

## **Electronic Supplementary Information**

### **Synthesis, Characterization and Oxidizing Properties of Diorgano Tellurone Carrying Bulky Aromatic Substituents**

Makoto Oba,<sup>†</sup> Yasunori Okada,<sup>†</sup> Kozaburo Nishiyama,<sup>†,\*</sup> Shigeru Shimada,<sup>‡</sup>

Wataru Ando<sup>‡,\*</sup>

<sup>†</sup>*Department of Materials Chemistry, Tokai University, 317 Nishino, Numazu, Shizuoka  
410-0395, Japan and* <sup>‡</sup>*National Institute of Advanced Industrial Science and Technology,  
1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

nishiyam@wing.ncc.u-tokai.ac.jp

### **Contents**

General experimental procedures	S2-S3
Computational details	S4
Cartesian coordinates of Tip <sub>2</sub> TeO <sub>2</sub> ( <b>2</b> )	S5-S6
<sup>1</sup> H, <sup>13</sup> C, and <sup>125</sup> Te NMR spectra of Tip <sub>2</sub> TeO <sub>2</sub> ( <b>2</b> )	S7-S9

## Experimental

**General.** Melting points were determined using a Yamato MP-21 melting point apparatus in open capillaries and are uncorrected.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{125}\text{Te}$  nuclear magnetic resonance (NMR) spectra were measured on a Varian Mercury plus 400 spectrometer at 400, 100, and 126 MHz, respectively. All chemical shifts are reported as  $\delta$  values (ppm) relative to residual chloroform ( $\delta_{\text{H}}$  7.26), the central peak of deuteriochloroform ( $\delta_{\text{C}}$  77.00), and dimethyl telluride ( $\delta_{\text{Te}}$  0); and  $J$  values are expressed in Hz. For  $^{125}\text{Te}$  NMR,  $\text{Tip}_2\text{TeO}$  ( $\delta_{\text{Te}}$  1314)<sup>1</sup> was used as a secondary external standard. Fast atom bombardment (FAB) mass spectra were obtained with a JEOL JMS-AX-500 spectrometer using 3-nitrobenzyl alcohol as a matrix. Infrared spectra were recorded with either KBr pellets or in a benzene solution on a JASCO IR Report-100 spectrometer.

Flash column chromatography was performed on a KANTO CHEMICAL Silica gel 60 N (spherical, neutral) 40–50  $\mu\text{m}$ . For analytical purposes, thin layer chromatography (TLC) was performed using Merck Silica gel 60 F<sub>254</sub> precoated aluminum sheets (Merck 5554) which were observed under ultraviolet irradiation. GC measurements were performed on a Shimadzu GC-18A gas chromatograph using a 50 m  $\times$  0.25 mm methyl silicone capillary column (Quadrex).

Bis(2,4,6-triisopropyl) telluride (**1**) was prepared according to the literature.<sup>2,3</sup> All remaining reagents and solvents were of commercial grade and used according to supplier instructions unless otherwise mentioned.

**NaIO<sub>4</sub>-Oxidation of Tip<sub>2</sub>Te (**1**) to Tip<sub>2</sub>TeO<sub>2</sub> (**2**).** To a stirred solution of bis(2,4,6-triisopropylphenyl) telluride (**1**, 536.3 mg, 1.00 mmol) in ethanol (10 ml) was added a solution of sodium periodate (480.5 mg, 2.25 mmol) in water (10 ml). After being stirred at room temperature overnight, the mixture was diluted with water and the

<sup>1</sup> Oba, M.; Endo, M.; Nishiyama, K.; Ouchi, A.; Ando, W. *Chem. Commun.* **2004**, 1672-1673.

<sup>2</sup> Kamigata, N.; Matsuhisa, A.; Taka, H.; Shimizu, T. *Org. Biomol. Chem.* **1995**, *7*, 821-7.

