

Supporting Information: Experimental Procedure and Spectral Data.

General. All reactions were carried out using standard Schlenk techniques. Preparative TLC was carried out using 20x 20 cm glass plates coated with silica gel 60 (1000-micron thickness) with fluorescent indicator (Analab). NMR spectra were obtained on a Bruker DRX-400. ^{31}P NMR spectra were referenced to external 85 % phosphoric acid, ^{13}C spectra to CDCl_3 , and ^1H spectra to tetramethylsilane. IR spectra were obtained on a Nicolet Impact 400D spectrometer with samples prepared as KBr disks. Elemental analyses were performed by Robertson Microlit Laboratories, Inc., Madison, NJ.

Potassium tetrachloroplatinate, tricyclohexylphosphine, tri-*n*-butylphosphine (10 wt% in hexanes), triethylphosphite, and triphenylphosphite were obtained from Strem Chemicals, Inc. and were used as received. *N, N*-Diisopropylethylamine (99%), $[\text{PtCl}_2(\text{cod})]$ (98 %), triphenylphosphine (99 %), ether (99+ %, anhydrous), and chloroform (99+ %, anhydrous) were obtained from Sigma-Aldrich, Inc. and used as received. Hexane (HPLC grade) and ethyl acetate (HPLC grade) were obtained from Burdick and Jackson and used as received. Ethanol (200 proof) was obtained from Aaper Chemical Co. and used as received. Copper(I) iodide (Fluka, > 98 %) was used as received. 4-(Acetylthio)phenylacetylene was prepared in three steps from 4-iodophenylsulfonyl chloride (pipsyl chloride, Aldrich) by the method of Lindsey, et al.¹

Dichloroplatinum complexes were prepared according to standard methods, which are summarized here for convenience. ***cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$.** $\text{K}_2\text{PtCl}_4 + 2.5 \text{ eq. PPh}_3$ in xylene, reflux 24 h, filter, wash with water. White powder, ^{31}P NMR (CDCl_3): δ 14.6, $J_{\text{PtP}} = 3670 \text{ Hz}$. ***cis*- $[\text{PtCl}_2(\text{PBu-}n)_2]$.** $\text{K}_2\text{PtCl}_4 + 2.1 \text{ equiv. PBu}_3$ in $\text{H}_2\text{O}/\text{hexanes}$, 65 °C, 1 h. Procedure gave a 2:1 mixture of *cis*-isomer and $[\text{PtCl}(\text{PBu}_3)_3]\text{Cl}$. The product was fused under nitrogen atmosphere

¹ Grykop, D. T.; Clausen, C.; Roth, K. M.; Dontha, N.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7345-7355.

at 160 °C for 1 h. A white solid and some yellow oil was obtained. The mixture was dissolved in hot EtOH and then cooled two days at -23 °C to give white prisms. ^{31}P NMR (CDCl_3): δ -2.7 (t, $J_{\text{PtP}} = 3515$ Hz). ***trans*-[PtCl₂(PCy₃)₂]**. K₂PtCl₄ + 3.0 equiv. PCy₃ in toluene, reflux 3 days, filter, wash with water. Light yellow powder, ^{31}P NMR (CDCl_3): δ 17.2 (t, $J_{\text{PtP}} = 2396$ Hz). ***cis*-[PtCl₂{P(OEt)₃}₂]**. PtCl₂(cod) + 2.0 equiv. P(OEt)₃ in CHCl₃, 10 min. Clear colorless oil, ^{31}P NMR (CDCl_3): δ -72.1 (t, $J_{\text{PtP}} = 5613$ Hz). ***cis*-[PtCl₂{P(OPh)₃}₂]**. PtCl₂(cod) + 2.0 equiv. P(OPh)₃ in CHCl₃, 10 min. White solid, ^{31}P NMR (CDCl_3): δ 60.1 (t, $J_{\text{PtP}} = 5794$ Hz).

***trans*-[4-AcSC₆H₄C≡C)₂Pt(PCy₃)₂] (1a)**. A Schlenk flask was charged with *trans*-[PtCl₂(PCy₃)₂] (0.350 g, 0.425 mmol), 4-AcSC₆H₄C≡CH (0.165 g, 0.936 mmol, 2.2 equiv.), CuI (0.020 g, 0.105 mmol), and CHCl₃ (15 mL). (*i*-Pr)₂NEt (1.0 mL, 5.7 mmol) was added and the reaction mixture was heated in an oil-bath to 55-60 °C. The reaction was followed by ^{31}P NMR. After 4 days, approximately 50 % conversion was achieved. The reaction mixture was filtered, concentrated to approximately 2-3 mL by rotary evaporation and diluted with EtOH. The resulting precipitate was washed with ether. The ether wh was evaporated to give 140 mg of a light yellow powder. The ethanol fraction was evaporated and washed with ether to give another 40 mg of material. The ether-soluble solids were combined and applied to a preparative TLC plate and developed with CHCl₃. Three bands were resolved; the middle band was isolated to give 140 mg of a pale yellow powder (30 % yield). ^{31}P NMR (CDCl_3): δ 24.5, (t, $J_{\text{PtP}} = 2399$ Hz). ^{13}C NMR (CDCl_3): δ 194.7, 133.7, 131.0, 130.8, 122.4, 115.1 (t, $J_{\text{PtC}} = 30$ Hz), 109.0, 33.2 (t, $J_{\text{PC}} = 14$ Hz), 39.9, 29.6, 27.6 (t, $J_{\text{PC}} = 11$ Hz), 26.5. ^1H NMR (CDCl_3): δ 7.26 (m, 8 H), 2.85 (unresolved multiplet, 6H), 2.42 (s, 6 H), 2.09 (d, $J_{\text{PC}} = 12$ Hz), 1.82-1.70 (broad singlets, 30 H), 1.24 (s, 18 H). IR (KBr disc) cm^{-1} : 2097 ($\nu\text{C}\equiv\text{C}$), 1712 ($\nu\text{C}=\text{O}$). Elemental analysis: calcd. for C₅₆H₈₀O₂P₂PtS₂ C 60.57, H 7.26, Pt 18.55; found C 60.79, H 7.29, Pt 17.63

***trans*-[4-AcSC₆H₄C≡C]₂Pt(PBu₃)₂] (1b).** A mixture of *cis*-[PtCl₂(PBu-*n*₃)₂] (0.54 g, 0.379 mmol), 4-AcSC₆H₄C≡CH (0.197 g, 1.25 mmol, 3.3 equiv.), CuI (0.010 g, 0.052 mmol), CHCl₃ (10 mL), and (*i*-Pr)₂NEt (0.5 mL, 2.8 mmol) was heated in an oil-bath to 55-60 °C overnight. The reaction mixture was filtered, taken to dryness by rotary evaporation, and applied to a prep TLC plate. After a second plate, a single component was isolated, giving 169 mg of yellow oil which solidified upon standing (47 % yield). ³¹P NMR (CDCl₃): δ -2.5 (t, *J*_{PtP} = 2253 Hz). ¹³C NMR (CDCl₃): δ 194.7, 134.0, 131.4, 130.4, 123.4, 111.6 (t, *J*_{PtC} = 14 Hz), 108.6, 30.1, 26.3, 24.4 (t, *J*_{PC} = 7 Hz), 23.9 (t, *J*_{PC} = 17 Hz), 13.9. ¹H NMR (CDCl₃): δ 7.42 (d, *J* = 8.4 Hz, 4 H), 7.23 (d, *J* = 8.4 Hz, 4 H), 2.37 (s, 6H), 2.01 (multiplet, 12 H), 1.51-1.39 (broad singlet, multiplet, 24 H), 0.93 (t, *J* = 7.3 Hz, 18 H). IR (KBr disc) cm⁻¹: 2098 (νC≡C), 1703 (νC=O). Elemental analysis: calcd. for C₄₄H₆₈O₂P₂PtS₂ C 55.62, H 7.21, Pt 20.53; found C 54.81, H 7.11, Pt 19.87.

***trans*-[(4-AcSC₆H₄C≡C)₂Pt(PPh₃)₂] (1c).** This compound has been previously reported,² but was obtained in higher yield (71 % v. 16 %) by this method. A mixture of *cis*-[PtCl₂(PPh₃)₂] (0.250 g, 0.316 mmol), 4-AcSC₆H₄C≡CH (0.123 g, 0.696 mmol, 2.2 equiv.), CuI (0.010 g, 0.052 mmol), CHCl₃ (15 mL), and (*i*-Pr)₂NEt (0.090 g, 0.696 mmol) was heated in an oil-bath to 55-60 °C. The reaction was monitored by ³¹P NMR. After 2.5 h, the PtCl₂(PPh₃)₂ was consumed, and two product peaks at 22.0 and 19.2 ppm were present in approximately a 2:1 ratio, presumed to be the mono- and di-substitution products. An additional 60 mg (0.34 mmol) of 4-AcSC₆H₄C≡CH and 39 mg (0.30 mmol) of (*i*-Pr)₂NEt were added and the reaction mixture was stirred and heated overnight. This resulted in complete conversion of the platinum complexes to a single product, as evidenced by ³¹P NMR. The reaction mixture was allowed to

² Mayor, M.; Weber, H. B.; von Hanisch, C.; Reichert, J.; Beckman, D. *Angew. Chem. Int. Ed.* **2002**, *41*, 1183-1186.

cool to room temperature and was then diluted with EtOH (25 mL). Within a few minutes a precipitate started to form. The mixture was cooled at $-10\text{ }^{\circ}\text{C}$ for 1 h, filtered, washed with water and EtOH, and air-dried to give 240 mg of orange needles (71% yield). ^{31}P NMR (CDCl_3): δ 19.6, $J_{\text{PtP}} = 2630\text{ Hz}$. ^{13}C NMR (CDCl_3): δ 194.8, 135.0 (t, $J_{\text{PC}} = 6\text{ Hz}$), 133.2, 131.5, 131.1 (t, $J_{\text{PC}} = 19\text{ Hz}$), 130.3, 129.9, 114.1, 112.8, 30.0. ^1H NMR (CDCl_3): δ 7.80 (multiplet, 12 H), 7.35 (multiplet, 18 H), 6.94 (d, $J = 12\text{ Hz}$, 4 H), 6.26 (d, $J = 12\text{ Hz}$, 4 H), 2.33 (s, 6 H). IR (KBr disc) cm^{-1} : 2105 ($\nu\text{C}\equiv\text{C}$), 1700 ($\nu\text{C}=\text{O}$).

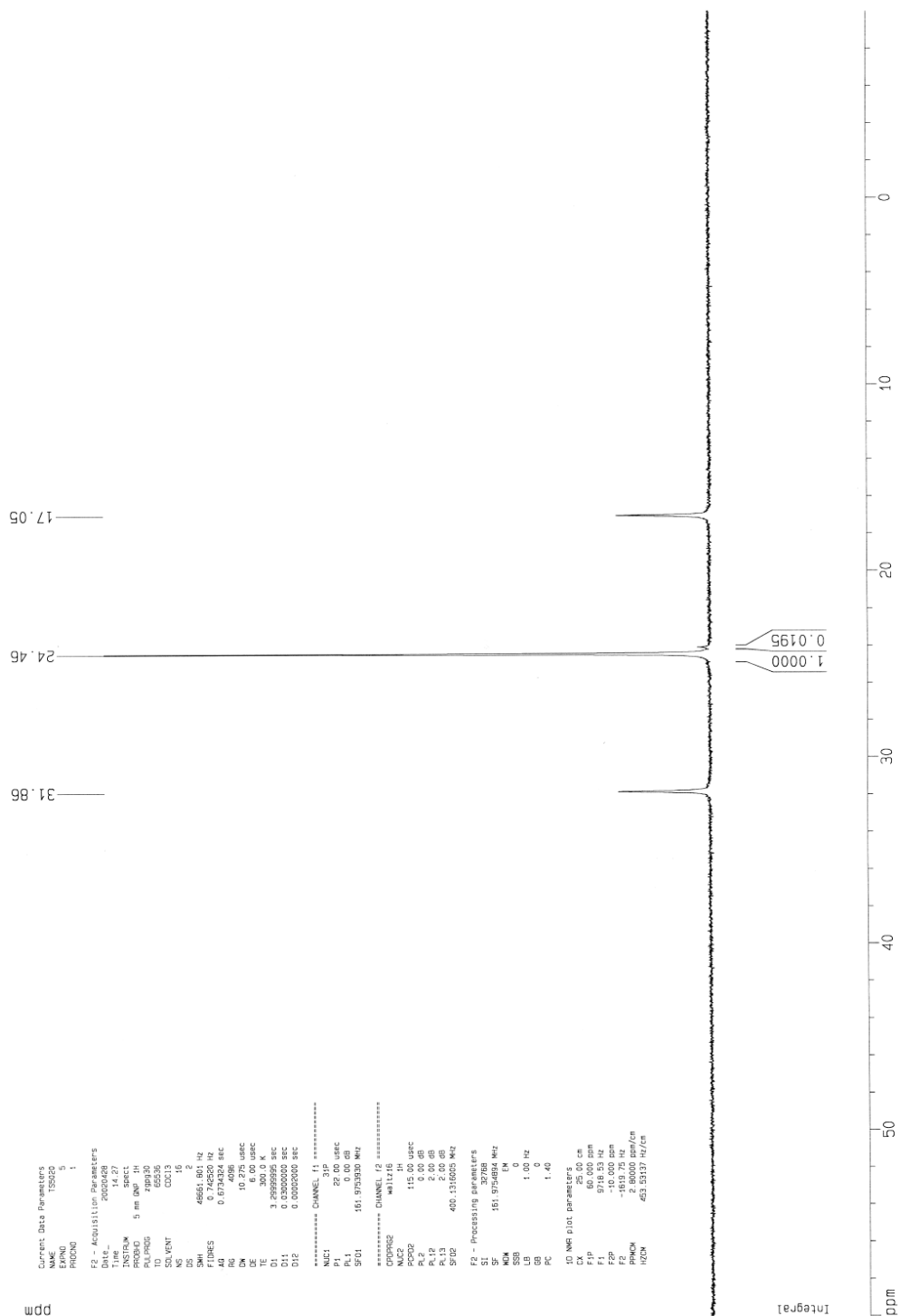
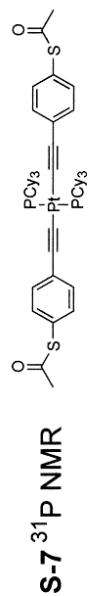
***trans*-[(4-AcSC₆H₄C \equiv C)₂Pt{P(POEt)₃}₂] (1d).** A mixture of *cis*-[PtCl₂{P(OEt)₃}₂] (0.299 g, 0.500 mmol), 4-AcSC₆H₄C \equiv CH (0.200 g, 1.13 mmol, 2.27 equiv.), CuI (0.020 g, 0.105 mmol), CHCl₃ (10 mL), and (*i*-Pr)₂NEt (1.0 mL, 5.7 mmol) was heated in an oil-bath to 55-60 $^{\circ}\text{C}$ overnight. Analysis by ^{31}P NMR showed two products in nearly equal proportions, presumed to be the *cis*- and *trans*-complexes. The solvent was removed under vacuum and the residue was stirred vigorously in ether-acetone to separate any amine salts. After filtering, the residue was applied to a prep TLC plate and developed using CHCl₃. The highest-R_f band was collected to give 200 mg of an orange oil. Analysis by ^{31}P NMR showed this fraction to be a mixture of the *trans*- and *cis*-complex in approximately a 2.5:1 ratio. A second prep TLC, developed with 3:1 hexane-ethyl acetate separated the isomers. The upper-R_f band gave 135 mg of a light yellow oil, identified as the *trans*-complex, while the lower-R_f band afforded 55 mg of the *cis*-complex. Both samples solidified upon standing overnight. Yield of the *trans*-complex was 31 %. ^{31}P NMR (CDCl_3): δ 99.8, $J_{\text{PtP}} = 4064\text{ Hz}$. ^{13}C NMR (CDCl_3): δ 194.3, 133.8, 131.8, 129.6, 124.2, 110.0 (t, $J_{\text{PC}} = 3\text{ Hz}$), 102.4 (t, $J_{\text{PC}} = 19\text{ Hz}$), 30.1, 16.3 (t, $J_{\text{PC}} = 4\text{ Hz}$). ^1H NMR (CDCl_3): δ 7.32 (d, $J = 8.4\text{ Hz}$, 4 H), 7.23 (d, $J = 8.4\text{ Hz}$, 4 H), 4.33 (m, 12 H), 2.39 (s, 6 H), 1.37 (t, $J_{\text{PH}} =$

