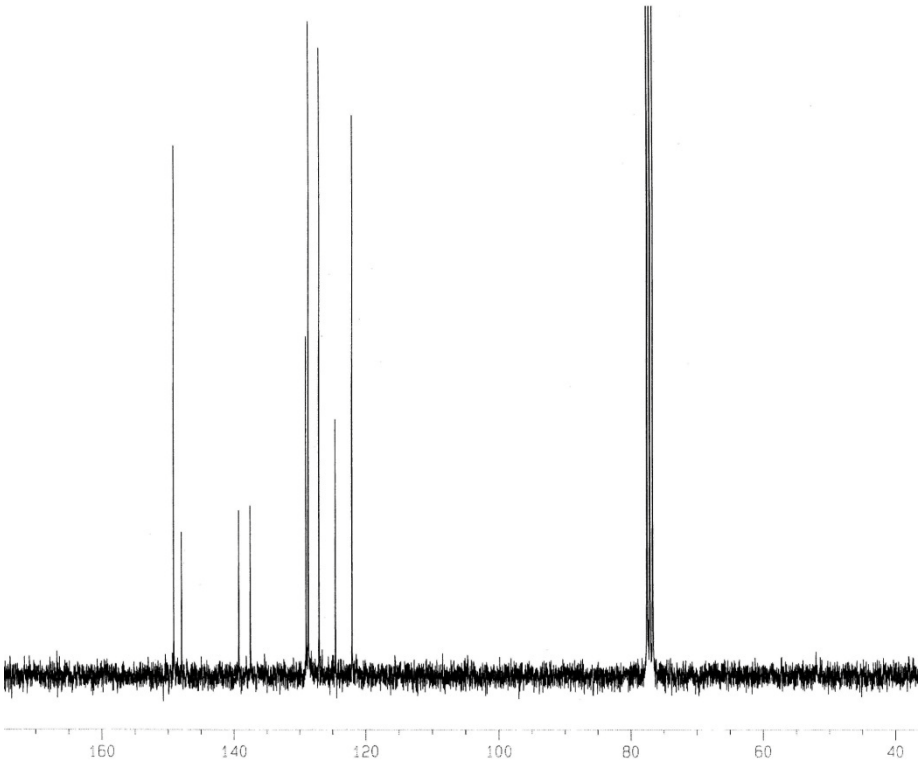

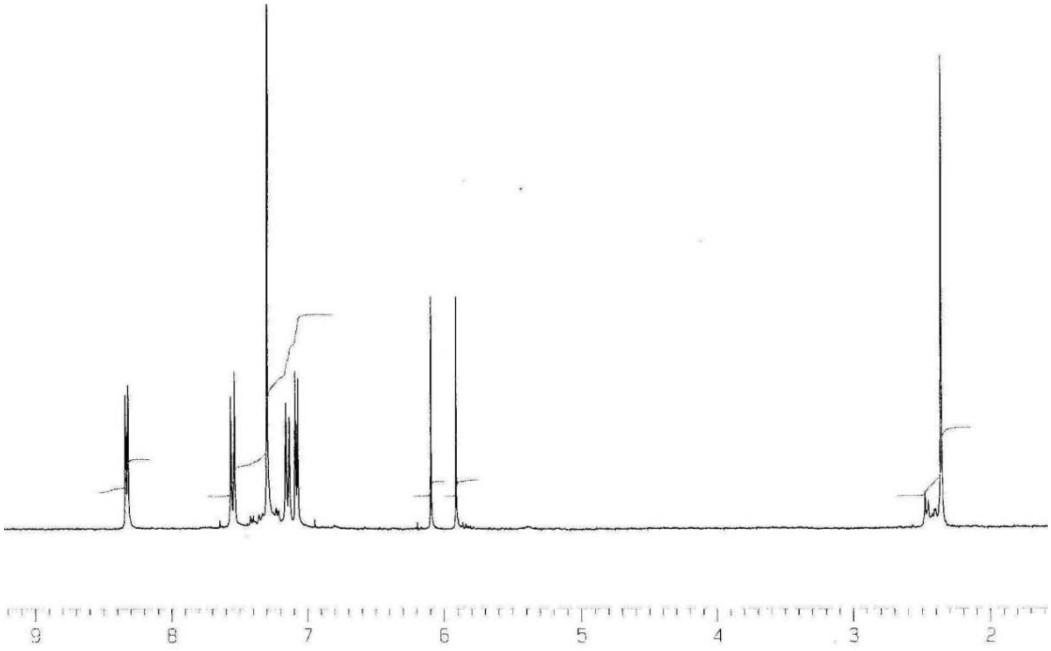

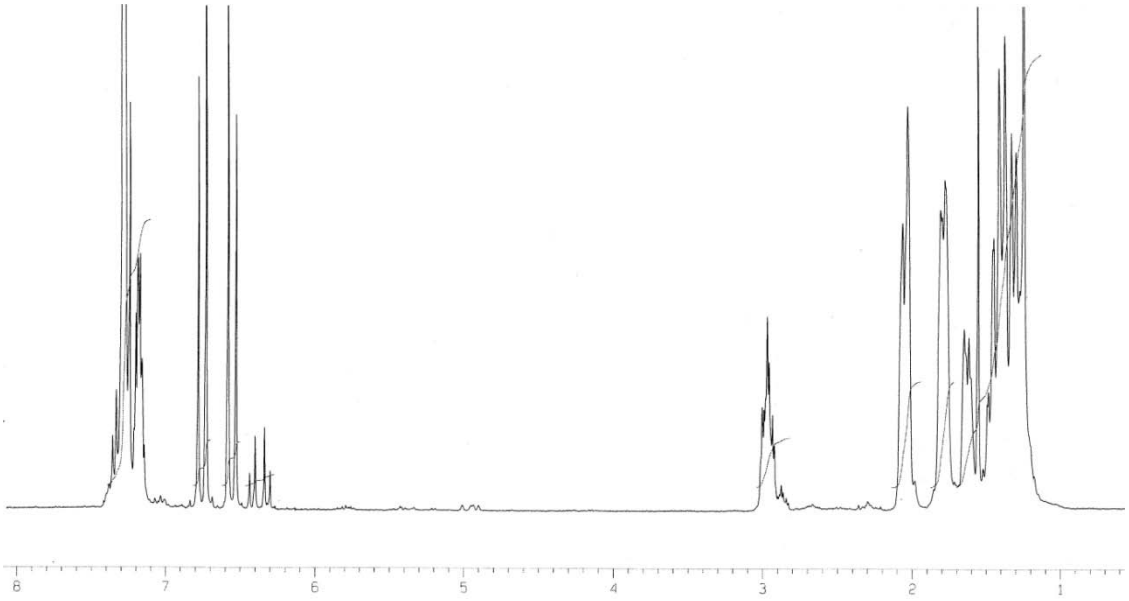

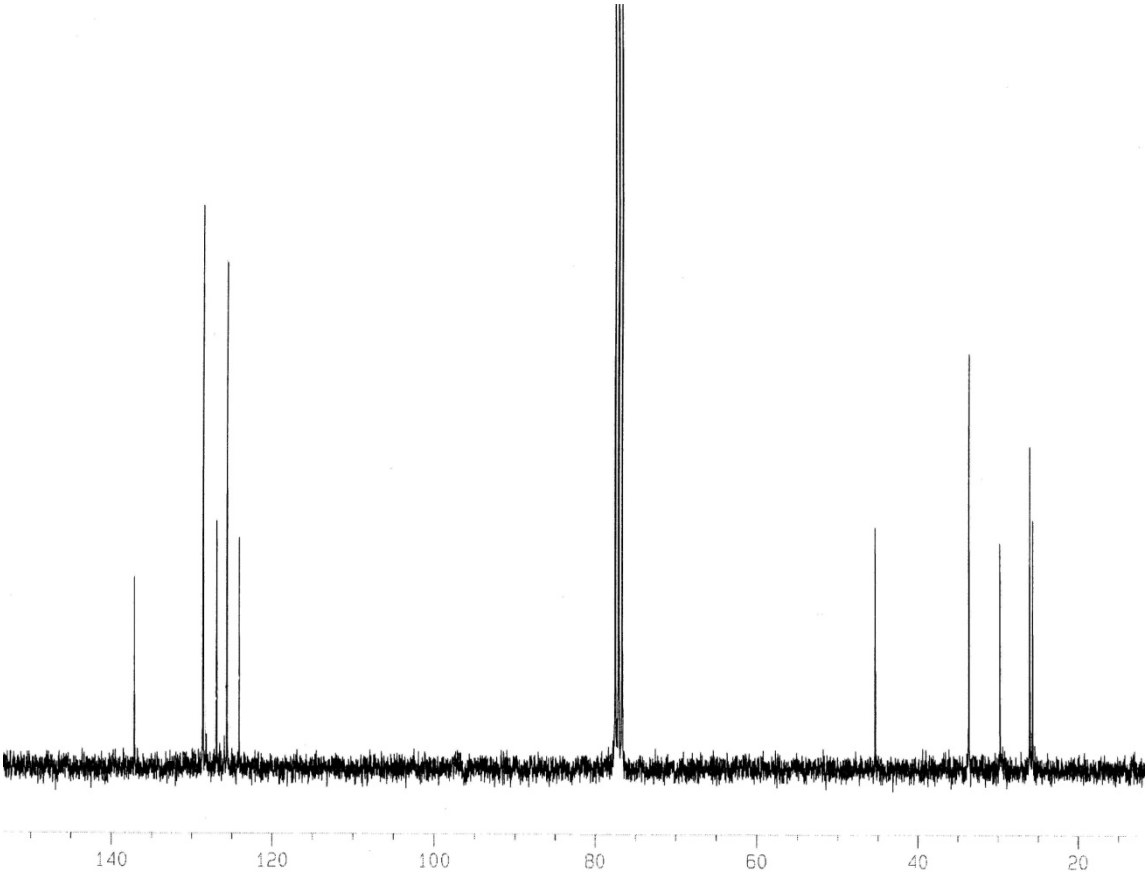

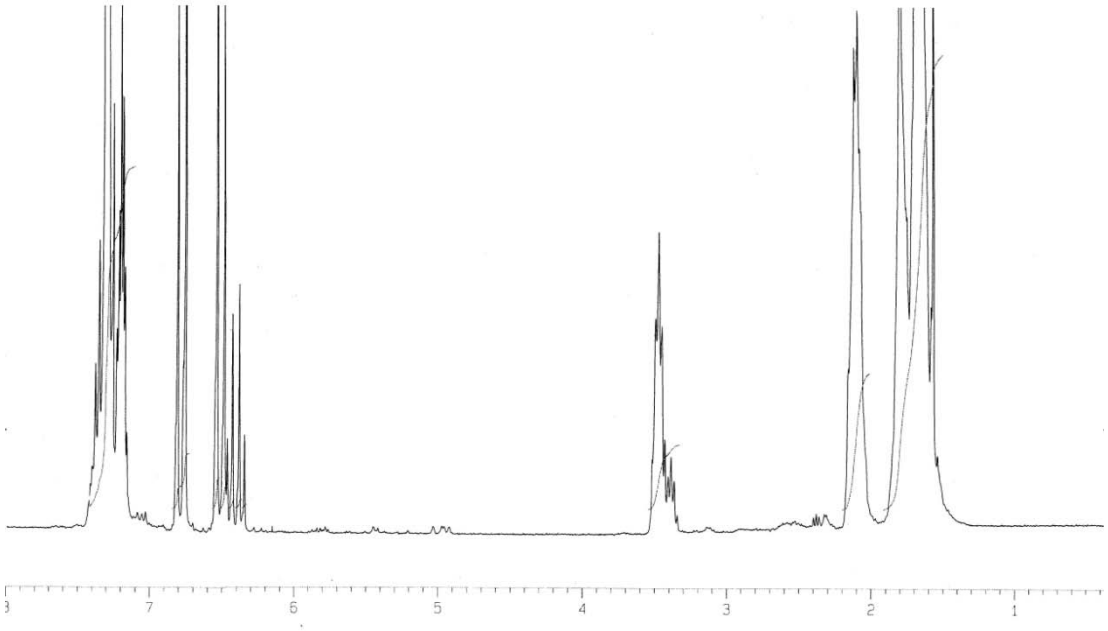
