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Tungsten catalysis has played an instrumental role in the history of organometallic chemistry, with electrophilic, fully oxidized W(VI) catalysts featuring prominently in olefin polymerization and metathesis reactions. Here, we report that the simple W(0) precatalyst, $W(CO)_6$, catalyzes the isomerization and hydrocarbonylation of alkenes via a W(0)/W(II) redox couple. The 6- to 7-coordinate geometry changes associated with this redox process are key in allowing isomerization to take place over multiple positions and stop at a defined unactivated internal site that is primed for in situ functionalization. DFT studies and crystallographic characterization of multiple directing-group-bound W(II) model complexes illuminate potential intermediates of this redox cycle and showcase the capabilities of the 7-coordinate W(II) geometry to facilitate challenging alkene functionalizations.

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Low-Valent Tungsten Redox Catalysis Enables Controlled Isomerization and Carbonylative Functionalization of Alkenes

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Abstract: Tungsten catalysis has played an instrumental role in the history of organometallic chemistry, with electrophilic, fully oxidized W(VI) catalysts featuring prominently in olefin polymerization and metathesis reactions. Here, we report that the simple W(0) precatalyst, W(CO)₆, catalyzes the isomerization and hydrocarbonylation of alkenes via a W(0)/W(II) redox couple. The 6- to 7-coordinate geometry changes associated with this redox process are key in allowing isomerization to take place over multiple positions and stop at a defined unactivated internal site that is primed for *in situ* functionalization. DFT studies and crystallographic characterization of multiple directing-group-bound W(II) model complexes illuminate potential intermediates of this redox cycle and showcase the capabilities of the 7-coordinate W(II) geometry to facilitate challenging alkene functionalizations.

Main Text: Tungsten is widely employed in commercial applications of central importance to modern society, including hard materials (e.g., tungsten carbide and metal alloys) and petroleum upgrading processes (1) (e.g., the Shell Higher Olefin Process and the Neohexene Process). Tungsten has also played an historically important role in the development of the field of homogeneous catalysis (2). Most notable in this context are catalytic processes that employ high-valent tungsten (e.g., +6) in a fixed oxidation state for alkene and alkyne metathesis (3) and polymerization reactions (4). Low-valent tungsten (e.g., +0), on the other hand, has a strikingly different reactivity profile, in that it possesses the potential for redox reactions, such as oxidative addition and reductive elimination. Moreover, the archetypal W(0) complex, W(CO)₆, is a bench-stable solid with high functional group tolerance, whereas fully oxidized W(VI) species are generally highly Lewis acidic and oxophilic, manifesting in sensitivity to air, moisture, and many common Lewis basic functional groups. Despite these promising features and the intriguing reactivity that has been demonstrated with stoichiometric low-valent tungsten, such as dearomatization (5-6) and alkene hydrofunctionalization (7-9), low-valent tungsten redox catalysis has been limited to a few specific types of transformations, including alkene isomerization, hydrogenation, and allylic substitution (10-12) (Fig. 1a).

Fig. 1. (a) Background of tungsten catalyzed reactions. (b) Coordination chemistry of W(0)/W(II) redox cycle. (c) Known regioselective methods for hydrocarbonylation reactions. (d) This work.

We were drawn to the W(0)/W(II) redox cycle because of the ability of the metal to naturally fluctuate between 6-coordinate octahedral and noncanonical 7-coordinate geometries (Fig. 1b). In theoretical (13-14) and experimental (15-17) studies it has been shown that the facile nature of migratory insertion and reductive elimination at 7-coordinate W(II) or Mo(II) is due to the spatial proximity of the ligands and attractive non-bonding interactions. Additionally, 6-coordinate alkyltungsten(II) species are known to undergo rapid β -H elimination to form 18-electron 7-coordinate W(II)-H species (18-19).

With these findings in mind, we hypothesized that the interplay between 6- and 7-coordinate species could be exploited to address a synthetically important problem, namely tandem isomerization and hydrocarbonylation of alkenes at a classically disfavored position. Alkene isomerization/hydroformylation is one of the highest volume homogenous catalytic reactions in the chemical industry (20), making it a useful reaction for benchmarking reactivity and selectivity patterns. Typically, in this family of reactions, the regioselectivity is dictated by thermodynamics, with functionalization occurring at the most stable alkylmetal intermediate (21-22). In particular, migration of the metal to the terminal position or to a carbon next to a π -system can reliably give linear or α -functionalized products, respectively, in high regioselectivity. Nevertheless, for a given molecule of interest, alternative positions cannot generally be functionalized with current methodology (Fig. 1c). More broadly speaking, controlled alkene isomerization to classically inaccessible internal positions has been limited to a few examples where the isomerization is coupled to an intramolecular cyclization or rearrangement, including 5-*endo* cyclizations by Kochi (23-26) and [3,3]-sigmatropic rearrangements by Marek (27). Capturing these intermediates via intermolecular functionalization, namely coupling with CO, would offer new possibilities in regiocontrolled alkene functionalization.

We reasoned that the isomerization and tandem carbonylation process could be guided to a traditionally unfavorable position via metallacycle ring contraction (28) or “metallacycle zipping,” with site-selectivity governed by the nature of the directing group employed (29). We envisioned the geometric flexibility of 7-coordinate W(II) would facilitate otherwise challenging endocyclic β -H eliminations required for the directed alkene isomerization. Stabilizing an alkylmetal species of a defined ring size through coordination of the directing group would then allow carbonylative functionalization (30) to take place (Fig. 1c) with high regioselectivity (31). The development of a W(0)-catalyzed directed migratory carbonylation would complement other substrate-directed tandem alkene isomerization/functionalization reactions, such as oxidative arylation and hydroalkylation catalyzed by nickel (32-33).

To initiate the study, we tested a library of known directing groups (DGs) for their ability to facilitate isomerization and carbonylation of an alkenyl carboxylic acid derivative with stoichiometric $W(CO)_6$ at 150 °C (Fig. 2a). Chatani’s NHPic (Pic = 2-picolinyl) directing group (**DG4**), which was originally developed for ruthenium-catalyzed $C(sp^2)$ -H carbonylation (34), gave quantitative yield of the desired product as a single regioisomer. All other directing groups examined failed to give any carbonylated products. Given that $W(CO)_6$ readily dissociates CO upon UV irradiation (7-8, 11, 18-19, 35-36) we questioned whether the reaction would take place at lower temperature (25 °C) under photocatalytic conditions. Indeed, the desired product was formed in good yield when using stoichiometric $W(CO)_6$ under an argon atmosphere with irradiation from a 450 Watt UV lamp (Fig. 2, entry 1). With 20 mol% $W(CO)_6$, there was evidence of turnover (entry 2), but all reactivity shut down with catalytic tungsten under an atmosphere of CO (Fig. 2, entries 3–6). One explanation is that the relatively high concentration of CO in solution at room temperature leads to poisoning of the catalyst. Under thermal conditions (150 °C), 93% of product **2a** was obtained using 20 mol% $W(CO)_6$ under 1 atm CO (entry 8). Other homoleptic metal carbonyls were less effective (Mo, entry 10) or ineffective all together (Cr and Fe, entries 11–12). Although molybdenum is known to exhibit similar reactivity and coordination chemistry to tungsten (9-11, 17) we attribute the higher yield of tungsten in this case to its greater kinetic stability (35). Additionally, a representative panel of Rh, Ru, Co, and Ir precatalysts failed to promote the reaction or did so with low efficiency (See SI for additional screening data).

Fig. 2. (a) Directing group optimization (see Supporting Information for details). (b) Reaction condition optimization. ^a1 atm of argon with no added CO. ^bYield determined by ¹H NMR.

Having optimized the reaction conditions, we next investigated the reaction scope (Fig. 3a). Notably, γ,δ -unsaturated amides bearing various substitution patterns are readily accessible via numerous robust organic reactions (37) including the Diels–Alder cycloaddition, Ireland- or Johnson–Claissen rearrangement, and Wittig olefination. γ,δ -Unsaturated amides containing a terminal alkene and α -monosubstitution afforded the products with high yields and moderate d.r. (2b–2c), while an α,α -disubstituted alkenyl amide (2d) gave lower yield. A derivative of (*S*)-allylglycine underwent the transformation (2e) and retained high *ee* (98%) at the α -stereocenter in the case of the major diastereomer. The minor diastereomer showed erosion to 52% *ee*, suggesting epimerization of the kinetically favored *cis* product to the thermodynamically preferred *trans* product. The reaction was effective with 1,1- and 1,2-disubstituted alkenes (2f–2h). The presence of a primary alkyl chloride (2i) or a second, more distal alkene (2j) was well tolerated.

Next, we investigated substrates that require thermodynamically uphill alkene isomerization, which we reasoned could be compensated for in the highly exergonic carbonylation step (vide infra). Indeed, trisubstituted alkenes were isomerized to disubstituted alkenes, which then afforded the desired carbonylated products (2k–2n, 2w) in moderate to high yields. Endocyclic alkenes represent another class of challenging substrates for selective alkene isomerization/functionalization reactions. Pleasingly, Diels–Alder-derived substrates bearing di- (2u–2v) or trisubstituted (2w) alkenes gave moderate yield with exclusively *cis* stereochemistry at the ring juncture. A cyclopentenyl substrate (2t) also reacted in high yield. Remarkably, exocyclic methyldiene cyclobutane was efficiently isomerized and carbonylated via the intermediacy of a highly strained endocyclic cyclobutene, providing 2o in modest yield and >20:1 dr. Various conjugated alkenes were next evaluated. An α,β -unsaturated ester (2q) provided the product in high yield and with high chemoselectivity. Styrenes with versatile (and potentially sensitive) functional handles, including aryl iodides, bromides, and nitriles (2q–2s) proceeded in high yields.

Lastly, we probed the distance dependence of this isomerization/carbonylation process (Fig. 3b). A substrate requiring no initial isomerization (2x) or isomerization over one position (2a) gave the corresponding products in greater than 90% yield. Moving the alkene farther away led to a gradual decrease in yield from 71% (2g) to 6% (2h). In cases with incomplete conversion to carbonylated product, we observed formation of a mixture of internal alkene isomers accompanied by gradual catalyst death, as evidenced by precipitation of tungsten black. We attribute the decrease in product yield over distance to increased activation entropy in the directed isomerization pathway and the sluggish nature of the alternative non-directed pathway (11). Synthesis of 2a on 5 mmol scale provided the product in 89% yield (951 mg), which could then be hydrolyzed to provide the corresponding 1,4-dicarboxylic acid in 92% yield (See SI).

We were then curious if chiral branched variants of **DG4** could control relative stereochemistry in the CO insertion step to provide diastereoselective carbonylated products (Fig. 3c). Introduction of a methyl group at the benzylic carbon (**DG7**) led to 5:1 d.r. and 82% yield, while progressively more bulky alkyl groups (**DG8–DG10**) did not lead to further improvement in diastereoselectivity and eventually led to a drastic drop in yield. Use of commercially available, enantiopure (*S*)-**DG7** under catalytic conditions provided the product 2aa in 75% yield and 5:1 d.r. (>99% *ee* for both diastereomers). Overall, this result establishes a platform for further development of chiral directing auxiliaries for stereocontrolled isomerization/hydrofunctionalization reactions.

Fig. 3. (a) Substrate scope. **(b)** Isomerization over multiple positions. **(c)** Progress towards stereocontrolled isomerization–carbonylation. ^a 1 equiv. W(CO)₆ under argon. ^b Yield determined by ¹H NMR. All reactions run on 0.1–0.2 mmol scale unless otherwise stated; See SI for full details.

The unique features of this catalytic isomerization/carbonylation process motivated us to interrogate the reaction mechanism and the underlying coordination chemistry of the intermediates involved. To examine the potential involvement of W(0)/W(II) redox processes, we first attempted direct synthesis of organometallic intermediates from an alkenyl amide starting material (**1xa**) by treatment with W(MeCN)₃(CO)₃ (1 equiv) in CDCl₃ at temperatures ranging from 3–60 °C, but

these experiments only showed formation of the organic product **2x** and unreacted starting material **1xa** by ^1H NMR (see SI). Thus, we next turned our attention to independent synthesis of isolable model complexes **W-1–W-3** in an effort to establish the feasibility of these W(II) intermediates to undergo CO migratory insertion and reductive elimination (Fig. 4a). Oxidative addition of alkyl iodide **SM-1** to $\text{W}(\text{MeCN})_3(\text{CO})_3$ furnished model complex **W-1** which is stable in solution for several days. After full conversion of **SM-1**, AgOTf and $\text{KOt-Bu}/18\text{-crown-6}$ were added to **W-1** at room temperature, triggering migratory insertion and reductive elimination to afford the desired product (**P-1**) in high yield. Due to our inability to isolate this alkyltungsten(II) intermediate in crystalline form, further studies focused on more thermally stable aryltungsten(II) species (**37**) to facilitate analysis by X-ray crystallography.

Fig. 4. (a) Synthesis and reactivity studies of organotungsten model complexes. (b) X-ray structures of complexes **W-3** (CCDC 2020047) and **W-3'** (CCDC 204639) with solvent omitted for clarity.

Using an analogous synthetic sequence, the complexes **W-2** and **W-3** were prepared by oxidative addition of the corresponding aryl iodides **SM-2** and **SM-3** to $\text{W}(0)$ (**39**). **W-3** was then treated with AgOTf to abstract the iodide, and further treatment with $\text{KOt-Bu}/18\text{-crown-6}$ deprotonated the amide. PMe_3 (2.5 equiv) was added to prevent migratory insertion and reductive elimination, as was observed with **W-1**. Without addition of PMe_3 , we were unable to isolate any organotungsten species at this stage, and other ligands (PPh_3 , PhCN , *tert*-butyl isocyanide, or pyridine) failed to form isolable complexes. While **W-2'** was found to be unisolable, **W-3'** is air- and moisture-stable and can be purified by column chromatography on neutral alumina. The X-ray structure of **W-3'** revealed the directing group to be bound in the amidate-form, demonstrating the feasibility of this coordination mode.

Having established plausible oxidation states and coordination structures for many of the key proposed intermediates, we next investigated the mechanism of alkene isomerization. Earlier observations that the amino acid substrate (**2e**) maintained its stereochemistry at the α -position and that the α,α -disubstituted substrate (**2d**) gave product indicated that the carbonylation reaction likely proceeds through the β,γ -unsaturated isomer (as drawn in Fig. 3a). To further exclude the alternative hypothesis that the carbonylation proceeds through the conjugated α,β -unsaturated amide, we subjected crotonyl amide **1xb** to the standard reaction conditions, and <10% product **23** was observed by ^1H NMR of the crude reaction mixture, with the remainder being unreacted starting material (Fig. 5).

Having established the positional aspects of isomerization, we then considered possible mechanisms, namely 1,2- and 1,3-hydride shift pathways (40-41), through a series of deuterium labeling experiments and DFT calculations. To test the feasibility of tungsten to undergo N-H oxidative addition and W(II)-H insertion into alkenes, we conducted a series of experiments in which the amide N-H was exchanged to N-D *in situ* via treatment with excess CH_3OD under the reaction conditions (see SI). Evaluation of different deuterated substrates with terminal alkenes (Fig. 5) of varying distances from the amide gave evidence for this mechanism with 52–96% deuterium incorporation into the terminal position.

Fig. 5. Mechanistic experiments and deuterium labeling studies.

Density functional theory (DFT) calculations were performed to identify the catalytically active W species and its reactivity in promoting N-H oxidative addition and alkene isomerization (Fig. 4b) (42). The six-coordinate W(0) complex **I-1** was found to be the most likely species in N-H oxidative addition (see SI for details), leading to a seven-coordinate W(II)-H (**I-2**). Subsequent metal-hydride insertion (**TS2**), endocyclic β -hydride elimination (**TS3**), and metal-hydride reinsertion (**TS4**) are all facile, leading to a more stable five-membered metallacycle (**I-5**). An agostic interaction with the endocyclic β -C-H bond in **I-3** promotes the otherwise challenging endocyclic β -hydride elimination (**TS3**). The seven-coordinate geometry of **TS3** and the flexibility of the DG are both critical to alleviate strain in the transition state with a bidentate DG. After CO insertion (**TS5**) and binding with another CO molecule, the C-N reductive elimination from the seven-coordinate W(II) (**I-7**) requires a very low barrier (**TS6**) and is highly exergonic. These DFT results in combination with the mechanistic experiments above show that this 1,2-hydride shift

pathway is the prevailing mode of isomerization, while 1,3-hydride shift is kinetically less favorable (see SI for details).

Fig. 6. DFT energy profile of the reaction from **1a** to **2a**.

During the course of the isomerization process, buildup of intermediate internal alkenes is detected for reactions halted prior to completion (see SI), suggesting substrate dissociation and re-association are likely occurring, which is further supported by incorporation of multiple deuterium equivalents at different chain positions. DFT also predicts that ligand exchange of the coordinated alkene with free CO is energetically feasible (see SI for details), which can explain why intermediate internal alkenes can be observed when stopping the reaction early. In chain-walking reactions, premature dissociation of the alkene from the substrate is typically deleterious and leads to side products or intermediates that cannot feed back into the catalytic cycle (43); however, in this reaction it appears to have little effect on the overall yield and regioselectivity.

The results with deuterium-labeled substrate **1g-d₃** revealed an unusual phenomenon (43) that isomerization proceeds in a uni-directional fashion exclusively towards the directing group. Running the complementary experiment with internal alkene **1gb** further corroborated the uni-directional nature of isomerization, as no deuterium was detected in the terminal position (Fig. 5). The uni-directional alkene isomerization is consistent with the greater stability of the π -complex with internal alkene (**I-4**) than the terminal alkene complex (**I-2**).

When compared to relevant industrial carbonylation processes, this method still has drawbacks that will be addressed in future work, namely the requirement for a stoichiometric auxiliary and relatively high catalyst loadings. Along these lines, directed alkene isomerization/functionalization employing native functional groups holds great promise owing the ability of W(0) to form table adducts with weakly Lewis basic groups (44). Nevertheless, these findings provide an experimental and computational framework for exploring W(0)/W(II) catalytic processes and illustrate how this catalytic cycle can enable exceptional regioselectivity with a diverse range of alkenes in a challenging tandem isomerization/functionalization transformation.

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Supplementary Materials:

Materials and Methods

Figures S1–S22

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SUPPORTING INFORMATION

Low-Valent Tungsten Redox Catalysis Enables Controlled Isomerization and Carbonylative Functionalization of Alkenes

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GENERAL INFORMATION

General Safety Considerations: Carbon monoxide (CO) is a colorless, odorless gas that is extremely toxic. Filling or opening reaction tubes that contain CO needs to be done in a well-ventilated fume hood with a CO monitor. $W(CO)_6$ and other $M(CO)_x$ complexes used in this study thermally decompose to give off free CO, so all reactions run with $M(CO)_x$ complexes should be handled with the same precautions as those using gaseous CO, while taking into account any potential hazards introduced by the metal carbonyl species themselves.

All sealed reactions run at or above the boiling point of the solvent were run with a blast shield placed in front of the stir plate. Upon completion, the reaction vessels were allowed to cool to room temperature before being carefully vented behind the blast shield.

All materials were used as received from commercial sources without further purification. $W(CO)_6$ was purchased from Strem Chemicals 99.9% purity (Lots 31397600 and 31679900). Carbon monoxide (CO) was purchased from Praxair at >99.99% purity. Toluene was purchased from MilliporeSigma in 100-mL Sure/Seal bottles and used as received. The Schlenk tubes used in this study were purchased from Chemglass and Synthware. 1H and ^{13}C NMR spectra were recorded on a Bruker DRX equipped with a 5 mm DCH cryoprobe (600 MHz and 151 MHz, respectively). 1H spectra were reported relative to residual solvent signals unless otherwise stated. ^{13}C NMR spectra were calibrated to residual solvent signals. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet and m = multiplet. High-resolution mass spectra (HRMS) were recorded on an Agilent LC/MSD TOF mass spectrometer by electrospray ionization (Positive mode) time of flight experiments. IR data was collected on a Thermo Fischer Nicolet 380 FTIR.

REACTION OPTIMIZATION

The following reactions were run according to “General Procedure A” substituting the catalysts shown in the table for $W(CO)_6$. Photochemical reactions were run in standard Schlenk tubes. For entries 1 and 2, a slightly modified procedure was used where the reaction was sealed inside the glovebox under argon and used directly without a gas exchange step. For reactions run at 0.1 atm, the same procedure was used from “General Procedure A”, but a 10% CO in argon mixture (mixture prepared by Praxair) was used instead. All yields were calculated by 1H NMR using CH_2Br_2 as an internal standard.

Figure S1 (a) Directing group optimization; (b) Reaction condition optimization. ^a 1 atm of Ar with no added CO. ^b Yield calculated by 1H NMR.

In section “a” the reactions were all analyzed by both LCMS and 1H NMR to detect possible products. No detectable amounts of product were found for any of directing groups screened except **DG4**. In all of the reactions, the starting material was consumed resulting in a mixture of various internal alkenes in both *E* and *Z* configuration. No reduced products were detected by LCMS ($M+2$), nor cyclized products that would likely result in a larger change in retention time.

Entry	Catalyst	x mol% catalyst	Yield 2a
1	$Ru_3(CO)_{10}$	5	<5%
2	$RhPPh_3Cl$	5	nd
3	$[Rh(COD)Cl]_2$	5	nd
4	$Rh(acac)(CO)_2$	5	12%
5	$[Ir(COD)OH]_2$	5	nd
6	$Co_2(CO)_8$	10	trace
8	$W(\eta\text{-}6\text{ toluene})(CO)_3$	20	32%

Table S1 Screening data of different metal pre-catalysts. All yields were determined by 1H NMR using CH_2Br_2 as an internal standard.

CONTROL EXPERIMENTS

To demonstrate that the observed reactivity did not arise from trace metal contaminants present in the stir bars, solvents, or the commercial tungsten source, we conducted an experiment in which W(CO)_6 underwent *in situ* sublimation from an open inner capillary into an outer vessel (disposable vial) containing the starting material and reaction solvent with no stir bar. As can be seen below, in this case the reaction still proceeded to furnish the product in 23% yield. We attribute the diminished yield compared to that obtained from General Procedure A to a combination of solid-state decomposition and incomplete transfer into the outer toluene solution. Here, we note that the W(CO)_6 used in this study was >99.9% pure (trace metals basis) and purified by sublimation by the vendor.

Scheme S1 *in situ* sublimation of W(CO)_6 to test rule out precious metal contamination

Experimental procedure: Outside of the glovebox, a disposable glass capillary was carefully filled with W(CO)_6 (70 mg, 0.2 mmol, 2 equiv.). The outside of the capillary was wiped with Kimwipes®. The 6-mL disposable reaction vial was charged with starting material **24b** (19 mg, 0.1 mmol, 1 equiv.) and then capped and moved inside an argon-filled glovebox along with the glass capillaries packed with W(CO)_6 . Once inside the glovebox, toluene (1 mL, from freshly opened Sure/Seal bottle) was added to the 6 mL vial to dissolve the starting material. The capillary was then carefully placed inside the 6-mL vial, which was capped and sealed with electrical tape. The reactions were removed from the glovebox and placed in a preheated oil bath at 150 °C for 24 h without stirring or agitation. The vials were then removed from the oil bath and allowed to cool to room temperature before being carefully vented to release pressure. The crude material from the outer 6-mL reaction vial was then passed through a plug of celite that was then washed with acetone, and the filtrate was evaporated to dryness. The crude reaction mixture was analyzed by ^1H NMR with CBr_2H_2 as an internal standard. A graphical representation of the experiments is shown below.

Experiments were conducted in triplicate using a different freshly opened bottle of toluene and a different batch of starting material for each trial, all of which resulted in >20% product formation.

Figure S2 Graphical depiction of *in situ* sublimation control reactions

Although other homoleptic metal carbonyls such as Fe(CO)_5 , Mo(CO)_6 and Cr(CO)_6 are potential contaminants in the commercial source and would also be volatile at the reaction temperature used in the above experiment, these complexes were independently tested under the optimized reaction conditions and were found to give no product or inferior yield to W(CO)_6 . Collectively this data is consistent with a mechanism in which tungsten acts as the catalyst, rather than a trace metal contaminant (<10 ppm).

EXPERIMENTAL PROCEDURES

General Procedure for Catalytic Reactions

Figure S3 A) Weighing out $W(CO)_6$ and starting material. B) Addition of solvent. C) Connecting CO tank to Schlenk line. D) Gas exchange of reaction. E) Heating of reaction. F) Letting reactions cool down before opening Schlenk tube.

Catalytic Carbonylation Procedure (General Procedure A) Inside an argon-filled glovebox (O_2 levels between 35.0–55.0 ppm, H_2O levels unknown), to an oven-dried 25-mL Schlenk tube with a Teflon-coated magnetic stir bar containing $W(CO)_6$ (14 mg, 0.4 mmol) and the appropriate alkene (0.2 mmol), toluene (2.0 mL) was added via micropipette, with care taken to ensure that solids on the wall were washed into the bottom of the tube. The flask was removed from the glovebox. A carbon monoxide tank was directly connected to a Schlenk line, and the line was

purged with CO for 5 min at flow rate that resulted in ~2 bubbles/second in the attached oil bubbler. The vessel was attached to the Schlenk line and the rubber tubing connection was exposed to vacuum. The reaction tube was submerged in a cooling bath of dry ice and acetone (-78 °C) for 1 min, and the reaction solution was then carefully exposed to vacuum until the pressure monitor for the line stabilized at 0.7–1.1 mTorr. CO was then back-filled into the Schlenk tube. The tube was immediately removed from the cooling bath with the line left open to CO for an additional 30 sec, before being sealed. The reaction vessel was allowed to warm room temperature and was then submerged into a preheated oil bath at 150 °C and heated for 24–72 h.

The vessel was allowed to cool to room temperature and was then carefully vented inside the fumehood. The reaction solution was diluted with acetone and filtered through a plug of celite, which was washed with additional acetone. The filtrate was then evaporated to dryness. The crude material was purified by flash silica gel column chromatography using 30–40% acetone:hexanes as eluent. The alkene starting material and isomerized intermediates can be recovered by using 50–60% acetone:hexanes as eluent.

Stoichiometric Carbonylation Procedure (General Procedure B) Inside an argon-filled glovebox (O₂ levels between 35.0–55.0 ppm, H₂O levels unknown), to an oven dried 6-mL vial with a Teflon-coated magnetic stir bar were added W(CO)₆ (36 mg, 0.1 mmol), the appropriate alkene (0.1 mmol), and toluene (1.0 mL), with care taken to ensure that solids on the wall were washed to the bottom of the tube. The vial was sealed tightly with a disposable cap, and electric tape was placed around the cap. The vial was placed in a preheated oil bath at 150 °C and allowed to heat for the allotted amount of time.

The vessel was allowed to cool to room temperature and was then carefully vented inside the fumehood. The reaction solution was diluted with acetone and filtered through a plug of celite, which was washed with additional acetone. The filtrate was then evaporated to dryness. The crude material was purified by flash silica gel column chromatography using 30–40% acetone:hexanes as eluent. The alkene starting material and isomerized intermediates can be recovered by using 50–60% acetone:hexanes as eluent.

Important notes about experimental setup:

- A standard freeze–pump–thaw procedure using liquid N₂ for ≥3 cycles results in only trace product formation. This is likely due to additional CO in the vessel inhibiting substrate association.
- Schlenk tubes that have additional head space will likely result in reduced yield. During the optimization process, when a 50-mL Schlenk tube was used for 0.2 mmol reaction under otherwise standard conditions, the yield of **2a** decreased by 15%.
- W(CO)₆ that is not washed off the walls into the bottom of the tube can decompose much faster, resulting in reduced yield.
- The reaction does not appear to be mass-transfer-limited, as different stir rates (250–1000 rpm) resulted in similar yields; however, “splashing” or uneven stirring can result in higher levels of tungsten deposition on the walls and can lead to lower yields.

Reaction Optimization Substrates

The starting materials below were prepared via amide coupling of 4-pentenoic acid with the corresponding amine according to the procedure below.

HATU-Mediated Amide Coupling (General Procedure C)

In a 50-mL round bottomed flask with Teflon-coated magnetic stir bar, the alkenyl carboxylic acid (1 mmol, 1.0 equiv), DCM (2 mL), and pyridine (0.24 mL, 3 mmol, 3 equiv) were added in that order. HATU (0.456 g, 1.2 mmol, 1.2 equiv) was added slowly, and after addition was complete addition, the amine (1 mmol, 1 equiv) was added dropwise by syringe. The reaction solution was allowed to stir for 24 h, at which point it was diluted with DCM (5 mL) and quenched with a saturated solution of aq. NaHCO₃ (5 mL). The aqueous layer was extracted with DCM (×3), and the organic layers were combined, washed successively with water and brine, dried over MgSO₄, filtered, evaporated to dryness. The crude material was purified by flash silica gel chromatography. Tetramethyl urea commonly co-eluted with the product and could be removed by under vacuum (1 mTorr at 50 °C).

CHARACTERIZATION OF NEW COMPOUNDS

N-(2-(methylthio)phenyl)pent-4-enamide (DG1-SM): The title compound was prepared according to the General Procedure C from 2-(methylthio)aniline (0.139 g, 1 mmol) to afford 180 mg (80% yield) of **DG1-SM** as a pale-yellow oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.39–8.21 (m, 2H), 7.47 (d, $J = 7.8$ Hz, 1H), 7.36–7.24 (m, 1H), 7.06 (t, $J = 7.5$ Hz, 1H), 5.90 (ddt, $J = 16.1, 11.3, 5.8$ Hz, 1H), 5.14 (d, $J = 17.1$ Hz, 1H), 5.05 (d, $J = 10.3$ Hz, 1H), 2.52 (q, $J = 5.6$ Hz, 4H), 2.37 (s, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.06, 138.41, 136.76, 133.03, 129.03, 125.20, 124.43, 120.76, 116.04, 37.29, 29.51, 19.09. **HRMS** calcd. for $\text{C}_{12}\text{H}_{15}\text{NOS}^+ [\text{M}+\text{H}]^+$: 222.0947, Found: 222.0948.

N-(2-(diphenylphosphaneyl)phenyl)pent-4-enamide (2-(pent-4-enamido)phenyl)diphenylphosphonium (DG2-SM): The title compound was prepared according to the General Procedure C using 2-(diphenylphosphaneyl)aniline (**42**) (0.279 g, 1 mmol) as the amine to afford 153 mg (42% yield) of **DG2-SM** as a white solid. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 10.95 (s, 1H), 8.78–8.01 (m, 1H), 7.74–7.23 (m, 12H), 7.21–6.71 (m, 2H), 5.75 (dtd, $J = 27.9, 16.9, 14.2, 8.3$ Hz, 1H), 5.26–4.73 (m, 2H), 2.50–2.18 (m, 4H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.29, 136.66 (d, $J = 16.0$ Hz), 133.97, 133.65 (d, $J = 19.3$ Hz), 133.42, 132.05 (d, $J = 10.0$ Hz), 130.58, 129.57, 128.95 (d, $J = 7.6$ Hz), 128.77 (d, $J = 12.5$ Hz), 124.82, 122.60, 115.50 (d, $J = 37.4$ Hz), 37.02 (d, $J = 83.1$ Hz), 30.95. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 37.49. **HRMS** calcd. for $\text{C}_{23}\text{H}_{23}\text{NOP}^+ [\text{M}+\text{H}]^+$: 360.1512, Found: 360.1514.

N-(quinolin-8-yl)pent-4-enamide (DG3-SM): This compound has previously been synthesized in our laboratory and the procedure and characterization has previously been reported (**42**).

N-(pyridin-2-ylmethyl)pent-4-enamide (DG4-SM): This compound has previously been synthesized in our laboratory and the procedure and characterization has previously been reported (**47**).

N-benzylpent-4-enamide (DG5-SM): This compound has previously been synthesized in our laboratory and the procedure and characterization has previously been reported (**47**).

N-([2,2'-bipyridin]-6-ylmethyl)pent-4-enamide (DG6-SM): The preparation of the crude amine used in the amide coupling is described below. LAH (314.2 mg, 1.5 equiv, 8.278 mmol) is suspended in THF (10 ml) and stirred at 0° C. [2,2'-bipyridine]-6-carbonitrile (1.000 g, 1 equiv, 5.519 mmol) is dissolved in THF (10 ml) and added to the suspension over 30 min. The reaction is stirred at 0 °C for 1 h. The

reaction is quenched by the addition of aq. Na₂SO₄ (27.0 ml). The reaction mixture is filtered, and diluted with EtOAc. The organic layer is dried over MgSO₄, filtered and concentrated to give a red oil which was used directly in the next step. The title compound was prepared according to the General Procedure C using [2,2'-bipyridin]-6-ylmethanamine (185mg, 1 mmol) as the amine to afford 177 mg (66 % yield) of **DG6-SM** as a white solid. ¹H NMR (600 MHz, d₆-DMSO) δ 8.69 (ddd, *J* = 4.7, 1.8, 0.9 Hz, 1H), 8.52 (t, *J* = 6.0 Hz, 1H), 8.42 (dt, *J* = 7.9, 1.1 Hz, 1H), 8.26 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.96 (td, *J* = 7.7, 1.8 Hz, 1H), 7.92 (t, *J* = 7.8 Hz, 1H), 7.46 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 7.34 (dd, *J* = 7.7, 0.9 Hz, 1H), 5.95–5.72 (m, 1H), 5.07 (dt, *J* = 17.0, 1.7 Hz, 1H), 5.03–4.84 (m, 1H), 4.46 (d, *J* = 6.0 Hz, 2H), 2.35–2.30 (m, 4H). ¹³C NMR (151 MHz, d₆-DMSO) δ 171.73, 158.56, 155.15, 154.51, 149.28, 137.83, 137.75, 137.22, 124.18, 121.26, 120.51, 118.61, 115.08, 44.25, 34.48, 29.26. HRMS calcd. for C₁₆H₁₈N₃O⁺ [M+H]⁺: 268.1444, Found: 268.1444.

N-(1-(pyridin-2-yl)ethyl)pent-4-enamide (DG7-SM): The title compound was prepared according to the general procedure C using 1-(pyridin-2-yl)ethan-1-amine (0.123 g, 1 mmol) as the amine to afford 145 mg (71 % yield) of **DG7-SM** as a white solid. ¹H NMR (600 MHz, CDCl₃) δ 8.54 (d, *J* = 4.2 Hz, 1H), 7.65 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.24–7.09 (m, 2H), 6.89 (s, 1H), 5.83 (tt, *J* = 11.7, 5.9 Hz, 1H), 5.14 (t, *J* = 6.9 Hz, 1H), 5.06 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.01–4.94 (m, 1H), 2.42 (p, *J* = 6.6 Hz, 2H), 2.33 (t, *J* = 7.7 Hz, 2H), 1.45 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.60, 161.14, 149.16, 137.24, 137.00, 122.48, 121.73, 115.59, 49.82, 36.17, 29.81, 23.00. HRMS calcd. for C₁₂H₁₇N₂O⁺ [M+H]⁺: 205.1335, Found: 205.1336.

N-(1(*S*)-(pyridin-2-yl)ethyl)pent-4-enamide ((*S*)-DG7-SM): The title compound was prepared according to the General Procedure C using 1-(pyridin-2-yl)ethan-1-amine (0.500 g, 1 mmol) as the amine to afford 350 mg (42 % yield) of (*S*)-**DG7-SM** as a white solid. The analytical data matches that of the racemic compound.

N-(2-methyl-1-(pyridin-2-yl)propyl)pent-4-enamide (DG8-SM): The title compound was prepared according to the General Procedure C using 2-methyl-1-(pyridin-2-yl)propan-1-amine (0.151 g, 1 mmol) as the amine to afford 132 mg (56 % yield) of **DG8-SM** as a white solid. ¹H NMR (600 MHz, CDCl₃) δ 8.54 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.62 (td, *J* = 7.6, 1.8 Hz, 1H), 7.21–7.14 (m, 2H), 6.73 (d, *J* = 8.7 Hz, 1H), 5.92–5.72 (m, 1H), 5.05 (dq, *J* = 17.1, 1.6 Hz, 1H), 4.97 (ddt, *J* = 10.1, 1.8, 1.2 Hz, 1H), 4.89 (dd, *J* = 8.7, 6.9 Hz, 1H), 2.45–2.28 (m, 4H), 2.10 (h, *J* = 6.8 Hz, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.86, 159.48, 149.19, 137.27, 136.35, 123.30, 122.39, 115.57, 58.93, 36.30, 34.14, 29.89, 19.28, 18.80. HRMS calcd. for C₁₄H₂₁N₂O⁺ [M+H]⁺: 233.1648, Found: 233.1648.

N-(2-phenyl-1-(pyridin-2-yl)ethyl)pent-4-enamide (DG9-SM): The preparation of the crude amine used in the amide coupling is described below. In a 100 mL Schlenk flask, picolinonitrile (1.0411 g, 1 equiv, 10.000 mmol) was dissolved ether (15 mL) at –10 °C. Once completely dissolved, benzylmagnesium chloride (1.5089 g, 10.000 mL, 1.0 molar in ether, 1 equiv, 10.000 mmol) was added dropwise then stirred for 3 h at temperature. The reaction was quenched with methanol (3.204 g, 4.05 mL, 10 equiv, 100.00 mmol) at –10 °C and

stirred for 10 min before the addition of sodium borohydride (454.0 mg, 1.2 equiv, 12.000 mmol). After stirring for 10 min at temperature the reaction was brought to room temperature and allowed to stir for an additional 3 h. The reaction was diluted with EtOAc (25 mL) and quenched with a saturated solution of aq. NaHCO₃ (5 mL). The aqueous layer was extracted with EtOAc x3 and the organic layers combined, washed with water then brine, and then dried with MgSO₄, filtered and evaporated to dryness. The crude material was then used directly for the subsequent amide coupling. Using the crude amine in the General Procedure C procedure using 2-phenyl-1-(pyridin-2-yl)ethan-1-amine (1.900 g, 4.79 mmol) as the amine afforded 930 mg (40 % yield) of **DG9-SM** as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.62 (d, *J* = 4.8 Hz, 1H), 7.58 (td, *J* = 7.6, 1.8 Hz, 1H), 7.24 (dt, *J* = 16.7, 5.6 Hz, 4H), 7.14–7.03 (m, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 5.88 (ddt, *J* = 16.8, 10.3, 6.2 Hz, 1H), 5.42 (td, *J* = 7.9, 5.8 Hz, 1H), 5.13 (d, *J* = 17.1 Hz, 1H), 5.06 (d, *J* = 10.3 Hz, 1H), 3.35 (dd, *J* = 13.3, 5.9 Hz, 1H), 3.17 (dd, *J* = 13.3, 8.0 Hz, 1H), 2.55–2.34 (m, 4H).. ¹³C NMR (126 MHz, CDCl₃) δ 171.69, 158.95, 149.14, 137.34, 137.16, 136.41, 129.64, 128.27, 126.55, 122.96, 122.60, 115.55, 55.38, 42.63, 36.05, 29.68. HRMS calcd. for C₁₈H₂₁N₂O⁺ [M+H]⁺: 281.1684, Found: 281.1684.

N-(2,2-dimethyl-1-(pyridin-2-yl)propyl)pent-4-enamide (DG10-SM): The title compound was prepared according to the General Procedure C using 2,2-dimethyl-1-(pyridin-2-yl)propan-1-amine (185mg, 1 mmol) as the amine to afford 37 mg (81% yield) of **DG10-SM** as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 8.57–8.48 (m, 1H), 7.59 (td, *J* = 7.7, 1.8 Hz, 1H), 7.17 (dd, *J* = 7.7, 4.2 Hz, 2H), 6.95 (d, *J* = 9.3 Hz, 1H), 5.80 (ddd, *J* = 16.9, 10.4, 6.3 Hz, 1H), 5.10–5.00 (m, 1H), 4.96 (dt, *J* = 10.3, 1.6 Hz, 1H), 4.92 (d, *J* = 9.3 Hz, 1H), 2.53–2.23 (m, 4H), 0.90 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 171.93, 158.56, 148.60, 137.26, 135.79, 124.46, 122.32, 115.53, 60.84, 36.38, 36.25, 29.90, 26.83. HRMS calcd. for C₁₅H₂₃N₂O⁺ [M+H]⁺: 247.1805, Found: 247.1850.

3-ethyl-1-(1-(pyridin-2-yl)ethyl)pyrrolidine-2,5-dione (DG7-P): The title compound was synthesized according to General Procedure B of **DG7-SM** (20 mg) with a reaction time of 24 h to afford 19 mg (82% yield; 5:1 d.r.) of **DG7-P** as a colorless oil. The two diastereomers could be separated analytically by SFC but could not be separated on a preparative scale. The two diastereomers are reported as mixture. ¹H NMR (600 MHz, CDCl₃) δ 8.52 (d, *J* = 4.9 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.18 (dd, *J* = 7.5, 5.0 Hz, 1H), 5.47 (q, *J* = 7.3 Hz, 1H), 2.93–2.74 (m, 2H), 2.49–2.35 (m, 1H), 1.97–1.84 (m, 1H), 1.82 (d, *J* = 7.4 Hz, 3H), 1.71–1.56 (m, 1H), 0.98 (m, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 179.82, 176.65, 158.16, 148.98, 148.93, 136.84, 136.80, 122.38, 120.95, 50.90, 50.81, 40.98, 40.96, 33.86, 33.80, 24.41, 24.35, 15.97, 15.94, 10.78, 10.73. HRMS calcd. for C₁₃H₁₇N₂O₂⁺ [M+H]⁺: 233.1285, Found: 233.1287.

