Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters
Tetrahedron Letters 47 (2006) 8877–8880

Synthesis and cyclometalation of a pyrido[3,2-*e*]-2,10b-diaza-cyclopenta[*c*]fluorene-1,3-dione scaffold

Seann P. Mulcahy, Patrick J. Carroll and Eric Meggers*

Department of Chemistry, University of Pennsylvania, 231 S. 34th St., Philadelphia, PA 19104, United States

Received 22 September 2006; accepted 10 October 2006

Abstract—The synthesis of a pyrido[3,2-*e*]-2,10b-diaza-cyclopenta[*c*]fluorene-1,3-dione scaffold is disclosed, which was synthesized using a Suzuki cross-coupling reaction and an intramolecular Heck cyclization as the key steps. This heterocyclic system can serve as a bidentate ligand as demonstrated by the formation and structural analysis of a derived ruthenium complex. The new scaffold constitutes an interesting candidate for the development of organometallic protein kinase inhibitors.

We recently started a research program that aims in exploring the scope of using substitutionally inert metal complexes to design bioactive small molecules.[1,2] In our concept we make use of the distinctive structural features of transition metals and thus the main purpose of the metal is to organize the organic ligands in the three-dimensional space. Following this strategy, we disclosed over the last two years a series of simple ruthenium-based protein kinase inhibitors such as **1**, which mimic the overall shape of the family of indolocarbazole alkaloids (e.g., staurosporine, see Fig. 1).[3] Almost all our compounds include the pyridocarbazole ligand **2** as a key pharmacophore, which substitutes for the indolocarbazole aglycone **3** of staurosporine. Heterocycle **2** serves as a very strong bidentate ligand in ruthenium complexes. Additional ligands in the coordination sphere of the metal substitute for the carbohydrate moiety of staurosporine, with the metal center serving as a 'glue' to unite all of the parts. This approach has resulted in the successful design of nanomolar and even picomolar protein kinase inhibitors.[1]

We became interested in designing ruthenium complexes with similar overall structures but modulated electron density at the metal center. This may allow us to design kinase inhibitors with additional functions such as luminescence, reactivity, or catalytic properties, which generally depend on the electronic nature of all involved ligands. Toward this goal we here disclose the synthesis of *N*-benzyl pyrido[3,2-*e*]-2,10b-diaza-cyclopenta[*c*]fluorene-1,3-dione **4**, which differs from pyridocarbazole **2** scaffold by the connectivity of the indole moiety. This heterocycle can serve as a bidentate ligand for ruthenium as demonstrated for complex **5**, forming a coordinative bond with the pyridine and a covalent bond with a carbon of the indole moiety.

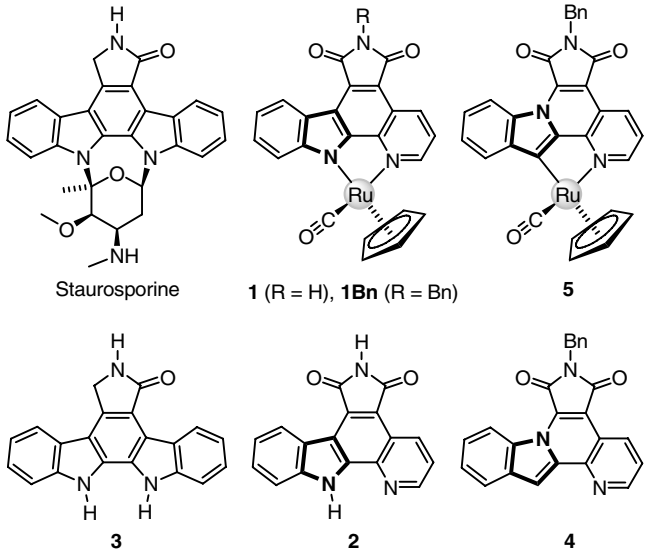
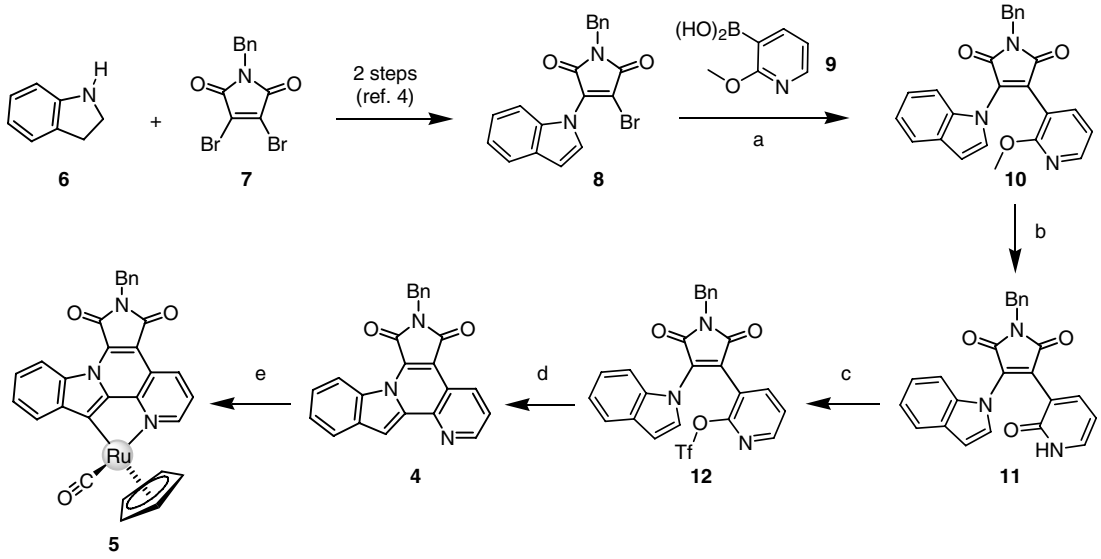


