Domino Reactions Initiated by Intramolecular Hydride Transfers from Tri(di)arylmethane Fragments to Ketenimine and Carbodiimide Functions

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General Methods

All melting points are uncorrected. Infrared (IR) spectra were recorded neat or as Nujol emulsions. ^{1}H NMR spectra were recorded in $CDCl_3$ at 200, 300 or 400 MHz. ^{13}C NMR spectra were recorded in $CDCl_3$ at 50, 75 or 100 MHz. ^{31}P NMR spectra were recorded in $CDCl_3$ at 121.4 or 161.9 MHz, using H_3PO_4 as internal reference. The chemical shifts are expressed in ppm, relative to Me_4Si at $\delta = 0.00$ ppm for ^{1}H, while the chemical shifts for ^{13}C are reported relative to the resonance of $CDCl_3$ $\delta = 77.1$ ppm. *J* values are given in Hz.

Materials: 3-methyl-2-nitrobenzaldehyde **7b**,[1] 1-diphenylmethyl-2-nitrobenzene **8a**,[2] 1-bis[4-(*N*,*N*-dimethylamino)phenyl]methyl-2-nitrobenzene **8c**,[3] 1-bis(4-methoxyphenyl)methyl-2-nitrobenzene **8f**,[3] 2-diphenylmethylaniline **9a**,[4] 2-bis[4-(*N*,*N*-dimethylamino)phenyl]-methylaniline **9c**,[3] 2-bis(4-methoxyphenyl)methylaniline **9f**,[3] 1-azido-2-diphenylmethyl-benzene **10a**,[3] 1-azido-2-bis[4-(*N*,*N*-dimethylamino)phenyl]methylbenzene **10c**,[3] 1-azido-2-bis(4-methoxyphenyl)methylbenzene **10f**,[3] 1-amino-4-chloro-2-[1-(4-methoxyphenyl)ethyl]-benzene **26**,[5] 1-azido-2-phenylmethylbenzene **31**,[6] methylphenylketene,[7] ethylphenylketene[8] and diphenylketene[9] were prepared following published experimental procedures.

Preparation of nitrobenzenes 8

Method A (R^1 = H, CH_3; R^2 = H)

Preparation of 3-methyl-2-nitro-1-diphenylmethylbenzene 8b (R^1 = CH_3, R^2 = H)

To a suspension of anhydrous aluminum chloride (5 g, 35 mmol) in anhydrous benzene (15 mL) 3-methyl-2-nitrobenzaldehyde **7b** (2.6 g, 16 mmol) was added, and the resulting mixture was stirred at 60 °C under nitrogen for 6 h. After cooling at room temperature, the reaction crude was poured into cold 6N HCl (50 mL), and extracted with dichloromethane (3 x 50 mL). The combined organic layers were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the resulting material was purified by column chromatography on silica gel, using hexanes/diethyl ether (7:3; v/v) as eluent.

3-Methyl-2-nitro-1-diphenylmethylbenzene 8b (R^1 = CH_3, R^2 = H). Yield = 2.28 g, 47%; mp 83-84 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1601 (m), 1527 (vs), 1495 (s), 1472 (m), 1450 (s), 1369 (s), 1265 (m), 1078 (w), 1032 (w), 852 (m), 779 (m), 735 (vs), 700 (vs); δ_H(200 MHz, $CDCl_3$) 2.26 (3H, s), 5.63 (1 H, s), 6.92 (1 H, d, *J* 7.6), 7.03-7.08 (4 H, m), 7.11-7.14 (1 H, m), 7.17-7.29 (7 H, m); δ_C(50 MHz, $CDCl_3$) 17.4, 51.2, 126.9, 128.5, 128.7, 129.3 129.6, 129.7, 135.0 (s), 141.7 (s), 151.9 (s); HRMS (ESI): Calcd for $C_{20}H_{21}N_2O_3$ $[M+NH_4]^+$ 321.1603, found 321.1602.

Method B (R^1 = H, CH_3; R^2 = $N(CH_3)_2$, *N*-morpholino)

Preparation of nitrobenzenes 8d,e

A mixture of anhydrous zinc chloride (3 g, 22 mmol), the corresponding nitrobenzaldehyde **7** (22 mmol) and *N*,*N*-dimethylaniline or *N*-phenylmorpholine (45 mmol) was heated at 80 °C under nitrogen for 6 h. After cooling at room temperature, water (50 mL) was added, the mixture extracted with dichloromethane (3 x 50 mL), and the combined organic phase was dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the resulting material was purified by column chromatography on silica gel, using hexanes/diethyl ether (7:3; v/v) as eluent.

1-Bis[4-(*N*,*N*-dimethylamino)phenyl]methyl-3-methyl-2-nitrobenzene 8d (R^1 = CH_3, R^2 = $N(CH_3)_2$). Yield = 6.25 g, 73%; mp 192-194 °C (pale green prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1612 (s), 1562 (w), 1520 (vs), 1479 (m), 1444 (m), 1352 (s), 1225 (w), 1165 (m), 950 (w), 765 (s); δ_H(400 MHz, $CDCl_3$) 2.31 (3 H, s), 2.94 (12 H, s), 5.47 (1 H, s), 6.66-6.68 (4 H, m), 6.95-6.98 (4 H, m), 7.02 (1 H, d, *J* 7.6), 7.14 (1 H, d, *J* 7.6), 7.26 (1 H, t, *J* 7.6); δ_C(100 MHz, $CDCl_3$) 17.4, 40.4, 49.4, 112.5, 128.7, 129.0, 129.2 (s), 129.5, 129.8, 130.4 (s), 136.7 (s), 149.2 (s), 151.9 (s); HRMS (ESI): Calcd for $C_{24}H_{28}N_3O_2$ $[M+H]^+$ 390.2176, found 390.2182.

1-Bis[4-(*N*-morpholino)phenyl]methyl-2-nitrobenzene 8e (R^1 = H, R^2 = *N*-morpholino). Yield = 6.67 g, 66%; mp 141-143 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1610 (s), 1514 (vs), 1450 (s), 1230 (vs), 1120 (s), 928 (m), 752 (m), 735 (m); δ_H(400 MHz, $CDCl_3$) 3.13-3.15 (8 H, m), 3.83-3.86 (8 H, m), 6.13 (1 H, s), 6.80-6.84 (4 H, m), 6.94-6.97 (4 H, m), 7.11 (1 H, dd, *J* 8.0 and 1.2), 7.35 (1 H, td, *J* 8.0 and 1.2), 7.47 (1 H, td, *J* 7.6 and 1.6),

7.83 (1 H, dd, *J* 7.6 and 1.6); δ_C(100 MHz, $CDCl_3$) 49.2, 49.7, 66.9, 115.5, 124.6, 127.2, 130.1, 131.9, 132.3, 133.7 (s), 139.1 (s), 149.8 (s); HRMS (ESI): Calcd for $C_{27}H_{30}N_3O_4$ $[M+H]^+$ 460.2231, found 460.2233.

Method C (R^1 = H, CH_3; R^2 = OCH_3)

Preparation of 1-bis(4-methoxyphenyl)methyl-3-methyl-2-nitrobenzene 8g (R^1 = CH_3, R^2 = OCH_3)

To 3-methyl-2-nitrobenzaldehyde **7b** (1.98 g, 12 mmol) and anhydrous aluminum chloride (0.64 g, 4.2 mmol), anisole (2.32 g, 24 mmol) was added dropwise during 5 min. The resulting mixture was stirred at room temperature under nitrogen for 12 h. Then water (25 ml) was added, the mixture extracted with diethyl ether (3 x 50 mL), and the organic phase dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel, using hexanes/dichloromethane (3:7; v/v) as eluent.

1-Bis(4-methoxyphenyl)methyl-3-methyl-2-nitrobenzene 8g (R^1 = CH_3, R^2 = OCH_3). Yield = 2.05 g, 47%; colourless oil; ν_{max}(neat)/cm^{-1} 1608 (s), 1583 (m), 1527 (vs), 1510 (vs), 1464 (m), 1367 (s), 1304 (s), 1250 (vs), 1178 (s), 1113 (w), 846 (m), 781 (m), 737 (m); δ_H(300 MHz, $CDCl_3$) 2.29 (3 H, s), 3.77 (6 H, s), 6.52 (1 H, s), 6.79-6.84 (4 H, m), 6.90-6.93 (1 H, m), 6.95-6.98 (4 H, m), 7.15 (1 H, d, *J* 7.5), 7.26 (1 H, t, *J* 7.5); δ_C(75 MHz, $CDCl_3$) 17.5, 49.5, 55.3, 113.9, 128.6, 129.4, 129.5 (s), 129.7, 130.2, 134.2 (s), 135.8 (s), 151.9 (s), 158.4 (s); HRMS (ESI): Calcd for $C_{22}H_{25}N_2O_4$ $[M+NH_4]^+$ 381.1814, found 381.1814.

Preparation of anilines 9

To a solution of the corresponding nitrobenzene **8** (10 mmol) in ethanol (200 mL) Pd on activated charcoal (0.1 g) was added. The reaction mixture was stirred at room temperature under hydrogen for 24 h. Then the solution was filtered through celite, the solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel.

2-Methyl-6-diphenylmethylaniline 9b (R^1 = CH_3, R^2 = H). Eluent for column chromatography: hexanes/diethyl ether (9.5:0.5, v/v). Yield = 2.27 g, 83%; colourless oil; ν_{max}(neat)/cm^{-1} 3456 (m), 3379 (m), 1621 (vs), 1599 (s), 1492 (s), 1465 (vs), 1435 (s), 1329 (w), 1274 (m), 1078 (m), 908 (m), 765 (s), 744 (vs); δ_H(200 MHz, $CDCl_3$) 2.10 (3 H, s), 3.41 (2 H, broad s), 5.46 (1 H, s), 6.50-6.64 (2 H, m), 6.96 (1 H, d, *J* 7.0), 7.08-7.12 (4 H, m), 7.14-7.30 (6 H, m); δ_C(50 MHz, $CDCl_3$) 17.7, 52.4, 117.8, 122.4 (s), 126.6, 128.0, 128.3 (s), 128.5, 128.8, 129.5, 142.3 (s), 142.7 (s); HRMS (ESI): Calcd for $C_{20}H_{20}N$ $[M+H]^+$ 274.1590, found 274.1593.

2-Bis[4-(*N*,*N*-dimethylamino)phenyl]methyl-6-methylaniline 9d (R^1 = CH_3, R^2 = $N(CH_3)_2$). Eluent for column chromatography: hexanes/diethyl ether (7:3, v/v). Yield = 3.02 g, 84%; mp 145-146 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 3440 (w), 3367 (m), 1608 (vs), 1583 (s), 1510 (vs), 1462 (vs), 1246 (vs), 1176 (s), 1111 (m), 1035 (s), 874 (w), 839 (m), 769 (s); δ_H(300 MHz, $CDCl_3$) 2.18 (3 H, s), 2.94 (12 H, s), 3.56 (2 H, broad s), 5.33 (1 H, s), 6.62-6.64 (2 H, m), 6.67-6.71 (4 H, m), 6.97-7.03 (5 H, m); δ_C(75 MHz, $CDCl_3$) 17.7, 40.7, 50.6, 112.7, 117.6, 122.1 (s), 127.9, 128.3, 129.9 (s), 130.1, 131.3 (s), 142.5 (s), 149.2 (s); HRMS (ESI): Calcd for $C_{24}H_{30}N_3$ $[M+H]^+$ 360.2434, found 360.2437.

2-Bis[4-(*N*-morpholino)phenyl]methylaniline 9e (R^1 = H, R^2 = *N*-morpholino). Eluent for column chromatography: hexanes/diethyl ether (3:7, v/v). Yield = 3.35 g, 78%; mp 106-108 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 3439 (w), 3360 (w), 1610 (s), 1492 (s), 1379 (s), 1304 (m), 1263 (vs), 1229 (vs), 1120 (vs), 928 (vs), 833 (m), 804 (m), 734 (vs); δ_H(300 MHz, $CDCl_3$) 3.11-3.15 (8 H, m), 3.48 (2 H, s), 3.82-3.86 (8 H, m), 5.32 (1 H, s), 6.64-6.68 (3 H, m), 6.81-6.86 (4 H, m), 6.99-7.10 (5 H, m); δ_C(75 MHz, $CDCl_3$) 49.3, 50.6, 67.0, 115.6, 116.1, 118.5, 127.2, 129.8, 129.9 (s), 130.2, 134.2 (s), 144.3 (s), 149.7 (s); HRMS (ESI): Calcd for $C_{27}H_{32}N_3O_2$ $[M+H]^+$ 430.2489, found 430.2492.

6-Bis(4-methoxyphenyl)methyl-2-methylaniline 9g (R^1 = CH_3, R^2 = OCH_3). Eluent for column chromatography: hexanes/diethyl ether (7:3, v/v). Yield = 2.17 g, 65%; colourless oil; ν_{max}(neat)/cm^{-1} 3454 (w), 3379 (w), 1620 (s), 1608 (s), 1508 (vs), 1463 (s), 1441 (s), 1302 (m), 1277 (m), 1176 (s), 1109 (m), 1034 (s), 835 (m), 737 (m); δ_H(300 MHz, $CDCl_3$) 2.15 (3 H, s), 3.49 (2 H, broad s), 3.78 (6 H, s), 5.37 (1 H, s), 6.52 (1 H, d, *J* 7.5), 6.61 (1 H, t, *J* 7.5), 6.79-6.88 (4 H, m), 6.97 (1 H, d, *J* 7.5), 6.98-7.04 (4 H, m); δ_C(75 MHz, $CDCl_3$) 17.8, 50.8,

55.3, 113.9, 117.8, 122.4 (s), 127.9, 128.7, 129.1 (s), 130.4, 135.1 (s), 142.4 (s), 158.3 (s); HRMS (ESI): Calcd for $C_{22}H_{24}NO_2$ $[M+H]^+$ 334.1802, found 334.1806.

Preparation of azides 10

Method A (R^1 = H, Me; R^2 = H, OMe).

Preparation of azides 10b,g.

To a solution of the corresponding aniline **9** (8.2 mmol) in a mixture of water (40 mL), concentrated sulfuric acid (10 mL) and 1,4-dioxane (40 mL), cooled at 0 °C, a solution of sodium nitrite (0.62 g, 9.0 mmol) in water (5 mL) was added dropwise. The reaction mixture was stirred at 0 °C for 30 min, and then a solution of sodium azide (0.59 g, 9 mmol) in water (5 mL) was added dropwise over 10 min. After stirring at room temperature for 16 h, the mixture was extracted with diethyl ether (3 x 50 mL) and the organic phase dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the resulting material was purified by column chromatography on silica gel.

2-Azido-3-methyl-1-(diphenylmethyl)benzene 10b (R^1 = CH_3, R^2 = H). Eluent for column chromatography: hexanes/diethyl ether (9.5:0.5, v/v). Yield = 2.18 g, 89%; colourless oil; ν_{max}(neat)/cm^{-1} 2110 (vs), 1599 (m), 1493 (s), 1450 (s), 1427 (s), 1288 (s), 1080 (m), 756 (vs), 700 (vs); δ_H(200 MHz, $CDCl_3$) 2.41 (3 H, s), 5.90 (1 H, s), 6.74 (1 H, dd, *J* 7.2 and 2.2), 6.97-7.01 (1 H, m), 7.05-7.10 (5 H, m), 7.21-7.33 (6 H, m); δ_C(50 MHz, $CDCl_3$) 18.1, 52.3, 125.9, 126.5, 128.4, 129.5, 129.7, 133.1 (s), 136.9 (s), 138.4 (s), 143.2 (s); HRMS (ESI): Calcd for $C_{20}H_{18}N_4$ $[M+H-N_2]^+$ 272.1439, found 272.1430.

2-Azido-1-bis(4-methoxyphenyl)methyl-3-methylbenzene 10g (R^1 = CH_3, R^2 = OCH_3). Eluent for column chromatography: hexanes/diethyl ether (9:1, v/v). Yield = 2.45 g, 83%; mp 74-75 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 2108 (vs), 1608 (s), 1583 (s), 1510 (vs), 1462 (s), 1302 (s), 1246 (vs), 1111 (m), 1035 (s), 739 (m); δ_H(300 MHz, $CDCl_3$) 2.40 (3 H, s), 3.78 (6 H, s), 5.80 (1 H, s), 6.74 (1 H, dd, *J* 7.2 and 1.5), 6.79-6.84 (4 H, m), 6.95-7.01 (4 H, m), 7.02 (1 H, d, *J* 7.2), 7.04 (1 H, d, *J* 1.5); δ_C(75 MHz, $CDCl_3$) 18.1,

50.6, 55.3, 113.7, 125.8, 128.3, 129.6, 130.3, 133.0 (s), 135.7 (s), 136.8 (s), 138.9 (s), 158.1 (s); HRMS (ESI): Calcd for $C_{22}H_{22}NO_2$ $[M+H-N_2]^+$ 332.1651, found 332.1650.

Method B (R^1 = H, Me; R^2 = NMe_2, *N*-morpholino).

Preparation of azides 10d,e.

To a solution of the corresponding aniline **9** (10 mmol) in a mixture of concentrated HCl and water (1:1, v/v) (10 mL), cooled at 0 °C, a solution of sodium nitrite (0.76 g, 11 mmol) in water (6 mL) was added dropwise. Next a solution of sodium azide (0.76 g, 12 mmol) and sodium acetate (7.6 g, 93 mmol) in water (20 mL) was added, and the reaction mixture was stirred at room temperature for 1 h. Then the reaction mixture was extracted with diethyl ether (3 x 50 mL) and the organic phase dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the resulting material was purified by column chromatography on silica gel.

2-Azido-1-bis[4-(*N*,*N*-dimethylamino)phenyl]methyl-3-methylbenzene 10d (R^1 = CH_3, R^2 = $N(CH_3)_2$). Eluent for column chromatography: hexanes/diethyl ether (9:1, v/v). Yield = 1.73 g, 45%; mp 117-118 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 2108 (vs), 1612 (s), 1518 (vs), 1444 (m), 1348 (m), 1163 (w), 1061 (w), 949 (w), 814 (w); δ_H(400 MHz, $CDCl_3$) 2.39 (3 H, s), 2.91 (12 H, s), 5.72 (1 H, s), 6.64-6.67 (4 H, m), 6.80 (1 H, dd, *J* 7.2 and 2.4), 6.92-6.98 (4 H, m), 6.99-7.03 (2 H, m); δ_C(100 MHz, $CDCl_3$) 18.2, 40.8, 50.3, 112.6, 125.7, 128.4, 129.2, 130.0, 132.0 (s), 132.7 (s), 136.8 (s), 139.7 (s), 149.1 (s); HRMS (ESI): Calcd for $C_{24}H_{28}N_5$ $[M+H]^+$ 386.2339, found 386.2346.

1-Azido-2-bis[4-(*N*-morpholino)phenyl]methylbenzene 10e (R^1 = H, R^2 = *N*-morpholino). Eluent for column chromatography: hexanes/diethyl ether (1:9, v/v). Yield = 3.28 g, 72%; mp 159-160 °C (yellow prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 2123 (vs), 1610 (m), 1510 (s), 1227 (m), 1184 (w), 1122 (m), 924 (w), 893 (m), 762 (w); δ_H(400 MHz, $CDCl_3$) 3.11-3.13 (8 H, m), 3.82-3.84 (8 H, m), 5.65 (1 H, s), 6.79-6.83 (4 H, m), 6.91-6.96 (5 H, m), 7.02 (1 H, td, *J* 5.7 and 0.9), 7.13 (1 H, dd, *J* 5.7 and 0.9 Hz), 7.24 (1 H, td, *J* 5.7 and 1.2); δ_C(100 MHz, $CDCl_3$) 49.0, 49.3, 67.0, 115.4, 118.1, 124.5, 127.6, 130.1, 130.8, 134.9 (s), 136.1 (s), 138.1 (s), 149.5 (s); HRMS (ESI): Calcd for $C_{27}H_{30}N_5O_2$ $[M+H]^+$ 456.2394, found 456.2396.

Preparation of iminophosphoranes 11

To a solution of the corresponding azide **10** (5 mmol) in anhydrous diethyl ether (20 mL) triphenylphosphine (1.30 g, 5 mmol) was added in five portions. The reaction mixture was stirred at room temperature under nitrogen for 16 h. Then, the precipitated compound **11** was isolated by filtration and washed with anhydrous diethyl ether (15 mL).
These compounds were used in the following step without further purification.
For analytical samples iminophosphoranes **11** were recrystallized from diethyl ether.

1-Diphenylmethyl-2-triphenylphosphoranylidenaminobenzene 11a (R^1 = H, R^2 = H). Yield = 2.49 g, 96%; mp 164-167 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1587 (s), 1477 (vs), 1437 (vs), 1338 (s), 1265 (m), 1220 (m), 1181 (s), 1024 (m), 999 (w), 777 (m), 740 (s), 696 (s), 609 (m); δ_H(300 MHz, $CDCl_3$) 6.48 (1 H, s), 6.52 (1 H, d, *J* 7.8), 6.60 (1 H, t, *J* 7.8), 6.76-6.84 (2 H, m), 7.12-7.25 (10 H, m), 7.34-7.40 (7 H, m), 7.45-7.51 (3 H, m), 7.55-7.62 (5 H, m); δ_C(75 MHz, $CDCl_3$) 52.1, 116.9, 121.0 (d, *J* 39.9), 125.3, 126.2, 127.2, 128.3 (d, *J* 11.9), 129.9, 131.3 (d, *J* 2.8), 131.4 (d, *J* 98.8) (s), 138.4 (d, *J* 21.7), 132.5 (d, *J* 9.5), 133.7 (d, *J* 19.3), 145.4 (s), 149.2 (s); δ_P(121.4 MHz, $CDCl_3$, H_3PO_4) 1.6; HRMS (ESI): Calcd for $C_{37}H_{31}NP$ $[M+H]^+$ 520.2189, found 520.2194.

3-Methyl-1-diphenylmethyl-2-triphenylphosphoranylidenaminobenzene 11b (R^1 = CH_3, R^2 = H). Yield = 2.48 g, 93%; mp 208-209 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1589 (w), 1456 (vs), 1433 (vs), 1342 (s), 1113 (m), 1028 (w), 932 (m), 891 (m), 754 (m), 696 (vs); δ_H(300 MHz, $CDCl_3$) 1.93 (3 H, s), 5.98 (1 H, s), 6.60-6.71 (6 H, m), 6.93-6.96 (1 H, m), 7.07-7.15 (6 H, m), 7.33-7.39 (7 H, m), 7.46-7.51 (8 H, m); δ_C(75 MHz, $CDCl_3$) 22.1, 51.6, 118.5 (d, *J* 3.1), 125.4, 127.7, 128.4 (d, *J* 23.6) (s), 128.5 (d, *J* 12.0), 128.6, 129.9, 131.2 (d, *J* 2.7), 132.4 (d, *J* 9.5), 132.8 (d, *J* 4.9), 133.0 (d, *J* 100.6) (s), 138.1 (d, *J* 9.1), 145.6 (s), 147.0 (d, *J* 1.3); δ_P(121.4 MHz, $CDCl_3$, H_3PO_4) - 7.0; HRMS (ESI): Calcd for $C_{38}H_{32}NP$ $[M+H]^+$ 534.2345, found 534.2349.

1-Bis[4-(*N*,*N*-dimethylamino)phenyl]methyl-2-triphenylphosphoranylideneamino-benzene 11c (R^1 = H, R^2 = NMe_2). Yield = 2.60 g, 86%; mp 209-211 °C (yellow prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1612 (s), 1587 (s), 1517 (vs), 1475 (vs), 1437 (vs), 1344 (vs), 1111 (s), 1024 (w), 947 (w), 814 (m), 715 (m), 694 (m); δ_H(400 MHz, $CDCl_3$) 2.86 (12 H, s), 6.26 (1 H, s), 6.47 (1H, d, *J* 7.8), 6.56 (1 H, t, *J* 7.4), 6.60 (4 H, d, *J* 8.5), 6.72-6.76 (1 H, m), 6.78-6.80 (1 H, m), 6.98 (4 H, d, *J* 8.5), 7.32-7.37 (6 H, m), 7.42-7.46 (3 H, m), 7.55-7.60 (6

H, m); δ_C(100 MHz, $CDCl_3$) 41.1, 50.0, 112.7, 117.0, 121.1 (d, *J* 9.7), 125.8, 128.3 (d, *J* 12.0), 130.0, 130.4, 131.3 (d, *J* 2.4), 131.7 (d, *J* 99.4) (s), 132.7 (d, *J* 9.6), 134.7 (s), 139.9 (d, *J* 21.1) (s), 148.6 (s), 149.1 (s); δ_P(121.4 MHz, $CDCl_3$, H_3PO_4) 0.8; HRMS (ESI): Calcd for $C_{41}H_{41}N_3P$ $[M+H]^+$ 606.3033, found 606.3036.

1-Bis[4-(*N*,*N*-dimethylamino)phenyl]methyl-3-methyl-2-triphenylphosphoranylidenaminobenzene 11d (R^1 = CH_3, R^2 = $N(CH_3)_2$). Yield = 3.07 g, 99%; mp 144-145 °C (yellow prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1612 (m), 1516 (vs), 1456 (s), 1435 (vs), 1344 (m), 1111 (s), 947 (w), 802 (m), 739 (s), 696 (s); δ_H(400 MHz, $CDCl_3$) 1.90 (3 H, s), 2.86 (12 H, s), 5.72 (1 H, s), 6.49-6.55 (7 H, m), 6.61-6.62 (2 H, m), 6.87-6.89 (1 H, m), 7.29-7.36 (8 H, m), 7.45-7.47 (8 H, m); δ_C(100 MHz, $CDCl_3$) 22.2, 41.1, 49.7, 112.6, 118.4, 127.7 (d, *J* 2.9), 128.3 (d, *J* 11.9), 128.5, 128.7 (d, *J* 18.4), 130.3, 131.0 (d, *J* 2.7), 132.5 (d, *J* 9.5), 133.1 (d, *J* 100.4) (s), 133.8 (d, *J* 19.4), 134.7 (s), 139.6 (d, *J* 8.9) (s), 146.8 (s), 148.5 (s); δ_P(121.4 MHz, $CDCl_3$, H_3PO_4) - 7.1; HRMS (ESI): Calcd for $C_{42}H_{43}N_3P$ $[M+H]^+$ 620.3189, found 620.3200.

1-Bis[4-(*N*-morpholino)phenyl]methyl-2-(triphenylphosphoranylidenamino)benzene 11e (R^1 = H, R^2 = *N*-morpholino). Yield = 3.41 g, 99%; mp 209-210 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1610 (s), 1512 (vs), 1475 (vs), 1340 (vs), 1228 (m), 1053 (m), 1024 (m), 931 (s), 819 (m); δ_H(300 MHz, $CDCl_3$) 3.06-3.09 (8 H, m), 3.82-3.85 (8 H, m), 6.28 (1 H, s), 6.47 (1 H, d, *J* 8.1), 6.56 (1 H, t, *J* 6.9), 6.73-6.78 (6 H, m), 6.97-7.02 (4 H, m), 7.32-7.39 (6 H, m), 7.44-7.48 (3 H, m), 7.49-7.55 (6 H, m); δ_C(75 MHz, $CDCl_3$) 49.8, 50.3, 67.1, 115.3, 117.0, 121.1 (d, *J* 9.7), 126.1, 128.4 (d, *J* 11.9), 129.9, 130.3, 131.4 (d, *J* 2.7), 131.6 (d, *J* 98.9) (s), 132.6 (d, *J* 9.6), 137.6 (s), 139.2 (d, *J* 21.3) (s), 149.0 (s), 149.2 (s); δ_P(121.4 MHz, $CDCl_3$, H_3PO_4) 1.1; HRMS (ESI): Calcd for $C_{45}H_{45}N_3O_2P$ $[M+H]^+$ 690.3244, found 690.3253.

1-Bis(4-methoxyphenyl)methyl-2-triphenylphosphoranylidenaminobenzene 11f (R^1 = H, R^2 = OCH_3). Yield = 2.75 g, 95%; mp 129-130 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1608 (s), 1587 (s), 1508 (s), 1475 (vs), 1438 (s), 1246 (s), 1174 (m), 1034 (m), 825 (w), 715 (w), 694 (m); δ_H(400 MHz, $CDCl_3$) 3.74 (6 H, s), 6.31 (1 H, s), 6.48 (1 H, d, *J* 7.8), 6.56 (1 H, t, *J* 7.4), 6.72 (4 H, d, *J* 8.4), 6.73-6.74 (1 H, m), 6.76 (1 H, t, *J* 7.8), 7.01 (4 H, d, *J* 8.4), 7.33-7.37 (6 H, m), 7.44-7.48 (3 H, m), 7.53-7.58 (6 H, m); δ_C(100 MHz,

$CDCl_3$) 50.4, 55.2, 113.2, 117.0, 121.2 (d, *J* 9.7), 126.2, 128.4 (d, *J* 12.0), 128.7 (d, *J* 18.2), 129.9, 130.8, 131.4 (d, *J* 2.3), 131.6 (d, *J* 99.5) (s), 132.6 (d, *J* 9.7), 133.8 (d, *J* 19.4), 138.0 (s), 139.1 (d, *J* 21.4) (s), 149.2 (s), 157.5 (s); δ_P(121.4 MHz, $CDCl_3$, H_3PO_4) 0.8; HRMS (ESI): Calcd for $C_{39}H_{35}NO_2P$ $[M+H]^+$ 580.2400, found 580.2402.

1-Bis(4-methoxyphenyl)methyl-3-methyl-2-triphenylphosphoranilydenaminobenzene 11g (R^1 = CH_3, R^2 = OCH_3). Yield = 2.58 g, 87%; mp 169-171 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1606 (s), 1587 (s), 1508 (vs), 1456 (vs), 1435 (vs), 1359 (s), 1244 (s), 1174 (s), 1109 (s), 1035 (s), 997 (m), 835 (m), 812 (m), 737 (s), 696 (s); δ_H(300 MHz, $CDCl_3$) 1.90 (3 H, s), 3.73 (6 H, s), 5.80 (1 H, s), 6.54-6.65 (10 H, m), 6.90 (1 H, d, *J* 6.6), 7.31-7.49 (15 H, m); δ_C(75 MHz, $CDCl_3$) 22.1, 49.9, 55.2, 113.1, 118.5 (d, *J* 3.1), 128.1, 128.4 (d, *J* 11.9), 130.6, 131.1 (d, *J* 2.7), 132.4 (d, *J* 9.5), 132.8 (d, *J* 4.9), 132.9 (d, *J* 100.9) (s), 138.0 (s), 138.8 (d, *J* 8.9) (s), 146.9 (s), 157.3 (s); δ_P(121.4 MHz, $CDCl_3$, H_3PO_4) - 7.0; HRMS (ESI): Calcd for $C_{40}H_{37}NO_2P$ $[M+H]^+$ 594.2556, found 594.2554.

Preparation of the Quinolines 13

To a solution of iminophosphorane **11** (1 mmol) in anhydrous dichloromethane (15 mL) ethylphenylketene (0.15 g, 1 mmol) or methylphenylketene (0.13 g, 1 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred at room temperature for 30 min. Then, the solvent was removed under reduced pressure and the resulting crude material was chromatographed on a silica gel column, using hexanes/diethyl ether (9:1, v/v) as eluent, to give the corresponding ketenimine **12**.

A solution of the ketenimine **12** (0.5 mmol) in anhydrous toluene (20 mL) was heated at reflux temperature under an atmosphere of nitrogen for 5-144 h. After cooling at room temperature, the solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel.

3-Methyl-3,4,4-triphenyl-3,4-dihydroquinoline 13a (R^1 = H; R^2 = H; R^3 = CH_3).. Reaction conditions: anhydrous toluene, 120 h. Eluent for column chromatography: hexanes/diethyl ether (9:1, v/v). Yield = 0.11 g, 60%; mp 194-195 ºC (colourless prisms from diethyl ether/hexane); ν_{max}(Nujol)/cm^{-1} 1633 (s), 1595 (m), 1493 (vs), 1471 (s), 1387 (w), 1265 (m), 1221 (w), 1031 (m), 939 (w), 791 (m), 758 (vs), 737 (vs), 698 (vs), 619 (s); δ_H(300 MHz; $CDCl_3$) 1.83 (3 H, s), 6.61 (2 H, d, *J* 7.5), 6.90 (4 H, t, *J* 7.2), 6.98-7.06 (4

H, m), 7.10-7.21 (6 H, m), 7.45 (1 H, dd, *J* 7.5 and 1.2), 7.55-7.58 (2 H, m), 8.21 (1 H, s); δ_C(75 MHz; $CDCl_3$) 20.2, 48.5 (s), 61.4 (s), 126.2, 126.3, 126.6, 126.7, 127.2, 127.5, 127.6, 127.9, 128.4, 128.6, 129.2, 131.8, 135.1 (s), 138.2 (s), 140.8 (s), 141.7 (s), 146.1 (s), 167.8; HRMS (ESI): Calcd for $C_{28}H_{24}N$ $[M+H]^+$ 374.1903, found 374.1907.

3-Ethyl-3,4,4-triphenyl-3,4-dihydroquinoline 13b (R^1 = H, R^2 = H, R^3 = CH_2CH_3). Reaction conditions: anhydrous *ortho*-xylene, 144 h. Eluent for column chromatography: hexanes/diethyl ether (9:1, v/v). Yield = 0.03 g, 15%; yellow oil; ν_{max}(neat)/cm^{-1} 1625 (s), 1597 (m), 1493 (s), 1452 (s), 1377 (w), 1263 (m), 1084 (w), 1036 (w), 874 (w), 773 (s), 737 (s), 702 (s); δ_H(300 MHz; $CDCl_3$) 0.80 (3 H, t, *J* 7.2), 2.00-2.10 (1 H, m), 2.53-2.62 (1 H, m), 6.61 (2 H, d, *J* 7.6), 6.93-7.25 (14 H, m), 7.41-7.46 (3 H, m), 8.63 (1 H, s,); δ_C(75 MHz; $CDCl_3$) 8.8, 24.8, 51.6 (s), 62.6 (s), 126.5, 126.6, 126.7, 126.8, 127.2, 127.3, 127.4, 127.8, 128.3, 129.0, 130.4, 130.5, 131.7, 135.2 (s), 135.3 (s), 141.8 (s), 142.3 (s), 144.0 (s), 167.7; HRMS (ESI): Calcd for $C_{29}H_{26}N$ $[M+H]^+$ 388.2060, found 388.2066.

3,8-Dimethyl-3,4,4-triphenyl-3,4-dihydroquinoline 13c (R^1 = CH_3, R^2 = H, R^3 = CH_3). Reaction conditions: anhydrous toluene, 30 h. Eluent for column chromatography: hexanes/diethyl ether (7:3, v/v). Yield = 0.19 g, 99%; mp 195-196 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1633 (m), 1304 (s), 1265 (s), 1155 (m), 1085 (m), 1034 (m), 939 (m), 891 (w), 779 (m), 765 (m), 740 (s), 721 (vs), 688 (m), 629 (m); δ_H(400 MHz; $CDCl_3$) 1.81 (3 H, s), 2.56 (3 H, s), 6.65 (2 H, d, *J* 10.0), 6.86-7.04 (10 H, m), 7.09-7.24 (4 H, m), 7.54-7.57 (2 H, m), 8.25 (1 H, s); δ_C(100 MHz; $CDCl_3$) 18.5, 20.6, 48.0 (s), 61.8 (s), 126.3, 126.6, 126.7, 127.1, 127.4, 127.5, 128.0, 128.8, 128.9, 132.1, 135.0 (s), 135.9 (s), 138.5 (s), 140.1 (s), 141.4 (s), 146.2 (s), 167.4; HRMS (ESI): Calcd for $C_{29}H_{26}N$ $[M+H]^+$ 388.2060, found 388.2066.

3-Ethyl-8-methyl-3,4,4-triphenyl-3,4-dihydroquinoline 13d (R^1 = CH_3, R^2 = H, R^3 = CH_2CH_3). Reaction conditions: anhydrous toluene, 96 h. Eluent for column chromatography: hexanes/diethyl ether (7:3, v/v). Yield = 0.12 g, 61%; mp 145-147 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1628 (m), 1597 (m), 1581 (m), 1495 (vs), 1464 (s), 1444 (s), 1375 (w), 1265 (s), 1089 (m), 1036 (m), 742 (s), 702 (vs); δ_H(400 MHz; $CDCl_3$) 0.78 (3 H, t, *J* 9.6), 1.96-2.08 (1 H, m), 2.54 (3 H, s), 2.58-2.63 (1 H, m), 6.57 (2 H, d, *J* 9.0), 6.91-7.20 (14 H, m), 7.43 (2 H, d, *J* 9.0), 8.68 (1 H, s); δ_C(100 MHz; $CDCl_3$) 8.80, 18.4, 24.9, 50.9 (s),

62.9 (s), 126.4, 126.5, 126.7, 126.8, 126.9, 127.1, 127.2, 127.3, 129.0, 130.4, 130.6, 131.9, 134.9 (s), 135.5 (s), 140.6 (s), 142.0 (s), 144.2 (s), 166.2; HRMS (ESI): Calcd for $C_{30}H_{28}N$ $[M+H]^+$ 402.2216, found 402.2219.

4,4-Bis[4-(*N*,*N*-dimethylamino)phenyl]-3-methyl-3-phenyl-3,4-dihydroquinoline 13e (R^1 = H, R^2 = $N(CH_3)_2$, R^3 = CH_3). Reaction conditions: anhydrous toluene, 6 h. Eluent for column chromatography: hexanes/diethyl ether (1:1, v/v). Yield = 0.14 g, 63%; mp 190-191 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1613 (s), 1519 (s), 1448 (s), 1359 (s), 1231 (w), 1207 (m), 1163 (w), 1063 (w), 950 (w), 818 (m), 800 (m), 761 (w), 695 (m); δ_H(300 MHz; $CDCl_3$) 1.77 (3 H, s), 2.90 (12 H, s), 6.37 (2 H, d, *J* 9.0), 6.50 (2 H, d, *J* 9.0), 6.65 (2 H, d, *J* 8.1), 6.72 (2 H, d, *J* 8.1), 6.93 (2 H, t, *J* 7.5), 6.99-7.04 (2 H, m), 7.10-7.20 (2 H, m), 7.37-7.42 (3 H, m), 8.23 (1 H, s); δ_C(75 MHz; $CDCl_3$) 20.6, 40.3, 40.7, 49.0 (s), 59.9 (s), 110.5, 111.2, 126.4, 126.6, 127.3, 127.8, 128.2, 129.0, 129.8, 132.6, 134.0 (s), 136.6 (s), 139.1 (s), 141.8 (s), 148.8 (s), 148.9 (s), 169.4 (s); HRMS (ESI): Calcd for $C_{32}H_{34}N_3$ $[M+H]^+$ 460.2747, found 460.2751.

4,4-Bis[4-(*N*,*N*-dimethylamino)phenyl]-3-ethyl-3-phenyl-3,4-dihydroquinoline 13f (R^1 = H, R^2 = $N(CH_3)_2$, R^3 = CH_2CH_3). Reaction conditions: anhydrous toluene, 20 h. Eluent for column chromatography: hexanes/diethyl ether (7:3, v/v). Yield = 0.19 g, 80%; mp 171-172 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1610 (s), 1518 (s), 1444 (s), 1354 (s), 1265 (m), 1163 (m), 1061 (w), 949 (w), 808 (m), 733 (m), 700 (m), 629 (s); δ_H(400 MHz; $CDCl_3$) 0.74 (3 H, t, *J* 7.3), 1.98-2.07 (1 H, m), 2.45-2.54 (1 H, m), 2.85 (6 H, s), 2.91 (6 H, s), 6.37 (2 H, d, *J* 9.1), 6.53 (2 H, d, *J* 9.1), 6.70 (2 H, d, *J* 7.7), 6.76 (2 H, d, *J* 7.7), 7.00-7.09 (4 H, m), 7.14-7.20 (2 H, m), 7.24-7.26 (2 H, m), 7.40 (1 H, dd, *J* 7.6 and 1.3), 8.63 (1 H, s); δ_C(100 MHz; $CDCl_3$) 9.0, 25.6, 40.4, 40.5, 52.0 (s), 60.9 (s), 110.5, 110.8, 126.4, 126.7, 127.1, 127.5, 128.0, 128.9, 129.9 (s), 130.6, 131.3 (s), 131.7, 132.2, 136.4 (s), 136.5 (s), 142.3 (s), 148.9 (s), 149.0 (s), 168.5; HRMS (ESI): Calcd for $C_{33}H_{36}N_3$ $[M+H]^+$ 474.2904, found 474.2910.

4,4-Bis[4-(*N*,*N*-dimethylamino)phenyl]-3,8-dimethyl-3-phenyl-3,4-dihydroquinoline 13g (R^1 = CH_3, R^2 = $N(CH_3)_2$, R^3 = CH_3). Reaction conditions: anhydrous toluene, 6 h. Eluent for column chromatography: hexanes/diethyl ether (1:1, v/v). Yield = 0.18 g, 78%; mp 170-171 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1610 (s), 1518 (vs), 1443 (m),

1352 (m), 1231 (m), 949 (w), 814 (w), 798 (m), 737 (m), 696 (m); δ_H(400 MHz; $CDCl_3$) 1.75 (3 H, s), 2.54 (3 H, s), 2.87 (6 H, s), 2.88 (6 H, s), 6.36 (2 H, d, *J* 8.8), 6.48-6.51 (2 H, m), 6.62 (2 H, d, *J* 7.6), 6.71 (2 H, d, *J* 8.8), 6.88-7.04 (6 H, m), 7.37-7.39 (2 H, m), 8.27 (1 H, s); δ_C(100 MHz; $CDCl_3$) 18.5, 20.9, 40.4, 40.7, 48.3 (s), 60.3 (s), 110.5, 111.2, 126.4, 126.8, 127.1, 127.3, 128.4, 129.1, 129.6 (s), 130.1, 132.7, 134.0 (s), 135.4 (s), 136.4 (s), 139.3 (s), 140.1 (s), 148.8 (s), 148.9 (s), 167.9; HRMS (ESI): Calcd for $C_{33}H_{36}N_3$ $[M+H]^+$ 474.2904, found 474.2909.

4,4-Bis[4-(*N*,*N*-dimethylamino)phenyl]-3-ethyl-8-methyl-3-phenyl-3,4-dihydroquinoline 13h (R^1 = CH_3, R^2 = $N(CH_3)_2$, R^3 = CH_2CH_3). Reaction conditions: anhydrous toluene, 5 h. Eluent for column chromatography: hexanes/diethyl ether (7:3, v/v). Yield = 0.18 g, 75%; mp 165-167 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1610 (s), 1517 (vs), 1466 (m), 1444 (m), 1352 (m), 1214 (w), 949 (w), 808 (w), 737 (m), 700 (s); δ_H(300 MHz; $CDCl_3$) 0.72 (3 H, t, *J* 7.2), 1.94-2.06 (1 H, m), 2.45-2.50 (1 H, m), 2.53 (3 H, s), 2.86 (6 H, s), 2.92 (6 H, s), 6.36 (2 H, d, *J* 9.0), 6.53 (2 H, d, *J* 9.0), 6.67 (2 H, d, *J* 8.1), 6.76 (2 H, d, *J* 8.1), 6.91-7.08 (6 H, m), 7.23-7.26 (2 H, m), 8.68 (1 H, s); δ_C(75 MHz; $CDCl_3$) 15.4, 18.4, 25.7, 40.5, 40.6, 51.4 (s), 61.2 (s), 110.4, 110.7, 126.3, 126.7, 126.9, 127.1, 128.4, 130.2 (s), 130.6, 131.7 (s), 131.8, 132.4, 135.1 (s), 136.2 (s), 136.8 (s), 140.6 (s), 148.9 (s), 149.0 (s), 167.0; HRMS (ESI): Calcd for $C_{34}H_{38}N_3$ $[M+H]^+$ 488.3060, found 488.3065.

3-Methyl-4,4-bis[4-(*N*-morpholino)phenyl]-3-phenyl-3,4-dihydroquinoline 13i (R^1 = H, R^2 = *N*-morpholino, R^3 = CH_3). Reaction conditions: anhydrous toluene, 12 h. Eluent for column chromatography: hexanes/diethyl ether (1:9, v/v). Yield = 0.18 g, 65%; mp 221-222 °C (orange prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1608 (s), 1512 (vs), 1448 (s), 1379 (m), 1304 (w), 1261 (m), 1238 (vs), 1122 (vs), 930 (s), 819 (m), 760 (m), 735 (m), 698 (m); δ_H(400 MHz; $CDCl_3$) 1.79 (3 H, s), 3.06-3.09 (8 H, m), 3.79-3.85 (8 H, m), 6.55 (2 H, d, *J* 8.4), 6.65-6.67 (4 H, m), 6.78 (2 H, d, *J* 8.4), 6.93 (2 H, t, *J* 7.6), 7.03 (2 H, t, *J* 8.4), 7.17 (2 H, t, *J* 7.6), 7.45 (3 H, m), 8.23 (1 H, s); δ_C(100 MHz; $CDCl_3$) 20.1, 48.2, 48.4 (s), 48.8, 59.7 (s), 66.4, 66.5, 112.9, 113.6, 126.2, 126.5, 127.0, 127.5, 127.9, 128.3 (s), 128.4, 128.5, 129.3, 131.8 (s), 132.2, 135.6 (s), 136.7 (s), 138.3 (s), 141.4 (s), 148.9 (s), 149.1 (s), 168.6; HRMS (ESI): Calcd for $C_{36}H_{38}N_3O_2$ $[M+H]^+$ 544.2959, found 544.2963.

3-Ethyl-4,4-bis[4-(*N*-morpholino)phenyl]-3-phenyl-3,4-dihydroquinoline 13j (R^1 = H, R^2 = *N*-morpholino, R^3 = CH_2CH_3). Reaction conditions: anhydrous toluene, reflux, 72 h. Eluent for column chromatography: hexanes/diethyl ether (1:9, v/v). Yield = 0.17 g, 60%; mp 184-185 °C (orange prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1713 (s), 1608 (s), 1512 (vs), 1450 (s), 1379 (m), 1363 (m), 1265 (s), 1238 (vs), 1122 (vs), 931 (s), 814 (m), 737 (vs), 702 (s); δ_H(400 MHz; $CDCl_3$) 0.76 (3 H, t, *J* 6.8), 1.94-2.04 (1 H, m), 2.45-2.52 (1 H, m), 3.07-3.16 (8 H, m), 3.81-3.86 (8 H, m), 6.54 (2 H, d, *J* 8.8), 6.67-6.72 (4 H, m), 6.80 (2 H, d, *J* 7.6), 7.00-7.11 (4 H, m), 7.15-7.21 (2 H, m), 7.29 (2 H, d, *J* 8.8), 7.41 (1 H, d, *J* 7.6), 8.60 (1 H, s); δ_C(100 MHz; $CDCl_3$) 8.4, 22.0, 48.3, 48.5, 51.4 (s), 60.6 (s), 66.4, 66.5, 112.7, 113.1, 126.1, 126.5, 126.8, 127.2, 127.6, 128.4, 130.1, 131.2, 131.8, 132.7 (s), 134.1 (s), 135.4 (s), 135.7 (s), 141.8 (s), 148.9 (s), 149.0 (s), 167.7; HRMS (ESI): Calcd for $C_{37}H_{40}N_3O_2$ $[M+H]^+$ 558.3115, found 558.3122.

4,4-Bis(4-methoxyphenyl)-3-methyl-3-phenyl-3,4-dihydroquinoline 13k (R^1 = H, R^2 = OCH_3, R^3 = CH_3). Reaction conditions: anhydrous toluene, 24 h. Eluent for column chromatography: hexanes/diethyl ether (4:1, v/v). Yield= 0.12 g, 57%; mp 168-170 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1606 (s), 1464 (s), 1443 (s), 1296 (m), 1252 (vs), 1184 (s), 1033 (s), 825 (w), 737 (w), 696 (w); δ_H(400 MHz; $CDCl_3$) 1.78 (3 H, s), 3.72 (3 H, s), 3.75 (3 H, s), 6.54 (2 H, d, *J* 9.0), 6.62 (2 H, d, *J* 7.7), 6.67 (2 H, d, *J* 9.0), 6.78 (2 H, d, *J* 8.4), 6.93 (2 H, t, *J* 7.7), 7.01-7.06 (2 H, m), 7.15-7.19 (2 H, m), 7.43-7.46 (3 H, m), 8.21 (1 H, s); δ_C(100 MHz; $CDCl_3$) 20.5, 48.8 (s), 55.2, 55.3, 60.2 (s), 111.8, 112.9, 126.7, 127.1, 127.6, 128.0, 128.5, 128.8, 128.9, 130.0, 132.9, 133.1 (s), 136.0 (s), 138.3 (s), 138.6 (s), 141.8 (s), 158.0 (s), 158.1 (s), 169.0; HRMS (ESI): Calcd for $C_{30}H_{28}NO_2$ $[M+H]^+$ 434.2115, found 434.2119.

3-Ethyl-4,4-bis(4-methoxyphenyl)-3-phenyl-3,4-dihydroquinoline 13l (R^1 = H, R^2 = OCH_3, R^3 = CH_2CH_3). Reaction conditions: anhydrous toluene, 120 h. Eluent for column chromatography: hexanes/diethyl ether (7:3, v/v). Yield= 0.12 g, 52%; mp 187-188 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1606 (s), 1508 (vs), 1464 (s), 1296 (m), 1254 (s), 1184 (s), 1036 (s), 819 (w), 737 (m), 702 (m); δ_H(400 MHz; $CDCl_3$) 0.77 (3 H, t, *J* 7.3), 1.96-2.05 (1 H, m), 2.45-2.55 (1 H, m), 3.73 (3 H, s), 3.78 (3 H, s), 6.55 (2 H, d, *J* 9.1), 6.67 (2 H, d, *J* 7.7), 6.71 (2 H, d, *J* 9.1), 6.82 (2 H, d, *J* 7.7), 7.01-7.05 (2 H, m), 7.07-7.10 (2 H, m), 7.15 (1 H, dd, *J* 7.8 and 1.3), 7.19 (1 H, td, *J* 7.4 and 1.4), 7.31 (2 H, d, *J* 8.5

Hz), 7.42 (1 H, dd, *J* 7.7 and 1.2), 8.63 (1 H, s); δ_C(100 MHz; $CDCl_3$) 8.9, 25.4, 51.8 (s), 55.2, 55.3, 61.2 (s), 111.8, 112.3, 126.7, 127.1, 127.3, 127.8, 128.2, 128.8, 130.4, 131.8, 132.6, 134.0, 135.7 (s), 135.8 (s), 135.9 (s), 142.2 (s), 158.1 (s), 158.3 (s), 168.1; HRMS (ESI): Calcd for $C_{31}H_{30}NO_2$ $[M+H]^+$ 448.2271, found 448.2273.

4,4-Bis(4-methoxyphenyl)-3,8-dimethyl-3-phenyl-3,4-dihydroquinoline 13m (R^1 = CH_3, R^2 = OCH_3, R^3 = CH_3). Reaction conditions: anhydrous toluene, 15 h. Eluent for column chromatography: hexanes/diethyl ether (7:3, v/v). Yield= 0.19 g, 85%; mp 158-160 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1629 (m), 1606 (s), 1581 (m), 1506 (vs), 1464 (s), 1385 (w), 1296 (s), 1252 (vs), 1184 (s), 1117 (w), 1036 (s), 810 (s), 737 (s), 698 (s); δ_H(300 MHz; $CDCl_3$) 1.76 (3 H, s), 2.55 (3 H, s), 3.72 (3 H, s), 3.74 (3 H, s), 6.53 (2 H, d, *J* 8.4), 6.59 (2 H, d, *J* 7.8), 6.67 (2 H, d, *J* 8.7), 6.76 (2 H, d, *J* 7.8), 6.92-7.02 (6 H, m), 7.44 (2 H, d, *J* 8.4), 8.26 (1 H, s); δ_C(75 MHz; $CDCl_3$) 18.5, 20.7, 48.1 (s), 55.1, 55.2, 60.5 (s), 111.6, 112.7, 126.6, 126.7, 127.3, 127.5, 128.8, 128.9, 130.1, 133.0, 133.5 (s), 135.7 (s), 135.8 (s), 138.2 (s), 138.7 (s), 140.0 (s), 157.9 (s), 158.0 (s), 167.6; HRMS (ESI): Calcd for $C_{31}H_{30}NO_2$ $[M+H]^+$ 448.2271, found 448.2276.

3-Ethyl-4,4-bis(4-methoxyphenyl)-8-methyl-3-phenyl-3,4-dihydroquinoline 13n (R^1 = CH_3, R^2 = OCH_3, R^3 = CH_2CH_3). Reaction conditions: anhydrous toluene, 48 h. Eluent for column chromatography: hexanes/diethyl ether (7:3, v/v). Yield = 0.23 g, 99%; colourless oil; ν_{max}(neat)/cm^{-1} 1606 (s), 1508 (vs), 1469 (s), 1296 (m), 1254 (vs), 1184 (s), 1036 (s), 835 (w), 810 (m), 734 (vs), 704 (s); δ_H(400 MHz; $CDCl_3$) 0.75 (3 H, t, *J* 7.2), 1.99 (1 H, m), 2.49 (1 H, m), 2.53 (3 H, s), 3.71 (3 H, s), 3.76 (3 H, s), 6.54 (2 H, d, *J* 8.8), 6.64 (2 H, d, *J* 7.6), 6.70 (2 H, d, *J* 8.8), 6.81 (2 H, d, *J* 8.0), 6.95-7.09 (6 H, m), 7.31 (2 H, d, *J* 8.0), 8.67 (1 H, s); δ_C(100 MHz; $CDCl_3$) 8.9, 18.3, 25.5, 51.1 (s), 55.1, 55.2, 61.4 (s), 111.7, 112.2, 126.5, 126.6, 127.1, 127.3, 128.9, 130.4, 131.9, 132.7, 134.2 (s), 135.4 (s), 135.5 (s), 135.9 (s), 136.2 (s), 140.5 (s), 158.0 (s), 158.2 (s), 166.6; HRMS (ESI): Calcd for $C_{32}H_{32}NO_2$ $[M+H]^+$ 462.2428, found 462.2436.

