

Supporting Information

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**Thiophosphoramidate-Based Cooperative Catalysts for Brønsted Acid Promoted Ionic Diels–Alder Reactions\*\***

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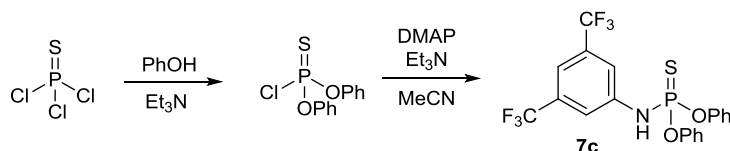
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Unless otherwise stated, all reagents were purchased from commercial suppliers and used without purification. Toluene (PhMe), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and diethyl ether (Et<sub>2</sub>O) were filtered through a column (Innovative Technology PS-MD-5) of activated alumina under nitrogen atmosphere. All reactions were carried out under an atmosphere of nitrogen in flame- or oven-dried glassware with magnetic stirring. Reactions were cooled via external cooling baths: ice water (0 °C), Neslab Cryotrol CB-80 immersion cooler (0 to -60 °C) or Neslab Cryocool immersion cooler CC-100 II. Purification of the reactions mixtures was performed by flash chromatography using SiliCycleSiliaFlash P60 (230-400 mesh) silica gel. All spectra were recorded on Varian vnmrs 700 (700 MHz), Varian vnmrs 500 (500 MHz), Varian MR400 (400 MHz), Varian Inova 500 (500 MHz) spectrometers and chemical shifts ( $\delta$ ) are reported in parts per million (ppm) and referenced to the <sup>1</sup>H signal of the internal tetramethylsilane according to IUPAC recommendations.<sup>1</sup> Data are reported as (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sext = sextet, m = multiplet; coupling constant(s) in Hz; integration). High resolution mass spectra (HRMS) were recorded on MicromassAutoSpecUltima or VG (Micromass) 70-250-S Magnetic sector mass spectrometers in the University of Michigan mass spectrometry laboratory. Infrared (IR) spectra were recorded as thin films on NaCl plates on a Perkin Elmer Spectrum BX FT-IR spectrometer. Absorption peaks were reported in wavenumbers (cm<sup>-1</sup>). All commercially unavailable acetals and ketals were prepared following the procedure reported by Lu and coworkers.<sup>2</sup> Commercially unavailable hydrogen bond donors were synthesized by previously reported procedures.<sup>3</sup>



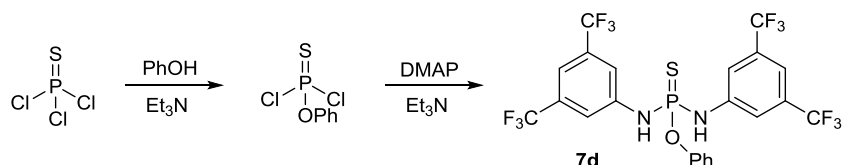
### Synthesis of thiophosphoramidate **7c**.

Phenol (1.11 g, 11.8 mmol) and triethylamine (1.81 mL, 18.9 mmol) were added to a flame-dried 200mL round bottom flask charged with 30 mL dry dichloromethane. Flask was cooled to 0 °C and thiophosphoryl chloride (0.60 mL, 5.9 mmol) was added dropwise. After two hours TLC indicated reaction went to completion. Solvent was evaporated and <sup>1</sup>H NMR confirmed desired diphenoxythiophosphoryl chloride. Compound was used directly in the following reaction without purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.44 (t, *J* = 7.6 Hz, 2 H), 7.37-7.27 (m, 3 H).<sup>4</sup>

Previously made diphenoxythiophosphoryl chloride (285 mg, 1 mmol) was dissolved in 3 mL of dry acetonitrile. 4-Dimethylaminopyridine (244.3 mg, 2 mmol) was then added followed by triethylamine (0.98 mL, 7 mmol), and 3,5-bis(trifluoromethyl)aniline (313  $\mu$ L, 2 mmol) at room temperature. The mixture was refluxed for 48 hours. Reaction was then quenched with saturated NaHCO<sub>3</sub>. The product was extracted with diethyl ether, and then organic layer was dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. Crude product was purified by column chromatography (3:1 hexanes/ethyl acetate) and all

fractions with product, including those with impurities were collected. Product was recrystallized from hexanes.

White solid, 62% yield (592 mg). IR (thin film,  $\text{cm}^{-1}$ ): 3246, 1717, 1621, 1490, 1471, 1391, 1276, 1183, 1136, 986, 927, 794, 686.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.66 (s, 2H), 7.58 (s, 1H), 7.36 (t,  $J = 7.7$  Hz, 4H), 7.24 (t,  $J = 7.7$  Hz, 2H), 7.18 (d,  $J = 7.7$  Hz, 4H), 6.01 (d,  $J = 15.0$  Hz, 1H);  $^{13}\text{C}$  NMR (175 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.1 (2C), 140.5, 133.0 (q,  $J = 34$  Hz, 2C), 129.8, 126.0, 123.7, 122.2, 121.0 (2C), 117.9, 116.2,  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  55.0 (s);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.1 (s); HRMS (ESI+) ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{15}\text{F}_6\text{NO}_2\text{PS}$  478.0453, found 478.0460.



### Synthesis of thiophosphoramidate 7d.

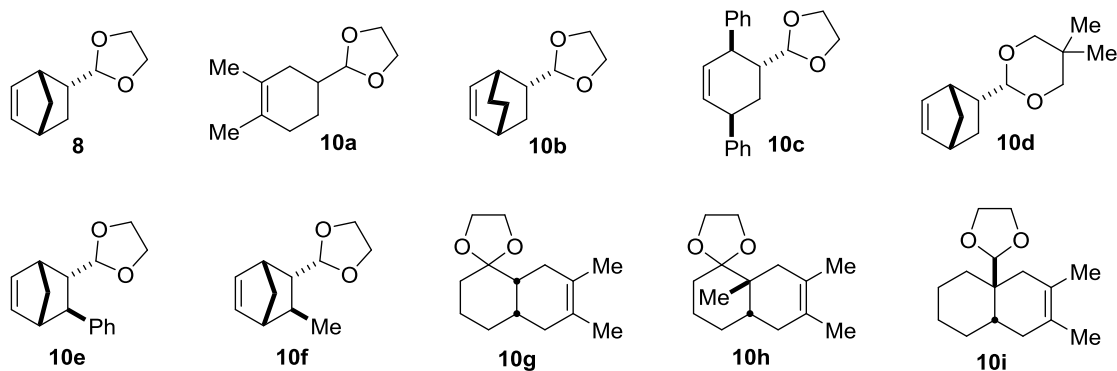
Phenol (277.6 mg, 2.95 mmol) and triethylamine (0.50 mL, 3.54 mmol) were added to a flame-dried 200mL round bottom flask charged with 30 mL dry dichloromethane. The mixture was cooled to 0 °C and thiophosphoryl chloride (0.30 mL, 2.95 mmol) was added dropwise. After two hours TLC indicated reaction went to completion. Solvent was evaporated and  $^1\text{H}$  NMR confirmed desired phenoxythiophosphoryl chloride. Compound used directly in following reaction without purification.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.44 (t,  $J = 7.6$  Hz, 2 H), 7.315 (m, 3 H).<sup>3</sup>

Phenoxythiophosphoryl chloride, together with 4-dimethylaminopyridine (1.194 g, 11.8 mmol) were added to a 200mL round bottom flask followed by triethylamine (15 mL, 88.5 mmol) and 3,5-bis(trifluoromethyl)aniline (2.7 g, 11.8 mmol). The mixture was refluxed for 48 hours. Reaction was then quenched saturated  $\text{NaHCO}_3$ . Products were extracted with diethyl ether. Organic layer was then dried over  $\text{MgSO}_4$ , filtered and concentrated. The product was purified by column chromatography using gradient from 5% to 20% dichloromethane in hexanes). All fractions with product, including those with impurities were collected. Product was then recrystallized from hexanes.

White solid, 40% yield (713 mg after 2 recrystallizations). IR (thin film,  $\text{cm}^{-1}$ ): 3414, 3239, 1622, 1592, 1491, 1471, 1388, 1279, 1188, 1133, 1004, 979, 928, 896, 683.  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.56 (s, 4H), 7.55 (s, 2H), 7.39 (t,  $J = 7.8$  Hz, 2H), 7.28 (t,  $J = 7.6$  Hz, 1H), 7.16 (d,  $J = 7.9$  Hz, 2H), 5.84 (d,  $J = 10.5$  Hz, 2H);  $^{13}\text{C}$  NMR (175 MHz,  $\text{CDCl}_3$ ) 149.1 (2C), 139.8, 133.0 (q,  $J = 33.7$  Hz, 6C), 130.1, 126.4, 125.1, 123.6, 122.0, 121.2 (2C), 118.5, 116.8;  $^{31}\text{P}$  NMR (283 MHz,  $\text{CDCl}_3$ )  $\delta$  51.2 (s);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.2 (s); HRMS (ESI+) ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{14}\text{F}_{12}\text{N}_2\text{OPS}$  613.0367, found 613.0361.

## Synthetic procedures and characterization data for the cycloadducts from Table 2.

The cycloadducts **8**,<sup>5</sup> **10a**,<sup>6</sup> **10b**,<sup>7</sup> **10d**,<sup>8</sup> **10e**,<sup>4</sup> **10f**<sup>9</sup> have been previously characterized. The characterization data for compounds **10c**, **10g**, **10h**, and **10i** is provided below.



## General procedure for catalyst screening, Table 1.

Reactions were run on 0.5-0.7 mmol scale based on dienophile. An oven-dried 4-mL scintillation vial was charged with anthracene, 3 mol% pTSA and 6 mol% catalyst **7**. The vial was then flushed with nitrogen. Dry solvent (toluene or diethyl ether) was added to ensure 0.3 M concentration of 2-vinyl-1,3-dioxolane. The reaction mixture was brought to -78 °C and then 2-vinyl-1,3-dioxolane (1 equiv, 0.5 mmol) and cyclopentadiene (3 equiv, 1.5 mmol) were added via micro syringe. The resulting mixture was stirred at the temperature indicated in Table 1 for the indicated time. The reaction was quenched with approximately 6 mol% of triethylamine. The conversions were determined using the following formula: conversion (%) = 100% - (yield (starting material, %)). Yield of the starting material (%) = 100% • [ $\nu(\text{starting material}) / \nu(\text{standard})$ ] •  $n$ , where  $\nu(\text{product}) / \nu(\text{standard})$  is the integral ratio of the corresponding  $^1\text{H}$  NMR peaks and  $n$  is the ratio of the standard to the initial amount of starting material (in mol).

## General procedure A for Diels-Alder reactions catalyzed by pTSA or pTSA/**7a**, Table 2 (entries 1–3, 6, 7)

Reactions were run on 0.5-0.9 mmol scale based on dienophile. An oven-dried 4-mL scintillation vial was charged with anthracene, 3 mol% pTSA and 6 mol% catalyst **7a**. The vial was then flushed with nitrogen. Dry toluene was added to ensure 0.3 M concentration of a dienophile. The reaction mixture was brought to 0 °C and then dienophile (1 equiv) and diene (5 equiv) were added via micro syringe. The resulting mixture was stirred at 0 °C for the time indicated in Table 2. The reaction was quenched with approximately 6 mol% of triethylamine. The  $^1\text{H}$  NMR yields were calculated using the following formula: yield (%) = 100% • [ $\nu(\text{product}) / \nu(\text{standard})$ ] •  $n$ , where  $\nu(\text{product}) / \nu(\text{standard})$  is the integral ratio of the corresponding  $^1\text{H}$  NMR peaks and  $n$  is the ratio of the standard to starting material (in mol).

