

Supporting Information for:

**Addition of Benzylzinc Halides to Alkenyl(phenyl)iodonium
Triflates: Stereoselective Synthesis of Trisubstituted Alkenes.**

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Experimental Section.

General: ^1H and ^{13}C NMR spectra were recorded on Varian Mercury 400 spectrometer and chemical shifts are reported in ppm downfield from internal TMS or residual protons in the deuterated chloroform (δ 7.26). IR spectra were obtained on a Perkin-Elmer 1600 FTIR as KBr pellets or neat on NaCl plates purchased from International Crystal Laboratories. GC-MS traces were recorded on a Hewlett Packard 5890 Series II gas chromatograph with an Ultra-1 crosslinked (methyl silicone gum; 12m x 0.2mm x 0.33mm) column, equipped with a 70eV HP 5971A mass selective detector. Purification was performed using flash grade silica gel or a Harrison Research Chromatotron using hexanes or hexanes/ethyl acetate as eluants.

Materials: Reactions were carried out in oven-dried glassware under nitrogen atmosphere unless otherwise indicated. Tetrahydrofuran was distilled from benzophenone/sodium, dichloromethane from CaH_2 and Fisher hexanes and ethyl acetate were used as received. All reagents were used as received unless otherwise noted. 4-Iodobenzotrifluoride and 1-iodo-3,5-bis(trifluoromethyl)benzene were purchased from Acros. Zinc dust, zinc foil (0.25 mm), 2,6-dichloro-a-bromotoluene, benzyl bromide and 1,2-dibromoethane were purchased from Aldrich Chemical Company. Flash grade silica gel (240-400 mesh) was purchased from either Aldrich or Fisher Scientific and all chromatography was performed using hexanes (Fisher) or hexanes/ethyl acetate as eluants. Salts **5a** – **5c** have been previously reported.¹

¹ Hinkle, R. J.; Stang, P. J. *Synthesis* **1994**, 393-396.

Representative Preparation of Organozinc Halide Reagents from Zinc foil.

Concentrations for reagents used in subsequent coupling reactions varied from 0.52

to 1.26 M. Preparation of (3): Zinc foil (0.615 g, 9.4 mmol) was placed in a 25 mL 3-necked round bottom flask equipped with a 10 mL addition funnel, stopper and N₂ inlet. Tetrahydrofuran (1.0 mL) was added via syringe and the zinc foil activated by addition of 1,2-dibromoethane (0.040 mL, 0.46 mmol) and heating to a gentle boil with a heat gun four times. A THF solution (5.0 mL) containing 2,6-dichloro- α -bromotoluene (0.752 g, 3.13 mmol) was placed in the addition funnel and the flask immersed in an ice-bath. The benzylic bromide solution was added at a rate of 1 drop each 5-10 sec. After the addition was complete, the zinc reagent solution was stirred at 0 – 5 C for ca. 3 h until the starting bromide was consumed (TLC). The resulting 0.52 M solution was used for the representative preparation of **6a**.

(E)-1-(2,6-Dichlorophenyl)-3-phenyl-2-pentene (6a):

THF was pre-cooled to -40 °C in a round bottom flask. Salt **5a** (0.120 g, 0.248 mmol) was placed in an oven-dried 13 x 100 mm borosilicate test tube equipped with a micro stir bar. Pre-cooled THF (1.0 mL) was added, followed immediately by a 0.52 M THF solution of organozinc reagent **3** (0.62 mL, 0.32 mmol) via syringe. The reaction was allowed to stir and slowly warm to rt over the course of several hours. After 14 h, sat'd NH₄Cl (2.0 mL) was added and the product extracted with 1/1 hexanes/EtOAc (4 x 2 mL). The combined organic phases were dried (MgSO₄) and concentrated in vacuo. The product was isolated by radial chromatography using hexanes as eluant to provide **6a** (0.060 g, 83%) as a colorless oil: IR (neat, NaCl) 3026 w, 2904 m, 2923 w, 1580 w, 1559

m, 1492 m, 1431 vs, 1087 m, 908 s, 770 s, 759 vs, 733 vs cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.07 (m, 8 H, Ar), 5.56 (t, $J = 6.96$ Hz, 1H, vinyl), 3.87 (d, $J = 6.96$ Hz, benzyl, 2H), 2.73 (q, $J = 7.70$ Hz, 2H), 1.06 (t, $J = 7.70$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.0, 142.5, 136.9, 135.4, 128.1, 128.0, 127.6, 126.6, 126.3, 122.9, 31.0, 23.4, 13.4. Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{Cl}_2$: C, 70.11; H, 5.54. Found: C, 70.07; H, 5.55.

