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Supplementary information

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Supplementary Information

Dual-Function Enzyme Catalysis for Enantioselective Carbon–Nitrogen Bond Formation

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I. General Procedures

(A) General

Unless otherwise noted, all chemicals and reagents were obtained from commercial suppliers (Millipore Sigma, VWR, TCI America and Fischer Scientific) and were used without further purification. NMR spectra of chemicals in DMSO-d_6 and $CDCl_3$ were obtained using a Bruker Prodigy 400 MHz spectrometer, and were referenced to residual solvent signals. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, bs = broad singlet), coupling constant (Hz), and integration. Sonication was performed using a Qsonica Q500 sonicator. High-resolution mass spectra were obtained at the California Institute of Technology Mass Spectral Facility. Reverse-phase high-performance liquid chromatography (HPLC) and liquid chromatography-mass spectroscopy (LC-MS) for analysis were carried out using Agilent 1200 series instruments, with a C8 (Agilent ZORBAX SB-C8, 4.6 × 50 mm, 3.5 µm) column. Water and acetonitrile containing 0.1% acetic acid were used as eluents. Normal-phase chiral HPLC was performed using Daicel Chiralpak IA and IC columns (4.6 × 250 mm, 5 µm) with hexane and isopropanol as the mobile phase.

(B) Cloning, mutagenesis, and expression of enzymes

Expression vector pET22b(+) (Novagen) was used for cloning and expression of all variants described in this paper. Site-specific mutagenesis was performed using polymerase chain reaction (PCR) with primers containing a mutated codon at the desired position. Primer sequences are available upon request. The PCR products were digested with *Dpn*I, purified with New England Biolabs gel purification kit, and the gaps were repaired using Gibson Mix™.[1] Without further purification after the Gibson step, 1 µL of the Gibson product was used to transform 50 µL of electrocompetent *Escherichia coli* BL21 *E. cloni*® (Lucigen) cells. BL21 *E. cloni*® cells transformed with pET22b(+) constructs encoding various $P411_{BM3}$ variants were grown overnight in 6 mL Luria-Bertani medium supplemented with 0.1 mg/mL ampicillin (LB_{amp}). Subsequently, 5 mL of this preculture were used to inoculate 45 mL of Hyperbroth medium supplemented with 0.1 mg/mL ampicillin (HB_{amp}). The expression culture was incubated at 37 °C and shaken at 230 rpm for 2 h and 15 min. Then, the expression culture was cooled on ice for 40 minutes and was induced with 1 mM 5-aminolevulinic acid (ALA) and 0.5 mM isopropyl *β*-D-1-thiogalactopyranoside (IPTG) (final concentrations). Cells were expressed at 22 °C and 140 rpm for 20–24 h, and the shaking radius was 25 mm. Once expression was finished, the cultures were centrifuged (4,000 × g, 4 minutes, and 4 °C) and the pellets were resuspended to an optical density at 600 nm (OD_{600}) of 33 in M9-N minimal medium with pH adjusted to 7.4. Aliquots of the cell suspension (3–4 mL) were used to determine protein concentration after lysis by sonication.

(C) Determination of haem protein concentration

Protein concentration in the cell was determined by performing hemochrome assay on the cell lysate.[2] Lysate was obtained by sonication (4 minutes, 1 second on, 1 second off, 30% amplitude, on wet ice). The cell debris was removed by centrifugation (14,000 × g, 10 minutes, 4 °C). To a cuvette, 500 µL of the lysate and 500 µL of solution I [0.2 M NaOH, 40% (v/v) pyridine, 0.5 mM $K_3Fe(CN)_6$] were added. The UV-Vis spectrum (380–620 nm) of the oxidized state (Fe^{III})

was recorded immediately. Sodium dithionite (10 µL of 0.5 M solution in water) was added and the UV-Vis spectrum of the reduced state (Fe^{II}) was recorded immediately. The protein concentration was calculated using the extinction coefficient and dilution factor (2× dilution in volume): $\varepsilon_[557_{reduced} - 540_{oxidized}] = 23.98\ mM^{-1}cm^{-1}$.

Please note that TTN values are lower bounds since the hemochrome assay detects the levels of haem, not necessarily concentration of the enzyme; however, haem concentration closely approximates enzyme concentration.

(D) Analytic reaction setup and product quantification

All the biocatalytic reactions were set up in an anaerobic chamber (oxygen level: < 40 ppm). To each 2-mL vial, 360 µL of resuspended cells (diluted to a given OD_{600} with M9-N minimal buffer, pH = 7.4) was added, followed by D-glucose (20 µL, 500 mM in M9-N), aniline derivatives (10 µL of an EtOH stock, 400 mM), and α-diazo-γ-lactone[3] (LAD, 10 µL of an EtOH stock, 400 mM). Final concentrations were typically 10.0 mM aniline derivative, 10.0 mM LAD, and 25 mM D-glucose; final reaction volume was 400 µL. The vials were sealed, shaken (550 rpm) inside the anaerobic chamber at room temperature for a set time. After the reaction was completed and the vials removed from the anaerobic chamber, the internal standard *p*-methyl anisole (600 µL of 0.833 mM stock solution in acetonitrile) was added. The mixture was transferred to a 1.7-mL Eppendorf tube, and then subjected to vortexing (15 s × 3) and centrifugation (14,000 × g, 5 min, 4 °C). A sample of the supernatant (0.2 mL) was transferred to a vial with an insert for reverse-phase HPLC analysis.

Another set of enzymatic reactions was set up following the same procedure. After the reactions were completed, extraction of products with 0.6 mL of hexane/ethyl acetate (2:3) followed by vortexing and centrifugation afforded the organic solutions of the desired products. Enantiomeric excess (e.e.) of the enzymatic reactions was measured using these organic solutions by normal-phase chiral HPLC.

(E) Purification of P411-L7_FL

To obtain purified protein of **L7_FL**, a single colony of *E. coli* BL21(DE3) freshly transformed with plasmid encoding this enzyme variant was used to inoculate 30 mL of LB_{amp} broth and the culture was grown at 37 ºC, 230 rpm for 14h. Subsequently, 950 mL of HB_{amp} broth in a 2.8-L flask were inoculated with 15 mL of the precultures and incubated at 37 ºC, 230 rpm for 2.5 h (to OD_{600} ~1.0). The flask was then cooled in an ice-water bath for 40 min and induced with 0.5 mM IPTG and 1.0 mM ALA (final concentrations). Expression was conducted at 22 ºC and 140 rpm for 22 h. Cultures were then centrifuged (5,000 × g, 5 min, 4 ºC), the supernatant was discarded, and the cell pellets were frozen on dry ice and stored at –78 ºC.

For protein purification, frozen cells were thawed on ice and resuspended in buffer A (25 mM tris, 20 mM imidazole, 100 mM NaCl, pH 7.5; 4 mL buffer per g of wet cell weight). The cell suspension was lysed by sonication (QSonica sonicator, 2 minutes, 1 second on, 1 second off, 35% amplitude, on wet ice). To pellet insoluble material, the crude extracts were centrifuged (20,000 × g, 15 min, 4 ºC), and the cleared lysate was filtered through a 0.45-µm filter unit. His-tagged P411 proteins were purified from the lysate using a nickel NTA column (1-mL HisTrap HP, GE Healthcare) using an Äkta purifier FPLC system (GE healthcare). Proteins were eluted with a

linear gradient from 100% buffer A to 100% buffer B (25 mM tris, 300 mM imidazole, 100 mM NaCl, pH 7.5). **L7_FL** eluted at 30–35 % buffer B. Fractions containing eluted protein were pooled and subjected to three rounds of buffer exchange to storage buffer (50 mM Kpi, pH 8.0) using centrifugal spin filters (30 kDa molecular weight cut-off, Amicon Ultra, Merck Millipore). Subsequently, the concentrated protein solution was divided into 50 µL aliquots, flash-frozen on powdered dry ice, and stored at –78 ºC. Protein concentrations were determined via the hemochrome assay specified above prior to setting up biocatalytic reactions.

II. Screening of Haem Proteins for Lactone Carbene N–H Insertion

General procedure:

Screening of the N–H insertion reaction with 40 haemprotein variants was performed in a 96-well plate. *E. coli* libraries for P411 or P450 variants were cultured in LB_{amp} (300 µL/well) at 37 ºC, 230 rpm and 80% relative humidity overnight. HB_{amp} (950 µL/well) was inoculated with the pre-culture (50 µL/well) and incubated at 37 ºC, 250 rpm, 80% humidity for 2 h and 45 min. The plates were cooled on ice for 40 minutes, and expression was induced with 0.5 mM IPTG and 1.0 mM ALA (final concentrations). Expression was conducted at 22 ºC and 230 rpm for 20–24 h.

Expression of *Rma* cytochrome *c* variants in 96-well plates employed a different protocol. *E. coli* libraries for *Rma* cytochrome *c* variants were induced with 20 µM IPTG and 0.2 mM ALA (final concentrations).

The cells were pelleted (4,500 × g, 4 min, 4 ºC) and resuspended with M9-N buffer (360 µL/well) and D-glucose solution (20 µL/well, 500 mM in M9-N). The 96-well plate was then transferred to an anaerobic chamber. In the anaerobic chamber, *N*-methylaniline (10 µL/well, 400 mM in EtOH) and LAD (10 µL/well, 400 mM in EtOH) were added. The plate was sealed with aluminum foil, removed from the anaerobic chamber, and shaken at 600 rpm.

After 12 h, the seal was removed and a solvent mixture of hexane and EtOAc (2:3 v/v) (600 µL/well) was added. The plate was tightly sealed with a reusable silicone mat, vortexed (15 s × 3) and centrifuged (4,500 × g, 5 min). The organic phase (200 µL/well) was filtered through an AcroPrep 96-well filter plate (0.2 µm) into a shallow-well plate for normal-phase HPLC analysis (Chiralpak IC, 25% *i*-PrOH in hexane, 1.5 mL/min, 32 ºC, 254 nm).

Figure 1. Summary of different haemproteins tested for *α*-amino lactone formation. The enantiomeric excesses (e.e.) of 40 enzymatic reactions were summarized. Protein identities are listed in **Table 1**.

Table 1. Information of haem protein variants[3,4] (corresponding to individual well positions in the summary chart of **Figure 1**).

Name	Mutations	Location
P450-WT (P450$_{BM3}$-wild type, CYP102A1)	-	D1
P450-C400S	C400S (relative to P450-WT)	D2
P411-CIS	V78A F87V P142S T175I A184V S226R H236Q E252G T268A A290V L353V I366V C400S E442K (relative to P450$_{BM3}$-wild type, CYP102A1)	D3
P411-CIS T438S	T438S (relative to P411-CIS)	D4
P411-CIS T268A F87A	T268A F87A (relative to P411-CIS)	D5
P411-CIS T268A F87V	T268A F87V (relative to P411-CIS)	D6
P411-"I263F"	I263F T438S (relative to P411-CIS)	A6
P411-"**G8**"	L437F T438Q (relative to P411-CIS)	A7
P411-"**G8**" L75Y	L75Y (relative to P411-"**G8**")	A8
P411-"**G8S**" (or P411-**VAC**$_{cis}$)	L75Y L181I (relative to P411-"**G8**")	A9
P411-"**G8**" L181V	L181V (relative to P411-"**G8**")	A10
P411-"**E12**"	I263G L437F (relative to P411-CIS)	B1
P411-"**E12**" V87L	V87L (relative to P411-"**E12**")	B2
P411-"**E12**" V87L L181R	V87L L181R (relative to P411-"**E12**")	B3
P411-"**F3**"	V87T T438C (relative to P411-CIS)	B4
P411-"**H9**"	I263G L437F (relative to P411-"**F3**")	B5
P411-"**6C9**"	V87T L181G I263M V281L T438C (relative to P411-CIS) *ΔFAD	B6
P411-"**P3**"	A328V V87A (relative to P411-"I263F")	A1
P411-"**P2**"	A328V (relative to P411-"I263F")	A2
P11-"A82L"	V87A A268G A328V A82L (relative to P411-"I263F")	A5
P411-"A82L" F263L A78V E267D	F263L A78V E267D (relative to P411-"A82L")	A3
P411-"**E10**"	A78V F263L (relative to P411-"A82L")	A4
P411-"**E10**" S438A	S438A (relative to P411-"**E10**")	B7
P411-"**E10**" V78F	V78F (relative to P411-"**E10**")	B8
P411-"**E10**" V78F S438A	V78F S438A (relative to P411-"**E10**")	B9
P411-"**C1**"	V87W A268G A328V (relative to P411-"I263F")	B10
P411-"**C2**"	L437G (relative to P411-"**C1**")	C1
P411-"**C4**"	T327V V328Y (relative to P411-"**C2**")	C2
P411-"**K1**"	V87F A268G A328V (relative to P411-"I263F")	C3

P411-“**K3**”	F261G T327P (relative to P411-“**K1**”)	C4
P411-“**K10**”	S72W A78S L188C T269L A330V T436M L437F (relative to P411-“**K3**”)	C5
P411-“**C10**” Y263W	N70E A74G A78L M118S F162L M177L F263W H266V A330Y I401L T436L L437Q (relative to P411-“A82L”) *ΔFAD	C6
P411-WIRF	S72F L436R Q437I (relative to P411-“**C10**” Y263W)	C7
P411-WIRF_GAK	E70K G74A S332G (relative to P411-WIRF)	C8
P411-“**L5**”	A87P S332A T327V Q437L (relative to P411-“**C10**”)	C9
P411-“**L7**”	V327P A264S (relative to P411-“**L5**”)	C10
Rma cyt *c*-wild type	-	D7
Rma cyt *c*-V75T M100D M103E	V75T M100D M103E (relative to *Rma* cyt *c*-wild type)	D8
Rma cyt *c*-V75R M100D M103T	V75R M100D M103T (relative to *Rma* cyt *c*-wild type)	D9
Rma cyt *c*-BOR^{LAC}	V75R M99Q M100D T101Y M103V (relative to *Rma* cyt *c*-wild type)	D10

*ΔFAD: FAD domain truncation.

III. Supporting Experimental Tables and Figures

Figure 2. Summary of amine substrates (**2a**–**2q**).

Figure 3. Other substrates tested for enzymatic N–H insertion.

Notes: The amine and diazo substrates listed here have been briefly tested for the N–H insertion chemistry catalyzed by **L7_FL**. However, these substrates only gave low enantioselectivity or reactivity, as preliminarily analyzed by LC-MS and chiral HPLC. These results are noteworthy, but they cannot be used for drawing final conclusions before further validation.

Table 2. Results of the Carbene N–H Insertion Reaction Catalyzed by Variants with Different Amino Acid Substitutions at Site 264.

L6_FL (264S) (*4.02 μM*)	81% yield, 2000 TTN, 94% e.e.
L5_FL (264A) (*5.07 μM*)	64% yield, 1270 TTN, –21% e.e.
L6_FL_264G (*1.83 μM*)	76% yield, 4180 TTN, 32% e.e.
L6_FL_264D (*1.36 μM*)	2% yield, 141 TTN, –8% e.e.
L6_FL_264T (*3.80 μM*)	3% yield, 82 TTN, 47% e.e.
L6_FL_264V (*1.82 μM*)	2% yield, 113 TTN, –2% e.e.
L6_FL_264C (*4.70 μM*)	3% yield, 57 TTN, 10% e.e.

Cell lysate L7_FL (*5.45 μM*)	96% yield, 1770 TTN, 95% e.e.
purified L7_FL (*4.73 μM*)	11% yield, 241 TTN, 96% e.e.

Cell lysate L7_FL (*5.45 μM*)	86% yield, 1570 TTN, 88% e.e.
purified L7_FL (*4.73 μM*)	61% yield, 1280 TTN, 89% e.e.

Figure 4. Enzymatic N–H insertion with cell lysate or purified **L7_FL**.

Table 3. Control experiments of lactone carbene N–H insertion.

Entry	*Conditions*	Result
1	10 μM free heme	full conversion, racemic
2	**L6** (induced with only IPTG)	~20% yield, 77% e.e.
3	only M9-N buffer	no reaction

IV. Preparation and Characterization of the Racemic Standards of Products

General procedure[5]:

Condition A: To a solution of arylamine (2.5 mmol) in DMF (1.5 mL) was added *α*-bromo-*γ*-butyrolactone (330 mg, 0.185 mL, 2 mmol). The resulting mixture was heated at 80 ºC for 24 h.

Condition B: To a solution of alkylamine (2.2 mmol) in DMF (1.5 mL) was added *α*-bromo-*γ*-butyrolactone (330 mg, 0.185 mL, 2 mmol). The resulting mixture was stirred at room temperature for 24 h.

Workup: After reaction completion, the mixture was extracted with EtOAc (7 mL × 3), and the combined organic layer was washed with saturated $NaHCO_3$ solution (15 mL) and brine (15 mL). The organic phase was further dried over Na_2SO_4 and concentrated to afford a brown residue. The final product was purified through silica gel column chromatography.

Notes: All aniline-derived products (**3a–3m**) were prepared under *Condition A*. Alkylamine-derived products (**3n–3q**) were prepared under *Condition B*.

3a **3-(methyl(phenyl)amino)dihydrofuran-2(3*H*)-one (3a): ^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.23–7.16 (m, 2H), 6.85 (m, 2H), 6.71 (tt, *J* = 7.3, 1.0 Hz, 1H), 5.09 (dd, *J* = 11.3, 8.8 Hz, 1H), 4.41 (td, *J* = 8.8, 1.5 Hz, 1H), 4.26 (ddd, *J* = 10.9, 8.8, 6.4 Hz, 1H), 2.74 (s, 3H), 2.46–2.21 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 175.1, 149.2, 129.0, 117.3, 113.2, 65.3, 58.1, 33.6, 24.4; **HRMS** (ESI) Calcd for $C_{11}H_{14}NO_2$ [M+H] 192.1025, found 192.1014.

3b **3-(ethyl(phenyl)amino)dihydrofuran-2(3*H*)-one (3b): ^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.21–7.15 (m, 2H), 6.78–6.72 (m, 2H), 6.71–6.63 (tt, *J* = 7.3, 1.0 Hz, 1H), 4.96 (dd, *J* = 11.5, 8.8 Hz, 1H), 4.42 (td, *J* = 8.8, 1.6 Hz, 1H), 4.25 (ddd, *J* = 10.8, 8.8, 6.4 Hz, 1H), 3.38–3.15 (m, 2H), 2.47–2.27 (m, 2H), 1.11 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 175.5, 147.1, 129.1, 116.9, 113.4, 65.2, 58.2, 42.6, 25.4, 13.6; **HRMS** (ESI) Calcd for $C_{12}H_{16}NO_2$ [M+H] 206.1181, found 206.1175.

3c **3-(methyl(*o*-tolyl)amino)dihydrofuran-2(3*H*)-one (3c): ^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.22–7.09 (m, 3H), 6.95 (td, *J* = 7.2, 1.6 Hz, 1H), 4.38–4.12 (m, 3H), 2.65 (s, 3H), 2.38 (dtd, *J* = 12.4, 10.5, 8.7 Hz, 1H), 2.45–2.20 (m, 4H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ

175.3, 150.5, 132.0, 130.9, 126.3, 123.1, 121.6, 65.1, 61.0, 35.2, 24.6, 17.9; **HRMS** (ESI) Calcd for $C_{12}H_{16}NO_2$ [M+H] 206.1181, found 206.1180.

3-(methyl(*p*-tolyl)amino)dihydrofuran-2(3*H*)-one (3d): ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.04–6.98 (m, 2H), 6.79–6.73 (m, 2H), 5.01 (dd, J = 11.2, 8.8 Hz, 1H), 4.39 (td, J = 8.8, 1.6 Hz, 1H), 4.24 (ddd, J = 10.7, 8.8, 6.4 Hz, 1H), 2.70 (s, 3H), 2.42–2.21 (m, 2H), 2.19 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 175.2, 147.2, 129.4, 126.0, 113.6, 65.3, 58.4, 33.7, 24.2, 19.9; **HRMS** (ESI) Calcd for $C_{12}H_{16}NO_2$ [M+H] 206.1181, found 206.1175.

3-((4-fluorophenyl)(methyl)amino)dihydrofuran-2(3*H*)-one (3e): ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.09–7.00 (m, 2H), 6.91–6.82 (m, 2H), 5.02 (dd, J = 11.3, 8.8 Hz, 1H), 4.39 (td, J = 8.8, 1.6 Hz, 1H), 4.24 (ddd, J = 10.8, 8.8, 6.4 Hz, 1H), 2.71 (s, 3H), 2.44–2.24 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 175.0, 155.2 (d, J = 234.0 Hz), 146.2 (d, J = 1.8 Hz), 115.3 (d, J = 21.9 Hz), 114.8 (d, J = 7.4 Hz), 65.3, 58.7, 34.0, 24.3; **^{19}F NMR (**280 MHz, DMSO-d_6) δ –127.8; **HRMS** (ESI) Calcd for $C_{11}H_{13}NO_2F$ [M+H] 210.0930, found 210.0939.

3-(indolin-1-yl)dihydrofuran-2(3*H*)-one (3f): ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.07–6.94 (m, 2H), 6.64–6.51 (m, 2H), 4.86 (dd, J = 11.2, 8.8 Hz, 1H), 4.41 (td, J = 8.8, 2.2 Hz, 1H), 4.26 (ddd, J = 10.2, 8.8, 6.6 Hz, 1H), 3.49–3.39 (m, 1H), 3.25–3.16 (m, 1H), 2.99–2.84 (m, 2H), 2.42–2.25 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 174.5, 150.5, 129.4, 127.0, 124.4, 117.7, 107.1, 65.5, 54.5, 48.0, 27.7, 23.6; **HRMS** (ESI) Calcd for $C_{12}H_{14}NO_2$ [M+H] 204.1025, found 204.1032.

3-(3,4-dihydroquinolin-1(2H)-yl)dihydrofuran-2(3*H*)-one (3g): ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.02–6.88 (m, 2H), 6.78–6.68 (m, 1H), 6.56 (td, J = 7.3, 1.0 Hz, 1H), 5.05 (dd, J = 11.1, 8.8 Hz, 1H), 4.42 (td, J = 8.8, 1.7 Hz, 1H), 4.26 (ddd, J = 10.7, 8.8, 6.5 Hz, 1H), 3.19–3.00 (m, 2H), 2.67 (t, 6.4 Hz, 2H), 2.46–2.23 (m, 2H), 1.94–1.74 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 175.0, 144.5, 129.1, 126.8, 123.1, 116.6, 111.2, 65.3, 56.8, 44.0, 27.4, 23.7, 21.7; **HRMS** (ESI) Calcd for $C_{13}H_{16}NO_2$ [M+H] 218.1181, found 218.1186.

3h

3-(phenylamino)dihydrofuran-2(3*H*)-one (3h): ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.14–7.04 (m, 2H), 6.67 (dt, *J* = 7.7, 1.1 Hz, 2H), 6.59 (tt, *J* = 7.3, 1.1 Hz, 1H), 5.93 (d, *J* = 7.8 Hz, 1H), 4.47 (dt, *J* = 10.7, 8.1 Hz, 1H), 4.38 (td, *J* = 8.7, 1.9 Hz, 1H), 4.24 (ddd, *J* = 10.6, 8.8, 6.1 Hz, 1H), 2.61 (dddd, *J* = 12.2, 8.1, 6.1, 1.9 Hz, 1H), 2.06 (dtd, *J* = 12.2, 10.7, 8.6 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 176.5, 147.5, 128.9, 116.6, 112.7, 65.3, 51.3, 29.6; **HRMS** (ESI) Calcd for $C_{10}H_{12}NO_2$ [M+H] 178.0868, found 178.0872.

3i

3-(*o*-tolylamino)dihydrofuran-2(3*H*)-one (3i): ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.07–6.96 (m, 2H), 6.67 (d, *J* = 7.9 Hz, 1H), 6.57 (td, *J* = 7.3, 1.1 Hz, 1H), 5.09 (d, *J* = 8.2 Hz, 1H), 4.55 (dt, *J* = 11.0, 8.3 Hz, 1H), 4.39 (td, *J* = 8.7, 1.5 Hz, 1H), 4.25 (ddd, *J* = 10.9, 8.8, 6.1 Hz, 1H), 2.61–2.54 (m, 1H), 2.19 (dtd, *J* = 12.0, 11.0, 8.7 Hz, 1H), 2.10 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 176.7, 145.2, 130.0, 126.6, 122.3, 116.8, 110.3, 65.2, 51.5, 29.3, 17.7; **HRMS** (ESI) Calcd for $C_{11}H_{14}NO_2$ [M+H] 192.1025, found 192.1028.

3j

3-(*m*-tolylamino)dihydrofuran-2(3*H*)-one (3j): ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.97 (t, *J* = 7.7 Hz, 1H), 6.52–6.38 (m, 3H), 5.83 (d, *J* = 7.9 Hz, 1H), 4.46 (dt, *J* = 10.8, 8.1 Hz, 1H), 4.37 (td, *J* = 8.6, 1.8 Hz, 1H), 4.24 (ddd, *J* = 10.6, 8.8, 6.1 Hz, 1H), 2.64–2.55 (m, 1H), 2.19 (s, 3H), 2.04 (dtd, *J* = 12.2, 10.7, 8.5 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 176.5, 147.5, 137.9, 128.7, 117.5, 113.3, 110.1, 65.3, 51.4, 29.6, 21.4; **HRMS** (ESI) Calcd for $C_{11}H_{14}NO_2$ [M+H] 192.1025, found 192.1027.

3k

3-(*p*-tolylamino)dihydrofuran-2(3*H*)-one (3k): ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.95–6.86 (m, 2H), 6.61–6.55 (m, 2H), 5.72 (d, *J* = 7.8 Hz, 1H), 4.47–4.32 (m, 2H), 4.23 (ddd, *J* = 10.6, 8.8, 6.1 Hz, 1H), 2.64–2.54 (m, 1H), 2.15 (s, 3H), 2.03 (dtd, *J* = 12.1, 10.6, 8.5 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 176.6, 145.2, 129.3, 125.1, 112.9, 65.3, 51.6, 29.6, 20.1; **HRMS** (ESI) Calcd for $C_{11}H_{14}NO_2$ [M+H] 192.1025, found 192.1027.

3l

3-((4-methoxyphenyl)amino)dihydrofuran-2(3*H*)-one (3l): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85–6.78 (m, 2H), 6.69–6.62 (m, 2H), 4.49 (td, *J* = 9.1, 1.2 Hz, 1H), 4.32 (ddd, *J* = 11.2, 9.3, 5.9 Hz, 1H), 4.06 (dd, *J* = 11.1, 8.0 Hz, 1H), 3.76 (s, 3H), 2.89–2.80 (m, 1H), 2.19 (dtd, *J* = 12.5, 11.2, 8.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.7, 153.4, 140.7, 115.3, 115.1, 65.9, 55.9, 54.0, 32.4; **HRMS** (ESI) Calcd for $C_{11}H_{14}NO_3$ [M+H] 208.0974, found 208.0975.

3m **3-((2,6-dimethylphenyl)amino)dihydrofuran-2(3*H*)-one (3m): ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06–6.99 (m, 2H), 6.94–6.88 (m, 1H), 4.47–4.39 (m, 1H), 4.18 (ddd, *J* = 11.1, 9.3, 5.7 Hz, 1H), 3.98 (dd, *J* = 11.5, 8.2 Hz, 1H), 3.62 (bs, 1H), 2.68–2.58 (m, 1H), 2.43–2.19 (m, 7H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.8, 143.5, 130.8, 129.2, 123.8, 65.4, 57.4, 31.8, 18.9; **HRMS** (ESI) Calcd for $C_{12}H_{16}NO_2$ [M+H] 206.1181, found 206.1186.

3n **3-(benzylamino)dihydrofuran-2(3*H*)-one (3n): ^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.40–7.20 (m, 5H), 4.30 (td, *J* = 8.6, 2.7 Hz, 1H), 4.13 (ddd, *J* = 9.7, 8.7, 6.4 Hz, 1H), 3.90–3.75 (m, 2H), 3.54–3.44 (m, 1H), 2.71 (s, 1H), 2.37 (dddd, *J* = 12.3, 8.2, 6.4, 2.7 Hz, 1H), 1.97 (dtd, *J* = 12.3, 9.8, 8.4 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 177.5, 140.3, 128.2, 128.0, 126.7, 65.5, 54.8, 50.4, 29.7; **HRMS** (ESI) Calcd for $C_{11}H_{14}NO_2$ [M+H] 192.1025, found 192.1025.

3o **3-((4-methoxybenzyl)amino)dihydrofuran-2(3*H*)-one (3o): ^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.35–7.20 (m, 2H), 6.92–6.83 (m, 2H), 4.29 (td, *J* = 8.6, 2.7 Hz, 1H), 4.12 (ddd, *J* = 9.7, 8.8, 6.4 Hz, 1H), 3.80–3.68 (m, 5H), 3.46 (dd, *J* = 9.8, 8.1 Hz, 1H), 2.61 (s, 1H), 2.35 (dddd, *J* = 12.3, 8.1, 6.4, 2.7 Hz, 1H), 1.95 (dtd, *J* = 12.3, 9.8, 8.4 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 177.6, 158.2, 132.1, 129.3, 113.6, 65.5, 55.0, 54.6, 49.8, 29.7; **HRMS** (FAB) Calcd for $C_{12}H_{15}NO_3$ [M+H] 222.1130, found 222.1111.

3p **3-((4-bromophenethyl)amino)dihydrofuran-2(3*H*)-one (3p): ^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.51–7.41 (m, 2H), 7.25–7.14 (m, 2H), 4.29 (td, *J* = 8.6, 2.6 Hz, 1H), 4.13 (ddd, *J* = 9.9, 8.8, 6.4 Hz, 1H), 3.63–3.52 (m, 1H), 2.96–2.85 (m, 1H), 2.81–2.64 (m, 3H), 2.40 (dddd, *J* = 12.2, 8.1, 6.4, 2.6 Hz, 1H), 2.23 (s, 1H), 1.92 (dtd, *J* = 12.2, 9.9, 8.4 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 177.4, 139.7, 131.1, 130.9, 118.9, 65.5, 55.5, 48.3, 35.1, 29.6; **HRMS** (ESI) Calcd for $C_{12}H_{15}NO_2Br$ [M+H] 284.0286, found 284.0305.

3q **3-(isoindolin-2-yl)dihydrofuran-2(3*H*)-one (3q): ^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.30–7.16 (m, 4H), 4.35 (td, *J* = 8.5, 2.7 Hz, 1H), 4.27–4.17 (m, 3H), 4.01–3.91 (m, 2H), 3.86 (dd, *J* = 10.2, 8.1 Hz, 1H), 2.42 (dddd, *J* = 12.4, 8.2, 6.4, 2.7 Hz, 1H), 2.27 (dtd, *J* = 12.4, 9.9, 8.3 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 175.8, 139.3, 126.7, 122.3, 65.5, 59.6, 55.7, 27.2; **HRMS** (ESI) Calcd for $C_{12}H_{14}NO_2$ [M+H] 204.1025, found 204.1027.

V. Analytic Scale Enzymatic Reactions and Calibration Curves for Products

All enzymatic reactions for lactone-carbene N–H insertion on analytical scale were conducted following the general procedure described in **Section I (D)**. Reactions for every substrate were set up in triplicate or quadruplicate. Product formation was quantified by reverse-phase HPLC based on the calibration curve of the corresponding racemic standard compound (**Section IV**). All TTNs for different products were calculated as the concentration of products divided by the concentration of haem proteins measured by the hemochrome assay (**Section I (C)**).

HPLC calibration curve:

Calibration curves of synthesized reference compounds were created for the determination of yield and TTN. For each substrate, five different concentrations of product (1.25, 2.50, 5.00, 7.50, and 10.0 mM) in 400-μL EtOH solutions were mixed each with 600 μL of 0.833 mM internal standard (*p*-methyl anisole) solution. The mixtures were vortexed and then analyzed by HPLC. All data points represent the average of duplicate runs. The calibration curves depict the ratio of product area to internal standard area (y-axis) against product concentration in mM (x-axis).