**General procedure B for Diels-Alder reactions catalyzed by pTSA/7e, Table 2 (entries 1–3, 6, 7)**

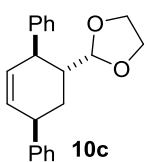
Reactions were run on 0.5-0.9 mmol scale based on dienophile. An oven-dried 4-mL scintillation vial was charged with 3 mol% pTSA and 6 mol% catalyst **7e**. The vial was then flushed with nitrogen. Dry toluene was added to ensure 0.3 M concentration of a dienophile. The reaction mixture was brought to 0 °C and then dienophile (1 equiv) and diene (5 equiv) were added via micro syringe. The resulting mixture was stirred at 0 °C for the time indicated in Table 2. The reaction was quenched with approximately 6 mol% of triethylamine. The mixture was directly subjected to column chromatography. Elution with hexanes allowed removal of excess toluene and diene. Subsequent purification of the cycloadduct was performed using 20:1 hexanes/diethyl ether.

**General procedure C for Diels-Alder reactions catalyzed by pTSA or pTSA/7a, Table 2 (entries 5, 8–10)**

Reactions were run on 0.3-0.7 mmol scale based on dienophile. An oven-dried 4-mL scintillation vial was charged with anthracene, 5 mol% pTSA and 10 mol% catalyst **7a**. The vial was then flushed with nitrogen. Dry dichloromethane was added to ensure 0.6 M concentration of a dienophile. The reaction mixture was brought to 0 °C and then dienophile (1 equiv) and diene (5 equiv) were added via micro syringe. The resulting mixture was stirred at the temperature indicated in Table 2 for the indicated time. The reaction was quenched with approximately 10 mol% of triethylamine. The <sup>1</sup>H NMR yields were calculated using the following formula: yield (%) = 100% • [v(product) / v(standard)] • *n*, where v(product) / v(standard) is the integral ratio of the corresponding <sup>1</sup>H NMR peaks and *n* is the ratio of the standard to starting material (in mol).

**General procedure D for Diels-Alder reactions catalyzed by pTSA/7e, Table 2 (entries 5, 8–10)**

Reactions were run on 0.3-0.7 mmol scale based on dienophile. An oven-dried 4-mL scintillation vial was charged with 5 mol% pTSA and 10 mol% catalyst **7e**. The vial was then flushed with nitrogen. Dry dichloromethane was added to ensure 0.6 M concentration of dienophile. The reaction mixture was brought to 0 °C and then dienophile (1 equiv) and diene (5 equiv) were added via micro syringe. The resulting mixture was stirred at the temperature indicated in Table 2 for the indicated time. The reaction was quenched with approximately 10 mol% of triethylamine. Volatiles were evaporated in vacuo and then the mixture was subjected to column chromatography using 20:1 hexanes/diethyl ether.

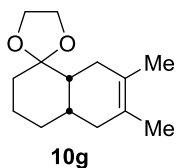


**Synthesis of 2-(1',2',3',4'-tetrahydro-[1,1':4',1''-terphenyl]-2'-yl)-1,3-dioxolane (**10c**, Entry 4)**

An oven-dried 4-mL scintillation vial was charged with 5 mol% (3.6 mg, 0.0209 mmol) pTSA and 10 mol% (31.2 mg, 0.0418 mmol) catalyst **7e**. The

vial was then flushed with nitrogen. In a separate vial a 0.9 M solution of 259 mg (1.25 mmol) (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene (3 equiv) in dry dichloromethane was made and added to the mixture of catalysts. Then 41.8  $\mu$ L (0.418 mmol) of 2-vinyl-1,3-dioxolane (1 equiv) and was added via micro syringe. The resulting mixture was stirred at room temperature for 5 h. The reaction was quenched with approximately 10 mol% of triethylamine. Volatiles were evaporated in vacuo and then the mixture was subjected to column chromatography using 1:1 hexanes/toluene. Reactions catalyzed by pTSA or pTSA/**7a** were analyzed by crude  $^1\text{H}$  NMR using anthracene as an internal standard.

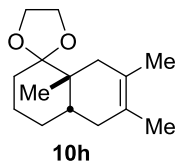
Colorless oil, 62% yield, 8.3:1 endo/exo; IR (thin film,  $\text{cm}^{-1}$ ) 3024, 2950, 2883, 1600, 1491, 1451, 1414, 1311, 1156, 1079, 1032, 957, 925, 857, 758, 701. *Endo product*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 7.6$  Hz, 2H), 7.39-7.33 (m, 4H), 7.33-7.28 (m, 2H), 7.27-7.19 (m, 2H), 6.02 (d,  $J = 10.1$  Hz), 5.89 (ddd,  $J = 10.1, 2.7, 2.4$  Hz, 1H), 4.07 (d,  $J = 8.4$  Hz, 1H), 4.00-3.87 (m, 2H), 3.85-3.76 (m, 2H), 3.72-3.66 (m, 1H), 3.63-3.53 (m, 1H), 2.22 (dddd,  $J = 13.2, 8.1, 5.5, 2.4$  Hz, 1H), 2.01 (dd,  $J = 12.9, 5.5$  Hz, 1H), 1.56 (q,  $J = 12.9$  Hz, 1H). *Distinct peaks for exo product*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.81 (d,  $J = 3.6$  Hz, 1H), 1.83 (dd,  $J = 10.5, 6.6$  Hz, 1H); *Endo only*:  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.3, 138.1, 135.4, 128.4, 128.1, 125.8, 106.8, 67.1, 51.5, 49.4, 47.0, 46.7, 44.3, 26.0; HRMS (ESI+) ( $m/z$ ):  $[\text{M}+\text{NH}_4]^+$  calcd for  $\text{C}_{17}\text{H}_{24}\text{NO}_2$  274.1802; found 274.1800.



**10g**

**6,7-Dimethyl-3,4,4a,5,8,8a-hexahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolane] (10g, Entry 8)**

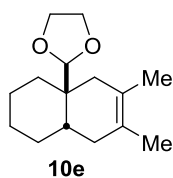
Colorless oil, 68% yield. IR (thin film,  $\text{cm}^{-1}$ ) 2927, 2829, 1717, 1441, 1377, 1354, 1298, 1160, 1098, 1087, 1050, 940, 876, 771.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.98-3.87 (m, 4H), 2.25 (d,  $J = 16.8$  Hz, 1H), 2.05-1.85 (m, 4H), 1.79-1.63 (m, 4H), 1.59 (br s, 6H), 1.54-1.47 (m, 1H), 1.37-1.17 (m, 2H).  $^{13}\text{C}$  NMR (175 MHz,  $\text{CDCl}_3$ )  $\delta$  123.5, 122.6, 64.1, 40.9, 37.9, 32.9, 29.8, 29.6, 26.0, 23.2, 19.1, 18.9. HRMS (EI) ( $m/z$ ):  $[\text{M}]^+$  calcd for  $\text{C}_{14}\text{H}_{22}\text{O}_2$  222.1620, found 222.1621.



**10h**

**6',7',8a'-trimethyl-3',4',4a',5',8',8a'-hexahydro-2'H-spiro[[1,3]dioxolane-2,1'-naphthalene] (10h, Entry 9)**

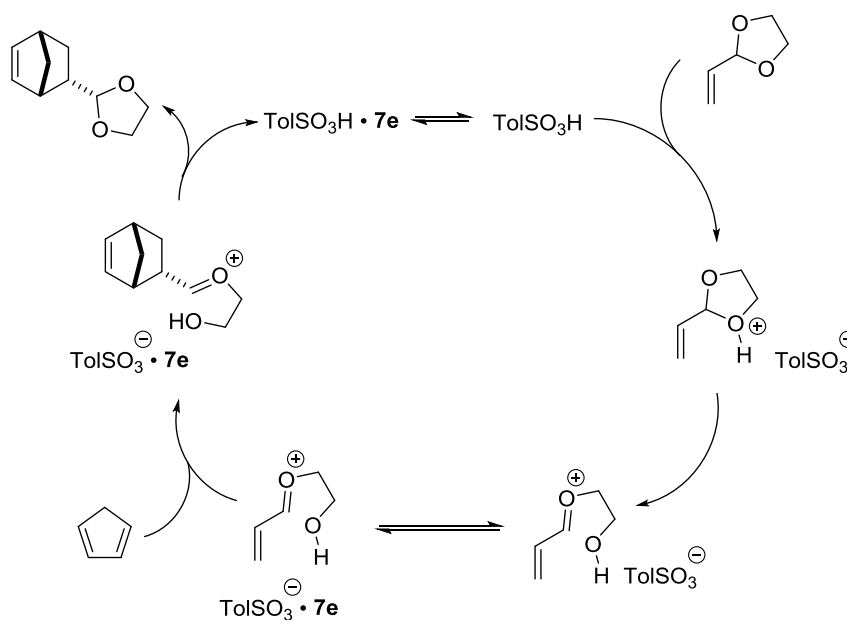
Pale yellow oil, 84% yield. IR (thin film,  $\text{cm}^{-1}$ ) 2927, 1448, 1368, 1172, 1085, 950.  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ )  $\delta$  3.98-3.92 (m, 4H), 2.27 (d,  $J = 18.2$  Hz, 1H), 2.22 (d,  $J = 18.2$  Hz, 1H), 1.73 (td,  $J = 13.3, 4.6$  Hz, 1H), 1.68-1.60 (m, 3H), 1.59 (s, 6H), 1.57-1.52 (m, 3H), 1.49 (qt,  $J = 13.3, 4.3$  Hz, 1H), 1.29 (qd,  $J = 13.3, 3.8$  Hz, 1H), 1.27-1.22 (m, 1H), 0.97-0.87 (m, 1H), 0.85-0.76 (m, 1H);  $^{13}\text{C}$  NMR (175 MHz,  $\text{CDCl}_3$ )  $\delta$  122.0, 121.9, 112.9, 65.0, 64.8, 41.3, 38.3, 36.2, 35.7, 30.3, 28.4, 22.8, 19.2, 19.0, 18.2. HRMS (ES+) ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{24}\text{O}_2$  237.1849, found 237.1841.



**6,7-Dimethyl-1,3,4,5,8,8a-hexahydronaphthalen-4a(2H-yl)-1,3-dioxolane (10i, Entry 10)**

Colorless oil, 59% yield. IR (thin film,  $\text{cm}^{-1}$ ) 2923, 2861, 1704, 1453, 1394, 1351, 1165, 1137, 1121, 1084, 1066, 955, 856.  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ )  $\delta$  4.87 (s, 1H), 3.95-3.90 (m, 1H), 3.89-3.79 (m, 3H), 2.35 (d,  $J = 18.3$  Hz, 1H), 2.19 (d,  $J = 18.3$ , 1H), 1.78-1.72 (m, 2H), 1.66-1.61 (m, 1H), 1.60 (s, 3H), 1.58 (s, 3H), 1.56-1.51 (m, 2H), 1.45-1.37 (m, 2H), 1.34-1.27 (m, 3H), 1.26-1.18 (m, 1H).  $^{13}\text{C}$  NMR (175 MHz,  $\text{CDCl}_3$ )  $\delta$  123.0, 121.8, 106.2, 65.3, 64.9, 39.2, 36.2, 34.9, 32.6, 29.2, 26.7, 25.8, 21.5, 19.0, 18.9. HRMS (EI) ( $m/z$ ):  $[\text{M}]^+$  calcd for  $\text{C}_{15}\text{H}_{24}\text{O}_2$  236.1776, found 236.1776.

**Proposed mechanism for the ionic Diels-Alder reaction**



**$^1\text{H}$  NMR continuous variation method (Job plot)**

Stock solutions of *N*-methylpyridinium tosylate and thiophosphoramidate in  $\text{CDCl}_3$ , both having a concentration of 5 mM, were prepared. Aliquots of each solution were mixed in several 5 mm NMR tubes such that the total volume in each tube was 1.0 mL and the mole fraction of catalyst was varied from 0.1 to 1.0 M across 10 samples.  $^1\text{H}$  NMR spectra were collected on a 500 MHz instrument at 25°C. The chemical shift of the amide proton of the catalyst ( $\delta_{\text{obs}}$ ) was noted in each sample and a Job plot was created by plotting  $(\delta_{\text{obs}} - \delta_{\text{free}}) \cdot [\text{catalyst}]_0$  against the mole fraction of the catalyst, where  $[\text{catalyst}]_0$  is the initial concentration of catalyst measured into each sample. The plot thus obtained showed a maxima at a mole fraction of 0.5, suggesting a 1:1 binding stoichiometry in the tosylate-thiophosphoramidate complex.



