

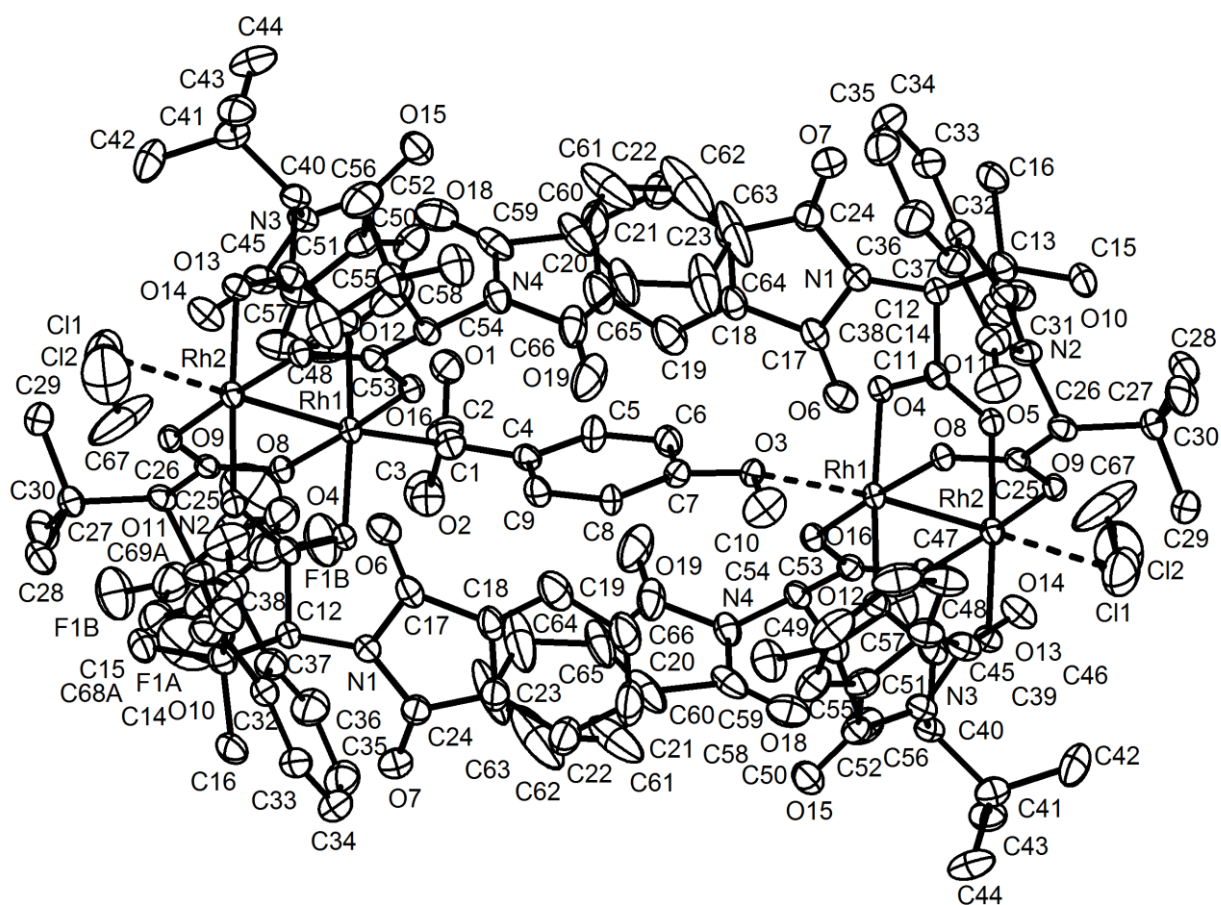
## Supporting Information

### **Stabilization of a Chiral Dirhodium Carbene by Encapsulation and a Discussion of the Stereochemical Implications**

*Christophe Werlé, Richard Goddard, Petra Philipps, Christophe Farès, and Alois Fürstner\**

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## CRYSTALLOGRAPHIC INFORMATION



**Figure S1.** Molecular structure of  $[(S^*-10)-(R^*-4)]$ . One component of the disordered carbene ligand is shown and H atoms are omitted for clarity.



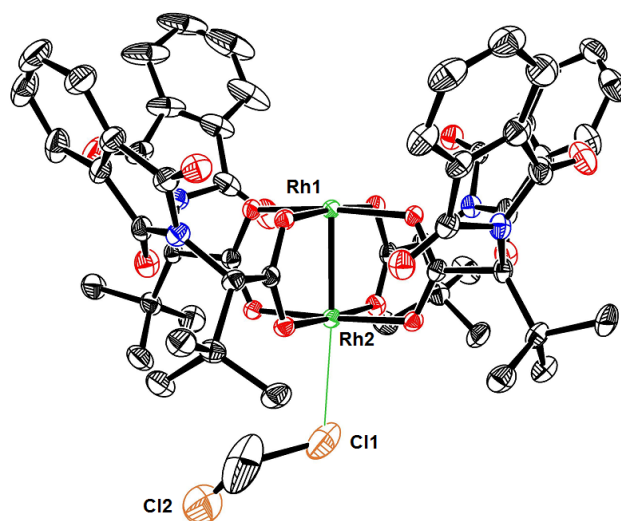
**Figure S2.** Photograph of a crystal of  $[(S^*-10)(R^*-4)]$

**X-ray Crystal Structure Analysis of [(S\*-10)·(R\*-4)]:**  $2(\text{C}_{124}\text{H}_{126}\text{Cl}_4\text{N}_8\text{O}_{35}\text{Rh}_4) \cdot 2(\text{C}_6\text{H}_5\text{F})$ ,  $M_r = 5875.72 \text{ g} \cdot \text{mol}^{-1}$ , green elongated plate, crystal size  $0.039 \times 0.049 \times 0.103 \text{ mm}^3$ , monoclinic, space group  $P2_1/n$ ,  $a = 13.480(8) \text{ \AA}$ ,  $b = 20.421(11) \text{ \AA}$ ,  $c = 23.499(13) \text{ \AA}$ ,  $\beta = 98.092(10)^\circ$ ,  $V = 6404(3) \text{ \AA}^3$ ,  $T = 100(2) \text{ K}$ ,  $Z = 1$ ,  $D_{\text{calc}} = 1.524 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 0.674 \text{ mm}^{-1}$ , Gaussian absorption correction ( $T_{\text{min}} = 0.95415$ ,  $T_{\text{max}} = 0.98016$ ), Bruker AXS Enraf-Nonius KappaCCD diffractometer,  $1.823 < \theta < 35.187^\circ$ , 233659 measured reflections, 28484 independent reflections, 17346 reflections with  $I > 2\sigma(I)$ ,  $R_{\text{int}} = 0.115$ .

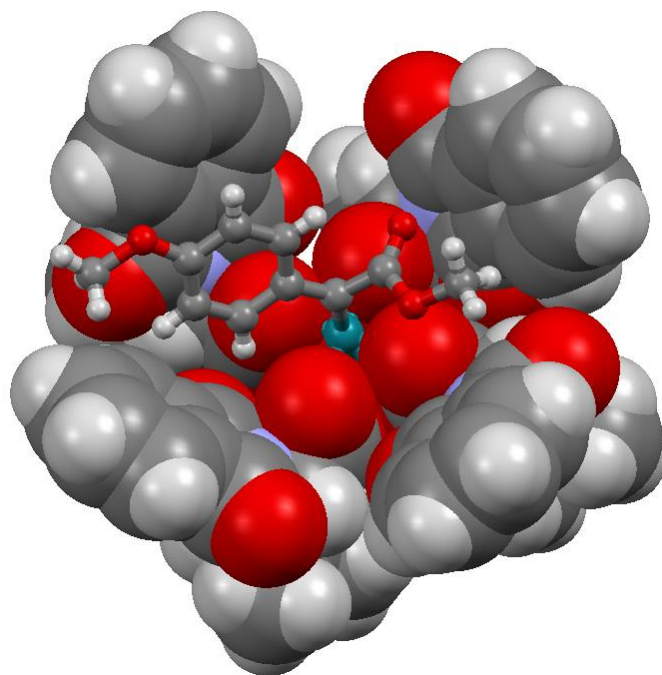
INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.55	440	443	99.3	11.40	27.95	54.91	0.0213	0.0117
2.55 - 1.69	1027	1027	100.0	12.16	17.81	45.34	0.0271	0.0131
1.69 - 1.34	1457	1457	100.0	12.11	9.64	34.21	0.0405	0.0175
1.34 - 1.17	1454	1454	100.0	11.62	6.14	25.24	0.0603	0.0253
1.17 - 1.06	1479	1479	100.0	10.72	5.03	20.48	0.0769	0.0335
1.06 - 0.98	1516	1516	100.0	9.97	4.21	16.90	0.0952	0.0427
0.98 - 0.92	1552	1552	100.0	9.34	3.42	13.50	0.1177	0.0549
0.92 - 0.87	1592	1592	100.0	8.83	2.76	10.58	0.1438	0.0700
0.87 - 0.84	1141	1141	100.0	8.36	2.37	8.89	0.1686	0.0852
0.84 - 0.80	1830	1830	100.0	8.09	1.96	7.50	0.2053	0.1057
0.80 - 0.77	1644	1644	100.0	7.64	1.67	6.13	0.2476	0.1309
0.77 - 0.75	1197	1197	100.0	7.36	1.35	4.86	0.3036	0.1678
0.75 - 0.73	1392	1392	100.0	7.11	1.30	4.48	0.3248	0.1814
0.73 - 0.71	1508	1508	100.0	6.86	1.17	3.97	0.3680	0.2116
0.71 - 0.69	1715	1715	100.0	6.63	1.03	3.37	0.4135	0.2506
0.69 - 0.68	921	921	100.0	6.41	0.95	3.06	0.4496	0.2840
0.68 - 0.66	2040	2046	99.7	6.19	0.74	2.30	0.5491	0.3759
0.66 - 0.65	1090	1090	100.0	6.01	0.64	1.99	0.5985	0.4470
0.65 - 0.63	2461	2483	99.1	5.72	0.46	1.36	0.7402	0.6534
0.63 - 0.62	1692	1752	96.6	4.92	0.38	1.04	0.8226	0.9439
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0.72 - 0.62	10710	10798	99.2	5.99	0.70	2.20	0.5555	0.4138
Inf - 0.62	29148	29239	99.7	8.10	3.36	11.10	0.1046	0.0697
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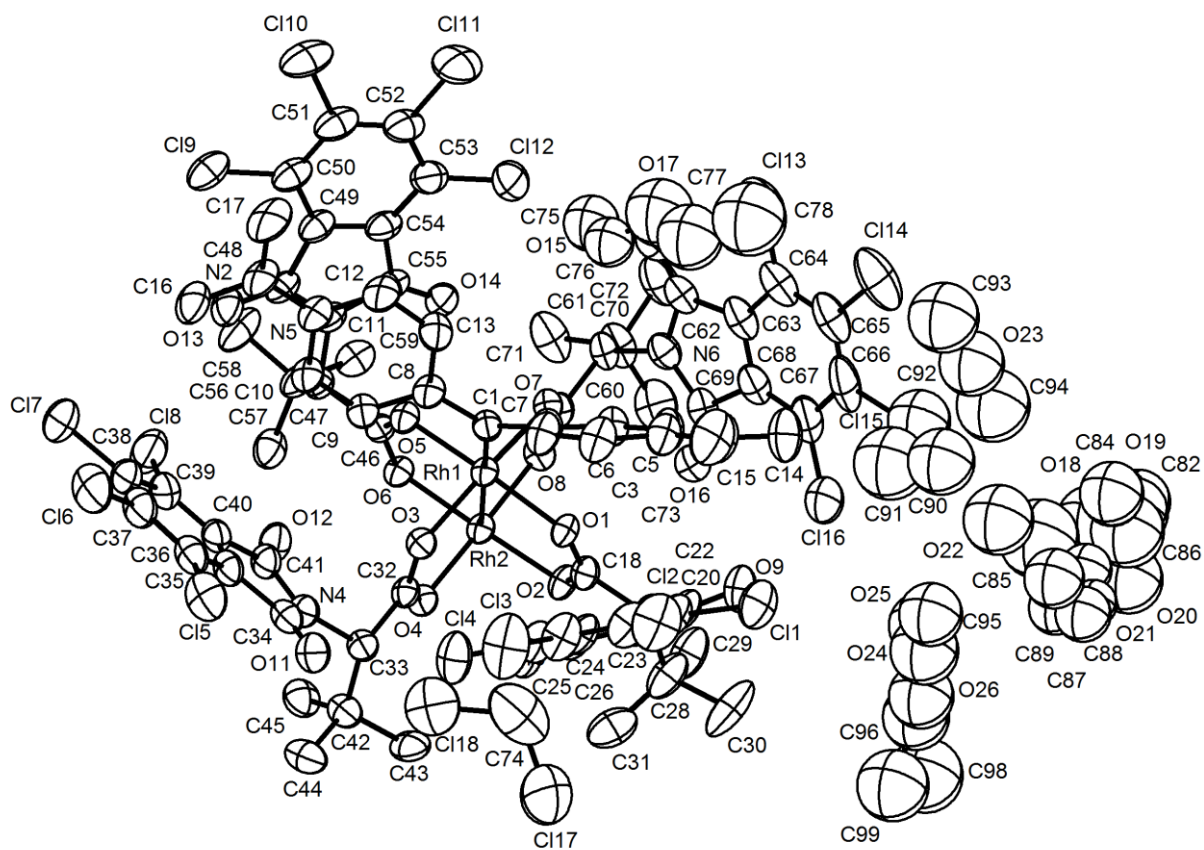
The structure was solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.059$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.173$ , 906 parameters. Several low-angle reflections were shadowed by the beamstop and removed from the data set before the final refinement cycles. The fluorobenzene solute is slightly disordered. The carbene ligand is disordered over two positions, each with half occupancy. The disorder could be resolved. Because of the closeness of C1 and O3[1-x, 1-y, 1-z] to one another, the atomic displacement parameters of C1 and O3 were restrained to be isotropic with an effective standard deviation of 0.001. H atoms riding,  $S = 1.244$ , residual electron density 3.12 (0.09  $\text{\AA}$  from Cl2)/ -3.01 (0.65  $\text{\AA}$  from Rh2)  $\text{e} \text{\AA}^{-3}$ . **CCDC-1481519**.



