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Pauson–Khand cycloaddition reactions of chiral ynamides. Observation of an unusual *endo*-addition with norbornadiene

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Abstract—Pauson–Khand cycloadditions using chiral ynamides are achieved in modest to good yields with excellent regioselectivity and modest stereoselectivity. An unusual *endo* addition is found when using norbornadiene and substituted ynamides, leading to cycloadducts that were not observed in previous studies using ynamides or ynamines.
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Ynamides are becoming synthetically useful synthons especially for use in transition metal-mediated processes.[1–4] The distinct stability of ynamides **1**–**3** (Fig. 1) over traditional ynamines[5] renders them viable substrates for developing stereoselective[6,7] and intramolecular reactions[8] that are otherwise challenging with ynamines. Our efforts in this area[4] and recent success in achieving a facile synthesis of chiral ynamides **3** via Cu-catalyzed cross-coupling[3] led us to examine the possibility of achieving auxiliary-driven asymmetric Pauson–Khand cycloadditions.[9–13] Co- or Fe-mediated Pauson–Khand cycloadditions using ynamides have been elegantly described recently by Rainier,[10] Witulski,[11] and Chen.[12] Specifically, Witulski[11] reported stereoselective intramolecular Pauson–Khand cycloadditions using tethered chiral sulfonyl-substituted ynamides **1**. However, Pauson–Khand reactions using chiral auxiliary-based ynamides such as **3** have not been explored.[7a,14] We report here our findings related to regio- and stereoselectivity issues in Pauson–Khand cycloadditions of chiral ynamides as well as an unusual *endo*-addition with norbornadiene.

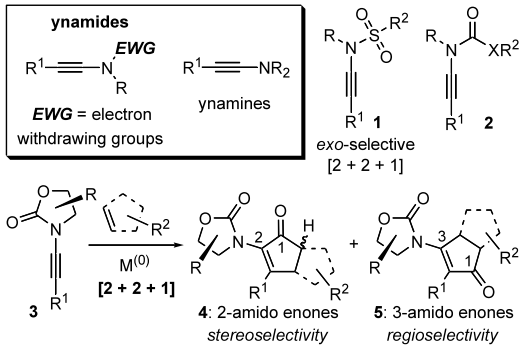
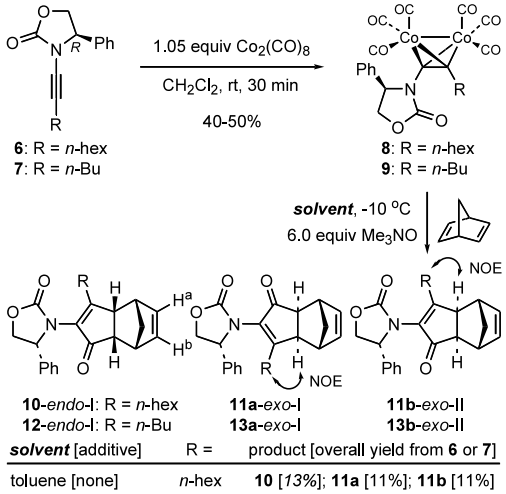


Figure 1.

To explore the feasibility ynamide Pauson–Khand cycloaddition, chiral ynamides **6** and **7** were treated with 1.05 equiv. of $Co_2(CO)_8$ at rt in CH_2Cl_2, providing the respective cobalt carbonyl complexes **8** and **9**[15] as deep purple solids in 40–50% yield (Scheme 1). All



solvent [additive]	R =	product [overall yield from **6** or **7**]
toluene [none]	*n*-hex	**10** [*13%*]; **11a** [11%]; **11b** [11%]
CH_2Cl_2 [none]	*n*-hex	**10** [*30%*]; **11a** [15%]; **11b** [15%]
CH_2Cl_2 [MS 4Å]	*n*-hex	**10** [*25%*]; **11a** [10%]; **11b** [10%]
CH_2Cl_2 [none]	*n*-Bu	**12** [*18%*]; **13a** [12%]; **13b** [6%]

Scheme 1.

