Electronic Supplementary Information

A New Oxapalladacycle Generated via *Ortho* C-H Activation of Phenylphosphinic Acid: Efficient Catalyst for Markovnikov-Type Additions of E-H Bonds to Alkynes

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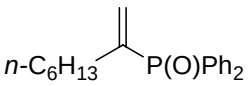
General. All reactions were carried out under nitrogen atmosphere in a sealed NMR or a Schlenk tube unless otherwise noted. Solvents were dried and purified under nitrogen before use by standard procedure. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL LA-500 instrument (500 MHz for ^{1}H, 125.4 MHz for ^{13}C, and 201.9 MHz for ^{31}P NMR spectroscopy). Unless otherwise noted, $CDCl_3$ was used as the solvent. Chemical shift values for ^{1}H and ^{13}C were referred to internal Me_4Si (0 ppm), and that for ^{31}P was referred to H_3PO_4 (85% solution in D_2O, 0 ppm). Mass spectra were measured on a Shimadzu GCMS-QP2010 spectrometer (EI). HRMS and elemental analysis was performed by the Analytical Center at the National Institute of Advanced Industrial Science and Technology. Preparative GPC was carried out on a Japan Analytical Industry LC-908 instrument (1H and 2H columns) with $CHCl_3$ as eluent.

X-ray Crystallography. Data collection was performed on a Bruker Smart Apex CCD diffractometer (Mo K*a* radiation, graphite monochromator). Data were corrected for absorption. For complex **3**, the structures were solved by the Patterson method.[1] Structure refinement was carried out by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically, with a similar U restraint for some of carbon atoms (C8-C12). All hydrogen atoms were located at calculated positions and refined with a riding model. Structure solution and refinement were performed using Crystal Structure software package[2] with SHELX-97 program.[3]

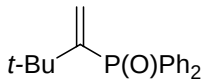
1) PATTY: Beurskens, P. T.; Admiraal, G.; Behm, H.; Beurskens, G.; Smits, J. M. M. and Smykalla, C. (1991). Z. f. Kristallogr. Suppl.4, p.99.
2) CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000-2010). Tokyo 196-8666, Japan.
3) SHELX97: Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.

Characterizations of Adducts

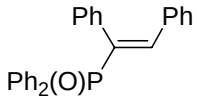


This compound is known: Han, L.-B.; Hua, R.-M.; Tanaka, M. *Angew. Chem. Int. Ed.*

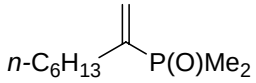
1998, *37*, 94.



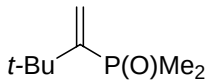
^{1}H NMR: δ 7.69-7.64 (m, 4H), 7.52-7.49 (m, 2H), 7.46-7.42 (m, 4H), 5.99 (d, $J_{P\text{-}H}$ = 45.2 Hz, 1H), 5.20 (d, $J_{P\text{-}H}$ = 22.0 Hz, 1H), 1.27 (s, 9H). ^{31}P NMR: δ 34.8. M/S (*m/z*) 284 (42, M^+), 228 (60), 227 (100), 201 (36). This compound is known: (a) Dobashi, N.; Fuse, K.; Hoshino, T.; Kanada, J.; Kashiwabara, T.; Kobata, C.; Nune, S. K.; Tanaka, M. *Tetrahedron Lett.* **2007**, *48*, 4669. (b) Takaki, K.; Takeda, M.; Koshiji, G.; Shishido, T.; Takehira, K. *Tetrahedron Lett.* **2001**, *42*, 6357.



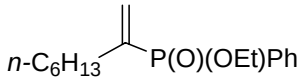
This compound is known: Han, L.-B.; Hua, R.-M.; Tanaka, M. *Angew. Chem. Int. Ed.* **1998**, *37*, 94.



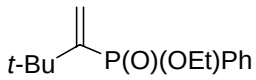
^{1}H NMR: δ 5.92 (d, $J_{P\text{-}H}$ = 19.5 Hz, 1H), 5.86 (d, $J_{P\text{-}H}$ = 39.1 Hz, 1H), 2.24-2.19 (m, 2H), 1.55 (d, $J_{P\text{-}H}$ = 12.2 Hz, 6H), 1.56-1.49 (m, 2H), 1.37-1.31 (m, 6H), 0.90 (t, $J_{H\text{-}H}$ = 6.1 Hz, 3H). ^{13}C NMR: δ 145.8 (d, $J_{C\text{-}P}$ = 87.8 Hz), 125.9 (d, $J_{C\text{-}P}$ = 7.2 Hz), 32.1, 31.6 (d, $J_{C\text{-}P}$ = 11.4 Hz), 29.4, 28.5 (d, $J_{C\text{-}P}$ = 6.2 Hz), 23.0, 16.6 (d, $J_{C\text{-}P}$ = 69.2 Hz), 14.5. ^{31}P NMR: δ 35.3. M/S (*m/z*) 187 (M^+-1), 173, 159, 145, 131, 104, 93, 78. HRMS Calcd for $C_{10}H_{21}OP$: 188.1330; found: 188.1325.



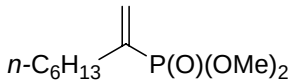
^{1}H NMR: δ 5.75 (d, $J_{P\text{-}H}$ = 42.7 Hz, 1H), 5.54 (d, $J_{P\text{-}H}$ = 22.0 Hz, 1H), 1.64 5.76 (d, $J_{P\text{-}H}$ = 12.2 Hz, 6H), 1.32 (s, 9H). ^{13}C NMR: δ 156.5 (d, $J_{C\text{-}P}$ = 82.7 Hz), 122.6 (d, $J_{C\text{-}P}$ = 11.4 Hz), 38.0 (d, $J_{C\text{-}P}$ = 9.3 Hz), 30.4 (d, $J_{C\text{-}P}$ = 4.1 Hz), 20.4 (d, $J_{C\text{-}P}$ = 70.3 Hz). ^{31}P NMR: δ 39.2. HRMS Calcd for $C_8H_{17}OP$: 160.1017; found: 160.1013.



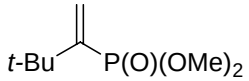
This compound is known: Han, L.-B.; Zhang, C.; Yazawa, H.; Shimada, S. *J. Am. Chem. Soc.* **2004**, *126*, 5080.



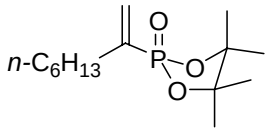
^{1}H NMR: δ 7.81-7.77 (m, 2H), 7.53-7.30 (m, 1H), 7.48-7.43 (m, 2H), 5.90 (d, $J_{P\text{-}H}$ = 44.0 Hz, 1H), 5.82 (d, $J_{P\text{-}H}$ = 22.0 Hz, 1H), 4.13-4.06 (m, 1H), 3.98-3.90 (m, 1H), 1.32 (t, $J_{H\text{-}H}$ = 7.4 Hz, 3H), 1.22 (s, 9H). ^{13}C NMR: δ 152.1 (d, $J_{C\text{-}P}$ = 117.8 Hz), 133.1 (d, $J_{C\text{-}P}$ = 129.2 Hz), 132.165 (d, $J_{C\text{-}P}$ = 3.1 Hz), 132.161 (d, $J_{C\text{-}P}$ = 10.3Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.4 Hz), 127.5 (d, $J_{C\text{-}P}$ = 10.3 Hz), 60.9 (d, $J_{C\text{-}P}$ = 6.2 Hz), 37.0 (d, $J_{C\text{-}P}$ = 11.4 Hz), 30.7 (d, $J_{C\text{-}P}$ = 4.1 Hz), 16.8 (d, $J_{C\text{-}P}$ = 6.2 Hz). ^{31}P NMR: δ 34.9. HRMS Calcd for $C_{14}H_{21}O_2P$: 252.1279; found: 252.1280.



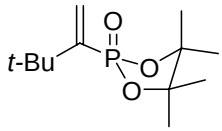
This compound is known: Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 1571.



^{1}H NMR: δ 6.03 (d, $J_{P\text{-}H}$ = 23.2 Hz, 1H), 5.90 (d, $J_{P\text{-}H}$ = 48.8 Hz, 1H), 3.72 (d, $J_{P\text{-}H}$ = 11.0 Hz, 6H), 1.23 (s, 9H). ^{13}C NMR: δ 147.9 (d, $J_{C\text{-}P}$ = 163.3 Hz), 128.7 (d, $J_{C\text{-}P}$ = 8.3 Hz), 52.6 (d, $J_{C\text{-}P}$ = 5.2 Hz), 36.0 (d, $J_{C\text{-}P}$ = 11.4 Hz), 30.4 (d, $J_{C\text{-}P}$ = 5.2 Hz). ^{31}P NMR: δ 23.0. HRMS Calcd for $C_8H_{17}O_3P$: 192.0915; found: 192.0925.