<sup>3</sup> Klapoetke, T.; Krumm, B.; Mayer, P.; Polborn, K.; Schwab, I. *Z. Anorg. Allg. Chem.* **2005**, 631 (13-14), 2677-2682.

precipitated solids were collected by filtration, affording bis(2,4,6-triisopropylphenyl) tellurone **2** (539.2 mg, 0.98 mmol) in 98% yield as colorless crystals (recrystallized from ethyl acetate), mp 108–110 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.12 (d,  $J = 7$  Hz, 24H), 1.21 (d,  $J = 7$  Hz, 12H), 2.88 (sept,  $J = 7$  Hz, 2H), 4.09 (sept,  $J = 7$  Hz, 4H), 7.14 (s, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  23.57, 24.26, 32.74, 34.24, 124.79, 137.82 ( $J_{\text{Te-C}} = 81$  Hz), 152.19, 154.87.  $^{125}\text{Te}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1326. FAB-MS (*m*-NBA)  $m/z$  569 ( $\text{MH}^+$ ). IR (KBr)  $\nu_{\text{max}}$  3470 (O–H), 3050 (C–H), 2960 (C–H), 825 (Te–O), 800 (Te–O)  $\text{cm}^{-1}$ . IR (benzene)  $\nu_{\text{max}}$  2960 (C–H), 835 (Te–O), 805 (Te–O)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{30}\text{H}_{46}\text{O}_2\text{Te}\cdot\text{H}_2\text{O}$ : C, 61.67; H, 8.28. Found: C, 61.82; H, 8.39.

**Oxidation of Alcohols with  $\text{Tip}_2\text{TeO}_2$  (**2**).** A typical experimental procedure for the oxidation of alcohols with tellurone **2** is as follows. A solution of 4-bromobenzyl alcohol (94.1 mg, 0.503 mmol) and **2** (584 mg, 1.03 mmol) in hexane (5 ml) was refluxed for 1 h. The  $^1\text{H}$  NMR analysis of the concentrated reaction mixture showed quantitative formation of 4-bromobenzaldehyde. Purification of the product was performed by flash column chromatography on silica gel and elution with hexane afforded 4-bromobenzaldehyde (90.4 mg, 0.489 mmol) in 97% yield. The structure was confirmed by comparison of the obtained  $^1\text{H}$  NMR spectrum and GC retention times with those of an authentic sample.

**Computational Methods.** All calculations were performed using the Gaussian 03 program package.<sup>4</sup> Geometry of  $\text{Tip}_2\text{TeO}_2$  (**2**) was fully optimized at the B3LYP<sup>5,6</sup> level of theory using the 6-31G(d)<sup>7</sup> basis set in combination with the LANL2DZdp<sup>8</sup> effective core potential basis set for Te atom. This combination is denoted 6-31G(d)+LANL2DZdp(Te). Stationary points were confirmed to be minima by vibrational frequency calculations which gave no imaginary frequencies.

---

<sup>4</sup> Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision D.02, Gaussian, Inc., Wallingford CT, 2004.

<sup>5</sup> Becke, A. D. *J. Chem. Phys.* 1993, 98, 5648-5652.

<sup>6</sup> Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785-789.

<sup>7</sup> (a) Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. *J. Comp. Chem.* **2001**, 22, 976-984. (b) Rassolov, V. A.; Pople, J. A.; Ratner, M. A.; Windus, T. L. *J. Chem. Phys.* **1998**, 109, 1223-1229. (c) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, 54, 724-728.

<sup>8</sup> (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, 82, 270-283. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, 82, 284-298. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, 82, 299-310. The diffuse and polarization functions are taken from C. E. Check, T. O. Faust, J. M. Bailey, B. J. Wright, T. M. Gilbert and L. S. Sunderlin, *J. Phys. Chem. A*, 2001, **105**, 8111-8116. Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/02/06, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy.

