Supporting Information

to

**Triazolyl- vs. Pyridyl-functionalized N-Heterocyclic Carbene Complexes: Impact of the Pendant N-donor Ligand on Intramolecular C–C Bond Formation**

Betty Y. T. Lee, Andrew D. Phillips, Muhammad Hanif, Tilo Söhnel, Christian G. Hartinger

---

a School of Chemical Sciences, The University of Auckland, Private Bag 92019, Auckland 1142, New Zealand. http://hartinger.auckland.ac.nz/

b School of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland.

E-mail: c.hartinger@auckland.ac.nz, andrew.phillips@ucd.ie.

---

**Table of Contents**

ESI-MS characterization data

Reactivity studies by MS and NMR spectroscopy

Density Functional Theory Calculations: Procedure, benchmarking and additional figures

UV/vis spectra

Fluorescence spectra

X-ray crystallography data and data collection parameters

\(^1\)H and \(^13\)C\{(\(^1\)H\} NMR and ESI-mass spectra used in the characterization of compounds
**Table S1.** Observed and calculated m/z values, and peak assignment of the most abundant peaks in the positive ion-mode ESI-mass spectra of compounds 3–5, 6a–d, 7a–d and 8’, and the adduct of 8’ with pta (8pta).

| Compound | m/z   | m/z(calculated) | Peak assignment  |
|----------|-------|-----------------|------------------|
| 3        | 347.1530 | 347.1543 | [M – Br]+         |
| 4        | 400.1811 | 400.1808 | [M – PF₆]+      |
| 5        | 480.2178 | 480.2183 | [M – PF₆]+      |
| 6a       | 670.1573 | 670.1565 | [M – PF₆]+      |
| 6b       | 760.2147 | 760.2120 | [M – PF₆]+      |
| 6c       | 672.1639 | 672.1649 | [M – PF₆]+      |
| 6d       | 762.2218 | 762.2215 | [M – PF₆]+      |
| 7a       | 750.1928 | 750.1937 | [M – PF₆]+      |
| 7b       | 840.2495 | 840.2495 | [M – PF₆]+      |
| 7c       | 752.2023 | 752.2027 | [M – PF₆]+      |
| 7d       | 842.2599 | 842.2601 | [M – PF₆]+      |
| 8’       | 716.2266 | 716.2260 | [M – OTf]+      |
| 8pta     | 873.3024 | 873.3024 | [8 – OTf + pta]+ |
Conversion of 7c to 8’

Table S2. Reaction conditions investigated involving 7c and various compounds used in the syntheses of 8’.

| Reaction | AgOTf | Ag₂O | AgNO₃ |
|----------|-------|------|-------|
| 1        | •     |      |       |
| 2        | •     | •    |       |
| 3        | •     | •    |       |
| 4        | •     | •    |       |
| 5        | •     | •    |       |

Reaction 1. Reaction of 7c with AgOTf
A mixture of 7c (4 mg, 4 µmol, 1 eq.) and AgOTf (1 mg, 4 µmol, 1 eq.) in 5 mL DCM was refluxed under nitrogen in darkness for 24 h. The reaction was monitored by ¹H NMR spectroscopy. Due to the number of additional resonances observed after 4 h of the reaction, unambiguous assignment of the signals formed proved difficult. Decomposition was observed after 24 h of the reaction.

Reaction 2. Reaction of 7c with Ag₂O
A mixture of 7c (6.0 mg, 7.0 µmol, 1.0 eq.) and Ag₂O (2.0 mg, 7.0 µmol, 1.0 eq.) in 10 mL DCM was refluxed under nitrogen in darkness for 4 h. The reaction was monitored by ¹H NMR spectroscopy. No reaction occurred during this time. Ag₂O (4.0 mg, 14 µmol, 2.0 eq.) was added to the solution and continued to be refluxed for 24 h, and a ¹H NMR spectrum was recorded which indicated decomposition.

Reaction 3. Reaction of 7c with Ag₂O
A mixture of 7c (5.0 mg, 6.0 µmol, 1.0 eq.) and Ag₂O (4.0 mg, 18 µmol, 3.0 eq.) in 10 mL DCM was refluxed under nitrogen in darkness for 2 h. Ag₂O (4.0 mg, 18 µmol, 3.0 eq.) was added to the solution and continued to be refluxed for another 2 h. The reaction was monitored by ¹H NMR spectroscopy. No reaction occurred during this time. The reaction mixture was
refluxed for another 24 h and the $^1$H NMR spectrum recorded after that period indicated decomposition.

**Reaction 4. Reaction of 7c with Ag$_2$O**

A mixture of 7c (5.0 mg, 6.0 µmol, 1.0 eq.) and Ag$_2$O (4.0 mg, 18 µmol, 3.0 eq.) in 10 mL DCM was refluxed under nitrogen in darkness for 24 h. The color of the solution changed from yellow to blue. $^1$H NMR and ESI-mass spectra of the blue reaction mixture were recorded (Figures 2 and S1). The reaction resulted in a mixture of 7c and 8' as demonstrated by $^1$H NMR spectroscopy (Figure 2). The formation of 8' was supported by ESI-MS (Figure S1) with a peak at $m/z$ 716.2244 being assigned to [M – PF$_6$]$^+$ ($m_{\text{calc}} = 716.2255$) and the presence of 7c was indicated by a peak at $m/z$ 752.2001 ([M – PF$_6$]$^+$, $m_{\text{calc}} = 752.2027$). The reaction mixture was continued to be refluxed for another 24 h. A $^1$H NMR spectrum was recorded which suggested decomposition (Figure 2).

![ESI-mass spectrum of reaction 4 between 7c and Ag$_2$O recorded after 24 h.](image)

**Figure S1.** ESI-mass spectrum of reaction 4 between 7c and Ag$_2$O recorded after 24 h.

**Reaction 5. Reaction of 7c with AgNO$_3$**

A mixture of 7c (5.0 mg, 6.0 µmol, 1.0 eq.) and AgNO$_3$ (2.0 mg, 12 µmol, 2.0 eq.) in 10 mL MeCN was refluxed under nitrogen in darkness for 24 h. The reaction was monitored by $^1$H NMR spectroscopy. Due to the number of additional resonances observed, unambiguous assignment of the signals formed proved difficult.
Figure S2. Molecular structure of the (protonated) pro-carbene 4 drawn at 50% probability level. The PF$_6^-$ counterion was omitted for clarity. Only one of the two independent molecules is shown and the disorder of the benzimidazolium moieties and the pyridyl groups was omitted.

Reaction of 8’ with 1,3,5-triaza-7-phosphaadamantane (pta)
A mixture of 8’ (5.0 mg, 5.8 µmol, 1.0 eq.) and pta (1.0 mg, 5.8 µmol, 1.0 eq.) in methanol (10 mL) was stirred for 24 h at room temperature. ESI-mass (Figure S3), and $^1$H and $^{31}$P{$^1$H} NMR spectra (Figures S4 and S5) of the reaction mixture were recorded.

Figure S3. ESI-mass spectrum of the reaction mixture of 8’ and pta.
Figure S4. $^1$H NMR spectrum of the reaction mixture of 8’ and pta in CDCl$_3$.