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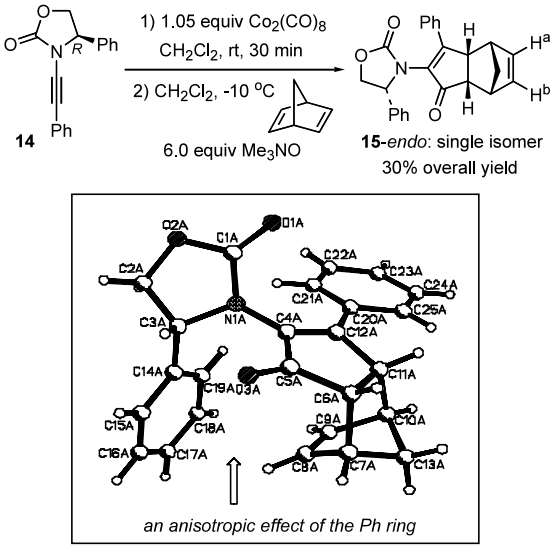
attempts to secure an X-ray structure of these complexes failed. Subsequent Pauson–Khand reactions of **8** and **9** with norbornadiene (NBD) were carried out in various solvents in the presence of 6.0 equiv. Me_3NO. In each case, a mixture of three isomers (**10**–**11a**,**b** from **8**, and **12**–**13a**,**b** from **9**) was isolated in 35–50% yield.

The expected *exo* products **11a**,**b** and **13a**,**b** exhibited excellent regioselectivity with only 2-amido enones (see regioisomer **4** in Fig. 1) being present as shown by NOE, although there is no diastereoselectivity. More interestingly, not only were we quite surprised with the finding of *endo* products **10** and **12**, but these *endo* products were also isolated as single regio- and stereoisomers. This result represents an unusual scenario in Pauson–Khand cycloadditions using NBD since *exo* products are formed almost exclusively.[7a,9,11] The related *endo* products were also not found in the work of Pericàs[7a,14] and Witulski[11] using ynamines and ynamides, respectively. However, it should be noted that Livinghouse[16a] and Carretero[16b,c] did report unusual *endo*-selective intramolecular Pauson–Khand cycloadditions. In addition, Pericàs[17] recently isolated *endo* products from Pauson–Khand cycloadditions of NBD with hetero bimetallic (Mo–Co) complexes of *N*-(2-alkynoyl)oxazolidinones or sultams, although *exo*-selectivity remained in reactions using dicobalt complexes of the same substrates.[16]

These *endo*-addition products were assigned initially based on NOE and the fact that the unusual shifting of olefinic protons H^a and H^b (see **10** and **12** in Scheme 1) toward upfield could only be explained by the close proximity of the phenyl ring on the Evans' oxazolidinone auxiliary.[18] However, the reaction of ynamide **14** with NBD allowed isolation of the crystalline *endo*-product **15** as a single diastereomer with an overall yield of 30% (Scheme 2).[19] The *endo* stereochemistry was unambiguously assigned using single crystal X-ray analysis that also distinctly revealed the same anisotropic effect of the Ph ring observed in ^1H NMR.

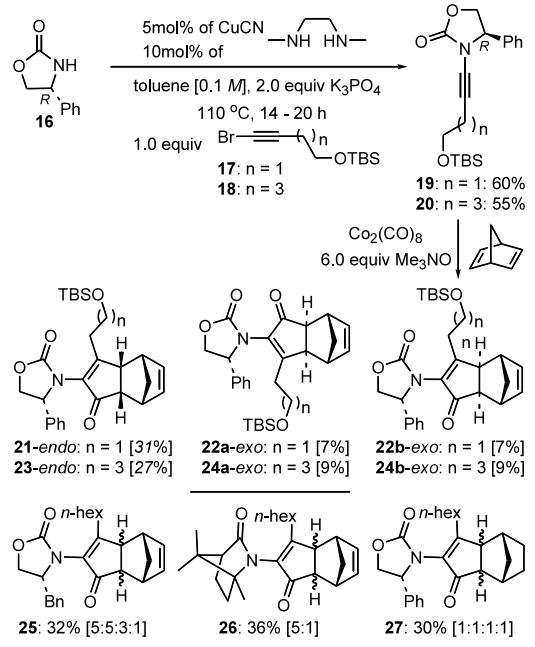


Scheme 2.