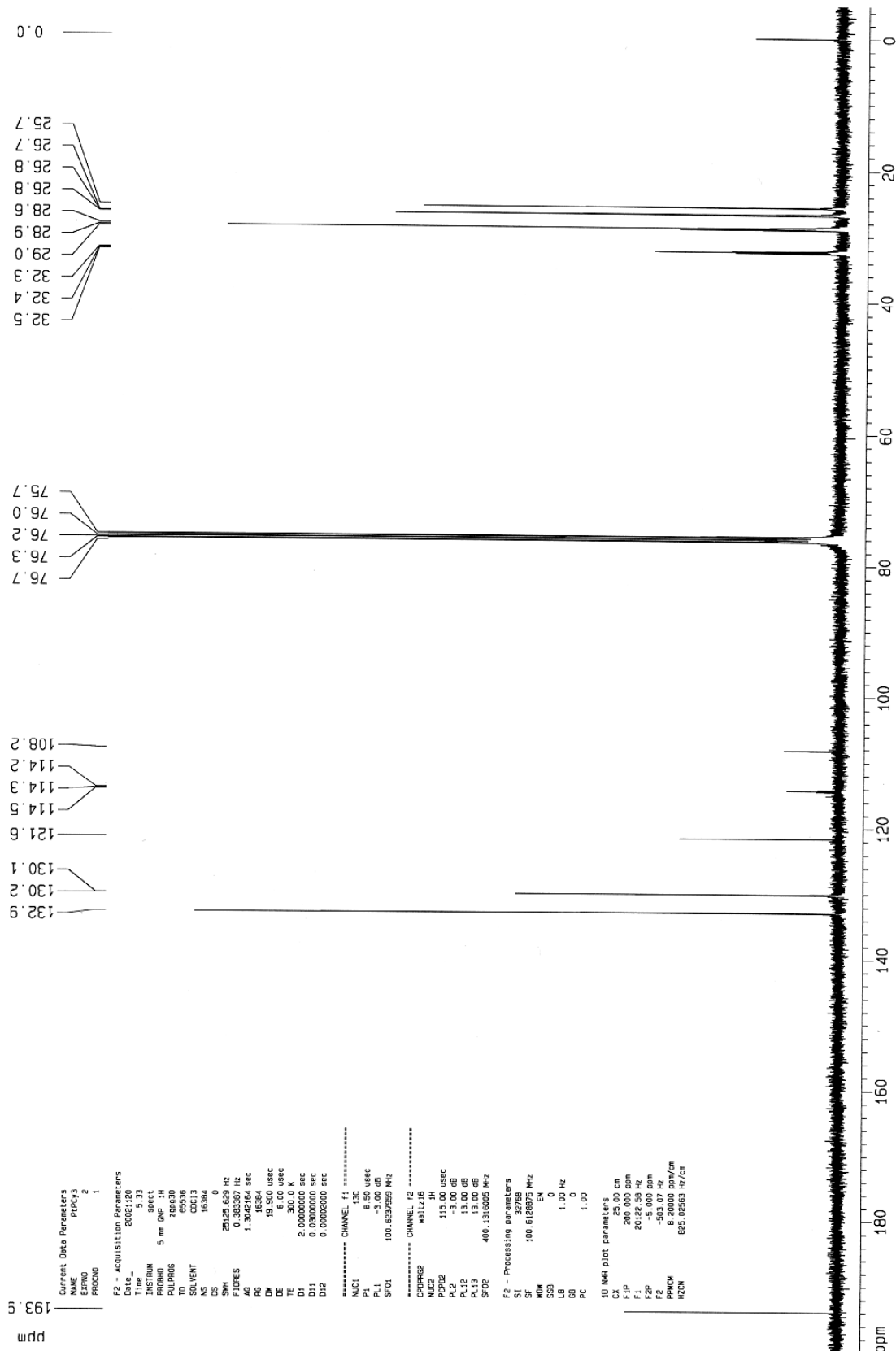
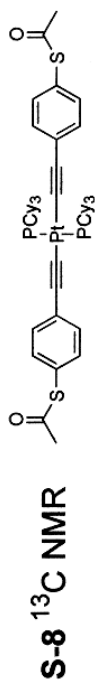
7.2 Hz, 18 H). IR (KBr disc) cm^{-1} : 2115 ($\nu\text{C}\equiv\text{C}$), 1702 ($\nu\text{C}=\text{O}$). Elemental analysis: calcd. for $\text{C}_{32}\text{H}_{44}\text{O}_8\text{P}_2\text{PtS}_2$ C 43.78, H 5.05, Pt 22.22; found C 43.75, H 4.88, Pt 21.41.

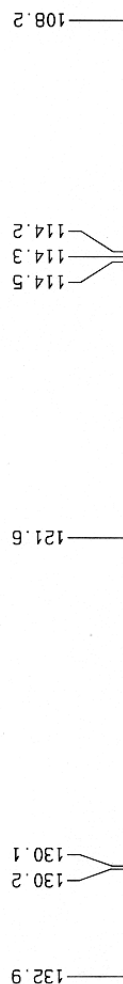
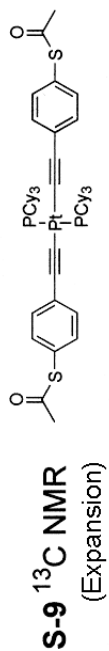
***trans*-[(4-AcSC₆H₄C \equiv C)₂Pt{P(OPh)₃}₂] (1d).** A mixture of *cis*-[PtCl₂{P(OPh)₃}₂] (0.443 g, 0.500 mmol), 4-AcSC₆H₄C \equiv CH (0.194 g, 1.10 mmol, 2.2 equiv.), CuI (0.020 g, 0.105 mmol), CHCl₃ (15 mL), and (*i*-Pr)₂NEt (1.0 mL, 5.7 mmol) was heated in an oil-bath to 55-60 °C four days. Analysis by ³¹P NMR showed that the starting material had been consumed, giving a mixture of the *trans*- and *cis*-complexes in approximately a 2:1 ratio. The reaction mixture was taken to dryness by rotary evaporation, redissolved in ca. 1 mL of CHCl₃, and applied to a prep TLC plate, eluting with CHCl₃. The highest and lowest-R_f bands were cut, and the middle fraction was rechromatographed using 2% MeOH-CHCl₃. A single band was isolated, giving 212 mg of an orange oil which solidified upon standing (36% yield). ³¹P NMR (CDCl₃): δ 79.5, J_{PtP} = 4590 Hz. ¹H NMR (CDCl₃): δ 7.30-7.08 (multiplets, 39 H), 2.33 (s, 6 H). IR (KBr disc) cm^{-1} : 2119 ($\nu\text{C}\equiv\text{C}$), 1712 ($\nu\text{C}=\text{O}$). Elemental analysis: calcd. for $\text{C}_{56}\text{H}_{44}\text{O}_8\text{P}_2\text{PtS}_2$ C 57.68, H 3.80; found C 57.45, H 3.83.

SAM Formation and Characterization. Gold on silicon surfaces were cleaned by a short rinse in acetone, followed by a 10 min air plasma cleaning. Flat substrates were used the same day they were cleaned. Gold wires (10 μm diam.) were cleaned by immersion in 30% hydrogen peroxide for 10 minutes, followed by rinses in deionized water and 100% ethanol. Gold wires were used that day, or stored for short periods (2-4 days) in 100% ethanol. Molecular wire solutions were made with oxygen free solvents and in an inert atmosphere glovebox, and all depositions were performed in an inert atmosphere glovebox to prevent polymerization. Solutions of the Pt wires were created by dissolving 1.4 mg of the platinum complex in 4 mL of THF and 60 μL of conc. Sulfuric acid. The molecules were allowed to

deprotect *in situ* and deposit on the gold substrates for 24 hours. After deposition substrates were rinsed in THF and 100% ethanol. Flat substrates were analyzed using multi-wavelength ellipsometry and contract angle measurements to characterize film quality.







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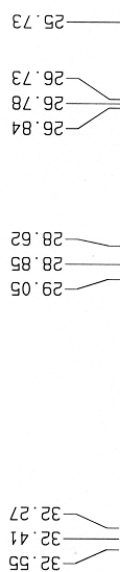
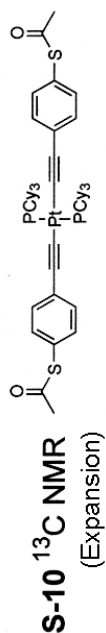
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ppm

