Experimental Section

General Methods. All NMR spectra were recorded on Varian 200 and 300 MHz instruments. Infrared spectra were recorded on a Fourier transform spectrometer and are reported in wavenumbers (cm^{-1}). Mass spectra were obtained on a VG 7070E spectrometer. A Fisher-Johns apparatus was used for melting point determinations.

$Pd(OAc)_2$, acid chlorides **2a-c**, **2e-f**, **2h-k** were purchased from commercial sources and were used as received. Acid chlorides **2d** and **2g** were prepared from *p*-chlorophenylacetic acid and phenylthioacetic acid respectively. THF was dried and distilled prior to use. 2-Iodoanilines **1b**,[1] **1c**[1], **1d**[2] **and 1e**[3] were prepared according to literature methods.

The following general procedure was used: a mixture of **1** (1 mmol), **2** (1 mmol), $Pd(OAc)_2$ (0.02 mmol), $(i\text{-Pr})_2EtN$ (3.0 mmol) and THF (5 mL) was reacted in an autoclave at 300 psi of carbon monoxide for 24 h at 100 °C. The reaction mixture was cooled to room temperature and excess carbon monoxide was released. The reaction mixture was filtered and the filtrate was concentrated by rotary evaporation. The residue was purified by silica gel column chromatography using ether-*n*-pentane (1:1) as the eluant.

2-Methyl-*4H*-3,1-benzoxazin-4-one, 3a;[4] mp 81-82 °C (80-81°C)[4]; IR 1646, 1758 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.42 (s, 3H, CH_3), 7.39-7.50 (m, 2H), 7.68-7.80 (m, 1H), 8.08-8.14 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 20.98, 116.85, 126.24, 128.05, 128.27, 136.30, 146.28, 159.50, 160.06; MS m/e 161 $[M]^+$

2-(Diphenylmethyl)-*4H*-3,1-benzoxazin-4-one, 3b; mp 120-122 °C; IR 1638, 1759 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.39 (s, 1H), 7.24-7.77 (m, 13H), 8.14-8.20 (m,, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 56.92, 116.79, 127.05, 127.45, 128.34, 128.48, 128.63, 128.88, 136.41, 138.37, 146.21, 159.45, 162.17; MS m/e 313 $[M]^+$ Anal Cald for $C_{21}H_{15}NO_2$; C 80.49, H 4.82, N 4.47; Found C 80.87, H 4.83, N 4.44.

6-Chloro 2-(diphenylmethyl)-*4H*-3,1-benzoxazin-4-one, 3c; mp 118-120 °C; IR 1634, 1766 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.36 (s, 1H), 7.24–7.41 (m, 10H), 7.55 (d, 1H, J = 8.6 Hz), 7.70 (dd, 1H J = 8.6 and 2.4 Hz), 8.10 (d, 1H, J = 2.4 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 56.93, 118.00, 118.78, 127.61, 127.77, 128.74, 128.89, 134.22, 136.72,

138.19, 144.74, 158.43, 162.55; MS m/e 347 $[M]^+$ Anal Cald for $C_{21}H_{14}ClNO_2$; C 72.52, H 4.06, N 4.03; Found C 72.11, H 4.08, N 4.01.

2-(Diphenylmethyl)-6-methyl-*4H*-3,1-benzoxazin-4-one, 3d; mp 122-123 °C; IR 1638, 1756 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.44, (s, 3H), 5.36 (s, 1H), 7.24–7.60 (m, 12H), 7.95-7.97 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 21.22, 56.90, 116.53, 126.88, 127.43, 127.95, 128.63, 128.91, 137.62, 138.54, 138.94, 144.10, 159.72, 161.38; MS m/e 327 $[M]^+$ Anal Cald for $C_{22}H_{17}NO_2$; C 80.71, H 5.23, N 4.28; Found C 80.54, H 5.32, N 4.26.

2-(Diphenylmethyl)-6-hydroxy-*4H*-3,1-benzoxazin-4-one, 3e; mp 189-191 °C; IR 1640, 1758 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$ and Acetone-d_6) δ 5.30 (s, 1H), 7.11- 7.50 (m, 13H), 8.88 (s (br), 1H, OH); ^{13}C-NMR (75 MHz, $CDCl_3$ and Acetone-d_6) δ 56.43, 111.90, 117.51, 125.05, 127.08, 128.32, 128.38, 128.65, 138.58, 139.18, 157.00, 159.11; 159.44; MS m/e 329 $[M]^+$ Anal Cald for $C_{21}H_{15}NO_3$; 329.1052; Found 329.1059.

2-(Diphenylmethyl)-6-cyano-*4H*-3,1-benzoxazin-4-one, 3f; mp 201-203 °C; IR 1638, 1774, 2231 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$ and DMSO-d_6) δ 5.49 (s, 1H), 7.23-7.37 (m, 10H), 7.67-7.71 (m, 1H), 8.04-8.16 (m, 1H), 8.42-8.45 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$ and DMSO-d_6); δ 54.35, 109.28, 115.47, 116.12, 125.67, 126.54, 126.86, 127.18, 131.07, 136.67, 137.31, 146.92, 155.73, 163.00 MS m/e 338 $[M]^+$ Anal Cald for $C_{22}H_{14}N_2O_2$; C 78.09, H 4.17, N 8.28; Found C 78.16, H 4.10, N 8.23.

2-(Benzyl)-*4H*-3,1-benzoxazin-4-one, 3g;[5] mp 86-88 °C; IR 1642, 1758 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.96 (s, 2H), 7.27-7.58 (m, 7H), 7.71-7.76 (m, 1H), 8.11-8.16 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 41.55, 116.77, 126.74, 127.43, 128.29, 128.37, 128.75, 129.23, 134.15, 136.40, 146.36, 159.52, 161.10; MS m/e 237 $[M]^+$ Anal Cald for $C_{15}H_{11}NO_2$; C 75.94, H 4.67, N 5.90; Found C 75.94, H 4.54, N 5.85.

2-(Benzyl)-6-methyl-*4H*-3,1-benzoxazin-4-one, 3h; mp 186-189 °C; IR 1642, 1756 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.94 (s, 2H), 7.24–7.58 (m, 7H), 7.91-7.93 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 21.17, 41.47, 116.43, 126.48, 127.38, 127.95, 128.73, 129.22, 134.26, 137.61, 138.70, 144.16, 159.72, 160.35; MS m/e 251 $[M]^+$ Anal Cald for $C_{16}H_{13}NO_2$; C 76.48, H 5.21, N 5.57; Found C 76.86, H 5.67, N 5.17.

