Supporting Information for:

Nickel-catalyzed synthesis of tetrasubstituted vinyl sulfides from thiocarbamates and alkynes

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Contents

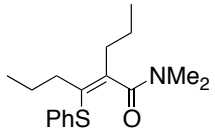
Instrumentation and Chemicals

All manipulations of oxygen- and moisture-sensitive materials were conducted in a dry box or with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on Varian UNITY INOVA 500 (^{1}H, 500 MHz; ^{13}C, 125.7 MHz) spectrometer using tetramethylsilane (^{1}H) as an internal standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), integration, and identification. High-resolution mass spectra were obtained with a Thermo Fisher SCIENTIFIC EXACTIVE spectrometer. Infrared spectra (IR) spectra were determined on a SHIMADZU IRAffinity-1 spectrometer. Melting points were determined using a YANAKO MP-500D. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} (0.25 mm) Plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating. Flash column chromatography was carried out using Kanto Chemical silica gel (spherical, 40–50 μm). Unless otherwise noted, commercially available reagents were used without purification. Toluene was purchased from Wako Pure Chemical Co. stored over slices of sodium. Tripropylphosphine was also purchased from Wako Pure Chemical Co. Bis(1,5-cyclooctadiene)nickel was purchased from Strem Chemicals, Inc.

Experimental Procedure and Characterization Data for Products.

General procedure. The reaction was performed in a 20 mL round-bottomed flask equipped with a Teflon-coated magnetic stirrer bar and Dimrotho reflux condenser. The top of condenser was connected with a balloon filled with argon gas (ca. 1 atm). A thiocarbamate (1.0 mmol) and an alkyne (2.0 mmol) were added to a solution of bis(1,5-dicyclooctadiene)nickel (0.10 mmol) and tripropylphosphine (0.40 mmol) in toluene (0.5 mL) in a dry box. The flask was taken outside the dry box and heated at 130 °C for the indicated time under argon atmosphere. The resulting reaction mixture was cooled to ambient temperature and filtered through a silica gel pad, concentrated in vacuo. The residue was purified by flash silica gel column chromatography (20 g, 2x15 cm, hexane/ethyl acetate = 3:1) to give the corresponding product.

(*Z*)-*N*,*N*-dimethyl-3-(phenylthio)-2-propylhex-2-enamide (**3aa**).



Yield: 84% (243.4 mg), pale yellow oil.

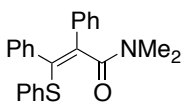
^{1}H NMR ($CDCl_3$) δ 7.34−7.32 (m, 2H; Ar−H), 7.27−7.24 (m, 2H; Ar−H), 7.19 (tt, *J* =7.0, 1.5 Hz, 1H; Ar—H), 3.00 (s, 3H; N–Me), 2.99 (s, 3H; N–Me), 2.44–2.10 (br, 4H; $2CH_2$), 1.58–1.50, 4H; $2CH_2$), 0.98 (t, *J* = 7.5 Hz,3H; Me), 0.86 (t *J* = 7.5 Hz, 3H; Me).

^{13}C NMR ($CDCl_3$) δ 170.9, 142.1, 134.5, 131.4, 130.7, 128.8, 126.6, 37.7, 34.0, 33.8, 32.9, 21.7, 21.6, 14.3, 13.8.

IR (neat): 2960, 2931, 2871, 1636, 1508, 1490, 1457, 1335 cm^{-1}.

HRMS (ESI+) found 292.1724, calcd for[M+H]+292.1730.

(*Z*)-*N*,*N*-dimethyl-2,3-diphenyl-3-(phenylthio)acrylamide (**3ab**).



Yield: 80% (288.7 mg), colorless crystal (m.p. 130–133 ºC).

^{1}H NMR ($CDCl_3$) δ 7.29–7.27 (m, 2H; Ar–H), 7.25–7.23 (m, 2H; Ar–H), 7.20–7.18

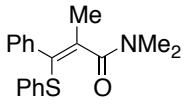
(m, 2H; Ar–H), 7.15–7.13 (m, 3H; Ar–H), 7.10–7.06 (m, 2H; Ar–H), 7.05–7.01 (m, 4H; Ar–H), 3.07 (s, 3H; N–Me), 3.06 (s, 3H; N–Me).

^{13}C NMR ($CDCl_3$) δ 169.8, 140.1, 136.6, 135.7, 134.4, 133.0, 131.6, 130.7, 129.2, 128.5, 128.2, 127.8, 127.7, 127.6, 126.9, 37.5, 34.4.

IR (KBr): 3061, 1637, 1581, 1491, 1479, 1439, 1396, 1147, 756, 742, 698, 689, 558 cm^{-1}.

HRMS (ESI+) found 360.1408, calcd for[M+H]+360.1417.

(*Z*)-*N*,*N*,2-trimethyl-3-phenyl-3-(phenylthio)acrylamide (**3ac**).



Yield: 39% (114.8 mg), dark red oil.

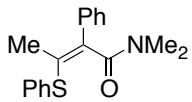
^{1}H NMR ($CDCl_3$) δ 7.48–7.46 (m, 2H; Ar–H), 7.44–7.42 (m, 2H; Ar–H), 7.38–7.35 (m, 2H; Ar–H), 7.34–7.25 (m, 4H; Ar–H), 3.03 (s, 3H; NMe_2), 3.01 (s, 3H; NMe_2), 1.94 (s, 3H; C=CCH_3).

^{13}C NMR ($CDCl_3$) δ 169.7, 139.8, 135.9, 133.3, 132.3, 130.8, 129.0, 128.7, 128.4, 127.8, 127.5, 37.6, 34.4, 19.9.

IR (neat): 2923, 1734, 1624, 1559, 1507, 1490, 1474, 1457, 1396 cm^{-1}.

HRMS (ESI+) found 298.1255, calcd for[M+H]+298.1260.

(*Z*)-*N*,*N*-dimethyl-2-phenyl-3-(phenylthio)but-2-enamide (**3ac'**).



Yield: 40% (119.3 mg), yellow solid (m.p. 109–111 ºC).

^{1}H NMR ($CDCl_3$) δ 7.30–7.28 (m, 2H; Ar–H), 7.22–7.17 (m, 4H; Ar–H), 7.15 (tt, *J* = 7.0, 1.5 Hz, 1H; Ar–H), 7.09–7.02 (m, 3H; Ar–H), 3.14 (s, 3H; NMe_2), 3.07 (s, 3H; NMe_2), 1.97 (s, 3H; C=CCH_3).

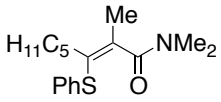
^{13}C NMR ($CDCl_3$) δ 171.3, 137.2, 136.9, 133.7, 131.7, 131.3, 129.6, 128.5, 127.9, 127.6, 126.7, 37.5, 34.2, 18.5.

IR (KBr): 3053, 2916, 1625, 1578, 1479, 1438, 1397, 1099, 742, 701, 692

cm^{-1}.

HRMS (ESI+) found 298.1256, calcd for[M+H]+298.1260.

(*Z*)-*N*,*N*,2-trimethyl-3-(phenylthio)oct-2-enamide (**3ad**).



Yield: 43% (125.9 mg), orange oil.

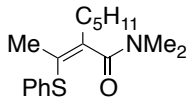
^{1}H NMR ($CDCl_3$) δ 7.33–7.31 (m, 2H; Ar–H), 7.29–7.25 (m, 2H; Ar–H), 7.20 (tt, *J* = 7.5, 2.5 Jz, 1H; Ar–H), 3.03 (s, 3H; N*Me*$_2$), 3.00 (s, 3H; N*Me*$_2$), 2,34 (br, 2H; C=CC*H*$_2$), 1.91 (s, 3H; C=CC*H*$_3$), 1.54–1.47 (m, 2H; C*H*$_2$), 1.34–1.31 (m, 4H; C*H*$_2$C*H*$_2$), 0.90 (t, *J* = 7.0 Hz, 3H; C*H*$_3$).

^{13}C NMR ($CDCl_3$) δ 171.0, 141.0, 134.3, 130.9, 128.9, 126.8, 126.4, 37.7, 34.1, 32.1, 32.0, 27.6, 22.4, 18.7, 14.0.

IR (neat): 2954, 2928, 2870, 1638, 1560, 1507, 1457, 1395 cm^{-1}.

HRMS (ESI+) found 292.1724, calcd for[M+H]+292.1730.

(*Z*)-*N*,*N*-dimethyl-2-(1-(phenylthio)ethylidene)heptanamide (**3ad'**).



Yield: 40% (117.2 mg), brown solid (59–61).

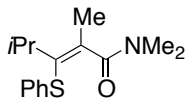
^{1}H NMR ($CDCl_3$) δ 7.34–7.32 (m, 2H; Ar–H), 7.28–7.24 (m, 2H; Ar–H), 7.19 (tt, *J* = 7.5, 1.5 Hz, 1H; Ar–H), 2.991 (s, 3H; N*Me*$_2$), 2.990 (s, 3H; N*Me*$_2$), 2.17 (br, 2H; C=CC*H*$_2$), 1.99 (s, 3H; C=C*Me*), 1.50 (pent, *J* = 2.5 Hz, 2H; C*H*$_2$), 1.26 (m, 4H; C*H*$_2$C*H*$_2$), 0.85 (t, *J* = 7.0 Hz, 3H; C*H*$_3$).

^{13}C NMR ($CDCl_3$) δ 171.6, 137.0, 134.5, 131.5, 130.9, 128.8, 126.7, 37.5, 34.1, 31.4, 31.1, 27.7, 22.4, 16.9, 13.9.

IR (KBr): 2952, 2922, 2854, 1628, 1472, 1397, 1137, 748, 692 cm^{-1}.

HRMS (ESI+) found 292.1724, calcd for[M+H]+292.1730.

(*Z*)-*N*,*N*,2,4-tetramethyl-3-(phenylthio)pent-2-enamide (**3ae**).



Yield: 36% (95.1 mg), brown solid (m.p. 48–50 °C).

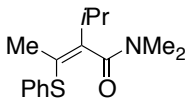
^{1}H NMR ($CDCl_3$) δ 7.43–7.41 (m, 2H; Ar–H), 7.22 (tt, *J* = 7.5, 2.0 Hz, 2H; Ar–H), 7.12 (tt, *J* = 7.5, 2.0 Hz, 1H; Ar–H), 3.03 (sept, *J* = 2.0 Hz, 1H; C*H*(CH_3)$_2$) 2.92 (s, 3H; NMe_2), 2.90 (s, 3H; NMe_2), 2.05 (s, 3H; C=CCH_3), 1.11 (d, *J* = 7.0 Hz, 3H; CH(C*H*$_3$)$_2$), 0.86 (d, *J* = 7.0 Hz, 3H; CH(C*H*$_3$)$_2$).

^{13}C NMR ($CDCl_3$) δ 171.5, 141.0, 136.7, 135.6, 129.6, 128.6, 126.0, 37.3, 34.0, 32.4, 21.5, 21.0, 16.8.

IR (KBr): 2971, 2936, 1623, 1468, 1395, 1361, 759 cm^{-1}.

HRMS (ESI+) found 264.1414, calcd for[M+H]+264.1417.

(*Z*)-2-isopropyl-*N*,*N*-dimethyl-3-(phenylthio)but-2-enamide (**3ae'**).



Yield: 34% (89.3 mg), brown solid (m.p. 67–68 °C).

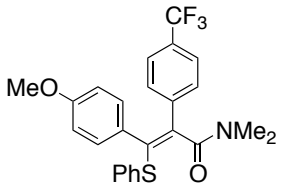
^{1}H NMR ($CDCl_3$) δ 7.32–7.30 (m, 2H; Ar–H), 7.29–7.25 (m, 2H; Ar–H), 7.20 (tt, *J* = 7.5, 2.0 Hz, 1H; Ar–H), 3.03 (s, 3H; N*Me*$_2$), 3.00 (s, 3H; N*Me*$_2$), 2.90 (sept, *J* = 2.0 Hz, 1H; C*H*(CH_3)$_2$), 1.93 (s, 3H; C=CC*H*$_3$), 1.25 (d, *J* = 7.0 Hz, 3H; CH(C*H*$_3$)$_2$), 1.08 (d, *J* = 7.0 Hz, 3H; CH(C*H*$_3$)$_2$).

^{13}C NMR ($CDCl_3$) δ 169.5, 146.1, 134.4, 130.7, 128.9, 126.7, 125.4, 38.1, 33.8, 31.0, 22.5, 19.9, 18.5.

IR (KBr): 2969, 2957, 2922, 1641, 1580, 1480, 1439, 1136, 1022, 752, 692 cm^{-1}.

HRMS (ESI+) found 264.1413, calcd for[M+H]+164.1417.

(*Z*)-3-(4-methoxyphenyl)-*N*,*N*-dimethyl-3-(phenylthio)-2-(4-(trifluoromethyl)phenyl)acrylamide (**3af**).



Yield: 34% (154.6 mg), white solid.

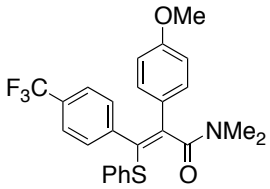
^{1}H NMR ($CDCl_3$) δ 7.38–7.36 (m, 2H; Ar–H), 7.31–7.28 (m, 4H; Ar–H), 7.12–7.08 (m, 4H; Ar–H), 7.07–7.04 (m, 1H; Ar–H), 6.70–6.67 (m, 2H; Ar–H), 3.75 (s, 3H; O*Me*), 3.07 (s, 3H; N*Me*$_2$), 3.02 (s, 3H; N*Me*$_2$).

^{13}C NMR ($CDCl_3$) δ 169.6, 159.4, 142.1, 141.1, 132.6, 131.5, 130.9, 130.5, 129.4, 128.7, 127.2, 124.8 (q, J = 3.9 Hz), 113.9, 55.2, 37.5, 34.4.

IR (KBr): 2933, 1733, 1635, 1511, 1323, 1251, 1125, 1109, 1067 cm^{-1}.

HRMS (ESI+) found 458.1392, calcd for[M+H]+458.1396.

(*Z*)-2-(4-methoxyphenyl)-*N*,*N*-dimethyl-3-(phenylthio)-3-(4-(trifluoromethyl)phenyl)acrylamide (**3af'**).



Yield: 38% (175.2 mg), brown solid.

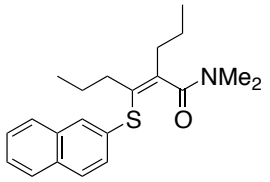
^{1}H NMR ($CDCl_3$) δ 7.40 (d, J = 8.5 Hz, 2H; Ar–H), 7.31–7.26 (m, 4H; Ar–H), 7.16–7.13 (m, 2H; Ar–H), 7.11–7.03 (m, 3H; Ar–H), 6.59–6.56 (m, 2H; Ar–H), 3.67 (s, 3H; O*Me*), 3.10 (s, 3H; N*Me*$_2$), 3.03 (s, 3H; N*Me*$_2$).

^{13}C NMR ($CDCl_3$) δ 169.4, 159.3, 139.70, 139.69, 136.9, 136.8, 132.6, 132.0, 131.6, 129.4, 129.1 (q, J = 32.4 Hz), 128.6, 127.9, 127.0, 125.2 (q, J = 3.9 Hz), 123.9 (q, J = 270.5 Hz), 113.4, 55.0, 37.5, 34.4.

IR (KBr): 1633, 1624, 1606, 1507, 1324, 1251, 1150, 1180, 1166, 1125, 1067 cm^{-1}.

HRMS (ESI+) found 458.1393, calcd for[M+H]+458.1396.

(*Z*)-*N*,*N*-dimethyl-3-(naphthalen-2-ylthio)-2-propylhex-2-enamide (**3ba**).



Yield: 79% (270.1 mg), pale yellow oil.

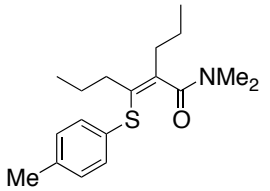
^{1}H NMR ($CDCl_3$) δ 7.80–7.73 (m, 4H; Ar–H), 7.47–7.42 (m, 3H; Ar–H), 3.04 (s, 3H; NCH_3), 3.01 (s, 3H; NCH_3), 2.49–2.13 (m, 4H; H_2CC=CCH_2), 1.60–1.54 (m, 4H; 2CH_2), 1.00 (t, J = 7.5 Hz, 3H; CH_3), 0.85 (t, J = 7.5 Hz, 3H; CH_3).

^{13}C NMR ($CDCl_3$) δ 170.9, 142.3, 133.9, 132.2, 132.0, 131.4, 129.2, 128.5, 128.4, 127.7, 127.3, 126.4, 125.9, 37.7, 34.1, 33.8, 33.0, 21.7, 21.6, 14.3, 13.8.

IR (neat): 2961, 2930, 1638, 1623, 1559, 1506, 1457 cm^{-1}.

HRMS (ESI+) found 342.1881, calcd for[M+H]+342.2886.

(Z)-N,N-dimethyl-2-propyl-3-(p-tolylthio)hex-2-enamide (**3ca**).



Yield: 79% (241.3 mg), pale yellow oil.

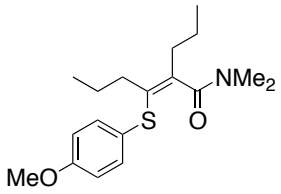
^{1}H NMR ($CDCl_3$) δ 7.26–7.23 (m, 2H; Ar–H), 7.08–7.06 (m, 2H; Ar–H), 3.01 (s, 3H; NCH_3), 2.99 (s, 3H; NCH_3), 2.43–2.08 (m, 4H; H_2CC=CCH_2), 2.31 (s, 3H; Ar–CH_3), 1.56–1.48 (m, 4H; 2CH_2), 0.96 (t, J = 7.5 Hz, 3H; CH_3), 0.85 (t, J = 7.5 Hz, 3H; CH_3).

^{13}C NMR ($CDCl_3$) δ 171.1, 140.8, 136.8, 132.0, 131.4, 130.6, 129.6, 37.7, 34.0, 33.8, 32.7, 21.7, 21.6, 21.1, 14.3, 13.8.

IR (neat): 2960, 2931, 2871, 1635, 1429, 1457, 1395, 1133, 809, 754 cm^{-1}.

HRMS (ESI+) found 306.1880, calcd for[M+H]+306.1886.

(*Z*)-3-((4-methoxyphenyl)thio)-*N*,*N*-dimethyl-2-propylhex-2-enamide (**3da**).



Yield: 78% (249.5 mg), pale yellow solid (m.p. 62–64 ºC).

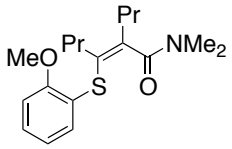
^{1}H NMR ($CDCl_3$) δ 7.35–7.31 (m, 2H; Ar–H), 6.83–6.80 (m, 2H; Ar–H), 3.78 (s, 3H; O*Me*), 3.02 (s, 3H; NMe_2), 3.00 (s, 3H; NMe_2), 2.38–2.04 (m, 4H; H_2CC=CCH_2), 1.55–1.47 (m, 4H; 2CH_2), 0.95 (t, *J* = 7.5 Hz, 3H; C*H3*), 0.84 (t, *J* = 7.5 Hz, 3H; C*H3*).

^{13}C NMR ($CDCl_3$) δ 171.2, 159.3, 139.4, 140.0, 132.9, 124.5, 114.5, 55.3, 37.7, 34.1, 33.8, 32.5, 21.6, 14.3, 13.8.

IR (KBr): 2968, 2960, 2931, 1623, 1492, 1395, 1283, 1247, 1024, 821 cm^{-1}.

HRMS (ESI+) found 322.1829, calcd for[M+H]+322.1835.

(*Z*)-3-((2-methoxyphenyl)thio)-*N*,*N*-dimethyl-2-propylhex-2-enamide (**3ea**).



Yield: 72% (230.8 mg), pale yellow liquid.

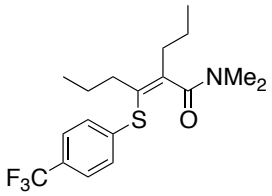
^{1}H NMR ($CDCl_3$) δ 7.23 (dd, *J* = 7.5, 1.5 Hz, 1H; Ar–H), 7.16 (ddd, *J* = 8.0, 7.5, 1.5 Hz, 1H; Ar–H), 6.99 (dt, *J* = 7.5, 1.0 Hz, 1H; Ar–H), 6.82 (dd, *J* = 8.0, 1.0 Hz, 1H; Ar–H), 3.84 (s, 3H; OCH_3), 3.00 (s, 3H; NMe_2), 2.97 (s, 3H; NMe_2), 2.45–2.17 (m, 4H; H_2C=CH_2), 1.59–1.51 (m, 4H; 2CH_2), 0.99 (t, *J* = 7.5 Hz, 3H; CH_3), 0.85 (t, *J* = 7.5 Hz, 3H; CH_3).

^{13}C NMR ($CDCl_3$) δ 170.8, 157.4, 142.3, 131.8, 130.6, 127.5, 123.0, 121.2, 110.7, 55.7, 37.6, 34.1, 33.9, 33.4, 21.9, 21.6, 14.3, 13.9.

IR (KBr): 2960, 2932, 2871, 1624, 1478, 1395, 1243 cm^{-1}.

HRMS (ESI+) found 322.1830, calcd for[M+H]+322.1835.

(*Z*)-*N*,*N*-dimethyl-2-propyl-3-((4-(trifluoromethyl)phenyl)thio)hex-2-enamide (**3fa**).



Yield: 37% (133.0 mg), pale yellow oil.

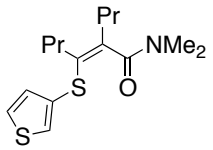
^{1}H NMR ($CDCl_3$) δ 7.50–7.48 (m, 2H; Ar–H), 7.39–7.37 (m, 2H; Ar–H), 2.97 3(s, 3H; N*Me*$_2$), 2.967 (s, 3H; N*Me*$_2$), 2.49–2.11 (m, 4H; *H*$_2$CC=CC*H*$_2$), 1.61–1.53 (m, 4H; 2C*H*$_2$), 1.00 (t, *J* = 7.5 Hz, 3H; C*H*$_3$), 0.89 (t, *J* = 7.5 Hz, 3H; C*H*$_3$).

^{13}C NMR ($CDCl_3$) δ 170.4, 145.8, 140.5, 129.5, 129.1, 128.2 (*J* = 32.5 Hz), 125.7 (*J* = 3.8 Hz), 123.1, 37.6, 34.0, 33.8, 33.6, 21.8, 21.6, 14.3, 13.8.

IR (neat): 2963, 2934, 2368, 1636, 1396, 1326, 1164, 1123, 1107, 1091, 1063 cm^{-1}.

HRMS (ESI+) found 360.1595, calcd for[M+H]+360.1603.

(*Z*)-*N*,*N*-dimethyl-2-propyl-3-(thiophen-3-ylthio)hex-2-enamide (**3ga**).



Yield: 76% (226.7 mg), pale yellow oil.

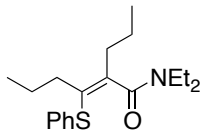
^{1}H NMR ($CDCl_3$) δ 7.29–7.27 (m, 2H; Ar–H), 7.03 (dd, *J* = 5.0, 1.0 Hz, 1H; Ar–H), 3.01 (s, 3H; N*Me*$_2$), 3.00 (s, 3H; N*Me*$_2$), 2.29–2.11 (m, 4H; *H*$_2$C=C*H*$_2$), 1,56–1,46 (m, 4H; 2C*H*$_2$), 0.95 (t, *J* = 7.5 Hz, 3H; C*H*$_3$), 0.86 (t, *J* = 7.5 Hz, 3H; C*H*$_3$)

^{13}C NMR ($CDCl_3$) δ 170.9, 139.5, 132.4, 131.2, 129.3, 126.8, 125.9, 37.7, 34.1, 33.8, 32.8, 21.6, 21.5, 14.2, 13.8.

IR (neat): 2959, 2931, 2871, 1632, 1492, 1457, 1395, 1132 cm^{-1}.

HRMS (ESI+) found 298.1289, calcd for[M+H]+298.1294.

(*Z*)-*N*,*N*-diethyl-3-(phenylthio)-2-propylhex-2-enamide (**3ha**).



Yield: 82% (263.2 mg), pale yellow oil.

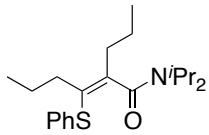
^{1}H NMR ($CDCl_3$) δ 7.36–7.34 (m, 2H; Ar–H), 7.27–7.23 (m, 2H; Ar–H), 7.18 (tt, *J* = 7.5, 2.0 Hz, 1H; Ar–H), 3.49–3.33 (m, 4H; N(CH_2CH_3)$_2$), 2.45–2.04 (m, 4H; H_2CC=CCH_2), 1.58–1.51 (m, 4H; 2CH_2), 1.18–1.16 (m, 6H; N(CH_2CH_3)$_2$), 0.98 (t, *J* = 7.0 Hz, 3H; CH_3), 0.85 (t, *J* = 7.5 Hz, 3H; CH_3).

^{13}C NMR ($CDCl_3$) δ 169.9, 142.8, 135.0, 131.2, 130.8, 128.8, 126.5, 42.0, 37.7, 33.9, 32.9, 21.74, 21.66, 14.3, 14.0, 13.7, 12.3.

IR (neat): 2962, 2933, 1623, 1617, 1559, 1507, 1473, 1457 cm^{-1}.

HRMS (ESI+) found 320.2037, calcd for[M+H]+320.2043.

(*Z*)-*N*,*N*-diisopropyl-3-(phenylthio)-2-propylhex-2-enamide (**3ia**).



Yield: 50% (173.8 mg), pale yellow solid (m.p. 62–65 ºC).