Notes: Pdt = product area, IS = internal standard area, [Pdt] = product concentration in reaction, [PC] = protein concentration in reaction, Avg. TTN = average total turnover number, SD TTN = standard deviation of TTN, Avg. Yield = average yield, SD Yield = standard deviation of yield.

3-(methyl(phenyl)amino)dihydrofuran-2(3*H*)-one (3a)
The calibration curve was generated based on UV absorbance at 270 nm on LC-MS.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2a** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	600.4	49.0	12.3	8.89	7.05	1300	40	92	3
2	613.4	48.2	12.7	9.23	7.05				
3	630.3	48.2	13.1	9.48	7.05				

Data analysis for **L6_FL** catalyzed carbene insertion of aniline **2a** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	535.1	46.9	11.4	8.27	4.02	2000	50	81	2
2	521.2	47.8	10.9	7.91	4.02				
3	536.5	48.8	11.0	7.97	4.02				

Data analysis for **L5_FL** catalyzed carbene insertion of aniline **2a** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	434.2	49.2	8.83	6.40	5.07	1270	5	64.3	0.3
2	450.3	50.6	8.90	6.45	5.07				
3	456.1	51.4	8.87	6.43	5.07				

Data analysis for **L1** catalyzed carbene insertion of aniline **2a** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	10.6	49.0	0.22	0.16	5.67	27.2	0.6	1.54	0.04
2	10.3	49.2	0.21	0.15	5.67				

Data analysis for **L2** catalyzed carbene insertion of aniline **2a** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	85.3	49.1	1.74	1.26	5.84	213	4	12.4	0.2
2	85.1	49.2	1.69	1.22	5.84				

Data analysis for **L3** catalyzed carbene insertion of aniline **2a** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	119.3	49	2.43	1.77	6.04	288	6	17.4	0.4
2	117.3	49.6	2.36	1.71	6.04				

Data analysis for **L4** catalyzed carbene insertion of aniline **2a** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	184.6	49.6	3.72	2.70	5.94	451	5	26.8	0.3
2	180.3	49.2	3.66	2.66	5.94				

Data analysis for **L5** catalyzed carbene insertion of aniline **2a** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	293.7	49.2	6.00	4.33	2.87	1480	40	43	1
2	286.7	49.8	5.76	4.17	2.87				

Data analysis for **L6** catalyzed carbene insertion of aniline **2a** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	505.4	49.5	10.2	7.40	2.23	3270	70	73	2
2	488.3	49.4	9.88	7.17	2.23				

Data analysis for **L7** catalyzed carbene insertion of aniline **2a** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	559.7	49.9	11.2	8.13	3.94	2060	3	81	0.1
2	552.9	49.4	11.2	8.12	3.94				

3-(ethyl(phenyl)amino)dihydrofuran-2(3*H*)-one (3b)
The calibration curve was generated based on UV absorbance at 220 nm on HPLC.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2b** (10 mM, OD_{600} = 30, 24 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	876.6	269.6	3.25	6.75	6.08	1160	70	71	4
2	938.9	280.5	3.34	6.94	6.08				
3	980.4	270.5	3.62	7.52	6.08				

3-(methyl(*o*-tolyl)amino)dihydrofuran-2(3*H*)-one (3c)
The calibration curve was generated based on UV absorbance at 220 nm on HPLC.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2c** (10 mM, OD_{600} = 30, 24 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	1454.2	258.5	5.63	7.61	6.08	1260	10	77	1
2	1534.8	266.7	5.75	7.78	6.08				
3	1499.5	264.3	5.67	7.67	6.08				

3-(methyl(*o*-tolyl)amino)dihydrofuran-2(3*H*)-one (3d)
The calibration curve was generated based on UV absorbance at 270 nm on LC-MS.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2d** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	707.1	50.0	14.1	10.1	7.05	1440	10	101	1
2	714.1	50.0	14.3	10.2	7.05				
3	719.4	51.2	14.1	10.1	7.05				

3-((4-fluorophenyl)(methyl)amino)dihydrofuran-2(3*H*)-one (3e)
The calibration curve was generated based on UV absorbance at 220 nm on HPLC.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2e** (10 mM, OD_{600} = 30, 12 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	930.6	293.2	3.17	6.86	6.83	986	17	67	1
2	891.3	289.5	3.08	6.66	6.83				
3	890.1	288.4	3.09	6.67	6.83				

3-(indolin-1-yl)dihydrofuran-2(3*H*)-one (3f)
The calibration curve was generated based on UV absorbance at 270 nm on LC-MS.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2f** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	686.2	50.2	13.7	10.0	7.05	1420	20	100	1
2	666.7	49.5	13.5	9.88	7.05				
3	683.5	49.5	13.8	10.1	7.05				

Data analysis for **L6_FL** catalyzed carbene insertion of aniline **2f** (10 mM, OD_{600} = 30, 24 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	588.1	47.4	12.4	9.10	4.02	2250	10	91	0.4
2	590	47.8	12.3	9.05	4.02				
3	578.6	47.1	12.3	9.01	4.02				

3-(3,4-dihydroquinolin-1(2*H*)-yl)dihydrofuran-2(3*H*)-one (3g)
The calibration curve was generated based on UV absorbance at 220 nm on HPLC.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2g** (10 mM, OD_{600} = 30, 24 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	2240.8	272.8	8.21	8.35	6.08	1380	30	84	2
2	2302.6	273.6	8.42	8.55	6.08				
3	2322.3	287.4	8.08	8.21	6.08				

Data analysis for **L6_FL** catalyzed carbene insertion of aniline **2g** (10 mM, OD_{600} = 30, 24 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	1963.7	270.7	7.25	7.37	4.02	1930	80	78	3
2	2090.2	264.9	7.89	8.02	4.02				
3	2006.6	259.2	7.74	7.87	4.02				

3-(phenylamino)dihydrofuran-2(3*H*)-one (3h)
The calibration curve was generated based on UV absorbance at 220 nm on HPLC.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2h** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	1118.7	271.2	4.12	8.18	6.08	1330	80	81	5
2	1055.8	278.0	3.80	7.53	6.08				
3	1126.8	264.2	4.26	8.46	6.08				

Data analysis for **L5_FL** catalyzed carbene insertion of aniline **2h** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	1062.3	278.6	3.81	7.56	5.07	1500	30	78	2
2	1080.1	285.2	3.79	7.51	5.07				
3	1065.1	271.0	3.93	7.80	5.07				

3-(*o*-tolylamino)dihydrofuran-2(3H)-one (3i)
The calibration curve was generated based on UV absorbance at 270 nm on LC-MS.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2i** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	399.4	49.7	8.04	9.43	7.05	1370	30	96	2
2	414.0	49.7	8.33	9.77	7.05				
3	411.5	49.8	8.26	9.70	7.05				

Data analysis for **L6_FL** catalyzed carbene insertion of aniline **2i** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	349.7	47.3	7.39	8.68	4.02	2230	60	90	2
2	367.1	47.5	7.73	9.07	4.02				
3	368.0	47.4	7.76	9.11	4.02				

Data analysis for **L5_FL** catalyzed carbene insertion of aniline **2i** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	352.9	50.7	6.96	8.17	5.07	1650	40	84	2
2	356.3	49.4	7.21	8.46	5.07				
3	361.4	49.8	7.26	8.52	5.07				

3-(*m*-tolylamino)dihydrofuran-2(3*H*)-one (3j)
The calibration curve was generated based on UV absorbance at 270 nm on LC-MS.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2j** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	411.3	49.5	8.31	9.25	7.05	1330	10	94	1
2	415.5	49.4	8.41	9.37	7.05				
3	423.3	50.0	8.47	9.43	7.05				

3-(*p*-tolylamino)dihydrofuran-2(3*H*)-one (3k)
The calibration curve was generated based on UV absorbance at 270 nm on LC-MS.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2k** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	369.1	49.4	7.47	9.11	7.05	1320	30	93	2
2	375.7	49.9	7.53	9.18	7.05				
3	389.7	49.9	7.81	9.52	7.05				

3-((4-methoxyphenyl)amino)dihydrofuran-2(3*H*)-one (3l)
The calibration curve was generated based on UV absorbance at 220 nm on HPLC.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2l** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	1349.1	261.3	5.16	10.3	6.08	1750	50	106	3
2	1475.4	270.8	5.45	10.9	6.08				
3	1479.1	277.8	5.32	10.7	6.08				

Data analysis for **L6_FL** catalyzed carbene insertion of aniline **2l** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	1176.9	259.6	4.53	9.07	4.02	2190	60	88	3
2	1165.4	271.7	4.29	8.59	4.02				
3	1152.5	265.0	4.35	8.71	4.02				

Data analysis for **L5_FL** catalyzed carbene insertion of aniline **2l** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	1197.5	279.1	4.29	8.59	5.07	1710	40	87	2
2	1250.5	280.9	4.45	8.91	5.07				
3	1199.2	280.7	4.27	8.55	5.07				

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2l** (10 mM, OD_{600} = 5, 12 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	1296.2	265.2	4.89	9.78	1.01	9640	20	98	0.2
2	1317.9	270.5	4.87	9.75	1.01				

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2l** (10 mM, OD_{600} = 1, 12 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	864.7	268.7	3.22	6.44	0.203	31700	60	64	0.1
2	852.2	265.5	3.21	6.42	0.203				

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2l** (10 mM, OD_{600} = 1, 24 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	1102.7	292.0	3.78	7.56	0.232	32100	600	75	1
2	1069.5	291.1	3.67	7.35	0.232				

3-((2,6-dimethylphenyl)amino)dihydrofuran-2(3*H*)-one (3m)
The calibration curve was generated based on UV absorbance at 220 nm on HPLC.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2m** (10 mM, OD_{600} = 30, 12 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	2538.2	291.3	8.71	6.94	6.83	1040	20	71	1
2	2614.9	291.4	8.97	7.15	6.83				
3	2641.8	291.6	9.06	7.22	6.83				

3-(benzylamino)dihydrofuran-2(3*H*)-one (3n)
The calibration curve was generated based on UV absorbance at 220 nm on HPLC.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2n** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	393.6	297.1	1.32	7.96	6.97	1120	30	78	2
2	373.3	293.1	1.27	7.66	6.97				

3-((4-methoxybenzyl)amino)dihydrofuran-2(3*H*)-one (3o)
The calibration curve was generated based on UV absorbance at 220 nm on HPLC.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2o** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	579.9	149.0	3.89	3.74	6.83	585	33	40	2
2	567.5	133.6	4.24	4.08	6.83				
3	619.2	143.0	4.33	4.16	6.83				

3-((4-bromophenethyl)amino)dihydrofuran-2(*3H*)-one (3p)
The calibration curve was generated based on UV absorbance at 220 nm on HPLC.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2p** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	832.6	146.2	5.69	4.73	6.83	693	10	47	1
2	855.3	147.7	5.79	4.81	6.83				
3	829.4	147.5	5.62	4.67	6.83				

3-(isoindolin-2-yl)dihydrofuran-2(3*H*)-one (3q)
The calibration curve was generated based on UV absorbance at 220 nm on HPLC.

Data analysis for **L7_FL** catalyzed carbene insertion of aniline **2m** (10 mM, OD_{600} = 30, 4 h):

Entry	Pdt	IS	Pdt/IS	[Pdt]/mM	[PC]/μM	Avg. TTN	SD TTN	Avg. Yield [%]	SD Yield [%]
1	272.9	153.4	1.78	4.14	6.83	628	19	43	1
2	280.6	149.2	1.88	4.38	6.83				
3	271.2	145.1	1.87	4.35	6.83				

VI. Preparative-scale Enzymatic Synthesis

General procedure for 1 mmol-scale enzymatic reactions:

To a 500 mL flask, a suspension of *E. coli* expressing **L7_FL** variant (OD_{600} = 15), aniline (1.0 mmol), LAD (123.2 mg, 1.1 mmol, 1.1 equiv.), D-glucose (20 mM), and M9-N buffer/EtOH (20:1 v/v) were added under anaerobic conditions. The flask was capped and sealed with parafilm inside the anaerobic chamber. The mixture was shaken at 250 rpm in a shaker outside of anaerobic chamber for 20 h.

After the reaction was completed, the reaction mixture was transferred to a 500 mL centrifuge bottle. The aqueous phase was extracted with organic solvent (hexane/EtOAc = 2:3, 100 mL × 4). The organic layers were combined in an Erlenmeyer flask, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by silica column chromatography with hexane/EtOAc as eluents afforded the desired *α*-amino lactone products. TTNs were calculated based on measured protein concentration and isolated product yield.

1 (1.1 equiv) **2e** (1 mmol) **3e**

(*S*)-3-((4-fluorophenyl)(methyl)amino)dihydrofuran-2(3*H*)-one

3e: 180 mg, 86% yield, 2780 TTN, 93% e.e. The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3e** are identical to the synthesized racemic standard of *rac*-**3e**. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.09–7.00 (m, 2H), 6.91–6.82 (m, 2H), 5.02 (dd, *J* = 11.3, 8.8 Hz, 1H), 4.39 (td, *J* = 8.8, 1.6 Hz, 1H), 4.24 (ddd, *J* = 10.8, 8.8, 6.4 Hz, 1H), 2.71 (s, 3H), 2.44–2.24 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 175.0, 155.2 (d, *J* = 234.0 Hz), 146.2 (d, *J* = 1.8 Hz), 115.3 (d, *J* = 21.9 Hz), 114.8 (d, *J* = 7.4 Hz), 65.3, 58.7, 34.0, 24.3; **^{19}F NMR (**280 MHz, DMSO-d_6) δ –127.8; **X-ray** (single-crystal) Colorless needle crystals of X-ray diffraction quality were obtained by vapor diffusion of hexanes into a saturated solution of **3e** in EtOAc (CCDC 2065484).

1 (1.1 equiv) **2l** (1 mmol) **3l**

(*S*)-3-((4-methoxyphenyl)amino)dihydrofuran-2(3*H*)-one

3l: 170 mg, 84% yield, 3570 TTN, 88% e.e. The ^{1}H NMR and ^{13}C NMR of **3l** are identical to the synthesized racemic standard of *rac*-**3l**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.85–6.78 (m, 2H), 6.69–6.62 (m, 2H), 4.49 (td, *J* = 9.1, 1.2 Hz, 1H), 4.32 (ddd, *J* = 11.2, 9.3, 5.9 Hz, 1H), 4.06 (dd, *J* = 11.1, 8.0 Hz, 1H), 3.76 (s, 3H), 2.89–2.80 (m, 1H), 2.19 (dtd, *J* = 12.5, 11.2, 8.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.7, 153.4, 140.7, 115.3, 115.1, 65.9, 55.9, 54.0, 32.4; **X-ray** (single-crystal) Colorless needle crystals of X-ray diffraction quality were obtained by vapor diffusion of hexanes into a saturated solution of **3l** in EtOAc (CCDC 2065489).

(*S*)-((2,6-dimethylphenyl)amino)dihydrofuran-2(3*H*)-one

3m, 148 mg, 72% yield, 3060 TTN, 91% e.e. The ^{1}H NMR and ^{13}C NMR of **3m** are identical to the synthesized racemic standard of *rac*-**3m**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06–6.99 (m, 2H), 6.94–6.88 (m, 1H), 4.47–4.39 (m, 1H), 4.18 (ddd, *J* = 11.1, 9.3, 5.7 Hz, 1H), 3.98 (dd, *J* = 11.5, 8.2 Hz, 1H), 3.62 (bs, 1H), 2.68–2.58 (m, 1H), 2.43–2.19 (m, 7H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.8, 143.5, 130.8, 129.2, 123.8, 65.4, 57.4, 31.8, 18.9.

General procedure for the gram-scale enzymatic reaction:

To a 1-L flask were added a suspension of *E. coli* expressing **L7_FL** variant (OD_{600} = 30), aniline (6.0 mmol), LAD (739.2, 6.6 mmol, 1.1 equiv.), D-glucose (20 mM), M9-N buffer/EtOH (20:1 v/v) under anaerobic conditions. The flask was capped and sealed with parafilm inside the anaerobic chamber. The mixture was shaken at 250 rpm in a shaker outside of anaerobic chamber for 20 h.

After the reaction was completed, the reaction mixture was transferred to two 500 mL centrifuge bottles. The aqueous phase was extracted with organic solvent (hexane/EtOAc = 2:3, 180 mL × 4). The organic layers were combined in an Erlenmeyer flask, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by silica column chromatography with hexane/EtOAc as eluents afforded the desired *α*-amino lactone products. TTNs were calculated based on measured protein concentration and isolated product yield.

(*S*)-3-(methyl(*p*-tolyl)amino)dihydrofuran-2(3*H*)-one

3d, 1.19 g, 97% yield, 3170 TTN, 96% e.e. The ^{1}H NMR and ^{13}C NMR of **3d** are identical to the synthesized racemic standard of *rac*-**3d**. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.04–6.98 (m, 2H), 6.79–6.73 (m, 2H), 5.01 (dd, *J* = 11.2, 8.8 Hz, 1H), 4.39 (td, *J* = 8.8, 1.6 Hz, 1H), 4.24 (ddd, *J* = 10.7, 8.8, 6.4 Hz, 1H), 2.70 (s, 3H), 2.42–2.21 (m, 2H), 2.19 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 175.2, 147.2, 129.4, 126.0, 113.6, 65.3, 58.4, 33.7, 24.2, 19.9.

VII. Assignment of Absolute Configuration through X-Ray Crystallography

(*S*)-3-((4-fluorophenyl)(methyl)amino)dihydrofuran-2(3*H*)-one (3e) (CCDC 2065484)

Table 4. Crystal data and structure refinement for **3e**.

Identification code	V20270	
Empirical formula	$C_{11}H_{12}FNO_2$	
Formula weight	209.22	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.4448(7) Å	a= 90°.
	b = 8.1264(11) Å	b= 90°.
	c = 22.523(3) Å	g = 90°.
Volume	996.6(2) $Å^3$	
Z	4	
Density (calculated)	1.394 Mg/m^3	
Absorption coefficient	0.913 mm^{-1}	
F(000)	440	
Crystal size	0.400 × 0.050 × 0.050 mm^3	
Theta range for data collection	3.925 to 74.374°.	
Index ranges	-6<=h<=6, -9<=k<=10, -28<=l<=26	
Reflections collected	11349	
Independent reflections	2013 [R(int) = 0.0931]	
Completeness to theta = 67.679°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7538 and 0.5211	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2013 / 0 / 137	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I)]	R1 = 0.0460, wR2 = 0.1159	
R indices (all data)	R1 = 0.0538, wR2 = 0.1198	
Absolute structure parameter	-0.2(2)	

Extinction coefficient	n/a
Largest diff. peak and hole	0.202 and -0.215 e.Å^{-3}

Table 5. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **3e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4986(4)	508(3)	9480(1)	30(1)
C(1)	5235(6)	2136(4)	9389(1)	26(1)
O(2)	7010(4)	2878(3)	9552(1)	32(1)
C(2)	2982(6)	2801(4)	9061(1)	26(1)
N(1)	3577(5)	4150(3)	8669(1)	26(1)
C(5)	5311(6)	3763(4)	8195(1)	28(1)
C(6)	1836(6)	5388(4)	8566(1)	24(1)
C(7)	1823(6)	6277(4)	8031(1)	27(1)
C(8)	157(6)	7559(4)	7933(1)	29(1)
C(9)	-1531(6)	7929(4)	8364(1)	28(1)
F(1)	-3173(4)	9174(2)	8269(1)	32(1)
C(10)	-1589(6)	7090(4)	8899(1)	28(1)
C(11)	79(6)	5834(4)	8998(1)	28(1)
C(3)	1886(6)	1221(4)	8790(1)	29(1)
C(4)	2643(5)	-69(4)	9245(2)	30(1)

Table 6. Bond lengths [Å] and angles [°] for **3e**.

O(1)-C(1)	1.346(4)
O(1)-C(4)	1.459(4)
C(1)-O(2)	1.197(4)
C(1)-C(2)	1.531(4)
C(2)-N(1)	1.445(4)
C(2)-C(3)	1.541(5)
C(2)-H(2)	1.0000
N(1)-C(6)	1.402(4)
N(1)-C(5)	1.458(4)

C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-C(7)	1.406(4)
C(6)-C(11)	1.411(4)
C(7)-C(8)	1.399(5)
C(7)-H(7)	0.9500
C(8)-C(9)	1.370(5)
C(8)-H(8)	0.9500
C(9)-F(1)	1.368(4)
C(9)-C(10)	1.384(4)
C(10)-C(11)	1.384(5)
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
C(3)-C(4)	1.522(5)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900

C(1)-O(1)-C(4)	110.4(2)
O(2)-C(1)-O(1)	122.0(3)
O(2)-C(1)-C(2)	128.1(3)
O(1)-C(1)-C(2)	109.8(3)
N(1)-C(2)-C(1)	112.5(2)
N(1)-C(2)-C(3)	118.5(3)
C(1)-C(2)-C(3)	102.0(3)
N(1)-C(2)-H(2)	107.8
C(1)-C(2)-H(2)	107.8
C(3)-C(2)-H(2)	107.8
C(6)-N(1)-C(2)	119.6(2)
C(6)-N(1)-C(5)	118.2(2)
C(2)-N(1)-C(5)	115.4(2)
N(1)-C(5)-H(5A)	109.5
N(1)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5

N(1)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
N(1)-C(6)-C(7)	120.9(3)
N(1)-C(6)-C(11)	122.0(3)
C(7)-C(6)-C(11)	117.1(3)
C(8)-C(7)-C(6)	121.4(3)
C(8)-C(7)-H(7)	119.3
C(6)-C(7)-H(7)	119.3
C(9)-C(8)-C(7)	119.2(3)
C(9)-C(8)-H(8)	120.4
C(7)-C(8)-H(8)	120.4
F(1)-C(9)-C(8)	119.3(3)
F(1)-C(9)-C(10)	119.1(3)
C(8)-C(9)-C(10)	121.6(3)
C(9)-C(10)-C(11)	119.2(3)
C(9)-C(10)-H(10)	120.4
C(11)-C(10)-H(10)	120.4
C(10)-C(11)-C(6)	121.5(3)
C(10)-C(11)-H(11)	119.2
C(6)-C(11)-H(11)	119.2
C(4)-C(3)-C(2)	101.7(2)
C(4)-C(3)-H(3A)	111.4
C(2)-C(3)-H(3A)	111.4
C(4)-C(3)-H(3B)	111.4
C(2)-C(3)-H(3B)	111.4
H(3A)-C(3)-H(3B)	109.3
O(1)-C(4)-C(3)	105.0(3)
O(1)-C(4)-H(4A)	110.7
C(3)-C(4)-H(4A)	110.7
O(1)-C(4)-H(4B)	110.7
C(3)-C(4)-H(4B)	110.7
H(4A)-C(4)-H(4B)	108.8

Symmetry transformations used to generate equivalent atoms:

Table 7. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3e**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	35(1)	18(1)	35(1)	0(1)	-2(1)	4(1)
C(1)	30(1)	21(2)	28(1)	0(1)	2(1)	0(1)
O(2)	35(1)	28(1)	34(1)	3(1)	-2(1)	-6(1)
C(2)	29(1)	18(2)	32(1)	1(1)	0(1)	1(1)
N(1)	27(1)	20(1)	32(1)	2(1)	3(1)	0(1)
C(5)	29(2)	24(2)	32(1)	-1(1)	1(1)	4(1)
C(6)	27(1)	14(2)	32(1)	-1(1)	-1(1)	-3(1)
C(7)	32(2)	18(2)	31(1)	0(1)	2(1)	-1(1)
C(8)	35(2)	20(2)	31(1)	3(1)	0(1)	0(1)
C(9)	31(1)	15(2)	36(2)	1(1)	-4(1)	-1(1)
F(1)	36(1)	23(1)	38(1)	2(1)	-1(1)	6(1)
C(10)	33(1)	19(2)	32(2)	0(1)	3(1)	-1(1)
C(11)	31(2)	19(2)	33(1)	2(1)	0(1)	-2(1)
C(3)	31(2)	18(2)	39(2)	0(1)	-4(1)	1(1)
C(4)	28(2)	20(2)	43(2)	0(1)	0(1)	1(1)

Table 8. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **3e**.

	x	y	z	U(eq)
H(2)	1799	3220	9365	31
H(5A)	6153	4770	8070	43
H(5B)	4423	3291	7857	43
H(5C)	6521	2966	8341	43
H(7)	2970	6001	7729	33
H(8)	195	8166	7573	35
H(10)	-2760	7373	9194	34
H(11)	40	5259	9365	33
H(3A)	77	1296	8755	35

H(3B)	2598	985	8395	35
H(4A)	1404	-154	9565	36
H(4B)	2831	-1160	9055	36

Table 9. Torsion angles [°] for **3e**.

C(4)-O(1)-C(1)-O(2)	179.2(3)
C(4)-O(1)-C(1)-C(2)	-1.0(3)
O(2)-C(1)-C(2)-N(1)	32.5(4)
O(1)-C(1)-C(2)-N(1)	-147.3(2)
O(2)-C(1)-C(2)-C(3)	160.5(3)
O(1)-C(1)-C(2)-C(3)	-19.3(3)
C(1)-C(2)-N(1)-C(6)	-148.6(3)
C(3)-C(2)-N(1)-C(6)	92.7(3)
C(1)-C(2)-N(1)-C(5)	60.9(3)
C(3)-C(2)-N(1)-C(5)	-57.8(4)
C(2)-N(1)-C(6)-C(7)	-152.2(3)
C(5)-N(1)-C(6)-C(7)	-2.5(4)
C(2)-N(1)-C(6)-C(11)	29.9(4)
C(5)-N(1)-C(6)-C(11)	179.5(3)
N(1)-C(6)-C(7)-C(8)	-177.4(3)
C(11)-C(6)-C(7)-C(8)	0.7(5)
C(6)-C(7)-C(8)-C(9)	-1.5(5)
C(7)-C(8)-C(9)-F(1)	-179.5(3)
C(7)-C(8)-C(9)-C(10)	1.5(5)
F(1)-C(9)-C(10)-C(11)	-179.7(3)
C(8)-C(9)-C(10)-C(11)	-0.8(5)
C(9)-C(10)-C(11)-C(6)	-0.1(5)
N(1)-C(6)-C(11)-C(10)	178.1(3)
C(7)-C(6)-C(11)-C(10)	0.1(5)
N(1)-C(2)-C(3)-C(4)	154.4(3)
C(1)-C(2)-C(3)-C(4)	30.3(3)
C(1)-O(1)-C(4)-C(3)	21.5(3)
C(2)-C(3)-C(4)-O(1)	-32.0(3)

(*S*)-3-((4-methoxyphenyl)amino)dihydrofuran-2(3*H*)-one (3l) (CCDC 2065489)

Table 10. Crystal data and structure refinement for **3l**.

Identification code	V20254	
Empirical formula	$C_{11}H_{13}NO_3$	
Formula weight	207.22	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 5.6898(6) Å	a= 90°.
	b = 7.6140(7) Å	b= 102.057(3)°.
	c = 11.6487(12) Å	g = 90°.
Volume	493.51(9) $Å^3$	
Z	2	
Density (calculated)	1.394 Mg/m^3	
Absorption coefficient	0.844 mm^{-1}	
F(000)	220	
Crystal size	0.200 × 0.150 × 0.050 mm^3	
Theta range for data collection	3.880 to 74.614°.	
Index ranges	-7<=h<=7, -9<=k<=9, -14<=l<=14	
Reflections collected	15186	
Independent reflections	1993 [R(int) = 0.0533]	
Completeness to theta = 67.679°	100.0%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7538 and 0.6431	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1993 / 2 / 141	
Goodness-of-fit on F^2	1.143	
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.1046	
R indices (all data)	R1 = 0.0381, wR2 = 0.1051	

Absolute structure parameter	0.1(2)
Extinction coefficient	0.014(4)
Largest diff. peak and hole	0.248 and -0.170 e.Å^{-3}

Table 11. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **3l**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	8327(3)	6270(3)	3761(2)	30(1)
C(1)	8352(4)	6057(3)	4911(2)	22(1)
O(2)	9860(3)	6761(3)	5653(2)	29(1)
C(2)	6299(4)	4855(3)	5072(2)	20(1)
N(1)	5177(4)	5365(3)	6020(2)	23(1)
C(5)	5966(4)	4798(3)	7176(2)	20(1)
C(6)	8143(4)	3949(3)	7576(2)	22(1)
C(7)	8877(4)	3470(4)	8756(2)	26(1)
C(8)	7438(5)	3880(4)	9551(2)	27(1)
O(3)	8024(4)	3530(3)	10738(2)	41(1)
C(11)	10466(5)	3249(4)	11248(2)	29(1)
C(9)	5249(4)	4713(4)	9157(2)	26(1)
C(10)	4514(4)	5159(3)	7984(2)	23(1)
C(3)	4621(4)	4929(3)	3868(2)	24(1)
C(4)	6330(5)	5286(4)	3051(2)	29(1)

Table 12. Bond lengths [Å] and angles [°] for **3l**.

O(1)-C(1)	1.347(3)
O(1)-C(4)	1.464(3)
C(1)-O(2)	1.208(3)
C(1)-C(2)	1.526(3)
C(2)-N(1)	1.440(3)
C(2)-C(3)	1.524(3)
C(2)-H(2)	1.0000
N(1)-C(5)	1.395(3)

N(1)-H(1N)	0.91(2)
C(5)-C(6)	1.389(3)
C(5)-C(10)	1.403(3)
C(6)-C(7)	1.399(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.394(4)
C(7)-H(7)	0.9500
C(8)-O(3)	1.379(3)
C(8)-C(9)	1.388(4)
O(3)-C(11)	1.408(3)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(9)-C(10)	1.385(3)
C(9)-H(9)	0.9500
C(10)-H(10)	0.9500
C(3)-C(4)	1.521(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900

C(1)-O(1)-C(4)	110.26(19)
O(2)-C(1)-O(1)	121.1(2)
O(2)-C(1)-C(2)	128.7(2)
O(1)-C(1)-C(2)	110.2(2)
N(1)-C(2)-C(3)	113.78(19)
N(1)-C(2)-C(1)	113.96(19)
C(3)-C(2)-C(1)	102.33(19)
N(1)-C(2)-H(2)	108.8
C(3)-C(2)-H(2)	108.8
C(1)-C(2)-H(2)	108.8
C(5)-N(1)-C(2)	123.48(19)
C(5)-N(1)-H(1N)	116(2)
C(2)-N(1)-H(1N)	116(2)
C(6)-C(5)-N(1)	123.5(2)

C(6)-C(5)-C(10)	118.4(2)
N(1)-C(5)-C(10)	118.1(2)
C(5)-C(6)-C(7)	120.9(2)
C(5)-C(6)-H(6)	119.6
C(7)-C(6)-H(6)	119.6
C(8)-C(7)-C(6)	119.9(2)
C(8)-C(7)-H(7)	120.0
C(6)-C(7)-H(7)	120.0
O(3)-C(8)-C(9)	115.6(2)
O(3)-C(8)-C(7)	124.8(2)
C(9)-C(8)-C(7)	119.6(2)
C(8)-O(3)-C(11)	117.6(2)
O(3)-C(11)-H(11A)	109.5
O(3)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
O(3)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(9)-C(8)	120.3(2)
C(10)-C(9)-H(9)	119.9
C(8)-C(9)-H(9)	119.9
C(9)-C(10)-C(5)	121.0(2)
C(9)-C(10)-H(10)	119.5
C(5)-C(10)-H(10)	119.5
C(4)-C(3)-C(2)	102.9(2)
C(4)-C(3)-H(3A)	111.2
C(2)-C(3)-H(3A)	111.2
C(4)-C(3)-H(3B)	111.2
C(2)-C(3)-H(3B)	111.2
H(3A)-C(3)-H(3B)	109.1
O(1)-C(4)-C(3)	105.08(19)
O(1)-C(4)-H(4A)	110.7
C(3)-C(4)-H(4A)	110.7
O(1)-C(4)-H(4B)	110.7
C(3)-C(4)-H(4B)	110.7
H(4A)-C(4)-H(4B)	108.8

Symmetry transformations used to generate equivalent atoms:

Table 13. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3l**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	26(1)	38(1)	27(1)	5(1)	10(1)	-2(1)
C(1)	18(1)	24(1)	26(1)	3(1)	6(1)	2(1)
O(2)	20(1)	34(1)	34(1)	0(1)	4(1)	-5(1)
C(2)	20(1)	19(1)	20(1)	1(1)	4(1)	1(1)
N(1)	16(1)	31(1)	22(1)	3(1)	6(1)	4(1)
C(5)	18(1)	19(1)	22(1)	-1(1)	4(1)	-3(1)
C(6)	18(1)	25(1)	22(1)	-1(1)	5(1)	-1(1)
C(7)	19(1)	32(1)	25(1)	4(1)	2(1)	-1(1)
C(8)	22(1)	36(1)	21(1)	2(1)	3(1)	-6(1)
O(3)	25(1)	78(2)	21(1)	10(1)	3(1)	-6(1)
C(11)	27(1)	34(1)	24(1)	3(1)	2(1)	3(1)
C(9)	22(1)	35(1)	24(1)	-2(1)	9(1)	-4(1)
C(10)	17(1)	26(1)	27(1)	0(1)	5(1)	-1(1)
C(3)	23(1)	24(1)	23(1)	1(1)	2(1)	-1(1)
C(4)	32(1)	33(1)	23(1)	0(1)	7(1)	1(1)

Table 14. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **3l**.

	x	y	z	U(eq)
H(2)	6929	3631	5217	24
H(1N)	3610(40)	5700(40)	5810(30)	27
H(6)	9147	3690	7041	26
H(7)	10354	2866	9014	31
H(11A)	11043	2209	10895	43
H(11B)	10647	3066	12095	43

H(11C)	11405	4277	11109	43
H(9)	4250	4978	9693	32
H(10)	3003	5717	7722	28
H(3A)	3765	3800	3675	29
H(3B)	3427	5885	3829	29
H(4A)	6906	4173	2769	35
H(4B)	5526	5987	2365	35

Table 15. Torsion angles [°] for **3l**.