Preparation of acridines 18, 2-arylquinolines 20 and quinolines 22

To a solution of iminophosphorane **11** (1 mmol) in anhydrous dichloromethane (15 mL) a solution of diphenylketene (0.19 g, 1 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred a room temperature under nitrogen for 30 min. Next the solvent was removed under reduced pressure and the resulting material was purified by column

chromatography on silica gel, using hexanes/diethyl ether (9:1; v/v) as eluent, to provide the expected ketenimine **15**.

A deoxygenated solution of the ketenimine **15** (0.5 mmol) in anhydrous *ortho*-xylene (20 mL) was heated in a sealed tube at 180 °C during 2-21 d. After cooling, the solvent was removed under reduced pressure. The resulting material was purified by column chromatography on silica gel.

10-(2,2-Diphenylethenyl)-9-phenyl-9,10-dihydroacridine 18a (R^1 = H, R^2 = H). Reaction time: 7 d. Eluent for column chromatography: hexanes/diethyl ether (9.5:0.5, v/v). Yield= 0.21 g, 95%; mp 191-192 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1589 (s), 1495 (s), 1308 (s), 1286 (s), 1261 (m), 1074 (w), 956 (w), 877 (w), 748 (vs), 700 (vs); δ_H(300 MHz; $CDCl_3$) 5.22 (1 H, s), 6.61 (1 H, s), 6.83-6.88 (4 H, m), 7.07-7.21 (14 H, m), 7.37-7.41 (3 H, m), 7.48-7.51 (2 H, m); δ_C(75 MHz; $CDCl_3$) 47.9, 114.0, 121.5, 124.0, 124.7 (s), 126.1, 127.2, 127.5, 127.8, 128.2, 128.3, 128.5, 128.6, 129.0, 129.6, 137.7 (s), 140.1 (s), 145.5 (s), 147.3 (s); HRMS (ESI): Calcd for $C_{33}H_{26}N$ $[M+H]^+$ 436.2060, found 436.2064.

10-(2,2-Diphenylethenyl)-3-methoxy-9-(4-methoxyphenyl)-9,10-dihydroacridine 18b (R^1 = H, R^2 = OCH_3). Reaction time: 5 d. Eluent for column chromatography: hexanes/diethyl ether (9:1, v/v). Yield = 0.15 g, 61%; mp 150-151 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1595 (vs), 1508 (vs), 1483 (vs), 1443 (vs), 1302 (m), 1269 (s), 1254 (s), 1213 (s), 1176 (m), 1038 (m), 752 (m), 698 (s); δ_H(400 MHz; $CDCl_3$) 3.72 (3 H, s), 3.73 (3 H, s), 5.12 (1 H, s), 6.42 (1 H, dd, *J* 8.4 and 2.8), 6.59 (1 H, s), 6.62-6.65 (2 H, m), 6.74 (1 H, d, *J* 2.4), 6.76-6.78 (2 H, m), 6.85 (1 H, m), 6.98 (1 H, d, *J* 8.0), 7.08 (2 H, d, *J* 7.2), 7.10-7.21 (6 H, m), 7.38-7.41 (3 H, m), 7.46-7.49 (2 H, m); δ_C(100 MHz; $CDCl_3$) 46.3, 55.3, 55.4, 100.5, 106.4, 113.9, 114.0, 117.8, 121.5, 123.9, 125.4 (s), 127.0, 127.8, 128.1, 128.2, 128.4, 128.5, 128.6, 129.0, 129.5, 130.2, 137.8 (s), 139.9 (s), 140.0 (s), 140.3 (s), 141.0 (s), 145.7 (s), 157.8 (s), 158.9 (s); HRMS (ESI): Calcd for $C_{35}H_{30}NO_2$ $[M+H]^+$ 496.2271, found 496.2275.

2,4-Bis[4-(*N*,*N*-dimethylamino)phenyl]-3,3-diphenyl-3,4-dihydroquinoline 20a (R^1 = H, R^2 = $N(CH_3)_2$). Reaction time: 1 d. Eluent for column chromatography: hexanes/diethyl ether

(7:3, v/v). Yield = 0.13 g, 50%; colourless oil; ν_{max}(neat)/cm^{-1} 1608 (vs), 1520 (vs), 1477 (m), 1444 (m), 1360 (s), 1265 (m), 1198 (m), 1167 (m), 947 (w), 818 (m), 737 (s), 700 (s); δ_H(400 MHz; $CDCl_3$) 2.82 (6 H, s), 2.89 (6 H, s), 4.56 (1 H, s), 6.31 (2 H, d, *J* 7.6), 6.40-6.43 (4 H, m), 6.57 (2 H, d, *J* 8.8), 6.79 (2 H, t, *J* 8.4), 6.93-6.98 (3 H, m), 7.08-7.18 (2 H, m), 7.21-7.23 (2 H, m), 7.31 (2 H, d, *J* 9.2), 7.40 (1 H, d, *J* 8.0), 7.63 (2 H, d, *J* 8.0); δ_C(100 MHz; $CDCl_3$) 40.1, 40.6, 54.6, 59.0 (s), 110.5, 112.2, 125.6, 125.9, 126.5, 126.7, 126.9, 127.2, 127.3 (s), 127.6, 127.9, 128.8 (s), 129.7, 131.1, 131.2, 131.4, 131.8, 142.0 (s), 142.1 (s), 144.1 (s), 149.6 (s), 150.7 (s), 171.7 (s); HRMS (ESI): Calcd for $C_{37}H_{36}N_3$ $[M+H]^+$ 522.2904, found 522.2908.

2,4-Bis[4-(*N*,*N*-dimethylamino)phenyl]- 8-methyl-3,3-diphenyl-3,4-dihydroquinoline 20b (R^1 = CH_3, R^2 = $N(CH_3)_2$). Reaction time: 2 d. Eluent for column chromatography: hexanes/diethyl ether (3:2, v/v). Yield = 0.25 g, 93%; mp 234-235 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1610 (m), 1519 (s), 1461 (vs), 1265 (m), 1120 (w), 1035 (m), 967 (w), 833 (s), 745 (m); δ_H(300 MHz; $CDCl_3$) 2.46 (3 H, s), 2.80 (6 H, s), 2.89 (6 H, s), 4.51 (1 H, s), 6.32 (2 H, d, *J* 7.5), 6.41 (4 H, t, *J* 8.7), 6.54 (2 H, d, *J* 8.7), 6.76-6.84 (4 H, m), 6.93-6.98 (2 H, m), 7.11-7.23 (3 H, m), 7.40 (2 H, d, *J* 9.0), 7.61 (2 H, d, *J* 7.5); δ_C(75 MHz; $CDCl_3$) 17.9, 40.2, 40.7, 55.0, 58.4 (s), 110.3, 112.3, 125.1, 125.6, 125.9, 126.2, 126.8, 127.7 (s), 127.8, 128.5, 129.2 (s), 129.7, 131.1, 131.3, 131.4, 134.8 (s), 142.3 (s), 142.4 (s), 142.5 (s), 149.5 (s), 150.5 (s), 168.6 (s); HRMS (ESI): Calcd for $C_{38}H_{38}N_3$ $[M+H]^+$ 536.3060, found 536.3062.

3,3-Diphenyl-8-diphenylmethyl-3,4-dihydroquinoline 22a (R^2 = H). Reaction time: 21 d. Eluent for column chromatography: hexanes/diethyl ether (9.5:0.5, v/v). Yield = 0.11 g, 51%; mp 159-161 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1599 (m), 1581 (m), 1493 (vs), 1444 (s), 1265 (w), 1078 (w), 1032 (w), 895 (w), 781 (w), 742 (s), 698 (vs), 621 (m); δ_H(400 MHz; $CDCl_3$) 3.47 (2 H, s), 6.55 (1 H, s), 6.81 (1 H, d, *J* 7.6), 6.95 (1 H, d, *J* 7.6), 7.00-7.07 (9 H, m), 7.17-7.28 (12 H, m), 8.22 (1 H, s); δ_C(100 MHz; $CDCl_3$) 38.1, 48.7 (s), 50.4, 125.9, 126.1, 126.5 (s), 127.4, 127.7, 127.8, 128.1, 128.7, 129.8, 140.0 (s), 140.8 (s), 143.8 (s), 144.3 (s), 166.7; HRMS (ESI): Calcd for $C_{34}H_{28}N$ $[M+H]^+$ 450.2216, found 450.2222.

8-Bis(4-methoxyphenyl)methyl-3,3-diphenyl-3,4-dihydroquinoline 22b (R^2 = OCH_3). Reaction time: 14 d. Eluent for column chromatography: hexanes/diethyl ether (9:1, v/v). Yield = 0.13 g, 50%; mp 147-149 °C (colourless prisms from diethyl ether/hexane); ν_{max}(Nujol)/cm^{-1} 1610 (s), 1578 (m), 1519 (vs), 1494 (vs), 1456 (s), 1367 (w), 1327 (m), 1284 (s), 1248 (vs), 1176 (s), 1070 (w), 1031 (s), 835 (m), 738 (s), 702 (m); δ_H(400 MHz; $CDCl_3$) 3.43 (2 H, s), 3.78 (6 H, s), 6.39 (1 H, s), 6.75-6.78 (4 H, m), 6.90-6.95 (5 H, m), 6.99 (1 H, d, *J* 7.6), 7.01-7.04 (5 H, m), 7.16-7.24 (6 H, m), 8.21 (1 H, s); δ_C(100 MHz; $CDCl_3$) 38.1, 48.6 (s), 48.7, 55.3, 113.5, 125.9, 126.4 (s), 126.7, 127.3, 127.8, 128.4, 128.5, 130.6, 136.9 (s), 140.6 (s), 140.7 (s), 143.8 (s), 157.7 (s), 166.6; HRMS (ESI): Calcd for $C_{36}H_{32}NO_2$ $[M+H]^+$ 510.2428, found 510.2433.

Preparation of Quinazolines 25

To a solution of iminophosphorane **11** (1 mmol) in anhydrous dichloromethane (15 mL) a solution of the aryl isocyanate (1 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure, and the oily residue was chromatographed on a silica gel column using hexanes/diethyl ether (7:3, v/v) as eluent to give the corresponding carbodiimides **23**.

A solution of the carbodiimide **23** (0.5 mmol) in anhydrous *o*-xylene (20 mL) was heated a 180 ºC, in a sealed tube, for 2-5 d. After cooling at room temperature, the solvent was removed under reduced pressure and the resulting material was purified by silica gel column chromatography.

3-(4-Bromophenyl)-4,4-bis[4-(*N*,*N*-dimethylamino)phenyl]-3,4-dihydroquinazoline 25a (R^1 = H; R^2 = $N(CH_3)_2$; R^3 = Br). Eluent for column chromatography: hexanes/diethyl ether (1:9, v/v). Yield = 0.22 g, 82%; mp 193-194 ºC (colourless prisms from diethyl ether/hexane); ν_{max}(Nujol)/cm^{-1} 1608 (s), 1564 (s), 1517 (s), 1355 (m), 1263 (m), 1190 (m), 1008 (w), 947 (w), 808 (w), 737 (m); δ_H(400 MHz; $CDCl_3$) 2.89 (12 H, s), 6.54-6.56 (4 H, m), 6.76-6.79 (3 H, m), 6.98-7.01 (1 H, m), 7.13-7.24 (8 H, m), 7.64 (1 H, s); δ_C(100 MHz; $CDCl_3$) 40.3, 71.9 (s), 111.3, 118.5 (s), 124.1, 125.3, 127.1, 127.2, 127.6, 129.0, 130.4, 131.2, 133.0 (s), 140.7 (s), 142.0 (s), 147.4, 149.3 (s); HRMS (ESI): Calcd for $C_{30}H_{30}BrN_4$ $[M+H]^+$ 525.1648, found 525.1655

3-(4-Chlorophenyl)-4,4-bis[4-(*N*,*N*-dimethylamino)phenyl]-8-methyl-3,4-dihydroquinazoline 25b (R^1 = CH_3, R^2 = $N(CH_3)_2$, R^3 = Cl). Eluent for column chromatography: hexanes/ethyl acetate (7:3, v/v). Yield = 0.21 g, 84%; mp 230-231 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1614 (vs), 1574 (vs), 1516 (s), 1489 (s), 1356 (s), 1292 (s), 1252 (m), 1092 (w), 948 (w), 816 (m), 737 (s); δ_H(300 MHz; $CDCl_3$) 2.41 (3 H, s), 2.90 (12 H, s), 6.52-6.57 (4 H, m), 6.61 (1 H, d, *J* 7.8), 6.83-6.87 (2 H, m), 6.91 (1 H, d, *J* 7.8), 7.00-7.04 (3 H, m), 7.11-7.16 (4 H, m), 7.70 (1 H, s); δ_C(75 MHz; $CDCl_3$) 17.8, 40.4, 71.9 (s), 111.3, 124.7, 125.1, 126.6, 128.3, 129.0, 129.2 (s), 130.3 (s), 130.4, 131.9 (s), 133.0 (s), 139.1 (s), 141.7 (s), 146.5, 149.3 (s); HRMS (ESI): Calcd for $C_{31}H_{32}ClN_4$ $[M+H]^+$ 495.2310, found 495.2317.

4,4-Bis[4-(*N*,*N*-dimethylamino)phenyl]-8-methyl-3-(4-methylphenyl)-3,4-dihydroquinazoline 25c (R^1 = CH_3, R^2 = $N(CH_3)_2$, R^3 = CH_3). Eluent for column chromatography: hexanes/diethyl ether (7:3, v/v). Yield = 0.18 g, 76%; mp 255-257 °C (yellow prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1713 (w), 1606 (vs), 1573 (vs), 1516 (vs), 1356 (s), 1300 (s), 1252 (s), 1224 (m), 1057 (w), 947 (w), 814 (m), 802 (m), 735 (m); δ_H(400 MHz; $CDCl_3$) 2.19 (3 H, s), 2.42 (3 H, s), 2.88 (12 H, s), 6.53-6.56 (4 H, m), 6.59 (1 H, d, *J* 7.6), 6.79-6.81 (2 H, m), 6.85-6.89 (3 H, m), 7.01 (1 H, d, *J* 7.6), 7.14-7.18 (4 H, m), 7.73 (1 H, s); δ_C(75 MHz; $CDCl_3$) 17.9, 20.8, 40.5, 71.8 (s), 111.3, 124.3, 125.1, 125.5, 128.8, 128.9, 129.9 (s), 130.6, 131.7 (s), 133.0 (s), 134.4 (s), 139.5 (s), 140.6 (s), 147.3, 149.2 (s); HRMS (ESI): Calcd for $C_{32}H_{35}N_4$ $[M+H]^+$ 475.2856, found 475.2860.

3-(4-Chlorophenyl)-4,4-bis(4-methoxyphenyl)-3,4-dihydroquinazoline 25d (R^1 = H, R^2 = OCH_3, R^3 = Cl). Eluent for column chromatography: hexanes/diethyl ether (1:9, v/v). Yield = 0.18 g, 78%; mp 96-97 °C (colourless prisms from diethyl ether/hexane); ν_{max}(Nujol)/cm^{-1} 1608 (s), 1585 (s), 1562 (s), 1510 (vs), 1491 (s), 1309 (m), 1296 (m), 1253 (vs), 1176 (s), 1033 (m), 822 (w), 771 (w); δ_H(300 MHz; $CDCl_3$) 3.71 (6 H, s), 6.72-6.82 (7 H, m), 7.01-7.06 (3 H, m), 7.19-7.26 (6 H, m), 7.66 (1 H, s); δ_C(75 MHz; $CDCl_3$) 55.3, 71.9 (s), 113.2, 124.4, 125.7, 126.9, 127.0, 128.1, 128.5, 130.8, 131.1 (s), 132.3 (s), 133.4 (s), 140.6 (s), 141.1 (s), 147.4, 158.8 (s); HRMS (ESI): Calcd for $C_{28}H_{24}ClN_2O_2$ $[M+H]^+$ 455.1521, found 455.1527.

3-(4-Bromophenyl)-4,4-bis(4-methoxyphenyl)-8-methyl-3,4-dihydroquinazoline 25e (R^1 = CH_3, R^2 = OCH_3, R^3 = Br). Eluent for column chromatography: hexanes/diethyl ether (1:1,

v/v). Yield = 0.16 g, 61%; mp 83-85 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1608 (vs), 1568 (s), 1542 (w), 1508 (s), 1488 (s), 1292 (s), 1253 (m), 1178 (m), 1074 (w), 1033 (s), 937 (m), 892 (w), 812 (s), 737 (vs); δ_H(400 MHz; $CDCl_3$) 2.42 (3 H, s), 3.76 (6 H, s), 6.55 (1 H, d, *J* 7.6), 6.73-6.77 (6 H, m), 6.93 (1 H, t, *J* 7.6), 7.06 (1 H, d, *J* 7.6), 7.17-7.22 (6 H, m), 7.70 (1 H, s); δ_C(100 MHz; $CDCl_3$) 15.3, 55.3, 71.9 (s), 113.2, 118.6 (s), 124.9, 125.1, 126.8, 129.5, 130.8, 131.4, 132.3 (s), 132.4 (s), 133.4 (s), 139.1 (s), 141.8 (s), 146.3, 158.8 (s); HRMS (ESI): Calcd for $C_{29}H_{26}BrN_2O_2$ $[M+H]^+$ 513.1172, found 513.1174.

Preparation of 4-chloro-2-[1-(4-methoxyphenyl)vinyl]-*N*-(2,2-diphenylvinyl)aniline 30

To a solution of 4-chloro-2-[1-(4-methoxyphenyl)ethyl]aniline **26** (5 g, 19 mmol) in a mixture of water (30 mL) and concentrated sulfuric acid (5 mL), cooled at 0 °C a solution of sodium nitrite (1.6 g, 23 mmol) in water (10 mL) was added dropwise. The resulting mixture was stirred at 0 °C for 30 min, and then a solution of sodium azide (1.5 g, 23 mmol) in water (10 mL) was added dropwise during 10 min. The reaction mixture was stirred at room temperature for 16 h, and then extracted with diethyl ether (3 x 50 mL). The organic phase was dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the resulting material was purified by column chromatography on silica gel, using hexanes as eluent, to give **1-azido-4-chloro-2-[1-(4-methoxyphenyl)ethyl]benzene** (4.15 g, yield 76%).

To a solution of 1-azido-4-chloro-2-[1-(4-methoxyphenyl)ethyl]benzene (1.9 g, 6.7 mmol) in anhydrous diethyl ether (20 mL) triphenylphosphine (1.9 g, 7.4 mmol) was added in five portions. The reaction mixture was stirred at room temperature under nitrogen for 16 h. The solvent was removed under reduced pressure, and the crude iminophosphorane **27** was purified by column chromatography on silica gel deactivated with triethylamine, using hexanes/diethyl ether (1:1, v/v) as eluent.

Iminophosphorane 27. Yield = 3.43 g, 98%; mp 51-52 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1610 (m), 1581 (s), 1510 (vs), 1475 (vs), 1437 (s), 1348 (vs), 1244

(vs), 1178 (s), 1034 (s), 999 (w), 908 (s), 860 (w), 831 (m), 812 (m), 846 (m); δ_H(400 MHz; $CDCl_3$) 1.57 (3 H, d, *J* 7.2), 3.70 (3 H, s), 5.06 (1 H, q, *J* 7.2), 6.35 (1 H, dd, *J* 8.4 and 1.2), 6.66 (1 H, dd, *J* 8.4 and 2.8), 6.68-6.72 (2 H, m), 6.99 (1 H, t, *J* 2.8), 7.11 (2 H, m), 7.35-7.40 (6 H, m), 7.44-7.49 (3 H, m), 7.59-7.64 (6 H, m); δ_C(100 MHz; $CDCl_3$) 21.1, 38.3, 55.2, 113.3, 121.9 (d, *J* 9.9), 122.0 (s), 125.6, 127.1, 128.5 (d, *J* 11.9), 128.8, 128.9 (d, *J* 89.2) (s), 131.5 (d, *J* 3.0), 132.5 (d, *J* 9.7), 139.4 (s), 142.6 (d, *J* 21.5) (s), 147.4 (s), 157.4 (s); δ_P(121.4 MHz; $CDCl_3$, H_3PO_4) 2.2; HRMS (ESI): Calcd for $C_{33}H_{30}ClNOP$ $[M+H]^+$ 522.1748, found 522.1748.

To a solution of iminophosphorane **27** (0.8 g, 1.5 mmol) in anhydrous dichloromethane (15 mL) a solution of diphenylketene (0.24 g, 1.5 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred a room temperature under nitrogen for 30 min. Next the solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel, using hexanes/diethyl ether (9.5:0.5; v/v) as eluent, to provide the ketenimine **28** (81% yield).

A solution of the ketenimine **28** (0.33 g, 0.75 mmol) in anhydrous *ortho*-xylene (20 mL) was heated at reflux temperature under nitrogen for 3 h. After cooling, the solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel, using hexanes/diethyl ether (9:1, v/v) as eluent.

4-Chloro-2-[1-(4-methoxyphenyl)vinyl]-*N*-(2,2-diphenylvinyl)aniline 30. Yield = 0.30 g, 91%; orange oil; ν_{max}(neat)/cm^{-1} 1659 (vs), 1578 (s), 1554 (w), 1510 (vs), 1446 (s), 1408 (m), 1176 (s), 1030 (m), 837 (m), 702 (vs), 638 (vs); δ_H(300 MHz; $CDCl_3$) 3.79 (3 H, s), 5.07 (1 H, d, *J* 0.9), 5.53 (1 H, d, *J* 0.9), 6.10 (1 H, d, *J* 12.0), 6.71-6.75 (2 H, m), 6.88-6.96 (3 H, m), 6.99-7.04 (2 H, m), 7.08-7.13 (3 H, m), 7.18-7.25 (7 H, m), 7.29-7.38 (1 H, m); δ_C(75 MHz; $CDCl_3$) 55.3, 112.7, 114.1, 115.4, 118.4 (s), 123.9, 124.0 (s), 125.6, 126.2, 126.8, 127.6, 128.3, 128.8, 129.0, 129.8, 130.5, 130.7 (s), 137.9 (s), 138.7 (s), 141.6 (s), 144.5 (s), 159.8 (s); HRMS (ESI): Calcd for $C_{29}H_{25}ClNO$ $[M+H]^+$ 438.1619, found 438.1619.

Preparation of 3,4-dihydroquinolines 34

To a solution of the azide **31** (2.2 g, 10 mmol) in anhydrous diethyl ether (20 mL) triphenylphosphine (2.75 g, 10 mmol) was added in five portions. The reaction mixture was stirred at room temperature under nitrogen for 16 h. Then, the precipitated 1-phenylmethyl-2-triphenylphosphoranylidenaminobenzene **32** was isolated by filtration and washed with anhydrous diethyl ether (15 mL).

This compound was used in the following step without further purification.
For an analytical sample this iminophosphorane was recrystallized from diethyl ether.

1-Phenylmethyl-2-triphenylphosphoranylidenaminobenzene 32. Yield = 4.26 g, 96%; mp 114-116 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1587 (s), 1445 (vs), 1377 (s), 1309 (s), 1259 (m), 1180 (w), 1157 (w), 1107 (vs), 1072 (w), 1053 (m), 1022 (m), 999 (w), 748 (s), 715 (vs), 700 (vs); δ_H(400 MHz; $CDCl_3$) 4.37 (2 H, s), 6.57 (1 H, d, *J* 7.6), 6.67 (1 H, t, *J* 7.6), 6.84 (1 H, t, *J* 7.6), 7.06 (1 H, d, *J* 7.6), 7.15-7.18 (1 H, m), 7.22-7.26 (2 H, m), 7.31-7.33 (2 H, m), 7.43-7.47 (6 H, m), 7.52-7.56 (3 H, m), 7.73-7.78 (6 H, m); δ_C(100 MHz; $CDCl_3$) 38.6, 117.4, 121.1 (d, *J* 9.7), 125.2, 126.3, 128.0, 128.5 (d, *J* 11.9), 129.2, 130.0 (d, *J* 1.7), 131.5 (d, *J* 97.4) (s), 131.6 (d, *J* 2.6), 132.6 (d, *J* 9.7), 135.6 (d, *J* 21.9) (s), 142.9 (s), 149.1 (s); δ_P(161.9 MHz; $CDCl_3$, H_3PO_4) 0.7; HRMS (ESI): Calcd for $C_{31}H_{27}NP$ $[M+H]^+$ 444.1876, found 444.1875.

To a solution of 1-phenylmethyl-2-triphenylphosphoranylidenaminobenzene **32** (0.5 g, 1.1 mmol) in anhydrous dichloromethane (15 mL) a solution of diphenylketene (1.1 mmol) or methylphenylketene (1.1 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred a room temperature under nitrogen for 30 min. Next the solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel, using hexanes/diethyl ether (9.5:0.5; v/v) as eluent, to provide ketenimine **33a** (91% yield) or ketenimine **33b** (70% yield), respectively.

A deoxygenated solution of ketenimine **33** (0.5 mmol) in anhydrous toluene (20 mL) was heated in a sealed tube at 160 °C during 36 h. After cooling, the solvent was removed under reduced pressure. The resulting material was purified by column chromatography on silica gel, using hexanes/diethyl ether (4:1) as eluent.

3,3,4-Triphenyl-3,4-dihydroquinoline 34a. Yield = 0.17 g, 97%; mp 192-194 °C (colourless prisms from diethyl ether); ν_{max}(Nujol)/cm^{-1} 1614 (s), 1595 (s), 1495 (vs), 1244 (w), 1180 (w), 1155 (w), 1103 (s), 1103 (s), 1034 (m), 972 (m), 908 (vs), 883 (w), 750 (vs), 735 (s), 698 (vs), 607 (s); δ_H(400 MHz; $CDCl_3$) 4.75 (1 H, s), 6.56 (2 H, d, *J* 7.2), 6.76-6.78 (2 H, m), 6.92-7.00 (3 H, m), 7.03-7.06 (3 H, m), 7.21-7.23 (4 H, m), 7.25-7.29 (2 H, m), 7.30-7.34 (2 H, m), 7.45 (1 H, d, *J* 7.2), 8.54 (1 H, s); δ_C(100 MHz; $CDCl_3$) 50.8, 54.2 (s), 126.3, 126.4, 127.0, 127.6, 127.7, 127.8, 127.9, 128.2, 128.4, 128.5, 128.9, 129.1, 130.1 (s), 139.6 (s), 141.8 (s), 143.1 (s), 144.3 (s), 165.5; HRMS (ESI): Calcd for $C_{27}H_{22}N$ $[M+H]^+$ 360.1747, found 360.1751.

3-Methyl-3,4-diphenyl-3,4-dihydroquinoline 34b. Yield = 0.10 g, 70%; colorless oil; ν_{max}(neat)/cm^{-1} 1622 (s), 1599 (s), 1494 (vs), 1477 (s), 1219 (w), 1106 (w), 1029 (m), 919 (w), 758 (vs), 732 (m), 698 (vs); δ_H(300 MHz; $CDCl_3$) 1.30 (3 H, s, minor isomer), 1.62 (3 H, s, major isomer), 4.02 (1 H, s, major isomer), 4.28 (1 H, s, minor isomer), 6.47-6.49 (3 H, m), 6.89-7.36 (23 H, m), 7.49 (1 H, d, *J* 7.5, minor isomer), 7.56 (1 H, d, *J* 7.8, major isomer), 7.90 (1 H, s, minor isomer), 8.05 (1 H, s, major isomer); δ_C(75 MHz; $CDCl_3$) 20.5 (minor isomer), 23.2 (major isomer), 45.4 (s, minor isomer), 46.3 (s, major isomer), 54.0 (minor isomer), 54.7 (major isomer), 126.6, 126.9, 127.0, 127.1, 127.3, 127.4, 127.6, 127.7, 127.89, 127.94, 128.0, 128.1, 128.4, 128.5, 128.8, 129.6, 129.8, 138.5 (s), 139.1 (s), 140.7 (s), 142.1 (s), 142.2 (s), 144.1 (s), 168.8; HRMS (ESI): Calcd for $C_{22}H_{20}N$ $[M+H]^+$ 298.1590, found 298.1594.

Figure S1: ORTEP representation of the crystal structure of **13e**

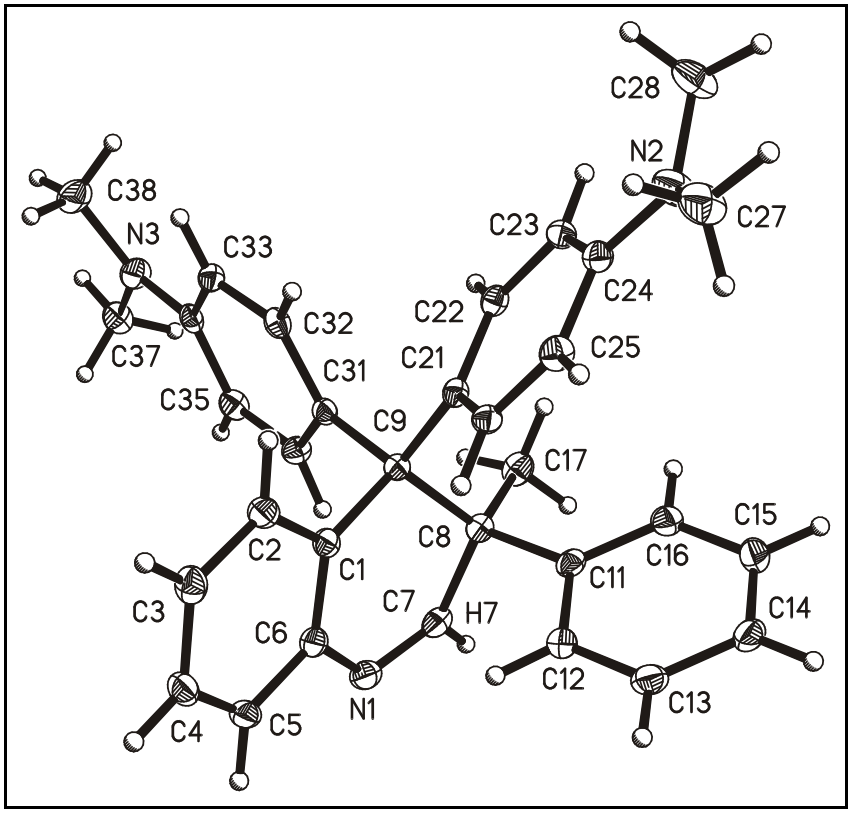


Figure S2: ORTEP representation of the crystal structure of **13k**

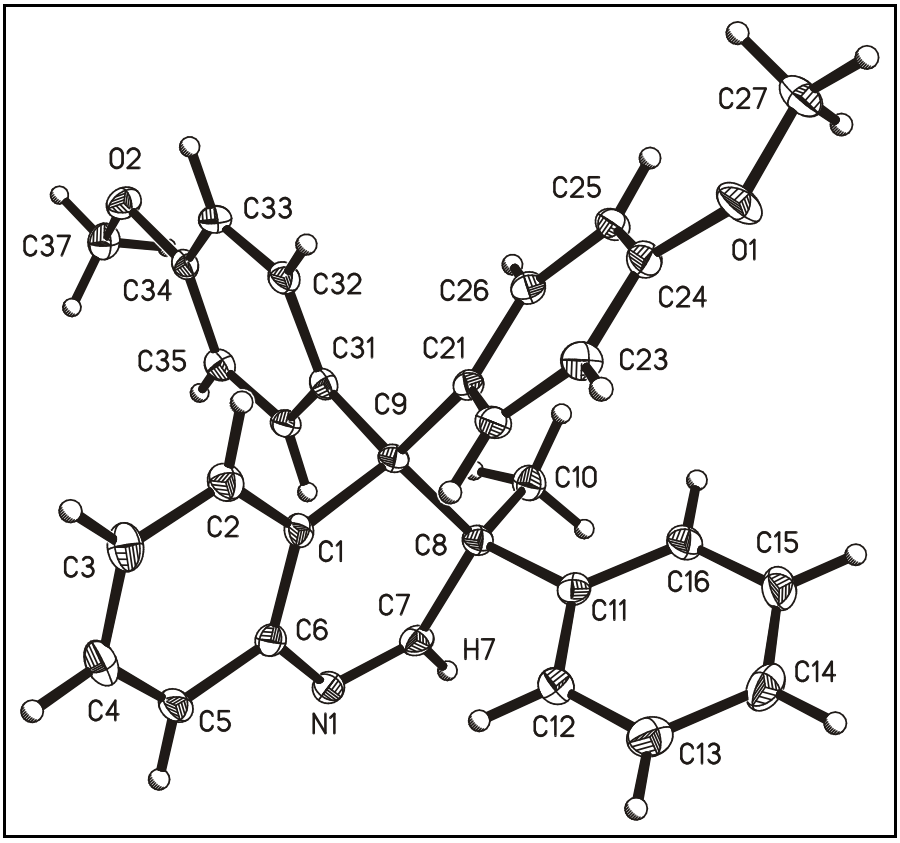


Figure S3: ORTEP representation of the crystal structure of **18a**

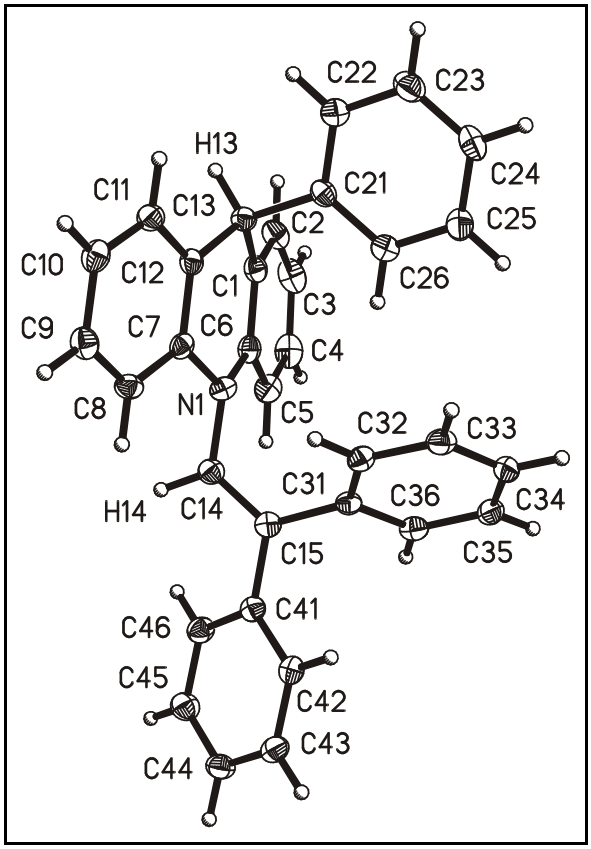
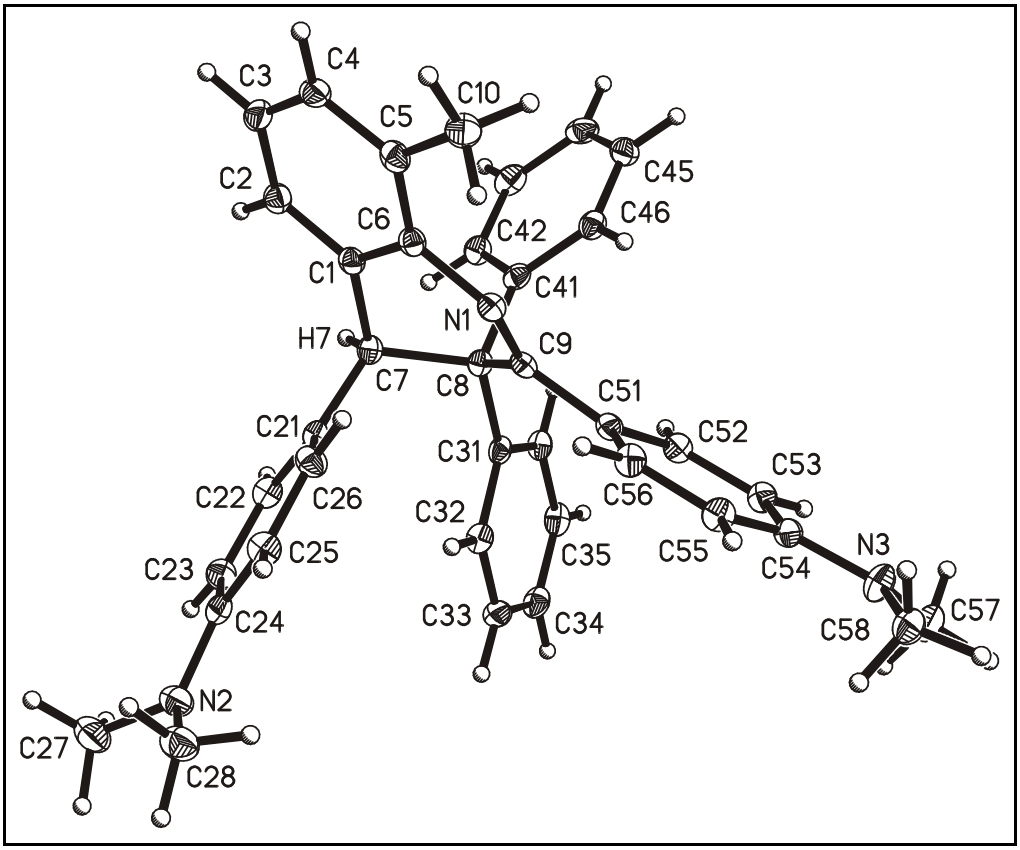


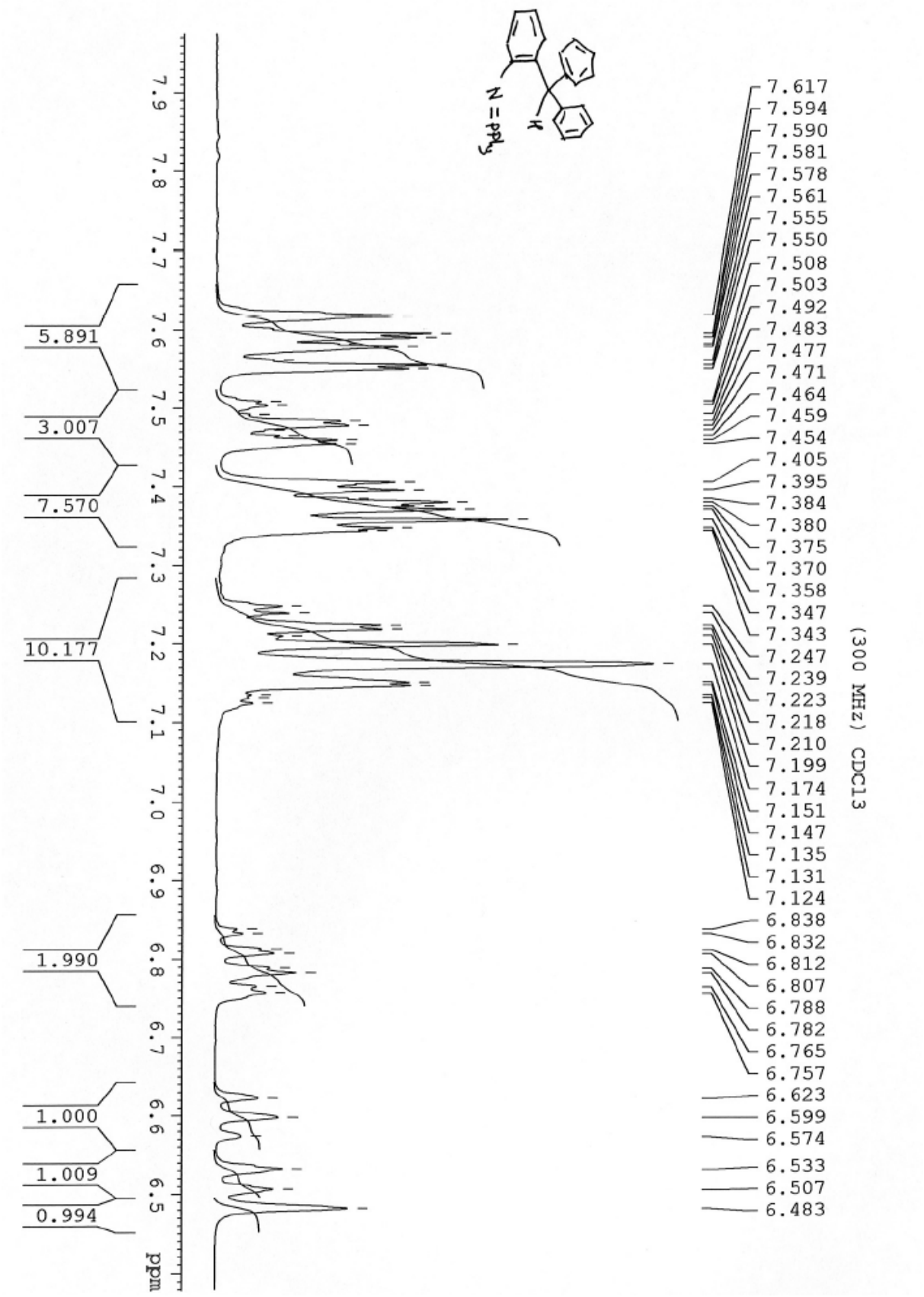
Figure S4: ORTEP representation of the crystal structure of **20b**



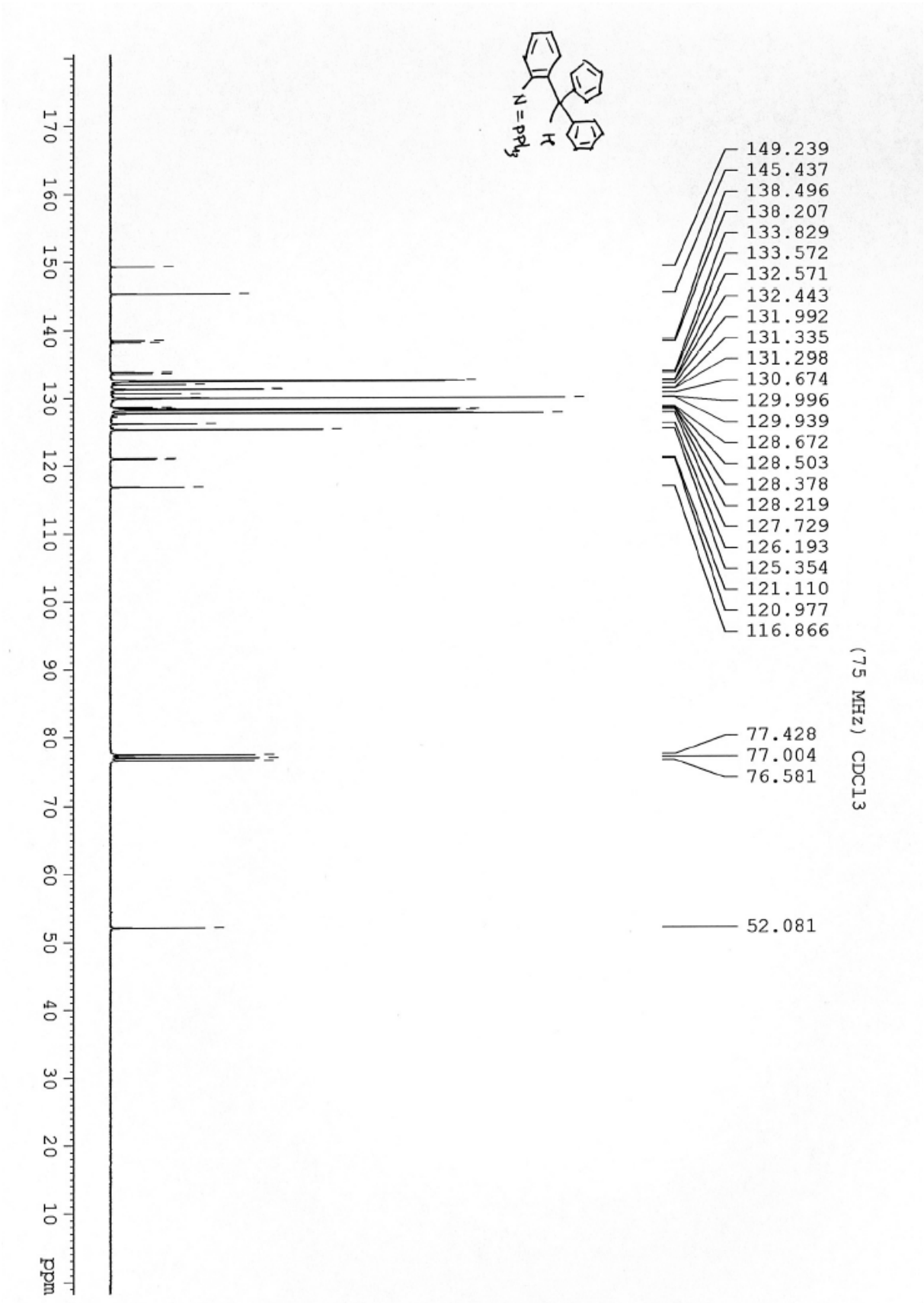
Copy of ^{1}H and ^{13}C NMR Spectra of Compounds 11, 13, 18, 20, 22, 25, 27, 30, 32 and 34.

Copy of ^{31}P NMR Spectra of Compounds 11, 27 and 32

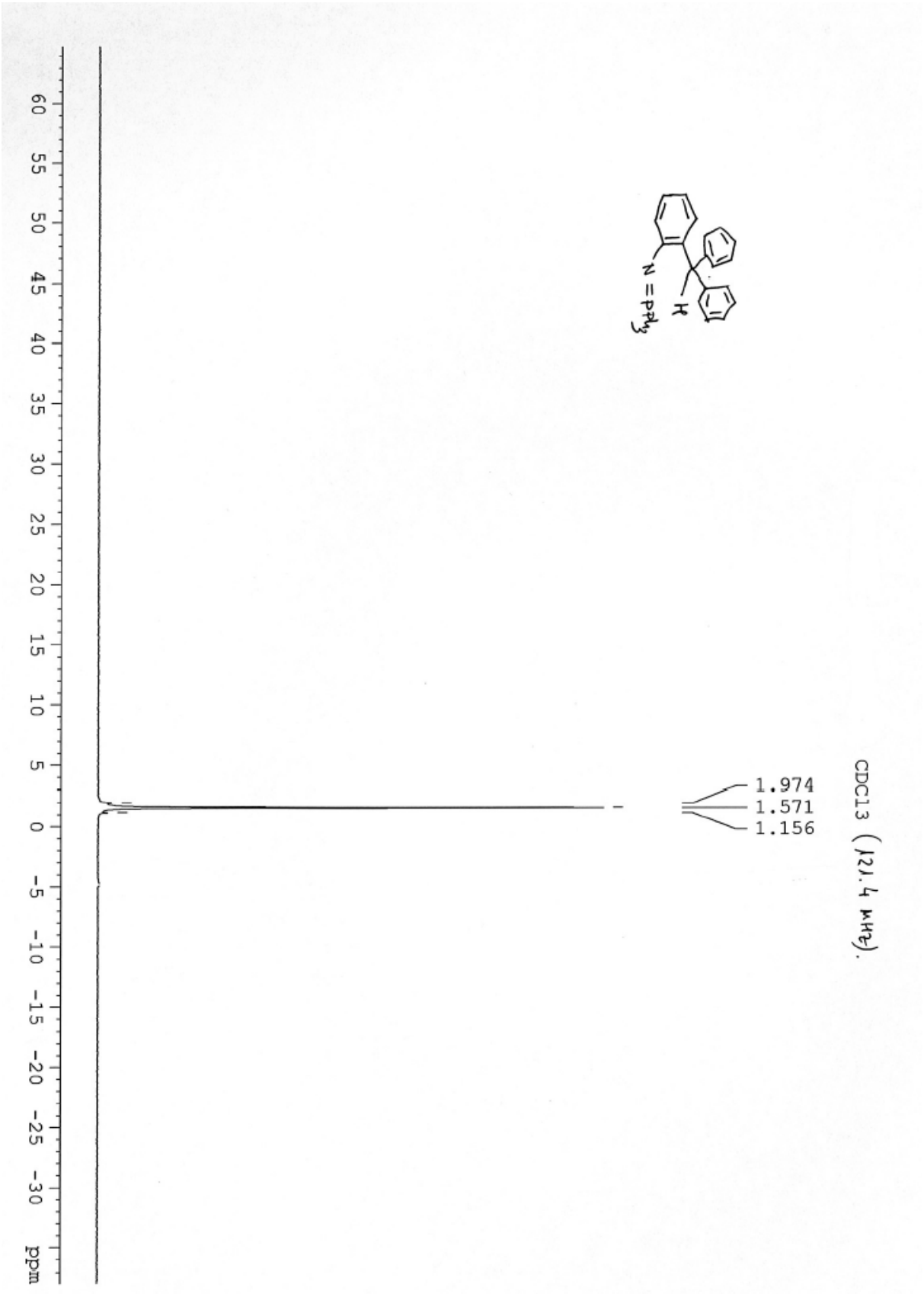
^{1}H NMR of **11a**



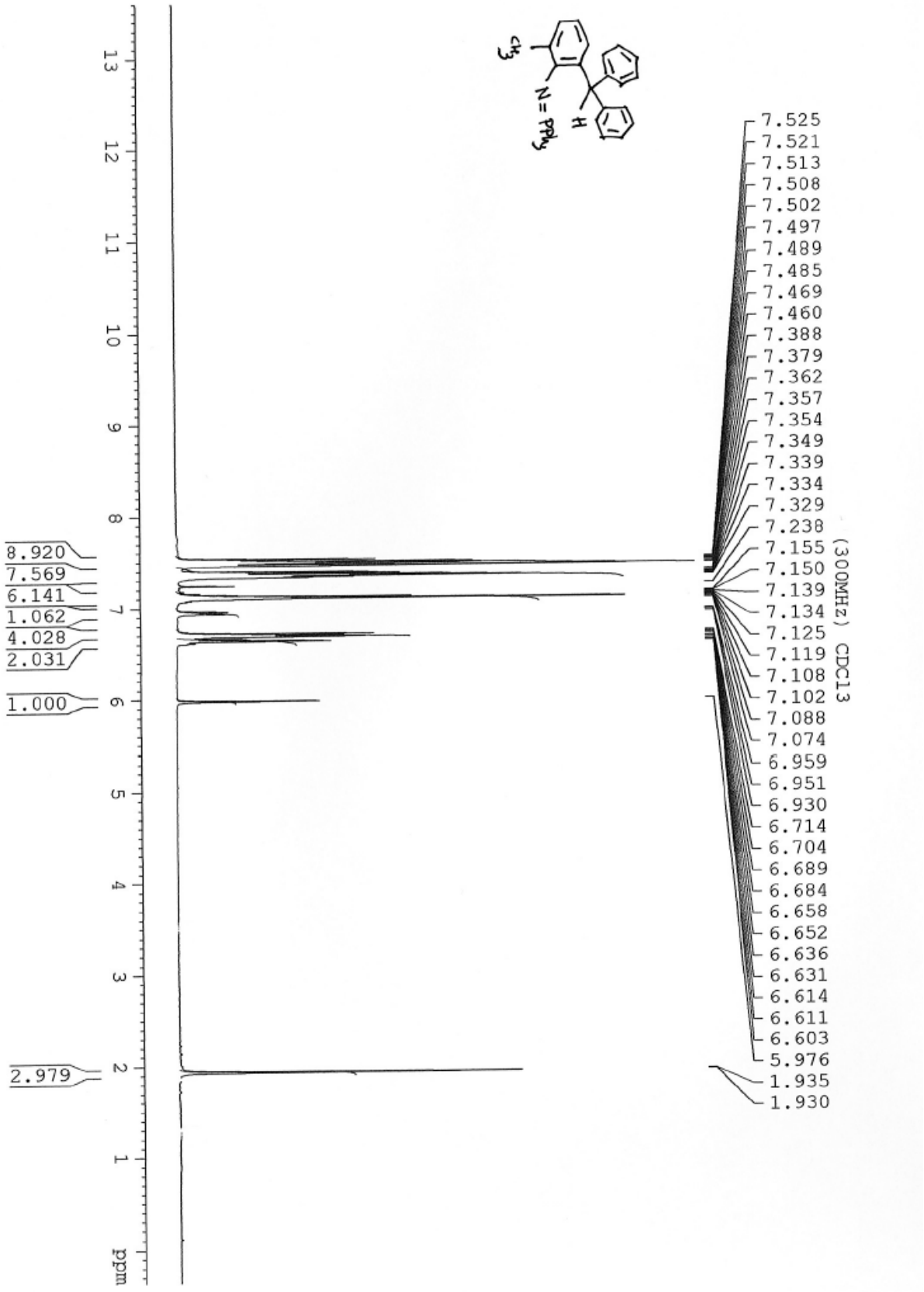
^{13}C NMR of **11a**



^{31}P NMR of **11a**



^{1}H NMR **11b**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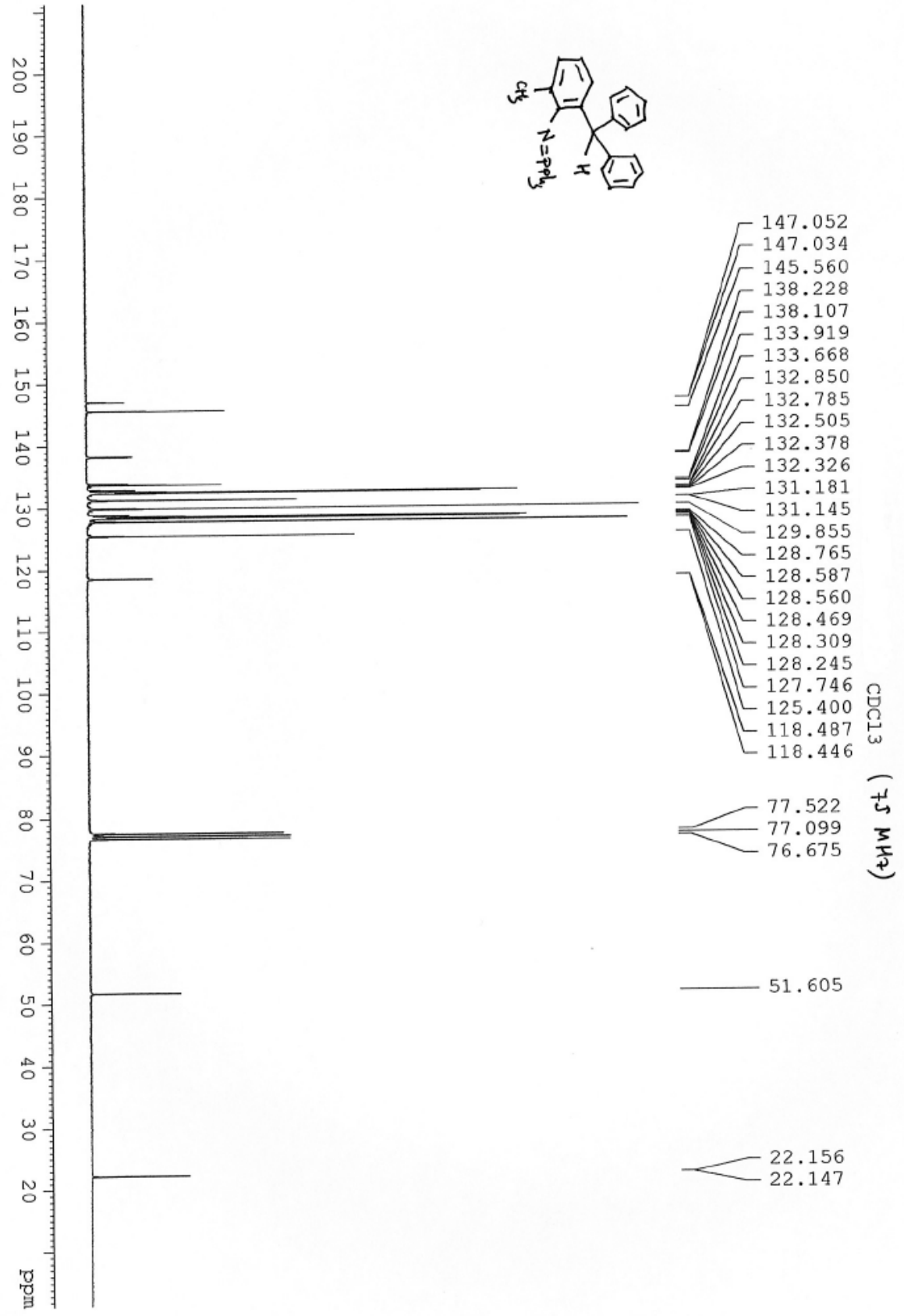
ppm

