SUPPORTING INFORMATION

Effective Modulation of the Donor Properties of N-Heterocyclic Carbene Ligands by "Through Space" Communication within a Planar Chiral Scaffold

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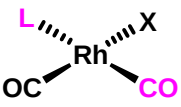
Assessment of the Donor Strength of Carbene Ligands & Compilation of Additional IR Data from the Literature

IR data of metal carbonyl complexes have been widely used to assess the overall donor strength of a bound carbene ligand.[1,2,3,4,5,6,7,8,9,12] Unfortunately, however, different authors have used different metal carbonyl templates for this purpose, which requires careful consideration upon comparison of the different scales.

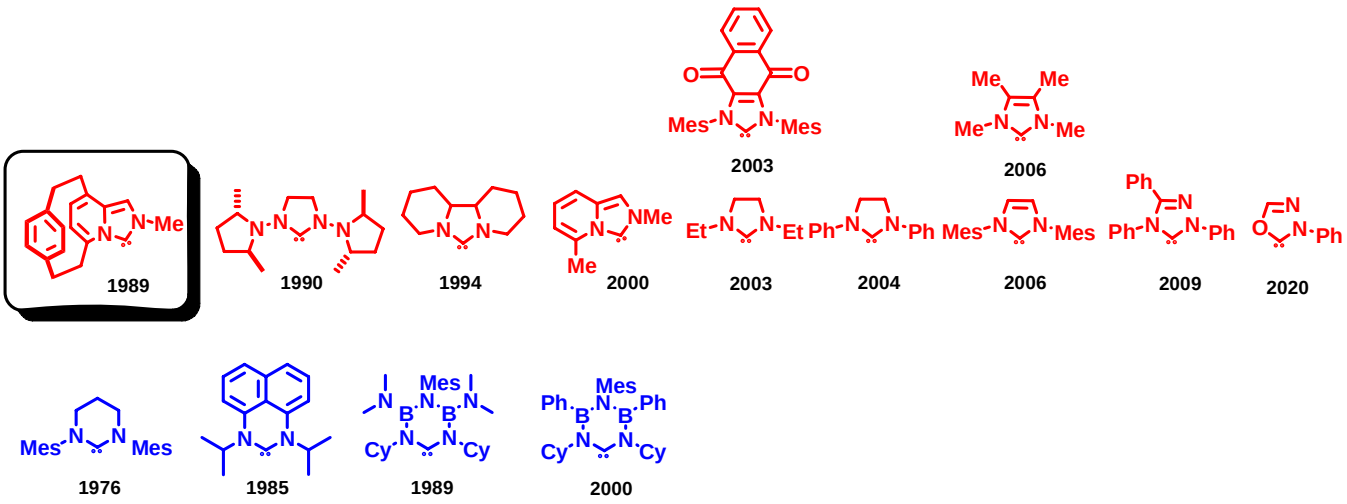
The "Rhodium and the Iridium Scale"



1a (X = Cl)
1b (X = I)

By far the largest data set is available for rhodium carbonyl complexes of type **1** (X = Cl, I), which have therefore also been chosen in the present study to allow for a proper comparison of the new carbenes with the established ligands. Thereby we rely on the stretching frequency ($\tilde{\nu}$) of the *trans*-CO moiety because it is least influenced by any steric effects and hence enables the most rigorous assessment of the electronic properties of the ligand in question. Although this is widely practiced in the literature, some authors chose the average CO stretching frequency of the *cis*- and the *trans*-disposed CO in **1** as parameter for such comparisons. It is of note that such an averaged scale is narrower, but the ranking of the ligands remains unaltered unless severe steric effects come into play.

Scheme S-1: Ranking of different carbene ligands according to the experimentally observed stretching frequency of the *trans*-CO ligand in complexes of type **1a** (X = Cl, $\tilde{\nu}$ in cm^{-1}):[6-12] Five-membered diamino-carbenes are color-coded in red, six-membered diamino-carbenes are shown in blue; Mes = 2,4,6-trimethylphenyl.



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1 For an in-depth theoretical analysis of the bonding situation of metal-NHC complexes see the following reference and literature cited therein: Hu, X.; Castro-Rodriguez, I.; Olsen, K.; Meyer, K. *Organometallics* **2004**, *23*, 755.

2 Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815.

3 Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663.

4 (a) Herrmann, W. A.; Schütz, J.; Frey, G. D.; Herdtweck, E. *Organometallics* **2006**, *25*, 2437. (b) Herrmann, W. A.; Baskakov, D.; Herdtweck, E.; Hoffmann, S. D.; Bunlaksananusorn, T.; Rampf, F.; Rodefeld, L. *Organometallics* 2006, 25, 2449.

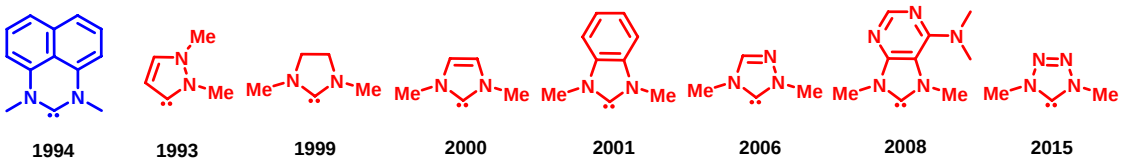
5 Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *J. Am. Chem. Soc.* **2004**, *126*, 15195.

6 (a) Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219. (b) Herrmann, W. A. ; Köcher, C. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162.

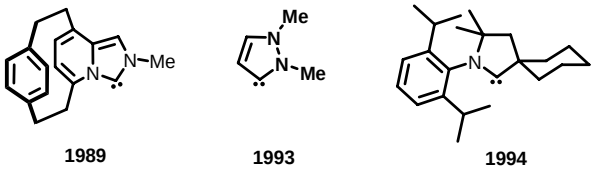
7 Bazinet, P.; Ong, T.-G.; O'Brien, J. S.; Lavoie, N.; Bell, E. ; Yap, G. P. A. ; Korobkov, I. ; Richeson, D. S. *Organometallics* **2007**, *26*, 2885.

8 Präsang, C.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2005**, *127*, 10182.

Scheme S-2: Ranking of different carbene ligands according to the experimentally observed stretching frequency of the *trans*-CO ligand in complexes of type **1b** (X = I, $\tilde{\nu}$ in cm^{-1}): Five-membered diamino-carbenes are color coded in red, six-membered diamino-carbenes are drawn in blue.



Scheme S-3: Comparison of the overall donor ability of the novel planar chiral carbene and cyclic "(alkyl)(amino)carbene" expressed in the stretching frequency of the *trans*-CO ligand in the corresponding complexes of type **1** ($\tilde{\nu}$ in cm^{-1}).



Several important conclusions can be drawn from the data compiled in Schemes S-1, S-2 and S-3:

- Exchange of the anionic ligand on rhodium in **1** from –Cl to –I causes only a very small shift of the scale to lower wavenumbers but does not alter the ranking
- Changing the size and character of the substituents on the N-atoms has very little influence on the donor ability, if any
- Annulation of one or two additional ring to the backbone engenders only a minor change, independent of its exact positioning. Even the annulation of a strongly electron withdrawing quinone ring has very little impact on the observed IR stretching frequencies of the corresponding rhodium complexes (cf. Scheme 1)[9]
- Triazolyl-ylidenes and tetrazol-ylidenes are weaker donors than their imidazol(idin)-2-ylidene counterparts
- Exchange of nitrogen for other heteroelements diminishes rather than increases the donor properties as evident from the oxadiazol-ylidene shown in Scheme S-1, which is the weakest donor amongst all 5-membered carbenes[10]
- (Alkyl)(amino)carbenes[4,11] and N,N'-bis(dialkylamino)imidazol-2-ylidenes[12] show the best donor abilities, but the new planar chiral NHC presented herein is an even stronger donor (Schemes S-1, S-3)

Overall, the parent planar chiral carbene presented in this paper is the strongest donor of all diamino-stabilized five-membered NHC's know to date, for which data on the "rhodium scale" are available. It even exceeds the donor capacity of five-membered carbenes, whose carbene center is flanked by only one N-atom.

Closely related data are extracted from the corresponding iridium complexes which have also found widespread use as a "scale" to measure the donor ability of various NHC's (Scheme S-4).[3,13] Again, variations of the N-substituents as well as steric modulations were found to induce little change. More interestingly, alkoxy substitutents at the C-4 and C-5 positions of the imidazol-2-ylidene scaffold, as

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9 Sandersen, M. D.; Kamplain, J. W.; Bielawski, C. W. *J. Am. Chem. Soc*. **2006**, *128*, 16514.

10 Alcarazo, M. ; Fernández, R. ; Alvarez, E. ; Lassaletta, J. M.; *J. Organomet. Chem*. **2005**, *690*, 5979.

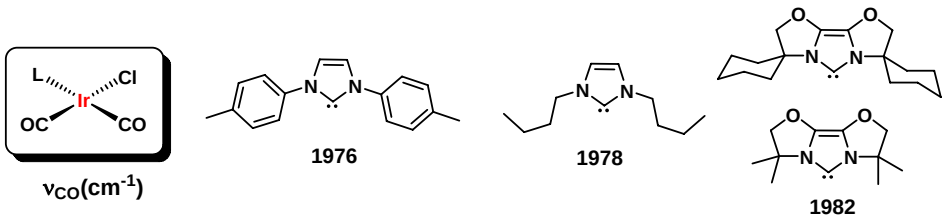
11 Lavallo, V.; Canac, Y.; DeHope, A.; Donnadieu, B.; Bertrand, G. *Angew. Chem. Int. Ed*. **2005**, *44*, 7236.

12 (a) Alcarazo, M.; Roseblade, S. J.; Alonso, E.; Fernández, R.; Alvarez, E.; Lahoz, F. J.; Lassaletta, J. M. *J. Am. Chem. Soc*. **2004**, *126*, 13242. (b) Ros, A.; Monge, D.; Alcarazo, M.; Alvarez, E.; Lassaletta, J. M.; Fernández, R. *Organometallics* **2006**, *25*, 6039.

13 Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *J. Am. Chem. Soc*. **2004**, *126*, 15195.

manifested in the bis-oxazoline derived NHC's developed by Glorius, have no profound effect on the donor capacity.

Scheme S-4: Comparison of the overall donor ability NHC's expressed in the stretching frequency of the corresponding iridium carbonyl complexes ($\tilde{\nu}$ in cm^{-1}).



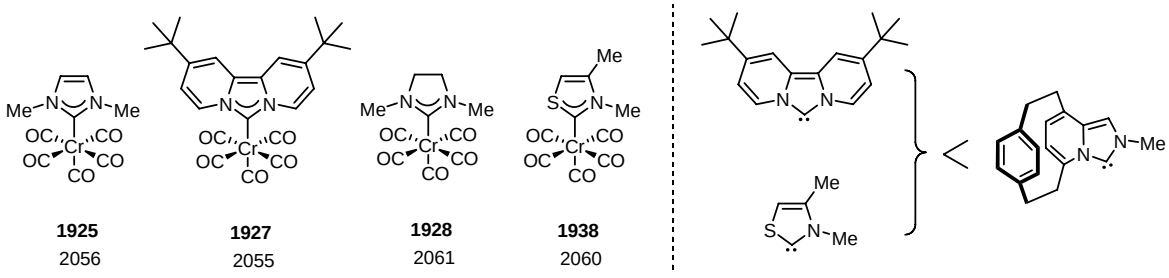
Other Scales

Other diamino-stabilized five-membered carbenes have been described in the literature, for which no IR data of the corresponding rhodium complexes **1** are available. Yet, it is possible to rank them relative to the carbenes shown in Schemes S-1, S-2 and S-3 by considering the following experimental and theoretical results.

Specifically, chromium carbonyl complexes of type $LCr(CO)_5$ have been used to investigate the donor ability of various N-heterocyclic carbenes. The data compiled in Schemes S-5 and S-6 allow one to draw the following conclusions:

- Even the lateral annulation of two rings to the parent imidazol-2-ylidene, as manifested in the corresponding dipyrido[1,2-c:2',1'-e]imidazolin-7-ylidene ligands, engenders little electronic changes. In fact, such bis-pyridino-annulated carbenes rank between that of the parent imidazol-2-ylidene and the imidazolidin-2-ylidene ligands.[14]
- As shown above, exchange of nitrogen for other heteroelements diminishes rather than increases the donor properties, as evident from the IR data of the thiazol-2-ylidene chromium carbonyl complex shown in Scheme S-5.[15]
- The computed vibrational frequency of the totally symmetric CO stretching mode of different chromium carbonyl complexes (Scheme S-6) show that substitution of the 4,5-positions of an imidazol-2-ylidene by electron withdrawing chlorine substituents also has very little influence; the dichorinated ligand is only a slightly weaker donor than the parent system.[16]

Scheme S-5: Comparison of the carbonyl stretching frequencies (IR in hexane solution) of chromium carbonyl complexes bearing different N-heterocyclic carbenes ($\tilde{\nu}$ in cm^{-1}).