3-ethyl-1-(2-methyl-1-(pyridin-2-yl)propyl)pyrrolidine-2,5-dione (DG8-P): The title compound was synthesized according to General Procedure B with 23 mg of **DG8-SM** and run for 24 h to afford 17 mg (73% yield; 5:1 d.r.) of **DG8-P** as a colorless oil. The two diastereomers could be separated analytically by LCMS, but could not be separated on a preparative scale. The two diastereomers are reported as mixture. ¹H NMR (600 MHz, CDCl₃) δ 8.55 (dt, *J* = 4.9, 1.3 Hz, 1H), 7.65 (td, *J* = 7.6, 1.8 Hz, 1H), 7.63–7.58 (m, 1H), 7.17 (ddd, *J* = 7.4, 4.9, 1.3 Hz, 1H), 4.92 (dd, *J* = 11.5, 1.7 Hz, 1H), 3.16 (dp, *J* = 11.4, 6.6 Hz, 1H), 2.82–2.62 (m, 2H), 2.40–2.29 (m, 1H), 1.86 (dddd, *J* = 21.4, 14.0, 7.3, 3.4 Hz, 1H), 1.63–1.52 (m, 1H), 0.94 (d, *J* = 6.7 Hz, 4H), 0.89 (t, *J* = 7.3 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 180.04, 179.99, 176.80, 176.77, 157.88, 157.84,

149.41, 149.39, 136.57, 136.54, 123.47, 122.86, 64.35, 40.85, 40.81, 33.70, 33.57, 26.96, 26.95, 24.59, 24.45, 20.65, 19.96, 19.92, 10.98, 10.65. **HRMS** calcd. for $C_{15}H_{21}N_2O_2^+$ $[M+H]^+$: 261.1598, Found: 261.1598.

3-ethyl-1-(2-phenyl-1-(pyridin-2-yl)ethyl)pyrrolidine-2,5-dione (DG9-P):

The title compound was synthesized according to General Procedure B with 28 mg of **DG9-SM** and run for 24 h to afford 17 mg (56% yield; 5:1 d.r.) of **DG9-P** as a colorless oil. The two diastereomers could be separated analytically by LCMS, but could not be separated on a preparative scale. The two diastereomers are reported as mixture. The assignments for major and minor are made when chemical shift distinct peaks are present. **1H NMR** (500 MHz, d_6 -DMSO) δ 8.54 (ddd, J = 4.8, 1.9, 1.0 Hz, 1H), 7.80 (td, J = 7.7, 1.9 Hz, 1H), 7.47 (ddq, J = 8.0, 2.3, 1.0 Hz, 1H), 7.32 (ddt, J = 7.5, 4.8, 0.9 Hz, 1H), 7.30–7.24 (m, 2H), 7.20 (td, J = 6.0, 5.5, 2.8 Hz, 3H), 5.51 (td, J = 11.6, 11.2, 5.2 Hz, 1H), 3.74–3.60 (m, 1H), 3.54 (ddd, J = 13.6, 11.6, 5.6 Hz, 1H), 2.85–2.60 (m, 2H), [major 2.24 (dd, J = 17.5, 3.7 Hz, 1H), minor 2.17 (dd, J = 18.2, 4.5 Hz, 1H)], [minor 1.60 (ddd, J = 13.6, 7.4, 5.1 Hz, 1H), major 1.47–1.35 (m, 1H), minor 1.34–1.28 (m, 1H), major 1.24–1.09 (m, 1H)], [minor 0.79 (t, J = 7.4 Hz, 1H), major 0.60 (t, J = 7.4 Hz, 3H)]. **^{13}C NMR** (126 MHz, d_6 -DMSO) δ 179.57, 176.66, 157.25, 148.74, 137.87, 136.79, 136.77, 128.93, 128.91, 128.88, 128.32, 128.30, 128.24, 126.43, 122.52, 121.03, 120.99, 56.16, 34.59, 32.82, 23.37, 9.99. **HRMS** calcd. for $C_{19}H_{21}N_2O_2^+$ $[M+H]^+$: 309.1598, Found: 309.1598.

1-(2,2-dimethyl-1-(pyridin-2-yl)propyl)-3-ethylpyrrolidine-2,5-dione (DG10-P):

The title compound was synthesized according to General Procedure B with 13.6 mg of **DG10-SM**, 19.5 mg of $W(CO)_6$ in 0.6 mL of toluene and run for 24 h to afford 6 mg (40% yield; 2:1 d.r.) of **DG10-P** in as a colorless oil. The two diastereomers could be separated analytically by LCMS, but could not be separated on a preparative scale. **1H NMR** (600 MHz, $CDCl_3$) δ 8.54 (ddd, J = 4.9, 1.9, 1.0 Hz, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.63 (ddd, J = 7.8, 6.7, 2.0 Hz, 1H), 7.17 (ddd, J = 7.5, 4.9, 1.2 Hz, 1H), 5.36 (d, J = 2.3 Hz, 1H), 2.87–2.67 (m, 2H), 2.48–2.34 (m, 1H), 1.90 (ddd, J = 19.0, 9.5, 4.6 Hz, 1H), 1.14 (s, 10H), 0.95 (dt, J = 15.3, 7.4 Hz, 3H). one sp^3 proton is chemical shift equivalent with water and cannot be seen. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 180.60, 177.42, 157.28, 148.75, 136.13, 124.75, 122.59, 66.66, 40.99, 36.07, 33.82, 33.73, 28.83, 24.67, 10.96, 10.83. **HRMS** calcd. for $C_{16}H_{23}N_2O_2^+$ $[M+H]^+$: 275.1754, Found: 275.1755.

Starting Material Synthesis (All yields unoptimized)

General amide coupling procedures

The starting materials below can be prepared directly via amide coupling of the commercial acid with 2-picolyl amine ($PicNH_2$) via General Procedure D or from reaction between with 2-picolyl amine ($PicNH_2$) and the corresponding commercial alcohol via General Procedure D. In some cases, the carboxylic acids were previously synthesized at The Scripps Research Institute and donated for this project. Their preparation and characterization have previously been published (44-45).

HATU-Mediated Amide Coupling (General Procedure D)

In a 50-mL round bottomed flask with Teflon coated magnetic stir bar, carboxylic acid (1.0 equiv), DCM (0.5 M), pyridine (3.0 equiv) were added in that order. HATU (1.2 equiv) was added slowly and after complete addition, PicNH₂ (1.0 equiv) was added dropwise by syringe. The reaction was allowed to stir for 24 h, at which point it was diluted with DCM (30 mL for 10 mmol scale) and quenched with a saturated solution of aq. NaHCO₃ (30 mL). The aqueous layer was extracted with DCM (×3), and the organic layers were combined, washed with water nad brine, dried over MgSO₄, filtered, and evaporated to dryness. The crude material was purified by flash silica chromatography using 55% acetone:hexanes to elute the product. Tetramethyl urea commonly co-eluted with the product and could be removed under vacuum (1 mTorr at 50 °C).

Ru-Catalyzed Amide Coupling (General Procedure E)

In an argon-filled glovebox, a 25-mL round-bottomed flask was charged with Ru-MACHO (0.015 equiv) and KH (0.1 equiv), and the solids were suspended in toluene [2 M]. Next, PicNH₂ (1 equiv) and alkenyl alcohol (1.2 equiv) were added in that order. A reflux condenser was attached, and the glassware was sealed inside the glovebox and removed. A steady flow of nitrogen was attached, and the reaction was run under reflux for 18 h. The reaction mixture was allowed to cool to room temperature and was then loaded directly onto a silica column and purified by flash silica chromatography using 55% acetone:hexanes to elute the product.

N-(pyridin-2-ylmethyl)pent-4-enamide (1a): The title compound was prepared according to General Procedure D using 4-pentenoic acid (10 mmol) as the carboxylic acid to afford 1.205 g (63% yield) of **1a** as a pale-yellow oil. ¹H NMR (600 MHz, d₆-DMSO) δ 8.55–8.48 (m, 1H), 8.43 (t, *J* = 6.1 Hz, 1H), 7.75 (td, *J* = 7.7, 1.9 Hz, 1H), 7.36–7.13 (m, 1H), 6.00–5.70 (m, 1H), 5.05 (dq, *J* = 17.1, 1.6 Hz, 1H), 4.97 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 4.35 (d, *J* = 6.0 Hz, 2H), 2.36–2.20 (m, 4H). ¹³C NMR (151 MHz, d₆-DMSO) δ 171.62, 158.78, 148.78, 137.74, 136.66, 122.03, 120.91, 115.07, 44.13, 34.44, 29.24. HRMS calcd. for C₁₁H₁₅N₂O⁺ [M+H]⁺: 191.1179, Found: 191.1180.

2-methyl-N-(pyridin-2-ylmethyl)pent-4-enamide (1b): The title compound was prepared according to General Procedure D using 2-methyl-4-pentenoic acid (10 mmol) as the carboxylic acid to afford 1.370 g (67% yield) of **1b** as a yellow oil. ¹H NMR (600 MHz, CDCl₃) δ 8.58–8.48 (m, 1H), 7.66 (td, *J* = 7.7, 1.8 Hz, 1H), 7.27–7.24 (m, 1H), 7.20 (dd, *J* = 7.5, 4.9 Hz, 1H), 6.74 (s, 1H), 5.82–5.68 (m, 1H), 5.06 (dq, *J* = 17.0, 1.6 Hz, 1H), 5.00 (dd, *J* = 10.3, 1.9 Hz, 1H), 4.56 (d, *J* = 4.9 Hz, 2H), 2.51–2.34 (m, 2H), 2.19 (dt, *J* = 13.6, 6.9 Hz, 1H), 1.20 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 175.94, 156.62, 149.11, 136.90, 136.04, 122.48, 122.31,

116.93, 44.47, 41.30, 38.54, 17.46. **HRMS** calcd. for $C_{12}H_{17}N_2O^+$ $[M+H]^+$: 205.1335, Found: 205.1336.

2-benzyl-N-(pyridin-2-ylmethyl)pent-4-enamide (1c): The title compound was prepared according to General Procedure D using 2-benzyl-4-pentenoic acid (10 mmol) as the carboxylic acid to afford 1.270 g (45% yield) of **1c** as a yellow oil. **1H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, J = 5.1 Hz, 1H), 7.66–7.50 (m, 1H), 7.24–7.09 (m, 1H), 7.03 (d, J = 7.9 Hz, 1H), 6.37 (s, 1H), 5.84–5.69 (m, 1H), 5.12–5.04 (m, 1H), 5.04–4.98 (m, 1H), 4.52–4.38 (m, 2H), 2.96 (dd, J = 13.6, 8.3 Hz, 1H), 2.77 (d, J = 5.2 Hz, 1H), 2.55–2.42 (m, 2H), 2.29 (q, J = 8.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.51, 156.78, 148.64, 139.78, 137.19, 135.73, 129.12, 128.51, 126.36, 122.44, 122.33, 117.19, 49.74, 44.32, 38.67, 36.92. **HRMS** calcd. $C_{18}H_{21}N_2O^+$ for $[M+H]^+$: 281.1648, Found: 281.1648.

2,2-dimethyl-N-(pyridin-2-ylmethyl)pent-4-enamide (1d): The title compound was prepared according to General Procedure D using 2,2-dimethyl-4-pentenoic acid (10 mmol) as the carboxylic acid to afford 0.935 g (43 % yield) of **1d** as a yellow oil. **1H NMR** (600 MHz, $CDCl_3$) δ 8.54 (dt, J = 5.0, 1.3 Hz, 1H), 7.66 (td, J = 7.7, 1.8 Hz, 1H), 7.25 (s, 1H), 7.23–7.17 (m, 1H), 7.00 (s, 1H), 5.74 (ddt, J = 17.4, 10.1, 7.4 Hz, 1H), 5.09–4.99 (m, 2H), 4.54 (d, J = 4.8 Hz, 2H), 2.32 (dt, J = 7.3, 1.2 Hz, 2H), 1.23 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.52, 156.73, 149.14, 136.84, 134.58, 122.42, 122.29, 118.02, 45.37, 44.60, 41.64, 25.23. **HRMS** calcd. $C_{13}H_{19}N_2O^+$ for $[M+H]^+$: 219.1492, Found: 219.1493.

tert-butyl (R)-(1-oxo-1-((pyridin-2-ylmethyl)amino)pent-4-en-2-yl)carbamate (1e): The title compound was prepared according to General Procedure D using (*S*)-*N*-Boc-allylglycine or (*R*)-*N*-Boc-allylglycine (10 mmol) as the carboxylic acid to afford 1.440 g (47 % yield) of **1e** as a yellow oil. Analytical data was identical for both enantiomers. **1H NMR** (600 MHz, $CDCl_3$) δ 8.55–8.50 (m, 1H), 7.72–7.68 (m, 1H), 7.35 (s, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.25–7.21 (m, 1H), 5.75 (tt, J = 17.0, 8.2 Hz, 1H), 5.24–5.00 (m, 3H), 4.58 (d, J = 5.3 Hz, 2H), 4.25 (s, 1H), 2.71–2.39 (m, 2H), 1.44 (s, J = 12.1 Hz, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.39, 156.39, 155.74, 145.68, 140.72, 132.93, 123.74, 119.51, 80.99, 54.46, 43.17, 36.55, 28.41. One sp^2 carbon could not be found likely due to chemical shift equivalence. **HRMS** calcd. for $C_{16}H_{24}N_3O_3^+$ $[M+H]^+$: 306.1810, Found: 306.1810.

4-methyl-N-(pyridin-2-ylmethyl)pent-4-enamide (1f): The title compound was prepared according to General Procedure E using 4-methyl-4-penten-1-ol (4.8 mmol) as the alcohol. The crude material was purified by flash silica chromatography 60% acetone:hexanes to afford 780 mg (96% yield) of **1f** as a yellowish oil. **1H NMR** (600 MHz, $CDCl_3$) δ 8.61–8.42 (m, 1H), 7.67 (dq, J = 7.7, 1.8 Hz, 1H), 7.27 (d, J = 9.2 Hz, 1H), 7.21 (t, J = 6.6 Hz, 1H), 6.79 (s, 1H), 4.73 (d, J = 17.6 Hz, 2H), 4.57 (d, J = 4.9 Hz, 2H), 2.50–2.30 (m, 4H), 1.74 (d,

$J = 13.3$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 172.61, 156.30, 148.85, 148.81, 144.49, 136.99, 122.45, 122.30, 110.47, 44.36, 34.83, 33.30, 22.53. HRMS calcd. for $\text{C}_{12}\text{H}_{17}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 205.1335, Found: 205.1337.

***N*-(pyridin-2-ylmethyl)hex-5-enamide (1ga):** The title compound was prepared according to General Procedure D using 5-hexenoic acid (10 mmol) as the carboxylic acid to afford 1.525 g (74% yield) of **1ga** as a yellowish oil. ^1H NMR (600 MHz, CDCl_3) δ 8.52–8.41 (m, 1H), 7.60 (tt, $J = 9.5$, 7.7, 3.4 Hz, 1H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.19–7.10 (m, 1H), 6.95 (d, $J = 34.3$ Hz, 1H), 5.72 (ddt, $J = 23.5$, 9.8, 6.4 Hz, 1H), 5.13–4.79 (m, 2H), 4.50 (dt, $J = 19.4$, 4.7 Hz, 2H), 2.23 (dt, $J = 15.0$, 7.6 Hz, 2H), 2.05 (dq, $J = 14.3$, 7.3 Hz, 2H), 1.72 (h, $J = 7.3$ Hz, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 173.11, 156.69, 149.08, 137.93, 136.84, 122.38, 122.13, 115.29, 44.45, 35.78, 33.19, 24.77. HRMS calcd. for $\text{C}_{12}\text{H}_{17}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 205.1335, Found: 205.1335.

(*Z*)-*N*-(pyridin-2-ylmethyl)hex-4-enamide (1gb): The title compound was prepared according to General Procedure E using *cis*-4-hexen-1-ol (4.8 mmol) as the alcohol. The crude material was purified by flash silica chromatography 60% acetone:hexanes to afford 755 mg (92% yield) **1gb** as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 8.54 (ddd, $J = 5.0$, 1.8, 0.9 Hz, 1H), 7.73 (ddt, $J = 9.5$, 5.8, 2.9 Hz, 1H), 7.36–7.31 (m, 1H), 7.28–7.25 (m, 1H), 6.99 (s, 1H), 5.49 (dqt, $J = 10.8$, 6.8, 1.5 Hz, 1H), 5.38 (dtdd, $J = 8.9$, 7.2, 3.5, 1.7 Hz, 1H), 4.59 (d, $J = 5.1$ Hz, 2H), 2.42 (ddddd, $J = 8.1$, 7.2, 6.4, 1.7, 0.9 Hz, 2H), 2.36–2.30 (m, 2H), 1.61 (ddt, $J = 6.8$, 1.8, 0.9 Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 172.87, 156.31, 148.19, 138.25, 128.76, 125.55, 122.90, 122.81, 44.18, 36.43, 23.20, 12.95. HRMS calcd. for $\text{C}_{12}\text{H}_{17}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 205.1335, Found: 205.1335.

(*Z*)-*N*-(pyridin-2-ylmethyl)hex-4-enamide-*d*3 (1gb-*d*3): The title compound was prepared according to General Procedure E using *cis*-4-hexen-1-ol-*d*3 (9.6 mmol) as the alcohol. The deuterium-labeled alcohol was prepared in a single step according to a known procedure (46). The purity of the alcohol is critical for obtaining high yield, as impurities can lead to reduced yields in the subsequent Ru-MACHO step. The crude material was purified by flash silica chromatography 60% acetone:hexanes to afford 495 mg (25% yield) **1gb-*d*3** as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 8.53 (d, $J = 5.0$ Hz, 1H), 7.68 (tt, $J = 7.6$, 1.6 Hz, 1H), 7.28 (d, $J = 7.8$ Hz, 1H), 7.24–7.18 (m, 1H), 6.80 (s, 1H), 5.48 (d, $J = 11.0$ Hz, 1H), 5.38 (dt, $J = 10.7$, 7.1 Hz, 1H), 4.57 (d, $J = 5.0$ Hz, 2H), 2.42 (q, $J = 7.3$ Hz, 2H), 2.33 (t, $J = 7.5$ Hz, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 172.82 (d, $J = 3.9$ Hz), 156.46 (d, $J = 2.6$ Hz), 148.60 (d, $J = 5.2$ Hz), 137.22 (d, $J = 4.4$ Hz), 128.69, 125.33, 122.51, 122.43, 44.34, 36.30, 36.29, 23.11. HRMS calcd. for $\text{C}_{12}\text{H}_{14}\text{D}_3\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 208.1524, Found: 208.1524.

***N*-(pyridin-2-ylmethyl)dec-9-enamide (1ha):** The title compound was prepared according to General Procedure D using 9-decenoic acid (10 mmol) as the carboxylic acid to afford 1.553 g (60% yield) of **1ha** as a pale-yellow oil. ^1H NMR (600 MHz, d_6 -DMSO) δ 8.49 (dt, $J = 4.4$, 1.7 Hz, 1H), 8.38 (t, $J = 6.0$ Hz, 1H), 7.75 (td, $J = 7.7$, 1.8 Hz, 1H), 7.26 (dd, $J = 7.6$, 4.4 Hz, 2H), 5.80 (ddt, $J = 17.0$, 10.2, 6.7 Hz, 1H), 5.10–

4.87 (m, 2H), 4.34 (d, $J = 6.0$ Hz, 2H), 2.17 (t, $J = 7.4$ Hz, 2H), 2.02 (tdd, $J = 8.0, 6.0, 1.5$ Hz, 2H), 1.53 (p, $J = 7.2$ Hz, 2H), 1.34 (p, $J = 7.0$ Hz, 2H), 1.26 (h, $J = 6.0, 5.0$ Hz, 8H). ^{13}C NMR (151 MHz, d_6 -DMSO) δ 172.32, 158.89, 148.77, 138.82, 136.63, 122.00, 120.85, 114.65, 44.09, 35.28, 33.16, 28.62, 28.57, 28.41, 28.21, 25.24. HRMS calcd. for $\text{C}_{16}\text{H}_{25}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 261.1961, Found: 261.1961.

(Z)-N-(pyridin-2-ylmethyl)dec-4-enamide (1hb): The title compound was prepared according to General Procedure E using *cis*-4-decen-1-ol (4.8 mmol) as the alcohol. The crude material was purified by flash silica chromatography 60% acetone:hexanes to afford 900 mg (86% yield) of **1hb** as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 8.54 (d, $J = 4.9$ Hz, 1H), 7.70 (td, $J = 7.7, 1.8$ Hz, 1H), 7.30 (d, $J = 7.8$ Hz, 1H), 7.23 (dd, $J = 7.4, 5.0$ Hz, 1H), 6.81 (s, 1H), 5.52–5.25 (m, 2H), 4.57 (d, $J = 5.0$ Hz, 2H), 2.45–2.28 (m, 4H), 2.03 (q, $J = 7.3$ Hz, 2H), 1.38–1.21 (m, 6H), 0.87 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 172.82, 156.41, 148.62, 137.46, 131.78, 127.74, 122.68, 122.66, 44.36, 36.71, 31.64, 29.46, 27.34, 23.59, 22.71, 14.20. HRMS calcd. for $\text{C}_{16}\text{H}_{25}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 261.1961, Found: 261.1962.

(Z)-9-chloro-N-(pyridin-2-ylmethyl)non-4-enamide (1i): The title compound was prepared via a 2-step sequence consisting of a Wittig reaction followed by amide coupling.

Step 1) Phosphonium salt (4.3 g, 10 mmol, 1 equiv) was suspended in THF (10 mL) and cooled to 0 °C. A solution of KHMDS in THF (20.5 mL, 1 M, 2.05 equiv) was added dropwise. The mixture was stirred for 1 h until an orange suspension formed. The mixture was then further cooled to –78 °C, and 5-chloropentanal (1.21 g, 10 mmol, 1 equiv) was added over 20 min. After addition was complete, the reaction was gradually warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure. The residue was dissolved in water and washed with diethyl ether ($\times 2$). The orange organic layer was discarded, while the aqueous layer was acidified with 2 M HCl until pH = 1. The aqueous layer was extracted with ethyl acetate ($\times 3$), and the combined organic layers were dried over anhydrous MgSO_4 . The solvent was removed in vacuo, and the resulting crude product was carried on to the next step without further purification (~58% yield).

Step 2) In a 50-mL round-bottomed flask with Teflon-coated magnetic stir bar, the crude acid was dissolved in DCM (6 mL), then DMAP (70 mg, 0.57 mmol, 0.1 equiv), HoBt (971 mg, 6.1 mmol, 1.1 equiv), and EDC (1.21 g, 6.1 mmol, 1.1 equiv) were added. 2-Picolyl amine (623 mg, 5.8 mmol, 1 equiv) was added dropwise by syringe and the reaction mixture was allowed to stir for 24 h, at which point it was diluted with DCM (3 mL) and quenched with a saturated solution of aq. NaHCO_3 (3 mL). The aqueous layer was extracted with DCM ($\times 3$), and the organic layers were combined, washed with water and brine, dried with MgSO_4 , filtered, and evaporated to dryness. The crude material was purified by flash silica chromatography using 55% acetone:hexanes to afford 976 mg (60% yield) of **1i** as a white solid. The product was obtained as an *E/Z* mixture and directly used for the catalytic reaction. The data listed below corresponds to the major (*Z*) isomer of the alkene. ^1H NMR (600 MHz, CDCl_3) δ 8.54 (ddd, $J = 5.0, 1.8, 1.0$ Hz, 1H), 7.70 (td, $J = 9.2, 8.3, 2.6$ Hz, 1H), 7.32–7.27 (m, 1H), 7.25–7.20 (m, 1H), 6.82 (s, 1H), 5.48–

5.34 (m, 2H), 4.57 (d, $J = 5.0$ Hz, 2H), 3.54–3.45 (m, 2H), 2.45–2.38 (m, 2H), 2.38–2.29 (m, 2H), 2.08 (td, $J = 7.5, 5.8$ Hz, 2H), 2.05–1.93 (m, 3H), 1.84–1.66 (m, 2H), 1.48 (dq, $J = 9.8, 7.5$ Hz, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 172.16, 156.34, 148.70, 137.68, 130.72, 128.57, 122.68, 122.62, 45.13, 44.37, 36.58, 32.26, 26.95, 26.55, 23.59. HRMS calcd. for $\text{C}_{15}\text{H}_{22}\text{ClN}_2\text{O}^+ [\text{M}+\text{H}]^+$: 281.1415, Found: 281.1415.

(Z)-7,11-dimethyl-N-(pyridin-2-ylmethyl)dodeca-4,10-dienamide (1j): The title compound was prepared via a 2-step sequence consisting of a Wittig reaction followed by amide coupling.

Step 1) Phosphonium salt (4.3 g, 10 mmol, 1 equiv) was suspended in THF (10 mL) and cooled to 0 °C. A solution of KHMDS in THF (20.5 mL, 1 M, 2.05 equiv) was added dropwise. The mixture was stirred for 1 h until an orange suspension formed. The mixture was then further cooled to –78 °C, and (±)-citronellal (1.543 g, 10 mmol, 1 equiv) was added over 20 min. After addition was complete, the reaction was gradually warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure. The residue was dissolved in water and washed with diethyl ether (×2). The orange organic layer was discarded, while the aqueous layer was acidified with 2 M HCl until pH = 1. The aqueous layer was extracted with ethyl acetate (×3), and the combined organic layers were dried over anhydrous MgSO_4 . The solvent was removed in vacuo, and the resulting crude product was carried on to the next step without further purification (~35% yield).

Step 2) In a 50-mL round-bottomed flask with Teflon-coated magnetic stir bar, the crude acid was dissolved in DCM (4 mL), and DMAP (32 mg, 0.27 mmol, 0.1 equiv), HoBt (450 mg, 2.9 mmol, 1.1 equiv), and EDC (564 mg, 2.9 mmol, 1.1 equiv) were added. 2-Picoyl amine (289 mg, 5.8 mmol, 1 equiv) was added dropwise by syringe, and the reaction mixture was allowed to stir for 24 h, at which point it was diluted with DCM (3 mL) and quenched with a saturated solution of aq. NaHCO_3 (3 mL). The aqueous layer was extracted with DCM (×3), and the organic layers were combined, washed with water and brine, dried over MgSO_4 , filtered, and evaporated to dryness. The crude material was purified by flash silica chromatography using 55% acetone:hexanes to afford 655 mg (78% yield) of **1j** as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 8.54 (dt, $J = 4.8, 1.4$ Hz, 1H), 7.70 (td, $J = 7.7, 1.8$ Hz, 1H), 7.30 (d, $J = 7.9$ Hz, 1H), 7.25–7.20 (m, 1H), 6.79 (s, 1H), 5.44–5.38 (m, 2H), 5.08 (tdd, $J = 7.2, 3.0, 1.6$ Hz, 1H), 4.58 (d, $J = 5.0$ Hz, 2H), 2.56–2.27 (m, 4H), 1.96 (dtd, $J = 41.7, 14.2, 7.5$ Hz, 4H), 1.67 (d, $J = 1.5$ Hz, 3H), 1.59 (s, 3H), 1.51–1.07 (m, 3H), 0.90–0.79 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.77, 137.46, 131.27, 130.24, 128.59, 124.99, 122.68, 122.60, 36.87, 36.65, 34.59, 33.09, 25.86, 25.81, 23.70, 19.59, 17.80. HRMS calcd. for $\text{C}_{20}\text{H}_{31}\text{N}_2\text{O}^+ [\text{M}+\text{H}]^+$: 315.2431, Found: 315.2432

(Z)-4-(bicyclo[2.2.1]heptan-2-ylidene)-N-(pyridin-2-ylmethyl)butanamide (1k): The title compound was prepared according to General Procedure D using (Z)-4-(bicyclo[2.2.1]heptan-2-ylidene)butanoic acid (**44**) (0.44 mmol) as the carboxylic acid to afford 98 mg (82% yield) of **1k** as a yellow solid. ^1H NMR (600 MHz, CDCl_3) δ 8.59–8.47 (m, 1H), 7.65 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.28–7.25 (m, 1H), 7.20 (ddd, $J = 7.7, 4.9, 1.2$ Hz, 1H), 6.72 (s, 1H), [mixture of *E/Z* vinyl protons, total of 1H, 5.17

(tt, $J = 6.3, 2.7$ Hz) and 4.98 (t, $J = 7.4$ Hz) 1H], 4.56 (t, $J = 5.2$ Hz, 2H), [mixture of *E/Z* allyl protons, total of 1H, 2.98–2.89 (m), 2.61–2.55 (m) 1H], 2.47–2.36 (m, 1H), 2.36–2.21 (m, 4H), 2.16–2.05 (m, 1H), 1.81 (dd, $J = 15.6, 5.4$ Hz, 1H), 1.63–1.48 (m, 2H), 1.32–1.11 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) (Carbon peaks listed below correspond to a mixture of *E* and *Z* isomers.) δ 173.05, 156.65, 149.10, 147.98, 147.18, 136.94, 122.49, 122.31, 115.91, 115.16, 45.43, 44.59, 40.28, 39.23, 39.21, 38.98, 37.33, 36.74, 36.60, 36.36, 35.85, 29.99, 29.50, 28.72, 28.51, 25.71, 25.10. **HRMS** calcd. for $\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}^+ [\text{M}+\text{H}]^+$: 271.1805, Found: 271.1804.

4-cyclohexylidene-*N*-(pyridin-2-ylmethyl)butanamide (1l):

The title compound was prepared according to General Procedure D using 4-cyclohexylidenebutanoic acid (**44**) (0.45 mmol) as the carboxylic acid to afford 90 mg (78% yield) of **1l** as a yellow oil.

^1H NMR (600 MHz, CDCl_3) δ 8.54 (ddd, $J = 5.0, 1.9, 1.0$ Hz, 1H), 7.67 (td, $J = 7.7, 1.8$ Hz, 1H), 7.29–7.26 (m, 1H), 7.21 (dddd, $J = 6.9, 4.5, 1.2, 0.6$ Hz, 1H), 6.73 (s, 1H), 5.07 (ddt, $J = 8.5, 7.2, 1.2$ Hz, 1H), 4.56 (d, $J = 5.0$ Hz, 2H), 2.42–2.34 (m, 2H), 2.30 (ddd, $J = 8.2, 6.7, 1.3$ Hz, 2H), 2.15–2.10 (m, 2H), 2.08–2.01 (m, 2H), 1.49 (dpd, $J = 17.6, 5.6, 5.0, 2.6$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 172.98, 156.62, 149.01, 141.51, 137.06, 122.54, 122.40, 119.48, 44.56, 37.25, 37.23, 28.83, 28.71, 27.94, 27.00, 23.54. **HRMS** calcd. for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{O}^+ [\text{M}+\text{H}]^+$: 259.1805, Found: 259.1804.

***tert*-butyl 4-(4-oxo-4-((pyridin-2-ylmethyl)amino)butylidene)piperidine-1-carboxylate (1m):**

The title compound was prepared according to General Procedure D using 4-(1-(*tert*-butoxycarbonyl)piperidin-4-ylidene)butanoic acid (**44**) (0.557 mmol) as the carboxylic acid to afford 127 mg (64% yield) of **1m** as a yellow solid.

^1H NMR (600 MHz, CDCl_3) δ 8.53 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 1H), 7.66 (td, $J = 7.7, 1.8$ Hz, 1H), 7.26 (m, 1H), 7.20 (dddt, $J = 7.4, 5.0, 1.3, 0.6$ Hz, 1H), 6.74 (s, 1H), 5.21 (t, $J = 7.2$ Hz, 1H), 4.55 (d, $J = 4.9$ Hz, 2H), 3.35 (t, $J = 5.9$ Hz, 4H), 2.40 (q, $J = 7.3$ Hz, 2H), 2.36–2.28 (m, 2H), 2.21 (s, 2H), 2.11 (d, $J = 6.2$ Hz, 2H), 1.46 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 172.58, 156.40, 154.93, 149.08, 137.01, 122.59, 122.38, 122.23, 81.58, 48.59, 44.53, 38.76, 36.90, 29.77, 23.47. **HRMS** calcd. for $\text{C}_{20}\text{H}_{30}\text{N}_3\text{O}_3^+ [\text{M}+\text{H}]^+$: 360.2282; Found: 360.2281.

(*Z*)-*N*-(pyridin-2-ylmethyl)-4-(1,4-dioxaspiro[4.5]decan-7-ylidene)butanamide (1n):

The title compound was prepared according to General Procedure D using 4-(1,4-dioxaspiro[4.5]decan-8-ylidene)butanoic acid (**44**) (0.883 mmol) as the carboxylic acid to afford 193 mg (69% yield) of **1n** as a white solid.

^1H NMR (600 MHz, CDCl_3) δ 8.57 (d, $J = 5.0$ Hz, 1H), 7.76 (td, $J = 7.7, 1.8$ Hz, 1H), 7.36 (d, $J = 7.8$ Hz, 1H), 7.29 (d, $J = 7.7$ Hz, 1H), 6.89 (s, 1H), 5.17 (t, $J = 7.3$ Hz, 1H), 4.61 (d, $J = 5.1$ Hz, 2H), 3.98 (s, 4H), 2.41 (q, $J = 7.4$ Hz, 2H), 2.32 (dt, $J = 18.2, 6.9$ Hz, 4H), 2.23 (t, $J = 6.5$ Hz, 2H), 1.66 (q, $J = 7.0$ Hz, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 172.88, 156.25, 148.25, 138.56, 137.90, 122.92, 122.83, 121.09, 109.09, 64.43, 44.16, 36.98, 36.30, 35.53, 33.63, 25.20, 23.80. **HRMS** calcd. for $\text{C}_{18}\text{H}_{25}\text{N}_2\text{O}_3^+ [\text{M}+\text{H}]^+$: 317.1860, Found: 317.1860.

3-methylene-*N*-(pyridin-2-ylmethyl)cyclobutane-1-carboxamide

(1o): The title compound was prepared according General Procedure D using 3-*exo* cyclobutene-1-carboxylic acid (5.35 mmol) as the carboxylic acid to afford 625 mg (74 % yield) of **1o** as a white solid. **¹H NMR** (600 MHz, CDCl₃) δ 8.60–8.50 (m, 1H), 7.78 (td, *J* = 7.7, 1.8 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.31 (dd, *J* = 7.5, 5.0 Hz, 1H), 6.95 (d, *J* = 18.8 Hz, 1H), 4.80 (p, *J* = 2.4 Hz, 2H), 4.62 (d, *J* = 5.2 Hz, 2H), 3.10–2.97 (m, 3H), 2.88 (ddt, *J* = 12.8, 8.5, 2.4 Hz, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ 174.74, 156.05, 147.68, 144.61, 138.52, 123.29, 123.05, 106.59, 43.93, 35.69, 34.90. **HRMS** calcd. for C₁₂H₁₅N₂O⁺ [M+H]⁺: 203.1179, Found: 203.1180.

butyl (*E*)-6-oxo-6-((pyridin-2-ylmethyl)amino)hex-2-enoate

(1p): The title compound was synthesized via cross-metathesis between compound **1a** and *n*-butyl acrylate. In an argon-filled glovebox, compound **1a** (250 mg, 1.3 mmol, 1 equiv), DCM (10 mL), Grubbs 2nd generation catalyst (55 mg, 0.065 mmol, 0.05 equiv) and butyl acrylate (1.32 mL, 9.1 mmol, 7 equiv) were added in that order to a 50-mL round-bottomed flask. A reflux condenser was attached inside the glovebox, and the system was sealed and removed from the glovebox. The flask was then attached to a steady flow of N₂ and placed in a preheated oil bath and brought to reflux for 16 h. The flask was removed, and the solvent was evaporated to dryness. The crude material was purified by flash silica chromatography 50% acetone:hexanes to afford 108 mg (28% yield, >10:1 *E/Z*) of **1p** as a colorless oil. The data below correspond to the *E* isomer: **¹H NMR** (600 MHz, CDCl₃) δ 8.52 (d, *J* = 5.0 Hz, 1H), 7.67 (td, *J* = 7.6, 1.7 Hz, 1H), 7.27 (s, 1H), 7.21 (dd, *J* = 7.5, 4.9 Hz, 1H), 6.97 (s, 1H), 6.94 (dt, *J* = 15.7, 6.8 Hz, 1H), 5.84 (d, *J* = 15.7 Hz, 1H), 4.55 (d, *J* = 4.9 Hz, 2H), 4.09 (t, *J* = 6.7 Hz, 2H), 2.64–2.52 (m, 2H), 2.42 (dd, *J* = 8.4, 6.6 Hz, 2H), 1.67–1.51 (m, 2H), 1.41–1.30 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 171.52, 166.63, 156.18, 148.78, 147.12, 137.26, 122.64, 122.48, 122.29, 64.26, 44.39, 34.60, 30.79, 27.95, 19.25, 13.82. **HRMS** calcd. for C₁₆H₂₃N₂O₃⁺ [M+H]⁺: 291.1703, Found: 291.1704.

(Z)-5-(4-bromophenyl)-*N*-(pyridin-2-ylmethyl)pent-4-enamide (1q): The title compound was prepared via a 2-step sequence consisting of a Wittig reaction followed by amide coupling.

Step 1) Phosphonium salt (0.50 g, 1.1 mmol, 1 equiv) was suspended in THF (1 mL) and cooled to 0 °C. A solution of KHMDS in THF (1.1 mL, 2 M, 2.05 equiv) was added dropwise. The mixture was stirred for 1 h until an orange suspension formed. The mixture was then further cooled to –78 °C, and 3-bromobenzaldehyde (215 mg, 1.1 mmol, 1 equiv) was added over 20 min. After addition was complete, the reaction was gradually warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure. The residue was dissolved in water and washed with diethyl ether (×2). The orange organic layer was discarded, while the aqueous layer was acidified with 2 M HCl until pH = 1. The aqueous layer was extracted with ethyl acetate (×3), and the combined organic layers were dried over anhydrous MgSO₄. The solvent was removed in vacuo, and the resulting crude product was carried on to the next step without further purification (~74% yield).

Step 2) In a 50 mL round bottomed flask with Teflon coated magnetic stir bar, the crude acid was dissolved in DCM (2 mL), then pyridine (0.22 mL, 2.7 mmol, 3 equiv) and HATU (386 mg, 1 mmol, 1.1 equiv) were added. 2-picoyl amine (71 mg, .9 mmol, 1 equiv) was added dropwise by syringe and the reaction was allowed to stir for 24 h then diluted with DCM (3 mL) and quenched with a saturated solution of aq. NaHCO₃ (3 mL). The aqueous layer was extracted with DCM (×3) and the organic layers combined, washed with water then brine, and then dried over MgSO₄, filtered and evaporated to dryness. The crude material was purified by flash silica chromatography using 55% acetone:hexanes to elute the product to afford 155 mg (70% yield) of **1q** as a brown oil. ¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, *J* = 4.9 Hz, 1H), 7.54 (td, *J* = 7.6, 1.7 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.23–7.13 (m, 1H), 7.09 (d, *J* = 8.1 Hz, 3H), 6.78 (s, 1H), 6.30 (d, *J* = 15.8 Hz, 1H), 6.14 (dt, *J* = 15.8, 6.7 Hz, 1H), 4.49 (d, *J* = 4.9 Hz, 2H), 2.51 (q, *J* = 7.1 Hz, 2H), 2.38 (t, *J* = 7.3 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 172.22, 156.36, 149.03, 136.96, 136.45, 131.65, 130.01, 129.80, 127.73, 122.53, 122.29, 120.86, 44.51, 36.17, 29.05. HRMS calcd. for C₁₇H₁₈BrN₂O⁺ [M+H]⁺: 345.0587, Found: 345.0587

(Z)-5-(4-iodophenyl)-N-(pyridin-2-ylmethyl)pent-4-enamide (1r): The title compound was prepared via a 2-step sequence consisting of a Wittig reaction followed by amide coupling.

Step 1) Phosphonium salt (2.0 g, 4.6 mmol, 1 equiv) was suspended in THF (5 mL) and cooled to 0 °C. A solution of KHMDS in THF (9.55 mL, 1 M, 2.05 equiv) was added dropwise. The mixture was stirred for 1 h until an orange suspension formed. The mixture was then further cooled to –78 °C, and 4-iodobenzaldehyde (1.21 g, 10 mmol, 1 equiv) was added over 20 min. After addition was complete, the reaction was gradually warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure. The residue was dissolved in water and washed with diethyl ether (×2). The orange organic layer was discarded, while the aqueous layer was acidified with 2 M HCl until pH = 1. The aqueous layer was extracted with ethyl acetate (×3), and the combined organic layers were dried over anhydrous MgSO₄. The solvent was removed in vacuo, and the resulting crude product was carried on to the next step without further purification (~68% yield).