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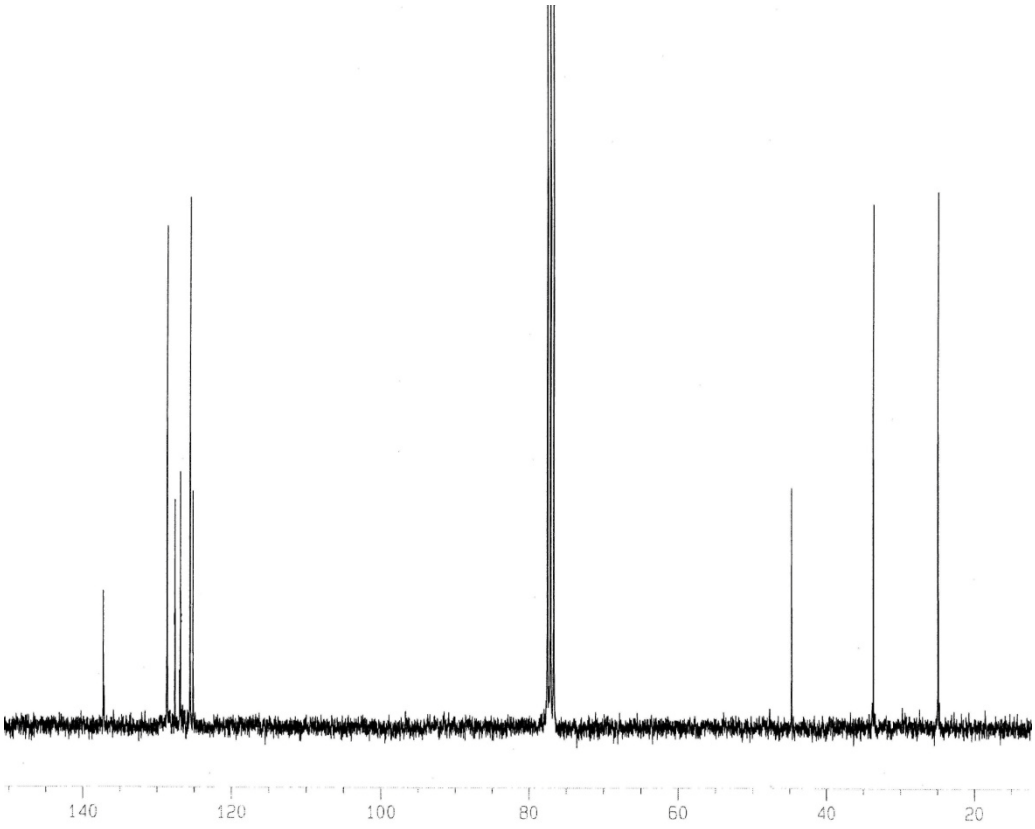
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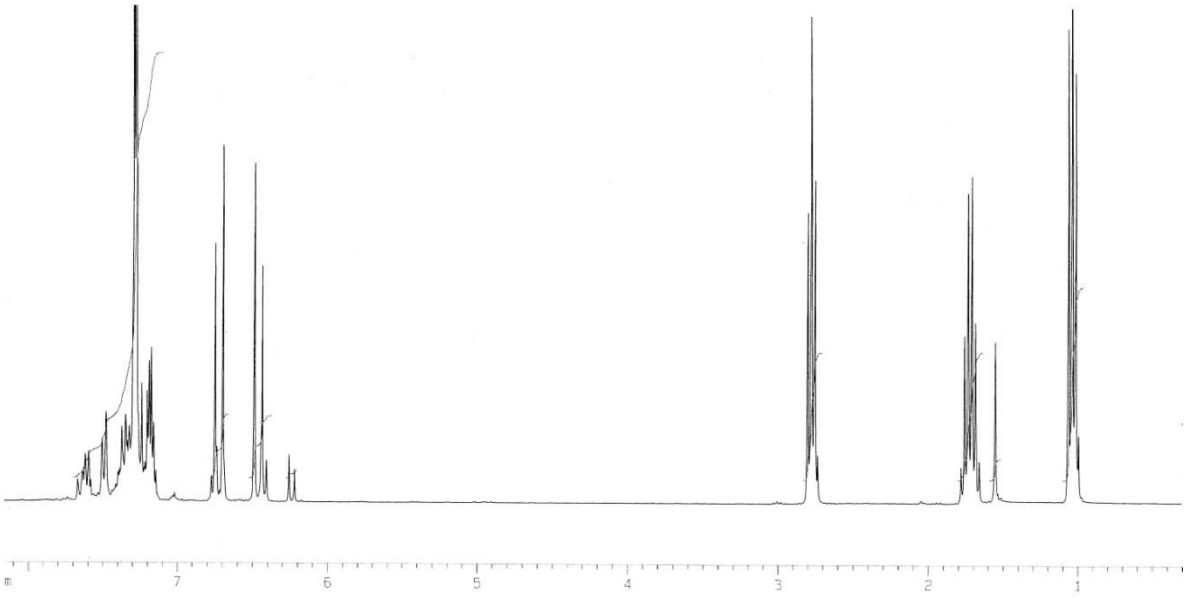
