Cover page for Supplementary Information

Manuscript Title:

Lewis acid-promoted reactions of zirconacyclopentadienes with isocyanates. One-pot three-component synthesis of multiply substituted iminocyclopentadienes from one isocyanate and two Alkynes

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Contents:

1) Experimental Details and Characterization Data;

2) Copies of ^{1}H NMR and ^{13}C NMR spectra for all new compounds;

1) Experimental Section

General: Unless otherwise noted, all starting materials were commercially available and were used without further purification. All reactions involving organometallic compounds were run under a slightly positive pressure of dry N_2 with use of standard Schlenk techniques. Zirconocene dichloride was obtained from Nichia. Boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$) and *n*BuLi was purchased from Acros, PhMgBr and $EtAlCl_2$ purchased from Kanto Chemicals. Toluene was refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere.

^1H and ^{13}C NMR spectra were recorded on a JEOL-300MHz spectrometer. IR spectra were recorded as neat liquids. GLC analysis was performed on a gas chromatograph (Shimadzu 14B) equipped with a flame ionization detector and a capillary column (CBP1-M25-25). GLC yields were determined using suitable hydrocarbons as internal standards.

General procedure for the preparation of multiply substituted iminocyclopentadiene derivatives (2a-2f). An alkyne (4.0 mmol) was added into a toluene solution of [Cp_2ZrBu_2] (Negishi reagent), prepared in situ from [Cp_2ZrCl_2] (2.0 mmol, 0.58 g) and *n*BuLi (4.0 mmol, 2.6 mL, 1.60M hexane solution) in toluene (20 mL) at -78°C. The reaction mixture was then stirred at room temperature for 1 h to afford zirconacyclopentadiene. Isocyanate (4.0 mmol) was added to this solution at room temperature, then $BF_3 \cdot Et_2O$ (8.0 mmol, 1.0 mL) were added to this solution at -78 °C. After stirring the reaction mixture at 0 °C for 1 h, raise the temperature to 80°C and stir the mixture for another 1h. The above reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with n-hexane. The extract was washed with water and brine and dried over Na_2SO_4. The solvent was then evaporated in vacuo to give red-brown oil, which was purified by column chromatograph to the products.

(3,5-Dichloro-phenyl)-(2,3,4,5-tetrapropyl-cyclopenta-2,4-dienylidene)-amine

(2a). Red liquid in 74% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.52 (b, 3H), 0.91 (b, 2H), 0.99 (t, *J* = 7.2 Hz, 9H), 1.45 (b, 6H), 1.57-1.62 (m, 2H), 2.20 (b, 6H), 6.72-7.30 (m, 3H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.97, 14.37, 14.60, 22.99, 23.93, 25.97, 27.31, 28.26, 116.69, 122.42, 123.77, 131.14, 134.50, 147.91, 153.20, 155.13, 171.86. HRMS calcd for $C_{23}H_{31}NCl_2$ 391.1834, found 391.1831.

(2,4-Dichloro-phenyl)-(2,3,4,5-tetrapropyl-cyclopenta-2,4-dienylidene)-amine (2b). Red liquid in 73% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.47 (b, 3H), 0.98 (b, 11H), 1.47-1.65 (m, 8H), 2.20-2.23 (m, 6H), 6.74-7.36 (m, 3H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.09, 14.34, 14.55, 22.99, 23.39, 23.90, 26.03, 27.33, 28.23, 120.39, 123.69, 124.11, 126.71, 128.23, 128.97, 131.29, 146.96, 147.78, 154.49, 172.94. HRMS calcd for $C_{23}H_{31}NCl_2$ 391.1834, found 391.1835.

(4-Bromo-phenyl)-(2,3,4,5-tetrapropyl-cyclopenta-2,4-dienylidene)-amine (2c). Red liquid in 81% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.45 (t, *J* = 7.2Hz, 3H), 0.89-1.00 (m, 11H), 1.47-1.61 (m, 8H), 2.17-2.26 (m, 6H), 6.68-7.37 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.95, 14.39, 14.60, 23.04, 23.70, 24.07, 26.01, 27.45, 28.21, 115.66, 119.96, 123.81, 131.09, 131.28, 147.29, 150.31, 154.37, 171.17. HRMS calcd for $C_{23}H_{32}NCl$ 401.1718, found 401.1721.

(4-Fluoro-phenyl)-(2,3,4,5-tetrapropyl-cyclopenta-2,4-dienylidene)-amine (2d). Red liquid in 77% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.45 (t, *J* = 7.2 Hz, 3H), 0.85-1.02 (m, 11H), 1.39-1.65 (m, 8H), 2.14-2.29 (m, 6H), 6.74-6.98 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.97, 14.41, 14.60, 23.09, 23.69, 24.13, 26.07, 27.59, 28.20, 28.29, 114.87 (d, *J* = 22.2Hz, 2C), 119.49 (d, *J* = 7.4Hz, 2C), 123.73, 131.45, 147.13, 147.43 (d, *J* = 3.1Hz, 1C), 154.25, 159.41 (d, *J* = 238.6Hz, 1C), 171.53. HRMS calcd for $C_{23}H_{32}NF$ 341.2519, found 341.2517.

(2-Chloro-phenyl)-(2,3,4,5-tetrapropyl-cyclopenta-2,4-dienylidene)-amine (2e). Red liquid in 75% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.41 (b, 3H), 0.97-1.00

(m, 11H), 1.45-1.64 (m, 8H), 2.17-2.29 (m, 6H), 6.80-7.35 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.05, 14.37, 14.56, 23.04, 23.46, 23.95, 26.07, 27.35, 28.20, 119.63, 122.87, 123.81, 124.31, 126.54, 129.30, 131.29, 147.44, 148.23, 153.97, 172.19. HRMS calcd for $C_{23}H_{32}NCl$ 357.2223, found 357.2224.

(2-Chloro-phenyl)-(2,3,4,5-tetraphenyl-cyclopenta-2,4-dienylidene)-amine (2f). Dark solid in 91% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 6.47-7.38 (m, 24H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 120.49, 123.04, 124.28, 125.85, 126.15, 127.02, 127.26, 127.51, 128.59, 129.76, 130.08, 131.29, 132.47, 132.77, 133.42, 133.62, 134.00, 147.19, 148.46, 153.87, 169.56. HRMS calcd for $C_{35}H_{24}NCl$ 493.1597, found 493.1592.

General procedure for the preparation of multiply substituted indenyl imines derivatives (2g-2i). A monoyne (2.0 mmol) was added to a solution of [Cp_2ZrPh_2] in toluene, prepared in situ from [Cp_2ZrCl_2] (2.0 mmol, 0.58 g) and PhLi (2.0 mmol, 1.0 mL, 2.0M dibutyl ether) in toluene (20 mL) at -78°C. The reaction mixture was then stirred at 100 °C for 9 h to afford zirconaindene. The solution was cooled to room temperature and isocyanate (4.0 mmol) was added. Then $BF_3{\cdot}Et_2O$ (8.0 mmol, 1.0 mL) were added to this solution at -78°C. After stirring the reaction mixture at 0°C for 1 h, raise the temperature to 80°C and stir the mixture for another 1h. The above reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with n-hexane. The extract was washed with water and brine and dried over Na_2SO_4. The solvent was then evaporated in vacuo to give red-brown oil, which was purified by column chromatograph to the products.

(2-Chloro-phenyl)-(2,3-dibutyl-inden-1-ylidene)-amine (2g). Orange liquid in 59% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.94 (t, J = 7.2Hz, 3H), 0.98 (t, J = 7.2Hz, 3H), 1.39-1.67 (m, 8H), 2.50-2.58 (m, 4H), 6.28-7.44 (m, 8H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.01, 14.13, 22.91, 23.13, 23.77, 25.72, 30.45, 32.29, 118.75, 119.61, 123.06, 124.35, 124.52, 126.20, 127.31, 129.12, 129.87, 130.96, 137.55, 146.08, 148.90, 149.50, 168.29. HRMS calcd for $C_{23}H_{26}NCl_2$ 351.1754, found 351.1756

(4-Methoxyl-phenyl)-(2,3-dibutyl-inden-1-ylidene)-amine (2h). Red liquid in 55% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.94 (t, *J* = 7.2Hz, 3H), 0.98 (t, *J* = 7.2Hz, 3H), 1.37-1.62 (m, 8H), 2.47-2.57 (m, 4H), 3.83 (s, 3H), 6.41-7.18 (m, 8H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.01, 14.11, 22.98, 23.12, 23.82, 25.66, 30.52, 32.51, 55.48, 114.29, 118.52, 119.59, 124.95, 125.83, 128.68, 130.42, 137.93, 145.42, 146.31, 148.35, 156.39, 167.26. HRMS calcd for $C_{24}H_{29}NO$ 347.2249, found 347.2254.

(4-Methyl-phenyl)-(2,3-dibutyl-inden-1-ylidene)-amine (2i). Red liquid in 51% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.94 (t, *J* = 7.2Hz, 3H), 0.97 (t, *J* = 7.2Hz, 3H), 1.37-1.62 (m, 8H), 2.38 (s, 3H), 2.47-2.57 (m, 4H), 6.35-7.16 (m, 8H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.01, 14.11, 20.98, 22.97, 23.12, 23.79, 25.66, 30.52, 32.50, 118.17, 118.52, 125.07, 125.78, 128.78, 129.56, 130.41, 133.01, 137.87, 146.31, 148.35, 149.58, 166.80. HRMS calcd for $C_{24}H_{29}N$ 331.2300, found 331.2302.

General procedure for the preparation of multiply substituted Hexa-2,4-dienedioic acid bisamide derivatives (3a-3e) and multiply substituted Penta-2,4-dienoic acid amide derivatives (4a-4d). A monoyne (4.0 mmol) was added into a toluene solution of [Cp_2ZrBu_2] (Negishi reagent), prepared in situ from [Cp_2ZrCl_2] (2.0 mmol, 0.58 g) and *n*BuLi (4.0 mmol, 2.6 mL, 1.60M hexane solution) in toluene (20 mL) at -78°C. The reaction mixture was then stirred at room temperature for 1 h to afford zirconacyclopentadiene. Isocyanate (4.0 mmol) and $EtAlCl_2$ (8.0 mmol, 8.8 mL, 0.9M hexane solution) were added to this solution at -78°C. After stirring the reaction mixture at -30°C for 1 h, the above reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with Et_2O. The extract was washed with water and brine and dried over Na_2SO_4. The solvent was then evaporated in vacuo to give yellow oil, which was purified by column chromatograph to the products.

(2Z,4Z)-N1,N6-bis(2,4-dichlorophenyl)-2,3,4,5-tetrapropyl hexa-2,4-dienediamide (3a). White solid in 89% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.89 (t, *J* = 7.5Hz, 6H), 0.92 (t, *J* = 7.5Hz, 6H), 1.34-1.51 (m, 8H), 2.14-2.20 (m, 4H), 2.34 (t, *J* = 7.8Hz, 4H), 7.21-8.24 (m, 6H), 8.88 (s, 2H), . ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.06, 14.75, 21.59, 22.03, 32.46, 36.96, 123.39, 124.35, 127.66, 128.88, 129.24, 133.28, 133.67, 144.37, 169.75. HRMS calcd for $C_{30}H_{36}N_2O_2Cl_4$ 596.1531, found 596.1518.

(2Z,4Z)-N1,N6-bis(2-chlorophenyl)-2,3,4,5-tetrapropyl hexa-2,4-dienediamide (3b). White solid in 80% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.89 (t, *J* = 7.2Hz, 6H), 0.92 (t, *J* = 7.2Hz, 6H), 1.33-1.57 (m, 8H), 2.15-2.22 (m, 4H), 2.35 (t, *J* = 7.8Hz, 4H), 6.99-8.27 (m, 8H), 8.88 (s, 2H), . ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.07, 14.77, 21.61, 22.01, 32.50, 37.01, 122.74, 123.82, 124.74, 127.45, 129.17, 133.40, 134.91, 144.12, 169.75. HRMS calcd for $C_{30}H_{38}N_2O_2Cl_2$ 528.2310, found 528.2310.

(2Z,4Z)-N1,N6-bis(4-chlorophenyl)-2,3,4,5-tetrapropyl hexa-2,4-dienediamide (3c). White solid in 23% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.86 (t, *J* = 7.2Hz, 12H), 1.24-1.49 (m, 8H), 2.08-2.13 (m, 4H), 2.30 (t, *J* = 7.8Hz, 4H), 7.25-7.57 (m, 8H), 9.17 (s, 2H), . ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.09, 14.69, 21.62, 22.11, 32.57, 36.96, 121.09, 128.94, 129.12, 134.22, 136.80, 142.55, 170.49. HRMS calcd for $C_{30}H_{38}N_2O_2Cl_2$ 528.2310, found 528.2303.

(2Z,4Z)-N1,N6-bis(4-fulorophenyl)-2,3,4,5-tetrapropyl hexa-2,4-dienediamide (3d). White solid in 26% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.85 (t, *J* = 7.2Hz, 6H), 0.87 (t, *J* = 7.2Hz, 6H), 1.22-1.50 (m, 8H), 2.10-2.20 (m, 4H), 2.26-2.34 (m, 4H), 6.96-7.59 (m, 8H), 9.30 (s, 2H), . ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.09, 14.70, 21.64, 22.10, 32.57, 36.96, 115.50 (d, *J* = 22.3Hz, 2C), 121.59 (d, *J* = 8.1Hz, 2C), 134.23, 134.33 (d, *J* = 3.1Hz, 1C), 142.33, 159.29 (d, *J* = 241.1Hz, 1C), 170.41. HRMS calcd for $C_{30}H_{38}N_2O_2F_2$ 496.2901, found 496.2902.

(2Z,4Z)-N1,N6-bis(4-methylphenyl)-2,3,4,5-tetrapropyl hexa-2,4-dienediamide (3e). White solid in 34% isolated yield. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.86 (t, *J* = 7.2Hz, 6H), 0.87 (t, *J* = 7.2Hz, 6H), 1.30-1.50 (m, 8H), 2.09-2.15 (m, 4H), 2.25-2.33 (m, 10H), 7.09-7.51 (m, 8H), 9.06 (s, 2H). ^{13}C NMR (CDCl$_3$, Me$_4$Si): δ 14.14, 14.74, 20.90, 21.63, 22.09, 32.60, 36.96, 119.92, 129.34, 133.57, 134.36, 135.80, 142.09, 170.23. HRMS calcd for $C_{32}H_{44}N_2O_2$ 488.3403, found 488.3407.

