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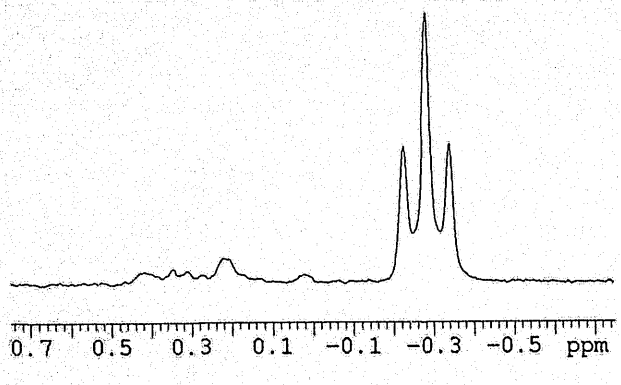
J11603-M1

Supplementary Material for "$^{6}Li/^{15}N$ NMR Based Solution Structural Determination of Et_2O- and TMEDA-Solvated Lithio-Phenylacetonitrile and a LiHMDS Mixed Aggregate"

A



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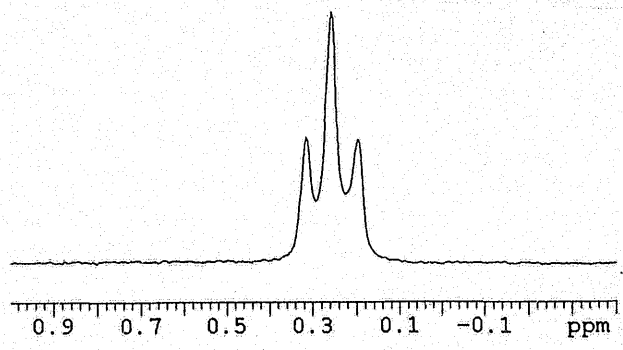

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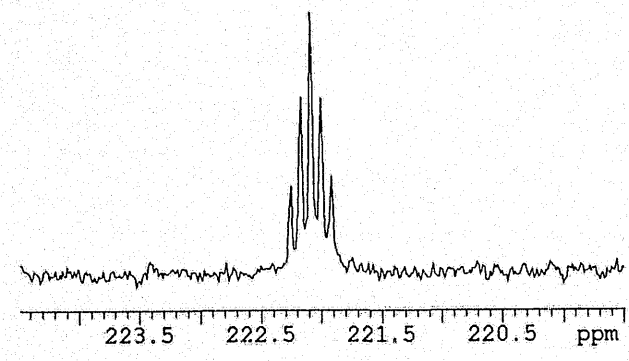

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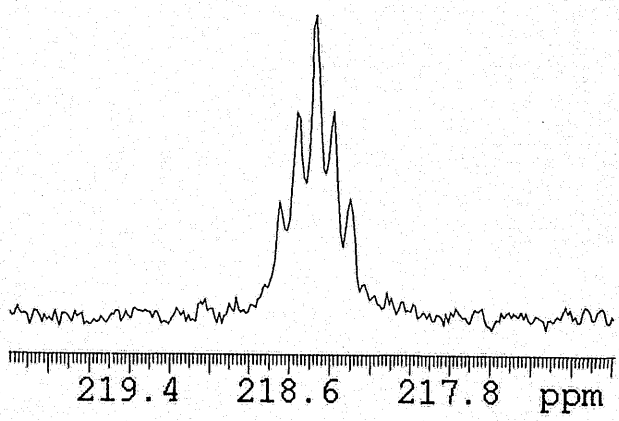

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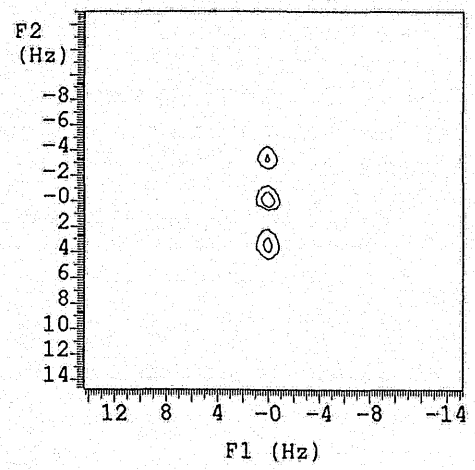