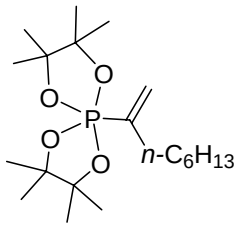


^{1}H NMR: δ 5.88 (d, $J_{P\text{-}H}$ = 23.2 Hz, 1H), 5.60 (d, $J_{P\text{-}H}$ = 50.0 Hz, 1H), 2.39-2.33 (m, 2H), 1.59-1.54 (m, 2H), 1.52 (s, 6H), 1.37-1.30 (m, 6H), 1.34 (s, 6H), 0.88 (t, $J_{H\text{-}H}$ = 6.1 Hz, 3H). ^{13}C NMR: δ 141.4 (d, $J_{C\text{-}P}$ = 166.4 Hz), 126.7 (d, $J_{C\text{-}P}$ = 9.3 Hz), 88.6, 33.3 (d, $J_{C\text{-}P}$ = 11.4 Hz), 32.0, 29.2, 28.4 (d, $J_{C\text{-}P}$ = 5.2 Hz), 25.4 (d, $J_{C\text{-}P}$ = 2.1 Hz), 24.5 (d, $J_{C\text{-}P}$ = 4.1 Hz), 23.0, 14.5. ^{31}P NMR: δ 31.1. HRMS Calcd for $C_{14}H_{27}O_3P$: 274.1698; found: 274.1695.

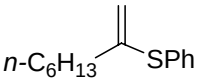


^{1}H NMR: δ 5.93 (d, $J_{P\text{-}H}$ = 24.4 Hz, 1H), 5.73 (d, $J_{P\text{-}H}$ = 50.0 Hz, 1H), 1.51 (s, 6H), 1.32 (s, 6H), 1.27 (s, 9H). ^{13}C NMR: δ 151.4 (d, $J_{C\text{-}P}$ = 158.1 Hz), 124.7 (d, $J_{C\text{-}P}$ = 8.3

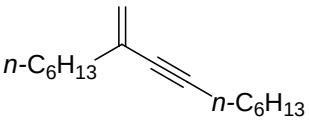
Hz), 88.4, 36.0 (d, $J_{C\text{-}P}$ = 13.4 Hz), 30.9 (d, $J_{C\text{-}P}$ = 5.2 Hz), 25.4 (d, $J_{C\text{-}P}$ = 4.1 Hz), 24.3 (d, $J_{C\text{-}P}$ = 5.2 Hz). ^{31}P NMR: δ 31.0. HRMS Calcd for $C_{12}H_{23}O_3P$: 246.1385; found: 246.1381.



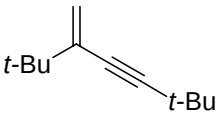
^{1}H NMR: δ 5.76 (d, $J_{P\text{-}H}$ = 25.6 Hz, 1H), 5.38 (d, $J_{P\text{-}H}$ = 56.1 Hz, 1H), 2.41-2.35 (m, 2H), 1.54-1.49 (m, 2H), 1.35-1.27 (m, 6H), 1.26 (s, 12H), 1.13 (s, 12H), 0.88 (t, $J_{H\text{-}H}$ = 7.4 Hz, 3H). ^{13}C NMR: δ 151.6 (d, $J_{C\text{-}P}$ = 204.6 Hz), 121.0 (d, $J_{C\text{-}P}$ = 7.2 Hz), 78.7, 33.3 (d, $J_{C\text{-}P}$ = 11.4 Hz), 32.2, 29.6, 28.6 (d, $J_{C\text{-}P}$ = 8.3 Hz), 24.9 (d, $J_{C\text{-}P}$ = 4.1 Hz), 24.2 (d, $J_{C\text{-}P}$ = 6.2 Hz), 23.1 (d, $J_{C\text{-}P}$ = 1.0 Hz), 14.5. ^{31}P NMR: δ -31.6. This compound is known: L.-B. Han, Y. Ono, Q. Xu, S. Shimada, *Bull. Chem. Soc. Jpn. in press*.



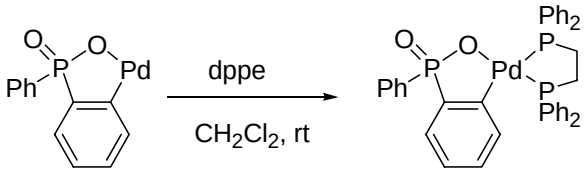
This compound is known: Ishiyama, T.; Nishijima, K.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 7219.



This compound is known: (a) Trost, B. M.; Chan, C.; Ruhter, G. *J. Am. Chem. Soc.* **1987**, *109*, 3486. (b) Trost, B. M.; Sorum, M.T.; Chan, C.; Harms, A. E.; Ruhter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698.

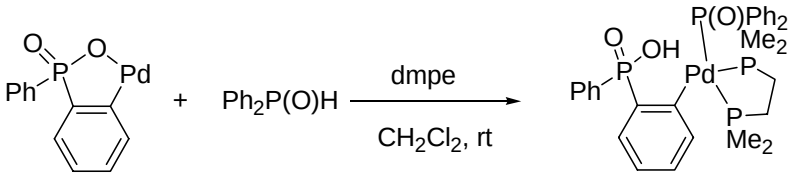


This compound is known: (a) Straub, T.; Haskel, A.; Eisen, M. *J. Am. Chem. Soc.* **1995**, *117*, 6364. (b) Haskel, A.; Straub, T.; Dash, A. K.; Eisen M. S. *J. Am. Chem. Soc.* **1999**, *121*, 3014.



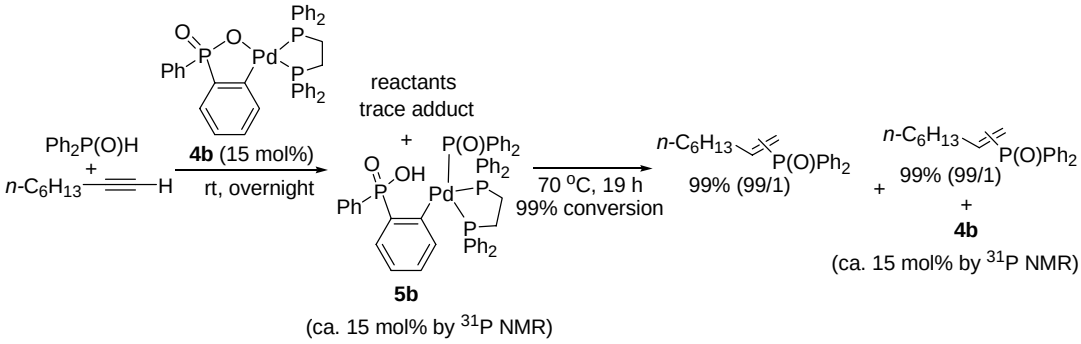
3 **4b**

Preparation of Complex 4b. The mixture of **3** (64.6 mg, 0.2 mmol) and dppe (80.0 mg, 0.2 mmol) in 4 mL CH_2Cl_2 was stirred at room temperature under nitrogen till **3** totally dissolved. Standing of the solution filtrate after adding drops of hexane at room temperature gave a white solid, which was collected and washed with CH_2Cl_2 and hexane. Dec. 168 °C. ^{1}H NMR (CD_2Cl_2): δ 7.99-7.58 (m, 9H), 7.56-6.99 (m, 17H), 6.87-6.84 (m, 1H), 6.61-6.54 (m, 2H), 2.62-2.37 (m, 2H), 2.34-2.21 (m, 1H), 2.16-2.02 (m, 1H). ^{31}P NMR (CD_2Cl_2): δ 61.3 (dd, $J_{P\text{-}P}$ = 29.4 Hz, $J_{P\text{-}P}$ = 7.4 Hz, 1P), 47.2 (dd, $J_{P\text{-}P}$ = 33.1 Hz, $J_{P\text{-}P}$ = 7.4 Hz, 1P), 38.2 (dd, $J_{P\text{-}P}$ = 33.1 Hz, $J_{P\text{-}P}$ = 29.4 Hz, 1P).



3 **5a**

Preparation of Complex 5a. The mixture of **3** (0.162 g, 0.5 mmol), dmpe (84 μL, 0.5 mmol) and $Ph_2P(O)H$ (0.101g, 0.5 mmol) in 5 mL CH_2Cl_2 was stirred at room temperature under nitrogen till **3** totally dissolved. Standing of the solution filtrate after adding drops of hexane at room temperature gave colorless crystals, which were collected and washed with CH_2Cl_2 and hexane. ^{31}P NMR (CD_2Cl_2): δ 71.9 (ddd, $J_{P\text{-}P}$ = 447.0 Hz, $J_{P\text{-}P}$ = 34.4 Hz, $J_{P\text{-}P}$ = 7.6 Hz, 1P), 32.1 (dd, $J_{P\text{-}P}$ = 447.0 Hz, $J_{P\text{-}P}$ = 26.8 Hz, 1P), 23.5 (dd, $J_{P\text{-}P}$ = 9.6 Hz, $J_{P\text{-}P}$ = 11.5 Hz, 1P), 20.3 (ddd, $J_{P\text{-}P}$ = 36.3 Hz, $J_{P\text{-}P}$ = 26.7 Hz, $J_{P\text{-}P}$ = 11.5 Hz, 1P).