Figure S5. $^{31}$P{$^1$H} NMR spectrum of the reaction mixture of 8’ and pta in CDCl$_3$. 
Figure S6. Ball and stick model of the DFT-calculated (ωB97xD) energy minimum of the cationic adduct formed between 8’ and pta with hydrogen atoms omitted for clarity. The reaction enthalpy between 8’ and pta in the gas phase is -25.88 kcal mol$^{-1}$.

In silico Density Functional Theory Studies

Computational Modeling Procedures
Geometry optimizations, frequency analyses, intrinsic reaction coordinates (IRCs), Mayer bond indexes, CM5 charges and energies were calculated using density functional theory as executed by the Gaussian 16 suite of programs, revision c01 running on ICHEC supercomputer cluster Kay (2 × 20 core 2.4 GHz Intel Gold Skylake 6148 processors). The three-parameter hybrid gradient-corrected functional (ωB97xD) was employed for all calculations as developed by Gordon-Head et al., and incorporates a modified version of Becke’s exchange functional (B97),$^1$ with the non-local correlation of Perdew-Wang. This functional contains a small degree of HF exchange to account for short range interactions.$^2$ Moreover, this particular DFT functional features a long-range empirical function to account for dispersion effects.

The reaction pathways were constructed from geometry-optimized structures representing energy minima or saddle points (transition states) using the ωB97xD level of theory, which has
an established reputation for producing highly accurate structural parameters for organometallic complexes.\textsuperscript{3-6} This method incorporates a modified version of Grimme’s D2 algorithm for calculating damped long-range dispersion corrections, which are beneficial in providing realistic energies for complexes where strong internal interactions between substituents are present.\textsuperscript{6,7} Calculated gas-phase energies were corrected through an applied approximated solvent potential using the SMD protocol, using MeCN as the solvent.\textsuperscript{8}

For each step of the geometry optimizations, self-consistent iterations were performed until a convergence criterion of $10^{-8}$ was obtained. A double zeta Gaussian-type basis set of Petersson was used and augmented with an additional set of $d$-orbitals for C, N and Cl and an additional $p$-orbital for hydrogen (6-31G(d,p)).\textsuperscript{9} In order to successfully locate the transition states involving hydroxide or water, a more polarized basis set (6-31+G(d,p)) for O was employed. The rhodium center was modelled with the Stoll and Preuss SDDAll basis set of double zeta quality, substituting the core electron wave-functions with an effective pseudopotential.\textsuperscript{10}

Optimized structures were verified to be stationary minima as indicated by the absence of imaginary frequencies or transition states as indicated by a single imaginary frequency. All transition states were verified to be connected to the appropriate minima by performing IRC analyses using the geometry and frequency analysis of the transition state as the starting point. Population analysis was performed using CM5 which employs the charge fitting methodology (Charge Model 5) as developed by Truhlar and Cramer \textit{et al}.\textsuperscript{11} Post-quantum analyses including both \textbf{VIIIa} and \textbf{VIIIb} were performed using the MULTIWFN program. Where appropriate, the density gradient was analyzed for covalent and non-covalent interactions and was performed using Density Overlap Regions Indicator algorithm (IRI) as developed by Hen and Lu,\textsuperscript{12} and implemented using the MULTIWFN program version 1.38.\textsuperscript{13} IRI plots were generated using VMD.\textsuperscript{14}

**Benchmarking of the employed DFT level of theory and basis set**

To validate the use of $\omega$-B97xD and the employed basis set, an optimization of the Ru(cym) complex \textbf{6a} was performed and compared to the experimentally obtained molecular structure (Tables S3 and S4). In this case, the unit cell contains two crystallographic independent molecules in the asymmetric unit (\textbf{6a'} and \textbf{6a''}), where the arrangement of the bidentate ligand occurs in two orientations. One of the orientations matches the structure modeled by the DFT calculations. A graphical comparison (Figure S7) shows an excellent match of all metal–ligand bond lengths (Table S3) with the major differences being the rotation of the $p$-cymene group.
and pendant anthracenyl unit. The RMS value was obtained by comparing the bond distance average of the two crystallographic independent molecules and the DFT calculated model (Table S3). A small RMS difference of 7.7% was found, thus indicating the chosen set of parameters for the DFT model is valid. Additionally, our previous study on the Rh complex B using the identical level of theory and the exact basis set including the SDDAll pseudo potential for Rh also indicated a high level of agreement.\textsuperscript{15}

**Calculation of the simulated UV-Visible absorption spectra for 8**

The gas phase geometries of the triazolyl metal-coordination and uncoordinated complexes were reoptimized using SMD solvent corrections, employing the dielectronic constant for methanol. The same basis set as described previously was employed. Upon confirming the absence of imaginary frequencies, the UV-visible spectra were calculated using 100 states. Analysis of the UV-visible transitions and determination of the % metal character for the MOs was preformed using the AOMIX program.\textsuperscript{16}

**Figure S7.** Overlay of one of the crystallographic independent molecules found in the unit cell (orange) and the DFT-calculated model (yellow) for Ru(cym) complex 6a with a pendant pyridyl group.
Table S3. Comparison of DFT modelled and experimental (two crystallographically independent structures 6a’ and 6a’’) bond lengths for complex 6a.

| Bond length     | X-ray 6a’ (Å) | X-ray 6a’’ (Å) | DFT ω-B97xD (Å) | Difference (Å) |
|-----------------|---------------|----------------|-----------------|----------------|
| Ru–C<sub>cym</sub> | 2.293         | 2.229          | 2.248           | 0.013          |
| Ru–C<sub>cym</sub> | 2.273         | 2.213          | 2.215           | 0.028          |
| Ru–C<sub>cym</sub> | 2.186         | 2.177          | 2.225           | -0.044         |
| Ru–C<sub>cym</sub> | 2.236         | 2.222          | 2.255           | -0.026         |
| Ru–C<sub>cym</sub> | 2.202         | 2.246          | 2.255           | -0.031         |
| Ru–C<sub>cym</sub> | 2.205         | 2.259          | 2.242           | -0.010         |
| Ru–Cl           | 2.39          | 2.391          | 2.401           | -0.010         |
| Ru–N            | 2.116         | 2.108          | 2.137           | -0.025         |
| Ru–C<sub>carbene</sub> | 2.036    | 2.045          | 2.068           | -0.028         |
**Table S4.** Summary of selected bond lengths (Å) and bond angles (°) on DFT calculated chlorido complexes with Cp* (M = Rh, Ir) or cym (M = Ru, Os) ligands and pendant pyridyl or triazolyl moieties.