2,3,4-Tripropyl-octa-2,4-dienoic acid (4-bromophenyl)-amide (4a). White solid in 54% isolated yield. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.80 (t, *J* = 7.2Hz, 3H), 0.89-0.98 (m, 9H), 1.18-1.50 (m, 8H), 1.91-1.99 (m, 2H), 2.09-2.18 (m, 4H), 2.33-2.38 (m, 2H), 5.45 (t, *J* = 7.2Hz, 1H), 7.21-7.41 (m, 5H). ^{13}C NMR (CDCl$_3$, Me$_4$Si): δ 13.88, 14.10, 14.77, 21.36, 22.26, 22.71, 22.85, 30.18, 32.23, 32.27, 33.09, 116.23, 120.73, 131.08, 131.87, 134.61, 137.41, 139.84, 145.16, 170.18. HRMS calcd for $C_{23}H_{34}NOBr$ 419.1824, found 419.1837.

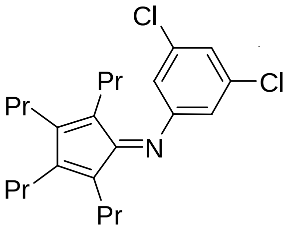
2,3,4-Tripropyl-octa-2,4-dienoic acid (4-chlorophenyl)-amide (4b). White solid in 30% isolated yield. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.80 (t, *J* = 7.5Hz, 3H), 0.90-0.98 (m, 9H), 1.20-1.25 (m, 2H), 1.36-1.48 (m, 6H), 1.94-1.97 (m, 2H), 2.10-2.19 (m, 4H), 2.33-2.39 (m, 2H), 5.46 (t, *J* = 7.2Hz, 1H), 7.22-7.42 (m, 5H). ^{13}C NMR (CDCl$_3$, Me$_4$Si): δ 13.88, 14.11, 14.76, 21.39, 22.26, 22.71, 22.86, 30.20, 32.26, 32.31, 33.08, 120.46, 128.68, 128.92, 131.06, 134.64, 136.97, 139.87, 145.11, 170.20. HRMS calcd for $C_{23}H_{34}NOCl$ 375.2329, found 375.2331.

2,3,4-Tripropyl-octa-2,4-dienoic acid (4-fluorophenyl)-amide (4c). White solid in 40% isolated yield. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.80 (t, *J* = 7.5Hz, 3H), 0.90-0.98 (m, 9H), 1.24-1.49 (m, 8H), 1.95-1.99 (m, 2H), 2.11-2.19 (m, 4H), 2.34-2.39 (m, 2H), 5.46 (t, *J* = 7.2Hz, 1H), 7.20-7.43 (m, 5H). ^{13}C NMR (CDCl$_3$, Me$_4$Si): δ 13.87, 14.11, 14.77, 21.40, 22.26, 22.69, 22.88, 30.21, 32.28, 32.33, 33.08, 115.52 (d, *J* = 22.2Hz, 2C), 121.00 (d, *J* = 7.4Hz, 2C), 130.93, 134.42(d, *J* = 2.5Hz, 1C), 134.70, 139.90, 144.85, 159.15 (d, *J* = 241.1Hz, 1C), 170.13. HRMS calcd for $C_{23}H_{34}NOF$ 359.2624, found 359.2637.

2,3,4-Tripropyl-octa-2,4-dienoic acid (4-methylphenyl)-amide (4d). White solid in 21% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.81 (t, J = 7.5Hz, 3H), 0.89-0.97 (m, 9H), 1.23-1.51 (m, 8H), 1.93-1.98 (m, 2H), 2.00-2.18 (m, 4H), 2.29 (s, 3H), 2.34-2.39 (m, 2H), 5.47 (t, J = 7.2Hz, 1H), 7.07-7.34 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.90, 14.12, 14.76, 20.84, 21.40, 22.24, 22.62, 22.86, 30.21, 32.34, 33.18, 119.41, 129.39, 130.80, 133.36, 134.91, 135.81, 139.93, 144.41, 170.02. HRMS calcd for $C_{24}H_{37}NO$ 355.2875, found 355.2871.

Procedure for the preparation of (2Z,4Z)-N1-(4-bromophenyl)-N6-(2,4-dichlorophenyl)-2,3,4,5-tetrapropylhexa-2,4-dienediamide (3f). 4-Octyne (2.0 mmol) was added into a toluene solution of [Cp_2ZrBu_2] (Negishi reagent), prepared *in situ* from Cp_2ZrCl_2 (1.0 mmol, 0.29 g) and *n*BuLi (2.0 mmol, 1.3 mL, 1.60M hexane solution) in toluene (10 mL) at -78^{o}C. The reaction mixture was then stirred at room temperature for 1h to afford zirconacyclopentadiene. 4-Bromophenyl isocyanate (1.4 mmol) and $EtAlCl_2$ (5.8 mmol, 6.2 mL, 0.9M hexane solution) were added to this solution at -78^{o}C and the reaction mixture was stirred at -35^{o}C for 1h. Then, 2,4-dichlorophenyl isocyanate (1.5 mmol) was added to the above reaction mixture at -35^{o}C. After stirring at room temperature for 12h, the above reaction mixture was quenched with 3N HCl and extracted with EtOAc. The extract was washed with water and brine and dried over $MgSO_4$. The solvent was then evaporated in vacuo to give yellow oil, which was purified by column chromatograph to the products as white solid in 39% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.79-0.92 (m, 12H), 1.22-1.52 (m, 8H), 2.01-2.22 (m, 6H), 2.42-2.48 (m, 2H), 7.26-7.54 (m, 6H), 7.85 (s, 1H), 8.28 (d, J = *8.7Hz*, 1H), 10.36 (s, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.96, 14.23, 14.67, 14.69, 21.26, 21.75, 21.84, 22.57, 32.23, 32.84, 36.91, 37.21, 115.82, 120.83, 122.92, 123.96, 128.08, 128.97, 129.96, 131.65, 131.74, 132.67, 136.12, 138.15, 139.39, 147.15, 169.46, 171.13. HRMS calcd for $C_{30}H_{37}BrCl_2N_2O_2$ 606.1416, found 606.1421.

Procedure for the preparation of (2Z,4E)-4-deutero-(4-bromophenyl)-2,3,4-triethylhepta-2,4-dienamide (4D). 3-Hexyne (4.0 mmol) was added into a toluene solution of [Cp_2ZrBu_2] (Negishi reagent), prepared *in situ* from Cp_2ZrCl_2 (2.0 mmol, 0.58 g) and *n*BuLi (4.0 mmol, 2.6 mL, 1.60M hexane solution) in toluene (20 mL) at -78°C. The reaction mixture was then stirred at room temperature for 1h to afford zirconacyclopentadiene. 4-Bromophenyl isocyanate (4.0 mmol) and $EtAlCl_2$ (8.0 mmol, 8.8 mL, 0.9M hexane solution) were added to this solution at -78°C. After stirring the reaction mixture at -30°C for 1h, the above reaction mixture was quenched with DCl (0.3ml, 20%) and extracted with Et_2O. The extract was washed with water and brine and dried over $MgSO_4$. The solvent was then evaporated in vacuo to give yellow oil, which was purified by column chromatograph to the products as yellow oil in 47% isolated yield, D > 90%. ^1H NMR ($CDCl_3$, Me_4Si): δ 0.84 (t, *J* = 7.5Hz, 3H), 0.96-1.10 (m, 9H), 1.97-2.06 (m, 2H), 2.15-2.26 (m, 4H), 2.41 (q, *J* = 7.5Hz, 2H), 7.26-7.41 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 12.77, 13.68, 13.80, 14.30, 21.17, 22.71, 23.27, 24.35, 116.29, 120.68, 131.92, 132.33, 135.52, 137.41, 140.22, 145.90, 169.93. HRMS calcd for $C_{19}H_{25}NOBrD$ 364.1261, found 364.1252.



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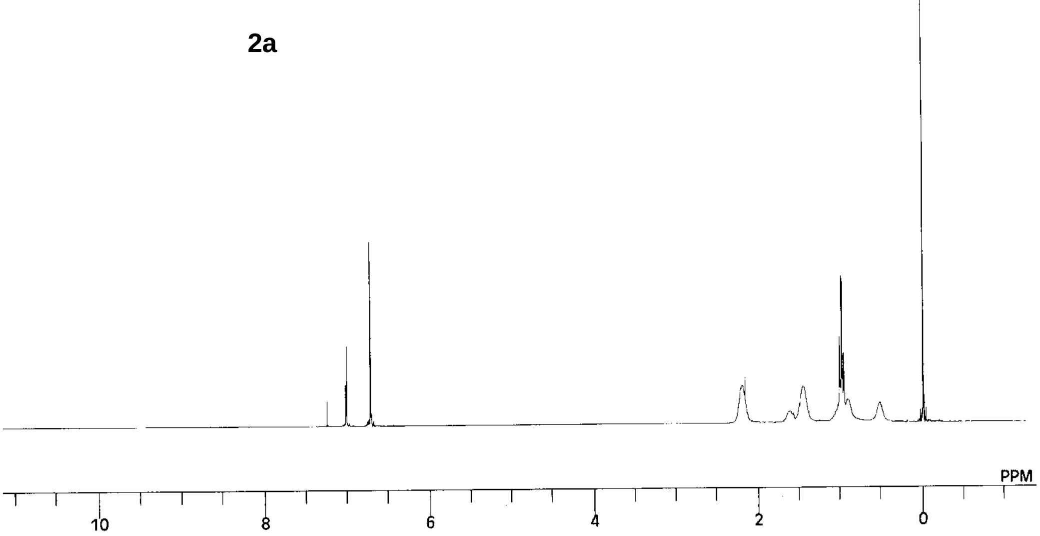