**Table S1.** Standard orientation of  $\text{Tip}_2\text{TeO}_2$  (**2**)<sup>a</sup>

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	52	0	-0.000171	-1.634673	-0.037761
2	8	0	-0.086365	-2.602072	1.462386
3	8	0	0.086623	-2.535121	-1.578986
4	6	0	-1.710614	-0.325999	-0.254129
5	6	0	-1.673052	0.602866	-1.318569
6	6	0	-2.784508	1.436549	-1.495305
7	6	0	-3.913638	1.365891	-0.680130
8	6	0	-3.921100	0.413517	0.340923
9	6	0	-2.845924	-0.450708	0.582857
10	6	0	-0.526206	0.729267	-2.321352
11	6	0	0.041615	2.158563	-2.386355
12	6	0	-0.957285	0.214874	-3.708233
13	6	0	-5.099112	2.292450	-0.912896
14	6	0	-5.340299	3.222454	0.291290
15	6	0	-6.375579	1.509331	-1.274103
16	6	0	-3.007218	-1.491337	1.693595
17	6	0	-4.028618	-2.569341	1.275514
18	6	0	-3.394995	-0.857980	3.043103
19	6	0	1.709187	-0.335274	0.236564
20	6	0	2.843102	-0.419736	-0.607336
21	6	0	3.920058	0.429407	-0.323380
22	6	0	3.914865	1.329515	0.744092
23	6	0	2.785804	1.363032	1.561768
24	6	0	1.672878	0.541045	1.344641
25	6	0	2.999746	-1.401672	-1.770744
26	6	0	4.026219	-2.497138	-1.416497
27	6	0	3.376463	-0.697042	-3.087918
28	6	0	5.104007	2.238171	1.024464
29	6	0	6.371463	1.431486	1.365332
30	6	0	5.363689	3.214371	-0.138735
31	6	0	0.525748	0.620024	2.351952
32	6	0	-0.025368	2.049111	2.503533
33	6	0	0.948042	0.015393	3.704743
34	1	0	-2.771960	2.158387	-2.308103
35	1	0	-4.799782	0.324836	0.973388
36	1	0	0.297954	0.085536	-2.007747
37	1	0	0.381236	2.495572	-1.400859
38	1	0	-0.698199	2.878188	-2.754176
39	1	0	0.898424	2.190379	-3.069096
40	1	0	-0.123283	0.291679	-4.415662
41	1	0	-1.795731	0.795805	-4.109683
42	1	0	-1.256408	-0.835723	-3.648337
43	1	0	-4.847382	2.926864	-1.773594
44	1	0	-4.446435	3.811528	0.523697