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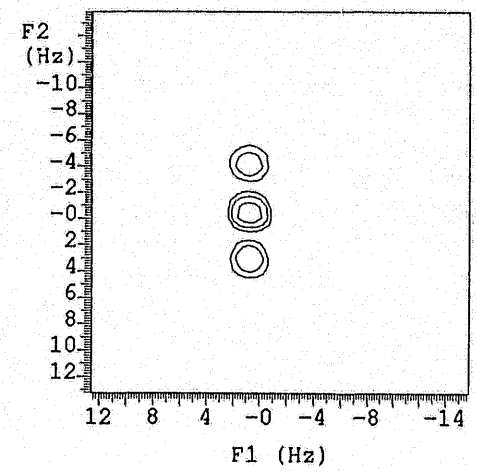
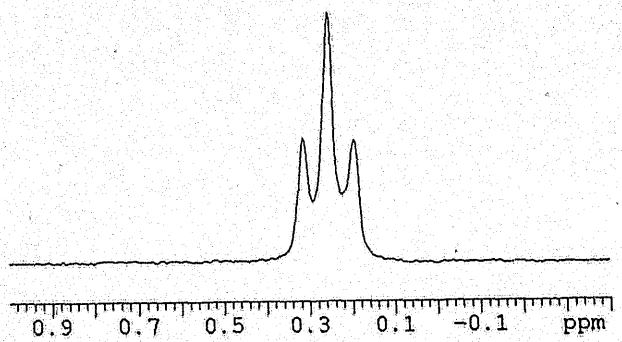


A-C: ^{6}Li, ^{15}N, and ^{6}Li-detected ^{15}N zero quantum NMR spectra for ether-solvated lithiophenylacetonitrile **6** (0.1M). **D-F:** Corresponding spectra for TMEDA-solvate **7**.

G



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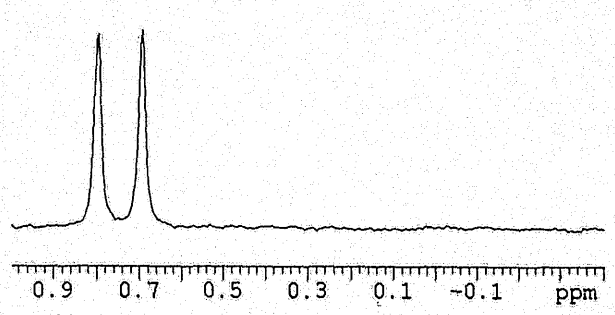

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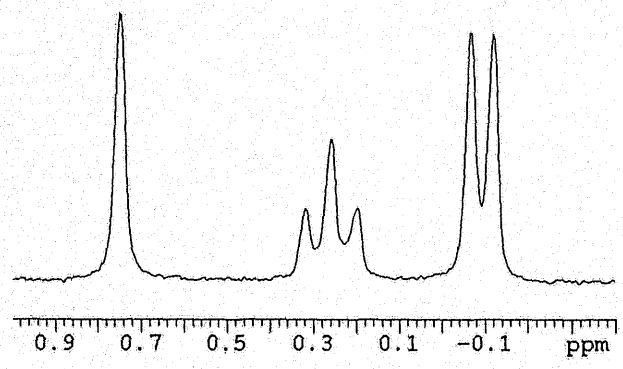

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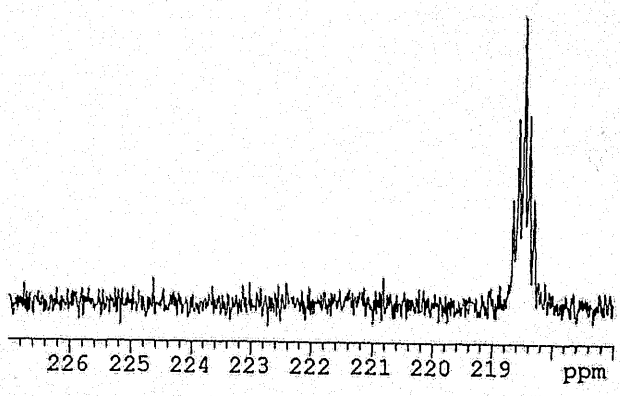