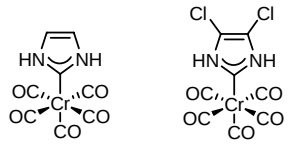


[14] (a) Nonnenmacher, M.; Kunz, D.; Rominger, F.; Oeser, T. *J. Organomet. Chem*. **2005**, *690*, 5647. (b) see also: Nonnenmacher, M.; Kunz, D.; Rominger, F.; Oeser, T. *Chem. Commun.* **2006**, 1378. (c) Weiss, R.; Reichel, S.; Handke, M.; Hampel, F. *Angew. Chem. Int. Ed*. **1998**, *37*, 344.

[15] Raubenheimer, H. G.; Stander, Y.; Marais, E. K.; Thompson, C.; Kruger, G. J.; Cronje, S.; Deetlefs, M. *J. Organomet. Chem*. **1999**, *590*, 158.

[16] Lee, M.-T.; Hu, C.-H. *Organometallics* **2004**, 23, 976.

Scheme S-6: Comparison of the computed totally symmetric CO stretching mode of chromium carbonyl complexes bearing differently substituted N-heterocyclic carbenes ($\tilde{\nu}$ in cm^{-1}).



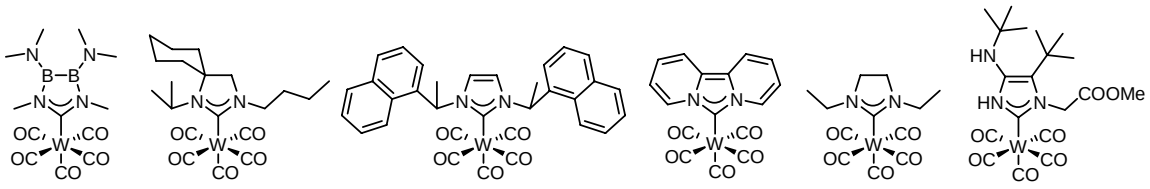
2136.8 **2139.9**

As the ranking of the imidazol-2-ylidenes and imidazolidin-2-ylidenes on the "rhodium scale" is well established, one may conclude that the donor capacity of the bis-pyridino-annulated carbenes as well as thiazol-2-ylidenes do not come close to that of the novel planar chiral carbene described in this paper.

The same conclusions are reached if one considers the corresponding tungsten complexes (Scheme S-7):[14,17]

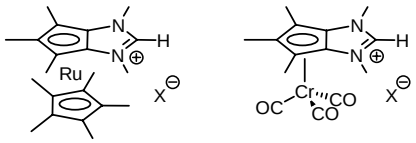
- The dipyrido[1,2-c:2',1'-e]imidazolin-7-ylidene ligand shows again a donor capacity comparable to that of the classical imidazolidin-2-ylidenes and the imidazol-2-ylidenes
- Additional electron donating substituents at the C-4 and C-5 positions hardly affect the donor properties
- The donor abilities of the analogous ligand featuring a diboron backbone also falls into the same range.[18]

Scheme S-7: Comparison of the A_1 stretching vibration of tungsten carbonyl complexes bearing different N-heterocyclic carbenes ($\tilde{\nu}$ in cm^{-1}).



2054 **2058** **2060** **2060** **2062** **2063**

Scheme S-8: Metallocene-fused imidazolium salts.



The only constitutionally distinct class of diamino-stabilized five-membered carbenes, which cannot be properly assessed to date, are the metallocene-fused imidazol-2-ylidene ligands derived from the salts

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17 (a) Ku, R.-Z.; Huang, J.-C.; Cho, J.-Y.; Kiang, F.-M.; Reddy, K. R.; Chen, Y.-C.; Lee, K.-J.; Lee, J.-H.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **1999**, *18*, 2145. (b) Herrmann, W. A.; Goossen, L. J.; Köcher, C.; Artus, G. R. J. *Angew.Chem. Int. Ed.* **1996**, *35*, 2805. (c) Kernbach, U.; Mühl, M.; Polborn, K.; Fehlhammer, W. P.; Jaouen, G. *Inorg. Chim. Acta* **2002**, *334*, 45. (d) Hahn, F. E.; Paas, M.; Van, D. L.; Fröhlich, R. *Chem. Eur. J.* **2005**, *11*, 5080.

18 Krahulic, K. E.; Enright, G. D.; Parvez, M.; Roesler, R. *J. Am. Chem. Soc.* **2005**, *127*, 4142.

shown in Scheme S-8.[19] To our knowledge, only a few mercury complexes and a single palladium complex have been reported, which do not allow us to draw firm conclusions about the donor properties of these interesting ligands. Since all available data, however, suggest that neither the annulation of an aromatic ring to the 4,5-position nor substitution of these positions with electron donating- or electron withdrawing substituents engenders any significant changes of the donor properties, one might expect that the metallocene-annulated systems also resemble the parent imidazol-2-ylidenes in electronic terms; this assumption, however, remains to be experimentally verified.

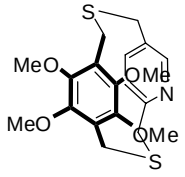
Experimental Section

General : All reactions were carried out in flame-dried glassware under Ar. All solvents were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg-anthracene), CH_2Cl_2, 1,2-dichloroethane (P_4O_{10}), MeCN, Et_3N (CaH_2), MeOH (Mg), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}; MS (EI): Finnigan MAT 8200 (70 eV); ESI-MS: Finnigan MAT 95; accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker DPX 300 or AV 400 spectrometer in the solvents indicated; ^1H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS, ^{19}F chemical shifts are reported in ppm relative to CF_3COOH, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale. Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Acros, Fluka, Lancaster, Aldrich) were used as received unless stated otherwise. 2,5-Bis(bromomethyl)pyridine (**9**), 2,11-dithia[3](1,4)benzeno[3](2,5)pyridinophane (**10**), [2](1,4)benzeno[2]-(2,5)pyridinophane (**11**), [2](1,4)benzeno[2](2,5)-pyridinophane *N*-oxide (**12**),[20] 1,4-bis(mercaptomethyl)-2,3,5,6-tetrafluorobenzene[21] and 1,4-bis(mercaptomethyl)-2,3,5,6-tetramethoxybenzene[22] were prepared according to literature procedures.

5,6,8,9-Tetrafluoro-2,11-dithia[3](1,4)benzeno[3] (2,5)pyridinophane: A solution of 2,5-di(bromo-

methyl)pyridine (2.27 g, 8.58 mmol) in a mixture of toluene (70 mL) and EtOH (10 mL) and a solution of 1,4-bis(mercaptomethyl)-2,3,5,6-tetrafluorobenzene (2.08 g, 8.58 mmol) in MeOH (110 mL) were simultaneously dropped via two dropping funnels over a period of 2.5 h into a 2 L flask containing MeOH (750 mL) and NaOH (0.68 g, 17.1 mmol). The resulting mixture was stirred under reflux for 16 h before the solvents were evaporated. The residue was suspended in CH_2Cl_2 (100 mL), undissolved materials were filtered off, the filtrate was evaporated, and the residue purified by flash chromatography (CH_2Cl_2:acetone = 20:1) to give the title compound as a white solid (1.98 g, 67%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.24 (s, 1H), 7.56 (dd, *J* = 2.0, 8.2 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 3.99-3.85 (m, 4H), 3.83 (d, *J* = 15.7 Hz, 1H), 3.74 (d, *J* = 15.7 Hz, 1H), 3.63-3.52 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.2, 147.2, 144.8 (m), 144.5 (m), 141.7 (m), 141.3 (m), 136.0, 129.7, 122.4, 114.6 (t, *J* = 16.2 Hz), 114.5 (t, *J* = 16.3 Hz), 38.3, 33.6, 23.5, 23.4. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –143.8, –143.0, –142.2, –141.8; IR (film): $\tilde{\nu}$ = 2940, 1565, 1480, 1409, 1286, 985, 735, 695 cm^{-1}; HRMS: *m/z*: calcd for $C_{15}H_{11}NS_2F_4$: 346.03418; found 346.03446.

5,6,8,9-Tetramethoxy-2,11-dithia[3](1,4)benzeno[3](2,5)pyridinophane: A cooled (–5 ºC) solution of



2,5-di(bromomethyl)pyridine (750 mg, 2.82 mmol) in EtOH (100 mL) and a solution of 1,4-bis(mercaptomethyl)-2,3,5,6-tetramethoxybenzene (820 mg, 2.82 mmol) and KO*t*Bu (700 mg, 5 mmol) in EtOH (100 mL) were simultaneously dropped via two dropping funnels over a period of 5 h into a 2 L flask containing boiling EtOH (1 L). Reflux was continued for 16 h before the solvent was evaporated. The residue was suspended in CH_2Cl_2 (100 mL), undissolved materials were filtered off, the filtrate was evaporated, and the residue purified by flash chromatography (CH_2Cl_2:acetone = 10:1) to give the title compound as a white solid (465 mg, 42%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* =

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19 (a) Arduengo, A. J.; Tapu, D.; Marshall, W. J. *J. Am. Chem. Soc*. **2005**, *127*, 16400. (b) Arduengo, A. J.; Tapu, D.; Marshall, W. J. *Angew. Chem. Int. Ed*. **2005**, *44*, 7240. (c) see also: Arduengo, A. J.; Bannenberg, T. P.; Tapu, D.; Marshall, W. J. *Chem. Lett*. **2005**, *34*, 1010.

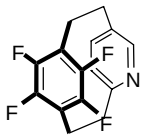
20 Wörsdörfer, U.; Vögtle, F.; Nieger, M.; Waletzke, M.; Grimme, S.; Glorius, F.; Pfaltz, A. *Synthesis* **1999**, *4*, 597-602.

21 Filler, R.; Cantrell, G. L.; Wolanin, D.; Naqvi, S. M. *J. Fluor. Chem.* **1986** , *30*, 399-414.

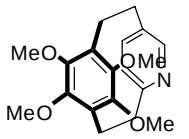
22 Staab, H. A.; Wahl, P.; Kay, K. Y. *Chem. Ber.* **1987**, *120*, 541-547.

1.9 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 4.05-3.53 (m, 8H), 3.88 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 3,74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2, 147.6, 146.5, 146.4, 146.2, 146.1, 136.3, 130.1, 124.0, 123.9, 122.5, 61.0, 60.9, 60.4, 60.3, 38.6, 34.0, 26.3, 26.1; IR (film): $\tilde{\nu}$ = 2938, 1464, 1411, 1275, 1058, 1022, 954 cm^{-1}; HRMS: *m/z*: calcd for $C_{19}H_{23}NO_4S_2Na$: 416.09607; found 416.09600; elemental analysis calcd (%) for $C_{19}H_{23}NO_4S_2$: C 57.99, H 5.89, N 3.56; found C 57.97, H 6.04, N 3.58.

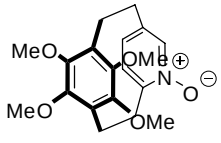
4,5,7,8-Tetrafluoro[2](1,4)benzeno[2](2,5)pyridinophane: 5,6,8,9-Tetrafluoro-2,11dithia[3](1,4) benzeno[3](2,5)pyridinophane (581 mg, 1.7 mmol) was suspended in $P(OMe)_3$ (80 mL) and the resulting mixture was irradiated with UV light (Hannovia lamp, 125W) overnight at ambient temperature. Excess $P(OMe)_3$ was removed by distillation and the desired product was isolated from the yellow viscous residue by flash chromatography (CH_2Cl_2:acetone = 10:1) as a white solid (205 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (s, 1H), 7.12-7.05 (m, 1H), 6.77 (dd, *J* = 2.6, 7.8 Hz, 1H), 3.32-3.24 (m, 1H), 3.19-2.85 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1, 149.6, 147.5 (m), 146.1(m), 144.9 (m), 144.2 (m), 136.0, 131.8, 121.9, 118.9 (t, *J* = 19.9 Hz), 118.4 (t, *J* = 20.0 Hz), 34.3, 29.9, 21.8, 20.7. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –136.9, –137.1, –138.2, –139.8; HRMS: *m/z*: calcd for $C_{15}H_{11}F_4NNa$: 304.07198; found 304.07221; elemental analysis calcd (%) for $C_{15}H_{11}NF_4$: C 64.06, H 3.94, N 4.98; found C 63.88, H 4.06, N 5.08.