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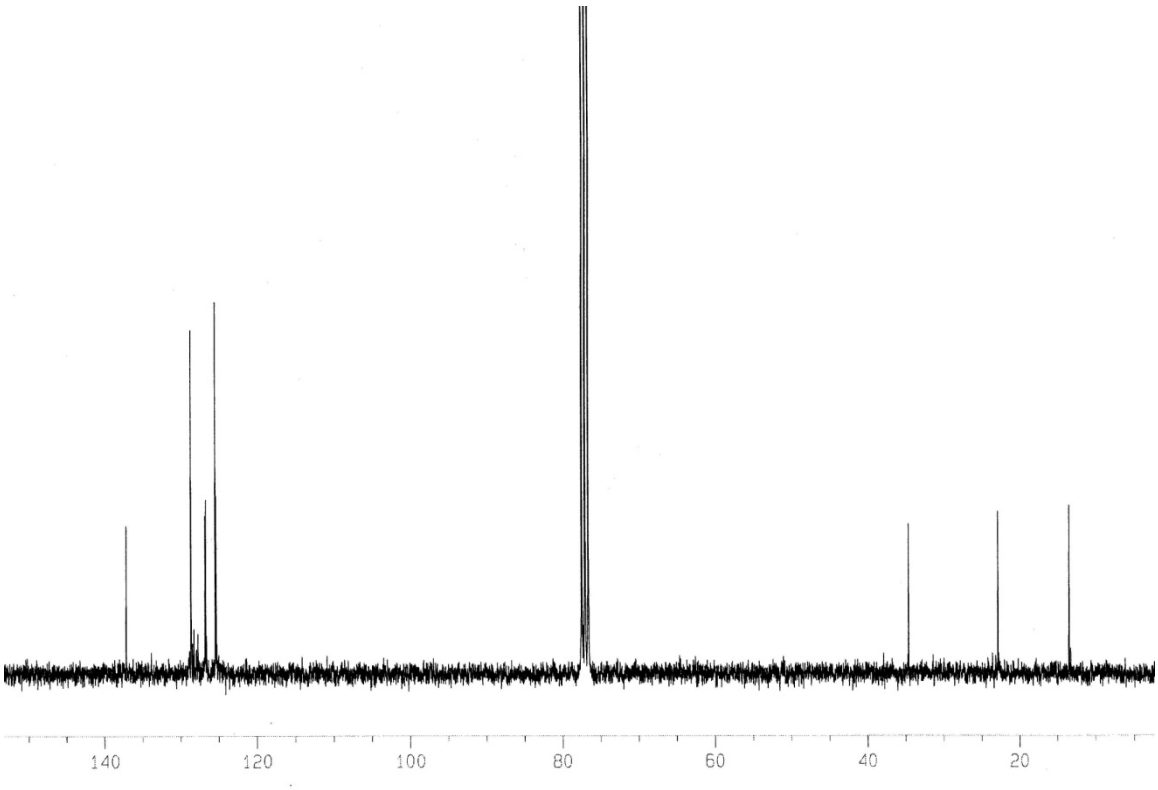
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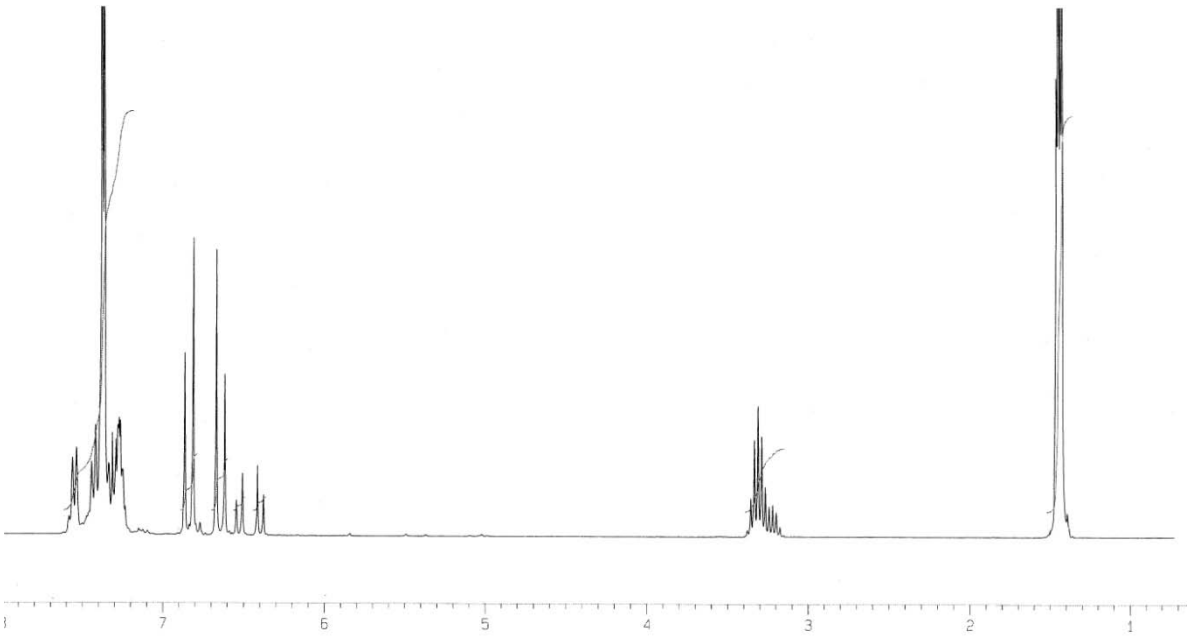