Figure 1. Staurosporine as a lead structure for the design of ruthenium-based protein kinase inhibitors.

* Corresponding author. Tel.: +1 215 573 1953; fax: +1 215 746 0348; e-mail: meggers@sas.upenn.edu

0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.10.054



Scheme 1. Reagents and conditions: (a) $Pd(dba)_2$ (10%), PPh_3 (20%), Na_2CO_3 (3.1 equiv), THF/H_2O (5:1), 75 °C, 7 h (70%); (b) TBDMSCl (3 equiv), NaI (4 equiv), MeCN, 0 °C to rt, 12 h (95%); (c) Tf_2O (2 equiv), pyridine, 0 °C to rt, 1 h (75%); (d) $Pd(PPh_3)_4$ (20%), Et_3N (3.1 equiv), DMF, 85 °C, 15 h (100%); (e) $[CpRu(CO)(MeCN)_2]^+PF_6^-$ (1.5 equiv), Et_3N (1.2 equiv), DMF, 55 °C, 2 h (61%).

The synthesis of heterocycle **4** is an overall six step route (Scheme 1). Michael addition/elimination of indoline **6** with *N*-benzyl dibromomaleimide **7** followed by DDQ oxidation afforded cross-coupling partner **8** according to a published procedure.[4] A Pd-mediated Suzuki cross-coupling[6] reaction in THF/H_2O (5:1) with commercially-available boronic acid **9**[5] (1.5 equiv) afforded the disubstituted maleimide **10** in a 70% yield.[7] It was important in this reaction to first reflux a solution of the substrates/reagents in THF prior to addition of H_2O, otherwise intractable precipitation of the catalyst occurred upon heating. The reaction did not proceed, however, without H_2O which is necessary to dissolve the base. The removal of the methyl group of **10** with BBr_3 resulted in decomposition of the starting material, but instead demethylation under milder conditions with NaI/TBDMSCl in MeCN gave pyridone **11** in a high yield of 95%.[8] Formation of triflate **12** was achieved with 2.0 equiv of Tf_2O in pyridine.[9] This choice of solvent is necessary to avoid formation of low-yielding mixtures of *O*- and *N*-triflates. An intramolecular Pd-catalyzed Heck reaction[6] was the final key step in the synthesis of ligand **4**.[10] Table 1 outlines a variety of conditions used to optimize this intramolecular cyclization. An initial stoichiometric C–C bond formation with $Pd(OAc)_2$ led only to decomposition of the starting material (entry 1). Subsequent catalytic couplings with $Pd(dba)_2$ or $PdCl_2(PPh_3)_2$ gave no cyclization product either (entries 2 and 3). Further couplings with $Pd(PPh_3)_4$ plus KOAc as a base (entry 4) and $Pd_2(dba)_3$ plus Et_3N (entry 5) gave the desired cyclization product in modest yields of 23% and 44%, respectively. We finally found that the combination of the electron-rich Pd(0) catalyst $Pd(PPh_3)_4$ in combination with 3.1 equiv Et_3N affords quantitative yields of the Heck coupling product **4** (entry 6). Thus, the right reaction conditions are highly critical for this intramolecular Heck coupling to occur in high yields. Ligand **4** is a deep purple solid and has a limited solubility profile due to its planarity and thus recrystallization from refluxing ethanol was used to purify this compound.[10]