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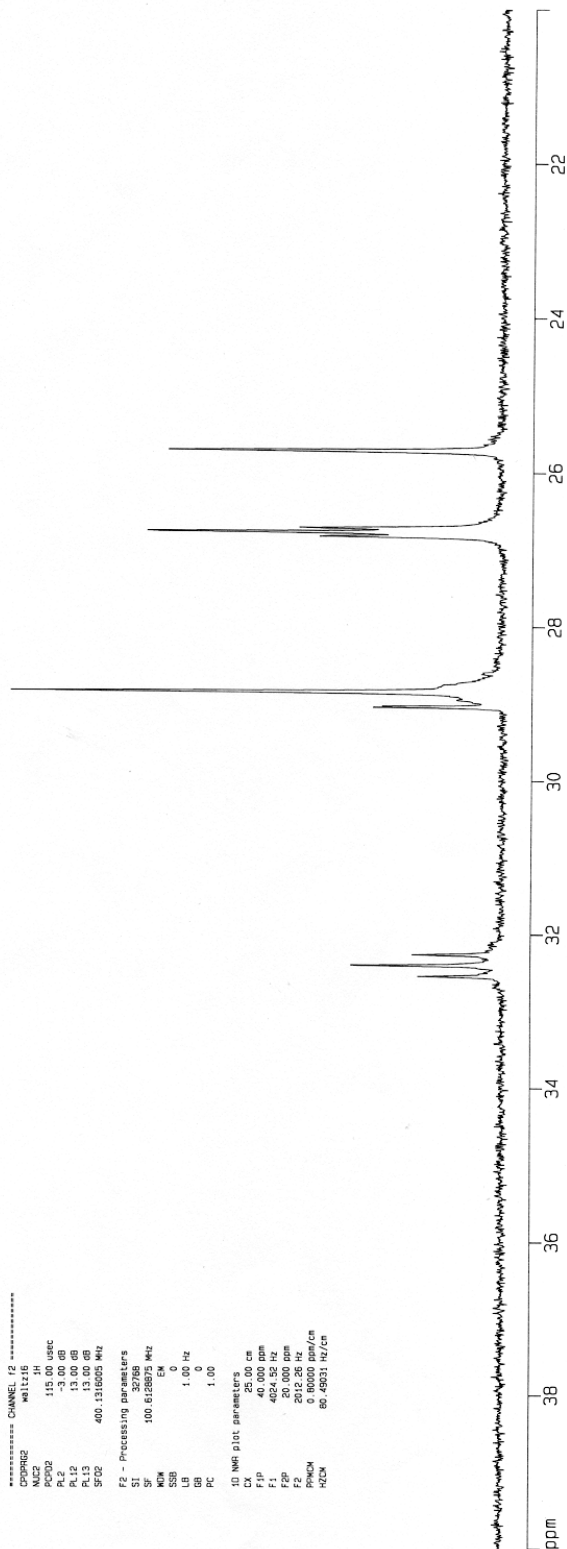
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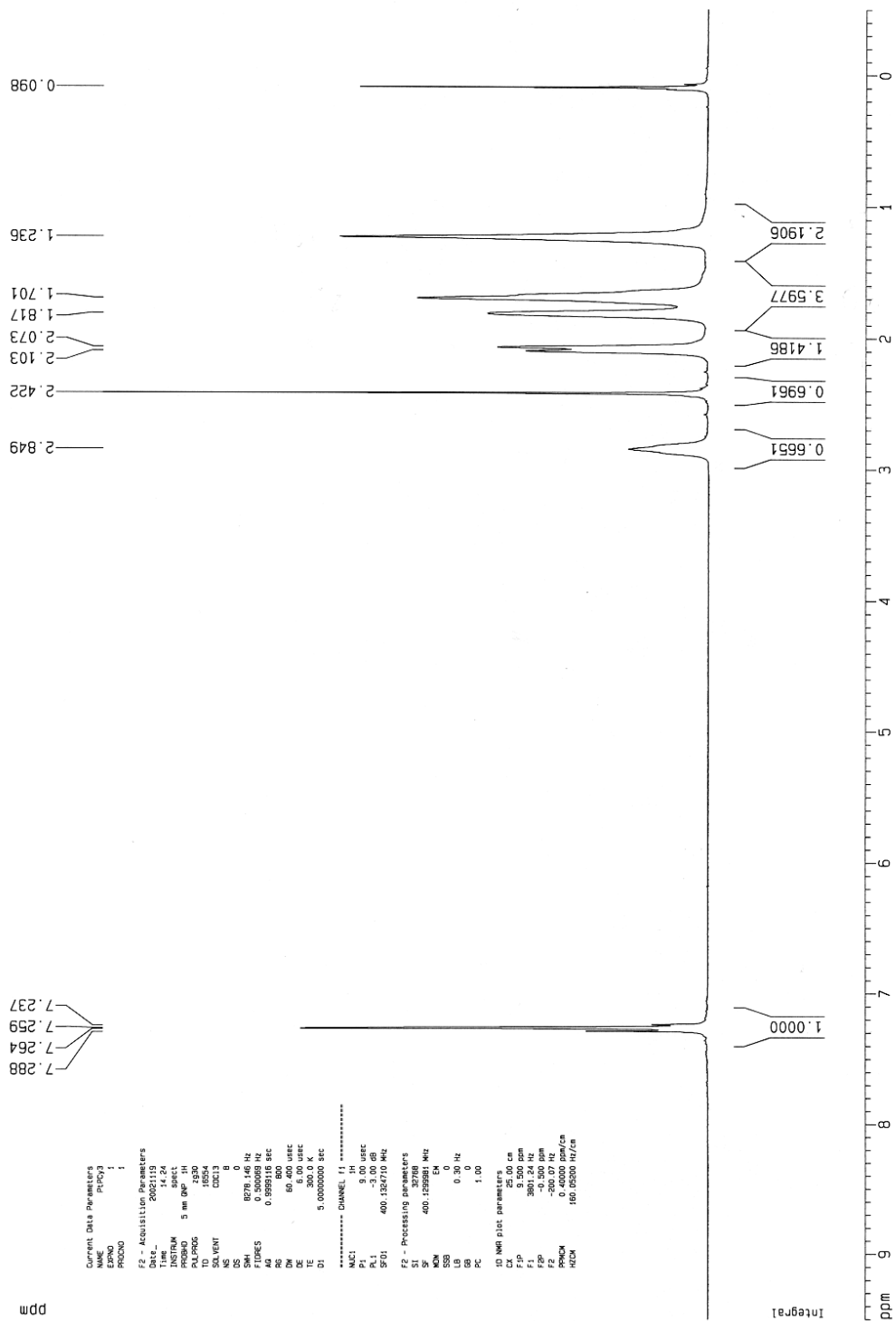
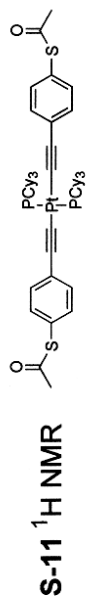
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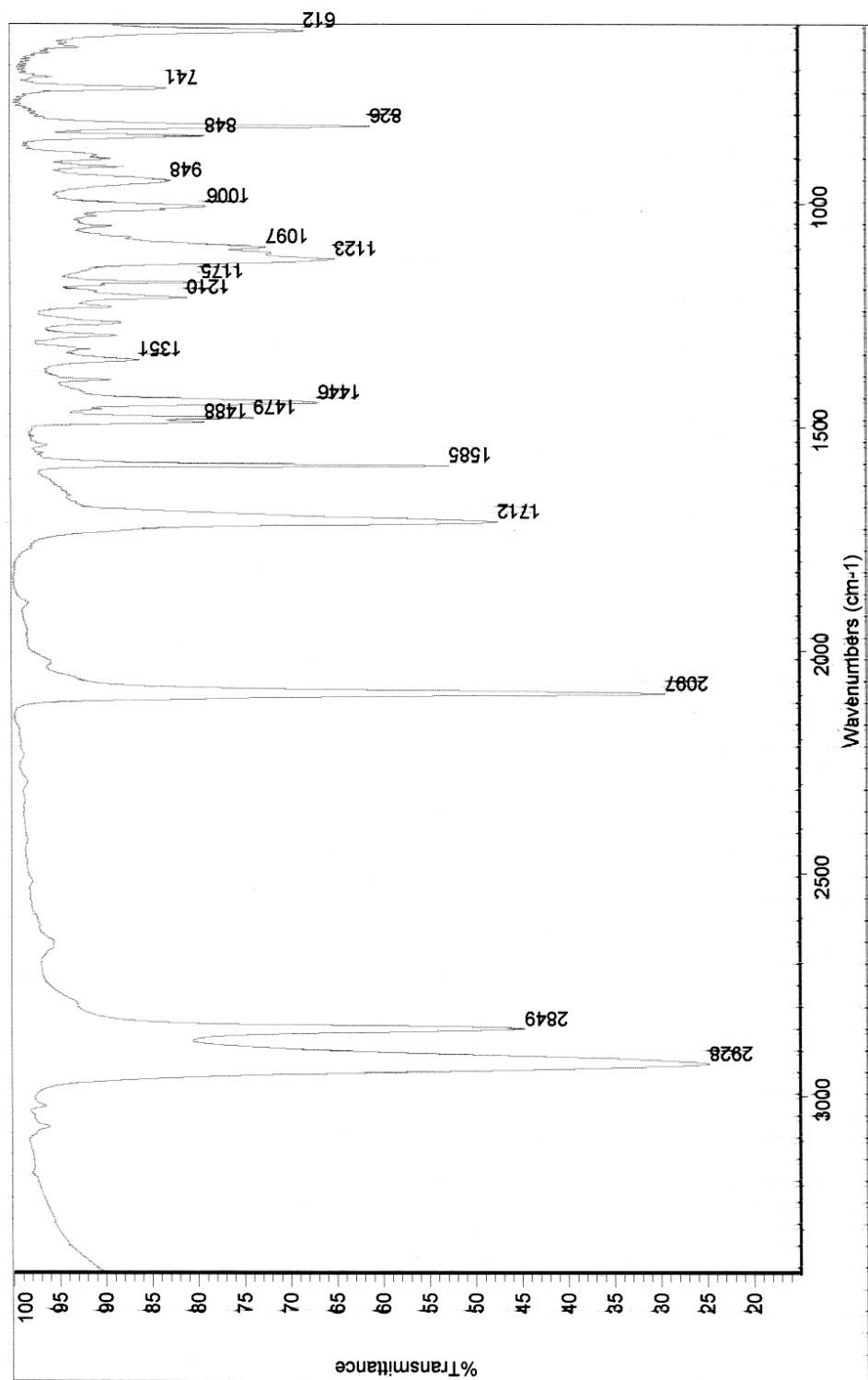
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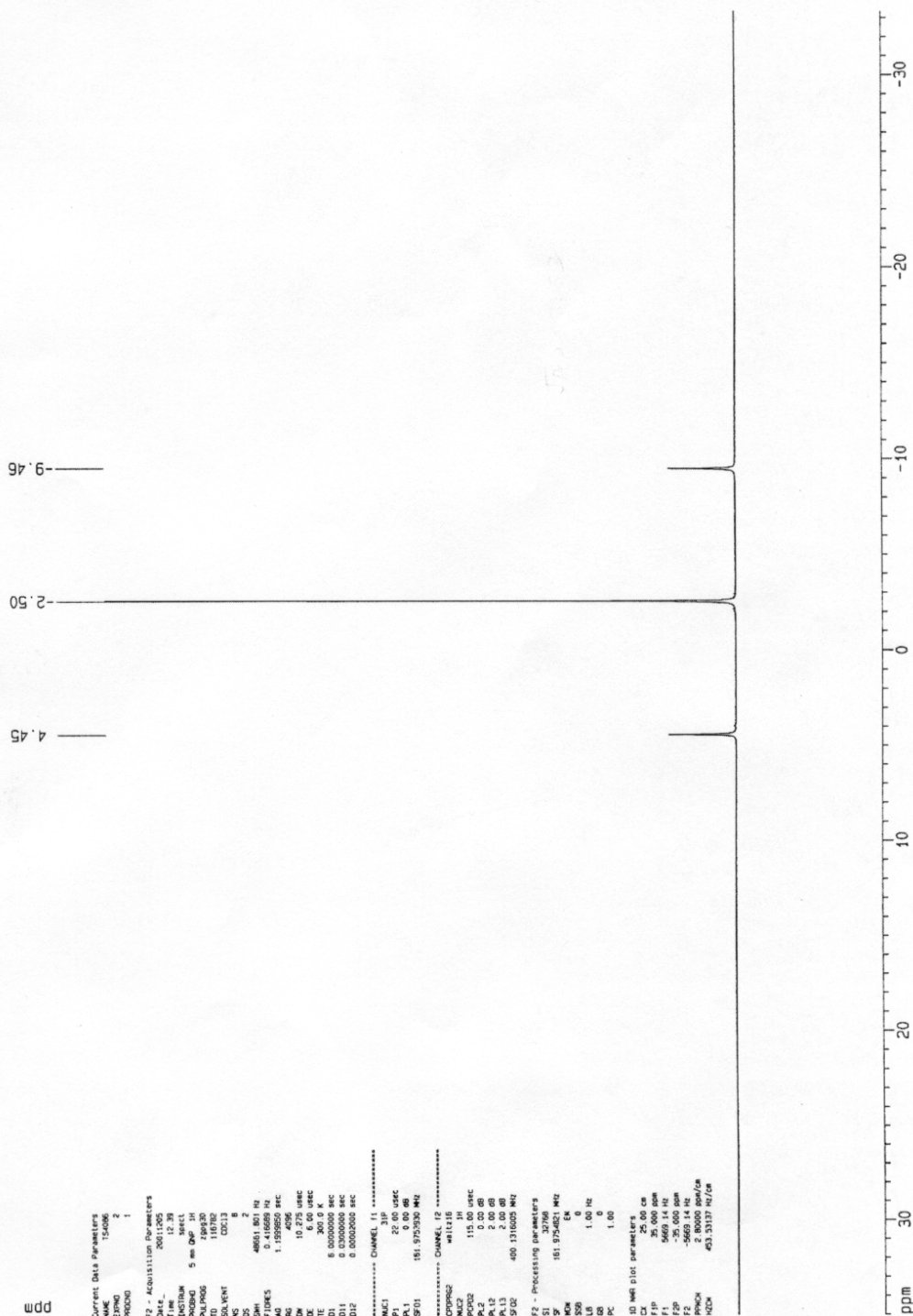
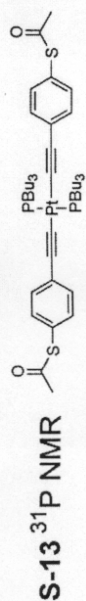
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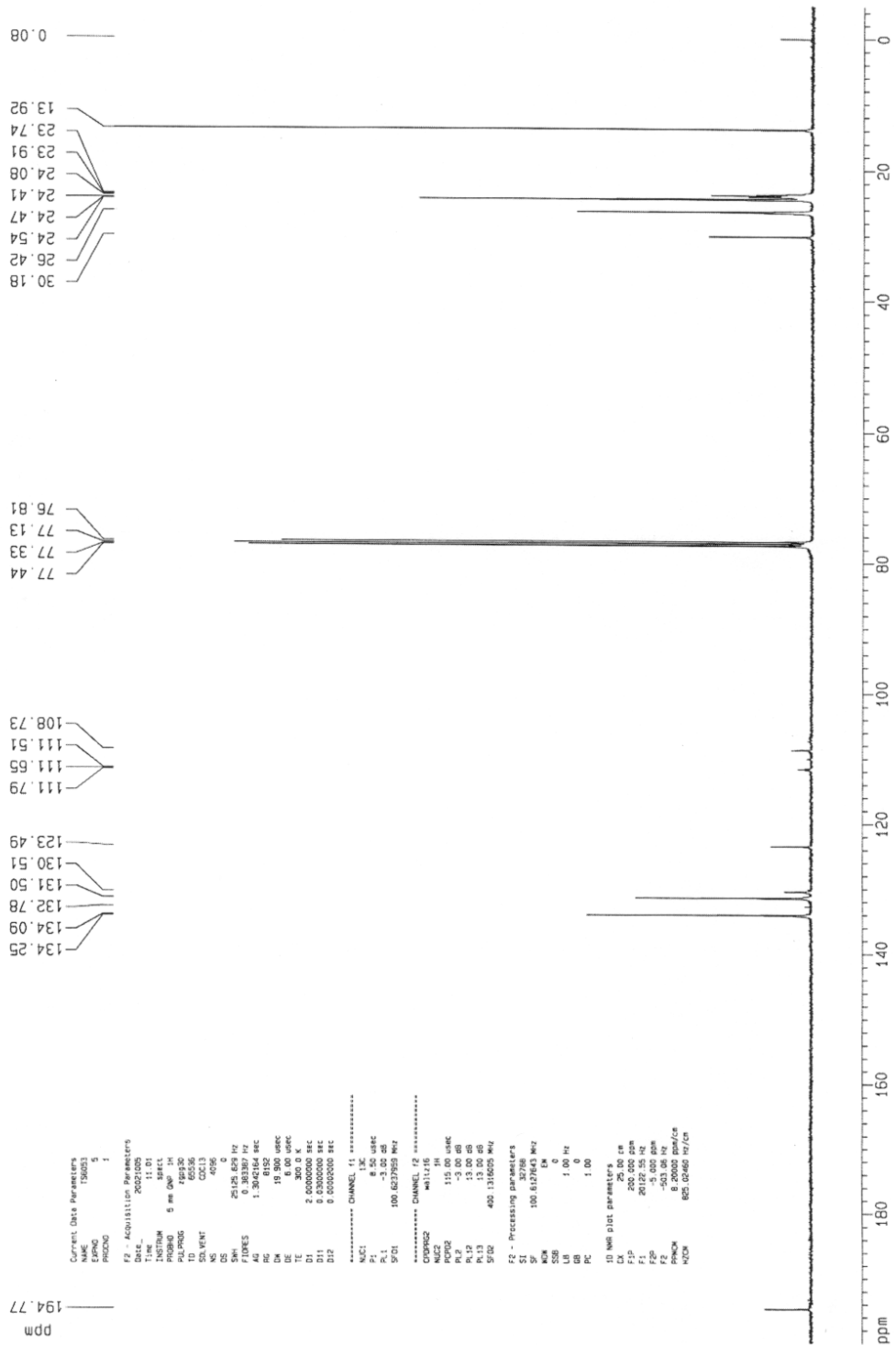
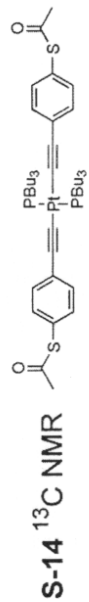
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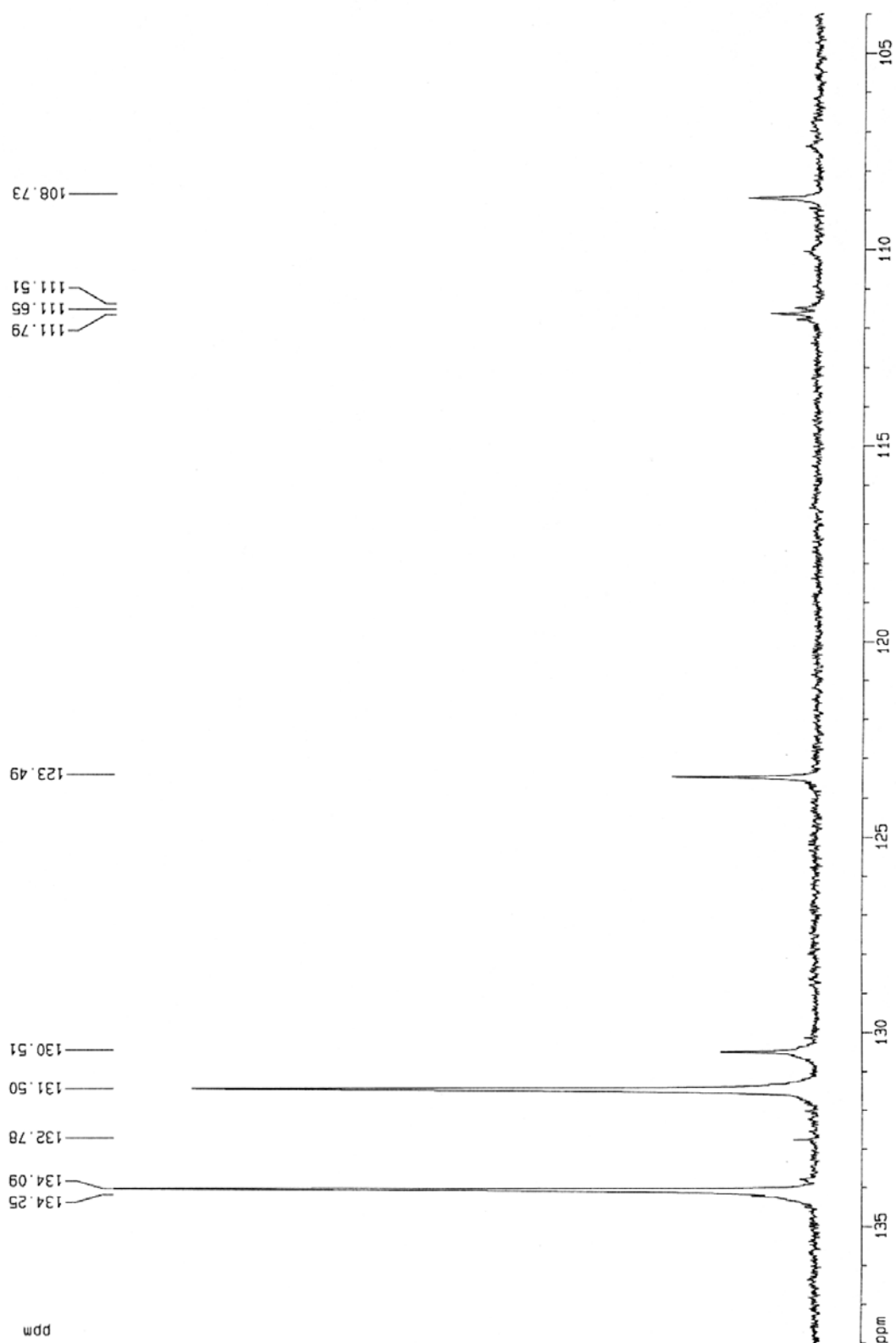
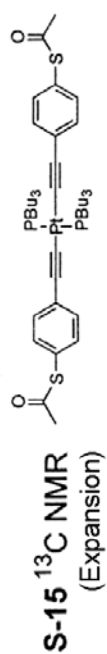


