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Supporting Information for

Intramolecular Iron-Mediated Diene/Olefin Cyclocoupling: Formation of Carbon Spirocycles

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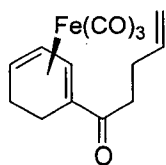
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General procedure for the preparation of homoallylic ketones. A flame dried round bottom flask was charged with the carboxylic acid complex, and with activated 4 Å molecular sieves (100 mg/mmol acid), then kept overnight under high vacuum (0.5 mmHg). The vacuum was broken with Ar, and then the acid was suspended in freshly distilled CH_2Cl_2 under argon. Then, 1.3 equivalents of freshly distilled (from CaH_2) triethylamine were added *via* syringe to the suspension. The yellow solution of alkylammonium salts (soluble in CH_2Cl_2) was cooled to 0 °C, then 2 equivalents of freshly distilled (from P_2O_5) methanesulfonyl chloride were added rapidly *via* syringe. The reaction mixture was stirred at 0 °C for 1 h (the reaction can be monitored by IR) under argon. The reaction mixture was then poured into chilled water, the phases were separated and the aqueous phase was extracted three times with CH_2Cl_2 . The combined organic layers were washed with 10% aq HCl, and then with sat aq sodium bicarbonate solution, dried (MgSO_4), filtered, and the solvent was evaporated *in vacuo*. The resulting brown viscous oil was placed under high vacuum (0.5 mm Hg) for 2 h, and then dissolved in freshly distilled (from Na/benzophenone) diethyl ether under argon. The solution was cooled to 0 °C, and 1.2 equiv of Grignard reagent was added dropwise over a period of 30 min. The reaction mixture was stirred at 0 °C for further 10 min, then

quenched with sat aq solution of NH_4Cl . The product mixture was partitioned and the aqueous layer was extracted 3 times with diethyl ether. The combined organic phases were washed with sat aq NaHCO_3 , 10% aq HCl , dried (MgSO_4), and concentrated under vacuum. Flash chromatography on silica gel or preparative TLC separation (EtOAc/hexanes , 2:8) afforded the desired racemic homoallylic ketone, usually as light brown oil. Deviations from this procedure are noted in the experimental data for the specific compound.

General procedure for the thermally induced cyclization. The complex was dissolved in freshly distilled (over sodium) di-*n*-butyl ether under argon. The solution was purged with CO for 1 min, and then refluxed under a balloon of CO for the required time. The cooled product mixture was diluted with ether, filtered through Celite, and concentrated. Flash chromatography or preparative TLC separation (EtOAc/hexanes) yielded the desired product. Deviations from this procedure are noted in the experimental data for the specific compound.

Tricarbonyl[1-4- η -1-(1,3-cyclohexadienyl)-4-penten-1-one]iron (7a).

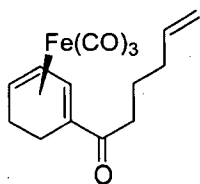


The acid **5** (300 mg, 1.14 mmol) in 3 mL of anhyd CH_2Cl_2 was reacted with 0.21 mL of anhyd Et_3N and 0.28 mL of methanesulfonyl chloride to yield 330.4 mg of mixed anhydride as a brown oil. This oil was then treated with 2.9 mL of anhyd Et_2O and 3-butenylmagnesium bromide (1.1 mL, 1.1 M solution in Et_2O) to yield 260 mg (89% yield) of the title compound as a light brown oil, along with 14 mg of recovered acid complex **5**. IR (cm^{-1} , neat): 2058, 1979, 1683. ^1H NMR (200 MHz, CDCl_3), δ 6.10 (dd, $J = 4.8, 1.7$ Hz, 1H),

5.83 (ddt, $J = 18.0, 10.2, 6.4$ Hz, 1H), 5.41 (ddd, $J = 6.3, 4.8, 0.9$ Hz, 1H), 5.07 (ddd, $J = 18.0, 3.3, 1.7$ Hz, 1H), 5.00 (ddd, $J = 10.2, 3.0, 1.7$ Hz, 1H), 3.40 (dddd, $J = 6.3, 4.3, 2.5, 1.7$ Hz, 1H), 2.66 (ddd, $J = 16.8, 8.5, 7.2$ Hz, 1H), 2.60 (apparent dt, $J = 16.8, 6.9$ Hz, 1H), 2.45-2.30 (2H), 2.18 (ddd, $J = 14.0, 11.4, 2.9$ Hz, 1H), 1.98 (apparent tt, $J = 11.4, 4.3$ Hz, 1H), 1.81 (m, 1H), 1.50 (ddd, $J = 14.0, 8.2, 3.1$ Hz, 1H) ^{13}C NMR (50 MHz, CDCl_3), δ 210.3, 204.2, 137.5, 115.2, 87.2, 85.7, 73.1, 63.1, 38.3, 28.1, 25.9, 23.1.

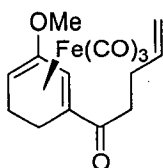
HRMS (m/z) for M^+ ($\text{C}_{14}\text{H}_{14}\text{FeO}_4$): calculated: 302.0241; found: 302.0242.

Tricarbonyl[1-4- η -1-(1,3-cyclohexadienyl)-5-hexen-1-one]iron (7b).



The acid **5** (200 mg, 0.76 mmol) in 2 mL of anhyd CH_2Cl_2 was treated with 0.14 mL of Et_3N and 0.89 mL of MsCl , then treated with 1.89 mL of Et_2O and 4-pentenylmagnesium bromide (0.76 mL, 1.1 M

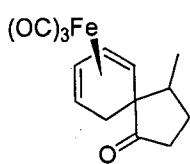
solution in Et_2O) to afford 172 mg of ketone **7b** (87%) as a light brown oil. IR (cm^{-1} , neat): 2056, 1991, 1677. ^1H NMR (200 MHz, CDCl_3), δ 6.09 (dd, $J = 4.2, 1.9$ Hz, 1H), 5.80 (apparent ddt, $J = 17.3, 10.1, 6.0$ Hz, 1H), 5.41 (dd, $J = 5.0, 4.2$ Hz, 1H), 5.06 (ddd, $J = 17.3, 3.5, 1.5$ Hz, 1H), 4.98 (ddd, $J = 10.1, 4.5, 1.5$ Hz, 1H), 3.40 (dddd, $J = 6.2, 4.2, 2.4, 1.9$ Hz, 1H), 2.52 (ddd, $J = 17.2, 7.8, 7.0$ Hz, 1H), 2.45 (ddd, $J = 17.2, 7.6, 6.4$ Hz, 1H), 2.25-1.64 (series of m, 7H), 1.45 (ddd, $J = 13.4, 7.9, 2.6$ Hz, 1H). ^{13}C NMR (50 MHz, CDCl_3), δ 210.3, 204.9, 138.2, 115.2, 87.1, 85.7, 73.3, 63.0, 38.1, 33.1, 25.8, 23.1, 23.0. HRMS (m/z) for $\text{M}^+ - \text{CO}$ ($\text{C}_{14}\text{H}_{16}\text{FeO}_3$): calculated: 288.0405; found: 288.0456.



Tricarbonyl[1-4- η -1-(3-methoxy-1,3-cyclohexadienyl)-4-penten-1-one]iron (7c).

Acid **5** (R = OMe (200 mg, 0.67 mmol) in 1.8 mL of Et₂O was treated with 125 μ L of Et₃N and 170 μ L of MsCl to afford 0.21 g of mixed anhydride as a brown oil. This oil was then treated with 2 mL of Et₂O and 3-butenylmagnesium bromide (0.67 mL, 1.1 M solution in Et₂O) to yield 133.9 mg (72% yield) of the title compound as a yellow solid. Mp 53-55 °C dec. IR (cm⁻¹, Et₂O): 2061, 1978, 1671. ¹H NMR (200 MHz, CDCl₃), δ 5.85 (apparent ddt, J = 17.4, 10.3, 6.6 Hz, 1H), 5.77 (d, J = 2.3 Hz, 1H), 5.04 (apparent dq, J = 17.4, 1.4 Hz, 1H), 5.00 (apparent dq, J = 10.3, 1.4 Hz, 1H), 3.69 (s, 3H), 3.59 (apparent q, J = 2.6 Hz, 1H), 2.67 (ddd, J = 17.6, 8.3, 7.4 Hz, 1H), 2.54 (apparent dt, J = 17.6, 7.0 Hz, 1H), 2.38 (m, 2H), 2.13-1.8 (series of m, 3H), 1.42 (ddd, J = 11.0, 5.6, 2.4 Hz, 1H). ¹³C NMR (50 MHz, CDCl₃), δ 206.1, 139.4, 137.5, 115.2, 67.6, 64.0, 55.6, 54.6, 38.9, 28.2, 26.7, 23.1. HRMS (m/z) for M⁺ (C₁₅H₁₆FeO₅): calculated: 332.0347; found: 332.0346.

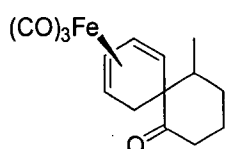
Tricarbonyl(6-9- η -1-oxo-4-methyl-spiro[4.5]deca-6,8-diene)iron (8a).



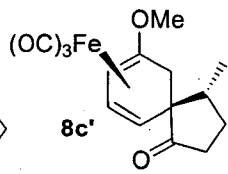
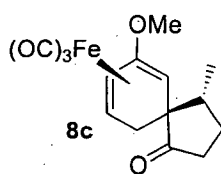
Ketone **7a** (200 mg, 0.66 mmol) dissolved in 35 mL of n-Bu₂O was heated for 5 h according to the general procedure to yield 188 mg (94% yield, yellow oil) after flash chromatography (1:4/EA:HEX¹) of the title product as 1.1:1 diastereomer mixture. IR (cm⁻¹, neat): 2050, 1962, 1732. ¹H NMR (200 MHz, CDCl₃), mixture of epimers, δ 5.54-5.36 (series of m, 3H), 5.24 (ddd, J = 5.9, 4.1, 1.3 Hz, 1H of one epimer), 3.38 (m, 1H of one epimer), 3.18 (m, 1H of one epimer), 2.91 (dd, J = 6.4, 1.2 Hz, 1H), 2.64 (dd, J = 6.6, 1.1 Hz, 1H), 2.33-1.61 (series of m, overlap with other epimer, 7H), 1.08 (d, J = 7.0 Hz, 3H), 0.86 (d, J = 7.3 Hz, 3H). ¹³C NMR (50 MHz, CDCl₃), 1:1.1 mixture of stereoisomers, δ 220.5, 219.9, 211.8, 211.5,

88.9, 86.8, 84.0, 81.6, 63.9, 63.5, 61.5, 59.8, 56.5, 42.8, 40.2, 39.3, 34.6, 33.4, 33.1, 26.2, 25.9, 15.7, 15.5. HRMS (m/z) for M^+ ($C_{14}H_{14}FeO_4$): calculated: 302.0241; found: 302.0230.

Tricarbonyl(6-9- η -5-methylspiro[5.5]undeca-7,9-dien-1-one)iron (8b).



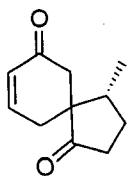
Ketone complex **7b** (101 mg, 0.32 mmol) dissolved in anhyd *n*-Bu₂O (16 mL) was heated for 7 h according to the general procedure to yield after preparative TLC (1:9/EA:HEX), the title compound as a white solid (60.9 mg, 60% yield), along with 18 mg of recovered starting material (83% yield of conversion), and 5.4 mg (5%) of demetallated spirocompound. Mp 58-60 °C dec. IR (cm⁻¹, neat): 2051, 1967, 1710. ¹H NMR (600 MHz, CDCl₃), First epimer: δ 5.26 (ddt, J = 6.6, 4.2, 1.2 Hz, 1H), 5.19 (ddd, J = 6.0, 4.2, 1.2 Hz, 1H), 3.26 (dtd, J = 6.6, 3.0, 1.2 Hz, 1H), 3.23 (dd, J = 6.0, 1.5 Hz, 1H), 2.75 (dd, J = 6.6, 1.2 Hz, 1H), 2.70-1.40 (series of m, overlap with other epimer, 9H), 0.70 (d, J = 7.2, 3H). Second epimer: δ 5.52 (ddd, J = 6.6, 4.2, 1.8 Hz, 1H), 5.16 (dddd, J = 6.0, 4.2, 1.8, 1.2 Hz, 1H), 3.02 (dtd, J = 6.0, 3.0, 1.8 Hz), 2.75 (dd, J = 6.6, 1.2 Hz), 2.70-1.40 (series of m, overlap with other epimer, 9H), 0.90 (d, J = 7.2 Hz, 3H). ¹³C NMR (50 MHz, CDCl₃), mixture of regioisomers, δ 213.0, 211.9, 211.6, 211.5, 89.6, 86.5, 84.4, 80.2, 64.1, 63.8, 61.9, 60.8, 56.6, 54.7, 41.9, 40.4, 40.0, 38.5, 38.3, 35.9, 28.4, 27.3, 22.6, 21.7, 15.7, 14.3. HRMS (m/z) for M^+ ($C_{15}H_{16}FeO_4$): calculated: 316.0398; found: 316.0393.



Tricarbonyl(6-9- η -7-methoxy-4-methylspiro[4.5]deca-6,8-dien-1-one)iron (8c/8c')

A solution of 139 mg (0.42 mmol) of ketone complex **7c** in 25 mL of anhyd *n*-Bu₂O was refluxed for 5 h according to the general procedure. After workup, spiroketones **8c** and **8c'** were isolated as a 1:1 mixture of regioisomers (brown oil, 125 mg, 90%). Spiroketone **8c** was isolated as a white solid by preparative TLC purification (1:4/EA:HEX). **8c**: Mp 40-45 °C dec. IR (cm⁻¹, CH₂Cl₂): 2046, 1966, 1737. ¹H NMR (200 MHz, CDCl₃), δ 5.14 (dd, *J* = 6.6, 1.8 Hz, 1H), 3.71 (s, 3H), 2.91 (d, *J* = 1.8 Hz, 1H), 2.69 (apparent dt, *J* = 6.6, 2.9 Hz, 1H), 2.28-1.83 (series of m, 5H), 1.66 (dd, *J* = 15.0, 3.2 Hz, 1H), 1.49 (dd, *J* = 15.0, 3.1 Hz, 1H), 1.1 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (50 MHz, CDCl₃), δ 221.2, 211.2, 140.5, 67.6, 58.3, 54.8, 53.7, 49.1, 42.4, 39.5, 34.2, 25.7, 15.8. HRMS (*m/z*) for M⁺ - CO (C₁₄H₁₆FeO₄): calculated: 304.0398; found: 304.0386. **8c'**: ¹H NMR (200 MHz, CDCl₃), δ 5.43 (d, *J* = 4.3 Hz, 1H), 4.92 (dd, *J* = 6.1, 4.3 Hz, 1H), 3.52 (s, 3H), 2.67 (d, *J* = 6.1 Hz, 1H, H₈), 2.4-2.1 (series of m, 2H), 1.88 (d, *J* = 14.8 Hz, 1H), 1.70-1.52 (series of m, 2H), 0.90 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (50 MHz, CDCl₃), δ 218.7, 212.2, 119.0, 80.0, 72.8, 65.9, 59.5, 56.5, 55.8, 40.1, 34.7, 26.0, 15.3.