| Parameter        | M = Rh Pyridyl 6c | M = Rh Triazolyl 7c | M = Ir Pyridyl 6d | M = Ir Triazolyl 7d | M = Ru Pyridyl 6a | M = Ru Triazolyl 7a | M = Os Pyridyl 6b | M = Os Triazolyl 7b |
|------------------|-------------------|---------------------|-------------------|---------------------|-------------------|-------------------|-------------------|-------------------|
| M–Cl             | 2.400             | 2.401               | 2.422             | 2.421               | 2.401             | 2.404             | 2.418             | 2.425             |
| M–N              | 2.134             | 2.100               | 2.139             | 2.101               | 2.137             | 2.082             | 2.152             | 2.095             |
| M–C<sub>carbene</sub> | 2.019             | 2.040               | 2.021             | 2.037               | 2.038             | 2.064             | 2.063             | 2.078             |
| M–C<sub>Cp*</sub> | 1.833             | 1.824               | 1.842             | 1.836               | 1.733             | 1.731             | 1.732             | 1.727             |
| Cl–M–C<sub>carbene</sub> | 91.18             | 93.32               | 90.52             | 93.04               | 87.48             | 85.39             | 86.94             | 85.18             |
| N–M–C<sub>carbene</sub> | 86.14             | 85.30               | 85.00             | 84.54               | 85.42             | 85.66             | 84.23             | 84.72             |
| N–M–Cl           | 86.61             | 87.60               | 85.59             | 85.78               | 83.71             | 83.80             | 83.25             | 82.63             |
| Cl–M–C<sub>Cp*</sub> | 122.67            | 122.39              | 123.10            | 122.61              | 124.87            | 125.59            | 125.40            | 125.86            |
| N–M–C<sub>Cp*</sub> | 127.81            | 128.70              | 128.19            | 129.64              | 128.69            | 132.49            | 132.18            | 128.44            |
| C<sub>carbene</sub>–M–C<sub>Cp*</sub> | 129.44            | 127.41              | 130.46            | 128.21              | 131.10            | 127.92            | 128.74            | 133.20            |
| C–N–M            | 123.33            | 124.31              | 123.04            | 124.52              | 123.96            | 127.90            | 123.81            | 127.96            |
| N–C<sub>H2</sub>–C<sub>ipso</sub>–C | -105.13           | -119.55             | -105.70           | -120.12             | -106.21           | -108.52           | -106.24           | -107.94           |
Figure S8. Ball and stick representations of the cationic (Cp*)RhIIICl and (Cp*)IrIIICl complexes 6c/6d (pendant pyridyl) and 7c/7d (pendant triazolyl) geometry-optimized structures using DFT (ω-B97xD).

Figure S9. Ball and stick representation of the cationic (cym)RuIIICl and (cym)OsIIICl complexes 6a/6b (pendant pyridyl) and 7a/7b (pendant triazolyl) geometry-optimized structures using DFT (ω-B97xD).
Figure S10. Detailed comparison of the reaction pathways for conversion of the (Cp*)Rh^III^Cl complexes Ia and Ib into the corresponding hydroxido-substituted species XIa and Xlb through pendant ligand associated/dissociation. Changes in key bond length metrics are given in Å.
Figure S11. Detailed comparison of reaction pathways for conversion of the RhIII–hydroxido complexes Xla and Xlb into metallo-cycloaddition products XVIIia and XVIIib through pendant ligand associated/dissociation. Changes in key bond length metrics are given in Å.
Figure S12. Cutaway core structural views of the modelled Rh(III) metallo-cycloaddition complexes XVIIIa (triazolyl) and XVIIIb (pyridyl) overlaid with the Mayer bond indices. The triazolyl-based complex with a Rh–N bond shows a single Rh–C9' bond, while the pyridyl species has no Rh–N bond, demonstrating an overall stronger interaction with the pendant anthracenyl group (0.577 + 0.229 = 0.806 versus 0.586).

A rationale for the difference between complexes XVIIIb (pyridyl) and XVIIIa (triazolyl) extend from the constrained geometry imposed by the cycloaddition and fusion of the pendant anthracenyl group with the Cp* ligand. The five-membered triazolyl ring is able to bind weakly to the Rh center, while the 6-membered pyridyl XVIIIb is too strained to form a successful orbital overlap with the metal. This was confirmed by several unsuccessful attempts to optimize a complex analogous to XVIIIa whereby the pendant pyridyl group was bound to Rh via the N center. Moreover, no convergence to a stable minimum during the optimization process was found when the Rh–N bond was fixed. To compensate for the lack of electron density offered by the 4th ligand in XVIIIb, an overall stronger interaction with the anthracenyl group is calculated. IRI analysis of the reduced electron density gradient (RDG; Figure S13) reveals one strong covalent between Rh and C9’, while two weaker flanking covalent interactions are noted as shown by the yellow arrows in Figure S13. In contrast, the additional electron density imparted by coordination of the triazolyl groups, reduces the anthracenyl interaction, restricting it to a single covalent bond.
**Figure S13.** Comparison of the isosurface maps through interaction region indicators (IRI) analysis (IRI = 1.0) for (top) XVIIIb (triazolyl) and (bottom) XVIIIa (pyridyl). Yellow arrows indicate the interaction between the Rh center and the anthracenyl pendant group. The included scale was adapted from ref. 12.
UV-visible spectroscopy

The compounds were dissolved in methanol \((1.7 \times 10^{-4} \text{ mol/L})\) and the UV-vis spectra were recorded on a Shimadzu UV-3600 Plus spectrophotometer.

**Figure S14.** UV-vis spectra of pro-carbenes 4 (A) and 5 (B) and the respective complexes 6a–d (A), 7a–d and 8' (B) were recorded in methanol.
Figure S15. TD-DFT (ωB97xD/SMD with CH₃OH) calculated spectra showing bands A to C, for the N-coordinated triazolyl species 8 (red) and the uncoordinated 8’ (blue) overlaid with the experimental spectrum (yellow) recorded in methanol. The inset shows an expansion of band B.
Figure S16. TD-DFT (ωB97xD/SMD with CH₃OH) calculated spectra for the N-coordinated triazolyl species 8 (top) and the uncoordinated 8’ (bottom). Blue lines represent the major transitions contributing to the bands. Due to strong metal-ligand coupling, none of the transitions is a pure MLCT, LMCT, d-d. Hence based on the % metal character (given in magenta) the dominant type of transition is indicated.
**Comparison of bonding between triazolyl coordinated 8 and uncoordinated 8’**

