

Supporting Information

Solution Structures of Lithium Enolates of Cyclopentanone, Cyclohexanone, Acetophenones and Benzyl Ketones. Triple Ions and Higher Lithiate Complexes

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Table of Contents

S1. General Experimental	3
S2. Synthesis	
1,3-Bis-(4-fluorophenyl)-2-propanone (5F-H)	3
1-Phenyl-2-(4-fluorophenyl)ethanone (6F-H)	3
1,3-Diphenyl-2-(trimethylsilyloxy)-1-propene (5H-Si)	4
1,3-Bis-(4-fluorophenyl)-2-(trimethylsilyloxy)-1-propene (5H-Si)	4
1-Phenyl-2-(4-fluorophenyl)-1-(trimethylsilyloxy)ethene (6F-Si)	4
S3. NMR Characterization of Enolate Structures	
General Preparation of Samples for Multinuclear NMR Spectroscopy	5
HMPA Titration of the Lithium Enolate of Cyclopentanone (1-Li)	6
HMPA Titration of the Lithium Enolate of Cyclohexanone (2-Li)	7
HMPA Titration of the Lithium Enolate of 4-Fluoroacetophenone (3F-Li)	8
HMPA Titration of the Lithium Enolate of Acetophenone (3H-Li)	9
TMEDA Titration of the Lithium Enolate of 4-Fluoroacetophenone (3F-Li)	10
PMDTA Titration of the Lithium Enolate of 4-Fluoroacetophenone (3F-Li)	11
HMPA Titration of Lithium 4-Fluorophenolate (4F-Li) in THF/Et ₂ O	12
HMPA Titration of Lithium 4-Fluorophenolate (4F-Li) in Et ₂ O	13
Kinetic and Thermodynamic Isomers of 1,3-Diphenyl-2-propanone Lithium Enolate (5H-Li)	14
¹ H NOE of the <i>E</i> and <i>Z</i> Isomers of Enol Silyl Ether of 1,3-Diphenyl-2-propanone	15
PMDTA Titration of the Lithium Enolate Z-5H-Li	16
TMTAN Titration of the Lithium Enolate Z-5H-Li	17
HMPA Titration of the Lithium Enolate Z-5H-Li	18
Kinetic and Thermodynamic Enolates of 1,3-Bis-(4-fluorophenyl)-2-propanone (5F-Li)	19
¹ H NOE of the of Enol Silyl Ether Isomers of 1,3-Bis-(4-fluorophenyl)-2-propanone (5F-Si)	20
Variable Temperature NMR Study of Dimers of Lithium Enolate <i>E/Z-5F-Li</i>	21
Variable Concentration Study of the Lithium Enolate Z-5F-Li in THF/Et ₂ O	22
Variable Temperature Study of Monomer Dimer Equilibrium of Lithium Enolate Z-5F-Li	23
P4- <i>t</i> Bu Titration of 1,3-Bis-(4-fluorophenyl)-2-propanone (5F-H)	24
Variable Temperature Study of Phenyl Ring Rotation in Z-5F-P4H	25
Variable Temperature Study of Phenyl Ring Rotation in Z-5F-Li	26
TMEDA Titration of Lithium Enolate Z-5F-Li in THF/Et ₂ O	27
TMTAN Titration of Lithium Enolate Z-5F-Li in THF/Et ₂ O	28
PMDTA Titration of Lithium Enolate Z-5F-Li in THF/Et ₂ O	29
PMDTA Titration of Lithium Enolate <i>E/Z-5F-Li</i> in THF/Et ₂ O	30
HMPA Titration of Lithium Enolate Z-5F-Li at -130 °C in THF/Et ₂ O	31
HMPA Titration of Lithium Enolate Z-5F-Li at -140 °C in THF/Et ₂ O	32

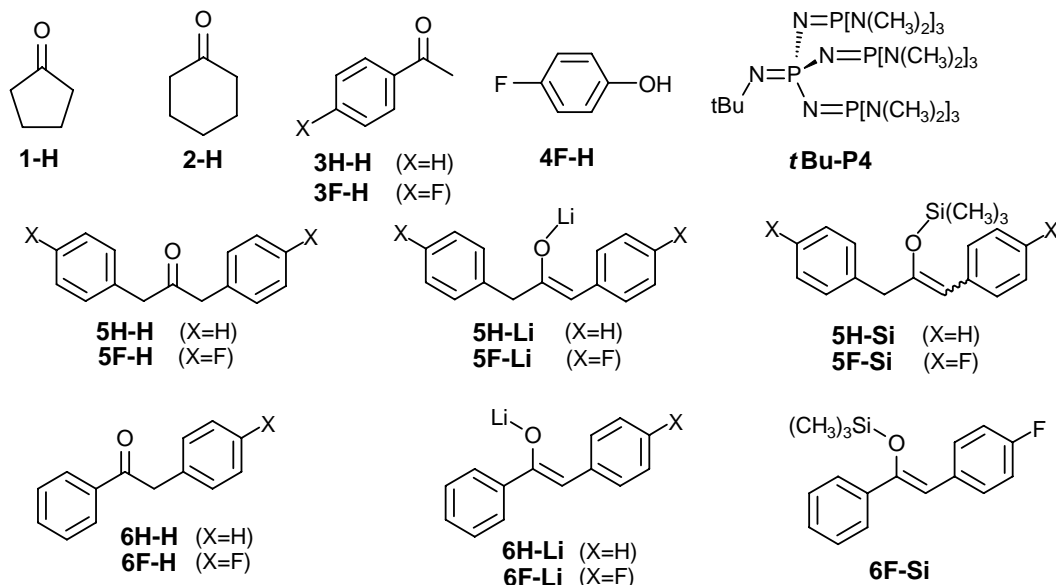
P4 Enolate Titration of Lithium Enolate Z-5F-Li in THF/Et ₂ O	33
Mixing Studies of P4 Enolate Generated Quadruple Ions of Z-5F and Z-6F	34
Dilution Study of Triple ion – Quadruple Ion Equilibrium for Z-5F	35
Variable Temperature Study of Quadruple Ion and Triple Ion of Z-5F	36
Variable Temperature Study of Z-5F-Li with 6 Equiv. HMPA in THF/Et ₂ O	37
HMPA Titration of Lithium Enolate E/Z-5F-Li in THF/Et ₂ O	38
HMPA Titration of Lithium Enolate E-5F-Li at -105 °C in Et ₂ O	39
HMPA Titration of Lithium Enolate E-5F-Li at -125 °C in Et ₂ O	40
HMPA Titration of Lithium Enolate Z-5F-Li at -140 °C in Et ₂ O/Me ₂ O	41
Dilution study of Lithium Enolate Z-5F-Li in Et ₂ O with 6 Equiv. of HMPA	42
HMPA Titration of Lithium Enolate of 1,2-Diphenylethanone (6H-Li) in THF/ Et ₂ O	43
Kinetic and Thermodynamic Deprotonation of 1-Phenyl-2-(4-fluorophenyl)ethanone (6F-H)	44
NOESY Study of Z-1-Phenyl-2-(4-fluorophenyl)-1-(trimethylsilyloxy)ethene (6F-Si)	45
HMPA Titration of Lithium Enolate 6F-Li in THF/ Et ₂ O	47
P4 Titration of 1-Phenyl-2-(4-fluorophenyl)ethanone (6F-H)	48
P4 Enolate Titration of Z Dimer of Lithium Enolate 6F-Li	49

S4. Crystallographic Section (Summary)

PMDTA Solvate of the Lithium Enolate of 1,3-Diphenyl-2-propanone (Z-5H-Li·PMDTA)	50
Lithium Enolate ((Z-5F-Li) ₂ ·(OEt) ₂)	51

S5. References

S6. NMR Spectra



S1. General Experimental.

All reactions requiring a dry atmosphere were performed in glassware flame-dried or dried overnight in a 110 °C oven, sealed with septa and flushed with dry N₂. Tetrahydrofuran (THF) and Et₂O were freshly distilled from sodium benzophenone ketyl under N₂. Commercially available starting materials and reagents were obtained from Aldrich Chemical Company and included: *n*-butyllithium, diisopropylamine, phosphazene base P4-*t*Bu (1-tert-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylideneamino]-2,4,5,4,5-catenadi(phosphazene)) 1 M solution in hexanes, cyclohexanone (**1-H**), cyclopentanone (**2-H**), 4-fluorophenol (**4F-H**), 4-fluoroacetophenone (**3F-H**), acetophenone (**3H-H**), and 1,3-diphenyl-2-propanone (**5H-H**), 1,3-bis-(4-fluorophenyl)-2-propanone (**5F-H**) and 1-phenyl-2-(4-fluorophenyl)ethanone (**6F-H**) were prepared according to previously published procedures.^[S1]

Low-temperature NMR spectra were acquired on a Bruker AVANCE spectrometer using a 10 mm broadband probe at the following frequencies: 360.131 MHz (¹H), 90.556 MHz (¹³C), 338.827 MHz (¹⁹F), 139.96 MHz (⁷Li) and 145.785 MHz (³¹P). All spectra were taken with the spectrometer unlocked. ¹³C NMR spectra were referenced internally to the C-O carbon of THF (δ 67.96), Et₂O (δ 66.57) or Me₂O (δ 60.25). Lorentzian multiplication (LB) of 2-6 Hz was applied to ¹³C NMR spectra. ³¹P NMR spectra were referenced externally to 1.0 M PPh₃ in THF (δ -6.00) or internally to free HMPA (δ 26.40). ¹⁹F NMR spectra were acquired without proton decoupling and were referenced internally to CFCl₃ (δ 0.0), 1,3-difluorobenzene (δ -110.8), or 1,2-difluorobenzene (δ -140). ⁷Li spectra were referenced externally to 0.3 M LiCl/MeOH standard (δ 0.00 ppm) or internally to free ⁷Li(HMPA)₄ (δ -0.40). Probe temperatures were measured internally with the ¹³C chemical shift thermometer: 10% ¹³C enriched (Me₃Si)₃CH.^[S2]

S2. Synthesis

1,3-Bis-(4-fluorophenyl)-2-propanone (5F-H): (See reference [S3] for an X-ray structure of **5F-H**) 4-Fluorophenylacetic acid (4.135 g, 26.8 mmol), 4-(dimethylamino)pyridine (3.53 g, 28.8 mmol), *N*-ethyl-*N'*-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI·HCl) (5.00 g, 26.0 mmol) and 80 mL of dichloromethane were added to a 250 mL round bottom flask. The solution was stirred for four days at room temperature, and 100 mL of 10% HCl solution was added. The organic layer was separated, washed with 10% HCl twice, saturated NaHCO₃ once, dried over MgSO₄ and the solvent was removed under vacuum. The resulting solid was recrystallized from ethanol to yield 2.35 g (74%) of **5F-H**. Melting Point 62-64 °C. ¹H NMR (300 MHz, CDCl₃), δ 3.69 (s, 4H), 6.99 (t, *J* = 8 Hz, 4H), 7.09 (dd, *J* = 5.5, 8.8, 4H). ¹³C NMR (75.4 MHz, CDCl₃), δ 48.4 (s), 115.8 (d, *J*_{CF} = 21.5 Hz), 129.7 (d, *J*_{CF} = 3.2Hz), 131.2 (d, *J*_{CF} = 7.8 Hz), 162.2 (d, *J*_{CF} = 246.6 Hz), 205.3 (s). ¹⁹F NMR (282 MHz, CDCl₃) δ -116 (tt, *J*_{FH} = 5.5, 8.8 Hz). HRMS (EI) (m/z): calcd. for C₁₅H₁₂F₂O (M+) 246.0856; found 246.0860.

1-Phenyl-2-(4-fluorophenyl)ethanone (6F-H). Prepared according to literature procedure.^[S4] ¹H NMR (300 MHz, CDCl₃), δ 4.262 (s, 2H), 7.02 (t, *J* = 8 Hz, 4H), 7.23 (dd, *J* = 5.5, 8 Hz, 2H), 7.47 (t, *J* = 8 Hz, 2H), 7.57 (t, *J* = 8 Hz, 1H), 8.02 (d, *J* = 8 Hz, 2H). ¹³C NMR (75.4 MHz, CDCl₃), δ 44.7 (s), 115.7 (d, *J*_{CF} = 21.5Hz), 128.7 (s), 128.9 (s), 130.4 (d, *J*_{CF} = 3.3Hz), 131.3 (d, *J*_{CF} = 8.1Hz), 133.5 (s), 136.7 (s), 162.16 (d, *J*_{CF} = 246.6Hz), 197.7 (s). ¹⁹F NMR (282 MHz, CDCl₃) δ -116.56 (tt, *J*_{FH} = 5.5, 8.8 Hz). HRMS (EI) (m/z): calcd. for C₁₅H₁₂F₂O (M+) 214.0789; found 214.0795.

1,3-Diphenyl-2-(trimethylsilyloxy)-1-propene (5H-Si). 1,3-Diphenyl-2-propanone (380 μ L, 0.78 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 °C to a 0.1 M solution (3:2 THF/Et₂O) of freshly prepared LiNⁱPr₂. After 10 min at -78 °C for 10 min Et₃N (84 μ L, 0.6 mmol) and Me₃SiCl (160 μ L, 1.2 mmol) were added. The sample was diluted with cold (ca 0 °C) pentane, washed with cold saturated NaHCO₃, dried over MgSO₄, and the solvent was removed under vacuum. The enol silyl ether mixture **5H-Si** was dissolved in *d*₆-benzene and ¹H, ¹⁹F and ¹³C NMR and HRMS spectra were obtained. *Z* Isomer: ¹H NMR (299.73 MHz, CDCl₃), δ 0.04 (s, 9H), 3.63 (s, 2H), 5.32 (s, 1H), 7.01-7.4 (m, 10H). ¹³C NMR (90.56 MHz, CDCl₃), δ 1.01 (s), 49.3 (s), 110.4 (s), 125.8 (s), 126.7 (s), 128.2 (s), 128.3 (s), 128.6 (s), 129.4 (s), 136.8 (s), 138.2 (s), 152.03 (s). *E* Isomer: ¹H NMR (299.73 MHz, CDCl₃), δ 0.06 (s, 9H), 3.53(s, 2H), 5.87 (s, 1H), 7.01-7.3 (m, 10 H). ¹³C NMR (75.37 MHz, CDCl₃), δ 0.45(s), 38.6 (s), 110.8 (s), 110.4 (s), 126.0 (s), 126.4 (s), 110.4 (s), 128.5 (s), 128.7 (s), 129.1 (s), 137.3 (s), 138.7 (s), 153.1(s). HRMS (ESI) (m/z): calcd. for C₁₈H₂₂O₂Si (M+) 282.1435; found 282.1436.

1,3-Bis-(4-fluorophenyl)-2-(trimethylsilyloxy)-1-propene (5F-Si): 1,3-Bis-(4-fluorophenyl)-2-propanone (380 μ L, 0.78 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 °C to a freshly prepared 0.1 M solution of LiNⁱPr₂ in 3:2 THF/Et₂O. Et₃N (84 μ L, 0.6 mmol) and Me₃SiCl (160 μ L, 1.2 mmol) were added at -78 °C. The sample was diluted with cold (ca 0 °C) pentane, washed with cold saturated NaHCO₃, dried over MgSO₄, and the solvent was removed under vacuum. ¹H, ¹⁹F and ¹³C NMR and HRMS were obtained on the resulting enol silyl ether mixture. *Z* Isomer: ¹H NMR (360.16 MHz, CDCl₃), δ 0.07 (s, 9H), 3.41 (s, 2H), 5.29(s, 1H), 6.89 (t, *J* = 8.6 Hz, 2H), 6.95 (*J* = 8.6 Hz, 2H), 7.17 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.38 (dd, *J* = 8.8, 5.5 Hz, 2H). ¹³C NMR (90.56 MHz, CDCl₃), δ 0.98 (s), 43.0 (s), 109.4 (s), 114.9 (d, *J*_{CF} = 21 Hz), 115.4 (d, *J*_{CF} = 21 Hz), 129.8 (d, *J*_{CF} = 8 Hz), δ 130.8 (d, *J*_{CF} = 8 Hz), 132.7 (d, *J*_{CF} = 3 Hz), 133.7 (d, *J*_{CF} = 3 Hz), 151.5 (s), 161.0 (d, *J*_{CF} = 246 Hz), 161.9 (d, *J*_{CF} = 246 Hz). ¹⁹F NMR (338.82 MHz, CDCl₃) δ -117.16 (tt, *J*_{FH} = 8.6, 5.5 Hz), -117.06 (tt, *J*_{FH} = 8.6, 5.5 Hz). *E* Isomer: ¹H NMR (300 MHz, CDCl₃), δ 0.07 (s, 9H), 3.46 (s, 2H), 5.83 (s, 1H), 6.89-6.976 (m, 4H), 7.12 (dd, *J* = 8.8, 5.5 Hz, 4H). ¹³C NMR (75.37 MHz, CDCl₃), δ 0.41(s), 37.6 (s), 109.5 (s), 115.3 (d, *J*_{CF} = 21 Hz), 115.4 (d, *J*_{CF} = 21 Hz), 130.3 (d, *J*_{CF} = 8 Hz), 130.5 (d, *J*_{CF} = 8 Hz), 133.2 (d, *J*_{CF} = 3 Hz), 134.2 (d, *J*_{CF} = 3 Hz), 153.0 (s), 161.5 (d, *J*_{CF} = 246 Hz), 161.8 (d, *J*_{CF} = 246 Hz). ¹⁹F NMR (338.82 MHz, CDCl₃) δ -117.30 (tt, *J*_{FH} = 8.6, 5.5 Hz), -117.66 (tt, *J*_{FH} = 8.6, 5.5 Hz). HRMS (ESI) (m/z): calcd. for C₁₈H₂₀OF₂Si (M+) 318.1247; found 318.1241.

1-Phenyl-2-(4-fluorophenyl)-1-(trimethylsilyloxy)ethene (6F-Si): Freshly prepared LiNⁱPr₂ (0.29 M, 4 mL) in 3:2 THF/Et₂O was added to a solution of 1-phenyl-2-(4-fluorophenyl)ethanone (0.247 g, 1.15 mmol) at -78 °C. The solution was allowed to warm to 0 °C for 1h, and Me₃SiCl (160 μ L, 1.2 mmol) was added. The sample was diluted with cold (ca 0 °C) pentane, washed with cold saturated NaHCO₃, dried over MgSO₄, and the solvent was removed under vacuum. ¹H and ¹³C NMR and HRMS were obtained on the resulting enol silyl ether. *Z* Isomer: ¹H NMR (299.87 MHz, CDCl₃), δ 0.02 (s, 9H), 6.04(s, 1H), 6.95 (t, *J* = 8.6 Hz, 2H), 7.27 (m, 3H), 7.51 (m, 2H), 7.57 (dd, *J* = 8.8, 5.5 Hz, 2H). ¹³C NMR (75.37 MHz, CDCl₃), δ 0.87 (s), 109.5 (s), 115.13 (d, *J*_{CF} = 21 Hz), 126.3 (s), 128.3 (s), 128.3 (s), 130.3 (d, *J*_{CF} = 8 Hz), 132.9 (d, *J*_{CF} = 3 Hz), 139.7 (s), 150.8 (s), 161.3 (d, *J*_{CF} = 246 Hz). ¹⁹F NMR (282 MHz, CDCl₃) δ -116.30 (tt, *J*_{FH} = 8.6, 5.5 Hz). *E* Isomer: ¹H NMR (300 MHz, CDCl₃), δ 0.07 (s, 9H), 5.83 (s, 1H), 6.89-6.976 (m, 4H), 7.12 (dd, *J* = 8.8, 5.5 Hz, 4H). HRMS (ESI) (m/z): calcd. for C₁₇H₁₉OFSi (M+) 286.1184; found 286.1190.

S3. NMR Characterization of Enolate Structures

General Preparation of Enolate Samples for Multinuclear NMR Spectroscopy. Lithium diisopropylamide was prepared fresh by the following procedure. Solvent was added (typically 1.8 mL of THF and 1.2 mL of Et₂O) including 1-2 μ L of 10% ¹³C enriched (Me₃Si)₃CH as a shift thermometer^[S2] to a dried thin-walled 10 mm NMR tube that had been stored under vacuum, fitted with septa, and flushed with N₂ or Ar. Silicon grease was applied to the interface between the tube and the septa before securing with parafilm for a better seal, as well as to the top of the septa to seal needle punctures. The NMR tube was cooled to -78 °C under positive N₂ or Ar pressure and diisopropylamine (42 μ L, 0.30 mmol) and *n*-BuLi (120 μ L, 2.5 M) were added to the solution. The solution was warmed to 0 °C in an ice bath for 5 min, and then cooled to -78 °C under positive N₂ or Ar pressure. The carbonyl compound was added by syringe either neat or as a solution in the desired solvent. Samples free of diisopropylamine were prepared from either crystallized material or from cleavage of the enol silyl ether. Experiments run using these samples did not differ from those containing diisopropylamine. Samples were stored at -78 °C. The spectrometer probe was cooled to <-78 °C, the sample was inserted and the probe was shimmed on the ¹³C FID of the THF peak. Spectra of NMR active nuclei which usually included ¹³C, ³¹P, ¹⁹F, ⁷Li and ¹H were acquired. At this point, a titration, variable temperature or variable concentration experiment could be performed. In the case of a titration experiment, for each addition the sample was ejected, placed in a -78 °C bath, the silicon grease was removed from the top of the septum, a desired amount of cosolvent was added, silicon grease was reapplied to the top of the septum and the NMR spectra were measured, including a ¹³C NMR spectrum to determine the sample temperature.

HMPA Titration of the Lithium Enolate of Cyclopentanone (1-Li). Cyclopentanone (300 μ L, 1.0 M solution in THF) was added to a freshly prepared solution of LiNⁱPr₂ in 3:2 THF/Et₂O and ¹³C and ⁷Li spectra were acquired at -120 °C. ¹³C, ⁷Li, and ³¹P spectra were obtained at -130 °C with 0, 0.25 (13 μ L), 0.5 (26 μ L), 1.0 (52 μ L), 2.0 (104 μ L) and 6.0 equiv. (312 μ L) of HMPA added. Spectra are shown in Figure 1 and S-1.

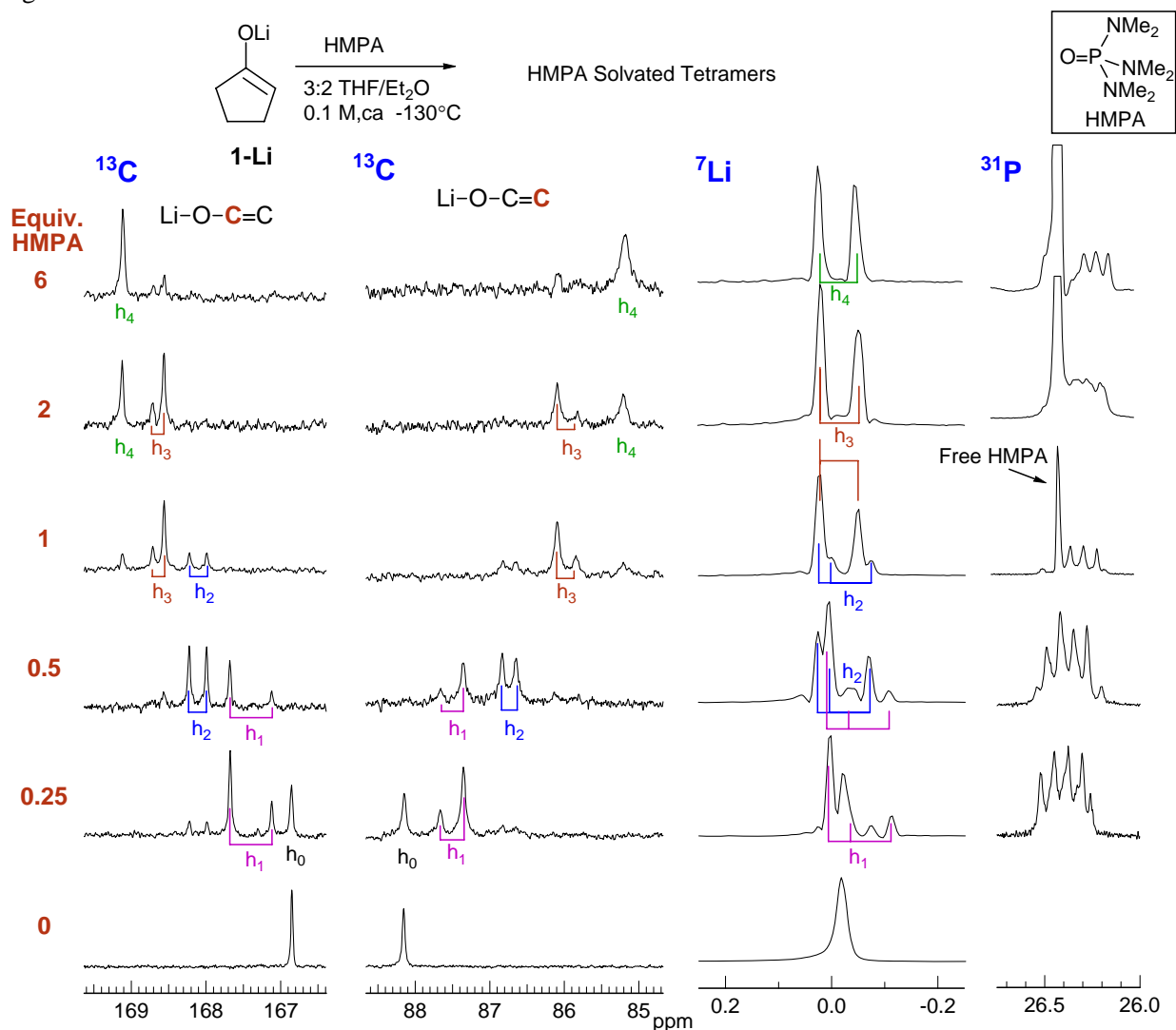


Figure S-1. HMPA titration of **1-Li** in 3:2 THF/ Et₂O at -122 °C. Sequential solvation of the aggregate was observed as the concentration of HMPA was increased. The individual HMPA solvated aggregates have differing ratios of NMR signals based on the symmetry of the aggregate. For example the mono HMPA solvated tetramer (h₁, shown in magenta above) appears as a 1:3 ratio of signals while the bis HMPA solvated tetramer (h₂, shown in blue above) appears as a 1:1 ratio of signals. Based upon the ratio of new NMR signals observed for the new HMPA solvates formed, the lithium enolate of cyclopentanone was assigned a tetrameric structure (h_n = number of coordinated HMPA molecules).

HMPA Titration of the Lithium Enolate of Cyclohexanone (2-Li). Cyclohexanone (300 μL , 1.0 M solution in THF) was added to a freshly prepared solution of LiN^iPr_2 in 3:2 THF/ Et_2O and ^{13}C and ^7Li spectra were acquired at $-125\text{ }^\circ\text{C}$. ^{13}C , ^7Li , and ^{31}P spectra were obtained at $-130\text{ }^\circ\text{C}$ with 0, 0.25 (13 μL), 0.5 (26 μL), 1.0 (52 μL), 2.0 (104 μL) and 6.0 equiv. (312 μL) of HMPA added. Spectra are shown in Figure S-2.

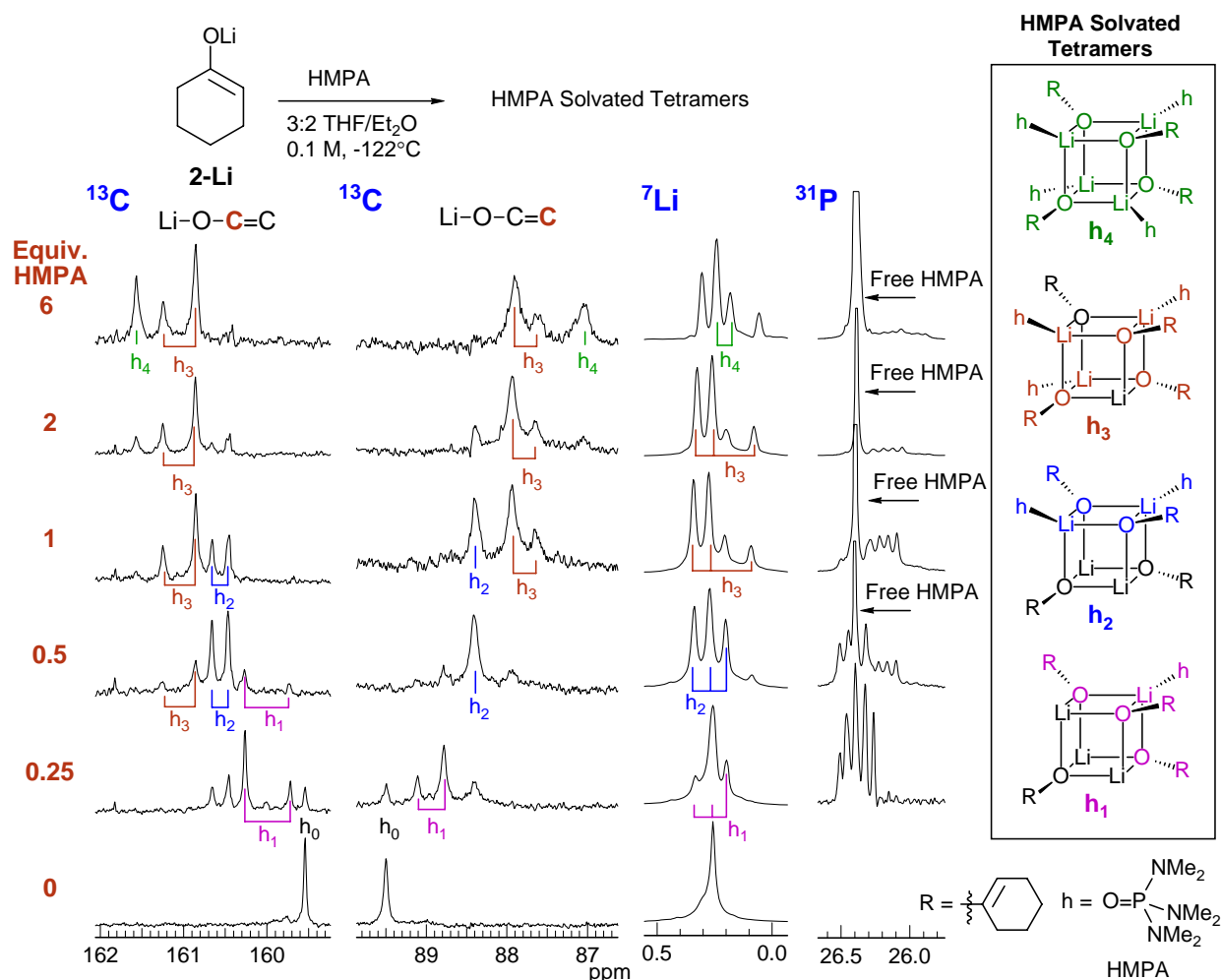


Figure S-2. HMPA titration of **2-Li** in 3:2 THF/ Et_2O at $-122\text{ }^\circ\text{C}$. (h = HMPA) Sequential solvation of the aggregate was observed as the concentration of HMPA was increased. The individual HMPA solvated aggregates have differing ratios of NMR signals based on the symmetry of the aggregate. For example the mono HMPA solvated tetramer (h_1 , shown in magenta above) appeared as a 1:3 ratio of signals while the bis HMPA solvated tetramer (h_2 , shown in blue above) appeared as a 1:1 ratio of signals. Based upon the ratio of new ^{13}C and ^7Li signals observed for each HMPA solvate, the lithium enolate of cyclohexanone was assigned a tetrameric structure (h_n = number of coordinated HMPA molecules).

HMPA Titration of the Lithium Enolate of 4-Fluoroacetophenone (3F-Li). 4-

Fluoroacetophenone (72 μL , 0.6 mmol) was added to a freshly prepared solution of 0.2 M LiN^iPr_2 in 3:2 THF/ Et_2O and ^{13}C , ^{19}F and ^7Li spectra were acquired at -120°C . ^{13}C , ^7Li , ^{19}F and ^{31}P spectra were obtained at -120°C with 0, 0.25 (26 μL), 0.5 (52 μL), 1.0 (104 μL), 2.0 (208 μL) and 6.0 equiv. (624 μL) of HMPA added. Spectra are shown in Figure 3 and S-3.

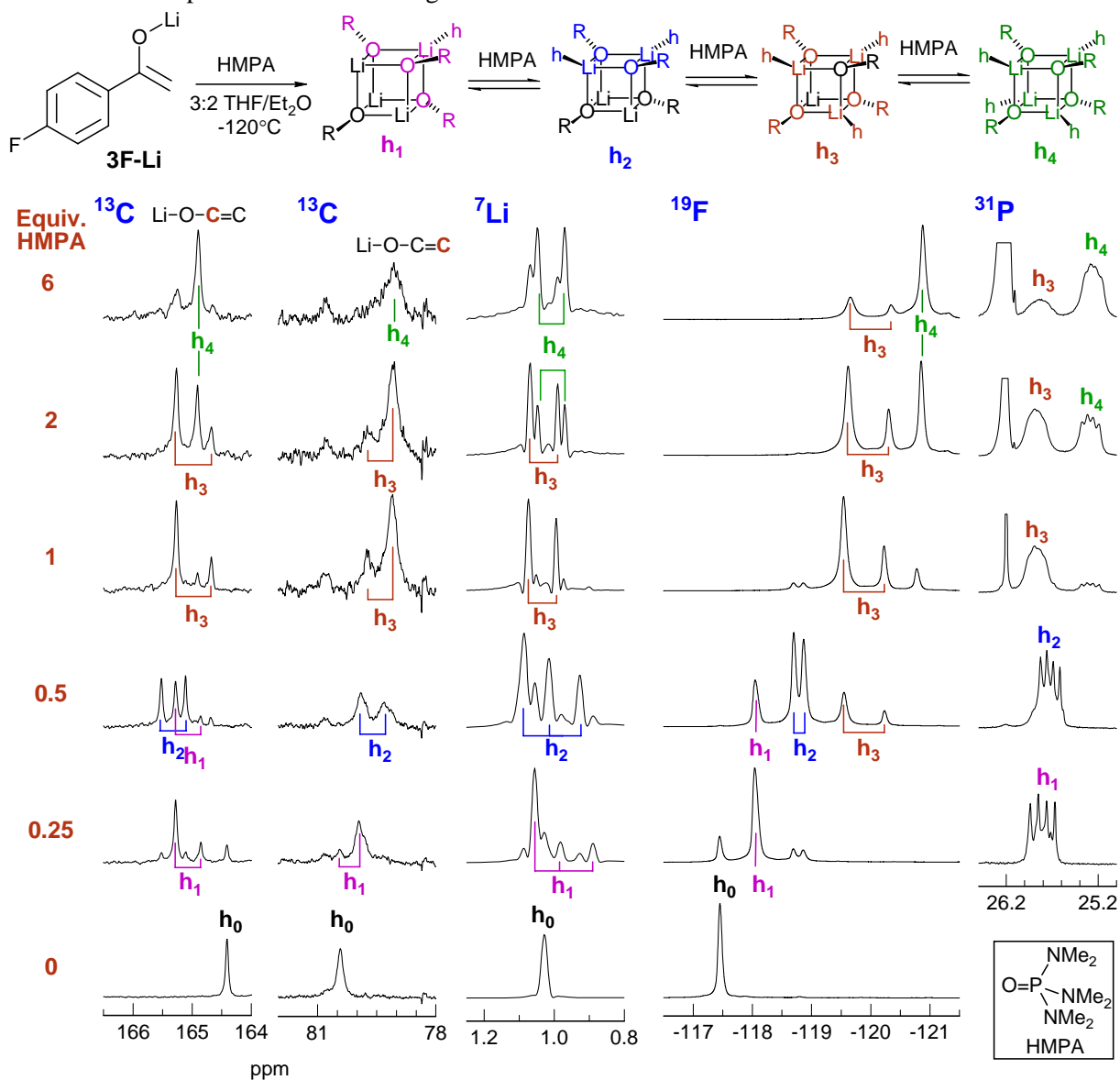


Figure S-3. HMPA titration of 3F-Li in 3:2 THF/ Et_2O at -120°C . (h = HMPA) Sequential solvation of the tetramer was observed as the concentration of HMPA was increased. The individual HMPA solvated aggregates have differing ratios of NMR signals based on the symmetry of the aggregate. For example the mono HMPA solvated tetramer (h_1 , shown in magenta above) appears as 1:3 ratio of signals while the bis HMPA solvated tetramer (h_2 , shown in blue above) appears as a 1:1 ratio of signals (h_n = number of coordinated HMPA molecules).

HMPA Titration of the Lithium Enolate of Acetophenone (3H-Li). Acetophenone (33 μ L, 0.3 mmol) was added to a 0.2 M solution (3:2 THF/Et₂O) of freshly prepared LiNⁱPr₂ and ¹³C, ¹⁹F and ⁷Li spectra were acquired at -125 °C. ¹³C, ⁷Li, ¹⁹F and ³¹P spectra were obtained at -125 °C with 0, 0.25 (13 μ L), 0.5 (26 μ L), 1.0 (52 μ L), and 2.0 equiv. (104 μ L) of HMPA added. Spectra are shown in Figure S-4.

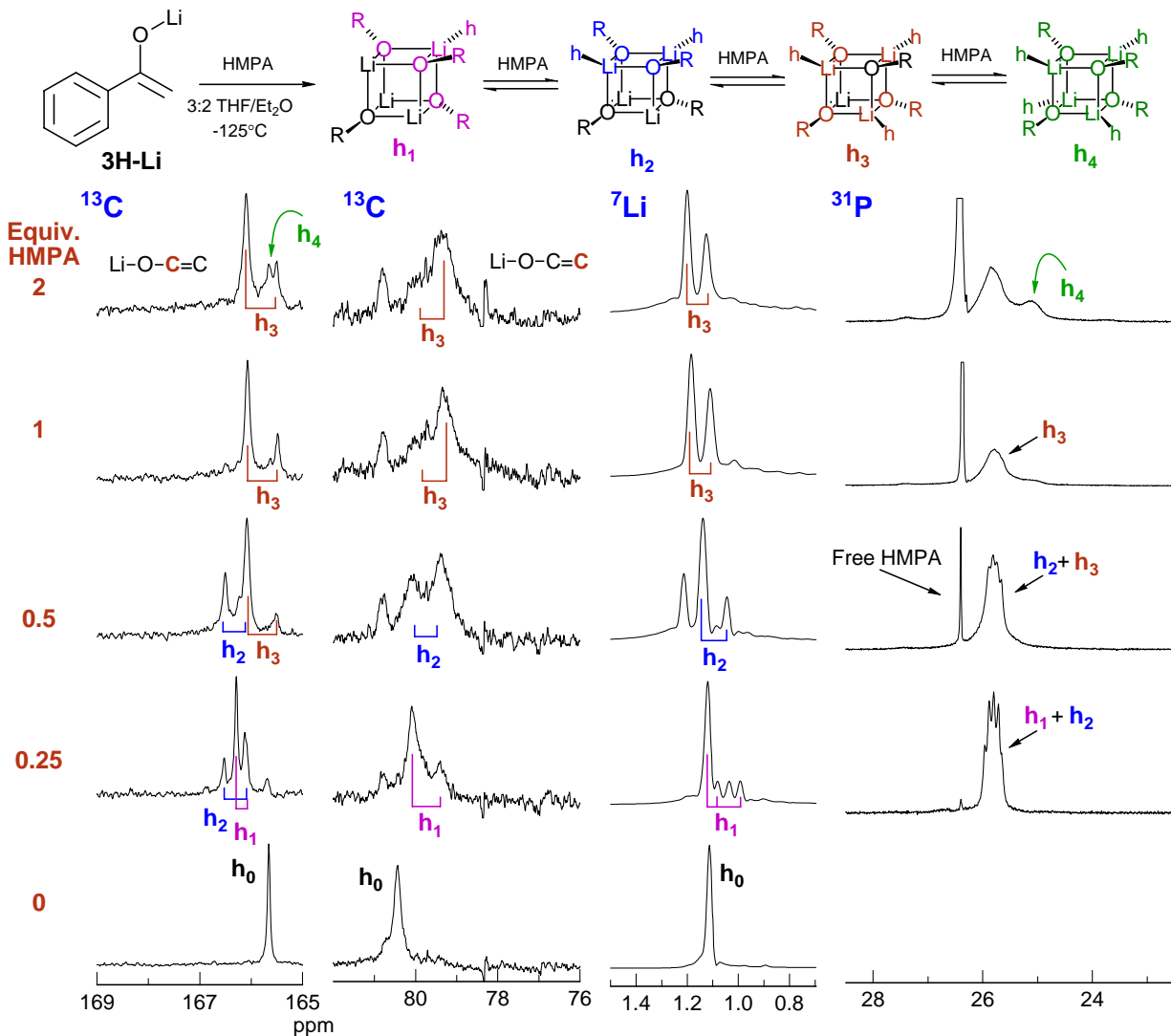


Figure S-4. HMPA titration of 3H-Li in 3:2 THF/ Et₂O at -125 °C. (h = HMPA) Sequential solvation of the tetramer was observed as the concentration of HMPA was increased.