C(4)-O(1)-C(1)-O(2)	-179.9(2)
C(4)-O(1)-C(1)-C(2)	0.3(3)
O(2)-C(1)-C(2)-N(1)	38.2(3)
O(1)-C(1)-C(2)-N(1)	-142.0(2)
O(2)-C(1)-C(2)-C(3)	161.5(2)
O(1)-C(1)-C(2)-C(3)	-18.8(2)
C(3)-C(2)-N(1)-C(5)	154.7(2)
C(1)-C(2)-N(1)-C(5)	-88.4(3)
C(2)-N(1)-C(5)-C(6)	11.9(4)
C(2)-N(1)-C(5)-C(10)	-170.3(2)
N(1)-C(5)-C(6)-C(7)	177.6(2)
C(10)-C(5)-C(6)-C(7)	-0.3(3)
C(5)-C(6)-C(7)-C(8)	-1.4(4)
C(6)-C(7)-C(8)-O(3)	-177.5(2)
C(6)-C(7)-C(8)-C(9)	2.1(4)
C(9)-C(8)-O(3)-C(11)	-159.2(3)
C(7)-C(8)-O(3)-C(11)	20.4(4)
O(3)-C(8)-C(9)-C(10)	178.6(2)
C(7)-C(8)-C(9)-C(10)	-1.0(4)
C(8)-C(9)-C(10)-C(5)	-0.7(4)
C(6)-C(5)-C(10)-C(9)	1.3(3)
N(1)-C(5)-C(10)-C(9)	-176.7(2)
N(1)-C(2)-C(3)-C(4)	151.8(2)
C(1)-C(2)-C(3)-C(4)	28.4(2)
C(1)-O(1)-C(4)-C(3)	18.5(3)

C(2)-C(3)-C(4)-O(1)	-29.1(2)

Symmetry transformations used to generate equivalent atoms:

Table 16. Hydrogen bonds for **3l** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(2)#1	0.91(2)	2.25(2)	3.150(3)	169(3)
C(6)-H(6)...O(1)#2	0.95	2.63	3.454(3)	145.9
C(3)-H(3A)...N(1)#3	0.99	2.69	3.478(3)	136.7
C(4)-H(4A)...O(3)#4	0.99	2.62	3.326(3)	128.3

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+2,y-1/2,-z+1 #3 -x+1,y-1/2,-z+1

#4 x,y,z-1

VIII. Chiral HPLC Traces

The absolute stereochemistry for α-amino lactone **3e** and **3l**-major was assigned to be *S* based on X-ray crystallography. The other products **3a–3d**, **3f–3k** and **3m–3q** were assigned by analogy.

(*S*)-3-(methyl(phenyl)amino)dihydrofuran-2(3*H*)-one (3a)
Chiral HPLC conditions: Chiralpak IC, 25% *i*-PrOH in hexane, 1.5 mL/min, 32 ºC, 254 nm

Racemic 3a:

#	Time	Area	Height	Width	Area%	Symmetry
1	9.813	3425.5	246.6	0.218	49.910	0.97
2	13.798	3437.8	171.4	0.318	50.090	0.962

Enzymatic preparation of 3a with L7_FL: 95% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	9.789	10232.7	724.8	0.2353	97.695	0.937
2	13.799	241.4	11.2	0.3581	2.305	0.889

Enzymatic preparation of 3a with L6_FL: 94% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	9.911	8049.4	561.7	0.2389	96.876	0.954
2	13.965	259.6	12.3	0.3506	3.124	1.088

Enzymatic preparation of 3a with L5_FL: –21% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	9.924	2865.2	207.6	0.23	39.632	0.974
2	13.93	4364.3	220.2	0.3303	60.368	0.973

(*S*)-3-(ethyl(phenyl)amino)dihydrofuran-2(3*H*)-one (3b)
Chiral HPLC conditions: Chiralpak IC, 25% *i*-PrOH in hexane, 1.5 mL/min, 32 ºC, 254 nm

Racemic 3b:

#	Time	Area	Height	Width	Area%	Symmetry
1	7.94	3204	282.9	0.1781	49.893	0.974
2	9.372	3217.8	236.5	0.2108	50.107	0.974

Enzymatic preparation of 3b with L7_FL: 98% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	7.927	8680.1	741.4	0.1951	98.862	0.941
2	9.377	99.9	7	0.2383	1.138	1.176

(*S*)-3-(methyl(*o*-tolyl)amino)dihydrofuran-2(3*H*)-one (3c)
Chiral HPLC conditions: Chiralpak IC, 25% *i*-PrOH in hexane, 1.5 mL/min, 32 ºC, 254 nm

Racemic 3c:

#	Time	Area	Height	Width	Area%	Symmetry
1	5.778	3021.2	382.8	0.1241	50.000	0.958
2	6.241	3021.2	352.6	0.134	50.000	0.947

Enzymatic preparation of 3c with L7_FL: 98% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	5.762	2800.6	341	0.1369	98.982	0.95
2	6.238	28.8	3.3	0.1436	1.018	0.883

(*S*)-3-(methyl(*p*-tolyl)amino)dihydrofuran-2(3*H*)-one (3d)

Chiral HPLC conditions: Chiralpak IC, 25% *i*-PrOH in hexane, 1.5 mL/min, 32 ºC, 254 nm

Racemic 3d:

#	Time	Area	Height	Width	Area%	Symmetry
1	11.364	7422.5	443.9	0.2611	49.963	0.941
2	15.983	7433.6	311.2	0.3687	50.037	0.923

Enzymatic preparation of 3d with L7_FL: 96% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	11.319	11443.4	680.7	0.2802	97.909	0.921
2	15.971	244.3	10.4	0.3922	2.091	0.96

Large-scale enzymatic preparation of 3d with L7_FL: 96% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	11.783	1665	99.2	0.2797	97.894	0.957
2	16.448	35.8	1.8	0.3251	2.106	0.696

(*S*)-3-((4-fluorophenyl)(methyl)amino)dihydrofuran-2(3*H*)-one (3e)
Chiral HPLC conditions: Chiralpak IC, 25% *i*-PrOH in hexane, 1.5 mL/min, 32 ºC, 254 nm

Racemic 3e:

#	Time	Area	Height	Width	Area%	Symmetry
1	7.567	3905.7	366.3	0.1664	49.850	0.939
2	10.996	3929.2	244.9	0.2472	50.150	0.94

Enzymatic preparation of 3e with L7_FL: 94% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	7.554	4670.5	427	0.1823	97.129	0.94
2	11.008	138	8.4	0.2752	2.871	1.05

Large-scale enzymatic preparation of 3e with L7_FL: 93% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	7.713	1650.9	151.6	0.1815	96.442	0.946
2	11.223	60.9	3.7	0.274	3.558	0.908

(*S*)-3-(indolin-1-yl)dihydrofuran-2(3*H*)-one (3f)
Chiral HPLC conditions: Chiralpak IC, 25% *i*-PrOH in hexane, 1.5 mL/min, 32 ºC, 254 nm

Racemic 3f:

#	Time	Area	Height	Width	Area%	Symmetry
1	13.907	3550.6	169.6	0.3262	50.350	0.908
2	15.155	3501.1	152.4	0.358	49.650	0.947

Enzymatic preparation of 3f with L7_FL: 88% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	13.885	7298.2	350	0.3475	94.089	0.908
2	15.164	458.5	20.4	0.3739	5.911	1.033

Enzymatic preparation of 3f with L6_FL: 87% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	14.023	6070.6	288.9	0.3502	93.495	0.931
2	15.287	422.3	18.6	0.3775	6.505	1.079

(*S*)-3-(3,4-dihydroquinolin-1(2*H*)-yl)dihydrofuran-2(3*H*)-one (3g)
Chiral HPLC conditions: Chiralpak IC, 25% *i*-PrOH in hexane, 1.5 mL/min, 32 ºC, 254 nm

Racemic 3g:

#	Time	Area	Height	Width	Area%	Symmetry
1	9.868	6050.5	405.1	0.2343	49.951	0.934
2	11.398	6062.5	351.3	0.2693	50.049	0.927

Enzymatic preparation of 3g with L7_FL: 90% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	9.842	8231.3	551.5	0.2488	95.210	0.909
2	11.392	414.1	24	0.2878	4.790	0.967

Enzymatic preparation of 3g with L6_FL: 92% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	9.898	7069.7	461.7	0.2552	96.122	0.944
2	11.454	285.2	16.2	0.2936	3.878	1.058

(*S*)-3-(phenylamino)dihydrofuran-2(3*H*)-one (3h)
Chiral HPLC conditions: Chiralpak IC, 25% *i*-PrOH in hexane, 1.5 mL/min, 32 ºC, 254 nm

Racemic 3h:

#	Time	Area	Height	Width	Area%	Symmetry
1	9.944	1811.1	127.9	0.2252	49.871	0.942
2	13.709	1820.4	91.1	0.305	50.129	0.922

Enzymatic preparation of 3h with L7_FL: 50% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	10.018	3210.6	231.8	0.2309	74.911	0.941
2	13.754	1075.3	54.5	0.3291	25.089	0.957

Enzymatic preparation of 3h with L5_FL: –57% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	9.934	874.8	61.3	0.2378	21.411	0.987
2	13.69	3210.9	158.2	0.3383	78.589	0.946

(*S*)-3-(*o*-tolylamino)dihydrofuran-2(3H)-one (3i)
Chiral HPLC conditions: Chiralpak IC, 25% *i*-PrOH in hexane, 1.5 mL/min, 32 ºC, 254 nm

Racemic 3i:

#	Time	Area	Height	Width	Area%	Symmetry
1	5.991	1330.2	155.8	0.1336	49.971	0.922
2	7.021	1331.7	132.6	0.1552	50.029	0.959

Enzymatic preparation of 3i with L7_FL: 91% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	5.991	3035.6	350.7	0.1443	95.403	0.912
2	7.036	146.3	14.6	0.1667	4.597	1.085

Enzymatic preparation of 3i with L6_FL: 90% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	6.015	2644.8	298.9	0.1475	95.069	0.932
2	7.059	137.2	13.5	0.1699	4.931	0.934

Enzymatic preparation of 3i with L5_FL: –7% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	6.008	1345.2	155.7	0.144	46.680	0.941
2	7.05	1536.5	150.6	0.17	53.320	0.951

(*S*)-3-(*m*-tolylamino)dihydrofuran-2(3*H*)-one (3j)
Chiral HPLC conditions: Chiralpak IC, 25% *i*-PrOH in hexane, 1.5 mL/min, 32 ºC, 254 nm

Racemic 3j:

#	Time	Area	Height	Width	Area%	Symmetry
1	9.79	2010.8	139.6	0.224	50.004	0.955
2	13.027	2010.4	101.7	0.2987	49.996	0.951

Enzymatic preparation of 3j with L7_FL: 85% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	9.789	5482.5	380.6	0.2401	92.302	0.944
2	13.049	457.3	23.9	0.3193	7.698	0.972

(*S*)-3-(*p*-tolylamino)dihydrofuran-2(3*H*)-one (3k)

Chiral HPLC conditions: Chiralpak IC, 25% *i*-PrOH in hexane, 1.5 mL/min, 32 ºC, 254 nm

Racemic 3k:

#	Time	Area	Height	Width	Area%	Symmetry
1	12.192	3516.3	195.5	0.2799	49.955	0.949
2	14.081	3522.6	167.3	0.3236	50.045	0.92

Enzymatic preparation of 3k with L7_FL: 87% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	12.185	6192.6	346.4	0.298	93.561	0.957
2	14.09	426.2	21	0.3381	6.439	0.884

(*S*)-3-((4-methoxyphenyl)amino)dihydrofuran-2(3*H*)-one (3l)

Chiral HPLC conditions: Chiralpak IC, 25% *i*-PrOH in hexane, 1.5 mL/min, 32 ºC, 254 nm

Racemic 3l:

#	Time	Area	Height	Width	Area%	Symmetry
1	20.126	4238	133.9	0.4773	49.975	0.87
2	23.391	4242.2	113.7	0.5472	50.025	0.857

Enzymatic preparation of 3l with L7_FL: 89% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	20.152	5858	189.8	0.5145	94.329	0.877
2	23.529	352.2	10.1	0.5794	5.671	0.959

Large-scale enzymatic preparation of 3l with L7_FL: 88% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	20.557	1181	38.3	0.5137	93.957	0.836
2	24.044	76	2.1	0.6004	6.043	1.357

Enzymatic preparation of 3l with L6_FL: 79% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	20.246	4922.2	156.5	0.524	89.435	0.904
2	23.587	581.5	16.1	0.6015	10.565	0.836

Enzymatic preparation of 3l with L5_FL: –53% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	20.333	1366.2	44.3	0.5138	23.520	0.949
2	23.57	4442.2	120.4	0.6149	76.480	0.865

(*S*)-3-((2,6-dimethylphenyl)amino)dihydrofuran-2(3*H*)-one (3m)

Chiral HPLC conditions: Chiralpak IA, 15% *i*-PrOH in hexane, 1.2 mL/min, 32 ºC, 254 nm

Racemic 3m:

#	Time	Area	Height	Width	Area%	Symmetry
1	5.46	523.9	63.7	0.1239	49.449	0.646
2	5.904	535.5	60.5	0.1313	50.551	0.654

Enzymatic preparation of 3m with L7_FL: 90% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	5.486	86.3	11.2	0.129	4.848	0.736
2	5.909	1693.4	197.2	0.1431	95.152	0.673

Large-scale enzymatic preparation of 3m with L7_FL: 91% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	5.59	21.4	2.9	0.1228	4.478	0.96
2	6.035	456.3	50.3	0.1513	95.522	0.67

(*S*)-3-(benzylamino)dihydrofuran-2(3*H*)-one (3n)
Chiral HPLC conditions: Chiralpak IA, 20% *i*-PrOH in hexane, 1.2 mL/min, 32 ºC, 220 nm

Racemic 3n:

#	Time	Area	Height	Width	Area%	Symmetry
1	5.611	4106.9	426	0.1607	50.468	0.505
2	6.184	4030.7	396.7	0.1693	49.532	0.535

Enzymatic preparation of 3n with L7_FL: 89% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	5.789	1065.2	102.9	0.1726	94.520	0.534
2	6.434	61.8	6.9	0.1502	5.480	0.848

(*S*)-3-((4-methoxybenzyl)amino)dihydrofuran-2(3*H*)-one (3o)
Chiral HPLC conditions: Chiralpak IA, 20% *i*-PrOH in hexane, 1.2 mL/min, 32 ºC, 220 nm

Racemic 3o:

#	Time	Area	Height	Width	Area%	Symmetry
1	7.438	10449.8	719.6	0.242	49.526	0.422
2	8.104	10649.9	693.6	0.2559	50.474	0.449

Enzymatic preparation of 3o with L7_FL: 88% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	7.503	2760.7	192.6	0.239	94.072	0.494
2	8.247	174	12.3	0.2354	5.928	0.624

(*S*)-3-((4-bromophenethyl)amino)dihydrofuran-2(*3H*)-one (3p)

Chiral HPLC conditions: Chiralpak IA, 20% *i*-PrOH in hexane, 1.2 mL/min, 32 ºC, 220 nm

Racemic 3p:

#	Time	Area	Height	Width	Area%	Symmetry
1	7.107	2817	186.8	0.222	49.672	0.424
2	8.026	2854.2	174.4	0.2409	50.328	0.45

Enzymatic preparation of 3p with L7_FL: 89% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	7.067	4520.1	309.6	0.2433	94.465	0.426
2	8.116	264.8	17.4	0.254	5.535	0.677

(*S*)-3-(isoindolin-2-yl)dihydrofuran-2(3*H*)-one (3q)
Chiral HPLC conditions: Chiralpak IA, 20% *i*-PrOH in hexane, 1.2 mL/min, 32 ºC, 210 nm

Racemic 3q:

#	Time	Area	Height	Width	Area%	Symmetry
1	6.587	754.6	54.4	0.2313	49.744	0.497
2	7.577	762.4	50	0.254	50.256	0.539

Enzymatic preparation of 3q with L7_FL: 66% e.e.

#	Time	Area	Height	Width	Area%	Symmetry
1	6.508	3224.9	218.8	0.2456	82.932	0.384
2	7.565	663.7	44.6	0.2479	17.068	0.463

IX. Sequence Information

Mutations present in P411 variants involved in this study[6]:

P411 variant	Mutations relative to wild-type P450$_{BM3}$
P411-**C10** (**L1**)	N70E A74G V78L A82L F87A M118S P142S F162L T175I M177L A184V S226R H236Q E252G I263Y H266V T268G A290V A328V A330Y L353V I366V C400S I401L T436L L437Q E442K ΔFAD*
L2	N70E A74G V78L A82L F87A M118S P142S F162L T175I M177L A184V S226R H236Q E252G I263Y H266V T268G A290V **T327V** A328V A330Y L353V I366V C400S I401L T436L L437Q E442K ΔFAD*
L3	N70E A74G V78L A82L F87A M118S P142S F162L T175I M177L A184V S226R H236Q E252G I263Y H266V T268G A290V **T327V** A328V A330Y L353V I366V C400S I401L T436L E442K ΔFAD*
L4	N70E A74G V78L A82L F87A M118S P142S F162L T175I M177L A184V S226R H236Q E252G I263Y H266V T268G A290V **T327V** A328V A330Y **S332A** L353V I366V C400S I401L T436L E442K ΔFAD*
L5	N70E A74G V78L A82L **F87P** M118S P142S F162L T175I M177L A184V S226R H236Q E252G I263Y H266V T268G A290V **T327V** A328V A330Y **S332A** L353V I366V C400S I401L T436L E442K ΔFAD*
L6	N70E A74G V78L A82L **F87P** M118S P142S F162L T175I M177L A184V S226R H236Q E252G I263Y **A264S** H266V T268G A290V **T327V** A328V A330Y **S332A** L353V I366V C400S I401L T436L E442K ΔFAD*
L7	N70E A74G V78L A82L **F87P** M118S P142S F162L T175I M177L A184V S226R H236Q E252G I263Y **A264S** H266V T268G A290V **T327P** A328V A330Y **S332A** L353V I366V C400S I401L T436L E442K ΔFAD*
L5_FL	N70E A74G V78L A82L **F87P** M118S P142S F162L T175I M177L A184V S226R H236Q E252G I263Y H266V T268G A290V **T327V** A328V A330Y **S332A** L353V I366V C400S I401L T436L E442K
L6_FL	N70E A74G V78L A82L **F87P** M118S P142S F162L T175I M177L A184V S226R H236Q E252G I263Y **A264S** H266V T268G A290V **T327V** A328V A330Y **S332A** L353V I366V C400S I401L T436L
L7_FL	N70E A74G V78L A82L **F87P** M118S P142S F162L T175I M177L A184V S226R H236Q E252G I263Y **A264S** H266V T268G A290V **T327P** A328V A330Y **S332A** L353V I366V C400S I401L T436L

*ΔFAD: FAD domain truncation.

Nucleotide and amino acid sequences of P411-C10 (L1):

ATGACAATTAAAGAAATGCCTCAGCCAAAAACGTTTGGAGAGCTTAAAAATTTACCGTTATTAAACACAG
ATAAACCGGTTCAAGCTTTGATGAAAATTGCGGATGAATTAGGAGAAATCTTTAAATTCGAGGCGCCTGG
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Nucleotide and amino acid sequences of P411-L2:

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Nucleotide and amino acid sequences of P411-L3:

ATGACAATTAAAGAAATGCCTCAGCCAAAAACGTTTGGAGAGCTTAAAAATTTACCGTTATTAAACACAG
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Nucleotide and amino acid sequences of P411-L4:

ATGACAATTAAAGAAATGCCTCAGCCAAAAACGTTTGGAGAGCTTAAAAATTTACCGTTATTAAACACAG
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Nucleotide and amino acid sequences of P411-L5:

ATGACAATTAAAGAAATGCCTCAGCCAAAAACGTTTGGAGAGCTTAAAAATTTACCGTTATTAAACACAG
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MTIKEMPQPKTFGELKNLPLLNTDKPVQALMKIADELGEIFKFEAPGRVTRYLSSQRLIKEACDESRFDK
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HFDFEDHTNYELDIKEL**L**TLKPKGFVVKAKSKKIPLGGIPSPSTEQSAKKVRKKAENAHNTPLLVLYGSN
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KGVRYSVFGCGDKNWATTYQKVPAFIDETLAAKGAENIADRGEADASDDFEGTYEEWREHMWSDVAAYFN
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Nucleotide and amino acid sequences of P411-L6:

ATGACAATTAAAGAAATGCCTCAGCCAAAAACGTTTGGAGAGCTTAAAAATTTACCGTTATTAAACACAG
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GAGTTAAGTCAAGGTCTGAAATTTCTGCGTGATTTTCTTGGAGACGGGTTA**CCG**ACAAGCTGGACGCATG
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MTIKEMPQPKTFGELKNLPLLNTDKPVQALMKIADELGEIFKFEAPGRVTRYLSSQRLIKEACDESRFDK
ELSQGLKFLRDFLGDGL**P**TSWTHEKNWKKAHNILLPSFSQQAMKGYHASMVDIAVQLVQKWERLNADEHI
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GDEVMVLIPQLHRDKTVWGDDVEEFRPERFENPSAIPQHAFKPFGNGQRASLGQQFALHEATLVLGMMLK
HFDFEDHTNYELDIKEL**L**TLKPKGFVVKAKSKKIPLGGIPSPSTEQSAKKVRKKAENAHNTPLLVLYGSN
MGTAEGTARDLADIAMSKGFAPQVATLDSHAGNLPREGAVLIVTASYNGHPPDNAKQFVDWLDQASADEV
KGVRYSVFGCGDKNWATTYQKVPAFIDETLAAKGAENIADRGEADASDDFEGTYEEWREHMWSDVAAYFN
LDIENSEDNKSTLSLQFVDSAADMPLAKMHGAFSTLEHHHHHH

Nucleotide and amino acid sequences of P411-L7:

ATGACAATTAAAGAAATGCCTCAGCCAAAAACGTTTGGAGAGCTTAAAAATTTACCGTTATTAAACACAG
ATAAACCGGTTCAAGCTTTGATGAAAATTGCGGATGAATTAGGAGAAATCTTTAAATTCGAGGCGCCTGG
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GAGTTAAGTCAAGGTCTGAAATTTCTGCGTGATTTTCTTGGAGACGGGTTA**CCG**ACAAGCTGGACGCATG
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ELSQGLKFLRDFLGDGL**P**TSWTHEKNWKKAHNILLPSFSQQAMKGYHASMVDIAVQLVQKWERLNADEHI
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LVKNPHVLQKVAEEAARVLVDPVPSYKQVKQLKYVGMVLNEALRLWP**P**VPYF**A**LYAKEDTVLGGEYPLEK
GDEVMVLIPQLHRDKTVWGDDVEEFRPERFENPSAIPQHAFKPFGNGQRASLGQQFALHEATLVLGMMLK
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Nucleotide and amino acid sequences of P411-L5_FL:

ATGACAATTAAAGAAATGCCTCAGCCAAAAACGTTTGGAGAGCTTAAAAATTTACCGTTATTAAACACAG
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MGTAEGTARDLADIAMSKGFAPQVATLDSHAGNLPREGAVLIVTASYNGHPPDNAKQFVDWLDQASADEV
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KQASITVSVVSGEAWSGYGEYKGIASNYLAELQEGDTITCFISTPQSEFTLPKDPETPLIMVGPGTGVAP
FRGFVQARKQLKEQGQSLGEAHLYFGCRSPHEDYLYQEELENAQSEGIITLHTAFSRMPNQPKTYVQHVM
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Nucleotide and amino acid sequences of P411-L6_FL:

ATGACAATTAAAGAAATGCCTCAGCCAAAAACGTTTGGAGAGCTTAAAAATTTACCGTTATTAAACACAG
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MTIKEMPQPKTFGELKNLPLLNTDKPVQALMKIADELGEIFKFEAPGRVTRYLSSQRLIKEACDESRFDK
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EHHHHHH

Nucleotide and amino acid sequences of P411-L7_FL:

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EHHHHHH

X. Computational Modelling

Computational Methods

Molecular dynamics (MD) simulations

Molecular Dynamics simulations were performed using the GPU code (*pmemd*)[7] of the AMBER 18 package.[8] Parameters for the lactone carbene covalently bound to Fe-haem Ser ligated cofactor, ylides and amine substrates, and Fe-haem Ser-ligated cofactor were generated within the *antechamber* and MCPB.py[9] modules in AMBER18 package using the general AMBER force field (*gaff*),[10] with partial charges set to fit the electrostatic potential generated at the B3LYP/6-31G(d) level by the RESP model.[11] The charges were calculated according to the Merz-Singh-Kollman scheme[12,13] using the Gaussian 09 package.[14]
Protonation states of protein residues were predicted using H++ server. Each protein was immersed in a pre-equilibrated truncated cuboid box with a 10 Å buffer of TIP3P[15] water molecules using the *leap* module, resulting in the addition of around 15,300 solvent molecules. The systems were neutralized by addition of explicit counter ions (Na^+ and Cl^-). All subsequent calculations were done using the widely tested Stony Brook modification of the Amber14 force field (*ff14sb*).[16] A two-stage geometry optimization approach was performed. The first stage minimizes the positions of solvent molecules and ions imposing positional restraints on the solute by a harmonic potential with a force constant of 500 $kcal \cdot mol^{-1} \cdot Å^{-2}$ and the second stage minimizes all the atoms in the simulation cell except those involved in the harmonic distance restraint. The systems were gently heated using six 50 ps steps, incrementing the temperature by 50 K for each step (0–300 K) under constant-volume and periodic-boundary conditions. Water molecules were treated with the SHAKE algorithm such that the angle between the hydrogen atoms was kept fixed. Long-range electrostatic effects were modelled using the particle-mesh-Ewald method.[17] An 8 Å cutoff was applied to Lennard–Jones and electrostatic interactions. Harmonic restraints of 30 $kcal \cdot mol^{-1}$ were applied to the solute and the Andersen equilibration scheme was used to control and equalize the temperature. The time step was kept at 2 fs during the heating stages, allowing potential inhomogeneities to self-adjust. Each system was then equilibrated for 2 ns with a 2-fs time step at a constant pressure of 1 atm. Finally, conventional MD trajectories at constant volume and temperature (300 K) were propagated.
Constrained-MD simulations included a restrained distance between the substrate amine N atom and the lactone carbene central C atom (up to 3.1–3.6 Å) or between the ylide lactone central C atom and Fe (up to 3.7–4.2 Å), that was defined by adding a harmonic potential with k = 50 and 200 $mol^{-1} \cdot Å^{-2}$ to the respective coordinate during the respective equilibrations and production runs. Trajectories were processed and analyzed using the cpptraj[18] module from AmberTools utilities.
The total simulation time accumulated for each system is detailed below:
- P411-**L1** variant in the apo state: 5 replicas of 1000 ns each (5,000 ns in total).
- P411 variants (**L5**, **L6**, and **L7**) in the apo state: 3 independent replicas of 500 ns each (1,500 ns in total).
- Lactone carbene bound into P411 studied variants (**L5**, **L6**, and **L7**): 5 independent replicas of 500 ns each (2500 ns in total).

- Amine substrate bound in a near attack conformation respect to the lactone carbene bound into P411 studied variants (**L5**, **L6**, and **L7**), through constrained-MD simulations: 2 sets of 3 independent replicas of 250 ns each (2 × 750 = 1,500 ns in total, for each system).
- Ylide bound into P411 studied variants (**L5**, **L6**, and **L7**) in a "just dissociated" conformation, through constrained-MD simulations: 3 independent replicas of 100 ns each (300 ns in total, for each system).

Quantum Mechanics Density Functional Theory (DFT) calculations

Density Functional Theory (DFT) calculations were carried out using Gaussian09.[14] A truncated computational model containing the porphyrin pyrrole core, Fe center and a methoxy group to mimic serine as Fe-axial ligand was used. Geometry optimizations and frequency calculations were performed using (U)B3LYP[19–21] functional with the SDD basis set for iron and 6-31G(d) on all other atoms. Transition states had one negative force constant corresponding to the desired reaction coordinate. All stationary points were verified as minima or first-order saddle points by a vibrational frequency analysis. Intrinsic reaction coordinate (IRC) calculations were performed to ensure that the optimized transition states connect the corresponding desired reactants and products. Enthalpies and entropies were calculated at 1 atm and 298.15 K. Single point (SP) energy calculations were performed using the dispersion-corrected functional (U)B3LYP-D3(BJ)[22,23] with the Def2TZVP basis set on all atoms. The CPCM polarizable conductor model (diethyl ether, $\varepsilon = 4$)[24,25] to have an estimation of the dielectric permittivity in the enzyme active site was included during the optimizations and SP calculations. The use of a dielectric constant $\varepsilon = 4$ has been proved to be a good and general model to account for electronic polarization and small backbone fluctuations in enzyme active sites.[26,27]
The methodology employed in this study, based on the use of (U)B3LYP density functional, is very similar to the previously used by us and other groups for the study of haem-iron carbene transfer reaction mechanisms.[3,28–32] Independent benchmark studies by Prof. Shaik[28] and Prof. Liu[31] groups demonstrated that this method performs very well in the computational modelling of these carbene transfer reactions.

The modeling of the open-shell electronic state was done by using a Gaussian09 "stable = opt" calculation[33–35] to generate a singlet open-shell orbital guess from the triplet optimized geometry, followed by a full optimization of the system starting from this guess. Using this approach, we could successfully determine the open-shell singlet pathway for the studied nucleophilic attack of the amine to the lactone carbene.
Optimized DFT structures are illustrated with CYLView.[36]

Computational protocol

1. Starting from the available crystal structure of P411-**E10** variant (PDB: 5UCW.pdb),[37] the P411-**C10** variant (P411-**L1**) was prepared using RosettaDesign.[38] P411-**L1** contains 13 mutations with respect to P411-**E10** (N70E, A74G, V78L, M118S, F162L, M177L, L263Y, H266V, A330Y, I401L, T436L, L437Q, S438T).