Next, we investigated the ability of **4** to serve as a bidentate ligand for ruthenium. Cyclometalation with the ruthenium precursor $[CpRu(CO)(MeCN)_2]^+PF_6^-$ in DMF at 55 °C afforded the coordinatively saturated complex **5** as a green solid.[11] A crystal structure of complex **5** is shown in Figure 2.[12] The structure demonstrates that the pyridoazafluorene heterocycle **4** can indeed serve as a bidentate ligand for ruthenium, having one classical coordination bond with the pyridine (Ru1–N19 = 2.15 Å) in addition to one covalent σ-bond with

Table 1. Optimization of the intramolecular Heck coupling with **12**

Entry	Catalyst (equiv)	Base (equiv)	Ligand[b] (equiv)	Solvent	Temperature (°C)	Yields (%)
1	$Pd(OAc)_2$ (1.0)	NaOAc (2.0)	PPh_3 (2.0) Bu_4NI (1.0)	Dioxane	85	0
2	$Pd(dba)_2$[a] (0.05)	Et_3N (3.0)	dppp (0.06)	DMF	85	0
3	$PdCl_2(PPh_3)_2$ (0.1)	Et_3N (1.1)	None	DMF	85	0
4	$Pd(PPh_3)_4$ (0.05)	KOAc (1.1)	None	DMF	130	23
5	$Pd_2(dba)_3$[a] (0.1)	Et_3N (2.1)	PPh_3 (0.2)	DMF	85	44
6	$Pd(PPh_3)_4$ (0.2)	Et_3N (3.1)	None	DMF	85	100

[a] dba = dibenzylideneacetone.
[b] dppp = 1,3-bis(diphenylphosphino)propane.

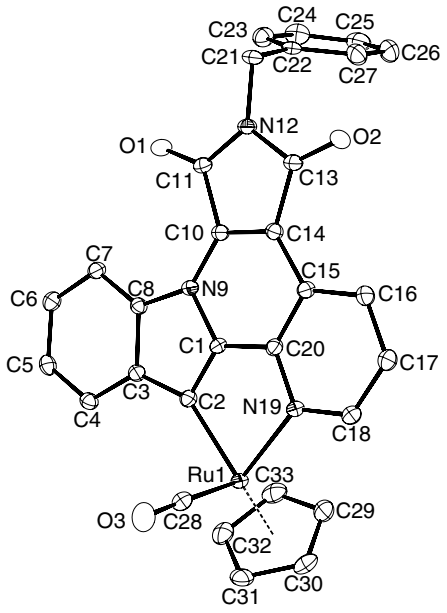


Figure 2. Crystal structure of the N-benzylated derivative of ruthenium complex **5**. ORTEP drawing with 30% probability thermal ellipsoids.

the indole moiety (Ru1–C2 = 2.08 Å). The coordination sphere is further filled up with an η^5-cyclopentadienyl and a CO group. With this, the structure is almost superimposable to the crystal structure of the analogous isomer **1Bn** (Fig. 1).[1b] Notably, the Ru–C bond with **5** and the Ru–N bond with **1Bn** of the indole moieties are virtually equidistant ($\Delta = 0.03$ Å).

Complex **5** is stable under neutral and slightly basic condition but decomposes under acidic and Lewis-acidic conditions with demetalation and recovery of the free ligand. For example, this has the consequence that purification by silica gel chromatography must be performed in presence of a base such as Et_3N.[11] This is in contrast to the isomeric pyridocarbazole complexes **1** and **1Bn**, which do not show this acid sensitivity.

