# Activation of water molecule under mild conditions by ruthenacyclopentatriene: Mechanism of hydrative cyclization of diynes

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## Supplementary Information

**General Considerations:** Column chromatography was performed on silica gel (Cica silica gel 60N) or neutral alumina (Merck Aluminum oxide 90 standardized) with mixed solvents. $^{1}$H and $^{13}$C NMR spectra were obtained for samples in $CDCl_3$ solutions at 25 ˚C. $^{1}$H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the singlet at 7.26 ppm for chloroform. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet. Coupling constants are reported in Hz. $^{13}$C NMR spectra were fully decoupled and are reported in terms of chemical shift (δ, ppm) relative to the triplet at 77.0 ppm for $CDCl_3$. Melting points were obtained in capillary tubes. [Cp*RuCl(cod)] (**1**),[1] and ruthenacyclopentatriene **3**[2] were prepared according to the reports. Diyne **2**,[3] ketone **5**,[4] and [Cp*RuCl(dppe)] (**7**)[4] were known compounds. Diphenylphosphinoethane, all silver salts, and solvents were purchaced and used as received.

**Genral procedure for Reaction of Ruthenacycle 3 with $H_2O$.**

**(a) Reaction in the absence of additives:** To a vigorously stirred solution of **3** (25.8 mg, 0.0498 mmol) in degassed THF (1.5 mL) was added degassed $H_2O$ (1.0 mL) under argon atmosphere. The mixture was stirred at 25 ˚C for 4 h. The solution was diluted with 20 mL of THF, dried over $K_2CO_3$, and filtrated. The residue was washed with THF and $CHCl_3$ (10 mL each). The combined filtrate was concentrated *in vacuo* to give a mixture of **3**, $\eta^5$-oxapentadiene complex **4**, ketone **5**, and furan **6**. Crude yields were determined as unreacted **3** (0.00782 mmol, 16%), **4** (0.0268 mmol,

54%), **5** (0.00233 mmol, 5%), and **6** (0.00137 mmol, 3%) by $^1$H NMR analysis with ethylbenzene (5.0 μL, 0.0410 mmol) as internal standard.

**(b) Reaction in the presence of a silver salt:** To a vigorously stirred solution of $AgNO_3$ (9.35 mg, 0.0550 mmol) in degassed $H_2O$ (1.0 mL) was added a solution of **3** (25.9 mg, 0.0500 mmol) in degassed THF (1.5 mL) under Ar atmosphere. The reaction mixture was stirred for 1 h at 25 ˚C. After diluted with THF (20 mL), the solution was dried over $K_2CO_3$, and filtrated. The residue was washed with THF and $CHCl_3$ (10 mL each). The combined organic layer was concentrated *in vacuo* to give a mixture of **4** (0.00371 mmol, 7%) and furan **6** ( 0.0261 mmol, 52%) as analyzed by $^1$H NMR analysis with ethylbenzene (5.0 mL, 0.0410 mmol) as internal standard. The crude mixture was purified with silica gel column chromatography (elution with hexane/$CH_2Cl_2$ 1:1 ~ 1:2) to give **6** (6.20 mg, 0.0236 mmol, 47 %) as colorless crystals (mp. 167.5–169.5 ˚C): $^1$H NMR (300 MHz, $CDCl_3$) δ 5.08 (s, 4 H), 7.26 (tt, *J* = 1.2, 7.4 Hz, 2 H), 7.38–7.44 (m, 4 H), 7.49–7.53 (m, 4 H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 66.5, 123.6, 126.8, 128.3, 128.7, 130.1, 141.3; HRMS (FAB) *m/z* calcd for $C_{18}H_{14}O_2$ 262.0994, found 262.0994 $[M]^+$.

**(c) Reaction in the presence of neutral alumina:** To a solution of **3** (25.9 mg, 0.0500 mmol) in degassed THF (1.5 mL) was added degassed water (1.0 mL) and $Al_2O_3$ (64.8 mg, 636 mmol). The reaction mixture was flushed with argon. The mixture was stirred at 25 °C for 4 h. Then the mixture was diluted with THF (20 mL), dried over $K_2CO_3$, and filtrated. The residue was washed with THF and $CHCl_3$ (10 mL each). The combined solution was concentrated in vacuo. The crude mixture was purified with alumina column chromatography. The yellow band eluted with a mixed solvent (hexane/$CHCl_3$ 1:1 ~ 0:1) was concentrated in vacuo to give **4** (18.1 mg, 73%) as orange micro crystals (mp 228.0–229.5 ˚C): $^1$H NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 15 H), 3.93 (s, 1 H), 4.57 (d, *J* = 11.1 Hz, 1 H), 4.90 (d, *J* = 10.2 Hz, 1 H), 5.01 (d, *J* = 11.1 Hz, 1 H), 5.32 (d, 10.2 Hz, 1 H), 7.16–7.22 (m, 1 H), 7.27–7.47(m, 7 H), 7.56–7.61 (m, 2 H); 13C NMR (75 MHz, CDCl3) δ

9.2, 69.4, 71.5, 72.7, 87.6, 91.4, 103.9, 124.3, 125.3, 127.1, 127.7, 128.1, 128.3, 128.6, 138.1, 141.7; HRMS (FAB) *m*/*z* calcd for $C_{28}H_{30}O_2Ru$ 500.1289, found 500.1300 $[M]^+$.

**Acid-promoted Decomposition of $\eta^4$-Oxapentadienyl Complex 4 with Diphenylphosphinoethane:** To a solution of **4** (24.9 mg, 0.0498 mmol) and diphenylphosphinoethane (20.9 mg, 0.0523 mmol) in degassed THF (10 mL) was added aqueous HCl (0.025 M, 2.0 mL, 0.050 mmol). The mixture was cooled to –78 ˚C, degassed, and backfilled with argon. This step was repeated twice. The solution was stirred at 70 ˚C for 12 h. After cooled to room temperature, the mixture was evaporated under reduced pressure to give a mixture of unreacted **4** (0.00680 mmol, 14%), ketone **5** (0.0421 mmol, 85%), and [Cp*RuCl(dppe)] (**7**) (0.0430 mmol, 86%) as analyzed by $^1$H NMR with *p*-xylene (10.0 μL, 0.0810 mmol) as an internal standard. The following spectral data of **7** were in good agreement with those of an authentic sample prepared according to the report:[5] $^1$H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 15 H), 2.05–2.20 (m, 2 H), 2.57–2.78 (m, 2 H), aromatic protons were obscure because of overlapping with those of **4**, **5**, and excess dppe. Spectral data for the authentic sample: $^1$H NMR (300 MHz, $CDCl_3$) δ 1.46 (s, 15 H), 2.05–2.30 (m, 2 H), 2.50–2.90 (m, 2 H), 7.14–7.74 (m, 20 H).

**Catalytic Hydrative Cyclization of Diyne 2.**

**(a) With Cp*RuCl(cod) (1)**: To a solution of **2** (73.8 mg, 0.300 mmol) and **1** (5.74 mg, 0.0151 mmol) in degassed THF (3.0 mL) was added degassed $H_2O$ (0.6 mL) under Ar atmosphere. The mixture was stirred at 70 ˚C for 24 h. After cooled to room temperature, the mixture was diluted with AcOEt (20 mL), dried over $MgSO_4$, and filtered. The residue was washed with AcOEt (10 mL), and combined filtrate was concentrated under reduced pressure. The crude product was purified with silica gel column chromatography (elution with hexane/EtOAc 17:1) to give recovered **2** (5.67 mg, 0.023 mmol, 8%). Further elution (hexane/EtOAc 15:1 ~ 13:1) afforded **5**

(50.9 mg, 0.193 mmol, 62 %) as colorless oil. Following spectral data are in good accordance with those previously reported:[4] $^{1}$H NMR (300 MHz, $CDCl_3$) δ 3.52 (s, 2 H), 4.68 (t, $J$ = 4.8 Hz, 2 H), 5.01–5.05 (m, 2 H), 7.07–7.10 (m, 2 H), 7.16–7.29 (m, 3 H), 7.45–7.51 (m, 2 H), 7.55–7.62 (m, 1 H), 7.81–7.85 (m, 2 H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 33.3, 77.7, 78.6, 126.5, 128.3, 128.45, 128.49, 132.8, 132.9, 136.8, 138.1, 146.4, 192.8; IR (KBr): 1644 $cm^{-1}$ (C=O); HRMS (FAB) *m/z* calcd for $C_{18}H_{17}O_2$ 265.1229, found 165.1221 $[M+H]^+$.

**(b) With $\eta^4$-oxapentadienyl complex 4:** To a solution of **2** (73.9 mg, 0.300 mmol) and **4** (7.48 mg, 0.0150 mmol) in degassed THF (3.0 mL) was added aqueous HCl (0.025 M, 0.6 mL, 0.0150 mmol) under Ar atmosphere. The mixture was stirred at 70 ˚C for 24 h. After cooled to room temperature, the solvent was removed under reduced pressure. The crude product was purified with silica gel column chromatography (elution with $CHCl_3$/hexane 3:1 then 1:0) to afford **5** (73.3 mg, 0.278 mmol, 88% based on **2** + **5**).