2-[(*p*-Chlorophenyl)methyl]-6-chloro-*4H*-3,1-benzoxazin-4-one, 3i; mp 143-145 °C; IR 1640, 1765 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.91 (s, 2H), 7.30 (s, 4H), 7.51 (d, 1H, *J* = 8.6), 7.72 (dd, 1H, *J* = 8.6 and 2.4 Hz), 8.08 (d, 1H, *J* = 2.4 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 40.76, 117.91, 127.79, 128.39, 128.98, 130.63, 132.27, 133.60, 134.14, 136.77, 144.72, 158.28, 160.85; MS m/e 304 $[M-2]^+$, 306 $[M]^+$ Anal Cald for $C_{15}H_9Cl_2NO_2$; C 58.85, H 2.96, N 4.58; Found C 58.87, H 2.88, N 4.51.

2-[(*p*-Chlorophenyl)methyl]-6-methyl-*4H*-3,1-benzoxazin-4-one, 3j; mp 119-121 °C; IR 1644, 1759 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.89 (s, 2H), 7.24-7.57 (m, 6H), 7.90-7.92 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 21.16, 40.72, 116.40, 126.51, 127.98, 128.85, 130.59, 132.68, 133.36, 137.65, 138.83, 144.05, 159.55, 159.73; MS m/e 285 $[M]^+$ HRMS Cald for $C_{16}H_{12}ClNO_2$; 285.0557; Found 285.0536.

2-(1-Phenylpropyl)-*4H*-3,1-benzoxazin-4-one, 3k; mp 135-136 °C; IR 1638, 1759 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.96 (t, 3H, *J* = 7.3 Hz), 1.95-2.10 (m, 1H), 2.22-2.41 (m, 1H), 3.77 (t, 1H, *J* =7.8 Hz), 7.24 – 7.79 (m, 8H), 8.12-8.15 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 12.15, 26.44, 53.18, 116.91, 126.82, 127.46, 128.16, 128.25, 128.31, 128.67, 135.32, 139.07, 146.39, 159.67, 163.50; MS m/e 265 $[M]^+$ Anal Cald for $C_{17}H_{15}NO_2$; C 76.96, H 5.70, N 5.28; Found C 77.20, H 5.91, N 4.92.

6-Chloro-2-(1-phenylpropyl)-*4H*-3,1-benzoxazin-4-one, 3l; mp 74-76 °C; IR 1635, 1765 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.95 (t, 3H, *J* = 7.3 Hz), 1.98-2.09, (m, 1H), 2.23-2.34 (m, 1H), 3.75 (t, 1H, *J* = 7.7 Hz), 7.24–8.10 (m, 8H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 12.12, 26.39, 53.14, 118.70, 127.58, 127.68, 128.12, 128.45, 128.75, 133.82, 135.60, 138.79, 144.88, 158.59, 163.85; MS m/e 299 $[M]^+$ Anal Cald for $C_{17}H_{14}ClNO_2$; C 68.12, H 4.71, N 4.67; Found C 68.18, H 4.60, N 4.64.

6-Cyano-2-(1-phenylpropyl)-*4H*-3,1-benzoxazin-4-one, 3m; mp 90-91 °C; IR 1634, 1770, 2232 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.95 (t, 3H, *J* =7.3 Hz), 1.97-2.38 (m, 2H), 3.78 (t, 1H, *J* = 7.8 Hz), 7.21-7.45 (m, 5H), 7.52 (dd, 1H, *J* = 8.4 and 0.6 Hz), 7.85 (dd, 1H, *J* = 8.4 and 2.0 Hz), 8.41 (dd, 1H, *J* = 2.0 and 0.6 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 12.05, 26.26, 53.26, 111.91, 117.02, 117.70, 127.75, 128.01, 128.12, 128.80, 133.07, 138.25, 138.56, 149.16, 157.63, 166.62; MS m/e 290 $[M]^+$ Anal Cald for $C_{18}H_{14}N_2O_2$; C 74.47, H 4.86, N 9.65; Found C 74.14, H 4.95, N 9.47.

2-[(Acetoxy)(phenyl)methyl]-6-chloro-*4H*-3,1-benzoxazin-4-one, 3n; mp 123-125 °C; IR 1650, 1751, 1770 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.24 (s, 3H), 6.34 (s, 1H), 7.23-7.41 (m, 3H), 7.53-7.73 (m, 4H), 8.06-8.08 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 20.76, 74.16, 118.20, 127.62, 127.84, 128.71, 128.88, 129.49, 133.95, 134.42, 136.75, 144.27, 157.47, 158.82, 169.93; MS m/e 290 $[M]^+$ Anal Cald for $C_{17}H_{12}ClNO_4$; C 61.92, H 3.67, N 4.25; Found C 62.01, H 3.55, N 4.20.

2-[(Acetoxy)(phenyl)methyl]-6-methyl-*4H*-3,1-benzoxazin-4-one, 3o; mp 136-138 °C; IR 1651, 1754, 1769 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.23 (s, 3H), 2.42 (s, 3H), 6.37 (s, 1H), 7.24 – 7.61 (m, 7H), 7.85-7.92 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 20.89, 21.24, 74.28, 116.81, 126.99, 127.71, 128.15, 128.88, 129.41, 134.38, 137.75, 139.31, 143.66, 157.75, 158.87, 170.02; MS m/e 309 $[M]^+$ HRMS Cald for $C_{18}H_{15}NO_4$; 309.1001; Found 309.1014.

2-[(Phenylthio)methyl]-*4H*-3,1-benzoxazin-4-one, 3p; mp 156-158 °C; IR 1638, 1760 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.98 (s, 2H), 7.21-7.32 (m, 3H), 7.44-7.54 (m, 4H), 7.72-7.77 (m, 1H), 8.13-8.18 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 37.78, 116.79, 126.84, 127.43, 128.51, 128.63, 129.08, 129.76, 130.92, 134.22, 136.53, 146.04, 159.11; MS m/e 269 $[M]^+$ HRMS Cald for $C_{15}H_{11}NO_2S$; 269.0510; Found 269.0509.