Compared to complex **1Bn**, the isomeric scaffold **5** provides a significant change in the electronic nature of the resulting metal complex. A substantial decrease of 22 cm^{-1} (1927 vs 1949 cm^{-1}) was observed for the CO stretch vibration in the infrared spectrum between **1Bn** and **5**, indicating an increase in electron density at the metal center of **5**. This is presumably due to the stronger σ-donating nature of the indole–carbon ligand of **5** compared to the analogous indole–nitrogen ligand in **1Bn**. The high electron density at this carbon may be also responsible for the acid sensitivity of **5**.

In summary, we have developed a straightforward synthetic strategy to the unique heterocycle **4** and we demonstrated its ability to serve as a chelating ligand in a ruthenium complex. Compared to the regioisomeric pyridocarbazole **2**, ligand **4** increases the electron density of the ruthenium center as demonstrated by probing the vibrational stretch frequency of a CO group in the coordination sphere of the ruthenium. Future work will evaluate the effect of this increased electron density for the design of organoruthenium kinase inhibitors with modulated physicochemical and reactive properties.

Acknowledgments

We thank the National Institutes of Health for a Grant (1 R01 GM071695-01A1) and a Chemistry–Biology Interface Training Grant Fellowship for S.P.M. (T32 GM 071339).

References and notes

1. Ruthenium complexes as protein kinase inhibitors: (a) Zhang, L.; Carroll, P. J.; Meggers, E. *Org. Lett.* **2004**, *6*, 521–523; (b) Bregman, H.; Williams, D. S.; Atilla, G. E.; Carroll, P. J.; Meggers, E. *J. Am. Chem. Soc.* **2004**, *126*, 13594–13595; (c) Bregman, H.; Williams, D. S.; Meggers, E. *Synthesis* **2005**, 1521–1527; (d) Williams, D. S.; Atilla, G. E.; Bregman, H.; Arzoumanian, A.; Klein, P. S.; Meggers, E. *Angew. Chem., Int. Ed.* **2005**, *117*, 1984–1987; (e) Bregman, H.; Carroll, P. J.; Meggers, E. *J. Am. Chem. Soc.* **2006**, *128*, 877–884; (f) Debreczeni, J. É.; Bullock, A. N.; Atilla, G. E.; Williams, D. S.; Bregman, H.; Knapp, S.; Meggers, E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1580–1585; (g) Atilla, G. E.; Williams, D. S.; Bregman, H.; Pagano, N.; Meggers, E. *ChemBioChem* **2006**, *7*, 1443–1450.
2. For bioorganometallic and medicinal organometallic chemistry, see: (a) Severin, K.; Bergs, R.; Beck, W. *Angew. Chem., Int. Ed.* **1998**, *37*, 1634–1654; (b) Grotjahn, D. B. *Coord. Chem. Rev.* **1999**, *190*, 1125–1141; (c) Jaouen, G., Ed. *J. Organomet. Chem.* **1999**, *589*, 1–126; (d) Metzler-Nolte, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1040–1043; (e) Fish, R. H.; Jaouen, G. *Organometallics* **2003**, *22*, 2166–2177; (f) Stodt, R.; Gencaslan, S.; Müller, I. M.; Sheldrick, W. S. *Eur. J. Inorg. Chem.* **2003**, 1873–1882; (g) Schlawe, D.; Majdalani, A.; Velcicky, J.; Heßler, E.; Wieder, T.; Prokop, A.; Schmalz, H.-G. *Angew. Chem., Int. Ed.* **2004**, *43*, 1731–1734; (h) Staveren, Van D. R.; Metzler-Nolte, N. *Chem. Rev.* **2004**, *104*, 5931–5985; (i) Yan, Y.; Melchart, K.; Habtemariam, M. A.; Sadler, P. J. *Chem. Commun.* **2005**, 4764–4776; (j) Dyson, P. J.; Sava, G. *Dalton Trans.* **2006**, 1929–1933; (k) Schatzschneider, U.; Metzler-Nolte, N. *Angew. Chem., Int. Ed.* **2006**, *45*, 1504–1507; (l) Stockland, R. A., Jr.; Kohler, M. C.; Guzei, I. A.; Kastner, M. E.; Bawiec, J. A., III; Labaree, D. C.; Hochberg, R. B. *Organometallics* **2006**, *25*, 2475–2485.
3. For indolocarbazole protein kinase inhibitors, see: (a) Kase, H.; Iwahashi, K.; Nakanishi, S.; Matsuda, Y.; Yamada, K.; Takahashi, M.; Murakata, C.; Sato, A.; Kaneko, M. *Biochem. Biophys. Res. Commun.* **1987**, *142*, 436–440; (b) Ruegg, U. T.; Burgess, G. M. *Trends Pharmacol. Sci.* **1989**, *10*, 218–220; (c) Martiny-Baron, G.; Kazanietz, M. G.; Mischak, H.; Blumberg, P. M.; Kochs, G.; Hug, H.; Marme, D.; Schachtele, C. *J. Biol. Chem.* **1993**, *268*, 9194–9197; (d) Caravatti, G.; Meyer, T.; Fredenhagen, A.; Trinks, U.; Mett, H.; Fabbro, D. *Bioorg. Med. Chem. Lett.* **1994**, *4*, 399–404; (e) Prudhomme, M. *Curr. Pharm. Des.* **1997**, *3*, 265–290; (f) Jackson, J. R.; Gilmartin, A.; Imburgia, C.; Winkler, J. D.; Marshall, L. A.; Roshak, A. *Cancer Res.* **2000**, *60*, 566.