(Z)-1-(2,6-Dichlorophenyl)-3-methyl-2-pentene (6b):

THF was pre-cooled to -40 C in a round bottom flask. Salt **5b** (0.100 g, 0.236 mmol) was placed in an oven-dried 13 x 100 mm borosilicate test tube equipped with a micro stir bar. Pre-cooled THF (1.0 mL) was added, followed immediately by a 0.66 M THF solution of organozinc reagent **3** (0.46 mL, 0.30 mmol) via syringe. The reaction was allowed to stir and slowly warm to rt over the course of several hours. After 14 h, sat'd NH_4Cl (2.0 mL) was added and the product extracted with 1/1 hexanes/EtOAc (4 x 2 mL). The combined organic phases were dried (MgSO_4) and concentrated in vacuo. Pure product was isolated by flash chromatography using hexanes as eluant to provide **6b** (0.026 g, 48%) as a colorless oil: IR (neat, NaCl) 2964 s, 2933 w, 1574 w, 1559 m, 1431 vs, 1374 m, 1133 m, 1082 m, 912 s, 774 vs cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.27 (d, $J = 8.06$ Hz, , 2 H, Ar), 7.05 (t, $J = 8.06$ Hz, 1H), 5.07 (t, $J = 6.60$ Hz, 1H, vinyl), 3.65 (d, $J = 6.60$ Hz, benzyl, 2H), 2.25 (q, $J = 7.70$ Hz, 2H), 1.69 (s, 3H), 1.05 (t, $J = 7.70$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.8, 137.5, 135.3, 128.1, 127.3, 119.0, 30.3, 25.2, 22.9, 12.7.

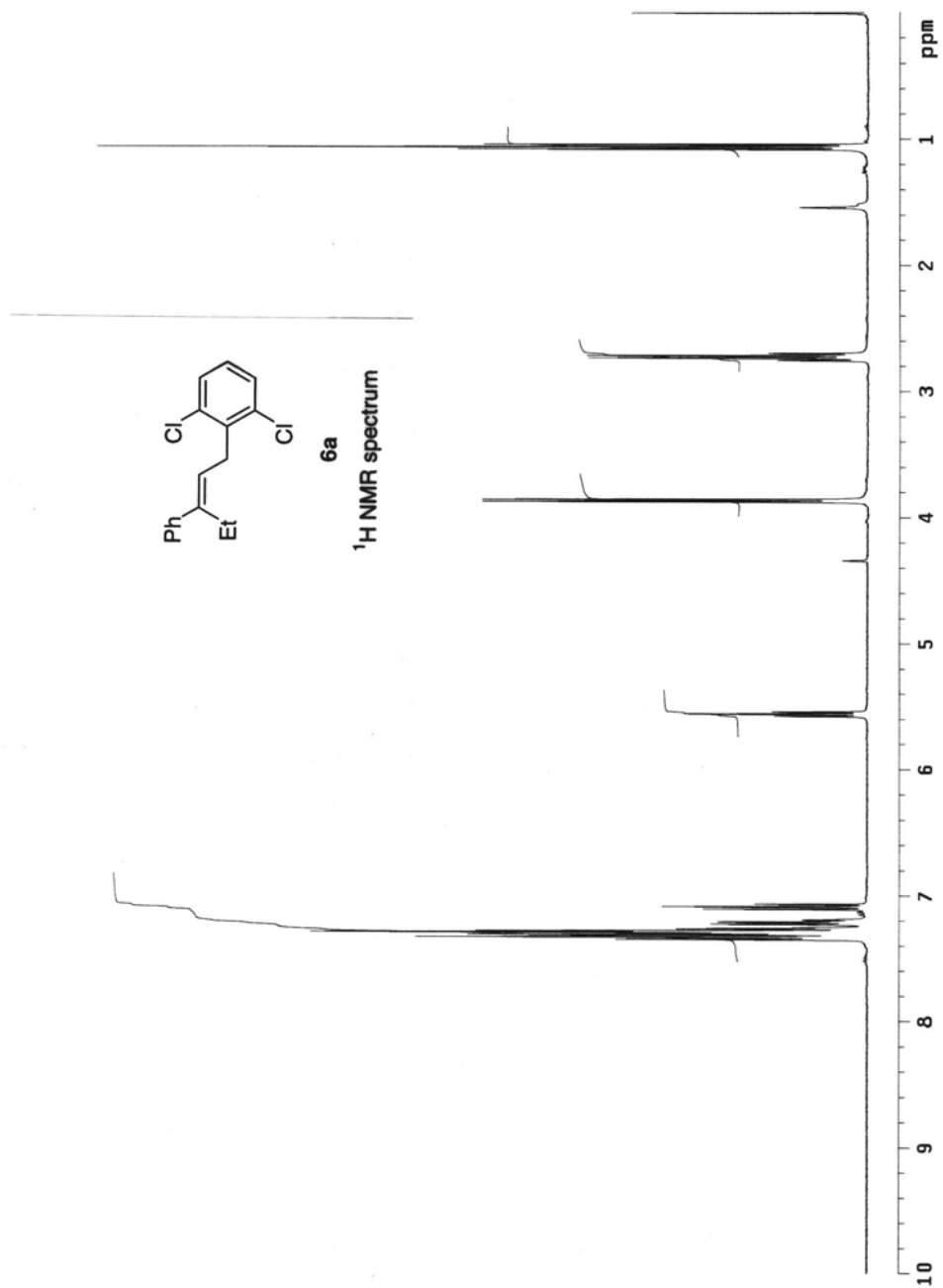
1-(2,6-Dichlorophenyl)-3-methyl-2-butene (6c):