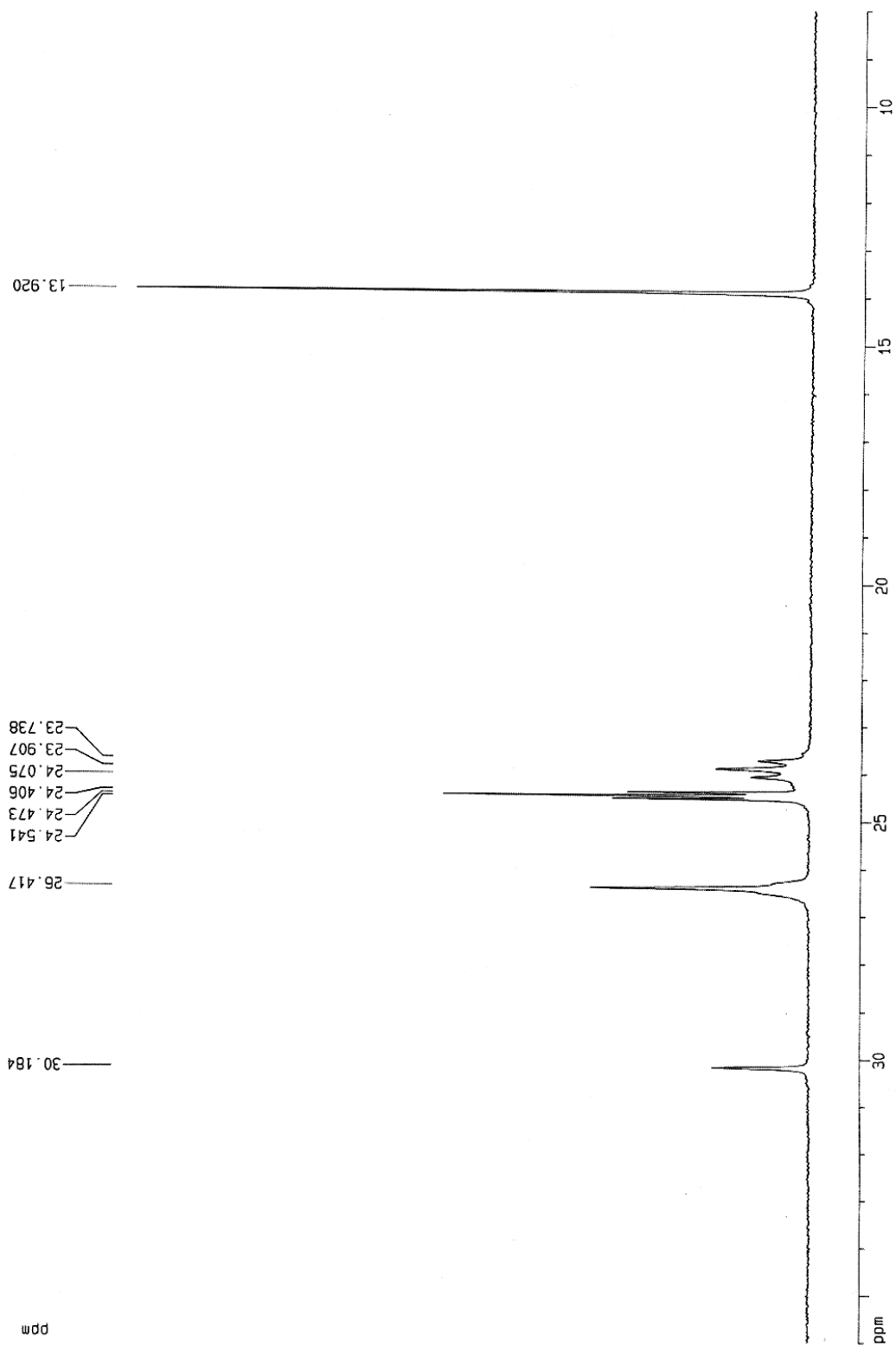
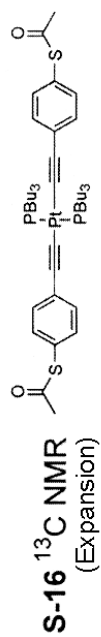