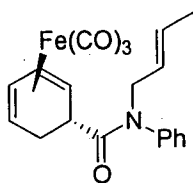
4-Methylspiro[4.5]dec-8-ene-1,7-dione (**9**).



The 1:1 mixture of spirocyclic ketone complexes **8c** (62 mg, 0.18 mmole) was placed under vacuum (0.5 mmHg) for 15 h (overnight). The vacuum was then broken with a flow of Ar, and the spirocyclic ketone complexes were dissolved in anhydrous C₆H₆ (10 mL). This solution was added via a syringe to a flame dried round bottom flask containing 35 equiv of anhydrous Me₃NO (536 mg) under Ar. The reaction mixture was stirred at rt under Ar for 16 h (the reaction was monitored by IR), then diluted with ether and filtered through Celite. The solution

was washed with H₂O, dried (MgSO₄), and concentrated. The demetallated product was then dissolved in methanol (5.5 mL), and added to a solution of oxalic acid (270 mg, 15.5 equiv) in water (1.4 mL). The reaction mixture was stirred at rt for 24 h, then poured into sat aq K₂CO₃ and extracted with ether. Preparative TLC (3:2/EA:HEX) yielded 27 mg (75% yield) of the α,β unsaturated ketone as a colorless oil. IR (cm⁻¹, CH₂Cl₂): 1729, 1679. ¹H NMR (200 MHz, CDCl₃), δ 6.89 (ddd, J = 10.2, 4.7, 3.1 Hz, 1H), 6.08 (br d, J = 10.2 Hz, 1H), 2.63 (apparent dt, J = 19.0, 3.1 Hz, 1H), 2.37-1.99 (series of m, 6H), 1.69-1.59 (series of m, 2H), 1.02 (d, J = 6.7 Hz, 3H). ¹³C NMR (50 MHz, CDCl₃), δ 219.2, 197.2, 147.0, 129.7, 53.9, 41.0, 39.1, 35.0, 32.8, 26.6, 16.2. HRMS (m/z) for MH⁺ (C₁₁H₁₅O₂): calculated: 179.1072; found: 179.1076.

Tricarbonyl[2-5- η - Cyclohexa-2,4-dienecarboxylic acid allyl-phenyl-amide]iron (14a).

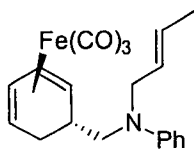


5-carboxylcyclohexa-1,3-dieneirontricarbonyl² (200 mg, 0.76 mmol) and 80 mg of 4 Å molecular sieves were dissolved in 2 mL of dry CH₂Cl₂, followed by sequential addition of 0.14 mL of Et₃N, and 0.12 mL of CH₃SO₂Cl. The reaction mixture was stirred at rt for 1h, 262 mg of N-crotylaniline and 0.28 mL of Et₃N were then added at 0 °C, stirred at rt for 12 h, washed with water, and dried (MgSO₄) to afford 273 mg (86% yield) of the title compound as a light brown oil after chromatography. R_f = 0.39 (1:9/ EA:HEX). IR (cm⁻¹, neat): 2046, 1965, 1651. ¹H NMR (300 MHz, CDCl₃), δ 7.50-7.10 (m, 5H), 5.53-5.40 (4H), 4.25-4.00 (2H), 3.07 (m, 1H), 2.88-2.73 (m, 2H), 1.75-1.65 (m, 2H), 1.62 (d, J = 5.7, 3H). ¹³C NMR (50 MHz, CDCl₃, δ): 211.7, 173.9, 142.1, 129.8, 129.6, 128.3, 128.1,

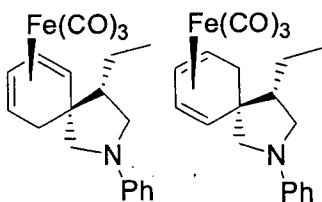
125.6, 86.3, 85.4, 60.7, 60.1, 52.1, 41.3, 30.0, 17.8. HRMS (m/z) for MH^+

($C_{20}H_{20}FeNO_4$): calculated: 394.0742; found: 394.0739.

Tricarbonyl[2-5- η - allyl-cyclohexa-2,4-dienylmethyl-phenyl-amine]iron (14b).



To 100 mg (0.25 mmol) of **14a** in 2 mL of CH_2Cl_2 was added DIBAL (2 mL, 1.5 M in toluene, 3.0 mmol) at $-78^\circ C$. The reaction mixture was warmed to rt over 2 h, stirred for 6 h, quenched with water at $0^\circ C$, extracted three times with CH_2Cl_2 , dried ($MgSO_4$), and concentrated under vacuum. Flash chromatography on silica gel afforded 93 mg (93% yield) of the title amine as a light brown oil. $R_f = 0.60$ (1:19/Hex:EA). 1H NMR (200 MHz, $CDCl_3$), δ 7.25-6.60 (5H), 5.60-5.20 (4H), 3.84 (d, $J = 4.4$ Hz, 2H), 3.23-3.00 (3H), 2.91 (dd, $J = 14.4, 8.6$ Hz, 1H), 2.50 (m, 1H), 2.00 (ddd, $J = 15.2, 10.5, 3.6$ Hz, 1H), 1.65 (d, $J = 5.8$, 3H), 1.72-1.50 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$), δ 211.9, 148.4, 129.2, 127.4, 126.4, 116.1, 112.3, 86.1, 84.8, 64.6, 59.8, 58.8, 36.7, 29.2, 17.7.

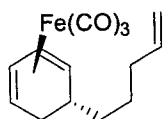


Tricarbonyl[6-9- η - 4-methyl-2-phenyl-2-aza-spiro[4.5]deca-6,8-diene]iron (15).

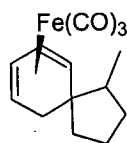
A solution of 45 mg of **14b** in 5 mL of n -Bu₂O was refluxed for 12 h according to the general procedure. Spiroamines **15** were isolated as a 1.3:1 mixture of epimers (brown oil, 36 mg, 50%), which also contained about 20% inseparable unreacted starting material. $R_f = 0.60$ (1:19/EA:HEX). 1H NMR (600 MHz, $CDCl_3$), mixture of epimers, δ 7.25-6.50 (5H), 5.45-5.32 (2H), 3.54 (dd, $J = 8.6, 6.6$ Hz, 1H, minor epimer), 3.31 (dd, $J = 9.0, 6.6$ Hz, 1H, major epimer), 3.24 (m, 1H, minor epimer), 3.20-2.90 (series of m, overlap with other epimer), 2.68 (d, $J = 8.4$ Hz, 1H,

major epimer), 2.20-1.00 (series of m, overlap with other epimer), 0.97 (t, $J = 7.8$, 3H, major epimer), 0.94 (t, $J = 7.8$, 3H). ^{13}C NMR (50 MHz, CDCl_3 , major epimer, δ): 211.9, 147.4, 129.2, 115.4, 111.1, 86.6, 83.3, 69.3, 63.5, 61.1, 51.5, 50.0, 43.3, 35.1, 29.8, 21.8, 12.6. HRMS (m/z) for MH^+ ($\text{C}_{20}\text{H}_{22}\text{FeNO}_3$): calculated: 380.0954; found: 380.0954.

Tricarbonyl[1-4- η - 5-pent-4-enyl-cyclohexa-1,3-diene]iron (16).



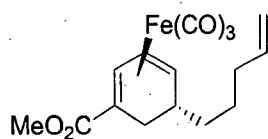
To 520 mg (1.37 mmol) of cation **13** in 10 mL of CH_2Cl_2 at -78°C , was added dropwise 4-pentenylmagnesium bromide (1.6 mL, 1.1 M solution in Et_2O) via syringe over 10 min. After being stirred for 2 h at -78°C , the reaction was warmed to 0°C , and quenched with 10 mL of water. The organic layer was separated, and the aqueous layer was extracted with 10 mL of CH_2Cl_2 and (2 x 10 mL) ether. The extracts were combined, dried (MgSO_4), and evaporated to give 285 mg (70% yield) of the title compound as a yellow oil after flash chromatography using hexane. ^1H NMR (200 MHz, CDCl_3), δ 5.75 (ddt, $J = 18.0, 10.2, 6.4$ Hz, 1H), 5.40-5.20 (2H), 5.03-4.85 (2H), 3.19-2.98 (2H), 2.15-1.90 (4H), 1.42-1.10 (5H). ^{13}C NMR (50 MHz, CDCl_3), δ 212.3, 138.8, 114.5, 85.5, 84.6, 67.2, 60.0, 39.6, 38.2, 33.9, 30.8, 32.6.



Tricarbonyl(6-9- η -4-methyl-spiro[4.5]deca-6,8-diene)iron (18).

Complex **16** (61 mg, 0.21 mmol) dissolved in 8 mL of $n\text{-Bu}_2\text{O}$ was heated for 12 h according to the general procedure to yield, after reverse phase PLC (pure methanol, $R_f = 0.47$), 41 mg (68% yield, yellow oil) of the title product as a mixture of epimers. ^1H NMR (200 MHz, CDCl_3), mixture of epimers, δ 5.36-5.24 (2H), 3.25-2.93 (2H), 2.00-1.00 (9H), 0.92 (d, $J = 7.0$ Hz, 3H), 0.84 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (50

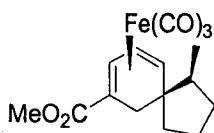
MHz, CDCl₃), major epimer, δ 212.5, 85.9, 82.2, 68.5, 61.7, 48.9, 44.9, 43.5, 42.0, 31.7, 22.4, 17.0. HRMS (m/z) for MH⁺ (C₁₄H₁₇FeO₃): calculated: 289.0528; found: 289.0799.



Tricarbonyl(6-9-η- 5-pent-4-enyl-cyclohexa-1,3-dienecarboxylic acid methyl ester)iron (20).

Cation **19** (211 mg, 0.5 mmol) was treated with 1.3 equiv of Grignard reagent according to the procedure for **16** to afford 103 mg (60% yield) of the title complex as a light brown oil after flash chromatography on silica gel. R_f = 0.31 (1:19/EA:HEX). ¹H NMR (200 MHz, CDCl₃), δ 6.08 (d, J = 4.4 Hz, 1H), 5.76 (ddt, J = 18.0, 10.0, 6.4 Hz, 1H), 5.34 (dd, J = 6.4, 4.4 Hz, 1H), 5.05–4.88 (2H), 3.69 (s, 3H), 3.30 (ddd, J = 6.4, 3.5, 1.1 Hz, 1H), 2.43 (dd, J = 14.6, 10.8 Hz, 1H), 2.22 (m, 1H), 1.65 (apparent t, J = 6.6, 2H), 1.42–1.15 (4H), 1.07 (dd, J = 14.6, 3.6 Hz, 1H). ¹³C NMR (50 MHz, CDCl₃), δ 210.3, 172.7, 138.6, 114.7, 88.6, 84.5, 68.0, 51.6, 39.6, 39.4, 33.8, 29.7, 27.4. HRMS (m/z) for MH⁺ (C₁₆H₁₉FeO₅): calculated: 347.0582; found: 347.0566.

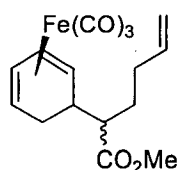
Tricarbonyl(6-9-η- 1-methyl-spiro[4.5]deca-7,9-diene-7-carboxylic acid methyl ester)iron (25b).



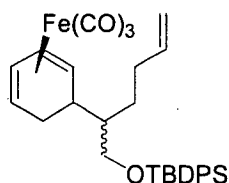
Complex **20** (40 mg) dissolved in anhyd *n*-Bu₂O (5 mL) was heated for 12 h according to the general procedure to yield the title compound as a yellow oil (20 mg, 50% yield), along with 30% of other inseparable isomers after preparative TLC. R_f = 0.35 (1:19/EA:HEX). ¹H NMR (200 MHz, CDCl₃), δ 6.09 (d, J = 4.4 Hz, 1H), 5.34 (dd, J = 6.4, 4.4 Hz, 1H), 3.71 (s, 3H), 3.14 (d, J = 6.4 Hz, 1H), 2.36 (d, J = 15.6 Hz, 1H), 1.40 (d, J = 15.6 Hz, 1H), 2.22–

1.15 (m, 7H), 0.92 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (50 MHz, CDCl_3), δ 210.4, 90.8, 87.8, 82.3, 73.0, 51.7, 48.4, 44.5, 42.6, 35.7, 32.1, 21.0, 16.5. HRMS (m/z) for MH^+ ($\text{C}_{16}\text{H}_{19}\text{FeO}_5$): calculated: 347.0582; found: 347.0550.

Tricarbonyl(2-5- η - 2-cyclohexa-2,4-dienyl-hex-5-enoic acid methyl ester)iron (26).