^{13}C NMR **11b**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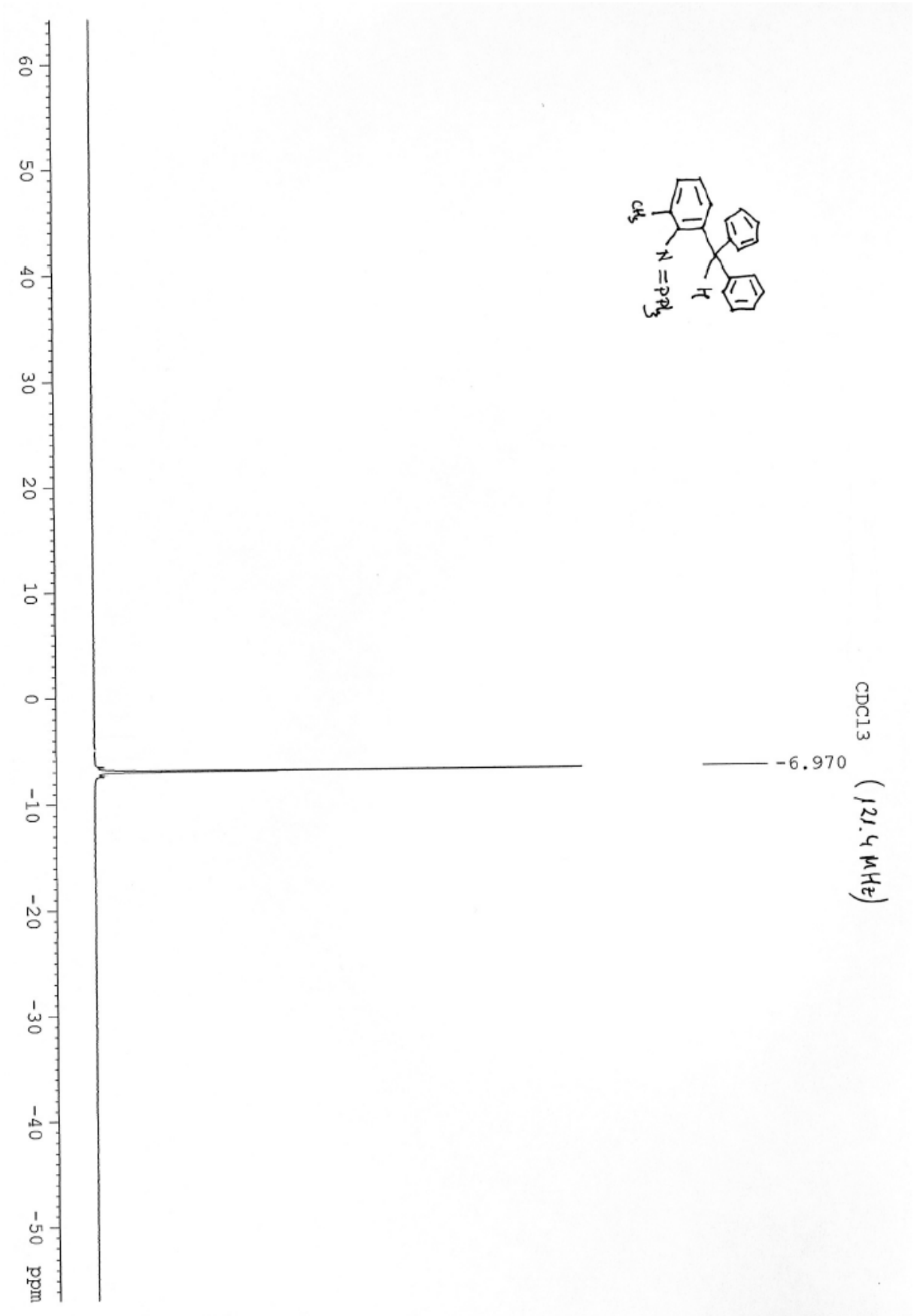
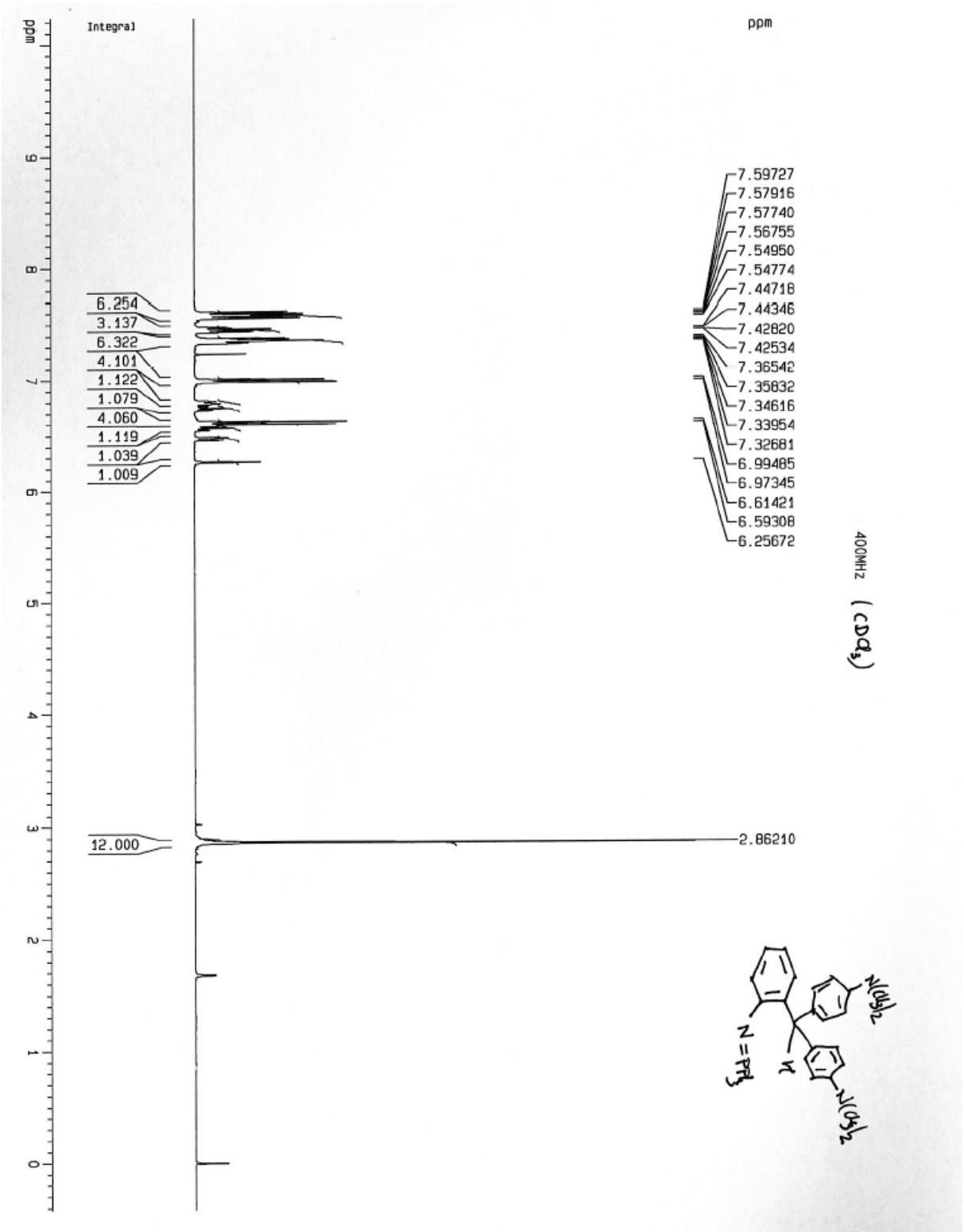
ppm

^{31}P NMR **11b**



^{1}H NMR **11c**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7.34616
7.33954
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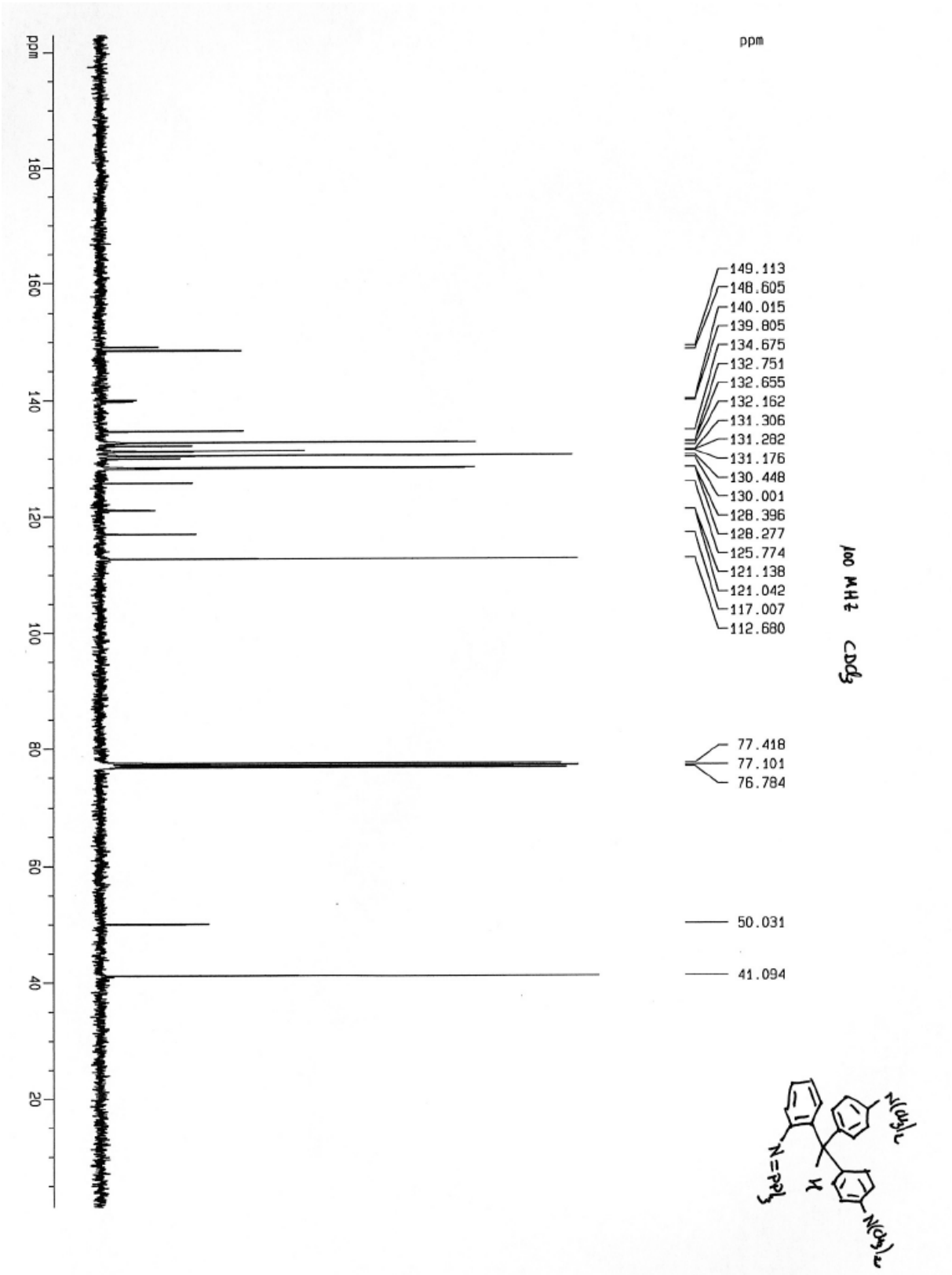
6.59308
6.25672
2.86210
400MHz (CDCl3)

^{13}C NMR **11c**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128.277
125.774
121.138
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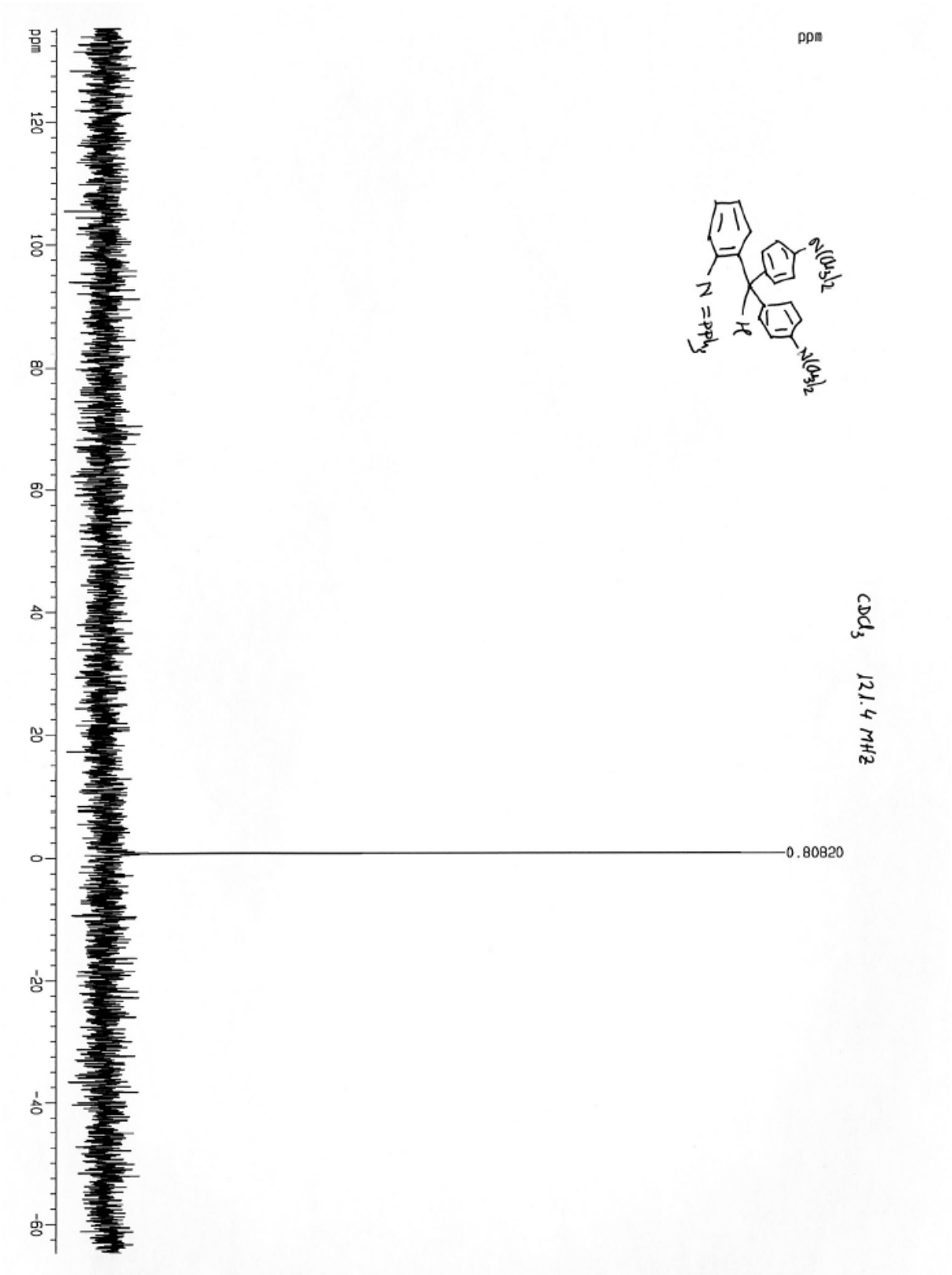
41.094
100 MHz CDCl3

^{31}P NMR **11c**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100
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20
0
-20
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-60
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H
N(CH3)2
CDCl3 121.4 MHz
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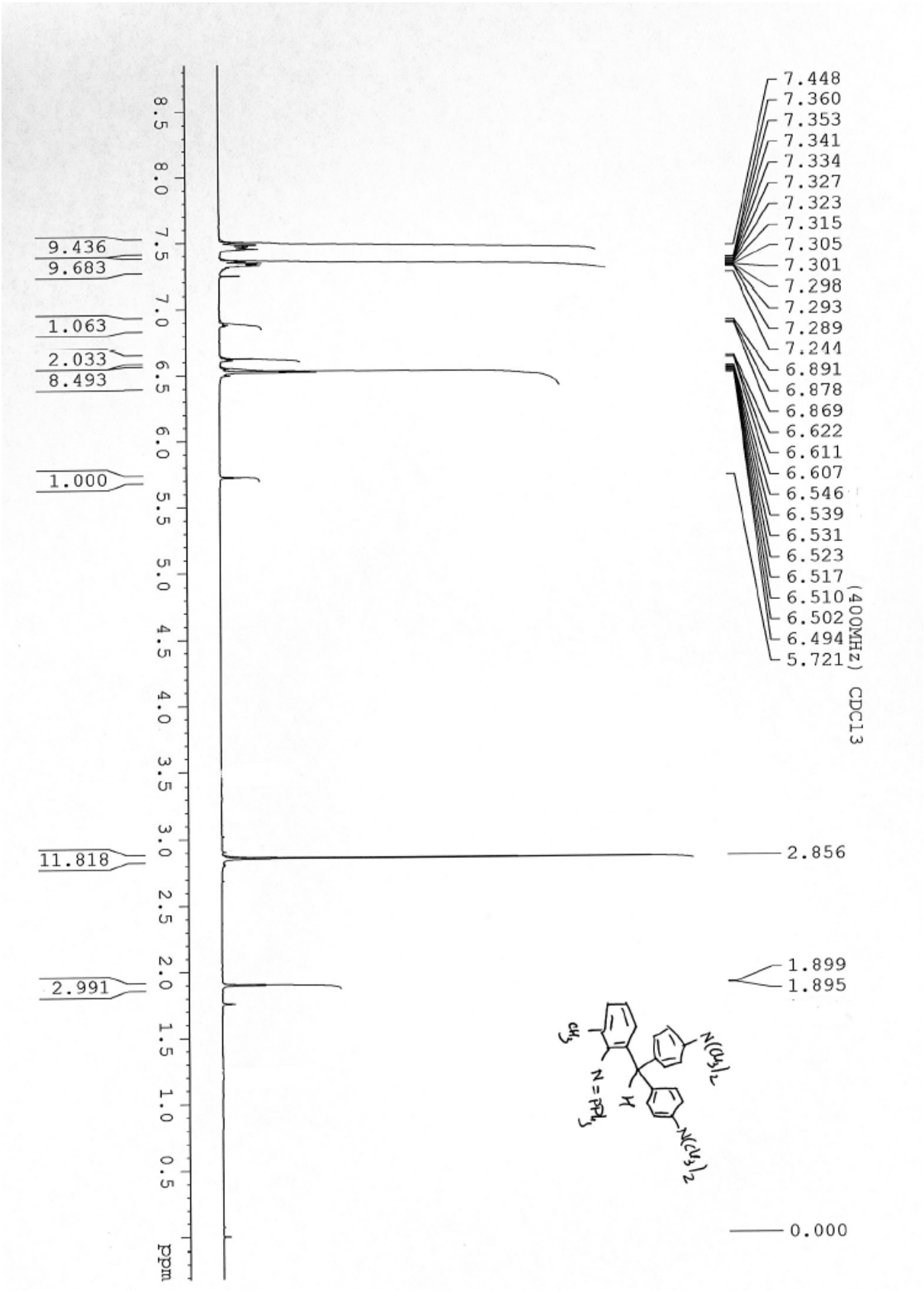
^{1}H NMR **11d**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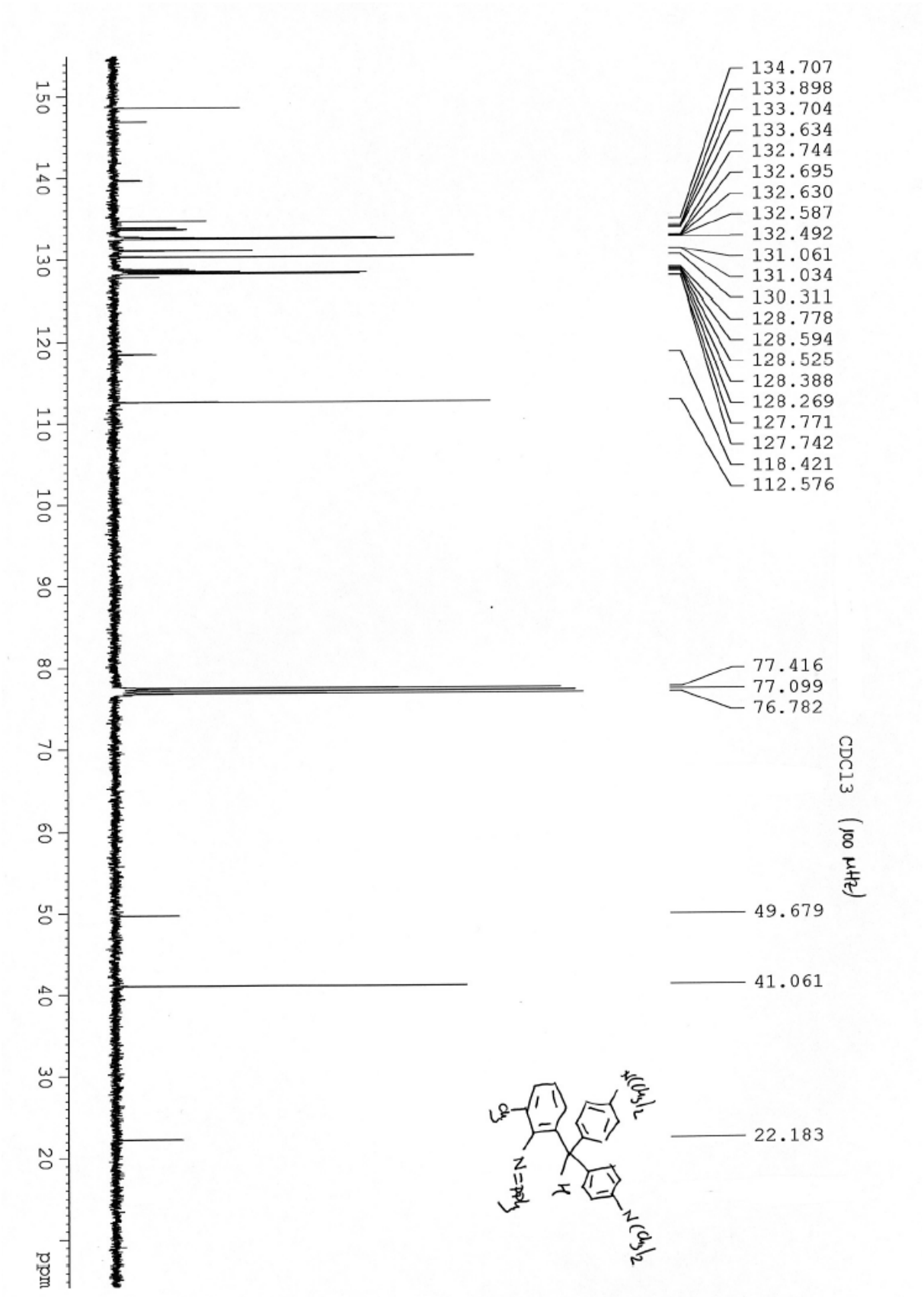
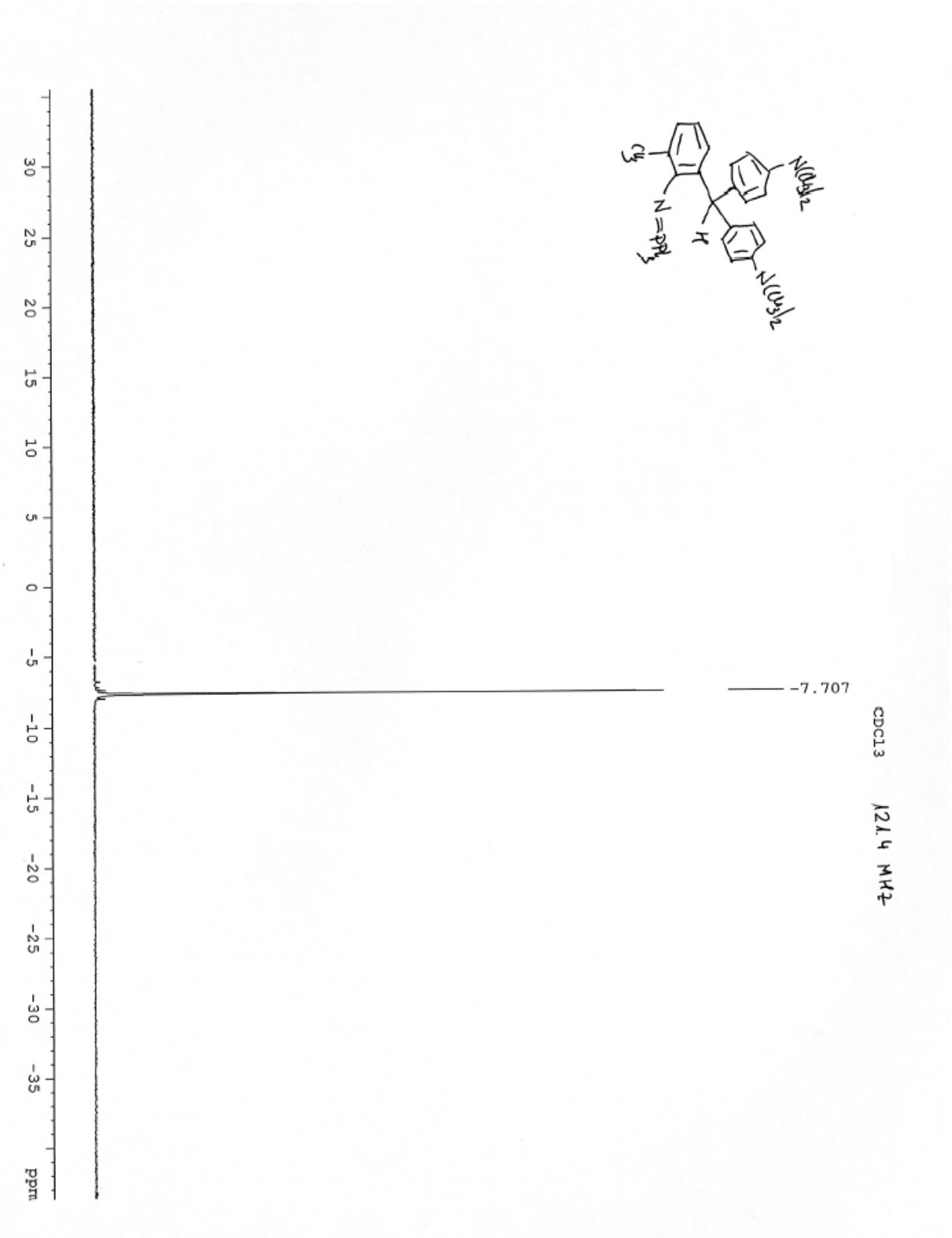
6.611
6.607
6.546
6.539
6.531
6.523
6.517
6.510
6.502
6.494
5.721
(400MHz) CDC13
9.436
9.683
1.063
2.033
8.493
1.000
11.818
2.991
2.856
1.899
1.895
0.000
ppm

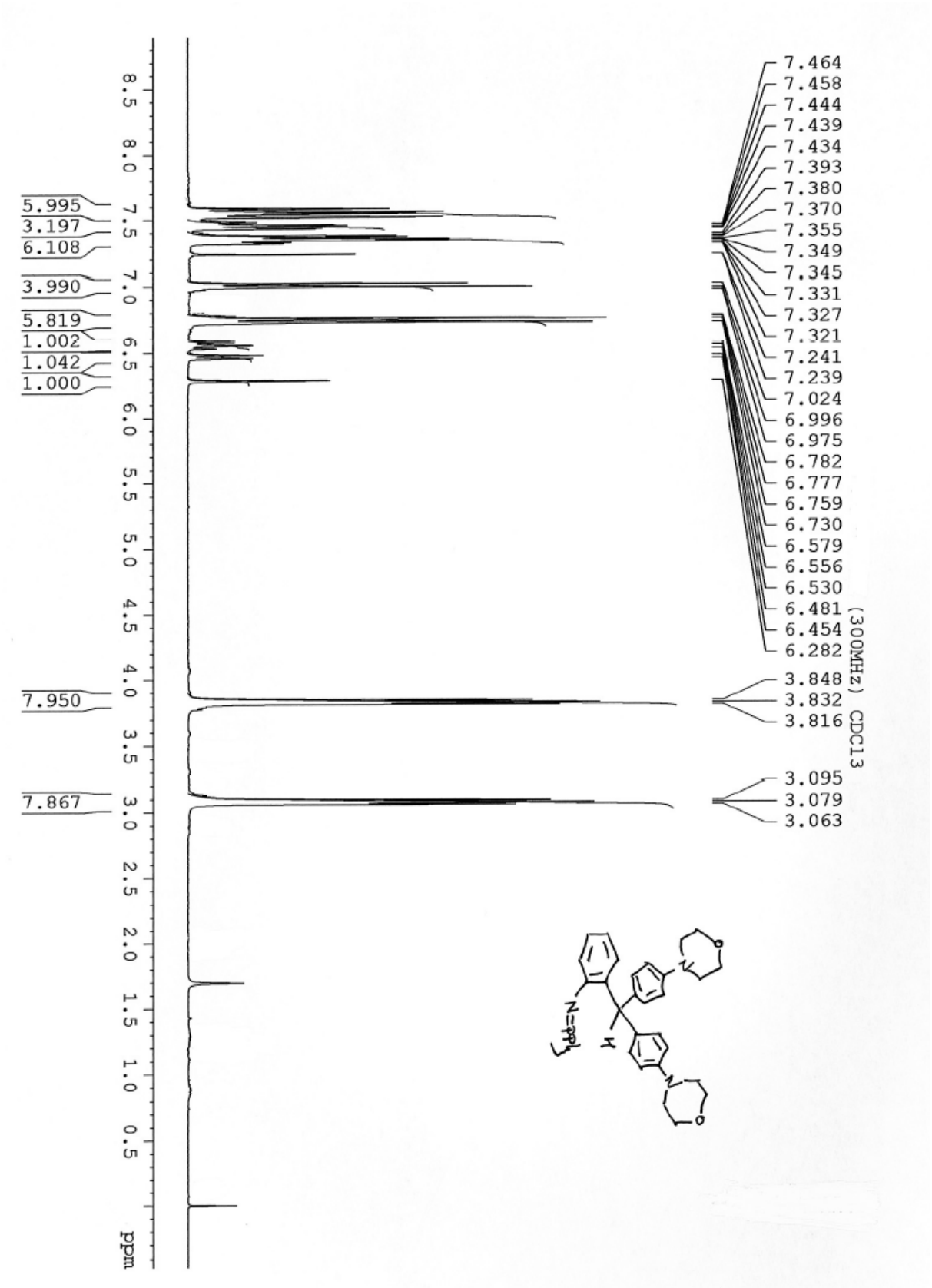
^{13}C NMR **11d**


134.707
133.898
133.704
133.634
132.744
132.695
132.630
132.587
132.492
131.061
131.034
130.311
128.778
128.594
128.525
128.388
128.269
127.771
127.742
118.421
112.576
77.416
77.099
76.782
CDC13 (100 MHz)
49.679
41.061
22.183
ppm

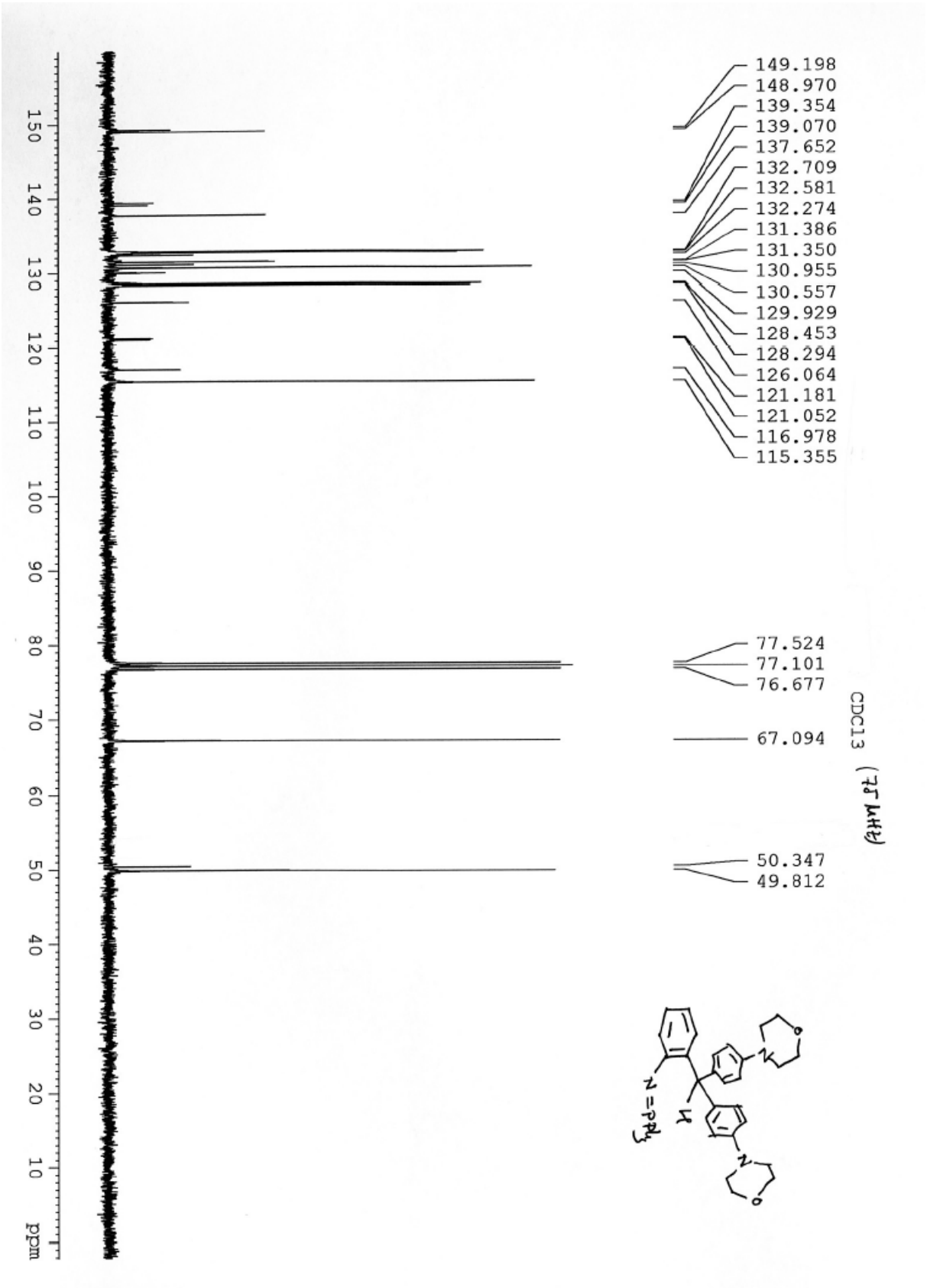
^{31}P NMR **11d**



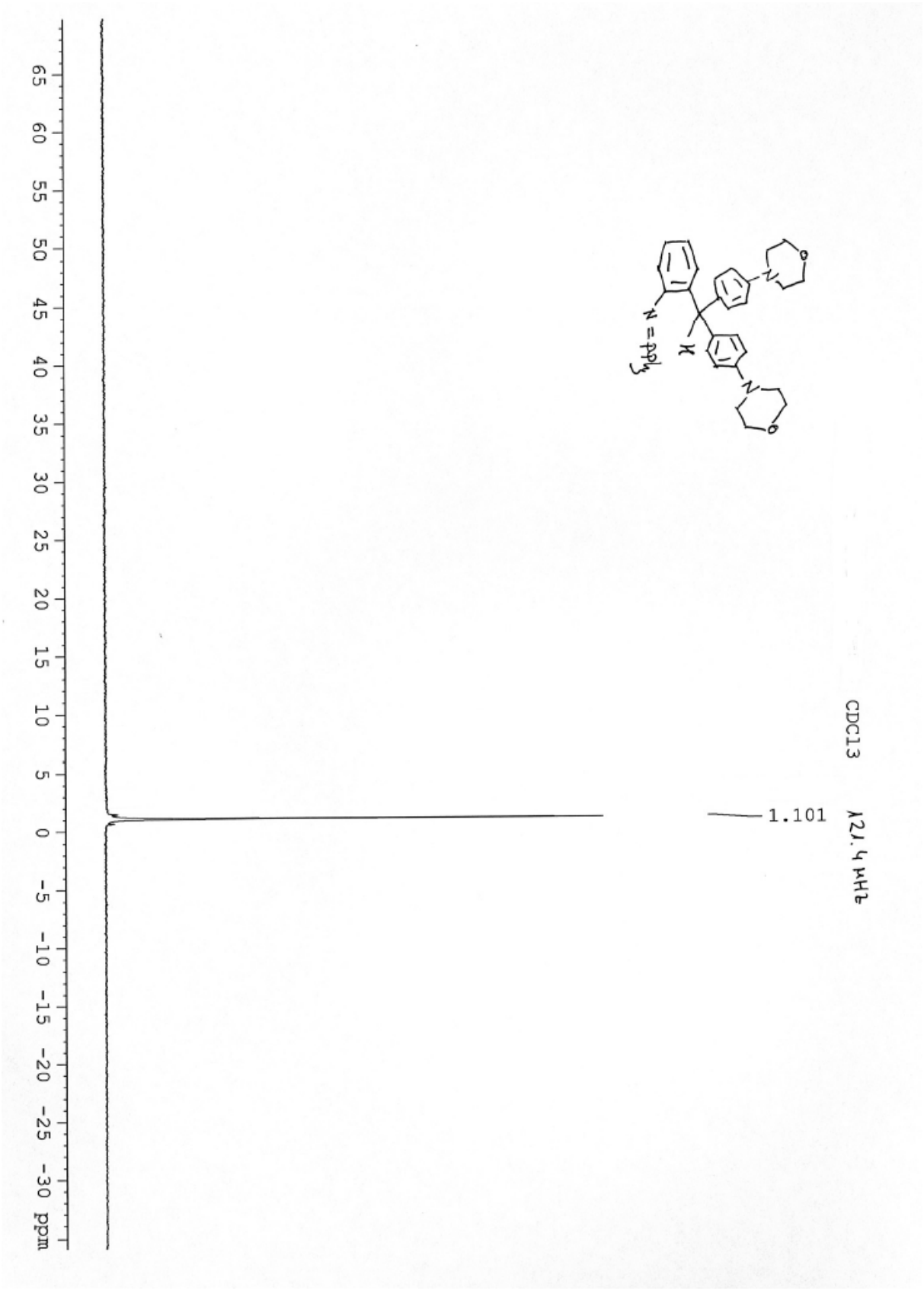
^{1}H NMR **11e**


7.464
7.458
7.444
7.439
7.434
7.393
7.380
7.370
7.355
7.349
7.345
7.331
7.327
7.321
7.241
7.239
7.024
6.996
6.975
6.782
6.777
6.759
6.730
6.579
6.556
6.530
6.481
6.454
6.282
3.848
3.832
3.816
3.095
3.079
3.063
5.995
3.197
6.108
3.990
5.819
1.002
1.042
1.000
7.950
7.867
(300MHz) CDCl3
ppm

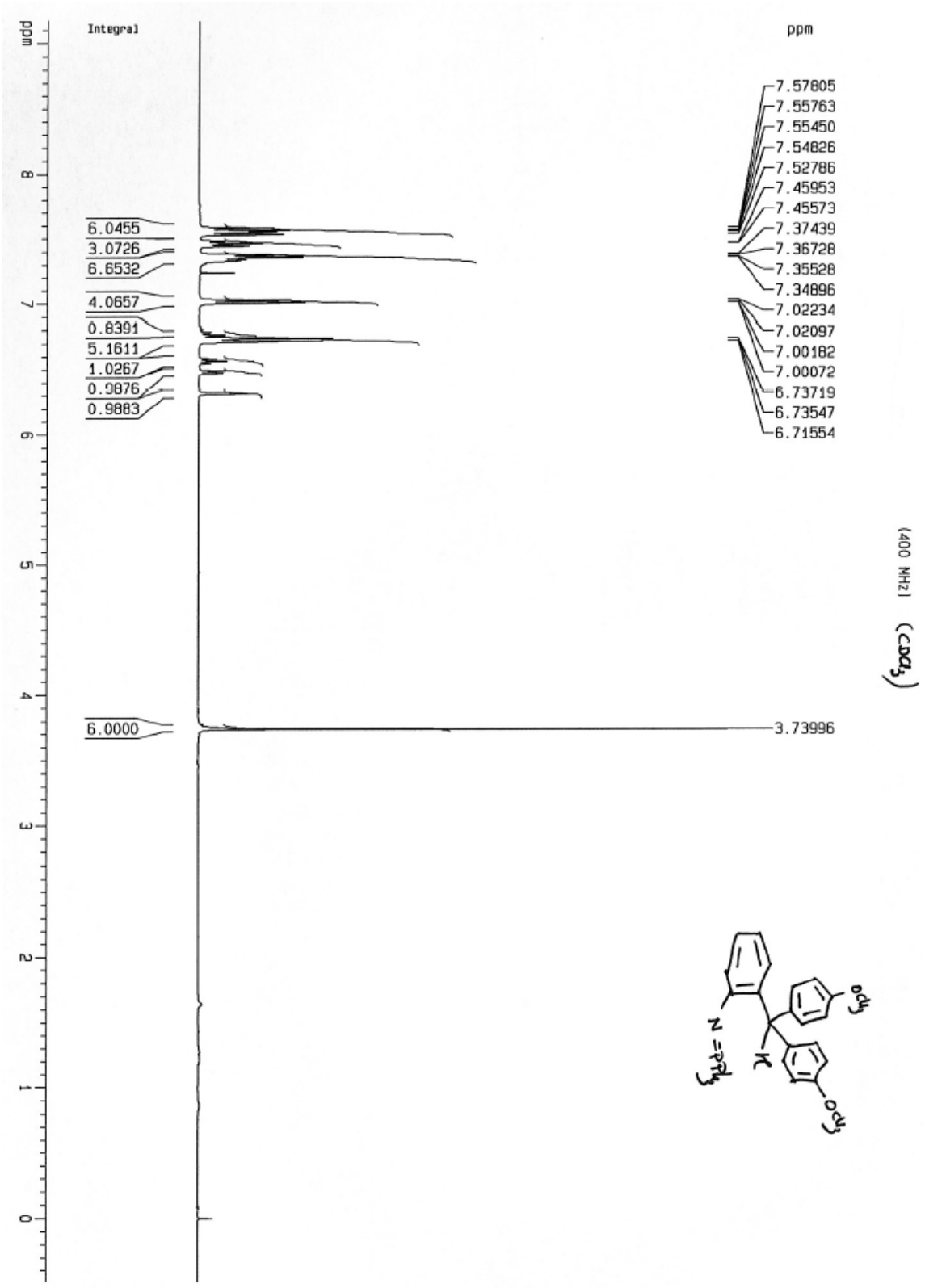
^{13}C NMR **11e**


149.198
148.970
139.354
139.070
137.652
132.709
132.581
132.274
131.386
131.350
130.955
130.557
129.929
128.453
128.294
126.064
121.181
121.052
116.978
115.355
77.524
77.101
76.677
67.094
50.347
49.812
CDCl3
(75 MHz)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
N=PPh2
H
N
O
N
O

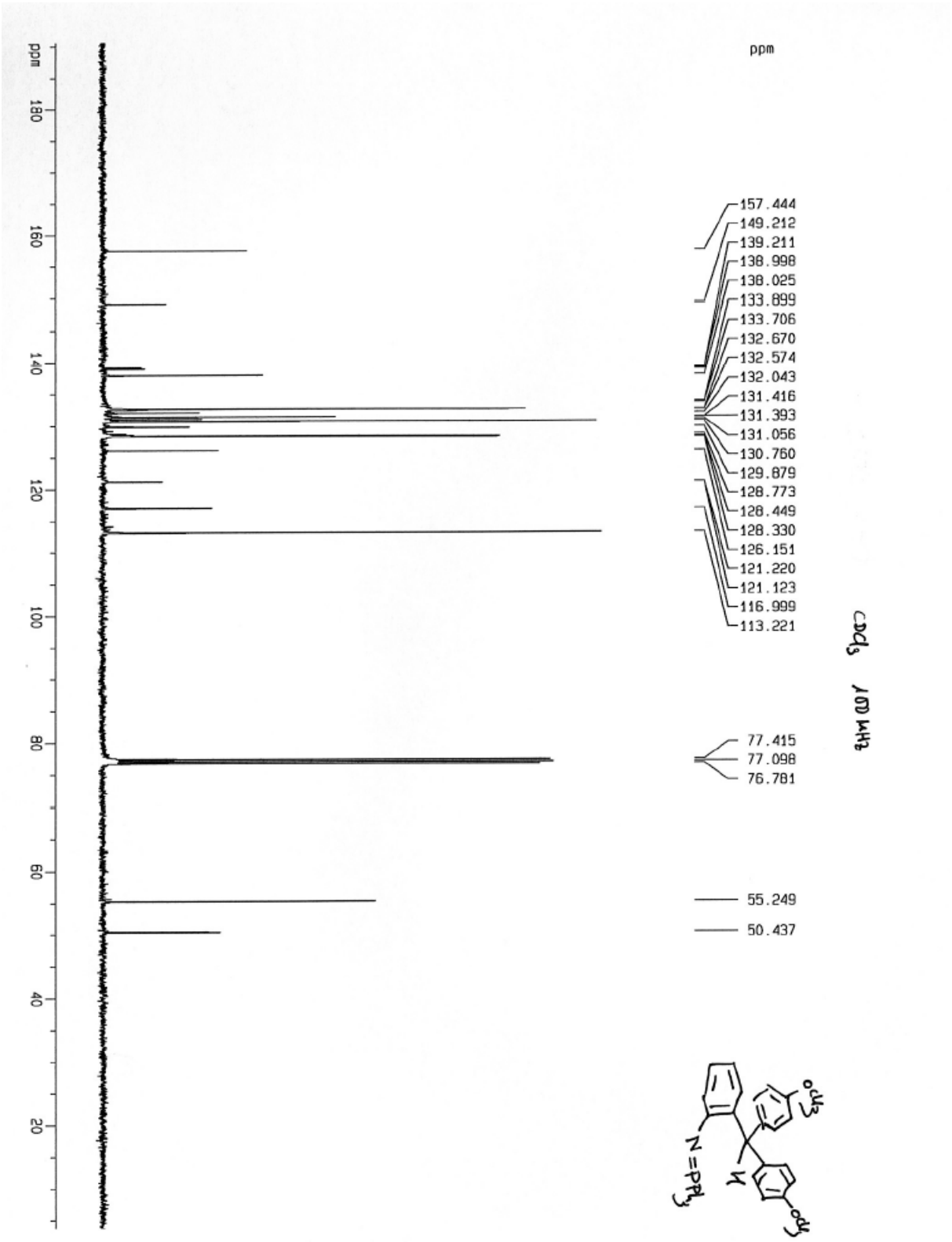
^{31}P NMR **11e**


65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm
1.101
CDC13
121.4 MHz

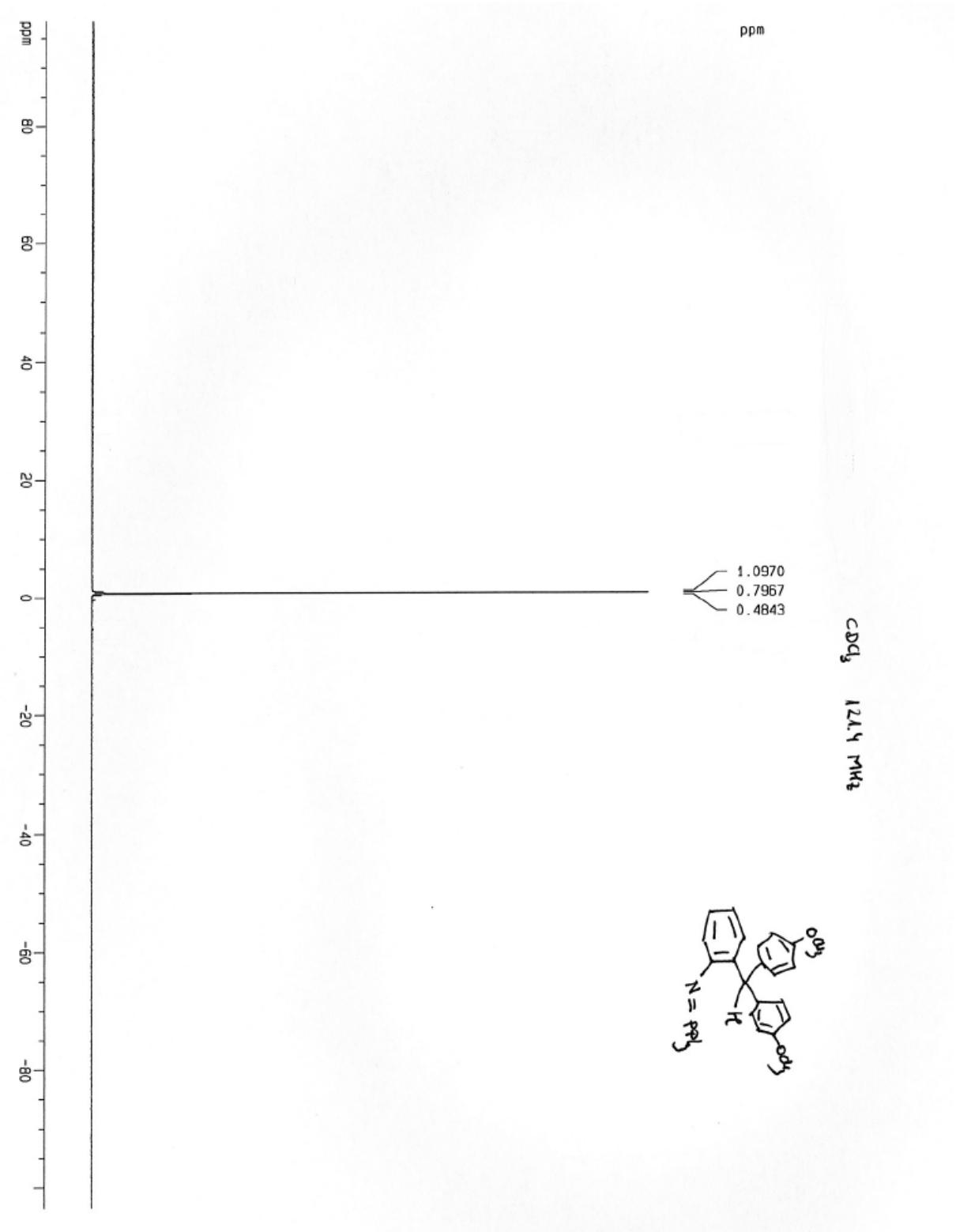
^{1}H NMR **11f**


Integral
ppm
7.57805
7.55763
7.55450
7.54826
7.52786
7.45953
7.45573
7.37439
7.36728
7.35528
7.34896
7.02234
7.02097
7.00182
7.00072
6.73719
6.73547
6.71554
6.0455
3.0726
6.6532
4.0657
0.8391
5.1611
1.0267
0.9876
0.9883
6.0000
3.73996
(400 MHz) (CDCl3)