From the geometry optimization of the cationic components of 8 and 8’, a charge decomposition analysis (CDA) and MBI analysis were performed to distinguish the nature of the bonding with the coupled anthracene ligand, particular in light that the two types of complexes only differ by 1.01 kcal/mol. The MBI analysis (Figure S17) shows the difference in the internal anthracenyl bonding and bonding to the Rh center. It is clear that in the Rh–N\textsubscript{triazolyl}-coordinated species 8, only a single relatively strong Rh-C(9’) bond is present. The CDA revealed no orbital between the C9a and C1 centers with Rh. Interestingly, the Rh–N\textsubscript{triazolyl} bond is almost half as weak as the Rh–C\textsubscript{anthracenyl} bond, which is consistent with experimental data where the phosphorus center of pta readily binds to the Rh center to form an adduct detectable by ESI-MS. CDA reveals that the principal MOs that contribute to the Rh–C9’ bond are HOMO, HOMO-14 and HOMO-16 where the primary interaction is between 4d\textsubscript{z2}-y\textsubscript{2} of Rh and 2p\textsubscript{z} of C9’, with much less Rh 4d\textsubscript{yz} involvement. Additionally, the CDA reveals no orbital overlap between C1 and C9a’ with the Rh center. Hence the ligand in 8 can be considered as octadentate. In contrast, for 8’ the CDA revealed multiple MOs containing overlaps between C1/C9a’ and the Rh center. The MBI map of 8’ (Figure S17) shows the extremely weak bonding between Rh and C9a’/C1, where the bonding strength between Rh and C9’ is practically unchanged. This additional metal coordination by the anthracenyl group weakens the C9a–C1 bond indicating some transfer of electron density to the metal. Analysis of the ligand fragment reveals coefficients on 2p\textsubscript{z} at C9a’ and C1 (a localized π-bond in HOFO-3; Figure S18). This MO interacts with both the Rh 4d\textsubscript{z2} and 4d\textsubscript{xz} orbitals and MO overlaps are observed in the HOMO, HOMO-10, HOMO-15 and weakly in HOMO-48 (not shown), whereas HOMO and HOMO-16 feature overlaps between the 2p\textsubscript{z} AO of C9’ and 4d\textsubscript{xz} and 4d\textsubscript{yz} of Rh. However, this 3-way π-type interaction with the Rh center cannot be considered a classical allylic type interaction due to the strong asymmetry of the three Rh–C bond strengths as indicated by the MBI analysis, but more appropriately as pseudo-allylic. Finally, the ligand in the triazolyl uncoordinated 8’ can be regarded as nonadentate, albeit with an extremely weak ninth coordination bond between C1 and the Rh center.
Figure S17. Mayer bond indices of the anthracenyl component in triazolyl coordinated 8 and uncoordinated 8'. 
Figure S18. (Top left) Highest occupied fragment orbital (HOFO) of the nonadentate ligand in 8’ with coefficients of C9a’ and C1 indicated. (Top right and bottom) MOs in 8’ where overlap between C9 and C1 with the d orbitals of Rh is present. All drawn with isovalues of 0.02 au.
Fluorescence spectroscopy

The compounds were dissolved in methanol (1.7 × 10^{-4} \text{ mol/L}) and the fluorescence emission spectra were collected on a JASCO FP-8600 NIR spectrofluorometer.

Figure S19. Fluorescence spectra of 4, 5, 6a–d, 7a–d and 8’ after excitation at λ_{ex} = 360 nm, with maxima (1–3) labelled were recorded in methanol.
Table S5. Maxima in the fluorescence emission spectra of 4, 5, 6a–d, 7a–d and 8’.

| Compound | Emission Maxima (nm) |
|----------|-----------------------|
|          | 1     | 2     | 3     |
| **4**    | 396   | 418   | 443   |
| **6a**   | 400   | 417   | 442   |
| **6b**   | 400   | 418   | 443   |
| **6c**   | 401   | 416   | 437   |
| **6d**   | 399   | 417   | 442   |
| **5**    | 395   | 417   | 444   |
| **7a**   | 399   | 415   | 439   |
| **7b**   | 399   | 414   | 439   |
| **7c**   | 399   | 414   | 439   |
| **7d**   | 399   | 414   | 438   |
| **8’**   | 392   | 415   | 439   |
Table S6. X-ray diffraction measurement parameters for 4 and 6a·½CHCl3.

|                           | 4                        | 6a-½CHCl3               |
|---------------------------|--------------------------|-------------------------|
| CCDC                      | 2101574                  | 2101573                 |
| Formula                   | C$_{28}$H$_{22}$N$_3$PF$_6$ | C$_{38.5}$H$_{35.5}$Cl$_{2.5}$N$_3$RuPF$_6$ |
| Molecular weight (g mol$^{-1}$) | 545.45                  | 874.86                  |
| Crystal size (mm)         | 0.14 × 0.12 × 0.10       | 0.08 × 0.08 × 0.08      |
| Radiation (Å)             | Cu Kα ($\lambda = 1.54184$) | Cu Kα ($\lambda = 1.54184$) |
| Temperature (K)           | 100.0(4)                 | 100.0(2)                |
| Crystal system            | monoclinic               | monoclinic              |
| Space group               | $P$n                     | $P_2_1/n$               |
| $a$ (Å)                   | 12.0723(2)               | 24.9866(2)              |
| $b$ (Å)                   | 10.7942(2)               | 11.2035(1)              |
| $c$ (Å)                   | 18.8432(3)               | 26.5555(2)              |
| $\alpha$ (°)             | 90                       | 90                      |
| $\beta$ (°)              | 91.696(1)                | 107.087(1)              |
| $\gamma$ (°)             | 90                       | 90                      |
| Volume (Å$^3$)            | 2452.40(7)               | 7105.21(11)             |
| Z                         | 4                        | 8                       |
| Calculated density (mg/mm$^3$) | 1.473                  | 1.636                   |
| Absorption coefficient (mm$^{-1}$) | 1.616                  | 6.302                   |
| F(000)                    | 1120                     | 3544                    |
| 2Theta range (°)          | 11.876 to 136.492        | 11.252 to 135.46        |
| Number of Parameters / Reflections (all) | 689/30887               | 955/94606               |
| Independent reflections   | 7945 [$R_{int} = 0.0426$, $R_{sigma} = 0.0388$] | 12866 [$R_{int} = 0.0401$, $R_{sigma} = 0.0238$] |
| Final R indices [I > 2σ(I)] | $R_1 = 0.0518$         | $R_1 = 0.0244$          |
|                           | $wR_2 = 0.1373$          | $wR_2 = 0.0575$         |
| R indices (all data)      | $R_1 = 0.0533$          | $R_1 = 0.0277$          |
|                           | $wR_2 = 0.1383$          | $wR_2 = 0.0588$         |
| Goodness-of-fit on $F^2$  | 1.058                    | 1.016                   |
| Largest diff. peak/hole (e Å$^{-3}$) | 0.72/-0.36            | 0.63/-0.52              |
| Flack parameter           | 0.018(12)               | -                       |
$^1$H and $^{13}$C($^1$H) NMR spectra

$^1$H NMR (400.13 MHz, DMSO-$d_6$): $\delta$ (ppm) = 8.51-8.52 (m, 1H), 8.37 (s, 1H), 7.77 (td, $^3J = 8$ Hz, $^4J = 2$ Hz, 1H), 7.63-7.68 (m, 1H), 7.45-7.50 (m, 1H), 7.26-7.31 (m, 2H), 7.15-7.21 (m, 2H), 5.59 (s, 2H).

Figure S20. $^1$H NMR spectrum of 1.

$^1$H NMR (400.13 MHz, CDCl$_3$): $\delta$ (ppm) = 8.63 (s, 1H), 8.29-8.35 (m, 1H), 8.08-8.14 (m, 4H), 7.81-7.84 (m, 1H), 7.70-7.73 (m, 1H), 7.49-7.55 (m, 4H), 7.45 (dt, $^3J = 7$ Hz, $^4J = 1$ Hz, 1H), 7.36 (dt, $^3J = 7$ Hz, $^4J = 1$ Hz, 1H), 6.19 (s, 2H).

Figure S21. $^1$H NMR spectrum of 2.
Figure S22. $^1$H NMR spectrum of 3.

$^1$H NMR (400.13 MHz, DMSO-$d_6$): $\delta$ (ppm) = 8.99 (s, 1H), 8.93 (s, 1H), 8.35-8.42 (m, 3H), 8.25-8.29 (m, 2H), 8.04-8.08 (m, 1H), 7.79-7.88 (m, 2H), 7.61-7.68 (m, 4H), 6.74 (s, 2H), 5.28 (d, $^3J$ = 3 Hz, 2H), 3.69 (t, $^3J$ = 3 Hz, 1H).