6-Methyl-2-[(phenylthio)methyl]-*4H*-3,1-benzoxazin-4-one, 3q; mp 173-175 °C; IR 1638, 1760 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.96 (s, 2H), 7.21-7.31 (m, 3H), 7.38-7.58 (m, 4H), 7.92-7.93 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 21.20, 37.68, 116.45, 126.60, 127.32, 128.05, 129.03, 130.80, 134.32, 137.67, 139.06, 143.86, 158.22, 159.26; MS m/e 283 $[M]^+$; HRMS Cald for $C_{16}H_{13}NO_2S$; 283.0667; Found 283.0672.

2-Phenyl-*4H*-3,1-benzoxazin-4-one, 3r;[4,5] mp 121-123 °C (123-124 °C)[4]; IR 1622, 1764 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.42- 7.76 (m, 6H), 8.16-8.27 (m, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 116.93, 127.13, 128.13, 128.21, 128.47, 128.64, 130.14, 132.51, 136.43, 146.86, 156.98, 159.39; MS m/e 223 $[M]^+$

2-(*o*-Methoxyphenyl)-6-methyl-*4H*-3,1-benzoxazin-4-one, 3s; mp 132-134 °C; IR 1626, 1754 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.45, (s, 3H), 3.89 (s, 3H), 6.96-7.06 (m, 2H), 7.40-7.58 (m, 3H), 7.79-7.84 (m, 1H), 7.99-8.00 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 21.21, 56.03, 112.08, 116.58, 120.48, 126.96, 127.88, 131.19, 132.93, 137.50,

138.67, 144.81, 156.87, 158.50, 159.93; MS m/e 267 $[M]^+$; HRMS Cald for $C_{16}H_{13}NO_3$; C 71.90, H 4.90, N 5.24; Found C 71.86, H 4.81, N 5.34.

(*E*)-2-Styryl-*4H*-3,1-benzoxazin-4-one, 3t;[5,6] mp 144-146 °C; IR 1635, 1758 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 6.76 (d, 1H, CH=**CH**, J = 16.2 Hz), 7.36- 7.59 (m, 7H), 7.77 (dd, 1H, J = 15.3 and 1.5 Hz), 7.82 (d, 1H, **CH**=CH, J = 16.2 Hz), 8.18 (dd, 1H, J = 7.8 and 1.5 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 116.90, 118.81, 126.86, 127.95, 128.07, 128.55, 128.94, 130.24, 134.58, 136.45, 141.90, 147.07, 157.24, 159.19; MS m/e 248 $[M-1]^+$,249 $[M]^+$.

2-*t*-Butyl-*4H*-3,1-benzoxazin-4-one, 3u;[5] mp 117-118 °C; IR 1636, 1762 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.35 (s, 9H), 7.35- 7.51 (m, 2H), 7.64-7.74 (m, 1H), 8.04-8.10 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 27.53, 37.75, 116.61, 126.75, 127.82, 128.04, 136.07, 146.37, 159.80, 168.02; MS m/e 203 $[M]^+$.

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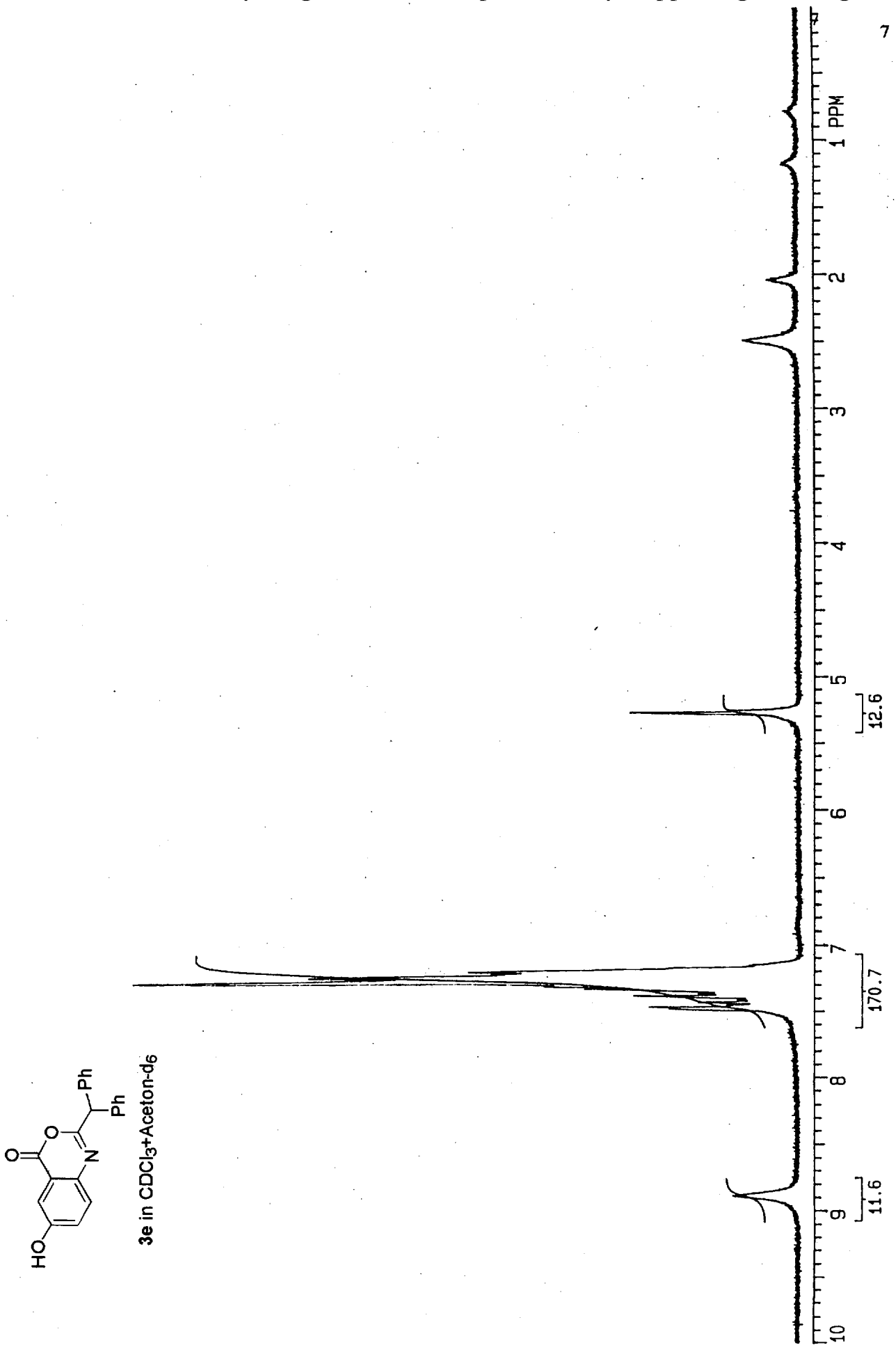