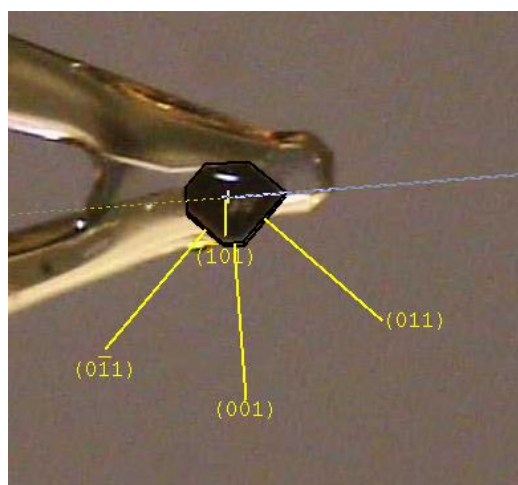
**Figure S3.** Projection showing that the aperture of the chiral calyx in [(*S*-10)·(*R*-4)] about Rh1 is larger than the pore on the backside, which, however, is still wide enough to accommodate a CH<sub>2</sub>Cl<sub>2</sub> ligand; the push/pull carbene unit bonded to Rh1 and the (*R*-4) unit have been removed for clarity



**Figure S4.** Space-filling model of the *S*-10 unit



**Figure S5.** Molecular structure of *S-13*; hydrogen atoms omitted for clarity



**Figure S6.** Photograph of the mounted crystal of *S-13*

**X-ray Crystal Structure Analysis of S-13:** (C<sub>73</sub>H<sub>60</sub>Cl<sub>16</sub>N<sub>6</sub>O<sub>16</sub>Rh<sub>2</sub>)·CH<sub>2</sub>Cl<sub>2</sub>·3(C<sub>4</sub>H<sub>10</sub>O),  $M_r = 2332.37 \text{ g} \cdot \text{mol}^{-1}$ , green-red prism, crystal size 0.090 x 0.174 x 0.184 mm<sup>3</sup>, monoclinic, space group  $P2_1$ ,  $a = 12.169(6) \text{ \AA}$ ,  $b = 21.543(12) \text{ \AA}$ ,  $c = 21.920(10) \text{ \AA}$ ,  $\beta = 105.183(10)^\circ$ ,  $V = 5546(5) \text{ \AA}^3$ ,  $T = 200(2) \text{ K}$ ,  $Z = 2$ ,  $D_{calc} = 1.397 \text{ g} \cdot \text{cm}^{-3}$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 0.792 \text{ mm}^{-1}$ , Gaussian absorption correction ( $T_{min} = 0.89426$ ,  $T_{max} = 0.93711$ ), Bruker AXS Enraf-Nonius KappaCCD diffractometer,  $2.923 < \theta < 28.476^\circ$ , 107627 measured reflections, 27743 independent reflections, 22737 reflections with  $I > 2\sigma(I)$ ,  $R_{int} = 0.043$ .

INTENSITY STATISTICS FOR DATASET

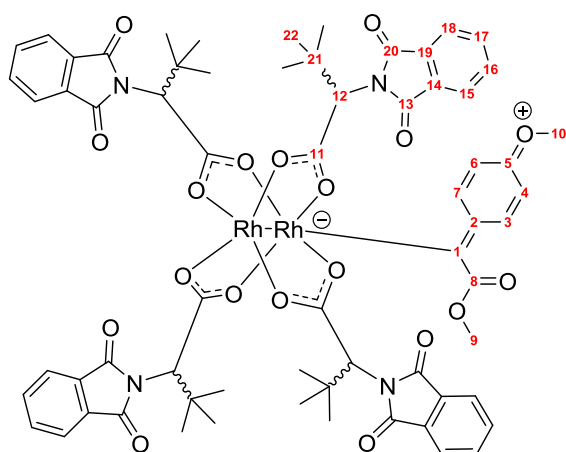
Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.98	420	443	94.8	4.76	126.17	60.43	0.0244	0.0153
2.98 - 2.00	994	1018	97.6	5.02	83.13	58.44	0.0220	0.0154
2.00 - 1.60	1376	1398	98.4	5.03	46.47	49.25	0.0243	0.0171
1.60 - 1.40	1379	1393	99.0	5.01	28.12	40.65	0.0297	0.0197
1.40 - 1.27	1445	1450	99.7	4.92	22.49	35.05	0.0345	0.0226
1.27 - 1.18	1360	1369	99.3	4.71	16.65	28.81	0.0420	0.0278
1.18 - 1.11	1429	1431	99.9	4.45	13.36	23.52	0.0466	0.0339
1.11 - 1.05	1555	1558	99.8	4.22	11.71	20.48	0.0543	0.0393
1.05 - 1.01	1226	1227	99.9	4.06	9.37	16.83	0.0639	0.0473
1.01 - 0.97	1490	1490	100.0	3.90	7.83	14.55	0.0750	0.0567
0.97 - 0.94	1228	1228	100.0	3.77	7.29	13.36	0.0790	0.0619
0.94 - 0.91	1431	1431	100.0	3.64	5.87	11.09	0.0958	0.0757
0.91 - 0.88	1609	1609	100.0	3.54	5.12	9.75	0.1124	0.0880
0.88 - 0.86	1232	1232	100.0	3.42	4.15	7.96	0.1311	0.1076
0.86 - 0.84	1375	1375	100.0	3.33	3.84	7.22	0.1390	0.1195
0.84 - 0.82	1447	1447	100.0	3.27	3.57	6.59	0.1517	0.1310
0.82 - 0.80	1614	1614	100.0	3.13	3.00	5.55	0.1819	0.1613
0.80 - 0.78	1813	1813	100.0	3.06	2.78	4.99	0.1948	0.1783
0.78 - 0.77	926	926	100.0	3.04	2.38	4.26	0.2189	0.2093
0.77 - 0.75	2443	2635	92.7	2.56	2.19	3.63	0.2530	0.2499
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0.85 - 0.75	8965	9157	97.9	2.98	2.83	5.06	0.1892	0.1770
Inf - 0.75	27792	28087	98.9	3.84	14.84	18.46	0.0420	0.0367
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The structure was solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.043 [I > 2\sigma(I)]$ ,  $wR_2 = 0.129$ , 1201 parameters. Several low-angle reflections were shadowed by the beamstop and removed from the data set before final refinement. The crystal contains non-disordered solute dichloromethane and partially-occupied diethylether molecules in the asymmetric unit, all but one of which are disordered. Disordered diethylether molecules were modelled by C and O atoms with varying occupancy and isotropic atomic displacement parameters, while maintaining an atomic ratio of 4 to 1, respectively. H atoms on disordered atoms could not be located, otherwise H atoms were calculated and refined using a riding model.  $S = 1.054$ , residual electron density 0.78 (0.91 Å from Rh1)/ -0.84 (0.78 Å from Rh1) e Å<sup>-3</sup>. **CCDC-1481518**.

