Supplementary Materials for

Asymmetric Induction and Enantiodivergence in Catalytic Radical C–H Amination via Enantiodifferentiative H-Atom Abstraction and Stereoretentive Radical Substitution

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Materials and Methods

Supplementary Text

Tables S1 to S3

Figures S1 to S14-2

Schemes S1 to S6

Captions for movies (SI-C and SI-D) to illustrate the major pathways leading to the enantiodifferentiative HAA and stereoretentive RS by [Co(**P4**)] and [Co(**P5**)]

CD Spectra

Density Functional Theory (DFT) Calculations

Other Supplementary Material for this manuscript includes the following:

Coordinates for DFT Calculated Structures (SI-B)

Movie for Major C–H Amination Pathway by [Co(**P4**)] (SI-C).

Movie for Major C–H Amination Pathway by [Co(**P5**)] (SI-D).

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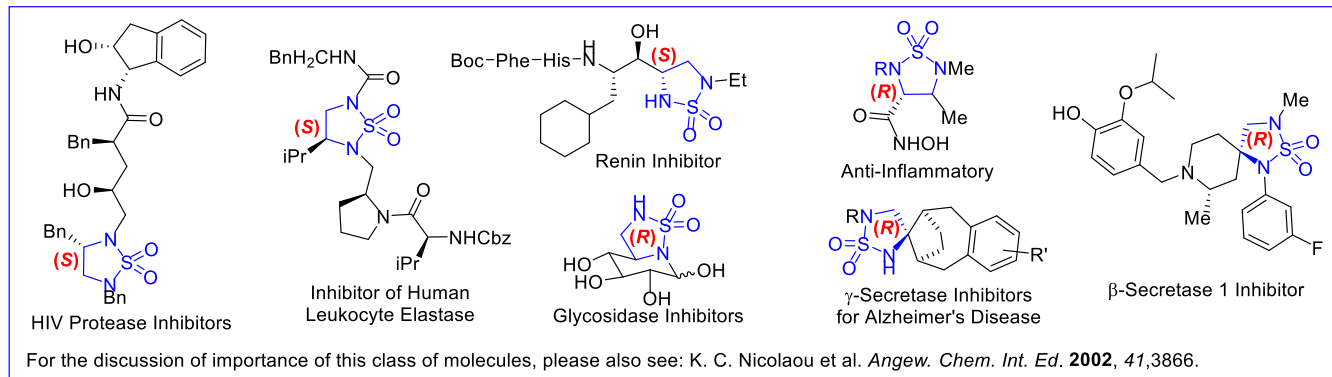
General Information

General Considerations. Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere in oven-dried glassware following standard Schlenk techniques. Gas tight syringes were used to transfer liquid reagents and solvents in catalytic reactions. Solvent was freshly distilled/degassed prior to use unless otherwise noted. Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254), visualizing with UV-light 254 nm or 365 nm fluorescence quenching, and cerium ammonium-molybdate (CAM) stain (ammonium pentamolybdate, cerium(IV) sulfate, sulfuric acid aqueous solution). Flash column chromatography was performed with ICN silica gel (60 Å, 230-400 mesh, 32-63 μm).

Materials. Commercial reagents were purchased from Sigma Aldrich, Acros, Alfa Aesar, Strem, Oakwood Products Inc., TCI, or Matrix Scientific and used as received with the following exceptions. Dichloromethane was distilled under nitrogen from calcium hydride. Tetrahydrofuran (THF) and toluene were distilled under nitrogen from sodium benzophenone ketyl. 1,4-Dioxane (inhibitor free, ACS reagent grade >99%) was freshly distilled from Na under an atmosphere of dry N_2 prior to use. Anhydrous cobalt(II) chloride, palladium(II) acetate, and 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthenes (Xantphos) were purchased from Strem.

Instrument. Proton nuclear magnetic resonance (^1H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Varian 600-MHz or Bruker 500-MHz or Bruker 400-MHz instrument. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$= 7.26 ppm, $(CH_3)_2CO$ = 2.05 ppm, $(CH_3)_2SO$ = 2.5 ppm). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = 77.00 ppm). Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart S8 Miracle accessory, HPLC measurements were carried out on a Shimadzu HPLC system with Chiralcel OD-H, AD-H and IC. GC measurements were carried out on a Shimadzu GCMS system with a Dex-CB column. Optical rotations were measured on a Rudolph Research Analytical AUTOPOL®IV digital polarimeter. High-resolution mass spectra were obtained on an Agilent 6220 using electrospray ionization time-of-flight (ESI-TOF). The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer (CuKα, λ= 1.54178 Å) and Bruker D8 Venture PHOTON 100 CMOS system equipped with a Cu $K_α$ INCOATEC Imus micro-focus source (λ = 1.54178 Å).

Figure S1. Select Examples of Biologically Important Molecules Containing Chiral Five-Membered Cyclic Sulfamide and Vicinal Diamine Motifs

A. Examples of Biologically Active Molecules Carrying Chiral Five-Membered Cyclic Sulfamide as the Key Motif

HIV Protease Inhibitors

Inhibitor of Human Leukocyte Elastase

Renin Inhibitor

Glycosidase Inhibitors

Anti-Inflammatory

γ-Secretase Inhibitors for Alzheimer's Disease

β-Secretase 1 Inhibitor

For the discussion of importance of this class of molecules, please also see: K. C. Nicolaou et al. *Angew. Chem. Int. Ed.* **2002**, *41*, 3866.

B. Method Demonstrated for Converting Cyclic Sulfamides into Diamines in our Previous Report

Zhang, et al. *Chem. Sci.* **2016**, *7*, 6934.

via a similar procedure

Zhang, et al. *J. Am. Chem. Soc.* **2017**, *139*, 9164.

Zhang, et al. *Angew. Chem. Int. Ed.* **2018**, *57*, 16837.
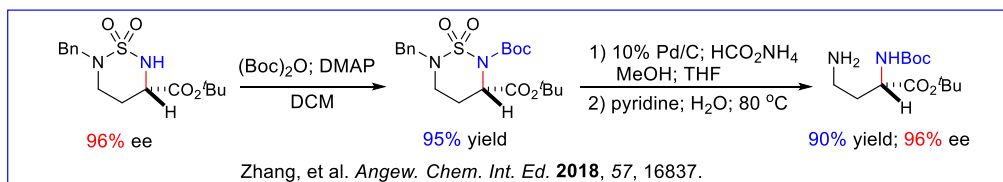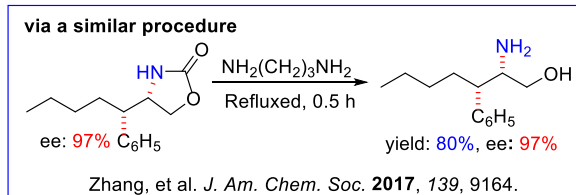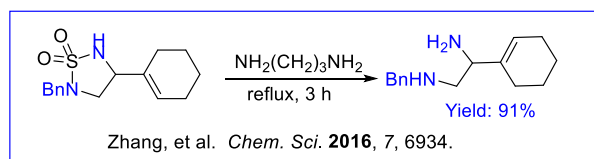
C. Examples of Biologically Important Molecules Containing Vicinal Diamine Motifs

U-50488(κ Agonist)

Biotin: Vitamin B₇

Tamiflu® (Antiviral Drug)

Eloxatin® (Anticancer Drug)

Penicillins (Antibiotics)
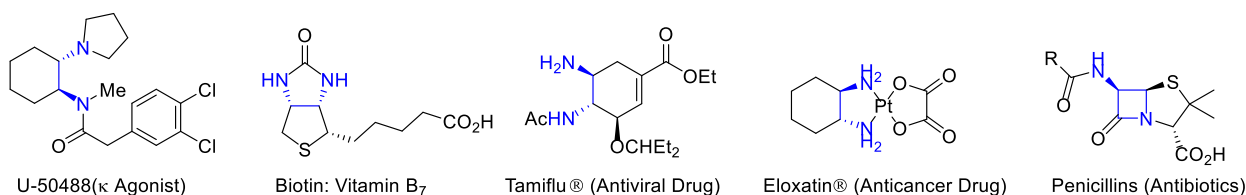
D. Selected Examples of Enantiomers of Vicinal Diamine Motifs for Entirely Different Therapeutic Possibilities

Indinavir (Crixivan®) (Anti-HIV Drug)

(R)-CPP Antagonist of NMDA

Levamisole (Ergamisol®)

1: treat worm infestations in both humans and animals 2: in combination with fluorouracil to treat colon cancer

Dexamisole

antidepressant

S5
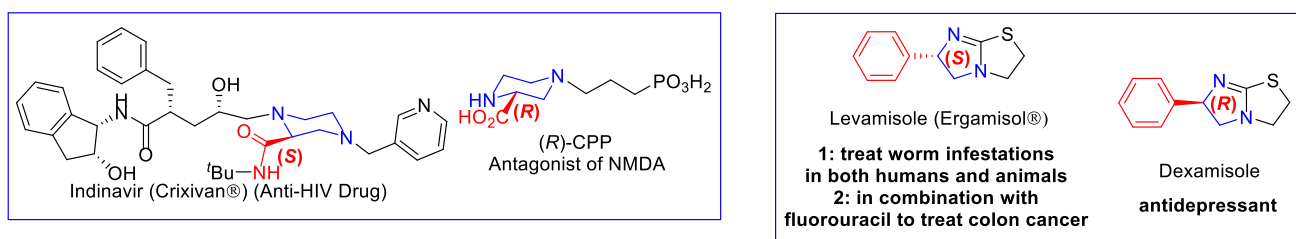
Figure S2. Summary of Structures Confirmed by X-ray

entry 1:(*R*)-**2a**

98% yield; er (*R*:*S*): 97:3

$[\alpha]_D^{25}$ = +89.1° (c 2.1, CHCl₃)

(*R*)-**2a**

entry 2: (*S*)-**2a**

75% yield; er (*R*:*S*): 6:94

$[\alpha]_D^{25}$ = -87.6.° (c 1.4, CHCl₃)

(S)-**2a**

entry 3: (*R*)-**2b**

97% yield; er (*R*:*S*): 98:2

$[\alpha]_D^{25}$ = +103.5° (c 2.3, CHCl₃)

(*R*)-**2b**

entry 4: (*S*)-**2b**

88% yield; er (*R*:*S*): 4:96

$[\alpha]_D^{25}$ = -84.5° (c 0.6, CHCl₃)

(S)-**2b**

entry 5: (*R*)-**2c**

98% yield; er (*R*:*S*): 98:2

$[\alpha]_D^{25}$ = +104.9° (c 1.5, CHCl₃)

(*R*)-**2c**

entry 6: (*S*)-**2c**

55% yield; er (*R*:*S*): 8:92

$[\alpha]_D^{25}$ = - 82.5° (c 1.2, CHCl₃);

(*S*)-**2c**

entry 21: (*R*)-**2k**

97% yield; er (*R*:*S*): 98:2

$[\alpha]_D^{25}$ = +70.8° (c 0.7, CHCl₃)

(*R*)-**2k**

entry 26: (*S*, *R*)-**2m**

79% yield; er (1*R*,2*S*:1*S*,2*R*): 9:91

$[\alpha]_D^{25}$ = -93.6° (c 1.4, CHCl₃)

(*S, R*)-**2m**

entry 33: (*S*, *S*)-**2s**

80% yield; er (1*R*,2*R*:1*S*,2*S*): 7:93

$[\alpha]_D^{24}$ = -17.8° (c 0.6, CHCl₃)

(*S, S*)-**2s**

X-Ray for P4 (3 conformers)

X-Ray for P5 (1 conformer)

P4 (1)

P4 (2)

P4 (3)

Figure S3. Summary of Library Synthesis of Co(II)-Based, Bridged Amidoporphyrins (4 Steps)

Step1: Synthesis of Catalyst Building Blocks

Pd(OAc)$_2$ (40 mol%), Xantphos (80 mol%)

Cs$_2$CO$_3$ (16 eq) dioxane,100 °C

68-88% yield

(12 eq)

same chiral source (recyclable after the reaction for up to 10 times without affecting the cross-coupling reaction)

Step 2: Synthesis of Ester Amidoporphyrins
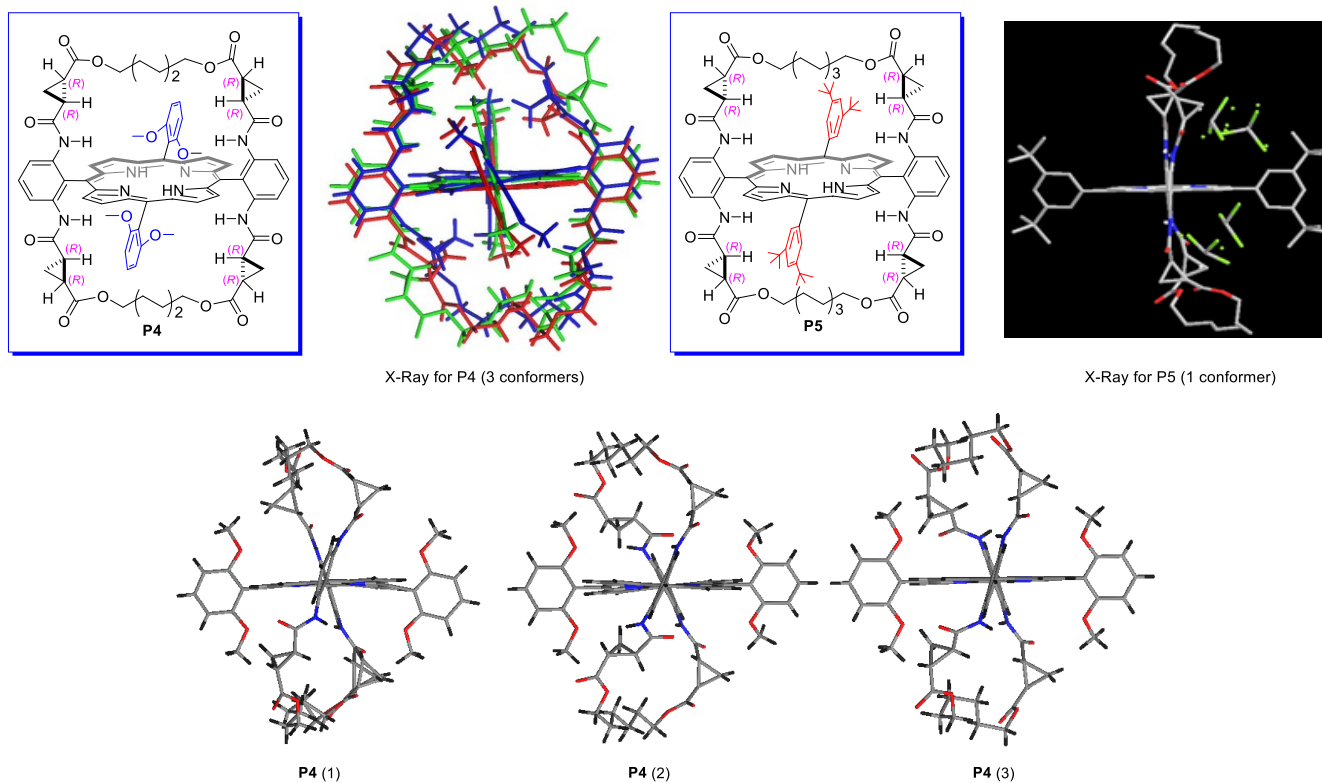
1. TFA

2. K$_2$CO$_3$, OTs

n = 1,2,3,4

65-95% yield

Step 3: Synthesis of Bridged Amidoporphyrins

1.Grubbs(II)

2. Pd/C, H$_2$

n = 1,2,3,4

65%-88% yield

Step 4: Synthesis of Co(II)-Based, Bridged Amidoporphyrins

CoCl$_2$, 2,6-lutidine

n = 1,2,3,4

88-95% yield

Synthesis and Characterization of of Catalyst Building Blocks

[Co(3,5-Di'Bu-ChenPhyrin)]

(1R,2R)-tert-Butyl 2-carbamoylcyclopropanecarboxylate was synthesized according to the reported procedure.[1] (S)-[Co(3,5-di'Bu-ChenPhyrin)][1] (400 mg, 0.3 mmol, 0.01 equiv), acryl amid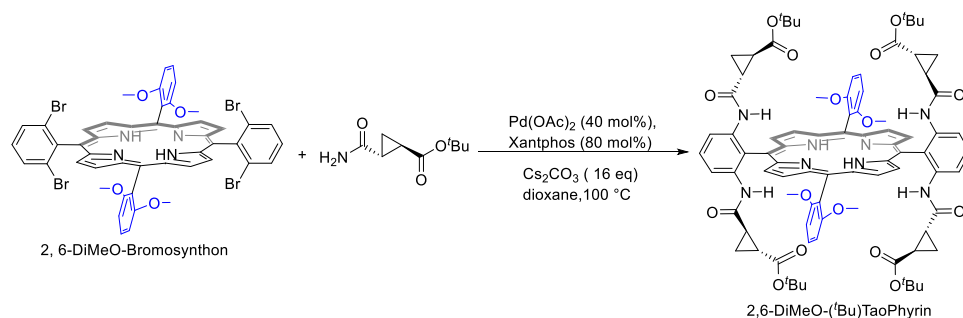e (10.6 g, 150 mmol, 5 equiv) and DMAP (1.83 g, 15 mmol, 0.5 equiv) were placed in an oven dried resealable Schlenk tube. The tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen. The screw cap was replaced with a rubber septum. Chlorobenzene (100 mL) was added via syringe. After the solution was cooled to 0 °C, 'BDA (4.4 mL, 30 mmol, 1 equiv) was added dropwise followed by the addition of 20 mL of chlorobenzene. The tube was purged with nitrogen for 1 min and sealed with Teflon screwcap. The reaction mixture was warmed up to r.t. and stirred for three days. After the reaction finished, the resulting mixture was purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1) to give tert-butyl (1R, 2R)-2-carbamoylcyclopropane-1-carboxylate (5.2 g, 93%),[2] TLC R_f = 0.25 (Hexanes/EtOAc 3:1) in 98% ee. **The following recrystallization gave >99% ee**. ^{1}H NMR (400 MHz, CDCl₃) δ ppm 5.84 (s, 1 H), 5.76 (s, 1 H), 2.07 (ddd, J = 3.8, 5.8, 9.5 Hz, 1 H), 1.93 (ddd, J = 3.8, 5.7, 9.4 Hz, 1 H), 1.44 (s, 9 H), 1.38 (ddd, J = 3.7, 5.7, 9.3 Hz, 1 H), 1.28 (ddd, J = 3.7, 5.8, 9.4 Hz, 1 H); ^{13}C NMR (125 MHz, CDCl₃) δ ppm 173.0, 171.7, 81.2, 28.1, 23.1, 23.0, 14.9; GC (DCB, 5 °C/min): Major t = 12.95 min., Minor t =11.77 min.

3,5-Di'Bu-Bromosynthon

LK-I-127B

3,5-Di'Bu-('Bu)TaoPhyrin
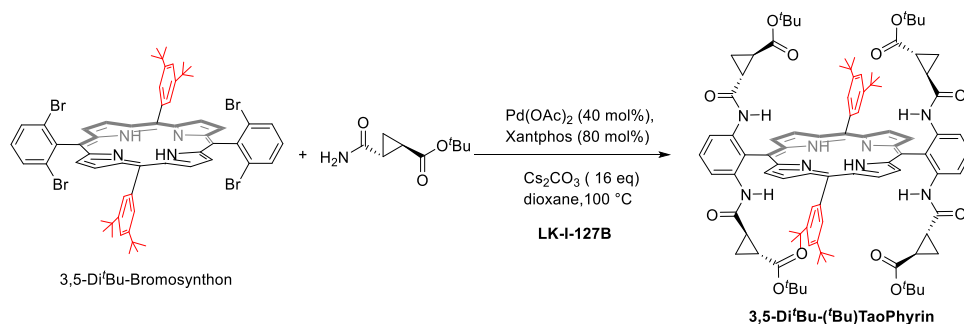
Representative procedure for the synthesis of (3,5-Di'Bu-Tao('Bu)Phyrin). 3,5-Di'Bu-Bromosynthon (686 mg, 0.59 mmol, 1 equiv),[1] the above synthesized chiral amide (tert-butyl (1R,2R)-2-carbamoylcyclopropane-1-carboxylate) (1.76 g, 9.5 mmol, 16 equiv), Pd(OAc)₂ (53 mg, 0.236 mmol, 0.4

equiv), Xantphos (274 mg, 0.47 mmol, 0.8 equiv) and Cs_2CO_3 (3.1 g, 9.5 mmol, 16 equiv) were placed in an oven dried Schlenk tube. The tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen. Under positive nitrogen atmosphere, the screw cap was replaced with a rubber septum. Dioxane (60 mL) was added via syringe and the tube was purged with nitrogen for 1 min and sealed with Teflon screwcap. Reaction mixture was stirred at 100 °C for three days prior to being cooled to r.t. The reaction mixture was filtered through a short pad of Celite. The solvent was removed and the residue was purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1) to give the title compound (820 mg, 88%); TLC R_f = 0.35 (Hexanes/EtOAc 4:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 9.02 (d, J = 4.6 Hz, 4 H), 8.79 (d, J = 4.6 Hz, 4 H), 8.53 (s, 4 H), 8.16 (d, J = 1.2 Hz, 4 H), 7.87 - 7.81 (m, 4 H), 6.66 (s, 4 H), 1.85 - 1.76 (m, 4 H), 1.59 - 1.50 (m, 40 H), 1.01 (s, 36H), 0.57 - 0.40 (m, 8 H), -2.43 (s, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 170.7, 168.7, 149.2, 140.0, 139.0, 130.3, 130.2, 123.2, 121.6, 121.2, 117.0, 107.0, 106.9, 80.7, 35.1, 31.7, 27.7, 24.1, 22.8, 15.1; HRMS (ESI) Calcd. for $C_{96}H_{114}N_8NaO_{12}^+$ [M+Na]$^+$: 1593.8448, Found: 1593.8510; UV–vis (CHCl$_3$), λmax nm (log ε): 421(5.27), 517(4.77), 552(4.37), 592(4.27), 648(4.18). (Note: To build up enough materials, multiple runs were conducted.)
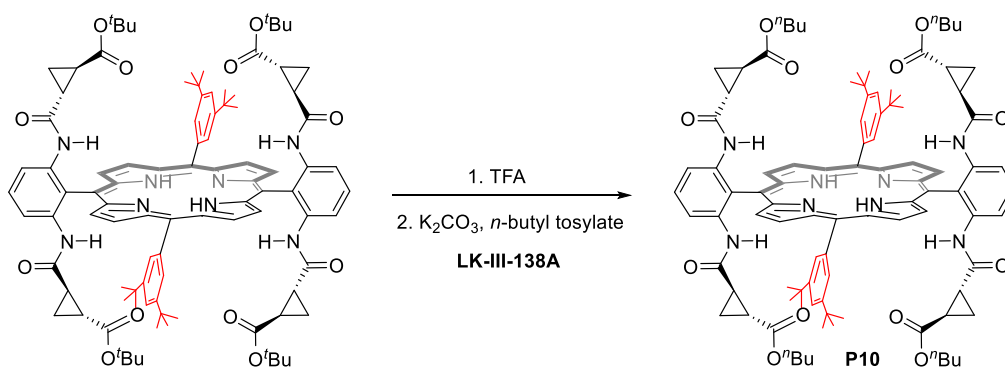

2, 6-DiMeO-Bromosynthon

2,6-DiMeO-(tBu)TaoPhyrin

Representative procedure for the synthesis of (2,6-DiMeO-Tao(tBu)Phyrin). 2, 6-DiMeO-Bromosynthon (800 mg, 0.76 mmol, 1 equiv),[1] the above synthesized chiral amide (*tert*-butyl (1*R*,2*R*)-2-carbamoylcyclopropane-1-carboxylate) (2.25 g, 12 mmol, 16 equiv), Pd(OAc)$_2$ (68 mg, 0.3 mmol, 0.4 equiv), Xantphos (356 mg, 0.61 mmol, 0.8 equiv) and Cs_2CO_3 (3.9 g, 12 mmol, 16 equiv) were placed in an oven dried Schlenk tube. The tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen. Under positive nitrogen atmosphere, the screw cap was replaced with a rubber septum. Dioxane (80 mL) was added via syringe and the tube was purged with nitrogen for 1 min and sealed with Teflon screwcap. The reaction mixture was stirred at 100 °C for three days prior to being cooled to r.t. The reaction mixture was filtered through a short pad of Celite. The solvent was removed and the residue was purified by silica gel column chromatography (eluent: Hexanes/EtOAc 2:1) to give the title compound (757 mg, 68%); TLC R_f = 0.30 (Hexanes/EtOAc 2:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 8.87 (d, J = 4.8

Hz, 4H), 8.73 (d, J = 4.7 Hz, 4H), 8.46 (br, 4H), 7.89 - 7.72 (m, 4H), 7.04 (d, J = 8.5 Hz, 4H), 6.74 (s, 4H), 3.54 (s, 12H), 1.85 (ddd, J = 3.9, 5.7, 9.3 Hz, 4H), 1.01 (s, 36H), 0.96 - 0.92 (m, 4H), 0.60 - 0.54 (m, 8H), -2.42 (s, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 170.5, 168.9, 160.3, 139.0, 130.9, 130.2, 121.9, 118.6, 117.8, 114.1, 106.4, 104.2, 80.6, 55.9, 27.7, 24.0, 22.8, 14.9; HRMS (ESI) m/z Calcd. for C$_{84}$H$_{91}$N$_8$O$_{16}$$^+$ [M+H]$^+$: 1467.6548, Found: 1467.6509; UV–vis (CHCl$_3$) λmax nm (log ε): 421(5.53), 515(4.34), 545(3.81), 590(3.85), 643(3.55). (Note: To build up enough materials, multiple runs were conducted.)

## General Procedure A (Synthesis of Ester Amidoporphyrins)

TFA (100 equiv) was added to a solution of the above synthesized **3,5-Di^{t}Bu-Tao(^{t}Bu)Phyrin** (1 equiv) or **2,6-DiMeO-Tao(^{t}Bu)Phyrin** (1 equiv) in DCM (0.5 M) at 0 °C. Then the reaction mixture was slowly warmed up to room temperature and stirred overnight. After the evaporation of all the volatiles, the residue was dissolved in DMF (0.1 M). K$_2$CO$_3$ (50 equiv) was added, followed by the addition of alkylating reagents (16 equiv). The reaction mixture was heated at 100 °C for 12 h. After cooling to the room temperature, the reaction mixture was diluted with EtOAc and water. The organic layer was separated and washed with brine 5 times. The organic solvent was removed under vacuum and the resulting oil was then purified by silica gel column chromatography (Conditions were given below) to afford the pure TaoPhyrin derivatives. (The reaction can be easily scaled up to 800 mg scale.)

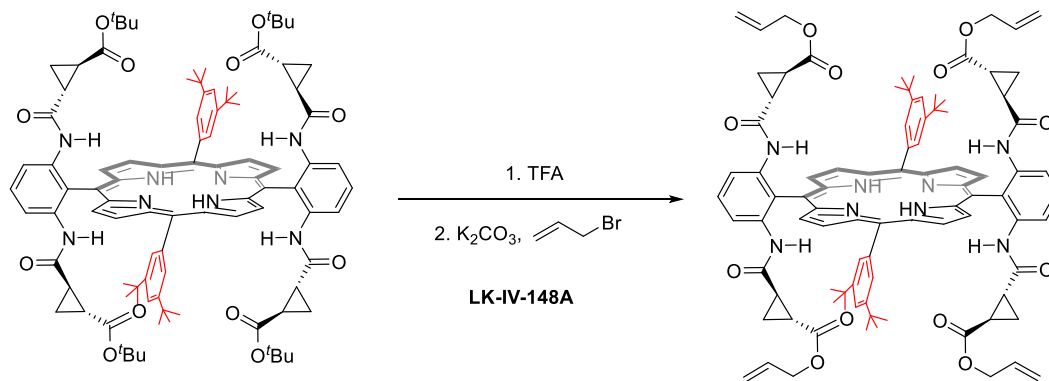## Characterization of Ester Amidoporphyrins

(3,5-Di^{t}Bu-Tao(nBu)Phyrin) (P10) was synthesized following **General Procedure A** using n-butyl 4-methylbenzenesulfonate as the alkylating reagent and **3,5-Di^{t}Bu-Tao(^{t}Bu)Phyrin** (48 mg, 0.031 mmol) as
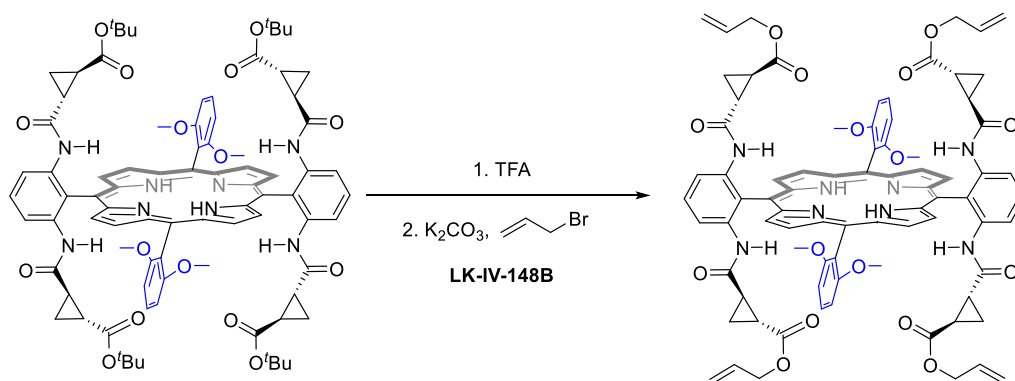
catalyst building block, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 6:1) to give the title compound in 82% yield (40 mg); TLC R_f = 0.35 (Hexanes/EtOAc 4:1). ^{1}H NMR (500 MHz , CDCl$_3$) δ ppm 9.03 (d, J = 5.3 Hz, 4 H), 8.79 (d, J = 5.3 Hz, 4 H), 8.65 - 8.39 (m, 4 H), 8.19 (d, J = 1.5 Hz, 4 H), 7.90 - 7.77 (m, 4 H), 6.68 (br. s., 4 H), 3.64 - 3.46 (m, 8 H), 1.87-1.85 (m, 4 H), 1.57 (s, 36 H), 1.24 - 1.21 (m, 8 H), 1.13 - 0.94 (m, 12 H), 0.65 - 0.63 (t, J = 7.2 Hz, 12 H), 0.62 - 0.60 (m, 4H), 0.55 - 0.37 (m, 4 H), -2.46 (s, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 171.7, 168.3, 149.2, 140.0, 139.0, 133.7, 130.4, 130.3, 129.7, 123.3, 121.6, 116.8, 106.7, 64.5, 35.1, 31.7, 30.2, 24.5, 21.7, 18.7, 15.2, 13.4; HRMS (ESI) m/z Calcd. for C$_{96}$H$_{115}$N$_8$O$_{12}$$^+$ [M+H]$^+$: 1571.8629, Found: 1571.8658; UV–vis (CHCl$_3$), λmax nm (log ε): 422(5.33), 522(4.09), 560(3.54), 598(3.55), 652(3.31).
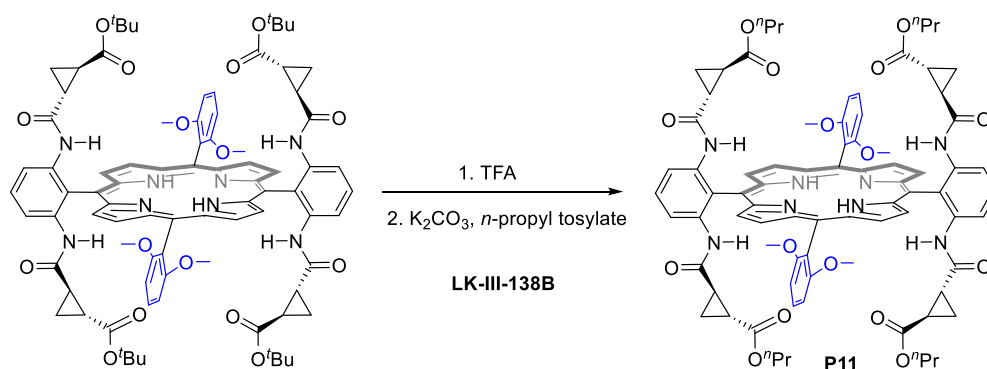
(2,6-DiMeO-Tao(nPr)Phyrin) (P11) was synthesized following **General Procedure A** using n-propyl 4-methylbenzenesulfonate as the alkylating reagent and **2,6-DiMeO-Tao(^{t}Bu)Phyrin** (76 mg, 0.052 mmol) as catalyst building block, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 3:1) to give the title compound in 82% yield (60 mg); TLC R_f = 0.30 (Hexanes/EtOAc 2:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 8.87 (d, J = 4.6 Hz, 4 H), 8.72 (d, J = 4.6 Hz, 4 H), 8.47 (br. s., 4 H), 7.83 (t, J = 8.4 Hz, 2 H), 7.78 (t, J = 8.4 Hz, 2 H), 7.04 (d, J = 9.2 Hz, 4 H), 6.76 (br. s., 4 H), 3.55 (s, 12 H), 3.54 - 3.46 (m, 8 H), 1.96 - 1.85 (m, 4 H), 1.36 - 1.17 (m, 8 H), 1.13 - 0.95 (m, 4 H), 0.60 (m, , 20 H), -2.42 (s, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 171.3, 168.5, 160.3, 138.9, 130.9, 130.3, 118.4, 117.6, 114.1, 106.3, 104.2, 66.0, 55.9, 24.4, 21.7, 21.5, 14.9, 10.0; HRMS (ESI) m/z Calcd. for C$_{80}$H$_{83}$N$_8$O$_{16}$$^+$ [M+H]$^+$: 1411.5922, Found: 1411.5939; UV–vis (CHCl$_3$), λmax nm (log ε): 424(5.54), 514(4.53), 556(3.80), 590(4.04), 644(3.68).
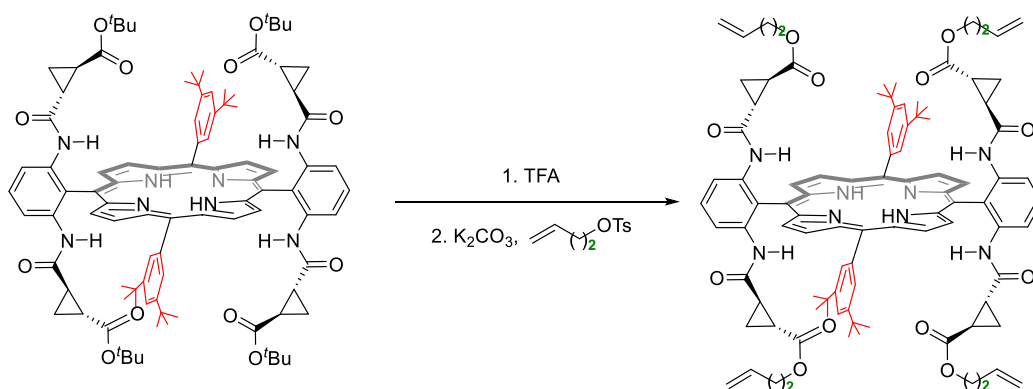
(3,5-Di^{t}Bu-Tao(Allyl)Phyrin) was synthesized following **General Procedure A** at 80 °C using allyl bromide as the alkylating reagent and **3,5-Di^{t}Bu-Tao(^{t}Bu)Phyrin** (139 mg, 0.088 mmol) as catalyst building block, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 6:1) to give the title compound in 90% yield (120 mg); TLC R_f = 0.35 (Hexanes/EtOAc 4:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 9.09 (d, J = 4.6 Hz, 4 H), 8.84 (d, J = 4.6 Hz, 4 H), 8.59 (d, J = 8.1 Hz, 4 H), 8.23 (d, J = 1.7 Hz, 4 H), 7.97 - 7.85 (m, 4 H), 6.74 (br. s., 4 H), 5.53 - 5.37 (m, 4 H), 5.01 - 4.82 (m, 8 H), 4.03 (dd, J = 4.6, 15.0 Hz, 8 H), 1.93 - 1.85 (m, 4 H), 1.56 (s, 36 H), 1.18 - 1.11 (m, 4 H), 0.65 (br. s., 4 H), 0.56 (br. s., 4 H), -2.42 (s, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 171.3, 168.1, 149.2, 140.0, 139.0, 131.4, 130.5, 130.2, 123.3, 121.6, 118.1, 117.0, 107.0, 65.1, 35.1, 31.8, 24.6, 21.6, 15.2; HRMS (ESI) m/z Calcd. for C$_{92}$H$_{98}$N$_8$NaO$_{12}^+$ [M+Na]$^+$: 1529.7196, Found: 1529.7243; UV–vis (CHCl$_3$), λmax nm (log ε): 422(5.33), 516(4.11), 550(3.68), 590(3.61), 646(3.45).
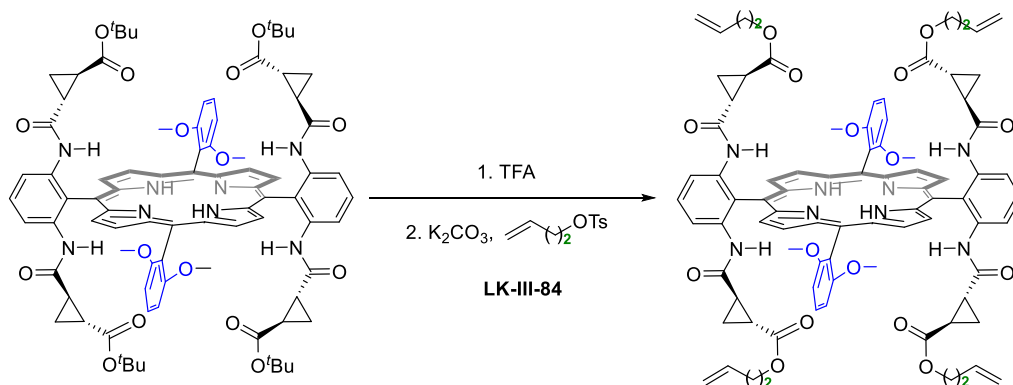

(2,6-DiMeO-Tao(Allyl)Phyrin) was synthesized following **General Procedure A** at 80 °C using allyl bromide as the alkylating reagent and **2,6-DiMeO-Tao(^{t}Bu)Phyrin** (139 mg, 0.095 mmol) as catalyst building block, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 3:1) to give the title compound in 75% yield (100 mg); TLC R_f = 0.30 (Hexanes/EtOAc 2:1). ^{1}H NMR (500 MHz, CDCl$_3$)
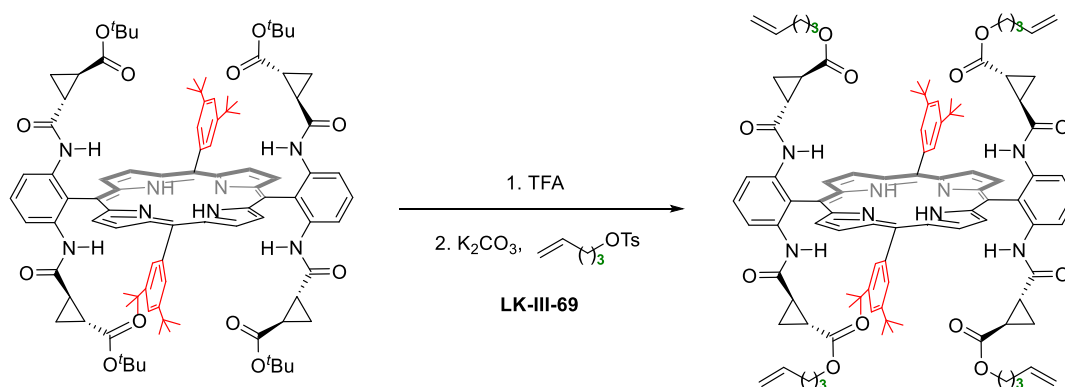
δ ppm 8.90 (d, J = 4.6 Hz, 4 H), 8.74 (d, J = 4.6 Hz, 4 H), 8.48 (d, J = 4.6 Hz, 4 H), 7.90 - 7.79 (m, 4 H), 7.08 (d, J = 8.7 Hz, 4 H), 6.82 (br. s., 4 H), 5.56 - 5.36 (m, 4 H), 5.08 - 4.68 (m, 8 H), 3.98 (d, J = 6.9 Hz, 8 H), 3.58 (s, 12 H), 1.85 (br. s, 4 H), 1.03 (br. s, 4 H), 0.62 (br. s, 4 H), 0.53 (br. s., 4 H), -2.42 (br. s, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 170.9, 168.4, 160.3, 138.9, 131.6, 131.0, 130.3, 121.7, 118.4, 118.0, 117.6, 114.2, 106.3, 104.3, 65.1, 55.9, 24.5, 21.6, 14.9; HRMS (ESI) m/z Calcd. for C$_{80}$H$_{75}$N$_8$O$_{16}$$^+$ [M+H]$^+$: 1403.5296, Found: 1403.5332; UV–vis (CHCl$_3$), λmax nm (log ε): 422(5.26), 514(4.10), 548(3.48), 588(3.60), 6.44(3.16).

(3,5-Di^{t}Bu-Tao(But-3-en-1-yl)Phyrin) was synthesized following **General Procedure A** using but-3-en-1-yl 4-methylbenzenesulfonate as the alkylating reagent and **3,5-Di^{t}Bu-Tao(^{t}Bu)Phyrin** (190 mg, 0.121 mmol) as catalyst building block, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 6:1) to give the title compound in 95% yield (180 mg); TLC R$_f$ = 0.35 (Hexanes/EtOAc 4:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 9.07 (d, J = 4.6 Hz, 4 H), 8.83 (d, J = 5.2 Hz, 4 H), 8.63 - 8.55 (m, 4 H), 8.21 (d, J = 1.7 Hz, 4 H), 7.90 (t, J = 2.0 Hz, 2 H), 7.87 (t, J = 8.7 Hz, 2 H), 6.70 (s, 4 H), 5.44 - 5.33 (m, 4 H), 4.80 - 4.66 (m, 8 H), 3.83 - 3.47 (m, 8H), 2.18 - 1.95 (m, 8H), 1.88 (ddd, J = 3.8, 5.3, 8.8 Hz, 4 H), 1.59(s, 36 H), 1.12 (ddd, J = 4.0, 5.5, 9.0 Hz, 4 H), 0.69 - 0.60 (m, 4 H), 0.56 - 0.47 (m, 4 H), -2.43 (s, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 171.6, 168.3, 149.3, 140.0, 139.0, 133.5, 130.5, 130.3, 123.3, 121.7, 117.0, 116.8, 106.8, 63.5, 35.2, 32.6, 31.8, 24.6, 21.7, 15.2; HRMS (ESI) m/z Calcd. for C$_{96}$H$_{106}$N$_8$NaO$_{12}$$^+$ [M+Na]$^+$: 1585.7822, Found: 1585.7854. UV–vis (CHCl$_3$), λmax nm (log ε): 422(5.26), 516(4.08), 552(3.81), 592(3.60), 648(3.50).
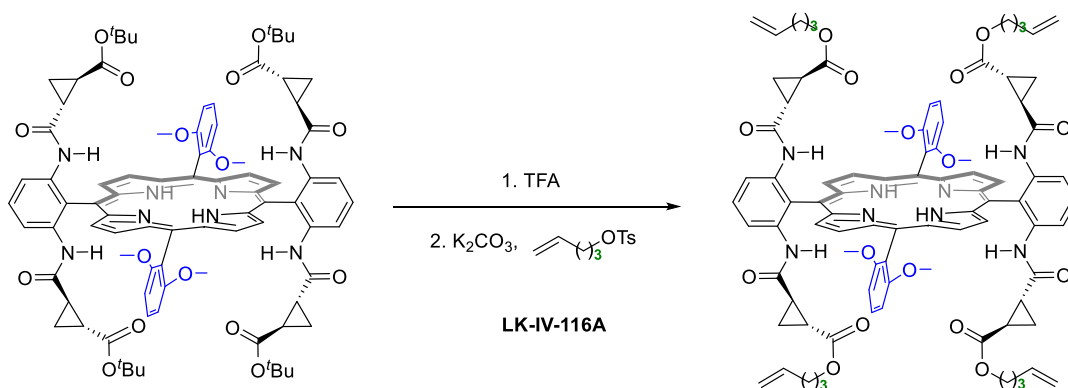
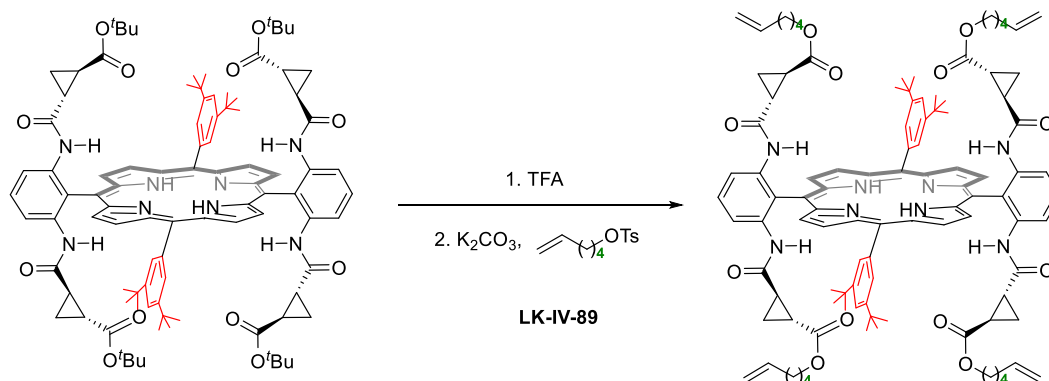(**2,6-DiMeO-Tao(But-3-en-1-yl)Phyrin**) was synthesized following **General Procedure A** using but-3-en-1-yl 4-methylbenzenesulfonate as the alkylating reagent and **2,6-DiMeO-Tao(^{t}Bu)Phyrin** (270 mg, 0.184 mmol) as catalyst building block, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 3:1) to give the title compound in 70% yield (188 mg); TLC R_f = 0.30 (Hexanes/EtOAc 2:1). ^{1}H NMR (500 MHz , CDCl$_3$) δ ppm 8.88 (d, J = 4.6 Hz, 4 H), 8.72 (d, J = 4.6 Hz, 4 H), 8.48 (d, J = 4.6 Hz, 4 H), 7.83 (t, J = 8.4 Hz, 2 H), 7.78 (t, J = 8.8 Hz, 2 H), 7.04 (d, J = 8.4 Hz, 4 H), 6.75 (br. s., 4 H), 5.63 - 5.25 (m, 4 H), 4.86 - 4.68 (m, 8 H), 3.62 - 3.52 (m, 8 H), 3.55 (s, 12 H), 1.97 (d, J = 5.3 Hz, 8 H), 1.92 - 1.83 (m, 4 H), 1.10 - 0.99 (m, 4 H), 0.65 - 0.58 (m, 8 H), -2.42 (s, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 171.2, 168.4, 160.3, 138.9, 133.5, 130.9, 130.3, 118.4, 117.5, 116.9, 114.2, 106.3, 104.2, 63.4, 55.9, 32.6, 24.4, 21.7, 14.9; HRMS (ESI) m/z Calcd. for C$_{84}$H$_{83}$N$_8$O$_{16}^+$ [M+H]$^+$: 1459.5922, Found: 1459.5950; UV–vis (CHCl$_3$) λmax nm (log ε): 424(5.26), 514(4.20), 546(3.59), 588(3.71), 644(3.27).

(**3,5-Di^{t}Bu-Tao(Pent-4-en-1-yl)Phyrin**) was synthesized following **General Procedure A** using pent-4-en-1-yl 4-methylbenzenesulfonate as the alkylating reagent and **3,5-Di^{t}Bu-Tao(^{t}Bu)Phyrin** (235 mg, 0.150 mmol) as catalyst building block, purified by silica gel column chromatography (eluent:
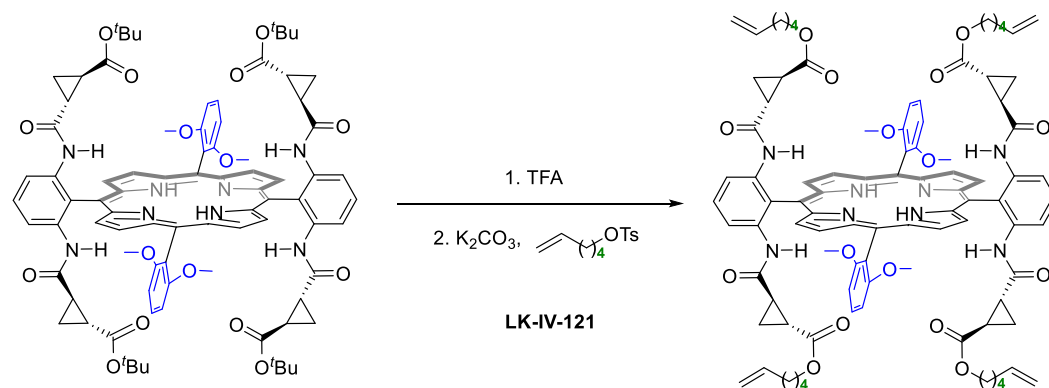
Hexanes/EtOAc 6:1) to give the title compound in 70% yield (170 mg); TLC R_f = 0.35 (Hexanes/EtOAc 4:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 9.08 (d, J = 4.6 Hz, 4 H), 8.84 (d, J = 4.6 Hz, 4 H), 8.60 (d, J = 8.1 Hz, 4 H), 8.23 (d, J = 1.7 Hz, 4 H), 7.91 (t, J = 1.7 Hz, 2 H), 7.89 (t, J = 8.4 Hz, 2 H), 6.73 (s, 4 H), 5.67 - 5.44 (m, 4 H), 4.82 - 4.62 (m, 8 H), 3.70 - 3.47 (m, 8 H), 1.91 (ddd, J = 3.8, 5.3, 8.8 Hz, 4 H), 1.86-1.76 (m, 8 H), 1.61 (s, 36 H), 1.44 - 1.33 (m, 8 H), 1.14 (ddd, J = 4.0, 5.1, 8.8 Hz, 4 H), 0.68-0.62 (m, 4 H), 0.57-0.50 (m, 4 H), -2.41 (s, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 171.7, 168.3, 149.3, 140.0, 139.0, 137.1, 130.5, 130.3, 123.4, 121.6, 116.8, 115.1, 106.8, 64.1, 35.2, 31.8, 29.7, 27.4, 24.6, 21.7, 15.3; HRMS (ESI) m/z Calcd. for C$_{100}$H$_{114}$N$_8$NaO$_{12}^+$ [M+Na]$^+$: 1641.8448, Found: 1641.8433; UV–vis (CHCl$_3$), λmax nm (log ε): 422(5.46), 516(4.22), 550(3.84), 590(3.74), 646(3.55).

(2,6-DiMeO-Tao(Pent-4-en-1-yl)Phyrin) was synthesized following **General Procedure A** using pent-4-en-1-yl 4-methylbenzenesulfonate as the alkylating reagent and **2,6-DiMeO-Tao(^{t}Bu)Phyrin** (75 mg, 0.051 mmol) as catalyst building block, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 3:1) to give the title compound in 90% yield (70 mg); TLC R_f = 0.30 (Hexanes/EtOAc 2:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 8.87 (d, J = 4.6 Hz, 4 H), 8.72 (d, J = 4.0 Hz, 4 H), 8.47 (br. s, 4 H), 7.83 (t, J = 8.4 Hz, 2 H), 7.78 (t, J = 8.4 Hz, 2 H), 7.04 (d, J = 8.7 Hz, 4 H), 6.76 (br. s, 4 H), 5.59 - 5.45 (m, 4 H), 4.85 - 4.73 (m, 8 H), 3.72 - 3.40 (m, 8 H), 3.54 (s, 12H), 1.91 (td, J = 4.6, 8.8 Hz, 4 H), 1.79 (d, J = 6.4 Hz, 8 H), 1.40 - 1.30 (m, 8 H), 1.09 - 0.97 (m, 4 H), 0.70-0.55 (m, 8 H), -2.43 (s, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 171.4, 168.5, 160.3, 138.9, 137.2, 131.0, 130.3, 118.4, 117.6, 115.1, 114.2, 110.0, 106.3, 104.2, 64.0, 55.9, 29.7, 27.4, 24.4, 21.7, 15.0; HRMS (ESI) m/z Calcd. for C$_{88}$H$_{91}$N$_8$O$_{16}^+$ [M+H]$^+$: 1515.6548, Found: 1515.6579; UV–vis (CHCl$_3$), λmax nm (log ε): 424(5.28), 514(4.25), 546(3.64), 588(3.75), 642(3.34).
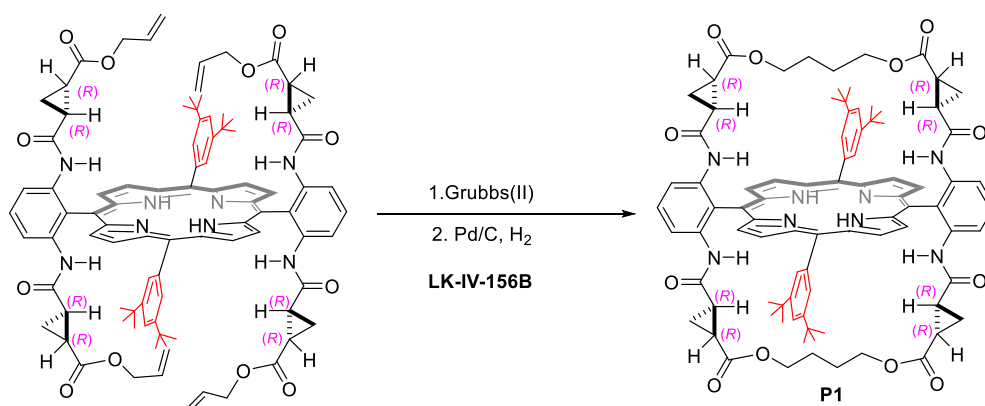
(3,5-Di^{t}Bu-Tao(Hex-5-en-1-yl)Phyrin) was synthesized following **General Procedure A** using hex-5-en-1-yl 4-methylbenzenesulfonate as the alkylating reagent and **3,5-Di^{t}Bu-Tao(^{t}Bu)Phyrin** (64 mg, 0.041 mmol) as catalyst building block, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 6:1) to give the title compound in 66% yield (45 mg); TLC R$_f$ = 0.35 (Hexanes/EtOAc 4:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 9.04 (d, J = 4.6 Hz, 4 H), 8.79 (d, J = 4.6 Hz, 4 H), 8.63 - 8.48 (m, 4 H), 8.19 (s, 4 H), 7.85 (d, J = 12.4 Hz, 4 H), 6.68 (br. s., 4 H), 5.63 - 5.51 (m, 4 H), 4.87 - 4.74 (m, 8 H), 3.63 - 3.44 (m, 8 H), 1.92 - 1.77 (m, 12 H), 1.57 (s, 36 H), 1.25-1.22 (m, 8 H), 1.18 - 1.04 (m, 12 H), 0.66 - 0.56 (m, 4 H), 0.54 - 0.42 (m, 4 H), -2.46 (s, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 171.8, 168.3, 149.2, 140.0, 139.0, 138.6, 138.0, 130.5, 130.3, 123.3, 121.6, 114.7, 64.6, 35.2, 33.5, 33.0, 31.8, 27.6, 24.8, 21.7, 15.3; HRMS (ESI) m/z Calcd. for C$_{104}$H$_{123}$N$_8$O$_{12}^+$ [M+H]$^+$: 1675.9255, Found: 1675.9187; UV–vis (CHCl$_3$), λmax nm (log ε): 424(5.27), 516(4.08), 552(3.67), 590(3.59), 646(3.41).

(2,6-DiMeO-Tao(Hex-5-en-1-yl)Phyrin) was synthesized following **General Procedure A** using hex-5-en-1-yl 4-methylbenzenesulfonate as the alkylating reagent and **2,6-DiMeO-Tao(^{t}Bu)Phyrin** (62 mg, 0.042 mmol) as catalyst building block, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1) to give the title compound in 65% yield (43 mg); TLC R$_f$ = 0.30 (Hexanes/EtOAc 3:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 8.87 (d, J = 4.6 Hz, 4 H), 8.72 (d, J = 4.6 Hz, 4 H), 8.46 (br. s., 4

H), 7.83 (t, $J = 8.5$ Hz, 2 H), 7.78 (t, $J = 8.5$ Hz, 2 H), 7.04 (d, $J = 8.7$ Hz, 4 H), 6.75 (br. s., 4 H), 5.59 (d, $J = 6.9$ Hz, 4 H), 4.87 - 4.78 (m, 8 H), 3.58 (br. s., 4 H), 3.55 (s, 12 H), 1.91 (td, $J = 4.6, 8.8$ Hz, 4 H), 1.83 (d, $J = 6.4$ Hz, 8 H), 1.36 - 1.21 (m, 12 H), 1.15 (d, $J = 6.4$ Hz, 8 H), 1.08 - 0.97 (m, 4 H), 0.60 (br. s., 8 H), -2.42 (s, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 171.4, 168.5, 162.6, 160.3, 138.9, 138.1, 131.0, 130.3, 118.4, 117.6, 115.2, 114.7, 114.2, 104.3, 64.5, 55.9, 33.1, 27.7, 24.9, 24.4, 21.7, 15.0; HRMS (ESI) m/z Calcd. for $C_{92}H_{99}N_8O_{16}^+$ [M+H]$^+$: 1571.7174, Found: 1571.7114; UV–vis (CHCl$_3$), λmax nm (log ε): 422(5.13), 516(4.06), 546(3.47), 590(3.56), 644(3.22).

General Procedure B (Synthesis of Bridged Amidoporphyrins)

Under nitrogen atmosphere, Grubbs 2nd generation catalyst (0.1 equiv) was added to a solution of the above synthesized porphyrins with olefin side chains (1 equiv) in DCM (0.001 M). The reaction mixture was stirred at 40 °C for 12 hours. The reaction mixture was directly poured onto a pad of silica gel (Hexanes/EtOAc = 1:1) to afford the mixture of *trans-cis* olefin metathesis isomers. The solvent was removed and the residue was dissolved in EtOAc-toluene (V/V 2 /1, 0.02 M) in the presence of 10%Pd/C (1 mg per mg of porphyrin). Hydrogen gas was bubbled through the reaction mixture until the reaction was completed (Typically for 30 min). The reaction mixture was pass through a short pad of Celite, the filtrate was concentrated and purified by silica gel column chromatography (Conditions were given below) to afford the desired product. (The reaction can be easily scaled up to 500 mg scale.)

Characterization of Bridged Amidoporphyrins

(3,5-Di^{t}Bu-Hu(C$_4$)Phyrin) (P1) was synthesized following General Procedure B from (3,5-Di^{t}BuTao-(Allyl)Phyrin) (73 mg, 0.049 mmol), purified by silica gel column chromatography (eluent:
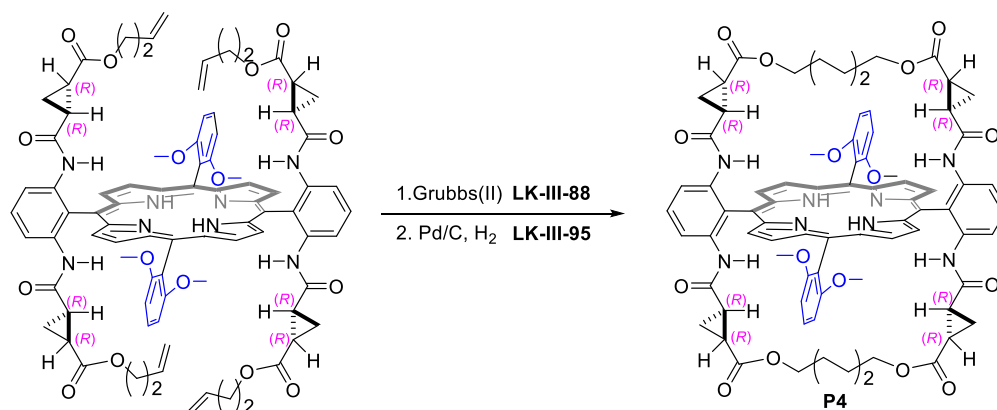
Hexanes/EtOAc 3:1) to give the title compound in 85% yield (60 mg); TLC R_f = 0.35 (Hexanes/EtOAc 2:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 9.14 (d, J = 5.2 Hz, 4 H), 8.92 (d, J = 4.6 Hz, 4 H), 8.45 (d, J = 8.7 Hz, 4 H), 8.14 (d, J = 1.7 Hz, 4 H), 7.95 - 7.89 (m, 4 H), 6.63 (s, 4 H), 3.63 - 3.54 (m, 4 H), 3.37 - 3.28 (m, 4 H), 1.80 (ddd, J = 4.0, 5.5, 9.0 Hz, 4 H), 1.61 (s, 36 H), 1.08 - 1.02 (m, 4 H), 0.95-0.89 (m, 8 H), 0.69 (dd, J = 4.6, 8.7 Hz, 4 H), 0.66 - 0.57 (m, 4 H), -2.53 (s, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 170.6, 168.1, 149.6, 139.4, 138.8, 130.6, 130.0, 123.2, 123.0, 122.1, 118.6, 108.1, 64.0, 35.1, 31.7, 24.6, 23.7, 22.0, 14.9; HRMS (ESI) m/z Calcd. for C$_{88}$H$_{94}$N$_8$NaO$_{12}^+$ [M+Na]$^+$: 1477.6883, Found: 1477.6867; UV−vis (CHCl$_3$), λmax nm (log ε): 424(5.29), 514(3.97), 552(3.67), 590(3.55), 644(3.36).
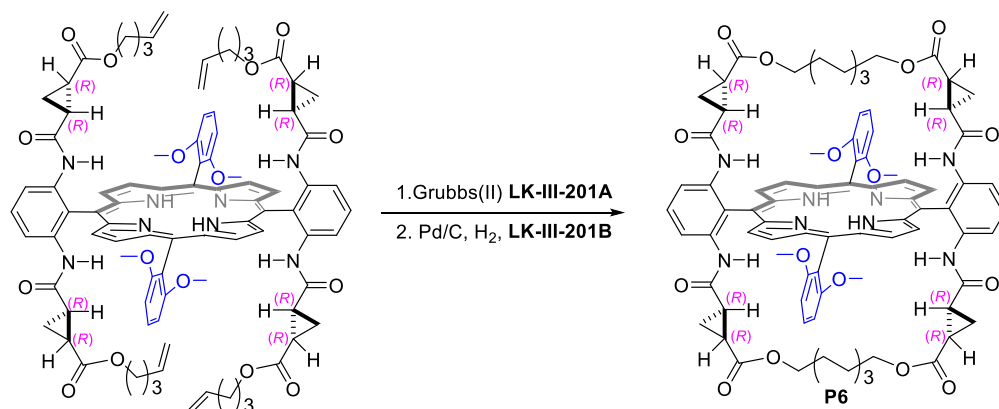

(2,6-DiMeO-Hu(C$_4$)Phyrin) (P2) was synthesized following **General Procedure B** from (**2,6-DiMeO-Tao(Allyl)Phyrin**) (89 mg, 0.063 mmol), purified by silica gel column chromatography (eluent: Hexanes/EtOAc 2:1) to give the title compound in 82% yield (70 mg); TLC R_f = 0.2 (Hexanes/EtOAc 1:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 8.98 (d,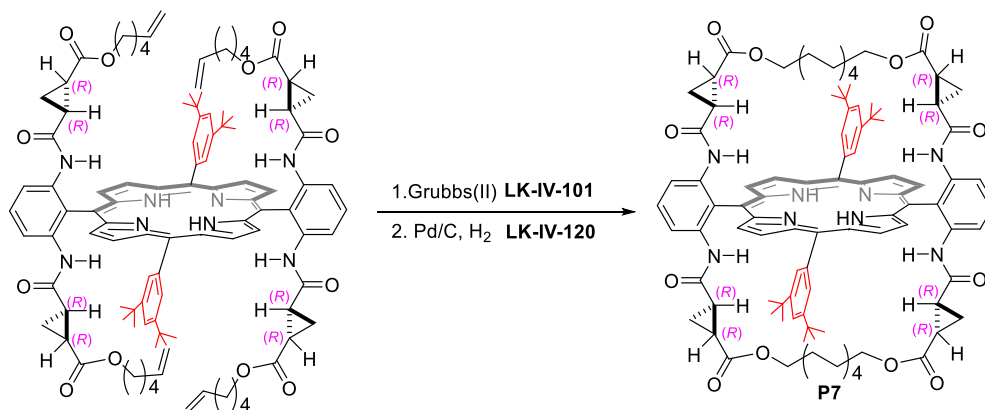 J = 4.6 Hz, 4 H), 8.82 (d, J = 4.6 Hz, 4 H), 8.46 (d, J = 8.7 Hz, 4 H), 7.92 - 7.83 (m, 4 H), 7.12 (d, J = 8.7 Hz, 4 H), 6.67 (s, 4 H), 3.67 - 3.59 (m, 12 H), 3.60 - 3.49 (m, 4 H), 3.35 - 3.26 (m, 4 H), 1.88 (ddd, J = 4.0, 5.5, 9.0 Hz, 4 H), 1.03 (td, J = 4.6, 8.8 Hz, 4 H), 0.98 - 0.84 (m, 8 H), 0.78 - 0.64 (m, 4 H), 0.58 (td, J = 4.6, 8.8 Hz, 4 H), -2.50 (s, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 170.6, 168.2, 160.2, 138.9, 131.3, 130.5, 122.5, 118.3, 117.8, 114.2, 107.0, 104.4, 64.1, 56.1, 24.6, 23.8, 22.2, 14.8; HRMS (ESI) m/z Calcd. for C$_{76}$H$_{71}$N$_8$O$_{16}^+$ [M+H]$^+$: 1351.4983, Found: 1351.4970; UV−vis (CHCl$_3$), λmax nm (log ε): 422(5.11), 514(4.06), 544 (3.42), 586(3.58), 640(3.10).

(3,5-Di*t*Bu-Hu(C₆)Phyrin) (P3) was synthesized following **General Procedure B** from (**3,5-Di*t*Bu-Tao(But-3-en-1-yl)Phyrin**) (168 mg, 0.107 mmol), purified by silica gel column chromatography (eluent: Hexanes/EtOAc 3:1) to give the title compound in 80% yield (130 mg); TLC R_f = 0.37 (Hexanes/EtOAc 2:1). ^{1}H NMR (400 MHz, CDCl₃) δ ppm 9.05 (d, J = 4.6 Hz, 4 H), 8.85 (d, J = 4.6 Hz, 4 H), 8.41 (d, J = 8.3 Hz, 4 H), 8.11 (d, J = 1.4 Hz, 4 H), 7.94 - 7.79 (m, 4 H), 6.64 (s, 4 H), 3.62 - 3.56 (m, 4 H), 3.50 - 3.44 (m, 4 H), 1.92 - 1.88 (m, 4 H), 1.57 (s, 36 H), 1.07 (dd, J = 3.7, 8.8 Hz, 4 H), 1.01 - 0.90 (m, 8 H), 0.78 (d, J = 2.8 Hz, 8 H), 0.67 - 0.49 (m, 8 H), -2.55 (s, 2 H); ^{13}C NMR (100 MHz, CDCl₃) δ ppm 171.1, 168.3, 149.4, 139.8, 138.7, 130.5, 130.4, 130.3, 130.2, 123.3, 122.4, 121.9, 118.6, 107.7, 64.3, 35.1, 31.8, 27.3, 24.2, 23.9, 22.1, 15.1; HRMS (ESI) m/z Calcd. for $C_{92}H_{102}N_8NaO_{12}^+$ [M+Na]$^+$: 1533.7515, Found: 1533.7542; UV–vis (CHCl₃), λmax nm (log ε): 424(5.43), 518(4.22), 554(3.83), 590(3.73), 646(3.58).
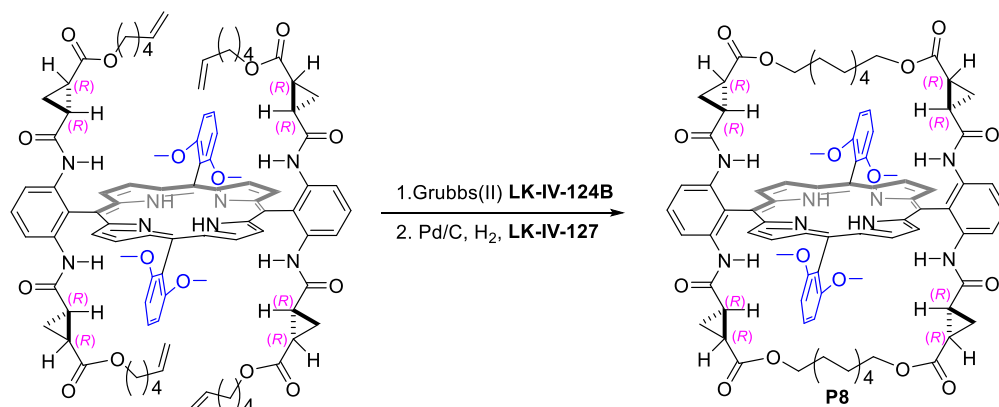

(2,6-DiMeO-Hu(C₆)Phyrin) (P4) was synthesized following **General Procedure B** from (**2,6-DiMeO-Tao(But-3-en-1-yl)Phyrin**) (171 mg, 0.117 mmol), purified by silica gel column chromatography (eluent: Hexanes/EtOAc 2:1) to give the title compound in 85% yield (140 mg); TLC R_f = 0.2 (Hexanes/EtOAc 1:1). ^{1}H NMR (500 MHz, CDCl₃) δ pm 8.88 (d, J = 4.6 Hz, 4 H), 8.76 (d, J = 4.6 Hz, 4 H), 8.35 (d, J =

8.4 Hz, 4 H), 7.83 (t, *J* = 8.4 Hz, 2 H), 7.79 (t, *J* = 8.5 Hz, 2 H), 7.05 (d, *J* = 8.6 Hz, 4 H), 6.70 (s, 4 H), 3.64 (dt, *J* = 7.0, 10.6 Hz, 4 H), 3.54 (s, 12 H), 3.44 - 3.38 (m, 4 H), 1.98 - 1.90 (m, 4 H), 1.06 (dt, *J* = 4.4, 8.8 Hz, 4 H), 1.00 - 0.88 (m, 8 H), 0.80 - 0.65 (m, 12 H), 0.57 (dd, *J* = 6.8, 10.9 Hz, 4 H), -2.50 (s, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 170.8, 168.3, 160.2, 138.6, 131.1, 130.3, 122.6, 118.9, 118.3, 114.2, 106.8, 104.3, 64.1, 55.9, 27.4, 24.4, 23.8, 22.1, 14.7; HRMS (ESI) *m/z* Calcd. for C$_{80}$H$_{79}$N$_8$O$_{16}^+$ [M+H]$^+$: 1407.5614, Found: 1407.5642; UV–vis (CHCl$_3$) λmax nm (log ε): 422(5.26), 516(4.08), 548(3.52), 588(3.59), 644(3.23).
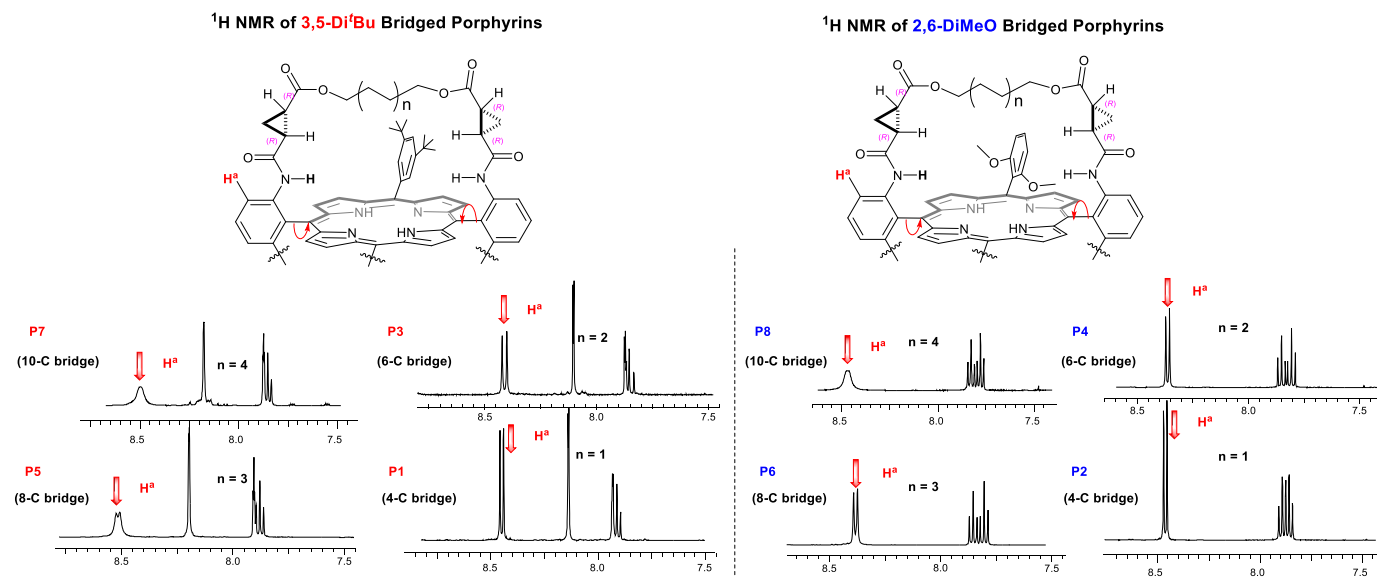

(**3,5-Di^{t}Bu-Hu(C$_8$)Phyrin) (P5)** was synthesized following **General Procedure B** from (**3,5-Di^{t}Bu-Tao(Pent-4-en-1-yl)Phyrin**) (158 mg, 0.098 mmol), purified by silica gel column chromatography (eluent: Hexanes/EtOAc 3:1) to give the title compound in 88% yield (135 mg); TLC R$_f$ = 0.37 (Hexanes/EtOAc 2:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 9.02 (d, *J* = 4.6 Hz, 4 H), 8.80 (d, *J* = 4.7 Hz, 4 H), 8.47 (d, *J* = 8.0 Hz, 4 H), 8.15 (s, 4 H), 7.88 - 7.81 (m, 4 H), 6.64 (s. 4 H), 3.72 - 3.61 (m, 4 H), 3.58 - 3.50 (m, 4 H), 1.94 - 1.84 (m, 4 H), 1.56 (s, 36 H), 1.25 - 1.15 (m, 4 H), 1.12-1.00 (m, 8 H), 0.94 - 0.80 (m, 16 H), 0.65 - 0.52 (m, 8 H), -2.49 (s, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 171.5, 168.4, 149.3, 140.0, 138.8, 130.5, 130.2, 123.3, 121.7, 117.8, 107.1, 63.8, 35.2, 31.8, 27.3, 26.8, 24.1, 21.9, 15.3; HRMS (ESI) m/z Calcd. for C$_{96}$H$_{110}$N$_8$NaO$_{12}^+$ [M+Na]$^+$ 1589.8341, Found: 1589.8372; UV–vis (CHCl$_3$), λmax nm (log ε): 424(5.17), 518(4.05), 552(3.67), 592(3.57), 646(3.43).

(2,6-DiMeO-Hu(C₈)Phyrin) (P6) was synthesized following **General Procedure B** from (**2,6-DiMeO-Tao(Pent-4-en-1-yl)Phyrin**) (59 mg, 0.039 mmol), purified by silica gel column chromatography (eluent: Hexanes/EtOAc/DCM 2:1:1) to give the title compound in 74% yield (42 mg); TLC R_f = 0.3 (Hexanes/EtOAc/DCM 1:1:1). ^{1}H NMR (500 MHz, CDCl₃) δ ppm 8.90 (d, J = 4.6 Hz, 4 H), 8.77 (d, J = 4.0 Hz, 4 H), 8.40 (d, J = 8.1 Hz, 4 H), 7.82 (t, J = 8.4 Hz, 2H), 7.78 (t, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 4 H), 6.81 (br. s., 4 H), 3.74 - 3.59 (m, 4 H), 3.59 - 3.41 (m, 16H), 2.03 - 1.89 (m, 4 H), 1.23 - 1.04 (m, 12 H), 0.89 - 0.76 (m, 16 H), 0.70 - 0.65 (m, 4H), 0.64 - 0.55 (m, 4H), -2.39 (s, 2 H); ^{13}C NMR (125 MHz, CDCl₃) δ ppm 171.1, 168.4, 160.3, 138.6, 130.9, 130.2, 122.5, 118.9, 118.4, 114.1, 106.5, 104.2, 64.0, 55.8, 27.2, 27.0, 24.2, 24.0, 21.8, 14.8; HRMS (ESI) m/z Calcd. for $C_{84}H_{87}N_8O_{16}^+$ [M+H]$^+$: 1463.6235, Found: 1463.6278; UV–vis (CHCl₃), λmax nm (log ε): 424(5.17), 516(4.17), 550(3.64), 590(3.68), 644(2.34).

(3,5-Di^{t}Bu-Hu(C₁₀)Phyrin) (P7) was synthesized following **General Procedure B** from (**3,5-Di^{t}Bu-Tao(Hex-5-en-1-yl)Phyrin**) (40 mg, 0.024 mmol), purified by silica gel column chromatography (eluent: Hexanes/EtOAc 5:1) to give the title compound in 65% yield (25 mg); TLC R_f = 0.35 (Hexanes/EtOAc 4:1). ^{1}H NMR (500 MHz, CDCl₃) δ ppm 9.03 (d, J = 4.9 Hz, 4 H), 8.80 (d, J = 4.6 Hz, 4 H), 8.56 - 8.41

(m, 4 H), 8.17 (s, 4 H), 7.90 - 7.80 (m, 4 H), 6.68 (s, 4 H), 3.77 - 3.67 (m, 4 H), 3.57 - 3.45 (m, 4 H), 1.94 - 1.86 (m, 4 H), 1.60 - 1.55 (m, 36 H), 1.36 - 1.24 (m, 12 H), 1.06 (d, J = 8.7 Hz, 4 H), 0.99 - 0.85 (m, 20 H), 0.58 (br. s., 8 H), -2.48(s, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 171.6, 168.4, 149.3, 140.0, 138.9, 130.9, 130.4, 130.2, 128.8, 123.2, 121.6, 107.7, 63.9, 35.1, 31.8, 27.5, 27.3, 26.7, 24.2, 24.0, 21.8, 15.3; HRMS (ESI) m/z Calcd for $C_{100}H_{119}N_8O_{12}^+$ [M+H]$^+$: 1623.8942, Found: 1623.8916; UV–vis (CHCl$_3$), λmax nm (log ε): 424(5.32), 518(4.07), 552(3.66), 592(3.56), 646(3.40).

(2,6-DiMeO-Hu(C$_{10}$)Phyrin) (P8) was synthesized following **General Procedure B** from (**2,6-DiMeO-Tao(Hex-5-en-1-yl)Phyrin**) (40 mg, 0.025 mmol), purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1) to give the title compound in 67% yield (26 mg); TLC R$_f$ = 0.2 (Hexanes/EtOAc 3:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 8.86 (d, J = 4.6 Hz, 4 H), 8.72 (d, J = 4.3 Hz, 4 H), 8.39 (d, J = 7.5 Hz, 4 H), 7.83 (t, J = 8.5 Hz, 2 H), 7.79 (t, J = 8.5 Hz, 2 H), 7.05 (d, J = 8.4 Hz, 4 H), 6.74 (br. s., 4 H), 3.62 (t, J = 6.6 Hz, 8 H), 3.55 (s, 12 H), 1.94 (ddd, J = 3.9, 5.5, 8.8 Hz, 4 H), 1.34 - 1.14 (m, 12 H), 1.04 (ddd, J = 3.9, 5.2, 8.8 Hz, 4 H), 0.99 - 0.83 (m, 20 H), 0.67 (br. s., 4 H), 0.57 (br. s., 4 H), -2.41 (s, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 187.6, 171.3, 168.5, 160.3, 138.7, 130.9, 130.2, 118.5, 114.1, 106.4, 104.2, 63.9, 55.9, 27.5, 27.4, 26.8, 24.2, 24.1, 21.7, 15.0; HRMS (ESI) m/z Calcd. for $C_{88}H_{95}N_8O_{16}^+$ [M+H]$^+$: 1519.6861, Found: 1519.6814; UV–vis (CHCl$_3$), λmax nm (log ε): 422(5.22), 516(4.11), 548(3.50), 588(3.62), 644(3.21).

Figure S4. ^{1}H NMR Spectra of Bridged Amidoporphyrins (Low-field Region)

General Procedure C (Synthesis of Co(II)-Based, Open and Bridged Amidoporphyrins)

The desired porphyrin starting material (1 equiv) and CoCl$_2$ (8 equiv) were placed in an oven dried Schlenk tube. The tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen. The screw cap was replaced with a rubber septum. 2,6-Lutidine (4 equiv) and THF (0.05 M) were added and the tube was purged with nitrogen for 1 min and sealed with Teflon screwcap. The reaction mixture was stirred at 100 °C for 12 h prior to being cooled to r.t. The reaction mixture was diluted with DCM and washed with brine. The organic layer was separated, dried, and concentrated. The residue was purified by silica gel column chromatography (eluent: Hexanes/EtOAc 1:1) to give the title compound.

## Characterization of Co(II)-Based, Open and Bridged Amidoporphyrins

[Co(3,5-Di^{t}Bu-Tao(nBu)Phyrin)] (**[Co(P10)]**) was synthesized in 95% yield (32 mg) following **General Procedure C** from (**3,5-Di^{t}Bu-Tao(nBu)Phyrin**) (**P10**) (33 mg, 0.021 mol). HRMS (ESI) m/z Calcd. for $C_{96}H_{113}CoN_8O_{12}^+$ [M+H]$^+$: 1628.7804, Found: 1628.7886; UV–vis (CHCl$_3$), λmax nm (log ε): 438(5,26), 550(4.24).

[Co(2,6-DiMeO-Tao(nPr)Phyrin)] (**[Co(P11)]**) was synthesized in 88% yield (26 mg) following **General Procedure C** from (**2,6-DiMeO-Tao(nPr)Phyrin**) (**P11**) (28 mg, 0.02 mmol). HRMS (ESI) m/z Calcd. for $C_{80}H_{81}CoN_8O_{16}^+$ [M+H]$^+$: 1468.5097, Found: 1468.5096; UV–vis (CHCl$_3$), λmax nm (log ε): 436(5.21), 546(4.24), 662(3.71).


[Co(3,5-Di^{t}Bu-Hu(C$_4$)Phyrin)] (**[Co(P1)]**) was synthesized in 84% yield (40 mg) following **General Procedure C** from (**3,5-Di^{t}Bu-Hu(C$_4$)Phyrin**) (**P1**) (46 mg, 0.032 mmol). HRMS (ESI) m/z Calcd. for $C_{88}H_{93}CoN_8O_{12}^+$ [M+H]$^+$: 1512.6239, Found: 1512.6259; UV–vis (CHCl$_3$), λmax nm (log ε): 438(4.78), 546(3.84), 662(3.49).

[Co(2,6-DiMeO-Hu(C$_4$)Phyrin)] ([Co(**P2**)]) was synthesized in 90% yield (55 mg) following **General Procedure C** from (**2,6-DiMeO-Hu(C$_4$)Phyrin**) (**P2**) (58 mg, 0.043 mmol). HRMS (ESI) m/z Calcd. for C$_{76}$H$_{69}$CoN$_8$O$_{16}$$^+$ [M+H]$^+$: 1408.4158, Found: 1408.4120; UV–vis (CHCl$_3$), λmax nm (log ε): 432(4.85), 542(3.96), 658(3.21).
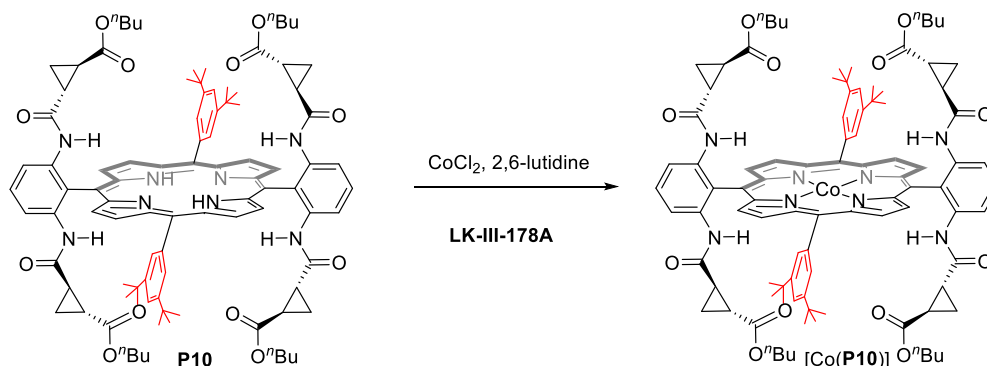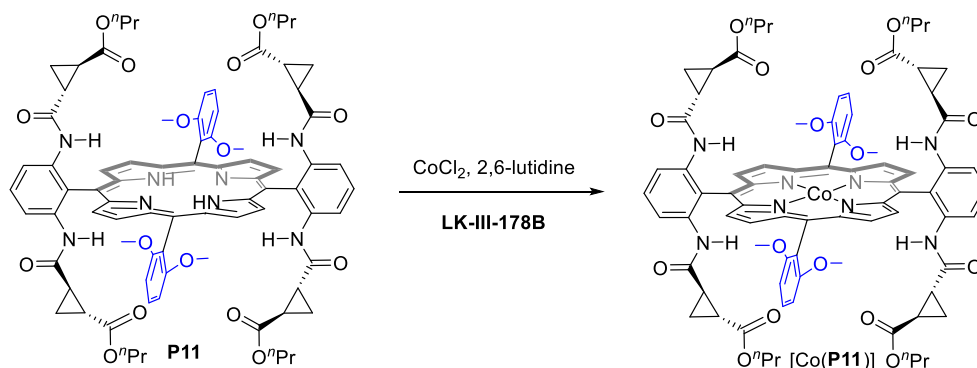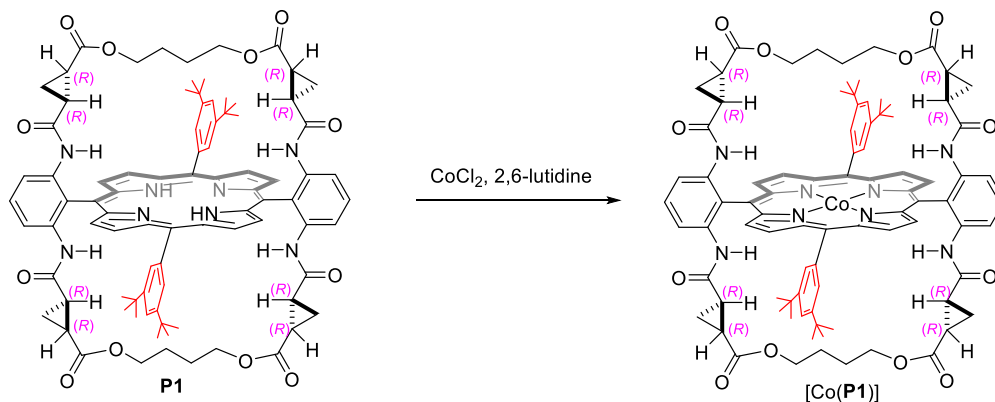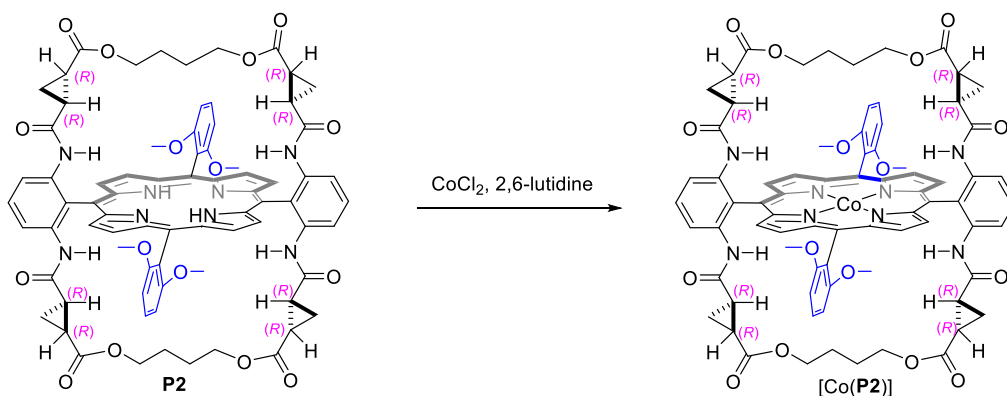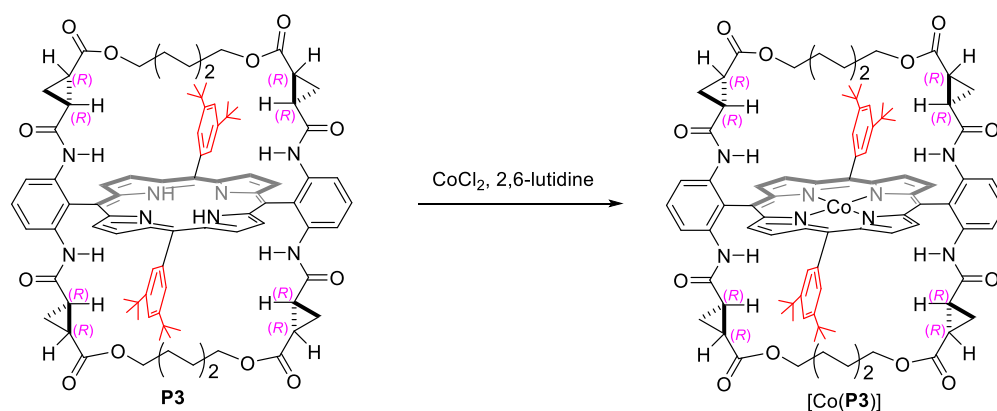
[Co(3,5-Di^{t}Bu-Hu(C$_6$)Phyrin)] ([Co(**P3**)]) was synthesized in 90% yield (170 mg) following **General Procedure C** from (**3,5-Di^{t}Bu-Hu(C$_6$)Phyrin**) (**P3**) (182 mg, 0.121 mmol). HRMS (ESI) m/z Calcd. for C$_{92}$H$_{101}$CoN$_8$O$_{12}$$^+$ [M+H]$^+$: 1568.6865, Found: 1568.6894; UV–vis (CHCl$_3$), λmax nm (log ε): 436(5.01), 548(4.03), 660(3.31).
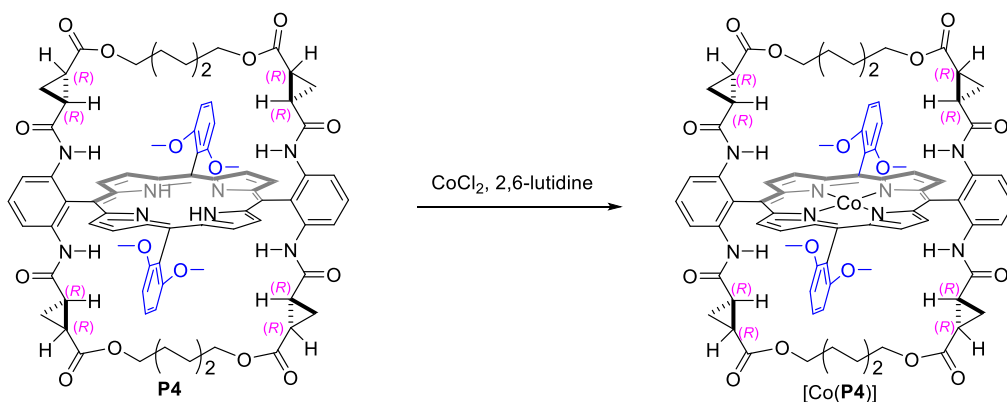
[Co(2,6-DiMeO-Hu(C$_6$)Phyrin)] ([Co(**P4**)]) was synthesized in 95% yield (50 mg) following **General Procedure C** from (**2,6-DiMeO-Hu(C$_6$)Phyrin**) (**P4**) (51 mg, 0.036 mmol). HRMS (ESI) *m/z* Calcd. for C$_{80}$H$_{77}$CoN$_8$O$_{16}^+$ [M+H]$^+$: 1464.4784, Found: 1464.4754; UV-vis (CHCl$_3$) λmax nm (log ε): 434(4.92), 544(3.94), 646(3.26). (The reaction can be easily scaled up to 400 mg scale.)
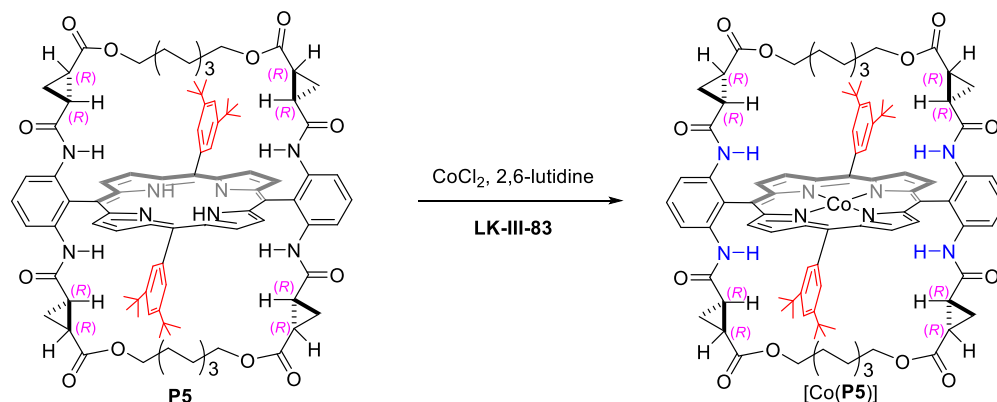
[Co(3,5-Di^{t}Bu-Hu(C$_8$)Phyrin)] ([Co(**P5**)]) was synthesized in 91% yield (128 mg) following **General Procedure C** from (**3,5-Di^{t}Bu-Hu(C$_8$)Phyrin**) (**P5**) (136 mg, 0.086 mmol). HRMS (ESI) m/z Calcd. for C$_{96}$H$_{109}$CoN$_8$O$_{12}^+$ [M+H]$^+$: 1624.7491, Found: 1624.7521; UV–vis (CHCl$_3$), λmax nm (log ε): 436(4.97), 550(3.97), 668(3.38). (The reaction can be easily scaled up to 500 mg scale.)
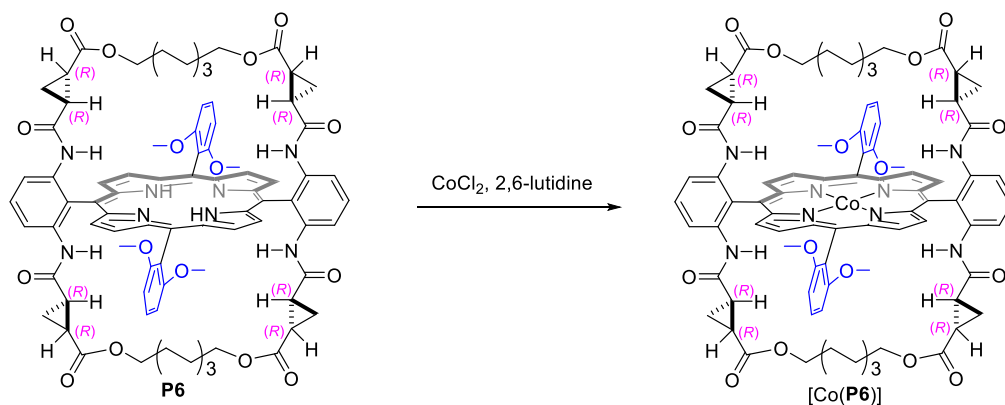
[Co(2,6-DiMeO-Hu(C8)Phyrin)] ([Co(**P6**)]) was synthesized in 95% yield (50 mg) following **General Procedure C** from (**2,6-DiMeO-Hu(C8)Phyrin**) (**P6**) (51 mg, 0.035 mmol). HRMS (ESI) m/z Calcd. for $C_{84}H_{85}CoN_8O_{16}^+$ [M+H]$^+$: 1520.5410, Found: 1520.5432; UV–vis (CHCl$_3$), λmax nm (log ε): 436(5.05), 544(4.08), 668(3.41).
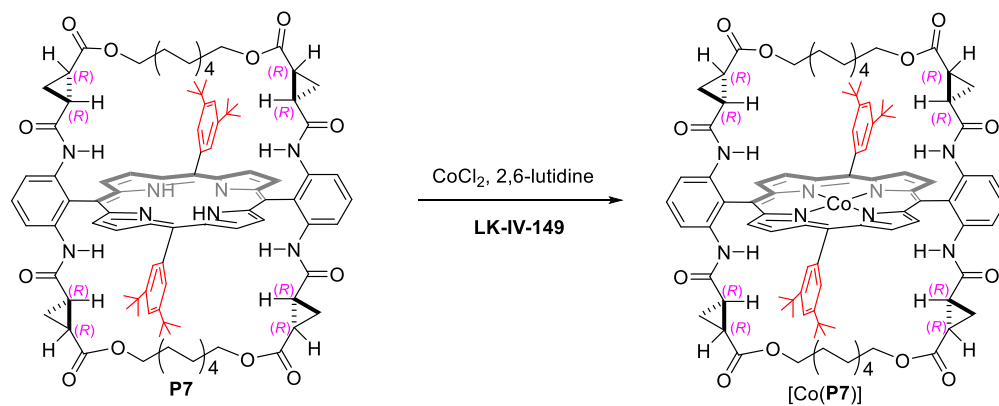
[Co(3,5-Di^{t}Bu-Hu(C10)Phyrin)] ([Co(**P7**)]) was synthesized in 92% yield (17 mg) following **General Procedure C** from (**3,5-Di^{t}Bu-Hu(C10)Phyrin**) (**P7**) (18 mg, 0.011 mmol). HRMS (ESI) m/z Calcd. for $C_{100}H_{117}CoN_8O_{12}^+$ [M+H]$^+$, 1680.8117, Found: 1680.8033; UV–vis (CHCl$_3$), λmax nm (log ε): 438(4.91), 550(3.94), 670(3.37).
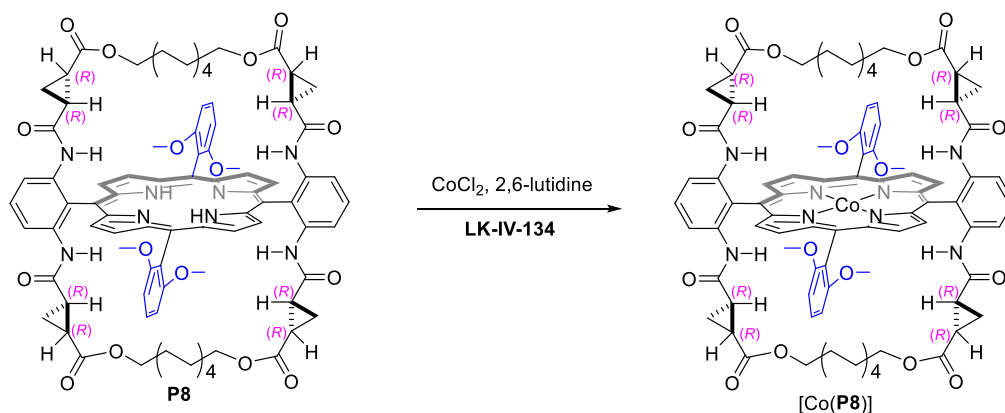
[Co(2,6-DiMeO-Hu(C$_{10}$)Phyrin)] ([Co(P8)]) was synthesized in 90% yield (18 mg) following **General Procedure C** from (**2,6-DiMeO-Hu(C$_{10}$)Phyrin**) (**P8**) (19 mg, 0.013 mmol). HRMS (ESI) *m*/*z* Calcd. for C$_{88}$H$_{93}$CoN$_8$O$_{16}^+$ [M+H]$^+$: 1576.6036, Found: 1576.5922; UV–vis (CHCl$_3$), λmax nm (log ε): 436(4.88), 546(3.91), 670(3.35).