N-H peak shift				
Mole fraction	$\delta_{\text{obs}}$	$\delta_{\text{obs}} - \delta_{\text{free}}$	$[\text{Phosph}]_0$	$(\delta_{\text{obs}} - \delta_{\text{free}}) \cdot [\text{Phosph}]_0$
0.1	8.1506	2.3925	0.0005	0.00119625
0.2	8.1448	2.3867	0.001	0.0023867
0.3	8.135	2.3769	0.0015	0.00356535
0.4	8.115	2.3569	0.002	0.0047138
0.5	8.0756	2.3175	0.0025	0.00579375
0.6	7.5603	1.8022	0.003	0.0054066
0.7	6.8571	1.099	0.0035	0.0038465
0.8	6.4503	0.6922	0.004	0.0027688
0.9	6.1046	0.3465	0.0045	0.00155925
1	5.7581	0	0.005	0



## <sup>1</sup>H NMR titrations

A 0.5 mM solution of thiophosphoramidate in CDCl<sub>3</sub> was prepared, of which 500  $\mu$ L was placed in a 5 mm NMR tube. A 2.5 mM solution of *N*-methylpyridinium tosylate in CDCl<sub>3</sub> containing 0.5 mM thiophosphoramidate **7e** was prepared as the titrant. Aliquots of 5 – 10  $\mu$ L of the second solution were sequentially added to the NMR tube and the <sup>1</sup>H NMR spectrum was collected after each addition on a 500 MHz instrument at 25°C. The chemical shift of the amide proton of the catalyst was noted in each sample. The binding constant was then calculated using the WinEQNMR program.<sup>10</sup> Three titrations were thus performed to furnish an averaged binding constant ( $K_a = 7.3 \cdot 10^4$ ).

## Computational Studies

Computational studies were performed using Spartan 2010. Geometry was optimized with MM2 (molecular mechanics) and then by DFT calculations:

Thiophosphoramidate Catalyst **7e**

Energy (kcal/mol): -2273472.26

Job type: Single point.

Method: RB3LYP

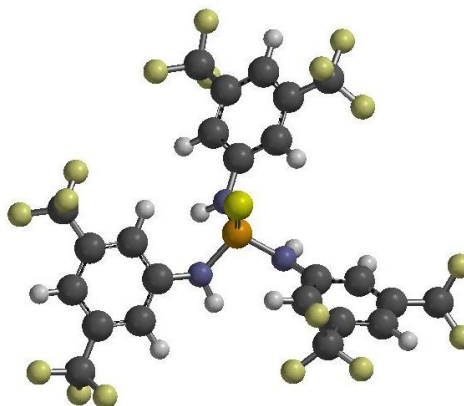
Basis set: 6-31+G\*

Number of shells: 261

Number of basis functions: 925

Multiplicity: 1

Coordinates (XYZ):



	X	Y	Z
P	-0.054160	0.009696	-0.189104
C	2.359336	-4.915996	0.058476
C	1.447459	-2.332969	-0.603251
C	3.146376	-4.059166	-0.714679
C	1.113154	-4.464877	0.491034
C	0.648562	-3.187890	0.165880
C	2.704656	-2.778032	-1.038428
H	-0.327224	-2.868146	0.514556
H	3.335131	-2.123795	-1.634109
C	-4.468079	1.312396	0.546018
C	-3.874591	-0.889114	-1.041591
C	-3.141999	1.046840	0.209496
C	-5.510446	0.497843	0.094649
C	-5.198292	-0.599878	-0.704581
C	-2.836358	-0.064459	-0.592187
H	-2.355444	1.697811	0.571914
H	-6.538528	0.719248	0.353674

H	-3.652505	-1.755958	-1.658715
C	3.352900	3.100822	0.540394
C	1.134808	3.771585	-0.992777
C	3.199705	4.418648	0.110055
C	2.420406	2.115252	0.210647
C	1.299119	2.447375	-0.561318
C	2.081254	4.740038	-0.661557
H	3.929937	5.175760	0.367739
H	2.566823	1.101499	0.565327
H	0.265380	4.046286	-1.584084
H	2.705760	-5.911041	0.308212
N	1.010518	-1.050273	-0.997629
H	1.611907	-0.583006	-1.668944
N	-1.515469	-0.348888	-0.997127
H	-1.426644	-1.108211	-1.665144
N	0.348374	1.482031	-0.952097
H	-0.358220	1.810150	-1.602496
C	0.223802	-5.354353	1.327080
C	4.523171	-4.495713	-1.154227
C	-6.285685	-1.504636	-1.231319
C	-4.789312	2.480919	1.447515
C	1.901285	6.142009	-1.190830
C	4.529729	2.711399	1.403730

F	-5.964778	3.064932	1.111939
F	-4.900023	2.094824	2.743620
F	-3.835993	3.441918	1.402666
F	-7.515251	-1.128024	-0.821119
F	-6.103386	-2.790321	-0.836088
F	-6.302597	-1.520320	-2.590920
F	0.701802	-6.614420	1.426227
F	0.081138	-4.879336	2.588899
F	-1.027117	-5.438976	0.802281
F	4.859821	-3.973518	-2.360292
F	4.624470	-5.840531	-1.253918
F	5.476562	-4.091913	-0.275394
F	0.604128	6.535116	-1.150711
F	2.293480	6.237039	-2.490231
F	2.620248	7.050389	-0.496100
F	5.500960	3.651330	1.403453
F	5.093426	1.549644	0.983239
F	4.159927	2.518729	2.694189
S	-0.064692	-0.034590	1.746971

Thiophosphoramidate Catalyst **7e** + Mesylate

Energy (kcal/mol): -2690086.83

Job type: Single point.

Method: RB3LYP

Basis set: 6-31+G\*

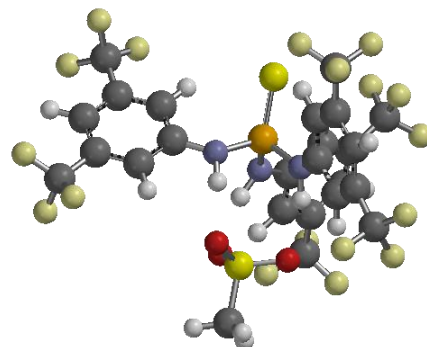
Number of shells: 293

Number of basis functions: 1030

Charge : -1

Multiplicity: 1

Coordinates (XYZ):



	<b>X</b>	<b>Y</b>	<b>Z</b>
P	-0.010625	0.013533	-0.740398
C	1.677731	-5.232520	-0.468896
C	0.420573	-2.712024	-0.206436
C	0.806370	-4.974540	0.592557
C	1.913017	-4.210784	-1.389866
C	1.298570	-2.962082	-1.274564
C	0.187630	-3.734832	0.733005
H	1.495461	-2.192254	-2.010312
H	-0.468465	-3.538845	1.575176
C	2.786153	3.745765	-1.280467
C	3.073421	2.035209	0.890391
C	1.995327	2.596226	-1.205134
C	3.724828	4.054411	-0.296411
C	3.855216	3.181874	0.788373
C	2.135044	1.723613	-0.114087
H	1.280144	2.376130	-1.987910
H	4.333707	4.948522	-0.367604

H	3.164586	1.379268	1.749923
C	-4.618481	0.660922	-1.445585
C	-3.359870	1.558378	0.862481
C	-5.393704	1.210925	-0.423859
C	-3.229448	0.559428	-1.339243
C	-2.583332	1.009287	-0.176112
C	-4.742726	1.659017	0.728551
H	-6.469888	1.286392	-0.520410
H	-2.649395	0.140951	-2.152858
H	-2.866699	1.885653	1.772846
H	2.159705	-6.197610	-0.572395
N	-0.257761	-1.500165	-0.016362
H	-0.698434	-1.431682	0.914235
N	1.404256	0.537191	0.035752
H	1.522747	0.107367	0.967375
N	-1.193258	0.969859	0.011178
H	-0.910978	1.256915	0.961997
C	2.812096	-4.488895	-2.565982
C	0.581688	-6.036600	1.635599
C	4.835770	3.529598	1.876476
C	2.672611	4.646328	-2.482375
C	-5.554033	2.195305	1.878042
C	-5.286490	0.218866	-2.721277

F	1.462470	4.576438	-3.083078
F	2.882651	5.953112	-2.166103
F	3.597109	4.338434	-3.437400
F	6.037047	3.925541	1.368585
F	5.084411	2.498192	2.715332
F	4.399001	4.564903	2.648686
F	2.147795	-5.118716	-3.577446
F	3.347936	-3.366190	-3.097779
F	3.849425	-5.306064	-2.235067
F	-0.616051	-5.914702	2.256893
F	1.528813	-6.002717	2.615025
F	0.628560	-7.291061	1.110961
F	-5.869203	1.223072	2.779200
F	-6.735885	2.731270	1.471575
F	-4.902773	3.161625	2.570394
F	-6.584443	-0.136570	-2.526907
F	-4.669218	-0.842586	-3.292648
F	-5.302070	1.207049	-3.661294
S	0.009403	0.034169	-2.696421
S	-0.043295	-0.079759	3.241550
O	-0.932373	-1.204407	2.799335
O	1.385606	-0.277328	2.827404
O	-0.576322	1.264187	2.837836

C	-0.054451	-0.109925	5.044604
H	0.589994	0.695028	5.404064
H	0.322743	-1.081951	5.369082
H	-1.082750	0.037785	5.381037

Thiourea Catalyst **7a**

Energy (kcal/mol):-1480032.09

Job type: Single point.

Method: RB3LYP

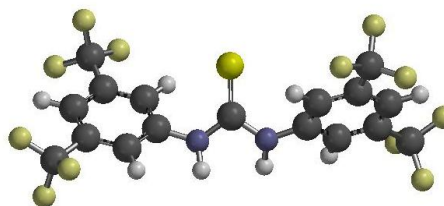
Basis set: 6-31+G\*

Number of shells: 177

Number of basis functions: 628

Multiplicity: 1

Coordinates (XYZ):



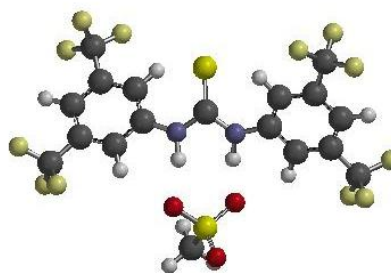
	<b>X</b>	<b>Y</b>	<b>Z</b>
C	0.000000	0.000000	0.247169
C	4.270519	1.094513	-0.600500
C	3.395253	-0.901622	1.125949
C	2.923564	1.032493	-0.251415
C	5.194294	0.174071	-0.093396
C	4.746340	-0.817699	0.776016
C	2.481704	0.021899	0.612949
H	2.224230	1.761286	-0.639156
H	6.240779	0.235222	-0.369543
H	3.055148	-1.695174	1.785260
C	-4.270519	-1.094513	-0.600500
C	-3.395253	0.901622	1.125949
C	-5.194294	-0.174071	-0.093396



C	-2.923564	-1.032493	-0.251415
C	-2.481704	-0.021899	0.612949
C	-4.746340	0.817699	0.776016
H	-6.240779	-0.235222	-0.369543
H	-2.224230	-1.761286	-0.639156
H	-3.055148	1.695174	1.785260
N	1.134252	-0.047417	1.041215
H	1.006729	-0.439253	1.968273
N	-1.134252	0.047417	1.041215
H	-1.006729	0.439253	1.968273
C	5.723410	-1.791359	1.386512
C	4.749230	2.152849	-1.565536
C	-5.723410	1.791359	1.386512
C	-4.749230	-2.152849	-1.565536
F	3.892747	3.196651	-1.649269
F	5.957957	2.650916	-1.204358
F	4.892101	1.655307	-2.820511
F	6.834392	-1.946038	0.633637
F	5.173678	-3.019878	1.555506
F	6.134298	-1.379822	2.616597
F	-6.134298	1.379822	2.616597
F	-6.834392	1.946038	0.633637
F	-5.173678	3.019878	1.555506

F	-5.957957	-2.650916	-1.204358
F	-3.892747	-3.196651	-1.649269
F	-4.892101	-1.655307	-2.820511
S	0.000000	0.000000	-1.412840