TMEDA Titration of the Lithium Enolate of 4-Fluoroacetophenone (3F-Li). 4-

Fluoroacetophenone (36 μL , 0.3 mmol) was added to a freshly prepared solution of 0.1 M LiN^iPr_2 in 3:2 THF/ Et_2O and ^{13}C , ^{19}F and ^7Li spectra were acquired at -125°C . ^{13}C , ^7Li , and ^{19}F spectra were obtained at -125°C with 0, 1.0 (45 μL), and 4.0 equiv. (180 μL) of TMEDA added. Spectra are shown in Figure S-5.

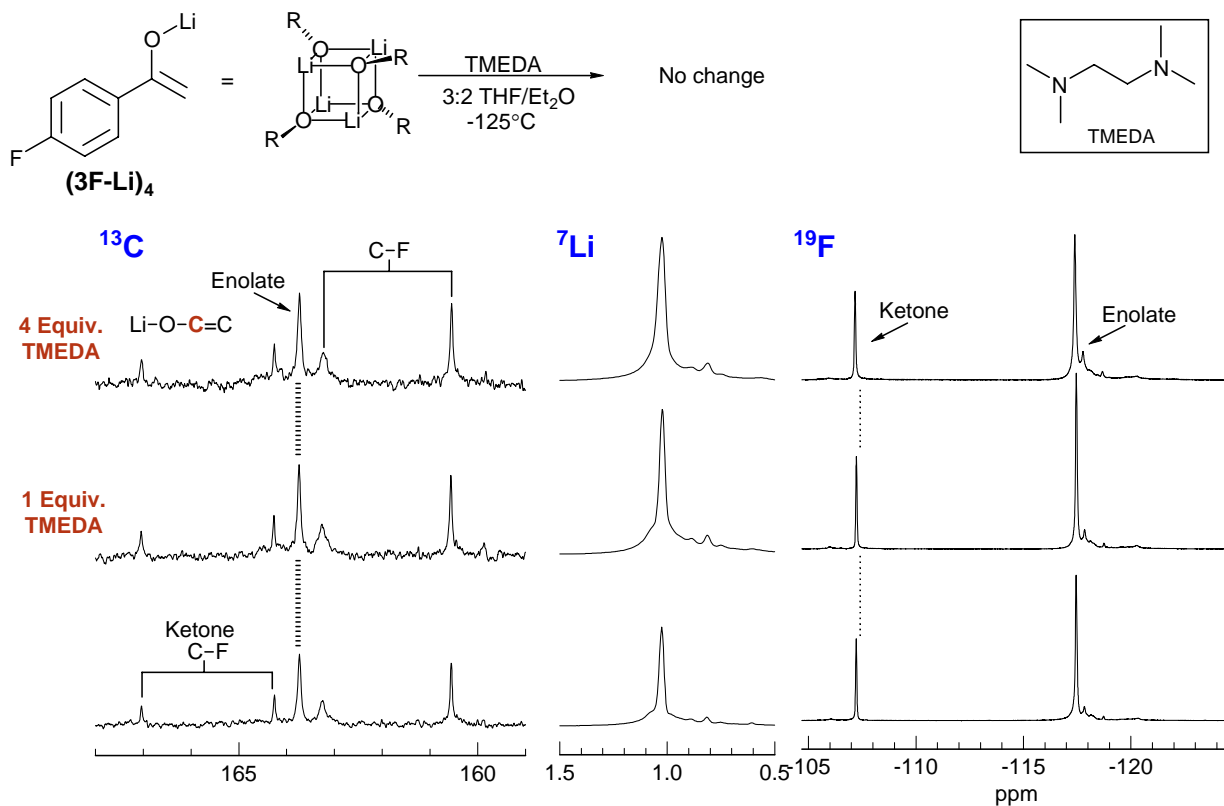


Figure S-5. TMEDA titration of 3F-Li in 3:2 THF/ Et_2O at -125°C . No change in the tetramer was observed up to four equivalents of TMEDA.

PMDTA Titration of the Lithium Enolate of 4-Fluoroacetophenone (**3F-Li**). 4-

Fluoroacetophenone (36 μL , 0.3 mmol) was added to a freshly prepared solution of 0.1 M LiN^iPr_2 in 3:2 THF/ Et_2O and ^{13}C , ^{19}F and ^7Li spectra were acquired at -125°C . ^{13}C , ^7Li , and ^{19}F spectra were obtained at -125°C with 0, 1.0 (62 μL), 4.0 (250 μL) and 10.0 equiv. (626 μL) of PMDTA added. Spectra are shown in Figure S-6.

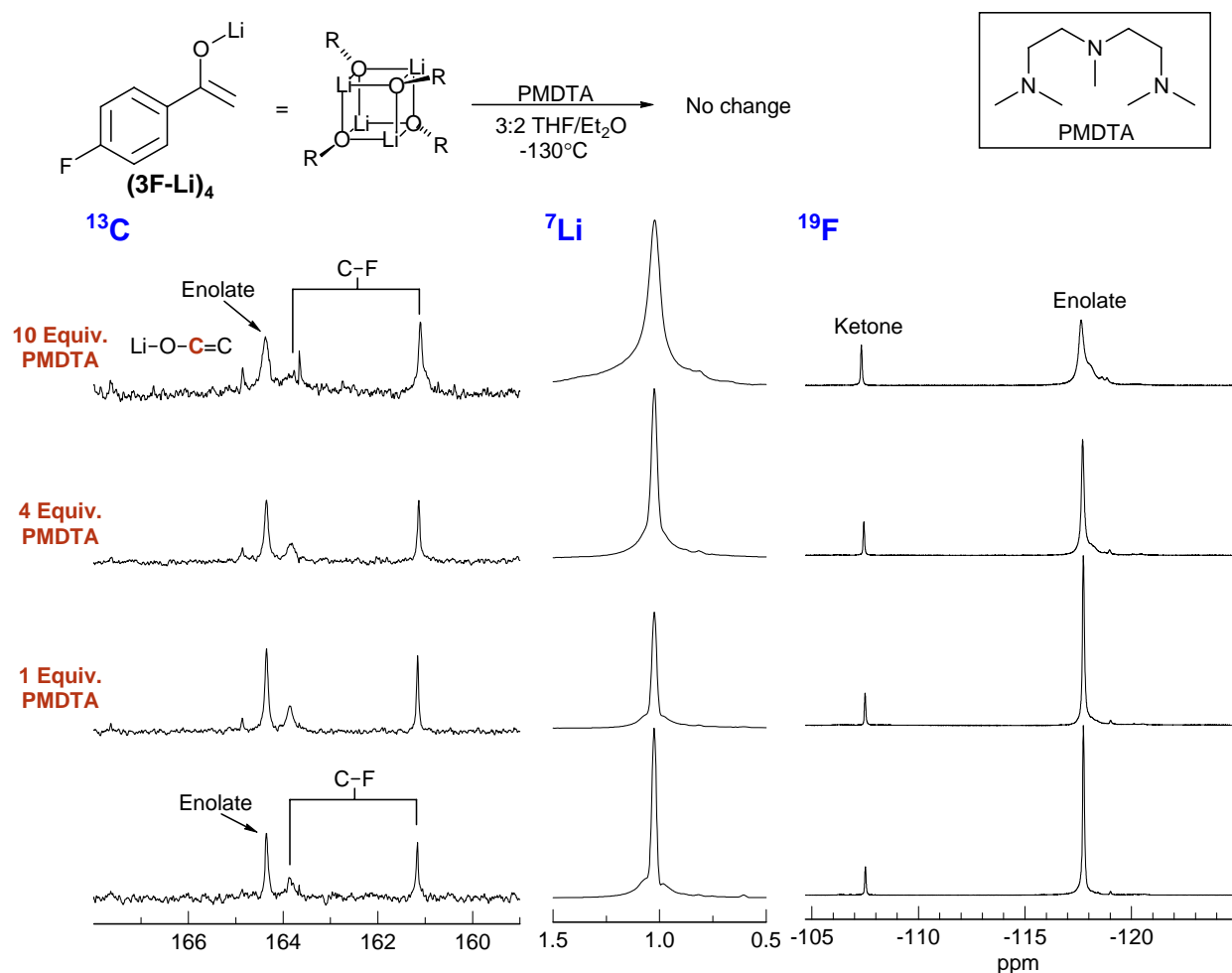


Figure S-6. PMDTA titration of **3F-Li** in 3:2 THF/ Et_2O at -125°C . No change in the tetramer is observed as the concentration of PMDTA was increased up to four equivalents. As the solution became increasingly concentrated in PMDTA at 10 equivalents (ca 5% of solution) broadening was observed in the ^{13}C and ^7Li NMR signals of the enolate and a broad shoulder appeared on the ^{19}F NMR signals of the lithium enolate. This may indicate that some solvation of the tetramer by the PMDTA is occurring at these higher concentrations of PMDTA.

HMPA Titration of Lithium 4-Fluorophenolate (4F-Li) in THF/Et₂O. 4-Fluorophenol (350 μ L, 0.85 M solution in THF/Et₂O) was added to a freshly prepared solution of 0.1 M LiⁿPr₂ in 3:2 THF/Et₂O. ¹³C, ⁷Li, ¹⁹F and ³¹P spectra were obtained at -120 °C with 0, 0.25 (13 μ L), 0.5 (26 μ L), 0.75 (39 μ L), 1.0 (52 μ L), 2.0 (104 μ L), 4.0 (208 μ L) and 6.0 equiv. (312 μ L) of HMPA added. Spectra are shown in Figure 4 and S-7.

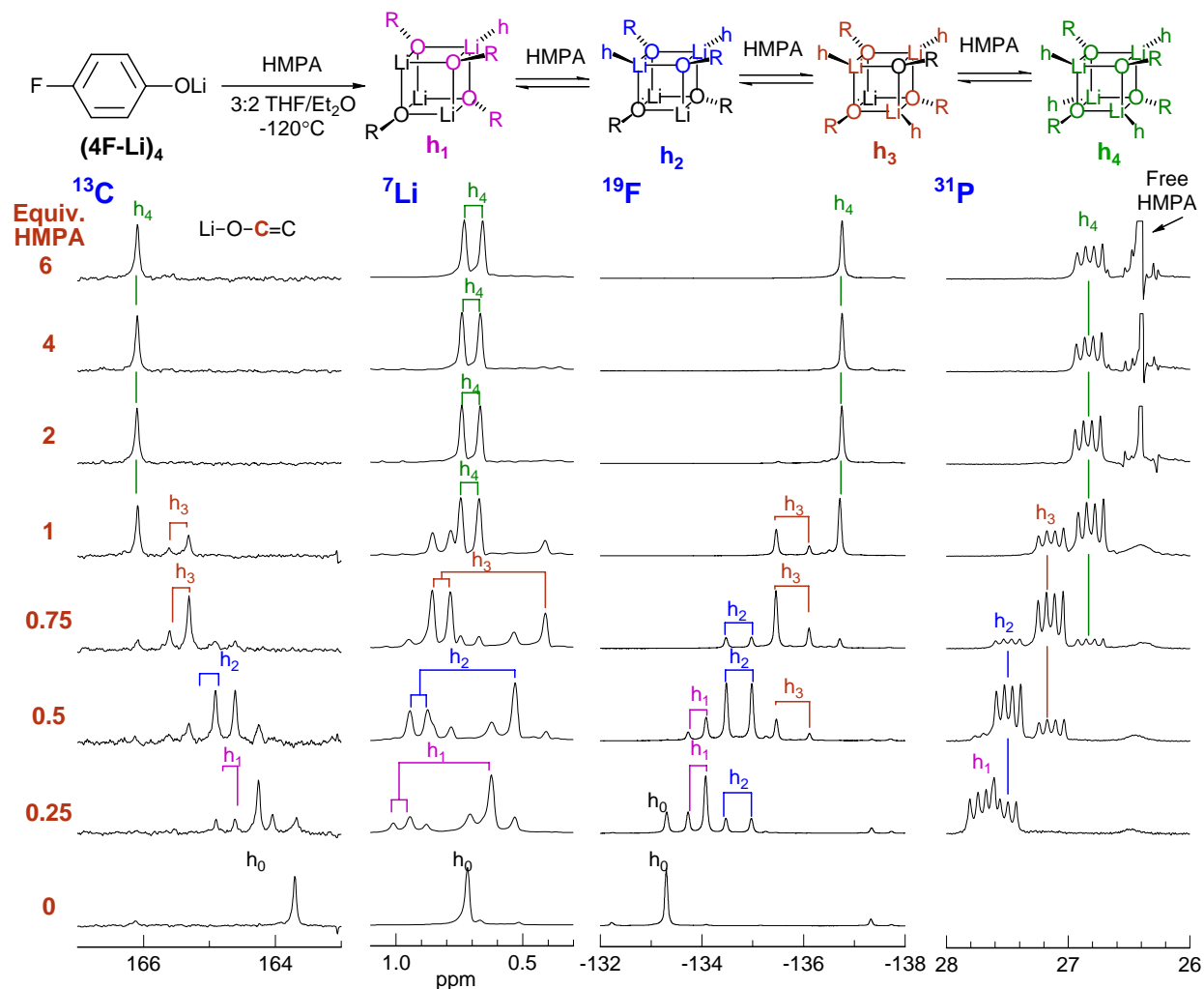


Figure S-7. HMPA titration of the lithium 4-fluorophenolate in 3:2 THF/ Et₂O at -120 °C. Sequential solvation of the aggregate was observed as the concentration of HMPA was increased. The individual HMPA solvated aggregates have differing ratios of NMR signals based on the symmetry of the aggregate. For example the mono HMPA solvated tetramer (h₁, shown in magenta above) appears as 1:3 ratio of signals while the bis HMPA solvated tetramer (h₂, shown in blue above) appears as a 1:1 ratio of signals. Based upon the ratio of new ¹³C, ¹⁹F and ⁷Li signals observed for the new HMPA solvates, the lithium 4-fluorophenolate can be assigned a tetrameric structure (h_n = number of coordinated HMPA molecules).

HMPA Titration of Lithium 4-Fluorophenolate (4F-Li) in Et₂O 4-Fluorophenol (530 μ L, 0.56 M solution in Et₂O) was added to a freshly prepared solution of LiN^tPr₂ in Et₂O. ¹³C, ⁷Li, ¹⁹F and ³¹P spectra were obtained at -120 °C with 0, 0.25 (13 μ L), 0.5 (26 μ L), 1.0 (52 μ L), 1.5 (78 μ L) and 3.0 equiv. (156 μ L) of HMPA added. Spectra are shown in Figure S-8.

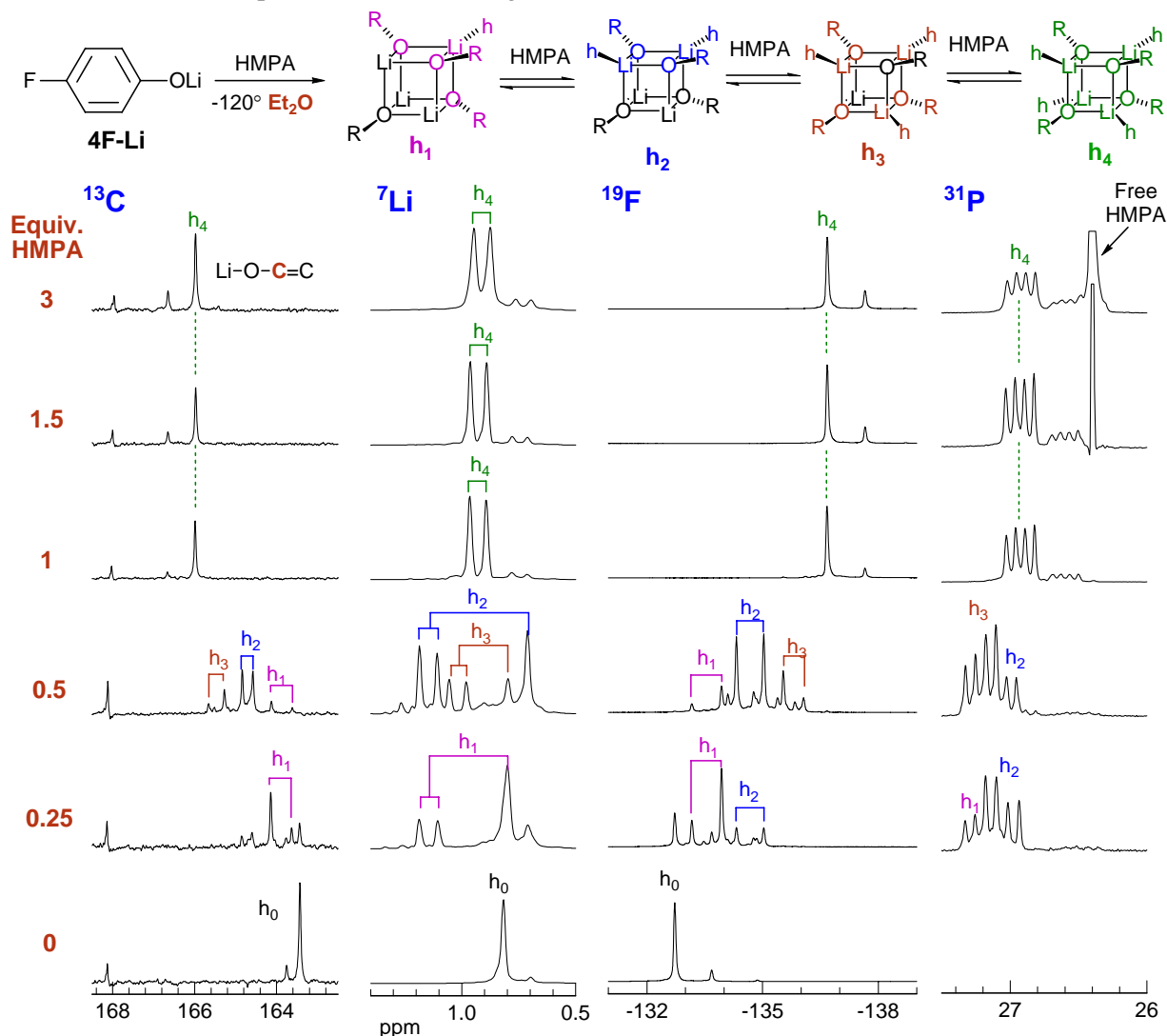


Figure S-8. HMPA titration of the lithium 4-fluorophenolate (4F-Li) in Et₂O at -120 °C. Sequential solvation of the aggregate was observed as the concentration of HMPA was increased. The individual HMPA solvated aggregates have differing ratios of NMR signals based on the symmetry of the aggregate. For example the mono HMPA solvated tetramer (h₁, shown in magenta above) appears as 1:3 ratio of signals while the bis HMPA solvated tetramer (h₂, shown in blue above) appears as a 1:1 ratio of signals. Based upon the ratio of new ¹³C, ¹⁹F and ⁷Li signals observed for the new HMPA solvates, lithium 4-fluorophenolate can be assigned a tetrameric structure (h_n = number of coordinated HMPA molecules).

Kinetic and Thermodynamic Isomers of the Lithium Enolate of 1,3-Diphenyl-2-propanone (5H-Li). 1,3-Diphenyl-2-propanone (380 μ L, 0.78 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 $^{\circ}$ C to a freshly prepared solution of 0.1 M LiNⁱPr₂ in 3:2 THF/Et₂O and ¹³C and ⁷Li spectra were acquired at -130 $^{\circ}$ C. The sample was allowed to warm to room temperature (ca 25 $^{\circ}$ C) for two hours after which the sample was recooled and ¹³C and ⁷Li spectra were acquired at -130 $^{\circ}$ C. Spectra are shown in Figure 5 and S-9.

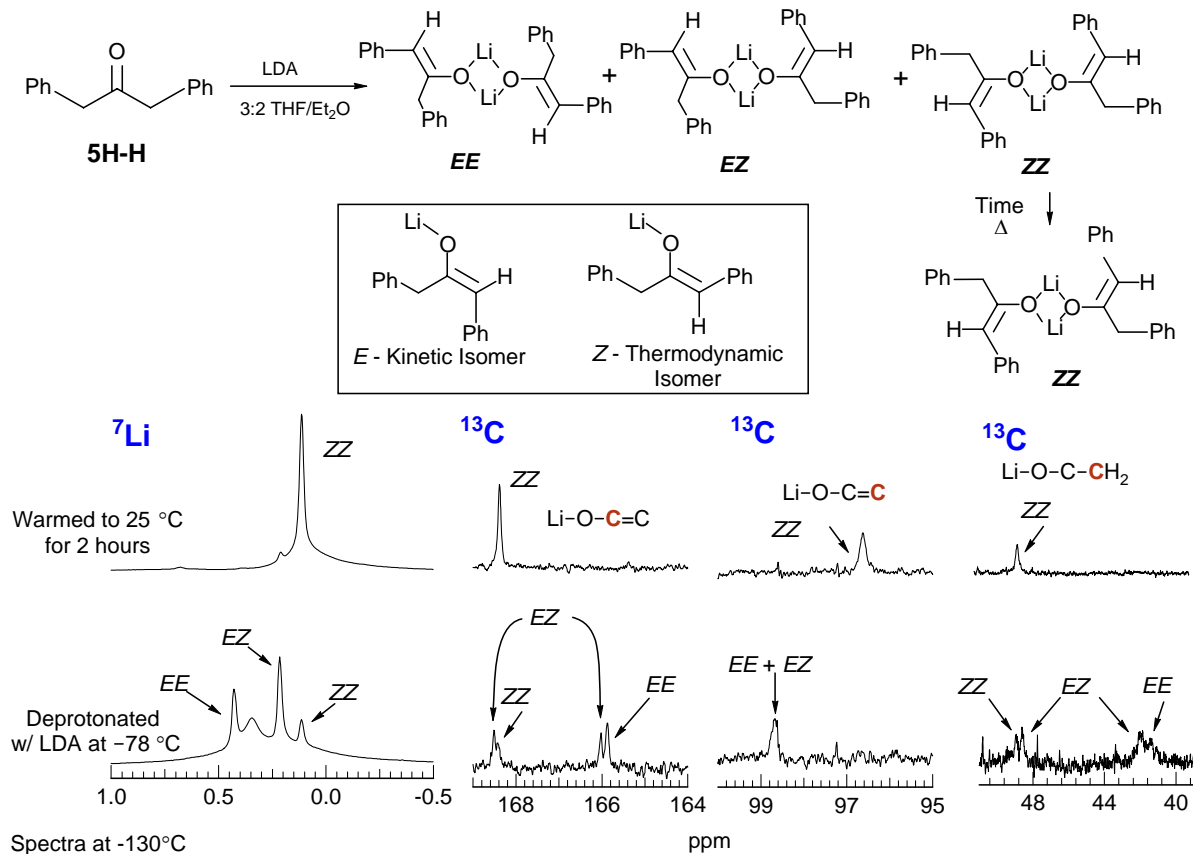


Figure S-9. NMR spectra of the 5H-Li dimer mixture that arises from the *E* and *Z* isomers generated by the kinetic deprotonation of 1,3-diphenyl-2-propanone in 3:2 THF/ Et₂O at -130 $^{\circ}$ C. Equilibration of the solution produced a single species identified as the *ZZ* dimer. *E* and *Z* isomers were assigned based on Me₃SiCl quenches and analysis of the NMR spectra of the resulting enol silyl ether mixture.

¹H NOE of the *E* and *Z* Isomers of the Enol Silyl Ethers of 1,3-Diphenyl-2-propanone. 1,3-Diphenyl-2-propanone (380 μ L, 0.78 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 $^{\circ}$ C to a freshly prepared solution of 0.1 M LiNⁱPr₂ in 3:2 THF/Et₂O. After 10 min at -78 $^{\circ}$ C, Et₃N (84 μ L, 0.6 mmol) and Me₃SiCl (160 μ L, 1.2 mmol) were added. The sample was diluted with cold (ca 0 $^{\circ}$ C) pentane, washed with cold saturated NaHCO₃, dried over MgSO₄, and the solvent was removed under vacuum. The enol silyl ether was dissolved in *d*₆-benzene and NMR spectra were obtained. Spectra are shown in Figure S-10.

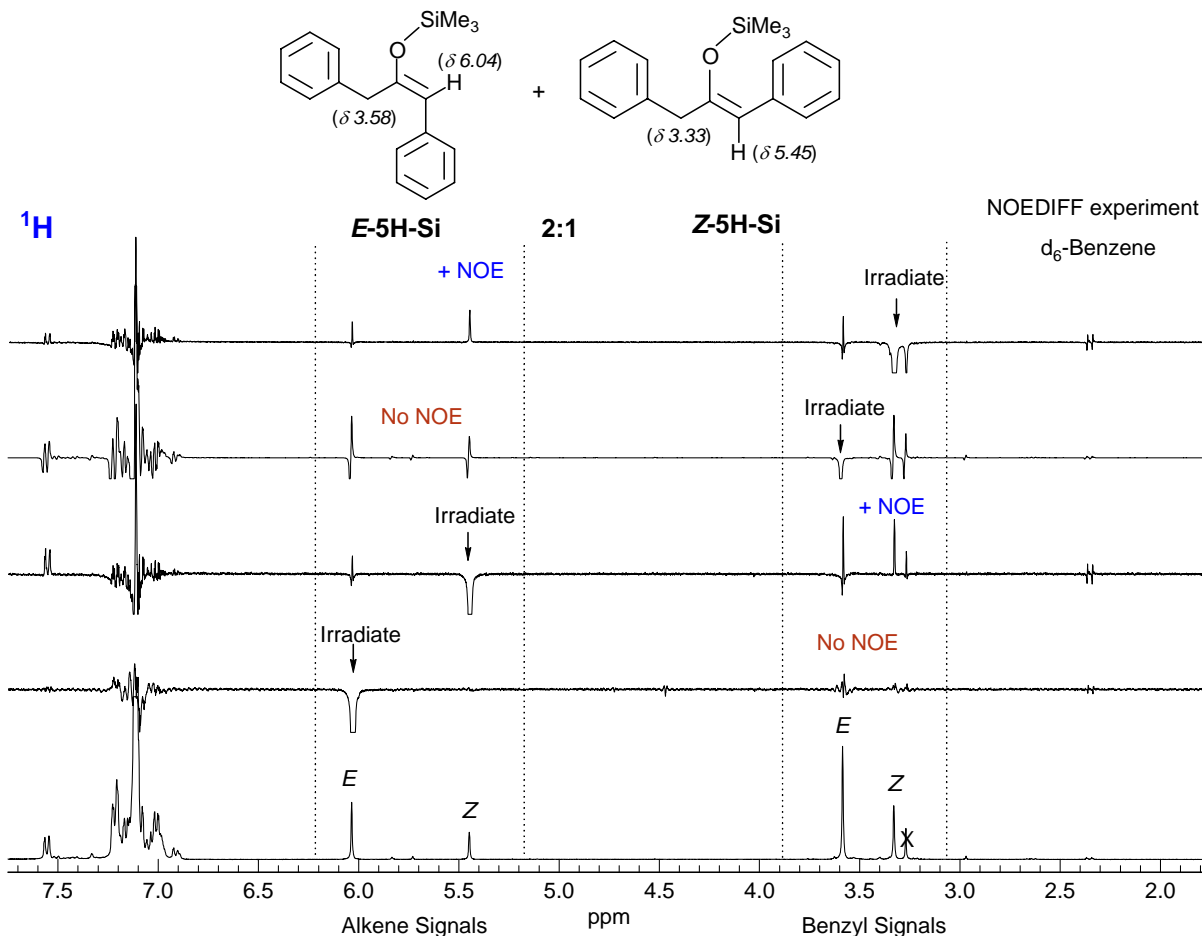


Figure S-10. NOE difference ¹H NMR spectra of the *E* and *Z* isomers (2:1) of the enol silyl ether of 1,3-diphenyl-2-propanone (**5H-Si**).

PMDTA Titration of Lithium Enolate of Z-5H-Li. 1,3-Diphenyl-2-propanone (410 μL , 0.73 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 $^{\circ}\text{C}$ to a freshly prepared solution of 0.1 M LiNⁱPr₂ in 3:2 THF/Et₂O. The solution was allowed to warm to room temperature (ca 25 $^{\circ}\text{C}$) for several hours before ¹³C and ⁷Li spectra were acquired at -130 $^{\circ}\text{C}$. ¹³C and ⁷Li spectra were obtained at -130 $^{\circ}\text{C}$ with 0, 0.5 (31 μL), 1.0 (62 μL), 1.5 (93 μL) and 2.0 equiv. (124 μL) of PMDTA added. Spectra are shown in Figure S-11.

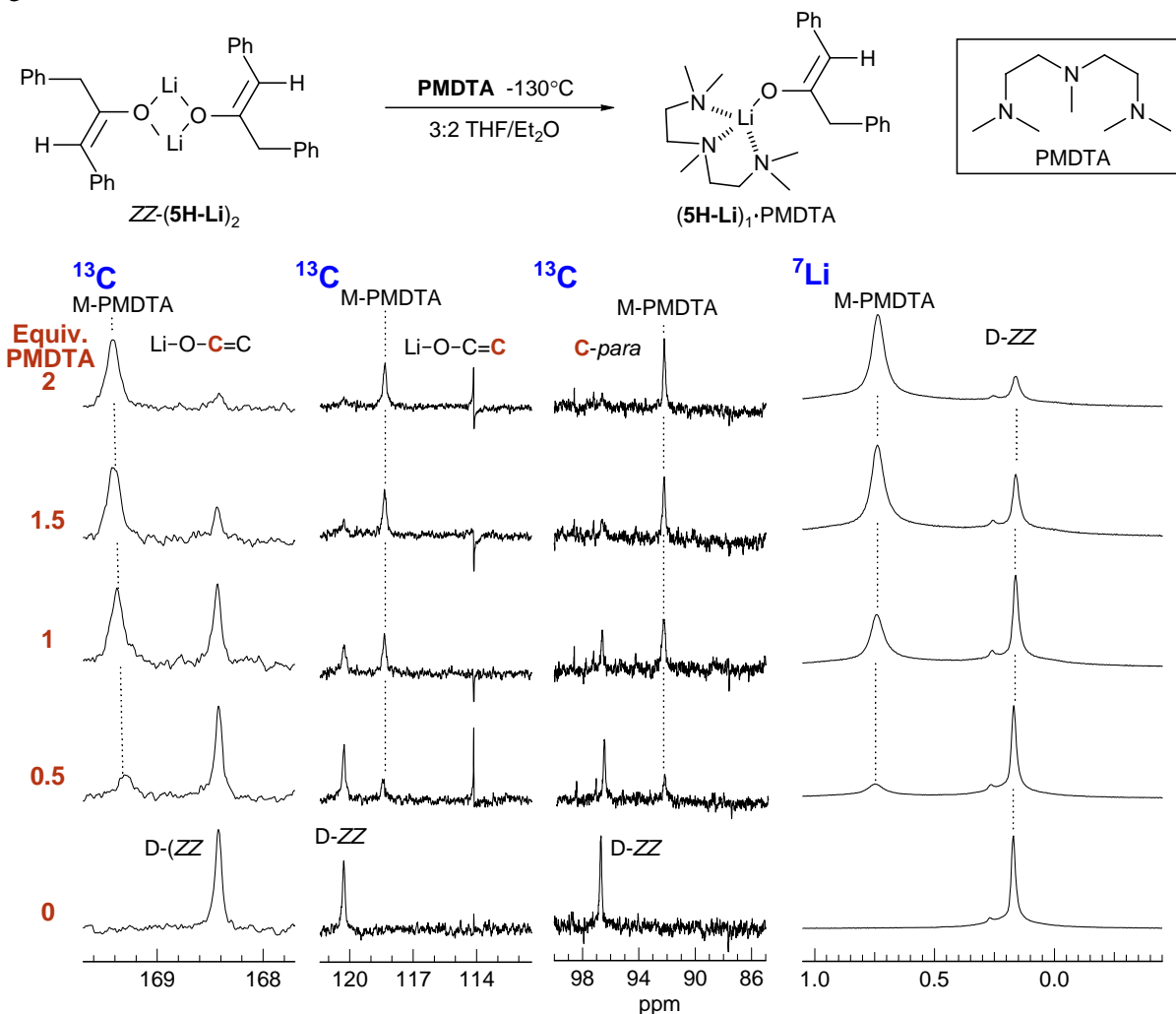


Figure S-11. PMDTA titration of **5H-Li** in 3:2 THF/ Et₂O at -130 $^{\circ}\text{C}$. Deaggregation of the dimer to a PMDTA solvated monomer was observed as the concentration of PMDTA was increased (M = monomer, D=dimer).

TMTAN Titration of Lithium Enolate of Z-5H-Li. 1,3-Diphenyl-2-propanone (640 μL , 0.46 M solution in 3:2 THF/ Et_2O , 0.3 mmol) was added at $-78\text{ }^\circ\text{C}$ to a freshly prepared solution of 0.1 M LiN^iPr_2 in 3:2 THF/ Et_2O . The solution was allowed to warm to room temperature (ca $25\text{ }^\circ\text{C}$) for several hours before ^{13}C and ^7Li spectra were acquired at $-130\text{ }^\circ\text{C}$. ^{13}C and ^7Li spectra were obtained at $-130\text{ }^\circ\text{C}$ with 0, 0.5 (29 μL), 1.0 (58 μL), and 1.5 equiv. (116 μL) of TMTAN added. Spectra are shown in Figure S-12.

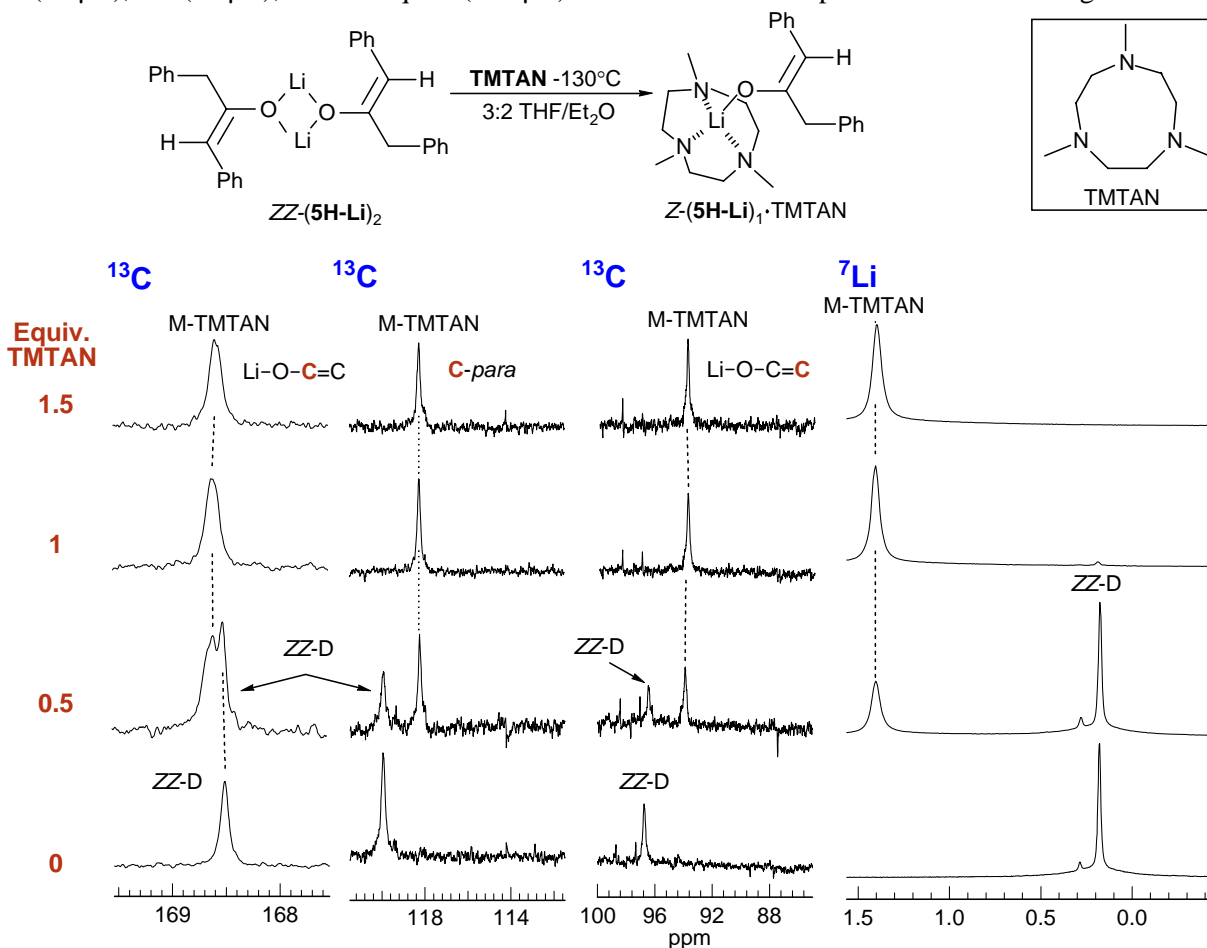


Figure S-12. TMTAN titration of Z-5H-Li in 3:2 THF/ Et_2O at $-130\text{ }^\circ\text{C}$. Deaggregation of the dimer was observed as the concentration of TMTAN was increased with formation of a mono-TMTAN solvated monomer (M = monomer, D = dimer).

HMPA Titration of Lithium Enolate of Z-5H-Li. 1,3-Diphenyl-2-propanone (380 μL , 0.78 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 °C to a freshly prepared solution of 0.1 M LiNⁱPr₂ in 3:2 THF/Et₂O. The solution was allowed to warm to room temperature (ca 25 °C) for several hours before ¹³C and ⁷Li spectra were acquired at -130 °C. ¹³C, ⁷Li, and ³¹P spectra were obtained at -125 °C with 0, 0.25 (13 μL), 0.5 (26 μL), 1.0 (52 μL), 2.0 (104 μL) and 6.0 equiv. (312 μL) of HMPA added. Spectra are shown in Figure S-13.