The P411-**L1** structure obtained from Rosetta was used as starting point for MD simulations. A total of 5 independent replicas of 1,000 ns each were carried out, accumulating a total of 5,000 ns (5 µs). The conformations visited by the enzyme along all this simulation time were clustered based on protein backbone RMSD, and the most populated cluster was selected as a representative structure of P411-**L1** apo state.

The representative structure obtained for P411-**L1** was used to prepare P411 variants **L5**, **L6** and **L7** using the mutagenesis tool from Pymol.[39] Variant **L5** includes 4 additional mutations with respect to **L1** (T327V, Q437L, S332A, A87P), **L6** has 1 additional mutation respect **L5** (A264S), and **L7** has 1 mutation respect to **L6** (V327P).

These structures generated for **L5**, **L6**, and **L7** were then used as starting points for MD simulations. A total of 3 independent replicas of 500 ns each were propagated, accumulating a total of 1,500 ns (1.5 µs) for each of these variants. These were clustered considering protein backbone RMSD, and the most populated cluster was selected as representative structure of P411-**L5**, **L6** and **L7** variants in the apo state, respectively.

2. The lactone carbene covalently bound to the iron was manually docked in the representative structures for P411 variants **L5**, **L6** and **L7** characterized previously in their apo state. For each system, 5 independent replicas of 500 ns each and starting from different orientations of the lactone carbene were carried out, accumulating a total of 2,500 ns (2.5 μs). The conformations explored by the lactone carbene and the interactions that it established with active site residues were analyzed. The most representative conformations visited by the enzyme along the accumulated simulation time were clustered based on protein backbone RMSD.

3. The amine substrate was docked in the lactone carbene-bound P411-**L5**, **L6**, and **L7** variants. Two different representative structures (the two most populated clusters) previously characterized for each system (in step 2) were used. Docking calculations were carried out using Autodock Vina.[40,41] Docking predictions were refined by performing constrained-MD simulations, where the distance between the amine and the carbene central C atom was kept restrained up to 3.6 Å. For each system 2 different structures were considered as starting points, and 3 independent replicas of 250 ns each were carried out, accumulating a total of 2 × 750 ns = 1,500 ns of sampling. The most representative conformations visited along the trajectories were characterized by clustering, considering the protein backbone RMSD. These simulations provided good descriptions of catalytically relevant binding poses explored by the amine substrate, in which it is in a near attack conformation to perform the nucleophilic attack to the carbene.

4. Next, the ylide-bound complex was prepared. The ylide was manually docked in P411 **L5**, **L6**, and **L7** variants, starting from the most populated clusters obtained from the amine and lactone carbene bound simulations (in step 3). The characterized amine substrate binding pose was used as a template, and the ylide was placed by superimposing it with the amine and the lactone carbene. Starting from these ylide bound structures constrained-MD simulations were performed, in which the distance between the ylide central C atom and the Fe was kept restrained up to 4.1 Å. With this geometric constraint it was aimed to characterize the dissociated ylide complex in the enzyme active site, mimicking the ylide complex characterized from model DFT calculations (see **Figure 14**). For each system, total of three replicas of 100 ns each were carried out, accumulating a total of 300 ns of simulation time.

5. Finally, visual inspections of the constrained-MD simulations of P411 **L6** and **L7** variants with ylide intermediate bound (from step 4) were carried out. This led to prepare different truncated active site models that included the ylide intermediate, S264 residue, and key active site water molecules, that were used to explore the possible ylide proton transfer pathways by DFT calculations.

a) Lactone carbene conformations in P411 variants:
P411 - L6 variant
P411 – L7 variant
P411 – L5 variant
Y263
d4
T438
d3
S264
d2
O2
d1
C2
O1
C1
Fe
N
A264
∠ N – Fe – C1 – C2 ~ - 90°
∠ N – Fe – C1 – C2 ~ + 120°
b) ∠ N – Fe – C1 – C2 dihedral along MD trajectories
∠ N – Fe – C1 – C2 (°)
L6 variant
L7 variant
L5 variant
Simulation time MD (ns)
c) Interaction between A264/S264 and lactone (O1)
d1 (S264 – LAC (O1)) (Å)
d1 (A264 – LAC (O1)) (Å)
d) Interaction between A264/S264 and lactone (O2)
d2 (Ser264 – LAC (O2)) (Å)
d2 (Ala264 – LAC (O2)) (Å)

Figure 5. Conformational control of lactone carbene formed in P411 variants. a, Representative snapshot corresponding to the most populated cluster extracted from Molecular Dynamics (MD) simulations describing the preferred orientation of the lactone carbene when formed in P411-**L6** (gray), P411-**L7** (cyan) and P411-**L5** (purple) variants. **b,** The ∠(N – Fe – C1 – C2) dihedral angle measured along independent MD trajectories (5 replicas, 500 ns each) describes the relative orientation explored by the carbene. In P411-**L6** and P411-**L7**, simulations show that the lactone preferentially explores a single conformation (dihedral angle ca. –90º), which is stabilized by H-bond interactions established between the carbene ester group and S264 and Y263 (see below). In P411-**L5**, simulations show that the lactone explores multiple orientations without a clear preference. **c,** Distance vs. time plot describing the H-bond interaction between the S264 hydroxyl group and the O1-oxygen of the lactone in P411-**L6** and P411-**L7**, and the A264 C_β and the O1-oxygen of the lactone in P411-**L5** (*d1*, as shown in **Figure 5a**). **d,** Distance vs. time plot describing the H-bond interaction between the S264 hydroxyl group and the O2-oxygen of the lactone in P411-**L6** and P411-**L7**, and the A264 C_β and the O2-oxygen of the lactone in P411-**L5** (*d2*, as shown in **Figure 5a**). **e,** Distance vs. time plot describing the H-bond interaction between the Y263 hydroxyl group and the O2-oxygen of the lactone in P411-**L6**, P411-**L7** and P411-**L5** (*d3*, as shown in **Figure 5a**). **f,** Distance vs. time plot describing the interaction between the Y263 hydroxyl group and the T438 hydroxyl group in P411-**L6**, P411-**L7** and P411-**L5** (*d4*, as shown in **Figure 5a**).

Figure 6. Binding of substrate 2a in a near attack conformation for N-nucleophilic attack. Representative snapshot corresponding to the most populated cluster extracted from constrained-MD simulations describing the binding of **2a** in a near attack conformation for the N-nucleophilic attack to the lactone carbene bound in variants P411-**L6** (gray), P411-**L7** (cyan) and P411-**L5** (purple). Substrate **2a** is shown in slate purple. The residues that are directly establishing hydrophobic interactions with the substrate are displayed as spheres. In P411-**L6** and P411-**L7**, hydrophobic interactions occurring between the aromatic ring of the aniline derivative and active site residues (L75, V328, L437, Y330, P329) stabilize this binding mode, while H-bond interactions between the carbene ester group and S264 are maintained (see **Figure 7**). On the other hand, in P411-**L5** variant the substrate is bound in a slightly different position in the active site, and interacts with residues P87, L75, V328, L437 and P329.

a) *Enantiospecific N-nucleophilic attack (**2a**):*

b) *Dihedral ∠ N – Fe – C1 – C2*

c) *Interaction between A264/S264 and lactone (O1)*

d) *Interaction between A264/S264 and lactone (O2)*

Figure 7. Analysis of substrate 2a binding in a near attack conformation for N-nucleophilic attack. a, Representative snapshot corresponding to the most populated cluster extracted from constrained-MD simulations describing the near attack conformations for the N-nucleophilic attack of **2a** to the lactone carbene in variants P411-**L6** (gray), P411-**L7** (cyan) and P411-**L5** (purple). **b,** The ∠(N – Fe – C1 – C2) dihedral angle measured along independent MD trajectories (2 different starting poses, 3 replicas of 250 ns for each) describes the relative orientation explored by the carbene in the presence of substrate **2a** in the active site. Lactone carbene does not reorient when the amine substrate is bound, and its initial conformation determines which face of the carbene will be exposed for the N-nucleophilic attack. **c,** Distance vs. time plot describing the H-bond interaction between the S264 hydroxyl group and the O1-oxygen of the lactone in P411-**L6** and P411-**L7**, and the A264 C_β and the O1-oxygen of the lactone in P411-**L5** (*d1*, as shown in **Figure 7a**). **d,** Distance vs. time plot describing the H-bond interaction between the S264 hydroxyl group and the O2-oxygen of the lactone in P411-**L6** and P411-**L7**, and the A264 C_β and the O2-oxygen of the lactone in P411-**L5** (*d2*, as shown in **Figure 7a**). **e,** Distance vs. time plot describing the H-bond interaction between the Y263 hydroxyl group and the O2-oxygen of the lactone in P411-**L6**, P411-**L7** and P411-**L5** (*d3*, as shown in **Figure 7a**). In P411-**L5**, the distance between Y263 and the lactone is significantly longer than in P411-**L6** and P411-**L7**. This affects to the positioning of specific water molecules in the active site (see also **Figure 8**) **f,** Distance vs. time plot describing the interaction between the Y263 hydroxyl group and the T438 hydroxyl group in P411-**L6**, P411-**L7** and P411-**L5** (*d4*, as shown in **Figure 7a**).

Figure 8. Precise positioning of waters in the active site upon 3a-ylide formation. a, Overlay of 3 representative snapshots from constrained-MD simulations exploring the active site arrangement in P411 variants when **3a**-ylide is formed. In P411-**L6** and P411-**L7**, water molecules are precisely positioned on the top-face of the lactone ring through *water channel 1* driven by Y263 and T438, and nearby the protonated ylide amine group through *water channel 2*. These water molecules are able to stereoselectively protonate the ylide intermediate from the pro-*S* face (see DFT model calculations in **Figure 18**). In P411-**L5** variant, water molecules cannot effectively access the top-face of lactone ring. Displayed water molecules are drawn from 25 random structures across the 100 ns MD trajectory. **b,** Representation of the normalized kernel density plot of the number of water molecules in the active site of P411 variants nearby the **3a**-ylide, considering its first solvation shell (using a distance cut-off of 3.4 Å). The average number

of water molecules in the active site is 1.8 ± 1.2 (P411-**L6**), 2.3 ± 1.0 (P411-**L7**) and 1.6 ± 0.7 (P411-**L5**), respectively. The presence of water molecules is monitored through visual inspection of MD trajectories and using the *watershell* function of cpptraj.[12]

Figure 9. Analysis of active site arrangement when 3a-ylide is formed. a, Representative snapshot corresponding to the most populated cluster extracted from constrained-MD simulations describing the active site arrangement when **3a**-ylide is formed (right after dissociation from Fe) in variants P411-**L6** (gray), P411-**L7** (cyan) and P411-**L5** (purple). **b,** Distance vs. time plot describing the H-bond interaction between the S264 hydroxyl group and the O1-oxygen of the lactone in P411-**L6** and P411-**L7**, and the A264 C_β and the O1-oxygen of the lactone in P411-**L5** (*d1*, as shown in **Figure 9a**). **c,** Distance vs. time plot describing the H-bond interaction between the S264 hydroxyl group and the O2-oxygen of the lactone in P411-**L6** and P411-**L7**, and the A264 C_β and the O2-oxygen of the lactone in P411-**L5** (*d2*, as shown in **Figure 9a**). **d,** Distance vs. time plot describing the H-bond interaction between the hydrogen of the Y263 hydroxyl group and the O2-oxygen of the lactone in P411-**L6**, P411-**L7** and P411-**L5** (*d3*, as shown in **Figure 9a**). In P411-**L5**, the distance between Y263 and the lactone is significantly longer than in P411-**L6** and P411-**L7**. This prevents the precise positioning of water molecules in the active site. **e,** Distance vs. time plot describing the interaction between the oxygen of the Y263 hydroxyl group and the T438 hydroxyl group in P411-**L6**, P411-**L7** and P411-**L5** (*d4*, as shown in **Figure 9a**).

Figure 10. Binding of substrate 2l in a near attack conformation for N-nucleophilic attack. Representative snapshot corresponding to the most populated cluster extracted from constrained-MD simulations describing the binding of **2l** in a near attack conformation for the N-nucleophilic attack to the lactone carbene bound in variants P411-**L6** (gray), P411-**L7** (cyan) and P411-**L5** (purple). Substrate **2l** is colored in light orange. The residues that are directly establishing hydrophobic interactions with the substrate are displayed as spheres. In P411-**L6** and P411-**L7**, hydrophobic interactions occurring between the aromatic ring of the aniline derivative and active site residues (L75, V328, L437, Y330, P329) stabilize this binding mode, while H-bond interactions between the carbene ester group and S264 are maintained (see **Figure 11**). On the other hand, in P411-**L5** the substrate is bound in a slightly different position in the active site, and interacts with residues P87, L75, V328, L437 and P329.

a) *Substrate **2l** binding in a catalytically competent pose:*

b) *∠ N – Fe – C1 – C2 dihedral along MD trajectories*

c) *Interaction between A264/S264 and lactone (O1)*

d) *Interaction between A264/S264 and lactone (O2)*

Figure 11. Analysis of substrate 2l binding in a near attack conformation for N-nucleophilic attack. a, Representative snapshot corresponding to the most populated cluster extracted from constrained-MD simulations describing the near attack conformations for the N-nucleophilic attack of **2l** to the lactone carbene in variants P411-**L6** (gray), P411-**L7** (cyan) and P411-**L5** (purple). **b,** The ∠(N – Fe – C1 – C2) dihedral angle measured along independent MD trajectories (2 different starting poses, 3 replicas of 250 ns for each) describes the relative orientation explored by the carbene in the presence of substrate **2l** in the active site. Lactone carbene does not reorient when the amine substrate is bound, and its initial conformation determines which face of the carbene will be exposed for the N-nucleophilic attack. **c,** Distance vs. time plot describing the H-bond interaction between the S264 hydroxyl group and the O1-oxygen of the lactone in P411-**L6** and P411-**L7**, and the A264 C_β and the O1-oxygen of the lactone in P411-**L5** (*d1*, as shown in **Figure 11a**). **d,** Distance vs. time plot describing the H-bond interaction between the S264 hydroxyl group and the O2-oxygen of the lactone in P411-**L6** and P411-**L7**, and the A264 C_β and the O2-oxygen of the lactone in P411-**L5** (*d2*, as shown in **Figure 11a**). **e,** Distance vs. time plot describing the H-bond interaction between the Y263 hydroxyl group and the O2-oxygen of the lactone in P411-**L6**, P411-**L7** and P411-**L5** (*d3*, as shown in **Figure 11a**). In P411-**L5**, the distance between Y263 and the lactone is significantly longer than in P411-**L6** and P411-**L7**. This affects to the positioning of specific water molecules in the active site (see also **Figure 12**) **f,** Distance vs. time plot describing the interaction between the Y263 hydroxyl group and the T438 hydroxyl group in P411-**L6**, P411-**L7** and P411-**L5** (*d4*, as shown in **Figure 11a**).
These observations for substrate **2l** are equivalent to those reported for substrate **2a** (**Figure 7**).

Figure 12. Precise positioning of waters in the active site upon 3l-ylide formation. a, Overlay of 3 representative snapshots from constrained-MD simulations exploring the active site arrangement in P411 variants when **3l**-ylide is formed. In P411-**L6** and P411-**L7**, water molecules are precisely positioned on the top-face of the lactone ring through *water channel 1* driven by Y263 and T438, and nearby the protonated ylide amine group through *water channel 2*. These water molecules are able to stereoselectively protonate the ylide intermediate from the pro-*S* face (see DFT model calculations in **Figure 19**). In P411-**L5** variant, water molecules cannot effectively access the top-face of lactone ring. Displayed water molecules are drawn from 25 random structures across the 100 ns MD trajectory. **b,** Representation of the normalized kernel density plot of the number of water molecules in the active site of P411 variants nearby the **3l**-ylide, considering its first solvation shell (using a distance cut-off of 3.4 Å). The average number of water molecules in the active site is 1.6 ± 1.1 (P411-**L6**), 0.8 ± 0.5 (P411-**L7**) and 1.3 ± 0.6

(P411-**L5**), respectively. The presence of water molecules is monitored through visual inspection of MD trajectories and using the *watershell* function of cpptraj.[12]
The results obtained for **3l**-ylide are very similar to those observed for **3a**-ylide (**Figure 8**).

Figure 13. Analysis of active site arrangement when 3l-ylide is formed. a, Representative snapshot corresponding to the most populated cluster extracted from constrained-MD simulations describing the active site arrangement when **3l**-ylide is formed (right after dissociation from Fe) in variants P411-**L6** (gray), P411-**L7** (cyan) and P411-**L5** (purple). **b,** Distance vs. time plot describing the H-bond interaction between the S264 hydroxyl group and the O1-oxygen of the lactone in P411-**L6** and P411-**L7**, and the A264 C_β and the O1-oxygen of the lactone in P411-**L5** (*d1*, as shown in **Figure 13a**). **c,** Distance vs. time plot describing the H-bond interaction between the S264 hydroxyl group and the O2-oxygen of the lactone in P411-**L6** and P411-**L7**, and the A264 C_β and the O2-oxygen of the lactone in P411-**L5** (*d2*, as shown in **Figure 13a**). **d,** Distance vs. time plot describing the H-bond interaction between the Y263 hydroxyl group and the O2-oxygen of the lactone in P411-**L6**, P411-**L7** and P411-**L5** (*d3*, as shown in **Figure 13a**). In P411-**L5**, the distance between Y263 and the lactone is significantly longer than in P411-**L6** and P411-**L7**. This prevents the precise positioning of water molecules in this region of the active site. **e,** Distance vs. time plot describing the interaction between the Y263 hydroxyl group and the T438 hydroxyl group in P411-**L6**, P411-**L7** and P411-**L5** (*d4*, as shown in **Figure 13a**).
The conclusions obtained for **3l**-ylide are very similar to those for **3a**-ylide (**Figure 9**).

Figure 14. Energy profile for lactone carbene N–H insertion involving model substrate **2l**. A truncated model that includes a methanol molecule to mimic P411-**L6** active site S264 has been used. Results obtained for different spin states are reported and the lowest in energy optimized geometries for each stationary point are shown. **3l**-ylide dissociation from **5l** – MeOH is found to be barrierless (see **Figure 16**). Proton transfer steps to yield the final product **3l** are studied in **Figure 17** and **18**. Electronic and Gibbs free energies are obtained at B3LYP-D3BJ/def2-TZVP// B3LYP/6-31G(d)-SDD. Energy values are given in kcal·mol^{-1}. Key distances and angles are given in Å and deg., respectively.

Figure 15. N-nucleophilic attack step for carbene N–H insertion reaction involving substrate **2l** in the absence of H-bond interaction with methanol molecule mimicking P411-**L6** active site S264. Results obtained for different spin states are reported. The lowest in energy optimized geometries for each stationary point are shown. Electronic and Gibbs free energies are obtained at B3LYP-D3BJ/def2-TZVP// B3LYP/6-31G(d)-SDD. Energy values are given in kcal·mol^{-1}. Key distances and angles are given in Å and deg., respectively.

The presence of MeOH (to mimic S264 H-bonding to the lactone ester group) decreases the N-nucleophilic attack barrier by ca. 1.5 kcal·mol^{-1} ($\Delta G^{\ddagger}_{(MeOH\text{-}model)}$ = 18.3 kcal·mol^{-1} from **Figure 14**, vs $\Delta G^{\ddagger}$ = 19.8 kcal·mol^{-1}). The presence of a H-bond interaction with the carbene ester group activating it is in line with observations from previous works.[32,42]

Figure 16. Potential energy scan (electronic energy) along Fe – C coordinate that describes **3l**-ylide dissociation, in the lowest energy closed-shell singlet electronic state, calculated at B3LYP/6-31G(d)-SDD level. The energies obtained at the lower computational level and do not include ZPE, Gibbs, or dispersion corrections. Relative energies are given in kcal·mol^{-1} and distances in Å.

The potential energy scan indicates a barrierless dissociation of the covalent **5l** intermediate to generate the ylide. All the attempts to optimize a dissociation transition state were unsuccessful. This is in line with previous work on a similar reaction.[28] No spontaneous proton transfer to form the enol is observed during dissociation (see also **Figure 20**).

a) 4 - MeOH
2.74
1.82
1.98
OSS
ΔΔG = 0.0
ΔΔE = 0.0
2.79
1.84
1.82
CSS
ΔΔG = 8.2
ΔΔE = 7.8
2.81
1.79
2.00
T
ΔΔG = 1.6
ΔΔE = 2.1
b) TS1-I - MeOH
1.84
2.79
2.04
109.3
2.01
OSS
ΔΔG = 0.0
ΔΔE = 0.0
1.82
2.82
2.06
107.7
2.11
CSS
ΔΔG = 0.5
ΔΔE = 0.3
2.96
1.83
2.18
110.4
1.94
T
ΔΔG = 6.4
ΔΔE = 8.6
c) 5I - MeOH
1.82
2.89
1.51
99.5
2.44
OSS
ΔΔG = 1.2
ΔΔE = 1.6
1.80
2.80
1.50
96.6
2.56
CSS
ΔΔG = 0.9
ΔΔE = 0.0
2.87
1.84
1.51
99.8
2.37
T
ΔΔG = 0.0
ΔΔE = 4.6

Figure 17. Optimized geometries for the different species reported in **Figure 14** and **15** in their different electronic states. Relative electronic and Gibbs free energies are obtained at B3LYP-D3BJ/def2-TZVP// B3LYP/6-31G(d)-SDD. Energy values are given in kcal·mol^{-1}. Key distances and angles are given in Å and deg., respectively.

Figure 18. Optimized model transition states (TSs) for stereoselective **3a** formation from **3a**-ylide. Computational models are built based on the conformations explored by the **3a**-ylide when formed in P411-**L6** active site and the arrangement of water molecules around the ylide as observed from MD simulations (**Figure 8**). Electronic and Gibbs free energies are obtained at B3LYP-D3BJ/def2-TZVP// B3LYP/6-31G(d)-SDD. Energy values are given in kcal·mol^{-1}. Key distances and angles are given in Å and deg., respectively. Optimizations are carried out in the absence of any geometrical constraint.

Model 1 includes a methanol molecule (model for active site S264 residue) and four water molecules: two on the top face (pro-*S* face) of the lactone, and two near the protonated amine.
Model 2 includes a methanol molecule (model for active site S264 residue) and two water molecules on the top face (pro-*S* face) of the lactone ring.
Model 3 includes a methanol molecule (model for active site S264 residue) and two water molecules: one on the top face (pro-*S* face) of the lactone, and another one near the protonated amine. Although the two water molecules are not directly interacting in the initial structure, they establish a new H-bond interaction upon geometry optimization. Additionally, the N–C(lactone) bond rotates during optimization to establish a new H-bond network between these two waters and the amine. All these interactions could probably not occur in the enzyme active site due to geometric restraints imposed to the ylide.

The low activation barriers calculated specially for Model 1 and Model 2 are indicating that this proton transfer step can rapidly take place in the active site once the ylide dissociates from the iron.

Figure 19. Optimized model transition states (TSs) for stereoselective **3l** formation from **3l**-ylide. Computational models are built based on the conformations explored by the **3l**-ylide when formed in P411-**L6** active site and the arrangement of water molecules around the ylide as observed from MD simulations (**Figure 12**). Electronic and Gibbs free energies are obtained at B3LYP-D3BJ/def2-TZVP// B3LYP/6-31G(d)-SDD. Energy values are given in kcal·mol^{-1}. Key distances and angles are given in Å and deg., respectively. Optimizations are carried out in the absence of any geometrical constraint. Models were constructed as described in **Figure 18**.

As found for *N*-methylated **3a**-ylide, model calculations for the enantioselective proton transfer involving **3l**-ylide describe low activation barriers calculated, indicating that this proton transfer step can rapidly take place in the active site once the ylide dissociates from the iron.

Figure 20. Computational explorations of enol formation from ylide considering **3l**-ylide as model substrate. **a)** Intramolecular **3l**-enol formation from **3l**-ylide. **b)** Equivalent enol formation from **3l**-ylide but considering the H-bond interactions that the lactone carbonyl is establishing with a molecule of methanol that mimics the side chain of active site S264 residue in P411-**L6**. **c)** Intramolecular enol formation from a model aliphatic-**3l**-ylide. Electronic and Gibbs free energies are obtained at B3LYP-D3BJ/def2-TZVP// B3LYP/6-31G(d)-SDD. Energy values are given in kcal·mol^{-1}. Optimizations are carried out in the absence of any geometrical constraint. Key distances and angles are given in Å and deg., respectively.

In a previous computational study on similar N–H carbene insertion reactions catalyzed by Fe-porphyrin,[28] it was described that dissociation of the ylide form the Fe center could involve a spontaneous proton transfer to form the corresponding enol. This proton transfer could occur during the dissociation, or through a very low in energy H-transfer step. In that case, the studied carbene includes an aliphatic ester, which is more flexible than the current lactone used in this study.

In our current case, no spontaneous enol formation is observed upon ylide dissociation from Fe (**Figure 16**). To rationalize these differences, we studied the intramolecular ylide-enol rearrangement using the models described in **Figure 20a-c**.

Enol formation from **3l**-ylide (**20a**) has a much higher barrier than enol formation when an aliphatic ester is present (**20c**). This is due to the higher strain on the 5-membered ring formed during the H-transfer transition state in the lactone system, than in the much more flexible aliphatic ester system. In addition, the presence of an additional H-bond interaction involving the carbonyl group of the lactone (**20b**), stabilizes the ylide form with respect to the enol and increases the intramolecular proton transfer barrier. Consequently, in this particular system the interaction established by the active site S264 side chain and the lactone disfavors even more the formation of the enol from the ylide when it is formed in the enzyme active site.

Figure 21. Alternative proton transfer rearrangements explored for model **3l**-ylide in the absence of geometrical restraints imposed by the enzyme active site (i.e. considering any possible geometry and water assistance) to stereoselectively yield **3l** product. **a**) Direct intramolecular proton transfer; **b**) and **c**) Proton transfer assisted by one or two water molecules, respectively; **d**) and **e**) first enol formation, followed by subsequent product formation assisted by one or two water molecules, respectively. Electronic and Gibbs free energies are obtained at B3LYP-D3BJ/def2-TZVP//

B3LYP/6-31G(d)-SDD. Energy values are given in kcal·mol^{-1}. Optimizations are carried out in the absence of any geometrical constraint. Key distances and angles are given in Å and deg., respectively.

- Direct intramolecular proton transfer to yield product **3l** has a very high barrier (**21a**).
- Intramolecular proton transfer assisted by one or two water molecules from the ylide to yield product **3l** would be possible (**21b-c**). However, the required conformations for the ylide and the specific positioning of the water molecules respect to the migrating proton from the amine and the lactone carbon are not possible in the enzyme active site (**Figure 12**).
- Although enol formation from **3l**-ylide via direct intramolecular proton transfer is very high in energy (**Figure 20**), this proton transfer assisted by a single water molecule would be feasible if the catalytic water molecule could interreact in a coplanar mode with a proton from the amine and the lactone carbonyl group (**21d**). However, geometrical restraints in enzyme active site prevent the ylide to explore those conformations.
- The direct formation of **3l** from **3l**-ylide is energetically more favorable (lower reaction barriers) than the pathway involving first the formation of the enol.

Table 17. Energies and thermochemistry parameters (at T=298.15K and P=1atm) of all DFT characterized stationary points: Electronic energies (E), electronic energies from high level single point calculations (E (SP)), Zero-point energy (ZPE), enthalpy (H), free energy (G(T)). All energies are given in a.u.