To a stirred solution of LDA (1 mmol, 0.5 mL, 2 M in heptane/THF) at -78°C under Ar was added 130 mg of methyl 5-hexenoate in 1 mL of THF. The mixture was stirred for 20 min, after which time the complex **13** (364 mg, 1 mmol) was added in one portion. Stirring was continued at -78°C for 30 min, and the reaction mixture was allowed to warm to rt. The title compound was obtained as a 2:1 mixture of diastereomers (223 mg, 70%) following workup as for **16** and flash chromatography. $R_f = 0.31$ (1:19/Hex:EA). ^1H NMR (200 MHz, CDCl_3), mixture of isomers, δ 5.82-5.60 (m, 1H), 5.40-5.26 (2H), 5.15-4.92 (2H), 3.69 (s, 3H, major isomer), 3.65 (s, 3H, minor isomer), 3.10-2.83 (series of m, 2H), 2.40-1.33 (series of m, 8H). ^{13}C NMR (50 MHz, CDCl_3 , δ): 211.8, 175.2, 137.6, 115.3, 85.6, 85.1, 62.7, 59.1, 53.4, 51.5, 40.8, 31.8, 30.4, 28.8. HRMS (m/z) for MH^+ ($\text{C}_{16}\text{H}_{19}\text{FeO}_5$): calculated: 347.0582; found: 347.0571.

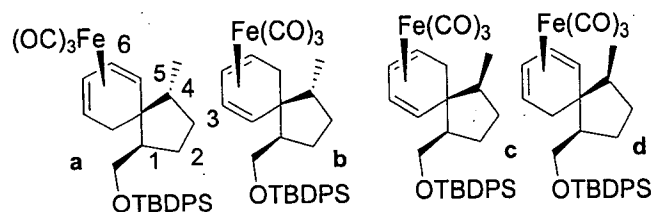


Tricarbonyl(2-5- η - tert-butyl-(2-cyclohexa-2,4-dienyl-hex-5-enyloxy)-diphenyl-silane)iron (28).

To a solution of 134 mg (0.39 mmol) of complex **26** in 1 mL of dichloromethane at -78°C under Ar was added 1 mL of 1.5 M DIBAL in Toluene. The

reaction mixture was stirred for 2 h, then warmed to 0 °C over 2 h, quenched with water at 0 °C, extracted three times with CH₂Cl₂, dried (MgSO₄), and concentrated under vacuum to give the intermediate alcohol. $R_f = 0.32$ (1:4/Hex:EA). The alcohol, 6.8 mg of DMAP, 55.8 mg of imidazole, and one drop of DMF were dissolved in 0.5 mL of dichloromethane at 0 °C. *t*-Butyldiphenylsilyl chloride (135 mg, 1.2 equiv) was added slowly. The reaction mixture was stirred at rt for 1 h, filtered through Celite, washed with sat. aq. NH₄Cl and H₂O, dried (MgSO₄), and evaporated. Chromatography gave the title compound (150 mg, 75% over two steps) as a 2:1 mixture of diastereomers (colorless oil). ¹H NMR (300 MHz, CDCl₃), mixture of isomers, δ 7.75-7.66 (4H), 7.50-7.30 (6H), 5.82-5.67 (m, 1H), 5.40-5.16 (2H), 5.05-4.90 (2H), 3.50 (2H), 3.00 (2H), 2.45 (m, 1H), 2.10-1.80 (series of m, 3H), 1.45-1.20 (4H), 1.07 (s, 9H). ¹³C NMR (75 MHz, CDCl₃), major isomer, δ 212.5, 139.0, 135.8, 133.9, 129.8, 127.8, 114.7, 85.6, 85.0, 65.2, 64.7, 46.8, 39.8, 32.1, 28.8, 27.7, 27.5, 27.1, 19.4. HRMS (m/z) for (M-3CO)⁺ (C₂₈H₃₆FeOSi): calculated: 472.1885; found: 472.1868.

Tricarbonyl(6-9- η - *tert*-Butyl-(4-methyl-spiro[4.5]deca-6,8-dien-1-ylmethoxy)-diphenylsilane)iron (30).



Complex **28** (70 mg)

dissolved in anhyd *n*-Bu₂O (5 mL)

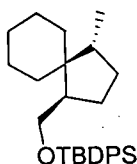
was heated for 12 h according to the

general procedure to yield after preparative TLC (1:9/EA:HEX), the title compound (56 mg, 80% yield) as a colorless oil, which contained four isomers

(**30a:30b:30c:30d**/4.5:4:1:1). ¹H NMR (600 MHz, CDCl₃, δ): characteristic peaks **30a**:

3.70 (dd, $J = 10.2, 3.6$ Hz, 1H), 3.32 (dd, $J = 10.2, 7.8$ Hz, 1H), 3.00 (m, 1H), 2.66 (dd, $J = 6.6, 1.2$ Hz, 1H), 1.04 (s, 9H), 0.93 (d, $J = 7.2$ Hz, 3H). **30b**: 3.65 (dd, $J = 10.2, 6.0$ Hz, 1H), 3.54 (dd, $J = 10.2, 7.2$ Hz, 1H), 3.08 (m, 1H), 2.64 (m, 1H), 1.05 (s, 9H), 0.83 (d, $J = 7.2$ Hz, 3H).

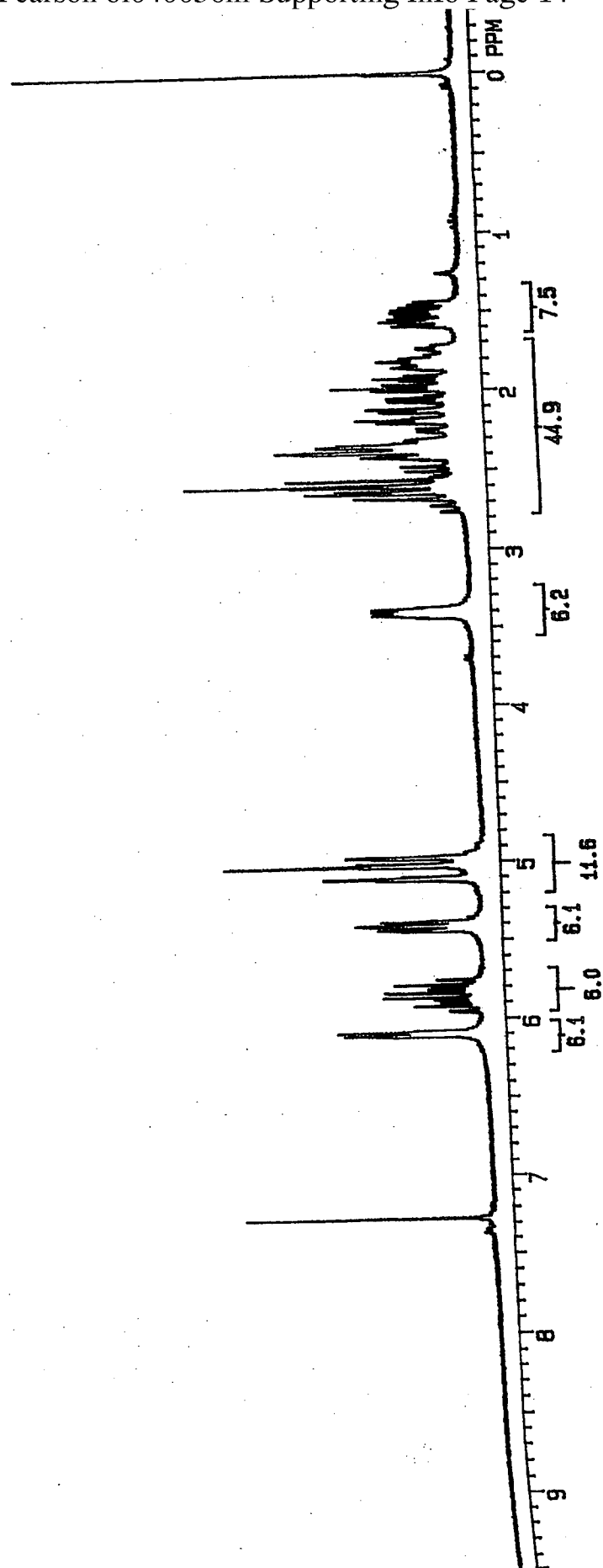
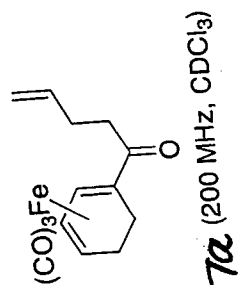
tert-Butyl-(4-methyl-spiro[4.5]dec-1-ylmethoxy)-diphenyl-silane (31).

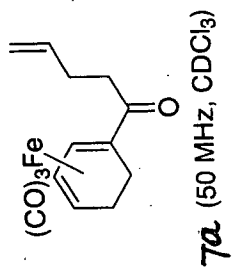


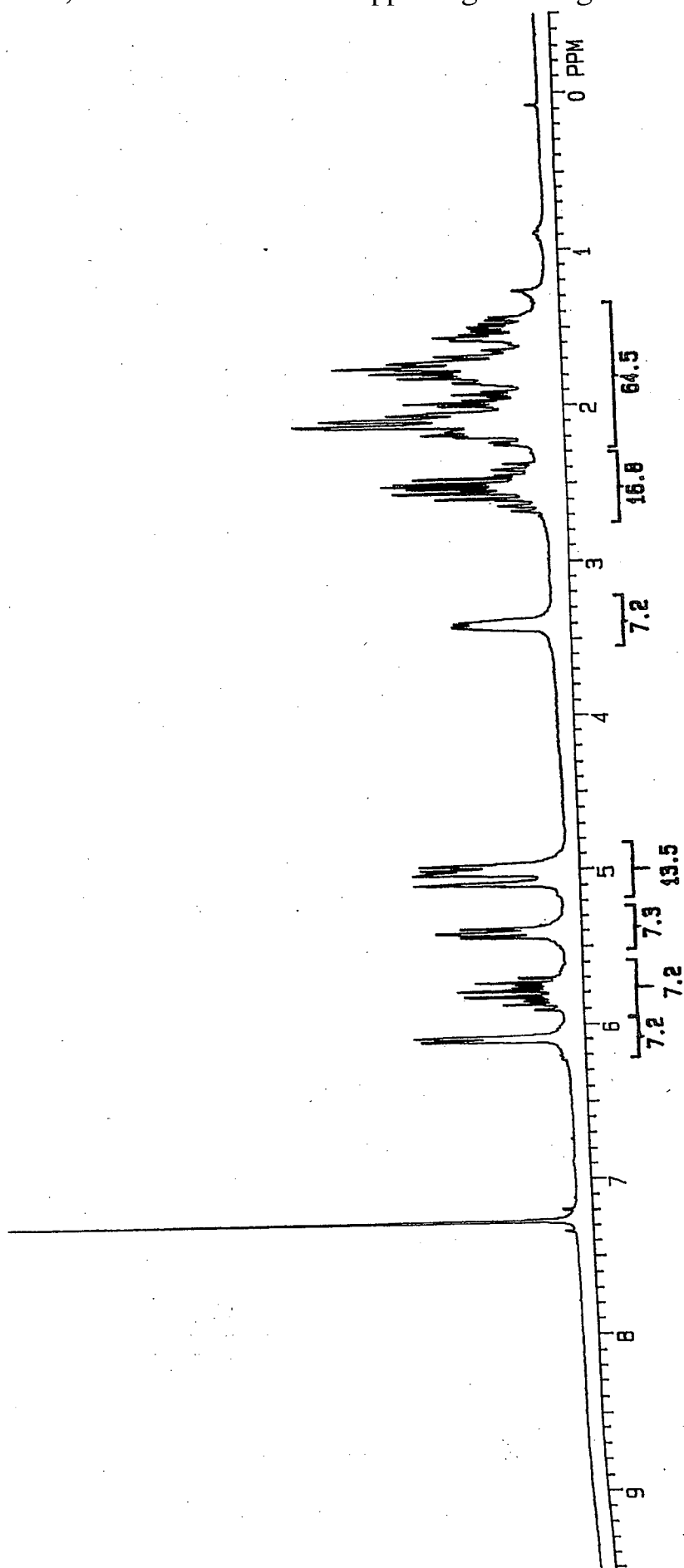
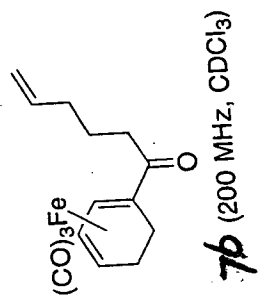
Complexes **30** (56 mg, 0.1 mmol) were treated with 30 mg of trimethylamine N-oxide in 1 mL of benzene. The reaction mixture was stirred at 60 °C for 2 h, filtered through Celite, evaporated, and dissolved in 1 mL of methanol containing 5 mg of 10% Pd on activated carbon under a balloon of hydrogen gas. After stirring at rt overnight, the reaction mixture was then filtered and concentrated to give 42 mg (>95% yield) of the title compound as a 4.5:1 mixture of diastereomers (colorless oil). ^1H NMR (200 MHz, CDCl_3), δ 7.75-7.66 (4H), 7.50-7.30 (6H), 3.74 (dd, $J = 9.8, 5.2$ Hz, 1H), 3.48 (dd, $J = 10.2, 8.8$ Hz, 1H), 2.10-1.00 (16H), 1.07 (s, 9H), 0.82 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (50 MHz, CDCl_3), δ 135.7, 134.2, 129.5, 127.6, 65.1, 46.3, 45.8, 40.0, 30.6, 30.5, 27.0, 26.8, 26.6, 25.4, 23.2, 22.9, 19.3, 15.1. HRMS (m/z) for (M-t-Bu) $^+$ ($\text{C}_{24}\text{H}_{31}\text{OSi}$): calculated: 363.2144; found: 363.2126.