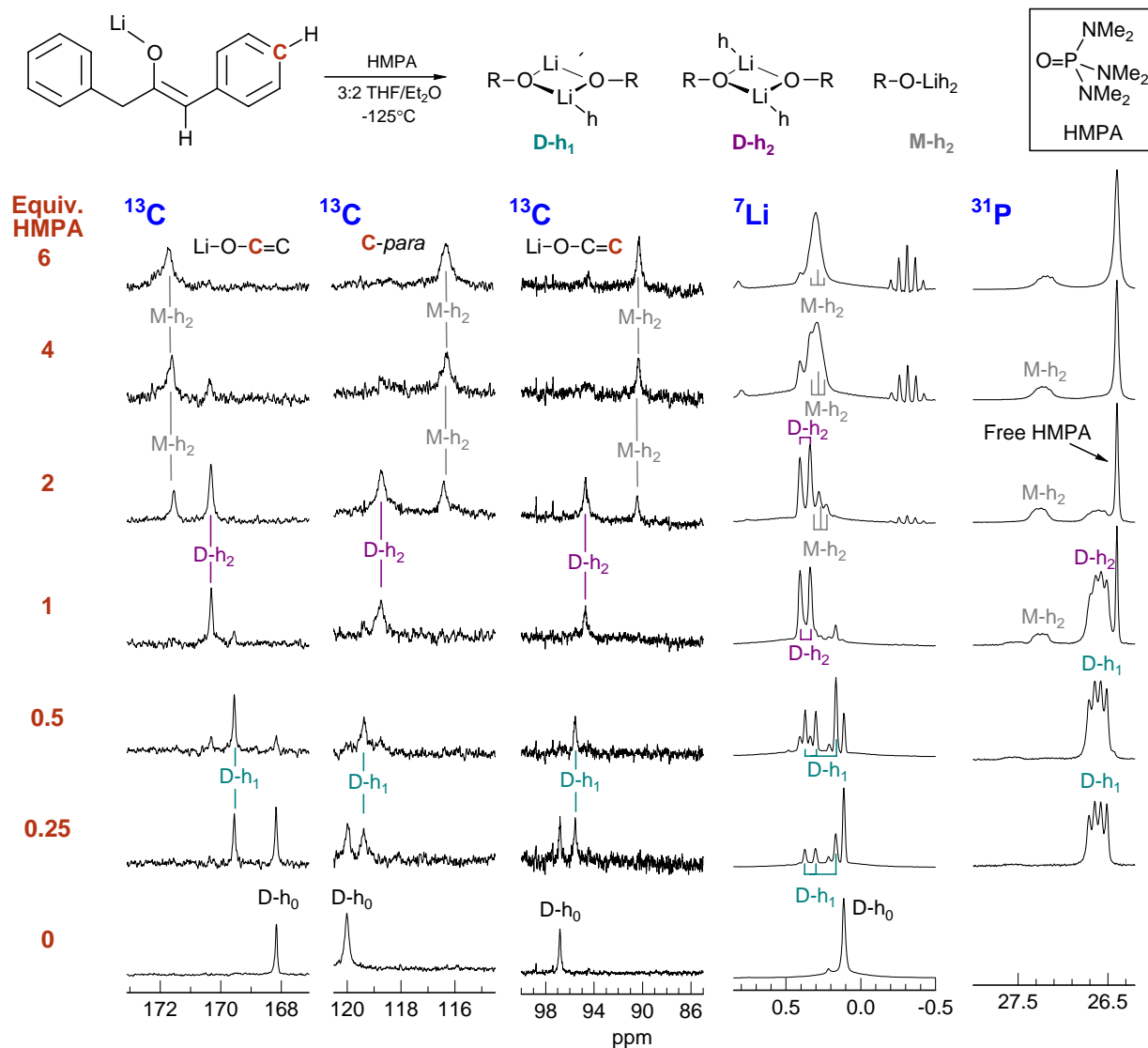


Figure S-13. HMPA titration of 5H-Li in 3:2 THF/ Et₂O at -125 °C. Sequential solvation of the dimer was observed as the concentration of HMPA was increased up to one equiv. Above one equiv. of HMPA dissociation to a HMPA solvated monomer was observed (h = HMPA; D = dimer; M = monomer).

Kinetic and Thermodynamic Enolates of 1,3-Bis-(4-fluorophenyl)-2- propanone (**5F-Li**).

Kinetic enolate : 1,3-bis-(4-fluorophenyl)-2- propanone (600 μ L, 0.5 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 $^{\circ}$ C to a freshly prepared solution of 0.1 M LiNⁱPr₂ in 3:2 THF/Et₂O and ¹³C and ⁷Li spectra were acquired at -120 $^{\circ}$ C. Et₃N (170 μ L, 1.2 mmol) and Me₃SiCl (80 μ L, 0.6 mmol) were added and ¹³C and ⁷Li spectra were acquired at -120 $^{\circ}$ C. Thermodynamic enolate: An identical sample was allowed to warm to room temperature (ca 25 $^{\circ}$ C) for 4 h. ¹³C and ⁷Li spectra were acquired at -120 $^{\circ}$ C. Et₃N (170 μ L, 1.2 mmol) and Me₃SiCl (80 μ L, 0.6 mmol) were added and ¹³C and ⁷Li spectra were acquired at -120 $^{\circ}$ C. Spectra are shown in Figure 5 and S-14.

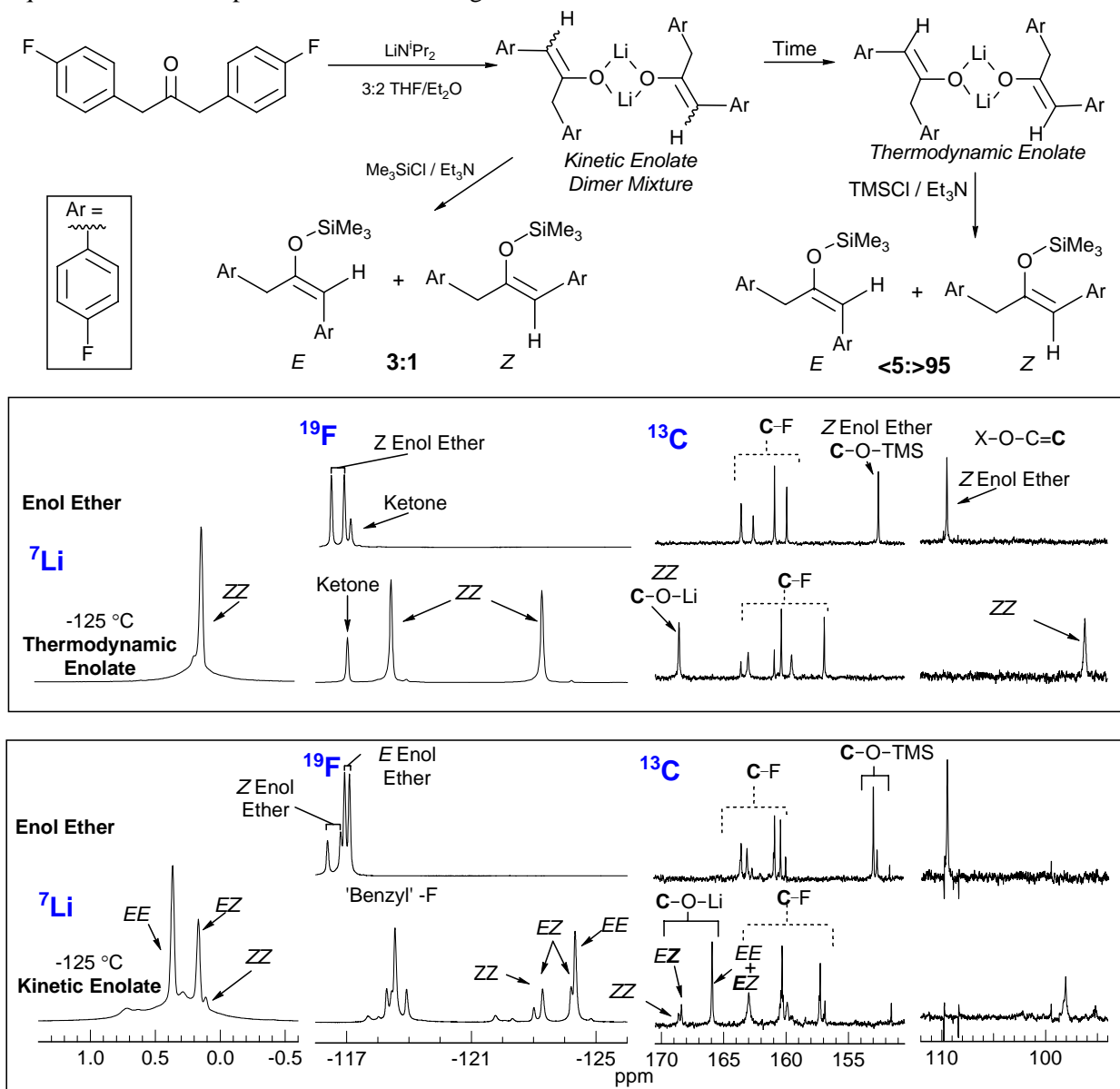


Figure S-14. NMR spectra of the dimer mixture that arises from the *E* and *Z* isomers generated by the kinetic deprotonation of **5F-H** in 3:2 THF/ Et₂O at -130 $^{\circ}$ C. Equilibration of the solution produced a single species identified as the ZZ dimer. Stereochemistry was assigned based on Me₃SiCl quenches and analysis of the resulting enol silyl ether NMR spectra.

¹H NOE of the *E* and *Z* Enol Silyl Ether of 1,3-Bis-(4-fluorophenyl)-2- propanone (5F-Si). *E/Z Mixture*: 1,3-Bis-(4-fluorophenyl)-2- propanone (380 μL, 0.78 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 °C to a freshly prepared solution of 0.1 M LiNⁱPr₂ in 3:2 THF/Et₂O. Et₃N (84 μL, 0.6 mmol) and Me₃SiCl (160 μL, 1.2 mmol) were added at -78 °C. The sample was diluted with cold (ca 0 °C) pentane, washed with cold saturated NaHCO₃, dried over MgSO₄, and the solvent was removed via vacuum. The resulting enol silyl ether mixture was dissolved in CDCl₃ and NMR experiments were performed. *Z Enol Ether*: The *Z* enol silyl ether was obtained in analogous fashion to the above procedure but the sample was allowed to warm to room temperature (ca 25 °C) for 2 h before the addition of Et₃N and Me₃SiCl. Spectra are shown in Figure S-15.

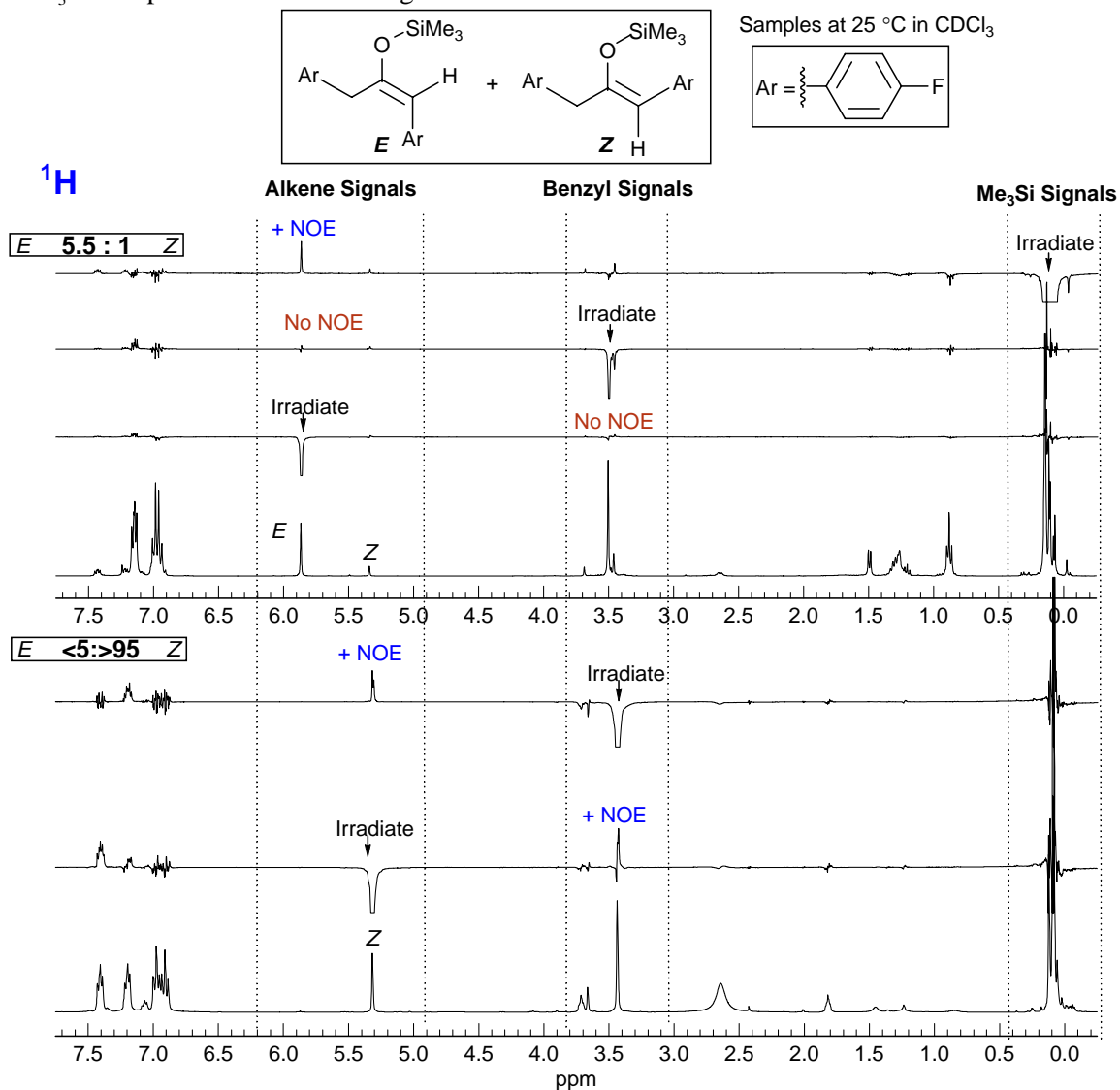


Figure S-15. NOE difference ¹H NMR spectra of the enol silyl ethers of 1,3-bis-(4-fluorophenyl)-2-propanone. The top set of spectra is of a mixture of *E* and *Z* isomers (5.5:1) based on NOE correlations observed the major isomer was determined to have the *E* configuration. The bottom set of spectra is a solution of predominately *Z* isomer (>95%) based on NOE correlations observed.

Variable Temperature NMR Study of Dimers of Lithium Enolate *E/Z*-5F-Li. 1,3-Bis-(4-fluorophenyl)-2-propanone (500 μ L, 0.58 M solution in 3:2 THF/ Et_2O , 0.3 mmol) was added at -78°C to a freshly prepared solution of 0.1 M LiN^iPr_2 in 3:2 THF/ Et_2O . ^{13}C , ^{19}F , and ^7Li spectra were acquired at -129°C . ^{13}C , ^7Li , and ^{19}F spectra were obtained at -130°C , -95°C , -45°C , 0°C , and 22°C . The sample was cooled to -133°C and ^{13}C , ^7Li , and ^{19}F spectra were acquired. Spectra are shown in Figure S-16.

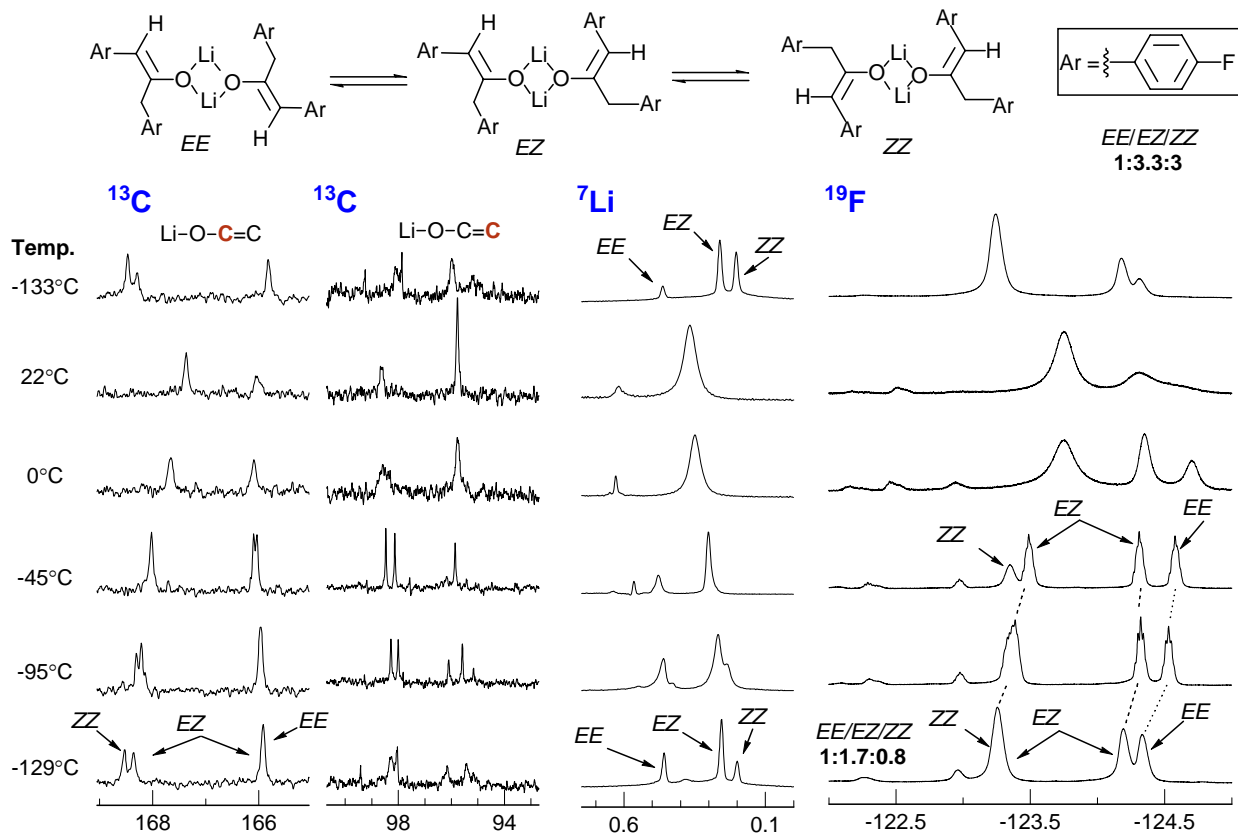


Figure S-16. A variable temperature NMR study of the dimers of **5F-Li** in 3:2 THF/ Et_2O . Over the course of the experiment, total ca 4 h (ca 40 min for each set of spectra), the ratio of *E* and *Z* isomers changed only slightly (from 52:48 to 36:64).

Variable Concentration Study of the Lithium Enolate Z-Q5F-Li in THF/Et₂O. A 10 mm NMR tube was sealed with a septa, purged with Ar, and cooled to -78 °C, and 3.5 mL of THF/ Et₂O were added. From a crystalized solution (See Crystallography section of Supplemental Information) of the lithium enolate of 1,3-bis-(4-fluorophenyl)-2- propanone (0.5 mL, 0.5 M solution in Et₂O, 0.12 mmol) was added at -78 °C. An internal standard, 1,3-difluorobenzene (8 μL), was added and ¹³C, ⁷Li, and ¹⁹F spectra were acquired at -120 °C of the 0.072 M sample. This sample was warmed to room temperature, 1.0 mL was removed by syringe and placed in a dry, purged 10 mm NMR tube sealed with a septum containing 3.0 mL of THF/ Et₂O. More internal standard, 1,3-difluorobenzene (6 μL), was added and ¹³C, ⁷Li, and ¹⁹F spectra were acquired at -120 °C of the 0.012 M sample.. From the original sample 0.5 mL was removed by syringe and placed in a dry, purged 10 mm NMR tube sealed with a septa containing 3.5 mL of THF/ Et₂O. More internal standard, 1,3-difluorobenzene (7 μL), was added and ¹³C, ⁷Li, and ¹⁹F spectra were acquired at -120 °C of the 0.006 M sample. Spectra are shown in Figure 6 and S-17.

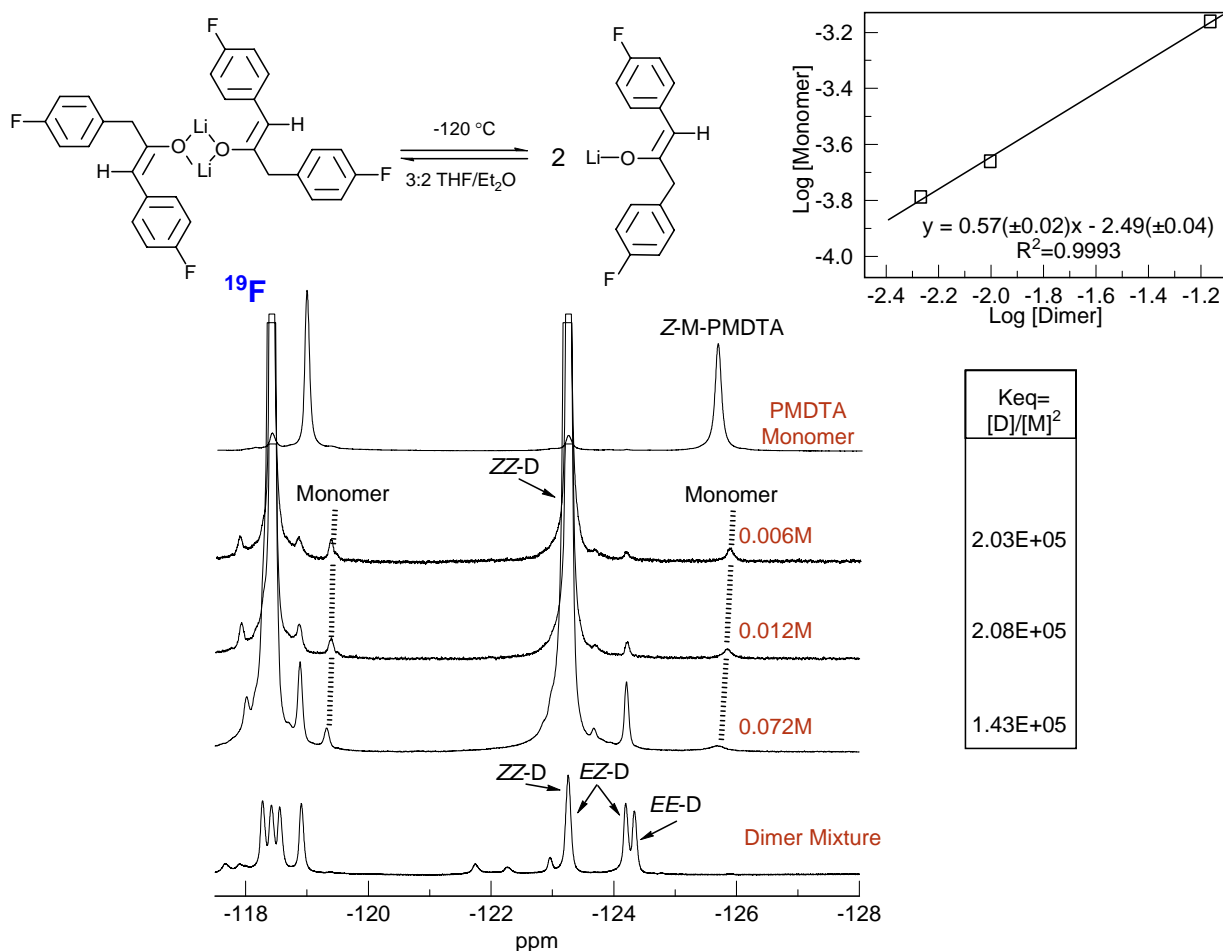


Figure S-17. Variable concentration study of the lithium enolate of 1,3-bis-(4-fluorophenyl)-2-propanone (**5F-Li**). Increasing amounts of monomer were observed in the ¹⁹F NMR spectra as the sample was diluted. The signal is very similar in chemical shift to that of the PMDTA solvated monomer (top spectrum) and a log plot of dimer and monomer concentration supports this assignment.

Variable Temperature Study of Monomer Dimer Equilibrium of Lithium Enolate Z-5F-Li. 1,3-Bis-(4-fluorophenyl)-2- propanone (1.0 mL, 0.32 M solution in 3:2 THF/ Et₂O, 0.31 mmol) was added at -78 °C to a freshly prepared solution of 0.1 M LiNⁱPr₂ in 3:2 THF/Et₂O. The sample was allowed to warm to room temperature (ca 25 °C) for several hours. ¹³C and ¹⁹F spectra were acquired at 211 K, 204 K, 189 K, 182 K, 178 K, 165 K, 162 K, and 143 K. Spectra are shown in Figure S-18.

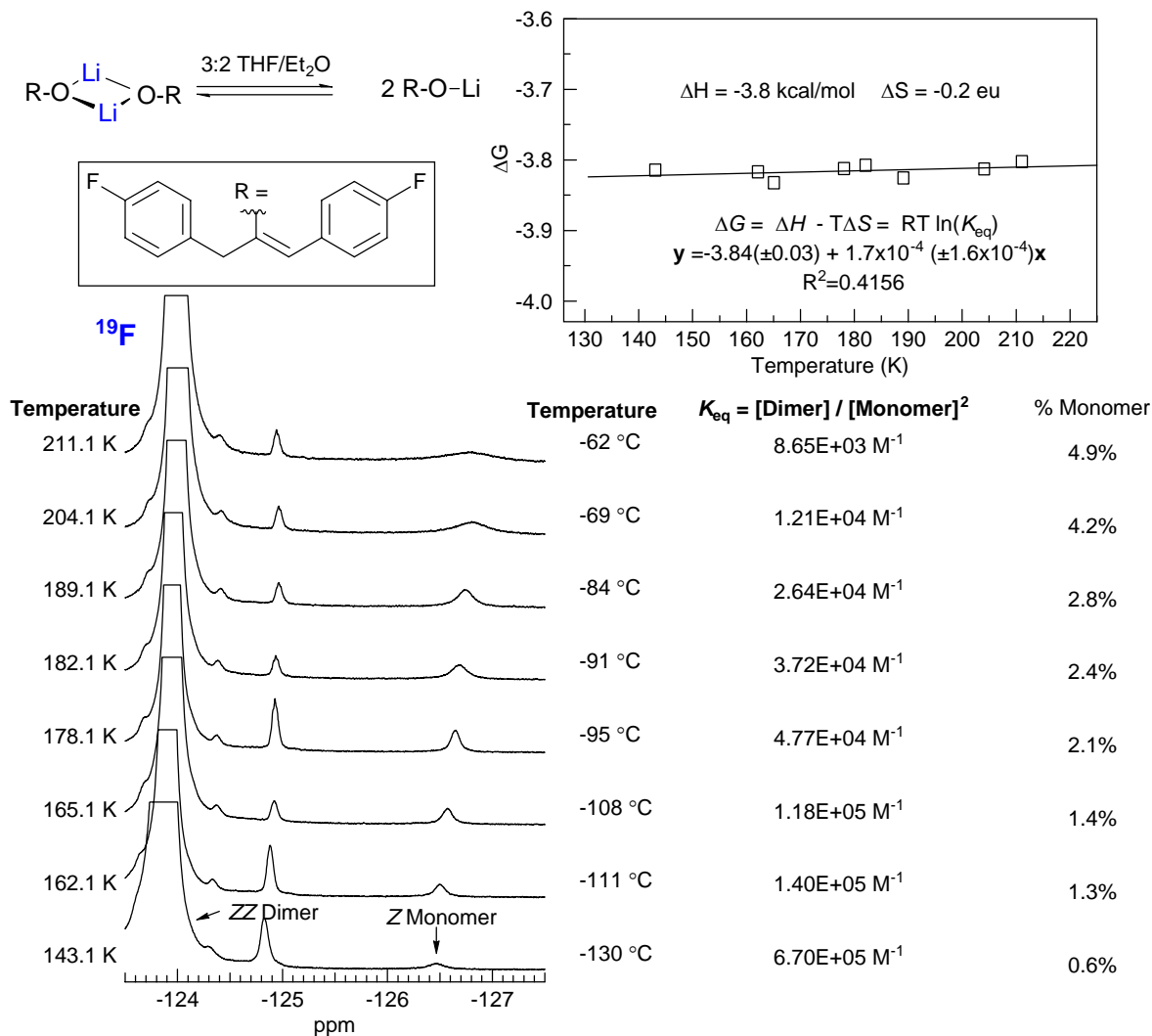


Figure S-18. Variable temperature study of the monomer-dimer equilibrium of the lithium enolate of 1,3-bis-(4-fluorophenyl)-2- propanone (**5F-Li**) observed by ¹⁹F NMR spectra. The signal is similar in chemical shift to that of the PMDTA solvated monomer (see experiment) and a plot of the association constant ($K_{\text{eq}} = [\text{Dimer}] / [\text{Monomer}]^2$), converted to Gibb's free energy (ΔG°), versus temperature gave the entropy and enthalpy of dimerization ($\Delta H = -3.8 \pm 0.1$ kcal/mol, $\Delta S = 0.17 \pm 0.16$ eu).

P4-*t*Bu Titration of 1,3-Bis-(4-fluorophenyl)-2-propanone (5F-H). A solution of 1,3-bis-(4-fluorophenyl)-2-propanone (74.8 mg, 0.3 mmol) in 3 mL of 3:2 THF/Et₂O was prepared in a 10 mm NMR tube sealed with a septum, purged with Ar. ¹³C, ¹H, ¹⁹F and ³¹P NMR spectra were obtained at -130 °C with 0, 0.1, 0.25, 0.4, 0.5, 0.75, and 1.0 equiv. of P4-*t*Bu added as a 1 M solution in hexanes. Spectra are shown in Figure S-19.

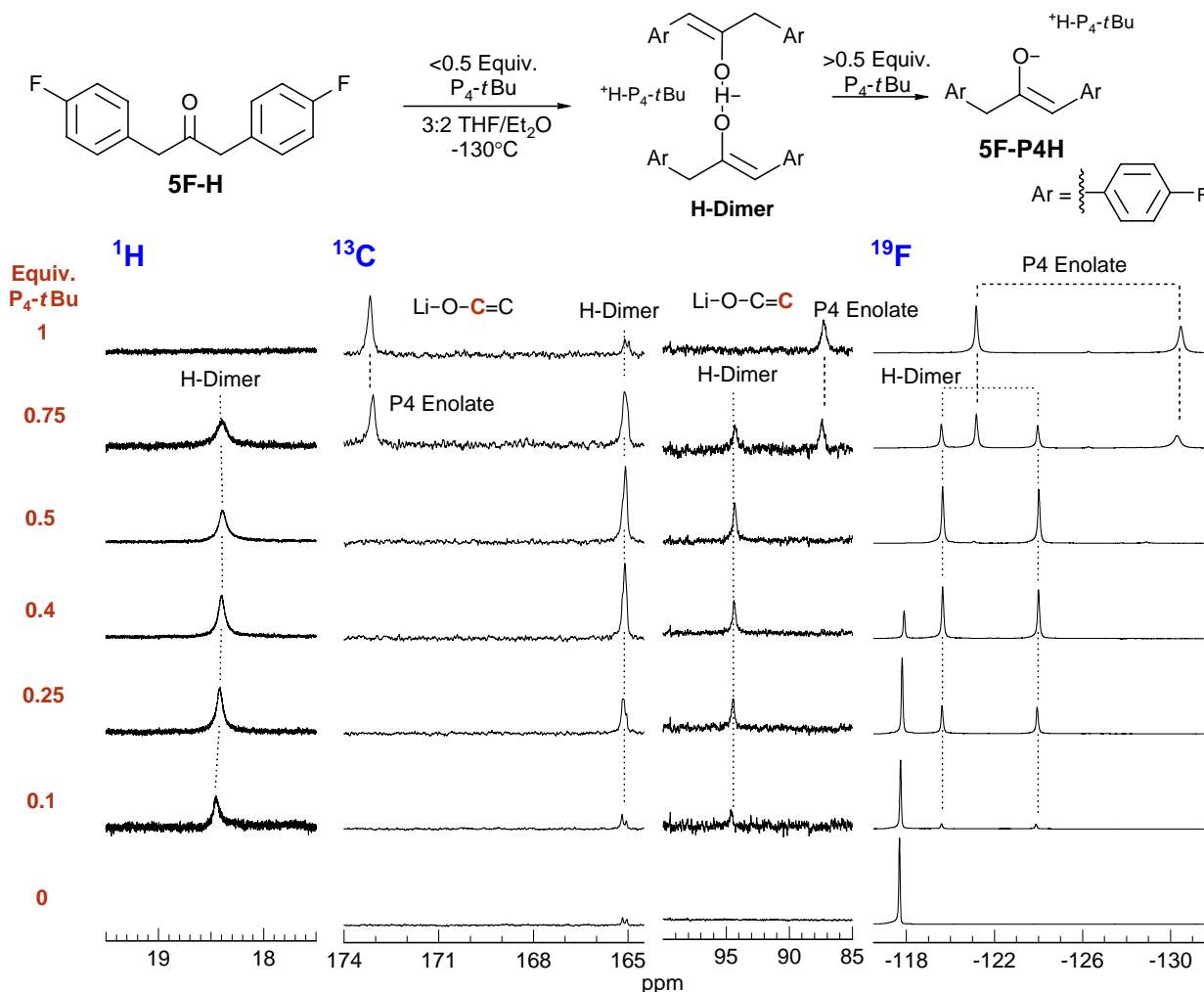


Figure S-19. P4-*t*Bu titration of 0.1 M 1,3-bis-(4-fluorophenyl)-2-propanone (5F-H) in 3:2 THF/Et₂O at -130 °C. The addition of less than a half of an equivalent of P4-*t*Bu produces a dimeric enolate species which is bridged by a low barrier hydrogen bond (δ 18.4). The ¹³C signals at δ 165.1 (C-O carbon) and δ 94.1 (β -carbon) are similar to those of the lithium enolate (5F-Li)₂ δ 168.6 (C-O carbon) and δ 96.2 (β -carbon). Upon the addition of a full equivalent of P4-*t*Bu a "naked" enolate was produced which has substantially shifted C-O carbon (δ 173.1) and β -carbon (δ 87.3), compared to the lithium enolate.

Variable Temperature Study of Phenyl Ring Rotation in Z-5F-P4H. A solution of 1,3-bis-(4-fluorophenyl)-2-propanone (55.0 mg , 0.22 mmol) was prepared using the general procedure for sample preparation in 3:1 Me₂O/Et₂O. P4-*t*Bu (1.0 equiv.) was added as a 1 M solution in hexanes and ¹³C, ¹H, and ¹⁹F NMR spectra were obtained at -95 °C, -83 °C, -77 °C, -71 °C, -64 °C, -54 °C, and -41 °C. Rates were determined by simulation of the coalescence of two doublets ($J(C,F) = 7$ Hz) with WINDNMR.^[S5] Spectra with simulated fits are shown in Figure 7 and S-20. Simulation data is presented in Table S-1.

Table S-1. Data for Simulation of the ¹³C Spectra of the rotation of the conjugated phenyl ring of **5F-P4H**.(Fig. S-20).

Temperature °C	-94.5	-82.9	-77.2	-70.9	-64	-53.6	-41
ν_a /Hz	13888	13889.3	13889.3	13889.3	13892.7	13893.5	13896.9
ν_b /Hz	13786.6	13787.9	13787.9	13787.9	13791.3	13792.1	13795.5
$k_{ab} + k_{ba}$ / sec ⁻¹	42	126	243	513	954	2428	5818
% a	50	50	50	50	50	50	50
W_a^a /Hz	2	2	2	2	2	2	2
W_b^a /Hz	2	2	2	2	2	2	2
k_{ab} / sec ⁻¹ ^b	21	63	121.5	256.5	477	1214	2909
ΔG^\ddagger / kcal/mol	9.19	9.40	9.43	9.45	9.53	9.62	9.79

^a Line width in the absence of exchange. ^b $k_{ab} = k_{ba}$ since %a = %b

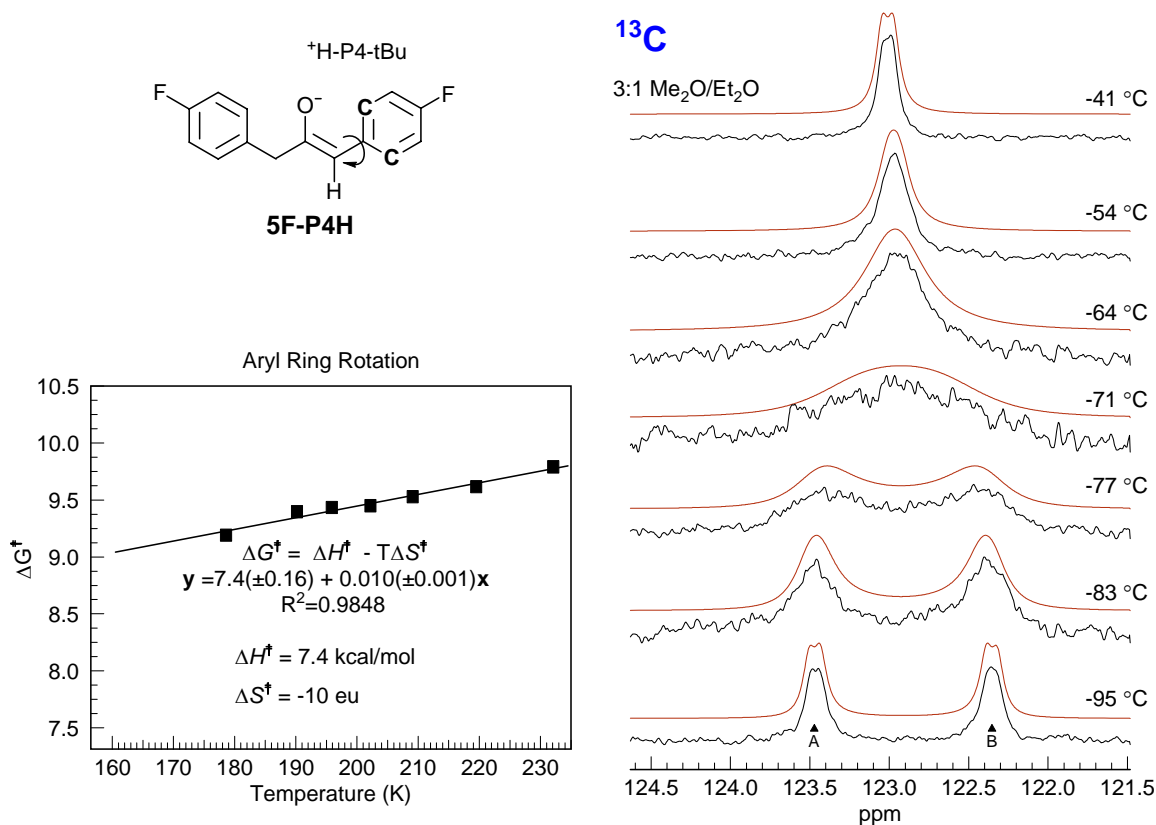


Figure S-20. DNMR study of the conjugated phenyl ring rotation of **Z-5F-P4H**. The upper lines are simulations using WINDNMR, using the “DNMR-dddd” option with three of the four coupling constants set to 0 to simulate two coalescing doublets.^[S5]

Variable Temperature Study of Phenyl Ring Rotation in Z-5F-Li. A solution of the lithium enolate of 1,3-bis-(4-fluorophenyl)-2-propanone was prepared by the addition of 1,3-bis-(4-fluorophenyl)-2-propanone (255.5 mg, 1.0 mmol) to a 0.17 M solution of lithium diisopropylamide in 2:1 Me₂O/Et₂O at -78 °C. ¹³C, ¹H, and ¹⁹F NMR spectra were obtained at -146 °C, -142 °C, -137 °C, -131 °C, -125 °C, -115 °C, and -104 °C. Rates were determined by simulation of the coalescence of two doublets (*J*(C,F) = 7 Hz) with WINDNMR.^[S5] Spectra with simulated fits are shown in Figure 7 and S-21. Simulation data is presented in Table S-2.

Table S-2. Data for DNMR Simulation of the rotation of the conjugated phenyl ring of the lithium enolate **5F-Li** (Fig. S-21).