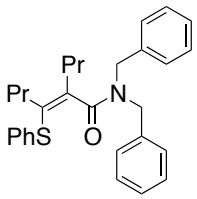
^{1}H NMR ($CDCl_3$) δ 7.37–7.34 (m, 2H; Ar–H), 7.27–7.23 (m, 2H; Ar–H), 7.16 (t, *J* = 7.5 Hz, 1H; Ar–H), 3.97 (sept, *J* = 7.0 Hz, 1H; NC*H*), 3.37 (sept, *J* = 7.0 Hz, 1H; NC*H*), 2.48–2.42 (m, 1H; C=CCH_2), 2.23–2.19 (m, 1H; C=CCH_2), 2.07–2.02 (m, 2H; H_2CC=CCH_2), 1.67–1.53 (m, 4H; 2CH_2), 1.48 (d, *J* = 7.0 Hz, 3H; NCHCH_3), 1.45 (d, *J* = 7.0 Hz, 3H; NCHCH_3), 1.20 (d, *J* = 7.0 Hz, 3H; NCHCH_3), 1.17 (d, *J* = 7.0 Hz, 3H; NCHCH_3), 0.98 (t, *J* = 7.5 Hz, 3H; CH_3), 0.84 (t, *J* = 7.5 Hz, 3H; CH_3).

^{13}C NMR ($CDCl_3$) δ 169.4, 144.2, 135.5, 130.3, 128.7, 126.2, 50.2, 45.5, 33.6, 32.7, 21.7, 21.6, 21.3, 21.0, 20.6, 20.1, 14.3, 13.6.

IR (KBr): 2965, 2931, 2363, 1616, 1369, 1332 cm^{-1}.

HRMS (ESI+) found 348.2349, calcd for[M+H]+348.2356.

(*Z*)-*N*,*N*-dibenzyl-3-(phenylthio)-2-propylhex-2-enamide (**3ja**).



Yield: 45% (200.1 mg), white solid (m.p. 81–83 ºC).

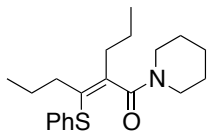
^{1}H NMR ($CDCl_3$) δ 7.34–7.35 (m, 2H; Ar–H), 7.33–7.32 (m, 2H; Ar–H), 7.30–7.28 (m, 1H; Ar–H), 7.27–7.18 (m, 10H; Ar–H), 4.73 (d, *J* = 14.5 Hz, 1H; NC*H*$_2$Ph), 4.45 (d, *J* = 10.0 Hz, 2H; NC*H*$_2$Ph), 4.37 (d, *J* = 15.5 Hz, 1H; NC*H*$_2$Ph), 2.53–2.48 (m, 1H; C*H*$_2$C=CCH$_2$), 2.27–2.21 (m, 1H; C*H*$_2$C=CCH$_2$), 2.11–2.10 (m, 2H; C*H*$_2$C=CC*H*$_2$), 1.74–1.69 (m, 1H; C*H*$_2$), 1.66–1.62 (m, 1H; C*H*$_2$), 1.52 (dq, *J* = 8.0, 7.0 Hz, 2H; 2C*H*$_2$), 1.00 (t, *J* = 7.5 Hz; C*H*$_3$), 0.81 (t, *J* = 7.5 Hz; C*H*$_3$).

^{13}C NMR ($CDCl_3$) δ 171.2, 142.1, 136.7, 136.0, 134.6, 132.6, 130.6, 128.9, 128.8, 128.7, 128.3, 127.7, 127.6, 127.2, 126.6, 50.6, 45.7, 33.8, 33.0, 22.1, 21.7, 14.2, 13.7.

IR (KBr): 2965, 1633, 1621, 1437, 1420, 1221, 749, 698 cm^{-1}.

HRMS (ESI+) found 444.2353, calcd for[M+H]+444.2356.

(*Z*)-3-(phenylthio)-1-(piperidin-1-yl)-2-propylhex-2-en-1-one (**3ka**).



Yield: 76% (252.3 mg), pale yellow oil.

^{1}H NMR ($CDCl_3$) δ 7.33–7.31 (m, 2H; Ar–H), 7.27–7.24 (m, 2H; Ar–H), 7.18 (tt, *J* = 7.5, 2.0 Hz, 1H; Ar–H), 3.71–3.68 (m, 1H; NC*H*$_2$), 3.55–3.50 (m, 1H; NC*H*$_2$), 2.40–3.36 (m, 2H; 2NC*H*$_2$), 2.48–2.43 (m, 1H; C=CC*H*$_2$), 2.27–2.17 (m, 2H; *H*$_2$CC=CC*H*$_2$), 2.11–2.05 (m, 1H; *H*$_2$CC=C), 1.63–1.51 (m, 10H; 2C*H*$_2$ + C*H*$_2$C*H*$_2$C*H*$_2$), 0.98 (t, *J* = 7.5 Hz, 3H; C*H*$_3$), 0.85 (t, *J* = 7.5 Hz, 3H; C*H*$_3$).

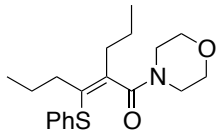
^{13}C NMR ($CDCl_3$) δ 169.2, 142.3, 134.9, 131.3, 130.6, 128.8, 126.5, 47.3, 41.8, 33.9,

32.9, 26.4, 25.4, 24.6, 21.75, 21.70, 14.3, 13.8.

IR (neat): 2960, 2936, 2870, 2857, 1624, 1437, 1284, 1228 748 cm^{-1}.

HRMS (ESI+) found 332.2035, calcd for[M+H]+332.2043.

(*Z*)-1-morpholino-3-(phenylthio)-2-propylhex-2-en-1-one (**3la**).



Yield: 85% (282.5 mg), colorless oil.

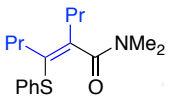
^{1}H NMR ($CDCl_3$) δ 7.32–7.30 (m, 2H; Ar–H), 7.28–7.25 (m, 2H; Ar–H), 7.20 (tt, *J* = 7.5, 2.0 Hz, 1H; Ar–H), 3.74–3.44 (m, 8H; N(C*H*$_2$C*H*$_2$)$_2$O), 2.45–2.11 (m, 4H; *H*$_2$CC=CC*H*$_2$), 1.57–1.53 (m, 4H; 2(C*H*$_2$)), 0.99 (t, *J* = 7.5Hz, 3H; C*H*$_3$), 0.85 (t, *J* = 7.5 Hz, 3H; C*H*$_3$).

^{13}C NMR ($CDCl_3$) δ 169.4, 141.2, 134.3, 132.4, 130.6, 129.0, 126.8, 66.8, 66.7, 46.7, 41.2, 33.9, 33.0, 21.8, 21.7, 14.3, 13.8.

IR (neat): 2961, 2930, 1636, 1457, 1430, 1424, 1115 cm^{-1}.

HRMS (ESI+) found 334.1828, calcd for[M+H]+334.1835.

^{1}H NMR and ^{13}C NMR Spectra of Products



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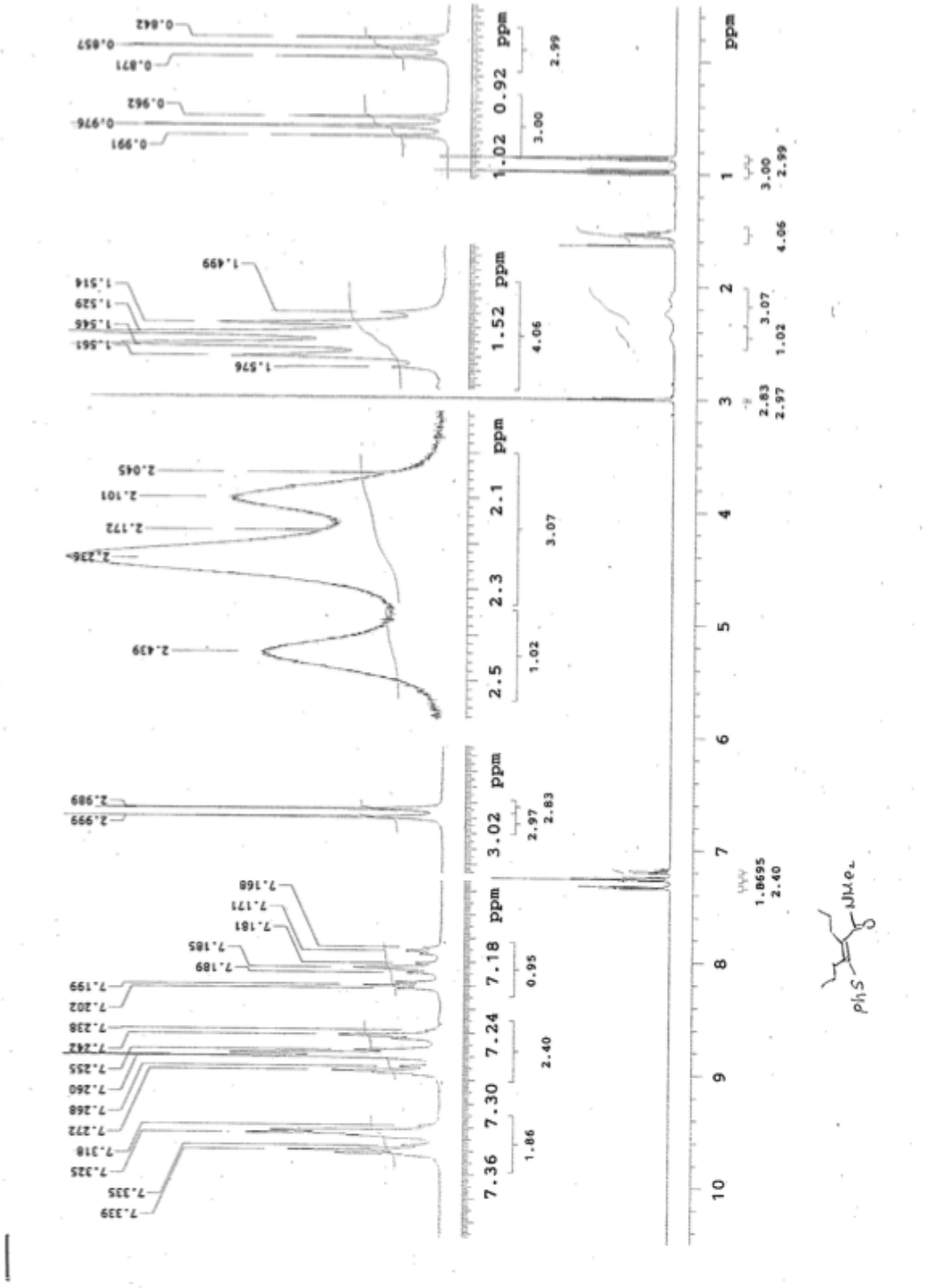

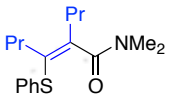
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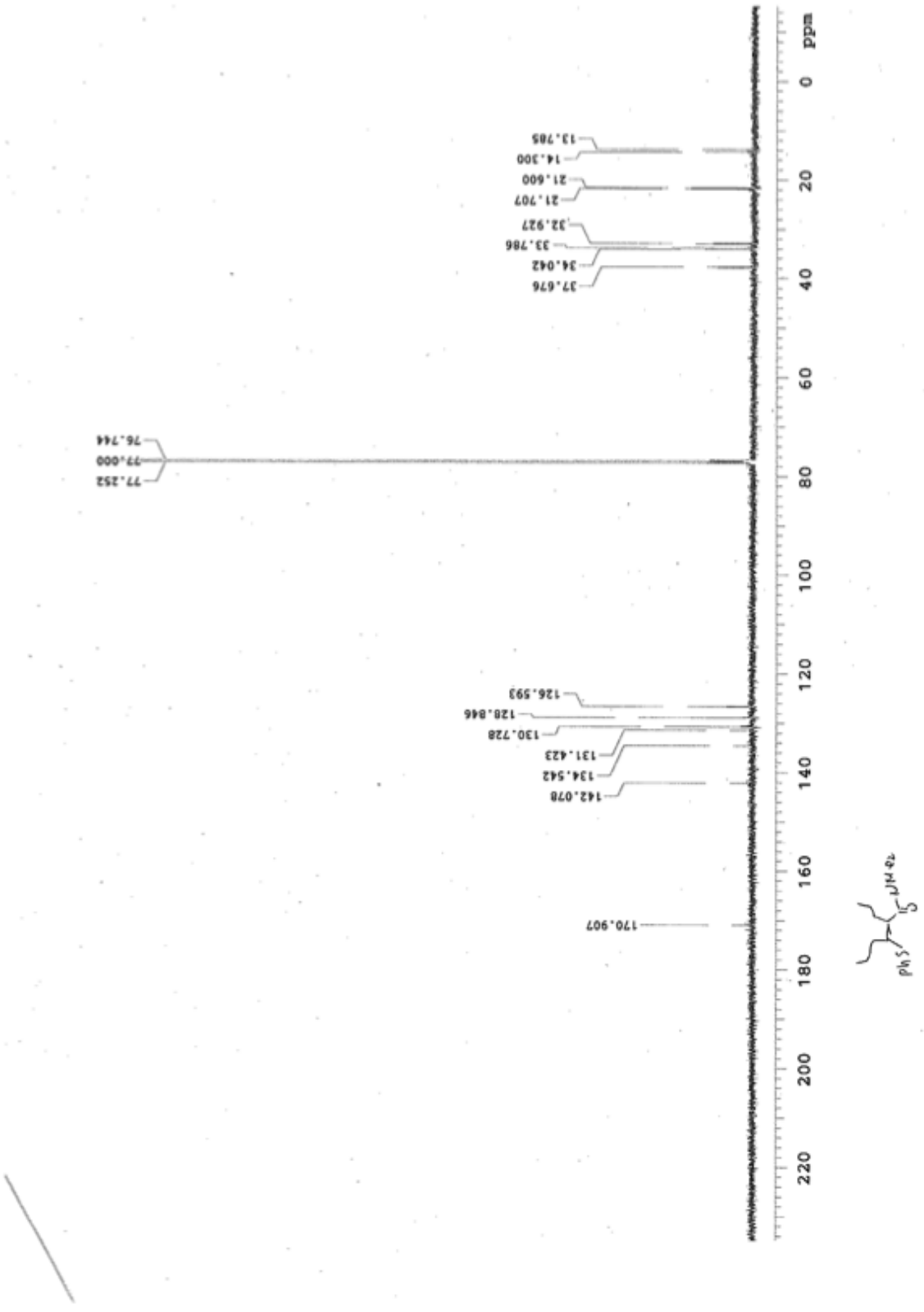
NMe2
PhS
O

3aa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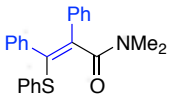
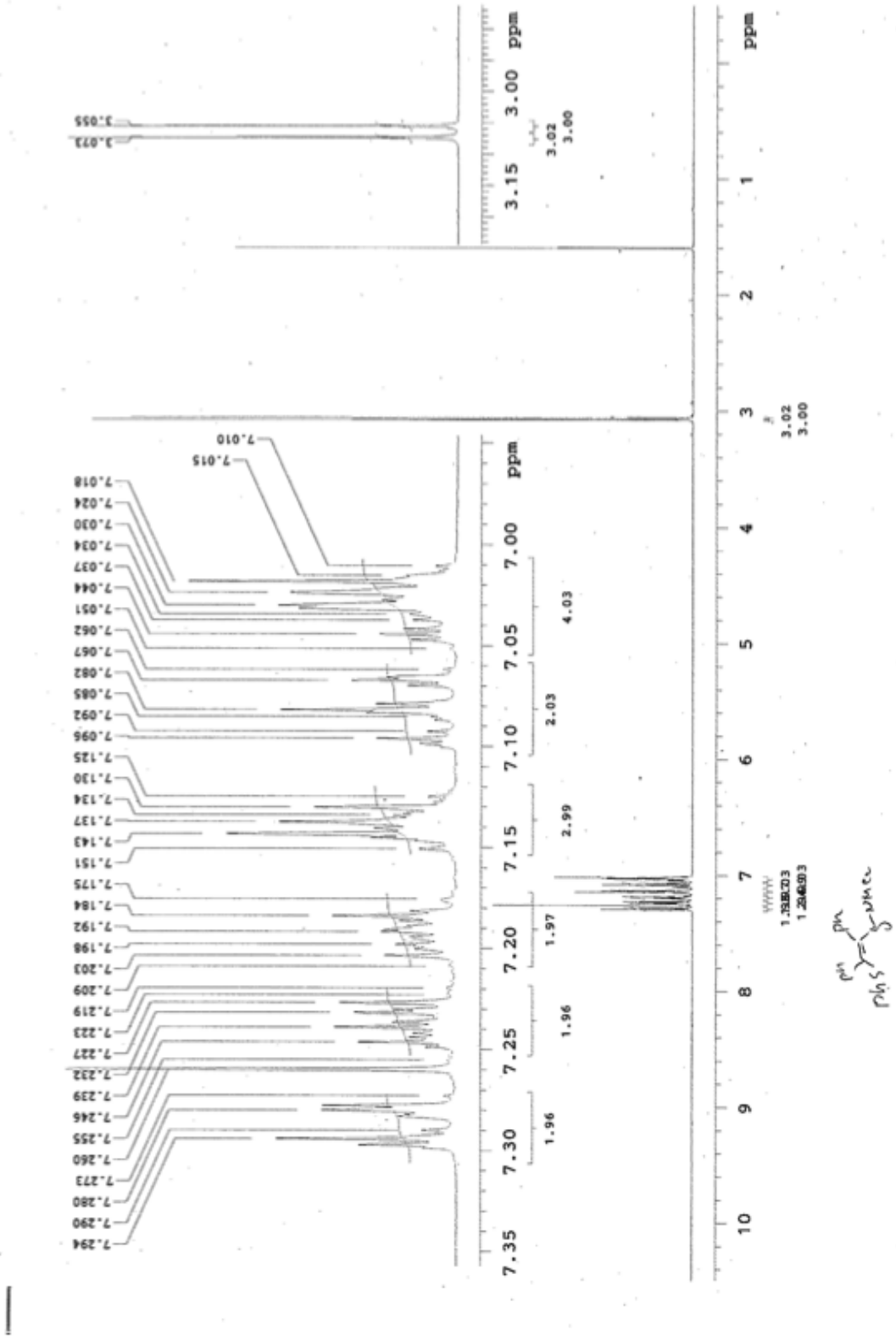
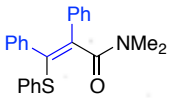
ppm



3ab

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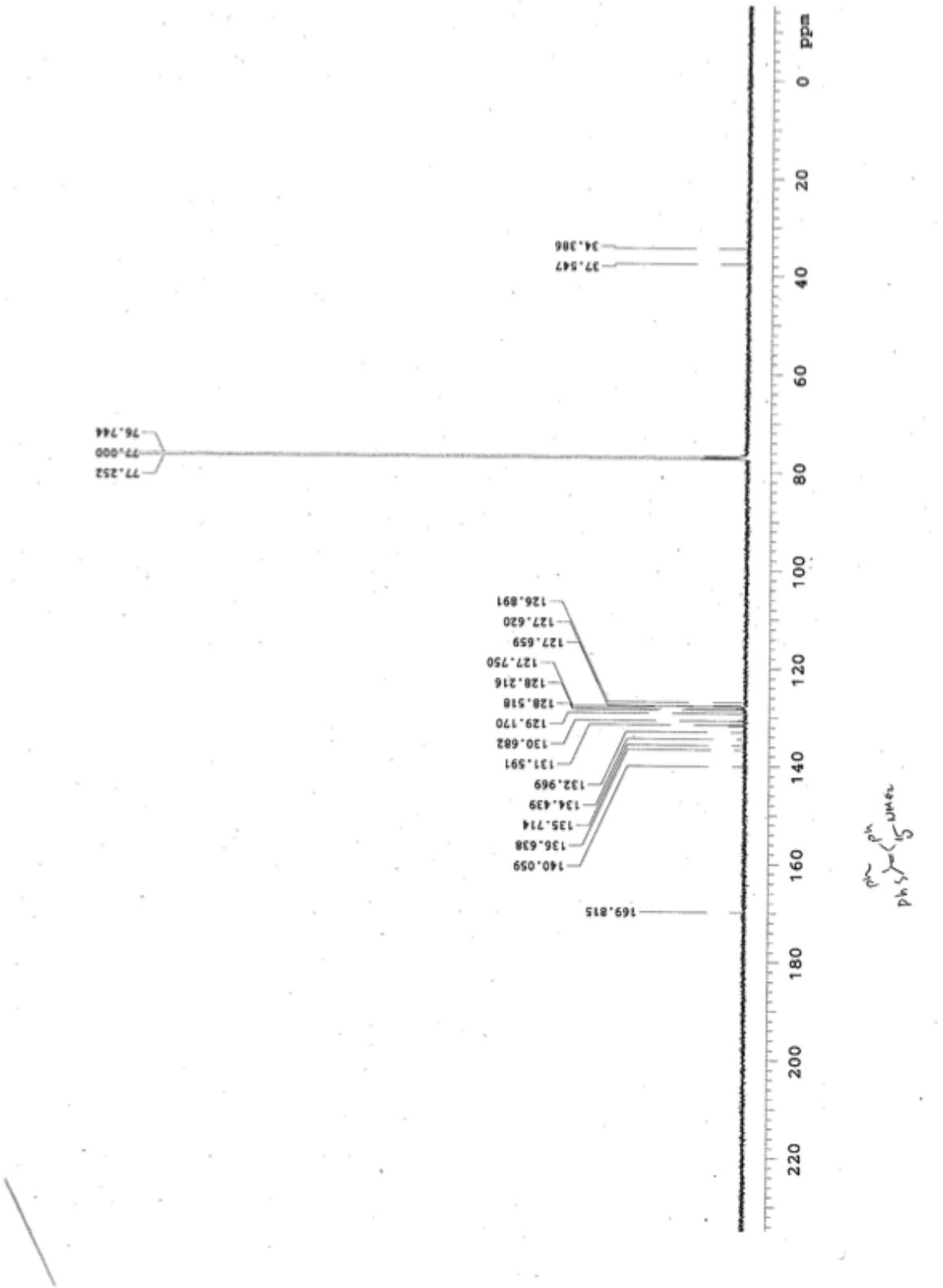
PhS
O

3ab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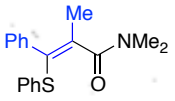
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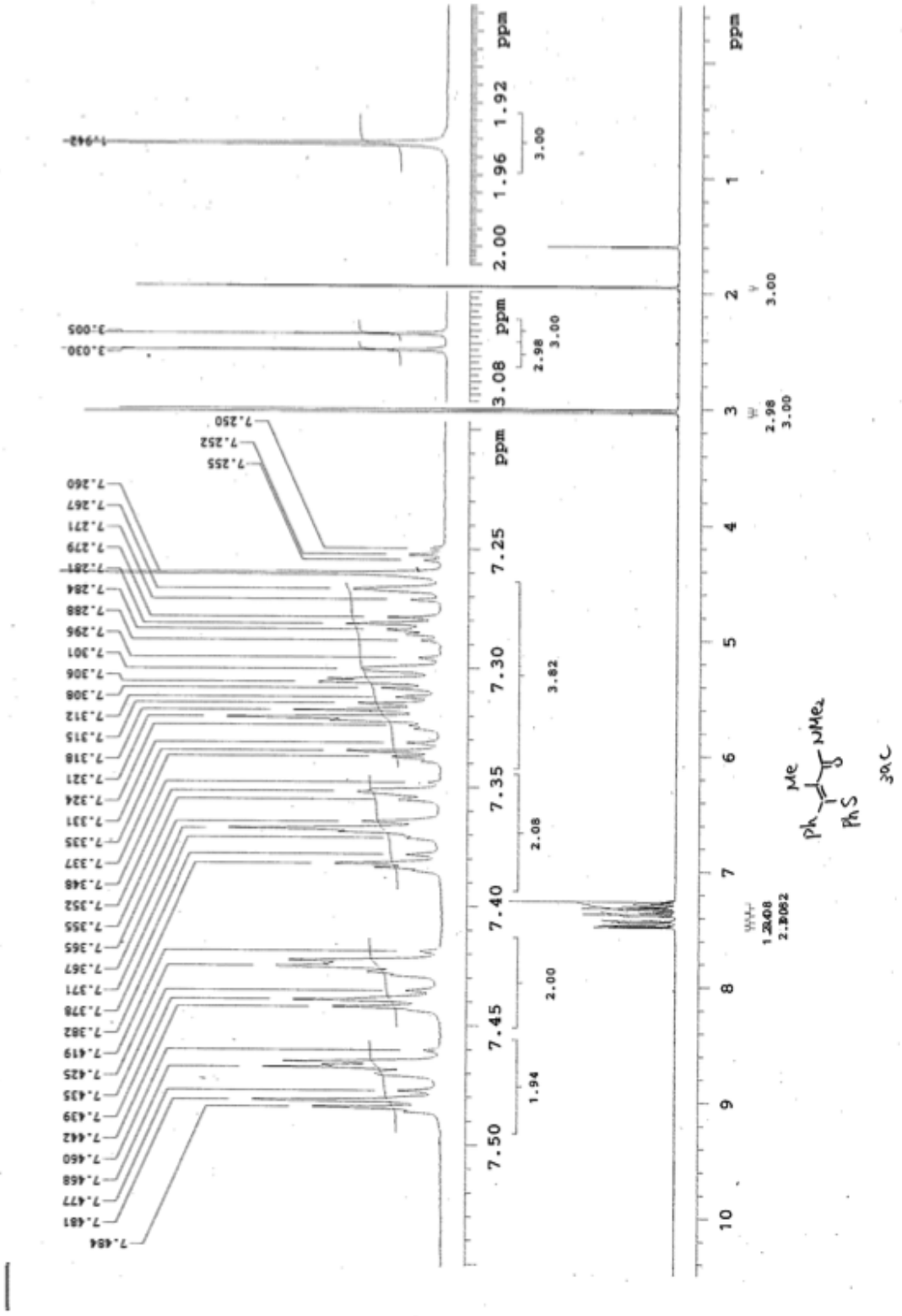
NMe2
PhS
O