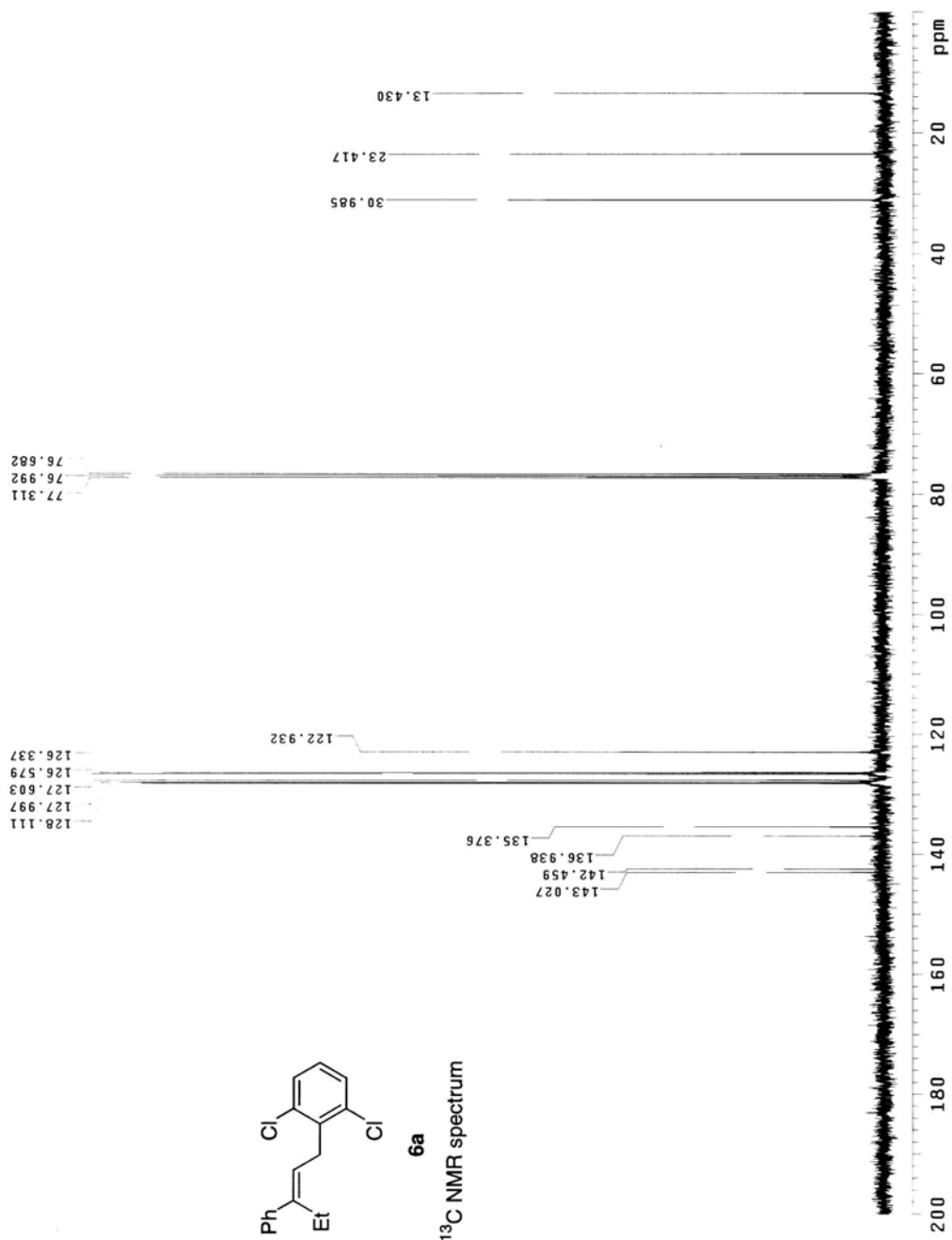
THF was pre-cooled to -40 C in a round bottom flask. Salt **5c** (0.124 g, 0.303 mmol) was placed in an oven-dried 13 x 100 mm borosilicate test tube equipped with a micro stir bar. THF (1.0 mL) was added, followed immediately by a 1.26 M THF solution of organozinc reagent **3** (0.29 mL, 0.37 mmol) via syringe. The reaction was allowed to stir and slowly warm to rt over the course of several hours. After 14 h, sat'd NH₄Cl (2.0 mL) was added and the product extracted with 1/1 hexanes/EtOAc (4 x 2 mL). The combined organic phases were dried (MgSO₄) and concentrated in vacuo. The product was isolated by flash chromatography using hexanes as eluant to provide **6c** (0.033 g, 50%) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, J = 8.06 Hz, 2 H), 5.11 (tt, J = 6.96, J = 1.46 Hz, 1H, vinyl), 3.87 (d, = 6.96 Hz, benzyl, 2H), 1.81 (s, 3H), 1.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 137.3, 135.2, 133.1, 128.0, 127.3, 119.5, 30.8, 25.9, 18.3. Anal. Calcd for C₁₁H₁₂Cl₂: C, 61.42; H, 5.65. Found: C, 61.44, 5.72.