Temperature °C	-146	-142	-137	-131	-125	-115	-104
<i>v</i> _a /Hz	14117.3	14117.3	14121.6	14122.7	14124.8	14115.1	14119.4
<i>v</i> _b /Hz	13925.9	13929	13932.3	13933.4	13935.5	13925.8	13930.1
<i>k</i> _{ab} + <i>k</i> _{ba} / sec ⁻¹	222	354	738	1935	4505	13205	31015
% a	50	50	50	50	50	50	50
<i>W</i> _a ^a /Hz	7	7	7	5	5	3	3
<i>W</i> _b ^a /Hz	7	7	7	5	5	3	3
<i>k</i> _{ab} / sec ⁻¹ ^b	111	177	369	967.5	2252.5	6602.5	15507.5
ΔG^\ddagger / kcal/mol	6.03	6.11	6.16	6.17	6.19	6.29	6.47

^a Line width in the absence of exchange. ^b *k*_{ab} = *k*_{ba} since %a = %b

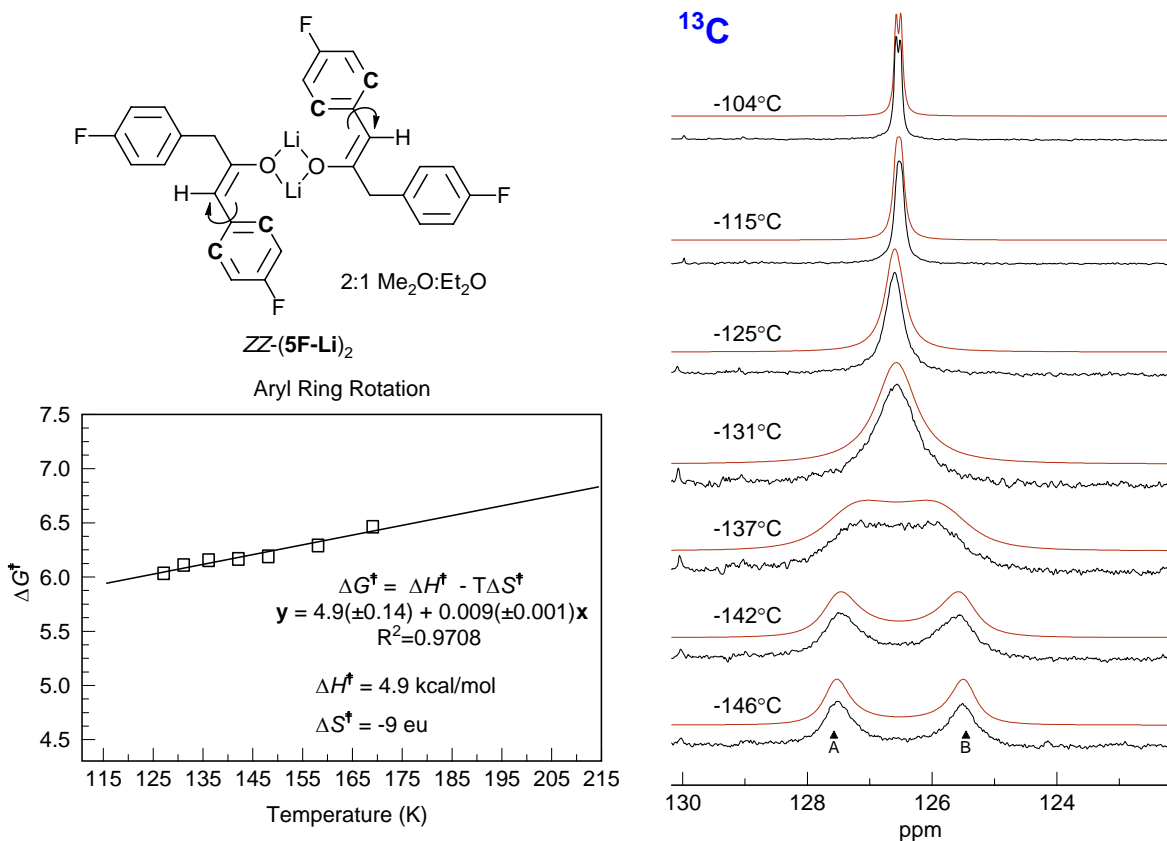


Figure S-21. DNMR study of the conjugated phenyl ring rotation of the lithium enolate **Z-5F-Li**. The upper lines are simulations using WINDNMR, using the “DNMR-dddd” option with three of the four coupling constants set to 0 to simulate two coalescing doublets.^[S5]

TMEDA Titration of Lithium Enolate Z-5F-Li in THF/Et₂O. 1,3-Bis-(4-fluorophenyl)-2-propanone (450 μ L, 0.65 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 $^{\circ}$ C to a freshly prepared solution of 0.1 M LiNⁱPr₂ in 3:2 THF/Et₂O. The sample was allowed to warm to room temperature (ca 25 $^{\circ}$ C) for 4 h. ¹³C, ⁷Li, and ¹⁹F spectra were obtained at -135 $^{\circ}$ C with 0, 0.25 (13 μ L), 0.5 (22 μ L), 1 (44 μ L), 2 (88 μ L), 4 (176 μ L), and 6 equiv.(264 μ L) of TMEDA added. From the ending solution 1 mL was removed and placed in a dry, sealed, and Ar purged 10 mm NMR tube containing 3 ml of 3:2 THF/ Et₂O. ¹³C, ⁷Li, and ¹⁹F spectra were obtained at -135 $^{\circ}$ C. Spectra are shown in Figure 8 and S-22.

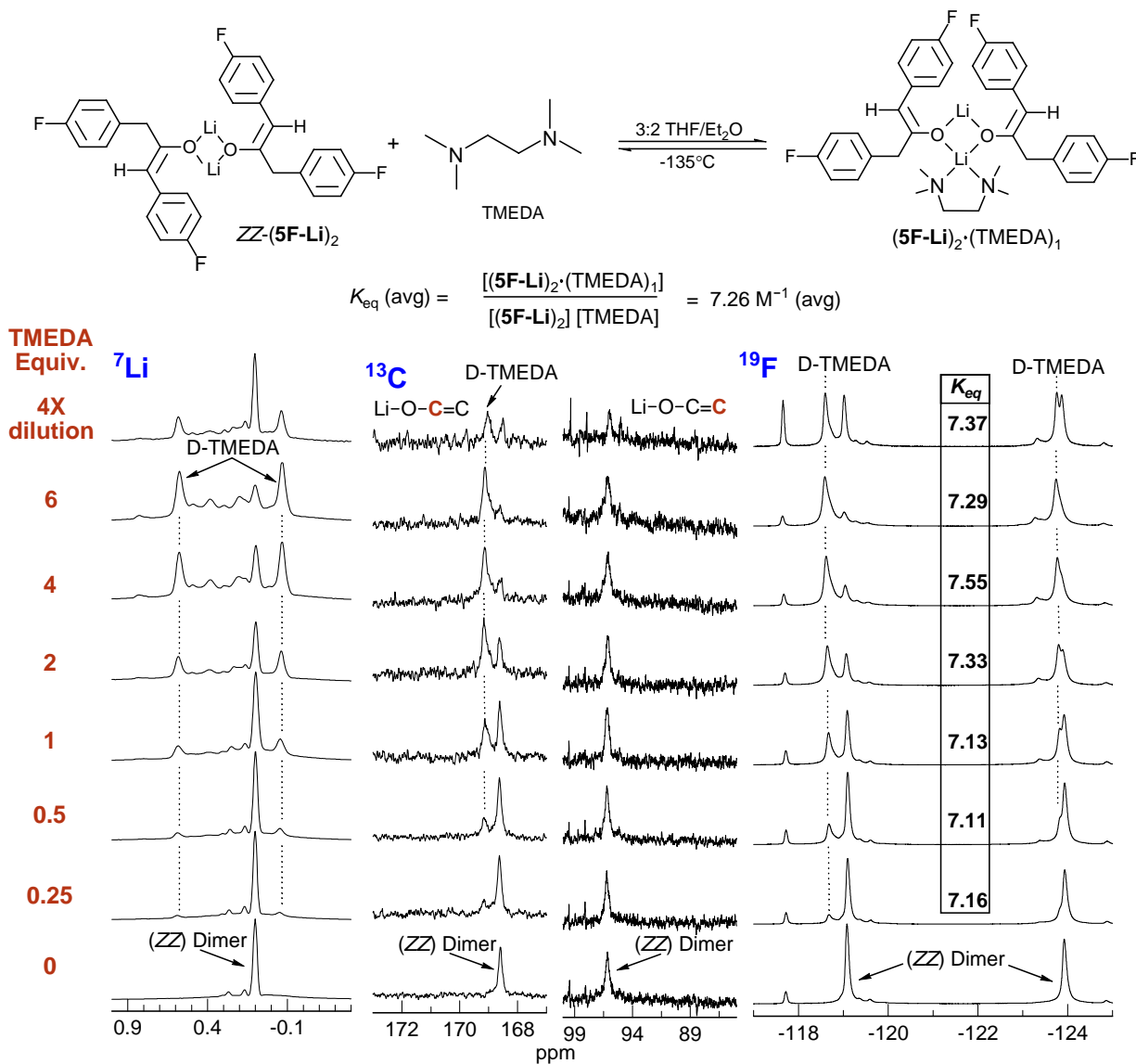


Figure S-22. TMEDA titration of Z-5F-Li in 3:2 THF/ Et₂O at -130 $^{\circ}$ C. Formation of a mono TMEDA solvated dimer was observed as the concentration of TMEDA was increased (D = dimer).

TMTAN Titration of Lithium Enolate Z-5F-Li in THF/Et₂O. 1,3-Bis-(4-fluorophenyl)-2-propanone (450 μ L, 0.65 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 $^{\circ}$ C to a freshly prepared solution of 0.1 M LiNⁱPr₂ in 3:2 THF/Et₂O. The sample was allowed to warm to room temperature (ca 25 $^{\circ}$ C) for 4 h. ¹³C, ⁷Li, and ¹⁹F spectra were obtained at -130 $^{\circ}$ C with 0, 0.5 (23 μ L), and 1 equiv.(46 μ L) of TMTAN added. Spectra are shown in Figure 8 and S-23.

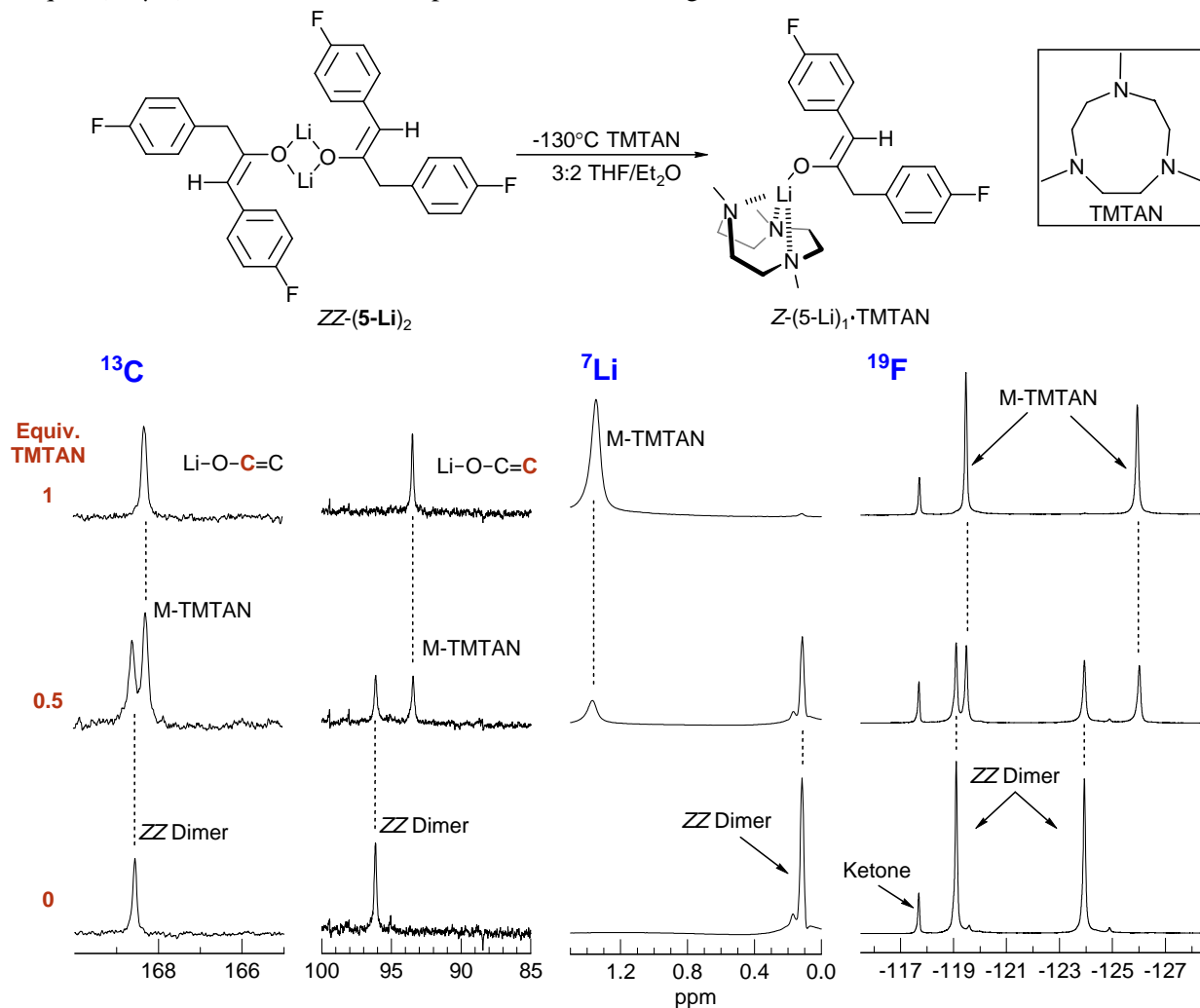


Figure S-23. TMTAN titration of the lithium enolate of Z-1,3-bis-(4-fluorophenyl)-2-propanone (**5F-Li**) in 3:2 THF/ Et₂O at -130 $^{\circ}$ C. Dissociation of the dimer to a TMTAN solvated monomer was observed as the concentration of TMTAN was increased (M = monomer).

PMDTA Titration of Lithium Enolate Z-5F-Li in THF/Et₂O. 1,3-Bis-(4-fluorophenyl)-2-propanone (800 μ L, 0.38 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 $^{\circ}$ C to a freshly prepared solution of 0.1 M LiNⁱPr₂ in 3:2 THF/Et₂O. The sample was allowed to warm to room temperature (ca 25 $^{\circ}$ C) for several hours. ¹³C, ⁷Li, and ¹⁹F spectra were obtained at -130 $^{\circ}$ C with 0, 0.5 (31 μ L), 1 (62 μ L), 2 (124 μ L) and 4 equiv. (248 μ L) of PMDTA added. Spectra are shown in Figure 8 and S-24.

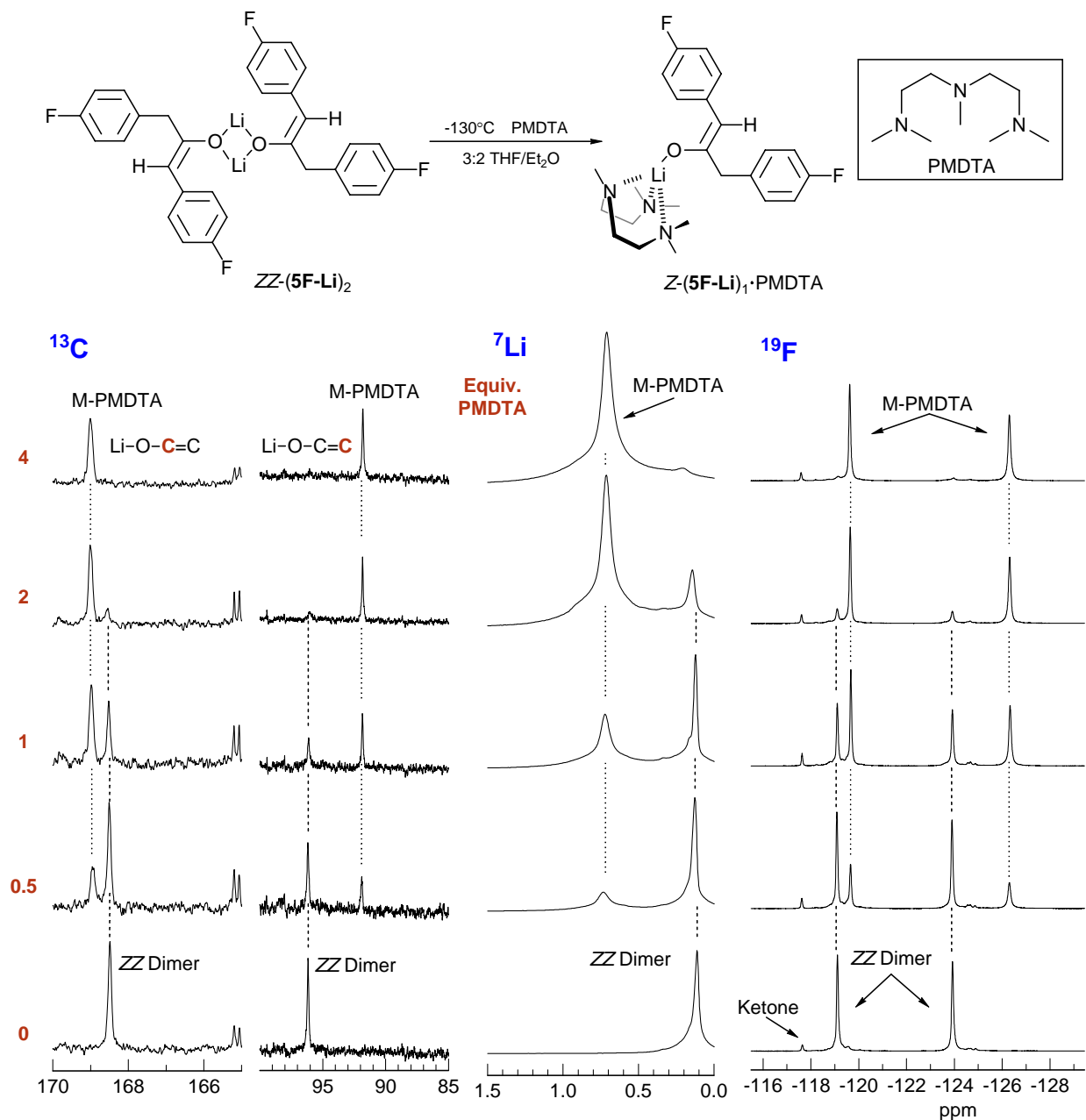


Figure S-24. PMDTA titration of 5F-Li in 3:2 THF/ Et₂O at -130 $^{\circ}$ C. Dissociation of the dimer to a PMDTA solvated monomer was observed as the concentration of PMDTA was increased (M = monomer).

PMDTA Titration of Lithium Enolate *E/Z*-5F-Li in THF/Et₂O. 1,3-Bis-(4-fluorophenyl)-2-propanone (450 μ L, 0.65 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 $^{\circ}$ C to a freshly prepared solution of 0.1 M LiNⁱPr₂ in 3:2 THF/Et₂O. ¹³C, ⁷Li, and ¹⁹F spectra were obtained at -130 $^{\circ}$ C with 0, 0.5 (13 μ L), 1 (52 μ L), and 2 equiv. (312 μ L) of PMDTA added. The sample was allowed to warm to room temperature (ca 25 $^{\circ}$ C) for 15 min after which ¹³C, ⁷Li, and ¹⁹F spectra were obtained at -130 $^{\circ}$ C. Spectra are shown in Figures 10 and S-25.

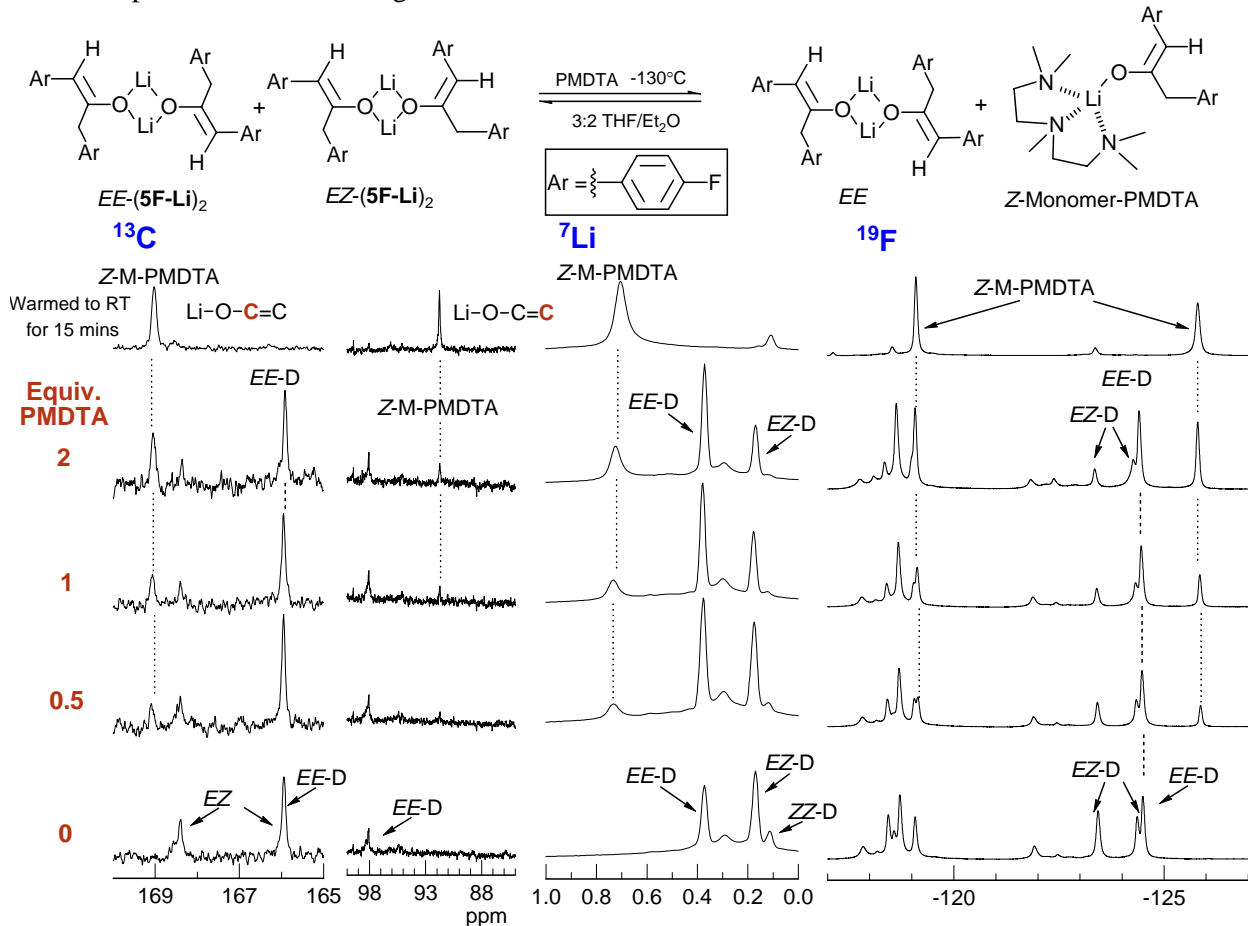


Figure S-25. PMDTA titration of the *EE* and *EZ* dimers of **5F-Li** in 3:2 THF/ Et₂O at -130 $^{\circ}$ C. Formation of the *Z* PMDTA solvated monomer was observed but no PMDTA solvated *E* monomer was detected (D = dimer; M = monomer).

HMPA Titration of Lithium Enolate Z-5F-Li at -130 °C in THF/Et₂O. 1,3-Bis-(4-fluorophenyl)-2-propanone (450 μL, 0.65 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 °C to a freshly prepared solution of 0.1 M LiNⁱPr₂ in 3:2 THF/Et₂O. The sample was allowed to warm to room temperature (ca 25 °C) for several hours. ¹³C, ⁷Li, ¹⁹F and ³¹P spectra were obtained at -130 °C with 0, 0.25 (13 μL), 0.5 (26 μL), 1 (52 μL), 2 (104 μL), 6 equiv. (312 μL), and 10 equiv. (520 μL) of HMPA added. Spectra are shown in Figures 11 and S-26.

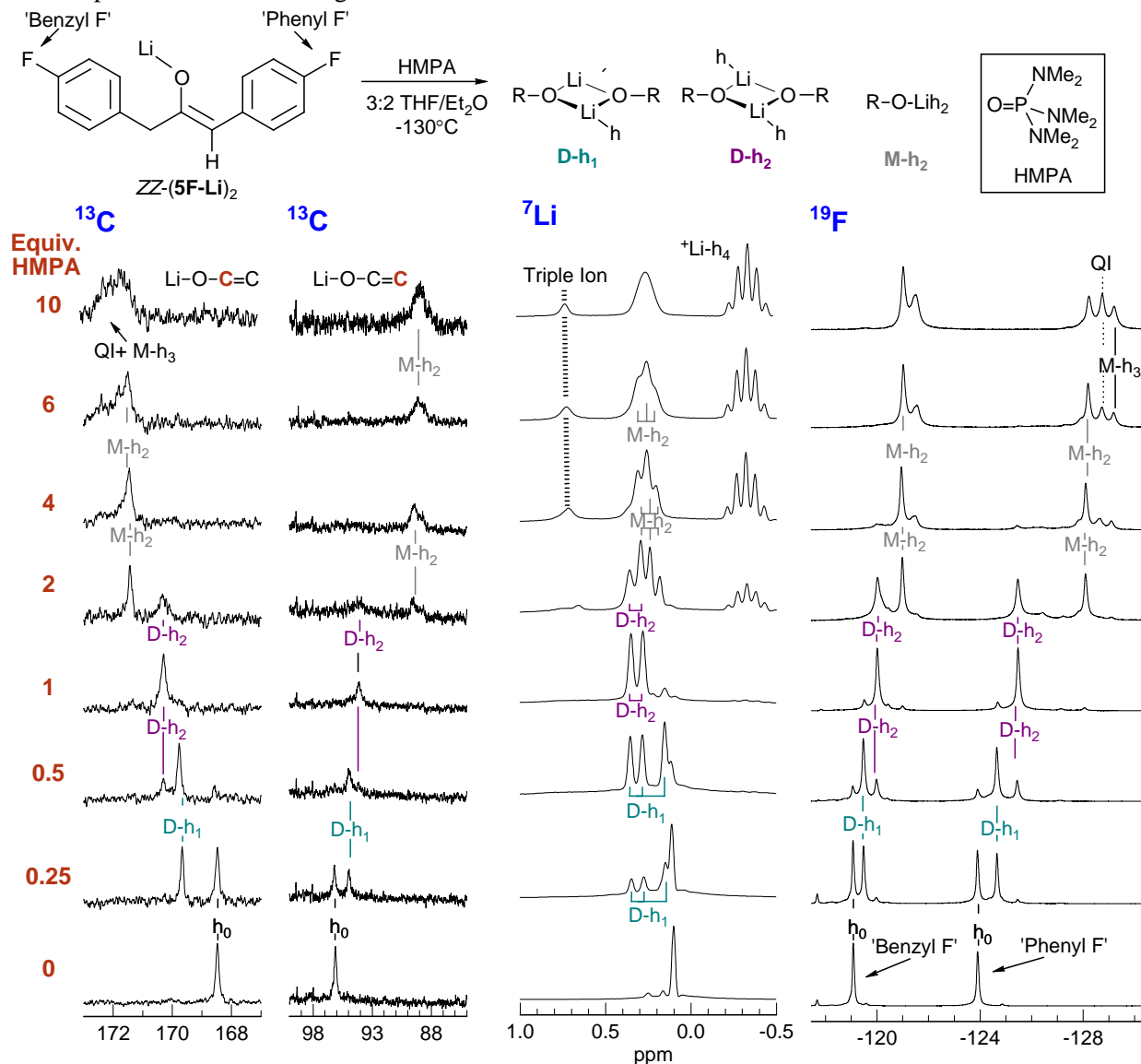


Figure S-26. HMPA titration of **5F-Li** in 3:2 THF/ Et₂O at -130 °C. Sequential solvation of the dimer was observed as HMPA was increased up to 1 equiv. Above 1 equiv. of HMPA dissociation to a HMPA solvated monomer was observed. Above 4 equiv. of HMPA the solution becomes more complex with the formation of a significant amount of ⁺Li(HMPA)₄. Two lithiate structures correlate with the formation of free Li⁺, a triple ion with a lithium to enolate ratio of 1:2, and a quadruple ion with a lithium to enolate ratio of 1:3. These species were generated and identified separately in the P4 enolate titration of lithium enolate **5F-Li** (h = HMPA; D = dimer; M = monomer; QI = quadruple ion).

HMPA Titration of Lithium Enolate **5F-Li at -140 °C in THF/Et₂O.** A 10 mm NMR tube was sealed with a septa, purged with Ar, and cooled to -78 °C, and 1 mL of THF and 1 mL of Me₂O were added. From a crystallized solution (See X-ray section) of the lithium enolate of 1,3-bis-(4-fluorophenyl)-2- propanone (1 mL, 0.12 M solution in Et₂O, 0.12 mmol) was added at -78 °C. ¹³C, ⁷Li, and ¹⁹F spectra were acquired at -130 °C. ¹³C, ⁷Li, ¹⁹F and ³¹P spectra were obtained at -130 °C with 0, 0.25 (13 μL), 0.5 (26 μL), 1 (52 μL), 2 (104 μL), 6 equiv. (312 μL), 10 equiv. (520 μL), 15 equiv. (780 μL), and 20 equiv. (1040 μL) of HMPA added. Spectra are shown in Figure S-27.

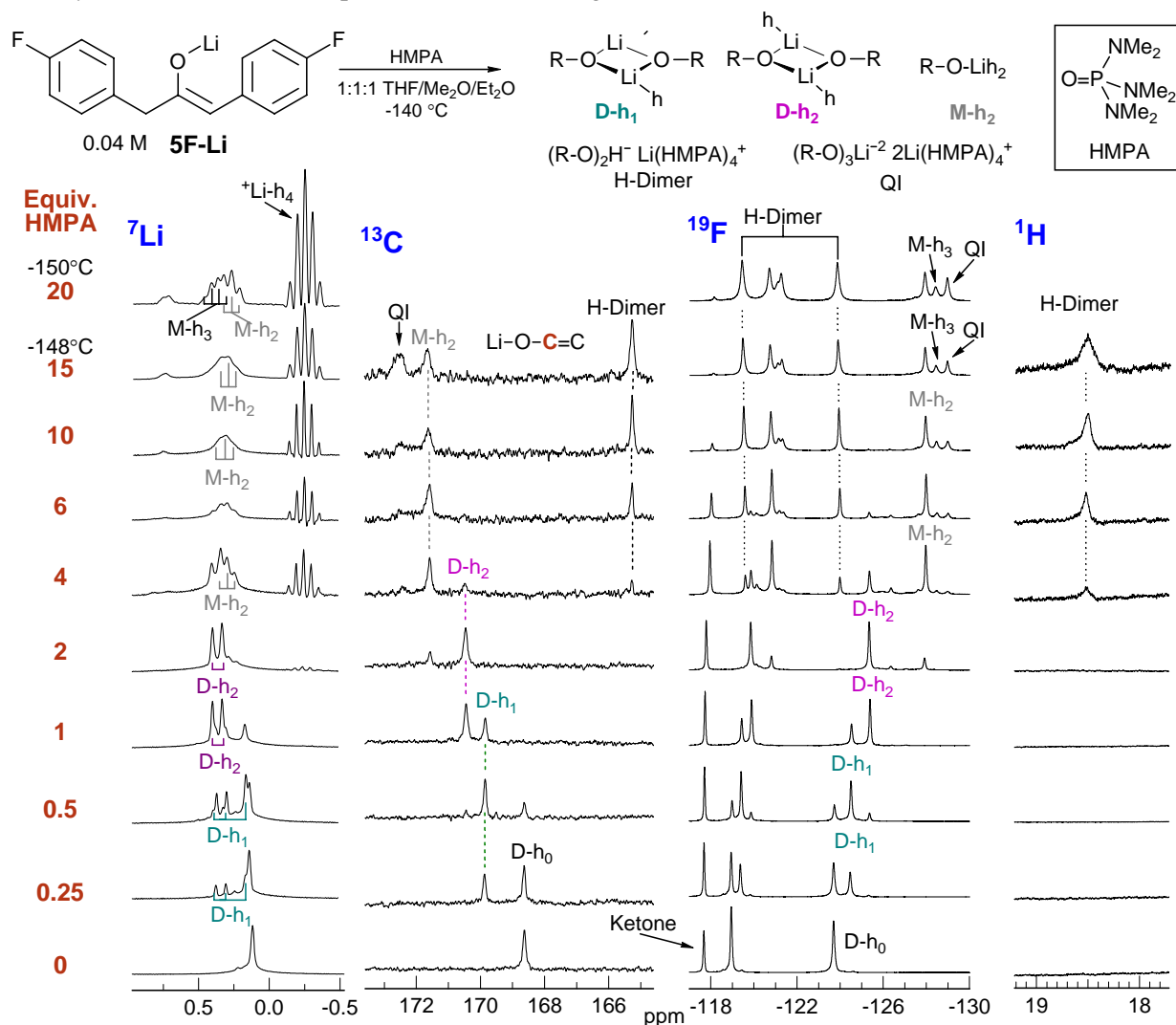


Figure S-27. The HMPA titration of 0.1 M **5F-Li** in 1:1:1 THF/Me₂O/Et₂O at -140 °C. Sequential solvation of the dimer was observed as the concentration of HMPA was increased up to one equiv. Above one equiv. dissociation to a HMPA solvated monomer was observed. Above four equiv. of HMPA the solution became more complex with the formation of a significant amount of separated Li(HMPA)₄⁺. Two ionic structures correlate with the formation of free Li⁺, a triple ion with a lithium to enolate ratio of 1:2, and a quadruple ion with a lithium to enolate ratio of 1:3. These species were generated and identified separately in the P4 enolate titration of lithium enolate **5F-Li** (Page S-33) (h = HMPA; D = dimer; M = monomer; QI = quadruple ion pair).

P4 Enolate Titration of Lithium Enolate Z-5F-Li in THF/Et₂O. 1,3-Bis-(4-fluorophenyl)-2-propanone (900 μ L, 0.64 M solution in 3:2 THF/ Et₂O, 0.6 mmol) was added at -78 $^{\circ}$ C to 3 mL of a freshly prepared solution of 0.1 M LiNⁱPr₂ in 3:2 THF/Et₂O (0.3 mmol). The sample was allowed to warm to room temperature (ca 25 $^{\circ}$ C) for several h to equilibrate to the Z isomer. ¹³C, ¹⁹F, and ⁷Li spectra were acquired at -125 $^{\circ}$ C of the Z-lithium enolate as well as after the addition of 0.5 (15 μ L) and 1 equiv. (30 μ L) of P4-*t*Bu (1.0 M solution in hexanes) to generate the P4 enolate in the presence of the lithium enolate at ratios of 0.5:1 and 1:1. ¹³C, ¹⁹F, and ⁷Li spectra were acquired with the addition of another 0.5 equiv. of **5F-P4H** (0.5 mL of a 0.3 M solution in 3:2 THF/ Et₂O, 0.3 mmol) at -125 $^{\circ}$ C and -115 $^{\circ}$ C bringing the ratio of P4 enolate to lithium enolate to 1.5:1. ¹³C, ¹⁹F, and ⁷Li spectra were acquired with the addition of another 0.5 equiv. of P4 enolate of **5F-P4H** (0.5 mL of a 0.3 M solution in 3:2 THF/ Et₂O, 0.3 mmol) at -115 $^{\circ}$ C. Spectra are shown in Figure 12 and S-28.

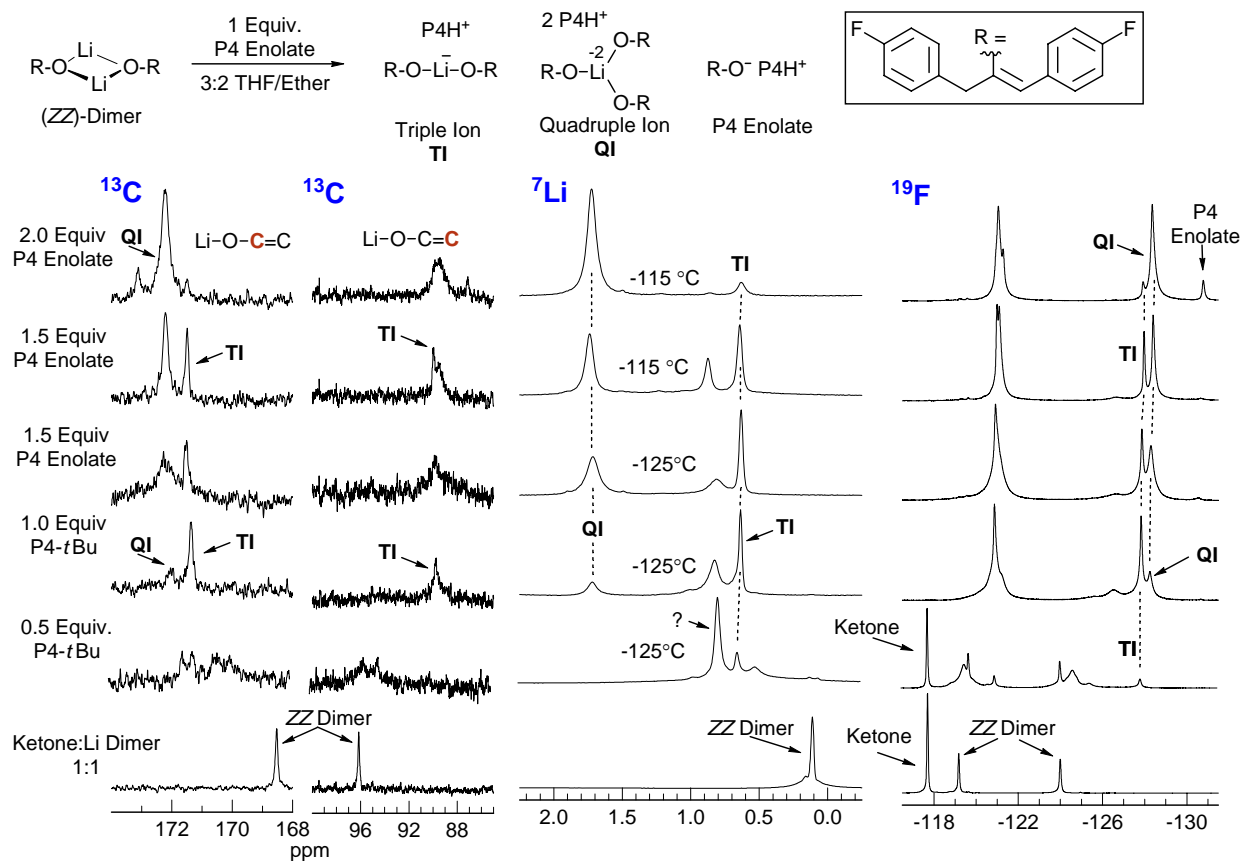


Figure S-28. The generation of the “naked” enolate in the presence of lithium enolate results in formation of complex lithiate species. The addition of a sub-stoichiometric amount of P4 to a solution of 1:1 ketone and enolate (1:1 **5F-H** : **5F-Li**) produced a complex solution which appears to be in rapid exchange. Addition of a full equivalent of P4 (1:1 **5F-P4H** : **5F-Li**) produced a solution which is mostly triple ion (TI). As the ratio of **5F-P4H** to **5F-Li** was further increased a new species appeared, leaving only small amounts of the triple ion at two equivalents of **5F-P4H**. We assigned the quadruple ion (QI) structure (RO)₃Li²⁻ (P4H⁺)₂ to this species.