3ac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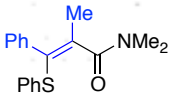
3ac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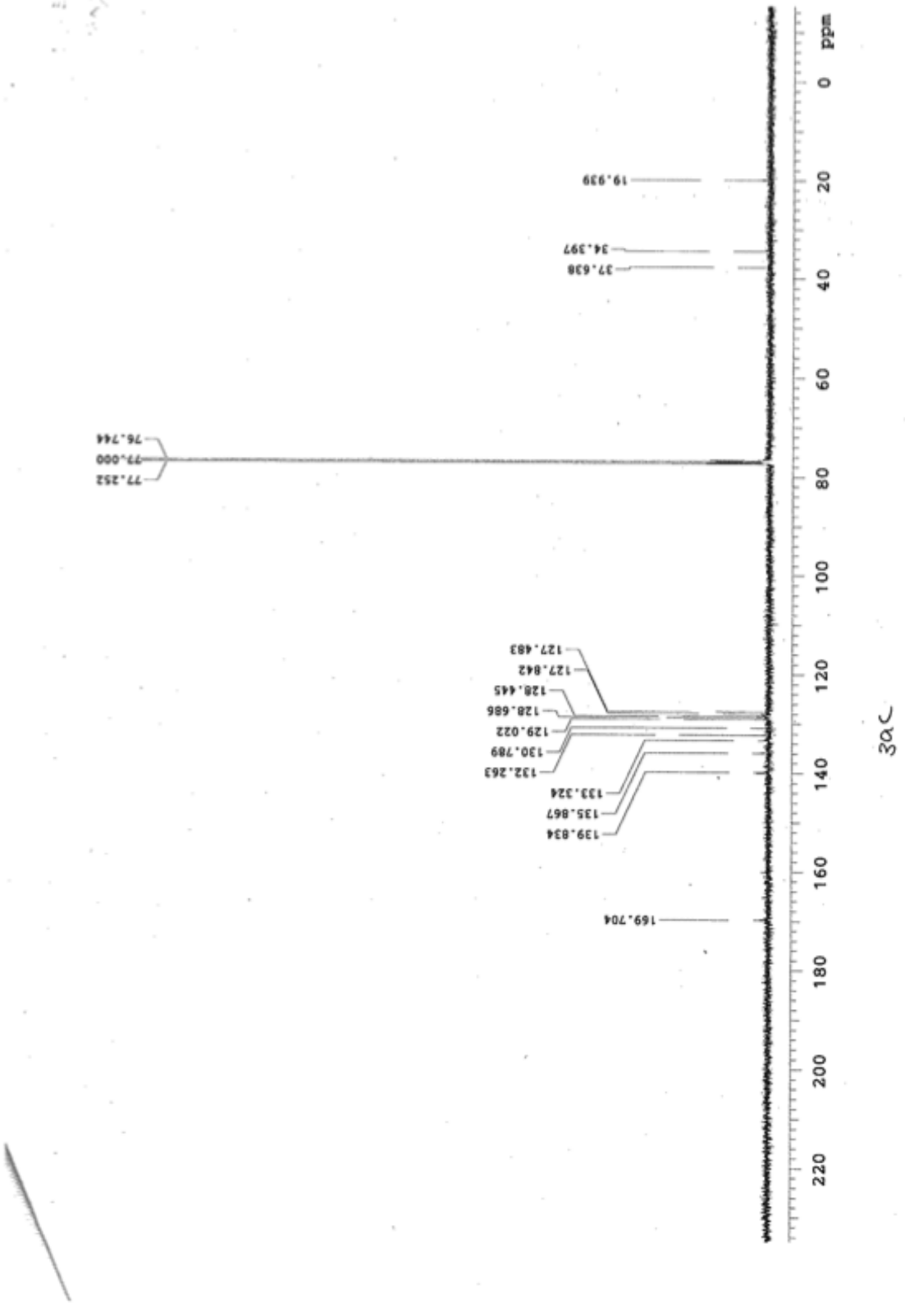
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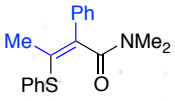
3ac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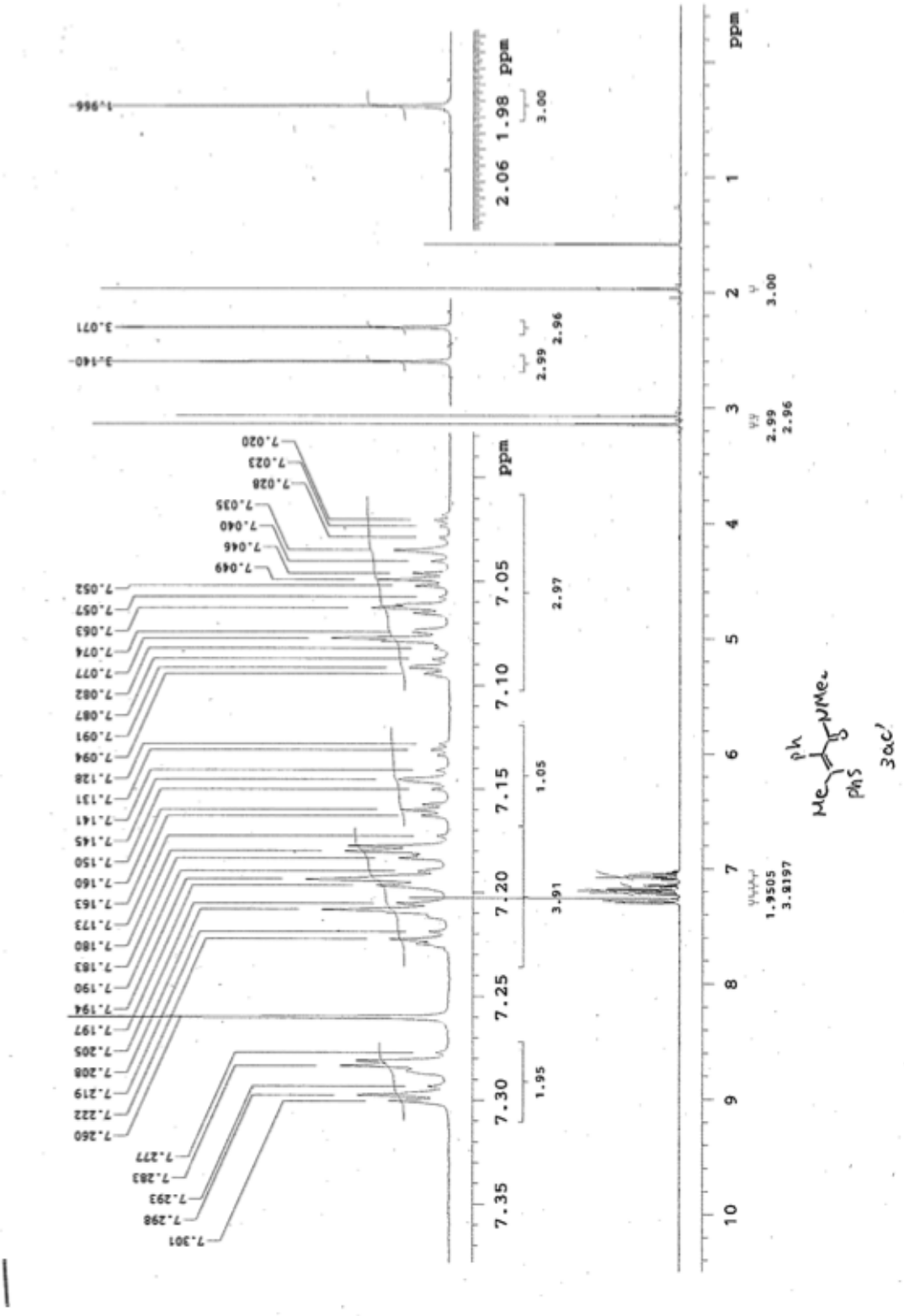
NMe2
PhS
O

3ac'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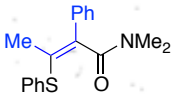
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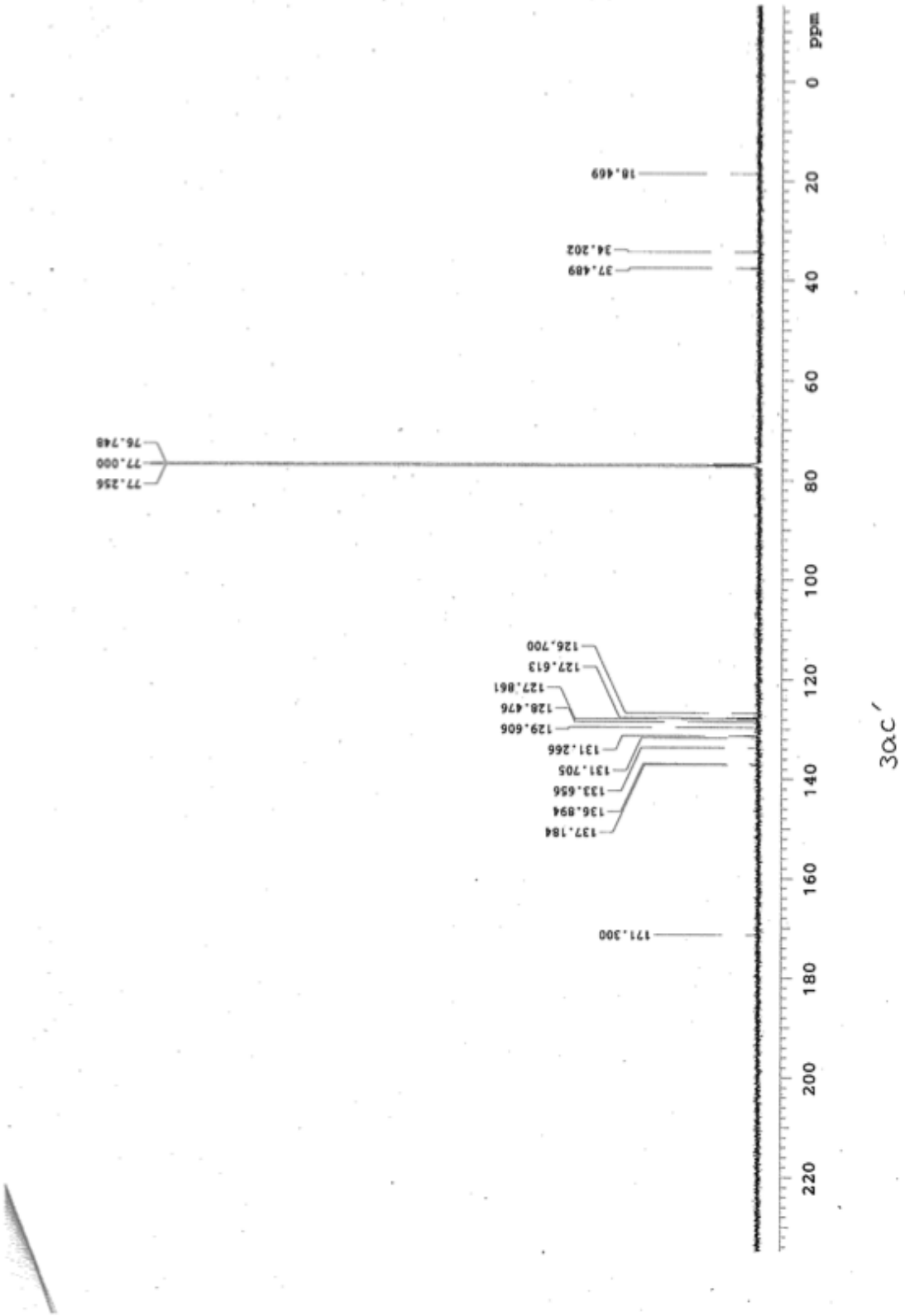
NMe2
PhS
O

3ac'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133.656
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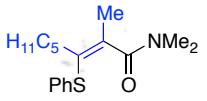
3ac'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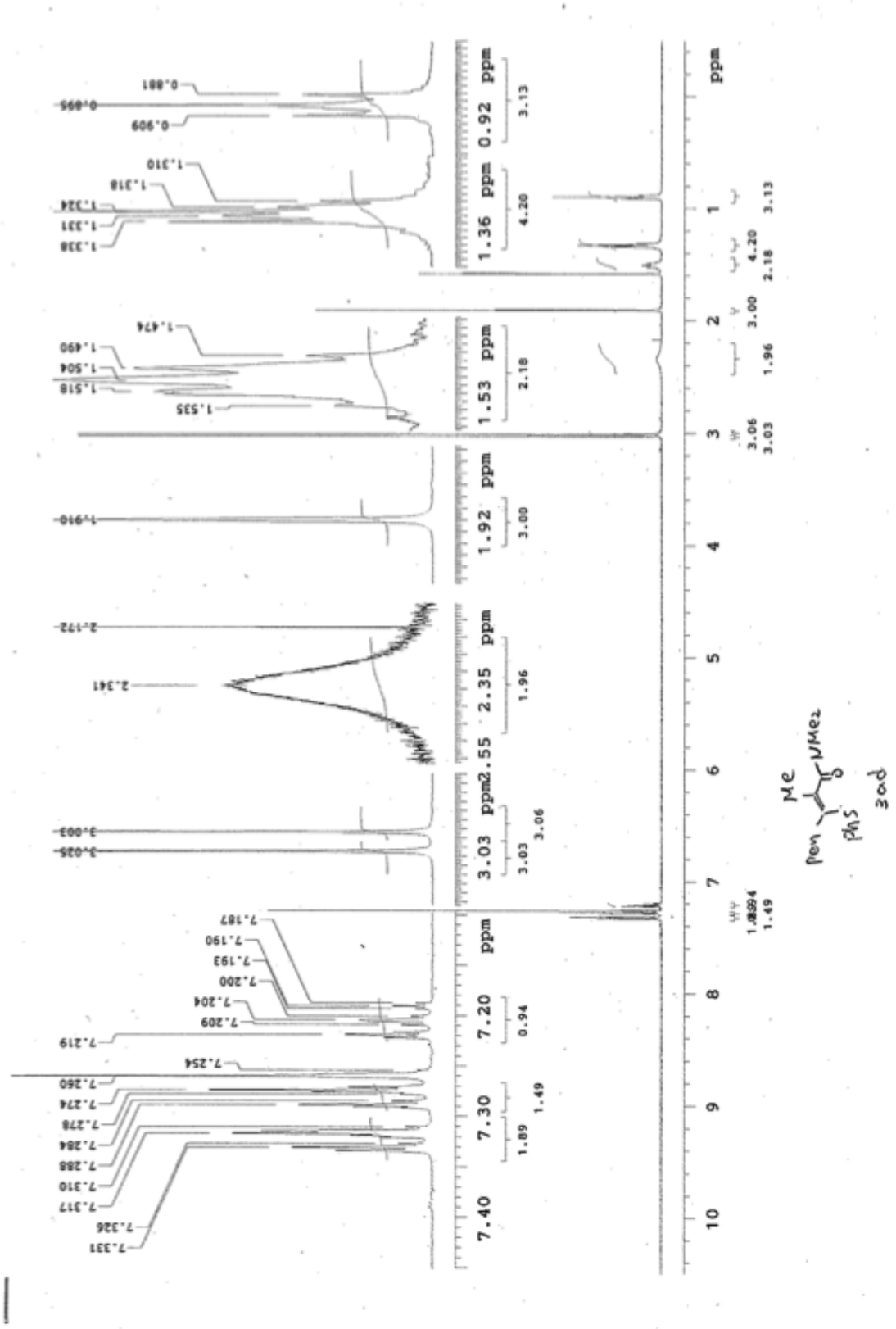
NMe$_2$
PhS
O

3ad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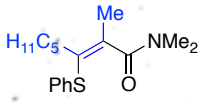
NMe2
Ph S
3ad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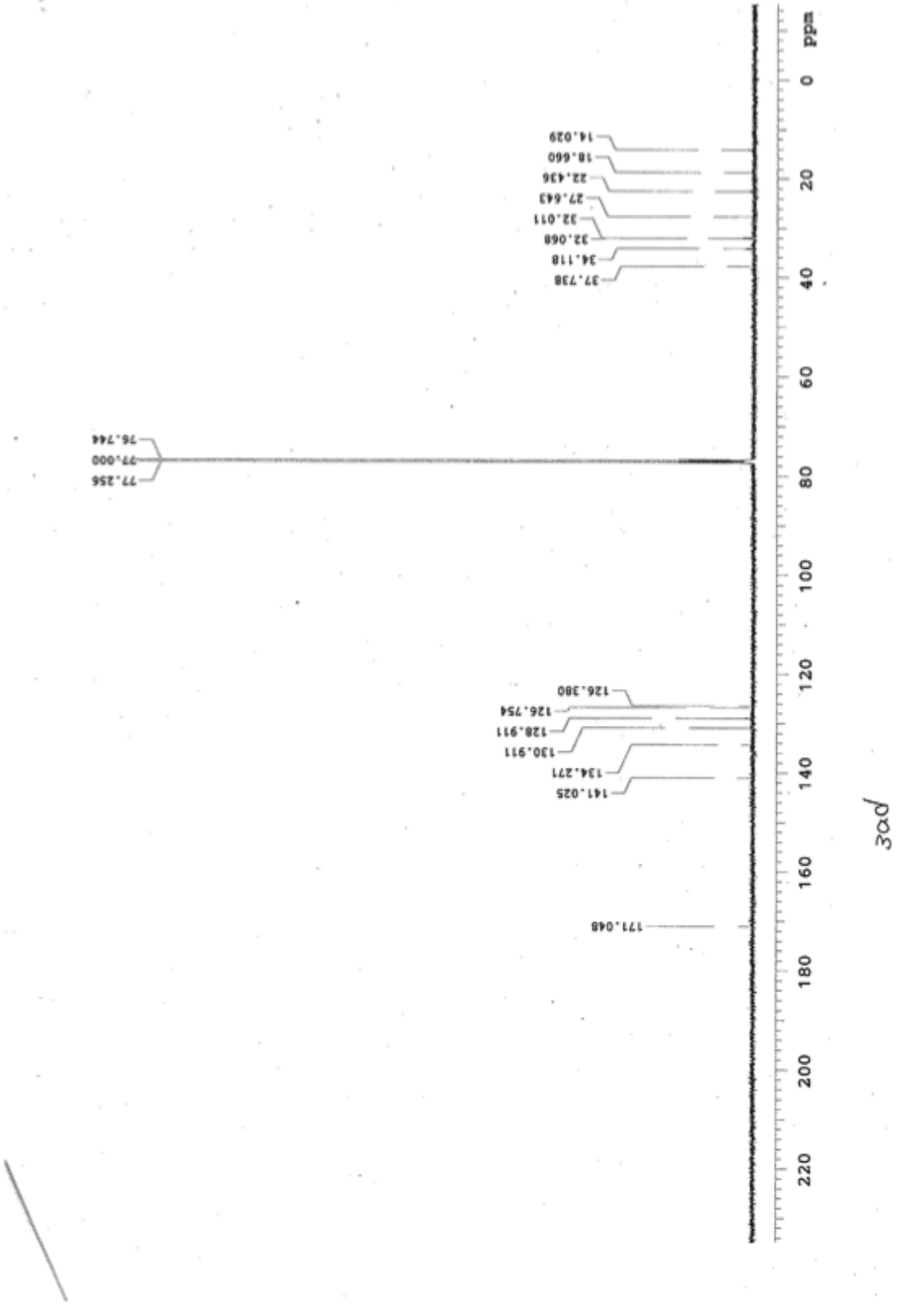
$H_{11}C_5$
NMe_2
PhS
O

3ad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0
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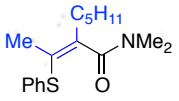
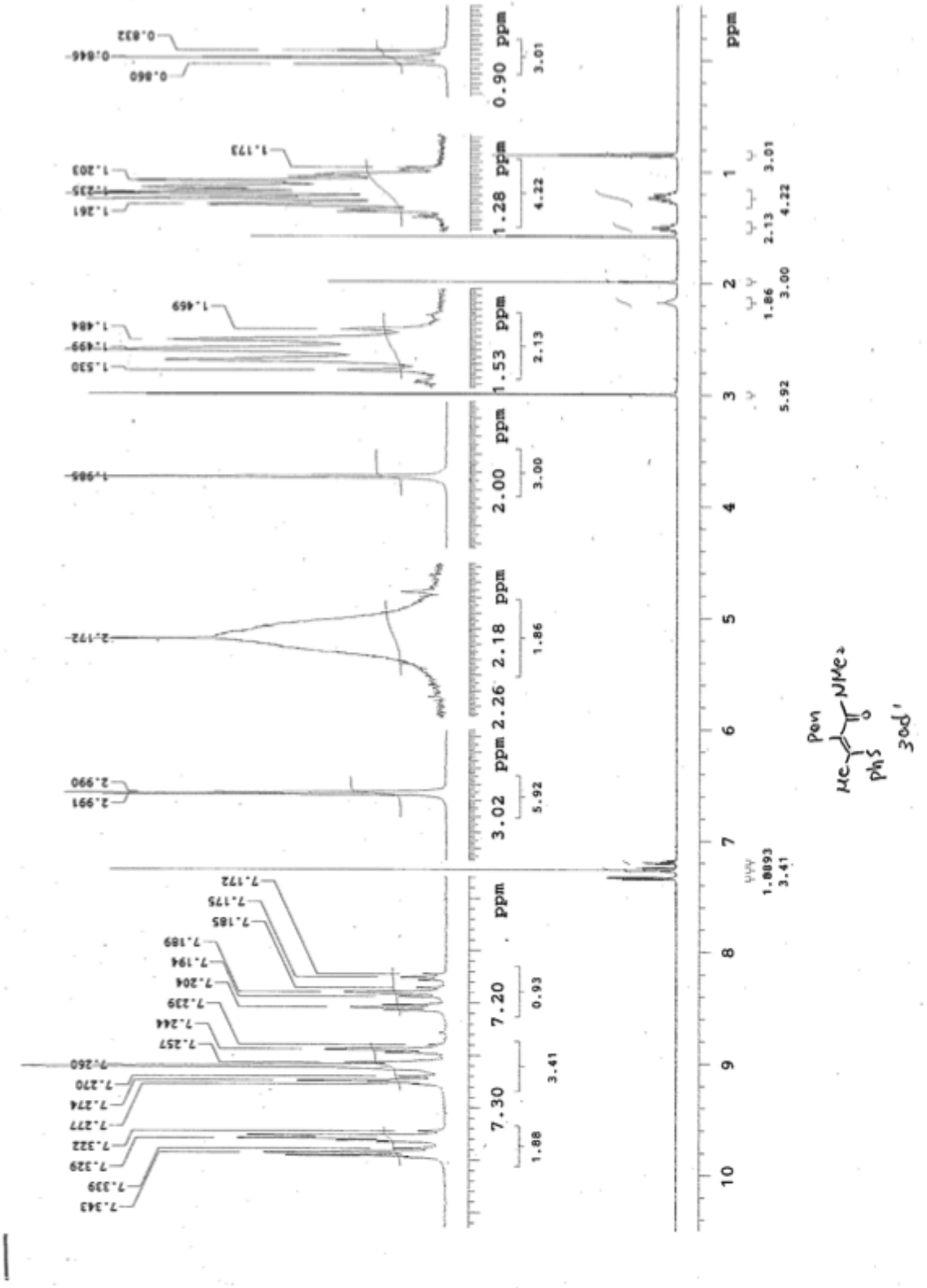
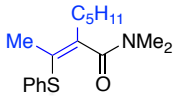
40
60
80
100
120
140
160
180
200
220
ppm

3ad

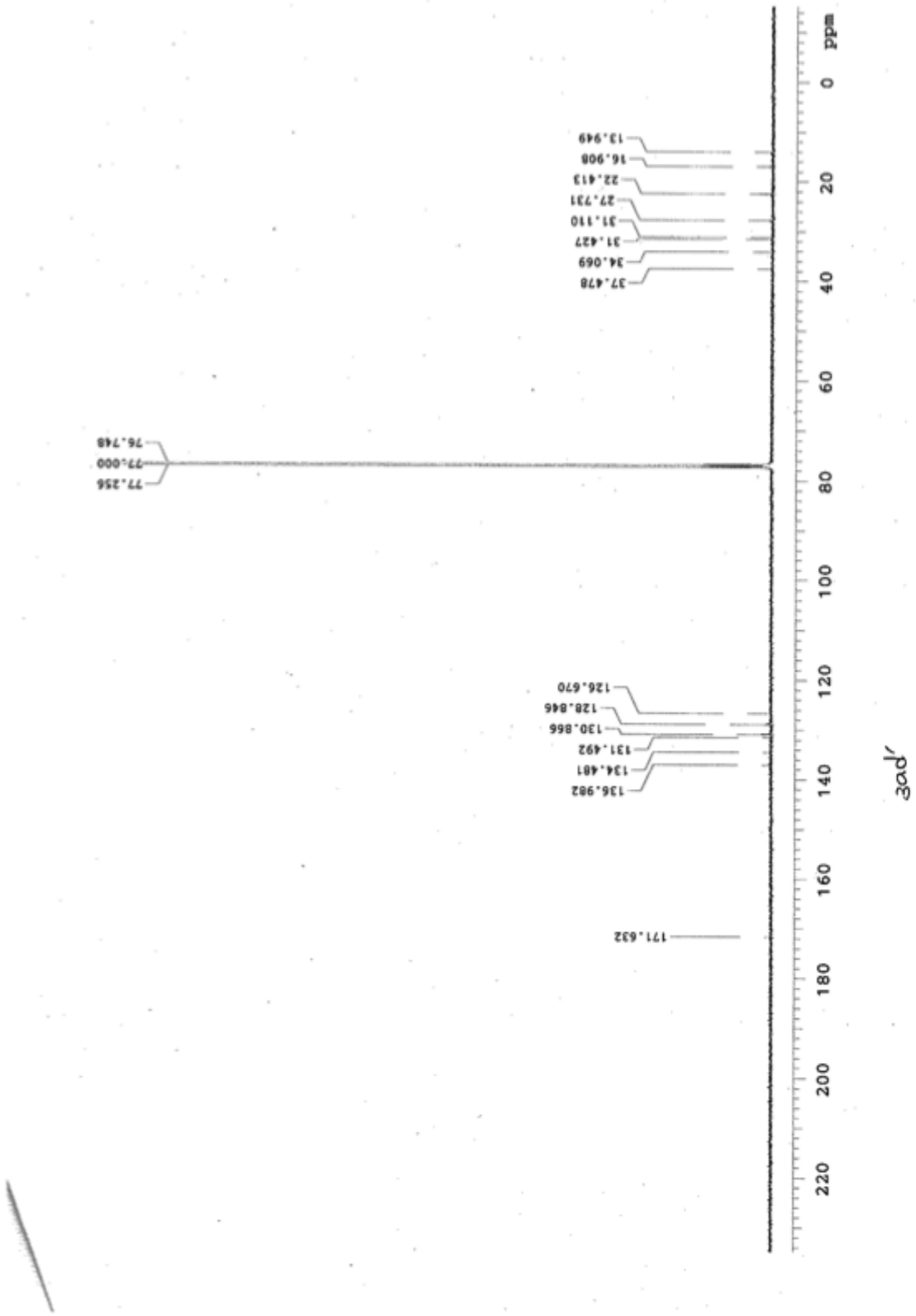

C5H11
Me
NMe2
PhS
O

3ad'