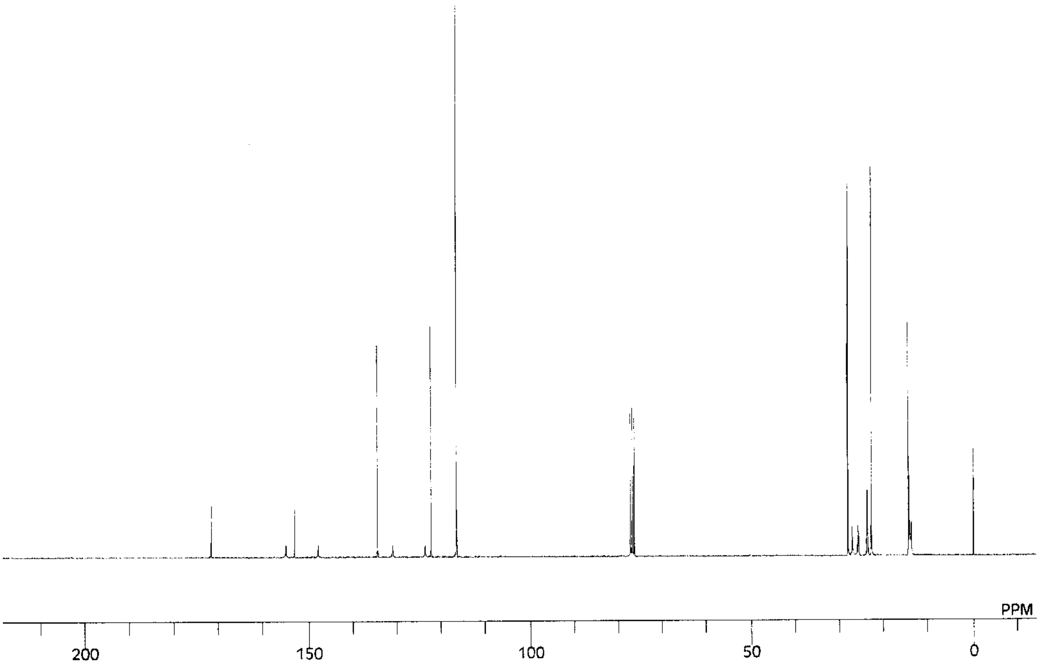

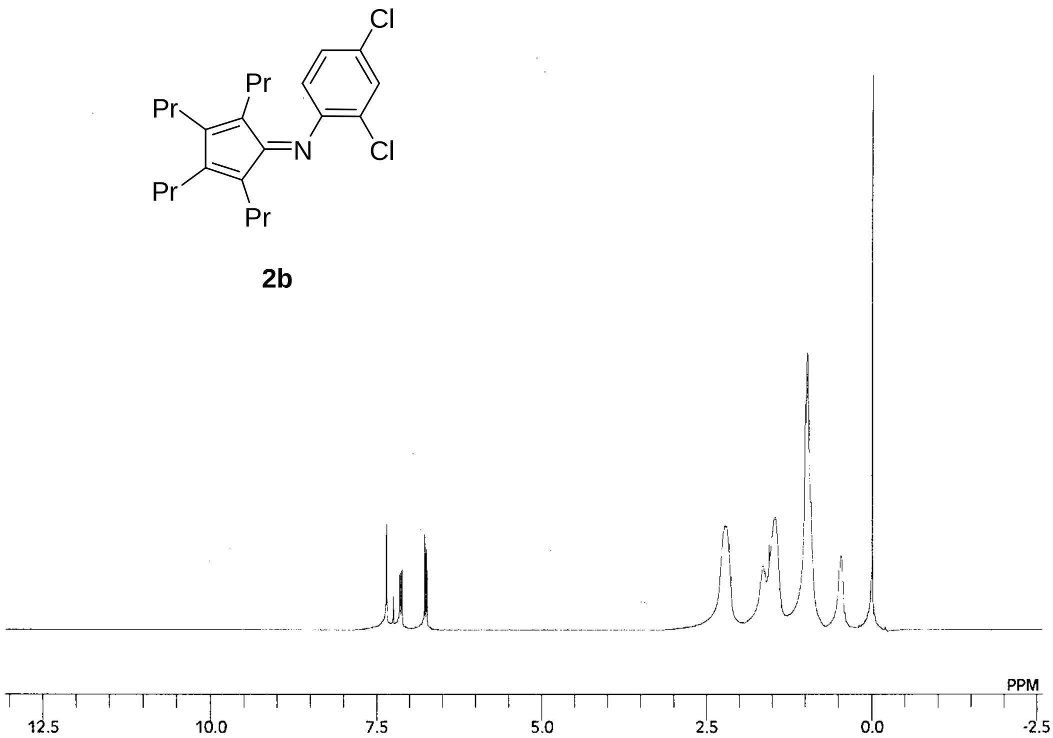

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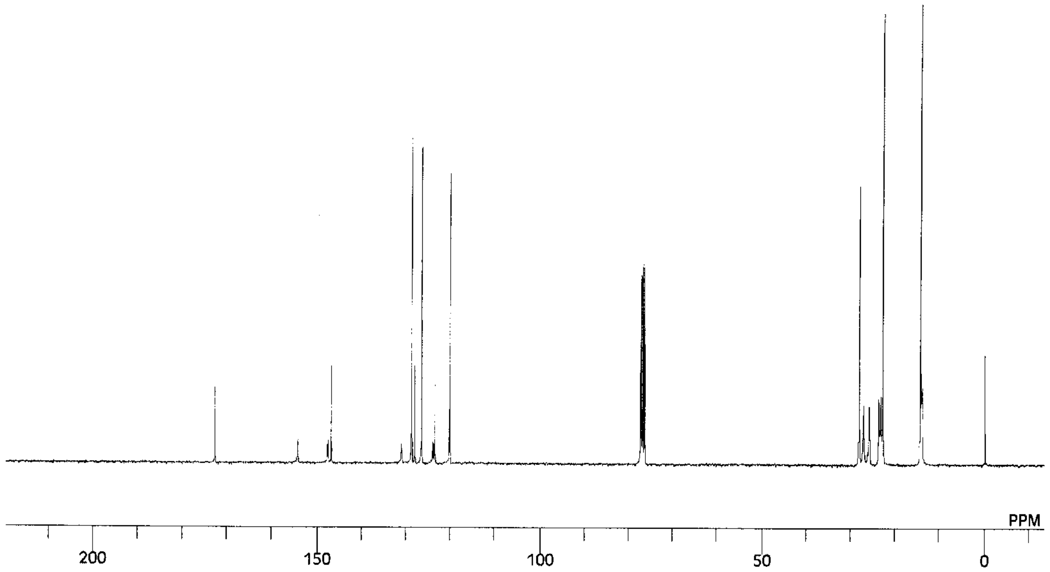

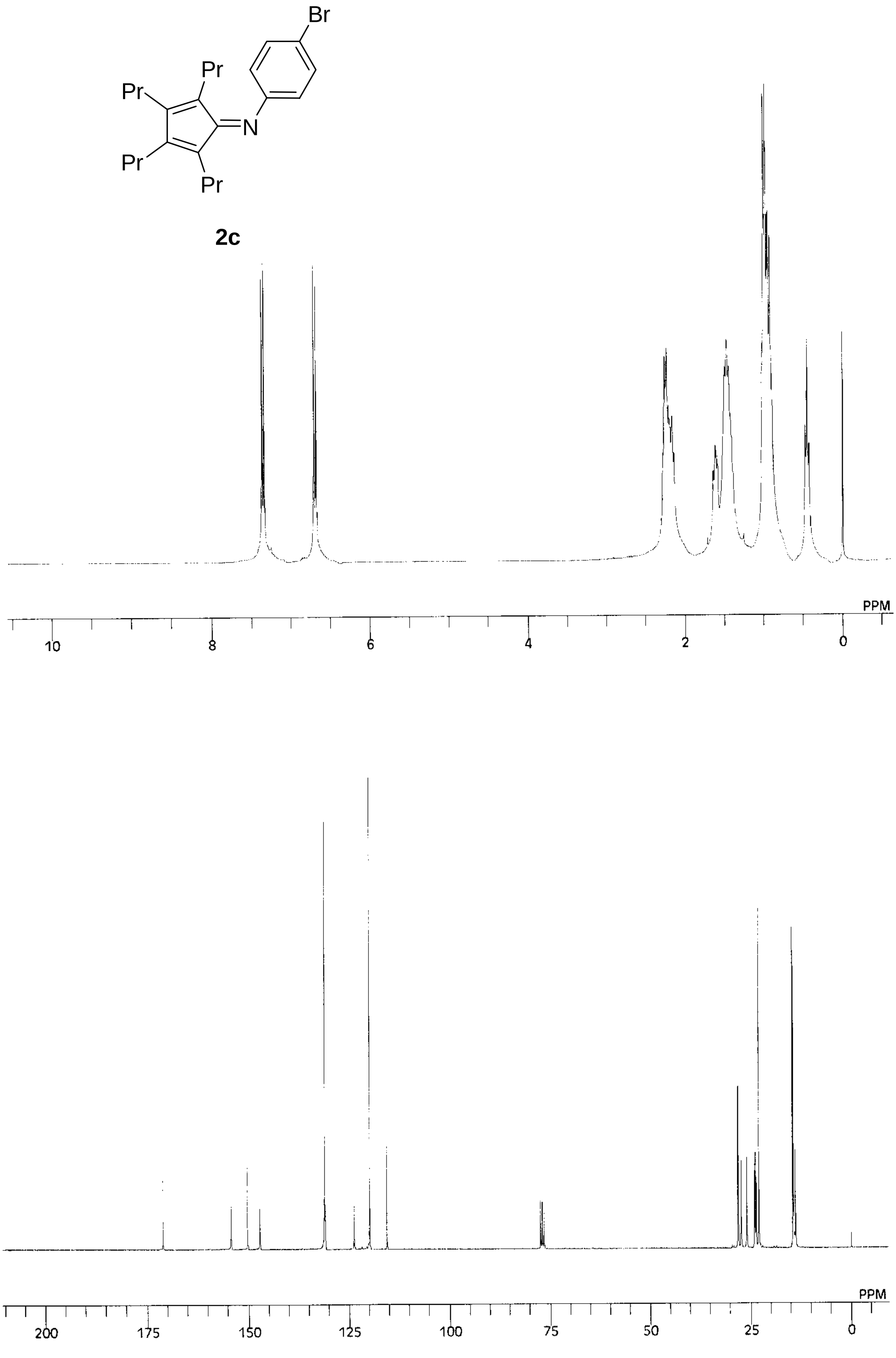

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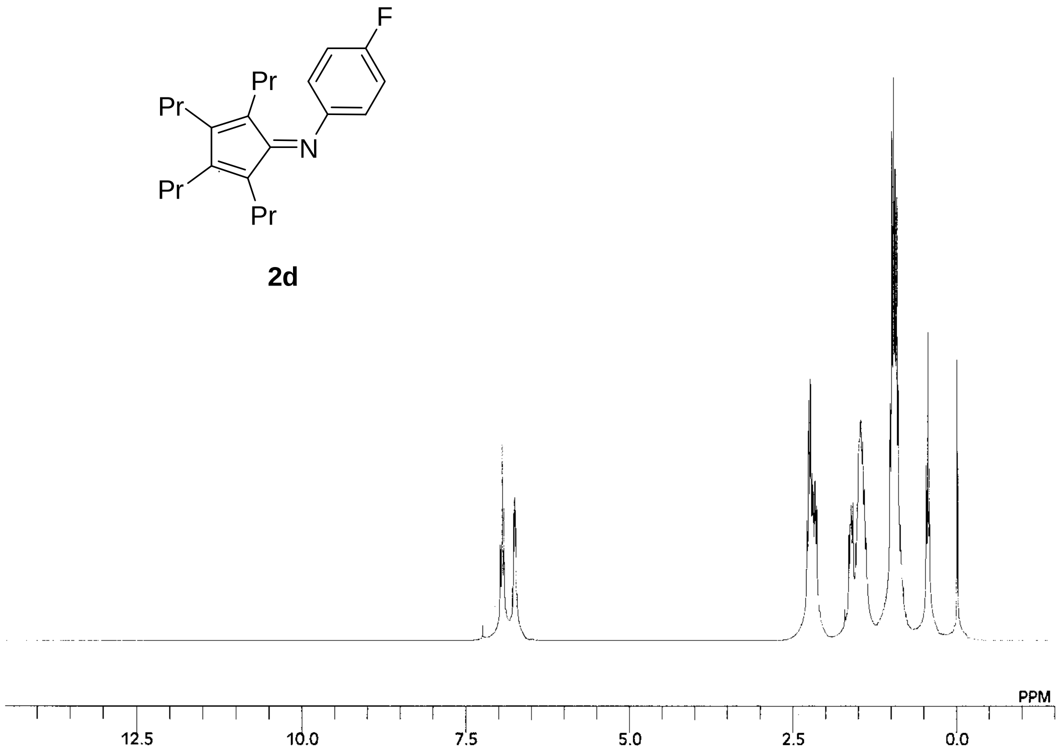
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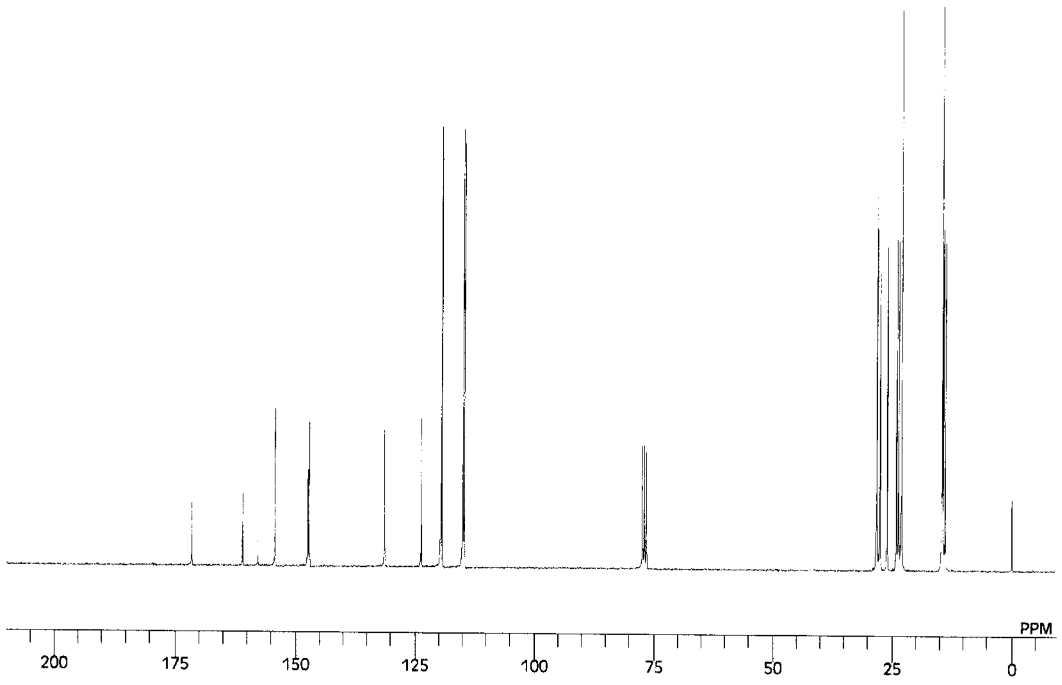
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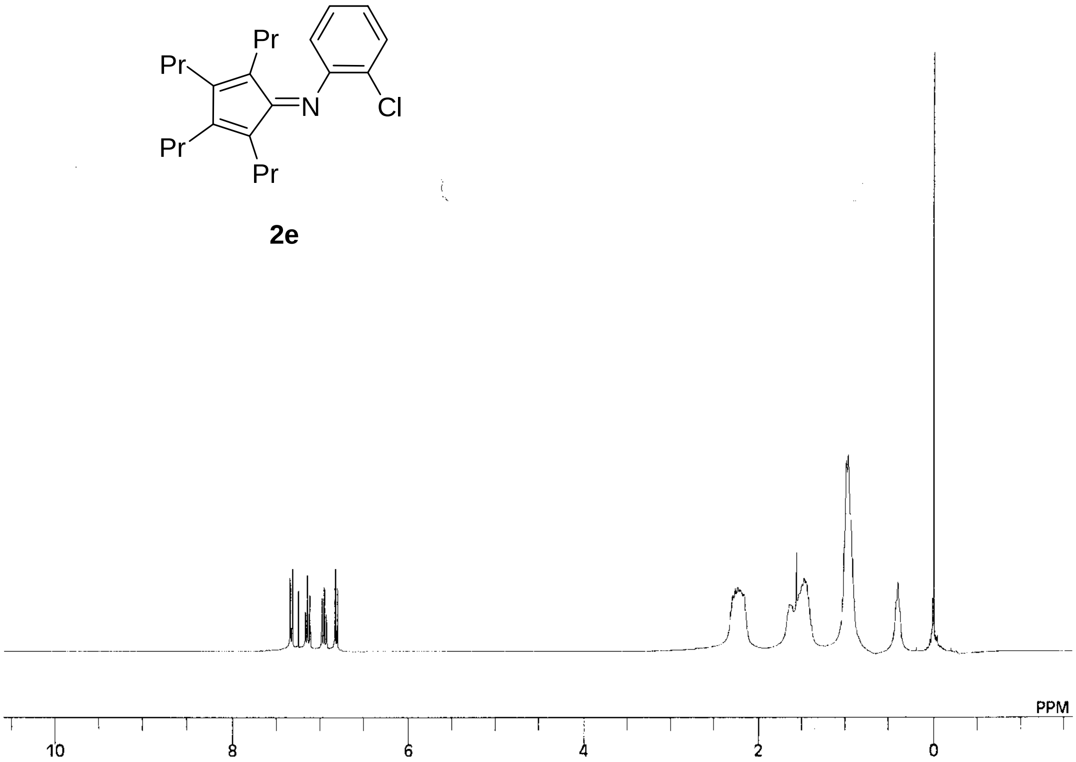