Mixing Studies of P4 Enolate Generated Quadruple Ions of Z-5F and Z-6F. *Spectrum A:* 1-Phenyl-2-(4-fluorophenyl)ethanone (800 μ L, 0.38 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 $^{\circ}$ C to a 0.1 M solution (3:2 THF/Et₂O) of freshly prepared LiNⁱPr₂. The sample was allowed to warm to ca 25 $^{\circ}$ C for two h after which 1-phenyl-2-(4-fluorophenyl)ethanone (1265 mg, 0.6 mmol) and P4-*t*Bu(0.6 mL, 1 M, hexane) were added. *Spectrum E:* 1,3-bis-(4-fluorophenyl)-2- propanone (900 μ L, 0.64 M solution in 3:2 THF/ Et₂O, 0.6 mmol) was added at -78 $^{\circ}$ C to a 0.1 M solution (3:2 THF/Et₂O) of freshly prepared LiNⁱPr₂. The sample was allowed to warm to ca 25 $^{\circ}$ C for several h. Two equivalents of P4 enolate of 1,3-bis-(4-fluorophenyl)-2- propanone (1.0 mL, 0.3 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added and ¹³C, ¹⁹F, and ⁷Li spectra were acquired at -125 $^{\circ}$ C. *Spectra B, C, and D:* appropriate ratios of solutions of the quadruple ions generated for spectra A and E were mixed in 10 mm NMR tubes sealed with septa and purged with Ar. ¹³C, ¹H and ¹⁹F NMR spectra were obtained at -130 $^{\circ}$ C. Spectra are shown in Figure 12 and S-29.

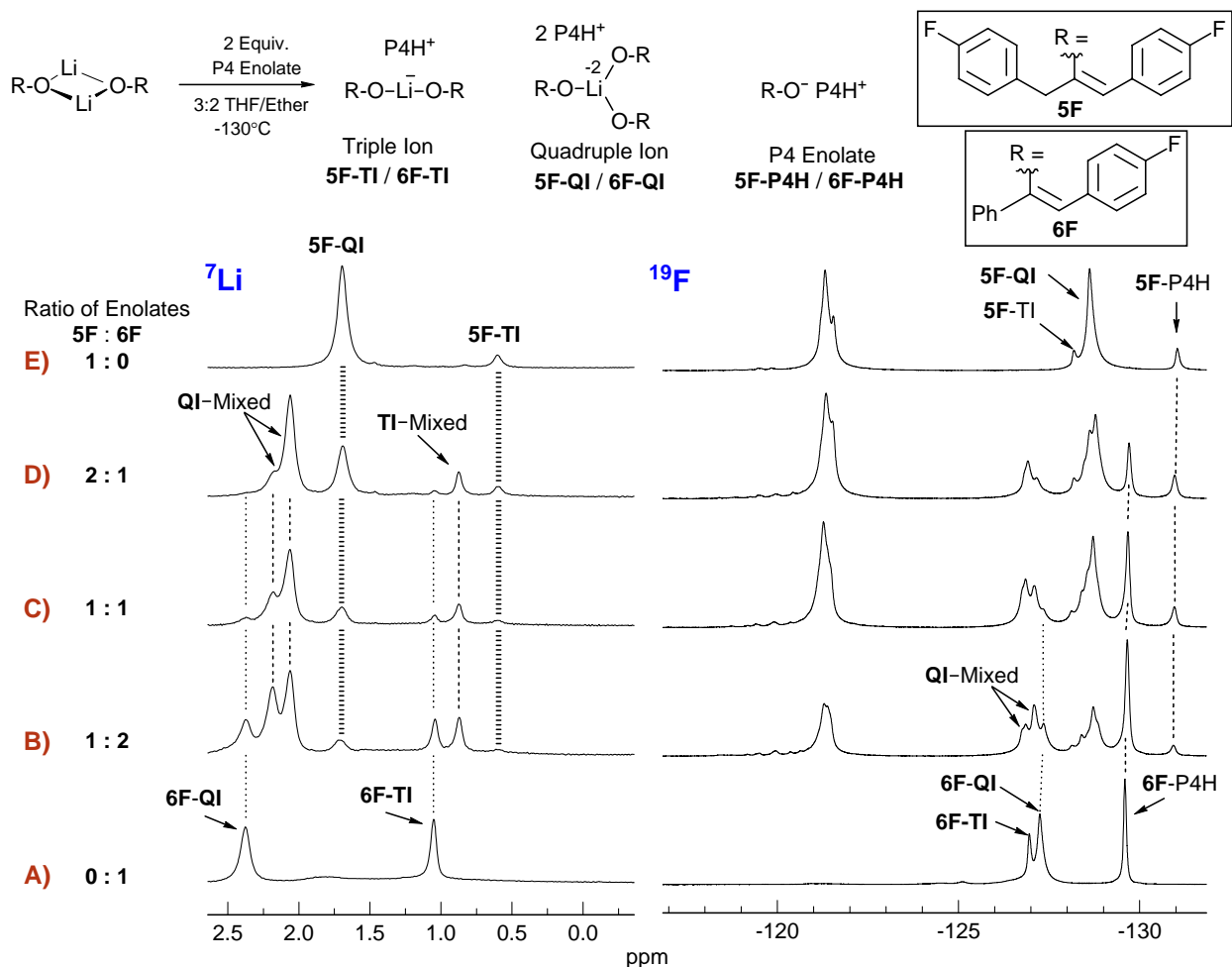


Figure S-29. Individual solution of the quadruple ions (5F)₃Li⁺² and (6F)₃Li⁺² were generated by the addition of 2 equiv of 5F-P4H to 5F-Li or 2 equiv of 6F-P4H to 6F-Li (Spectra E and A). When solutions of the two quadruple ions were mixed in several ratios, two new sets of signals were observed in the ¹⁹F and ⁷Li NMR spectra in addition to those of the homo-aggregates. The new signals are due to the formation of the 2:1 and 1:2 mixed quadruple ions (5F)₁(6F)₂Li⁺² and (5F)₂(6F)₁Li⁺² (Spectra B, C, and D). Small amounts of the triple ions and mixed triple ion were also formed.

Dilution Study of Triple Ion–Quadruple Ion Equilibrium of Z-5F. 1,3-Bis-(4-fluorophenyl)-2-propanone (1.00 mL, 0.97 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 °C to a 0.1 M solution (3:2 THF/Et₂O) of freshly prepared LiNⁱPr₂ (0.3 mmol). The sample was allowed to warm to ca 25 °C for several hours, cooled to -78 °C, and 1,3-difluorobenzene (8 μL) was added. P4-*t*Bu (600 μL, 1.0 M solution in hexanes, 0.6 mmol) was added to produce a solution of ca 2:1 **5F-P4H** to **5F-Li**. ¹³C, ⁷Li, and ¹⁹F spectra were obtained at -115 °C. *2X Dilution:* This sample was warmed to ca 25 °C, 2.0 mL was removed via syringe and placed in a dry, purged 10 mm NMR tube sealed with a septa containing 2.0 mL of 3:2 THF/ Et₂O and 1,3-difluorobenzene internal standard (4 μL). ¹³C, ⁷Li, and ¹⁹F spectra were acquired at -115 °C. *4X Dilution:* From the original sample 1.0 mL was removed via syringe and placed in a dry, purged 10 mm NMR tube sealed with a septa containing 3.0 mL of 3:2 THF/ Et₂O and 1,3-difluorobenzene (6 μL). ¹³C, ⁷Li, and ¹⁹F spectra were acquired at -115 °C. *8X Dilution:* From the original sample 0.5 mL was removed via syringe and placed in a dry, purged 10 mm NMR tube sealed with a septa containing 3.5 mL of 3:2 THF/ Et₂O and 1,3-difluorobenzene (7 μL). ¹³C, ⁷Li, and ¹⁹F spectra were acquired at -115 °C. Spectra and results are shown in Figure 13 and S-30.

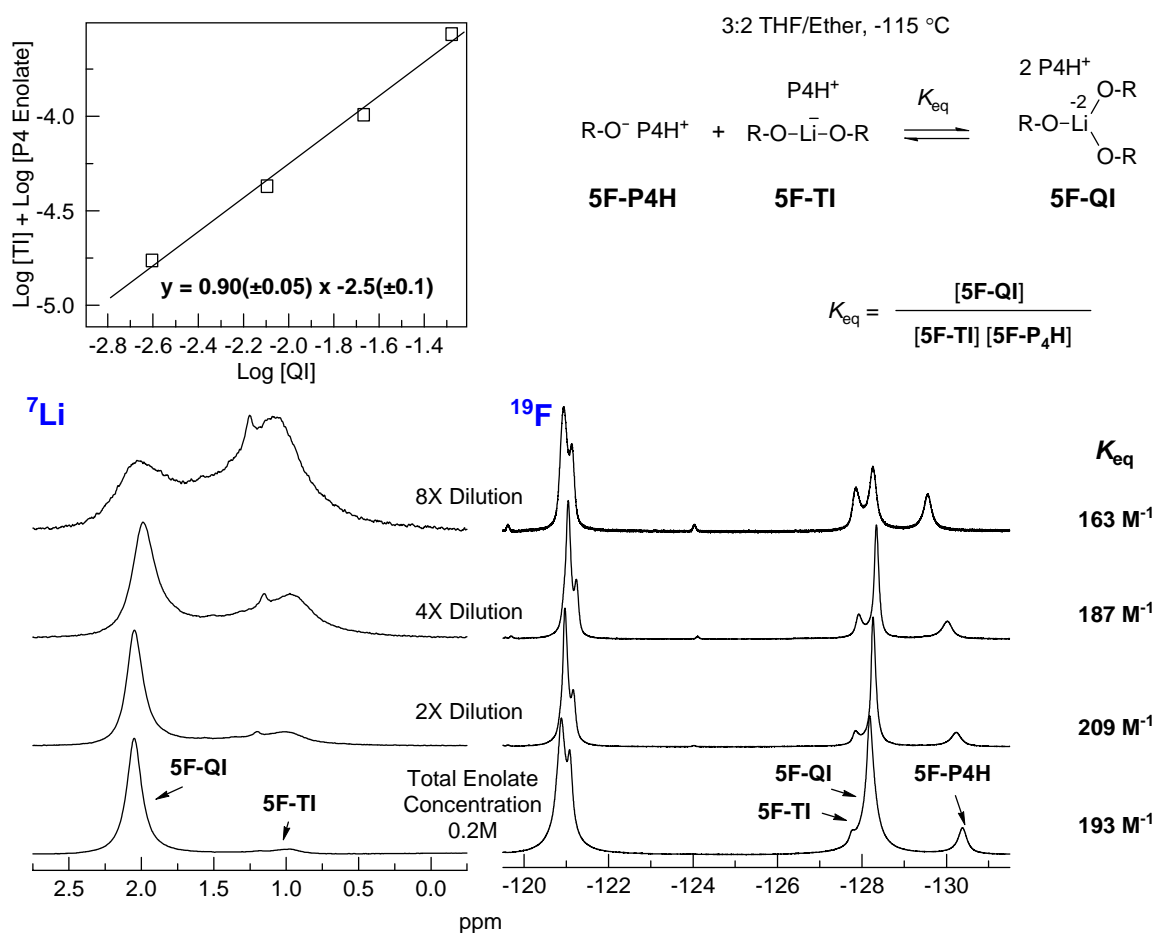


Figure S-30. Dilution study of the quadruple ion equilibrium of **5F** in 3:2 THF/ Et₂O at -115 °C. Concentrations were determined by ¹⁹F NMR against an internal standard, 1,3 difluorobenzene. Due to overlap of **QI** and **TI** signals the ratios of these species were determined using lineshape simulation using WinDNMR.^[S5]

Variable Temperature Study of Z-5F-Li with 6 Equiv. HMPA in THF/Et₂O. ¹³C, ⁷Li, and ¹⁹F spectra were acquired at -115 °C, -125 °C, and -140 °C of the sample at the end of experiment titled P4 Enolate Titration of Z Dimer of Lithium Enolate of 1,3-bis-(4-fluorophenyl)-2-propanone (**5F-Li**) which had been stored at -78 °C for 12 h. Spectra are shown in Figure S-31.

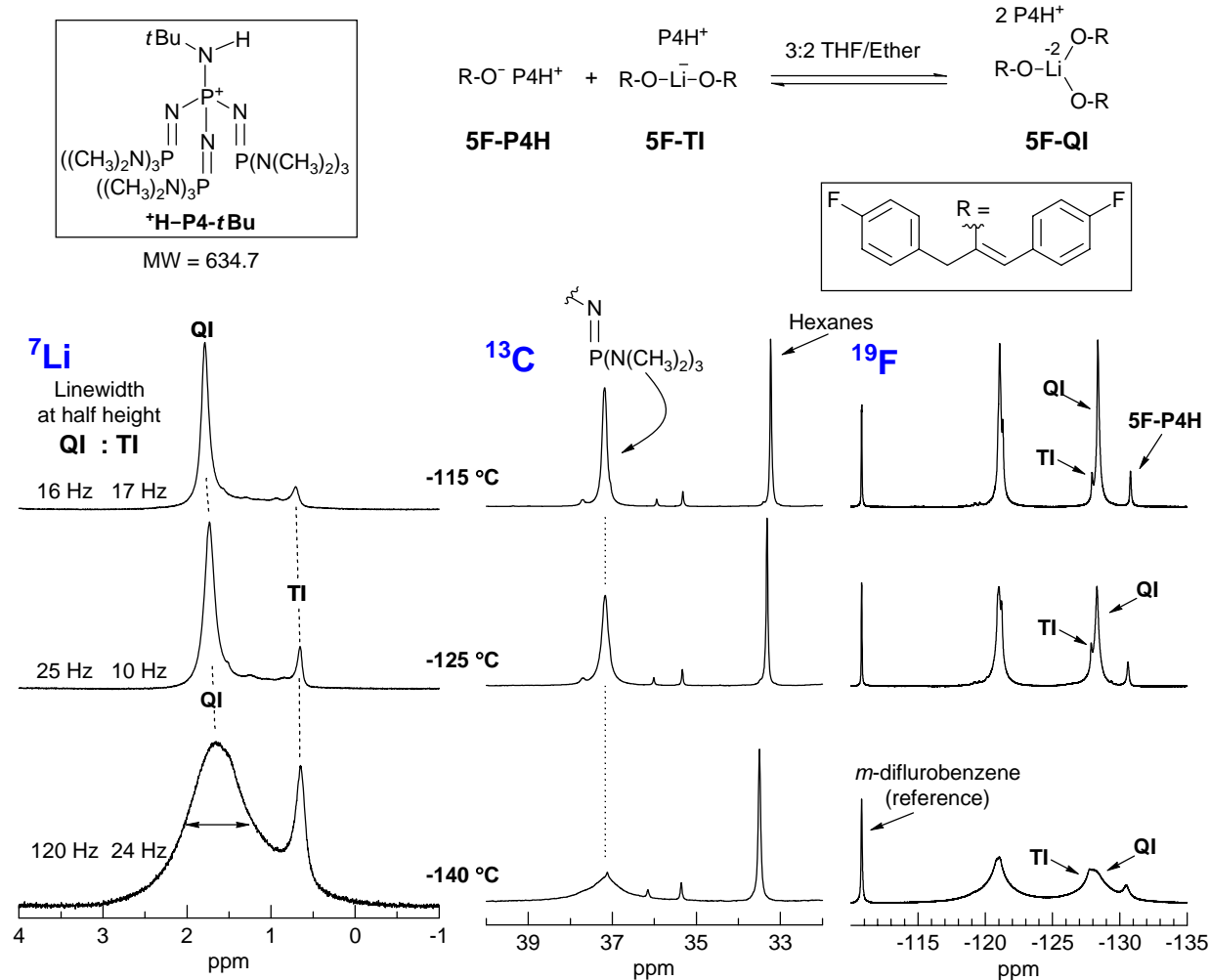


Figure S-31. ⁷Li, ¹³C, and ¹⁹F NMR spectra of a sample consisting of ca 2:1 ratio of **5F-P4H** to **5F-Li**. The linewidth of the ⁷Li and ¹⁹F NMR signals assigned to QI broadened significantly more than the signals assigned to TI upon cooling to -140 °C (HMPA titration conditions). The source of this broadening is unknown. One possibility is a slowing of some ion pair association processes between the quadruple ion and the P4H⁺ counterion ion. ¹³C NMR signals assigned to the P4H⁺ counterion ion were also found to broaden at -140 °C.

Variable Temperature Study of Z-5F-Li with 6 equiv. HMPA in THF/Et₂O. 1,3-Bis-(4-fluorophenyl)-2-propanone (850 μ L, 0.35 M solution in 3:2 THF/Et₂O, 0.3 mmol) was added at -78 $^{\circ}$ C to a freshly prepared solution of 0.1 M LiNⁱPr₂ in 3:2 THF/Et₂O. The sample was allowed to warm to room temperature (ca 25 $^{\circ}$ C) for several hours. ¹³C, ⁷Li, ¹⁹F and ³¹P spectra were obtained at -125 $^{\circ}$ C. HMPA was added (0.32 mL, 6.0 Equiv.) and ¹³C, ⁷Li, ¹⁹F and ³¹P spectra were obtained at -125 $^{\circ}$ C, -135 $^{\circ}$ C, and -140 $^{\circ}$ C. HMPA was added (0.48mL, 15.0 Equiv. total) and ¹³C, ⁷Li, ¹⁹F and ³¹P spectra were obtained at -125 $^{\circ}$ C, -135 $^{\circ}$ C, and -140 $^{\circ}$ C. Spectra are shown in Figure S-32.

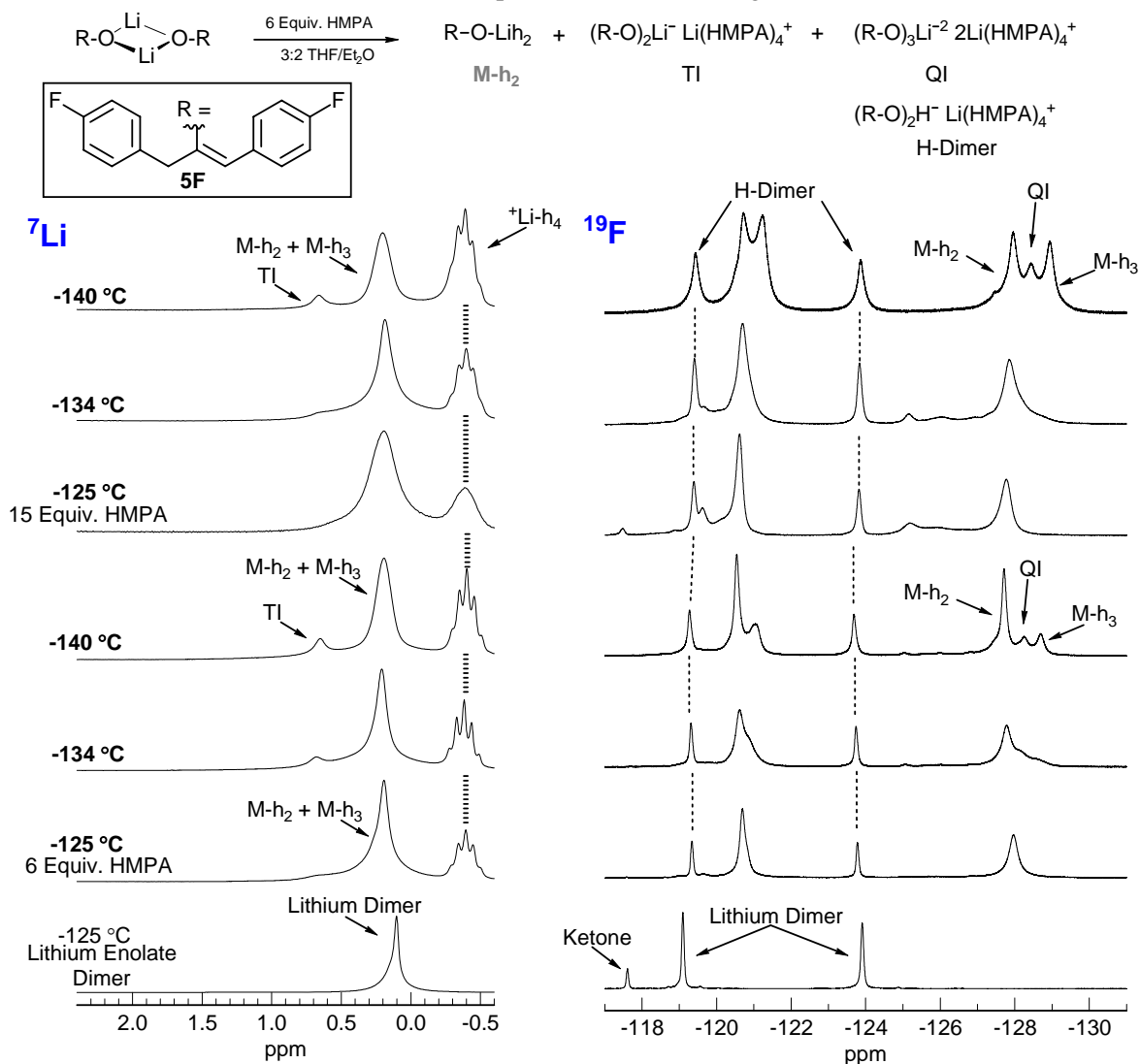


Figure S-32. ⁷Li and ¹⁹F NMR spectra of a sample of lithium enolate **5F-Li** with 6 equiv. and 15 equiv. of HMPA at -125 to -140 $^{\circ}$ C. Coalescence of the ¹⁹F NMR signals attributed to M-(HMPA)₂, QI, and M(HMPA)₃ was observed over this temperature range.

HMPA Titration of Lithium Enolate *E/Z*-5F-Li in THF/Et₂O. 1,3-Bis-(4-fluorophenyl)-2-propanone (450 μ L, 0.65 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 $^{\circ}$ C to a 0.1 M solution (3:2 THF/Et₂O) of freshly prepared LiNⁱPr₂. ¹³C, ⁷Li, ¹⁹F and ³¹P spectra were obtained at -130 $^{\circ}$ C with 0, 0.25 (13 μ L), 0.5 (26 μ L), 1 (52 μ L), 2 (104 μ L), and 6 equiv. (312 μ L) of HMPA added. Spectra are shown in Figure S-33.

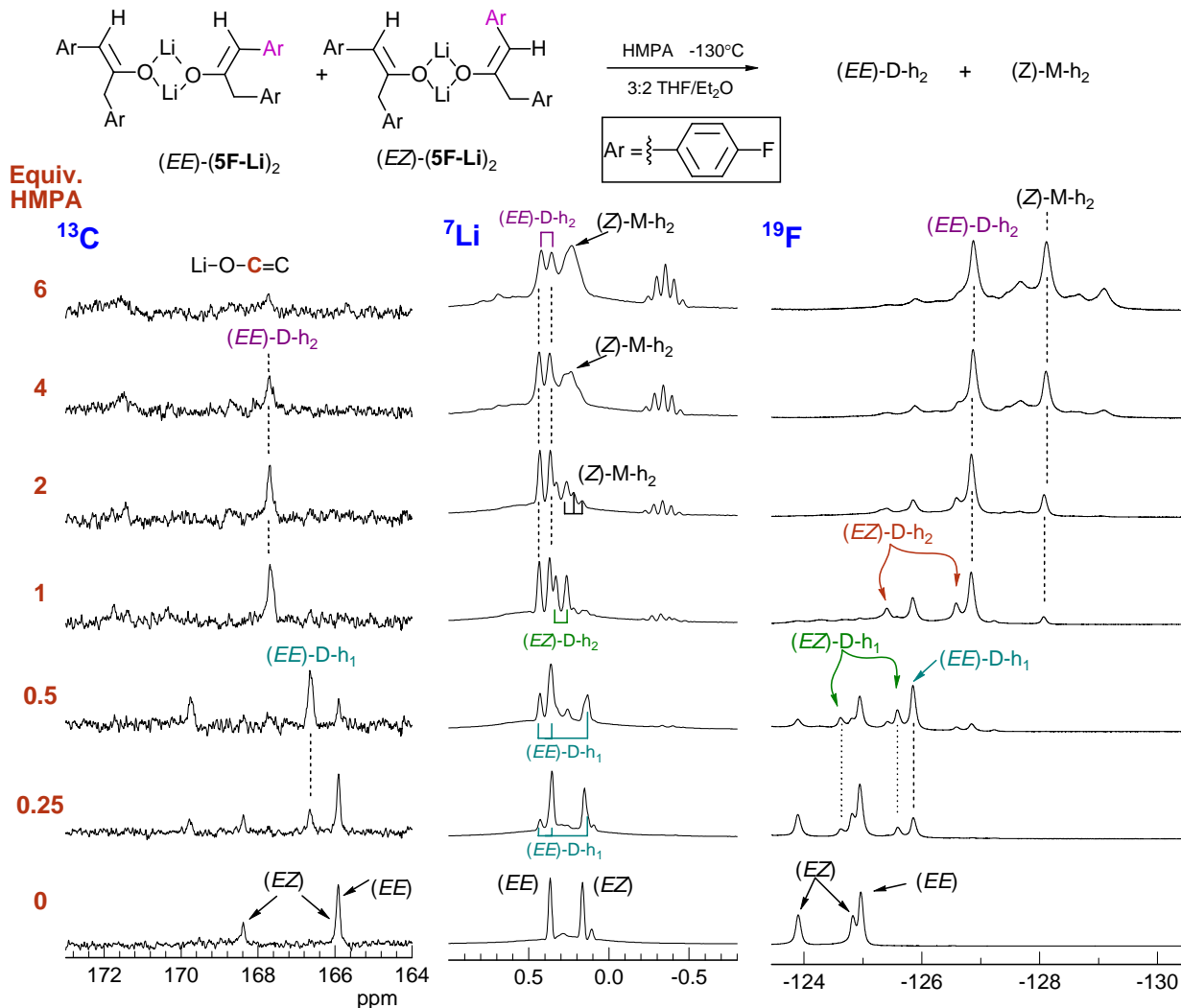


Figure S-33. HMPA titration of the *EE* and *EZ* dimers of **5F-Li** in 3:2 THF/ Et₂O at -130 $^{\circ}$ C. Sequential solvation of the *EE* and *EZ* dimer was observed as the concentration of HMPA was increased up to one equiv. Above one equiv. of HMPA formation of the *Z* HMPA solvated monomer was observed but formation of the *E* HMPA solvated monomer was not (h = HMPA; D = dimer; M = monomer).

HMPA Titration of Lithium Enolate *E*-5F-Li at -105 °C in Et₂O. 1,3-Bis-(4-fluorophenyl)-2-propanone (450 μ L, 0.65 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 °C to a 0.1 M solution (Et₂O) of freshly prepared LiNⁱPr₂. ¹³C, ⁷Li, ¹⁹F and ³¹P spectra were obtained at -105 °C with 0, 0.25 (13 μ L), 0.5 (26 μ L), 0.75 (39 μ L), and 1 equiv. (52 μ L) of HMPA added. The sample was quenched with the addition of Et₃N (84 μ L, 0.6 mmol) and Me₃SiCl (160 μ L, 1.2 mmol). The resulting enol silyl ether was determined to be a 85:15 mixture of *E* and *Z* isomer. Spectra are shown in Figure 15 and S-34.

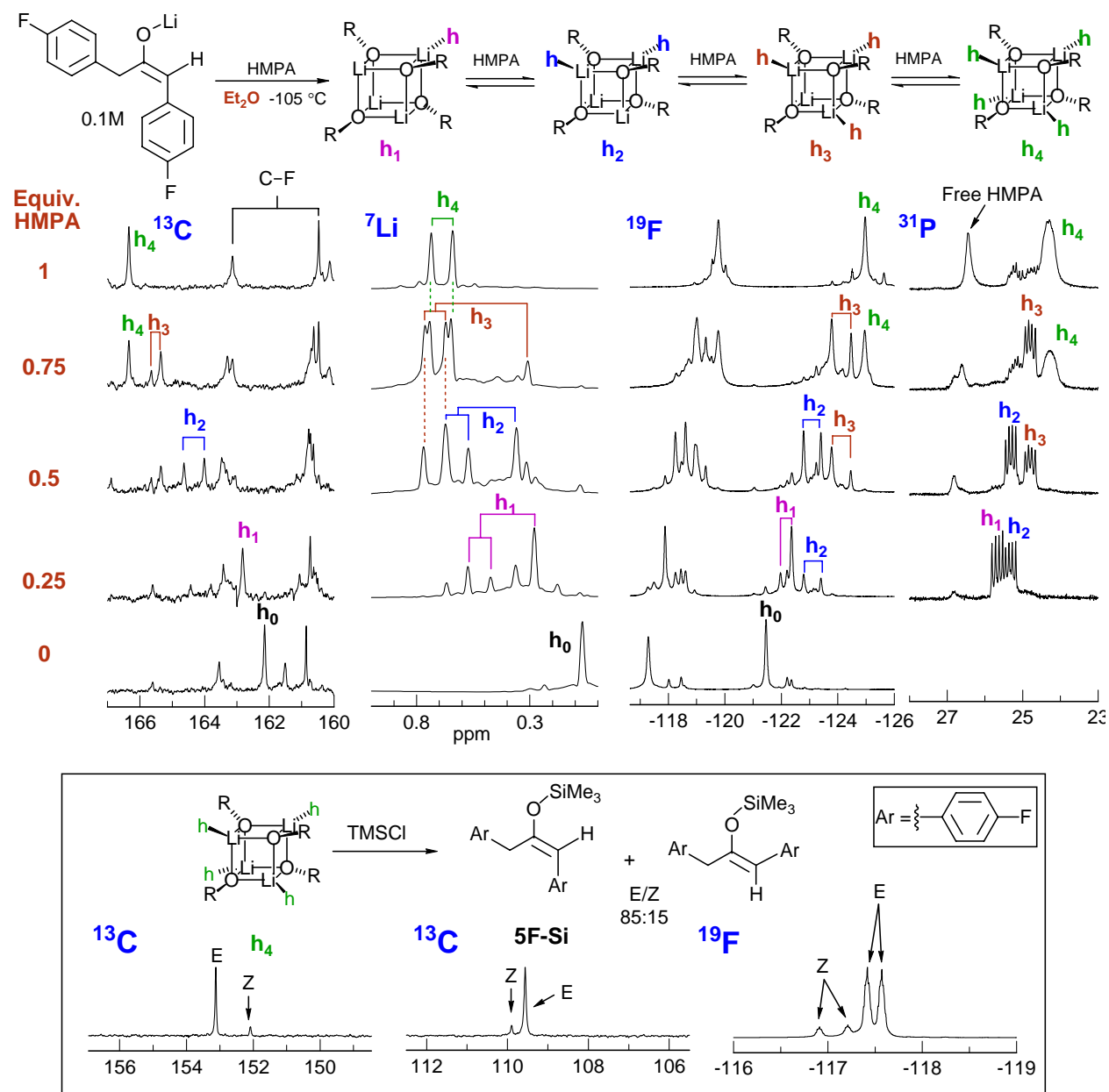


Figure S-34. HMPA titration of the tetramer of *E*-5F-Li in Et₂O at -105 °C. Sequential solvation of the *E* tetramer was observed as the concentration of HMPA was increased up to one equiv. Quenching the solution with Me₃SiCl resulted in an enol silyl ether a mixture of 85:15, *E* and *Z* isomers. (h = HMPA)

HMPA Titration of Lithium Enolate *E*-5F-Li at -125 °C in Et₂O. 1,3-Bis-(4-fluorophenyl)-2-propanone (450 μ L, 0.65 M solution in Et₂O, 0.3 mmol) was added at -78 °C to a 0.1 M solution (Et₂O) of freshly prepared LiNⁱPr₂ in Et₂O. ¹³C, ⁷Li, ¹⁹F and ³¹P spectra were obtained at -122 °C with 0, 0.25 (13 μ L), and 0.5 (26 μ L) equiv. of HMPA and at -105 °C with 0.5, 0.75 (39 μ L), 1 (52 μ L), 2 (104 μ L), 3 (156 μ L), 4 (208 μ L) and 6 equiv. (312 μ L) of HMPA. The sample was quenched with Et₃N (84 μ L, 0.6 mmol) and Me₃SiCl (160 μ L, 1.2 mmol). Spectra are shown in Figure S-35.

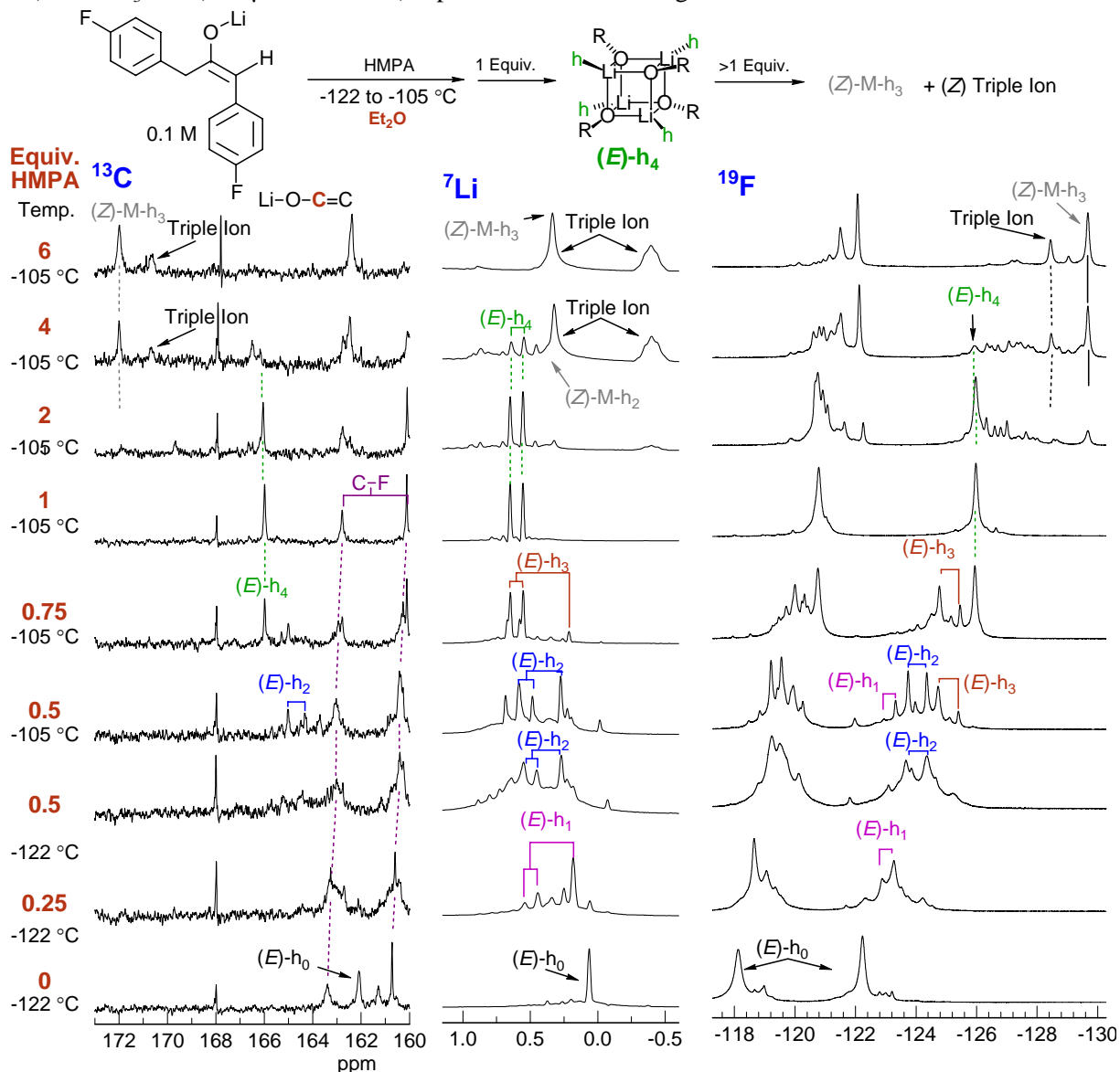


Figure S-35. HMPA titration of the tetramer of *E*-5F-Li in Et₂O at various temperatures from -122 to -105 °C. Sequential solvation of the *E* tetramer was observed as the concentration of HMPA was increased up to one equivalent. Above one equivalent, the tetra-HMPA solvated *E* tetramer was converted to triple ion and *Z* HMPA-solvated monomer with the solution consisting largely of these two species at six equivalents of HMPA. Quenching the sample with Me₃SiCl resulted in exclusively (>95%) *Z* enol silyl ether. (h = HMPA)

HMPA Titration of Lithium Enolate Z-5F-Li at -140 °C in Et₂O/Me₂O. 1,3-Bis-(4-fluorophenyl)-2-propanone (450 μL, 0.65 M solution in Et₂O, 0.3 mmol) was added at -78 °C to a 0.1 M solution (Et₂O) of freshly prepared LiNⁱPr₂. The solution was allowed to warm to room temperature for several hours. The sample was cooled to -78 °C and via cannula ca 0.5 mL of Me₂O was added. ¹³C, ⁷Li, ¹⁹F and ³¹P spectra were obtained at -133 °C with 0, 0.25 (13 μL), 0.5 (26 μL), 1 (52 μL), 1.5 (78 μL), 2 (104 μL), 4 (208 μL) and 6 equiv. (312 μL) of HMPA added. Spectra are shown in Figure S-36.

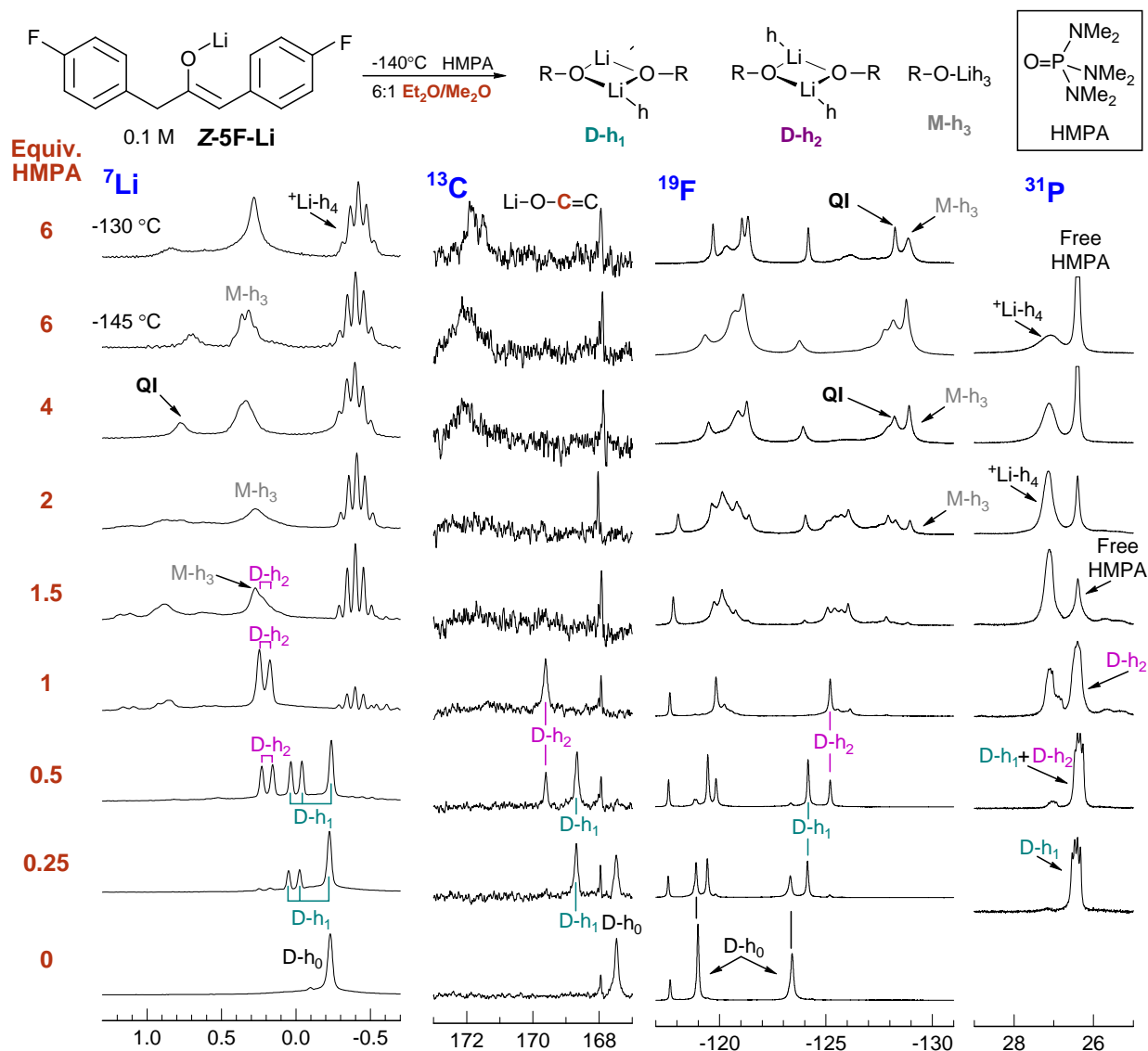


Figure S-36. HMPA titration of Z-5F-Li in Et₂O at -140 °C. Sequential solvation of the dimer was observed as the concentration of HMPA was increased up to one equiv. Above one equiv. of HMPA the solution became more complex with the formation of a number of broad signals. The addition of >4 equiv. of HMPA produces a solution consisting of the previously identified tris-HMPA monomer and quadruple ion (h = HMPA; D = dimer; M = monomer).