Thiourea Catalyst **7a** + Mesylate  
 Energy (kcal/mol): -1896642.93  
 Job type: Single point.  
 Method: RB3LYP  
 Basis set: 6-31+G\*  
 Number of shells: 209  
 Number of basis functions: 733  
 Charge : -1  
 Multiplicity: 1  
 Coordinates (XYZ):



	<b>X</b>	<b>Y</b>	<b>Z</b>
C	0.007778	-0.728897	-0.084693
C	-4.343415	-1.617060	0.692652
C	-3.375901	0.593532	-0.686417
C	-2.966388	-1.390787	0.642416
C	-5.249046	-0.765620	0.057173
C	-4.746195	0.343879	-0.626421
C	-2.467334	-0.281610	-0.061024
H	-2.285575	-2.060342	1.147351
H	-6.315109	-0.956757	0.098572
H	-2.995089	1.468765	-1.203274
C	4.411972	-1.655478	-0.606802

C	3.386635	0.691371	0.468922
C	5.294270	-0.706340	-0.095310
C	3.027096	-1.462245	-0.584139
C	2.497675	-0.284967	-0.031865
C	4.760001	0.471508	0.437775
H	6.364908	-0.873379	-0.112332
H	2.365025	-2.214818	-0.986315
H	2.983181	1.618719	0.864718
N	-1.113337	0.069294	-0.123433
H	-0.971052	1.076239	-0.329541
N	1.137548	0.043229	0.028108
H	0.982183	1.037723	0.278592
C	-5.708810	1.307299	-1.267259
C	-4.867844	-2.827352	1.418215
C	5.706225	1.527049	0.944547
C	4.952852	-2.954644	-1.141817
F	-4.031997	-3.256092	2.394212
F	-6.072683	-2.590795	2.007989
F	-5.062314	-3.887095	0.582572
F	-6.809364	0.677847	-1.765317
F	-5.156400	1.999786	-2.288896
F	-6.176509	2.231152	-0.379006
F	6.246878	2.260348	-0.069627

F	6.763223	0.981012	1.611862
F	5.119934	2.403881	1.788568
F	6.229040	-2.839036	-1.599501
F	4.213466	-3.448186	-2.164828
F	4.982307	-3.927048	-0.186176
S	-0.025474	-2.412307	-0.170634
S	0.002866	3.645398	0.031812
O	0.683763	4.646309	-0.814114
O	-1.044412	2.827253	-0.681626
O	0.929243	2.738776	0.806460
C	-0.900061	4.571612	1.298294
H	-1.421069	3.861758	1.944682
H	-1.612919	5.229511	0.795716
H	-0.178264	5.157310	1.872345

<sup>1</sup> Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Goodfellow, R.; Granger, P. *Pure Appl. Chem.* **2001**, *73*, 1795.

<sup>2</sup> Lu, T.-J.; Yang, J.-F.; Sheu, L.-J. *J. Org. Chem.* **1995**, *60*, 2931–2934.

<sup>3</sup> a) Kim, H. Y.; Oh, K. *Org. Lett.* **2011**, *13*, 1306–1309; b) Liu, H.; Tomooka, C. S.; Moore, H. W. *Synth. Commun.* **1997**, *27*, 2177–2180; c) Rodriguez, A. A.; Yoo, H.; Ziller, J. W.; Shea, K. J. *Tetrahedron Lett.* **2009**, *50*, 6830–6833.

<sup>4</sup> Hoque, M. E. U.; Dey, S.; Guha, A. K.; Kim, C. K.; Lee, B.-S.; Lee, H. W. *J. Org. Chem.* **2007**, *72*, 5493–5499.

<sup>5</sup> Chavan, S. P.; Sharma, A. K. *Synlett* **2001**, *2001*, 0667–0669.

<sup>6</sup> Borovika, A.; Nagorny, P. *Tetrahedron* **2013**, *69*, 5719–5725.

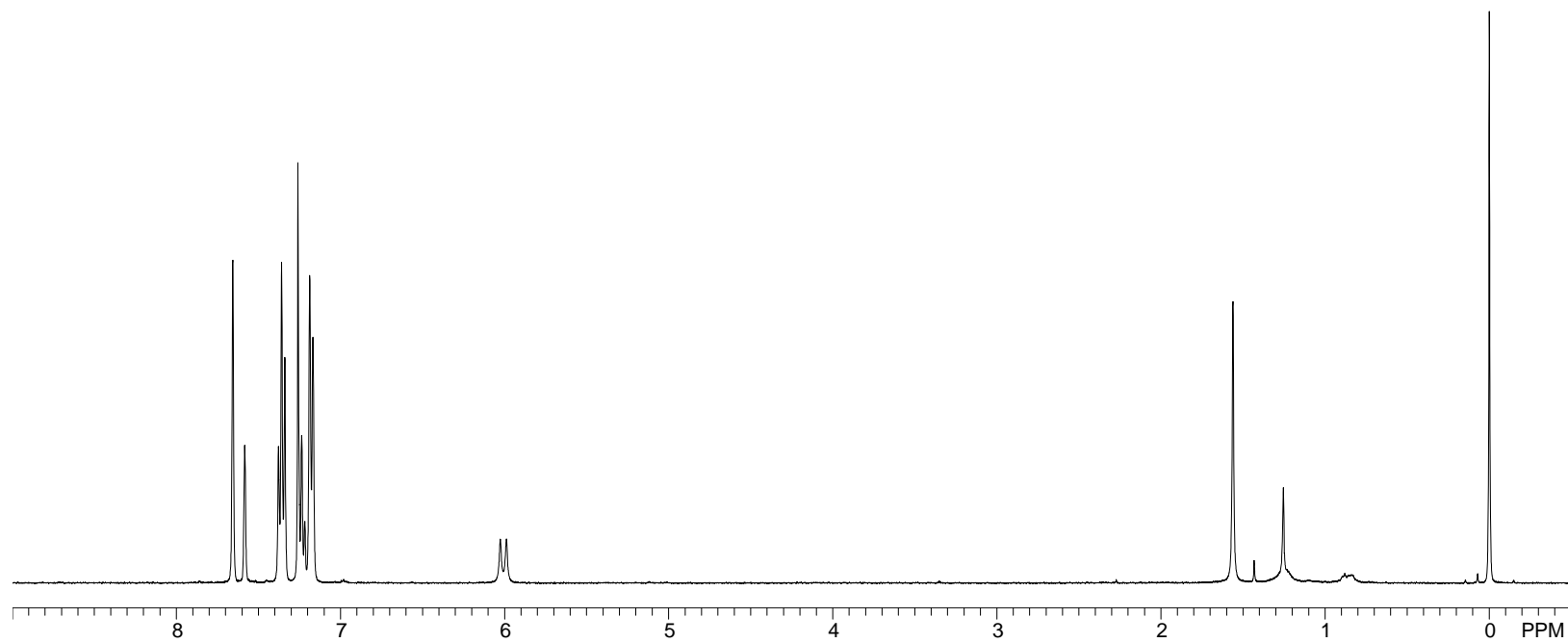
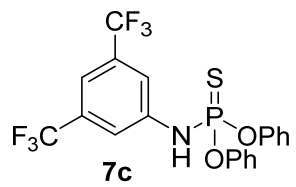
<sup>7</sup> Chavan, S. P.; Ethiraj, K. S.; Dantale, S. W. *Synthetic Commun* **2007**, *37*, 2337–2343.

<sup>8</sup> Inokuchi, T.; Tanigawa, S.; Torii, S. *J. Org. Chem.* **1990**, *55*, 3958–3961.

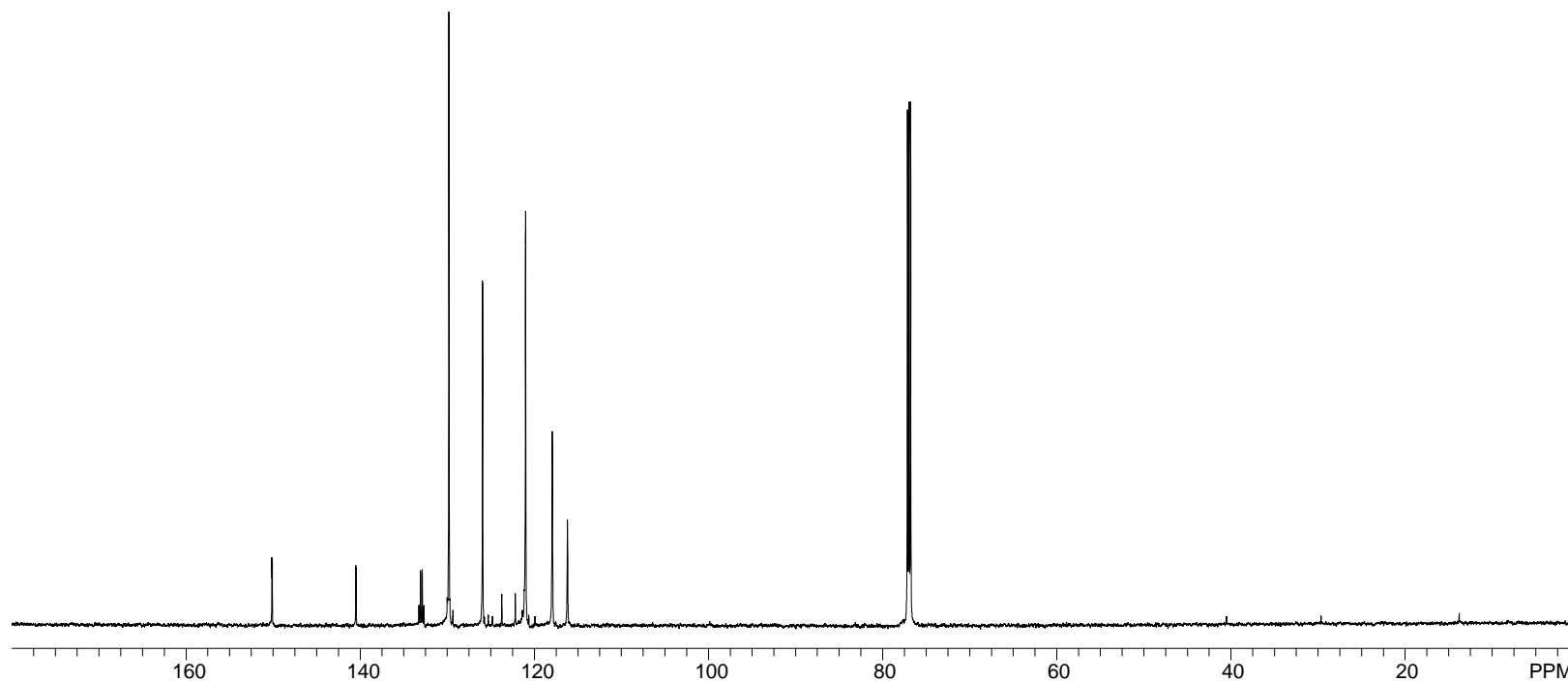
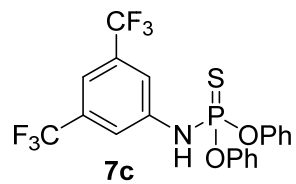
<sup>9</sup> Kumareswaran, R. *Tetrahedron* **1999**, *55*, 1099–1110.

<sup>10</sup> We thank Dr. Hynes for providing us permission to use WinEQNMR for calculating the  $K_a$  of **7e**: M. J. Hynes, *J. Chem. Soc., Dalton Trans.* **1993**, 311.