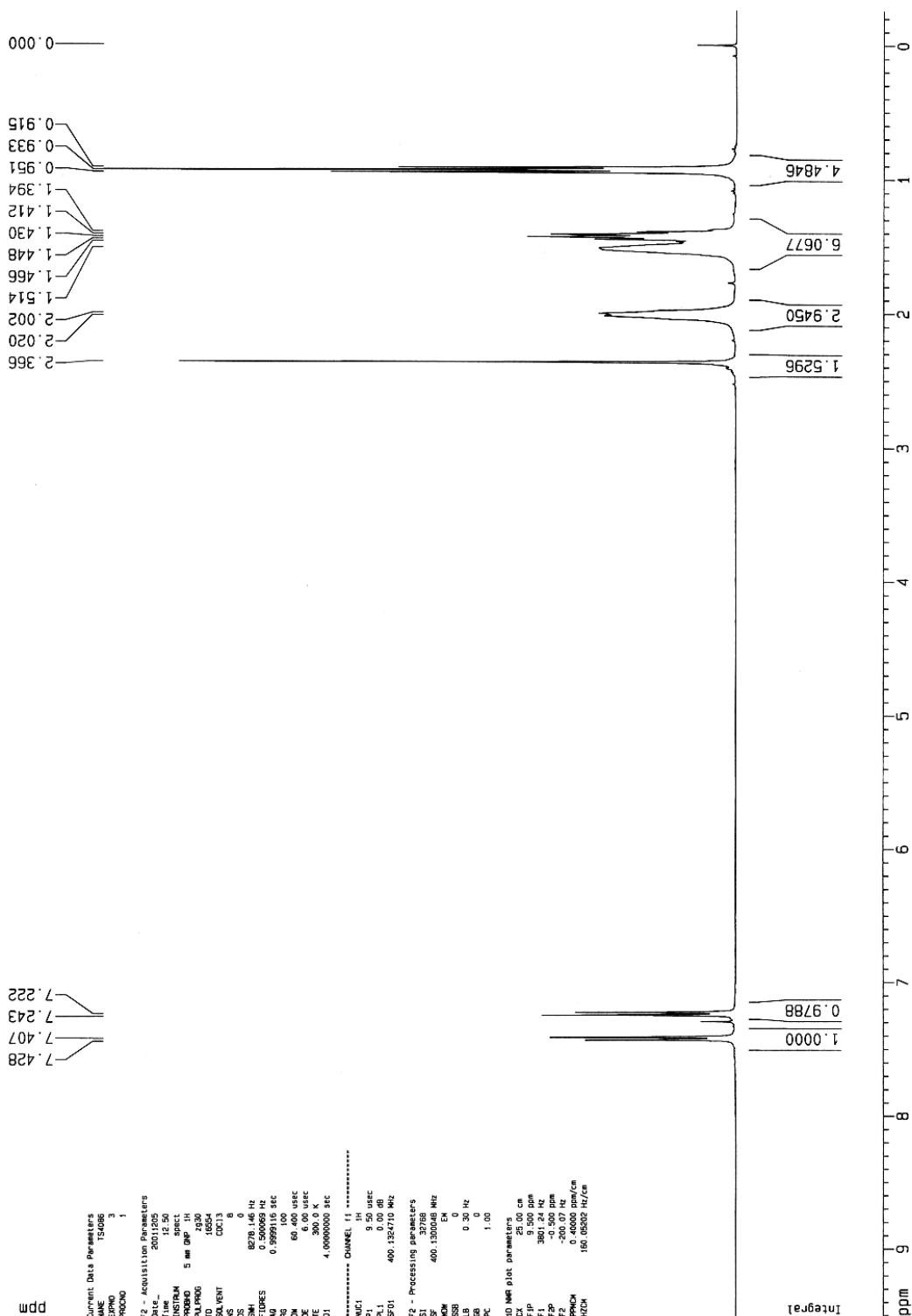


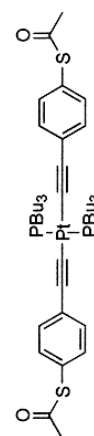
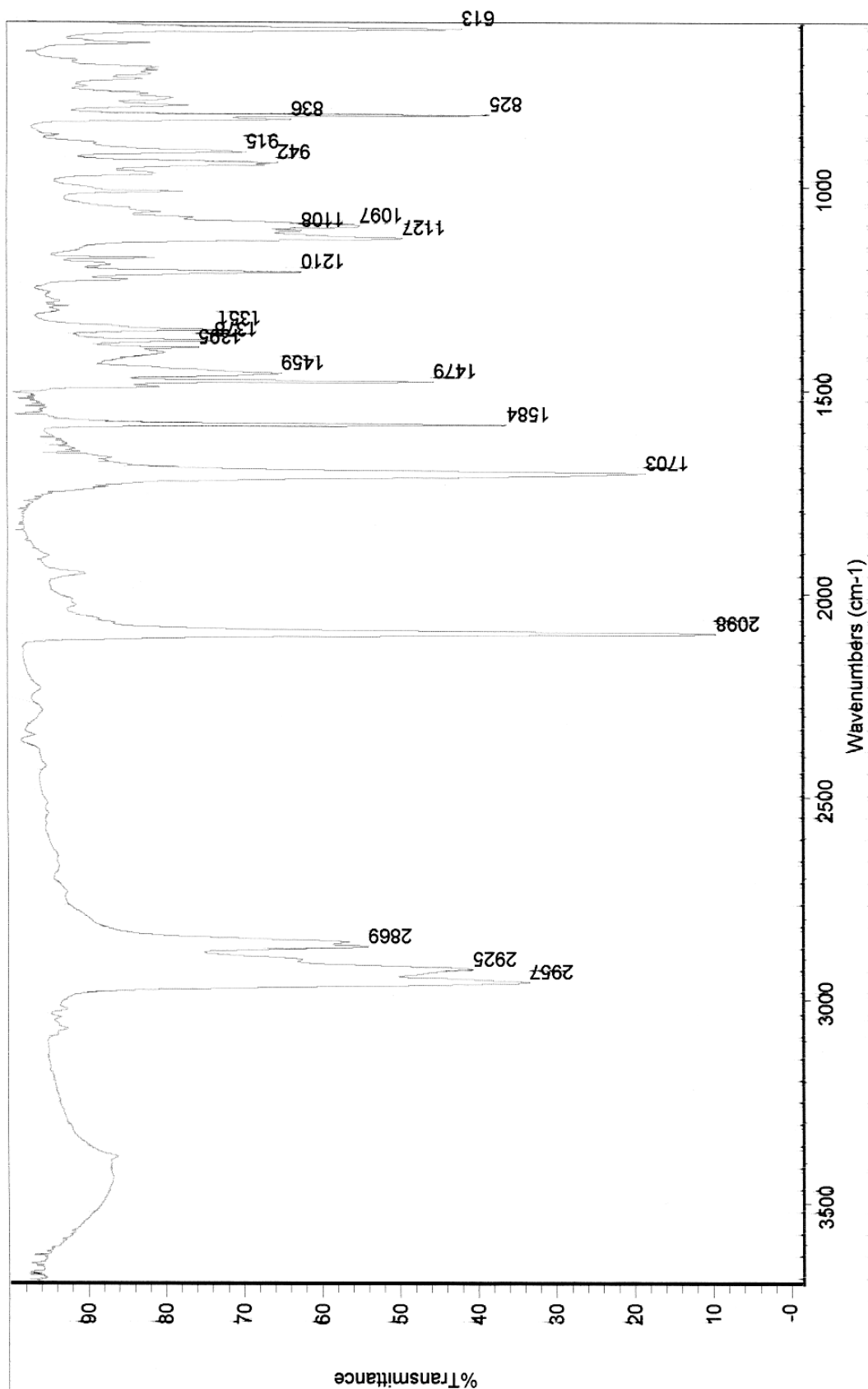






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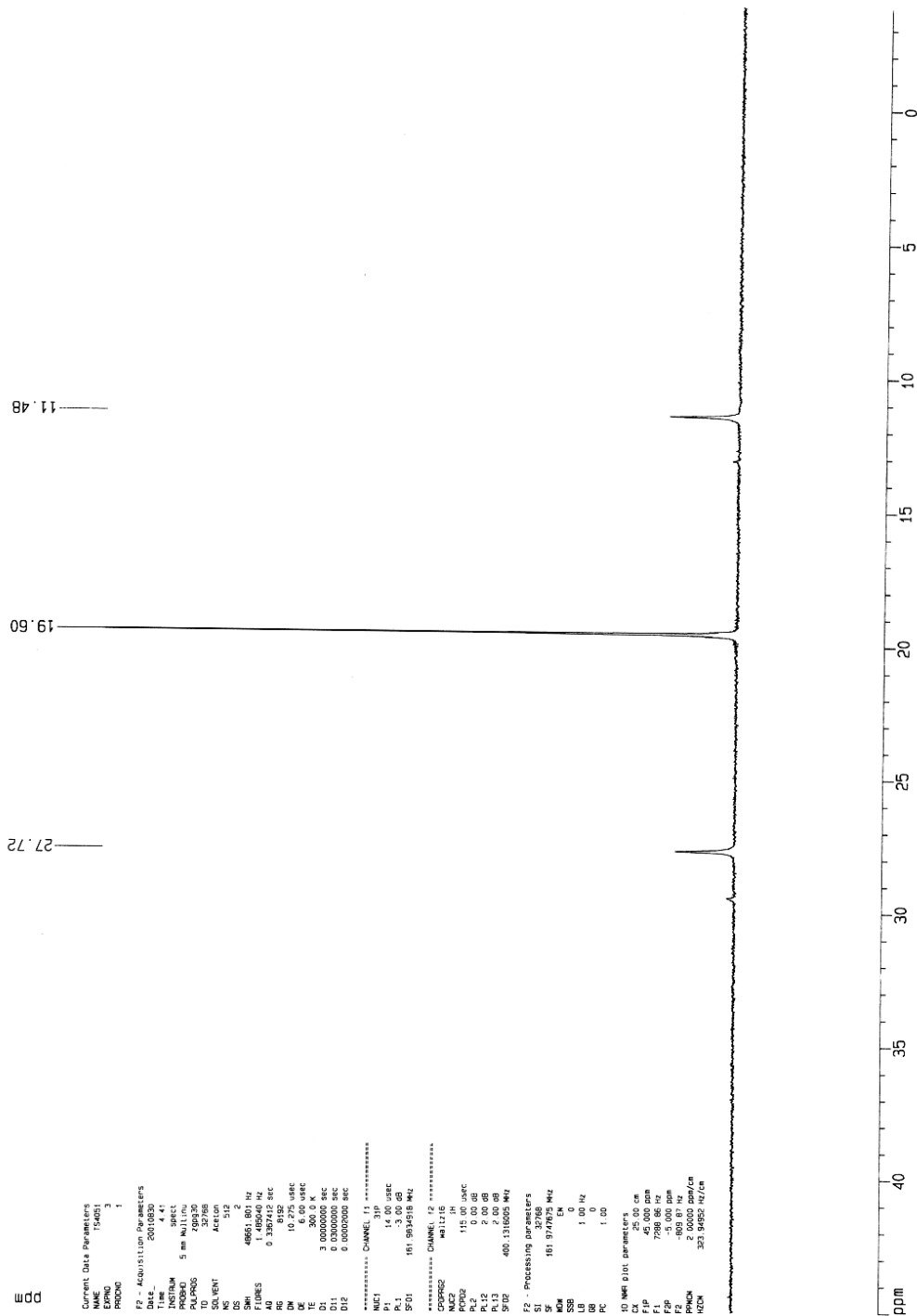
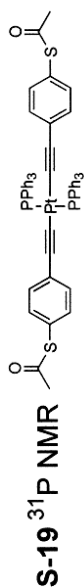