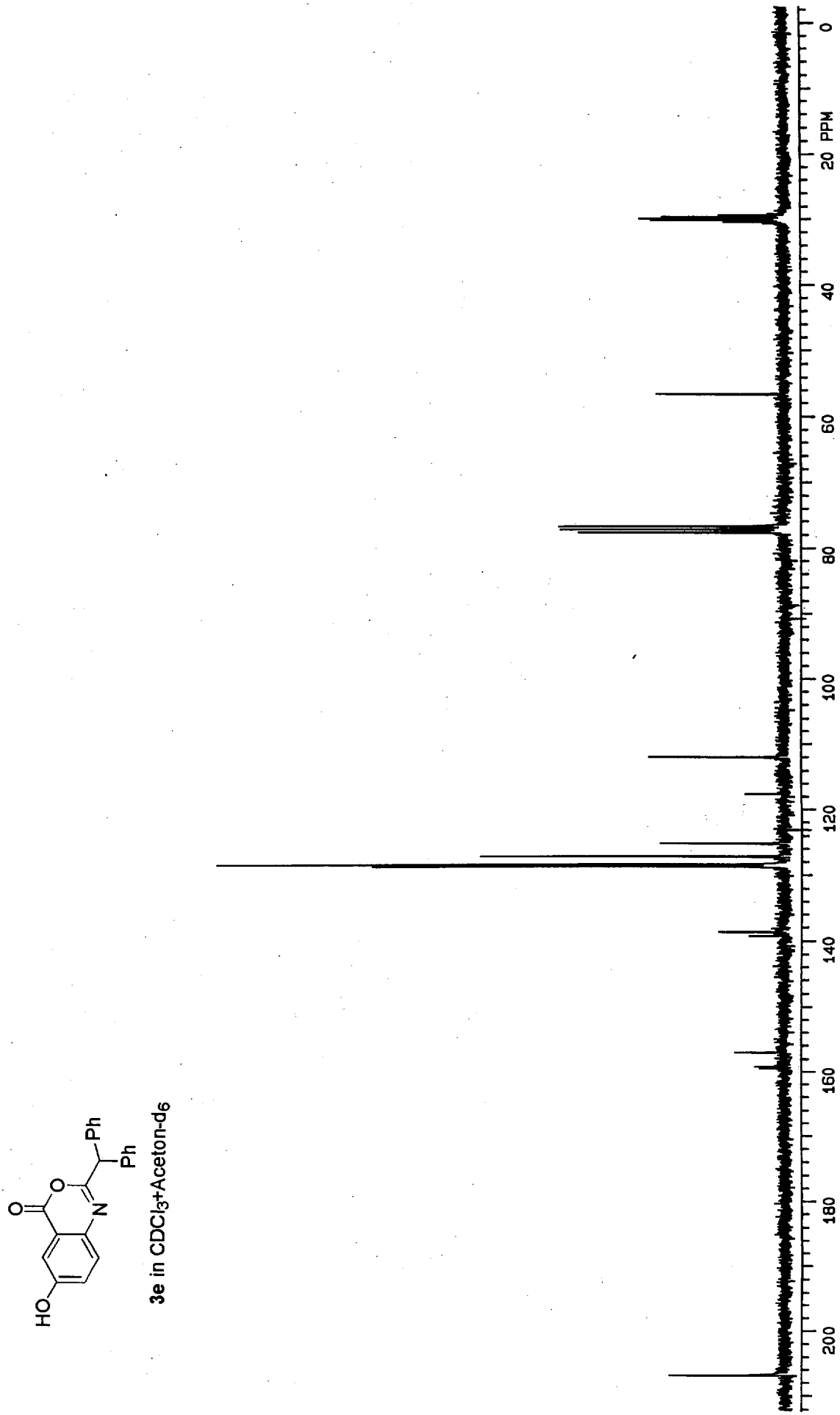

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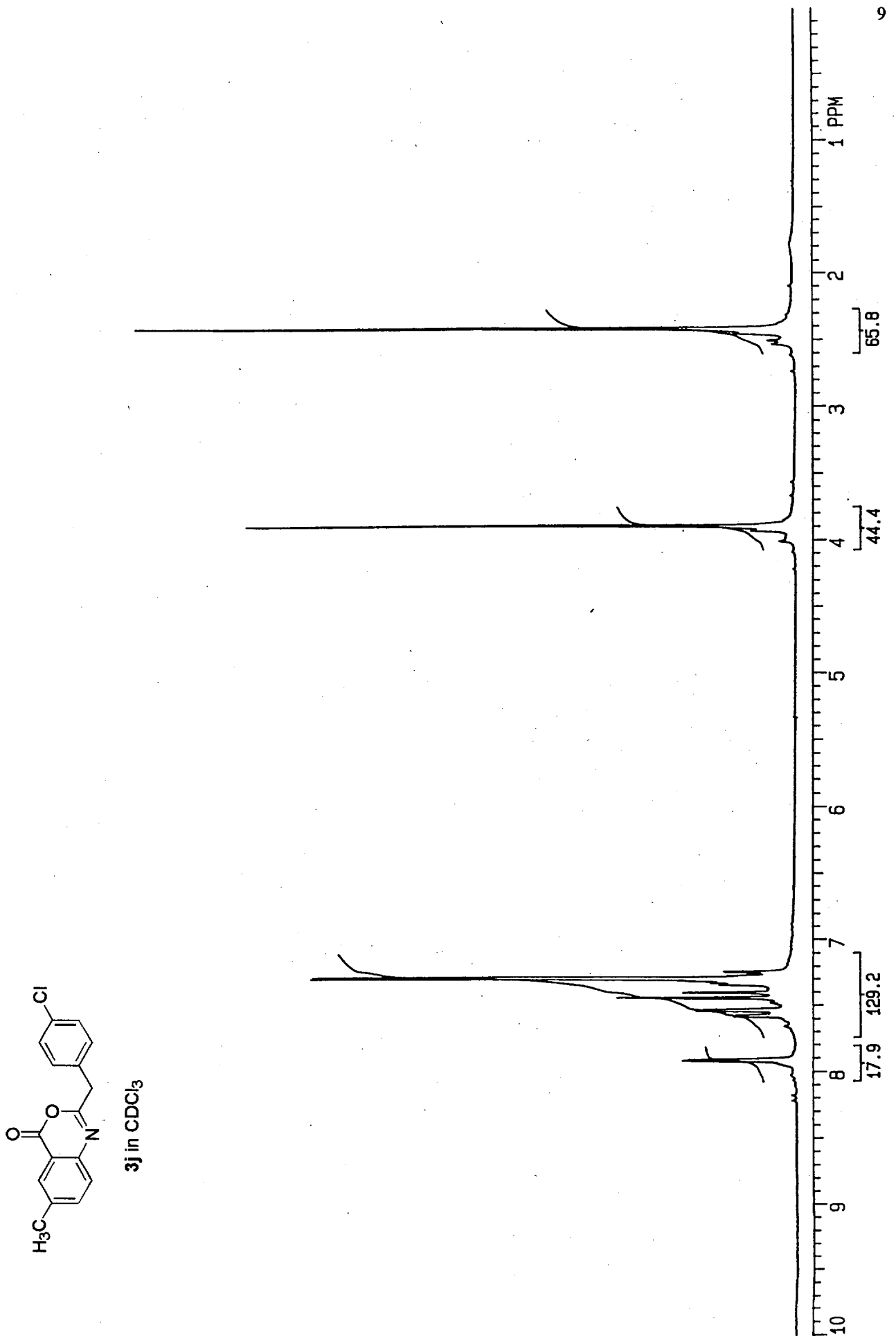