General Procedure D (Amine Synthesis).

Procedure D1 (S$_N$2 Amination)
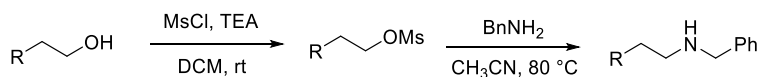
Methanesulfonyl chloride (0.58 mL, 7.5 mmol) was added to a round bottom flask containing alcohol precursor (5 mmol) in DCM (15 mL), followed by the addition of triethyl amine (1.41 mL, 10 mmol). The precipitate was formed immediately. The reaction mixture was stirred at room temperature for 1 or 2 hours until the alcohol was fully consumed based on TLC. DCM (30 mL) was added and the reaction mixture was washed with water (50 mL). The aqueous solution was extracted by DCM (3 × 20 mL). The combined organic layer was dried over anhydrous sodium sulfate. The solvent was removed and CH$_3$CN (20 mL) was added, followed by the benzyl amine (10 mmol) and the reaction was heated at 80 °C for 6 hours. Then the solvent was removed and the residue was purified by silica gel column chromatography (gradient elution: Hexanes/EtOAc 8:1 to 1:1) to give the desired amine products, which were used directly for the next step.
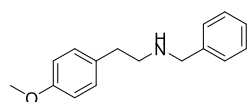
Procedure D2 (Reductive Amination)
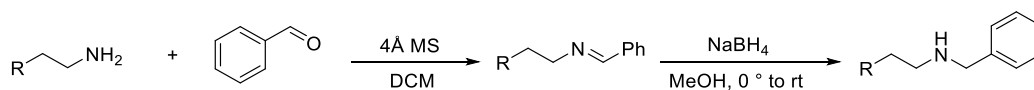
Oven-dried 4 Å molecular sieves (1.0 g) were added to a solution of primary amine (5 mmol) and benzaldehyde (0.53 mL, 5 mmol) in dichloromethane (30 mL). The reaction mixture was stirred for 2 hours at room temperature. Then the solvent was removed under reduced pressure and MeOH (25 mL) was added into the residue. The reaction mixture was cooled to 0 °C, followed by the addition of NaBH$_4$ (570 mg, 15 mmol) in several portions. After the reaction became less vigorous, the reaction was slowly warmed up to room temperature and stirred for another hour. Then the solvent was removed and the residue was purified by silica gel column chromatography (gradient elution: Hexanes/EtOAc 8:1 to 1:1) to give the desired amine products, which were used directly for the next step.

Procedure D3 (Amide Reduction)
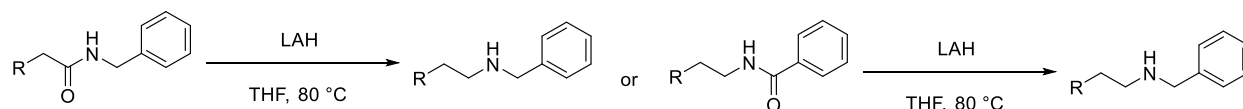
LiAlH$_4$ (1.5 mmol) was added to a sealed tube containing amide (5 mmol) in newly distilled anhydrous THF (15 mL). The reaction mixture was heated to 80 °C for 2 days. After quenching the excess amount of LiAlH$_4$ following Fieser method, the reaction mixture was filtrated through a short pad of Celite. Then the solvent was removed and the residue was purified by silica gel column chromatography (gradient elution: Hexanes/EtOAc 8:1 to 1:1) to give the desired amine products, which were used directly for the next step.

Characterization of Amines

N-Benzyl-2-phenylethan-1-amine was prepared in 75% yield (790 mg) as yellow oil through **General Procedure D2** from 2-phenylethan-1-amine (commercially available, cas: 64-04-0) (605 mg, 5 mmol). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.44 - 7.24 (m, 10 H), 3.88 (s, 2 H), 3.03 - 2.96 (m, 2 H), 2.94 - 2.87 (m, 2 H), 1.50 (br. s., 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 140.4, 140.1, 128.8, 128.5, 128.1, 127.0, 126.2, 54.0, 50.7, 36.5; HRMS (ESI) *m/z* Calcd. for C$_{15}$H$_{18}$N$^+$ [M+H]$^+$: 212.1434, Found: 212.1429; IR (neat, cm^{-1}): 2923, 2815, 1736, 1602, 1494, 1452, 1240, 733, 696.
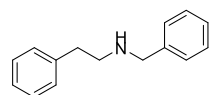
***N*-Benzyl-2-(4-methoxyphenyl)ethan-1-amine** was prepared in 82% yield (980 mg) as yellow oil through **General Procedure D1** from 2-(4-methoxyphenyl)ethan-1-ol (commercially available, cas: 702-23-8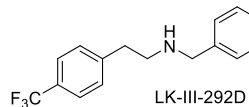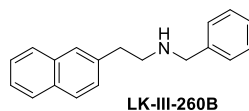) (760 mg, 5 mmol). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.42 - 7.27 (m, 5 H), 7.22 - 7.16 (m, 2 H), 6.93 - 6.87 (m, 2 H), 3.87 (s, 2 H), 3.85 (s, 3 H), 2.98 - 2.91 (m, 2 H), 2.87 - 2.80 (m, 2 H), 1.57 (br. s., 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 158.1, 140.4, 132.1, 129.7, 128.4, 128.2, 127.0, 113.9, 55.3, 53.9, 50.8, 35.5; HRMS (ESI) *m/z* Calcd. for C$_{16}$H$_{20}$NO$^+$ [M+H]$^+$: 242.1539, Found: 242.1527; IR (neat, cm^{-1}): 2932, 2834, 1611, 1583, 1511, 1453, 1244, 907, 727, 697.

***N*-Benzyl-2-(4-chlorophenyl)ethan-1-amine** was prepared in 86% yield (1.05 g) as yellow oil through **General Procedure D1** from 2-(4-chlorophenyl)ethan-1-ol (commercially available, cas: 1875-88-3) (780 mg, 5 mmol). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.41 - 7.20 (m, 7 H), 7.17 - 7.12 (m, 2 H), 3.81 (s, 2 H), 2.91 - 2.87 (m, 2 H), 2.83 - 2.77 (m, 2 H), 1.61 (br. s., 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 140.1, 138.5, 131.9, 130.1, 128.6, 128.4, 128.1, 127.0, 53.9, 50.3, 35.7; HRMS (ESI) *m/z* Calcd. for C$_{15}$H$_{17}$ClN$^+$ [M+H]$^+$: 246.1044, Found: 248.1041; IR (neat, cm^{-1}): 2925, 2817, 1668, 1599, 1491, 1453, 1089, 1014, 730, 697.
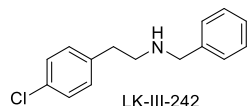
***N*-Benzyl-2-(4-(trifluoromethyl)phenyl)ethan-1-amine** was prepared in 70% yield (976 mg) as yellow oil through **General Procedure D1** from 2-(4-(trifluoromethyl)phenyl) ethan-1-ol (commercially available, cas: 2968-93-6) (950 mg, 5 mmol). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.56 (d, *J* = 8.3 Hz, 2 H), 7.39 - 7.24 (m, 7 H), 3.83 (s, 2 H), 2.99 - 2.92 (m, 2 H), 2.93 - 2.84 (m, 2 H), 1.41 (br. s., 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 144.2, 140.1, 129.0, 128.5 (q, *J* = 32.5 Hz), 128.4, 128.0, 127.0, 125.3 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 270.0 Hz), 53.8, 50.1, 36.2; HRMS (ESI) *m/z* Calcd. for C$_{16}$H$_{17}$F$_3$N$^+$ [M+H]$^+$: 280.1308, Found: 280.1306; IR (neat, cm^{-1}): 2928, 1618, 1454, 1323, 1066, 907, 730, 698.

***N*-Benzyl-2-(naphthalen-2-yl)ethan-1-amine** was prepared in 74% yield (970 mg) as yellow oil through **General Procedure D3** from *N*-benzyl-2-(naphthalen-2-yl)acetamide (1.37 g, 5 mmol) which was prepared using 2-(naphthalen-2-yl)acetic acid (commercially available, cas: 581-96-4) and benzylamine.[3] ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.93 - 7.77 (m, 3 H), 7.66 (s, 1 H), 7.51 - 7.40 (m, 2 H), 7.38 - 7.19 (m, 6 H), 3.83 (s, 2 H), 3.01 (s, 4 H), 1.55 (br. s., 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 140.2, 137.5, 133.5, 132.1, 128.4, 128.1, 128.0, 127.6,

127.4, 127.3, 127.0, 126.9, 126.0, 125.3, 53.9, 50.3, 36.4; HRMS (ESI) *m/z* Calcd. for $C_{19}H_{20}N^+$ [M+H]$^+$: 262.1590, Found: 262.1589; IR (neat, cm^{-1}): 2924, 2853, 1728, 1601, 1552, 1260, 1077, 907, 730, 647.
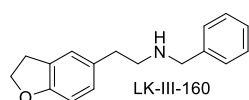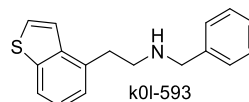
N-Benzyl-2-(1H-indol-3-yl)ethan-1-amine was prepared in 83% yield (1.04 g) as yellow oil through **General Procedure D2** from Tryptamine (commercially available, cas: 61-54-1) (800 mg, 5 mmol). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 8.15 (br. s., 1 H), 7.68 (d, *J* = 7.8 Hz, 1 H), 7.40 (d, *J* = 7.8 Hz, 1 H), 7.37 - 7.27 (m, 5 H), 7.27 - 7.22 (m, 1 H), 7.20 - 7.13 (m, 1 H), 7.05 (d, *J* = 2.0 Hz, 1 H), 3.88 (s, 2 H), 3.15 - 3.01 (m, 4 H), 1.62 (br. s., 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 140.3, 136.3, 128.3, 128.1, 127.4, 126.8, 122.0, 121.9, 119.2, 118.9, 114.0, 111.1, 53.9, 49.4, 25.8; HRMS (ESI) *m/z* Calcd. for $C_{17}H_{19}N_2^+$ [M+H]$^+$: 251.1543, Found: 215.1543; IR (neat, cm^{-1}): 3457, 3055, 2917, 2836, 1618, 1454, 735, 696.
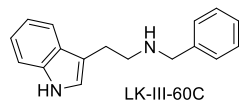
N-Benzyl-2-(2,3-dihydrobenzofuran-5-yl)ethan-1-amine was prepared in 65% yield (822 mg) as yellow oil through **General Procedure D3** from *N*-benzyl-2-(2,3-dihydrobenzofuran-5-yl)acetamide (1.34 g, 5 mmol) which was prepared using 2-(2,3-dihydrobenzofuran-5-yl)acetic acid (commercially available, cas: 69999-16-2) and benzylamine following the literature procedure.[3] ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.43 - 7.21 (m, 5 H), 7.04 (s, 1 H), 6.99 - 6.88 (m, 1 H), 6.75 - 6.67 (m, 1 H), 4.64 - 4.51 (m, 2 H), 3.89 - 3.77 (m, 2 H), 3.28 - 3.12 (m, 2 H), 2.95 - 2.82 (m, 2 H), 2.81 - 2.69 (m, 2 H), 1.77 (br. s., 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 159.7, 140.2, 131.8, 128.5, 128.4, 128.1, 127.5, 127.4, 125.2, 109.1, 71.4, 53.9, 50.9, 35.7, 29.7; HRMS (ESI) *m/z* Calcd. for $C_{17}H_{20}NO^+$ [M+H]$^+$: 254.1539, Found: 254.1527; IR (neat, cm^{-1}): 2893, 2854, 1613, 1490, 1242, 982, 728, 698.

N-Benzyl-2-(benzo[b]thiophen-4-yl)ethan-1-amine was prepared in 59% yield (340 mg) as yellow oil through **General Procedure D3** from *N*-benzyl-2-(benzo[b]thiophen-4-yl)acetamide (600 mg, 2.1 mmol) which was prepared using 2-(benzo[b]thiophen-4-yl)acetic acid (commercially available, cas: 2635-75-8) and benzylamine following the literature procedure. ^{1}H NMR (600 MHz, CDCl$_3$) δ ppm 7.75 (d, *J* = 8.1 Hz, 1H), 7.33 - 7.21 (m, 8H), 7.19 (d, *J* = 7.1 Hz, 1H), 3.82 (s, 2H), 3.18 (t, *J* = 7.2 Hz, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 1.49 (br. s., 1H); ^{13}C NMR (150 MHz, CDCl$_3$) δ ppm 140.4, 140.3, 139.0, 135.1, 128.5, 128.2, 127.1, 126.2, 124.5, 124.4, 121.9, 120.8, 54.0, 50.0, 34.7; HRMS (ESI) *m/z* Calcd. for $C_{17}H_{18}NS^+$ [M+H]$^+$: 268.1154, Found: 268.1155; IR (neat, cm^{-1}): 2818, 1452, 1411, 1105, 907, 729, 698.

(*E*)-*N*-Benzylhex-3-en-1-amine was prepared in 65% yield (614 mg) as yellow oil through **General Procedure D1** from (*E*)-hex-3-en-1-ol (commercially available, cas: 928-97-2) (500 mg, 5 mmol). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.42 - 7.35 (m, 4 H), 7.34 - 7.28 (m, 1 H), 5.64 - 5.56 (m, 1 H), 5.46 - 5.38 (m, 1 H), 3.86 (s, 2 H), 2.75 - 2.70 (m, 2 H), 2.28 (dq, *J* = 1.0, 6.8 Hz, 2 H), 2.13 - 2.01 (m, 2 H), 1.74 (br. s., 1 H), 1.02 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 140.3, 134.3, 128.4, 128.2, 127.0, 126.4, 53.9, 48.9, 33.0, 25.7, 13.9; HRMS (ESI) *m/z* Calcd. for C$_{13}$H$_{20}$N$^+$ [M+H]$^+$: 190.1590, Found: 190.1601; IR (neat, cm^{-1}): 2960, 2929, 1453, 1404, 1286, 966, 732, 697.
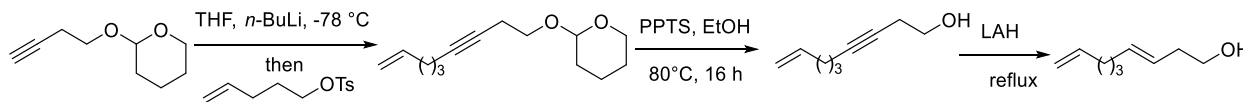
2-(But-3-yn-1-yloxy)tetrahydro-2*H*-pyran (1.7 g, 11 mmol) was dissolved into THF (10 mL) under nitrogen atmosphere and cooled down to -78˚C. *n*-BuLi (2.5 M solution in Hexane) (4.8 mL, 12.1 mmol) was added slowly into this solution and the reaction mixture was warmed up to room temperature and stirred for 30 min. Then the reaction solution was cooled down to -78˚C. Pent-4-en-1-yl 4-methylbenzenesulfonate (2.9 g, 12.1 mmol) in THF (5 mL) was added slowly into the alkynyllithium solution and the reaction was heated up to reflux for 24 h. The solvent was removed and the residue was purified by silica gel column chromatography (eluent: Hexanes/EtOAc 30:1), to give 2-(non-8-en-3-yn-1-yloxy)tetrahydro-2*H*-pyran as colorless oil, TLC R$_f$ = 0.7 (Hexanes/EtOAc 9:1) (1.0 g, 65% yield).
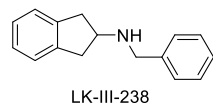
2-(Non-8-en-3-yn-1-yloxy)tetrahydro-2*H*-pyran (1.0 g, 4.5 mmol) was dissolved into ethanol (40 mL). PPTS (150 mg, 0.6 mmol) was added. The reaction mixture was stirred at 80 ˚C for 16 h. The solvent was removed and the residue was purified by silica gel column chromatography (eluent: Hexanes/EtOAc 8:1) to give non-8-en-3-yn-1-ol as colorless oil, TLC R$_f$ = 0.5 (Hexanes/EtOAc 8:1) (620 mg, 98% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 5.79 (tdd, *J* = 6.6, 10.3, 17.1 Hz, 1 H), 5.03 (qd, *J* = 1.6, 17.1 Hz, 1 H), 5.00 - 4.95 (m, 1 H), 3.68 (t, *J* = 6.4 Hz, 2 H), 2.43 (tt, *J* = 2.4, 6.4 Hz, 2 H), 2.22 - 2.16 (m, 2 H), 2.16 - 2.08 (m, 2 H), 1.89 (s, 1 H), 1.59 (quin, *J* = 7.2 Hz, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 137.9, 115.1, 82.3, 76.6, 61.4, 32.8, 28.1, 23.2, 18.1.

(*E*)-Nona-3,8-dien-1-ol was prepared according to the following procedure. A solution of non-8-en-3-yn-1-ol (500 mg, 3.62 mmol) was added to a cold (0˚ C) suspension of LiAlH$_4$ (412 mg, 10.8 mmol) in a mixture of digylme (5.5 mL) and THF (1.6 mL). The reaction mixture was heated to reflux for 72 h. The

reaction was quenched using H_2O (0.4 mL) followed by 10% NaOH (0.4 mL) and H_2O (1.2 mL). Then the reaction mixture was poured into 10% HCl and extracted with pentane (3× 40 mL). The combined organic layer was concentrated under high vacuum to give **(*E*)-nona-3,8-dien-1-ol**, as a colorless oil (450 mg, 90% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 5.79 (tdd, J = 6.7, 10.2, 17.1 Hz, 1 H), 5.59 - 5.47 (m, 1 H), 5.45 - 5.30 (m, 1 H), 4.99 (qd, J = 1.6, 17.1 Hz, 1 H), 4.96 - 4.91 (m, 1 H), 3.64 - 3.57 (m, 2 H), 2.26 (q, J = 6.4 Hz, 2 H), 2.12 - 2.00 (m, 4 H), 1.99 (s, 1 H), 1.51 - 1.43 (m, 2 H).

(*E*)-*N*-Benzylnona-3,8-dien-1-amine was prepared in 50% yield (300 mg) as yellow oil through **General**

LK-III-216
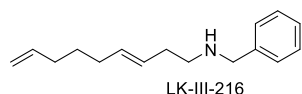
Procedure D1 from **(*E*)-nona-3,8-dien-1-ol** (364 mg, 2.6 mmol). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.39 - 7.31 (m, 4 H), 7.29 - 7.22 (m, 1 H), 5.81 (tdd, J = 6.6, 10.3, 17.1 Hz, 1 H), 5.55 - 5.46 (m, 1 H), 5.43 - 5.34 (m, 1 H), 5.01 (qd, J = 1.6,

17.1 Hz, 1 H), 4.98 - 4.92 (m, 1 H), 3.80 (s, 2 H), 2.68 (t, J = 6.8 Hz, 2 H), 2.23 (q, J = 6.8 Hz, 2 H), 2.10 - 1.98 (m, 4 H), 1.46 (quin, J = 7.5 Hz, 2 H), 1.39 (br. s., 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 140.5, 138.8, 132.2, 128.4, 128.1, 127.9, 126.8, 114.5, 53.9, 48.9, 33.2, 33.1, 32.0, 28.7; HRMS (ESI) *m/z* Calcd. for $C_{16}H_{24}N^+$ [M+H]$^+$: 230.1903, Found: 230.1895; IR (neat, cm^{-1}): 2924, 2840, 1640, 1453, 968, 908, 730, 690.

_N_-Benzyl-2-(cyclohex-1-en-1-yl)ethan-1-amine was prepared in 84% yield (900 mg) as yellow oil

LK-III-189
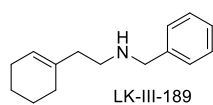
through **General Procedure D2** from 2-(cyclohex-1-en-1-yl)ethan-1-amine (commercially available, cas: 3399-73-3) (625 mg, 5 mmol). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.37 - 7.29 (m, 4 H), 7.29 - 7.21 (m, 1 H), 5.50 - 5.45 (m, 1 H), 3.81 (s,

2 H), 2.71 (t, J = 7.1 Hz, 2 H), 2.18 (t, J = 7.1 Hz, 2 H), 2.04 - 1.96 (m, 2 H), 1.92 - 1.84 (m, 2 H), 1.66 - 1.59 (m, 2 H), 1.59 - 1.53 (m, 2 H), 1.47 (br. s., 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 140.5, 135.4, 128.4, 128.1, 126.8, 122.8, 53.9, 46.9, 38.3, 28.1, 25.3, 23.0, 22.5; HRMS (ESI) *m/z* Calcd. for $C_{15}H_{22}N^+$ [M+H]$^+$: 216.1747, Found: 216.1742; IR (neat, cm^{-1}): 2923, 2833, 2855, 1494, 1452, 1114, 907, 728, 697.
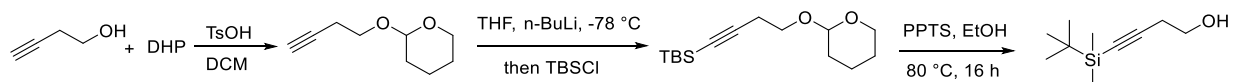
Under nitrogen atmosphere, *p*-toluenesulfonic acid (63 mg, 0.33 mmol) was added to a round-bottom flask containing but-3-yn-1-ol (2.52 mL, 33 mmol) in DCM (36 mL) followed by the slow addition of dihydropyran (3.2 mL, 35 mmol). The reaction mixture was stirred for 2 hours at room temperature until the consumption of but-3-yn-1-ol based on TLC. Then the solvent was removed and the residue was

purified by silica gel column chromatography (eluent: Hexanes/EtOAc 30:1) to give 2-(but-3-yn-1-yloxy)tetrahydro-2*H*-pyran as colorless oil, TLC R_f = 0.3 (Hexanes/EtOAc 9:1) (5.1 g, 99% yield).[4]

The above DHP protected alkyne (1.5 g, 10 mmol) was dissolved into THF (10 mL) under nitrogen atmosphere and cooled down to -78˚C. *n*-BuLi (2.5 M solution in Hexane) (4.3 mL, 10.7 mmol) was added slowly into this solution and the reaction mixture was warmed up to room temperature and stirred for 30 min. Then the reaction solution was cooled down to -78˚C. *tert*-Butyldimethylsilyl chloride (1.6 g, 10.6 mmol) in THF (5 mL) was added slowly into the alkynyllithium solution and the reaction was warmed up to room temperature and stirred for 3 h. The solvent was removed and the residue was purified by silica gel column chromatography (eluent: Hexanes/EtOAc 30:1) to give *tert*-butyldimethyl(4-((tetrahydro-2*H*-pyran-2-yl)oxy)but-1-yn-1-yl)silane as colorless oil, TLC R_f = 0.6 (Hexanes/EtOAc 9:1) (1.2 g, 46% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 4.66 (t, *J* = 3.4 Hz, 1 H), 3.89 (ddd, *J* = 2.9, 8.7, 11.4 Hz, 1 H), 3.82 (td, *J* = 7.2, 9.7 Hz, 1 H), 3.61 - 3.40 (m, 2 H), 2.53 (t, *J* = 7.1 Hz, 2 H), 1.83 (dd, *J* = 3.4, 9.3 Hz, 1 H), 1.75 - 1.66 (m, 1 H), 1.63 - 1.56 (m, 2 H), 1.55 - 1.45 (m, 2 H), 0.92 (s, 9 H), 0.07 (s, 6 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 104.5, 98.6, 83.6, 65.7, 61.9, 30.5, 26.0, 25.4, 21.4, 19.2, 16.5, -4.5.

tert-Butyldimethyl(4-((tetrahydro-2*H*-pyran-2-yl)oxy)but-1-yn-1-yl)silane (1.2 g, 4.4 mmol) was dissolved into ethanol (40 mL). PPTS (150 mg, 0.6 mmol) was added. The reaction mixture was stirred at 80 ˚C for 16 h. The solvent was removed and the residue was purified by silica gel column chromatography (eluent: Hexanes/EtOAc 16:1) to give **4-(*tert*-butyldimethylsilyl)but-3-yn-1-ol** as colorless oil, TLC R_f = 0.4 (Hexanes/EtOAc 8:1) (800 mg, 98% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 3.71 (t, *J* = 6.4 Hz, 2 H), 2.50 (t, *J* = 6.4 Hz, 2 H), 2.01 (s, 1 H), 0.92 (s, 9 H), 0.09 (s, 6 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 103.8, 85.1, 61.0, 26.0, 24.2, 16.4, -4.52.

N-Benzyl-4-(*tert*-butyldimethylsilyl)but-3-yn-1-amine was prepared in 36% yield (402 mg) as yellow oil through **General Procedure D1** from the above synthesized 4-(*tert*-butyldimethylsilyl)but-3-yn-1-ol (750 mg, 4.1 mmol). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.40 - 7.29 (m, 4 H), 7.29 - 7.24 (m, 1 H), 3.83 (s, 2 H), 2.80 (t, *J* = 6.6 Hz, 2 H), 2.48 (t, *J* = 6.6 Hz, 2 H), 1.88 (br. s., 1 H), 0.93 (s, 9 H), 0.10 (s, 6 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 140.0, 128.4, 128.1, 127.0, 105.5, 84.2, 53.3, 47.4, 26.1, 20.9, 16.5, -4.5; HRMS (ESI) *m/z* Calcd. for C$_{17}$H$_{28}$NSi$^+$ [M+H]$^+$: 274.1986, Found: 274.1977; IR (neat, cm^{-1}): 2952, 2927, 2855, 2171, 1461, 1249, 809, 836, 824, 732, 697.

N-Benzyl-2,3-dihydro-1H-inden-2-amine was prepared in 38% yield (420 mg) as yellow oil through **General Procedure D1** from 2,3-dihydro-1H-inden-2-ol (commercially available, cas: 4254-29-9) (690 mg, 5 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.38 - 7.29 (m, 4 H), 7.28 - 7.22 (m, 1 H), 7.22 - 7.16 (m, 2 H), 7.16 - 7.07 (m, 2 H), 3.86 (s, 2 H), 3.68 (quin, J = 6.8 Hz, 1 H), 3.17 (dd, J = 7.2, 15.4 Hz, 2 H), 2.81 (dd, J = 6.8, 15.4 Hz, 2 H), 1.57 (br. s., 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 141.7, 140.3, 128.4, 128.2, 127.0, 126.4, 124.7, 59.0, 52.3, 40.0; HRMS (ESI) m/z Calcd. for C$_{16}$H$_{18}$N^{+} [M+H]$^{+}$: 224.1434, Found: 224.1430; IR (neat, cm^{-1}): 2932, 2835, 1603, 1453, 1124, 738, 697.

N-Isopropyl-2,3-dihydro-1H-inden-2-amine was prepared in 50% yield (437 mg) as yellow oil through **General Procedure D1** between 2,3-dihydro-1H-inden-2-ol (commercially available, cas: 4254-29-9) (690 mg, 5 mmol) and propan-2-amine. ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.24 - 7.18 (m, 2 H), 7.18 - 7.13 (m, 2 H), 3.76 (quin, J = 7.3 Hz, 1 H), 3.19 (dd, J = 7.3, 15.7 Hz, 2 H), 3.00 (td, J = 6.4, 12.6 Hz, 1 H), 2.74 (dd, J = 7.1, 15.7 Hz, 2 H), 1.48 (br. s., 1 H), 1.11 (d, J = 6.4 Hz, 6 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 141.8, 126.4, 124.7, 57.0, 46.6, 40.3, 23.2; HRMS (ESI) m/z Calcd. for C$_{12}$H$_{18}$N^{+} [M+H]$^{+}$: 176.1434, Found: 176.1437; IR (neat, cm^{-1}): 2963, 2837, 1617, 1459, 1173, 908, 728, 640.
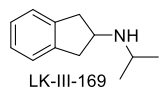
N-Phenethyl-3-phenylpropan-1-amine was prepared in 83% yield (1.0 g) as yellow oil through **General Procedure D1** between 3-phenylpropan-1-ol (commercially available, cas: 122-97-4) (680 mg, 5 mmol) and 2-phenylethan-1-amine (commercially available, cas: 64-04-0) (1.2 g, 10 mmol). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.39 - 7.11 (m, 10 H), 2.93 - 2.87 (m, 2 H), 2.86 - 2.79 (m, 2 H), 2.66 (td, J = 7.5, 14.4 Hz, 4 H), 1.83 (td, J = 7.5, 15.0 Hz, 2 H), 1.23 (br. s., 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 142.1, 140.1, 128.7, 128.4, 128.3, 128.2, 126.1, 125.7, 51.1, 49.2, 36.3, 33.6, 31.6; HRMS (ESI) m/z Calcd. for C$_{17}$H$_{22}$N^{+} [M+H]$^{+}$: 240.1747, Found: 240.1738; IR (neat, cm^{-1}): 2931, 2856, 1602, 1495, 1453, 908, 728, 697.
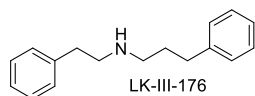
**N-Benzyl-2-(furan-2-yl)ethan-1-amine** was prepared in 57% yield as yellow oil through **General Procedure D2** from 2-(furan-2-yl)ethan-1-amine (222 mg, 2 mmol) (synthesized according to the literature[5]). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36 - 7.29 (m, 5 H), 7.28 - 7.22 (m, 1 H), 6.30 (dd, J = 2.0, 2.9 Hz, 1 H), 6.12 - 6.01 (m, 1 H), 3.82 (s, 2 H), 2.97 -
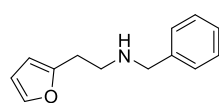
2.91 (m, 2 H), 2.89 - 2.83 (m, 2 H), 1.61 (br. s., 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 154.1, 141.2, 140.2, 128.4, 128.1, 127.0, 110.2, 105.8, 53.7, 47.5, 28.7; HRMS (ESI) *m/z* Calcd. for C$_{13}$H$_{16}$NO$^+$ [M+H]$^+$: 202.1226, Found: 202.1205; IR (neat, cm^{-1}): 2923, 2821, 1496, 1453, 1157, 873, 729, 697, 599.

***N*-Benzyl-2-cyclopropylethan-1-amine** was prepared in 58% yield (1.02 g) as yellow oil through **General Procedure D1** from 2-cyclopropylethan-1-ol (commercially available, cas: 2566-44-1) (500 mg, 5.8 mmol). ^{1}H NMR (600 MHz, CDCl$_3$) δ ppm 7.36 - 7.30 (m, 3H), 7.27 - 7.23 (m, 2H), 3.81 (s, 2H), 2.74 (t, *J* = 7.1 Hz, 2H), 1.43 (dd, *J* = 14.1, 7.0 Hz, 2H), 1.40 (br.s, 1H), 0.75 - 0.64 (m, 1H), 0.48 - 0.40 (m, 2H), 0.09 - 0.03 (m, 2H); ^{13}C NMR (150 MHz, CDCl$_3$) δ ppm 140.7, 128.5, 128.2, 127.0, 54.3, 49.7, 35.2, 9.0, 4.3; HRMS (ESI) *m/z* Calcd. for C$_{12}$H$_{18}$N$^+$ [M+H]$^+$: 176.1434, Found: 176.1422; IR (neat, cm^{-1}): 2915, 1453, 751.
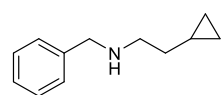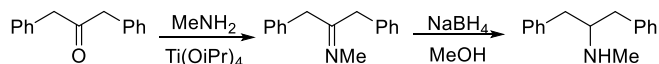
***N*-Methyl-1,3-diphenylpropan-2-amine** was synthesized according to the following method: At room temperature, Ti(OiPr)$_4$ (1.5 mL, 5.2 mmol) was added to a 1,3-diphenylpropanone (commercially available, cas: 102-04-5) (1.0 g, 4.7 mmol) DCM solution (20 mL), followed by the addition of MeNH$_2$ (3.5 mL, 7 mmol, 2M in MeOH). The reaction mixture was stirred for 1 hour and the solvent was removed. The residue was dissolved into MeOH (20 mL) and cooled to 0 ˚C. Then NaBH$_4$ (0.53 g, 14.1 mmol) was added to this solution and the reaction mixture was slowly warmed up to room temperature and stirred for 2 hours. Then the solvent was removed and the residue was purified by silica gel column chromatography (gradient elution: Hexanes/EtOAc 8:1 to 1:1) to give the desired amine product as yellow oil (600 mg, 56% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.38 - 7.12 (m, 10 H), 3.01 - 2.91 (m, 1 H), 2.82 - 2.73 (m, 2 H), 2.71 - 2.62 (m, 2 H), 2.42 (s, 3 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 139.5, 129.3, 128.4, 126.2, 62.8, 40.2, 34.2; HRMS (ESI) *m/z* Calcd. for C$_{16}$H$_{20}$N$^+$ [M+H]$^+$: 226.1590, Found: 226.1576; IR (neat, cm^{-1}): 2930, 2851, 1737, 1601, 1494, 1452, 748, 697.
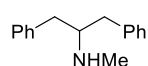
***N*-Benzyl-2-(ferrocenyl)ethan-1-amine** was prepared in 63% yield (340 mg) as yellow oil through **General Procedure D2** from 2-(ferrocenyl)ethan-1-amine (390 mg, 1.7 mmol) (synthesized according to the literature.[6]). ^{1}H NMR (600 MHz, CDCl$_3$) δ ppm 7.36 - 7.24 (m, 5 H), 4.10 (s, 7 H), 4.07 (s, 2 H), 3.81 (s, 2 H), 2.79 (t, *J* = 7.0 Hz, 2 H), 2.58 (t, *J* = 7.0 Hz, 2 H), 1.61 (br. s., 1 H); ^{13}C NMR (150 MHz, CDCl$_3$) δ ppm 140.3, 128.4, 128.1, 126.9, 86.5, 68.5, 68.3, 67.3, 53.9,
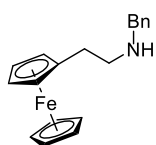
50.4, 30.1; HRMS (ESI) *m/z* Calcd. for $C_{19}H_{22}FeN^+$ [M+H]$^+$: 320.1102, Found: 320.1110; IR (neat, cm^{-1}): 1739, 1365, 1229, 1217.

General Procedure E (Synthesis of Sulfamoyl Azide 1)

Sulphuryl Azide ($N_3SO_2N_3$) was prepared according to our reported procedure without further optimization.[7] Sulfuryl chloride (9.72 mL, 120 mmol) was added dropwise for 1 h to a solution of sodium azide (29.25 g, 450 mmol) and pyridine (19.44 mL, 250 mmol) in acetonitrile (600 mL) at 0 °C. Then the reaction mixture was stirred for one hour at room temperature followed by the addition of 100 mL DCM. The mixture was poured into ice-cold water and extracted with DCM (3 x 100 mL). The combined organic layer was washed sequentially with hydrochloric acid (1 mol/L in H_2O), water, potassium hydroxide (1 mol/L in H_2O), hydrochloric acid (1 mol/L in H_2O), and water. After drying (Na_2SO_4), the sulphuryl azide solution was used directly for the further reaction. This solution (0.3 M in DCM) can be stored in the refrigerator at -20 °C for at least six months without significant decomposition.
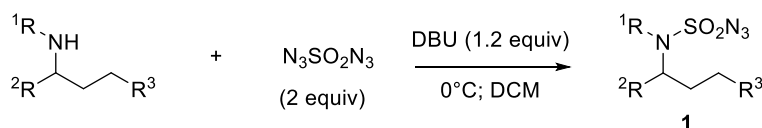
A mixture of amine (1 equiv) and DBU (1.2 equiv) in DCM was added dropwise via pipette to a solution of $N_3SO_2N_3$ (2 equiv, 0.3 M in DCM) at 0 °C. After the reaction was completed based on TLC (~ 1 h), the majority of the solvent was removed under reduced pressure at room temperature. Purification of this mixture by silica gel column chromatography (Conditions were given below.) afforded the sulfamoyl azide. **Note: Some azides could be explosive and should be handled carefully.**

Characterization of Sulfamoyl Azides (1a-1u)

***N*-Benzyl-2-phenylethan-1-sulfamoyl azide** (**1a**) was obtained in 88% yield (560 mg) as colorless oil
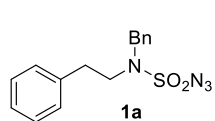
through **General Procedure E** from *N*-benzyl-2-phenylethan-1-amine starting from 2 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), TLC R_f = 0.6 (Hexanes/EtOAc 8:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.44 - 7.37 (m, 2 H), 7.37 - 7.32 (m, 2 H), 7.32 - 7.26 (m, 2 H), 7.26 - 7.20 (m, 2 H), 7.10 (d, *J* = 6.8 Hz, 2 H), 4.43 (s, 2 H), 3.48 - 3.40 (m, 2 H), 2.88 - 2.81 (m, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 137.6, 134.5,

129.0, 128.8, 128.7, 128.6, 128.5, 126.8, 53.0, 50.0, 34.4; IR (neat, cm^{-1}): 2123, 1380, 1204, 1164, 734, 697.

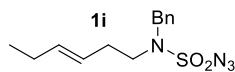**N-Benzyl-2-(4-methoxyphenyl)ethan-1-sulfamoyl azide** (**1b**) was obtained in 85% yield (294 mg) as colorless oil through **General Procedure E** from *N*-benzyl-2-(4-methoxyphenyl)ethan-1-amine starting from 1 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), TLC R$_f$ = 0.3 (Hexanes/EtOAc 8:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.55 - 7.26 (m, 5 H), 7.08 - 6.94 (m, 2 H), 6.86 - 6.69 (m, 2 H), 4.39 (s, 2 H), 3.76 (s, 3 H), 3.44 - 3.26 (m, 2 H), 2.87 - 2.66 (m, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 158.4, 134.5, 129.7, 129.5, 128.9, 128.6, 128.5, 114.1, 55.2, 53.0, 50.2, 33.4; IR (neat, cm^{-1}): 2126, 1611, 1513, 1456, 1379, 1205, 1165, 905, 726, 699.

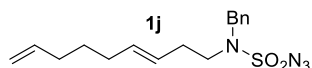**N-Benzyl-2-(4-chlorophenyl)ethan-1-sulfamoyl azide** (**1c**) was obtained in 88% yield (310 mg) as colorless oil through **General Procedure E** from *N*-benzyl-2-(4-chlorophenyl) ethan-1-amine starting from 1 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), TLC R$_f$ = 0.4 (Hexanes/EtOAc 8:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.42 - 7.13 (m, 7 H), 7.06 - 6.86 (m, 2 H), 4.39 (s, 2 H), 3.50 - 3.28 (m, 2 H), 2.88 - 2.66 (m, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 136.0, 134.3, 132.6, 130.1, 129.0, 128.8, 128.6, 53.2, 49.9, 33.8; IR (neat, cm^{-1}): 2128, 1493, 1380, 1264, 1167, 733, 703,610, 593.

N-Benzyl-2-(4-(trifluoromethyl)phenyl)ethan-1-sulfamoyl azide (**1d**) was obtained in 90% yield (355 mg) as colorless oil through **General Procedure E** from *N*-benzyl-2-(4-(trifluoromethyl)phenyl)ethan-1-amine starting from 1 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), TLC R$_f$ = 0.7 (Hexanes/EtOAc 8:1). ^{1}H NMR (600 MHz, CDCl$_3$) δ ppm 7.51 (d, *J* = 8.0 Hz, 2 H), 7.40 - 7.36 (m, 3 H), 7.33 - 7.28 (m, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 4.42 (s, 2 H), 3.57 - 3.33 (m, 2 H), 2.95 - 2.78 (m, 2 H); ^{13}C NMR (150 MHz, CDCl$_3$) δ ppm 141.6, 134.2, 129.2 (q, *J* = 32.0 Hz), 129.1, 129.0, 128.7, 128.6, 125.6 (q, *J* = 3.0 Hz), 124.1 (q, *J* = 272.0 Hz), 53.4, 49.8, 34.3; ^{19}F NMR (470 MHz, CFCl$_3$, CDCl$_3$) δ ppm -63.05 (s, 3F); IR (neat, cm^{-1}): 2128, 1619, 1380, 1325, 1264, 1123, 1067, 733, 702, 609, 593.

N-Benzyl-2-(naphthalen-2-yl)ethan-1-sulfamoyl azide (**1e**) was obtained in 80% yield (292 mg) as
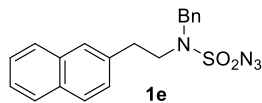
colorless wax through **General Procedure E** from *N*-benzyl-2-(naphthalen-2-yl)ethan-1-amine starting from 1 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), TLC R_f = 0.7 (Hexanes/EtOAc 8:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.88 - 7.70 (m, 3 H), 7.54 (s, 1 H), 7.53 - 7.41 (m, 2 H), 7.41 - 7.13 (m, 6 H), 4.44 (s, 2 H), 3.53 (t, *J* = 7.8 Hz, 2 H), 3.01 (t, *J* = 7.8 Hz, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 135.0, 134.5, 133.5, 132.3, 128.9, 128.7, 128.6, 128.4, 127.7, 127.5, 127.3, 126.9, 126.2, 125.7, 53.1, 50.0, 34.6; IR (neat, cm^{-1}): 2124, 1600, 1496, 1455, 1378, 1206, 1164, 907, 751,1 730, 609, 591.

N-Benzyl-2-(1H-indol-3-yl)ethan-1-sulfamoyl azide was obtained in 87% yield (620 mg) as yellow wax
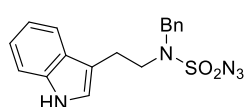
through **General Procedure E** from *N*-benzyl-2-(1*H*-indol-3-yl)ethan-1-amine starting from 2 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 8:1), TLC R_f = 0.25 (Hexanes/EtOAc 8:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.99 (br. s., 1 H), 7.45 - 7.31 (m, 7 H), 7.21 (dt, *J* = 1.0, 7.6 Hz, 1 H), 7.15 - 7.07 (m, 1 H), 6.98 (d, *J* = 2.4 Hz, 1 H), 4.47 (s, 2 H), 3.61 - 3.41 (m, 2 H), 3.10 - 2.94 (m, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 136.2, 134.6, 128.9, 128.7, 128.5, 127.0, 122.3, 122.2, 119.6, 118.5, 111.8, 111.2, 53.1, 49.1, 24.2.
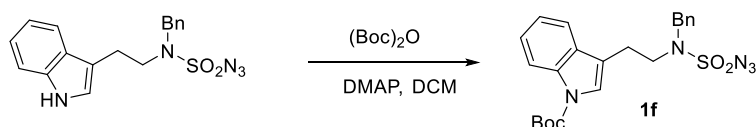
N-Benzyl-2-(1-(*tert*-butoxycarbonyl)-1H-indol-3-yl) ethan-1-sulfamoyl azide (1f) was obtained
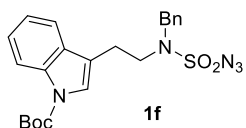
according to the following procedure. DMAP (12 mg, 0.1 mmol) and (Boc)$_2$O (231 mg, 1.2 mmol) were added to a solution of *N*-benzyl-2-(1*H*-indol-3-yl)ethan-1-sulfamoyl azide (355 mg, 1 mmol) in DCM (4 mL). The reaction mixture was stirred for 2h. The solvent was removed and the residue was purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), to give *N*-benzyl-2-(1-(*tert*-butoxycarbonyl)-1*H*-indol-3-yl) ethan-1-sulfamoyl azide as colorless wax, TLC R_f = 0.7 (Hexanes/EtOAc 8:1) (450 mg, 95% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 8.24 - 7.98 (m, 1 H), 7.44 - 7.19 (m, 9 H), 4.49 (s, 2 H), 3.60 - 3.42 (m, 2 H), 3.03 - 2.85 (m, 2 H), 1.68 (s, 9 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 149.6, 135.4, 134.4, 129.9, 128.9, 128.6, 124.5, 123.4, 122.5, 118.6, 116.2, 115.3, 83.7, 53.4, 48.5, 28.2, 24.0; IR (neat, cm^{-1}): 2125, 1728, 1453, 1369, 1161, 1095, 906, 727, 698, 609, 592.

N-Benzyl-2-(2,3-dihydrobenzofuran-5-yl)ethan-1-sulfamoyl azide (**1g**) was obtained in 95%   yield (340 mg) as colorless wax through **General Procedure E** from *N*-benzyl-2-(2,3-dihydrobenzofuran-5-yl)ethan-1-amine starting from 1 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), TLC R_f = 0.6 (Hexanes/EtOAc 8:1). ^{1}H NMR (600 MHz, CDCl) δ ppm 7.41 - 7.35 (m, 3 H), 7.32 (d, *J* = 6.8 Hz, 2 H), 6.91 (s, 1H), 6.79 (d, *J* = 8.0 Hz, 1 H), 6.68 (d, *J* = 8.1 Hz, 1 H), 4.54 (t, *J* = 8.7 Hz, 2 H), 4.42 (s, 2 H), 3.45 - 3.33 (m, 2 H), 3.15 (t, *J* = 8.7 Hz, 2 H), 2.79 - 2.71 (m, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 158.9, 134.5, 129.4, 128.9, 128.6, 128.5, 128.2, 127.4, 125.2, 109.3, 71.2, 53.0, 50.4, 33.8, 29.7; IR (neat, cm^{-1}): 2126, 1735, 1614, 1492, 1264, 1165, 732, 701, 608, 593.
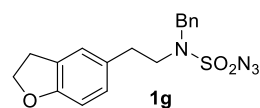
N-Benzyl-2-(benzo[b]thiophen-4-yl)ethan-1-sulfamoyl azide (**1h**) was obtained in 88% yield (330 mg) as colorless wax through **General Procedure E** from *N*-benzyl-2-(benzo[b]thiophen-4-yl)ethan-1-amine starting from 1 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), TLC R_f = 0.55 (Hexanes/EtOAc 8:1). ^{1}H NMR (600 MHz, CDCl$_3$) δ ppm 7.75 (d, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 5.5 Hz, 1H), 7.40 - 7.34 (m, 2H), 7.25-7.15 (m, 2H), 7.24 (dd, *J* = 12.4, 4.7 Hz, 2H), 7.16 (d, *J* = 5.5 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 4.42 (s, 2H), 3.47 (t, *J* = 7.9 Hz, 2H), 3.145(t, *J* = 7.9 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 140.4, 138.7, 134.6, 132.5, 129.1, 128.9, 128.8, 126.9, 124.8, 124.5, 121.5, 121.4, 53.6, 49.6, 33.3; IR (neat, cm^{-1}): 2122, 1454, 1378, 1164, 760, 592.
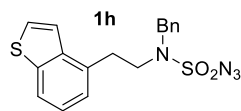
(E)-N-Benzylhex-3-en-1-sulfamoyl azide (**1i**) was obtained in 89% yield (265 mg) as colorless oil through **General Procedure E** from (*E*)-*N*-benzylhex-3-en-1-amine starting from 1 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), TLC R_f = 0.7 (Hexanes/EtOAc 8:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.52 - 7.31 (m, 5 H), 5.62 - 5.47 (m, 1 H), 5.26 (td, *J* = 6.8, 15.2 Hz, 1 H), 4.49 (s, 2 H), 3.36 - 3.19 (m, 2 H), 2.33 - 2.21 (m, 2 H), 2.06 - 1.92 (m, 2 H), 1.05 - 0.90 (m, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 135.6, 134.7, 128.8, 128.5, 128.4, 124.0, 52.6, 48.5, 30.8, 25.5, 13.5; IR (neat, cm^{-1}): 2124, 1496, 1455, 1379, 1204, 1166, 906, 727, 697, 593.

(E)-N-Benzylnona-3,8-dien-1- sulfamoyl azide (**1j**) was prepared in 95% yield (317 mg) as colorless oil through **General Procedure E** from (*E*)-*N*-benzylnona-3,8-dien-1-amine

starting from 1 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), TLC R_f = 0.7 (Hexanes/EtOAc 8:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.39 - 7.30 (m, 5 H), 5.77 (tdd, J = 6.7, 10.3, 16.9 Hz, 1 H), 5.43 (td, J = 6.7, 15.0 Hz, 1 H), 5.29 - 5.13 (m, 1 H), 5.04 - 4.84 (m, 2 H), 4.45 (s, 2 H), 3.35 - 3.12 (m, 2 H), 2.22 (q, J = 7.2 Hz, 2 H), 2.08 - 1.84 (m, 4 H), 1.40 (quin, J = 7.5 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 138.6, 134.6, 133.7, 128.8, 128.5, 128.4, 125.2, 114.5, 52.6, 48.5, 33.1, 31.9, 30.8, 28.4; IR (neat, cm^{-1}): 2123, 1640, 1496, 1455, 1379, 1204, 1165, 907, 728, 697, 592.

N-Benzyl-2-(cyclohex-1-en-1-yl)ethan-1-sulfamoyl azide (**1k**) was obtained in 80% yield (255 mg) as colorless oil through **General Procedure E** from N-benzyl-2-(cyclohex-1-en-1-yl)ethan-1-amine starting from 1 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), TLC R_f = 0.7 (Hexanes/EtOAc 8:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.48 - 7.33 (m, 5 H), 5.52 - 5.36 (m, 1 H), 4.51 (s, 2 H), 3.41 - 3.22 (m, 2 H), 2.26 - 2.16 (m, 2 H), 2.05 - 1.94 (m, 2 H), 1.92 - 1.80 (m, 2 H), 1.65 - 1.59 (m, 2 H), 1.58 - 1.52 (m, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 134.7, 133.5, 128.8, 128.5, 128.4, 124.1, 52.3, 47.2, 35.8, 28.1, 25.2, 22.7, 22.1; IR (neat, cm^{-1}): 2122, 1381, 1205, 1165, 768, 735, 698.

N-Benzyl-4-(*tert*-butyldimethylsilyl)but-3-yn-1-sulfamoyl azide (**1l**) was obtained in 82% yield (310 mg) as colorless wax through **General Procedure E** from N-benzyl-4-(*tert*-butyldimethylsilyl)but-3-yn-1-amine starting from 1 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), TLC R_f = 0.7 (Hexanes/EtOAc 8:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.43 - 7.26 (m, 5 H), 4.59 (s, 2 H), 3.38 (t, J = 7.2 Hz, 2 H), 2.50 (t, J = 7.2 Hz, 2 H), 0.91 (s, 9 H), 0.07 (s, 6 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 134.6, 129.0, 128.5, 103.1, 85.7, 53.2, 47.1, 26.0, 19.6, 16.4, -4.6; IR (neat, cm^{-1}): 2176, 2133, 1471, 1456, 1382, 1201, 1165, 837, 809, 774, 736, 596.

N-Benzyl-2,3-dihydro-1*H*-inden-2-sulfamoyl azide (**1m**) was obtained in 70% yield (230 mg) as colorless oil through **General Procedure E** from N-benzyl-2,3-dihydro-1*H*-inden-2-amine starting from 1 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), TLC R_f = 0.7 (Hexanes/EtOAc 8:1). ^{1}H NMR (400 MHz, CDCl$_3$)
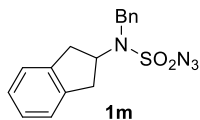
δ ppm 7.34 - 7.26 (m, 3 H), 7.22 - 7.05 (m, 6 H), 4.89 - 4.79 (m, 1 H), 4.40 (s, 2 H), 3.21 - 3.12 (m, 2 H), 3.09 - 3.00 (m, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 139.7, 136.5, 128.6, 127.8, 127.1, 127.0, 124.4, 60.0, 49.4, 36.6; IR (neat, cm^{-1}): 2129, 1421, 1264, 1169, 908, 732, 703.

N-Isopropyl-2,3-dihydro-1H-inden-2-sulfamoyl azide (1m′) was obtained in 70% yield (196 mg) as colorless oil through **General Procedure E** from N-isopropyl-2,3-dihydro-1H-inden-2-amine starting from 1 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), TLC R$_f$ = 0.8 (Hexanes/EtOAc 8:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.24 - 7.17 (m, 4 H), 4.45 (quin, J = 8.8 Hz, 1 H), 3.97 (td, J = 6.8, 13.7 Hz, 1 H), 3.35 (dd, J = 9.3, 15.7 Hz, 2 H), 3.15 (dd, J = 8.3, 15.7 Hz, 2 H), 1.38 (d, J = 6.8 Hz, 6 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 139.9, 127.0, 124.5, 57.6, 51.3, 37.2, 21.3; IR (neat, cm^{-1}): 2122, 1462, 1369, 1264, 1190, 1147, 733, 703, 642, 619.

**N-Phenethyl-3-phenylpropan-1-azide (1n)** was obtained in 90% yield (310 mg) as colorless oil through **General Procedure E** from N-phenethyl-3-phenylpropan-1-amine starting from 1 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), TLC R$_f$ = 0.7 (Hexanes/EtOAc 8:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.40 - 7.30 (m, 4 H), 7.30 - 7.23 (m, 2 H), 7.22 - 7.14 (m, 4 H), 3.60 - 3.44 (m, 2 H), 3.35 - 3.20 (m, 2 H), 3.00 - 2.85 (m, 2 H), 2.64 (t, J = 7.6 Hz, 2 H), 2.03 - 1.87 (m, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 140.5, 137.5, 128.7, 128.6, 128.3, 126.9, 126.2, 51.0, 49.3, 34.8, 32.6, 29.3; IR (neat, cm^{-1}): 2122, 1603, 1496, 1454, 1379, 1203, 1163, 906, 727, 698, 598.

N-Benzyl-2-(vinyl)ethan-1-sulfamoyl azide was obtained in 85% yield (2.1 g) through **General Procedure E** from N-benzylbut-3-en-1-amine (commercially available, cas: 17150-62-8) (1.5 g, 9.3 mmol). Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), colorless oil, TLC R$_f$ = 0.5 (Hexanes/EtOAc 8:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.64 - 7.29 (m, 5H), 5.78 - 5.58 (m, 1H), 5.17 - 5.00 (m, 2H), 4.49 (s, 2H), 3.41-3.19 (m, 2H), 2.43-2.22 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 134.6, 133.8, 128.9, 128.5, 117.8, 52.6, 47.9, 31.9; IR (neat, cm^{-1}): 2122, 1377, 1204, 1165, 923, 763, 735, 698.
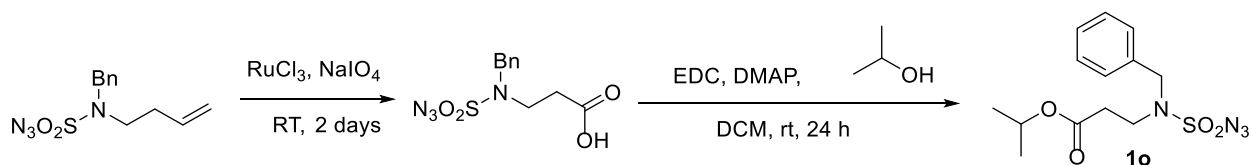
Sodium periodate (2.6 g, 12 mmol) and ruthenium(III) chloride hydrate (60 mg, 0.25 mmol) were added to a solution of *N*-benzyl-2-(vinyl)ethan-1-sulfamoyl azide (1.6 g, 6 mmol) in CH_3CN (3 mL), CCl_4 (4 mL) and H_2O (4 mL). The reaction mixture was stirred for 48 h at room temperature until the consumption of starting material based on TLC. After addition of 50 ml of EtOAc, the reaction mixture was washed by water (80 mL) and the aqueous layer was extracted by EtOAc (3 x 40 mL). The combined organic layer was dried over anhydrous sodium sulfate. The solvent was removed by vacuum and the residue was purified by silica gel column chromatography (gradient elution: Hexanes/EtOAc 3:1 to 1:1) to give the desired carboxylic acid azide intermediate as yellow oil (1.28 g, 75% yield), TLC R_f = 0.3 (Hexanes/EtOAc 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 - 7.32 (m, 5 H), 4.50 (s, 2 H), 3.54 (t, *J* = 7.3 Hz, 2 H), 2.73 - 2.56 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 134.3, 129.1, 128.7, 128.5, 53.6, 44.0, 32.7; IR (neat, cm[-1]): 2129, 1712, 1378, 1266, 1195, 1166, 733, 700.

EDC (180 mg, 1.1 mmol), DMAP (12 mg, 0.1 mmol) and [i]PrOH (0.8 mL, 10 mmol) were added to a solution of the above carboxylic acid azide (284 mg, 1 mmol) in DCM (10 mL) at 0° C. The reaction mixture was stirred at room temperature for 16 h. The solvent was removed and the residue was purified by silica gel column chromatography (gradient elution: Hexanes/EtOAc 8:1 to 4:1) to give the desired product **1o** in 85% yield (277 mg), colorless oil, TLC R_f = 0.5 (Hexanes/EtOAc 3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.50 - 7.32 (m, 5 H), 4.99 (td, *J* = 6.3, 12.3 Hz, 1 H), 4.51 (s, 2 H), 3.55 (t, *J* = 7.3 Hz, 2 H), 2.57 (t, *J* = 7.3 Hz, 2 H), 1.23 (d, *J* = 5.9 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 170.3, 134.5, 129.0, 128.6, 128.5, 68.5, 53.3, 44.4, 33.2, 21.8; IR (neat, cm[-1]): 2125, 1726, 1455, 1375, 1196, 1164, 753, 591.

***N*-Benzyl-2-(furan-2-yl)ethan-1-sulfamoyl azide (1p)** was obtained in 90% yield (275 mg) through
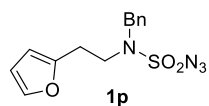
General Procedure E from *N*-benzyl-2-(furan-2-yl)ethan-1-amine starting from 1 mmol scale. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 16:1), colorless oil TLC R_f = 0.6 (Hexanes/EtOAc 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ

ppm 7.41-7.30 (m, 6H), 6.28 (dd, J = 2.0, 3.2 Hz, 1H), 6.05 (dd, J = 0.8, 3.2 Hz, 1H), 4.35 (s, 2H), 3.51 (t, J = 7.2 Hz, 2H), 2.90 (t, J = 7.2 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 151.4, 141.6, 134.5, 128.9, 128.5, 128.4, 110.5, 107.0, 52.8, 47.0, 26.8; IR (neat, cm^{-1}): 2126, 1379, 1194, 1165, 906, 727.

N-Benzyl-2-(thiophen-2-yl)ethan-1-sulfamoyl azide (1q) was obtained in 88% yield (283 mg) through
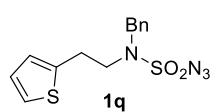
General Procedure E from *N*-benzyl-2-(thiophen-2-yl)ethan-1-amine (Synthesized according to the known procedure[8]), starting from 1 mmol scale. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 16:1), colorless oil, TLC R_f = 0.55 (Hexanes/EtOAc 10:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 - 7.32 (m, 5H), 7.16 (d, J = 4.4 Hz, 1H), 6.94 - 6.91 (m, 1H), 6.78 (d, J = 2.8 Hz, 1H), 4.42 (s, 2 H), 3.48 (t, J = 7.6 Hz, 2H), 3.05 (t, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 139.6, 134.4, 129.0, 128.6, 128.6, 127.1, 125.7, 124.2, 53.2, 50.0, 28.5; IR (neat, cm^{-1}): 2126, 1380, 1204, 1167, 905, 727, 698.

N-Benzyl-2-(cyclopropyl)ethan-1-sulfamoyl azide (1r) was obtained in 75% yield (300 mg) through
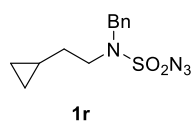
General Procedure E from *N*-benzyl-2-cyclopropylethan-1-amine, starting from 1.4 mmol scale. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 16:1), colorless oil, TLC R_f = 0.65 (Hexanes/EtOAc 10:1). ^{1}H NMR (600 MHz, CDCl$_3$) δ ppm 7.42 - 7.31 (m, 5 H), 4.46 (s, 2 H), 3.32 - 3.28 (m, 2 H), 1.45 (dd, J = 7.3, 15.2 Hz, 2 H), 0.56 (ddd, J = 5.1, 7.8, 12.5 Hz, 1 H), 0.42 (dt, J = 5.1, 5.5 Hz, 2 H), 0.03 - 0.04 (m, 2 H); [13]H NMR (150 MHz, CDCl$_3$) δ ppm 134.8, 129.0, 128.7, 128.6, 52.8, 48.8, 32.8, 8.3, 4.5; IR (neat, cm^{-1}): 2127, 1383, 1166.

N-Methyl-1,3-diphenylpropan-2-sulfamoyl azide (1s) was obtained in 85% yield (280 mg) through
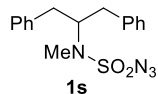
General Procedure E from *N*-methyl-1,3-diphenylpropan-2-amine starting from 1 mmol scale. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 16:1), colorless oil TLC R_f = 0.6 (Hexanes/EtOAc 8:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.39 - 7.31 (m, 4 H), 7.30 - 7.24 (m, 2 H), 7.24 - 7.17 (m, 4 H), 4.54 - 4.40 (m, 1 H), 2.95 - 2.84 (m, 4 H), 2.94 (s, 3 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 137.2, 129.0, 128.7, 127.0, 62.9, 38.1, 30.0; IR (neat, cm^{-1}): 2126, 1496, 1454, 1370, 1264, 1201, 1162, 960, 933, 733, 700, 612.
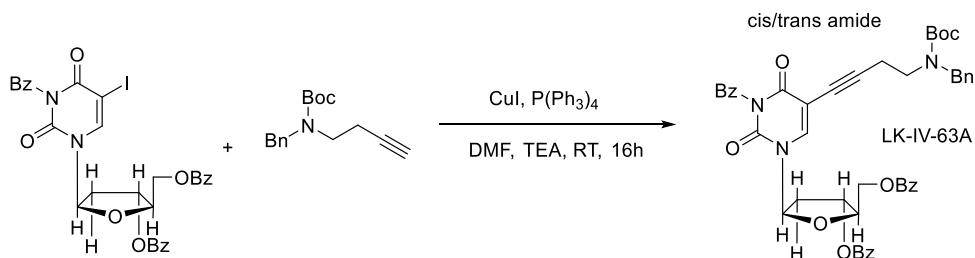
Deoxyuridine-based sulfamoyl azide (1t) was synthesized according to the following procedure. *tert*-Butyl (azidosulfonyl)(but-3-yn-1-yl) carbamate (800 mg, 3.06 mmol), triethylamine (0.42 mL, 3.06 mmol), Pd(PPh$_3$)$_4$ (105 mg, 0.09 mmol) and CuI (35 mg, 0.185 mmol) were added to a solution of 3-*N*-benzoyl 3'5-di-*O*-benzoyl-5-iodo-2'-deoxyuridine (1.0 g, 1.53 mmol) in anhydrous DMF (10 mL). The reaction was stirred at room temperature for 24 h. The solution was concentrated in vacuo and the residue was purified by silica gel column chromatography (eluent: Hexanes/EtOAc 7:1) to obtain the product, R$_f$ = 0.42 (Hexanes/EtOAc 1:1) (812 mg, 68% yield) as yellow solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 8.11 - 8.01 (m, 4 H), 7.92 (d, J = 7.8 Hz, 2 H), 7.86 (br. s, 1 H), 7.70 - 7.64 (m, 1 H), 7.63 - 7.54 (m, 2 H), 7.48 (td, J = 7.8, 19.6 Hz, 7 H), 7.36 - 7.29 (m, 2 H), 7.26 - 7.16 (m, 2 H), 6.39 (dd, J = 5.4, 8.3 Hz, 1 H), 5.64 (d, J = 6.4 Hz, 1 H), 4.85 - 4.71 (m, 2 H), 4.61 (br. s., 1 H), 4.54 - 4.46 (m, 2 H), 3.32 (br. s., 1 H), 3.23 (br. s., 1 H), 2.80 (d, J = 11.7 Hz, 1 H), 2.46 (d, J = 18.1 Hz, 2 H), 2.42 - 2.30 (m, 2 H), 1.49 (br. s., 5 H), 1.44 (br. s., 4 H); HRMS (ESI) Calcd. for C$_{46}$H$_{43}$N$_3$NaO$_{10}^+$ [M+Na]$^+$: 820.2841, Found: 820.2855.
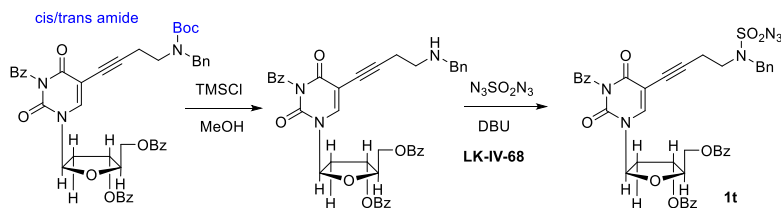
The deprotection of the Boc-substituted substrate was conducted according to the following procedure. The Boc-protected amine (500 mg, 1 mmol) was set to stir in MeOH (10 mL) and DCM (5 mL) in a round-bottom flask and put under a nitrogen atmosphere. The stirring solution was then cooled to 0 °C in an ice bath and then TMSCl (1.26 mL, 10 mmol) was added slowly over the course of 30 minutes. The reaction was allowed to slowly warm to room temperature and left to react for 3 h. After the reaction had completed, all volatiles were removed under reduced pressure. The non-volatile products dissolved in DCM (20 mL), Et$_3$N (2.0 ml) and brine (20 mL), then extracted with DCM (2 x 20 mL). The organic extracts were dried over Na$_2$SO$_4$, filtered, and concentrated under vacuum to give crude amine (350 mg, Yield: about 80%) which was used directly in the next step (**Note, this compound is unstable and needs to be converted immediately**).

Deoxyuridine-based sulfamoyl azide (1t) was synthesized from above obtained crude amine through

General Procedure E, purified by silica gel column chromatography (gradient elution: DCM/EtOAc 20:1 to 10:1) to give the desired product in 65% yield,
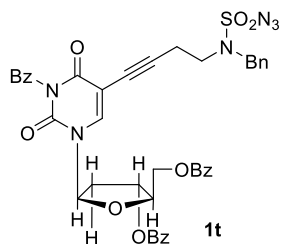
white powder, TLC R_f = 0.5 (Hexanes/EtOAc 1:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 8.02 (dt, J = 1.0, 7.5 Hz, 4 H), 7.92 - 7.85 (m, 3 H), 7.69 - 7.61 (m, 1 H), 7.61 - 7.54 (m, 2 H), 7.53 - 7.39 (m, 6 H), 7.38 - 7.27 (m, 5 H), 6.37 (dd, J = 5.5, 8.2 Hz, 1 H), 5.65 - 5.58 (m, 1 H), 4.80 - 4.67 (m, 2 H), 4.62 - 4.56 (m, 1 H), 4.52 (s, 2 H), 3.30 (t, J = 7.2 Hz, 2 H), 2.79 (ddd, J = 1.6, 5.6, 14.4 Hz, 1 H), 2.52 - 2.43 (m, 2 H), 2.37 (ddd, J = 6.6, 8.1, 14.5 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 167.6, 166.0, 165.8, 160.3, 148.2, 140.9, 135.3, 134.4, 133.8, 133.6, 131.1, 130.5, 129.7, 129.5, 129.2, 129.1, 128.9, 128.8, 128.6, 128.5, 100.7, 91.2, 86.1, 83.3, 77.2, 74.8, 72.8, 64.3, 53.2, 46.8, 38.6, 19.3; IR (neat, cm^{-1}): 2130, 1755, 1714, 1673, 1378, 1264, 1168, 1096, 733, 704.

N-Benzyl-2-(ferrocenyl)ethan-1-sulfamoyl azide (1u) was synthesized from *N*-benzyl-2-(ferrocenyl)ethan-1-amine (270 mg, 0.85 mmol) through **General Procedure E**, purified by silica gel column chromatography (gradient elution: Hexanes/EtOAc 20/1) to give the desired product in 94% yield (340 mg) yellow oil, TLC R_f = 0.65 (Hexanes/EtOAc 8:1). ^{1}H NMR (600 MHz, CDCl$_3$) δ ppm 7.43 - 7.32 (m, 5 H), 4.43 (s, 2 H), 4.11 - 4.06 (m, 7 H), 4.01 (s, 2 H), 3.43 - 3.32 (m, 2 H), 2.62 - 2.52 (m, 2 H); ^{13}C NMR (150 MHz, CDCl$_3$) δ ppm 134.5, 128.9, 128.6, 128.5, 84.2, 68.7, 68.2, 67.8, 52.9, 49.2, 27.9; IR (neat, cm^{-1}): 2126, 1383, 1208, 1167, 740, 612.

General Procedure F (Co(II)-Catalyzed Intramolecular Radical 1,5-C–H Amination)
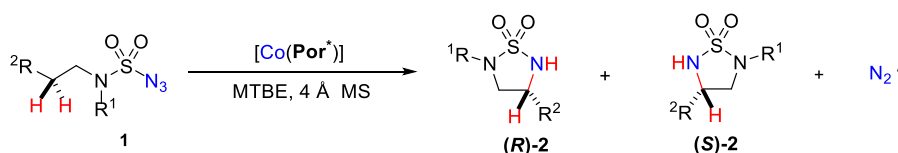
An oven dried Schlenk tube was charged with catalyst (0.002 mmol) or (0.005 mmol) and 4Å molecular sieves (50 mg). This reaction vessel was evacuated and backfilled with nitrogen several times. The Teflon screw cap was replaced with a rubber septum and the azide substrate (0.1 mmol) was added followed by the addition of 1.0 mL of methyl *tert*-butyl ether (HPLC plus, residue analysis 99.9% from Aldrich). The Schlenk tube was then purged with nitrogen for 2 minutes and the rubber septum was replaced with a Teflon screw cap. The Schlenk tube was then placed in an oil bath at the indicated temperature while stirring. After the indicated time, the reaction mixture was purified by silica gel column chromatography (Conditions were given below.). The fractions containing product were collected and concentrated by rotary evaporation to obtain the target compound. All the racemic products (for HPLC) were obtained

following the same procedure with achiral catalyst [Co(**P9**)][Co(3,5-Di*t*Bu-IbuPhyrin)][7] and please find the references therein[7] for the synthesis for this catalyst.

Achiral Catalyst used:

[Co(**P9**)] (**P9**: 3,5-Di*t*Bu-IbuPhyrin)
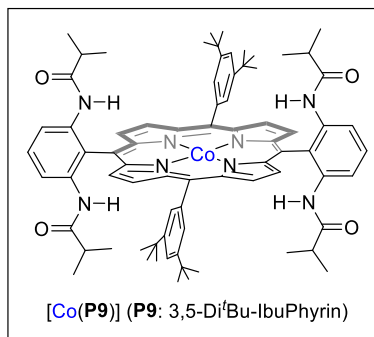
Figure S5. Representative Survey of Open Catalysts for Asymmetric Radical 1,5-C–H Amination of Sulfamoyl Azide **2a**
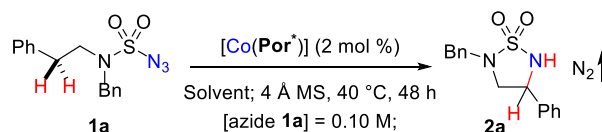
Our previous work has demonstrated the synthesis of the catalysts [Co(P12)],[1] [Co(P13)][1] and [Co(P14)].[9] [Co(P15)] was synthesized through a similar procedure.

in Benzene
95% yield
er of **2a** (R:S): 31:69

in MTBE
76% yield
er of **2a** (R:S): 26:74

[Co(**P12**)]

in MTBE
97% yield
er of **2a** (R:S): 34:66

[Co(**P13**)]

[Co(**P10**)] in MTBE
95% yield
er of **2a** (R:S): 54:46

[Co(**P11**)] in MTBE
89% yield
er of **2a** (R:S): 23:77

[Co(**P14**)] in MTBE
95% yield
er of **2a** (R:S): 75:25

[Co(**P15**)] in MTBE
92% yield
er of **2a** (R:S): 74:26
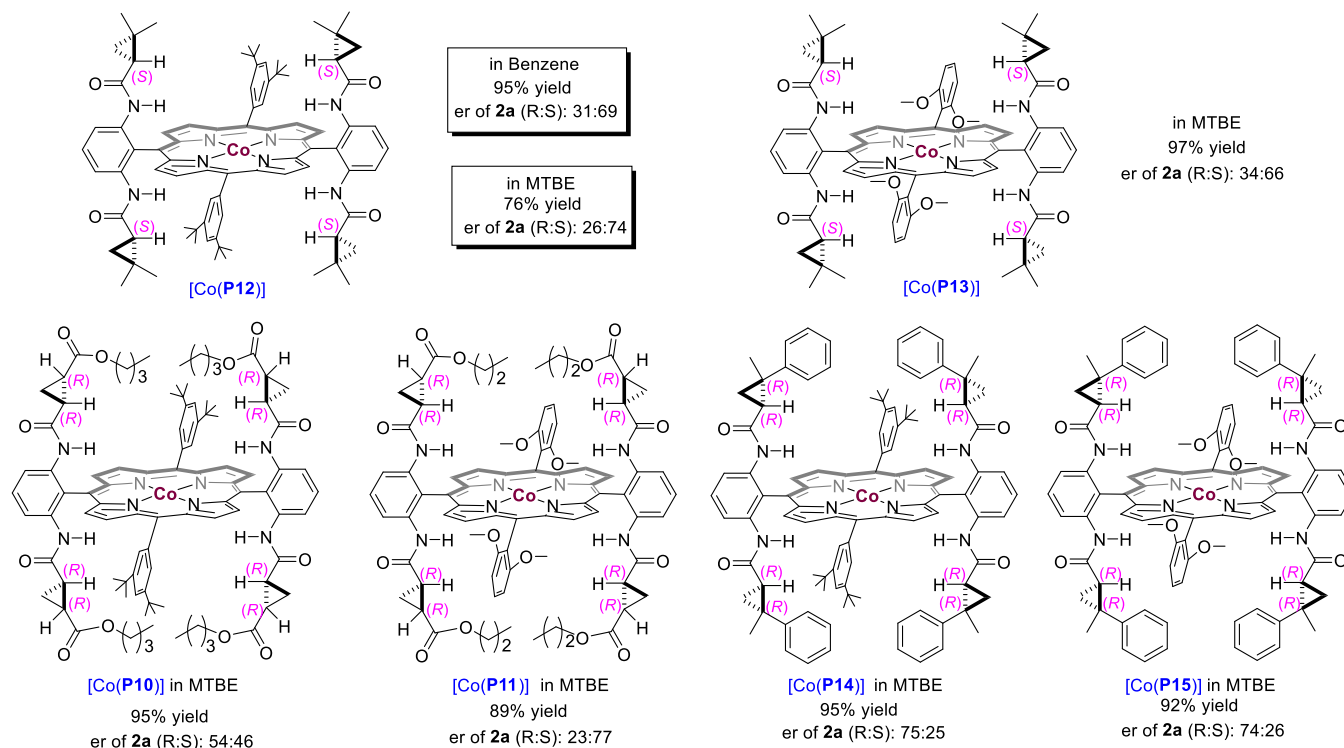
Table S1. Systematic Control of Degree and Sense of Asymmetric Induction for Intramolecular Radical 1,5-C–H Amination of Sulfamoyl Azide **1a** by [Co(HuPhyrin)] [a,b,c,d]
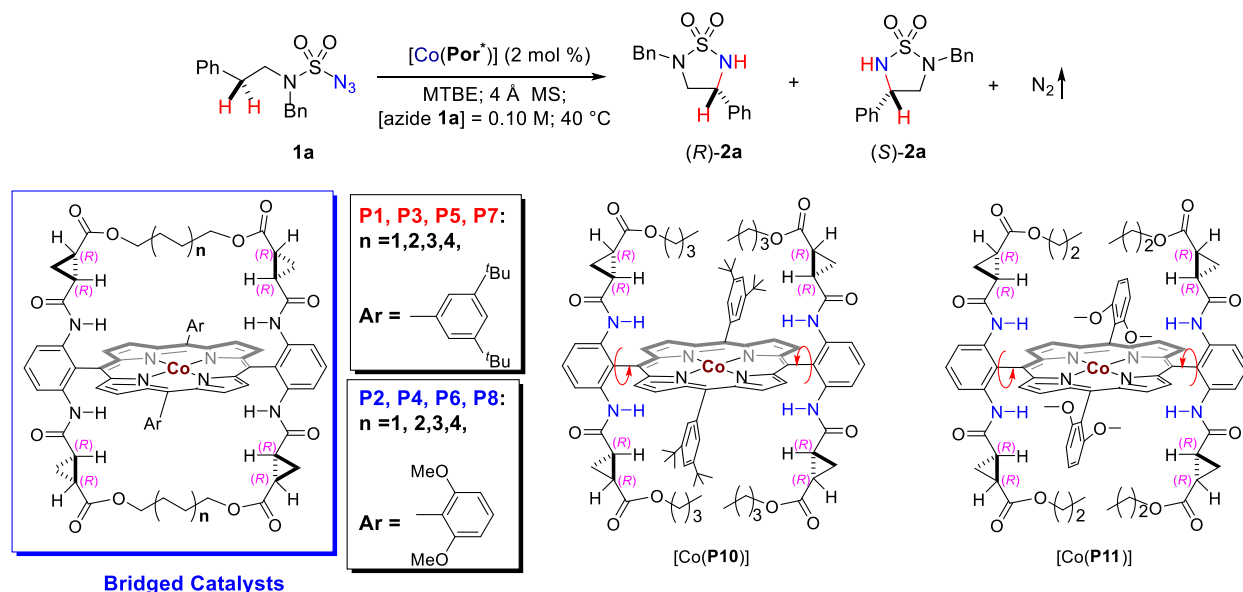
Entry	[Co(**Por***)] (2 mol%)	*meso*-Substituent	Methylene Chain Length	Yield (%)[b]	(R)/(S)[c]	er (R:S)[d]
1	[Co(**P1**)]	3,5-Di*t*Bu Phenyl	4	85	R	52:48
2	[Co(**P2**)]	2,6-DiMeO Phenyl	4	10	S	32:68
3	[Co(**P3**)]	3,5-Di*t*Bu Phenyl	6	89	S	30:70
4	[Co(**P4**)]	2,6-DiMeO Phenyl	6	68	S	6:94
5	[Co(**P5**)]	3,5-Di*t*Bu Phenyl	8	92	R	97:3
6	[Co(**P6**)]	2,6-DiMeO Phenyl	8	76	R	62:38
7	[Co(**P7**)]	3,5-Di*t*Bu Phenyl	10	90	R	87:13
8	[Co(**P8**)]	2,6-DiMeO Phenyl	10	95	S	36:64
9	[Co(**P10**)]	3,5-Di*t*Bu Phenyl	non-Bridged	95	R	54:46
10	[Co(**P11**)]	2,6-DiMeO Phenyl	non-Bridged	89	S	23:77

[a] All reactions were performed on a 0.1 mmol scale of sulfamoyl azides **1a** using 2 mol % of [Co(**Por***)] in 1 mL of MTBE at 40 ºC. [b] Isolated yields. [c] Absolute stereochemistry assigned by X-ray crystal structure. [d] Enantiomeric ratios (er) were determined by chiral HPLC analysis using ADH column. MTBE: Methyl *t*-butyl ether.
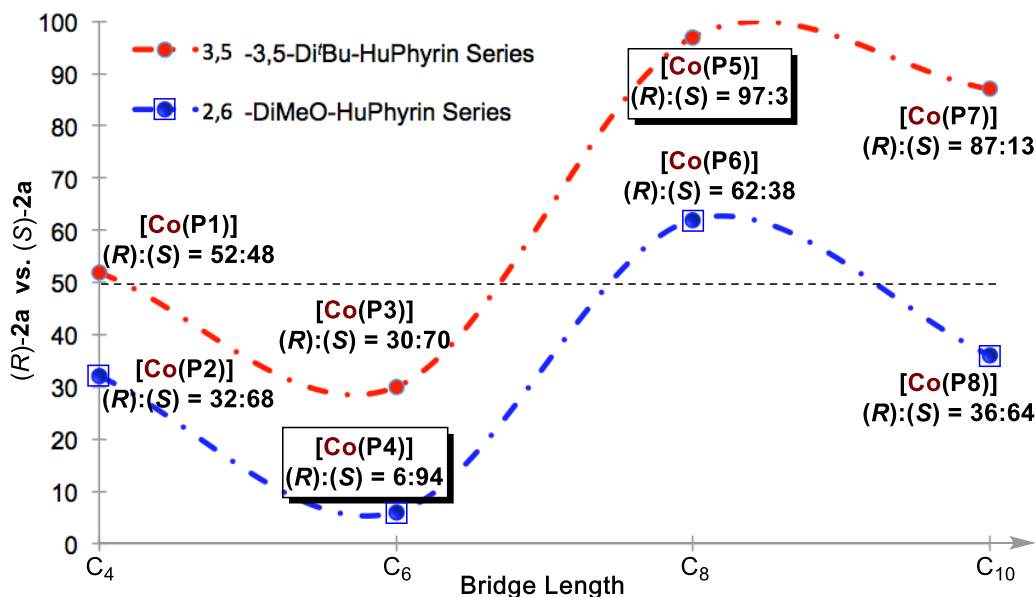
Characterization of Sulfamides (2a-2m′)

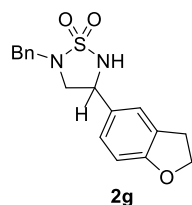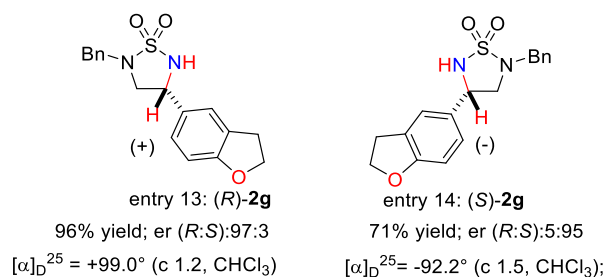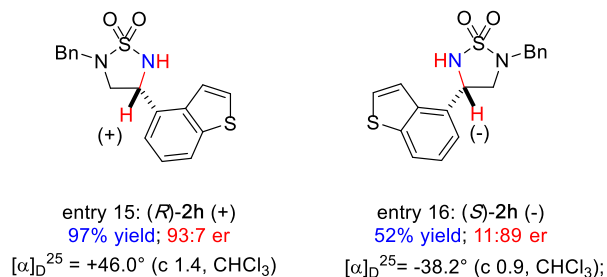**2-Benzyl-4-phenyl-1,2,5-thiadiazolidine 1,1-dioxide** (**2a**) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R_f = 0.35 (Hexanes/EtOAc 4:1); For **[Co(3,5-Di^{t}Bu-Hu(C$_8$)Phyrin)]** ([Co(**P5**)]), 2 mmol % of catalyst was used (92 % yield) and the reaction was run at 40 ˚C for 48h; for **[Co(2,6-DiMeO-Hu(C$_6$)Phyrin)]** ([Co(**P4**)]), 2 mmol % of catalyst was used and the reaction was run at 40 ºC for 48h (68% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.44 - 7.26 (m, 10 H), 4.85 - 4.74 (m, 1 H), 4.71 (d, J = 5.9 Hz, 1 H), 4.35, 3.98 (AB q, J = 13.3 Hz, each 1 H), 3.54 (dd, J = 7.2, 9.6 Hz, 1 H), 3.11 (dd, J = 8.2, 9.4 Hz, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 138.4, 134.8, 129.0, 128.8, 128.7, 128.2, 126.4, 55.8, 55.1, 50.5; HRMS (ESI) m/z Calcd. for C$_{15}$H$_{17}$N$_2$O$_2$S$^+$ [M+H]$^+$: 289.1005, Found: 289.0991; IR (neat, cm^{-1}): 1331, 1285, 1153, 1096, 1019, 753, 696, 684; Enantiomeric excess was determined by HPLC with an ADH column (90:10 n-hexane: isopropanol, 0.8 mL/min); R-enantiomer: t_r = 34.4 min; S- enantiomer: t_r = 24.7 min; Absolute configurations of both enantiomer products were confirmed by X-ray.
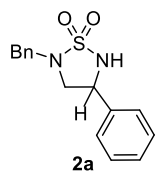
Both reactions were successfully scaled up to 2 mmol without any notable change for enantioselectivities. For **[Co(3,5-Di^{t}Bu-Hu(C$_8$)Phyrin)]** ([Co(**P5**)]), 2 mmol % of catalyst was used (98 % yield, 97:3 er) and the reaction was run at 40 ˚C for 48h; for **[Co(2,6-DiMeO-Hu(C$_6$)Phyrin)]** ([Co(**P4**)]), 2 mmol % of catalyst was used and the reaction was run at 40 ºC for 48h (75% yield, 6:94 er).

entry 1:(*R*)-**2a**
98% (95%) yield; er (*R*:*S*): 97
[α]$_D^{25}$ = +89.1° (c 2.1, CHCl$_3$)

(*R*)-**2a**

entry 2: (*S*)-**2a**
75% (68%) yield; er (*R*:*S*): 6:94
[α]$_D^{25}$ = -87.6.° (c 1.4, CHCl$_3$)

(*S*)-**2a**
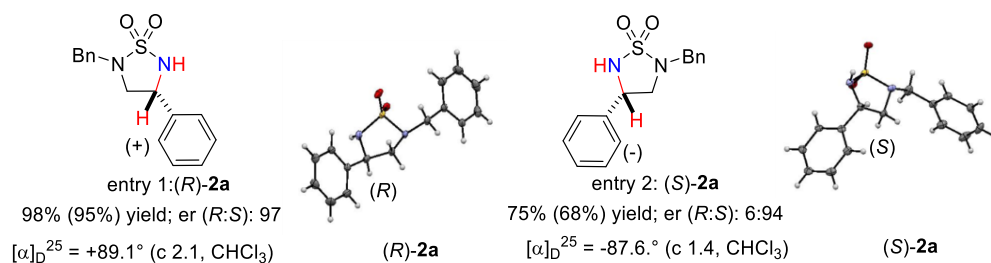
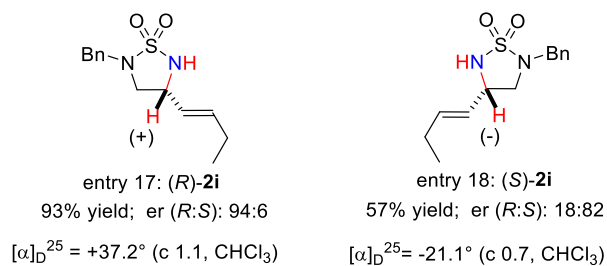**2-Benzyl-4-(4-methoxyphenyl)-1,2,5-thiadiazolidine 1,1-dioxide (2b)** was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R$_f$ = 0.32 (Hexanes/EtOAc 4:1); For **[Co(3,5-Di^{t}BuHu-(C$_8$)Phyrin)]** ([Co(**P5**)]), 2 mmol % of catalyst was used (97 % yield) for 48h; for **[Co(2,6-DiMeO-Hu(C$_6$)Phyrin)]** ([Co(**P4**)]), 2 mmol % of catalyst was used and the reaction was run at 40 ºC for 72h (88% yield). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.39 - 7.32 (m, 5 H), 7.30 (d, *J* = 8.7 Hz, 2 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 4.74 (dd, *J* = 7.1, 14.5 Hz, 1 H), 4.65 (d, *J* = 6.2 Hz, 1 H), 4.36, 4.02 (AB q, *J* = 13.6 Hz, each 1 H), 3.79 (s, 3 H), 3.51 (dd, *J* = 7.1, 9.6 Hz, 1 H), 3.16 - 3.09 (m, 1 H); ^{13}C NMR (150 MHz, CDCl$_3$) δ ppm 160.1, 135.1, 130.4, 128.9, 128.8, 128.3, 127.9, 114.5, 55.7, 55.5, 55.4, 50.6; HRMS (ESI) *m/z* Calcd. for C$_{16}$H$_{19}$N$_2$O$_3$S$^+$ [M+H]$^+$: 319.1111, Found: 319.1099; IR (neat, cm^{-1}): 1613, 1515, 1307, 1264, 1163, 896, 833, 731, 701; Enantiomeric excess was determined by HPLC with an ADH column (90:10 *n*-hexane: isopropanol, 1.0 mL/min); *R*- enantiomer: t$_r$ = 42.0 min; *S*- enantiomer: t$_r$ = 25.0 min; Absolute configurations of both enantiomer products were confirmed by X-ray.

entry 3: (*R*)-**2b**
97% yield; er (*R*:*S*): 98:2
[α]$_D^{25}$ = +103.5° (c 2.3, CHCl$_3$)

(*R*)-**2b**

entry 4: (*S*)-**2b**
88% yield; er (*R*:*S*): 4:96
[α]$_D^{25}$ = -84.5° (c 0.6, CHCl$_3$)

(*S*)-**2b**
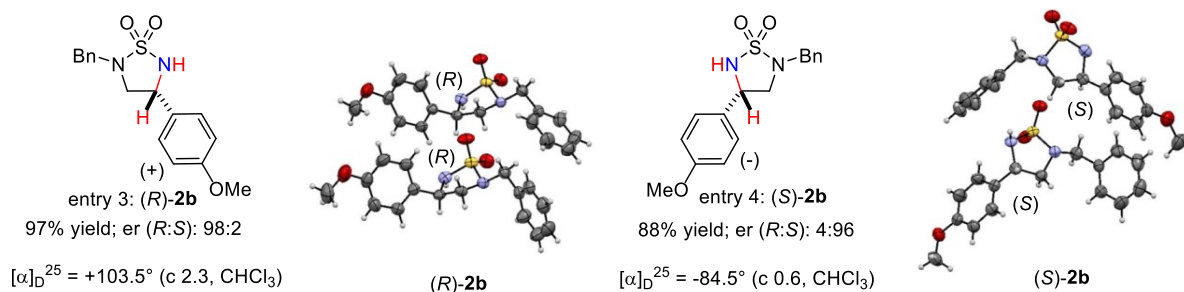
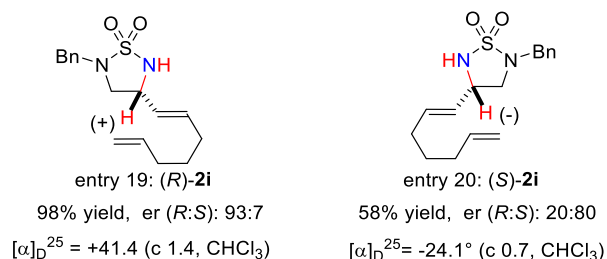**2-Benzyl-4-(4-chlorophenyl)-1,2,5-thiadiazolidine 1,1-dioxide (2c)** was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R$_f$ = 0.3 (Hexanes/EtOAc 4:1); For **[Co(3,5-Di^{t}BuHu-(C$_8$)Phyrin)]** ([Co(**P5**)]), 2 mmol % of catalyst was used (98% yield) for 48h; for **[Co(2,6-DiMeO-Hu(C$_6$)Phyrin)]** ([Co(**P4**)]), 5 mmol % of catalyst was used and the reaction was run for 72h (55% yield). ^{1}H NMR (600 MHz, CDCl$_3$) δ ppm 7.38 - 7.30 (m, 9 H), 4.77 (dd, *J* = 7.2,

14.7 Hz, 1 H), 4.72 (br. s, 1H), 4.38 3.98 (AB q, J = 13.6 Hz, each 1H), 3.56 (dd, J = 7.3, 9.7 Hz, 1H), 3.06 (dd, J = 8.2, 9.7 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 137.0, 134.6, 129.2, 128.8, 128.7, 128.3, 127.8, 55.2, 54.8, 50.5; HRMS (ESI) m/z Calcd. for $C_{15}H_{16}ClN_2O_2S^+$ [M+H]$^+$: 323.0616, Found: 323.0595; IR (neat, cm^{-1}): 1493, 1455, 1339, 1264, 1153, 1059, 827, 733, 698; Enantiomeric excess was determined by HPLC with an ADH column (90:10 n-hexane: isopropanol, 1.0 mL/min); R- enantiomer: t$_r$ = 31.2 min; S- enantiomer: t$_r$ = 19.5 min; Absolute configurations of both enantiomer products were confirmed by X-ray.

entry 5: (R)-**2c**
98% yield; er (R:S): 98:2
$[\alpha]_D^{25}$ = +104.9° (c 1.5, CHCl$_3$)

(R)-**2c**

entry 6: (S)-**2c**
55% yield; er (R:S): 8:92
$[\alpha]_D^{25}$ = - 82.5° (c 1.2, CHCl$_3$);

(S)-**2c**
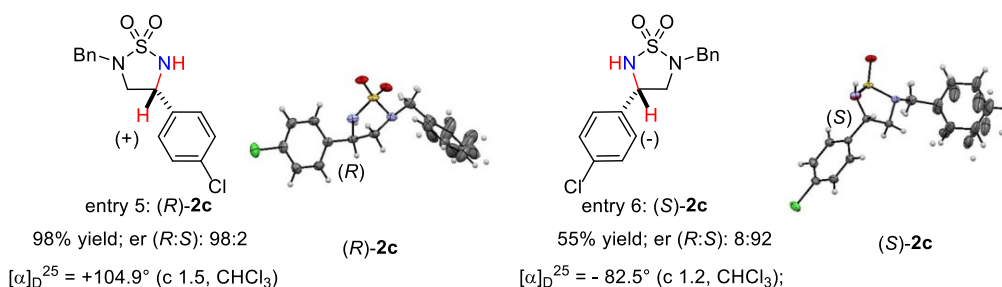
2-Benzyl-4-(4-(trifluoromethyl)phenyl)-1,2,5-thiadiazolidine 1,1-dioxide (**2d**) was obtained through

General Procedure F. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R$_f$ = 0.4 (Hexanes/EtOAc 4:1); For **[Co(3,5-Di^{t}Bu-Hu(C$_8$)Phyrin)]** ([Co(**P5**)]), 2 mmol % of catalyst was used (98% yield) for 48h; for **[Co(2,6-DiMeO-Hu(C$_6$)Phyrin)]** ([Co(**P4**)]), 5 mmol % of catalyst was used and the reaction was run for 72h (89% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.63 (d, J = 8.1 Hz, 2 H), 7.53 (d, J = 8.0 Hz, 2 H), 7.44 - 7.30 (m, 5 H), 4.97 - 4.77 (m, 2 H), 4.40, 3.96 (AB q, J = 13.5 Hz, each 1H), 3.63 (dd, J = 5.6, 11.4 Hz, 1 H), 3.05 (dd, J = 5.8, 11.4 Hz, 1 H); ^{13}C NMR (150 MHz, CDCl$_3$) δ ppm 142.7, 134.7, 131.1 (q, J = 33.0 Hz), 129.0, 128.9, 128.5, 126.9, 126.5 (q, J = 4.5 Hz), 123.9 (q, J = 271.5 Hz), 55.4, 54.8, 50.7; ^{19}F NMR (470 MHz, CFCl$_3$, CDCl$_3$) δ ppm -63.27 (s, 3F); HRMS (ESI) m/z Calcd. for $C_{16}H_{15}F_3N_2NaO_2S^+$ [M+Na]$^+$: 379.0699, Found: 379.0721; IR (neat, cm^{-1}): 1620, 1496, 1456, 1423, 1400, 1324, 1286, 1153, 1110, 1016, 840, 684, 700, 657; Enantiomeric excess was determined by HPLC with an ADH column (90:10 n-hexane: isopropanol, 1.0 mL/min); R- enantiomer: t$_r$ = 28.1 min; S-enantiomer: t$_r$ = 14.5 min; Absolute configurations of the products were determined by analogy.