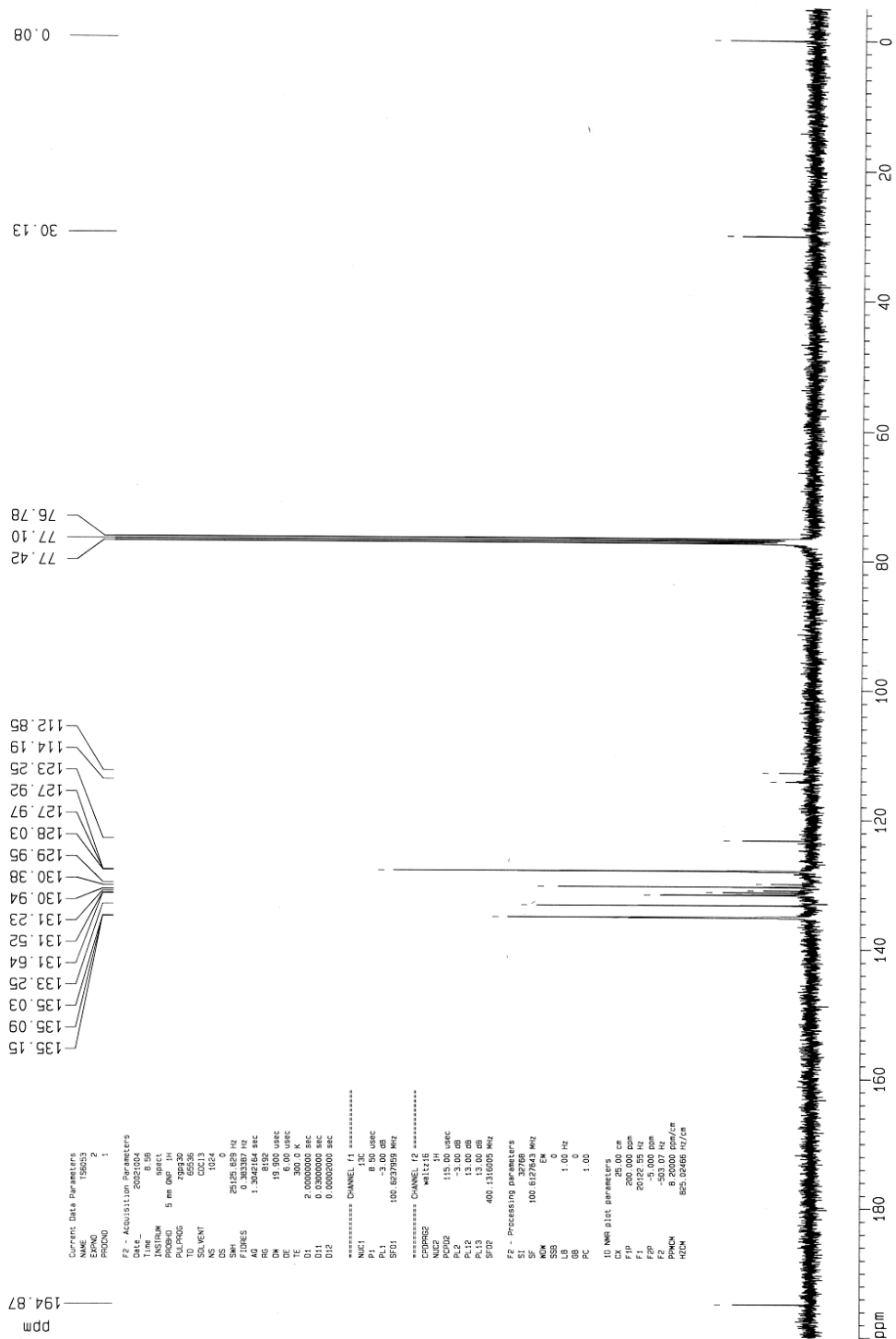
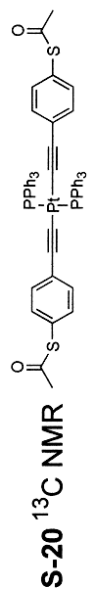
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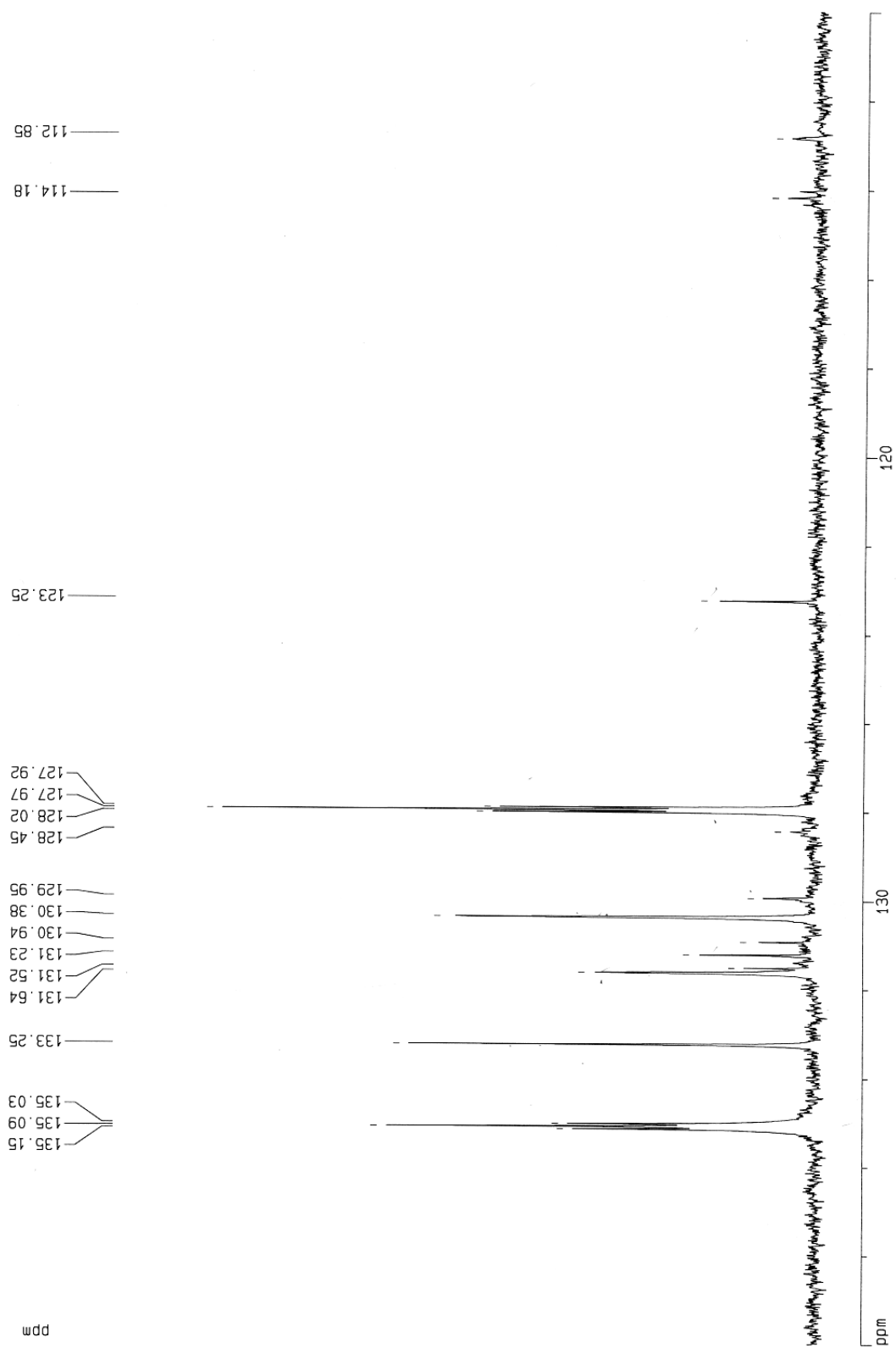
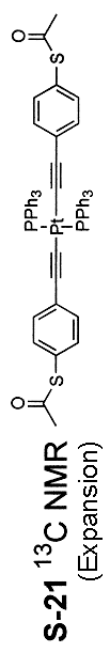
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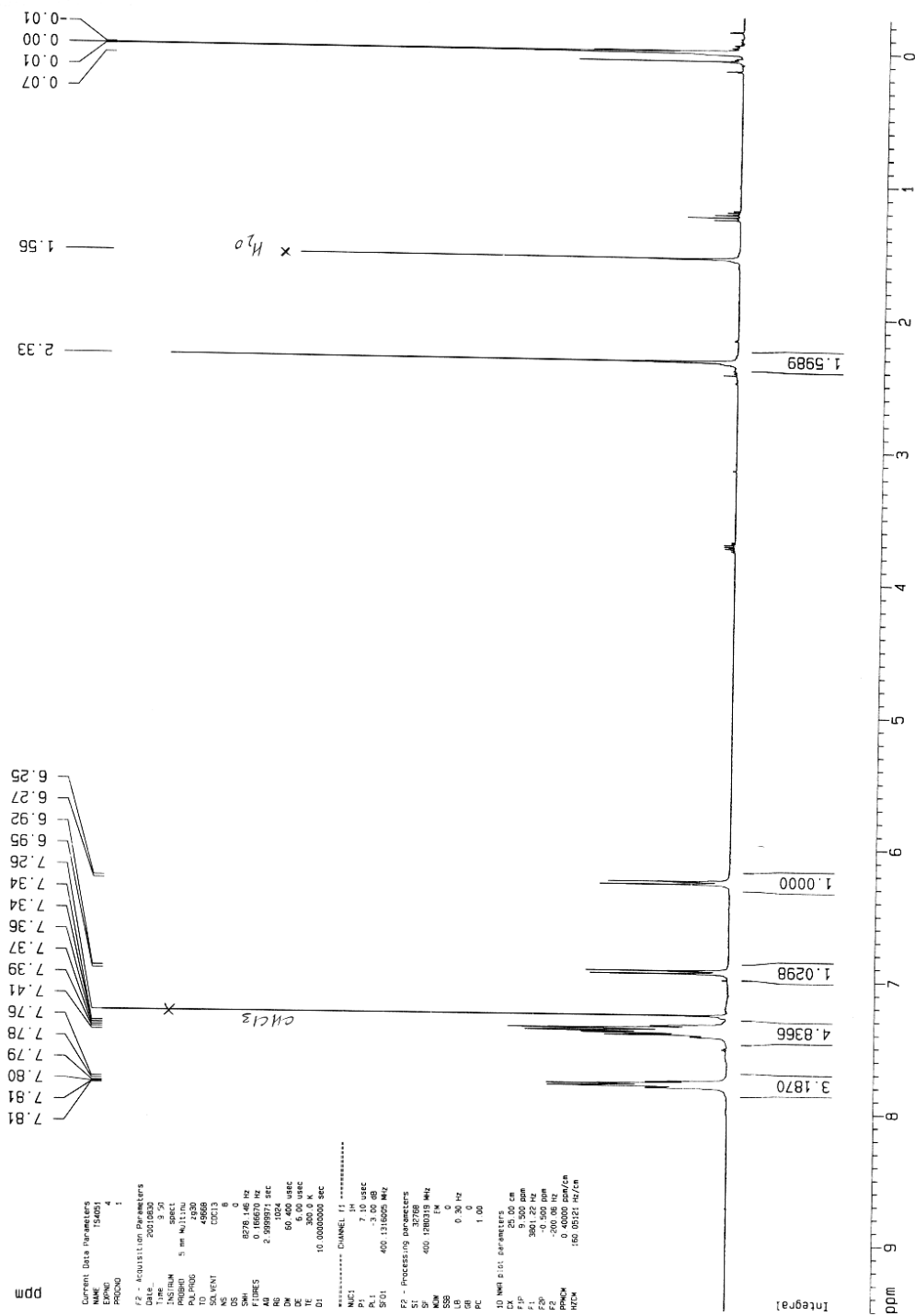
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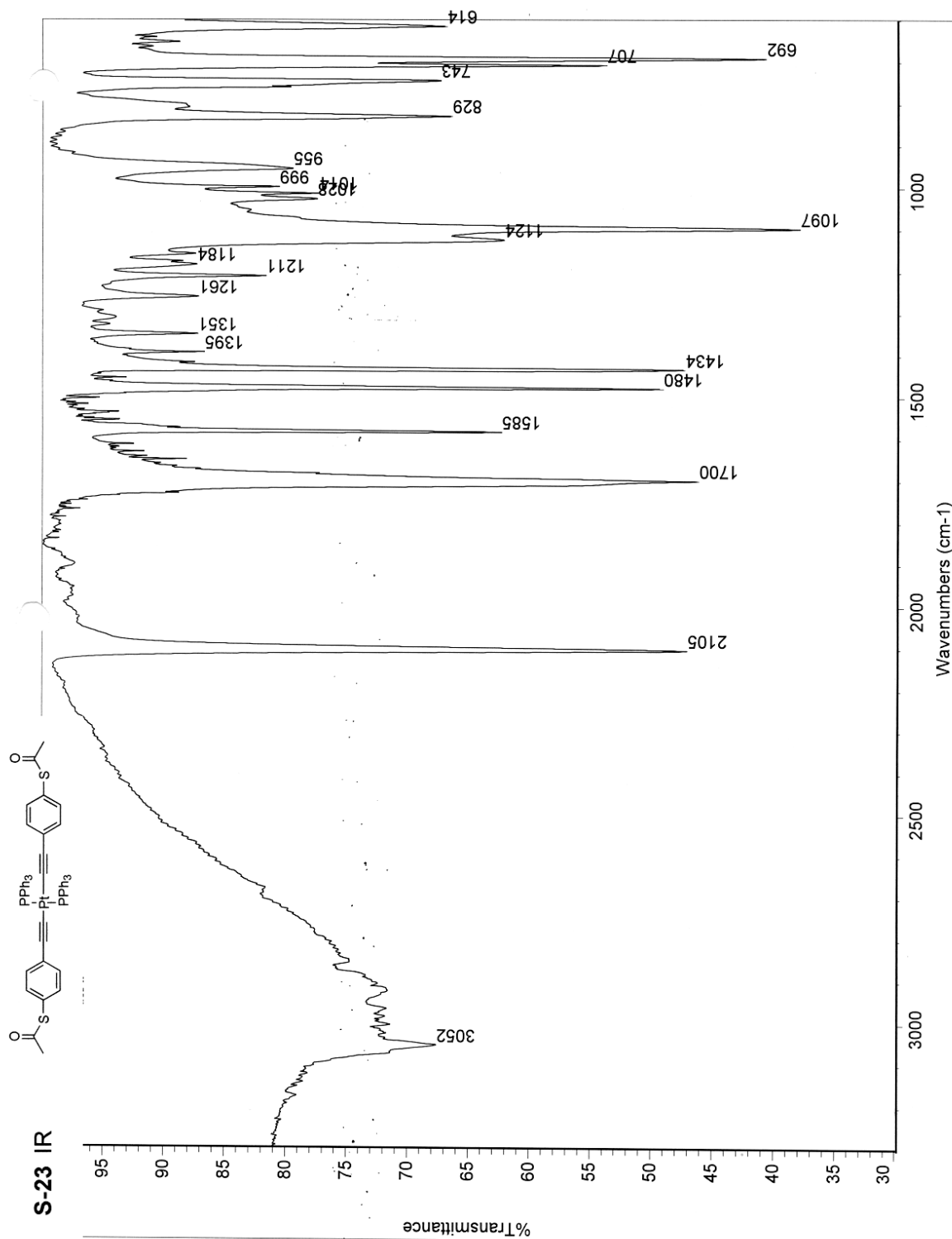
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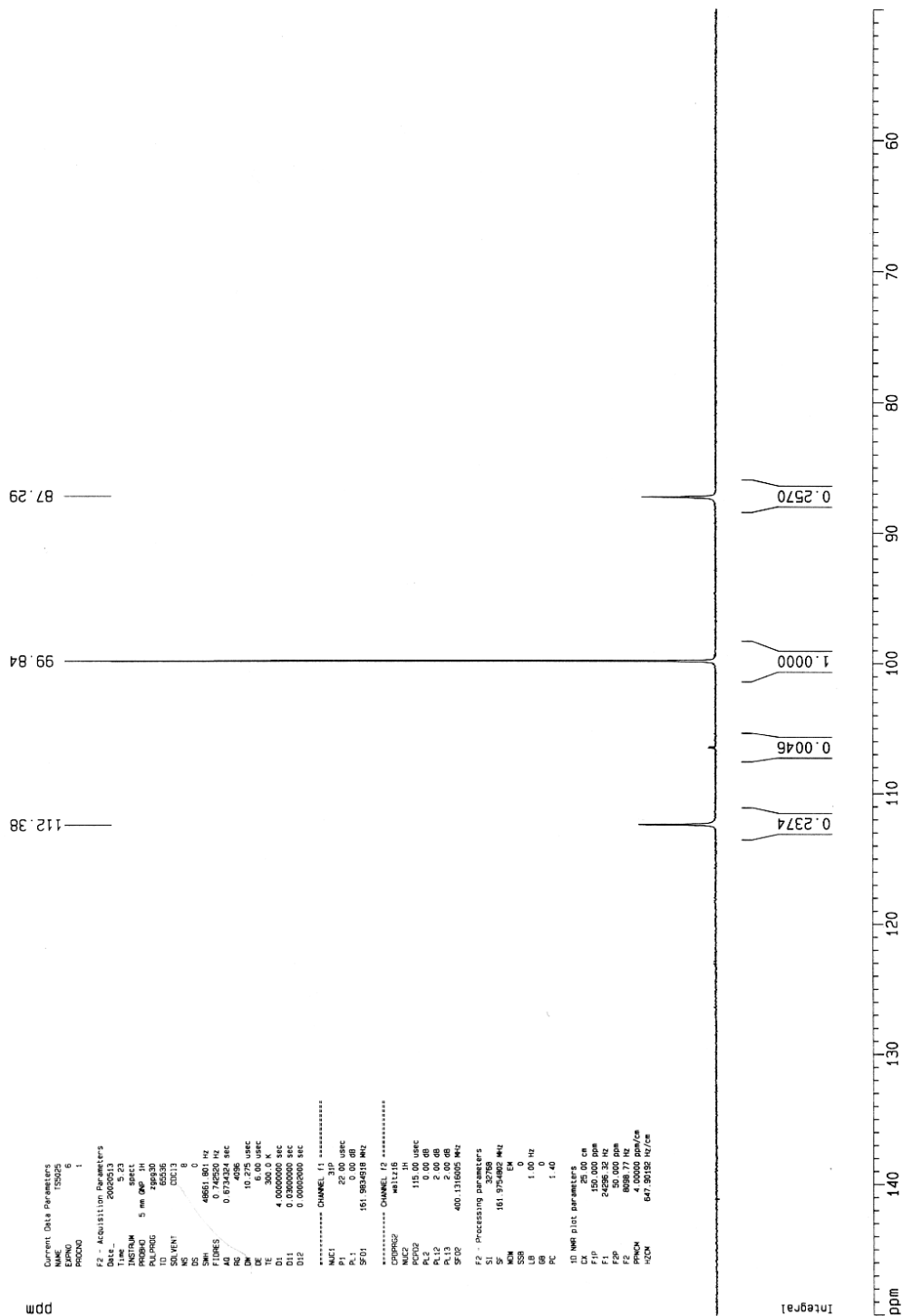
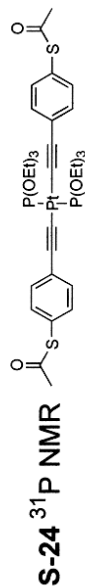