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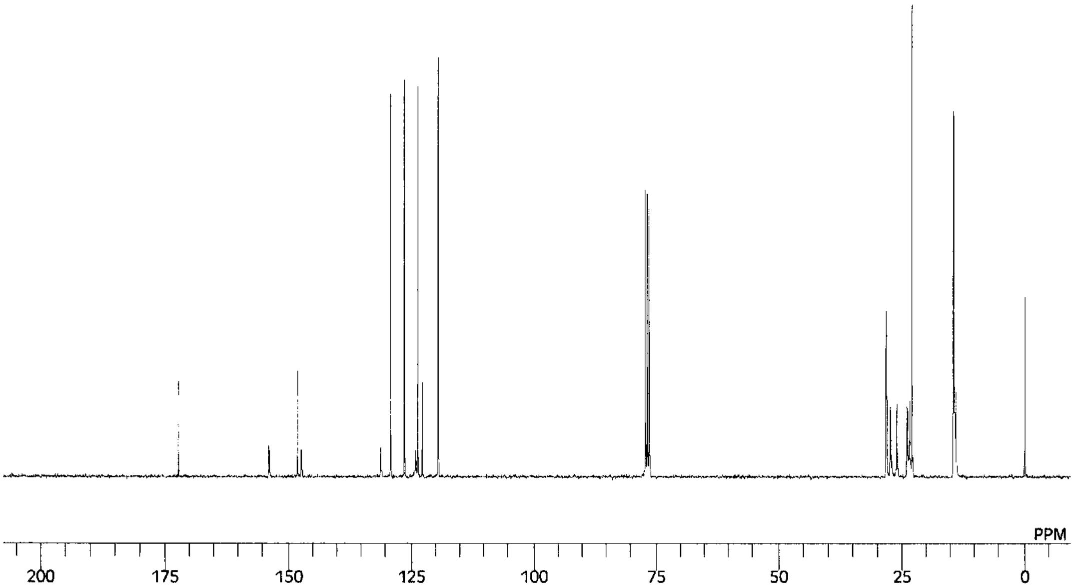

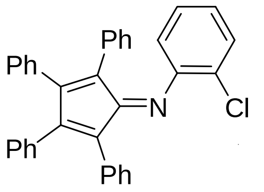

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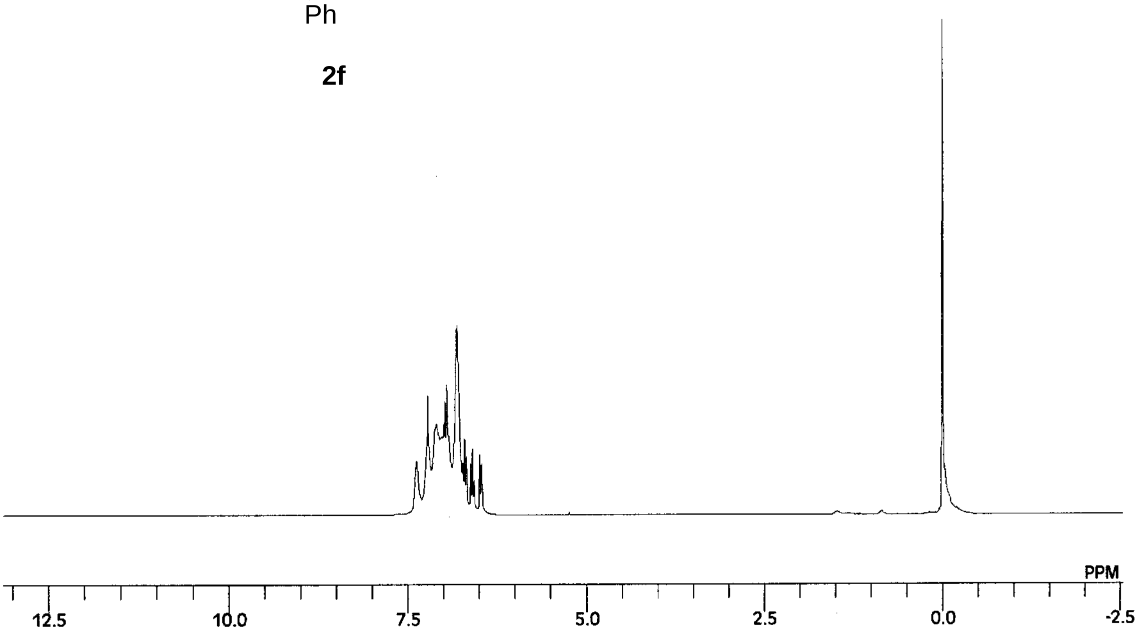

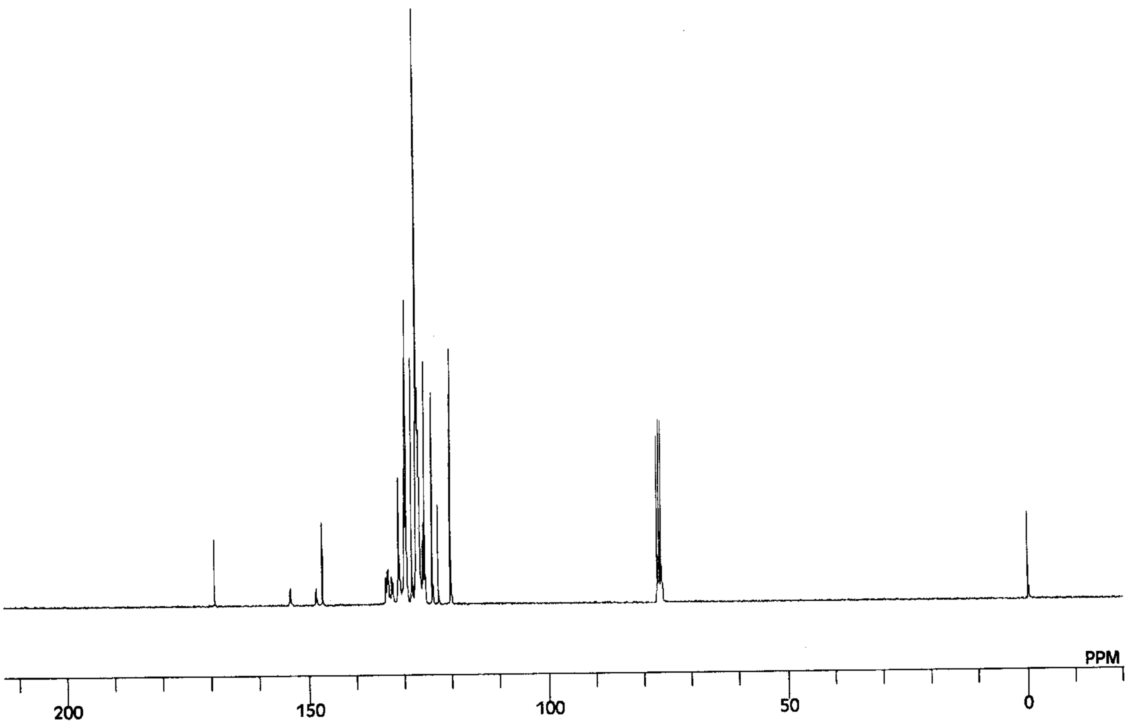

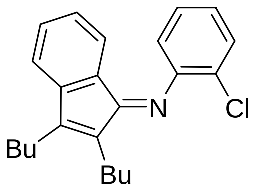

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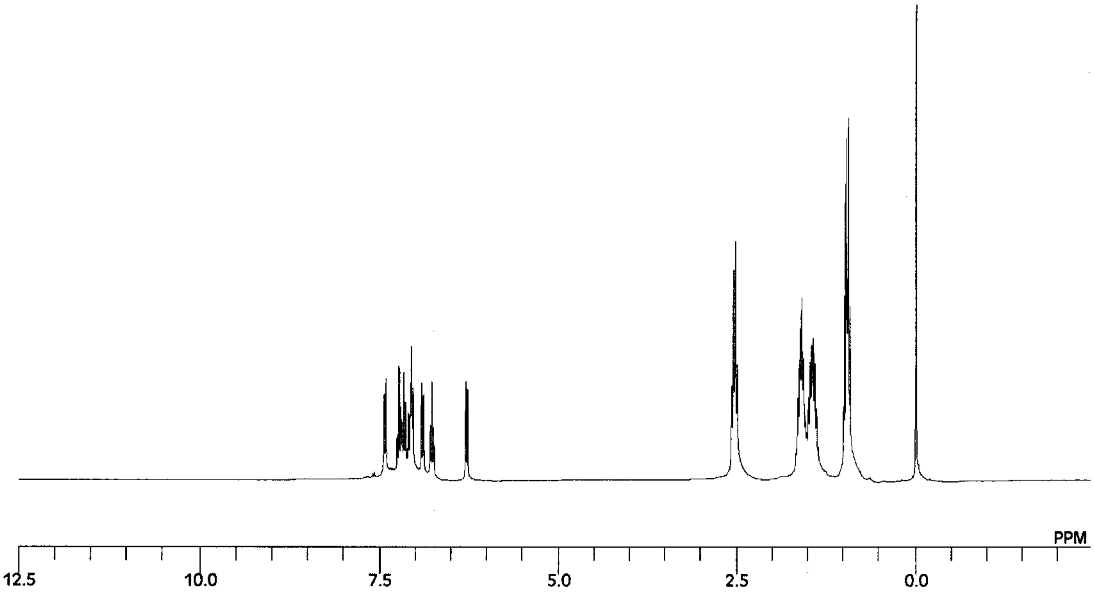

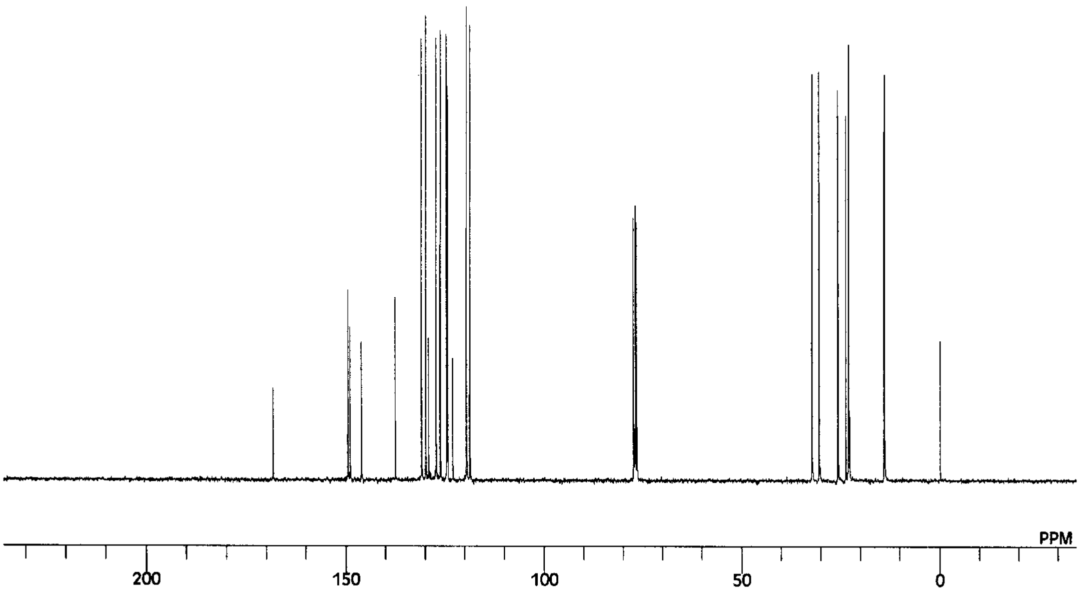

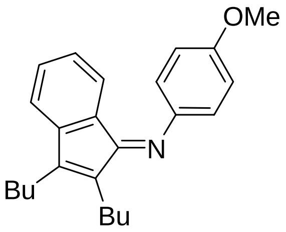

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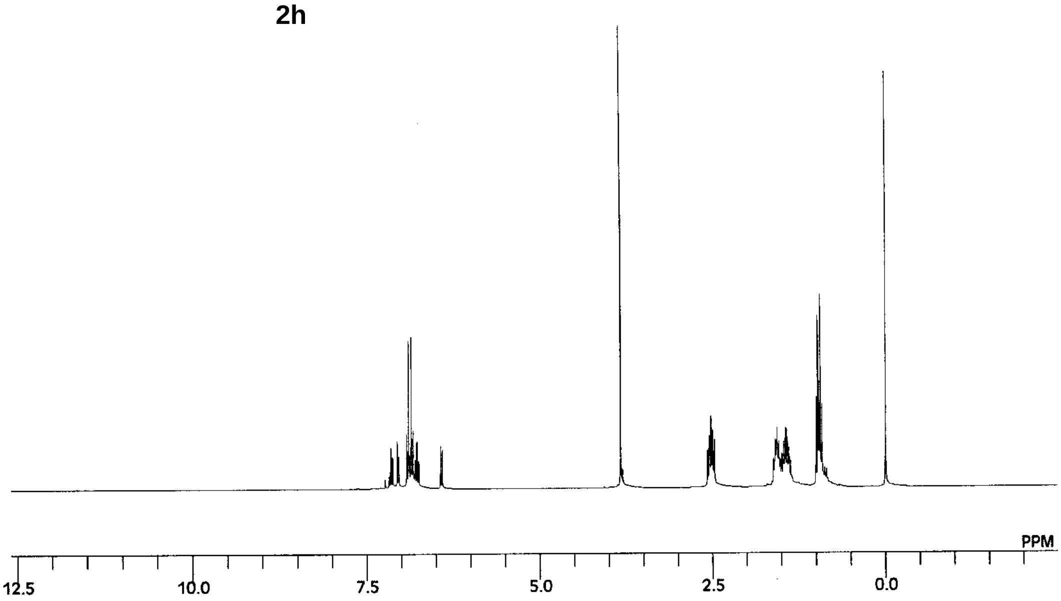