Step 2) In a 50 mL round bottomed flask with Teflon coated magnetic stir bar, the crude acid was dissolved in DCM (4 mL), then DMAP (38 mg, 0.31 mmol, 0.1 equiv), HoBt (529 mg, 3.4 mmol, 1.1 equiv), and EDC (663 mg, 3.4 mmol, 1.1 equiv) were added. 2-picoyl amine (340 mg, 3.1 mmol, 1 equiv) was added dropwise by syringe and the reaction was allowed to stir for 24 h then diluted with DCM (3 mL) and quenched with a saturated solution of aq. NaHCO₃ (3 mL). The aqueous layer was extracted with DCM (×3). and the organic layers combined, washed with water then brine, and then dried over MgSO₄, filtered and evaporated to dryness. The crude material was purified by flash silica chromatography using 55% acetone:hexanes to elute the product to afford 700 mg (56% yield) of **1r** as a white solid. ¹H NMR (600 MHz, CDCl₃) δ 8.48 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.63 (td, *J* = 7.6, 1.8 Hz, 1H), 7.61–7.56 (m, 2H), 7.25 (t, *J* = 1.0 Hz, 1H), 7.19 (ddd, *J* = 7.7, 4.9, 1.1 Hz, 1H), 7.10–7.00 (m, 2H), 6.84 (s, 1H), 6.37–6.32 (m, 1H), 6.23 (dt, *J* = 15.8, 6.8 Hz, 1H), 4.57 (d, *J* = 5.0 Hz, 2H), 2.66–2.52 (m, 2H), 2.45 (dd, *J* = 8.0, 6.8 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 172.21, 156.30, 148.86, 137.64, 137.15, 137.06, 130.14, 129.95, 128.03, 122.60, 122.42, 92.26, 44.43, 36.17, 29.05. HRMS calcd. for C₁₇H₁₈IN₂O⁺ [M+H]⁺: 393.0458, Found: 393.0457.

(Z)-5-(2-cyanophenyl)-N-(pyridin-2-ylmethyl)pent-4-enamide (1s): The title compound was prepared via a 2-step sequence consisting of a Wittig reaction followed by amide coupling.

Step 1) Phosphonium salt (0.50 g, 1.1 mmol, 1 equiv) was suspended in THF (1 mL) and cooled to 0 °C. A solution of KHMDS in THF (1.1 mL, 2 M, 2.05 equiv) was added dropwise. The mixture was stirred for 1 h until an orange suspension formed. The mixture was then further cooled to -78 °C, and 2-cyanobenzaldehyde (152 mg, 1.1 mmol, 1 equiv) was added over 20 min. After addition was complete, the reaction was gradually warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure. The residue was dissolved in water and washed with diethyl ether (×2). The orange organic layer was discarded, while the aqueous layer was acidified with 2 M HCl until pH = 1. The aqueous layer was extracted with ethyl acetate (×3), and the combined organic layers were dried over anhydrous MgSO₄. The solvent was removed in vacuo, and the resulting crude product was carried on to the next step without further purification (~77% yield).

Step 2) In a 50 mL round bottomed flask with Teflon coated magnetic stir bar, the crude acid was dissolved in DCM (2 mL), then pyridine (0.19 mL, 2.3 mmol, 3 equiv) and HATU (332 mg, .875 mmol, 1.1 equiv) were added. 2-picoyl amine (86 mg, 0.8 mmol, 1 equiv) was added dropwise by syringe and the reaction was allowed to stir for 24 h then diluted with DCM (3 mL) and quenched with a saturated solution of aq. NaHCO₃ (3 mL). The aqueous layer was extracted with DCM x3 and the organic layers combined, washed with water then brine, and then dried with MgSO₄, filtered and evaporated to dryness. The crude material was purified by flash silica chromatography using 65% acetone:hexanes to elute the product to afford 110 mg (60% yield) of **1s** as a yellow oil. The product was obtained as a mixture of *E/Z* isomers. Only the *Z* isomer is reported below. ¹H NMR (600 MHz, CDCl₃) δ 8.65–8.42 (m, 1H), 7.68 (dtd, *J* = 11.7, 7.7, 1.8 Hz, 1H), 7.56–7.45 (m, 1H), 7.38–7.26 (m, 4H), 7.25–7.17 (m, 1H), 6.85 (s, 1H), 6.80 (d, *J* = 1.6 Hz, 1H), 6.50 (dt, *J* = 15.8, 6.9 Hz, 1H), 4.60 (dd, *J* = 18.3, 4.9 Hz, 2H), 2.84–2.62 (m, 2H), 2.57–2.41 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 171.94, 156.32, 149.14, 140.87, 136.94, 134.80, 133.01, 132.78, 127.35, 127.03, 125.75, 122.53, 122.30, 118.19, 110.74, 44.56, 35.86, 30.11. HRMS calcd. for C₁₈H₁₈N₃O⁺ [*M*+H]⁺: 292.1444, Found: 292.1442.

N-(pyridin-2-ylmethyl)cyclopent-3-ene-1-carboxamide (1t): The title compound was prepared according to General Procedure D using 3-cyclopentene-1-carboxylic acid (10 mmol) as the carboxylic acid to afford 1.589 g (78% yield) of **1t** as a white solid. ¹H NMR (600 MHz, CDCl₃) δ 8.51 (dd, *J* = 5.0, 1.6 Hz, 1H), 7.66 (tt, *J* = 7.7, 1.8 Hz, 1H), 7.31–7.23 (m, 1H), 7.23–7.15 (m, 1H), 6.88 (s, 1H), 5.82–5.49 (m, 2H), 4.55 (d, *J* = 5.1 Hz, 2H), 3.20–2.97 (m, 1H), 2.74–2.42 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 176.19, 156.67, 148.90, 137.11, 129.33, 122.51, 122.34, 122.33, 44.57, 43.54, 37.07. HRMS calcd. for C₁₂H₁₅N₂O⁺ [*M*+H]⁺: 203.1179, Found: 203.1178.

N-(pyridin-2-ylmethyl)cyclohex-3-ene-1-carboxamide (1u): The title compound was prepared according to General Procedure D using 3-cyclohexene-1-carboxylic acid (10 mmol) as the carboxylic acid to afford 1.265 g (58% yield) of **1u** as a white solid. ¹H NMR (600 MHz, CDCl₃) δ 8.50 (d, *J* = 4.9 Hz, 1H),

7.63 (td, $J = 7.7, 1.8$ Hz, 1H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.17 (dd, $J = 7.5, 4.9$ Hz, 1H), 6.93 (s, 1H), 5.68 (s, 2H), 4.54 (d, $J = 5.0$ Hz, 2H), 2.48–2.43 (dddd, $J = 11.7, 10.1, 5.5, 2.9$ Hz, 1H), 2.32–2.23 (m, 2H), 2.14–2.06 (m, 2H), 1.97–1.93 (ddt, $J = 12.6, 4.7, 2.5$ Hz, 1H), 1.77–1.69 (m, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 176.00, 156.64, 149.05, 136.86, 126.83, 125.53, 122.41, 122.17, 44.42, 41.32, 28.24, 25.84, 24.80. HRMS calcd. for $\text{C}_{13}\text{H}_{17}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 217.1335, Found: 217.1336.

trans-6-methyl-N-(pyridin-2-ylmethyl)cyclohex-3-ene-1-carboxamide (1v): The title compound was prepared according to General Procedure D using trans-6-methylcyclohex-3-ene-1-carboxylic acid (**45**) (1.66 mmol) to afford 186 mg (49% yield) of **1v** as a yellow solid. ^1H NMR (600 MHz, d_6 -DMSO) δ 8.52 (t, $J = 6.4$ Hz, 2H), 7.81 (t, $J = 7.9$ Hz, 1H), 7.48–7.11 (m, 2H), 5.86–5.45 (m, 2H), 4.39 (qd, $J = 15.9, 5.8$ Hz, 2H), 2.36–1.96 (m, 4H), 1.96–1.50 (m, 2H), 0.85 (dd, $J = 21.0, 6.6$ Hz, 3H). ^{13}C NMR (151 MHz, d_6 -DMSO) δ 174.87, 158.62, 148.32, 137.27, 126.17, 125.58, 122.23, 121.08, 47.15, 43.84, 33.11, 30.17, 29.07, 19.55. HRMS calcd. for $\text{C}_{14}\text{H}_{19}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$ 231.1492, Found: 231.1493.

4-methyl-N-(pyridin-2-ylmethyl)cyclohex-3-ene-1-carboxamide (1w): The title compound was prepared according to General Procedure D using 4-methylcyclohex-3-ene-1-carboxylic acid (10 mmol) as the carboxylic acid to afford 1.890 g (82% yield) of **1w** as a yellow solid. ^1H NMR (600 MHz, CDCl_3) δ 8.59–8.44 (m, 1H), 7.66 (td, $J = 7.7, 1.8$ Hz, 1H), 7.25 (s, 1H), 7.19 (dd, $J = 7.5, 4.9$ Hz, 1H), 6.83 (s, 1H), 5.49–5.32 (m, 1H), 4.57 (d, $J = 4.9$ Hz, 2H), 2.42 (dddd, $J = 11.9, 9.0, 5.8, 2.8$ Hz, 1H), 2.34–2.15 (m, 2H), 2.10–1.92 (m, 3H), 1.77 (dtd, $J = 12.3, 10.5, 10.0, 5.7$ Hz, 1H), 1.68–1.64 (m, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 176.11, 156.68, 149.15, 136.89, 134.11, 122.47, 122.26, 119.53, 44.48, 41.31, 29.65, 28.52, 26.27, 23.59. HRMS calcd. for $\text{C}_{14}\text{H}_{19}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$ 231.1492, Found: 231.1493.

N-(pyridin-2-ylmethyl)but-3-enamide (1xa): The title compound was previously prepared in our laboratory according to the published procedure (**43**). Analytical data are reproduced below for the reader's convenience. ^1H NMR (400 MHz, CDCl_3) δ 8.54 (d, $J = 4.1$ Hz, 1H), 7.66 (td, $J = 7.7, 1.8$ Hz, 1H), 7.35–7.11 (m, 3H), 6.87 (s, 2H), 6.12–5.90 (m, 1H), 5.43–5.12 (m, 3H), 4.56 (d, $J = 5.0$ Hz, 3H), 3.10 (d, $J = 7.1, 1.4$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 170.87, 156.49, 149.21, 137.03, 131.47, 122.61, 122.37, 119.90, 44.70, 41.77. HRMS calcd. for $\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 177.1022, Found: 177.1022.

N-(pyridin-2-ylmethyl)hept-6-enamide (1y): The title compound was prepared according to General Procedure D using 6-pentenoic acid (10 mmol) as the carboxylic acid to afford 1.436 g (66% yield) of **1y** as a pale-yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 8.29–8.13 (m, 1H), 7.49 (t, $J = 5.7$ Hz, 1H), 7.40 (td, $J = 7.7, 1.8$ Hz, 1H), 7.03 (dt, $J = 7.8, 1.0$ Hz, 1H), 6.93 (ddd, $J = 7.5, 4.9, 1.2$ Hz, 1H), 5.54 (ddt, $J = 16.9, 10.2, 6.7$ Hz, 1H), 4.75 (dq, $J = 17.1, 1.7$ Hz, 1H), 4.69 (ddt, $J = 10.2, 2.3, 1.2$ Hz, 1H), 4.28 (d, $J = 5.7$ Hz, 2H), 2.10–2.01 (m, 2H), 1.86–1.76 (m, 2H), 1.46–1.37 (m, 2H), 1.17 (tt, $J = 9.8, 6.5$ Hz, 2H). ^{13}C NMR (151

MHz, CDCl₃) δ 173.23, 157.01, 146.85, 138.12, 136.39, 121.77, 121.39, 114.09, 44.21, 35.75, 33.02, 28.05, 24.77. **HRMS** calcd. for C₁₃H₁₉N₂O⁺ [M+H]⁺: 219.1492, Found: 219.1492.

N-(pyridin-2-ylmethyl)oct-7-enamide (1z): The title compound was prepared according to General Procedure D using 7-octenoic acid (10 mmol) as the carboxylic acid to afford 1.890 g (81 % yield) of **1z** as a pale-yellow oil. **¹H NMR** (600 MHz, CDCl₃) δ 8.54 (dd, J = 5.0, 1.7 Hz, 1H), 7.66 (ddt, J = 7.9, 5.0, 2.5 Hz, 1H), 7.25 (s, 1H), 7.20 (dd, J = 7.6, 4.7 Hz, 1H), 6.73 (s, J = 22.4 Hz, 1H), 5.86–5.68 (m, 1H), 4.98 (dq, J = 17.0, 1.9 Hz, 1H), 4.95–4.90 (m, 1H), 4.56 (t, J = 4.7 Hz, 2H), 2.39–2.19 (m, 2H), 2.04 (q, J = 7.0 Hz, 2H), 1.68 (q, J = 7.5 Hz, 3H), 1.47–1.26 (m, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 173.29, 156.57, 149.13, 139.03, 136.92, 122.51, 122.32, 114.52, 44.53, 36.78, 33.73, 28.92, 28.75, 25.71. **HRMS** calcd. for C₁₄H₂₁N₂O⁺ [M+H]⁺: 233.1648, Found: 233.1648.

PRODUCT CHARACTERIZATION

3-ethyl-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2a): The title compound was synthesized from alkene **1a** (38 mg, 0.2 mmol) according to General Procedure A with a reaction time of 24 h. The product was isolated by flash silica chromatography to afford 40 mg (92% yield) of **2a** as a yellow oil. The reaction was also conducted on a large scale following General Procedure A (using a 500-mL Schlenk tube) using alkene **1a** (951 mg, 5.00 mmol) according with a reaction time of 24 h. The product was isolated by flash silica chromatography to afford 970 mg (89% yield) of **2a** as a yellow oil. The analytical data for the large-scale reaction matched that of the smaller scale reaction. **¹H NMR** (600 MHz, CDCl₃) δ 8.50 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H), 7.62 (td, J = 7.7, 1.8 Hz, 1H), 7.21 (dt, J = 7.8, 0.9 Hz, 1H), 7.15 (ddd, J = 7.6, 4.9, 1.1 Hz, 1H), 4.81 (s, 2H), 2.96–2.82 (m, 2H), 2.48 (dd, J = 17.8, 4.0 Hz, 1H), 1.95 (dq, J = 13.7, 7.5, 4.6 Hz, 1H), 1.70–1.60 (m, 1H), 1.00 (t, J = 7.4 Hz, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 179.82, 176.67, 154.71, 149.75, 136.71, 123.36, 121.84, 43.60, 41.41, 33.47, 24.54, 11.05. **HRMS** calcd. for C₁₂H₁₅N₂O₂⁺ [M+H]⁺: 219.1128, Found: 219.1129.

(cis)-3-ethyl-4-methyl-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2b) (Major diastereomer): The title compound was synthesized from alkene **1b** (42 mg, 0.2 mmol) according to General Procedure A with a reaction time of 48 h. The product was isolated by flash silica chromatography to afford 39.5 mg (85% yield; 3:1 d.r.) of **2b** as a yellow oil. The two diastereomers were obtained as a mixture, and peaks corresponding to each of the isomers could be assigned in the ¹H NMR spectrum of the mixture; the ¹³C NMR spectral data correspond to the mixture. **¹H NMR** (600 MHz, CDCl₃) δ 8.55–8.49 (m, 1H), 7.64 (td, J = 7.7, 1.8 Hz, 1H), 7.22 (t, J = 7.3 Hz, 1H), 7.19–7.14 (m, 1H), 4.82 (d, J = 4.3 Hz, 2H), 3.13–3.03 (m, major, 1H), 2.85 (td, J = 8.2, 6.2 Hz, major, 1H), 2.63 (qd, J = 7.4, 4.9 Hz, minor, 1H), 2.45 (dt, J = 8.2, 4.9 Hz, minor, 1H), 1.96 (dtd, J = 15.0, 7.5, 5.0 Hz, minor, 1H), 1.86 (tt, J = 13.8, 7.4 Hz, 1H), 1.71 (tt, J = 14.6, 7.5 Hz, major, 1H), 1.41 (d, J = 7.4 Hz, minor, 3H), 1.31 (d, J = 7.5 Hz, major, 3H), 1.09 (t, J = 7.4 Hz, major, 3H), 1.06 (t, J = 7.4 Hz, minor, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 180.44, 179.90, 179.46, 179.01, 154.86, 154.78, 149.71, 149.70, 136.69, 122.55, 121.77, 121.67, 49.53, 45.31, 43.54, 43.35, 40.57, 38.48, 23.77, 19.81, 16.60, 12.56, 11.76, 11.18. **HRMS** calcd. for C₁₃H₁₇N₂O₂⁺ [M+H]⁺: 233.1285, Found: 233.1285.

(*cis*)-3-benzyl-4-ethyl-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2c) (Major diastereomer):

The title compound was synthesized from alkene **1c** (56 mg, 0.2 mmol) according to General Procedure A with a reaction time of 48 h. The product was isolated by flash silica chromatography to afford 49 mg (79% yield; 3:1 d.r.) of **2c** as a yellow oil. The diastereomeric mixture of **2c** was further purified by preparative

HPLC to afford 31 mg (50% yield; 9:1 d.r.) of the major diastereomer of **2c**. The analytical data for the major diastereomer is reported below. ¹H NMR (600 MHz, CDCl₃) δ 8.55 (dtd, *J* = 6.3, 3.2, 2.7, 1.8 Hz, 1H), 7.65 (td, *J* = 7.6, 1.8 Hz, 1H), 7.39–7.34 (m, 2H), 7.33–7.27 (m, 3H), 7.26–7.22 (m, 1H), 7.21–7.16 (m, 1H), 4.89 (d, *J* = 3.8 Hz, 2H), 3.75 (d, *J* = 5.0 Hz, 1H), 3.00 (dt, *J* = 8.6, 5.0 Hz, 1H), 1.98 (dddd, *J* = 13.8, 9.6, 6.8, 5.1 Hz, 1H), 1.80–1.71 (m, 1H), 1.52–1.40 (m, 1H), 0.90 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 178.48, 176.78, 153.82, 149.04, 137.25, 136.24, 128.66, 127.48, 127.33, 122.10, 121.25, 52.38, 48.80, 43.09, 32.86, 19.56, 13.37. HRMS calcd. for C₁₉H₂₁N₂O₂⁺ [M+H]⁺: 309.1598, Found: 309.1599.

4-ethyl-3,3-dimethyl-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2d):

The title compound was synthesized from alkene **1d** (44 mg, 0.2 mmol) according to General Procedure A with a reaction time of 48 h. The product was isolated by flash silica chromatography to afford 19.5 mg (40% yield) of **2d** as a yellow oil. ¹H NMR (600 MHz, CDCl₃) δ 8.50 (d, *J* = 4.9 Hz,

1H), 7.62 (td, *J* = 7.6, 1.8 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.15 (dd, *J* = 7.5, 4.9 Hz, 1H), 4.78 (s, 2H), 2.46 (t, *J* = 7.2 Hz, 1H), 1.91 (dp, *J* = 14.5, 7.4 Hz, 1H), 1.67–1.52 (m, 1H), 1.38 (s, 3H), 1.25 (d, *J* = 4.7 Hz, 3H), 1.14 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 182.97, 178.80, 154.99, 149.76, 136.71, 122.55, 121.67, 52.83, 43.88, 43.37, 25.58, 21.10, 19.72, 13.21. HRMS calcd. for C₁₄H₁₉N₂O₂⁺ [M+H]⁺: 247.1441, Found: 247.1440.

tert-butyl ((3*S*,4*R*)-4-ethyl-2,5-dioxo-1-(pyridin-2-ylmethyl)pyrrolidin-3-yl)carbamate (2e) (Major diastereomer):

The title compound was synthesized from alkene **1e-(S)** (53 mg, 0.19 mmol) according to General Procedure A with a reaction time of 24 h. The product was isolated by flash silica chromatography to afford 51 mg (87% yield; 2.1:1 d.r.) of **2e** as a

yellow oil. The mixture of diastereomers could be separated by preparative HPLC to afford the major diastereomer of **2e** in 50% yield (29 mg; 98% *ee*) as a yellow wax. The purified major diastereomer was determined to have been formed in 98% *ee* according to the method below. The same procedure using **2e-(R)** instead of **2e-(S)** provided the product which matched the analytical data for the product of **2e-(S)**. ¹H NMR (600 MHz, CD₃OD) δ 8.45 (d, *J* = 4.9 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.31 (t, *J* = 6.3 Hz, 1H), 4.86 (d, *J* = 1.4 Hz, 2H), 4.71 (d, *J* = 9.0 Hz, 1H), 2.95 (q, *J* = 8.0 Hz, 1H), 1.74 (dt, *J* = 14.4, 7.2 Hz, 1H), 1.63 (dt, *J* = 14.4, 7.4 Hz, 1H), 1.46 (s, 9H), 1.07 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (151 MHz, CD₃OD) δ 179.91, 177.66, 158.14, 156.35, 149.80, 138.82, 124.05, 123.28, 80.98, 53.41, 46.47, 44.09, 28.63, 20.56, 12.85. HRMS calcd. for C₁₇H₂₄N₃O₄⁺ [M+H]⁺: 334.1761, Found: 334.1762.

tert-butyl ((3*S*,4*S*)-4-ethyl-2,5-dioxo-1-(pyridin-2-ylmethyl)pyrrolidin-3-yl)carbamate (2e) (Minor diastereomer):

The title compound was synthesized as described in the preceding entry. Purification by flash silica chromatography followed by preparative HPLC afforded 10 mg (17% yield; 51.7% *ee*) of the minor diastereomer of **2e** in as a yellow wax. The purified minor diastereomer of **2e**-(*S*) was determined to have been formed in 51.7% *ee* according to the method below. The same procedure using **2e**-(*R*) instead of **2e**-(*S*) provided the product which matched the analytical data for the product of **2e**-(*S*). ¹H NMR (600 MHz, CD₃OD) δ 8.51–8.43 (m, 1H), 7.80 (td, *J* = 7.8, 1.8 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.33 (dd, *J* = 7.6, 5.0 Hz, 1H), 4.83 (s, 2H), 4.22 (d, *J* = 6.3 Hz, 1H), 2.93–2.83 (m, 1H), 2.10–1.92 (m, 1H), 1.84–1.67 (m, 1H), 1.48 (s, 9H), 1.09 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (151 MHz, CD₃OD) δ 178.47, 177.28, 157.67, 156.33, 149.83, 138.82, 124.02, 122.98, 81.10, 56.45, 44.17, 28.66, 23.16, 11.43. One carbon underneath solvent peak could not be cleanly assigned for minor diastereomer, but is detectable in major diastereomer at δ46.47. HRMS calcd. for C₁₇H₂₄N₃O₄⁺ [M+H]⁺: 334.1761, Found: 334.1762.

3-isopropyl-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2f): The title compound was synthesized from alkene **1f** (58 mg, 0.2 mmol) according to General Procedure A with a reaction time of 48 h. The product was isolated by flash silica chromatography to afford 30 mg (65% yield) of **2f** as a yellow oil. ¹H NMR (600 MHz, CDCl₃) δ 8.50 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.62 (td, *J* = 7.7, 1.8 Hz, 1H), 7.22 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.15

(ddd, *J* = 7.6, 4.9, 1.1 Hz, 1H), 4.81 (s, 2H), 2.89 (dt, *J* = 9.1, 4.5 Hz, 1H), 2.76 (dd, *J* = 18.4, 9.3 Hz, 1H), 2.55 (dd, *J* = 18.4, 4.6 Hz, 1H), 2.35 (pd, *J* = 6.9, 4.4 Hz, 1H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 179.36, 176.86, 154.73, 149.68, 136.74, 122.63, 121.92, 43.59, 30.45, 28.86, 20.30, 17.47. HRMS calcd. for C₁₃H₁₇N₂O₂⁺ [M+H]⁺: 233.1285, Found: 233.1285.

3-propyl-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2g): The title compound was synthesized from alkene **1ga** or **1gb** (37 mg, 0.2 mmol) according to General Procedure A with a reaction time of 48 h. The product was isolated by flash silica chromatography to afford 33 mg (71% yield) from **1gb** and 43 mg (92% yield) from **1ga** as a yellow oil. The spectra of the product from **1fa** and **1fb** were identical. ¹H NMR (600 MHz, CDCl₃)

δ 8.50 (d, *J* = 4.8 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.22 (s, 1H), 7.15 (dd, *J* = 7.5, 4.9 Hz, 1H), 4.80 (s, 2H), 2.96–2.86 (m, 2H), 2.51–2.43 (m, 1H), 1.92 (tt, *J* = 12.8, 5.4 Hz, 1H), 1.54 (ddd, *J* = 14.1, 9.3, 5.7 Hz, 1H), 1.43 (h, *J* = 9.2, 8.2 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 180.02, 176.67, 154.71, 149.74, 136.73, 122.62, 121.87, 43.58, 39.99, 34.55, 33.57, 20.17, 13.90. HRMS calcd. for C₁₃H₁₇N₂O₂⁺ [M+H]⁺: 233.1285, Found: 233.1286.

d3-3-propyl-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2g-d3):

The title compound was synthesized from alkene **1g-d3** (41 mg, 0.2 mmol) according to General Procedure A with a reaction time of 48 h. The product was isolated by flash silica chromatography to afford 41 mg

(88% yield) of **2g-d3** as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 8.50 (dd, $J = 5.1, 1.7$ Hz, 1 H), 7.61 (td, $J = 7.7, 1.8$ Hz, 1 H), 7.20 (d, $J = 7.8$ Hz, 1 H), 7.15 (dd, $J = 7.6, 4.9$ Hz, 1 H), 4.80 (s, 2 H), 2.93–2.84 (m, 2 H), 2.60–2.39 (m, 1 H), 1.91 (dddd, $J = 13.6, 9.2, 7.1, 4.8$ Hz, 1 H), 1.65–1.47 (m, 1 H), 1.41 (q, $J = 8.5, 7.8$ Hz, 2 H). ^{13}C NMR (151 MHz, CDCl_3) δ 179.87, 176.52, 153.84, 147.84, 138.68, 123.22, 122.55, 42.54, 40.56, 40.42, 40.28, 40.14, 40.03, 40.00, 39.86, 39.72, 34.57, 33.27, 19.84. HRMS calcd. For $\text{C}_{13}\text{H}_{14}\text{D}_3\text{N}_2\text{O}_4^+$ $[\text{M}+\text{H}]^+$: 236.1473, Found: 236.1473.

3-heptyl-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2h): The title compound was synthesized from alkene **1ha** or **1hb** (52 mg, 0.2 mmol) according to General Procedure A with a reaction time of 72 h for **1ha** and 48h for **1hb**. Starting from **1hb**, the product was isolated by flash silica chromatography to afford 47 mg (85% yield) of **2h** as a yellow oil. Starting from **1ha**, the yield was found to be 6% as determined by ^1H NMR using CH_2Br_2 as an internal standard. ^1H NMR (600 MHz, CDCl_3) δ 8.51 (dd, $J = 4.9, 1.6$ Hz, 1H), 7.62 (td, $J = 7.7, 1.8$ Hz, 1H), 7.22 (d, $J = 7.8$ Hz, 1H), 7.16 (dd, $J = 7.5, 4.9$ Hz, 1H), 4.81 (s, 2H), 2.96–2.84 (m, 2H), 2.50–2.45 (m, 1H), 1.99–1.89 (m, 1H), 1.57 (dd, $J = 13.8, 6.6$ Hz, 2H), 1.42–1.34 (m, 2H), 1.34–1.21 (m, 7H), 0.88 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 180.03, 176.70, 154.74, 149.75, 136.73, 122.63, 121.89, 43.60, 40.19, 34.56, 31.87, 31.50, 29.42, 29.20, 26.85, 22.75, 14.21. HRMS calcd. for $\text{C}_{17}\text{H}_{25}\text{N}_2\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 289.1911, Found: 289.1910.

3-(6-chlorohexyl)-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2i): The title compound was synthesized from alkene **1i** (58 mg, 0.2 mmol) according to General Procedure A with a reaction time of 72 h. The product was isolated by flash silica chromatography to afford 49 mg (76% yield) as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 8.53 (ddd, $J = 4.9, 1.9, 0.9$ Hz, 1H), 7.66 (td, $J = 7.7, 1.8$ Hz, 1H), 7.25 (dt, $J = 7.8, 1.0$ Hz, 1H), 7.19 (ddd, $J = 7.7, 4.8, 1.1$ Hz, 1H), 4.83 (s, 2H), 3.55 (t, $J = 6.7$ Hz, 2H), 2.99–2.87 (m, 2H), 2.52–2.48 (m, 1H), 2.00–1.92 (m, 1H), 1.78 (dq, $J = 7.9, 6.7$ Hz, 2H), 1.66–1.57 (m, 1H), 1.51–1.34 (m, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 179.87, 176.56, 154.62, 149.66, 136.83, 122.67, 121.94, 45.11, 43.54, 40.10, 34.54, 32.56, 31.38, 28.74, 26.77, 26.68. HRMS calcd. for $\text{C}_{16}\text{H}_{22}\text{ClN}_2\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 309.1364, Found: 309.1363.

3-(4,8-dimethylnon-7-en-1-yl)-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2j): The title compound was synthesized from alkene **1j** (67 mg, 0.2 mmol) according to General Procedure A with a reaction time of 72 h. The product was isolated by flash silica chromatography to afford 53 mg (74% yield; 1:1 d.r.) of **2j** as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 8.48 (d, $J = 5.0$ Hz, 1H), 7.66–7.57 (m, 1H), 7.20 (d, $J = 7.9$ Hz, 1H), 7.14 (dd, $J = 7.6, 4.9$ Hz, 1H), 5.07 (t, $J = 7.2$ Hz, 1H), 4.79 (s, 2H), 2.96–2.84 (m, 2H), 2.52–2.43 (m, 1H), 2.07–1.84 (m, 3H), 1.66 (s, 3H), 1.58 (s, 3H), 1.57–1.49 (m, 2H), 1.45–1.25 (m, 4H), 1.20–1.05 (m, 2H), 0.84 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 179.86, 176.54, 154.58, 149.57, 136.62, 131.15, 124.81, 122.49, 121.76, 43.43, 40.06, 40.02, 37.03, 36.97, 36.62, 36.57, 34.42, 34.37, 32.21, 32.20, 31.67, 31.60, 25.73, 25.52, 25.50, 24.14, 24.10, 19.49, 19.44, 17.65. The peaks reported for ^{13}C

NMR correspond to both diastereomers which are present in a 1:1 to ratio. 9 of the 12 *sp*³ carbons were chemical shift distinct and peaks are reported to include both diastereomers. **HRMS** calcd. For C₂₁H₃₁N₂O₂⁺ [M+H]⁺: 343.2380, Found: 343.2381.

3-((bicyclo[2.2.1]heptan-2-yl)methyl)-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2k): The title compound was synthesized from alkene **1k** (55 mg, 0.2 mmol) according to General Procedure A with a reaction time of 72 h. The product was isolated by flash silica chromatography to afford 22 mg (40% yield; 1:1 d.r.) of **2j** as a colorless oil. **¹H NMR** (600 MHz, CDCl₃) δ 8.51 (dt, *J* = 4.7, 2.2 Hz, 1H), 7.62 (td, *J* = 7.7, 1.9 Hz, 1H), 7.21 (dd, *J* = 7.9, 3.9 Hz, 1H), 7.16 (dd, *J* = 7.5, 4.9 Hz, 1H), 4.81 (d, *J* = 2.6 Hz, 2H), 3.00 – 2.72 (m, 2H), 2.61 – 2.40 (m, 1H), 2.30 – 2.13 (m, 1H), 2.07 – 1.96 (m, 1H), 1.96 – 1.85 (m, 1H), 1.78 (m, *J* = 14.6, 10.5, 5.5 Hz, 1H), 1.53 (m, *J* = 20.7, 14.0, 7.0, 3.5 Hz, 4H), 1.43 – 1.28 (m, 2H), 1.14 (m, *J* = 21.6, 14.6, 8.6, 2.3 Hz, 2H), 0.67 (m, *J* = 14.7, 11.9, 5.3, 2.3 Hz. **¹³C NMR** (151 MHz, CDCl₃) δ 180.16, 180.12, 176.68, 176.63, 154.76, 154.74, 149.77, 136.71, 122.61, 121.89, 121.87, 121.86, 43.60, 43.58, 41.94, 40.76, 40.26, 40.13, 39.96, 39.94, 39.85, 39.65, 39.41, 39.27, 38.65, 38.64, 38.51, 38.34, 37.53, 37.33, 37.29, 37.18, 36.80, 36.61, 36.47, 35.48, 35.40, 35.11, 34.94, 34.89, 34.62, 34.50, 30.25, 30.19, 30.10, 28.78, 28.74, 22.69, 22.34. For C₁₈H₂₃N₂O₂⁺ [M+H]⁺: 299.1754, Found: 299.1753.

3-(cyclohexylmethyl)-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2l): The title compound was synthesized from alkene **1l** (52 mg, 0.2 mmol) according to General Procedure A with a reaction time of 72 h. The product was isolated by flash silica chromatography to afford 48 mg (84% yield) of **2l** as a yellow oil. **¹H NMR** (600 MHz, CDCl₃) δ 8.51 (d, *J* = 5.0 Hz, 1H), 7.62 (td, *J* = 7.7, 3.8 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.16 (dd, *J* = 7.6, 4.9 Hz, 1H), 4.81 (s, 2H), 3.02–2.83 (m, 2H), 2.46 (dd, *J* = 17.2, 3.4 Hz, 1H), 1.89 (td, *J* = 11.0, 10.5, 4.7 Hz, 1H), 1.83–1.61 (m, 5H), 1.40 (ddt, *J* = 14.8, 9.1, 5.5 Hz, 2H), 1.35–1.08 (m, 3H), 1.08–0.86 (m, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ 180.83, 176.54, 154.01, 149.61, 136.61, 122.49, 121.74, 43.45, 39.23, 37.82, 35.48, 35.04, 33.80, 32.26, 26.37, 26.17, 26.05. **HRMS** calcd. for C₁₇H₂₃N₂O₂⁺ [M+H]⁺: 287.1754, Found: 287.1754.

tert-butyl 4-((2,5-dioxo-1-(pyridin-2-ylmethyl)pyrrolidin-3-yl)methyl)piperidine-1-carboxylate (2m): The title compound was synthesized from alkene **1m** (36 mg, 0.1 mmol) according to General Procedure A with a reaction time of 72 h. The product was isolated by flash silica chromatography to afford 36 mg (93% yield) of **2m** as a hard yellow oil. **¹H NMR** (600 MHz, Acetone) δ 8.61 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.86 (td, *J* = 7.7, 1.8 Hz, 1H), 7.42–7.36 (m, 2H), 4.85 (d, *J* = 1.6 Hz, 2H), 4.18 (s, 2H), 3.11 (ddt, *J* = 10.0, 9.0, 4.6 Hz, 1H), 3.05 (dd, *J* = 17.7, 9.0 Hz, 1H), 2.59 (dd, *J* = 17.8, 4.4 Hz, 1H), 2.10 (p, *J* = 2.5 Hz, 3H), 1.93 (ddd, *J* = 13.4, 8.3, 4.7 Hz, 1H), 1.86 (dt, *J* = 12.9, 2.9 Hz, 1H), 1.83–1.74 (m, 2H), 1.63 (ddd, *J* = 13.6, 10.1, 5.5 Hz, 1H), 1.57 (s, 9H), 1.21 (dtdd, *J* = 39.2, 12.7, 11.3, 4.4 Hz, 2H). 1 proton could not be detected and likely sits underneath

the solvent peaks. ^{13}C NMR (151 MHz, Acetone) δ 181.21, 177.57, 156.24, 155.40, 150.14, 137.68, 123.41, 122.28, 79.57, 43.98, 38.68, 38.33, 35.45, 34.51, 28.53. HRMS calcd. for $\text{C}_{21}\text{H}_{30}\text{N}_3\text{O}_4^+ [\text{M}+\text{H}]^+$: 388.2231, Found: 388.2231.

3-((1,4-dioxaspiro[4.5]decan-8-yl)methyl)-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2n): The title compound was synthesized from alkene **1n** (60.5 mg, 0.19 mmol) according to General Procedure A with a reaction time of 72 h. The product was isolated by flash silica chromatography to afford 56.5 mg (86% yield) of **2n** as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 8.51 (d, $J = 4.9$ Hz, 1H), 7.64 (qd, $J = 7.9, 1.9$ Hz, 1H), 7.23 (t, $J = 7.9$ Hz, 1H), 7.16 (dd, $J = 7.6, 5.0$ Hz, 1H), 4.81 (d, $J = 9.3$ Hz, 2H), 3.94 (qt, $J = 8.5, 5.5, 4.1$ Hz, 2H), 3.06–2.90 (m, 2H), 2.58–2.29 (m, 2H), 2.10 (dddt, $J = 19.2, 12.8, 5.8, 3.0$ Hz, 1H), 2.04–1.90 (m, 1H), 1.75 (tq, $J = 10.1, 3.4$ Hz, 3H), 1.57–1.39 (m, 5H), 1.39–1.22 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 180.84, 176.66, 149.76, 136.81, 122.75, 122.68, 122.07, 121.96, 108.86, 64.41, 43.59, 40.66, 40.59, 38.38, 38.22, 38.09, 37.86, 35.32, 34.52, 34.43, 34.40, 33.95, 32.89, 32.20, 30.66, 29.57. HRMS calcd. for $\text{C}_{19}\text{H}_{25}\text{N}_2\text{O}_4^+ [\text{M}+\text{H}]^+$: 345.1809, Found: 345.1808.

cis-6-methyl-3-(pyridin-2-ylmethyl)-3-azabicyclo[3.2.0]heptane-2,4-dione (2o): The title compound was synthesized from alkene **1o** (20.5 mg, 0.2 mmol) according to General Procedure B with a reaction time of 24 h. The product was isolated by flash silica chromatography to afford 15 mg (65% yield; >20:1 d.r.) of **2o** as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 8.52 (dd, $J = 5.0, 1.6$ Hz, 1H), 7.67 (td, $J = 7.7, 1.8$ Hz, 1H), 7.28–7.23 (m, 1H), 7.19 (dd, $J = 7.5, 4.9$ Hz, 1H), 4.86 (s, 2H), 3.31 (ddd, $J = 10.7, 6.6, 4.1$ Hz, 1H), 2.97 (dd, $J = 6.6, 4.3$ Hz, 1H), 2.68 (ddddd, $J = 14.0, 11.3, 9.1, 5.6$ Hz, 1H), 2.45 (ddd, $J = 12.8, 8.6, 4.0$ Hz, 1H), 2.20 (ddd, $J = 12.8, 10.6, 6.6$ Hz, 1H), 1.35 (dd, $J = 7.1, 0.9$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 180.06, 179.11, 178.43, 154.68, 149.40, 137.23, 122.77, 121.98, 46.19, 43.17, 35.65, 33.10, 31.00, 22.28. HRMS calcd. for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_2^+ [\text{M}+\text{H}]^+$: 231.1128, Found: 231.1127.

butyl 3-(2,5-dioxo-1-(pyridin-2-ylmethyl)pyrrolidin-3-yl)propanoate (2p): The title compound was synthesized from alkene **1p** (50 mg, 0.17 mmol) according to General Procedure A with a reaction time of 48 h. The product was isolated by flash silica chromatography to afford 45 mg (82% yield) of **2p** as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 8.49 (ddd, $J = 4.9, 1.9, 0.9$ Hz, 1H), 7.63 (td, $J = 7.7, 1.8$ Hz, 1H), 7.22 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.16 (ddd, $J = 7.5, 4.9, 1.1$ Hz, 1H), 4.81 (s, 2H), 4.08 (t, $J = 6.7$ Hz, 2H), 3.05–2.82 (m, 2H), 2.57–2.40 (m, 3H), 2.26–2.16 (m, 1H), 2.01–1.90 (m, 1H), 1.64–1.55 (m, 2H), 1.43–1.31 (m, 2H), 0.93 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 179.22, 176.10, 172.77, 154.41, 149.68, 136.82, 122.69, 121.92, 64.73, 43.50, 39.22, 34.60, 31.56, 30.75, 26.81, 19.25. HRMS calcd. For $\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}_4^+ [\text{M}+\text{H}]^+$: 319.1652, Found: 319.1653.

4-(4-bromophenethyl)-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2q): The title compound was synthesized from alkene **1q** (32 mg, 0.093 mmol) according to General Procedure A with a reaction time of 48 h. The product was isolated by flash silica

chromatography to afford 32 mg (93% yield) of **2q** as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 8.49 (dt, $J = 4.7, 1.6$ Hz, 1H), 7.67–7.59 (m, 1H), 7.42–7.40 (m, 2H), 7.24–7.02 (m, 4H), 4.81 (s, 2H), 2.98–2.66 (m, 4H), 2.54–2.43 (m, 1H), 2.37–2.21 (m, 1H), 1.87 (dtd, $J = 14.6, 8.9, 6.0$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 179.54, 176.24, 154.47, 149.70, 139.57, 136.79, 131.79, 130.34, 122.69, 121.96, 120.25, 43.54, 39.25, 34.60, 33.05, 32.49. HRMS calcd. for $\text{C}_{18}\text{H}_{18}\text{BrN}_2\text{O}_2^+ [\text{M}+\text{H}]^+$ 373.0546, Found: 373.0548.