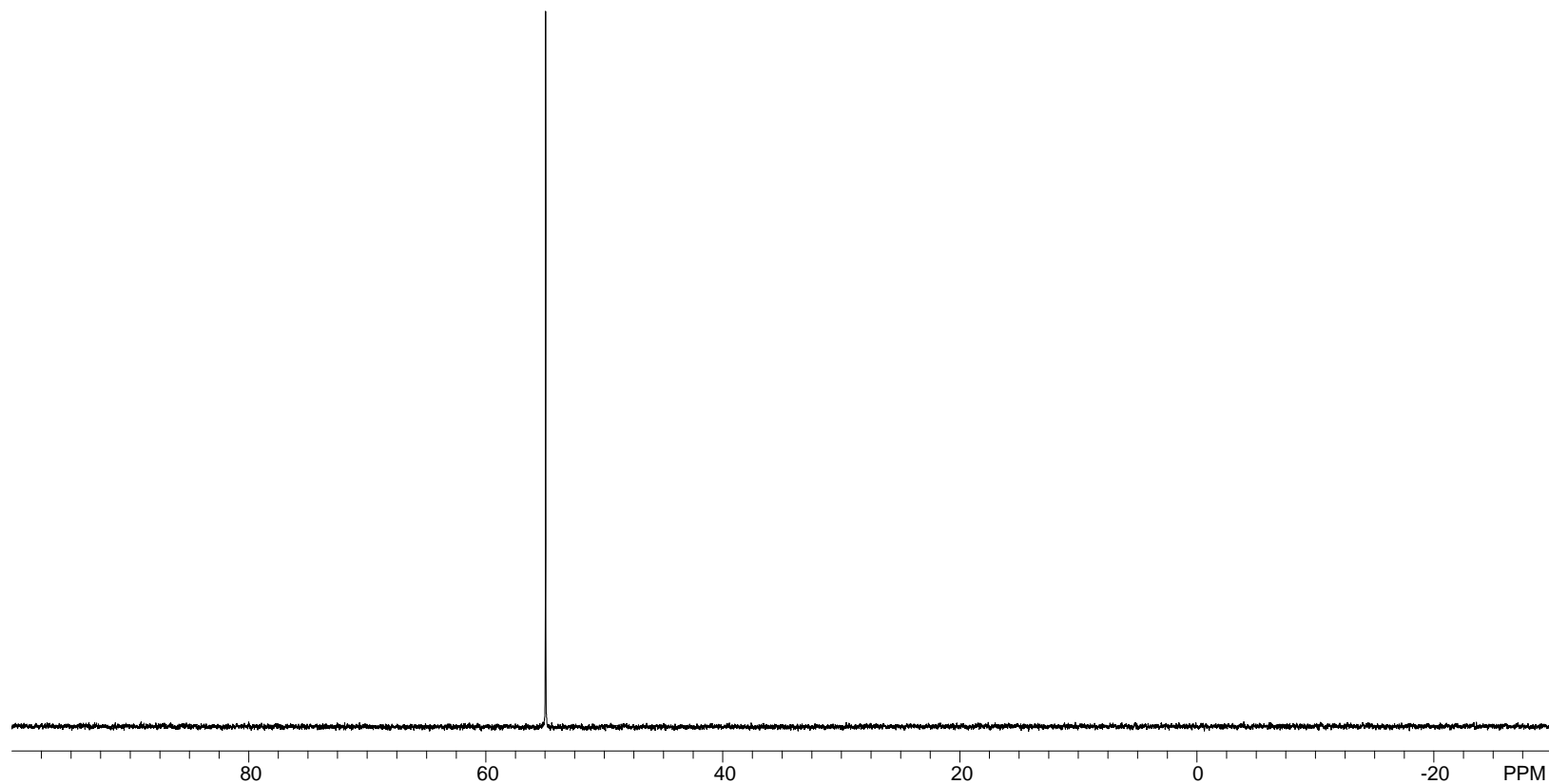
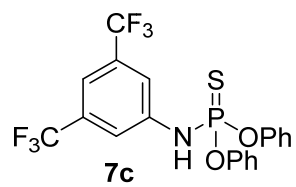
$^1\text{H}$  NMR 400 Hz



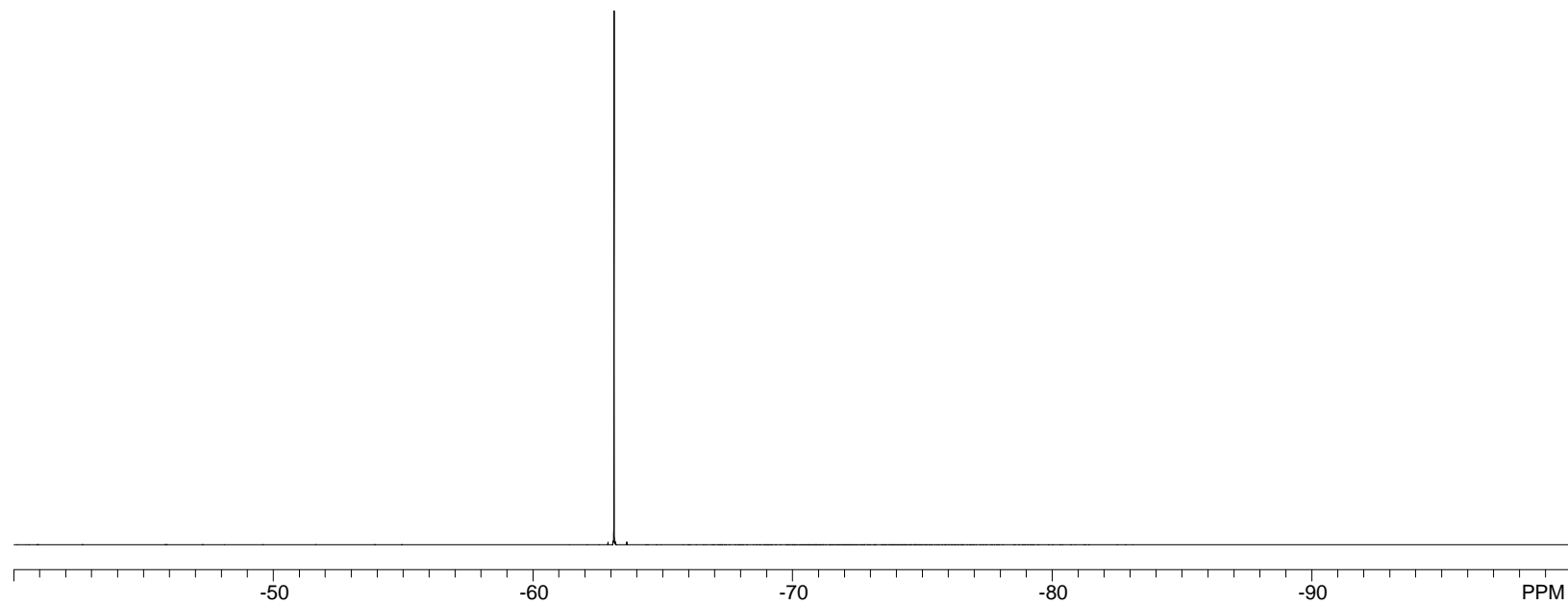
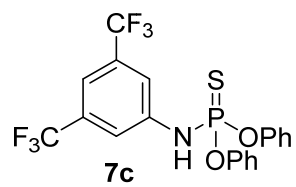
$^{13}\text{C}$  NMR, 175 MHz



$^{31}\text{P}$  NMR, 162 MHz

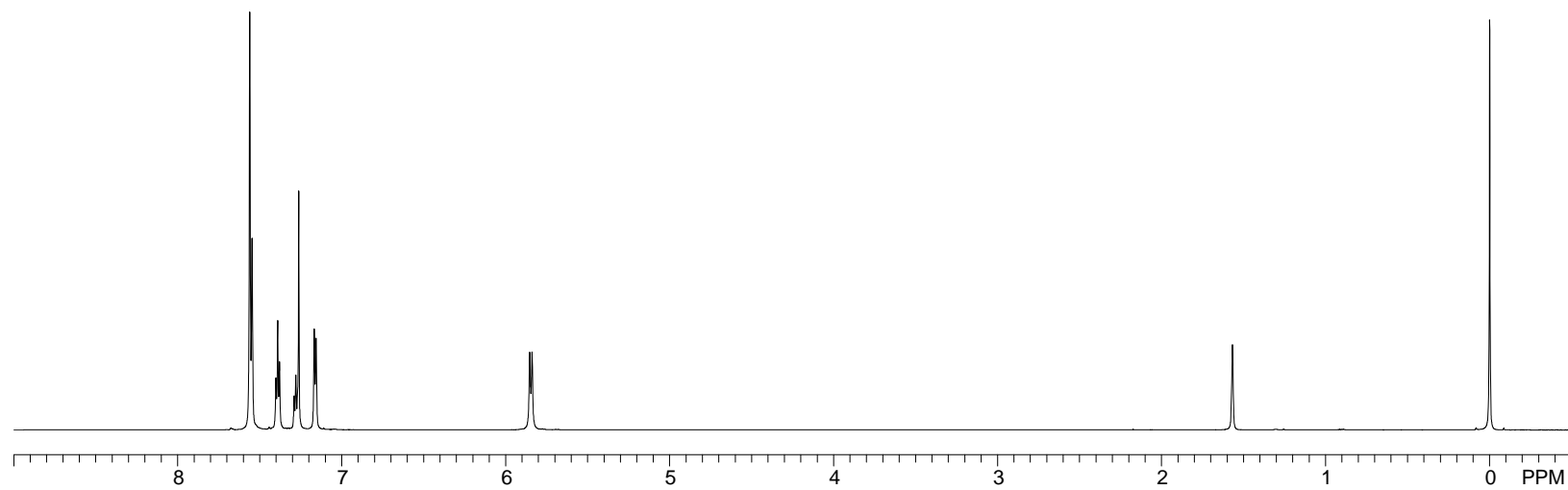
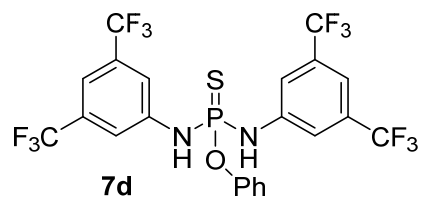


$^{19}\text{F}$  NMR, 376 MHz

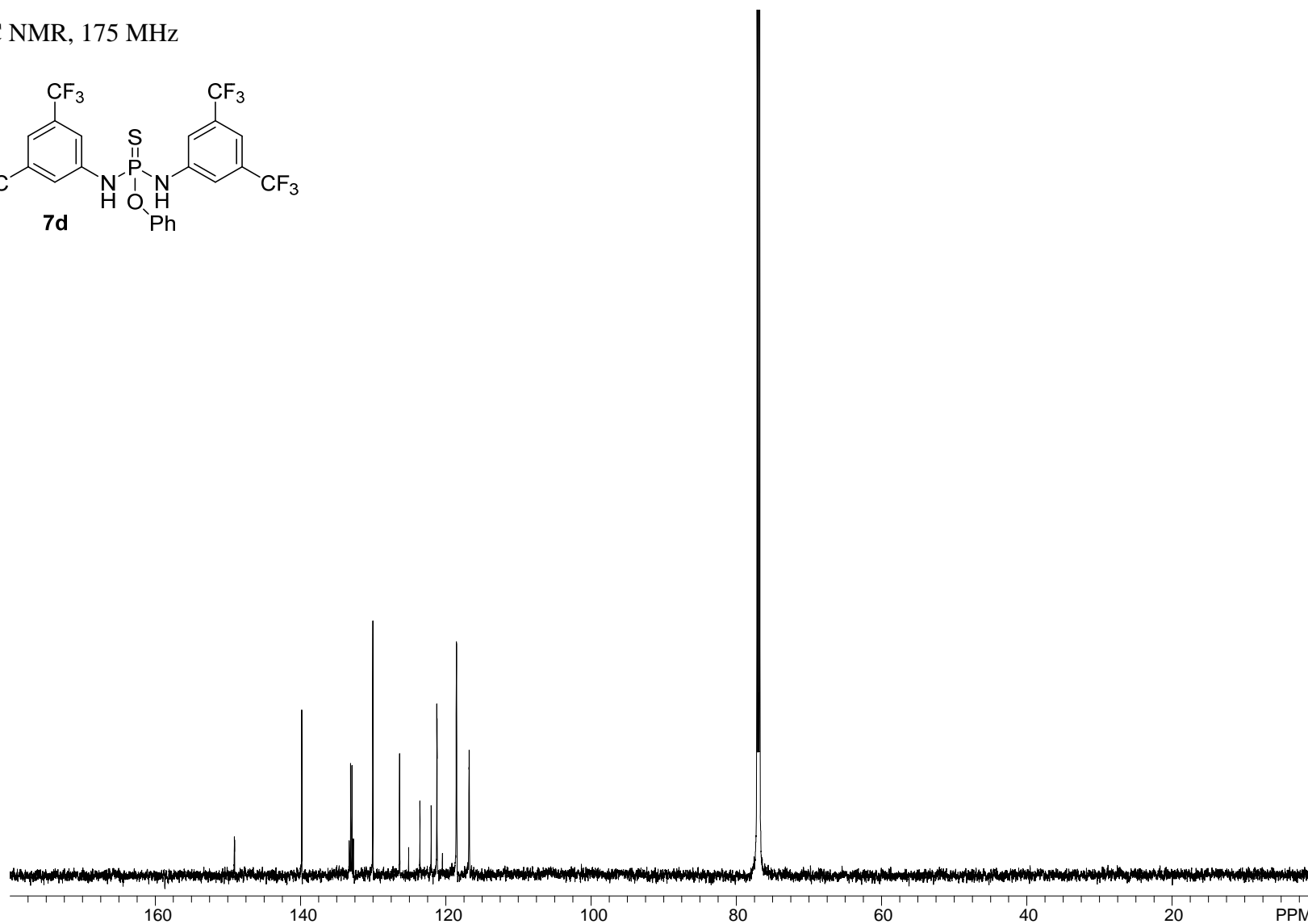
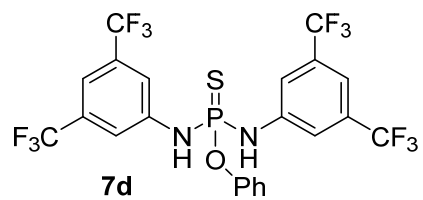