Structure	E	ZPE	H	G(T)	E (SP)
Model1-3a-ylide	-1053.583145	0.381333	-1053.174130	-1053.259323	-1054.175740
Model1-TS-3a-ylide	-1053.571696	0.376835	-1053.167740	-1053.252862	-1054.164323
Model2-3a-ylide	-900.705795	0.328634	-900.353540	-900.433153	-901.195271
Model2-TS-3a-ylide	-900.696962	0.325201	-900.349189	-900.425909	-901.185462
Model3-3a-ylide	-900.726606	0.330610	-900.374442	-900.448537	-901.213151
Model3-TS-3a-ylide	-900.711604	0.325688	-900.364425	-900.437173	-901.197301
Model1-3l-ylide	-1128.806672	0.386436	-1128.391826	-1128.478746	-1129.433305
Model1-TS-3l-ylide	-1128.78644528	0.381588	-1128.376580	-1128.464730	-1129.413659
Model2-3l-ylide	-975.906405	0.333299	-975.563260	-975.646178	-976.446330
Model2-TS-3l-ylide	-975.911388	0.329366	-975.557920	-975.639189	-976.434438
Model3-3l-ylide	-975.943508	0.335141	-975.584721	-975.663187	-976.464603
Model3-TS-3l-ylide	-975.931517	0.329844	-975.578764	-975.655803	-976.451885
2l	-402.116304	0.149497	-401.957196	-402.002284	-402.316508
4 OSS	-1532.812711	0.391585	-1532.393700	-1532.475392	-2673.347061
4 Triplet	-1532.808652	0.391568	-1532.389657	-1532.472143	-2673.343653
4 CSS	-1532.796511	0.546437	-1934.350026	-1532.458448	-2673.334674
TS1-2l OSS	-1934.911322	0.544686	-1934.330788	-1934.431251	-3075.660765
TS1-2l Triplet	-1934.898038	0.542646	-1934.319163	-1934.421510	-3075.646929
TS1-2l CSS	-1934.910289	0.544809	-1934.329639	-1934.429948	-3075.660239
5l OSS	-1934.932568	0.546437	-1934.350026	-1934.451233	-3075.683195
5l Triplet	-1934.927889	0.546411	-1934.345160	-1934.453294	-3075.678432
5l CSS	-1934.934316	0.547939	-1934.350428	-1934.450953	-3075.685750
3l	-707.400899	0.230147	-707.156437	-707.211976	-707.747667
Fe(II)-Porph Quintet	-1227.611354	0.312870	-1227.275946	-1227.348912	-2367.973500
Fe(II)-Porph Triplet	-1227.563719	0.313730	-1227.228052	-1227.298927	-2367.942248
Fe(II)-Porph CSS	-1227.574526	0.315417	-1227.237735	-1227.305947	-2367.950916
4-MeOH OSS	-1648.543127	0.444907	-1648.066975	-1648.158665	-2789.143348
4-MeOH Triplet	-1648.539427	0.445022	-1648.062299	-1648.157778	-2789.141130
4-MeOH CSS	-1648.525939	0.445555	-1648.048550	-1648.142251	-2789.130645
TS1-2l – MeOH OSS	-2050.640831	0.598022	-2050.002189	-2050.114960	-3191.458146
TS1-2l – MeOH Triplet	-2050.628093	0.596315	-2049.990991	-2050.104935	-3191.444845
TS1-2l – MeOH CSS	-2050.640644	0.598599	-2050.001557	-2050.113662	-3191.457259

5l – MeOH OSS	-2050.661374	0.600108	-2050.021335	-2050.131999	-3191.480819
5l – MeOH Triplet	-2.050.657518	0.600439	-2050.016395	-2050.129389	-3191.475924
5l – MeOH CSS	-2050.664888	0.601598	-2050.022706	-2050.134630	-3191.488622
Fe(II)-Porph + 3l-ylide-MeOH CSS	-2050.665072	0.601380	-2050.022790	-2050.136633	-3191.479127
3l-ylide	-707.344084	0.230950	-707.098887	-707.154237	-707.695908
TS-3l-enol	-707.330337	0.225995	-707.090436	-707.145314	-707.680946
3l-enol	-707.357771	0.228203	-707.114621	-707.171523	-707.708070
3l-ylide - MeOH	-823.074808	0.284174	-822.771582	-822.840709	-823.491907
TS-3l-enol - MeOH	-823.060072	0.279736	-822.761840	-822.828299	-823.475381
3l-enol - MeOH	-823.08431	0.281958	-822.782670	-822.853785	-823.500950
aliphatic-3l-ylide	-708.556210	0.249772	-708.289811	-708.351316	-708.909898
TS-aliphatic-3l-enol	-708.551015	0.245620	-708.289233	-708.349117	-708.904483
aliphatic-3l-enol	-708.570100	0.249102	-708.304409	-708.365350	-708.923480
TS-intra-3l	-707.291099	0.224394	-707.052240	-707.109041	-707.641571
3-ylide - H2O	-783.774581	0.255643	-783.501926	-783.563759	-784.179479
TS-3l - H2O	-783.761372	0.250873	-783.494364	-783.554598	-784.164749
3l - H2O	-783.826230	0.255523	-783.553672	-783.615289	-784.227975
3l-ylide 2 H2O	-860.214791	0.281697	-859.914264	-859.979329	-860.669958
TS-3l 2 H2O	-860.205153	0.276870	-859.910254	-859.973382	-860.659120
3l - 2 H2O	-860.259589	0.280533	-859.959181	-860.027278	-860.712251
3l-ylide - H2O (conf.2)	-783.782574	0.255261	-783.510627	-783.572191	-784.185376
TS1-3l-enol - H2O	-783.776660	0.248982	-783.511848	-783.571515	-784.180238
3l-enol - H2O	-783.794547	0.254621	-783.523062	-783.584661	-784.197045
TS2-3l-enol - H2O	-783.749858	0.248370	-783.485549	-783.544261	-784.152916
TS1-3l-enol - 2 H2O	-860.197513	0.272283	-859.907096	-859.972383	-860.654321
3l-enol - 2 H2O	-860.214790	0.278629	-859.916106	-859.984237	-860.672267
TS2-3l-enol - 2 H2O	-860.194119	0.272522	-859.903518	-859.967122	-860.650064

Cartesian coordinates of DFT optimized stationary points in xyz format (Å):

Model1-3a-ylide

C	3.078183	1.993114	-0.774670
H	4.156000	2.067914	-0.618573
H	2.756113	2.751387	-1.496597
C	1.621363	0.224165	-0.794778
O	1.220564	-0.903396	-1.143781
O	2.799606	0.687551	-1.335153
C	1.077831	1.196284	0.087811
N	0.173642	0.665502	1.163028
C	2.242690	2.076299	0.512542
H	1.987383	3.117413	0.738455
H	2.805985	1.671360	1.370773
C	-1.067302	0.011337	0.672688
C	-1.422788	-1.216582	1.227968
C	-1.887656	0.650844	-0.253861
C	-2.615056	-1.826370	0.831124
H	-0.771632	-1.699512	1.949035
C	-3.078928	0.034406	-0.638589
H	-1.602485	1.609360	-0.668594
C	-3.444475	-1.202850	-0.101909
H	-2.888400	-2.788879	1.252873
H	-3.722662	0.526507	-1.361659
H	0.713523	-0.065789	1.694364
H	0.311116	2.550922	-1.046025
O	-0.006210	3.388178	-1.501819
H	2.671385	-2.025459	-1.469098
O	3.291649	-2.765383	-1.269933
C	4.416495	-2.212924	-0.589736
H	5.116139	-3.031875	-0.400170
H	4.920550	-1.451502	-1.197947
H	4.134459	-1.762253	0.372552
O	1.828137	-1.259813	2.314626
H	1.682722	-1.592799	3.213953
H	1.694524	-2.049260	1.713064
O	1.242684	-3.170587	0.520384
H	0.790690	-2.495897	-0.026606
H	-1.113030	4.076260	-0.276504
O	-1.634432	4.340948	0.517672
H	-1.114190	5.061853	0.904482
H	2.057229	-3.314219	-0.019760
C	-0.188466	1.736250	2.160539
H	0.726850	2.082578	2.641564
H	-0.688517	2.560415	1.643744
H	-0.851079	1.291158	2.904160
H	-0.397045	3.087008	-2.337618
H	-4.371164	-1.677712	-0.410439

Model1-TS-3a-ylide

C	3.441770	0.951610	-0.754247
H	4.466300	0.629365	-0.564504
H	3.439764	1.760488	-1.491402
C	1.468630	-0.218238	-0.834931
O	0.717619	-1.141568	-1.134334
O	2.729148	-0.180479	-1.329441
C	1.239142	0.967527	0.018448
N	0.235786	0.718024	1.124649
C	2.648938	1.334100	0.499169
H	2.761954	2.400282	0.715471
H	2.971401	0.730014	1.357865
C	-1.141665	0.383685	0.667874
C	-1.779335	-0.700552	1.270427
C	-1.788004	1.189101	-0.267944
C	-3.091528	-1.006601	0.902867
H	-1.262012	-1.300303	2.012473
C	-3.100208	0.867707	-0.623769
H	-1.269459	2.049589	-0.693573
C	-3.751725	-0.225695	-0.047903
H	-3.591765	-1.853811	1.362390
H	-3.615577	1.482640	-1.356075
H	0.591142	-0.111307	1.666237
H	0.836487	2.002536	-0.608154
O	0.416763	3.262750	-0.950609
H	1.689879	-2.722356	-1.499163
O	2.016765	-3.620999	-1.272855
C	3.311768	-3.480007	-0.686024
H	3.675950	-4.486450	-0.464182
H	4.012079	-2.994461	-1.376389
H	3.276504	-2.902512	0.247937
O	1.381698	-1.572847	2.185287
H	1.329974	-1.818412	3.122202
H	0.965592	-2.332098	1.683561
O	0.126994	-3.438604	0.696069
H	-0.400397	-2.794461	0.192020
H	1.664065	4.181447	-0.365148
O	2.472369	4.641327	0.026286
H	3.110246	4.636481	-0.703309
H	0.806852	-3.715799	0.029721
C	0.184048	1.900875	2.059219
H	1.156006	2.014612	2.538945
H	-0.055307	2.786850	1.471128
H	-0.584679	1.707571	2.807688
H	0.451322	3.292084	-1.921684
H	-4.771584	-0.465465	-0.334472

Model2-3a-ylide

C	0.788029	-3.332385	0.048958
H	0.511105	-4.287093	0.500232
H	1.445447	-3.513554	-0.809906
C	-0.322670	-1.344648	-0.206269
O	-1.264653	-0.605248	-0.508480
O	-0.420672	-2.698219	-0.427854
C	0.961062	-1.048040	0.360949
N	1.003172	0.202784	1.193173
C	1.434357	-2.333224	1.022119
H	2.519666	-2.475686	1.045161
H	1.039137	-2.478986	2.044693
C	0.611535	1.455293	0.483477
C	-0.353711	2.264685	1.074552
C	1.262276	1.826657	-0.690330
C	-0.687893	3.477154	0.468718
H	-0.853883	1.954550	1.988631
C	0.919104	3.042530	-1.284183
H	2.010465	1.181828	-1.139027
C	-0.051461	3.867674	-0.710454
H	-1.446908	4.109094	0.919551
H	1.415085	3.342293	-2.202501
H	0.338838	0.114632	1.976386
H	2.287198	-0.940267	-0.963847

O	3.134572	-0.866691	-1.510571
H	-2.716842	-1.289218	-1.375266
O	-3.576138	-1.535443	-1.782512
C	-4.572616	-0.793928	-1.112540
H	-5.540821	-1.056043	-1.554205
H	-4.624262	-1.020717	-0.034104
H	-4.439836	0.295952	-1.217840
H	4.224845	-2.037148	-0.664219
O	4.702952	-2.691565	-0.103730
H	4.467692	-3.544874	-0.498253
C	2.361056	0.385083	1.827951
H	2.562317	-0.468205	2.474458
H	3.101825	0.434736	1.031030
H	2.348435	1.309257	2.406239
H	2.873005	-1.108490	-2.414074
H	-0.312497	4.810112	-1.182596

Model2-TS-3a-ylide

C	2.156706	2.187469	0.262085
H	2.999308	2.564703	0.842595
H	2.090779	2.729078	-0.686489
C	1.274790	0.076318	0.052254
O	1.266540	-1.135905	-0.096864
O	2.423873	0.788598	-0.035176
C	0.147699	1.007922	0.314486
N	-0.989007	0.372606	1.091967
C	0.814702	2.200842	1.003724
H	0.288690	3.144060	0.829338
H	0.968632	2.044705	2.082328
C	-1.599043	-0.832724	0.454630
C	-1.660396	-2.005069	1.201691
C	-2.141179	-0.735026	-0.824538
C	-2.279702	-3.125909	0.646572
H	-1.224894	-2.057244	2.196526
C	-2.754516	-1.867423	-1.364592
H	-2.070020	0.205391	-1.372300
C	-2.826303	-3.057725	-0.636413
H	-2.328199	-4.048199	1.217169
H	-3.179172	-1.814479	-2.362750
H	-0.624129	0.060207	1.999567
H	-0.405977	1.479651	-0.723328
O	-1.257177	2.159948	-1.575904
H	2.811900	-2.062778	-0.648072
O	3.634483	-2.535524	-0.885443
C	4.640022	-2.090930	0.003367
H	5.582379	-2.559983	-0.299562
H	4.777357	-0.998870	-0.024320
H	4.442944	-2.379482	1.049882
H	-0.956390	3.711769	-1.081005
O	-0.700064	4.605111	-0.688115
H	0.085536	4.858894	-1.195802
C	-2.061364	1.402290	1.387812
H	-1.633250	2.178090	2.021981
H	-2.381819	1.821825	0.434601
H	-2.878740	0.896079	1.900880
H	-0.894063	2.044879	-2.469961
H	-3.305996	-3.931242	-1.068048

Model3-3a-ylide

C	1.324588	-1.832682	1.781198
H	1.230098	-1.305658	2.738022
H	1.736635	-2.828420	1.954553
C	1.552488	-0.312020	0.088567
O	2.178726	0.447478	-0.689865
O	2.266518	-1.101143	0.958644
C	0.171104	-0.521651	0.270747
N	-0.724196	-0.123185	-0.853586
C	-0.011984	-1.821433	1.015835
H	-0.092224	-2.706109	0.360061
H	-0.859730	-1.849597	1.708462
C	-2.156149	-0.123540	-0.468688
C	-2.735383	1.080835	-0.069827
C	-2.899281	-1.303129	-0.499472
C	-4.081043	1.100994	0.300796
H	-2.146954	1.990960	-0.040941
C	-4.244729	-1.270986	-0.126353
H	-2.449343	-2.240214	-0.807765
C	-4.838034	-0.071901	0.272490
H	-4.534010	2.038377	0.608969
H	-4.825755	-2.187984	-0.150109
H	-0.464534	0.885544	-1.051839
H	0.029321	1.270938	1.429958
O	-0.029215	2.245529	1.599618
O	0.303078	2.416648	-1.139900
H	0.206755	2.629098	-0.179013
H	1.163657	1.936271	-1.159373
H	0.798186	2.461268	2.060119
C	-0.456314	-0.862460	-2.142415
H	-0.570445	-1.933900	-1.983161
H	-1.153459	-0.513975	-2.906556
H	0.570858	-0.635709	-2.427402
H	-5.885034	-0.051955	0.559922
H	3.937151	0.756396	-0.319196
O	4.893397	0.896823	-0.145712
C	5.534063	-0.343236	-0.363632
H	6.592283	-0.224786	-0.104519
H	5.118064	-1.149626	0.260253
H	5.482287	-0.672111	-1.415763

Model3-TS-3a-ylide

C	1.304712	-2.098309	1.416553
H	1.370109	-1.797684	2.466437
H	1.607161	-3.141237	1.316101
C	1.620528	-0.297140	0.026445
O	2.239414	0.533955	-0.635894
O	2.264110	-1.294777	0.670225
C	0.179973	-0.345224	0.344238
N	-0.709014	0.190264	-0.764713
C	-0.069806	-1.771665	0.812058
H	-0.301461	-2.458459	-0.013642
H	-0.865116	-1.857154	1.556747
C	-2.151553	0.031530	-0.430881
C	-2.671964	0.795765	0.617657
C	-2.961965	-0.850879	-1.145844
C	-4.024842	0.674005	0.937233
H	-2.022656	1.444085	1.199432
C	-4.314922	-0.961228	-0.812414
H	-2.569455	-1.450929	-1.957546
C	-4.850640	-0.198477	0.224542

H	-4.431055	1.268281	1.750462
H	-4.944279	-1.646871	-1.371863
H	-0.486215	1.248302	-0.758101
H	0.069016	0.585926	1.265138
O	-0.094468	1.756236	1.906286
O	0.172145	2.697752	-0.457404
H	0.115089	2.504815	0.559369
H	1.090720	2.455199	-0.676144
H	0.688986	1.875370	2.467771
C	-0.344014	-0.290248	-2.138263
H	-0.372530	-1.379476	-2.179336
H	-1.045502	0.134534	-2.856902
H	0.663365	0.062560	-2.349364
H	-5.903179	-0.285096	0.477938
H	4.078760	0.258209	-0.965139
O	5.033809	0.098421	-1.099398
C	5.618230	-0.017606	0.183691
H	6.675040	-0.270043	0.045528
H	5.569390	0.921066	0.760609
H	5.152966	-0.810590	0.789232

Model1-3l-ylide

C	-1.346431	-2.957164	-0.347372
H	-2.200372	-3.494062	0.070558
H	-0.874643	-3.569386	-1.125142
C	-0.931745	-0.732130	-0.734792
O	-1.198679	0.402074	-1.182375
O	-1.841949	-1.744910	-0.963562
C	0.175412	-1.243131	-0.015672
N	0.980797	-0.303039	0.822699
C	-0.310507	-2.497449	0.688759
H	0.453582	-3.266231	0.850137
H	-0.786530	-2.284456	1.661085
C	1.588978	0.862309	0.152384
C	1.314874	2.141239	0.620416
C	2.487878	0.673258	-0.899926
C	1.921429	3.253004	0.027958
H	0.621599	2.284400	1.442147
C	3.095114	1.772449	-1.490024
H	2.709910	-0.327418	-1.250673
C	2.813997	3.072330	-1.034926
H	1.686069	4.241755	0.402549
H	3.795232	1.648240	-2.309854
H	0.389260	0.036651	1.623100
H	1.468210	-2.236115	-1.048152
O	2.257571	-2.845017	-1.182855
H	-3.055055	0.646569	-1.215146
O	-3.915807	0.998074	-0.888410
C	-4.751991	-0.101096	-0.545662
H	-5.684378	0.310918	-0.148789
H	-4.990138	-0.717501	-1.423313
H	-4.298262	-0.747633	0.217341
O	-0.970704	0.538838	2.648043
H	-0.745609	1.089846	3.413837
H	-1.500099	1.135823	2.044535
O	-2.071368	2.159428	0.807209
H	-1.486086	1.819004	0.097162
H	3.026232	-2.404285	0.358483
O	3.148803	-2.017831	1.263182
H	2.991860	-2.757301	1.871244
H	-2.946295	1.873114	0.454908
H	2.636300	-2.600898	-2.041978
H	1.766256	-0.883591	1.205269
O	3.458414	4.078422	-1.686174
C	3.196536	5.419734	-1.284961
H	3.799411	6.049644	-1.940540
H	2.136708	5.673619	-1.408536
H	3.493112	5.590661	-0.242728

Model1-TS-3l-ylide

C	0.240330	-3.181767	-0.387484
H	-0.295021	-4.051693	-0.005740
H	0.970399	-3.497064	-1.138981
C	-0.455350	-1.029692	-0.790331
O	-1.195834	-0.137181	-1.190595
O	-0.739095	-2.326719	-1.049468
C	0.807913	-0.948649	-0.025710
N	0.853109	0.231419	0.913698
C	0.885017	-2.301048	0.688315
H	1.916579	-2.609429	0.887803
H	0.291303	-2.320945	1.612066
C	0.946883	1.590764	0.321130
C	0.094177	2.578414	0.800750
C	1.915910	1.872874	-0.645339
C	0.183288	3.879544	0.298430
H	-0.642335	2.349252	1.564127
C	2.001595	3.167344	-1.141686
H	2.579348	1.078062	-0.998452
C	1.140024	4.178005	-0.680642
H	-0.491548	4.637587	0.676805
H	2.739779	3.421574	-1.895903
H	0.000509	0.186957	1.537214
H	1.844667	-0.896753	-0.730540
O	3.169579	-0.859502	-1.195969
H	-2.999253	-0.711147	-1.344785
O	-3.930658	-0.743141	-1.034844
C	-4.077518	-1.906570	-0.218496
H	-5.122941	-1.948083	0.097773
H	-3.841302	-2.819550	-0.778572
H	-3.439157	-1.862579	0.674548
O	-1.563792	-0.078450	2.195489
H	-1.722783	0.201099	3.110686
H	-2.213532	0.438251	1.635558
O	-3.094505	1.356175	0.510190
H	-2.360828	1.540907	-0.102639
H	3.829371	-2.090950	-0.346333
O	4.130069	-2.872726	0.223803
H	3.988316	-3.638066	-0.353755
H	-3.607539	0.671033	0.010234
H	3.101243	-1.117194	-2.130542
H	1.672194	0.084544	1.513406
O	1.314837	5.404536	-1.239824
C	0.469954	6.470641	-0.816317
H	0.781725	7.343459	-1.391449
H	-0.584012	6.252596	-1.027292
H	0.593039	6.676797	0.254002

Model2-3l-ylide

C	1.555046	-2.525440	0.228293
H	1.865799	-3.422488	0.767026
H	1.924637	-2.571804	-0.803015
C	-0.317142	-1.207687	0.341057
O	-1.523700	-0.950199	0.398548
O	0.107021	-2.508318	0.193054
C	0.822820	-0.345012	0.403697

N	0.580820	0.928162	1.159989
C	1.975562	-1.203707	0.893533
H	2.967821	-0.895279	0.546214
H	2.007212	-1.316809	1.992632
C	-0.327428	1.934459	0.549927
C	-1.475852	2.305505	1.233332
C	0.010874	2.519263	-0.671452
C	-2.317144	3.284716	0.699755
H	-1.739046	1.831414	2.174654
C	-0.822867	3.494507	-1.201246
H	0.894708	2.198802	-1.214689
C	-1.990493	3.886358	-0.522507
H	-3.215062	3.558628	1.239611
H	-0.589283	3.967327	-2.149525
H	0.233628	0.742431	2.114413
H	1.552286	0.081766	-1.284111
O	2.129693	0.376361	-2.057705
H	-2.715630	-2.327560	0.492880
O	-3.361291	-3.067273	0.519456
C	-3.116198	-3.867609	-0.618379
H	-3.775527	-4.741359	-0.562993
H	-3.334346	-3.343692	-1.564930
H	-2.076371	-4.226585	-0.666913
H	3.792422	-0.125181	-1.592115
O	4.643669	-0.431144	-1.200379
H	4.687015	-1.365771	-1.452666
H	1.714274	-0.009407	-2.845486
H	1.496290	1.369725	1.293729
O	-2.731430	4.847606	-1.132130
C	-3.939716	5.272881	-0.506773
H	-4.363676	6.031555	-1.165745
H	-4.648089	4.442287	-0.402910
H	-3.745151	5.713435	0.478649

Model2-TS-3l-ylide

C	-2.486996	1.738227	-0.585417
H	-3.249638	1.802547	-1.362961
H	-2.783000	2.358679	0.266776
C	-1.139879	-0.006406	0.095447
O	-0.873630	-1.135076	0.485191
O	-2.432873	0.358495	-0.137480
C	-0.275824	1.158940	-0.133065
N	1.149256	0.918068	-0.602451
C	-1.067481	2.074745	-1.059409
H	-0.833804	3.135103	-0.918879
H	-0.941600	1.813808	-2.122818
C	1.872827	-0.292913	-0.164466
C	1.999394	-1.374811	-1.023734
C	2.447530	-0.306455	1.106953
C	2.705686	-2.506491	-0.611542
H	1.549691	-1.356055	-2.012744
C	3.147925	-1.430165	1.520300
H	2.344164	0.559050	1.753205
C	3.279041	-2.540229	0.667463
H	2.797542	-3.345895	-1.289661
H	3.605987	-1.470947	2.502916
H	1.206568	0.994451	-1.624575
H	0.123152	1.923166	0.896819
O	0.991455	2.755793	1.343767
H	-2.246362	-2.309746	0.950933
O	-2.974447	-2.933873	1.149400
C	-3.815403	-2.963237	0.013992
H	-4.674526	-3.600199	0.251640
H	-4.194296	-1.966045	-0.258390
H	-3.318672	-3.388706	-0.874782
H	0.341439	4.244322	0.817451
O	-0.124580	5.021686	0.401262
H	-0.954308	5.076608	0.899013
H	1.046541	2.629820	2.303527
H	1.635625	1.737142	-0.181344
O	3.983203	-3.587130	1.168975
C	4.130304	-4.755708	0.366022
H	4.707738	-5.458275	0.968076
H	3.156187	-5.196974	0.123715
H	4.674622	-4.536855	-0.560715

Model3-3l-ylide

C	-1.250582	-1.848340	-1.773053
H	-1.147983	-1.355992	-2.747146
H	-1.626689	-2.862729	-1.917414
C	-1.576146	-0.279052	-0.139355
O	-2.244994	0.471543	0.607053
O	-2.237469	-1.116422	-1.003508
C	-0.178598	-0.433945	-0.294089
N	0.647462	-0.043908	0.881387
C	0.060547	-1.761074	-0.971474
H	0.144790	-2.604210	-0.262611
H	0.932047	-1.800060	-1.633437
C	2.108467	-0.089066	0.682326
C	2.721650	0.806880	-0.187972
C	2.863043	-1.025805	1.389091
C	4.107392	0.770476	-0.353813
H	2.133430	1.530275	-0.743218
C	4.242533	-1.065006	1.226040
H	2.380728	-1.724844	2.067484
C	4.875949	-0.165923	0.353477
H	4.571973	1.476164	-1.031712
H	4.847670	-1.785081	1.766654
H	0.352811	0.950455	1.139436
H	-0.050546	1.329576	-1.381923
O	0.077775	2.305656	-1.526943
O	-0.402845	2.446250	1.194508
H	-0.241163	2.679020	0.247424
H	-1.266411	1.973676	1.148817
H	-0.663463	2.578426	-2.091642
H	-4.002580	0.720421	0.188039
O	-4.960726	0.817101	-0.003247
C	-5.558488	-0.430122	0.285224
H	-6.614676	-0.371070	-0.000888
H	-5.099021	-1.259273	-0.274930
H	-5.516749	-0.685986	1.357945
H	0.430753	-0.625219	1.704374
O	6.226754	-0.282756	0.263331
C	6.930286	0.608361	-0.598560
H	7.983022	0.337279	-0.509713
H	6.610390	0.491208	-1.641010
H	6.794972	1.651866	-0.289685

Model3-TS-3l-ylide

C	-1.237886	-2.030685	-1.519427
H	-1.401447	-1.740835	-2.561729
H	-1.438591	-3.095988	-1.400901
C	-1.605845	-0.257826	-0.114558
O	-2.216749	0.499167	0.637067

O	-2.209953	-1.313191	-0.703286
C	-0.203435	-0.170328	-0.553248
N	0.654053	0.446220	0.524479
C	0.140821	-1.580607	-1.008577
H	0.474541	-2.223041	-0.181075
H	0.895714	-1.622092	-1.797975
C	2.107196	0.386470	0.295523
C	2.661754	1.032373	-0.815218
C	2.911364	-0.289704	1.204833
C	4.037031	0.989002	-0.998769
H	2.016531	1.545497	-1.525182
C	4.296500	-0.329382	1.021781
H	2.474891	-0.788647	2.066578
C	4.865380	0.313566	-0.084849
H	4.497037	1.480439	-1.850033
H	4.908739	-0.858640	1.741505
H	0.323735	1.480262	0.575159
H	-0.164836	0.770358	-1.480338
O	-0.007042	1.929195	-2.104985
O	-0.387653	2.879360	0.245909
H	-0.301034	2.683178	-0.766344
H	-1.292771	2.590418	0.462255
H	-0.754807	2.015894	-2.718544
H	-3.975191	0.050074	1.135675
O	-4.900570	-0.186212	1.345640
C	-5.608352	-0.207869	0.121194
H	-6.630176	-0.540143	0.333694
H	-5.669796	0.785779	-0.353413
H	-5.167649	-0.904052	-0.609264
H	0.449583	0.028215	1.439210
O	6.195584	0.340657	-0.362525
C	7.089576	-0.314980	0.532393
H	6.882270	-1.390694	0.587593
H	8.088114	-0.159178	0.122123
H	7.036902	0.119050	1.538332

2l

N	0.382071	-0.689105	0.358877
C	-0.088139	-1.601597	-0.596247
C	0.357079	-2.935693	-0.597694
C	-1.061066	-1.220921	-1.537973
C	-0.158770	-3.858307	-1.506452
H	1.112674	-3.249097	0.119255
C	-1.574882	-2.145680	-2.445548
H	-1.414810	-0.192486	-1.556854
C	-1.125563	-3.468597	-2.436563
H	0.197759	-4.884624	-1.509719
H	-2.317576	-1.842057	-3.178161
H	1.307743	-0.900575	0.714204
H	0.329902	0.280461	0.067244
O	-1.600701	-4.375074	-3.371259
C	-2.764140	-5.087724	-2.953360
H	-3.601729	-4.405183	-2.754833
H	-3.032224	-5.760132	-3.772226
H	-2.567721	-5.678035	-2.047917

4 OSS

Fe	-0.058357	0.023969	-0.386027
N	-1.538469	1.418933	-0.388555
N	-1.485165	-1.428783	-0.466887
N	1.350933	1.466890	-0.338196
N	1.401544	-1.370398	-0.418146
C	-1.361204	2.772737	-0.305733
C	-1.258452	-2.778114	-0.454484
C	-2.886490	1.209558	-0.496628
C	-2.840683	-1.263676	-0.567782
C	1.120857	2.813636	-0.252619
C	1.222788	-2.727732	-0.402061
C	2.709169	1.307399	-0.389678
C	2.753226	-1.159050	-0.459734
C	-2.642812	3.446696	-0.356408
C	-2.514011	-3.494807	-0.542611
C	-3.589851	2.475318	-0.481289
C	-3.496431	-2.553947	-0.619818
C	2.378478	3.532131	-0.243407
C	2.506326	-3.398948	-0.428430
C	3.364097	2.596932	-0.336928
C	3.455947	-2.424192	-0.474831
C	-0.131861	3.423525	-0.218418
C	-0.005615	-3.385754	-0.400340
C	3.371244	0.086538	-0.467563
C	-3.501588	-0.037208	-0.590856
H	-0.150537	4.508361	-0.155755
H	0.016758	-4.472251	-0.392187
H	4.456985	0.106959	-0.502302
H	-4.584936	-0.055092	-0.673317
C	0.976786	0.082886	-3.144824
H	1.673363	0.925745	-2.967393
H	1.578786	-0.842534	-3.051616
H	0.669096	0.150000	-4.206859
C	-0.152008	-0.016222	1.573896
C	-1.419975	0.086239	2.383531
C	-1.022849	-0.389130	3.791057
H	-1.279832	-1.444973	3.951465
H	-1.458158	0.199678	4.604858
H	-2.247526	-0.491818	1.962408
H	-1.757233	1.135249	2.408350
O	-0.137041	0.103947	-2.318328
C	0.925722	-0.109473	2.565760
O	2.141317	-0.065610	2.446965
O	0.404459	-0.251362	3.854857
H	2.473603	4.609644	-0.182256
H	4.436678	2.746697	-0.364678
H	-2.779149	4.520706	-0.313018
H	-4.664779	2.586658	-0.559727
H	-4.566647	-2.700694	-0.704205
H	-2.610524	-4.573936	-0.553974
H	2.641286	-4.473943	-0.420392
H	4.533403	-2.532002	-0.506980

4 Triplet

Fe	-0.038512	0.030117	-0.402090
N	-1.577507	1.359556	-0.418701
N	-1.352409	-1.510725	-0.321338
N	1.262377	1.577620	-0.489803
N	1.479349	-1.287523	-0.401331
C	-1.493374	2.724854	-0.391853
C	-1.060204	-2.843356	-0.195170
C	-2.910713	1.053844	-0.475817
C	-2.717492	-1.417550	-0.388096
C	0.971545	2.913578	-0.458077
C	1.402823	-2.647774	-0.258314
C	2.617701	1.478985	-0.636512

C	2.805133	-0.987498	-0.553702
C	-2.818407	3.306908	-0.427146
C	-2.279770	-3.620955	-0.176928
C	-3.698537	2.268572	-0.489145
C	-3.308579	-2.736279	-0.305786
C	2.188071	3.691962	-0.576446
C	2.726962	-3.228818	-0.313227
C	3.209214	2.800219	-0.699341
C	3.595841	-2.198538	-0.509971
C	-0.308365	3.456852	-0.380572
C	0.223974	-3.379072	-0.135248
C	3.338326	0.290425	-0.694221
C	-3.446112	-0.232627	-0.481326
H	-0.390885	4.540037	-0.363212
H	0.312356	-4.456950	-0.031403
H	4.415751	0.367470	-0.810361
H	-4.528367	-0.319115	-0.526120
C	-0.061642	-1.092722	-3.096580
H	0.855087	-1.696021	-2.951238
H	-0.917125	-1.768860	-2.907295
H	-0.099209	-0.825167	-4.169280
C	-0.048274	0.106548	1.595127
C	-1.296075	0.255168	2.428515
C	-0.841524	-0.091251	3.857570
H	-1.073670	-1.135078	4.113098
H	-1.268026	0.554919	4.632274
H	-2.122965	-0.376873	2.089394
H	-1.661891	1.294090	2.376239
O	-0.087377	0.058059	-2.316795
C	1.054521	0.094465	2.536162
O	2.271227	0.111320	2.377294
O	0.580613	0.078827	3.862276
H	2.231704	4.774440	-0.576524
H	4.268127	2.997624	-0.815331
H	-3.027162	4.369953	-0.418664
H	-4.780361	2.303081	-0.538406
H	-4.372327	-2.939223	-0.340010
H	-2.324262	-4.699635	-0.086641
H	2.941632	-4.286764	-0.222595
H	4.674259	-2.234753	-0.606972

4 CSS

Fe	-0.061886	0.033782	-0.308492
N	-1.501328	1.471666	-0.340300
N	-1.526974	-1.375381	-0.467542
N	1.390163	1.439524	-0.302388
N	1.362797	-1.397208	-0.411344
C	-1.285865	2.819130	-0.245394
C	-1.337232	-2.730466	-0.480879
C	-2.852871	1.302853	-0.467850
C	-2.875579	-1.170866	-0.578252
C	1.197597	2.791163	-0.205120
C	1.146015	-2.748822	-0.424611
C	2.741528	1.244869	-0.382725
C	2.718166	-1.222163	-0.475428
C	-2.547162	3.531275	-0.302331
C	-2.611725	-3.411135	-0.595052
C	-3.520154	2.589111	-0.446737
C	-3.566743	-2.442104	-0.661553
C	2.474737	3.477298	-0.213617
C	2.410167	-3.455575	-0.486173
C	3.432330	2.517063	-0.332880
C	3.385528	-2.506648	-0.527987
C	-0.038164	3.433516	-0.153273
C	-0.101005	-3.372159	-0.433480
C	3.368858	0.007443	-0.483793
C	-3.501366	0.075019	-0.586602
H	-0.026679	4.518170	-0.083306
H	-0.108173	-4.458964	-0.450877
H	4.453886	-0.000867	-0.542376
H	-4.584016	0.088969	-0.680596
C	0.952534	0.123157	-3.122628
H	1.661446	0.959159	-2.950877
H	1.555322	-0.806126	-3.052863
H	0.632133	0.203986	-4.181798
C	-0.156092	-0.020726	1.504899
C	-1.404804	0.073105	2.346188
C	-1.013616	-0.540952	3.697488
H	-1.278697	-1.604345	3.753579
H	-1.435579	-0.029523	4.567575
H	-2.270304	-0.413505	1.891159
H	-1.668805	1.135827	2.469915
O	-0.139355	0.141885	-2.275672
C	0.940059	-0.166902	2.507635
O	2.148090	-0.084216	2.388677
O	0.418009	-0.423931	3.766839
H	2.599521	4.551583	-0.147556
H	4.507840	2.638484	-0.382824
H	-2.652381	4.608582	-0.252475
H	-4.590325	2.732710	-0.538404
H	-4.639579	-2.557583	-0.761085
H	-2.737718	-4.486735	-0.631331
H	2.514877	-4.533807	-0.507004
H	4.458857	-2.643370	-0.584872