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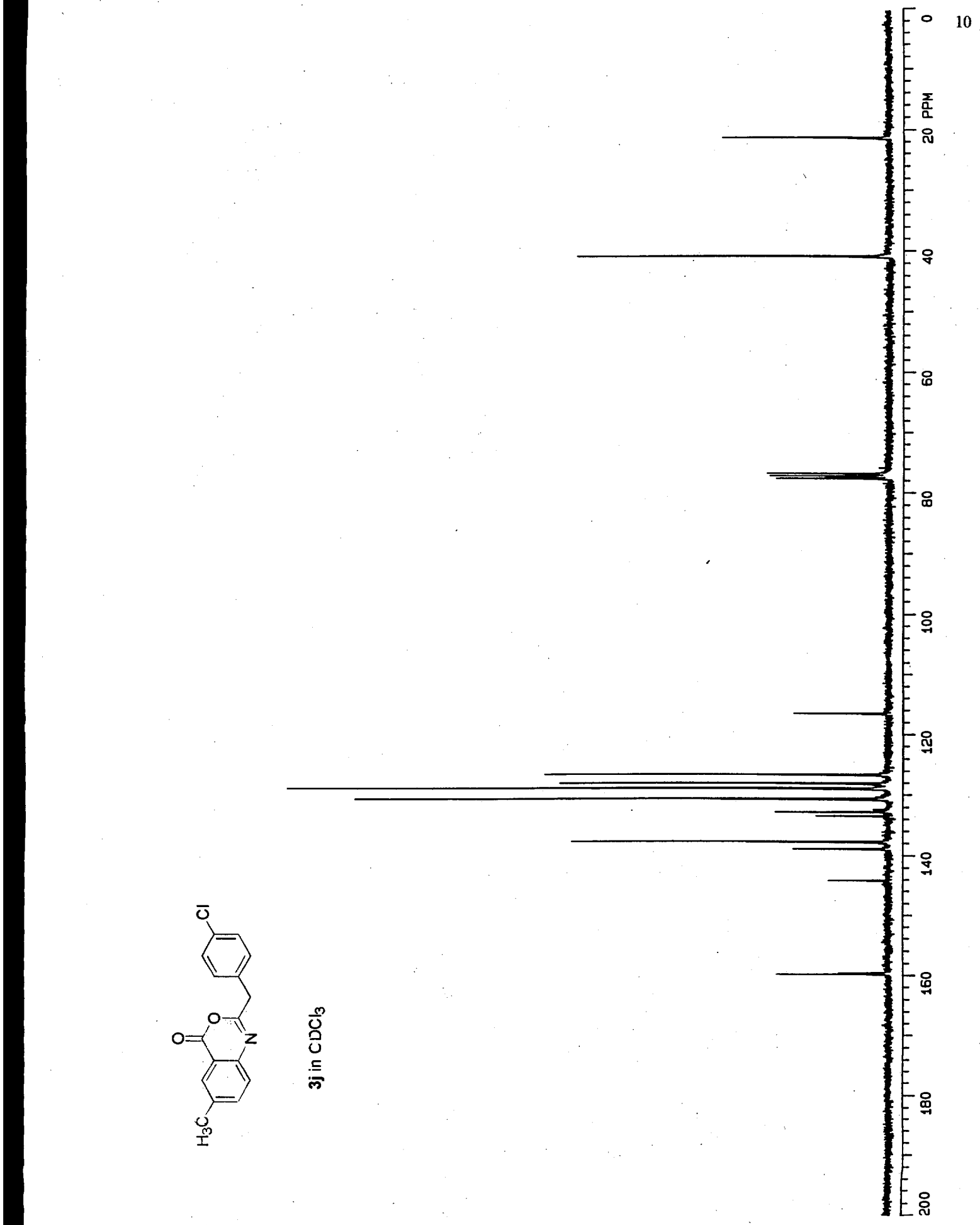