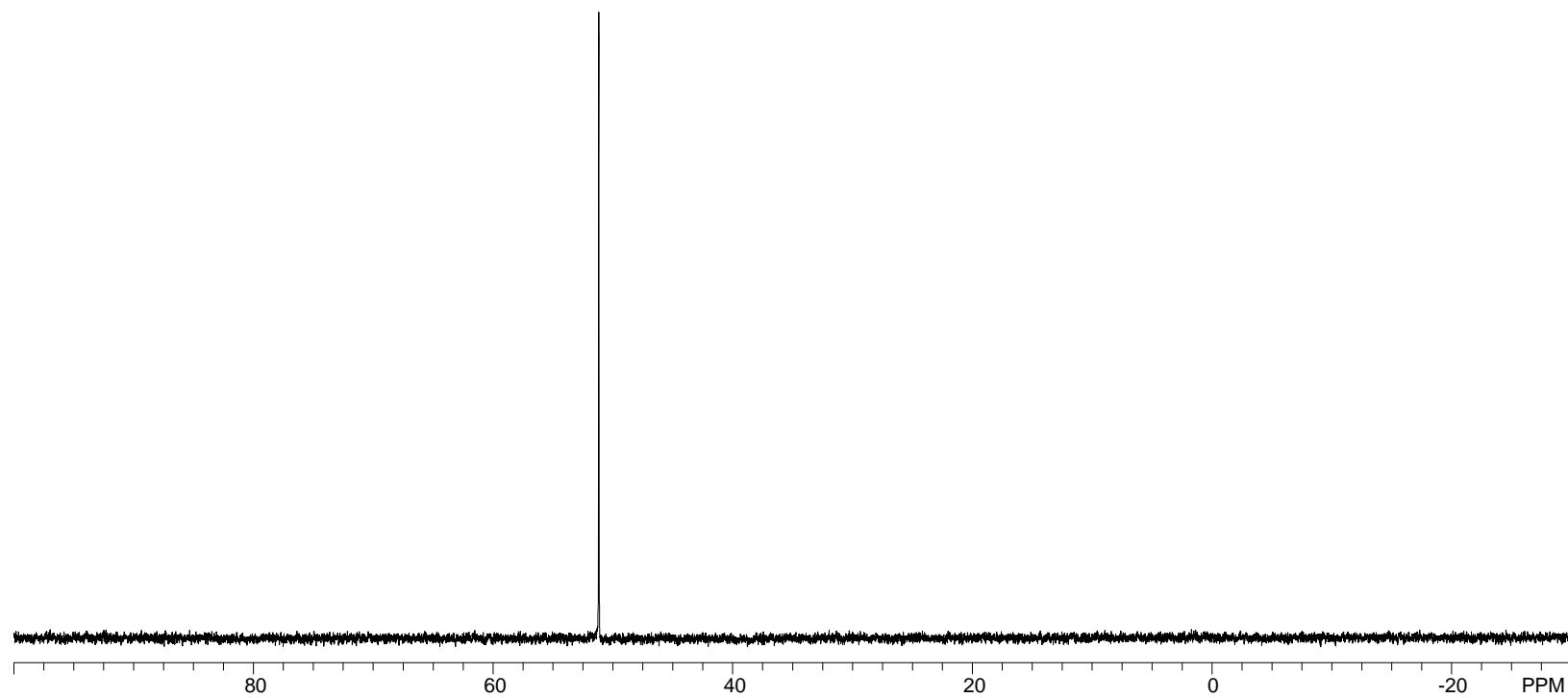
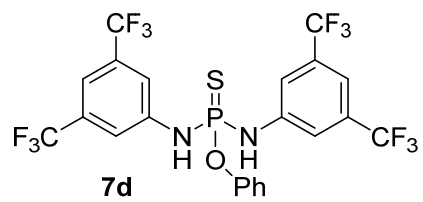
$^1\text{H}$  NMR, 700 MHz



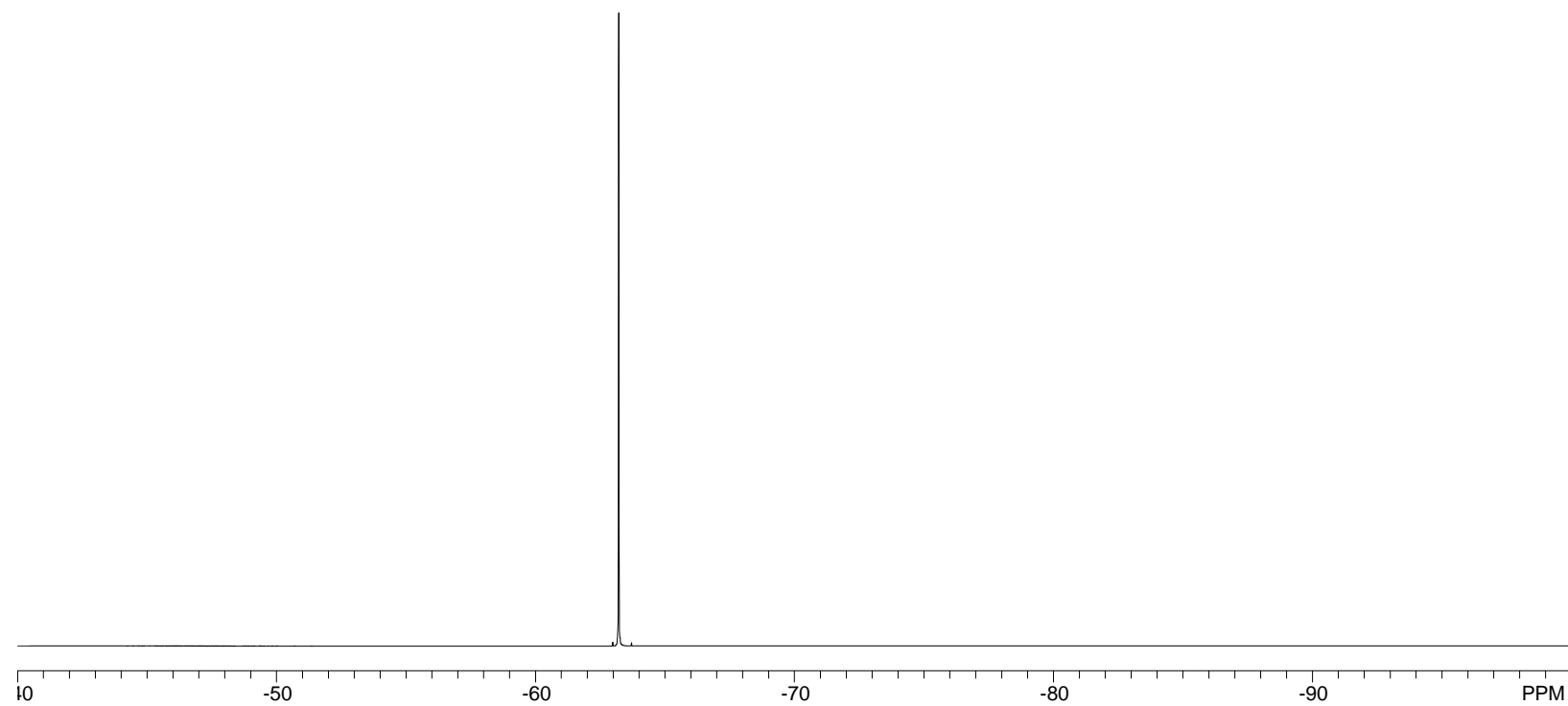
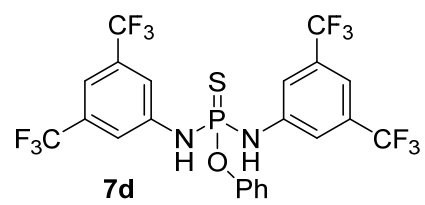
$^{13}\text{C}$  NMR, 175 MHz



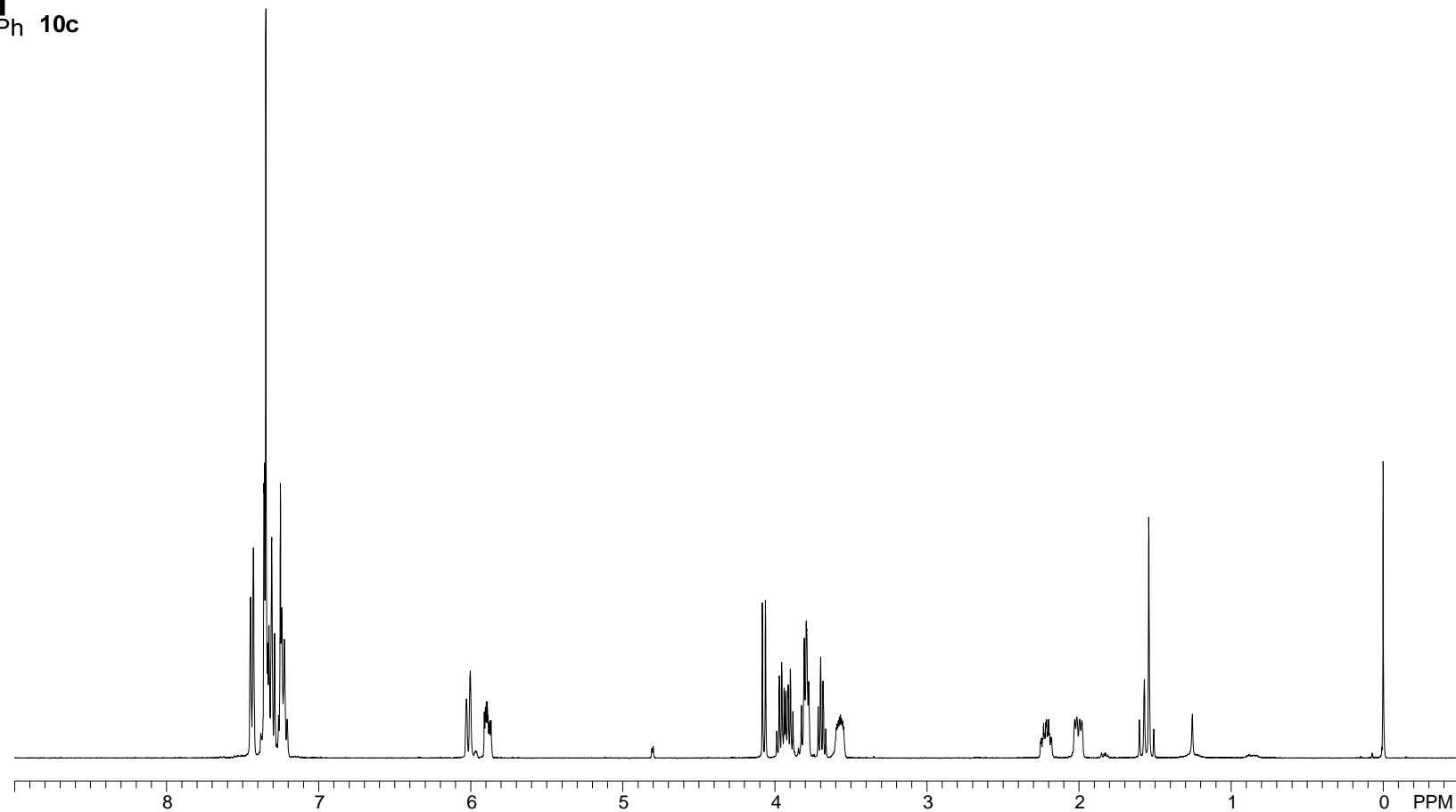
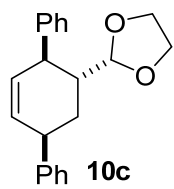
$^{31}\text{P}$  NMR, 283 MHz