Monitoring ^{31}P NMR Spectra of 4b-Catalyzed Addition of $Ph_2P(O)H$ to 1-Octyne. **4b** (11 mg, 0.015 mmol, 15 mol%; Chart 1) was added to a mixture of $Ph_2P(O)H$ (20.2 mg, 0.1 mmol) and 1-octyne (16 µL, 0.11 mmol) dissolved in CD_2Cl_2 (0.5 mL) in a NMR tube. After 2 h, ^{31}P NMR showed the complete conversion of **4b** to **5b** (ca. 15 mol%; Chart 2). The solvent was changed to d_8-toluene, and the tube was heated at 70 °C overnight (19 h). ^{31}P NMR showed that all starting $Ph_2P(O)H$ and **5b** were completely disappeared, and 99% yield of the adducts (branched/linear ratio = 99/1) together with **4b** (ca.15 mol%) were obtained (Chart 3).

Chart 1. ^{31}P NMR of **4b**.

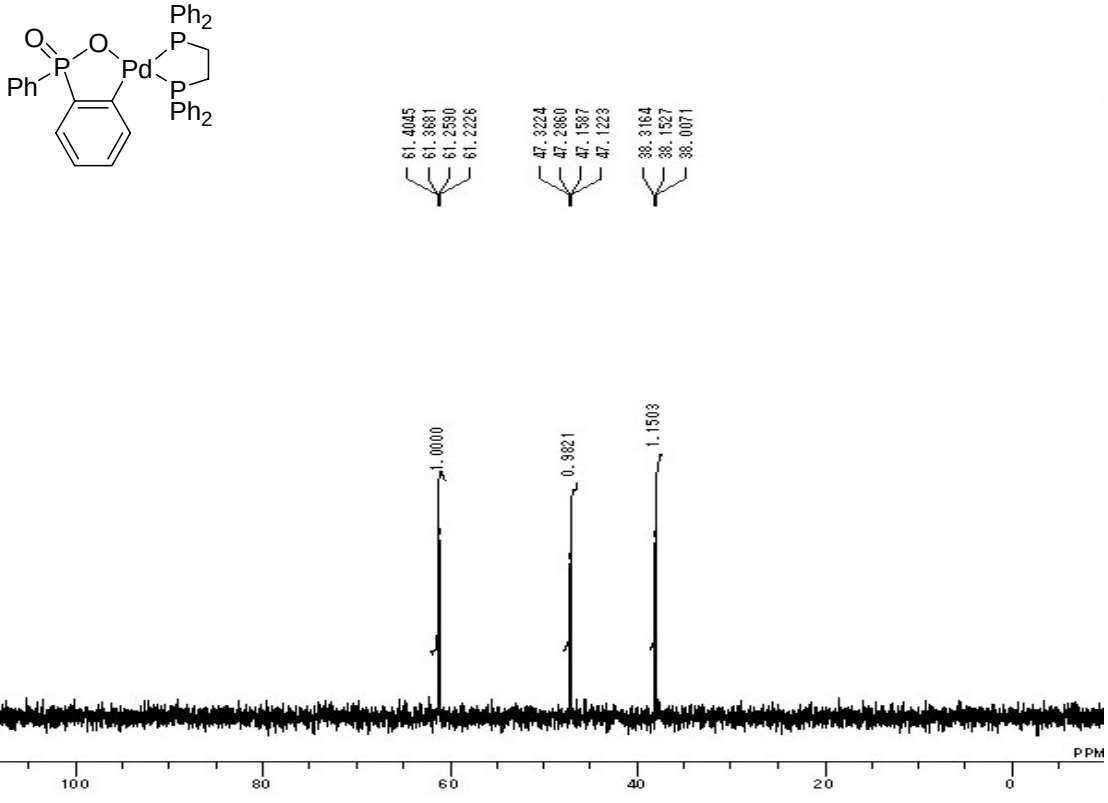


Chart 2. After 2 h at room temperature of a mixture of **4b** with $Ph_2P(O)H$ and 1-octyne: **4b** totally converted to **5b** (ca. 15 mol%); trace adduct (29.97 ppm) was also observed.

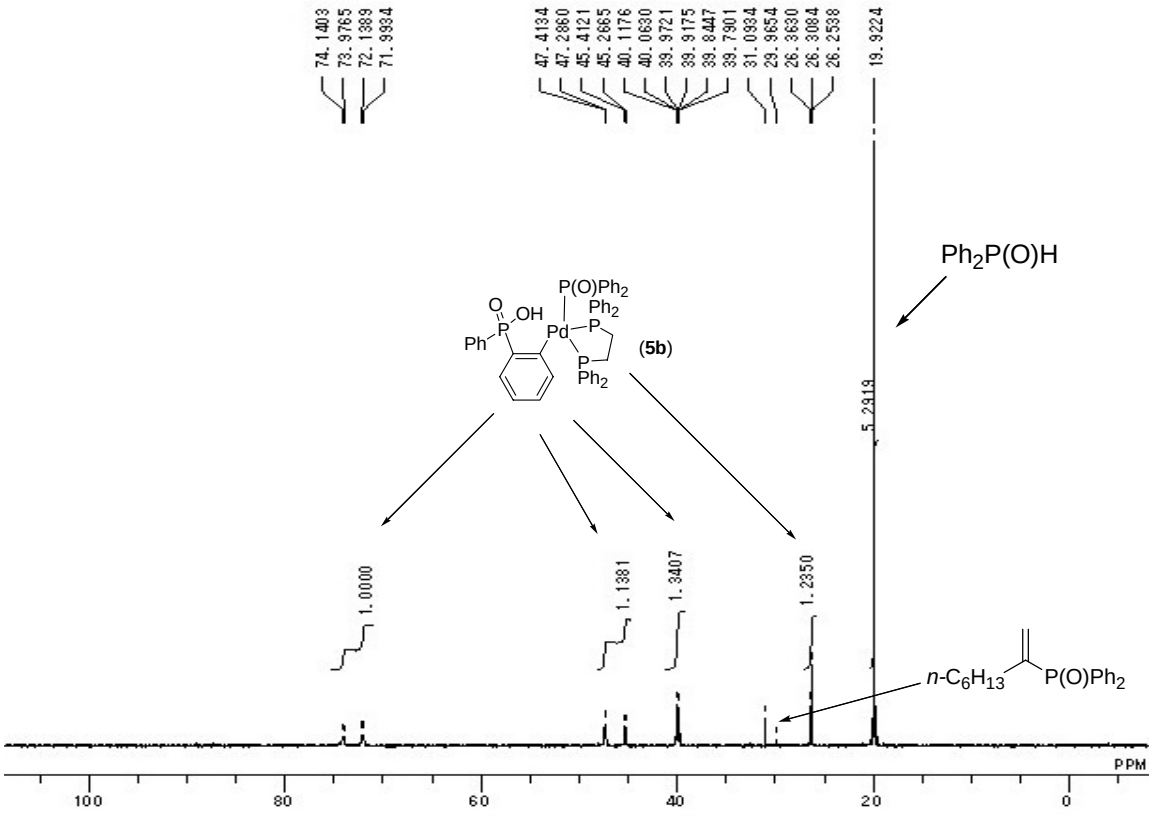
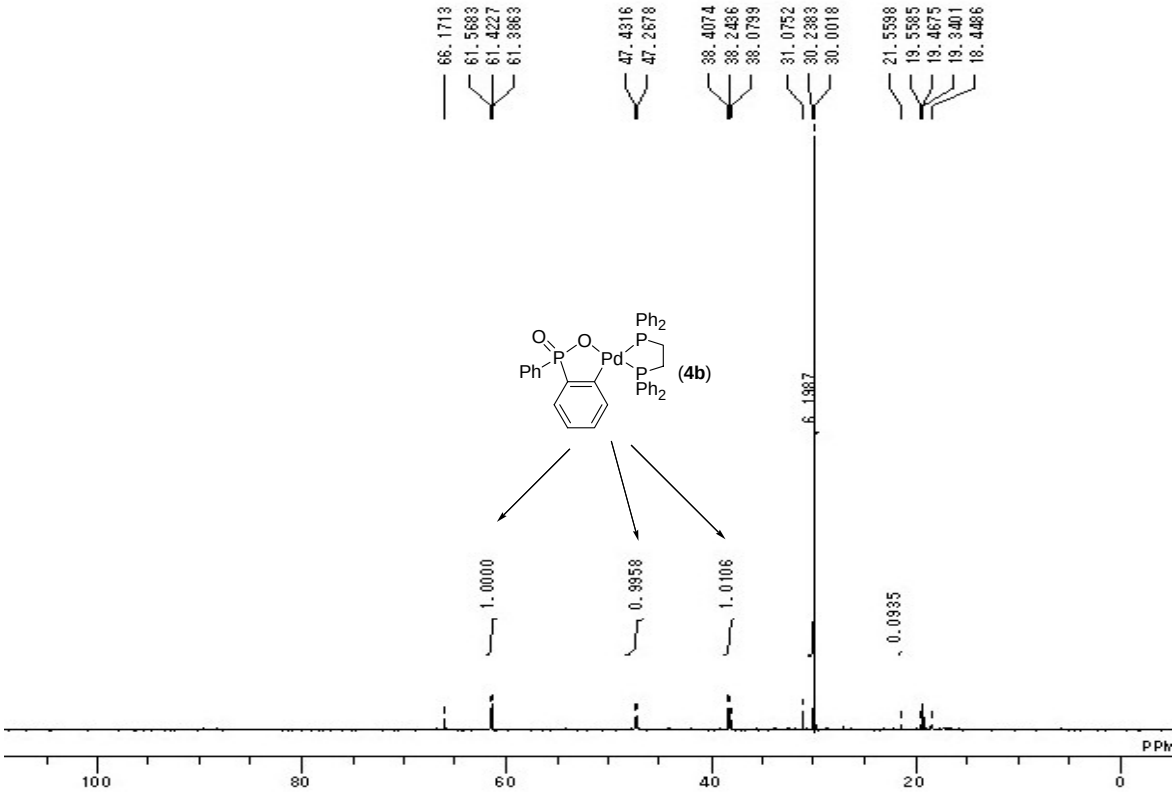
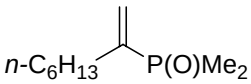