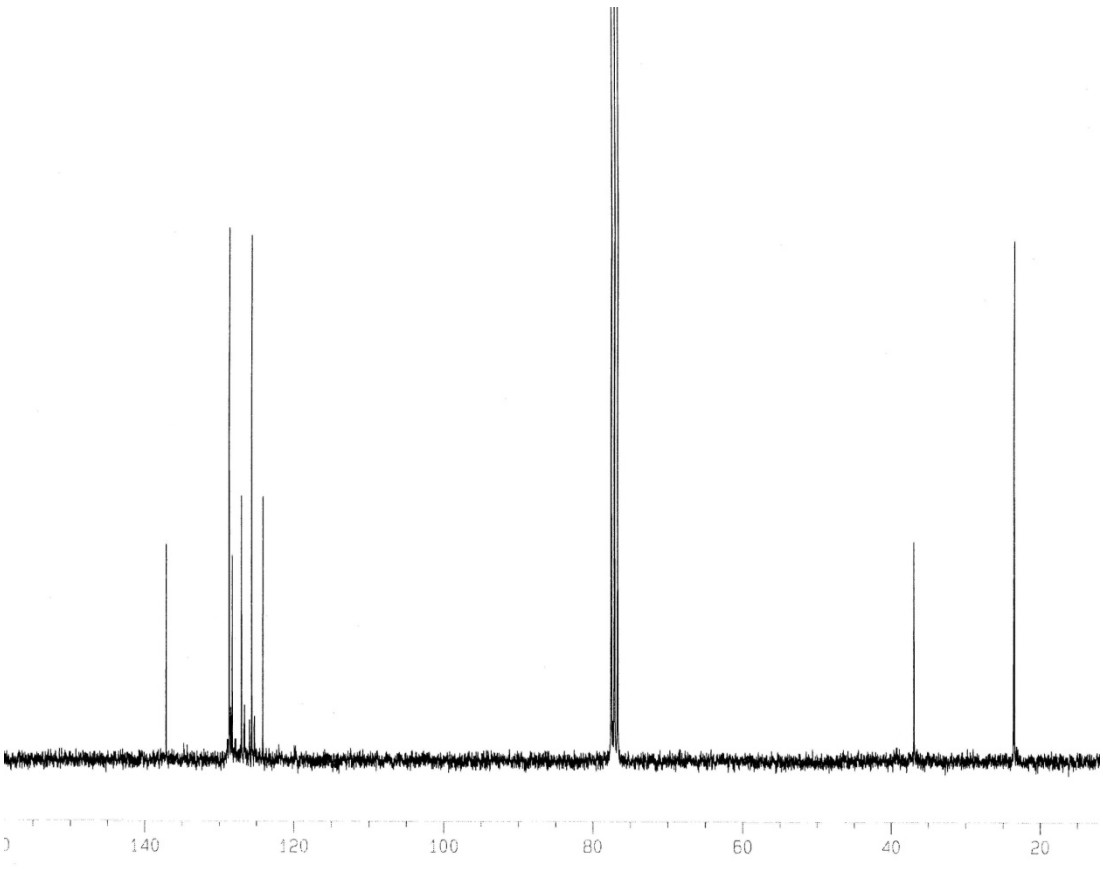

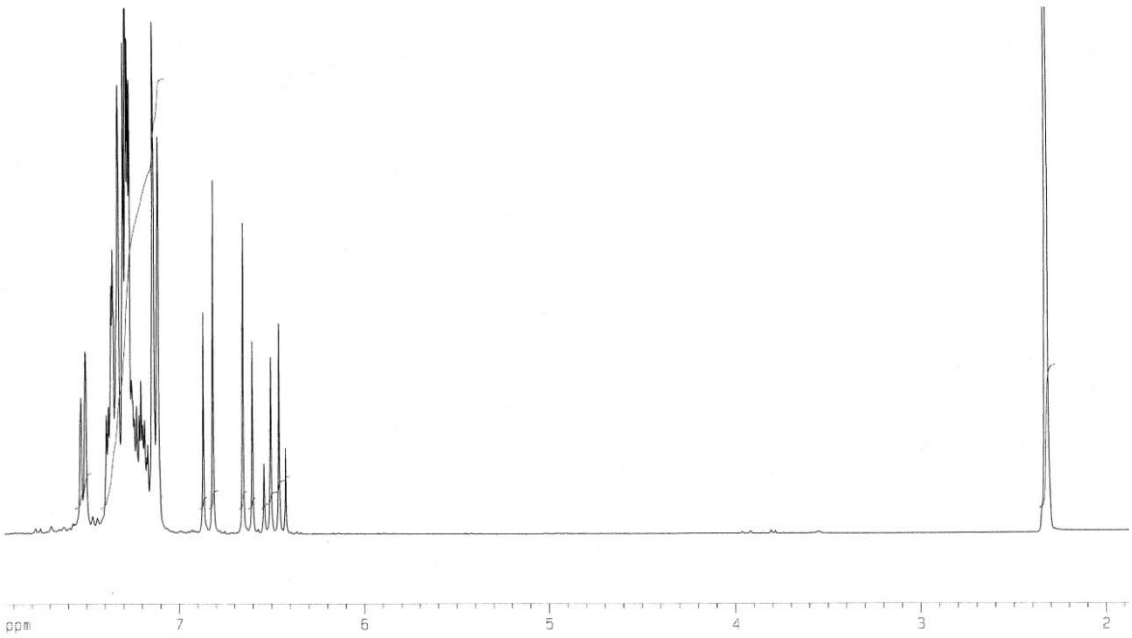
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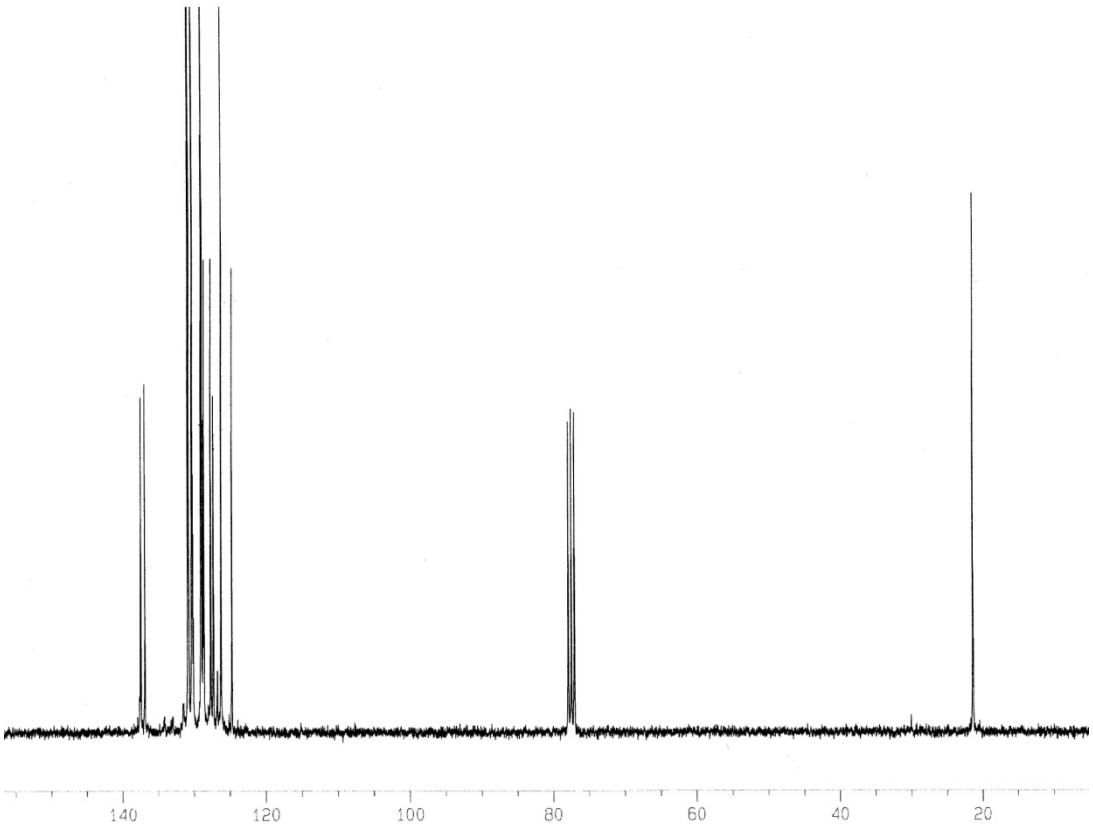