**General.** All reactions were carried out under argon in flame-dried glassware, ensuring rigorously inert conditions. The solvents were purified by distillation over the indicated drying agents and were stored/handled under argon: CH<sub>2</sub>Cl<sub>2</sub> (CaH<sub>2</sub>), diethylether (CaH<sub>2</sub>), fluorobenzene (CaH<sub>2</sub>), hexane (Na/K), pentane (Na/K), toluene (Na/K). NMR: Spectra were recorded on Bruker AV300, AV400, AV500, or AV600 spectrometers at the indicated temperatures with the chemical shifts ( $\delta$ ) given in ppm relative to TMS and the coupling constants ( $J$ ) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CD<sub>2</sub>Cl<sub>2</sub>:  $\delta_{\text{H}}$  = 5.32 ppm,  $\delta_{\text{C}}$  = 53.8 ppm); <sup>15</sup>N NMR spectra are referenced to external H<sub>3</sub>CNO<sub>2</sub>; UV/VIS: UV-1650PC spectrophotometer (Shimadzu). HRMS (ESI): ESQ3000 (Bruker). The different rhodium precursors were purchased from Strem Chemicals or TCI Europe and used as received. The different diazoalkane derivatives were prepared according to literature procedures.<sup>1</sup>

### Preparation of the Chiral Rhodium Carbenes

**Complex [(S\*-10)(R\*-4)].** A solution of diazoalkane **9a** (2.90 mg, 0.01 mmol) in fluorobenzene (0.5

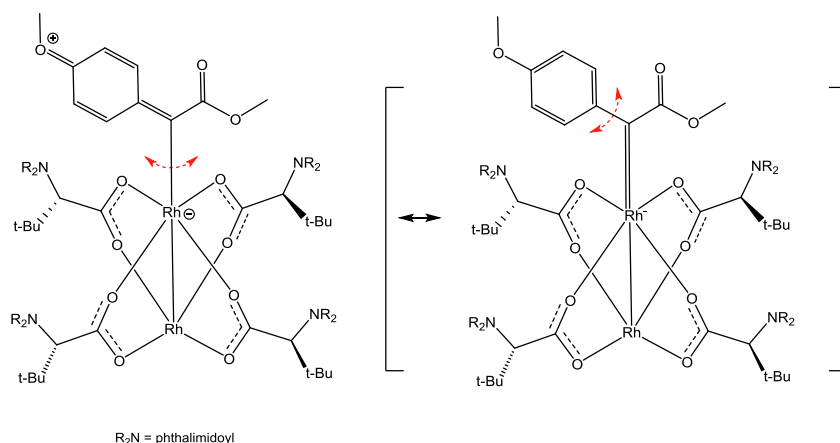


mL) was quickly added to a solution of a 1:1 mixture of [Rh<sub>2</sub>(S-PTTL)<sub>4</sub>].2EtOAc and [Rh<sub>2</sub>(R-PTTL)<sub>4</sub>].2EtOAc (10 mg each, 0.01 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) at -5 °C under rigorously inert conditions. A vigorous effervescence and concomitant color change were observed. Emerald green crystals of the resulting carbene suitable for X-ray diffraction were obtained by layering the solution with cold toluene (1 mL) and hexane (5 mL) at -30 °C.

For the characterization of the complex by NMR, the following procedure was used: A solution of diazoalkane **9a** (2.90 mg, 0.01 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (1 mL) was quickly added to a solution of a 1:1 mixture of [Rh<sub>2</sub>(S-PTTL)<sub>4</sub>].2EtOAc and [Rh<sub>2</sub>(R-PTTL)<sub>4</sub>].2EtOAc (10 mg each, 0.01 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (1 mL) at -5 °C under rigorously inert conditions. A vigorous effervescence and concomitant color change were observed. The solution was stirred at -5 °C for 2 min before it was transferred into a carefully dried NMR tube under inert conditions via canula and cooled to -50 °C. The complex showed the following spectral characteristics: UV/VIS:  $\lambda_{\text{max}}$  [nm] = 725; <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223 K):  $\delta$  = 7.76 (br. s, 4H,

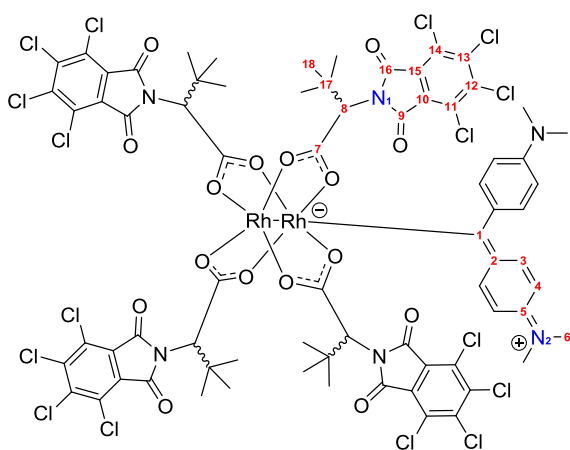
<sup>1</sup> a) Chan, W.-W.; Yeung, S.-H.; Zhou, Z.; Chan, A. S. C.; Yu, W.-Y. *Org. Lett.* **2010**, *12*, 604; b) Hu, M.; He, Z.; Gao, B.; Li, L.; Ni, C.; Hu, J. *J. Am. Chem. Soc.* **2013**, *135*, 17302; c) Miller, J. B. *J. Org. Chem.* **1959**, *24*, 560; d) Kumar, S.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 1040; e) for the synthesis of the required imines used as starting materials, see: Fergus, S.; Eustace, S. J.; Hegarty, A. F. *J. Org. Chem.* **2004**, *69*, 4663; f) Pickard, P. L.; Tolbert, T. L. *J. Org. Chem.* **1961**, *26*, 4886.

H<sub>18</sub>), 7.74 – 7.72 (m, 4H, H<sub>15</sub>), 7.68 – 7.62 (m, 9H, H<sub>7</sub>, H<sub>17</sub>, H<sub>16</sub>), 7.56 (d, *J* = 7.2, 1H, H<sub>3</sub>), 6.29 (br. s, 1H, H<sub>4</sub>), 4.83 (br. s, 1H, H<sub>6</sub>), 4.67 (s, 4H, H<sub>12</sub>), 3.44 (br. s, 3H, H<sub>9</sub>), 2.69 (br. s, 3H, H<sub>10</sub>), 0.99 (s, 36H, H<sub>22</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223 K): δ = 240.7 (br. s, C<sub>1</sub>), 185.6 (C<sub>11</sub>), 173.5 (br., C<sub>8</sub>), 170.5 (C<sub>5</sub>), 168.1 (C<sub>13</sub>), 166.9 (C<sub>20</sub>), 147.5 (br., C<sub>7</sub>), 142.7 (br., C<sub>2</sub>), 137.6 (C<sub>3</sub>), 133.7 (C<sub>17</sub>), 133.5 (C<sub>16</sub>), 131.6 (C<sub>14</sub>), 131.5 (C<sub>19</sub>), 123.1 (C<sub>18</sub>), 122.7 (C<sub>15</sub>), 115.5 (C<sub>4</sub>), 114.8 (br., C<sub>6</sub>), 60.6 (C<sub>12</sub>), 56.8 (C<sub>9</sub>), 50.0 (C<sub>10</sub>), 35.4 (C<sub>21</sub>), 27.3 (C<sub>22</sub>); <sup>15</sup>N NMR (51 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223 K): δ = -213.2; HRMS (ESI<sup>+</sup>): calcd. for [C<sub>66</sub>H<sub>67</sub>N<sub>4</sub>O<sub>19</sub>Rh<sub>2</sub>]<sup>+</sup>: 1425.24900, found 1425.24848.



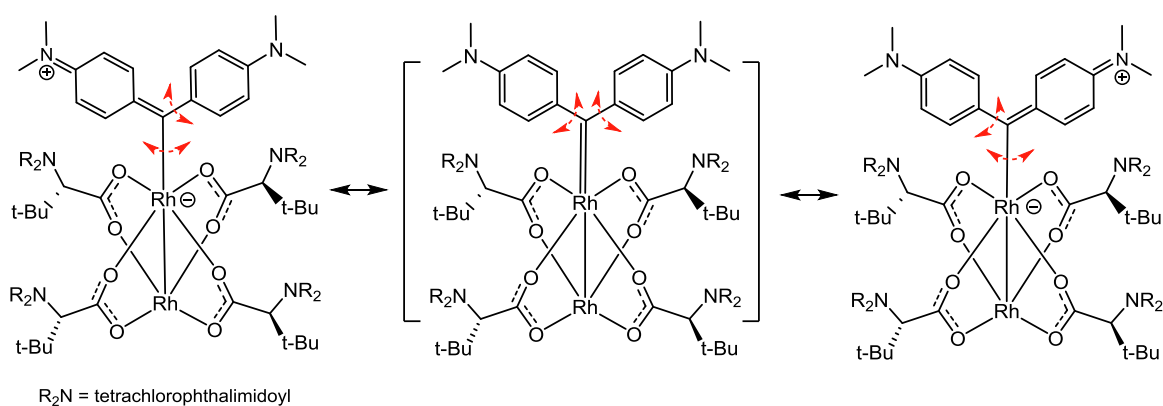
The unique set of NMR chemical shifts for the four coordinated ligands in the di-rhodium complex point to a 4-fold symmetry, indicating rotation of the carbene ligand about the Rh-C1 bond that is faster than the NMR time scale (> 10 μs) as well as equivalent conformational space available to the four chiral ligands. Conversely, the electron-donating methoxyphenyl substituent presents two inequivalent yet slowly exchangeable halves (as determined by NOESY/EXSY), suggesting a predominantly hindered rotation about the C1-C2 bond. Therefore, it is proposed that the electronic distribution is such that the C1-C2 has higher bond order than the C1-Rh bond.

**Complex S-13.** A solution of diazoalkane **12** (2.84 mg, 0.01 mmol) in fluorobenzene (0.5 mL) was added dropwise to a solution of a 1:1 mixture of [Rh<sub>2</sub>(S-TCPTTL)<sub>4</sub>]<sub>2</sub>·2EtOAc and [Rh<sub>2</sub>(R-TCPTTL)<sub>4</sub>]<sub>2</sub>·2EtOAc (10 mg each, 0.01 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) at 0 °C under rigorously inert conditions. A vigorous effervescence and concomitant color change were observed. Red-green crystals of the resulting carbene suitable for X-ray diffraction were obtained by layering the solution with cold diethylether/toluene (0.5/0.5 mL) and hexane (5 mL) at -20 °C.