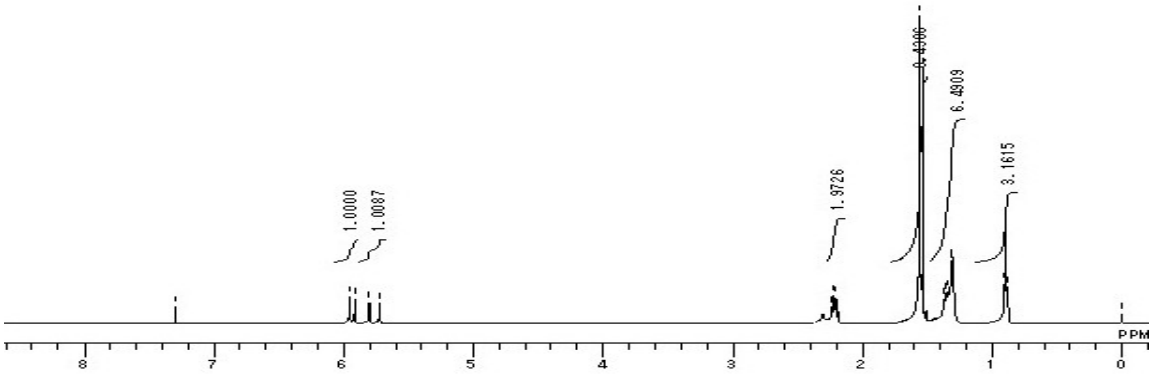
Chart 3. Heating at 70 ^{o}C for 19 h: $Ph_2P(O)H$ and **5b** completely disappeared to give the adducts (branched/linear 99/1), while **4b** was regenerated (cat. 15 mol%).