**Crystallographic Structural Determinations:** A single crystal suitable for X-ray analysis was mounted on a glass fiber, and diffraction data were collected at 153 K on a Brucker SMART APEX CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The absorption correction was made using SADABS. The structure was solved by direct methods and refined by the full-matrix least-squares on $F^2$ by using SHELXTL.[6] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. CCDC 766961 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

**Table S1**. Selected crystallographic data and collection parameters for **4**.

| | **4** |
|---|---|
| Formula | $C_{28}H_{30}O_2Ru$ |
| Fw | 499.59 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ (#14) |
| *a* [Å] | 8.2716(8) |
| *b* [Å] | 23.868(2) |
| *c* [Å] | 11.4379(11) |
| $\alpha$ [°] | |
| $\beta$ [°] | 93.401(2) |
| $\gamma$ [°] | |
| V [Å$^3$] | 2254.1(4) |
| *Z* | 4 |
| $D_{calc}$ [g cm$^{-3}$] | 1.472 |
| μ [mm$^{-1}$] | 0.718 |
| *F*(000) | 1032 |
| Crystal size [mm$^3$] | 0.5 × 0.3 × 0.3 |
| Reflections collected | 16230 |
| Independent reflections | 5576 ($R_{int}$ = 0.0312) |
| GOF on $F^2$ | 1.106 |
| $R_1$ [$I$>2σ($I$)][a] | 0.0554 |
| $wR_2$ (all data)[b] | 0.1514 |
| Largest diff. peak and hole [e Å$^{-3}$] | 5.061 / –1.023 |

[a] $R_1 = \Sigma||(F_o-F_c)|/\Sigma(F_o)$. [b] $wR_2 = \{\Sigma[(w(F_o^2-F_c^2)^2)]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

**Theoretical Calculations:** The Gaussian 03 program package was used for all geometry optimizations.[7] The geometries of stationary points **A–H** and transition states **TS-BC–TS-GH** were fully optimized by means of the Becke's three-parameter hybrid density functional method (B3LYP)[8] with the basis set, consisting of a double-ζ basis set with the relativistic effective core potential of Hay and Wadt (LanL2DZ)[9] for Ru and the 6-31G(d)[10] basis sets for other elements (BS-I). The vibrational frequencies and zero-point energy (ZPE) were calculated at the same level of theory. The obtained structures were characterized by the number of imaginary frequencies (one or zero for transition or ground states, respectively). The connectivity of each step was further confirmed by IRC calculation[11] from **TS-BC–TS-GH** followed by optimization of the resulted geometries. Single-point energies for geometries obtained by the above method were calculated at the same level using the basis sets consisting of a [6*s*5*p*3*d*2*f*1*g*] contracted valence basis set with the Stuttgart-Dresden-Bonn energy-consistent pseudopotential (SDD)[12,13] for Ru and the 6-311++G(2d,p) basis sets[14] for other elements (BS-II). Relative energies were corrected with unscaled ZPE obtained at the B3LYP/BS-I level.

**Table S2. Summary of Theoretical Calculations**

| Model | Energy/au | ZPE/kcal mol$^{-1}$ (IF/cm$^{-1}$) |
|---|---|---|
| **s1** | –519.57026878 | 0.173944 |
| **sTS** | –519.52150090 | 0.169190 (1267.24i) |
| **s2** | –519.56302775 | 0.174840 |
| **B** | –519.17709823 | 0.161484 |
| **TS-BC** | –519.14992458 | 0.161241 (365.02i) |
| **C** | –519.17000366 | 0.164301 |
| **TS-CD** | –519.14479230 | 0.158489 (1476.54i) |
| **D** | –519.18976710 | 0.160578 |
| **TS-DE** | –519.18476799 | 0.159476 (752.60i) |
| **E** | –519.20313838 | 0.163538 |
| **F** | –671.87401769 | 0.203908 |
| **TS-FG** | –671.87295542 | 0.203390 (111.74i) |
| **G** | –671.90769958 | 0.204152 |
| **TS-GH** | –671.88832376 | 0.203525 (130.61i) |
| **H** | –671.93334603 | 0.206048 |

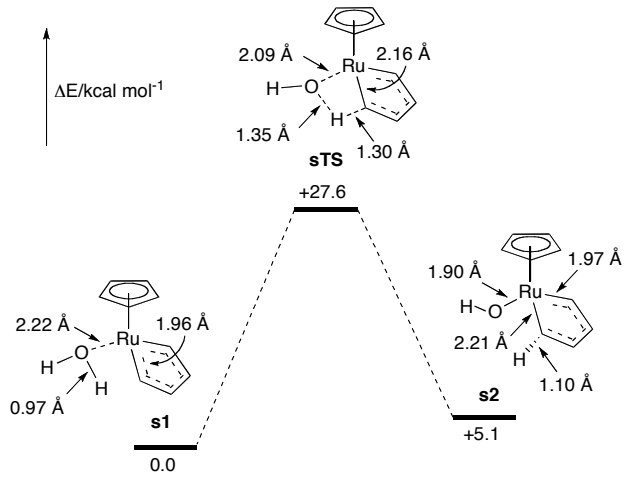


**Fig S1**. Reaction profile for protonation of cataionic ruthenacycle.

## Standard Orientations for Models.

Standard orientations for **s1**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | 0.013251 | 0.179453 | -0.119340 |
| 2 | 6 | 0 | 1.230341 | -1.358700 | 0.882857 |
| 3 | 1 | 0 | 0.762693 | -2.182318 | 1.405185 |
| 4 | 6 | 0 | 1.653968 | -0.113672 | 1.465052 |
| 5 | 1 | 0 | 1.491766 | 0.193507 | 2.490130 |
| 6 | 6 | 0 | 2.359954 | 0.620776 | 0.471687 |
| 7 | 1 | 0 | 2.784556 | 1.608877 | 0.599547 |
| 8 | 6 | 0 | 2.378351 | -0.147283 | -0.723115 |
| 9 | 1 | 0 | 2.830470 | 0.147331 | -1.662137 |
| 10 | 6 | 0 | 1.683523 | -1.365178 | -0.481588 |
| 11 | 1 | 0 | 1.547650 | -2.173054 | -1.188859 |
| 12 | 6 | 0 | -1.357127 | -0.990822 | -0.873396 |
| 13 | 1 | 0 | -1.132414 | -1.755694 | -1.619639 |
| 14 | 6 | 0 | -2.658857 | -0.844828 | -0.366855 |
| 15 | 1 | 0 | -3.539396 | -1.294428 | -0.823114 |
| 16 | 6 | 0 | -2.692885 | -0.095206 | 0.819604 |
| 17 | 1 | 0 | -3.600411 | 0.093983 | 1.390132 |
| 18 | 6 | 0 | -1.415276 | 0.324535 | 1.215530 |
| 19 | 1 | 0 | -1.230462 | 0.669494 | 2.234865 |
| 20 | 1 | 0 | -1.665413 | 2.111016 | -1.149481 |
| 21 | 8 | 0 | -0.695562 | 2.033340 | -1.110640 |
| 22 | 1 | 0 | -0.359547 | 2.240884 | -1.999203 |

Standard orientations for **sTS**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 44 | 0 | 0.054351 | 0.191671 | -0.287226 |
| 2 | 6 | 0 | 1.045125 | -1.271214 | 1.030107 |
| 3 | 1 | 0 | 0.457700 | -1.960187 | 1.621611 |
| 4 | 6 | 0 | 1.480906 | 0.044899 | 1.436766 |
| 5 | 1 | 0 | 1.246148 | 0.524782 | 2.378370 |
| 6 | 6 | 0 | 2.348470 | 0.566997 | 0.422123 |
| 7 | 1 | 0 | 2.810126 | 1.546118 | 0.431707 |
| 8 | 6 | 0 | 2.382620 | -0.357717 | -0.635300 |
| 9 | 1 | 0 | 2.902105 | -0.229299 | -1.577363 |
| 10 | 6 | 0 | 1.558344 | -1.491176 | -0.278904 |
| 11 | 1 | 0 | 1.429481 | -2.387463 | -0.871777 |
| 12 | 6 | 0 | -1.354596 | -1.057957 | -0.916985 |
| 13 | 1 | 0 | -1.114894 | -1.759475 | -1.720077 |
| 14 | 6 | 0 | -2.597514 | -1.046254 | -0.325896 |
| 15 | 1 | 0 | -3.434113 | -1.647544 | -0.677262 |
| 16 | 6 | 0 | -2.678890 | -0.204795 | 0.816819 |
| 17 | 1 | 0 | -3.511902 | -0.269429 | 1.516536 |
| 18 | 6 | 0 | -1.605692 | 0.648223 | 1.017300 |
| 19 | 1 | 0 | -1.454907 | 1.102251 | 1.997882 |
| 20 | 1 | 0 | -1.375293 | 1.577181 | 0.141332 |
| 21 | 8 | 0 | -0.408476 | 2.207610 | -0.561955 |
| 22 | 1 | 0 | -0.550747 | 2.422608 | -1.503580 |