Figure S23. $^1$H NMR spectrum of 4.

$^1$H NMR (400.13 MHz, DMSO-$d_6$): $\delta$ (ppm) = 9.22 (s, 1H), 8.92 (s, 1H), 8.42 (d, $^3J$ = 8 Hz, 2H), 8.26-8.32 (m, 4H), 7.91 (d, $^3J$ = 8 Hz, 1H), 7.74-7.82 (m, 2H), 7.61-7.70 (m, 5H), 7.45 (d, $^3J$ = 8 Hz, 1H), 7.29 (dd, $^3J$ = 5 Hz, $^4J$ = 1 Hz, 1H), 6.81 (s, 2H), 5.73 (s, 2H).
Figure S24. $^{13}$C{$^1$H} NMR spectrum of 4.

$^1$H NMR (400.13 MHz, DMSO-$d_6$); $\delta$ (ppm) = 9.16 (s, 1H), 8.93 (s, 1H), 8.37-8.38 (m, 2H), 8.29-8.32 (d, $^3J = 8$ Hz, 1H), 8.25-8.29 (m, 2H), 8.18 (s, 1H), 8.05 (d, $^3J = 8$ Hz, 1H), 7.71-7.81 (m, 2H), 7.61-7.65 (m, 4H), 7.31-7.37 (m, 3H), 7.22-7.24 (m, 2H), 6.73 (s, 2H), 5.65 (s, 1H), 5.55 (s, 1H).

Figure S25. $^1$H NMR spectrum of 5.
Figure S26. $^{13}$C$[^1]$H NMR spectrum of 5.

$^1$H NMR (400.13 MHz, CDCl$_3$): δ (ppm) = 9.26 (dd, $^3$$J$ = 6 Hz, $^4$$J$ = 1 Hz, 1H), 8.65 (s, 1H), 8.41 (m, 1H), 8.04-8.10 (m, 3H), 7.91 (td, $^3$$J$ = 8 Hz, $^4$$J$ = 1 Hz, 1H), 7.79 (d, $^3$$J$ = 8 Hz, 1H), 7.58 (d, $^3$$J$ = 8 Hz, 1H), 7.45-7.56 (m, 3H), 7.39-7.44 (m, 2H), 7.09-7.16 (m, 2H), 6.59-6.65 (m, 2H), 5.76-5.83 (m, 3H), 5.62 (dd, $^3$$J$ = 6 Hz, 1H), 5.56 (dd, $^3$$J$ = 6 Hz, 1H), 5.54 (dd, $^3$$J$ = 6 Hz, 1H), 5.28 (d, $^3$$J$ = 16 Hz, 1H), 2.96 (sept, $^3$$J$ = 7 Hz, 1H), 2.23 (s, 3H), 1.25 (d, $^3$$J$ = 7 Hz, 3H).

Figure S27. $^1$H NMR spectrum of 6a.
$^{13}$C($^1$H) NMR (100.61 MHz, CDCl$_3$): δ (ppm) = 188.4 (C, 1C), 157.7 (CH, 1C), 156.3 (C, 1C), 139.8 (CH, 1C), 134.9 (C, 1C), 134.0 (C, 4C), 131.4 (C, 4C), 129.9 (CH, 2C), 129.2 (CH, 1C), 127.5 (CH, 2C), 126.1 (CH, 1C), 125.7 (CH, 1C), 125.5 (CH, 1C), 124.8 (CH, 1C), 124.2 (C, 1C), 123.9 (CH, 1C), 123.8 (CH, 1C), 123.7 (CH, 1C), 122.8 (CH, 1C), 113.9 (C, 1C), 111.9 (CH, 1C), 110.0 (CH, 1C), 101.8 (C, 1C), 88.8 (CH, 1C), 87.9 (CH, 1C), 85.6 (CH, 1C), 85.1 (CH, 1C), 51.5 (NCH$_2$, 1C), 48.6 (NCH$_2$, 1C), 31.4 (CH, 1C), 23.8 (CH$_3$, 1C), 21.1 (CH$_3$, 1C), 18.8 (CH$_3$, 1C).

Figure S28. $^{13}$C($^1$H) NMR spectrum of 6a.

Figure S29. $^1$H-$^{13}$C HSQC NMR spectrum of 6a.
**Figure S30.** $^1$H-$^{13}$C HMBC NMR spectrum of 6a.

![Figure S30](image)

$^1$H NMR (400.13 MHz, CDCl$_3$): $\delta$ (ppm) = 9.09 (d, $^3J = 6$ Hz, 1H), 8.65 (s, 1H), 8.34-8.47 (m, 1H), 8.02-8.18 (m, 3H), 7.84-7.90 (m, 2H), 7.59 (d, $^3J = 8$ Hz, 1H), 7.43-7.55 (m, 4H), 7.34 (t, $^3J = 6$ Hz, 1H), 7.07-7.14 (m, 2H, H15), 6.55-6.62 (m, 2H, H15), 5.86 (d, $^3J = 16$ Hz, 1H), 5.81 (d, $^3J = 6$ Hz, 1H), 5.76 (d, $^3J = 8$ Hz, 1H), 5.65-5.73 (m, 3H), 5.25 (d, $^3J = 16$ Hz, 1H), 2.90 (sept, $^3J = 7$ Hz, 1H), 2.36 (s, 3H), 1.28 (d, $^3J = 7$ Hz, 3H), 1.21 (d, $^3J = 7$ Hz, 3H).

**Figure S31.** $^1$H NMR spectrum of 6b.

![Figure S31](image)
$^{13}$C ($^1$H) NMR (100.61 MHz, CDCl$_3$): $\delta$ (ppm) = 172.7 (C, 1C), 157.8 (CH, 1C), 155.3 (C, 1C), 140.2 (CH, 1C), 134.6 (C, 1C), 133.4 (C, 1C), 129.9 (CH, 1C), 129.2 (CH, 1C), 127.5 (CH, 2C), 125.6 (CH, 2C), 125.2 (CH, 2C), 124.4 (CH, 1C), 124.3 (C, 1C), 123.9 (CH, 1C), 123.8 (CH, 1C), 123.2 (CH, 1C), 111.9 (CH, 1C), 110.3 (CH, 1C), 104.8 (C, 1C), 93.9 (C, 1C), 80.3 (CH, 1C), 79.5 (CH, 1C), 76.5 (CH, 1C), 76.2 (CH, 1C), 52.0 (C, 1C), 48.6 (C, 1C), 31.3 (CH, 1C), 24.4 (CH$_3$, 1C), 21.1 (CH$_3$, 1C), 18.7 (CH$_3$, 1C).

**Figure S32.** $^{13}$C ($^1$H) NMR spectrum of 6b.

$^1$H-$^{13}$C HSQC NMR spectrum of 6b.