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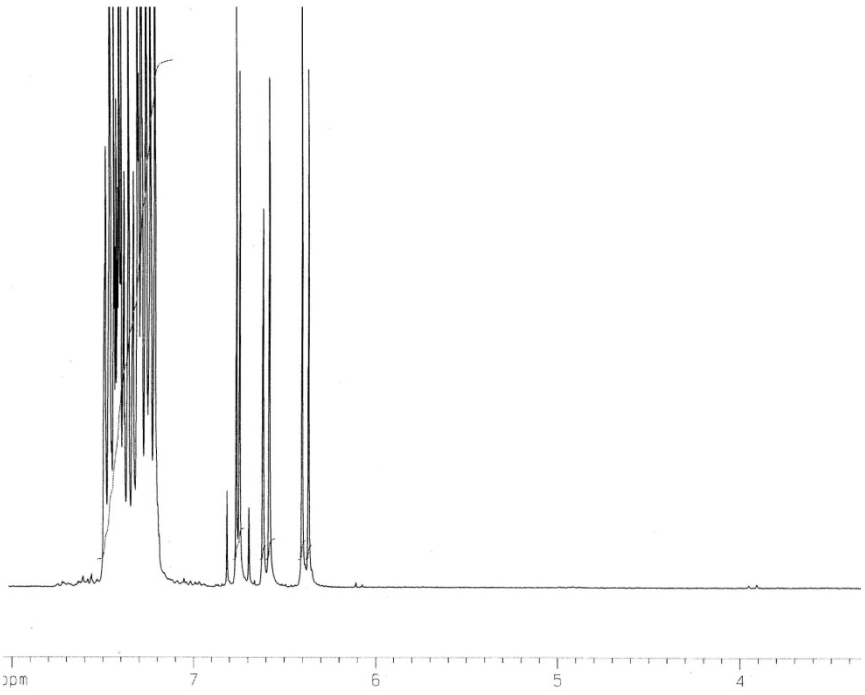
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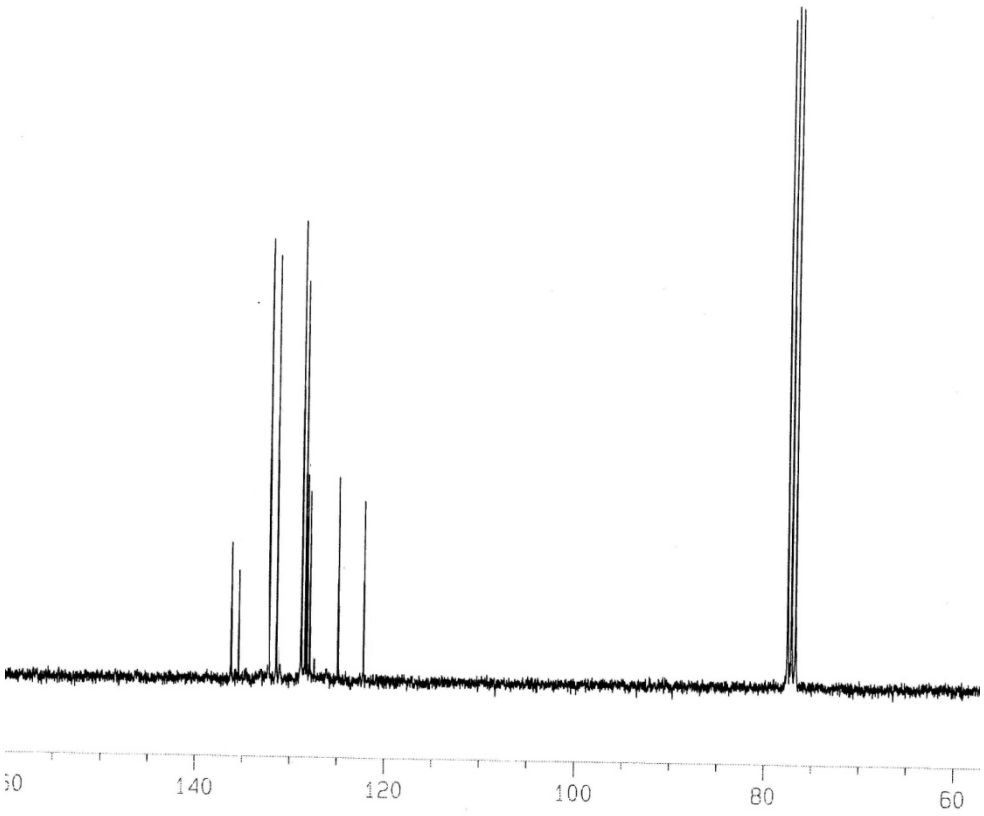