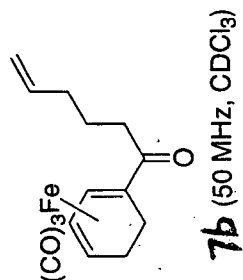
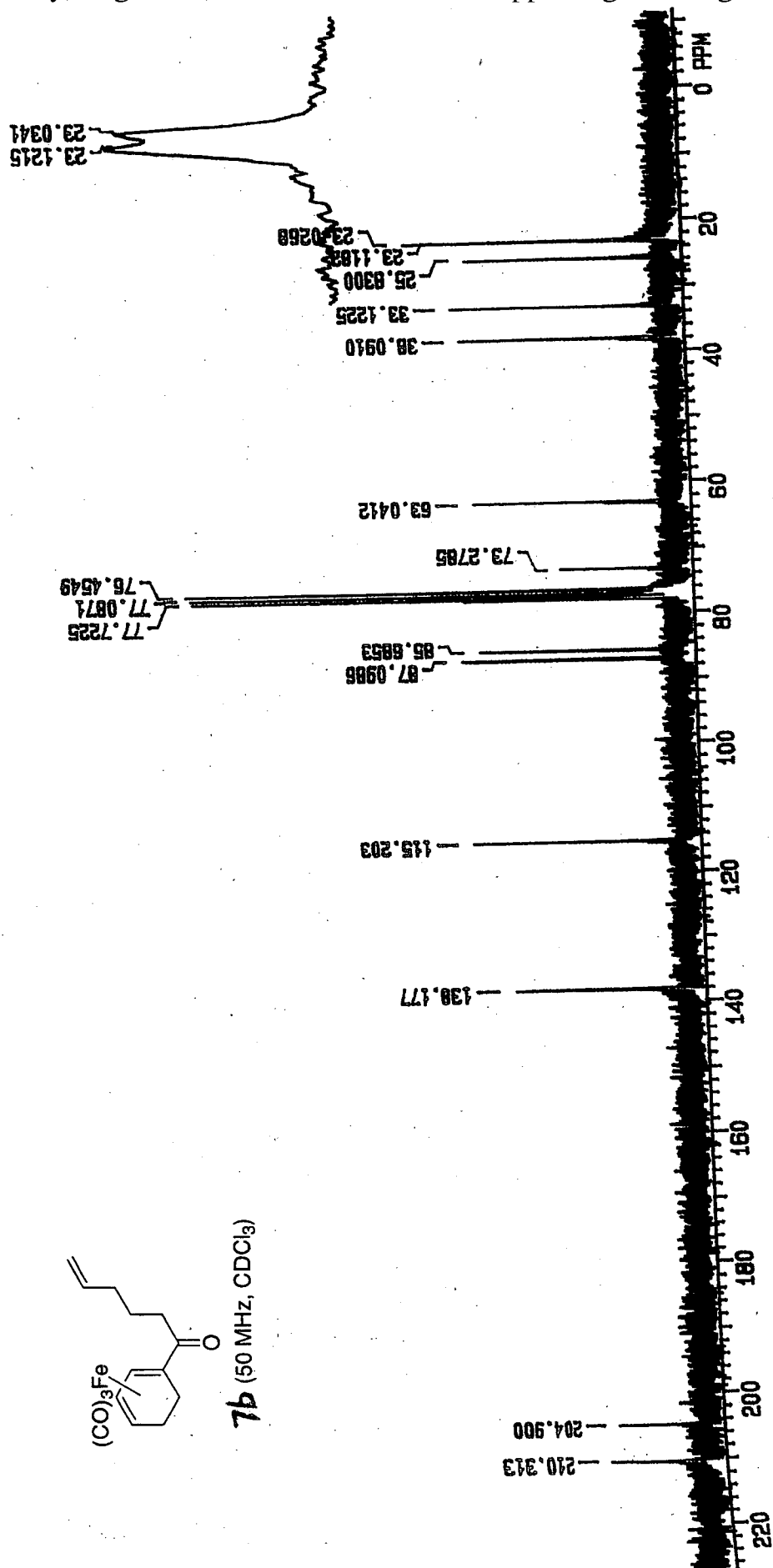
¹ EA:HEX=Ethyl acetate:Hexane

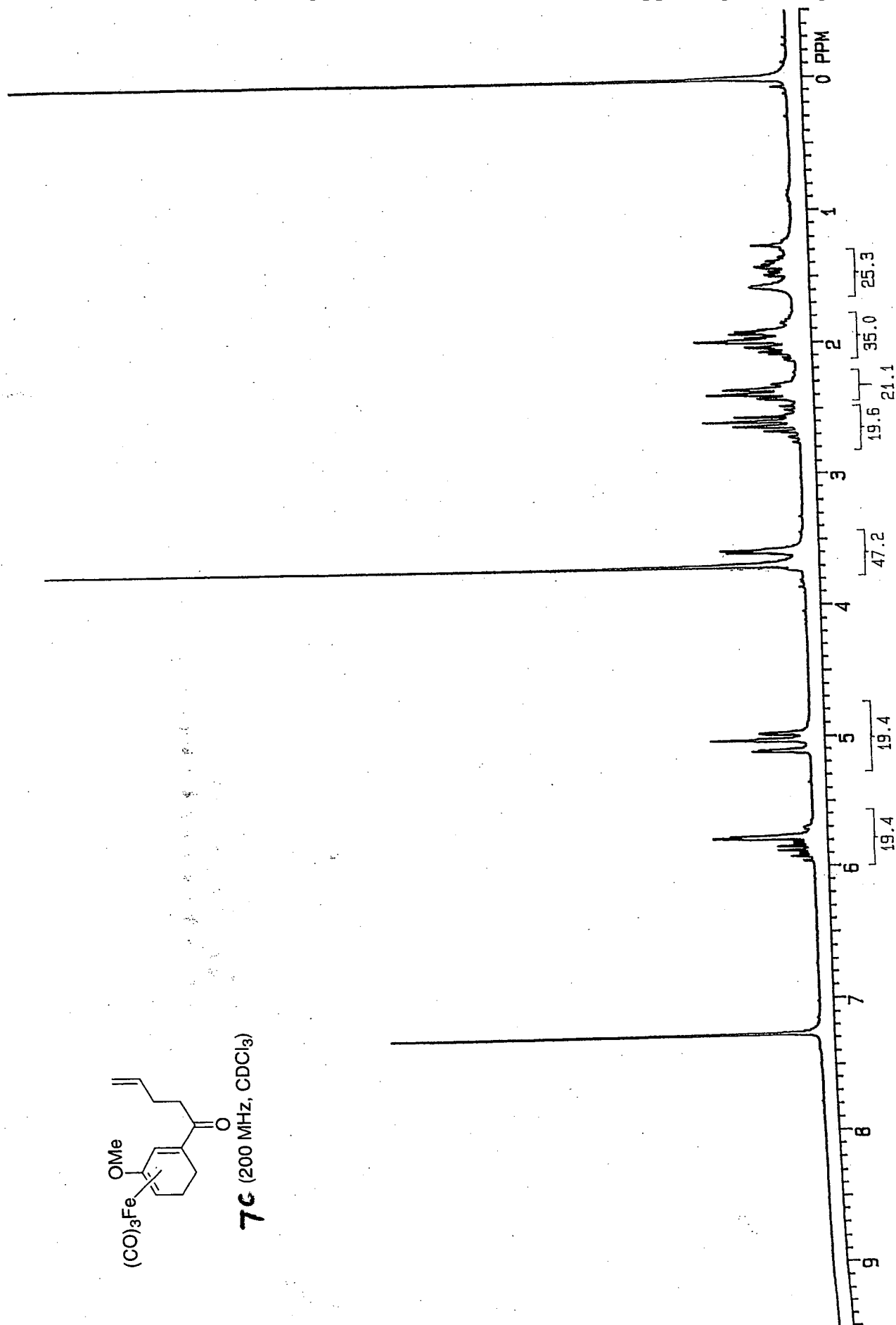
² Bandara, B. M. R.; Birch, A. J.; Raverty, W. D. *J. Chem. Soc., Perkin Trans. I* **1982**, 1755.

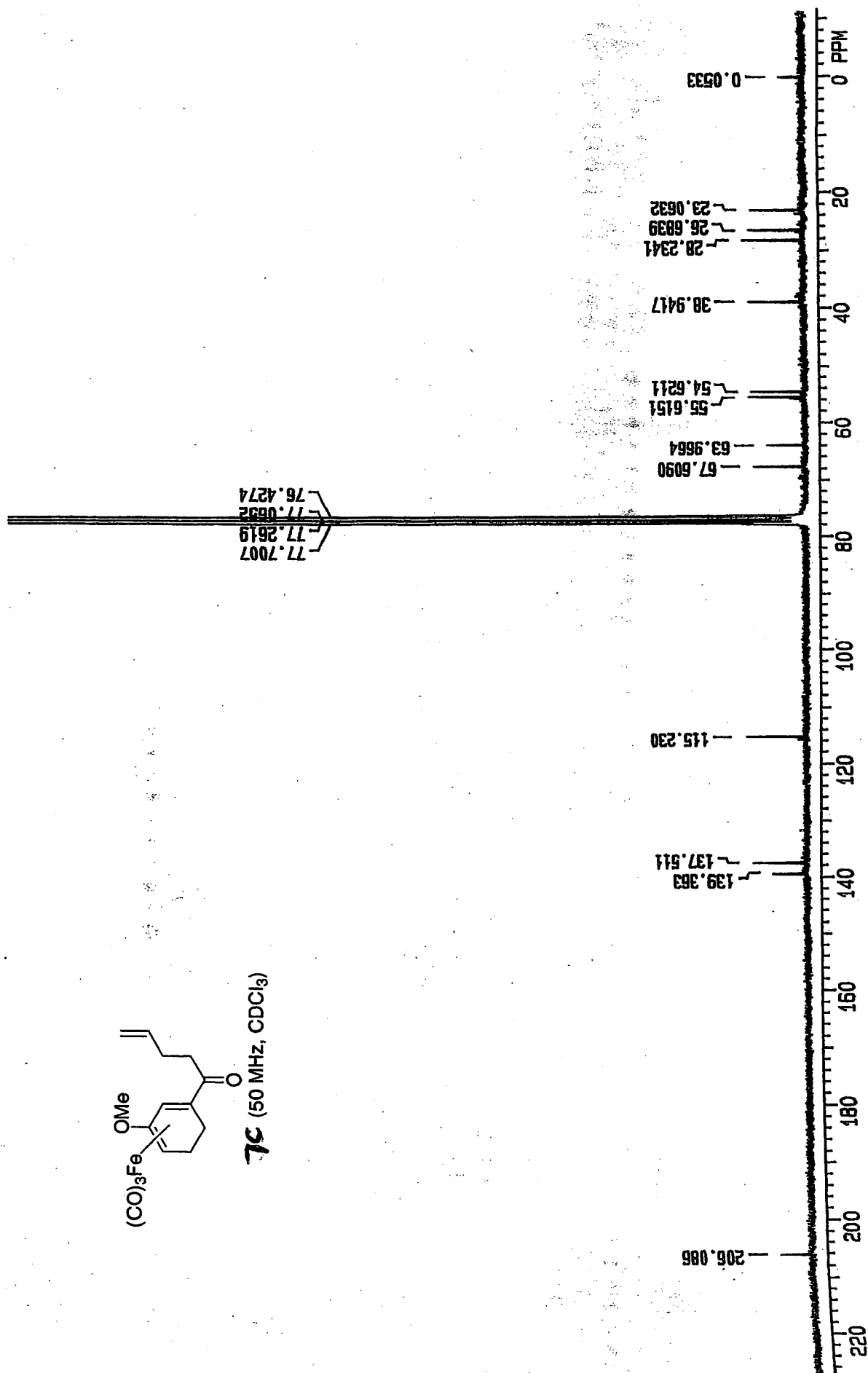


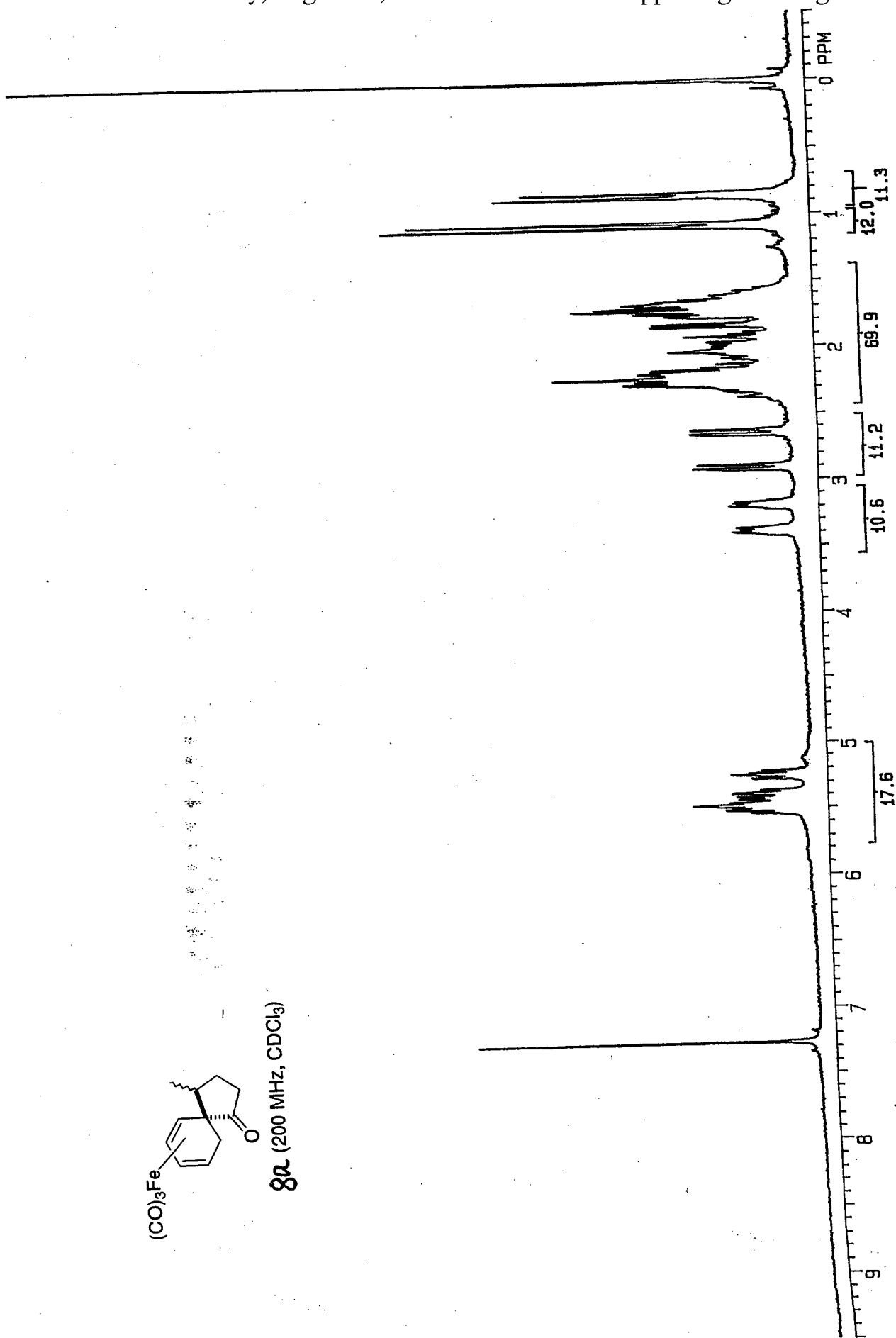
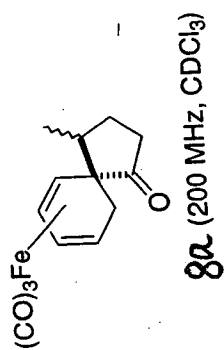