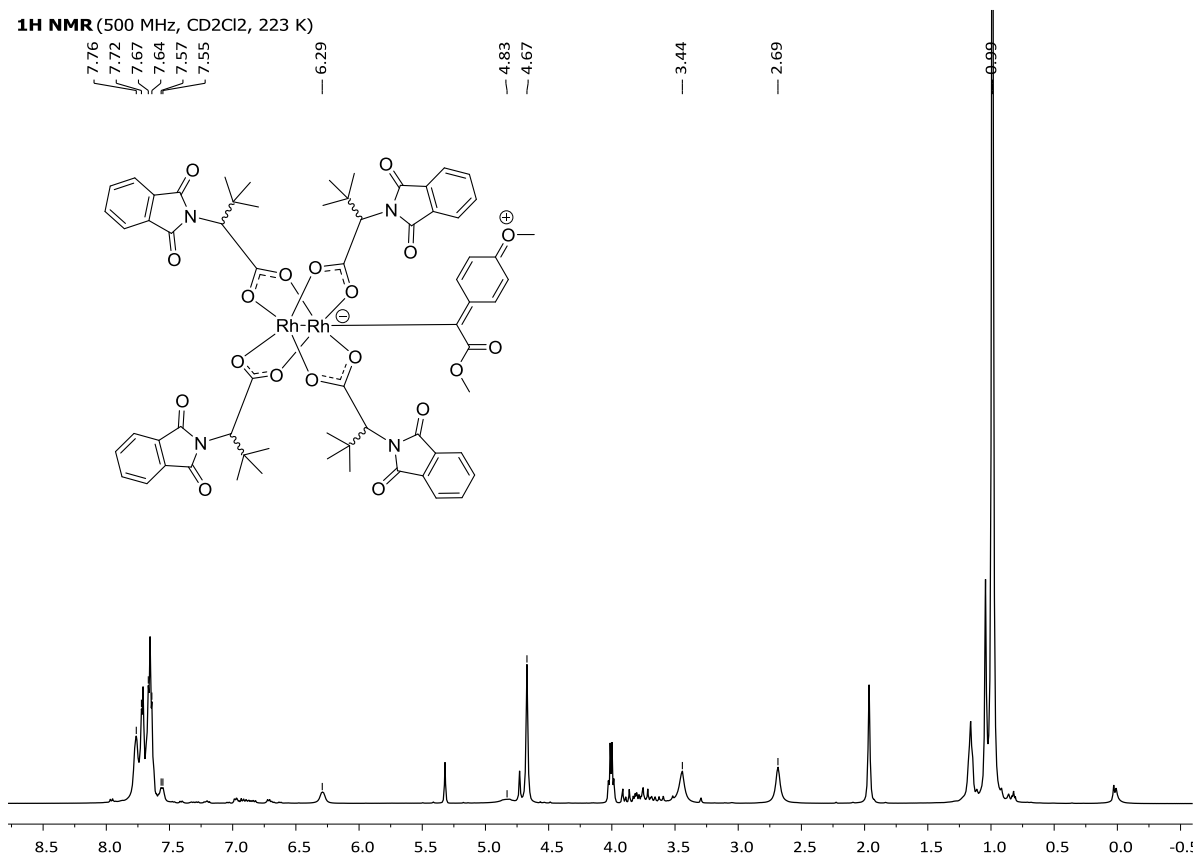


For the characterization of the complex by NMR, the following procedure was used: A solution of diazoalkane **12** (2.84 mg, 0.01 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (1 mL) was added dropwise to a solution of a 1:1 mixture of [Rh<sub>2</sub>(*S*-TCPTTL)<sub>4</sub>]-2EtOAc and [Rh<sub>2</sub>(*R*-TCPTTL)<sub>4</sub>]-2EtOAc (10 mg each, 0.01 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (1 mL) at 0 °C under rigorously inert conditions. A vigorous effervescence and concomitant color were observed. The solution was stirred at 0 °C for 5 min before it was transferred into a carefully dried NMR tube under inert conditions via canula. The complex showed the following spectral characteristics: UV/VIS: λ<sub>max</sub> [nm] = 582; <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 273 K): δ = 6.87 (d, *J*=9.2, 4H, H<sub>3</sub>), 5.65 (d, *J*=9.2, 4H, H<sub>4</sub>), 4.61 (s, 4H, H<sub>8</sub>), 2.78 (s, 12H, H<sub>6</sub>), 1.02 (s, 36H, H<sub>18</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 273 K): δ = 252.0 (br. s, C<sub>1</sub>), 183.1 (C<sub>7</sub>), 163.5 (C<sub>9</sub>), 162.6 (C<sub>16</sub>), 153.0 (C<sub>5</sub>), 139.8 (C<sub>2</sub>), 139.4 (C<sub>12</sub>), 139.2 (C<sub>13</sub>), 136.3 (C<sub>3</sub>), 129.5 (C<sub>10</sub>), 129.0 (C<sub>15</sub>), 127.6 (C<sub>11</sub>), 127.5 (C<sub>14</sub>), 108.7 (C<sub>4</sub>), 62.0 (C<sub>8</sub>), 40.3 (C<sub>6</sub>), 35.9 (C<sub>17</sub>), 27.7 (C<sub>18</sub>); <sup>15</sup>N NMR (51 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 273 K): δ -310.99 (N<sub>2</sub>), -210.79 (N<sub>1</sub>); HRMS (ESI+): calcd. for [C<sub>73</sub>H<sub>60</sub>N<sub>6</sub>O<sub>16</sub>Cl<sub>16</sub>Rh<sub>2</sub>]<sup>+</sup>: 2041.71868, found 2041.71963.

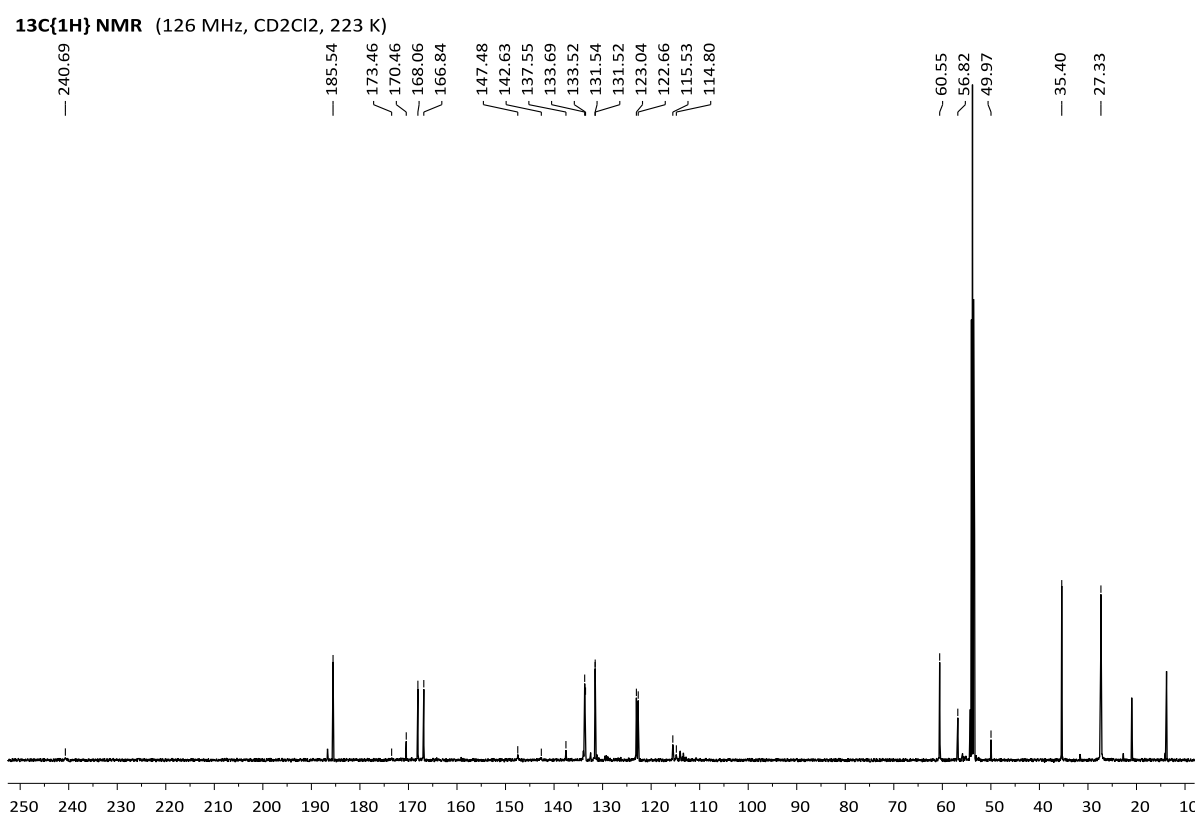


A single set of NMR chemical shifts at 273K indicate a 4-fold symmetry, implying again relatively facile rotation of the carbene ligand about the Rh-C1 bond and identical average conformation of the chiral ligands in **S-13**. In contrast to [(*S*\*-**10**)(*R*\*-**4**)], however, the NMR degeneracy within the aromatic dimethylaminophenyl groups also suggests facile rotation about the C1-C2 bond (faster than μs). Since the carbene has two equivalent electron-donating substituents, it is conceivable that the partial π-character of the C1-C2 bond is shared between each halves; in so doing, it averages out and allows for some degree of rotational freedom at the somewhat higher temperature used to record the spectra (273K compared with 223K for [(*S*\*-**10**)(*R*\*-**4**)]).

**<sup>1</sup>H NMR** (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223 K)



**<sup>13</sup>C{<sup>1</sup>H} NMR** (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223 K)



NS07A99

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 P1: 10.00 usec  
 P2: 24.00000000 W

===== CHANNEL f2 =====  
 Name: 499.873019 MHz  
 P1: 10.00 usec  
 P2: 24.00000000 W

===== Processing parameters =====  
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 ASB: 0  
 ZF: 0.30 Hz  
 GB: 0  
 PC: 1.00

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 FIDRES: 0.250967 Hz  
 AQ: 1.397560 sec  
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 DE: 10.00 usec  
 TE: 320.0 K  
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 DS: 2  
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 FIDRES: 0.250967 Hz  
 AQ: 1.397560 sec  
 RG: 50.8  
 DF: 60.800 usec  
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===== Processing parameters =====  
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 ASB: 0  
 ZF: 0.30 Hz  
 GB: 0  
 PC: 1.00

===== Acquisition Parameters =====  
 Date\_: 20160302  
 Time: 15.59  
 INSTRUM: spect  
 PROGRAM: zgpg30  
 PULPROG: zgpg30  
 SOLVENT: DMS  
 DS: 2  
 SWH: 8223.685 Hz  
 FIDRES: 0.250967 Hz  
 AQ: 1.397560 sec  
 RG: 50.8  
 DF: 60.800 usec  
 DE: 10.00 usec  
 TE: 320.0 K  
 TD: 0.01000001 sec  
 TDO: 0

===== Processing parameters =====  
 SI: 32768  
 SF: 499.8700195 MHz  
 ASB: 0  
 ZF: 0.30 Hz  
 GB: 0  
 PC: 1.00

===== Acquisition Parameters =====  
 Date\_: 20160302  
 Time: 15.59  
 INSTRUM: spect  
 PROGRAM: zgpg30  
 PULPROG: zgpg30  
 SOLVENT: DMS  
 DS: 2  
 SWH: 8223.685 Hz  
 FIDRES: 0.250967 Hz  
 AQ: 1.397560 sec  
 RG: 50.8  
 DF: 60.800 usec  
 DE: 10.00 usec  
 TE: 320.0 K  
 TD: 0.01000001 sec  
 TDO: 0