3-(4-iodophenethyl)-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2r): The title compound was synthesized from alkene **1r** (78 mg, 0.2 mmol) according to General Procedure A with a reaction time of 48 h. The product was isolated by flash silica chromatography to afford 65 mg (78% yield) of **2r** as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ

8.49 (ddd, $J = 4.8, 1.9, 1.0$ Hz, 1H), 7.66–7.58 (m, 3H), 7.23 (dt, $J = 7.9, 1.0$ Hz, 1H), 7.16 (ddd, $J = 7.6, 4.9, 1.1$ Hz, 1H), 6.97–6.94 (m, 2H), 4.81 (s, 2H), 2.92 (dd, $J = 17.7, 9.1$ Hz, 1H), 2.89–2.82 (m, 1H), 2.72 (dddd, $J = 41.7, 14.0, 9.1, 6.4$ Hz, 2H), 2.48 (dd, $J = 17.7, 4.2$ Hz, 1H), 2.25 (dddd, $J = 13.7, 9.3, 6.8, 5.3$ Hz, 1H), 1.87 (dtd, $J = 13.8, 8.8, 6.0$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 179.55, 176.26, 154.44, 149.66, 140.26, 137.79, 136.88, 130.70, 122.72, 121.99, 91.58, 43.52, 39.27, 34.63, 33.03, 32.61. HRMS calcd. for $\text{C}_{18}\text{H}_{18}\text{IN}_2\text{O}_2^+ [\text{M}+\text{H}]^+$: 421.0407, Found: 421.0408.

2-(2-(2,5-dioxo-1-(pyridin-2-ylmethyl)pyrrolidin-3-yl)ethyl)benzonitrile (2s): The title compound was synthesized from alkene **1s** (40 mg, 0.13 mmol) according to General Procedure A with a reaction time of 72 h. The product was isolated by flash silica chromatography to afford 30 mg (68% yield) of **2s** as a yellow

oil. ^1H NMR (600 MHz, CDCl_3) δ 8.49 (d, $J = 4.9$ Hz, 1H), 7.69–7.59 (m, 2H), 7.53 (t, $J = 7.7$ Hz, 1H), 7.38 (d, $J = 7.8$ Hz, 1H), 7.33 (t, $J = 7.6$ Hz, 1H), 7.23 (d, $J = 7.9$ Hz, 1H), 7.16 (dd, $J = 7.5, 5.1$ Hz, 1H), 4.82 (s, 2H), 3.09–2.96 (m, 3H), 2.92 (d, $J = 5.1$ Hz, 1H), 2.57 (dd, $J = 18.1, 4.6$ Hz, 1H), 2.32 (dq, $J = 10.9, 4.2, 2.8$ Hz, 1H), 1.97 (dt, $J = 14.3, 7.9$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 179.26, 176.09, 154.47, 149.77, 144.73, 136.78, 133.21, 133.12, 129.90, 127.23, 122.69, 121.95, 118.02, 112.56, 43.63, 39.49, 34.66, 32.66, 31.91. HRMS calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_3\text{O}_2^+ [\text{M}+\text{H}]^+$: 320.1394, Found: 320.1393.

(cis)-2-(pyridin-2-ylmethyl)tetrahydrocyclopentapyrrole-1,3(2H,3H)-dione (2t): The title compound was synthesized from alkene **1t** (40.5 mg, 0.2 mmol) according to General Procedure A with a reaction time of 24 h.

The product was isolated by flash silica chromatography to afford 39 mg (85% yield) of **2t** as a white solid. ^1H NMR (600 MHz, CDCl_3) δ 8.49 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 1H), 7.62 (td, $J = 7.7, 1.8$ Hz, 1H), 7.20 (dt, $J = 7.8, 0.9$ Hz, 1H), 7.15 (ddd, $J = 7.6, 4.9, 1.1$ Hz, 1H), 4.79 (s, 2H), 3.30–3.18 (m, 2H), 2.20 (ddd, $J = 13.1, 6.4, 1.8$ Hz, 2H), 1.96–1.84 (m, 2H), 1.77 (dddt, $J = 12.8, 6.4, 4.4, 2.0$ Hz, 1H), 1.52 (dp, $J = 18.7, 6.3$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 180.41, 154.65, 150.16, 137.28, 122.60, 121.69, 45.95, 43.24, 30.65, 25.32. HRMS calcd. for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_2^+ [\text{M}+\text{H}]^+$: 231.1128, Found: 231.1128.

(cis)-2-(pyridin-2-ylmethyl)hexahydro-1H-isoindole-1,3(2H)-dione

(2u): The title compound was synthesized from alkene **1u** (43 mg, 0.2 mmol) according to General Procedure A with a reaction time of 24 h. The product was isolated by flash silica chromatography to afford 33 mg (65% yield) of **2u** as a white solid. Single crystals suitable for X-Ray diffraction were grown by slow diffusion of hexanes into a concentrated solution of

product in acetone. The product partially isomerizes to the trans configuration if left heating for 48-72 h. ¹H NMR (600 MHz, CDCl₃) δ 8.50 (d, *J* = 4.9 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.15 (dd, *J* = 7.5, 4.9 Hz, 1H), 4.80 (s, 2H), 2.95 (p, *J* = 7.8 Hz, 2H), 1.87 (q, *J* = 6.3 Hz, 4H), 1.47 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 179.75, 155.02, 149.69, 136.71, 122.57, 121.81, 43.28, 40.04, 23.88, 21.82. HRMS calcd. for C₁₄H₁₇N₂O₂⁺ [M+H]⁺ 245.1285, Found: 245.1285. X-ray: CCDC (2008992).

(cis)-4-methyl-2-(pyridin-2-ylmethyl)hexahydro-1H-isoindole-1,3(2H)-dione (2v): The title compound was synthesized from alkene **1v** (46 mg, 0.2 mmol) according to General Procedure A with a reaction time of 48 h. The product was isolated by flash silica chromatography to afford 21 mg (42% yield; 2.1:1 d.r.) of **2v** as a yellow oil. The two diastereomers could be separated analytically by LCMS, but could not be separated on a preparative

scale. The methyl group on cyclohexyl ring shows a clear doublet with 2 distinct chemical shifts at 1.18 and 1.12 ppm. The integration of these peaks corresponded to a 2.1:1 ratio. The relative stereochemistry of this methyl group could not be assigned from the mixture, however the two bridging hydrogens show a clear NOE and are in agreement with related compounds **2t** and **2u** which were isolated as single diastereomers and are assigned to be in the cis configuration to one another as confirmed by X-ray crystallography for **2u**. All data given below is for the mixture of diastereomers. ¹H NMR (600 MHz, CDCl₃) δ 8.43 (d, *J* = 4.7 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 1H), 7.08 (dd, *J* = 7.5, 5.0 Hz, 1H), 4.81–4.62 (m, 2H), 2.93 (ddd, *J* = 16.7, 8.2, 3.7 Hz, 1H), 2.42 (t, *J* = 8.7 Hz, 1H), 2.17 (dt, *J* = 13.3, 4.4 Hz, 1H), 2.02–1.79 (m, 1H), 1.76–1.47 (m, 4H), 1.18 (d, *J* = 7.1 Hz, minor), 1.12 (d, *J* = 6.4 Hz, major, 3H), 1.07–0.88 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 180.14, 179.30, 179.18, 178.46, 155.12, 149.69, 149.65, 136.70, 122.55, 122.53, 121.94, 121.69, 47.38, 44.57, 43.26, 43.21, 41.25, 40.50, 33.19, 32.10, 29.36, 28.14, 23.53, 22.27, 21.81, 21.02, 19.80, 18.76. HRMS calcd. for C₁₅H₁₉N₂O₂⁺ [M+H]⁺: 259.1441, Found: 259.1441

(cis)-5-methyl-2-(pyridin-2-ylmethyl)hexahydro-1H-isoindole-1,3(2H)-dione (2w):

The title compound was synthesized from alkene **1w** (46 mg, 0.2 mmol) according to General Procedure A with a reaction time of 48 h. The product was isolated by flash silica chromatography to afford 20 mg (40% yield; 1.9:1 d.r.) of **2w** as a yellow oil. The two diastereomers could be separated analytically by LCMS, but could not be separated on a preparative scale. The methyl group on cyclohexyl

ring shows a clear doublet with 2 distinct chemical shifts at 0.95 and 0.92 ppm. The integration of these peaks corresponded to a 1.9:1 ratio. The relative stereochemistry of this methyl group could not be assigned from the mixture, however the two bridging hydrogens show a clear NOE and are in agreement with related compounds **2u** and **2t**, which were isolated as single diastereomers and

are assigned to be in the *cis* configuration to one another as confirmed by X-ray crystallography for **2u**. All data given below is for the mixture of diastereomers. **¹H NMR** (600 MHz, CDCl₃) δ 8.51 (s, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.19 (m, 2H), 4.79 (s, 2H), 3.05 (td, *J* = 7.4, 2.6 Hz, 1H), 2.99–2.92 (m, 1H), 2.88 (dt, *J* = 10.0, 7.4 Hz, 1H), 2.39–2.26 (m, 1H), 2.15 (dddd, *J* = 13.9, 7.0, 5.5, 3.8 Hz, 1H), 1.76–1.58 (m, 4H), 1.54–1.38 (m, 2H), 1.27 (ddd, *J* = 14.0, 11.6, 6.9 Hz, 1H), 1.08–0.96 (m, 1H), 0.95 (d, *J* = 6.5 Hz, major) and 0.92 (d, *J* = 6.5 Hz, minor, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 180.09, 180.04, 179.37, 179.12, 136.68, 43.30, 40.79, 40.38, 39.83, 39.69, 35.21, 30.83, 30.03, 29.41, 28.25, 26.30, 22.42, 22.17, 21.66. **HRMS** calcd. for C₁₅H₁₉N₂O₂⁺ [M+H]⁺ 259.1441, Found: 259.1443.

3-methyl-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2x): The title compound was synthesized from alkene **1wa** (35 mg, 0.2 mmol) according to General Procedure A with a reaction time of 24 h. The product was isolated by flash silica chromatography to afford 37 mg (91% yield) of **2x** as a yellow oil.

¹H NMR (600 MHz, CDCl₃) δ 8.51 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.63 (td, *J* = 7.7, 1.8 Hz, 1H), 7.22 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.16 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 4.81 (s, 2H), 3.09–2.87 (m, 2H), 2.41 (dd, *J* = 17.7, 4.1 Hz, 1H), 1.38 (d, *J* = 7.2 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 180.55, 176.45, 154.67, 149.77, 136.68, 122.65, 121.91, 43.60, 36.66, 34.98, 16.97. **HRMS** calcd. for C₁₁H₁₃N₂O₂⁺ [M+H]⁺: 205.0972, Found: 205.0974.

3-butyl-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2y): The title compound was synthesized from alkene **1y** (44 mg, 0.2 mmol) according to General Procedure A with a reaction time of 48 h. The product was isolated by flash silica chromatography to afford 16.5 mg (33% yield) of **2y** as a yellow oil.

¹H NMR (600 MHz, CDCl₃) δ 8.51 (d, *J* = 4.8 Hz, 1H), 7.63 (td, *J* = 7.7, 1.8 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.16 (dd, *J* = 7.2, 5.2 Hz, 1H), 4.81 (s, 2H), 2.96–2.85 (m, 2H), 2.53–2.44 (m, 1H), 1.95 (td, *J* = 9.1, 5.0 Hz, 1H), 1.57 (dt, *J* = 14.1, 8.3 Hz, 1H), 1.40–1.32 (m, 4H), 0.94–0.89 (m, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ 180.05, 176.72, 154.73, 149.75, 136.74, 122.64, 121.91, 43.60, 40.17, 34.56, 31.21, 29.00, 22.57, 14.02. **HRMS** calcd. for C₁₄H₁₉N₂O₂⁺ [M+H]⁺: 247.1441, Found: 247.1441.

3-pentyl-1-(pyridin-2-ylmethyl)pyrrolidine-2,5-dione (2z): The title compound was synthesized from alkene **1z** (46 mg, 0.2 mmol) according to General Procedure A with a reaction time of 72 h. The product was isolated by flash silica chromatography to afford 9 mg (17% yield) of **2z** as a yellow oil.

¹H NMR (600 MHz, *d*₆-DMSO) δ 8.42 (dt, *J* = 4.8, 1.4 Hz, 1H), 7.72 (td, *J* = 7.6, 1.8 Hz, 1H), 7.24 (ddd, *J* = 7.4, 6.3, 1.4 Hz, 2H),

4.62 (s, 2H), 2.93–2.82 (m, 2H), 2.44 (d, $J = 7.8$ Hz, 1H), 1.75–1.65 (m, 1H), 1.51–1.42 (m, 1H), 1.35–1.16 (m, 6H), 0.86–0.80 (m, 3H). ^{13}C NMR (151 MHz, d_6 -DMSO) δ 179.89, 176.67, 155.46, 149.05, 136.83, 122.50, 121.14, 42.67, 40.05, 33.89, 31.03, 30.41, 25.77, 21.97, 13.91. HRMS calcd. for $\text{C}_{15}\text{H}_{21}\text{N}_2\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 261.1598, Found: 261.1597.

3-ethyl-1(*S*)-(1-(pyridin-2-yl)ethyl)pyrrolidine-2,5-dione (2aa): The title compound was synthesized from alkene (*S*)-**DG7-SM** (41 mg, 0.2 mmol) according to modified General Procedure A using $\text{W}(\text{CO})_6$ (25 mg, 0.055 mmol) with a reaction time of 48 h. The product was isolated by flash silica chromatography to afford 35 mg (75% yield; 5.3:1 d.r.; >99% *ee*) of **2aa** as a colorless oil. The two diastereomers and pairs of enantiomers were separated by SFC with the method shown below. The two diastereomers are reported as mixture. The spectra matched that from the racemic compound. ^1H NMR (600 MHz, CDCl_3) δ 8.52 (d, $J = 4.9$ Hz, 1H), 7.68 (t, $J = 7.5$ Hz, 1H), 7.37 (d, $J = 7.9$ Hz, 1H), 7.18 (dd, $J = 7.5, 5.0$ Hz, 1H), 5.47 (q, $J = 7.3$ Hz, 1H), 2.93–2.74 (m, 2H), 2.49–2.35 (m, 1H), 1.97–1.84 (m, 1H), 1.82 (d, $J = 7.4$ Hz, 3H), 1.71–1.56 (m, 1H), 0.98 (m, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 179.82, 176.65, 158.16, 148.98, 148.93, 136.84, 136.80, 122.38, 120.95, 50.90, 50.81, 40.98, 40.96, 33.86, 33.80, 24.41, 24.35, 15.97, 15.94, 10.78, 10.73. HRMS calcd. for $\text{C}_{13}\text{H}_{17}\text{N}_2\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 233.1285, Found: 233.1287.

REMOVAL OF DIRECTING GROUP FROM **2a**

Scheme S2 Directing group removal

To a 5-mL disposable vial equipped with magnetic stir bar, **2a** (100 mg, 0.458 mmol) and KOH (116 mg, 2.06 mmol) were added. The solids were dissolved in H₂O (340 μ L) and ethanol (4.5 mL). The vial was sealed and placed in a preheated oil bath at 100 °C for 18 h. The reaction was then allowed to cool to room temperature, and the organic solvent was removed by rotary evaporator. The crude was then diluted with DCM and aq. NaHCO₃, and the organic phase was discarded. The aqueous layer was extracted with DCM ($\times 2$). Next, the aqueous layer was acidified with 6 M HCl until it had reached pH < 1, as monitored by pH paper. The aqueous layer was then extracted with EtOAc ($\times 3$), and the organic layers were combined, dried over MgSO₄, filtered, and evaporated to dryness. The resulting solid was washed with cold Et₂O and then dried under vacuum, to afford 61 mg (92% yield) of **3a** as a white solid. Analytical data match previously published data (48).

SYNTHESIS AND REACTIVITY OF ORGANOTUNGSTEN COMPLEXES

Scheme S3 Stoichiometric NMR monitored reaction

$\text{W}(\text{MeCN})_3(\text{CO})_3$ (12 mg, 0.030 mmol) and **1xa** (5.2 mg, 0.030 mmol) were added to a J Young NMR tube followed by 0.75 mL of CDCl_3 . The NMR tube was shaken vigorously for 2 minutes, at which point data collection ensued. The stacked spectra below show data collected at 10 minutes (top) and 1 h (bottom). The sweep width for these experiments was from 10 ppm to -15 ppm to account for possible formation of a metal hydride; however, no signals were observed in the hydride region (<0 ppm).

Figure S4 Time-monitored progress of stoichiometric reaction followed by ^1H NMR. The top ^1H spectrum corresponds to a timepoint $t = 10$ min after the reaction started. The bottom ^1H spectrum corresponds to a timepoint $t = 1$ hour after the reaction started. Both spectra were acquired at room temperature, and the NMR tube was allowed to stand at room temperature in between acquisitions.

2-iodo-*N*-(pyridin-2-ylmethyl)benzamide (SM-3): The title compound was prepared according to the General Procedure D using 2-iodobenzoic acid (1.500 g, 4.44 mmol) as the carboxylic acid. The product was isolated by flash silica chromatography to afford 1.105 g (71% yield) of **SM-3** as a white solid. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.56 (d, J = 4.9 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.82 (t, J = 7.7 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 7.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.36–7.29 (m, 2H), 7.11 (t, J = 7.7 Hz, 1H), 4.82 (d, J = 5.1 Hz, 2H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 169.53, 155.42, 147.69, 141.76, 140.15, 138.54, 131.38, 128.51, 128.32, 123.50, 123.19, 92.76, 44.32; **HRMS** calcd. for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{OI}^+$ $[\text{M}+\text{H}]^+$: 338.9989, Found: 338.9989.

4-bromo-2-iodo-*N*-(pyridin-2-ylmethyl)benzamide (SM-2): The title compound was prepared according to General Procedure D using 2-iodo-4-bromo benzoic acid (1.500 g, 3.66 mmol) as the carboxylic acid. The product was isolated by flash silica chromatography to afford 1.125g (58% yield) of **SM-2** as a white solid. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.57 (d, J = 6.2 Hz, 1H), 8.04 (d, J = 4.5 Hz, 1H), 7.89 (dq, J = 15.8, 7.6 Hz, 1H), 7.66–7.30 (m, 4H), 4.93–4.76 (m, 2H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 168.66, 154.83, 147.46, 142.31, 142.29, 140.14, 131.55, 129.55, 124.74, 124.23, 123.65, 93.40, 43.80; **HRMS** calcd. for $\text{C}_{13}\text{H}_{11}\text{N}_2\text{OIBr}^+$ $[\text{M}+\text{H}]^+$: 416.9094, Found: 416.9096.

3-iodo-*N*-(pyridin-2-ylmethyl)propenamide (SM-1): A flame-dried 10-mL Schlenk tube equipped with magnetic stir bar was charged with 3-iodopropenoic acid (2.00 g, 10.00 mmol) and DMF (40 μL , 0.05 mmol) and was then cooled to 0 $^\circ\text{C}$. Oxalyl chloride (875 μL , 10.00 mmol) was added dropwise over 15 min, and the reaction solution was allowed to continue stirring at 0 $^\circ\text{C}$ for 30 min before being allowed to warm to room temperature and stir for an additional 1 h. The reaction was then cooled back down to 0 $^\circ\text{C}$, and under vigorous stirring 2-picolyamine (1.622 g, 15.00 mmol) was added. The reaction mixture was stirred for 10 min, at which point it was diluted with EtOAc and quenched by addition of a saturated solution of aqueous NH_4Cl . The organic layer was separated, evaporated to dryness, redissolved in MeOH (4 mL), and purified by HPLC. The product-containing fractions were combined and lyophilized to afford 455 mg (16% yield) of **SM-1** as a white powder in which was stored at $-40\text{ }^\circ\text{C}$. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.53 (d, J = 5.1 Hz, 1H), 7.70 (tt, J = 7.5, 1.8 Hz, 1H), 7.32 (d, J = 7.8 Hz, 1H), 7.24 (dd, J = 7.5, 5.0 Hz, 1H), 7.02 (s, 1H), 4.59 (d, J = 4.9 Hz, 2H), 3.41 (td, J = 7.1, 1.7 Hz, 2H), 2.91 (td, J = 7.0, 1.7 Hz, 2H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 170.55, 155.93, 148.65, 137.47, 122.78, 122.67, 44.38, 40.61, -1.77; **HRMS** calcd. for $\text{C}_9\text{H}_{12}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 290.9989, Found: 290.9990.

Inside an argon-filled glovebox, a 1 dram vial containing of **SM-2** (106 mg, 0.255 mmol) and $\text{W}(\text{MeCN})_3(\text{CO})_3$ (100 mg, 0.255 mmol) was dissolved in 2 mL of THF then stirred and heated at 45 $^\circ\text{C}$ for 1 h. The solution turned a vibrant yellow. After 1 h it was then allowed to cool to room temperature and then filtered through a PFE syringe filter into a vial of ether. The filtered solution

was then allowed to slowly evaporate in the glovebox brought to saturation to afford red cube crystals. The crystals were collected by filtration and washed with hexanes to afford 45 mg (26% yield) of **W-2** as red cubic crystals. The above procedure was not optimized for isolated yield. The single crystals collected were used for x-ray crystallography, NMR, HRMS, and IR characterization. Oil and grease appear in the NMR as the crystals collected for diffraction were all submerged in oil for initial characterization by x-ray crystallography and these were used for characterization. **¹H NMR** (600 MHz, THF) δ 11.82 (s, 1H), 8.94 (d, J = 5.6 Hz, 1H), 8.06–7.92 (m, 2H), 7.73 (d, J = 8.3 Hz, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.47 (t, J = 6.6 Hz, 1H), 7.33 (dd, J = 8.3, 1.9 Hz, 1H), 5.78–5.56 (m, 2H). **¹³C NMR** (151 MHz, THF) δ 226.12, 223.68, 221.56, 169.34, 166.36, 166.09, 154.19, 146.70, 140.88, 137.76, 129.26, 127.11, 126.80, 125.56, 123.24, 57.09. **IR** (cm⁻¹) 1998, 1907, 1865, 1604, 1566, 1397, 1242, 1164, 1043, 1017, 875, 821, 770, 749, 725, 672. **HRMS** calcd. For C₁₆H₁₀N₂O₄BrIW⁺ [M]⁺: 683.8372. Found 683.4350. **X-ray** (CCDC 2020047).

Inside an argon filled glovebox, a 1 dram vial containing of **SM-3** (50 mg, 0.15 mmol) and W(MeCN)₃(CO)₃ (58 mg, 0.255 mmol) was dissolved in 2 mL of THF then stirred and heated at 45 °C for 1 h. The solution turned brown. After 1 h it was then allowed to cool to room temperature and then filtered through a PFE syringe filter. The filtered solution was then allowed to slowly evaporate in the glovebox and brought to saturation at which point the solution was subject to slow vapor diffusion with pentanes to afford red cube crystals. The crystals were collected by filtration and washed with hexanes to afford 16 mg (18% yield) of **W-3** as red cubic crystals. The above procedure was not optimized for isolated yield. The single crystals collected were used for x-ray crystallography, NMR, HRMS, and IR characterization. Oil and grease appear in the NMR as the crystals collected were all submerged in oil for initial characterization by x-ray crystallography. **¹H NMR** (600 MHz, CD₂Cl₂) δ 8.88 (d, J = 5.4 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 6.2 Hz, 1H), 7.28 (d, J = 7.9 Hz, 1H), 7.22 (d, J = 7.8 Hz, 1H), 5.64 (s, 2H). **¹³C NMR** (151 MHz, CD₂Cl₂) δ 223.55, 218.12, 216.25, 167.54, 165.05, 162.21, 153.46, 144.97, 140.23, 136.94, 131.81, 127.10, 124.90, 123.47, 122.48, 56.33. **IR** (cm⁻¹) 1998.5, 1879.2 (d), 1557.5, 1523.6, 1392.1, 762.5, 737.7. **HRMS** calcd. For C₁₆H₁₀N₂O₄IW⁺ [M]⁺: 606.9346, Found: 606.9350. **X-ray** (CCDC 2050458).

In a argon-filled glovebox, to a 20-mL vial were added 2-iodo-*N*-(pyridin-2-ylmethyl)benzamide (100 mg, 0.30 mmol), W(MeCN)₃(CO)₃ (116 mg, 0.30 mmol), and THF (4 mL). The reaction was heated to 45 °C for 2 h resulting in a homogenous brown solution. After complete conversion of the starting material, the reaction vessel was removed from the heat source and allowed to cool to room temperature, at which point silver trifluoromethylsulfonate (76 mg, 0.30 mmol) was added to the solution. The reaction mixture was heated to 45 °C for 30 min. The reaction was cooled to room temperature and filtered, and the filtrate was transferred into a separate vial containing trimethylphosphine (49.5 mg, 0.65 mmol). The reaction mixture was stirred for 15 min at room temperature, resulting in a dark-red solution. Potassium *tert*-butoxide (33 mg, 0.30 mmol) was added to the reaction mixture, resulting in immediate formation of a dark-purple solution. Next, 18-crown-6 (78 mg, 0.30 mmol) was added, resulting in formation of yellow/orange solution. The reaction mixture was stirred for 1 h at room

temperature, resulting in slow precipitation of KOTf–18C6. The reaction solution was filtered to remove KOTf–18C6. Slow evaporation of the solvent resulted in further precipitation of the remaining KOTf–18C6. A second filtration was then performed. The product can be isolated by flash chromatography on neutral alumina using DCM/MeOH (97/3) as the eluent to afford 56 mg (31% overall yield) of **W-3'** as a yellow solid. Vapor diffusion of pentane into a concentrated solution of **W-3'** provided single crystals suitable for X-ray diffraction. ¹H NMR (600 MHz, CD₂Cl₂) δ 8.75 (d, *J* = 5.7 Hz, 1H), 7.83 (t, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 6.7 Hz, 1H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 5.21 (d, *J* = 22.1 Hz, 1H), 5.06 (d, *J* = 22.1 Hz, 1H), 1.02 (d, *J* = 8.0 Hz, 10H), 0.75 (d, *J* = 8.2 Hz, 10H). ¹³C NMR (151 MHz, CD₂Cl₂) δ 177.30, 167.86, 165.58, 165.40, 153.09, 145.48, 142.19 (d, *J* = 3.2 Hz), 138.98, 129.30–129.19 (m), 128.89, 128.15 (d, *J* = 221.6 Hz), 127.42, 127.27, 124.12, 123.36, 122.12 (d, *J* = 2.4 Hz), 56.64, 14.86 (d, *J* = 24.2 Hz), 12.62 (d, *J* = 26.5 Hz). ³¹P NMR (162 MHz, CD₂Cl₂) δ -15.83 (d, *J* = 170.2 Hz), -18.38 (d, *J* = 168.1 Hz). IR (cm⁻¹) 1886.6, 1809.8, 1102.0, 944, 892.5, 726.3, 669, 630. HRMS calcd. For C₂₁H₂₉N₂O₃P₂W⁺ [M+H]⁺: 603.1157, Found: 603.1157. X-ray (CCDC 2045639).

Inside an argon-filled glovebox, W(MeCN)₃(CO)₃ (40 mg, 0.102 mmol) and **SM-1** (30 mg, 0.102 mmol) were added to a 20 mL vial equipped with magnetic stir bar and dissolved in 3 mL of THF. The stir rate was set to 1000 rpm and stirred for 2 h at 25 °C. After 2 h, silver trifluoromethanesulfonate (26 mg, 0.102 mmol), potassium tert-butoxide (11.5 mg, 0.102 mmol), and 18-crown-6 (27 mg, 0.102 mmol) were added, the vial was removed from the glovebox and allowed to stir for 48 h. The crude material was filtered through celite and GCMS analysis of the crude material showed **P-1** and small amounts of proto-demetalated material. The product was isolated by PTLC (1:1 acetone:hexanes) to afford 15 mg (76% yield) of **P-1** as a colorless oil.

This intermediate is detecting *in situ*. Upon evaporation of solvent a dark brown oil resulted and various attempts at crystallization were unsuccessful resulting only in formation of oils or decomposition to form **P-1** in some cases. ¹H NMR (600 MHz, THF) δ 12.15 (s, 1H), 8.82 (d, *J* = 5.7 Hz, 1H), 7.87 (td, *J* = 7.7, 1.6 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.37–7.28 (m, 1H), 5.01 (d, *J* = 12.0 Hz, 2H), 3.50 (dt, *J* = 17.3, 6.0 Hz, 1H), 3.32–3.19 (m, 1H), 2.50 (dt, *J* = 11.9, 6.1 Hz, 1H), 2.41 (ddd, *J* = 11.3, 8.0, 5.8 Hz, 1H). ¹³C NMR (151 MHz, THF) δ 175.37, 164.46, 153.54, 139.81, 124.98, 123.04, 55.26, 42.57, 5.83. IR (cm⁻¹) 1989.5, 1886.7, 1857.6, 1611.9, 1403.7, 1232.6, 1090, 887.8, 763.9, 628.1. The parent compound could not be detected by HRMS, with the major mass signal being the organic product below.

¹H NMR (600 MHz, CDCl₃) δ 8.54 (dt, *J* = 5.0, 1.4 Hz, 1H), 7.68 (td, *J* = 7.7, 1.8 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.23–7.19 (m, 1H), 4.85 (s, 2H), 2.82 (s, 4H). **¹³C NMR** (151 MHz, CDCl₃) δ 177.17, 154.40, 149.52, 137.81, 122.91, 122.31, 43.45, 28.50. **HRMS** calcd. For C₁₀H₁₁N₂O₂⁺ [M]⁺: 191.0815, Found 191.0815.

MONITORING REACTION PROGRESS OF FORMATION OF 2a

Scheme S4 Catalytic reaction stopped early to detect isomerized intermediates

The following reaction was run to determine the buildup of intermediate alkenes. The alkene **1a** (38 mg, 0.2 mmol) was subject to General Procedure A with an abridged reaction time of 12 h. The crude material was then analyzed by ^1H NMR using CBr_2H_2 as an internal standard. The presence of internal alkenes suggests that the substrate can dissociate from the catalyst during the course of the isomerization/carbonylation sequence.

DETERMINATION OF DEUTERIUM INCORPORATION

Deuterium Labeling Procedure: Inside an argon-filled glovebox (O_2 levels between 35.0–55.0 ppm, H_2O levels unknown), an oven dried 6-mL vial containing a Teflon-coated magnetic stir bar was charged with $W(CO)_6$ (36 mg, 0.1 mmol), the alkene of interest (0.1 mmol), d_4 -methanol (75 μ L, 1.00 mmol) and toluene (1.0 mL), with care taken to ensure that the solids on the wall were washed into the bottom of the tube. The vial was sealed tightly with a disposable cap and electric tape. The vial was placed in a preheated oil bath and allowed to heat for the allotted amount of time. The vessel was allowed to cool to room temperature and was then carefully vented. The crude reaction mixture was diluted with acetone and filtered through a plug of celite and evaporated to dryness. The crude material was purified by flash silica column chromatography using 30–40% acetone:hexanes, and the purified product was analyzed by 1H NMR to determine the site(s) and extent of deuterium incorporation.

Deuterium Labeling Control: Inside an argon-filled glovebox (O_2 levels between 35.0–55.0 ppm, H_2O levels unknown), a J. Young tube, was charged with alkene **1a** (0.1 mmol), MeOD (37 μ L, 1.00 mmol), and d_8 -toluene (1.0 mL). The tube was heated to 150 $^{\circ}C$ for 1 h and was then allowed to cool to room temperature. 1H NMR analysis of the crude mixture showed partial chemical shift overlap of the N–H proton with one aromatic proton. Nevertheless, the integration of these two protons together was 1.02 H, showing that the conditions used in the following experiments for in situ N–H to N–D exchange provide sufficiently high levels of D incorporation. The 1H NMR data for these experiments is shown below.

Figure S5 The top spectra corresponds to the **1xa** in d_8 -toluene. The bottom spectra is **1xa** in d_8 -toluene with 10 equiv MeOD after heating to 150 °C for 1 h.

All compounds were analyzed by quantitative ^1H NMR using standard protocols outlined by Bruker, and the integral values below are reported as their relative quantities. d_6 -DMSO or C_6D_6 were used as the solvent of choice, as the water and grease chemical shifts in these solvents did not overlap with the peaks of interest in the compound being analyzed. The ^{13}C NMR spectra showed several peaks with low signal intensity due to the high levels of deuterium incorporation and the presence of multiple deuterium atoms per molecule; therefore, this spectral data is not included below. ^{13}C NMR spectral data for the corresponding non-deuterated products are given above.

^1H NMR (600 MHz, CDCl_3) δ 8.58–8.42 (m, 0.98H), 7.63 (td, $J = 7.7, 1.8$ Hz, 1.03H), 7.22 (d, $J = 7.8$ Hz, 0.97H), 7.16 (dd, $J = 7.6, 4.9$ Hz, 1.00H), 4.81 (s, 1.98H), 3.07–2.85 (m, 1.64H, **a**), 2.44–2.36 (m, 0.92H, **b**), 1.41–1.34 (m, 2.10H, **c**).

^1H NMR (600 MHz, d_6 -DMSO) δ 8.46 (d, $J = 4.9$ Hz, 1.18H), 7.76 (td, $J = 7.7, 1.8$ Hz, 1.00H), 7.27 (t, $J = 6.5$ Hz, 2.00H), 4.66 (s, 1.96H), 2.97–2.84 (m, 1.66H, **a,b**), 1.72 (d, $J = 13.9$ Hz, 0.45H, **c**), 1.48 (dt, $J = 15.3, 6.6$ Hz, 0.55H, **c**), 1.37 (dq, $J = 13.7, 7.1, 6.5$ Hz, 1.21H, **d**), 0.89 (d, $J = 8.4$ Hz, 3.00H, **e**).

^1H NMR (600 MHz, C_6D_6) δ 8.35 (d, $J = 6.0$ Hz, 1.00H), 6.96 (td, $J = 7.6, 1.8$ Hz, 1.00H), 6.81 (d, $J = 7.8$ Hz, 1.00H), 6.53 (dd, $J = 7.5, 4.8$ Hz, 0.99H), 4.73 (s, 1.95H), 2.24–2.10 (m, 1.52H, **a**), 1.89–1.80 (m, 0.97H, **b**), 1.66–1.50 (m, 0.41H, **c**), 1.38 (m, 0.70H, **c**), 1.14–0.89 (m, 1.61H, **c**), 0.65 (q, $J = 10.2, 9.1$ Hz, 2.04H, **d**).

^1H NMR (600 MHz, C_6D_6) δ 8.38–8.24 (m, 0.95H), 6.94 (td, $J = 7.7, 1.8$ Hz, 1.01H), 6.76 (d, $J = 7.8$ Hz, 0.96H), 6.51 (dd, $J = 7.5, 4.8$ Hz, 1.00H), 4.78–4.64 (m, 1.98H), 2.04 (d, $J = 7.5$ Hz, 0.38H,

b), 1.78–1.64 (m, 0.37H, **c**), 1.29–1.19 (m, 0.44H, **c**), 1.09 (d, $J = 1.8$ Hz, 2.94H, **a**), 1.00 (s, 2.83H, **a**), 0.91 (m, 2.37H, **d**).

Scheme S5 Potential pathway that can lead to multiple deuterium incorporations on the same molecule. Substrate **1c** was used as a model for this scheme, but an analogous pathway with the other molecules examined would lead to multiple deuterium per molecule.

DETERMINATION OF ENANTIOMERIC EXCESS OF COMPOUNDS **2e** AND DG7-P

Scheme S6 Synthesis and isolation of both diastereomers of **(3R)-2e**

Figure S6 Mixing of both enantiomers to create the racemic mixture for chiral SFC analysis

Two samples of product **2e** were synthesized according to General Procedure A starting from either the *(R)*- or *(S)*-configured starting material. The *(3R)*- and *(3S)*-configured products (**2e**) were isolated by reverse phase HPLC, which allowed for separation of the major and minor diastereomers, and the enantiomeric excess of both diastereomers was then determined. The samples were analyzed on a Waters UPC2 SFC with a Daicel IC (major diastereomer) and Daicel IA (minor diastereomer) column (3 μm , 4.6 $\times$ 250 mm) under isocratic conditions (4 mL/min, 35% MeOH / CO₂, 1600 psi backpressure) at 30 $^{\circ}\text{C}$. The enantiomers were detected by UV light (260 nm). “Racemic” samples of both the major and the minor diastereomers were made by preparing a 1 mg/mL solution of the major and minor products from arising from each of the enantiomeric starting materials and combining them in equal portions; deviation from 0% ee was due to weighing errors. The major diastereomer of **2e** was found to be enantiomerically pure (98% ee by SFC) starting from either the *(R)*- or *(S)*-configured starting material. The minor diastereomer of **2e** was found to have 52% ee starting from the *(S)*-configured starting material.

Entry	% Area Ent1	% Area Ent2	ee	Area Ent1	Area Ent2
2e major (“racemic”)	55.94	44.06	11.88	325658	256479
2e minor (“racemic”)	67.35	32.65	34.70	172413	83582

Table S2 Integrations for “racemic” samples of major and minor diastereomers of **2e**

Figure S7 “Racemic” sample of the major diastereomer of **2e**

Figure S8 “Racemic” sample of minor diastereomer of **2e**

Entry	% Area Ent1	% Area Ent2	ee	Area Ent1	Area Ent2
(3 <i>S</i>)- 2e major	99.04	0.96	98.08	275520	2665

Table S3 Integrations for (3*S*)-**2e** (major diastereomer)

Figure S9 Chromatogram for major diastereomer of (3*S*)-**2e**

Entry	% Area Ent1	% Area Ent2	ee	Area Ent1	Area Ent2
(3 <i>S</i>)- 2e minor	75.83	24.17	51.66	230606	73507

Table S4 Integration for minor diastereomer of (3*S*)-**2e**.

Figure S10 Chromatogram for minor diastereomer of (3*S*)-**2e**.

Racemic and enantioenriched samples of compound **DG7-SM** were synthesized according to General Procedure C from (rac)- and (*S*)-1-(pyridin-2-yl)ethan-1-amine. The compounds were then used as starting materials in the carbonylation reaction according to General Procedure A. Products from both reactions were isolated by flash silica chromatography. The racemic product was analyzed on a Waters UPC2 SFC with a Daicel CEL1 column (3 μ m, 4.6 $\times$ 250 mm) under isocratic conditions (4 mL/min, 3% IPA/ CO₂, 1600 psi backpressure) at 30 °C. Separation conditions were able to all four diastereomers in a single run. The two sets of enantiomers were detected by UV light (212 nm). When the (*S*)-configured starting material was used, both major and minor diastereomers were found to be enantiomerically pure (>99% *ee* by SFC).

Entry	%Area Ent_1	% Area Ent_2	<i>ee</i>	Area Ent_1	Area Ent_2
DG7-P major (racemic)	59.18	49.82	0.36	122446	121560
DG7-P minor (racemic)	49.87	50.13	-0.27	23616	23742

Table S5 Integration for the four diastereomers of (*rac*)-**2aa** . Using this separation method, the diastereomeric ratio (d.r. = 5:1) was found to be consistent with ¹H NMR data.

Figure S11 Separation of the four diastereomers of (*rac*)-**2aa**. The peaks labeled EntB_1 and EntB_2 correspond to the major diastereomers.

Figure S12 Separation of the four diastereomers of (*rac*)-**2aa**. The peaks labeled EntA_1 and EntA_2 correspond to the minor diastereomers.

Entry	% Area Ent 1	% Area Ent 2	ee	Area Ent 1	Area Ent 2
(<i>S</i>)- DG7-P major	n.d.	100.00	100.00	n.d.	320557
(<i>S</i>)- DG7-P minor	n.d.	100.00	100.00	n.d.	69303

Table S6 Integration for both diastereomers of the racemic mixture **2aa**. Using this separation method, the diastereomeric ratio (d.r.= 5:1) was also confirmed to be consistent with ¹H NMR data. n.d. = not detectable.

Figure S13 Chromatogram of product (*S*)-**DG7-P** from the reaction run with enantiopure starting material, (*S*)-**DG7-SM**. The major diastereomer (EntB_2) and minor diastereomer (retention time: 7.686) were determined to be >99% ee with no detectable amounts of opposite enantiomer.

X-RAY CRYSTALOGRAPHY

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker X8 APEX II CCD diffractometer equipped with Mo K $_{\alpha}$ radiation ($\lambda = 0.71073$). Crystals of the subject compound were used as received (grown from Ethylacetate/Hexane). A 0.250 x 0.20 x 0.20 mm colorless plate was mounted on a Cryoloop with Paratone oil.

Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ω scans. Crystal-to-detector distance was 40 mm using exposure time 5.0s (depending on the detector 2θ position) with a scan width of 0.70° . Data collection was 100.0% complete to 25.242° in θ . A total of 13272 reflections were collected covering the indices, $-9 \leq h \leq 9$, $-11 \leq k \leq 11$, $-12 \leq l \leq 12$. 2651 reflections were found to be symmetry independent, with a R_{int} of 0.0507. Indexing and unit cell refinement indicated a Primitive, **Triclinic** lattice. The space group was found to be ***P*-1**. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Crystallographic data are summarized in Table S6.

Table S7 Crystal data and structure refinement for **2u** (CCDC 2008992).

Empirical formula	C ₁₄ H ₁₆ N ₂ O ₂	
Molecular formula	C ₁₄ H ₁₆ N ₂ O ₂	
Formula weight	244.29	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.7012(7) Å	α = 64.252(2)°.
	b = 9.2939(8) Å	β = 83.457(2)°.
	c = 9.4109(8) Å	γ = 85.058(2)°.
Volume	602.24(9) Å ³	
Z	2	
Density (calculated)	1.347 Mg/m ³	
Absorption coefficient	0.091 mm ⁻¹	
F(000)	260	

Crystal size	0.25 x 0.2 x 0.2 mm ³
Crystal color, habit	colorless plate
Theta range for data collection	2.412 to 27.103°.
Index ranges	-9<=h<=9, -11<=k<=11, -12<=l<=12
Reflections collected	13272
Independent reflections	2651 [R(int) = 0.0507]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.7011
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2651 / 0 / 163
Goodness-of-fit on F ²	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0371, wR2 = 0.0913
R indices (all data)	R1 = 0.0428, wR2 = 0.0961
Largest diff. peak and hole	0.382 and -0.189 e.Å ⁻³

Table S8 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2u**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	8146(1)	3162(1)	1259(1)	21(1)
O(2)	4026(1)	2716(1)	5292(1)	21(1)
N(1)	6280(1)	3191(1)	3346(1)	15(1)
N(2)	8992(1)	1753(1)	5292(1)	18(1)
C(1)	9926(2)	858(2)	6521(2)	21(1)
C(2)	10155(2)	1285(2)	7726(1)	22(1)
C(3)	9368(2)	2702(2)	7675(2)	22(1)
C(4)	8409(2)	3651(2)	6402(2)	20(1)
C(5)	8263(2)	3135(1)	5242(1)	15(1)
C(6)	7290(2)	4157(1)	3800(1)	17(1)
C(7)	6861(2)	2688(1)	2171(1)	15(1)
C(8)	4694(2)	2559(1)	4137(1)	15(1)
C(9)	5634(2)	1428(1)	2323(1)	16(1)
C(10)	5386(2)	1319(1)	792(1)	19(1)
C(11)	4167(2)	2656(1)	-252(1)	18(1)
C(12)	2422(2)	2686(2)	680(1)	19(1)
C(13)	2674(2)	2999(1)	2105(1)	17(1)
C(14)	3974(2)	1773(1)	3222(1)	15(1)

Table S9 Bond lengths [Å] and angles [°] for **2u**.

O(1)-C(7)	1.2099(15)	C(14)-H(14)	1.0000
O(2)-C(8)	1.2113(15)		
N(1)-C(6)	1.4570(14)	C(7)-N(1)-C(6)	124.04(10)
N(1)-C(7)	1.3937(15)	C(8)-N(1)-C(6)	123.12(10)
N(1)-C(8)	1.3882(15)	C(8)-N(1)-C(7)	112.63(10)
N(2)-C(1)	1.3410(16)	C(5)-N(2)-C(1)	117.20(10)
N(2)-C(5)	1.3407(15)	N(2)-C(1)-H(1)	118.2
C(1)-H(1)	0.9500	N(2)-C(1)-C(2)	123.53(12)
C(1)-C(2)	1.3867(18)	C(2)-C(1)-H(1)	118.2
C(2)-H(2)	0.9500	C(1)-C(2)-H(2)	120.7
C(2)-C(3)	1.3859(19)	C(3)-C(2)-C(1)	118.66(11)
C(3)-H(3)	0.9500	C(3)-C(2)-H(2)	120.7
C(3)-C(4)	1.3887(17)	C(2)-C(3)-H(3)	120.7
C(4)-H(4)	0.9500	C(2)-C(3)-C(4)	118.55(11)
C(4)-C(5)	1.3882(17)	C(4)-C(3)-H(3)	120.7
C(5)-C(6)	1.5148(16)	C(3)-C(4)-H(4)	120.6
C(6)-H(6A)	0.9900	C(5)-C(4)-C(3)	118.81(11)
C(6)-H(6B)	0.9900	C(5)-C(4)-H(4)	120.6
C(7)-C(9)	1.5157(16)	N(2)-C(5)-C(4)	123.23(11)
C(8)-C(14)	1.5190(16)	N(2)-C(5)-C(6)	116.00(10)
C(9)-H(9)	1.0000	C(4)-C(5)-C(6)	120.74(11)
C(9)-C(10)	1.5220(15)	N(1)-C(6)-C(5)	111.63(9)
C(9)-C(14)	1.5405(16)	N(1)-C(6)-H(6A)	109.3
C(10)-H(10A)	0.9900	N(1)-C(6)-H(6B)	109.3
C(10)-H(10B)	0.9900	C(5)-C(6)-H(6A)	109.3
C(10)-C(11)	1.5295(16)	C(5)-C(6)-H(6B)	109.3
C(11)-H(11A)	0.9900	H(6A)-C(6)-H(6B)	108.0
C(11)-H(11B)	0.9900	O(1)-C(7)-N(1)	124.55(11)
C(11)-C(12)	1.5236(17)	O(1)-C(7)-C(9)	128.33(11)
C(12)-H(12A)	0.9900	N(1)-C(7)-C(9)	107.07(10)
C(12)-H(12B)	0.9900	O(2)-C(8)-N(1)	123.90(11)
C(12)-C(13)	1.5257(16)	O(2)-C(8)-C(14)	128.66(11)
C(13)-H(13A)	0.9900	N(1)-C(8)-C(14)	107.33(9)
C(13)-H(13B)	0.9900	C(7)-C(9)-H(9)	106.9
C(13)-C(14)	1.5517(16)	C(7)-C(9)-C(10)	115.65(10)

C(7)-C(9)-C(14)	103.22(9)
C(10)-C(9)-H(9)	106.9
C(10)-C(9)-C(14)	116.55(10)
C(14)-C(9)-H(9)	106.9
C(9)-C(10)-H(10A)	109.1
C(9)-C(10)-H(10B)	109.1
C(9)-C(10)-C(11)	112.68(10)
H(10A)-C(10)-H(10B)	107.8
C(11)-C(10)-H(10A)	109.1
C(11)-C(10)-H(10B)	109.1
C(10)-C(11)-H(11A)	109.6
C(10)-C(11)-H(11B)	109.6
H(11A)-C(11)-H(11B)	108.1
C(12)-C(11)-C(10)	110.28(10)
C(12)-C(11)-H(11A)	109.6
C(12)-C(11)-H(11B)	109.6
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
C(11)-C(12)-C(13)	110.93(10)
H(12A)-C(12)-H(12B)	108.0
C(13)-C(12)-H(12A)	109.5
C(13)-C(12)-H(12B)	109.5
C(12)-C(13)-H(13A)	109.0
C(12)-C(13)-H(13B)	109.0
C(12)-C(13)-C(14)	113.00(10)
H(13A)-C(13)-H(13B)	107.8
C(14)-C(13)-H(13A)	109.0
C(14)-C(13)-H(13B)	109.0
C(8)-C(14)-C(9)	102.43(9)
C(8)-C(14)-C(13)	107.50(9)
C(8)-C(14)-H(14)	111.2
C(9)-C(14)-C(13)	112.92(9)
C(9)-C(14)-H(14)	111.2
C(13)-C(14)-H(14)	111.2

Table S10 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2u**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	18(1)	25(1)	19(1)	-10(1)	0(1)	-1(1)
O(2)	25(1)	23(1)	16(1)	-11(1)	1(1)	-1(1)
N(1)	16(1)	14(1)	14(1)	-7(1)	-4(1)	0(1)
N(2)	19(1)	18(1)	17(1)	-7(1)	-2(1)	1(1)
C(1)	19(1)	20(1)	20(1)	-6(1)	-2(1)	2(1)
C(2)	17(1)	27(1)	16(1)	-4(1)	-4(1)	-2(1)
C(3)	22(1)	31(1)	17(1)	-12(1)	-3(1)	-6(1)
C(4)	22(1)	20(1)	20(1)	-11(1)	-3(1)	-1(1)
C(5)	14(1)	16(1)	15(1)	-6(1)	-1(1)	-2(1)
C(6)	21(1)	14(1)	16(1)	-7(1)	-5(1)	-1(1)
C(7)	17(1)	15(1)	13(1)	-6(1)	-6(1)	4(1)
C(8)	19(1)	12(1)	14(1)	-4(1)	-4(1)	2(1)
C(9)	20(1)	13(1)	14(1)	-6(1)	-4(1)	2(1)
C(10)	26(1)	18(1)	17(1)	-10(1)	-5(1)	1(1)
C(11)	23(1)	19(1)	14(1)	-6(1)	-4(1)	-1(1)
C(12)	19(1)	21(1)	17(1)	-6(1)	-6(1)	-3(1)
C(13)	15(1)	20(1)	17(1)	-7(1)	-3(1)	-1(1)
C(14)	18(1)	14(1)	13(1)	-5(1)	-1(1)	-2(1)

Table S11 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **2u**.

	x	y	z	U(eq)
H(1)	10460	-121	6569	25
H(2)	10838	618	8570	26
H(3)	9481	3019	8493	27
H(4)	7864	4635	6327	24
H(6A)	6492	4937	4032	20
H(6B)	8139	4764	2906	20
H(9)	6146	370	3050	19
H(10A)	4900	273	1051	23
H(10B)	6540	1370	192	23
H(11A)	4717	3698	-632	22
H(11B)	3970	2482	-1186	22
H(12A)	1866	1649	1047	23
H(12B)	1633	3534	-18	23
H(13A)	1528	2963	2711	21
H(13B)	3111	4087	1724	21
H(14)	3388	763	3955	18

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker APEX II Ultra CCD diffractometer equipped with Mo K $_{\alpha}$ radiation ($\lambda = 0.71073$). Crystals of the subject compound were used as received (grown from THF/Et₂O). A 0.000 x 0.075 x 0.070 mm yellow block was mounted on a Cryoloop with Paratone oil.

Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 45 mm using exposure time 1.0s (depending on the detector 2θ position) with a scan width of 0.75° . Data collection was 100.0% complete to 25.242° in θ . A total of 18321 reflections were collected covering the indices, $-12 \leq h \leq 12$, $-13 \leq k \leq 13$, $-14 \leq l \leq 14$. 4457 reflections were found to be symmetry

independent, with a R_{int} of 0.0405. Indexing and unit cell refinement indicated a **Primitive, Triclinic** lattice.

The space group was found to be **P-1**. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Crystallographic data are summarized in Table S10.

Notes: Excellent data and refinement, THF solvent “hold” by OH bond

Table S12 Crystal data and structure refinement for **W-2** (CCDC 2020047).

Empirical formula	C ₂₀ H ₁₈ Br I N ₂ O ₅ W	
Molecular formula	C ₁₆ H ₁₀ Br I N ₂ O ₄ W, C ₄ H ₈ O	
Formula weight	757.02	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.8119(8) Å	α = 115.3720(10)°.
	b = 11.1754(9) Å	β = 96.9760(10)°.
	c = 11.6513(10) Å	γ = 102.9580(10)°.
Volume	1090.09(16) Å ³	
Z	2	
Density (calculated)	2.306 Mg/m ³	
Absorption coefficient	8.581 mm ⁻¹	
F(000)	708	
Crystal size	0.1 x 0.075 x 0.07 mm ³	
Crystal color, habit	yellow block	
Theta range for data collection	1.996 to 26.369°.	
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14	
Reflections collected	18321	
Independent reflections	4457 [R(int) = 0.0405]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.4915 and 0.3653
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4457 / 0 / 272
Goodness-of-fit on F^2	1.040
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0178$, $wR2 = 0.0445$
R indices (all data)	$R1 = 0.0188$, $wR2 = 0.0450$
Largest diff. peak and hole	0.716 and -0.453 e. $\text{\AA}^{-3}$

Table S13 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **W-2**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
W(1)	4042(1)	3810(1)	1908(1)	12(1)
I(1)	4806(1)	2724(1)	3625(1)	18(1)
Br(1)	270(1)	7380(1)	1743(1)	25(1)
O(1)	1355(2)	1142(2)	248(2)	26(1)
O(2)	3214(2)	3837(2)	-747(2)	23(1)
O(3)	1720(2)	4316(2)	3570(2)	22(1)
O(4)	7294(2)	7851(2)	3962(2)	19(1)
N(1)	5787(3)	2995(3)	1101(2)	15(1)
N(2)	6069(3)	5471(2)	2947(2)	14(1)
C(1)	2348(3)	2104(3)	864(3)	17(1)
C(2)	3541(3)	3866(3)	229(3)	17(1)
C(3)	2578(3)	4155(3)	2989(3)	16(1)
C(4)	5542(3)	1760(3)	48(3)	18(1)
C(5)	6612(3)	1154(3)	-289(3)	20(1)
C(6)	8007(3)	1866(3)	477(3)	22(1)
C(7)	8282(3)	3160(3)	1539(3)	21(1)
C(8)	7156(3)	3701(3)	1829(3)	16(1)
C(9)	7401(3)	5095(3)	2998(3)	18(1)
C(10)	6112(3)	6755(3)	3338(3)	16(1)
C(11)	4755(3)	6986(3)	3007(3)	16(1)
C(12)	3579(3)	5770(3)	2241(3)	15(1)
C(13)	2252(3)	5934(3)	1847(3)	17(1)
C(14)	2135(3)	7248(3)	2240(3)	18(1)
C(15)	3289(3)	8457(3)	3008(3)	20(1)
C(16)	4605(3)	8309(3)	3379(3)	19(1)
O(5)	9481(2)	7775(3)	5427(2)	30(1)
C(17)	10787(4)	7435(4)	5201(4)	30(1)
C(18)	11948(4)	8816(4)	5819(4)	35(1)
C(19)	11499(4)	9634(4)	7068(4)	31(1)
C(20)	9867(5)	9026(5)	6654(4)	54(1)

Table S14 Bond lengths [Å] and angles [°] for **W-2**.

W(1)-I(1)	2.8567(3)	N(2)-W(1)-N(1)	72.41(9)
W(1)-N(1)	2.237(2)	N(2)-W(1)-C(12)	73.43(10)
W(1)-N(2)	2.168(2)	C(1)-W(1)-I(1)	89.80(9)
W(1)-C(1)	1.994(3)	C(1)-W(1)-N(1)	99.72(10)
W(1)-C(2)	1.989(3)	C(1)-W(1)-N(2)	171.88(10)
W(1)-C(3)	2.018(3)	C(1)-W(1)-C(3)	76.73(12)
W(1)-C(12)	2.218(3)	C(1)-W(1)-C(12)	114.03(11)
Br(1)-C(14)	1.908(3)	C(2)-W(1)-I(1)	158.16(8)
O(1)-C(1)	1.149(4)	C(2)-W(1)-N(1)	84.48(10)
O(2)-C(2)	1.128(4)	C(2)-W(1)-N(2)	103.23(10)
O(3)-C(3)	1.141(4)	C(2)-W(1)-C(1)	77.52(12)
O(4)-C(10)	1.330(4)	C(2)-W(1)-C(3)	114.21(11)
N(1)-C(4)	1.340(4)	C(2)-W(1)-C(12)	68.88(11)
N(1)-C(8)	1.350(4)	C(3)-W(1)-I(1)	79.24(8)
N(2)-C(9)	1.461(4)	C(3)-W(1)-N(1)	159.12(10)
N(2)-C(10)	1.295(4)	C(3)-W(1)-N(2)	109.86(10)
C(4)-C(5)	1.381(4)	C(3)-W(1)-C(12)	68.72(11)
C(5)-C(6)	1.383(5)	C(12)-W(1)-I(1)	132.94(7)
C(6)-C(7)	1.381(5)	C(12)-W(1)-N(1)	129.77(9)
C(7)-C(8)	1.384(4)	C(4)-N(1)-W(1)	123.90(19)
C(8)-C(9)	1.508(4)	C(4)-N(1)-C(8)	118.2(2)
C(10)-C(11)	1.451(4)	C(8)-N(1)-W(1)	117.20(19)
C(11)-C(12)	1.408(4)	C(9)-N(2)-W(1)	118.24(18)
C(11)-C(16)	1.399(4)	C(10)-N(2)-W(1)	120.3(2)
C(12)-C(13)	1.405(4)	C(10)-N(2)-C(9)	120.6(3)
C(13)-C(14)	1.376(4)	O(1)-C(1)-W(1)	178.0(3)
C(14)-C(15)	1.393(4)	O(2)-C(2)-W(1)	176.8(3)
C(15)-C(16)	1.380(4)	O(3)-C(3)-W(1)	178.0(3)
O(5)-C(17)	1.440(4)	N(1)-C(4)-C(5)	123.0(3)
O(5)-C(20)	1.435(4)	C(4)-C(5)-C(6)	118.6(3)
C(17)-C(18)	1.503(5)	C(7)-C(6)-C(5)	118.9(3)
C(18)-C(19)	1.531(5)	C(6)-C(7)-C(8)	119.5(3)
C(19)-C(20)	1.517(5)	N(1)-C(8)-C(7)	121.7(3)
		N(1)-C(8)-C(9)	116.9(2)
N(1)-W(1)-I(1)	80.18(6)	C(7)-C(8)-C(9)	121.3(3)
N(2)-W(1)-I(1)	86.89(6)	N(2)-C(9)-C(8)	108.7(2)

O(4)-C(10)-C(11)	118.3(3)
N(2)-C(10)-O(4)	125.5(3)
N(2)-C(10)-C(11)	116.2(3)
C(12)-C(11)-C(10)	115.1(3)
C(16)-C(11)-C(10)	123.5(3)
C(16)-C(11)-C(12)	121.4(3)
C(11)-C(12)-W(1)	114.6(2)
C(13)-C(12)-W(1)	127.8(2)
C(13)-C(12)-C(11)	117.5(3)
C(14)-C(13)-C(12)	119.8(3)
C(13)-C(14)-Br(1)	117.1(2)
C(13)-C(14)-C(15)	123.2(3)
C(15)-C(14)-Br(1)	119.7(2)
C(16)-C(15)-C(14)	117.6(3)
C(15)-C(16)-C(11)	120.6(3)
C(20)-O(5)-C(17)	107.2(3)
O(5)-C(17)-C(18)	104.8(3)
C(17)-C(18)-C(19)	101.7(3)
C(20)-C(19)-C(18)	102.8(3)
O(5)-C(20)-C(19)	108.2(3)

Table S15 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **W-2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
W(1)	10(1)	12(1)	12(1)	5(1)	3(1)	2(1)
I(1)	21(1)	19(1)	16(1)	10(1)	5(1)	6(1)
Br(1)	21(1)	26(1)	32(1)	15(1)	7(1)	13(1)
O(1)	17(1)	18(1)	32(1)	6(1)	2(1)	0(1)
O(2)	24(1)	28(1)	17(1)	10(1)	9(1)	9(1)
O(3)	20(1)	28(1)	23(1)	13(1)	11(1)	9(1)
O(4)	14(1)	16(1)	22(1)	7(1)	0(1)	1(1)
N(1)	13(1)	17(1)	17(1)	10(1)	5(1)	5(1)
N(2)	11(1)	16(1)	14(1)	7(1)	3(1)	2(1)
C(1)	14(1)	17(1)	20(2)	8(1)	7(1)	6(1)
C(2)	11(1)	15(1)	23(2)	6(1)	6(1)	3(1)
C(3)	16(1)	16(1)	16(1)	8(1)	1(1)	3(1)
C(4)	17(2)	19(2)	17(2)	7(1)	4(1)	4(1)
C(5)	26(2)	18(2)	21(2)	9(1)	10(1)	11(1)
C(6)	23(2)	25(2)	26(2)	15(1)	14(1)	14(1)
C(7)	16(2)	27(2)	26(2)	16(1)	7(1)	8(1)
C(8)	17(1)	18(1)	16(1)	11(1)	6(1)	5(1)
C(9)	12(1)	21(2)	20(2)	9(1)	2(1)	4(1)
C(10)	18(1)	16(1)	12(1)	5(1)	5(1)	2(1)
C(11)	17(1)	17(1)	16(1)	8(1)	7(1)	5(1)
C(12)	16(1)	16(1)	12(1)	7(1)	5(1)	5(1)
C(13)	15(1)	17(1)	19(2)	7(1)	5(1)	4(1)
C(14)	18(2)	23(2)	20(2)	12(1)	6(1)	10(1)
C(15)	27(2)	15(1)	22(2)	9(1)	10(1)	8(1)
C(16)	22(2)	15(1)	17(2)	6(1)	6(1)	3(1)
O(5)	21(1)	28(1)	30(1)	6(1)	4(1)	6(1)
C(17)	22(2)	27(2)	38(2)	13(2)	6(2)	11(1)
C(18)	26(2)	38(2)	44(2)	21(2)	13(2)	11(2)
C(19)	34(2)	26(2)	30(2)	13(2)	3(2)	6(2)
C(20)	36(2)	44(2)	39(2)	-12(2)	10(2)	2(2)

Table S16 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **W-2**.

	x	y	z	U(eq)
H(4)	7919	7655	4348	28
H(4A)	4587	1280	-492	22
H(5)	6393	267	-1033	24
H(6)	8765	1471	276	26
H(7)	9237	3675	2067	26
H(9A)	7675	5044	3818	21
H(9B)	8194	5810	2983	21
H(13)	1437	5139	1311	21
H(15)	3174	9351	3267	25
H(16)	5417	9113	3893	23
H(17A)	10715	6917	4251	35
H(17B)	10987	6862	5616	35
H(18A)	11949	9263	5245	42
H(18B)	12914	8720	6024	42
H(19A)	11913	9485	7796	37
H(19B)	11804	10643	7342	37
H(20A)	9512	8815	7327	64
H(20B)	9426	9703	6557	64

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker APEX II Ultra diffractometer equipped with Mo K $_{\alpha}$ radiation ($\lambda = 0.71073$). Crystals of the subject compound were used as received (grown from THF/Pentane). A 0.160 x 0.160 x 0.060 mm yellow crystal was mounted on a Cryoloop with Paratone oil.

Data were collected in a nitrogen gas stream at 100(2) K using ϕ and π scans. Crystal-to-detector distance was 40 mm using exposure time 2.0 s (depending on the detector 2θ position) with a scan width of 0.75° . Data collection was 100.0% complete to 25.242° in θ . A total of 10663 reflections were collected. 10663 reflections were found to be symmetry independent, with a R_{int} of 0.0416. Indexing and unit cell refinement indicated a **Primitive, Triclinic** lattice. The space group was found to be ***P*-1**. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Crystallographic data are summarized in Table S15.

Notes: Excellent data and refinement.

Minor Dizo on THF.

Table S17 Crystal data and structure refinement for **W-3** (CCDC 2050458).

Empirical formula	C20 H19 I N2 O5 W	
Molecular formula	C16 H11 I N2 O4 W, C4 H8 O	
Formula weight	678.12	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.5844(7) Å	$\alpha = 114.892(2)^\circ$.
	b = 10.9537(8) Å	$\beta = 104.036(2)^\circ$.
	c = 11.6929(9) Å	$\gamma = 99.239(2)^\circ$.
Volume	1031.06(13) Å ³	
Z	2	
Density (calculated)	2.184 Mg/m ³	
Absorption coefficient	7.133 mm ⁻¹	
F(000)	640	
Crystal size	0.18 x 0.18 x 0.06 mm ³	
Crystal color, habit	yellow plate	
Theta range for data collection	2.047 to 26.021°.	
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14	
Reflections collected	10663	
Independent reflections	4065 [R(int) = 0.0416]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0937 and 0.0586	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4065 / 7 / 270	
Goodness-of-fit on F ²	1.055	

Final R indices [$I > 2\sigma(I)$]

$R_1 = 0.0248$, $wR_2 = 0.0605$

R indices (all data)

$R_1 = 0.0266$, $wR_2 = 0.0617$

Largest diff. peak and hole

1.663 and $-0.657 \text{ e.}\text{\AA}^{-3}$

Table S18 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **W-3** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
W(1)	6496(1)	6017(1)	3150(1)	18(1)
I(1)	5525(1)	7187(1)	1434(1)	28(1)
O(1)	8585(4)	5327(3)	1404(3)	34(1)
O(2)	7731(4)	5969(3)	5837(3)	35(1)
O(3)	9413(3)	8619(3)	4899(3)	31(1)
O(4)	2772(3)	2212(3)	1173(3)	28(1)
N(1)	4898(4)	7015(4)	4046(3)	20(1)
N(2)	4286(4)	4475(3)	2143(3)	19(1)
C(1)	7810(5)	5544(4)	2021(4)	26(1)
C(2)	7257(5)	5935(4)	4863(5)	25(1)
C(3)	8340(5)	7674(4)	4234(4)	22(1)
C(4)	5340(5)	8255(4)	5169(4)	23(1)
C(5)	4347(5)	8955(5)	5621(5)	32(1)
C(6)	2817(5)	8315(5)	4883(5)	36(1)
C(7)	2350(5)	7018(5)	3742(5)	33(1)
C(8)	3408(5)	6394(5)	3341(4)	23(1)
C(9)	2980(5)	5002(5)	2097(4)	25(1)
C(10)	4143(5)	3156(4)	1760(4)	21(1)
C(11)	5539(5)	2789(4)	2027(4)	24(1)
C(12)	5595(5)	1413(5)	1623(4)	28(1)
C(13)	6951(6)	1149(5)	1938(5)	35(1)
C(14)	8253(6)	2280(5)	2705(6)	36(1)
C(15)	8221(5)	3646(5)	3107(5)	32(1)
C(16)	6857(5)	3949(4)	2761(4)	23(1)
O(5)	1999(4)	-115(4)	1310(5)	48(1)
C(17)	728(5)	-16(5)	1754(5)	29(1)
C(18)	201(7)	-1364(6)	1789(6)	48(1)
C(19)	1047(16)	-2368(13)	1076(13)	33(3)
C(19A)	650(11)	-2350(12)	620(10)	33(3)
C(20)	1616(13)	-1600(8)	368(10)	34(2)
C(20A)	2267(11)	-1430(9)	1066(12)	34(2)

Table S18 Bond lengths [Å] and angles [°] for **W-3**.

W(1)-I(1)	2.8588(3)	C(15)-H(15)	0.9500
W(1)-N(1)	2.234(3)	C(15)-C(16)	1.407(6)
W(1)-N(2)	2.166(3)	O(5)-C(17)	1.437(5)
W(1)-C(1)	2.009(4)	O(5)-C(20)	1.449(8)
W(1)-C(2)	2.004(5)	O(5)-C(20A)	1.424(8)
W(1)-C(3)	1.992(4)	C(17)-H(17A)	0.9900
W(1)-C(16)	2.218(4)	C(17)-H(17B)	0.9900
O(1)-C(1)	1.141(5)	C(17)-C(18)	1.503(7)
O(2)-C(2)	1.101(5)	C(18)-H(18A)	0.9900
O(3)-C(3)	1.152(5)	C(18)-H(18B)	0.9900
O(4)-H(4)	0.8400	C(18)-H(18C)	0.9900
O(4)-C(10)	1.340(5)	C(18)-H(18D)	0.9900
N(1)-C(4)	1.339(5)	C(18)-C(19)	1.551(8)
N(1)-C(8)	1.352(5)	C(18)-C(19A)	1.552(8)
N(2)-C(9)	1.459(5)	C(19)-H(19A)	0.9900
N(2)-C(10)	1.292(5)	C(19)-H(19B)	0.9900
C(4)-H(4A)	0.9500	C(19)-C(20)	1.532(8)
C(4)-C(5)	1.382(6)	C(19A)-H(19C)	0.9900
C(5)-H(5)	0.9500	C(19A)-H(19D)	0.9900
C(5)-C(6)	1.391(7)	C(19A)-C(20A)	1.534(8)
C(6)-H(6)	0.9500	C(20)-H(20A)	0.9900
C(6)-C(7)	1.382(7)	C(20)-H(20B)	0.9900
C(7)-H(7)	0.9500	C(20A)-H(20C)	0.9900
C(7)-C(8)	1.377(6)	C(20A)-H(20D)	0.9900
C(8)-C(9)	1.500(6)		
C(9)-H(9A)	0.9900	N(1)-W(1)-I(1)	80.51(8)
C(9)-H(9B)	0.9900	N(2)-W(1)-I(1)	87.55(9)
C(10)-C(11)	1.457(6)	N(2)-W(1)-N(1)	71.83(13)
C(11)-C(12)	1.392(6)	N(2)-W(1)-C(16)	73.41(14)
C(11)-C(16)	1.410(6)	C(1)-W(1)-I(1)	79.31(13)
C(12)-H(12)	0.9500	C(1)-W(1)-N(1)	159.37(16)
C(12)-C(13)	1.373(7)	C(1)-W(1)-N(2)	111.38(15)
C(13)-H(13)	0.9500	C(1)-W(1)-C(16)	69.13(16)
C(13)-C(14)	1.386(7)	C(2)-W(1)-I(1)	158.36(12)
C(14)-H(14)	0.9500	C(2)-W(1)-N(1)	84.76(15)
C(14)-C(15)	1.375(6)	C(2)-W(1)-N(2)	102.85(15)

C(2)-W(1)-C(1)	113.29(18)	N(2)-C(9)-H(9B)	110.1
C(2)-W(1)-C(16)	68.60(16)	C(8)-C(9)-H(9A)	110.1
C(3)-W(1)-I(1)	89.60(12)	C(8)-C(9)-H(9B)	110.1
C(3)-W(1)-N(1)	98.01(14)	H(9A)-C(9)-H(9B)	108.4
C(3)-W(1)-N(2)	169.77(15)	O(4)-C(10)-C(11)	123.5(4)
C(3)-W(1)-C(1)	77.67(16)	N(2)-C(10)-O(4)	120.4(4)
C(3)-W(1)-C(2)	76.80(17)	N(2)-C(10)-C(11)	116.1(4)
C(3)-W(1)-C(16)	115.33(16)	C(12)-C(11)-C(10)	123.7(4)
C(16)-W(1)-I(1)	132.99(11)	C(12)-C(11)-C(16)	121.5(4)
C(16)-W(1)-N(1)	129.46(13)	C(16)-C(11)-C(10)	114.8(4)
C(10)-O(4)-H(4)	109.5	C(11)-C(12)-H(12)	119.8
C(4)-N(1)-W(1)	123.4(3)	C(13)-C(12)-C(11)	120.5(4)
C(4)-N(1)-C(8)	118.6(4)	C(13)-C(12)-H(12)	119.8
C(8)-N(1)-W(1)	117.6(3)	C(12)-C(13)-H(13)	120.6
C(9)-N(2)-W(1)	117.5(3)	C(12)-C(13)-C(14)	118.8(4)
C(10)-N(2)-W(1)	120.6(3)	C(14)-C(13)-H(13)	120.6
C(10)-N(2)-C(9)	121.2(3)	C(13)-C(14)-H(14)	119.2
O(1)-C(1)-W(1)	177.5(4)	C(15)-C(14)-C(13)	121.6(5)
O(2)-C(2)-W(1)	175.8(4)	C(15)-C(14)-H(14)	119.2
O(3)-C(3)-W(1)	177.4(4)	C(14)-C(15)-H(15)	119.5
N(1)-C(4)-H(4A)	118.5	C(14)-C(15)-C(16)	121.0(4)
N(1)-C(4)-C(5)	123.1(4)	C(16)-C(15)-H(15)	119.5
C(5)-C(4)-H(4A)	118.5	C(11)-C(16)-W(1)	114.8(3)
C(4)-C(5)-H(5)	121.0	C(15)-C(16)-W(1)	128.6(3)
C(4)-C(5)-C(6)	117.9(5)	C(15)-C(16)-C(11)	116.5(4)
C(6)-C(5)-H(5)	121.0	C(17)-O(5)-C(20)	103.5(5)
C(5)-C(6)-H(6)	120.3	C(20A)-O(5)-C(17)	109.8(5)
C(7)-C(6)-C(5)	119.3(4)	O(5)-C(17)-H(17A)	110.5
C(7)-C(6)-H(6)	120.3	O(5)-C(17)-H(17B)	110.5
C(6)-C(7)-H(7)	120.2	O(5)-C(17)-C(18)	105.9(4)
C(8)-C(7)-C(6)	119.5(4)	H(17A)-C(17)-H(17B)	108.7
C(8)-C(7)-H(7)	120.2	C(18)-C(17)-H(17A)	110.5
N(1)-C(8)-C(7)	121.6(4)	C(18)-C(17)-H(17B)	110.5
N(1)-C(8)-C(9)	116.2(4)	C(17)-C(18)-H(18A)	112.1
C(7)-C(8)-C(9)	122.2(4)	C(17)-C(18)-H(18B)	112.1
N(2)-C(9)-C(8)	108.2(3)	C(17)-C(18)-H(18C)	110.4
N(2)-C(9)-H(9A)	110.1	C(17)-C(18)-H(18D)	110.4

C(17)-C(18)-C(19)	106.8(5)
C(17)-C(18)-C(19A)	98.2(6)
H(18A)-C(18)-H(18B)	109.8
H(18C)-C(18)-H(18D)	108.6
C(19)-C(18)-H(18C)	110.4
C(19)-C(18)-H(18D)	110.4
C(19A)-C(18)-H(18A)	112.1
C(19A)-C(18)-H(18B)	112.1
C(18)-C(19)-H(19A)	111.9
C(18)-C(19)-H(19B)	111.9
H(19A)-C(19)-H(19B)	109.6
C(20)-C(19)-C(18)	99.2(7)
C(20)-C(19)-H(19A)	111.9
C(20)-C(19)-H(19B)	111.9
C(18)-C(19A)-H(19C)	112.1
C(18)-C(19A)-H(19D)	112.1
H(19C)-C(19A)-H(19D)	109.8
C(20A)-C(19A)-C(18)	98.2(7)
C(20A)-C(19A)-H(19C)	112.1
C(20A)-C(19A)-H(19D)	112.1
O(5)-C(20)-C(19)	104.8(8)
O(5)-C(20)-H(20A)	110.8
O(5)-C(20)-H(20B)	110.8
C(19)-C(20)-H(20A)	110.8
C(19)-C(20)-H(20B)	110.8
H(20A)-C(20)-H(20B)	108.9
O(5)-C(20A)-C(19A)	99.9(7)
O(5)-C(20A)-H(20C)	111.8
O(5)-C(20A)-H(20D)	111.8
C(19A)-C(20A)-H(20C)	111.8
C(19A)-C(20A)-H(20D)	111.8
H(20C)-C(20A)-H(20D)	109.5

Table S19 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **W-3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
W(1)	21(1)	14(1)	19(1)	6(1)	10(1)	4(1)
I(1)	43(1)	20(1)	21(1)	11(1)	14(1)	6(1)
O(1)	35(2)	31(2)	34(2)	10(2)	22(2)	5(1)
O(2)	61(2)	25(2)	29(2)	16(2)	25(2)	13(2)
O(3)	27(2)	23(2)	38(2)	11(2)	12(1)	1(1)
O(4)	31(2)	18(2)	25(2)	9(1)	4(1)	-3(1)
N(1)	21(2)	21(2)	19(2)	12(2)	8(1)	6(1)
N(2)	23(2)	15(2)	15(2)	7(1)	5(1)	1(1)
C(1)	28(2)	15(2)	26(2)	4(2)	10(2)	-1(2)
C(2)	21(2)	11(2)	35(3)	6(2)	4(2)	6(2)
C(3)	28(2)	16(2)	22(2)	7(2)	14(2)	7(2)
C(4)	27(2)	21(2)	22(2)	10(2)	11(2)	7(2)
C(5)	43(3)	26(3)	35(2)	15(2)	24(2)	15(2)
C(6)	32(3)	35(3)	59(3)	29(3)	28(2)	20(2)
C(7)	23(2)	30(3)	51(3)	24(2)	13(2)	11(2)
C(8)	23(2)	25(2)	29(2)	20(2)	11(2)	8(2)
C(9)	21(2)	24(2)	27(2)	15(2)	2(2)	2(2)
C(10)	25(2)	20(2)	14(2)	7(2)	7(2)	-1(2)
C(11)	36(2)	17(2)	21(2)	7(2)	17(2)	8(2)
C(12)	39(3)	20(2)	27(2)	9(2)	19(2)	4(2)
C(13)	47(3)	21(2)	48(3)	15(2)	34(2)	17(2)
C(14)	38(3)	26(3)	58(3)	20(2)	30(2)	19(2)
C(15)	29(2)	23(2)	45(3)	14(2)	20(2)	11(2)
C(16)	27(2)	15(2)	27(2)	8(2)	16(2)	6(2)
O(5)	46(2)	34(2)	89(3)	35(2)	47(2)	20(2)
C(17)	29(2)	29(3)	27(2)	12(2)	12(2)	10(2)
C(18)	57(3)	38(3)	73(4)	32(3)	47(3)	22(3)
C(19)	35(6)	26(3)	51(7)	24(5)	21(6)	18(4)
C(19A)	35(6)	26(3)	51(7)	24(5)	21(6)	18(4)
C(20)	36(5)	32(4)	45(5)	23(4)	22(4)	16(4)
C(20A)	36(5)	32(4)	45(5)	23(4)	22(4)	16(4)

Table S20 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **W-3**.

	x	y	z	U(eq)
H(4)	2849	1441	1129	42
H(4A)	6386	8674	5680	28
H(5)	4698	9845	6410	38
H(6)	2099	8764	5160	43
H(7)	1307	6559	3237	39
H(9A)	2125	4324	2056	30
H(9B)	2668	5121	1288	30
H(12)	4690	651	1127	34
H(13)	6996	209	1636	42
H(14)	9190	2107	2959	44
H(15)	9135	4397	3625	38
H(17A)	-82	86	1122	34
H(17B)	1027	806	2658	34
H(18A)	-899	-1650	1598	57
H(18B)	744	-1306	2655	57
H(18C)	-901	-1789	1316	57
H(18D)	434	-1181	2729	57
H(19A)	1886	-2417	1726	39
H(19B)	360	-3330	428	39
H(19C)	619	-3268	596	39
H(19D)	14	-2506	-263	39
H(20A)	2511	-1843	168	41
H(20B)	822	-1853	-484	41
H(20C)	2930	-1376	1890	41
H(20D)	2705	-1769	347	41

Table S21 Hydrogen bonds for **W-3** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4)...O(5)	0.84	1.89	2.621(5)	145.3

Symmetry transformations used to generate equivalent atoms:

Table S22 Crystal data and structure refinement for **W-3'** (CCDC 2045639).

Empirical formula	C ₂₁ H ₂₈ N ₂ O ₃ P ₂ W	
Molecular formula	C ₂₁ H ₂₈ N ₂ O ₃ P ₂ W	
Formula weight	602.24	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 2 ₁ /n 1	
Unit cell dimensions	a = 15.2659(4) Å	α = 90°.
	b = 9.7429(2) Å	β = 111.3810(10)°.
	c = 16.2231(4) Å	γ = 90°.
Volume	2246.86(9) Å ³	
Z	4	
Density (calculated)	1.780 Mg/m ³	
Absorption coefficient	5.308 mm ⁻¹	
F(000)	1184	
Crystal size	0.16 x 0.115 x 0.08 mm ³	
Crystal color, habit	yellow block	
Theta range for data collection	1.569 to 26.373°.	
Index ranges	-19 ≤ h ≤ 15, -12 ≤ k ≤ 12, -13 ≤ l ≤ 20	
Reflections collected	30856	
Independent reflections	4596 [R(int) = 0.0756]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.1467 and 0.1020	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4596 / 0 / 268	
Goodness-of-fit on F ²	1.049	
Final R indices [I > 2σ(I)]	R1 = 0.0245, wR2 = 0.0566	
R indices (all data)	R1 = 0.0301, wR2 = 0.0601	
Largest diff. peak and hole	0.823 and -0.524 e.Å ⁻³	

Table S23 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **W-3'**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
W(1)	2300(1)	3595(1)	5190(1)	11(1)
P(1)	1914(1)	1327(1)	4401(1)	17(1)
P(2)	3010(1)	5643(1)	6134(1)	14(1)
O(1)	1479(2)	3390(3)	6695(2)	22(1)
O(2)	110(2)	3442(3)	4387(2)	22(1)
O(3)	3920(2)	4979(2)	3680(2)	17(1)
N(1)	3551(2)	2329(3)	6028(2)	14(1)
N(2)	3368(2)	3814(3)	4622(2)	14(1)
C(1)	1779(3)	3448(3)	6121(2)	15(1)
C(2)	924(3)	3526(3)	4676(2)	16(1)
C(3)	1825(3)	5331(3)	4243(2)	14(1)
C(4)	1037(3)	6192(3)	4029(2)	15(1)
C(5)	837(3)	7180(4)	3368(2)	18(1)
C(6)	1422(3)	7387(4)	2895(2)	18(1)
C(7)	2222(3)	6579(3)	3103(2)	16(1)
C(8)	2420(2)	5563(3)	3761(2)	14(1)
C(9)	3305(3)	4764(3)	4006(2)	14(1)
C(10)	4270(3)	3111(4)	4997(2)	16(1)
C(11)	4305(3)	2284(3)	5782(2)	15(1)
C(12)	5084(3)	1471(3)	6236(3)	20(1)
C(13)	5088(3)	672(4)	6926(2)	21(1)
C(14)	4306(3)	707(4)	7179(2)	21(1)
C(15)	3567(3)	1548(3)	6723(2)	18(1)
C(16)	2865(3)	255(4)	4331(3)	34(1)
C(17)	1150(3)	1462(4)	3255(3)	26(1)
C(18)	1281(4)	196(4)	4871(3)	38(1)
C(19)	3876(3)	6657(4)	5880(3)	23(1)
C(20)	2187(3)	6914(4)	6235(3)	21(1)
C(21)	3655(3)	5186(4)	7292(2)	23(1)

Table S24 Bond lengths [Å] and angles [°] for **W-3'**.