0.832
0.846
0.860
1.173
1.203
1.235
1.261
1.459
1.484
1.499
1.530
1.985
2.172
2.991
2.990
7.172
7.175
7.185
7.189
7.194
7.204
7.239
7.244
7.257
7.260
7.270
7.274
7.277
7.322
7.329
7.339
7.343
0.90 ppm
3.01
1.28 ppm
4.22
1.53 ppm
2.13
2.00 ppm
3.00
2.18 ppm
1.86
2.26
3.02 ppm
5.92
7.20 ppm
0.93
7.30
1.88
3.41
ppm
1
2
3
4
5
6
7
8
9
10
1.86
2.13
3.01
3.00
4.22
5.92
1.8893
3.41


C5H11
Me
NMe2
PhS
O

3ad'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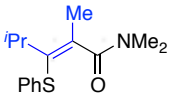
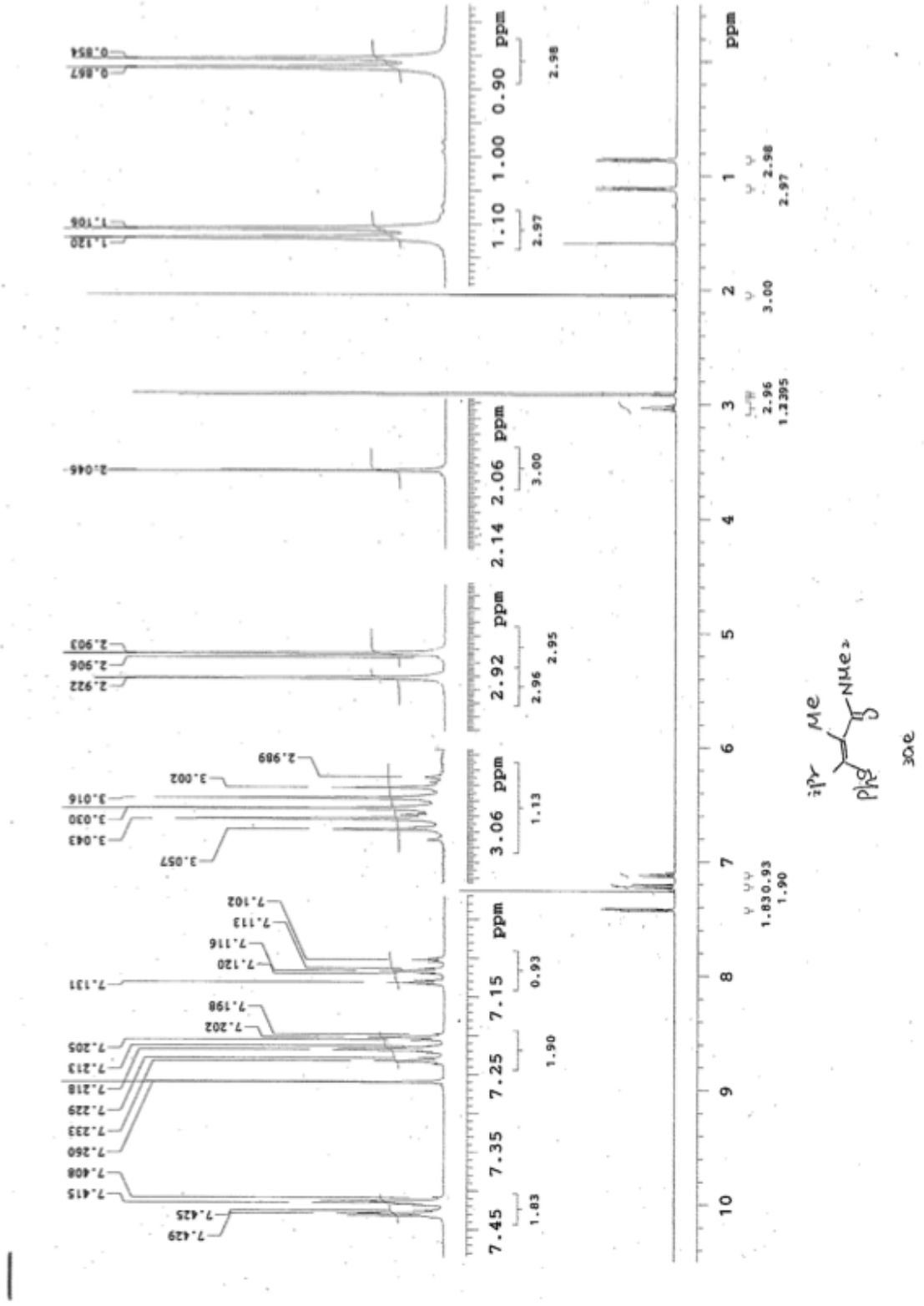
16.908
22.413
27.731
31.110
31.427
34.069
37.478
76.748
77.000
77.256
126.670
128.846
130.866
131.492
134.481
136.982
171.632
0
20
40
60
80
100
120
140
160
180
200
220
ppm
3ad'


Me
iPr
NMe2
PhS
O

3ae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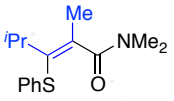
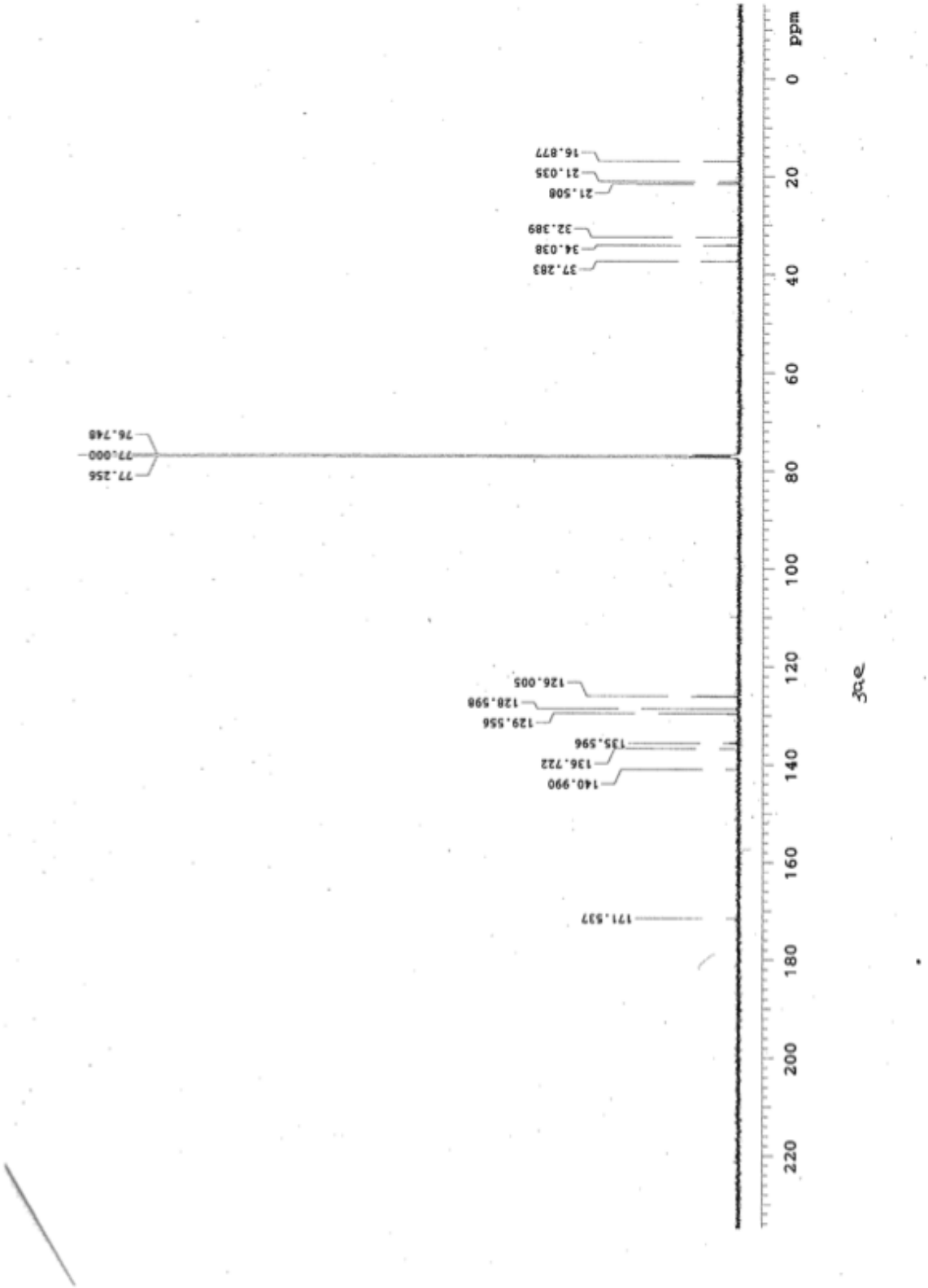
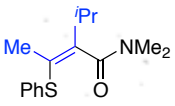
0.867
1.106
1.120
2.046
2.903
2.906
2.922
2.989
3.002
3.016
3.030
3.043
3.057
7.102
7.113
7.116
7.120
7.131
7.198
7.202
7.205
7.213
7.218
7.229
7.233
7.260
7.408
7.415
7.425
7.429
7.45
7.35
7.25
7.15
3.06 ppm
2.92 ppm
2.14 2.06 ppm
1.10 1.00 0.90 ppm
ppm
1.83
1.90
0.93
1.13
2.96
2.95
3.00
2.97
2.98
1.830.93
1.90
3.00
2.96
1.3395
2.98
2.97
iPr
Me
NMe2
PhS
O
3ae

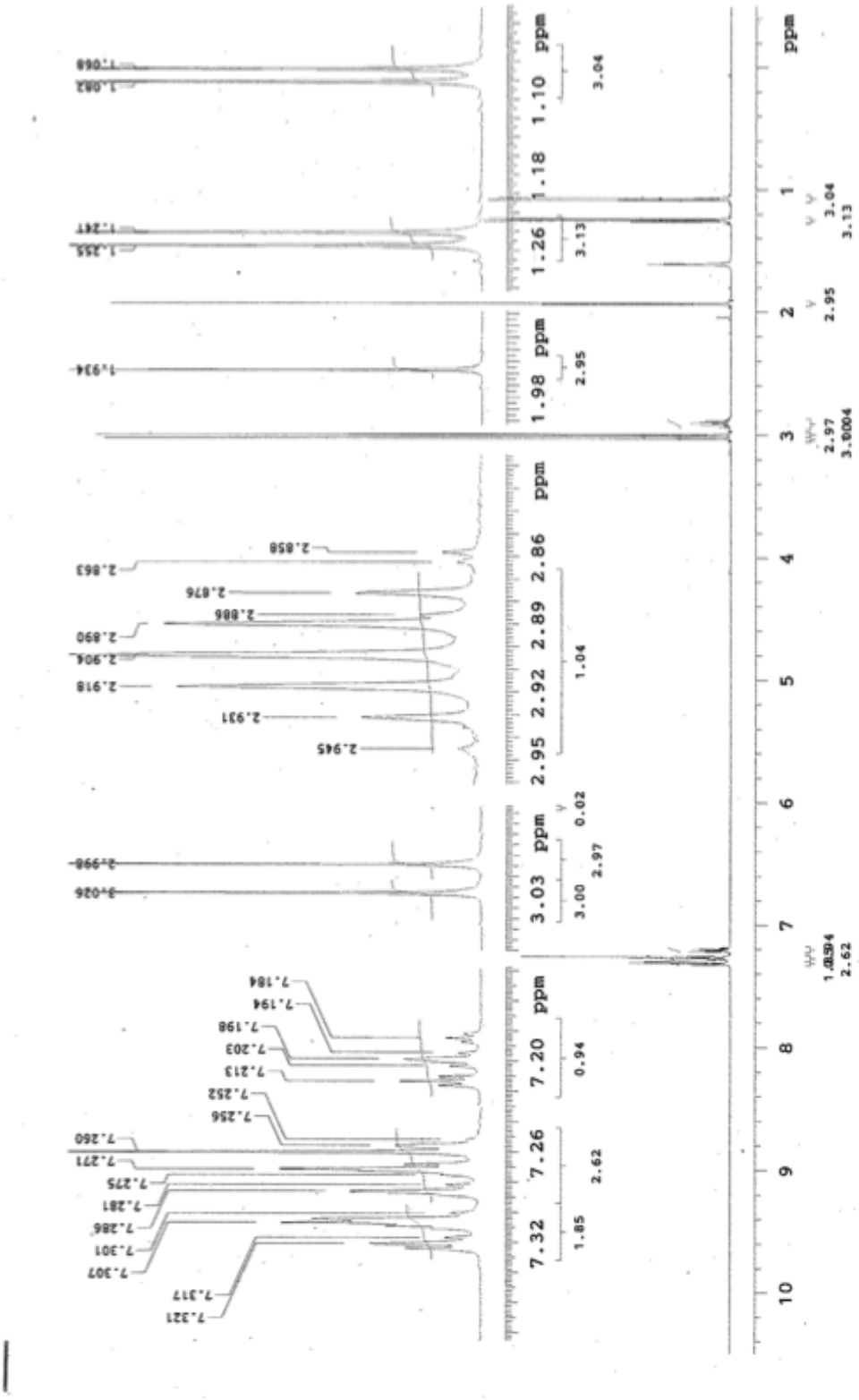

Me
iPr
NMe2
PhS
O

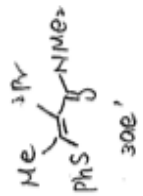
3ae

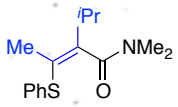

ppm
0
20
40
60
80
100
120
140
160
180
200
220
16.877
21.035
21.508
32.389
34.038
37.283
76.748
77.000
77.256
126.005
128.598
129.556
135.596
136.722
140.990
171.537
3ae


iPr
Me
NMe2
PhS
O

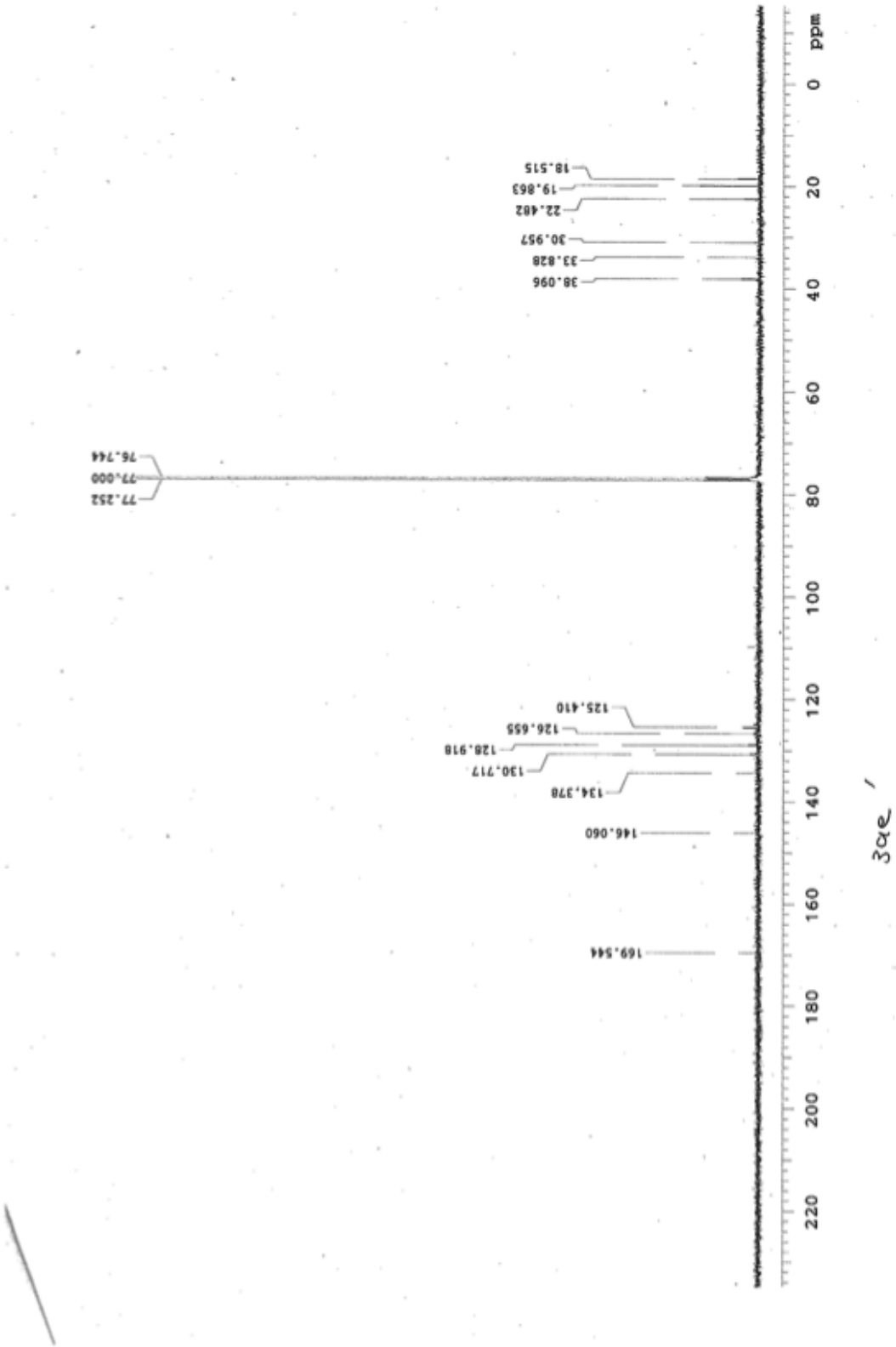
3ae'

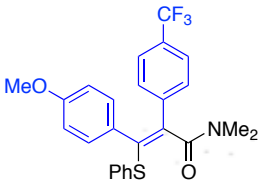

7.068
7.082
7.247
7.255
7.934
2.858
2.863
2.876
2.886
2.890
2.904
2.918
2.931
2.945
2.998
3.026
7.184
7.194
7.198
7.203
7.213
7.252
7.256
7.260
7.271
7.275
7.281
7.286
7.301
7.307
7.317
7.321
7.32
7.26
7.20
3.03
2.95
2.92
2.89
2.86
1.98
1.26
1.18
1.10
ppm


Me
iPr
PhS
NMe2
30e'

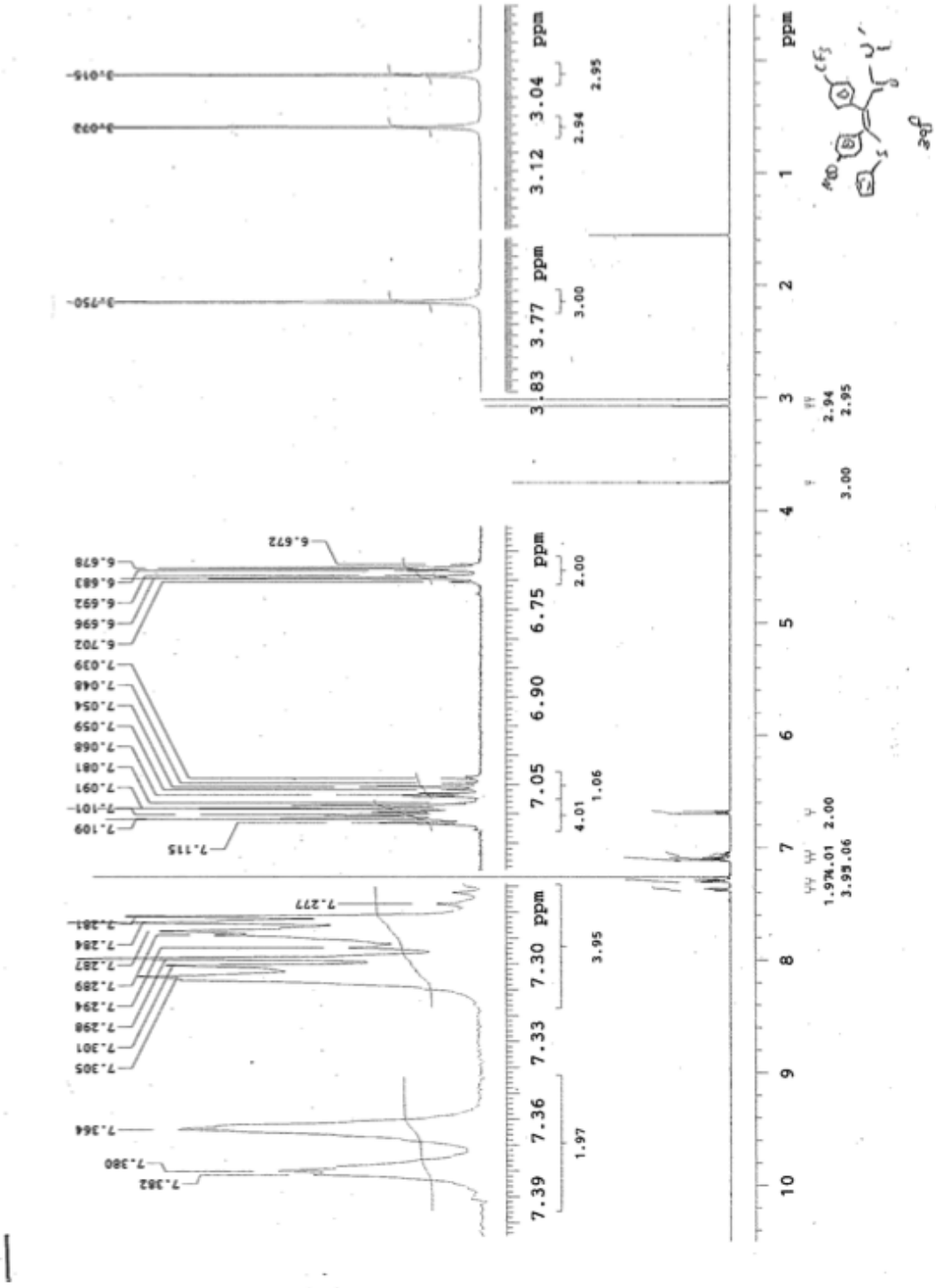

iPr
Me
NMe2
PhS
O

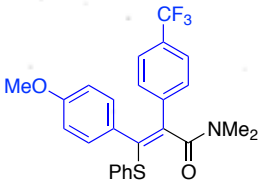
3ae'


18.515
19.863
22.482
30.957
33.828
38.096
76.744
77.000
77.252
125.410
126.655
128.918
130.717
134.378
146.060
169.544
0
20
40
60
80
100
120
140
160
180
200
220
ppm
3ae'