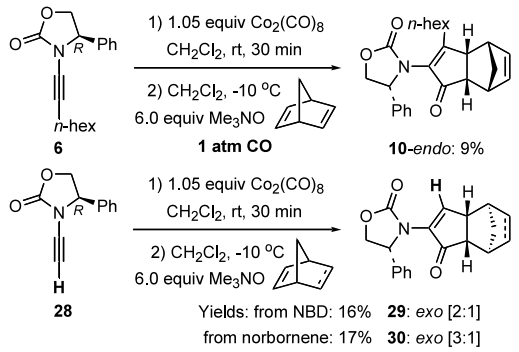
Pauson–Khand reactions of synthetically useful chiral ynamides are shown in Scheme 3. Ynamides **19** and **20** were prepared from alkynyl bromides **17** and **18**, respectively, in good yields using Cu-catalyzed cross-coupling.[3a] Subsequent cycloadditions of **19** and **20** afforded separable mixtures of *endo* (**21** and **23**, respectively) and *exo* (**22a**,**b** and **24a**,**b**, respectively) isomers in modest overall yields[19] with the *endo* addition again being stereoselective.

We briefly examined other chiral auxiliaries as shown in products **25** and **26**, and *endo* isomers were again observed,[20] although it was non-stereoselective, leading to all four possible isomers. In addition, the reaction of **6** with norbornene led to **27** also as a mixture of four isomers. By comparing with reactions of ynamides **6**, **7**, **14**, **19**–**20** with NBD, these latter results imply that the Ph group on the oxazolidinone auxiliary and the usage of NBD are important in providing the selectivity for the *endo* addition.

To improve the efficiency of this cycloaddition, we examined two variables as shown in Scheme 4. Initially, we were concerned there was an insufficient amount of CO to render Co-insertion effective, but the reaction of ynamide **6** with NBD under a blanket of 1 atm of CO led to **10** in 9% yield. Also, both Pericàs[7a] and Witulski[11] had employed terminal unsubstituted ynamines or ynamides and indicated that substituted ynamines or ynamides gave lower yields; however, the opposite was true in our work. However, reactions of ynamide **28** with NBD and norbornene led to cycloadducts **29** and **30** in only 16 and 17% yield, respectively.[21]



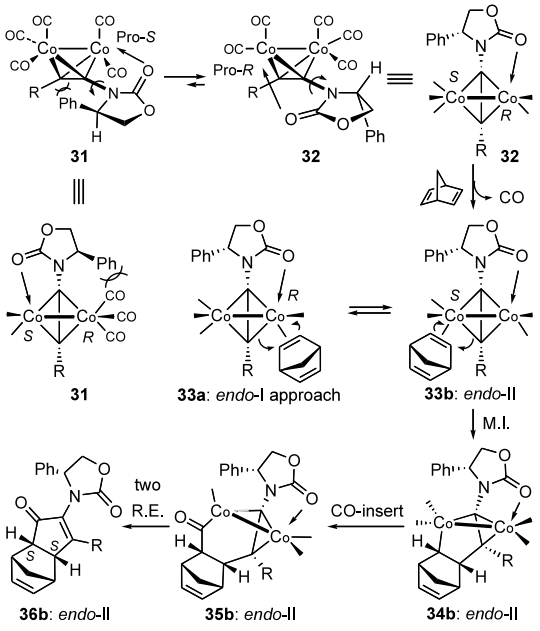
Scheme 3.



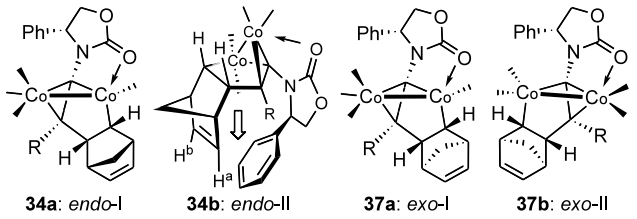
Scheme 4.

While we are further exploring optimization issues, it has become quite intriguing mechanistically especially since we now only observe *exo* products when using unsubstituted ynamides.[7a,11,22] To rationalize these results, a mechanistic working model is illustrated in Schemes 5–7.