4. Lakatosh, S. A.; Luzikov, Y. N.; Preobrazhenskaya, M. N. *Org. Biomol. Chem.* **2003**, *1*, 826–833.
5. 2-Methoxy-3-pyridyl boronic acid was either purchased commercially or synthesized from 2-methoxypyridine: Thompson, A. E.; Hughes, G.; Batsanov, A. S.; Bryce, M. R.; Parry, P. R.; Tarbit, B. *J. Org. Chem.* **2005**, *70*, 388–390.
6. (a) Routier, S.; Coudert, G.; Mérour, J.-Y. *Tetrahedron Lett.* **2001**, *42*, 7025–7028; (b) Wang, J.; Soundarajan, N.; Liu, N.; Zimmermann, K.; Naidu, B. N. *Tetrahedron Lett.* **2005**, *46*, 907–910; (c) Routier, S.; Peixoto, P.; Mérour, J.-Y.; Coudert, G.; Dias, N.; Bailly, C.; Pierré, A.; Léonce, S.; Caignard, D.-H. *J. Med. Chem.* **2005**, *48*, 1401–1413; (d) Routier, S.; Mérour, J.-Y.; Dias, N.; Lansiaux, A.; Bailly, C.; Lozach, O.; Meijer, L. *J. Med. Chem.* **2006**, *49*, 789–799.
7. *Synthesis of compound* **10**: To a solution of compound **8** (1.58 g, 4.15 mmol) in THF (125 mL) were added compound **9** (0.95 g, 6.22 mmol), Na_2CO_3 (1.21 g, 11.40 mmol), PPh_3 (220 mg, 0.83 mmol), and $Pd(dba)_2$ (238 mg, 0.42 mmol), and the resulting solution was purged with Ar for 10 min and then refluxed. After 1 h, H_2O was added and heated to 75 °C for an additional 6 h and then cooled to rt. The mixture was poured into 250 mL of H_2O and extracted with EtOAc (3 × 200 mL), washed with brine (100 mL), and dried over $MgSO_4$. Purification by column chromatography was performed on silica gel with 20:1 hexanes/EtOAc as the eluent to give disubstituted maleimide **10** as a viscous orange oil (1.2 g, 70%): IR (thin film, cm^{-1}) ν 3031, 2929, 1705, 1644, 1573, 1457, 1396, 1351, 1204, 1118, 1011, 743. ^1H NMR (DMSO-d_6) δ (ppm) 8.15 (dd, $J = 1.8$, 4.9 Hz, 1H), 8.07 (dd, $J = 1.8$, 7.5 Hz, 1H), 7.61 (d, $J = 3.6$ Hz, 1H), 7.60 (d, $J = 8.3$ Hz, 1H), 7.40 (d, $J = 7.1$ Hz, 2H), 7.36 (t, $J = 7.8$ Hz, 2H), 7.30 (t, $J = 7.1$ Hz, 1H), 7.17 (dd, $J = 4.9$, 7.5 Hz, 1H), 7.05 (t, $J = 7.3$ Hz, 1H), 6.82 (d, $J = 3.6$ Hz, 1H), 6.82 (t, $J = 7.3$ Hz, 1H), 6.59 (d, $J = 8.3$ Hz, 1H), 4.79 (s, 2H), 2.89 (s, 3H). ^{13}C NMR (DMSO-d_6) δ (ppm) 169.1, 166.9, 160.3, 148.4, 140.3, 136.5, 134.6, 133.3, 129.1, 128.6, 128.4, 127.7, 127.5, 122.1, 121.6, 120.8, 119.2, 116.9, 111.9, 111.7, 106.6, 52.9, 41.5. HRMS (CI) calcd for $C_{25}H_{19}N_3O_3$ $(M)^+$ 409.1426, found $(M)^+$ 409.1426.