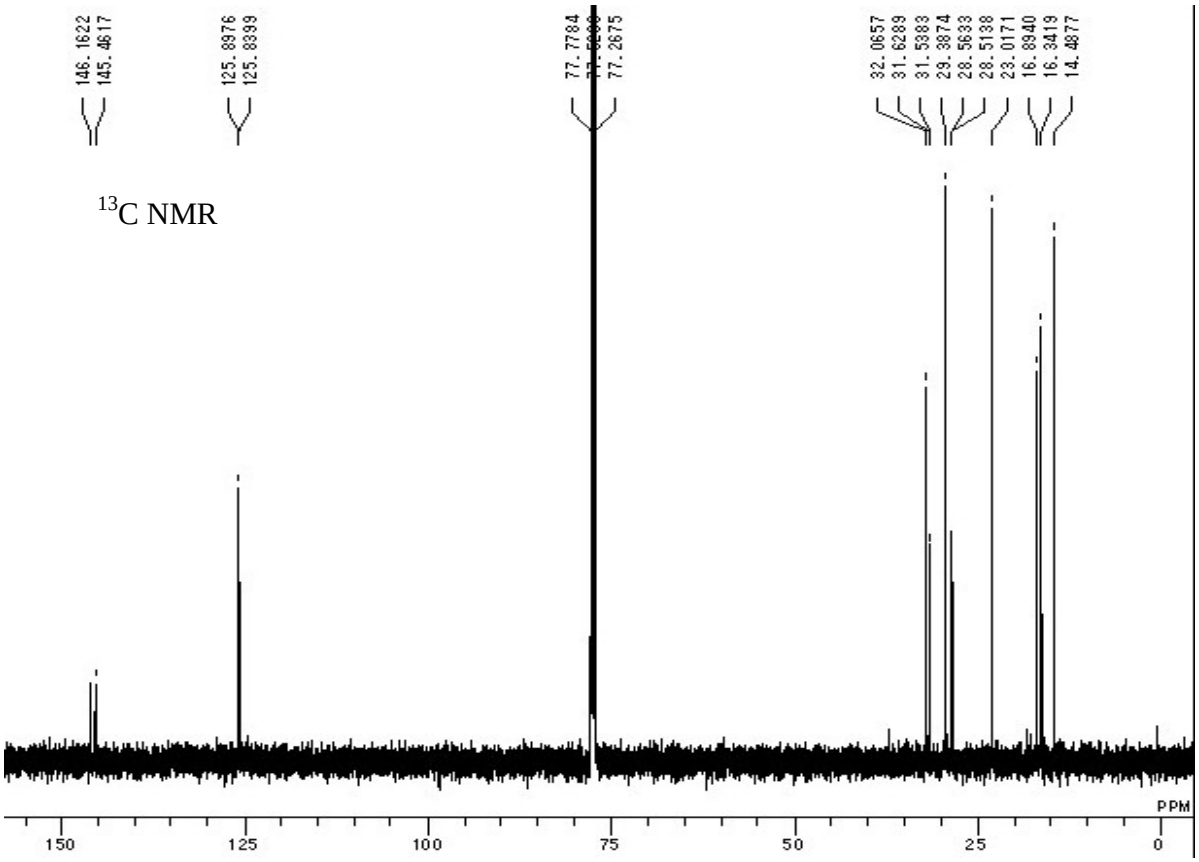


^{1}H NMR and ^{13}C NMR Spectra of New Compounds

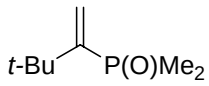


^{1}H NMR

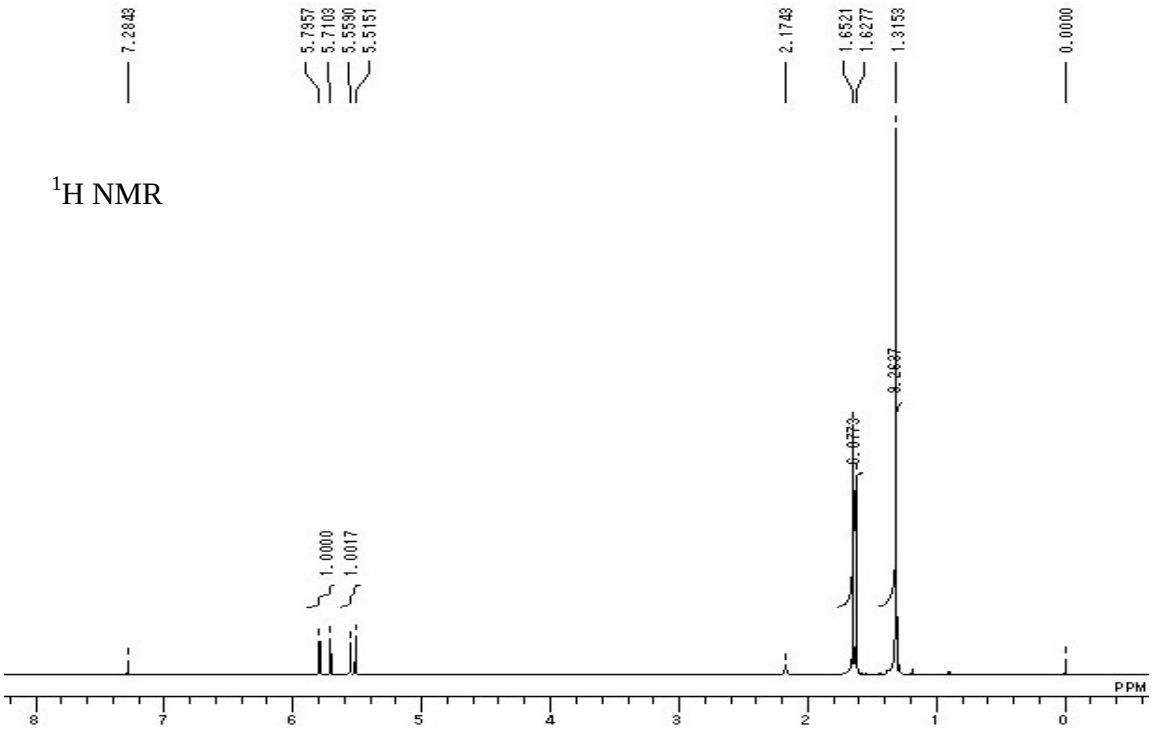




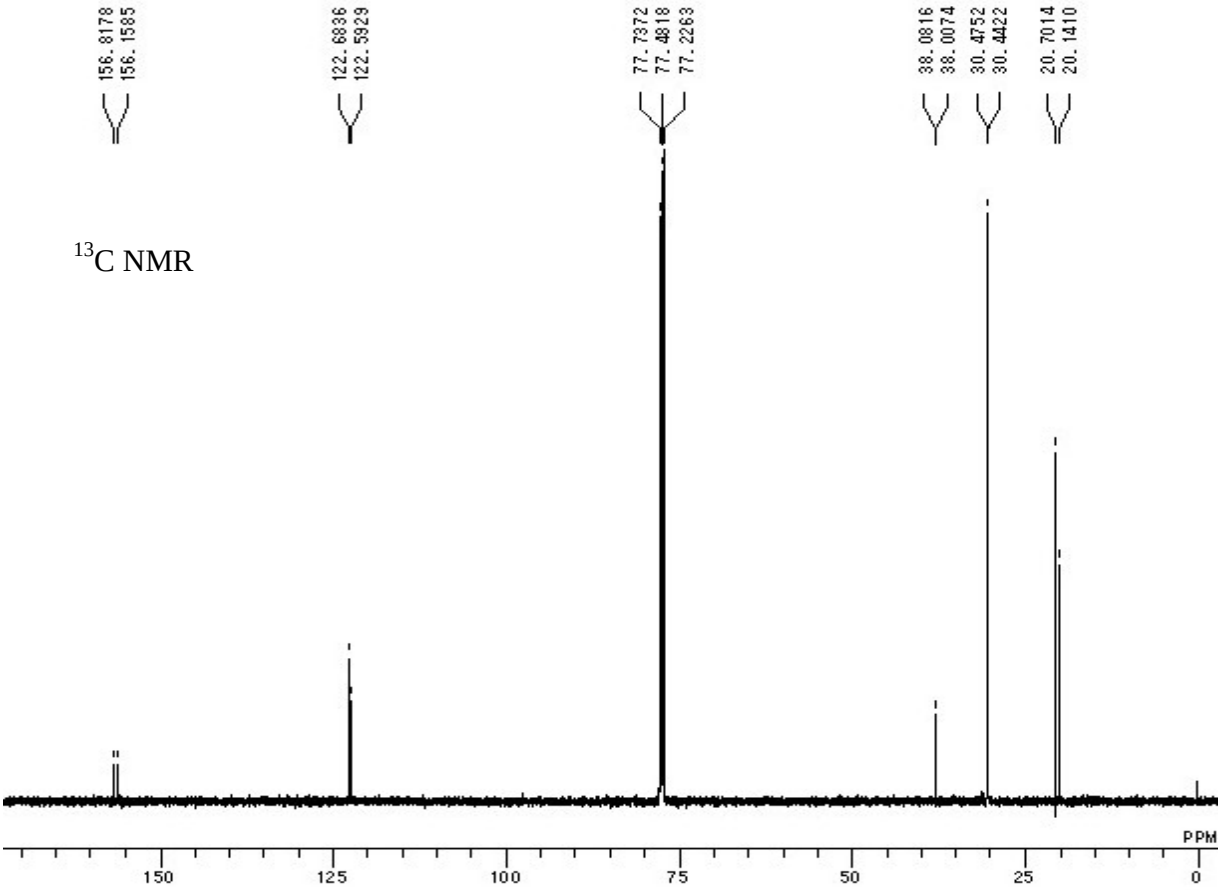
^{13}C NMR

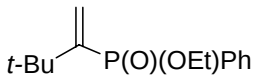


^{1}H NMR

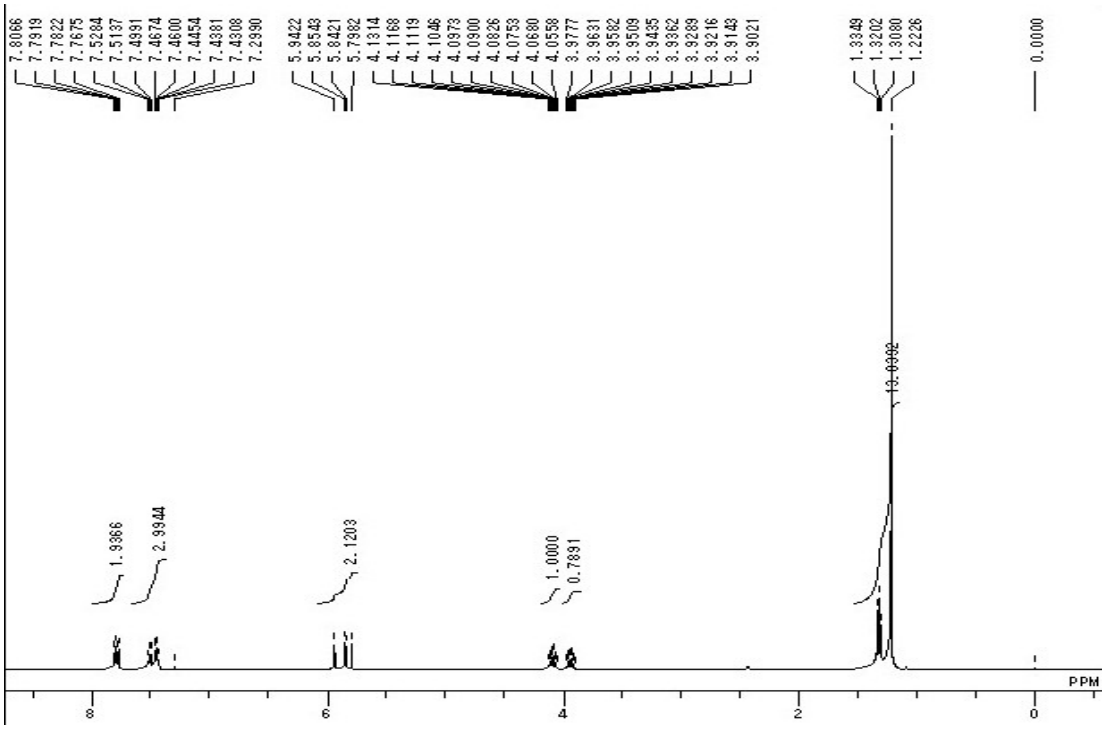


^{13}C NMR





^{1}H NMR



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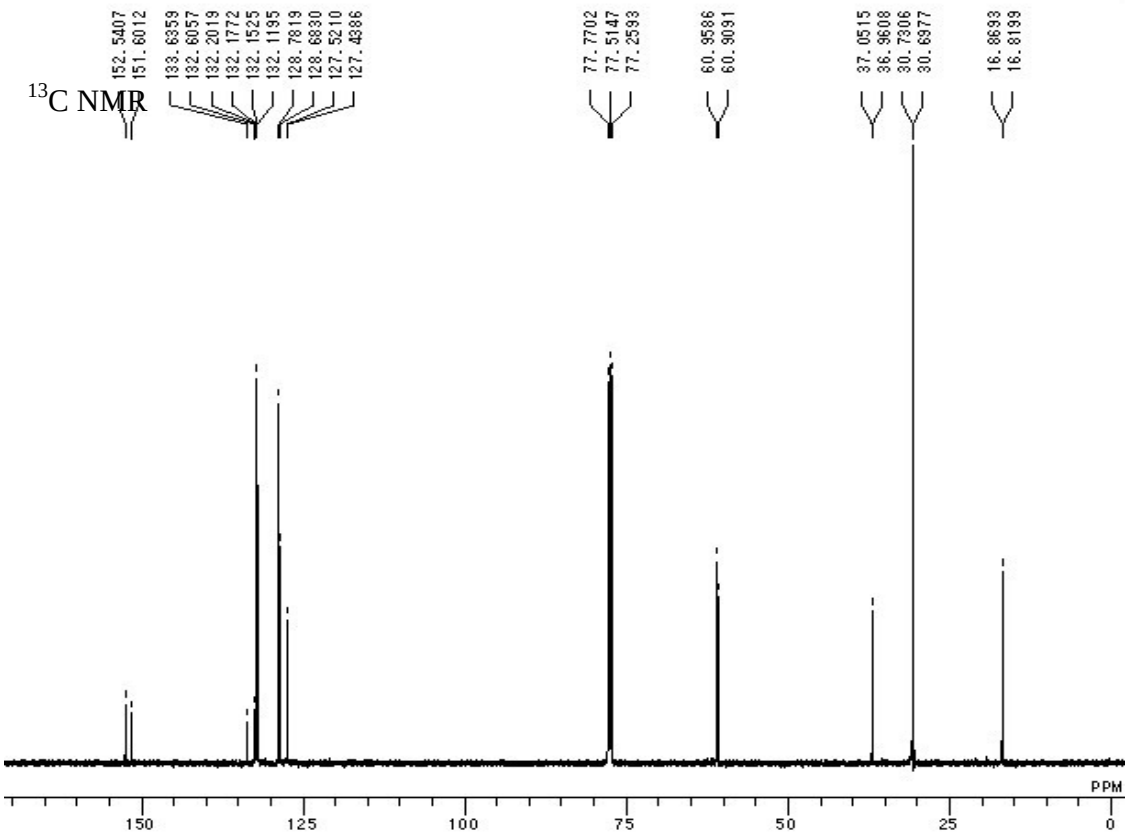