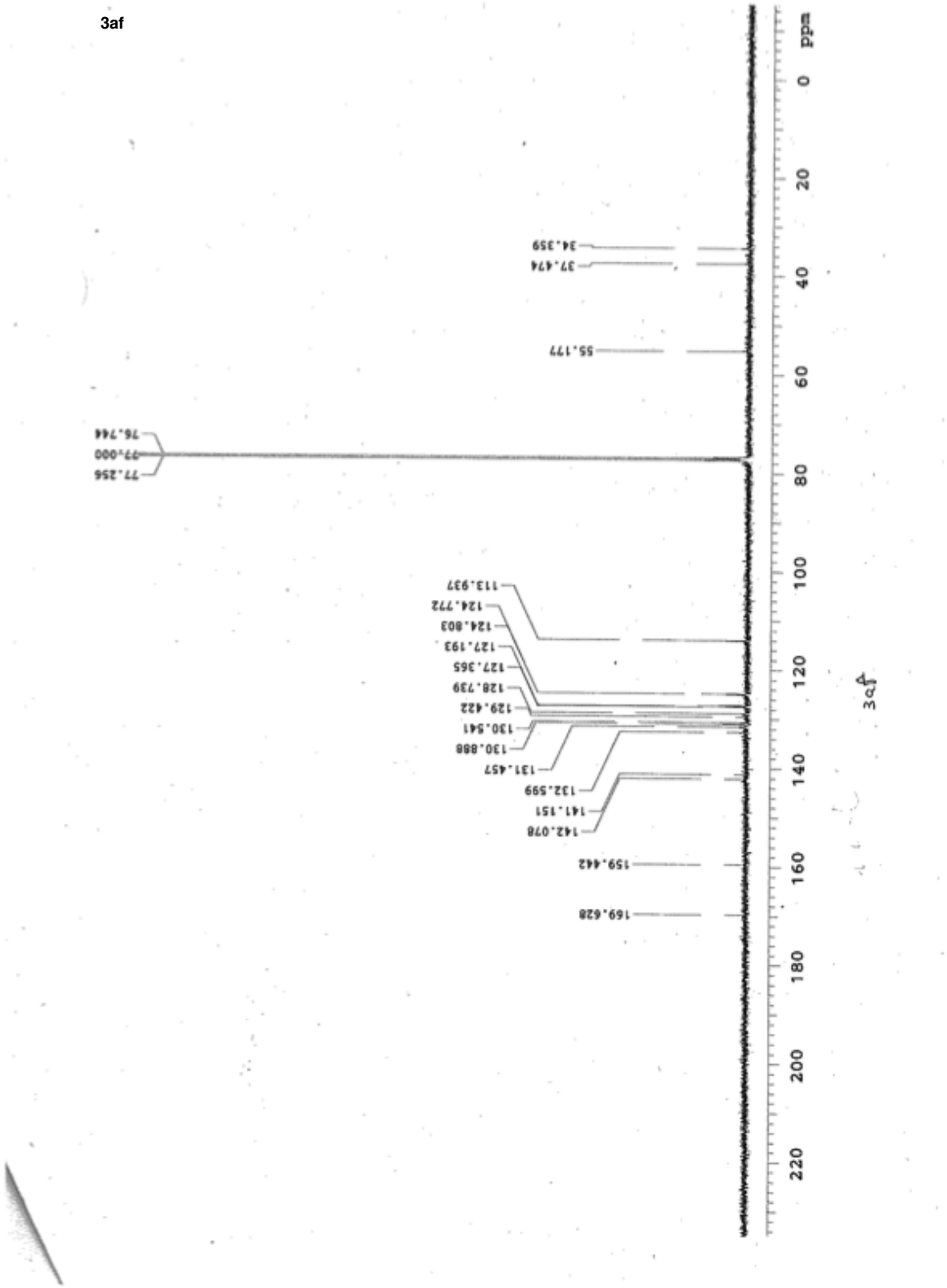


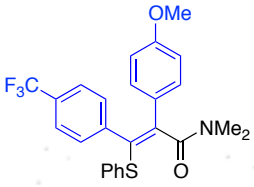
3af



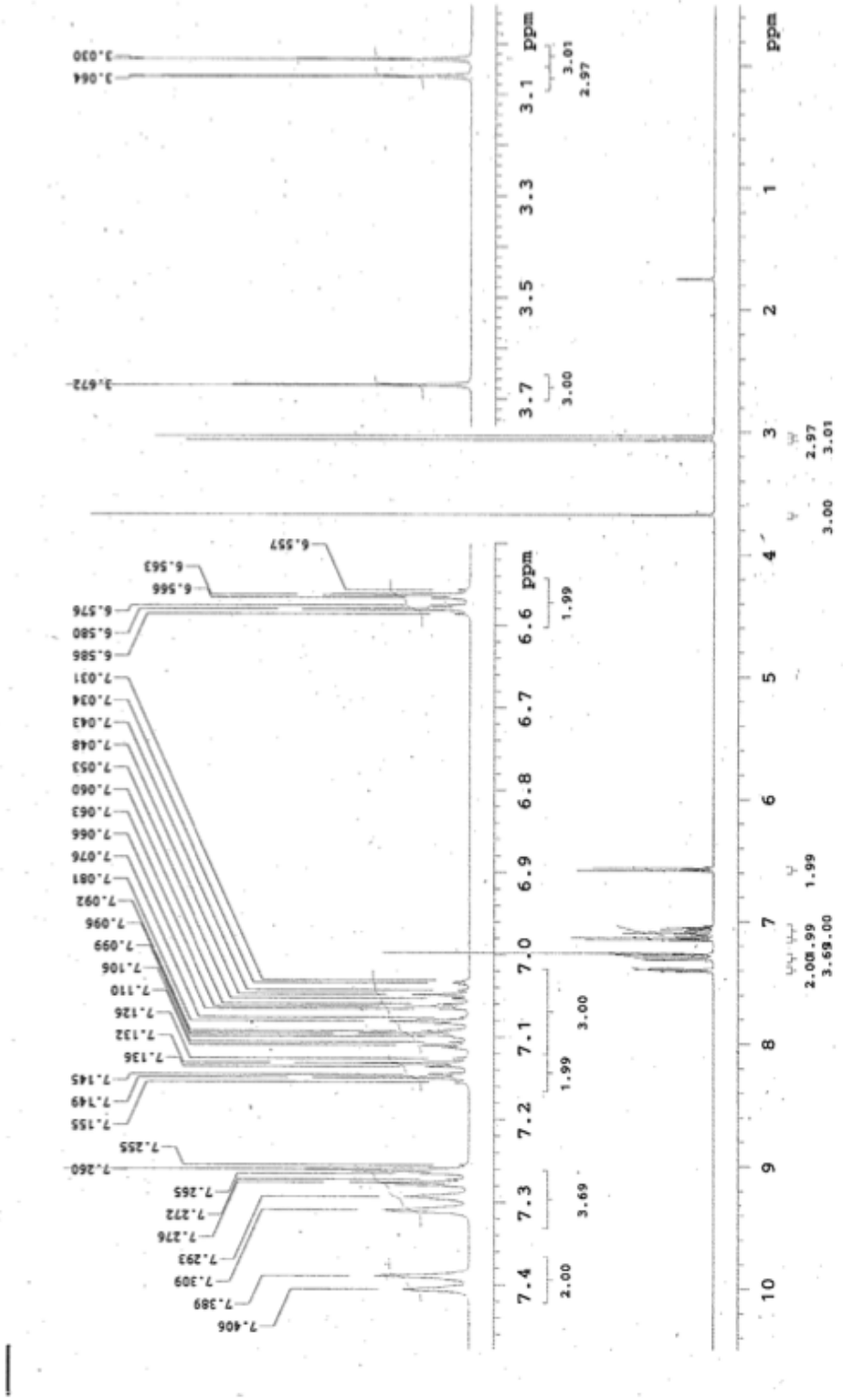

CF3
MeO
NMe2
PhS
O

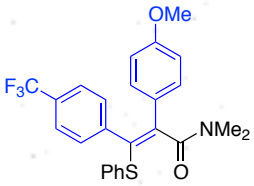
3af


34.359
37.474
55.177
76.744
77.000
77.256
113.937
124.772
124.803
127.193
127.365
128.739
129.422
130.541
130.888
131.457
132.599
141.151
142.078
159.442
169.628
0
20
40
60
80
100
120
140
160
180
200
220
ppm
3af

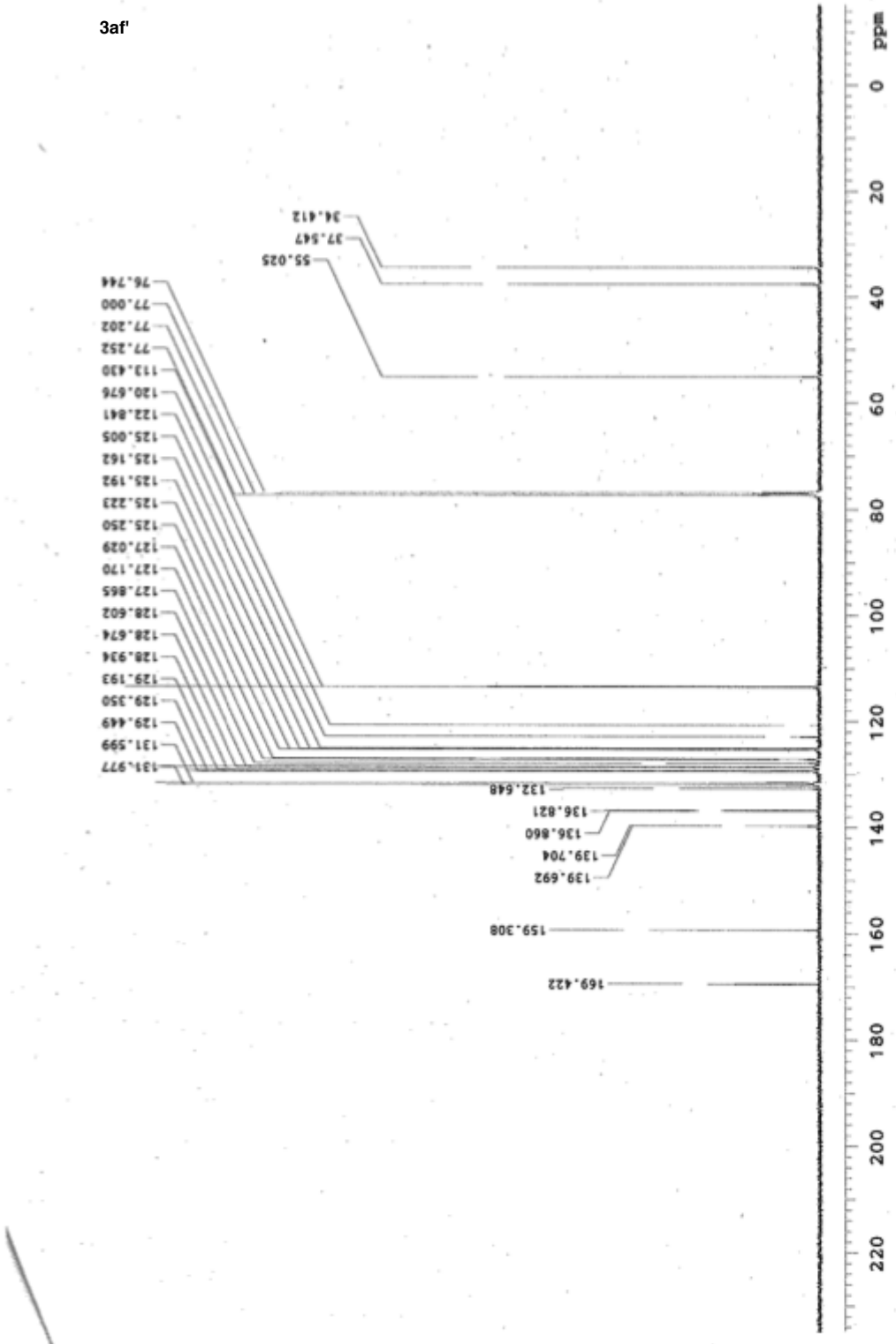

OMe
F3C
NMe2
PhS
O

3af'

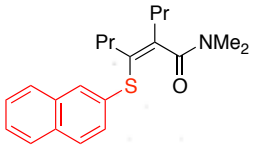

3.030
3.064
3.672
6.537
6.563
6.566
6.576
6.580
6.586
7.031
7.034
7.043
7.048
7.053
7.060
7.063
7.066
7.076
7.081
7.092
7.096
7.099
7.106
7.110
7.126
7.132
7.136
7.145
7.149
7.155
7.255
7.260
7.265
7.272
7.276
7.293
7.309
7.389
7.406
ppm
3.7
3.5
3.3
3.1
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
1
2
3
4
5
6
7
8
9
10
3.00
3.01
2.97
1.99
2.00
3.69
2.08.99
3.69.00


OMe
F3C
NMe2
PhS
O

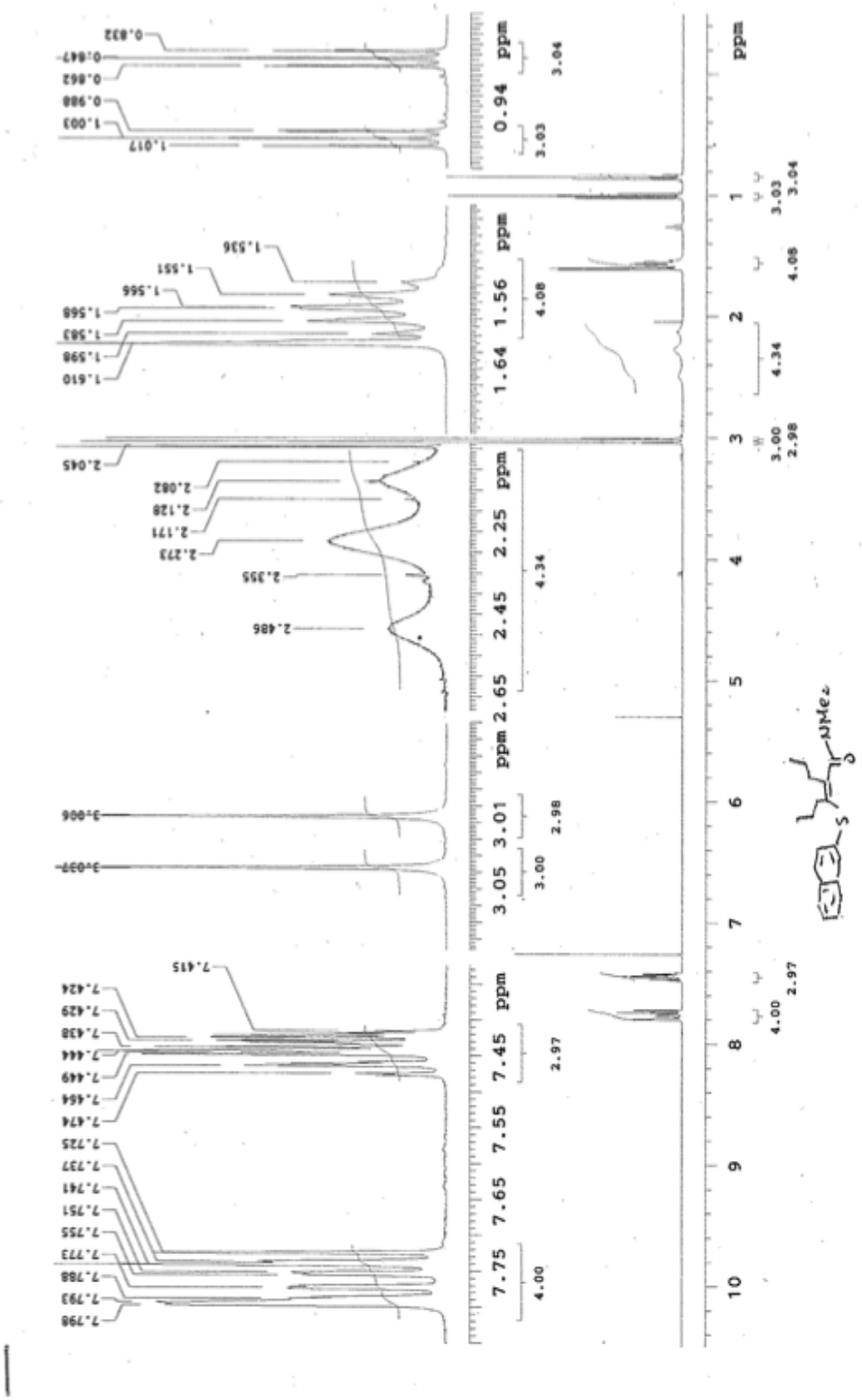
3af'

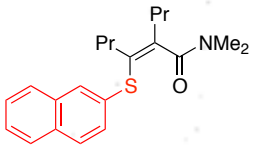

34.412
37.547
55.025
76.744
77.000
77.202
77.252
113.430
120.676
122.841
125.005
125.162
125.192
125.223
125.250
127.029
127.170
127.865
128.602
128.674
128.934
129.193
129.350
129.449
131.599
131.977
132.648
136.821
136.860
139.704
139.692
159.308
169.422
ppm
0
20
40
60
80
100
120
140
160
180
200
220

3af'

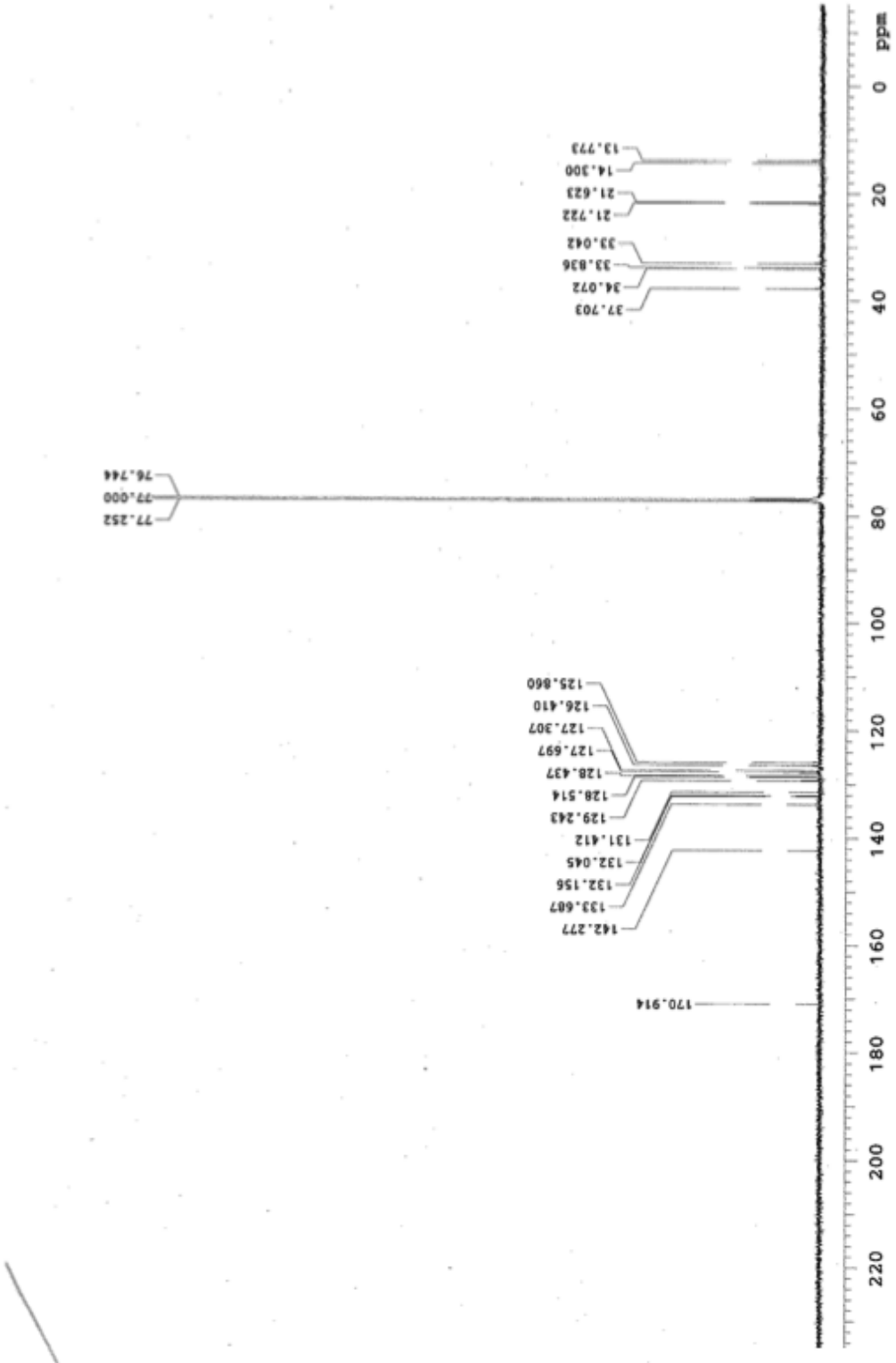


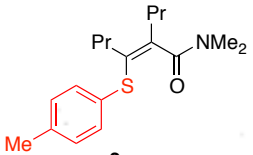
3ba



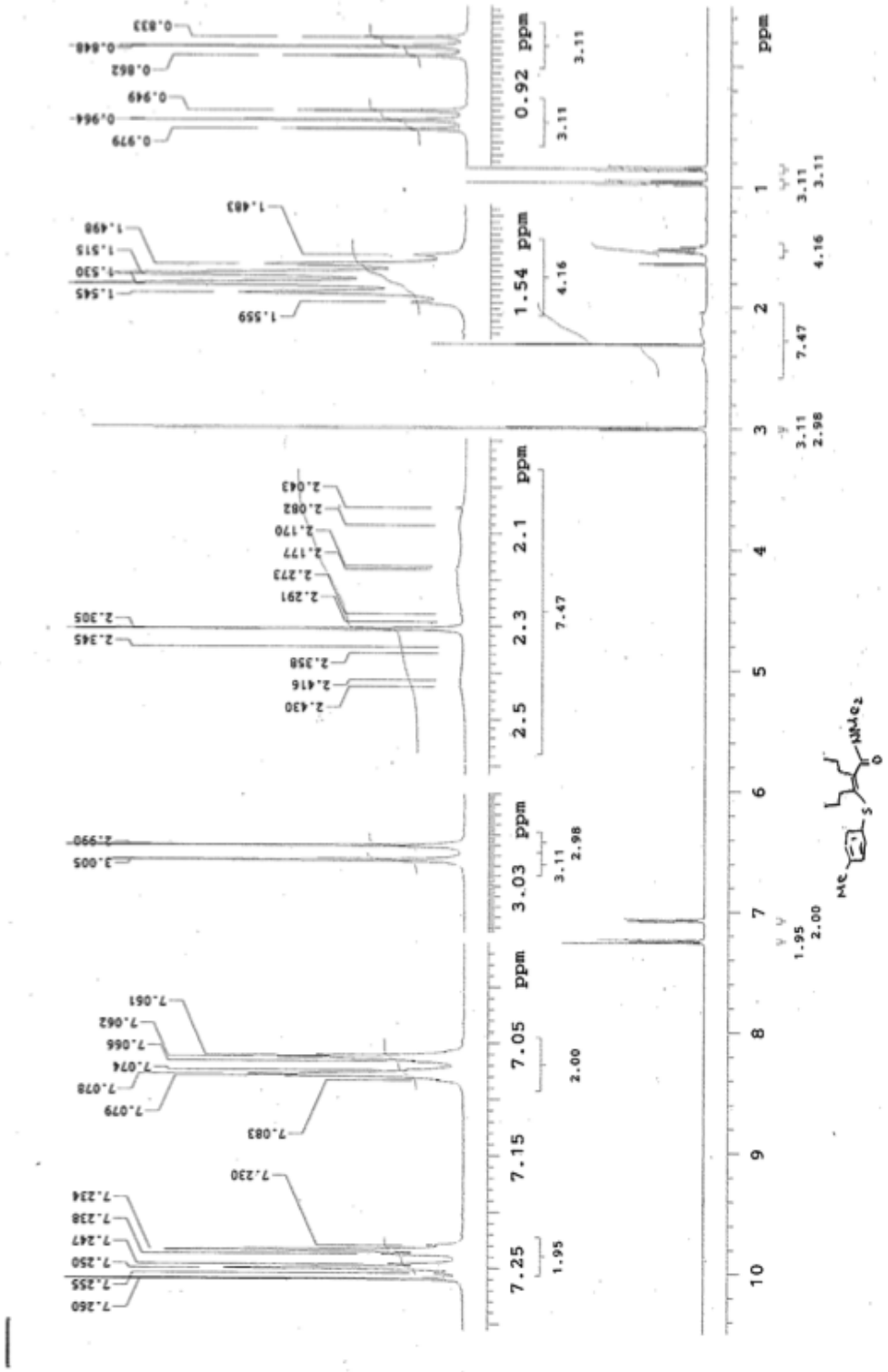

Pr
Pr
NMe2
S
O

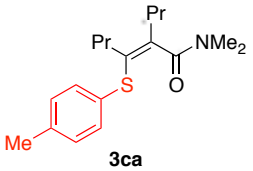
3ba


13.773
14.300
21.623
21.722
33.042
33.836
34.072
37.703
76.744
77.000
77.252
125.860
126.410
127.307
127.697
128.437
128.514
129.243
131.412
132.045
132.156
133.687
142.277
170.914
ppm
0
20
40
60
80
100
120
140
160
180
200
220