8. *Synthesis of compound* **11**: A solution of compound **10** (250 mg, 0.61 mmol) in MeCN (73 mL) was cooled to 0 °C, purged with Ar, then treated with anhydrous NaI (366 mg, 2.45 mmol) and TBDMSCl (276 mg, 1.83 mmol) sequentially, and subsequently slowly warmed to rt. An orange suspension slowly evolved and the mixture was stirred for 12 h. The mixture was quenched with H_2O and extracted into 200 mL EtOAc. The organic layer was washed with aq 5% $NaHCO_3$ (2 × 75 mL), brine (2 × 75 mL), dried over $MgSO_4$, and concentrated. The crude residue was purified by column chromatography on silica gel with 200:1 CH_2Cl_2/MeOH as the eluent to afford **11** as an orange foam (230 mg, 95%): IR (thin film, cm^{-1}) ν 3037 (br), 2857, 1701, 1633, 1552, 1454, 1431, 1395, 1355, 1242, 1206, 1118, 1053, 742. ^1H NMR (DMSO-d_6) δ (ppm) 7.89 (dd, $J = 1.0$, 7.0 Hz, 1H), 7.63 (d, $J = 3.5$ Hz, 1H), 7.57 (d, $J = 8.1$ Hz, 1H), 7.47 (dd, $J = 1.0$, 6.1 Hz, 1H), 7.39 (d, $J = 5.7$ Hz, 2H), 7.36 (t, $J = 7.7$ Hz, 2H), 7.29 (t, $J = 6.8$ Hz, 1H), 7.08 (t, $J = 6.8$ Hz, 1H), 6.96 (m, $J = 6.8$, 7.5 Hz, 1H), 6.94 (d, $J = 8.1$ Hz, 1H), 6.74 (d, $J = 3.5$ Hz, 1H), 6.37 (t, $J = 6.8$ Hz, 1H), 4.73 (s, 2H). ^{13}C NMR (DMSO-d_6) δ (ppm) 169.2, 167.1, 158.8, 143.3, 137.6, 136.6, 135.2, 133.0, 128.9, 128.6, 128.5, 127.6, 127.5, 122.0, 121.3, 120.8, 120.2, 119.8, 111.8, 106.3, 104.9, 41.4. HRMS calcd for $C_{24}H_{17}N_3O_3$ $(M+Na)^+$ 418.1167, found 418.1183 $(M+Na)^+$.
9. *Synthesis of compound* **12**: A solution of compound **11** (1.05 g, 2.65 mmol) in pyridine (26.5 mL) was cooled to 0 °C and stirred under Ar. Tf_2O (898 μL, 5.31 mmol) was added dropwise over 30 min, then warmed to rt, and stirred for another 30 min. The orange mixture was diluted to 250 mL with H_2O and extracted with EtOAc (3 × 200 mL). The organic layer was washed with aq 10% HCl (50 mL), brine (50 mL), dried over $MgSO_4$, and concentrated. The crude residue was dry-loaded onto silica gel and purified by column chromatography with 4:1 hexanes/EtOAc as the eluent to provide **12** as an orange foam (1.05 g, 75%): IR (thin film, cm^{-1}) ν 3041, 2933, 1710, 1651, 1597, 1464, 1420, 1395, 1356, 1214, 1130, 1076, 894, 855, 747, 599. ^1H NMR (DMSO-d_6) δ (ppm) 8.47 (dd, $J = 1.9$, 8.5 Hz, 1H), 8.29 (dd, $J = 1.9$, 7.7 Hz, 1H), 7.75 (dd, $J = 4.8$, 7.7 Hz, 1H), 7.62 (d, $J = 7.8$ Hz, 1H), 7.60 (d, $J = 3.6$ Hz, 1H), 7.43 (d, $J = 7.4$ Hz, 2H), 7.36 (t, $J = 7.7$ Hz, 2H), 7.30 (t, $J = 7.2$ Hz, 1H), 7.10 (t, $J = 7.4$ Hz, 1H), 6.88 (d, $J = 3.7$ Hz, 1H), 6.88 (t, $J = 8.4$ Hz, 1H), 6.69 (d, $J = 8.3$ Hz, 1H), 4.86 (s, 2H). ^{13}C NMR (DMSO-d_6) δ (ppm) 168.0, 166.0, 152.5, 149.3, 143.2, 136.1, 135.8, 133.9, 129.7, 128.5, 127.9, 127.5, 127.5, 125.0, 122.5, 122.4, 121.2, 119.0, 116.7, 115.6, 112.2, 108.1, 41.6. HRMS calcd for $C_{25}H_{16}N_3O_5SF_3$ $(M+Na)^+$ 550.0660, found 550.0651 $(M+Na)^+$.
10. *Synthesis of compound* **4**: A solution of compound **12** (150 mg, 0.3 mmol) in dry DMF (3.7 mL) was treated with Et_3N (123 μL, 0.9 mmol). After the addition of $Pd(PPh_3)_4$ (60 mg, 0.06 mmol), the solution was purged with Ar 10 min, and then heated to 85 °C for 15 h. The purplish-red mixture was cooled to rt and diluted with 100 mL CH_2Cl_2. The organic extract was washed with brine (2 × 20 mL), dried over $MgSO_4$, and concentrated. Recrystallization from refluxing EtOH gave **4** as a purple solid (160 mg, 100%): IR (thin film, cm^{-1}) ν 1688, 1624, 1583, 1556, 1478, 1446, 1396, 1341, 1322, 1222, 1131, 953, 815, 779, 742. ^1H NMR ($CDCl_3$) δ (ppm) 9.41 (m, 1H), 8.89 (dd, $J = 1.7$, 8.1 Hz, 1H), 8.84 (dd, $J = 1.7$, 4.6 Hz, 1H), 7.89 (m, 1H), 7.87 (s, 1H), 7.71 (m, 2H), 7.46 (dd, $J = 4.6$, 8.1 Hz, 1H), 7.34–7.52 (m, 5H), 4.92 (s, 2H). HRMS (ESI) calcd for $C_{24}H_{15}N_3O_2$ 378.1242 $(M+H)^+$, found $(M+H)^+$ 378.1250.
11. *Synthesis of complex* **5**: A solution of compound **4** (10 mg, 0.027 mmol) in dry DMF (1.8 mL) was treated with Et_3N (4.4 μL, 0.032 mmol) and $[CpRu(CO)(MeCN)_2]^+PF_6^-$ (17 mg, 0.04 mmol) and heated to 55 °C for 2 h. The resulting greenish-brown mixture was diluted with 20 mL EtOAc, washed with brine (20 mL), dried over $MgSO_4$, and concentrated. Purification by column chromatography on silica gel with 50:1:0.01 hexanes/EtOAc/Et_3N as the eluent afforded **5** as a green solid (9 mg, 61%): IR (thin film, cm^{-1}) ν 3078, 2930, 1927, 1706, 1564, 1540, 1466, 1432, 1393, 1123, 805, 743. ^1H NMR (DMSO-d_6) δ (ppm) 9.04 (m, 1H), 8.89 (dd, $J = 1.1$, 5.6 Hz, 1H), 8.28 (dd, $J = 1.1$, 7.7 Hz, 1H), 7.99 (m, 1H), 7.53 (m, 2H), 7.27–7.41 (m, 5H), 7.19 (dd, $J = 5.6$, 7.7 Hz, 1H), 5.31 (s, 5H), 4.92 (s, 2H).
12. Crystals were grown by the slow evaporation of a solution of **5** in MeCN to give an opaque green solid suitable for X-ray crystallographic analysis. CCDC 621757 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.