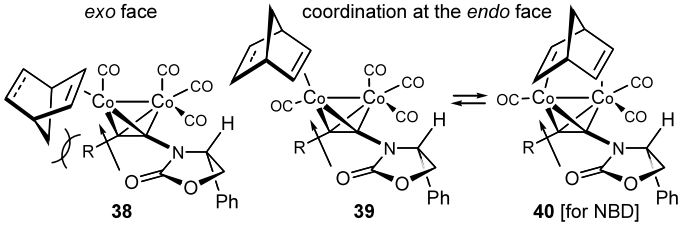
Based on related transition metal carbonyl complexes containing Evans' type auxiliary,[23] it may be proposed that cobalt complexes **31** and **32** can have the carbonyl group of oxazolidinone coordinated to either diastereotopic (Pro-*R* or *S* before coordination) Co metal with **32** being favored for having less steric congestion (Scheme 5). Loss of a CO ligand in **32** would allow coordination of NBD at its *endo* (or *exo*, not shown) face to either the *R*- or *S*-Co metal. This would lead to two diastereomeric *endo*-coordinated complexes **33a** and **33b** with the favored product **36b** (*endo*-II) being derived from **33b** through migratory insertion (MI) and CO-insertion intermediates **34b** and **35b**.



Scheme 5.



Scheme 6.



Scheme 7.

Presently, we are uncertain as to why the *endo*-coordinated complex-II **33b** would be favored over **33b** to undergo MI, while the corresponding *exo*-coordinated complexes (not shown) do not appear to have any preferences. Unfortunately, preliminary low-level (PM3) calculations were inconclusive. By comparing stabilities of migratory-inserted intermediates,[7a] one postulation would be that the migratory-inserted *endo*-intermediate-II **34b** (a different perspective shown in Scheme 6) is favored over *endo*-intermediate-I **34a** because of the orbital overlap or π-stacking between the Ph ring of the auxiliary and the second olefin of NBD seen in the modeling of **34b** (see the arrow). This π-stacking is absent in the *endo*-intermediate-I **34a** as well as in both *exo*-intermediates **37a** and **37b**.

In addition, support for this stacking could be found in both the X-ray structure of **15** and in the ^{1}H NMR of cycloadducts **10**, **12**, **21**, and **23** in which both olefinic protons (H^a and H^b) are unusually upfield shifted, suggesting an anisotropic effect of the phenyl ring. This observation is also in good agreement with results from using other ynamides that lack this particular phenyl ring (see **25**), or norbornene that lacks this extra double bond (see **27**), the selectivity for *endo* products is lost, leading to both *endo*-I and -II products.

A second factor would be the observation of the *endo* addition product only when using substituted ynamides. To address this issue, our molecular modeling reveals that although being less congested, coordination at the *exo* face of NBD or norbornene would lead to the unwanted steric interaction with the R group as shown in **38** (Scheme 7). Thus, when R = H, we as well as others[7a,11] have observed only the *exo* addition. On the other hand, despite being more congested, coordination at the *endo* face of NBD (or norbornene, see **39**) would be devoid of such steric interaction, and in the case of NBD, it could also benefit from a double coordination with both Co metals (see **40**).

We have described here Pauson–Khand cycloaddition reactions of chiral ynamides. These reactions can be achieved in excellent regioselectivity, although in modest stereoselectivity. When norbornadiene and substituted ynamides were used, an unusual *endo* addition occurred leading to cycloadducts that were not observed in previous studies using ynamines or ynamides. Efforts are underway to further investigate the mechanism and to develop applications of this cycloaddition.

Acknowledgements

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15. **General procedure for the Pauson–Khand reaction of ynamides**: To a solution of an appropriate ynamide (0.2 mmol) in CH_2Cl_2 (2 mL) was added $Co_2(CO)_8$ (72.8 mg, 0.21 mmol). The mixture was stirred at rt for 30 min until the complex was formed completely as indicated by TLC. The respective alkene (2.0 mmol) was then added to the reaction mixture, and after cooling to −10°C, a solution of TMANO (1.2 mmol) in CH_2Cl_2 (1 ml) was added to dropwise. The reaction was warmed to rt and allowed to react for 10–16 h. Once completed, the reaction mixture was filtered through a small bed of celite and concentrated under reduced pressure. Purification of the crude material using silica gel column chromatography (gradient eluent: 10% to 50% EtOAc in hexanes) afforded the respective cycloadduct.