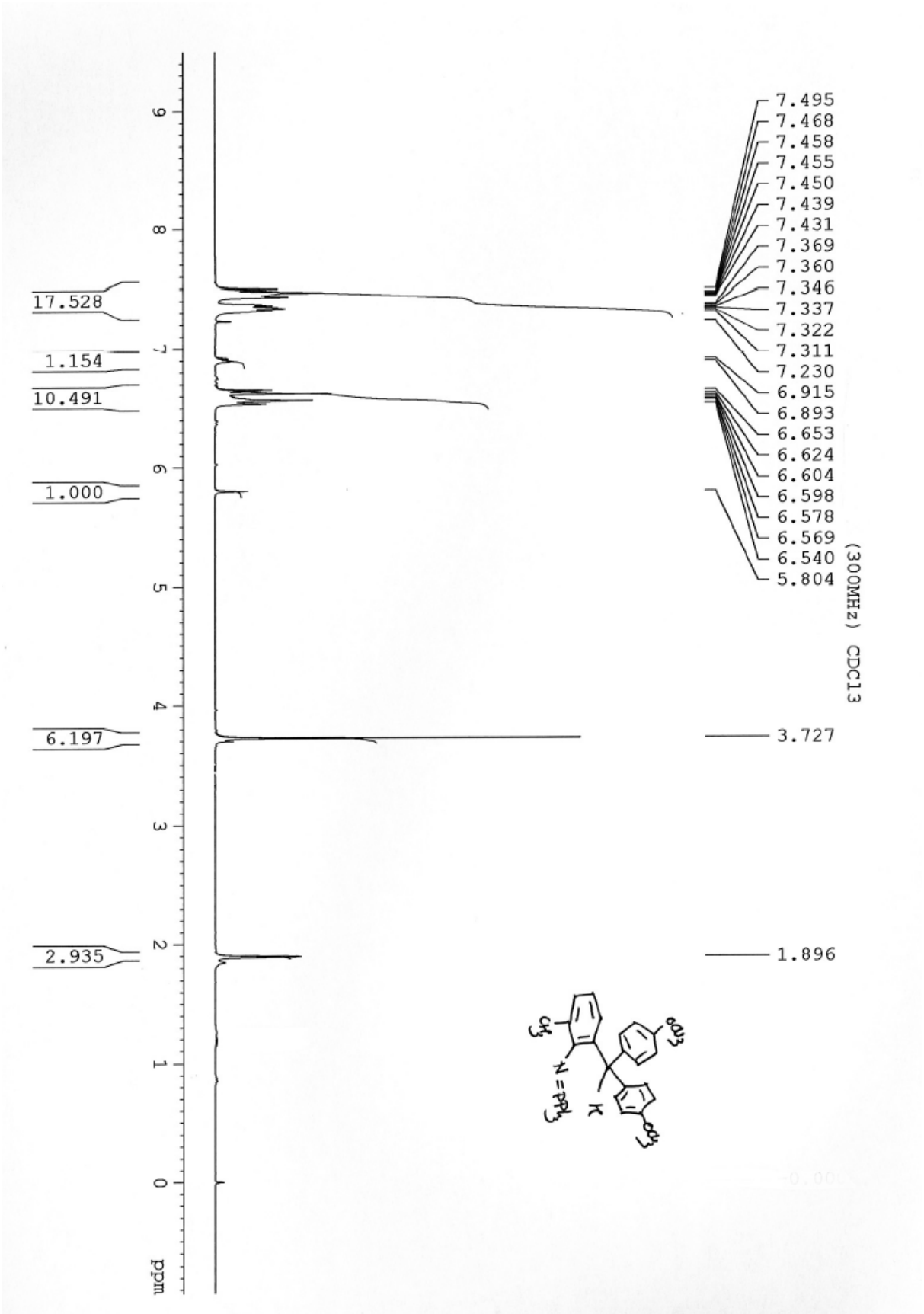
^{13}C NMR **11f**


ppm
180
160
140
120
100
80
60
40
20
ppm
157.444
149.212
139.211
138.998
138.025
133.899
133.706
132.670
132.574
132.043
131.416
131.393
131.056
130.760
129.879
128.773
128.449
128.330
126.151
121.220
121.123
116.999
113.221
77.415
77.098
76.781
55.249
50.437
CDCl3
OMe
NH2
OMe
N=PPh3
H

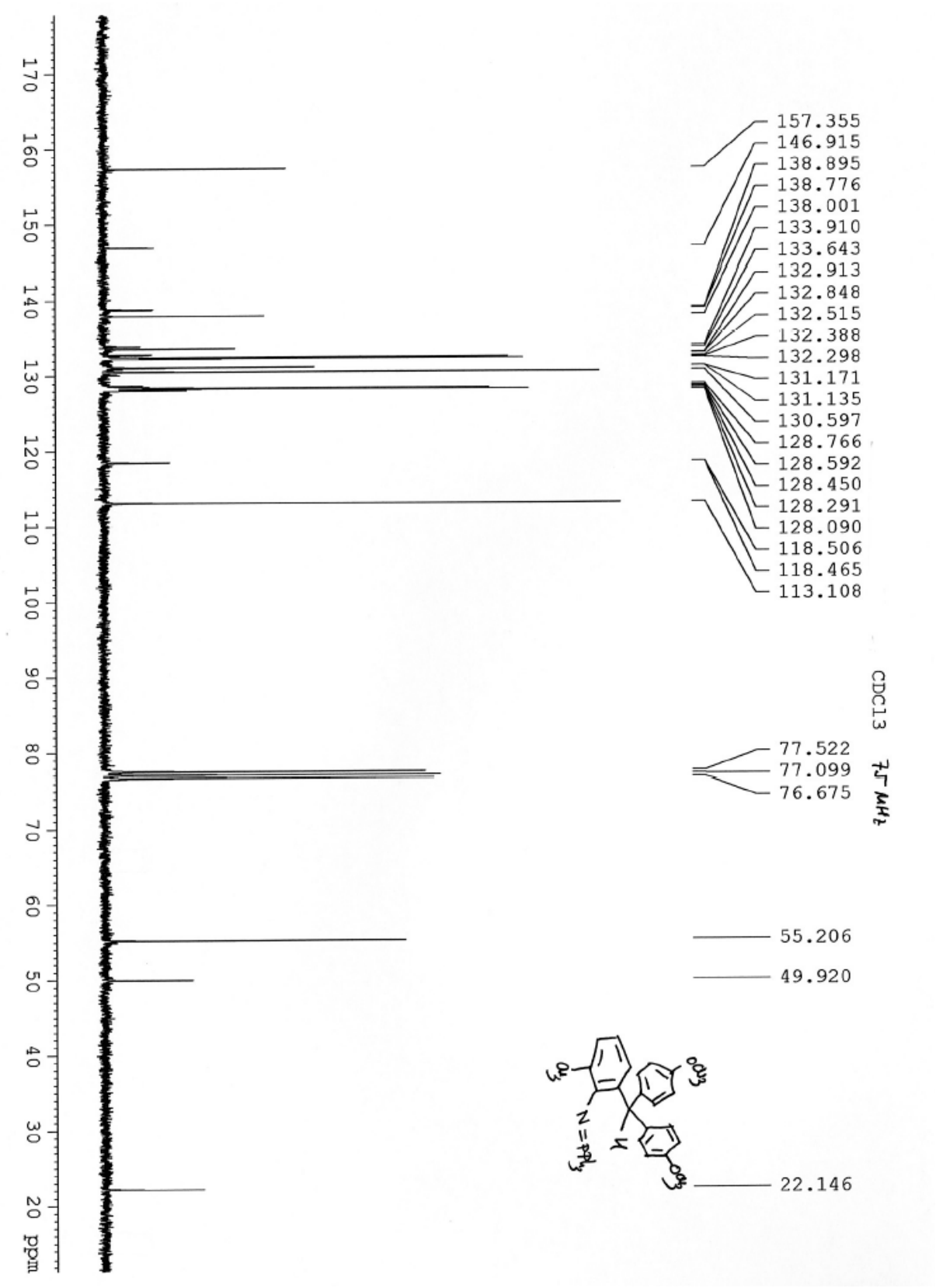
^{31}P NMR **11f**



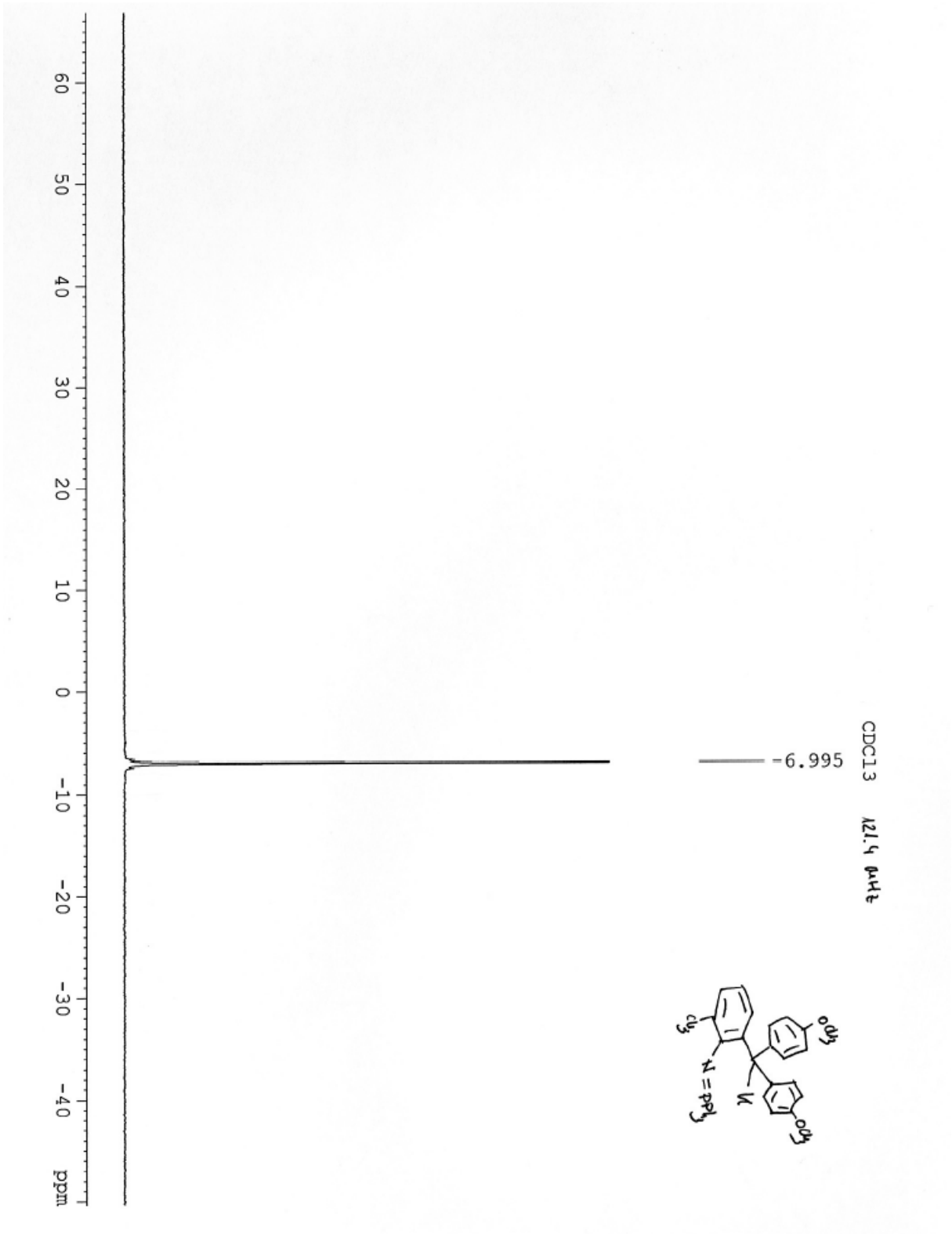
^{1}H NMR **11g**


7.495
7.468
7.458
7.455
7.450
7.439
7.431
7.369
7.360
7.346
7.337
7.322
7.311
7.230
6.915
6.893
6.653
6.624
6.604
6.598
6.578
6.569
6.540
5.804
3.727
1.896
17.528
1.154
10.491
1.000
6.197
2.935
(300MHz) CDC13
ppm

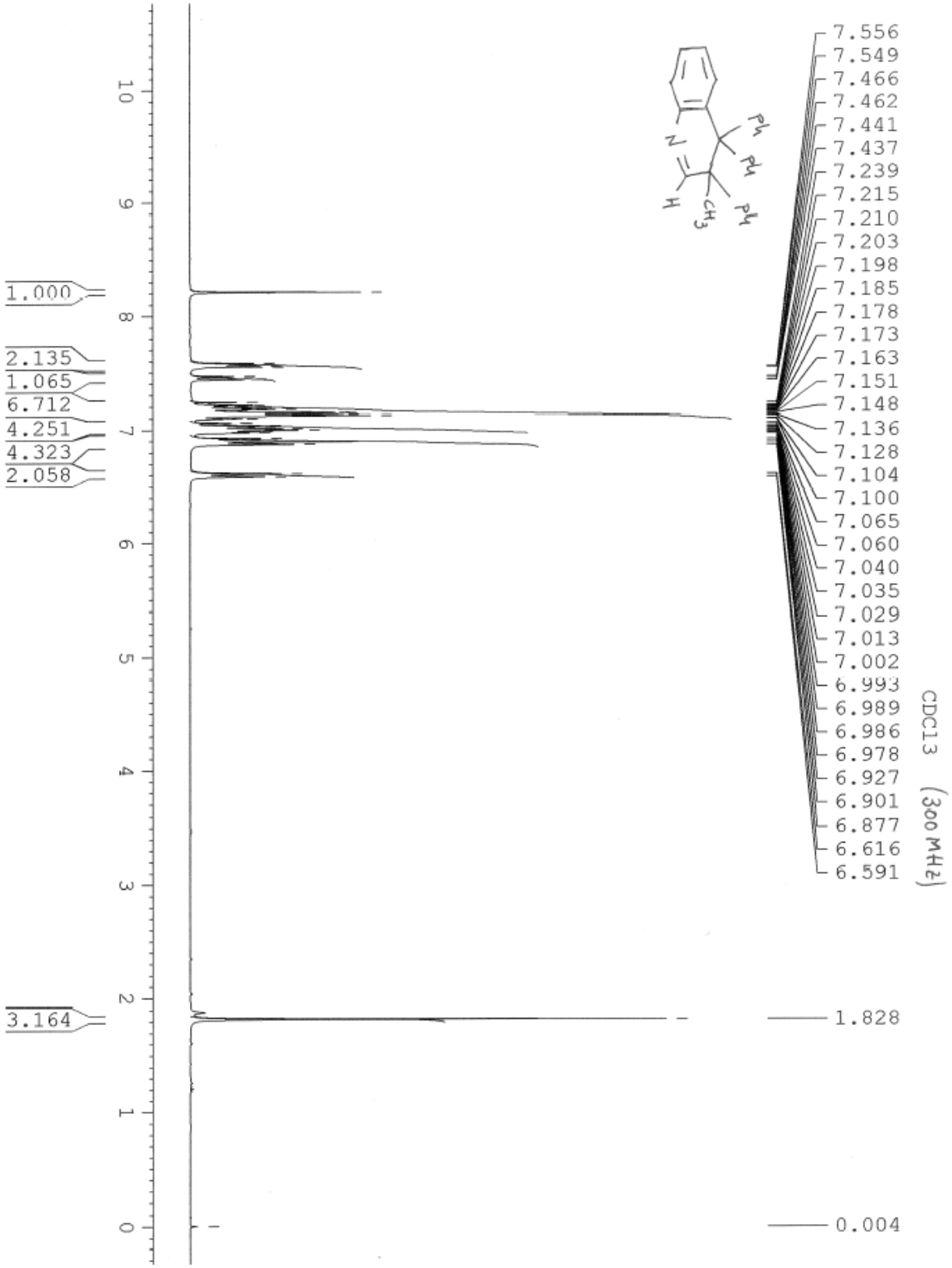
^{13}C NMR **11g**


157.355
146.915
138.895
138.776
138.001
133.910
133.643
132.913
132.848
132.515
132.388
132.298
131.171
131.135
130.597
128.766
128.592
128.450
128.291
128.090
118.506
118.465
113.108
77.522
77.099
76.675
55.206
49.920
22.146
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

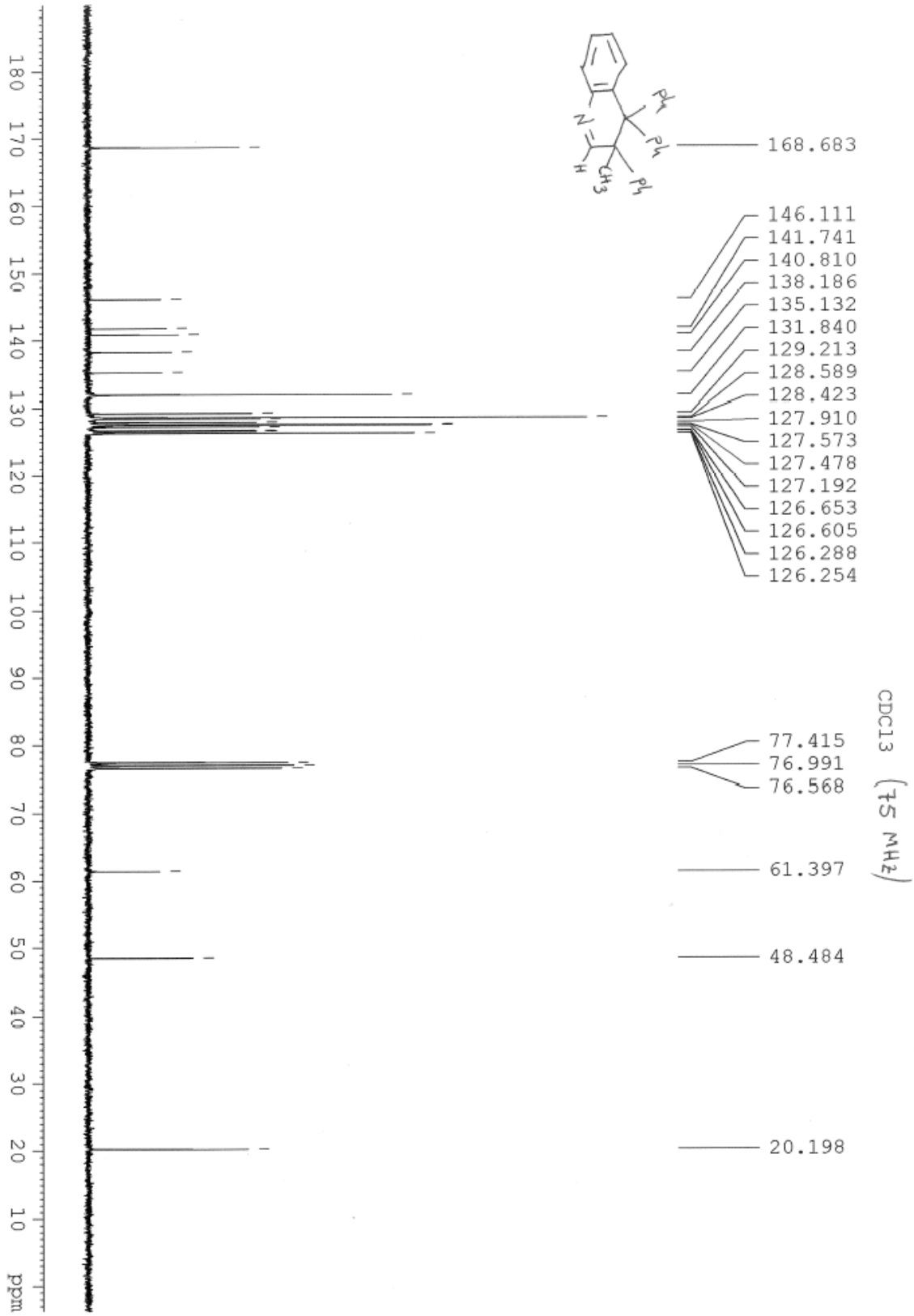
^{31}P NMR **11g**



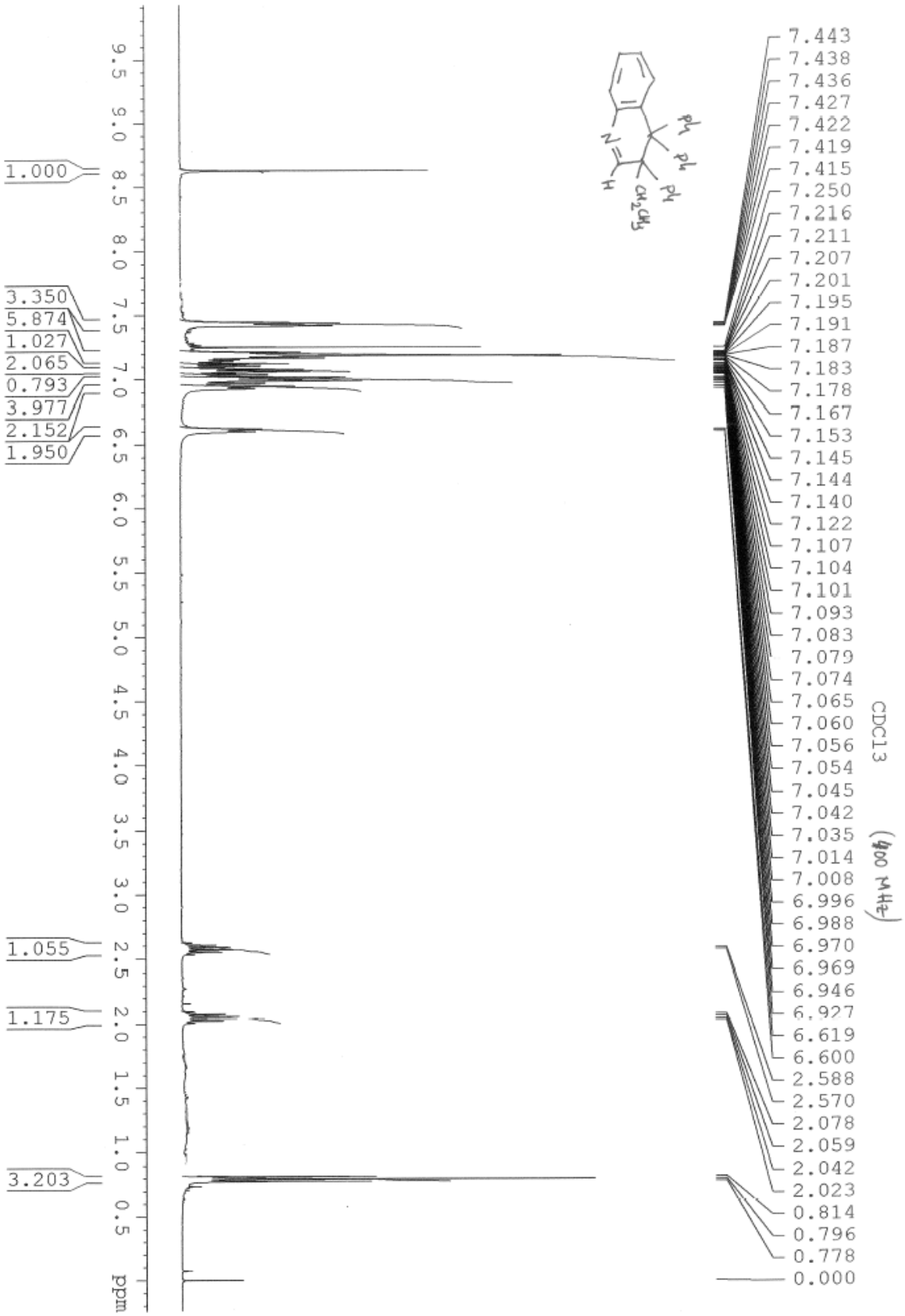
^{1}H NMR of **13a**


7.556
7.549
7.466
7.462
7.441
7.437
7.239
7.215
7.210
7.203
7.198
7.185
7.178
7.173
7.163
7.151
7.148
7.136
7.128
7.104
7.100
7.065
7.060
7.040
7.035
7.029
7.013
7.002
6.993
6.989
6.986
6.978
6.927
6.901
6.877
6.616
6.591
CDCl3 (300 MHz)
1.000
2.135
1.065
6.712
4.251
4.323
2.058
3.164
1.828
0.004
Ph
Ph
Ph
N
H
CH3

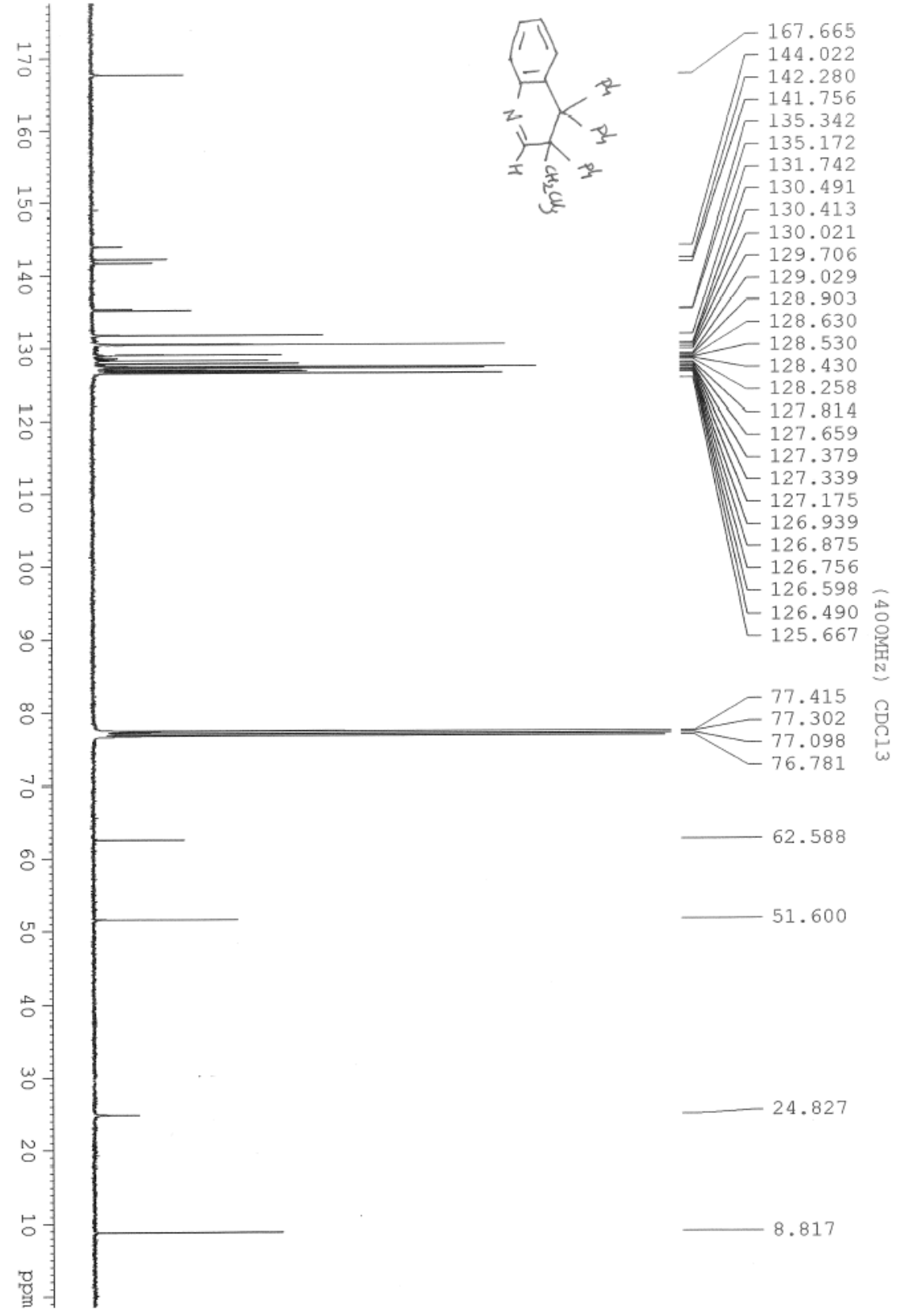
^{13}C NMR of **13a**



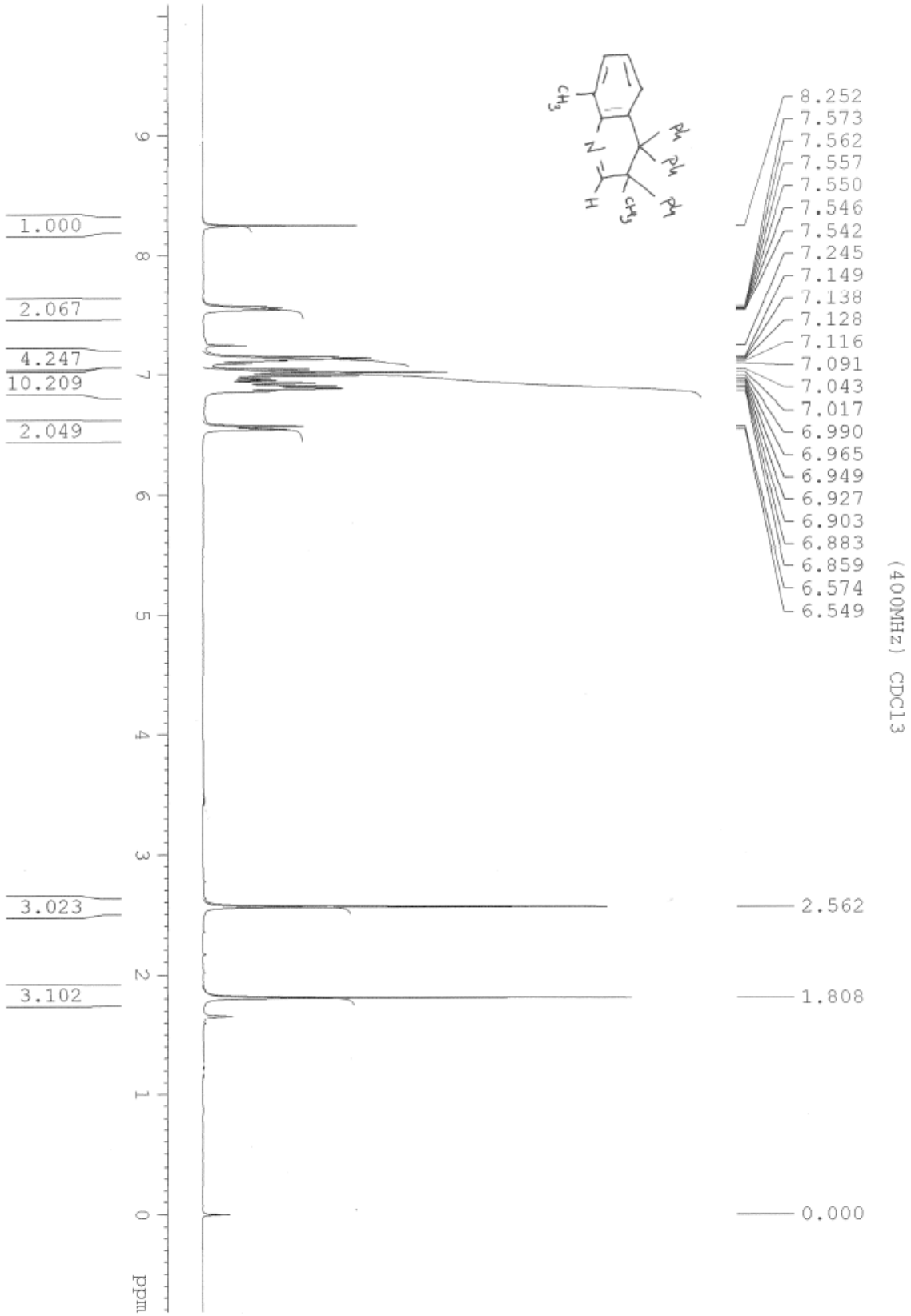
^{1}H NMR **13b**


1.000
3.350
5.874
1.027
2.065
0.793
3.977
2.152
1.950
1.055
1.175
3.203
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
Ph Ph Ph
N
H
CH2CH3
7.443
7.438
7.436
7.427
7.422
7.419
7.415
7.250
7.216
7.211
7.207
7.201
7.195
7.191
7.187
7.183
7.178
7.167
7.153
7.145
7.144
7.140
7.122
7.107
7.104
7.101
7.093
7.083
7.079
7.074
7.065
7.060
7.056
7.054
7.045
7.042
7.035
7.014
7.008
6.996
6.988
6.970
6.969
6.946
6.927
6.619
6.600
2.588
2.570
2.078
2.059
2.042
2.023
0.814
0.796
0.778
0.000
CDC13 (400 MHz)

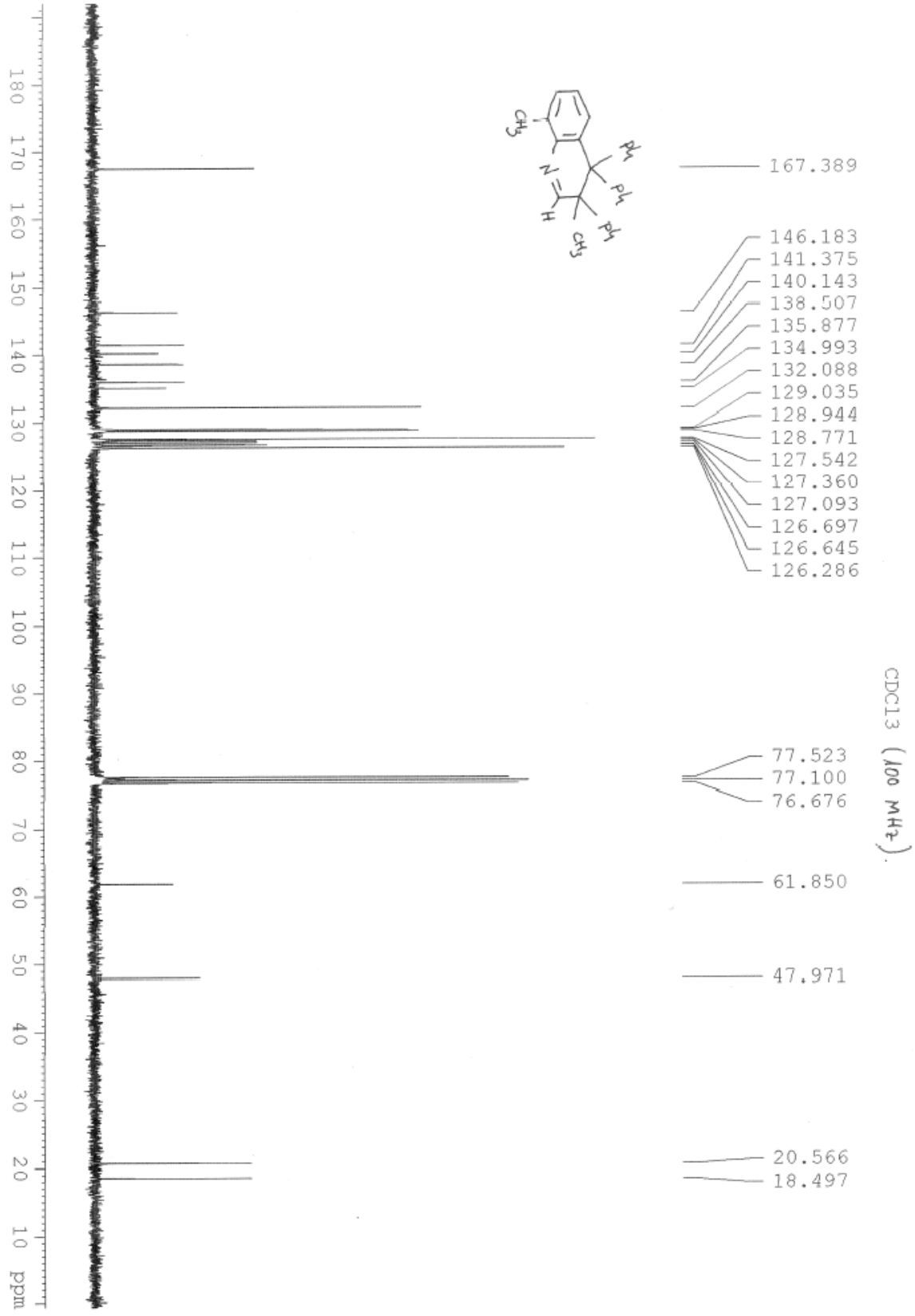
^{13}C NMR **13b**


167.665
144.022
142.280
141.756
135.342
135.172
131.742
130.491
130.413
130.021
129.706
129.029
128.903
128.630
128.530
128.430
128.258
127.814
127.659
127.379
127.339
127.175
126.939
126.875
126.756
126.598
126.490
125.667
77.415
77.302
77.098
76.781
62.588
51.600
24.827
8.817
(400MHz) CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

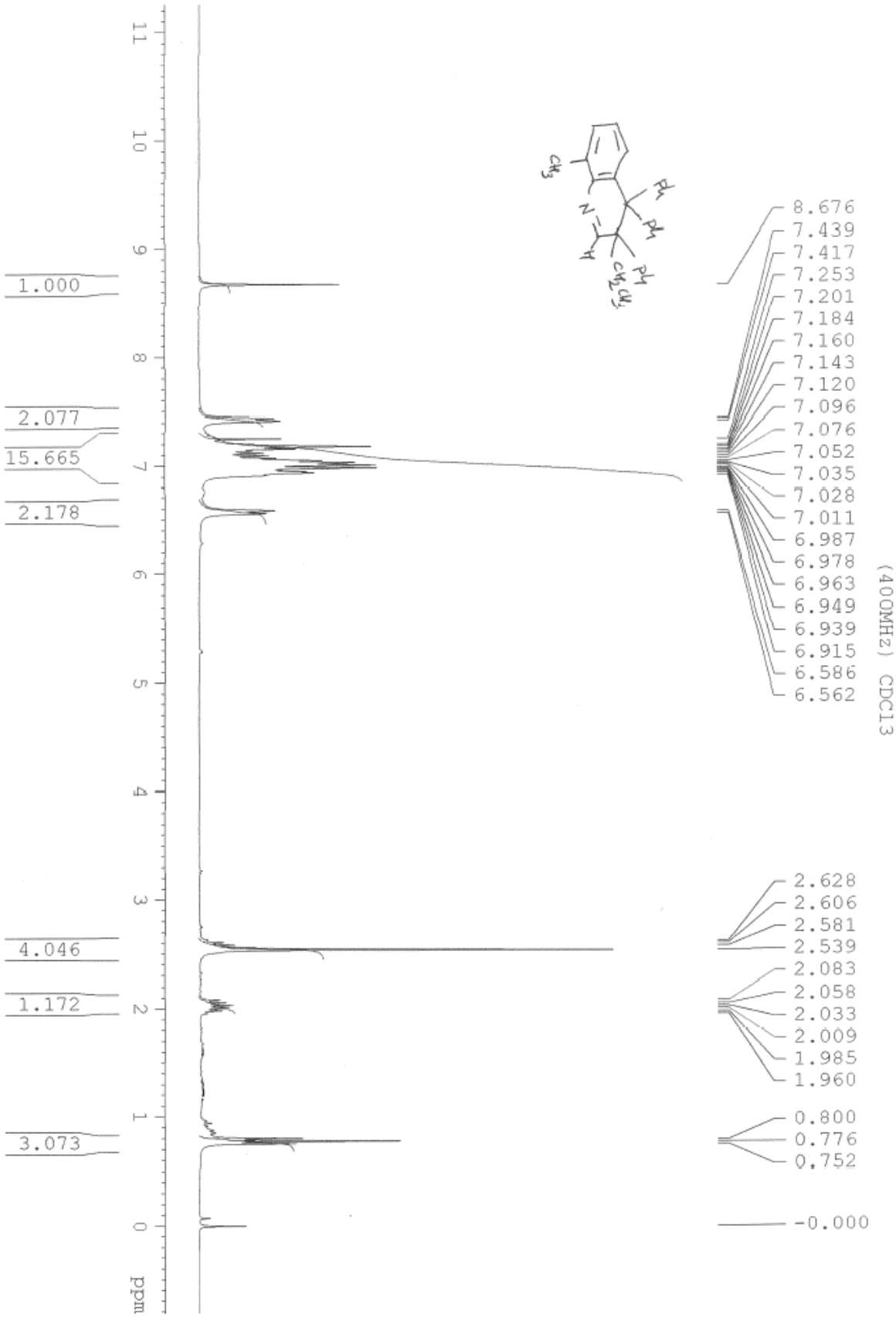
^{1}H NMR **13c**


1.000
2.067
4.247
10.209
2.049
3.023
3.102
8.252
7.573
7.562
7.557
7.550
7.546
7.542
7.245
7.149
7.138
7.128
7.116
7.091
7.043
7.017
6.990
6.965
6.949
6.927
6.903
6.883
6.859
6.574
6.549
2.562
1.808
0.000
(400MHz) CDCl3
ppm

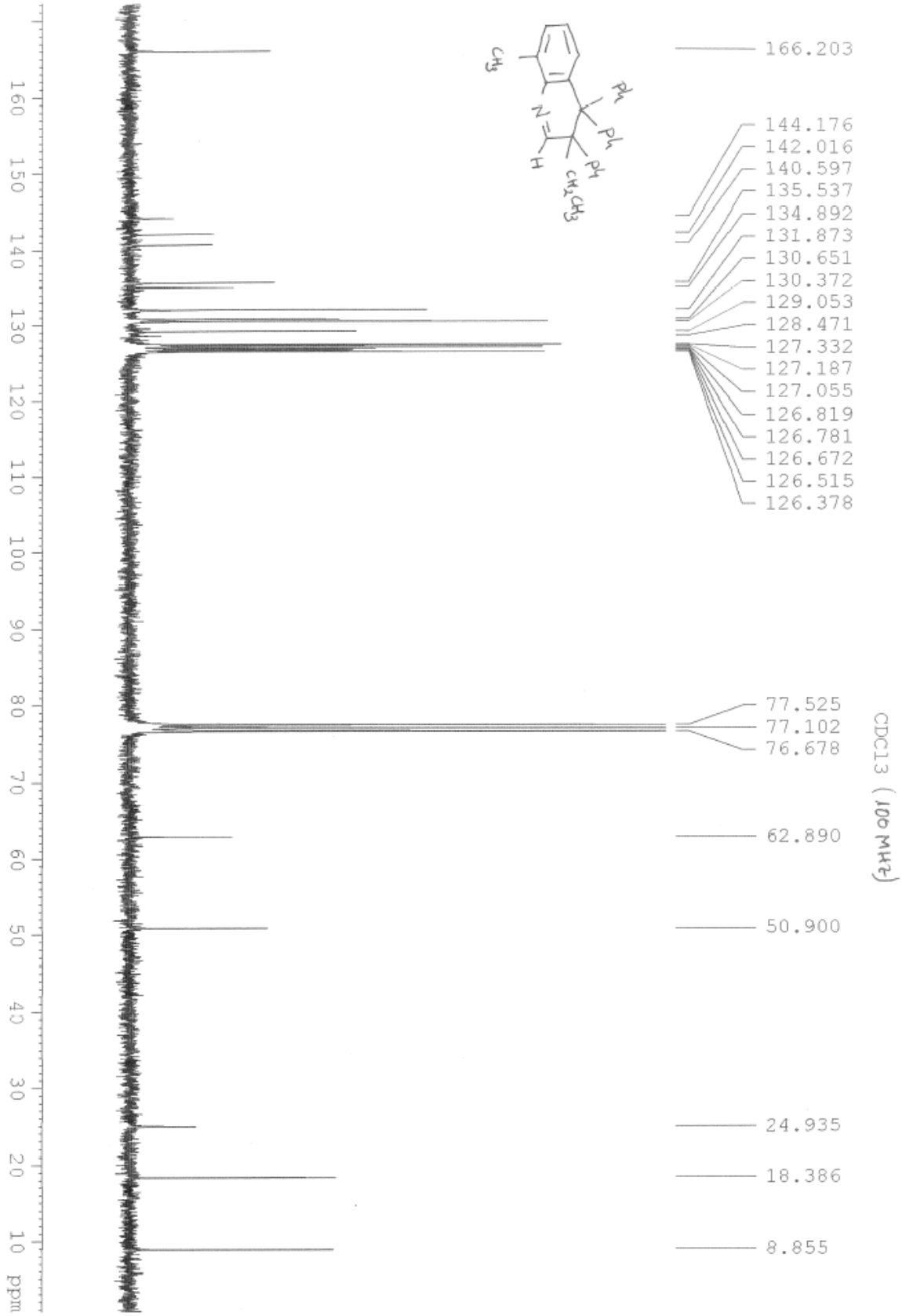
^{13}C NMR **13c**


167.389
146.183
141.375
140.143
138.507
135.877
134.993
132.088
129.035
128.944
128.771
127.542
127.360
127.093
126.697
126.645
126.286
77.523
77.100
76.676
61.850
47.971
20.566
18.497
CDCl3 (100 MHz)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

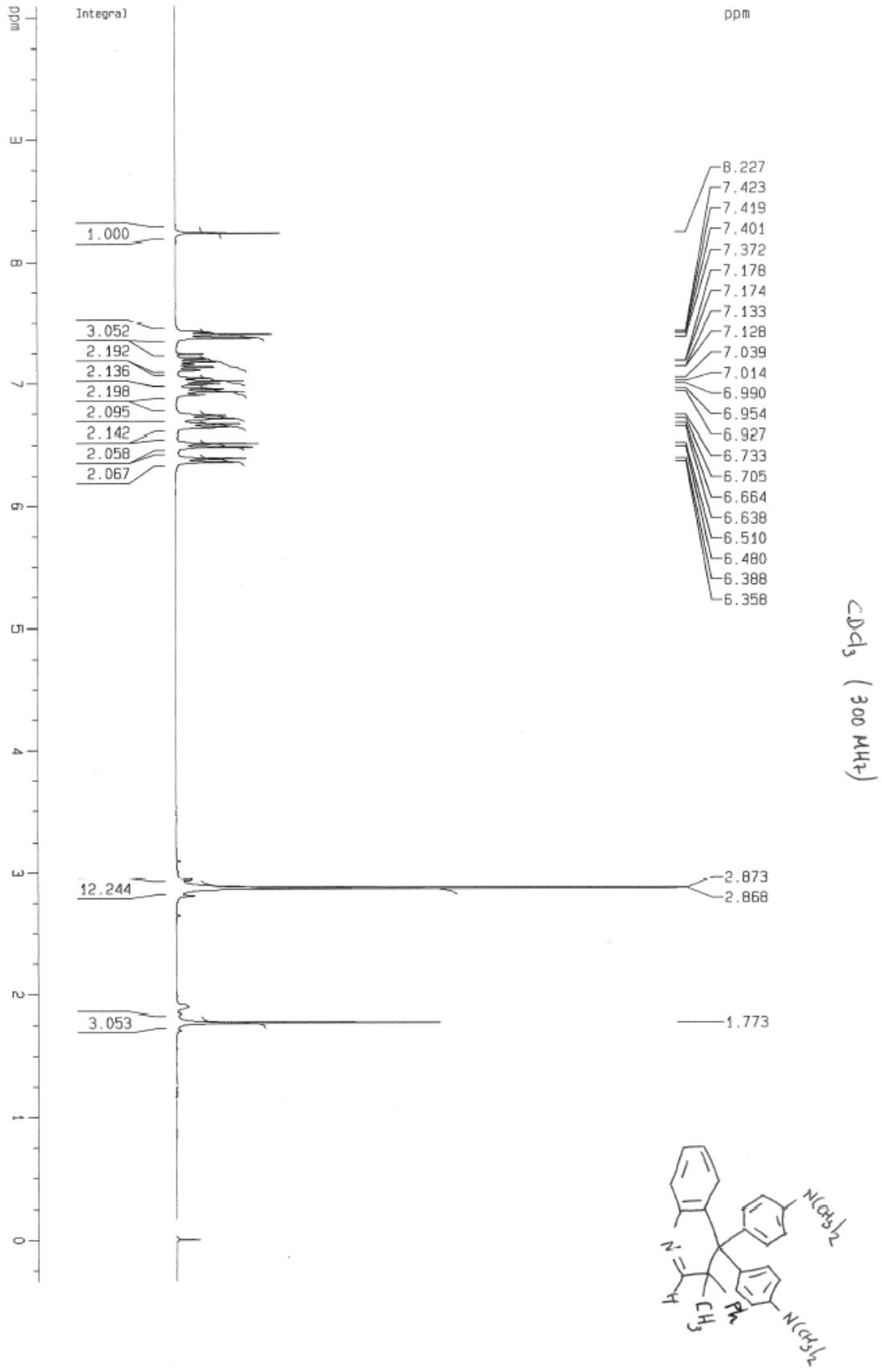
^{1}H NMR **13d**


1.000
2.077
15.665
2.178
4.046
1.172
3.073
8.676
7.439
7.417
7.253
7.201
7.184
7.160
7.143
7.120
7.096
7.076
7.052
7.035
7.028
7.011
6.987
6.978
6.963
6.949
6.939
6.915
6.586
6.562
2.628
2.606
2.581
2.539
2.083
2.058
2.033
2.009
1.985
1.960
0.800
0.776
0.752
-0.000
(400MHz) CDCl3
ppm

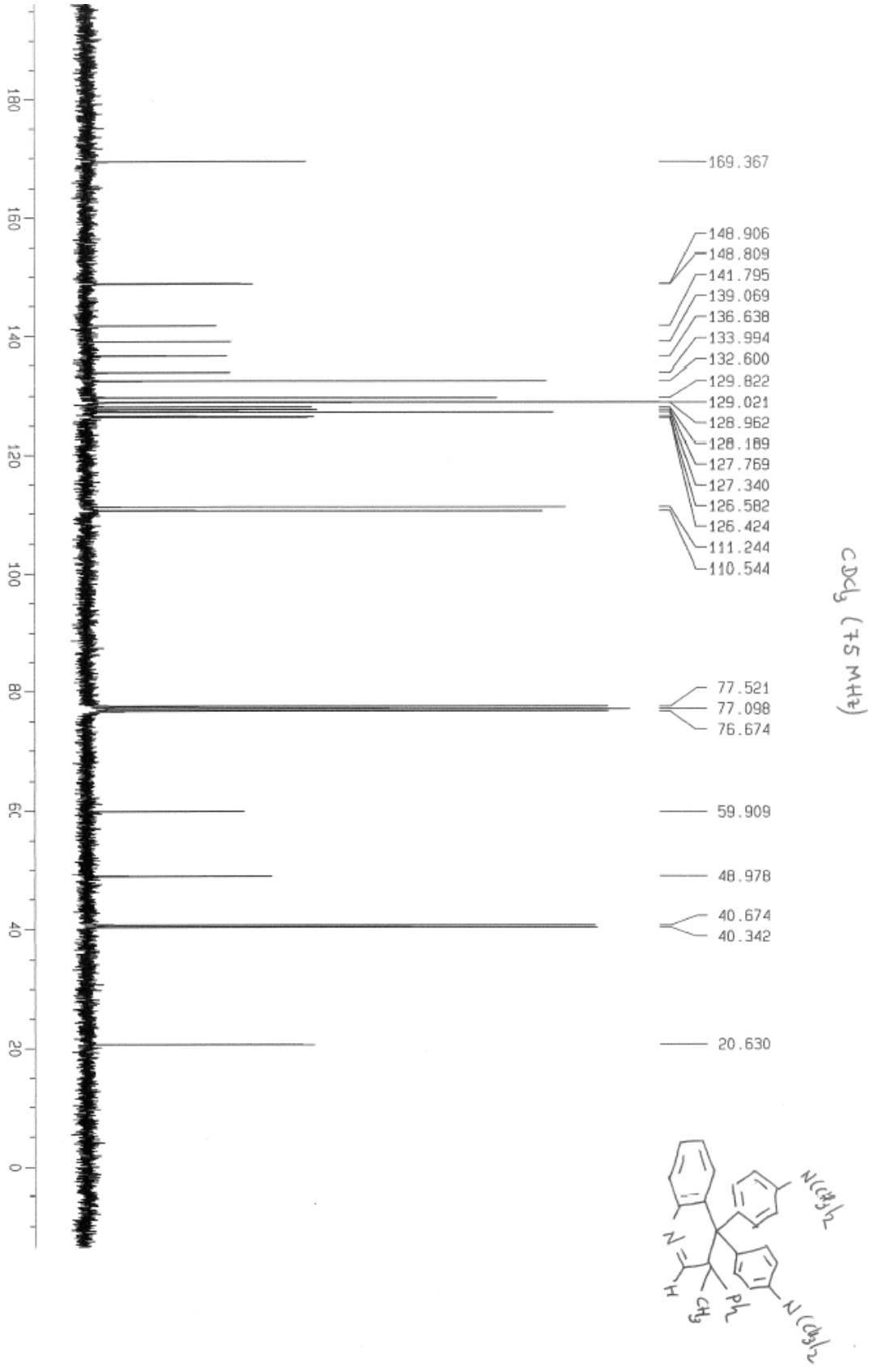
^{13}C NMR **13d**


166.203
144.176
142.016
140.597
135.537
134.892
131.873
130.651
130.372
129.053
128.471
127.332
127.187
127.055
126.819
126.781
126.672
126.515
126.378
77.525
77.102
76.678
62.890
50.900
24.935
18.386
8.855
CDCl3 (100 MHz)
ppm