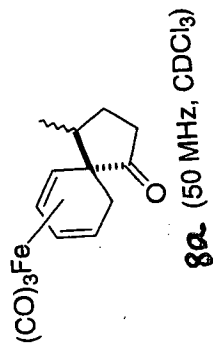




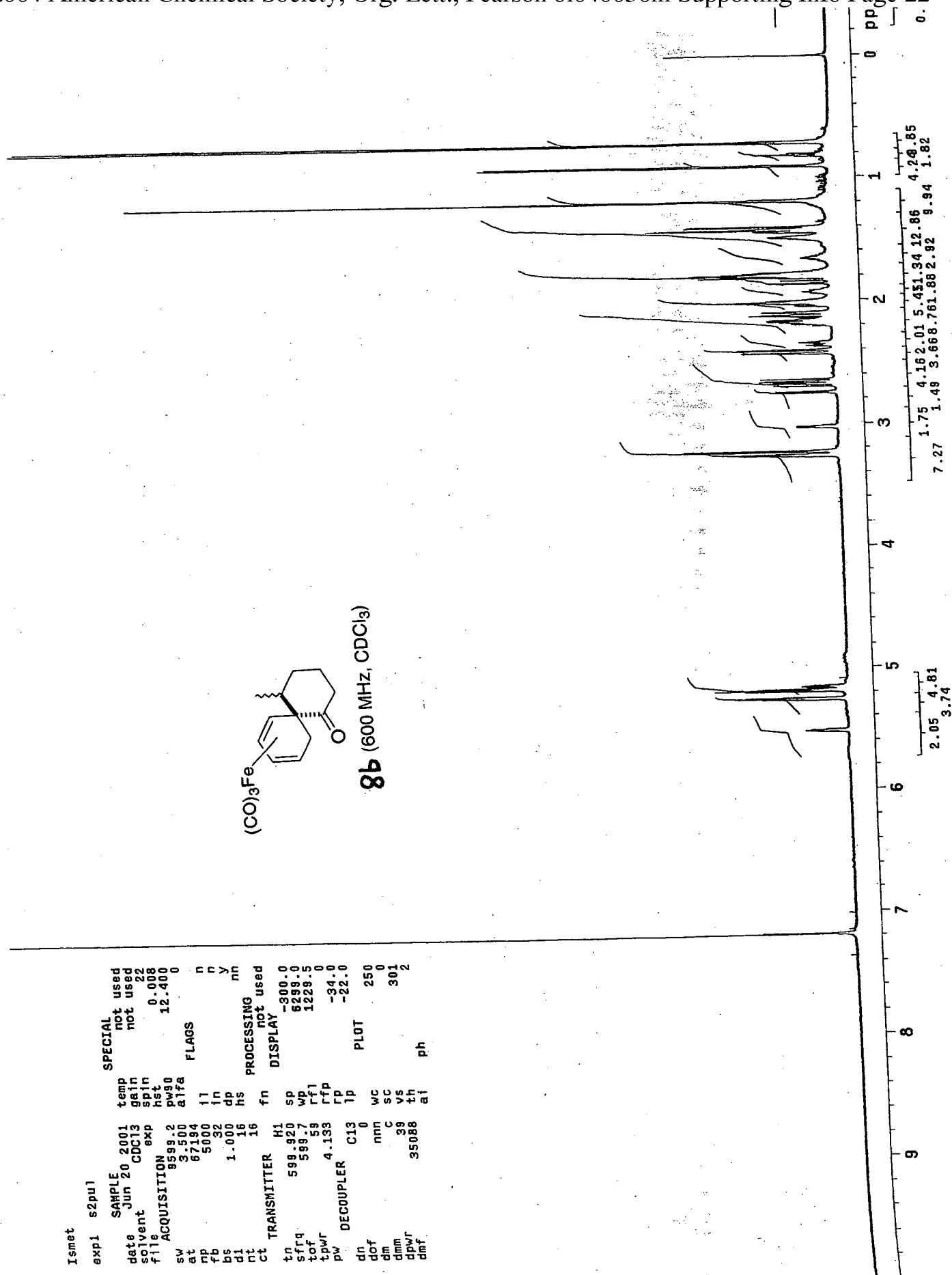
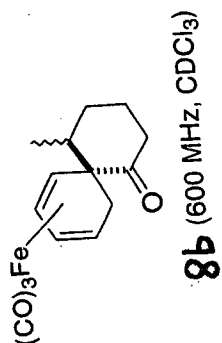




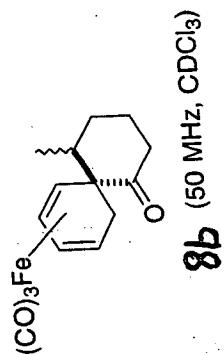
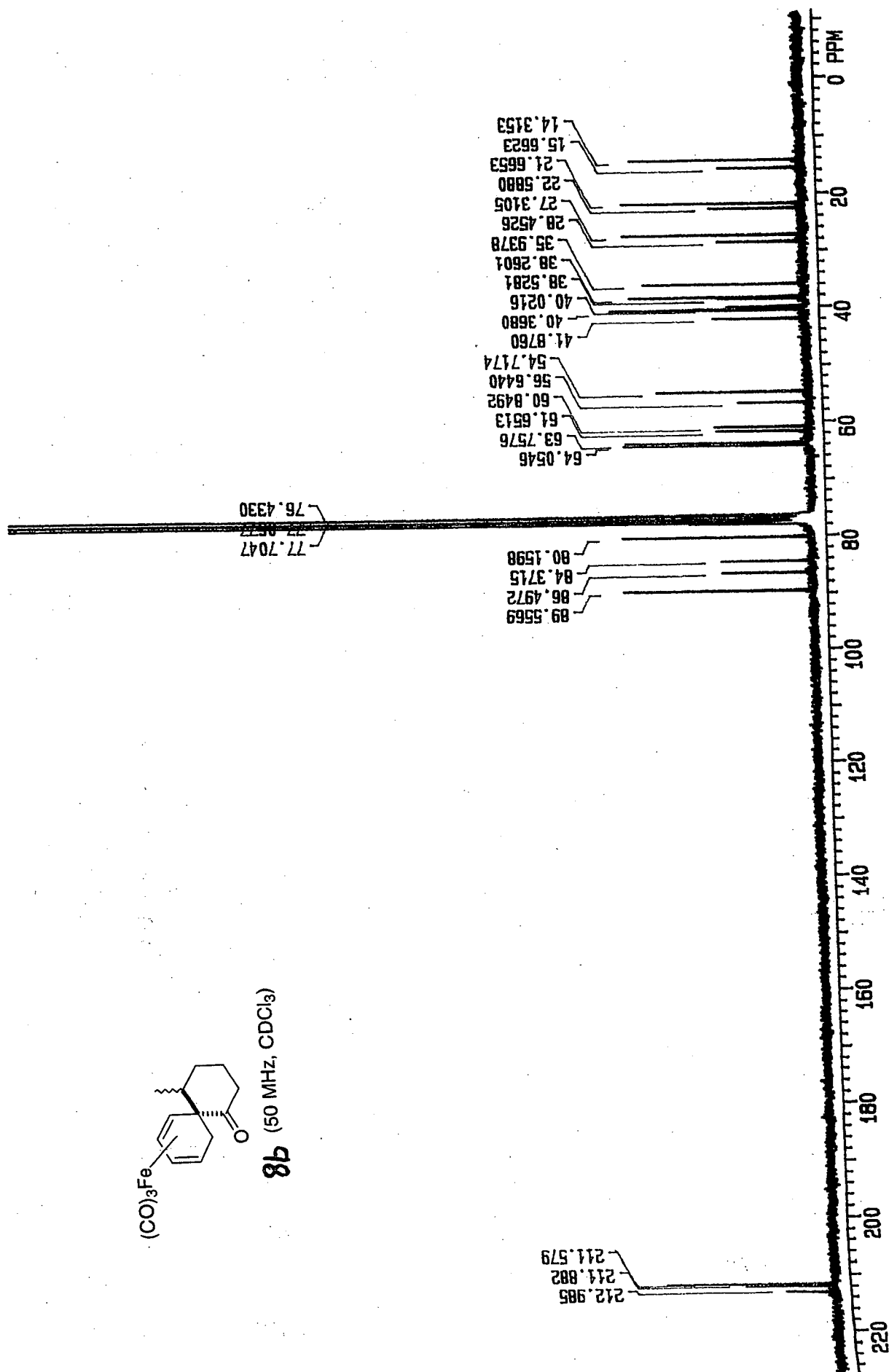




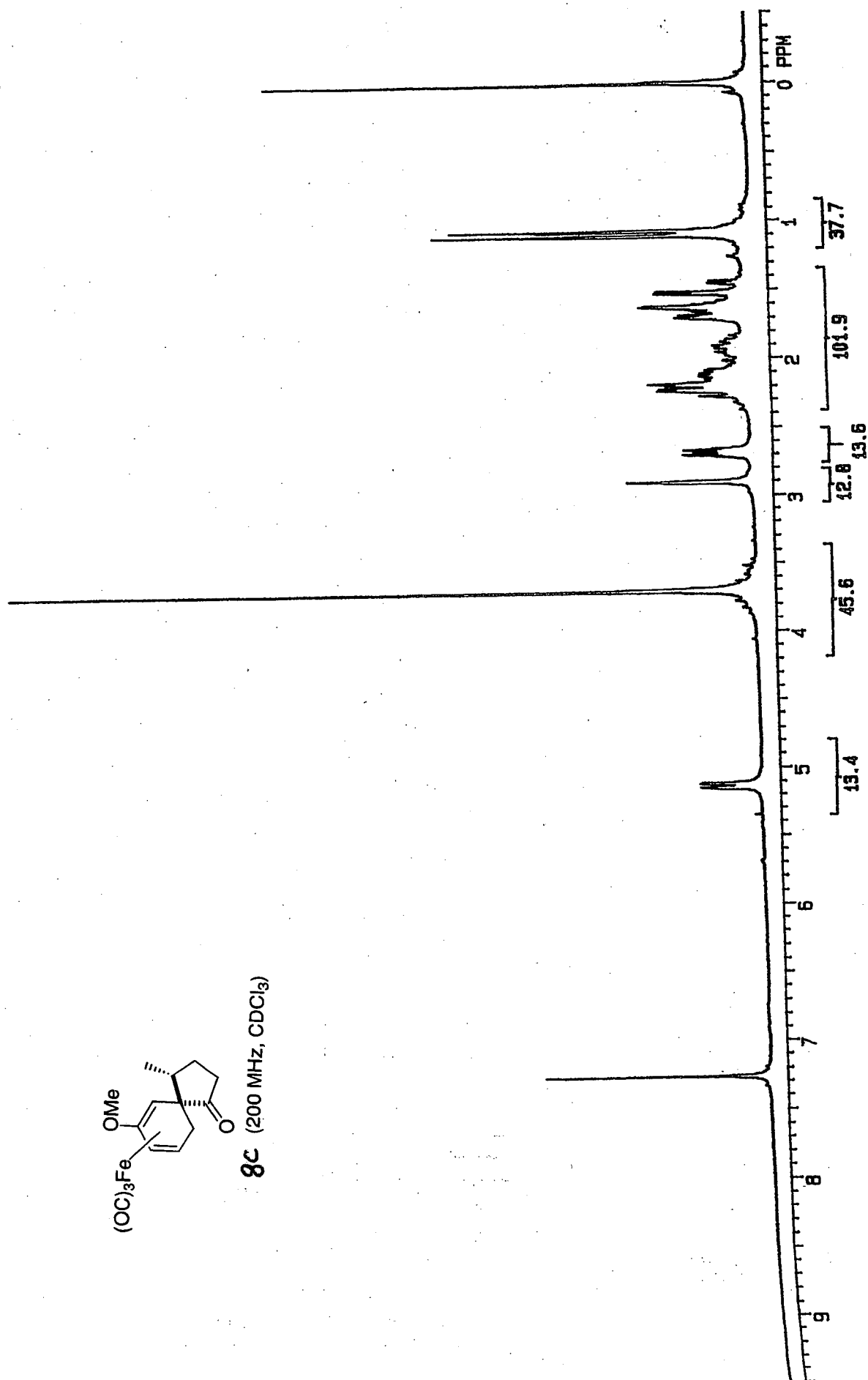
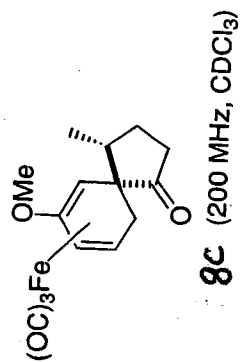
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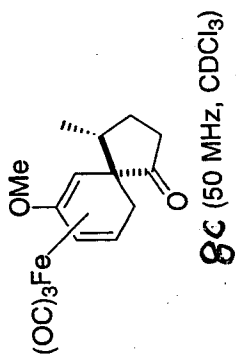