Standard orientations for **s2**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 44 | 0 | 0.055784 | 0.260177 | -0.351194 |
| 2 | 6 | 0 | 0.973159 | -1.468670 | 0.896557 |
| 3 | 1 | 0 | 0.376660 | -2.313331 | 1.212500 |
| 4 | 6 | 0 | 1.233447 | -0.298170 | 1.641101 |
| 5 | 1 | 0 | 0.866779 | -0.086852 | 2.636896 |
| 6 | 6 | 0 | 2.116599 | 0.554681 | 0.882066 |
| 7 | 1 | 0 | 2.498832 | 1.513093 | 1.210043 |
| 8 | 6 | 0 | 2.351906 | -0.062409 | -0.358566 |
| 9 | 1 | 0 | 2.975643 | 0.312711 | -1.160458 |
| 10 | 6 | 0 | 1.604120 | -1.307430 | -0.381191 |
| 11 | 1 | 0 | 1.618332 | -2.040143 | -1.178728 |
| 12 | 6 | 0 | -1.462060 | -0.908641 | -0.798006 |
| 13 | 1 | 0 | -1.373525 | -1.580286 | -1.656492 |
| 14 | 6 | 0 | -2.553294 | -1.027378 | 0.068652 |
| 15 | 1 | 0 | -3.356856 | -1.745566 | -0.076422 |
| 16 | 6 | 0 | -2.465866 | -0.190219 | 1.169921 |
| 17 | 1 | 0 | -3.055643 | -0.347252 | 2.072743 |
| 18 | 6 | 0 | -1.502340 | 0.875976 | 1.085471 |
| 19 | 1 | 0 | -1.186690 | 1.354616 | 2.010503 |
| 20 | 1 | 0 | -1.771808 | 1.614994 | 0.320528 |
| 21 | 8 | 0 | -0.290863 | 1.598693 | -1.652384 |
| 22 | 1 | 0 | 0.506647 | 2.074269 | -1.955515 |

Standard orientations for **B**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 44 | 0 | -0.053726 | -0.200844 | -0.266706 |
| 2 | 6 | 0 | 1.284154 | 0.887286 | 1.233534 |
| 3 | 1 | 0 | 0.812358 | 1.482879 | 2.002386 |
| 4 | 6 | 0 | 1.700519 | 1.339503 | -0.056211 |
| 5 | 1 | 0 | 1.573102 | 2.341673 | -0.444710 |
| 6 | 6 | 0 | 2.369679 | 0.264199 | -0.717680 |
| 7 | 1 | 0 | 2.797844 | 0.303387 | -1.711609 |
| 8 | 6 | 0 | 2.331868 | -0.863010 | 0.132265 |
| 9 | 1 | 0 | 2.725829 | -1.846905 | -0.090285 |
| 10 | 6 | 0 | 1.639229 | -0.493738 | 1.326285 |
| 11 | 1 | 0 | 1.457070 | -1.136150 | 2.178126 |
| 12 | 6 | 0 | -1.435542 | -0.725085 | 1.049334 |
| 13 | 1 | 0 | -1.271867 | -1.567638 | 1.725122 |
| 14 | 6 | 0 | -2.578120 | 0.039373 | 1.108222 |
| 15 | 1 | 0 | -3.422986 | -0.184065 | 1.759467 |
| 16 | 6 | 0 | -2.538211 | 1.171202 | 0.247742 |
| 17 | 1 | 0 | -3.349907 | 1.895215 | 0.178197 |
| 18 | 6 | 0 | -1.365304 | 1.267550 | -0.465351 |
| 19 | 1 | 0 | -1.141523 | 2.135432 | -1.089901 |
| 20 | 8 | 0 | -0.779815 | -1.280192 | -1.715553 |
| 21 | 1 | 0 | -0.027096 | -1.668849 | -2.196154 |

Standard orientations for **TS-BC**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 44 | 0 | -0.010882 | -0.048511 | -0.167557 |
| 2 | 6 | 0 | 1.537932 | 0.745891 | 1.256858 |
| 3 | 1 | 0 | 1.224364 | 1.251523 | 2.160393 |
| 4 | 6 | 0 | 1.795732 | 1.364616 | -0.012720 |
| 5 | 1 | 0 | 1.676526 | 2.416614 | -0.237870 |
| 6 | 6 | 0 | 2.299706 | 0.368151 | -0.897658 |
| 7 | 1 | 0 | 2.589438 | 0.517025 | -1.929623 |
| 8 | 6 | 0 | 2.333664 | -0.861888 | -0.187618 |
| 9 | 1 | 0 | 2.617457 | -1.820763 | -0.603539 |
| 10 | 6 | 0 | 1.882116 | -0.642628 | 1.139191 |
| 11 | 1 | 0 | 1.811156 | -1.385576 | 1.922367 |
| 12 | 6 | 0 | -1.571900 | -0.759573 | 0.835913 |
| 13 | 1 | 0 | -1.504720 | -1.635753 | 1.479714 |
| 14 | 6 | 0 | -2.804951 | -0.087096 | 0.644272 |
| 15 | 1 | 0 | -3.767053 | -0.453520 | 0.994754 |
| 16 | 6 | 0 | -2.636726 | 1.068800 | -0.099860 |
| 17 | 1 | 0 | -3.475425 | 1.696782 | -0.407081 |
| 18 | 6 | 0 | -1.290442 | 1.335069 | -0.494623 |
| 19 | 1 | 0 | -1.050902 | 2.312289 | -0.924328 |
| 20 | 8 | 0 | -0.952399 | -1.790919 | -0.809678 |
| 21 | 1 | 0 | -1.293636 | -1.624847 | -1.707398 |

Standard orientations for **C**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 44 | 0 | 0.046984 | -0.021814 | -0.160124 |
| 2 | 6 | 0 | 1.577765 | 0.682778 | 1.286008 |
| 3 | 1 | 0 | 1.281036 | 1.146612 | 2.217303 |
| 4 | 6 | 0 | 1.781839 | 1.360782 | 0.027929 |
| 5 | 1 | 0 | 1.645032 | 2.420048 | -0.148225 |
| 6 | 6 | 0 | 2.287885 | 0.410710 | -0.908539 |
| 7 | 1 | 0 | 2.562179 | 0.606213 | -1.936198 |
| 8 | 6 | 0 | 2.386864 | -0.840640 | -0.234762 |
| 9 | 1 | 0 | 2.694629 | -1.773942 | -0.691871 |
| 10 | 6 | 0 | 1.978565 | -0.683048 | 1.110140 |
| 11 | 1 | 0 | 1.956348 | -1.455953 | 1.867014 |
| 12 | 6 | 0 | -1.593263 | -0.930389 | 0.654415 |
| 13 | 1 | 0 | -1.527374 | -1.593567 | 1.516846 |
| 14 | 6 | 0 | -2.855443 | -0.144823 | 0.457134 |
| 15 | 1 | 0 | -3.836226 | -0.540087 | 0.718407 |
| 16 | 6 | 0 | -2.648972 | 1.033136 | -0.176554 |
| 17 | 1 | 0 | -3.465761 | 1.694950 | -0.469431 |
| 18 | 6 | 0 | -1.247458 | 1.324006 | -0.480336 |
| 19 | 1 | 0 | -1.017509 | 2.349362 | -0.792739 |
| 20 | 8 | 0 | -1.305336 | -1.716815 | -0.549604 |
| 21 | 1 | 0 | -1.923649 | -1.434372 | -1.251449 |

Standard orientations for **TS-CD**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 44 | 0 | 0.038723 | -0.019476 | -0.152796 |
| 2 | 6 | 0 | 1.705922 | 0.769903 | 1.178412 |
| 3 | 1 | 0 | 1.475149 | 1.369338 | 2.048890 |
| 4 | 6 | 0 | 1.891828 | 1.261870 | -0.161310 |
| 5 | 1 | 0 | 1.835379 | 2.296896 | -0.472411 |
| 6 | 6 | 0 | 2.246009 | 0.152638 | -0.984666 |
| 7 | 1 | 0 | 2.464769 | 0.189606 | -2.043212 |
| 8 | 6 | 0 | 2.278076 | -1.010281 | -0.160300 |
| 9 | 1 | 0 | 2.478673 | -2.018205 | -0.501941 |
| 10 | 6 | 0 | 1.954311 | -0.636405 | 1.167487 |
| 11 | 1 | 0 | 1.892670 | -1.298575 | 2.021037 |
| 12 | 6 | 0 | -1.678950 | -1.021898 | 0.527636 |
| 13 | 1 | 0 | -1.561471 | -1.733375 | 1.347196 |
| 14 | 6 | 0 | -2.892216 | -0.137890 | 0.473183 |
| 15 | 1 | 0 | -3.888835 | -0.533495 | 0.665132 |
| 16 | 6 | 0 | -2.646963 | 1.123202 | 0.061848 |
| 17 | 1 | 0 | -3.432479 | 1.862068 | -0.097366 |
| 18 | 6 | 0 | -1.242768 | 1.386429 | -0.229523 |
| 19 | 1 | 0 | -0.982230 | 2.423306 | -0.473082 |
| 20 | 8 | 0 | -1.345558 | -1.557136 | -0.691038 |
| 21 | 1 | 0 | -0.912461 | -0.568925 | -1.479519 |