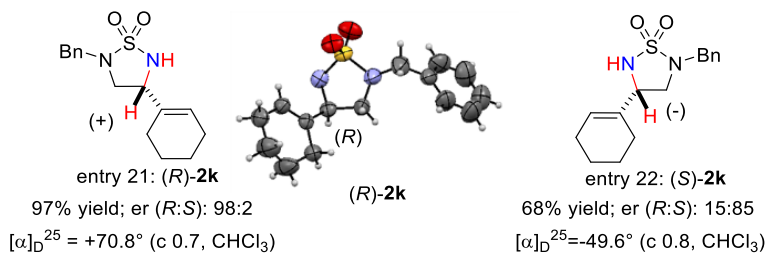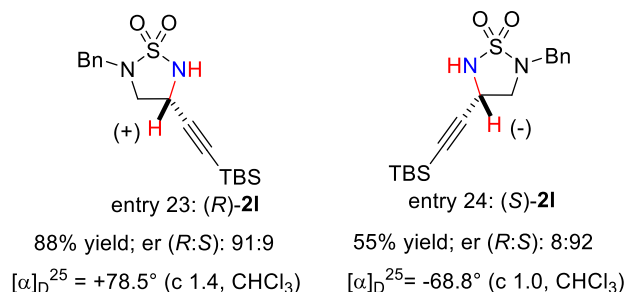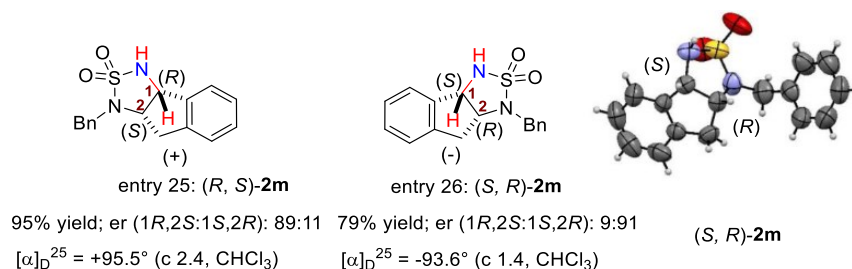entry 7: (*R*)-**2d**
98% yield; er (*R:S*): 98:2
$[\alpha]_D^{25}$ = +86.5° (c 1.7, CHCl$_3$)

entry 8: (*S*)-**2d**
89% yield; er (*R:S*): 5:95
$[\alpha]_D^{25}$ = -74.2° (c 1.4, CHCl$_3$)
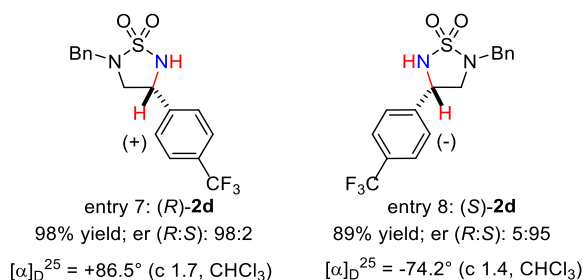
2-Benzyl-4-(naphthalen-2-yl)-1,2,5-thiadiazolidine 1,1-dioxide (**2e**) was obtained through **General**
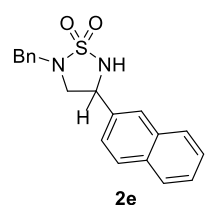
Procedure F. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R$_f$ = 0.5 (Hexanes/EtOAc 4:1); For **[Co(3,5-Di^{t}BuHu-(C$_8$)Phyrin)]** ([Co(**P5**)]), 2 mmol % of catalyst was used (97% yield) for 48h; for **[Co(2,6-DiMeO-Hu(C$_6$)Phyrin)]** ([Co(**P4**)]), 5 mmol % of catalyst was used and the reaction was run at 40 ºC for 72h (53% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.90 - 7.79 (m, 5 H), 7.57 - 7.47 (m, 2 H), 7.43 - 7.30 (m, 5 H), 5.00 - 4.94 (m, 1 H), 4.93 - 4.88 (m, 1 H), 4.42, 4.03 (AB q, *J* = 13.7 Hz, each 1 H), 3.64 (dd, *J* = 7.3, 9.8 Hz, 1 H), 3.21 (dd, *J* = 8.3, 9.8 Hz, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 135.6, 134.8, 133.3, 133.0, 129.1, 128.8, 128.7, 128.2, 128.0, 127.7, 126.7, 126.6, 125.7, 123.6, 56.1, 54.9, 50.6; HRMS (ESI) *m/z* Calcd. for C$_{19}$H$_{18}$N$_2$NaO$_2$S$^+$ [M+Na]$^+$: 361.0981, Found: 361.0964; IR (neat, cm^{-1}): 1724, 1494, 1455, 1378, 1283, 1158, 1122, 1049, 1030, 904, 891, 821, 730, 594; Enantiomeric excess was determined by HPLC with an ADH column (90:10 *n*-hexane: isopropanol, 1.0 mL/min); *R*- enantiomer: t$_r$ = 34.0 min; *S*- enantiomer: t$_r$ = 24.0 min; Absolute configurations of the products were determined by analogy.

entry 9: (*R*)-**2e**
97% yield; er (*R:S*): 99:1
$[\alpha]_D^{25}$ = +147.9° (c 2.1, CHCl$_3$)

entry 10: (*S*)-**2e**
53% yield; er (*R:S*): 6:94
$[\alpha]_D^{25}$ = -151.1° (c 0.8, CHCl$_3$)
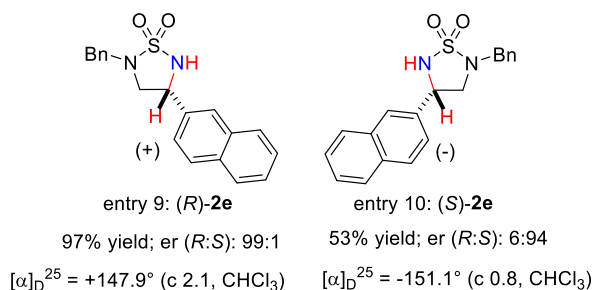
***tert*-Butyl 3-(5-benzyl-1,1-dioxido-1,2,5-thiadiazolidin-3-yl)-1*H*-indole-1-carboxylate** (**2f**) was
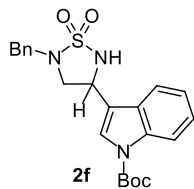
obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R$_f$ = 0.2 (Hexanes/EtOAc 4:1); For **[Co(3,5-Di^{t}Bu-Hu(C$_8$)Phyrin)]** ([Co(**P5**)]), 2 mmol % of catalyst was used (98% yield) for 48h; for **[Co(2,6-DiMeO-Hu(C$_6$)Phyrin)]** ([Co(**P4**)]), 5 mmol % of catalyst was used and the reaction was run at 40 ºC for 72h (92% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 8.18 - 8.08 (m, 1 H), 7.68 (d, *J* = 7.8 Hz, 1 H), 7.58 (s, 1 H), 7.42 - 7.25 (m, 6 H), 7.26-7.22 (m, 1 H), 5.04 (q, *J*

= 7.4 Hz, 1 H), 4.67 (d, J = 6.6 Hz, 1 H), 4.36, 4.11 (AB q, J = 13.7 Hz, each 1 H), 3.55 (dd, J = 7.0, 9.8 Hz, 1 H), 3.41 (dd, J = 8.2, 9.4 Hz, 1 H), 1.64 (s, 9 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 149.2, 135.8, 134.9, 128.8, 128.7, 128.2, 127.4, 125.2, 124.0, 123.1, 119.2, 117.2, 115.6, 84.4, 53.2, 50.5, 49.5, 28.1; HRMS (ESI) m/z Calcd. for C$_{22}$H$_{26}$N$_3$O$_4$S$^+$ [M+H]$^+$: 428.1639, Found: 428.1623; IR (neat, cm^{-1}): 1732, 1608, 1571, 1476, 1452, 1368, 1256, 1150, 1093, 732, 697. Enantiomeric excess was determined by HPLC with an ODH column (85:15 n-hexane: isopropanol, 1.0 mL/min); R- enantiomer: t_r = 25.6 min; S-enantiomer: t_r = 16.5 min; Absolute configurations of the products were determined by analogy.

entry 11: (R)-**2f**
98% yield; er (R:S): 97:3
$[\alpha]_D^{25}$ = +73.3° (c 0.9, CHCl$_3$)

entry 12: (S)-**2f**
92% yield; er (R:S): 8:92
$[\alpha]_D^{25}$ = -67.1° (c 0.7, CHCl$_3$)
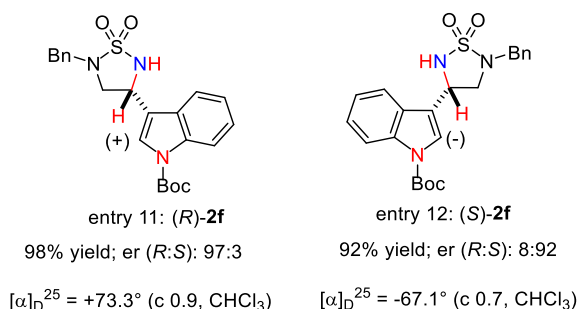
2-Benzyl-4-(2,3-dihydrobenzofuran-5-yl)-1,2,5-thiadiazolidine 1,1-dioxide (**2g**) was obtained through

General Procedure F. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R$_f$ = 0.5 (Hexanes/EtOAc 4:1); For **[Co(3,5-Di^{t}Bu-Hu(C$_8$)Phyrin)]** ([Co(**P5**)]), 2 mmol % of catalyst was used (96% yield) for 48h; for **[Co(2,6-DiMeO-Hu(C$_6$)Phyrin)]** ([Co(**P4**)]), 5 mmol % of catalyst was used and the reaction was run for 72h (71% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.43 - 7.30 (m, 5 H), 7.28 (s, 1 H), 7.07 (d, J = 8.3 Hz, 1 H), 6.73 (d, J = 8.3 Hz, 1 H), 4.73 (q, J = 7.2 Hz, 1 H), 4.65 (d, J = 6.4 Hz, 1 H), 4.58 (t, J = 8.6 Hz, 2 H), 4.38, 4.02 (AB q, J = 13.7 Hz, each 1 H), 3.50 (dd, J = 7.1, 9.5 Hz, 1 H), 3.20 (t, J = 8.8 Hz, 2 H), 3.12 (dd, J = 8.3, 9.8 Hz, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 160.6, 134.9, 130.2, 128.8, 128.7, 128.2, 126.7, 123.2, 109.4, 71.5, 55.9, 55.3, 50.5, 29.5; HRMS (ESI) m/z Calcd. for C$_{17}$H$_{19}$N$_2$O$_3$S$^+$ [M+H]$^+$: 331.1111, Found: 331.1135; IR (neat, cm^{-1}): 1615, 1493, 1455, 1264, 1162, 731, 697, 597; Enantiomeric excess was determined by HPLC with an ADH column (90:10 n-hexane: isopropanol, 1.0 mL/min); R- enantiomer: t_r 43.8 min; S- enantiomer: t_r = 31.6 min; Absolute configurations of the products were determined by analogy.
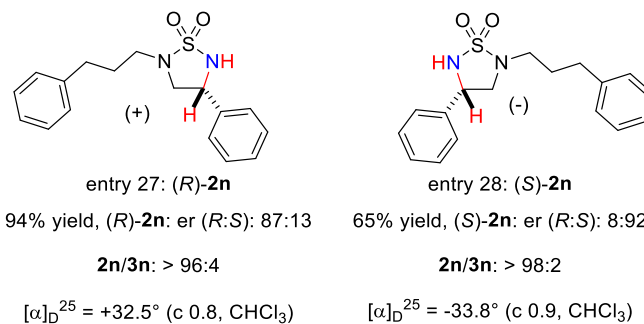
entry 13: (*R*)-**2g**
96% yield; er (*R*:*S*):97:3
$[\alpha]_D^{25}$ = +99.0° (c 1.2, CHCl₃)

entry 14: (*S*)-**2g**
71% yield; er (*R*:*S*):5:95
$[\alpha]_D^{25}$= -92.2° (c 1.5, CHCl₃);

2-Benzyl-4-(benzo[b]thiophen-4-yl)-1,2,5-thiadiazolidine 1,1-dioxide (**2h**) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC $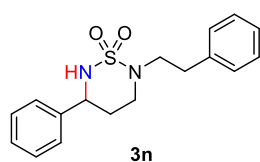R_f$ = 0.5 (Hexanes/EtOAc 3:1); For **[Co(3,5-Di^{t}Bu-Hu(C₈)Phyrin)]** ([Co(**P5**)]), 2 mmol % of catalyst was used (97% yield) for 48h; for **[Co(2,6-DiMeO-Hu(C₆)Phyrin)]** ([Co(**P4**)]), 5 mmol % of catalyst was used and the reaction was run at 40 °C for 72h (52% yield). ^{1}H NMR (500 MHz, acetone-D_6) δ ppm 7.95 (d, *J* = 8.1 Hz, 1 H), 7.76 (d, *J* = 5.6 Hz, 1 H), 7.71 (d, *J* = 5.6 Hz, 1 H), 7.66 (d, *J* = 7.4 Hz, 1 H), 7.42 (t, *J* = 6.4 Hz, 2 H), 7.40-7.39 (m, 1H), 7.36 (t, *J* = 7.3 Hz, 2 H), 7.32-7.29 (m, 1 H), 6.97 (d, *J* = 6.9 Hz, 1 H), 5.47 (dd, *J* = 7.7, 15.1 Hz, 1 H), 4.35, 3.98 (AB q, *J* = 13.8 Hz, each 1 H), 3.91 - 3.85 (m, 1 H), 3.15 (t, *J* = 9.1 Hz, 1 H); ^{13}C NMR (150 MHz, CDCl₃) δ ppm 141.1, 136.8, 134.9, 132.5, 129.0, 128.9, 128.4, 128.0, 124.6, 123.3, 122.5, 120.7, 54.9, 54.2, 50.7; HRMS (ESI) *m/z* Calcd. for $C_{17}H_{17}N_2O_2S_2^+$ [M+H]$^+$: 345.0726, Found: 345.0726; IR (neat, cm^{-1}): 1214, 1164, 750, 668; Enantiomeric excess was determined by HPLC with an ADH column (90:10 *n*-hexane: isopropanol, 1.0 mL/min); *R*- enantiomer: t_r 32.6 min; *S*-enantiomer: t_r = 28.7 min; Absolute configurations of the products were determined by analogy.

entry 15: (*R*)-**2h** (+)
97% yield; 93:7 er
$[\alpha]_D^{25}$ = +46.0° (c 1.4, CHCl₃)

entry 16: (*S*)-**2h** (-)
52% yield; 11:89 er
$[\alpha]_D^{25}$= -38.2° (c 0.9, CHCl₃);

(*E*)-2-Benzyl-4-(but-1-en-1-yl)-1,2,5-thiadiazolidine 1,1-dioxide (**2i**) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/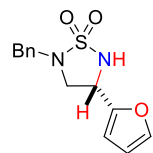EtOAc 4:1), white solid, TLC R_f = 0.4 (Hexanes/EtOAc 4:1); For **[Co(3,5-Di^{t}Bu-Hu(C₈)Phyrin)]** ([Co(**P5**)]), 2 mmol % of catalyst was used (93% yield) for 48h; for **[Co(2,6-DiMeO-Hu(C₆)Phyrin)]** ([Co(**P4**)]), 5 mmol % of catalyst was used and the reaction was run at 40 °C for 72h (57% yield). ^{1}H NMR (500 MHz, CDCl₃) δ ppm 7.45 - 7.29 (m, 5 H), 5.79 (td, *J* = 6.2, 15.5

Hz, 1 H), 5.41 (dd, J = 7.8, 15.2 Hz, 1 H), 4.40 (d, J = 5.9 Hz, 1 H), 4.28, 4.05 (AB q, J = 13.7 Hz, each 1 H), 4.19 (quin, J = 7.1 Hz, 1 H), 3.33 (dd, J = 6.8, 9.8 Hz, 1 H), 2.99 (dd, J = 8.1, 9.5 Hz, 1 H), 2.12 - 1.98 (m, 2 H), 0.97 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 138.1, 135.1, 128.8, 128.6, 128.1, 125.4, 54.8, 53.4, 50.4, 25.1, 13.0; HRMS (ESI) m/z Calcd. for $C_{13}H_{19}N_2O_2S^+$ [M+H]$^+$: 267.1162, Found: 267.1170; IR (neat, cm^{-1}): 1671, 1496, 1455, 1299, 1265, 1163, 1055, 1027, 773, 731, 697; Enantiomeric excess was determined by HPLC with an ADH column (90:10 n-hexane: isopropanol, 0.8 mL/min); R- enantiomer: t_r = 19.9 min; S- enantiomer: t_r = 15.9 min; Absolute configurations of the products were determined by analogy.

entry 17: (R)-**2i**
93% yield; er (R:S): 94:6
$[\alpha]_D^{25}$ = +37.2° (c 1.1, CHCl$_3$)

entry 18: (S)-**2i**
57% yield; er (R:S): 18:82
$[\alpha]_D^{25}$= -21.1° (c 0.7, CHCl$_3$)

(E)-2-Benzyl-4-(hepta-1,6-dien-1-yl)-1,2,5-thiadiazolidine 1,1-dioxide (2j) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes /EtOAc 4:1), white solid, TLC R$_f$ = 0.4 (Hexanes/EtOAc 4:1); For **[Co(3,5-Di^{t}Bu-Hu(C$_8$)Phyrin)]** ([Co(**P5**)]), 2 mmol % of catalyst was used (98% yield) for 48h; for **[Co(2,6-DiMeO-Hu(C$_6$)Phyrin)]** ([Co(**P4**)]), 5 mmol % of catalyst was used and the reaction was run at 40 ºC for 72h (58% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.38 (d, J = 4.4 Hz, 4 H), 7.34 (td, J = 3.8, 8.1 Hz, 1 H), 5.83 - 5.70 (m, 2 H), 5.44 (dd, J = 7.8, 15.2 Hz, 1 H), 5.05 - 4.93 (m, 2 H), 4.37 (d, J = 6.4 Hz, 1 H), 4.29, 4.06 (AB q, J = 14.2 Hz, each 1 H), 4.24 - 4.16 (m, 1 H), 3.34 (dd, J = 6.8, 9.8 Hz, 1 H), 2.99 (dd, J = 7.8, 9.3 Hz, 1 H), 2.13 - 1.95 (m, 4 H), 1.45 (quin, J = 7.6 Hz, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 138.2, 136.2, 135.1, 128.8, 128.6, 128.2, 126.7, 114.9, 54.7, 53.4, 50.4, 33.1, 31.4, 27.9; HRMS (ESI) m/z Calcd. for $C_{16}H_{23}N_2O_2S^+$ [M+H]$^+$: 307.1475, Found: 307.1464; IR (neat, cm^{-1}): 1639, 1496, 1455, 1395, 1303, 1266, 1162, 731, 969, 613; Enantiomeric excess was determined by HPLC with an ADH column (95:5 n-hexane: isopropanol, 0.8 mL/min); R- enantiomer: t_r = 40.2 min; S- enantiomer: t_r = 30.6 min; Absolute configurations of the products were determined by analogy.

entry 19: (*R*)-**2i**
98% yield, er (*R:S*): 93:7
$[\alpha]_D^{25}$ = +41.4 (c 1.4, CHCl$_3$)

entry 20: (*S*)-**2i**
58% yield, er (*R:S*): 20:80
$[\alpha]_D^{25}$= -24.1° (c 0.7, CHCl$_3$)

2-Benzyl-4-(cyclohex-1-en-1-yl)-1,2,5-thiadiazolidine 1,1-dioxide (2k) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R$_f$ = 0.4 (Hexanes/EtOAc 4:1); For **[Co(3,5-Di^{t}Bu-Hu (C$_8$)Phyrin)]** (**[Co(P5)]**), 2 mmol % of catalyst was used (97% yield) for 48h; for **[Co(2,6-DiMeO-Hu(C$_6$)Phyrin)]** (**[Co(P4)]**), 5 mmol % of catalyst was used and the reaction was run at 40 ºC for 72h (68% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.40 - 7.36 (m, 4 H), 7.36 - 7.32 (m, 1 H), 5.79-5.74 (m, 1 H), 4.33, 3.99 (AB q, *J* = 13.7 Hz, each 1 H), 4.33 - 4.32 (m, 1 H), 4.17 (q, *J* = 7.5 Hz, 1 H), 3.30 (dd, *J* = 7.1, 9.5 Hz, 1 H), 3.03 (t, *J* = 8.8 Hz, 1 H), 2.11 - 1.87 (m, 4 H), 1.72 - 1.49 (m, 4 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 135.1, 133.9, 128.8, 128.6, 128.1, 126.3, 57.8, 51.8, 50.5, 24.9, 23.7, 22.3, 22.1; HRMS (ESI) *m/z* Calcd. for C$_{15}$H$_{21}$N$_2$O$_2$S$^+$ [M+H]$^+$: 293.1318, Found: 293.1320; IR (neat, cm^{-1}): 1323, 1276, 1152, 909, 755, 698, 684; Enantiomeric excess was determined by HPLC with an ADH column (90:10 *n*-hexane: isopropanol, 1.0 mL/min); *R*- enantiomer: t$_r$ = 17.7 min; *S*- enantiomer: t$_r$ = 15.8 min; Absolute configurations of the products were determined by X-ray and analogy.
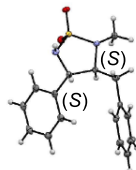

entry 21: (*R*)-**2k**
97% yield; er (*R:S*): 98:2
$[\alpha]_D^{25}$ = +70.8° (c 0.7, CHCl$_3$)

(*R*)-**2k**

entry 22: (*S*)-**2k**
68% yield; er (*R:S*): 15:85
$[\alpha]_D^{25}$=-49.6° (c 0.8, CHCl$_3$)

2-Benzyl-4-((*tert*-butyldimethylsilyl)ethynyl)-1,2,5-thiadiazolidine 1,1-dioxide (2l) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R$_f$ = 0.5 (Hexanes/EtOAc 4:1); For **[Co(3,5-Di^{t}Bu-Hu(C$_8$)Phyrin)]** (**[Co(P5)]**), 2 mmol % of catalyst was used for 48h (88% yield); for **[Co(2,6-DiMeO-Hu(C$_6$)Phyrin)]** (**[Co(P4)]**), 5 mmol % of catalyst was used and the reaction was run at 40 ºC for 72h (55% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.39 - 7.27 (m, 5 H), 4.50 - 4.44 (m, 1 H), 4.43-4.38 (m, 1 H), 4.26 - 4.14 (m, 2 H), 3.43 (dd, *J* = 6.6, 9.8 Hz, 1 H), 3.34 - 3.22 (m, 1 H), 0.89 (s, 9 H), 0.08 (s, 6 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 134.8, 128.8, 128.5, 128.2,

100.7, 90.5, 53.8, 50.5, 44.4, 25.9, 16.3, -4.9; HRMS (ESI) *m/z* Calcd. for $C_{17}H_{27}N_2O_2SSi^+$ [M+H]$^+$: 351.1557, Found: 351.1541; IR (neat, cm^{-1}): 1496, 1455, 1471, 1330, 1265, 1168, 839, 824, 810, 777, 733, 698, 622; Enantiomeric excess was determined by HPLC with an ADH column (98:2 *n*-hexane: isopropanol, 0.8 mL/min); *R*- enantiomer: t_r = 46.1 min; *S*- enantiomer: t_r = 40.2 min; Absolute configurations of the products were determined by analogy.

entry 23: (*R*)-**2l**
88% yield; er (*R:S*): 91:9
$[\alpha]_D^{25}$ = +78.5° (c 1.4, CHCl$_3$)

entry 24: (*S*)-**2l**
55% yield; er (*R:S*): 8:92
$[\alpha]_D^{25}$= -68.8° (c 1.0, CHCl$_3$)

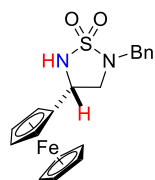**3-Benzyl-3,3a,8,8a-tetrahydro-1*H*-indeno[1,2-c][1,2,5]thiadiazole 2,2-dioxide** (**2m**) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R$_f$ = 0.4 (Hexanes/EtOAc 4:1); For **[Co(3,5-Di^{t}Bu-Hu(C$_8$)Phyrin)]** ([Co(**P5**)]), 2 mmol % of catalyst was used (95% yield) for 48h; for **[Co(2,6-DiMeO-Hu(C$_6$)Phyrin)]** ([Co(**P4**)]), 5 mmol % of catalyst was used and the reaction was run for 72h (79% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.48 - 7.34 (m, 6 H), 7.33 - 7.25 (m, 2 H), 7.14 (d, *J* = 7.3 Hz, 1 H), 5.12 (t, *J* = 7.8 Hz, 1 H), 4.51 (d, *J* = 14.2 Hz, 1 H), 4.35 (d, *J* = 8.3 Hz, 1 H), 4.22 - 4.10 (m, 2 H), 3.01 - 2.89 (m, 1 H), 2.88 - 2.75 (m, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 141.5, 138.0, 135.1, 130.0, 129.2, 128.8, 128.3, 127.9, 125.5, 125.2, 63.3, 61.0, 50.2, 38.1; HRMS (ESI) *m/z* Calcd. for $C_{16}H_{17}N_2O_2S^+$ [M+H]$^+$: 301.1005, Found: 301.1001; IR (neat, cm^{-1}): 1727, 1496, 1480, 1403, 1321, 1303, 1154, 1029, 786, 738, 701, 620; Enantiomeric excess was determined by HPLC with an ODH column (90:10 *n*-hexane: isopropanol, 1.0 mL/min); (1*R*,2*S*)- enantiomer: t_r = 27.0 min; (1*S*,2*R*)- enantiomer: t_r = 36.2 min; Absolute configurations of the products were determined by X-ray and analogy.

entry 25: (*R*, *S*)-**2m**
95% yield; er (1*R*,2*S*:1*S*,2*R*): 89:11
$[\alpha]_D^{25}$ = +95.5° (c 2.4, CHCl$_3$)

entry 26: (*S*, *R*)-**2m**
79% yield; er (1*R*,2*S*:1*S*,2*R*): 9:91
$[\alpha]_D^{25}$ = -93.6° (c 1.4, CHCl$_3$)

(*S*, *R*)-**2m**

1-Isopropyl-3,3a,8,8a-tetrahydro-1H-indeno[1,2-c][1,2,5]thiadiazole 2,2-dioxide (**2m′**) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R_f = 0.4 (Hexanes/EtOAc 4:1); For **[Co(3,5-Di^tBu-Hu(C_8)Phyrin)]** ([Co(**P5**)]), 2 mmol % of catalyst was used (61 % yield) for 48h.
^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.44 - 7.32 (m, 2 H), 7.32 - 7.21 (m, 2 H), 5.08 (t, J = 8.1 Hz, 1 H), 4.33 (dt, J = 5.1, 7.7 Hz, 1 H), 4.25 (d, J = 8.8 Hz, 1 H), 3.77 (td, J = 6.6, 13.2 Hz, 1 H), 3.42 (dd, J = 8.1, 16.9 Hz, 1 H), 3.22 (dd, J = 5.1, 16.9 Hz, 1 H), 1.39 (dd, J = 2.2, 6.6 Hz, 6 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 142.1, 137.6, 130.1, 127.8, 125.6, 125.5, 60.9, 60.2, 48.4, 40.9, 22.2, 20.6; HRMS (ESI) m/z Calcd. for C$_{12}$H$_{17}$N$_2$O$_2$S$^+$ [M+H]$^+$: 253.1005, Found: 253.1011; IR (neat, cm^{-1}): 1627, 1483, 1461, 1391, 1325, 1285, 1175, 1144, 1046, 874, 1017, 751; Enantiomeric excess was determined by HPLC with an ODH column (90:10 n-hexane: isopropanol, 1.0 mL/min); R- enantiomer: t_r = 29.0 min; S- enantiomer: t_r = 18.2 min; Absolute configurations of the products were determined by analogy.
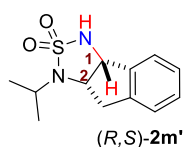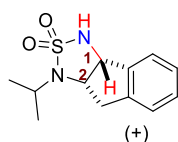
(+)
entry 25: (*R*,*S*)-**2m'**
R = iPr: 61% yield; er (1*R*,2*S*:1*S*,2*R*): 94:6
$[\alpha]_D^{25}$ = +154.4° (c 0.9, CHCl$_3$)

Table S2. Ligand Effect on Co(II)-Catalyzed Selective Formation of 5-Membered Ring Structures (Open vs Bridged Catalysts)

entry	cat	2n:3n (1,5/1,6)	er of 2n (*R*:*S*)^b	er of 3n	yield (%)
1	[Co(P4)]	>98:2	8:92	ND	65
2	[Co(P5)]	>96:4	87:13	ND	94
3	[Co(P10)]	74:26	44:56	59:41	94
4	[Co(P11)]	81:19	22:78	23:77	90
5	[Co(P9)]	70:30	-	-	98

[Co(P4)] [Co(P5)] [Co(P10)] [Co(P11)] [Co(P9)]
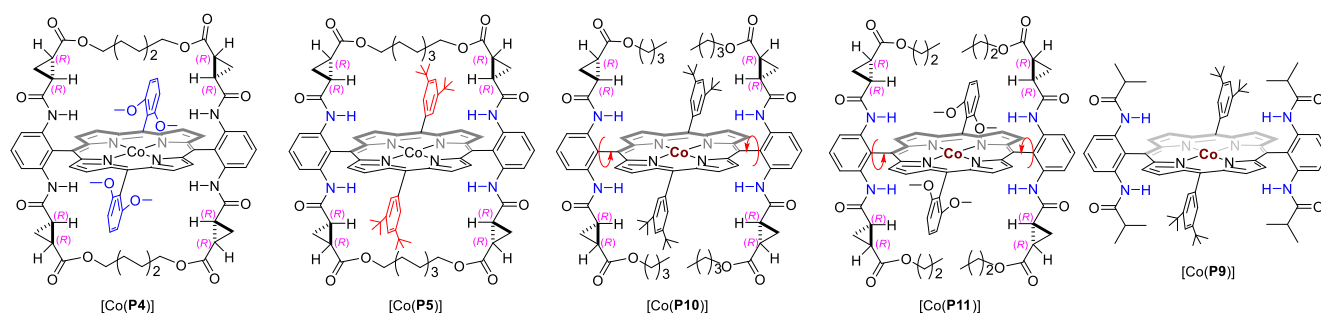
[a] Reactions were performed at room temperature with 5 mol % [Co(Por*)]. [b] Absolute configuration determined by analogy.

Characterization of Sulfamides (2n-2u)

4-Phenyl-2-(3-phenylpropyl)-1,2,5-thiadiazolidine 1,1-dioxide (2n) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes /EtOAc 4:1), white solid, TLC R_f = 0.3 (Hexanes/EtOAc 4:1); For **[Co(3,5-Di^{t}Bu-Hu (C$_8$)Phyrin)]** ([Co(**P5**)]), 5 mmol % of catalyst was used for 48h (94 % yield); for **[Co(2,6-DiMeO-Hu(C$_6$)Phyrin)]** ([Co(**P4**)]), 5 mmol % of catalyst was used and the reaction was run for 72h (65% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.48 - 7.34 (m, 5 H), 7.33 - 7.28 (m, 2 H), 7.24 - 7.17 (m, 3 H), 4.88 - 4.77 (m, 1 H), 4.61 (d, J = 5.4 Hz, 1 H), 3.71 (dd, J = 6.8, 9.3 Hz, 1 H), 3.22 (dd, J = 8.3, 9.3 Hz, 1 H), 3.16 (td, J = 7.3, 12.7 Hz, 1 H), 2.99 (td, J = 7.1, 12.7 Hz, 1 H), 2.74 (t, J = 7.6 Hz, 2 H), 1.99 (q, J = 7.3 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 141.0, 138.5, 129.1, 128.8, 128.5, 128.4, 126.4, 126.1, 56.0, 55.8, 46.3, 32.9, 29.3; HRMS (ESI) m/z Calcd. for C$_{17}$H$_{21}$N$_2$O$_2$S$^+$ [M+H]$^+$: 317.1318, Found: 317.1330; IR (neat, cm^{-1}): 1602, 1496, 1454, 1286, 1265, 1155, 1028, 733, 698; Enantiomeric excess was determined by HPLC with an ODH column (90:10 n-hexane: isopropanol, 1.0 mL/min); R- enantiomer: t_r = 63.0 min; S- enantiomer: t_r = 97.1 min; Absolute configurations of product were determined by analogy.

entry 27: (R)-**2n**

94% yield, (R)-**2n**: er (R:S): 87:13

2n/3n: > 96:4

$[\alpha]_D^{25}$ = +32.5° (c 0.8, CHCl$_3$)

entry 28: (S)-**2n**

65% yield, (S)-**2n**: er (R:S): 8:92

2n/3n: > 98:2

$[\alpha]_D^{25}$ = -33.8° (c 0.9, CHCl$_3$)

2-Phenethyl-5-phenyl-1,2,6-thiadiazinane 1,1-dioxide (3n) was obtained through **General Procedure F** together with **2n-a** using **[Co(3,5-Di^tBu-(nBu)TaoPhyrin)]** (**[Co(P10)]**) (5 mol %) for 48h and **[Co(2,6-DiMeO-(nPr)TaoPhyrin)]** (**[Co(P11)]**) (5 mol %) for 72h (**Table S2**). Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R_f = 0.5 (Hexanes/EtOAc 4:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.43 - 7.25 (m, 7 H), 7.23 - 7.18 (m, 3 H), 4.77 - 4.65 (m, 1 H), 4.05 (d, J = 7.4 Hz, 1 H), 3.69 (dt, J = 3.1, 13.3 Hz, 1 H), 3.47 - 3.32 (m, 2 H), 3.31 - 3.18 (m, 1 H), 3.02 - 2.85 (m, 2 H), 2.05 - 1.88 (m, 1 H), 1.87 - 1.77 (m, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 139.3, 138.5, 129.0, 128.8, 128.6, 126.6, 126.3, 59.7, 50.8, 49.6, 35.1, 29.5; HRMS (ESI) m/z Calcd. for C$_{17}$H$_{21}$N$_2$O$_2$S$^+$[M+H]$^+$: 317.1318, Found: 317.1331; IR (neat, cm^{-1}): 1728, 1603, 1495, 1456, 1425, 1324, 1295, 1145, 1026, 950, 774, 744, 694; Enantiomeric excess was determined by HPLC with an ODH column (90:10 n-hexane: isopropanol, 1.0 mL/min); enantiomer A: t_r = 28.5 min; enantiomer: B t_r = 33.7 min.

Isopropyl (S)-5-benzyl-1,2,5-thiadiazolidine-3-carboxylate 1,1-dioxide ((R)-2o) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R_f = 0.3 (Hexanes/EtOAc 3:1) with **[Co(3,5-Di^tBu-Hu(C$_8$)Phyrin)]** (**[Co(P5)]**). 5 mmol % of catalyst was used and the reaction was run at 40 ˚C for 72h (53% yield, er (R:S) = 93:7). For **[Co(2,6-DiMeO-Hu(C$_6$) Phyrin)]** (**[Co(P4)]**), 5 mmol % of catalyst was used at 40 ºC for 72h (<10% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.41 - 7.31 (m, 5 H), 5.20 (br. s., 1 H), 5.12 (td, J = 6.4, 12.7 Hz, 1 H), 4.33, 3.97 (AB q, J = 13.7 Hz, each 1 H), 4.13 (br. s., 1 H), 3.48 - 3.38 (m, 2 H), 1.27 (dd, J = 1.0, 6.4 Hz, 3 H), 1.21(dd, J = 1.0, 6.4 Hz, 3 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 169.3, 134.6, 128.8, 128.4, 128.3, 71.3, 52.9, 50.2, 49.7, 21.6, 21.5; HRMS (ESI) m/z Calcd. for C$_{13}$H$_{18}$N$_2$NaO$_4$S$^+$ [M+Na]$^+$: 321.0879, Found: 321.0856; IR (neat, cm^{-1}): 1736, 1455, 1332, 1264, 1170, 1102, 896, 732, 702; Enantiomeric excess was determined by HPLC with an ODH column (97:3 n-hexane: isopropanol, 1.0 mL/min); R- enantiomer: t_r = 94.7 min; S- enantiomer: t_r = 80.8 min; Absolute configurations of product were determined by analogy.

entry 29: (R)-**2o**

53% yield; er (R:S): 93:7

$[α]_D^{25}$ = -13.9° (c 0.9, CHCl$_3$)

**(R)-2-Benzyl-4-(furan-2-yl)-1,2,5-thiadiazolidine 1,1-dioxide** (**(R)-2p**) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R_f = 0.3 (Hexanes/EtOAc 4:1) with **[Co(3,5-Di^{t}Bu-Hu(C$_8$)Phyrin)]** ([Co(**P5**)]). 2 mmol % of catalyst was used for 48h (94% yield, er (R:S) = 98:2). For **[Co(2,6-DiMeO-Hu(C$_6$) Phyrin)]** ([Co(**P4**)]), 5 mmol % of catalyst was used at 40 ºC for 72h (<10% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.55 - 7.30 (m, 6 H), 6.45 - 6.31 (m, 2 H), 4.86 (q, J = 7.3 Hz, 1 H), 4.76 (d, J = 6.4 Hz, 1 H), 4.34, 4.14 (AB q, J = 13.7 Hz, each 1 H), 3.59 - 3.48 (m, 1 H), 3.46 - 3.33 (m, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 150.0, 143.2, 134.9, 128.8, 128.6, 128.2, 110.7, 108.5, 52.1, 50.5, 49.7; IR (neat, cm^{-1}): 1332, 1304, 1265, 1166, 731, 699; HRMS (ESI) m/z Calcd. for $C_{13}H_{14}N_2NaO_3S$ [M+Na]$^+$: 301.0623, Found: 301.0610; Enantiomeric excess was determined by HPLC with an ADH column (90:10 n-hexane: isopropanol, 1.0 mL/min); R- enantiomer: t_r = 20.7 min; S-enantiomer: t_r = 26.5 min; Absolute configurations of product were determined by analogy.

entry 30:(R)-**2p**

94% yield; er (R:S): 98:2

$[\alpha]_D^{25}$ = + 103.5 ° (c 2.0, CHCl$_3$)

(R)-2-Benzyl-4-(thiophen-2-yl)-1,2,5-thiadiazolidine 1,1-dioxide (**(R)-2q**) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R_f = 0.25 (Hexanes/EtOAc 4:1) with **[Co(3,5-Di^{t}Bu-Hu(C$_8$)Phyrin)]** ([Co(**P5**)]). 2 mmol % of catalyst was used for 48h (95% yield, er (R:S) = 97:3). For **[Co(2,6-DiMeO-Hu(C$_6$) Phyrin)]** ([Co(**P4**)]), 5 mmol % of catalyst was used at 40 ºC for 72h (<10% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.40-7.29 (m, 5H), 7.29 (d, J = 5.0 Hz, 1H), 7.05 (d, J = 3.5 Hz, 1H), 6.97-6.95 (m, 1H), 5.06 (q, J = 7.0 Hz, 1H), 4.78 (d, J = 5.5 Hz, 1H), 4.32, 4.13 (AB q, J = 14.0 Hz, each 1H), 3.58 (dd, J = 7.0, 10.0 Hz, 1H), 3.30 (dd, J = 7.5, 10.0 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 141.2, 134.8, 128.8, 128.7, 128.3, 127.1, 126.3, 126.0, 55.1, 51.9, 50.4; IR (neat, cm^{-1}): 1455, 1387, 1367, 1300, 1285, 1265, 1155, 1126, 1017, 727; HRMS (ESI) m/z Calcd. For $C_{13}H_{15}N_2O_2S_2$ [M+H]$^+$: 295.0575, Found: 295.0570; Enantiomeric excess was determined by HPLC with an ODH column (90:10 n-hexane: isopropanol, 1.0 mL/min); R- enantiomer: t_r = 33.3 min; S- enantiomer: t_r = 45.6 min; Absolute configurations of product were determined by analogy.

entry 31: (R)-**2q**

95% yield; er (R:S): 97:3

$[\alpha]_D^{24}$ = +98.4° (c 2.6, CHCl$_3$)

(R)-2-Benzyl-4-cyclopropyl-1,2,5-thiadiazolidine 1,1-dioxide ((R)-2r) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), colorless oil, TLC R_f = 0.30 (Hexanes/EtOAc 3:1) with **[Co(3,5-Di^{t}Bu-Hu(C$_8$)Phyrin)]** ([Co(**P5**)]). 5 mmol % of catalyst was used for 48h (95% yield, er (R:S) = 93:7). For **[Co(2,6-DiMeO-Hu(C$_6$) Phyrin)]** ([Co(**P4**)]), 5 mmol % of catalyst was used at 40 ºC for 72h (98 % yield, er (R:S) = 58:42). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.39-7.30 (m, 5 H), 4.57 (d, J = 3.8 Hz, 1 H), 4.23, 4.09 (AB q, J = 13.7 Hz, each 1 H), 3.37-3.28 (m, 1 H), 3.13-3.03 (m, 2 H), 1.07-0.97 (m, 1 H), 0.63-0.55 (m, 1 H), 0.56 - 0.48 (m, 1 H), 0.36 (td, J = 4.9, 10.0 Hz, 1 H), 0.24-0.17 (m, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 135.3, 128.9, 128.7, 128.3, 57.4, 53.2, 50.5, 14.7, 3.1, 2.5; IR (neat, cm^{-1}): 3247, 1289, 1165; HRMS (ESI) m/z Calcd. For C$_{12}$H$_{17}$N$_2$O$_2$S [M+H]$^+$: 253.1005, Found: 253.1002; Enantiomeric excess was determined by HPLC with an ODH column (90:10 n-hexane: isopropanol, 1.0 mL/min); R-enantiomer: t_r = 70.9 min; S- enantiomer: t_r = 76.1 min; Absolute configurations of product were determined by analogy.

entry 32: (R)-**2r**

95% yield; er (R:S): 93:7

[α]$_D^{24}$ = +15.0° (c 2.0, CHCl$_3$)

(3S,4S)-3-Benzyl-2-methyl-4-phenyl-1,2,5-thiadiazolidine 1,1-dioxide ((S,S)-**2s**) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R_f = 0.35 (Hexanes/EtOAc 4:1) with **[Co(2,6-DiMeO-Hu(C$_6$) Phyrin)]** ([Co(**P4**)]), (2 mol %) at 40 ºC for 72 h (80% yield, er (1R,2R:1S,2S) = 7:93). For **[Co(3,5-Di^{t}Bu-Hu (C$_8$)Phyrin)]** ([Co(**P5**)]), 2 mmol % of catalyst was used for 72h (98 % yield, er (1R,2R:1S,2S) = 58:42). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.56 - 7.21 (m, 8 H), 7.20 - 7.09 (m, 2 H), 4.64 (d, J = 6.4 Hz, 1 H), 4.44 (t, J = 7.1 Hz, 1 H), 3.55 (ddd, J = 4.9, 6.4, 7.3 Hz, 1 H), 3.14 - 3.03 (m, 1 H), 3.00 - 2.93 (m, 1 H), 2.69 (s, 3 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 138.2, 135.9, 129.6, 128.9, 128.7, 127.2, 127.1, 69.8, 60.5, 36.9, 32.8; IR (neat, cm^{-1}):1603, 1495, 1454, 1298, 1266, 1153, 1028, 750, 735, 698; HRMS (ESI) m/z Calcd. for C$_{16}$H$_{19}$N$_2$O$_2$S$^+$[M+H]$^+$: 303.1162, Found: 303.1148; Enantiomeric excess was determined by HPLC with an ODH column (90:10 n-hexane: isopropanol, 1.0 mL/min); (1R,2R)- enantiomer: t_r = 27.7 min; (1S,2S)- enantiomer: t_r = 35.6 min; Absolute configurations of product were determined by analogy.
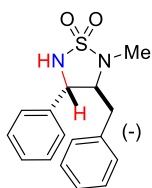
entry 33:(S,S)-**2s**

80% yield; er (1R,2R:1S,2S): 7:93

[α]$_D^{24}$ = -17.8° (c 0.6, CHCl$_3$)

Product ((S)-**2t**) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 2:1), white solid, TLC R_f = 0.45 (Hexanes/EtOAc 1:1) with **[Co(2,6-DiMeO-Hu(C$_6$)Phyrin)]** ([Co(**P4**)]), (2 mol %) for 96 h (88% yield, dr = 10:90). For **[Co(3,5-Di^{t}Bu-Hu (C$_8$)Phyrin)]** ([Co(**P5**)]), 2 mmol % of catalyst was used for 72h (82 % yield, dr = 60:40). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 8.09 - 8.01 (m, 4 H), 7.99 (s, 1 H), 7.90 (d, J = 8.3 Hz, 2 H), 7.72 - 7.65 (m, 1 H), 7.64 - 7.56 (m, 2 H), 7.55 - 7.44 (m, 6 H), 7.40 - 7.30 (m, 5 H), 6.36 (dd, J = 5.9, 7.8 Hz, 1 H), 5.64 (d, J = 6.4 Hz, 1 H), 4.83 - 4.74 (m, 2 H), 4.70 (d, J = 6.4 Hz, 1 H), 4.64 (d, J = 1.5 Hz, 1 H), 4.45 (q, J = 6.5 Hz, 1 H), 4.27 (d, J = 14.2 Hz, 1 H), 4.11 (d, J = 13.7 Hz, 1 H), 3.38 (dd, J = 7.6, 9.5 Hz, 1 H), 3.27 - 3.22 (m, 1 H), 2.86 (dd, J = 5.4, 14.2 Hz, 1 H), 2.39 (td, J = 7.3, 14.3 Hz, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 167.4, 166.0, 165.8, 160.1, 148.0, 142.5, 135.4, 134.7, 133.8, 133.7, 130.9, 130.5, 129.7, 129.6, 129.2, 129.1, 128.8, 128.6, 128.2, 99.1, 89.3, 86.5, 83.4, 76.5, 74.7, 64.2, 53.4, 50.6, 44.1, 38.6; The diastereomeric ratio was determined by both ^{1}H NMR and ^{13}C NMR spectroscopic integration; IR (neat, cm^{-1}): 1754, 1712, 1671, 1450, 1315, 1266, 1167, 1095, 1070, 907, 727, 712; HRMS (ESI) m/z Calcd. For C$_{41}$H$_{34}$N$_4$NaO10S$^+$ [M+Na]$^+$: 797.1888, Found: 797.1842.
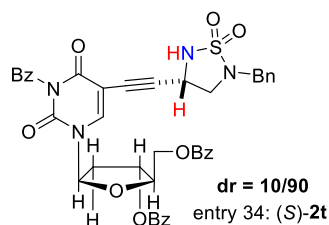
(S)-2-Benzyl-4-(ferrocenyl)-1,2,5-thiadiazolidine 1,1-dioxide ((S)-2u) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), yellow solid, TLC R_f = 0.35 (Hexanes/EtOAc 4:1) with **[Co(2,6-DiMeO-Hu(C$_6$)Phyrin)]** ([Co(**P4**)]), (5 mol %) at 40 ºC for 72 h (41% yield). For **[Co(3,5-Di^{t}Bu-Hu (C$_8$)Phyrin)]** ([Co(**P5**)]), 2 mmol % of catalyst was used for 48h (73 % yield, er (R:S) = 58:42). ^{1}H NMR (500 MHz, acetone-D_6) δ ppm 7.49 - 7.43 (m, 2 H), 7.41 - 7.36 (m, 2 H), 7.34 (d, J = 6.8 Hz, 1 H), 6.38 - 6.29 (m, 1 H), 4.67 - 4.63 (m, 1 H), 4.32 - 4.29 (m, 1 H), 4.26 - 4.23 (m, 1 H), 4.23, 4.07 (AB q, J = 15.0 Hz, each 1H), 4.18 (s, 5 H), 4.17 - 4.15 (m, 2 H), 3.62 (dd, J = 7.3, 9.8 Hz, 1 H), 3.21 (dd, J = 8.1, 9.5 Hz, 1 H); ^{13}C NMR (150 MHz, acetone-D_6) 127.3, 119.6, 118.8, 78.4, 59.6, 59.3, 59.0, 58.1, 57.4, 45.6, 42.5, 41.4; IR (neat, cm^{-1}): 3263, 2921, 2852, 1709, 1576, 1317, 774; HRMS (DART) m/z Calcd. for C$_{19}$H$_{21}$FeN$_2$O$_2$S$^+$ [M+H]$^+$: 397.0668, Found: 397.0679; Enantiomeric excess was determined by HPLC with an ADH column (90:10 n-hexane: isopropanol, 1.0 mL/min); S- enantiomer: t_r = 42.0 min; R-enantiomer: t_r = 56.8 min; Absolute configurations of product were determined by analogy.

Table S3. KIE Studies on Catalytic C–H Amination of Enantiopure Isotopomeric Azides via Co(II)-Based MRC [a,b,c]

Comments

free Re←→Si face rotation occurred during cyclization

High KIE allowed for highly enantioenriched radical intermmediate formation through HAA

Optimized bridged catalysts are highly enantioselective during HAA with minimum Re←→Si face rotation during cyclization

Entry	Azide	Catalyst	KIE[b]	Re:Si of IIa[c]	ee%[cal,d]	ee%[exp,e]	yield (%)[a]
1	(S)-1a_D	[Co(P9)] (achiral)	23.0	96:4	92 (R)	4 (R)	80
2[f]	(S)-1a_D	[Co(P4)]	2.0	67:33	34 (R)	-4 (S)	64
3	(S)-1a_D	[Co(P5)]	96.0	99:1	98 (R)	94 (R)	98
4	(R)-1a_D	[Co(P9)] (achiral)	23.0	4:96	-92 (S)	-4 (S)	85
5[f]	(R)-1a_D	[Co(P4)]	61.0	2:98	-96 (S)	-94 (S)	80
6	(R)-1a_D	[Co(P5)]	0.8	57:43	14 (R)	32 (R)	98

[a] Reactions were performed on a 0.10 mmol scale of sulfamoyl azide (R)-**1a_D** or (S)-**1a_D** using 2 mol % of [Co(Por)] in 1 mL of MTBE at 40 ºC; Isolated Yield; [b] Ratio of H:D determined by ¹H-NMR spectroscopy (see the following spectrum section for detail). [c] Calculated based on the ratio of H:D. [d] Calculated on the basis of stereoretentive RS. [e] Determined by chiral HPLC analysis, which offered no separation of (R)-**2a_H** from (R)-**2a_D** and (S)-**2a_H** from (S)-**2a_D**. [f] 5 mol % [Co(**P4**)].

(For NMR spectra and HPLC, see the following section for the details). (Note: there was an overlap of N-H proton and chiral benzylic proton for H- vs. D-derivative analysis. This issue was solved by simply adding one drop of D₂O to the CDCl₃ solution for NH proton exchange. The complete

disappearance of NH proton allowed accurate integration (500 MHz machine with cryogenically cooled probe) of benzylic proton and calculation of the ratios of **H**:**D**. Please see the following spectrum section. for the detailed spectra.)

Key Information of Asymmetric Induction Process Obtained from the Results in Table S3

1. For bridged catalysts [Co(**P4**)] and [Co(**P5**)], **HAA** is highly enantioselective, **radical substitution** is stereoretentive due to either the stereochemistry retention of facial chirality through cavity-like ligand environments or the cavity-favored rapid radical substitution before the rotation/racemization occurs, or the combined effects.

2. For the achiral open catalyst [Co(**P9**)], high values of intramolecular KIE (23.0) were consistently obtained from both isotopic enantiomers (*S*)-**1a$_D$** or (*R*)-**1a$_D$**, generating the highly enantio-enriched radical intermediates (*Re*)-**IIa$_D$** or (*Si*)-**IIa$_D$**. However, the facile rotation of α-C–C bond of radical (*Re*)-**IIa$_D$** or (*Si*)-**IIa$_D$** inside such flexible cavity led to the erosion of enantiopurity in radical intermediates (*Re*)-**IIa$_D$** or (*Si*)-**IIa$_D$**. Therefore, the cyclization product **2a$_H$** was obtained with poor enantiomeric ratios.

Synthesis and Characterization of Deuterated Azides (*S*)-1a$_D$, (*R*)-1a$_D$ and Products 2a$_H$

(*R*)-*N*-Benzyl-2-phenylethan-2-d-1-amine was prepared in 65% yield (550 mg) through **General Procedure D1** from (*R*)-2-phenylethan-2-d-1-ol which was prepared according to the reported procedure[10] from (*R*)-mandelic acid (commercially available, cas: 611-71-2). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.36 - 7.16 (m, 10 H), 3.81 (s, 2 H), 2.91 (d, *J* = 7.3 Hz, 2 H), 2.85 - 2.76 (m, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm 140.3, 140.0, 128.7, 128.4, 128.1, 126.9, 126.1, 53.9, 50.5, 36.0 (t, *J* = 18.8 Hz); HRMS (ESI) *m/z* Calcd. For C$_{15}$H$_{17}$DN$^+$ [M+H]$^+$: 213.1497, Found: 213.1503.
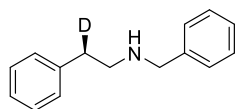
(*S*)-*N*-Benzyl-2-phenylethan-2-d-1-amine was prepared in 45% yield (350 mg) through **General Procedure D1** from (*S*)-2-phenylethan-2-d-1-ol which was prepared according to the reported procedure[10] from (*S*)-mandelic acid (commercially available, cas: 17199-29-0).
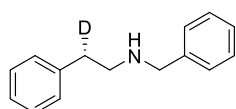
(*R*)-*N*-Benzyl-2-phenylethan-2-d-1-sulfamoyl azide was obtained in 67% yield (160 mg) as colorless oil
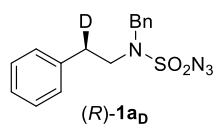
through **General Procedure E** from (*R*)-*N*-Benzyl-2-phenylethan-2-d-1-amine starting from 0.75 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), TLC R_f = 0.6 (Hexanes/EtOAc 8:1). ^{1}H NMR (600 MHz, CDCl$_3$) δ ppm 7.42 - 7.35 (m, 3 H), 7.35 - 7.31 (m, 2 H), 7.31 - 7.26 (m, 2 H), 7.25 - 7.18 (m, 1 H), 7.12 - 7.05 (m, 2 H), 4.42 (s, 2 H), 3.42 (d, *J* = 8.3 Hz, 2 H), 2.81 (t, *J* = 8.1 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 137.5, 134.5, 128.9, 128.7, 128.6, 126.8, 53.0, 49.9, 34.0 (t, *J* = 19.0 Hz). Enantiopurity > 99% based on the method used and the product ^{1}H NMR (t=35; T1=66; ø=45° C) on a 600 MHz machine. Non-deuterated **1a** is < 1%, falling into the ^{1}H NMR integration error. **Therefore, it is a reasonable approximation for the above KIE studies by assuming that the isotopomeric sulfamoyl azides are the only component.**

(*S*)-*N*-Benzyl-2-phenylethan-2-d-1-sulfamoyl azide was obtained in 79% yield (250 mg) as colorless oil
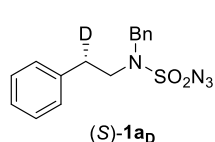
through **General Procedure E** from (*S*)-*N*-Benzyl-2-phenylethan-2-d-1-amine starting from 1.0 mmol scale, purified by silica gel column chromatography (eluent: Hexanes/EtOAc 40:1), TLC R_f = 0.6 (Hexanes/EtOAc 8:1).

2-Benzyl-4-phenyl-1,2,5-thiadiazolidine 1,1-dioxide-4d (2a$_H$) was obtained through **General Procedure F**. Purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), white solid, TLC R_f = 0.35 (Hexanes/EtOAc 4:1); For **[Co(3,5-Di^{t}Bu-Hu(C$_8$)Phyrin)]** (**[Co(P5)]**), 2 mmol % of catalyst was used and the reaction was run at 40 ºC for 48 h (98% yield with both (*R*)-**1a$_D$** and (*S*)-**1a$_D$** as starting azides); for **[Co(2,6-DiMeOHu-(C$_6$)Phyrin)]** (**[Co(P4)]**), 5 mmol % of catalyst was used and the reaction was run at 40 ˚C for 48h (80% yield for (*R*)-**1a$_D$**; 64% yield for (*S*)-**1a$_D$**); for **[Co(3,5-Di^{t}Bu-IbuPhyrin)]** (**[Co(P9)]**), 2 mmol % of catalyst was used and the reaction was run at 40 ˚C for 48h (85% yield for (*R*)-**1a$_D$**; 80% yield for (*S*)-**1a$_D$**). ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 7.48 - 7.28 (m, 10 H), 4.87 (br. s., 1 H), 4.38, 4.01 (AB q, *J* = 15.0 Hz, each 1 H), 3.56 (d, *J* = 9.8 Hz, 1 H), 3.13 (d, *J* = 9.3 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm 138.3, 134.8, 129.0, 128.8, 128.7, 128.2, 126.4, 55.8 - 55.1 (m); 55.0, 50.5; HRMS (ESI) *m/z* Calcd. For C$_{15}$H$_{16}$DN$_2$O$_2$S$^+$ [M+H]$^+$: 290.1068, Found: 290.1055; Enantiomeric excess was determined by HPLC with an ADH column (90:10 *n*-hexane: isopropanol, 0.8 mL/min); *R*- enantiomer: t_r = 34.4 min; *S*- enantiomer: t_r = 24.7 min.
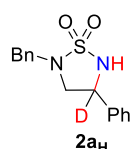
(R)-**2a_H**(+): er (R:S): 97:3   (S)-**2a_H** (-): er (R:S): 3:97

$[\alpha]_D^{25}$ = +86.0° (c 1.1, CHCl$_3$) $[\alpha]_D^{25}$ = -85.4° (c 1.2, CHCl$_3$)
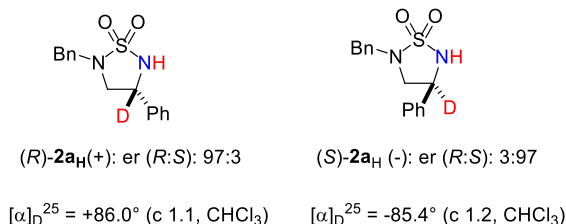
Experimental Evidence for Radical Mechanism

1. TEMPO Trapping Experiment
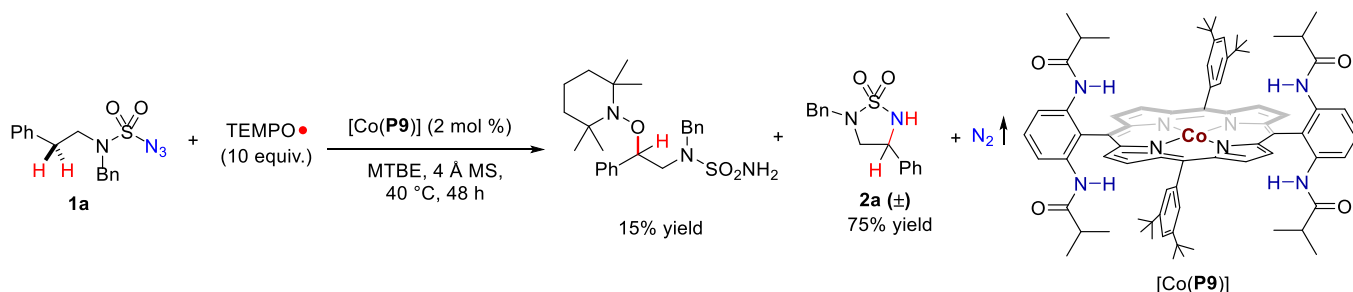
An oven dried Schlenk tube was charged with catalyst [Co(**P9**)] (0.002 mmol) and 4Å molecular sieves

(50 mg). This reaction vessel was evacuated and backfilled with nitrogen several times. The Teflon screw cap was replaced with a rubber septum and azide **1a** (0.1 mmol) was added followed methyl *tert*-butyl ether (0.5 mL), TEMPO (1 mmol) and the remaining methyl *tert*-butyl ether (0.5 mL). The Schlenk tube was then purged with nitrogen for

2 minutes and the rubber septum was replaced with a Teflon screw cap. The Schlenk tube was then placed in an oil bath at 40 ºC while stirring. After 48h, the reaction mixture was purified by silica gel column chromatography (eluent: Hexanes/EtOAc 4:1), to give the TEMPO-trapped product in 15% yield as yellow solid (TLC R$_f$ = 0.15 (Hexanes/EtOAc 1:1)) together with amination product **2a(±)** in 75% yield. **For TEMPO-trapped product**: ¹H NMR (500 MHz, CDCl$_3$) δ ppm 7.45 - 7.38 (m, 4 H), 7.37 - 7.28 (m, 6 H), 4.86 (dd, *J* = 5.1, 10.5 Hz, 1 H), 4.17 - 4.07 (m, 2 H), 3.82 - 3.75 (m, 1 H), 3.73 - 3.64 (m, 1 H), 3.45 (s, 2 H), 1.50 - 1.38 (m, 6 H), 1.17 - 0.93 (m, 12 H); ¹³C NMR (100 MHz, CDCl$_3$) δ ppm 141.9, 135.6, 128.7, 128.5, 128.3, 128.1, 128.0, 84.4, 77.2, 51.5, 50.6, 40.4, 29.7, 17.1; IR (neat, cm⁻¹): 2925, 1554, 1495, 1454, 1333, 1361, 1155, 1132, 1008, 940, 756, 733, 700, 547; HRMS (ESI) *m/z* Calcd. For C$_{24}$H$_{36}$N$_3$O$_3$S$^+$ [M+H]$^+$: 446.2472, Found: 446.2459.

2. EPR Experiment
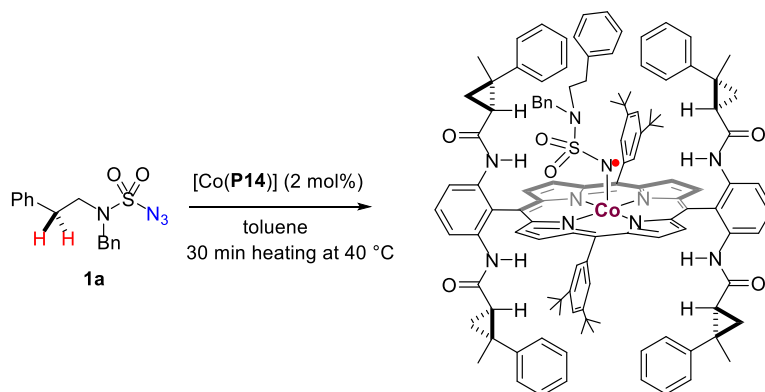
An oven-dried EPR tube was cooled down under nitrogen atmosphere and charged with catalyst [Co(**P14**)] (0.002 mmol mmol). This EPR tube was then capped with a red rubber septum, which was fastened with parafilm. The tube was evacuated and backfilled with nitrogen three times. Then the sulfamoyl azide **1a** (0.1 mmol in 0.4 mL of anhydrous toluene) was added into this tube through a gas-tight syringe. The cap of the EPR tube was further sealed with vacuum grease. The reaction mixture was shaken well followed by the reaction at 40 ºC for 30 minutes. Then the sample was ready for EPR experiment at room temperature.

X-band EPR spectra were recorded on a Bruker EMX-Plus spectrometer (Bruker BioSpin). Simulations of the EPR spectra were performed by using the EPR simulation program SpinFit in Xenon. Experimental X-band EPR spectra of α-Co(III)-Aminyl Radical **I** in toluene were recorded at room temperature. (Freq = 9.42731 GHz; mod. amp. = 1 G; microwave power = 63.25 mW) (**Figure S-6**).

Figure S6. Experimental and Simulated X-Band EPR Spectra for α-Co(III)-Aminyl Radical **I** in Toluene at RT

A second species (minor) was also observed in this spectrum based on 2nd Harmonic spectrum

From simulation: $g_{iso(major)}$: 2.00772;

From simulation: $g_{iso(minor)}$: 1.99725;
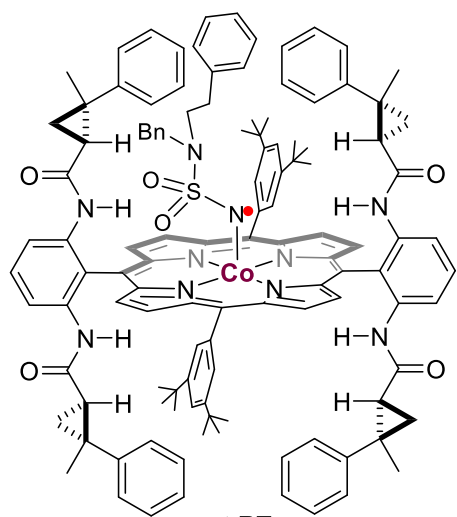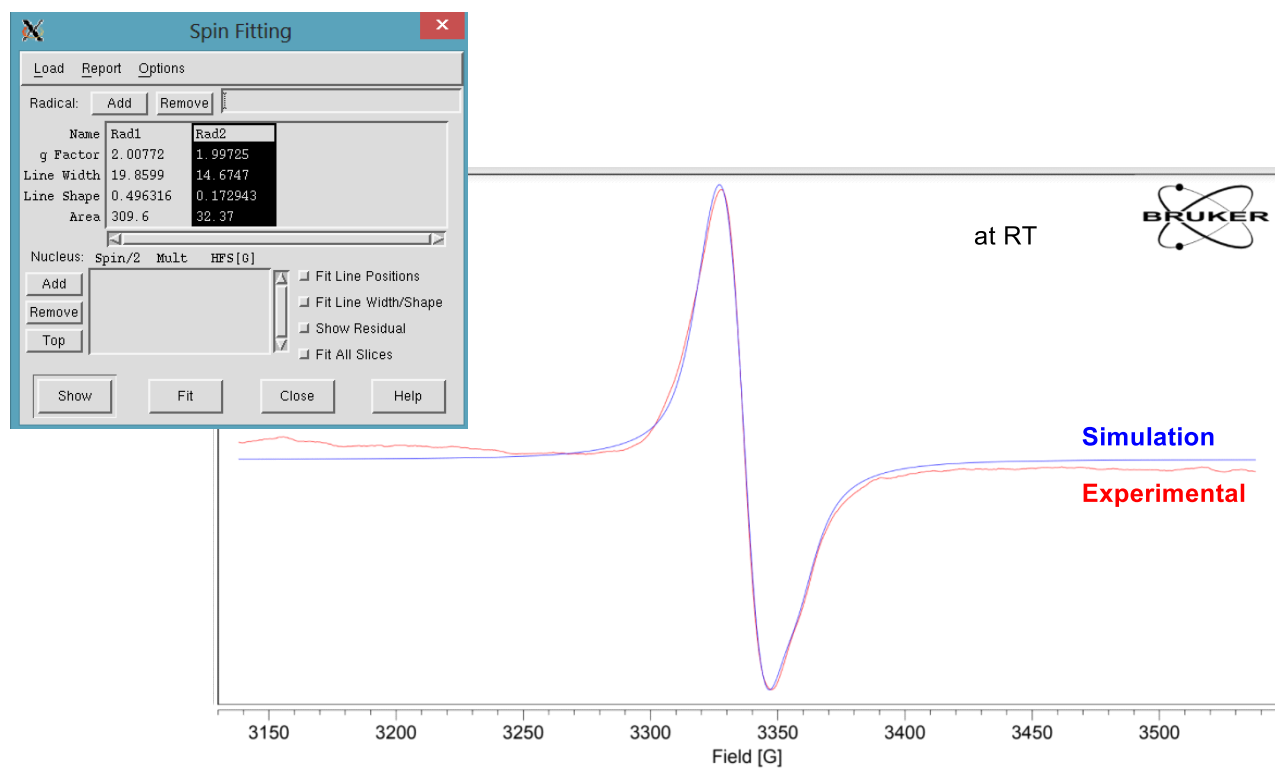
α-Co(III)-aminyl radical **I**

From Experimental: g_{iso}: 2.00753

3. HRMS Experiment

α-Co(III)-aminyl radical **I**

Chemical Formula: $C_{119}H_{120}CoN_{10}O_6S^+$
Exact Mass: 1875.8440
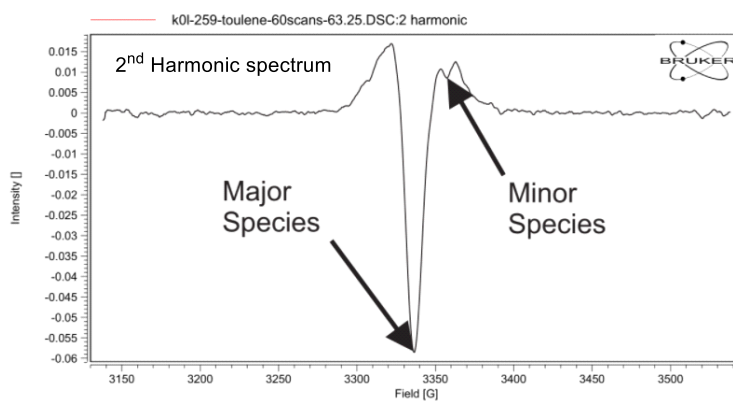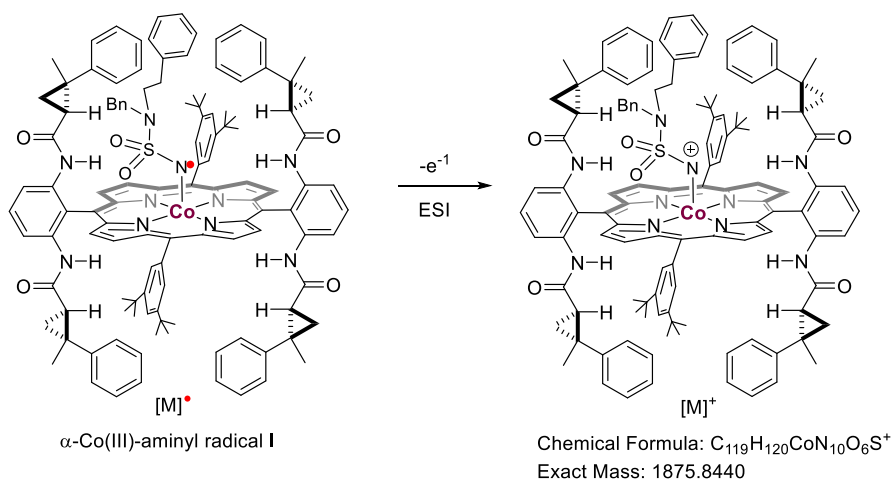
Through a gas-tight syringe, the same EPR solution was transferred to a sealed HRMS sample vial, which was pre-evacuated and backfilled with nitrogen. The high-resolution mass spectra (CH_3CN as solvent for LC-HRMS) (ESI) in the absence of any additives such as formic acids that commonly act as electron carriers for ionization allowed for the detection of the molecular ion signals corresponding to the α-Co(III)-aminyl radical **I** ($[M]^+$ m/z = 1875.8391 (observed)), by the loss of one electron (**Figure S-7**).

sCLIPS Report - F:\Agilent6220_1054.d\AcqData\MSProfile.bin

Self-Calibration Mass Range (Da)
        Start: -0.55
        End: 0.55

RT Windows
    Scan 35 at 0.576

sCLIPS Parameters
    Accurate Mass: 1875.8391
    Charge: 1
    Mass Tolerance (mDa):   250.00
    Electron State: Both

    Double Bond Equivalent Range
        Minimum: -1.00
        Maximum: 150.00

    Profile Mass Range (Da)
        Start: -2.00
        End: 5.50

    Empirical Rules: Enabled
      Empirical Elemental Limits: Wiley
      H/C Ratio: Extended
      Heteroatom Ratios: Extended

[M]⁺
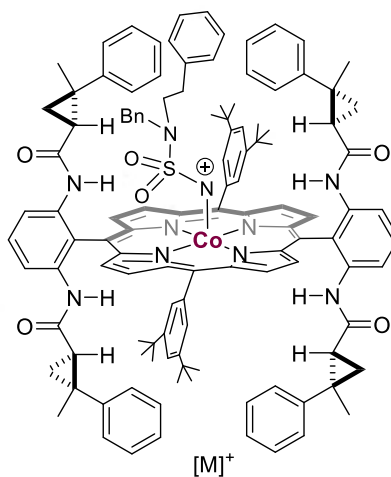
Element	Minimum	Maximum
C	115	120
H	115	125
N	9	10
O	5	6
Co	1	1
S	1	1

sCLIPS Search Results

	Formula	Mono Isotope	Mass Error (mDa)	Mass Error (PPM)	Spectral Accuracy	RMSE	DBE
1	C120H124N10O5CoS	1,875.8803	-41.2395	-21.9845	93.8647	1,326	64.0
2	C120H122N9O6CoS	1,875.8565	-17.4300	-9.2918	93.7782	1,345	64.5
3	C119H120N10O6CoS	1,875.8440	-4.8539	-2.5876	93.4843	1,409	65.0

Figure S7. Observed and Simulated ESI-MS Spectra with Isotope Distribution (Corresponding to [α-Co(III)-aminyl radical $\mathbf{I} - e^{-1}$]$^+$ ([M]$^+$ m/z = 1875.8391)
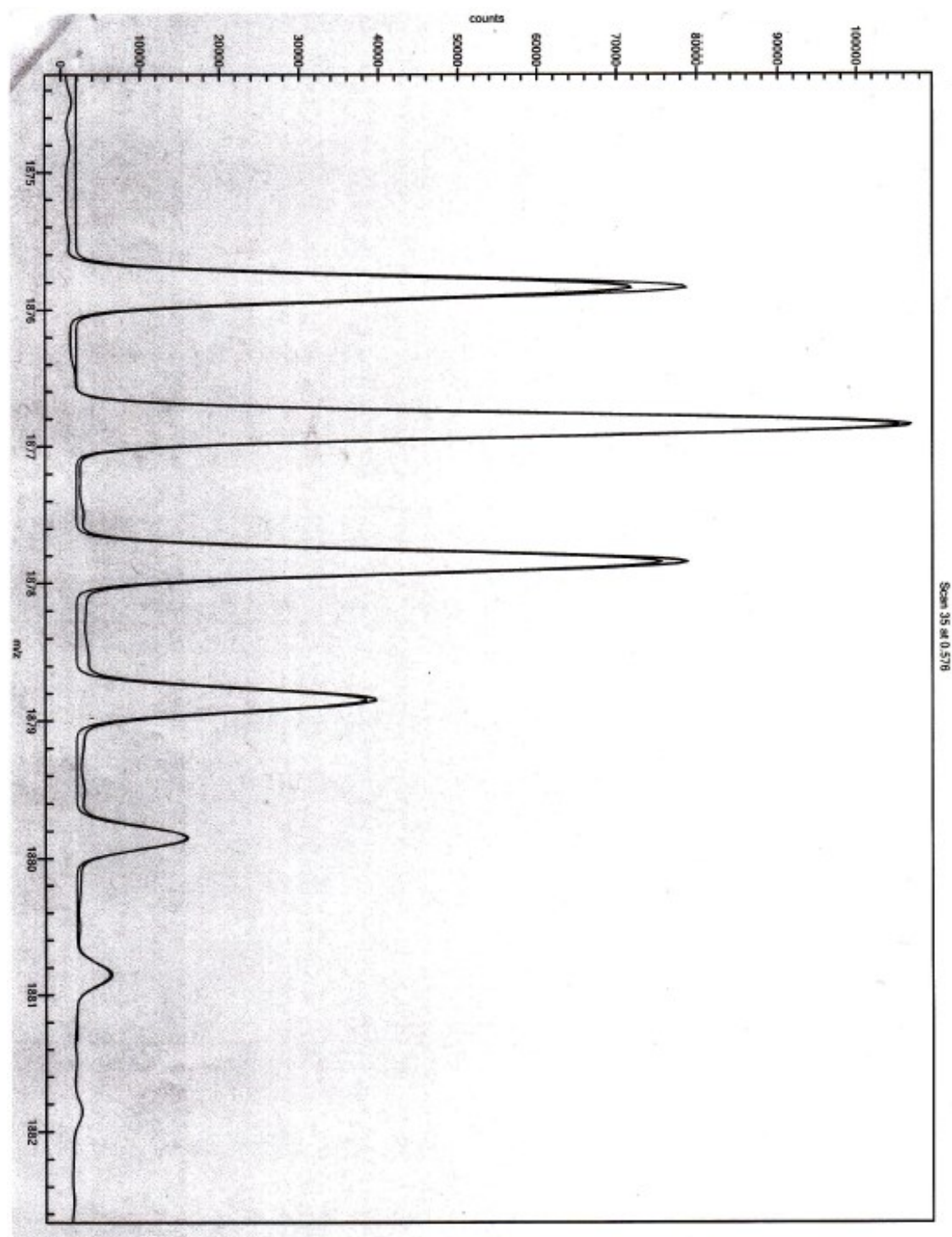
Assigned as the neutral α-Co(III)-aminyl radical $\mathbf{I}$ with catalyst [Co(**P14**)], by the loss of one electron, from electrospray ionization mass spectrometry (ESI-MS).

X-ray Crystallography and Data Interpretation

The X-ray diffraction data for (*R*)-**2a (LK-3-247C-0m)**, (*S*)-**2a (lk-3-186c)**, (*R*)-**2c (LK-3-68B)**, (*S*)-**2c (LK-3-68C)**, (*S, R*)-**2m (LK-3-237B-0m)**, (*S, S*)-**2s (LK_4_13c)**, **P4 (lk_3_95_2nd)** and **P5 (LK-3-74A)** were measured on a Bruker D8 Venture PHOTON 100 CMOS system equipped with a Cu K$_\alpha$ INCOATEC Imus micro-focus source (λ = 1.54178 Å). X-ray diffraction data for (*R*)-**2b (LK-3-29A)**, (*S*)-**2b (LK-3-36-3rd)** **and** (*R*)-**2k (LK-3-198B)**, were collected using Bruker-AXS SMART-APEXII CCD diffractometer) using Kα radiation (λ = 1.54178 Å). Indexing was performed using *APEX2* [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01 [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX2 [1]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-2013 [7] (full-matrix least-squares on F^2) contained in APEX2 [1,7], WinGX v1.70.01 [4,5,6,7] and OLEX2 [7,8]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of –CH, -CH$_2$, -CH$_3$ groups were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH,-CH$_2$) and Uiso(H) = 1.5Ueq(-CH$_3$). **For CIF-check files, please see the following sections together with the compound NMR spectra and HPLC.**

(*R*)-**2a**
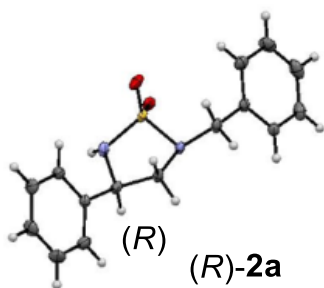
(*R*)-**2a (LK_3_247C_0m):** Hydrogen atom of –NH group has been found from difference Fourier map and was freely refined. The remaining hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). Crystal data and refinement conditions are shown in **Table 1**.

Table 1 Crystal data and structure refinement for (*R*)-2a (LK-3-247C-0m).	
Identification code	(*R*)-**2a** (LK-3-247C-0m)
Empirical formula	C$_{15}$H$_{16}$N$_2$O$_2$S
Formula weight	288.36
Temperature/K	99.97
Crystal system	monoclinic

Space group	P2$_1$/c
a/Å	14.6858(3)
b/Å	5.83800(10)
c/Å	17.4091(4)
α/°	90
β/°	110.6117(5)
γ/°	90
Volume/Å^3	1397.04(5)
Z	4
ρ$_{calc}$g/cm^3	1.371
μ/mm^{-1}	2.085
F(000)	608.0
Crystal size/mm^3	0.32 × 0.05 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.43 to 137.95
Index ranges	-17 ≤ h ≤ 17, -6 ≤ k ≤ 7, -21 ≤ l ≤ 21
Reflections collected	16268
Independent reflections	2561 [R$_{int}$ = 0.0554, R$_{sigma}$ = 0.0356]
Data/restraints/parameters	2561/0/185
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R$_1$ = 0.0376, wR$_2$ = 0.0961
Final R indexes [all data]	R$_1$ = 0.0401, wR$_2$ = 0.0982
Largest diff. peak/hole / e Å^{-3}	0.68/-0.41

(*S*)-**2a**

(*S*)-**2a (lk-3-186c):** The crystal was a twin with two components related by (1 0 0 0 -1 0 -0.88 0 -1) symmetry operation. Two crystal lattices were identified in RLAT [1] and the data have been integrated with SAINT [2] using two different orientation matrices. Subsequently the TWINABS was used to perform scaling and absorption corrections and HKLF5 type reflection file has been used for structure refinement (BASF = 0.179(3)). Hydrogen atom of –NH group has been found from difference Fourier map and was freely refined. The remaining hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). Crystal data and refinement conditions are shown in **Table 2**.

Table 2 Crystal data and structure refinement for (*S*)-2a (lk-3-186c-0m).

Identification code	(*S*)-**2a** (lk-3-186c-0m)
Empirical formula	$C_{15}H_{16}N_2O_2S$
Formula weight	288.36
Temperature/K	100.01
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.4266(2)
b/Å	6.1137(2)
c/Å	13.0269(3)
α/°	90
β/°	108.7061(9)
γ/°	90
Volume/Å^3	711.10(3)
Z	2
ρ_{calc}g/cm^3	1.347
μ/mm^{-1}	2.048
F(000)	304.0
Crystal size/mm^3	0.12 × 0.04 × 0.01
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.164 to 138.148
Index ranges	-11 ≤ h ≤ 11, -7 ≤ k ≤ 7, -15 ≤ l ≤ 15
Reflections collected	2435
Independent reflections	2435 [R_{int} = ?, R_{sigma} = 0.0520]
Data/restraints/parameters	2435/1/186
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0471, wR_2 = 0.1261
Final R indexes [all data]	R_1 = 0.0476, wR_2 = 0.1266
Largest diff. peak/hole / e Å^{-3}	0.54/-0.43
Flack parameter	0.087(16)

(*R*)-**2b**
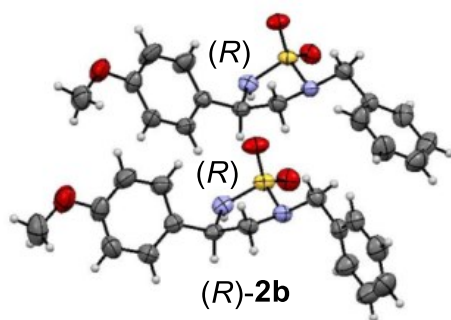
(*R*)-**2b (LK_3_29A):** Hydrogen atom of -NH group have been found from difference Fourier map and were refined with Uiso(H) = 1.2Ueq(-NH). Crystal data and refinement conditions are shown in **Table 3**.

Table 3 Crystal data and structure refinement for (*R*)-2b (LK-3-29A-0m).	
Identification code	(*R*)-**2b** (LK-3-29A-0m)
Empirical formula	$C_{32}H_{36}N_4O_6S_2$
Formula weight	636.77
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.25630(10)
b/Å	11.77610(10)
c/Å	13.42920(10)
α/°	90
β/°	101.6400(10)
γ/°	90
Volume/Å^3	1588.61(2)
Z	2
ρ_{calc}mg/mm^3	1.331
m/mm^{-1}	1.933
F(000)	672.0
Crystal size/mm^3	0.32 × 0.1 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection	6.72 to 141.798°
Index ranges	-12 ≤ h ≤ 11, -14 ≤ k ≤ 13, -15 ≤ l ≤ 15
Reflections collected	19445
Independent reflections	5527 [R_{int} = 0.0309, R_{sigma} = 0.0326]
Data/restraints/parameters	5527/1/405
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0324, wR_2 = 0.0826
Final R indexes [all data]	R_1 = 0.0350, wR_2 = 0.0842
Largest diff. peak/hole / e Å^{-3}	0.13/-0.23
Flack parameter	0.041(8)

(S)-2b
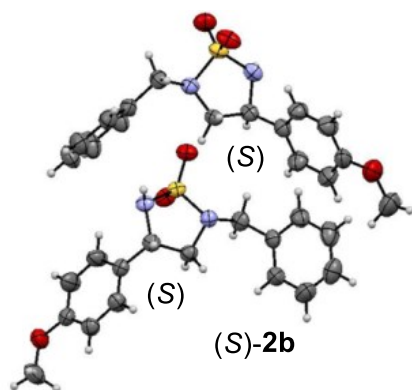
(S)-2b (LK-3-36-3rd): Hydrogen atom of -NH group have been found from difference Fourier map and were freely refined. Crystal data and refinement conditions are shown in **Table 4**.

Table 4 Crystal data and structure refinement for (S)-2b (LK-3-36-3rd_0m).	
Identification code	(S)-2b (LK-3-36-3rd-0m)
Empirical formula	$C_{16}H_{18}N_2O_3S$
Formula weight	318.38
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.2613(3)
b/Å	11.7758(3)
c/Å	13.4262(4)
α/°	90
β/°	101.6390(10)
γ/°	90
Volume/Å^3	1589.00(8)
Z	4
ρ_{calc}mg/mm^3	1.331
m/mm^{-1}	1.933
F(000)	672.0
Crystal size/mm^3	0.24 × 0.14 × 0.03
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection	6.722 to 137.448°
Index ranges	-12 ≤ h ≤ 11, -14 ≤ k ≤ 13, -16 ≤ l ≤ 15
Reflections collected	14363
Independent reflections	5466 [R_{int} = 0.0266, R_{sigma} = 0.0352]
Data/restraints/parameters	5466/1/407
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0289, wR_2 = 0.0760
Final R indexes [all data]	R_1 = 0.0309, wR_2 = 0.0773

Largest diff. peak/hole / e Å⁻³	0.12/-0.26
Flack parameter	0.039(6)

(R) (R)-2c
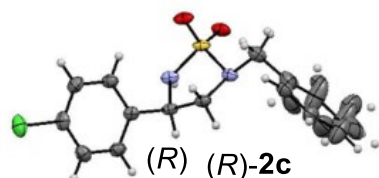
(R)-2c (LK-3-68B): Hydrogen atom of -NH group have been found from difference Fourier map and was freely refined. Disordered phenyl group has been refined with RIGU restraint. Crystal data and refinement conditions are shown in **Table 5**.

Table 5 Crystal data and structure refinement for (R)-2c (LK-3-68B_0m).

Identification code	(R)-2c (LK-3-68B-0m)
Empirical formula	$C_{15}H_{15}ClN_2O_2S$
Formula weight	322.80
Temperature/K	99.98
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	4.97110(10)
b/Å	11.8495(2)
c/Å	25.3307(5)
α/°	90
β/°	90
γ/°	90
Volume/Å³	1492.11(5)
Z	4
ρ_{calc}mg/mm³	1.437
m/mm⁻¹	3.625
F(000)	672.0
Crystal size/mm³	0.15 × 0.04 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection	6.98 to 137.846°
Index ranges	-5 ≤ h ≤ 5, -14 ≤ k ≤ 14, -30 ≤ l ≤ 30
Reflections collected	19052
Independent reflections	2720 [R_{int} = 0.0843, R_{sigma} = 0.0448]
Data/restraints/parameters	2720/90/225
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0430, wR_2 = 0.1010
Final R indexes [all data]	R_1 = 0.0509, wR_2 = 0.1053
Largest diff. peak/hole / e Å⁻³	0.34/-0.24

Flack parameter	0.076(13)

(S)

(S)-**2c**
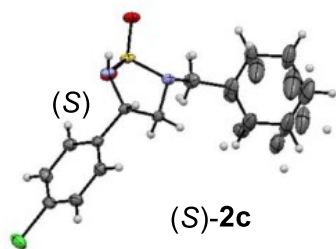
(*S*)-**2c (LK-3-68c-2nd):** Hydrogen atom of -NH group have been found from difference Fourier map and was freely refined. Disordered phenyl group has been refined with RIGU, SIMU restraints. Crystal data and refinement conditions are shown in **Table 6**.

Table 6 Crystal data and structure refinement for (*S*)-2c (LK-3-68c-2nd-0m).	
Identification code	(*S*)-**2c** (LK-3-68c-2nd-0m)
Empirical formula	$C_{15}H_{15}ClN_2O_2S$
Formula weight	322.80
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	4.96390(10)
b/Å	11.8448(3)
c/Å	25.3491(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1490.44(6)
Z	4
ρ_{calc}mg/mm^3	1.439
m/mm^{-1}	3.629
F(000)	672.0
Crystal size/mm^3	0.24 × 0.12 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection	6.974 to 137.818°
Index ranges	-5 ≤ h ≤ 5, -14 ≤ k ≤ 14, -30 ≤ l ≤ 30
Reflections collected	19015
Independent reflections	2715 [R_{int} = 0.0568, R_{sigma} = 0.0341]
Data/restraints/parameters	2715/78/225
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0348, wR_2 = 0.0855
Final R indexes [all data]	R_1 = 0.0388, wR_2 = 0.0878

Largest diff. peak/hole / e Å^{-3}	0.32/-0.23
Flack parameter	0.066(9)

(R)

(R)-**2k**
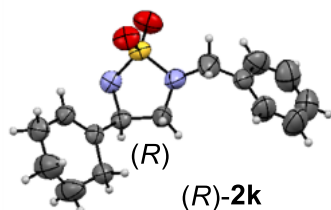
(*R*)-**2k (LK-3-198b-0m):** Non-aromatic ring is conformationally disordered over two positions with 3:1 occupancy ratio and has been refined using SADI restraint. Hydrogen atom of –NH group has been found from difference Fourier map and was freely refined. The remaining hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). Crystal data and refinement conditions are shown in **Table 7**.

Table 7 Crystal data and structure refinement for (*R*)-2k (LK-3-198b-0m).

Identification code	(*R*)-**2k** (LK-3-198b-0m)
Empirical formula	$C_{15}H_{20}N_2O_2S$
Formula weight	292.39
Temperature/K	296.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.06640(10)
b/Å	11.9606(3)
c/Å	24.9189(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1510.02(6)
Z	4
ρ_{calc}g/cm^3	1.286
μ/mm^{-1}	1.930
F(000)	624.0
Crystal size/mm^3	0.18 × 0.18 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.094 to 142.914
Index ranges	-5 ≤ h ≤ 6, -13 ≤ k ≤ 14, -29 ≤ l ≤ 29
Reflections collected	18700

Independent reflections	2870 [R_{int} = 0.0466, R_{sigma} = 0.0285]
Data/restraints/parameters	2870/1/204
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0449, wR_2 = 0.1150
Final R indexes [all data]	R_1 = 0.0507, wR_2 = 0.1195
Largest diff. peak/hole / e Å^{-3}	0.53/-0.30
Flack parameter	0.044(13)
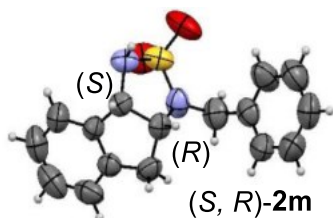
(S, R)-**2m**

(*S, R*)-**2m (LK-3-237B-0m):** Hydrogen atom of –NH group has been found from difference Fourier map and was freely refined. Crystals did not diffract past approximately 0.9Å resolution. The remaining hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). Crystal data and refinement conditions are shown in **Table 8**.

Table 8 Crystal data and structure refinement for (*S, R*)-2m (LK-3-237B_0m).	
Identification code	(*S, R*)-**2m** (LK-3-237B-0m)
Empirical formula	$C_{16}H_{16}N_2O_2S$
Formula weight	300.37
Temperature/K	298(2)
Crystal system	orthorhombic
Space group	$P22_12_1$
a/Å	5.0613(4)
b/Å	13.3347(10)
c/Å	22.6731(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1530.2(2)
Z	4
ρ_{calc}g/cm^3	1.304
μ/mm^{-1}	1.927
F(000)	632.0
Crystal size/mm^3	0.21 × 0.05 × 0.01
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.692 to 117.802

Index ranges	$-5 \leq h \leq 5$, $-14 \leq k \leq 14$, $-25 \leq l \leq 25$
Reflections collected	10778
Independent reflections	2206 [R_{int} = 0.0793, R_{sigma} = 0.0543]
Data/restraints/parameters	2206/0/194
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0515, wR_2 = 0.1183
Final R indexes [all data]	R_1 = 0.0671, wR_2 = 0.1273
Largest diff. peak/hole / e Å^{-3}	0.15/-0.23
Flack parameter	0.14(2)
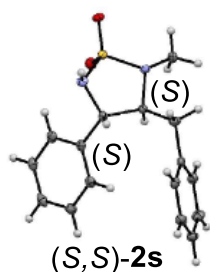
(*S*,*S*)-**2s**

(*S, S*)-**2s** (**LK_4_13c**): Hydrogen atoms of –CH, –CH$_2$ and –CH$_3$ groups were placed in geometrically calculated positions and were included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2(1.5)Ueq(-CH,-CH$_2$,(-CH$_3$)). Hydrogen atoms of –NH groups have been found from difference Fourier map and were freely refined. Crystal data and refinement conditions are shown in **Table 9**.

Table 9 Crystal data and structure refinement for (*S, S*)-2s (LK_4_13c_0m).	
Identification code	(*S, S*)-**2s** (LK_4_13c)
Empirical formula	$C_{16}H_{18}N_2O_2S$
Formula weight	302.38
Temperature/K	100.01
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.6293(2)
b/Å	7.4200(2)
c/Å	34.2745(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1431.63(8)
Z	4
ρ_{calc}g/cm^3	1.403
μ/mm^{-1}	2.060

F(000)	640.0
Crystal size/mm^3	0.08 × 0.04 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	10.324 to 137.944
Index ranges	-6 ≤ h ≤ 6, -8 ≤ k ≤ 8, -41 ≤ l ≤ 41
Reflections collected	17701
Independent reflections	2635 [R_{int} = 0.0886, R_{sigma} = 0.0505]
Data/restraints/parameters	2635/0/195
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0374, wR_2 = 0.0813
Final R indexes [all data]	R_1 = 0.0472, wR_2 = 0.0854
Largest diff. peak/hole / e Å^{-3}	0.22/-0.38
Flack parameter	0.055(15)
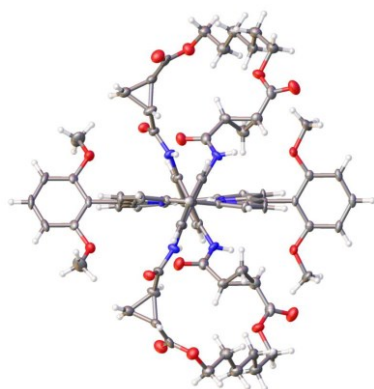
X-ray of P4

P4 (lk_3_95_2nd): There are total two porphyrin molecules in an asymmetric unit (1 full and 2 halves located on 2- fold and 2-fold screw rotation axes). In all porphyrin molecules the NHCOO(C)$_6$NHCOO chains are disordered with 0.85:0.15 occupancy ratio. There also exists disorder of C$_6$H$_3$(OCH$_3$)2 groups. The major part of disorder has been refined anisotropically, whereas minor part was refined isotropically and using restraints to keep the geometry within reasonable range. Targeted values of bond and angular 1-3 distances were taken from CSD search of similar fragments. Disordered chloroform molecules in the structure were refined using restraints as well. It has been noticed, that there exists pseudotranslation in the structure, along [100] or **a** direction. Processing the data with the smaller unit cell however, leads to 50:50 disorder of C$_6$H$_3$(OCH$_3$)$_2$ group and much worse R-factor. It was concluded therefore, that the pseudo translation is caused by the disorder of side chains and structure was analyzed using larger unit cell. All hydrogen atoms were placed in geometrically calculated positions and included in the refinement

process using riding model with isotropic thermal parameters: Uiso(H) = 1.2(1.5)Ueq(-CH,-CH$_2$,-NH(-CH$_3$)). Crystal data and refinement conditions are shown in **Table 10**.