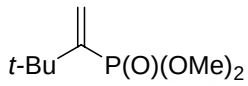

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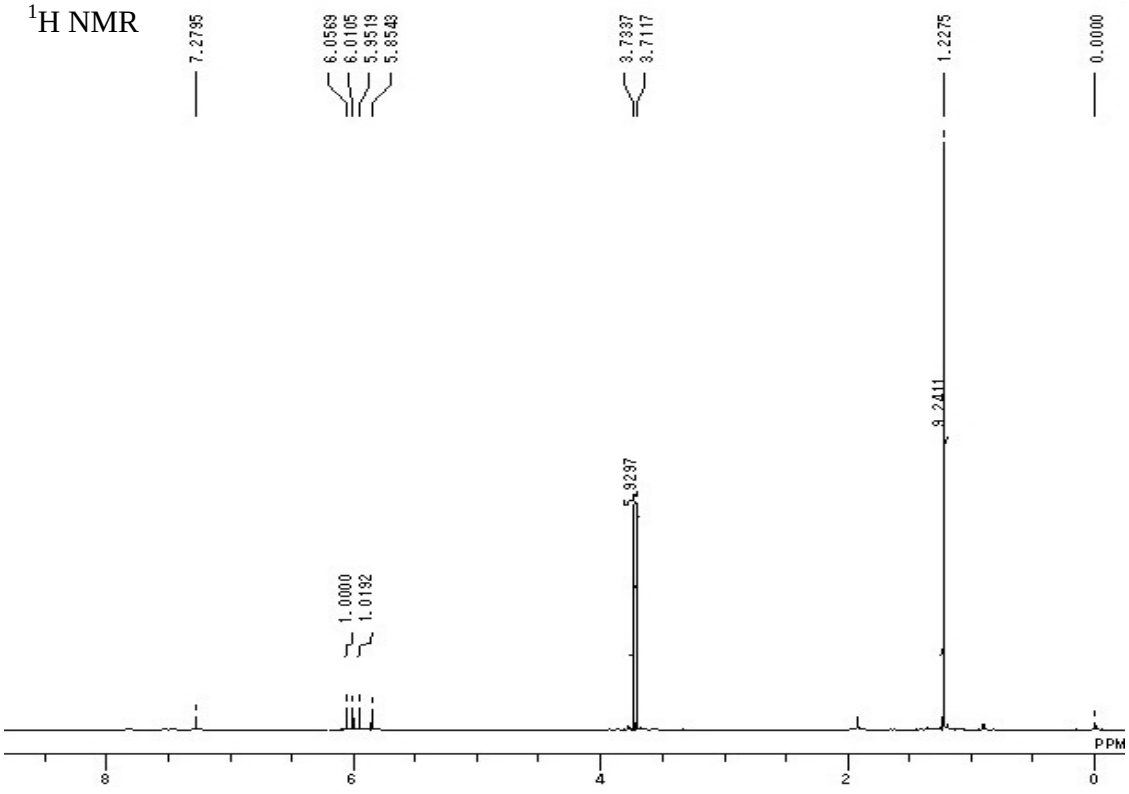

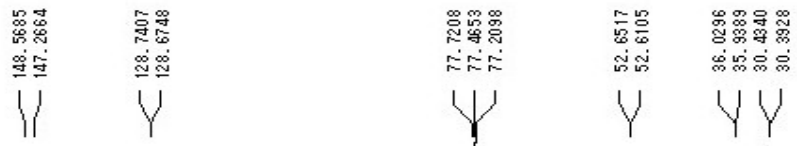

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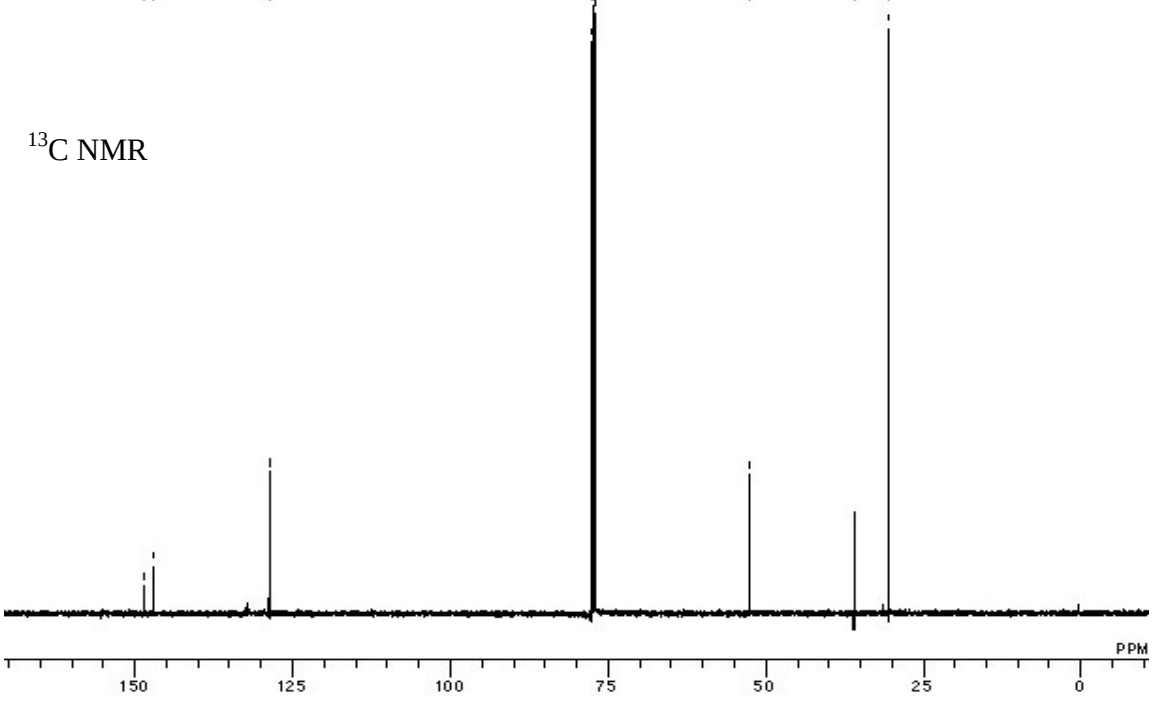

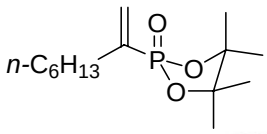

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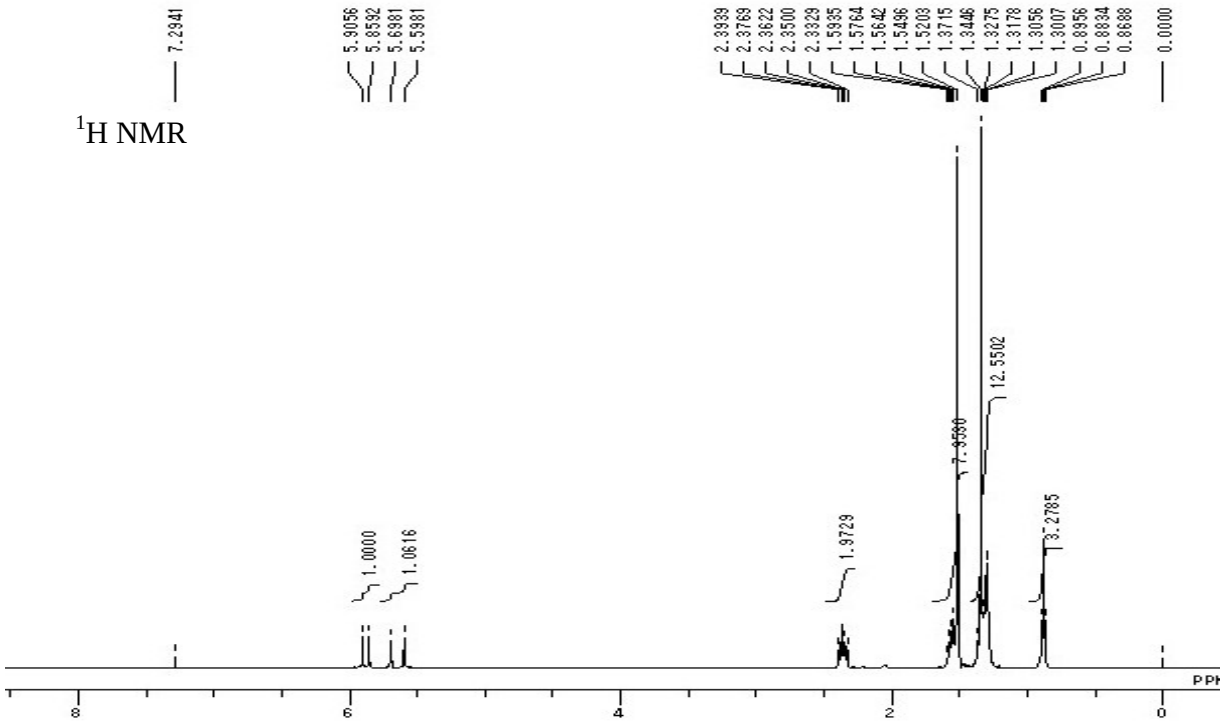