**Figure S33.** $^1$H-$^{13}$C HSQC NMR spectrum of 6b.
$^1$H NMR (400.13 MHz, CDCl$_3$): $\delta$ (ppm) = 9.03 (d, $^3J = 6$ Hz, 1H), 8.66 (s, 1H), 8.38 (d, $^3J = 9$ Hz, 1H), 8.16 (m, 2H), 8.00-8.04 (m, 3H), 7.71 (d, $^3J = 8$ Hz, 1H), 7.53-7.61 (m, 3H), 7.47 (d, $^3J = 14$ Hz, 1H), 7.39-7.43 (m, 1H), 7.28-7.32 (m, 1H), 7.08 (td, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 6.47 (td, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 6.36 (d, $^3J = 14$ Hz, 1H), 6.01 (d, $^3J = 16$ Hz, 1H), 5.36 (d, $^3J = 8$ Hz, 1H), 5.25 (d, $^3J = 16$ Hz, 1H), 1.82 (s, 15H).

Figure S34. $^1$H-$^{13}$C HMBC NMR spectrum of 6b.

$^1$H NMR spectrum of 6c.

Figure S35. $^1$H NMR spectrum of 6c.
$^{13}$C\textsuperscript{1H} NMR (100.61 MHz, CDCl\textsubscript{3}): $\delta$ (ppm) = 181.8 (d, $^1J = 51$ Hz, C, 1C), 155.5 (CH, 1C), 155.4 (C, 1C), 140.4 (CH, 1C), 134.6 (C, 1C), 134.3 (C, 1C), 132.3 (C, 1C), 131.7 (C, 1C), 131.3 (C, 1C), 131.2 (C, 1C), 130.1 (CH, 1C), 130.0 (CH, 1C), 128.9 (CH, 1C), 127.8 (CH, 1C), 127.5 (CH, 1C), 126.8 (CH, 1C), 126.1 (CH, 1C), 125.8 (CH, 1C), 125.3 (CH, 1C), 124.9 (CH, 1C), 124.0 (CH, 1C), 123.9 (CH, 1C), 123.4 (C, 1C), 122.5 (CH, 1C), 112.2 (CH, 1C), 110.8 (CH, 1C), 99.4 (d, $^1J = 7$ Hz, C, Cp*), 50.9 (NCH\textsubscript{2}, 1C), 48.3 (NCH\textsubscript{2}, 1C), 9.9 (CH\textsubscript{3}, Cp*).

Figure S36. $^{13}$C\textsuperscript{1H} NMR spectrum of 6c.

Figure S37. $^1$H-$^{13}$C HSQC NMR spectrum of 6c.
Figure S38. $^1$H-$^{13}$C HMBC NMR spectrum of 6c.

$^1$H NMR (400.13 MHz, CDCl$_3$): $\delta$ (ppm) = 8.96 (dd, $^3J = 6$ Hz, $^4J = 1$ Hz, 1H), 8.66 (s, 1H), 8.40 (d, $^3J = 8$ Hz, 1H), 8.15 (d, $^3J = 8$ Hz, 1H), 8.13 (d, $^3J = 8$ Hz, 1H), 8.02-8.04 (m, 2H), 7.98 (td, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 7.71 (d, $^3J = 8$ Hz, 1H), 7.49-7.60 (m, 3H), 7.42 (d, $^2J = 14$ Hz, 1H), 7.40 (td, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 7.28-7.33 (m, 1H), 7.04 (td, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 6.42 (td, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 6.32 (d, $^2J = 14$ Hz, 1H), 5.98 (d, $^2J = 16$ Hz, 1H), 5.32 (d, $^2J = 8$ Hz, 1H), 5.04 (d, $^2J = 16$ Hz, 1H), 1.83 (s, 15H).

Figure S39. $^1$H NMR spectrum of 6d.
$^{13}$C$\{^1$H$\}$ NMR (100.61 MHz, CDCl$_3$): $\delta$ (ppm) = 166.8 (C, 1C), 156.0 (CH, 1C), 155.1 (C, 1C), 140.8 (CH, 1C), 134.4 (C, 1C), 133.8 (C, 1C), 132.3 (C, 1C), 131.7 (C, 1C), 131.3 (C, 1C), 131.2 (C, 1C), 130.1 (CH, 1C), 130.0 (CH, 1C), 128.9 (CH, 1C), 127.8 (CH, 1C), 127.4 (CH, 1C), 126.7 (CH, 1C), 126.5 (CH, 1C), 125.8 (CH, 1C), 125.4 (CH, 1C), 124.8 (CH, 1C), 123.9 (CH, 1C), 123.8 (CH, 1C), 123.4 (C, 1C), 122.6 (CH, 1C), 112.3 (CH, 1C), 110.8 (CH, 1C), 92.0 (C, Cp*), 51.4 (NCH$_2$, 1C), 47.9 (NCH$_2$, 1C), 9.66 (CH$_3$, Cp*).

Figure S40. $^{13}$C$\{^1$H$\}$ NMR spectrum of 6d.

Figure S41. $^1$H-$^{13}$C HSQC NMR spectrum of 6d.
Figure S42. $^1$H-$^{13}$C HMBC NMR spectrum of 6d.

$^1$H NMR (400.13 MHz, CDCl$_3$): $\delta$ (ppm) = 8.65 (s, 1H), 8.41 (d, $^3J = 8$ Hz, 1H), 8.20 (d, $^3J = 8$ Hz, 1H), 8.15 (d, $^3J = 8$ Hz, 1H), 8.06 (d, $^3J = 8$ Hz, 1H), 7.86 (s, 1H), 7.49-7.59 (m, 3H), 7.46 (d, $^3J = 8$ Hz, 1H), 7.34-7.43 (m, 6H), 7.19 (d, $^2J = 16$ Hz, 1H), 7.03 (td, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 6.64 (d, $^2J = 16$ Hz, 1H), 6.52 (td, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 5.96 (dd, $^3J = 6$ Hz, 1H), 5.78-5.34 (m, 2H), 5.59-5.73 (m, 4H), 5.53 (dd, $^3J = 6$ Hz, 1H), 5.16 (d, $^2J = 16$ Hz, 1H), 2.94 (sept, $^3J = 7$ Hz, 1H), 2.23 (s, 3H), 1.32 (d, $^3J = 7$ Hz, 3H), 1.22 (d, $^3J = 7$ Hz, 3H).

Figure S43. $^1$H NMR spectrum of 7a.
$^{13}$C-$^1$H NMR (100.61 MHz, CDCl$_3$): δ (ppm) = 187.1 (C, 1C), 141.4 (C, 1C), 134.7 (C, 1C), 134.3 (C, 1C), 132.6 (C, 1C), 132.0 (C, 1C), 131.4 (C, 2C), 131.2 (C, 1C), 130.1 (CH, 1C), 129.9 (CH, 1C), 129.6 (CH, 1C), 129.4 (CH, 2C), 129.1 (CH, 1C), 128.9 (CH, 2C), 127.5 (CH, 2C), 125.9 (CH, 1C), 125.3 (CH, 1C), 124.7 (CH, 1C), 124.1 (C, 1C), 124.0 (CH, 1C), 123.7 (CH, 1C), 123.6 (CH, 1C), 122.7 (CH, 1C), 112.9 (C, 1C), 111.9 (CH, 1C), 109.8 (CH, 1C), 101.4 (C, 1C), 88.4 (CH, 1C), 88.2 (CH, 1C), 87.8 (CH, 1C), 84.7 (CH, 1C), 56.1 (NCH$_2$, 1C), 49.4 (NCH$_2$, 1C), 40.7 (NCH$_2$, 1C), 31.3 (CH, 1C), 23.8 (CH$_3$, 1C), 20.7 (CH$_3$, 1C), 19.2 (CH$_3$, 1C).