Standard orientations for **D**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 44 | 0 | 0.035924 | 0.051000 | -0.263924 |
| 2 | 6 | 0 | 1.607809 | 0.766032 | 1.248425 |
| 3 | 1 | 0 | 1.309162 | 1.401252 | 2.071658 |
| 4 | 6 | 0 | 1.954459 | 1.206009 | -0.071638 |
| 5 | 1 | 0 | 2.032213 | 2.231918 | -0.405038 |
| 6 | 6 | 0 | 2.337354 | 0.038294 | -0.821746 |
| 7 | 1 | 0 | 2.663160 | 0.031090 | -1.853072 |
| 8 | 6 | 0 | 2.191781 | -1.093570 | 0.011240 |
| 9 | 1 | 0 | 2.350991 | -2.122584 | -0.283377 |
| 10 | 6 | 0 | 1.724399 | -0.653805 | 1.285843 |
| 11 | 1 | 0 | 1.519288 | -1.285679 | 2.140043 |
| 12 | 6 | 0 | -1.589532 | -1.125610 | 0.442797 |
| 13 | 1 | 0 | -1.337774 | -1.763532 | 1.302341 |
| 14 | 6 | 0 | -2.823545 | -0.282689 | 0.529044 |
| 15 | 1 | 0 | -3.786665 | -0.736348 | 0.760665 |
| 16 | 6 | 0 | -2.667922 | 1.026328 | 0.221672 |
| 17 | 1 | 0 | -3.499433 | 1.729701 | 0.180271 |
| 18 | 6 | 0 | -1.323359 | 1.388878 | -0.166052 |
| 19 | 1 | 0 | -1.171843 | 2.427868 | -0.479261 |
| 20 | 8 | 0 | -1.247924 | -1.525685 | -0.760419 |
| 21 | 1 | 0 | -0.145026 | 0.428584 | -1.815738 |

Standard orientations for **TS-DE**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 44 | 0 | 0.043168 | 0.074083 | -0.180644 |
| 2 | 6 | 0 | 1.663636 | 0.557538 | 1.305314 |
| 3 | 1 | 0 | 1.407806 | 1.024480 | 2.246880 |
| 4 | 6 | 0 | 1.943974 | 1.234440 | 0.072356 |
| 5 | 1 | 0 | 1.994172 | 2.305517 | -0.071951 |
| 6 | 6 | 0 | 2.297190 | 0.232338 | -0.900556 |
| 7 | 1 | 0 | 2.566162 | 0.419338 | -1.931624 |
| 8 | 6 | 0 | 2.192508 | -1.033014 | -0.288212 |
| 9 | 1 | 0 | 2.328954 | -1.987630 | -0.779321 |
| 10 | 6 | 0 | 1.771830 | -0.847035 | 1.065804 |
| 11 | 1 | 0 | 1.615304 | -1.631242 | 1.794365 |
| 12 | 6 | 0 | -1.589456 | -1.132736 | 0.428772 |
| 13 | 1 | 0 | -1.395541 | -1.763871 | 1.307874 |
| 14 | 6 | 0 | -2.857807 | -0.332078 | 0.399533 |
| 15 | 1 | 0 | -3.822913 | -0.827719 | 0.500320 |
| 16 | 6 | 0 | -2.722004 | 0.983667 | 0.129894 |
| 17 | 1 | 0 | -3.568215 | 1.661448 | 0.020886 |
| 18 | 6 | 0 | -1.352605 | 1.411121 | -0.105026 |
| 19 | 1 | 0 | -1.209637 | 2.479636 | -0.296646 |
| 20 | 8 | 0 | -1.163714 | -1.534004 | -0.749795 |
| 21 | 1 | 0 | -0.589382 | 0.886966 | -1.491344 |

Standard orientations for **E**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 44 | 0 | 0.072296 | -0.049289 | -0.224923 |
| 2 | 6 | 0 | 1.475535 | 0.776334 | 1.212055 |
| 3 | 1 | 0 | 1.111767 | 1.339036 | 2.060815 |
| 4 | 6 | 0 | 1.875098 | 1.298802 | -0.056801 |
| 5 | 1 | 0 | 1.871806 | 2.339792 | -0.350298 |
| 6 | 6 | 0 | 2.387687 | 0.205918 | -0.841004 |
| 7 | 1 | 0 | 2.746921 | 0.283372 | -1.860014 |
| 8 | 6 | 0 | 2.276089 | -0.981525 | -0.100328 |
| 9 | 1 | 0 | 2.524125 | -1.976847 | -0.443855 |
| 10 | 6 | 0 | 1.648746 | -0.653384 | 1.154608 |
| 11 | 1 | 0 | 1.439951 | -1.346260 | 1.959725 |
| 12 | 6 | 0 | -1.688395 | -1.128657 | 0.453306 |
| 13 | 1 | 0 | -1.639496 | -1.706715 | 1.387530 |
| 14 | 6 | 0 | -2.881588 | -0.254546 | 0.264425 |
| 15 | 1 | 0 | -3.874386 | -0.685085 | 0.402696 |
| 16 | 6 | 0 | -2.682333 | 1.027944 | -0.050383 |
| 17 | 1 | 0 | -3.522181 | 1.690809 | -0.275767 |
| 18 | 6 | 0 | -1.282947 | 1.567838 | -0.079255 |
| 19 | 1 | 0 | -1.084451 | 2.184520 | 0.807597 |
| 20 | 8 | 0 | -1.050630 | -1.665519 | -0.572184 |
| 21 | 1 | 0 | -1.117367 | 2.217910 | -0.954102 |

Standard orientations for **F**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 44 | 0 | 0.799601 | -0.068572 | -0.252700 |
| 2 | 6 | 0 | 2.139346 | 0.793424 | 1.221004 |
| 3 | 1 | 0 | 1.735340 | 1.303078 | 2.084912 |
| 4 | 6 | 0 | 2.509249 | 1.381404 | -0.028347 |
| 5 | 1 | 0 | 2.443321 | 2.429415 | -0.287520 |
| 6 | 6 | 0 | 3.101080 | 0.349734 | -0.841547 |
| 7 | 1 | 0 | 3.461940 | 0.483497 | -1.854174 |
| 8 | 6 | 0 | 3.063858 | -0.864794 | -0.139783 |
| 9 | 1 | 0 | 3.378782 | -1.830328 | -0.512421 |
| 10 | 6 | 0 | 2.405355 | -0.619221 | 1.117995 |
| 11 | 1 | 0 | 2.237852 | -1.350222 | 1.898680 |
| 12 | 6 | 0 | -0.862630 | -1.344481 | 0.380735 |
| 13 | 1 | 0 | -0.755492 | -1.961931 | 1.283689 |
| 14 | 6 | 0 | -2.096644 | -0.529798 | 0.250148 |
| 15 | 6 | 0 | -2.003032 | 0.778964 | 0.009303 |
| 16 | 6 | 0 | -0.670299 | 1.451672 | -0.053426 |
| 17 | 1 | 0 | -0.495420 | 2.087983 | 0.824110 |
| 18 | 1 | 0 | -0.579650 | 2.106135 | -0.936931 |
| 19 | 8 | 0 | -0.190529 | -1.761628 | -0.674771 |
| 20 | 6 | 0 | -3.542277 | -0.944296 | 0.341982 |
| 21 | 1 | 0 | -3.813367 | -1.362623 | 1.325056 |
| 22 | 1 | 0 | -3.816780 | -1.693195 | -0.418185 |
| 23 | 8 | 0 | -4.279946 | 0.264195 | 0.116850 |
| 24 | 6 | 0 | -3.387556 | 1.356051 | -0.135925 |
| 25 | 1 | 0 | -3.583468 | 2.165957 | 0.585138 |
| 26 | 1 | 0 | -3.570414 | 1.766909 | -1.143039 |

Standard orientations for **TS-FG**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 44 | 0 | 0.820104 | -0.039848 | -0.164601 |
| 2 | 6 | 0 | 2.271618 | 0.912745 | 1.136290 |
| 3 | 1 | 0 | 1.955388 | 1.504166 | 1.984822 |
| 4 | 6 | 0 | 2.513638 | 1.380703 | -0.191366 |
| 5 | 1 | 0 | 2.438840 | 2.402484 | -0.537805 |
| 6 | 6 | 0 | 2.990127 | 0.257214 | -0.968420 |
| 7 | 1 | 0 | 3.235140 | 0.286612 | -2.022975 |
| 8 | 6 | 0 | 3.036049 | -0.882754 | -0.147049 |
| 9 | 1 | 0 | 3.290581 | -1.886388 | -0.460069 |
| 10 | 6 | 0 | 2.513213 | -0.508504 | 1.138724 |
| 11 | 1 | 0 | 2.405607 | -1.163622 | 1.993612 |
| 12 | 6 | 0 | -0.970127 | -1.466926 | 0.358321 |
| 13 | 1 | 0 | -0.959784 | -2.177577 | 1.197467 |
| 14 | 6 | 0 | -2.139284 | -0.581068 | 0.209753 |
| 15 | 6 | 0 | -2.007371 | 0.738018 | 0.015133 |
| 16 | 6 | 0 | -0.693872 | 1.418891 | 0.172987 |
| 17 | 1 | 0 | -0.584240 | 1.792825 | 1.199656 |
| 18 | 1 | 0 | -0.578826 | 2.281467 | -0.499175 |
| 19 | 8 | 0 | -0.168992 | -1.743804 | -0.627173 |
| 20 | 6 | 0 | -3.599501 | -0.964035 | 0.215500 |
| 21 | 1 | 0 | -3.940143 | -1.352412 | 1.190068 |
| 22 | 1 | 0 | -3.842805 | -1.725023 | -0.542255 |
| 23 | 8 | 0 | -4.293583 | 0.250110 | -0.093092 |
| 24 | 6 | 0 | -3.369315 | 1.335094 | -0.232548 |
| 25 | 1 | 0 | -3.612705 | 2.126348 | 0.495015 |
| 26 | 1 | 0 | -3.462062 | 1.777741 | -1.237730 |