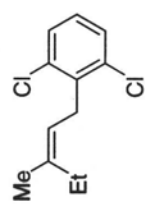
1-(3-cyanophenyl)-3-methyl-2-butene (7c):

THF was pre-cooled to -40 C in a round bottom flask. Salt **5c** (0.103 g, 0.253mmol) was placed in an oven-dried 13 x 100 mm borosilicate test tube equipped with a micro stir bar. THF (1.0 mL) was added, followed immediately by a 0.53 M THF solution of organozinc reagent **4** (0.62 mL, 0.33 mmol) via syringe. The reaction was allowed to stir and slowly warm to rt over the course of several hours. After 18 h, sat'd

NH₄Cl (2.0 mL) was added and the product extracted with 1/1 hexanes/EtOAc (4 x 2 mL). The combined organic phases were dried (MgSO₄) and concentrated in vacuo. The product was isolated by flash chromatography using 95/5 hexanes/EtOAc as eluant to provide **7c** (0.032 g, 74%) as a colorless oil: IR (neat, cm⁻¹), 3082 m, 3013 m, 2967 s, 2932 s, 2875 m, 2229 s, 1601 m, 1584 m, 1474 m, 1445 m, 788 s, 759 s, 690 vs; ¹H NMR (400 MHz, CDCl₃) δ 7.50-7.35 (m, 3 H), 5.27 (tt, J = 7.33, J = 1.46 Hz, 1H, vinyl), 3.37 (d, J = 7.33 Hz, benzyl, 2H), 1.77 (s, 3H), 1.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.0, 134.1, 132.7, 131.7, 129.4, 128.9, 121.3, 119.0, 112.2, 33.9, 25.8, 18.0.