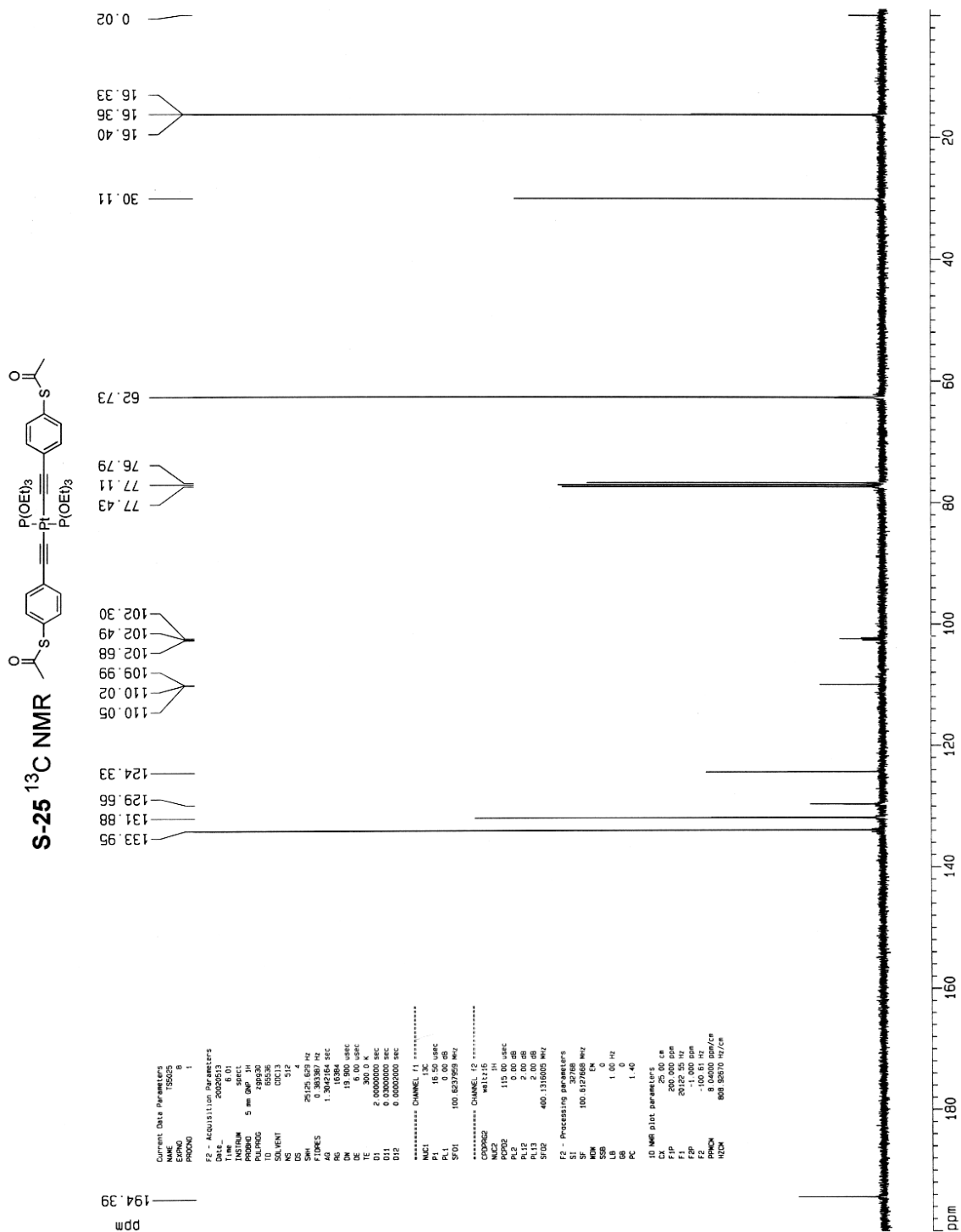


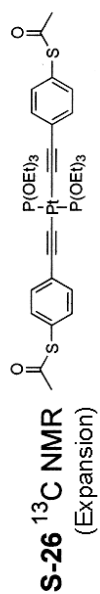








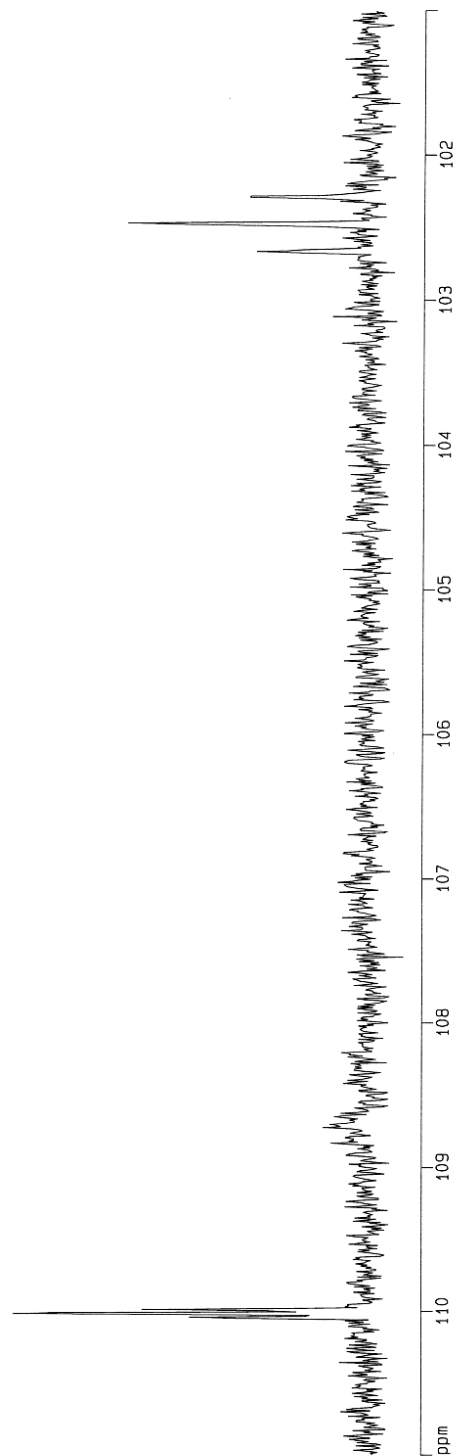


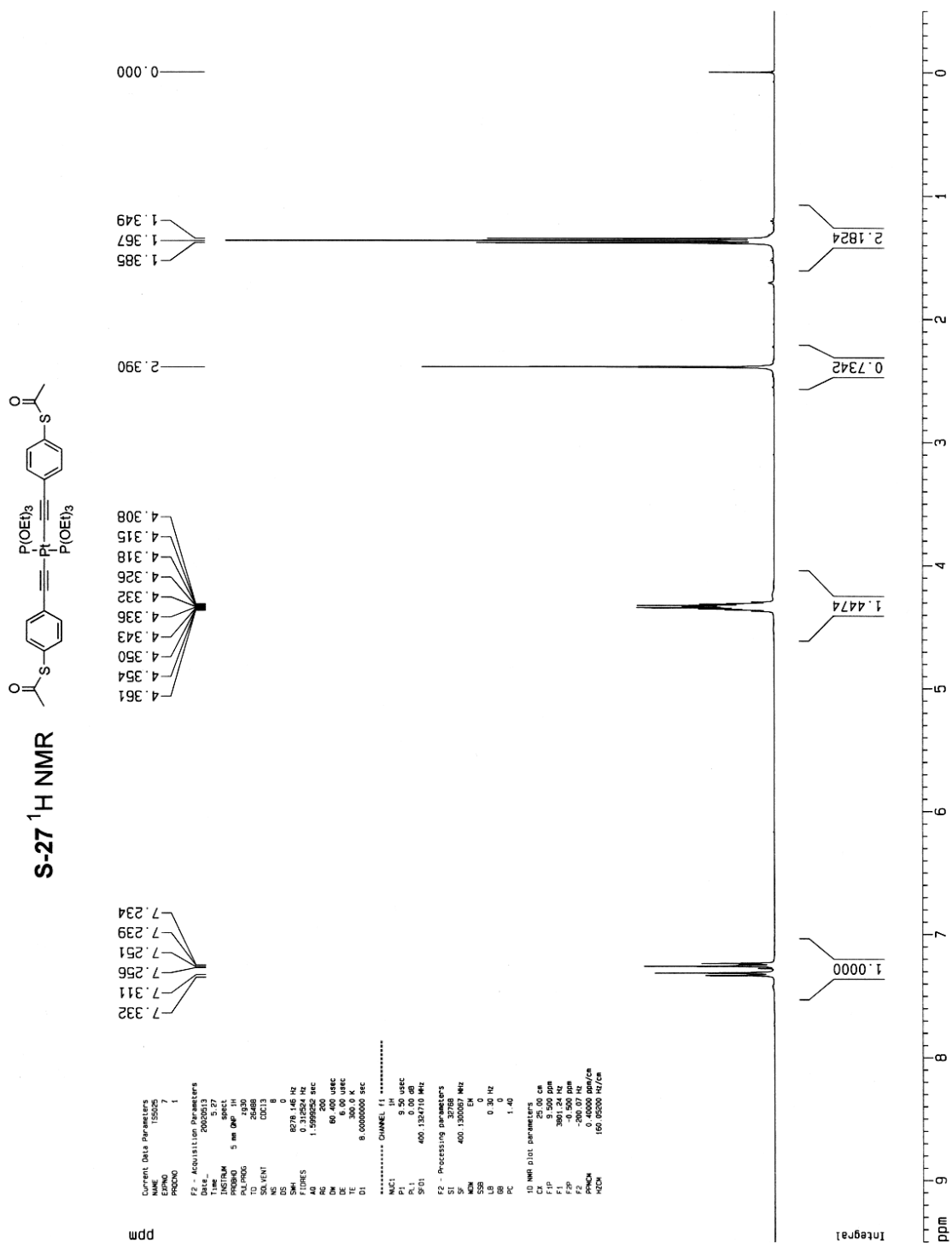


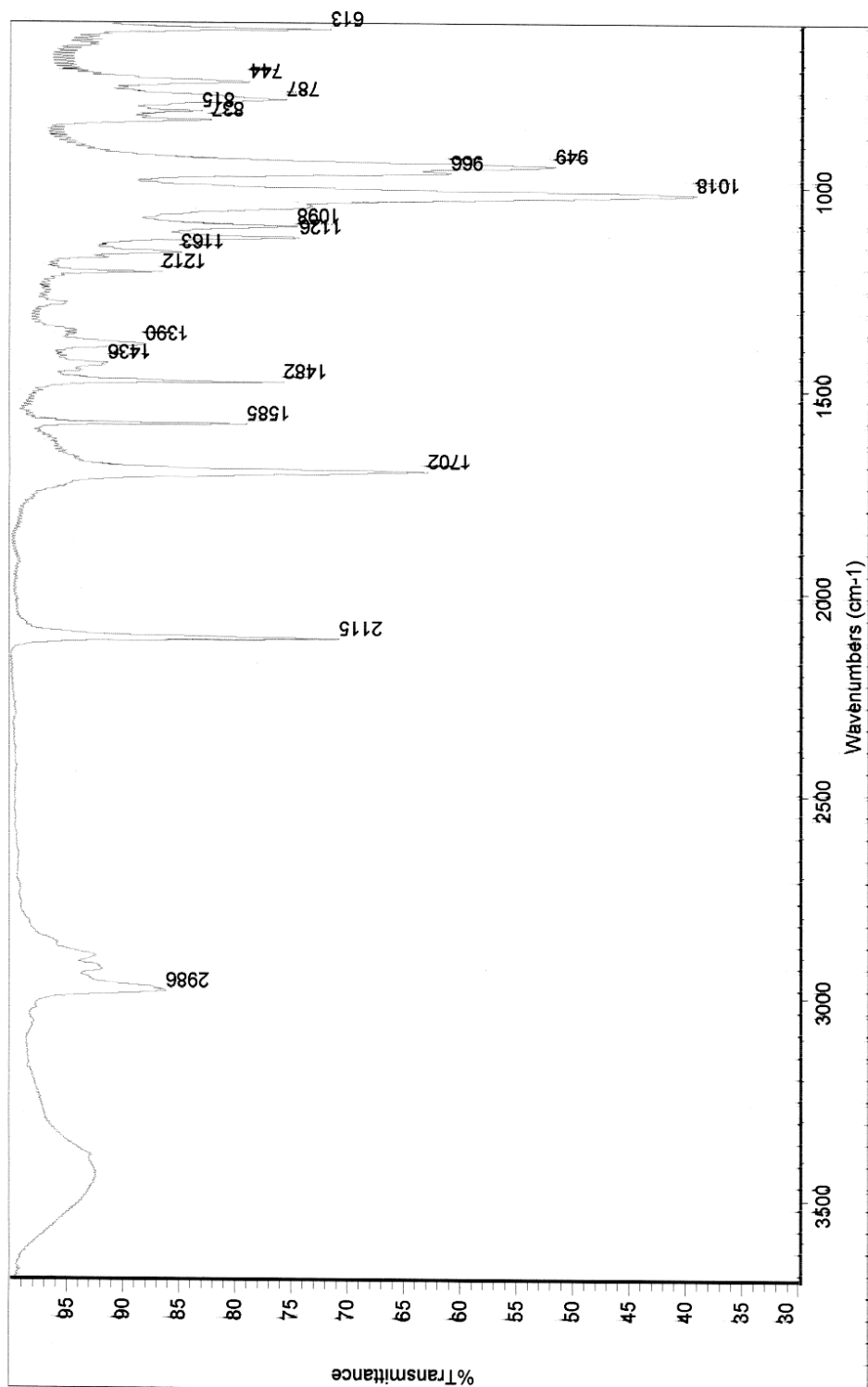
102.68
102.49
102.30

110.05
110.02
109.99

ppm



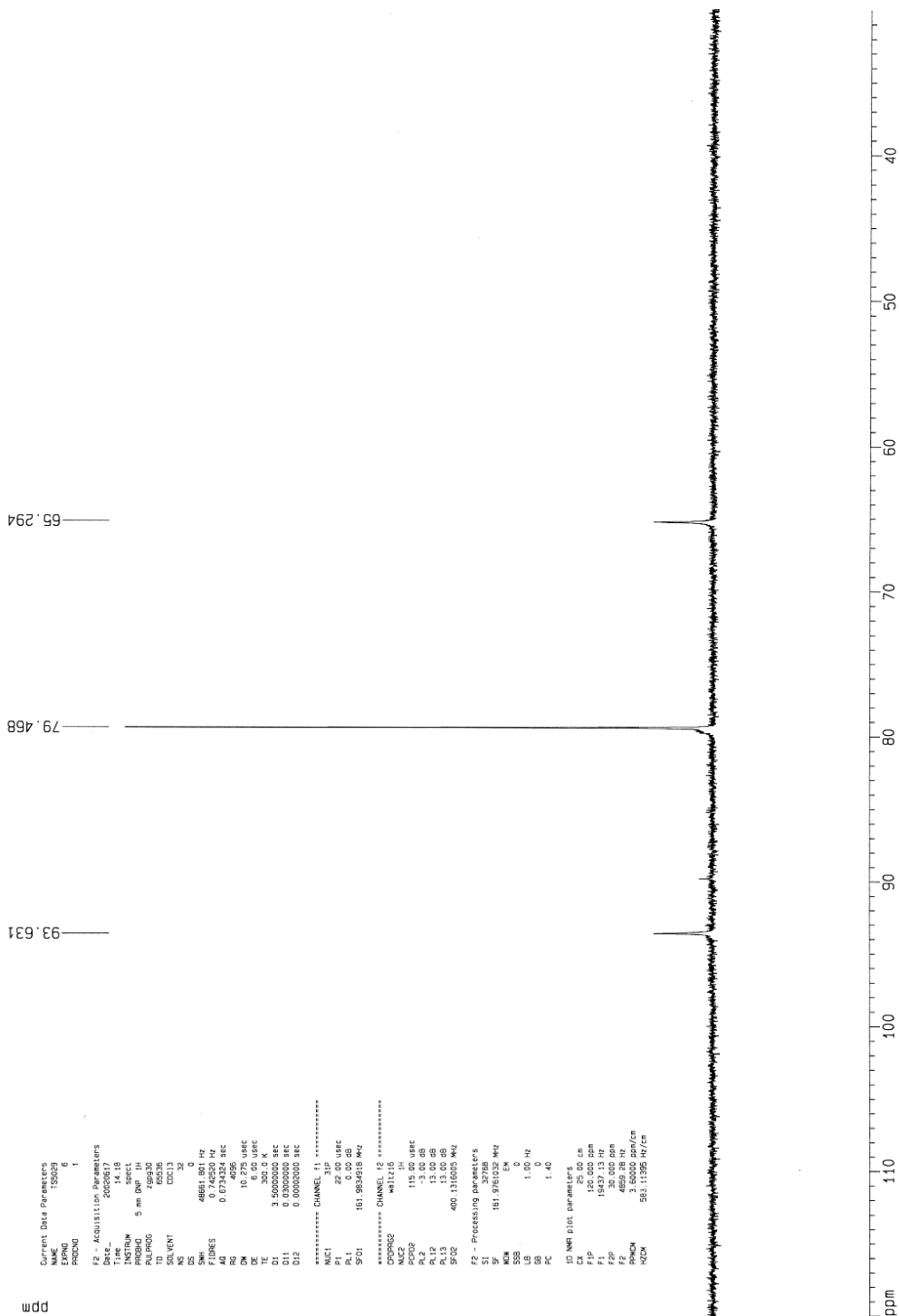