Standard orientations for **G**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 44 | 0 | -0.960582 | 0.045784 | -0.114662 |
| 2 | 6 | 0 | -2.412593 | -1.028910 | 1.086604 |
| 3 | 1 | 0 | -2.130814 | -1.732072 | 1.858792 |
| 4 | 6 | 0 | -2.670855 | -1.333154 | -0.281304 |
| 5 | 1 | 0 | -2.614609 | -2.308893 | -0.744765 |
| 6 | 6 | 0 | -2.995712 | -0.095099 | -0.942636 |
| 7 | 1 | 0 | -3.216485 | 0.016467 | -1.996541 |
| 8 | 6 | 0 | -3.028992 | 0.954540 | 0.029553 |
| 9 | 1 | 0 | -3.230086 | 1.998853 | -0.166577 |
| 10 | 6 | 0 | -2.617116 | 0.395298 | 1.270664 |
| 11 | 1 | 0 | -2.491326 | 0.933904 | 2.200799 |
| 12 | 6 | 0 | 1.547314 | 1.759057 | -0.056623 |
| 13 | 1 | 0 | 1.961487 | 2.775565 | -0.014499 |
| 14 | 6 | 0 | 2.422697 | 0.678370 | -0.160562 |
| 15 | 6 | 0 | 2.025145 | -0.659758 | -0.208595 |
| 16 | 6 | 0 | 0.743294 | -1.172490 | -0.495899 |
| 17 | 1 | 0 | 0.647434 | -2.259212 | -0.498652 |
| 18 | 1 | 0 | 0.290320 | -0.745870 | -1.451619 |
| 19 | 8 | 0 | 0.277040 | 1.682768 | 0.087924 |
| 20 | 6 | 0 | 3.930100 | 0.726940 | -0.021318 |
| 21 | 1 | 0 | 4.287297 | 1.455180 | 0.716398 |
| 22 | 1 | 0 | 4.435567 | 0.943214 | -0.979080 |
| 23 | 8 | 0 | 4.285103 | -0.581153 | 0.438940 |
| 24 | 6 | 0 | 3.254872 | -1.494797 | 0.081512 |
| 25 | 1 | 0 | 3.102994 | -2.201778 | 0.907785 |
| 26 | 1 | 0 | 3.537766 | -2.082746 | -0.810212 |

Standard orientations for **TS-GH**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 44 | 0 | -0.844847 | 0.112710 | -0.212262 |
| 2 | 6 | 0 | -1.842953 | -1.445188 | 0.896825 |
| 3 | 1 | 0 | -1.355677 | -2.346245 | 1.245463 |
| 4 | 6 | 0 | -2.492833 | -1.267522 | -0.361642 |
| 5 | 1 | 0 | -2.587766 | -2.004136 | -1.148143 |
| 6 | 6 | 0 | -2.980535 | 0.091801 | -0.403769 |
| 7 | 1 | 0 | -3.504733 | 0.548473 | -1.233643 |
| 8 | 6 | 0 | -2.715808 | 0.714699 | 0.865136 |
| 9 | 1 | 0 | -2.947024 | 1.736818 | 1.132192 |
| 10 | 6 | 0 | -1.974893 | -0.211714 | 1.645801 |
| 11 | 1 | 0 | -1.569078 | -0.030874 | 2.632815 |
| 12 | 6 | 0 | 1.524547 | 1.948042 | -0.007395 |
| 13 | 1 | 0 | 2.074725 | 2.858024 | 0.289541 |
| 14 | 6 | 0 | 2.196964 | 0.702834 | 0.042088 |
| 15 | 6 | 0 | 1.765646 | -0.431815 | -0.648491 |
| 16 | 6 | 0 | 0.706511 | -0.562560 | -1.590991 |
| 17 | 1 | 0 | 0.613982 | -1.529613 | -2.083954 |
| 18 | 1 | 0 | 0.566094 | 0.288465 | -2.268629 |
| 19 | 8 | 0 | 0.326220 | 2.099139 | -0.363383 |
| 20 | 6 | 0 | 3.466200 | 0.364085 | 0.796594 |
| 21 | 1 | 0 | 3.486052 | 0.725699 | 1.831545 |
| 22 | 1 | 0 | 4.375587 | 0.740762 | 0.293183 |
| 23 | 8 | 0 | 3.477568 | -1.066406 | 0.834216 |
| 24 | 6 | 0 | 2.696622 | -1.555878 | -0.247874 |
| 25 | 1 | 0 | 2.161946 | -2.457555 | 0.073737 |
| 26 | 1 | 0 | 3.332037 | -1.831618 | -1.108939 |

Standard orientations for **H**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 44 | 0 | -0.475252 | 0.263043 | -0.127748 |
| 2 | 6 | 0 | -1.344907 | -1.038670 | 1.463332 |
| 3 | 1 | 0 | -0.734915 | -1.624858 | 2.137509 |
| 4 | 6 | 0 | -1.805856 | -1.456454 | 0.171329 |
| 5 | 1 | 0 | -1.626288 | -2.421148 | -0.284852 |
| 6 | 6 | 0 | -2.597773 | -0.392208 | -0.386238 |
| 7 | 1 | 0 | -3.102972 | -0.398748 | -1.341855 |
| 8 | 6 | 0 | -2.595777 | 0.676484 | 0.557259 |
| 9 | 1 | 0 | -3.056053 | 1.645268 | 0.410388 |
| 10 | 6 | 0 | -1.841194 | 0.281859 | 1.703190 |
| 11 | 1 | 0 | -1.665219 | 0.883230 | 2.584872 |
| 12 | 6 | 0 | 1.106561 | 1.784026 | 0.175366 |
| 13 | 1 | 0 | 1.277452 | 2.357306 | 1.097433 |
| 14 | 6 | 0 | 1.750952 | 0.516223 | 0.015865 |
| 15 | 6 | 0 | 1.429556 | -0.407971 | -1.028441 |
| 16 | 6 | 0 | 0.508527 | -0.161423 | -2.071676 |
| 17 | 1 | 0 | 0.192627 | -1.010630 | -2.674558 |
| 18 | 1 | 0 | 0.475062 | 0.806873 | -2.555866 |
| 19 | 8 | 0 | 0.316571 | 2.241207 | -0.735803 |
| 20 | 6 | 0 | 2.652141 | -0.198036 | 0.996413 |
| 21 | 1 | 0 | 2.402832 | -0.025832 | 2.047619 |
| 22 | 1 | 0 | 3.704266 | 0.098907 | 0.837478 |
| 23 | 8 | 0 | 2.479431 | -1.587906 | 0.711903 |
| 24 | 6 | 0 | 2.106528 | -1.713978 | -0.660054 |
| 25 | 1 | 0 | 1.463701 | -2.592322 | -0.770591 |
| 26 | 1 | 0 | 3.000043 | -1.857441 | -1.293525 |