W(1)-P(1)	2.5135(9)	C(12)-C(13)	1.362(5)
W(1)-P(2)	2.5087(9)	C(13)-H(13)	0.9500
W(1)-N(1)	2.263(3)	C(13)-C(14)	1.397(5)
W(1)-N(2)	2.156(3)	C(14)-H(14)	0.9500
W(1)-C(1)	1.953(4)	C(14)-C(15)	1.372(5)
W(1)-C(2)	1.959(4)	C(15)-H(15)	0.9500
W(1)-C(3)	2.221(3)	C(16)-H(16A)	0.9800
P(1)-C(16)	1.825(4)	C(16)-H(16B)	0.9800
P(1)-C(17)	1.804(4)	C(16)-H(16C)	0.9800
P(1)-C(18)	1.807(4)	C(17)-H(17A)	0.9800
P(2)-C(19)	1.815(4)	C(17)-H(17B)	0.9800
P(2)-C(20)	1.813(4)	C(17)-H(17C)	0.9800
P(2)-C(21)	1.829(4)	C(18)-H(18A)	0.9800
O(1)-C(1)	1.179(4)	C(18)-H(18B)	0.9800
O(2)-C(2)	1.160(5)	C(18)-H(18C)	0.9800
O(3)-C(9)	1.251(4)	C(19)-H(19A)	0.9800
N(1)-C(11)	1.350(4)	C(19)-H(19B)	0.9800
N(1)-C(15)	1.353(4)	C(19)-H(19C)	0.9800
N(2)-C(9)	1.339(4)	C(20)-H(20A)	0.9800
N(2)-C(10)	1.458(4)	C(20)-H(20B)	0.9800
C(3)-C(4)	1.403(5)	C(20)-H(20C)	0.9800
C(3)-C(8)	1.416(5)	C(21)-H(21A)	0.9800
C(4)-H(4)	0.9500	C(21)-H(21B)	0.9800
C(4)-C(5)	1.389(5)	C(21)-H(21C)	0.9800
C(5)-H(5)	0.9500		
C(5)-C(6)	1.389(5)	P(2)-W(1)-P(1)	168.31(3)
C(6)-H(6)	0.9500	N(1)-W(1)-P(1)	79.45(7)
C(6)-C(7)	1.387(5)	N(1)-W(1)-P(2)	89.12(7)
C(7)-H(7)	0.9500	N(2)-W(1)-P(1)	86.76(8)
C(7)-C(8)	1.407(5)	N(2)-W(1)-P(2)	87.52(8)
C(8)-C(9)	1.482(5)	N(2)-W(1)-N(1)	72.98(11)
C(10)-H(10A)	0.9900	N(2)-W(1)-C(3)	74.69(12)
C(10)-H(10B)	0.9900	C(1)-W(1)-P(1)	104.08(10)
C(10)-C(11)	1.491(5)	C(1)-W(1)-P(2)	78.03(10)
C(11)-C(12)	1.394(5)	C(1)-W(1)-N(1)	89.31(13)
C(12)-H(12)	0.9500	C(1)-W(1)-N(2)	157.38(14)

C(1)-W(1)-C(2)	69.51(15)	C(4)-C(5)-C(6)	121.5(3)
C(1)-W(1)-C(3)	117.90(13)	C(6)-C(5)-H(5)	119.3
C(2)-W(1)-P(1)	74.77(10)	C(5)-C(6)-H(6)	121.0
C(2)-W(1)-P(2)	116.36(10)	C(7)-C(6)-C(5)	118.0(3)
C(2)-W(1)-N(1)	140.92(12)	C(7)-C(6)-H(6)	121.0
C(2)-W(1)-N(2)	133.03(13)	C(6)-C(7)-H(7)	119.6
C(2)-W(1)-C(3)	72.68(14)	C(6)-C(7)-C(8)	120.7(3)
C(3)-W(1)-P(1)	111.13(9)	C(8)-C(7)-H(7)	119.6
C(3)-W(1)-P(2)	77.06(9)	C(3)-C(8)-C(9)	118.3(3)
C(3)-W(1)-N(1)	145.26(12)	C(7)-C(8)-C(3)	121.9(3)
C(16)-P(1)-W(1)	119.36(14)	C(7)-C(8)-C(9)	119.7(3)
C(17)-P(1)-W(1)	113.84(13)	O(3)-C(9)-N(2)	124.8(3)
C(17)-P(1)-C(16)	101.9(2)	O(3)-C(9)-C(8)	123.4(3)
C(17)-P(1)-C(18)	103.6(2)	N(2)-C(9)-C(8)	111.9(3)
C(18)-P(1)-W(1)	112.55(14)	N(2)-C(10)-H(10A)	109.6
C(18)-P(1)-C(16)	103.8(2)	N(2)-C(10)-H(10B)	109.6
C(19)-P(2)-W(1)	118.82(13)	N(2)-C(10)-C(11)	110.2(3)
C(19)-P(2)-C(21)	101.65(19)	H(10A)-C(10)-H(10B)	108.1
C(20)-P(2)-W(1)	116.04(13)	C(11)-C(10)-H(10A)	109.6
C(20)-P(2)-C(19)	103.59(19)	C(11)-C(10)-H(10B)	109.6
C(20)-P(2)-C(21)	101.87(18)	N(1)-C(11)-C(10)	117.8(3)
C(21)-P(2)-W(1)	112.60(12)	N(1)-C(11)-C(12)	121.2(3)
C(11)-N(1)-W(1)	117.6(2)	C(12)-C(11)-C(10)	121.0(3)
C(11)-N(1)-C(15)	118.0(3)	C(11)-C(12)-H(12)	119.8
C(15)-N(1)-W(1)	124.2(2)	C(13)-C(12)-C(11)	120.4(4)
C(9)-N(2)-W(1)	121.9(2)	C(13)-C(12)-H(12)	119.8
C(9)-N(2)-C(10)	115.8(3)	C(12)-C(13)-H(13)	120.7
C(10)-N(2)-W(1)	121.4(2)	C(12)-C(13)-C(14)	118.6(4)
O(1)-C(1)-W(1)	178.1(3)	C(14)-C(13)-H(13)	120.7
O(2)-C(2)-W(1)	177.6(3)	C(13)-C(14)-H(14)	120.7
C(4)-C(3)-W(1)	131.4(3)	C(15)-C(14)-C(13)	118.7(3)
C(4)-C(3)-C(8)	115.6(3)	C(15)-C(14)-H(14)	120.7
C(8)-C(3)-W(1)	112.9(2)	N(1)-C(15)-C(14)	123.1(4)
C(3)-C(4)-H(4)	118.9	N(1)-C(15)-H(15)	118.4
C(5)-C(4)-C(3)	122.2(3)	C(14)-C(15)-H(15)	118.4
C(5)-C(4)-H(4)	118.9	P(1)-C(16)-H(16A)	109.5
C(4)-C(5)-H(5)	119.3	P(1)-C(16)-H(16B)	109.5

P(1)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
P(1)-C(17)-H(17A)	109.5
P(1)-C(17)-H(17B)	109.5
P(1)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
P(1)-C(18)-H(18A)	109.5
P(1)-C(18)-H(18B)	109.5
P(1)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
P(2)-C(19)-H(19A)	109.5
P(2)-C(19)-H(19B)	109.5
P(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
P(2)-C(20)-H(20A)	109.5
P(2)-C(20)-H(20B)	109.5
P(2)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
P(2)-C(21)-H(21A)	109.5
P(2)-C(21)-H(21B)	109.5
P(2)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

Table S25 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **W-3'**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
W(1)	10(1)	11(1)	11(1)	0(1)	4(1)	0(1)
P(1)	16(1)	14(1)	18(1)	-4(1)	5(1)	-1(1)
P(2)	12(1)	14(1)	15(1)	-1(1)	4(1)	-1(1)
O(1)	23(2)	24(1)	22(2)	3(1)	13(1)	4(1)
O(2)	13(2)	27(2)	24(2)	-2(1)	4(1)	-2(1)
O(3)	16(1)	22(1)	18(1)	3(1)	9(1)	2(1)
N(1)	14(2)	12(1)	14(2)	-1(1)	3(1)	-2(1)
N(2)	15(2)	13(1)	16(2)	4(1)	8(1)	4(1)
C(1)	11(2)	15(2)	17(2)	2(1)	2(2)	3(1)
C(2)	20(2)	14(2)	14(2)	1(1)	8(2)	1(2)
C(3)	17(2)	13(2)	9(2)	-2(1)	2(1)	0(1)
C(4)	12(2)	16(2)	14(2)	-4(1)	3(2)	0(1)
C(5)	13(2)	16(2)	18(2)	-1(2)	-1(2)	5(2)
C(6)	22(2)	14(2)	13(2)	1(2)	0(2)	-1(2)
C(7)	19(2)	16(2)	13(2)	-1(1)	5(2)	-4(2)
C(8)	12(2)	13(2)	16(2)	-4(1)	3(1)	-3(1)
C(9)	14(2)	13(2)	13(2)	-4(1)	3(1)	-3(1)
C(10)	12(2)	17(2)	17(2)	-1(2)	3(2)	1(2)
C(11)	16(2)	10(2)	17(2)	-3(1)	4(2)	-3(1)
C(12)	15(2)	23(2)	21(2)	-2(2)	5(2)	-1(2)
C(13)	19(2)	19(2)	22(2)	5(2)	5(2)	6(2)
C(14)	22(2)	18(2)	19(2)	5(2)	5(2)	1(2)
C(15)	18(2)	21(2)	17(2)	2(2)	7(2)	0(2)
C(16)	25(2)	27(2)	42(3)	-22(2)	4(2)	2(2)
C(17)	21(2)	35(2)	19(2)	-10(2)	3(2)	6(2)
C(18)	52(3)	25(2)	41(3)	-8(2)	23(2)	-16(2)
C(19)	23(2)	23(2)	26(2)	-9(2)	11(2)	-11(2)
C(20)	19(2)	20(2)	21(2)	-6(2)	4(2)	5(2)
C(21)	24(2)	19(2)	21(2)	-2(2)	2(2)	-1(2)

Table S26 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **W-3'**.

	x	y	z	U(eq)
H(4)	626	6096	4346	18
H(5)	287	7726	3237	22
H(6)	1279	8062	2442	22
H(7)	2641	6715	2798	20
H(10A)	4786	3794	5176	19
H(10B)	4359	2502	4546	19
H(12)	5615	1476	6062	24
H(13)	5612	101	7228	25
H(14)	4287	161	7657	25
H(15)	3042	1583	6904	22
H(16A)	3198	748	4007	51
H(16B)	2602	-599	4019	51
H(16C)	3305	41	4929	51
H(17A)	528	1777	3218	39
H(17B)	1092	561	2971	39
H(17C)	1416	2119	2953	39
H(18A)	694	639	4844	57
H(18B)	1669	1	5490	57
H(18C)	1136	-663	4535	57
H(19A)	4434	6095	5963	35
H(19B)	4054	7454	6274	35
H(19C)	3608	6970	5264	35
H(20A)	1876	7365	5662	32
H(20B)	2526	7600	6678	32
H(20C)	1714	6463	6418	32
H(21A)	3238	4683	7523	35
H(21B)	3878	6023	7640	35
H(21C)	4194	4607	7332	35

Table S27 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **W-3'**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
W(1)	3077(1)	7113(1)	4911(1)	11(1)
P(1)	2533(1)	5879(1)	3510(1)	14(1)
P(2)	3330(1)	8224(1)	6338(1)	15(1)
O(1)	5337(2)	7168(2)	5686(2)	21(1)
O(2)	4027(2)	8457(2)	3618(2)	21(1)
O(3)	19(2)	7275(2)	4479(2)	23(1)
N(1)	3094(2)	5210(3)	5515(2)	12(1)
N(2)	1626(2)	6729(3)	4987(2)	15(1)
C(1)	4492(3)	7130(3)	5374(2)	15(1)
C(2)	3667(3)	7954(3)	4108(2)	15(1)
C(3)	3884(3)	4472(4)	5759(2)	17(1)
C(4)	3866(3)	3284(4)	6069(2)	19(1)
C(5)	2980(3)	2807(3)	6111(3)	20(1)
C(6)	2161(3)	3536(3)	5856(2)	17(1)
C(7)	2240(2)	4738(3)	5575(2)	14(1)
C(8)	1374(3)	5580(3)	5344(2)	15(1)
C(9)	1012(3)	5790(4)	6159(2)	19(1)
C(10)	901(3)	7516(4)	4613(2)	16(1)
C(11)	1273(3)	8733(4)	4412(2)	16(1)
C(12)	634(3)	9726(4)	4173(2)	24(1)
C(13)	979(3)	10896(4)	4081(3)	31(1)
C(14)	1970(3)	11063(4)	4215(3)	29(1)
C(15)	2604(3)	10075(4)	4433(2)	21(1)
C(16)	2285(3)	8876(3)	4548(2)	15(1)
C(17)	3451(3)	5259(4)	3043(2)	23(1)
C(18)	1748(3)	4544(4)	3478(3)	35(1)
C(19)	1798(3)	6818(4)	2629(2)	23(1)
C(20)	3822(3)	7227(4)	7289(2)	21(1)
C(21)	2295(3)	8976(4)	6587(2)	20(1)
C(22)	4209(3)	9486(4)	6515(2)	21(1)

Table S28 Bond lengths [Å] and angles [°] for **W-3'**.

W(1)-P(1)	2.5259(9)	C(11)-C(16)	1.417(5)
W(1)-P(2)	2.5013(10)	C(12)-H(12)	0.9500
W(1)-N(1)	2.264(3)	C(12)-C(13)	1.378(6)
W(1)-N(2)	2.159(3)	C(13)-H(13)	0.9500
W(1)-C(1)	1.960(4)	C(13)-C(14)	1.390(6)
W(1)-C(2)	1.940(4)	C(14)-H(14)	0.9500
W(1)-C(16)	2.208(4)	C(14)-C(15)	1.382(5)
P(1)-C(17)	1.811(4)	C(15)-H(15)	0.9500
P(1)-C(18)	1.821(4)	C(15)-C(16)	1.401(5)
P(1)-C(19)	1.812(4)	C(17)-H(17A)	0.9800
P(2)-C(20)	1.831(4)	C(17)-H(17B)	0.9800
P(2)-C(21)	1.828(4)	C(17)-H(17C)	0.9800
P(2)-C(22)	1.824(4)	C(18)-H(18A)	0.9800
O(1)-C(1)	1.176(4)	C(18)-H(18B)	0.9800
O(2)-C(2)	1.179(4)	C(18)-H(18C)	0.9800
O(3)-C(10)	1.251(4)	C(19)-H(19A)	0.9800
N(1)-C(3)	1.351(4)	C(19)-H(19B)	0.9800
N(1)-C(7)	1.354(4)	C(19)-H(19C)	0.9800
N(2)-C(8)	1.450(5)	C(20)-H(20A)	0.9800
N(2)-C(10)	1.347(4)	C(20)-H(20B)	0.9800
C(3)-H(3)	0.9500	C(20)-H(20C)	0.9800
C(3)-C(4)	1.376(5)	C(21)-H(21A)	0.9800
C(4)-H(4)	0.9500	C(21)-H(21B)	0.9800
C(4)-C(5)	1.391(5)	C(21)-H(21C)	0.9800
C(5)-H(5)	0.9500	C(22)-H(22A)	0.9800
C(5)-C(6)	1.378(5)	C(22)-H(22B)	0.9800
C(6)-H(6)	0.9500	C(22)-H(22C)	0.9800
C(6)-C(7)	1.386(5)		
C(7)-C(8)	1.501(5)	P(2)-W(1)-P(1)	169.72(3)
C(8)-H(8)	1.0000	N(1)-W(1)-P(1)	81.99(7)
C(8)-C(9)	1.541(5)	N(1)-W(1)-P(2)	93.90(8)
C(9)-H(9A)	0.9800	N(2)-W(1)-P(1)	83.08(8)
C(9)-H(9B)	0.9800	N(2)-W(1)-P(2)	86.70(8)
C(9)-H(9C)	0.9800	N(2)-W(1)-N(1)	72.53(11)
C(10)-C(11)	1.485(5)	N(2)-W(1)-C(16)	75.25(13)
C(11)-C(12)	1.393(5)	C(1)-W(1)-P(1)	111.85(11)

C(1)-W(1)-P(2)	77.23(11)	C(3)-C(4)-C(5)	118.0(4)
C(1)-W(1)-N(1)	87.73(13)	C(5)-C(4)-H(4)	121.0
C(1)-W(1)-N(2)	153.68(13)	C(4)-C(5)-H(5)	120.3
C(1)-W(1)-C(16)	119.67(14)	C(6)-C(5)-C(4)	119.4(4)
C(2)-W(1)-P(1)	75.59(11)	C(6)-C(5)-H(5)	120.3
C(2)-W(1)-P(2)	113.09(11)	C(5)-C(6)-H(6)	120.3
C(2)-W(1)-N(1)	138.35(13)	C(5)-C(6)-C(7)	119.3(4)
C(2)-W(1)-N(2)	136.81(13)	C(7)-C(6)-H(6)	120.3
C(2)-W(1)-C(1)	69.37(15)	N(1)-C(7)-C(6)	122.1(3)
C(2)-W(1)-C(16)	73.28(14)	N(1)-C(7)-C(8)	117.3(3)
C(16)-W(1)-P(1)	102.22(9)	C(6)-C(7)-C(8)	120.6(3)
C(16)-W(1)-P(2)	76.10(9)	N(2)-C(8)-C(7)	109.5(3)
C(16)-W(1)-N(1)	146.74(12)	N(2)-C(8)-H(8)	108.4
C(17)-P(1)-W(1)	118.27(12)	N(2)-C(8)-C(9)	112.5(3)
C(17)-P(1)-C(18)	102.2(2)	C(7)-C(8)-H(8)	108.4
C(17)-P(1)-C(19)	102.89(18)	C(7)-C(8)-C(9)	109.4(3)
C(18)-P(1)-W(1)	118.69(14)	C(9)-C(8)-H(8)	108.4
C(19)-P(1)-W(1)	111.08(13)	C(8)-C(9)-H(9A)	109.5
C(19)-P(1)-C(18)	101.35(19)	C(8)-C(9)-H(9B)	109.5
C(20)-P(2)-W(1)	113.17(13)	C(8)-C(9)-H(9C)	109.5
C(21)-P(2)-W(1)	119.08(12)	H(9A)-C(9)-H(9B)	109.5
C(21)-P(2)-C(20)	103.43(18)	H(9A)-C(9)-H(9C)	109.5
C(22)-P(2)-W(1)	114.72(13)	H(9B)-C(9)-H(9C)	109.5
C(22)-P(2)-C(20)	102.59(18)	O(3)-C(10)-N(2)	124.5(4)
C(22)-P(2)-C(21)	101.81(18)	O(3)-C(10)-C(11)	123.6(3)
C(3)-N(1)-W(1)	124.5(2)	N(2)-C(10)-C(11)	111.9(3)
C(3)-N(1)-C(7)	117.5(3)	C(12)-C(11)-C(10)	119.3(3)
C(7)-N(1)-W(1)	117.8(2)	C(12)-C(11)-C(16)	121.9(4)
C(8)-N(2)-W(1)	122.3(2)	C(16)-C(11)-C(10)	118.5(3)
C(10)-N(2)-W(1)	119.6(3)	C(11)-C(12)-H(12)	119.9
C(10)-N(2)-C(8)	117.8(3)	C(13)-C(12)-C(11)	120.3(4)
O(1)-C(1)-W(1)	176.9(3)	C(13)-C(12)-H(12)	119.9
O(2)-C(2)-W(1)	179.6(3)	C(12)-C(13)-H(13)	120.5
N(1)-C(3)-H(3)	118.1	C(12)-C(13)-C(14)	119.0(4)
N(1)-C(3)-C(4)	123.7(4)	C(14)-C(13)-H(13)	120.5
C(4)-C(3)-H(3)	118.1	C(13)-C(14)-H(14)	119.6
C(3)-C(4)-H(4)	121.0	C(15)-C(14)-C(13)	120.9(4)

C(15)-C(14)-H(14)	119.6	P(2)-C(22)-H(22A)	109.5
C(14)-C(15)-H(15)	119.0	P(2)-C(22)-H(22B)	109.5
C(14)-C(15)-C(16)	121.9(4)	P(2)-C(22)-H(22C)	109.5
C(16)-C(15)-H(15)	119.0	H(22A)-C(22)-H(22B)	109.5
C(11)-C(16)-W(1)	112.2(3)	H(22A)-C(22)-H(22C)	109.5
C(15)-C(16)-W(1)	131.8(3)	H(22B)-C(22)-H(22C)	109.
C(15)-C(16)-C(11)	116.0(3)		
P(1)-C(17)-H(17A)	109.5		
P(1)-C(17)-H(17B)	109.5		
P(1)-C(17)-H(17C)	109.5		
H(17A)-C(17)-H(17B)	109.5		
H(17A)-C(17)-H(17C)	109.5		
H(17B)-C(17)-H(17C)	109.5		
P(1)-C(18)-H(18A)	109.5		
P(1)-C(18)-H(18B)	109.5		
P(1)-C(18)-H(18C)	109.5		
H(18A)-C(18)-H(18B)	109.5		
H(18A)-C(18)-H(18C)	109.5		
H(18B)-C(18)-H(18C)	109.5		
P(1)-C(19)-H(19A)	109.5		
P(1)-C(19)-H(19B)	109.5		
P(1)-C(19)-H(19C)	109.5		
H(19A)-C(19)-H(19B)	109.5		
H(19A)-C(19)-H(19C)	109.5		
H(19B)-C(19)-H(19C)	109.5		
P(2)-C(20)-H(20A)	109.5		
P(2)-C(20)-H(20B)	109.5		
P(2)-C(20)-H(20C)	109.5		
H(20A)-C(20)-H(20B)	109.5		
H(20A)-C(20)-H(20C)	109.5		
H(20B)-C(20)-H(20C)	109.5		
P(2)-C(21)-H(21A)	109.5		
P(2)-C(21)-H(21B)	109.5		
P(2)-C(21)-H(21C)	109.5		
H(21A)-C(21)-H(21B)	109.5		
H(21A)-C(21)-H(21C)	109.5		
H(21B)-C(21)-H(21C)	109.5		

NMR AND IR SPECTRA

W

NMR SPECTRA FOR DEUTERIUM INCORPORATION EXPERIMENTS

COMPUTATIONAL DETAILS

Computational Methods

All density functional theory (DFT) calculations were carried out using the Gaussian 16 program (50). Geometries of intermediates and transition states were optimized using the B3LYP functional (51) with Grimme's DFT-D3 dispersion correction (52) and a mixed basis set of LANL2DZ (53) for W and 6-31G(d) for other atoms. Vibrational frequency calculations were performed for all intermediates and transition states to confirm if each optimized structure is a local minimum or a transition state structure. Each optimized transition state structure has only one imaginary (negative) frequency, and all minima have no imaginary frequencies. Single-point energy calculations were performed using the M06 functional (54) with Grimme's DFT-D3 dispersion correction and a mixed basis set of SDD (55) for W and 6-311+G(d,p) for other atoms in toluene solvent using the SMD continuum solvation model (56). The reported Gibbs free energies and enthalpies include thermal corrections at 298 K. Gibbs free energies and enthalpies at 150 °C were also calculated and are provided below. All reported W species have singlet spin state.

Catalyst Activation and Substrate Coordination Steps to Form the Reactant Complex I-1

The computed reaction energy profile to form the substrate complex **I-1** from the W(CO)_6 precatalyst is shown in Figure S14. W(CO)_6 is known to be relatively stable due to its 18-electron configuration (57). The catalyst initiation process requires dissociation of one of the CO ligands to form W(CO)_5 (57). W(CO)_5 then undergoes facile ligand exchange to replace a second CO ligand with the substrate (**1a**) to form **I-9**. The alkenyl group can then coordinate to the W center, replacing a third CO ligand to form π -alkene complex **I-1**.

Figure S14 Substrate coordination to the W center.

Several isomers of the π -alkene complex **I-1** were located (Figure S15). The most stable isomer **I-1** has a *facial* coordination geometry, in which the pyridine and amide nitrogen atoms and the alkene are all *cis* to one another. The *meridional* isomer **I-1a**, in which the pyridine and amide nitrogen atoms and the alkene are coplanar, is less stable by 3.1 kcal/mol. Here, the *meridional* isomer is destabilized due to the strong trans effect of the *trans* positioned CO ligands. Dissociation of the alkenyl group from **I-1** to form five-coordinate W complex **I-1b** is endergonic by 12.0 kcal/mol. Other isomers of the five-coordinate W complex (**I-1c-e**) are also much less stable than the six-coordinate octahedral complex **I-1**. Dissociation of the pyridine from **I-1** to form five-coordinate complex **I-1f** is endergonic by 16.7 kcal/mol. Taken together, these results indicate that the octahedral W(0) complexes **I-1** and **I-1a** are the most stable complexes formed after the substrate binds to the W.

Figure S15 Isomers of the substrate complex **I-1**.

Next, we considered the N–H oxidative addition transition states from both **I-1** and **I-1a** and the resulting W–hydride complexes (Figure S16). The *facial* complex **I-1** leads to transition

state **TS1**, which then forms W(II) complex **I-2a**. On the other hand, the *meridional* complex **I-1a** leads to **TS1a**, which then forms W(II) complex **I-2**. In both **TS1** and **I-2a**, the pyridine and amide N atoms and the alkene are *cis* to one another. The planar geometry of the sp^2 -hybridized amide N leads to substantial distortion of the substrate in **I-2a**. **TS1**, the *facial* isomer, is 12.9 kcal/mol lower in energy than the *meridional* isomer, **TS1a**, while the product of **TS1** (**I-2**) is 2.7 kcal/mol less stable than **I-2a**. These results indicate that by a difference of 12.9 kcal/mol, the most favorable N–H oxidative addition process occurs from the *facial* W(0) complex **I-1** via **TS1** to form W(II) complex **I-2a**, which then isomerizes to the more stable isomer **I-2** prior to hydrometallation across the alkene. In **I-2** and subsequent intermediates in the alkene isomerization process, the pyridine N, the amide N, and the alkene are coplanar. This geometry is consistent with the crystal structures of the seven-coordinated W(II) complexes.

Figure S16 Isomers of the N–H oxidative addition transition state **TS1** and the seven-coordinate W(II) hydride complex **I-2**. All Gibbs free energies and enthalpies are with respect to **I-1**.

Alternative Reaction Pathways

1,3-Hydride Shift

We considered the 1,3-hydride shift pathway, which initiates via the oxidative addition of the allylic C–H bond in substrate complex **I-1** to form a π -allyltungsten–hydride complex, followed by C–H reductive elimination to shuttle the H atom to the terminal carbon of the allyl moiety, thereby forming the isomerized alkene with an internal C=C double bond. We carefully considered various isomers of the allylic C–H oxidative addition transition state. Because complex **I-1** is already six-coordinate, one of the ligands from **I-1** needs to dissociate prior to the allylic C–H oxidative addition step. We have considered the following possibilities: dissociation of the amide N (**TS7a**), dissociation of the pyridine (**TS7b**), dissociation of one of the CO ligands (**TS7c**), and dissociation of the alkenyl group (**TS7d**) from **I-1** (Figure S17). Our calculations indicate that

the most favorable allylic C–H oxidative addition is **TS7a**, which requires 27.5 kcal/mol with respect to **I-1**. Because the N–H oxidative addition from **I-1** (**TS1**) requires a lower barrier ($\Delta G^\ddagger = 22.8$ kcal/mol), the 1,2-hydride shift pathway via N–H oxidative addition is more favorable than the 1,3-hydride shift pathway.

Figure S17 Isomers of the allylic C–H oxidative addition transition states. All Gibbs free energies and enthalpies are with respect to **I-1**.

Other N–H Oxidative Addition Transition States

Besides **TS1** and **TS1a** discussed above, we have considered several N–H oxidative addition transition states, including reactions from both five- and six-coordinated W(0) complexes with and without the alkenyl group of the substrate binding to the W center. Figure S18 illustrates the alternative pathway involving the N–H oxidative addition from two different five-coordinate W complexes (**I-10** and **I-1c**), formed by dissociation of a CO ligand and the alkenyl group, respectively, from the octahedral complex **I-1**. Formation of both five-coordinated complexes are endergonic (by 27.2 and 11.2 kcal/mol to form **I-10** and **I-1c**, respectively). Subsequent N–H oxidative addition (**TS1b** and **TS1c**) requires activation free energies of 48.1 and 34.2 kcal/mol, respectively. Both are much less favorable than N–H oxidative addition from the octahedral complex **I-1**. These results indicate the oxidative addition with a six-coordinate, 18-electron W(0) complex to form a seven-coordinate W(II)–hydride intermediate is much more favorable than the oxidative addition with a five-coordinate, 16-electron W(0) complex to form a six-coordinate W(II)–hydride.

Figure S18 Alternative N–H oxidative addition pathways. All Gibbs free energies and enthalpies are with respect to **I-1**.

Next, we considered the N–H oxidative addition from an octahedral complex **I-9**, which involves the *N,N*-bidentate coordination of the substrate onto a W(0) center with four carbonyl ligands. Complex **I-9** is 14.3 kcal/mol more stable than **I-1** in terms of Gibbs free energy (Figure S19), indicating that **I-9** may accumulate, especially under relatively high CO concentrations. Nonetheless, **I-9** is less reactive than **I-1** in the N–H oxidative addition step, which requires an activation free energy of 36.8 kcal/mol (**TS1d**) with respect to **I-9**, much higher than the N–H oxidative addition barrier from **I-1** (22.8 kcal/mol). Therefore, **I-9** is unlikely to be the active species involved in the N–H oxidative addition step.

Figure S19 The N–H oxidative addition pathway via six-coordinate W complex **I-9**.

Reaction Energy Profile of a Bis(CO)-Ligated Pathway Involving Five- and Six-Coordinate W Complexes

Here, we compared the two reaction pathways of N–H oxidative addition and alkene isomerization through a hydride shift process via the six-coordinate tris(CO)-ligated W(0) complex **I-1** and the five-coordinate bis(CO)-ligated W(0) complex **I-10**, respectively (Figures S20 and S21). In the former pathway, a seven-coordinate W(II)–hydride intermediate (**I-2**) is formed after the N–H oxidative addition, which then promotes the alkene migration, shuttling between seven- and six-coordinate W(II) complexes. In the alternative pathway involving **I-10**, a six-coordinate W(II)–hydride intermediate is formed, and the subsequent alkene migration involves six- and five-coordinate W(II) complexes. As discussed in the earlier section, the N–H oxidative addition from **I-10** is highly unfavorable, because of the highly endergonic dissociation of one CO molecule from **I-1** to form **I-10** and another 20.9 kcal/mol required to reach the N–H oxidative addition transition state **TS1b**. After the N–H oxidative addition via **TS1b** to form **I-2b**, the six- and five-coordinate W(II) intermediates (**I-2b**, **I-3a**, and **I-4a**) and the hydride migration transition states (**TS2a**, **TS3a**, and **TS4a**) in this bis(CO)-ligated pathway are all less stable than the corresponding seven- and six-coordinate W(II) complexes and transition states in tris(CO)-ligated pathway. Therefore, these results indicate that the tris(CO)-ligated pathway involving seven- and six-coordinate W species is more favorable in both N–H oxidative addition and alkene isomerization steps.

Figure S20 Reaction energy profiles of the N-H oxidative addition and alkene isomerization pathways involving of six-coordinate W complex **I-1** (in solid lines) and five-coordinate W complex **I-10** (in dashed lines). All Gibbs free energies and enthalpies are with respect to **I-1**.

Figure S21 3D structures of transition states in the bis(CO)-ligated reaction pathway.

Agostic Interactions with β -C–H Bonds in Alkyl–W(II) Complexes

Agostic interactions between the W(II) center and β -C–H bonds are observed in alkyl W(II) complexes **I-3** and **I-5** (Figure S22). Two different isomers of **I-3** (**I-3** and **I-3b**) were located, which involve agostic interactions with the endo- and exocyclic β -C–H bonds, respectively. The β -C–H agostic interactions in the six-membered metallacycle (**I-3** and **I-3b**) are stronger than in the five-membered metallacycle **I-5**, as evidenced by the shorter W–H distances and longer C–H distances in **I-3/I-3b** than in **I-5**. The relatively strong agostic interaction in **I-3** promotes the subsequent endocyclic β -H elimination (**TS3**), which requires a low barrier (4.6 kcal/mol) with respect to **I-3**.

$\Delta G = 10.7$ kcal/mol
 $\Delta H = 11.7$ kcal/mol

$\Delta G = 11.7$ kcal/mol
 $\Delta H = 12.9$ kcal/mol

$\Delta G = -5.1$ kcal/mol
 $\Delta H = -4.1$ kcal/mol

Figure 22 3D structures of agostic interactions with β -C-H bonds in complexes **I-3**, **I-3b**, and **I-5**. All Gibbs free energies and enthalpies are with respect to **I-1**.

Energy profile with ΔG and ΔH calculated at 150 °C

Figure S23 Reaction energy profile with ΔG and ΔH calculated at 150 °C

Cartesian Coordinates and Energies of All Optimized Structures

I-1

B3LYP-D3 electronic energy: -1020.264850 a.u.
B3LYP-D3 enthalpy: -1019.977753 a.u.
B3LYP-D3 free energy: -1020.048093 a.u.
M06-D3 SCF energy in solution: -1019.169244 a.u.
M06-D3 enthalpy in solution: -1018.882147 a.u.
M06-D3 free energy in solution: -1018.952487 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.592193000	-0.523893000	0.059753000
6	0.886202000	-2.152469000	-0.969673000
6	0.322364000	-1.602381000	1.699553000
6	2.518613000	-0.388566000	0.478977000
8	0.158321000	-2.229240000	2.673062000
8	0.992669000	-3.113699000	-1.634672000
8	3.646879000	-0.238167000	0.759008000
7	-1.683273000	-0.395728000	-0.129934000
6	-2.344517000	0.519267000	0.614014000
6	-2.389428000	-1.140950000	-1.006740000
6	-3.714854000	0.731370000	0.475951000
6	-1.542376000	1.250407000	1.666854000
6	-3.760012000	-0.999384000	-1.182364000
1	-1.813927000	-1.864558000	-1.572700000
6	-4.438450000	-0.037553000	-0.432555000
1	-4.201404000	1.493064000	1.076875000
1	-2.025099000	2.200096000	1.916658000
1	-1.494753000	0.622240000	2.562879000
7	-0.146518000	1.473493000	1.246144000
1	-4.276941000	-1.628186000	-1.899444000
1	-5.507095000	0.111557000	-0.553453000
6	0.103736000	2.583653000	0.396530000
6	1.571210000	2.849839000	0.124469000
8	-0.814196000	3.173541000	-0.139093000
1	1.745937000	3.924521000	0.245144000
1	2.207579000	2.307649000	0.829397000
6	1.937591000	2.438879000	-1.323294000
1	1.464230000	3.156352000	-2.004582000
1	3.020096000	2.558457000	-1.428971000
6	1.544417000	1.031397000	-1.768355000
1	2.352984000	0.417300000	-2.154130000
6	0.245618000	0.677625000	-2.078020000
1	0.043330000	-0.158745000	-2.740733000
1	-0.563525000	1.393690000	-1.955303000
1	0.524750000	1.383990000	2.004655000

TS1

B3LYP-D3 electronic energy: -1020.220051 a.u.
B3LYP-D3 enthalpy: -1019.940935 a.u.
B3LYP-D3 free energy: -1020.011912 a.u.
M06-D3 SCF energy in solution: -1019.124279 a.u.
M06-D3 enthalpy in solution: -1018.845163 a.u.
M06-D3 free energy in solution: -1018.916140 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.450126000	-0.573082000	0.121057000
6	0.482673000	-2.414242000	-0.697285000
6	-0.186116000	-1.497331000	1.764162000
6	2.397510000	-0.881408000	0.421388000
8	-0.589261000	-2.037985000	2.711548000
8	0.475911000	-3.469513000	-1.184750000
8	3.539371000	-1.040996000	0.584361000
7	-1.763161000	-0.152059000	-0.223924000
6	-2.234010000	0.963751000	0.380135000
6	-2.604605000	-0.904505000	-0.959466000
6	-3.566263000	1.353402000	0.243121000
6	-1.244064000	1.716637000	1.236277000
6	-3.943315000	-0.577482000	-1.133734000
1	-2.172869000	-1.792237000	-1.409137000
6	-4.434240000	0.577257000	-0.521663000
1	-3.908254000	2.258914000	0.734008000
1	-1.480329000	2.783662000	1.276063000
1	-1.312172000	1.313207000	2.259437000
7	0.110210000	1.537839000	0.730971000
1	-4.580491000	-1.215999000	-1.736150000
1	-5.474018000	0.867706000	-0.639819000
6	0.843811000	2.672488000	0.470855000
6	2.265436000	2.426336000	-0.017128000
8	0.393615000	3.814075000	0.575718000
1	2.799307000	3.374629000	0.084762000
1	2.770252000	1.676663000	0.598858000
6	2.311414000	1.995265000	-1.503485000
1	1.811671000	2.775508000	-2.091241000
1	3.361128000	1.983707000	-1.816967000
6	1.696495000	0.653660000	-1.867481000
1	2.388346000	-0.135677000	-2.150179000
6	0.363727000	0.473826000	-2.128235000
1	0.012999000	-0.395942000	-2.679495000
1	-0.329888000	1.306577000	-2.048482000
1	0.927831000	0.436317000	1.491052000

I-2

B3LYP-D3 electronic energy: -1020.24472 a.u.
 B3LYP-D3 enthalpy: -1019.963578 a.u.
 B3LYP-D3 free energy: -1020.033628 a.u.
 M06-D3 SCF energy in solution: -1019.153350 a.u.
 M06-D3 enthalpy in solution: -1018.872208 a.u.
 M06-D3 free energy in solution: -1018.942258 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.427963000	-0.641053000	0.054251000
6	0.061802000	-1.158238000	1.978990000
6	0.280733000	-2.386909000	-0.588497000
8	0.772790000	-3.378085000	-0.987459000
8	0.328453000	-1.512025000	3.045772000
7	1.729077000	0.053361000	-0.134036000

6	1.995571000	1.211774000	0.515915000
6	2.718043000	-0.563046000	-0.813853000
6	3.269901000	1.776645000	0.490691000
6	0.827292000	1.810807000	1.256314000
6	4.006973000	-0.050960000	-0.877727000
1	2.456263000	-1.488522000	-1.311044000
6	4.290149000	1.143329000	-0.213353000
1	3.441569000	2.711304000	1.014362000
1	0.820556000	1.396046000	2.277026000
1	0.932434000	2.896894000	1.323558000
7	-0.408469000	1.454851000	0.569760000
1	4.765615000	-0.581538000	-1.442819000
1	5.286088000	1.575097000	-0.249653000
6	-1.009455000	2.509005000	-0.075597000
6	-2.310429000	2.202637000	-0.820304000
8	-0.589092000	3.669330000	-0.054795000
1	-2.825476000	3.162374000	-0.920140000
1	-2.080064000	1.871383000	-1.838645000
6	-3.232779000	1.196503000	-0.117524000
1	-3.407031000	1.557255000	0.902835000
1	-4.208157000	1.212305000	-0.622415000
6	-0.715444000	-0.217867000	-1.922407000
8	-0.843482000	-0.059776000	-3.060079000
1	-1.078065000	-2.320451000	-0.196742000
6	-2.801879000	-0.265692000	-0.040759000
1	-3.181923000	-0.915205000	-0.825886000
6	-2.495277000	-0.848138000	1.196529000
1	-2.680330000	-1.900122000	1.389192000
1	-2.477012000	-0.211034000	2.077739000

TS2

B3LYP-D3 electronic energy: -1020.227829 a.u.

B3LYP-D3 enthalpy: -1019.94845 a.u.

B3LYP-D3 free energy: -1020.018797 a.u.

M06-D3 SCF energy in solution: -1019.135985 a.u.