4,5,7,8-Tetramethoxy[2](1,4)benzeno[2](2,5)pyridinophane: Prepared analogously from 5,6,8,9-tetramethoxy-2,11dithia[3](1,4) benzeno[3](2,5)pyridinophane (420 mg, 1.07 mmol) as a white solid (220 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 2.1 Hz 1H), 6.96 (dd, *J* = 2.1, 7.7 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 3.65 (s, 3H), 3.62 (s, 3H), 3.18-3.13 (m, 1H), 3.05-2.98 (m, 2H), 2.80-2.92 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 149.8, 148.7, 148.4, 148.2, 135.4, 131.4, 128.2, 126.5, 126.1, 121.2, 61.8, 61.5, 61.1, 61.0, 34.1, 29.7, 23.5, 23.0; HRMS: *m/z*: calcd for $C_{19}H_{23}NO_4Na$: 352.15193; found 352.15197; elemental analysis calcd (%) for $C_{19}H_{23}NO_4$: C 69.28, H 7.04, N 4.25; found C 69.35, H 7.00, N 4.21.



4,5,7,8-Tetrafluoro[2](1,4)benzeno[2](2,5)pyridinophane *N*-oxide: *m*CPBA (351 mg, 2.03 mmol) was added to a solution of 4,5,7,8-tetrafluoro[2](1,4)benzeno[2](2,5)pyridinophane (179 mg, 0.64 mmol) in CH_2Cl_2 (25 mL) and the resulting mixture was stirred for 16 h. For work up, the mixture was diluted with CH_2Cl_2 (20 mL) and successively washed with aq. NaOH (5% *w/w*, 10 mL) and brine (10 mL), the organic phase was dried over Na_2SO_4 and evaporated, and the residue purified by flash chromatography (CH_2Cl_2:MeOH = 20:1) to give the title compound as a white solid (249 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (s, 1H), 6.91 (dd, *J* = 3.4, 8.1 Hz, 1H), 6.81-6.74 (m, 1H), 3.87-3.57 (m, 2H), 3.18-2.72 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.2, 141.9, 137.6, 127.5, 127. 0, 30.4, 30.0, 22.4, 19.6 (quaternary carbons coupled with ^{19}F were not detected in this experiment); IR (film): $\tilde{\nu}$ = 2950, 1746, 1469, 1390, 1272, 1260, 1152, 1021, 974, 893 cm^{-1}; HRMS: *m/z*: calcd for $C_{15}H_{11}F_4NONa$: 320.06690; found 320.06697.



4,5,7,8-Tetramethoxy[2](1,4)benzeno[2](2,5)pyridinophane *N*-oxide: A suspension of 4,5,7,8-tetramethoxy[2](1,4)benzeno[2](2,5)pyridinophane (72 mg, 0.218 mmol), sodium percarbonate (111 mg, 0.70 mmol), methyltrioxorhenium (11 mg, 0.044 mmol) and acetic acid (0.2 mL) in acetonitrile (10 mL) was stirred at 60 ºC for 24 h before additional sodium percarbonate (119 mg, 0.75 mmol) and methyltrioxorhenium (17 mg, 0.07 mmol) were added and stirring at 60ºC was continued for 4 d. After this time, the solvents were evaporated and the residue repeatedly extracted with CH_2Cl_2 and H_2O. The combined organic phases were dried over Na_2SO_4 and evaporated, and the residue purified by flash chromatography (CH_2Cl_2:MeOH = 20:1→ 10:1) to give the title compound as a white solid (58 mg, 77%).^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 1.3 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.64 (dd, *J* = 1.5, 8.0 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.64 (s, 3H), 3.63-3.55 (m, 1H), 3.59 (s, 3H), 2.96-2.66 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.4, 148.8, 148.2, 147.5, 140.5, 136.6, 126.6, 125.7, 125.6, 125.4, 125.2, 63.1, 61.8, 61.3, 61.0, 29.6, 29.5, 23.3, 21.3; IR (film): $\tilde{\nu}$ = 2937, 1465, 1405, 1268, 1249, 1059, 1028, 985 cm^{-1}; HRMS: *m/z*: calcd for $C_{19}H_{23}NO_5$: 345.15762; found 345.15725.

Compound 13: A solution of *N*,*N*-dimethylcarbamoyl chloride (133 mg, 1.23 mmol) in CH_2Cl_2 (2 mL) was slowly added to a solution of *N*-oxide **12** (200 mg, 0.89 mmol) in CH_2Cl_2 (10 mL). After stirring for 30 min at ambient temperature, a solution of TMSCN (139 mg, 1.3 mmol) in CH_2Cl_2 (2 mL) was added and stirring continued for 24 h. The mixture was extracted with sat. aq. $NaHCO_3$ and CH_2Cl_2 (4 x 10 mL), the organic phase was washed with brine (2 x 15 mL), dried over $MgSO_4$, filtered, and the filtrate was evaporated. Compound **13** was isolated by flash chromatography (CH_2Cl_2:MeOH = 30:1) as a white solid (128 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.90 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 5.29 (s, 1H), 5.24 (d, *J* = 13.5 Hz, 1H), 5.14 (d, *J* = 13.5 Hz, 1H), 3.01 (s, 6H), 2.94 (t, *J* = 7.1 Hz, 2H), 2.83 (t, *J* = 7.1 Hz, 2H), 2.60-2.40 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 154.8, 153.6, 138.9, 138.6, 130.9, 129.7, 128.7, 127.4, 116.5, 104.1, 38.7, 36.1, 33.2, 30.9 (the signals of O*C*ONMe$_2$ and N(*C*H$_3$)$_2$ were not observed); IR (film): $\tilde{\nu}$ = 3042, 2933, 2212, 1727, 1435, 1384, 1154, 1137, 1017, 902, 863, 749 cm^{-1}; HRMS: *m/z*: calcd for $C_{19}H_{21}N_3O_2Na$: 346.15260; found 346.15249.

Compound 13a: Prepared analogously from 4,5,7,8-tetrafluoro[2](1,4)benzeno[2](2,5)pyridinophane *N*-oxide (115 mg, 0.39 mmol) as a white solid (33 mg, 28%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.60 (d, *J* = 13.3 Hz, 1H), 5.52 (d, *J* = 13.5 Hz, 1H), 5.49 (s, 1H), 3.40-3.00 (bs, 4H), 2.96 (s, 6H), 2.80-2.60 (bs, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.0, 156.7, 153.7, 152.7, 131.4, 129.2, 118.3 (m), 116.8 (m), 107.5, 37.1 (bs), 36.6 (bs), 34.8, 32.5, 20.6, 19.8. (the four *C*F were observed as a broad signal centred at 144.4 ppm); IR (film): $\tilde{\nu}$ = 2939, 2217, 1743, 1485, 1381, 1140, 1010, 906, 853, 752 cm^{-1}; MS (EI): *m/z* (%): 395 (38) [M]$^+$, 307 (100), 176 (22), 146 (21), 118 (48), 72 (58).

Compound 13b: Prepared analogously from 4,5,7,8-tetramethoxy[2](1,4)benzeno[2](2,5)pyridinophane *N*-oxide (50 mg, 0.144 mmol) as a colorless oil (18 mg, 29%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.52 (d, *J* = 13.4 Hz, 1H), 5.41 (d, *J* = 13.4 Hz, 1H), 5.32 (s, 1H), 3.90-3.50 (bs, 12H), 3.10-2.50 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 155.7, 153.5, 148.3, 129.8, 127.1, 126.0, 124.4, 116.5, 105.0, 34.5, 32.2, 22.2, 20.9 (the signals of the carbamoyl carbonyl group and of two *C*OMe were not detected; the four O*C*H$_3$ appear as a broad singlet centred at 61.2 ppm, and the two N*C*H$_3$ appear as a broad singlet at 36.3 ppm); MS (EI): *m/z* (%): 443 (21) [M]$^+$, 428 (10), 354 (53), 339 (38), 323 (67), 284 (27), 249 (20), 72 (100).

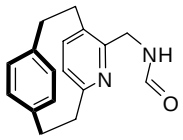
13-Cyano[2](1,4)benzeno[2](2,5)pyridinophane (14): A solution of *N*,*N*-dimethylcarbamoyl chloride (1.02 g, 9.5 mmol) in CH_2Cl_2 (15 mL) was slowly added to a solution of *N*-oxide **12** (1.55 g, 6.88 mmol) in CH_2Cl_2 (50 mL). The resulting mixture was stirred for 30 min before a solution of TMSCN (0.88 g, 8.5 mmol) in CH_2Cl_2 (15 mL) was introduced and stirring continued for 16 h. The organic solvent was evaporated, $ClCH_2CH_2Cl$ (30 mL) was added and the solution stirred under reflux for 5 h. The mixture was extracted with sat. aq. $NaHCO_3$ and CH_2Cl_2 (4 x 20 mL), the organic phase was dried over $MgSO_4$ and filtered, and the filtrate was evaporated. Compound **14** was isolated by flash chromatography (hexanes:AcOEt = 1:3) as a white solid (870 mg, 54%). Its analytical and spectral properties match those reported in the literature.

4,5,7,8-Tetrafluoro-13-cyano[2](1,4)benzeno[2](2,5)pyridinophane: Prepared analogously from 4,5,7,8-tetrafluoro[2](1,4)benzeno[2](2,5)pyridinophane *N*-oxide (249 mg, 0.83 mmol) as a pale yellow solid (870 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (dd, *J* = 3.1, 8.0 Hz, 1H), 6.94 (dd, *J* = 2.6, 8.0 Hz, 1H), 3.53-3.40 (m, 1H), 3.36-3.15 (m, 3H), 315-2.90 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.9, 147.6 (m), 145.4 (m), 144.4(m), 143. 3 (m), 137.6, 136.9, 132.6, 124.7, 118.4 (m), 118.2 (m), 115.3, 34.3, 29.8, 21.3, 20.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –136.1, –136.5, –136.7, –137.2; IR (film): $\tilde{\nu}$ = 2946, 2227, 1571, 1470, 1267, 1160, 1019, 946, 894, 744 cm^{-1}; HRMS: *m/z*: calcd for $C_{16}H_{10}F_4N_2Na$: 329.06723; found 329.06735; elemental analysis calcd (%) for $C_{16}H_{10}N_2F_4$: C 62.75, H 3.29, N 9.15; found C 63.18, H 3.12, N 9.03.

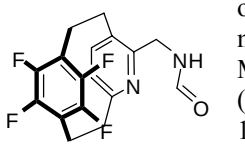
4,5,7,8-Tetramethoxy-13-cyano[2](1,4)benzeno[2](2,5)pyridinophane: Prepared analogously from 4,5,7,8-tetramethoxy[2](1,4)benzeno[2](2,5)pyridinophane *N*-oxide (125 mg, 0.36 mmol) using toluene as the solvent in the electrocyclization step; white solid (65 mg, 51%).^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 7.9 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 3.99 (s, 3H), 3.81 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.44-3.37 (m, 1H), 3.29-2.87 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4, 149.1, 148.6, 148.5, 137.2, 137.1, 136.9, 130.8, 126.1, 125.7, 124.2, 116.0, 61.9, 61.8, 61.2, 60.5,

34.1, 29.4, 23.0, 22.9; HRMS: *m/z*: calcd for $C_{20}H_{22}N_2O_4$: 354.15796; found 354.15788; elemental analysis calcd (%) for $C_{20}H_{22}N_2O_4$: C 67.78, H 6.26, N 7.90; found C 67.59, H 6.31, N 7.80.

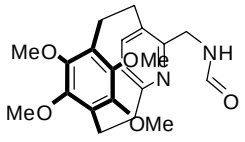
13-Formylaminomethyl[2](1,4)benzeno[2](2,5)pyridinophane (15): A solution of compound **14** (400 mg, 1.70 mmol) in acetic acid (30 mL) was stirred under an atmosphere of H_2 (5 bar) in the presence of Pd/C (10% *w/w*, 150 mg). After 3 h, the catalyst was filtered off through a pad of Celite which was carefully rinsed with hot acetic acid (3 x 5 mL). The combined filtrates were evaporated and the residue dissolved in methyl formiate (10 mL). Et_3N (440 µL, 3.4 mmol) was added and the resulting mixture refluxed for 2 h. Evaporation of all volatile materials and purification of the residue by flash chromatography (CH_2Cl_2:MeOH = 10:1) afforded formamide **15** as a yellow oil (308 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31 (s, 1H), 7.50 (bs, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.67 (dd, *J* = 1.8, 7.9 Hz, 1H), 6.58 (dd, *J* = 1.8, 7.9 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 2H), 6.41 (dd, *J* = 1.7, 7.9 Hz, 1H), 4.47 (dd, *J* = 5.1, 15.2 Hz, 1H), 4.29 (dd, *J* = 5.1, 15.2 Hz, 1H), 3.36-2.96 (m, 7H), 2.91-2.78 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.4, 158.7, 152.1, 141.6, 139.4, 138.5, 133.6, 132.4, 132.2, 130.3, 128.1, 123.5, 40.5, 36.1, 34.2, 33.8, 31.3; IR (film): $\tilde{\nu}$ = 3316, 2930, 2856, 1683, 1572, 1500, 1452, 1383, 1233, 902, 800, 724 cm^{-1}; HRMS: *m/z*: calcd for $C_{17}H_{18}N_2ONa$: 289.13113; found 289.13130.