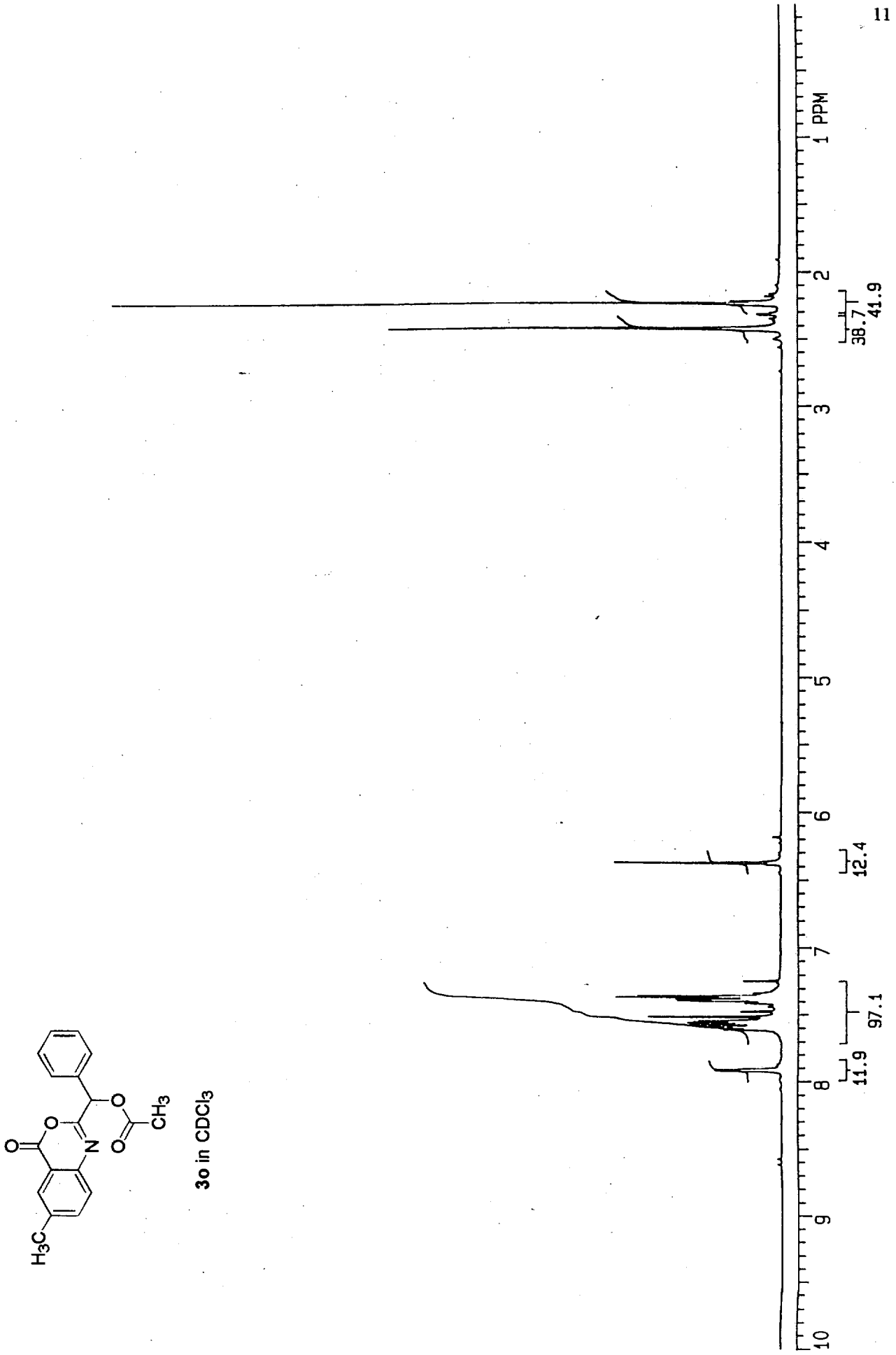

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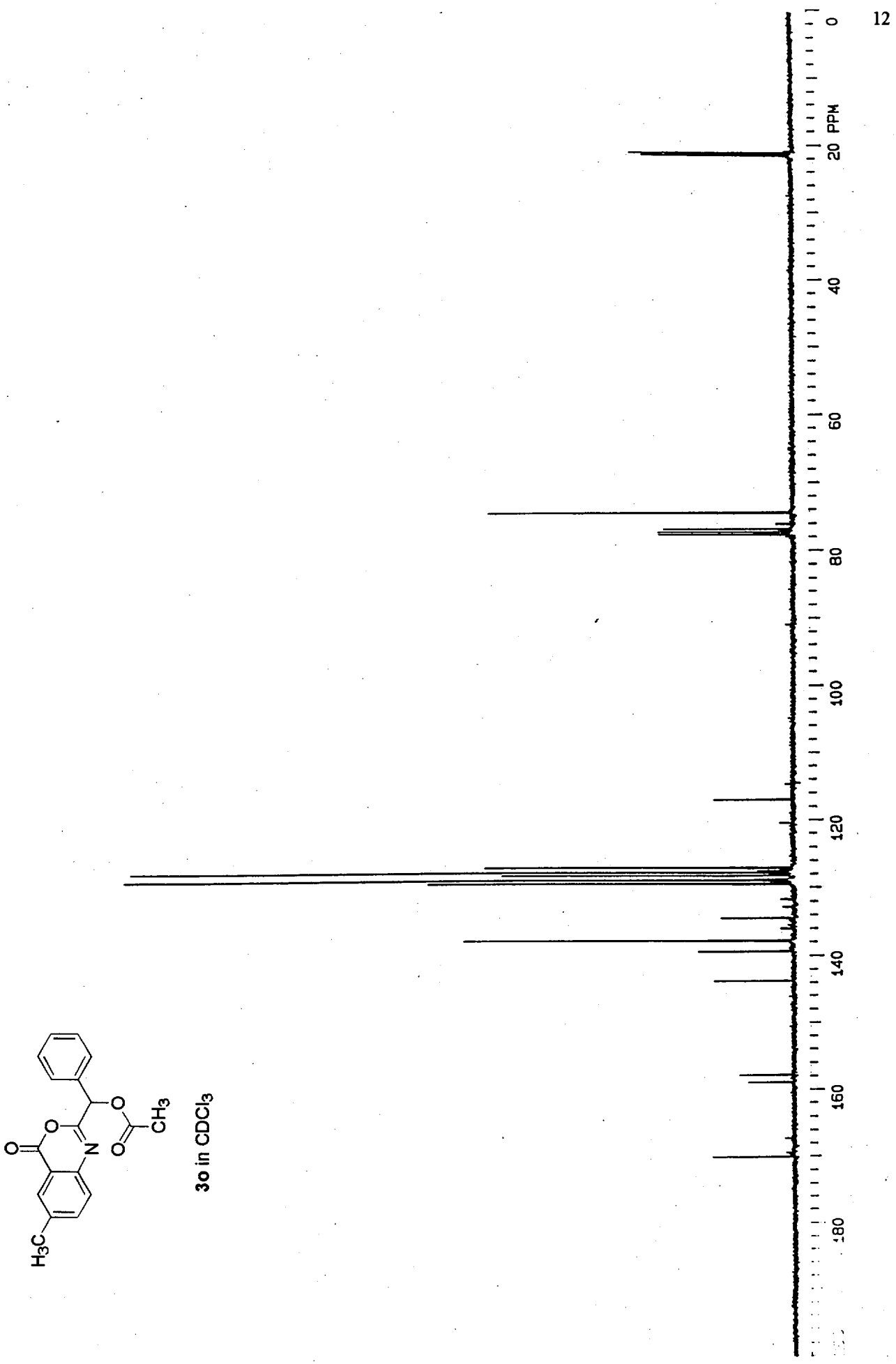