Figure S44. $^{13}$C-$^1$H NMR spectrum of 7a.

Figure S45. $^1$H-$^{13}$C HSQC NMR spectrum of 7a.
$^1$H NMR (400.13 MHz, CDCl$_3$): $\delta$ (ppm) = 8.65 (s, 1H), 8.44 (d, $^3J = 8$ Hz, 1H), 8.04-8.17 (m, 3H), 7.88 (s, 1H), 7.48-7.56 (m, 3H), 7.43-7.47 (m, 2H), 7.35-7.43 (m, 5H), 7.17 (d, $^2J = 16$ Hz, 1H), 7.02 (td, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 6.57 (d, $^2J = 16$ Hz, 1H), 6.49 (td, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 5.98 (d, $^3J = 6$ Hz, 1H), 5.87 (d, $^3J = 6$ Hz, 1H), 5.81 (d, $^3J = 6$ Hz, 1H), 5.75 (d, $^3J = 6$ Hz, 1H), 5.72 (d, $^3J = 6$ Hz, 1H), 5.67 (d, $^3J = 6$ Hz, 1H), 5.60-5.65 (m, 2H), 5.14 (d, $^2J = 16$ Hz, 1H), 2.88 (sept, $^3J = 7$ Hz, 1H), 2.38 (s, 3H), 1.27 (d, $^3J = 7$ Hz, 3H), 1.26 (d, $^3J = 7$ Hz, 3H).

**Figure S46.** $^1$H-$^{13}$C HMBC NMR spectrum of 7a.

**Figure S47.** $^1$H NMR spectrum of 7b.
$^{13}$C\{$^1$H\} NMR (100.61 MHz, CDCl$_3$): $\delta$ (ppm) = 170.9 (C, 1C), 139.9 (C, 1C), 134.3 (C, 1C), 133.6 (C, 1C), 132.6 (C, 1C), 131.9 (C, 1C), 131.4 (C, 1C), 131.3 (C, 1C), 131.2 (C, 1C), 130.1 (CH, 1C), 129.9 (CH, 1C), 129.4 (CH, 3C), 129.1 (CH, 1C), 128.9 (CH, 2C), 127.5 (CH, 1C), 127.4 (CH, 1C), 125.8 (CH, 1C), 125.3 (CH, 1C), 124.5 (CH, 1C), 124.2 (C, 1C), 123.7 (CH, 2C), 123.6 (CH, 1C), 122.6 (CH, 1C), 112.1 (CH, 1C), 109.9 (CH, 1C), 103.9 (C, 1C), 93.4 (C, 1C), 79.9 (CH, 1C), 79.8 (CH, 1C), 79.1 (CH, 1C), 75.8 (CH, 1C), 55.9 (NCH$_2$, 1C), 49.4 (NCH$_2$, 1C), 40.9 (NCH$_2$, 1C), 31.3 (CH, 1C), 24.3 (CH$_3$, 1C), 20.7 (CH$_3$, 1C), 19.2 (CH$_3$, 1C).

**Figure S48.** $^{13}$C\{$^1$H\} NMR spectrum of 7b.

$^1$H-$^{13}$C HSQC NMR spectrum of 7b.

**Figure S49.** $^1$H-$^{13}$C HSQC NMR spectrum of 7b.
Figure S50. $^1$H-$^{13}$C HMBC NMR spectrum of $7b$. 

$^1$H NMR (400.13 MHz, CDCl$_3$): $\delta$ (ppm) = 8.65 (s, 1H), 8.41 (d, $^3J = 8$ Hz, 1H), 8.15-8.20 (m, 3H), 8.02 (d, $^3J = 8$ Hz, 1H), 7.55-7.61 (m, 3H), 7.51 (d, $^3J = 16$ Hz, 1H), 7.37-7.46 (m, 6H), 7.31-7.36 (m, 1H), 7.05 (td, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 6.46 (td, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H), 6.34 (d, $^3J = 16$ Hz, 1H), 5.99 (d, $^3J = 16$ Hz, 1H), 5.69 (s, 2H), 5.35 (d, $^3J = 8$ Hz, 1H), 5.15 (d, $^3J = 16$ Hz, 1H), 1.81 (s, 15H).

Figure S51. $^1$H NMR spectrum of $7c$. 

$\text{PF}_5$
$^{13}$C($^1$H) NMR (100.61 MHz, CDCl$_3$): $\delta$ (ppm) = 180.7 (d, $^1J = 51$ Hz, C, 1C), 141.3 (C, 1C), 134.5 (C, 1C), 134.4 (C, 1C), 132.8 (C, 1C), 132.5 (C, 1C), 131.7 (C, 1C), 131.4 (C, 1C), 131.2 (C, 1C), 130.1 (CH, 2C), 129.5 (CH, 2C), 129.4 (CH, 2C), 128.9 (CH, 2C), 128.8 (CH, 1C), 127.6 (CH, 2C), 125.9 (CH, 1C), 125.2 (CH, 1C), 125.1 (CH, 2C), 124.0 (CH, 1C), 123.9 (CH, 1C), 123.5 (C, C1), 112.5 (CH, 1C), 112.3 (CH, 1C), 110.5 (CH, 1C), 99.4 (d, $^1J = 7$ Hz, C, Cp*), 56.2 (NCH$_2$, 1C), 48.7 (NCH$_2$, 1C), 40.7 (NCH$_2$, 1C), 9.9 (CH, Cp*).

Figure S52. $^{13}$C($^1$H) NMR spectrum of 7c.

Figure S53. $^1$H-$^{13}$C HSQC NMR spectrum of 7c.
Figure S54. $^1$H-$^{13}$C HMBC NMR spectrum of 7c.

$^1$H NMR (400.13 MHz, CDCl$_3$): $\delta$ (ppm) = 8.66 (s, 1H), 8.43 (d, $^3$J = 8 Hz, 1H), 8.20 (s, 1H), 8.14-8.18 (m, 2H), 8.03 (d, $^3$J = 8 Hz, 1H), 7.49-7.61 (m, 3H), 7.38-7.46 (m, 7H), 7.32-7.37 (m, 1H), 7.02 (t, $^3$J = 8 Hz, 1H), 6.43 (t, $^3$J = 8 Hz, 1H), 6.29 (d, $^3$J = 15 Hz, 1H), 5.96 (d, $^3$J = 16 Hz, 1H), 5.70 (s, 2H), 5.32 (d, $^3$J = 8 Hz, 1H), 5.04 (d, $^3$J = 16 Hz, 1H), 1.83 (s, 15H).