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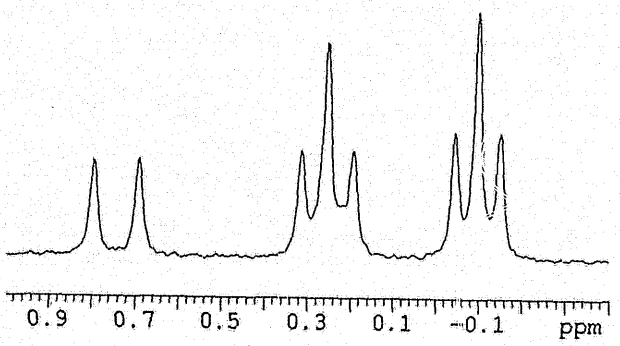
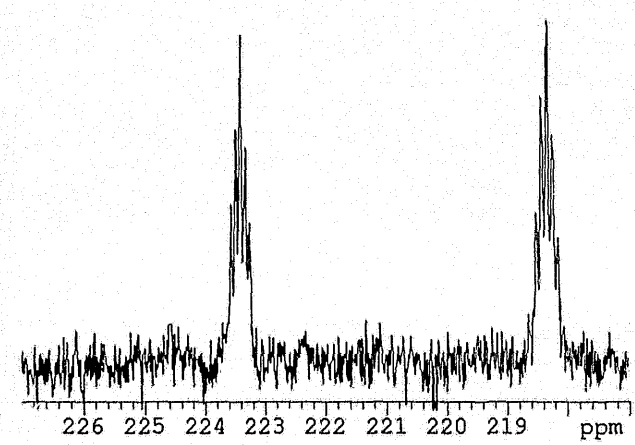
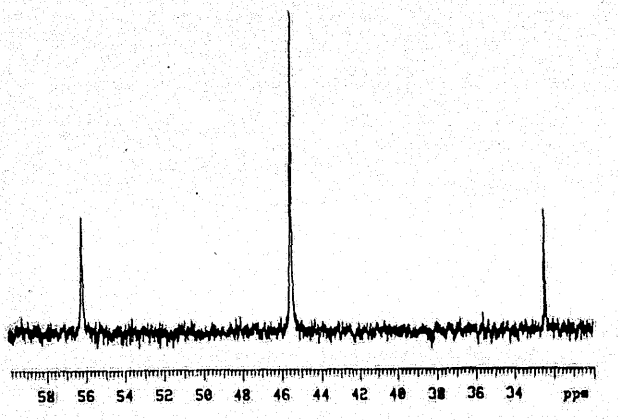


L



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

M



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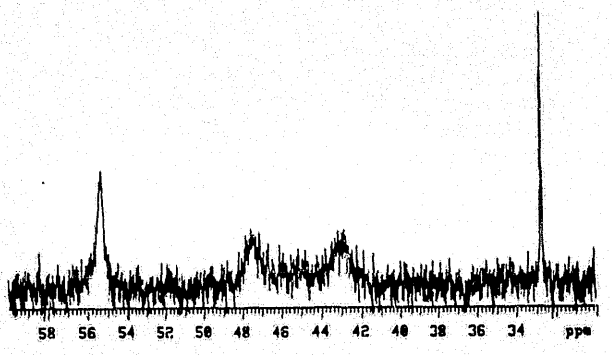
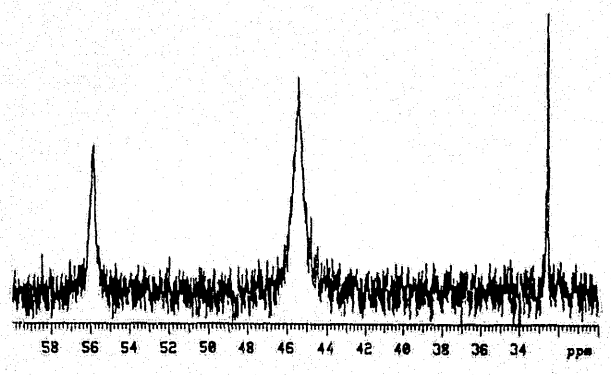
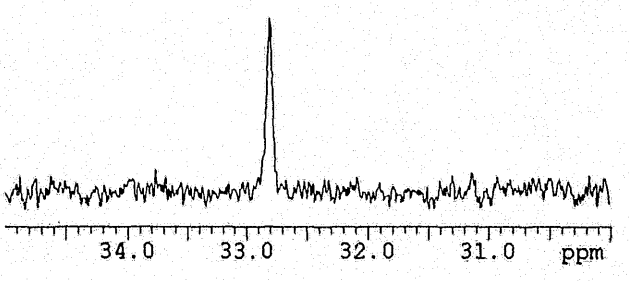