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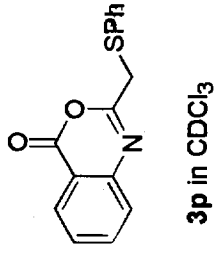

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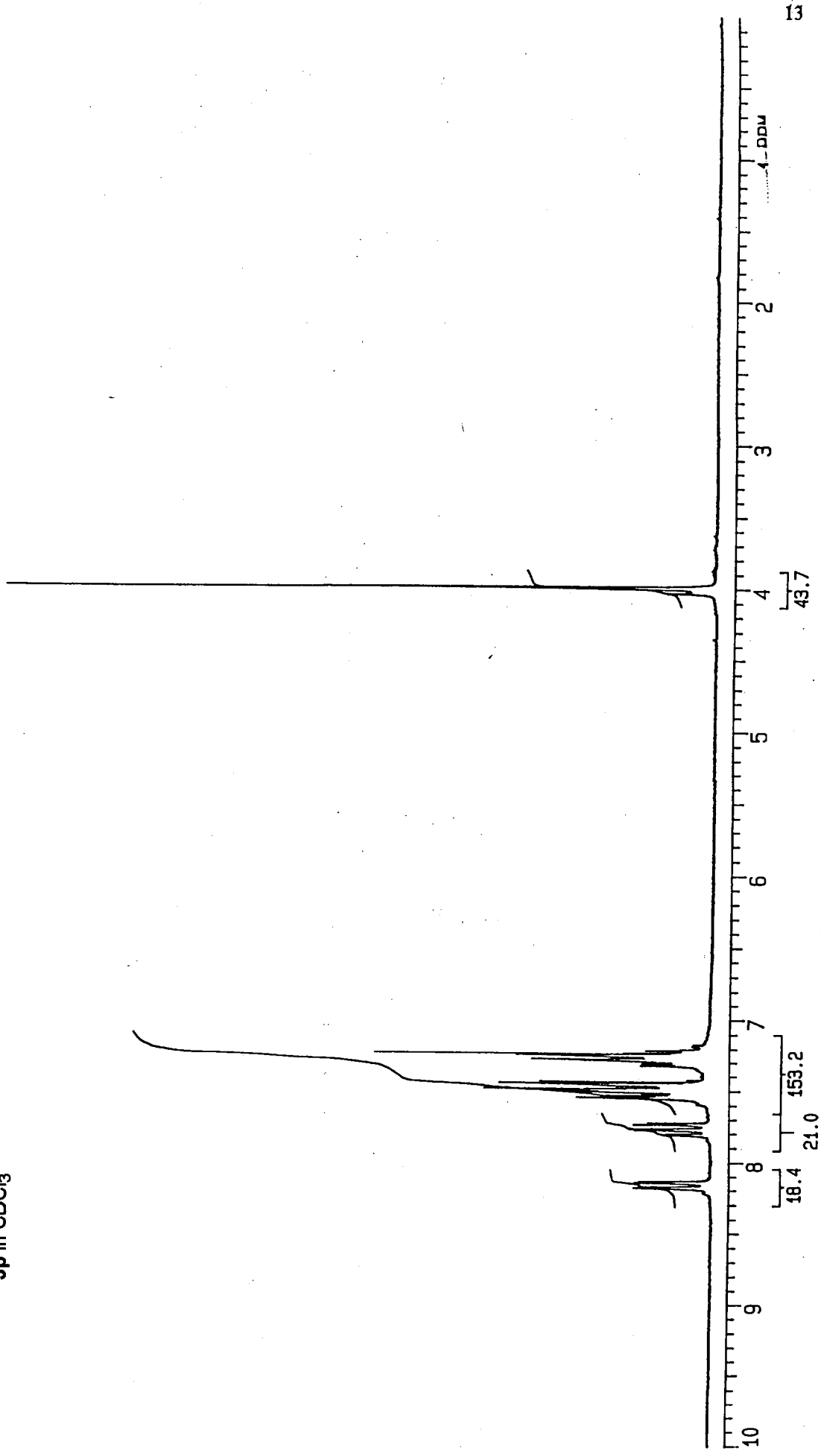