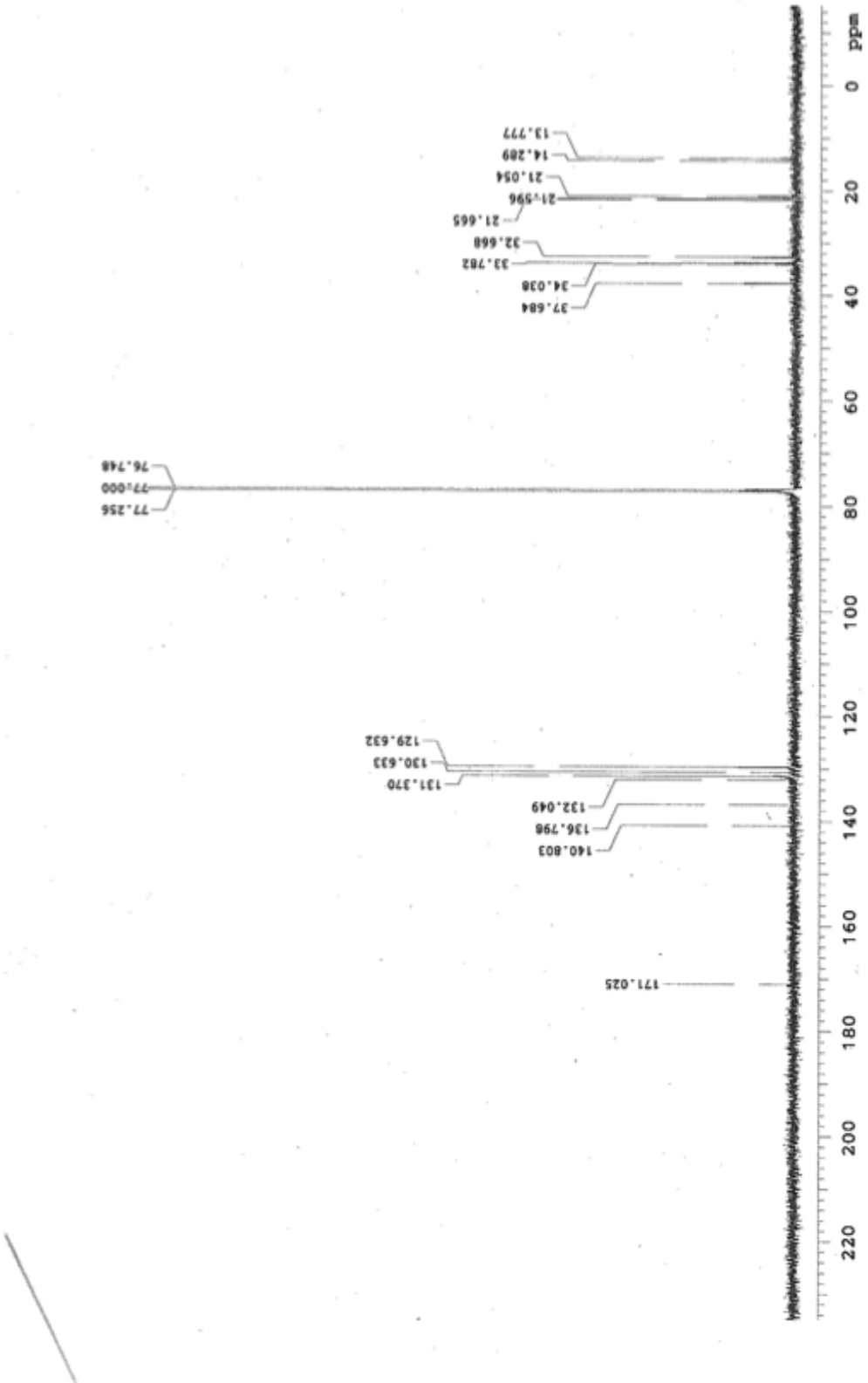


3ca




Pr
Pr
NMe2
S
O
Me

3ca


13.777
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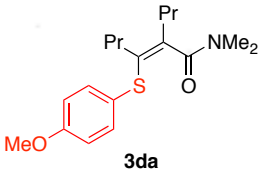
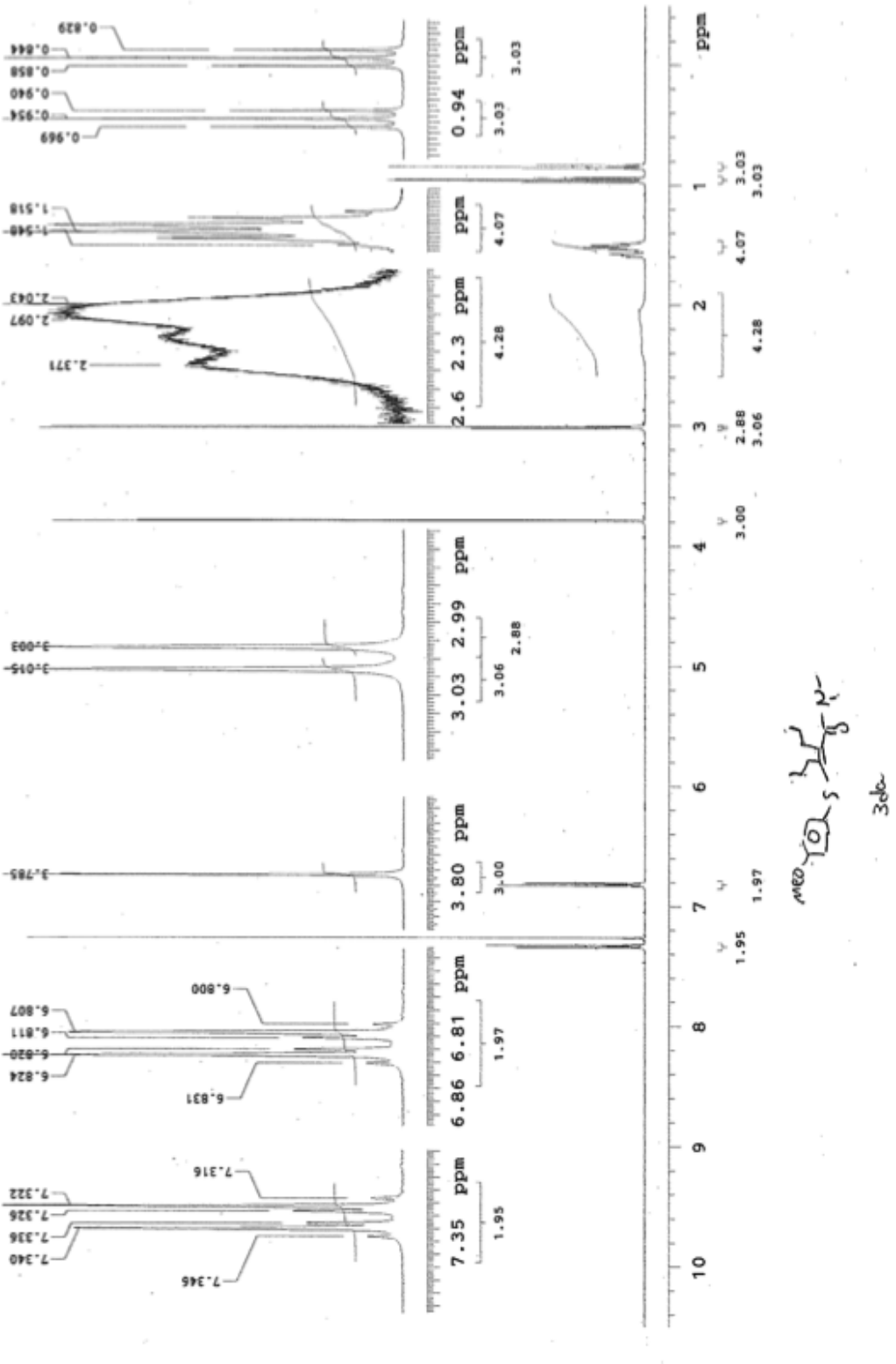
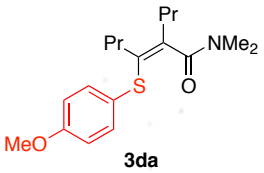
21.665
32.668
33.782
34.038
37.684
76.748
77.000
77.256
129.632
130.633
131.370
132.049
136.798
140.803
171.025
ppm
0
20
40
60
80
100
120
140
160
180
200
220

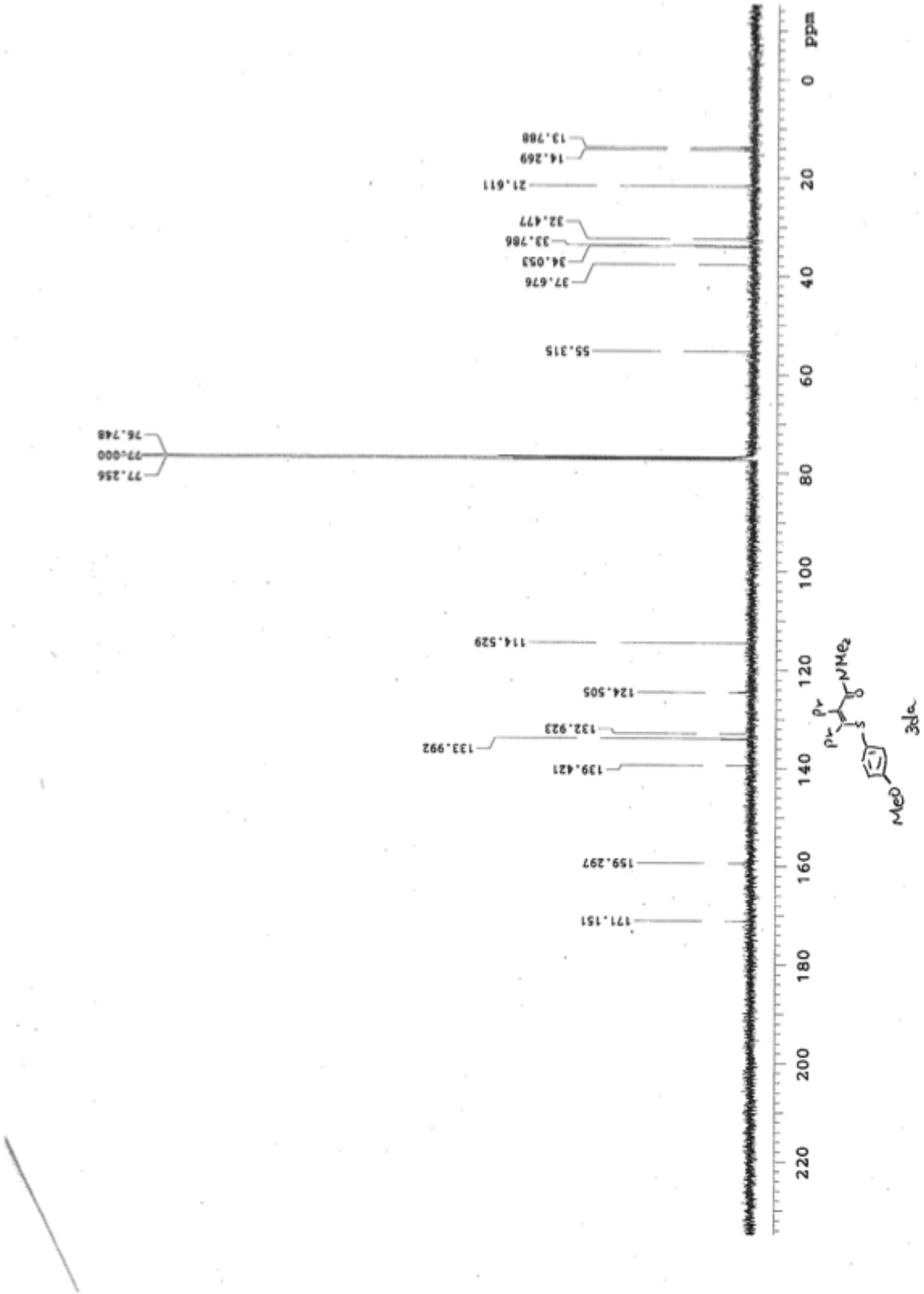

Pr
Pr
NMe2
S
O
MeO

3da


0.829
0.844
0.858
0.940
0.954
0.969
1.518
1.548
2.043
2.097
2.371
3.003
3.015
3.785
6.800
6.807
6.811
6.820
6.824
6.831
7.316
7.322
7.326
7.336
7.340
7.346
0.94 ppm 3.03
2.6 2.3 ppm 4.28
4.07
3.03 2.99 ppm 3.06 2.88
3.80 ppm 3.00
6.86 6.81 ppm 1.97
7.35 ppm 1.95
ppm
3.03
4.07
4.28
2.88
3.06
3.00
1.97
1.95
MeO
S
N
3da


Pr
Pr
NMe2
S
O
MeO

3da


13.788
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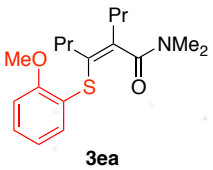
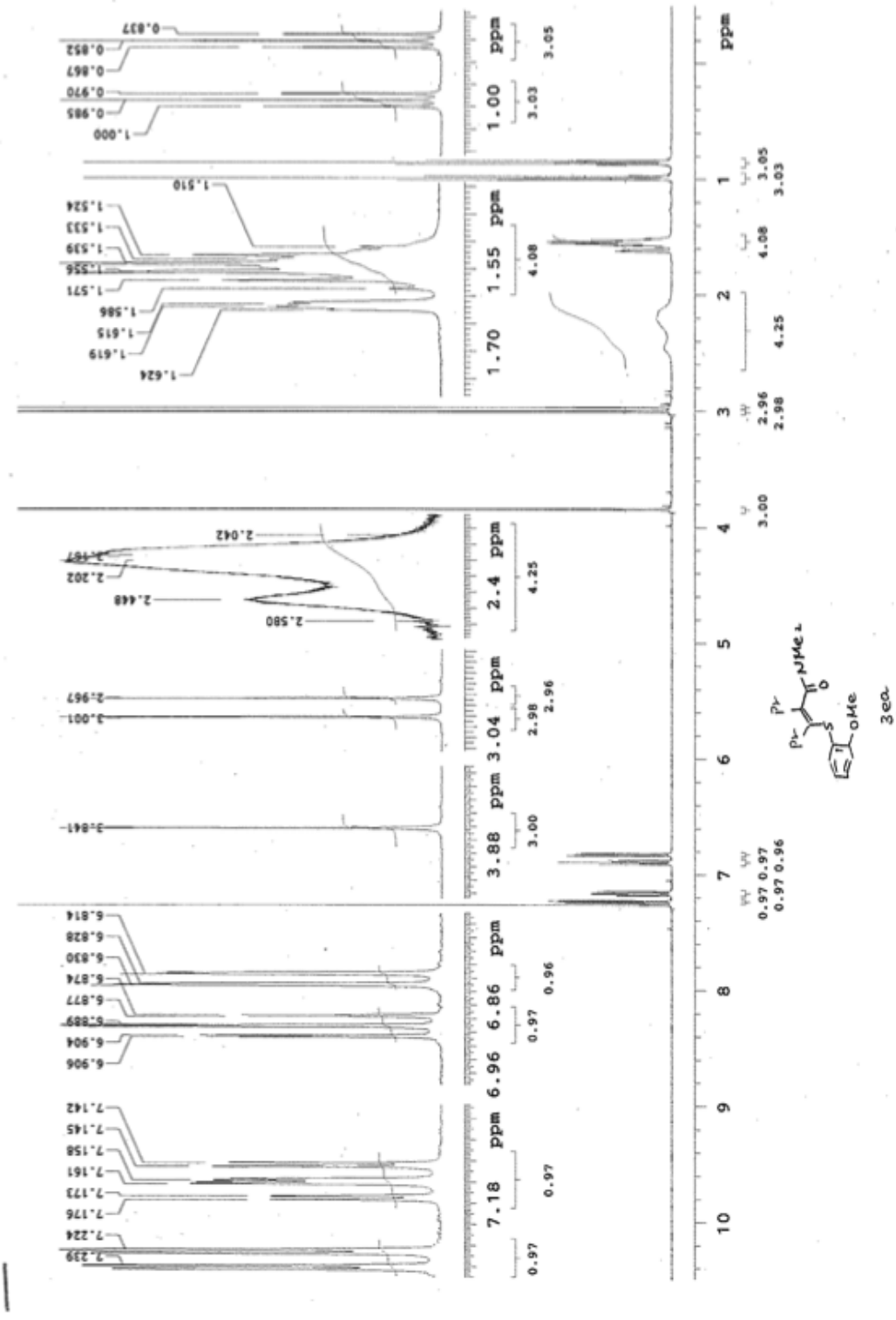
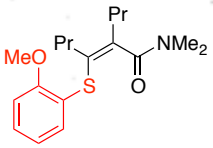
21.611
32.477
33.786
34.053
37.676
55.315
76.748
77.000
77.256
114.529
124.505
132.923
133.992
139.421
159.297
171.151
0
20
40
60
80
100
120
140
160
180
200
220
ppm
NMe2
Pr
Pr
S
MeO
3da

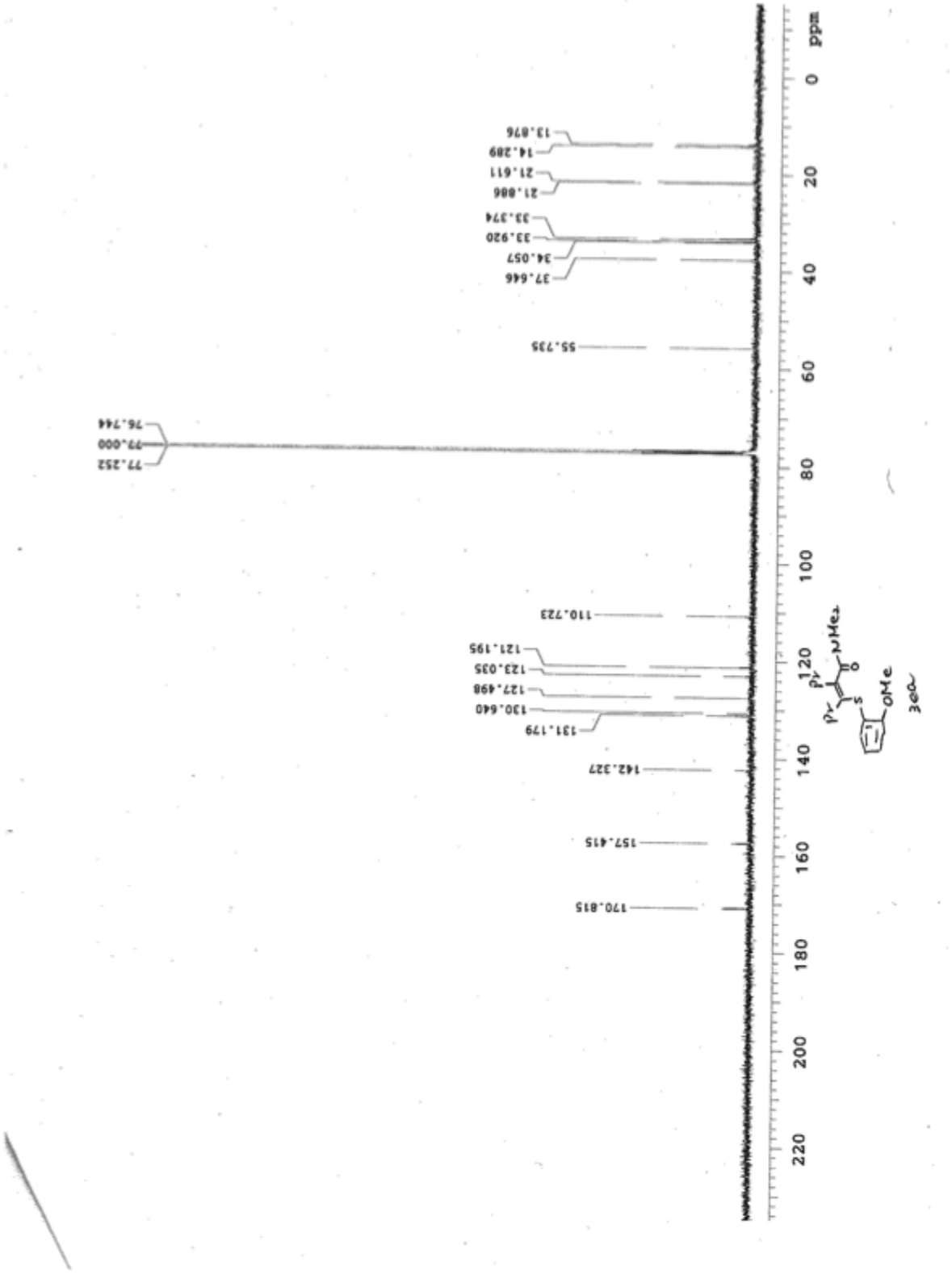

Pr
Pr
NMe2
MeO
S
O

3ea


0.837
0.852
0.867
0.970
0.985
1.000
1.510
1.524
1.533
1.539
1.556
1.571
1.586
1.615
1.619
1.624
2.042
2.187
2.202
2.448
2.580
2.967
3.001
3.841
6.814
6.828
6.830
6.874
6.877
6.889
6.904
6.906
7.142
7.145
7.158
7.161
7.173
7.176
7.224
7.239
1.70 1.55 ppm
1.00 ppm
2.4 ppm
3.88 ppm 3.04 ppm
7.18 ppm 6.96 6.86 ppm
ppm
3ea


Pr
Pr
NMe2
MeO
S
O

3ea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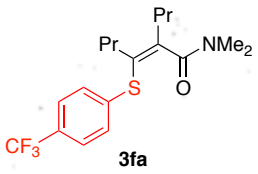
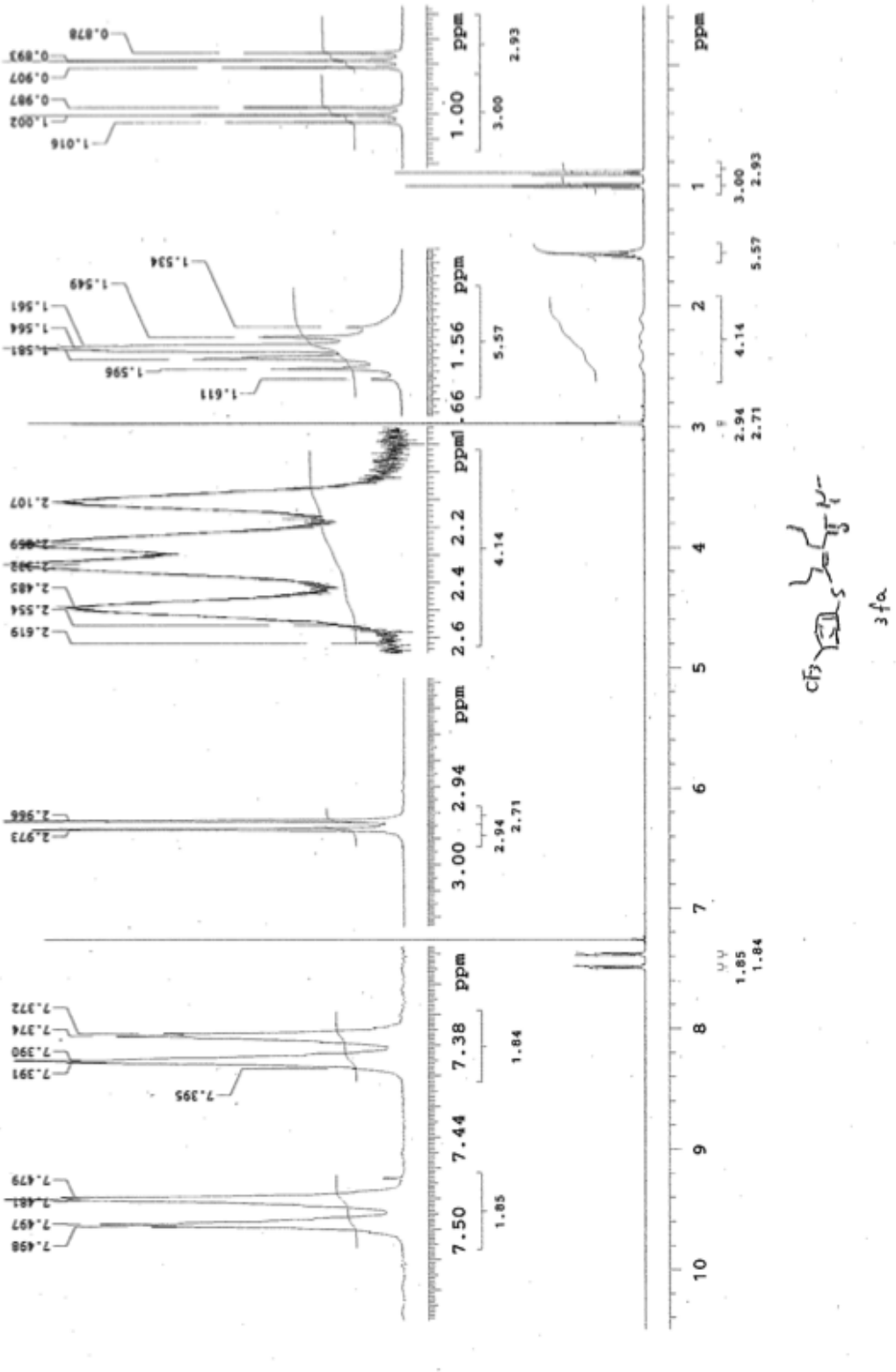
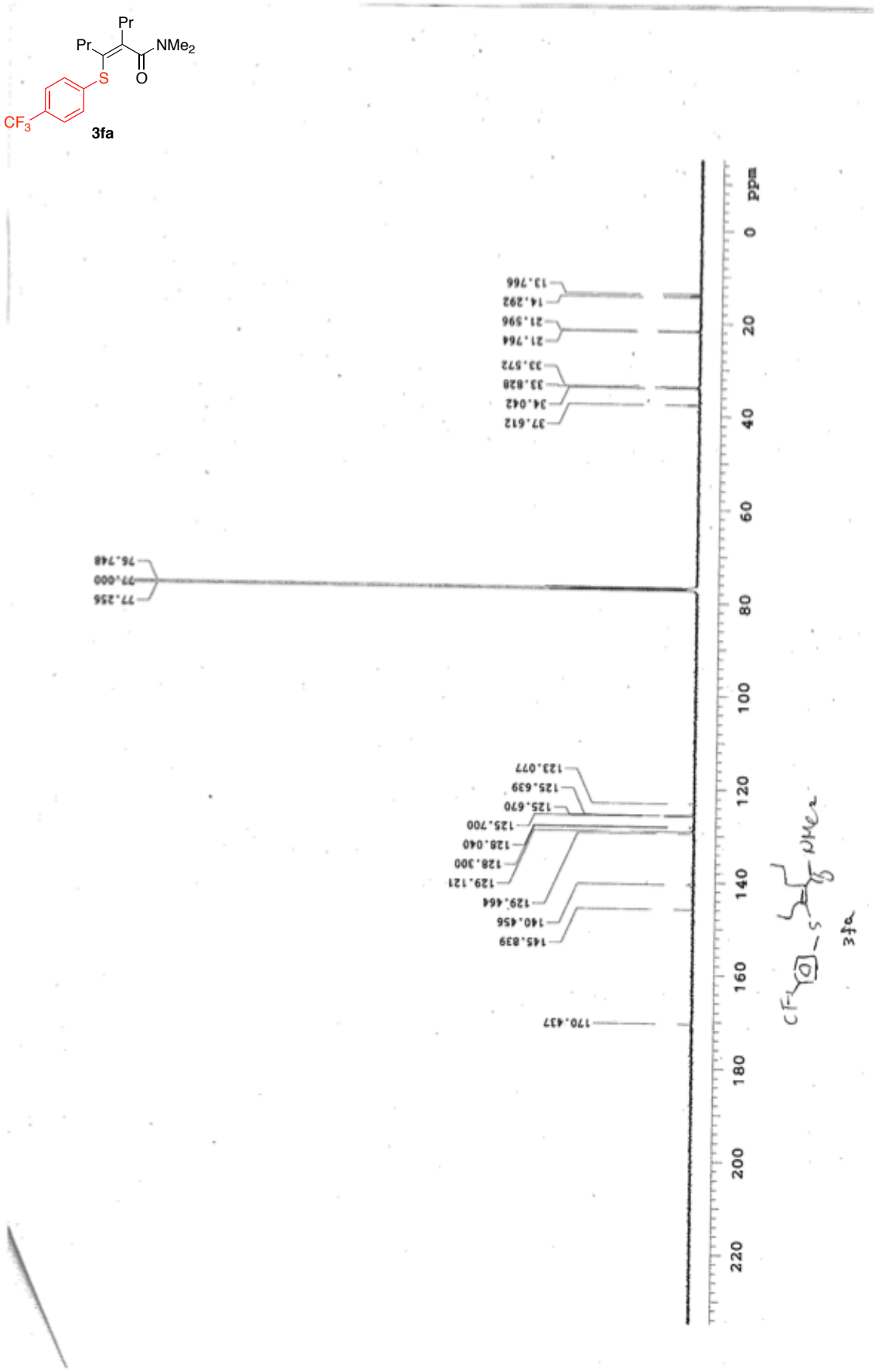
34.057
37.646
55.735
76.744
77.000
77.252
110.723
121.195
123.035
127.498
130.640
131.179
142.327
157.415
170.815
0
20
40
60
80
100
120
140
160
180
200
220
ppm
Pr
Pr
NMe2
O
S
OMe
3ea