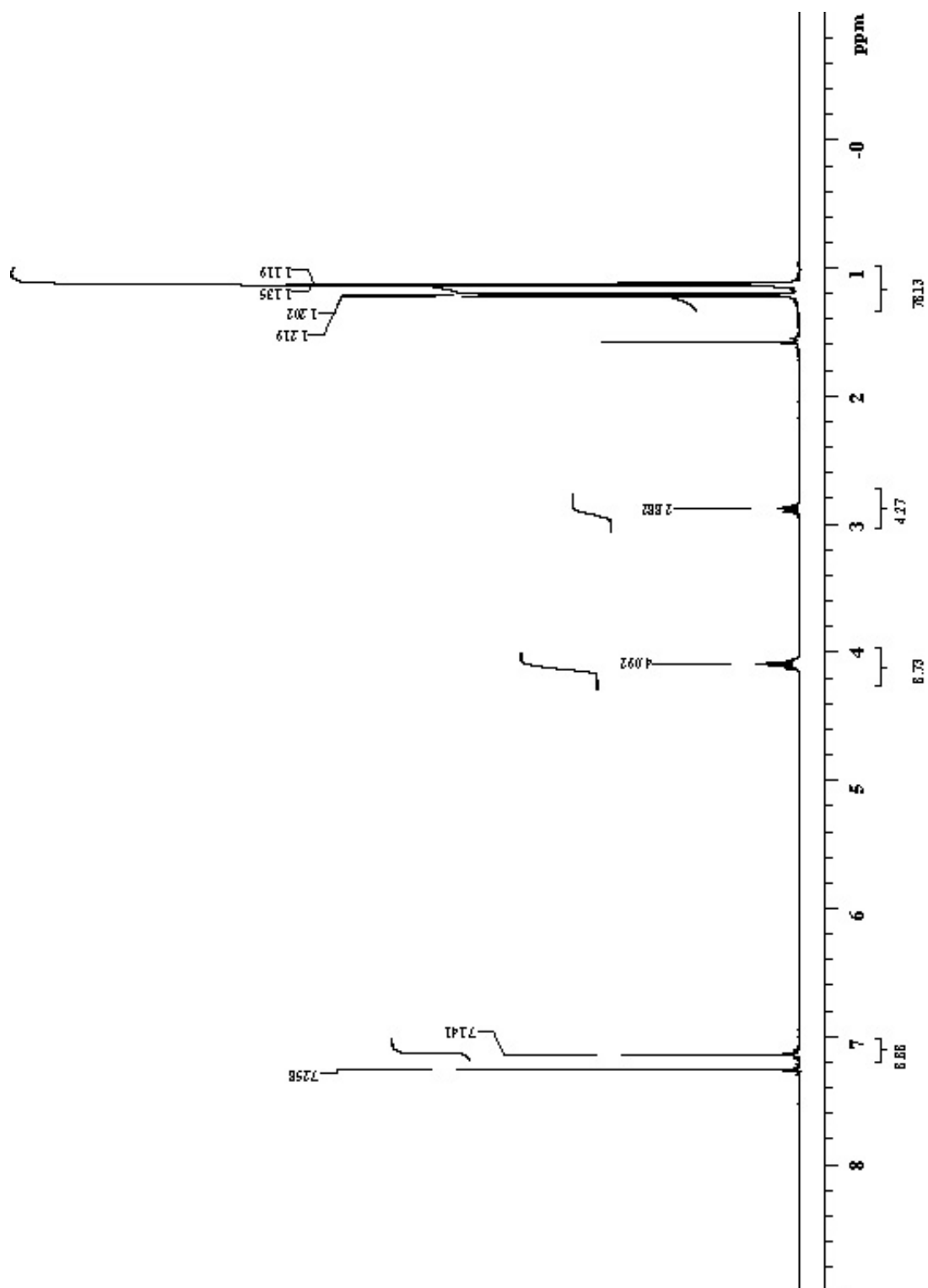
45	1	0	-6.161999	3.916953	0.080820
46	1	0	-5.607867	2.652130	1.188536
47	1	0	-6.216062	0.871809	-2.150351
48	1	0	-7.197671	2.199167	-1.497990
49	1	0	-6.697387	0.866301	-0.446528
50	1	0	-2.053453	-1.999933	1.844107
51	1	0	-3.729134	-3.060468	0.343091
52	1	0	-5.028670	-2.144213	1.125397
53	1	0	-4.101312	-3.338875	2.052577
54	1	0	-2.675003	-0.089800	3.347516
55	1	0	-4.388553	-0.394950	3.019120
56	1	0	-3.411198	-1.629375	3.821270
57	1	0	4.798485	0.371634	-0.959717
58	1	0	2.773924	2.044728	2.408490
59	1	0	2.045989	-1.903874	-1.941914
60	1	0	4.095268	-3.225361	-2.232724
61	1	0	3.734102	-3.036308	-0.508603
62	1	0	5.026551	-2.078172	-1.251524
63	1	0	3.393907	-1.427321	-3.904812
64	1	0	4.366894	-0.228616	-3.045050
65	1	0	2.649678	0.080687	-3.348971
66	1	0	4.848576	2.839157	1.907660
67	1	0	6.693991	0.817274	0.516412
68	1	0	7.197460	2.105418	1.621150
69	1	0	6.200068	0.762793	2.215718
70	1	0	5.642491	2.679177	-1.054044
71	1	0	6.184023	3.897646	0.110194
72	1	0	4.474570	3.814831	-0.360077
73	1	0	-0.305721	0.007925	1.997329
74	1	0	-0.357966	2.449718	1.539691
75	1	0	0.720993	2.736384	2.917071
76	1	0	-0.884338	2.048872	3.184346
77	1	0	1.232775	-1.033497	3.579792
78	1	0	1.794073	0.559198	4.140795
79	1	0	0.114678	0.059922	4.415646

---

<sup>a</sup> Total energy = -1328.6542 a.u. (including zero-point vibrational energy correction scaled by 0.9804<sup>9</sup>)

---

<sup>9</sup> Bauschlicher, C. W.; Partridge, H. *J. Chem. Phys.* **1995**, *103*, 1788-1791