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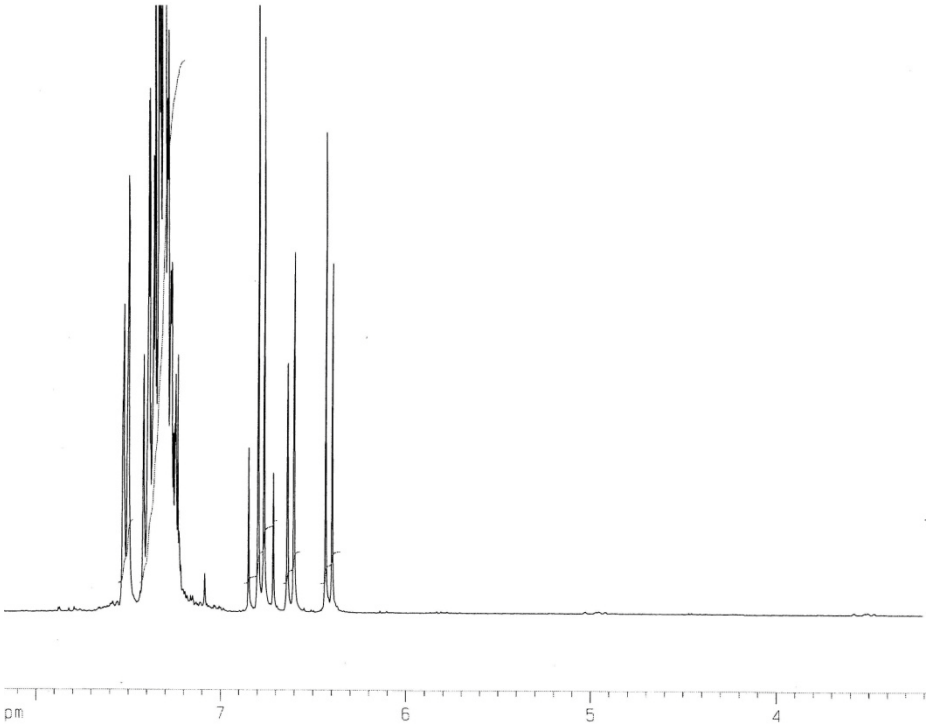
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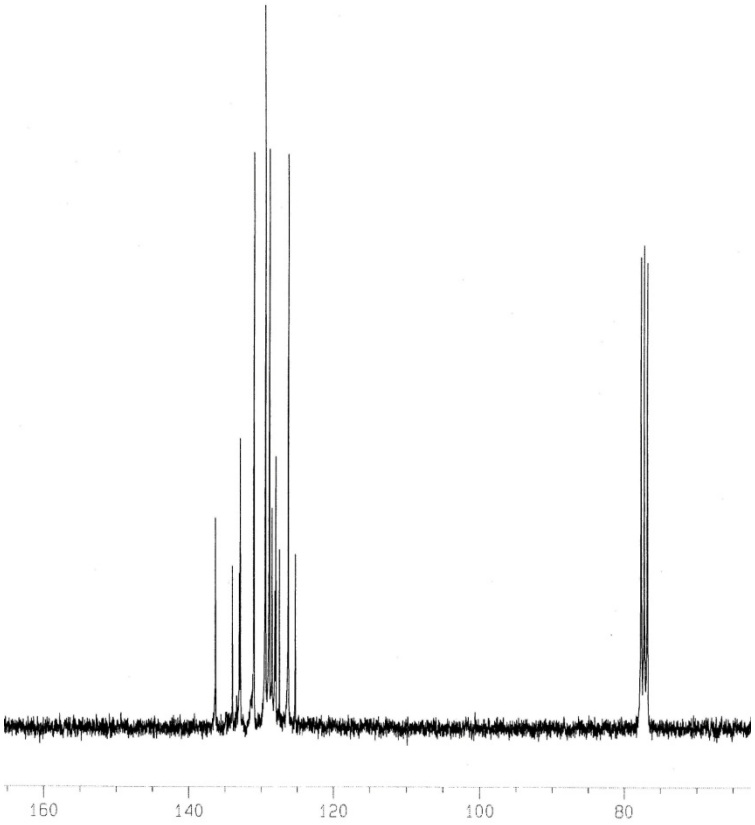
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