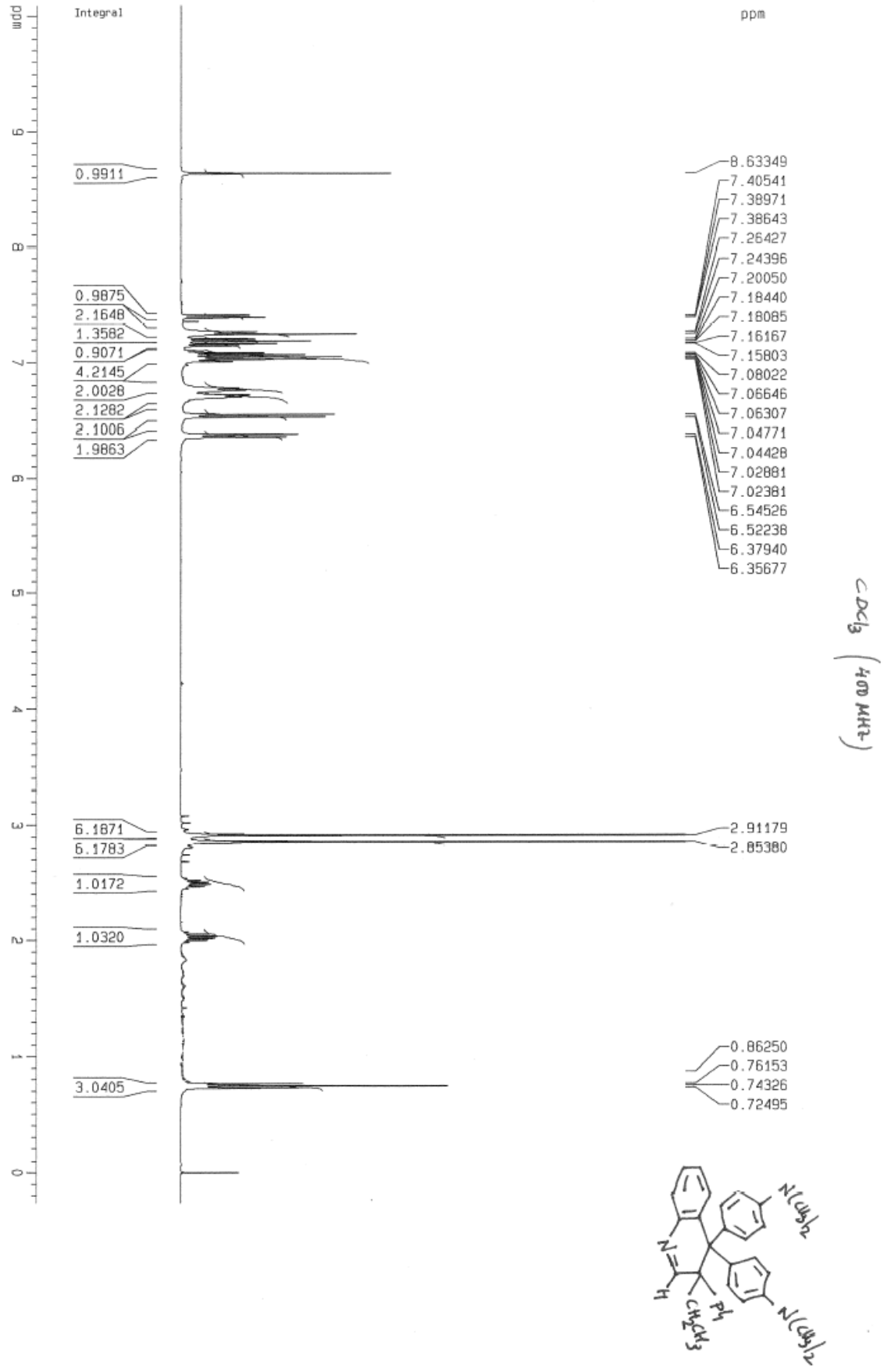
^{1}H NMR **13e**


Integral
ppm
1.000
3.052
2.192
2.136
2.198
2.095
2.142
2.058
2.067
12.244
3.053
8.227
7.423
7.419
7.401
7.372
7.178
7.174
7.133
7.128
7.039
7.014
6.990
6.954
6.927
6.733
6.705
6.664
6.638
6.510
6.480
6.388
6.358
2.873
2.868
1.773
CDCl3 (300 MHz)
N(CH3)2
N
H
CH3
Ph
N(CH3)2

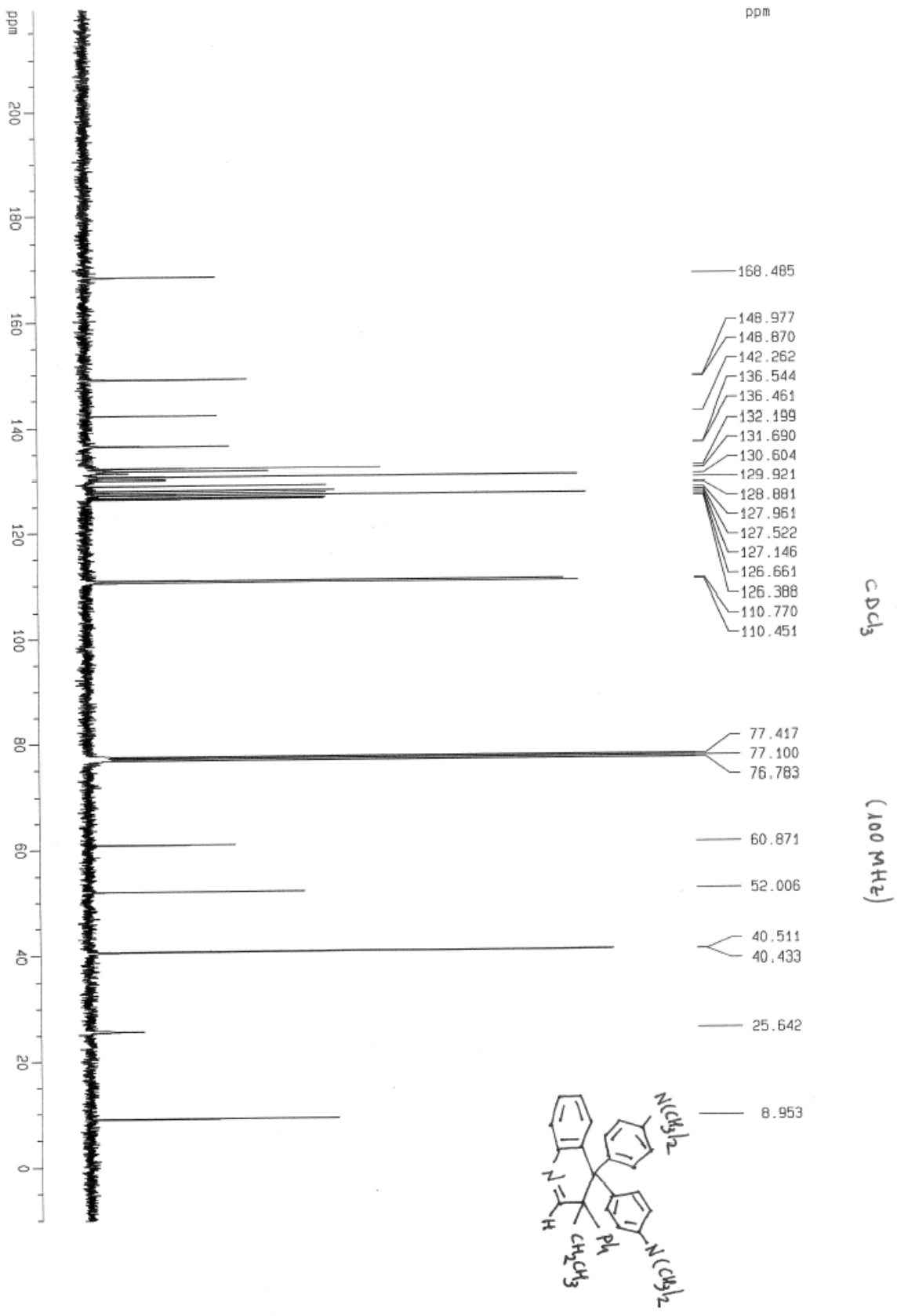
^{13}C NMR **13e**


169.367
148.906
148.809
141.795
139.069
136.638
133.994
132.600
129.822
129.021
128.962
128.189
127.769
127.340
126.582
126.424
111.244
110.544
77.521
77.098
76.674
59.909
48.978
40.674
40.342
20.630
CDCl3 (75 MHz)
N(CH3)2
N
H
CH3
Ph
N(CH3)2

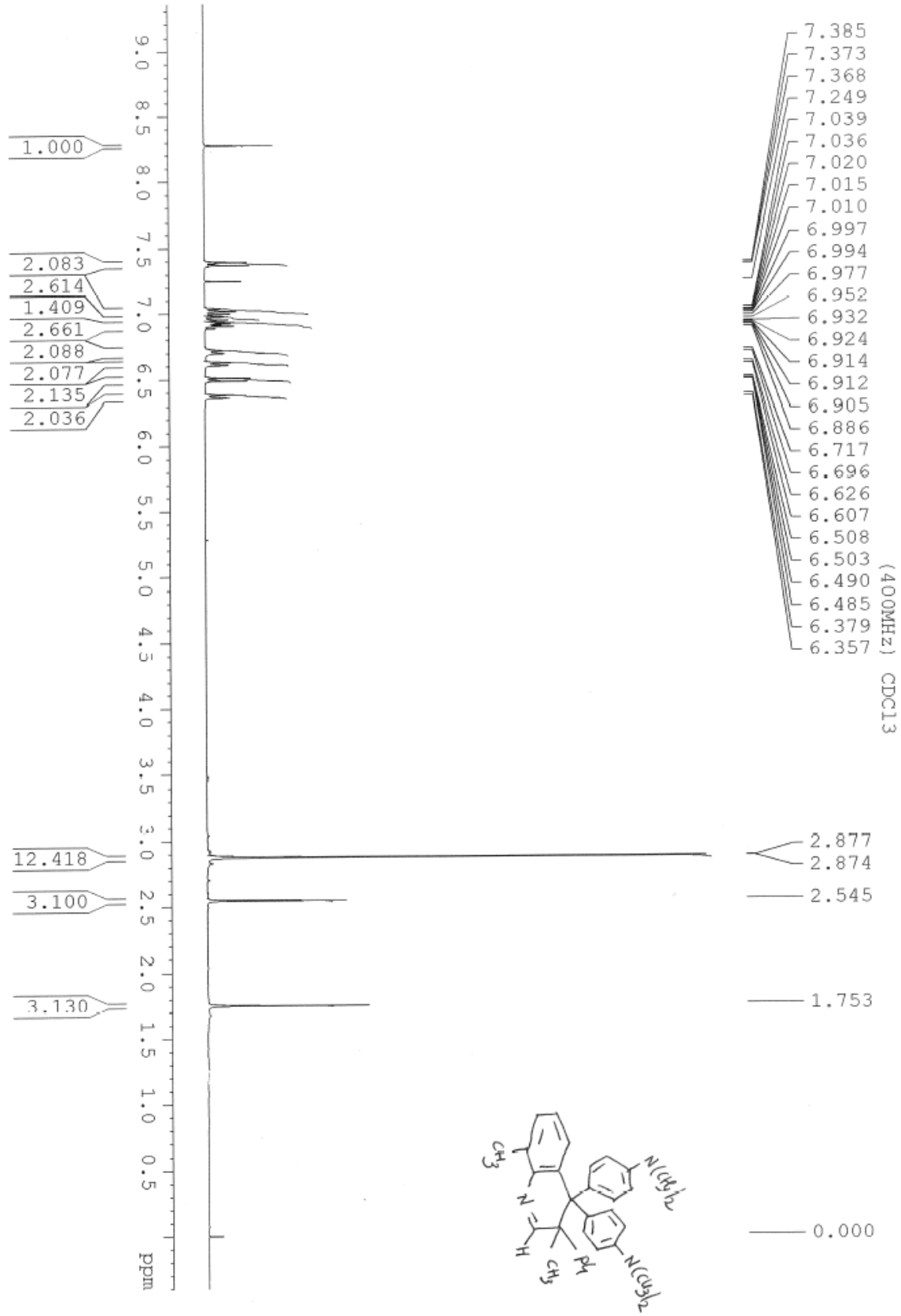
^{1}H NMR **13f**


Integral
ppm
0.9911
0.9875
2.1648
1.3582
0.9071
4.2145
2.0028
2.1282
2.1006
1.9863
6.1871
6.1783
1.0172
1.0320
3.0405
8.63349
7.40541
7.38971
7.38643
7.26427
7.24396
7.20050
7.18440
7.18085
7.16167
7.15803
7.08022
7.06646
7.06307
7.04771
7.04428
7.02881
7.02381
6.54526
6.52238
6.37940
6.35677
2.91179
2.85380
0.86250
0.76153
0.74326
0.72495
CDCl3 (400 MHz)
N(CH3)2
N
H
CH2CH3
Ph
N(CH3)2

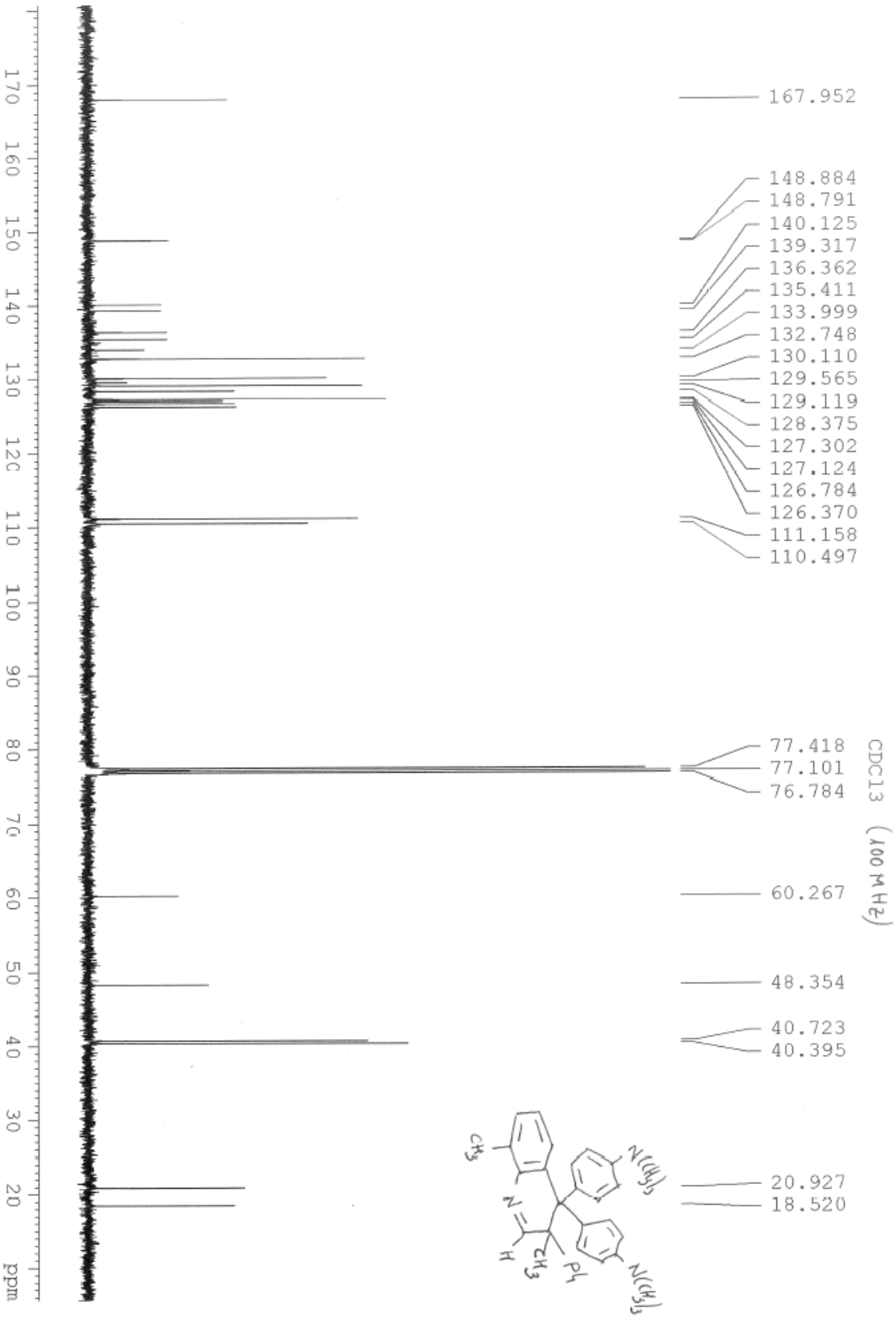
^{13}C NMR **13f**


ppm
168.485
148.977
148.870
142.262
136.544
136.461
132.199
131.690
130.604
129.921
128.881
127.961
127.522
127.146
126.661
126.388
110.770
110.451
77.417
77.100
76.783
60.871
52.006
40.511
40.433
25.642
8.953
CDCl3
(100 MHz)

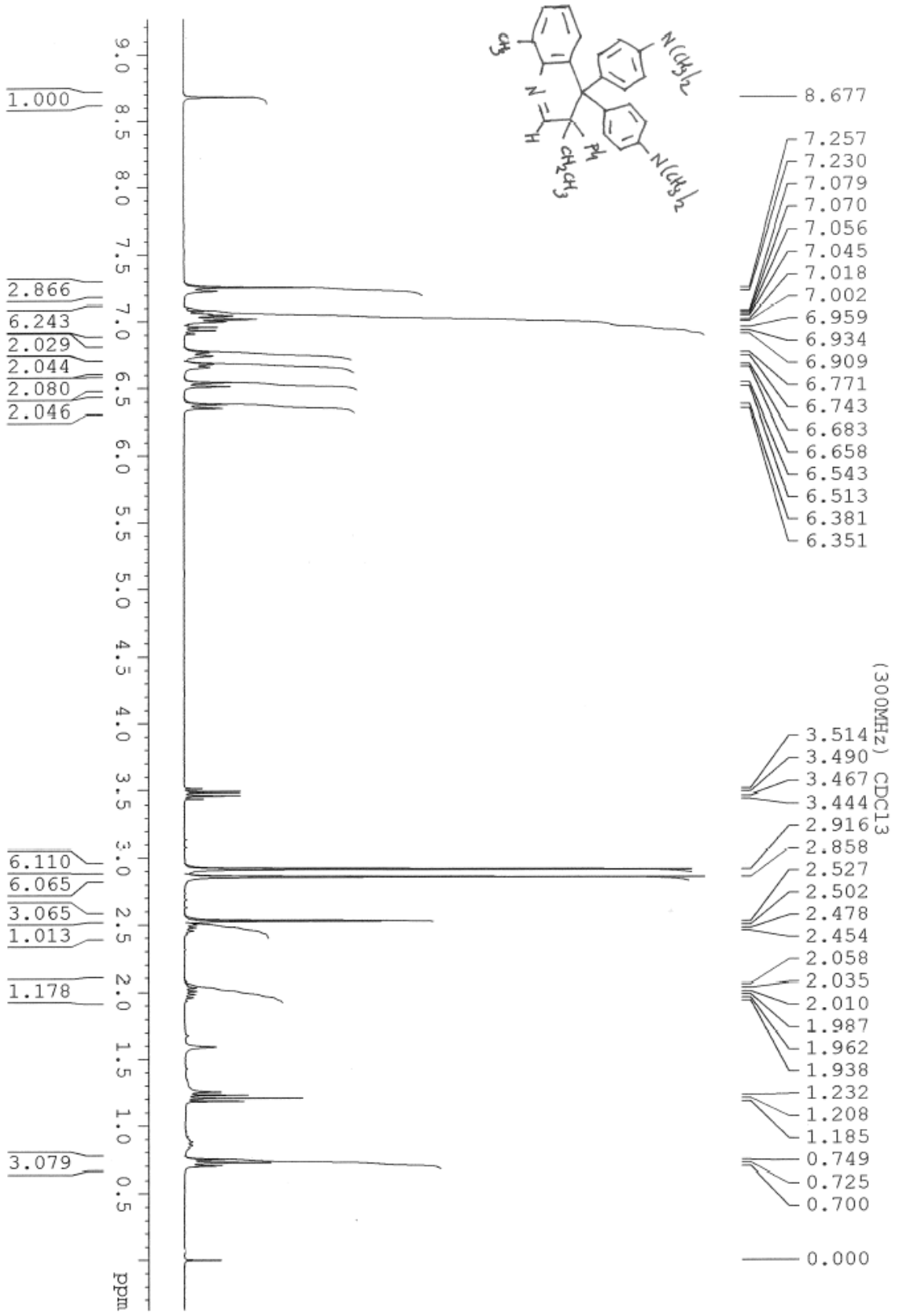
^{1}H NMR **13g**


7.385
7.373
7.368
7.249
7.039
7.036
7.020
7.015
7.010
6.997
6.994
6.977
6.952
6.932
6.924
6.914
6.912
6.905
6.886
6.717
6.696
6.626
6.607
6.508
6.503
6.490
6.485
6.379
6.357
(400MHz) CDCl3
2.877
2.874
2.545
1.753
0.000
1.000
2.083
2.614
1.409
2.661
2.088
2.077
2.135
2.036
12.418
3.100
3.130
ppm
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

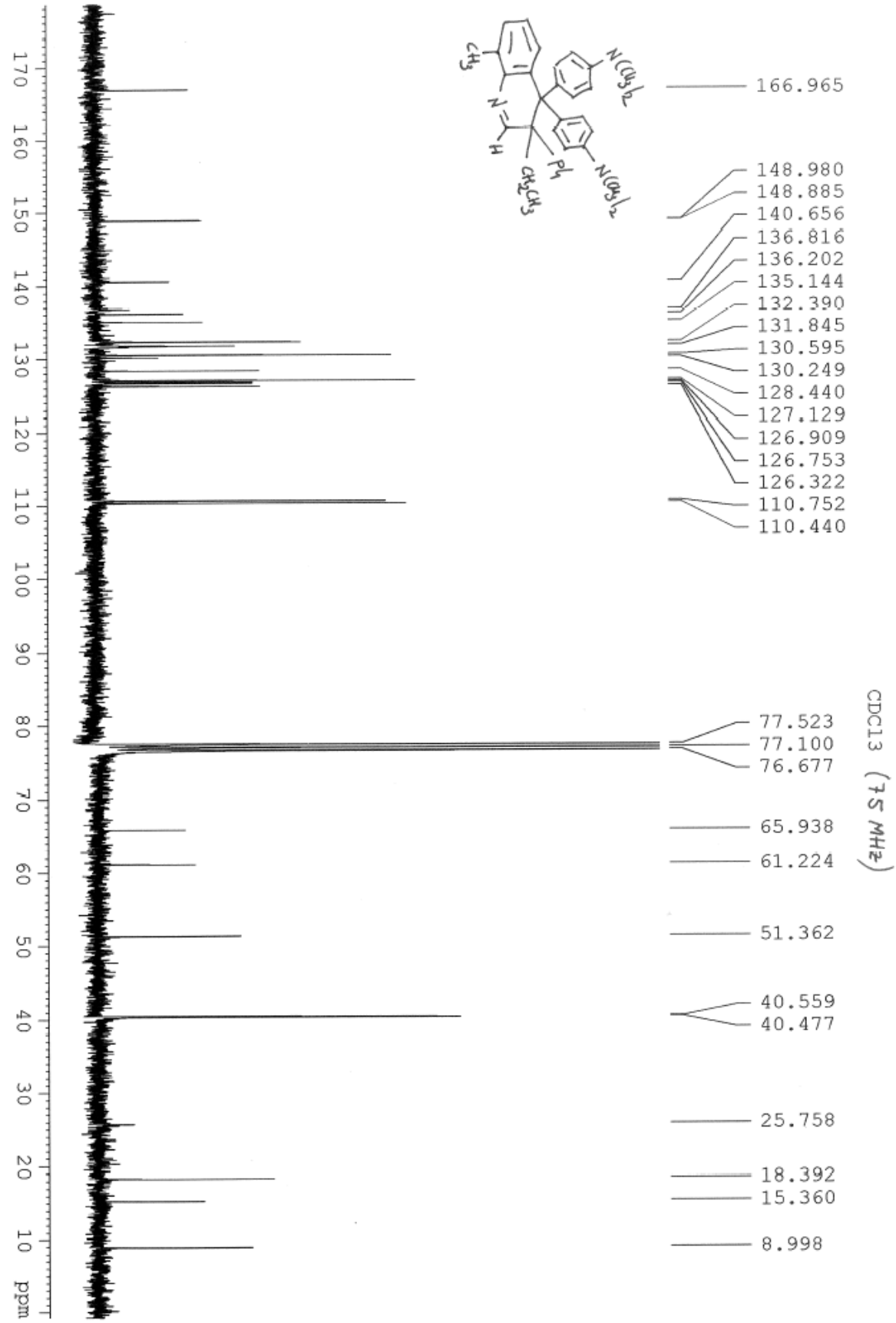
^{13}C NMR **13g**


167.952
148.884
148.791
140.125
139.317
136.362
135.411
133.999
132.748
130.110
129.565
129.119
128.375
127.302
127.124
126.784
126.370
111.158
110.497
77.418
77.101
76.784
60.267
48.354
40.723
40.395
20.927
18.520
CDC13 (100 MHz)
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
CH3
N
H
CH3
Ph
N(CH3)2
N(CH3)2

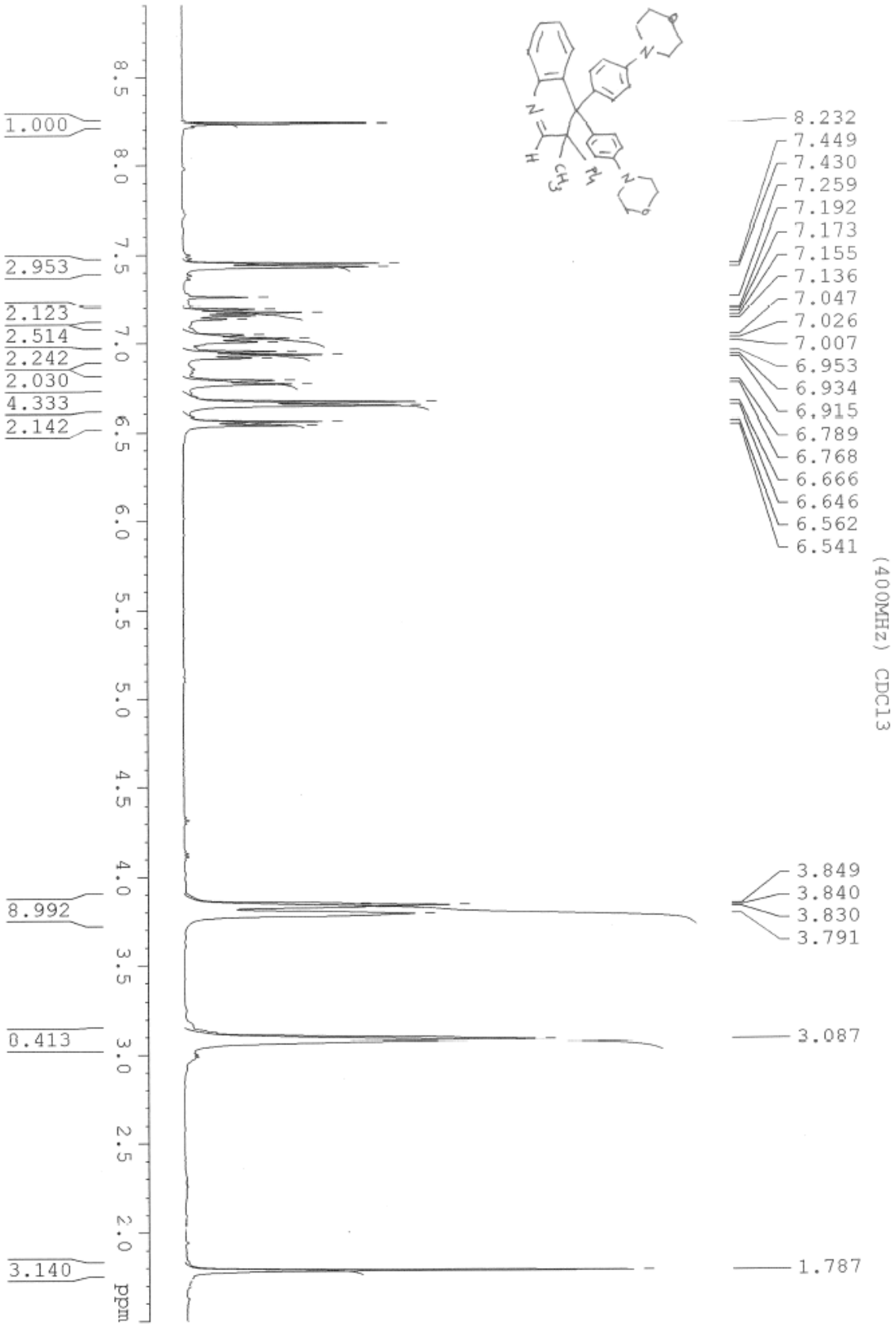
^{1}H NMR **13h**


1.000
2.866
6.243
2.029
2.044
2.080
2.046
6.110
6.065
3.065
1.013
1.178
3.079
ppm
8.677
7.257
7.230
7.079
7.070
7.056
7.045
7.018
7.002
6.959
6.934
6.909
6.771
6.743
6.683
6.658
6.543
6.513
6.381
6.351
3.514
3.490
3.467
3.444
2.916
2.858
2.527
2.502
2.478
2.454
2.058
2.035
2.010
1.987
1.962
1.938
1.232
1.208
1.185
0.749
0.725
0.700
0.000
(300MHz) CDCl3

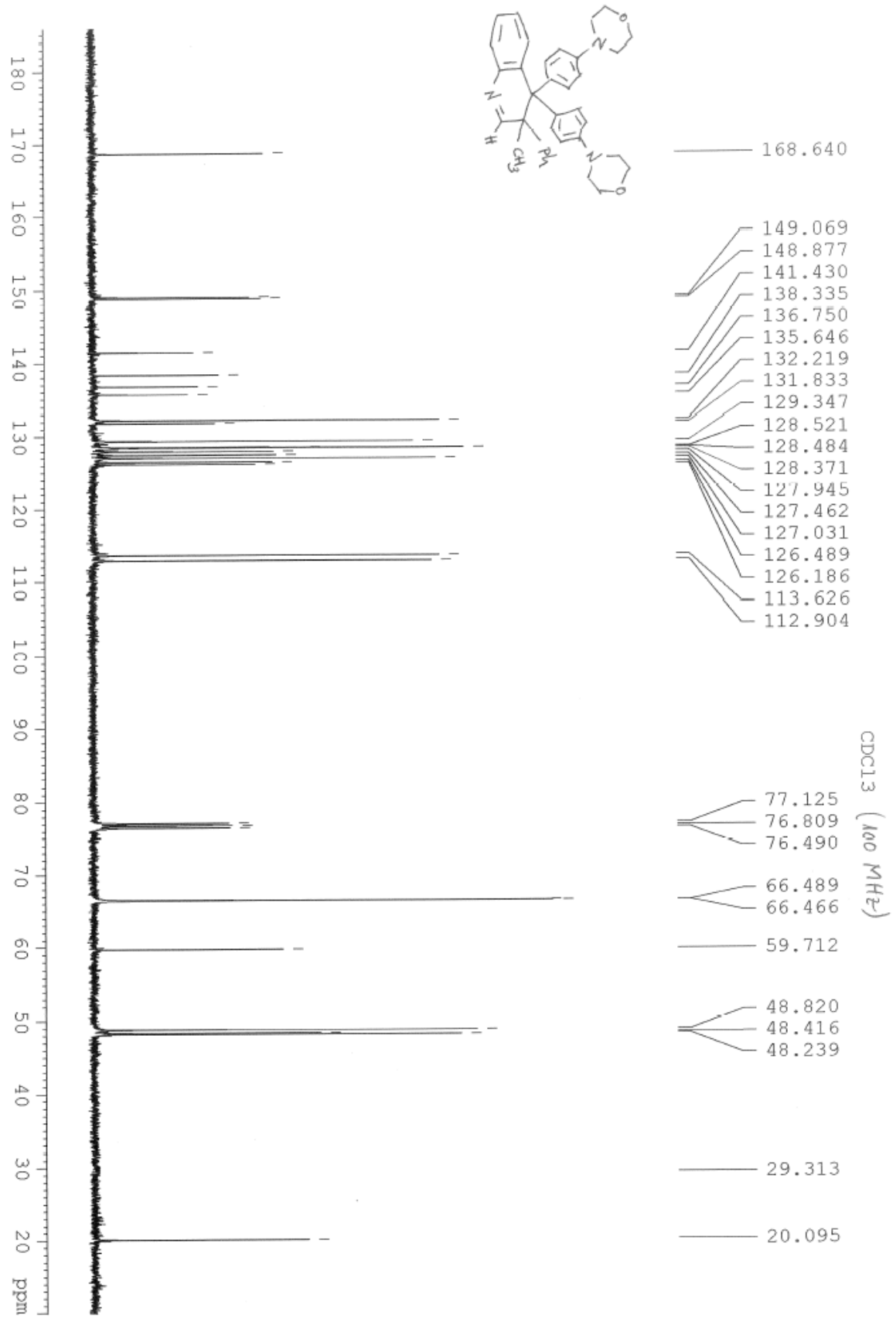
^{13}C NMR **13h**


166.965
148.980
148.885
140.656
136.816
136.202
135.144
132.390
131.845
130.595
130.249
128.440
127.129
126.909
126.753
126.322
110.752
110.440
77.523
77.100
76.677
65.938
61.224
51.362
40.559
40.477
25.758
18.392
15.360
8.998
CDCl3 (75 MHz)
ppm

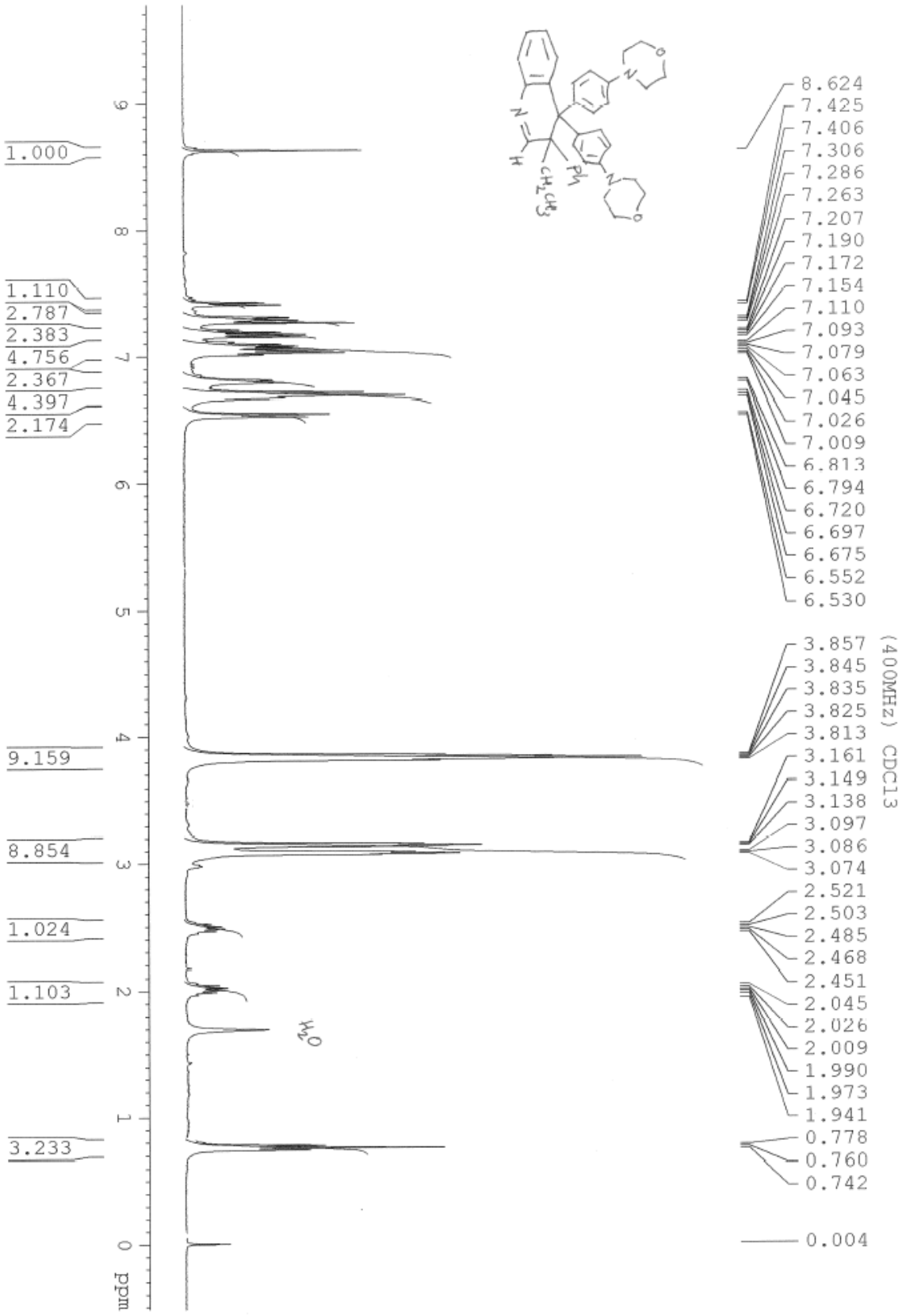
^{1}H NMR **13i**


1.000
2.953
2.123
2.514
2.242
2.030
4.333
2.142
8.992
0.413
3.140
ppm
8.232
7.449
7.430
7.259
7.192
7.173
7.155
7.136
7.047
7.026
7.007
6.953
6.934
6.915
6.789
6.768
6.666
6.646
6.562
6.541
3.849
3.840
3.830
3.791
3.087
1.787
(400MHz) CDCl3

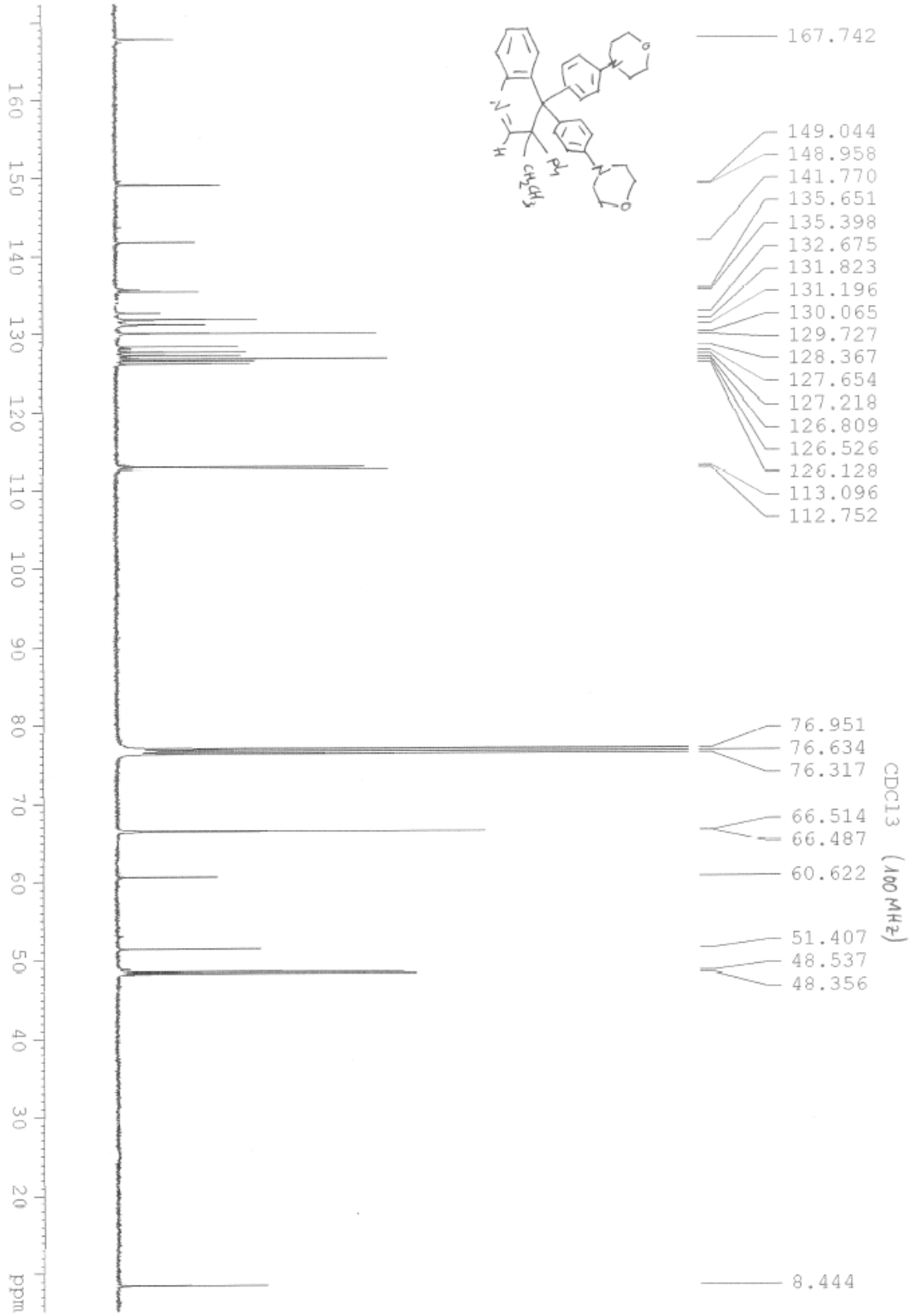
^{13}C NMR **13i**


168.640
149.069
148.877
141.430
138.335
136.750
135.646
132.219
131.833
129.347
128.521
128.484
128.371
127.945
127.462
127.031
126.489
126.186
113.626
112.904
77.125
76.809
76.490
66.489
66.466
59.712
48.820
48.416
48.239
29.313
20.095
CDCl3 (100 MHz)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

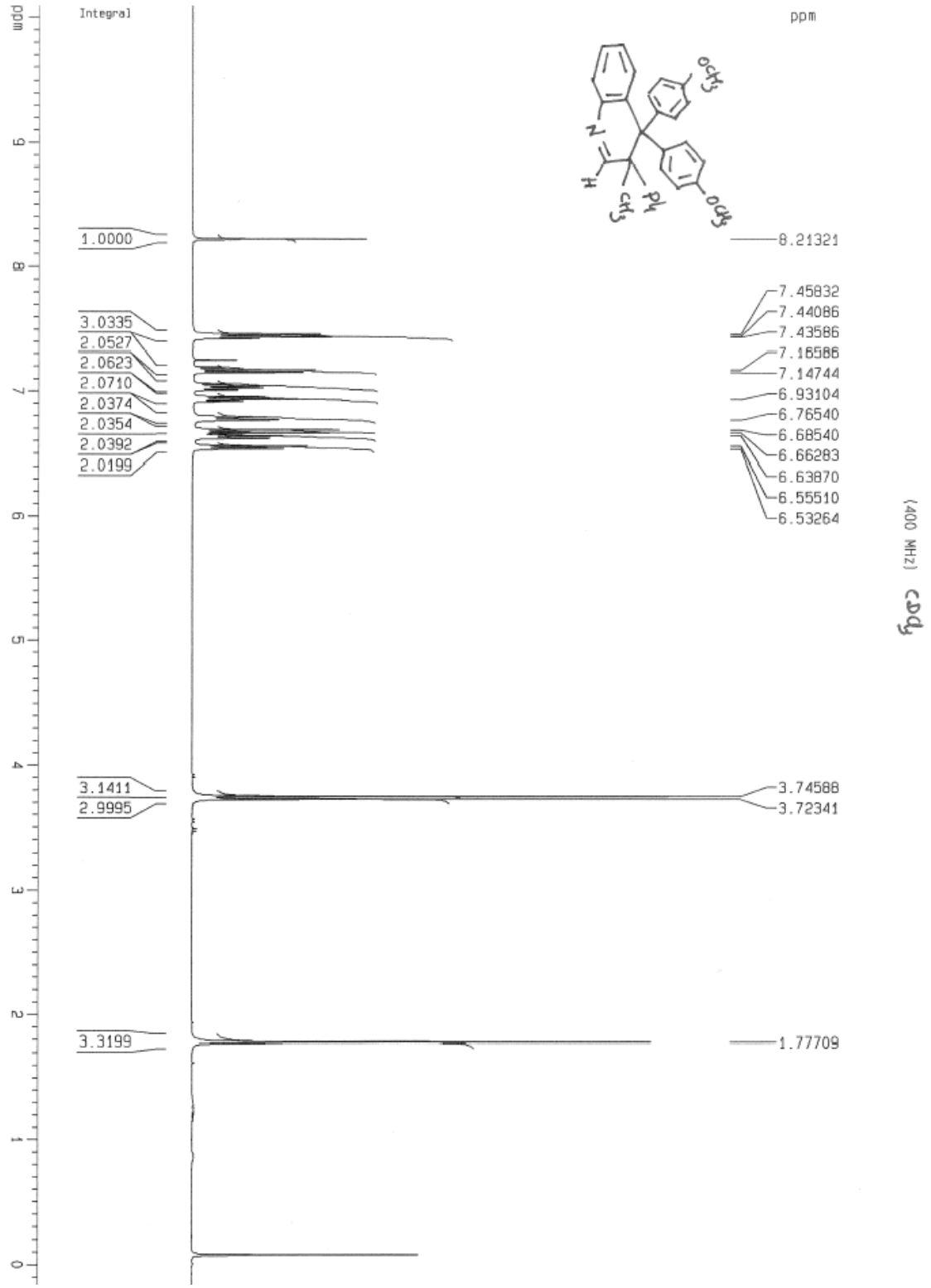
^{1}H NMR **13j**


1.000
1.110
2.787
2.383
4.756
2.367
4.397
2.174
9.159
8.854
1.024
1.103
3.233
H2O
ppm
8.624
7.425
7.406
7.306
7.286
7.263
7.207
7.190
7.172
7.154
7.110
7.093
7.079
7.063
7.045
7.026
7.009
6.813
6.794
6.720
6.697
6.675
6.552
6.530
3.857
3.845
3.835
3.825
3.813
3.161
3.149
3.138
3.097
3.086
3.074
2.521
2.503
2.485
2.468
2.451
2.045
2.026
2.009
1.990
1.973
1.941
0.778
0.760
0.742
0.004
(400MHz) CDCl3

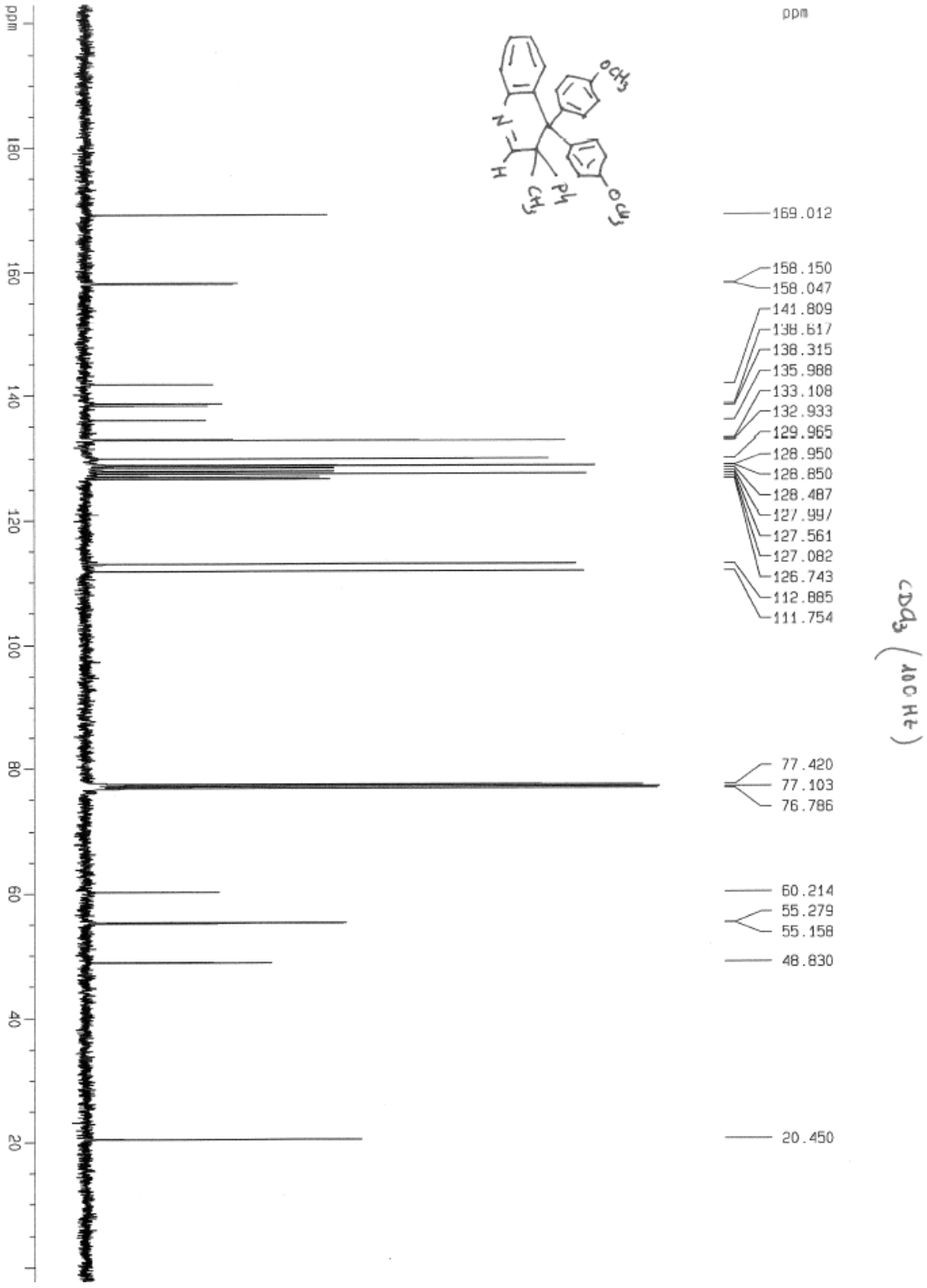
^{13}C NMR **13j**


167.742
149.044
148.958
141.770
135.651
135.398
132.675
131.823
131.196
130.065
129.727
128.367
127.654
127.218
126.809
126.526
126.128
113.096
112.752
76.951
76.634
76.317
66.514
66.487
60.622
51.407
48.537
48.356
8.444
CDCl3 (100 MHz)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

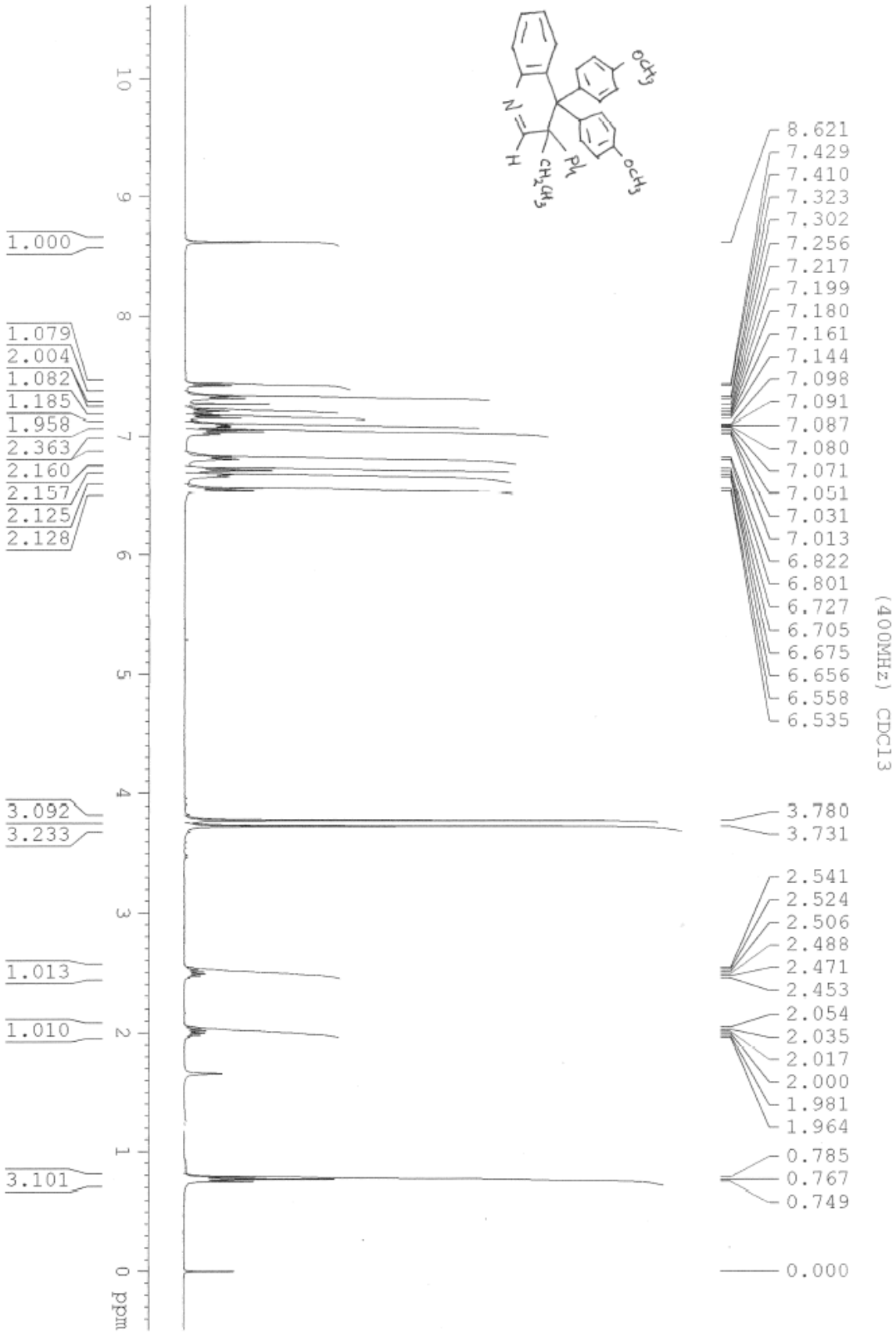
^{1}H NMR **13k**


Integral
ppm
1.0000
3.0335
2.0527
2.0623
2.0710
2.0374
2.0354
2.0392
2.0199
3.1411
2.9995
3.3199
8.21321
7.45832
7.44086
7.43586
7.16586
7.14744
6.93104
6.76540
6.68540
6.66283
6.63870
6.55510
6.53264
3.74588
3.72341
1.77709
(400 MHz) cdcl3