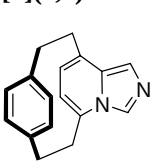
4,5,7,8-Tetrafluoro-13-formylaminomethyl[2](1,4)benzeno[2](2,5)pyridinophane: Prepared analogously from 4,5,7,8-tetrafluoro-13-cyano[2](1,4)benzene [2](2,5)-pyridinophane (91 mg, 0.30 mmol) as an oil that solidifies on standing (92 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 0.9 Hz, 1H), 7.32 (bs, 1H), 7.20-7.10 (m, 1H), 6,83 (dt, *J* = 2.9, 7.6 Hz, 1H), 4.58 (dd, *J* = 3.6, 17.5 Hz, 1H) 4.52 (dd, *J* = 4.9, 16.1 Hz, 1H), 3.46-2.94 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.0, 157.4, 152.6, 148.8 (m), 147.7 (m), 145.2 (m), 144.4 (m), 138.1, 129.2, 121.1, 118.6 (t, *J* = 20.0 Hz), 118.0 (t, *J* = 20.0 Hz), 39.8, 33.8, 28.9, 20.8, 20,7; IR (film): $\tilde{\nu}$ = 3221, 2961, 2853, 1676, 1470, 1378, 1264, 1153, 1027, 895 cm^{-1}; HRMS: *m/z*: calcd for $C_{17}H_{14}F_4N_2O$: 361.09344; found 361.09357; elemental analysis calcd (%) for $C_{17}H_{14}N_2F_4O$: C 60.36, H 4.17, N 8.28; found C 60.11, H 4.66, N 8.20.



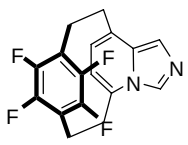
4,5,7,8-Tetramethoxy-13-formylaminomethyl[2](1,4)benzeno[2](2,5)pyridinophane: Prepared analogously from 4,5,7,8-tetramethoxy-13-cyano[2](1,4)benzene [2](2,5)-pyridinophane (60 mg, 0.17 mmol) as white solid (39 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 1H), 7.43 (bs, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 3.47-3.42 (m, 2H), 3.72 (s, 3H), 3.65 (s, 3H), 3.64 (s, 3H), 3.22 (s, 3H), 3.36-2.85 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0, 156.9, 151.5, 149.4, 149.3, 149.0, 148.7, 138.2, 129.3, 126.5, 125.6, 121.1, 62.2, 61.8, 61.7, 61.5, 39.1, 33.3, 28.6, 22.9, 22.8; IR (film): $\tilde{\nu}$ = 3383, 2941, 2837, 1685, 1405, 1248, 1059, 1027, 978, 811 cm^{-1}; HRMS: *m/z*: calcd for $C_{21}H_{26}N_2O_5$: 386.18418; found 386.18400.



[2](1,4)Benzeno[2](5,8)imidazo[1,5-a]pyridinophane: $POCl_3$ (605 mg, 3.9 mmol) was added to a solution of formamide **15** (350 mg, 1.31 mmol) in toluene (5 mL) and the resulting mixture was stirred at 80 ºC for 3 h. After cooling to room temperature, the solvents were evaporated, the residue was dissolved in $CHCl_3$ (10 mL), the organic phase was washed twice with NaOH (2 M) and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash chromatography (CH_2Cl_2:acetone = 10:1) to give the title compound as a yellow solid (198 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (s, 1H), 7.12 (s, 1H), 6.58 (dd, *J* = 1.8, 7.8 Hz, 1H), 6.51 (dd, *J* = 1.8, 7.9 Hz, 1H), 6.12 (d, *J* = 7.0 Hz, 1H), 6.09 (dd, *J* = 1.9, 7.8 Hz, 1H), 5.95 (dd, *J* = 1.9, 7.8 Hz, 1H), 5.90 (d, *J* = 6.8 Hz, 1H), 3.40-2.85 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.0, 135.0, 134.6, 132.1, 130.5, 130.4, 129.8, 126.9, 126.0, 123.6, 121.8, 121.1, 118.2, 34.1, 32.3, 31.3, 31.1; IR (film): $\tilde{\nu}$ = 2932, 2859, 1496, 1446, 1266, 1115, 919, 802, 721, 650, 584 cm^{-1}; HRMS: *m/z*: calcd for $C_{17}H_{16}N_2Na$: 271.12057; found 271.12070. Separation of the enantiomers was achieved on a preparative scale (Chiralpak AS; n-heptane:2-propanol = 80:20; 308 K). The retention times of the two enantiomers are 26.1 min and 30.1 min, respectively.



4,5,7,8-Tetrafluoro-[2](1,4)benzeno[2](5,8)imidazo[1,5-a]pyridinophane: Prepared analogously from 4,5,7,8-tetrafluoro-13-formylaminomethyl [2](1,4)benzeno[2](2,5)pyridinophane (71 mg, 0.21 mmol) as a white solid (58 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (s, 1H), 7.32 (s, 1H), 6.38 (dd, *J* = 3.8, 6.9 Hz, 1H), 6.27 (dd, *J* = 3.8, 7.0 Hz, 1H), 3.62-3.02 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.9 (m), 147.7 (m), 144.7 (m), 144.3 (m), 133.2, 131.6, 129.1, 128.5, 122.3, 121.6, 118.4 (m), 117.5, 115.9 (m), 30.4, 30.2, 21.6, 20.1; IR (film): $\tilde{\nu}$ = 3142, 2958, 1474, 1263, 1065, 992, 915, 893, 771,



658 cm^{-1}; HRMS: *m/z*: calcd for $C_{17}H_{12}F_4N_2Na$: 343.08285; found 343.08259; elemental analysis calcd (%) for $C_{17}H_{12}N_2F_4$: C 63.75, H 3.78, N 8.75; found C 63.68, H 3.71, N 8.68.

4,5,7,8-Methoxy-[2](1,4)benzeno[2](5,8)imidazo[1,5-a]pyridinophane: Prepared analogously from 4,5,7,8-tetramethoxy-13-formylaminomethyl [2](1,4)benzeno[2](2,5)-pyridinophane (25 mg, 0.065 mmol) as a pale brown solid (15 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 1H), 7.18 (s, 1H), 6.30 (d, *J* = 6.9 Hz, 1H), 6.19 (d, *J* = 6.9 Hz, 1H), 3.78 (bs, 6H), 3.53 (s, 3H), 3.23 (s, 3H), 3.35-3.08 (m, 5H), 3.04-2.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.8, 148.6, 148.5, 132.5, 130.9, 128.2, 127.2, 125.5, 123.2, 121.8, 119.4, 116.9, 62.9, 62.6, 61.5, 61.4, 29.9, 29.8, 23.2, 21.5; IR (film): $\tilde{\nu}$ = 2935, 1449, 1402, 1243, 1074, 1030, 985, 760 cm^{-1}; HRMS: *m/z*: calcd for $C_{21}H_{24}N_2O_4$: 368.17361; found 368.17355.

[2](1,4)Benzeno[2](5,8)-2-methylimidazo[1,5-a]pyridiniumphane iodide (16): MeI (193 μL, 3.1 mmol) was added to a suspension of [2](1,4)benzeno[2](5,8)imidazo[1,5-a]pyridinephane (155 mg, 0.62 mmol) in THF (2 mL) and the mixture was stirred at 60 ºC overnight. Pentane addition (5 mL) caused the precipitation of the desired product as a yellow solid that was washed twice with pentane (2 mL each) and dried in vacuo (210 mg, 87%). ^{1}H NMR (300 MHz, d_6- DMSO): δ = 9.67 (s, 1H), 8.07 (s, 1H), 6.70 (d, *J* = 7.1 Hz, 1H), 6.68-6.62 (m, 2H), 6.57 (d, *J* = 7.1 Hz, 1H), 6.16 (dd, *J* = 1.5, 8.0 Hz, 1H), 6.00 (dd, *J* = 1.3, 7.8 Hz, 1H), 4.16 (s, 3H), 3.45-2.90 (m, 8H); ^{13}C NMR (75 MHz, d_6- DMSO): δ = 137.4, 136.0, 133.9, 133.5, 132.3, 132.0, 129.6, 129.1, 127.2, 126.7, 123.1, 122.9, 116.1, 37.3, 33.3, 31.5, 30.5, 30.2; IR (film): $\tilde{\nu}$ = 3115, 2933, 2862, 1645, 1549, 1499, 1415, 1177, 1157, 803, 776, 725, 613 cm^{-1}; HRMS: *m/z*: calcd for $C_{18}H_{19}N_2$: 263.15428; found 263.15417; elemental analysis calcd (%) for $C_{18}H_{19}N_2$: C 55.40, H 4.91, N 7.18; found C 55.31, H 4.78, N 7.09.

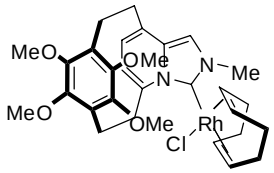
4,5,7,8-Tetrafluoro-[2](1,4)benzeno[2](5,8)-2-methylimidazo[1,5-a]pyridiniumphane iodide: Prepared analogously from 4,5,7,8-tetrafluoro[2](1,4)benzeno[2](5,8)-imidazo [1,5-a]pyridinophane (58 mg, 0.18 mmol) as a yellow solid (70 mg, 84%). ^{1}H NMR (400 MHz, d_6-DMSO): δ = 10.06 (s, 1H), 8.46 (s, 1H), 6.98 (bs, 2H), 4.19 (s, 3H), 3.78-3.15 (m, 8H); ^{13}C NMR (75 MHz, d_6-DMSO): δ = 146.9 (m), 146.5 (m), 143.5 (m), 143.3 (m), 132.7, 132.1, 128.6, 128.2, 126.8, 121.0, 118.1 (t, *J* = 19.7 Hz), 116.4 (t, *J* = 19.5 Hz) 115.8, 36.8, 28.9, 28.6, 20.9, 19.2; IR (film): $\tilde{\nu}$ = 3026, 2951, 1471, 1266, 1037, 989, 896, 789 cm^{-1}; HRMS: *m/z*: calcd for $C_{18}H_{15}F_4N_2$: 335.11658; found 335.11651; elemental analysis calcd (%) for $C_{18}H_{15}N_2F_4$: C 46.77, H 3.27, N 6.06; found C 46.71, H 3.24, N 6.01.

Complex 17: A suspension of compound **16** (100 mg, 0.25 mmol) in CH_2Cl_2 (3 mL) was treated with Ag_2O (30.1 mg, 0.13 mmol). After stirring for 3 h, $[RhCl(cod)]_2$ (64 mg, 0.13 mmol) was added and stirring continued overnight. Removal of the precipitated silver salts through a pad of silica, evaporation of the filtrate, and purification of the residue by flash chromatography (AcOEt:hexanes = 1:2) afforded complex **17** as a yellow solid (94 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.78 (s, 1H), 6.69 (dd, *J* = 1.5, 7.8 Hz, 1H), 6.55 (d, *J* = 1.6 Hz, 1H), 6.54 (d, *J* = 1.6 Hz, 1H), 6.29-6.26 (m, 1H), 5.98 (dd, *J* = 1.7, 7.9 Hz, 1H), 5.91 (d, *J* = 6.8 Hz, 1H), 5.85 (d, *J* = 6.8 Hz, 1H), 5.02 (bs, 2H), 4.35 (s, 3H), 3.72 (dt, *J* = 4.5, 7.8 Hz, 1H), 3.13 (dt, *J* = 4.5, 8.1 Hz, 1H), 3.97-2.66 (m, 7H), 2.48-2.17 (m, 4H), 1.98-1.62 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.6 (d, *J* = 51.5), 138.6, 137.6, 137.5, 136.5, 131.0, 130.7, 128.6, 127.9, 126.4, 126.2, 119.3, 112.4, 97.7 (d, *J* = 7.5 Hz), 96.4 (d, *J* = 7.0 Hz), 69.2 (d, *J* = 14.5 Hz), 68.0 (d, *J* = 14.0 Hz), 39.6, 34.6, 33.5, 33.3, 32.0, 31.7, 31.0, 29.3, 28.0; IR (film): $\tilde{\nu}$ = 2931, 2873, 2828, 1640, 1447, 1363, 1180, 1086, 806, 659 cm^{-1}; HRMS: *m/z*: calcd for $C_{26}H_{30}N_2Rh$: 473.14515; found 473.14532; elemental analysis calcd (%) for $C_{26}H_{30}N_2Rh$: C 61.36, H 5.94, N 5.50; found C 61.28, H 5.85, N 5.34.

