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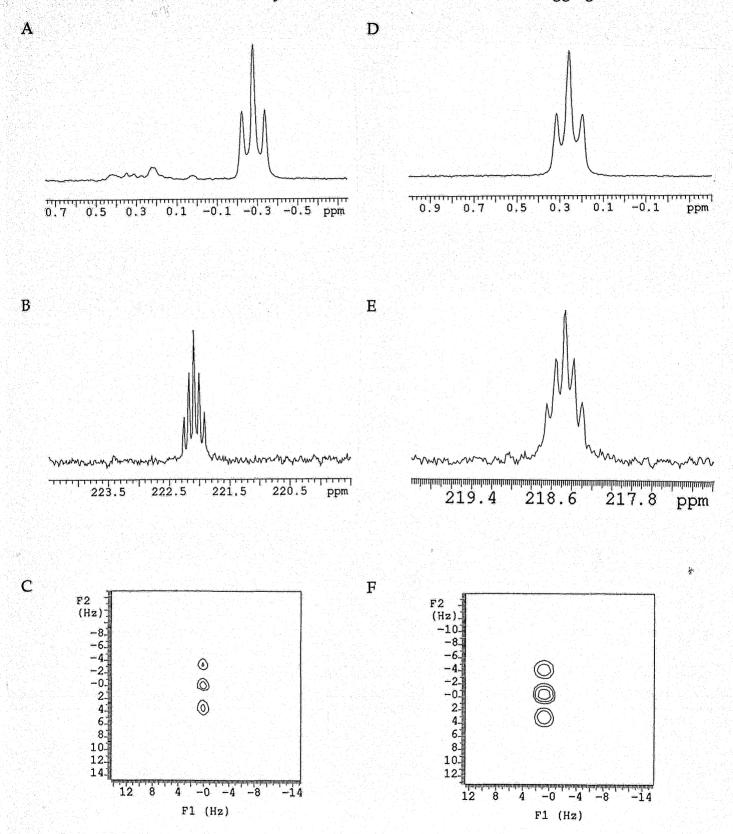
## CARLIER 11602-11603

## **Terms & Conditions**

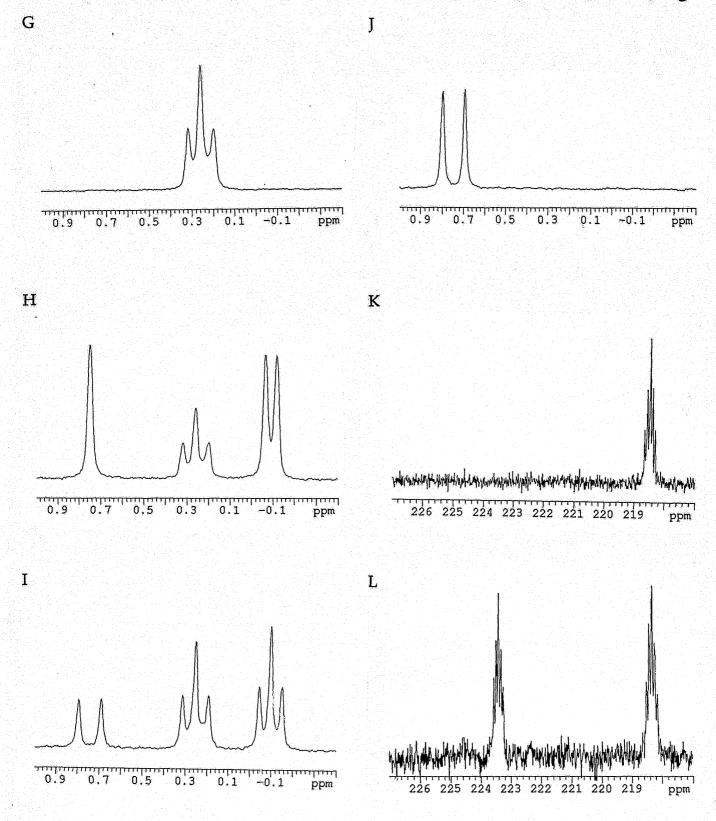
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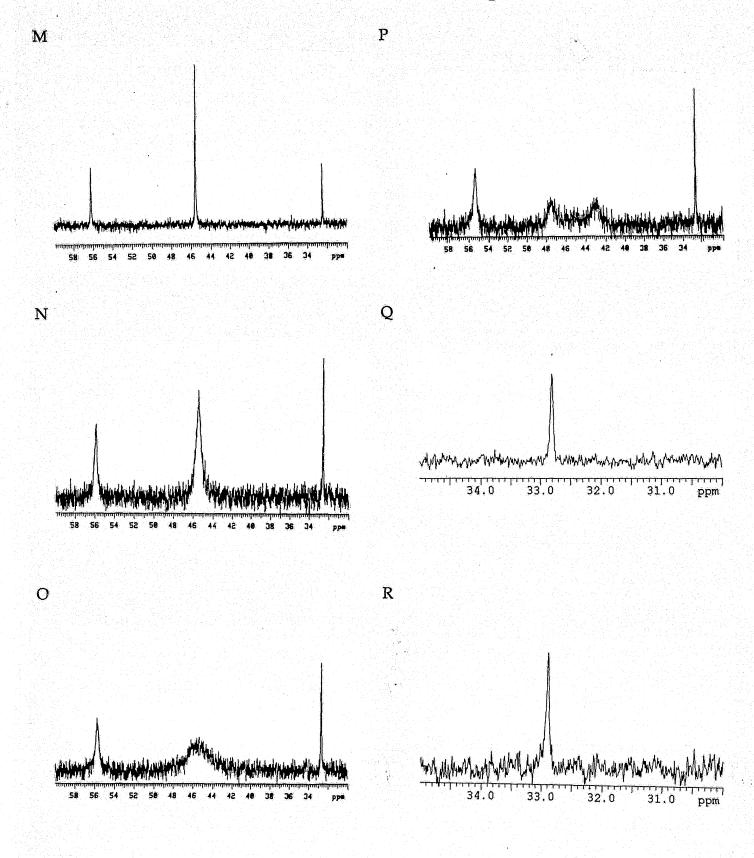
Supplementary Material for "<sup>6</sup>Li/<sup>15</sup>N NMR Based Solution Structural Determination of Et<sub>2</sub>O-and TMEDA-Solvated Lithio-Phenylacetoni<sup>4</sup>rile and a LiHMDS Mixed Aggregate"