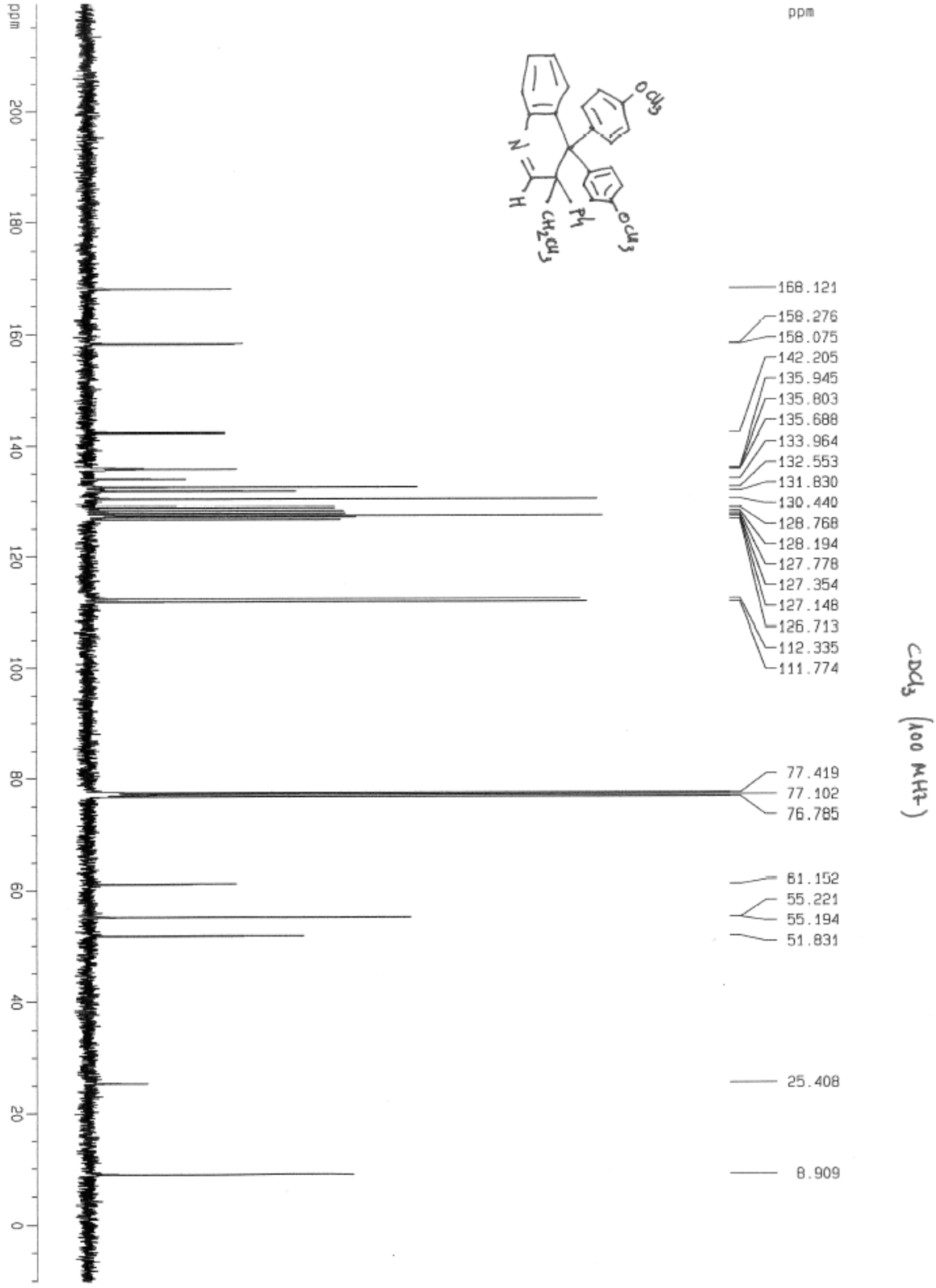
^{13}C NMR **13k**


ppm
180
160
140
120
100
80
60
40
20
ppm
169.012
158.150
158.047
141.809
138.617
138.315
135.988
133.108
132.933
129.965
128.950
128.850
128.487
127.997
127.561
127.082
126.743
112.885
111.754
77.420
77.103
76.786
60.214
55.279
55.158
48.830
20.450
CDCl3 (100 Hz)

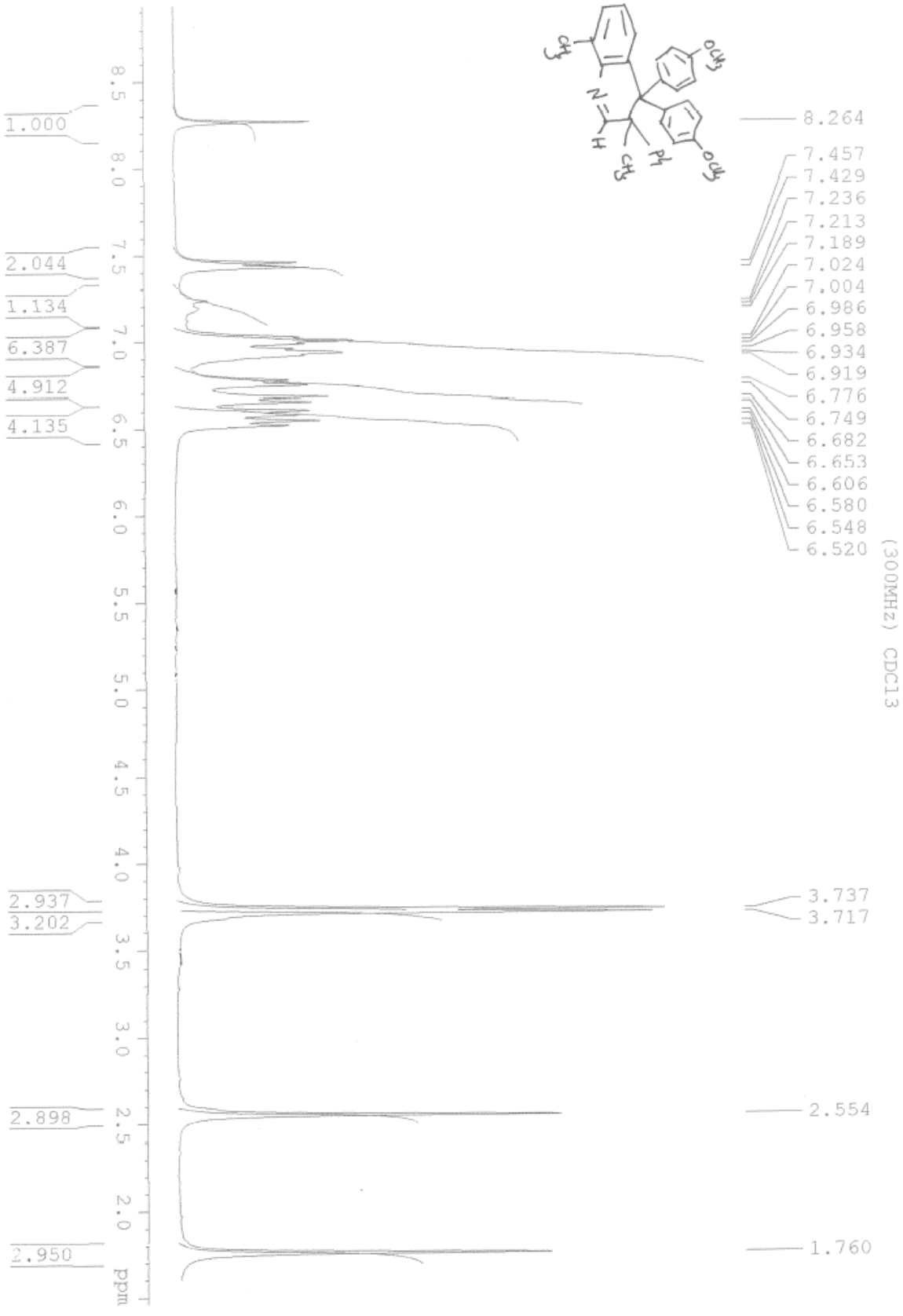
^{1}H NMR **13l**


OCH3
N
H
CH2CH3
Ph
OCH3
1.000
1.079
2.004
1.082
1.185
1.958
2.363
2.160
2.157
2.125
2.128
3.092
3.233
1.013
1.010
3.101
10
9
8
7
6
5
4
3
2
1
0 ppm
8.621
7.429
7.410
7.323
7.302
7.256
7.217
7.199
7.180
7.161
7.144
7.098
7.091
7.087
7.080
7.071
7.051
7.031
7.013
6.822
6.801
6.727
6.705
6.675
6.656
6.558
6.535
3.780
3.731
2.541
2.524
2.506
2.488
2.471
2.453
2.054
2.035
2.017
2.000
1.981
1.964
0.785
0.767
0.749
0.000
(400MHz) CDCl3

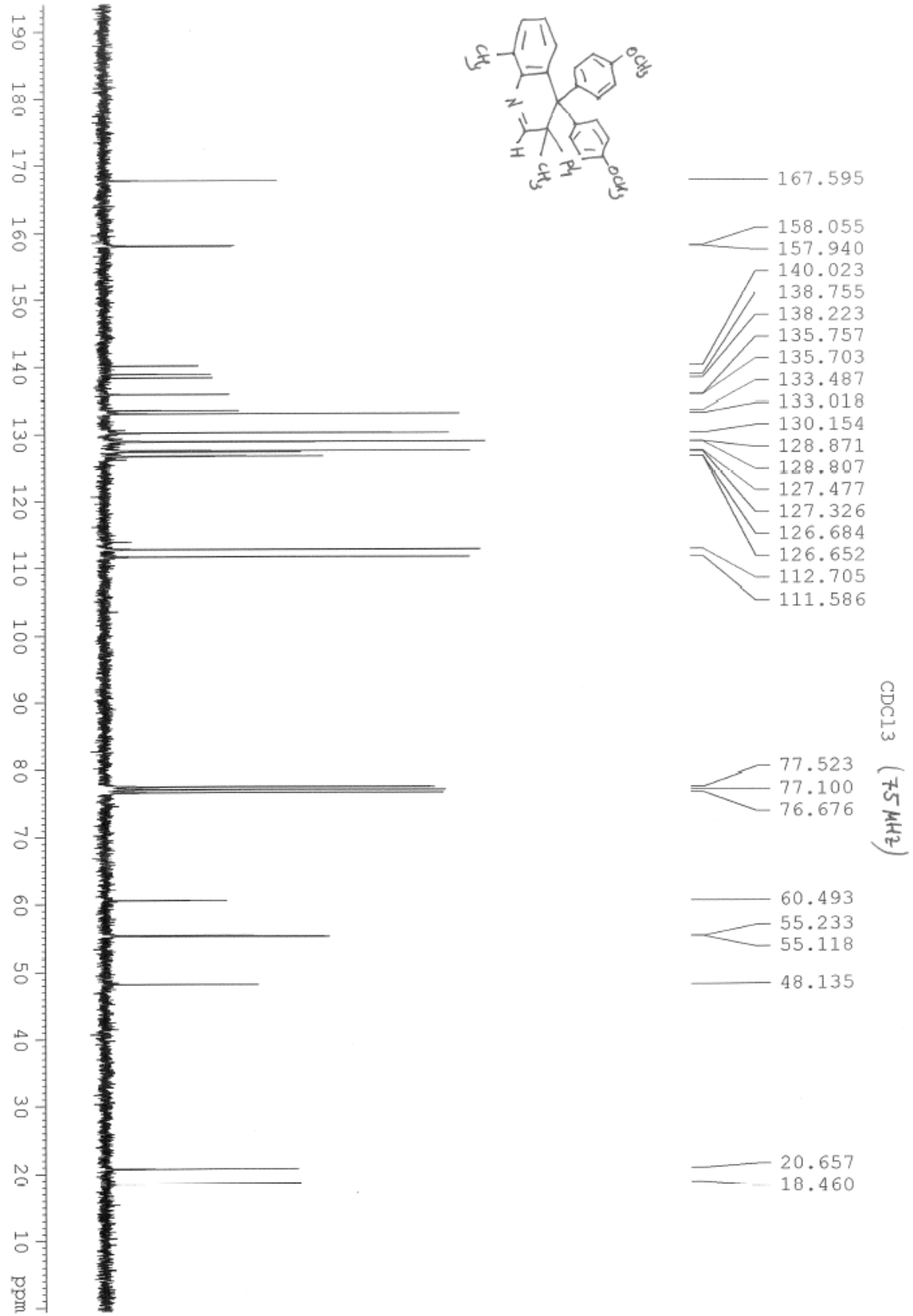
^{13}C NMR **13l**


ppm
200
180
160
140
120
100
80
60
40
20
0
ppm
168.121
158.276
158.075
142.205
135.945
135.803
135.688
133.964
132.553
131.830
130.440
128.768
128.194
127.778
127.354
127.148
126.713
112.335
111.774
77.419
77.102
76.785
61.152
55.221
55.194
51.831
25.408
8.909
CDCl3 (100 MHz)

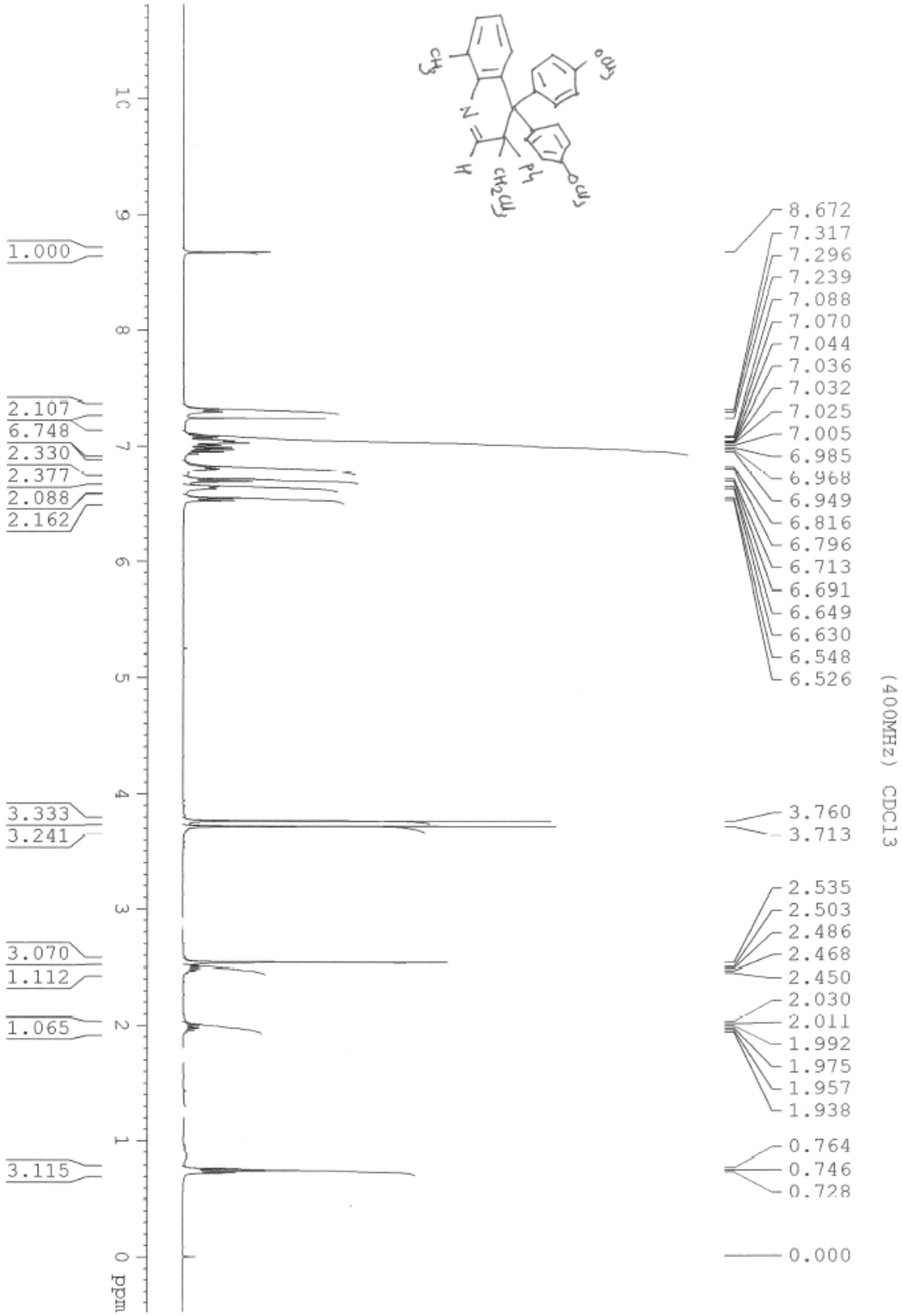
^{1}H NMR **13m**


1.000
2.044
1.134
6.387
4.912
4.135
2.937
3.202
2.898
2.950
8.264
7.457
7.429
7.236
7.213
7.189
7.024
7.004
6.986
6.958
6.934
6.919
6.776
6.749
6.682
6.653
6.606
6.580
6.548
6.520
3.737
3.717
2.554
1.760
(300MHz) CDCl3
ppm

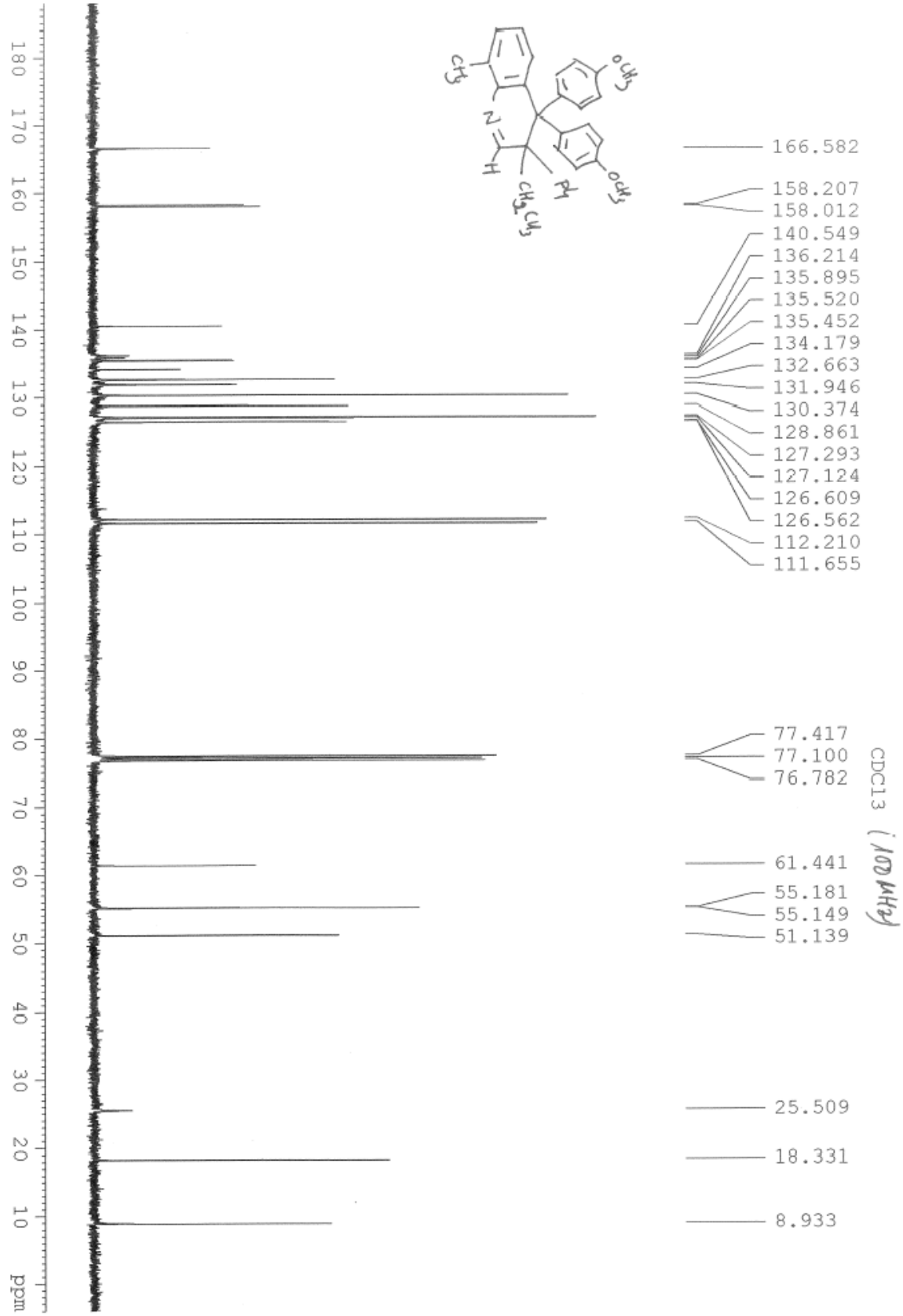
^{13}C NMR **13m**


167.595
158.055
157.940
140.023
138.755
138.223
135.757
135.703
133.487
133.018
130.154
128.871
128.807
127.477
127.326
126.684
126.652
112.705
111.586
77.523
77.100
76.676
60.493
55.233
55.118
48.135
20.657
18.460
CDCl3 (75 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

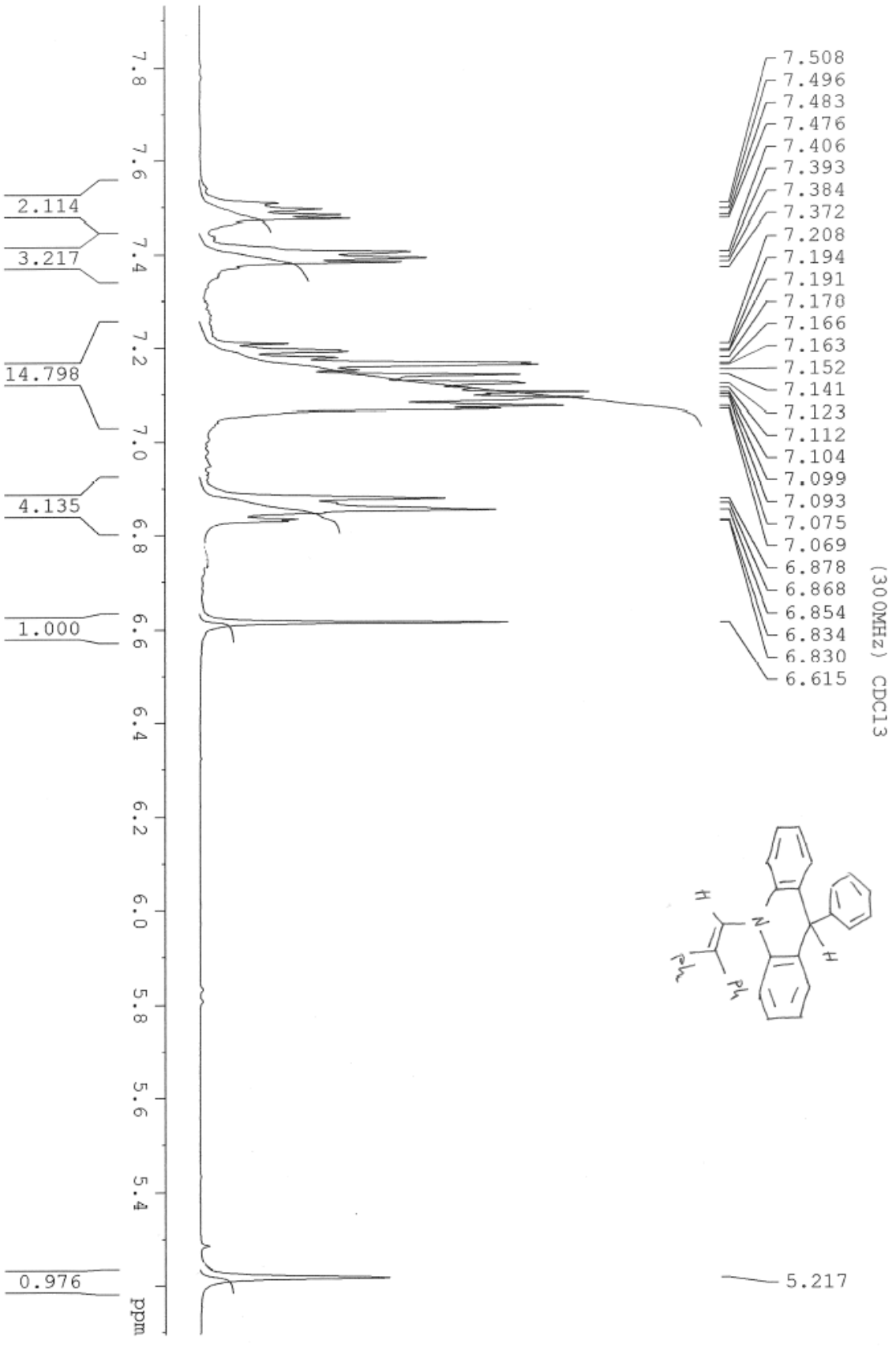
^{1}H NMR **13n**


1.000
2.107
6.748
2.330
2.377
2.088
2.162
3.333
3.241
3.070
1.112
1.065
3.115
8.672
7.317
7.296
7.239
7.088
7.070
7.044
7.036
7.032
7.025
7.005
6.985
6.968
6.949
6.816
6.796
6.713
6.691
6.649
6.630
6.548
6.526
3.760
3.713
2.535
2.503
2.486
2.468
2.450
2.030
2.011
1.992
1.975
1.957
1.938
0.764
0.746
0.728
0.000
(400MHz) CDCl3
ppm

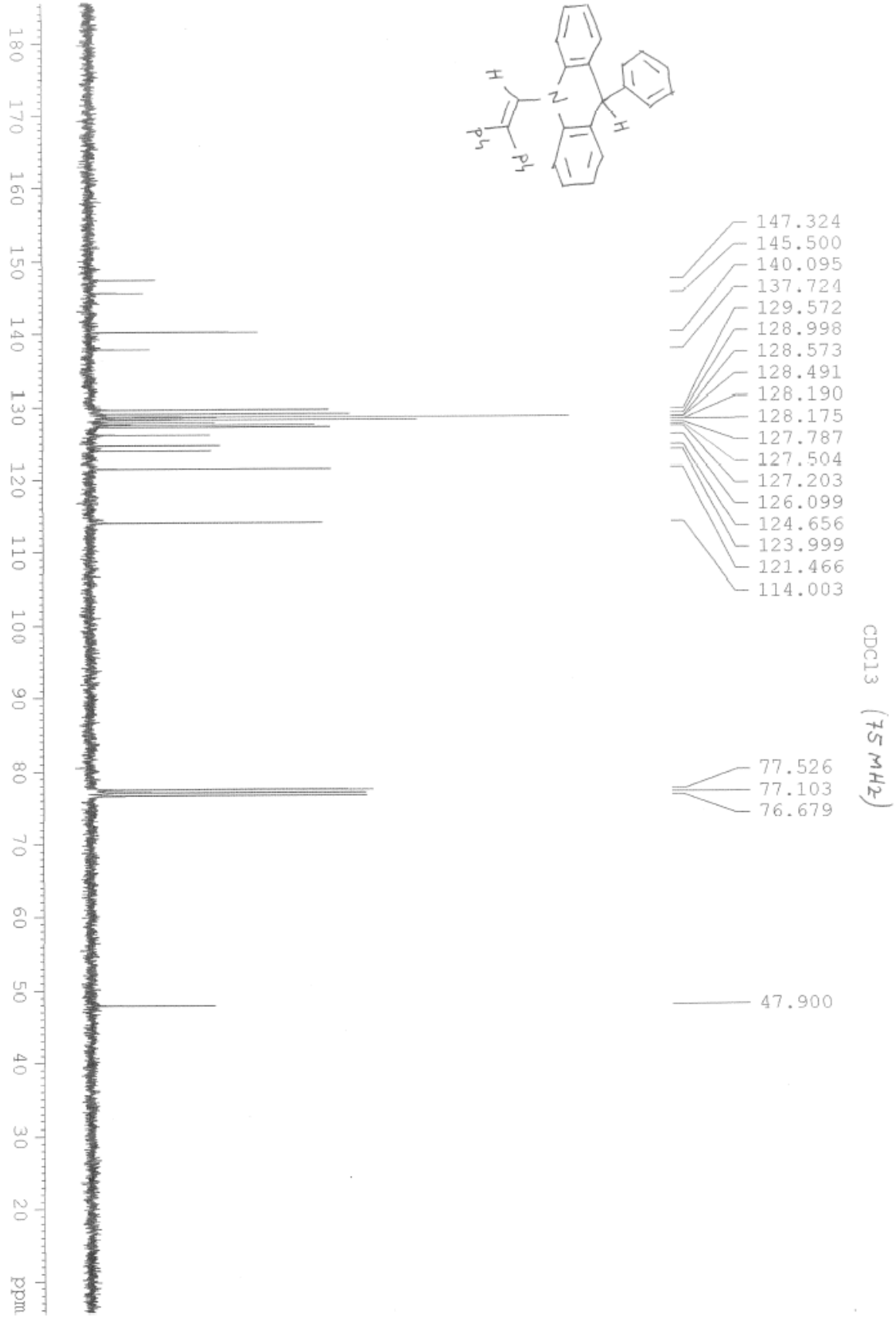
^{13}C NMR **13n**


166.582
158.207
158.012
140.549
136.214
135.895
135.520
135.452
134.179
132.663
131.946
130.374
128.861
127.293
127.124
126.609
126.562
112.210
111.655
77.417
77.100
76.782
CDCl3 (100 MHz)
61.441
55.181
55.149
51.139
25.509
18.331
8.933
ppm

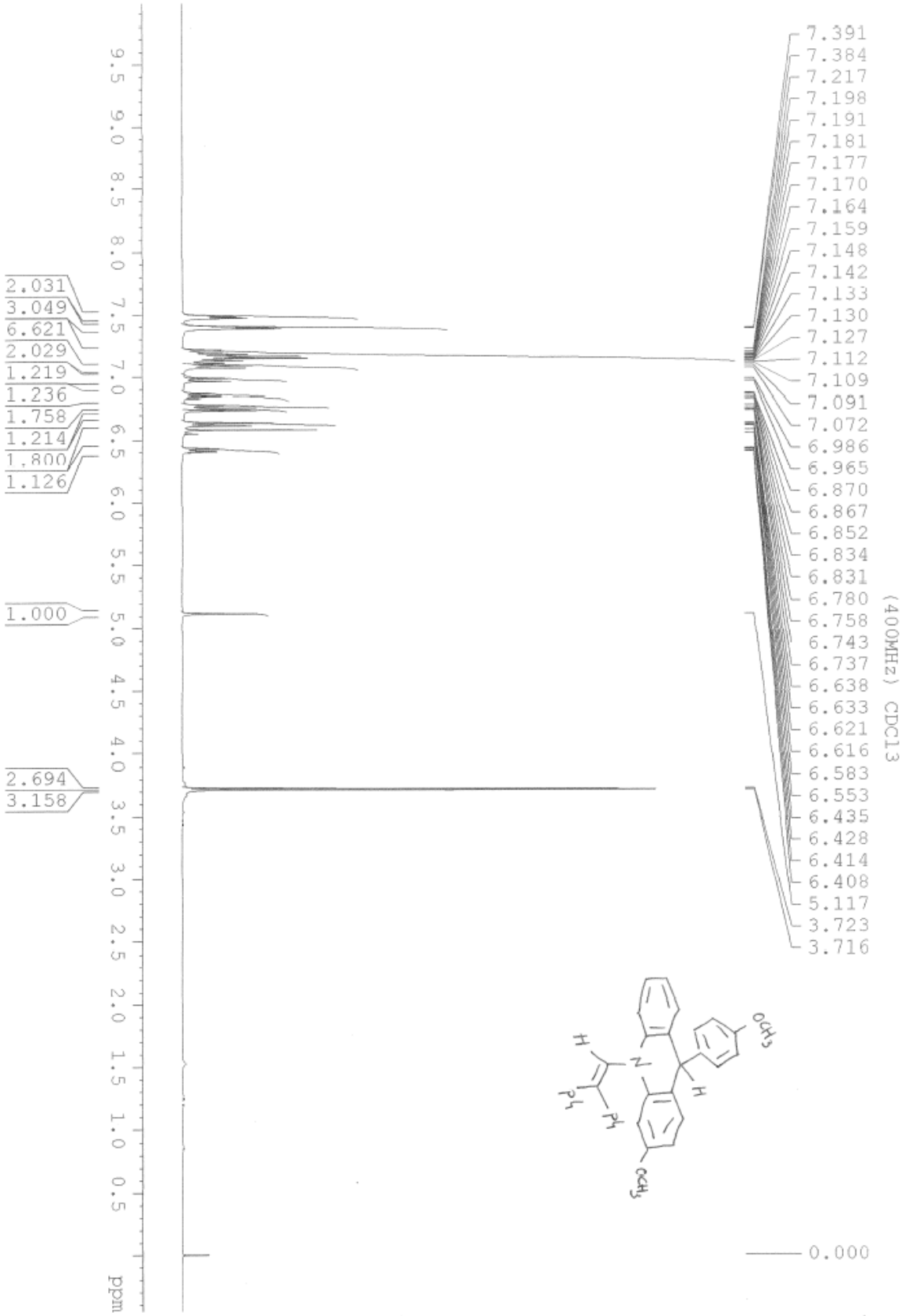
^{1}H NMR **18a**


7.508
7.496
7.483
7.476
7.406
7.393
7.384
7.372
7.208
7.194
7.191
7.170
7.166
7.163
7.152
7.141
7.123
7.112
7.104
7.099
7.093
7.075
7.069
6.878
6.868
6.854
6.834
6.830
6.615
5.217
2.114
3.217
14.798
4.135
1.000
0.976
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
ppm
(300MHz) CDCl3
H
N
Ph
Ph
H

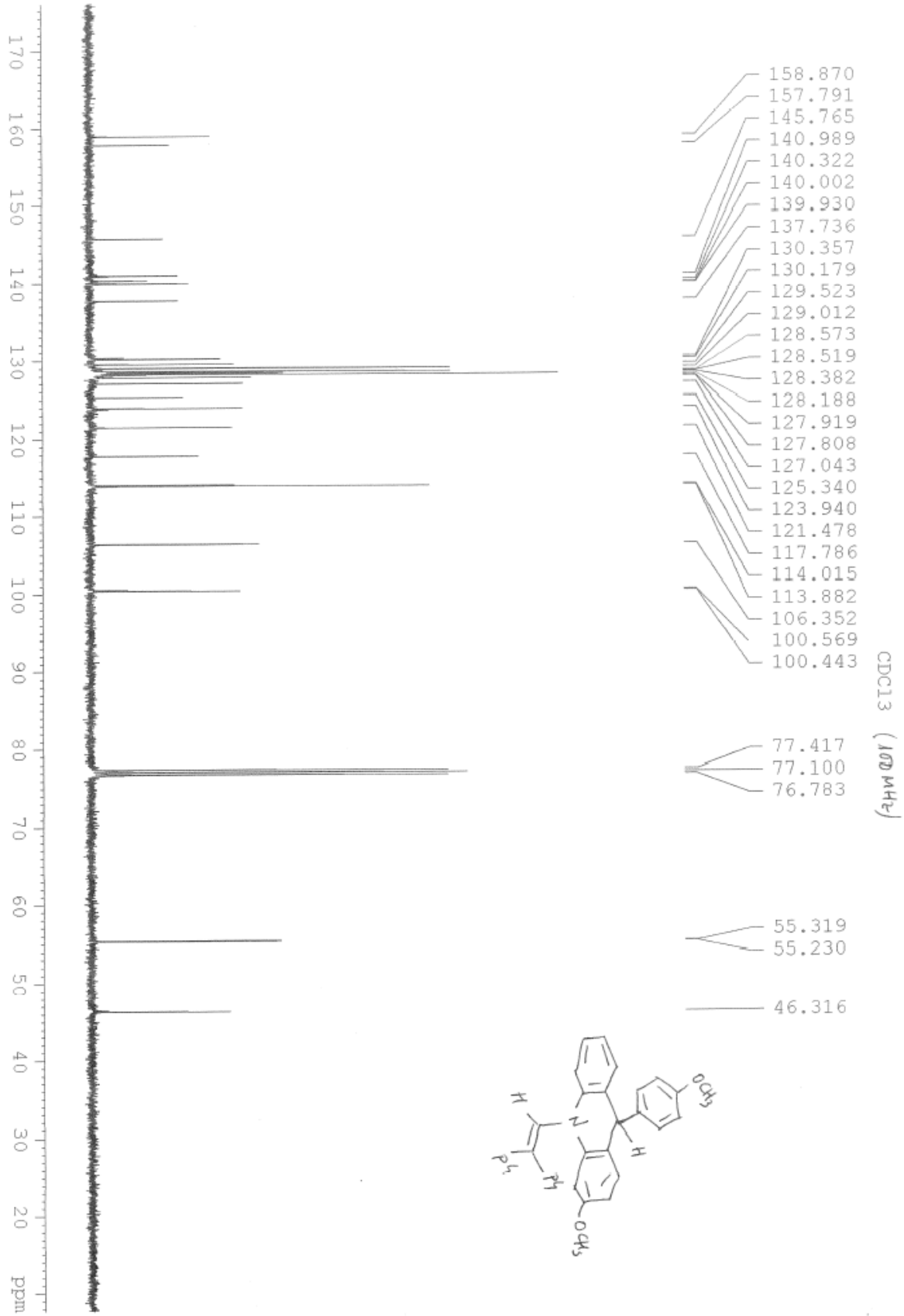
^{13}C NMR **18a**


147.324
145.500
140.095
137.724
129.572
128.998
128.573
128.491
128.190
128.175
127.787
127.504
127.203
126.099
124.656
123.999
121.466
114.003
77.526
77.103
76.679
47.900
CDCl3 (75 MHz)
ppm

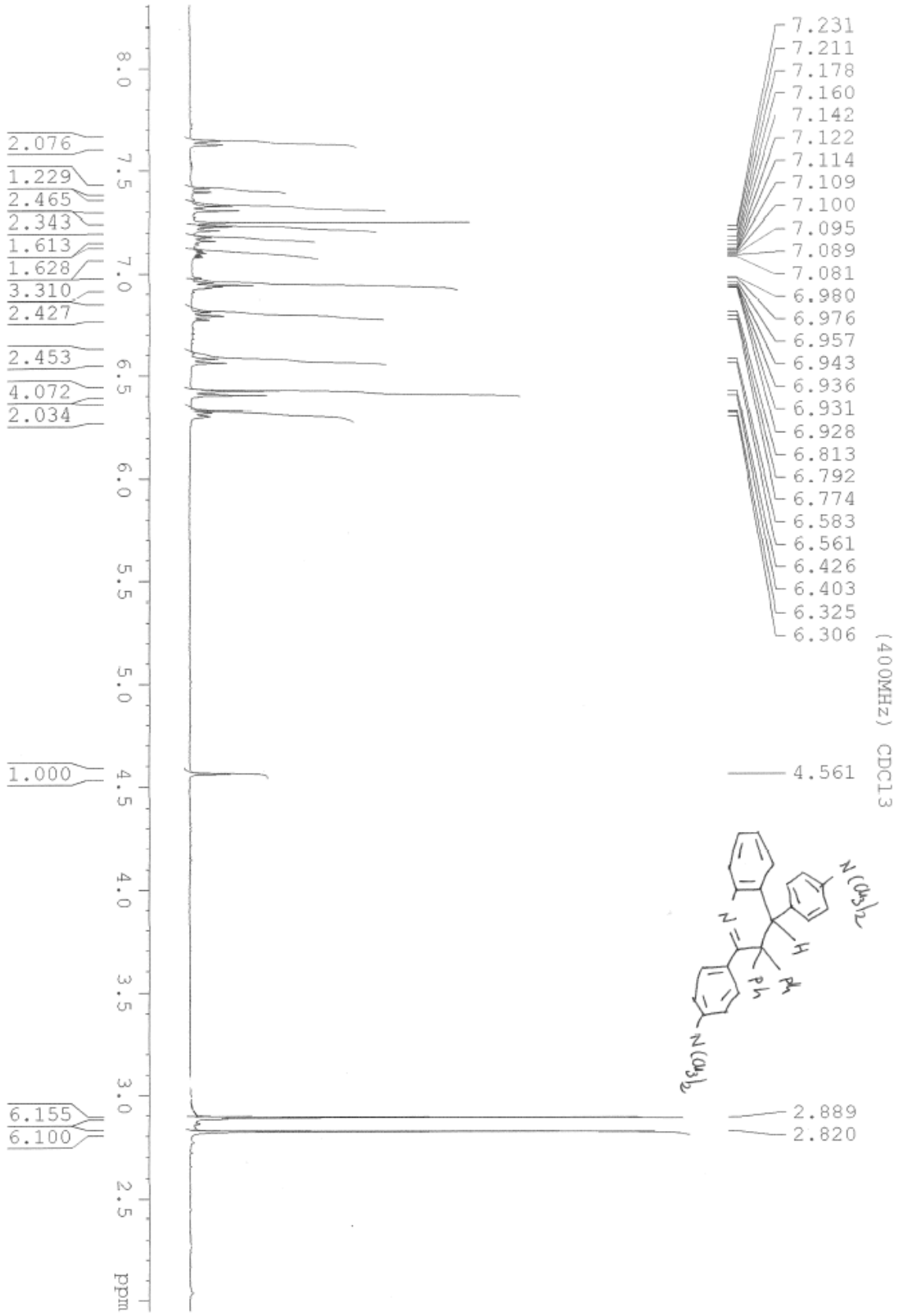
^{1}H NMR **18b**


7.391
7.384
7.217
7.198
7.191
7.181
7.177
7.170
7.164
7.159
7.148
7.142
7.133
7.130
7.127
7.112
7.109
7.091
7.072
6.986
6.965
6.870
6.867
6.852
6.834
6.831
6.780
6.758
6.743
6.737
6.638
6.633
6.621
6.616
6.583
6.553
6.435
6.428
6.414
6.408
5.117
3.723
3.716
(400MHz) CDCl3
0.000
2.031
3.049
6.621
2.029
1.219
1.236
1.758
1.214
1.800
1.126
1.000
2.694
3.158
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm
OCH3
H
N
H
Ph
Ph
OCH3

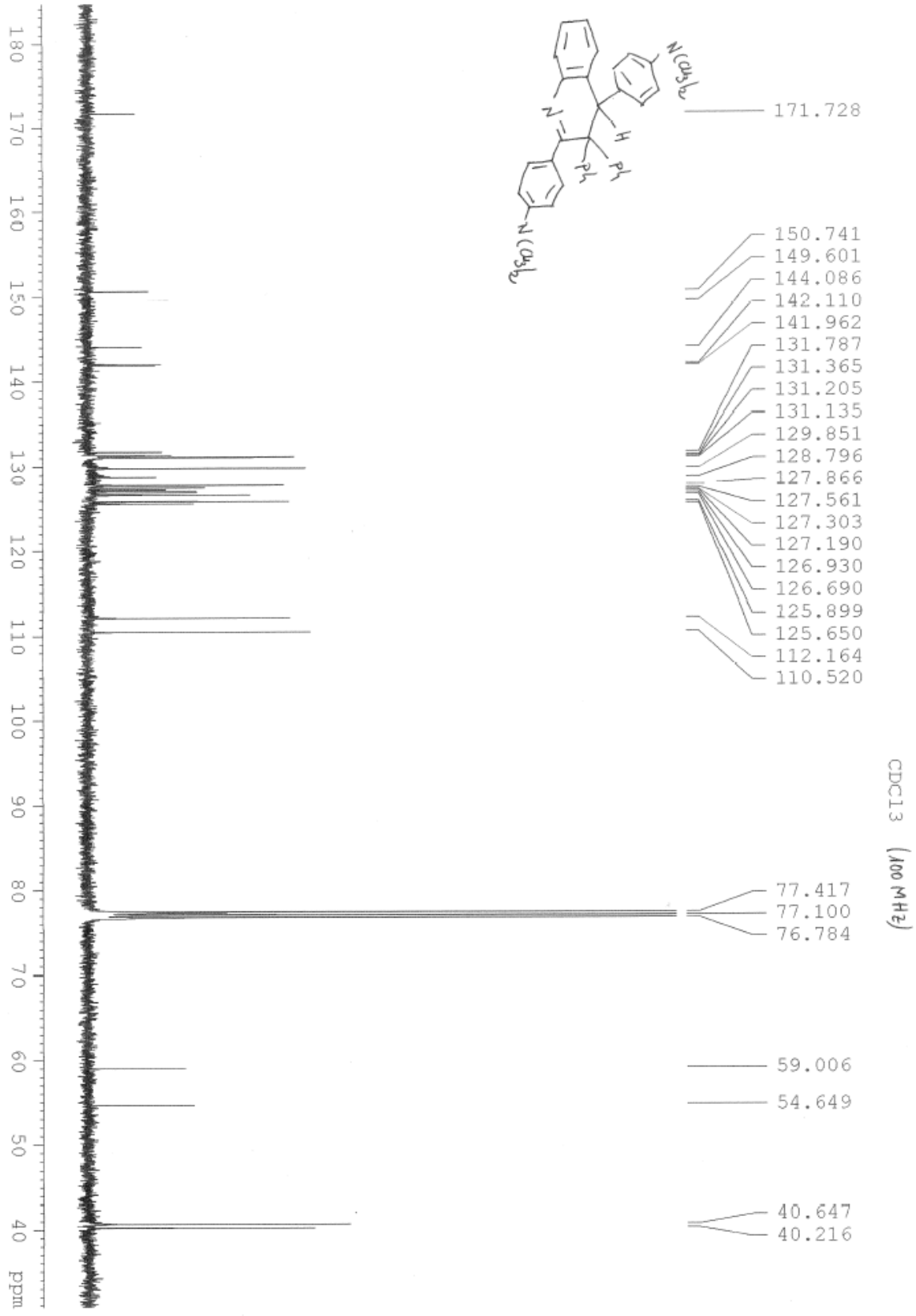
^{13}C NMR **18b**


158.870
157.791
145.765
140.989
140.322
140.002
139.930
137.736
130.357
130.179
129.523
129.012
128.573
128.519
128.382
128.188
127.919
127.808
127.043
125.340
123.940
121.478
117.786
114.015
113.882
106.352
100.569
100.443
77.417
77.100
76.783
55.319
55.230
46.316
CDC13 (100 MHz)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
OCH3
H
N
H
Ph
Ph
OCH3

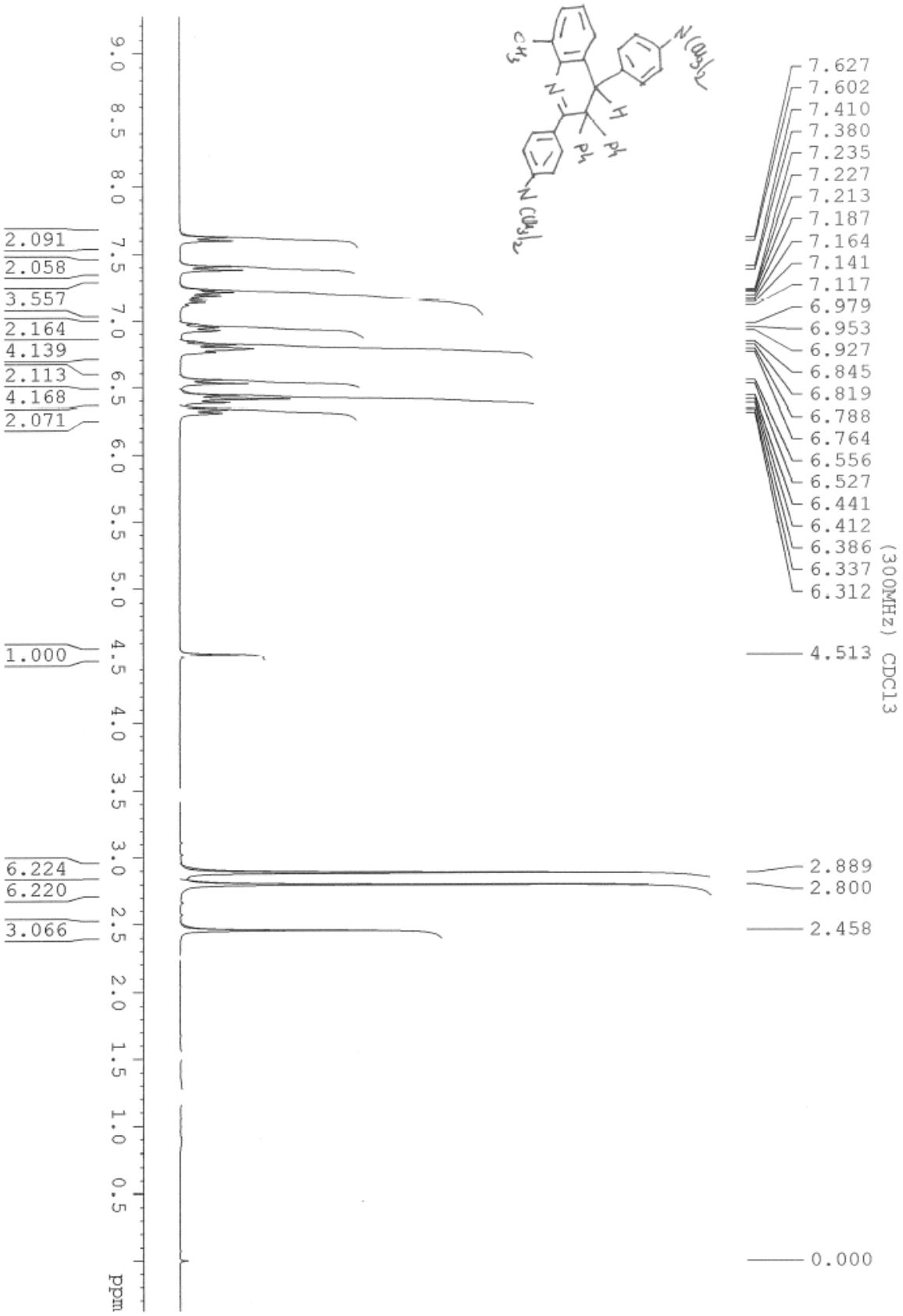
^{1}H NMR **20a**


7.231
7.211
7.178
7.160
7.142
7.122
7.114
7.109
7.100
7.095
7.089
7.081
6.980
6.976
6.957
6.943
6.936
6.931
6.928
6.813
6.792
6.774
6.583
6.561
6.426
6.403
6.325
6.306
(400MHz) CDCl3
4.561
2.889
2.820
2.076
1.229
2.465
2.343
1.613
1.628
3.310
2.427
2.453
4.072
2.034
1.000
6.155
6.100
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
N(CH3)2
N
H
Ph
Ph
N(CH3)2

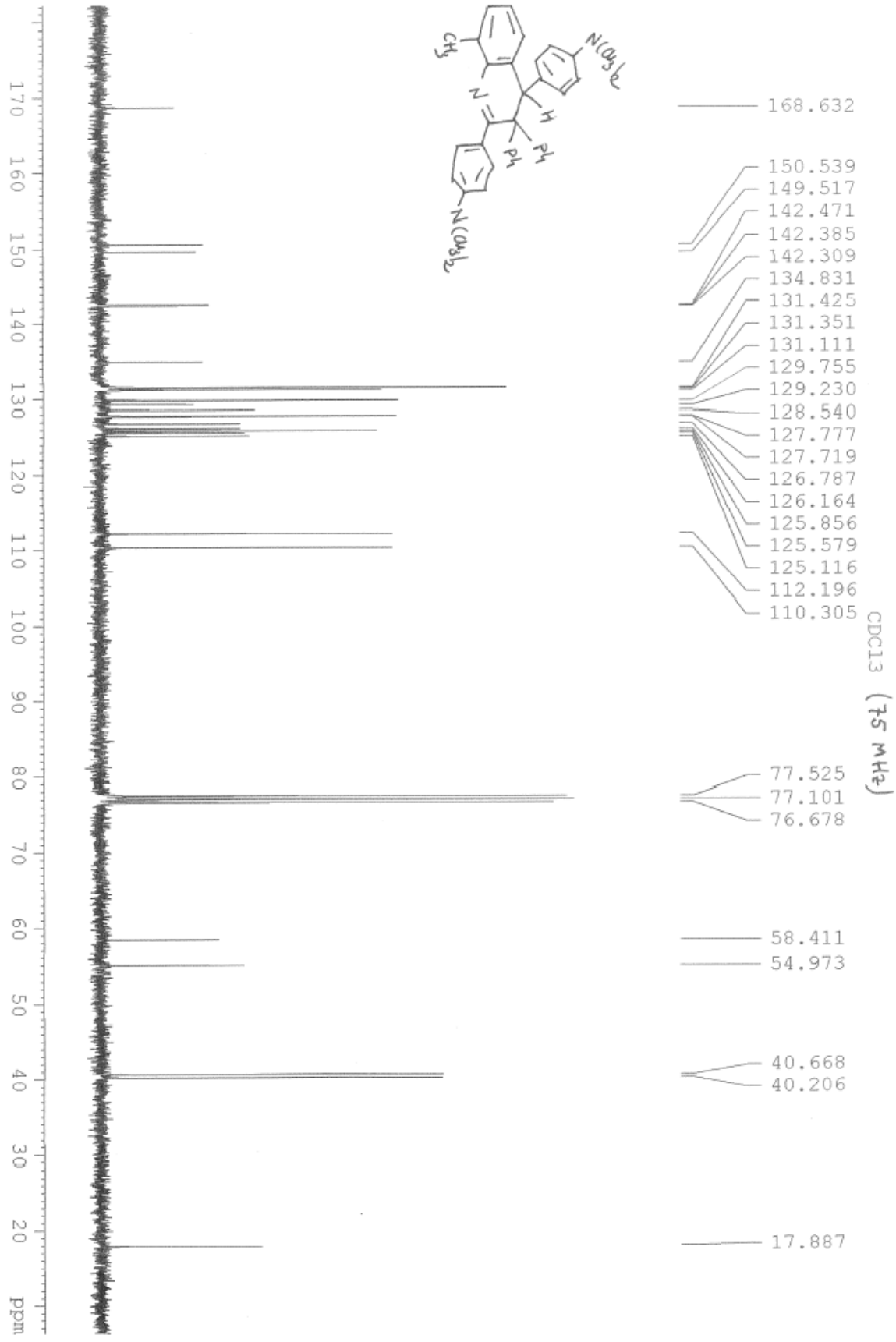
^{13}C NMR **20a**


171.728
150.741
149.601
144.086
142.110
141.962
131.787
131.365
131.205
131.135
129.851
128.796
127.866
127.561
127.303
127.190
126.930
126.690
125.899
125.650
112.164
110.520
77.417
77.100
76.784
59.006
54.649
40.647
40.216
CDCl3 (100 MHz)
ppm