TS1-2l OSS

Fe	-1.428318	0.138908	0.369937
N	-2.127646	1.442985	-1.024795
N	-0.516963	1.685943	1.323397
N	-2.420763	-1.379736	-0.527630
N	-0.860046	-1.124301	1.858004
C	-2.948062	1.139507	-2.080179
C	0.169901	1.624218	2.508173
C	-1.898683	2.793126	-1.093842
C	-0.478903	3.000761	0.928661
C	-3.190890	-1.295681	-1.656162
C	-0.173805	-0.791566	2.995958
C	-2.513736	-2.674874	-0.097187
C	-1.170716	-2.454397	1.973349
C	-3.239218	2.333570	-2.848274
C	0.686399	2.933239	2.859354
C	-2.584326	3.360406	-2.235537
C	0.281988	3.786880	1.877081
C	-3.767834	-2.590120	-1.969491
C	-0.017276	-1.954630	3.846964
C	-3.346780	-3.446066	-0.999244
C	-0.637964	-2.987472	3.209994
C	-3.430963	-0.132735	-2.385384
C	0.332512	0.477413	3.289445
C	-1.926790	-3.182892	1.058594
C	-1.116666	3.520439	-0.195471
H	-4.070779	-0.221027	-3.259840
H	0.886290	0.586602	4.218390
H	-2.094070	-4.234222	1.278825

H	-1.012684	4.587240	-0.377398
C	-3.544161	1.604702	1.841880
H	-2.873705	2.095023	2.582083
H	-3.690466	2.346039	1.027259
H	-4.530121	1.513232	2.346394
C	0.414141	0.335845	-3.038750
H	1.140820	0.546719	-3.828590
H	-0.569895	0.700945	-3.341878
O	-3.100771	0.371495	1.408073
C	0.329657	-1.425040	-1.559259
O	0.452453	-2.590492	-1.213545
O	0.345743	-1.105602	-2.893089
H	-4.414899	-2.791117	-2.815160
H	-3.576521	-4.498509	-0.881198
H	-3.866603	2.364245	-3.731270
H	-2.567353	4.408776	-2.510161
H	0.459249	4.853047	1.796014
H	1.262240	3.153324	3.750690
H	0.491196	-1.958877	4.803940
H	-0.746480	-4.014311	3.539121
C	0.202027	-0.184889	-0.734589
N	1.754713	-0.742973	0.505430
H	1.410485	-1.697462	0.588087
H	1.509756	-0.206156	1.332407
C	0.820427	0.861735	-1.649737
H	0.458213	1.872861	-1.472851
H	1.916970	0.871727	-1.575103
C	3.108366	-0.633198	0.118843
C	3.707403	-1.624384	-0.681520
C	3.858185	0.496757	0.469702
C	5.024542	-1.487418	-1.097505
H	3.130021	-2.496853	-0.971983
C	5.184202	0.636413	0.052344
H	3.404344	1.272976	1.081000
C	5.776734	-0.358581	-0.734525
H	5.495261	-2.251671	-1.708598
H	5.738069	1.519748	0.348612
O	7.065725	-0.326753	-1.194179
C	7.867152	0.796298	-0.856545
H	8.840371	0.621109	-1.318694
H	7.441517	1.728495	-1.250232
H	7.993585	0.889682	0.230009

TS1-2l Triplet

Fe	-1.509763	0.148694	0.427138
N	-2.131574	1.626010	-0.842952
N	-0.547157	1.507001	1.585757
N	-2.438073	-1.204585	-0.764275
N	-0.912911	-1.317562	1.700927
C	-2.883005	1.492124	-1.979801
C	0.181019	1.271214	2.723362
C	-1.929333	2.975879	-0.667879
C	-0.550527	2.875794	1.399024
C	-3.141057	-0.968110	-1.917378
C	-0.167533	-1.185833	2.845778
C	-2.535780	-2.554489	-0.516607
C	-1.241562	-2.652424	1.602262
C	-3.150486	2.787963	-2.553982
C	0.685274	2.521569	3.255617
C	-2.557178	3.710462	-1.732618
C	0.224044	3.511439	2.438345
C	-3.679231	-2.213521	-2.432280
C	-0.006149	-2.466629	3.480653
C	-3.306554	-3.191440	-1.562983
C	-0.681422	-3.377587	2.706519
C	-3.348785	0.276516	-2.499004
C	0.381633	0.021901	3.311397
C	-1.996689	-3.222083	0.572160
C	-1.196713	3.554014	0.375378
H	-3.936285	0.313725	-3.411943
H	0.974196	-0.015984	4.221060
H	-2.167436	-4.294306	0.626586
H	-1.112947	4.638051	0.373654
C	-3.243682	0.319691	2.735253
H	-3.072180	-0.699130	3.128691
H	-2.541203	0.989572	3.262166
H	-4.263987	0.615901	3.040338
C	0.517737	0.862530	-2.963155
H	1.297190	1.190887	-3.656857
H	-0.443281	1.287297	-3.266640
O	-3.134183	0.395035	1.348414
C	0.306419	-1.110067	-1.791962
O	0.376637	-2.324532	-1.637713
O	0.437128	-0.578766	-3.057360
H	-4.269591	-2.301420	-3.336507
H	-3.527568	-4.251524	-1.606155
H	-3.722450	2.958873	-3.458226
H	-2.548586	4.790013	-1.828888
H	0.380719	4.580552	2.523389
H	1.292749	2.611848	4.148397
H	0.545987	-2.639249	4.396917
H	-0.791989	-4.443693	2.866551
C	0.197363	-0.032798	-0.781116
N	1.735750	-0.860435	0.383886
H	1.354732	-1.795834	0.255455
H	1.491049	-0.485668	1.296356
C	0.825601	1.155079	-1.482597
H	0.432370	2.119516	-1.164720
H	1.915906	1.166040	-1.332069
C	3.084005	-0.706172	0.018286
C	3.655423	-1.532067	-0.971211
C	3.865255	0.314914	0.579189
C	4.972970	-1.346094	-1.363713
H	3.053785	-2.314733	-1.423511
C	5.191903	0.502279	0.184348
H	3.433767	0.964721	1.336558
C	5.755373	-0.329766	-0.791255
H	5.421231	-1.984190	-2.119465
H	5.769765	1.295607	0.644503
O	7.042633	-0.236988	-1.250298
C	7.873198	0.778158	-0.706522
H	8.838926	0.676231	-1.205119
H	7.468084	1.779537	-0.902781
H	8.009358	0.651923	0.375644

TS1-2l CSS

Fe	-1.428749	0.132048	0.346998
N	-2.136638	1.428214	-1.059107
N	-0.559285	1.696826	1.312839
N	-2.409934	-1.399354	-0.554907
N	-0.890015	-1.114062	1.857966
C	-2.929432	1.109414	-2.130150
C	0.113354	1.645680	2.505310
C	-1.932573	2.780561	-1.121687

C	-0.542115	3.010573	0.920851
C	-3.153132	-1.329069	-1.702198
C	-0.220158	-0.770535	3.001883
C	-2.510750	-2.687647	-0.112082
C	-1.202656	-2.441190	1.980284
C	-3.229986	2.299073	-2.902522
C	0.602005	2.963507	2.864844
C	-2.609548	3.337938	-2.275499
C	0.193140	3.811228	1.880050
C	-3.721181	-2.628136	-2.014021
C	-0.076307	-1.926063	3.866853
C	-3.323465	-3.471723	-1.023431
C	-0.687994	-2.964080	3.231430
C	-3.383961	-0.171636	-2.443945
C	0.276912	0.502573	3.291982
C	-1.943383	-3.180707	1.061009
C	-1.175359	3.520232	-0.211415
H	-4.002658	-0.270511	-3.332489
H	0.815718	0.621082	4.228732
H	-2.113846	-4.229377	1.291329
H	-1.088769	4.589086	-0.390229
C	-3.584805	1.579786	1.816737
H	-2.923511	2.051743	2.578541
H	-3.717691	2.344119	1.019388
H	-4.578948	1.484401	2.306578
C	0.498284	0.346059	-3.006360
H	1.260089	0.567455	-3.758937
H	-0.475528	0.695037	-3.358610
O	-3.139854	0.358612	1.358027
C	0.361523	-1.416146	-1.529661
O	0.481334	-2.577346	-1.177358
O	0.446177	-1.096440	-2.859980
H	-4.349235	-2.840172	-2.871299
H	-3.556022	-4.522655	-0.897826
H	-3.842149	2.319069	-3.796508
H	-2.609804	4.387123	-2.547328
H	0.350774	4.880719	1.802784
H	1.162319	3.192940	3.763746
H	0.417485	-1.921264	4.831539
H	-0.801908	-3.987692	3.568587
C	0.157863	-0.166870	-0.718605
N	1.816407	-0.763039	0.583180
H	1.457598	-1.711996	0.642806
H	1.557445	-0.223234	1.402748
C	0.824315	0.877817	-1.598440
H	0.450457	1.887865	-1.441628
H	1.914353	0.888076	-1.462106
C	3.159178	-0.644827	0.184778
C	3.761867	-1.636210	-0.614071
C	3.903097	0.496927	0.512309
C	5.071135	-1.487957	-1.050710
H	3.191419	-2.518183	-0.889576
C	5.221814	0.647866	0.074722
H	3.449204	1.274704	1.121571
C	5.815293	-0.347038	-0.710497
H	5.541398	-2.252669	-1.661709
H	5.768574	1.541224	0.353919
O	7.097578	-0.304256	-1.190057
C	7.886922	0.834929	-0.880648
H	8.855096	0.668695	-1.356634
H	7.440578	1.755447	-1.279138
H	8.030016	0.945090	0.202350

5l OSS

Fe	-1.444747	0.202821	0.440955
N	-1.737026	1.938117	-0.530123
N	-0.156928	1.146931	1.753940
N	-2.671046	-0.741363	-0.862338
N	-1.089189	-1.525210	1.412649
C	-2.616251	2.162862	-1.576459
C	0.454699	0.608019	2.883098
C	-1.189024	3.159806	-0.222127
C	0.176793	2.484368	1.743555
C	-3.418971	-0.163998	-1.865448
C	-0.335666	-1.721406	2.566214
C	-3.012874	-2.064978	-0.846013
C	-1.656791	-2.746977	1.116917
C	-2.593584	3.558480	-1.948840
C	1.199607	1.615221	3.562773
C	-1.708092	4.177075	-1.119817
C	1.031211	2.787647	2.854438
C	-4.230072	-1.153503	-2.510635
C	-0.413046	-3.108868	2.971561
C	-3.976012	-2.345321	-1.877587
C	-1.225393	-3.740154	2.082913
C	-3.395009	1.197751	-2.190247
C	0.373971	-0.747682	3.245705
C	-2.532299	-3.009817	0.078012
C	-0.284551	3.419451	0.801370
H	-4.041460	1.523715	-3.001916
H	0.915262	-1.054984	4.136968
H	-2.892001	-4.030019	-0.024254
H	0.057546	4.444779	0.915202
C	-2.955028	0.656215	2.859832
H	-2.530477	-0.241224	3.344966
H	-2.380388	1.524773	3.234081
H	-3.987176	0.768370	3.242738
C	-0.009835	0.337126	-3.148120
H	0.467029	0.543656	-4.109898
H	-1.026323	0.731468	-3.147082
O	-2.991513	0.567691	1.472107
C	0.245692	-1.441884	-1.727612
O	0.399942	-2.612101	-1.397143
O	-0.082641	-1.106879	-3.006740
H	-4.909185	-0.959628	-3.333001
H	-4.403517	-3.320655	-2.078192
H	-3.189988	3.993614	-2.742722
H	-1.429212	5.223969	-1.089547
H	1.433300	3.769004	3.077580
H	1.774564	1.456918	4.468043
H	0.089590	-3.523638	3.837893
H	-1.524954	-4.781460	2.066039
C	0.421904	-0.231604	-0.913230
N	1.467260	-0.544407	0.136921
H	1.193452	-1.477866	0.473466
H	1.270877	0.100923	0.919207
C	0.798048	0.832519	-1.936128
H	0.518837	1.849232	-1.657476
H	1.872100	0.820326	-2.177086
C	2.898949	-0.517987	-0.195836
C	3.482816	-1.583633	-0.888452
C	3.659687	0.582686	0.183368
C	4.835474	-1.535372	-1.198197
H	2.878680	-2.435948	-1.180424

C	5.021208	0.635096	-0.129071
H	3.199563	1.403109	0.728943
C	5.614080	-0.426823	-0.824072
H	5.313336	-2.351392	-1.730759
H	5.599322	1.499295	0.175007
O	6.927825	-0.482315	-1.178814
C	7.767288	0.615311	-0.836865
H	8.757917	0.362635	-1.217860
H	7.422440	1.544474	-1.307216
H	7.820298	0.755808	0.249855

5l Triplet

Fe	-1.431009	0.137086	0.483844
N	-1.707707	2.036900	-0.170209
N	-0.085669	0.791984	1.910108
N	-2.704573	-0.514919	-0.950533
N	-1.085112	-1.757859	1.121602
C	-2.598633	2.465550	-1.129878
C	0.517637	0.051944	2.922919
C	-1.122020	3.167245	0.356779
C	0.279977	2.109661	2.127718
C	-3.461631	0.243832	-1.811574
C	-0.337842	-2.170096	2.209691
C	-3.089674	-1.819789	-1.147115
C	-1.706767	-2.889631	0.621078
C	-2.552590	3.913772	-1.229698
C	1.289668	0.905836	3.752944
C	-1.640375	4.345626	-0.320920
C	1.144794	2.194612	3.252084
C	-4.318131	-0.595324	-2.586239
C	-0.456467	-3.609889	2.363077
C	-4.083380	-1.890581	-2.170335
C	-1.295107	-4.048209	1.387375
C	-3.408641	1.652001	-1.897252
C	0.408128	-1.354772	3.042252
C	-2.608860	-2.928038	-0.419667
C	-0.189937	3.211424	1.375568
H	-4.064298	2.130143	-2.620376
H	0.947532	-1.826774	3.858771
H	-3.007817	-3.901296	-0.693767
H	0.178649	4.191366	1.668249
C	-2.927932	-0.049026	2.930697
H	-2.786351	-1.136978	3.046927
H	-2.167063	0.447847	3.556303
H	-3.916276	0.200186	3.356228
C	-0.057672	0.900605	-3.045045
H	0.403130	1.285197	-3.958581
H	-1.070795	1.291852	-2.947203
O	-2.899806	0.363905	1.597369
C	0.201112	-1.118595	-1.997396
O	0.356815	-2.329869	-1.898637
O	-0.140272	-0.544164	-3.182457
H	-5.011585	-0.245552	-3.342234
H	-4.548711	-2.804581	-2.520734
H	-3.154578	4.501879	-1.912848
H	-1.340046	5.363219	-0.098612
H	1.569205	3.113309	3.640612
H	1.870489	0.581696	4.608630
H	0.040472	-4.186671	3.134564
H	-1.628771	-5.060992	1.192974
C	0.400211	-0.086497	-0.966377
N	1.454617	-0.608489	-0.011914
H	1.182047	-1.591215	0.128976
H	1.264947	-0.133201	0.886174
C	0.777381	1.147455	-1.777017
H	0.519542	2.096509	-1.306663
H	1.847274	1.164577	-2.034886
C	2.884780	-0.509878	-0.336291
C	3.469886	-1.397332	-1.244959
C	3.645159	0.478188	0.280134
C	4.824314	-1.285064	-1.530418
H	2.866996	-2.164912	-1.718417
C	5.008185	0.594290	-0.006304
H	3.183702	1.157907	0.992638
C	5.603101	-0.289744	-0.915469
H	5.303872	-1.964848	-2.227350
H	5.586220	1.367454	0.485228
O	6.919372	-0.270458	-1.264647
C	7.761717	0.711041	-0.669832
H	8.755730	0.542904	-1.086957
H	7.429991	1.726891	-0.917819
H	7.800617	0.597509	0.420653

5l CSS

Fe	-1.436673	0.186946	0.417525
N	-1.785137	1.946167	-0.511155
N	-0.197019	1.136627	1.754828
N	-2.651208	-0.754790	-0.872545
N	-1.077190	-1.558320	1.393063
C	-2.650117	2.164938	-1.550521
C	0.410200	0.596273	2.872937
C	-1.272058	3.173504	-0.179984
C	0.098306	2.481130	1.776160
C	-3.397414	-0.181619	-1.867611
C	-0.333699	-1.750794	2.535445
C	-2.977594	-2.084434	-0.871969
C	-1.624306	-2.780468	1.089691
C	-2.670402	3.571344	-1.905410
C	1.128473	1.621860	3.594790
C	-1.809814	4.198390	-1.056478
C	0.937692	2.790016	2.912936
C	-4.203659	-1.185540	-2.537495
C	-0.393137	-3.139603	2.946022
C	-3.940452	-2.369267	-1.920249
C	-1.196837	-3.777064	2.049498
C	-3.402002	1.176125	-2.184207
C	0.360693	-0.753966	3.224029
C	-2.496114	-3.028925	0.032291
C	-0.380686	3.421284	0.864026
H	-4.051237	1.492582	-2.997282
H	0.900400	-1.053642	4.118896
H	-2.849971	-4.050219	-0.085196
H	-0.063786	4.451609	1.008106
C	-3.099223	0.371593	2.869874
H	-2.922257	-0.681691	3.184690
H	-2.374512	0.985102	3.452298
H	-4.101169	0.636654	3.274216
C	0.039346	0.433035	-3.171041
H	0.511782	0.673564	-4.127530
H	-0.980268	0.820449	-3.156612
O	-3.054000	0.575193	1.507916
C	0.310521	-1.379654	-1.796951

O	0.456804	-2.563683	-1.500323
O	-0.024019	-1.013593	-3.072609
H	-4.879642	-0.989356	-3.361596
H	-4.354865	-3.348083	-2.131594
H	-3.274238	4.003853	-2.694832
H	-1.562507	5.252379	-1.002998
H	1.308015	3.778463	3.159360
H	1.692143	1.459651	4.506139
H	0.107869	-3.550985	3.814670
H	-1.487471	-4.820928	2.028961
C	0.480648	-0.198931	-0.964244
N	1.496800	-0.522852	0.104156
H	1.217361	-1.463534	0.415025
H	1.283877	0.103688	0.894399
C	0.842148	0.904996	-1.944348
H	0.537144	1.906843	-1.635495
H	1.917150	0.929987	-2.186404
C	2.936490	-0.491580	-0.198470
C	3.527683	-1.539656	-0.911691
C	3.694506	0.595955	0.220320
C	4.885211	-1.488308	-1.198267
H	2.923422	-2.379847	-1.236969
C	5.061436	0.652052	-0.068840
H	3.228772	1.404189	0.779026
C	5.661759	-0.393382	-0.781690
H	5.368759	-2.291344	-1.745314
H	5.637294	1.506271	0.266285
O	6.981381	-0.444837	-1.116427
C	7.819167	0.638687	-0.729408
H	8.815466	0.392038	-1.099501
H	7.486957	1.582311	-1.179754
H	7.853366	0.748993	0.361608

3l

C	-0.512212	-1.005450	3.538934
H	-0.905210	-1.949323	3.920527
H	-0.551283	-0.253588	4.334280
C	1.225081	-0.568248	2.068867
O	2.342497	-0.596787	1.615266
O	0.885121	-1.227112	3.203716
C	-0.005349	0.189930	1.534424
N	-0.030891	0.344304	0.095904
H	-0.457515	1.217751	-0.184751
C	-1.174732	-0.521384	2.245732
C	-0.333412	-0.705871	-0.791280
C	0.017106	-2.041966	-0.551607
C	-0.968775	-0.405638	-2.013287
C	-0.258893	-3.044186	-1.489507
H	0.529530	-2.324922	0.360930
C	-1.233169	-1.394061	-2.950946
H	-1.254213	0.621981	-2.228941
C	-0.884432	-2.729042	-2.698115
H	0.030936	-4.063038	-1.259066
H	-1.720825	-1.149777	-3.890007
O	-1.197200	-3.630547	-3.682404
C	-0.842274	-4.989463	-3.473658
H	-1.347067	-5.408440	-2.593013
H	-1.169467	-5.527288	-4.365393
H	0.242664	-5.109700	-3.355705
H	0.096083	1.203186	1.945533
H	-1.519069	-1.368115	1.644618
H	-2.024363	0.139163	2.434165

Fe(II)-Porph Quintet

Fe	-1.973614	0.206216	0.958277
N	-1.793751	2.091062	-0.102379
N	-0.157495	0.826134	1.962714
N	-2.808195	-0.530507	-0.899539
N	-1.168459	-1.795733	1.164443
C	-2.564270	2.482913	-1.162278
C	0.580163	0.051816	2.816674
C	-1.153805	3.205834	0.363561
C	0.251024	2.120064	2.139726
C	-3.437636	0.229760	-1.846242
C	-0.290183	-2.202615	2.131490
C	-3.113198	-1.837140	-1.165020
C	-1.704812	-2.924659	0.607863
C	-2.424154	3.913940	-1.368071
C	1.483248	0.891106	3.583773
C	-1.549024	4.362729	-0.421046
C	1.279468	2.174260	3.163224
C	-4.190174	-0.628564	-2.744092
C	-0.278089	-3.652752	2.204577
C	-3.989426	-1.911085	-2.320960
C	-1.155765	-4.100895	1.259027
C	-3.339461	1.624380	-1.954768
C	0.502829	-1.345712	2.908467
C	-2.618173	-2.941244	-0.456166
C	-0.224320	3.221471	1.413314
H	-3.899424	2.087060	-2.764405
H	1.155989	-1.819377	3.638028
H	-2.953691	-3.920336	-0.790538
H	0.200943	4.189381	1.669046
C	-3.470041	0.047383	3.527430
H	-3.370434	-1.044187	3.702163
H	-2.664746	0.531258	4.117268
H	-4.423479	0.347310	4.006682
O	-3.448691	0.389566	2.182474
H	-4.778990	-0.287990	-3.588027
H	-4.381686	-2.825509	-2.751031
H	-2.921531	4.486153	-2.142736
H	-1.190007	5.374143	-0.269109
H	1.781143	3.074667	3.498723
H	2.183947	0.536304	4.330862
H	0.331221	-4.240065	2.881907
H	-1.404060	-5.126496	1.011068

Fe(II)-Porph Triplet

Fe	-1.662370	0.154693	0.680630
N	-1.735217	2.005960	-0.124657
N	-0.200112	0.787774	1.939636
N	-2.762751	-0.522735	-0.888980
N	-1.173719	-1.745760	1.132963
C	-2.511775	2.428970	-1.196837
C	0.561749	0.022946	2.811282
C	-1.222464	3.160153	0.444426
C	0.126436	2.100313	2.222220
C	-3.394325	0.226746	-1.867840
C	-0.298672	-2.183349	2.121577
C	-3.182867	-1.821792	-1.092688
C	-1.815226	-2.884457	0.669260
C	-2.447347	3.869439	-1.316698
C	1.368178	0.855650	3.630189
C	-1.663794	4.320694	-0.303706

C	1.091444	2.161572	3.265333
C	-4.200661	-0.605065	-2.690415
C	-0.382717	-3.621228	2.254629
C	-4.072811	-1.892082	-2.201284
C	-1.319730	-4.051263	1.370403
C	-3.265505	1.619407	-2.011594
C	0.511683	-1.380527	2.888337
C	-2.754923	-2.929537	-0.335557
C	-0.385884	3.219047	1.535615
H	-3.825600	2.090745	-2.814739
H	1.148673	-1.861555	3.625763
H	-3.166668	-3.900183	-0.597833
H	-0.051840	4.199433	1.863860
C	-2.957404	0.085445	3.154703
H	-2.504482	-0.896189	3.355875
H	-2.364274	0.847805	3.683011
H	-3.970767	0.084655	3.587728
O	-3.076241	0.358638	1.780881
H	-4.789220	-0.260027	-3.532369
H	-4.532400	-2.801742	-2.569617
H	-2.953113	4.441552	-2.085714
H	-1.387097	5.341476	-0.067359
H	1.519766	3.075747	3.659143
H	2.058524	0.499545	4.385827
H	0.209938	-4.206345	2.948124
H	-1.655226	-5.064521	1.182842

Fe(II)-Porph CSS

Fe	-1.621532	0.109421	0.651168
N	-1.794104	1.995388	-0.063140
N	-0.213448	0.750430	1.953663
N	-2.759997	-0.559413	-0.879988
N	-1.177301	-1.801068	1.142328
C	-2.586807	2.418360	-1.104440
C	0.526077	-0.015571	2.826037
C	-1.231350	3.134821	0.461343
C	0.151159	2.053511	2.205462
C	-3.425946	0.199179	-1.812380
C	-0.313329	-2.233734	2.121876
C	-3.124968	-1.860251	-1.130035
C	-1.744058	-2.940070	0.618874
C	-2.516875	3.857398	-1.243225
C	1.370212	0.823526	3.647779
C	-1.676936	4.303380	-0.268141
C	1.134703	2.109573	3.264753
C	-4.223122	-0.644258	-2.677270
C	-0.336201	-3.677507	2.217576
C	-4.038495	-1.924818	-2.250956
C	-1.227619	-4.116389	1.285786
C	-3.350997	1.585403	-1.915705
C	0.476471	-1.403830	2.911246
C	-2.665466	-2.968091	-0.423523
C	-0.336355	3.166148	1.526508
H	-3.934195	2.057158	-2.702743
H	1.116413	-1.880159	3.649916
H	-3.035641	-3.942490	-0.732636
H	0.035098	4.139801	1.836213
C	-3.030359	0.378866	3.129620
H	-2.432129	-0.427897	3.603098
H	-2.556001	1.336109	3.436526
H	-4.023204	0.356592	3.624992
O	-3.182996	0.237993	1.761722
H	-4.836789	-0.287040	-3.495945
H	-4.466947	-2.837336	-2.648726
H	-3.046036	4.432974	-1.993630
H	-1.371364	5.320763	-0.053607
H	1.583096	3.019962	3.644971
H	2.050448	0.459804	4.408994
H	0.259388	-4.261229	2.909674
H	-1.513306	-5.135365	1.052338

4-MeOH OSS

Fe	-0.639438	0.015498	-0.466740
N	-1.917888	1.392803	0.312548
N	-1.850598	-1.453474	0.244857
N	0.549136	1.483663	-1.187478
N	0.603192	-1.352471	-1.278053
C	-1.758380	2.751139	0.270451
C	-1.633741	-2.798462	0.122234
C	-3.112278	1.162301	0.939890
C	-3.051757	-1.310217	0.886022
C	0.371645	2.828989	-1.001026
C	0.478274	-2.712009	-1.179143
C	1.677741	1.344612	-1.950812
C	1.718411	-1.121086	-2.037240
C	-2.887445	3.405128	0.899439
C	-2.728284	-3.535283	0.719866
C	-3.731707	2.417670	1.309538
C	-3.611862	-2.610593	1.189256
C	1.428773	3.565649	-1.661787
C	1.554933	-3.364128	-1.895997
C	2.234666	2.643960	-2.258549
C	2.320217	-2.375542	-2.435293
C	-0.685489	3.421854	-0.313536
C	-0.544788	-3.387828	-0.517399
C	2.219531	0.133457	-2.367586
C	-3.650092	-0.094054	1.209474
H	-0.692170	4.507198	-0.259735
H	-0.507924	-4.473787	-0.530477
H	3.119577	0.169290	-2.974742
H	-4.609645	-0.128801	1.717986
C	-1.270990	0.092420	-3.333169
H	-0.684987	1.009818	-3.536809
H	-0.620867	-0.761968	-3.604519
H	-2.112073	0.089556	-4.053192
C	0.339406	-0.001065	1.248577
C	-0.303603	0.157054	2.604581
C	0.760175	-0.324884	3.603698
H	0.594040	-1.364856	3.912007
H	0.854957	0.294192	4.500479
H	-1.245321	-0.390744	2.697950
H	-0.545065	1.218848	2.773514
O	-1.754575	0.026168	-2.033389
C	1.765558	-0.148763	1.529818
O	2.738306	-0.172299	0.774285
O	2.008318	-0.261705	2.889286
H	1.519322	4.645262	-1.665828
H	3.127660	2.808928	-2.849224
H	-3.006856	4.477842	0.993807
H	-4.686340	2.511625	1.813231
H	-4.558003	-2.774590	1.691063
H	-2.800374	-4.615769	0.753863
H	1.686401	-4.436882	-1.970806
H	3.214046	-2.466906	-3.040342

C	5.428966	0.570313	2.771865
H	6.383143	0.458035	3.300562
H	4.628532	0.648971	3.523707
H	5.463709	1.525165	2.219029
O	5.267362	-0.547537	1.924950
H	4.374162	-0.467827	1.520515

4-MeOH Triplet

Fe	-0.565547	0.004531	-0.492331
N	-1.336403	1.871329	-0.259388
N	-2.220227	-0.795178	0.367380
N	1.077411	0.815866	-1.345575
N	0.177997	-1.847488	-0.740772
C	-0.731906	3.059189	-0.569005
C	-2.444079	-2.114908	0.663024
C	-2.580761	2.182513	0.219516
C	-3.334611	-0.112071	0.779209
C	1.368756	2.143225	-1.496691
C	-0.364592	-3.029779	-0.311000
C	2.107173	0.124550	-1.919375
C	1.329742	-2.168386	-1.406093
C	-1.621116	4.162590	-0.274774
C	-3.739525	-2.272861	1.286472
C	-2.772979	3.617284	0.207262
C	-4.295697	-1.030300	1.351581
C	2.638792	2.301092	-2.176102
C	0.476139	-4.137217	-0.711255
C	3.091649	1.046265	-2.448813
C	1.521406	-3.602285	-1.401724
C	0.541666	3.196367	-1.115434
C	-1.572619	-3.160535	0.369880
C	2.217270	-1.261229	-1.976707
C	-3.517415	1.267223	0.694435
H	0.897411	4.205211	-1.305303
H	-1.879333	-4.162699	0.655990
H	3.094947	-1.670143	-2.469208
H	-4.461118	1.665369	1.057008
C	-2.137764	-1.064209	-2.699494
H	-1.633374	-2.048218	-2.668414
H	-3.081089	-1.173901	-2.131387
H	-2.419267	-0.882515	-3.753331
C	0.273002	0.162510	1.311701
C	-0.360105	0.871267	2.483396
C	0.518273	0.486136	3.687215
H	0.076352	-0.332283	4.271057
H	0.741437	1.315270	4.365644
H	-1.411342	0.603623	2.631485
H	-0.341947	1.960172	2.316494
O	-1.336927	-0.025360	-2.235593
C	1.577454	-0.251575	1.772510
O	2.525263	-0.773543	1.172406
O	1.757335	0.023534	3.126286
H	3.097362	3.252721	-2.416272
H	4.002618	0.752098	-2.955910
H	-1.382757	5.207512	-0.432640
H	-3.675357	4.122522	0.530169
H	-5.262359	-0.743842	1.748341
H	-4.155885	-3.217027	1.616318
H	0.271821	-5.178355	-0.492829
H	2.357903	-4.113569	-1.862473
C	5.333021	0.819888	1.682158
H	6.396239	1.047632	1.825354
H	4.750534	1.555498	2.262991
H	5.091925	0.973241	0.617705
O	5.109442	-0.508362	2.104672
H	4.170114	-0.706434	1.884759