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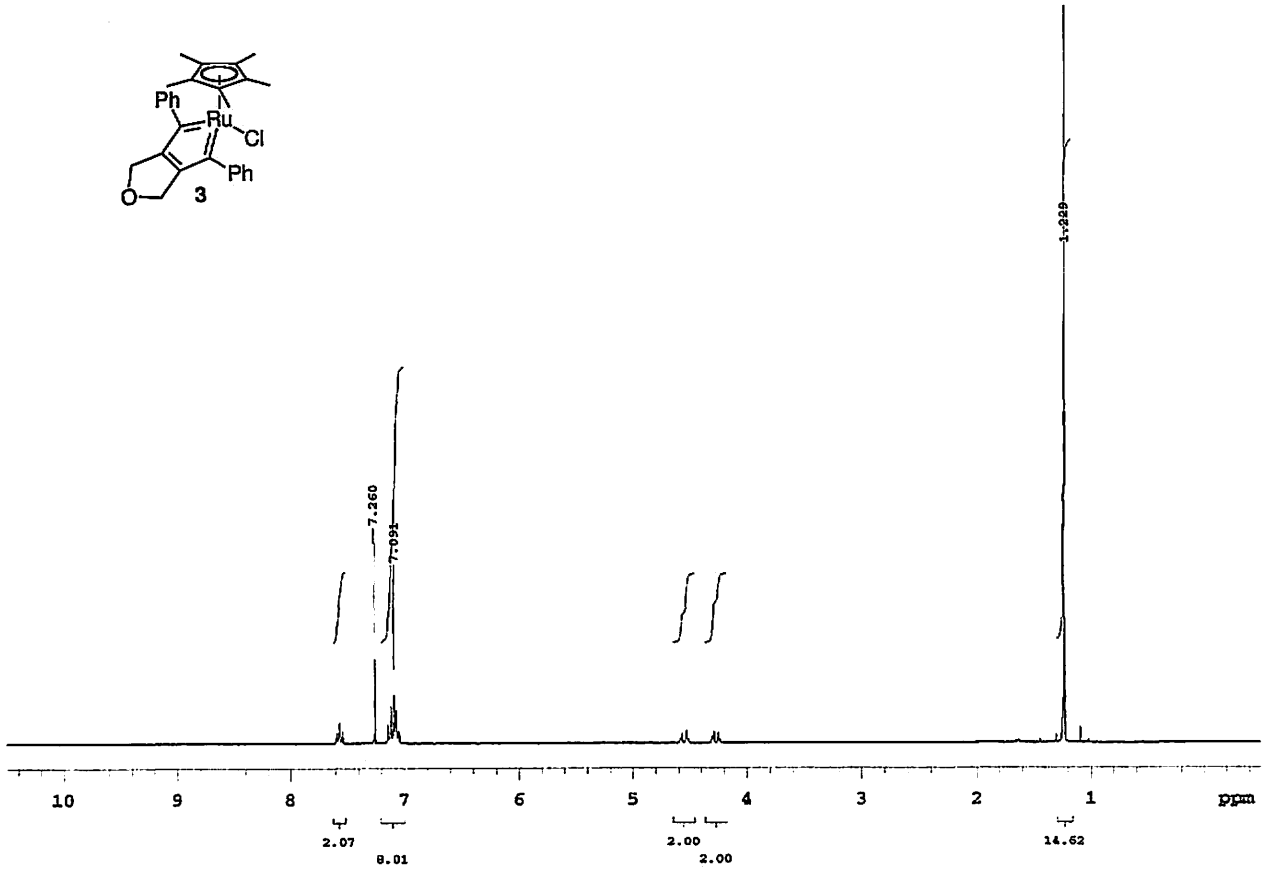
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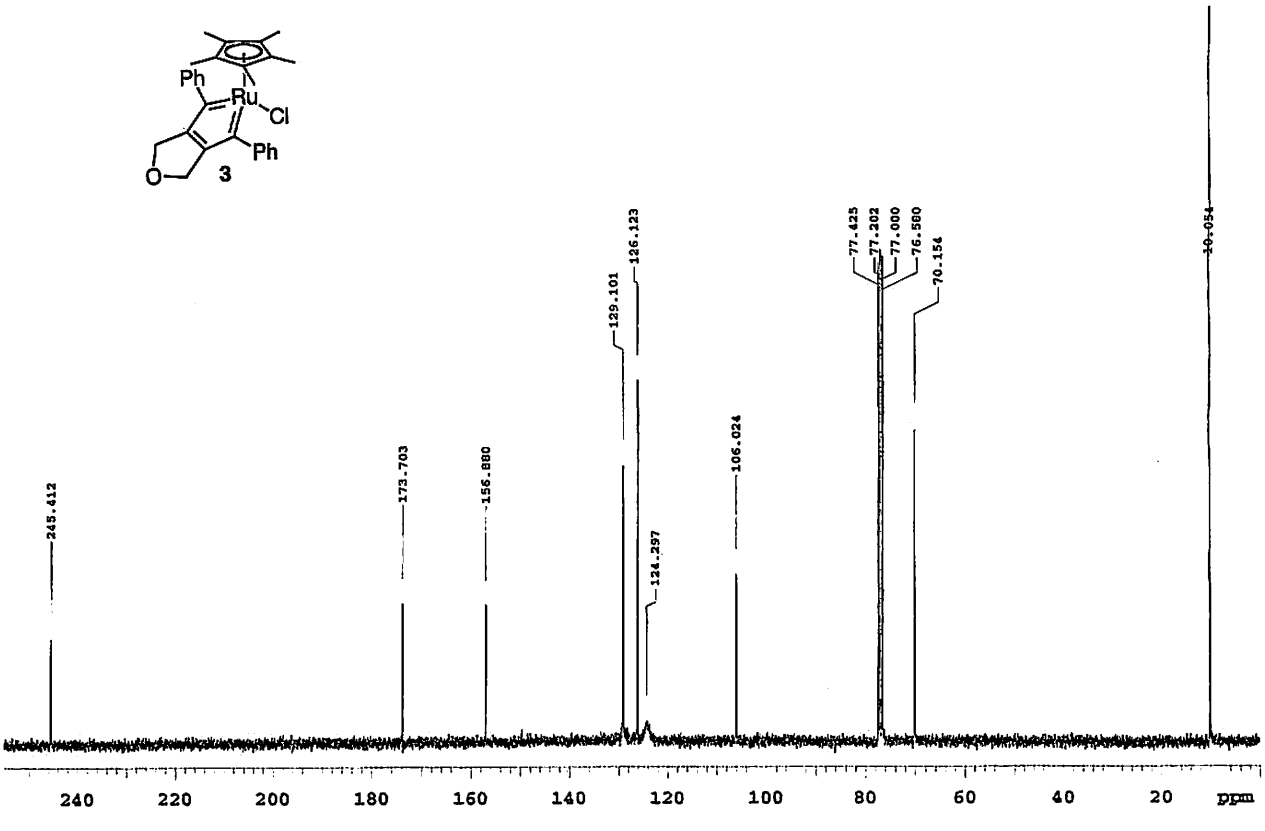
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77.425
77.202
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160
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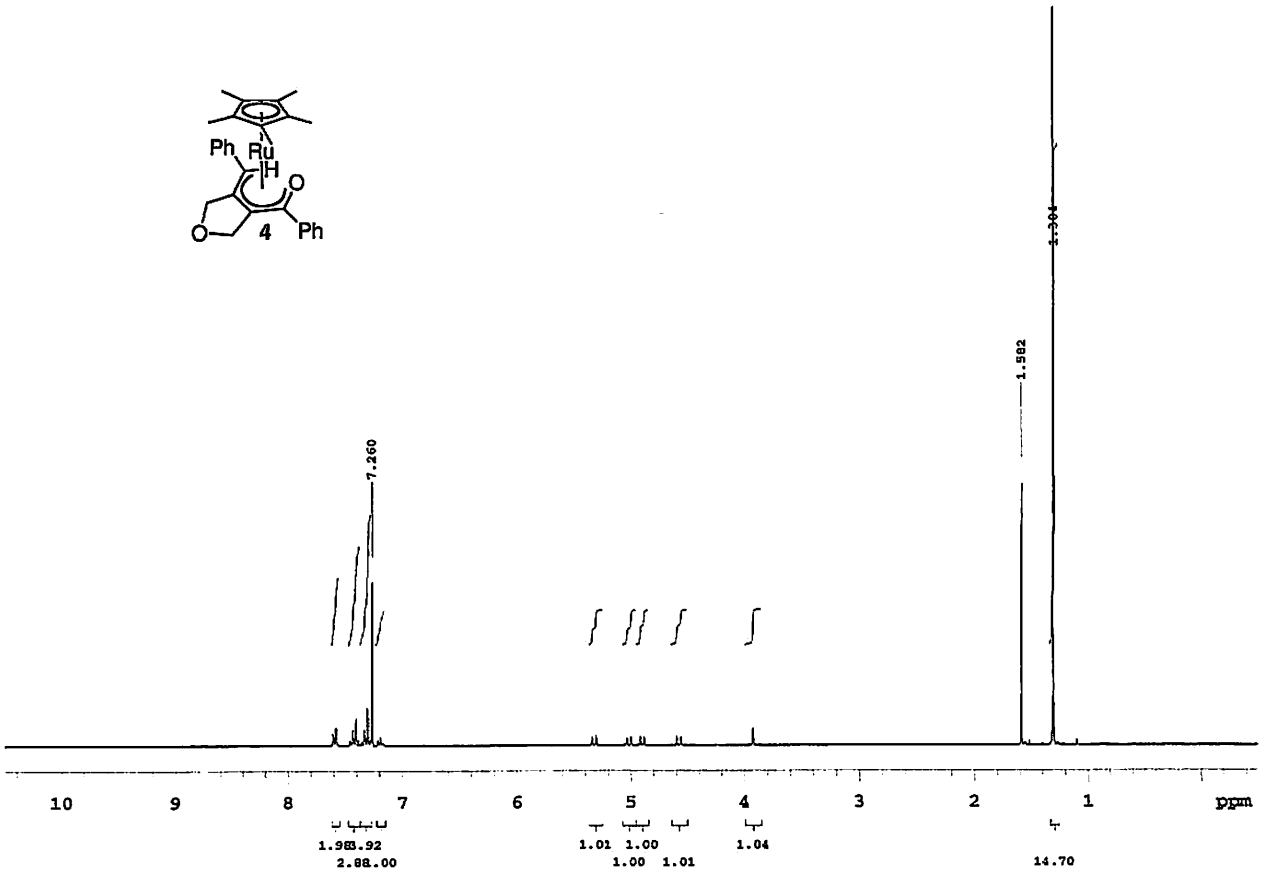
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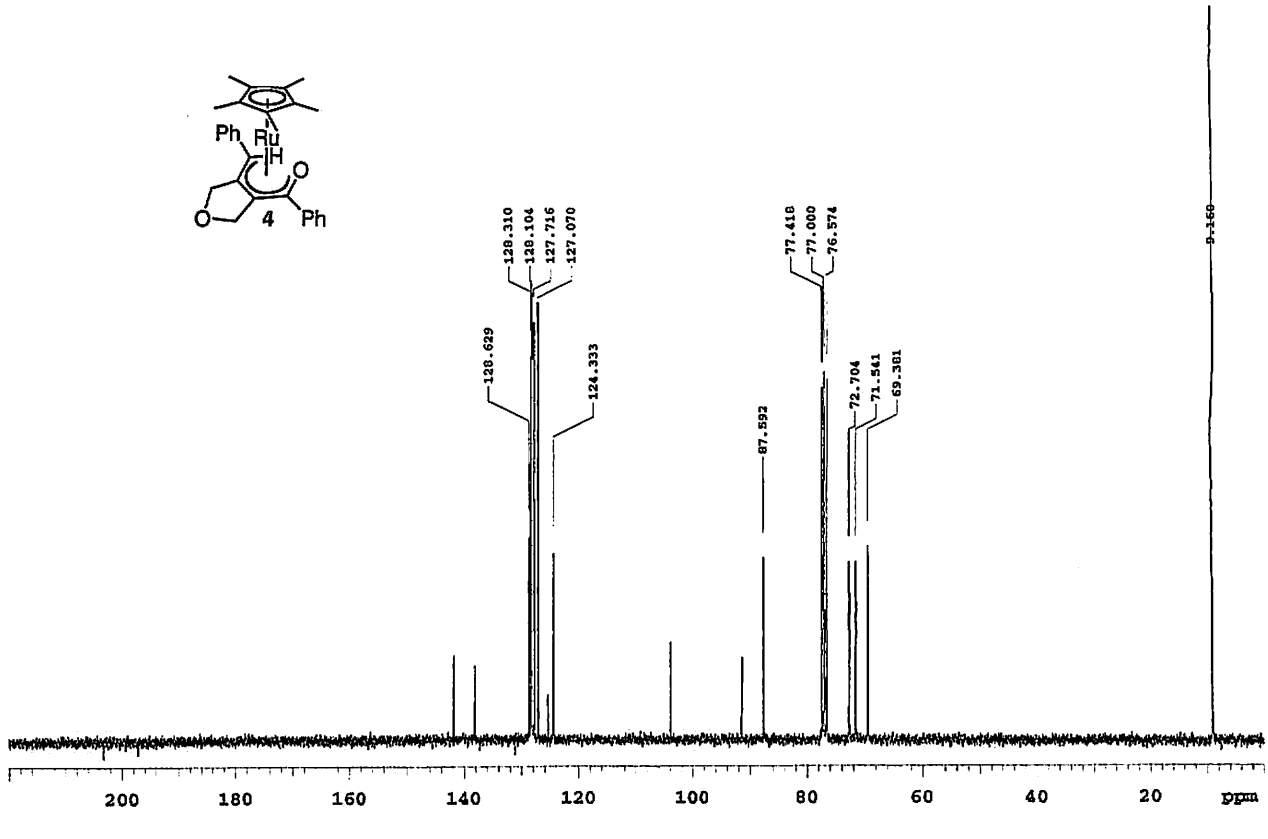