A-C: <sup>6</sup>Li, <sup>15</sup>N, and <sup>6</sup>Li-detected <sup>15</sup>N zero quantum NMR spectra for ether-solvated lithiophenylacetonitrile 6 (0.1M). D-F: Corresponding spectra for TMEDA-solvate 7.



G: <sup>6</sup>Li spectrum of 7 (0.1M). H-I: <sup>6</sup>Li spectra of 0.1M [<sup>6</sup>Li]LiHMDS and 0.1M [<sup>6</sup>Li,<sup>15</sup>N]LiHMDS respectively, each containing 0.5 eq. [<sup>15</sup>N]phenylacetonitrile and 1 eq. TMEDA. J: <sup>6</sup>Li spectrum of [<sup>6</sup>Li,<sup>15</sup>N]-9 (0.05M). K: <sup>15</sup>N spectrum of 7 (0.1M). L: <sup>15</sup>N NMR spectrum of 0.1M [<sup>6</sup>Li]LiHMDS containing 0.5 eq. [<sup>15</sup>N]phenylacetonitrile and 1 eq. TMEDA.



**M-P:** TMEDA and α-cyano carbon region of  $^{13}$ C NMR spectra of 0.1M [ $^{6}$ Li, $^{14}$ N]-7 at -20, -55, -70, and -90 °C respectively ( $^{4}$ 8-toluene). **Q-R:** α-cyano carbon region of  $^{13}$ C NMR spectra of 0.1M [ $^{6}$ Li, $^{15}$ N]-5 in 1:2  $^{4}$ 8-toluene: $^{4}$ 8-THF at -90 and -110 °C respectively.

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## Preparation of [15N]phenylacetonitrile:

A 100 ml 24/40 round-bottom flask equipped with a magnetic stirring bar was charged with [<sup>15</sup>N]KCN (1.038 g, 15.7 mmol, Cambridge Isotope Lab, dried under vacuum at 50 °C for 45 minutes), 18-crown-6 (4.18 g, 15.8 mmol) and 30 mL of acetonitrile (dried by 3A molecular sieves). Benzyl bromide (7.5 mL, 62.8 mmol) was added by pipet over 5 minutes and the reaction was then put under Argon; a mild exotherm ensued during which nearly all of the solids dissolved. The reaction was monitored by Gas Chromatography (50M Carbowax, 100 °C for 2 minutes, then 10 °C/min for 10 minutes, hold at 200 °C for 2 minutes) by determining the ratio of phenylacetonitrile to remaining benzyl bromide. After 2.5 hours 90% conversion had been achieved, and after 5 hours the reaction was cooled to 0 °C and quenched by the addition of triethylamine (13 mL, 95 mmol). After stirring for 45 minutes at 0 °C and 90 minutes at room temperature, the reaction was poured into 100 mL H<sub>2</sub>O, and extracted with diethyl ether (1x200 mL, 2x50 mL). The combined ether extracts were washed (2x50 mL 2N HCl, 1x25 mL H<sub>2</sub>O), dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo* to give 1.74g of a yellow oil. Kugelröhr distillation (1mm, 80-100 °C) afforded 1.59 g of a colorless oil (86% yield based on KCN, purity 96 area% by Gas Chromatography).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 3.85 (2H, s), 7.3-7.45 (5H, m).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): 23.57 (d,  ${}^{2}J_{15N-13C} = 3.0$  Hz), 117.82 (d,  ${}^{1}J_{15N-13C} = 16.8$  Hz), 127.89, 128.02, 129.11, 129.85.

 $^{15}$ N NMR (1:1 Et<sub>2</sub>O: Toluene, -90 °C): 247.07 (externally referenced to dimethylethylamine at 25.7 ppm).

IR (NaCl): 2222 cm<sup>-1</sup> (CN stretch of [<sup>14</sup>N]phenylacetonitrile occurs at 2255 cm<sup>-1</sup>).