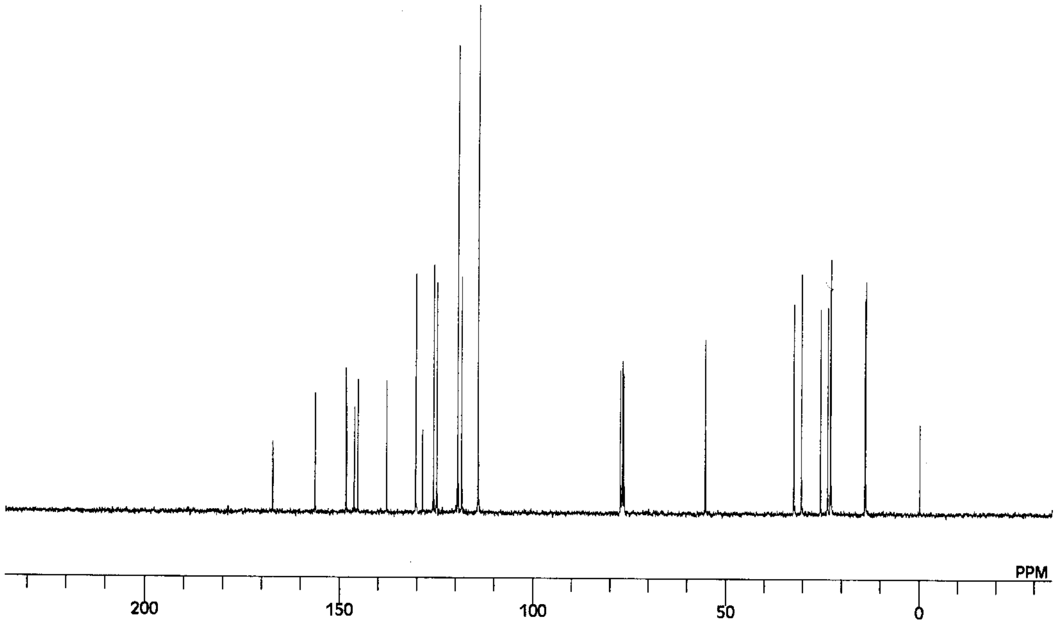

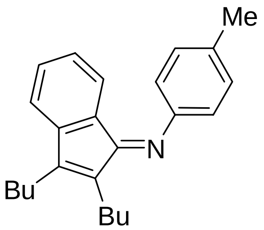

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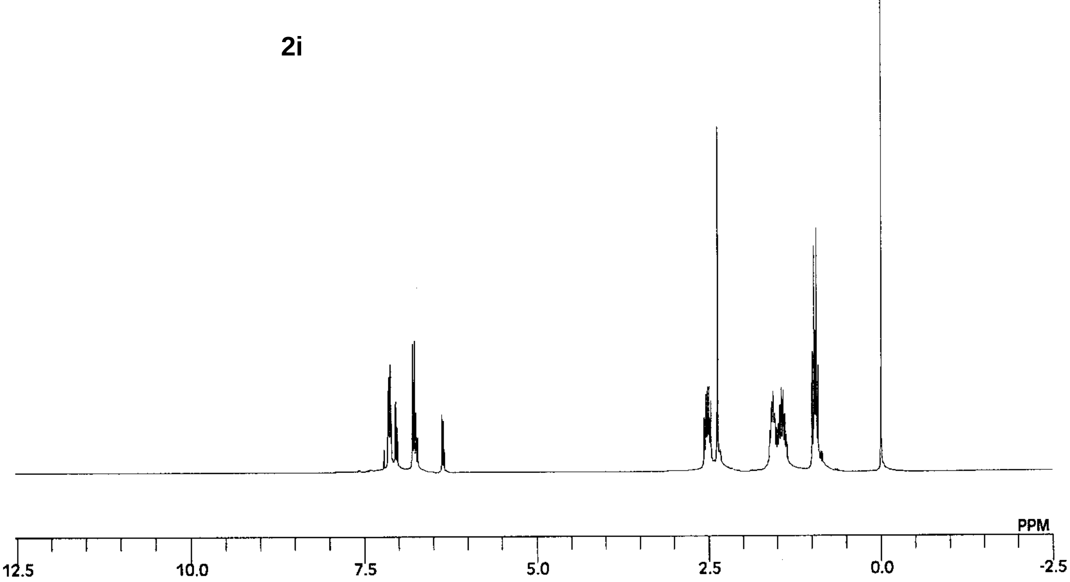

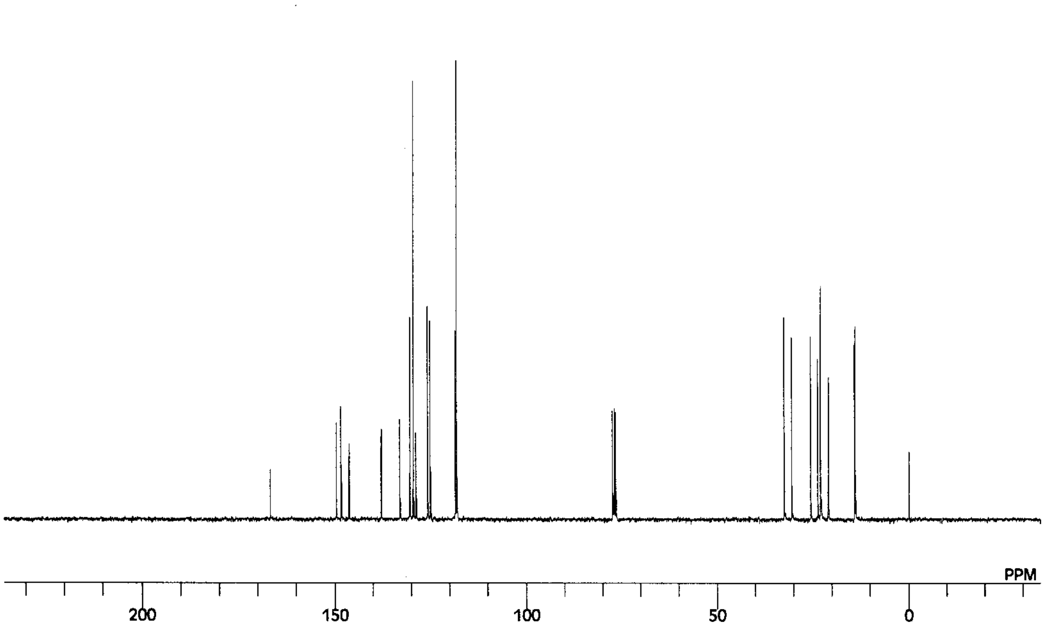

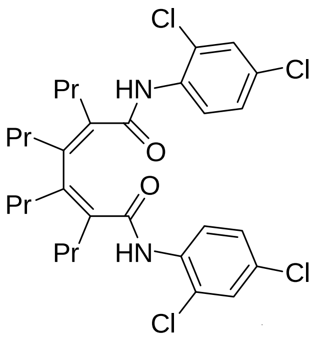

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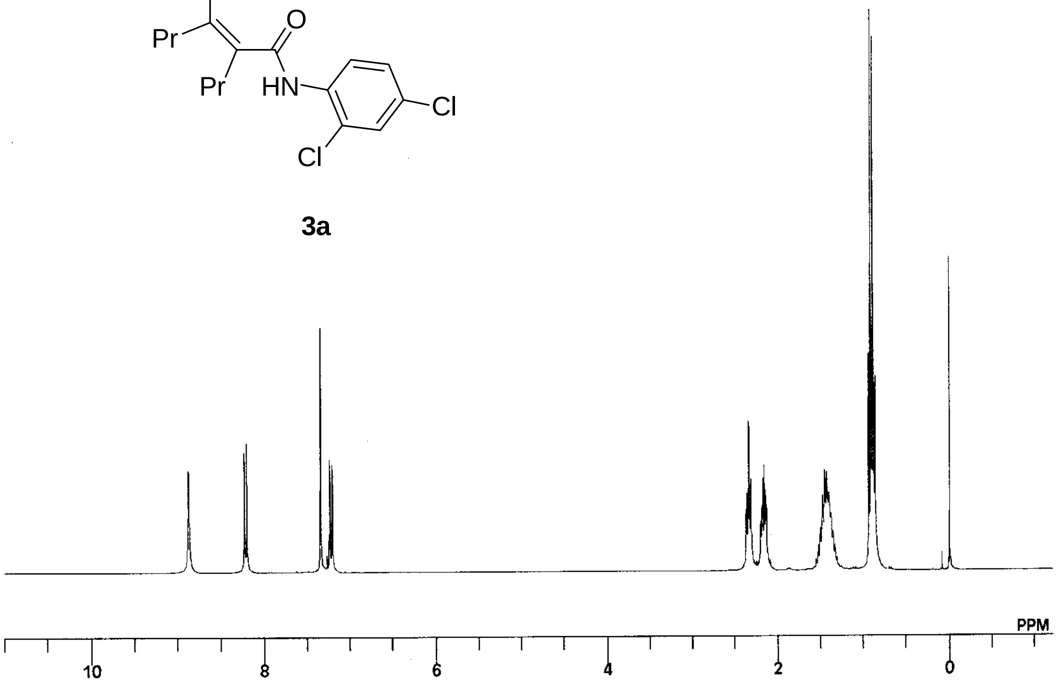

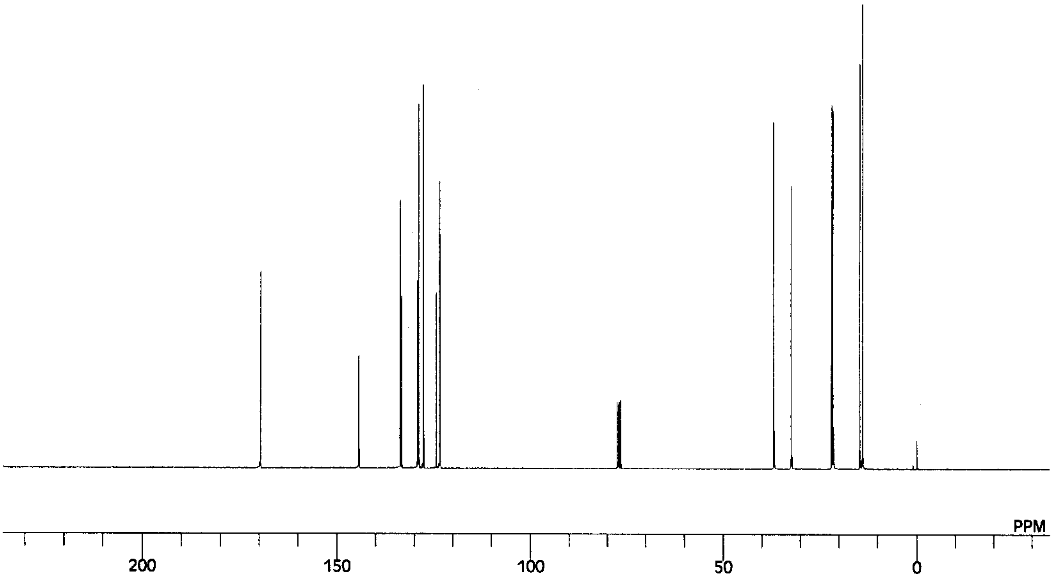

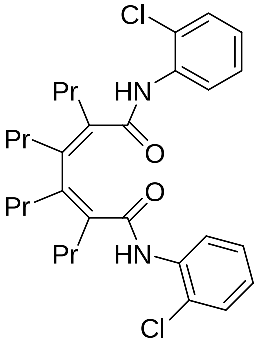

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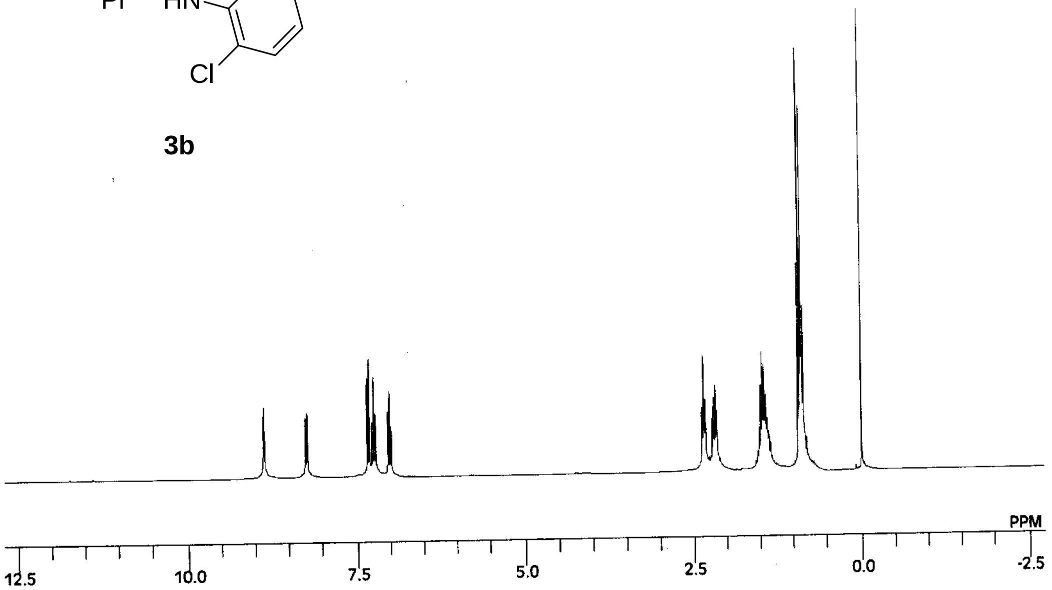