Table 10 Crystal data and structure refinement for P4 (lk_3_95_2nd).	
Identification code	**P4** (lk_3_95_2nd)
Empirical formula	C$_{331.89}$H$_{325.58}$Cl$_{34.75}$N$_{32}$O$_{65}$
Moiety formula	4(C$_{80}$H$_{78}$N$_8$O$_{16}$)·11.6(CHCl$_3$)·H$_2$O
Formula weight	7034.32
Temperature/K	100
Crystal system	orthorhombic
Space group	P2$_1$2$_1$2
a/Å	37.7211(9)
b/Å	20.6072(5)
c/Å	21.3384(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	16586.9(7)
Z	2
ρ$_{calc}$g/cm^3	1.408
μ/mm^{-1}	3.282
F(000)	7303.0
Crystal size/mm^3	0.11 × 0.04 × 0.03
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.758 to 138.154
Index ranges	-44 ≤ h ≤ 45, -23 ≤ k ≤ 22, -25 ≤ l ≤ 25
Reflections collected	115894
Independent reflections	30115 [R$_{int}$ = 0.0824, R$_{sigma}$ = 0.0685]
Data/restraints/parameters	30115/336/2497
Goodness-of-fit on F^2	1.010
Final R indexes [I>=2σ (I)]	R$_1$ = 0.0624, wR$_2$ = 0.1527
Final R indexes [all data]	R$_1$ = 0.0844, wR$_2$ = 0.1675
Largest diff. peak/hole / e Å^{-3}	0.87/-0.39
Flack parameter	0.034(5)
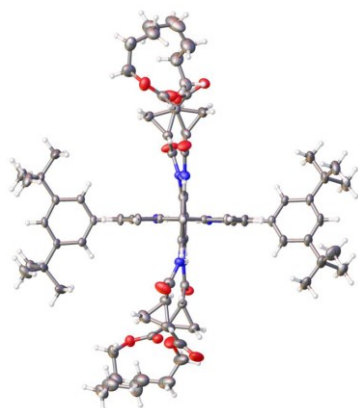
X-ray of P5

P5 (LK_3_74A): The disordered chloroform molecules have been refined using restraints (DFIX, DANG, SIMU) and occupancy factors have been refined as free variables. Crystal data and refinement conditions are shown in **Table 11**.

Table 11 Crystal data and structure refinement for P5 (LK-3-74-0m).	
Identification code	**P5** (LK-3-74-0m)
Empirical formula	$C_{99.18}H_{113.18}Cl_{9.53}N_8O_{12}$
Moiety Formula	$C_{96}H_{110}N_8O_{12}$, 3.17 $(CHCl_3)$,
Formula weight	1947.03
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	14.8069(3)
b/Å	23.9156(5)
c/Å	15.4586(3)
$\alpha/°$	90
$\beta/°$	108.2750(10)
$\gamma/°$	90
Volume/Å^3	5198.03(18)
Z	2
ρ_{calc}mg/mm^3	1.244
m/mm^{-1}	2.827
F(000)	2044.0
Crystal size/mm^3	0.09 × 0.09 × 0.01
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection	6.02 to 133.212°
Index ranges	-17 ≤ h ≤ 17, -28 ≤ k ≤ 27, -18 ≤ l ≤ 18
Reflections collected	45025
Independent reflections	16669 [R_{int} = 0.0495, R_{sigma} = 0.0563]
Data/restraints/parameters	16669/38/1242

Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	$R_1 = 0.0593$, $wR_2 = 0.1475$
Final R indexes [all data]	$R_1 = 0.0720$, $wR_2 = 0.1571$
Largest diff. peak/hole / e Å^{-3}	1.01/-0.35
Flack parameter	0.045(6)

[1] Bruker (2013). *APEX2* (Version 2013.6-2). Bruker AXS Inc., Madison, Wisconsin, USA.

[2] Bruker (2013). SAINT-V8.32A. Data Reduction Software.

[3] Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption*

Correction. University of Gottingen, Germany.

[4] Farrugia L.J. Appl. Cryst. (1999). 32, 837±838

[5] Sheldrick, G.M. (1997) SHELXL-97. Program for the Refinement of Crystal

[6] Sheldrick, G.M. (1990) Acta Cryst. A46, 467-473

[7] Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.

[8] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program (2009). J. Appl. Cryst., 42, 339-341.

General Procedure for CD Spectra Study

A stock solution of [Co(II)(D_2-Por*)] in CH$_3$CN (6.7×10^{-5} M) was prepared. This solution was used for CD study at 25 ˚C. The nearly identical CD spectra between [Co(**P3**)] and [Co(**P5**)] or between [Co(**P4**)] and [Co(**P6**)] likely suggested the similar type of chiral conformations taken by these catalysts.

Figure S-8. CD Spectra of (a) [Co(**P3**)], (b) [Co(**P5**)] at 25 ˚C.
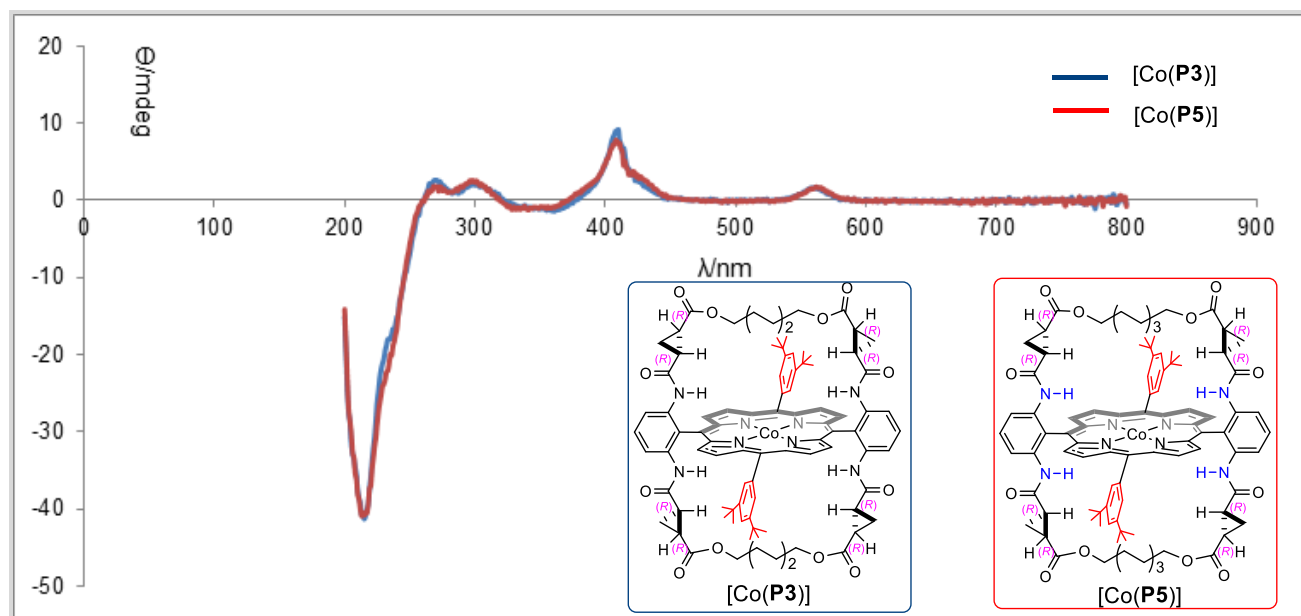
Figure S-9. CD Spectra of (a) [Co(**P4**)], (b) [Co(**P6**)] at 25 ˚C.

3,5-Di-tBu-Tao(^{t}Bu)Phyrin

^{1}H NMR, 500MHz, CDCl$_3$

−2.43

0.47
0.50

1.01
1.54
1.55
1.78
1.79
1.80
1.81
1.82

6.66

7.27

7.81
7.83
7.85

8.16

8.54

8.79
8.80

9.01
9.02

6.66

7.27

7.81
7.83
7.85
8.16
8.54
8.79
8.80
9.01
9.02

−2.43

0.47
0.50

−1.01

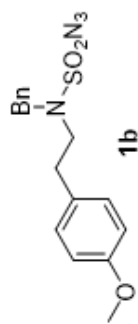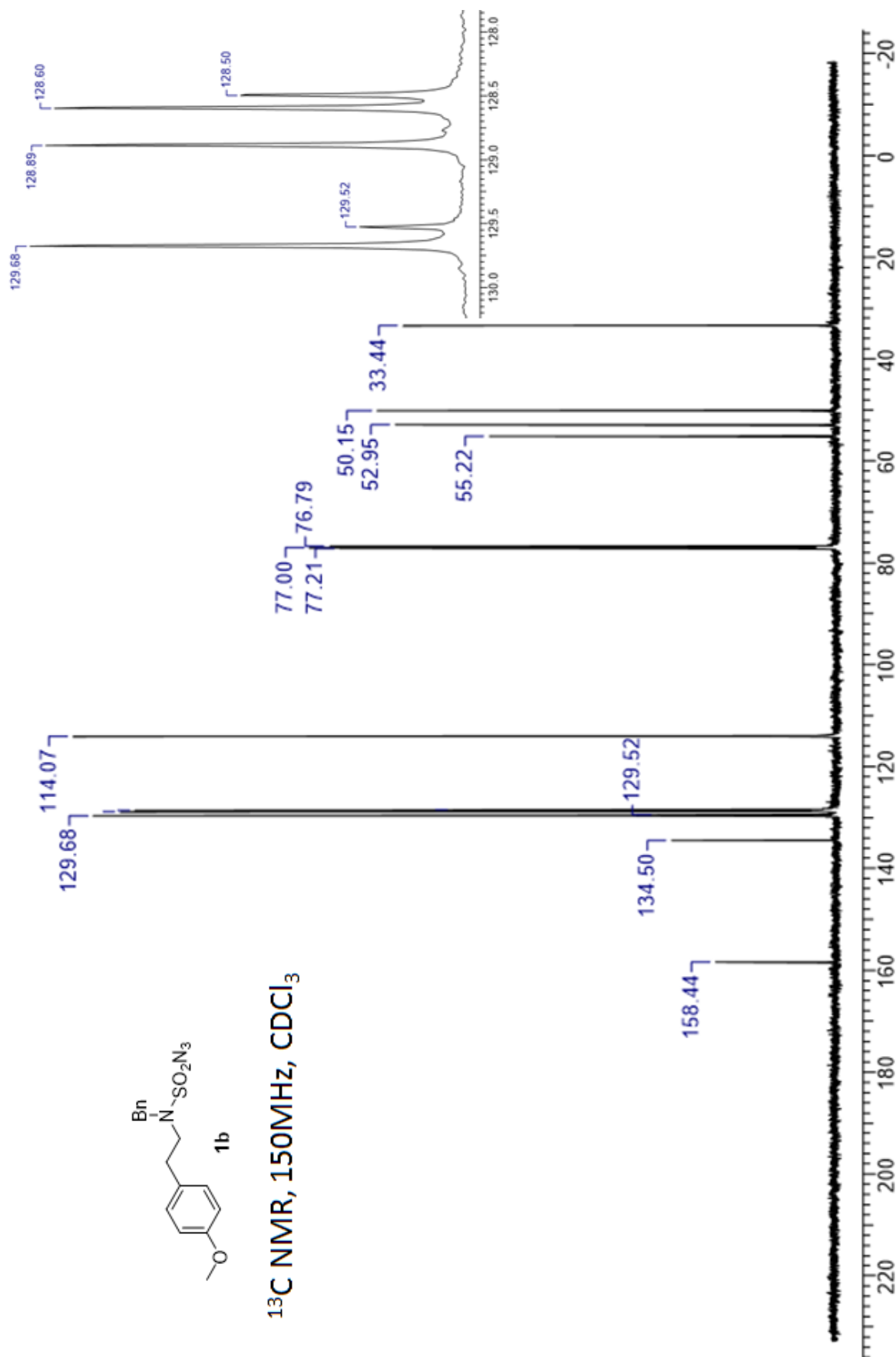1.54
1.55
1.78
1.79
1.80
1.81
1.82

4.00

4.24

4.28

3.97

3.93

4.19

8.17

37.59

38.30

4.31

f1 (ppm)

S89

^{13}C NMR, 100MHz, CDCl$_3$

3,5-Di^{t}Bu-Tao(^{t}Bu)Phyrin

S90

^1H NMR, 500MHz, $CDCl_3$

2,6-DiMeO-Tao(^{t}Bu)Phyrin

^{13}C NMR, 100MHz, CDCl$_3$

2,6-DiMeO-Tao(^{t}Bu)Phyrin

170.46
168.88
160.34
139.00
130.88
130.16
121.85
118.58
117.77
114.12
106.42
104.26
80.56
77.35
77.23
77.03
76.71
55.89
27.69
24.02
22.80
14.91

P1

(3,5-Di^tBu-Hu(C₄)Phyrin)

^{1}H NMR, 500MHz, CDCl$_3$

^{13}C NMR, 125MHz, CDCl$_3$

(3,5-Di^{t}Bu-Hu(C$_4$)Phyrin)

P1

^{1}H NMR, 500MHz, CDCl$_3$

(2,6-DiMeO-Hu(C$_4$)Phyrin)

P2

13C NMR, 125MHz, CDCl₃

P2
(2,6-DiMeO-Hu(C₄)Phyrin)

S96

P3

(3,5-Di^{t}Bu-Hu(C$_6$)Phyrin)

^{1}H NMR, 400MHz, CDCl$_3$

f1 (ppm)

^{13}C NMR, 100MHz, CDCl$_3$

P3

(3,5-Di^{t}Bu-Hu(C$_6$)Phyrin)

171.06
168.30
149.44
139.80
138.74
130.48
130.17
123.29
122.42
121.93
118.60
107.73
77.39
77.08
76.76
64.26
35.14
31.76
27.33
24.19
23.88
22.09
15.07

^{1}H NMR, 500MHz, CDCl$_3$

P4

(2,6-DiMeO-Hu(C$_6$)Phyrin)
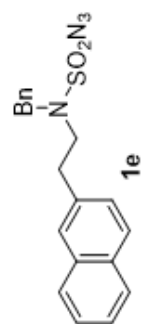
^{13}C NMR, 100MHz, CDCl$_3$

P4

(2,6-DiMeO-Hu(C$_6$)Phyrin)

14.70
23.81
22.05
24.38
27.42
55.87
64.10
76.67
76.99
77.31
104.29
106.80
114.19
118.33
118.94
122.57
130.27
131.06
138.62
160.24
168.28
170.75

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: I

Bond precision: C-C = 0.0097 A   Wavelength=1.54178

Cell:	a=37.7211(9)	b=20.6072(5)	c=21.3384(5)
	alpha=90	beta=90	gamma=90

Temperature: 100 K

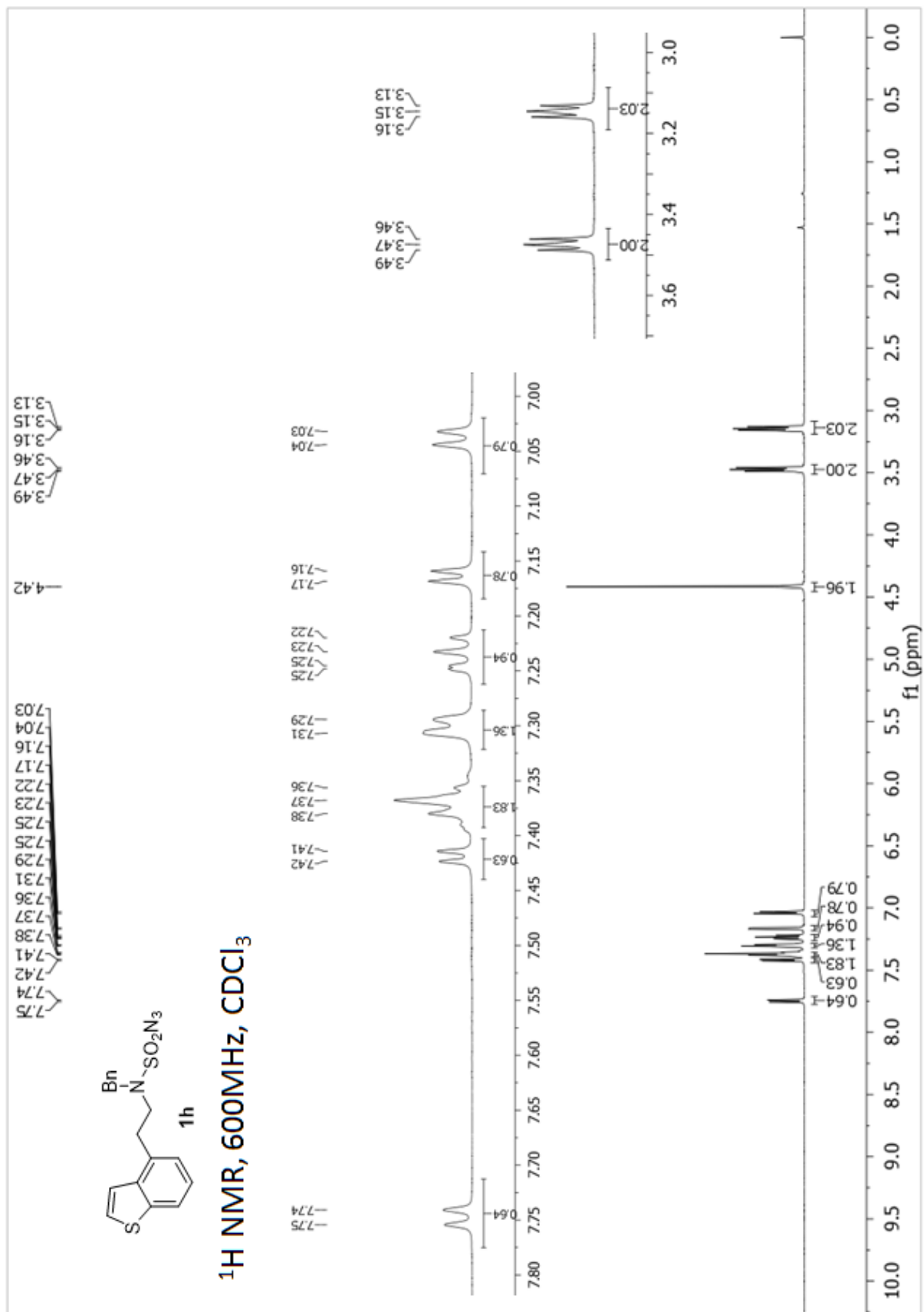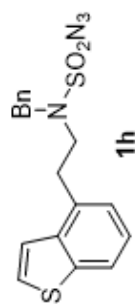|	Calculated	Reported
Volume	16586.9(7)	16586.9(7)
Space group	P 21 21 2	P 21 21 2
Hall group	P 2 2ab	P 2 2ab
Moiety formula	2(C80 H78 N8 O16),	11.59(C H C13), 4(C80 H78
	2(C79.70 H77.55 N8	N8 O16), H2O
	O15.85), 10.186(C H C13),	
Sum formula	C331.89 H323.59 C134.76	C331.89 H325.58 C134.75
	N32 O65	N32 O65
Mr	7032.63	7034.32
Dx,g cm-3	1.408	1.408
Z	2	2
Mu (mm-1)	3.283	3.282
F000	7299.6	7303.0
F000'	7344.57	
h,k,lmax	45,24,25	45,23,25
Nref	30884[16586]	30115
Tmin,Tmax	0.854,0.906	0.635,0.753
Tmin'	0.697	

Correction method= MULTI-SCAN

Data completeness= 1.82/0.98   Theta(max)= 69.077

R(reflections)= 0.0624(23665)   wR2(reflections)= 0.1675(30115)

S = 1.010   Npar= 2497
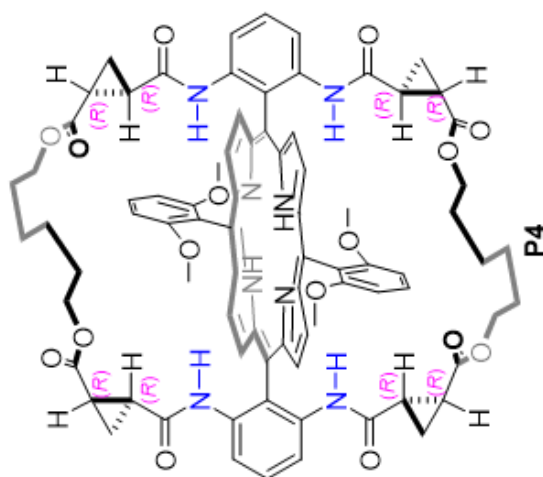
P4

The following ALERTS were generated. Each ALERT has the format

    test-name ALERT alert-type alert-level.

Click on the hyperlinks for more details of the test.

● **Alert level B**

PLAT201_ALERT_2_B	Isotropic non-H Atoms in Main Residue(s)	....		1	Report
PLAT220_ALERT_2_B	Large Non-Solvent	C	Ueq(max)/Ueq(min) Range	7.3	Ratio
PLAT220_ALERT_2_B	Large Non-Solvent	C	Ueq(max)/Ueq(min) Range	6.7	Ratio

● **Alert level C**

PLAT041_ALERT_1_C	Calc. and Reported SumFormula Strings Differ			Please	Check
PLAT068_ALERT_1_C	Reported F000 Differs from Calcd (or Missing).			Please	Check
PLAT089_ALERT_3_C	Poor Data / Parameter Ratio (Zmax < 18)	....		6.64	Note
PLAT094_ALERT_2_C	Ratio of Maximum / Minimum Residual Density	....		2.25	Report
PLAT213_ALERT_2_C	Atom O14	has ADP max/min Ratio	.....		3.4	prolat
PLAT220_ALERT_2_C	Large Non-Solvent	O	Ueq(max)/Ueq(min) Range	4.4	Ratio
PLAT220_ALERT_2_C	Large Non-Solvent	C	Ueq(max)/Ueq(min) Range	5.2	Ratio
PLAT220_ALERT_2_C	Large Non-Solvent	O	Ueq(max)/Ueq(min) Range	3.4	Ratio
PLAT220_ALERT_2_C	Large Non-Solvent	O	Ueq(max)/Ueq(min) Range	5.1	Ratio
PLAT222_ALERT_3_C	Large Non-Solvent	H	Uiso(max)/Uiso(min)	7.0	Ratio
PLAT222_ALERT_3_C	Large Non-Solvent	H	Uiso(max)/Uiso(min)	6.4	Ratio
PLAT222_ALERT_3_C	Large Non-Solvent	H	Uiso(max)/Uiso(min)	5.8	Ratio
PLAT234_ALERT_4_C	Large Hirshfeld Difference C154 -- C162			0.18	Ang.
PLAT234_ALERT_4_C	Large Hirshfeld Difference C90 -- C114			0.16	Ang.
PLAT242_ALERT_2_C	Low	Ueq as Compared to Neighbors for	.....		O240	Check
PLAT242_ALERT_2_C	Low	Ueq as Compared to Neighbors for	.....		C98	Check
PLAT242_ALERT_2_C	Low	Ueq as Compared to Neighbors for	.....		C106	Check
PLAT309_ALERT_2_C	Single Bonded Oxygen (C-O > 1.3 Ang)	.....		O252	Check
PLAT340_ALERT_3_C	Low Bond Precision on C-C Bonds	....		0.0097	Ang.
PLAT411_ALERT_2_C	Short Inter H...H Contact H128 .. H183			2.02	Ang.
PLAT420_ALERT_2_C	D-H Without Acceptor N9 .. H9			Please	Check
PLAT420_ALERT_2_C	D-H Without Acceptor N11 .. >N11			Please	Check
PLAT420_ALERT_2_C	D-H Without Acceptor N12 .. H12			Please	Check
PLAT420_ALERT_2_C	D-H Without Acceptor >N13 .. >N13			Please	Check
PLAT420_ALERT_2_C	D-H Without Acceptor N14 .. H14			Please	Check
PLAT420_ALERT_2_C	D-H Without Acceptor N16 .. H16			Please	Check
PLAT790_ALERT_4_C	Centre of Gravity not Within Unit Cell: Resd. #			1	Note
	C80 H78 N8 O16				

● **Alert level G**

FORMU01_ALERT_1_G There is a discrepancy between the atom counts in the
    _chemical_formula_sum and _chemical_formula_moiety. This is
    usually due to the moiety formula being in the wrong format.
    Atom count from _chemical_formula_sum: C331.8899 H325.58 C134.75 N
    Atom count from _chemical_formula_moiety:C331.59 H325.5899 C134.77 N
FORMU02_ALERT_2_G There is a discrepancy between the atom counts in the
    _chemical_formula_sum and the formula from the _atom_site* data.
    Atom count from _chemical_formula_sum:C331.8899 H325.58 C134.75 N32
    Atom count from the _atom_site data: C331.8856 H323.5854 C134.75799
CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.
CELLZ01_ALERT_1_G WARNING: H atoms missing from atom site list. Is this intentional?
    From the CIF: _cell_formula_units_Z   2
    From the CIF: _chemical_formula_sum   C331.89 H325.58 C134.75 N32 O65
    TEST: Compare cell contents of formula and atom_site data

atom	Z*formula	cif sites	diff
C	663.78	663.77	0.01
H	651.16	647.17	3.99

P4

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|---|---|---|---|---|---|
C1		69.50	69.52	-0.02	
N		64.00	64.00	0.00	
O		130.00	130.00	0.00	

PLAT002_ALERT_2_C Number of Distance or Angle Restraints on AtSite ... 99 Note
PLAT003_ALERT_2_C Number of Uiso or Uij Restrained non-H Atoms ... 56 Report
PLAT005_ALERT_5_C No _iucr_refine_instructions_details in the CIP Please Do !
PLAT007_ALERT_5_C Number of Unrefined Donor-H Atoms ... 18 Report
PLAT033_ALERT_4_C Flack x Value Deviates > 2*sigma from Zero ... 0.034 Note
PLAT042_ALERT_1_C Calc. and Reported MoietyFormula Strings Differ Please Check
PLAT083_ALERT_4_C SHELXL Second Parameter in WGHT Unusually Large. 12.37 Why ?
PLAT301_ALERT_3_C Main Residue Disorder .... Percentage = 26 Note
PLAT302_ALERT_4_C Anion/Solvent Disorder .... Percentage = 100 Note
PLAT311_ALERT_2_C Isolated Disordered Oxygen Atom (No H's ?) ... O1 Check
PLAT432_ALERT_2_C Short Inter X...Y Contact C16 .. C224 .. 2.61 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact C11A .. C173 .. 1.32 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact C11C .. C170 .. 3.11 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact C112 .. C173 .. 1.70 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact C113 .. C154 .. 3.20 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact C114 .. C173 .. 1.63 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact C115 .. C173 .. 1.78 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact C115 .. C26 .. 3.15 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact C120 .. C165 .. 3.16 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact C126 .. C173 .. 1.75 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact C130 .. C173 .. 2.28 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact C133 .. C145 .. 2.73 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact C134 .. C173 .. 1.55 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact O1 .. C173 .. 2.97 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact O150 .. C191 .. 2.98 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact O256 .. C137 .. 2.62 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact O256 .. C99 .. 2.99 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact O256 .. C157 .. 3.00 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact C25 .. C185 .. 3.13 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact C66 .. C185 .. 3.16 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact C87 .. C185 .. 2.66 Ang.
PLAT432_ALERT_2_C Short Inter X...Y Contact C173 .. C224 .. 1.08 Ang.
PLAT720_ALERT_4_C Number of Unusual/Non-Standard Labels .... 9 Note
PLAT779_ALERT_4_C Suspect or Irrelevant (Bond) Angle in CIF ..... # 1 Check
CL1A -CL6 -C173 1.555 1.555 1.555 44.80 Deg.
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Read. # 8 Note
CL1A -CL6 -C173
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Read. # 9 Note
C_H C13
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Read. # 14 Note
C_H C13
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Read. # 15 Note
C_C1
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Read. # 17 Note
C1
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Read. # 18 Note
C1
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Read. # 19 Note
C1
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Read. # 20 Note
C1
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Read. # 21 Note
O
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Read. # 23 Note
H
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Read. # 24 Note
H
PLAT791_ALERT_4_C The Model has Chirality at C82 (Chiral SPGR) R Verify
PLAT791_ALERT_4_C The Model has Chirality at C85 (Chiral SPGR) R Verify

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```
PLAT791_ALERT_4_G The Model has Chirality at C86   (Chiral SPGR)  R Verify
PLAT791_ALERT_4_G The Model has Chirality at C90   (Chiral SPGR)  R Verify
PLAT791_ALERT_4_G The Model has Chirality at C98   (Chiral SPGR)  R Verify
PLAT791_ALERT_4_G The Model has Chirality at C102  (Chiral SPGR)  R Verify
PLAT791_ALERT_4_G The Model has Chirality at C103  (Chiral SPGR)  R Verify
PLAT791_ALERT_4_G The Model has Chirality at C107  (Chiral SPGR)  R Verify
PLAT791_ALERT_4_G The Model has Chirality at C123  (Chiral SPGR)  R Verify
PLAT791_ALERT_4_G The Model has Chirality at C129  (Chiral SPGR)  R Verify
PLAT791_ALERT_4_G The Model has Chirality at C130  (Chiral SPGR)  R Verify
PLAT791_ALERT_4_G The Model has Chirality at C153  (Chiral SPGR)  R Verify
PLAT791_ALERT_4_G The Model has Chirality at C167  (Chiral SPGR)  R Verify
PLAT791_ALERT_4_G The Model has Chirality at C176  (Chiral SPGR)  R Verify
PLAT791_ALERT_4_G The Model has Chirality at C101  (Chiral SPGR)  R Verify
PLAT791_ALERT_4_G The Model has Chirality at C177  (Chiral SPGR)  R Verify
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ......   ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints ...............  336 Note
```

```
 0 ALERT level A = Most likely a serious problem - resolve or explain
 3 ALERT level B = A potentially serious problem, consider carefully
27 ALERT level C = Check. Ensure it is not caused by an omission or oversight
67 ALERT level G = General information/check it is not something unexpected

 6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
47 ALERT type 2 Indicator that the structure model may be wrong or deficient
 7 ALERT type 3 Indicator that the structure quality may be low
34 ALERT type 4 Improvement, methodology, query or suggestion
 3 ALERT type 5 Informative message, check
```

checkCIF publication errors

● Alert level A

PUBL002_ALERT_1_A The contact author's address is missing,
        _publ_contact_author_address.
PUBL005_ALERT_1_A _publ_contact_author_email, _publ_contact_author_fax and
        _publ_contact_author_phone are all missing.
        At least one of these should be present.
PUBL006_ALERT_1_A _publ_requested_journal is missing
        e.g. 'Acta Crystallographica Section C'
PUBL008_ALERT_1_A _publ_section_title is missing. Title of paper.
PUBL009_ALERT_1_A _publ_author_name is missing. List of author(s) name(s).
PUBL010_ALERT_1_A _publ_author_address is missing. Author(s) address(es).
PUBL012_ALERT_1_A _publ_section_abstract is missing.
        Abstract of paper in English.

 7 ALERT level A = Data missing that is essential or data in wrong format
 0 ALERT level G = General alerts. Data that may be required is missing
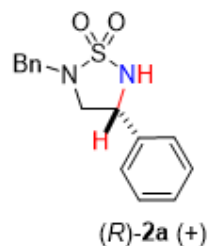
P4

Publication of your CIF

You should attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the nature of your study may justify the reported deviations from journal submission requirements and the more serious of these should be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. *checkCIF* was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

If level A alerts remain, which you believe to be justified deviations, and you intend to submit this CIF for publication in a journal, you should additionally insert an explanation in your CIF using the Validation Reply Form (VRF) below. This will allow your explanation to be considered as part of the review process.
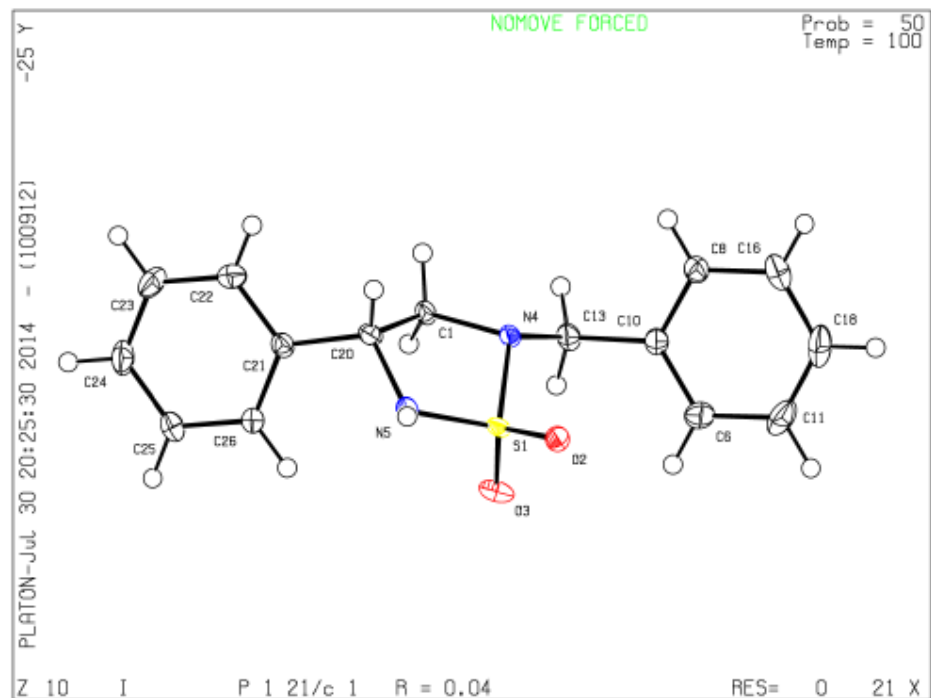
Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PUBL002_GLOBAL
;
PROBLEM: The contact author's address is missing.
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
```


P4

S105

PLATON version of 20/08/2014; check.def file version of 19/12/2014

^{1}H NMR, 500MHz, CDCl$_3$

(3,5-Di^{t}Bu-Hu(C$_8$)Phyrin)

P5

P5
(3,5-Di^{t}Bu-Hu(C$_8$)Phyrin)
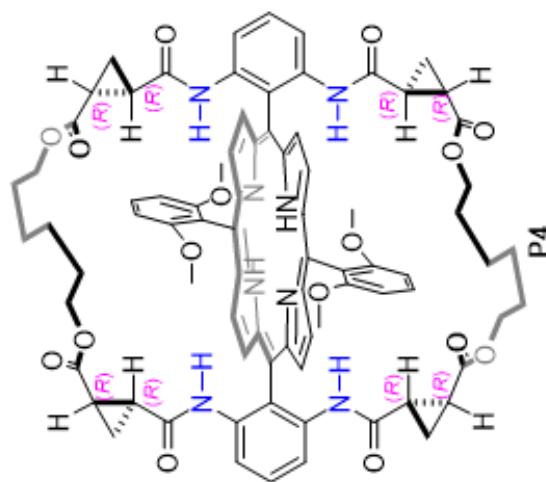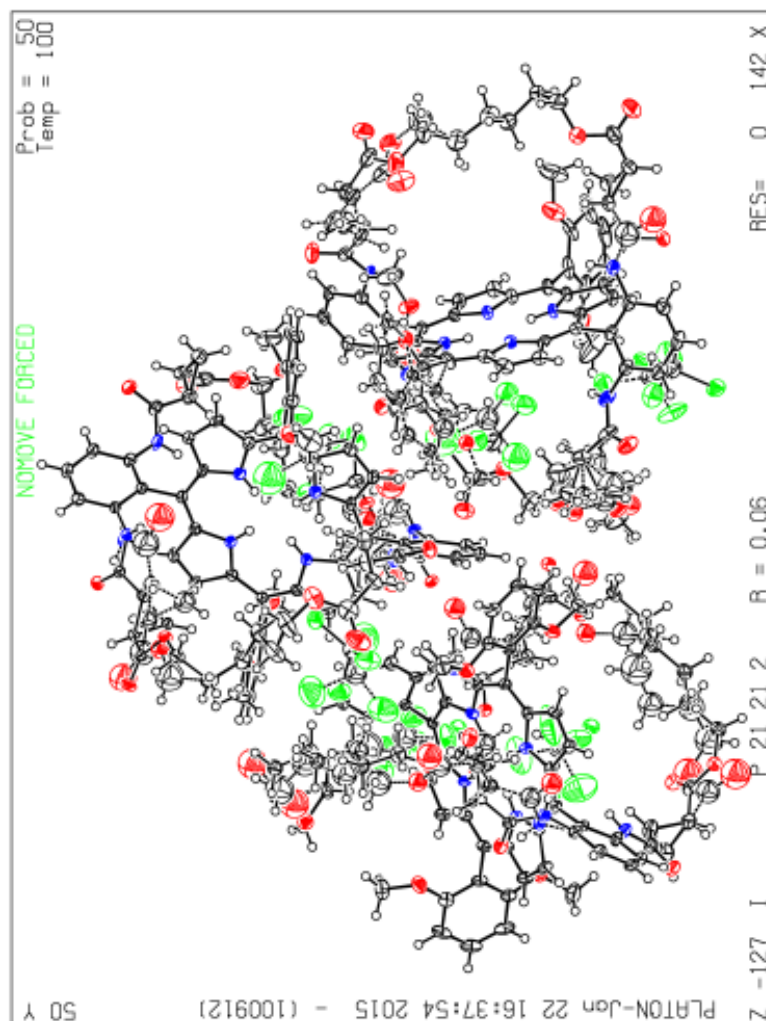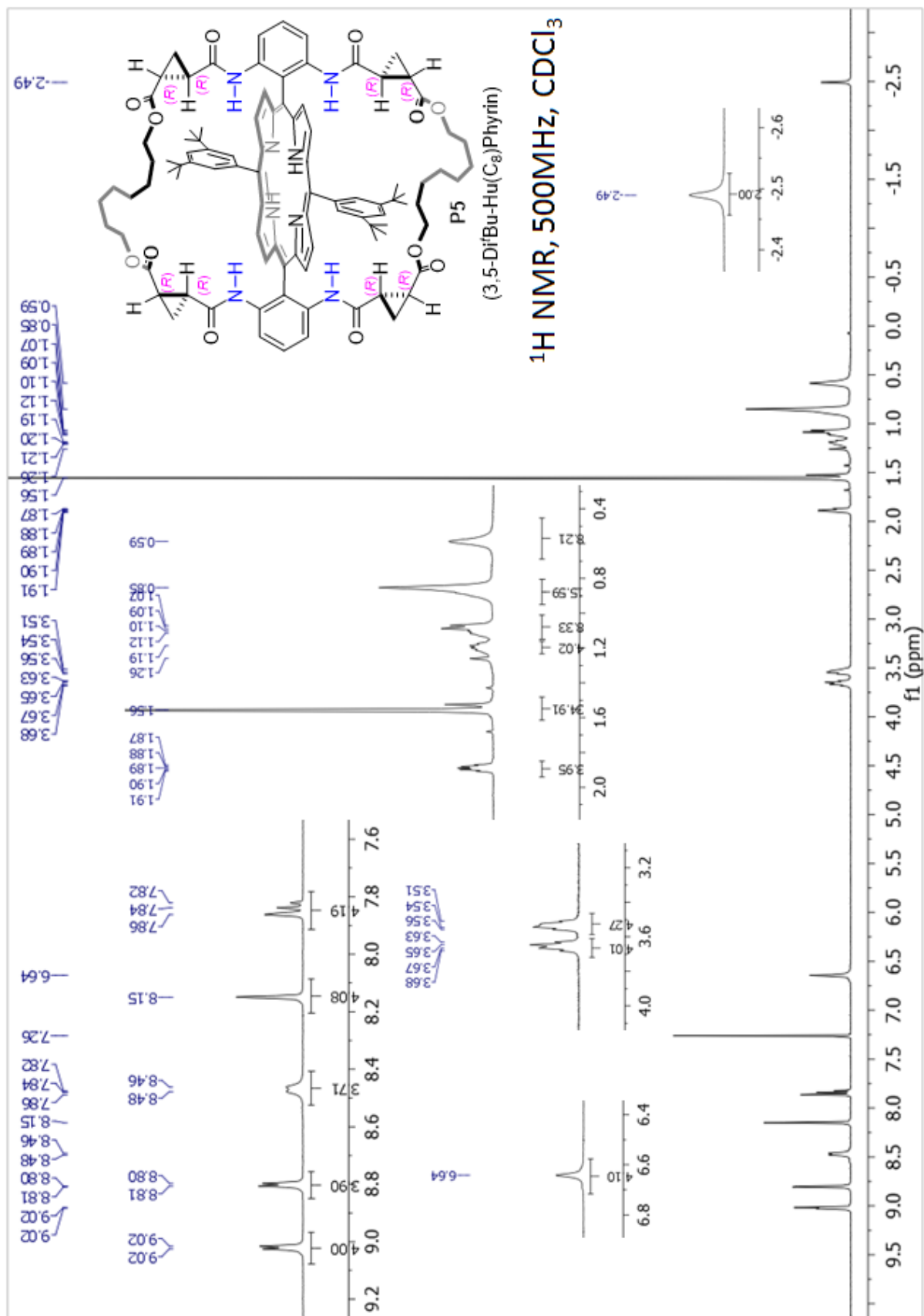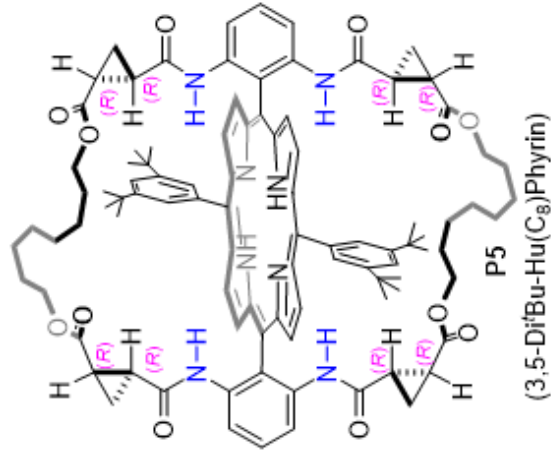
^{13}C NMR, 125MHz, CDCl$_3$

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE
FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED
CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: I

Bond precision:	C-C = 0.0089 A		Wavelength=1.54178
Cell:	a=14.8069(3)	b=23.9156(5)	c=15.4586(3)
	alpha=90	beta=108.275(1)	gamma=90
Temperature:	100 K		

	Calculated	Reported
Volume	5198.03(18)	5198.03(18)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C96 H110 N8 O12, 3.17(C H C13)	3.17(C H C13), C96 H110 N8 O12
Sum formula	C99.18 H113.18 C19.53 N8 O12	C99.18 H113.18 C19.53 N8 O12
Mr	1946.92	1947.03
Dx,g cm-3	1.244	1.244
Z	2	2
Mu (mm-1)	2.826	2.827
F000	2044.3	2044.0
F000'	2056.30	
h,k,lmax	17,28,18	17,28,18
Nref	18398[9443]	16669
Tmin,Tmax	0.814,0.972	0.592,0.753
Tmin'	0.738	

Correction method= MULTI-SCAN

Data completeness= 1.77/0.91   Theta (max) = 66.606

R(reflections) = 0.0593(14262)   wR2 (reflections) = 0.1571(16669)

S = 1.030   Npar= Npar =1242
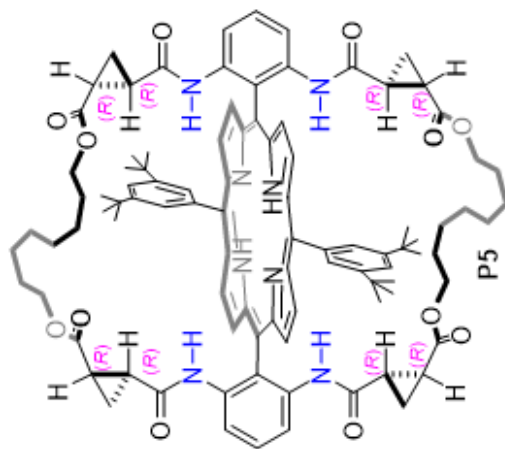
P5

The following ALERTS were generated. Each ALERT has the format
      test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

● Alert level C

PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)...   Please Check
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....   2.86 Why ?
PLAT202_ALERT_3_C Isotropic non-H Atoms in Anion/Solvent   1
PLAT220_ALERT_2_C Large Non-Solvent   C   Ueq(max)/Ueq(min) Range   5.4 Ratio
PLAT222_ALERT_3_C Large Non-Solvent   H   U1so(max)/U1so(min) .   5.2 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C91   --   C93 .   0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C91   --   C97 .   0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C92   --   C95 .   0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C97   --   C98 .   0.16 Ang.
PLAT241_ALERT_2_C High   Ueq as Compared to Neighbors for ....   C66 Check
PLAT241_ALERT_2_C High   Ueq as Compared to Neighbors for ....   C95 Check
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of   C65 Check
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ....   0.0089 Ang.
PLAT420_ALERT_2_C D-H Without Acceptor   N6   ..   H6 ..   Please Check
PLAT420_ALERT_2_C D-H Without Acceptor   N7   ..   H7 ..   Please Check
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of .   49 Ang3

● Alert level G

FORMU01_ALERT_1_G There is a discrepancy between the atom counts in the
      chemical_formula_sum and _chemical_formula_moiety. This is
      usually due to the moiety formula being in the wrong format.
      Atom count from _chemical_formula_sum: C99.18 H113.18 C19.53 N8 O1
      Atom count from _chemical_formula_moiety:C99.17 H113.17 C19.51 N8 O1
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite   22 Note
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ....   8 Why ?
PLAT033_ALERT_4_G Flack x Value Deviates > 2*sigma from Zero ....   0.045 Note
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ   Please Check
PLAT302_ALERT_4_G Anion/Solvent Disorder .... Percentage -   84 Note
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Read. #   3 Note
                  C H C13
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Read. #   4 Note
                  C H C13
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Read. #   5 Note
                  C H C13
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Read. #   6 Note
                  C H C13
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Read. #   7 Note
                  C H C13
PLAT791_ALERT_4_G The Model has Chirality at C45 ....   R Verify
PLAT791_ALERT_4_G The Model has Chirality at C47 ....   R Verify
PLAT791_ALERT_4_G The Model has Chirality at C48 ....   R Verify
PLAT791_ALERT_4_G The Model has Chirality at C51 ....   R Verify
PLAT791_ALERT_4_G The Model has Chirality at C52 ....   R Verify
PLAT791_ALERT_4_G The Model has Chirality at C53 ....   R Verify
PLAT791_ALERT_4_G The Model has Chirality at C58 ....   R Verify
PLAT791_ALERT_4_G The Model has Chirality at C77 ....   R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints ....   38 Note

  0 ALERT level A - Most likely a serious problem - resolve or explain
  0 ALERT level B - A potentially serious problem, consider carefully
 16 ALERT level C - Check. Ensure it is not caused by an omission or oversight
 20 ALERT level G - General information/check it is not something unexpected

P5

S110
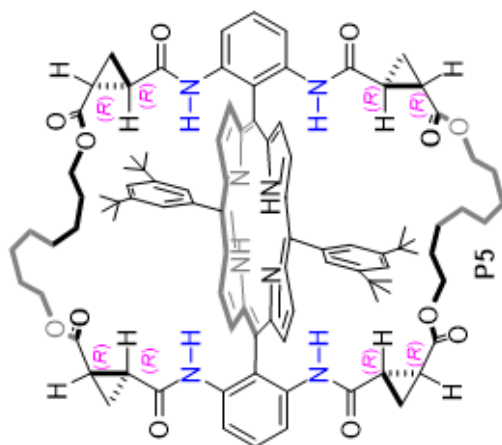
```
3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
8 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
20 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check
```

checkCIF publication errors

🔴 Alert level A

```
PUBL002_ALERT_1_A   The contact author's address is missing,
                    _publ_contact_author_address.
PUBL005_ALERT_1_A   _publ_contact_author_email, _publ_contact_author_fax and
                    _publ_contact_author_phone are all missing.
                    At least one of these should be present.
PUBL006_ALERT_1_A   _publ_requested_journal is missing
                    e.g. 'Acta Crystallographica Section C'
PUBL008_ALERT_1_A   _publ_section_title is missing. Title of paper.
PUBL009_ALERT_1_A   _publ_author_name is missing. List of author(s) name(s).
PUBL010_ALERT_1_A   _publ_author_address is missing. Author(s) address(es).
PUBL012_ALERT_1_A   _publ_section_abstract is missing.
                    Abstract of paper in English.
```

```
7 ALERT level A - Data missing that is essential or data in wrong format
0 ALERT level G - General alerts. Data that may be required is missing
```

Publication of your CIF

You should attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the nature of your study may justify the reported deviations from journal submission requirements and the more serious of these should be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. *checkCIF* was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

If level A alerts remain, which you believe to be justified deviations, and you intend to submit this CIF for publication in a journal, you should additionally insert an explanation in your CIF using the Validation Reply Form (VRF) below. This will allow your explanation to be considered as part of the review process.

```
# start Validation Reply Form
_vrf_PUBL002_GLOBAL
;
PROBLEM: The contact author's address is missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
```


P5

P5

;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;

_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;

_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;

_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;

_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;

_vrf_PUBL012_GLOBAL
;
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;

end Validation Reply Form

If you wish to submit your CIF for publication in Acta Crystallographica Section C or E, you should upload your CIF via the web. If your CIF is to form part of a submission to another IUCr journal, you will be asked, either during electronic submission or by the Co-editor handling your paper, to upload your CIF via our web site.

PLATON version of 05/02/2014; check.def file version of 05/02/2014

^{1}H NMR, 500MHz, CDCl$_3$

(2,6-DiMeO-Hu(C$_8$)Phyrin)

P6

S114

¹³C NMR, 125MHz, CDCl₃

P6
(2,6-DiMeO-Hu(C₈)Phyrin)

^{1}H NMR, 500MHz, CDCl$_3$

P7

(3,5-Di^{t}Bu-Hu(C$_{10}$)Phyrin)

¹³C NMR, 125MHz, CDCl₃

P7
(3,5-Di'Bu-Hu(C₁₀)Phyrin)

S117

^{1}H NMR, 500MHz, CDCl$_3$

P8

(2,6-DiMeO-Hu(C$_{10}$)Phyrin)

¹³C NMR, 125MHz, CDCl₃

^{13}C NMR, 125MHz, CDCl$_3$

P8
(2,6-DiMeO-Hu(C$_{10}$)Phyrin)

Peaks: 171.27, 168.54, 160.31, 138.72, 130.92, 130.20, 118.47, 114.08, 106.39, 104.23, 77.02, 76.77, 63.94, 55.88, 27.45, 27.36, 26.84, 24.15, 24.05, 21.69, 14.96

P10

(3,5-Di^{t}Bu-Tao(nBu)Phyrin)

^{1}H NMR, 500MHz, CDCl$_3$

^{13}C NMR, 100MHz, CDCl$_3$

P10
(3,5-Di^{t}Bu-Tao(nBu)Phyrin)
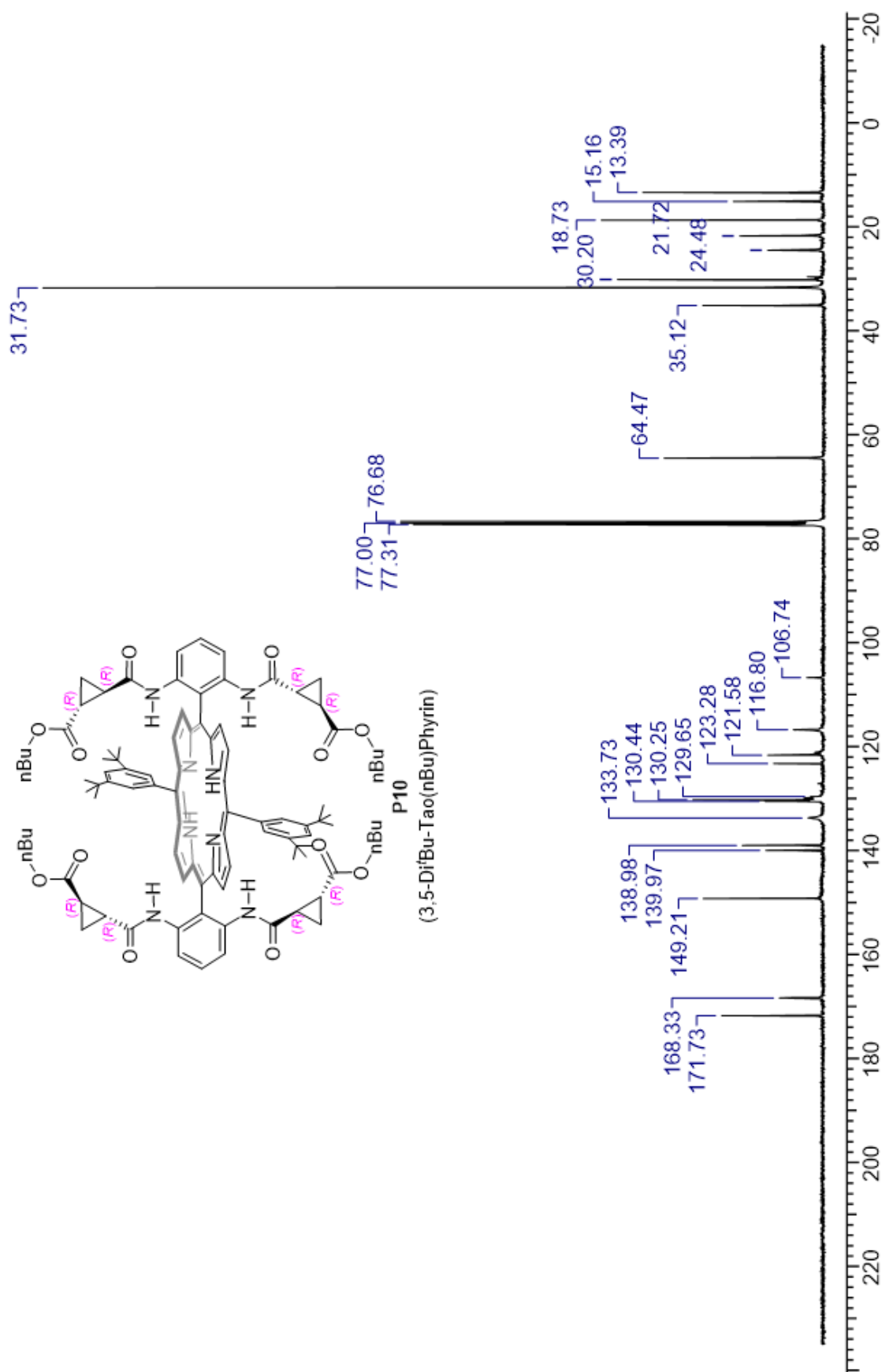
1H NMR, 500MHz, CDCl3

LK-III-138B_PROTON_027

P11
(2,6-DiMeO-Tao(nPr)Phyrin)

^{13}C NMR, 100MHz, CDCl$_3$

P11

(2,6-DiMeO-Tao(nPr)Phyrin)

77.32
77.00
66.04
55.85
24.35
21.72
21.52
14.90
10.00
104.23
106.29
114.13
117.59
118.42
130.25
130.91
138.91
160.28
168.49
171.34

*

220 200 180 160 140 120 100 80 60 40 20 0 -20

^{1}H NMR, 500MHz, CDCl$_3$

Bn
N–SO$_2$N$_3$

1a

^{13}C NMR, 100MHz, CDCl$_3$

128.74
128.67
128.77
128.60
126.85
128.98

128.67
128.77

128.60
126.85
128.98

134.52
137.63

76.85
77.11
77.37

50.02
53.00

34.40

Bn
|
N–SO$_2$N$_3$

1a

¹H NMR, 400MHz, CDCl₃

1b

^{13}C NMR, 150MHz, CDCl$_3$

1b

^{1}H NMR, 400MHz, CDCl$_3$

1c

^{13}C NMR, 100MHz, CDCl$_3$

1c

^{1}H NMR, 600MHz, CDCl$_3$

Structure label: 1d (F$_3$C-substituted phenethyl, N-Bn, N-SO$_2$N$_3$)

Peak assignments:
- 7.52
- 7.50
- 7.38
- 7.37
- 7.31
- 7.31
- 7.30
- 7.26
- 7.16
- 7.15
- 4.42
- 3.44
- 3.43
- 3.42
- 2.88
- 2.87
- 2.85

^{13}C NMR, 150MHz, CDCl$_3$

1d

^{1}H NMR, 500MHz, CDCl$_3$

1e

13C NMR, 125MHz, CDCl₃

^{1}H NMR, 500MHz, CDCl$_3$

1f

¹³C NMR, 100MHz, CDCl₃

1f

^{1}H NMR, 600MHz, CDCl$_3$

1g

^{13}C NMR, 100MHz, CDCl$_3$

1g

128.59
128.88
158.95
134.53
129.38
128.49
128.19
127.42
125.24
109.25
77.31
77.00
76.68
52.96
71.20
50.40
33.75
29.65
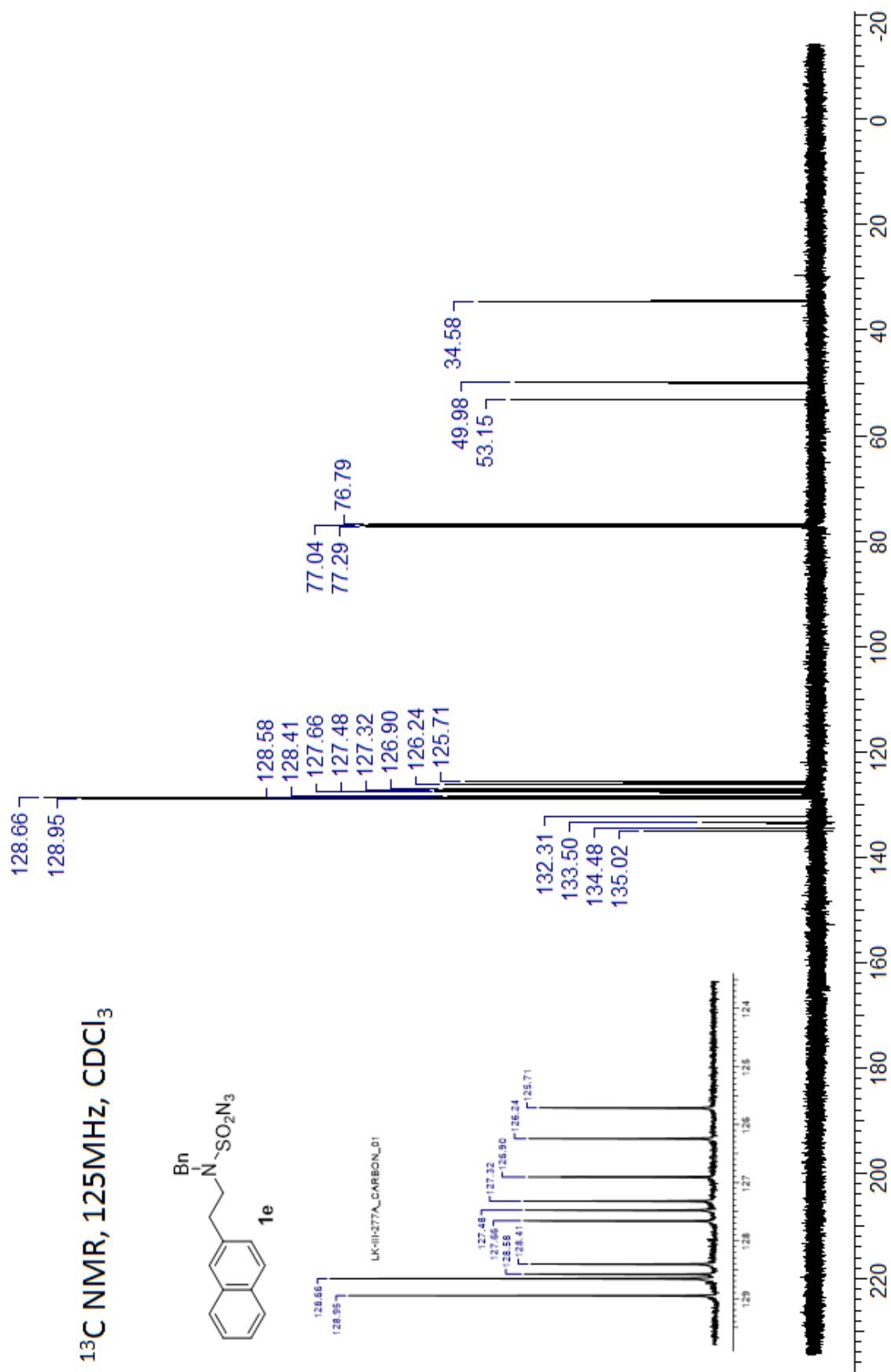
^{1}H NMR, 600MHz, CDCl$_3$

1h

^{13}C NMR, 125MHz, CDCl$_3$
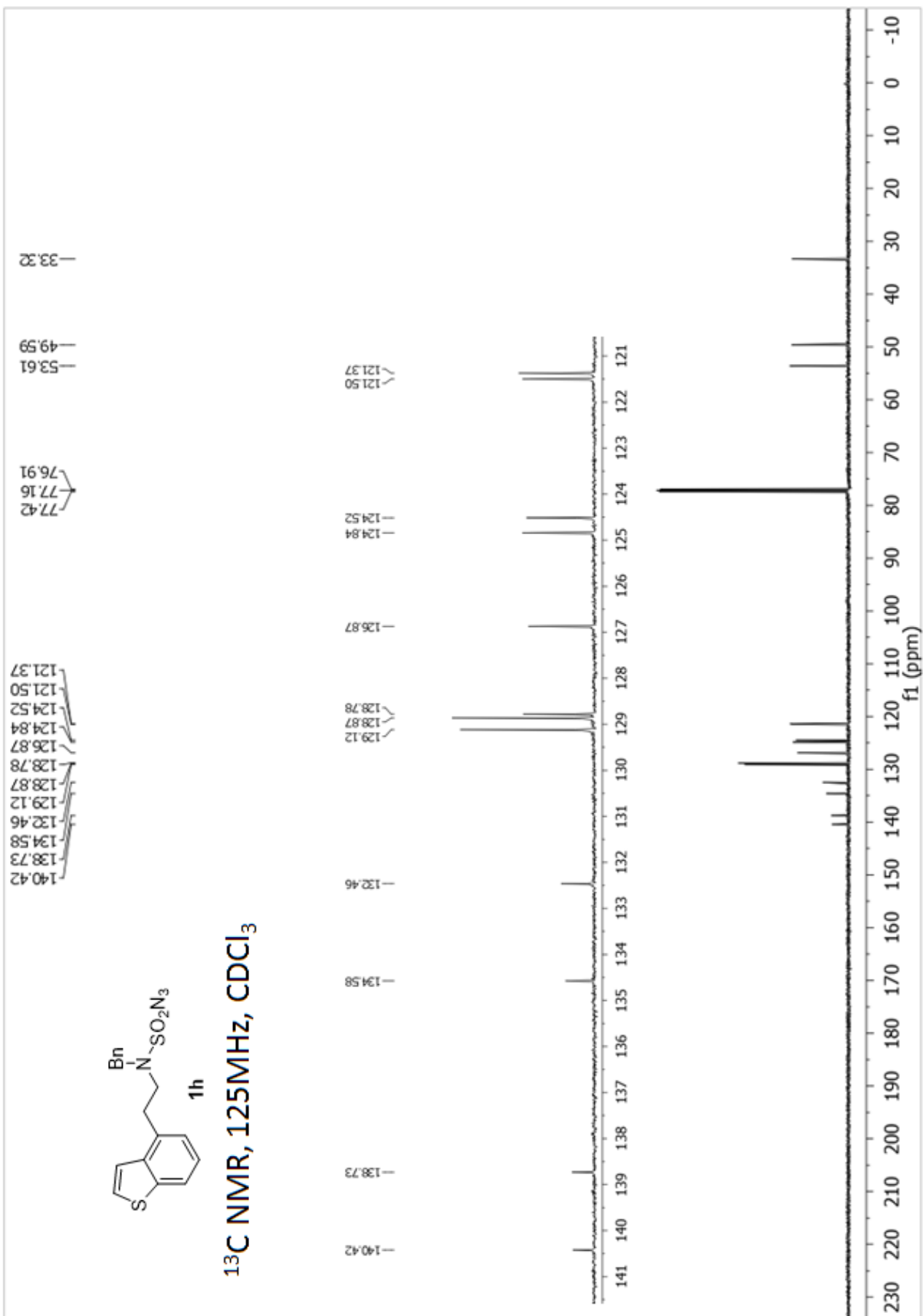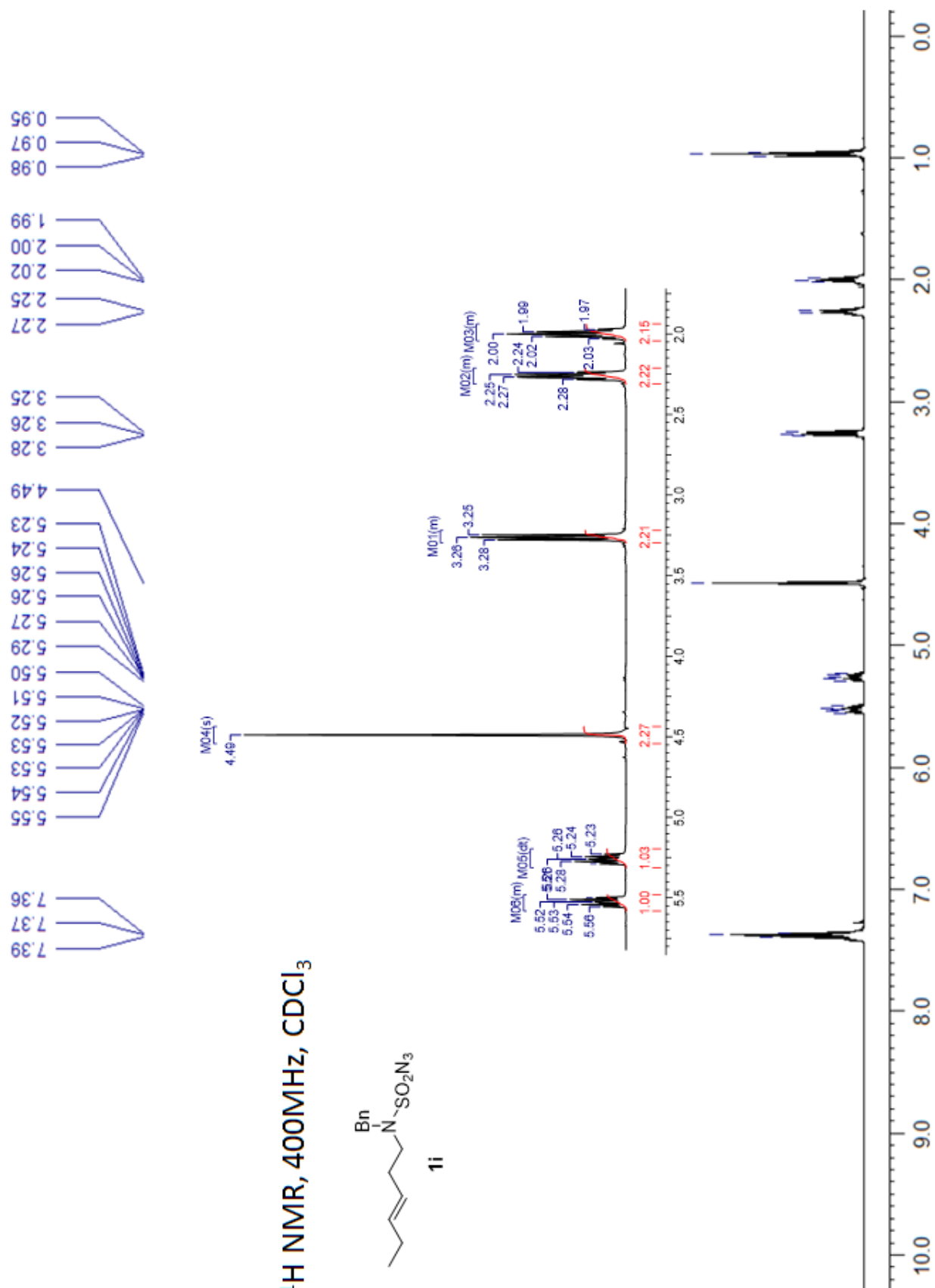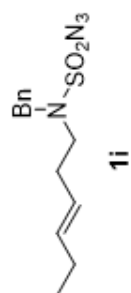
1h

33.32

49.59
53.61

76.91
77.16
77.42

121.37
121.50
124.52
124.84
126.87
128.78
128.87
129.12
132.46
134.58
138.73
140.42

121.37
121.50

124.52
124.84

126.87

128.78
128.87
129.12

132.46

134.58

138.73

140.42

f1 (ppm)

^{1}H NMR, 400MHz, CDCl$_3$

1i

¹³C NMR, 100MHz, CDCl₃

13.53
25.52
48.48
30.75
52.55
76.68
76.99
77.31
128.39
123.91
128.46
128.84
134.65
135.58

^{1}H NMR, 400MHz, CDCl$_3$

1j

¹³C NMR, 100MHz, CDCl₃

134.62
138.58
133.68
128.47
128.84
128.40
125.24
114.54
76.99
76.67
77.31
31.89
33.12
48.48
52.57
30.80
28.40

^{1}H NMR, 500MHz, CDCl$_3$

1k

^{13}C NMR, 125MHz, CDCl$_3$

1k

^{1}H NMR, 400MHz, CDCl$_3$

1l

^{13}C NMR, 100MHz, CDCl$_3$

1l

^{1}H NMR, 400MHz, CDCl$_3$

1m

13C NMR, 100MHz, CDCl₃

1m

S149

^{1}H NMR, 500MHz, CDCl$_3$

1m'

LK-III-177_CARBON_01

¹³C NMR, 125MHz, CDCl₃

21.33
37.24
51.28
57.62
76.78
77.03
77.29
124.48
126.99
139.92

1m'

^{1}H NMR, 400MHz, CDCl$_3$

1.90
1.92
1.94
2.59
2.61
2.63
2.87
2.88
2.90
3.22
3.24
3.26
3.43
3.44
3.45
3.47

7.14
7.16
7.23
7.28
7.28
7.29
7.30
7.31

1.92
1.91
1.90
1.88
1.92
1.94
1.96
1.98

1.98

1.98

2.00

1.96

2.00

2.61
2.59
2.87
2.63
2.88
2.90
3.22
3.44
3.43
3.24
3.26
3.45
3.47

1n

^{13}C NMR, 100MHz, CDCl$_3$

1n

128.73
128.56
128.26
126.85
126.24
137.50
140.54
77.01
77.33
76.69
49.27
50.92
34.76
32.63
29.33

^{1}H NMR, 500MHz, CDCl$_3$

^{13}C NMR, 125MHz, CDCl$_3$

128.97

128.56

134.51

170.32

68.54

76.78
77.04
77.29

53.30

44.36

33.23

21.76

128.97
128.56
128.51
134.51

1o

^{1}H NMR, 400MHz, CDCl$_3$

2.86
2.88
2.89
3.47
3.49
3.51

4.33

6.04
6.05
6.27
6.28
6.28
6.29
7.24
7.29
7.29
7.30
7.31
7.31
7.32
7.34
7.34
7.34
7.36
7.36
7.37
7.38
7.38

1p

LK-III-22B_CARBON_01

^{13}C NMR, 125MHz, CDCl$_3$

1p

128.50
128.89
106.98
110.49
134.47
141.64
151.39
76.99
76.67
77.31
52.84
46.98
26.83

^{1}H NMR, 400MHz, CDCl$_3$

1q

^{13}C NMR, 125MHz, CDCl$_3$

1q

76.67

139.56
134.37

128.95
128.60

127.09
125.71
124.20

53.21
50.03
28.47

^{1}H NMR, 600MHz, CDCl$_3$

1r

Bn
N–SO$_2$N$_3$

7.38
7.37
7.36
7.34
7.36

4.46

3.31
3.30
3.29

1.47
1.45
1.44
1.43

0.44
0.43
0.42
0.42
0.41

0.00
0.00
0.00

^{13}C NMR, 150MHz, CDCl$_3$

4.47
8.29
32.75
48.76
52.81
76.95
77.16
77.37
128.58
128.69
129.00
134.84

128.58
128.69
129.00

1r

Bn
N—SO$_2$N$_3$

f1 (ppm)

^{1}H NMR, 500MHz, CDCl$_3$

2.85
2.87
2.88
2.89
2.91
2.92
2.94
2.95

4.43
4.44
4.46
4.47
4.49

7.20
7.22
7.26
7.27
7.28
7.32
7.34
7.35

1s

^{13}C NMR, 125MHz, CDCl$_3$

1s

128.73
129.00
126.95
137.20
77.30
77.05
76.79
62.88
38.11
30.03

^{1}H NMR, 400MHz, CDCl$_3$

S164

^{13}C NMR, 100MHz, CDCl$_3$

1t

^{1}H NMR, 600MHz, CDCl$_3$

1u

^{13}C NMR, 150MHz, CDCl$_3$

1u

^{1}H NMR, 400MHz, CDCl$_3$

2a

¹³C NMR, 125MHz, CDCl₃

2a

1: 215 nm, 4 nm Results

Pk #	Retention Time	Area Percent
1	24.788	49.728
2	34.872	50.272

Totals	
	100.000
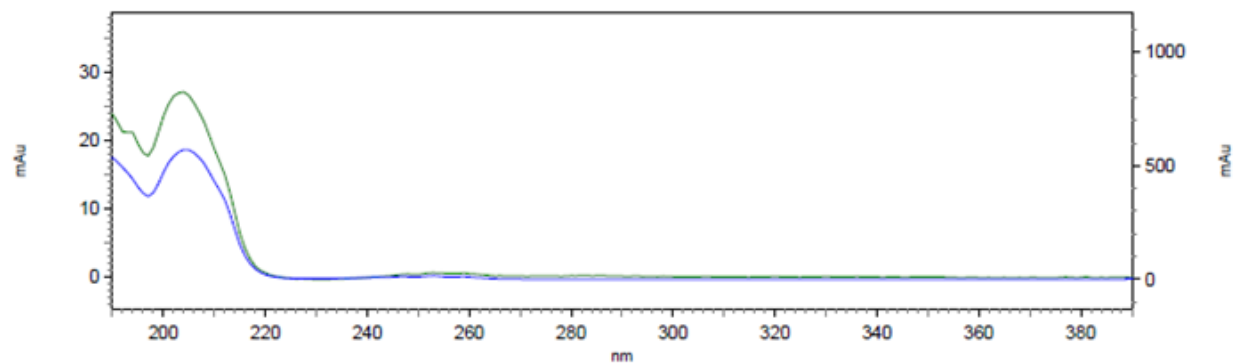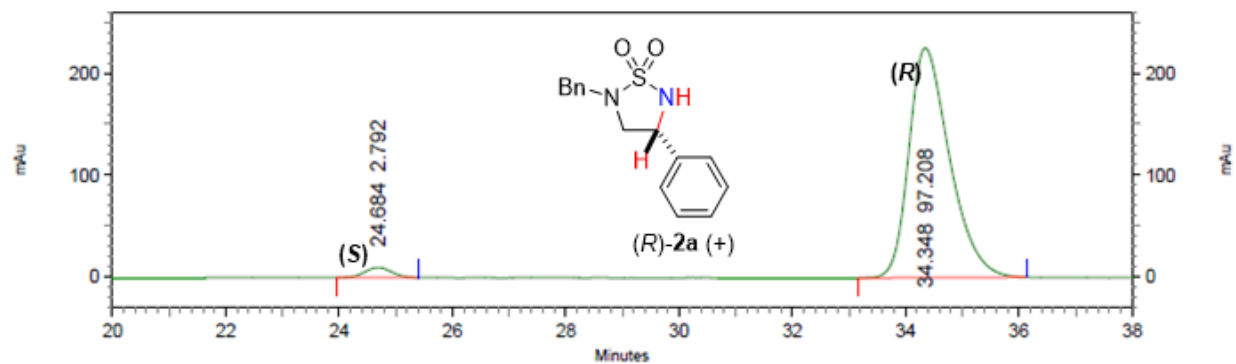
3: 219 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	24.684	2.792	1
	34.348	97.208	2

Totals		
	100.000	

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

(R)-2a (+)
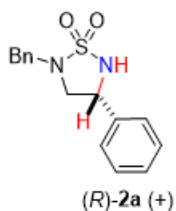
Datablock: I

```
Bond precision:   C-C = 0.0027 A          Wavelength=1.54178

Cell:          a=14.6858(3)     b=5.8380(1)        c=17.4091(4)
               alpha=90         beta=110.6117(5)   gamma=90
Temperature:   100 K

               Calculated                Reported
Volume         1397.04(5)                1397.04(5)
Space group    P 21/c                    P 1 21/c 1
Hall group     -P 2ybc                   -P 2ybc
Moiety formula C15 H16 N2 O2 S           C15 H16 N2 O2 S
Sum formula    C15 H16 N2 O2 S           C15 H16 N2 O2 S
Mr             288.36                    288.36
Dx,g cm-3      1.371                     1.371
Z              4                         4
Mu (mm-1)      2.085                     2.085
F000           608.0                     608.0
F000'          610.97
h,k,lmax       17,7,21                   17,7,21
Nref           2588                      2561
Tmin,Tmax      0.882,0.901               0.370,0.753
Tmin'          0.513

Correction method= MULTI-SCAN

Data completeness= 0.990         Theta(max)= 68.975

R(reflections)= 0.0376( 2375)    wR2(reflections)= 0.0982( 2561)

S = 1.063                Npar= 185
```

The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

(R)-**2a** (+)

S173

Publication of your CIF

You should attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the nature of your study may justify the reported deviations from journal submission requirements and the more serious of these should be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. *checkCIF* was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

If level A alerts remain, which you believe to be justified deviations, and you intend to submit this CIF for publication in a journal, you should additionally insert an explanation in your CIF using the Validation Reply Form (VRF) below. This will allow your explanation to be considered as part of the review process.

```
# start Validation Reply Form
_vrf_PUBL002_GLOBAL
;
PROBLEM: The contact author's address is missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
```
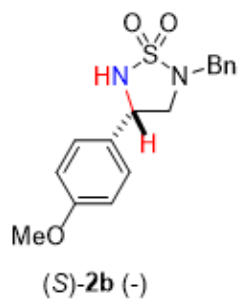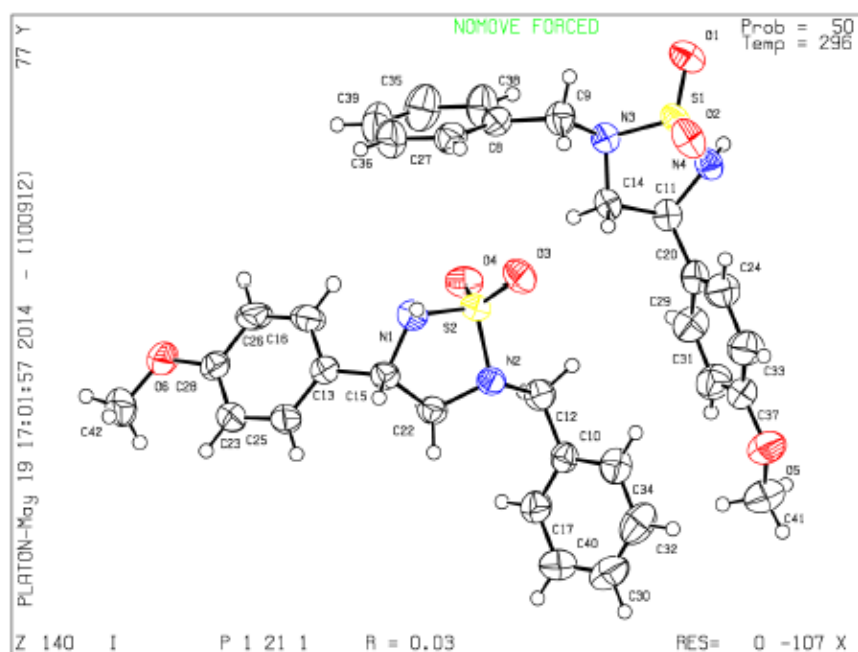

(R)-2a (+)

(R)-2a (+)

PLATON version of 24/07/2014; check.def file version of 24/07/2014

Datablock I - ellipsoid plot

3: 219 nm, 4 nm
 Results

Name	Retention Time	Area Percent	Pk #
	24.644	93.582	1
	34.764	6.418	2

Totals		
	100.000	

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

(S)-2a (-)

Datablock: I

```
Bond precision:   C-C = 0.0066 A            Wavelength=1.54178

Cell:             a=9.4266(2)     b=6.1137(2)        c=13.0269(3)
                  alpha=90        beta=108.7061(9)   gamma=90
Temperature:      100 K

                  Calculated                 Reported
Volume            711.10(3)                  711.10(3)
Space group       P 21                       P 1 21 1
Hall group        P 2yb                      P 2yb
Moiety formula    C15 H16 N2 O2 S            C15 H16 N2 O2 S
Sum formula       C15 H16 N2 O2 S            C15 H16 N2 O2 S
Mr                288.36                     288.36
Dx,g cm-3         1.347                      1.347
Z                 2                          2
Mu (mm-1)         2.048                      2.048
F000              304.0                      304.0
F000'             305.48
h,k,lmax          11,7,15                    11,7,15
Nref              2663[ 1466]                2435
Tmin,Tmax         0.906,0.980                0.327,0.753
Tmin'             0.782

Correction method= MULTI-SCAN

Data completeness= 1.66/0.91       Theta(max)= 69.074

R(reflections)= 0.0471( 2394)      wR2(reflections)= 0.1266( 2435)

S = 1.076                Npar= 186
```

The following ALERTS were generated. Each ALERT has the format
     test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

(S)-2a (-)

○ **Alert level C**
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ....   0.0066 Ang.

○ **Alert level G**
PLAT033_ALERT_4_G Flack x Value Deviates > 2*sigma from Zero 0.087
PLAT791_ALERT_4_G The Model has Chirality at C7   ....   S Verify

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  2 ALERT level G = General information/check it is not something unexpected

  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  0 ALERT type 2 Indicator that the structure model may be wrong or deficient
  1 ALERT type 3 Indicator that the structure quality may be low
  2 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check
```

checkCIF publication errors
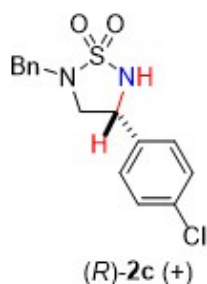
🔴 **Alert level A**
PUBL002_ALERT_1_A The contact author's address is missing,
           _publ_contact_author_address.
PUBL005_ALERT_1_A _publ_contact_author_email, _publ_contact_author_fax and
           _publ_contact_author_phone are all missing.
           At least one of these should be present.
PUBL006_ALERT_1_A _publ_requested_journal is missing
           e.g. 'Acta Crystallographica Section C'
PUBL008_ALERT_1_A _publ_section_title is missing. Title of paper.
PUBL009_ALERT_1_A _publ_author_name is missing. List of author(s) name(s).
PUBL010_ALERT_1_A _publ_author_address is missing. Author(s) address(es).
PUBL012_ALERT_1_A _publ_section_abstract is missing.
           Abstract of paper in English.

```
  7 ALERT level A = Data missing that is essential or data in wrong format
  0 ALERT level G = General alerts. Data that may be required is missing
```

S178

Publication of your CIF

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(S)-**2a** (-)

```
# start Validation Reply Form
_vrf_PUBL002_GLOBAL
;
PROBLEM: The contact author's address is missing.
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
```
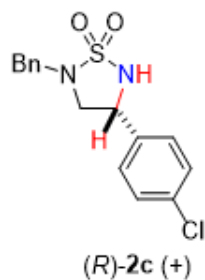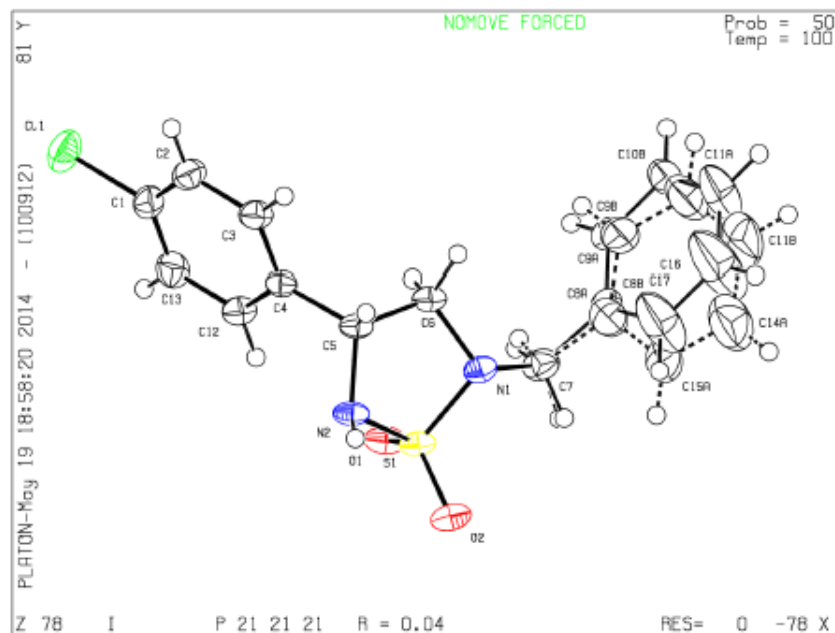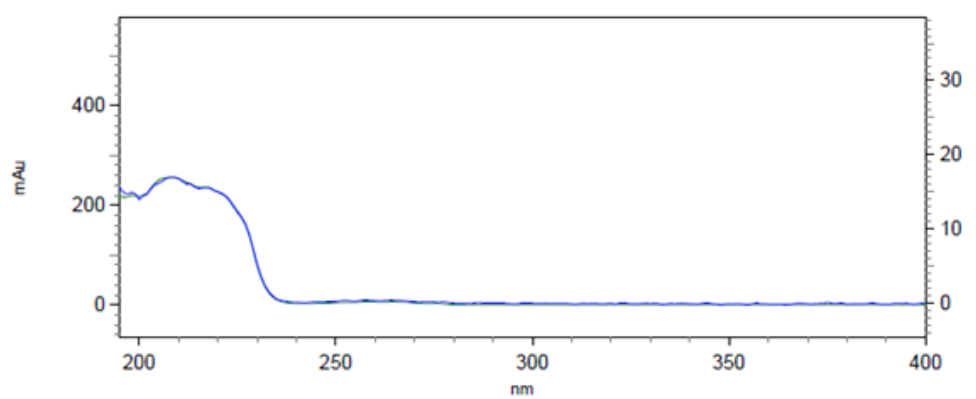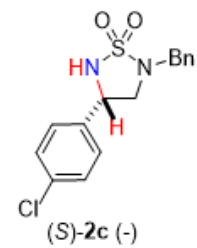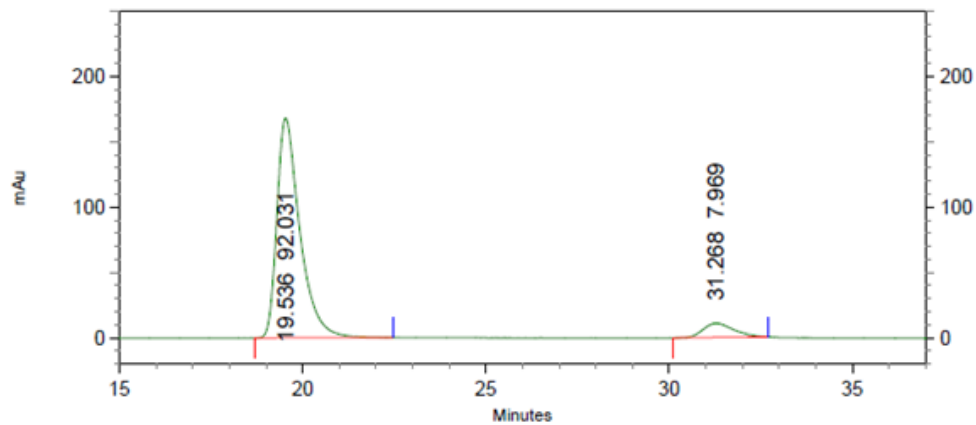
If you wish to submit your CIF for publication in Acta Crystallographica Section C or E, you should upload your CIF via the web. If your CIF is to form part of a submission to another IUCr journal, you will be asked, either during electronic submission or by the Co-editor handling your paper, to upload your CIF via our web site.

(S)-**2a** (-)

PLATON version of 24/07/2014; check.def file version of 24/07/2014

Datablock I - ellipsoid plot

Systematic Control of Degree and Sense of Asymmetric Induction for Intramolecular Radical 1,5-C–H Amination of Sulfamoyl Azide

[Co(P1)]
(4-C bridge)

(S)

(R)

24.836 47.592

34.976 52.408

(R):(S) = 52:48

[Co(P2)]
(4-C bridge)

(S)

(R)

24.852 67.942

35.140 32.058

(R):(S) = 32:68

[Co(P3)]
(6-C bridge)

(S)

(R)

24.784 69.749

34.964 30.251

(R):(S) = 30:70

[Co(P4)]
(6-C bridge)

(S)

(R)

24.644 93.582

34.764 6.418

(R):(S) = 6:94

Systematic Control of Degree and Sense of Asymmetric Induction for Intramolecular Radical 1,5–C–H Amination of Sulfamoyl Azide

^{1}H NMR, 600MHz, CDCl$_3$

2b

^{13}C NMR, 150 MHz, CDCl$_3$

2b
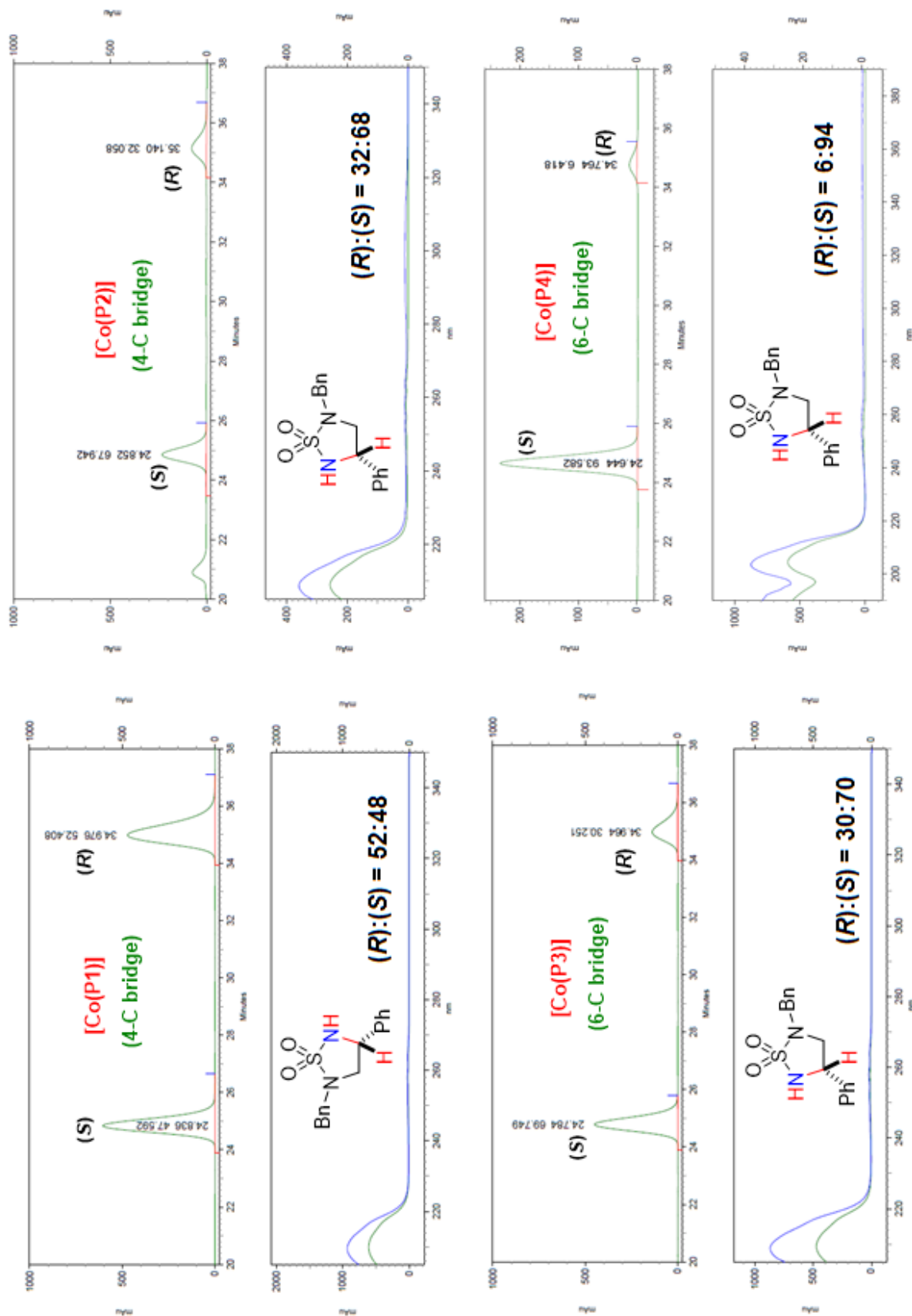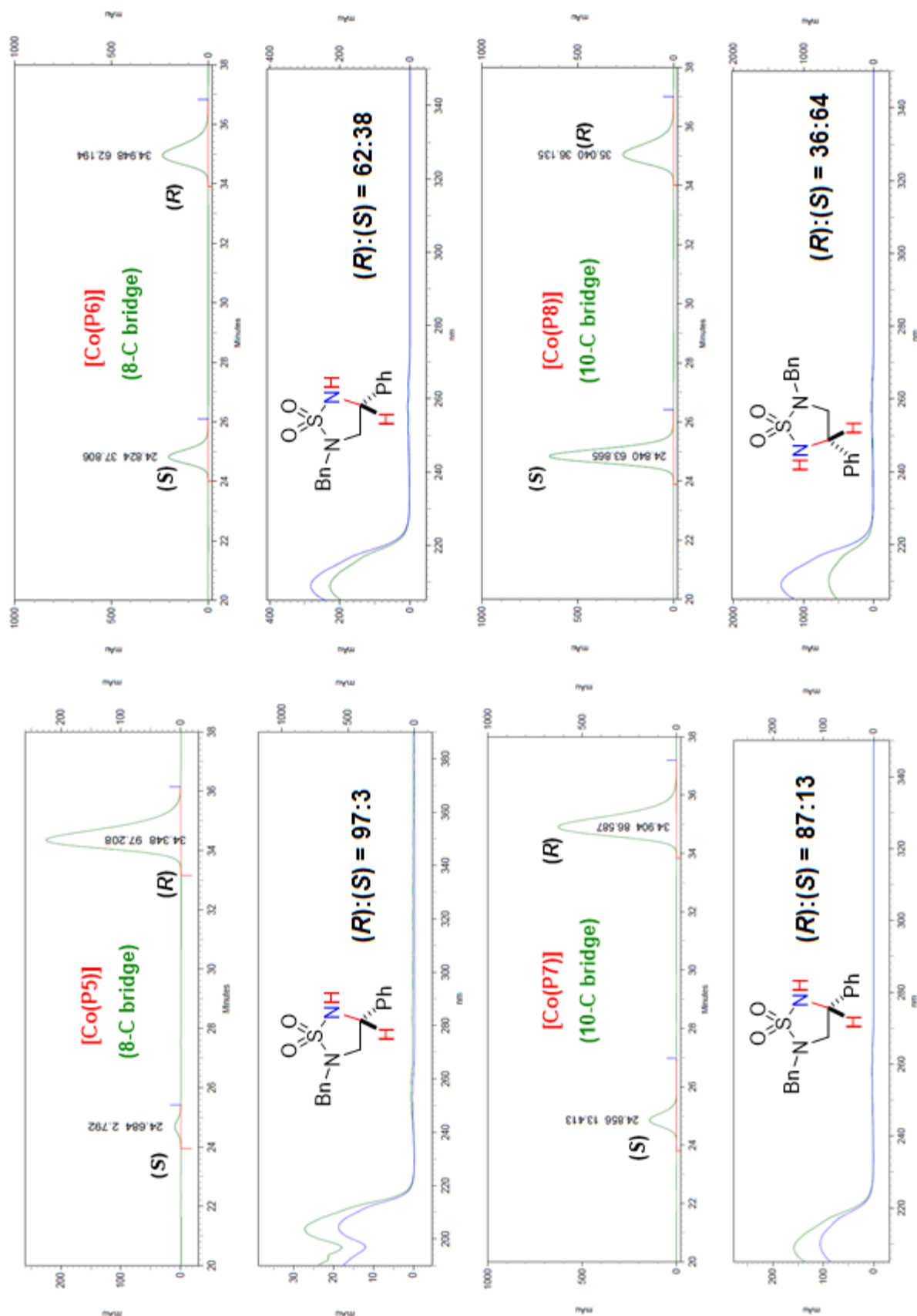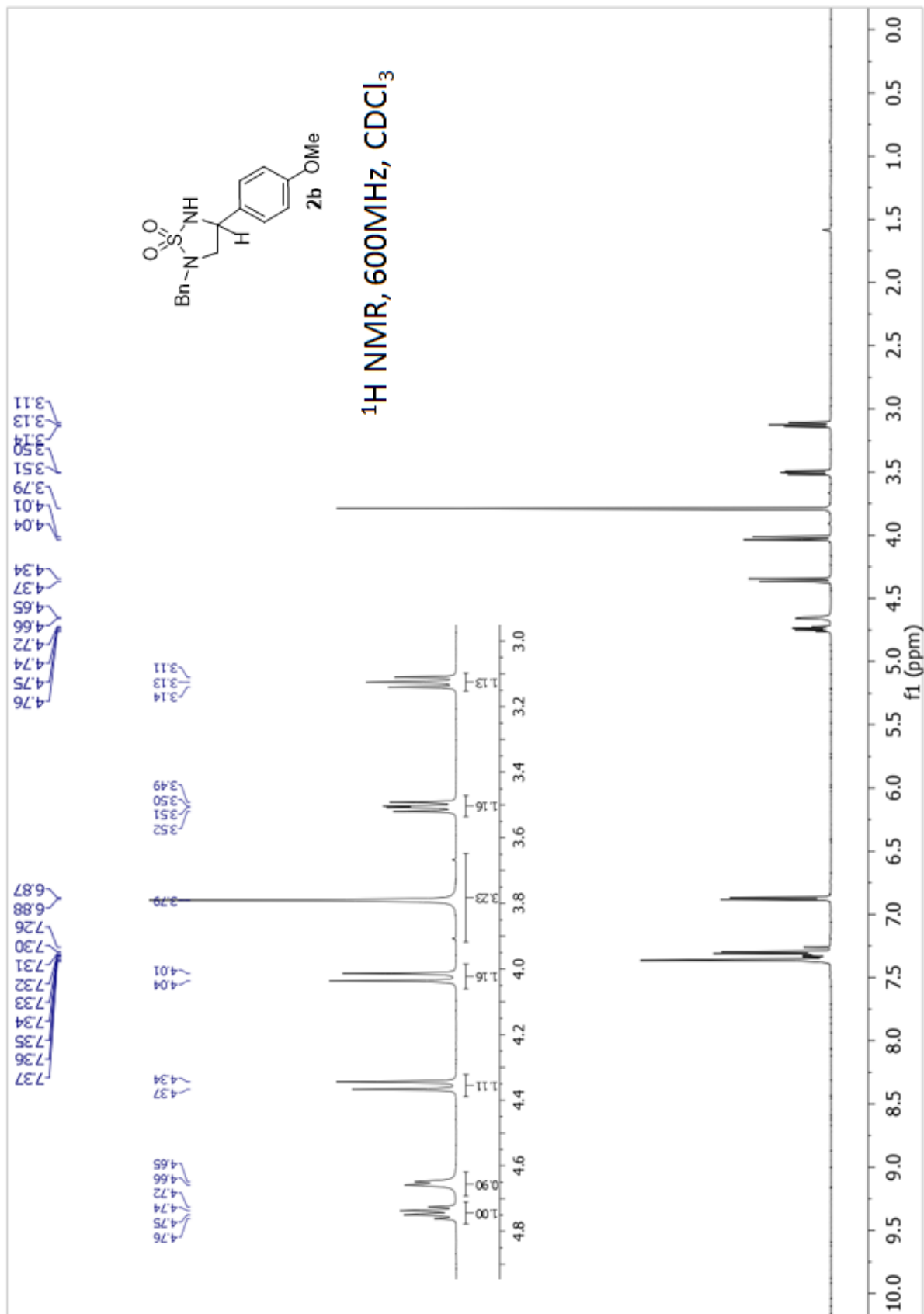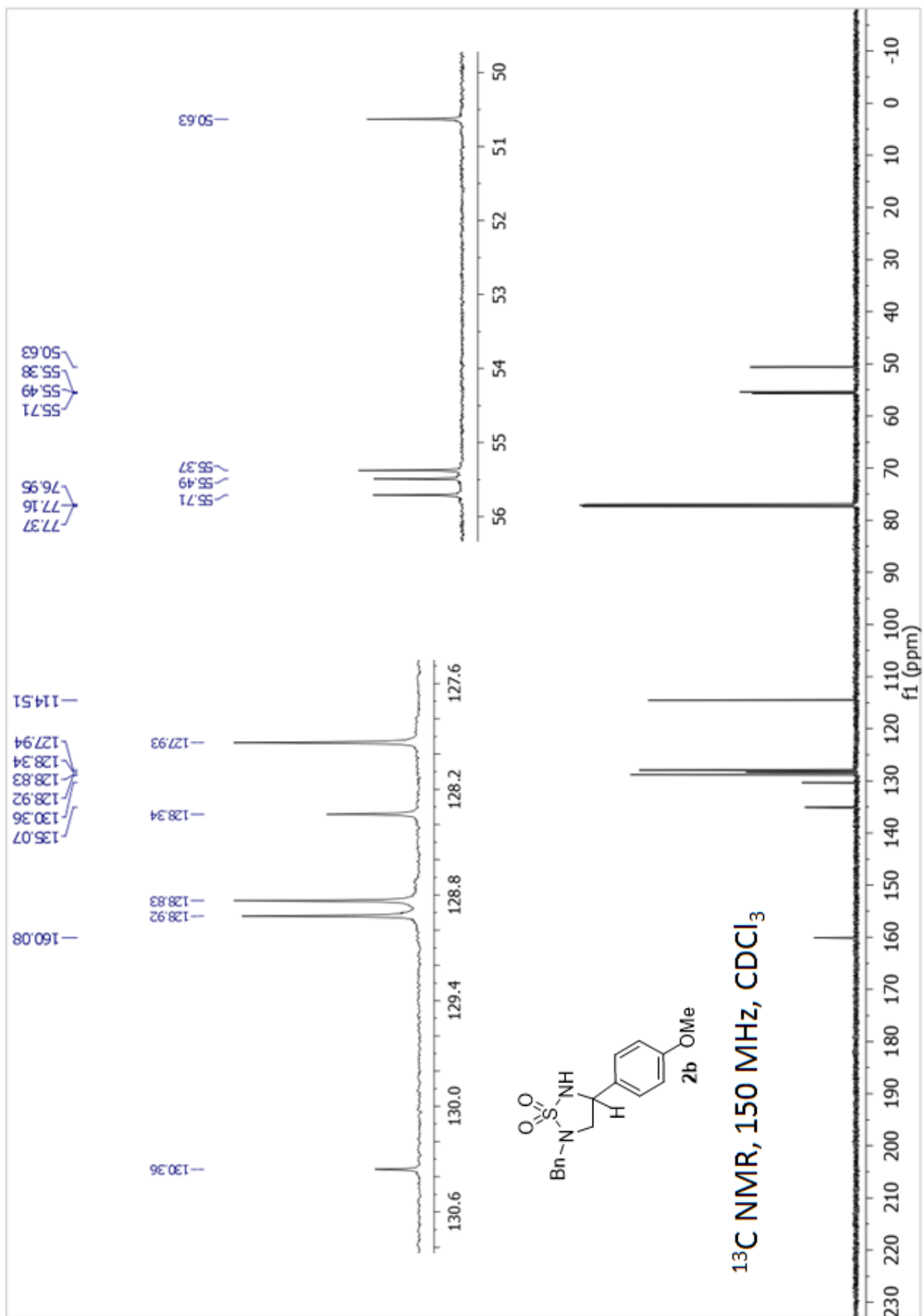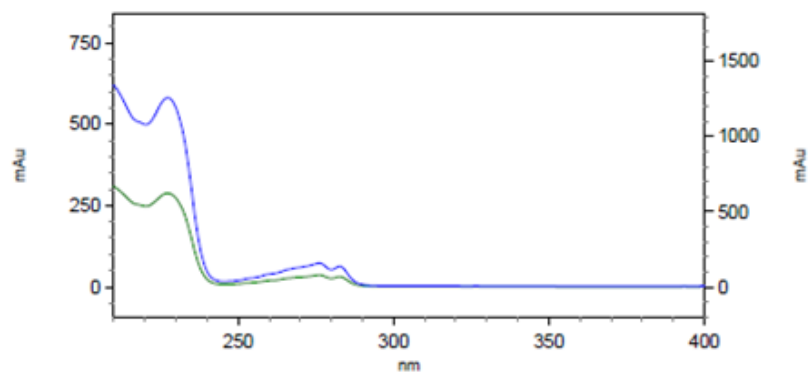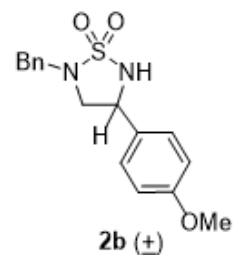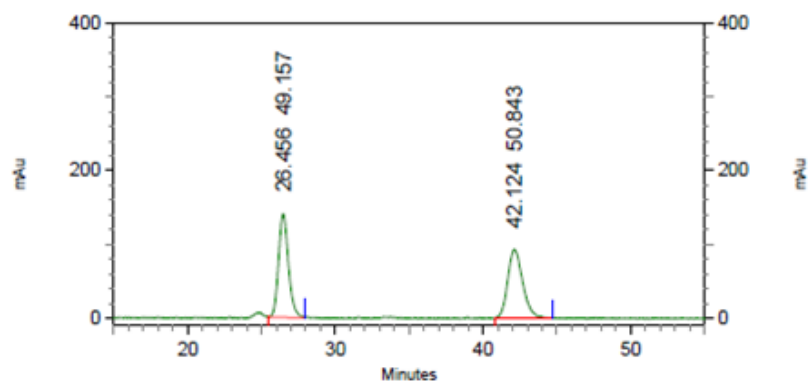
3: 196 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	26.456	49.157	1
	42.124	50.843	2

Totals		
	100.000	

(R)-2b (+)
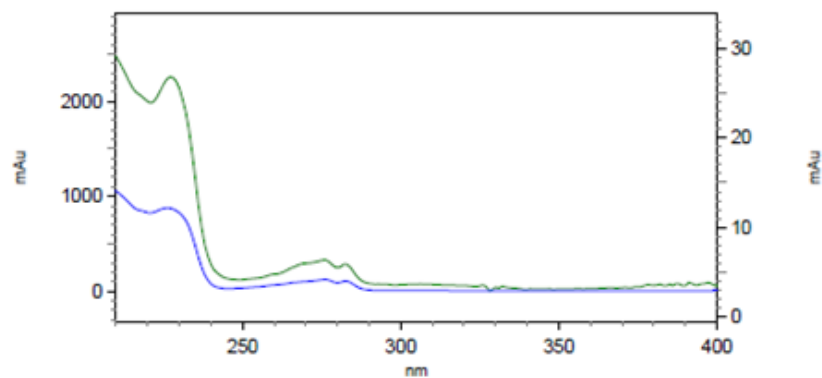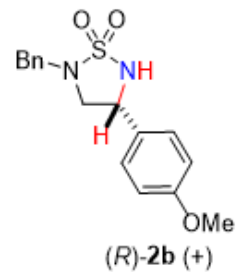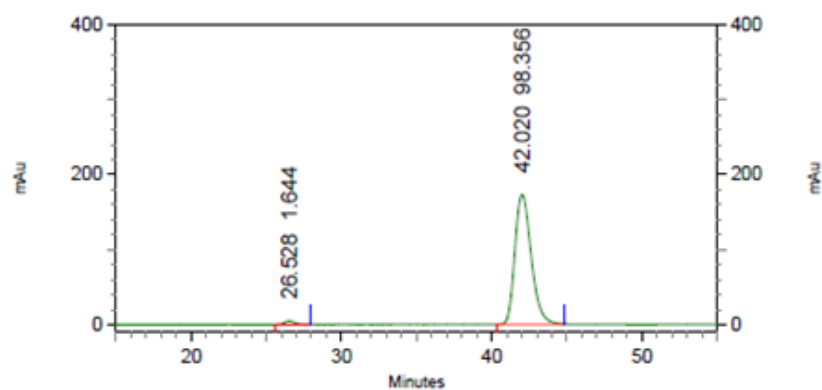
3: 226 nm, 4 nm
 Results

Name	Retention Time	Area Percent	Pk #
	26.528	1.644	1
	42.020	98.356	2

Totals		
	100.000	

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report
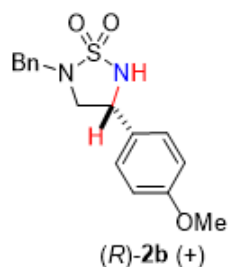
Datablock: I