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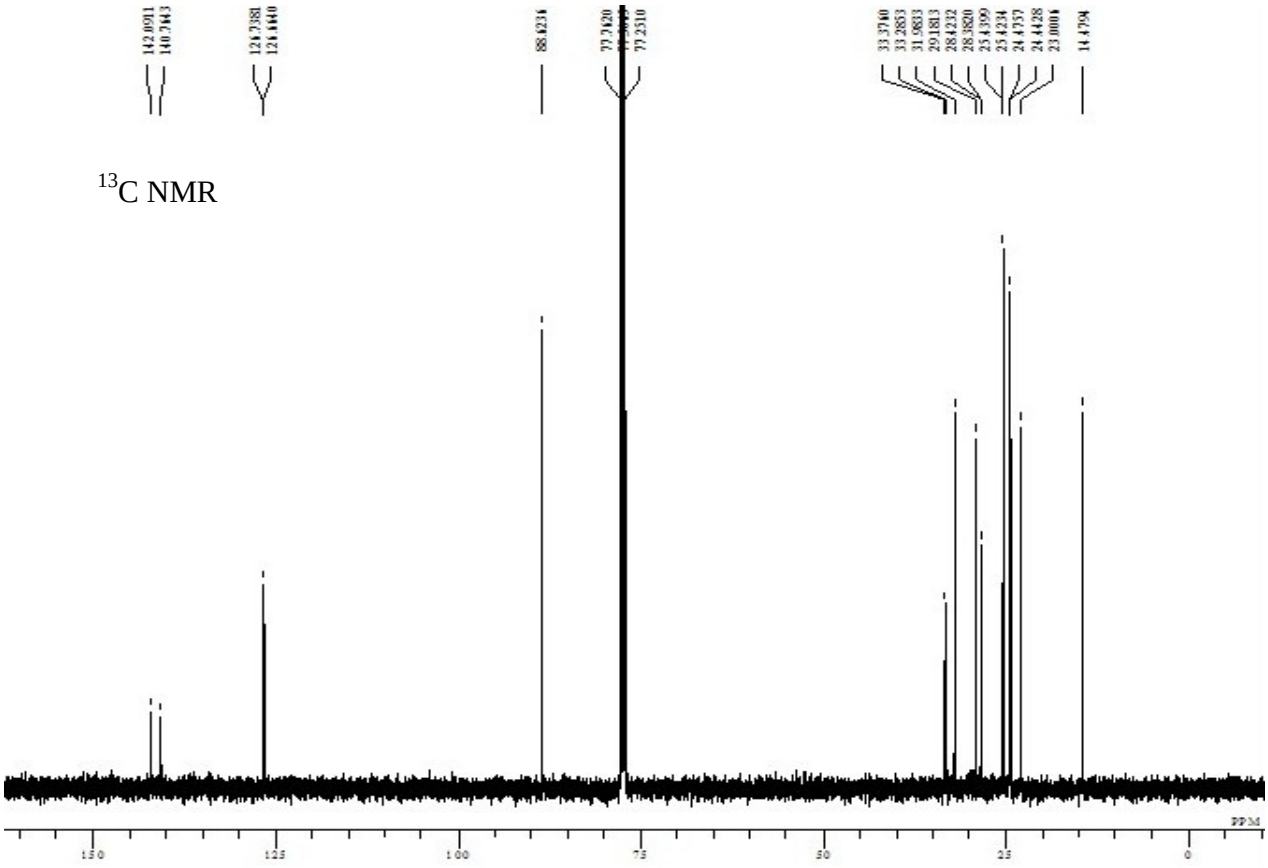
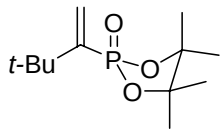
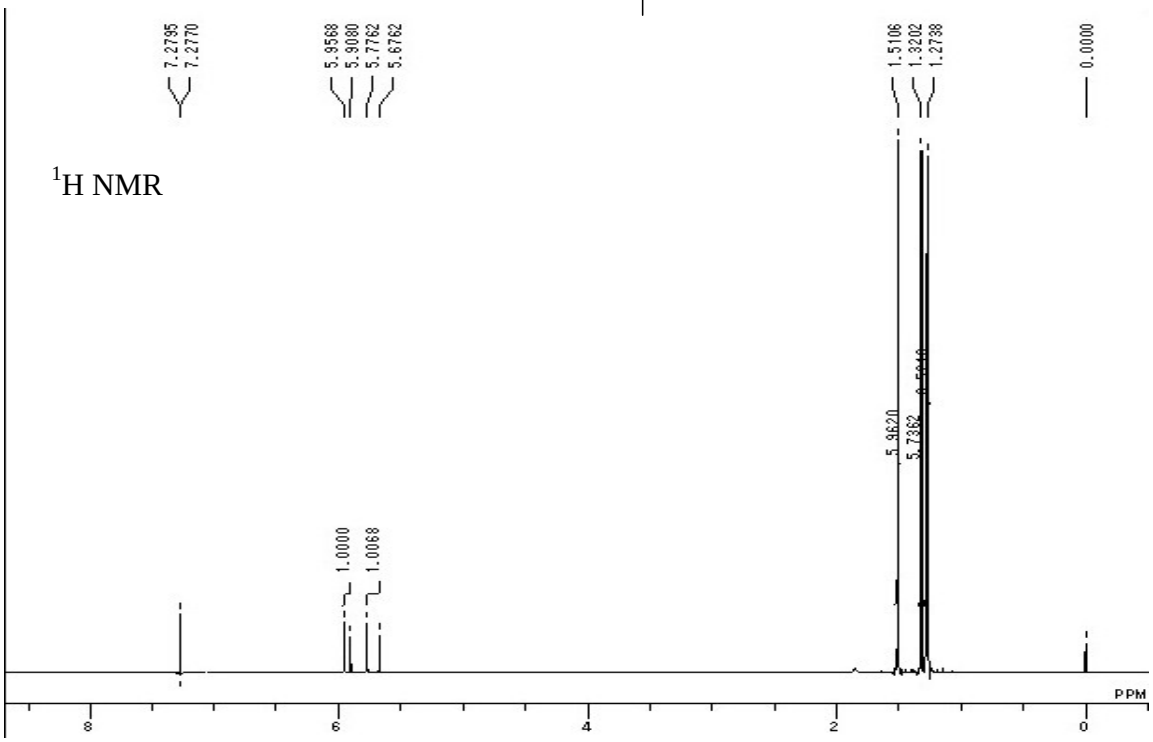
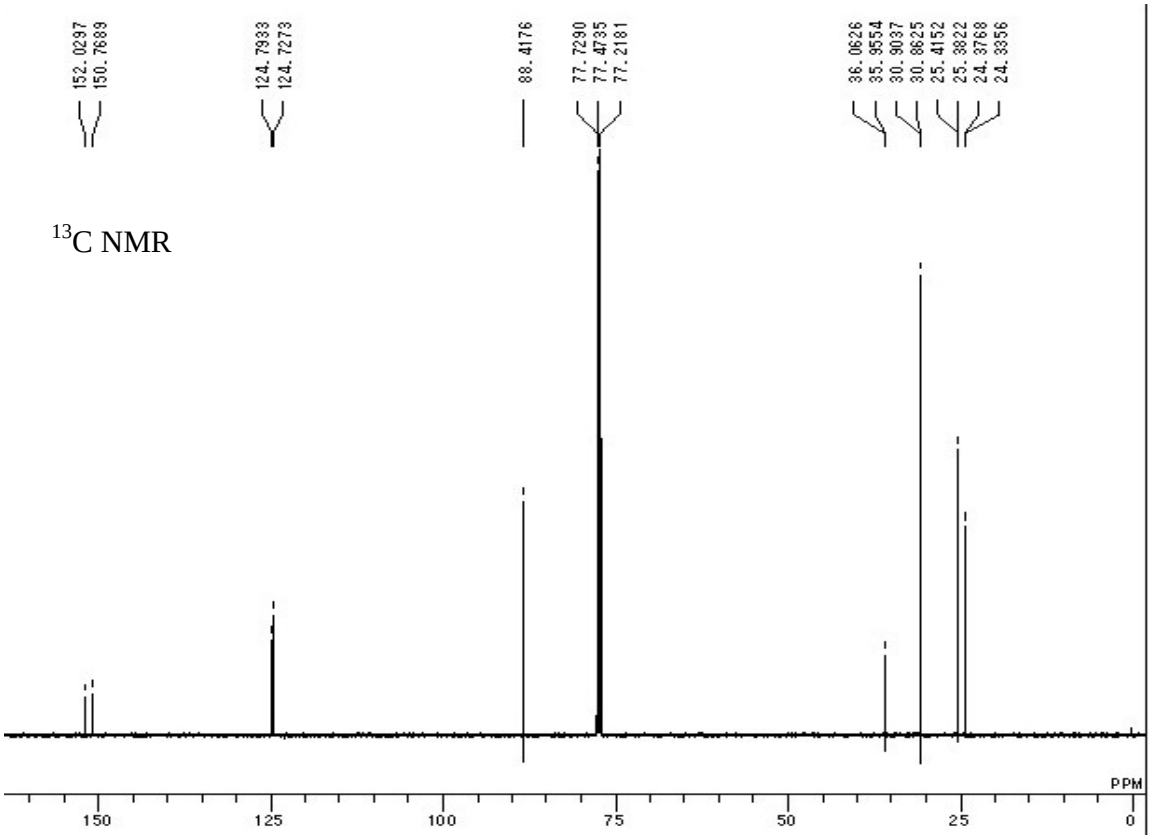