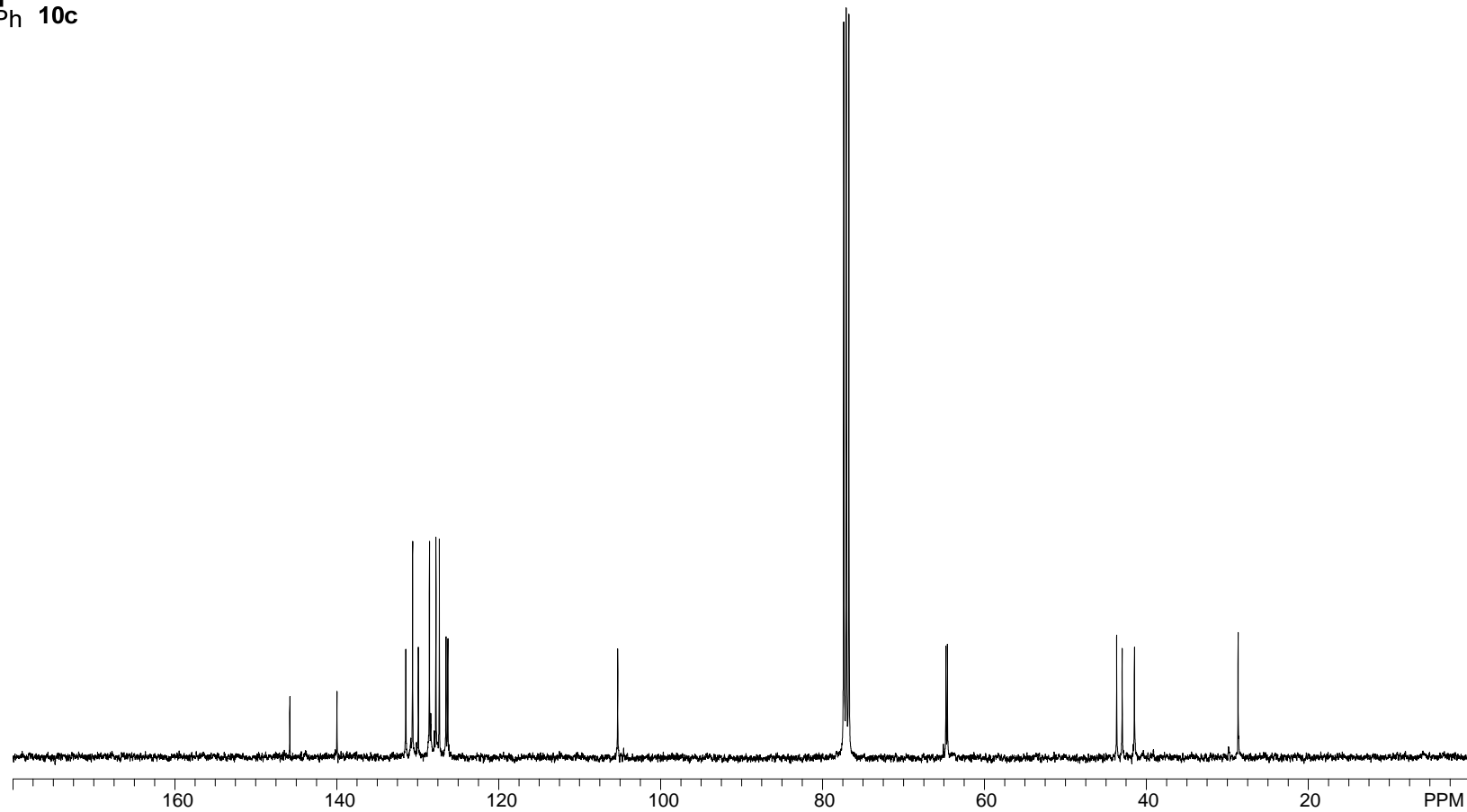
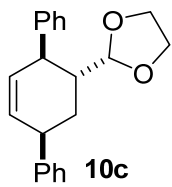
$^{19}\text{F}$  NMR, 376 MHz



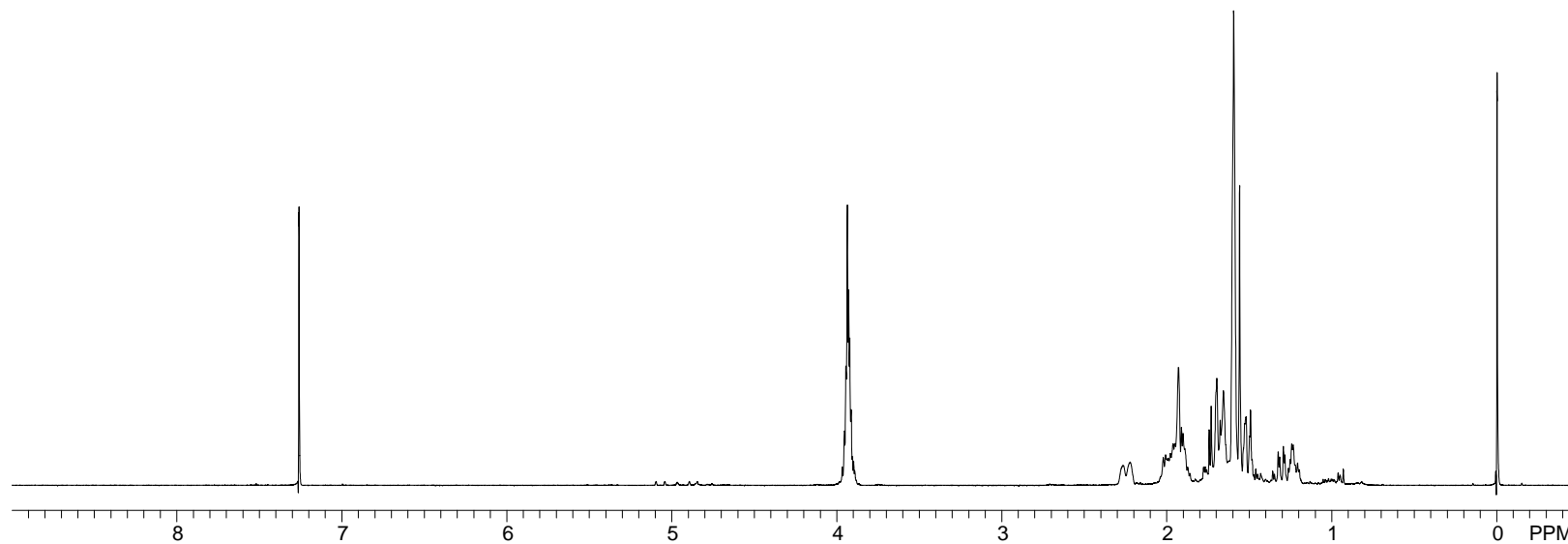
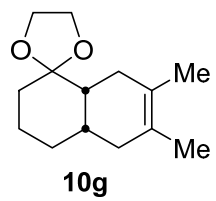
$^1\text{H}$  NMR, 400 MHz



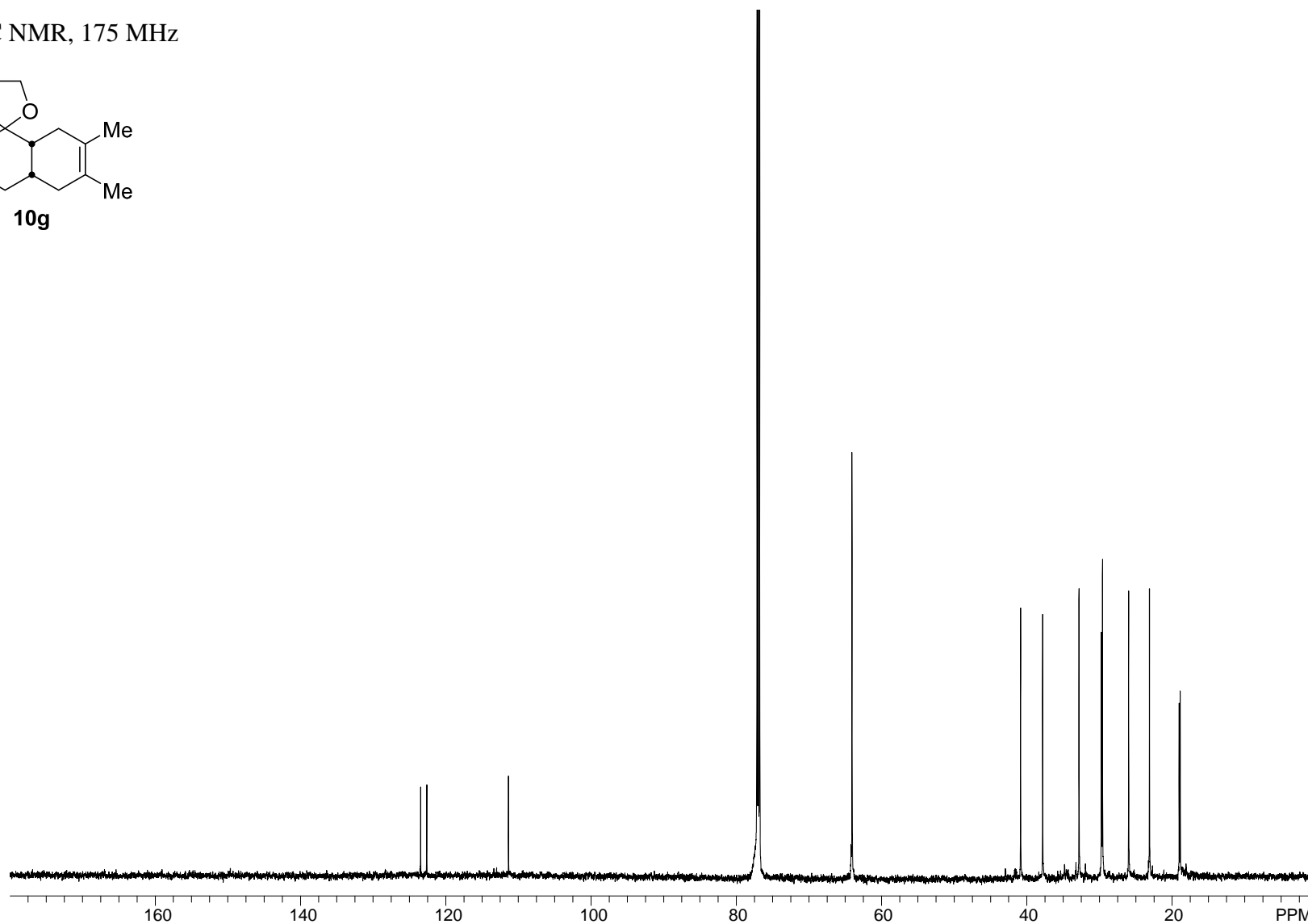
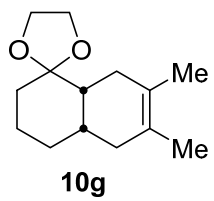
$^{13}\text{C}$  NMR, 101 MHz