Complex 21: Prepared analogously from 4,5,7,8-tetrafluoro [2](1,4)benzeno[2](5,8)-2-methylimidazo-[1,5-a]pyridiniumphane iodide (40 mg, 0.087 mmol) as a yellow solid (44 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.91 (s, 1H), 6.24-6.11 (m, 3H), 5.23 (bs, 2H), 4.32 (s, 3H), 4.38-3.97 (s, 1H), 3.35-3.31 (m, 1H), 3.16-2.99 (m, 2H), 2.99-2.78 (m, 4H), 2.64-2.61 (m, 1H), 2.44-2.40 (m, 1H), 2.32-2.20 (m, 3H), 2.00-1.86 (m, 1H), 1.84-1.63 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.7 (d, *J* = 50.6), 136.8, 135.8, 127.8, 123.4, 117.9, 117.4 (m), 116.9 (m), 112.1, 97.7 (d, *J* = 7.1 Hz), 96.8 (d, *J* = 7.1 Hz), 69.2 (d, *J* = 14.2 Hz), 68.3 (d, *J* = 14.1 Hz), 39.4, 33.9, 33.2, 31.7, 29.3, 28.4, 28.0, 21.0, 20.7 (the four *C*F were not detected); ^{19}F NMR (282 MHz,

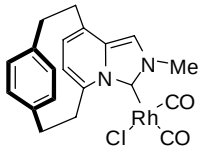
$CDCl_3$): δ = –138.7, –139.5, –141.2, –147.7; IR (film): $\tilde{\nu}$ = 3089, 2936, 2871, 2829, 1474, 1268, 987, 892, 663 cm^{-1}; HRMS: *m/z*: calcd for $C_{26}H_{26}N_2F_4Rh$: 545.10746; found 545.10741; elemental analysis calcd (%) for $C_{26}H_{26}N_2F_4Rh$: C 53.76, H 4.51, N 4.82; found C 53.84, H 4.46, N 4.75.

[Rhodium chloro 1,5-cyclooctadiene 4,5,7,8-tetramethoxy[2](1,4)benzeno[2](5,8)-2-methylimidazo [1,5-a]pyridin-3-ylidenephane]: MeI (13 μL, 0.2 mmol) was added to a suspension of 4,5,7,8-tetramethoxy[2](1,4)-benzeno[2](5,8)imidazo[1,5-a]pyridinophane (15 mg, 0.04 mmol) in THF (0.5 ml) and the resulting mixture was stirred at 60 ºC overnight. Pentane addition (3 mL) caused the precipitation of the corresponding salt as a pale brown solid that was washed twice with pentane (1 mL each) and dried in vacuo.

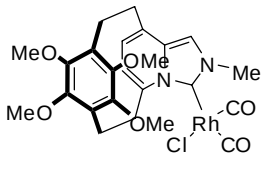


This material was suspended in CH_2Cl_2 (1 mL) was treated with Ag_2O (5 mg, 0.02 mmol). After 3 h at ambient temperature, $[RhCl(cod)]_2$ (9.8 mg, 0.02 mmol) was added and stirring continued overnight. Removal of the precipitated silver salts, evaporation of the filtrate, and purification of the residue by flash chromatography (MeOH:CH_2Cl_2 = 1:50) afforded the title complex as a yellow solid (10 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.82 (s, 1H), 6.19 (s, *J* = 6.9 Hz, 1H), 6.12 (d, *J* = 6.9 Hz, 1H), 5.78 (dd, *J* = 8.7, 12.6 Hz, 1H), 5.02 (s, 2H), 4.38 (s, 3H), 3.96-3.88 (m, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 3.63 (s, 3H), 3.60 (s, 3H) 3.40-3.26 (m, 1H), 3.10-2.92 (m, 3H), 2.90-2.74 (m, 3H), 2.67-2.60 (m, 1H), 2.58-2.44 (m, 1H), 2.41-2.17 (m, 3H), 2.09-1.93 (m, 1H), 1.90-1.71 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.7 (d, *J* = 53.0), 150.4, 149.4, 148.5, 148.3, 136.4, 136.3, 127.0, 125.1, 125.0, 122.7, 117.9, 111.6, 96.5 (d, *J* = 7.3 Hz), 95.8 (d, *J* = 7.2 Hz), 69.0 (d, *J* = 14.6 Hz), 67.8 (d, *J* = 14.8 Hz), 62.9, 62.2, 61.7, 61.2, 39.1, 34.2, 33.5, 31.5, 29.5, 28.3, 27.9, 23.7, 23.1; IR (film): $\tilde{\nu}$ = 2930, 2826, 1460, 1402, 1244, 1074, 1035, 987, 813 cm^{-1}; MS (EI)): *m/z* (%): 628 (100) $[M]^+$, 592 (25), 562 (11), 482 (15), 419 (50), 385 (44), 369 (21), 260 (68), 224 (17), 159 (69); elemental analysis calcd (%) for $C_{30}H_{38}N_2O_4ClRh$: C 57.29, H 6.09, N 4.45; found C 57.20, H 6.02, N 4.38.

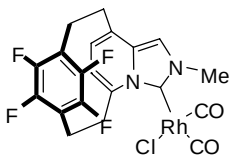
Complex 18: CO was bubbled for 5 min through a solution of complex **17** (25 mg, 0.055 mmol) in THF (2 mL). Once the color of the mixture had changed to a very pale yellow, the solvent was evaporated and the residue washed with pentane (1 mL), thus furnishing the desired carbonyl complex **18** as a light brown solid (22 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.91 (s, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.55 (bs, 2H), 6.08 (d, *J* = 7.0 Hz, 1H), 6.02 (d, *J* = 8.0 Hz,1H), 5.99-5.94 (m, 1H), 5.29 (dd, *J* = 10.6, 12.3 Hz, 1H), 4.13 (s, 3H), 3.57 (dt, *J* = 10.8, 5.3 Hz, 1H), 3.10-2.82 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.9 (d, *J* = 54.6), 181.8 (d, *J* = 74.9), 162.5 (d, *J* = 44.7), 137.8, 136.6, 136.2, 131.3, 131.0, 130.8, 128.4, 127.6, 126.7, 126.0, 120.5, 113.5, 40.3, 35.0, 33.3, 30.9, 30.8; IR (film): $\tilde{\nu}$ = 2068, 1989 cm^{-1}; MS (EI): *m/z* (%): 456 (21) $[M]^+$, 428 (24), 400 (81), 368 (69), 260 (100), 182 (20), 57 (49), 43 (70);



Complex 19: Prepared analogously as a pale yellow solid (5 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.85 (s, 1H), 6.20 (d, *J* = 7.2 Hz, 1H), 6.16 (d, *J* = 7.2 Hz, 1H), 4.97 (dd, *J* = 9.3, 13.1 Hz, 1H), 4.04 (s, 3H), 3.65 (s, 3H), 3.64 (s, 3H), 3.52 (s, 3H), 3.41 (s, 3H), 3.33-3.04 (m, 2H), 3.03-2.76 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 185.3 (d, *J* = 55.7), 183.5 (d, *J* = 75.1), 164.8 (d, *J* = 48.2), 149.5, 149.3, 136.1, 135.8, 127.2, 126.7, 126.0, 125.0, 124.7, 123.9, 119.5, 112.8, 62.8, 62.7, 62.0, 61.6, 40.1, 35.2, 29.3, 23.6, 21.7; IR (film): $\tilde{\nu}$ = 2072, 1989 cm^{-1}; HRMS: *m/z*: calcd for $C_{24}H_{26}N_2O_6Rh$: 541.08334; found 541.08391; elemental analysis calcd (%) for $C_{24}H_{26}N_2O_6Rh$: C 49.97, H 4.54, N 4.86; found C 50.10, H 4.51, N 4.82.



Complex 22: Prepared analogously from complex **21** (18 mg, 0.033 mmol) as a pale brown solid (13.7 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (s, 1H), 6.35 (dd, *J* = 4.0, 7.2 Hz, 1H), 6.28 (dd, *J* = 3.9, 7.0 Hz, 1H), 5.35 (dd, *J* = 9.3, 13.0 Hz, 1H), 4.13 (s, 3H), 3.45-2.96 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 185.8 (d, *J* = 54.4), 183.2 (d, *J* = 73.7), 167.2 (d, *J* = 47.2), 148.6 (m), 148.3 (m), 145.7 (m), 145.2 (m), 136.7, 136.4, 127.8, 125.7, 119.9, 118.3 (t, *J* = 19.6), 117.6 (t, *J* = 20.1), 113.6, 41.0, 35.2, 29.8, 21.6, 21.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –137.7, –138.8, –144.1, –145.2; IR (film): $\tilde{\nu}$ = 2073, 2004 cm^{-1}; HRMS: *m/z*: calcd for $C_{20}H_{14}N_2O_2F_4Rh$: 493.00339; found 493.00408; elemental analysis calcd (%) for $C_{20}H_{14}N_2O_2F_4Rh$: C 45.44, H 2.67, N 5.30; found C 45.40, H 2.63, N 5.24.



ADDITIONAL STRUCTURAL INFORMATION

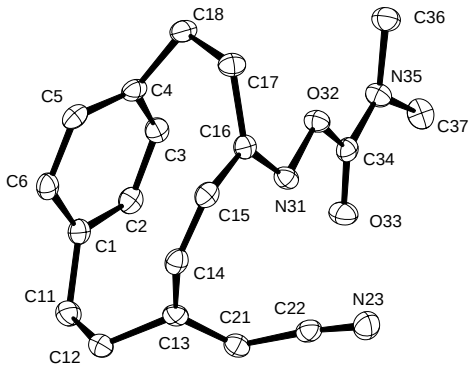


Figure S-1. Molecular crystal structure of compound **13**. Anisotropic displacement parameters are shown at the 50% probability level, hydrogen atoms are omitted for clarity.

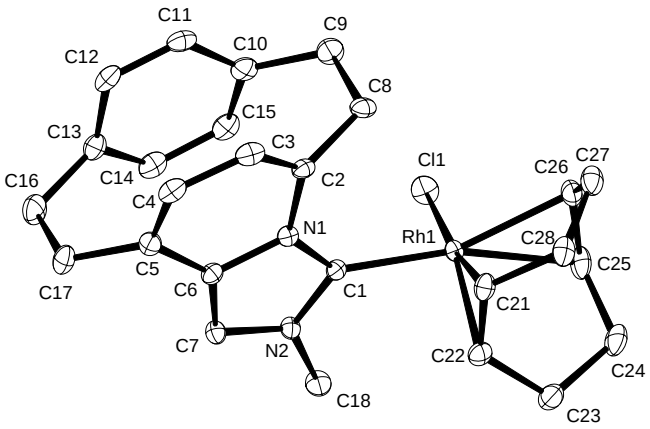


Figure S-2. Molecular crystal structure of compound **17**. Anisotropic displacement parameters are shown at the 50% probability level, hydrogen atoms are omitted for clarity.

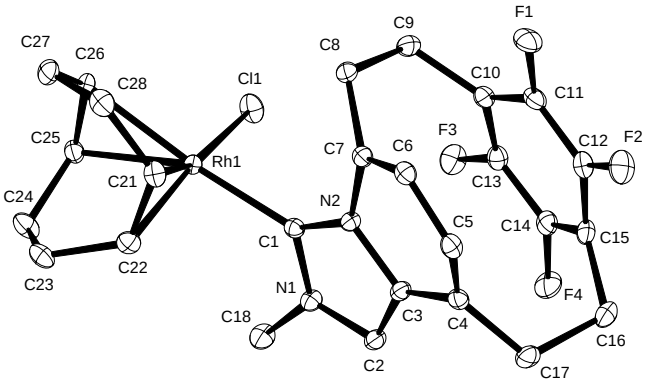


Figure S-3. Molecular crystal structure of compound **21**. Anisotropic displacement parameters are shown at the 50% probability level, hydrogen atoms are omitted for clarity.

A comparison of the molecular crystal structures of **17** and **21** reveals an almost exact agreement of the bond lenghts (average difference 0.002 Å) in the imidazo[1,5-a]pyridine-3-ylidene moiety and only slightly larger differences for the aromatic caps. Due to the ethylene bridges in the cyclophanes, all aromatic rings adopt a saddle shape but remain essentially parallel to each other (2.8° for the tetrafluoro compound and 3.9° for the unsubstituted ligand). Similarly the perpendicular distance between the ring centroid of the pyridine ring and the least-squares plane of the cap is almost the same for both compounds (2.917 and 2.937 Å). As indicated by Figure S-4, which shows the superposition of the two ligands, there is a slightly larger fold angle between the five and the six membered ring in the fluorinated compound (9.8° compared to 4.2°). Larger deviations are observed for the dihedral angles of the ethylene bridges. While for the unsubstituted cyclophane a nearly eclipsed arrangement is observed, a considerable twist is found in the fluorinated cyclophane (see Figure S-5 and Tables S-1 and S-2). In terms of the observed electronic properties, these seem to have little effect on molecular shape or intramolecular bond lengths. One would however expect, that there is a large difference in the local quadrupole moments of the fluorinated and the unsubstituted caps, which will have a strong through space influence on the electron distribution in the other half of the cyclophane.