M06-D3 enthalpy in solution: -1018.856606 a.u.

M06-D3 free energy in solution: -1018.926953 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.393410000	-0.615209000	-0.105484000
6	-0.013119000	-0.612552000	-2.136710000
6	-0.218170000	-2.455204000	0.366275000
8	-0.606698000	-3.510716000	0.678953000
8	-0.252085000	-0.621600000	-3.265447000
7	-1.780583000	-0.005680000	0.116341000
6	-2.070520000	1.256269000	-0.276948000
6	-2.777185000	-0.784895000	0.591404000
6	-3.371738000	1.757144000	-0.210247000
6	-0.915155000	2.053766000	-0.807620000
6	-4.091309000	-0.349298000	0.678366000
1	-2.499039000	-1.781151000	0.909536000
6	-4.397674000	0.950262000	0.269377000
1	-3.558381000	2.777635000	-0.528655000
1	-0.915472000	1.948869000	-1.907107000

1	-1.042615000	3.116366000	-0.579807000
7	0.343597000	1.570889000	-0.256168000
1	-4.851458000	-1.017476000	1.068457000
1	-5.413943000	1.327844000	0.334595000
6	1.106156000	2.556628000	0.310113000
6	2.507219000	2.148082000	0.757233000
8	0.760471000	3.738741000	0.418467000
1	3.090242000	3.071556000	0.799485000
1	2.467832000	1.749252000	1.780211000
6	3.162581000	1.120739000	-0.176988000
1	2.931083000	1.363002000	-1.220853000
1	4.256325000	1.179456000	-0.068992000
6	0.692220000	-0.483786000	1.902308000
8	0.865945000	-0.414911000	3.044074000
1	1.255117000	-2.040146000	-0.712891000
6	2.761433000	-0.300427000	0.132583000
1	3.070597000	-0.635958000	1.121839000
6	2.664403000	-1.304513000	-0.849695000
1	3.025248000	-2.305476000	-0.618189000
1	2.755077000	-1.030188000	-1.898087000

I-3

B3LYP-D3 electronic energy: -1020.233099 a.u.
 B3LYP-D3 enthalpy: -1019.950957 a.u.
 B3LYP-D3 free energy: -1020.022862 a.u.
 M06-D3 SCF energy in solution: -1019.145707 a.u.
 M06-D3 enthalpy in solution: -1018.863565 a.u.
 M06-D3 free energy in solution: -1018.935470 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.409014000	-0.348440000	0.158177000
6	0.178770000	-0.654448000	2.116191000
6	-0.917576000	-2.258442000	0.381953000
8	-1.240433000	-3.375454000	0.511562000
8	0.513249000	-0.991185000	3.171448000
7	1.779952000	-0.199827000	-0.105457000
6	2.274498000	1.047652000	-0.309192000
6	2.623417000	-1.256195000	-0.060075000
6	3.648963000	1.242731000	-0.470035000
6	1.305429000	2.199828000	-0.370721000
6	3.994126000	-1.119643000	-0.215932000
1	2.153877000	-2.217771000	0.106996000
6	4.517755000	0.158457000	-0.425338000
1	4.018622000	2.251158000	-0.627071000
1	1.649159000	3.008005000	0.292826000
1	1.344008000	2.632193000	-1.386349000
7	-0.032584000	1.770442000	-0.026889000
1	4.630458000	-1.996636000	-0.172159000
1	5.586692000	0.305215000	-0.549096000
6	-0.927366000	2.767499000	0.152083000
6	-2.324301000	2.291071000	0.587003000
8	-0.689842000	3.973524000	0.027209000
1	-2.471453000	2.616757000	1.624519000
1	-3.068456000	2.820233000	-0.016927000

6	-2.550333000	0.780750000	0.466301000
1	-1.861441000	0.271900000	1.297443000
6	-2.343559000	0.186418000	-0.887035000
1	-2.127865000	0.956185000	-1.629101000
6	-3.322617000	-0.867150000	-1.368942000
1	-4.288995000	-0.410837000	-1.627433000
1	-3.497787000	-1.628310000	-0.601829000
6	-0.250314000	-0.945601000	-1.777104000
8	-0.212083000	-1.397202000	-2.842574000
1	-2.947591000	-1.375578000	-2.262783000
1	-3.492259000	0.442731000	0.916193000

TS3

B3LYP-D3 electronic energy: -1020.222274 a.u.
 B3LYP-D3 enthalpy: -1019.94403 a.u.
 B3LYP-D3 free energy: -1020.015846 a.u.
 M06-D3 SCF energy in solution: -1019.13453 a.u.
 M06-D3 enthalpy in solution: -1018.856286 a.u.
 M06-D3 free energy in solution: -1018.928102 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.423493000	-0.321074000	-0.143745000
6	-0.059179000	-1.096859000	-1.916837000
6	1.196918000	-2.163262000	-0.029217000
8	1.680725000	-3.220291000	0.066987000
8	-0.334976000	-1.590855000	-2.934315000
7	-1.814237000	-0.270182000	0.038481000
6	-2.360504000	0.937821000	0.319045000
6	-2.619531000	-1.343048000	-0.120409000
6	-3.744780000	1.084904000	0.429950000
6	-1.409709000	2.081626000	0.548775000
6	-4.000189000	-1.259153000	-0.018184000
1	-2.116271000	-2.277815000	-0.335906000
6	-4.575723000	-0.017550000	0.260388000
1	-4.152502000	2.067088000	0.646862000
1	-1.799165000	3.008976000	0.109790000
1	-1.360504000	2.263364000	1.639401000
7	-0.106210000	1.754049000	0.011754000
1	-4.604255000	-2.149155000	-0.156534000
1	-5.653550000	0.087620000	0.342188000
6	0.695164000	2.806273000	-0.279568000
6	2.043846000	2.393427000	-0.889846000
8	0.409827000	3.995965000	-0.124834000
1	1.976707000	2.564973000	-1.971431000
1	2.812825000	3.073106000	-0.506064000
6	2.454191000	0.956480000	-0.620020000
1	1.284091000	0.216636000	-1.603559000
6	2.510323000	0.423526000	0.688027000
1	2.172406000	1.104026000	1.471002000
6	3.549103000	-0.589275000	1.116392000
1	4.455150000	-0.075393000	1.466105000
1	3.828722000	-1.249601000	0.289847000
6	0.194462000	-0.734917000	1.899359000
8	0.204374000	-1.115484000	2.988369000

1	3.184516000	-1.217450000	1.934868000
1	3.150531000	0.521400000	-1.337867000

I-4

B3LYP-D3 electronic energy: -1020.254023 a.u.
 B3LYP-D3 enthalpy: -1019.973918 a.u.
 B3LYP-D3 free energy: -1020.045163 a.u.
 M06-D3 SCF energy in solution: -1019.163283 a.u.
 M06-D3 enthalpy in solution: -1018.883178 a.u.
 M06-D3 free energy in solution: -1018.954423 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.420195000	-0.459976000	0.089278000
6	0.337247000	-0.901001000	-1.905386000
6	0.012954000	-2.366004000	0.538305000
8	-0.275189000	-3.470270000	0.802893000
8	0.330896000	-1.198554000	-3.022987000
7	-1.811422000	-0.123223000	-0.013495000
6	-2.194896000	1.091623000	-0.481847000
6	-2.760588000	-1.014240000	0.350136000
6	-3.545419000	1.426312000	-0.590505000
6	-1.096387000	2.032695000	-0.906991000
6	-4.117408000	-0.738787000	0.263765000
1	-2.406319000	-1.968867000	0.717542000
6	-4.520843000	0.508332000	-0.216167000
1	-3.812702000	2.409714000	-0.963898000
1	-1.030856000	1.991737000	-2.010598000
1	-1.338787000	3.069774000	-0.645688000
7	0.144303000	1.627409000	-0.293684000
1	-4.836000000	-1.490779000	0.571081000
1	-5.574490000	0.760451000	-0.291301000
6	1.007082000	2.595722000	0.102915000
6	2.248174000	2.029003000	0.811189000
8	0.847427000	3.808683000	-0.045084000
1	3.110383000	2.641573000	0.520886000
1	2.104986000	2.184201000	1.887801000
6	2.522476000	0.558836000	0.529225000
1	1.439921000	-1.902556000	0.370505000
6	2.597631000	0.065451000	-0.782804000
1	2.385824000	0.778599000	-1.579074000
6	3.487921000	-1.090024000	-1.180926000
1	3.668611000	-1.764494000	-0.338153000
1	4.457108000	-0.700108000	-1.521966000
6	0.377815000	-0.057376000	2.098563000
8	0.365435000	0.149900000	3.234179000
1	3.058468000	-1.674238000	-2.000541000
1	3.066146000	0.012568000	1.298268000

TS4

B3LYP-D3 electronic energy: -1020.237110 a.u.
 B3LYP-D3 enthalpy: -1019.958547 a.u.
 B3LYP-D3 free energy: -1020.031354 a.u.
 M06-D3 SCF energy in solution: -1019.143542 a.u.
 M06-D3 enthalpy in solution: -1018.864979 a.u.

M06-D3 free energy in solution: -1018.937786 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.408479000	-0.379223000	0.078894000
6	-0.184912000	0.014744000	2.084043000
6	-0.226299000	-2.378780000	0.108493000
8	-0.090493000	-3.535523000	0.086015000
8	-0.053409000	0.234883000	3.210626000
7	1.828912000	-0.282272000	-0.032714000
6	2.371859000	0.927003000	-0.322844000
6	2.663986000	-1.320283000	0.215356000
6	3.757074000	1.106925000	-0.367195000
6	1.430755000	2.061469000	-0.616057000
6	4.043868000	-1.201710000	0.189010000
1	2.194501000	-2.268680000	0.440314000
6	4.608502000	0.040478000	-0.110039000
1	4.146147000	2.093290000	-0.600006000
1	1.753592000	2.970597000	-0.089689000
1	1.506523000	2.303693000	-1.691857000
7	0.080534000	1.705946000	-0.252138000
1	4.657554000	-2.071039000	0.399105000
1	5.686068000	0.171337000	-0.138324000
6	-0.793972000	2.730452000	-0.115042000
6	-2.176704000	2.222207000	0.318766000
8	-0.537655000	3.925160000	-0.274348000
1	-2.201677000	2.179699000	1.416281000
1	-2.930900000	2.949759000	-0.001663000
6	-2.476245000	0.863247000	-0.268155000
1	-1.670252000	-1.375283000	0.780006000
6	-2.974852000	-0.217728000	0.453859000
1	-3.112857000	-0.080375000	1.525801000
6	-3.826559000	-1.286387000	-0.196186000
1	-3.503188000	-1.468084000	-1.225144000
1	-4.869542000	-0.943291000	-0.215045000
6	-0.629047000	-0.691755000	-1.918139000
8	-0.803162000	-0.900740000	-3.045488000
1	-3.790327000	-2.233229000	0.349764000
1	-2.651295000	0.858860000	-1.343392000

I-5

B3LYP-D3 electronic energy: -1020.263138 a.u.

B3LYP-D3 enthalpy: -1019.979245 a.u.

B3LYP-D3 free energy: -1020.05119 a.u.

M06-D3 SCF energy in solution: -1019.172528 a.u.

M06-D3 enthalpy in solution: -1018.888635 a.u.

M06-D3 free energy in solution: -1018.96058 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.430700000	-0.342226000	0.194806000
6	-2.060353000	-1.102280000	1.059368000
8	-3.007788000	-1.539269000	1.571714000
7	1.815043000	-0.309223000	-0.290487000
6	2.432623000	0.882472000	-0.108505000

6	2.555383000	-1.380875000	-0.656046000
6	3.812646000	1.015931000	-0.284756000
6	1.566263000	2.037726000	0.306823000
6	3.926963000	-1.314280000	-0.843353000
1	2.014599000	-2.308192000	-0.798506000
6	4.571185000	-0.088359000	-0.652977000
1	4.270818000	1.988145000	-0.132314000
1	1.809643000	2.298352000	1.351531000
1	1.804243000	2.932328000	-0.283738000
7	0.169847000	1.687083000	0.161392000
1	4.473466000	-2.204520000	-1.135050000
1	5.643863000	0.002104000	-0.796614000
6	-0.703069000	2.738966000	0.077994000
6	-2.143301000	2.251424000	-0.013288000
8	-0.379216000	3.925524000	0.085072000
1	-2.588057000	2.321689000	0.987714000
1	-2.710176000	2.934862000	-0.660049000
6	-2.210719000	0.812186000	-0.502553000
6	-1.691768000	0.561396000	-1.923555000
1	-1.434463000	1.518763000	-2.394947000
6	-2.624986000	-0.287869000	-2.789475000
1	-3.576505000	0.232363000	-2.943988000
1	-2.836363000	-1.243623000	-2.297917000
6	-0.478577000	-2.218504000	-0.508423000
8	-0.457926000	-3.277847000	-0.994195000
1	-2.185546000	-0.499035000	-3.770355000
1	-3.214119000	0.402087000	-0.386101000
6	0.217675000	-0.600132000	2.052132000
8	0.616451000	-0.681756000	3.137849000
1	-0.685772000	0.044360000	-1.935492000

I-6

B3LYP-D3 electronic energy: -1133.60247 a.u.
B3LYP-D3 enthalpy: -1133.307005 a.u.
B3LYP-D3 free energy: -1133.384956 a.u.
M06-D3 SCF energy in solution: -1132.480477 a.u.
M06-D3 enthalpy in solution: -1132.185012 a.u.
M06-D3 free energy in solution: -1132.262963 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.167144000	-0.554636000	-0.037444000
6	1.695988000	-1.821722000	0.243034000
8	2.571417000	-2.559240000	0.433368000
7	-2.085560000	0.092605000	0.074772000
6	-2.285435000	1.404217000	0.342040000
6	-3.164161000	-0.701624000	-0.098715000
6	-3.571370000	1.938232000	0.452233000
6	-1.049721000	2.236349000	0.536489000
6	-4.467304000	-0.236124000	-0.003183000
1	-2.967823000	-1.741386000	-0.325267000
6	-4.677892000	1.114868000	0.280494000
1	-3.684257000	2.996932000	0.662867000
1	-1.178242000	3.243940000	0.125044000
1	-0.891169000	2.355850000	1.624610000

7	0.080252000	1.584108000	-0.084371000
1	-5.293805000	-0.921961000	-0.154636000
1	-5.683970000	1.516867000	0.355525000
6	0.987982000	2.386885000	-0.711317000
6	2.144924000	1.568520000	-1.267781000
8	0.904503000	3.610345000	-0.818442000
1	1.906385000	1.277006000	-2.297768000
1	3.026372000	2.217577000	-1.329837000
6	2.432418000	0.338659000	-0.402583000
6	3.070270000	0.690629000	0.945963000
1	2.433042000	1.418703000	1.463196000
6	4.497806000	1.250970000	0.814253000
1	4.518266000	2.203311000	0.274723000
1	5.147710000	0.545304000	0.282512000
6	-0.628627000	-2.430734000	-0.163036000
8	-1.114978000	-3.478113000	-0.252597000
1	4.930865000	1.424362000	1.806071000
1	3.069552000	-0.356770000	-0.954078000
6	0.165770000	-0.615902000	-2.089626000
8	0.161675000	-0.677311000	-3.241552000
1	3.111854000	-0.198814000	1.584166000
6	0.151316000	-0.376245000	2.020699000
8	0.153875000	-0.290270000	3.170118000

TS5

B3LYP-D3 electronic energy: -1133.559798 a.u.
 B3LYP-D3 enthalpy: -1133.266233 a.u.
 B3LYP-D3 free energy: -1133.343845 a.u.
 M06-D3 SCF energy in solution: -1132.447049 a.u.
 M06-D3 enthalpy in solution: -1132.153484 a.u.
 M06-D3 free energy in solution: -1132.231096 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.102975000	-0.459908000	0.091439000
6	0.922288000	-2.085155000	0.941606000
8	1.450153000	-2.983806000	1.457539000
7	-2.108188000	-0.095704000	-0.126671000
6	-2.467164000	1.206838000	0.012913000
6	-3.063438000	-1.010736000	-0.410150000
6	-3.794243000	1.607309000	-0.154171000
6	-1.392431000	2.184316000	0.407800000
6	-4.396917000	-0.672906000	-0.578872000
1	-2.728792000	-2.036140000	-0.499198000
6	-4.772578000	0.666363000	-0.454127000
1	-4.040425000	2.658833000	-0.046792000
1	-1.539987000	3.149232000	-0.090036000
1	-1.498197000	2.381428000	1.490631000
7	-0.076114000	1.649818000	0.106263000
1	-5.119799000	-1.448668000	-0.806428000
1	-5.806720000	0.968466000	-0.589217000
6	0.910162000	2.587988000	-0.077700000
6	2.313066000	2.029315000	-0.345613000
8	0.720808000	3.801133000	-0.017265000
1	2.591785000	2.302213000	-1.371073000

1	2.996913000	2.563537000	0.322708000
6	2.441590000	0.511842000	-0.170857000
6	-0.289722000	-1.923857000	-1.203341000
8	-0.542772000	-2.717744000	-2.011004000
6	1.406805000	-0.067193000	-1.419944000
8	1.804349000	0.056650000	-2.538938000
6	-0.553546000	-0.335723000	2.165204000
8	-0.773384000	-0.376582000	3.292156000
6	3.809701000	-0.113177000	-0.466031000
1	3.713891000	-1.204164000	-0.391785000
6	4.915794000	0.369323000	0.479391000
1	4.068271000	0.109933000	-1.507374000
1	4.670349000	0.148256000	1.525712000
1	5.080521000	1.448802000	0.393360000
1	5.863260000	-0.129402000	0.246174000
1	2.209461000	0.277598000	0.883167000

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B3LYP-D3 electronic energy: -1246.928254 a.u.
B3LYP-D3 enthalpy: -1246.621312 a.u.
B3LYP-D3 free energy: -1246.704444 a.u.
M06-D3 SCF energy in solution: -1245.78241 a.u.
M06-D3 enthalpy in solution: -1245.475468 a.u.
M06-D3 free energy in solution: -1245.5586 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.343354000	-0.838432000	-0.037736000
6	0.906152000	-2.355261000	0.296473000
8	1.650322000	-3.226705000	0.493745000
7	-1.590787000	1.037765000	-0.240285000
6	-1.476629000	1.931662000	0.765949000
6	-2.353275000	1.345744000	-1.307773000
6	-2.143406000	3.156488000	0.726865000
6	-0.609032000	1.513493000	1.924739000
6	-3.043836000	2.544620000	-1.412680000
1	-2.395164000	0.596576000	-2.090184000
6	-2.937974000	3.469535000	-0.371872000
1	-2.023656000	3.853198000	1.550222000
1	-0.144836000	2.379712000	2.406295000
1	-1.253828000	1.040163000	2.686756000
7	0.417468000	0.586997000	1.467245000
1	-3.642383000	2.746906000	-2.294206000
1	-3.458692000	4.421304000	-0.421781000
6	1.653973000	0.748336000	2.032267000
6	2.765111000	0.006538000	1.298160000
8	1.886539000	1.477667000	2.996456000
1	3.713702000	0.312570000	1.743757000
1	2.661860000	-1.068175000	1.460660000
6	2.762029000	0.341723000	-0.220805000
6	0.321316000	-0.897361000	-1.944624000
8	0.681701000	-1.001443000	-3.042988000
6	1.352299000	0.758745000	-0.676031000
8	1.043389000	1.783652000	-1.204653000
6	-1.396540000	-1.521422000	1.663969000

8	-1.933360000	-2.017251000	2.549734000
6	3.788000000	1.435668000	-0.581935000
1	4.739972000	1.147784000	-0.118295000
1	3.480718000	2.377609000	-0.111735000
6	3.997972000	1.628591000	-2.086858000
1	3.086927000	1.982962000	-2.576085000
1	4.788850000	2.363550000	-2.273099000
1	4.298410000	0.687232000	-2.564115000
1	2.988879000	-0.568206000	-0.792139000
6	-1.749331000	-1.975608000	-0.951766000
8	-2.608630000	-2.564855000	-1.458141000

TS6

B3LYP-D3 electronic energy: -1246.92825 a.u.
 B3LYP-D3 enthalpy: -1246.622247 a.u.
 B3LYP-D3 free energy: -1246.702661 a.u.
 M06-D3 SCF energy in solution: -1245.781779 a.u.
 M06-D3 enthalpy in solution: -1245.475776 a.u.
 M06-D3 free energy in solution: -1245.55619 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.339976000	-0.841699000	-0.039663000
6	0.933722000	-2.340673000	0.275064000
8	1.694626000	-3.200690000	0.460719000
7	-1.612211000	1.018826000	-0.228177000
6	-1.480277000	1.927006000	0.762880000
6	-2.409172000	1.304256000	-1.276810000
6	-2.161766000	3.143833000	0.727402000
6	-0.579553000	1.534226000	1.904923000
6	-3.116345000	2.493800000	-1.376952000
1	-2.465292000	0.544107000	-2.047643000
6	-2.991183000	3.433593000	-0.351708000
1	-2.026817000	3.852462000	1.538141000
1	-0.113864000	2.412523000	2.362803000
1	-1.199520000	1.065882000	2.690173000
7	0.444304000	0.609531000	1.437684000
1	-3.742745000	2.677478000	-2.243069000
1	-3.524236000	4.378645000	-0.398541000
6	1.672116000	0.739934000	2.030327000
6	2.788180000	0.019796000	1.282916000
8	1.891038000	1.432615000	3.023434000
1	3.735434000	0.340698000	1.721014000
1	2.705825000	-1.057289000	1.442226000
6	2.758607000	0.363109000	-0.232804000
6	0.308824000	-0.860380000	-1.953625000
8	0.658927000	-0.939840000	-3.057219000
6	1.342122000	0.793767000	-0.655251000
8	1.021885000	1.816608000	-1.179764000
6	-1.362697000	-1.520094000	1.680562000
8	-1.889655000	-2.013128000	2.574094000
6	3.782593000	1.454131000	-0.609204000
1	4.742332000	1.157456000	-0.167559000
1	3.491126000	2.395126000	-0.127029000
6	3.961494000	1.654645000	-2.117117000

1	3.041730000	2.015390000	-2.584900000
1	4.751477000	2.387211000	-2.316024000
1	4.247396000	0.714605000	-2.605667000
1	2.968727000	-0.542797000	-0.815978000
6	-1.727413000	-2.011069000	-0.937512000
8	-2.576013000	-2.624764000	-1.433509000

I-8

B3LYP-D3 electronic energy: -1246.98671 a.u.
B3LYP-D3 enthalpy: -1246.677876 a.u.
B3LYP-D3 free energy: -1246.759371 a.u.
M06-D3 SCF energy in solution: -1245.834413 a.u.
M06-D3 enthalpy in solution: -1245.525579 a.u.
M06-D3 free energy in solution: -1245.607074 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.520940000	-0.854689000	-0.185708000
6	0.748575000	-2.374133000	-0.216297000
8	1.567998000	-3.208926000	-0.209689000
7	-1.685167000	1.083202000	-0.031819000
6	-1.232284000	2.042142000	0.805296000
6	-2.758003000	1.357824000	-0.804634000
6	-1.829562000	3.298777000	0.879729000
6	-0.086844000	1.667521000	1.708930000
6	-3.411277000	2.582597000	-0.774329000
1	-3.082224000	0.556830000	-1.458596000
6	-2.936642000	3.576753000	0.082333000
1	-1.422820000	4.046236000	1.553064000
1	0.438475000	2.566097000	2.047957000
1	-0.457599000	1.127114000	2.586077000
7	0.873040000	0.753048000	1.059211000
1	-4.269187000	2.748919000	-1.416779000
1	-3.415715000	4.550115000	0.124833000
6	1.653200000	-0.118433000	1.921665000
6	2.950416000	-0.442682000	1.207404000
8	1.310083000	-0.417412000	3.037634000
1	3.769927000	-0.142977000	1.871523000
1	3.028104000	-1.521737000	1.051542000
6	2.944699000	0.368940000	-0.106876000
6	0.190796000	-0.273555000	-2.007462000
8	0.604834000	0.013640000	-3.052329000
6	1.753375000	1.310533000	0.058927000
8	1.539059000	2.381193000	-0.457283000
6	-1.279668000	-1.523674000	1.604684000
8	-1.726027000	-1.948261000	2.583338000
6	4.255381000	1.107645000	-0.424127000
1	5.075430000	0.389956000	-0.293299000
1	4.412783000	1.900134000	0.319973000
6	4.298152000	1.691545000	-1.840270000
1	3.508581000	2.433652000	-1.980201000
1	5.264649000	2.170298000	-2.031397000
1	4.158105000	0.903165000	-2.589737000
1	2.704941000	-0.298866000	-0.941946000
6	-1.899608000	-1.903612000	-1.116415000

8 -2.751347000 -2.475836000 -1.672136000

W(CO)₆

B3LYP-D3 electronic energy: -747.942706 a.u.

B3LYP-D3 enthalpy: -747.877781 a.u.

B3LYP-D3 free energy: -747.934072 a.u.

M06-D3 SCF energy in solution: -747.03465 a.u.

M06-D3 enthalpy in solution: -746.969725 a.u.

M06-D3 free energy in solution: -747.026016 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.000000000	0.000000000	0.000000000
6	0.000000000	0.000000000	2.069526000
6	0.000000000	2.069526000	0.000000000
6	-2.069526000	0.000000000	0.000000000
6	0.000000000	-2.069526000	0.000000000
6	2.069526000	0.000000000	0.000000000
6	0.000000000	0.000000000	-2.069526000
8	3.220379000	0.000000000	0.000000000
8	0.000000000	-3.220379000	0.000000000
8	0.000000000	0.000000000	3.220379000
8	-3.220379000	0.000000000	0.000000000
8	0.000000000	3.220379000	0.000000000
8	0.000000000	0.000000000	-3.220379000

W(CO)₅

B3LYP-D3 electronic energy: -634.559789 a.u.

B3LYP-D3 enthalpy: -634.505631 a.u.

B3LYP-D3 free energy: -634.558168 a.u.

M06-D3 SCF energy in solution: -633.689332 a.u.

M06-D3 enthalpy in solution: -633.635174 a.u.

M06-D3 free energy in solution: -633.687711 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.000000000	0.000000000	0.249185000
6	-2.062051000	0.000000000	0.269799000
6	0.000000000	-2.062051000	0.269799000
6	2.062051000	0.000000000	0.269799000
6	0.000000000	2.062051000	0.269799000
6	0.000000000	0.000000000	-1.707285000
8	0.000000000	3.214620000	0.258532000
8	3.214620000	0.000000000	0.258532000
8	0.000000000	-3.214620000	0.258532000
8	-3.214620000	0.000000000	0.258532000
8	0.000000000	0.000000000	-2.868021000

W(CO)₄

B3LYP-D3 electronic energy: -521.135937 a.u.

B3LYP-D3 enthalpy: -521.09269 a.u.

B3LYP-D3 free energy: -521.142007 a.u.

M06-D3 SCF energy in solution: -520.301232 a.u.

M06-D3 enthalpy in solution: -520.257985 a.u.

M06-D3 free energy in solution: -520.307302 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.000003000	0.000174000	0.000000000
6	-0.000358000	-0.000332000	2.044874000
6	-0.688562000	-1.925061000	0.000000000
6	-0.000358000	-0.000332000	-2.044874000
6	0.688935000	1.925352000	0.000000000
8	-0.000358000	-0.000696000	-3.201423000
8	-1.077846000	-3.014205000	0.000000000
8	-0.000358000	-0.000696000	3.201423000
8	1.078842000	3.014266000	0.000000000

CO

B3LYP-D3 electronic energy: -113.306913 a.u.
 B3LYP-D3 enthalpy: -113.298571 a.u.
 B3LYP-D3 free energy: -113.321014 a.u.
 M06-D3 SCF energy in solution: -113.281218 a.u.
 M06-D3 enthalpy in solution: -113.272876 a.u.
 M06-D3 free energy in solution: -113.295319 a.u.

Cartesian coordinates

ATOM	X	Y	Z
8	0.000000000	0.000000000	0.487595000
6	0.000000000	0.000000000	-0.650127000

I-1a

B3LYP-D3 electronic energy: -612.331963 a.u.
 B3LYP-D3 enthalpy: -612.082219 a.u.
 B3LYP-D3 free energy: -612.141014 a.u.
 M06-D3 SCF energy in solution: -612.061983 a.u.
 M06-D3 enthalpy in solution: -611.812239 a.u.
 M06-D3 free energy in solution: -611.871034 a.u.

Cartesian coordinates

ATOM	X	Y	Z
7	-2.179566000	0.986714000	-0.184484000
6	-2.304295000	-0.324442000	0.056651000
6	-3.288769000	1.739723000	-0.195826000
6	-3.546234000	-0.928649000	0.295220000
6	-1.038089000	-1.159136000	0.065001000
6	-4.564679000	1.229811000	0.029959000
1	-3.141873000	2.799470000	-0.395539000
6	-4.691421000	-0.139272000	0.281300000
1	-3.602721000	-1.996776000	0.487002000
1	-0.932195000	-1.669742000	1.032741000
1	-1.112885000	-1.960693000	-0.683849000
7	0.124033000	-0.340845000	-0.194472000
1	-5.430573000	1.884130000	0.009575000
1	-5.667153000	-0.581440000	0.463128000
1	-0.053394000	0.644260000	-0.349883000
6	1.368812000	-0.883448000	-0.243535000
6	2.501086000	0.088157000	-0.571639000
8	1.567115000	-2.081081000	-0.050877000
1	2.743276000	-0.043356000	-1.635733000

1	2.186805000	1.131476000	-0.445464000
6	3.752407000	-0.204320000	0.276242000
1	3.534832000	-0.006527000	1.333511000
1	3.958845000	-1.278831000	0.191451000
6	4.941130000	0.599958000	-0.168328000
1	5.267020000	0.430273000	-1.196830000
6	5.595057000	1.488640000	0.581245000
1	6.450104000	2.042259000	0.201963000
1	5.301687000	1.690915000	1.609891000

I-9

B3LYP-D3 electronic energy: -1133.613675 a.u.
B3LYP-D3 enthalpy: -1133.317052 a.u.
B3LYP-D3 free energy: -1133.397641 a.u.
M06-D3 SCF energy in solution: -1132.486607 a.u.
M06-D3 enthalpy in solution: -1132.189984 a.u.
M06-D3 free energy in solution: -1132.270573 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.216592000	-0.676520000	0.104452000
6	0.211195000	-0.270731000	2.117194000
6	0.985222000	-2.456167000	0.455075000
6	0.142485000	-1.121511000	-1.884269000
6	-1.615261000	-1.416111000	0.289950000
8	0.073632000	-1.393831000	-3.011567000
8	1.513581000	-3.481019000	0.642968000
8	0.182255000	-0.080806000	3.259046000
8	-2.700658000	-1.838978000	0.389964000
7	2.223313000	0.361359000	-0.170961000
6	2.246420000	1.715015000	-0.168214000
6	3.379951000	-0.299314000	-0.389108000
6	3.416416000	2.434504000	-0.403056000
6	0.946348000	2.398327000	0.162424000
6	4.586196000	0.351999000	-0.616637000
1	3.311803000	-1.380826000	-0.375856000
6	4.607815000	1.746953000	-0.628126000
1	3.388061000	3.519695000	-0.402478000
1	0.805928000	2.429498000	1.247514000
1	0.938888000	3.433008000	-0.200496000
7	-0.204033000	1.636288000	-0.372270000
1	5.485642000	-0.230367000	-0.785255000
1	5.531158000	2.288366000	-0.810032000
1	-0.241303000	1.666189000	-1.390266000
6	-1.485461000	1.977854000	0.202915000
6	-2.679582000	1.632400000	-0.663854000
8	-1.547494000	2.512109000	1.287555000
1	-2.875036000	2.506368000	-1.305075000
1	-2.439129000	0.794542000	-1.325792000
6	-3.926124000	1.302588000	0.178123000
1	-3.696296000	0.448854000	0.821344000
1	-4.137823000	2.155680000	0.833409000
6	-5.107091000	0.985392000	-0.699391000
1	-5.560687000	1.829238000	-1.222935000
6	-5.586880000	-0.244849000	-0.888799000

1	-6.432344000	-0.433662000	-1.545468000
1	-5.142030000	-1.105541000	-0.394517000

I-1a

B3LYP-D3 electronic energy: -1020.258031 a.u.
 B3LYP-D3 enthalpy: -1019.972431 a.u.
 B3LYP-D3 free energy: -1020.04348 a.u.
 M06-D3 SCF energy in solution: -1019.162028 a.u.
 M06-D3 enthalpy in solution: -1018.876428 a.u.
 M06-D3 free energy in solution: -1018.947477 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.310446000	-0.544804000	0.005860000
6	-0.796489000	0.090574000	1.877941000
6	0.048083000	-2.354613000	0.705120000
6	0.103285000	-1.222159000	-1.856254000
8	0.324118000	-1.625139000	-2.927261000
8	0.290206000	-3.419734000	1.119739000
8	-1.100789000	0.400828000	2.956608000
7	1.816106000	0.113432000	0.143968000
6	2.132565000	1.401018000	-0.142080000
6	2.837476000	-0.749001000	0.368951000
6	3.451683000	1.835000000	-0.255018000
6	0.992320000	2.377570000	-0.227407000
6	4.172070000	-0.376780000	0.301392000
1	2.550389000	-1.768090000	0.596204000
6	4.495247000	0.940011000	-0.030404000
1	3.650241000	2.873063000	-0.504389000
1	0.774517000	2.755119000	0.776989000
1	1.259155000	3.240598000	-0.848144000
7	-0.270068000	1.765033000	-0.695821000
1	4.940363000	-1.118217000	0.493666000
1	5.529097000	1.260845000	-0.110773000
1	-0.315663000	1.677934000	-1.708706000
6	-1.462496000	2.395406000	-0.166630000
6	-2.766185000	2.025680000	-0.837585000
8	-1.396430000	3.116960000	0.804166000
1	-3.459273000	2.849252000	-0.646106000
1	-2.637656000	1.921727000	-1.923227000
6	-3.308509000	0.697147000	-0.260228000
1	-3.320731000	0.760372000	0.834283000
1	-4.353222000	0.584912000	-0.588812000
6	-2.477916000	-0.484876000	-0.722155000
1	-2.515510000	-0.608491000	-1.808231000
6	-2.377756000	-1.686751000	0.027199000
1	-2.351039000	-2.643428000	-0.486934000
1	-2.797016000	-1.731989000	1.030443000

I-1b

B3LYP-D3 electronic energy: -1020.23203 a.u.
 B3LYP-D3 enthalpy: -1019.946327 a.u.
 B3LYP-D3 free energy: -1020.02237 a.u.
 M06-D3 SCF energy in solution: -1019.143032 a.u.
 M06-D3 enthalpy in solution: -1018.857329 a.u.

M06-D3 free energy in solution: -1018.933372 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.236702000	-0.685130000	-0.086819000
6	-0.297839000	-0.845487000	1.756981000
6	0.926884000	-2.509352000	-0.017602000
6	-1.520812000	-1.393712000	-0.598291000
8	1.416970000	-3.575398000	0.006719000
8	-0.603726000	-0.898517000	2.887707000
8	-2.565395000	-1.796987000	-0.953515000
7	2.266319000	0.278957000	-0.120769000
6	2.333529000	1.635629000	-0.141670000
6	3.413384000	-0.423046000	-0.285890000
6	3.533423000	2.311848000	-0.347834000
6	1.049773000	2.363073000	0.148144000
6	4.644781000	0.187879000	-0.484261000
1	3.313017000	-1.501339000	-0.246009000
6	4.708843000	1.581711000	-0.520813000
1	3.542105000	3.397209000	-0.364109000
1	0.886841000	2.402968000	1.229871000
1	1.085698000	3.394817000	-0.220689000
7	-0.122711000	1.639943000	-0.400501000
1	5.532127000	-0.423524000	-0.607753000
1	5.654584000	2.090869000	-0.679618000
1	-0.224688000	1.790691000	-1.405777000
6	-1.377362000	1.926199000	0.282390000
6	-2.629447000	1.689774000	-0.535149000
8	-1.368684000	2.364286000	1.410407000
1	-2.935419000	2.672013000	-0.927487000
1	-2.429149000	1.039998000	-1.391854000
6	-3.765298000	1.093099000	0.320528000
1	-3.458979000	0.099202000	0.658096000
1	-3.886079000	1.719145000	1.212242000
6	-5.050331000	1.012225000	-0.459006000
1	-5.564169000	1.959177000	-0.636654000
6	-5.557970000	-0.117390000	-0.954394000
1	-6.484534000	-0.124786000	-1.523145000
1	-5.055264000	-1.070911000	-0.812941000

I-1c

B3LYP-D3 electronic energy: -1020.232948 a.u.

B3LYP-D3 enthalpy: -1019.947254 a.u.

B3LYP-D3 free energy: -1020.023445 a.u.

M06-D3 SCF energy in solution: -1019.144098 a.u.

M06-D3 enthalpy in solution: -1018.858404 a.u.

M06-D3 free energy in solution: -1018.934595 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.228095000	-0.665500000	-0.183913000
6	-0.951653000	-2.384116000	-0.767330000
6	-0.167402000	-1.347272000	1.606213000
6	1.590025000	-1.368251000	-0.468562000
8	-0.154276000	-1.714602000	2.723967000

8	-1.457084000	-3.384494000	-1.111494000
8	2.678156000	-1.771301000	-0.642915000
7	-2.222195000	0.374949000	-0.057988000
6	-2.260491000	1.725545000	0.058049000
6	-3.392782000	-0.304931000	0.001016000
6	-3.452986000	2.417878000	0.259408000
6	-0.949498000	2.453500000	-0.097046000
6	-4.616658000	0.321261000	0.190209000
1	-3.313673000	-1.380512000	-0.102068000
6	-4.651606000	1.710653000	0.325717000
1	-3.435459000	3.498718000	0.360541000
1	-0.773151000	2.686220000	-1.152493000
1	-0.964652000	3.404309000	0.448446000
7	0.200529000	1.622399000	0.326560000
1	-5.521486000	-0.275205000	0.234561000
1	-5.591204000	2.231593000	0.482300000
1	0.304708000	1.584385000	1.339177000
6	1.452843000	1.902815000	-0.338497000
6	2.690376000	1.612657000	0.483931000
8	1.451412000	2.353073000	-1.465676000
1	2.868037000	2.494847000	1.119876000
1	2.502753000	0.767553000	1.154299000
6	3.920189000	1.327602000	-0.396191000
1	3.691979000	0.477754000	-1.044542000
1	4.096308000	2.194202000	-1.044388000
6	5.131314000	1.022710000	0.444846000
1	5.597021000	1.870282000	0.951283000
6	5.620887000	-0.205310000	0.623287000
1	6.486161000	-0.389706000	1.254931000
1	5.162322000	-1.068728000	0.146296000

I-1d

B3LYP-D3 electronic energy: -1020.205675 a.u.
 B3LYP-D3 enthalpy: -1019.921367 a.u.
 B3LYP-D3 free energy: -1019.996039 a.u.
 M06-D3 SCF energy in solution: -1019.110968 a.u.
 M06-D3 enthalpy in solution: -1018.82666 a.u.
 M06-D3 free energy in solution: -1018.901332 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.199481000	-0.381241000	0.177689000
6	-0.156444000	0.354152000	2.074975000
6	-0.159580000	-2.165772000	0.962355000
6	-0.448102000	-1.308656000	-1.605084000
8	-0.642064000	-1.897222000	-2.594656000
8	-0.053005000	-3.246837000	1.411384000
8	-0.191564000	0.712062000	3.181751000
7	1.929316000	-0.164671000	-0.086420000
6	2.397565000	1.084003000	-0.384789000
6	2.826384000	-1.181222000	-0.047500000
6	3.738046000	1.320784000	-0.668763000
6	1.388019000	2.205121000	-0.336910000
6	4.177647000	-1.003984000	-0.309055000
1	2.415325000	-2.150250000	0.205973000

6	4.652408000	0.268377000	-0.630758000
1	4.057610000	2.329666000	-0.911999000
1	1.229123000	2.527136000	0.698145000
1	1.731663000	3.074583000	-0.908865000
7	0.075936000	1.724202000	-0.809896000
1	4.842006000	-1.860365000	-0.259985000
1	5.702721000	0.437802000	-0.845463000
1	0.044314000	1.549799000	-1.812245000
6	-1.106821000	2.363934000	-0.308608000
6	-2.400989000	1.757496000	-0.835447000
8	-1.057047000	3.231823000	0.536263000
1	-3.156157000	2.550205000	-0.853607000
1	-2.280005000	1.363822000	-1.850333000
6	-2.890494000	0.617176000	0.092724000
1	-2.232092000	-0.298473000	0.113190000
1	-2.963243000	0.995447000	1.116866000
6	-4.204880000	0.050954000	-0.379525000
1	-5.053821000	0.733642000	-0.329775000
6	-4.352399000	-1.184357000	-0.856930000
1	-5.315038000	-1.552682000	-1.199559000
1	-3.510255000	-1.871889000	-0.915130000

I-1e

B3LYP-D3 electronic energy: -1020.195286 a.u.