```
Bond precision:   C-C = 0.0048 A            Wavelength=1.54178

Cell:             a=10.2563(1)    b=11.7761(1)         c=13.4292(1)
                  alpha=90        beta=101.640(1)      gamma=90
Temperature:      296 K

                  Calculated                Reported
Volume            1588.61(2)                1588.61(2)
Space group       P 21                      P 1 21 1
Hall group        P 2yb                     P 2yb
Moiety formula    C16 H18 N2 O3 S           2(C16 H18 N2 O3 S)
Sum formula       C16 H18 N2 O3 S           C32 H36 N4 O6 S2
Mr                318.39                    636.77
Dx,g cm-3         1.331                     1.331
Z                 4                         2
Mu (mm-1)         1.933                     1.933
F000              672.0                     672.0
F000'             675.23
h,k,lmax          12,14,16                  12,14,15
Nref              6140[ 3229]               5527
Tmin,Tmax         0.793,0.962               0.581,0.753
Tmin'             0.539

Correction method= MULTI-SCAN

Data completeness= 1.71/0.90       Theta(max)= 70.899

R(reflections)= 0.0324( 5145)      wR2(reflections)= 0.0842( 5527)

S = 1.025                    Npar= Npar = 405
```

The following ALERTS were generated. Each ALERT has the format
        test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

(R)-**2b** (+)
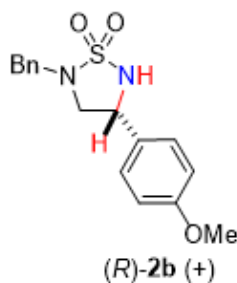
Alert level C
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ....   0.0048 Ang.

Alert level G
PLAT033_ALERT_4_G Flack x Value Deviates > 2*sigma from Zero 0.041
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ   Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by ....   2.00 Ratio
PLAT142_ALERT_4_G su on b - Axis Small or Missing ....   0.00010 Ang.
PLAT143_ALERT_4_G su on c - Axis Small or Missing ....   0.00010 Ang.
PLAT791_ALERT_4_G The Model has Chirality at C8   ....   R Verify
PLAT791_ALERT_4_G The Model has Chirality at C11   ....   R Verify

   0 **ALERT** level A - Most likely a serious problem - resolve or explain
   0 **ALERT** level B - A potentially serious problem, consider carefully
   1 **ALERT** level C - Check. Ensure it is not caused by an omission or oversight
   7 **ALERT** level G - General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   0 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   5 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check

checkCIF publication errors

Alert level A
PUBL002_ALERT_1_A The contact author's address is missing,
          _publ_contact_author_address.
PUBL005_ALERT_1_A _publ_contact_author_email, _publ_contact_author_fax and
          _publ_contact_author_phone are all missing.
          At least one of these should be present.
PUBL006_ALERT_1_A _publ_requested_journal is missing
          e.g. 'Acta Crystallographica Section C'
PUBL008_ALERT_1_A _publ_section_title is missing. Title of paper.
PUBL009_ALERT_1_A _publ_author_name is missing. List of author(s) name(s).
PUBL010_ALERT_1_A _publ_author_address is missing. Author(s) address(es).
PUBL012_ALERT_1_A _publ_section_abstract is missing.
          Abstract of paper in English.

   7 **ALERT** level A - Data missing that is essential or data in wrong format
   0 **ALERT** level G - General alerts. Data that may be required is missing

Publication of your CIF

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(R)-2b (+)

```
# start Validation Reply Form
_vrf_PUBL002_GLOBAL
;
PROBLEM: The contact author's address is missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
```

(R)-**2b** (+)

If you wish to submit your CIF for publication in Acta Crystallographica Section C or E, you should upload your CIF via the web. If your CIF is to form part of a submission to another IUCr journal, you will be asked, either during electronic submission or by the Co-editor handling your paper, to upload your CIF via our web site.
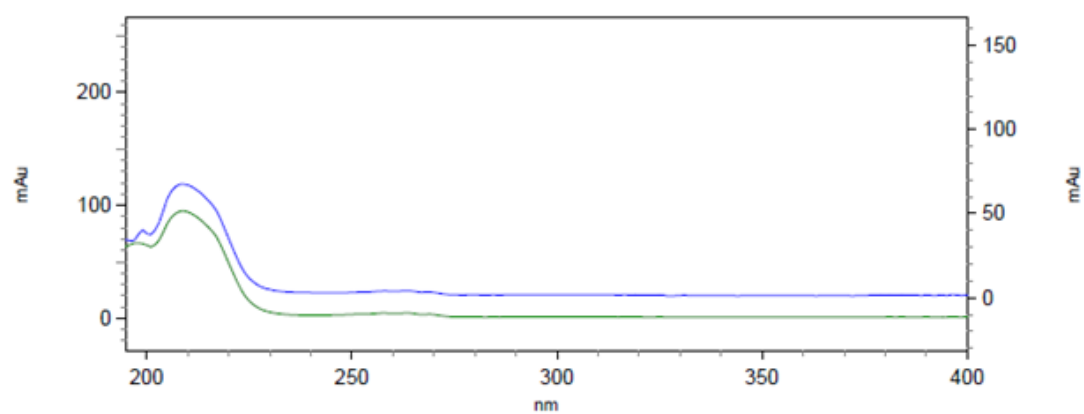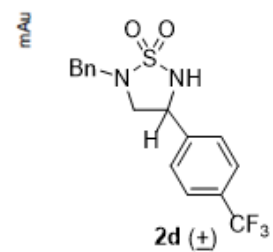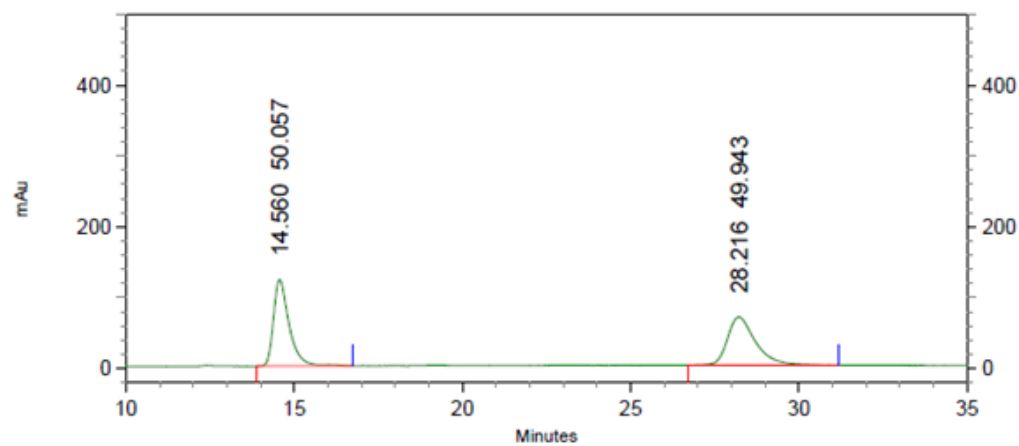
PLATON version of 05/02/2014; check.def file version of 05/02/2014

Datablock I - ellipsoid plot

1: 196 nm, 4 nm
 Results

Name	Retention Time	Area Percent	Pk #
	25.036	95.839	1
	39.808	4.161	2

Totals			
		100.000	

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found.   CIF dictionary   Interpreting this report
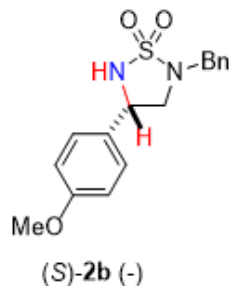
Datablock: I

```
Bond precision:    C-C = 0.0042 A              Wavelength=1.54178

Cell:              a=10.2613(3)     b=11.7758(3)         c=13.4262(4)
                   alpha=90         beta=101.639(1)      gamma=90
Temperature:       296 K

                   Calculated                   Reported
Volume             1589.00(8)                   1589.00(8)
Space group        P 21                         P 1 21 1
Hall group         P 2yb                        P 2yb
Moiety formula     C16 H18 N2 O3 S              C16 H18 N2 O3 S
Sum formula        C16 H18 N2 O3 S              C16 H18 N2 O3 S
Mr                 318.39                       318.38
Dx,g cm-3          1.331                        1.331
Z                  4                            4
Mu (mm-1)          1.933                        1.933
F000               672.0                        672.0
F000'              675.23
h,k,lmax           12,14,16                     12,14,16
Nref               5892[ 3102]                  5466
Tmin,Tmax          0.759,0.944                  0.573,0.753
Tmin'              0.599

Correction method= MULTI-SCAN

Data completeness= 1.76/0.93       Theta(max)= 68.724

R(reflections)= 0.0289( 5145)      wR2(reflections)= 0.0773( 5466)

S = 1.066                     Npar= Npar = 407
```

The following ALERTS were generated. Each ALERT has the format
     test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

(S)-**2b** (-)

checkCIF publication errors

Publication of your CIF

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(S)-**2b** (-)

```
# start Validation Reply Form
_vrf_PUBL002_GLOBAL
;
PROBLEM: The contact author's address is missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
```

(S)-**2b** (-)

If you wish to submit your CIF for publication in Acta Crystallographica Section C or E, you should upload your CIF via the web. If your CIF is to form part of a submission to another IUCr journal, you will be asked, either during electronic submission or by the Co-editor handling your paper, to upload your CIF via our web site.

PLATON version of 05/02/2014; check.def file version of 05/02/2014

Datablock I - ellipsoid plot

^{1}H NMR, 600MHz, CDCl$_3$

2c

^{13}C NMR, 100MHz, CDCl$_3$

2c
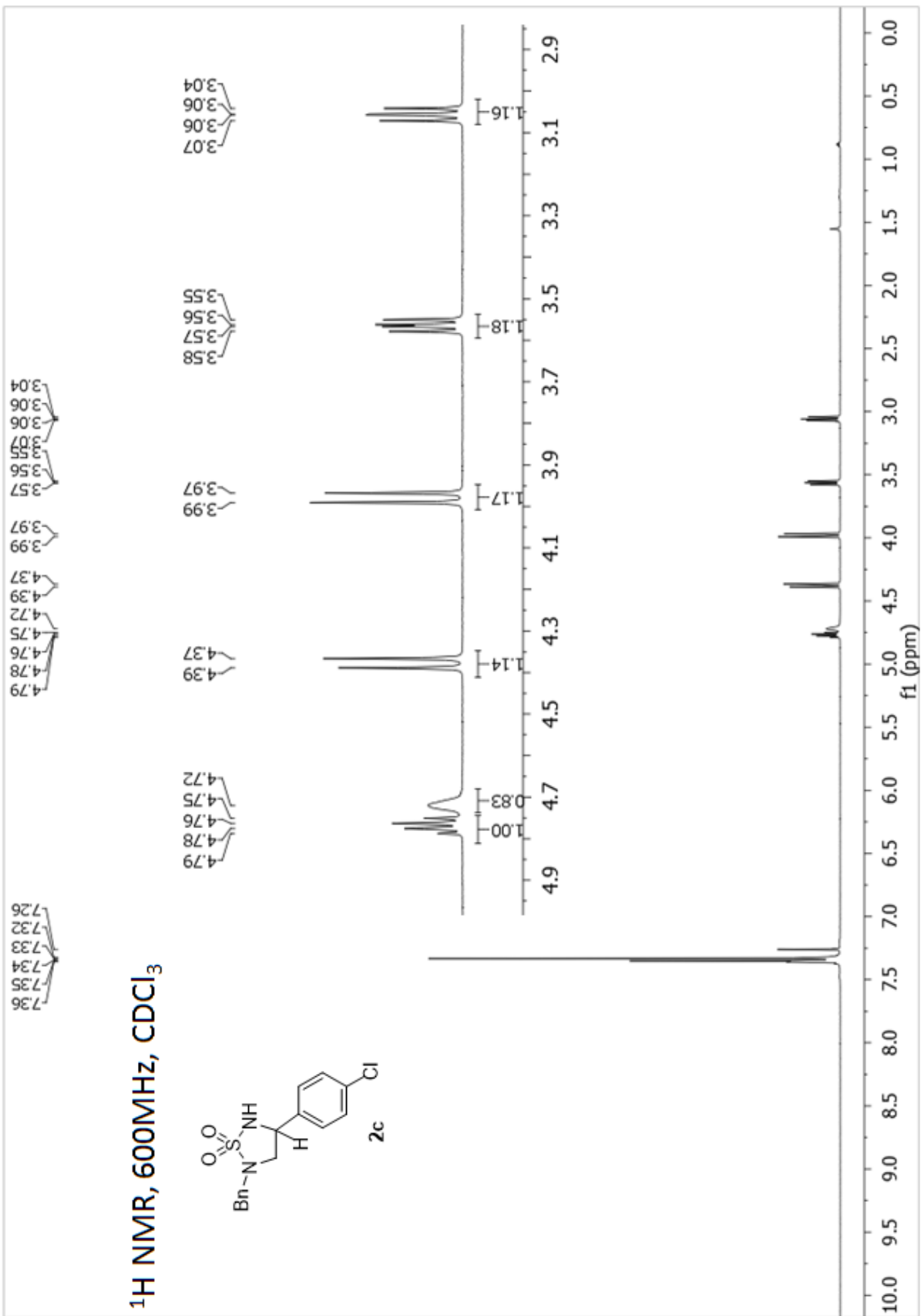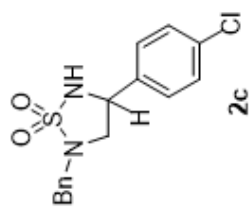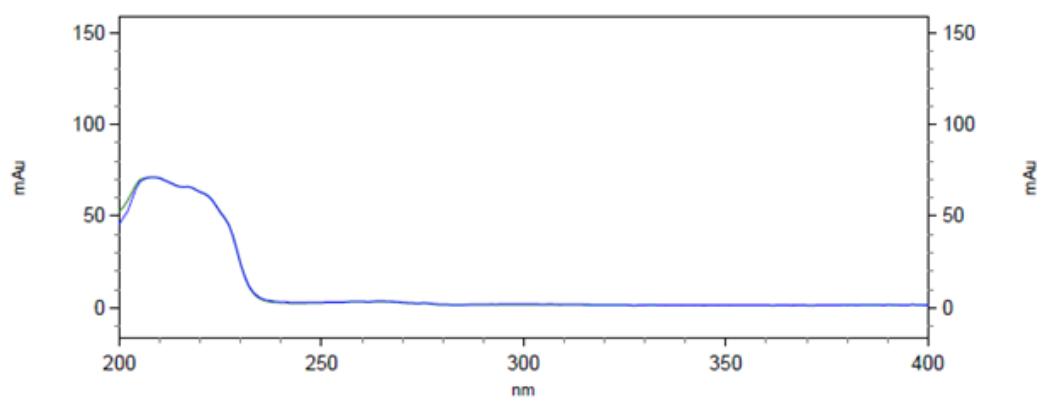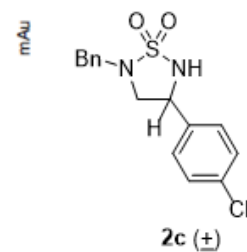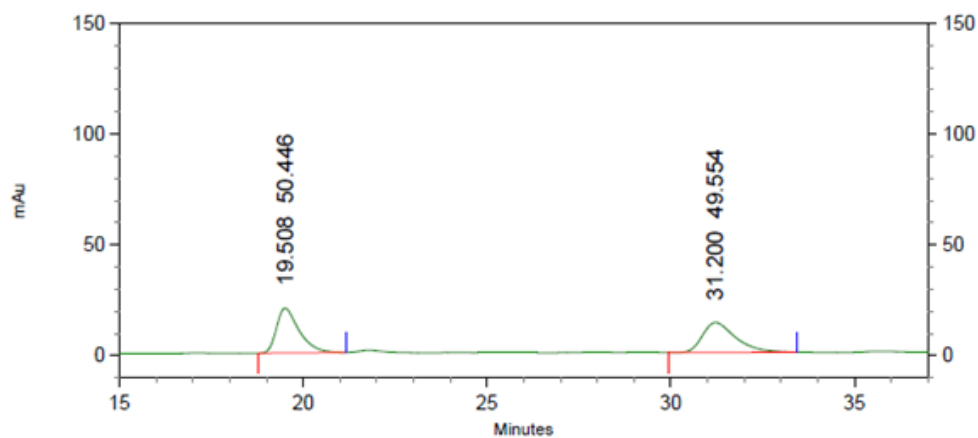
4: 230 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	19.508	50.446
2	31.200	49.554

(R)-2c (+)
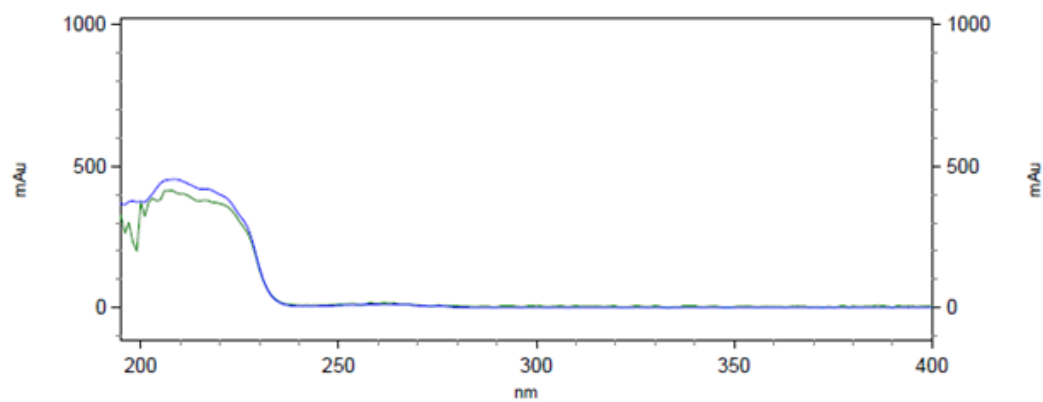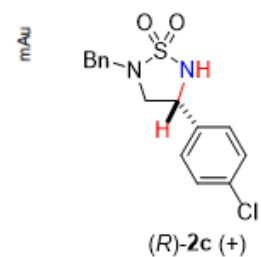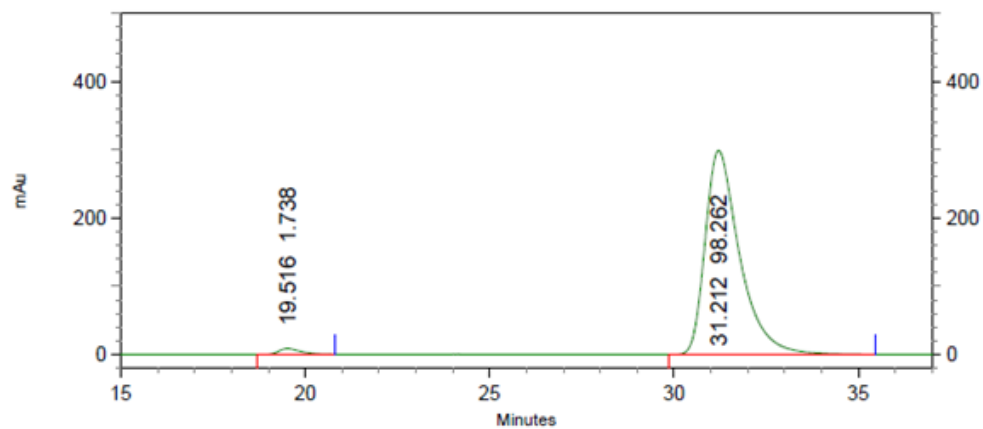
4: 230 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	19.516	1.738
2	31.212	98.262

Totals	
	100.000

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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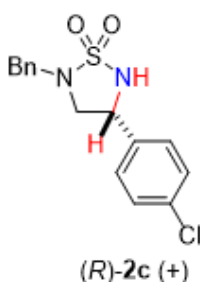
No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: I

```
Bond precision:   C-C = 0.0063 A              Wavelength=1.54178

Cell:             a=4.9711(1)      b=11.8495(2)      c=25.3307(5)
                  alpha=90         beta=90           gamma=90
Temperature:      100 K

                  Calculated               Reported
Volume            1492.11(5)               1492.11(5)
Space group       P 21 21 21               P 21 21 21
Hall group        P 2ac 2ab                P 2ac 2ab
Moiety formula    C15 H15 Cl N2 O2 S       C15 H15 Cl N2 O2 S
Sum formula       C15 H15 Cl N2 O2 S       C15 H15 Cl N2 O2 S
Mr                322.81                   322.80
Dx,g cm-3         1.437                    1.437
Z                 4                        4
Mu (mm-1)         3.625                    3.625
F000              672.0                    672.0
F000'             676.44
h,k,lmax          6,14,30                  5,14,30
Nref              2748[ 1638]              2720
Tmin,Tmax         0.840,0.930              0.608,0.753
Tmin'             0.581

Correction method= MULTI-SCAN

Data completeness= 1.66/0.99      Theta(max)= 68.923

R(reflections)= 0.0430( 2437)      wR2(reflections)= 0.1053( 2720)

S = 1.039                    Npar= Npar = 225
```

The following ALERTS were generated. Each ALERT has the format
        test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

(R)-2c (+)
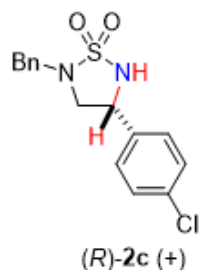
Alert level C
```
PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) ........      7.28 Note
PLAT220_ALERT_2_C Large Non-Solvent  C    Ueq(max)/Ueq(min) Range        5.0 Ratio
PLAT222_ALERT_3_C Large Non-Solvent     H    Uiso(max)/Uiso(min) ..       6.4 Ratio
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............    0.0063 Ang.
```

Alert level G
```
PLAT033_ALERT_4_G Flack x Value Deviates > 2*sigma from Zero .....     0.076
PLAT301_ALERT_3_G Main Residue  Disorder ............ Percentage =       29 Note
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........        4 Note
PLAT791_ALERT_4_G The Model has Chirality at C5       .............        R Verify
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ....        1 Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............       90 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   6 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   1 ALERT type 2 Indicator that the structure model may be wrong or deficient
   5 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

checkCIF publication errors

Alert level A
```
PUBL002_ALERT_1_A  The contact author's address is missing,
          _publ_contact_author_address.
PUBL005_ALERT_1_A  _publ_contact_author_email, _publ_contact_author_fax and
          _publ_contact_author_phone are all missing.
          At least one of these should be present.
PUBL006_ALERT_1_A  _publ_requested_journal is missing
          e.g. 'Acta Crystallographica Section C'
PUBL008_ALERT_1_A  _publ_section_title is missing. Title of paper.
PUBL009_ALERT_1_A  _publ_author_name is missing. List of author(s) name(s).
PUBL010_ALERT_1_A  _publ_author_address is missing. Author(s) address(es).
PUBL012_ALERT_1_A  _publ_section_abstract is missing.
          Abstract of paper in English.
```

```
   7 ALERT level A = Data missing that is essential or data in wrong format
   0 ALERT level G = General alerts. Data that may be required is missing
```

Publication of your CIF

You should attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the nature of your study may justify the reported deviations from journal submission requirements and the more serious of these should be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. *checkCIF* was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

If level A alerts remain, which you believe to be justified deviations, and you intend to submit this CIF for publication in a journal, you should additionally insert an explanation in your CIF using the Validation Reply Form (VRF) below. This will allow your explanation to be considered as part of the review process.

```
# start Validation Reply Form
_vrf_PUBL002_GLOBAL
;
PROBLEM: The contact author's address is missing.
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
```

(R)-2c (+)

If you wish to submit your CIF for publication in Acta Crystallographica Section C or E, you should upload your CIF via the web. If your CIF is to form part of a submission to another IUCr journal, you will be asked, either during electronic submission or by the Co-editor handling your paper, to upload your CIF via our web site.

PLATON version of 05/02/2014; check.def file version of 05/02/2014

Datablock I - ellipsoid plot

4: 230 nm, 4
nm Results

| Pk #	Retention Time	Area Percent
1	19.536	92.031
2	31.268	7.969

Totals	
	100.000

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: I
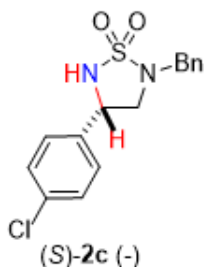
```
Bond precision:    C-C = 0.0049 A           Wavelength=1.54178

Cell:              a=4.9639(1)      b=11.8448(3)      c=25.3491(6)
                   alpha=90         beta=90           gamma=90
Temperature:       100 K

                   Calculated                Reported
Volume             1490.44(6)                1490.44(6)
Space group        P 21 21 21                P 21 21 21
Hall group         P 2ac 2ab                 P 2ac 2ab
Moiety formula     C15 H15 Cl N2 O2 S        C15 H15 Cl N2 O2 S
Sum formula        C15 H15 Cl N2 O2 S        C15 H15 Cl N2 O2 S
Mr                 322.81                    322.80
Dx,g cm-3          1.439                     1.439
Z                  4                         4
Mu (mm-1)          3.629                     3.629
F000               672.0                     672.0
F000'              676.45
h,k,lmax           6,14,30                   5,14,30
Nref               2747[ 1637]               2715
Tmin,Tmax          0.623,0.930               0.583,0.753
Tmin'              0.399

Correction method= MULTI-SCAN

Data completeness= 1.66/0.99       Theta(max)= 68.909

R(reflections)= 0.0348( 2547)      wR2(reflections)= 0.0878( 2715)

S = 1.065                  Npar= Npar = 225
```
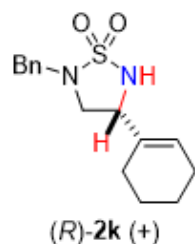
The following ALERTS were generated. Each ALERT has the format
      test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

(S)-2c (-)

(S)-2c (-)

checkCIF publication errors

(S)-2c (-)

checkCIF publication errors

Publication of your CIF

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```
# start Validation Reply Form
_vrf_PUBL002_GLOBAL
;
PROBLEM: The contact author's address is missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
```

(S)-2c (-)

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PLATON version of 05/02/2014; check.def file version of 05/02/2014

Datablock I - ellipsoid plot

^{1}H NMR, 500MHz, CDCl$_3$

2d

^{13}C NMR, 150MHz, CDCl$_3$

2d

quartet (J = 271.5 Hz)

quartet (J = 33.0 Hz)

quartet (J = 4.5 Hz)

50.65
54.81
55.36

76.95
77.16
77.37

121.23
123.03
124.84
126.11
126.13
126.16
126.18
126.64
126.90
128.53
128.87
129.01
130.82
131.03
131.25
131.47
134.68
142.73

130.82
131.03
131.25
131.47

126.11
126.13
126.16
126.18

126.10
126.20

4: 222 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	14.560	50.057
2	28.216	49.943

Totals	
	100.000
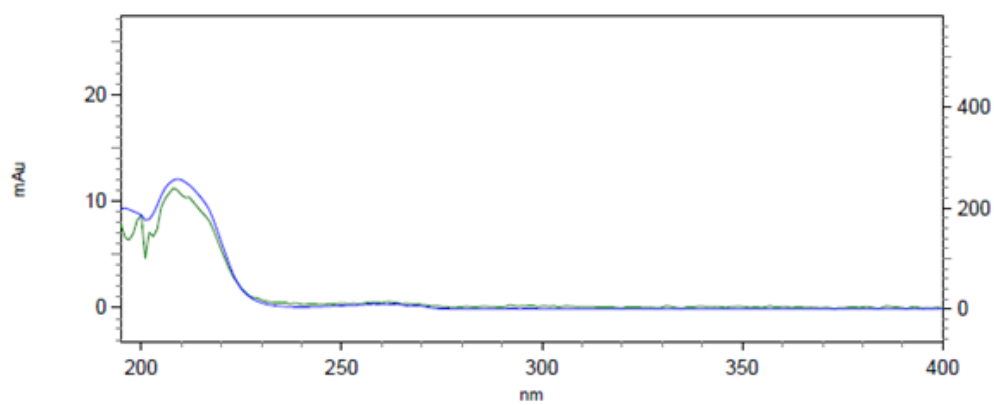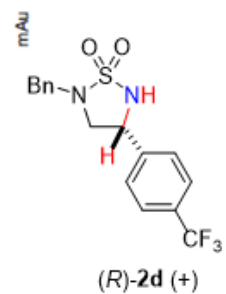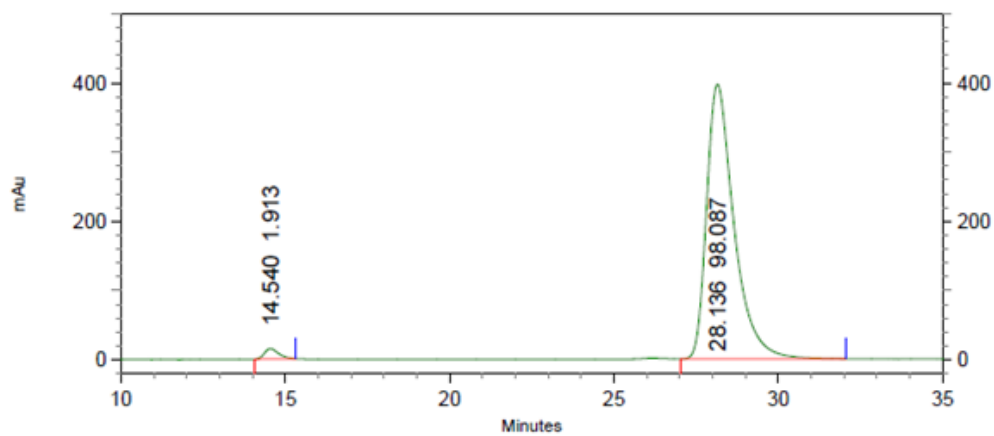
4: 220 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	14.540	1.913
2	28.136	98.087

Totals	
	100.000

(S)-2d (-)
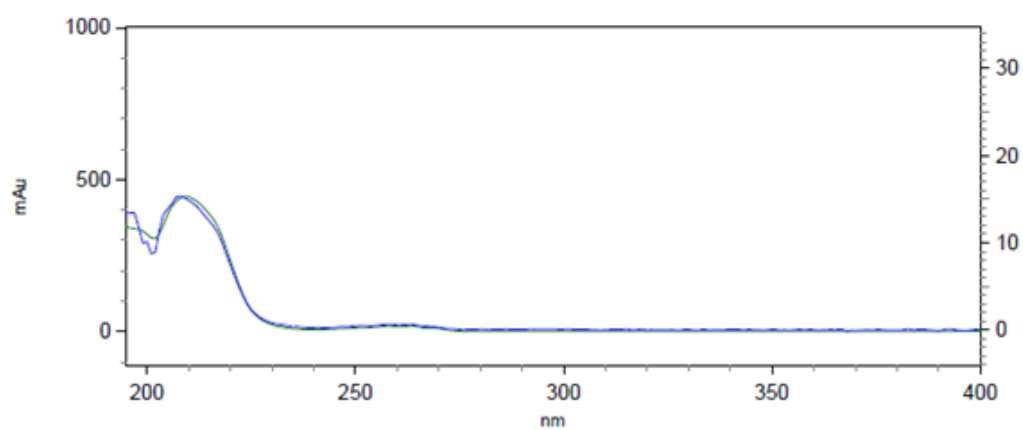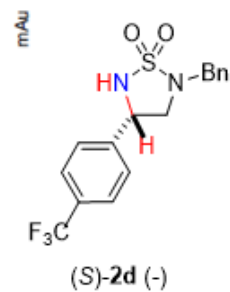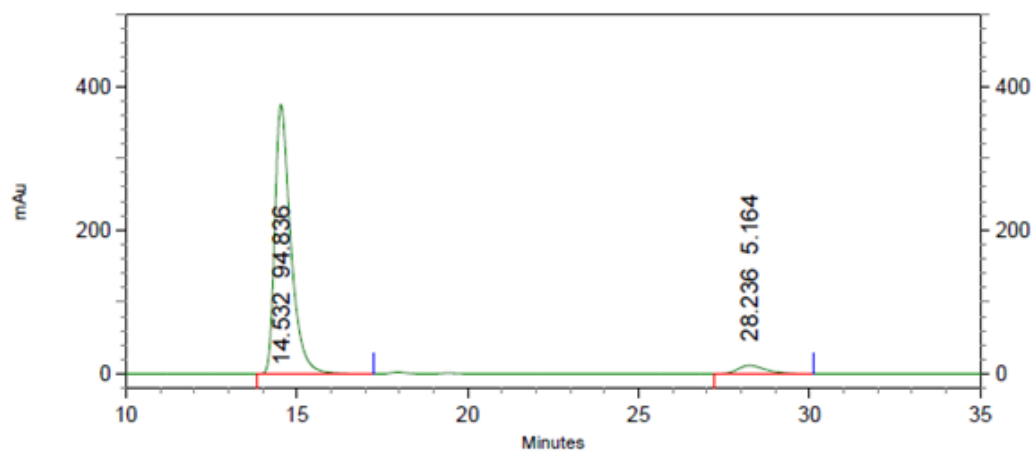
4: 220 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	14.532	94.836
2	28.236	5.164

Totals	
	100.000

¹H NMR, 500MHz, CDCl₃

2e

13C NMR, 125MHz, CDCl₃

2e

2e (±)
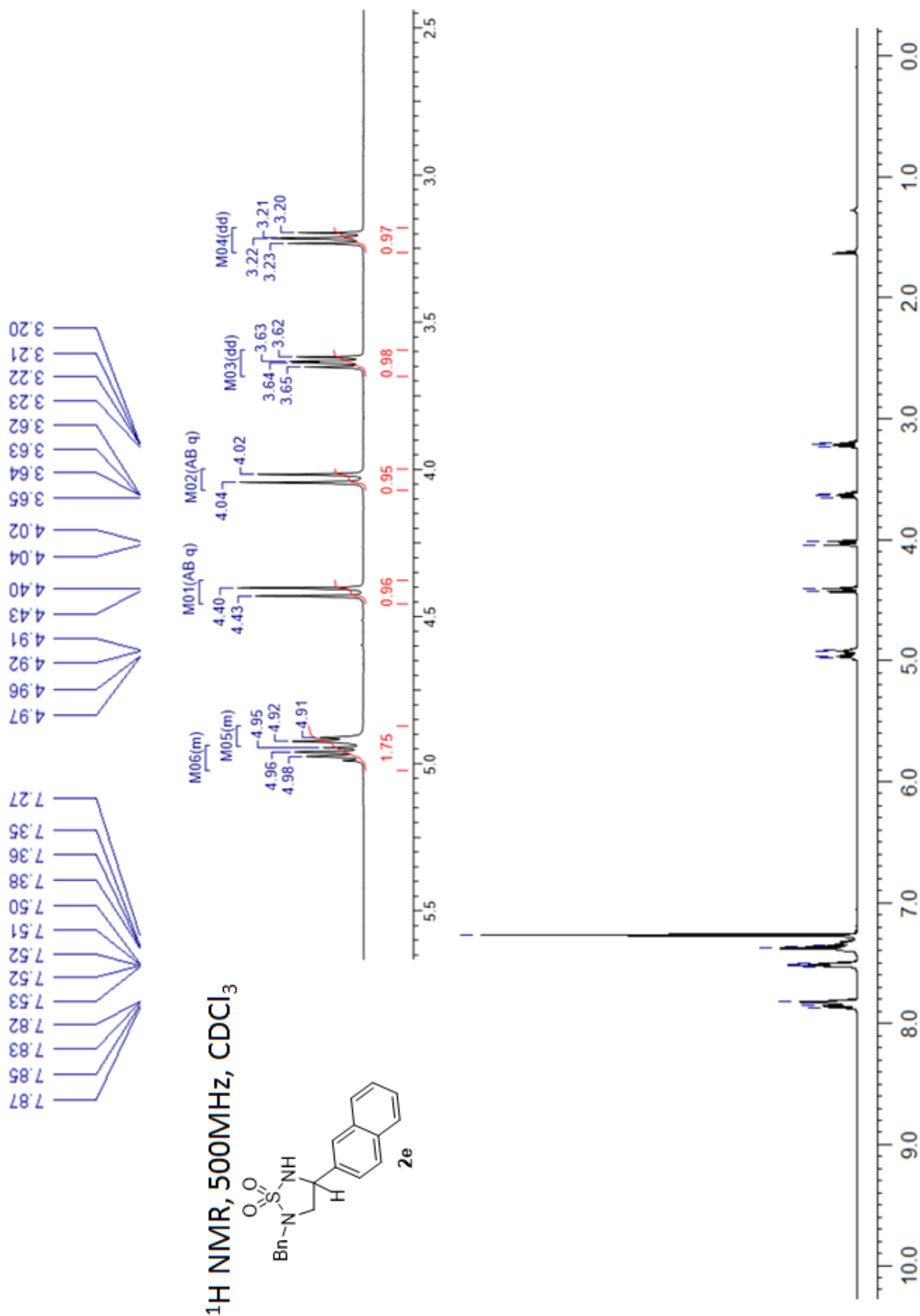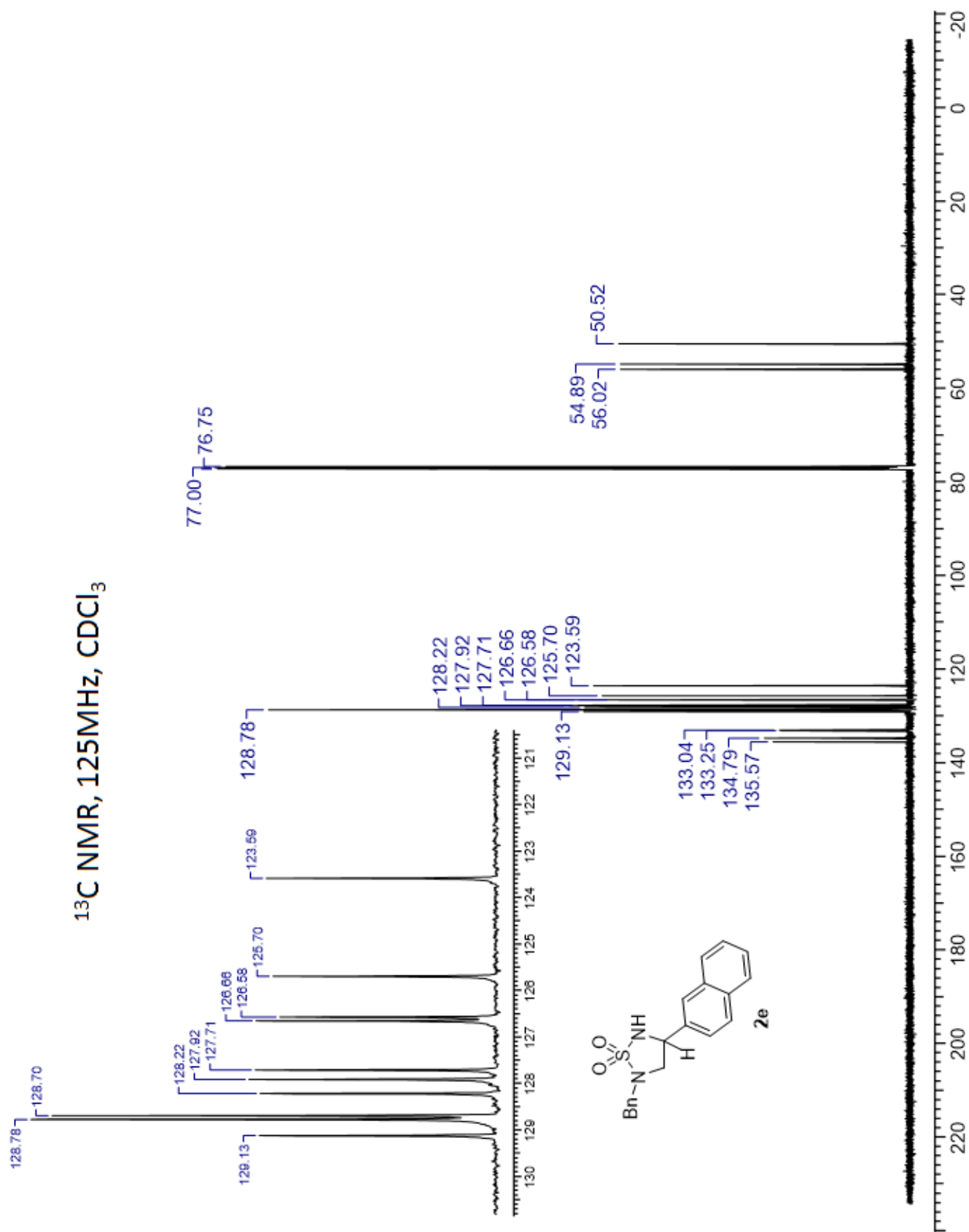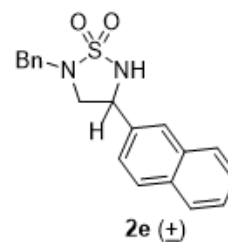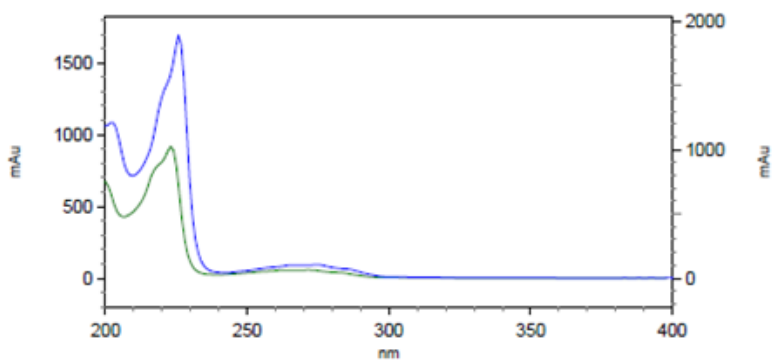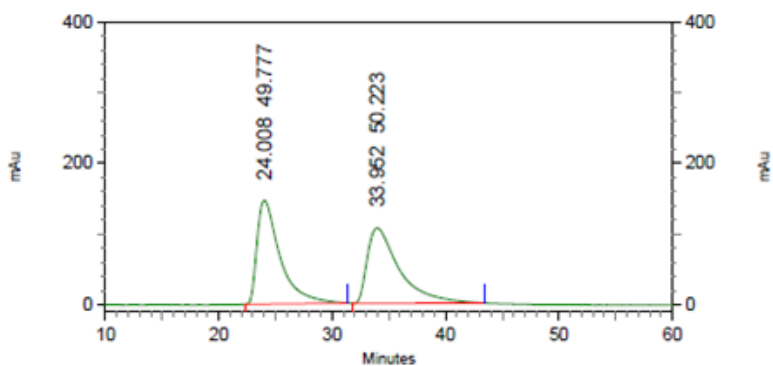
1: 232 nm, 4 nm
 Results

Name	Retention Time	Area Percent	Pk #
	24.008	49.777	1
	33.952	50.223	2

Totals	
	100.000

(R)-2e (+)
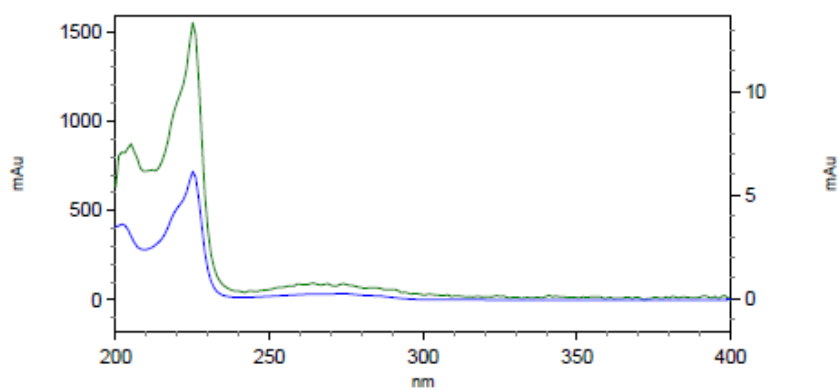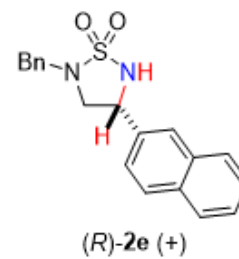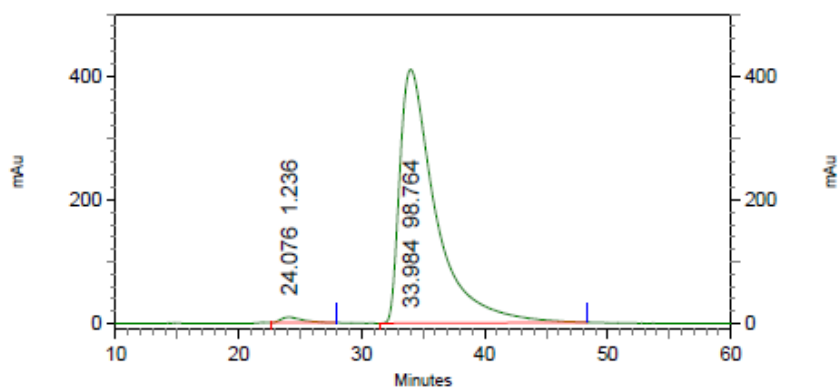
1: 223 nm, 4 nm

Results

Name	Retention Time	Area Percent	Pk #
	24.076	1.236	1
	33.984	98.764	2

Totals			
		100.000	
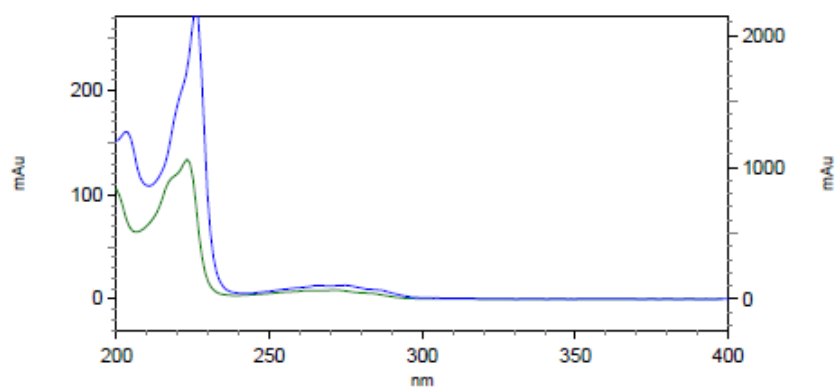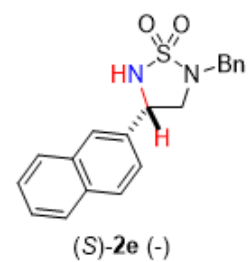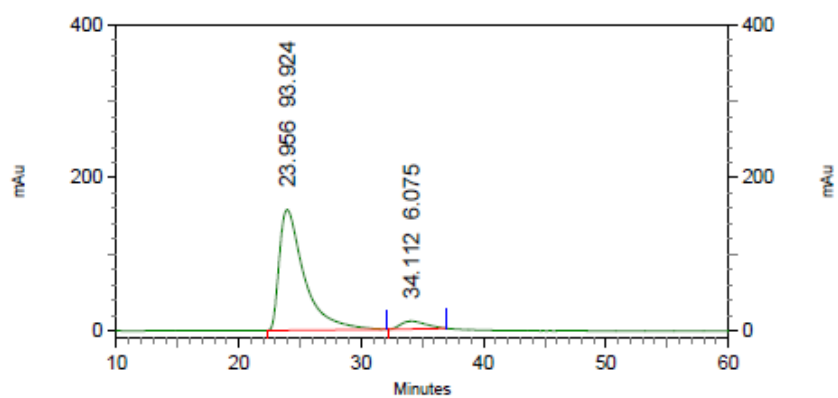
1: 232 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	23.956	93.924	1
	34.112	6.075	2
Totals			
		100.000	

¹H NMR, 400MHz, CDCl₃

2f

^{13}C NMR, 100MHz, CDCl$_3$

28.12
49.47
50.46
53.15
76.99
76.67
77.31
84.35
115.57
117.15
119.18
123.05
124.01
125.16
127.42
128.24
128.68
128.79
134.85
135.86
149.24

2f
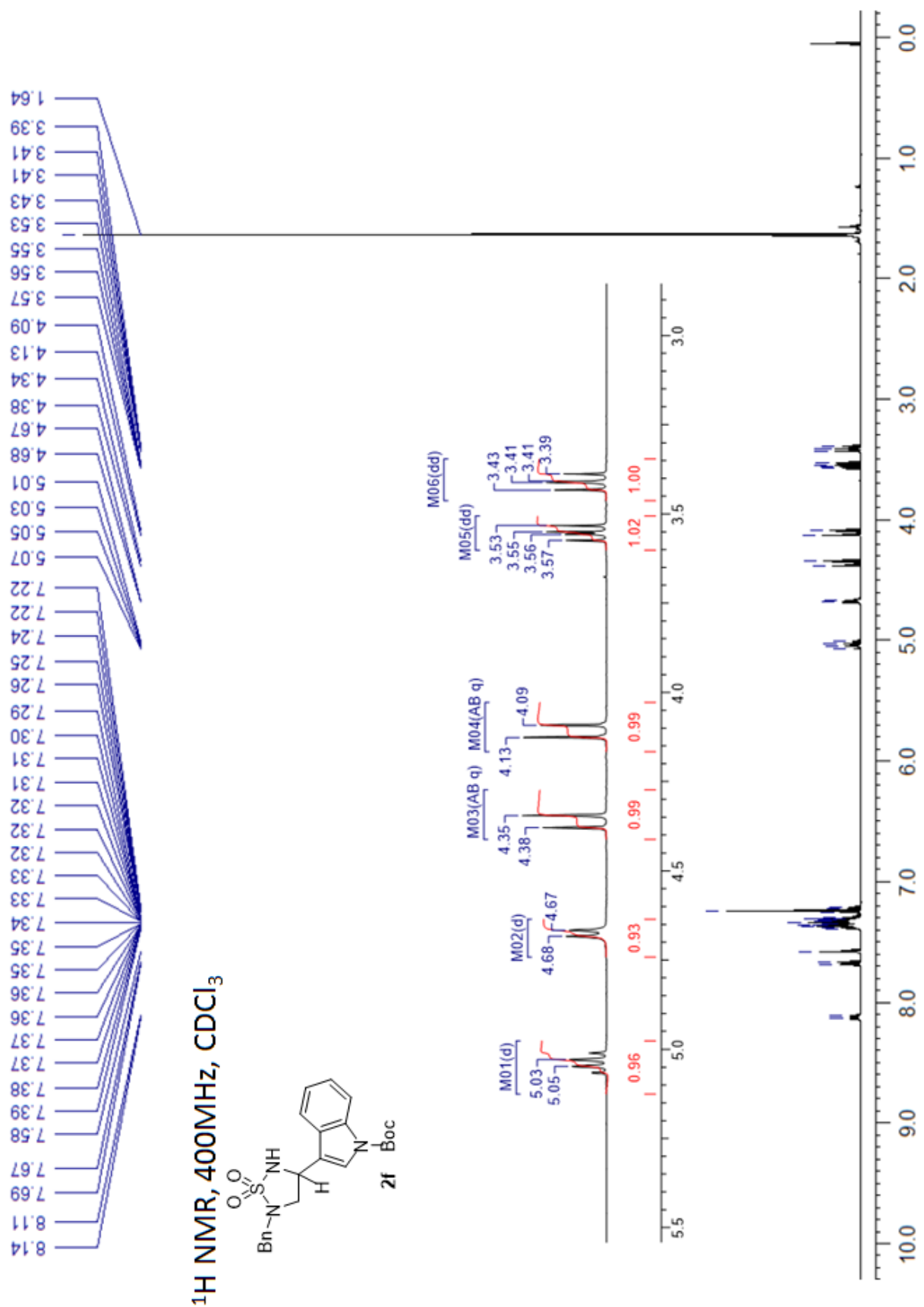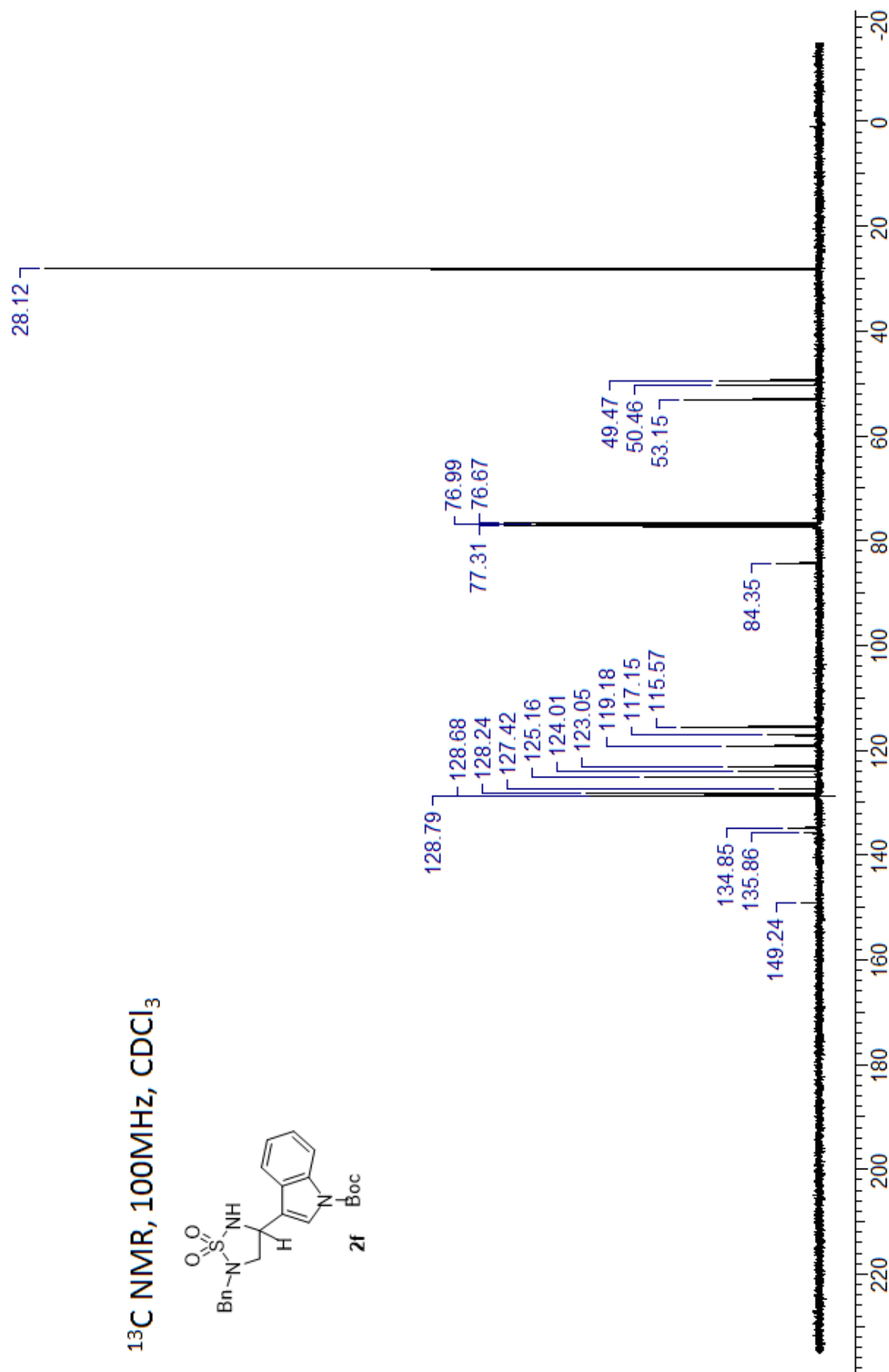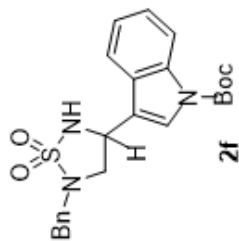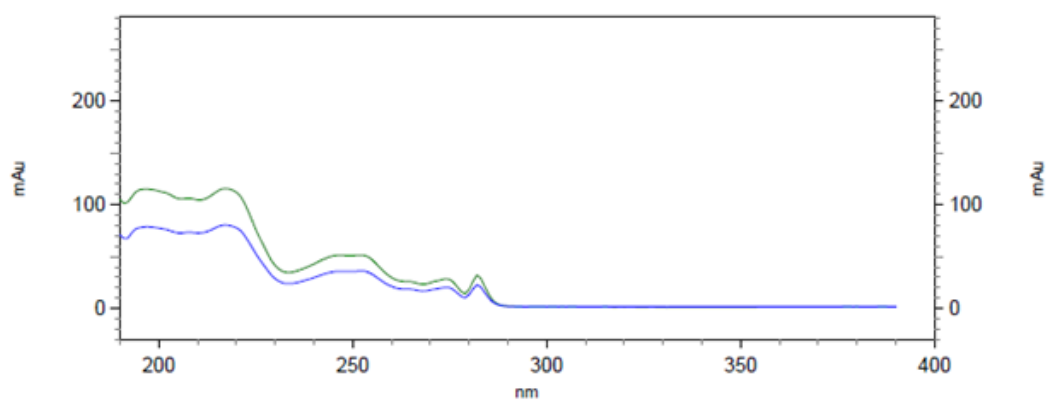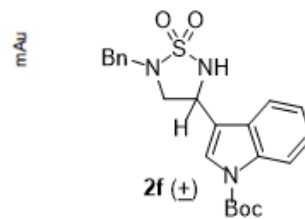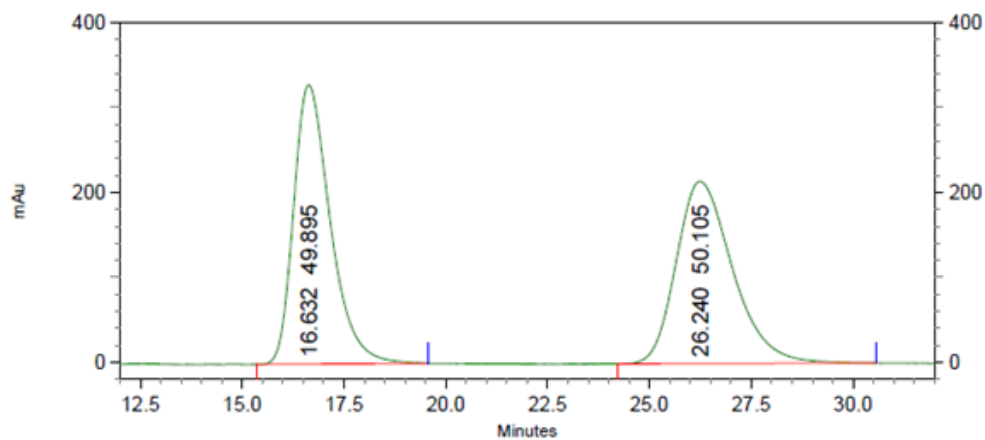
4: 235 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	16.632	49.895
2	26.240	50.105

Totals	
	100.000

(R)-**2f** (+)
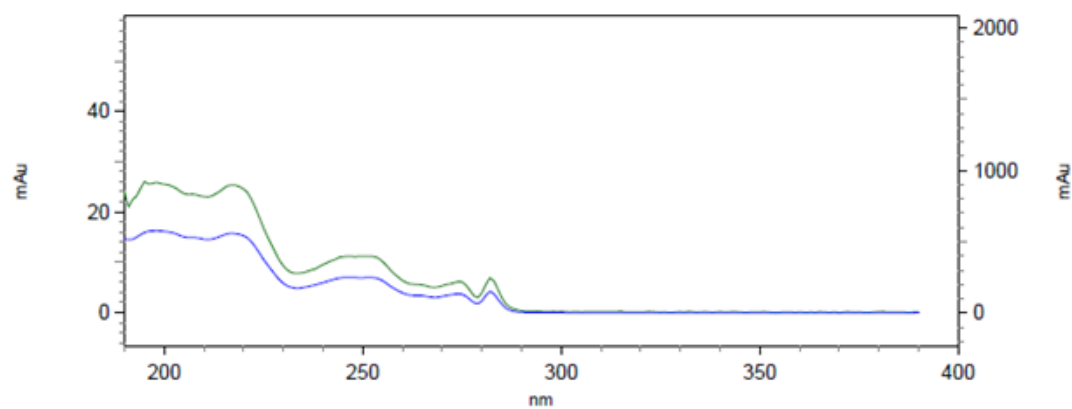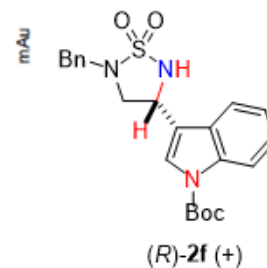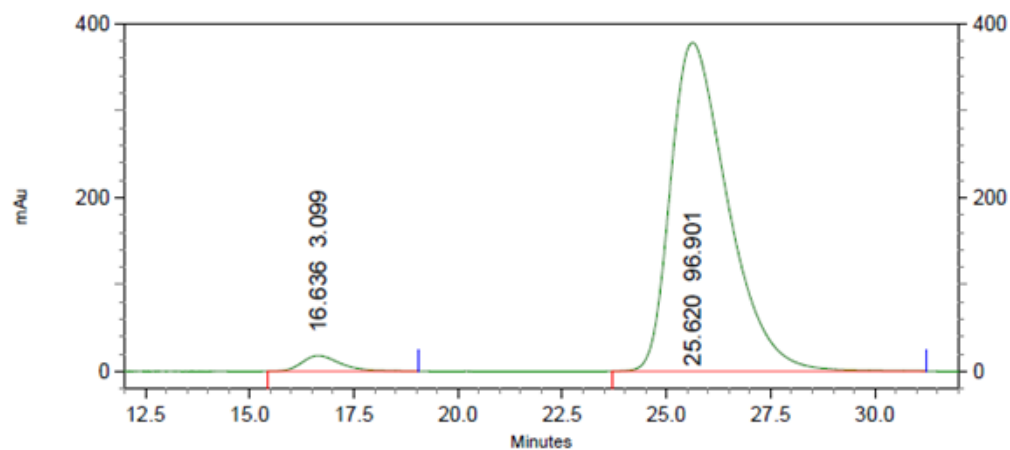
4: 235 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	16.636	3.099
2	25.620	96.901

Totals	
	100.000

(S)-**2f** (-)
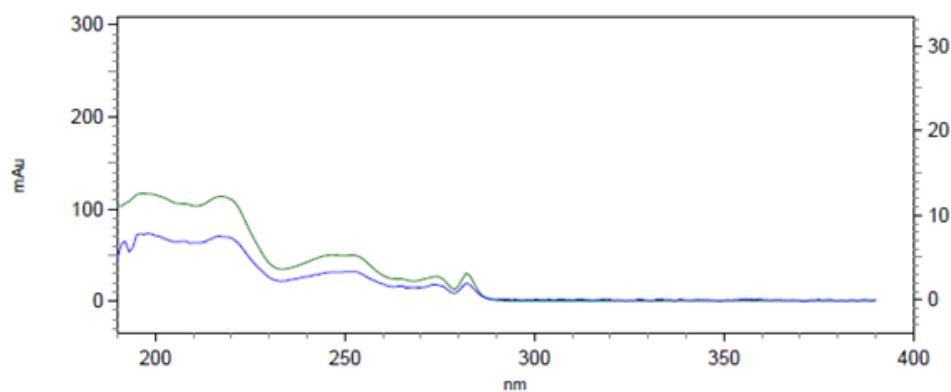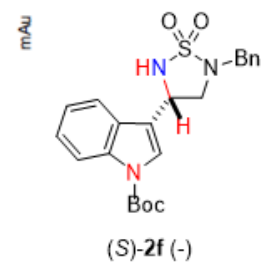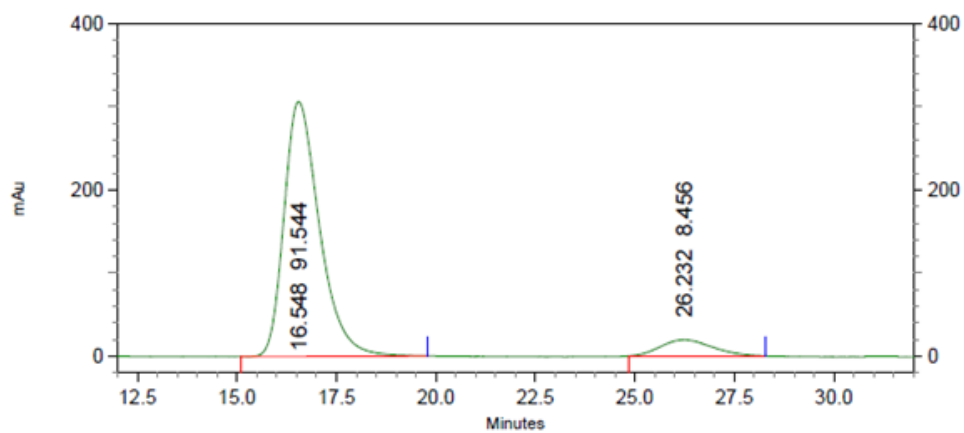
4: 235 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	16.548	91.544
2	26.232	8.456

Totals	
	100.000
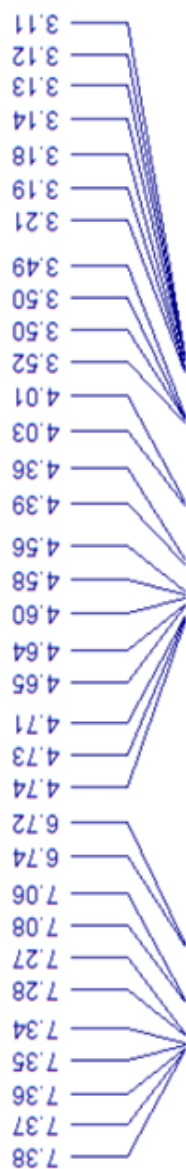
^{1}H NMR, 500MHz, CDCl$_3$

2g

Peak assignments:
- M01 (AB q): 4.56, 4.36
- M02 (AB q): 4.01
- M03 (dd): 3.49, 3.50, 3.50, 3.52
- M04 (t): 3.20, 3.21
- M05 (dd): 3.18, 3.14, 3.13, 3.12, 3.11
- M06 (t)
- M07 (d): 4.58
- M08 (q)
- M09 (d): 6.72, 6.74
- M10 (d): 7.08, 7.06

Chemical shifts listed:
3.11, 3.12, 3.13, 3.14, 3.18, 3.19, 3.21, 3.49, 3.50, 3.50, 3.52, 4.01, 4.03, 4.36, 4.39, 4.56, 4.58, 4.60, 4.64, 4.65, 4.71, 4.73, 4.74, 6.72, 6.74, 7.06, 7.08, 7.27, 7.28, 7.34, 7.35, 7.36, 7.37, 7.38

Integrations: 2.02, 1.05, 1.05, 1.04, 1.10, 2.02, 1.08, 1.10, 0.98, 0.93, 1.00

13C NMR, 125MHz, CDCl$_3$

2g
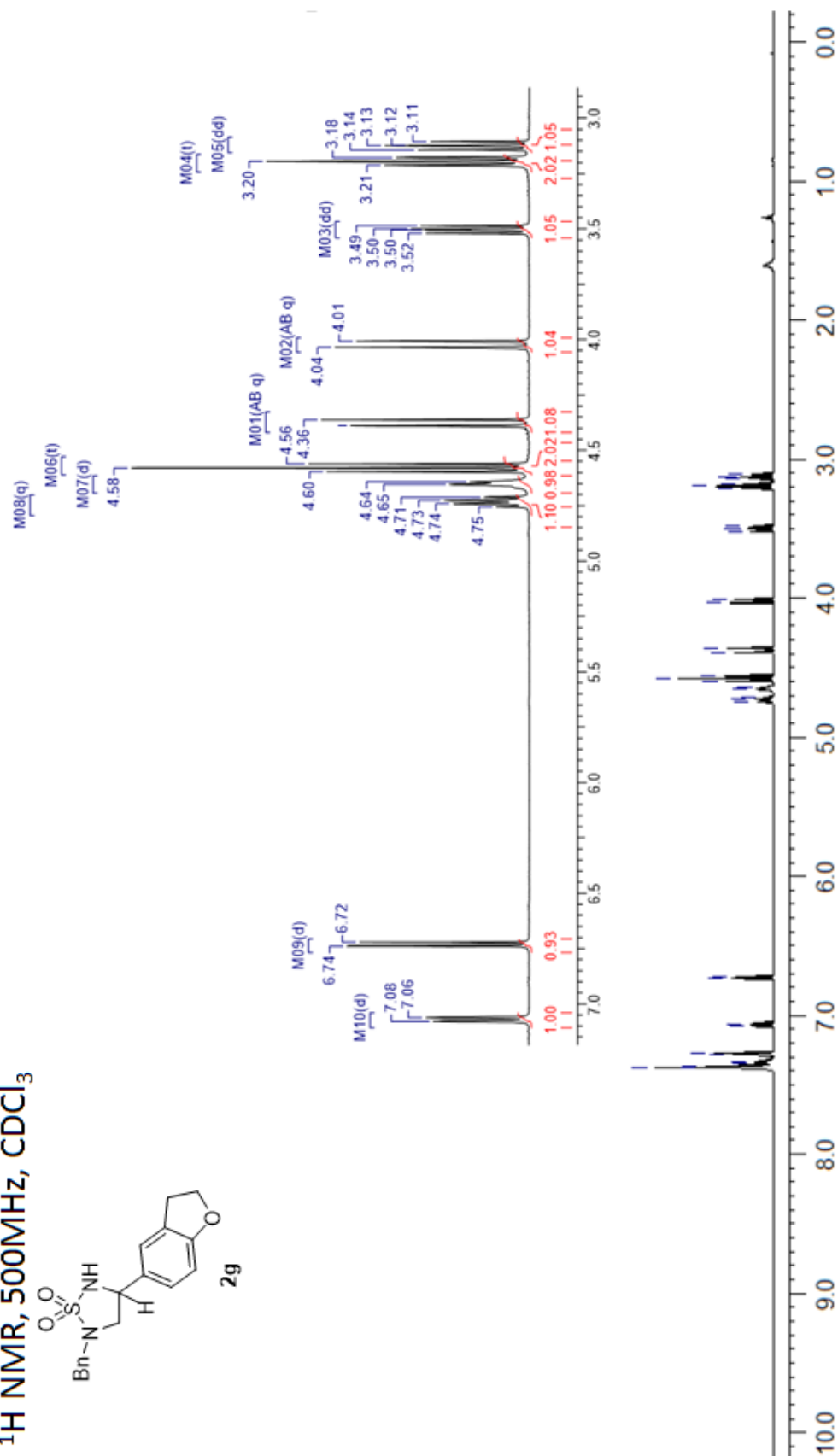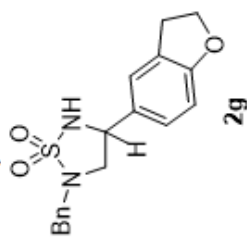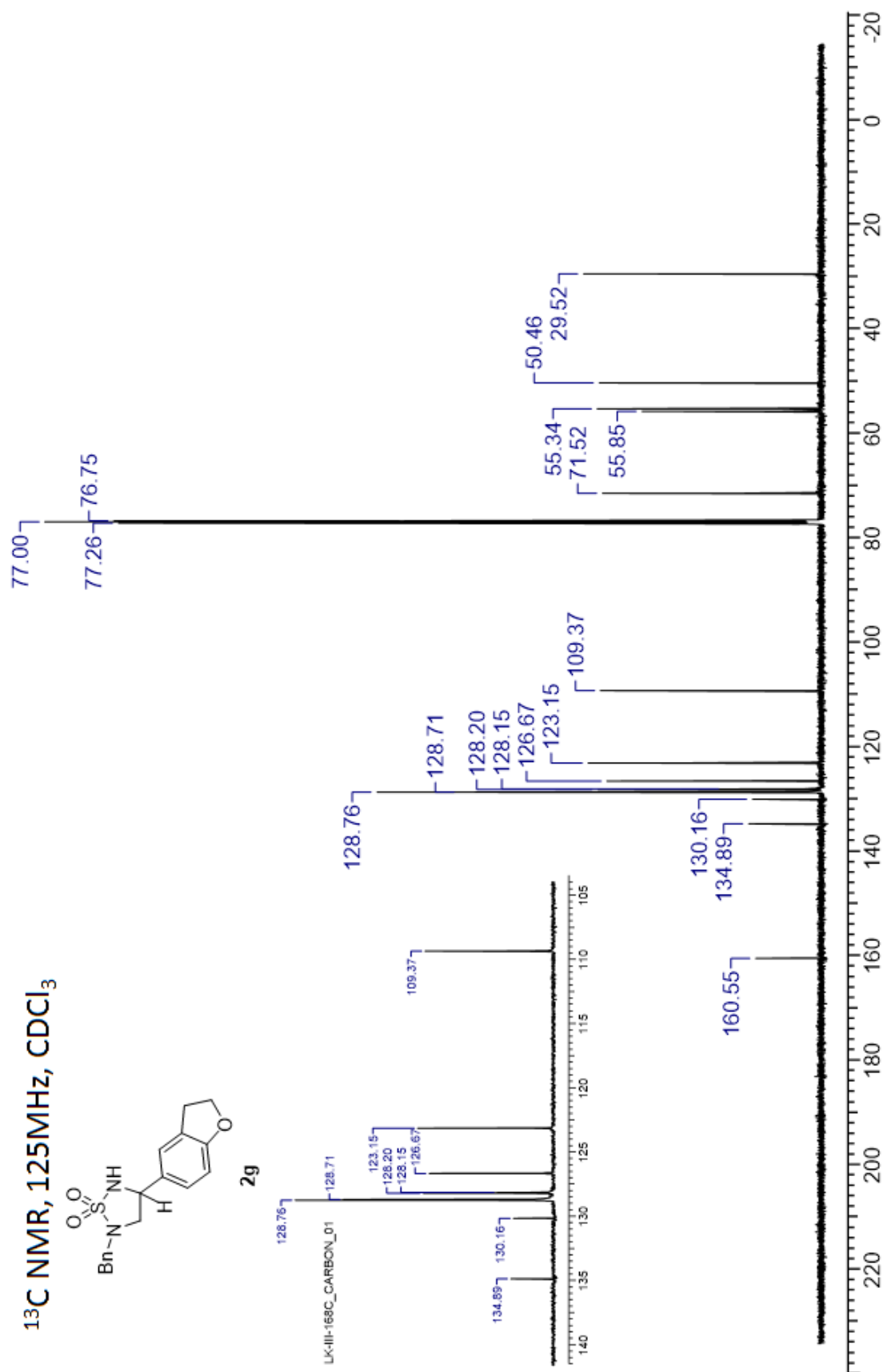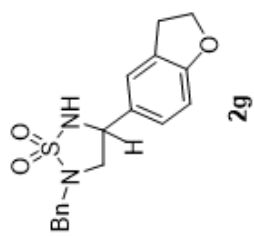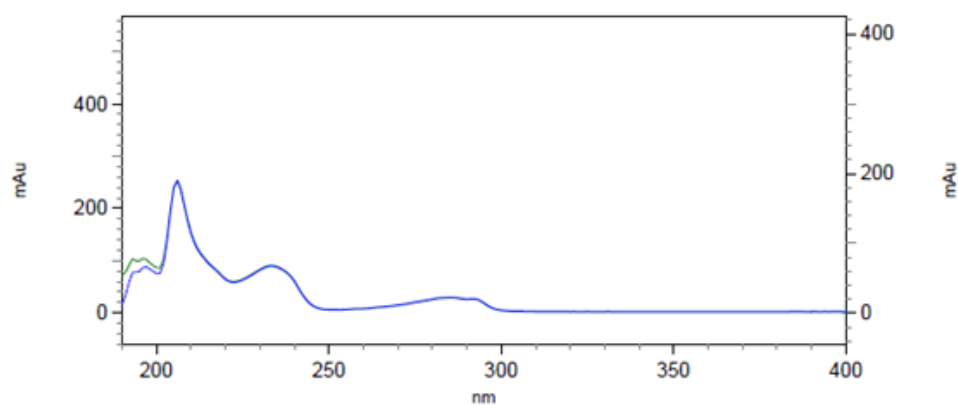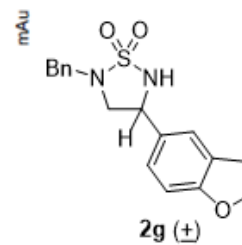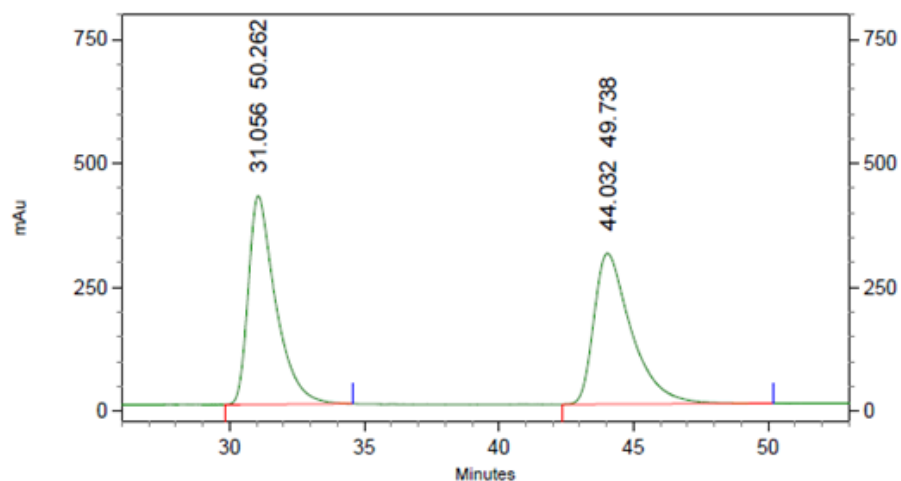
1: 222 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	31.056	50.262
2	44.032	49.738

Totals	
	100.000
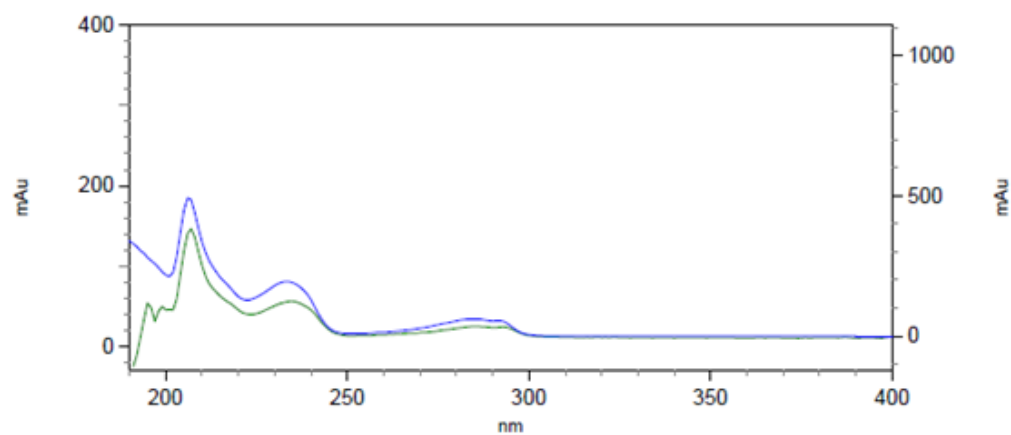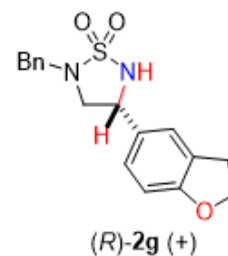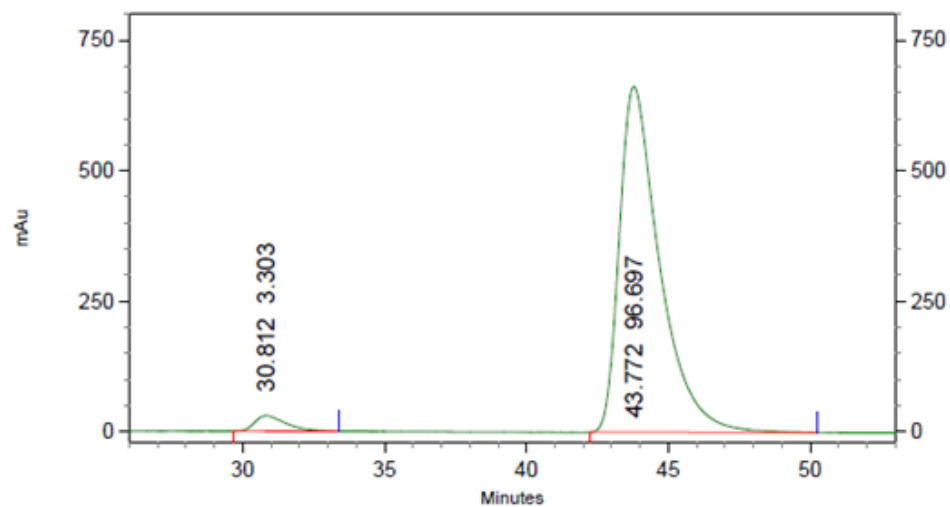
1: 222 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	30.812	3.303
2	43.772	96.697

Totals	
	100.000

(S)-**2g** (-)
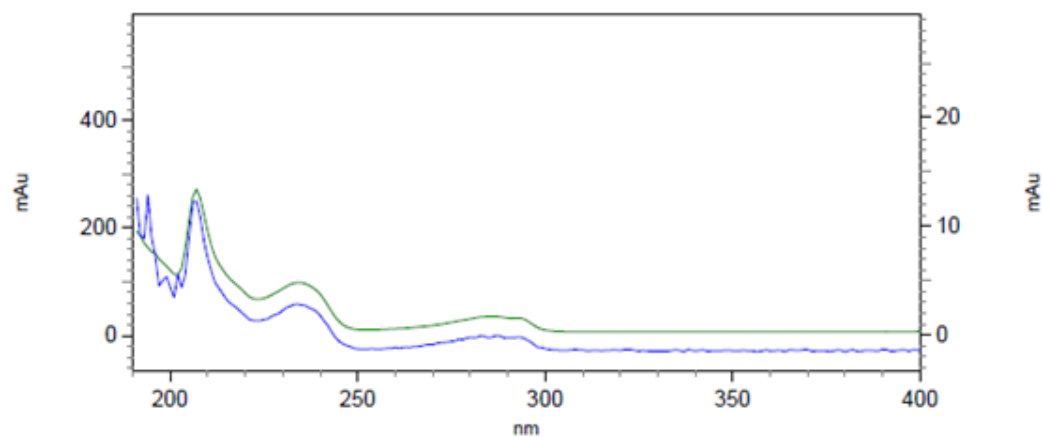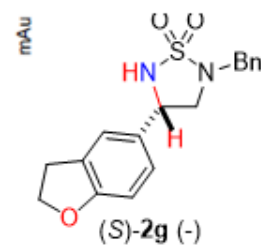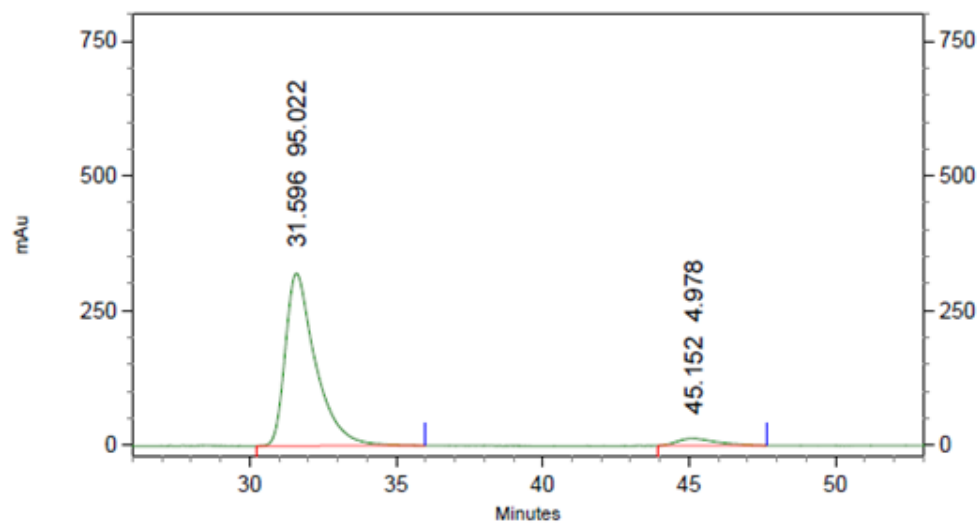
1: 222 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	31.596	95.022
2	45.152	4.978

Totals	
	100.000

^{1}H NMR, 500MHz, Acetone-D_6

2h

^{13}C NMR, 150 MHz, CDCl$_3$

141.07
136.80
134.90
132.46
128.96
128.90
128.42
128.02
124.55
123.25
122.52
120.70

50.74
54.15
54.90

76.95
77.16
77.37

120.70
122.52
123.25
124.55
128.02
128.42
128.90
128.96
132.46
134.90
136.80
141.07

2h
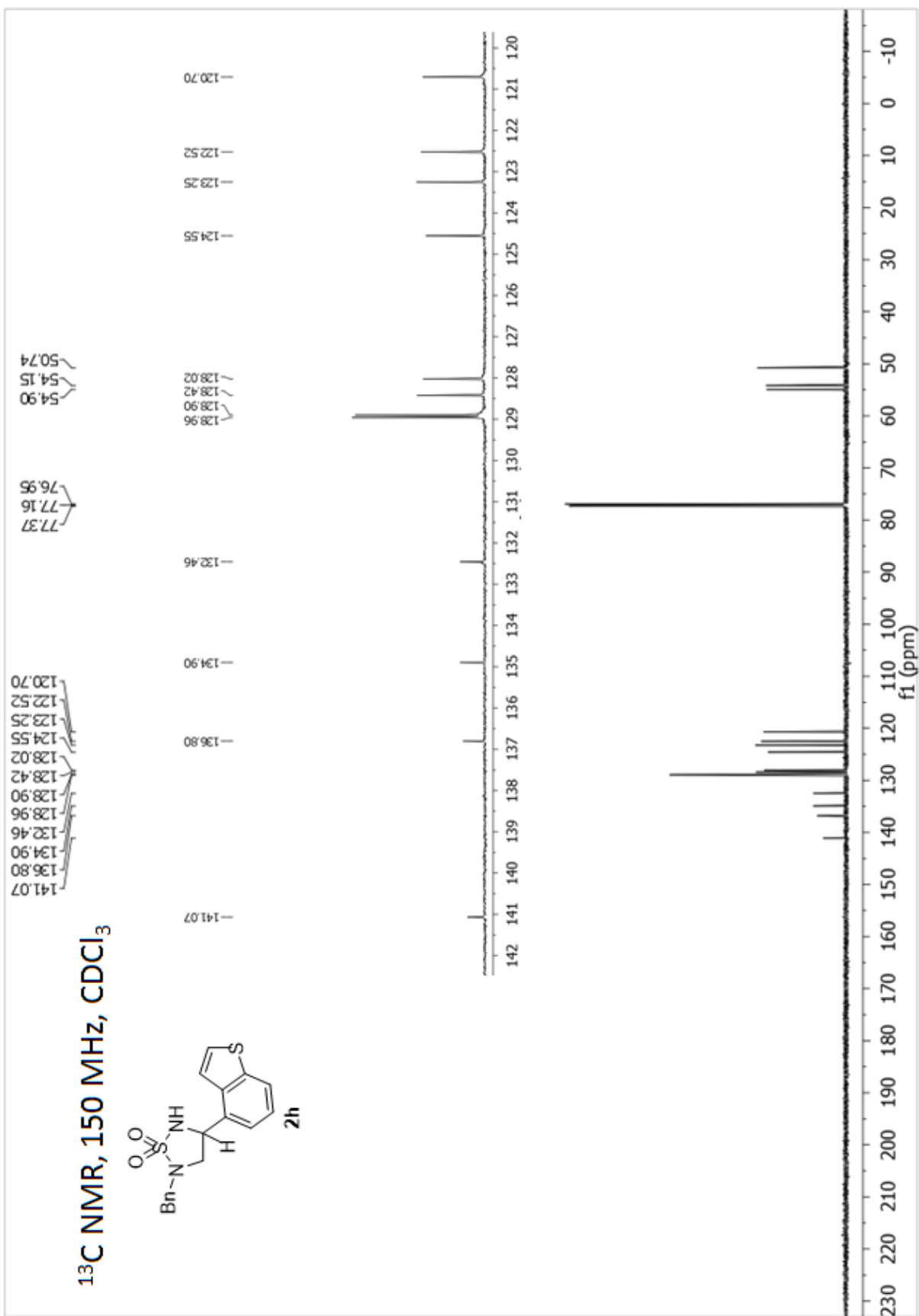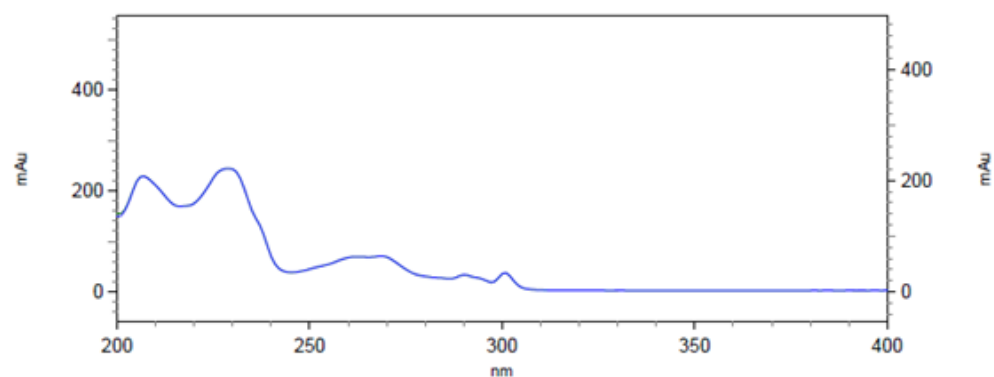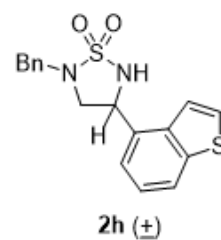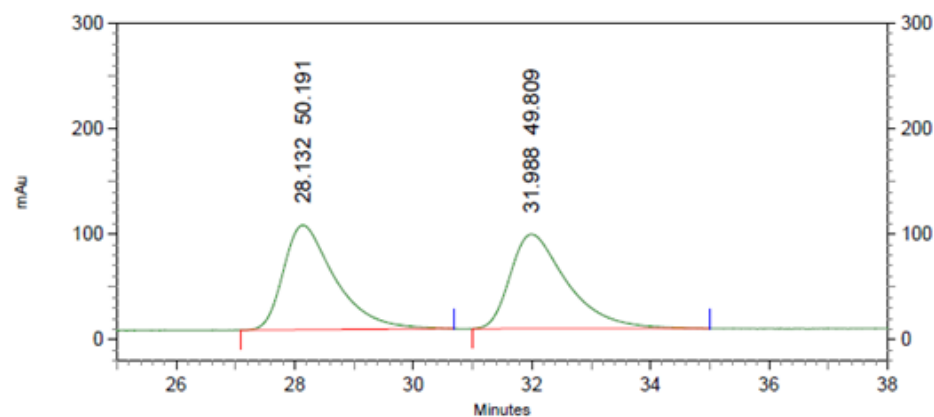
4: 284 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	28.132	50.191
2	31.988	49.809

Totals	
	100.000
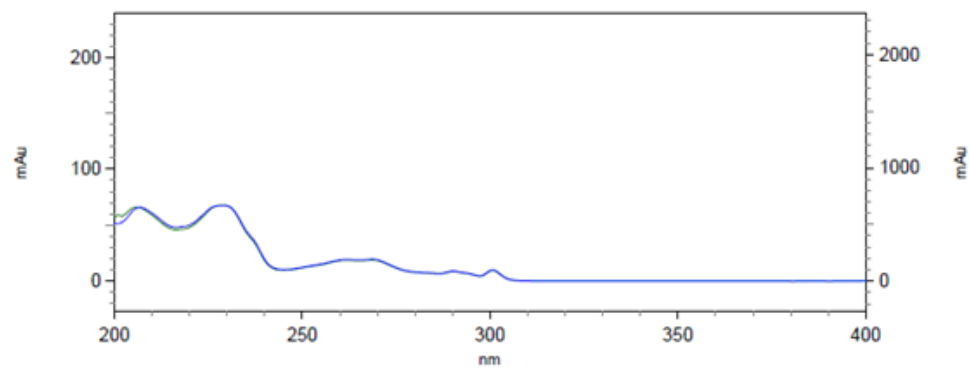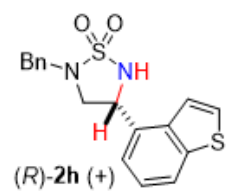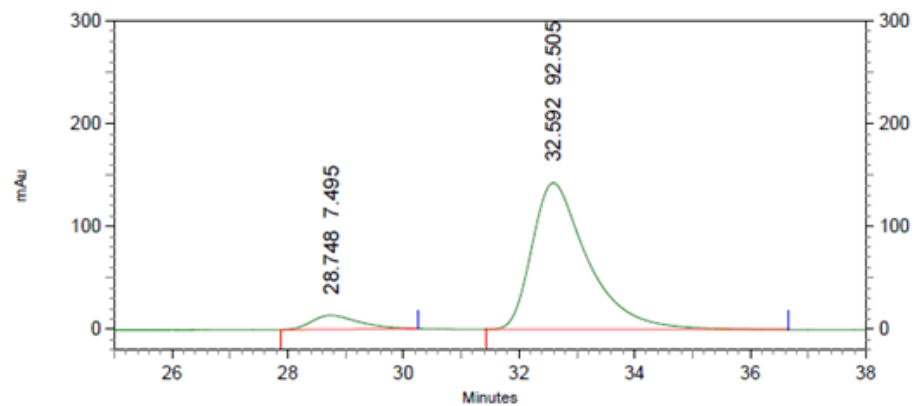
4: 284 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	28.748	7.495
2	32.592	92.505

Totals	
	100.000
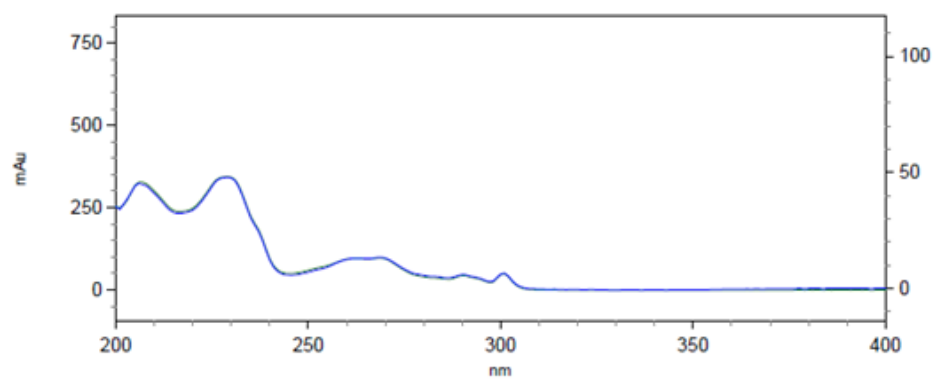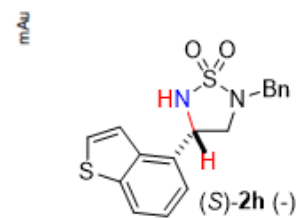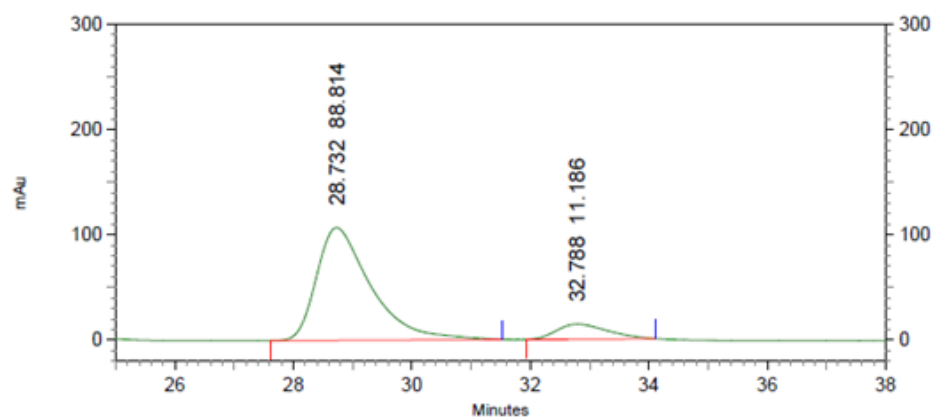
4: 284 nm, 4
nm Results

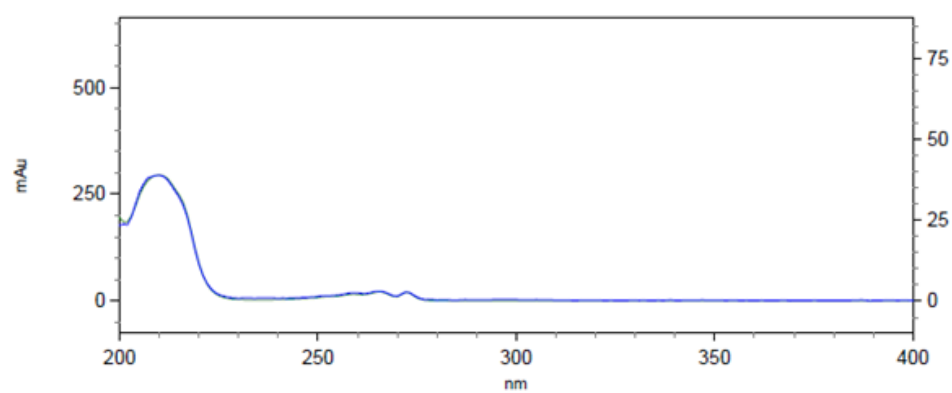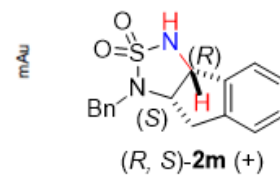| Pk #	Retention Time	Area Percent
1	28.732	88.814
2	32.788	11.186

Totals	
	100.000

¹H NMR, 500MHz, CDCl₃

2i

^{13}C NMR, 125MHz, CDCl$_3$

2i

12.97

25.07

50.39
53.44
54.74

76.74
77.00

128.12
125.38

128.60
128.73

135.05
138.08
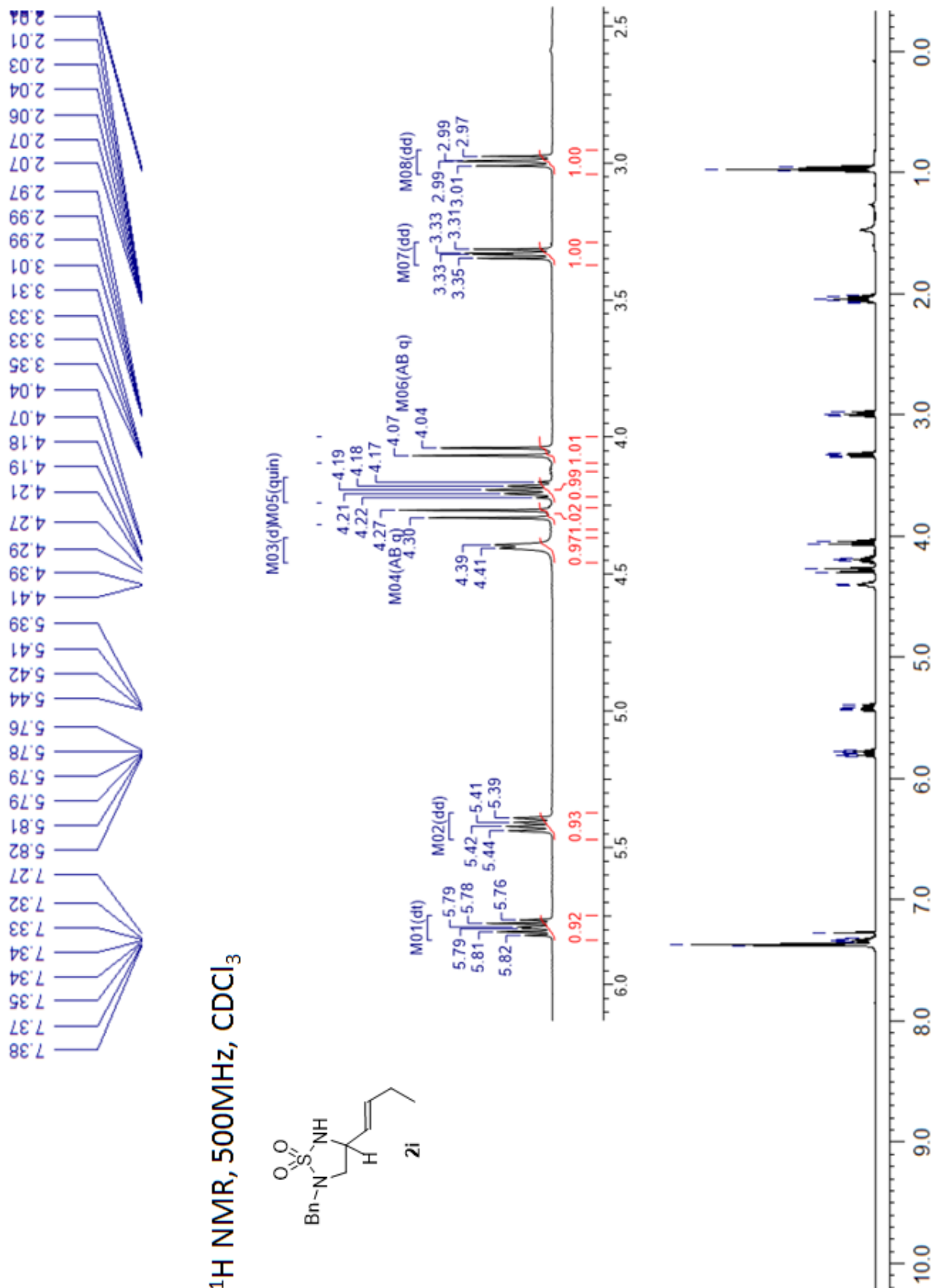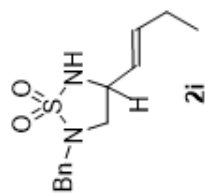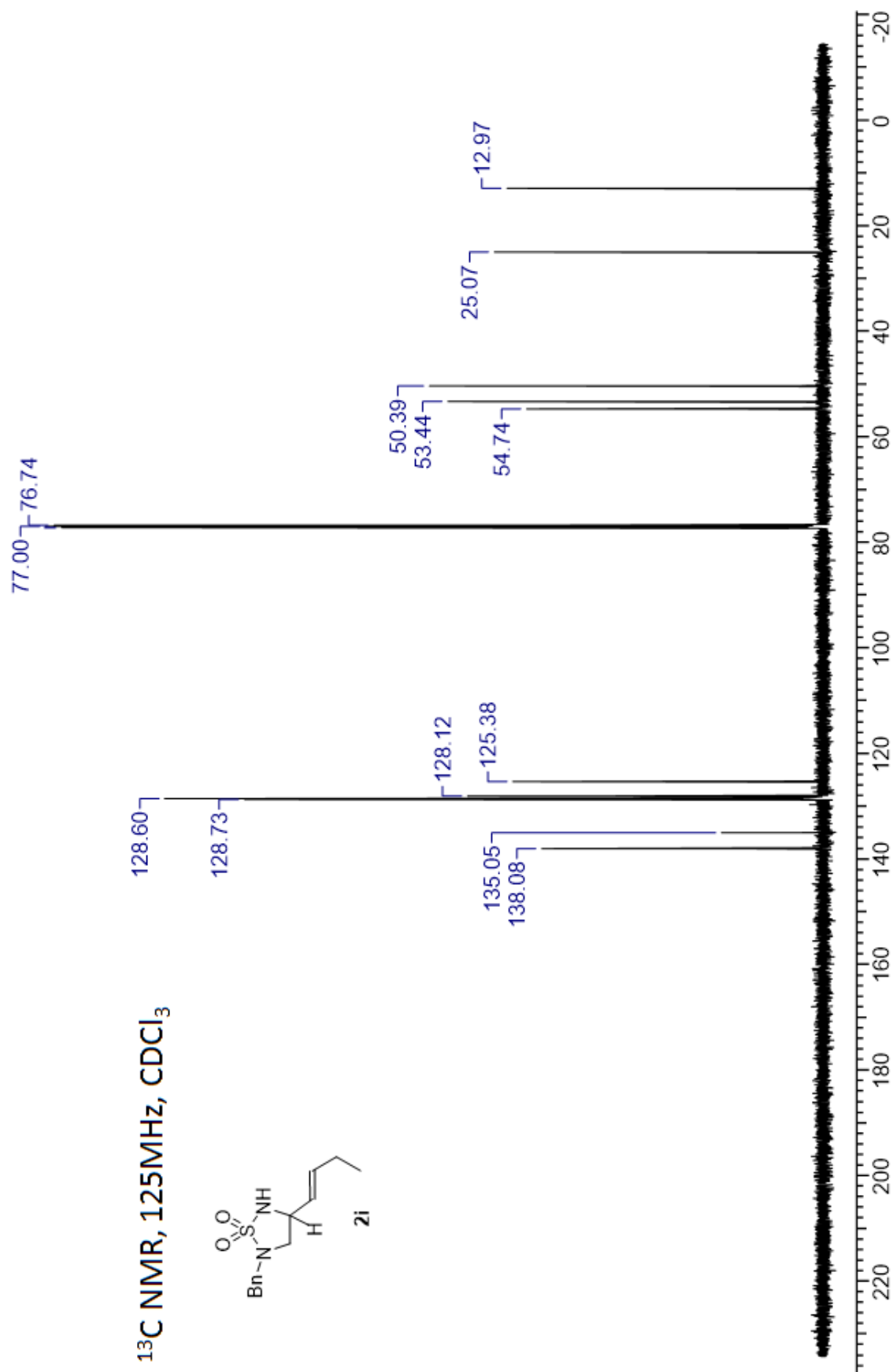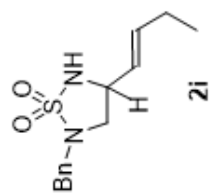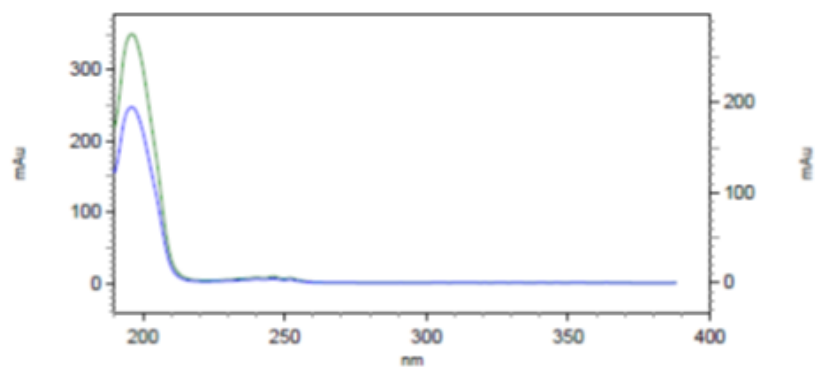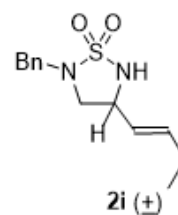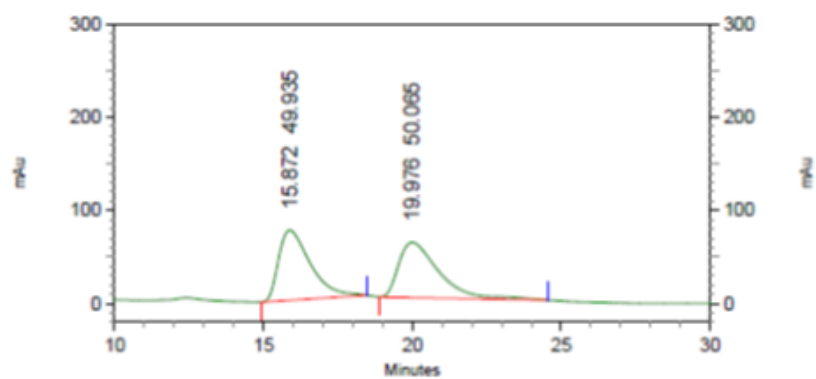
5: 201 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	15.872	49.935	1
	19.976	50.065	2

Totals		
	100.000	
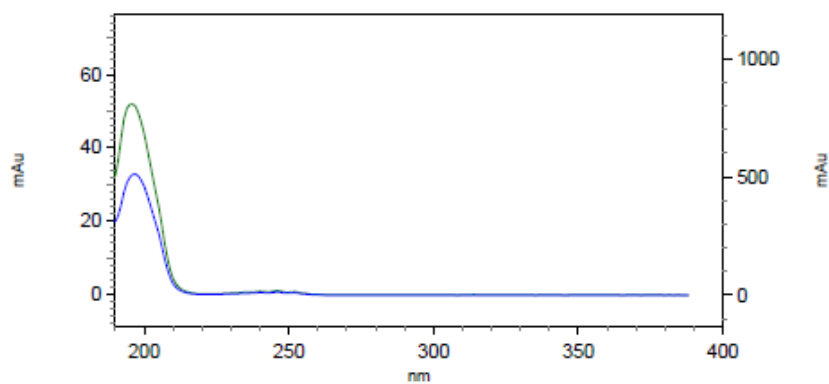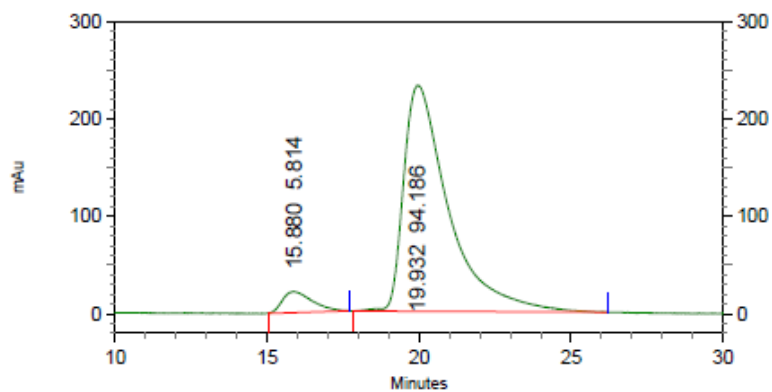
5: 196 nm, 4 nm
 Results

Name	Retention Time	Area Percent	Pk #
	15.880	5.814	1
	19.932	94.186	2

Totals		
	100.000	
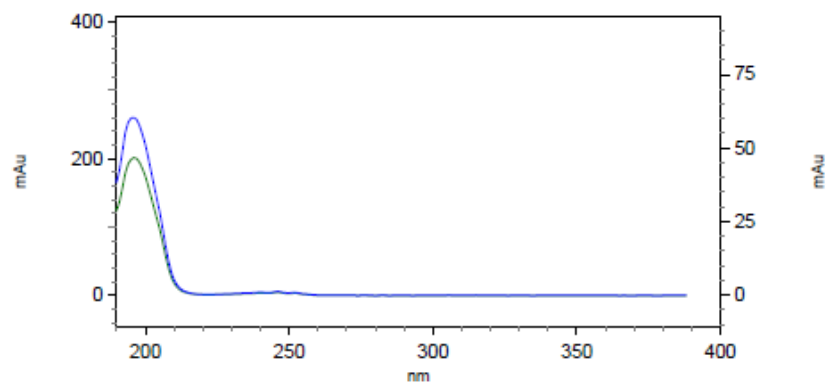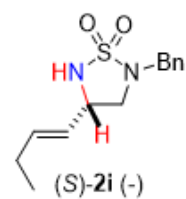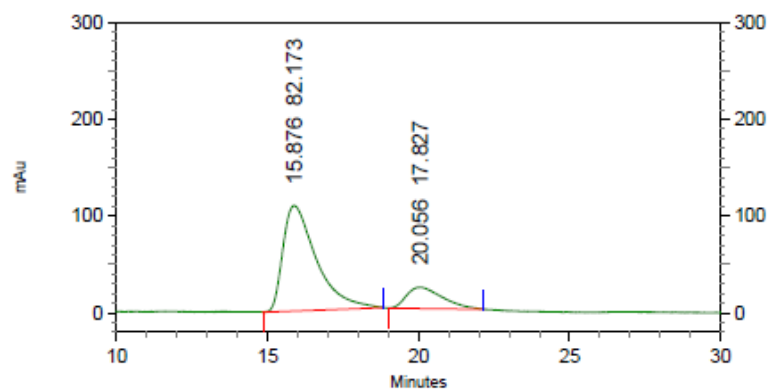
5: 196 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	15.876	82.173	1
	20.056	17.827	2

Totals		
	100.000	

¹H NMR, 500MHz, CDCl₃

2j

^{13}C NMR, 125MHz, CDCl$_3$

2j

128.62
128.16
126.68
114.90
135.07
136.22
138.20
77.28
77.02
76.77
53.44
54.71
27.87
50.34.40
33.05
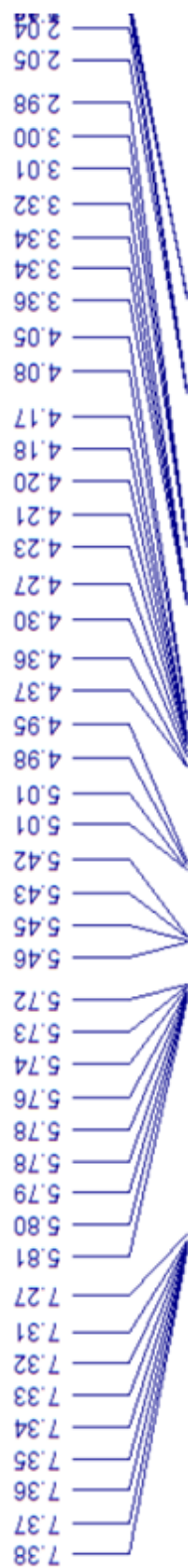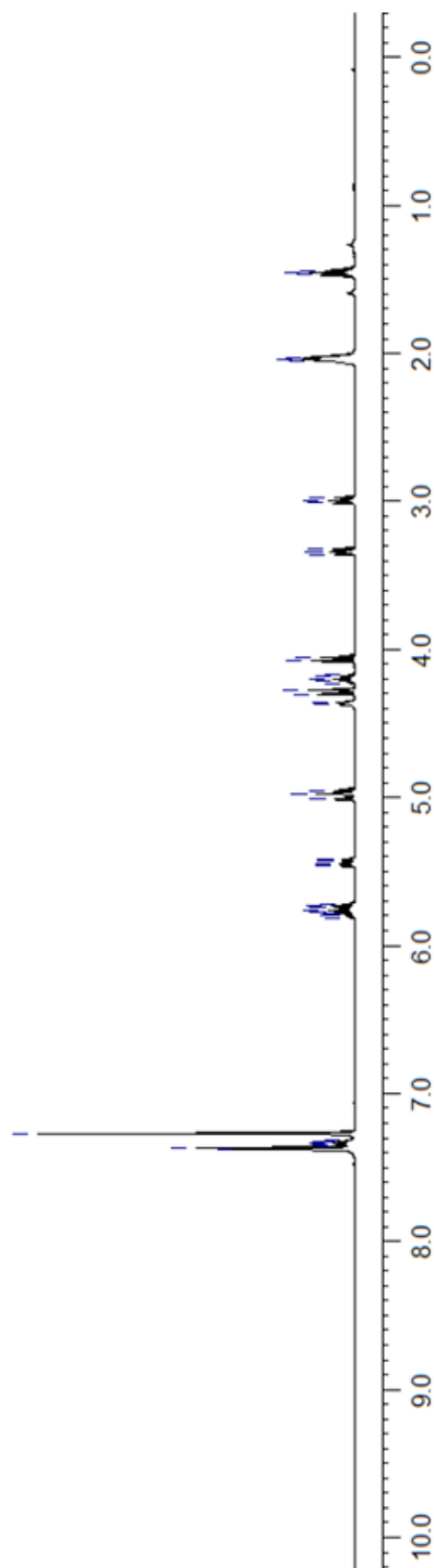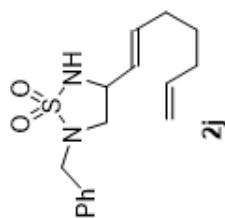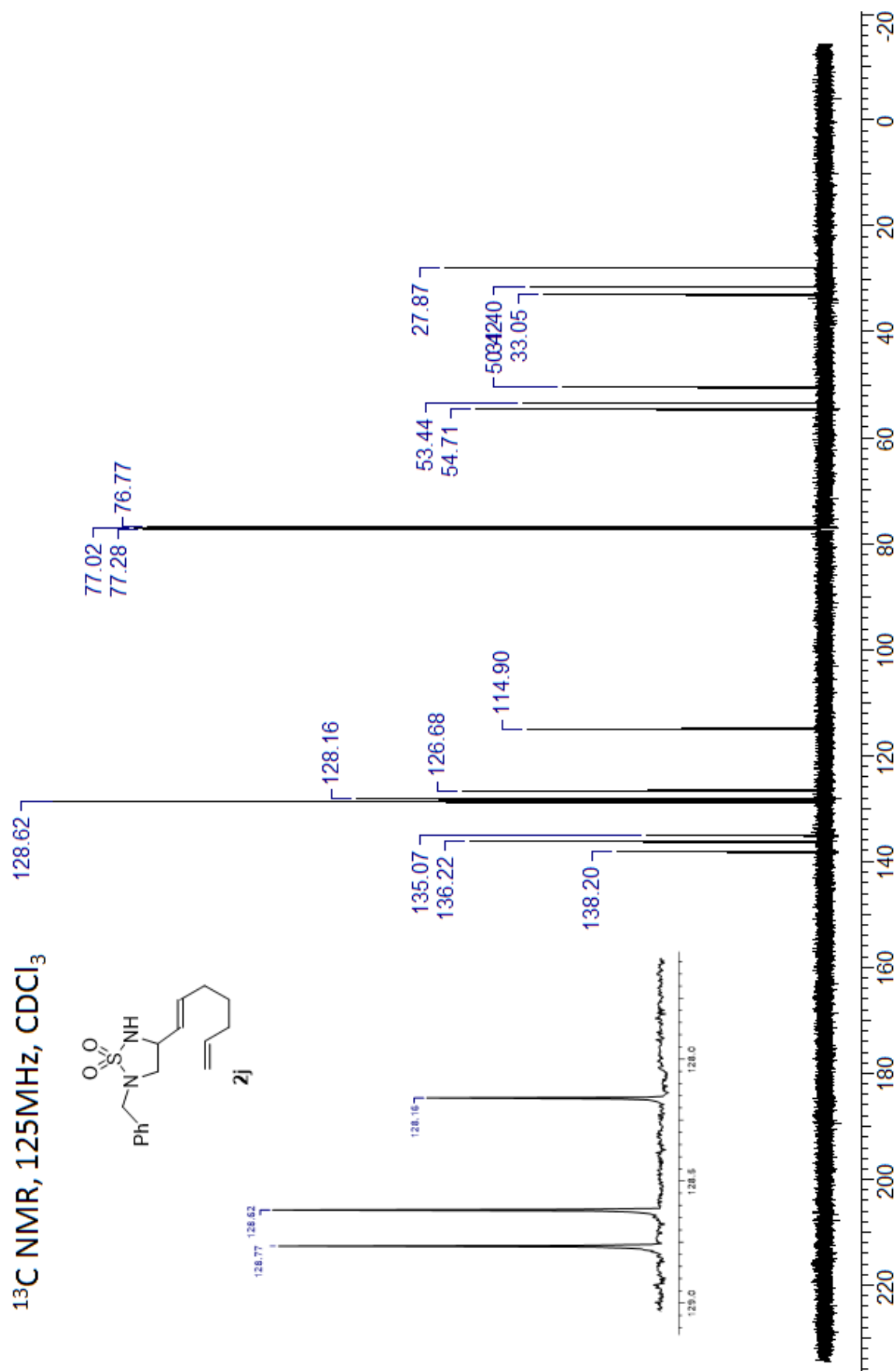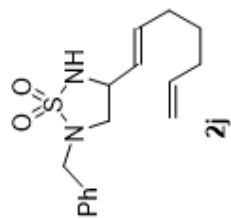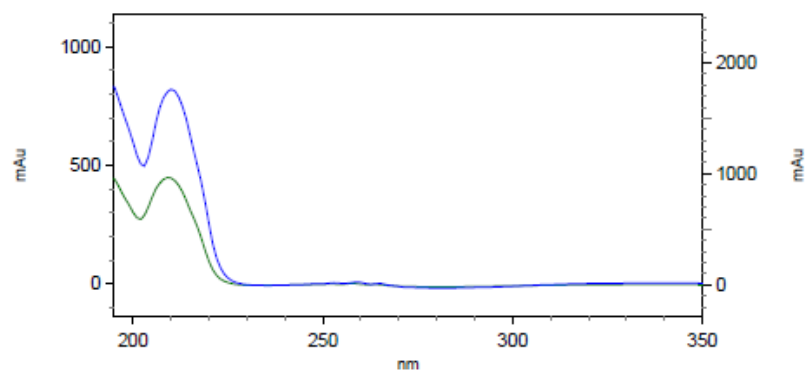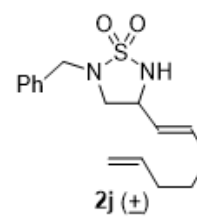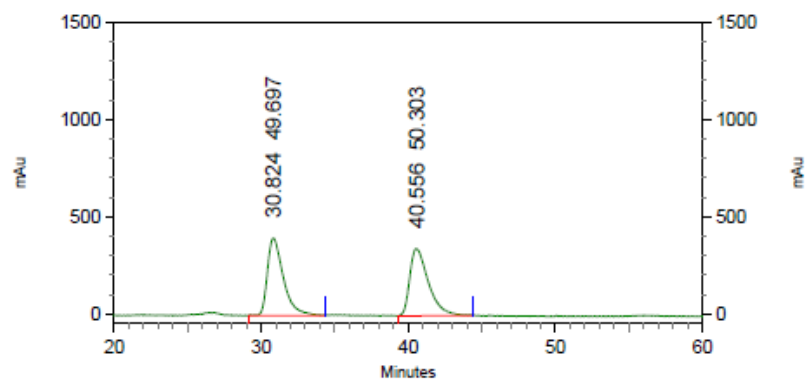
3: 205 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	30.824	49.697	1
	40.556	50.303	2

Totals		
	100.000	

(R)-**2j** (+)
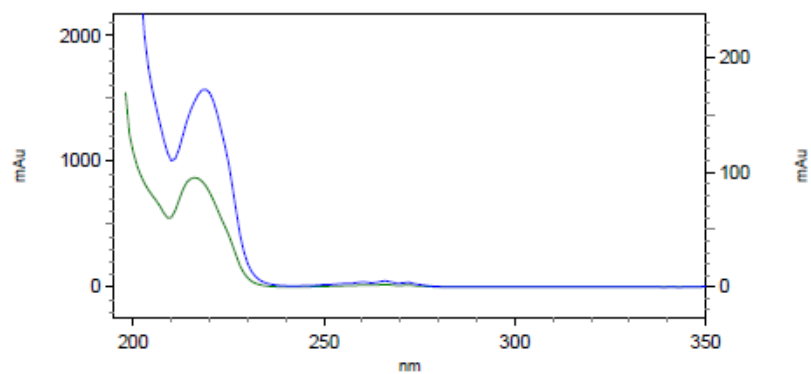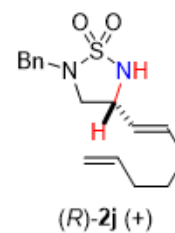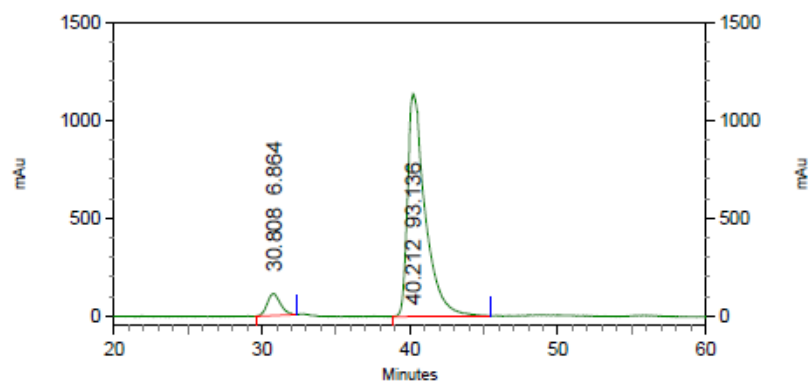
3: 195 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	30.808	6.864	1
	40.212	93.136	2

Totals	
	100.000
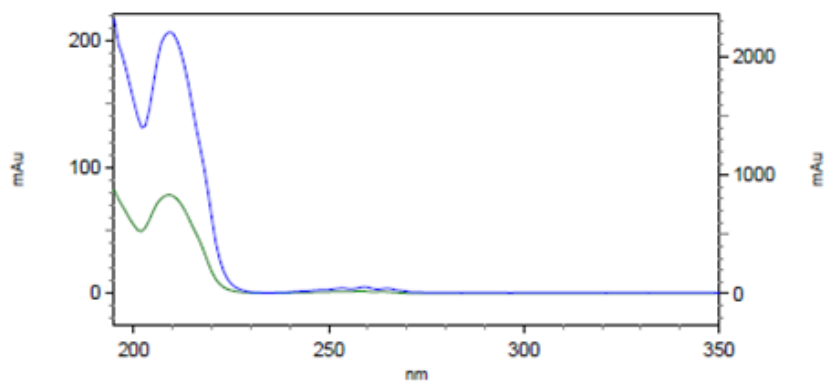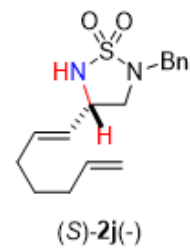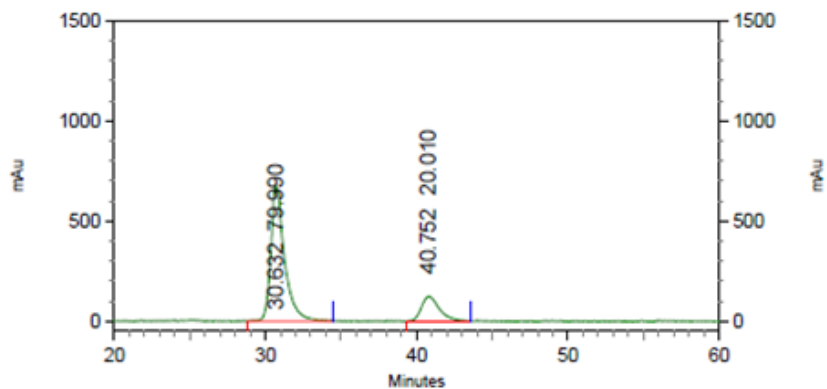
3: 193 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	30.632	79.990	1
	40.752	20.010	2

Totals		
	100.000	

^{1}H NMR, 500MHz, CDCl$_3$

2k

^{13}C NMR, 100MHz, CDCl$_3$

2k
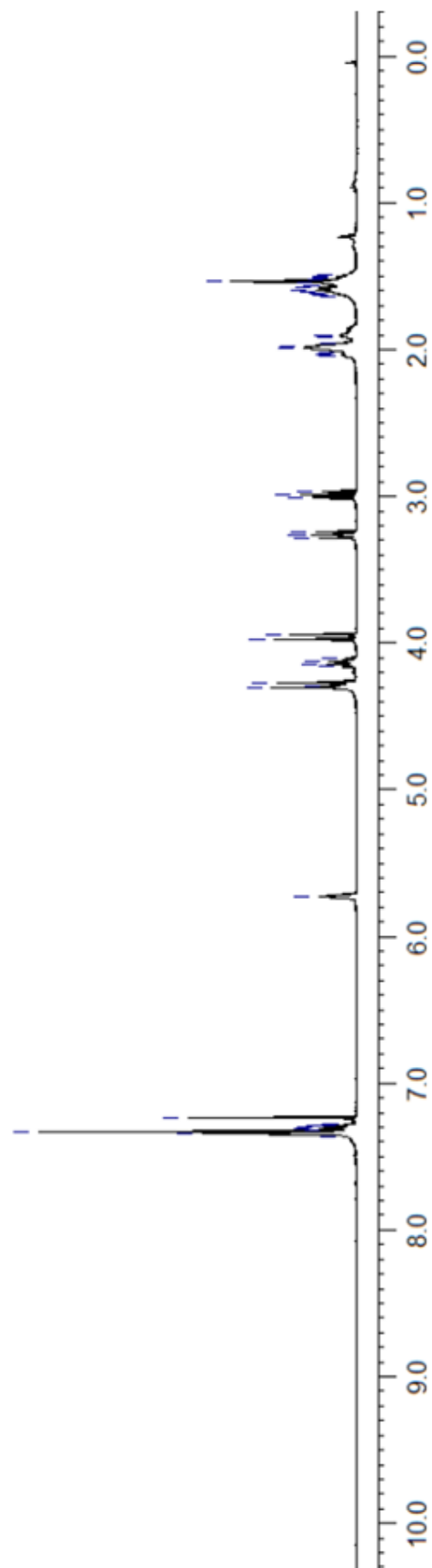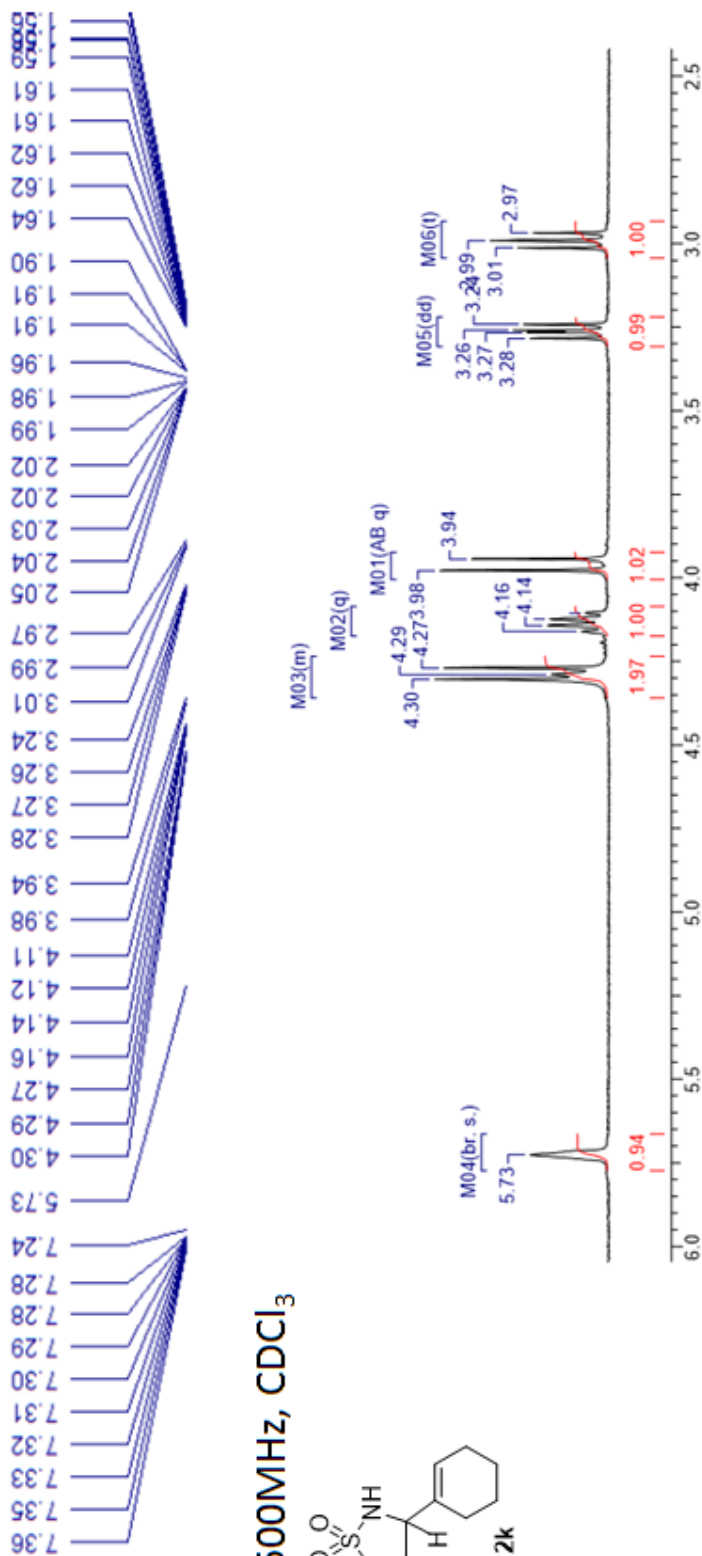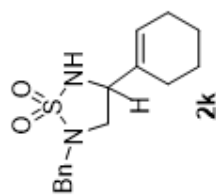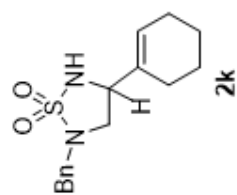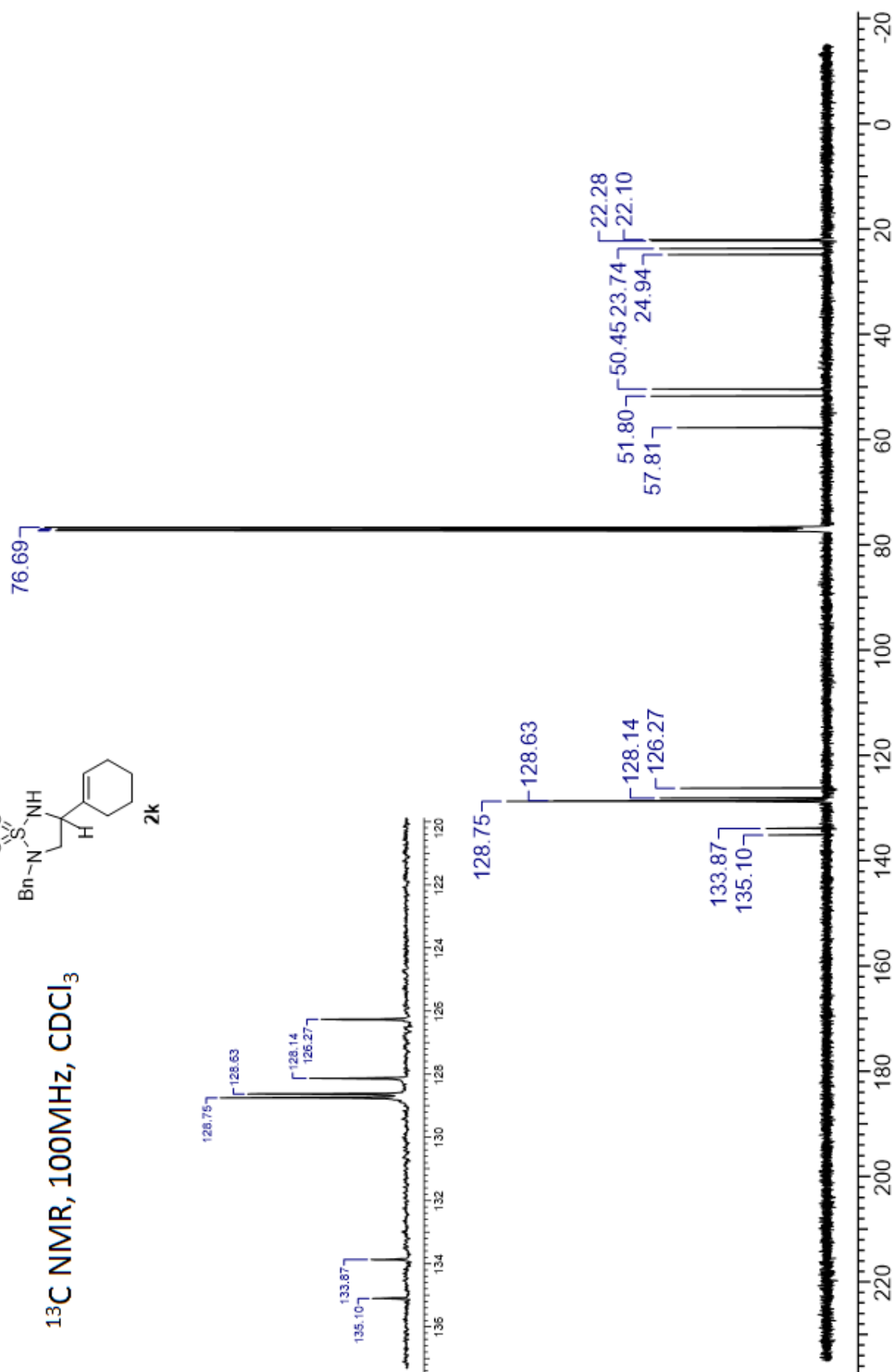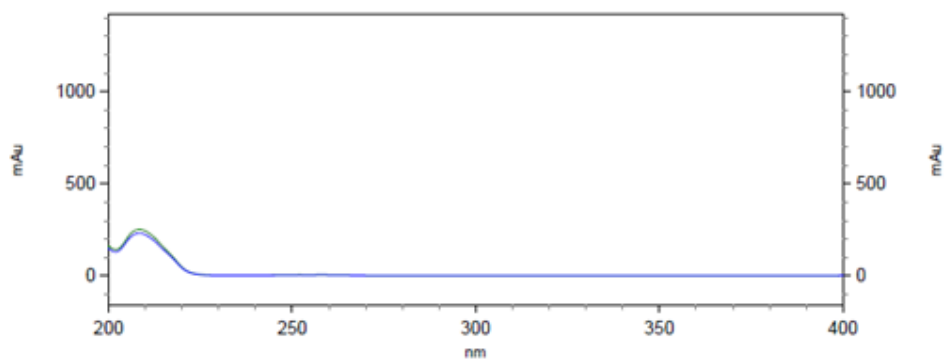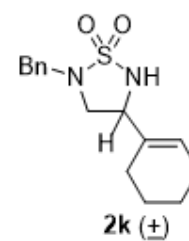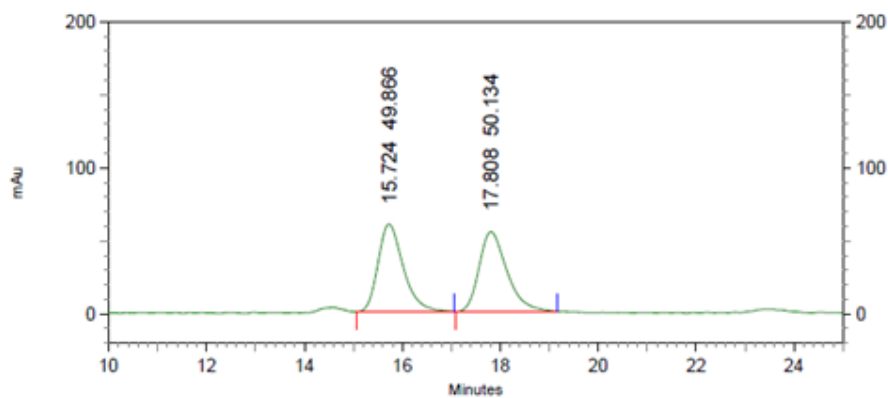
4: 214 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	15.724	49.866
2	17.808	50.134

(R)-**2k** (+)
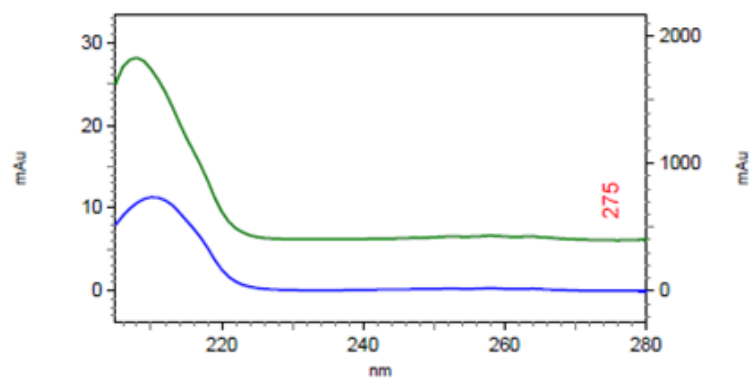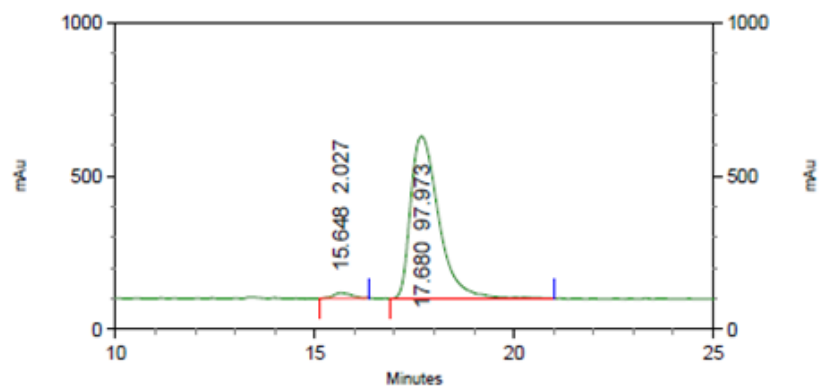
3: 205 nm, 4 nm
 Results

Pk # Name	Retention Time	Area Percent
1	15.648	2.027
2	17.680	97.973
Totals		100.000

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: I

(R)-2k (+)
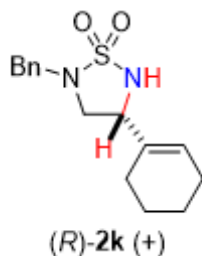
```
Bond precision:   C-C = 0.0072 A            Wavelength=1.54178