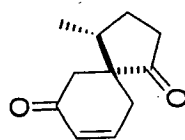
S23



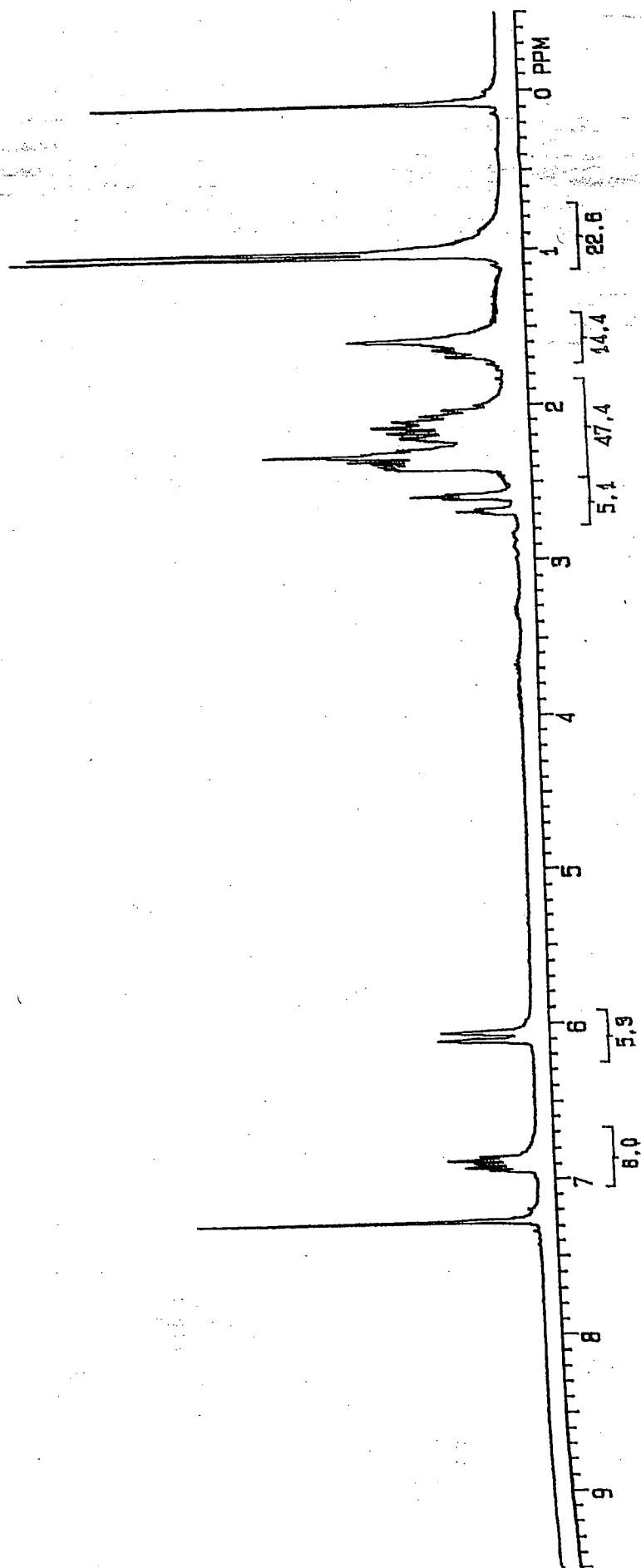
S 24

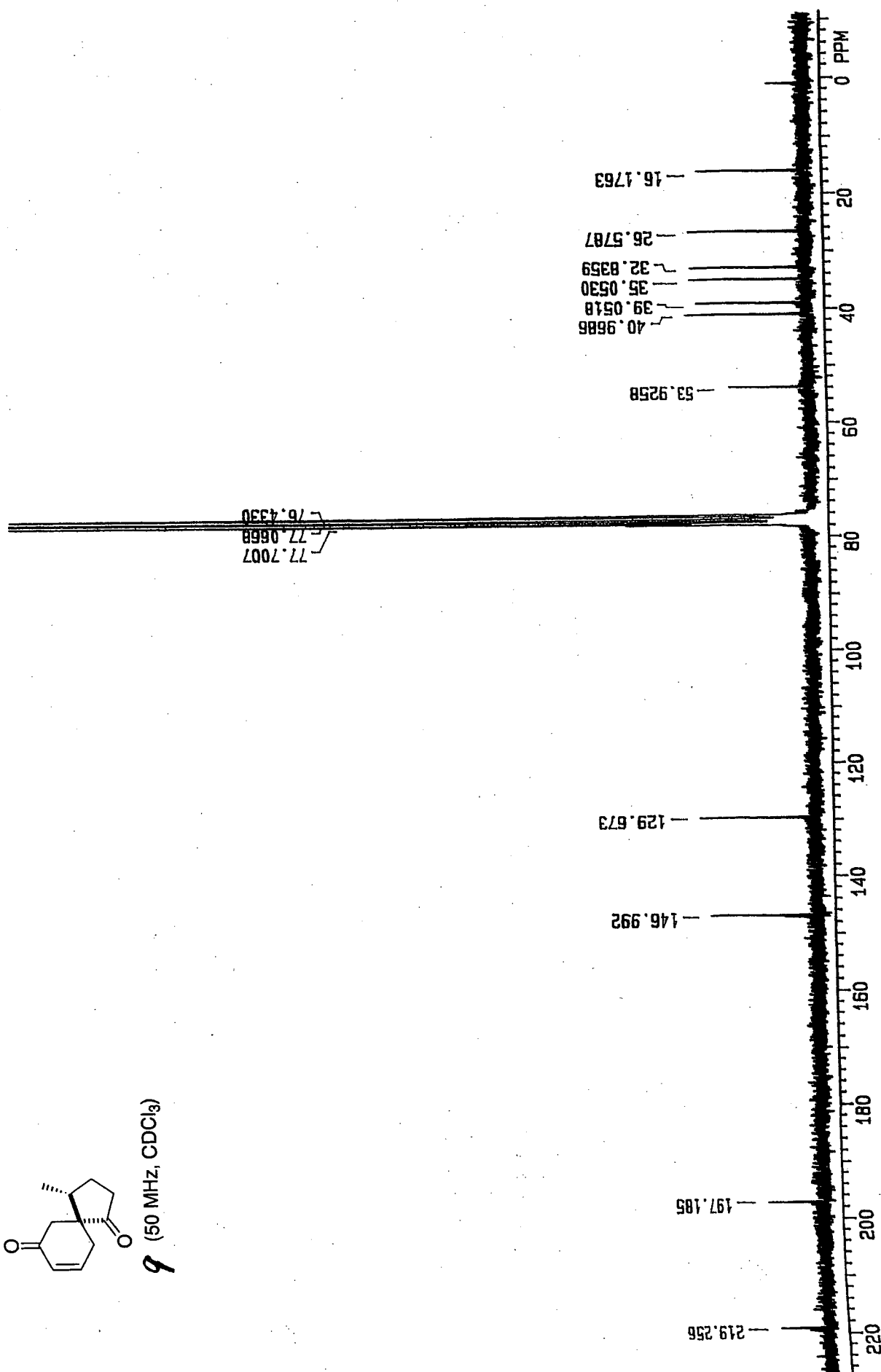
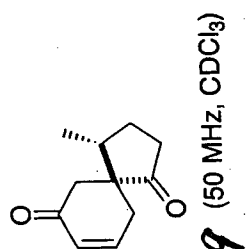


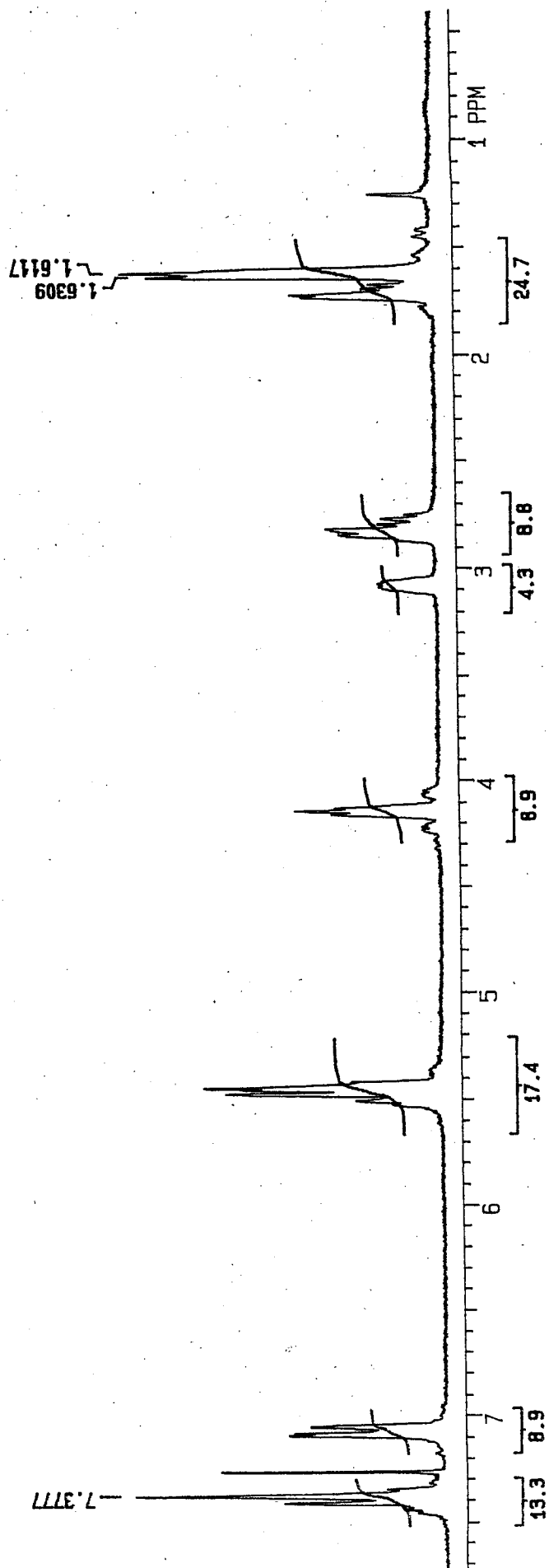
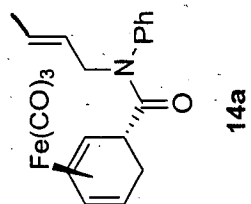


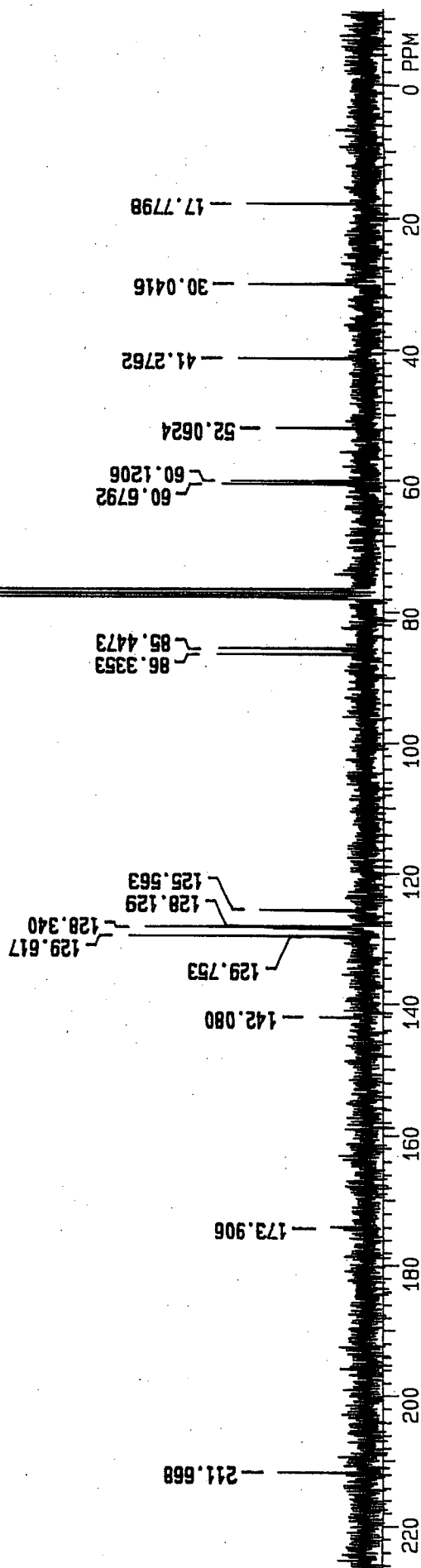
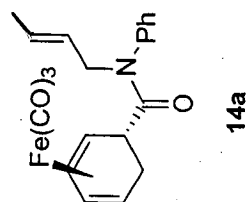


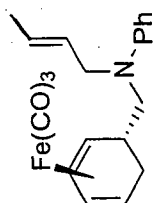
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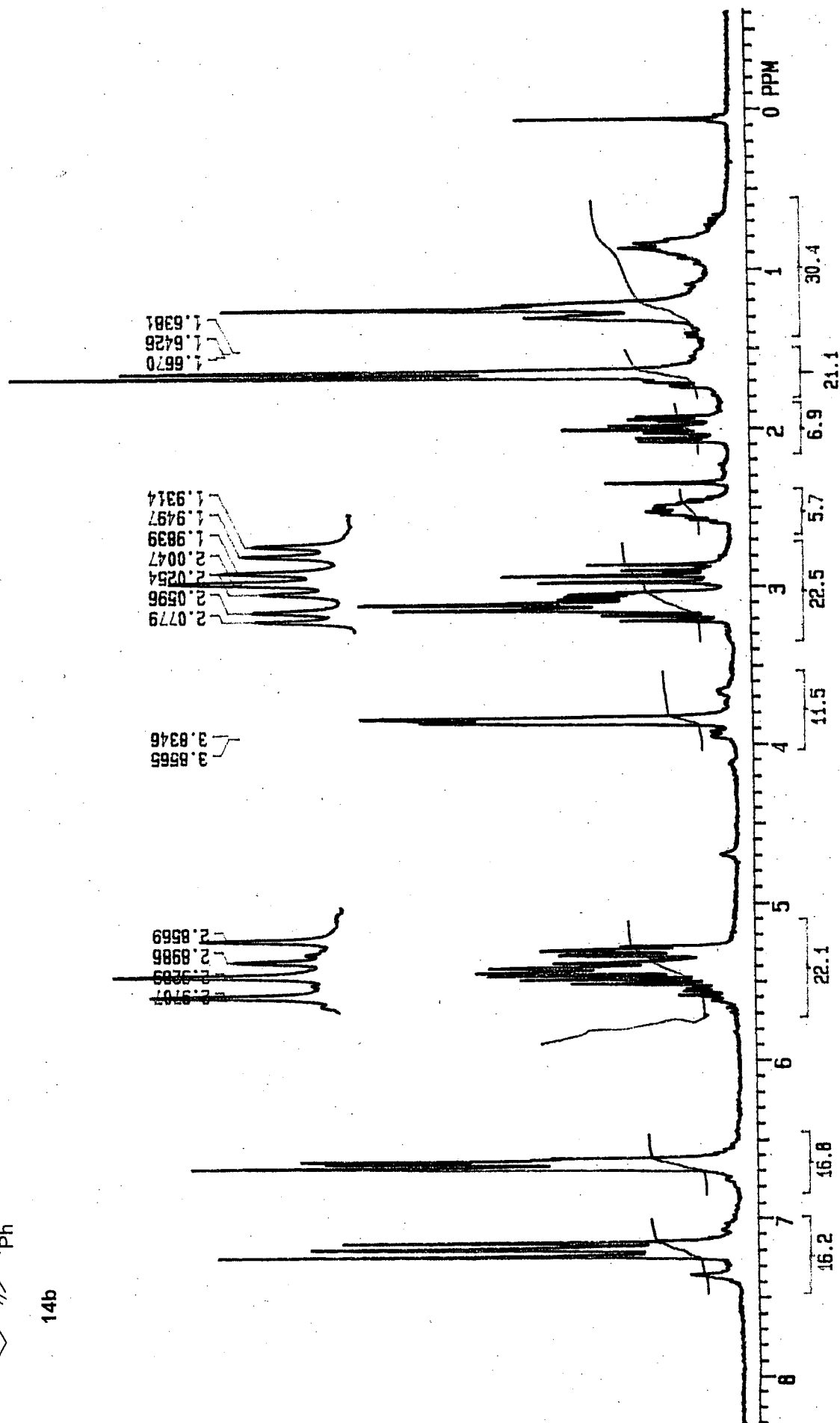