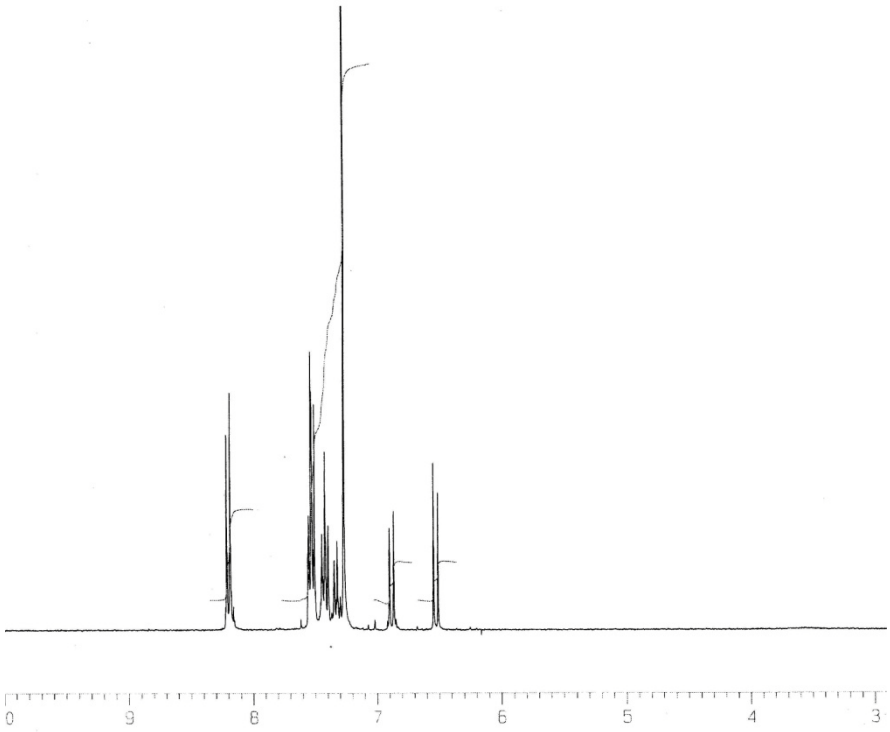
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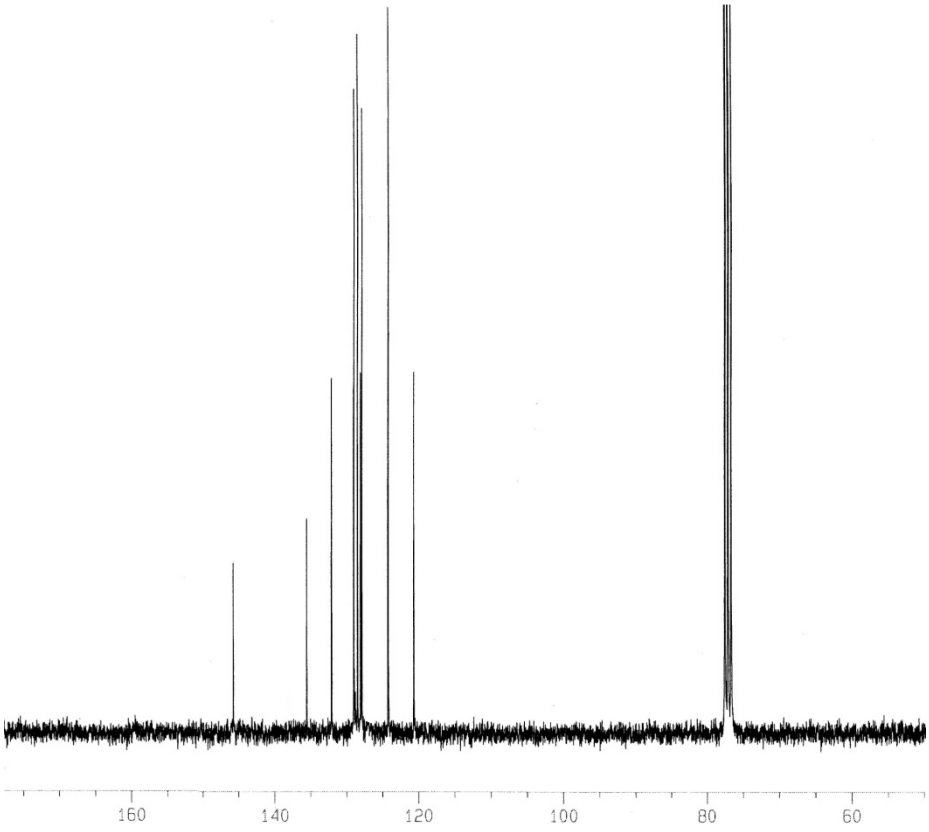
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