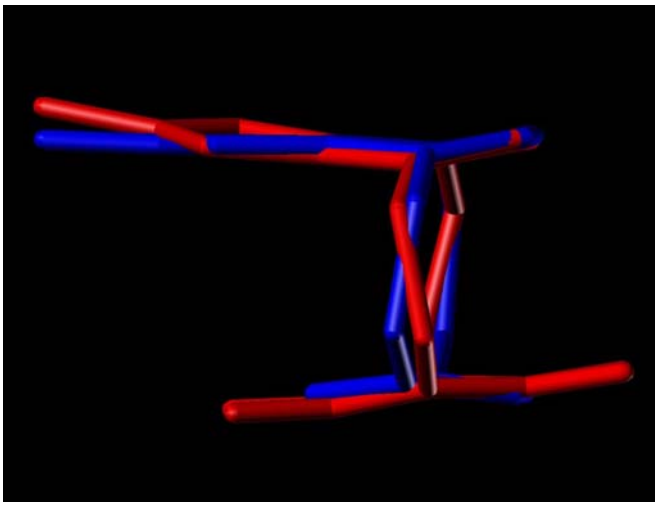


Figure S-4: Superposition of the carbene ligands of **17** (blue) and **21** (red) illustrating the saddle shape of the aromatic rings and slightly larger folding between the five and six membered rings in the fluorinated ligand of **21**.

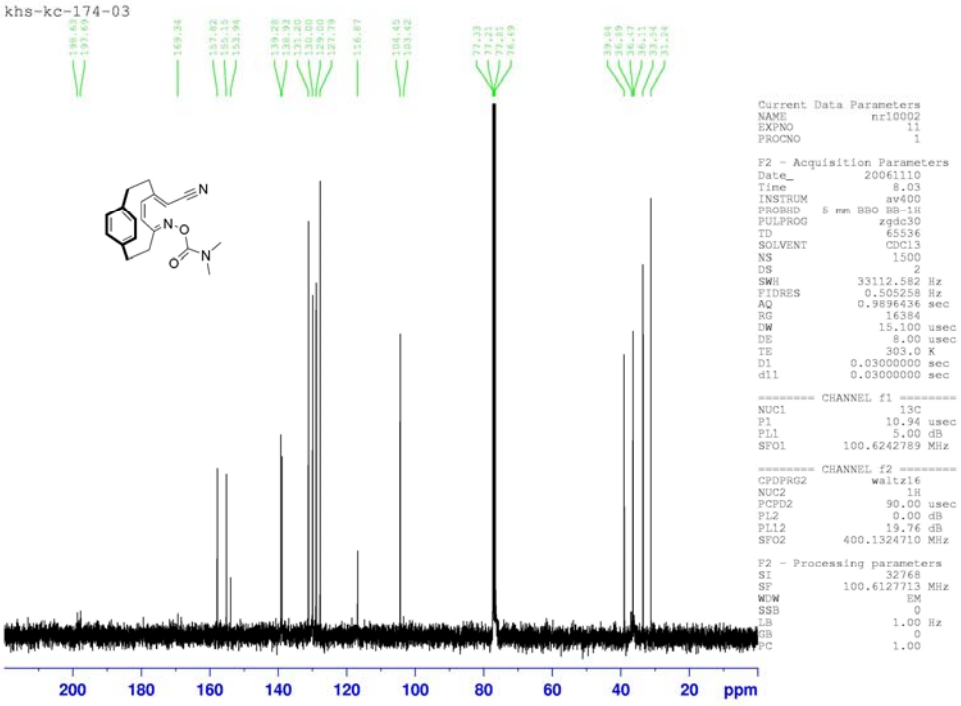
Figure S-5: Side-by-side view of the cyclophane ligands of **17** and **21** showing the different twisting of the ethylene bridges.

Table S-1. Interplanar angles and dihedral angles in complex **21**

Planes (defining atoms)		Interplanar Angle
Plane 1 (C10/C13/C14/C15)	Plane 2 (C10/C11/C12/C15)	11.98(16)°
Plane 3 (C7/N2/C3/C4)	Plane 4 (C7/C6/C5/C4)	16.38(16)°
Plane 5 (C11/C12/C13/C14)	Plane 7 (C12/C14/C15)	9.19(33)°
Plane 5	Plane 8 (C10/C11/C13)	9.83(32)°
Plane 6 (C6/C5/C3/N2)	Plane 9 (C3/C4/C5)	12.64(30)°
Plane 6	Plane 10 (C6/C7/N2)	14.28(30)°
Plane 11 (C1/N1/N2/C2/C3)	Plane 12 (N2/C3/C4/C5/C6/C7)	9.83(14)°
Plane 12	Plane 13 (C10/C11/C12/C13/C14/C15)	2.78(13)°
Torsional angle	C4-C17-C16-C15	-14.23(25)°
	C7-C8-C9-C10	-19.68(24)°

Table S-1. Interplanar angles and dihedral angles in complex **17**

Planes (defining atoms)		Interplanar Angle
Plane 1 (C10/C13/C14/C15)	Plane 2 (C10/C11/C12/C13)	12.62(46)°
Plane 3 (C2/C3/C4/C5)	Plane 4 (C2/N1/C6/C5)	15.09(43)°
Plane 5 (C11/C12/C14/C15)	Plane 7 (C11/C10/C15)	10.22(61)°
Plane 5	Plane 8 (C12/C13/C14)	10.58(79)°
Plane 6 (C3/C4/C6/N1)	Plane 9 (C3/C2/N1)	12.97(72)°
Plane 6	Plane 10 (C4/C5/C6)	11.64(55)°
Plane 11 (C1/N2/C7/C6/N1)	Plane 12 (N1/C2/C3/C4/C5/C6)	2.75(33)°
Plane 12	Plane 13 (C10/C11/C12/C13/C14/C15)	2.43(31)°
Torsional angle	C5-C17-C16-C13	-9.64(66)°
	C2-C8-C9-C10	2.71(65)°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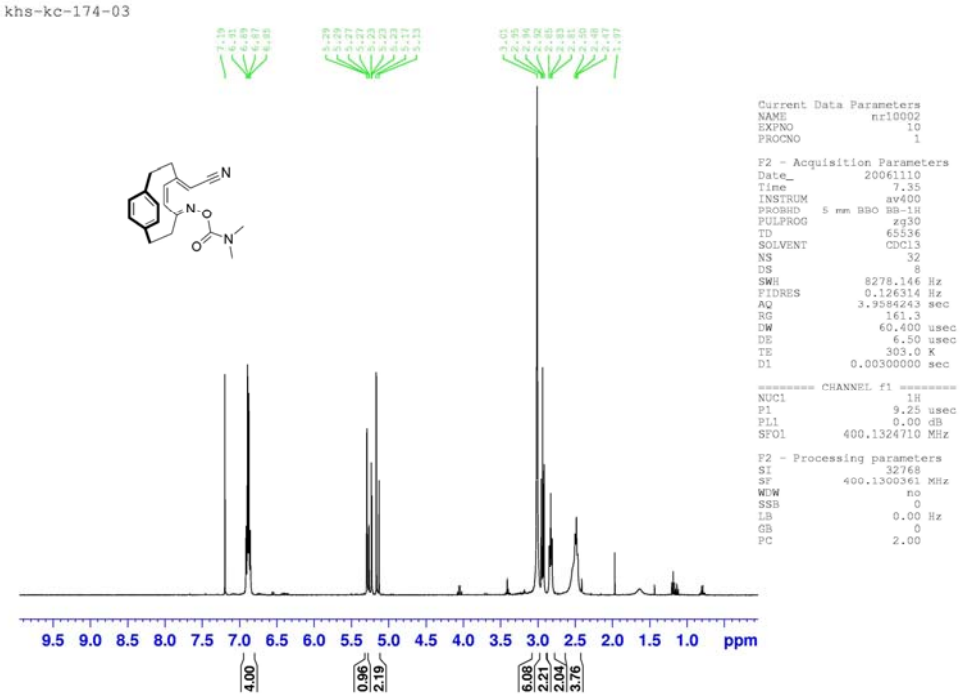
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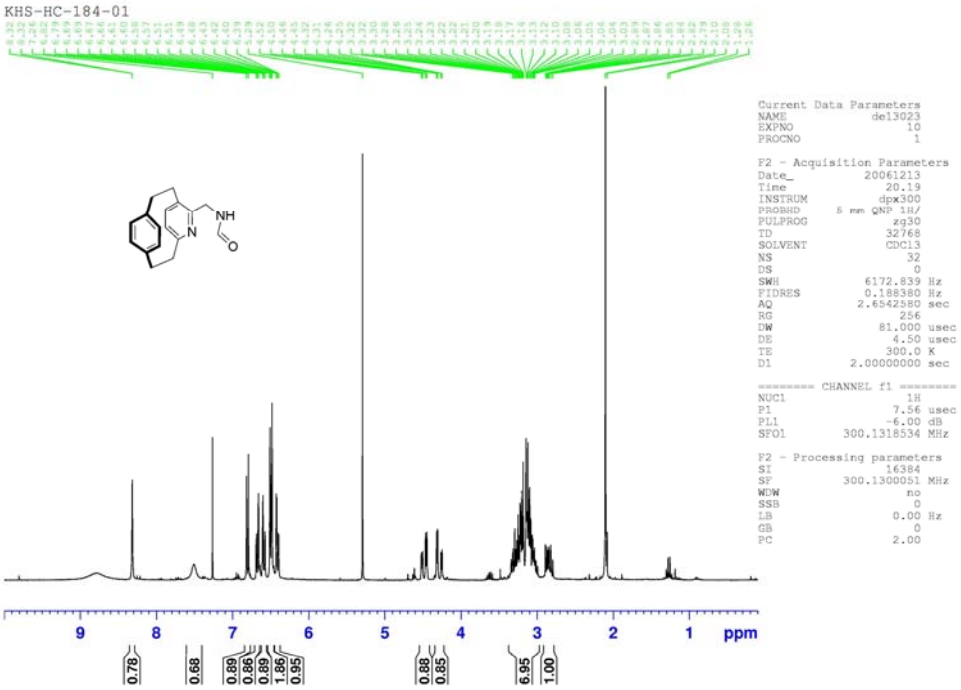
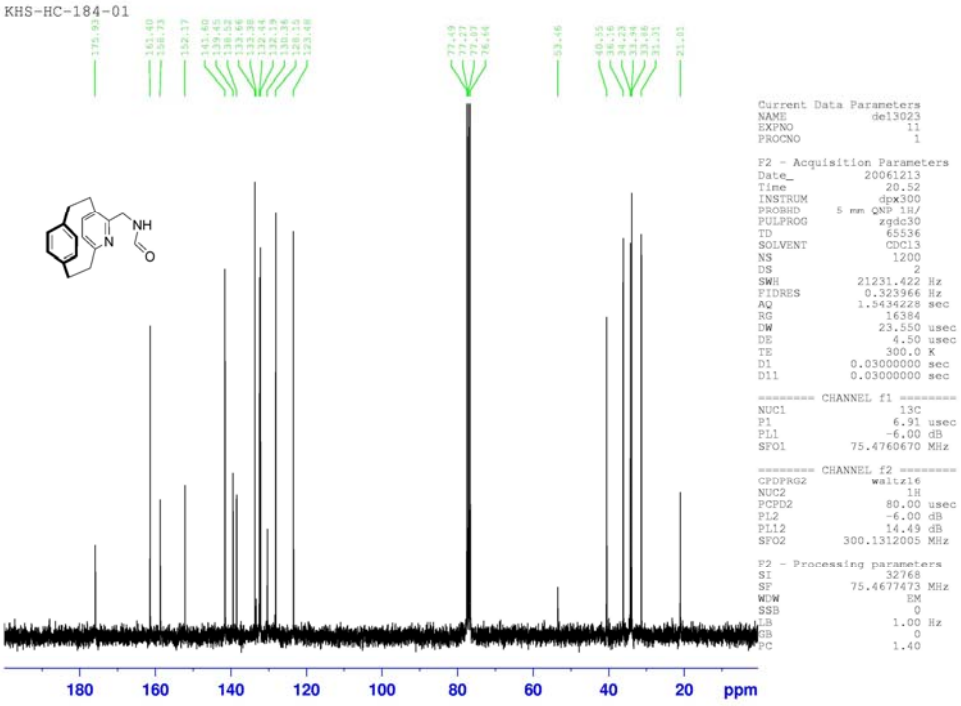
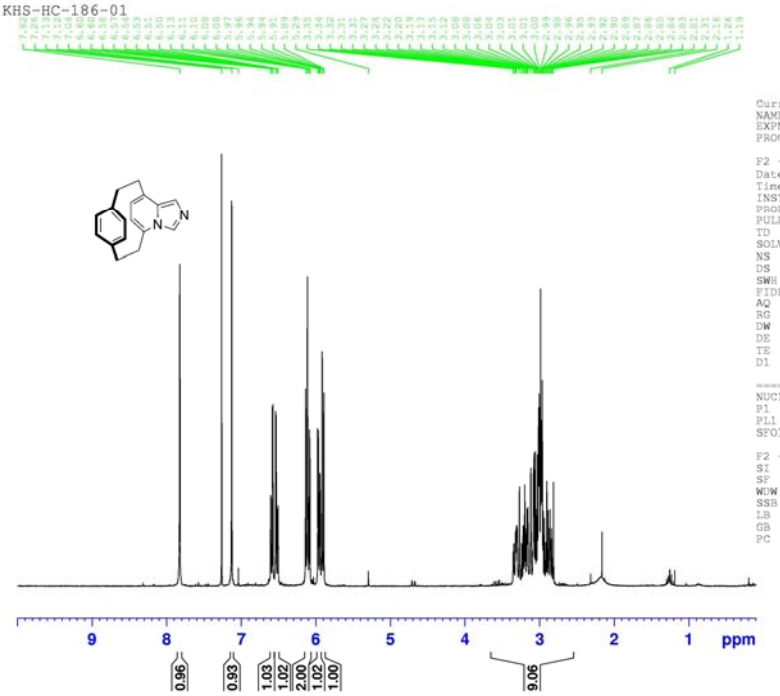
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 8
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 161.3
DW 60.400 usec
DE 6.50 usec
TE 303.0 K
D1 0.00300000 sec
CHANNEL f1
NUC1 1H
P1 9.25 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300361 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00