$^1\text{H}$  NMR, 400 MHz

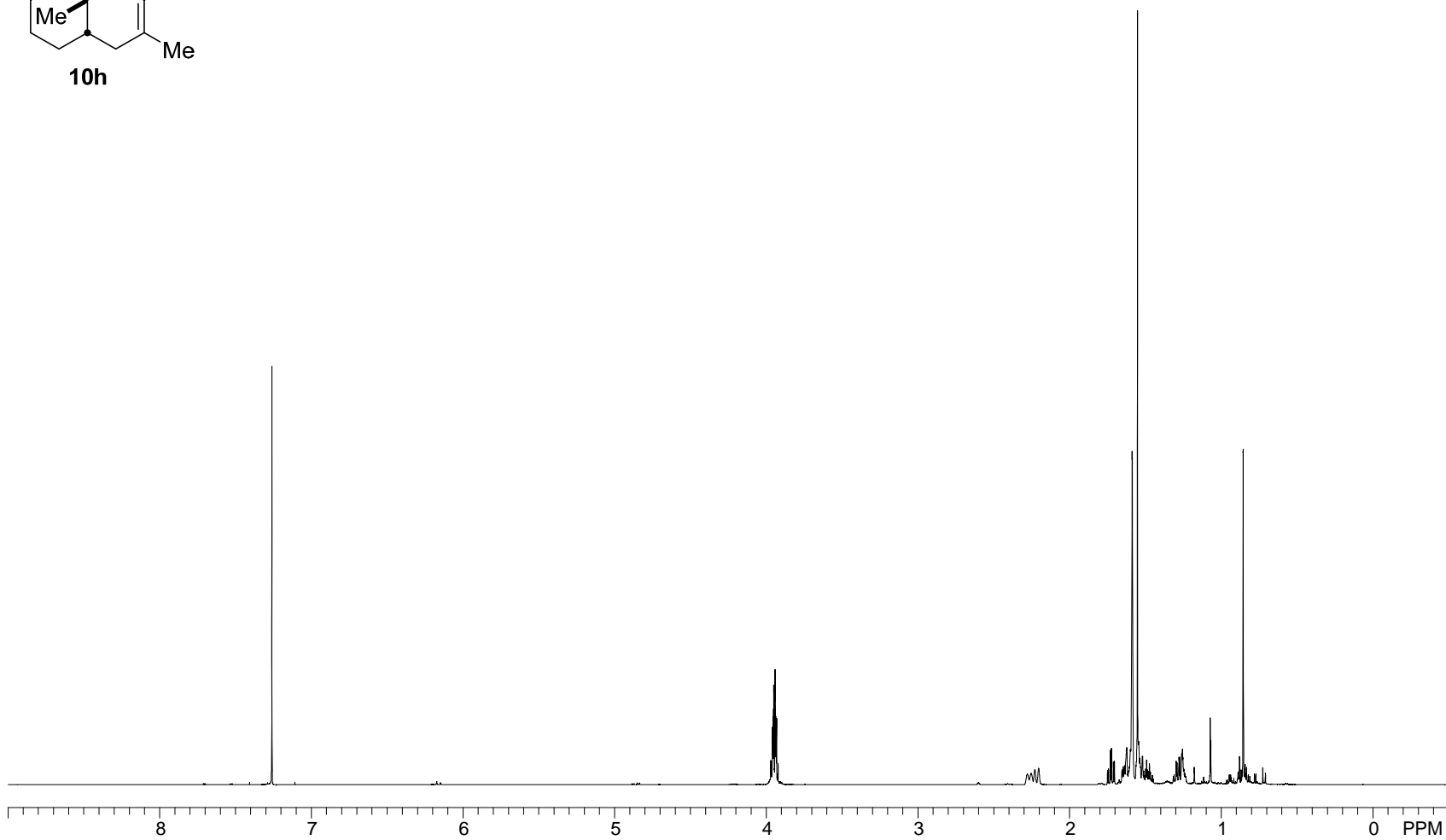
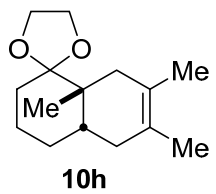


$^{13}\text{C}$  NMR, 175 MHz

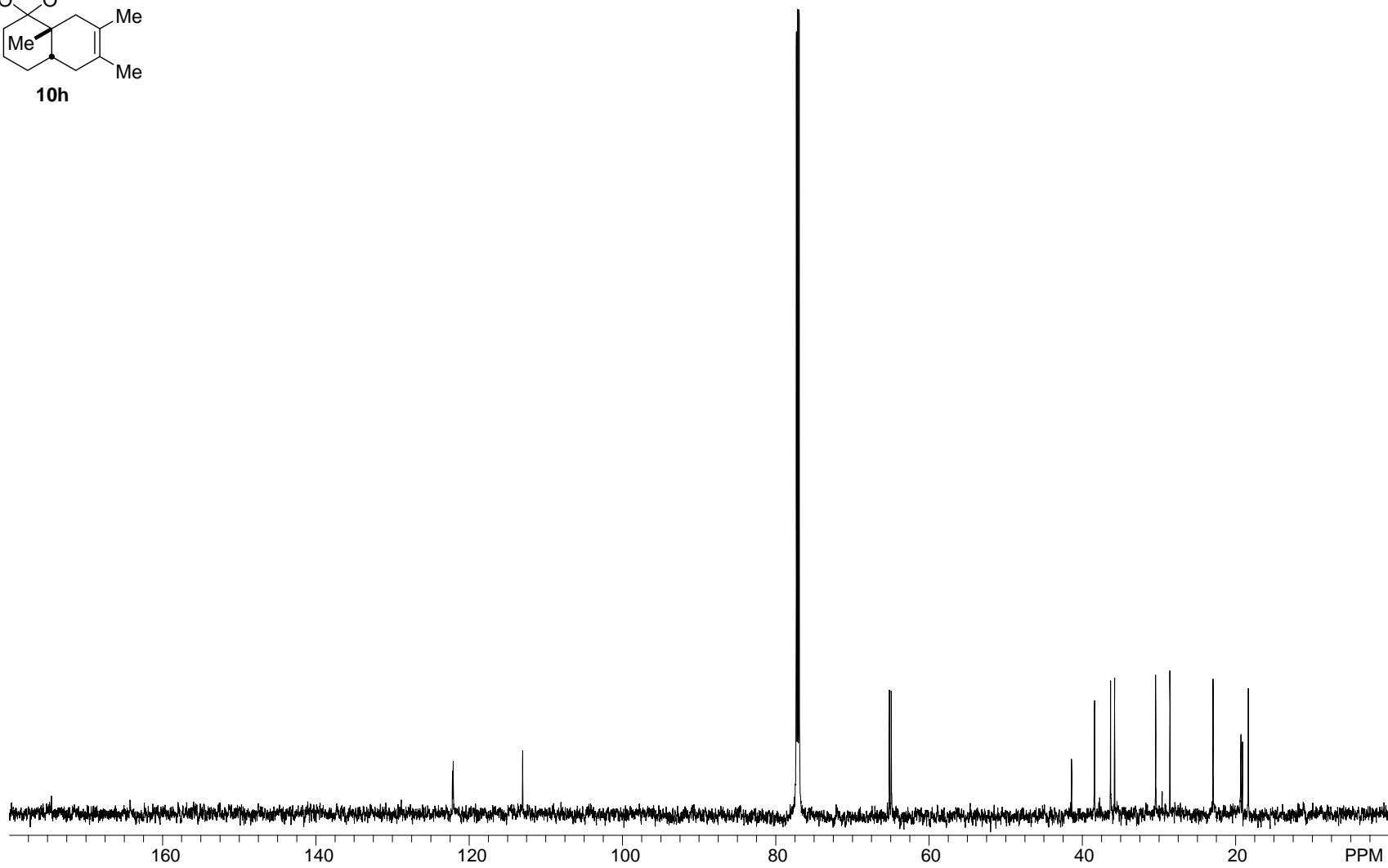
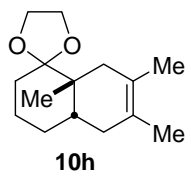




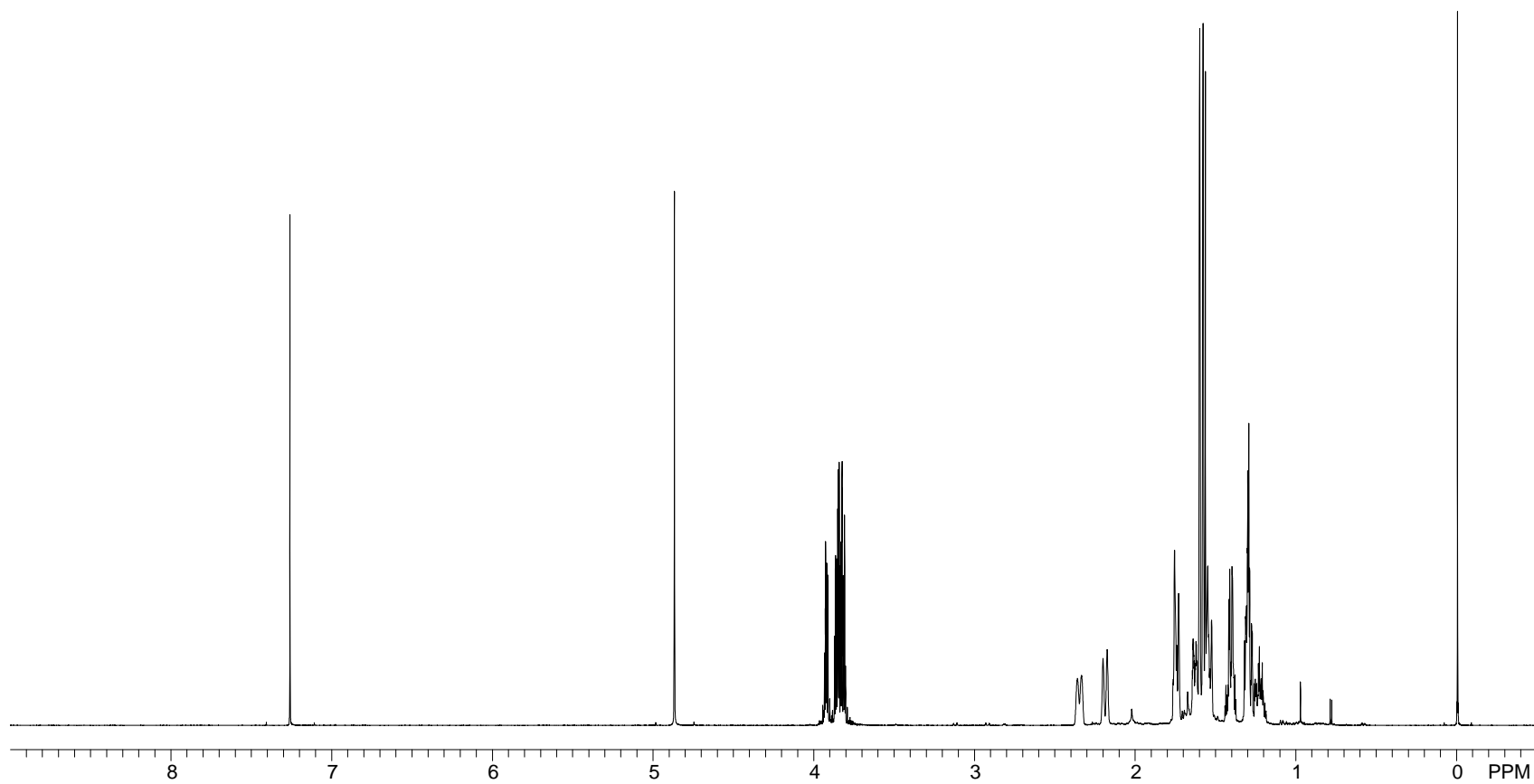
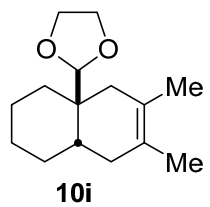
$^1\text{H}$  NMR, 700 MHz



$^{13}\text{C}$  NMR, 175 MHz



$^1\text{H}$  NMR, 700 MHz



$^{13}\text{C}$  NMR, 175 MHz