Characterization of selected new compounds: **10**: $R_f=0.18$ (33% EtOAc in hexanes); $[\alpha]_D^{23}=-80.8°$ (*c* 0.34, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, 3H, $J=7.0$ Hz), 1.25–1.42 (m, 6H), 1.49 (d, 1H, $J=8.0$ Hz), 1.63 (d, 1H, $J=8.0$ Hz), 1.83–1.89 (m, 1H), 2.40–2.46 (m, 1H), 2.76 (t, 1H, $J=5.0$ Hz), 2.83 (brd, 1H), 3.03 (brd, 1H), 3.25 (t, 1H, $J=5.0$ Hz), 4.24 (t, 1H, $J=9.0$ Hz), 4.73 (t, 1H, $J=9.0$ Hz), 4.85 (dd, 1H, $J=3.0$, 6.0 Hz), 5.17 (dd, 1H, $J=3.0$, 6.0 Hz), 5.62 (t, 1H, $J=9.0$ Hz), 7.23–7.25 (m, 2H), 7.32–7.36 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.96, 22.43, 26.51, 29.80, 30.32, 31.44, 43.63, 43.89, 45.26, 49.28, 51.63, 59.45, 70.31, 127.83, 128.50, 128.90, 131.47, 132.64, 134.52, 137.24, 155.60, 176.77, 204.20; IR (thin film) cm^{-1} 2928 (m), 2857 (m), 1762 (s), 1700 (s), 1405 (m), 1212 (m); LC–MS: *m*/*e* (% relative intensity) 392 (100) ($M+H^+$), 326 (18).

11a: $R_f=0.44$ (50% EtOAc in hexanes); $[\alpha]_D^{23}=-138.6°$ (*c* 0.49, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, 1H, $J=7.0$ Hz), 1.05–1.07 (m, 1H), 1.16–1.29 (m, 8H), 1.42–1.46 (m, 1H), 2.09 (d, 1H, $J=5.0$ Hz), 2.31–2.36 (m, 1H), 2.47–2.53 (m, 1H), 2.57 (d, 1H, $J=5.0$ Hz), 2.76 (brd, 1H), 2.88 (brd, 1H), 4.31 (t 1 H, $J=7.0$ Hz), 4.77 (t, 1H, $J=8.5$ Hz), 5.71 (t, 1H, $J=8.0$ Hz), 6.17 (dd, 1H, $J=3.0$, 6.0 Hz), 6.23 (dd, 1H, $J=3.0$, 5.5 Hz), 7.30–7.38 (m, 5H); IR (thin film) cm^{-1} 2928 (m), 2854 (m), 1767 (s), 1634 (s), 1401 (m), 1200 (m); LC–MS: *m*/*e* (% relative intensity) 392 (100) ($M+H^+$).

11b: $R_f=0.38$ (50% EtOAc in hexanes); $[\alpha]_D^{23}=-148.5°$ (*c* 0.51, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.14 (d, 1H, $J=9.0$ Hz), 0.90 (t, 1H, $J=7.0$ Hz), 1.23–1.34 (m, 8H), 2.05–2.09 (m, 1H), 2.19 (d, 1H, $J=5.0$ Hz), 2.47–2.53 (m, 1H), 2.50 (brd, 1H), 2.67 (d, 1H, $J=5.0$ Hz), 70 (brd, 1H), 4.33 (t 1 H, $J=9.0$ Hz), 4.78 (t, 1H, $J=8.5$ Hz), 5.75 (t, 1H, $J=8.0$ Hz), 6.14 (dd, 1H, $J=2.5$, 5.0 Hz), 6.18 (dd, 1H, $J=2.5$, 5.0 Hz), 7.30–7.35 (m, 5H); IR (thin film) cm^{-1} 2930 (m), 2859 (m), 1766 (s), 1703 (s), 1403 (m); LC–MS: *m*/*e* (% relative intensity) 392 (100) ($M+H^+$).