KHS-HC-184-01
NH
O
9
8
7
6
5
4
3
2
1
ppm
0.78
0.68
0.89
0.86
0.89
1.86
0.95
0.88
0.85
6.95
1.00
Current Data Parameters
NAME de13023
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20061213
Time 20.19
INSTRUM dpx300
PROBHD 5 mm QNP 1H/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 256
DW 81.000 usec
DE 4.50 usec
TE 300.0 K
D1 2.00000000 sec
CHANNEL f1
NUC1 1H
P1 7.56 usec
PL1 -6.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 16384
SF 300.1300051 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

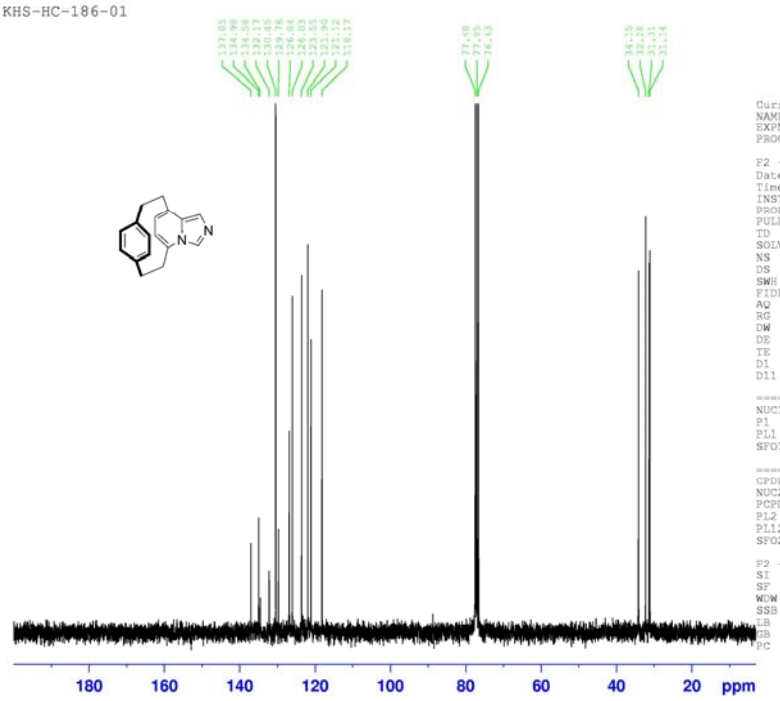

KHS-HC-184-01
175.93
161.40
158.73
152.17
141.60
139.45
136.62
133.66
133.38
132.44
132.19
130.36
128.15
123.48
77.49
77.17
76.84
53.46
40.55
36.16
34.29
31.34
31.16
31.01
21.01
NH
O
180
160
140
120
100
80
60
40
20
ppm
Current Data Parameters
NAME de13023
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20061213
Time 20.52
INSTRUM dpx300
PROBHD 5 mm QNP 1H/
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 1200
DS 2
SWH 21231.422 Hz
FIDRES 0.323966 Hz
AQ 1.5434228 sec
RG 16384
DW 23.550 usec
DE 4.50 usec
TE 300.0 K
D1 0.03000000 sec
D11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 6.91 usec
PL1 -6.00 dB
SFO1 75.4760670 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.49 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677473 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

KHS-HC-186-01



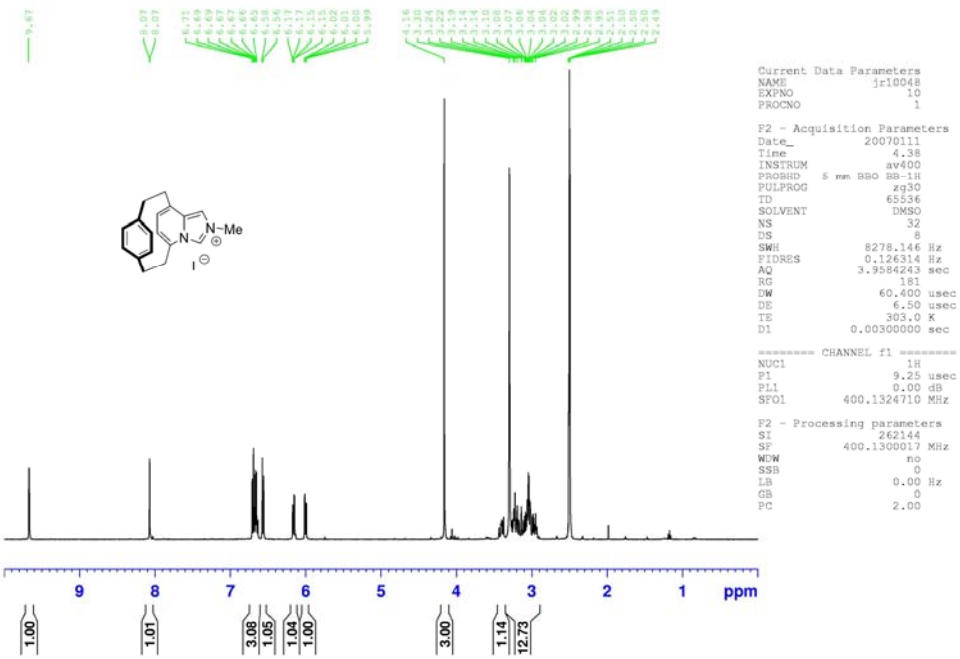

```
Current Data Parameters
NAME                  del18015
EXPNO                       10
PROCNO                       1

F2 - Acquisition Parameters
Date_               20061218
Time                   15.26
INSTRUM                dpx300
PROBHD     5 mm QNP 1H/
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        32
DS                         0
SWH                6172.839 Hz
FIDRES             0.188380 Hz
AQ                 2.6542580 sec
RG                     406.4
DW                  81.000 usec
DE                   4.50 usec
TE                   300.0 K
D1                2.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                       7.56 usec
PL1                     -6.00 dB
SFO1             300.1318534 MHz

F2 - Processing parameters
SI                         16384
SF                300.1300061 MHz
WDW                           no
SSB                            0
LB                          0.00 Hz
GB                             0
PC                         10.00
```

KHS-HC-186-01



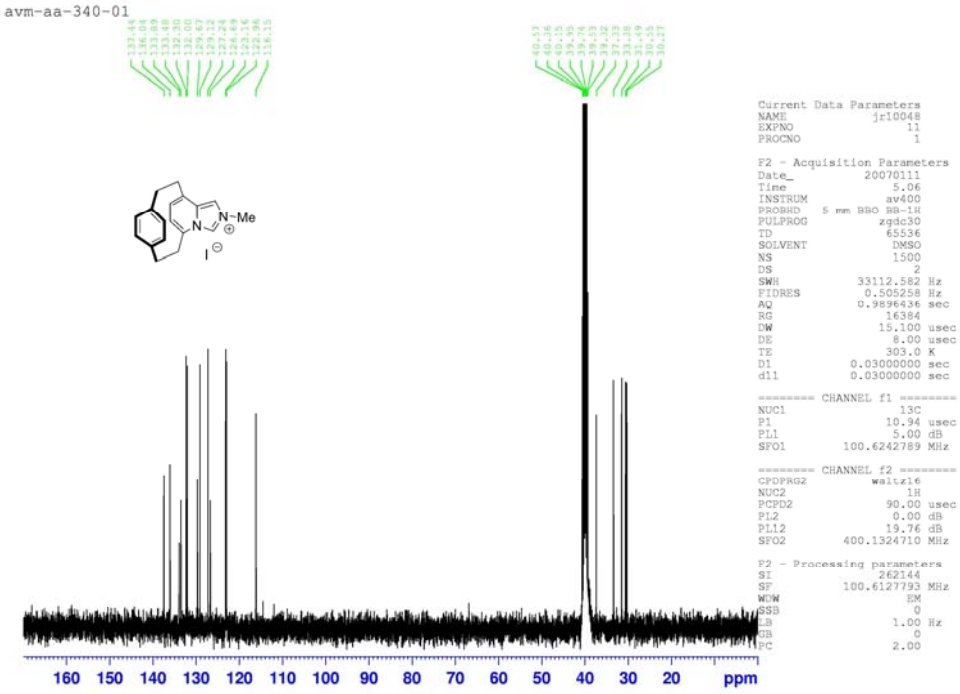

```
Current Data Parameters
NAME                  del18015
EXPNO                       11
PROCNO                       1

F2 - Acquisition Parameters
Date_               20061218
Time                   15.58
INSTRUM                dpx300
PROBHD     5 mm QNP 1H/
PULPROG              zgdc30
TD                     65536
SOLVENT                CDCl3
NS                      1200
DS                         2
SWH               21231.422 Hz
FIDRES             0.323966 Hz
AQ                 1.5434228 sec
RG                    7298.2
DW                  23.550 usec
DE                   4.50 usec
TE                   300.0 K
D1                0.03000000 sec
D11               0.03000000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                       6.91 usec
PL1                     -6.00 dB
SFO1             75.4760670 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                     -6.00 dB
PL12                    14.49 dB
SFO2             300.1312005 MHz

F2 - Processing parameters
SI                         32768
SF                75.4677477 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```

avm-aa-340-01

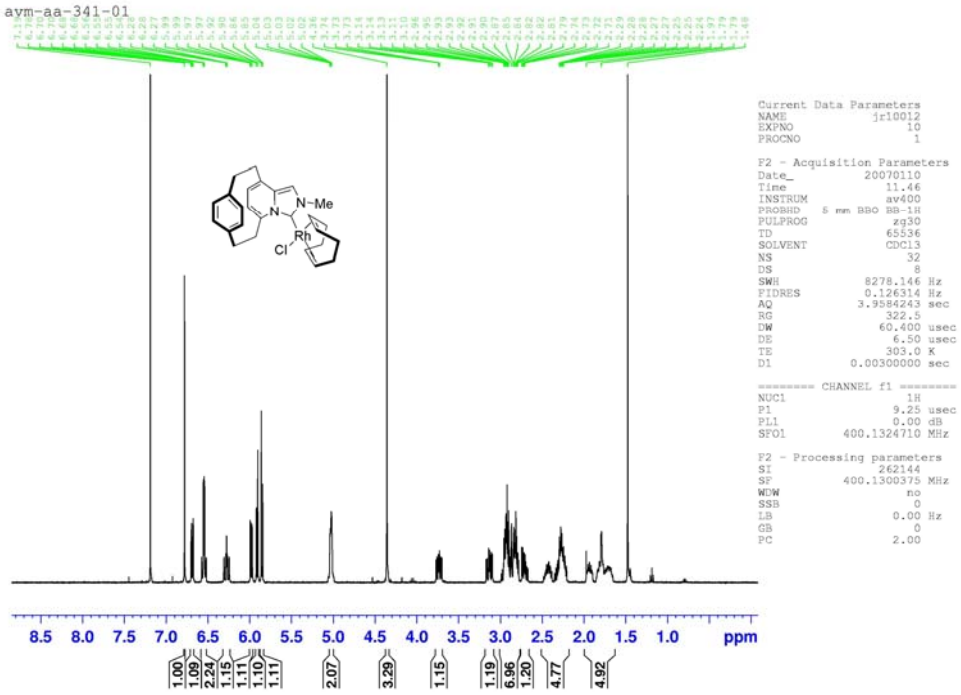


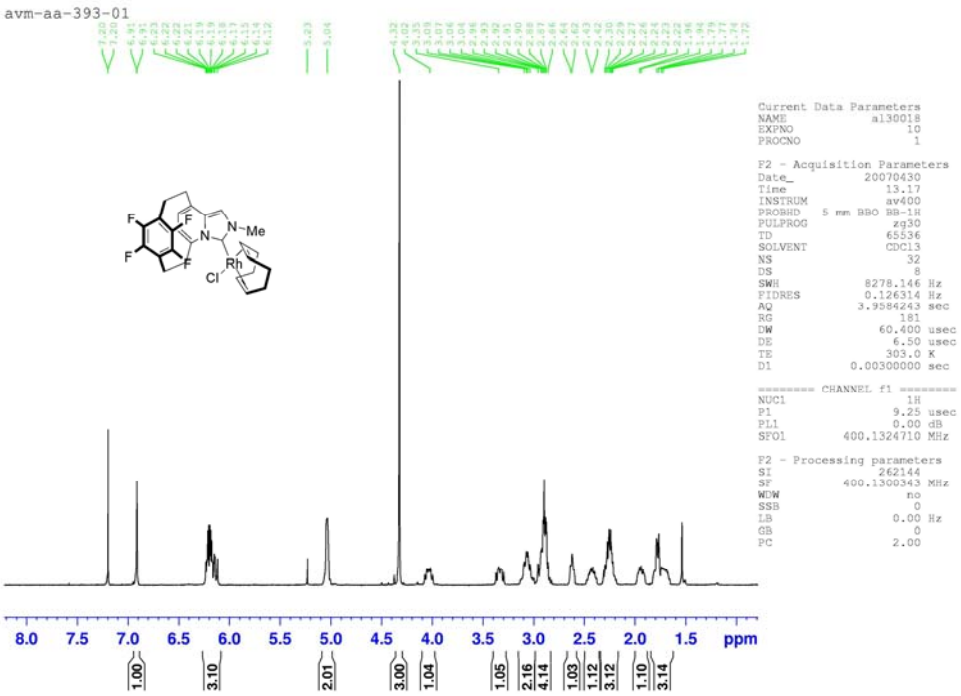