Dilution study of Lithium Enolate Z-5F-Li in Et₂O with 6 equiv. of HMPA. 1,3-Bis-(4-fluorophenyl)-2-propanone (1.13 mL, 0.80 M solution Et₂O, 0.3 mmol) was added at -78 °C to a 0.3 M solution of freshly prepared LiN^hPr₂ in Et₂O. HMPA (6 equiv., 120 μL) was added and the sample was allowed to warm to room temperature (ca 25 °C) for 15 min. ¹³C, ⁷Li, and ¹⁹F spectra were obtained at -125 °C. From this sample 1 mL was removed and placed in a dry, purged 10 mm NMR tube sealed with a septa containing 2.0 mL of Et₂O. ¹³C, ⁷Li, and ¹⁹F spectra were obtained at -125 °C. From the original sample 0.5 mL was removed and placed in a dry, purged 10 mm NMR tube sealed with a septa containing 2.5 mL of Et₂O. ¹³C, ⁷Li, and ¹⁹F spectra were obtained at -125 °C. From the original sample 0.2 mL was removed and placed in a dry, purged 10 mm NMR tube sealed with a septa containing 3.8 mL of Et₂O. ¹³C, ⁷Li, and ¹⁹F spectra were obtained at -125 °C. Spectra are shown in Figure S-37.

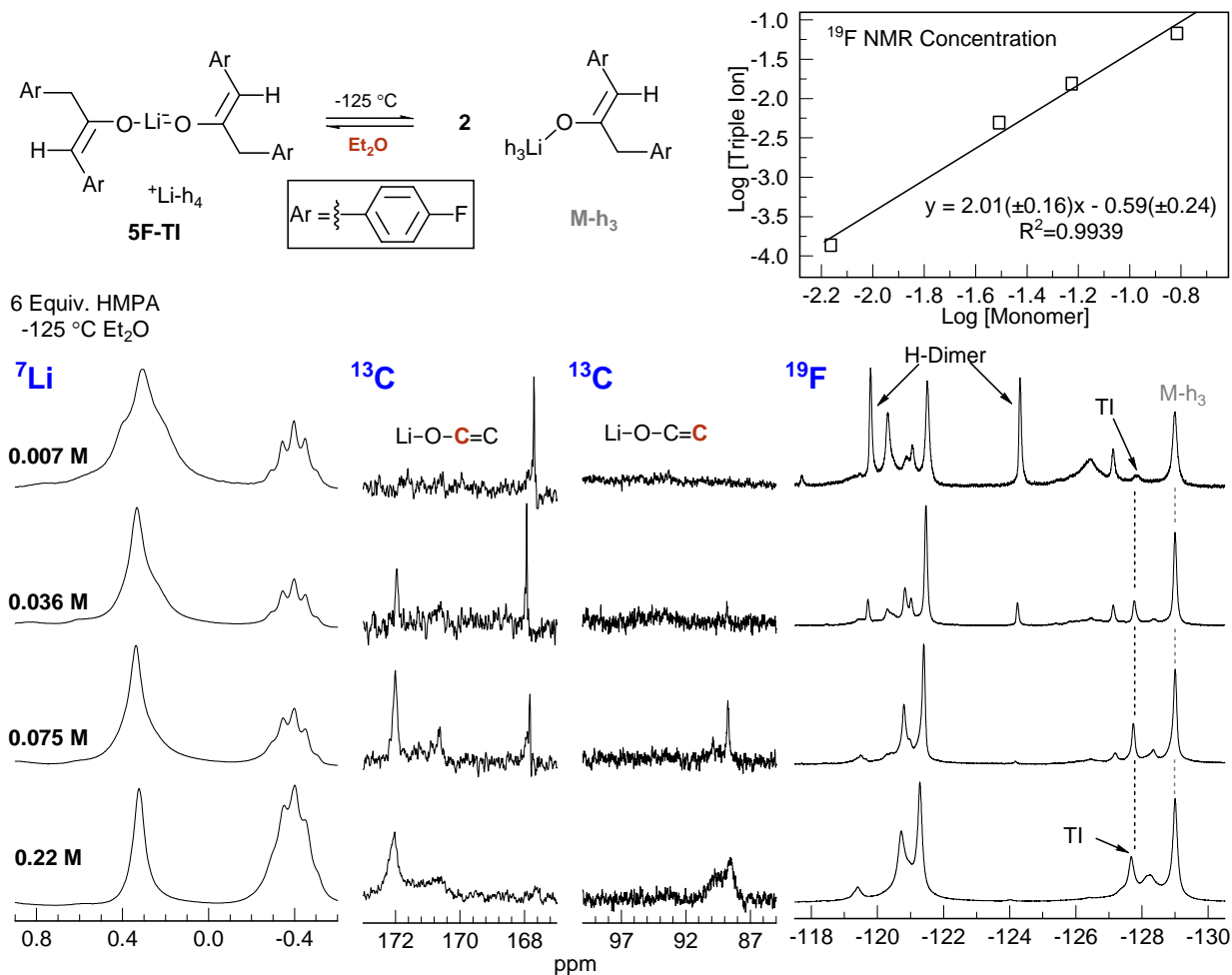


Figure S-37. Variable concentration experiment of an Et₂O solution of the lithium enolate of **5F-Li** containing 6 equiv. of HMPA at -125 °C. Based on the integration of ¹⁹F NMR spectra the triple ion decreased and the amount of tris-HMPA monomer increased as the solution was diluted (h = HMPA).

HMPA Titration of Lithium Enolate of 1,2-Diphenylethanone (6H-Li) in THF/Et₂O. 1,2-Diphenylethanone (480 μ L, 0.62 M solution in 3:2 THF/Et₂O, 0.3 mmol) was added at -78 $^{\circ}$ C to a 0.1 M solution of freshly prepared LiNⁱPr₂ in 3:2 THF/Et₂O. The sample was allowed to warm to room temperature (ca 25 $^{\circ}$ C) for 2 h, recooled to -130 $^{\circ}$ C and ¹³C and ⁷Li spectra were acquired. ¹³C, ⁷Li and ³¹P spectra were obtained at -130 $^{\circ}$ C with 0.25 (13 μ L), 0.5 (26 μ L), 0.75 (39 μ L), 1 (52 μ L), 2 (104 μ L), 4 (208 μ L) and 6 equiv. (312 μ L) of HMPA added. Spectra are shown in Figure S-38.

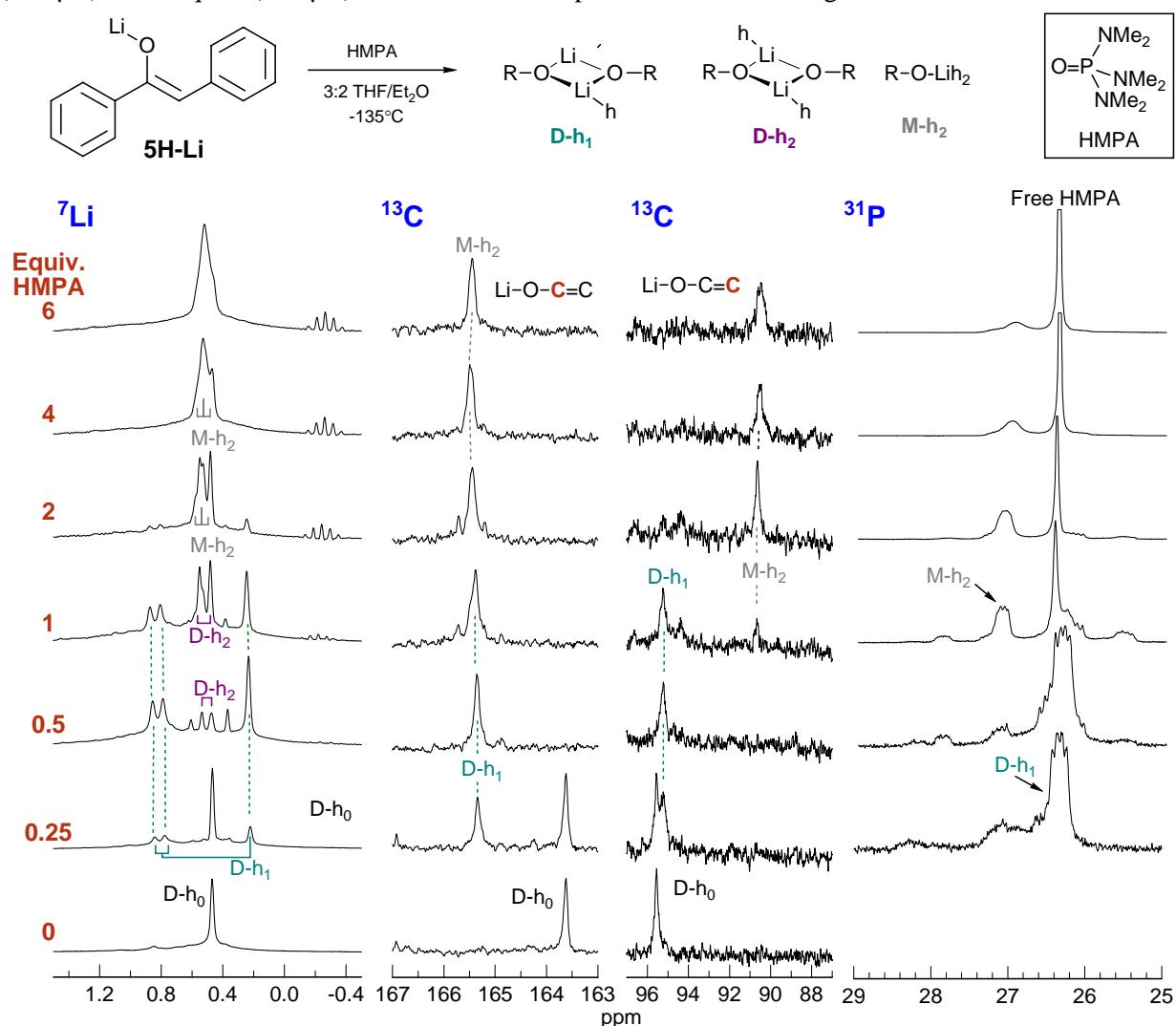


Figure S-38. HMPA titration of the lithium enolate of 0.1 M **6H-H** in 3:2 THF/Et₂O at -130 $^{\circ}$ C. Solvation of the dimer by HMPA was observed, followed by dissociation to monomer upon increasing the concentration of HMPA (D = 4-center dimer, M = monomer, h_n = number of coordinated HMPA molecules).

Kinetic and Thermodynamic Deprotonation of 1-Phenyl-2-(4-fluorophenyl)ethanone (6F-H). *Kinetic Conditions:* 1-Phenyl-2-(4-fluorophenyl)ethanone (400 μ L, 0.67 M solution in 3:2 THF/Et₂O, 0.3 mmol) was added at -78 $^{\circ}$ C to a 0.1 M solution of freshly prepared LiNⁱPr₂ in 3:2 THF/Et₂O and ¹³C, ¹⁹F and ⁷Li spectra were acquired at -130 $^{\circ}$ C. The sample was quenched with the addition of Me₃SiCl (100 μ L, 0.8 mmol) and ¹³C, ¹⁹F and ⁷Li spectra were acquired at -130 $^{\circ}$ C. *Thermodynamic Conditions:* An identical sample was allowed to warm to room temperature (ca 25 $^{\circ}$ C) for several hours after which the sample was cooled and ¹³C, ¹⁹F and ⁷Li spectra were acquired at -130 $^{\circ}$ C. The sample was quenched with the addition of Me₃SiCl (100 μ L, 0.8 mmol) and ¹³C, ¹⁹F and ⁷Li spectra were acquired at -130 $^{\circ}$ C. Spectra are shown in Figure S-39.

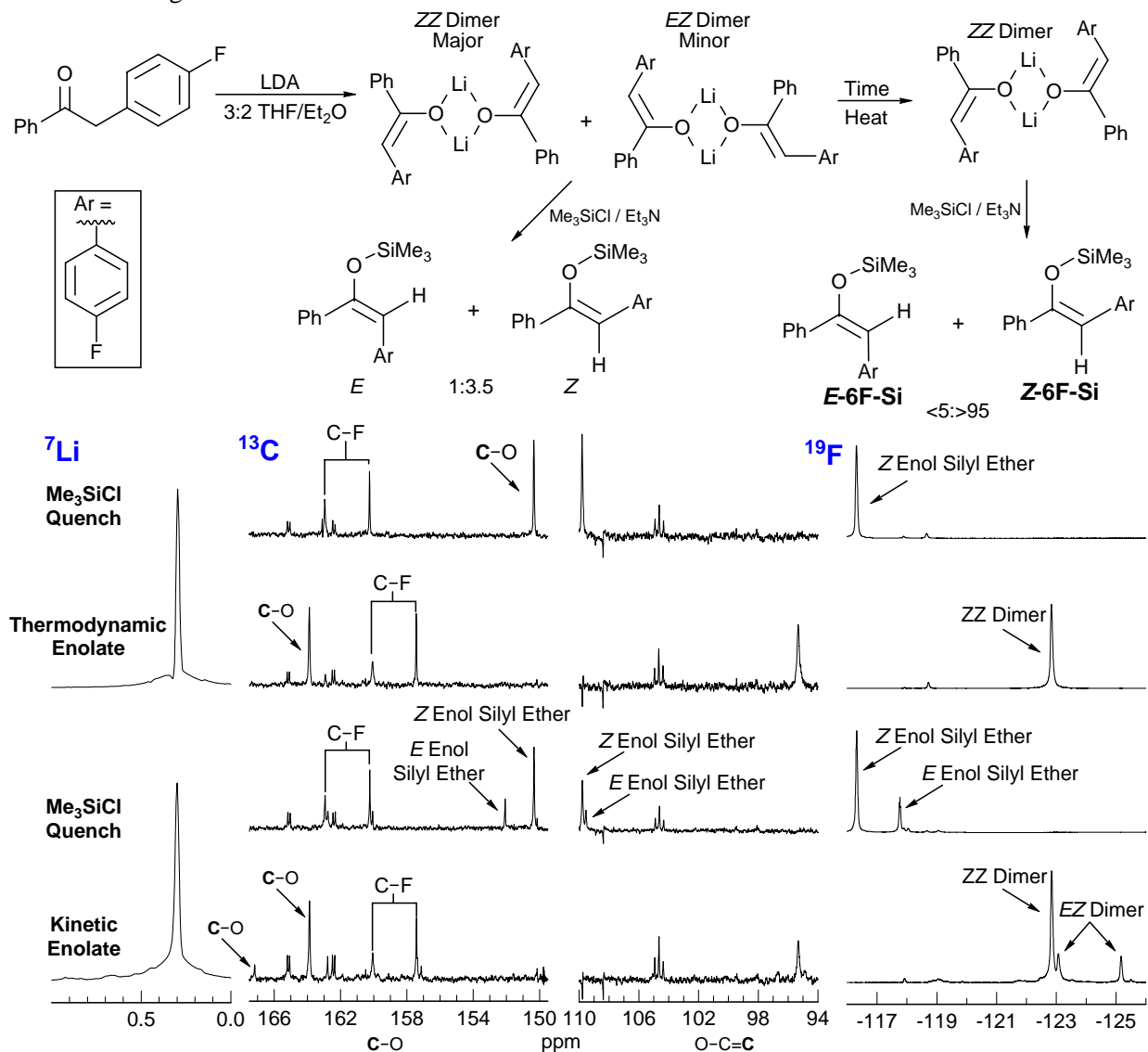


Figure S-39. Deprotonation of 1-phenyl-2-(4-fluorophenyl)ethanone (6F-H) with 0.1 M LiNⁱPr₂ in 3:2 THF/Et₂O under kinetic and thermodynamic conditions. Samples were quenched with Me₃SiCl for further analysis of the resulting enol silyl ether.

NOESY Study of Z-1-Phenyl-2-(4-fluorophenyl)-1-(trimethylsilyloxy)ethene (6F-Si). Z-1-Phenyl-2-(4-fluorophenyl)-1-(trimethylsilyloxy)ethene was synthesized and isolated as described in the synthesis section. A sample was prepared in dry CDCl₃ and selective ¹H NOESY experiments were run irradiating H_a (Figure S-40) and the Me₃Si protons (Figure S-41) using standard Varian pulse sequences. The mixing time (time for NOE buildup) was varied to distinguish real NOEs from artifacts (Figure S-40) and to determine relative distances

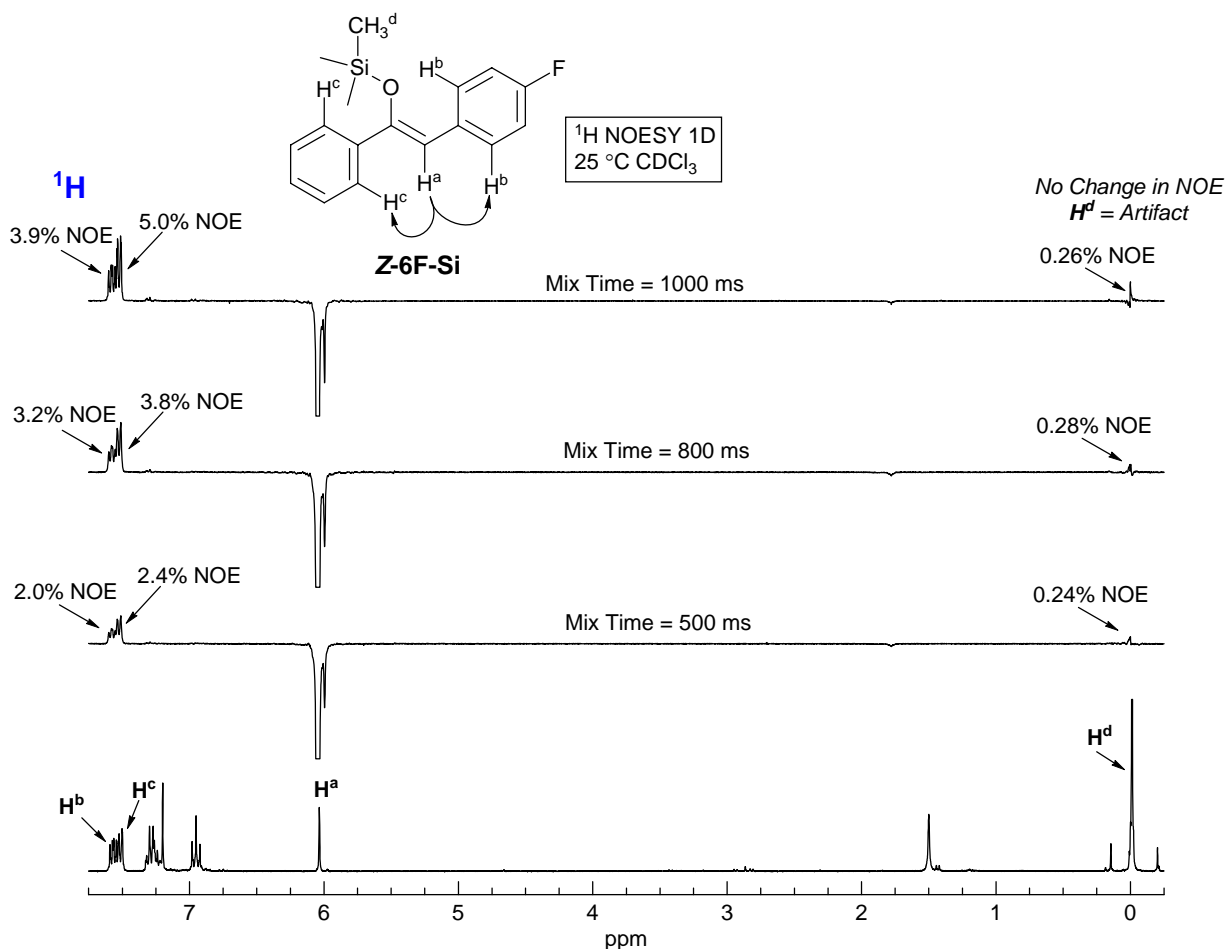


Figure S-40. Selective ¹H NOESY experiments of **6F-Si** were performed with varying mix times to distinguish artifacts observed from the intense (CH₃)₃Si signal when the vinyl proton signal was selectively inverted.

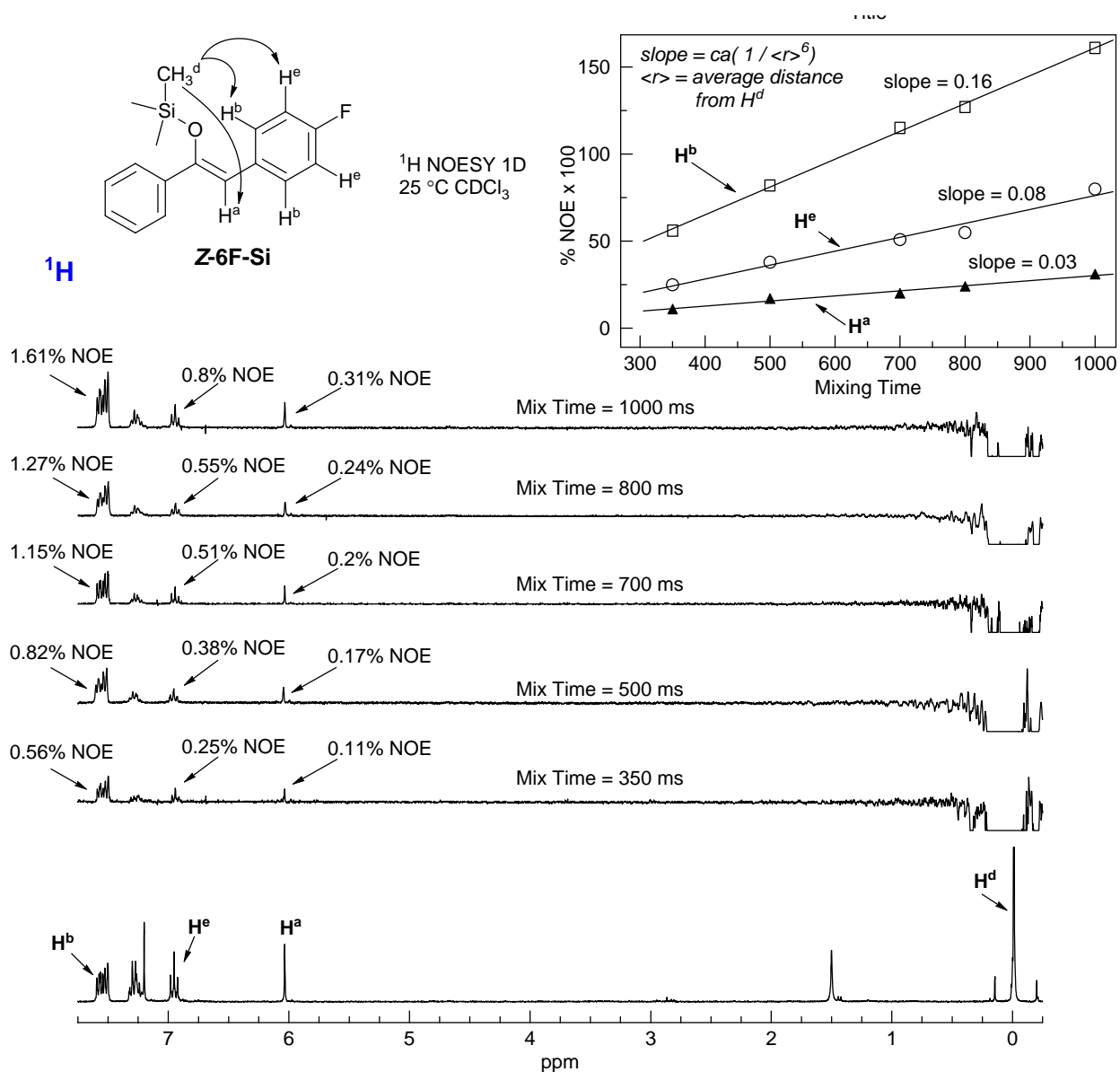


Figure S-41. Selective ¹H NOESY experiments of **6F-Si** were performed with varying mix times to determine the relative distance from (CH₃)₃Si based on the observed NOE when the (CH₃)₃Si signal, **H^d**, was selectively inverted. The measurement of relative distances was made from a plot of the percent NOE versus mixing time where the slope of the line for **H^a**, **H^b**, and **H^e** are proportional to 1/*r*⁶, where *r* is equal to the average distance from **H^d**.

HMPA Titration of Lithium Enolate 6F-Li in THF/ Et₂O. 1-Phenyl-2-(4-fluorophenyl)ethanone (800 μ L, 0.38 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 $^{\circ}$ C to a freshly prepared 0.1 M solution of LiNⁱPr₂ in 3:2 THF/Et₂O. The sample was allowed to warm to room temperature (ca 25 $^{\circ}$ C) for 2 h, was cooled to -130 $^{\circ}$ C. ¹³C, ⁷Li, ¹⁹F and ³¹P spectra were obtained at -130 $^{\circ}$ C with 0, 0.25 (13 μ L), 0.5 (26 μ L), 0.75 (39 μ L), 1 (52 μ L), 2 (104 μ L), 4 (208 μ L) and 6 equiv. (312 μ L) of HMPA added. Spectra are shown in Figure S-42.

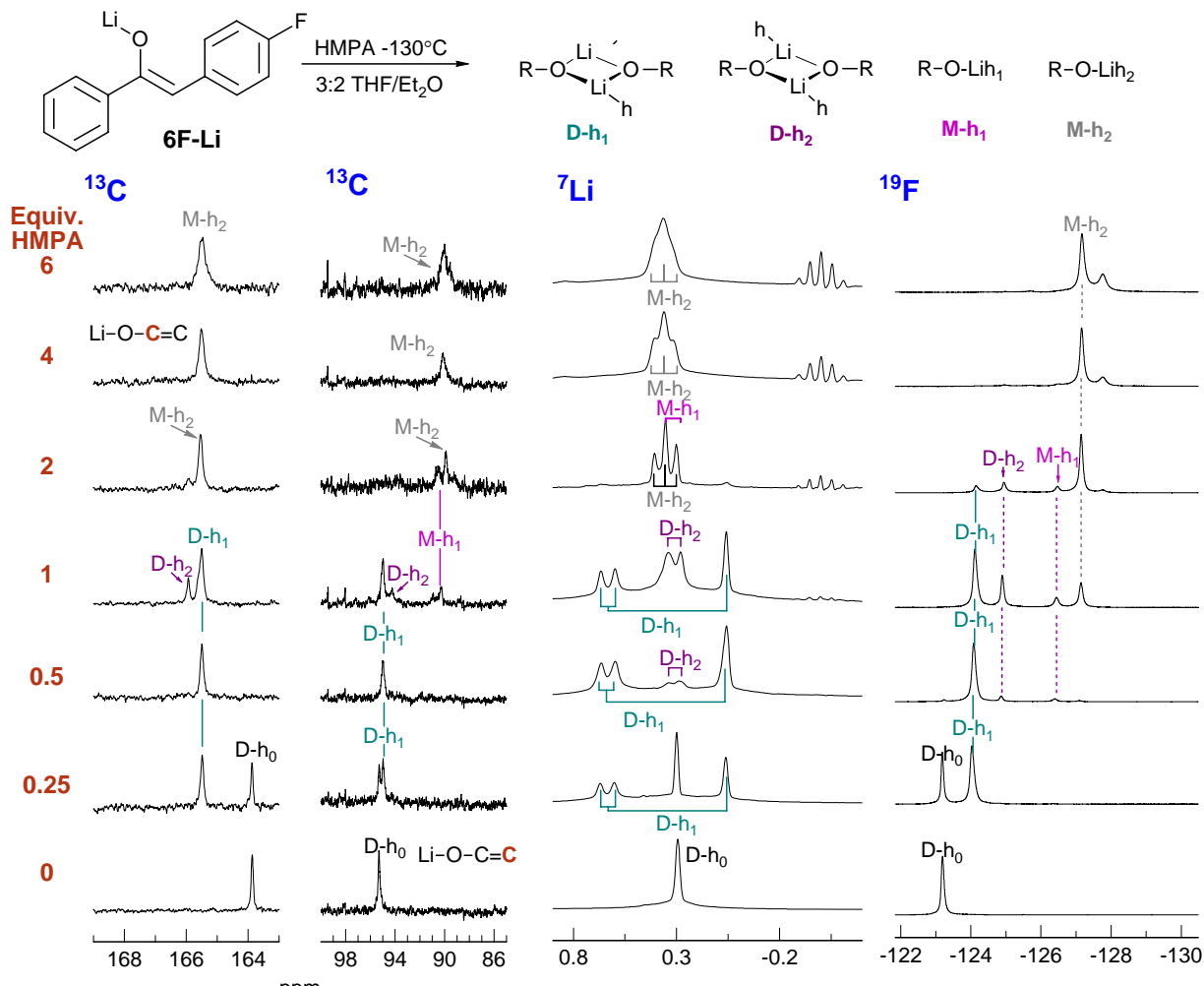


Figure S-42. HMPA titration of 0.1 M **6H-Li** in 3:2 THF/Et₂O at -130 $^{\circ}$ C. Solvation of the dimer by HMPA was observed but this enolate dissociates to monomer easily with both mono-HMPA monomer and bis-HMPA monomer observed with half an equivalent of HMPA (D = 4-center dimer, M = monomer, h_n = number of coordinated HMPA molecules).

P4 Titration of 1-Phenyl-2-(4-fluorophenyl)ethanone (6F-H). A solution of 1-phenyl-2-(4-fluorophenyl)ethanone (82 mg, 0.38 mmol) was prepared in a 10 mm NMR tube sealed with a septa, purged with Ar, containing 3 mL of 3:2 THF/Et₂O. ¹³C, ¹H and ¹⁹F NMR spectra were obtained at -130 °C. P₄-tBu was added as a 1 M solution in hexane and ¹³C, ¹H, ¹⁹F and ³¹P NMR spectra were obtained at -130 °C with 0.3, 0.6, 0.9, and 1.2 equiv. of P₄-tBu. Spectra are shown in Figure S-43.

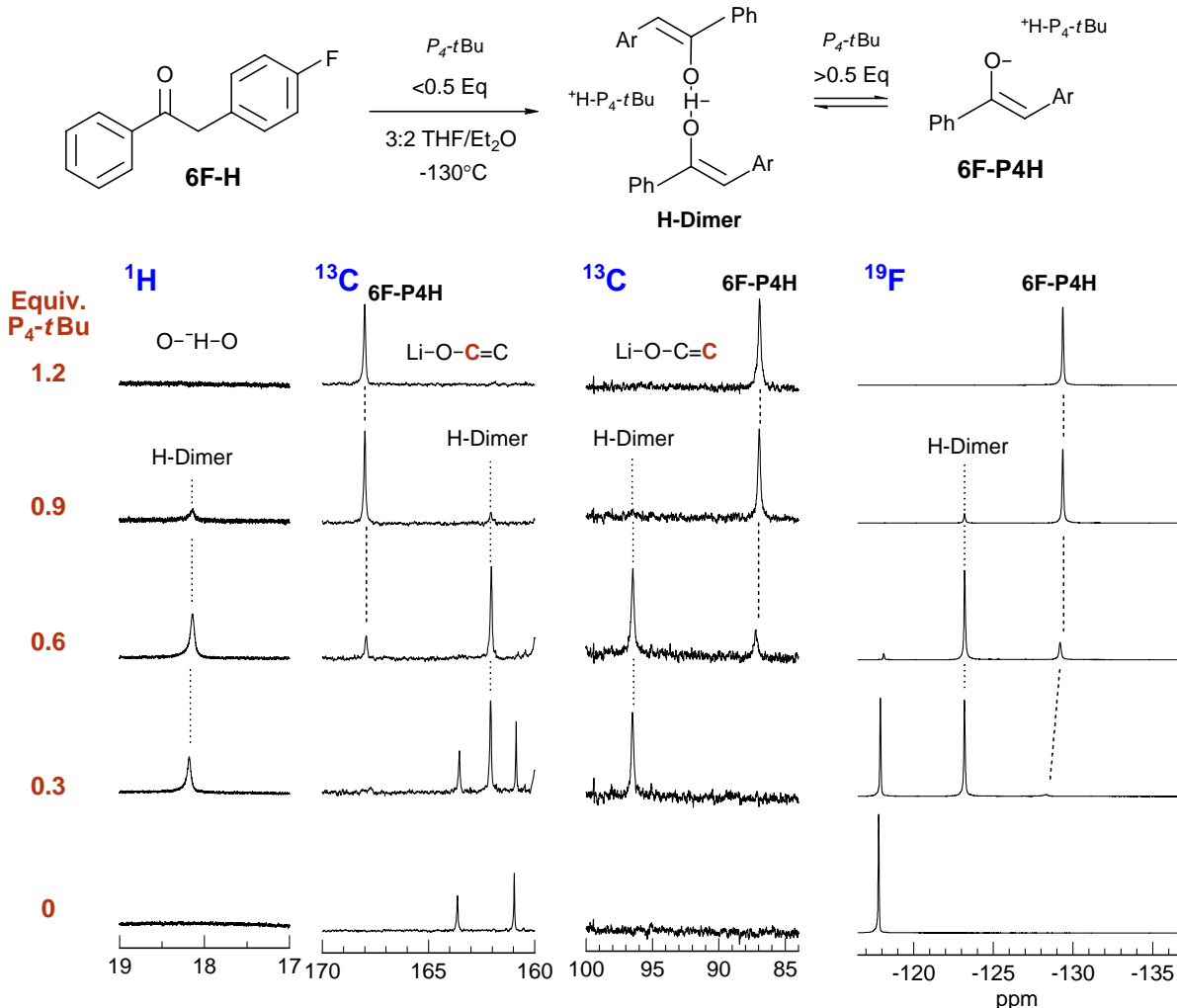


Figure S-43. P₄-tBu titration of 0.1 M 6F-H in 3:2 THF/Et₂O at -130 °C. The addition of less than 0.5 equivalent of P₄-tBu produced a dimeric enolate species which is bridged by a low barrier hydrogen bond (δ 18.2). The ¹³C signals at δ 162.1 (C-O carbon) and δ 96.5 (β-carbon) are similar to those of the lithium enolate δ 163.9 (C-O carbon) and δ 95.3 (β-carbon). Upon the addition of a full equivalent of P₄-tBu thea “naked” enolate 6F-P4H was produced, with substantially shifted C-O carbon (δ 168.0) and β-carbon (δ 87.1), compared to 6F-Li.

P4 Enolate Titration of Z Dimer of Lithium Enolate 6F-Li. 1-Phenyl-2-(4-fluorophenyl)ethanone (800 μ L, 0.38 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 $^{\circ}$ C to a 0.1 M solution of freshly prepared LiNⁱPr₂ in 3:2 THF/Et₂O. The sample was allowed to warm to room temperature (ca 25 $^{\circ}$ C) for 2 h and recooled to -130 $^{\circ}$ C. ¹³C, ¹⁹F and ⁷Li spectra were acquired on this sample, and after the addition of 1-phenyl-2-(4-fluorophenyl)ethanone (635 mg, 0.3 mmol) and P4-*t*Bu(0.3 mL, 1 M, hexane), as well as after the addition of 1-phenyl-2-(4-fluorophenyl)ethanone (540 mg, 0.25 mmol) and P4-*t*Bu(0.25 mL, 1 M, hexane). Spectra are shown in Figure S-44.

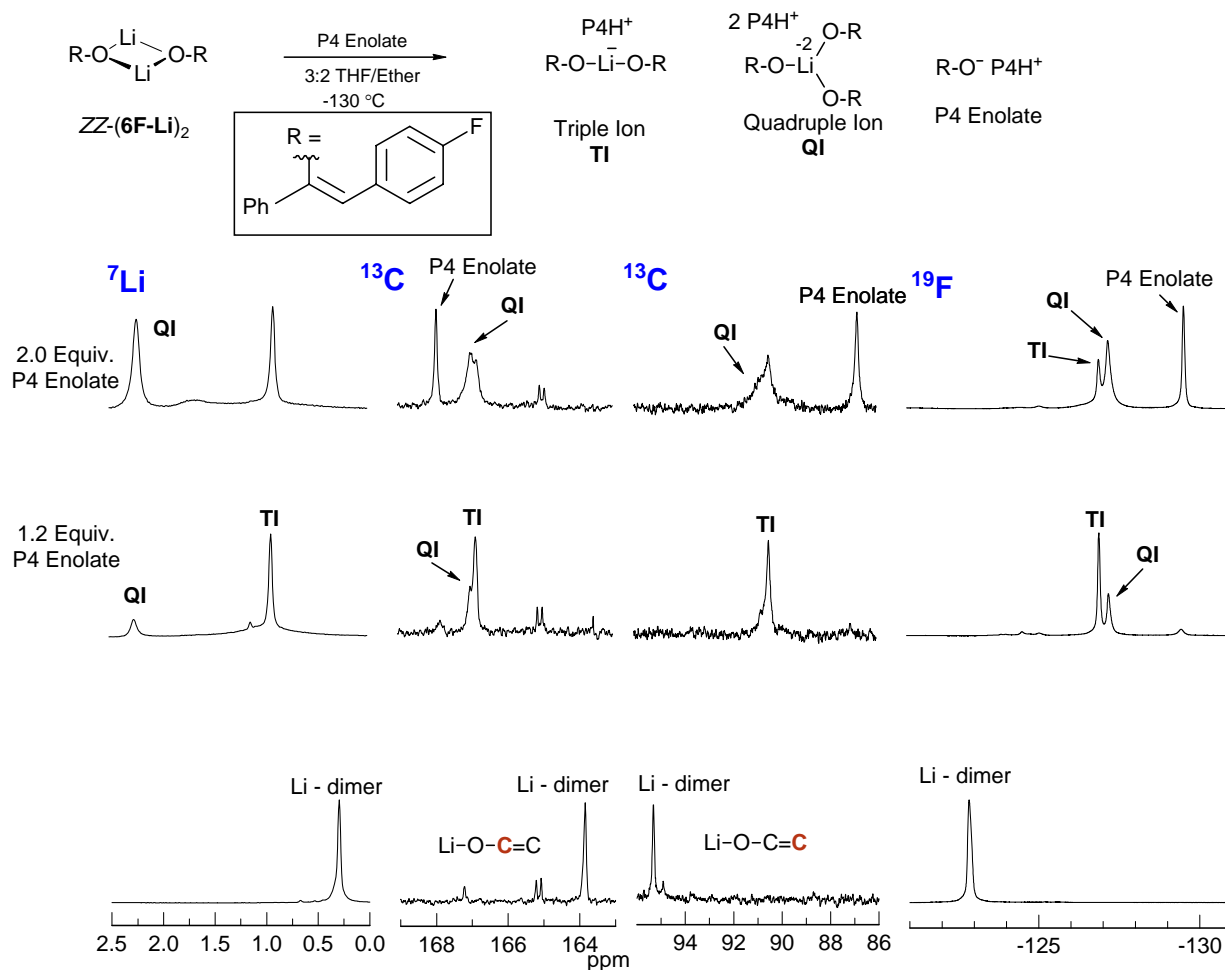


Figure S-44. The generation of the P4 enolate **6F-P4H** in the presence of lithium enolate **6F-Li** results in formation of complex ionic species. Addition of a full equivalent of **6F-P4H** to the lithium enolate produced a solution which is mostly triple ion (TI). Past one equiv of P4 enolate a new species appeared at the expense of the TI, which reached 49% of the total at two equivalents of **6F-P4H** leading to the assignment of the quadruple ion structure (**6F**)₃Li⁻² (P4H⁺)₂.