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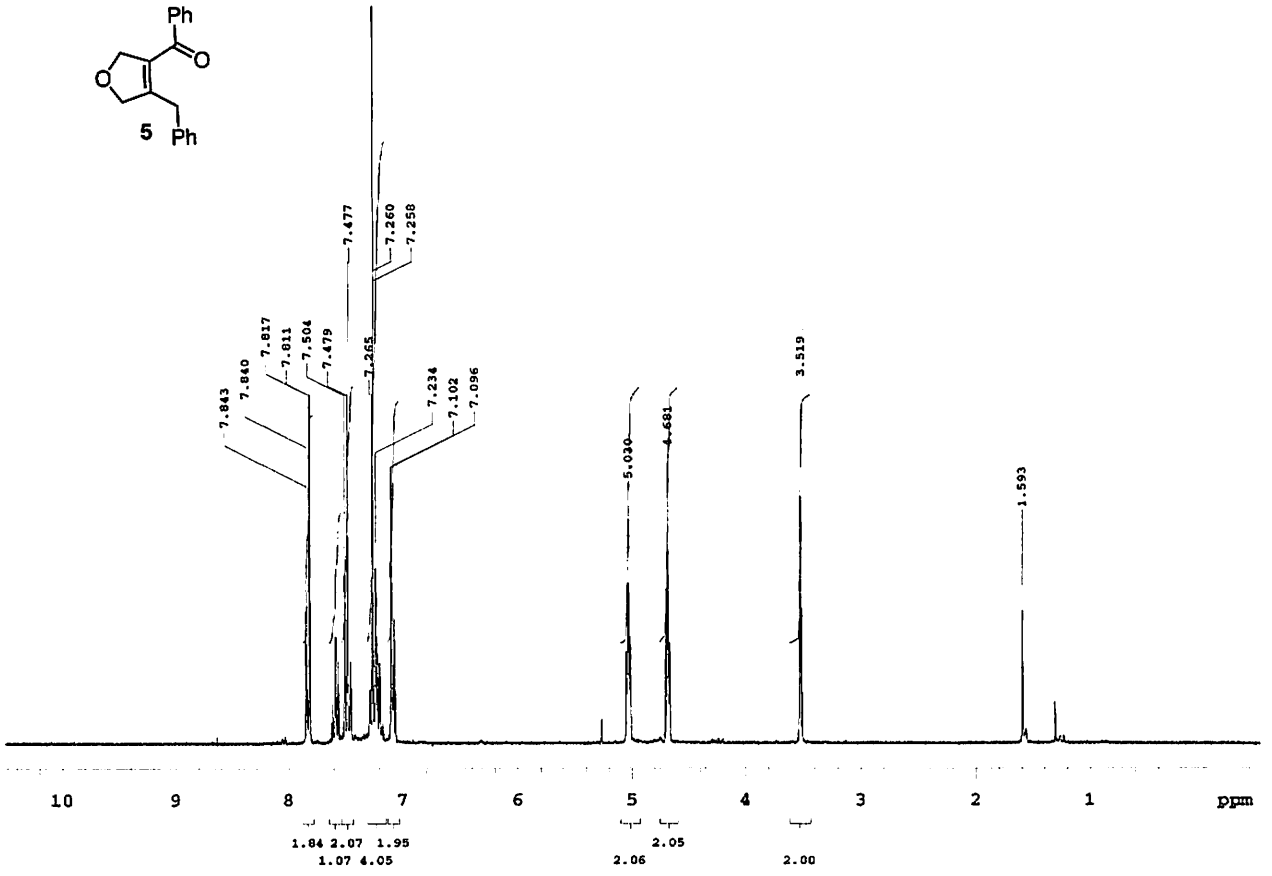
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7.234
7.102
7.096
5.030
4.681
3.519
1.593
10
9
8
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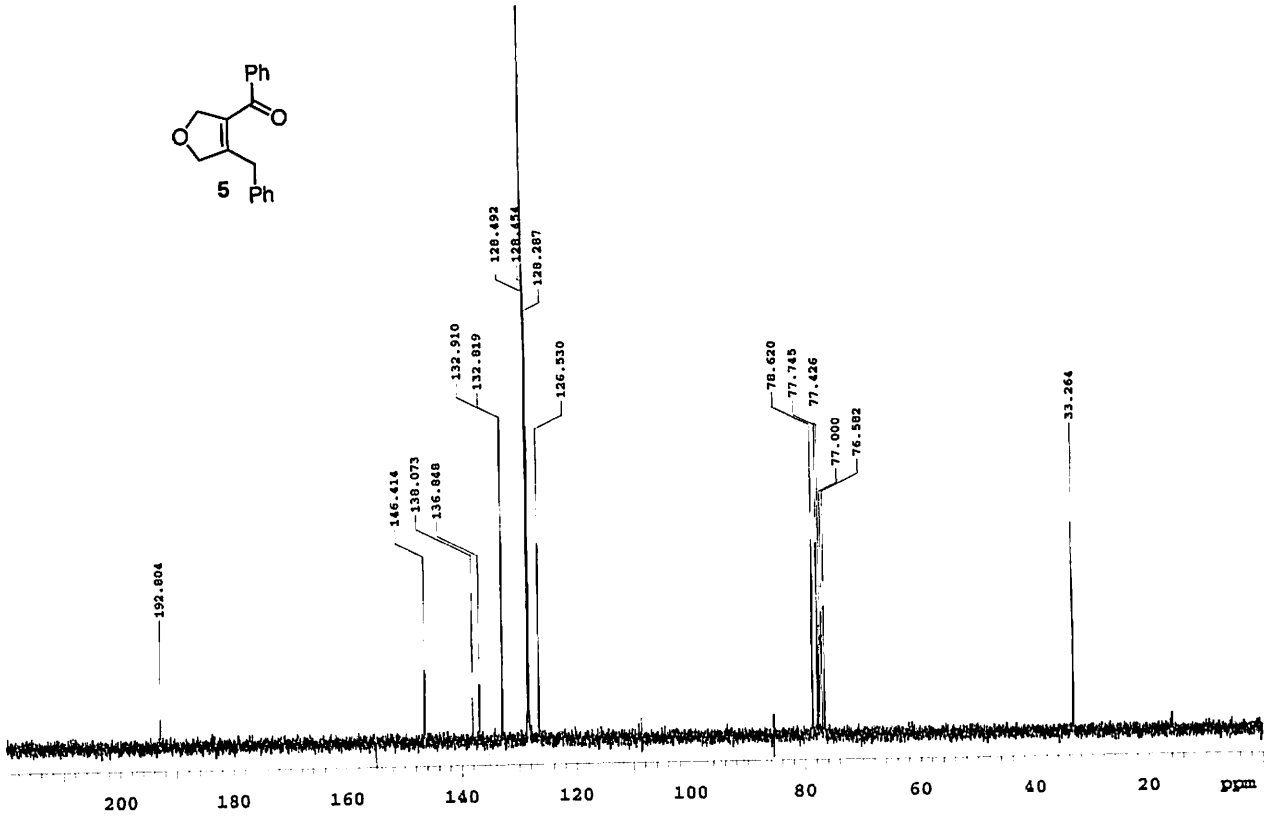
4
3
2
1
ppm
1.84 2.07 1.95
1.07 4.05
2.06
2.05
2.00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126.530
78.620
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77.000