N



Q



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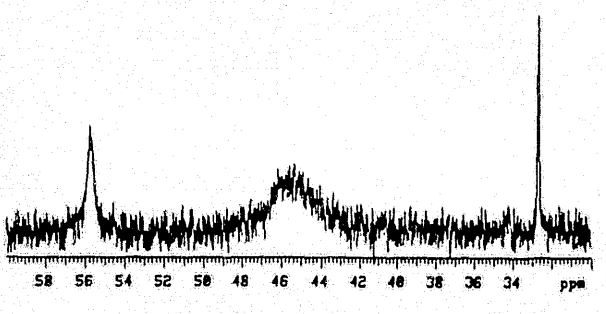

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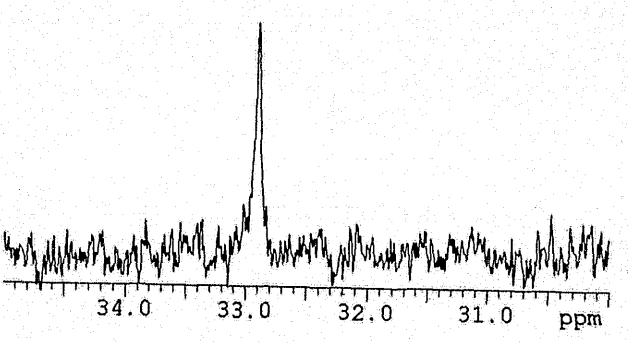

M-P: TMEDA and α-cyano carbon region of ^{13}C NMR spectra of 0.1M [^{6}Li,^{14}N]-7 at -20, -55, -70, and -90 °C respectively (d_8-toluene). **Q-R:** α-cyano carbon region of ^{13}C NMR spectra of 0.1M [^{6}Li,^{15}N]-5 in 1:2 d_8-toluene:d_8-THF at -90 and -110 °C respectively.

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p. 11602 Carlier

Preparation of [^{15}N]phenylacetonitrile:

A 100 ml 24/40 round-bottom flask equipped with a magnetic stirring bar was charged with [^{15}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_2O, and extracted with diethyl ether (1x200 mL, 2x50 mL). The combined ether extracts were washed (2x50 mL 2N HCl, 1x25 mL H_2O), dried over $MgSO_4$, 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).

^{1}H NMR ($CDCl_3$): 3.85 (2H, s), 7.3-7.45 (5H, m).
^{13}C NMR ($CDCl_3$): 23.57 (d, $^2J_{15N\text{-}13C}$ = 3.0 Hz), 117.82 (d,$^1J_{15N\text{-}13C}$ = 16.8 Hz), 127.89, 128.02, 129.11, 129.85.
^{15}N NMR (1:1 Et_2O: Toluene, –90 °C): 247.07 (externally referenced to dimethylethylamine at 25.7 ppm).
IR (NaCl): 2222 cm^{-1} (CN stretch of [^{14}N]phenylacetonitrile occurs at 2255 cm^{-1}).