===== Processing parameters =====  
 SI: 32768  
 SF: 499.8700195 MHz  
 ASB: 0  
 ZF: 0.30 Hz  
 GB: 0  
 PC: 1.00

===== Acquisition Parameters =====  
 Date\_: 20160302  
 Time: 15.59  
 INSTRUM: spect  
 PROGRAM: zgpg30  
 PULPROG: zgpg30  
 SOLVENT: DMS  
 DS: 2  
 SWH: 8223.685 Hz  
 FIDRES: 0.250967 Hz  
 AQ: 1.397560 sec  
 RG: 50.8  
 DF: 60.800 usec  
 DE: 10.00 usec  
 TE: 320.0 K  
 TD: 0.01000001 sec  
 TDO: 0

===== Processing parameters =====  
 SI: 32768  
 SF: 499.8700195 MHz  
 ASB: 0  
 ZF: 0.30 Hz  
 GB: 0  
 PC: 1.00

===== Acquisition Parameters =====  
 Date\_: 20160302  
 Time: 15.59  
 INSTRUM: spect  
 PROGRAM: zgpg30  
 PULPROG: zgpg30  
 SOLVENT: DMS  
 DS: 2  
 SWH: 8223.685 Hz  
 FIDRES: 0.250967 Hz  
 AQ: 1.397560 sec  
 RG: 50.8  
 DF: 60.800 usec  
 DE: 10.00 usec  
 TE: 320.0 K  
 TD: 0.01000001 sec  
 TDO: 0

===== Processing parameters =====  
 SI: 32768  
 SF: 499.8700195 MHz  
 ASB: 0  
 ZF: 0.30 Hz  
 GB: 0  
 PC: 1.00

===== Acquisition Parameters =====  
 Date\_: 20160302  
 Time: 15.59  
 INSTRUM: spect  
 PROGRAM: zgpg30  
 PULPROG: zgpg30  
 SOLVENT: DMS  
 DS: 2  
 SWH: 8223.685 Hz  
 FIDRES: 0.250967 Hz  
 AQ: 1.397560 sec  
 RG: 50.8  
 DF: 60.800 usec  
 DE: 10.00 usec  
 TE: 320.0 K  
 TD: 0.01000001 sec  
 TDO: 0

===== Processing parameters =====  
 SI: 32768  
 SF: 499.8700195 MHz  
 ASB: 0  
 ZF: 0.30 Hz  
 GB: 0  
 PC: 1.00

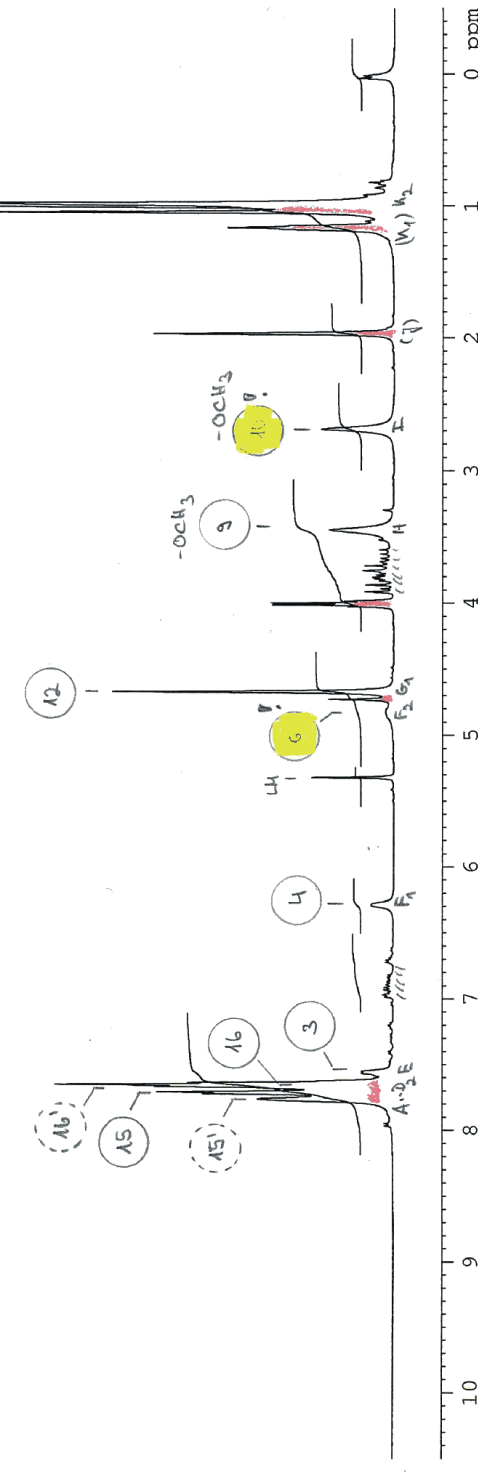
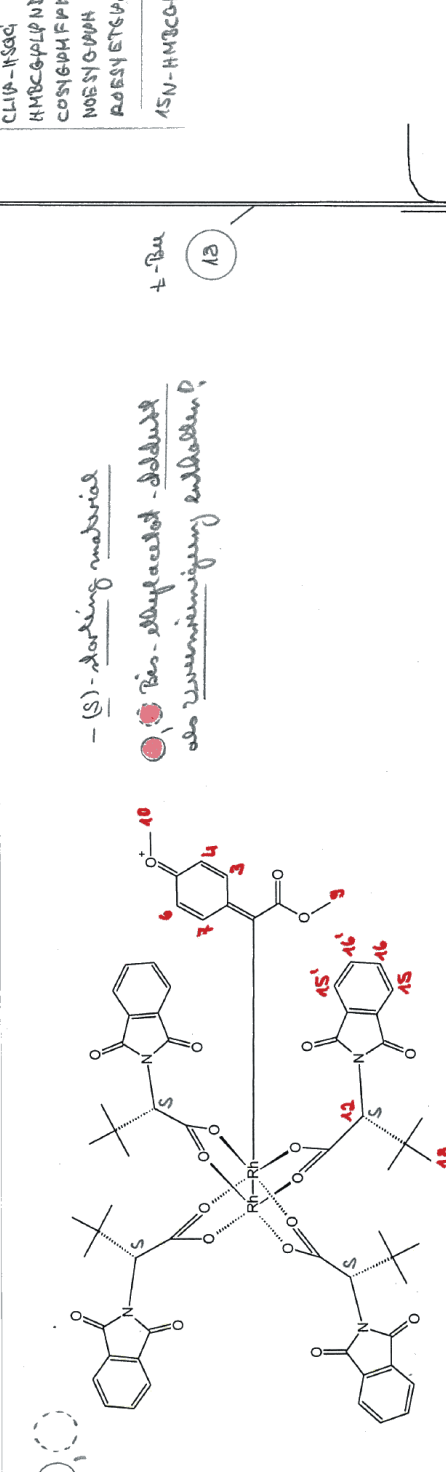
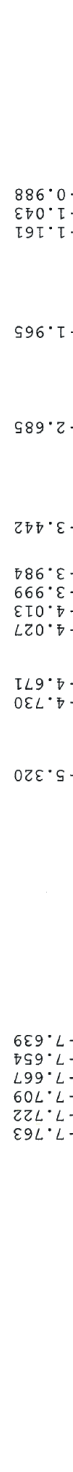
===== Acquisition Parameters =====  
 Date\_: 20160302  
 Time: 15.59  
 INSTRUM: spect  
 PROGRAM: zgpg30  
 PULPROG: zgpg30  
 SOLVENT: DMS  
 DS: 2  
 SWH: 8223.685 Hz  
 FIDRES: 0.250967 Hz  
 AQ: 1.397560 sec  
 RG: 50.8  
 DF: 60.800 usec  
 DE: 10.00 usec  
 TE: 320.0 K  
 TD: 0.01000001 sec  
 TDO: 0

===== Processing parameters =====  
 SI: 32768  
 SF: 499.8700195 MHz  
 ASB: 0  
 ZF: 0.30 Hz  
 GB: 0  
 PC: 1.00

===== Acquisition Parameters =====  
 Date\_: 20160302  
 Time: 15.59  
 INSTRUM: spect  
 PROGRAM: zgpg30  
 PULPROG: zgpg30  
 SOLVENT: DMS  
 DS: 2  
 SWH: 8223.685 Hz  
 FIDRES: 0.250967 Hz  
 AQ: 1.397560 sec  
 RG: 50.8  
 DF: 60.800 usec  
 DE: 10.00 usec  
 TE: 320.0 K  
 TD: 0.01000001 sec  
 TDO: 0

===== Processing parameters =====  
 SI: 32768  
 SF: 499.8700195 MHz  
 ASB: 0  
 ZF: 0.30 Hz  
 GB: 0  
 PC: 1.00

===== Acquisition Parameters =====  
 Date\_: 20160302  
 Time: 15.59  
 INSTRUM: spect  
 PROGRAM: zgpg30  
 PULPROG: zgpg30  
 SOLVENT: DMS  
 DS: 2  
 SWH: 8223.685 Hz  
 FIDRES: 0.250967 Hz  
 AQ: 1.397560 sec  
 RG: 50.8  
 DF: 60.800 usec  
 DE: 10.00 usec  
 TE: 320.0 K  
 TD: 0.01000001 sec  
 TDO: 0



WEC-WA-501-01  
 1H - 50degC  
 (\*223K/1100lph)  
 AV500as  
 P. P. Williams

c507200

Current Data Parameters  
 NAME wcv50101\_223K\_I1  
 PROCNO 2

F2 - Acquisition Parameters  
 Date\_ 20160902  
 Time\_ 12:00:00  
 INSTRUM 5 mm PABBO BB-  
 FPROBHD 5 mm PABBO BB-  
 PULPROG zgpg30  
 TD 6556  
 AQC 0.0500000  
 SOLVENT 6000  
 NS 16  
 SWE 39062.500 Hz  
 FIDRES 0.390625 Hz  
 AQ 0.390625 Hz  
 RG 327.680  
 DW 12.800 usec  
 DE 10.00 usec  
 TE 223.0 K  
 D1 0.1000000 sec  
 D11 0.0300000 sec  
 TD0 1