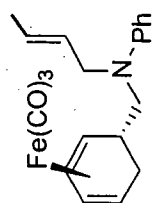




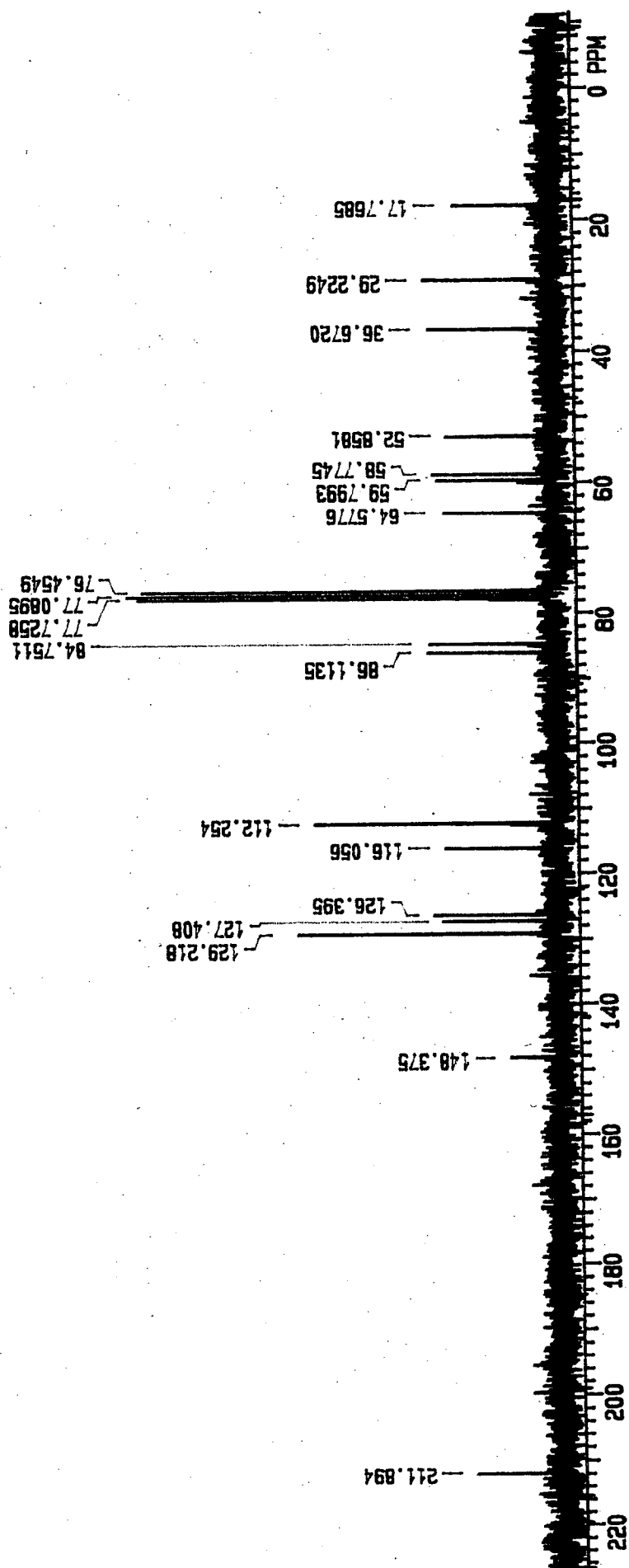


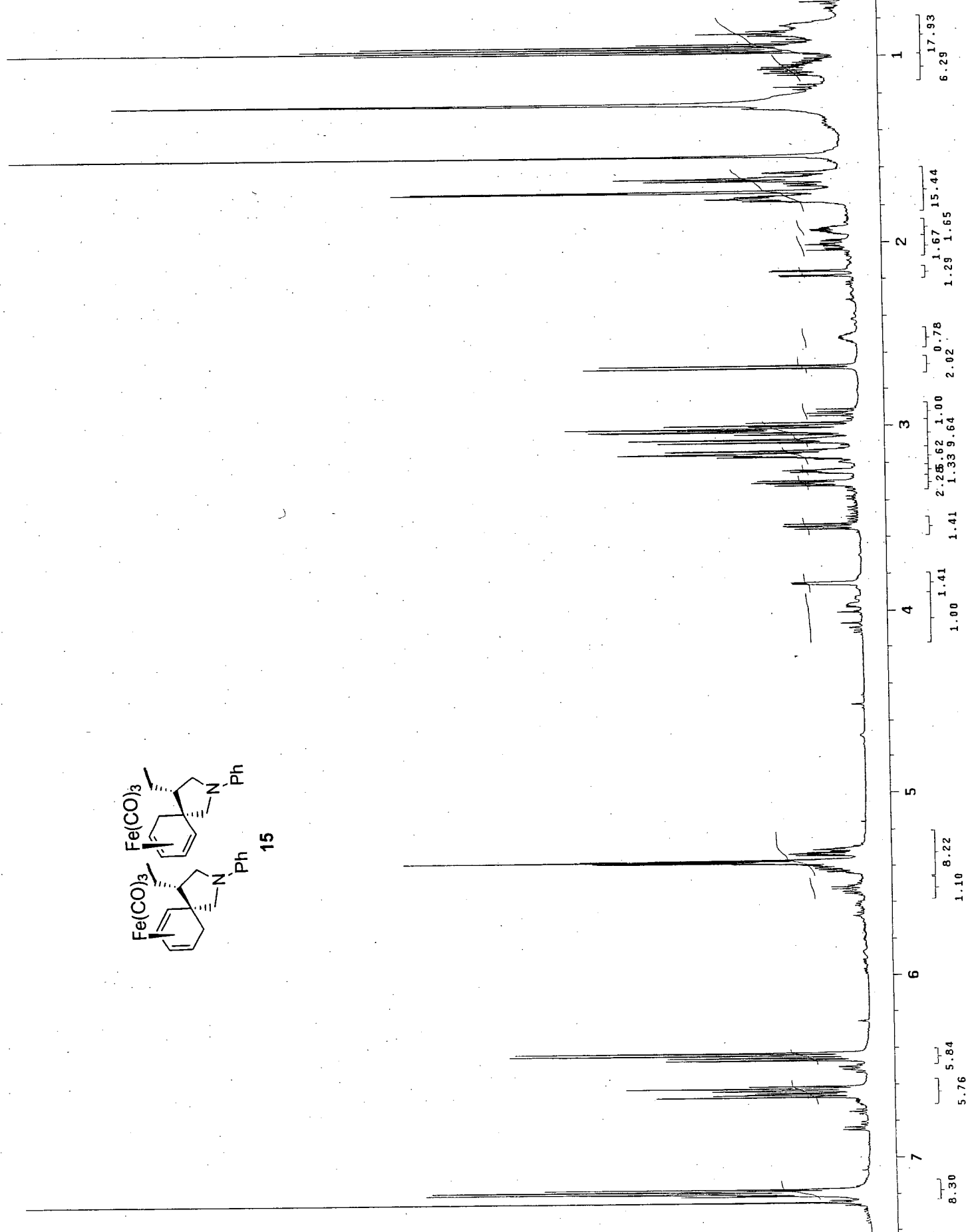
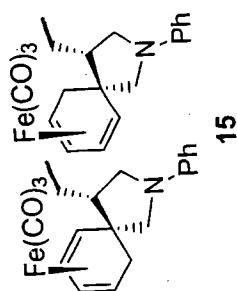
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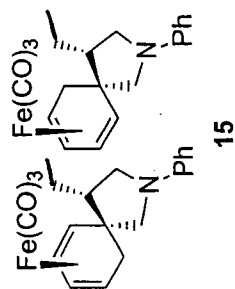


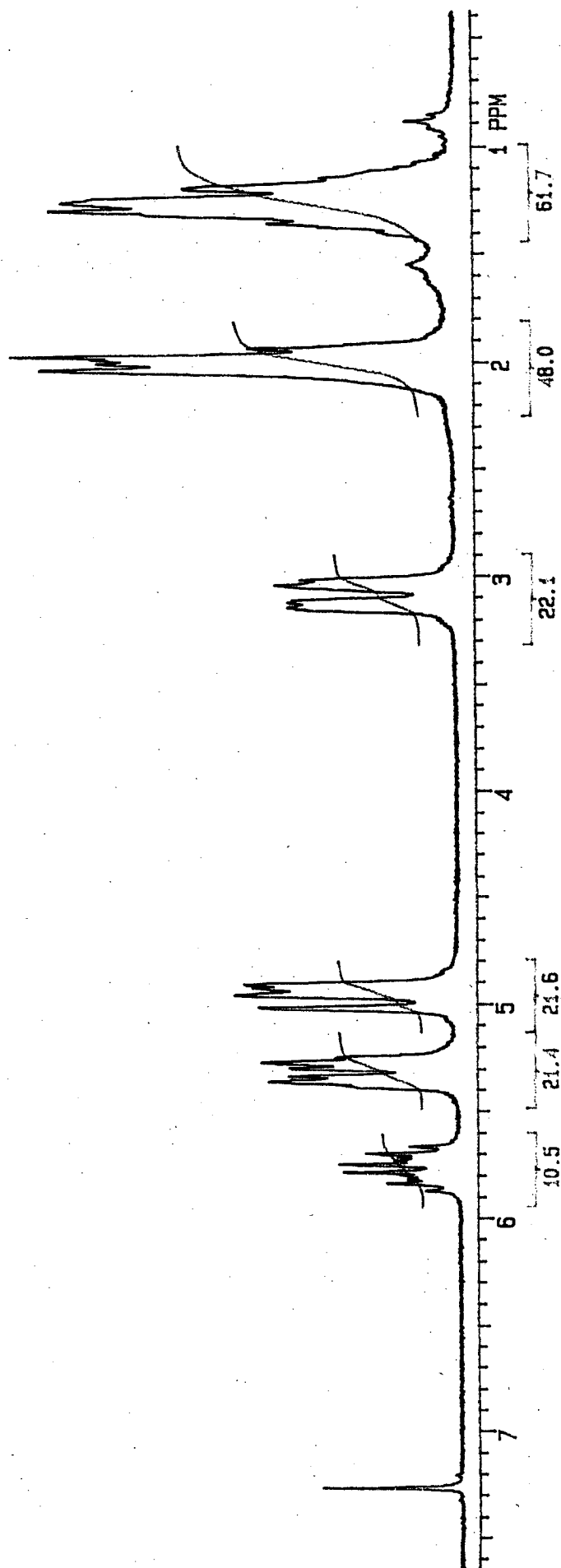
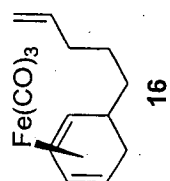


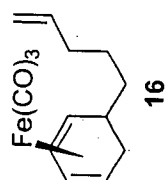
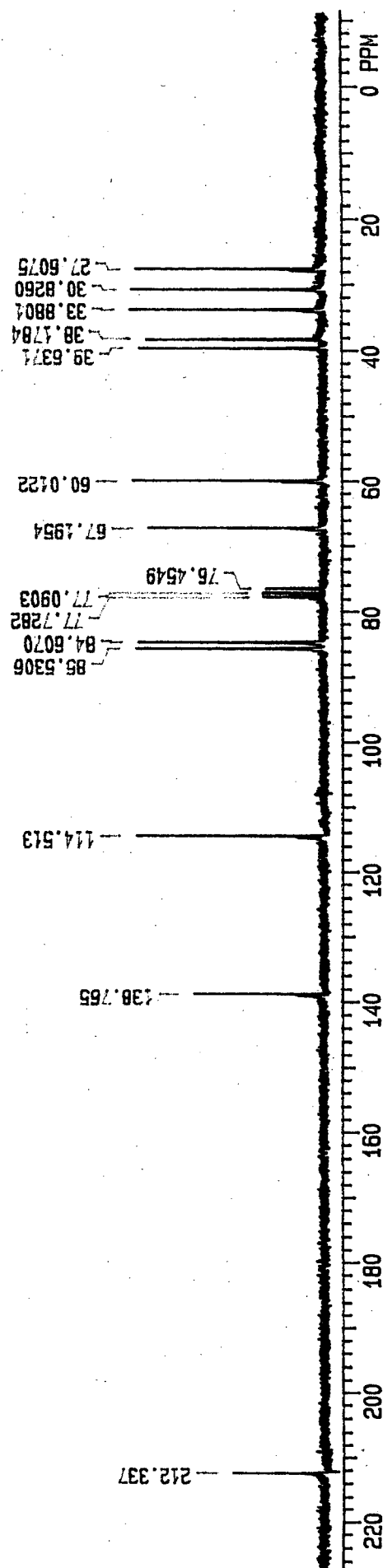
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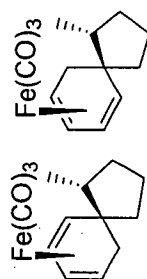