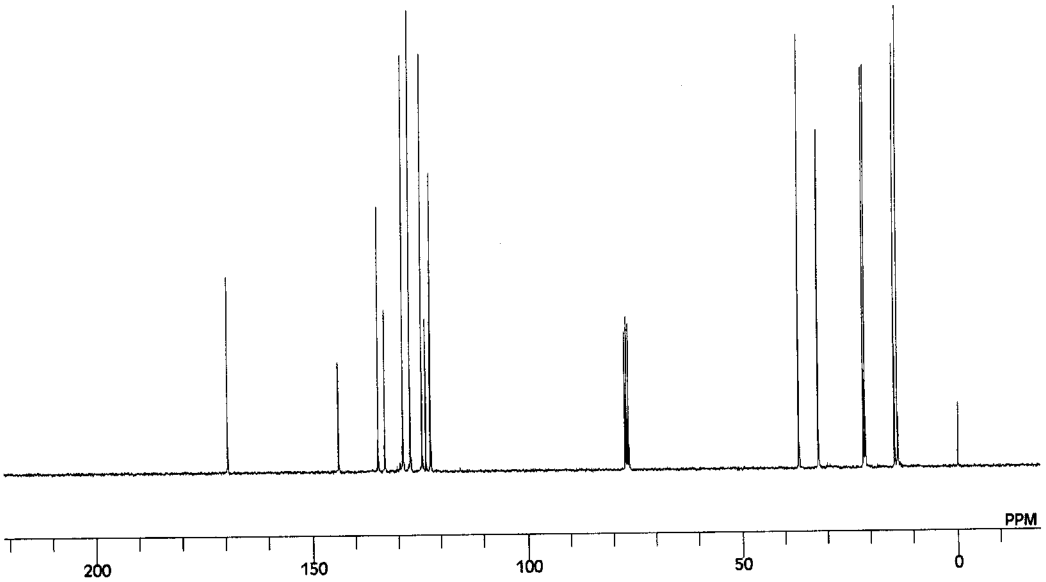

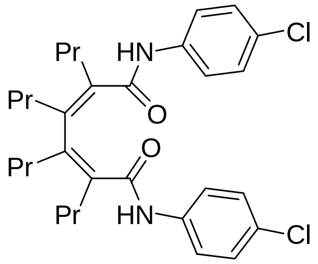

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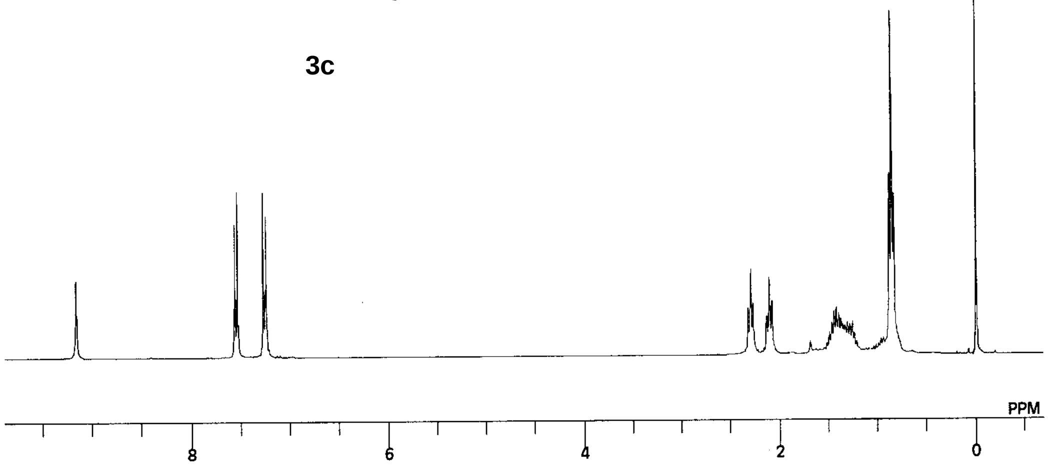

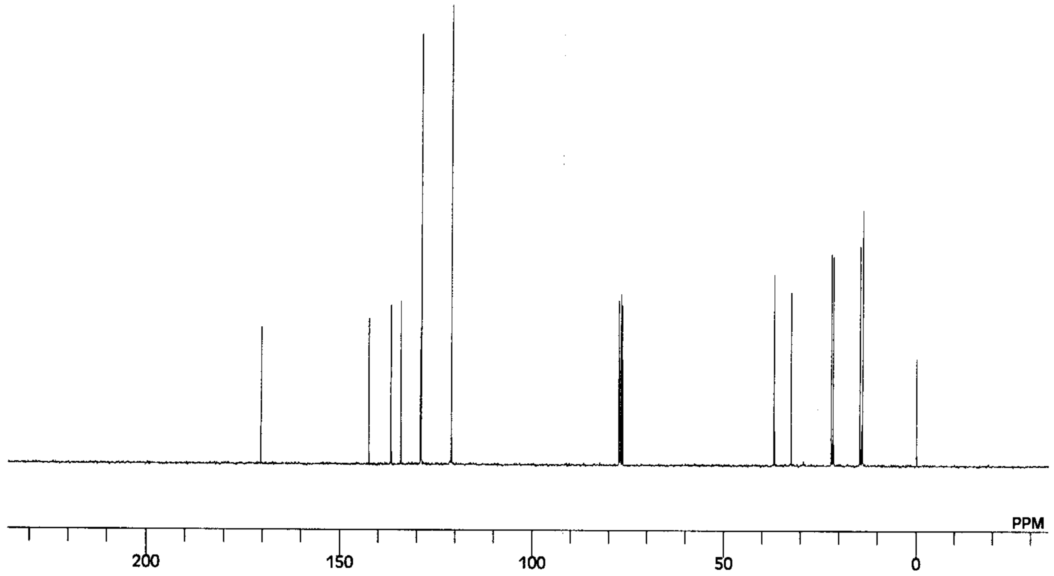

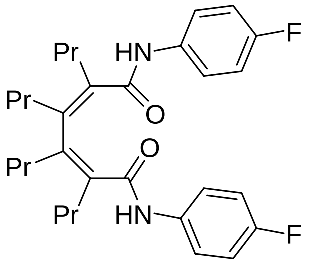
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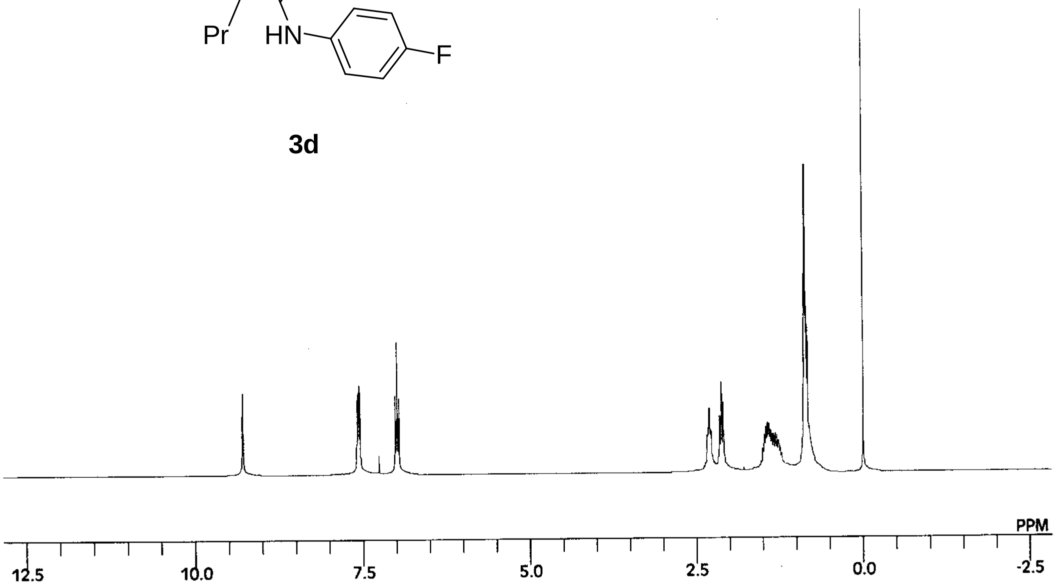
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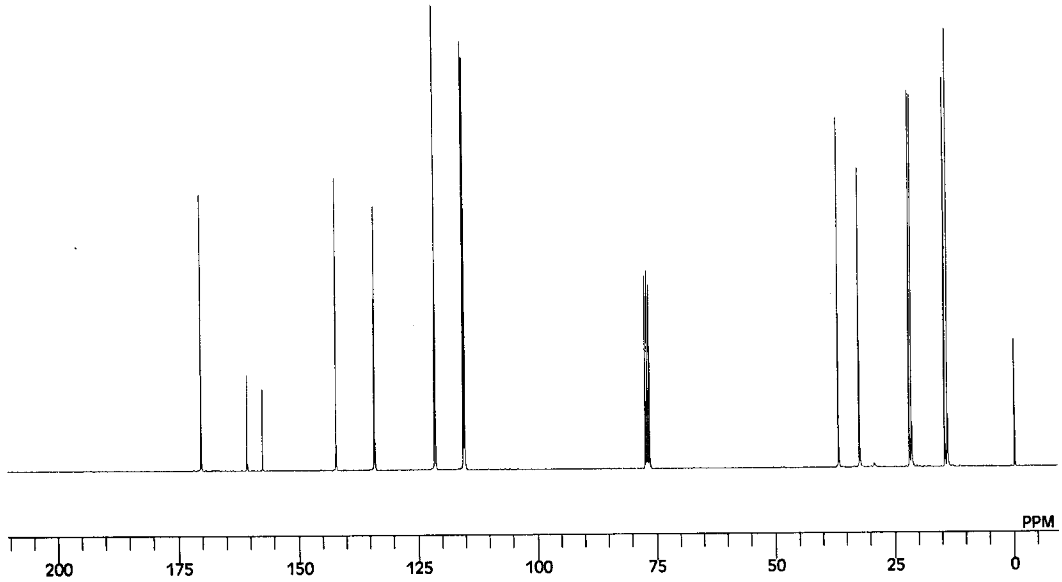
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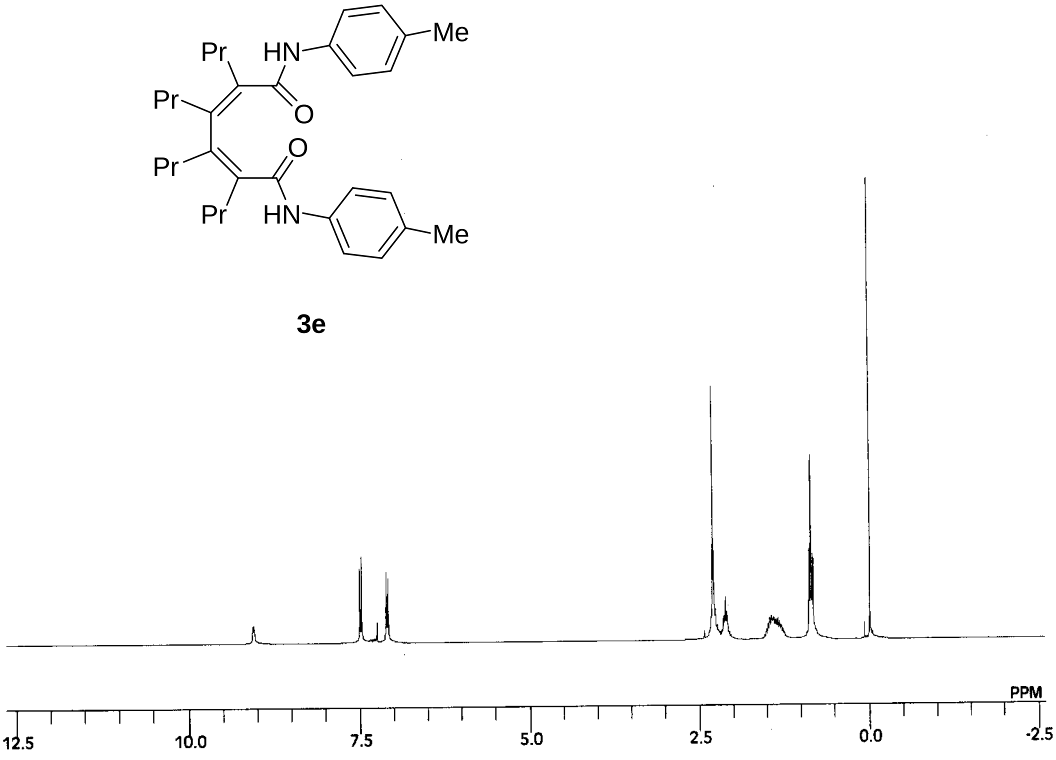
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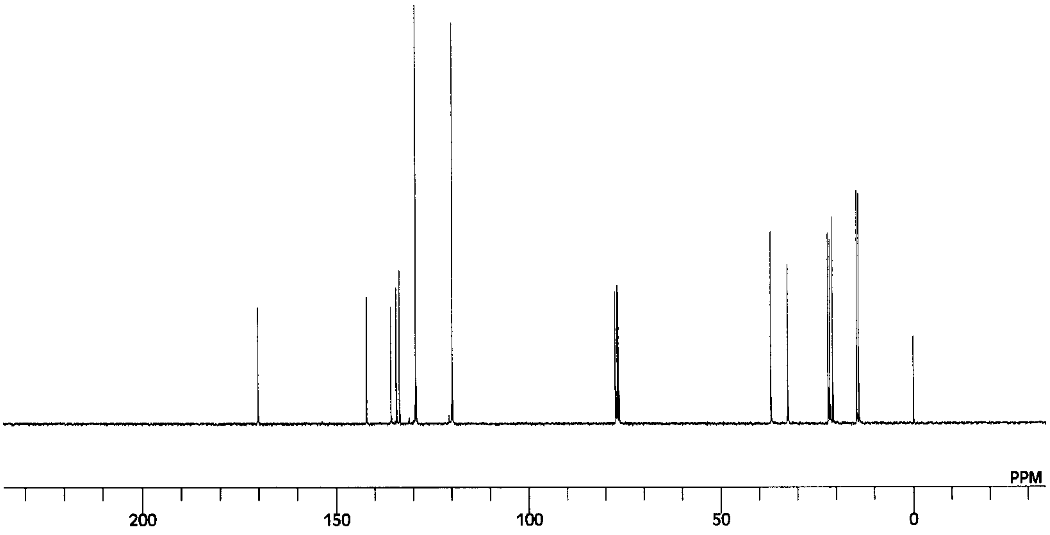
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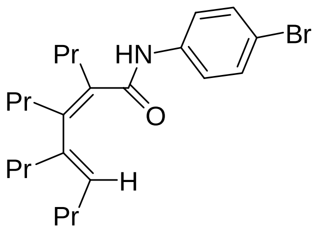