Cell:             a=5.0664(1)      b=11.9606(3)       c=24.9189(6)
                  alpha=90         beta=90            gamma=90
Temperature:      296 K

                  Calculated                  Reported
Volume            1510.02(6)                  1510.02(6)
Space group       P 21 21 21                  P 21 21 21
Hall group        P 2ac 2ab                   P 2ac 2ab
Moiety formula    C15 H20 N2 O2 S             C15 H20 N2 O2 S
Sum formula       C15 H20 N2 O2 S             C15 H20 N2 O2 S
Mr                292.39                      292.39
Dx,g cm-3         1.286                       1.286
Z                 4                           4
Mu (mm-1)         1.930                       1.930
F000              624.0                       624.0
F000'             626.97
h,k,lmax          6,14,30                     6,14,29
Nref              2941[ 1746]                 2870
Tmin,Tmax         0.742,0.962                 0.576,0.753
Tmin'             0.673

Correction method= MULTI-SCAN

Data completeness= 1.64/0.98       Theta(max)= 71.457

R(reflections)= 0.0449( 2559)      wR2(reflections)= 0.1195( 2870)

S = 1.040                Npar= 204
```

The following ALERTS were generated. Each ALERT has the format
        test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

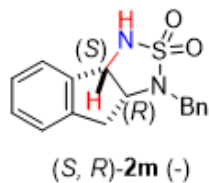(R)-2k (+)

checkCIF publication errors

Publication of your CIF

You should attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the nature of your study may justify the reported deviations from journal submission requirements and the more serious of these should be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. *checkCIF* was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

If level A alerts remain, which you believe to be justified deviations, and you intend to submit this CIF for publication in a journal, you should additionally insert an explanation in your CIF using the Validation Reply Form (VRF) below. This will allow your explanation to be considered as part of the review process.
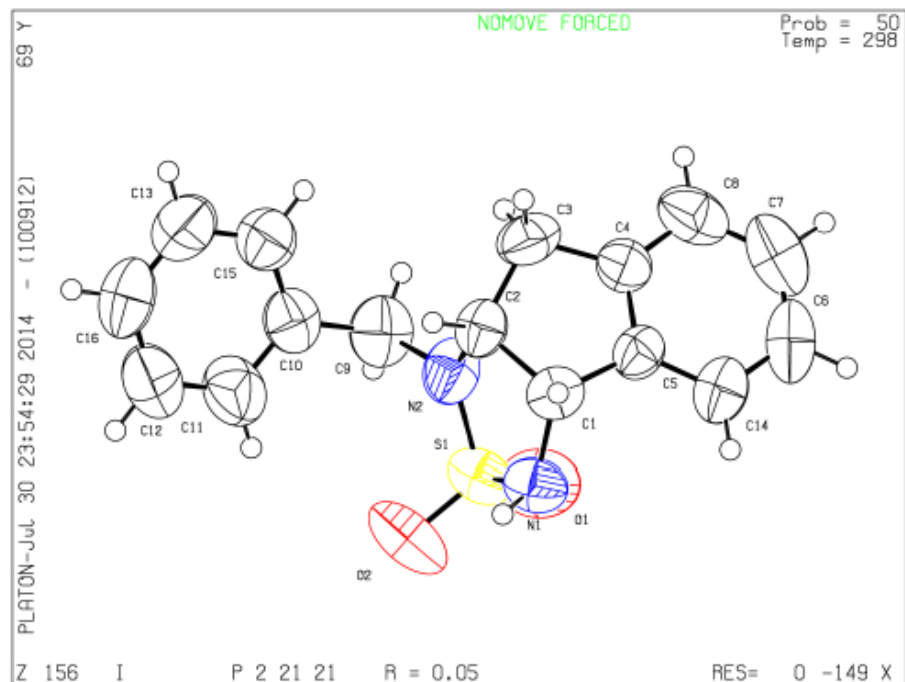

(R)-**2k** (+)

```
# start Validation Reply Form
_vrf_PUBL002_GLOBAL
;
PROBLEM: The contact author's address is missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
```
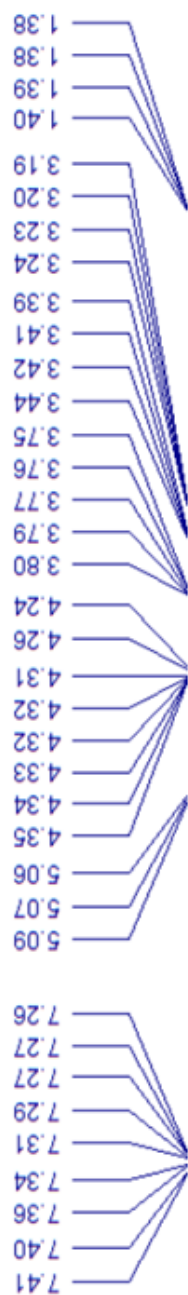
If you wish to submit your CIF for publication in Acta Crystallographica Section C or E, you should upload your CIF via the web. If your CIF is to form part of a submission to another IUCr journal, you will be asked, either during electronic submission or by the Co-editor handling your paper, to upload your CIF via our web site.

_____

PLATON version of 24/07/2014; check.def file version of 24/07/2014

(*R*)-**2k** (+)

Datablock I - ellipsoid plot

4: 214 nm, 4 nm
Results

Pk # Name	Retention Time	Area Percent
1	15.820	84.789
2	17.860	15.211
Totals		100.000

^{1}H NMR, 400MHz, CDCl$_3$

21

¹³C NMR, 100MHz, CDCl₃

2l

-4.93
16.34
25.92
44.42
50.47
53.84
76.67
76.98
77.30
90.47
100.69
128.24
128.49
128.79
134.80
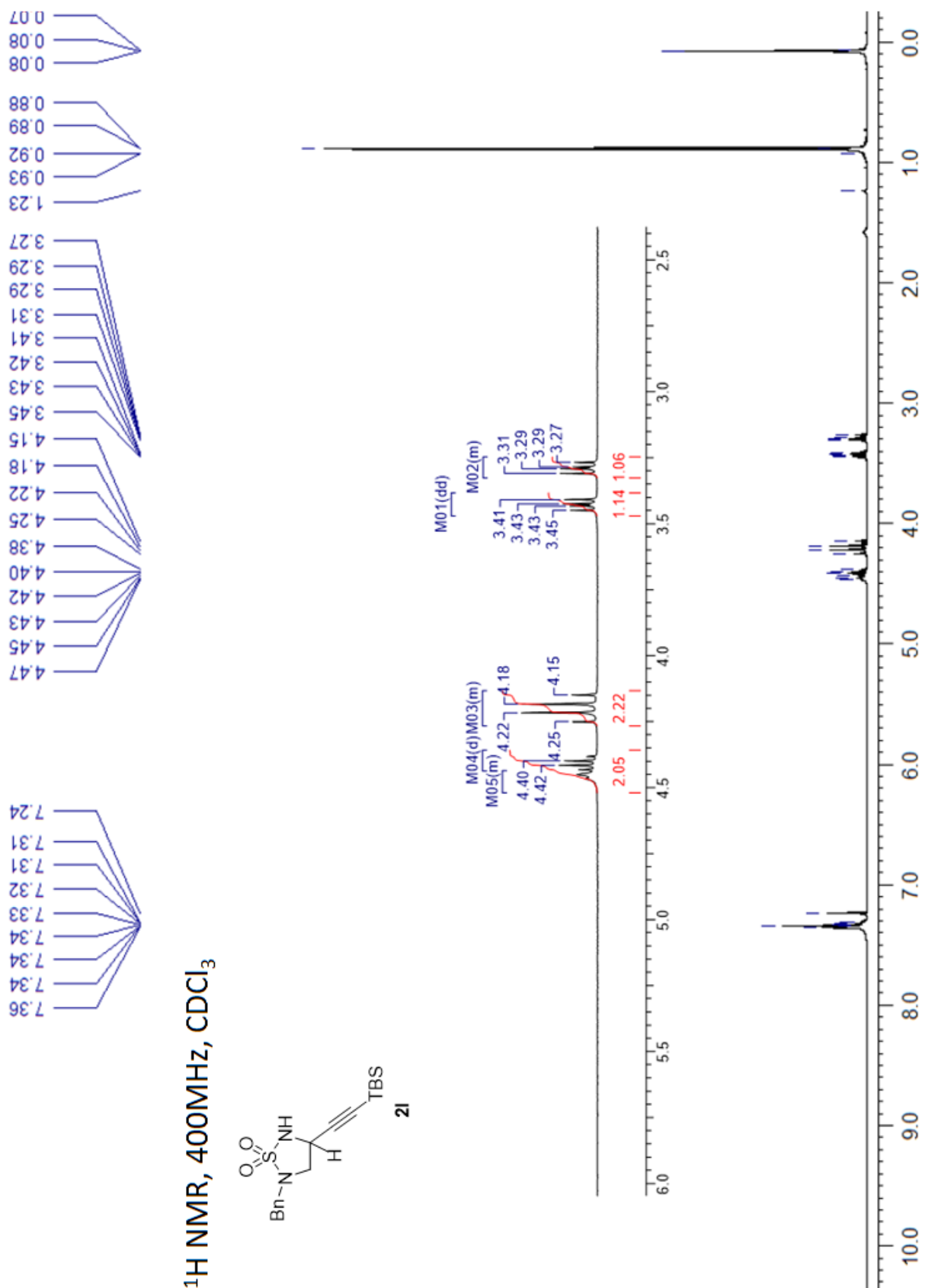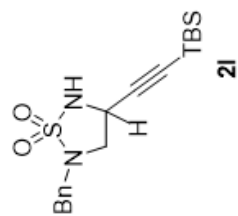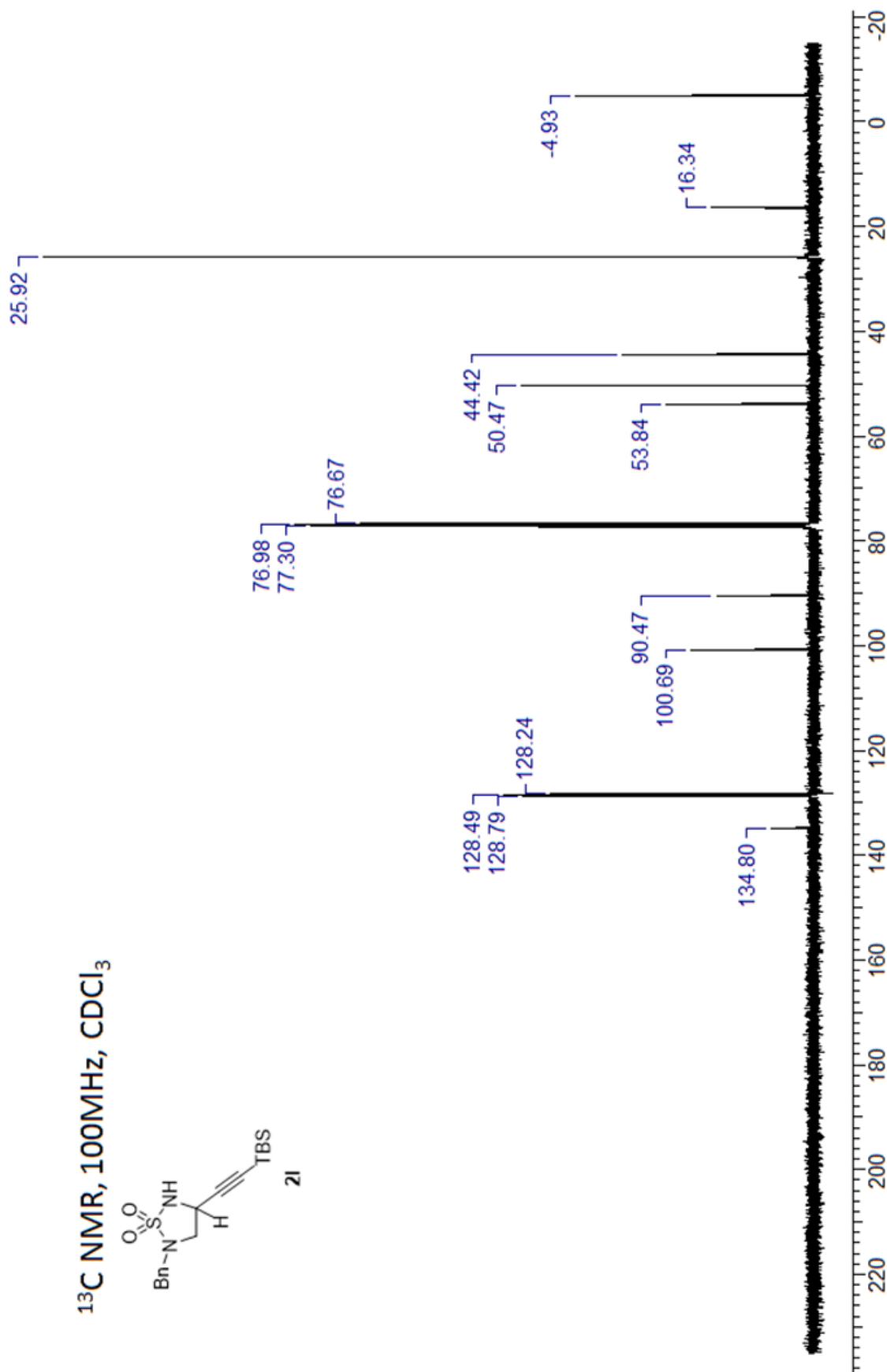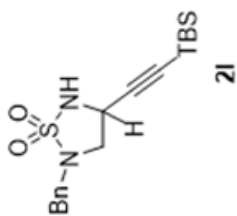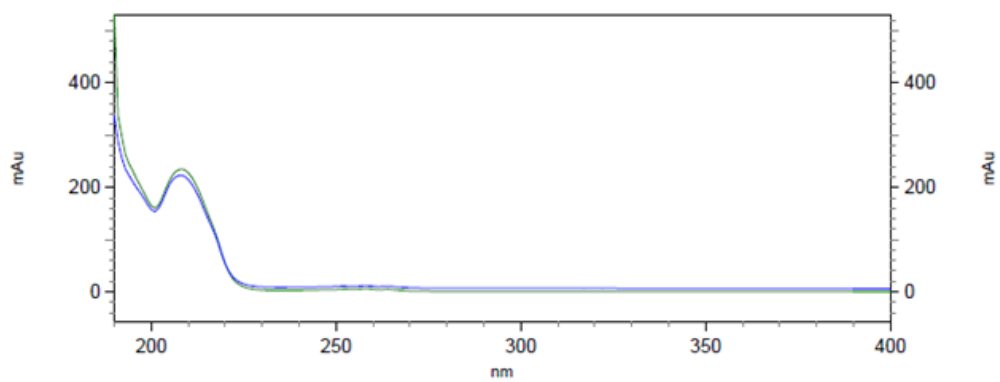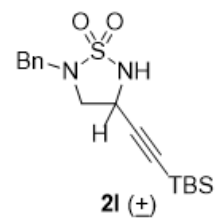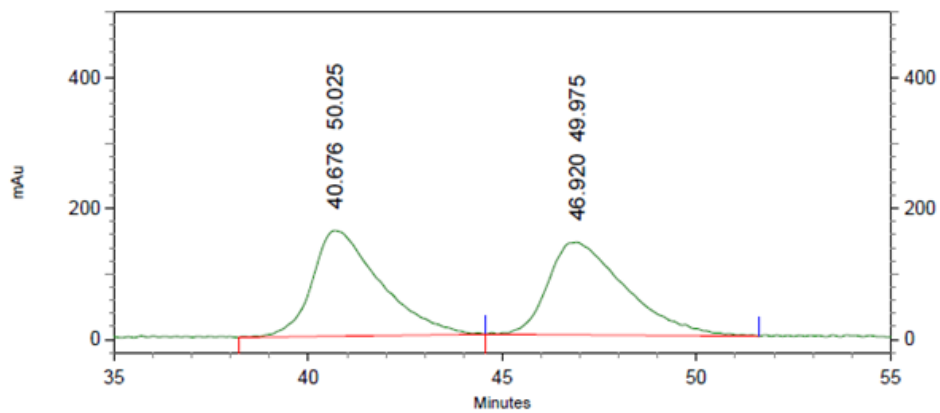
4: 220 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	40.676	50.025
2	46.920	49.975

Totals	
	100.000
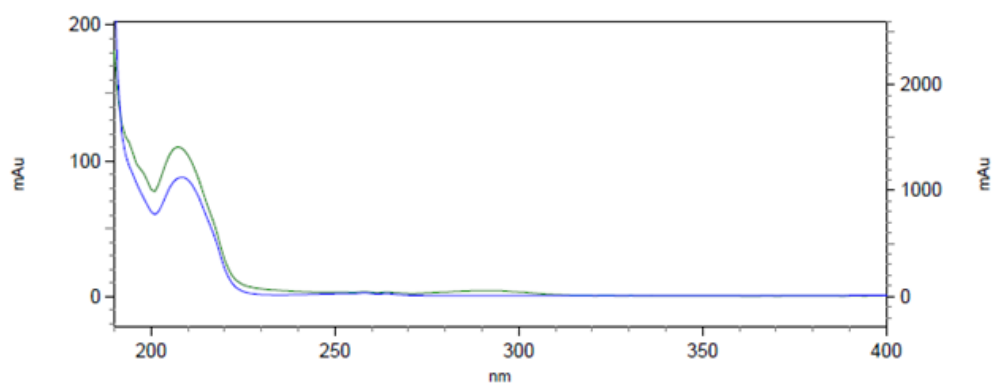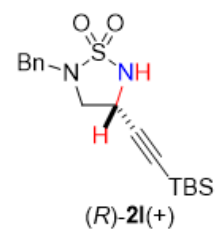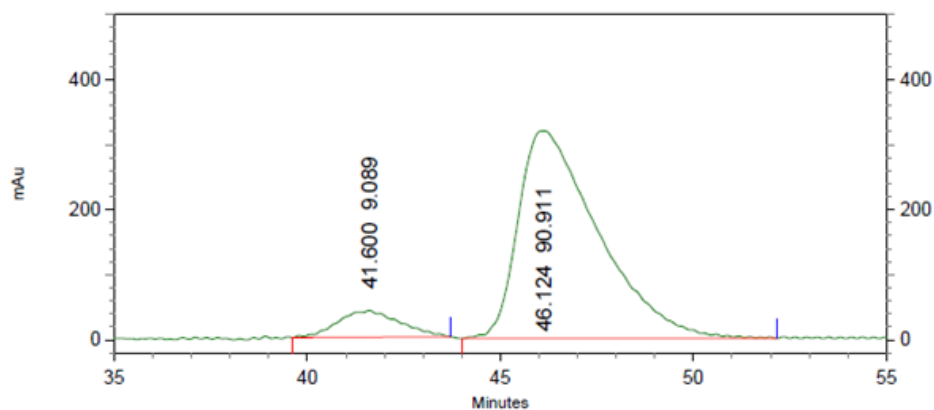
4: 220 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	41.600	9.089
2	46.124	90.911

Totals	
	100.000
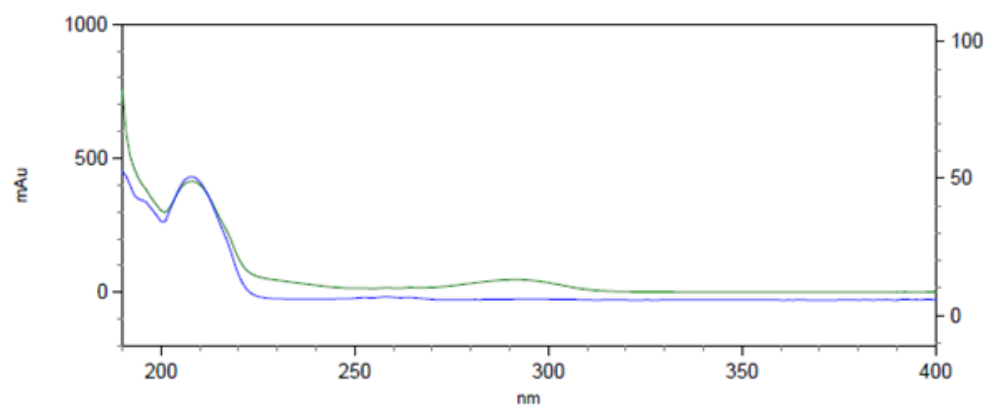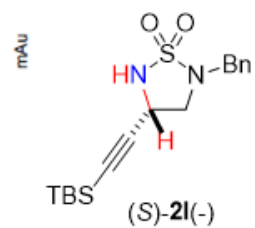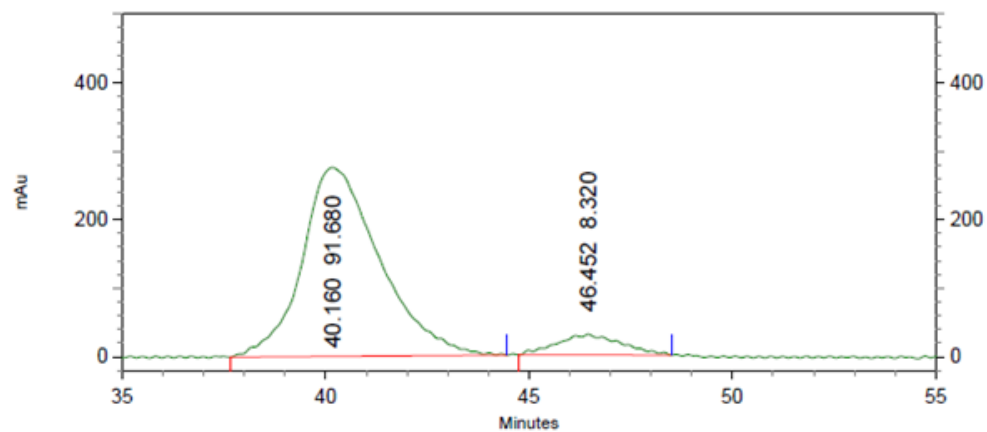
4: 220 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	40.160	91.680
2	46.452	8.320

Totals	
	100.000
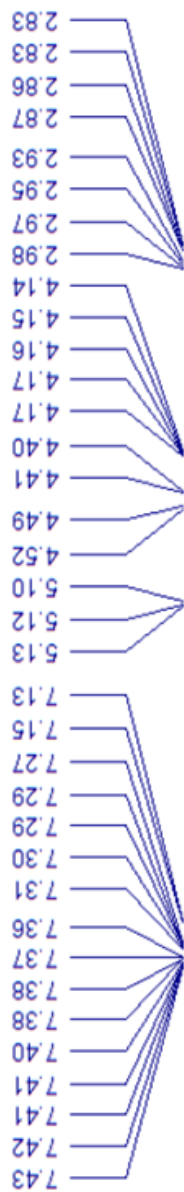
^{1}H NMR, 500MHz, CDCl$_3$

2m

^{13}C NMR, 125MHz, CDCl$_3$

2m
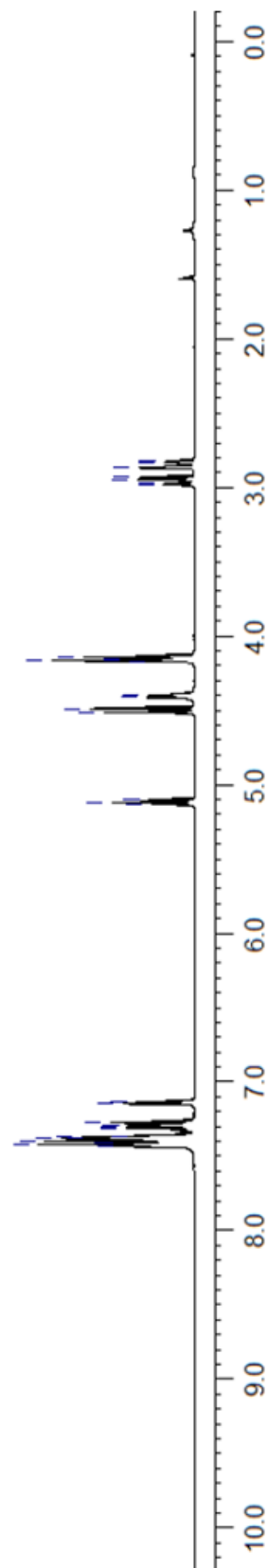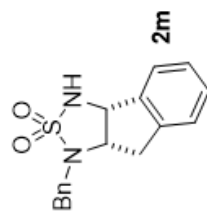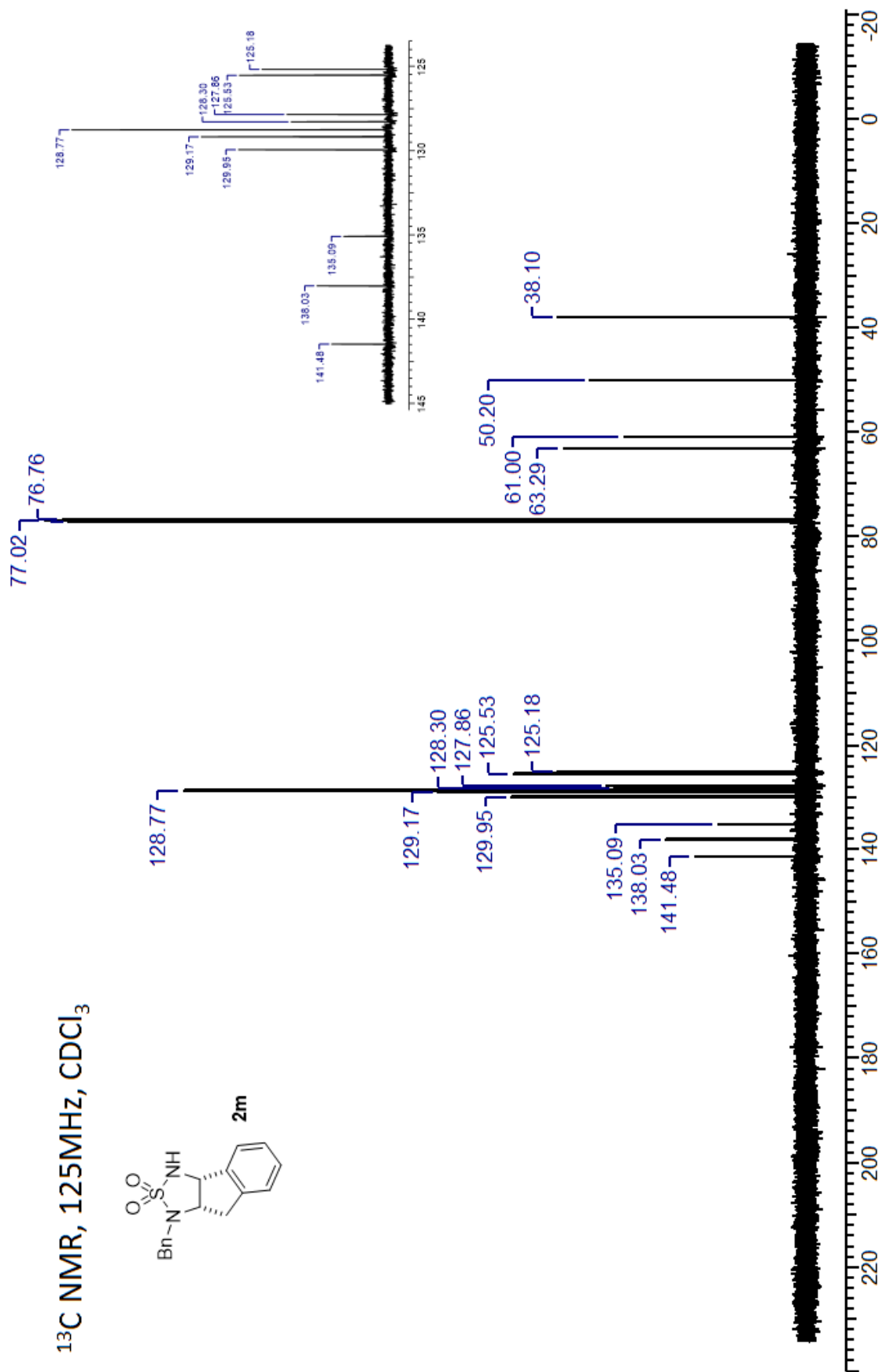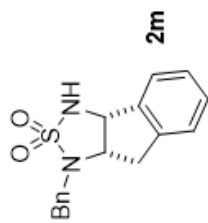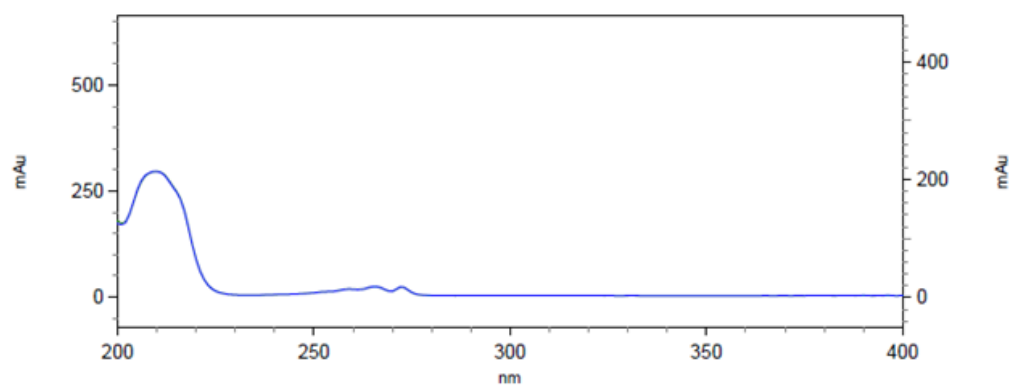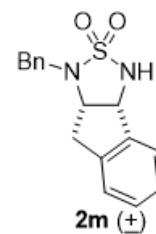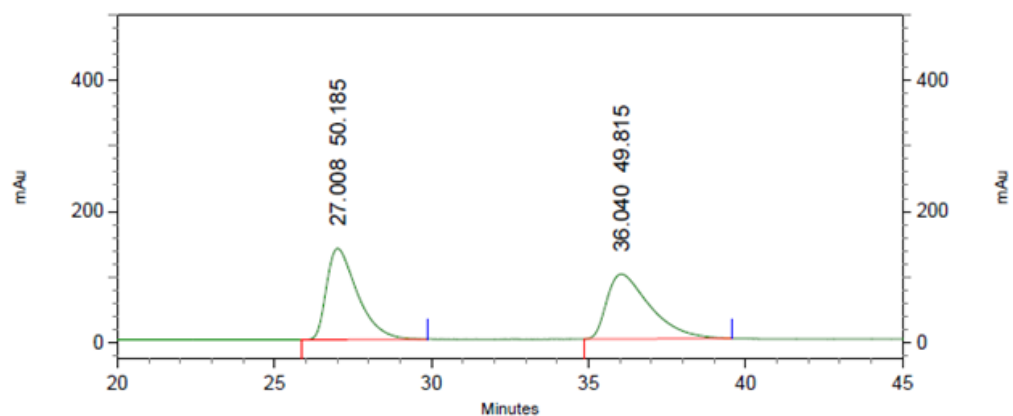
4: 222 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	27.008	50.185
2	36.040	49.815

Totals	
	100.000
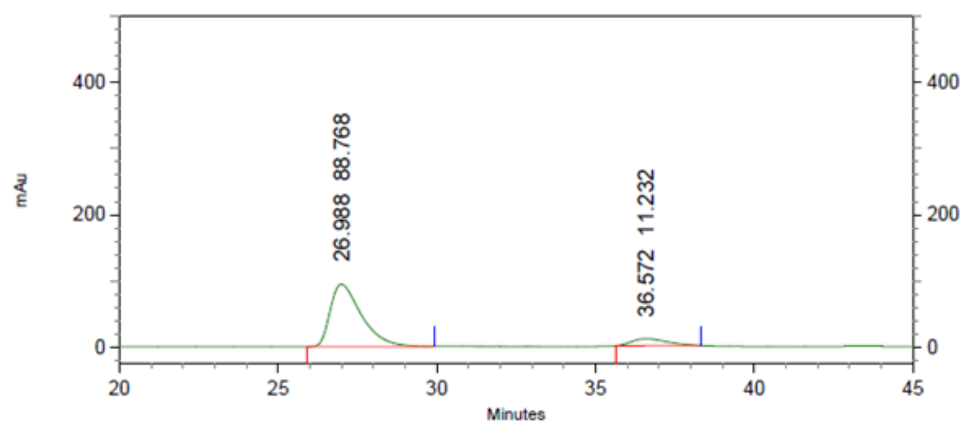
4: 222 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	26.988	88.768
2	36.572	11.232

Totals	
	100.000
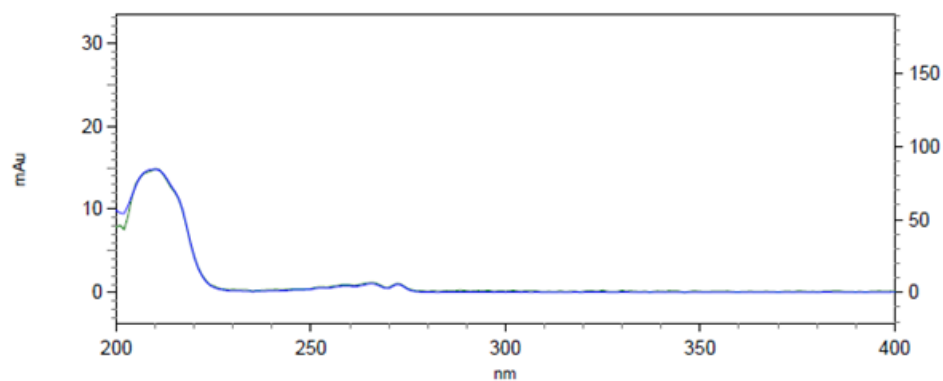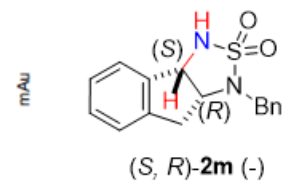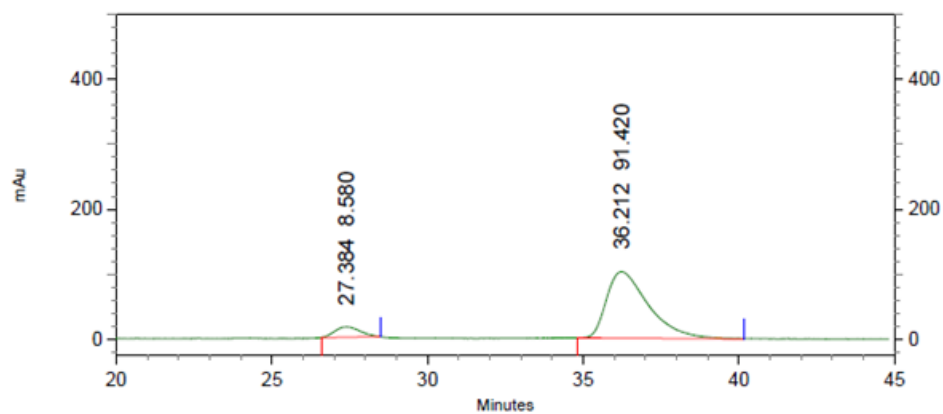
4: 222 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	27.384	8.580
2	36.212	91.420

Totals	
	100.000

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report
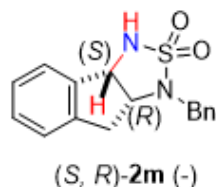
Datablock: I

```
Bond precision:   C-C = 0.0103 A               Wavelength=1.54178

Cell:                a=5.0613(4)     b=13.3347(10)      c=22.6731(18)
                     alpha=90        beta=90            gamma=90
Temperature:        298 K

                    Calculated                 Reported
Volume              1530.2(2)                  1530.2(2)
Space group         P 2 21 21                  P 2 21 21
Hall group          P 2bc 2                    P 2bc 2
Moiety formula      C16 H16 N2 O2 S            C16 H16 N2 O2 S
Sum formula         C16 H16 N2 O2 S            C16 H16 N2 O2 S
Mr                  300.37                     300.37
Dx,g cm-3           1.304                      1.304
Z                   4                          4
Mu (mm-1)           1.927                      1.927
F000                632.0                      632.0
F000'               635.04
h,k,lmax            5,14,25                    5,14,25
Nref                2207[ 1328]                2206
Tmin,Tmax           0.891,0.981                0.485,0.753
Tmin'               0.667

Correction method= MULTI-SCAN

Data completeness= 1.66/1.00        Theta(max)= 58.901

R(reflections)= 0.0515( 1792)       wR2(reflections)= 0.1273( 2206)

S = 1.044                  Npar= 194
```

The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

(S, R)-2m (-)

(S, R)-2m (-)

Alert level B

```
        Crystal system given = orthorhombic
THETM01_ALERT_3_B  The value of sine(theta_max)/wavelength is less than 0.575
        Calculated sin(theta_max)/wavelength =    0.5554
PLAT023_ALERT_3_B Resolution (too) Low [sin(theta)/Lambda < 0.6]..      58.90 Degree
PLAT340_ALERT_3_B Low Bond Precision on  C-C Bonds ...............      0.0103 Ang.
```

Alert level C

```
PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) ........       6.85 Note
PLAT241_ALERT_2_C High       Ueq as Compared to Neighbors for .....         C3 Check
PLAT242_ALERT_2_C Low        Ueq as Compared to Neighbors for .....         S1 Check
PLAT242_ALERT_2_C Low        Ueq as Compared to Neighbors for .....        C10 Check
PLAT331_ALERT_2_C Small Average Phenyl   C-C Dist. C10     -C15        1.36 Ang.
PLAT334_ALERT_2_C Small Average Benzene  C-C Dist. C4      -C8         1.37 Ang.
```
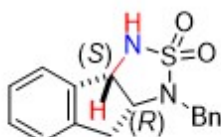
Alert level G

```
PLAT033_ALERT_4_G Flack x Value Deviates > 2*sigma from Zero .....      0.140
PLAT128_ALERT_4_G Alternate Setting for Input Space Group  P22121      P21212 Note
PLAT791_ALERT_4_G The Model has Chirality at C1        .............        S Verify
PLAT791_ALERT_4_G The Model has Chirality at C2        .............        R Verify
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   3 ALERT level B = A potentially serious problem, consider carefully
   6 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   4 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   5 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   4 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

checkCIF publication errors

Alert level A

```
PUBL002_ALERT_1_A  The contact author's address is missing,
        _publ_contact_author_address.
PUBL005_ALERT_1_A  _publ_contact_author_email, _publ_contact_author_fax and
        _publ_contact_author_phone are all missing.
        At least one of these should be present.
PUBL006_ALERT_1_A  _publ_requested_journal is missing
        e.g. 'Acta Crystallographica Section C'
PUBL008_ALERT_1_A  _publ_section_title is missing. Title of paper.
PUBL009_ALERT_1_A  _publ_author_name is missing. List of author(s) name(s).
PUBL010_ALERT_1_A  _publ_author_address is missing. Author(s) address(es).
PUBL012_ALERT_1_A  _publ_section_abstract is missing.
        Abstract of paper in English.
```

```
   7 ALERT level A = Data missing that is essential or data in wrong format
   0 ALERT level G = General alerts. Data that may be required is missing
```

Publication of your CIF

You should attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the nature of your study may justify the reported deviations from journal submission requirements and the more serious of these should be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. *checkCIF* was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

If level A alerts remain, which you believe to be justified deviations, and you intend to submit this CIF for publication in a journal, you should additionally insert an explanation in your CIF using the Validation Reply Form (VRF) below. This will allow your explanation to be considered as part of the review process.

```
# start Validation Reply Form
_vrf_PUBL002_GLOBAL
;
PROBLEM: The contact author's address is missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
```


(*S, R*)-**2m** (-)

(S, R)-2m (-)

PLATON version of 24/07/2014; check.def file version of 24/07/2014

Datablock I - ellipsoid plot

¹H NMR, 500MHz, CDCl₃

(*R*, *S*)-**2m'**

^{13}C NMR, 125MHz, CDCl$_3$

142.07
137.57
130.11
125.56
125.51
77.28
77.02
76.77
60.89
60.17
48.43
40.88
22.19
20.61

(R, S)-2m'

4: 221 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	17.540	50.064
2	28.772	49.936

Totals	
	100.000

(*R, S*)-**2m'** (+)
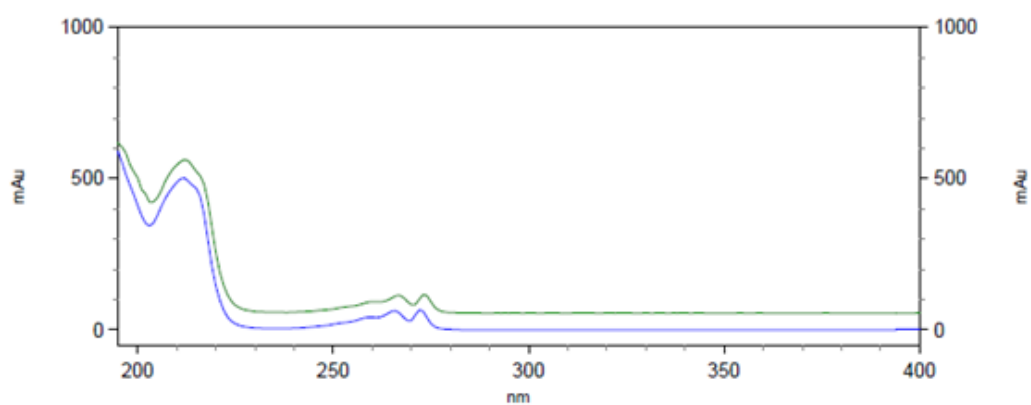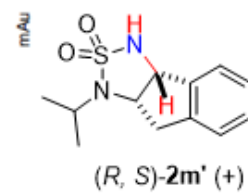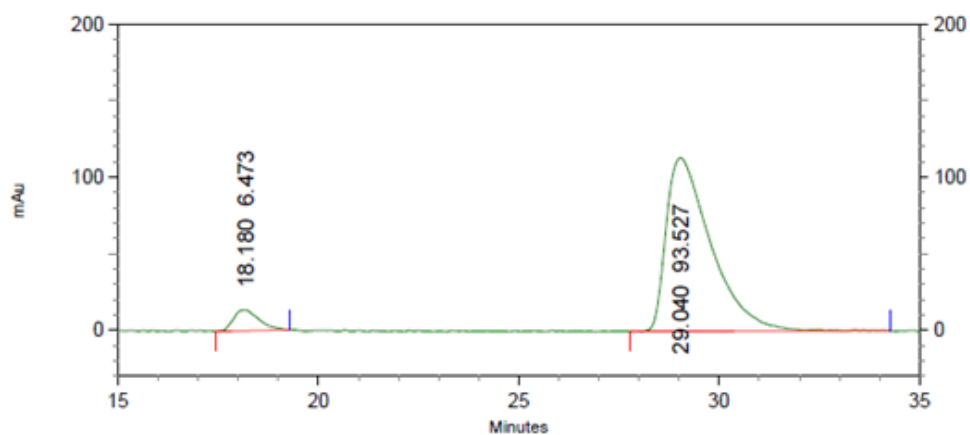
4: 221 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	18.180	6.473
2	29.040	93.527