S4. Crystallographic Section (Summary)

A full reporting of the crystallographic data is presented in the second section of the Supplemental Information. Reported here is a summary of this data which includes the synthetic procedures used to generate crystals suitable for X-ray diffraction study and ORTEP diagrams of the respective molecules.

PMDTA Solvate of the Lithium Enolate of 1,3-Diphenyl-2-propanone (5H-Li·PMDTA). 1,3-Diphenyl-2-propanone (410 μL , 0.73 M solution in 3:2 THF/ Et₂O, 0.3 mmol) was added at -78 °C to a 0.1 M solution (3:2 THF/Et₂O) of freshly prepared LiNⁱPr₂. The solution was allowed to warm to room temperature (ca 25 °C) for several hours after which the sample was recooled to -78 °C and 2.0 equiv. (124 μL) of PMDTA added. Upon standing for several days at -78 °C crystals formed.

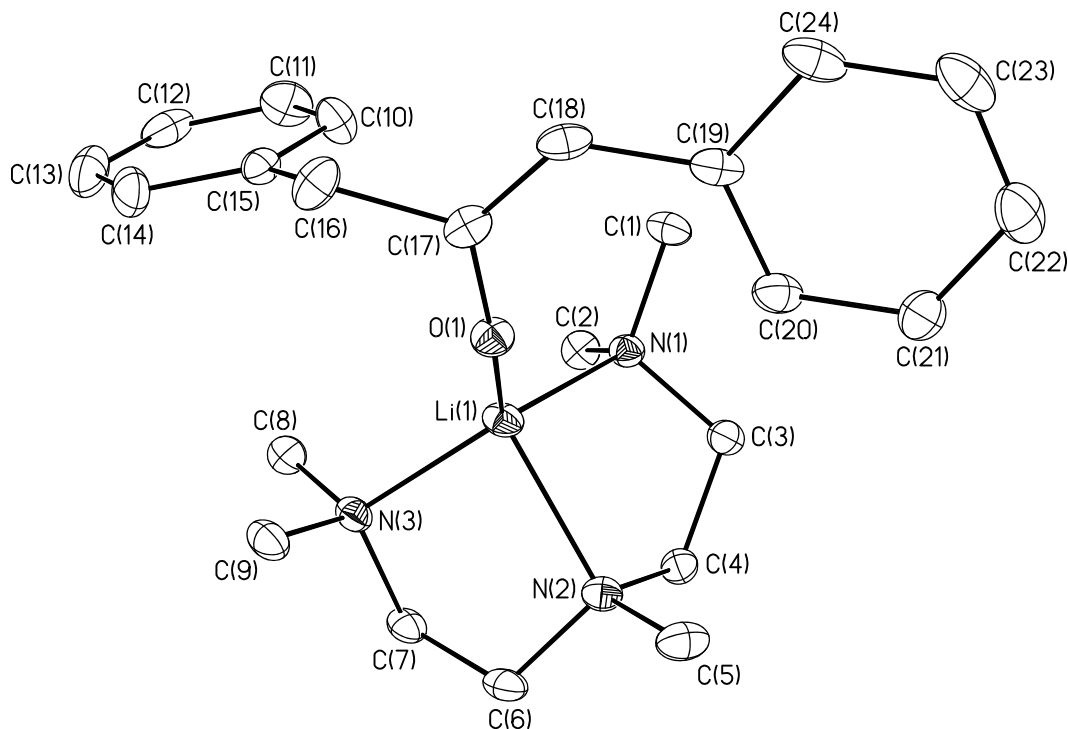


Figure S-45. Lithium enolate of 1,3-diphenyl-2-propanone PMDTA solvate (**5H-Li·PMDTA**). All H atoms have been omitted.

Lithium Enolate ((Z-5F-Li)₂(OEt₂)₂). 1,3-Bis-(4-fluorophenyl)-2- propanone (0.768 g, 3.2 mmol) was placed in a 15 mL conical vial, dissolved in 1 mL of Et₂O and cooled to 0 °C. Diisopropylamine (0.46 mL, 3.3 mmol) and 2 ml of Et₂O was placed in to a flame dried and argon purged 5 mL round bottom flask and cooled to -78 °C. *n*-Butyllithium (1.5mL, 3.2 mmol) was added and the solution was warmed to 0 °C for 5 min. The freshly prepared lithium diisopropylamide (LiNⁱPr₂) was added to a conical flask by cannula at 0 °C and the flask was shaken to mix the reactants. The solution was allowed to warm to room temperature for 30 min and cooled to -20 °C. Upon standing overnight at -20 °C crystals formed. Crystals for X-ray diffraction study could be removed or a solution of crystalized enolate could be prepared by removing the solvent via cannula, and placing the crystals under vacuum for 2 min. The flask was then back filled with argon and the crystals were dissolved in 5 mL of 3:2 THF/Et₂O to make up a 0.6 M solution. ^[S3]

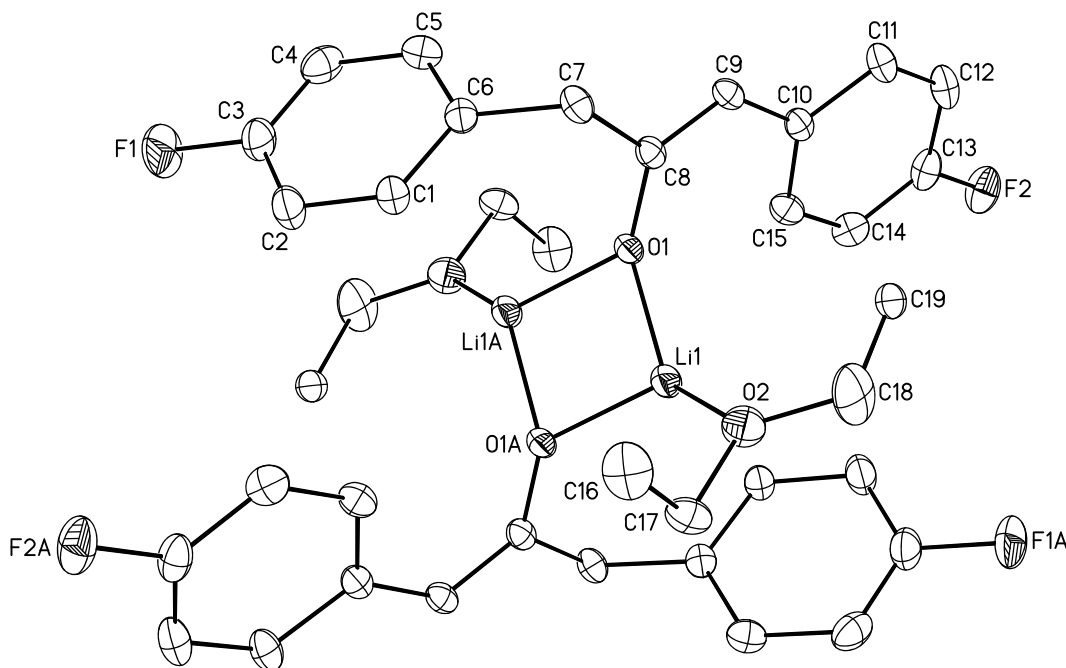


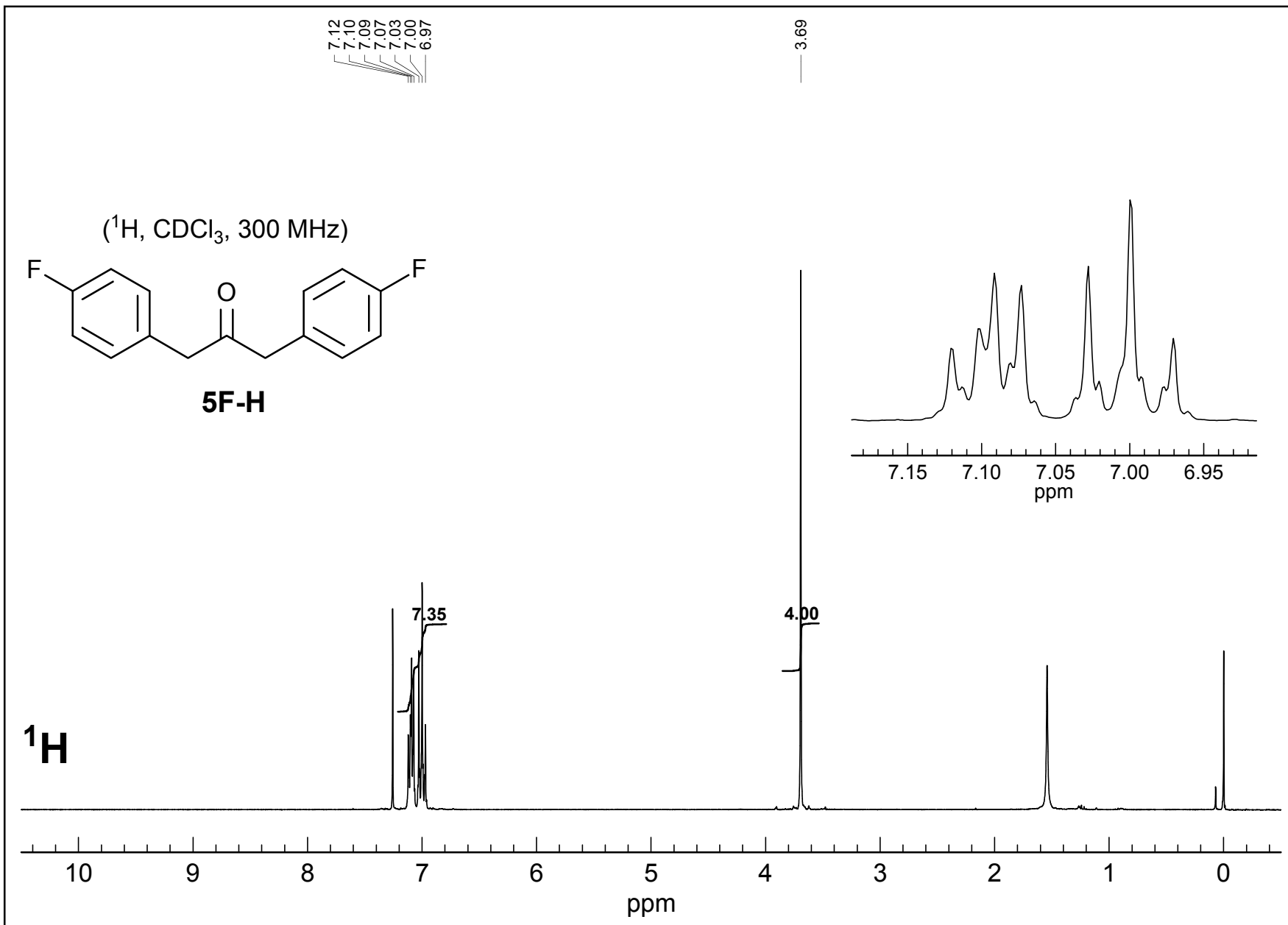
Figure S-46. A molecular drawing of ((Z-5F-Li)₂(OEt₂)₂) shown with 30% probability ellipsoids. The minor components of the disordered atoms and the H atoms are omitted.

S5. References

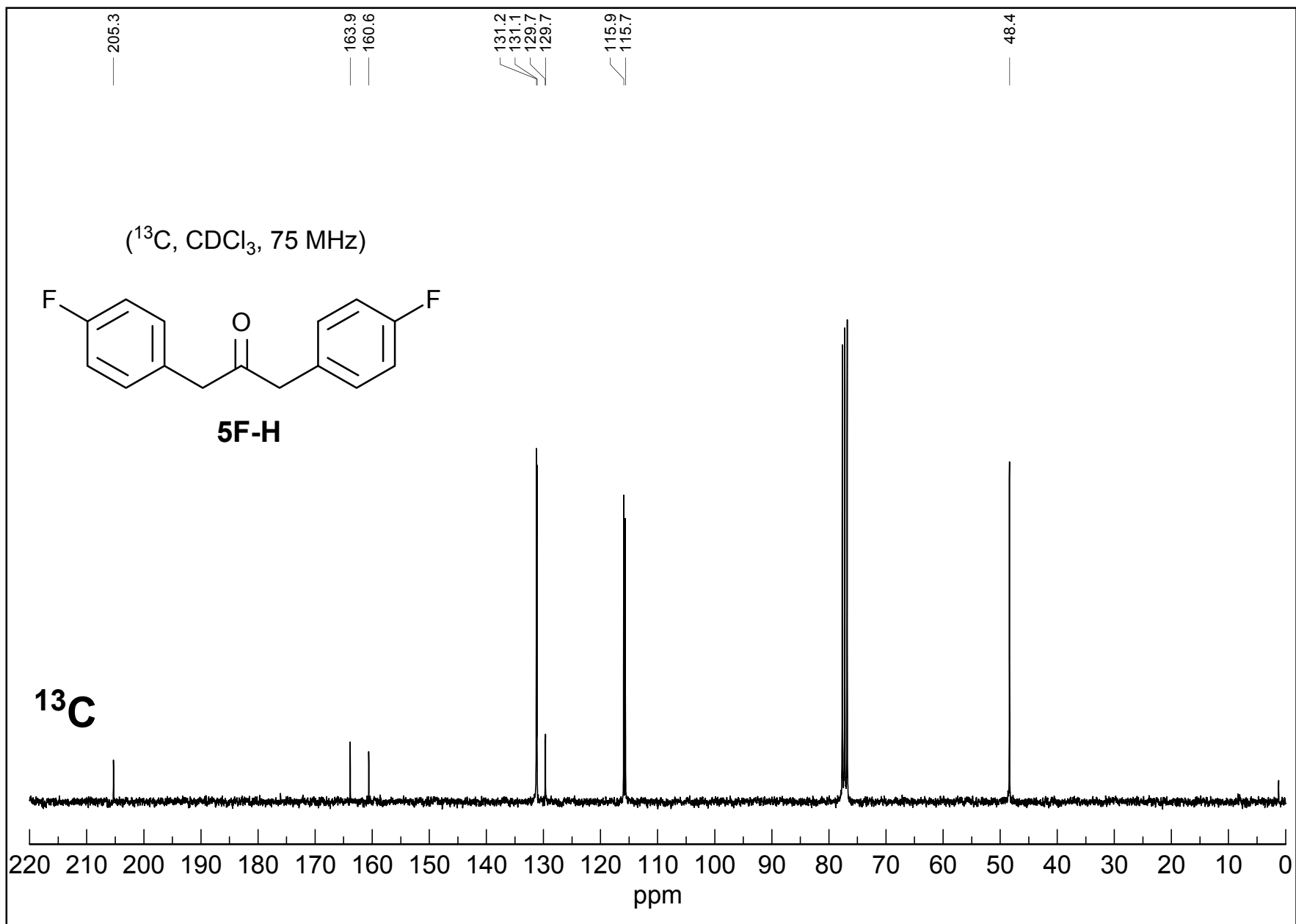
- [S1] Kolonko, K. J.; Reich, H. J. *J. Amer. Chem.* **2008**, *130*, 9668-9669.
- [S2] Sikorski, W. H.; Sanders, A. W.; Reich, H. J. *Magn. Reson. Chem.* **1998**, *36*, S118 -S124.
- [S3] Guzei, I. A.; Kolonko, K. J.; Reich, H. J. *Acta Cryst.* **2007**, *E63*, o4094.
- [S4] Denney, D. B.; Denney, D. Z.; Pastor, S. D. *Phosphorus Sulfur Silicon Relat. Elem.* **1985**, *22*, 191-197.
- [S5] DNMR simulations were performed with a version of the computer program WINDNMR (Reich, H. J. *J. Chem. Educ. Software* **1996**, *3D*, 2; <http://www.chem.wisc.edu/areas/reich/plt/-windnrmr.htm>)

S5. Spectra

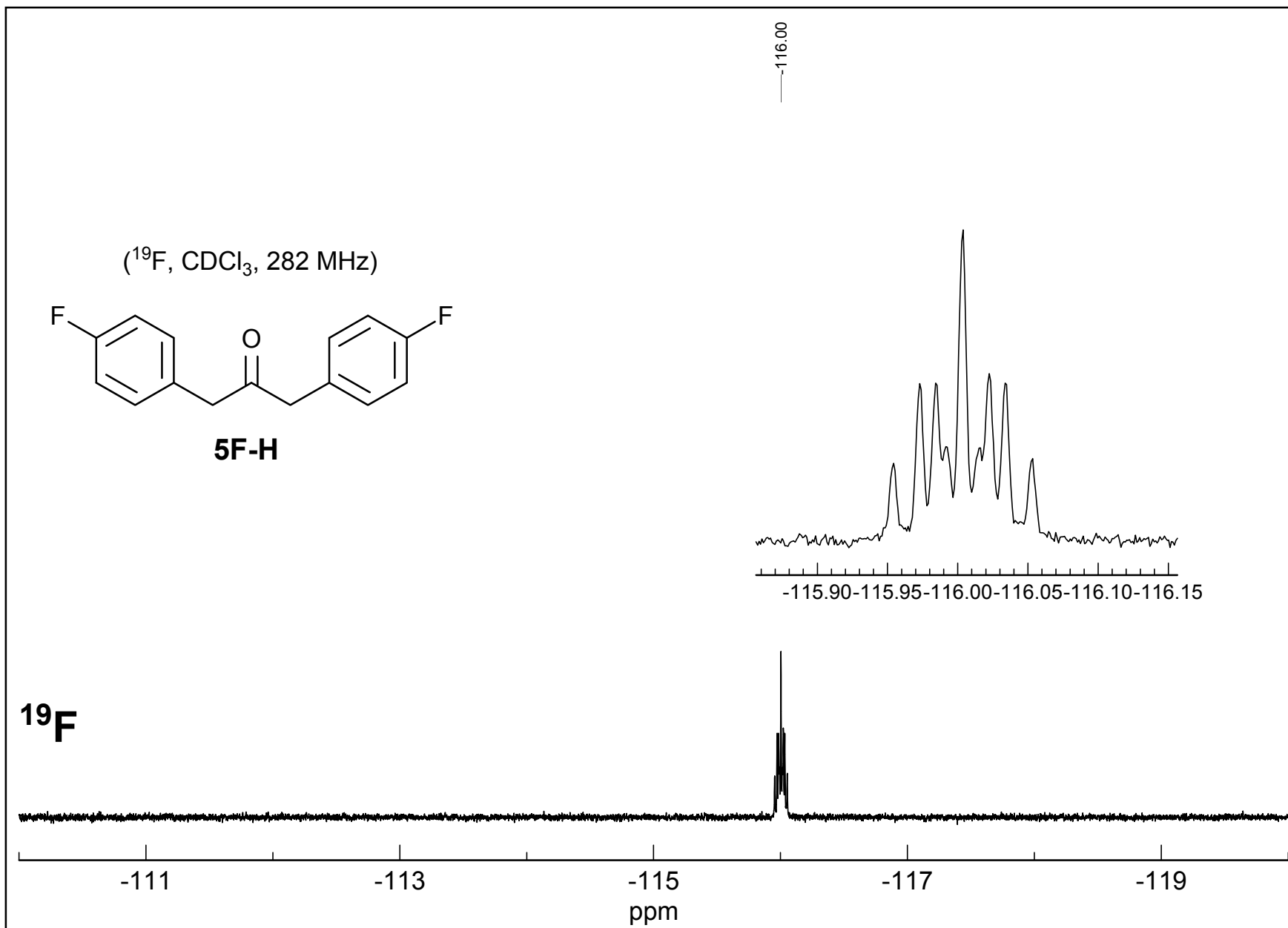
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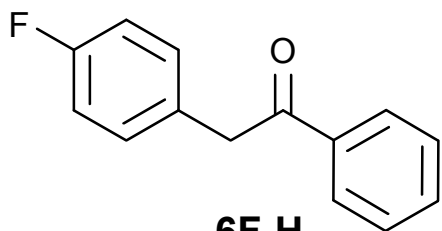
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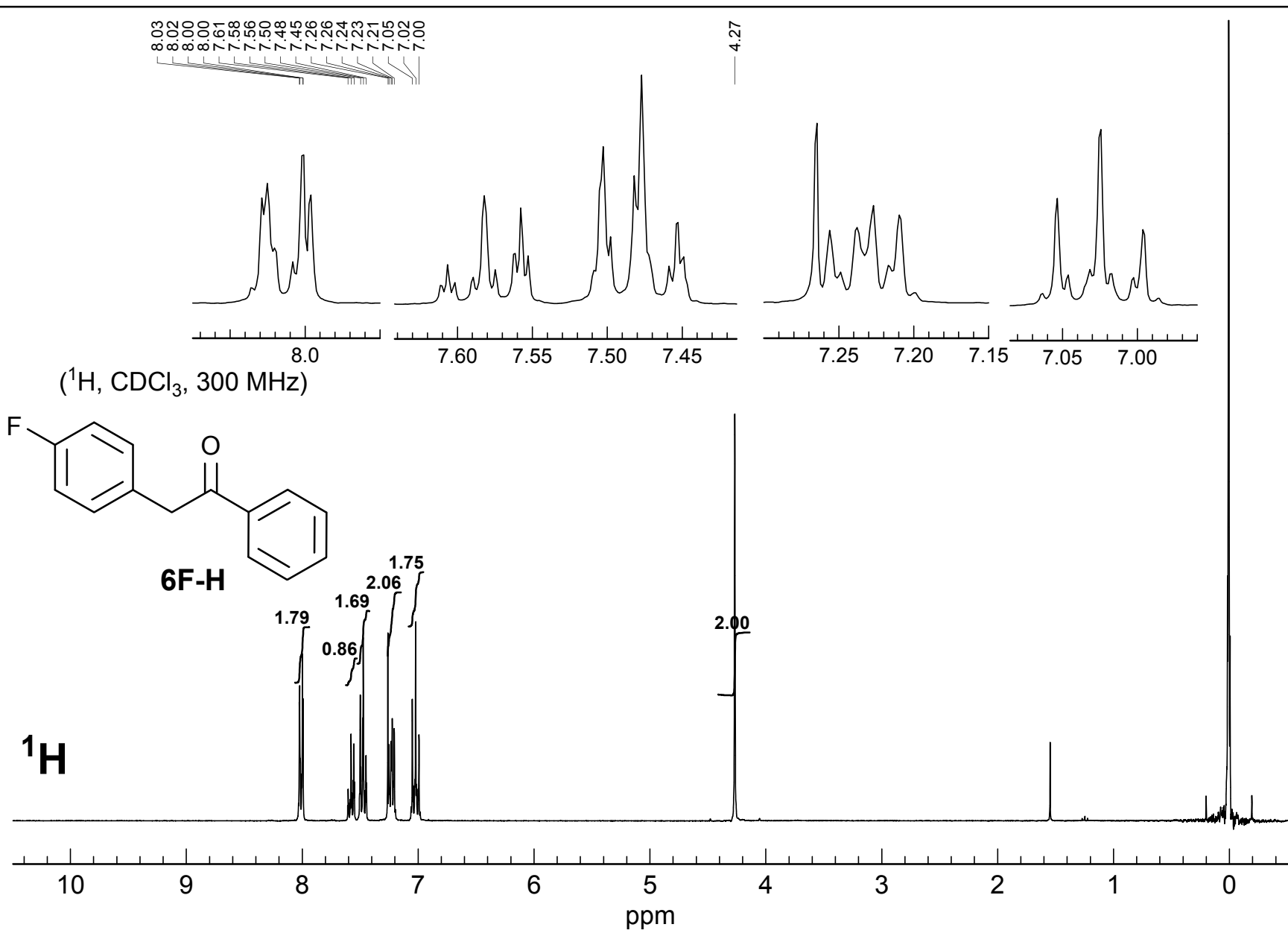
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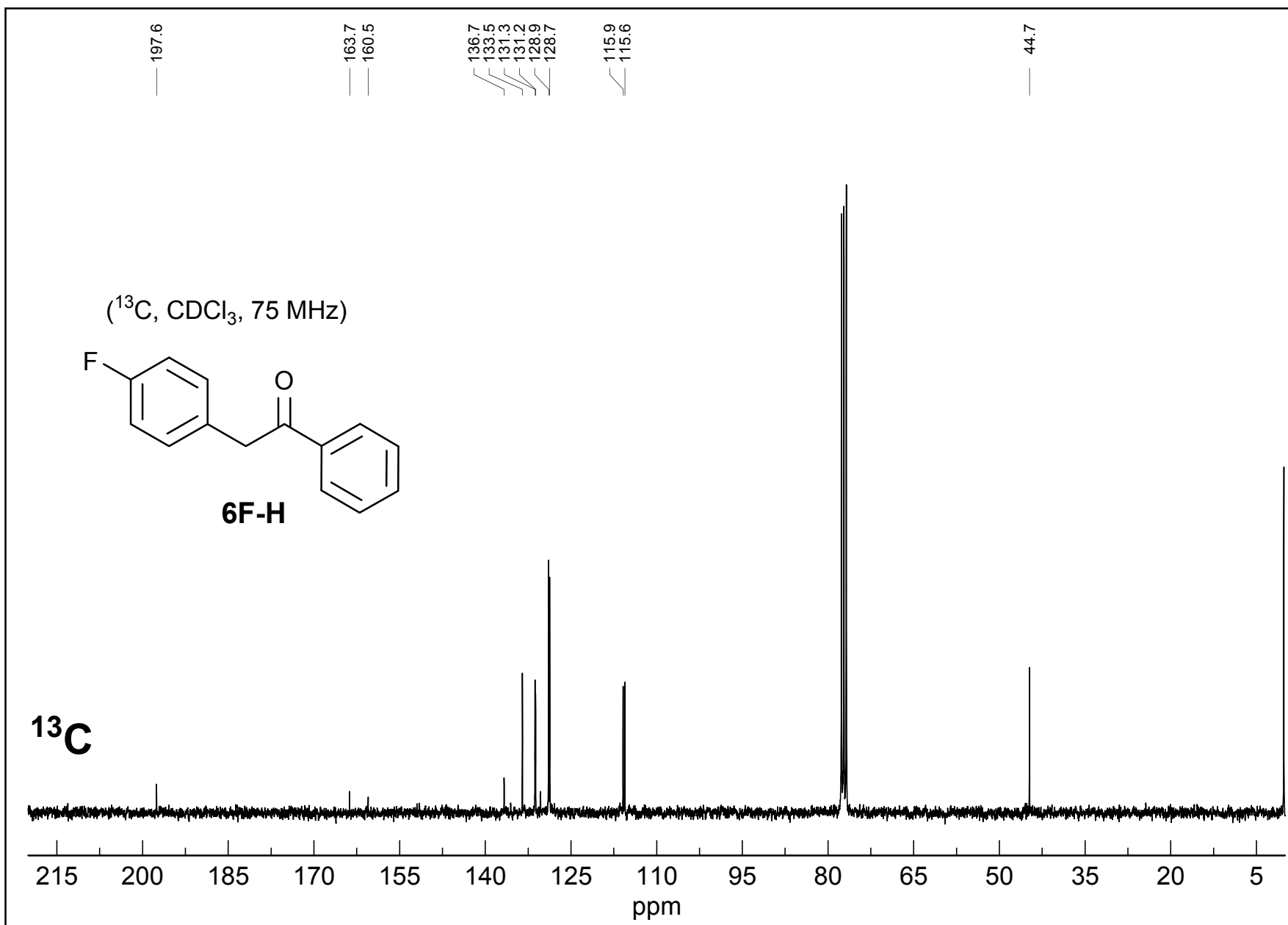
S-56



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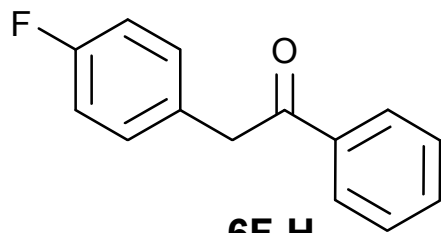


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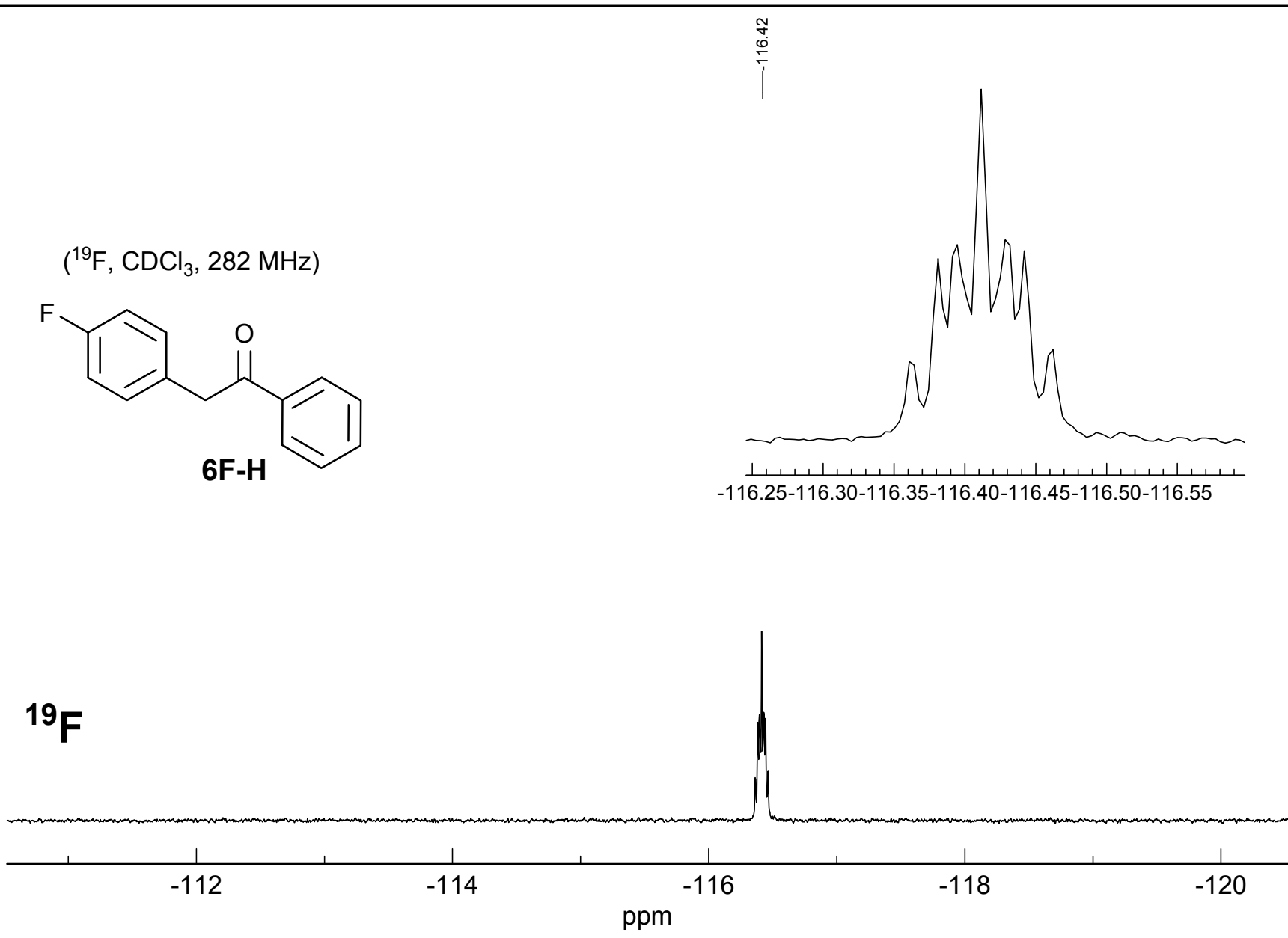


S-58

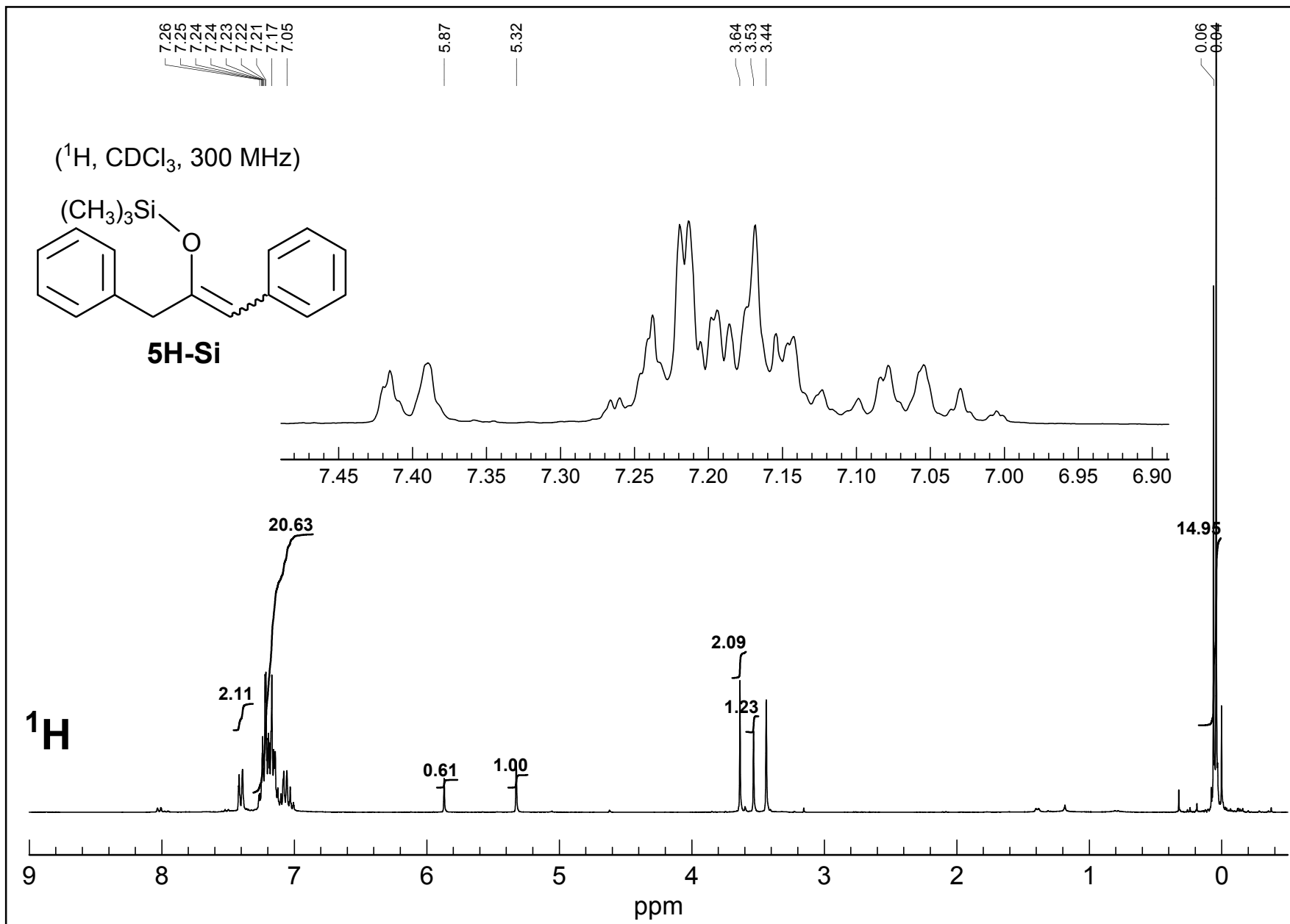
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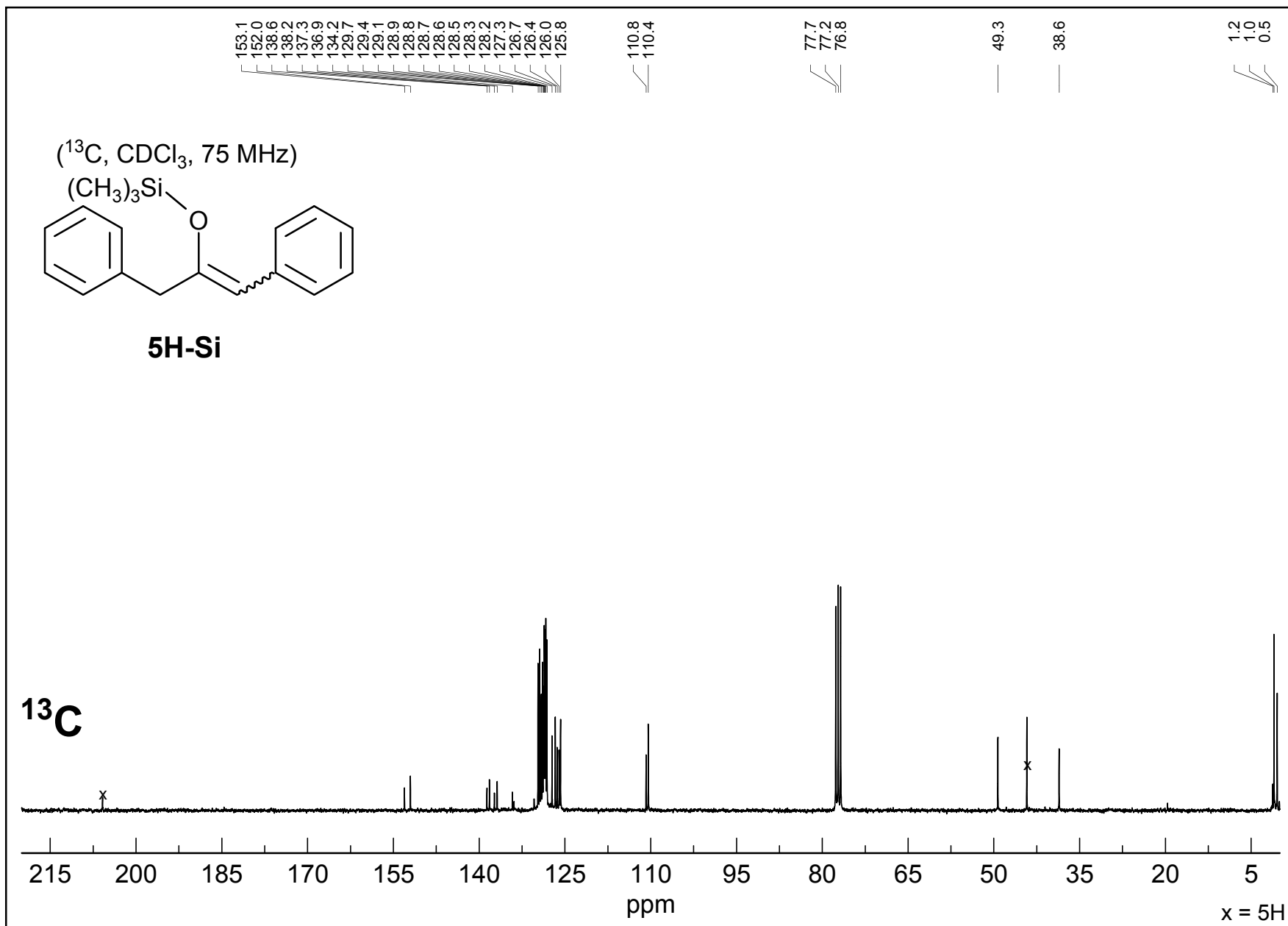
^{19}F