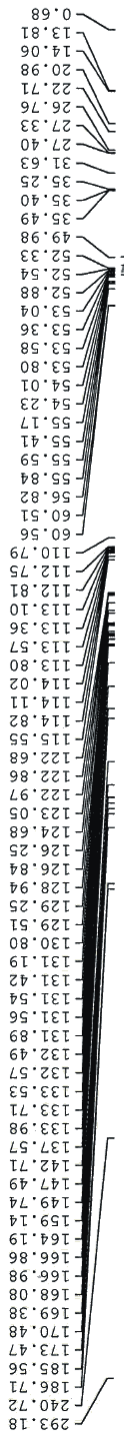
==== CHANNEL F1 =====  
 SFO1 125.712649 MHz  
 NUC1 13C  
 P1 10.00 usec  
 PLW1 98.00000000 W  
 ===== CHANNEL F2 =====  
 SFO2 499.8730869 MHz  
 NUC2 1H  
 P2 10.00 usec  
 PLW2 24.00000000 W  
 PLW12 0.37500000 W

F2 - Processing parameters  
 SI 32768  
 SF 125.692446 MHz  
 WDW EM  
 SSB 0 0.80 Hz  
 LB 0  
 GC 0  
 PC 1.00

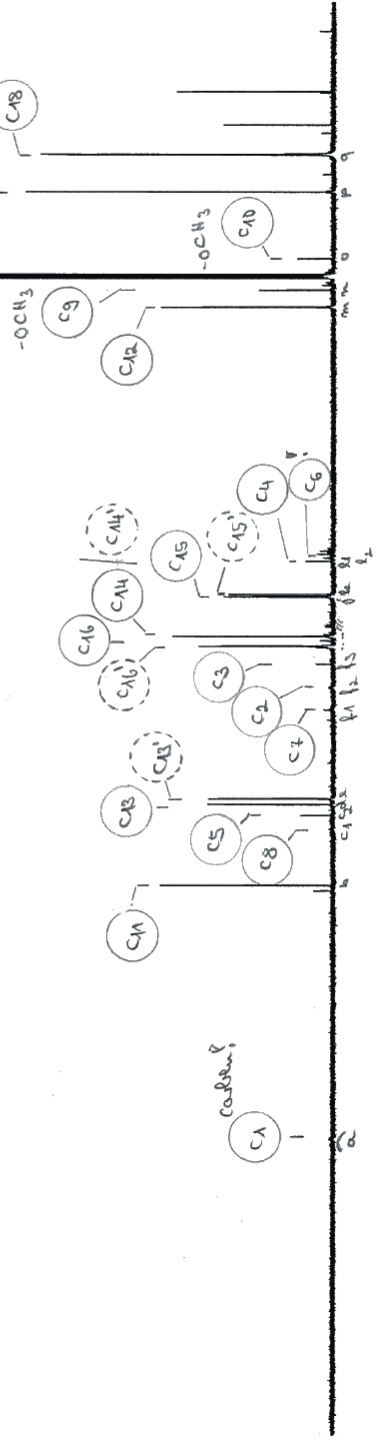
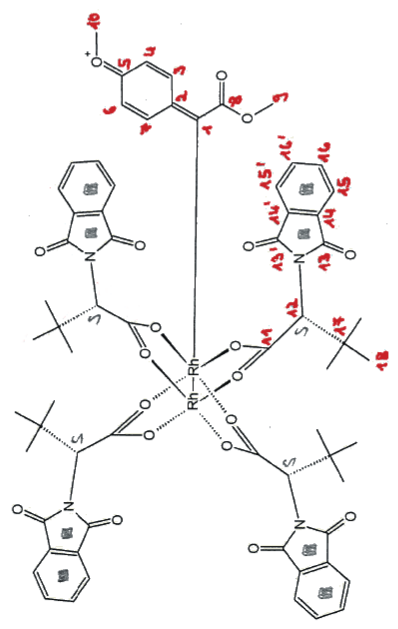
2. Affinity!  
 SW = 33.04

(1) 3rd. Edition  
 WEC-WA-501-01  
 13C{1H} -50degC  
 (\*223K/11001ph)  
 AV500as

P. D. ...



(S) starting material  
 Bis-styrylacet - alcohol  
 abs. 2,2,2-trifluoroethanol  
 -  $\delta_{ASN} = -213.5$  ppm