**Figure S1.** <sup>1</sup>H NMR spectrum of Tip<sub>2</sub>TeO<sub>2</sub> (2)

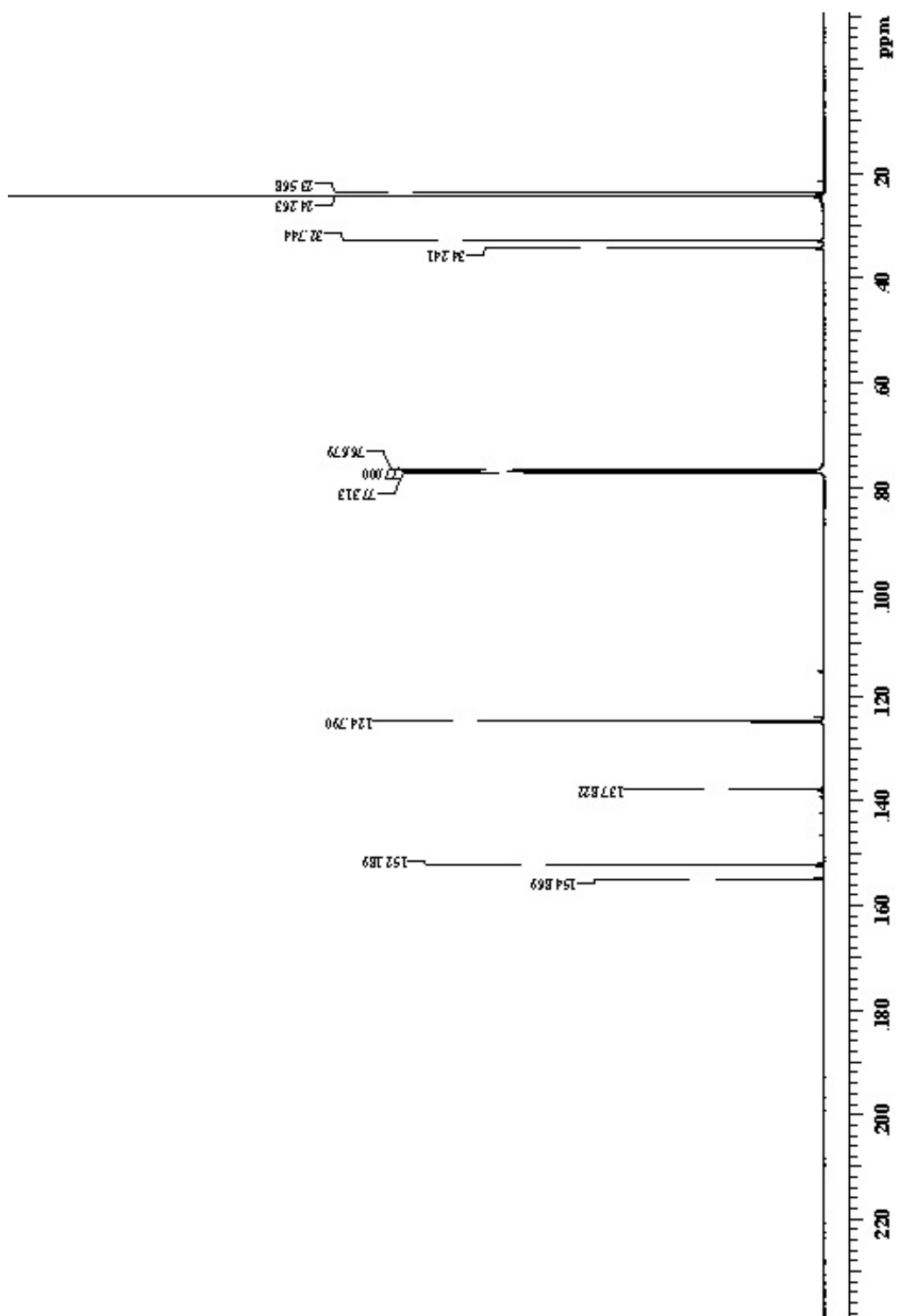
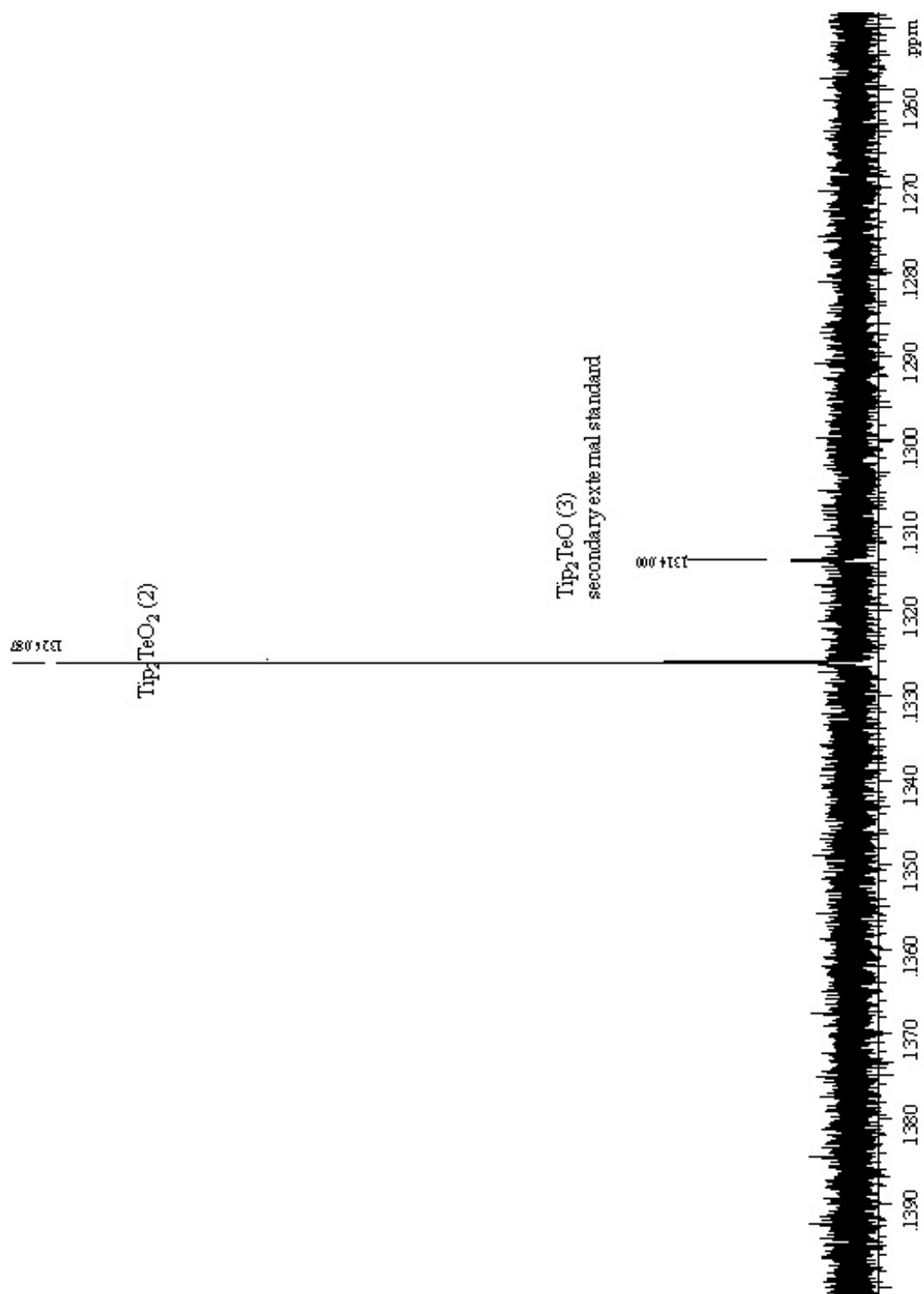


Figure S2.  $^{13}\text{C}$  NMR spectrum of  $\text{Tip}_2\text{TeO}_2$  (2)





**Figure S3.**  $^{125}\text{Te}$  NMR spectrum of  $\text{Tip}_2\text{TeO}_2$  (2)