B3LYP-D3 enthalpy: -1019.909802 a.u.

B3LYP-D3 free energy: -1019.98522 a.u.

M06-D3 SCF energy in solution: -1019.103461 a.u.

M06-D3 enthalpy in solution: -1018.817977 a.u.

M06-D3 free energy in solution: -1018.893395 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.249118000	-0.783083000	0.357551000
6	0.221435000	0.082026000	2.200740000
6	0.104903000	-1.738151000	-1.417641000
6	-1.606278000	-1.328994000	0.681010000
8	-0.035504000	-2.290187000	-2.437388000
8	0.147894000	0.543048000	3.266691000
8	-2.726995000	-1.646753000	0.850846000
7	2.335843000	-0.055465000	-0.117773000
6	2.438244000	1.260972000	-0.428074000
6	3.448516000	-0.815707000	-0.186200000
6	3.646696000	1.836267000	-0.813701000
6	1.172323000	2.060546000	-0.290909000
6	4.689732000	-0.308271000	-0.548794000
1	3.315341000	-1.865700000	0.056119000
6	4.794525000	1.046386000	-0.869629000
1	3.682221000	2.892379000	-1.062516000
1	1.022701000	2.364399000	0.749798000
1	1.203633000	2.969748000	-0.903005000
7	-0.007914000	1.225182000	-0.638306000
1	5.551013000	-0.966857000	-0.583438000
1	5.747012000	1.476969000	-1.162720000
1	-0.040326000	1.038850000	-1.640581000
6	-1.284087000	1.786809000	-0.196971000

6	-2.481822000	1.354117000	-1.015878000
8	-1.313284000	2.583566000	0.713676000
1	-2.581490000	2.076625000	-1.842395000
1	-2.304560000	0.370589000	-1.459031000
6	-3.771210000	1.332699000	-0.173727000
1	-3.625211000	0.644342000	0.662187000
1	-3.928070000	2.332551000	0.247942000
6	-4.953334000	0.899216000	-0.998488000
1	-5.339335000	1.627305000	-1.714776000
6	-5.508311000	-0.311578000	-0.922395000
1	-6.350305000	-0.595684000	-1.548760000
1	-5.127772000	-1.060795000	-0.231674000

I-1f

B3LYP-D3 electronic energy: -1020.229072 a.u.
 B3LYP-D3 enthalpy: -1019.943741 a.u.
 B3LYP-D3 free energy: -1020.017187 a.u.
 M06-D3 SCF energy in solution: -1019.137689 a.u.
 M06-D3 enthalpy in solution: -1018.852358 a.u.
 M06-D3 free energy in solution: -1018.925804 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.884295000	-0.506724000	-0.085440000
6	1.818980000	-2.230748000	-0.300524000
6	-0.014956000	-0.875083000	-1.835406000
6	-0.532411000	-1.439259000	0.812670000
8	-0.526110000	-1.087852000	-2.860592000
8	2.380320000	-3.243842000	-0.432822000
8	-1.387454000	-1.974348000	1.413197000
7	-2.633321000	1.132676000	1.016867000
6	-2.531295000	0.898327000	-0.301526000
6	-3.547869000	0.444922000	1.707529000
6	-3.328825000	-0.027311000	-0.973939000
6	-1.467051000	1.706751000	-1.006365000
6	-4.405095000	-0.488567000	1.123130000
1	-3.592510000	0.645781000	2.775731000
6	-4.287565000	-0.730320000	-0.244176000
1	-3.176892000	-0.211591000	-2.032577000
1	-1.246561000	1.323909000	-2.000389000
1	-1.788756000	2.750600000	-1.116010000
7	-0.233428000	1.670467000	-0.175078000
1	-5.126748000	-1.024027000	1.731508000
1	-4.918597000	-1.466540000	-0.733594000
6	0.751706000	2.646564000	-0.524063000
6	1.703975000	3.041194000	0.592763000
8	0.821071000	3.076894000	-1.655780000
1	2.269872000	3.902904000	0.231475000
1	1.122289000	3.357083000	1.469775000
6	1.936490000	0.699070000	1.601815000
1	1.194648000	0.938950000	2.366661000
6	2.535292000	-0.564737000	1.642271000
1	2.238569000	-1.300594000	2.383409000
1	3.523074000	-0.718916000	1.209621000
1	-0.529809000	1.743378000	0.803144000

6	2.656379000	1.898458000	1.001700000
1	3.380274000	2.297056000	1.727411000
1	3.251434000	1.595174000	0.126590000

TS1a

B3LYP-D3 electronic energy: -1020.196266 a.u.
 B3LYP-D3 enthalpy: -1019.917983 a.u.
 B3LYP-D3 free energy: -1019.989823 a.u.
 M06-D3 SCF energy in solution: -1019.101988 a.u.
 M06-D3 enthalpy in solution: -1018.823705 a.u.
 M06-D3 free energy in solution: -1018.895545 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.311181000	-0.566640000	0.008928000
6	-0.612954000	-0.097905000	2.023268000
6	0.275172000	-2.413241000	0.560000000
6	-0.316428000	-1.361034000	-1.833483000
8	-0.373347000	-1.847646000	-2.888416000
8	0.676398000	-3.459345000	0.864093000
8	-0.871638000	0.125062000	3.124071000
7	1.845328000	0.093420000	-0.017323000
6	2.093978000	1.421204000	0.015645000
6	2.894386000	-0.756123000	-0.108951000
6	3.396827000	1.923168000	-0.040124000
6	0.916504000	2.340661000	0.153887000
6	4.211295000	-0.325554000	-0.152263000
1	2.649731000	-1.809956000	-0.150455000
6	4.472198000	1.046301000	-0.118115000
1	3.548463000	2.997803000	-0.019991000
1	0.855770000	2.672490000	1.205543000
1	1.074732000	3.253046000	-0.432067000
7	-0.337111000	1.698263000	-0.222737000
1	5.010822000	-1.055329000	-0.221150000
1	5.490488000	1.421089000	-0.159761000
1	-0.208619000	0.551525000	-1.368813000
6	-1.379164000	2.581694000	-0.366610000
6	-2.746398000	2.039150000	-0.757939000
8	-1.218632000	3.790490000	-0.176207000
1	-3.434755000	2.880898000	-0.650027000
1	-2.729355000	1.770127000	-1.824498000
6	-3.226659000	0.824718000	0.053219000
1	-3.039215000	0.981743000	1.123098000
1	-4.317979000	0.738205000	-0.064678000
6	-2.586556000	-0.459781000	-0.421247000
1	-2.754034000	-0.637626000	-1.485454000
6	-2.426869000	-1.607419000	0.379052000
1	-2.471191000	-2.594919000	-0.070618000
1	-2.699188000	-1.583037000	1.432271000

I-2a

B3LYP-D3 electronic energy: -1020.236356 a.u.
 B3LYP-D3 enthalpy: -1019.955724 a.u.
 B3LYP-D3 free energy: -1020.028525 a.u.
 M06-D3 SCF energy in solution: -1019.14588 a.u.

M06-D3 enthalpy in solution: -1018.865248 a.u.
M06-D3 free energy in solution: -1018.938049 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.463494000	-0.545417000	0.173156000
6	0.101827000	-2.453726000	-0.395912000
6	-0.104162000	-1.245299000	1.938436000
6	2.299123000	-1.294982000	0.045235000
8	-0.451328000	-1.649213000	2.969876000
8	-0.170026000	-3.540439000	-0.703705000
8	3.379766000	-1.713817000	-0.064151000
7	-1.728408000	-0.091022000	-0.291353000
6	-2.191474000	1.043253000	0.283097000
6	-2.573876000	-0.856560000	-1.013237000
6	-3.526183000	1.429904000	0.140018000
6	-1.191120000	1.829782000	1.084236000
6	-3.906673000	-0.523250000	-1.202418000
1	-2.154976000	-1.760178000	-1.440698000
6	-4.394727000	0.644915000	-0.610626000
1	-3.862865000	2.346630000	0.613241000
1	-1.399214000	2.903795000	1.034632000
1	-1.296707000	1.538559000	2.144628000
7	0.147397000	1.548968000	0.588589000
1	-4.544187000	-1.168922000	-1.796583000
1	-5.433135000	0.937089000	-0.736754000
6	0.988590000	2.622595000	0.590567000
6	2.335731000	2.409173000	-0.097362000
8	0.686153000	3.745245000	1.012206000
1	2.899184000	3.337191000	0.022765000
1	2.907256000	1.596219000	0.362680000
6	2.127878000	2.124723000	-1.607170000
1	1.369631000	2.817596000	-1.989724000
1	3.062294000	2.347429000	-2.138775000
6	1.749395000	0.708100000	-1.958778000
1	2.578983000	0.012669000	-2.069273000
6	0.506469000	0.293077000	-2.323374000
1	0.347187000	-0.676568000	-2.786475000
1	-0.321971000	0.994915000	-2.349273000
1	1.735755000	-0.195583000	1.285361000

TS7a

B3LYP-D3 electronic energy: -1020.212723 a.u.
B3LYP-D3 enthalpy: -1019.932454 a.u.
B3LYP-D3 free energy: -1020.002884 a.u.
M06-D3 SCF energy in solution: -1019.118579 a.u.
M06-D3 enthalpy in solution: -1018.83831 a.u.
M06-D3 free energy in solution: -1018.90874 a.u.

Cartesian coordinates

ATOM	X	Y	Z
7	-1.367714000	-0.767755000	-0.097082000
6	-2.458199000	-0.346280000	0.585751000
6	-1.542380000	-1.786275000	-0.971049000
6	-3.708773000	-0.951459000	0.417124000

6	-2.357979000	0.788744000	1.597944000
6	-2.751445000	-2.430810000	-1.189116000
1	-0.657882000	-2.098811000	-1.511593000
6	-3.867242000	-2.007678000	-0.469683000
1	-4.555923000	-0.569644000	0.977518000
1	-3.374027000	1.121718000	1.829639000
1	-1.915151000	0.408802000	2.523873000
7	-1.555424000	1.921061000	1.173891000
1	-2.805240000	-3.242858000	-1.906365000
1	-4.836358000	-2.478511000	-0.605692000
1	-0.642169000	1.991601000	1.600590000
6	-1.670451000	2.405960000	-0.103579000
6	-0.419953000	3.109231000	-0.620572000
8	-2.654206000	2.191629000	-0.801715000
1	-0.705335000	3.697390000	-1.498280000
1	-0.009622000	3.789294000	0.133933000
6	0.644733000	2.073056000	-1.004238000
1	1.049579000	1.587488000	0.608298000
6	0.255165000	0.993015000	-1.872215000
1	-0.815175000	0.852222000	-2.010061000
6	1.109778000	0.014920000	-2.392239000
1	0.673823000	-0.769988000	-3.002615000
1	2.169405000	0.195092000	-2.546886000
1	1.635742000	2.496717000	-1.157200000
74	0.984575000	-0.101555000	0.047999000
6	2.912423000	0.287520000	0.084114000
6	1.567691000	-2.032005000	0.000628000
6	0.765050000	-0.316763000	2.020188000
8	2.000188000	-3.108418000	-0.056955000
8	4.055317000	0.521325000	0.070517000
8	0.538857000	-0.397744000	3.160263000

TS7b

B3LYP-D3 electronic energy: -1020.199897 a.u.

B3LYP-D3 enthalpy: -1019.920568 a.u.

B3LYP-D3 free energy: -1019.992629 a.u.

M06-D3 SCF energy in solution: -1019.105141 a.u.

M06-D3 enthalpy in solution: -1018.825812 a.u.

M06-D3 free energy in solution: -1018.897873 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.985991000	-0.366891000	0.053423000
6	-2.388933000	-1.723365000	0.310180000
6	-0.627427000	-0.517782000	2.035283000
6	0.511821000	-1.675780000	-0.244039000
8	-0.435346000	-0.592204000	3.176090000
8	-3.259813000	-2.484686000	0.459099000
8	1.394214000	-2.400622000	-0.465479000
7	2.714627000	0.652265000	-1.038164000
6	2.663727000	0.688299000	0.302572000
6	3.609635000	-0.156153000	-1.615769000
6	3.505894000	-0.075746000	1.111391000
6	1.629302000	1.625830000	0.885111000
6	4.497270000	-0.952942000	-0.892810000

1	3.611374000	-0.168893000	-2.703564000
6	4.441113000	-0.909240000	0.499772000
1	3.415378000	-0.028585000	2.192418000
1	1.327003000	1.319366000	1.887323000
1	2.030681000	2.644765000	0.959445000
7	0.448103000	1.624109000	-0.003308000
1	5.199851000	-1.598165000	-1.410170000
1	5.104115000	-1.524864000	1.100767000
6	-0.434678000	2.744983000	0.155358000
6	-1.603970000	2.764829000	-0.827686000
8	-0.282796000	3.551381000	1.043520000
1	-2.358303000	3.422535000	-0.392106000
1	-1.271103000	3.220289000	-1.771552000
6	-1.404524000	0.529470000	-1.995776000
1	-0.500575000	0.936542000	-2.449075000
6	-1.705220000	-0.825729000	-2.208488000
1	-1.043353000	-1.405998000	-2.844576000
1	-2.724805000	-1.193604000	-2.139439000
1	0.808993000	1.535877000	-0.960036000
6	-2.153193000	1.357460000	-1.068812000
1	-3.237675000	1.271206000	-1.085958000
1	-2.112339000	0.949079000	0.569980000

TS7c

B3LYP-D3 electronic energy: -906.851797 a.u.
 B3LYP-D3 enthalpy: -906.583623 a.u.
 B3LYP-D3 free energy: -906.647952 a.u.
 M06-D3 SCF energy in solution: -905.786963 a.u.
 M06-D3 enthalpy in solution: -905.518789 a.u.
 M06-D3 free energy in solution: -905.583118 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.713799000	-0.295372000	0.015870000
6	1.134812000	-1.918822000	-0.999519000
8	1.351497000	-2.861257000	-1.660559000
7	-1.500691000	-0.542989000	-0.133160000
6	-2.293744000	0.375778000	0.473729000
6	-2.101160000	-1.531023000	-0.835829000
6	-3.680194000	0.346542000	0.364158000
6	-1.597474000	1.399541000	1.340322000
6	-3.480142000	-1.641424000	-0.954036000
1	-1.434719000	-2.235116000	-1.318563000
6	-4.292579000	-0.679234000	-0.353648000
1	-4.268039000	1.122219000	0.844884000
1	-2.209744000	2.301839000	1.431072000
1	-1.435021000	0.966963000	2.333839000
7	-0.260525000	1.713225000	0.802942000
1	-3.900849000	-2.461422000	-1.526453000
1	-5.373349000	-0.722283000	-0.445925000
1	0.393774000	1.996876000	1.528633000
6	-0.235823000	2.606053000	-0.336144000
6	1.158748000	2.800302000	-0.916484000
8	-1.262029000	3.052178000	-0.792719000
1	1.028526000	3.296244000	-1.879930000

1	1.734349000	3.475195000	-0.265703000
6	1.871439000	1.448327000	-1.055662000
1	2.351731000	1.284673000	-2.019755000
6	2.535543000	0.924167000	0.127156000
1	2.656762000	1.544571000	1.017372000
6	3.045254000	-0.409072000	0.064979000
1	3.507211000	-0.814567000	0.961744000
1	3.482524000	-0.771734000	-0.864181000
6	0.651793000	-1.166143000	1.807617000
8	0.674142000	-1.596834000	2.896071000
1	0.566480000	0.599776000	-1.562067000

TS7d

B3LYP-D3 electronic energy: -1020.191424 a.u.
 B3LYP-D3 enthalpy: -1019.912167 a.u.
 B3LYP-D3 free energy: -1019.984312 a.u.
 M06-D3 SCF energy in solution: -1019.098621 a.u.
 M06-D3 enthalpy in solution: -1018.819364 a.u.
 M06-D3 free energy in solution: -1018.891509 a.u.

Cartesian coordinates

ATOM	X	Y	Z
7	1.606747000	-0.213135000	0.552096000
6	2.505654000	0.130053000	-0.401447000
6	2.044207000	-0.366037000	1.819530000
6	3.852199000	0.328219000	-0.110376000
6	1.961425000	0.264774000	-1.806305000
6	3.374810000	-0.195495000	2.181314000
1	1.284789000	-0.639023000	2.543026000
6	4.299786000	0.158472000	1.198254000
1	4.533894000	0.619396000	-0.902977000
1	2.587629000	0.941374000	-2.394675000
1	1.932731000	-0.717482000	-2.289036000
7	0.564757000	0.748892000	-1.724316000
1	3.671989000	-0.334331000	3.215304000
1	5.346089000	0.308103000	1.446594000
1	0.039755000	0.585035000	-2.583367000
6	0.466049000	2.144432000	-1.296480000
6	-0.906661000	2.504795000	-0.807337000
8	1.464024000	2.814408000	-1.172747000
1	-0.967487000	3.594102000	-0.703931000
1	-1.686259000	2.164223000	-1.497936000
6	-1.071318000	1.805327000	0.575914000
1	-0.318114000	2.239309000	1.243104000
6	-2.442031000	2.040442000	1.118042000
1	-3.261752000	1.704882000	0.483515000
6	-2.710955000	2.601645000	2.300362000
1	-3.731284000	2.726739000	2.651886000
1	-1.919391000	2.941616000	2.966047000
1	-0.836170000	0.326965000	1.400077000
74	-0.557566000	-0.502973000	-0.087428000
6	-2.362393000	-0.462235000	-0.881808000
6	-1.293267000	-1.703323000	1.306968000
6	-0.015425000	-2.205970000	-1.047204000
8	-1.702111000	-2.412562000	2.136944000

8	-3.414745000	-0.356098000	-1.384192000
8	0.299135000	-3.203469000	-1.554879000

I-10

B3LYP-D3 electronic energy: -906.883131 a.u.
B3LYP-D3 enthalpy: -906.609273 a.u.
B3LYP-D3 free energy: -906.67457 a.u.
M06-D3 SCF energy in solution: -905.822409 a.u.
M06-D3 enthalpy in solution: -905.548551 a.u.
M06-D3 free energy in solution: -905.613848 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.304404000	-0.581022000	-0.136861000
6	-0.709320000	-0.399056000	1.716643000
6	0.100905000	-2.480075000	0.162242000
8	0.370219000	-3.606520000	0.334899000
8	-1.033590000	-0.260085000	2.843324000
7	1.795748000	0.019449000	-0.040054000
6	2.099660000	1.352765000	-0.073903000
6	2.840345000	-0.852687000	-0.107716000
6	3.397360000	1.819999000	-0.239650000
6	0.943652000	2.275725000	0.174770000
6	4.158824000	-0.447351000	-0.246058000
1	2.579177000	-1.902143000	-0.050462000
6	4.455925000	0.914856000	-0.331312000
1	3.573463000	2.890989000	-0.276254000
1	0.712394000	2.284108000	1.245021000
1	1.169998000	3.303845000	-0.129867000
7	-0.282195000	1.776208000	-0.488497000
1	4.939322000	-1.199804000	-0.292900000
1	5.476768000	1.261668000	-0.454563000
1	-0.260809000	1.929026000	-1.497427000
6	-1.523712000	2.282033000	0.075811000
6	-2.763522000	2.033383000	-0.758233000
8	-1.528113000	2.824585000	1.156478000
1	-3.520409000	2.742906000	-0.414069000
1	-2.556007000	2.239646000	-1.818116000
6	-3.259598000	0.577026000	-0.613450000
1	-3.444147000	0.367301000	0.446032000
1	-4.225382000	0.492179000	-1.135447000
6	-2.250067000	-0.415268000	-1.163574000
1	-2.056013000	-0.262338000	-2.239411000
6	-2.182043000	-1.780352000	-0.740715000
1	-2.014908000	-2.561114000	-1.481686000
1	-2.761042000	-2.110045000	0.120021000

TS1b

B3LYP-D3 electronic energy: -906.843545 a.u.
B3LYP-D3 enthalpy: -906.576028 a.u.
B3LYP-D3 free energy: -906.641759 a.u.
M06-D3 SCF energy in solution: -905.782380 a.u.
M06-D3 enthalpy in solution: -905.514863 a.u.
M06-D3 free energy in solution: -905.580594 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.412326000	-0.574441000	-0.000772000
6	0.090975000	-2.502687000	-0.433367000
6	0.241709000	-1.224799000	1.791563000
8	0.126799000	-1.594062000	2.903242000
8	-0.100008000	-3.626421000	-0.670957000
7	-1.703420000	-0.041552000	-0.209352000
6	-2.046558000	1.200017000	0.230037000
6	-2.660934000	-0.805918000	-0.789398000
6	-3.339639000	1.693290000	0.089840000
6	-0.946906000	1.969898000	0.905852000
6	-3.965008000	-0.366353000	-0.966602000
1	-2.353057000	-1.797144000	-1.100348000
6	-4.317758000	0.907778000	-0.519034000
1	-3.567281000	2.690337000	0.453091000
1	-1.100307000	3.047927000	0.822072000
1	-0.950006000	1.705054000	1.974232000
7	0.355490000	1.614638000	0.331765000
1	-4.688081000	-1.021114000	-1.441241000
1	-5.330100000	1.280672000	-0.640715000
6	1.175886000	2.687334000	-0.005524000
6	2.610211000	2.372992000	-0.421225000
8	0.793878000	3.851955000	0.049104000
1	2.935567000	3.226275000	-1.022548000
1	3.217256000	2.392454000	0.496378000
6	2.856955000	1.051945000	-1.157646000
1	2.201066000	0.990011000	-2.040238000
1	3.884575000	1.058465000	-1.551743000
6	2.674102000	-0.172434000	-0.275658000
1	3.261244000	-0.154082000	0.641811000
6	2.392254000	-1.434720000	-0.847191000
1	2.744831000	-2.341275000	-0.363709000
1	2.306812000	-1.517000000	-1.932518000
1	1.203811000	0.626597000	1.044696000

TS1c

B3LYP-D3 electronic energy: -1020.196015 a.u.
 B3LYP-D3 enthalpy: -1019.917285 a.u.
 B3LYP-D3 free energy: -1019.992694 a.u.
 M06-D3 SCF energy in solution: -1019.101341 a.u.
 M06-D3 enthalpy in solution: -1018.822611 a.u.
 M06-D3 free energy in solution: -1018.89802 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.005431000	-0.689523000	0.182457000
6	1.842817000	-1.356089000	0.485643000
6	-0.252635000	-2.379481000	-0.876606000
6	-0.794966000	-1.727948000	1.621633000
8	-0.407910000	-3.337278000	-1.517146000
8	2.936196000	-1.730746000	0.627466000
8	-1.324724000	-2.289960000	2.497791000
7	-1.931299000	0.242296000	-0.483915000
6	-2.215255000	1.431197000	0.101069000

6	-2.803862000	-0.273121000	-1.377553000
6	-3.385827000	2.126900000	-0.195560000
6	-1.210783000	1.918569000	1.111566000
6	-3.982720000	0.371606000	-1.724705000
1	-2.531793000	-1.231836000	-1.804348000
6	-4.281157000	1.595270000	-1.121056000
1	-3.580206000	3.076758000	0.291909000
1	-1.173910000	3.010017000	1.143271000
1	-1.518595000	1.561607000	2.105293000
7	0.128152000	1.398587000	0.804730000
1	-4.650269000	-0.080833000	-2.449929000
1	-5.194150000	2.127432000	-1.371138000
6	1.147189000	2.362150000	0.766158000
6	2.552491000	1.863859000	0.483801000
8	0.909083000	3.558874000	0.881396000
1	3.232241000	2.648111000	0.828300000
1	2.777970000	0.946290000	1.033300000
6	2.770739000	1.620026000	-1.030368000
1	2.105149000	0.816689000	-1.376654000
1	2.483668000	2.532116000	-1.571806000
6	4.197049000	1.256109000	-1.338704000
1	4.931413000	2.046458000	-1.175632000
6	4.601241000	0.054885000	-1.751981000
1	5.648917000	-0.162292000	-1.941670000
1	3.899746000	-0.762560000	-1.902452000
1	0.586665000	0.219876000	1.608008000

TS1d

B3LYP-D3 electronic energy: -1133.543694 a.u.
 B3LYP-D3 enthalpy: -1133.254604 a.u.
 B3LYP-D3 free energy: -1133.33596 a.u.
 M06-D3 SCF energy in solution: -1132.419726 a.u.
 M06-D3 enthalpy in solution: -1132.130636 a.u.
 M06-D3 free energy in solution: -1132.211992 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.220768000	-0.698853000	0.060733000
6	0.285463000	-0.607259000	2.175741000
6	1.187631000	-2.458393000	0.291955000
6	0.075338000	-1.321973000	-1.849789000
6	-1.621378000	-1.428986000	0.308216000
8	-0.022591000	-1.711089000	-2.937266000
8	1.815992000	-3.426206000	0.405495000
8	0.249426000	-0.666177000	3.321662000
8	-2.697986000	-1.835393000	0.462124000
7	2.179909000	0.430508000	-0.178846000
6	2.133258000	1.747395000	0.121494000
6	3.336586000	-0.099264000	-0.627298000
6	3.255340000	2.565043000	-0.021192000
6	0.821019000	2.260266000	0.650653000
6	4.490818000	0.654708000	-0.787652000
1	3.314599000	-1.158478000	-0.856271000
6	4.450052000	2.015879000	-0.477758000
1	3.178360000	3.619643000	0.222546000

1	0.835600000	2.151743000	1.751906000
1	0.697179000	3.326544000	0.441264000
7	-0.298065000	1.503155000	0.102157000
1	5.396590000	0.181536000	-1.151049000
1	5.332465000	2.637707000	-0.596297000
1	-0.086367000	0.479996000	-1.215298000
6	-1.443045000	2.235111000	-0.121300000
6	-2.617440000	1.557476000	-0.810441000
8	-1.541894000	3.411338000	0.235093000
1	-2.921939000	2.228546000	-1.622652000
1	-2.357514000	0.593318000	-1.252897000
6	-3.801038000	1.385012000	0.168336000
1	-3.523912000	0.675618000	0.956392000
1	-3.976281000	2.357463000	0.646599000
6	-5.043255000	0.916057000	-0.537125000
1	-5.473280000	1.621820000	-1.250761000
6	-5.615338000	-0.277489000	-0.371069000
1	-6.508649000	-0.564236000	-0.920311000
1	-5.204242000	-1.013033000	0.315943000

I-2b

B3LYP-D3 electronic energy: -906.888030 a.u.
 B3LYP-D3 enthalpy: -906.618141 a.u.
 B3LYP-D3 free energy: -906.685058 a.u.
 M06-D3 SCF energy in solution: -905.828011 a.u.
 M06-D3 enthalpy in solution: -905.558122 a.u.
 M06-D3 free energy in solution: -905.625039 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.397940000	-0.595573000	0.021097000
6	-0.358296000	-1.732776000	-1.392094000
6	-0.197522000	-1.741431000	1.481082000
8	-0.596917000	-2.328281000	2.427400000
8	-0.855331000	-2.311684000	-2.271784000
7	-1.712542000	0.196205000	0.133916000
6	-1.875927000	1.477765000	-0.248275000
6	-2.805030000	-0.543256000	0.437972000
6	-3.145092000	2.053861000	-0.351444000
6	-0.624366000	2.233720000	-0.554761000
6	-4.091157000	-0.034888000	0.355321000
1	-2.615793000	-1.560909000	0.754544000
6	-4.267016000	1.291510000	-0.051001000
1	-3.232841000	3.090584000	-0.660755000
1	-0.575607000	2.430721000	-1.636758000
1	-0.649163000	3.217879000	-0.075729000
7	0.566888000	1.486700000	-0.124652000
1	-4.935010000	-0.667073000	0.609290000
1	-5.261640000	1.721693000	-0.122467000
6	1.594846000	2.361147000	0.240195000
6	2.886614000	1.761813000	0.768348000
8	1.477633000	3.581795000	0.156768000
1	3.595810000	2.590035000	0.843307000
1	2.723237000	1.369629000	1.781218000
6	3.414835000	0.646919000	-0.137914000

1	3.348627000	0.971205000	-1.184644000
1	4.482412000	0.488098000	0.068695000
1	0.802392000	-2.244451000	0.658051000
6	2.694736000	-0.673728000	0.044527000
1	3.010603000	-1.227303000	0.930034000
6	2.275943000	-1.425012000	-1.079981000
1	2.319722000	-2.509363000	-1.094096000
1	2.340797000	-0.967172000	-2.067666000

TS2a

B3LYP-D3 electronic energy: -906.878175 a.u.
 B3LYP-D3 enthalpy: -906.609379 a.u.
 B3LYP-D3 free energy: -906.674607 a.u.
 M06-D3 SCF energy in solution: -905.816990 a.u.
 M06-D3 enthalpy in solution: -905.548194 a.u.
 M06-D3 free energy in solution: -905.613422 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.310086000	-0.556097000	-0.098768000
6	-0.250722000	-2.391679000	0.392106000
8	-0.669742000	-3.432862000	0.723467000
7	-1.867792000	-0.004750000	-0.039544000
6	-2.143238000	1.316394000	0.056032000
6	-2.897292000	-0.878481000	-0.181550000
6	-3.457697000	1.793262000	-0.001033000
6	-0.982117000	2.234304000	0.254628000
6	-4.217920000	-0.470806000	-0.239160000
1	-2.625304000	-1.924454000	-0.241596000
6	-4.506024000	0.896534000	-0.149560000
1	-3.635791000	2.861277000	0.075989000
1	-1.043977000	3.071462000	-0.455291000
1	-1.062647000	2.703691000	1.246557000
7	0.289531000	1.530677000	0.121903000
1	-5.003997000	-1.209446000	-0.352164000
1	-5.532071000	1.249858000	-0.193592000
6	1.356224000	2.392683000	0.363351000
6	2.760262000	1.862917000	0.095177000
8	1.186353000	3.557132000	0.718380000
1	3.402241000	2.745750000	0.034702000
1	3.099071000	1.273350000	0.956572000
6	2.856838000	1.011547000	-1.184149000
1	2.243787000	1.467976000	-1.972105000
1	3.894775000	1.027542000	-1.546844000
6	1.540596000	-0.979934000	1.337625000
8	2.289049000	-1.200241000	2.208535000
1	0.297307000	-1.638282000	-1.499024000
6	2.443873000	-0.433812000	-0.970040000
1	3.194477000	-1.018438000	-0.440523000
6	1.684584000	-1.144389000	-1.953803000
1	1.937981000	-2.183757000	-2.156558000
1	1.366118000	-0.600287000	-2.844591000

I-3a

B3LYP-D3 electronic energy: -906.904611 a.u.

B3LYP-D3 enthalpy: -906.632546 a.u.
 B3LYP-D3 free energy: -906.698188 a.u.
 M06-D3 SCF energy in solution: -905.842579 a.u.
 M06-D3 enthalpy in solution: -905.570514 a.u.
 M06-D3 free energy in solution: -905.636156 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.385945000	-0.325064000	0.174235000
6	-0.524509000	-1.670602000	1.595975000
6	-0.381958000	-2.068733000	-0.752107000
8	-0.311791000	-3.069491000	-1.354575000
8	-0.582964000	-2.439421000	2.479613000
7	1.758226000	-0.154871000	-0.103288000
6	2.244414000	1.116835000	-0.126866000
6	2.630867000	-1.192082000	-0.197958000
6	3.615028000	1.360714000	-0.249353000
6	1.255821000	2.244870000	-0.020214000
6	3.995426000	-1.008163000	-0.327834000
1	2.188106000	-2.179299000	-0.168933000
6	4.500806000	0.296680000	-0.353779000
1	3.966190000	2.387802000	-0.262336000
1	1.525952000	2.886291000	0.832056000
1	1.337312000	2.892527000	-0.905734000
7	-0.091649000	1.724849000	0.122892000
1	4.647921000	-1.871151000	-0.402380000
1	5.567471000	0.475404000	-0.451452000
6	-1.087063000	2.679365000	0.100924000
6	-2.510625000	2.130290000	0.257774000
8	-0.878474000	3.881264000	-0.025411000
1	-2.888760000	2.504241000	1.217378000
1	-3.126684000	2.593783000	-0.520297000
6	-2.174708000	-0.056637000	-1.075657000
1	-1.897789000	0.673415000	-1.844322000
6	-3.048617000	-1.161385000	-1.638738000
1	-3.986597000	-0.756091000	-2.046292000
1	-3.301448000	-1.893623000	-0.863430000
1	-2.537908000	-1.697651000	-2.444683000
6	-2.637682000	0.603019000	0.191101000
1	-3.629555000	0.252921000	0.499683000
1	-2.047690000	0.172449000	1.113532000

TS3a

B3LYP-D3 electronic energy: -906.893787 a.u.
 B3LYP-D3 enthalpy: -906.625577 a.u.
 B3LYP-D3 free energy: -906.691273 a.u.
 M06-D3 SCF energy in solution: -905.831352 a.u.
 M06-D3 enthalpy in solution: -905.563142 a.u.
 M06-D3 free energy in solution: -905.628838 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.399377000	-0.313210000	0.186637000
6	-0.294635000	-1.801934000	1.479190000
6	-0.598230000	-1.956179000	-0.883512000

8	-0.667575000	-2.894592000	-1.579951000
8	-0.177055000	-2.646808000	2.279565000
7	1.779660000	-0.157657000	-0.073003000
6	2.280425000	1.095062000	-0.224091000
6	2.626886000	-1.215868000	-0.097774000
6	3.649932000	1.304728000	-0.407489000
6	1.299495000	2.231240000	-0.183253000
6	3.992390000	-1.070203000	-0.272222000
1	2.165107000	-2.187231000	0.028380000
6	4.514688000	0.217911000	-0.431734000
1	4.017834000	2.319004000	-0.526274000
1	1.595839000	2.948403000	0.596671000
1	1.347656000	2.795317000	-1.126996000
7	-0.037753000	1.720742000	0.056389000
1	4.630588000	-1.946850000	-0.283853000
1	5.581263000	0.367594000	-0.571653000
6	-1.017158000	2.685588000	0.159014000
6	-2.389640000	2.124372000	0.534090000
8	-0.817969000	3.886143000	0.013739000
1	-2.528846000	2.344612000	1.600045000
1	-3.149856000	2.701196000	-0.005637000
6	-2.582197000	0.633775000	0.292915000
1	-1.574963000	-0.151996000	1.439243000
6	-2.397710000	0.045886000	-0.984669000
1	-2.038388000	0.712019000	-1.771826000
6	-3.310945000	-1.058943000	-1.467101000
1	-4.246345000	-0.629081000	-1.852620000
1	-3.560545000	-1.742571000	-0.648539000
1	-2.858472000	-1.648691000	-2.268868000
1	-3.359340000	0.183679000	0.910079000

I-4a

B3LYP-D3 electronic energy: -906.904521 a.u.
 B3LYP-D3 enthalpy: -906.635479 a.u.
 B3LYP-D3 free energy: -906.702224 a.u.
 M06-D3 SCF energy in solution: -905.842407 a.u.
 M06-D3 enthalpy in solution: -905.573365 a.u.
 M06-D3 free energy in solution: -905.640110 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	-0.451285000	-0.348184000	0.154576000
6	-0.090134000	-1.676214000	1.551228000
6	-0.338957000	-1.652375000	-1.315291000
8	-0.236891000	-2.336436000	-2.253804000
8	0.172536000	-2.396947000	2.443227000
7	1.768057000	-0.132837000	0.002953000
6	2.242238000	1.116243000	-0.211671000
6	2.644685000	-1.164094000	0.063714000
6	3.607929000	1.356873000	-0.380474000
6	1.223232000	2.214444000	-0.263468000
6	4.009380000	-0.991313000	-0.097432000
1	2.211485000	-2.139019000	0.248407000
6	4.504008000	0.296536000	-0.325471000
1	3.947693000	2.373657000	-0.551110000

1	1.475227000	3.004905000	0.456873000
1	1.246772000	2.699919000	-1.250271000
7	-0.097523000	1.668157000	0.012356000
1	4.668738000	-1.850543000	-0.041097000
1	5.568842000	0.466883000	-0.453197000
6	-1.092993000	2.631356000	0.116062000
6	-2.451593000	2.059271000	0.497812000
8	-0.889488000	3.827517000	-0.040582000
1	-2.653717000	2.416957000	1.514525000
1	-3.206023000	2.529229000	-0.145914000
6	-2.536314000	0.539530000	0.463477000
1	-1.403330000	-1.711387000	0.811468000
6	-2.592718000	-0.167347000	-0.763052000
1	-2.419576000	0.421386000	-1.669290000
6	-3.458419000	-1.386904000	-0.979236000
1	-4.456601000	-1.078698000	-1.321661000
1	-3.577820000	-1.951871000	-0.048691000
1	-3.039724000	-2.060139000	-1.734181000
1	-3.051979000	0.088007000	1.310405000

TS4a

B3LYP-D3 electronic energy: -906.890493 a.u.

B3LYP-D3 enthalpy: -906.622177 a.u.

B3LYP-D3 free energy: -906.689304 a.u.

M06-D3 SCF energy in solution: -905.826747 a.u.

M06-D3 enthalpy in solution: -905.558431 a.u.

M06-D3 free energy in solution: -905.625558 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.395546000	-0.272293000	-0.106213000
7	-1.805535000	-0.299738000	0.012984000
6	-2.429330000	0.903072000	-0.073239000
6	-2.569336000	-1.418818000	0.111362000
6	-3.823002000	1.002680000	-0.089186000
6	-1.550659000	2.114771000	-0.140818000
6	-3.952200000	-1.384388000	0.096720000
1	-2.029474000	-2.352237000	0.201676000
6	-4.597150000	-0.146866000	-0.007345000
1	-4.279050000	1.985146000	-0.162192000
1	-1.779390000	2.688797000	-1.051086000
1	-1.784464000	2.792188000	0.693095000
7	-0.151848000	1.722778000	-0.101721000
1	-4.511214000	-2.310618000	0.173350000
1	-5.681255000	-0.084866000	-0.014963000
6	0.718975000	2.784410000	0.067830000
6	2.184707000	2.359628000	0.134258000
8	0.365810000	3.954112000	0.144376000
1	2.655883000	2.717285000	-0.791156000
1	2.645356000	2.928836000	0.948317000
6	2.421560000	0.868497000	0.323115000
6	0.954810000	-1.264271000	1.461739000
8	1.322254000	-1.790734000	2.444433000
6	0.350987000	-2.202462000	-0.656332000
8	0.247791000	-3.320191000	-0.975265000

1	1.396488000	-0.598355000	-1.479704000
6	2.791777000	0.055060000	-0.765746000
1	2.896230000	0.560031000	-1.727564000
1	2.774386000	0.569672000	1.307739000
6	3.660203000	-1.173169000	-0.602486000
1	3.512284000	-1.628766000	0.379996000
1	3.444752000	-1.928505000	-1.364312000
1	4.715850000	-0.884544000	-0.699825000

I-3b

B3LYP-D3 electronic energy: -1020.235130 a.u.
 B3LYP-D3 enthalpy: -1019.952530 a.u.
 B3LYP-D3 free energy: -1020.024674 a.u.
 M06-D3 SCF energy in solution: -1019.144268 a.u.
 M06-D3 enthalpy in solution: -1018.861668 a.u.
 M06-D3 free energy in solution: -1018.933812 a.u.

Cartesian coordinates

ATOM	X	Y	Z
74	0.366452000	-0.631284000	0.034140000
6	0.354904000	-0.429512000	-1.999668000
6	-0.474807000	-2.494417000	0.106546000
8	-1.008679000	-3.517339000	0.224274000
8	0.286514000	-0.310414000	-3.148596000
7	-1.773960000	0.081142000	-0.090390000
6	-2.014184000	1.339928000	0.337544000
6	-2.799139000	-0.636414000	-0.603913000
6	-3.292175000	1.898891000	0.277242000
6	-0.825592000	2.062620000	0.881746000
6	-4.091375000	-0.141891000	-0.688813000
1	-2.561706000	-1.630952000	-0.960233000
6	-4.348137000	1.154378000	-0.235675000
1	-3.435990000	2.915940000	0.627032000
1	-0.916110000	3.142519000	0.737811000
1	-0.790367000	1.884936000	1.973286000
7	0.392525000	1.570133000	0.249296000
1	-4.874244000	-0.762823000	-1.110804000
1	-5.347361000	1.575693000	-0.293296000
6	1.303140000	2.558426000	0.014918000
6	2.721977000	2.212163000	-0.445834000
8	1.077220000	3.760478000	0.218455000
1	2.954601000	2.890599000	-1.273300000
1	3.359456000	2.540154000	0.386643000
6	3.075414000	0.771802000	-0.809179000
1	2.696196000	0.518268000	-1.806371000
1	4.173103000	0.685367000	-0.870701000
6	2.544933000	-0.212424000	0.214894000
1	2.833900000	0.053390000	1.232960000
6	2.648726000	-1.655836000	-0.087655000
1	3.037978000	-2.275424000	0.722566000
1	3.123839000	-1.882168000	-1.046096000
6	0.352333000	-0.707062000	2.065930000
8	0.366239000	-0.765252000	3.222825000
1	1.592852000	-2.163115000	-0.262332000

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