4-MeOH CSS

Fe	-0.547505	-0.006280	-0.428445
N	-1.651201	1.605042	0.127220
N	-1.994631	-1.212285	0.336679
N	0.817886	1.196083	-1.317966
N	0.482700	-1.620425	-1.094781
C	-1.291752	2.916627	-0.039546
C	-1.961526	-2.581823	0.371974
C	-2.861429	1.612922	0.770322
C	-3.161046	-0.837018	0.950690
C	0.822479	2.563172	-1.294111
C	0.164259	-2.930443	-0.863288
C	1.880565	0.817536	-2.088287
C	1.592988	-1.627408	-1.890815
C	-2.308287	3.784626	0.517597
C	-3.146685	-3.090705	1.029902
C	-3.284914	2.975336	1.015914
C	-3.893563	-2.007823	1.385497
C	1.941507	3.071986	-2.064504
C	1.124261	-3.800505	-1.515183
C	2.591913	1.986837	-2.565869
C	2.005777	-2.989912	-2.161719
C	-0.136711	3.365204	-0.678206
C	-0.952005	-3.381291	-0.161037
C	2.241818	-0.495064	-2.372959
C	-3.575648	0.478971	1.150513
H	0.004967	4.440952	-0.741114
H	-1.069214	-4.456926	-0.058535
H	3.114467	-0.648309	-3.002052
H	-4.524915	0.632193	1.656806
C	-2.776395	0.169707	-2.381859
H	-3.417646	-0.558879	-1.845526
H	-3.123714	1.174587	-2.065308
H	-3.029210	0.077881	-3.457224
C	0.328022	0.032216	1.167580
C	-0.288197	0.286913	2.520888
C	0.761310	-0.181625	3.538908
H	0.554052	-1.191529	3.911910
H	0.896040	0.487262	4.393281
H	-1.251935	-0.213068	2.648876
H	-0.483057	1.365617	2.628167
O	-1.423687	-0.033197	-2.177564
C	1.772363	-0.149222	1.458341
O	2.733843	-0.224162	0.701669
O	2.005888	-0.220782	2.812972
H	2.169704	4.121954	-2.203810
H	3.470232	1.958827	-3.199570
H	-2.268008	4.867365	0.510385
H	-4.211024	3.256599	1.503050
H	-4.851515	-1.985309	1.891386
H	-3.365339	-4.140795	1.183278
H	1.098193	-4.883197	-1.483751
H	2.859301	-3.267424	-2.768399
C	5.436487	0.708604	2.587333
H	6.410662	0.676264	3.089306
H	4.655556	0.779122	3.360470
H	5.399357	1.634319	1.987668

O	5.315105	-0.457788	1.800380
H	4.412178	-0.442595	1.414090

TS1-2l – MeOH OSS

Fe	1.439476	-0.636316	0.247609
N	2.144797	-0.778426	-1.647695
N	0.562230	-2.454101	0.042487
N	2.385057	1.144018	0.486009
N	0.858070	-0.564556	2.201858
C	2.944514	0.133632	-2.287273
C	-0.122969	-3.144247	1.008867
C	1.953148	-1.809328	-2.531973
C	0.556743	-3.252395	-1.075241
C	3.130174	1.800325	-0.455454
C	0.183230	-1.540079	2.888129
C	2.449995	1.904259	1.622684
C	1.146867	0.416738	3.116227
C	3.259414	-0.329633	-3.623927
C	-0.607559	-4.403652	0.477087
C	2.641401	-1.535618	-3.775378
C	-0.182780	-4.469711	-0.816313
C	3.663673	3.033247	0.093485
C	0.012817	-1.152968	4.274448
C	3.240220	3.095964	1.385910
C	0.613328	0.062726	4.414647
C	3.388434	1.339183	-1.745276
C	-0.303148	-2.725483	2.329871
C	1.874882	1.572855	2.846835
C	1.201741	-2.957164	-2.274594
H	4.009407	1.966437	-2.379627
H	-0.851893	-3.393536	2.988680
H	2.020464	2.269918	3.668130
H	1.125559	-3.690708	-3.073323
C	3.629447	-2.632956	0.427922
H	2.965208	-3.513408	0.567156
H	3.878697	-2.606125	-0.654402
H	4.576403	-2.883159	0.951227
C	-0.465747	1.150936	-2.628172
H	-1.207064	1.429940	-3.381621
H	0.513665	1.042003	-3.098995
O	3.108177	-1.449716	0.913385
C	-0.347632	1.740612	-0.412465
O	-0.443949	2.503637	0.548394
O	-0.394009	2.246952	-1.676647
H	4.288468	3.733252	-0.448478
H	3.442596	3.860772	2.126342
H	3.876260	0.206514	-4.335413
H	2.651617	-2.194427	-4.635878
H	-0.333795	-5.267063	-1.534668
H	-1.176634	-5.134984	1.038973
H	-0.490967	-1.747976	5.027066
H	0.705952	0.669638	5.307646
C	-0.225653	0.259964	-0.437265
N	-1.738573	-0.022149	0.896024
H	-1.405067	0.688713	1.543709
H	-1.490422	-0.946126	1.239488
C	-0.844980	-0.080203	-1.787430
H	-0.468454	-1.002893	-2.223954
H	-1.939886	-0.151917	-1.726190
C	-3.096029	0.111532	0.521285
C	-3.699280	1.381427	0.457240
C	-3.837814	-1.012141	0.136192
C	-5.014187	1.510009	0.031899
H	-3.128836	2.261128	0.739732
C	-5.161233	-0.884826	-0.292411
H	-3.379447	-1.997250	0.175483
C	-5.758070	0.380740	-0.347385
H	-5.488372	2.485584	-0.014778
H	-5.709501	-1.775346	-0.577140
O	-7.043089	0.620447	-0.750667
C	-7.833038	-0.487489	-1.159359
H	-8.803276	-0.076255	-1.443588
H	-7.390147	-1.001495	-2.022308
H	-7.970152	-1.208240	-0.342762
C	0.364543	5.584905	-0.882972
H	0.324071	6.664023	-1.072850
H	0.261361	5.063882	-1.847681
H	1.362547	5.347079	-0.480953
O	-0.675491	5.266625	0.020459
H	-0.615618	4.302240	0.193922

TS1-2l – MeOH Triplet

Fe	1.509513	-0.711225	0.176209
N	2.125845	-0.743297	-1.774360
N	0.559076	-2.485871	-0.062284
N	2.430469	1.085767	0.387773
N	0.916467	-0.687693	2.117546
C	2.873565	0.196598	-2.432697
C	-0.158048	-3.185065	0.874870
C	1.926562	-1.773820	-2.664426
C	0.567130	-3.259696	-1.206592
C	3.135277	1.787682	-0.555638
C	0.182317	-1.635549	2.786025
C	2.526163	1.799777	1.559252
C	1.245321	0.275446	3.046402
C	3.139148	-0.236608	-3.782760
C	-0.650811	-4.420568	0.299836
C	2.550043	-1.465525	-3.923276
C	-0.193446	-4.466525	-0.984359
C	3.674038	3.000532	0.031253
C	0.026931	-1.258153	4.165733
C	3.298119	3.004213	1.339536
C	0.695124	-0.070151	4.326315
C	3.340955	1.392990	-1.871864
C	-0.358008	-2.792430	2.198808
C	1.990785	1.428818	2.783405
C	1.203346	-2.942037	-2.398328
H	3.927202	2.049261	-2.508650
H	-0.942155	-3.450621	2.835550
H	2.159461	2.103128	3.619096
H	1.122734	-3.664374	-3.206791
C	3.266383	-2.511118	1.602961
H	3.116424	-2.106349	2.620412
H	2.563412	-3.354336	1.484114
H	4.287149	-2.933516	1.570935
C	-0.541637	1.324221	-2.622088
H	-1.324531	1.623307	-3.324098
H	0.417910	1.271858	-3.143291
O	3.135917	-1.544218	0.608411
C	-0.315754	1.771554	-0.380820
O	-0.367057	2.474740	0.634904
O	-0.457808	2.359043	-1.610232
H	4.268473	3.731773	-0.503293
H	3.518466	3.741455	2.102476

H	3.707969	0.326476	-4.513044
H	2.542070	-2.112250	-4.792959
H	-0.343608	-5.244360	-1.724015
H	-1.247391	-5.153264	0.830270
H	-0.515782	-1.831711	4.907680
H	0.807200	0.521000	5.227558
C	-0.220124	0.306648	-0.490540
N	-1.713863	-0.026880	0.885867
H	-1.353533	0.682743	1.520958
H	-1.459572	-0.957446	1.207161
C	-0.842574	0.028270	-1.847544
H	-0.438462	-0.849637	-2.348935
H	-1.931745	-0.101500	-1.759930
C	-3.069813	0.123603	0.534555
C	-3.661197	1.402277	0.500707
C	-3.832311	-0.986799	0.145138
C	-4.982782	1.550740	0.105738
H	-3.075028	2.270618	0.786676
C	-5.162648	-0.837748	-0.252438
H	-3.384050	-1.977186	0.160031
C	-5.747107	0.435167	-0.274452
H	-5.447628	2.531773	0.084500
H	-5.727007	-1.717500	-0.539484
O	-7.038683	0.695276	-0.645824
C	-7.850604	-0.397883	-1.049518
H	-8.823213	0.027518	-1.303502
H	-7.435502	-0.904833	-1.930400
H	-7.975325	-1.128773	-0.239834
C	0.402409	5.663304	-0.513997
H	0.342668	6.753527	-0.615395
H	0.285865	5.220388	-1.515807
H	1.412857	5.410190	-0.154031
O	-0.612604	5.256225	0.381265
H	-0.547280	4.278772	0.459435

TS1-2l – MeOH CSS

Fe	1.603269	-0.387027	0.235614
N	2.261662	-0.751533	-1.657282
N	0.878588	-2.281660	0.326754
N	2.437403	1.466702	0.184301
N	1.116192	-0.090861	2.190224
C	2.958108	0.117273	-2.455495
C	0.295449	-2.878931	1.413214
C	2.120330	-1.907391	-2.377223
C	0.895101	-3.225813	-0.667285
C	3.093739	2.032559	-0.875132
C	0.546292	-1.005745	3.034813
C	2.500032	2.375920	1.202893
C	1.372266	1.021321	2.946860
C	3.260065	-0.506554	-3.728948
C	-0.101963	-4.235778	1.087145
C	2.738645	-1.764883	-3.680255
C	0.271851	-4.450578	-0.205272
C	3.564623	3.360179	-0.524358
C	0.408361	-0.445028	4.365592
C	3.196857	3.572205	0.768462
C	0.922945	0.814753	4.310166
C	3.325926	1.416319	-2.104125
C	0.136045	-2.290757	2.670600
C	1.999554	2.177368	2.487972
C	1.467892	-3.057042	-1.927175
H	3.871356	1.991563	-2.848200
H	-0.327883	-2.898186	3.443654
H	2.131103	2.986323	3.202190
H	1.420963	-3.900990	-2.610911
C	3.955461	-2.194454	0.603490
H	3.361014	-3.075565	0.933754
H	4.136710	-2.344802	-0.483652
H	4.948869	-2.306658	1.089896
C	-0.550410	0.971035	-2.691361
H	-1.352333	1.101035	-3.422308
H	0.414553	0.947782	-3.202786
O	3.387276	-0.978195	0.917914
C	-0.395829	1.737230	-0.531705
O	-0.537885	2.548318	0.378197
O	-0.575086	2.136597	-1.820872
H	4.113915	4.018164	-1.187428
H	3.380521	4.441757	1.388383
H	3.806083	-0.033680	-4.536744
H	2.771346	-2.537859	-4.439216
H	0.159896	-5.350914	-0.798029
H	-0.581523	-4.923308	1.774083
H	-0.015916	-0.964446	5.216782
H	1.009808	1.543245	5.107689
C	-0.075539	0.277130	-0.471352
N	-1.671981	-0.003888	0.980509
H	-1.432580	0.840217	1.494095
H	-1.292033	-0.824514	1.442335
C	-0.734319	-0.229044	-1.746350
H	-0.282342	-1.136625	-2.140978
H	-1.807554	-0.412983	-1.603950
C	-3.019758	-0.115702	0.587196
C	-3.798932	1.031394	0.337566
C	-3.585141	-1.378211	0.362014
C	-5.108189	0.901028	-0.106844
H	-3.383159	2.025039	0.487015
C	-4.902028	-1.508964	-0.085953
H	-2.990375	-2.270421	0.542327
C	-5.673787	-0.365671	-0.322685
H	-5.716587	1.780722	-0.294489
H	-5.307592	-2.501833	-0.242998
O	-6.971083	-0.375426	-0.760527
C	-7.583522	-1.633781	-1.002755
H	-8.597379	-1.414757	-1.342747
H	-7.053692	-2.196919	-1.782188
H	-7.631164	-2.242093	-0.090065
C	-2.789071	4.836375	-1.119042
H	-3.735348	5.385898	-1.171059
H	-2.837440	3.997259	-1.828385
H	-1.985179	5.512989	-1.450064
O	-2.615898	4.406901	0.220021
H	-1.799015	3.863791	0.250612

5l – MeOH OSS

Fe	1.510319	-0.691430	0.307847
N	1.610789	-1.885765	-1.295248
N	0.181837	-2.007981	1.204891
N	2.765910	0.625900	-0.583690
N	1.312654	0.515329	1.893463
C	2.413618	-1.708634	-2.409617
C	-0.343928	-1.935570	2.490631
C	0.979978	-3.096909	-1.470582

C	-0.233738	-3.220918	0.693921
C	3.421159	0.465965	-1.782815
C	0.588846	0.290399	3.058302
C	3.227612	1.798630	-0.052169
C	1.966330	1.716302	2.081165
C	2.252904	-2.822901	-3.318206
C	-1.114373	-3.100566	2.771137
C	1.365030	-3.678679	-2.745165
C	-1.048968	-3.905857	1.651449
C	4.297879	1.574597	-2.022419
C	0.770690	1.399759	3.973697
C	4.177539	2.411907	-0.940569
C	1.619728	2.274201	3.375675
C	3.251176	-0.631675	-2.637547
C	-0.170698	-0.830253	3.341528
C	2.845151	2.315550	1.197668
C	0.116876	-3.712164	-0.575024
H	3.828204	-0.636583	-3.559247
H	-0.665577	-0.866043	4.308688
H	3.283634	3.263407	1.497641
H	-0.290028	-4.678666	-0.860636
C	3.002732	-2.306231	2.164244
H	2.575997	-1.779121	3.036332
H	2.428420	-3.244184	2.040147
H	4.033690	-2.597635	2.439543
C	0.002455	0.944275	-2.925266
H	-0.471912	1.217876	-3.870630
H	1.023663	0.607141	-3.104346
O	3.046803	-1.526472	1.012293
C	-0.261491	1.829363	-0.838722
O	-0.424210	2.708021	0.017888
O	0.064387	2.151727	-2.113421
H	4.926228	1.691645	-2.897908
H	4.684476	3.351418	-0.754753
H	2.769069	-2.922414	-4.266184
H	1.001467	-4.627638	-3.121742
H	-1.498755	-4.880126	1.500100
H	-1.637585	-3.289736	3.701387
H	0.306804	1.470169	4.950804
H	1.995834	3.216465	3.756371
C	-0.435663	0.395398	-0.691225
N	-1.444085	0.152004	0.402881
H	-1.204997	0.853025	1.118275
H	-1.188678	-0.763360	0.816208
C	-0.798594	-0.073067	-2.093368
H	-0.497218	-1.095664	-2.323384
H	-1.873536	0.030395	-2.306895
C	-2.884783	0.198183	0.107299
C	-3.527016	1.424953	-0.089963
C	-3.590722	-0.996047	0.017822
C	-4.885247	1.442530	-0.377754
H	-2.968191	2.352337	-0.016877
C	-4.957714	-0.981230	-0.273719
H	-3.083878	-1.944293	0.180415
C	-5.610056	0.241813	-0.474264
H	-5.408445	2.380899	-0.530659
H	-5.493478	-1.920557	-0.337923
O	-6.934398	0.373440	-0.762059
C	-7.720951	-0.807498	-0.878787
H	-8.731617	-0.470324	-1.113536
H	-7.355668	-1.453301	-1.686874
H	-7.735187	-1.373703	0.060752
C	-0.245633	6.162706	0.023722
H	-0.562010	7.197560	-0.151962
H	0.800583	6.068893	-0.310453
H	-0.266135	5.984918	1.111921
O	-1.124569	5.315088	-0.685952
H	-0.828078	4.393537	-0.521132

5 – MeOH Triplet

Fe	1.359407	-0.832515	0.269225
N	1.715589	-1.559681	-1.587133
N	-0.042917	-2.305816	0.612431
N	2.680156	0.667426	-0.086898
N	0.929082	-0.081370	2.108642
C	2.662349	-1.117455	-2.485164
C	-0.721213	-2.584138	1.795636
C	1.139849	-2.682323	-2.141370
C	-0.381036	-3.317385	-0.270521
C	3.493338	0.823267	-1.185820
C	0.126906	-0.639027	3.089944
C	3.044630	1.650089	0.804530
C	1.555258	1.010513	2.689368
C	2.663878	-1.975765	-3.657063
C	-1.516710	-3.748727	1.635671
C	1.724541	-2.934254	-3.449266
C	-1.305642	-4.206545	0.340451
C	4.367004	1.935979	-0.999067
C	0.215166	0.157992	4.300541
C	4.085063	2.455613	0.249519
C	1.089869	1.168169	4.052164
C	3.478901	-0.016263	-2.320338
C	-0.645537	-1.778319	2.957855
C	2.504908	1.813235	2.096953
C	0.161027	-3.470428	-1.567664
H	4.179042	0.216451	-3.118391
H	-1.234713	-2.090078	3.815749
H	2.896514	2.636572	2.688597
H	-0.193080	-4.320805	-2.144938
C	2.714352	-2.600441	2.073748
H	2.572608	-1.963930	2.963132
H	1.914543	-3.359613	2.083117
H	3.674476	-3.130907	2.198257
C	0.083637	1.263045	-2.744076
H	-0.357674	1.689101	-3.648130
H	1.083890	0.885666	-2.958291
O	2.762628	-1.869447	0.883874
C	-0.148505	1.892883	-0.557705
O	-0.242209	2.660532	0.402799
O	0.211981	2.347753	-1.780606
H	5.104397	2.273988	-1.717752
H	4.551909	3.296351	0.749183
H	3.313663	-1.843318	-4.514438
H	1.444717	-3.755972	-4.098456
H	-1.726198	-5.086258	-0.132934
H	-2.152297	-4.176853	2.401954
H	-0.325176	-0.055976	5.215397
H	1.414702	1.955536	4.722434
C	-0.429256	0.458805	-0.599537
N	-1.495449	0.142492	0.421371
H	-1.185661	0.640380	1.266923
H	-1.369481	-0.859837	0.639709
C	-0.796765	0.206816	-2.056263
H	-0.569319	-0.797923	-2.412943

H	-1.858010	0.417035	-2.258533
C	-2.913378	0.413729	0.138165
C	-3.416883	1.715863	0.216291
C	-3.741318	-0.648943	-0.207580
C	-4.759267	1.943261	-0.056657
H	-2.762307	2.537091	0.488138
C	-5.092262	-0.422537	-0.484549
H	-3.343003	-1.659700	-0.256156
C	-5.606130	0.878557	-0.410333
H	-5.176595	2.943273	0.002219
H	-5.723866	-1.261548	-0.750245
O	-6.902695	1.212614	-0.656451
C	-7.811425	0.176692	-1.014774
H	-8.775986	0.664618	-1.162294
H	-7.507535	-0.317987	-1.945547
H	-7.899998	-0.571437	-0.217330
C	1.441962	5.465996	-0.805055
H	1.723861	6.520797	-0.906327
H	1.231232	5.069334	-1.810916
H	2.308943	4.914738	-0.408925
O	0.317712	5.400853	0.051090
H	0.113386	4.449066	0.175132

5 – MeOH CSS

Fe	1.323180	-0.908119	0.268054
N	1.270638	-1.982478	-1.432445
N	-0.182560	-2.064876	1.055767
N	2.769419	0.257528	-0.499171
N	1.305040	0.191396	1.965807
C	2.102705	-1.850460	-2.513905
C	-0.681598	-2.033784	2.345239
C	0.454307	-3.047846	-1.711734
C	-0.774576	-3.150354	0.446702
C	3.411063	0.092275	-1.698122
C	0.558844	-0.021010	3.102294
C	3.365986	1.332326	0.104264
C	2.094187	1.282330	2.234932
C	1.787940	-2.846213	-3.520249
C	-1.625433	-3.108330	2.539767
C	0.758971	-3.587178	-3.024907
C	-1.687413	-3.797948	1.361293
C	4.439048	1.101756	-1.865083
C	0.874514	0.975920	4.106680
C	4.408254	1.876220	-0.745896
C	1.827177	1.784592	3.567046
C	3.109225	-0.894351	-2.635929
C	-0.355097	-1.059462	3.288405
C	3.045114	1.818381	1.370699
C	-0.504847	-3.581842	-0.851737
H	3.700739	-0.910057	-3.548230
H	-0.849452	-1.117425	4.254859
H	3.601968	2.682318	1.724701
H	-1.059698	-4.446312	-1.208463
C	2.977007	-2.343867	2.218288
H	3.436398	-1.435749	2.669988
H	2.115892	-2.604609	2.871136
H	3.720479	-3.157178	2.363178
C	0.123853	1.272861	-2.820777
H	-0.254844	1.695205	-3.754897
H	1.086146	0.789652	-2.994811
O	2.657734	-2.217173	0.881236
C	-0.094429	1.998451	-0.668056
O	-0.130584	2.811894	0.271295
O	0.336800	2.381690	-1.902554
H	5.087115	1.189907	-2.729196
H	5.027612	2.730245	-0.498438
H	2.301659	-2.953288	-4.468521
H	0.254643	-4.431461	-3.480374
H	-2.276012	-4.678162	1.130093
H	-2.160688	-3.304259	3.461444
H	0.420944	1.029727	5.089474
H	2.316207	2.641745	4.014593
C	-0.498850	0.624509	-0.676353
N	-1.507780	0.377390	0.401625
H	-1.193471	0.985265	1.171803
H	-1.348115	-0.591974	0.730037
C	-0.862725	0.321419	-2.115975
H	-0.695077	-0.712696	-2.424385
H	-1.901897	0.593158	-2.364918
C	-2.938652	0.600605	0.132335
C	-3.434796	1.902435	0.015170
C	-3.778186	-0.496455	-0.016687
C	-4.784358	2.095095	-0.247624
H	-2.766973	2.749871	0.133064
C	-5.137405	-0.306201	-0.283594
H	-3.383682	-1.504892	0.080441
C	-5.645201	0.993586	-0.399740
H	-5.196975	3.094809	-0.337140
H	-5.779346	-1.171699	-0.394543
O	-6.948946	1.294089	-0.653869
C	-7.869797	0.220605	-0.816674
H	-8.838222	0.685103	-1.008144
H	-7.596651	-0.415677	-1.667612
H	-7.933521	-0.393287	0.090362
C	2.033367	5.335811	-0.442324
H	2.400018	6.314216	-0.775672
H	2.318010	4.587459	-1.197515
H	2.559982	5.080649	0.493336
O	0.634276	5.429265	-0.273027
H	0.317423	4.516387	-0.087272

Fe(II)-Porph + 3l-ylide – MeOH

Fe	1.492126	-1.099635	0.391546
N	1.498228	-1.955229	-1.444410
N	-0.187561	-2.146399	0.847261
N	2.939228	0.168937	-0.204362
N	1.233259	-0.001231	2.065722
C	2.392788	-1.719704	-2.459693
C	-0.880816	-2.121841	2.037918
C	0.662022	-2.942745	-1.909926
C	-0.786607	-3.127744	0.088382
C	3.644514	0.124157	-1.383158
C	0.337090	-0.237015	3.084803
C	3.453720	1.236264	0.493642
C	1.973021	1.086987	2.467774
C	2.115492	-2.577510	-3.592470
C	-1.938068	-3.107545	2.028602
C	1.036575	-3.335579	-3.252363
C	-1.882352	-3.729484	0.815022
C	4.643197	1.172317	-1.418703
C	0.520132	0.722901	4.152451
C	4.522396	1.865213	-0.253457
C	1.532586	1.547906	3.766163
C	3.408513	-0.768375	-2.424188

C	-0.627761	-1.239891	3.086666
C	3.010543	1.661887	1.740954
C	-0.395365	-3.496544	-1.195832
H	4.046436	-0.689226	-3.300921
H	-1.259876	-1.320446	3.967376
H	3.507735	2.522812	2.179930
H	-0.966988	-4.283010	-1.682404
C	3.420689	-2.171360	2.218095
H	4.076795	-1.285665	2.089496
H	2.838471	-1.994087	3.147416
H	4.095229	-3.024363	2.436583
C	0.177752	1.673252	-2.946884
H	-0.084052	2.022710	-3.948548
H	1.209011	1.300748	-2.944197
O	2.643024	-2.460797	1.108964
C	-0.365722	2.353603	-0.836278
O	-0.461968	3.126559	0.147392
O	0.111097	2.812372	-2.052846
H	5.325062	1.348827	-2.242093
H	5.086461	2.727432	0.081760
H	2.678194	-2.580616	-4.518597
H	0.530646	-4.092680	-3.839923
H	-2.511593	-4.526927	0.437241
H	-2.626251	-3.285229	2.846593
H	-0.065185	0.752992	5.063909
H	1.951491	2.395255	4.295660
C	-0.705773	1.012366	-0.947920
N	-1.522551	0.476614	0.151998
H	-1.220240	1.029263	0.969433
H	-1.283285	-0.497718	0.364321
C	-0.780728	0.595478	-2.382684
H	-0.394945	-0.407758	-2.603345
H	-1.789095	0.673662	-2.828679
C	-2.999615	0.579269	0.016934
C	-3.585239	1.847339	-0.013423
C	-3.765412	-0.571290	-0.101153
C	-4.961255	1.951458	-0.153364
H	-2.963562	2.732200	0.081884
C	-5.153184	-0.467889	-0.250413
H	-3.299948	-1.553514	-0.069879
C	-5.754996	0.796071	-0.275613
H	-5.447762	2.921321	-0.169476
H	-5.742352	-1.372207	-0.342393
O	-7.091559	1.014274	-0.410920
C	-7.952169	-0.113079	-0.536122
H	-8.960876	0.291610	-0.630280
H	-7.711276	-0.702762	-1.429174
H	-7.899238	-0.756829	0.350540
C	1.997644	5.329058	-0.553002
H	2.530528	6.277837	-0.691863
H	2.000665	4.790793	-1.513741
H	2.571950	4.721398	0.165946
O	0.692658	5.623937	-0.101797
H	0.230660	4.757498	-0.007164

3l-ylide

C	-0.961000	-0.414096	3.351264
H	-0.426533	-0.133104	4.266831
H	-1.943699	-0.810791	3.617789
C	-0.192291	0.793221	1.569339
O	-0.123278	1.721769	0.742809
O	-1.164884	0.779936	2.560082
C	0.599014	-0.355299	1.677250
N	1.345778	-0.618158	0.429440
H	1.375797	0.329119	0.006309
C	-0.102678	-1.388168	2.502719
H	-0.737965	-2.082267	1.923506
H	0.533140	-1.999850	3.157035
C	0.750142	-1.562979	-0.547197
C	1.312139	-2.825184	-0.726413
C	-0.391260	-1.178005	-1.242594
C	0.725973	-3.711739	-1.623409
H	2.201229	-3.120561	-0.175121
C	-0.978472	-2.062893	-2.147305
H	-0.814849	-0.191143	-1.082216
C	-0.421202	-3.336866	-2.340936
H	1.142236	-4.700849	-1.783215
H	-1.861367	-1.750338	-2.691445
O	-0.914244	-4.272249	-3.195031
C	-2.077570	-3.953726	-3.954536
H	-1.901030	-3.095210	-4.613765
H	-2.288324	-4.837217	-4.558452
H	-2.934676	-3.744297	-3.303260
H	2.317353	-0.897475	0.602908

TS-3l-enol

C	-3.626597	-1.200671	1.039172
H	-4.527827	-0.753857	1.469846
H	-3.625734	-2.275024	1.229454
C	-2.868386	-0.004911	-0.693524
O	-2.630153	0.459984	-1.874084
O	-3.712427	-1.025224	-0.417569
C	-2.188271	0.474037	0.389154
N	-1.134773	1.338698	-0.133658
H	-1.664974	1.183245	-1.308232
C	-2.346174	-0.464531	1.546490
H	-1.501935	-1.161031	1.680235
H	-2.545088	-0.003123	2.522193
C	0.251194	0.900219	-0.040679
C	1.225984	1.755374	0.480357
C	0.613173	-0.365523	-0.497223
C	2.553504	1.346172	0.542534
H	0.949934	2.743715	0.840941
C	1.943573	-0.785058	-0.434321
H	-0.142037	-1.027497	-0.909436
C	2.923138	0.071471	0.087384
H	3.320162	1.999697	0.946387
H	2.201096	-1.772938	-0.797395
O	4.246623	-0.237754	0.195532
C	4.679568	-1.515958	-0.256820
H	4.483592	-1.649659	-1.327985
H	5.755677	-1.546399	-0.079600
H	4.195800	-2.325183	0.304415
H	-1.204304	2.309884	0.176380

3l-enol

C	-0.639509	-0.476275	3.774413
H	-0.613727	-1.527074	4.082450
H	-1.192776	0.104364	4.514009
C	1.146969	0.018944	2.491250
O	2.447409	0.291007	2.300248
O	0.739824	0.011585	3.790168

C	0.183413	-0.199665	1.577638
N	0.358607	-0.149417	0.177422
H	0.179409	0.755028	-0.247941
C	-1.138475	-0.319385	2.324043
H	-1.767230	0.575182	2.194965
H	-1.737236	-1.183565	2.014580
C	-0.016051	-1.226221	-0.643827
C	-0.028741	-2.549497	-0.163754
C	-0.344416	-1.012851	-1.990399
C	-0.360497	-3.607572	-1.002409
H	0.236088	-2.740788	0.871741
C	-0.670560	-2.074907	-2.838617
H	-0.343890	0.000271	-2.387921
C	-0.684553	-3.384785	-2.347805
H	-0.368920	-4.627024	-0.627246
H	-0.916101	-1.862135	-3.873111
O	-0.996825	-4.499675	-3.087327
C	-1.327036	-4.314983	-4.454482
H	-0.495282	-3.868162	-5.015634
H	-1.535405	-5.309908	-4.852872
H	-2.218116	-3.684097	-4.574793
H	2.892106	0.258759	3.164856

3l-ylide – MeOH

C	-3.643194	0.175148	-1.217373
H	-4.531296	-0.448453	-1.370380
H	-3.660473	1.006958	-1.924800
C	-2.881194	-0.021343	0.925112
O	-2.768622	0.222548	2.151420
O	-3.712484	0.732783	0.119850
C	-2.242410	-0.993676	0.167651
N	-1.081840	-1.598890	0.841639
H	-1.287630	-1.421267	1.840616
C	-2.354797	-0.685942	-1.292266
H	-1.505782	-0.110420	-1.700765
H	-2.513410	-1.547045	-1.954862
C	0.262757	-1.052197	0.521377
C	1.175322	-1.825127	-0.192788
C	0.570221	0.243853	0.920220
C	2.419858	-1.290630	-0.507922
H	0.925535	-2.836608	-0.503412
C	1.820078	0.780387	0.611098
H	-0.158268	0.828472	1.473911
C	2.751357	0.014062	-0.108122
H	3.150513	-1.868381	-1.064104
H	2.054973	1.787153	0.934135
O	3.990802	0.441879	-0.462467
C	4.388210	1.760120	-0.091827
H	4.397180	1.882440	0.997895
H	5.400246	1.884022	-0.479054
H	3.731061	2.515182	-0.539691
H	-1.053147	-2.618369	0.727342
H	-3.989352	1.233059	2.977032
O	-4.625813	1.840959	3.419040
C	-4.544042	3.075176	2.739111
H	-5.319319	3.736633	3.143372
H	-3.570992	3.578289	2.879156
H	-4.712400	2.973357	1.655850