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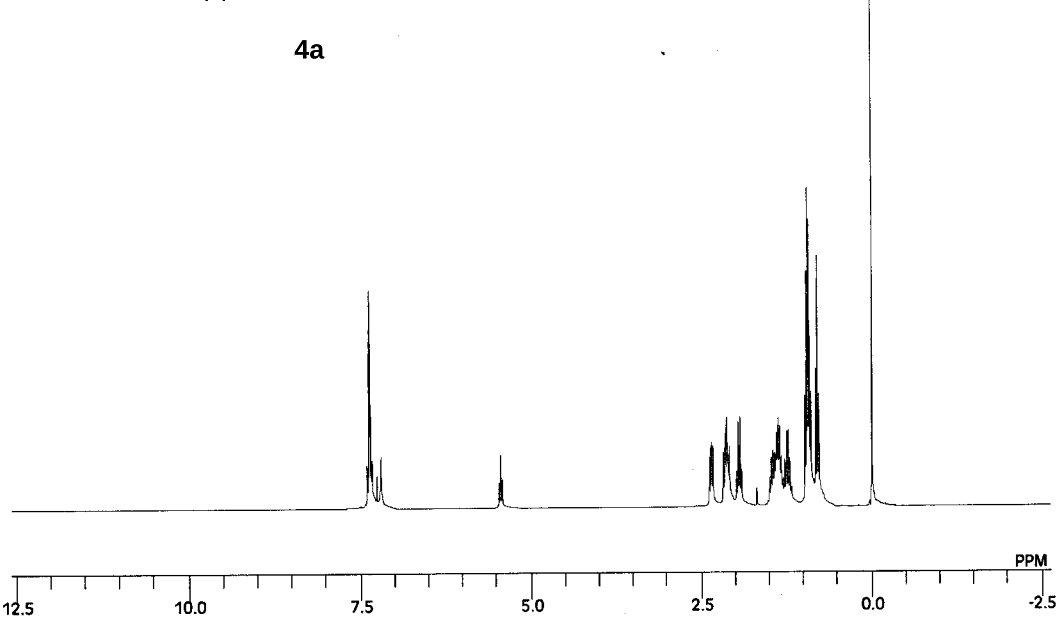

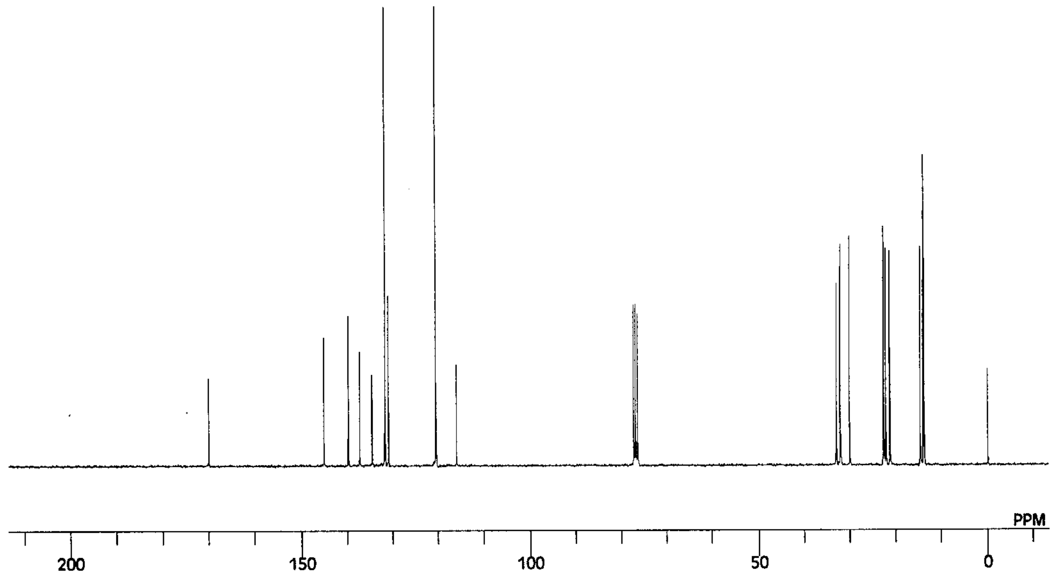

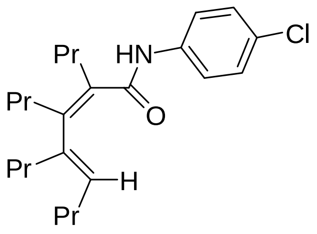

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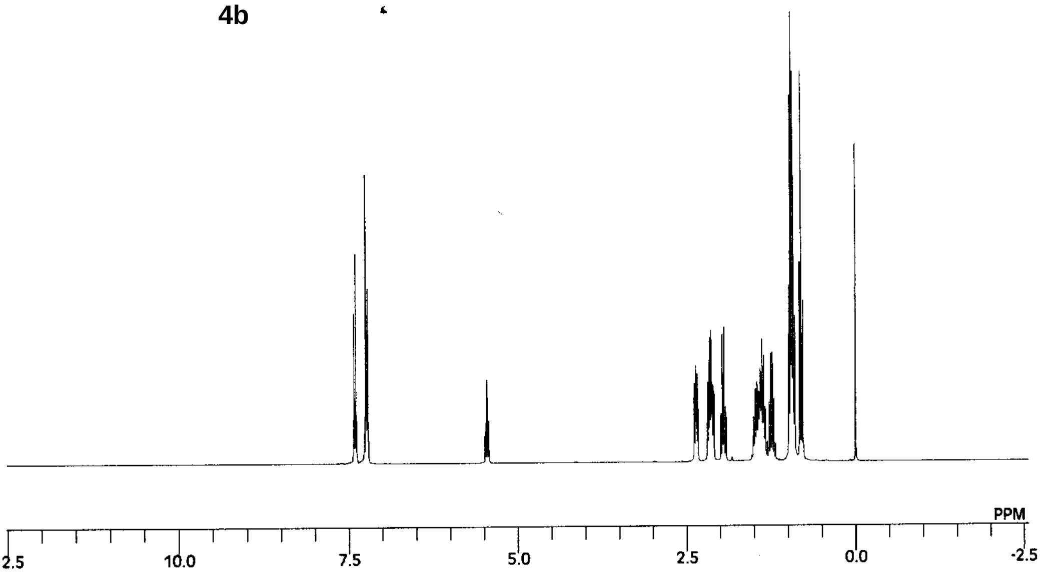

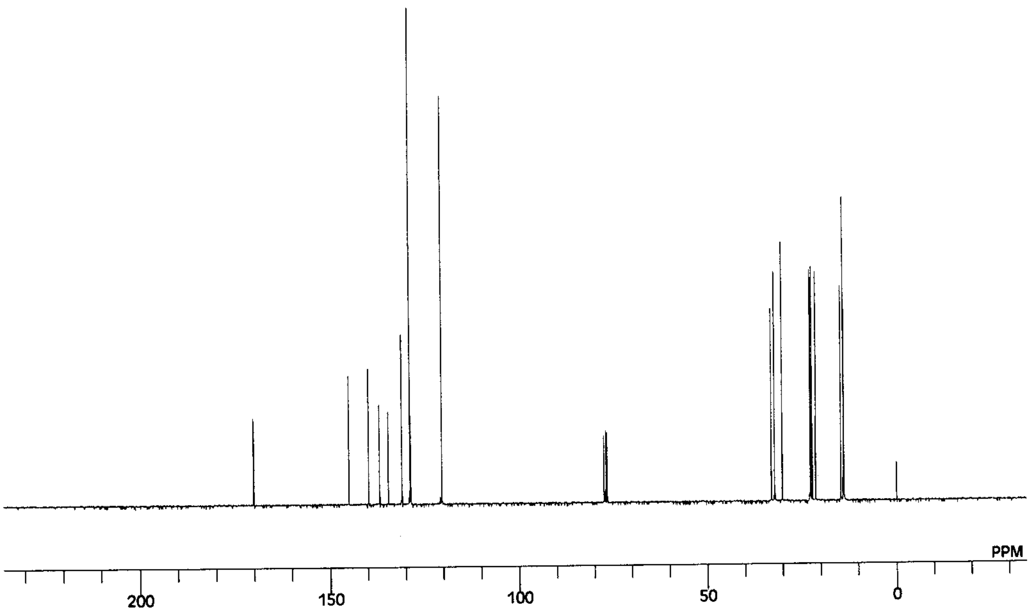

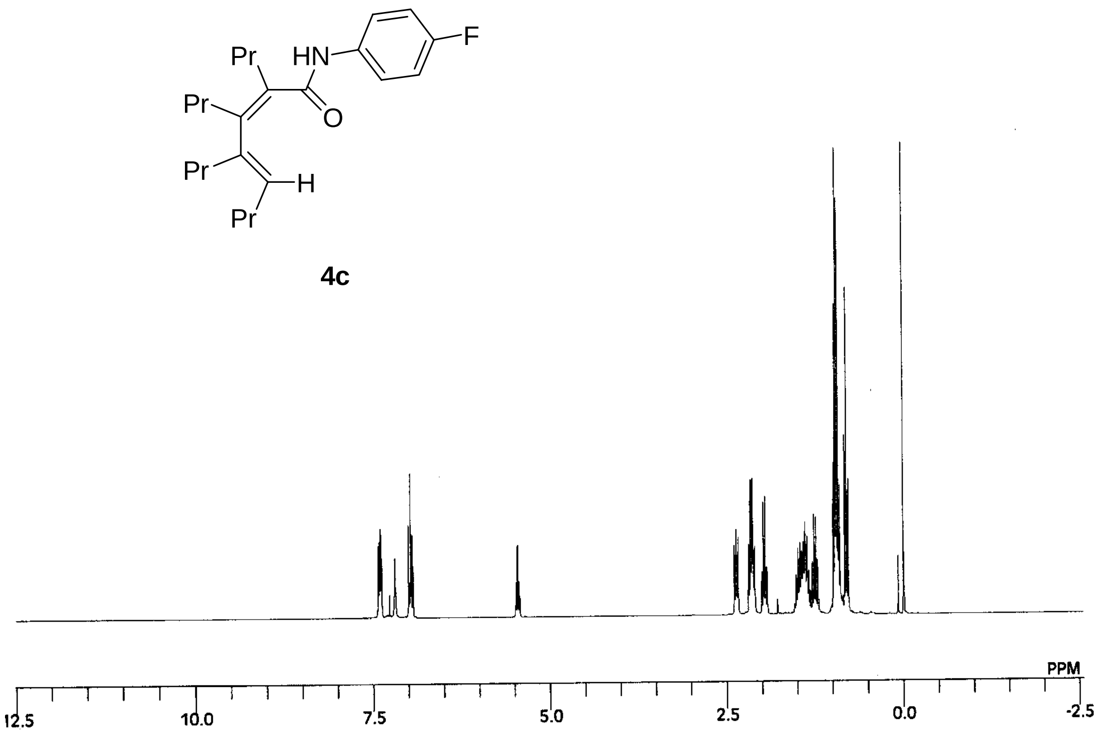

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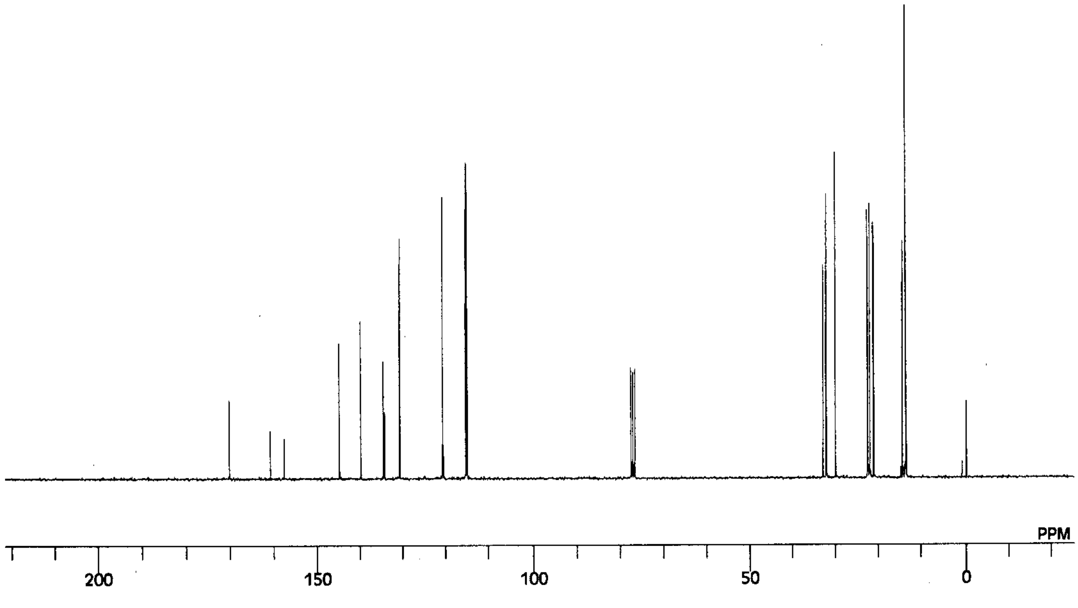

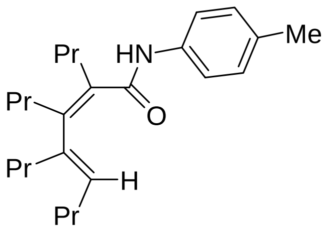

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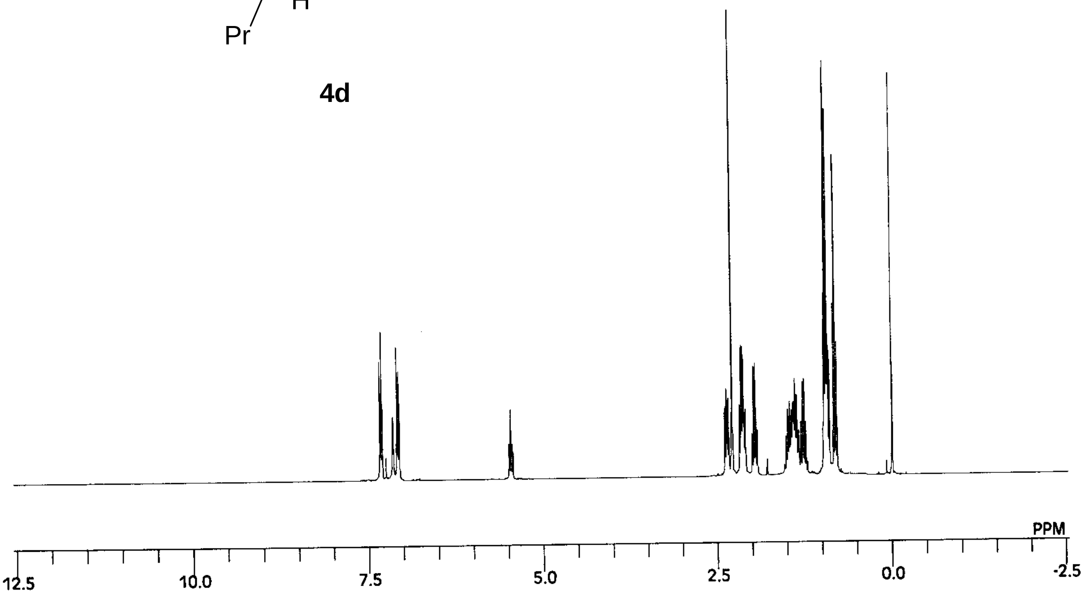