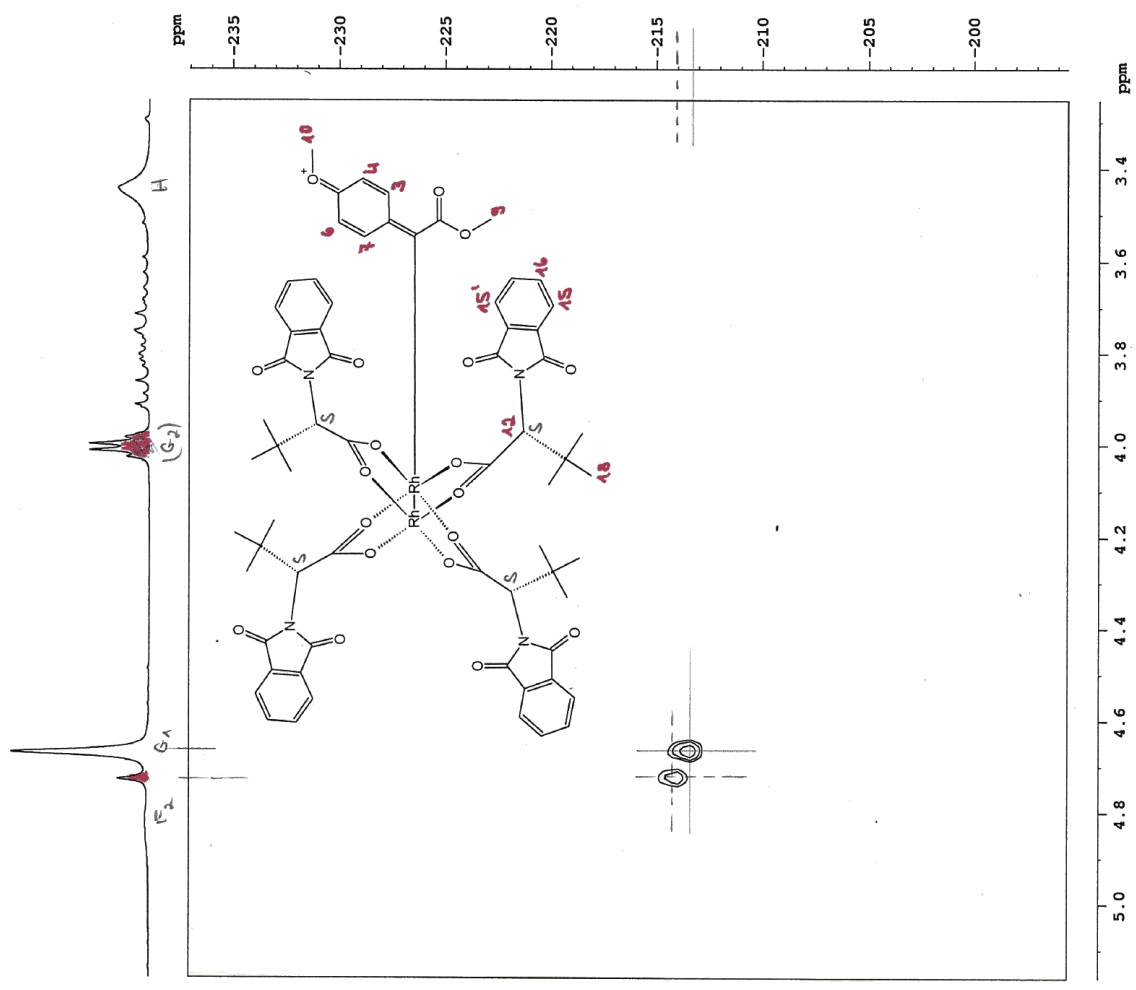


```

Current data Parameters
Name: WECWA501_23_K11
EXPNO: 23
PROCNO: 1
F2 - Acquisition Parameters
Date_: 20160302
Time: 23:53
INSTRUM: spect
PROBHD: 5 mm PABBO BB
PULPROG: hmcgprdgf
TD: 1024
AQ: 0.1306624 sec
RG: 203
AQ: 0.1306624 sec
RG: 203
DS: 16
SFR: 319.495 Hz
AQ: 0.1306624 sec
RG: 203
TE: 223.0 K
CNSX13: 10.000000
D0: 0.000000 sec
D1: 0.000000 sec
D2: 0.000000 sec
D5: 0.0500000 sec
D6: 0.0002000 sec
D16: 0.0001640 sec
INU: 0.0001640 sec
===== CHANNEL f1 =====
SFO1: 499.8721494 MHz
NUC1: 15N
P1: 10.00 usec
P2: 20.00 usec
P3: 20.00 usec
P4: 20.00 usec
P5: 20.00 usec
P6: 20.00 usec
P7: 20.00 usec
P8: 20.00 usec
P9: 20.00 usec
P10: 20.00 usec
P11: 20.00 usec
P12: 20.00 usec
P13: 20.00 usec
P14: 20.00 usec
P15: 20.00 usec
P16: 20.00 usec
P17: 20.00 usec
P18: 20.00 usec
P19: 20.00 usec
P20: 20.00 usec
P21: 20.00 usec
P22: 20.00 usec
P23: 20.00 usec
P24: 20.00 usec
P25: 20.00 usec
P26: 20.00 usec
P27: 20.00 usec
P28: 20.00 usec
P29: 20.00 usec
P30: 20.00 usec
P31: 20.00 usec
P32: 20.00 usec
P33: 20.00 usec
P34: 20.00 usec
P35: 20.00 usec
P36: 20.00 usec
P37: 20.00 usec
P38: 20.00 usec
P39: 20.00 usec
P40: 20.00 usec
P41: 20.00 usec
P42: 20.00 usec
P43: 20.00 usec
P44: 20.00 usec
P45: 20.00 usec
P46: 20.00 usec
P47: 20.00 usec
P48: 20.00 usec
P49: 20.00 usec
P50: 20.00 usec
P51: 20.00 usec
P52: 20.00 usec
P53: 20.00 usec
P54: 20.00 usec
P55: 20.00 usec
P56: 20.00 usec
P57: 20.00 usec
P58: 20.00 usec
P59: 20.00 usec
P60: 20.00 usec
P61: 20.00 usec
P62: 20.00 usec
P63: 20.00 usec
P64: 20.00 usec
P65: 20.00 usec
P66: 20.00 usec
P67: 20.00 usec
P68: 20.00 usec
P69: 20.00 usec
P70: 20.00 usec
P71: 20.00 usec
P72: 20.00 usec
P73: 20.00 usec
P74: 20.00 usec
P75: 20.00 usec
P76: 20.00 usec
P77: 20.00 usec
P78: 20.00 usec
P79: 20.00 usec
P80: 20.00 usec
P81: 20.00 usec
P82: 20.00 usec
P83: 20.00 usec
P84: 20.00 usec
P85: 20.00 usec
P86: 20.00 usec
P87: 20.00 usec
P88: 20.00 usec
P89: 20.00 usec
P90: 20.00 usec
P91: 20.00 usec
P92: 20.00 usec
P93: 20.00 usec
P94: 20.00 usec
P95: 20.00 usec
P96: 20.00 usec
P97: 20.00 usec
P98: 20.00 usec
P99: 20.00 usec
P100: 20.00 usec
===== CHANNEL f2 =====
SFO2: 50.6655893 MHz
NUC2: 15N
P1: 10.00 usec
P2: 20.00 usec
P3: 20.00 usec
P4: 20.00 usec
P5: 20.00 usec
P6: 20.00 usec
P7: 20.00 usec
P8: 20.00 usec
P9: 20.00 usec
P10: 20.00 usec
P11: 20.00 usec
P12: 20.00 usec
P13: 20.00 usec
P14: 20.00 usec
P15: 20.00 usec
P16: 20.00 usec
P17: 20.00 usec
P18: 20.00 usec
P19: 20.00 usec
P20: 20.00 usec
P21: 20.00 usec
P22: 20.00 usec
P23: 20.00 usec
P24: 20.00 usec
P25: 20.00 usec
P26: 20.00 usec
P27: 20.00 usec
P28: 20.00 usec
P29: 20.00 usec
P30: 20.00 usec
P31: 20.00 usec
P32: 20.00 usec
P33: 20.00 usec
P34: 20.00 usec
P35: 20.00 usec
P36: 20.00 usec
P37: 20.00 usec
P38: 20.00 usec
P39: 20.00 usec
P40: 20.00 usec
P41: 20.00 usec
P42: 20.00 usec
P43: 20.00 usec
P44: 20.00 usec
P45: 20.00 usec
P46: 20.00 usec
P47: 20.00 usec
P48: 20.00 usec
P49: 20.00 usec
P50: 20.00 usec
P51: 20.00 usec
P52: 20.00 usec
P53: 20.00 usec
P54: 20.00 usec
P55: 20.00 usec
P56: 20.00 usec
P57: 20.00 usec
P58: 20.00 usec
P59: 20.00 usec
P60: 20.00 usec
P61: 20.00 usec
P62: 20.00 usec
P63: 20.00 usec
P64: 20.00 usec
P65: 20.00 usec
P66: 20.00 usec
P67: 20.00 usec
P68: 20.00 usec
P69: 20.00 usec
P70: 20.00 usec
P71: 20.00 usec
P72: 20.00 usec
P73: 20.00 usec
P74: 20.00 usec
P75: 20.00 usec
P76: 20.00 usec
P77: 20.00 usec
P78: 20.00 usec
P79: 20.00 usec
P80: 20.00 usec
P81: 20.00 usec
P82: 20.00 usec
P83: 20.00 usec
P84: 20.00 usec
P85: 20.00 usec
P86: 20.00 usec
P87: 20.00 usec
P88: 20.00 usec
P89: 20.00 usec
P90: 20.00 usec
P91: 20.00 usec
P92: 20.00 usec
P93: 20.00 usec
P94: 20.00 usec
P95: 20.00 usec
P96: 20.00 usec
P97: 20.00 usec
P98: 20.00 usec
P99: 20.00 usec
P100: 20.00 usec
===== GRADIENT CHANNEL =====
GENDI: 0.000000 sec
GENAM[1]: SINE.100
GENAM[2]: SINE.100
GENAM[3]: SINE.100
GENE1: 70.00 %
GENE2: 70.00 %
GENE3: 50.10 %
GENE4: 50.10 %
P16: 1000.00 usec
F1 - Acquisition parameters
TD: 1024
SFO1: 50.66559 MHz
AQ: 0.1306624 sec
RG: 203
SFR: 299.75246 PPM
PROBHD: 5 mm PABBO BB
===== Processing parameters =====
SI: 1024
SF: 499.8700197 MHz
WDW: 0
SSB: 0 Hz
GB: 0
PC: 1.40
F1 - Processing parameters
SI: 1024
AQ: 0.1306624 sec
SFR: 299.75246 PPM
PROBHD: 5 mm PABBO BB
===== Processing parameters =====
SI: 1024
SF: 499.8700197 MHz
WDW: 0
SSB: 0 Hz
GB: 0
PC: 1.40

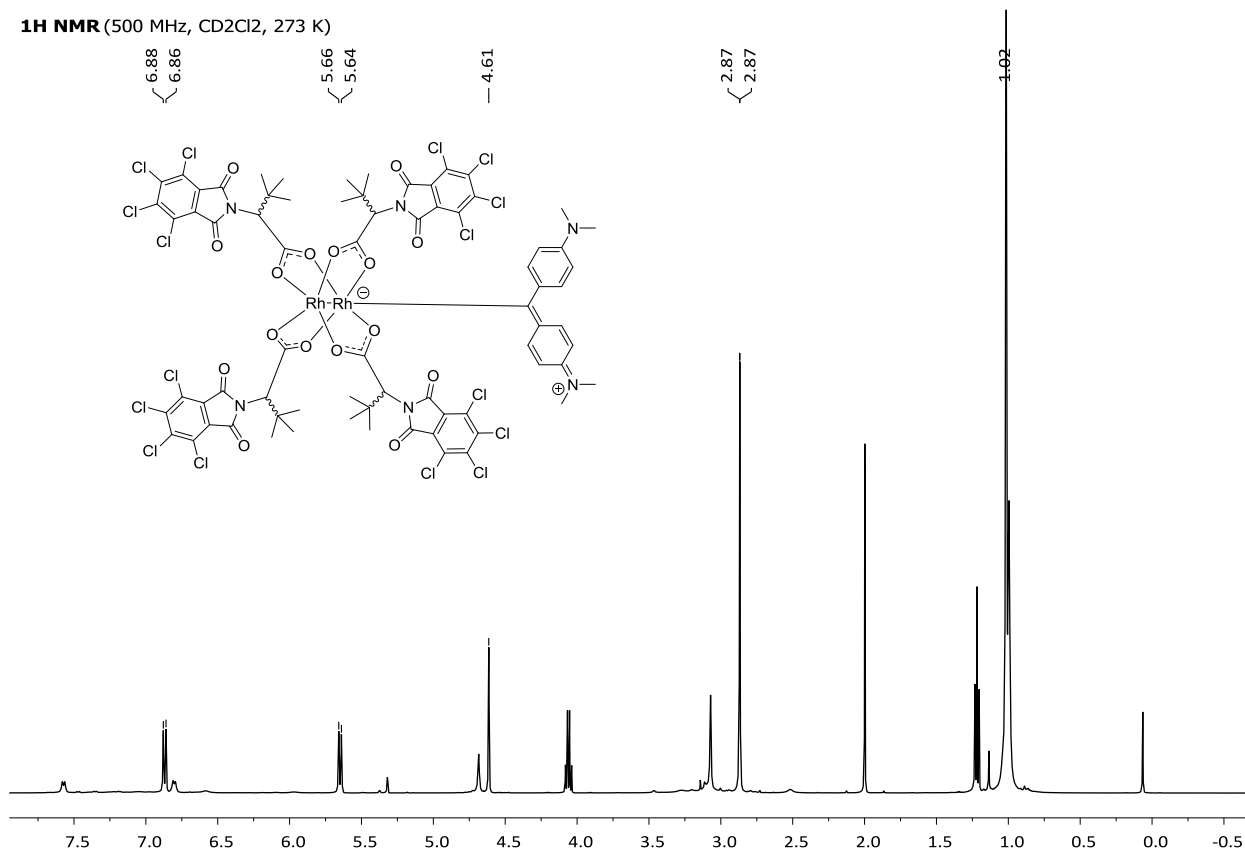
```

$\delta_{15N} = -214.1$   
 $S/N = -213.5$

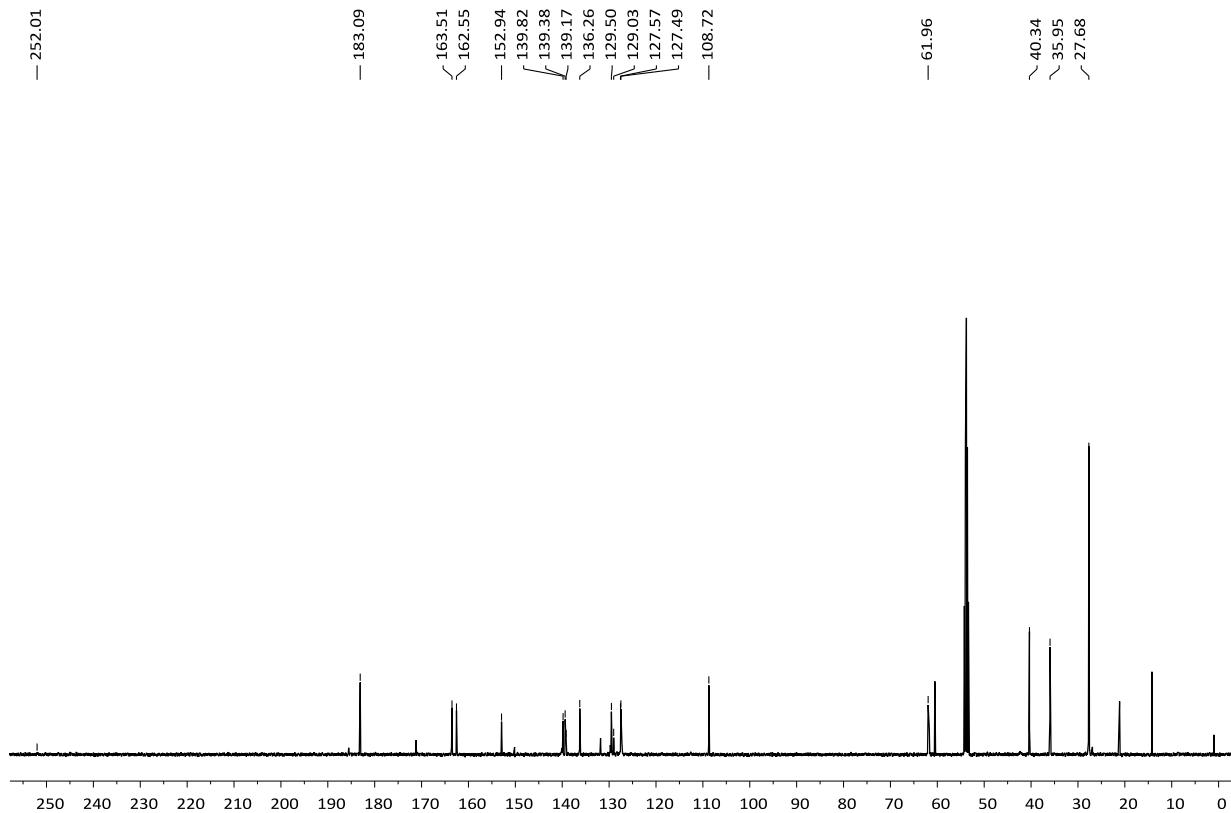


WEC-WA-501-01  
15N HMBC -50degc  
(\*223K/11001ph)  
AV500as

**<sup>1</sup>H NMR** (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 273 K)



**<sup>13</sup>C{<sup>1</sup>H} NMR** (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 273 K)



CULTURE DATA Parameters  
 NAME WECWA9701\_273K  
 PROCNO 1  
 PRORUN 1

P2 - Acquisition Parameters  
 DATE\_ TIME 21.03.13  
 INSTRUM spect  
 PULPROG zgpg30  
 TD 32768  
 SOLVENT CDCl3  
 DS 4  
 SWH 8223.685 Hz  
 FIDRES 0.192284 Hz  
 AQ 1.992284 sec  
 RG 114  
 DW 60.000 usec  
 DE 1.500 usec  
 TE 273.0 K  
 D1 0.1000000 sec  
 TDO 1