```
Current Data Parameters
NAME                  jr10048
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_              20070111
Time                   4.38
INSTRUM               av400
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      32
DS                       8
SWH               8278.146 Hz
FIDRES               0.126314 Hz
AQ                3.9584243 sec
RG                     181
DW                  60.400 usec
DE                   6.50 usec
TE                  303.0 K
D1                0.00300000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    9.25 usec
PL1                   0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                     262144
SF                400.1300017 MHz
WDW                        no
SSB                         0
LB                    0.00 Hz
GB                          0
PC                    2.00
```

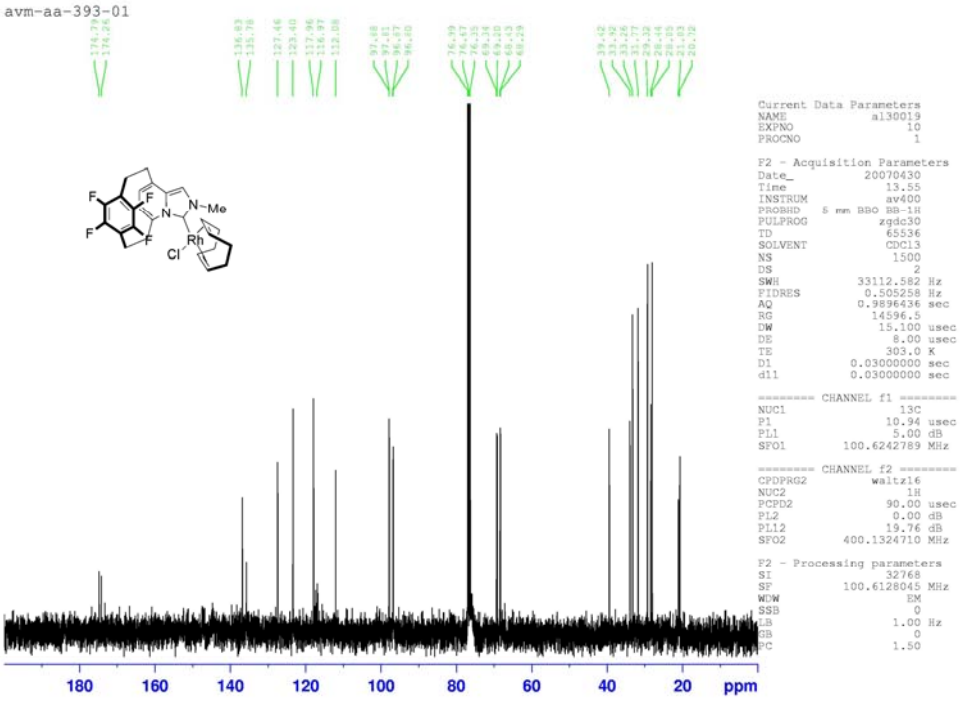
avm-aa-340-01

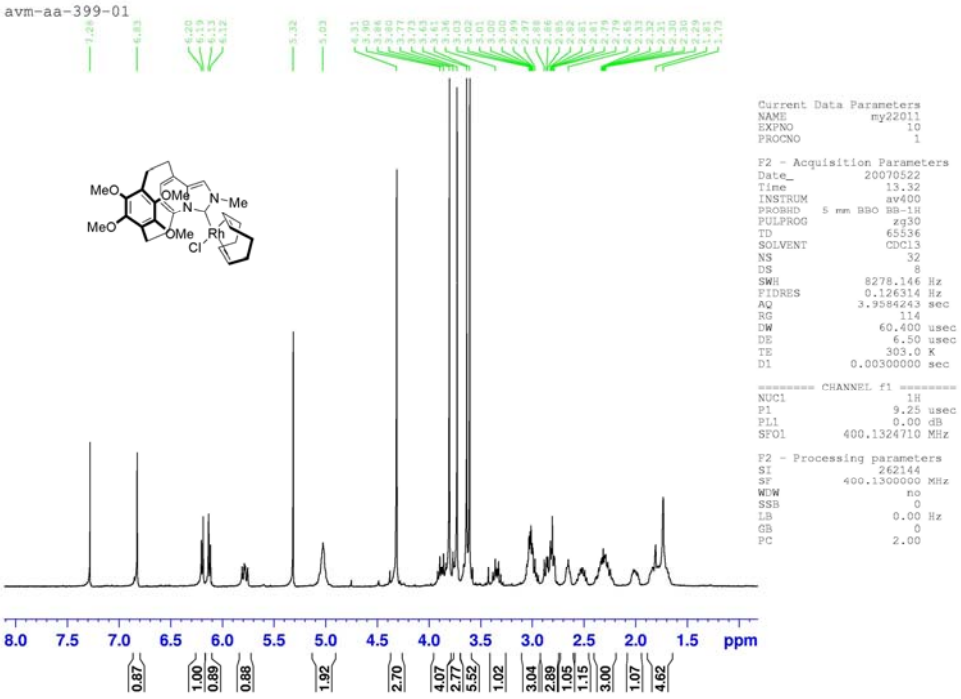


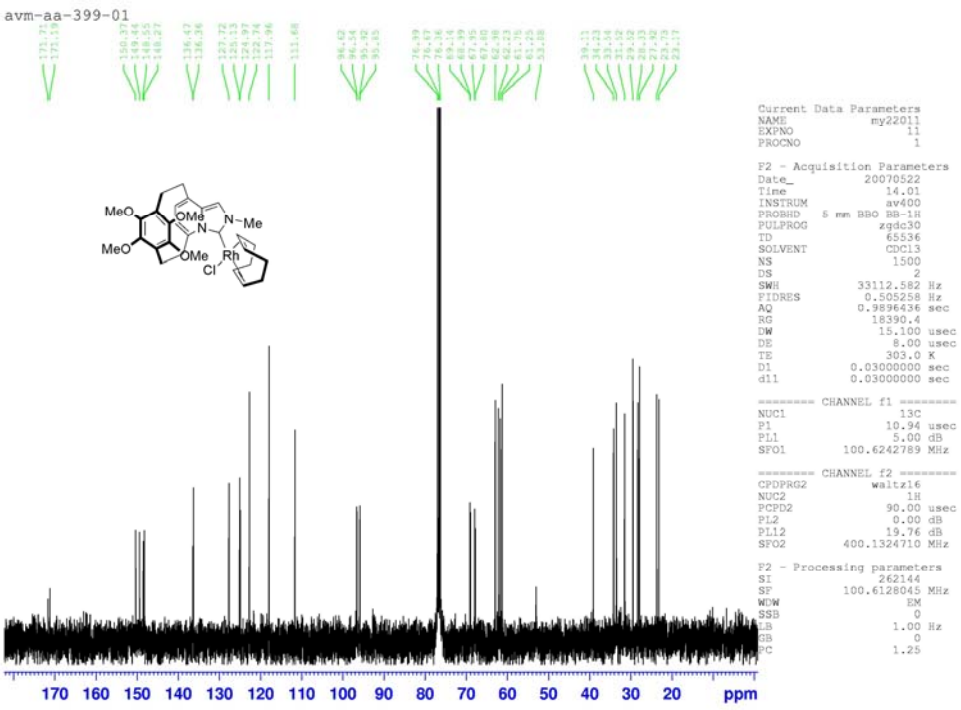

```
Current Data Parameters
NAME                  jr10048
EXPNO                      11
PROCNO                      1

F2 - Acquisition Parameters
Date_              20070111
Time                   5.06
INSTRUM               av400
PROBHD    5 mm BBO BB-1H
PULPROG            zgdc30
TD                   65536
SOLVENT               DMSO
NS                    1500
DS                       2
SWH              33112.582 Hz
FIDRES               0.505258 Hz
AQ                0.9896436 sec
RG                     16384
DW                  15.100 usec
DE                   8.00 usec
TE                  303.0 K
D1                0.03000000 sec
d11               0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                   10.94 usec
PL1                   5.00 dB
SFO1           100.6242789 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                90.00 usec
PL2                   0.00 dB
PL12                 19.76 dB
SFO2           400.1324710 MHz

F2 - Processing parameters
SI                     262144
SF                100.6127793 MHz
WDW                        EM
SSB                         0
LB                    1.00 Hz
GB                          0
PC                    2.00
```


avm-aa-341-01
N
N-Me
Rh
Cl
Current Data Parameters
NAME jr10012
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070110
Time 11.46
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 8
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 322.5
DW 60.400 usec
DE 6.50 usec
TE 303.0 K
D1 0.00300000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.25 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 262144
SF 400.1300375 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00 1.09 2.24 1.15 1.11 1.10 1.11 2.07 3.29 1.15 1.19 6.96 1.20 4.77 4.92


avm-aa-393-01
F
F
F
N
N-Me
Rh
Cl
Current Data Parameters
NAME al30018
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070430
Time 13.17
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 8
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 181
DW 60.400 usec
DE 6.50 usec
TE 303.0 K
D1 0.00300000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.25 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 262144
SF 400.1300343 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
1.00 3.10 2.01 3.00 1.04 1.05 2.16 4.14 1.03 1.12 3.12 1.10 3.14


avm-aa-393-01
Current Data Parameters
NAME a130019
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070430
Time 13.55
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 1500
DS 2
SWH 33112.582 Hz
FIDRES 0.505258 Hz
AQ 0.9896436 sec
RG 14596.5
DW 15.100 usec
DE 8.00 usec
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.94 usec
PL1 5.00 dB
SFO1 100.6242789 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 19.76 dB
SFO2 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 100.6128045 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.50
180 160 140 120 100 80 60 40 20 ppm


avm-aa-399-01
Current Data Parameters
NAME my22011
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070522
Time 13.32
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 8
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 114
DW 60.400 usec
DE 6.50 usec
TE 303.0 K
D1 0.00300000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.25 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 262144
SF 400.1300000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
0.87 1.00 0.89 0.88 1.92 2.70 4.07 2.77 5.52 1.02 3.04 2.89 1.05 1.15 3.00 1.07 4.62


avm-aa-399-01
MeO
OMe
N
Me
MeO
OMe
Rh
Cl
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
Current Data Parameters
NAME my22011
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070522
Time 14.01
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 1500
DS 2
SWH 33112.582 Hz
FIDRES 0.505258 Hz
AQ 0.9896436 sec
RG 18390.4
DW 15.100 usec
DE 8.00 usec
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.94 usec
PL1 5.00 dB
SFO1 100.6242789 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 19.76 dB
SFO2 400.1324710 MHz
F2 - Processing parameters
SI 262144
SF 100.6128045 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.25