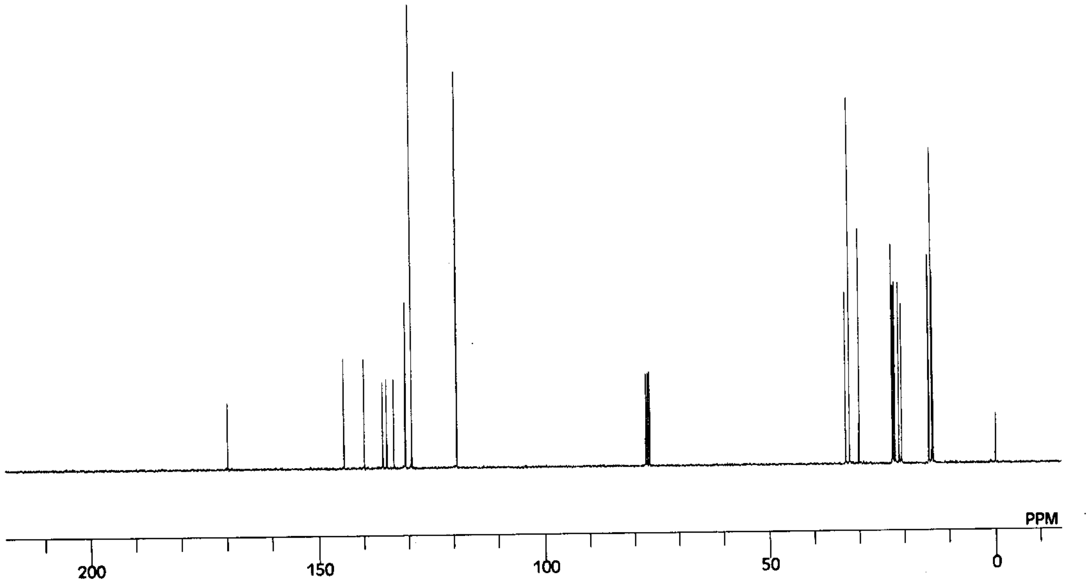

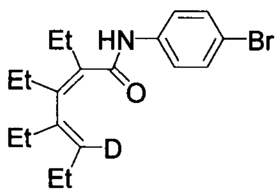

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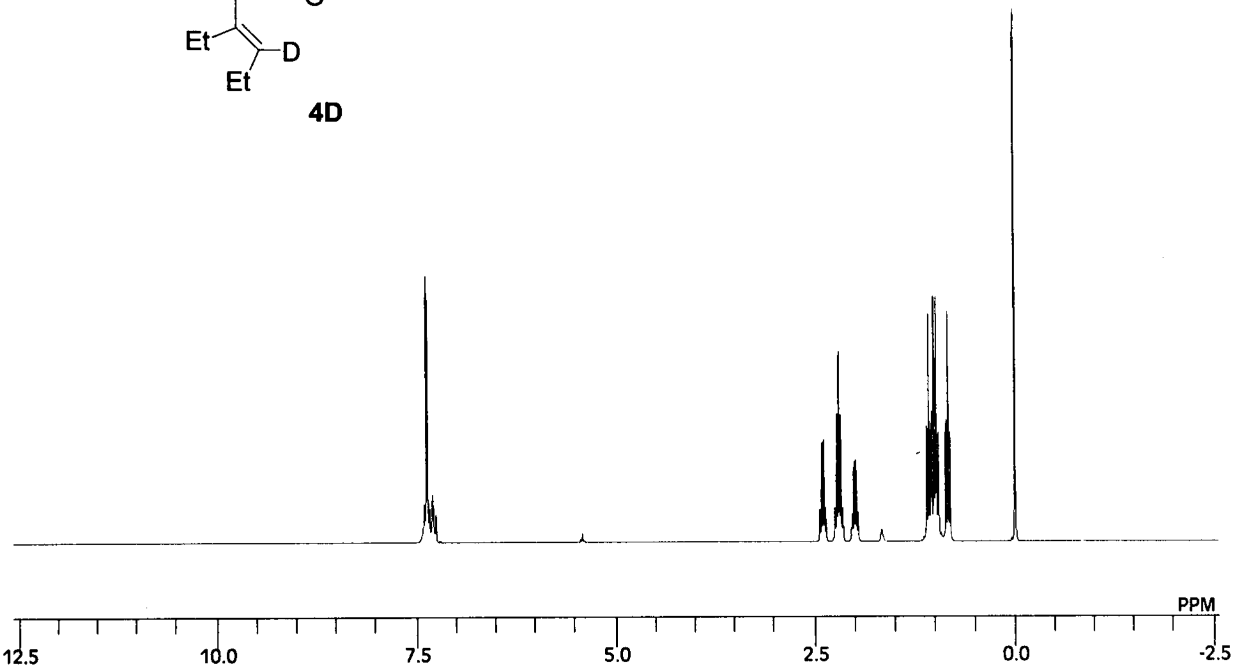

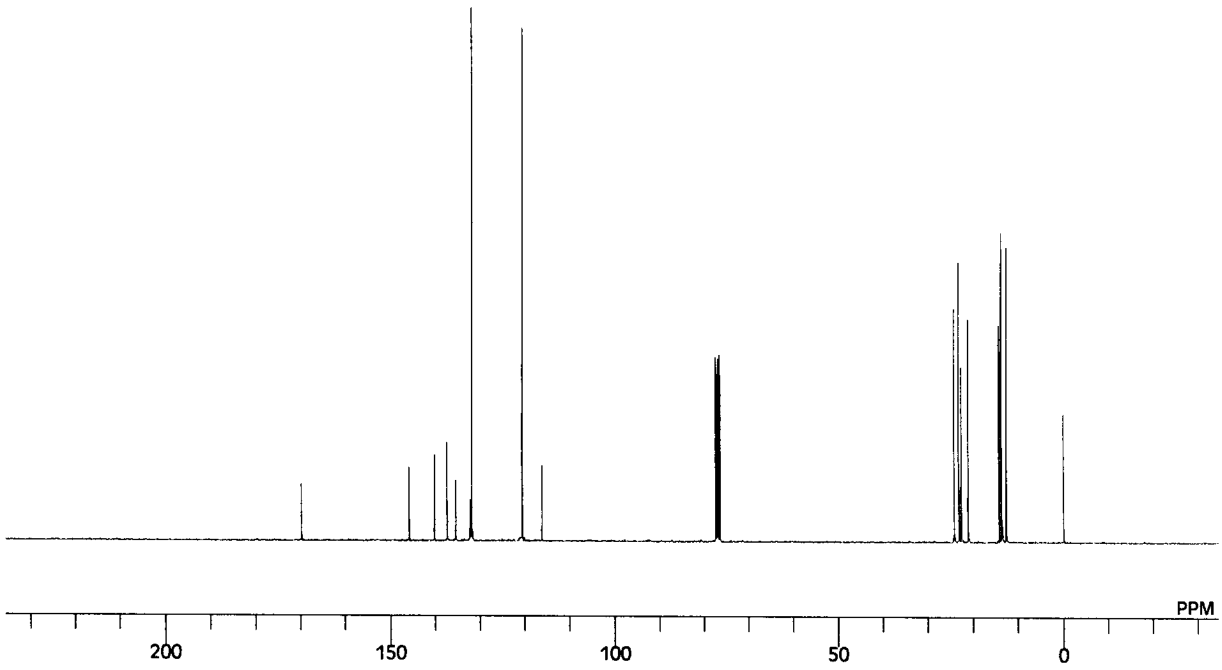

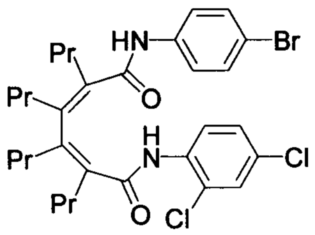
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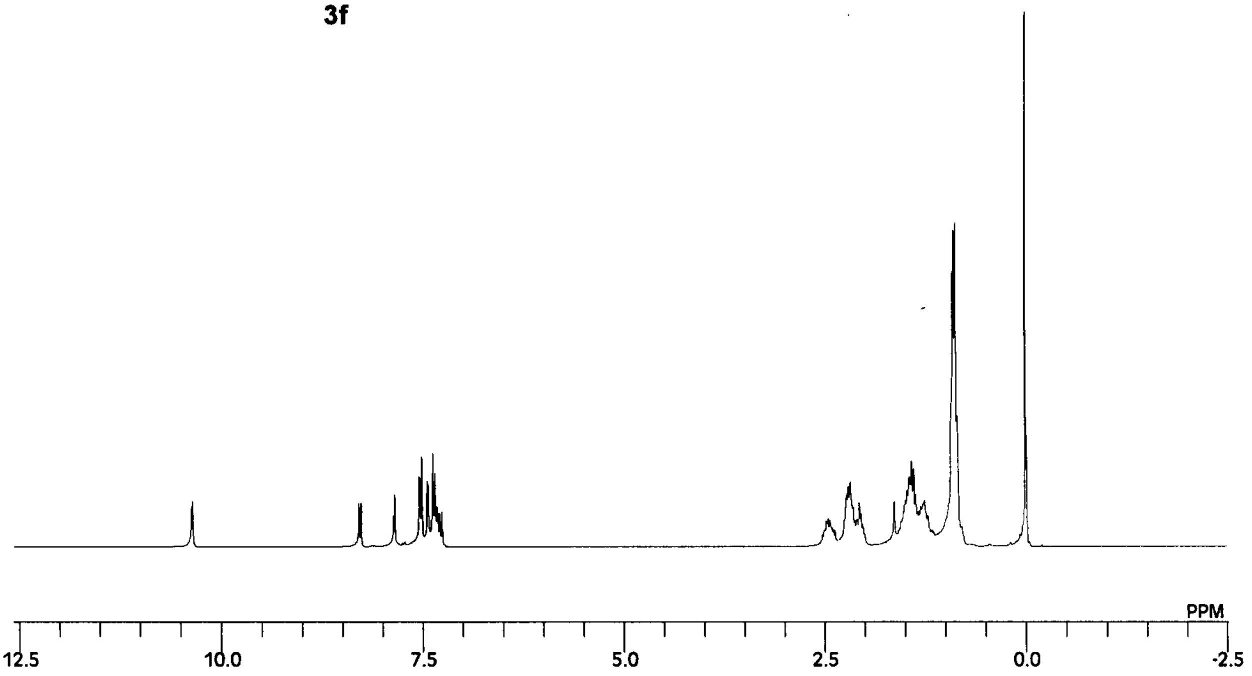
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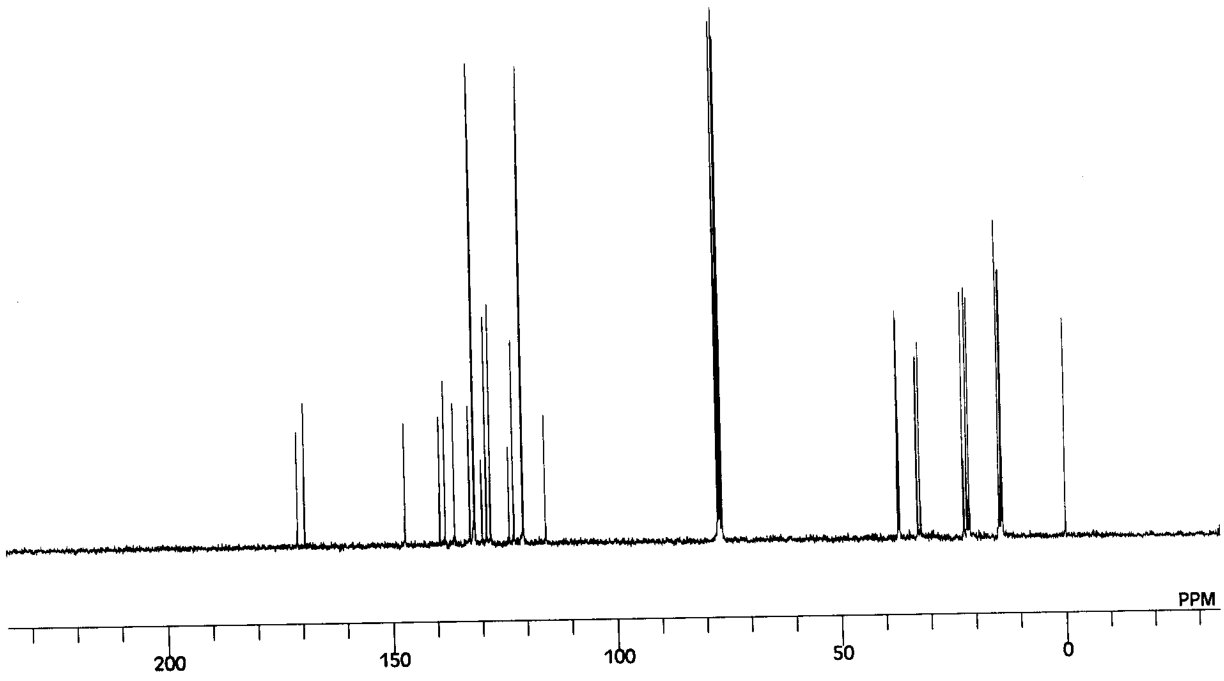
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