Figure S55. $^1$H NMR spectrum of 7d.
$^{13}$C($^1$H) NMR (100.61 MHz, CDCl$_3$): $\delta$ (ppm) = 164.7 (C, 1C), 140.6 (C, 1C), 134.2 (C, 1C), 133.9 (C, 1C), 132.8 (C, 1C), 132.5 (C, 1C), 131.7 (C, 1C), 131.3 (C, 1C), 131.2 (C, 1C), 130.2 (CH, 1C), 130.1 (CH, 1C), 129.5 (CH, 1C), 129.4 (CH, 2C), 128.9 (CH, 2C), 128.8 (CH, 1C), 127.6 (CH, 1C), 127.5 (CH, 1C), 125.9 (CH, 1C), 125.2 (CH, 1C), 124.9 (CH, 1C), 124.8 (CH, 1C), 124.0 (CH, 1C), 123.9 (CH, 1C), 123.5 (C, 1C), 122.5 (CH, 1C), 112.3 (CH, 1C), 110.5 (CH, 1C), 92.2 (C, Cp$^*$), 56.2 (NCH$_2$, 1C), 48.5 (NCH$_2$, 1C), 40.9 (NCH$_2$, 1C), 9.64 (CH$_3$, Cp$^*$).

Figure S56. $^{13}$C($^1$H) NMR spectrum of 7d.

$^1$H-$^{13}$C HSQC NMR spectrum of 7d.

Figure S57. $^1$H-$^{13}$C HSQC NMR spectrum of 7d.
Figure S58. $^1$H-$^{13}$C HMBC NMR spectrum of 7d.

$^1$H NMR (400.13 MHz, CDCl$_3$): δ (ppm) = 7.94 (s, 1H), 7.63 (t, $^3$J = 8 Hz, 2H), 7.43 (d, $^3$J = 8 Hz, 1H), 7.35-7.39 (m, 4H), 7.28-7.34 (m, 6H), 7.21 (t, $^3$J = 8 Hz, 2H), 6.52 (d, $^3$J = 8 Hz, 2H), 5.94 (s, 2H), 5.51 (s, 2H), 4.81 (t, $^3$J = 4 Hz, 1H), 4.58 (s, 2H), 2.22 (d, $^3$J = 4 Hz, 2H), 1.77 (s, 6H), 0.40 (s, 6H).

Figure S59. $^1$H NMR spectrum of 8'.

S45
$^{13}$C-$^1$H NMR (100.61 MHz, CDCl$_3$): δ (ppm) = 129.8 (CH, 3C), 128.9 (CH, 2C), 128.7 (CH, 2C), 128.5 (CH, 1C), 128.4 (CH, 1C), 127.9 (CH, 2C), 124.4 (CH, 1C), 124.2 (CH, 1C), 123.7 (CH, 1C), 118.3 (CH, 1C), 112.1 (CH, 1C), 110.9 (CH, 1C), 54.2 (NCH$_2$, 1C), 50.4 (NCH$_2$, 1C), 45.3 (CH, 1C), 44.6 (NCH$_2$, 1C), 29.4 (CH$_2$, 1C), 11.0 (CH$_3$, 2C), 5.89 (CH$_3$, 2C).

Figure S60. $^{13}$C-$^1$H NMR spectrum of 8'.

Figure S61. $^1$H-$^{13}$C HSQC NMR spectrum of 8'.
Figure S62. $^1$H-$^{13}$C HMBC NMR spectrum of 8'.

ESI-mass spectra

Figure S63. ESI-mass spectrum of 3.
Figure S64. ESI-mass spectrum of 4.

Figure S65. ESI-mass spectrum of 5.
**Figure S66.** ESI-mass spectrum of 6a.

**Figure S67.** ESI-mass spectrum of 6b.
Figure S68. ESI-mass spectrum of 6c.

Figure S69. ESI-mass spectrum of 6d.
Figure S70. ESI-mass spectrum of 7a.

Figure S71. ESI-mass spectrum of 7b.
Figure S72. ESI-mass spectrum of 7c.

Figure S73. ESI-mass spectrum of 7d.
Figure S74. ESI-mass spectrum of 8'. 
References

(1) Becke, A. D., Density-functional thermochemistry. V. Systematic optimization of exchange-correlation functionals. *J. Chem. Phys.* **1997**, *107*, 8554-8560.

(2) Chai, J.-D.; Head-Gordon, M., Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615-6620.

(3) Śliwa, P.; Handzlik, J., Assessment of density functional methods for the study of olefin metathesis catalysed by ruthenium alkylidene complexes. *Chem. Phys. Lett.* **2010**, *493*, 273-278.

(4) Kulkarni, A. D.; Truhlar, D. G., Performance of Density Functional Theory and Møller–Plesset Second-Order Perturbation Theory for Structural Parameters in Complexes of Ru. *J. Chem. Theory Comput.* **2011**, *7*, 2325-2332.

(5) Minenkov, Y.; Singstad, Å.; Occhipinti, G.; Jensen, V. R., The accuracy of DFT-optimized geometries of functional transition metal compounds: a validation study of catalysts for olefin metathesis and other reactions in the homogeneous phase. *Dalton Trans.* **2012**, *41*, 5526-5541.

(6) Sperger, T.; Sanhueza, I. A.; Kalvet, I.; Schoenebeck, F., Computational Studies of Synthetically Relevant Homogeneous Organometallic Catalysis Involving Ni, Pd, Ir, and Rh: An Overview of Commonly Employed DFT Methods and Mechanistic Insights. *Chem. Rev.* **2015**, *115*, 9532-9586.

(7) Bursch, M.; Caldeveyher, E.; Hansen, A.; Neugebauer, H.; Ehler, S.; Grimme, S., Understanding and Quantifying London Dispersion Effects in Organometallic Complexes. *Acc. Chem. Res.* **2019**, *52*, 258-266.

(8) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

(9) Petersson, G. A.; Al-Laham, M. A., A complete basis set model chemistry. II. Open-shell systems and the total energies of the first-row atoms. *J. Chem. Phys.* **1991**, *94*, 6081-6090.

(10) Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, H., Energy-adjusted ab initio pseudopotentials for the second and third row transition elements. *Theor. Chim. Acta* **1990**, *77*, 123-141.
(11) Marenich, A. V.; Jerome, S. V.; Cramer, C. J.; Truhlar, D. G., Charge Model 5: An Extension of Hirshfeld Population Analysis for the Accurate Description of Molecular Interactions in Gaseous and Condensed Phases. J. Chem. Theory Comput. 2012, 8, 527-541.

(12) Lu, T.; Chen, Q., Interaction Region Indicator: A Simple Real Space Function Clearly Revealing Both Chemical Bonds and Weak Interactions. Chemistry – Methods 2021, 1, 231-239.

(13) Lu, T.; Chen, F., Multiwfn: A multifunctional wavefunction analyzer. J. Comput. Chem. 2012, 33, 580-592.

(14) Humphrey, W.; Dalke, A.; Schulten, K., VMD: Visual molecular dynamics. J. Mol. Graphics 1996, 14, 33-38.

(15) Lee, B. Y. T.; Phillips, A. D.; Hanif, M.; Tong, K. K. H.; Söhnel, T.; Hartinger, C. G., Heptadentate, octadentate or even nonadentate? Denticity in the unexpected formation of an all-carbon donor atom ligand in RhIII(Cp*)(anthracenyl-NHC) complexes. Inorg. Chem. 2021, 60, 8734–8741.

(16) S. I. Gorelsky, AOMix: Program for Molecular Orbital Analysis; version 6.90, 2018, http://www.sg-chem.net/; S. I. Gorelsky, A. B. P. Lever. Electronic structure and spectra of ruthenium diimine complexes by density functional theory and INDO/S. Comparison of the two methods. J. Organomet. Chem. 2001, 635, 187-196.