Totals	
	100.000

^{1}H NMR, 500MHz, CDCl$_3$

Product Crude Mixture
by [Co(**P5**)]
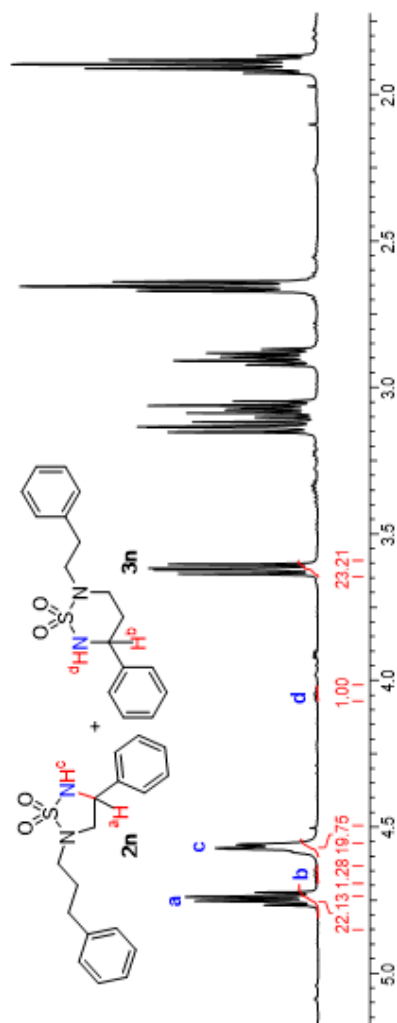
2n major
3n trace amount

Product Crude Mixture by
[Co(**P5**)]

2n major
3n trace amount

3n (synthesized
from open catalyst)

2n

^{1}H NMR, 500MHz, CDCl$_3$

2n

^{13}C NMR, 100MHz, CDCl$_3$

2n

140.95
138.49
129.05
128.80
128.45
128.44
126.38
126.06
77.30
76.67
55.97
55.84
46.29
32.89
29.28

2n (±)
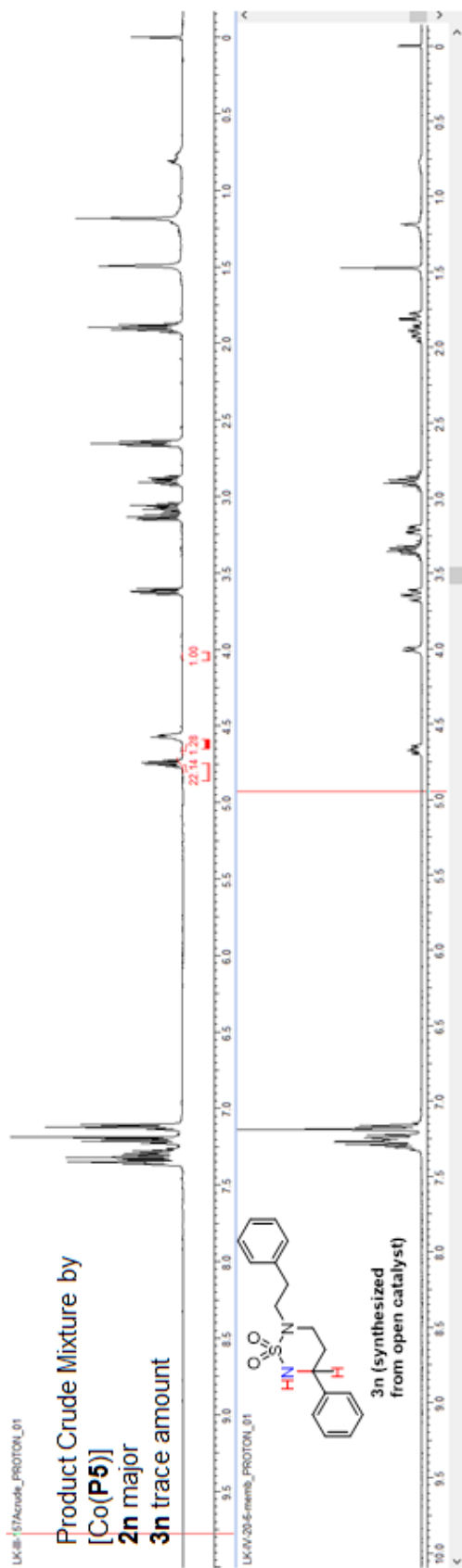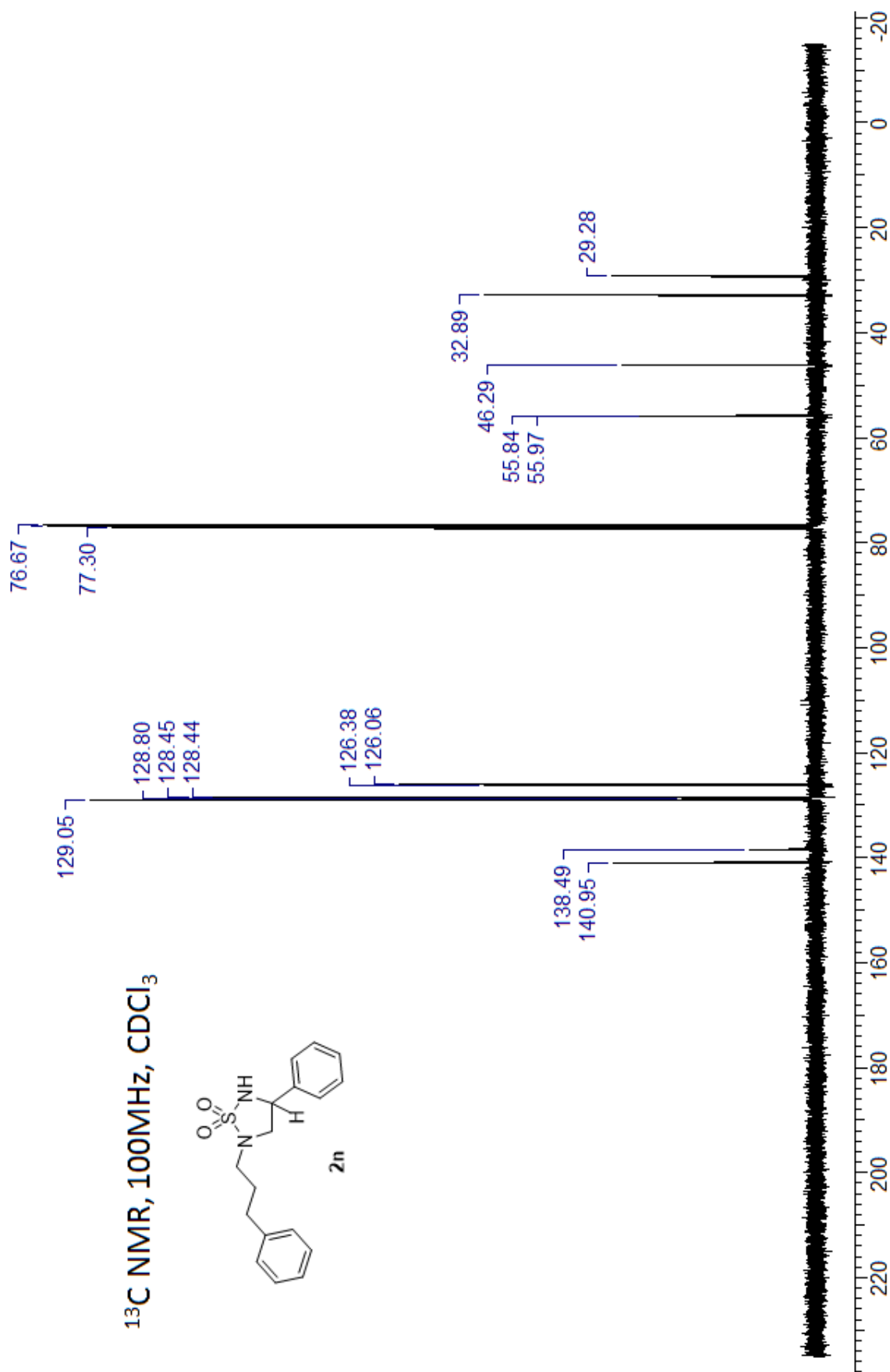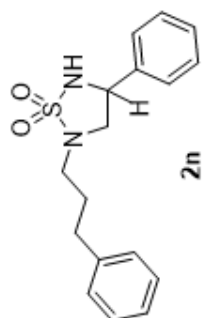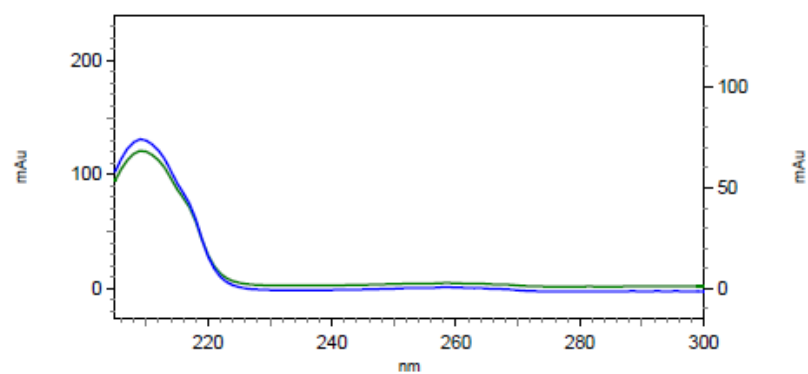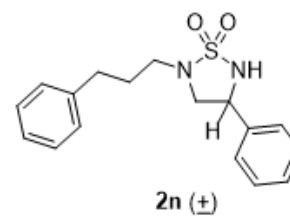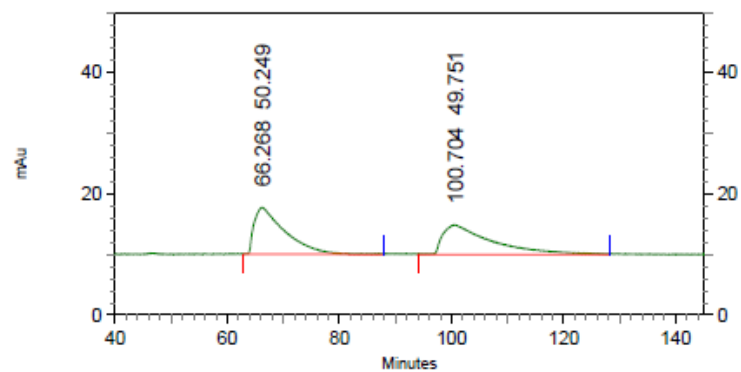
2: 216 nm, 4 nm
Results

Pk # Name	Retention Time	Area Percent
1	66.268	50.249
2	100.704	49.751

Totals	
	100.000

(R)-2n (+)
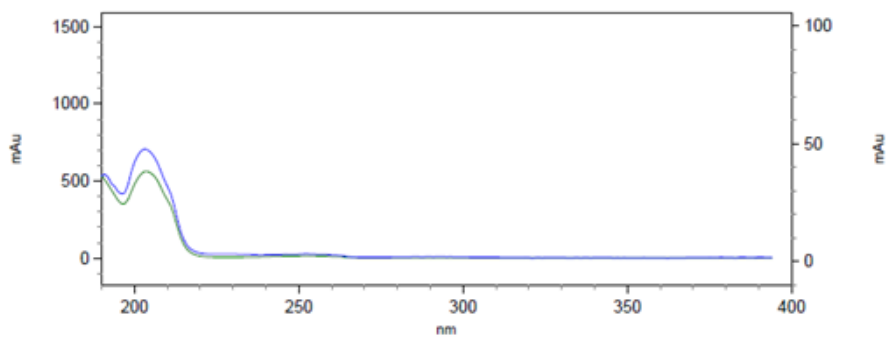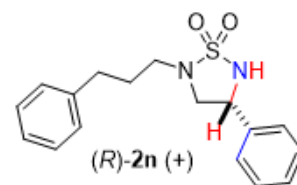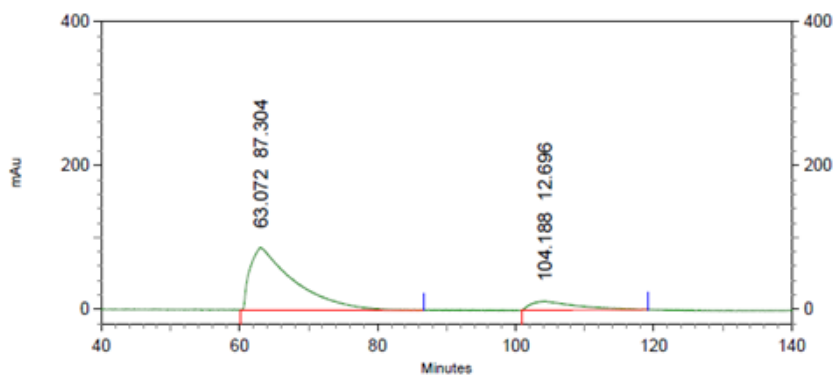
4: 195 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	63.072	87.304
2	104.188	12.696

Totals	
	100.000
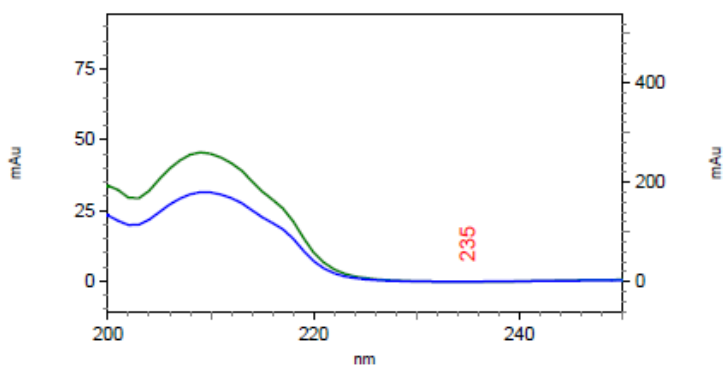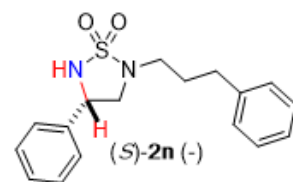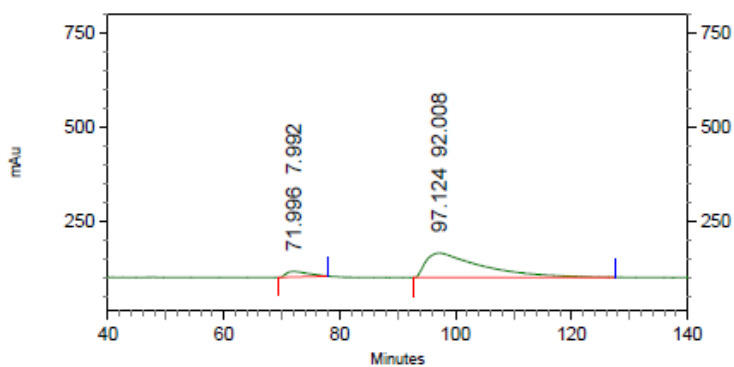
12: 219 nm, 4 nm
Results

Pk # Name	Retention Time	Area Percent
1	71.996	7.992
2	97.124	92.008
Totals		100.000

¹H NMR, 400MHz, CDCl₃

3n

^{13}C NMR, 125MHz, CDCl$_3$

3n

76.75
77.01

128.58
126.56
126.26
128.83
128.98

138.53
139.32

50.78
59.65

29.52
35.13
49.56

3n (±)
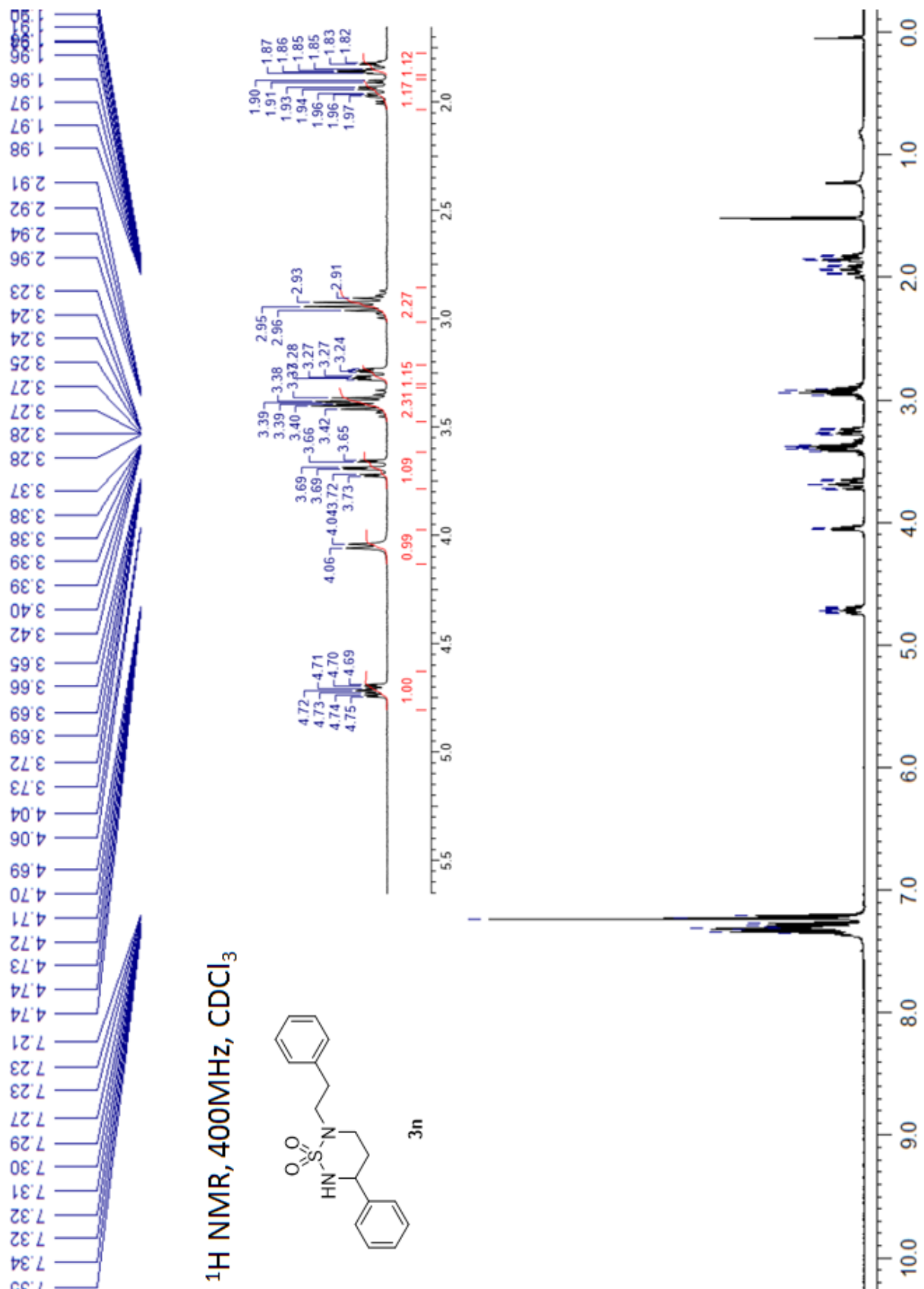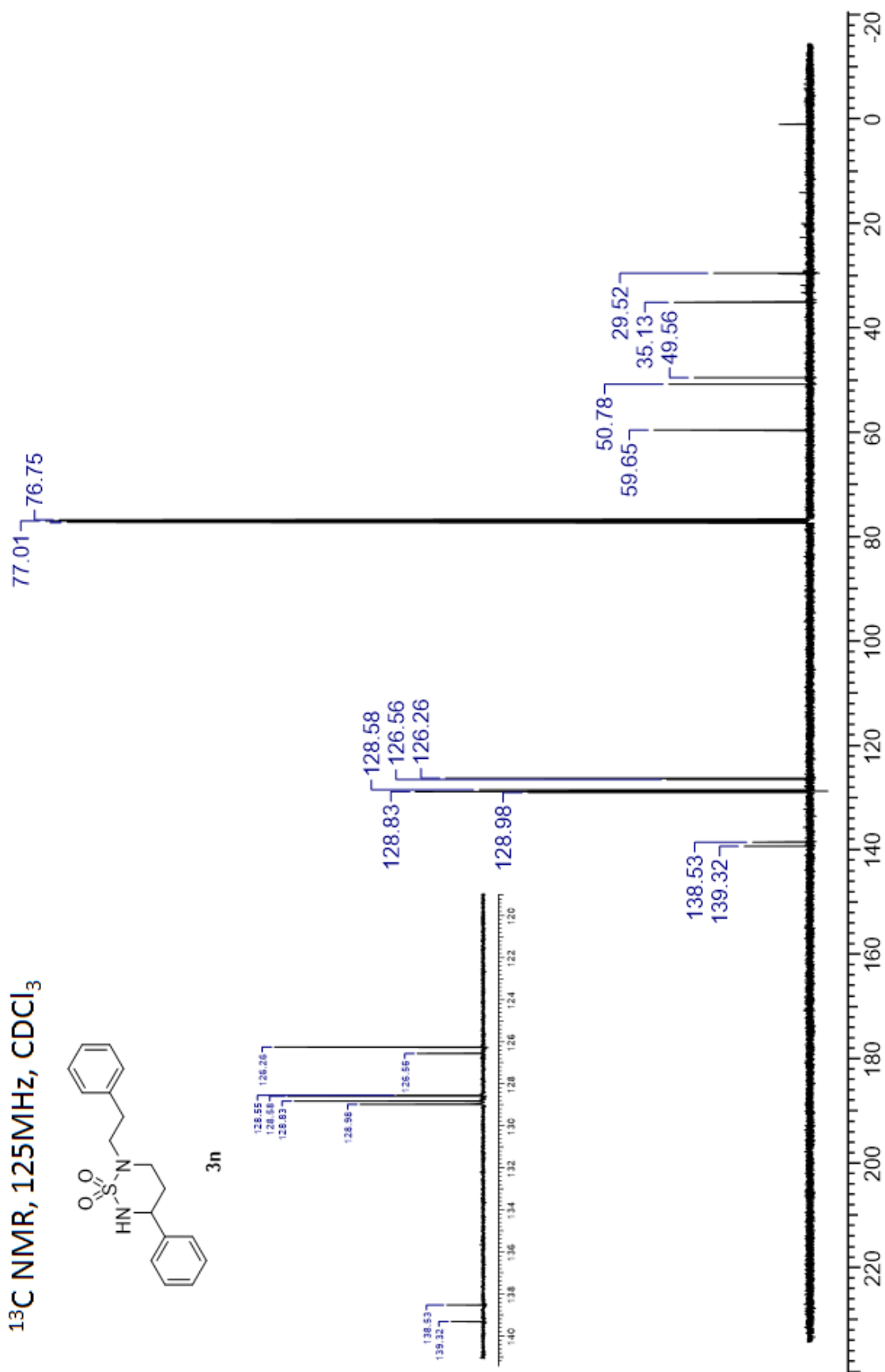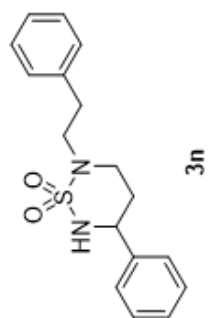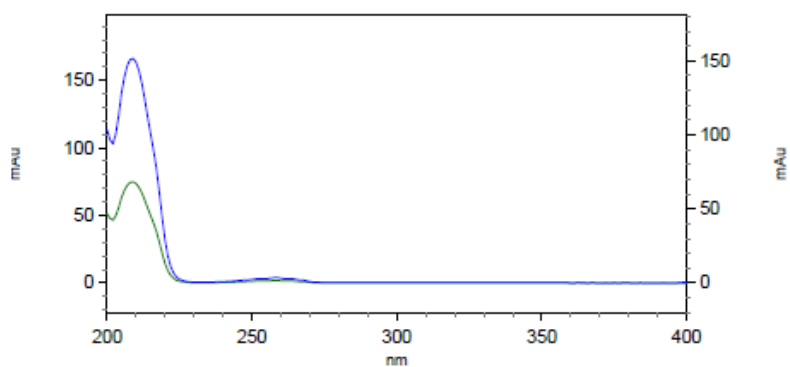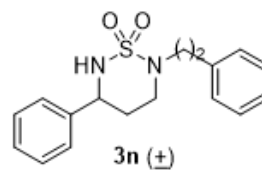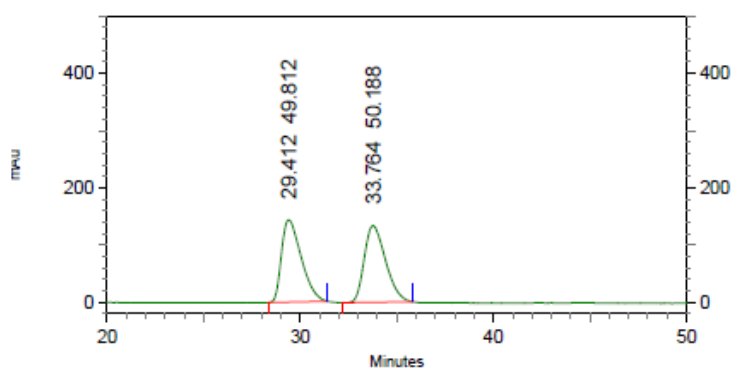
4: 210 nm, 4 nm
 Results

Name	Retention Time	Area Percent	Pk #
	29.412	49.812	1
	33.764	50.188	2

Totals			
	100.000		
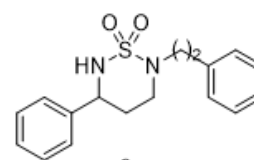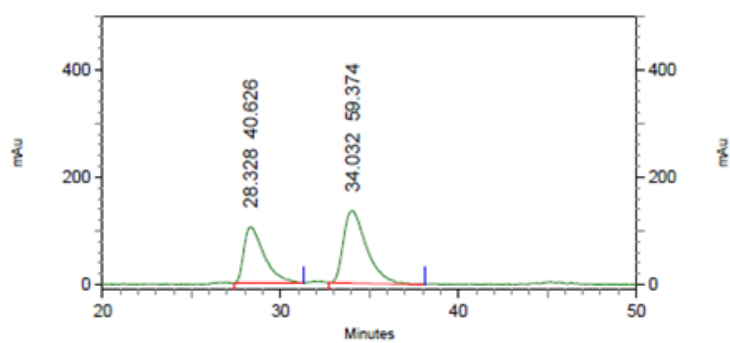
3n

[Co(**P10**)]

er = 59:41
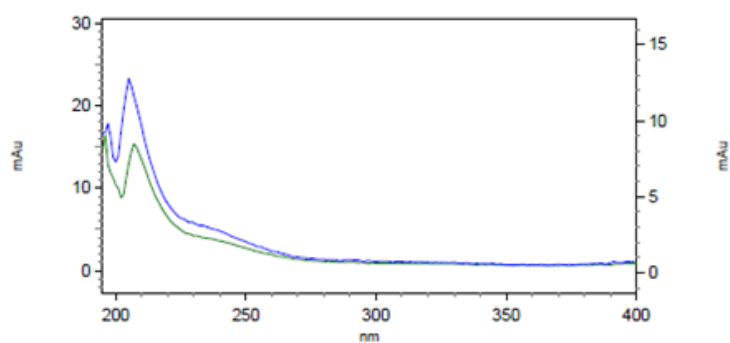
7: 210 nm, 4 nm
Results

Pk # Name	Retention Time	Area Percent
1	28.328	40.626
2	34.032	59.374

Totals	
	100.000
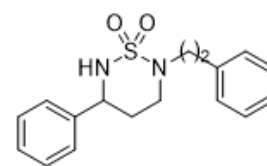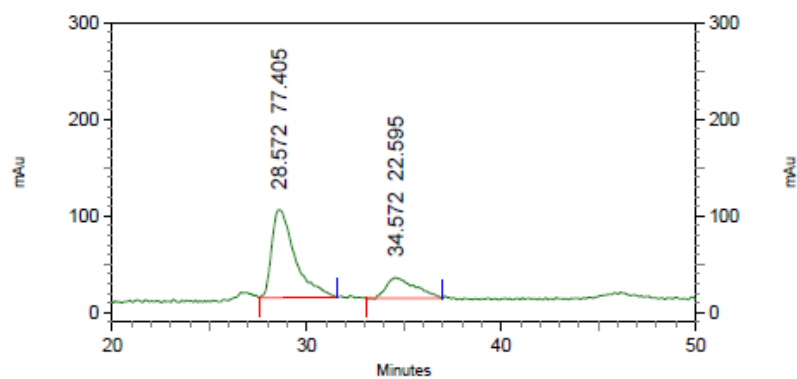
3n

[Co(**P11**)]

er = 23: 77
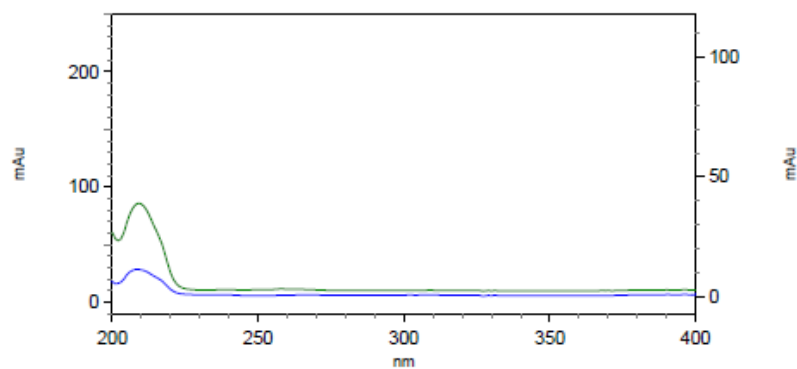
1: 217 nm, 4 nm

Results

Name	Retention Time	Area Percent	Pk #
	28.572	77.405	1
	34.572	22.595	2
Totals			
		100.000	

^{1}H NMR, 500MHz, CDCl$_3$

(R)-2o

1.20
1.22
1.26
1.27

3.42
3.43
3.43
3.96
3.98
4.13
4.32
4.35
5.10
5.11
5.12
5.13
5.15
5.20

7.27
7.33
7.34
7.36
7.37

M04(m)
3.42
3.43
3.43
3.46
3.41
3.40
2.10

M03(br. s.)
M02(AB q)
3.96
3.99
M01(AB q)
4.13
4.32
4.35
1.09
1.03
1.29

M06(br. s.)
M05(m)
5.12
5.13
5.11
5.15
5.16
5.20
5.10
1.00 1.11

^{13}C NMR, 125MHz, CDCl$_3$

(R)-**2o**
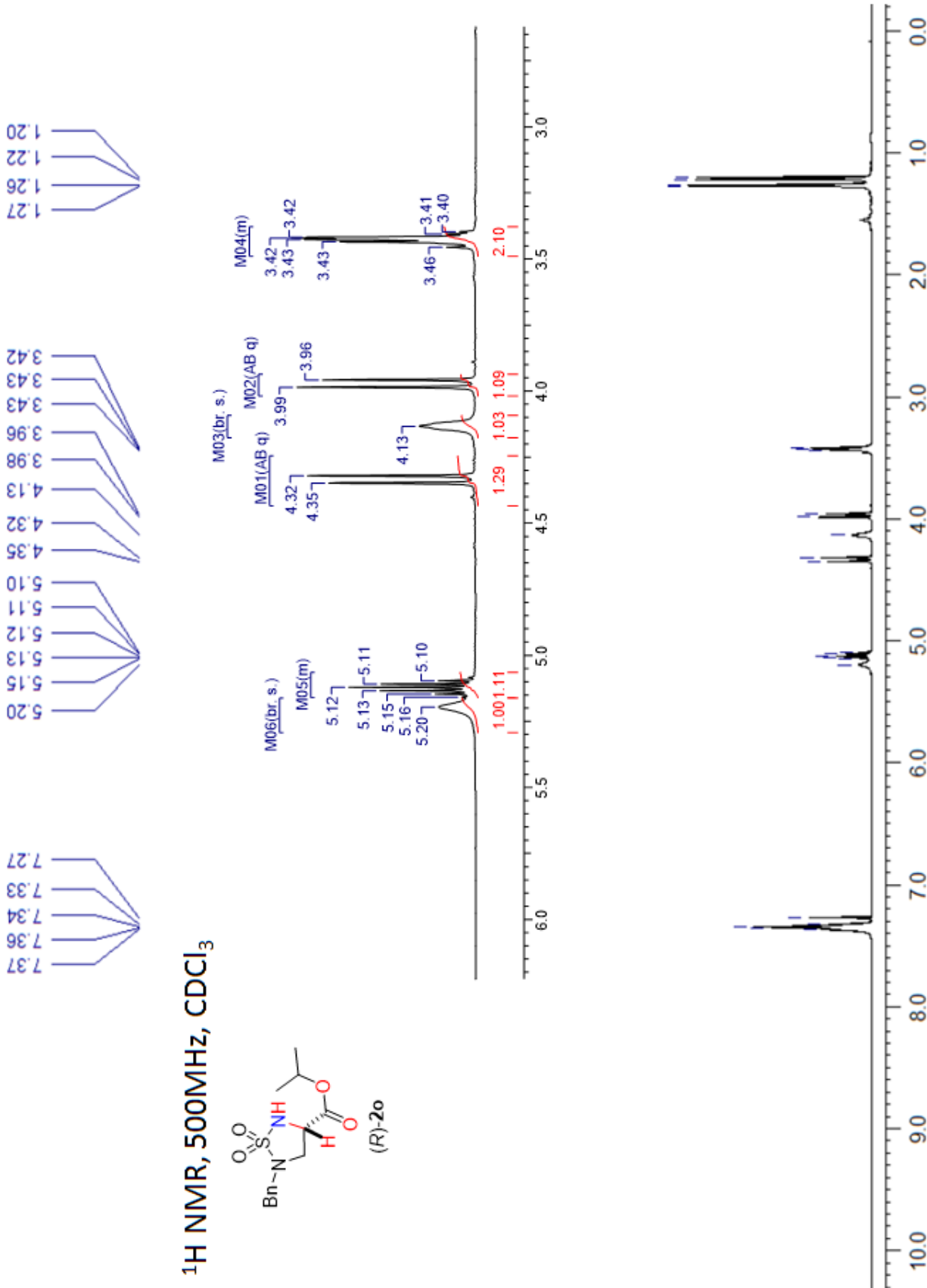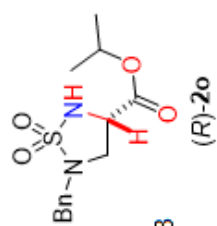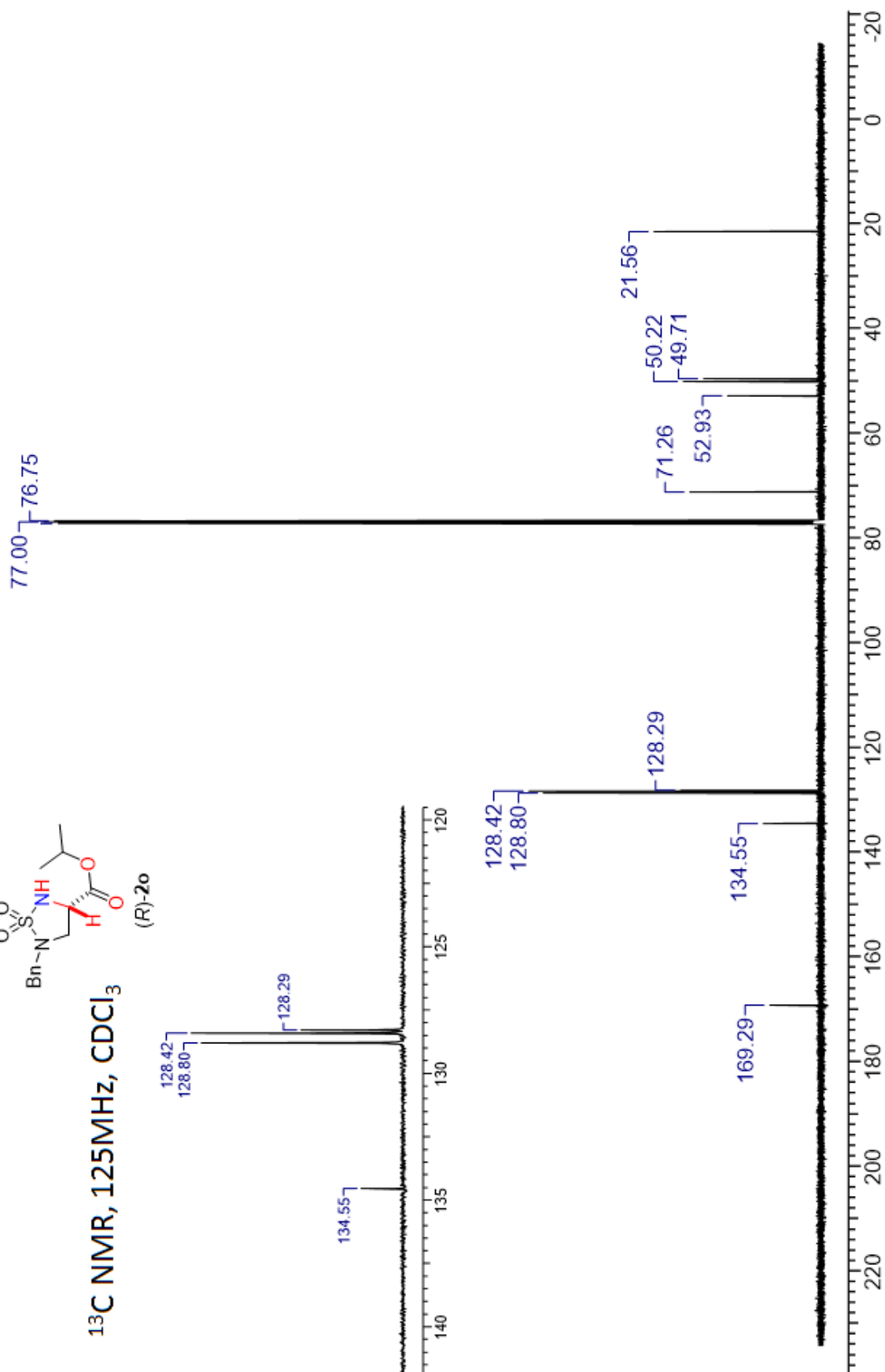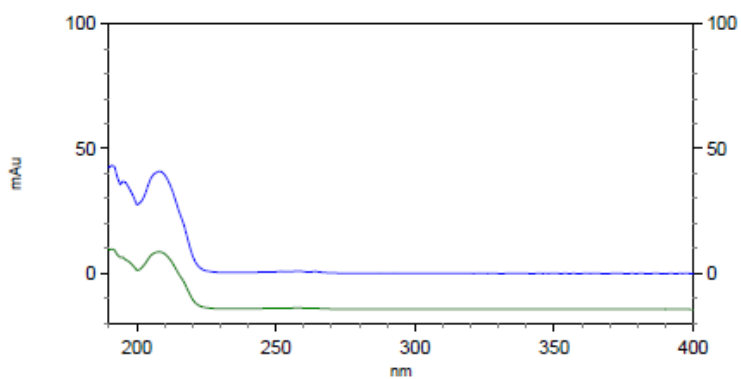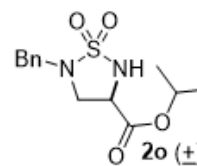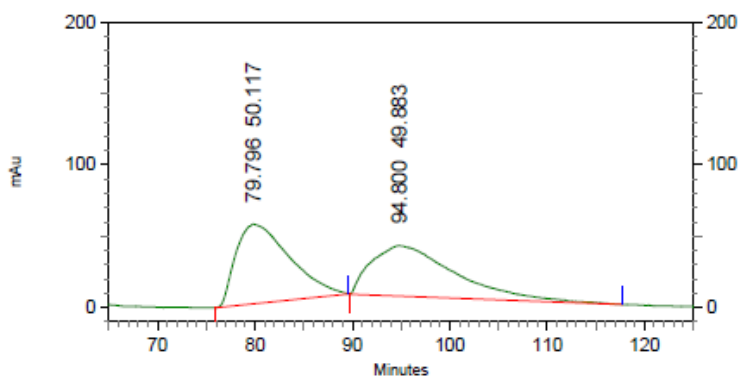
1: 212 nm, 4 nm
 Results

Name	Retention Time	Area Percent	Pk #
	79.796	50.117	1
	94.800	49.883	2

Totals		
	100.000	
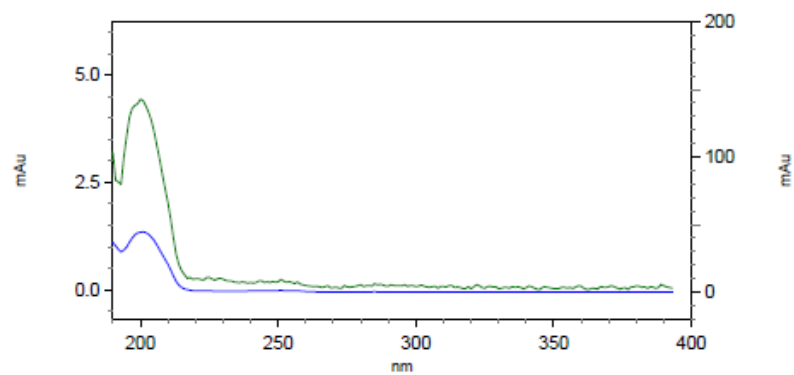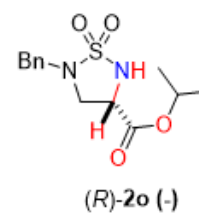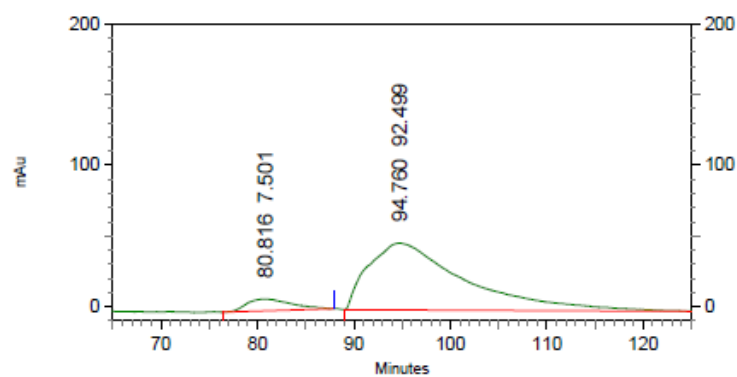
1: 212 nm, 4 nm
 Results

Name	Retention Time	Area Percent	Pk #
	80.816	7.501	1
	94.760	92.499	2

Totals		
	100.000	

^{1}H NMR, 500MHz, CDCl$_3$

(R)-2p
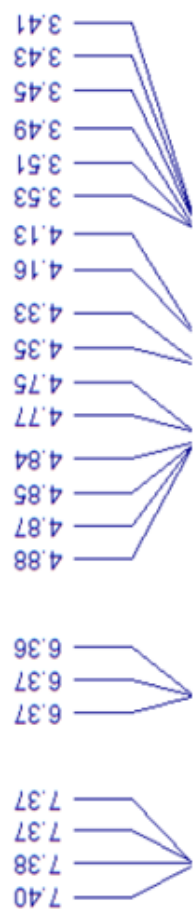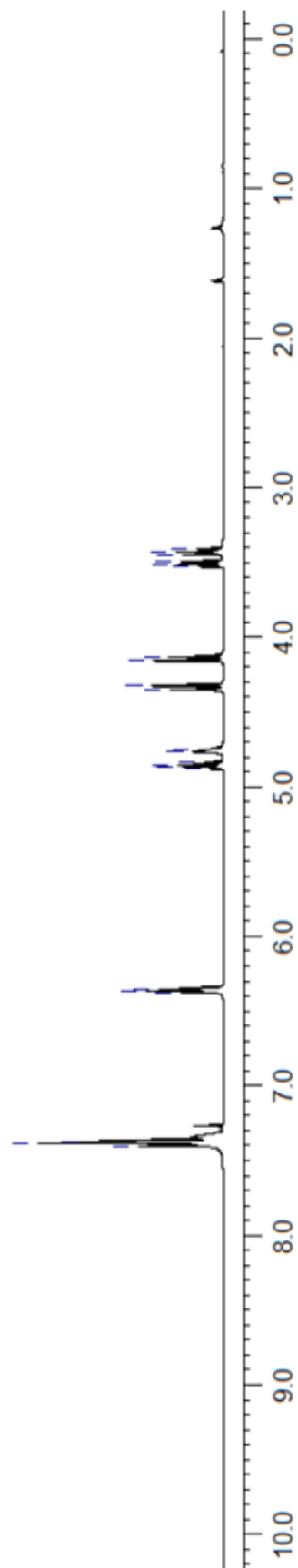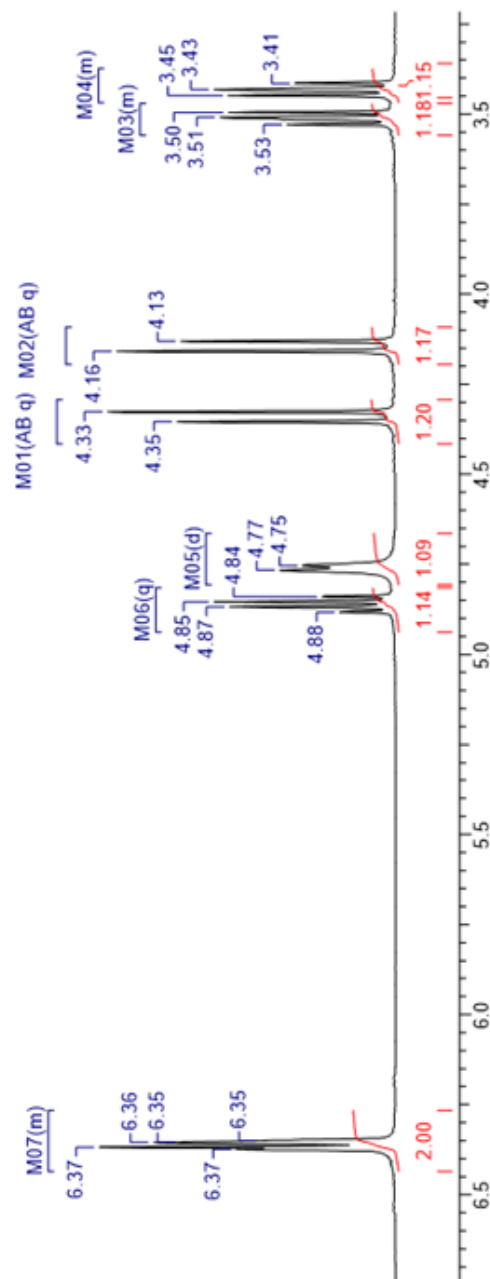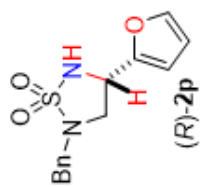
^{13}C NMR, 125MHz, CDCl$_3$
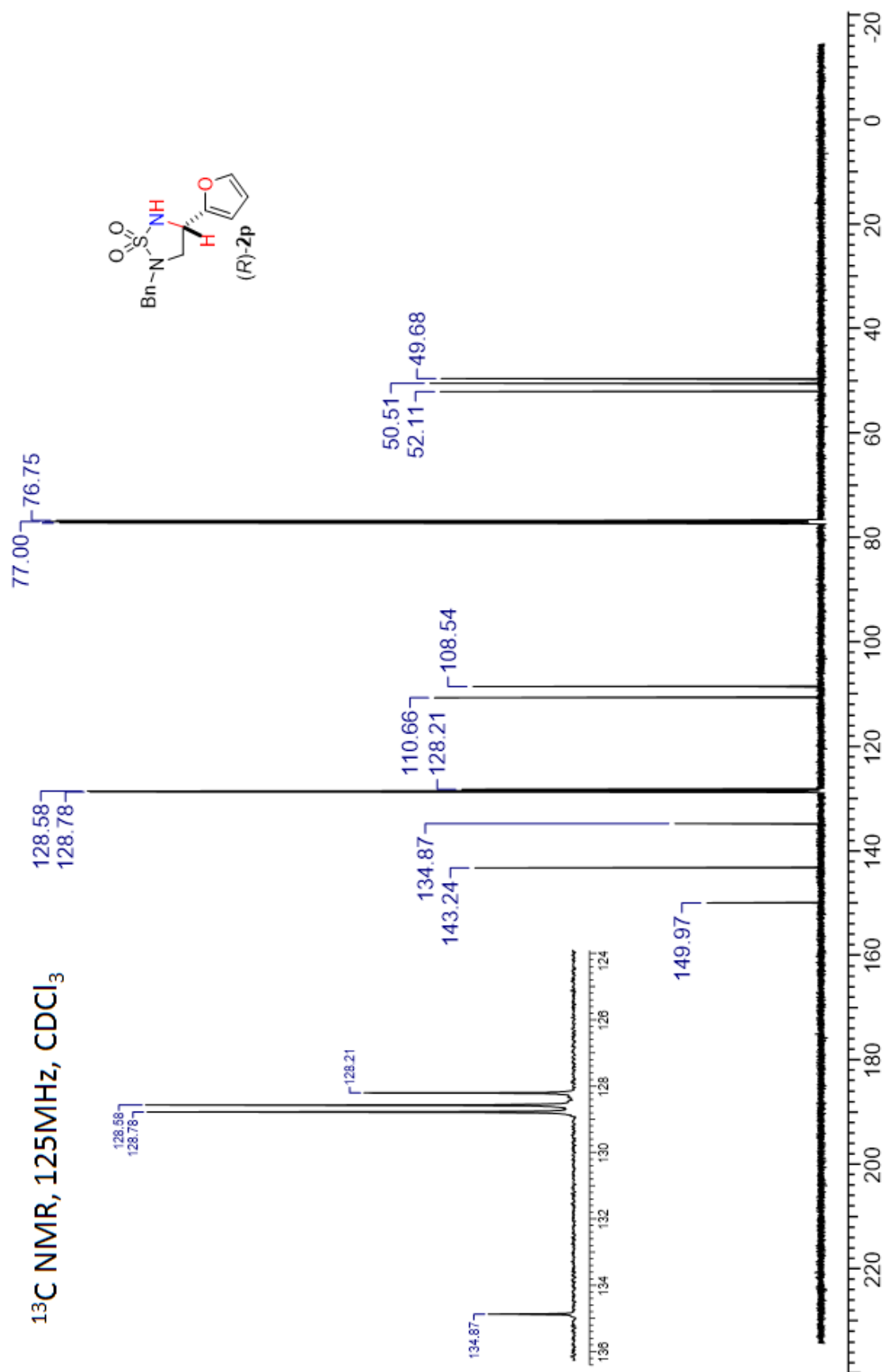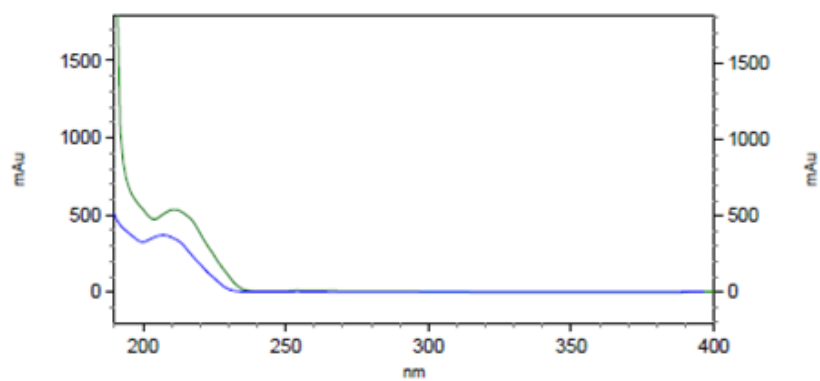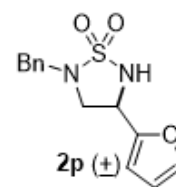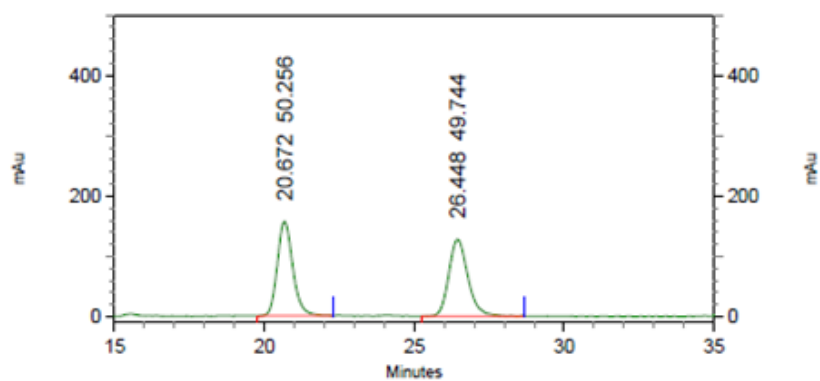
1: 214 nm, 4 nm
Results

Pk # Name	Retention Time	Area Percent
1	20.672	50.256
2	26.448	49.744

Totals	
	100.000

(R)-**2p** (+)
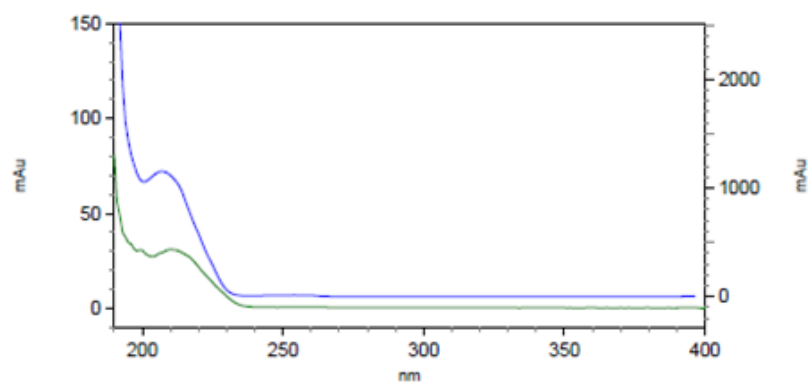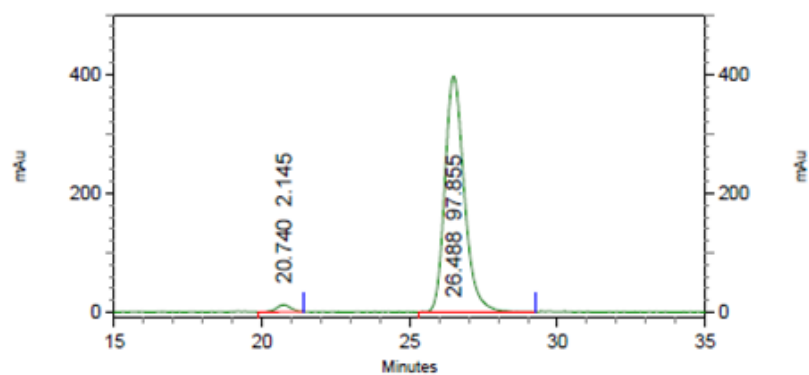
1: 214 nm, 4 nm
 Results

Pk # Name	Retention Time	Area Percent
1	20.740	2.145
2	26.488	97.855

Totals	
	100.000

¹H NMR, 500MHz, CDCl₃

(R)-2q

13C NMR, 125MHz, CDCl₃

(R)-2q
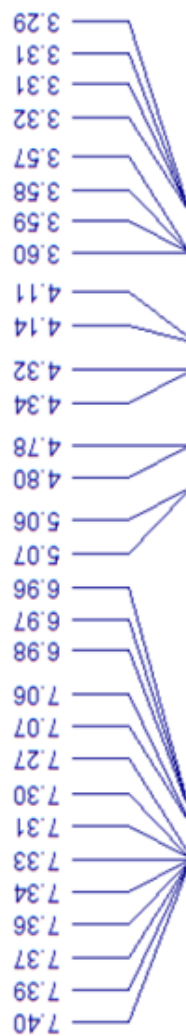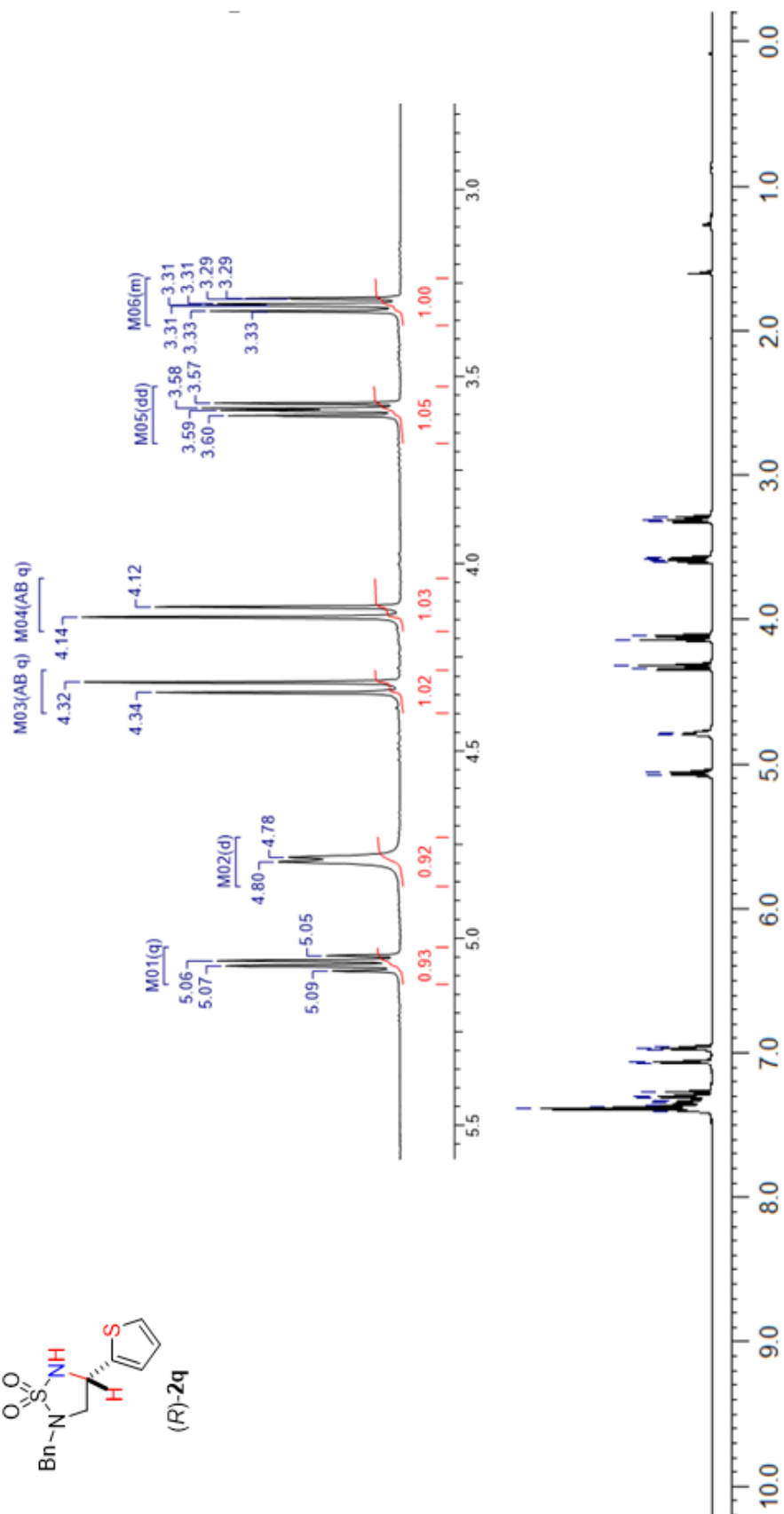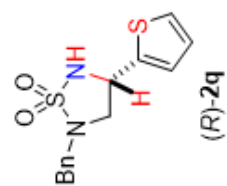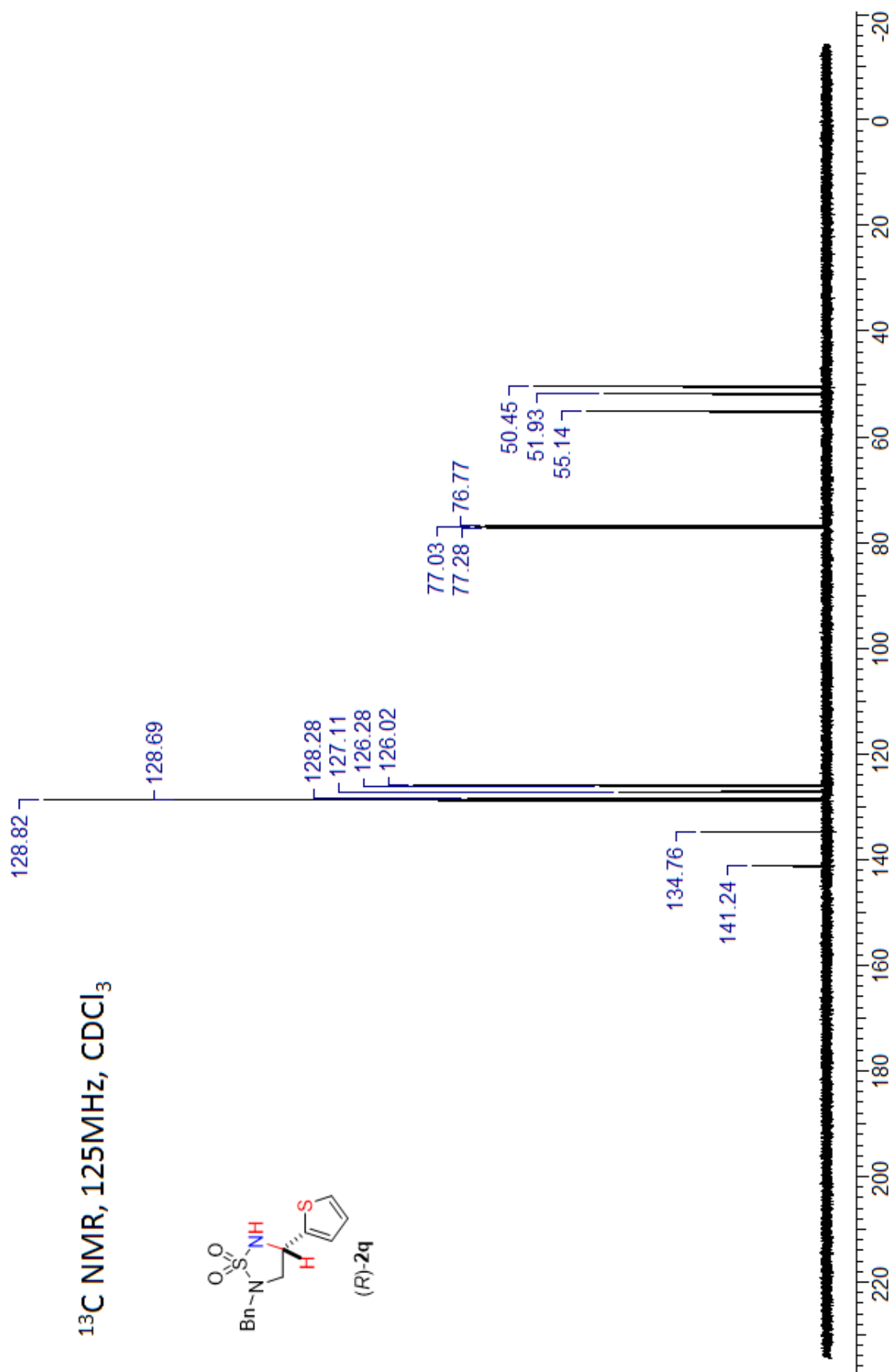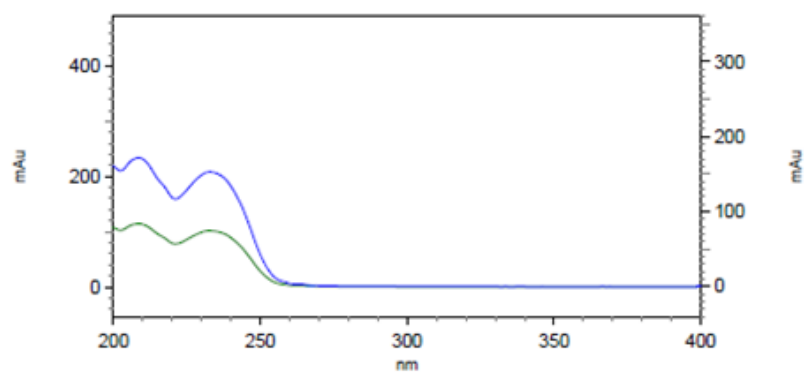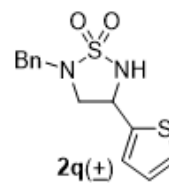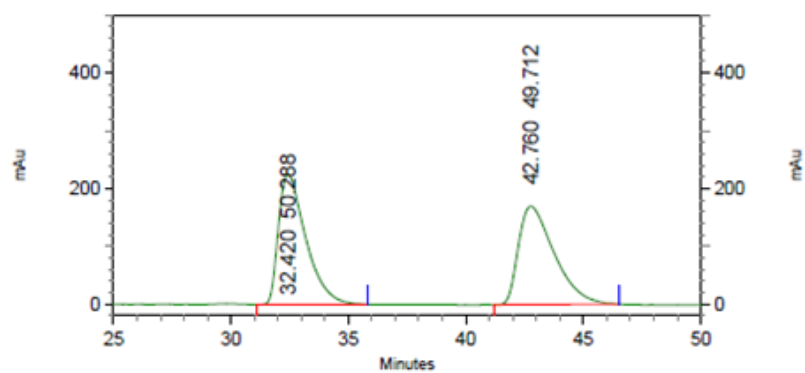
4: 210 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	32.420	50.288	1
	42.760	49.712	2

Totals	
	100.000

(R)-2q (+)
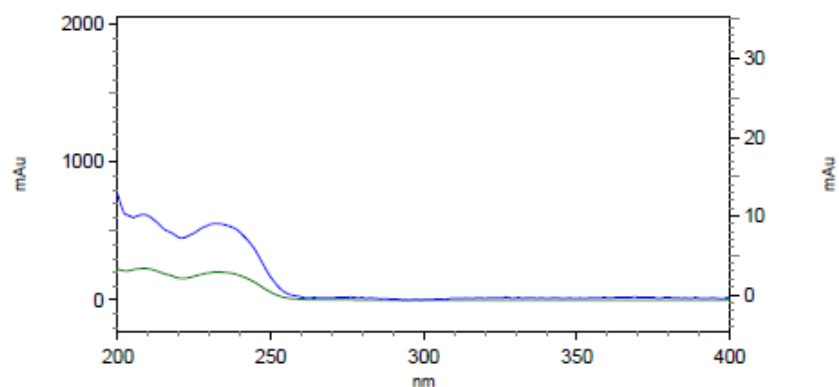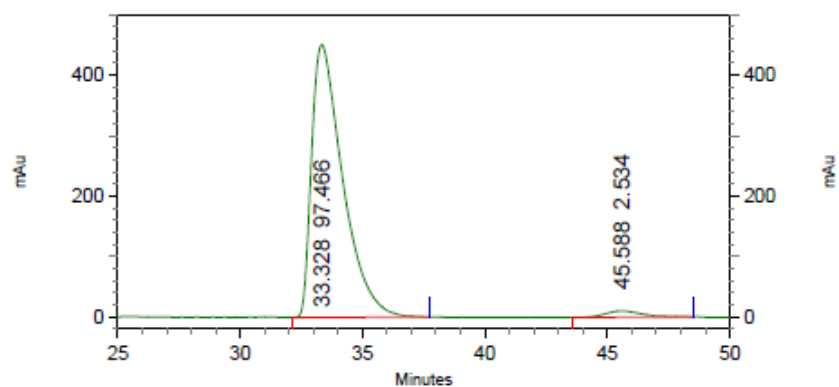
4: 210 nm, 4 nm
 Results

Name	Retention Time	Area Percent	Pk #
	33.328	97.466	1
	45.588	2.534	2

Totals		
	100.000	

^{1}H NMR, 500MHz, CDCl$_3$

(R)-2r

^{13}C NMR, 125MHz, CDCl$_3$

(R)-**2r**

2.53
3.13
14.68
50.46
53.19
57.44
76.91
77.16
77.41
128.25
128.72
128.88
135.29

128.25
128.72
128.88
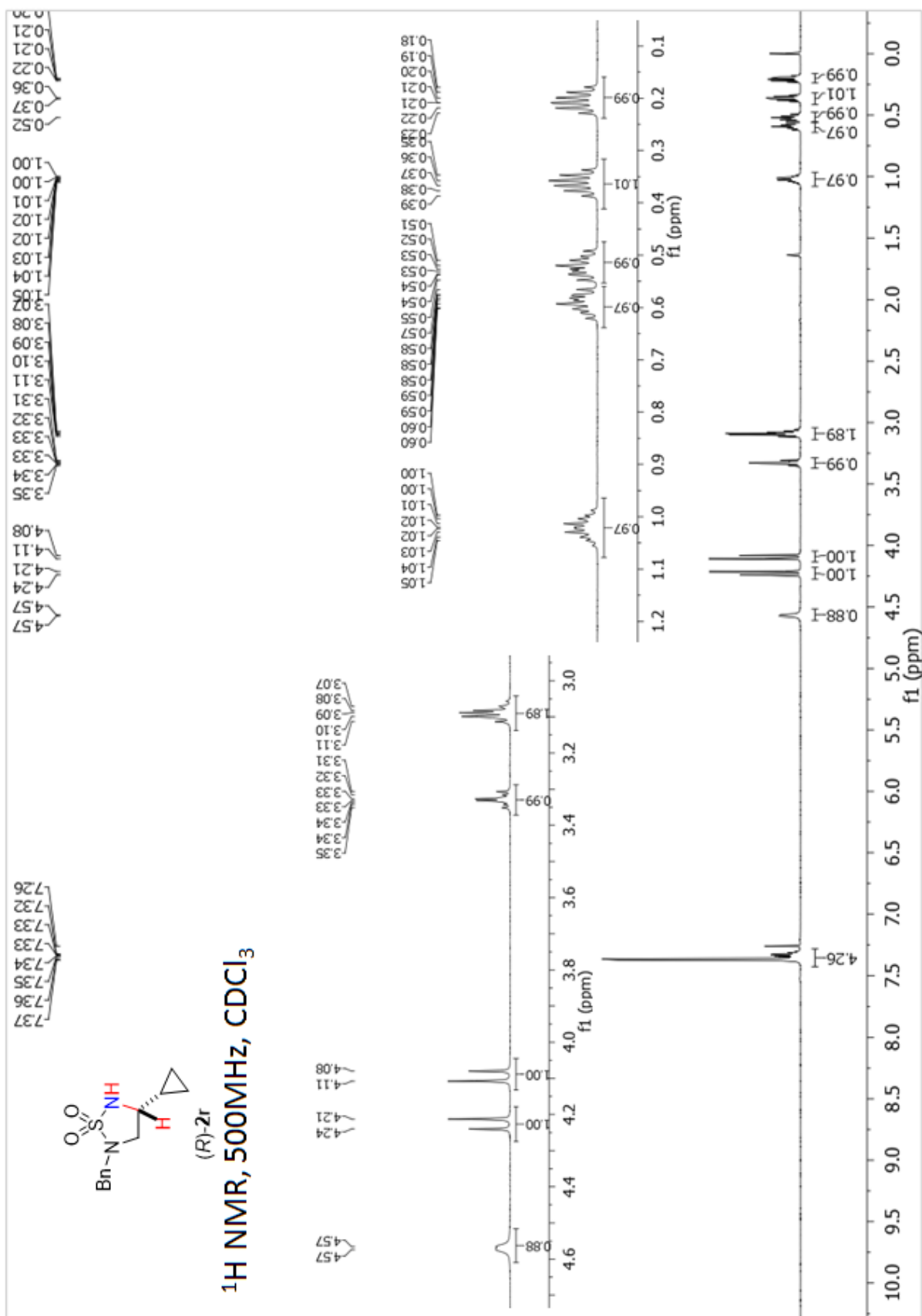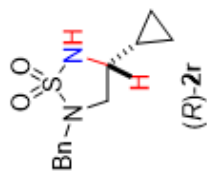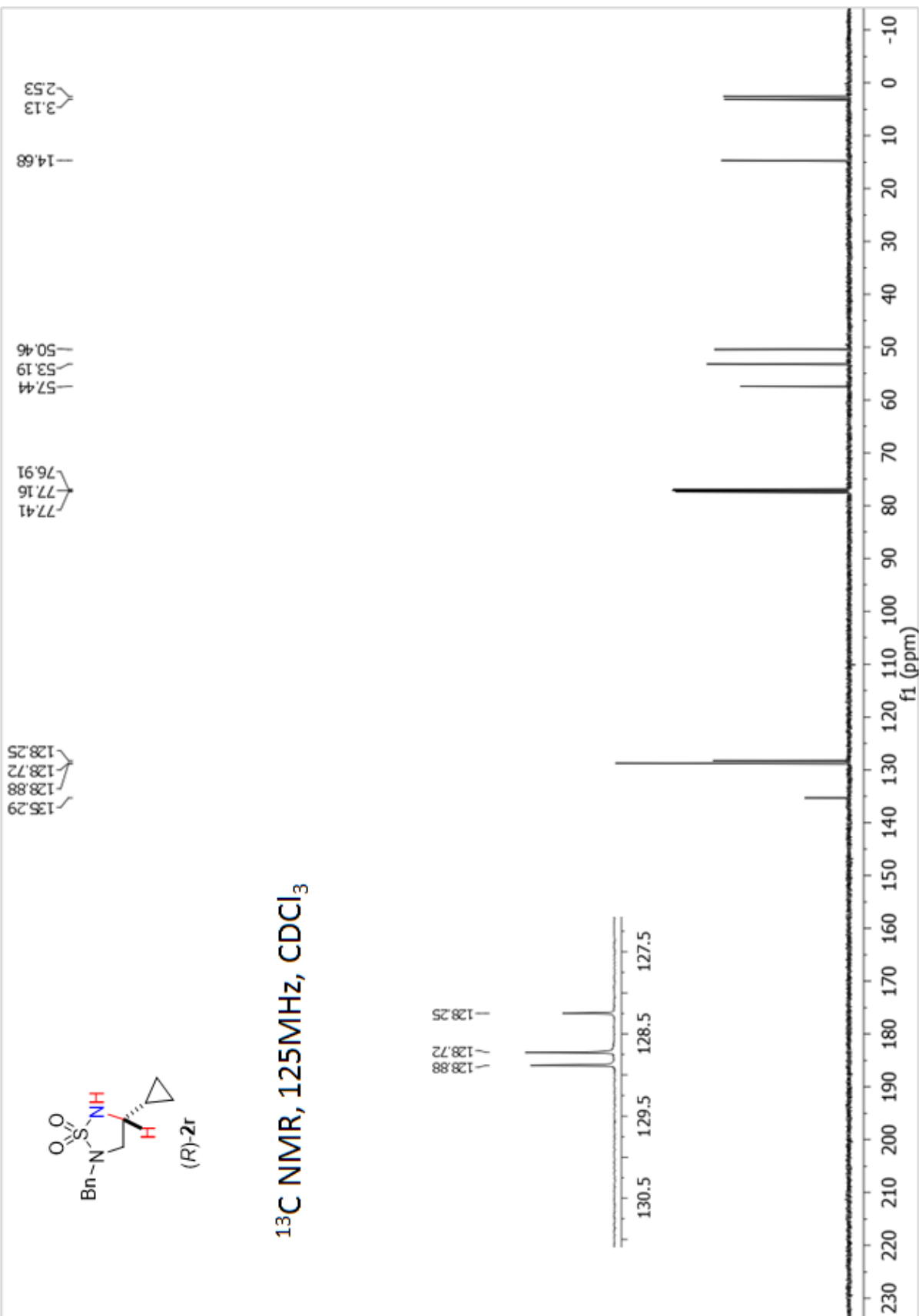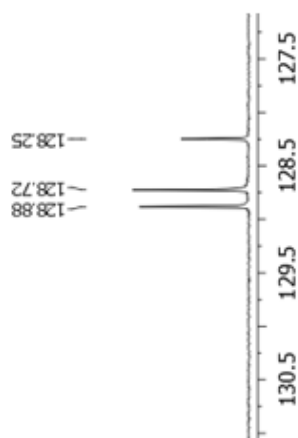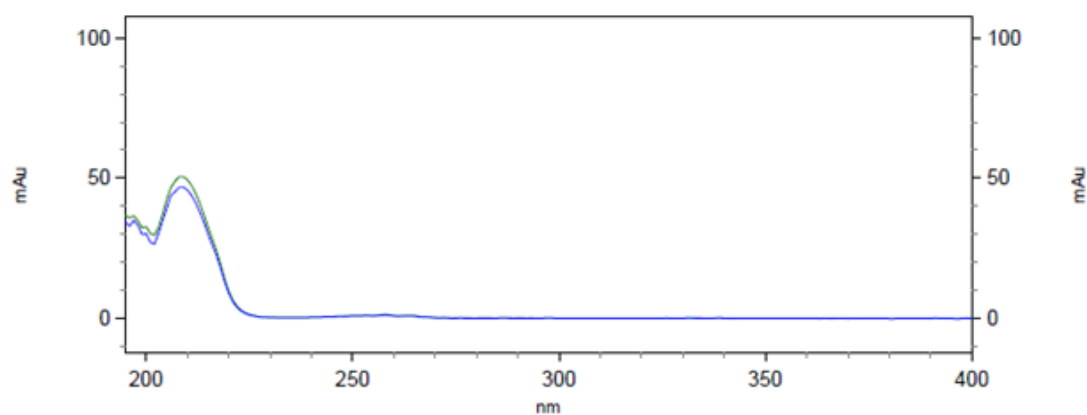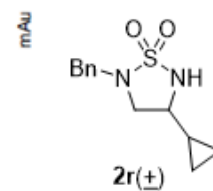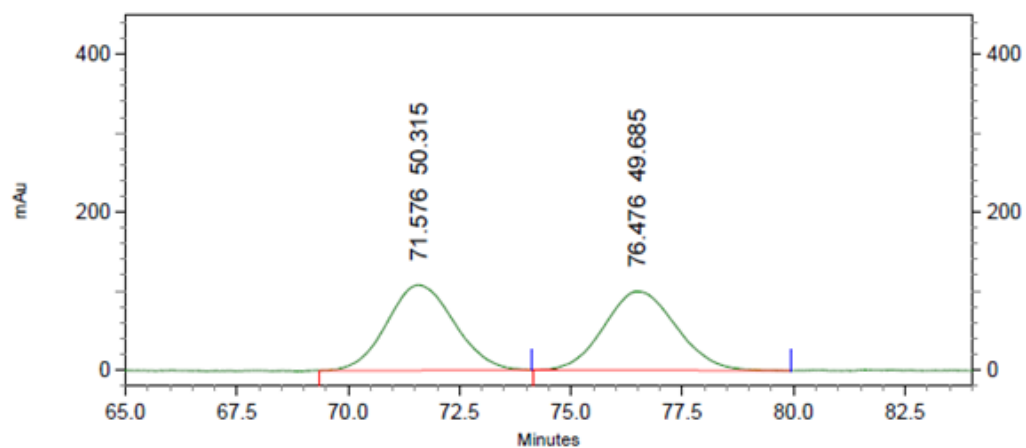
4: 220 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	71.576	50.315
2	76.476	49.685

Totals	
	100.000
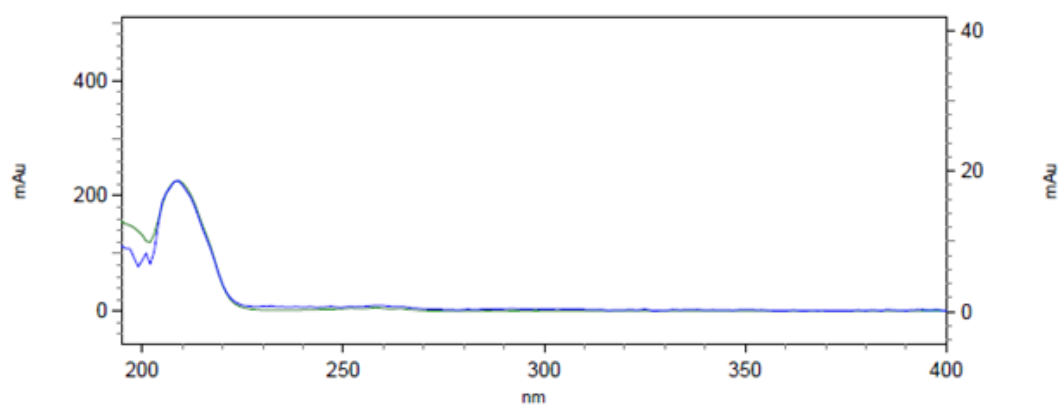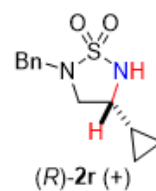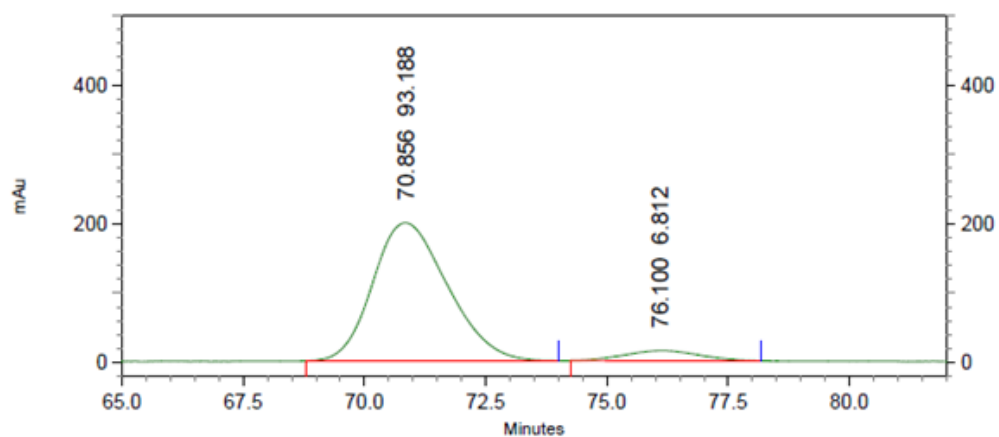
4: 220 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	70.856	93.188
2	76.100	6.812

Totals	
	100.000
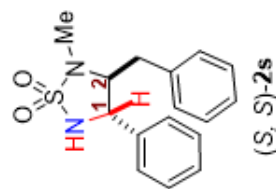
^{1}H NMR, 500MHz, CDCl$_3$

2.69, 2.94, 2.95, 2.97, 2.98, 3.06, 3.07, 3.08, 3.09, 3.53, 3.54, 3.55, 3.56, 4.42, 4.44, 4.45, 4.64, 4.65

7.16, 7.17, 7.27, 7.28, 7.30, 7.33, 7.34, 7.34, 7.35

(S, S)-**2s**

^{13}C NMR, 125MHz, CDCl$_3$

(S, S)-**2s**
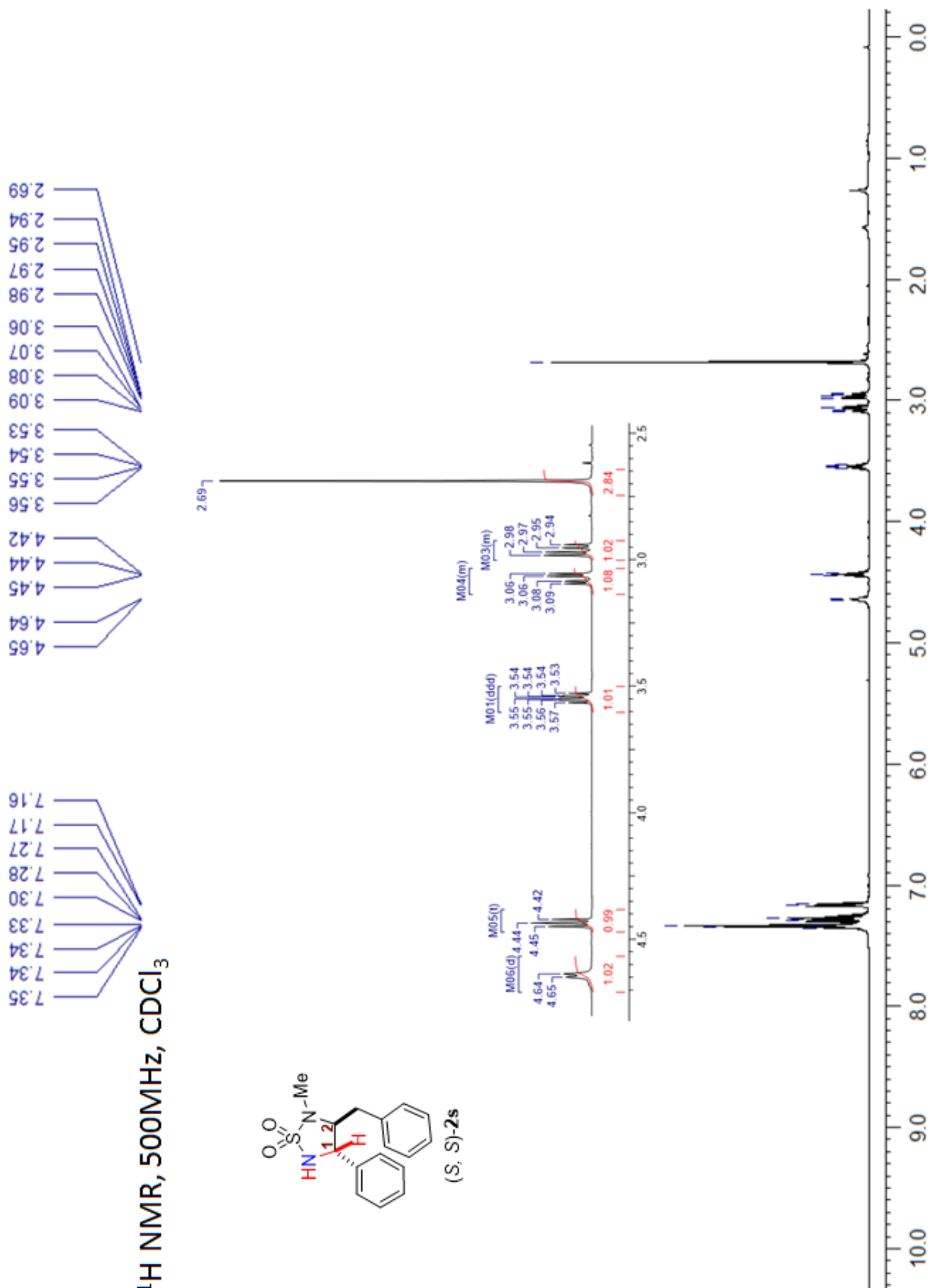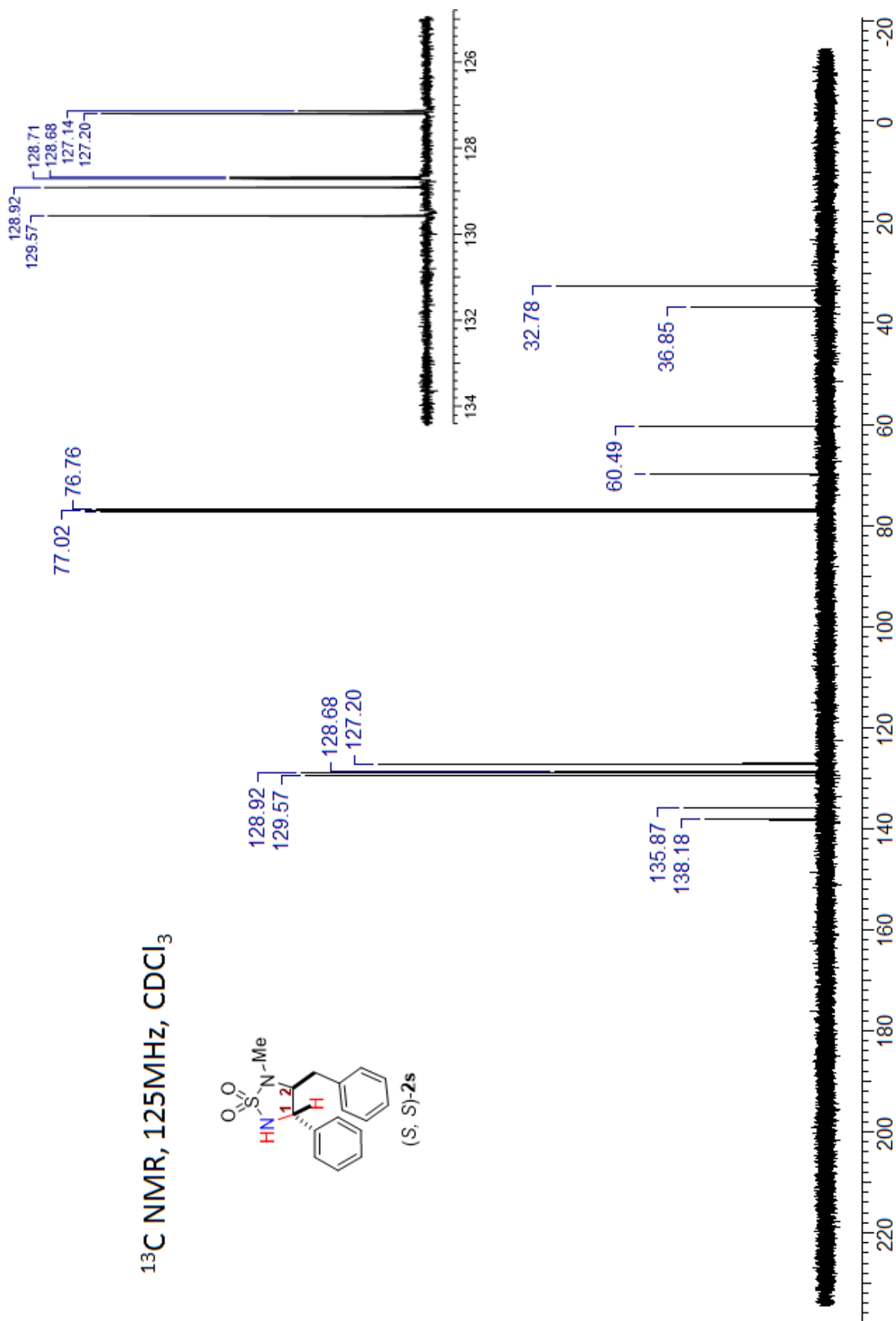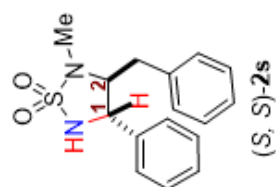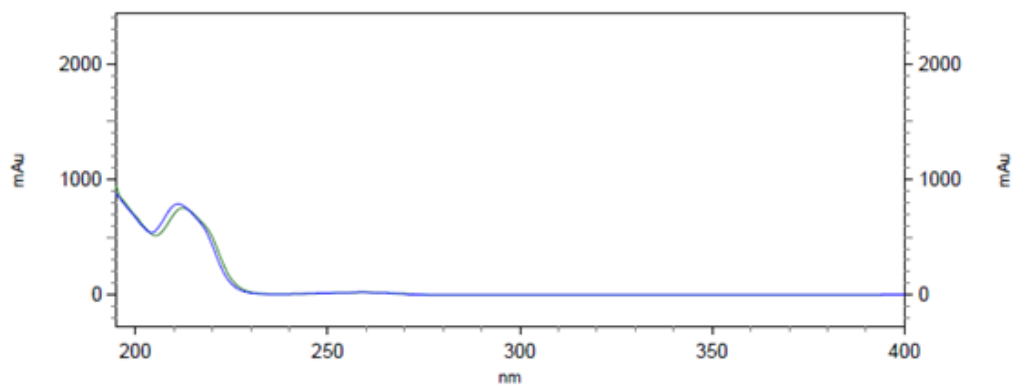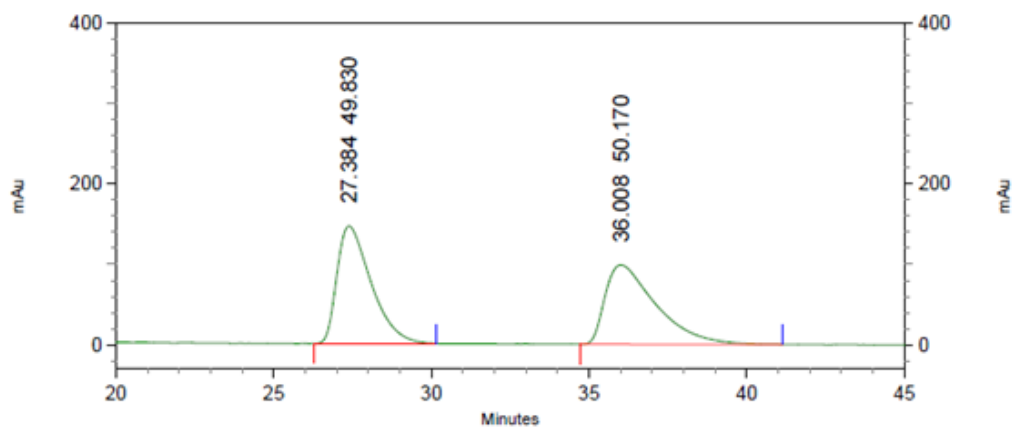
4: 224 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	27.384	49.830
2	36.008	50.170

Totals	
	100.000

(*S*, *S*)-**2s** (-)
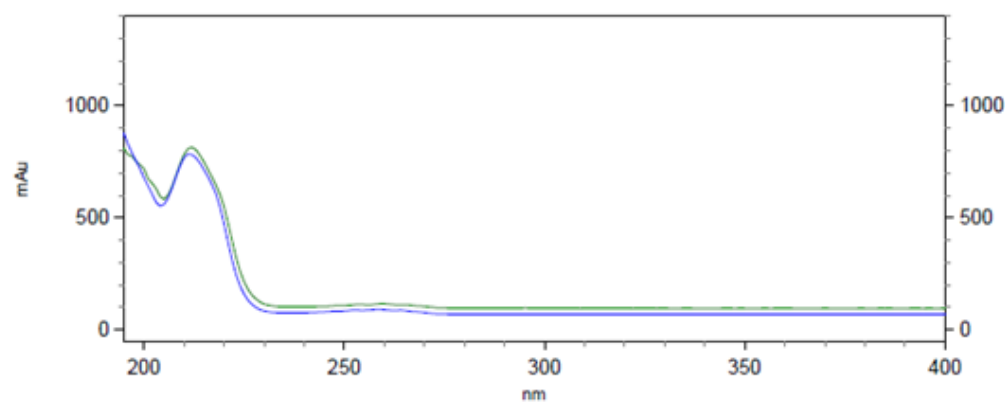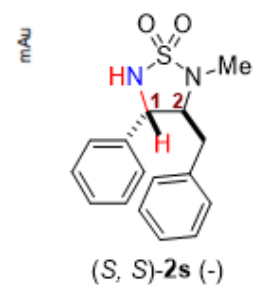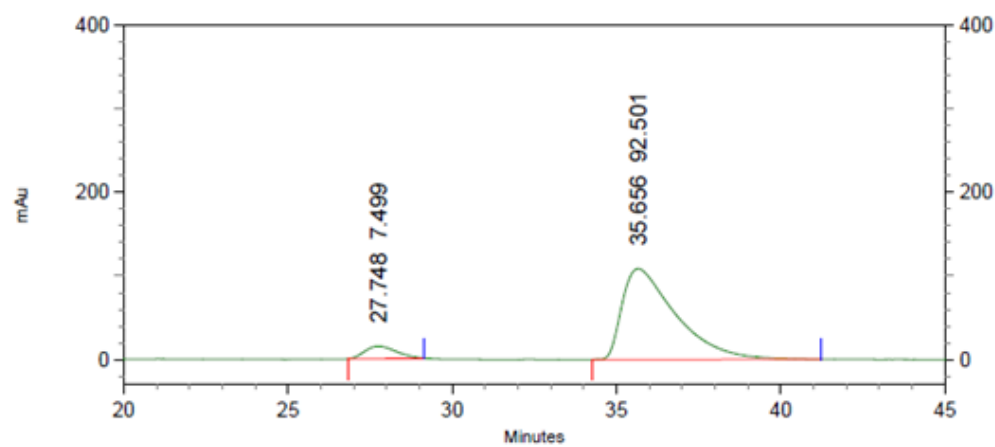
4: 224 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	27.748	7.499
2	35.656	92.501