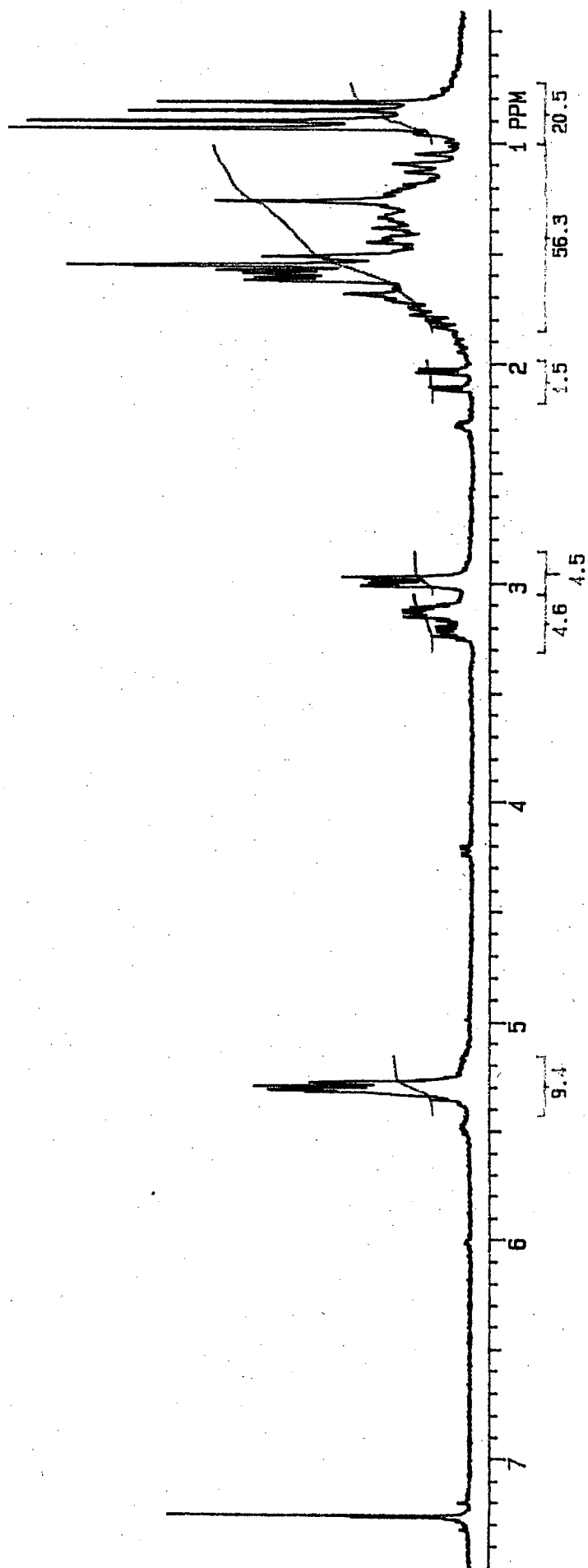


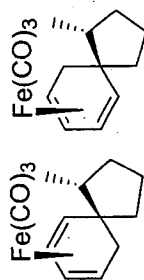
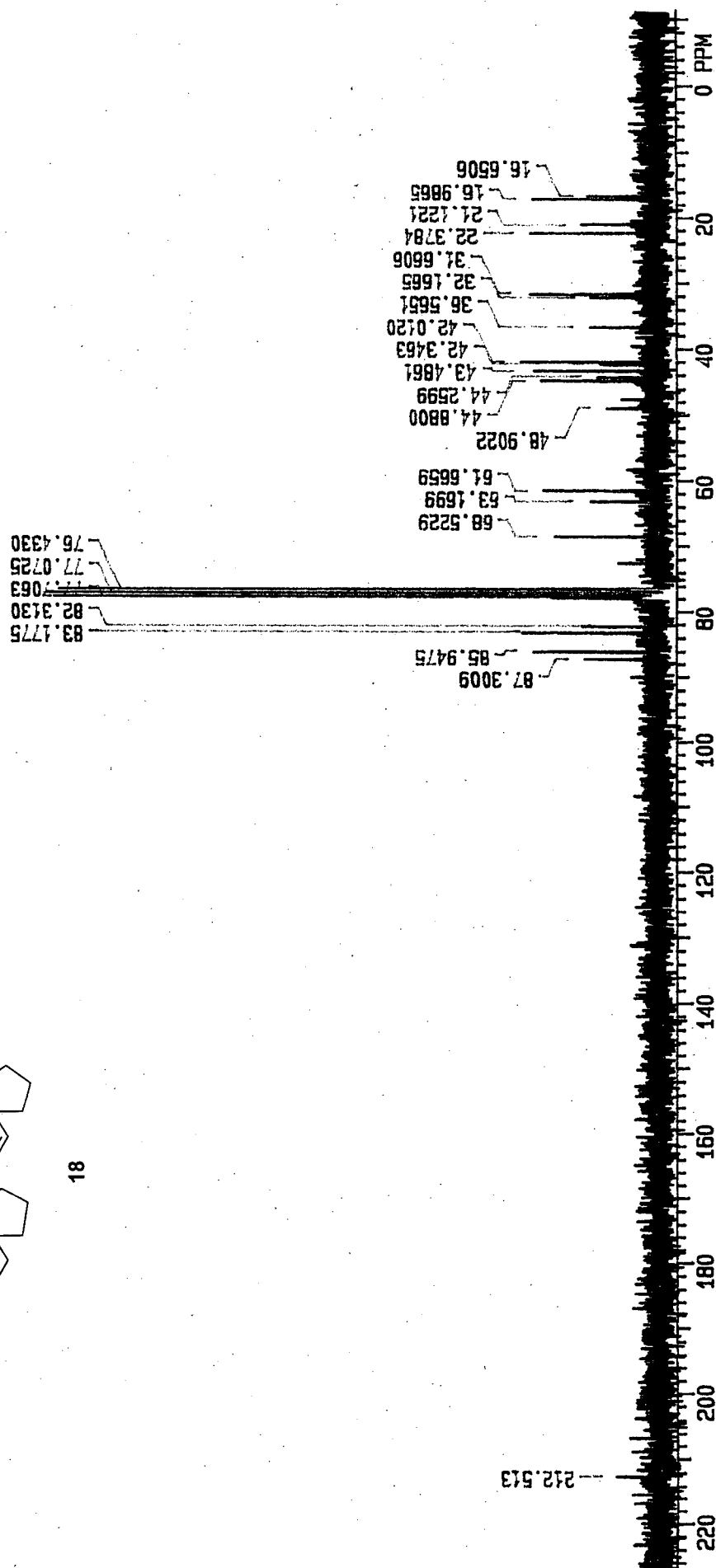




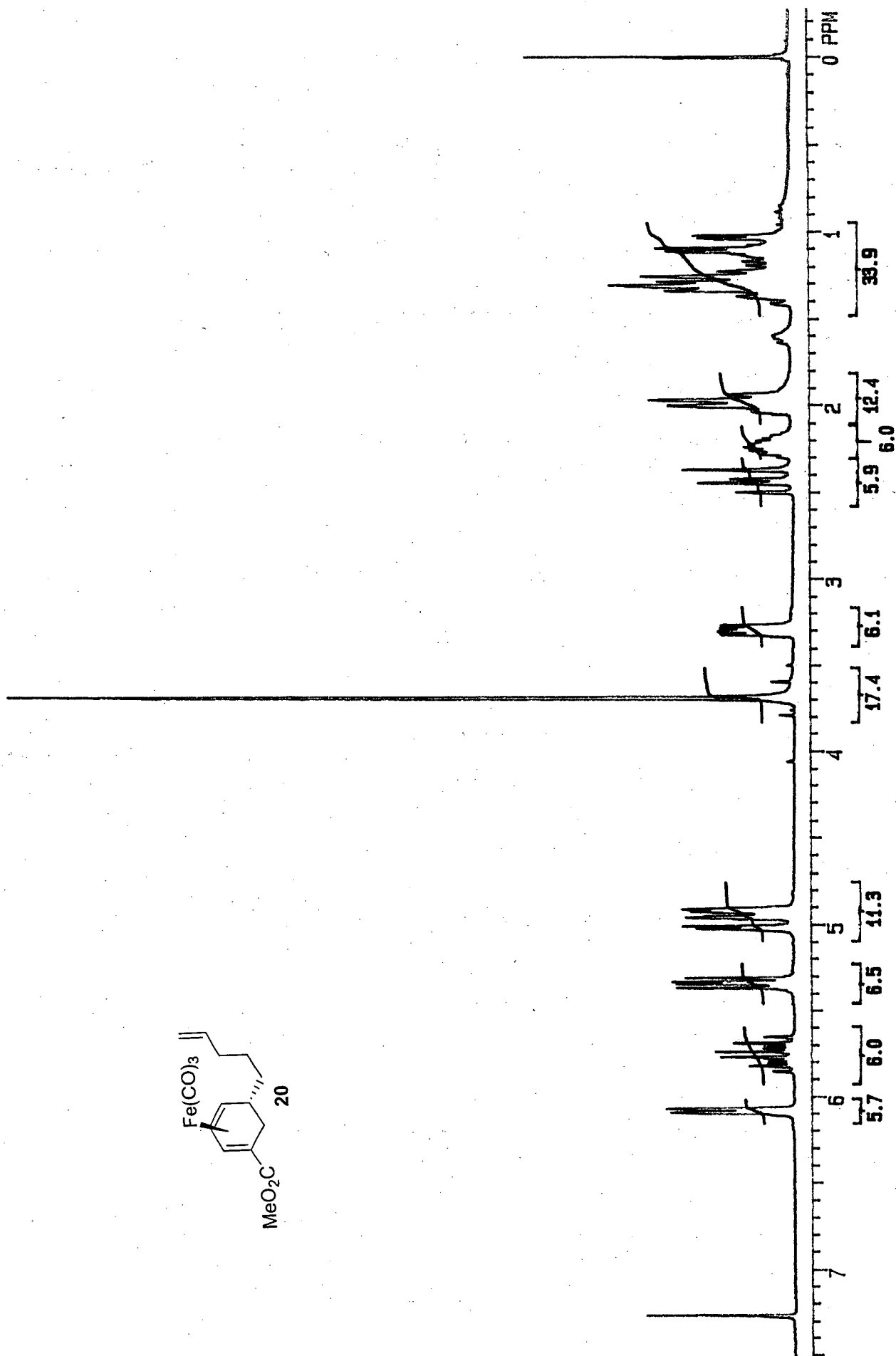
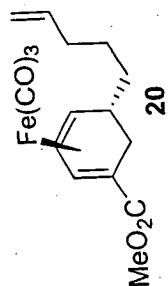


18

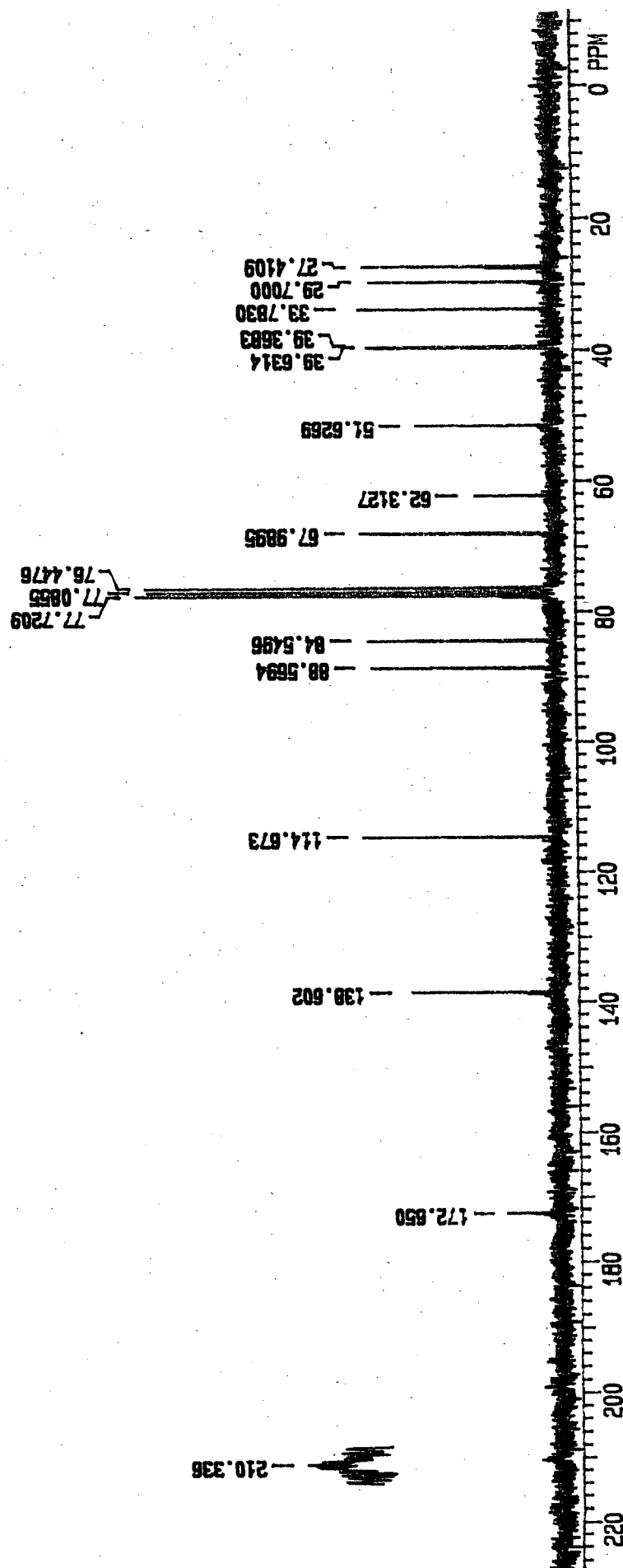
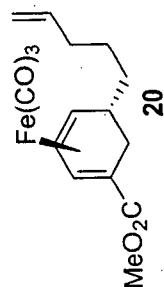




18



S39



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 INOVA-600 "larry"

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 Pulse 45.0 degrees
 Acq. time 3.494 sec
 Width 6000.6 Hz
 32 repetitions

OBSERVE H1, 599.9093321 MHz
 DATA PROCESSING
 FT size 65536
 Total time 2 min, 24 sec