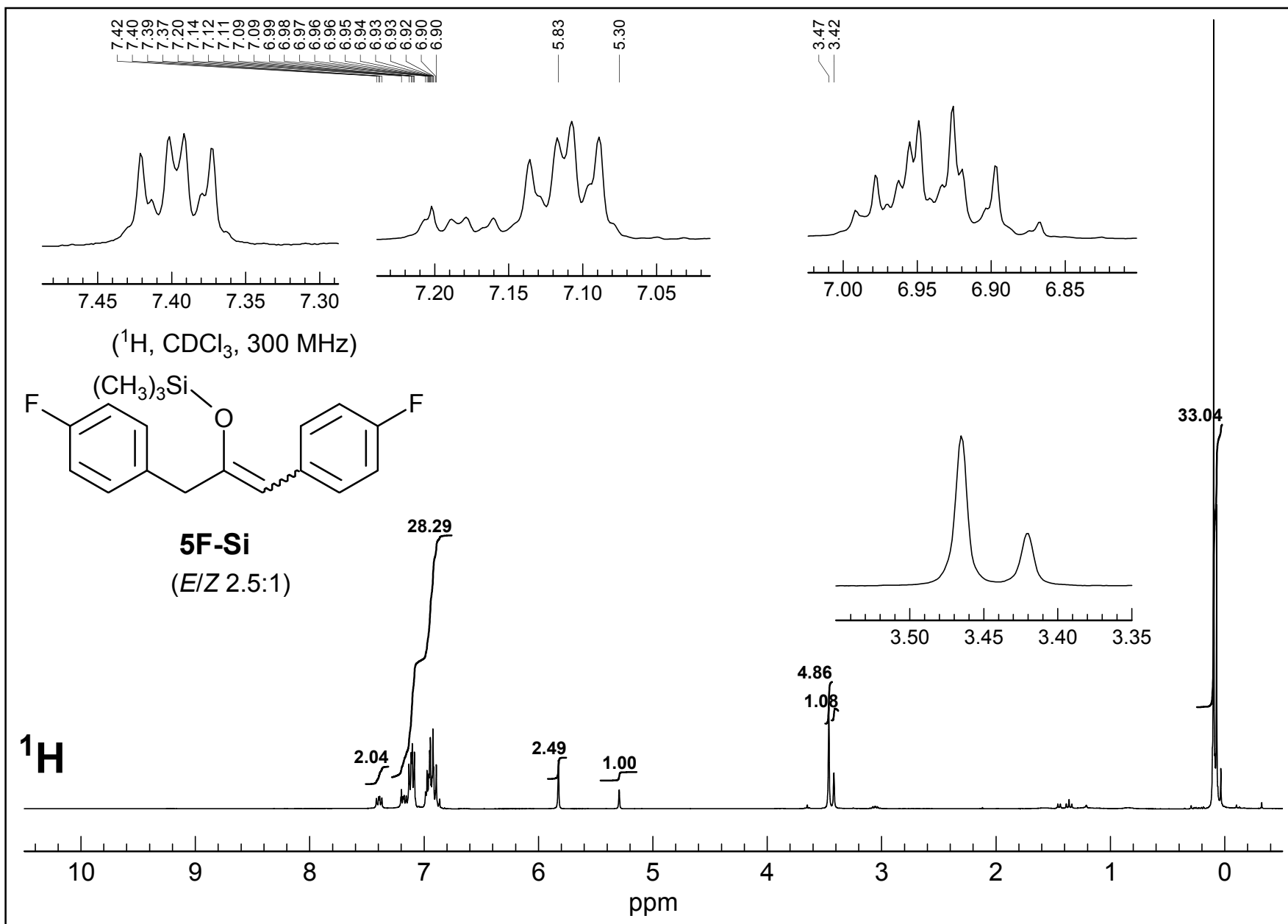
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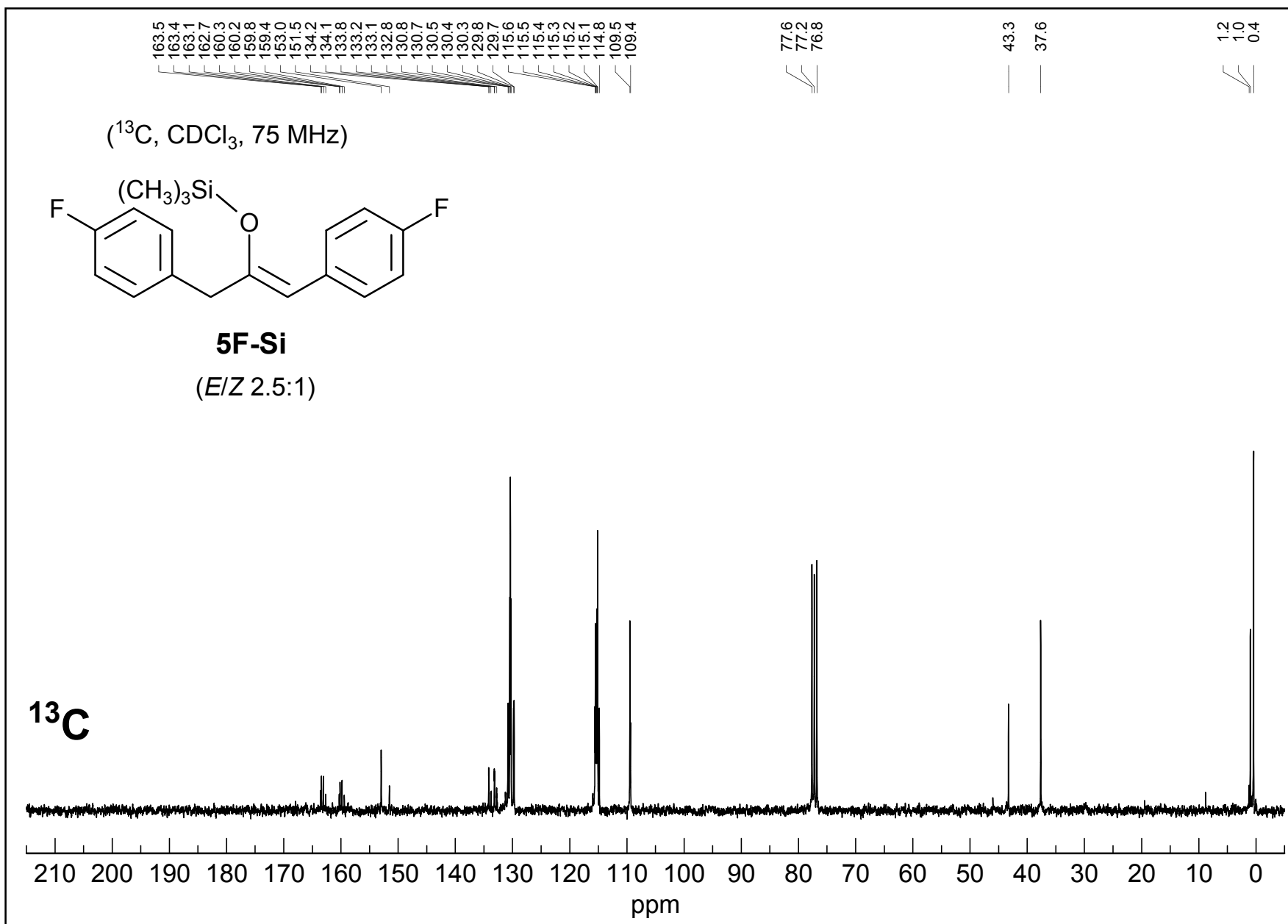


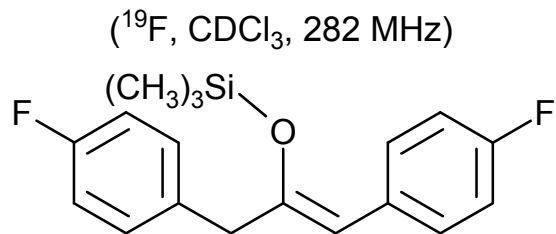
09-S



S-61



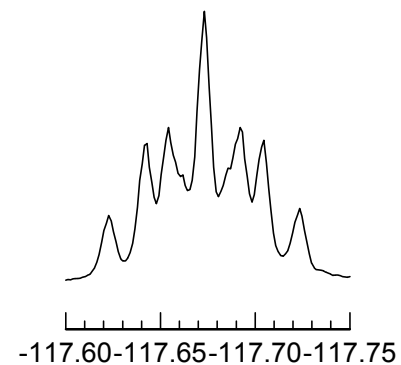
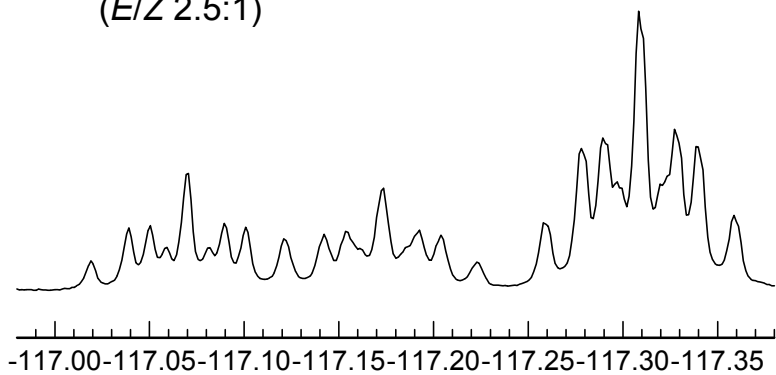




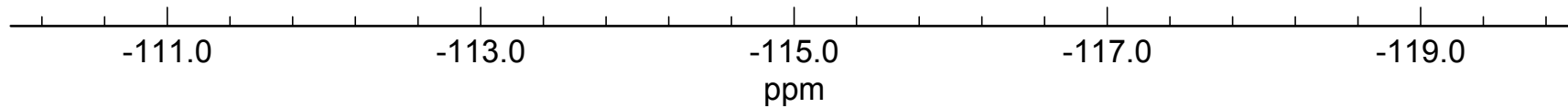
5F-Si
(*E/Z* 2.5:1)

117.07
117.18
117.31
117.68

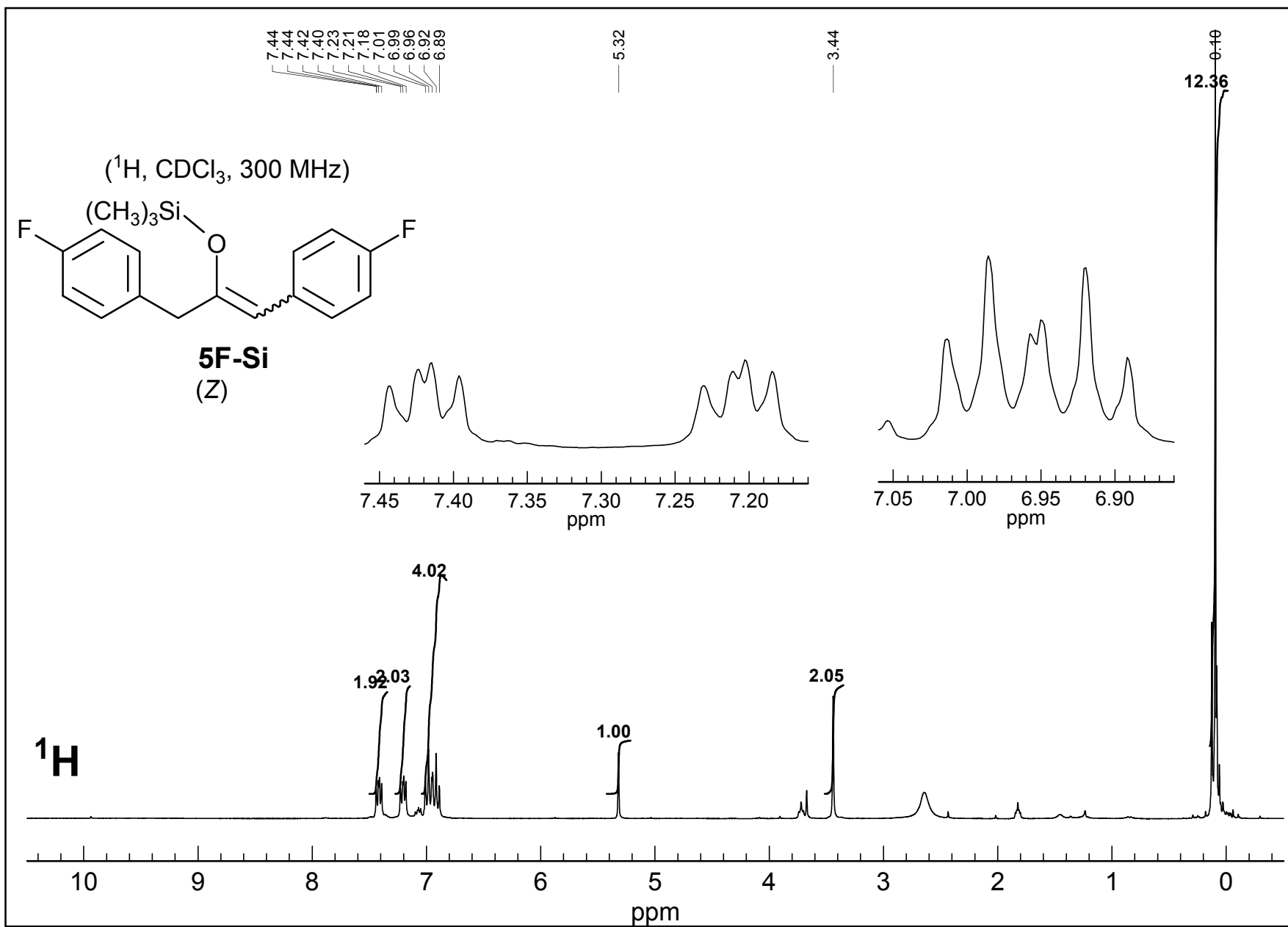
£9-S



¹⁹F

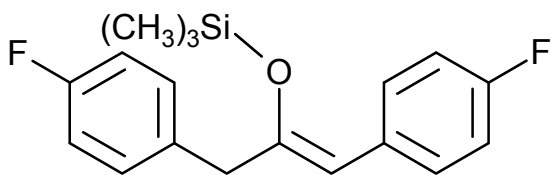


S-64



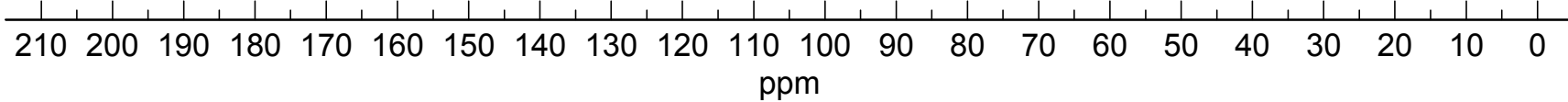
59-S

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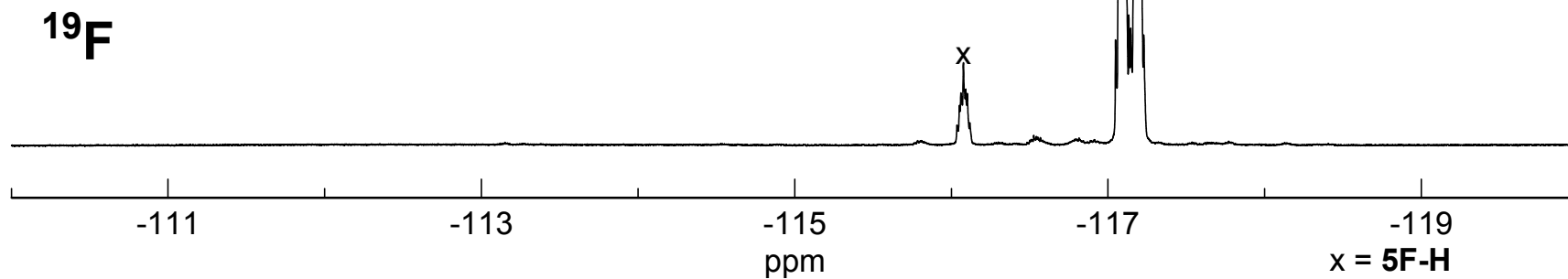
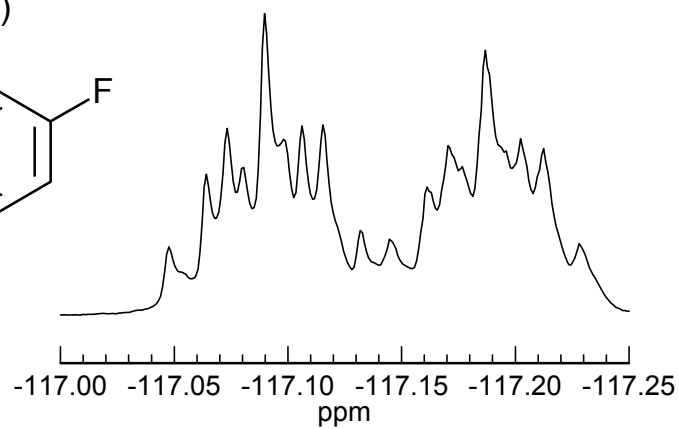
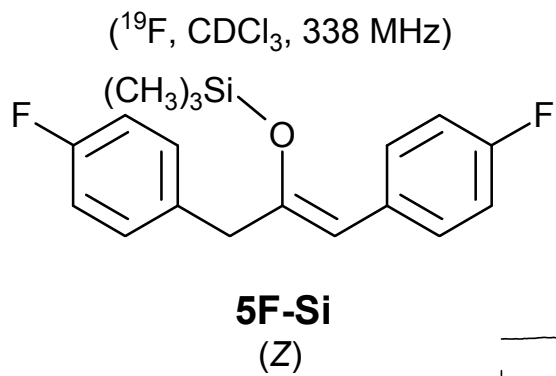


5F-Si
(Z)

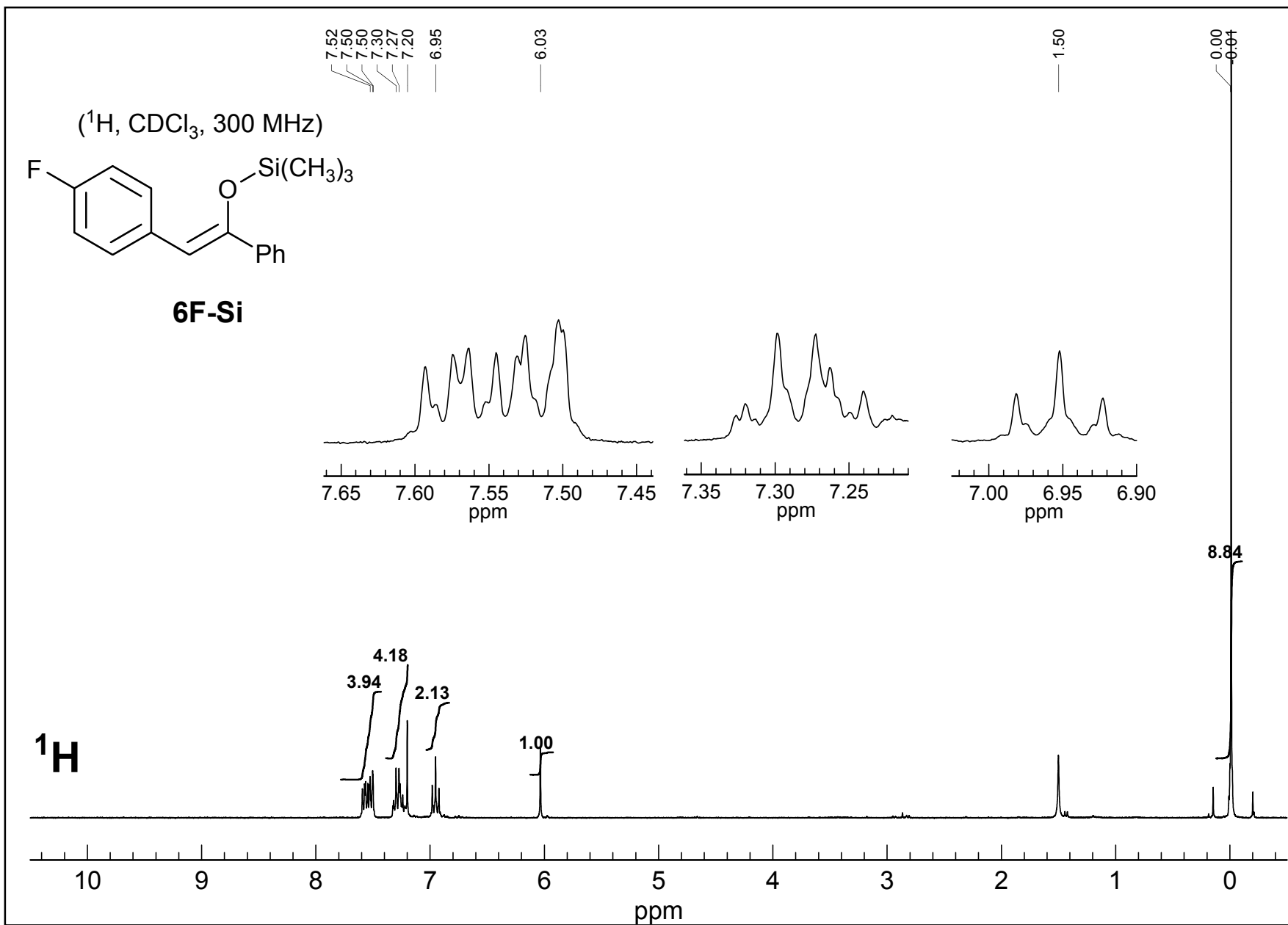
¹³C



99-S

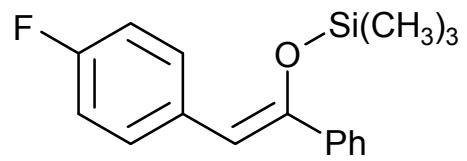


S-67

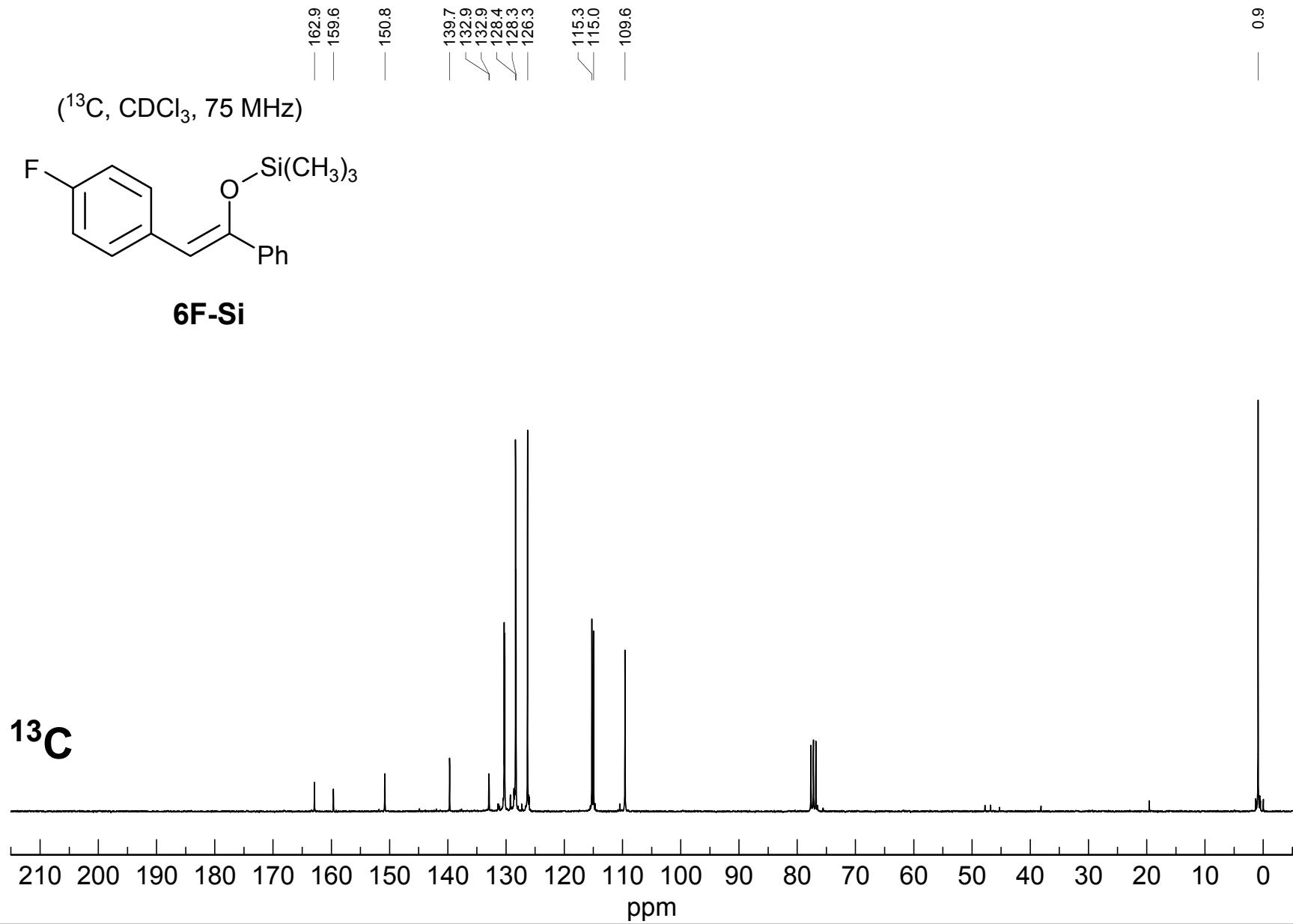


89-S

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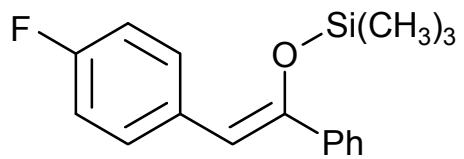


6F-Si



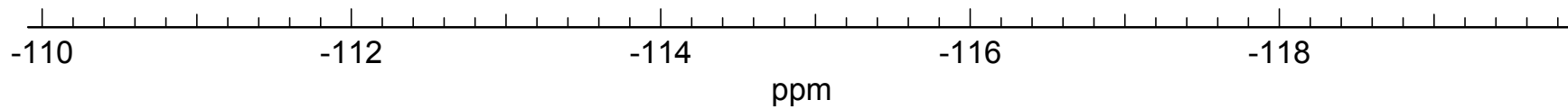
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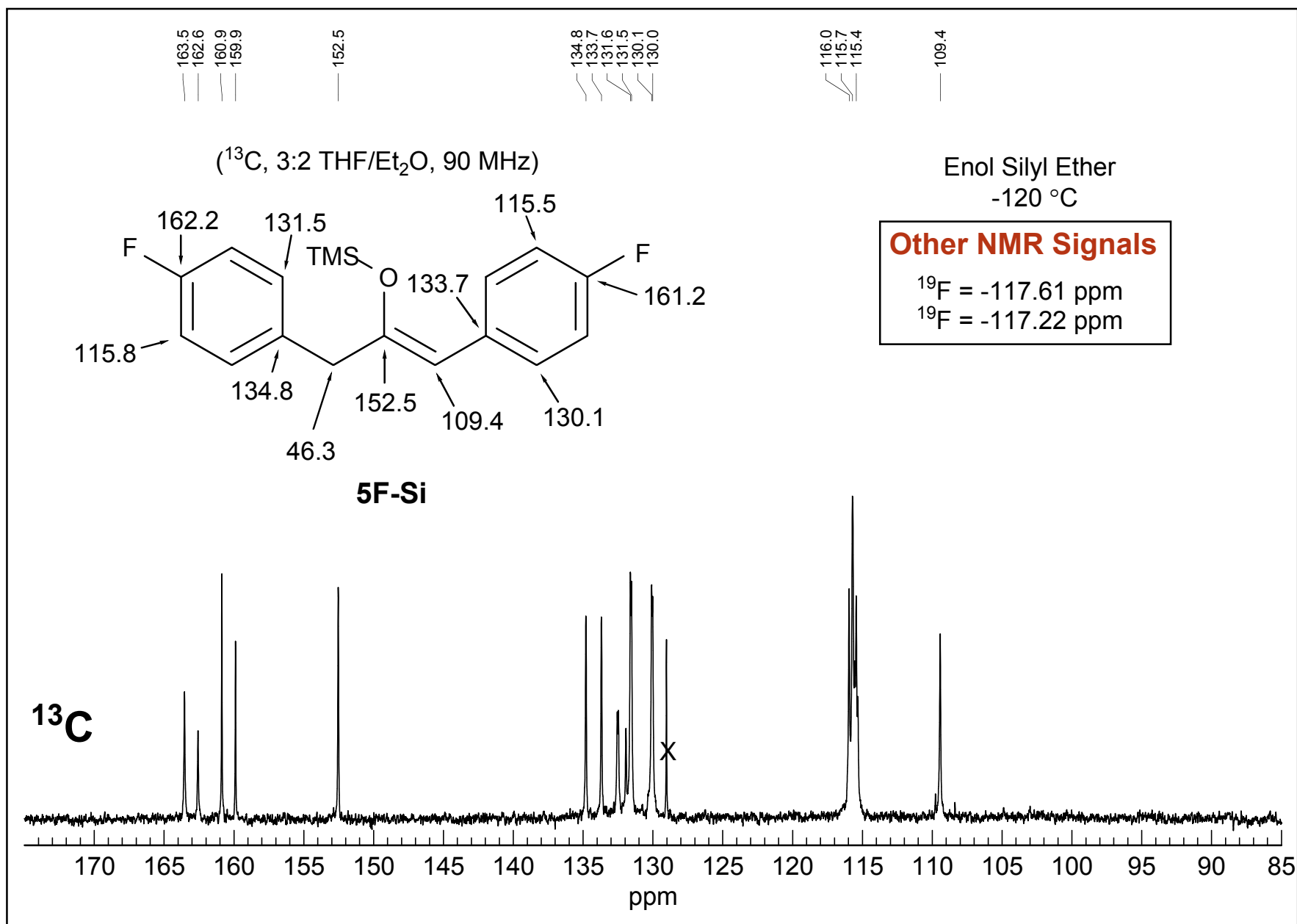


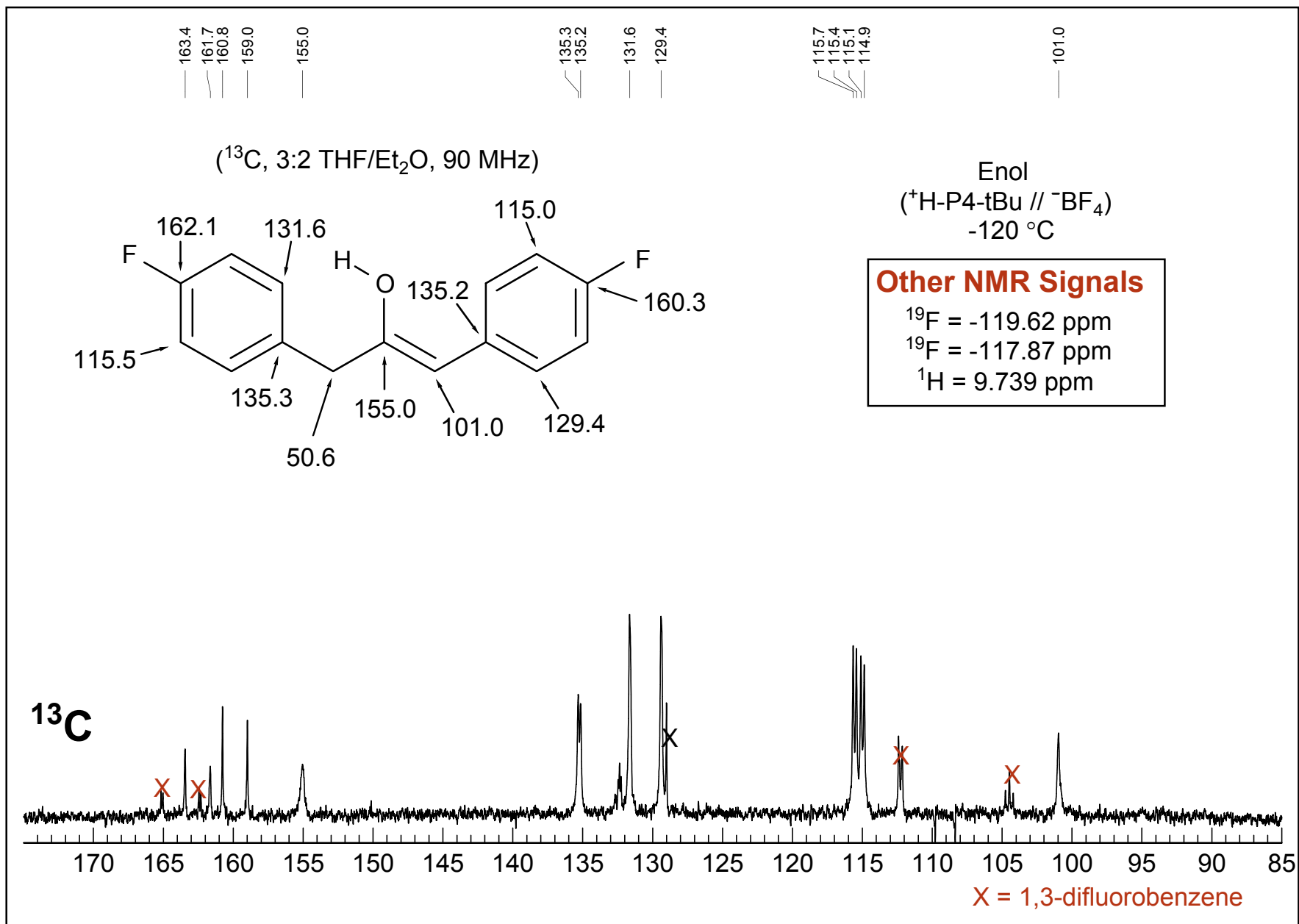
6F-Si

^{19}F

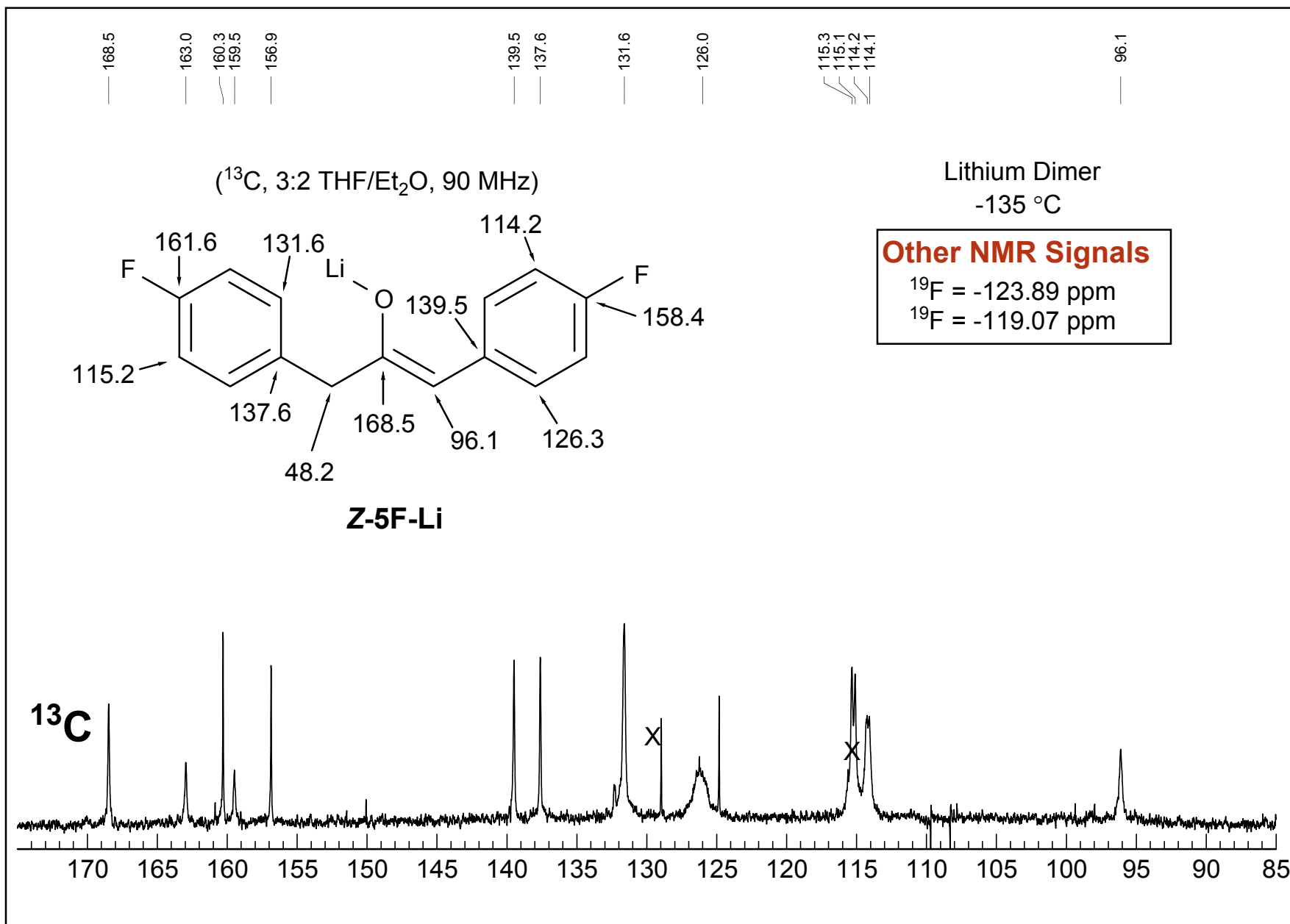


S-70

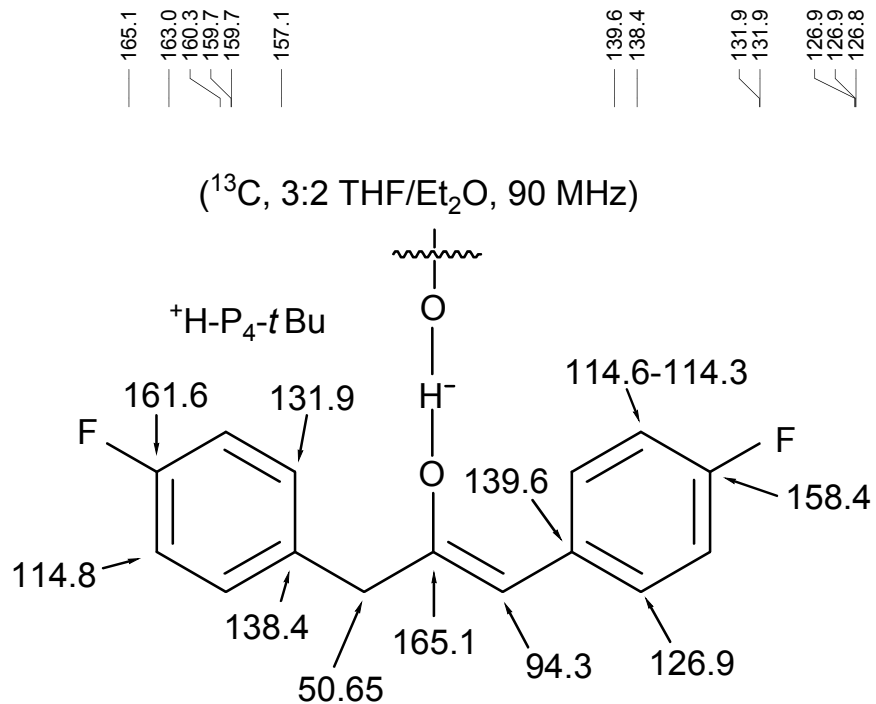




S-72



S-78



Hydrogen Dimer
-120 °C

Other NMR Signals

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^{19}F = -119.53 ppm

^1H = 18.398 ppm