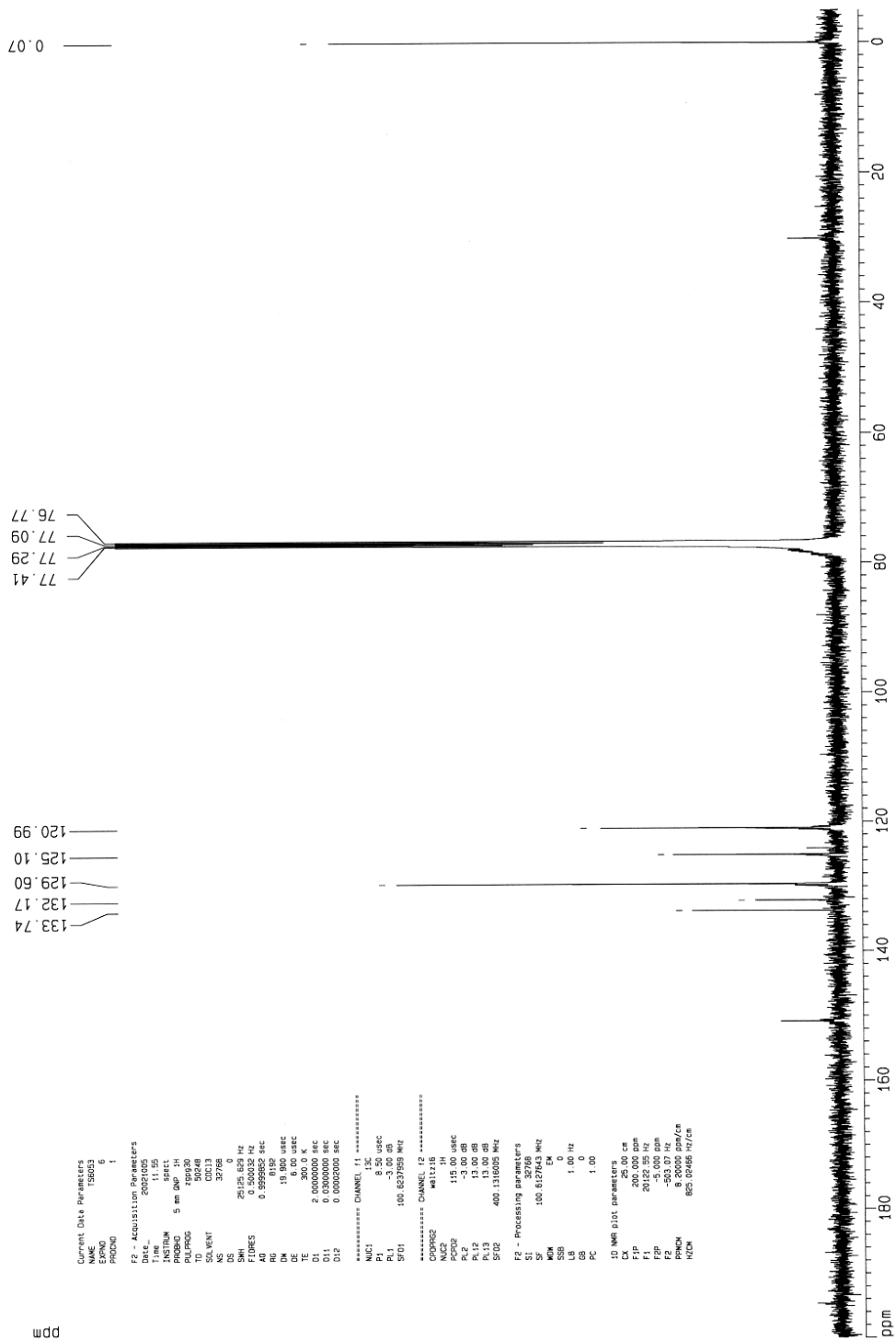
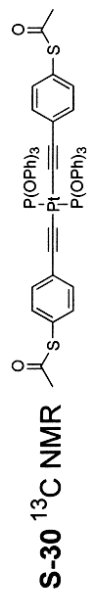


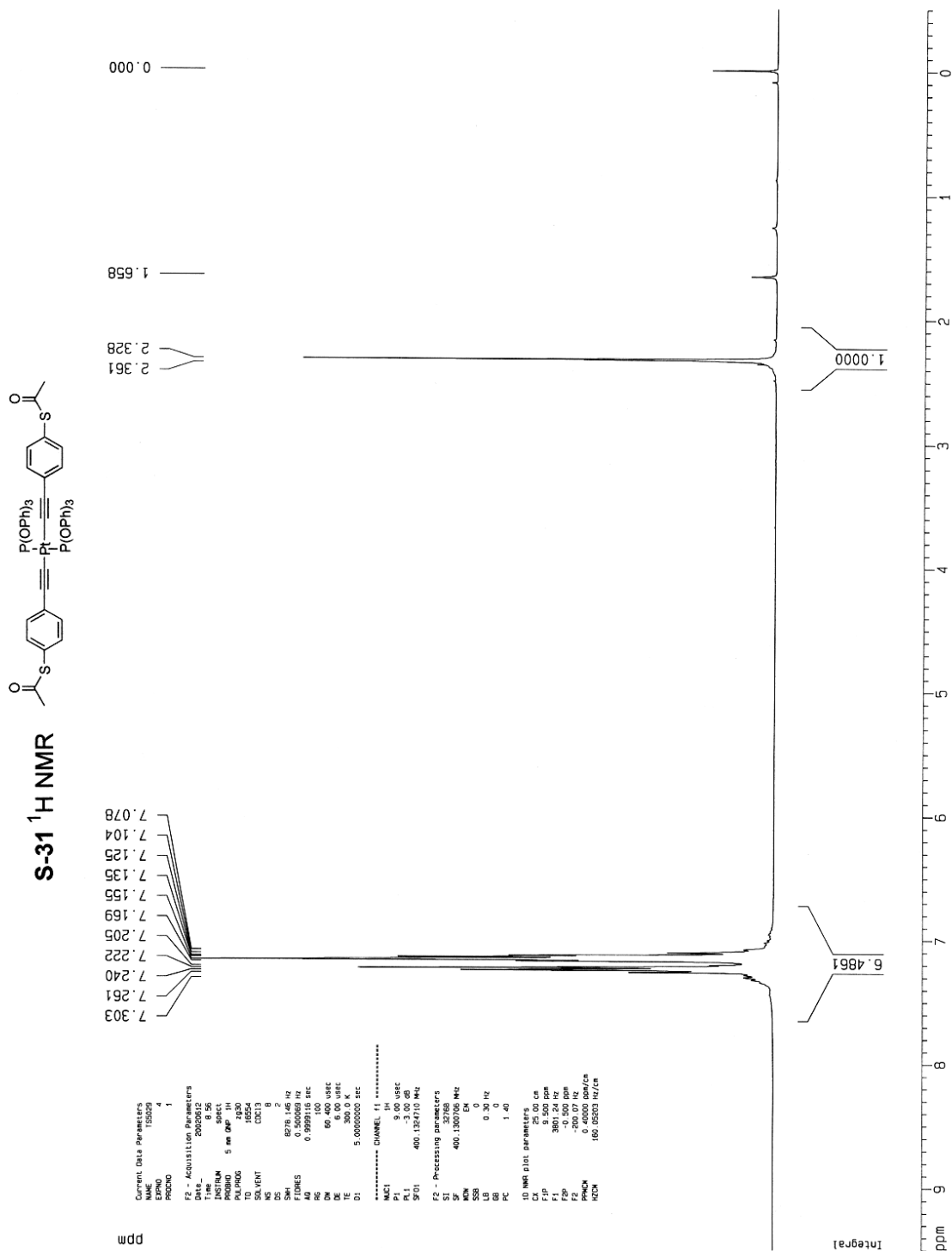
Date: Thu Oct 03 16:26:12 2002

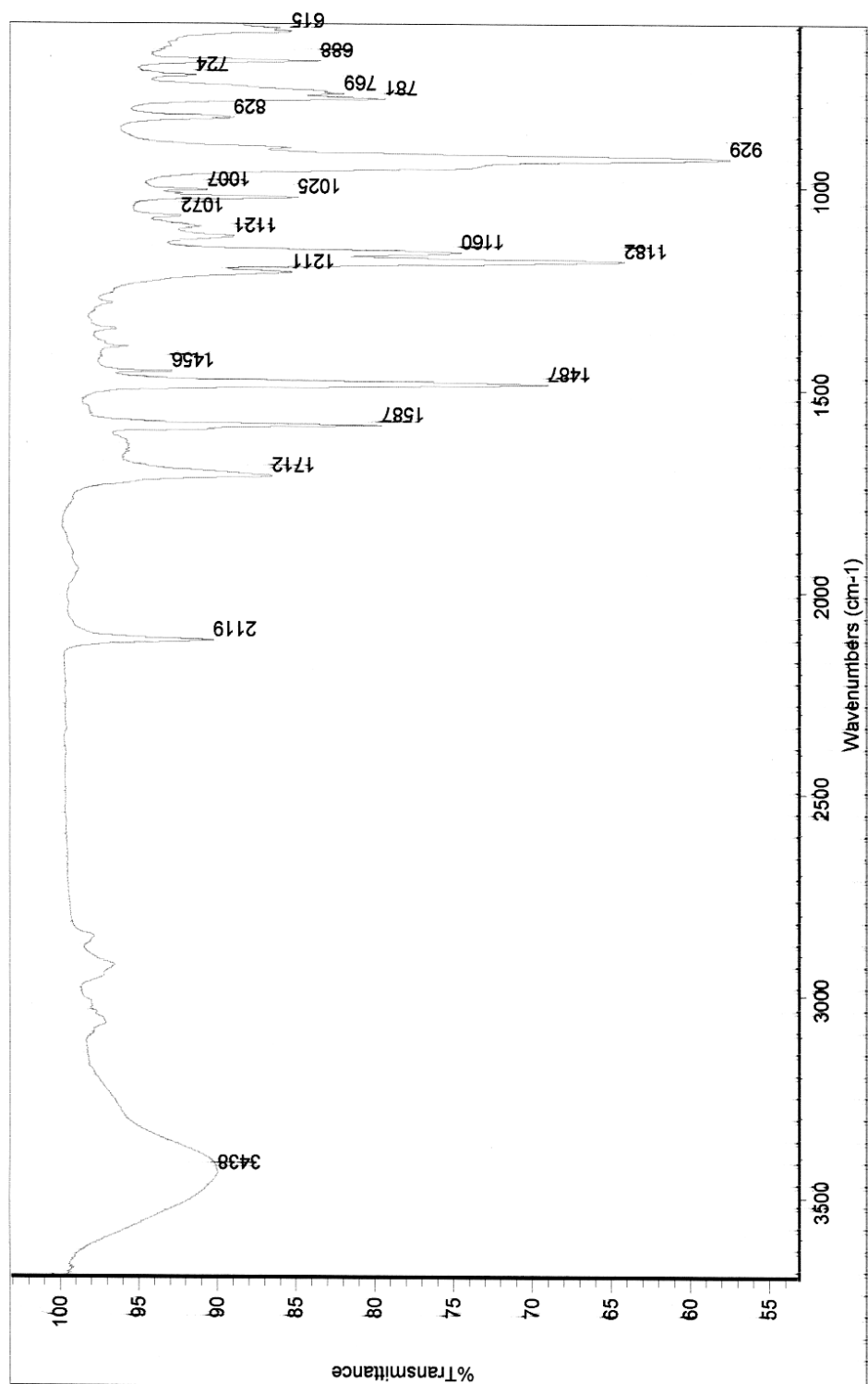
Scans: 64

Resolution: 2.000









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Date: Thu Oct 03 18:28:08 2002

Scans: 64

Resolution: 2.000