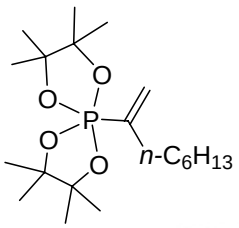


^{1}H NMR

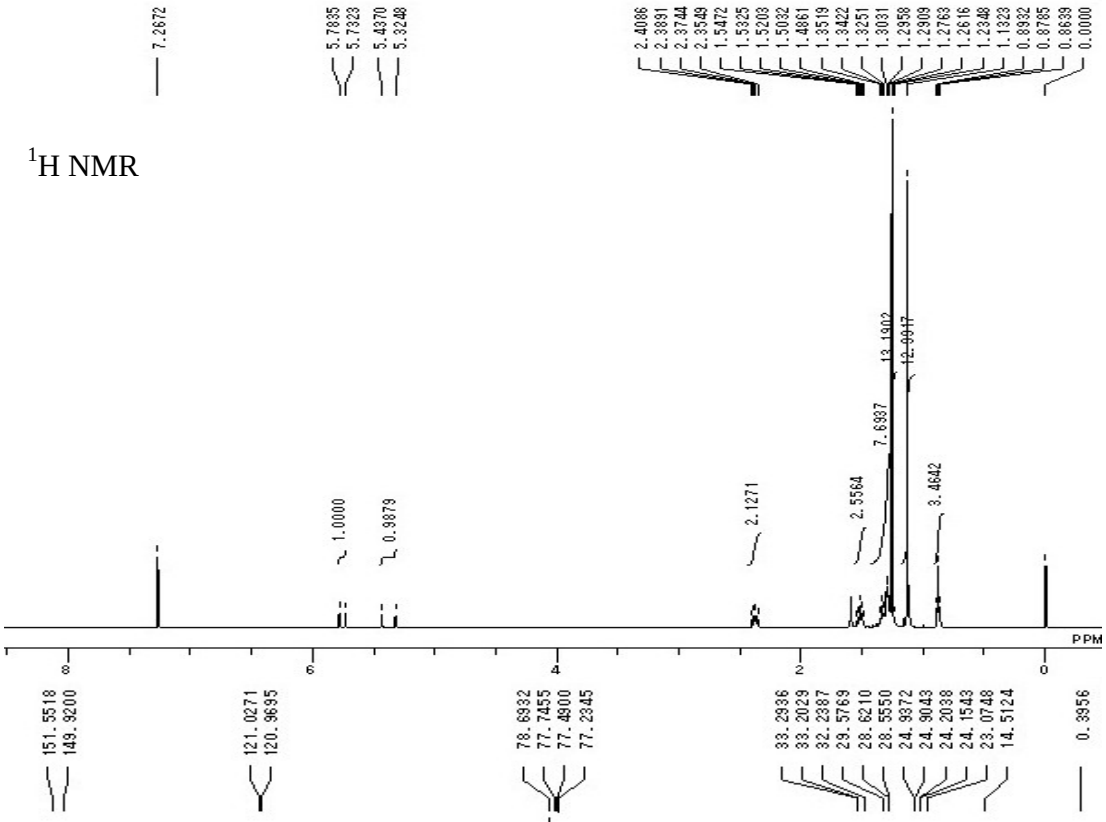


^{13}C NMR

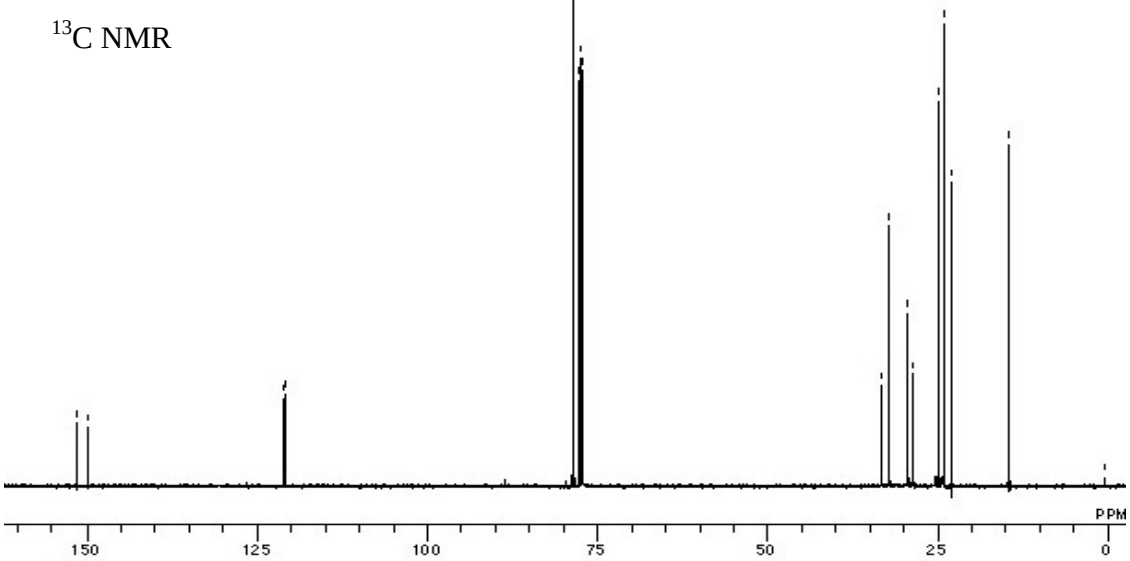




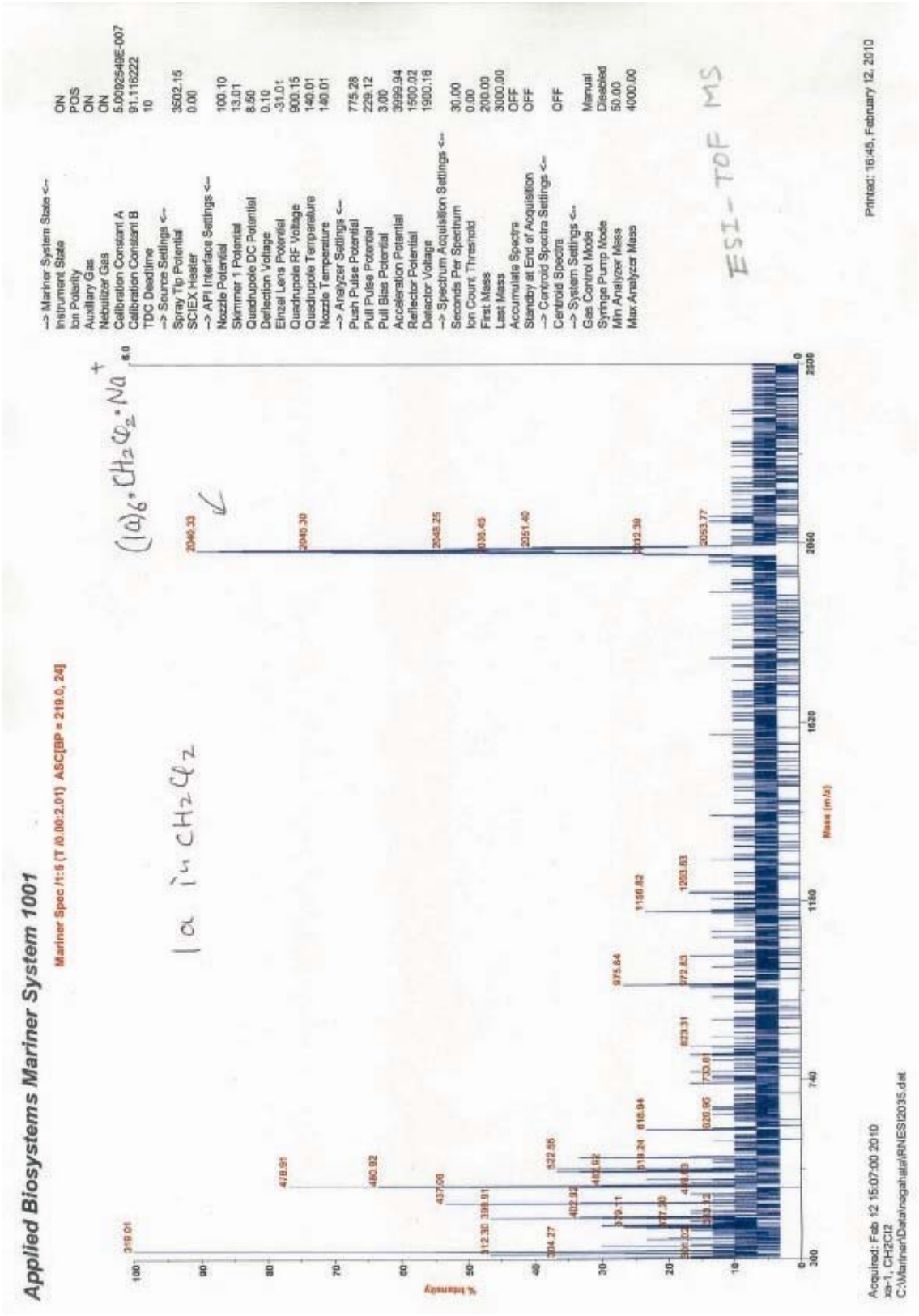
^{1}H NMR



^{13}C NMR



ESI-TOF MS of **3** in CH_2Cl_2



ESI-TOF MS of **3** (with 1% DMSO) in $CHCl_3$