TS-3l-enol – MeOH

C	4.070185	-0.516816	-0.662258
H	4.880430	-0.140126	-1.292639
H	4.256042	-1.561995	-0.412704
C	3.099206	1.106074	0.526931
O	2.779511	1.968248	1.456987
O	4.129871	0.239363	0.602156
C	2.317904	0.984079	-0.572607
N	1.132745	1.803452	-0.358178
H	1.710825	2.223280	0.764058
C	2.677847	-0.261001	-1.325411
H	1.982697	-1.097267	-1.152903
H	2.795703	-0.150880	-2.410616
C	-0.150730	1.131698	-0.190870
C	-1.181348	1.353688	-1.108174
C	-0.353326	0.278046	0.892890
C	-2.410847	0.725009	-0.943985
H	-1.024429	2.017627	-1.955152
C	-1.584749	-0.359944	1.058767
H	0.431158	0.118733	1.628982
C	-2.620789	-0.140541	0.139985
H	-3.220360	0.888264	-1.648274
H	-1.724415	-1.013181	1.911958
O	-3.856473	-0.712242	0.212750
C	-4.128407	-1.595175	1.295691
H	-4.041219	-1.083349	2.262087
H	-5.157078	-1.930836	1.155654
H	-3.457689	-2.463359	1.283363
H	1.033464	2.563911	-1.033638
H	2.236959	1.020371	2.959828
O	1.862969	0.349538	3.569115
C	2.921614	-0.515698	3.950055
H	3.651130	-0.017358	4.607814
H	2.482734	-1.351414	4.504813
H	3.464011	-0.919420	3.083488

3l-enol – MeOH

C	-3.432048	1.150484	-1.075149
H	-4.408003	0.895820	-1.490406
H	-3.052230	2.050207	-1.568067
C	-2.672256	0.869387	1.016752
O	-2.638166	1.171573	2.329772
O	-3.647785	1.500753	0.334649
C	-1.892790	0.027587	0.319077
N	-0.883251	-0.755436	0.932342
C	-2.404318	-0.008510	-1.110009
H	-1.625737	0.175256	-1.859649
H	-2.874724	-0.971273	-1.358581
C	0.469604	-0.623338	0.528789
C	1.357535	-1.701475	0.691780
C	0.972193	0.576372	0.013882
C	2.699576	-1.577867	0.354634
H	0.990306	-2.645687	1.088829
C	2.321771	0.704775	-0.331790
H	0.304189	1.423088	-0.112474
C	3.197079	-0.372722	-0.162769
H	3.382067	-2.413024	0.481397
H	2.671321	1.651073	-0.729130
O	4.533844	-0.355943	-0.468082
C	5.079724	0.845155	-0.992435
H	4.976942	1.678526	-0.284871
H	6.139465	0.646151	-1.162388
H	4.606618	1.122723	-1.943695

H	-1.140931	-1.731039	1.061764
H	-4.397324	0.984125	3.212038
O	-5.307193	0.866642	3.537211
C	-6.076804	1.939325	3.019193
H	-7.117690	1.765196	3.310115
H	-5.769383	2.915831	3.426773
H	-6.028694	1.997290	1.922043
H	-1.921349	0.624906	2.710202

aliphatic-3l-ylide

C	-4.810969	0.351389	-0.915114
H	-5.216364	0.838505	-0.021376
H	-5.391063	0.649223	-1.791663
C	-2.554482	0.455544	-0.201141
O	-2.897787	-0.202454	0.825981
O	-3.473494	0.768704	-1.178459
C	-1.262939	0.910824	-0.429898
N	-0.390260	0.453457	0.672807
H	-1.098220	-0.081127	1.239441
C	-0.649023	1.615510	-1.589150
H	-0.132847	2.547857	-1.309275
H	0.085352	1.002568	-2.142474
C	0.274519	1.483428	1.498588
C	1.657423	1.458328	1.667063
C	-0.500240	2.466503	2.102889
C	2.270780	2.428908	2.452355
H	2.259079	0.689329	1.188081
C	0.108264	3.437805	2.898215
H	-1.574251	2.475152	1.946536
C	1.500847	3.423760	3.074974
H	3.346554	2.435231	2.593599
H	-0.507211	4.195147	3.368528
O	2.193345	4.325642	3.821792
C	1.469688	5.364513	4.475197
H	0.750332	4.958087	5.196522
H	2.215986	5.959050	5.003833
H	0.942787	5.999857	3.752876
H	0.326364	-0.217714	0.363053
H	-4.874476	-0.732583	-0.777721
H	-1.439984	1.882780	-2.295328

TS-aliphatic-3l-enol

C	-4.778807	-1.439536	-0.375854
H	-4.251375	-2.289005	-0.820932
H	-5.570615	-1.798867	0.283946
C	-2.846487	-0.093470	-0.154520
O	-2.662164	-0.228146	-1.439335
O	-3.908981	-0.667014	0.457048
C	-1.937438	0.650162	0.559150
N	-0.956538	1.132311	-0.428822
H	-1.577724	0.534636	-1.320605
C	-1.883348	1.043532	1.994562
H	-0.941816	0.748890	2.482308
H	-1.996346	2.129239	2.150307
C	0.440255	0.747326	-0.285395
C	1.451505	1.665975	-0.581517
C	0.773834	-0.548264	0.100273
C	2.786433	1.288009	-0.493795
H	1.197858	2.680580	-0.880648
C	2.113017	-0.935055	0.191889
H	-0.016144	-1.253571	0.338391
C	3.128599	-0.016776	-0.106638
H	3.581250	1.992621	-0.717033
H	2.347827	-1.948290	0.495935
O	4.464284	-0.288129	-0.046966
C	4.868815	-1.596003	0.341039
H	4.495823	-2.355371	-0.357626
H	5.959685	-1.589949	0.319549
H	4.526717	-1.837598	1.355255
H	-1.011326	2.143330	-0.586140
H	-5.207727	-0.828967	-1.175943
H	-2.698896	0.552095	2.534348

aliphatic-3l-enol

C	-4.968353	0.381563	-0.603459
H	-5.204438	0.777293	0.387543
H	-5.616766	0.841209	-1.350663
C	-2.620757	0.232485	-0.253748
O	-2.935741	-0.018058	1.040407
O	-3.632413	0.724807	-0.997036
C	-1.380183	0.033413	-0.752687
N	-0.413609	-0.435545	0.210772
C	-0.983401	0.247546	-2.185655
H	-0.189763	1.001549	-2.279535
H	-0.597140	-0.678986	-2.636261
C	0.701700	0.379653	0.545116
C	1.912059	-0.214085	0.943773
C	0.617132	1.776043	0.548101
C	2.994269	0.563953	1.336895
H	2.003590	-1.298443	0.946738
C	1.705194	2.564715	0.936627
H	-0.309825	2.253921	0.245819
C	2.903081	1.963430	1.336327
H	3.927660	0.101366	1.643885
H	1.599716	3.643700	0.922133
O	4.027644	2.639415	1.735593
C	3.978154	4.058120	1.752594
H	3.207897	4.427603	2.442475
H	4.959133	4.390231	2.097567
H	3.788748	4.468245	0.751728
H	-0.118626	-1.393677	0.033023
H	-5.113559	-0.704522	-0.606874
H	-1.837785	0.580825	-2.780753
H	-2.091821	-0.353470	1.418630

TS-intra-3l

C	-3.37830	1.46080	-1.04600
H	-4.00810	1.11510	-1.87300
H	-3.40570	2.55130	-1.00070
C	-3.21460	-0.15560	0.57120
O	-3.45060	-0.76150	1.61130
O	-3.93600	0.95490	0.19340
C	-2.20950	-0.41090	-0.42050
N	-1.05590	-1.33550	0.14270
H	-1.38900	-1.64970	1.05940
C	-1.95140	0.87430	-1.15490
H	-1.21960	1.52670	-0.65340
H	-1.64860	0.77070	-2.20190
C	0.31510	-0.90280	0.06120
C	1.17050	-1.49060	-0.87730
C	0.79780	0.09800	0.90630
C	2.49400	-1.07840	-0.96940

H	0.79500	-2.27570	-1.52690
C	2.12980	0.50970	0.82920
H	0.13580	0.55550	1.63620
C	2.98450	-0.07650	-0.11590
H	3.17010	-1.52460	-1.69160
H	2.48490	1.28140	1.50170
O	4.29430	0.25220	-0.28200
C	4.85220	1.26130	0.55450
H	4.80880	0.97320	1.61190
H	5.89460	1.35850	0.24810
H	4.34120	2.22210	0.41710
H	-1.77120	-1.65730	-0.73810

3-ylide - H_2O

C	-2.93750	-1.34700	1.61840
H	-3.90640	-0.91100	1.88920
H	-2.70210	-2.16050	2.30810
C	-2.51150	-1.00900	-0.60030
O	-2.45710	-1.24840	-1.81370
O	-3.05050	-1.91420	0.28970
C	-2.06280	0.13940	0.10170
N	-1.05360	0.89040	-0.70400
H	-1.27310	0.57960	-1.66740
C	-1.84820	-0.25240	1.54030
H	-0.85070	-0.67520	1.74750
H	-2.03580	0.53200	2.28310
C	0.37800	0.66430	-0.43300
C	1.11570	1.63290	0.24700
C	0.96530	-0.53090	-0.83530
C	2.45910	1.40170	0.51950
H	0.64870	2.56220	0.56220
C	2.31440	-0.76550	-0.56630
H	0.37480	-1.27580	-1.36070
C	3.06810	0.20250	0.11520
H	3.05650	2.13910	1.04540
H	2.76240	-1.69650	-0.89150
O	4.38470	0.07510	0.42760
C	5.06050	-1.12160	0.05000
H	5.06030	-1.25370	-1.03880
H	6.08670	-1.00600	0.40090
H	4.60960	-2.00140	0.52480
H	-1.29170	1.89790	-0.65610
H	-3.09900	1.87910	0.05340
O	-2.95040	2.84470	-0.13910
H	-3.48610	3.01240	-0.93120

TS-3l - H_2O

C	-2.97390	-1.17370	1.70040
H	-3.81660	-0.60430	2.10560
H	-2.78800	-2.04550	2.32990
C	-2.78950	-0.85270	-0.55770
O	-2.89710	-1.06640	-1.75720
O	-3.35020	-1.66130	0.38290
C	-2.08000	0.24780	0.09980
N	-0.99960	0.79270	-0.81820
H	-1.23850	0.42360	-1.75080
C	-1.73820	-0.27870	1.48140
H	-0.81790	-0.87790	1.50120
H	-1.66260	0.49390	2.25240
C	0.40710	0.55980	-0.50670
C	1.09490	1.50280	0.26220
C	1.04850	-0.58900	-0.95900
C	2.43090	1.28960	0.57430
H	0.58510	2.39760	0.60770
C	2.39320	-0.80660	-0.65040
H	0.50830	-1.31930	-1.55540
C	3.09050	0.13410	0.12110
H	2.98710	2.00900	1.16630
H	2.87990	-1.70290	-1.01530
O	4.39670	0.02260	0.47880
C	5.12350	-1.12550	0.04910
H	5.16630	-1.18400	-1.04530
H	6.13230	-1.00350	0.44550
H	4.68430	-2.04800	0.44750
H	-1.29190	1.84000	-0.78840
H	-2.65960	1.46290	0.13320
O	-2.47430	2.73260	-0.10320
H	-3.11390	2.94130	-0.80460

3l - H_2O

C	-3.00000	-2.05900	-0.74540
H	-4.05070	-2.20420	-0.47460
H	-2.67670	-2.88050	-1.38620
C	-2.46770	0.19140	-0.79150
O	-2.35860	1.30510	-1.25590
O	-2.91140	-0.84040	-1.53530
C	-2.20730	-0.28810	0.64840
N	-1.12200	0.42160	1.33780
H	-1.38210	2.45060	1.14180
C	-2.10600	-1.81490	0.47180
H	-1.07130	-2.09390	0.25030
H	-2.43760	-2.37200	1.35140
C	0.22860	0.15680	0.91160
C	1.04560	-0.76230	1.58930
C	0.76630	0.86340	-0.16800
C	2.36100	-0.97380	1.19170
H	0.64920	-1.31210	2.44010
C	2.07920	0.64040	-0.59050
H	0.16100	1.61770	-0.65730
C	2.88540	-0.28170	0.08910
H	2.99830	-1.67780	1.71780
H	2.46450	1.20680	-1.43040
O	4.18040	-0.56850	-0.23180
C	4.76640	0.11280	-1.33500
H	4.79430	1.19690	-1.16860
H	5.78630	-0.26710	-1.41340
H	4.22790	-0.09630	-2.26790
H	-1.20980	0.23260	2.33350
H	-3.12670	-0.04410	1.19860
O	-1.58710	3.30410	0.70980
H	-1.96760	2.97880	-0.12340

3l-ylide 2 H_2O

C	2.89840	-2.17670	1.02850
H	2.99430	-1.86160	2.07480
H	3.20690	-3.22030	0.93720
C	3.07550	-0.35870	-0.35760
O	3.66350	0.46200	-1.07990
O	3.79960	-1.37530	0.22970
C	1.70870	-0.46130	0.03770

N	0.74550	0.13870	-0.93340
H	0.80690	-0.31420	-1.85760
C	1.48520	-1.88240	0.49570
H	1.22850	-2.57270	-0.32890
H	0.73060	-2.01250	1.27900
C	-0.67020	0.11930	-0.52600
C	-1.09290	0.88040	0.56810
C	-1.57580	-0.64620	-1.24910
C	-2.43410	0.86710	0.92480
H	-0.38370	1.47140	1.13820
C	-2.92770	-0.66200	-0.89240
H	-1.24220	-1.23900	-2.09720
C	-3.36240	0.09870	0.19960
H	-2.78920	1.45140	1.76740
H	-3.61860	-1.26500	-1.46880
O	-4.64810	0.16100	0.63640
C	-5.63770	-0.59120	-0.05990
H	-5.71840	-0.27210	-1.10620
H	-6.57890	-0.39150	0.45370
H	-5.42240	-1.66600	-0.02160
H	1.06300	1.14710	-1.08140
H	1.84540	1.06240	1.34560
O	1.82350	2.00540	1.68100
O	1.92890	2.59160	-1.02390
H	1.92090	2.66240	-0.03770
H	2.73720	2.04740	-1.18650
H	2.65930	2.12300	2.16070

TS-3l 2 H_2O

C	2.94090	-2.13750	1.00030
H	3.19650	-1.82850	2.01920
H	3.15630	-3.20030	0.87980
C	3.11020	-0.36840	-0.45290
O	3.62250	0.38970	-1.26490
O	3.80170	-1.41010	0.08260
C	1.75680	-0.32140	0.13400
N	0.77430	0.24680	-0.86230
H	0.89080	-0.19450	-1.78160
C	1.50370	-1.73580	0.62900
H	1.11090	-2.39660	-0.15850
H	0.83250	-1.79770	1.48990
C	-0.64480	0.16560	-0.48120
C	-1.09220	0.81510	0.67480
C	-1.52780	-0.53490	-1.29400
C	-2.43950	0.74950	1.00280
H	-0.38630	1.34950	1.30690
C	-2.88510	-0.59770	-0.96540
H	-1.17460	-1.03610	-2.19200
C	-3.34620	0.04760	0.18890
H	-2.81670	1.24300	1.89270
H	-3.55970	-1.14600	-1.61130
O	-4.64020	0.05290	0.60610
C	-5.60860	-0.63770	-0.17780
H	-5.67520	-0.21950	-1.18970
H	-6.56100	-0.49820	0.33540
H	-5.38180	-1.70920	-0.24000
H	1.07470	1.28080	-0.97830
H	1.78730	0.65830	1.05040
O	1.68260	1.81260	1.64380
O	1.83940	2.69410	-0.77830
H	1.84470	2.53800	0.23840
H	2.69980	2.33350	-1.06620
H	2.48900	1.91670	2.17510

3l - 2 H_2O

C	3.07730	-2.13110	1.10270
H	3.29850	-1.77590	2.11390
H	3.39790	-3.16900	1.00600
C	3.14200	-0.37920	-0.40020
O	3.61790	0.39830	-1.20130
O	3.88100	-1.34710	0.17330
C	1.70670	-0.44000	0.13550
N	0.72900	-0.03820	-0.87820
H	0.85060	-0.59220	-1.72360
C	1.62570	-1.87210	0.69420
H	1.31920	-2.56470	-0.09820
H	0.93020	-1.97270	1.52980
C	-0.64760	-0.04350	-0.48290
C	-1.07640	0.68150	0.64330
C	-1.60130	-0.71670	-1.24980
C	-2.42220	0.70940	0.98640
H	-0.36000	1.24010	1.23920
C	-2.96050	-0.67440	-0.91990
H	-1.28890	-1.28250	-2.12510
C	-3.37810	0.03550	0.20990
H	-2.75860	1.26760	1.85490
H	-3.67010	-1.20490	-1.54420
O	-4.67370	0.13600	0.63620
C	-5.67910	-0.51980	-0.12430
H	-5.72300	-0.13430	-1.15110
H	-6.62340	-0.30930	0.38070
H	-5.51800	-1.60530	-0.15390
H	1.23190	1.83870	-1.23610
H	1.67090	0.29880	0.94850
O	1.66940	2.52370	1.60010
O	1.81020	2.63370	-1.16980
H	1.73100	2.70020	0.62840
H	2.67920	2.21710	-1.32180
H	2.57230	2.66100	1.92540

3l-ylide - H_2O (conf.2)

C	3.21570	-2.20790	-0.18140
H	2.89760	-2.64390	-1.13680
H	3.88910	-2.90720	0.32080
C	3.10630	0.08960	-0.26490
O	3.55170	1.22210	-0.57900
O	3.95300	-1.00000	-0.45900
C	1.89870	-0.36630	0.25110
N	0.90030	0.53600	0.82610
H	0.92140	0.50860	1.85720
C	1.98800	-1.80330	0.66280
H	2.17100	-1.94450	1.74560
H	1.11770	-2.42140	0.40460
C	-0.50470	0.29630	0.41650
C	-0.81080	0.20690	-0.94210
C	-1.49800	0.19150	1.37900
C	-2.12890	0.01770	-1.33070
H	-0.01510	0.27160	-1.67710
C	-2.82840	-0.00590	0.99370
H	-1.25270	0.25860	2.43660
C	-3.14820	-0.09130	-0.36690

H	-2.39610	-0.05270	-2.38010
H	-3.59190	-0.09340	1.75690
O	-4.40260	-0.28300	-0.85600
C	-5.47950	-0.40290	0.06850
H	-5.58980	0.50570	0.67310
H	-6.37600	-0.54700	-0.53590
H	-5.34350	-1.26710	0.73030
H	2.51330	2.46160	-0.32800
H	1.15590	1.54140	0.56950
O	1.72870	3.00060	0.00850
H	2.08950	3.51360	0.75000

TS1-3l-enol - H_2O

C	3.21470	-2.16490	-0.08330
H	2.85270	-2.68370	-0.97900
H	3.95020	-2.79650	0.41990
C	3.03890	0.10240	-0.30720
O	3.43840	1.22900	-0.78280
O	3.89140	-0.95890	-0.51340
C	1.91980	-0.29230	0.38540
N	0.88790	0.61160	0.86860
H	0.89600	0.65520	1.89440
C	2.03830	-1.72720	0.81590
H	2.27340	-1.84150	1.88910
H	1.14680	-2.33710	0.61890
C	-0.48650	0.31910	0.44930
C	-0.76270	0.07820	-0.89970
C	-1.51950	0.33370	1.37940
C	-2.07090	-0.14550	-1.30660
H	0.05090	0.05800	-1.61770
C	-2.84070	0.10960	0.97700
H	-1.30790	0.51790	2.43050
C	-3.12140	-0.13110	-0.37290
H	-2.30480	-0.33400	-2.34960
H	-3.62820	0.12030	1.72110
O	-4.36570	-0.36500	-0.87770
C	-5.46950	-0.35630	0.02040
H	-5.57860	0.61880	0.51150
H	-6.35220	-0.55530	-0.58900
H	-5.37110	-1.13820	0.78390
H	2.61740	2.13520	-0.46660
H	1.20430	1.74580	0.48570
O	1.73460	2.77770	-0.05480
H	2.10240	3.33710	0.65040

3l-enol - H_2O

C	3.25280	-2.16920	0.06020
H	2.91540	-2.75450	-0.80240
H	4.00970	-2.73780	0.60380
C	3.01960	0.05490	-0.28760
O	3.44240	1.16600	-0.87790
O	3.89780	-0.97070	-0.45410
C	1.92300	-0.26600	0.44280
N	0.87200	0.62130	0.84220
H	0.89550	0.79520	1.84780
C	2.06640	-1.69670	0.92340
H	2.28660	-1.75440	2.00170
H	1.17460	-2.30950	0.74420
C	-0.46880	0.29000	0.45140
C	-0.73790	-0.26130	-0.81020
C	-1.54070	0.57300	1.30130
C	-2.04580	-0.52040	-1.20190
H	0.08690	-0.48450	-1.47990
C	-2.86010	0.32120	0.91110
H	-1.35280	0.99750	2.28570
C	-3.12050	-0.23080	-0.34770
H	-2.25720	-0.94850	-2.17720
H	-3.66500	0.55300	1.59910
O	-4.36720	-0.52420	-0.83160
C	-5.48680	-0.24100	-0.00470
H	-5.55460	0.82950	0.22970
H	-6.36690	-0.54090	-0.57630
H	-5.45160	-0.81250	0.93210
H	2.81190	1.92720	-0.70650
H	1.18470	2.32860	0.18230
O	1.66800	3.05800	-0.28960
H	2.04410	3.60740	0.41750

TS2-3l-enol - H_2O

C	3.68190	-1.76670	0.27840
H	4.23150	-2.53310	-0.27100
H	3.90760	-1.85980	1.34570
C	3.15860	0.37740	-0.29320
O	3.40080	1.61390	-0.45010
O	4.19770	-0.46980	-0.14730
C	1.89060	-0.23890	-0.08180
N	0.79680	0.25220	-0.87130
H	0.92140	0.18850	-1.87760
C	2.16800	-1.74120	0.00830
H	1.61440	-2.26280	0.79590
H	1.92440	-2.23450	-0.94460
C	-0.53770	0.08900	-0.47670
C	-0.90510	-0.25940	0.83730
C	-1.56960	0.30560	-1.40480
C	-2.24440	-0.36480	1.20080
H	-0.13610	-0.45320	1.57820
C	-2.91410	0.19430	-1.04530
H	-1.31710	0.57240	-2.42900
C	-3.26410	-0.14020	0.26810
H	-2.51870	-0.63340	2.21700
H	-3.67320	0.37140	-1.79910
O	-4.55100	-0.27700	0.73050
C	-5.60970	-0.05720	-0.18750
H	-5.57420	-0.76670	-1.02530
H	-6.53380	-0.21050	0.37340
H	-5.59490	0.96620	-0.58620
H	2.44890	2.12930	0.37220
H	1.65170	0.94330	1.04850
O	1.67800	2.05730	1.19710
H	2.13890	2.23440	2.03870

TS1-3l-enol - 2 H_2O

C	-2.66510	-2.75050	0.15730
H	-2.18700	-3.32770	-0.64520
H	-3.33370	-3.41220	0.71460
C	-2.76150	-0.51780	-0.36980
O	-3.26160	0.46190	-1.02420
O	-3.46790	-1.71630	-0.44960
C	-1.64520	-0.67110	0.41250
N	-0.71340	0.37680	0.76760

H	-0.74060	0.55080	1.77790
C	-1.60740	-2.04370	1.03000
H	-1.88440	-2.04620	2.09970
H	-0.63410	-2.54720	0.95510
C	0.68130	0.15830	0.40300
C	1.00800	-0.37830	-0.84750
C	1.70150	0.54930	1.26700
C	2.33890	-0.51990	-1.21980
H	0.21020	-0.69280	-1.51330
C	3.04430	0.41200	0.89930
H	1.45870	0.96660	2.24210
C	3.36960	-0.12570	-0.35120
H	2.60460	-0.93860	-2.18570
H	3.81550	0.72040	1.59540
O	4.64150	-0.31010	-0.81360
C	5.72310	0.06690	0.02910
H	5.69850	1.13970	0.25930
H	6.63210	-0.16160	-0.52960
H	5.72020	-0.50390	0.96650
H	-3.57700	1.63200	-0.37950
H	-1.02620	1.66300	0.26790
O	-1.21740	2.74170	-0.02210
O	-3.62870	2.62300	0.06670
H	-2.37850	2.82320	0.01510
H	-4.08620	3.19190	-0.57540
H	-0.95080	2.82550	-0.95470

3l-enol - 2 H_2O

C	3.24030	-2.26710	0.35660
H	3.19610	-2.32010	1.45090
H	3.82380	-3.10800	-0.02150
C	3.01270	-0.12400	-0.30260
O	3.52880	1.07880	-0.51860
O	3.95730	-1.04860	0.00900
C	1.74390	-0.61370	-0.39030
N	0.67390	0.10000	-0.97770
H	0.76260	0.28130	-1.97260
C	1.83480	-2.12750	-0.25250
H	1.75640	-2.61950	-1.23470
H	1.07270	-2.57460	0.39460
C	-0.65770	-0.03940	-0.55980
C	-1.00190	-0.49710	0.72650
C	-1.70190	0.31470	-1.42830
C	-2.33380	-0.58740	1.11810
H	-0.22340	-0.77300	1.43010
C	-3.03960	0.22870	-1.03710
H	-1.46640	0.66950	-2.42950
C	-3.36760	-0.22740	0.24470
H	-2.59130	-0.93930	2.11290
H	-3.81040	0.51620	-1.74340
O	-4.64520	-0.35760	0.73150
C	-5.71840	0.00830	-0.12130
H	-5.66440	1.06690	-0.40910
H	-6.63190	-0.16190	0.45170
H	-5.74240	-0.60800	-1.03020
H	2.81560	1.78730	-0.57500
H	1.51050	0.75260	1.51970
O	1.39880	1.59420	2.00800
O	1.80230	3.07280	-0.26920
H	1.49450	2.69380	0.59280
H	2.36050	3.82800	-0.02120
H	2.22030	1.68390	2.51830

TS2-3l-enol - 2 H_2O

C	3.34940	-2.15210	0.32730
H	3.51080	-2.11890	1.41160
H	3.84950	-3.03250	-0.08140
C	3.02830	-0.04150	-0.47780
O	3.40820	1.08220	-0.90960
O	3.98770	-0.97980	-0.24720
C	1.72790	-0.50920	-0.14290
N	0.64550	0.09530	-0.86820
H	0.76150	0.11390	-1.87760
C	1.86160	-2.02890	-0.02410
H	1.63490	-2.52530	-0.98150
H	1.22900	-2.49010	0.74140
C	-0.69460	-0.02720	-0.48520
C	-1.09150	-0.43700	0.80350
C	-1.70920	0.29130	-1.40470
C	-2.43810	-0.50460	1.14830
H	-0.34210	-0.69190	1.54370
C	-3.06090	0.22000	-1.06270
H	-1.43570	0.60680	-2.40970
C	-3.43830	-0.17960	0.22430
H	-2.73360	-0.81940	2.14530
H	-3.80360	0.47700	-1.80990
O	-4.73540	-0.28800	0.66840
C	-5.77330	0.03300	-0.24280
H	-5.71120	1.07730	-0.57760
H	-6.70950	-0.11460	0.29950
H	-5.75890	-0.62440	-1.12290
H	2.57600	2.15160	-0.46870
H	1.63180	0.42850	1.23850
O	1.50790	1.29600	1.88670
O	2.02830	2.87380	0.11250
H	1.75100	2.22160	1.03910
H	2.66310	3.56210	0.38080
H	2.22710	1.25310	2.54180

XI. NMR Spectra

Et
N
O
O
3b
DMSO-d6
1.96
2.01
0.96
1.00
1.00
1.00
2.00
1.98
2.99
f1 (ppm)

175.5
147.1
129.1
116.9
113.4
65.2
58.2
42.6
25.4
13.6
Et
N
O
O
3b
f1 (ppm)

Me
Me
N
O
O
3c
2.92
0.97
3.00
3.03
5.00
f1 (ppm)

175.3
150.5
132.0
130.9
126.3
123.1
121.6
65.1
61.0
35.2
24.6
17.9
Me
Me
N
O
O
3c
f1 (ppm)

Me
N
O
O
Me
3d
f1 (ppm)

175.2
147.2
129.4
126.0
113.6
65.3
58.4
33.7
24.2
19.9
Me
N
O
O
Me
3d
f1 (ppm)

3d, enzymatic product after purification

Me
N
O
O
F
3e
f1 (ppm)

Me
N
O
O
F
3e
f1 (ppm)

3e, enzymatic product after purification

LZ-NH insertion-NMepF-enzymatic-DMSO.2.fid
175.0
156.3
154.0
146.2
115.4
115.2
114.9
114.8
65.3
58.7
34.0
24.3
Me
N
O
O
F
3e
f1 (ppm)

LZ-NMe4F-enzymatic-F.3.fid
-127.8
Me
N
O
O
F
3e
f1 (ppm)

3f
f1 (ppm)

174.5
150.5
129.4
127.0
124.4
117.7
107.1
65.5
54.5
48.0
27.7
23.6
3f
f1 (ppm)

3g
DMSO-d6
1.98
1.03
0.98
1.00
1.01
1.00
1.97
2.07
2.02
2.05
f1 (ppm)

3g
175.0
144.5
129.1
128.8
123.0
116.5
111.2
65.4
56.8
44.0
27.4
23.7
21.7
f1 (ppm)

3h
f1 (ppm)

3h
f1 (ppm)

Me
H
N
O
O
3i
DMSO-d6
1.98
1.06
0.96
1.00
1.03
1.03
0.99
1.04
4.05
f1 (ppm)

176.7
145.2
130.0
126.6
122.3
116.8
110.3
65.2
51.5
29.3
17.7
Me
H
N
O
O
3i
f1 (ppm)

Me
H
N
O
O
3j
f1 (ppm)

176.5
147.5
137.9
128.7
117.5
113.3
110.1
65.3
51.4
29.6
21.3
Me
H
N
O
O
3j
f1 (ppm)

3k
Me
f1 (ppm)

3k
Me
176.6
145.2
129.3
125.1
112.9
65.3
51.6
29.6
20.1
f1 (ppm)

MeO
H
N
O
O
3l
f1 (ppm)

176.7
153.4
140.7
115.3
115.1
65.8
55.9
54.0
32.4
MeO
H
N
O
O
3l
f1 (ppm)

3l, enzymatic product after purification

Me
H
N
O
O
Me
3m
f1 (ppm)

Me
H
N
O
O
Me
3m
176.8
143.5
130.8
129.2
123.8
65.4
57.4
31.8
18.9
f1 (ppm)

3m, enzymatic product after purification

3n
f1 (ppm)

3n
f1 (ppm)

MeO
H
N
O
O
3o
f1 (ppm)

177.56
158.16
132.10
129.25
113.56
65.49
55.00
54.61
49.83
29.70
MeO
H
N
O
O
3o
f1 (ppm)

Br
H
N
O
O
3p
f1 (ppm)

177.4
139.7
131.1
130.9
118.9
65.5
55.5
48.3
35.1
29.6
Br
H
N
O
O
3p
f1 (ppm)

3q
f1 (ppm)

3q
175.8
139.3
126.7
122.3
65.5
59.6
55.7
27.2
f1 (ppm)

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