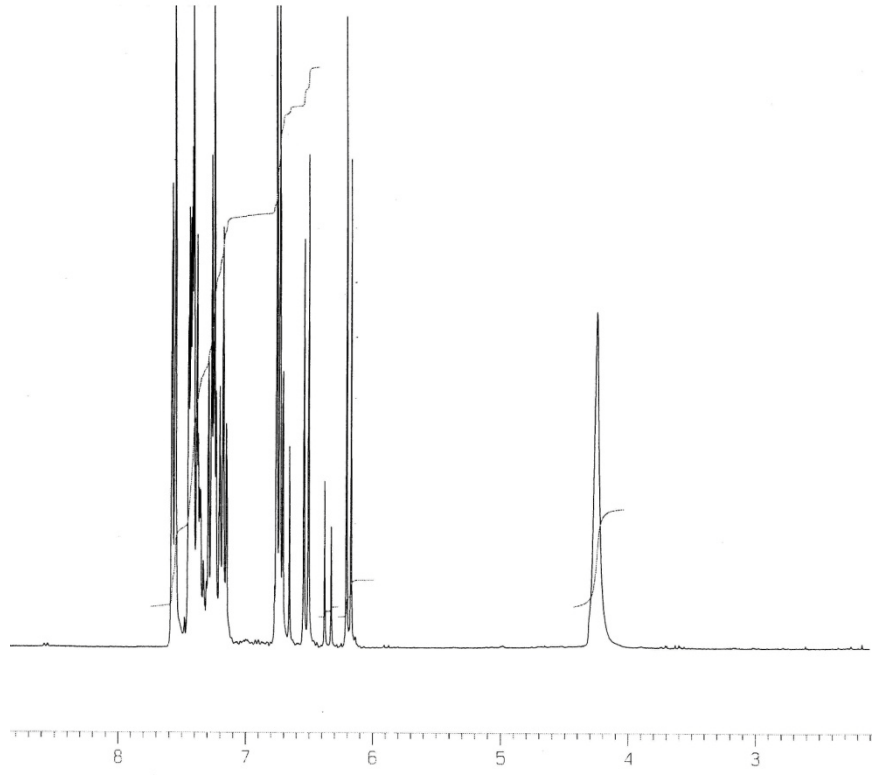
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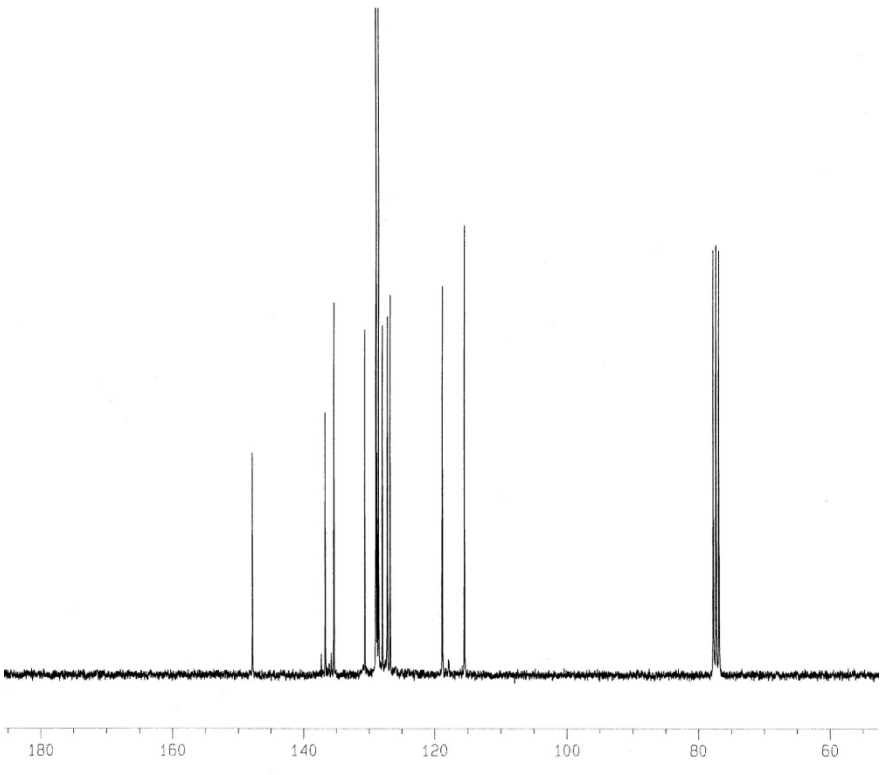
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