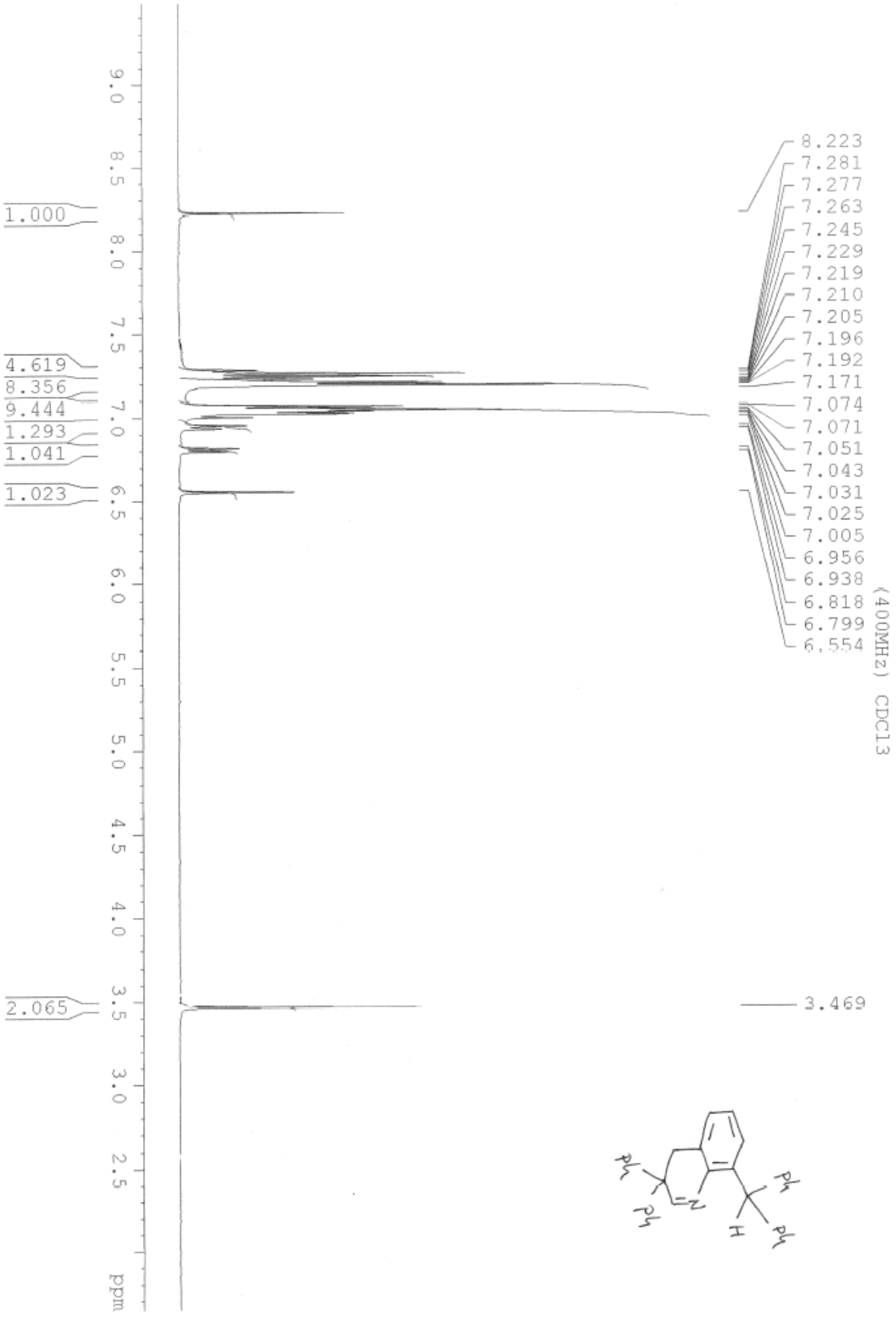
^{1}H NMR **20b**


7.627
7.602
7.410
7.380
7.235
7.227
7.213
7.187
7.164
7.141
7.117
6.979
6.953
6.927
6.845
6.819
6.788
6.764
6.556
6.527
6.441
6.412
6.386
6.337
6.312
4.513
2.889
2.800
2.458
0.000
(300MHz) CDC13
2.091
2.058
3.557
2.164
4.139
2.113
4.168
2.071
1.000
6.224
6.220
3.066
ppm

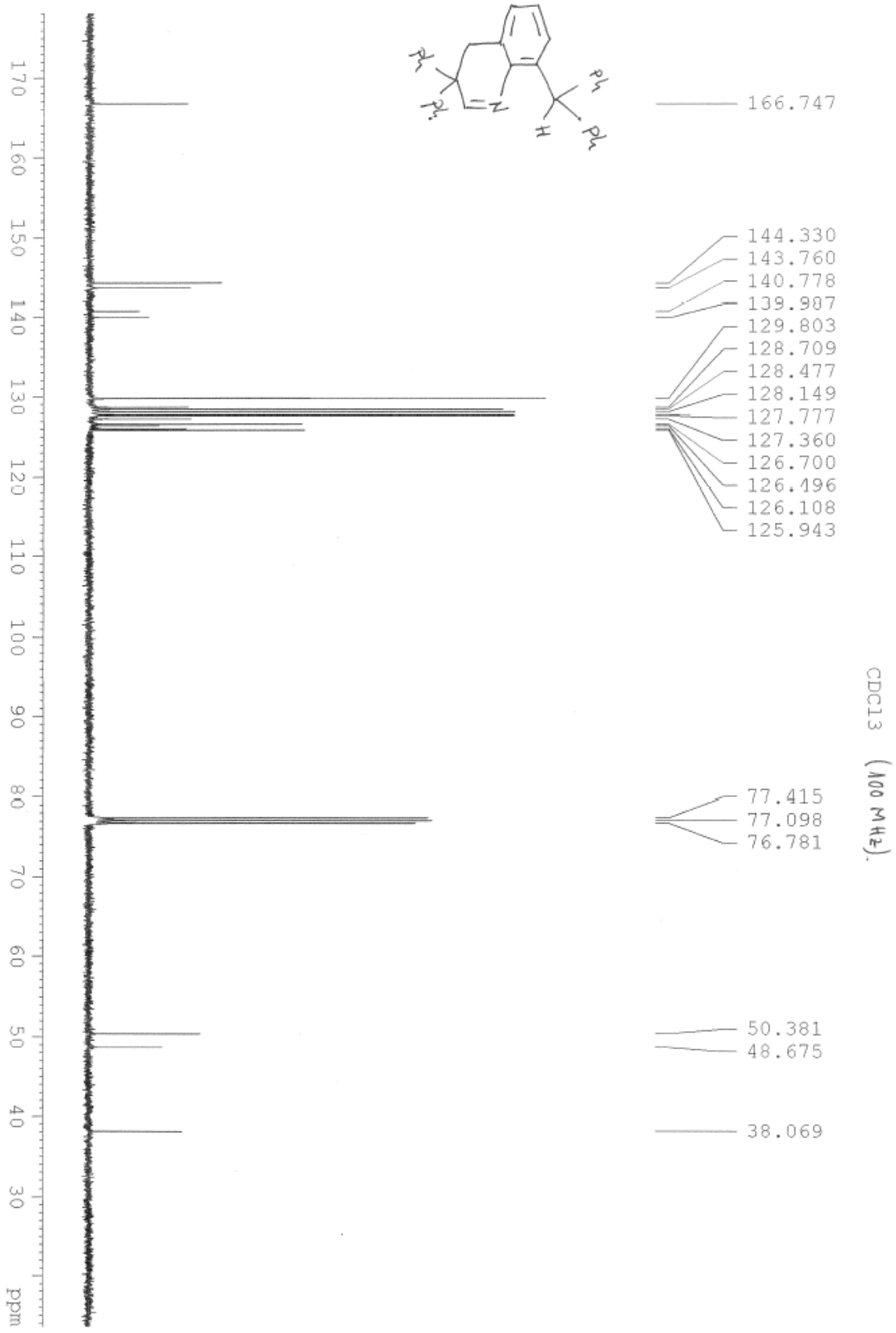
^{13}C NMR **20b**


168.632
150.539
149.517
142.471
142.385
142.309
134.831
131.425
131.351
131.111
129.755
129.230
128.540
127.777
127.719
126.787
126.164
125.856
125.579
125.116
112.196
110.305
77.525
77.101
76.678
58.411
54.973
40.668
40.206
17.887
CDCl3 (75 MHz)
ppm

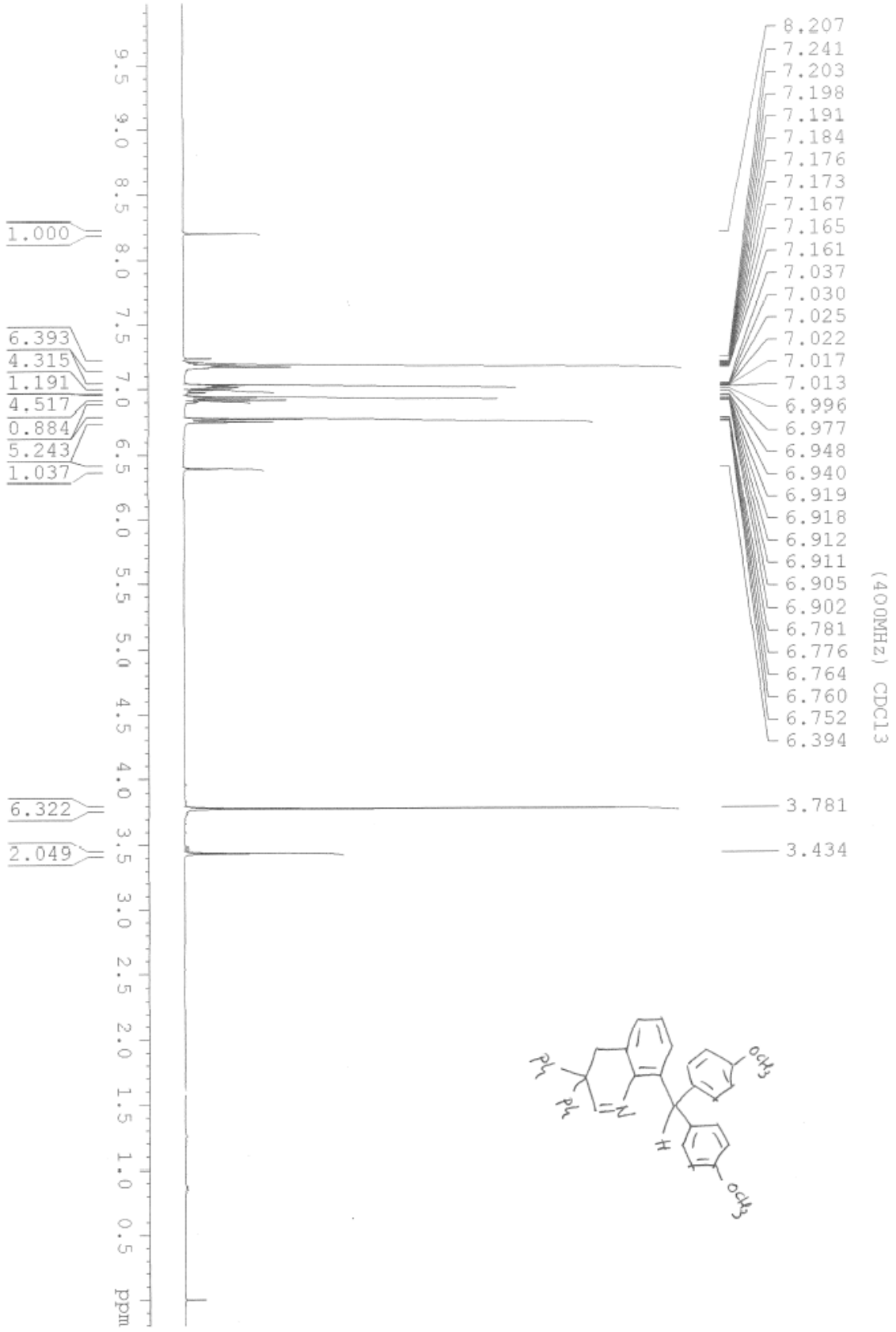
^{1}H NMR **22a**


1.000
4.619
8.356
9.444
1.293
1.041
1.023
2.065
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
8.223
7.281
7.277
7.263
7.245
7.229
7.219
7.210
7.205
7.196
7.192
7.171
7.074
7.071
7.051
7.043
7.031
7.025
7.005
6.956
6.938
6.818
6.799
6.554
(400MHz) CDCl3
3.469
Ph
Ph
N
H
Ph
Ph

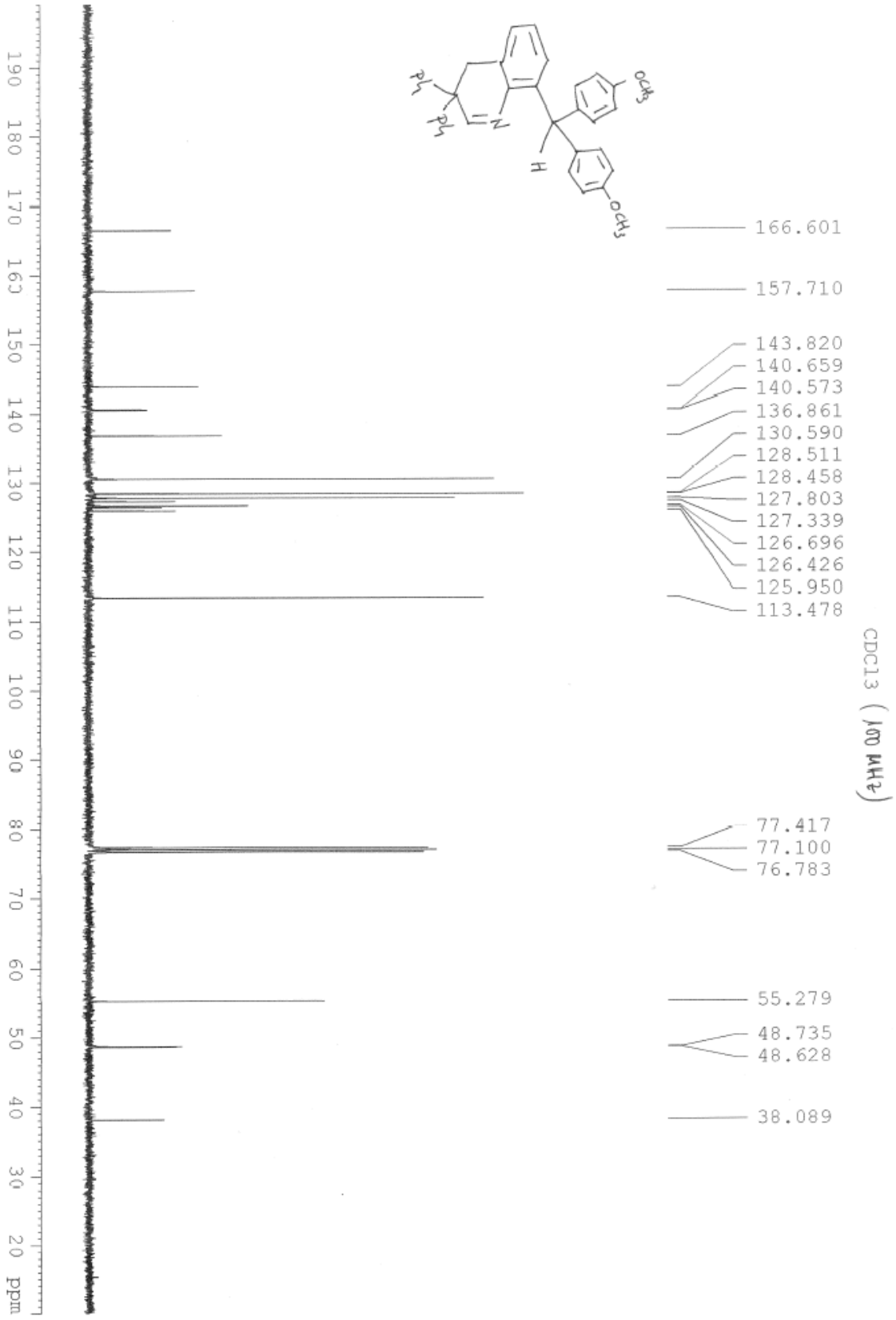
^{13}C NMR **22a**


166.747
144.330
143.760
140.778
139.987
129.803
128.709
128.477
128.149
127.777
127.360
126.700
126.496
126.108
125.943
77.415
77.098
76.781
50.381
48.675
38.069
CDCl3 (100 MHz).
ppm

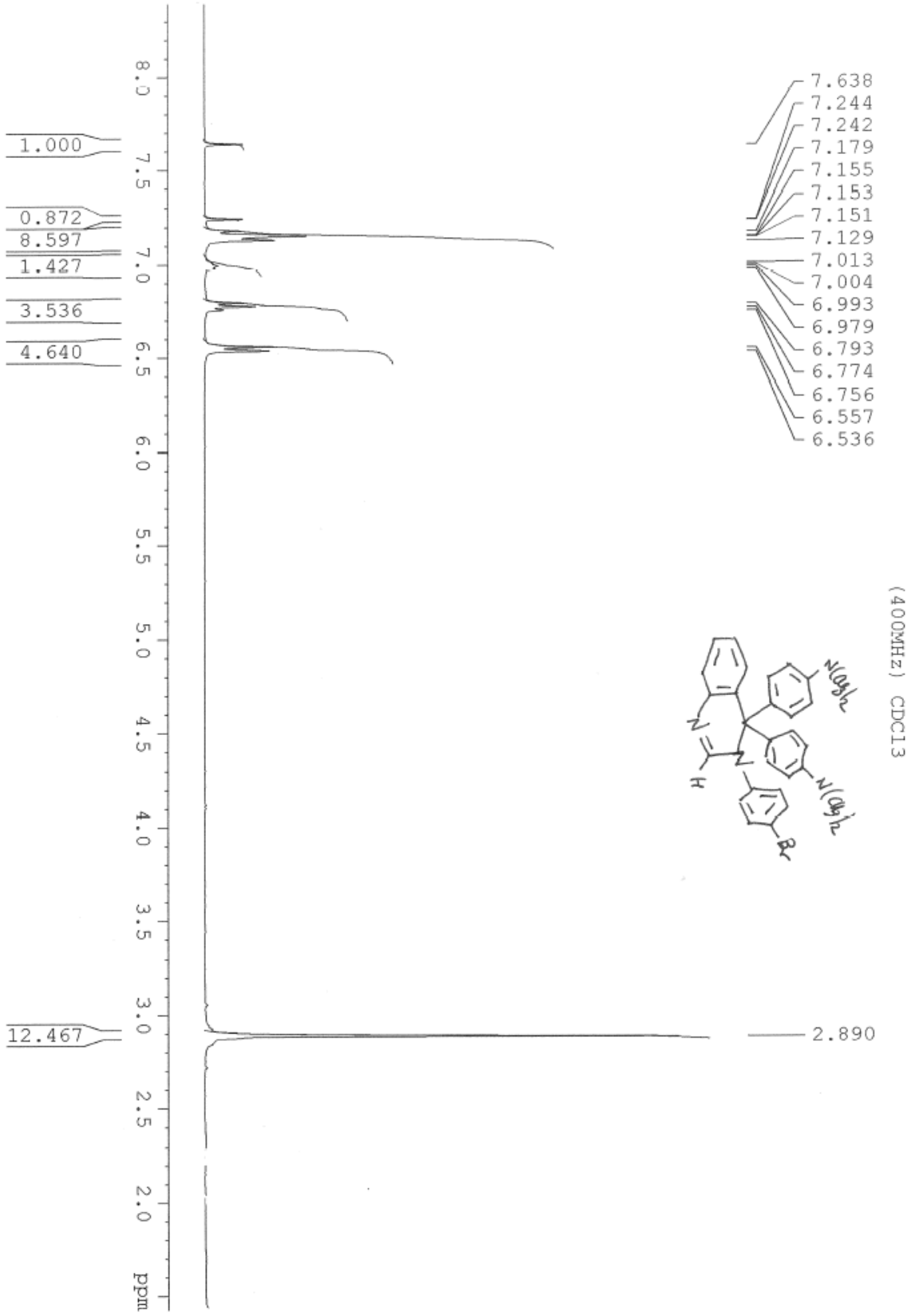
^{1}H NMR **22b**


8.207
7.241
7.203
7.198
7.191
7.184
7.176
7.173
7.167
7.165
7.161
7.037
7.030
7.025
7.022
7.017
7.013
6.996
6.977
6.948
6.940
6.919
6.918
6.912
6.911
6.905
6.902
6.781
6.776
6.764
6.760
6.752
6.394
3.781
3.434
1.000
6.393
4.315
1.191
4.517
0.884
5.243
1.037
6.322
2.049
(400MHz) CDCl3
ppm
Ph
Ph
N
H
OCH3
OCH3

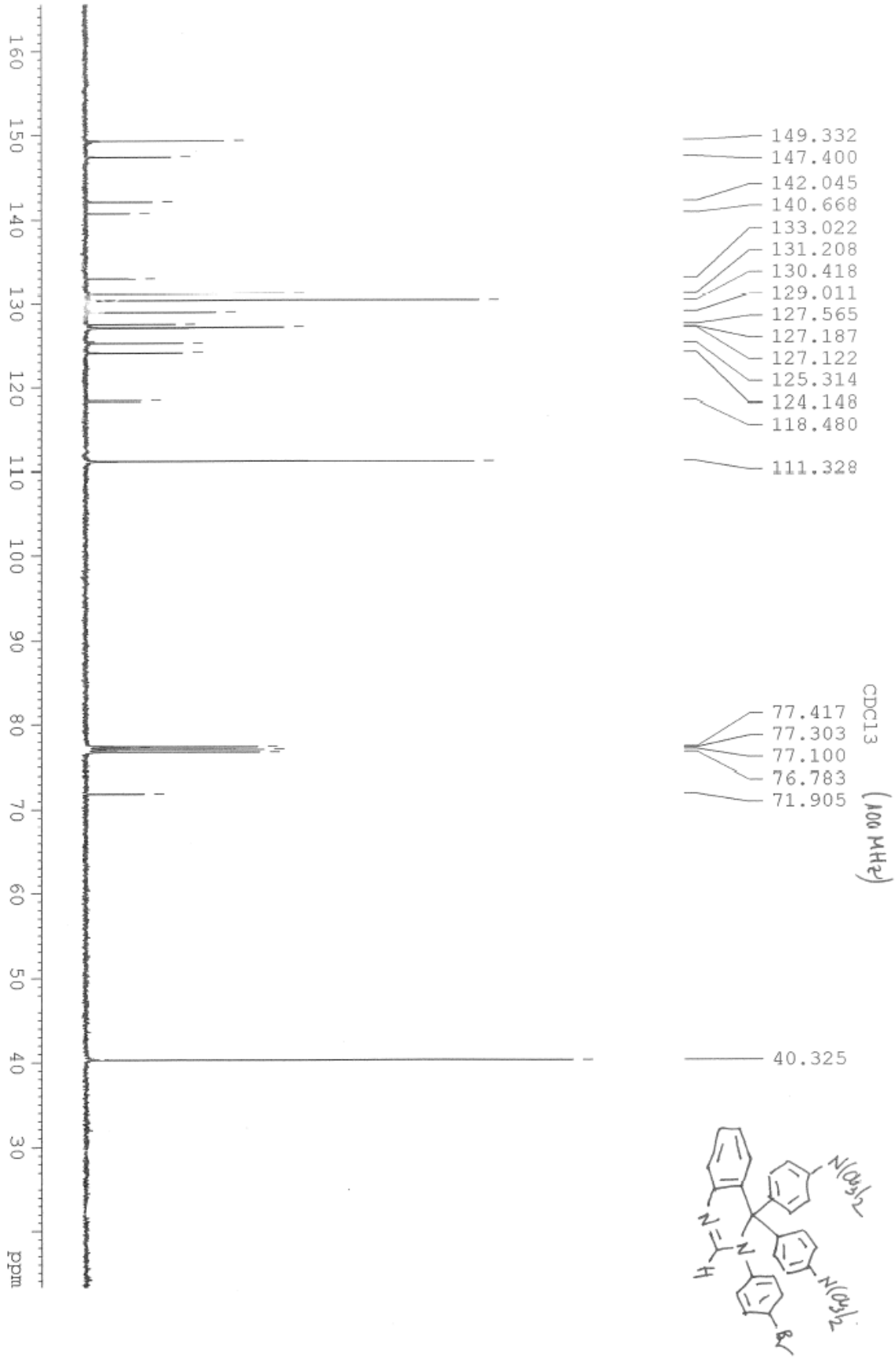
^{13}C NMR **22b**


166.601
157.710
143.820
140.659
140.573
136.861
130.590
128.511
128.458
127.803
127.339
126.696
126.426
125.950
113.478
77.417
77.100
76.783
55.279
48.735
48.628
38.089
CDCl3 (100 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

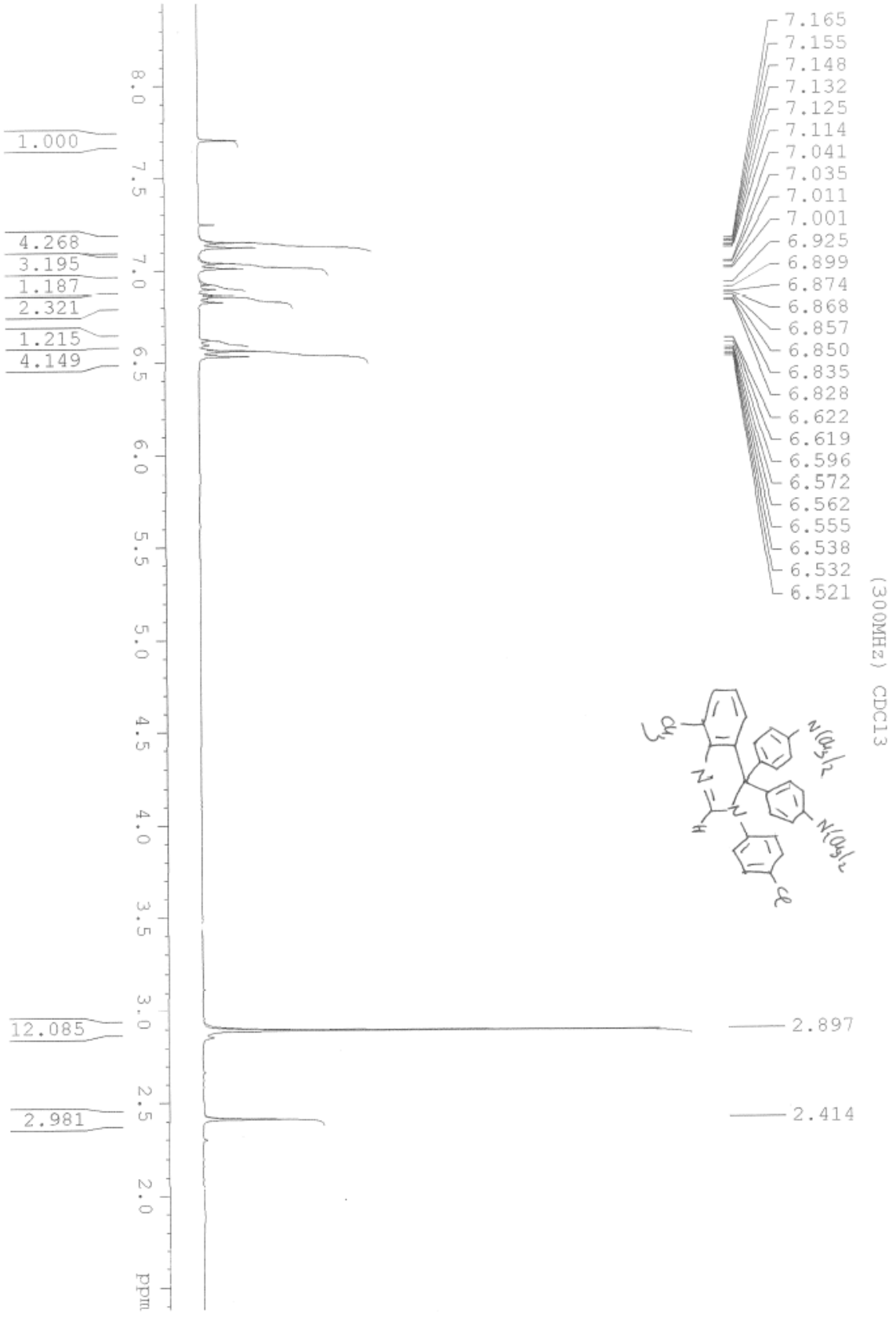
^{1}H NMR **25a**


7.638
7.244
7.242
7.179
7.155
7.153
7.151
7.129
7.013
7.004
6.993
6.979
6.793
6.774
6.756
6.557
6.536
2.890
1.000
0.872
8.597
1.427
3.536
4.640
12.467
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
(400MHz) CDCl3

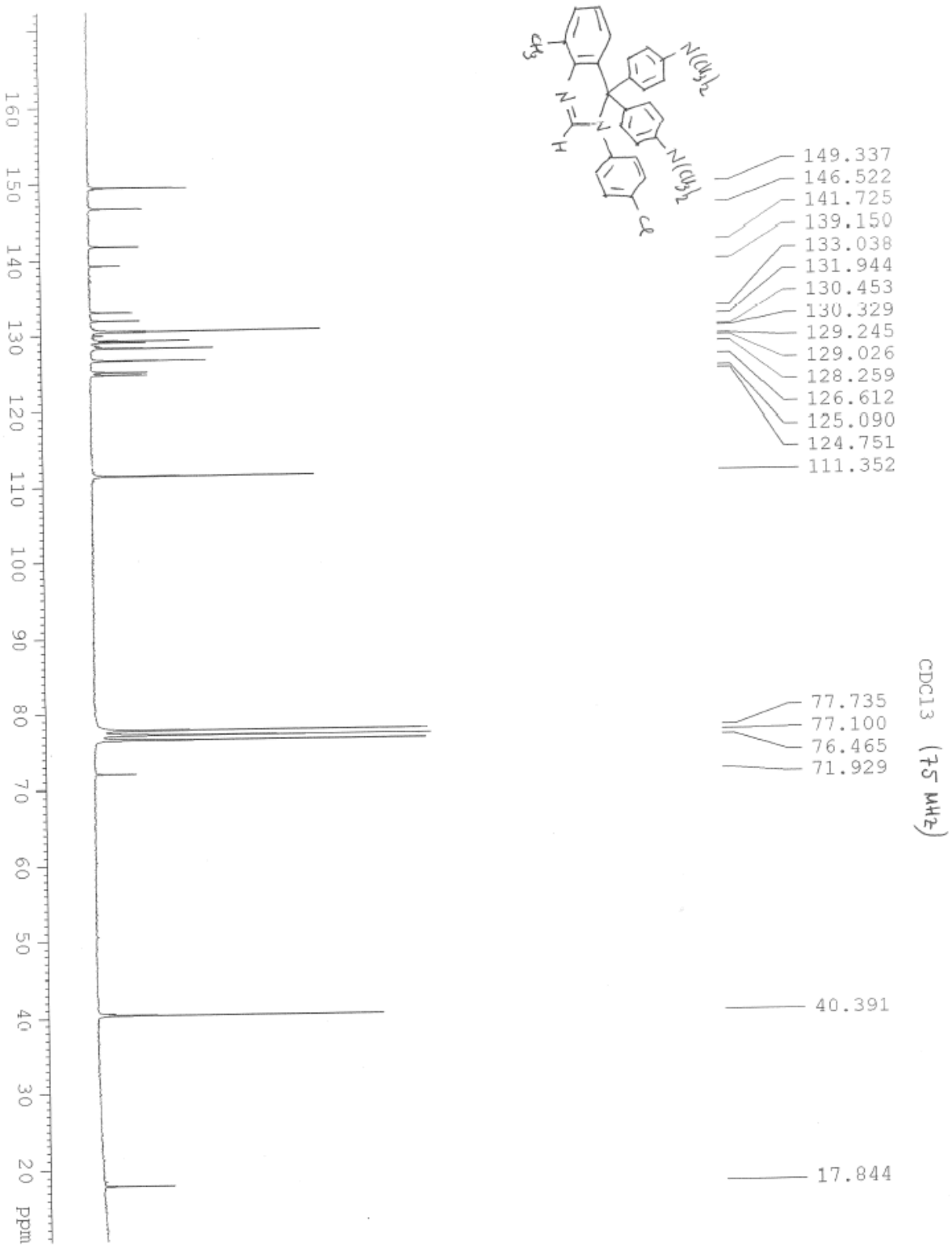
^{13}C NMR **25a**


149.332
147.400
142.045
140.668
133.022
131.208
130.418
129.011
127.565
127.187
127.122
125.314
124.148
118.480
111.328
77.417
77.303
77.100
76.783
71.905
CDCl3
(100 MHz)
40.325
ppm

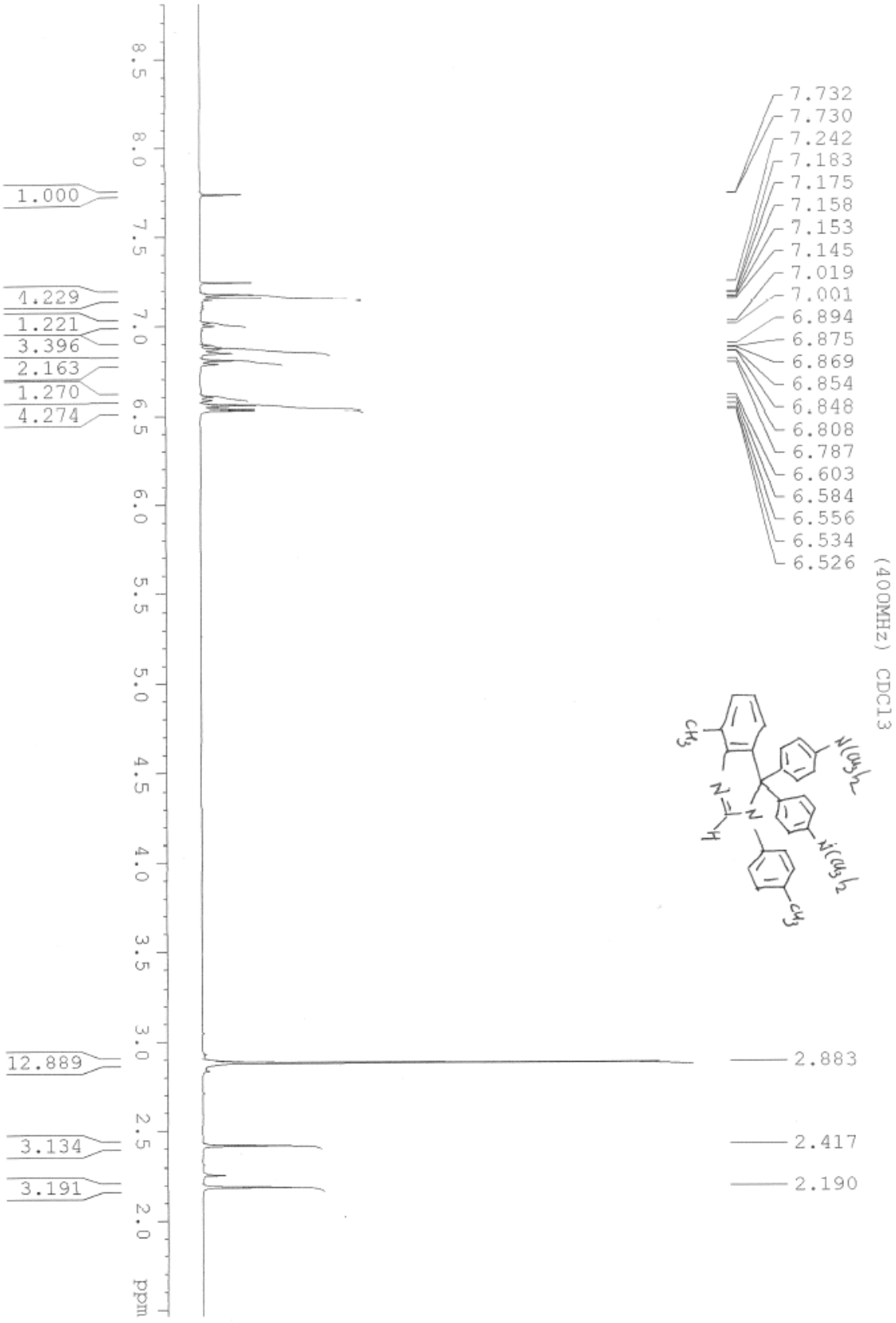
^{1}H NMR **25b**


7.165
7.155
7.148
7.132
7.125
7.114
7.041
7.035
7.011
7.001
6.925
6.899
6.874
6.868
6.857
6.850
6.835
6.828
6.622
6.619
6.596
6.572
6.562
6.555
6.538
6.532
6.521
(300MHz) CDCl3
1.000
4.268
3.195
1.187
2.321
1.215
4.149
12.085
2.981
2.897
2.414
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

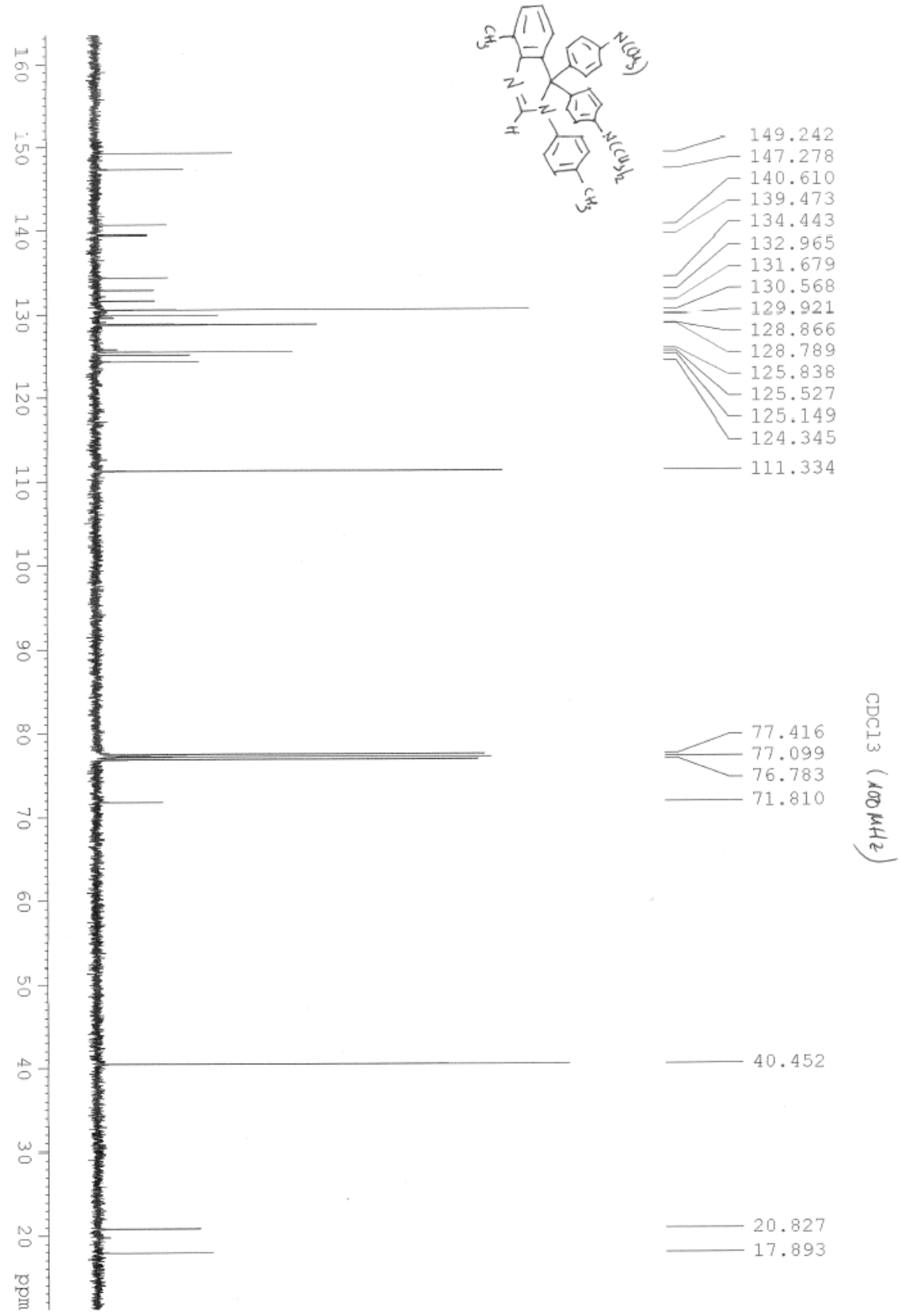
^{13}C NMR **25b**


149.337
146.522
141.725
139.150
133.038
131.944
130.453
130.329
129.245
129.026
128.259
126.612
125.090
124.751
111.352
77.735
77.100
76.465
71.929
40.391
17.844
CDCl3 (75 MHz)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

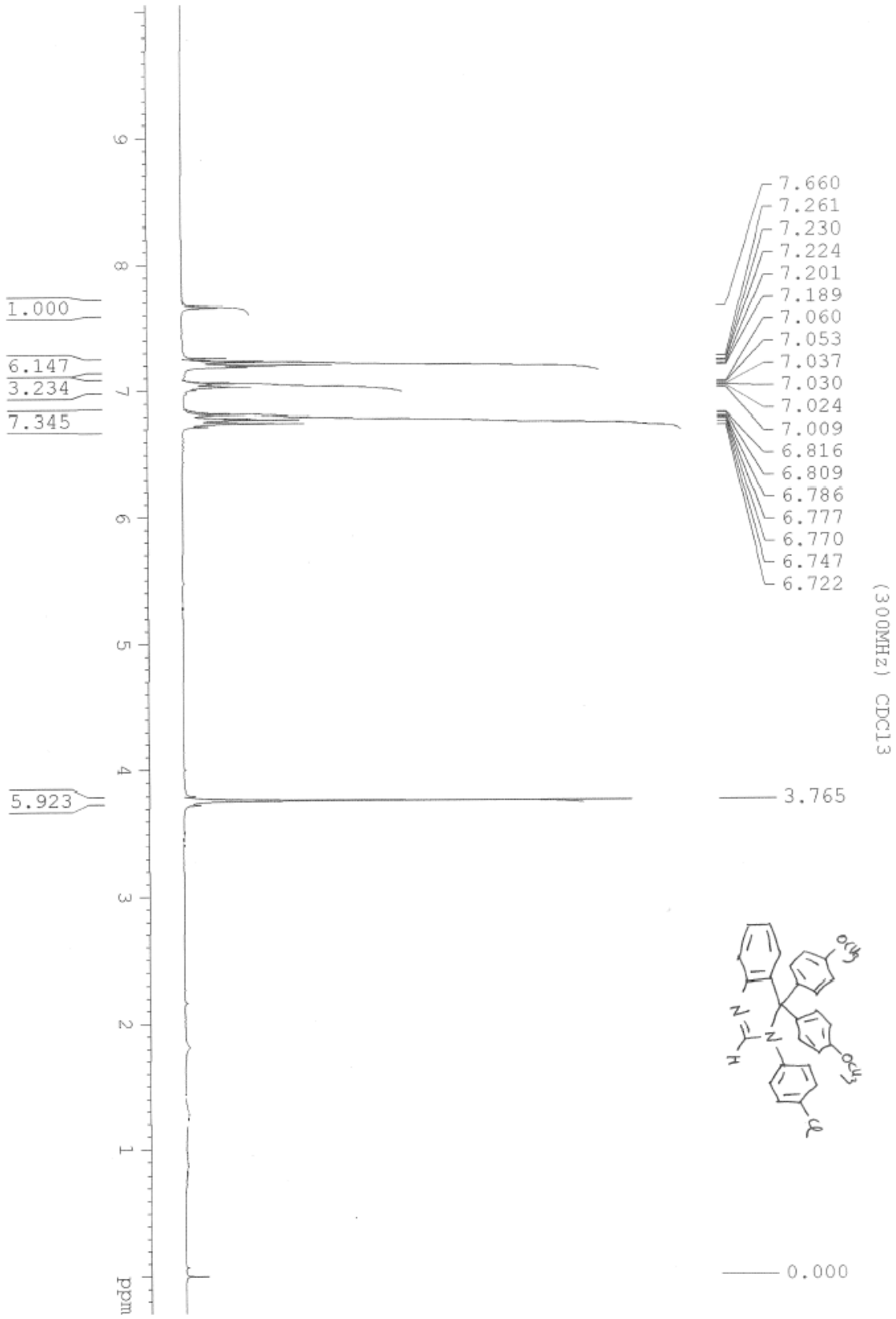
^{1}H NMR **25c**


7.732
7.730
7.242
7.183
7.175
7.158
7.153
7.145
7.019
7.001
6.894
6.875
6.869
6.854
6.848
6.808
6.787
6.603
6.584
6.556
6.534
6.526
(400MHz) CDCl3
1.000
1.229
1.221
3.396
2.163
1.270
4.274
12.889
3.134
3.191
2.883
2.417
2.190
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

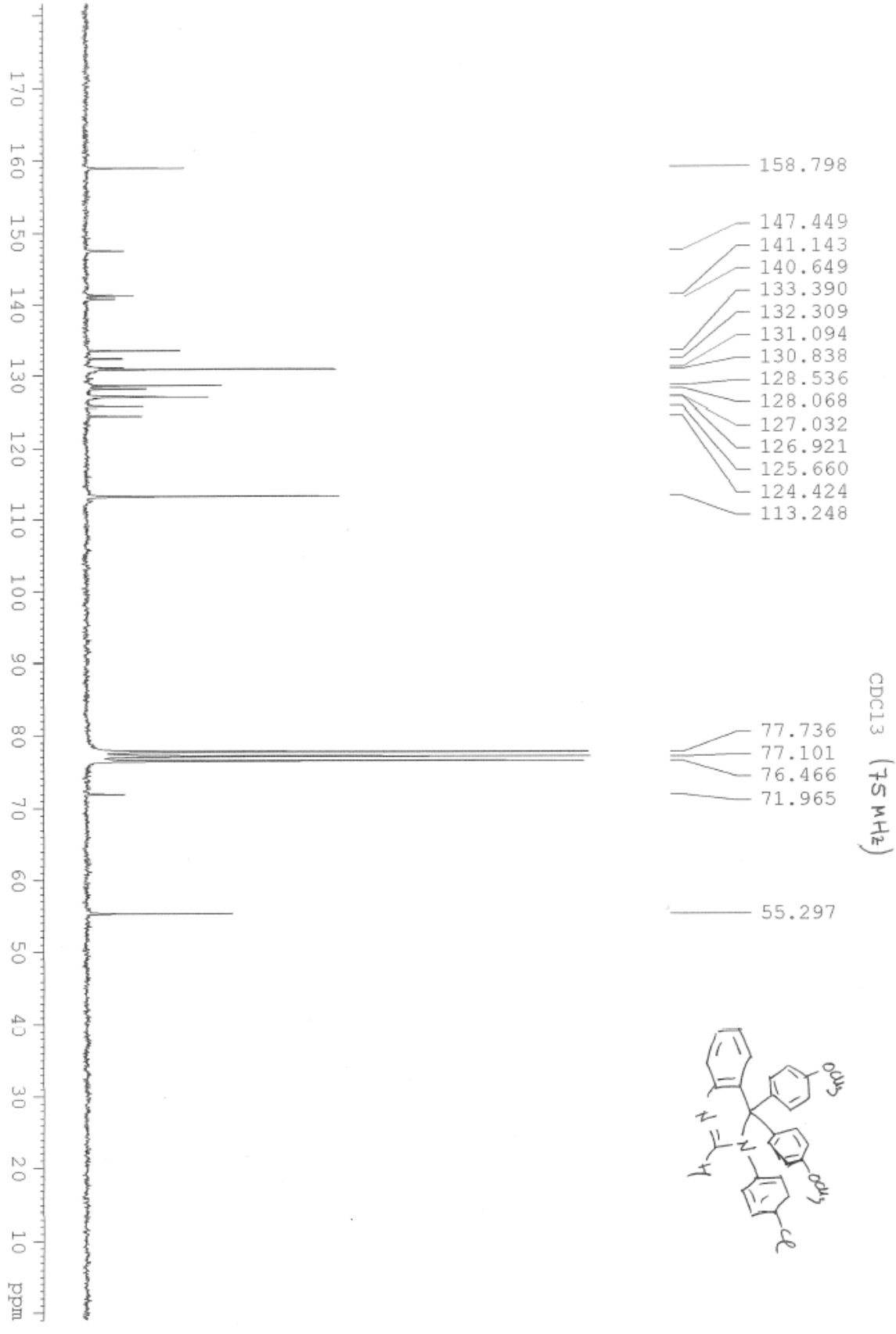
^{13}C NMR **25c**


149.242
147.278
140.610
139.473
134.443
132.965
131.679
130.568
129.921
128.866
128.789
125.838
125.527
125.149
124.345
111.334
77.416
77.099
76.783
71.810
40.452
20.827
17.893
CDCl3 (100 MHz)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

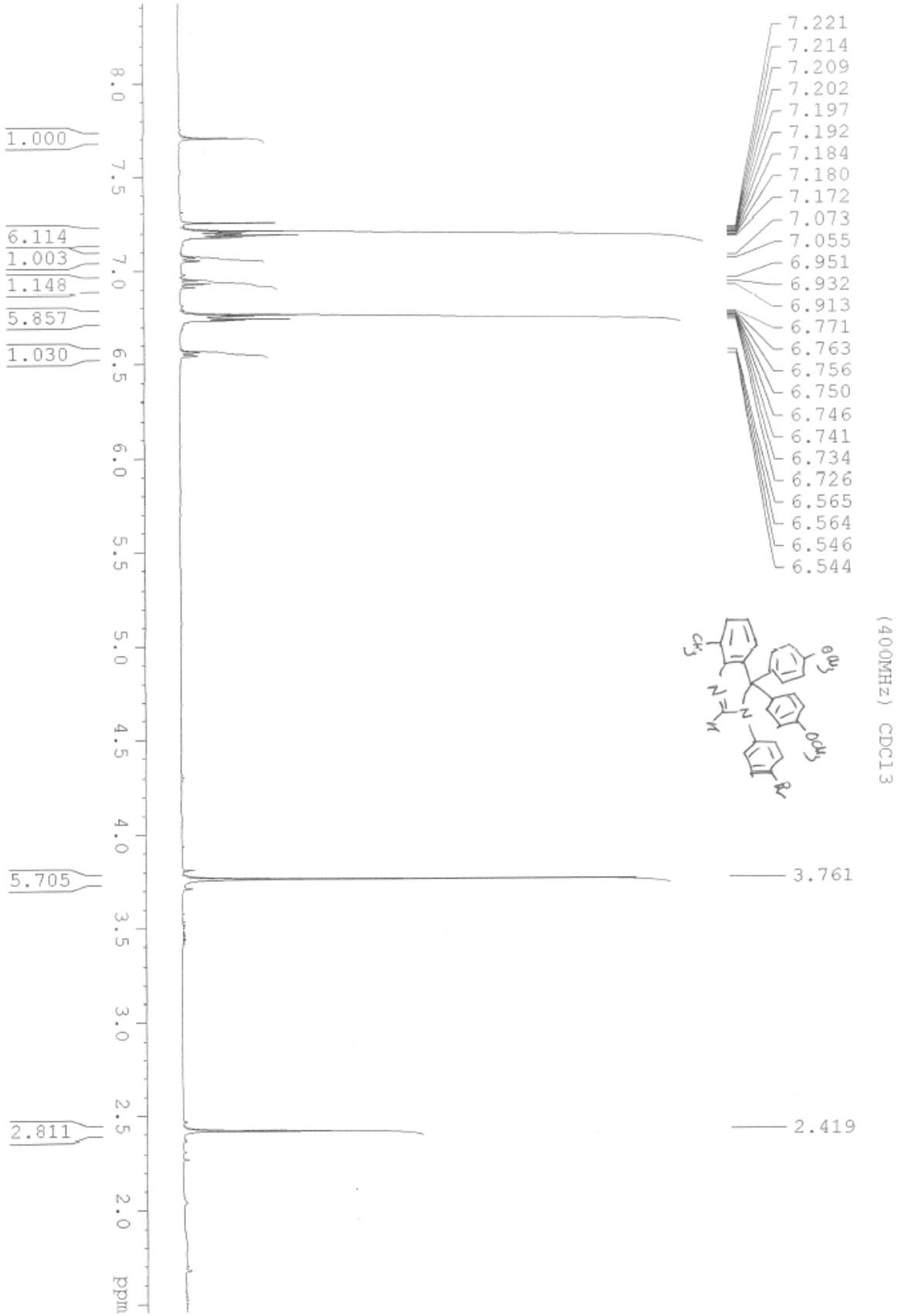
^{1}H NMR **25d**


1.000
6.147
3.234
7.345
5.923
7.660
7.261
7.230
7.224
7.201
7.189
7.060
7.053
7.037
7.030
7.024
7.009
6.816
6.809
6.786
6.777
6.770
6.747
6.722
3.765
0.000
(300MHz) CDCl3
ppm