76.582
33.264
200
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140
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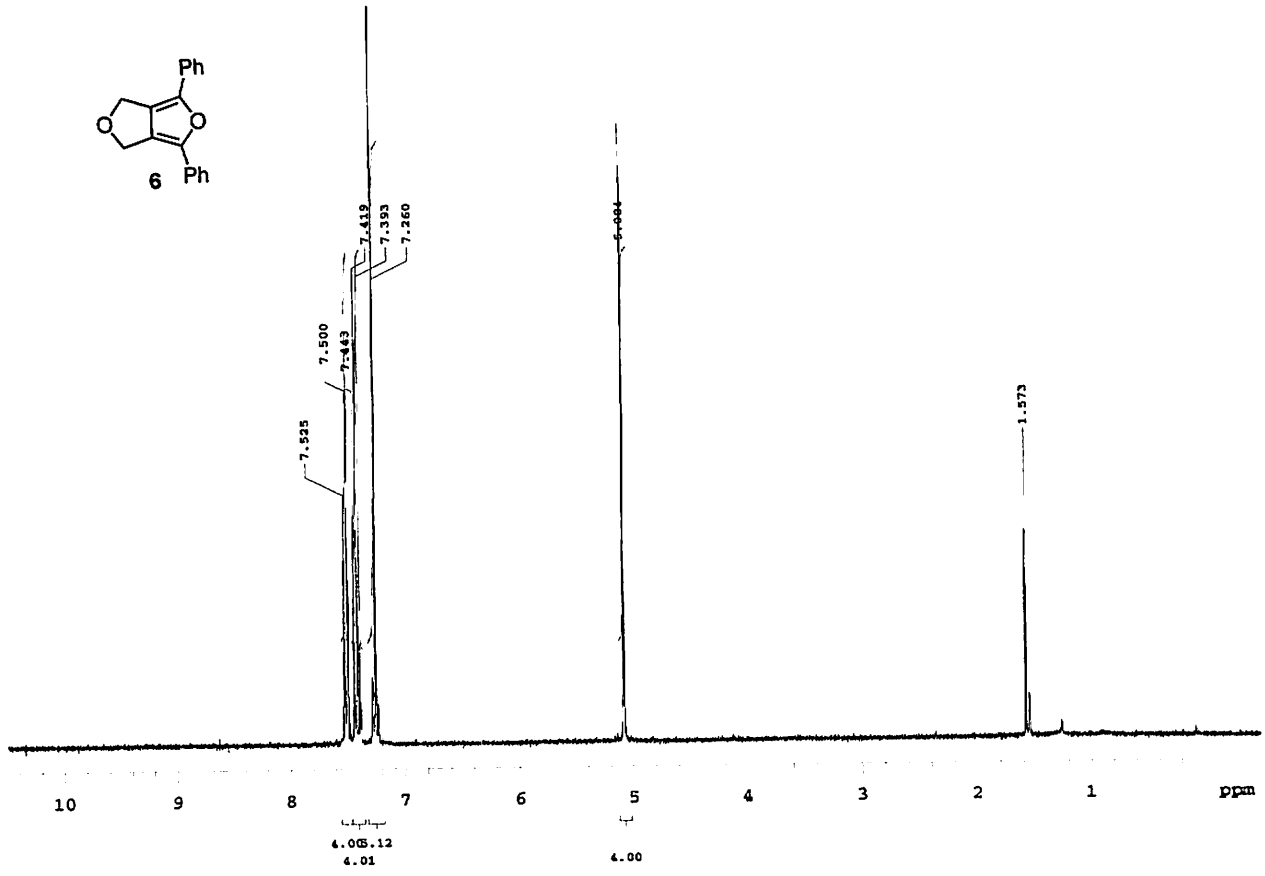
20
ppm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O
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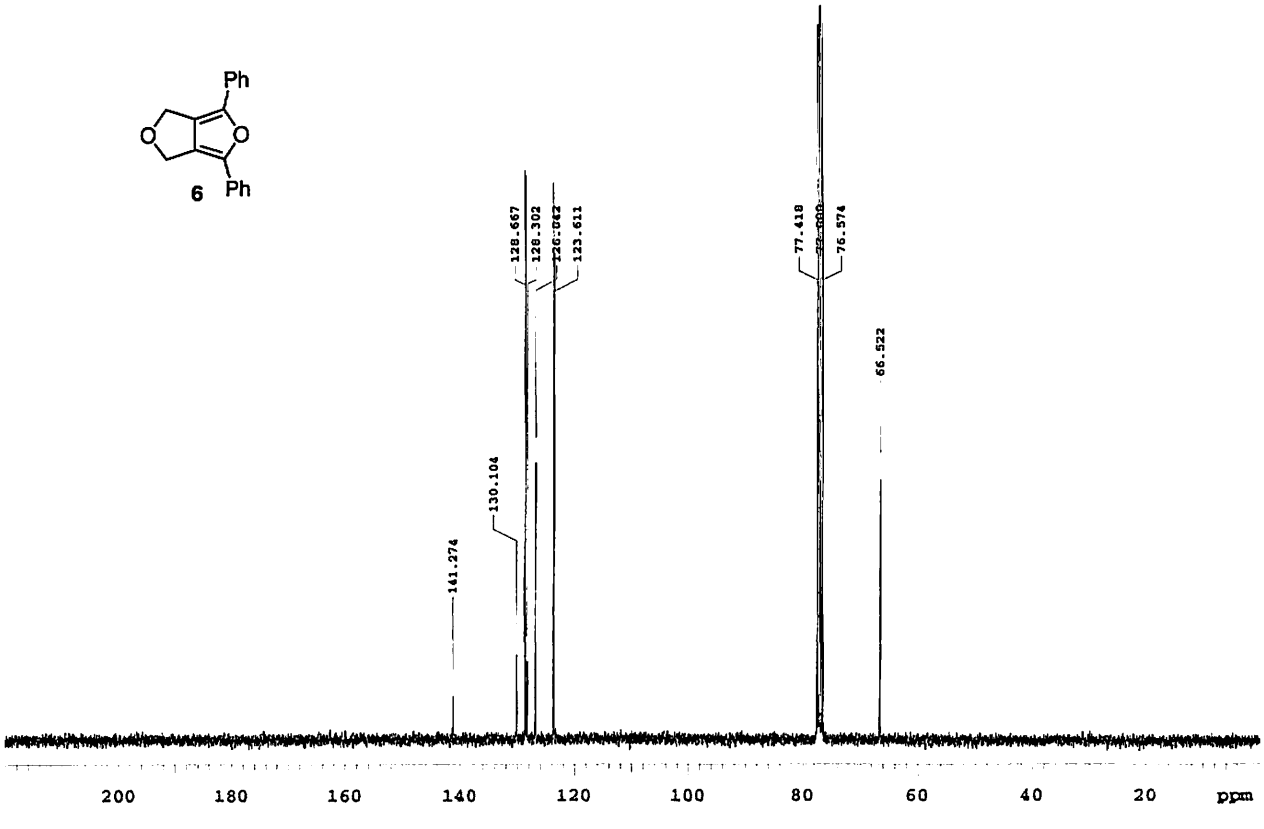
9
8
7
6
5
4
3
2
1
ppm
4.05
5.12
4.01
4.00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200
180
160
140
120
100
80
60
40
20
ppm