12: $R_f=0.57$ (50% EtOAc in hexanes); $[\alpha]_D^{23}=-127.74°$ (*c* 0.58, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, 3H, $J=6.9$ Hz), 1.31–1.38 (m, 4H), 1.42 (d, 1H, $J=8.4$ Hz), 1.54 (d, 1H, $J=8.4$ Hz), 1.75–1.86 (m, 1H), 2.32–2.43 (m, 1H), 2.69 (t, 1H, $J=5.4$ Hz), 2.78 (brd, 1H), 2.96 (brd, 1H), 3.19 (t, 1H, $J=5.4$ Hz), 4.17 (t, 1H, $J=8.7$ Hz), 4.65 (t, 1H, $J=8.7$ Hz), 4.79 (dd, 1H, $J=2.7$, 5.4 Hz), 5.12 (dd, 1H, $J=2.7$, 5.4 Hz), 5.53 (t, 1H, $J=8.7$ Hz), 7.21–7.25 (m, 2H), 7.30–7.35 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.72, 22.81, 28.56, 29.95, 43.57, 43.86, 45.19, 49.22, 51.58, 59.45, 70.25, 127.80, 128.46, 128.86, 131.47, 132.56, 134.54, 137.17, 155.57, 176.73, 204.11; IR (thin film) cm^{-1} 2958 (m), 1762 (s), 1699 (s), 1406 (m), 1210 (m), 702 (m); LC–MS: *m*/*e* (% relative intensity) 364 (100) ($M+H^+$), 298 (10).

15: $R_f=0.37$ (50% EtOAc in hexanes); $[\alpha]_D^{23}=+42.3°$ (*c* 0.53, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.58 (d, 1H, $J=8.5$ Hz), 1.66 (dt, 1H, $J=8.5$, 2.0 Hz), 2.91 (t, 1H, $J=5.5$ Hz), 2.96 (brd, 1H), 3.18 (brd, 1H), 3.61 (dd 1 H, $J=4.0$, 5.5 Hz), 4.23 (t, 1H, $J=9.0$ Hz), 4.67 (t, 1H, $J=8.5$ Hz), 5.03 (dd, 1H, $J=3.0$, 5.5 Hz), 5.47 (t, 1H, $J=9.0$ Hz), 5.56 (dd, 1H, $J=3.0$, 5.5 Hz), 7.06–7.08 (m, 2H), 7.20–7.28 (m, 2H), 7.39–7.46 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.60, 44.68, 46.47, 49.37, 51.70, 126.09, 126.45, 127.78, 127.91, 128.14, 128.33, 128.47, 128.63, 130.40, 133.24, 133.97, 136.20, 156.09, 204.09; IR (thin film) cm^{-1} 2925 (m), 1761 (s), 1700 (s), 1395 (m), 1209 (m); LC–MS: *m*/*e* (% relative intensity) 384 (100) ($M+H^+$), 318 (10).

21: $R_f=0.63$ (50% EtOAc in hexanes); $[\alpha]_D^{23}=-58.57°$ (*c* 0.40, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.08 (s, 6H), 0.90 (s, 9H), 1.46 (d, 1H, $J=7.5$ Hz), 1.58 (dt, 1H, $J=7.5$, 1.5 Hz), 2.08–2.11 (m, 1H), 2.65–2.68 (m, 1H), 2.74 (t, 1H, $J=5.0$ Hz), 2.90 (brd, 1H), 3.01 (brd, 1H), 3.40 (t, 1H, $J=5.0$ Hz), 3.86–3.92 (m, 2H), 4.22 (t, 1H, $J=9.5$ Hz), 4.73 (t, 1H, $J=9.0$ Hz), 4.86 (dd, 1H, $J=3.0$, 6.0 Hz), 5.07 (dd, 1H, $J=3.0$, 6.0 Hz), 5.68 (t, 1H, $J=9.5$ Hz), 7.22–7.26 (m, 2H), 7.33–7.36 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.50, 18.12, 25.78, 33.50, 43.63, 44.07, 46.37, 49.35, 51.53, 59.25, 60.44, 70.41, 127.78, 128.57, 128.96, 131.57, 132.42, 135.15, 137.13, 174.06, 204.27 (missing 1 signal due to overlap); IR (thin film) cm^{-1} 2952 (m), 2854 (m), 1762 (s), 1700 (s), 1401 (m), 1251 (m); LC–MS: *m*/*e* (% relative intensity) 466 (100) ($M+H^+$), 334 (30).