3fa




Pr
Pr
NMe2
S
O
CF3
3fa
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14.292
21.596
21.764
33.572
33.828
34.042
37.612
76.748
77.000
77.256
123.077
125.639
125.670
125.700
128.040
128.300
129.121
129.464
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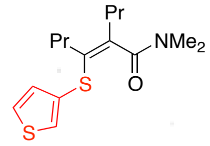
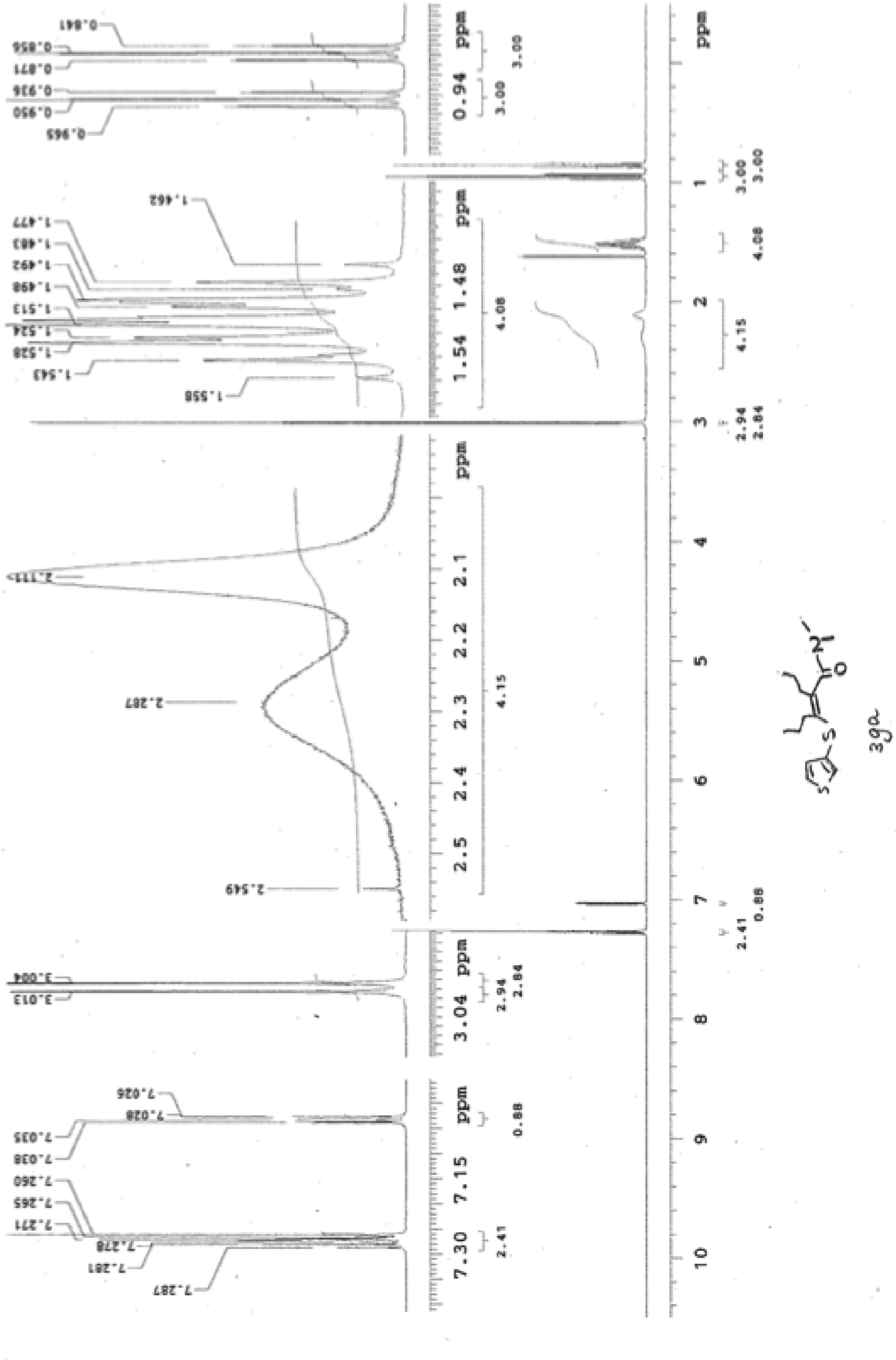
145.839
170.437
0
20
40
60
80
100
120
140
160
180
200
220
ppm


Pr
Pr
NMe2
S
O
S

3ga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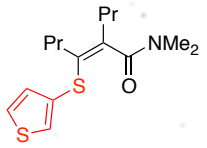
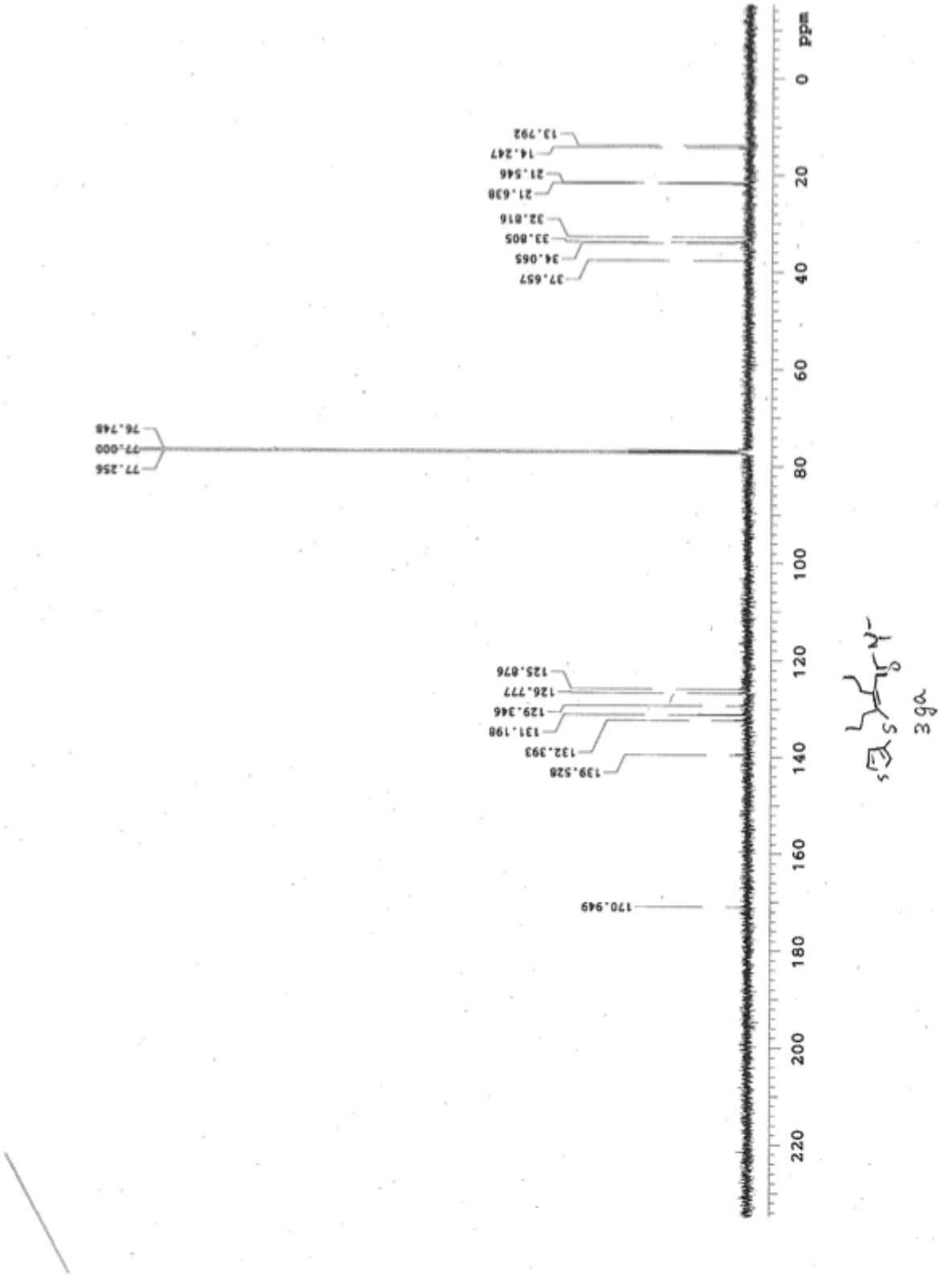
0.856
0.871
0.936
0.950
0.965
1.462
1.477
1.483
1.492
1.498
1.513
1.524
1.528
1.543
1.558
2.111
2.287
2.549
3.004
3.013
7.026
7.028
7.035
7.038
7.260
7.265
7.271
7.278
7.281
7.287
ppm
3.00
3.00
4.08
4.15
2.94
2.84
0.88
2.41
3ga


Pr
Pr
NMe2
S
O
S

3ga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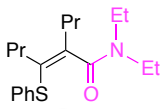
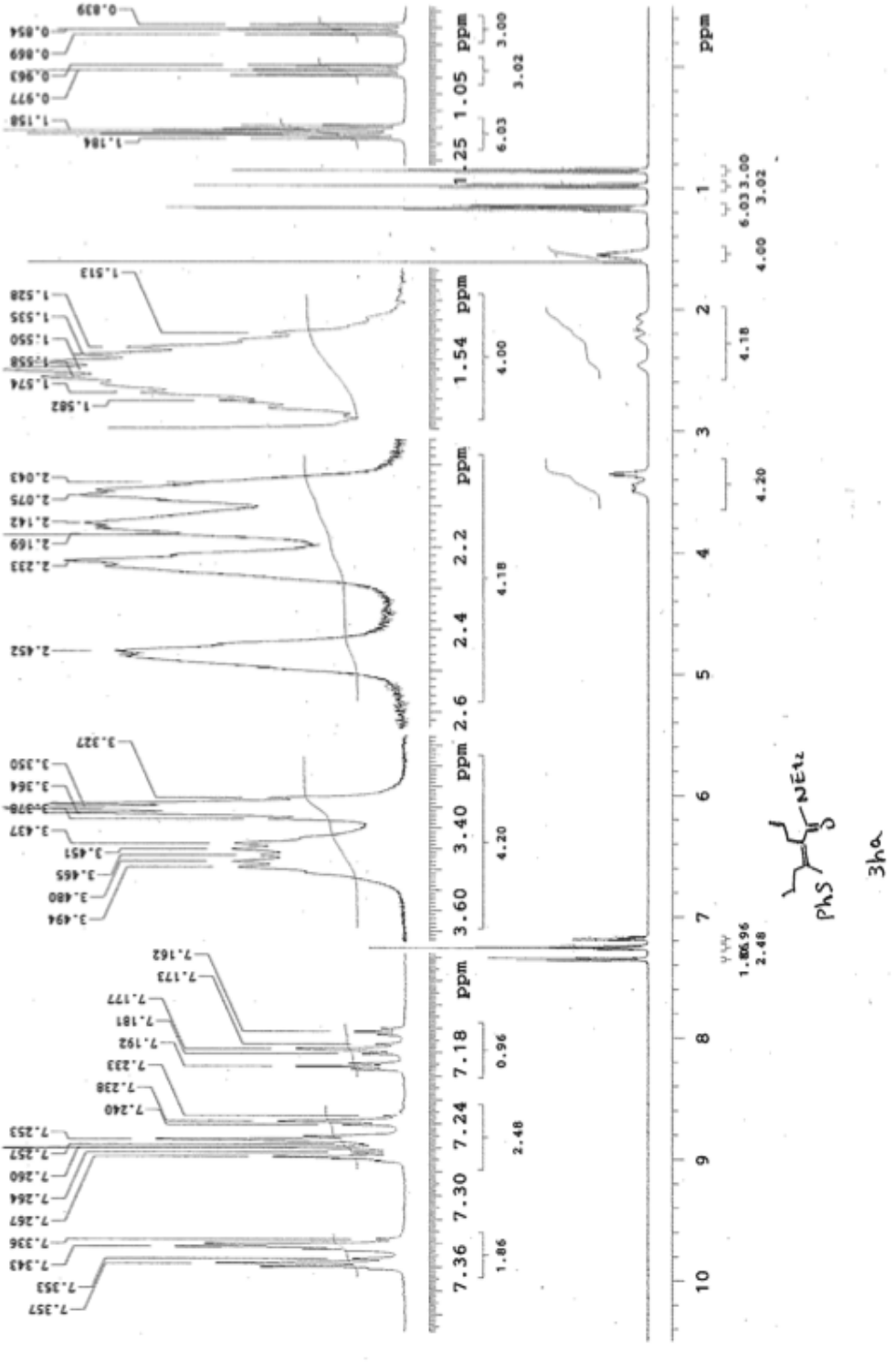
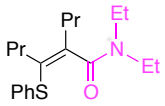
21.546
21.638
32.816
33.805
34.065
37.657
76.748
77.000
77.256
125.876
126.777
129.346
131.198
132.393
139.528
170.949
0
20
40
60
80
100
120
140
160
180
200
220
ppm
3ga

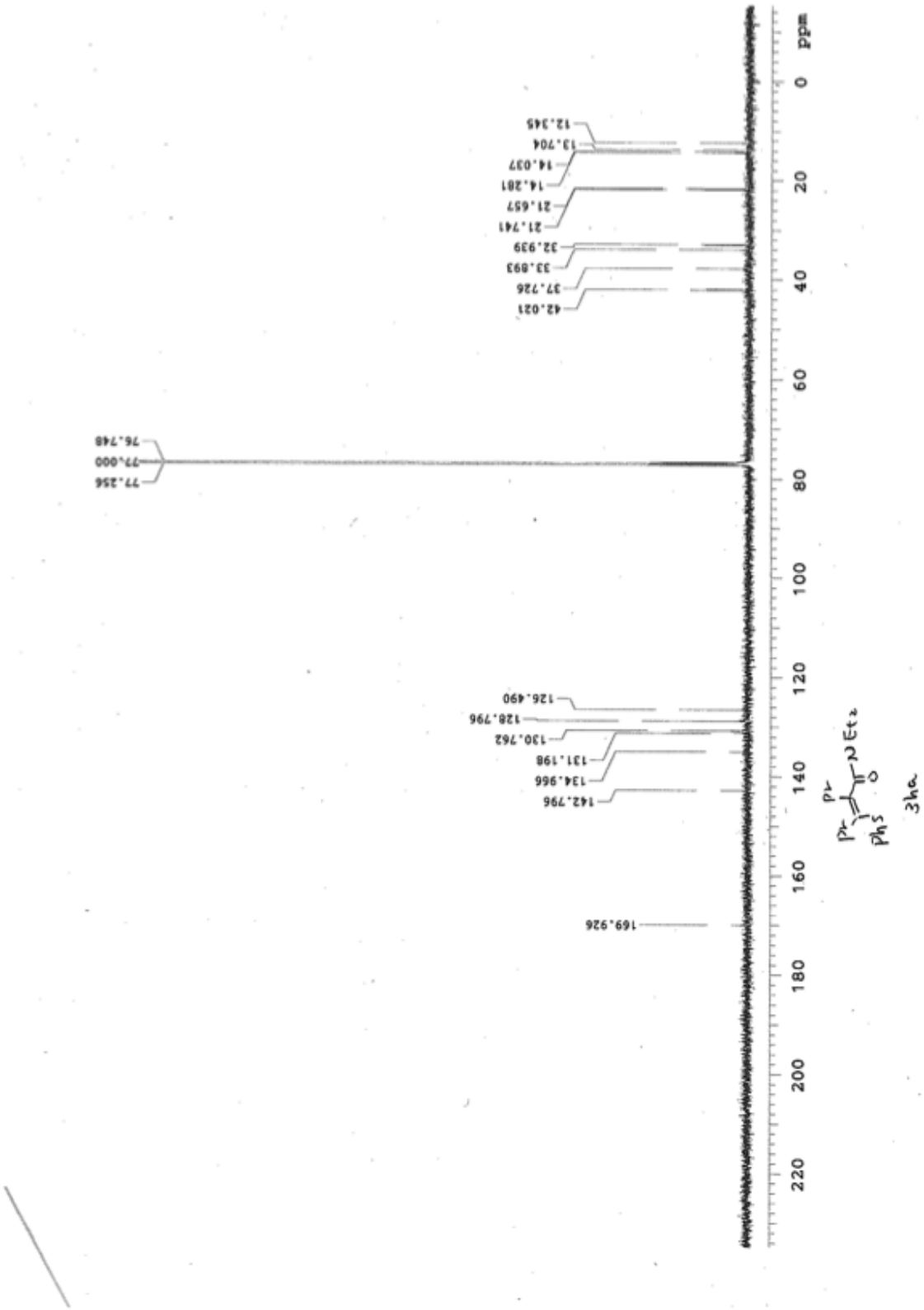

Pr
Et
Pr
N
Et
PhS
O

3ha


0.839
0.854
0.869
0.963
0.977
1.158
1.184
1.25 1.05 ppm
6.03 3.00
3.02
1.513
1.528
1.535
1.550
1.558
1.574
1.582
1.54 ppm
4.00
2.043
2.075
2.142
2.169
2.233
2.452
2.4 2.2 ppm
4.18
3.327
3.350
3.364
3.378
3.437
3.451
3.465
3.480
3.494
2.6 3.40 ppm
3.60
4.20
7.162
7.173
7.177
7.181
7.192
7.233
7.238
7.240
7.253
7.257
7.260
7.264
7.267
7.336
7.343
7.353
7.357
7.18 ppm
0.96
7.24
2.48
7.30
7.36
1.86
1 2 3 4 5 6 7 8 9 10 ppm
6.03 3.00
3.02
4.00
4.18
4.20
1.86 96
2.48
NEt2
PhS
3ha


Pr
Et
Pr
N
Et
PhS
O

3ha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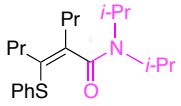
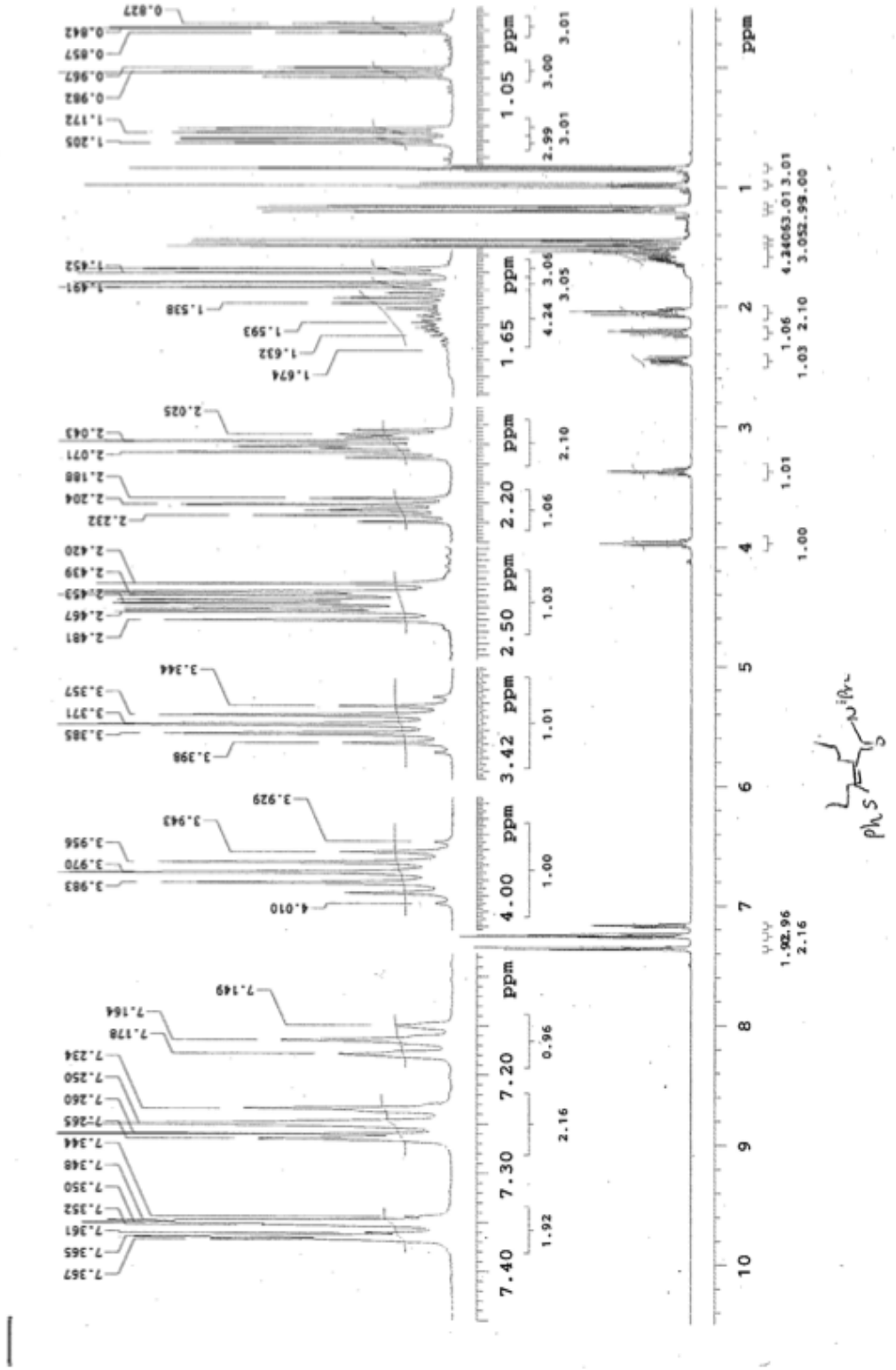
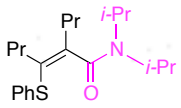
32.939
33.093
37.726
42.021
76.748
77.000
77.256
126.490
128.796
130.762
131.198
134.966
142.796
169.926
0
20
40
60
80
100
120
140
160
180
200
220
ppm
Pr
NEt2
PhS
O
3ha