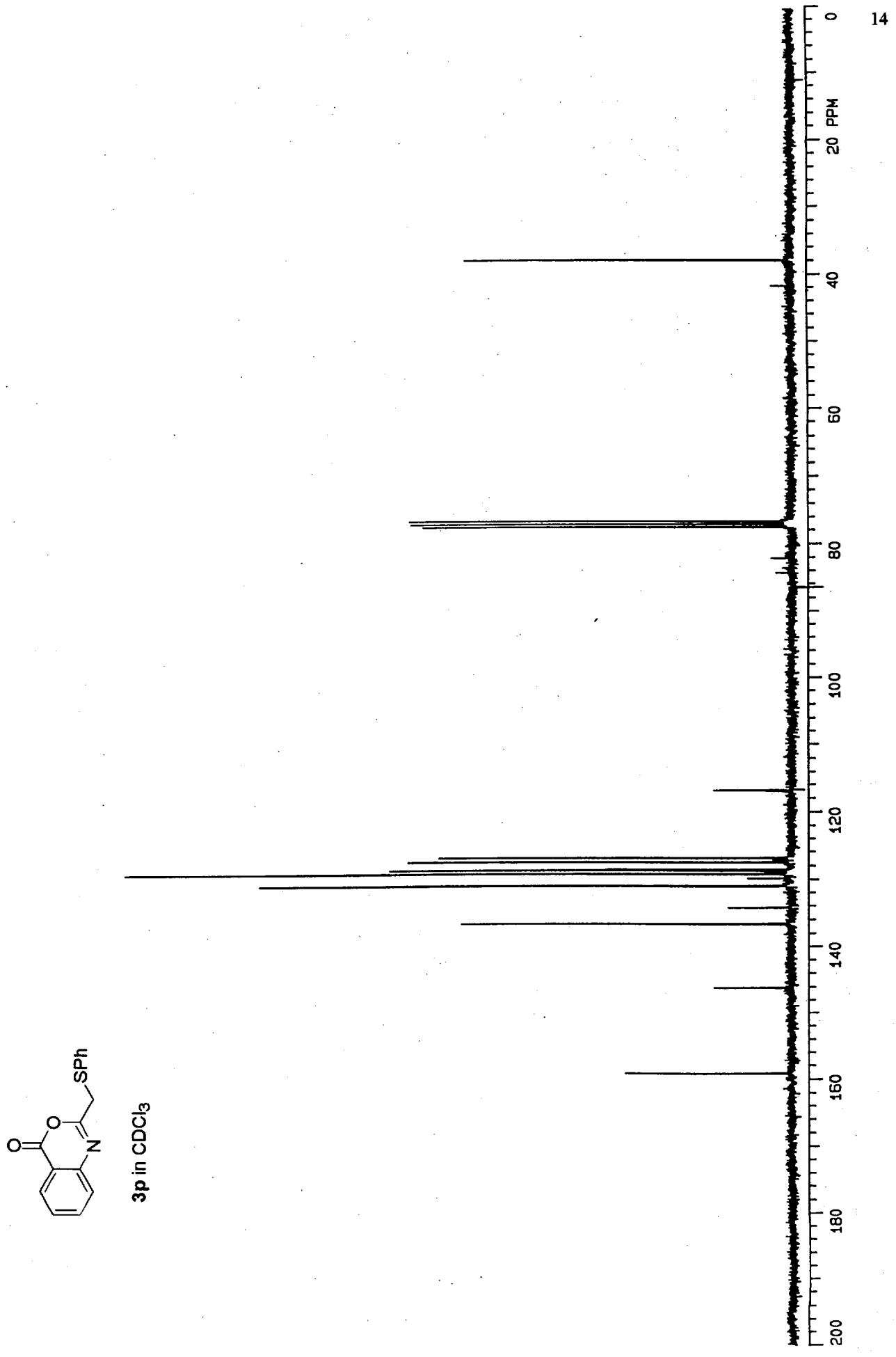
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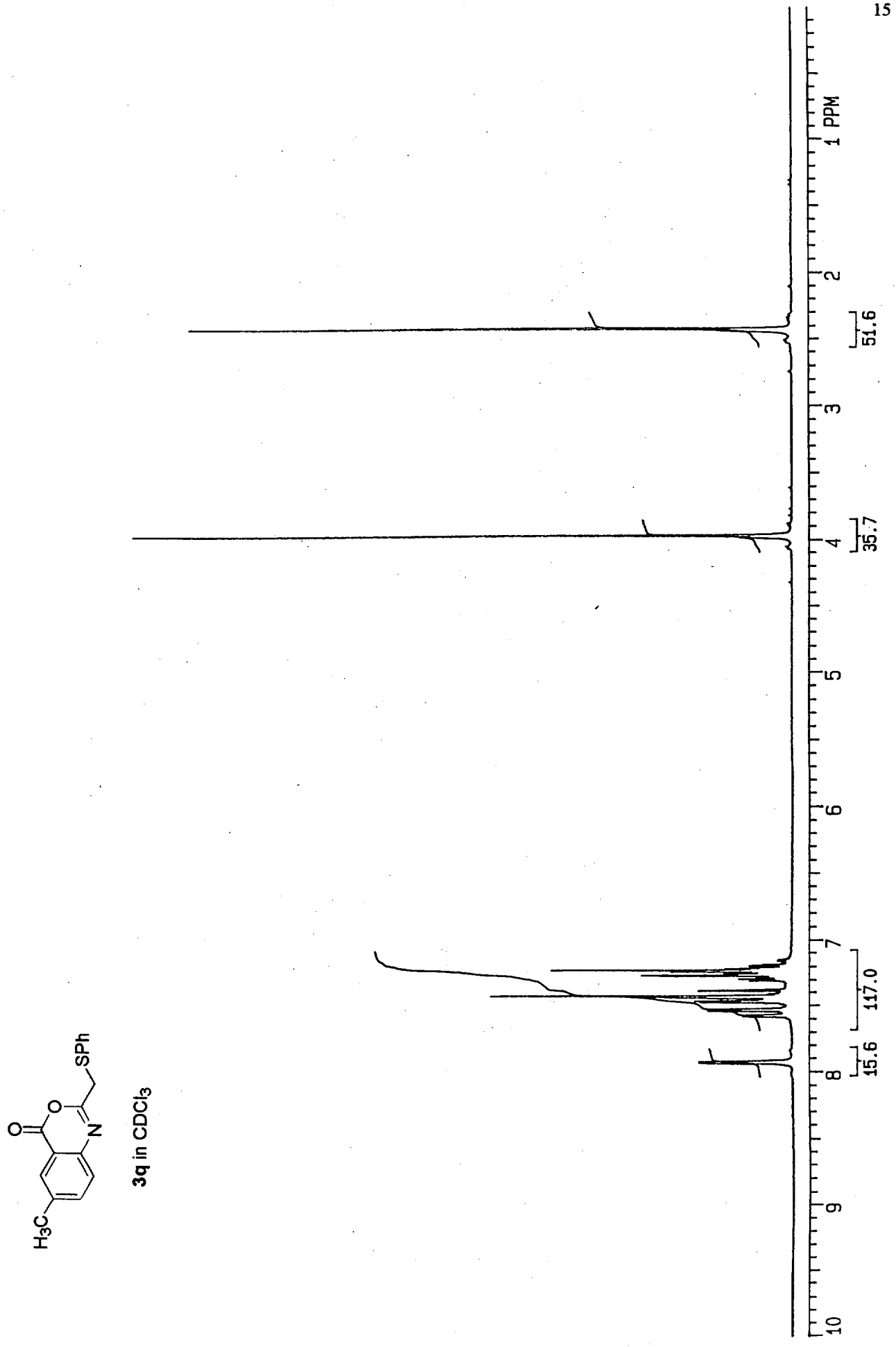

3q in $CDCl_3$