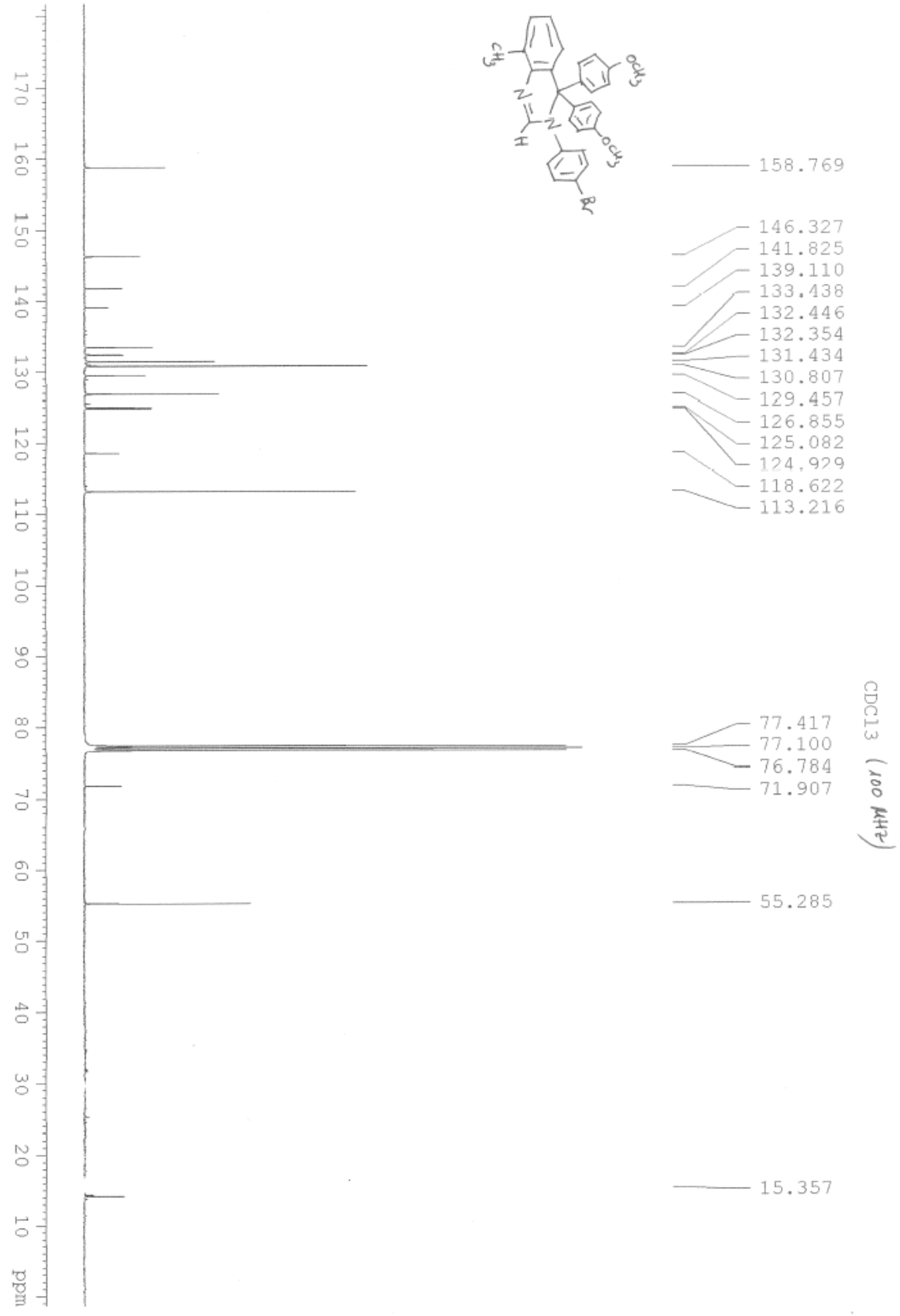
^{13}C NMR **25d**


158.798
147.449
141.143
140.649
133.390
132.309
131.094
130.838
128.536
128.068
127.032
126.921
125.660
124.424
113.248
77.736
77.101
76.466
71.965
55.297
CDCl3 (75 MHz)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

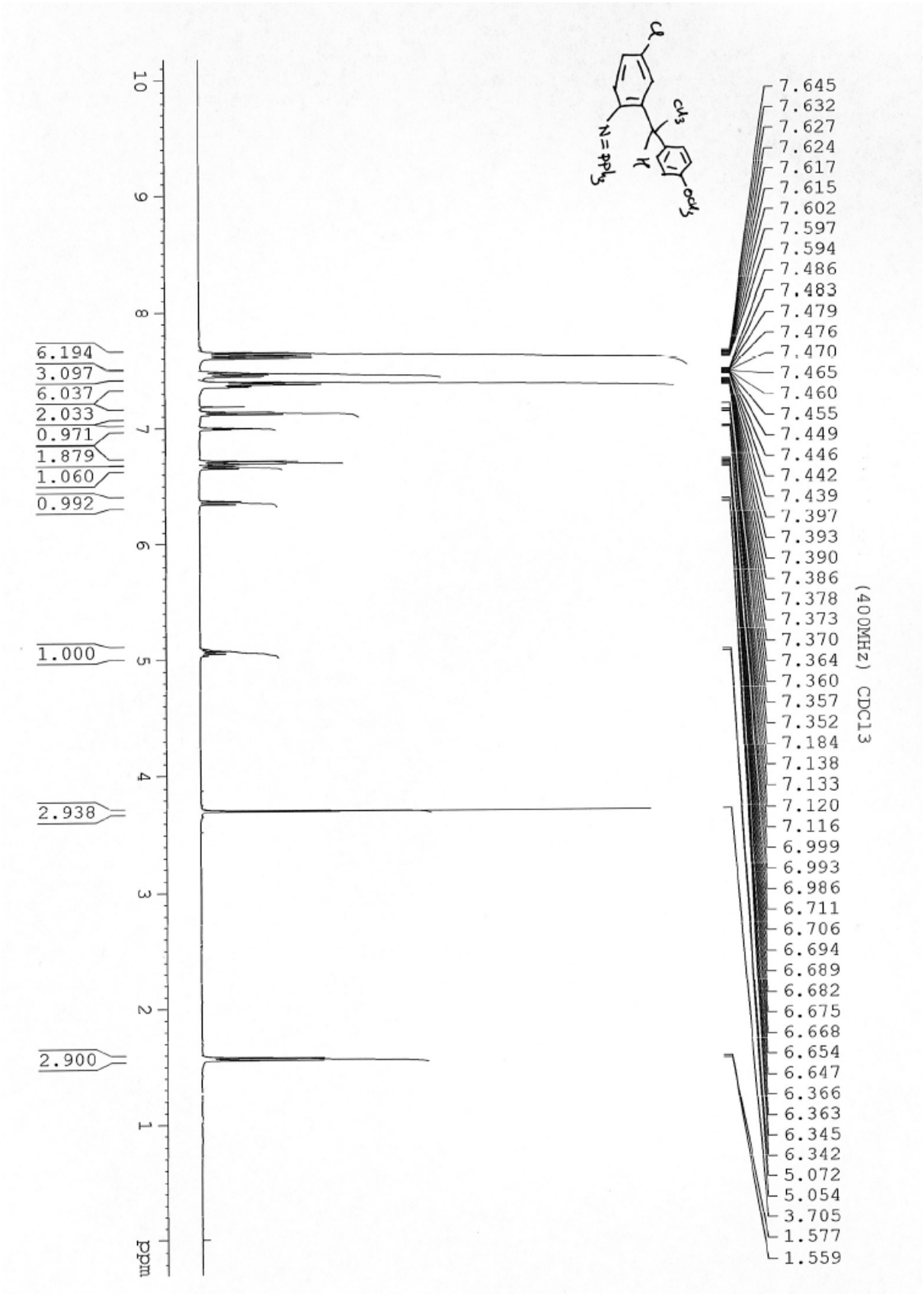
^{1}H NMR **25e**


7.221
7.214
7.209
7.202
7.197
7.192
7.184
7.180
7.172
7.073
7.055
6.951
6.932
6.913
6.771
6.763
6.756
6.750
6.746
6.741
6.734
6.726
6.565
6.564
6.546
6.544
1.000
6.114
1.003
1.148
5.857
1.030
5.705
2.811
3.761
2.419
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
(400MHz) CDCl3

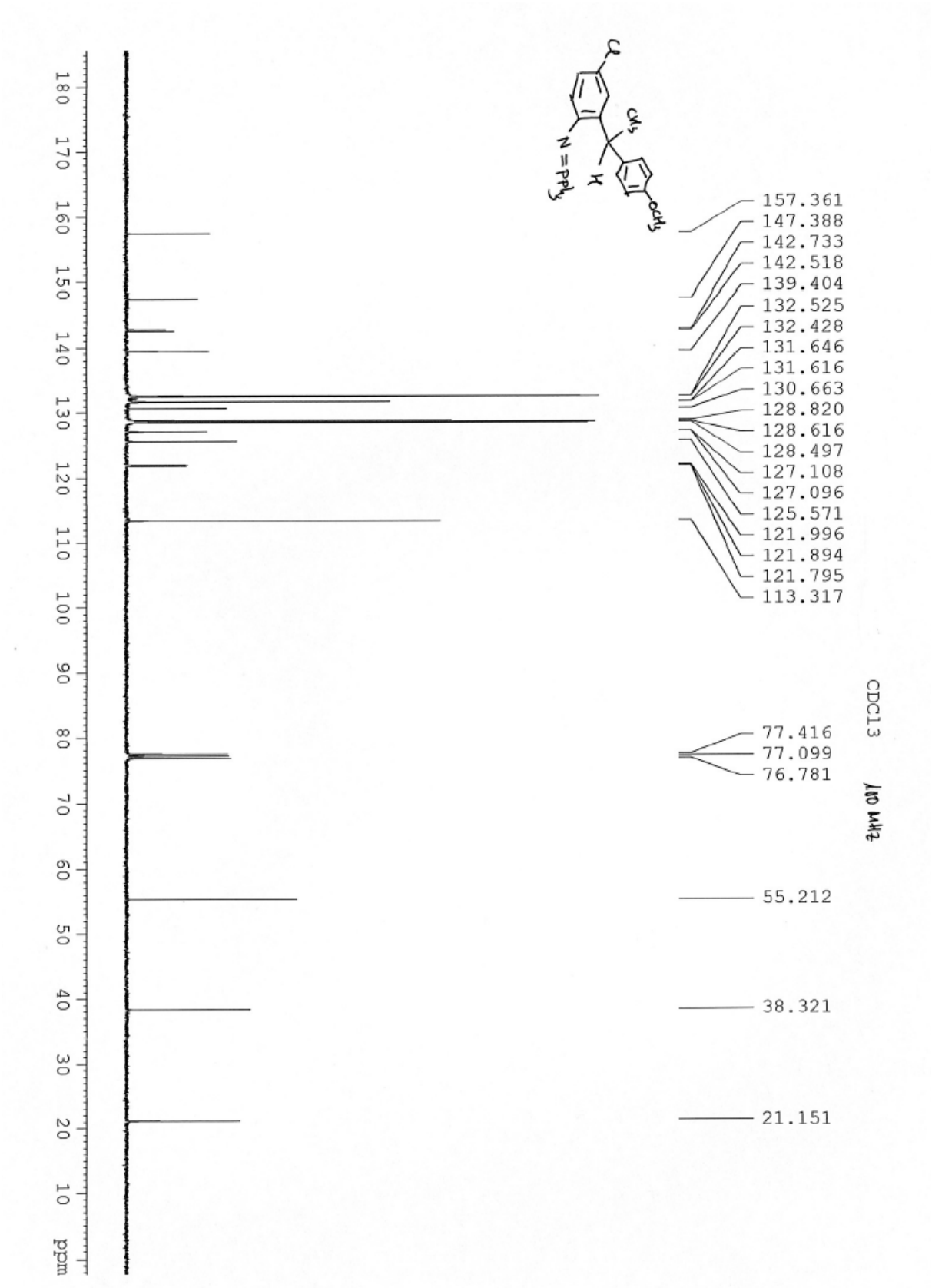
^{13}C NMR **25e**


158.769
146.327
141.825
139.110
133.438
132.446
132.354
131.434
130.807
129.457
126.855
125.082
124.929
118.622
113.216
77.417
77.100
76.784
71.907
55.285
15.357
CDCl3 (100 MHz)
ppm

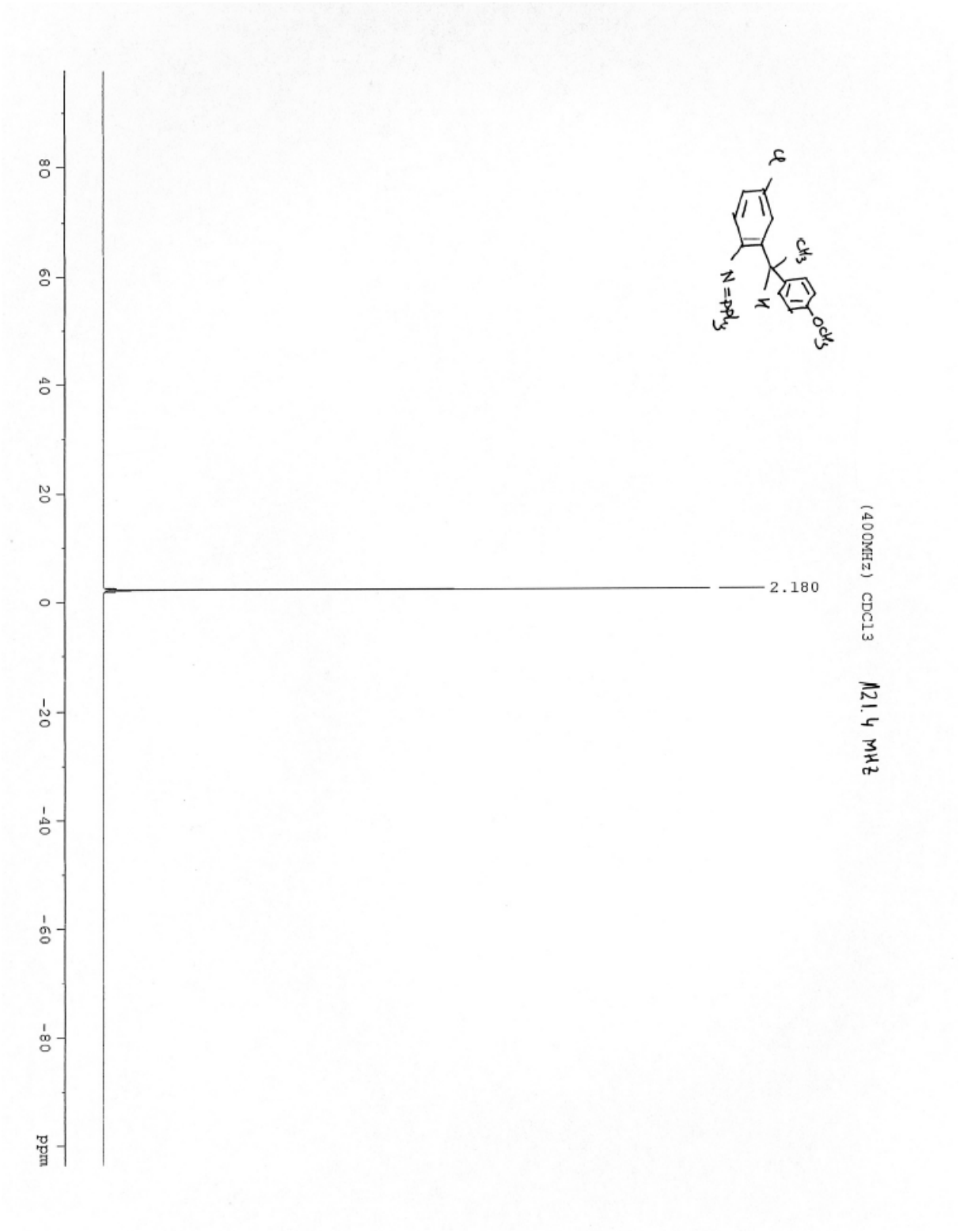
^{1}H NMR **27**


6.194
3.097
6.037
2.033
0.971
1.879
1.060
0.992
1.000
2.938
2.900
ppm
7.645
7.632
7.627
7.624
7.617
7.615
7.602
7.597
7.594
7.486
7.483
7.479
7.476
7.470
7.465
7.460
7.455
7.449
7.446
7.442
7.439
7.397
7.393
7.390
7.386
7.378
7.373
7.370
7.364
7.360
7.357
7.352
7.184
7.138
7.133
7.120
7.116
6.999
6.993
6.986
6.711
6.706
6.694
6.689
6.682
6.675
6.668
6.654
6.647
6.366
6.363
6.345
6.342
5.072
5.054
3.705
1.577
1.559
(400MHz) CDCl3

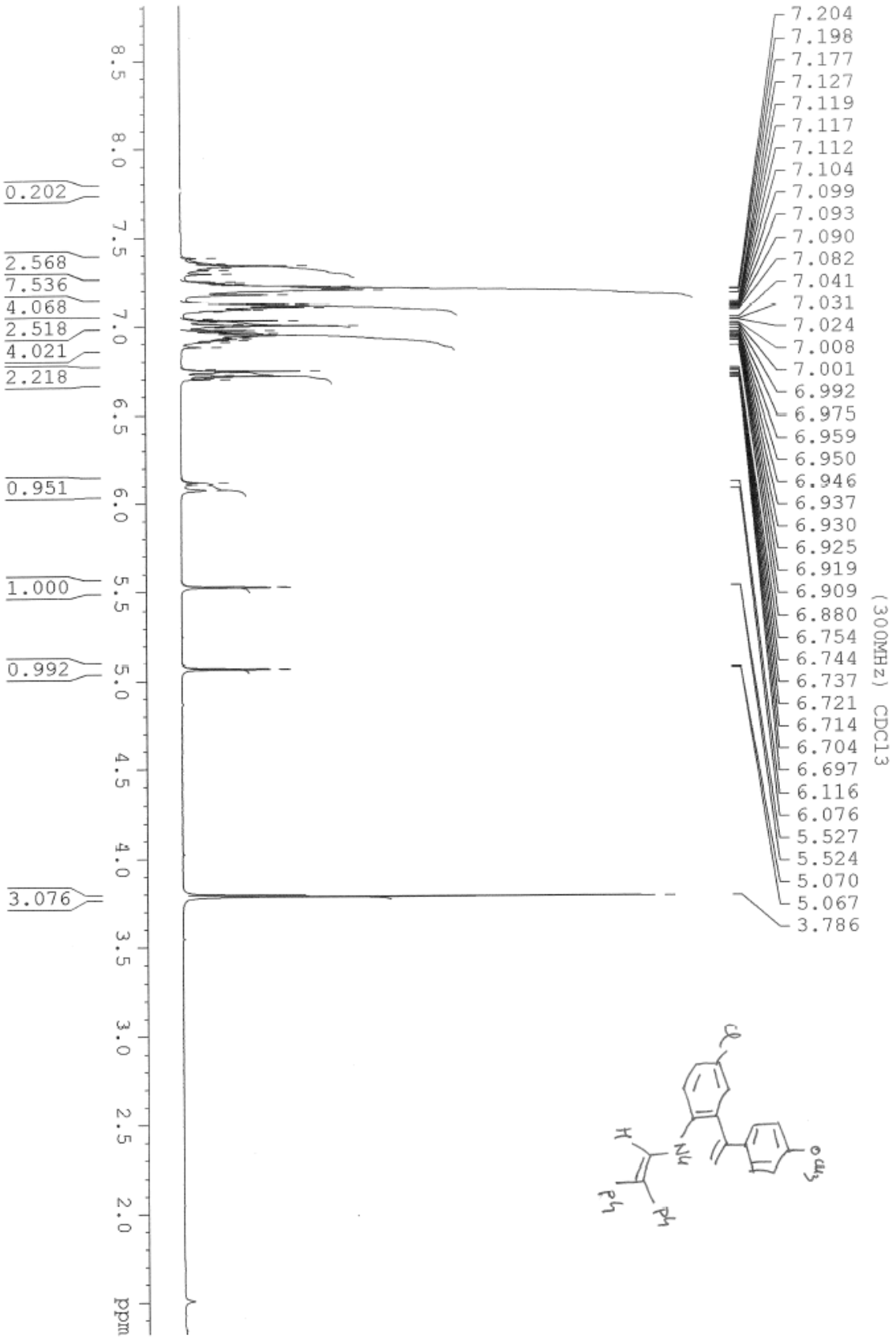
^{13}C NMR **27**


157.361
147.388
142.733
142.518
139.404
132.525
132.428
131.646
131.616
130.663
128.820
128.616
128.497
127.108
127.096
125.571
121.996
121.894
121.795
113.317
77.416
77.099
76.781
55.212
38.321
21.151
CDCl3
ppm

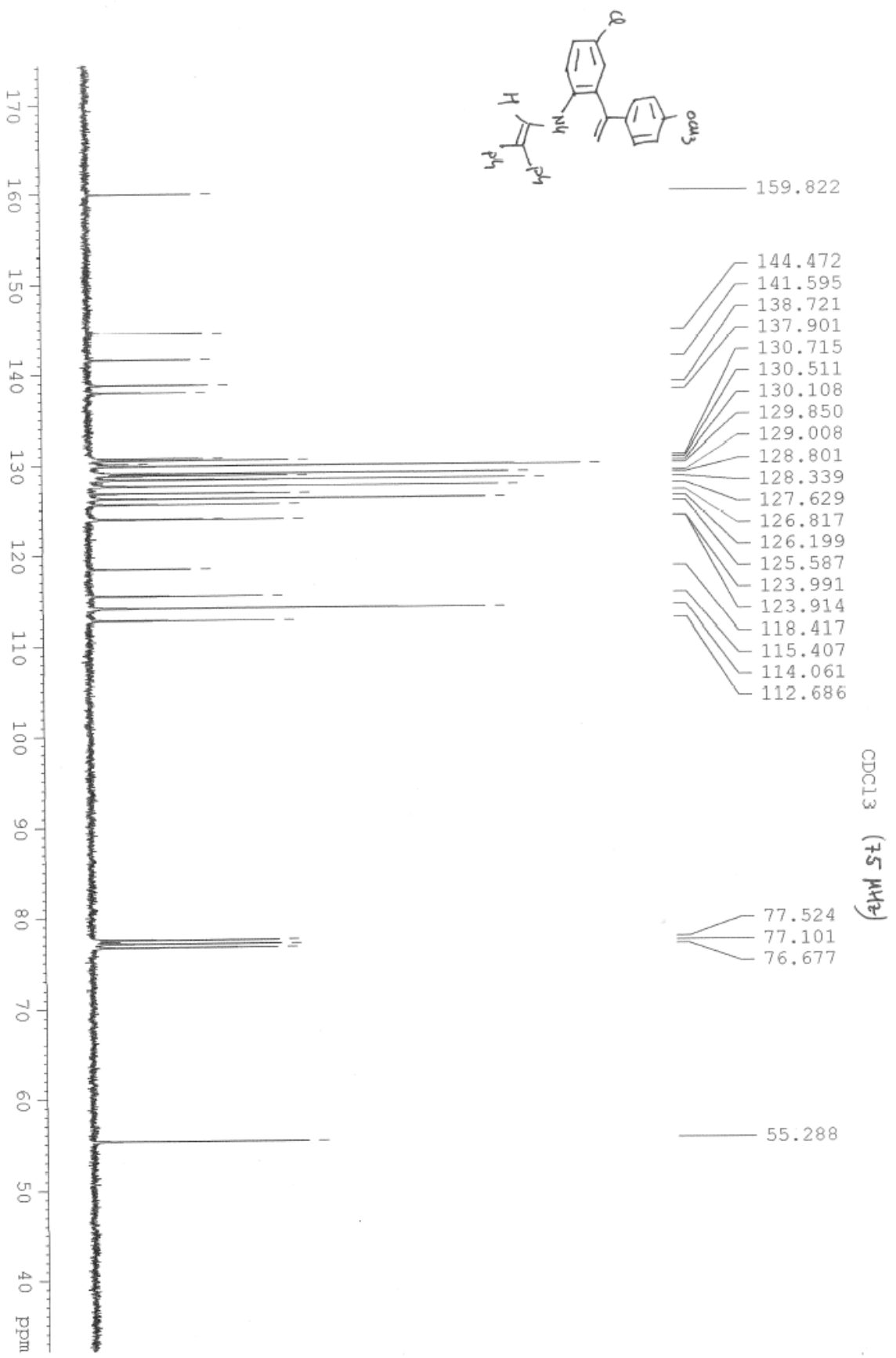
^{31}P NMR **27**



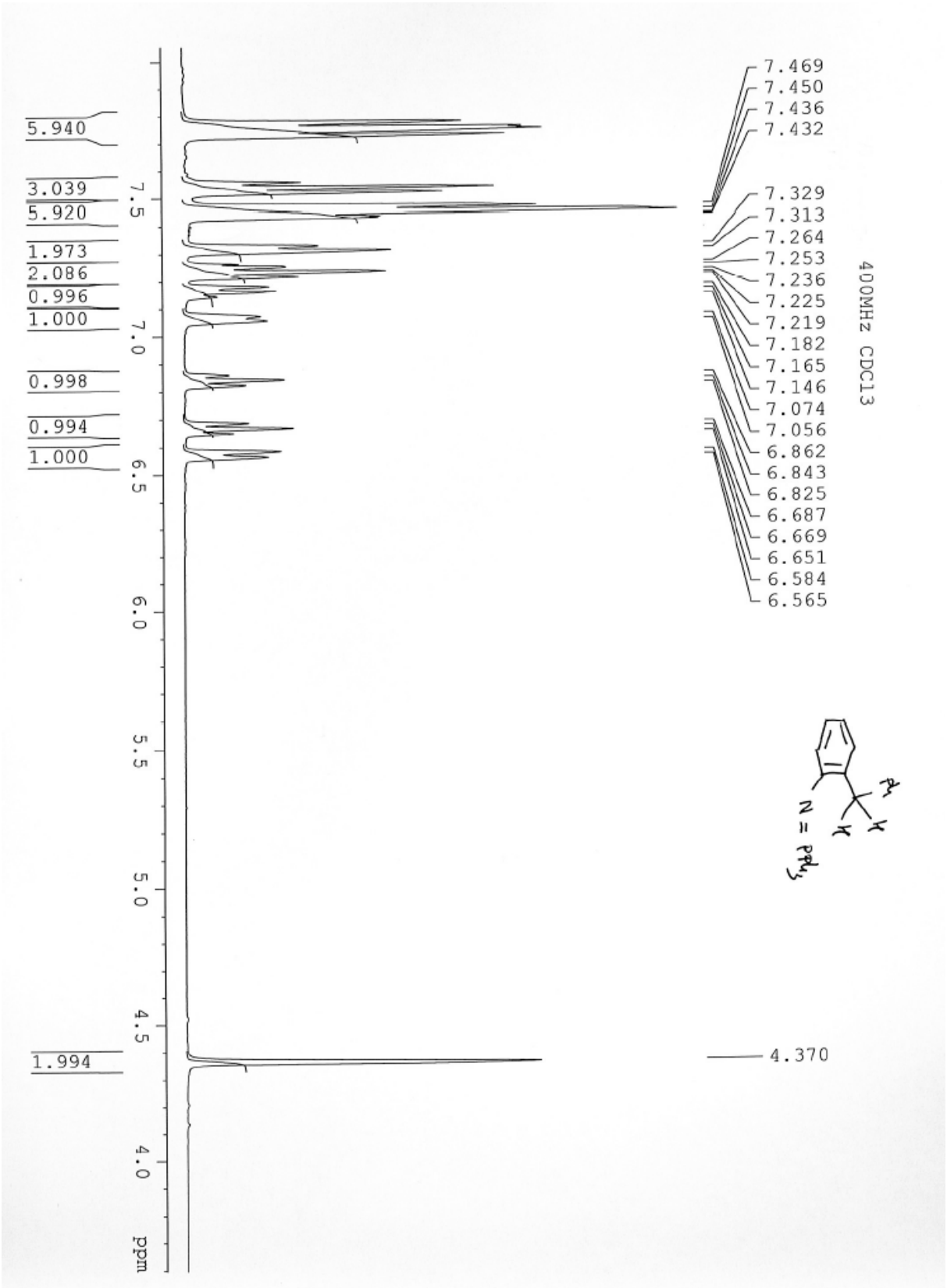
^{1}H NMR **30**


7.204
7.198
7.177
7.127
7.119
7.117
7.112
7.104
7.099
7.093
7.090
7.082
7.041
7.031
7.024
7.008
7.001
6.992
6.975
6.959
6.950
6.946
6.937
6.930
6.925
6.919
6.909
6.880
6.754
6.744
6.737
6.721
6.714
6.704
6.697
6.116
6.076
5.527
5.524
5.070
5.067
3.786
0.202
2.568
7.536
4.068
2.518
4.021
2.218
0.951
1.000
0.992
3.076
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
(300MHz) CDCl3
Cl
H
NH
Ph
Ph
OMe

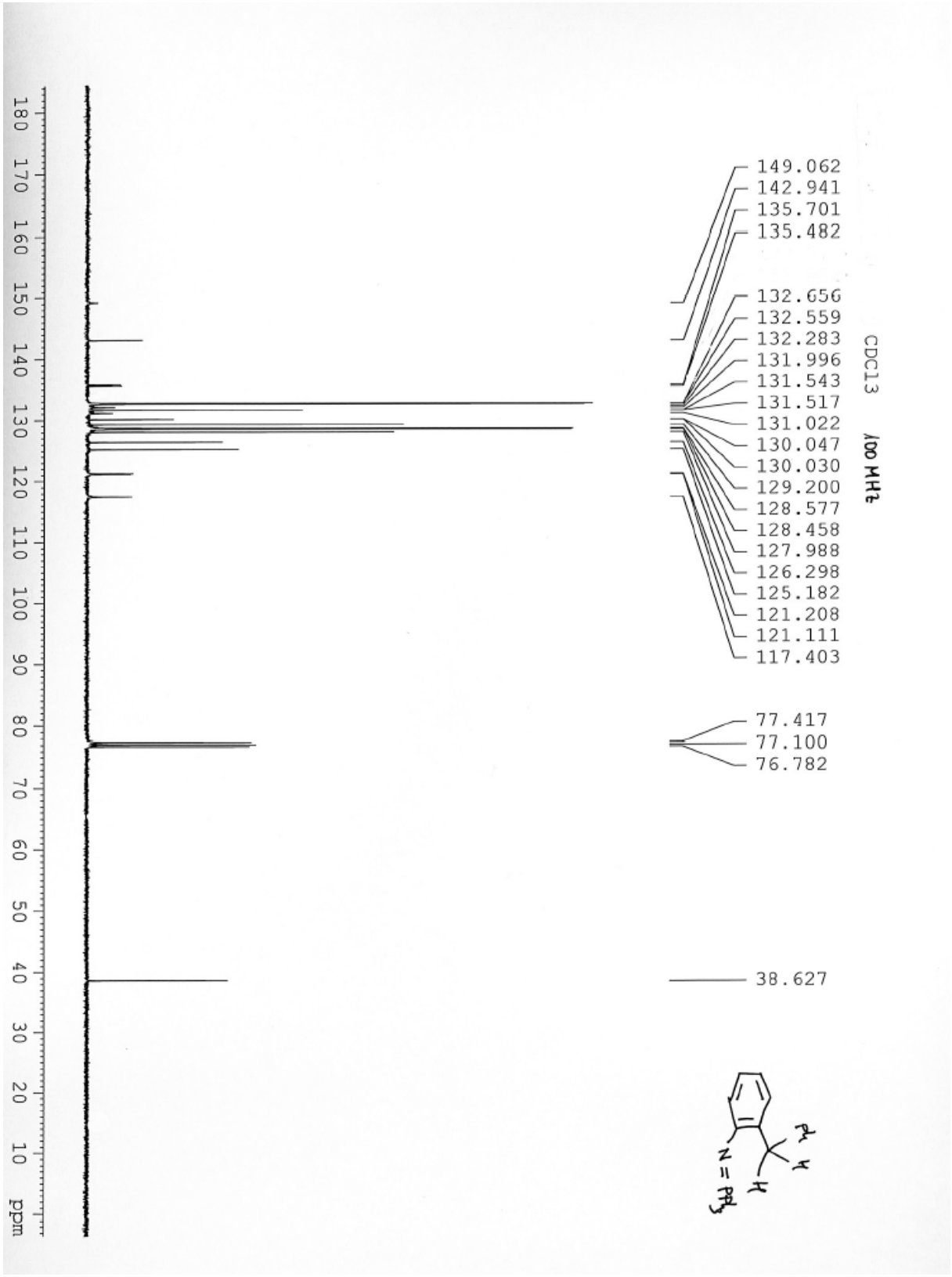
^{13}C NMR **30**


159.822
144.472
141.595
138.721
137.901
130.715
130.511
130.108
129.850
129.008
128.801
128.339
127.629
126.817
126.199
125.587
123.991
123.914
118.417
115.407
114.061
112.686
77.524
77.101
76.677
55.288
CDCl3 (75 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

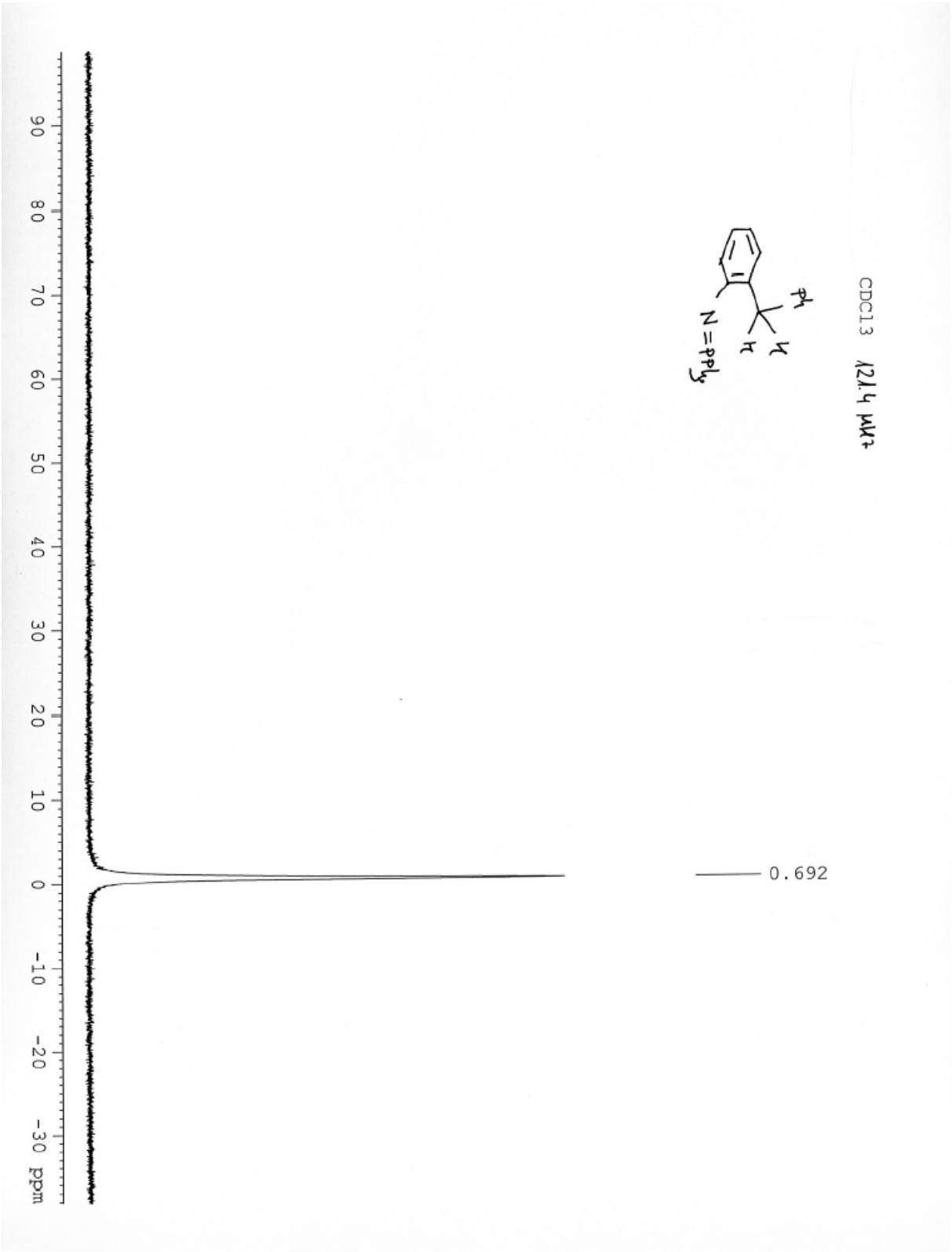
^{1}H NMR **32**


7.469
7.450
7.436
7.432
7.329
7.313
7.264
7.253
7.236
7.225
7.219
7.182
7.165
7.146
7.074
7.056
6.862
6.843
6.825
6.687
6.669
6.651
6.584
6.565
400MHz CDCl3
5.940
3.039
5.920
1.973
2.086
0.996
1.000
0.998
0.994
1.000
1.994
4.370
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm
N = PPh3

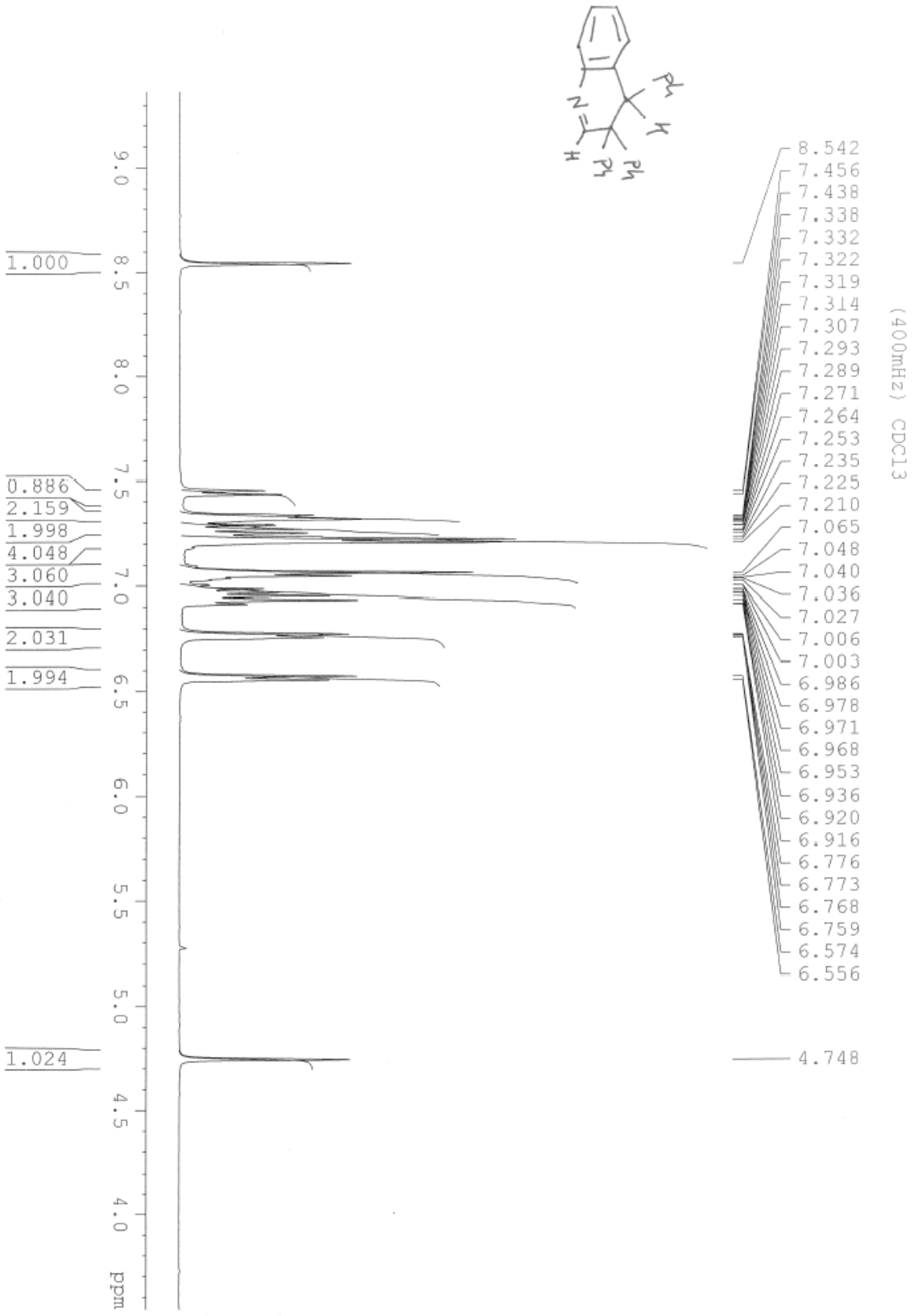
^{13}C NMR **32**


149.062
142.941
135.701
135.482
132.656
132.559
132.283
131.996
131.543
131.517
131.022
130.047
130.030
129.200
128.577
128.458
127.988
126.298
125.182
121.208
121.111
117.403
77.417
77.100
76.782
38.627
CDCl3 100 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

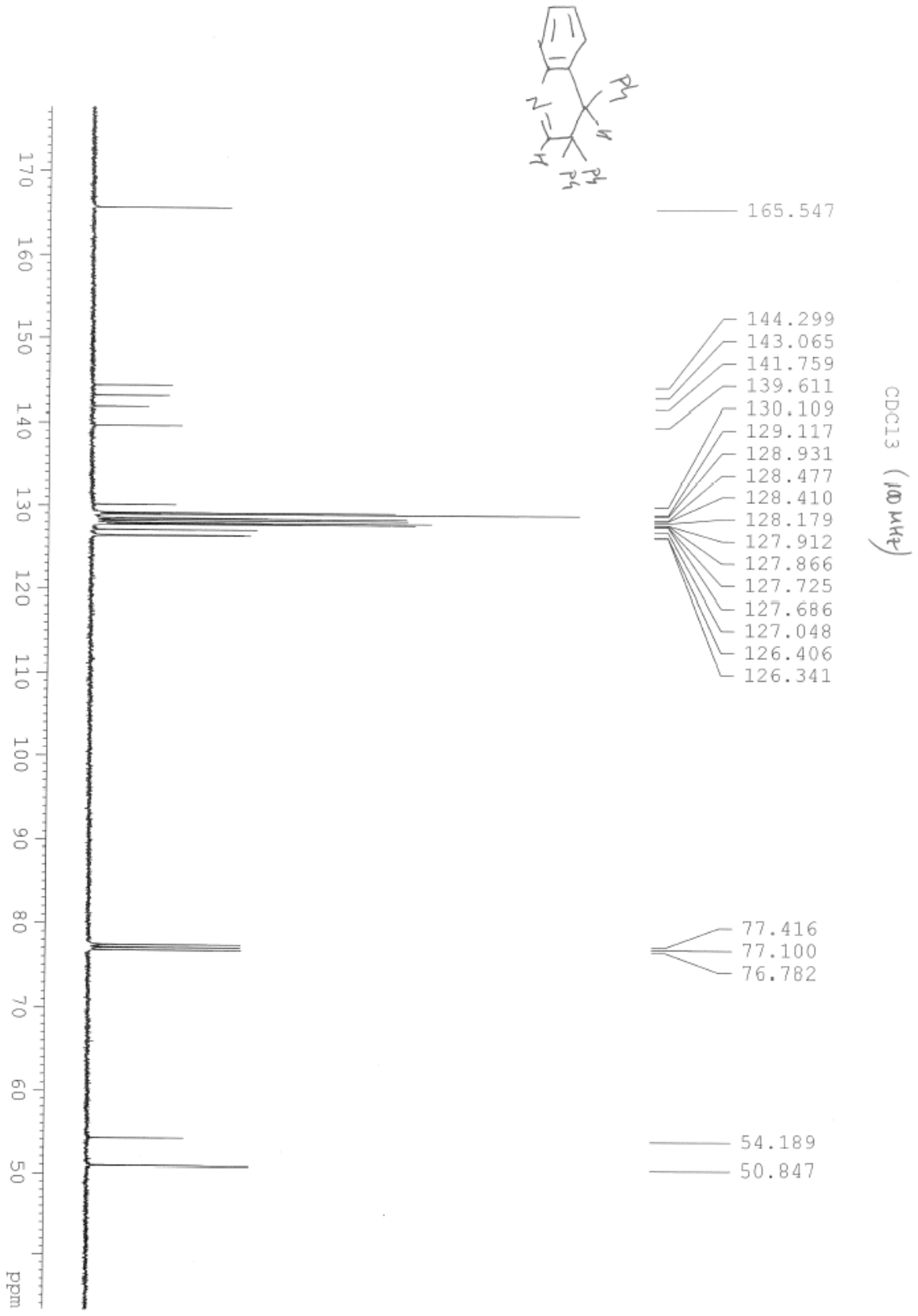
^{31}P NMR **32**


CDCl3 121.4 MHz
Ph
H
H
N=PPh3
0.692
90
80
70
60
50
40
30
20
10
0
-10
-20
-30 ppm

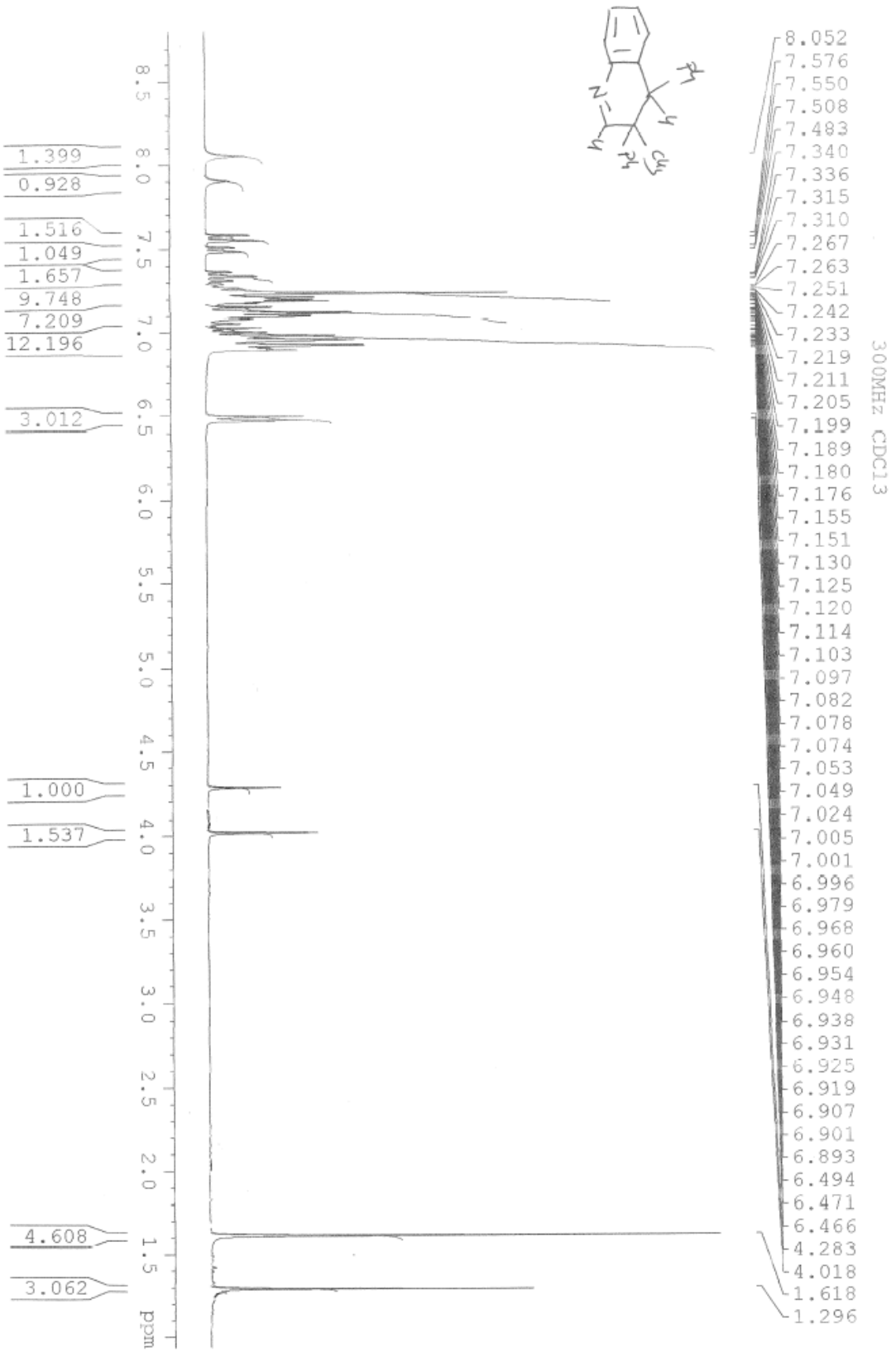
^{1}H NMR **34a**


8.542
7.456
7.438
7.338
7.332
7.322
7.319
7.314
7.307
7.293
7.289
7.271
7.264
7.253
7.235
7.225
7.210
7.065
7.048
7.040
7.036
7.027
7.006
7.003
6.986
6.978
6.971
6.968
6.953
6.936
6.920
6.916
6.776
6.773
6.768
6.759
6.574
6.556
4.748
(400mHz) CDCl3
1.000
0.886
2.159
1.998
4.048
3.060
3.040
2.031
1.994
1.024
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm

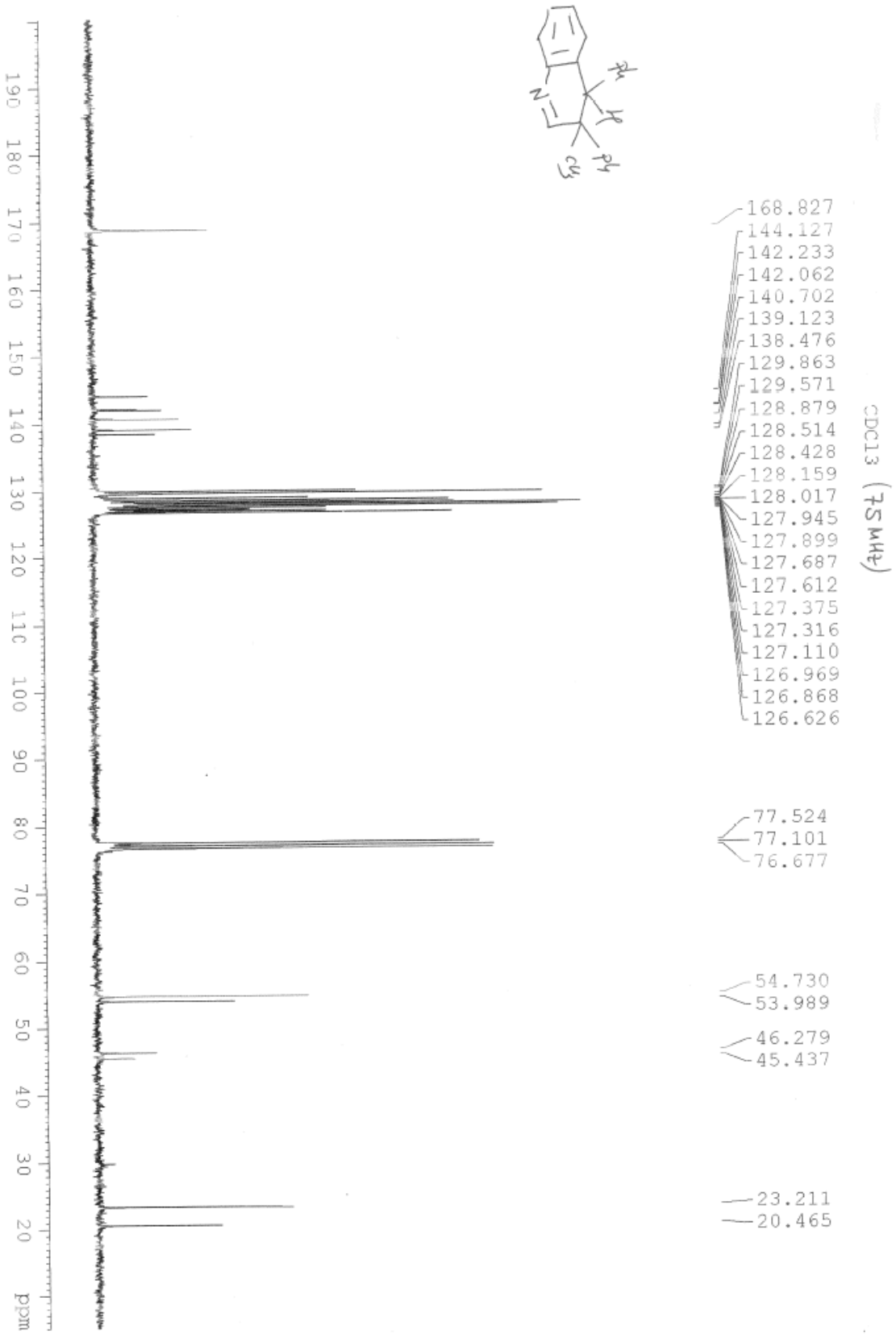
^{13}C NMR **34a**


165.547
144.299
143.065
141.759
139.611
130.109
129.117
128.931
128.477
128.410
128.179
127.912
127.866
127.725
127.686
127.048
126.406
126.341
77.416
77.100
76.782
54.189
50.847
CDCl3 (100 MHz)
ppm

^{1}H NMR **34b**


8.052
7.576
7.550
7.508
7.483
7.340
7.336
7.315
7.310
7.267
7.263
7.251
7.242
7.233
7.219
7.211
7.205
7.199
7.189
7.180
7.176
7.155
7.151
7.130
7.125
7.120
7.114
7.103
7.097
7.082
7.078
7.074
7.053
7.049
7.024
7.005
7.001
6.996
6.979
6.968
6.960
6.954
6.948
6.938
6.931
6.925
6.919
6.907
6.901
6.893
6.494
6.471
6.466
4.283
4.018
1.618
1.296
300MHz CDC13
1.399
0.928
1.516
1.049
1.657
9.748
7.209
12.196
3.012
1.000
1.537
4.608
3.062
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

^{13}C NMR **34b**


Ru
N
Ph
Cy
168.827
144.127
142.233
142.062
140.702
139.123
138.476
129.863
129.571
128.879
128.514
128.428
128.159
128.017
127.945
127.899
127.687
127.612
127.375
127.316
127.110
126.969
126.868
126.626
CDCl3 (75 MHz)
77.524
77.101
76.677
54.730
53.989
46.279
45.437
23.211
20.465
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

References

[1] J. C. Cuevas, J. De Mendoza, P. Prados,. *J. Org. Chem.,* 1988, **53**, 2055-2066.

[2] H. E. Ungnade, E. W. Crandall, *J. Am. Chem. Soc.,* 1949, **71**, 2209-2210.

[3] R. N. Carde, G. Jones, W. H. McKinley, C Price, *J. Chem. Soc., Perkin Trans. 1,* 1978, 1211-1218.

[4] F. Bickelhaupt, C. Jongsma, P. De Koe, R. Lourens, N. R. Mast, G. L. Van Mourik, H. Vermeer, R. J. M. Weustink, *Tetrahedron,* 1976, **32**, 1921-1930.

[5] K. Marcsekova, S. Doye, *Synthesis,* 2007, 145-154.

[6] L. Krbechek, H. Takimoto, *J. Org. Chem.,* 1968, **33**, 4286-4288.

[7] H. Pracejus, G. Wallura, *J. Prakt. Chem. (Leipzig),* 1962, **19**, 33-36.

[8] L. M: Baigrie, H. R. Seiklay, T. T. Tidwell, *J. Am. Chem. Soc.,* 1985, **107**, 5391-5396.

[9] E. C. Taylor, A. McKillop, G. H. Hawks, *Org. Synth.,* 1972, **52**, 36-38.