22a,**b**: $R_f=0.68$ (50% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) **22a**: δ 0.01–0.03 (m, 7H), 0.84–0.87 (m, 10H), 2.08 (d, 1H, $J=4.5$ Hz), 2.73 (d, 1H, $J=5.0$ Hz), 2.74–2.79 (m, 1H), 2.83 (brd, 1H), 2.87 (brd, 1H), 3.38–3.42 (m, 1H), 3.86–3.95 (m, 2H), 4.28 (t 1 H, $J=8.5$ Hz), 4.77 (t, 1H, $J=9.0$ Hz), 5.76 (t, 1H, $J=8.5$ Hz), 6.16 (dd, 1H, $J=3.0$, 6.0 Hz), 6.22 (dd, 1H, $J=2.5$, 5.0 Hz), 7.29–7.36 (m, 5H); **22b**: δ 0.05–0.08 (m, 7H), 0.91–0.93 (m, 10H), 2.18 (d, 1H, $J=5.5$ Hz), 2.28–2.34 (m, 1H), 2.54–2.60 (m, 1H), 2.61 (brd, 1H), 2.66 (brd, 1H), 2.85 (d, 1H, $J=5.0$ Hz), 3.66–3.70 (m, 2H), 4.31 (t 1 H, $J=8.5$ Hz), 4.78 (t, 1H, $J=9.0$ Hz), 5.80 (t, 1H, $J=8.5$ Hz), 6.13 (dd, 1H, $J=3.0$, 5.5 Hz), 6.16 (dd, 1H, $J=3.0$, 6.0 Hz), 7.29–7.36 (m, 5H); LC–MS: *m*/*e* (% relative intensity) 466 (100) ($M+H^+$).

23: $R_f=0.47$ (50% EtOAc in hexanes); mp 94–96°C; $[\alpha]_D^{23}=-54.89°$ (*c* 0.63, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.07 (s, 6H), 0.90 (s, 9H), 0.48 (d, 1H, $J=9.0$ Hz), 1.51–1.56 (m, 2H), 1.60 (dt, 1H, $J=9.0$, 2.0 Hz), 1.64–1.70 (m, 2H), 1.88–1.94 (m, 1H), 2.42–2.48 (m, 1H), 2.75 (t, 1H, $J=5.0$ Hz), 2.83 (brd, 1H), 3.03 (brd, 1H), 3.25 (t, 1H, $J=5.0$ Hz), 3.63–3.66 (m, 2H), 4.23 (t, 1H, $J=8.5$ Hz), 4.72 (t, 1H, $J=9.0$ Hz), 4.84 (dd, 1H, $J=3.0$, 6.0 Hz), 5.16 (dd, 1H, $J=3.0$, 6.0 Hz), 5.61 (t, 1H, $J=9.0$ Hz), 7.22–7.24 (m, 2H), 7.34–7.35 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.38, 18.21, 22.93, 25.84, 30.02, 32.97, 43.65, 43.91, 45.21, 49.30, 51.67, 59.45, 62.50, 70.36, 127.84, 128.54, 128.93, 131.47, 132.66, 134.67, 137.22,

176.57, 204.26 (missing 1 signal due to overlap); IR (thin film) cm^{-1} 2932 (m), 2858 (m), 1764 (s), 1702 (s), 1406 (m); LC–MS: *m*/*e* (% relative intensity) 494 (100) ($M+H^+$).