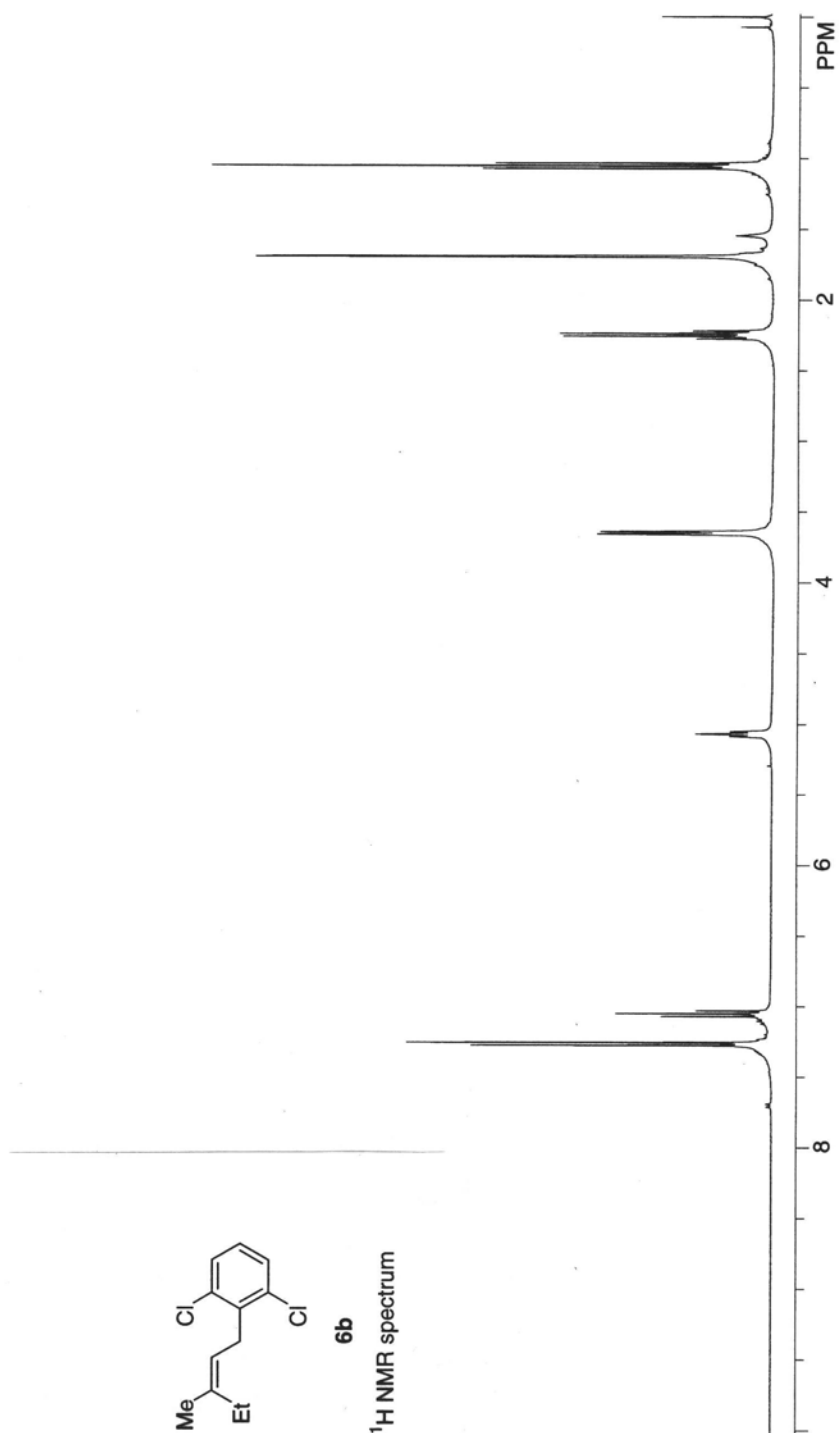


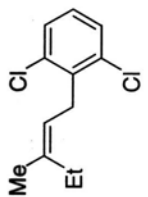