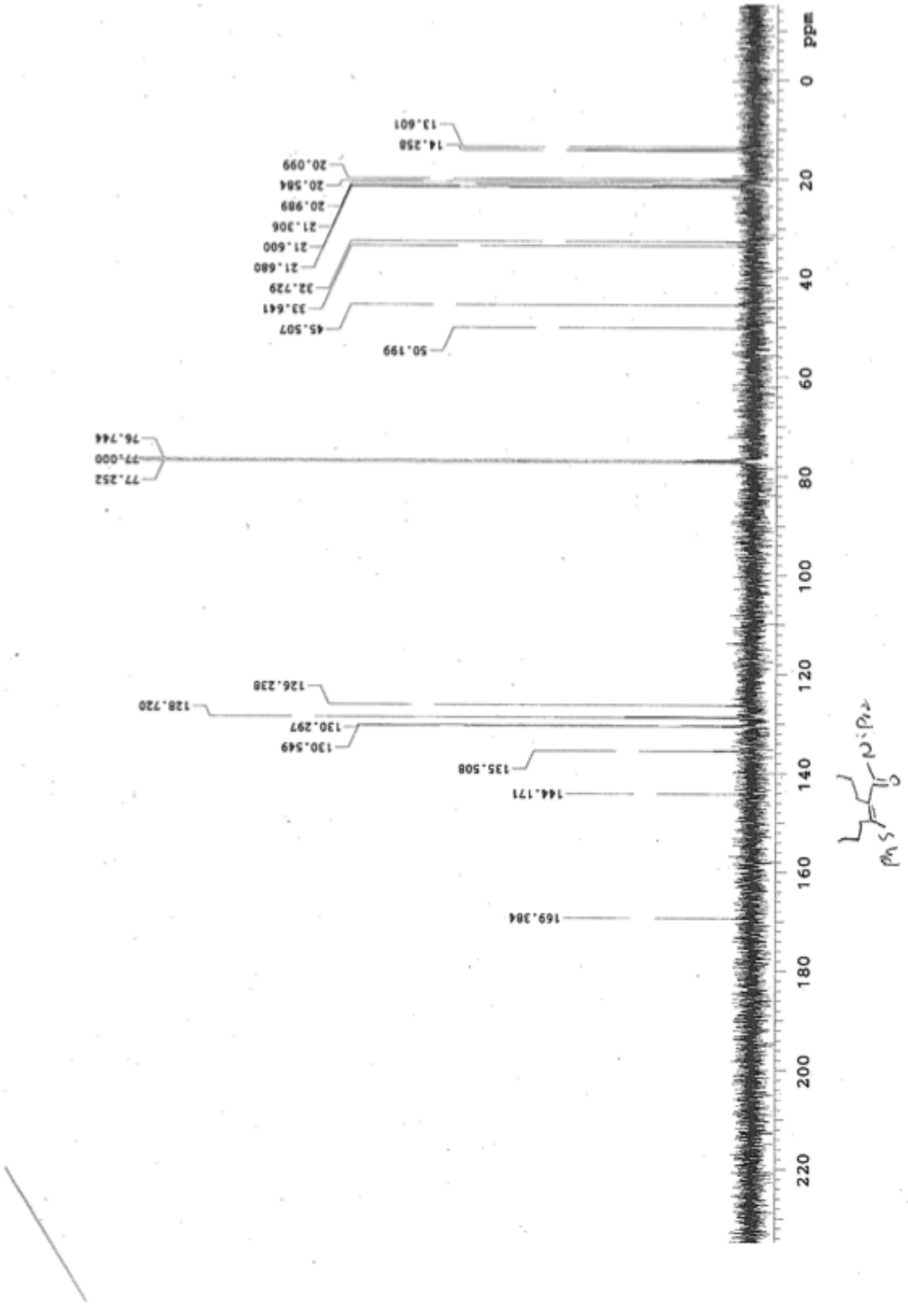


3ia




Pr
i-Pr
Pr
N
i-Pr
PhS
O

3ia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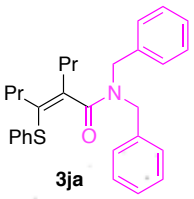
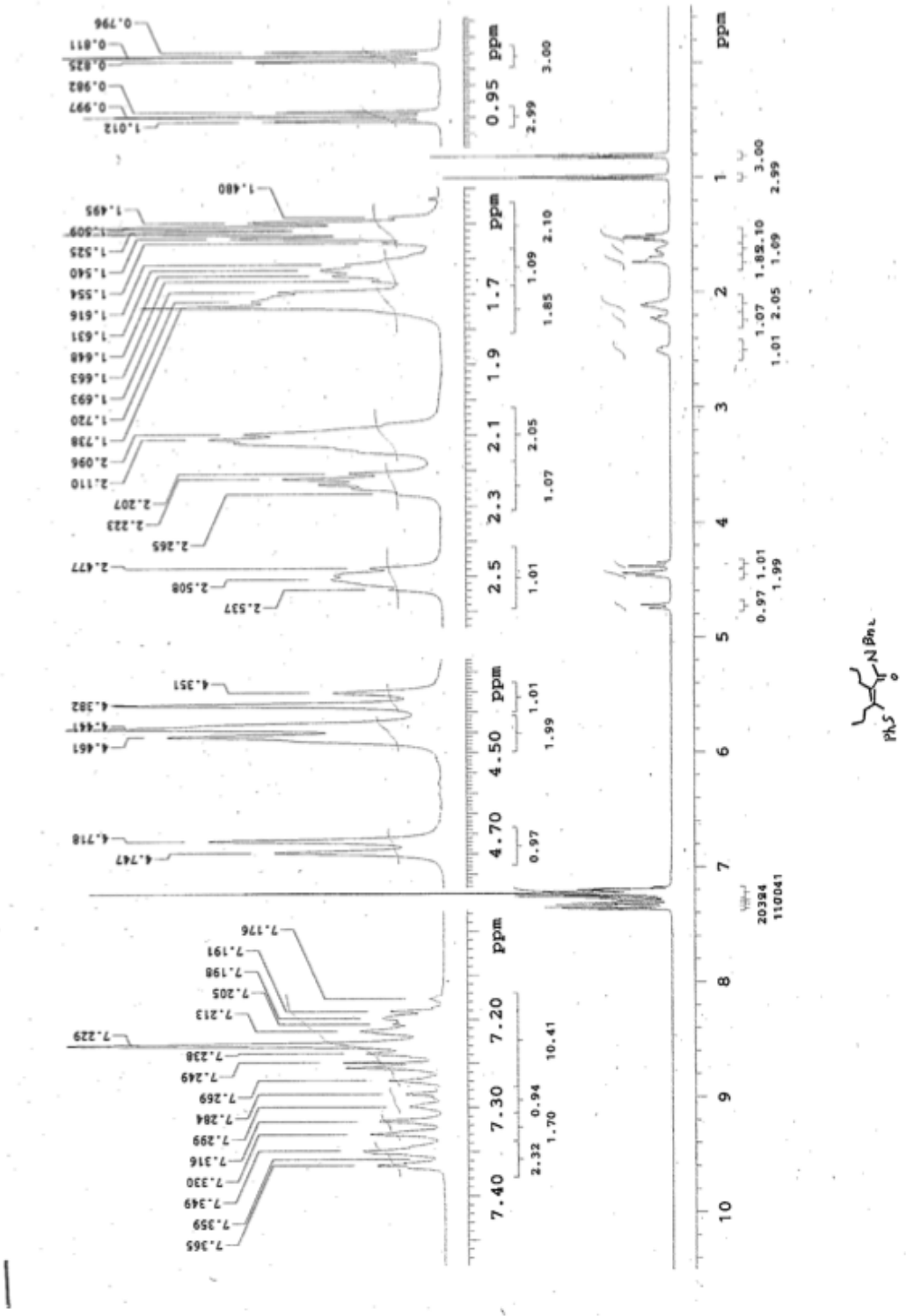
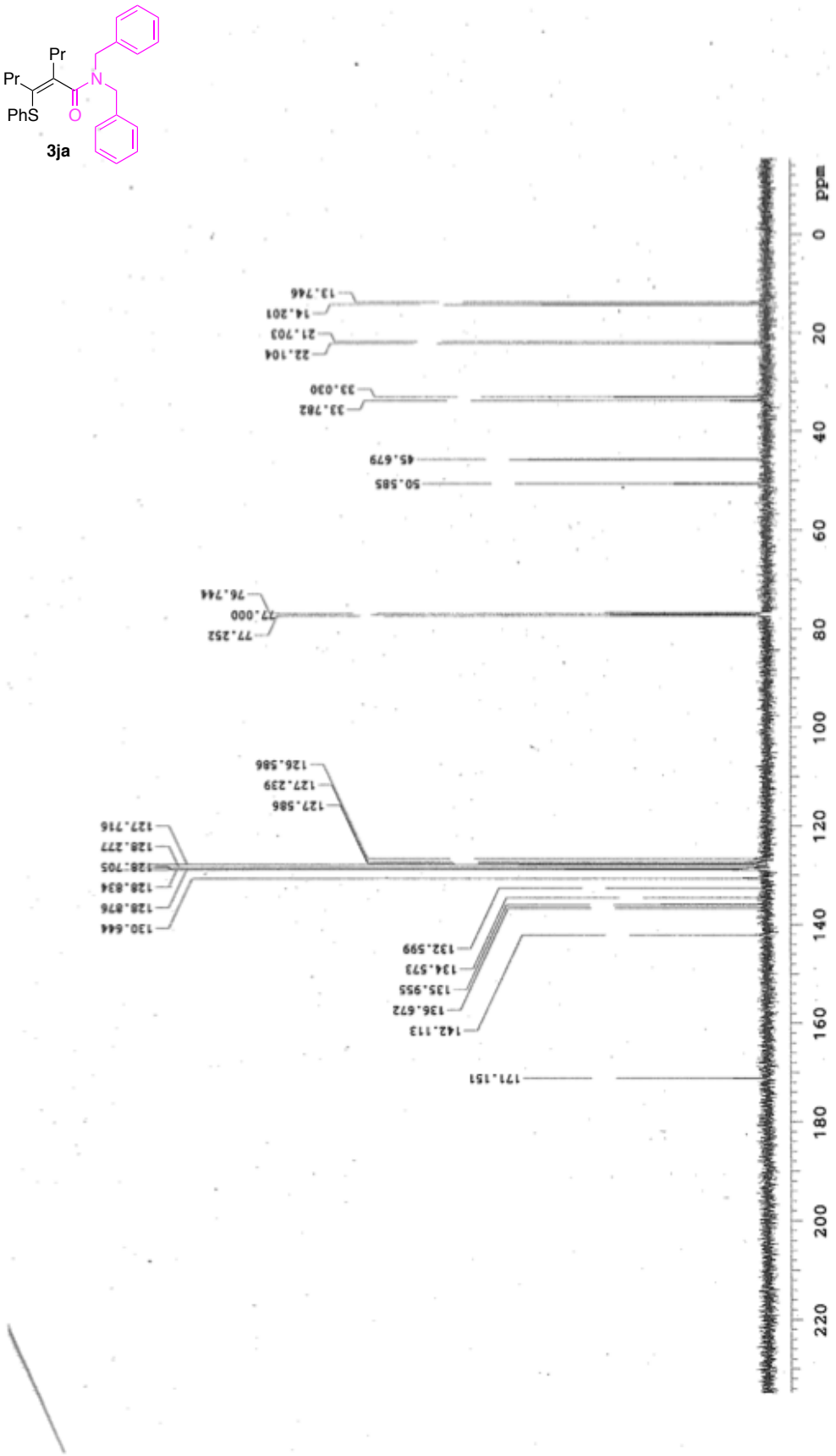
20.584
20.989
21.306
21.600
21.680
32.729
33.641
45.507
50.199
76.744
77.000
77.252
126.238
128.720
130.297
130.549
135.508
144.171
169.384
0
20
40
60
80
100
120
140
160
180
200
220
ppm



3ja




Pr
Pr
PhS
N
O
3ja
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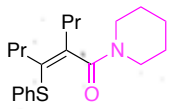
22.104
33.030
33.782
45.679
50.585
76.744
77.000
77.252
126.586
127.239
127.586
127.716
128.277
128.705
128.834
128.876
130.644
132.599
134.573
135.955
136.672
142.113
171.151
ppm
0
20
40
60
80
100
120
140
160
180
200
220



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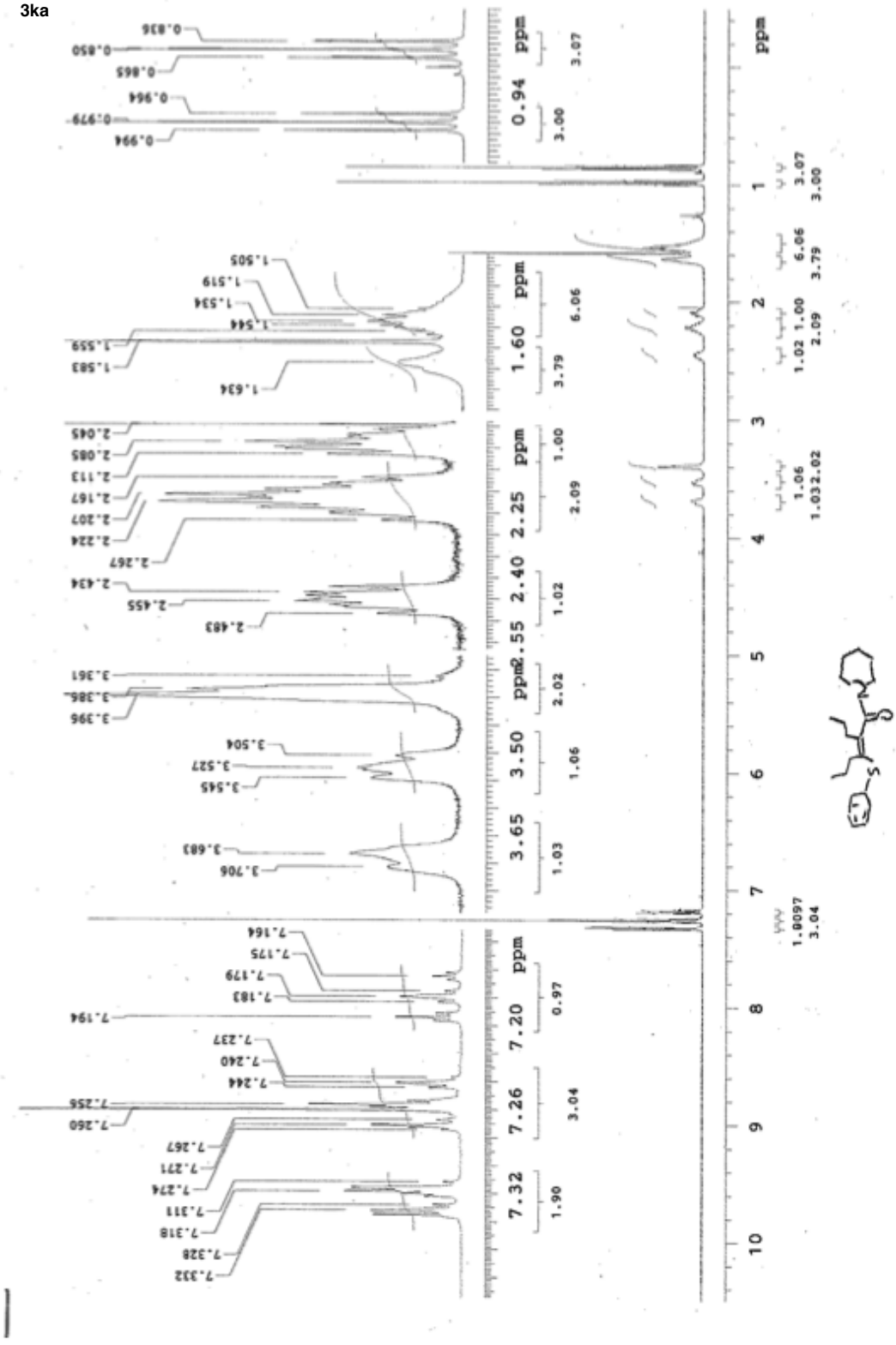
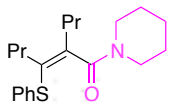
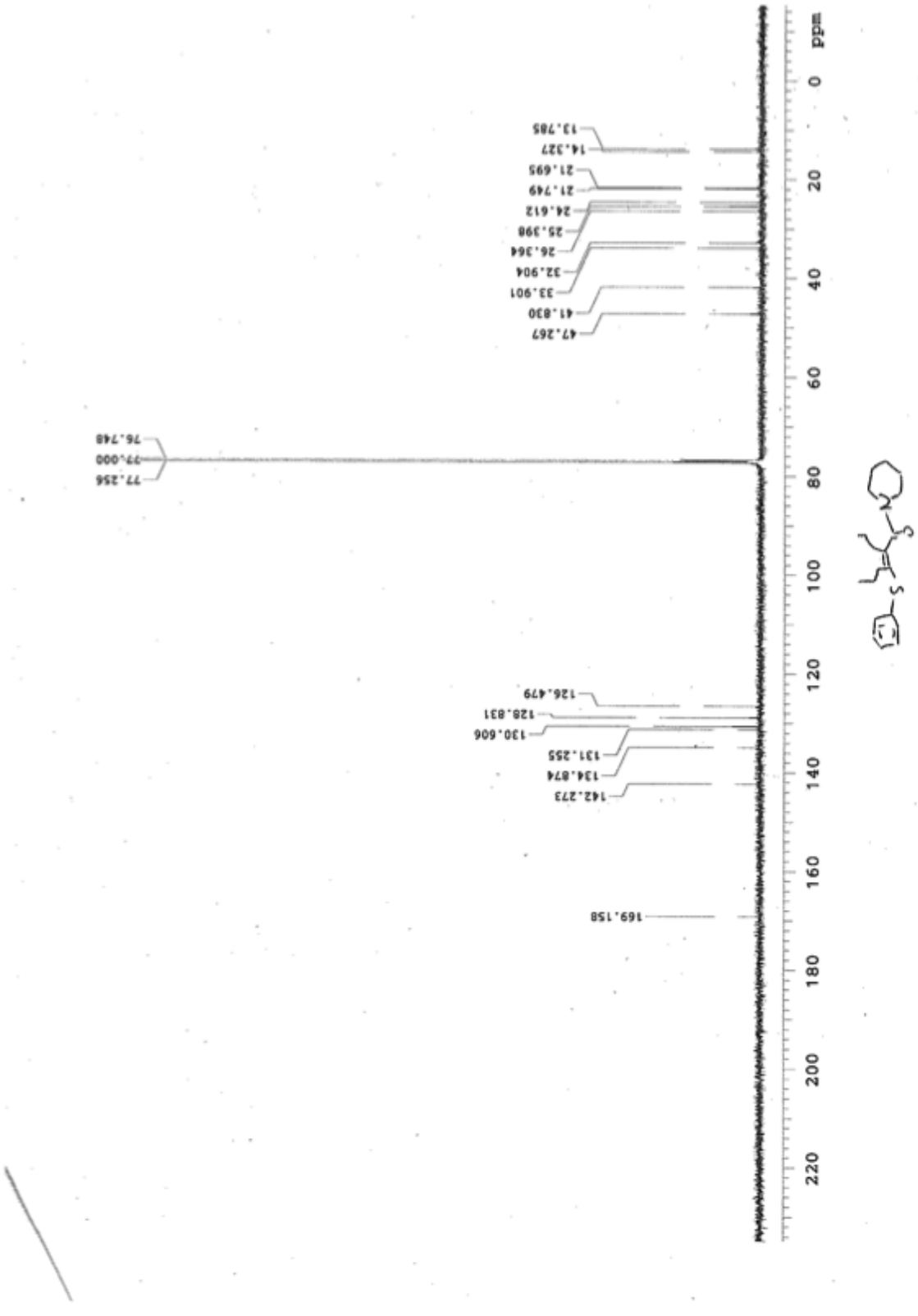



Pr
Pr
N
PhS
O

3ka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21.695
21.749
24.612
25.398
26.364
32.904
33.901
41.830
47.267
76.748
77.000
77.256
126.479
128.831
130.606
131.255
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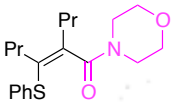
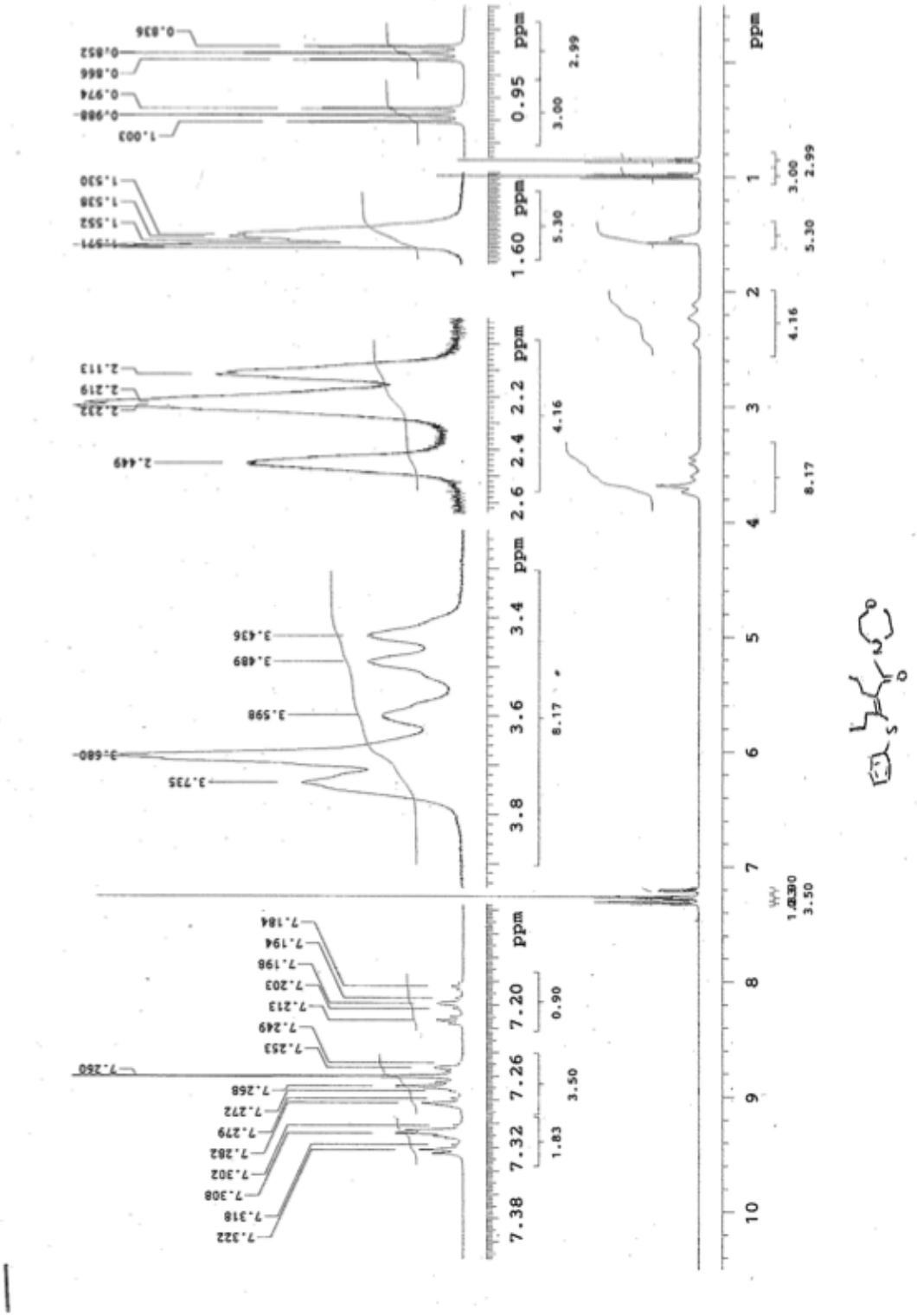
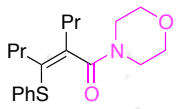
142.273
169.158
0
20
40
60
80
100
120
140
160
180
200
220
ppm

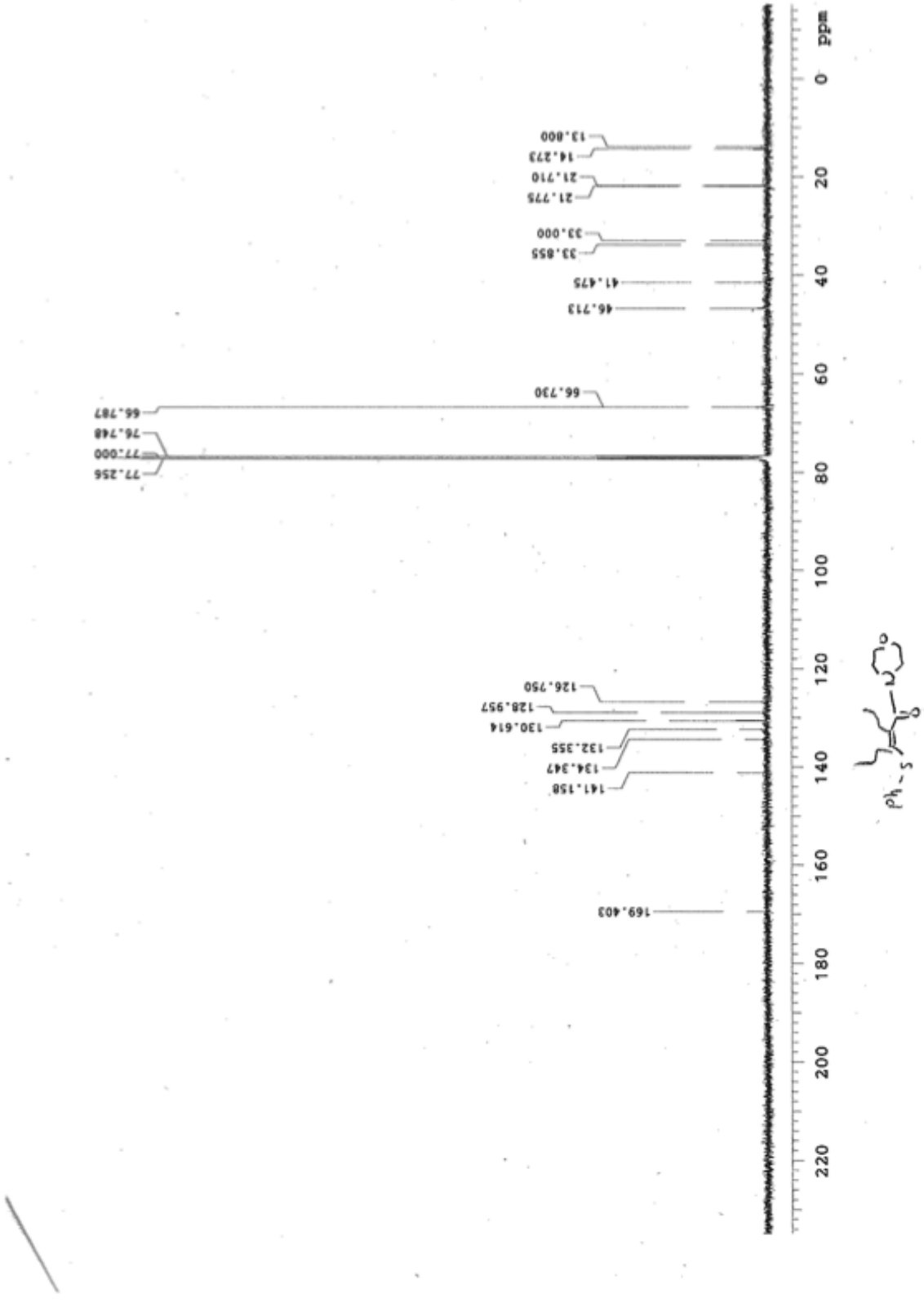


3la




Pr
Pr
PhS
N
O
O

3la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14.273
21.710
21.775
33.000
33.855
41.475
46.713
66.730
66.787
76.748
77.000
77.256
126.750
128.957
130.614
132.355
134.347
141.158
169.403
0
20
40
60
80
100
120
140
160
180
200
220
ppm