29a,**b**: $R_f=0.43$ (25% EtOAc in hexanes); ^1H NMR (300 MHz, $CDCl_3$) **29a**: δ 1.25 (d, 1H, $J=9.6$ Hz), 1.35 (d, 1H, $J=9.6$ Hz), 2.03–2.05 (m, 1H), 2.62–2.64 (m, 1H), 2.76 (brd, 1H), 2.86 (brd, 1H), 4.23 (dd, 1H, $J=4.2$, 8.7 Hz), 4.72 (t, 1H, $J=8.7$ Hz), 6.04 (dd, 1H, $J=3.9$, 9.0 Hz), 6.13 (dd, 1H, $J=3.0$, 5.4 Hz), 6.26 (dd, 1H, $J=3.0$, 5.4 Hz), 7.21–7.24 (m, 2H), 7.30–7.34 (m, 3H), 7.80 (d, 1H, $J=3.3$ Hz); **29b**: δ 0.27 (d, 1H, $J=9.6$ Hz), 0.95–0.97 (m, 1H), 2.15–2.17 (m, 1H), 2.50 (brd, 1H), 2.55 (brd, 1H), 2.62–2.65 (m, 1H), 2.71–2.73 (m, 1H), 4.30 (dd, 1H, $J=4.2$, 8.7 Hz), 4.75 (t, 1H, $J=8.7$ Hz), 6.01 (dd, 1H, $J=3.6$, 8.4 Hz), 6.10 (dd, 1H, $J=3.0$, 5.4 Hz), 6.22 (dd, 1H, $J=3.0$, 5.4 Hz), 7.21–7.24 (m, 2H), 7.30–7.34 (m, 3H), 7.70 (d, 1H, $J=3.0$ Hz); IR (thin film) cm^{-1} 2975 (m), 1762 (s), 1703 (s), 1400 (s); GC–MS: *m*/*e* (% relative intensity) 307 (100) ($M+H^+$), 241 (54), 196 (72).

30a,**b**: $R_f=0.38$ (33% EtOAc in hexanes); ^1H NMR (300 MHz, $CDCl_3$) **30a**: δ 0.96 (d, 1H, $J=10.5$ Hz), 1.06 (d, 1H, $J=10.8$ Hz), 1.18–1.28 (m, 2H), 1.48–1.72 (m, 2H), 1.99 (d, 1H, $J=5.4$ Hz), 2.25 (d, 1H, $J=4.2$ Hz), 2.35 (d, 1H, $J=4.2$ Hz), 2.54–2.56 (m, 1H), 4.24 (dd, 1H, $J=4.2$, 8.7 Hz), 4.72 (t, 1H, $J=9.0$ Hz), 6.07 (dd, 1H, $J=3.9$, 9.0 Hz), 7.20–7.23 (m, 2H), 7.29–7.37 (m, 3H), 7.76 (d, 1H, $J=3.3$ Hz); **30b**: δ 0.09 (d, 1H, $J=11.4$ Hz), 0.55 (d, 1H, $J=10.8$ Hz), 1.18–1.28 (m, 2H), 1.48–1.72 (m, 2H), 1.98–2.00 (m, 1H), 2.09 (d, 1H, $J=4.8$ Hz), 2.54–2.56 (m, 1H), 2.61–2.64 (m, 1H), 4.31 (dd, 1H, $J=4.2$, 8.7 Hz), 4.76 (t, 1H, $J=8.7$ Hz), 6.03 (dd, 1H, $J=3.9$, 9.0 Hz), 7.20–7.23 (m, 2H), 7.29–7.37 (m, 3H), 7.63 (d, 1H, $J=3.0$ Hz); IR (thin film) cm^{-1} 2953 (m), 2872 (m), 1754 (s), 1700 (s), 1399 (s); GC–MS: *m*/*e* (% relative intensity) 309 (3) ($M+H^+$), 265 (100), 198 (54).

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19. Despite being modest, the overall yield implies the cycloaddition step occurred in about 60% since our best yield for the formation of the cobalt complex is around 50%. This is the case with later examples as well.
20. The *endo*/*exo* stereochemistry in **26** was not vigorously assigned.
21. We did use other alkenes such as cyclopentene, cyclohexene, and allyl alcohol. Unfortunately, they all led to their respective cycloadducts in $\leq 10\%$ yield. We are currently examining this limitation.
22. The *exo* stereochemistry in **29** was assigned using NOE.
23. For an example, see: Powers, T. S.; Wulff, W. D.; Quinn, J.; Shi, Y.; Jiang, W. Q.; Hsung, R. P.; Parisi, M.; Rahm, A.; Jiang, X. W.; Yap, G. A.; Rheingold, A. L. *J. Organomet. Chem.* **2001**, *617*, 182.