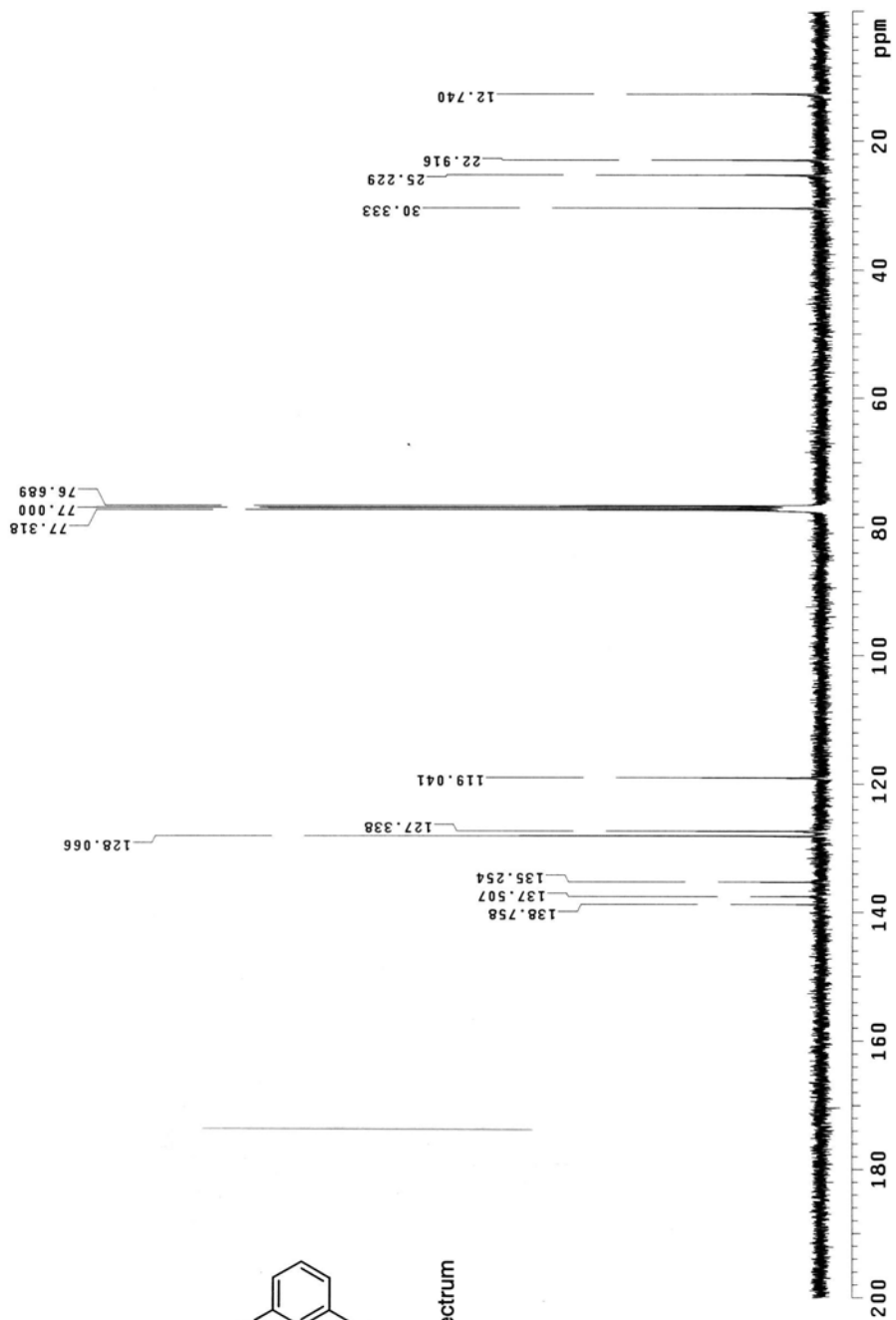




6b

¹H NMR spectrum





6b
¹³C NMR spectrum