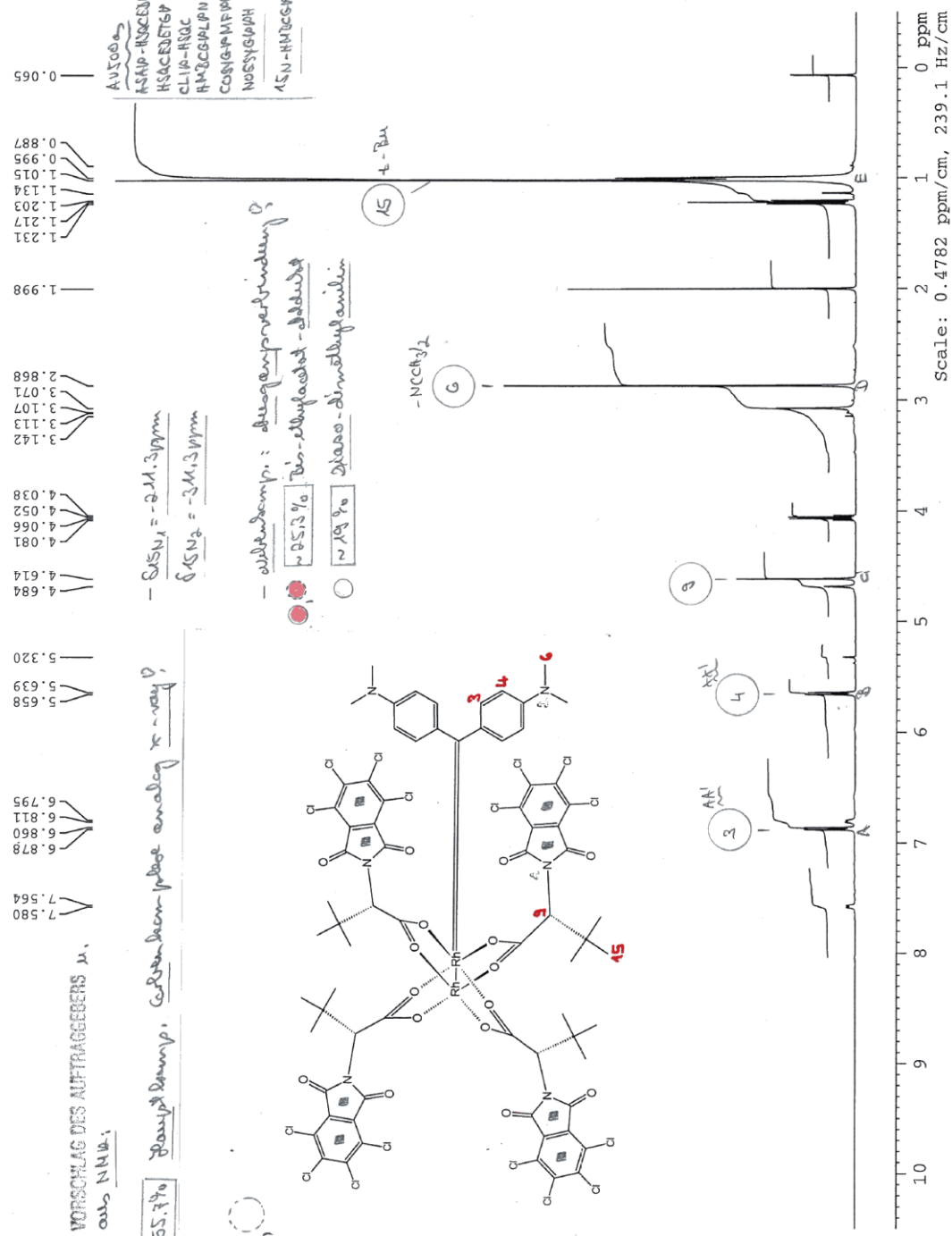
CHANNEL f1  
 SPOL 499.873069 MHz  
 PC1 10.00 usec  
 P1 24.0000000 W  
 P2 - Processing parameters  
 SI 32768  
 SF 499.873069 MHz  
 SD 0  
 LB 0 0.30 Hz  
 GB 0  
 PC 1.00

0.5, 30 ml, CD<sub>2</sub>O<sub>2</sub>  
 \*9734 (100)

SIA = 18.77

WEC-WA-497-01  
 1H 0degC  
 (\*273K/6001ph)  
 AV500as

P. Pindl/Mr



VORSCHLAG DES AUFTRAGGEBERS M.  
 aus NMR:

~55.3% Hauptkomponente, Carbonium-Ionen analog x-ray?



CSO 7222  
 Current Data Parameters  
 NAME vecwa49701\_273K  
 EXPNO 18  
 PROCNO 1

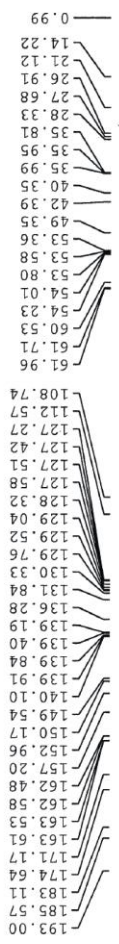
F2 - Acquisition Parameters  
 Date\_ 20160303  
 Time\_ 13:00:00  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB-  
 PULPROG zgpg30  
 SOLVENT CDCl3  
 NS 6000  
 DS 4  
 SWH 39063.16 Hz  
 FWHZ 0.556046 Hz  
 EXPTES 0.8188608 sec  
 AQ 0.03000000 sec  
 RG 203  
 DM 12.800 usec  
 DE 273.0 K  
 TE 273.0 K  
 D1 0.01000000 sec  
 D11 0.03000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 SF01 125.7112649 MHz  
 NUC1 13C  
 PUL1 13C usec  
 FLM1 98.0000000 W

===== CHANNEL f2 =====  
 SF02 499.8750000 MHz  
 NUC2 1H  
 PUL2 1H usec  
 FLM2 1H usec  
 PCYPRG12 waltz16  
 FCD22 80.00 usec  
 FLM12 0.3750000 W

F2 - Processing parameters  
 SF 125.692894 MHz  
 WDW EM  
 SSB 0 0.80 Hz  
 GB 0  
 PC 1.00

0.5, 0.0, 0.2, 0.2, 0.2, 0.2  
 (0%)  
 SA = -21.65



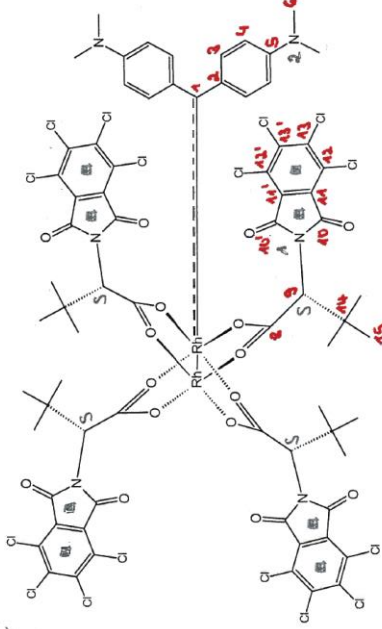
193.00  
185.57  
183.11  
174.64  
171.17  
163.53  
162.58  
162.48  
157.20  
152.96  
150.17  
149.54  
140.10  
139.84  
139.40  
139.19  
136.28  
131.84  
130.33  
129.76  
129.52  
128.32  
127.58  
127.51  
127.42  
127.27  
112.57  
108.74

AV500as  
 ASAP-HSCENETGPGP  
 HSCENETGPGP  
 CLIP-KSQC  
 HMTC-GALVANZGF  
 CONGP-PHPPPP  
 NOEN-GVPH  
 ASU-HHGGIANDGF

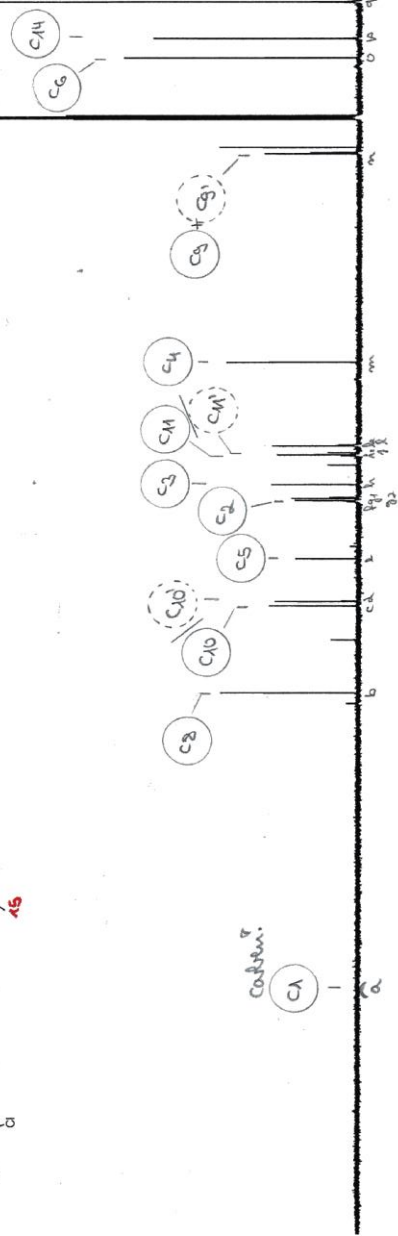
→ Doppelte Signale für die  
 Polhalbind-Subst.  
 → Die in 813c sind in der  
 Handen!

S15N1 = -21.3 ppm  
 S15N2 = -21.3 ppm

Waldenamp: dungen perind, ?  
 nBS 3% Res. abgefasst - Substanz  
 nAG 4% Mass. dimethylphenol



VORSCHLAG DES AUFTRAGGEBERS u. aus NMR:  
 n 55.74% Kampfbamp. Carbonkämpfer analog x-ray?



Carbon  
 CA

(170, 220, 240)  
 WEC-WA-497-01  
 13C{1H} 0degc  
 (\*273K/600lph)

P. Rüdiger