Totals	
	100.000

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: I

```
Bond precision:   C-C = 0.0048 A            Wavelength=1.54178

Cell:             a=5.6293(2)      b=7.4200(2)      c=34.2745(11)
                  alpha=90         beta=90          gamma=90
Temperature:      100 K

                  Calculated              Reported
Volume            1431.63(8)              1431.63(8)
Space group       P 21 21 21              P 21 21 21
Hall group        P 2ac 2ab               P 2ac 2ab
Moiety formula    C16 H18 N2 O2 S         C16 H18 N2 O2 S
Sum formula       C16 H18 N2 O2 S         C16 H18 N2 O2 S
Mr                302.38                  302.38
Dx,g cm-3         1.403                   1.403
Z                 4                       4
Mu (mm-1)         2.060                   2.060
F000              640.0                   640.0
F000'             643.04
h,k,lmax          6,8,41                  6,8,41
Nref              2658[ 1594]             2635
Tmin,Tmax         0.906,0.960             0.515,0.753
Tmin'             0.848

Correction method= # Reported T Limits: Tmin=0.515 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 1.65/0.99      Theta(max)= 68.972

R(reflections)= 0.0374( 2328)     wR2(reflections)= 0.0854( 2635)

S = 1.056                  Npar= 195
```

```
The following ALERTS were generated. Each ALERT has the format
        test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```
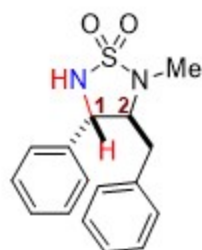
(S, S)-**2s** (-)

(*S*, *S*)-**2s** (-)

🟡 **Alert level C**
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds .... 0.0048 Ang.

⚪ **Alert level G**
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF   Please Do !
PLAT033_ALERT_4_G Flack x Value Deviates > 2*sigma from Zero .....   0.055 Note
PLAT791_ALERT_4_G The Model has Chirality at C7   (Chiral SPGR)   S Verify
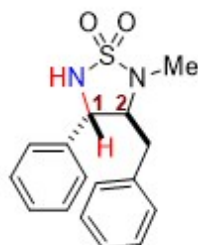PLAT791_ALERT_4_G The Model has Chirality at C8   (Chiral SPGR)   S Verify

---

   0 **ALERT level A** = Most likely a serious problem - resolve or explain
   0 **ALERT level B** = A potentially serious problem, consider carefully
   1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
   4 **ALERT level G** = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   0 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check

---

checkCIF publication errors

🔴 **Alert level A**
PUBL002_ALERT_1_A The contact author's address is missing,
             _publ_contact_author_address.
PUBL005_ALERT_1_A _publ_contact_author_email, _publ_contact_author_fax and
             _publ_contact_author_phone are all missing.
          At least one of these should be present.
PUBL006_ALERT_1_A _publ_requested_journal is missing
             e.g. 'Acta Crystallographica Section C'
PUBL008_ALERT_1_A _publ_section_title is missing. Title of paper.
PUBL009_ALERT_1_A _publ_author_name is missing. List of author(s) name(s).
PUBL010_ALERT_1_A _publ_author_address is missing. Author(s) address(es).
PUBL012_ALERT_1_A _publ_section_abstract is missing.
             Abstract of paper in English.

---

   7 **ALERT level A** = Data missing that is essential or data in wrong format
   0 **ALERT level G** = General alerts. Data that may be required is missing

---

Publication of your CIF

You should attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the nature of your study may justify the reported deviations from journal submission requirements and the more serious of these should be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. *checkCIF* was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

If level A alerts remain, which you believe to be justified deviations, and you intend to submit this CIF for publication in a journal, you should additionally insert an explanation in your CIF using the Validation Reply Form (VRF) below. This will allow your explanation to be considered as part of the review process.

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PUBL002_GLOBAL
;
PROBLEM: The contact author's address is missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
.
```


(*S*, *S*)-**2s** (-)

(S, S)-**2s** (-)

PLATON version of 21/06/2015; check.def file version of 21/06/2015

Datablock I - ellipsoid plot
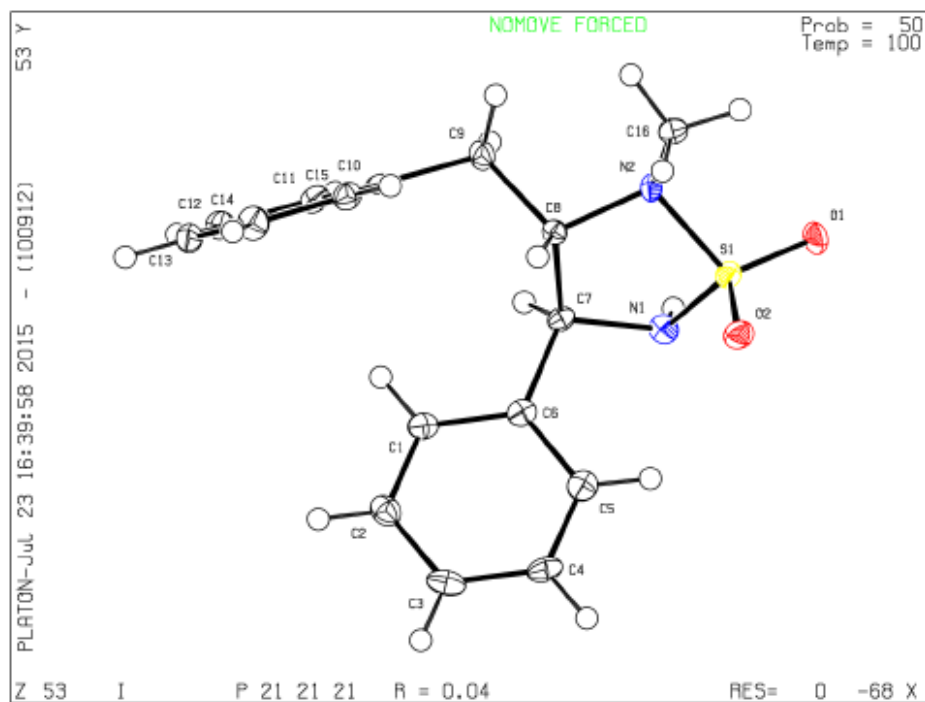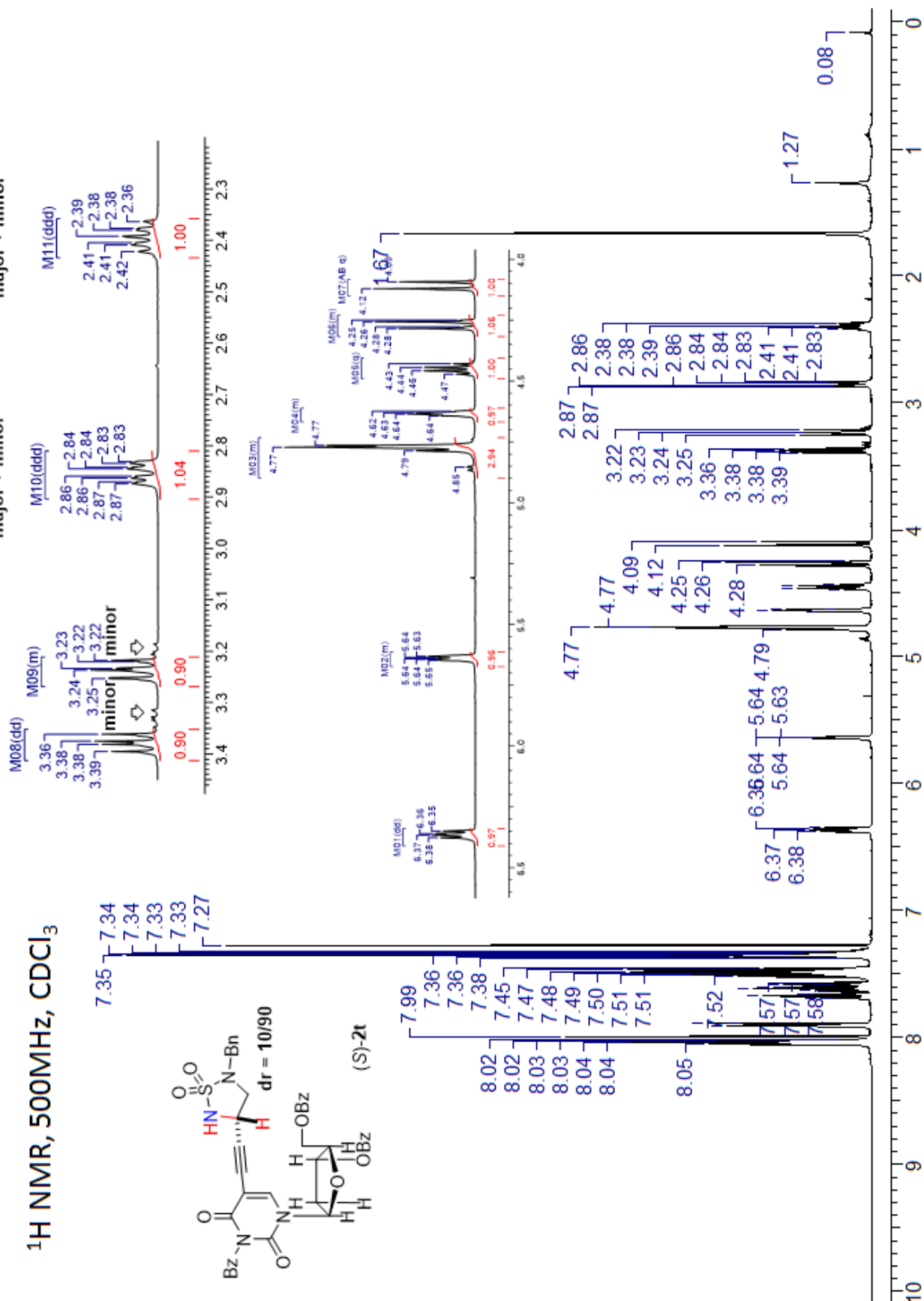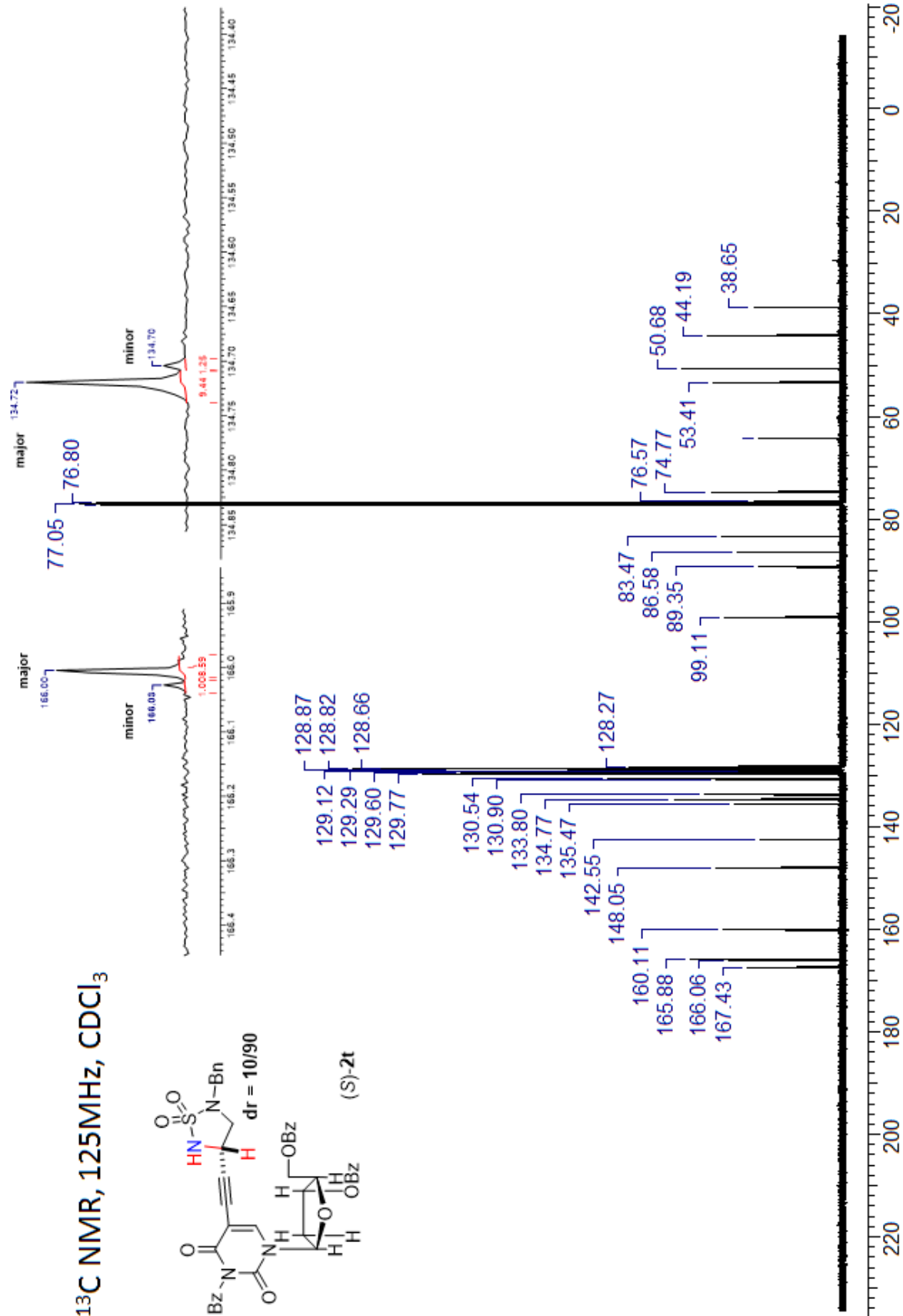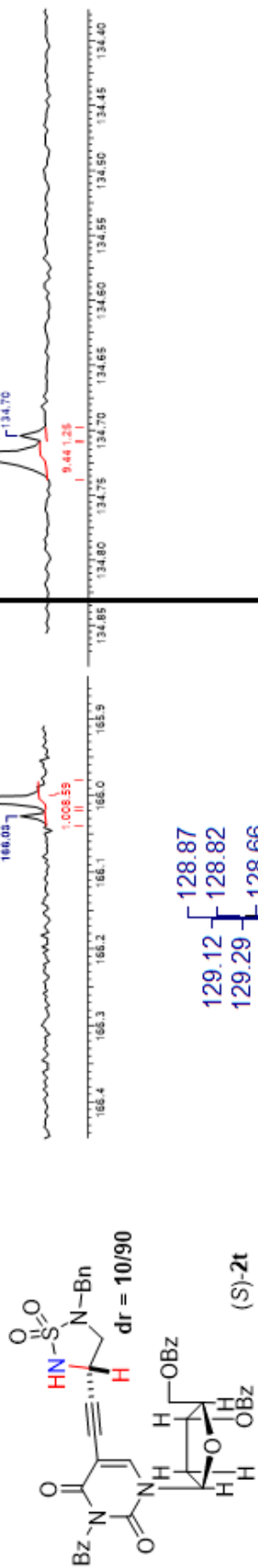
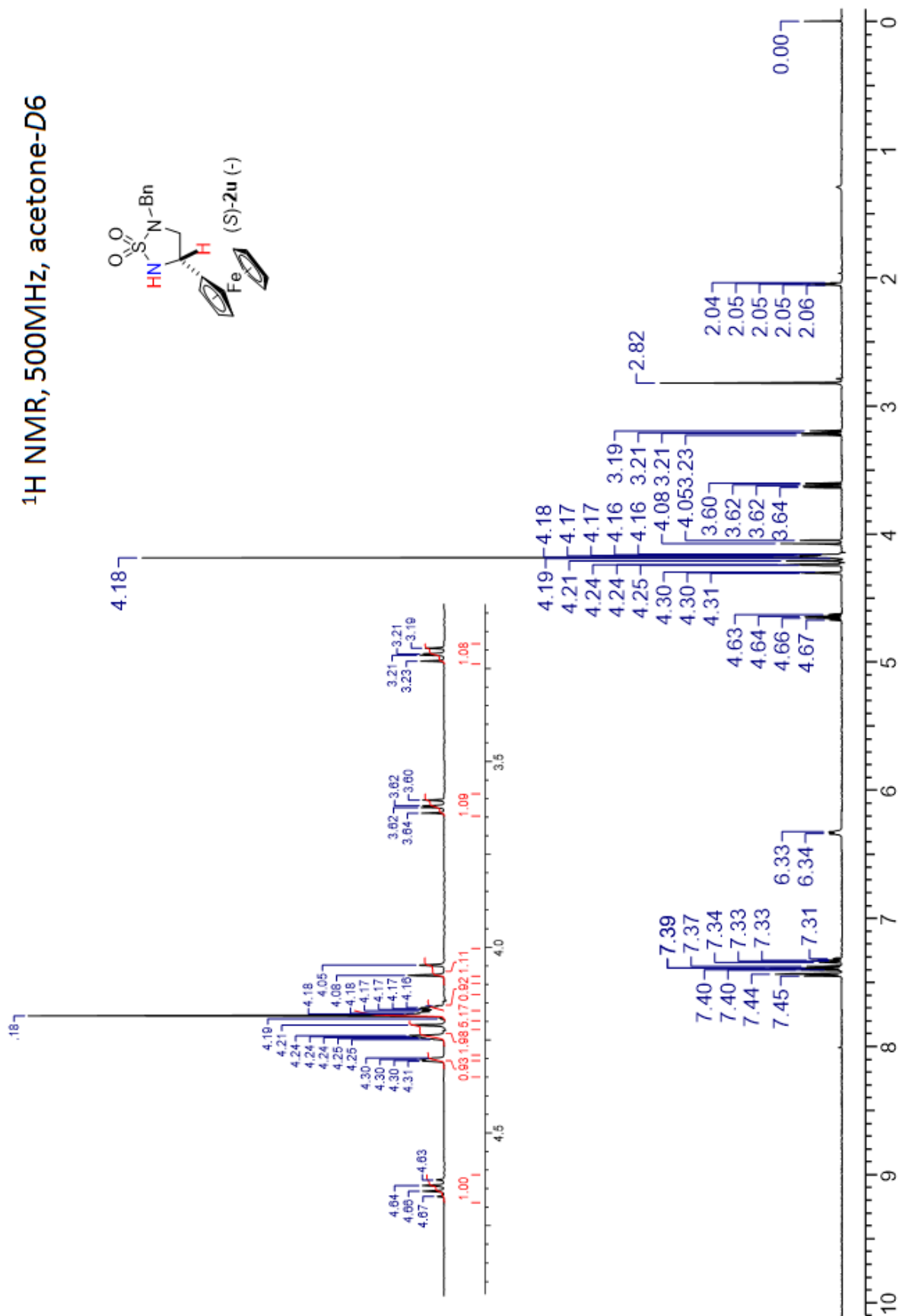¹H NMR, 500MHz, CDCl₃

major + minor

major + minor

minor

(S)-2t

dr = 10/90

S306

^{13}C NMR, 125MHz, CDCl$_3$

dr = 10/90

(S)-2t

¹H NMR, 500MHz, acetone-*D*6

(S)-**2u** (-)

^{13}C NMR, 150MHz, acetone-$D6$

(S)-2u (-)

S309

Chromatogram

mAU

1PDA Multi 1 254nm,4nm
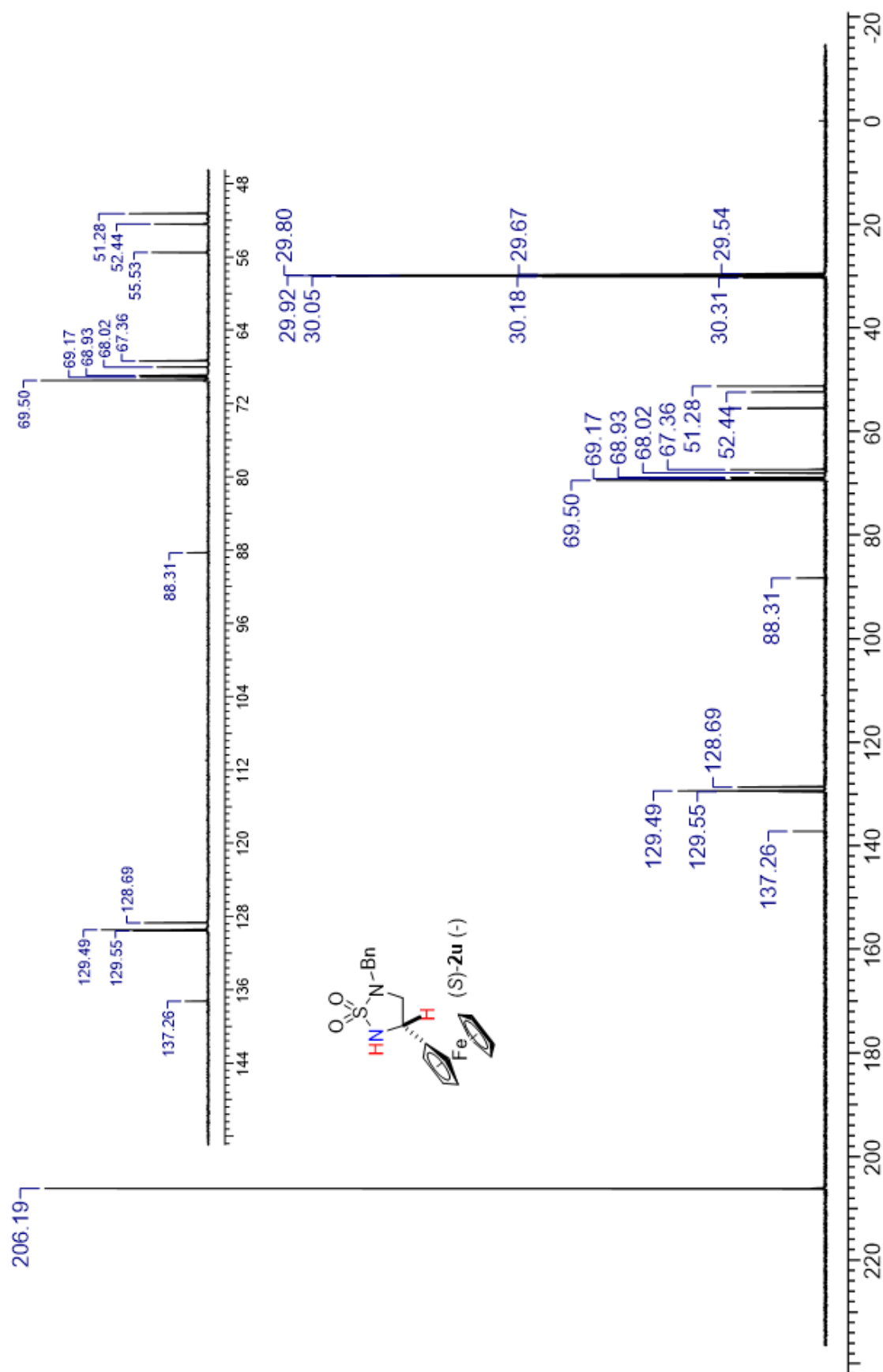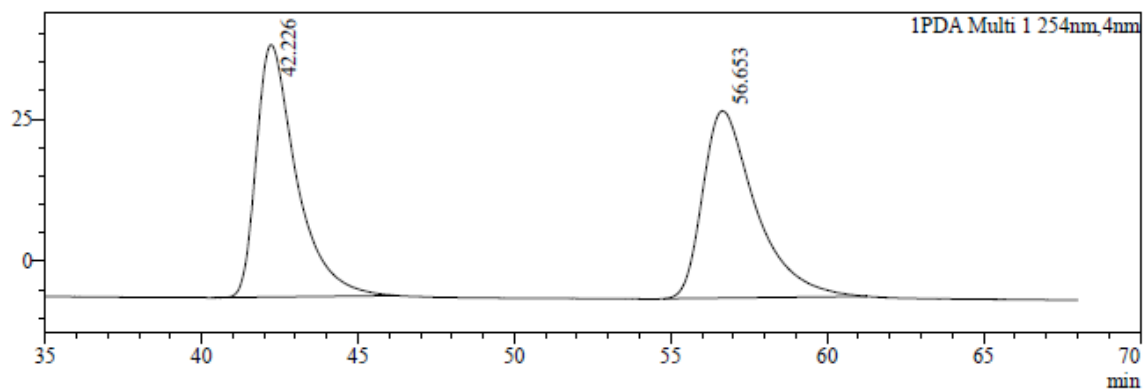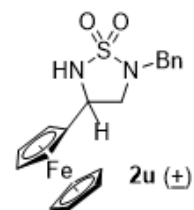
42.226

56.653

UV Spectrum

lk-v-168c10%1ML.lcd

mAU
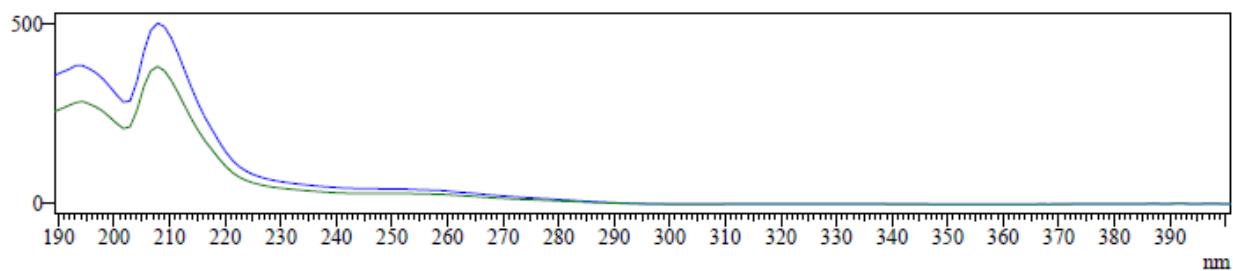
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	42.226	3951498	50.405
2	56.653	3888058	49.595
Total		7839556	100.000

(S)-**2u** (-)

Chromatogram

mAU

1PDA Multi 1 254nm,4nm

42.032

56.771

UV Spectrum

lk-v-168A10%1ML.lcd

mAU
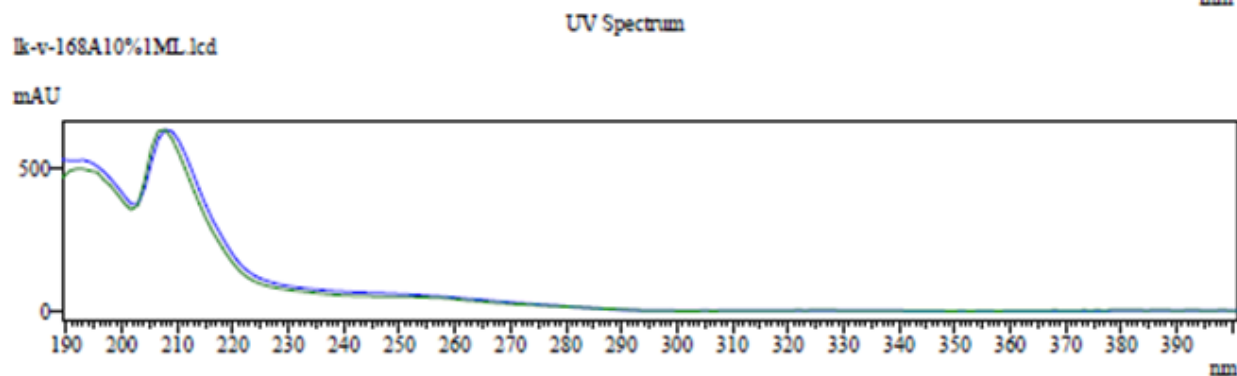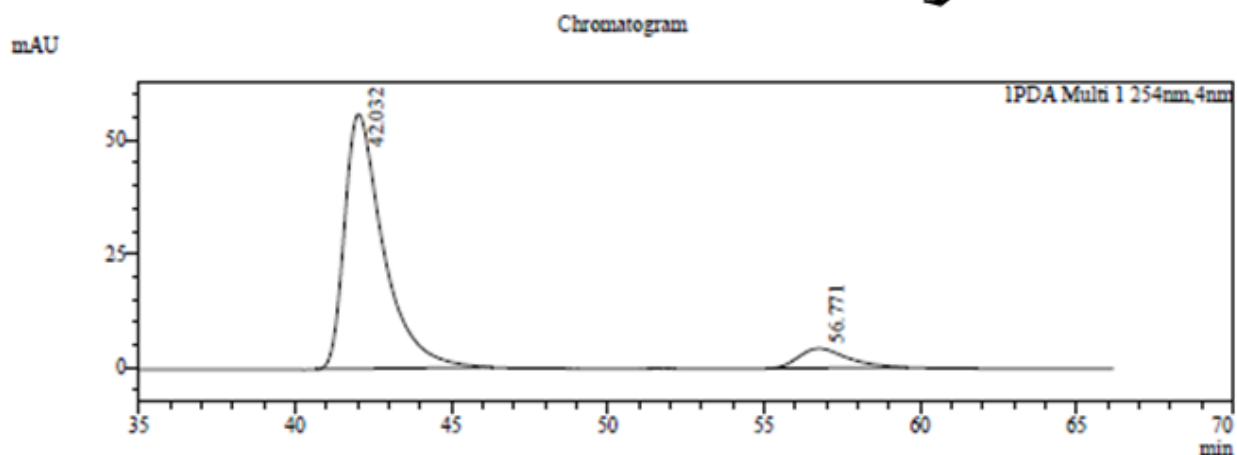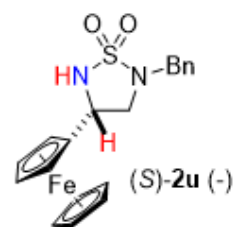
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	42.032	4836069	91.256
2	56.771	463366	8.744
Total		5299435	100.000

^{1}H NMR, 600MHz, CDCl$_3$

^{1}H NMR (t=35; T1=66; ø=45°C) on a 600 M Hz machine
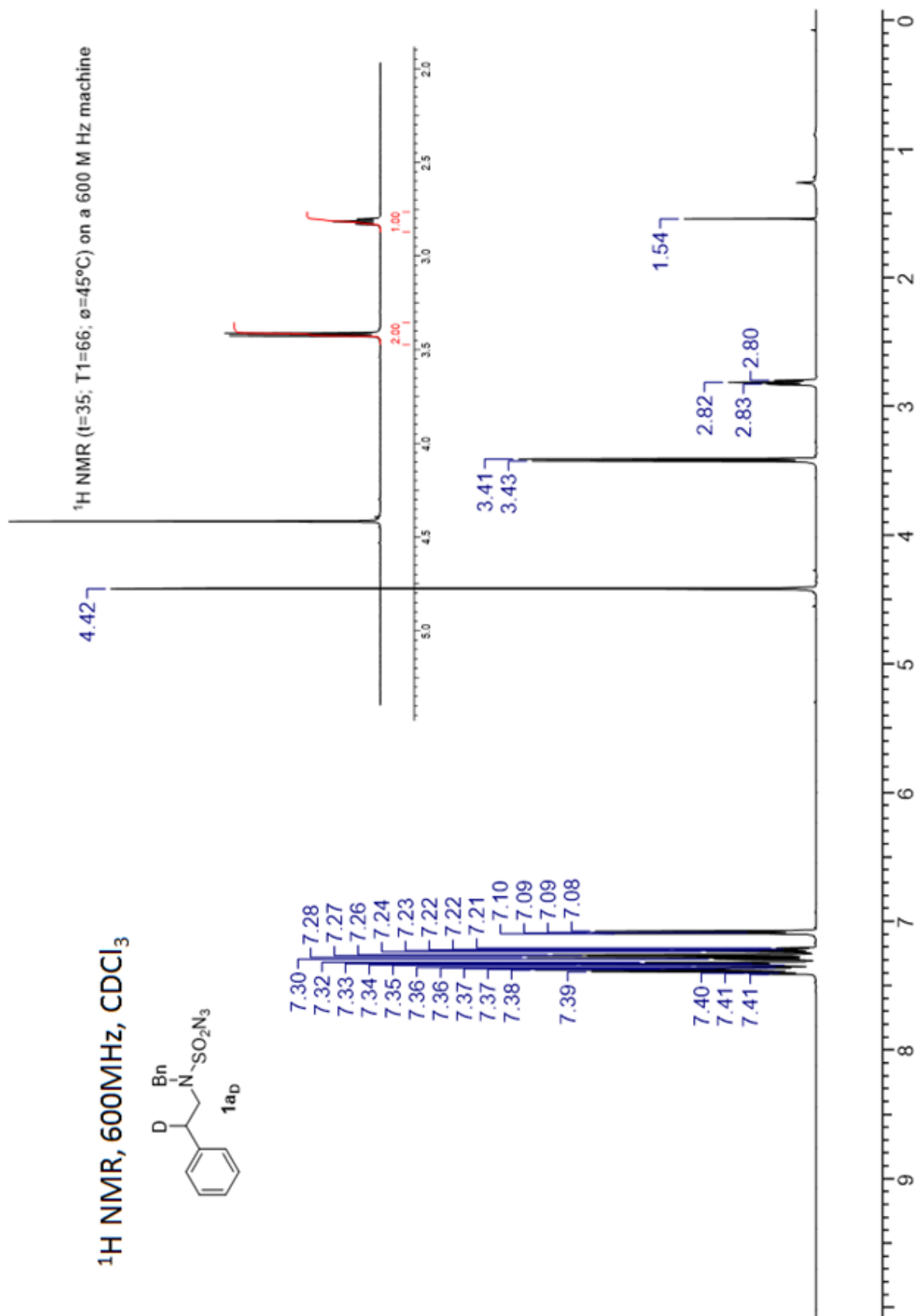
^{13}C NMR, 100MHz, CDCl$_3$

LK-V-117_CARBON_01
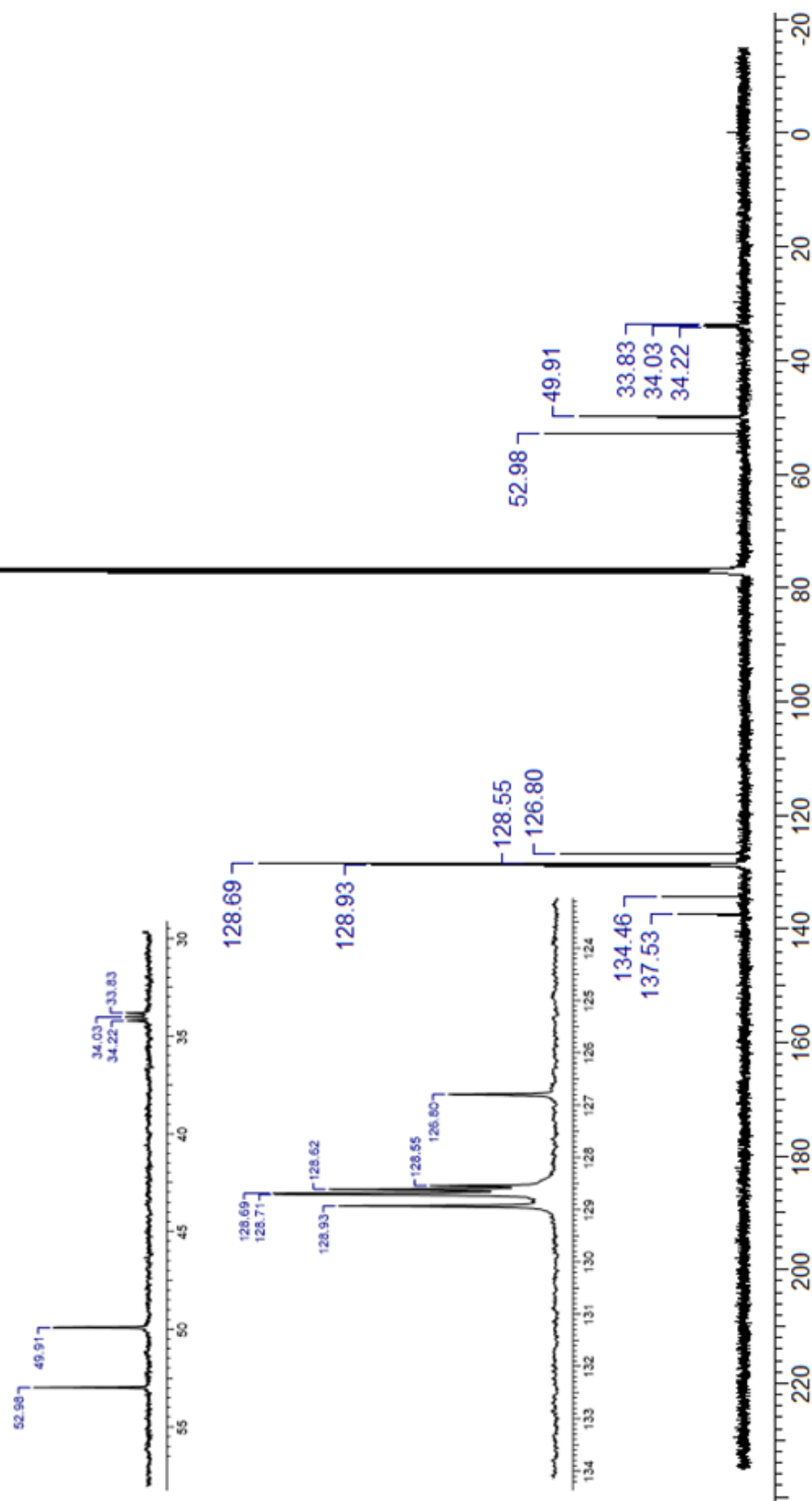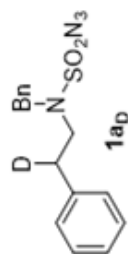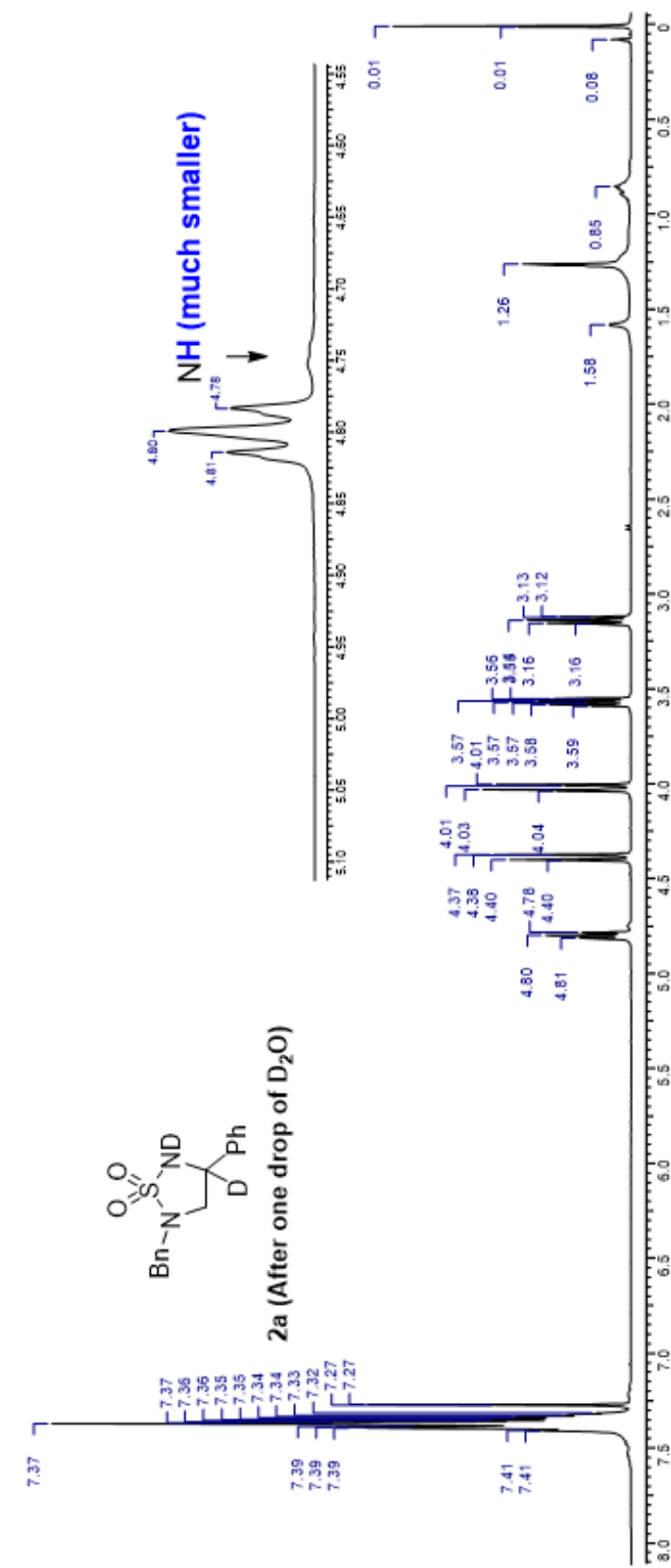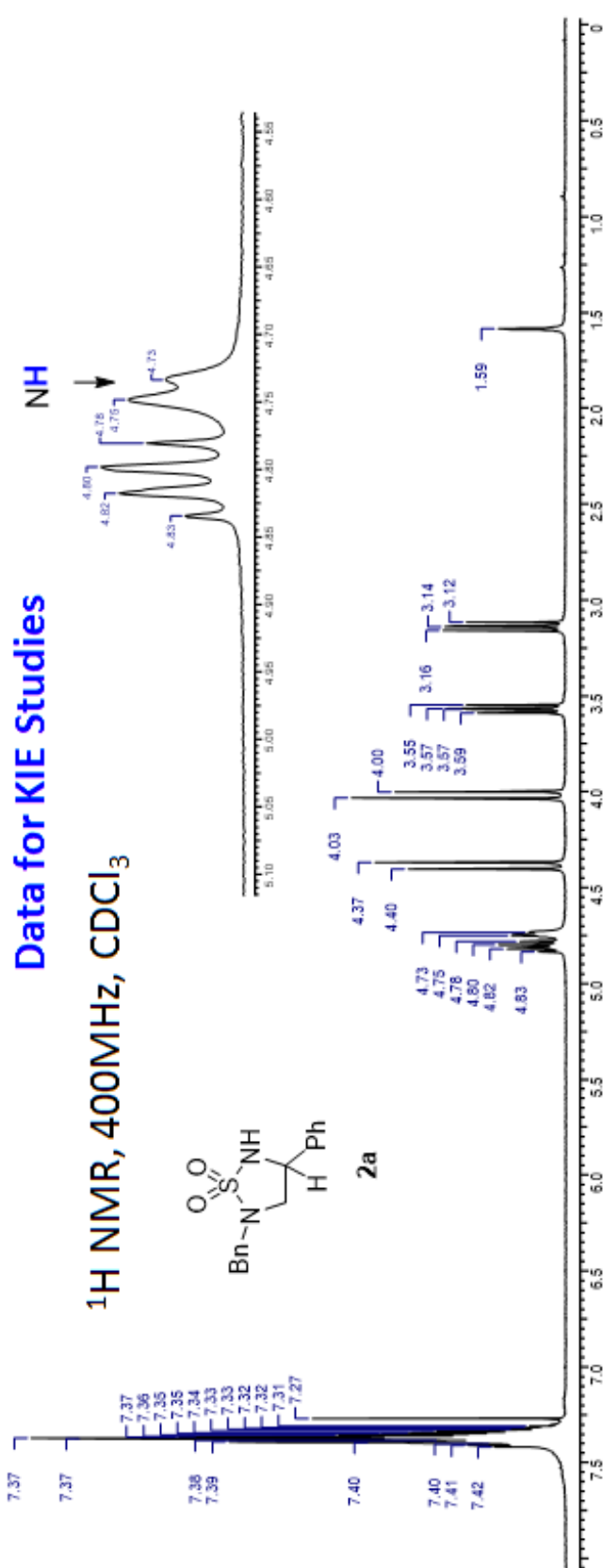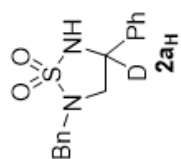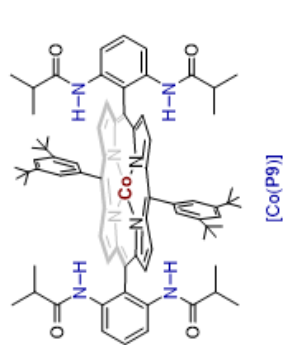
77.00
76.68
52.98
49.91
34.22
34.03
33.83
137.53
134.46
128.93
128.69
128.55
126.80

128.71
128.69
128.62
128.93
126.80
128.55
34.03
34.22
33.83
52.98
49.91

1a$_D$

Data for KIE Studies

^1H NMR, 400MHz, $CDCl_3$

2a

NH

2a (After one drop of D_2O)

NH (much smaller)

Table 2, entries 1 and 4

^{1}H NMR, 500MHz, CDCl$_3$

[Co(**P9**)]

(After one drop of D$_2$O)

= 23:1

2a$_D$

;

2a$_H$

(R)-**1a$_D$**

or

(S)-**1a$_D$**

[Co(**P9**)]

2a$_H$

Table 2, entry 1

5: 213 nm, 4 nm
 Results

Name	Retention Time	Area Percent	Pk #
	24.564	48.406	1
	34.384	51.594	2
Totals		100.000	

Table 2, entry 4

5: 213 nm, 4 nm
Results
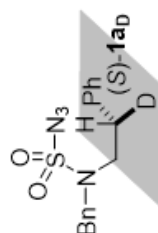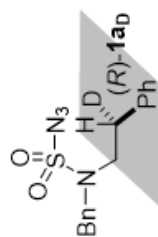
Name	Retention Time	Area Percent	Pk #
	24.556	51.857	1
	34.456	48.143	2
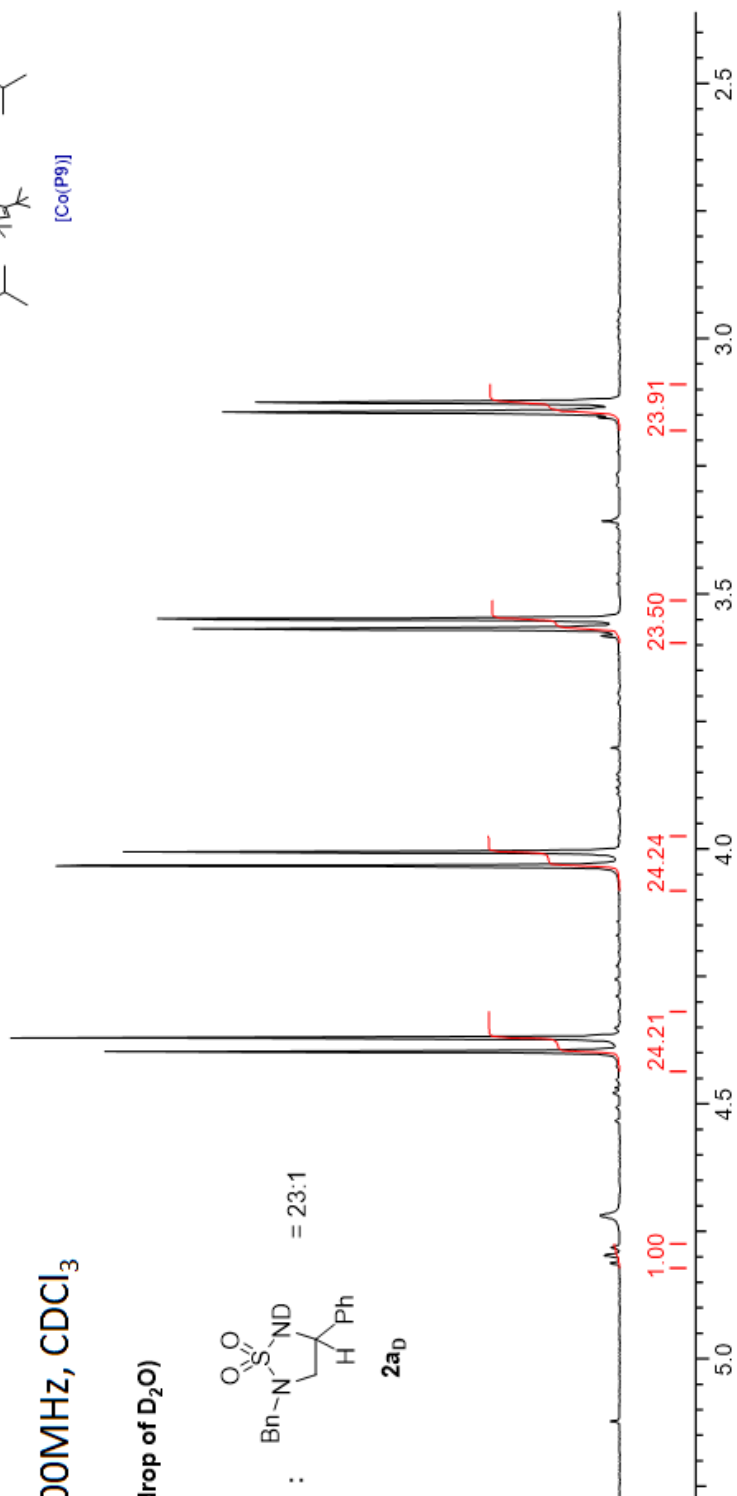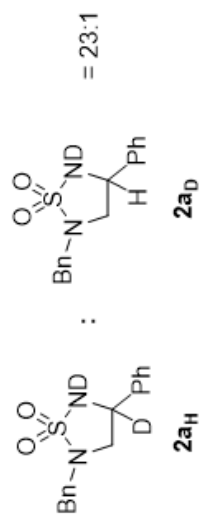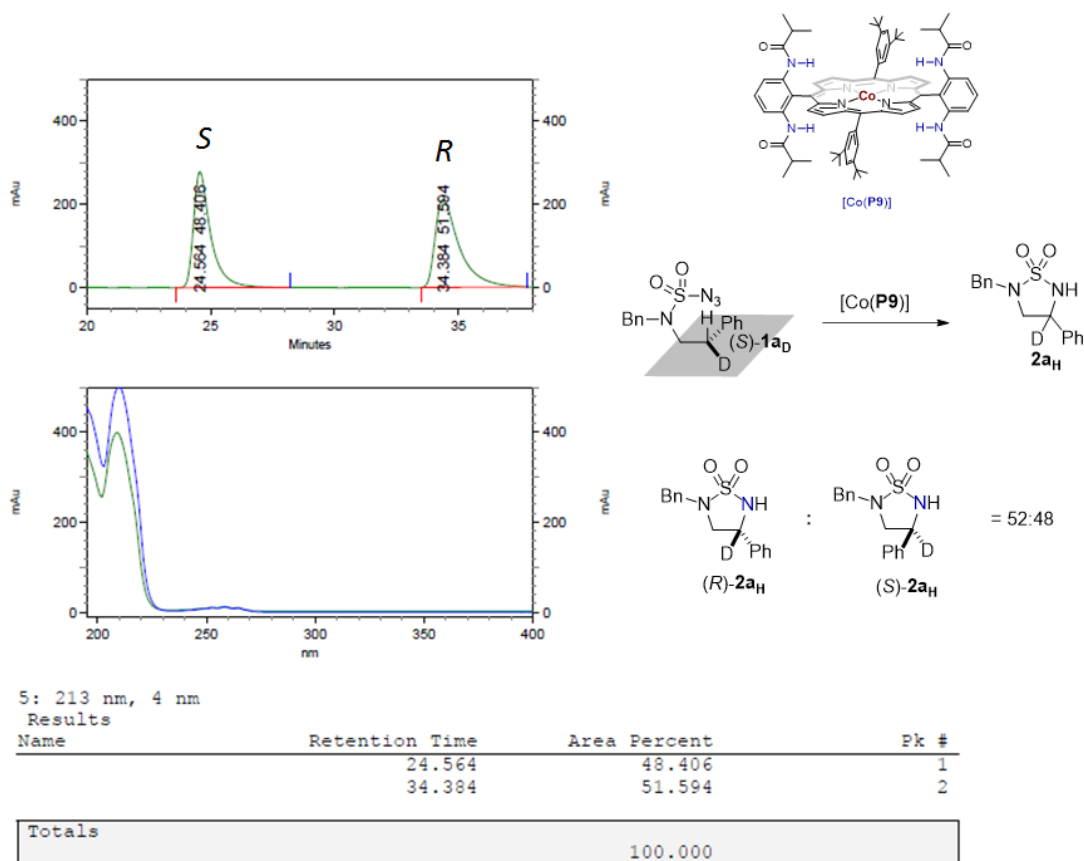
Totals			
		100.000	

Table 2, entry 2

^1H NMR, 500MHz, $CDCl_3$
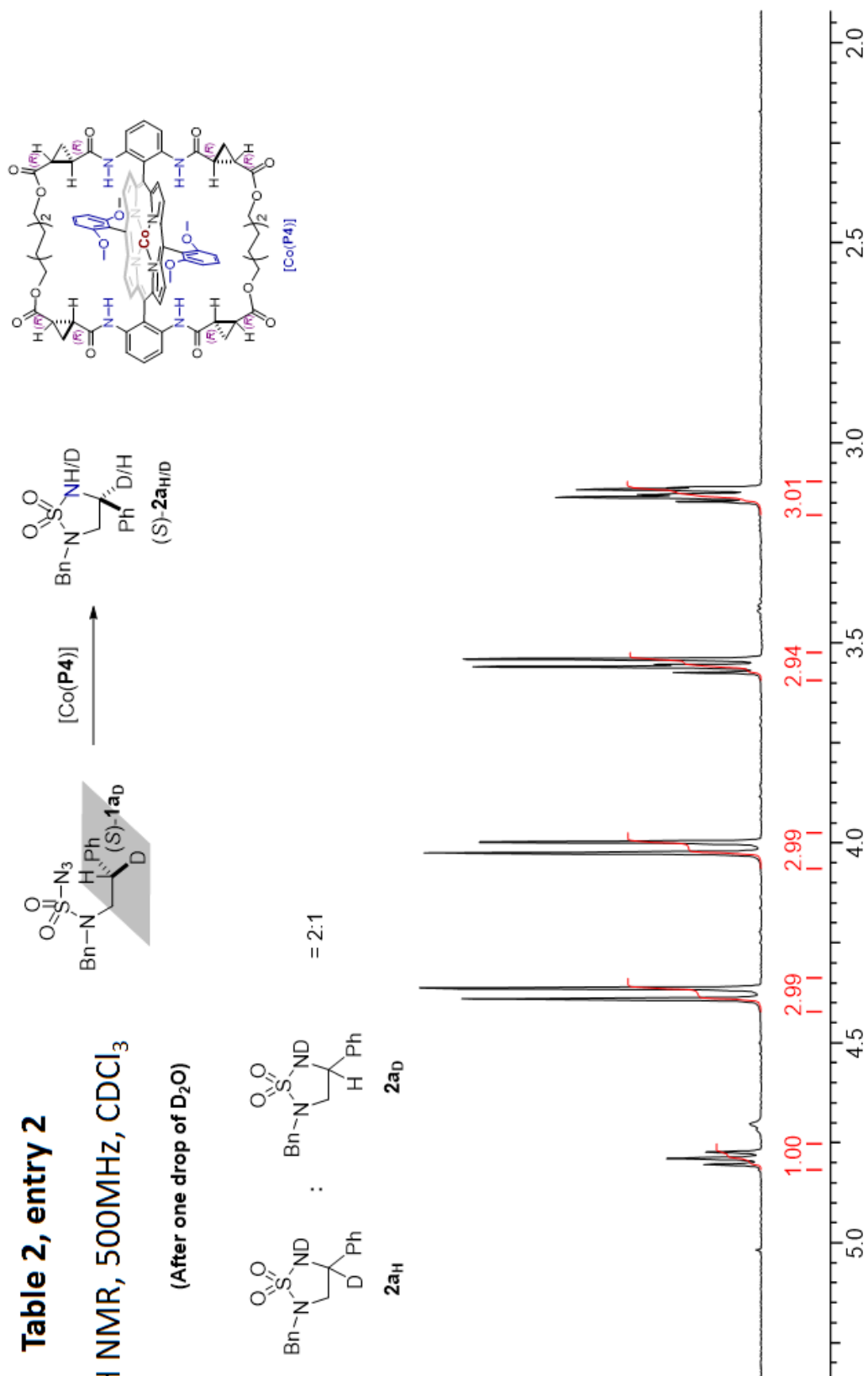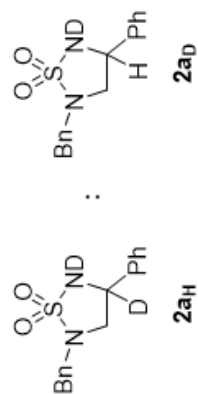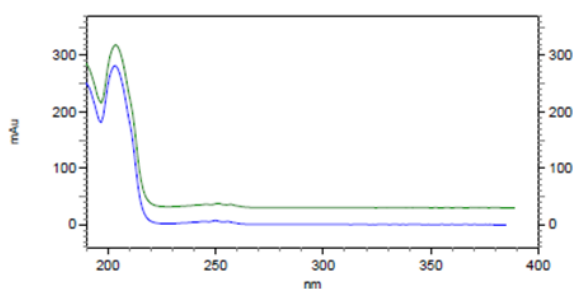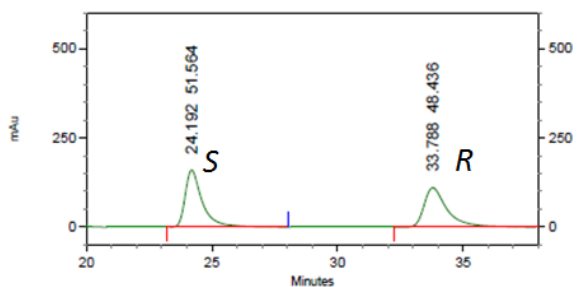
(After one drop of D_2O)

= 2:1

$[Co(\mathbf{P4})]$

$(S)\text{-}\mathbf{1a_D}$

$\mathbf{2a_D}$: $\mathbf{2a_H}$

$(S)\text{-}\mathbf{2a_{H/D}}$

$[Co(\mathbf{P4})]$

Table 2, entry 2

Table 2, entry 3

^{1}H NMR, 500MHz, CDCl$_3$

13C NMR, 100MHz, CDCl₃

2aH

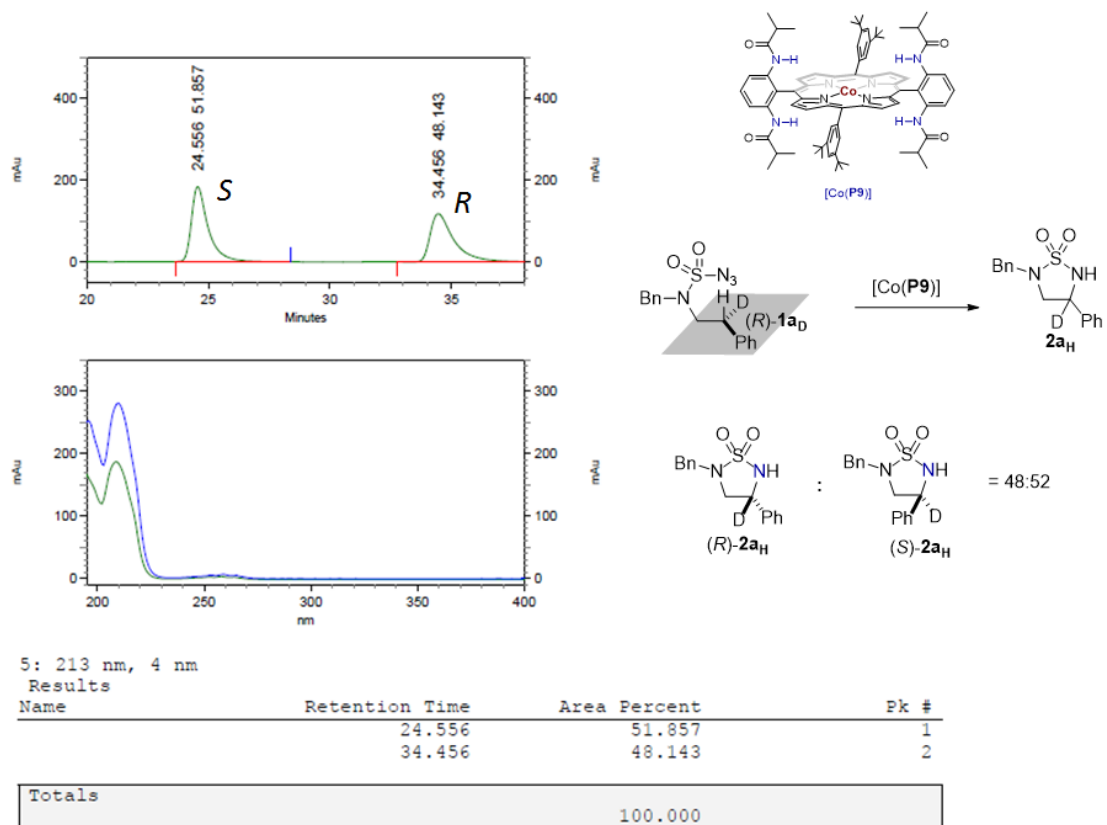S321
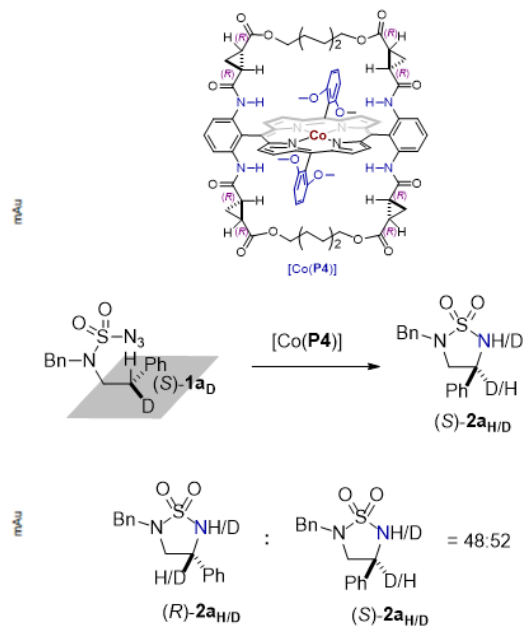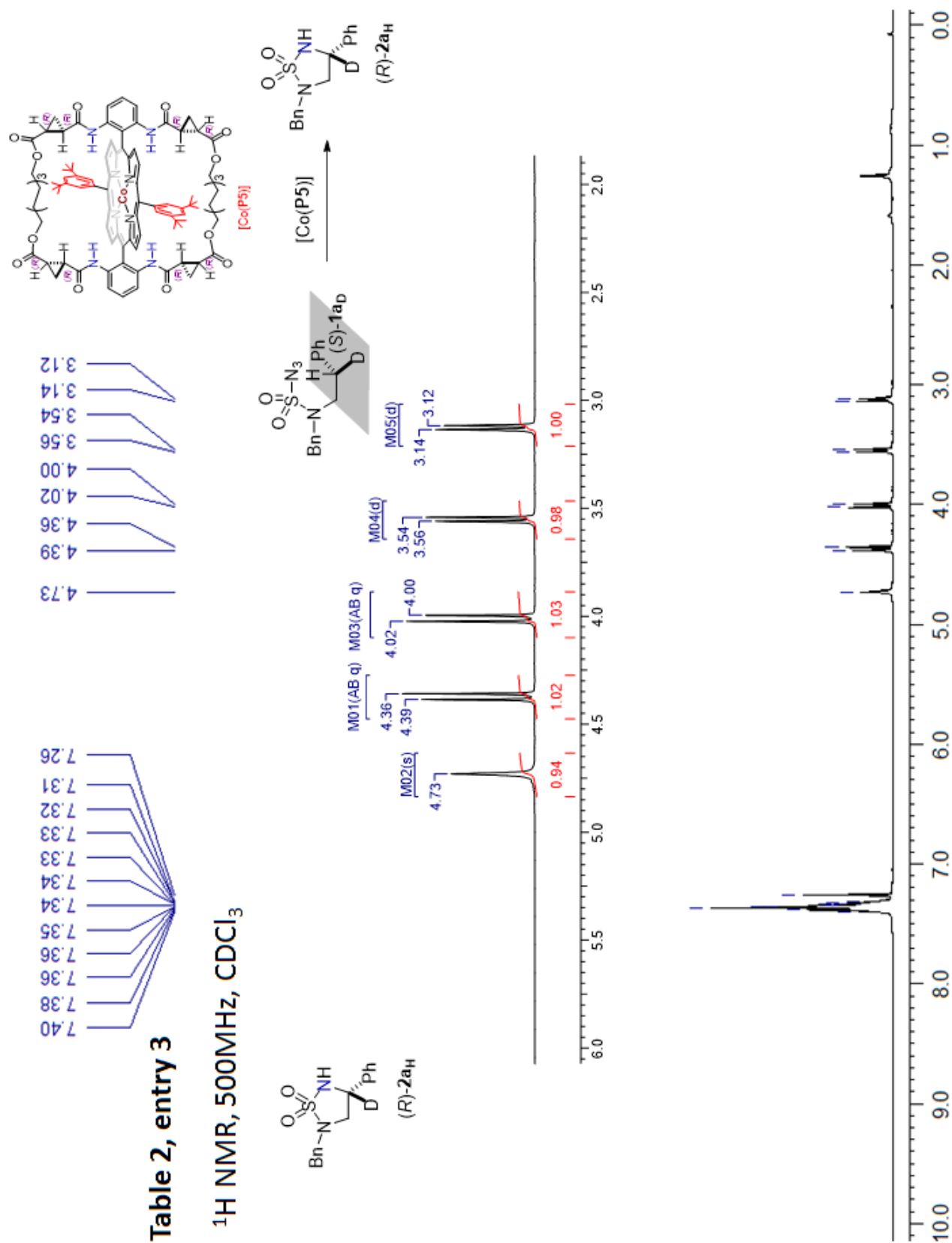
Table 2, entry 3

^{1}H NMR, 500MHz, CDCl$_3$

Table 2, entry 3

^{1}H NMR, 500MHz, CDCl$_3$

[Co(P5)]

(After one drop of D$_2$O)

= 96:1

S323

Table 2, entry 3

6: 220 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	24.064	2.609	1
	33.352	97.391	2

Table 2, entry 5

^{1}H NMR, 500MHz, CDCl$_3$

(S)-2a$_H$ (-)

(R)-1a$_D$

[Co(P4)]

(S)-2a$_H$

[Co(P4)]

Table 2, entry 5

^{1}H NMR, 500MHz, CDCl$_3$

S326

Table 2, entry 5

^{1}H NMR, 500MHz, CDCl$_3$

S327
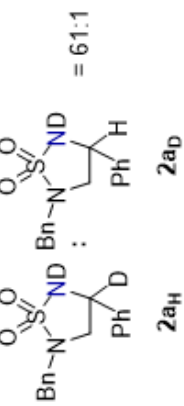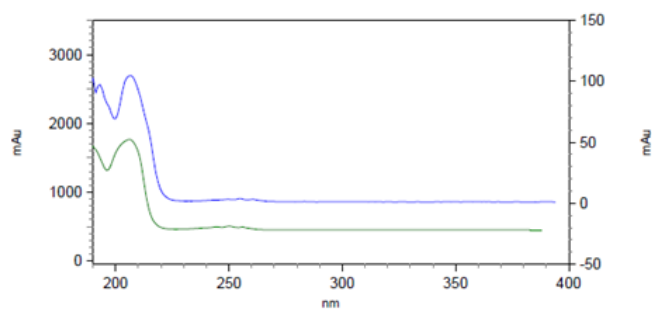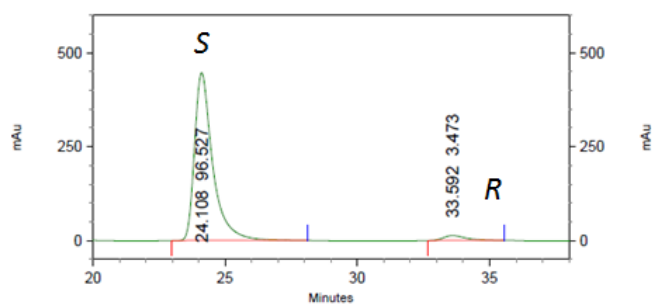
Table 2, entry 5

3: 220 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	24.108	96.527	1
	33.592	3.473	2

Totals		
		100.000
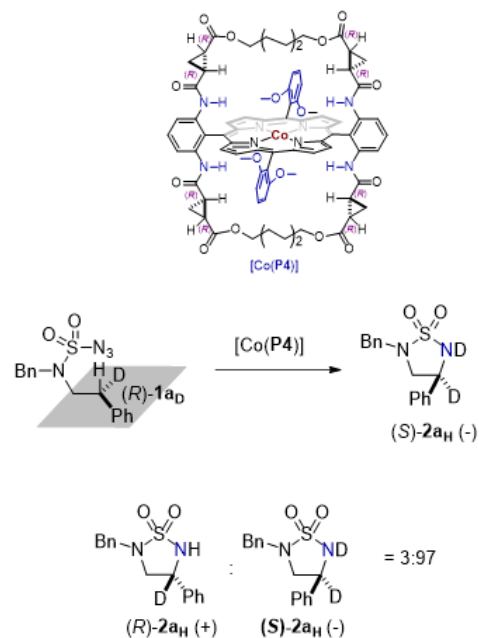
Table 2, entry 6

¹H NMR, 500MHz, CDCl₃

(After one drop of D₂O)

= 0.8:1
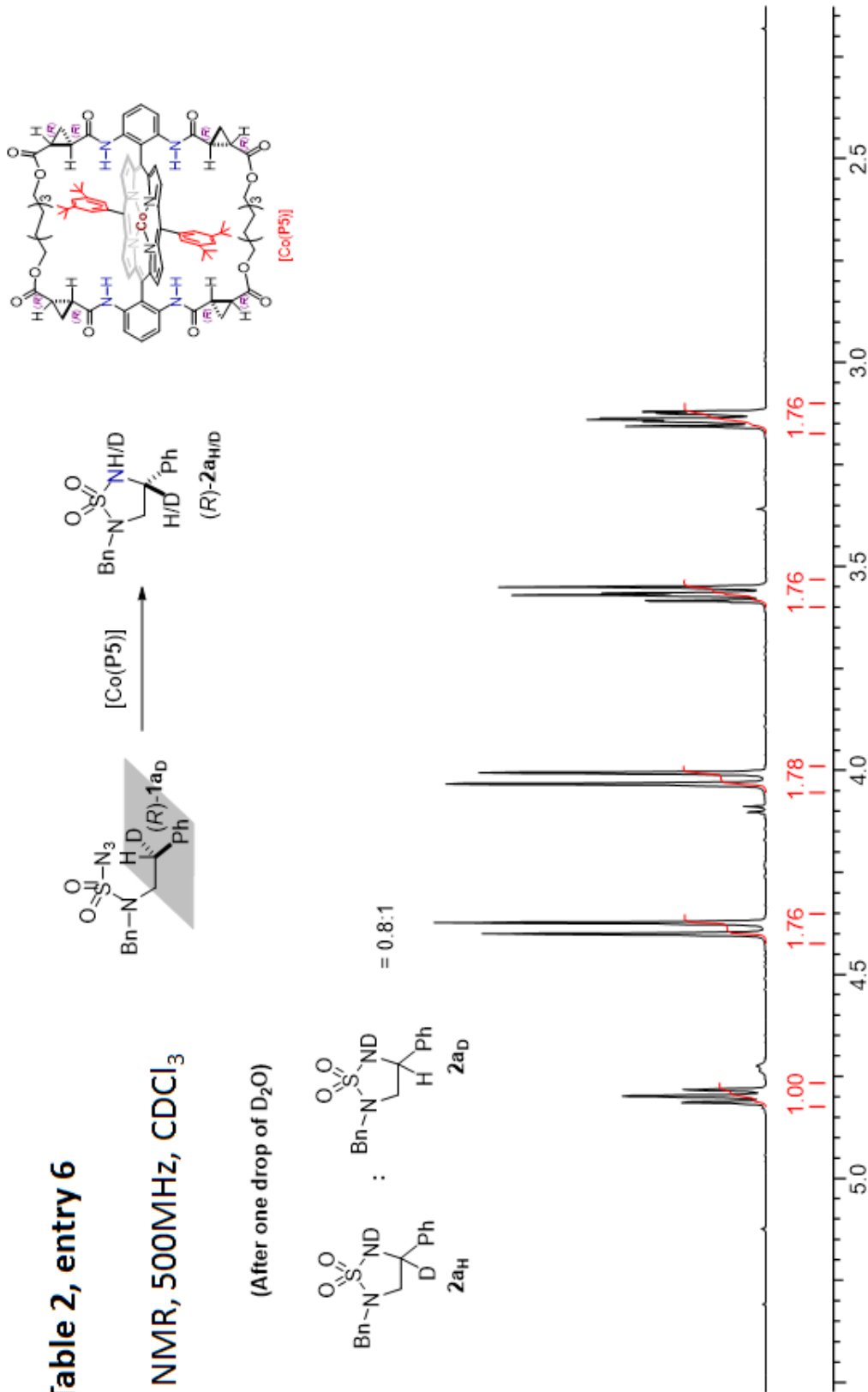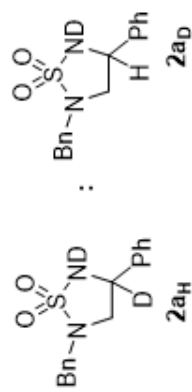
Table 2, entry 6
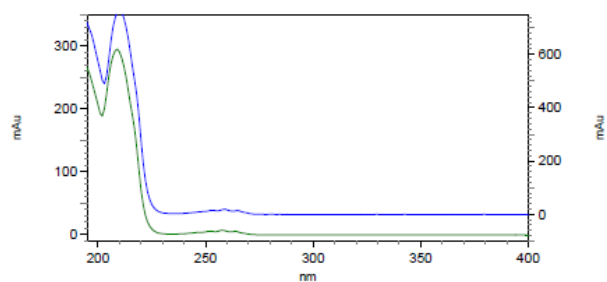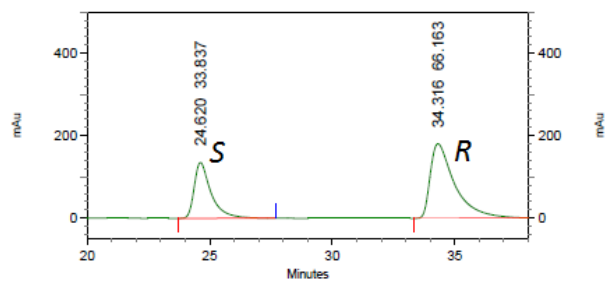
5: 218 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	24.620	33.837	1
	34.316	66.163	2

Totals			
		100.000	

^{1}H NMR, 500MHz, CDCl$_3$

7.42
7.41
7.39
7.35
7.34
7.32
7.31
7.27

4.88
4.87
4.86
4.85
4.11
3.80
3.79
3.78
3.77
3.72
3.70
3.69
3.67
3.45

1.58
1.37
1.27
1.03

M01(dd)
4.88
4.87
4.86
4.85

M04(s)
4.11

M02(m)
3.80
3.79
3.78
3.77

M03(m)
3.72
3.70
3.69
3.67

M05(s)
3.45

1.09
2.28
4.14
1.15 1.14
2.00
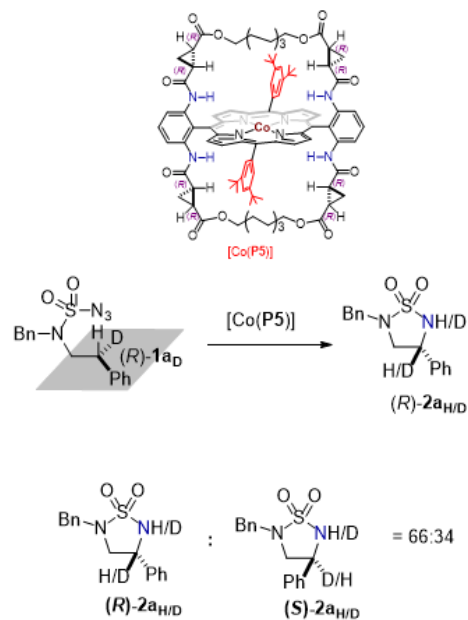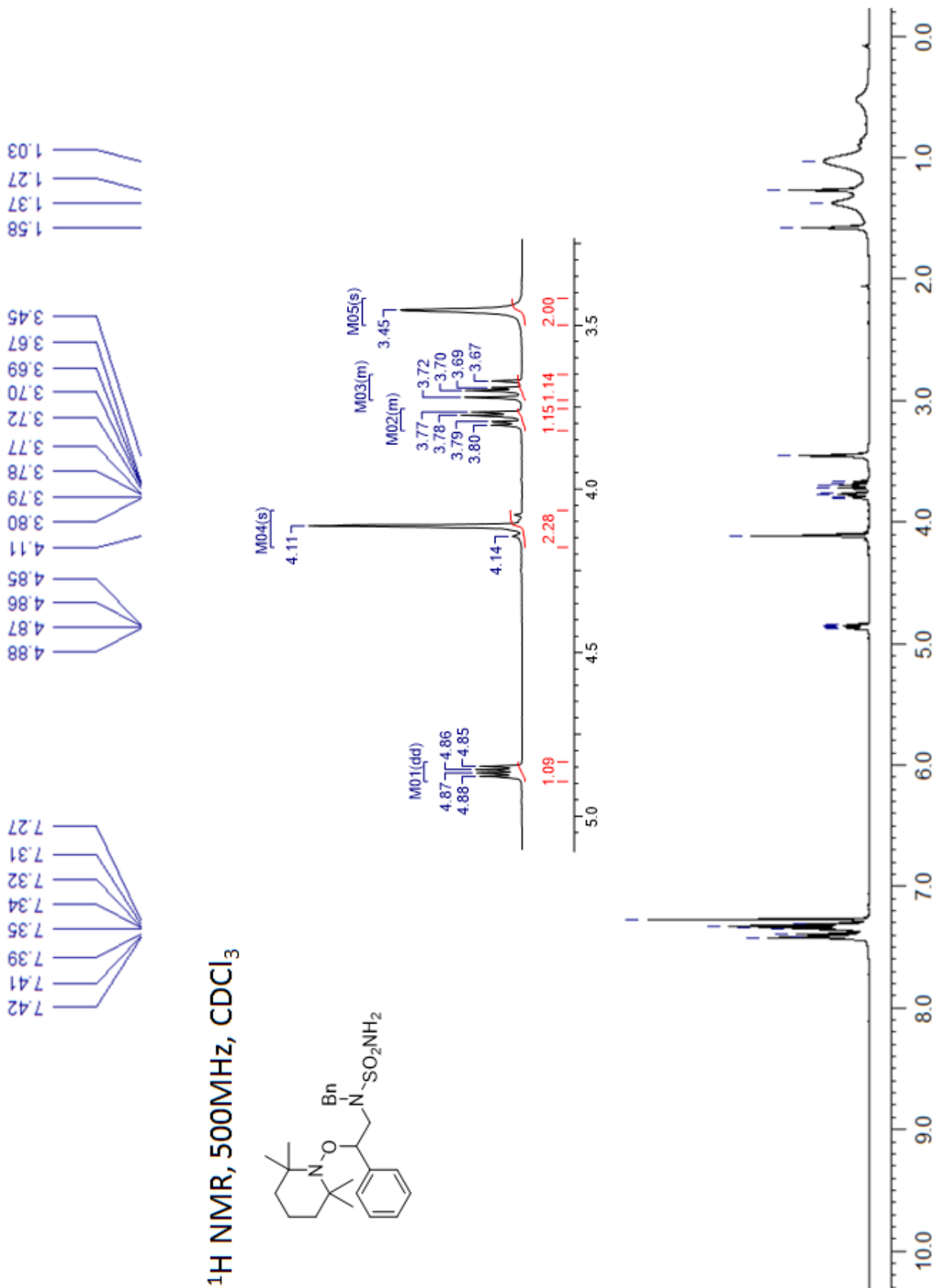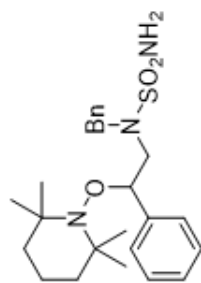
^{13}C NMR, 100MHz, CDCl$_3$
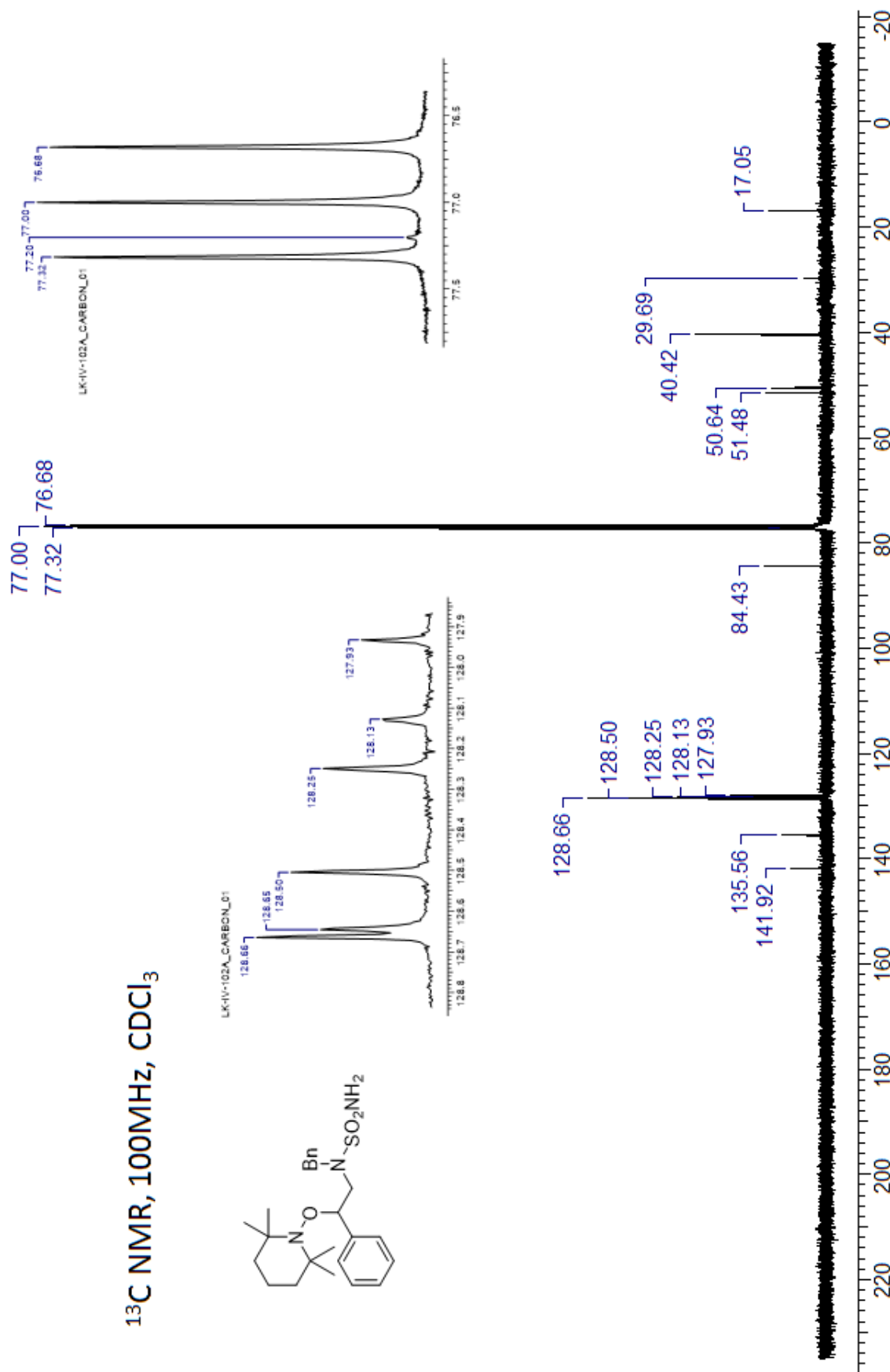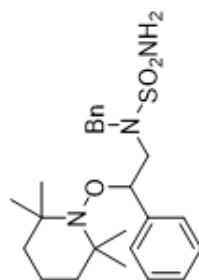
Density Functional Theory (DFT) Calculations

1. Methods

Initial screening of conformational space. Calculations were performed on a truncated model system, wherein the linker on the bottom side of the porphyrin ring has been reduced to methyl groups (**[Co(P4)]$_{model}$** and **[Co(P5)]$_{model}$**, Scheme S1) in order to reduce conformational complexity and cost. Initial screening of the conformational space was performed with molecular mechanics (MMFF) implemented in the Spartan04 software. The critical distances to the hydrogen radical in the HAA transition states have been constrained during the force field calculations (1.30 Å for C$\cdots$H and N$\cdots$H distances). From the initial global screening, a number of relevant modes have been identified (**A1−D2**, Schemes S2−S3) and these have been subjected to a second round of conformational screening with frozen hydrogen bonds between the amide proton of the bridge and one of the O(=S) atoms of the substrate (O^1 or O^2). A selection of conformers thus obtained has been subjected to DFT calculations[11-21] performed with the Gaussian 09 suite of programs.[22] Geometries of the radical species (doublet spin state) were optimized in gas phase with the M06L[23] functional in combination with the LANL2DZ basis set, which has been chosen due to the large size of the system. Stationary points were probed through vibrational analysis (1 negative frequency for transition states) and Gibbs free energy corrections were performed under standard conditions (298.15 K, 1.0 atm). Additionally, we probed the performance of various density functionals through single point energy calculations at the geometries optimized at the levels described above by means of the SMD solvation model[24] with benzene as solvent and the larger Def2TZVPP[25] basis set. Since the optimal density functional for the current system is not known we tested three additional state of the art approaches that have been developed over the past decade: [11-21,26-31] ωB97XD,[32] M06[23] and MN12SX.[33] The Gibbs free energies for all conformers are provided in Figs. S10−1 to S10−4.

Calculations on smaller model systems. To gain a better understanding of the conformational preferences during HAA in absence of the bridge (i.e., by eliminating any strain induced by the bridge), additional model calculations have been performed on a further truncated model system at the M06L/Def2SVP level (**[Co]$_{model01}$**, Scheme S4, below).

Calculation of free energy surface. In order to construct the free energy surface, we reoptimized the three most stable transition state conformers of the preferred reaction mode (obtained with M06L/LANL2DZ) for both catalyst systems (**[Co(P4)]**$_{model}$ and **[Co(P5)]**$_{model}$) with M06L/Def2SVP. From the optimized transition state structures, we performed Intrinsic Reaction Coordiante calculations (IRC) employing the L(ocal) Q(uadratic) A(approximation) method[34,35] and reoptimized the end points with M06L/Def2SVP. The lowest of the three values after single point calculations with ωB97XD/Def2TZVPP$_{benzene(SMD)}$//M06L/Def2SVP was chosen to construct the graph in Scheme S5.

Calculations of HAA transition states leading to 5- or 6-membered ring product. Finally, we investigated the kinetic selectivity between HAA transition states leading to the 5- or 6-membered ring products, also at the M06L/Def2SVP level (**[Co]**$_{model02}$, Scheme S6).

Coordinates file. A file for convenient viewing of computed geometries with the program Mercury 3.3 (or higher) is appended as separate "coordinates.xyz" file.[36]

Scheme S1. Truncated catalyst models **[Co(P4)]**$_{model}$ and **[Co(P5)]**$_{model}$
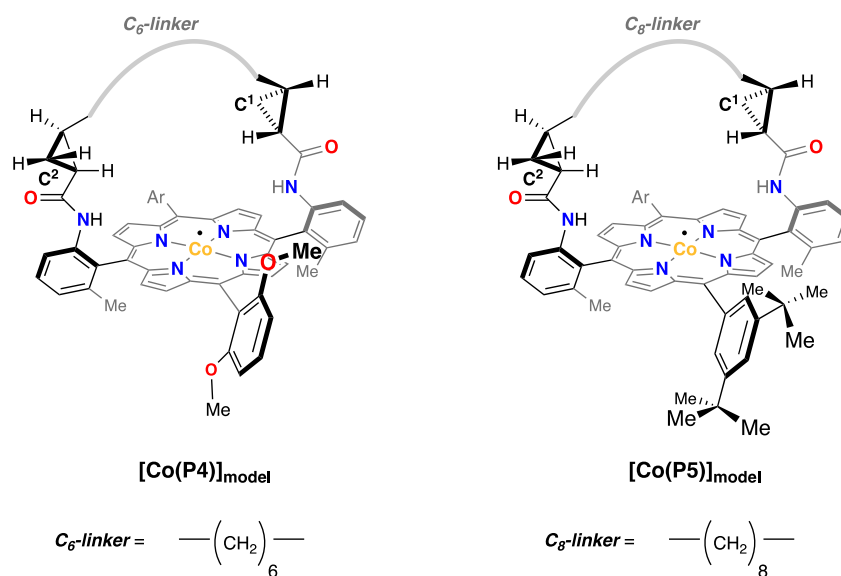
Scheme S2. Investigated transition state conformations for HAA with **[Co(P4)]**_{model} and substrate **1a**
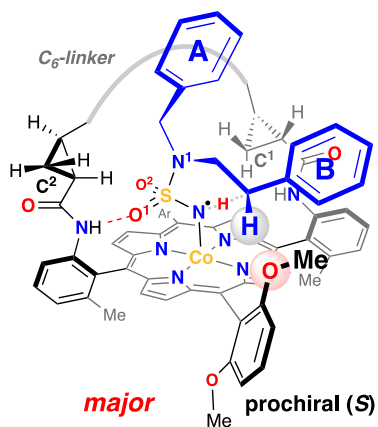
HAA transition state (Mode A1)
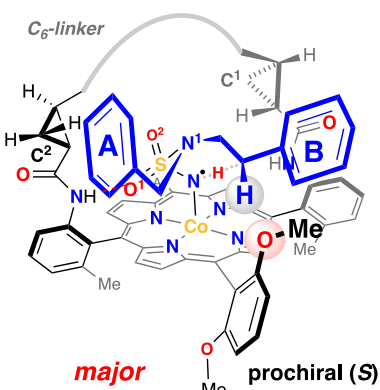
HAA transition state (Mode A2)

HAA transition state (Mode B1)
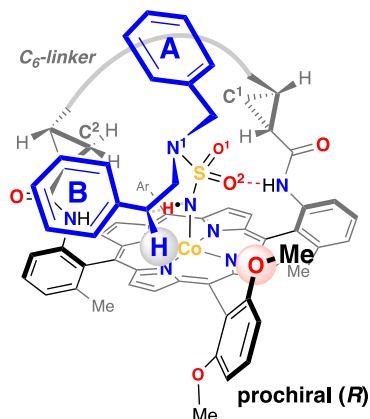
HAA transition state (Mode C1)
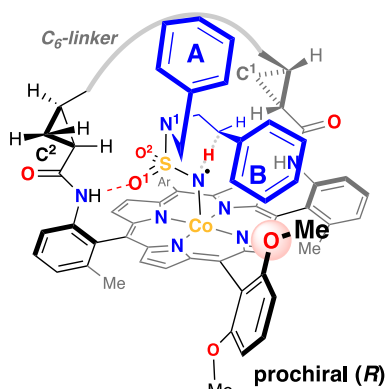
HAA transition state (Mode C2)
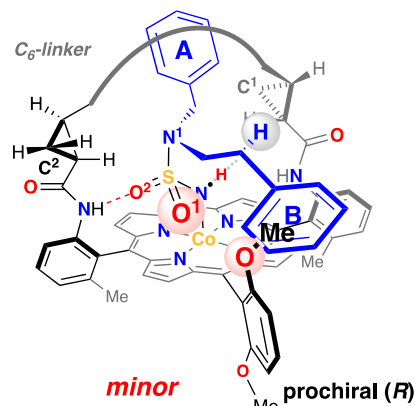
HAA transition state (Mode D1)

Scheme S3. Investigated transition state conformations for HAA with **[Co(P5)]$_{model}$** and substrate **1a**

prochiral (*S*)
minor

HAA transtion state (Mode A1)

prochiral (*S*)

HAA transtion state (Mode A2)

prochiral (*S*)

HAA transtion state (Mode B1)

prochiral (*S*)

HAA transtion state (Mode B2)

prochiral (*R*)

HAA transtion state (Mode C1)

prochiral (*R*)

HAA transtion state (Mode C2)

prochiral (*R*)
major

HAA transtion state (Mode D1)

prochiral (*R*)

HAA transtion state (Mode D2)
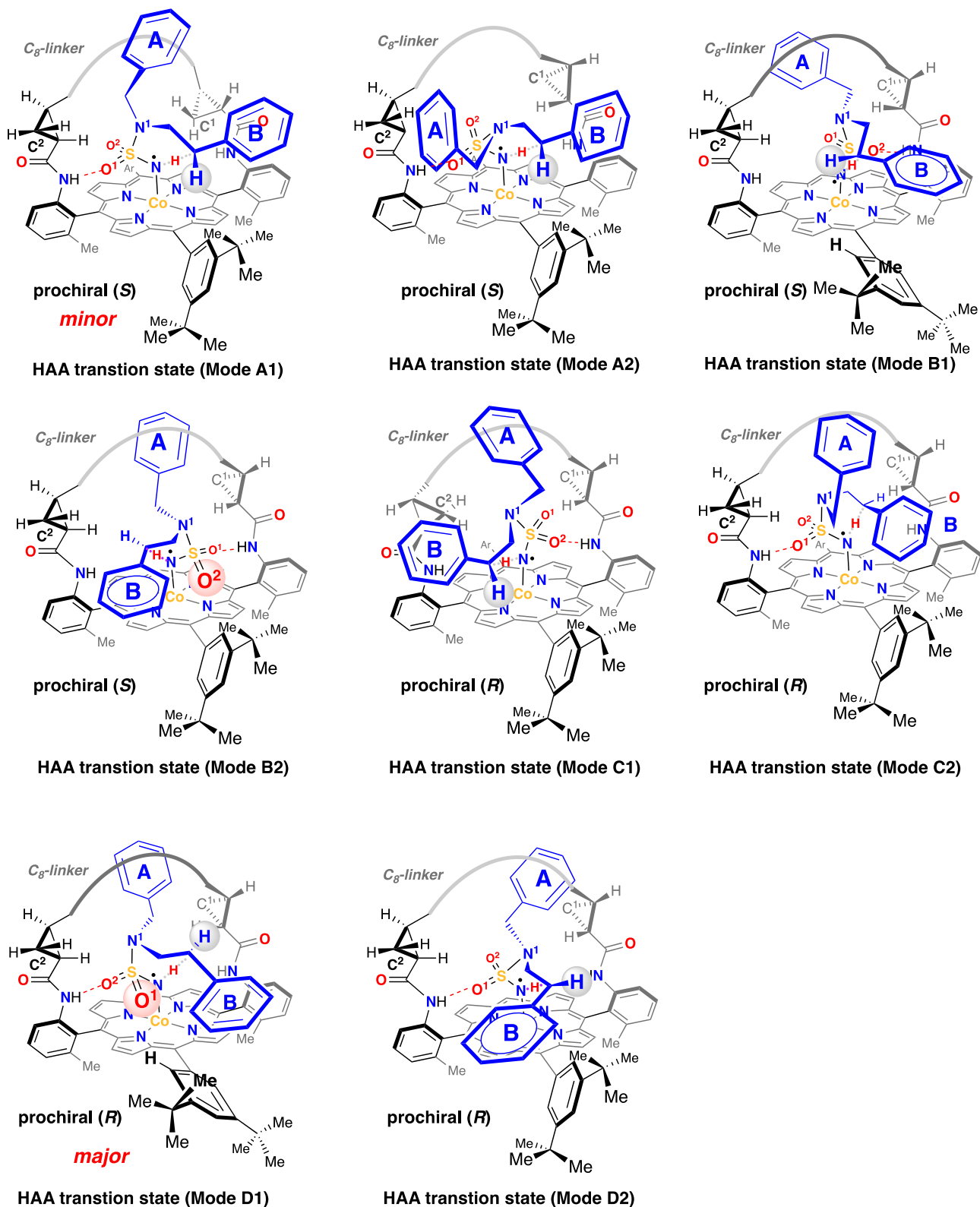
2. Challenges and Simplifications

(1) Considering the large complexity of the system under investigation we assumed that the second bridge on the bottom side of the porphyrin ring has little influence on HAA occurring at the top side (i.e., we used a truncated model system; cf. Scheme S1).

(2) Due to the large size of the system under investigation we used the small LANL2DZ basis set for geometry optimization, which will lead to significant basis set superposition error. The optimized structures have been subjected to single point energy calculations with the larger Def2TZVPP basis set and four density functionals (ωB97XD, M06, MN12SX and M06L).

(3) As a consequence of the above uncertainties we also focus on chemically meaningful trends rather than relying solely on exact free energy differences between the transition states leading to the major and minor enantiomer (on the order of 2 kcal/mol). That is, the resulting stereochemical model has to be in agreement with characteristic selectivity trends arising from variations of the substrates. In particular the model should account for:

(a) Reactions of sterically hindered substrates (i.e., **1s**, **1t** and **1u**) are selective only with **[Co(P4)]** (cf. Fig. 3C). They are facile but nonselective with **[Co(P5)]**.

(b) Low yields are obtained when substrates containing moieties with heteroatoms (ester, **1o**; furyl, **1p**; and thienyl, **1q**) are used in reactions with **[Co(P4)]**. These reactions proceed smoothly with **[Co(P5)]** (cf. Fig. 3B).

(c) Significantly higher levels of enantioselectivity are obtained when reactions with substrates containing small alkenyl moieties (**1i** and **1j**) or a cyclopropyl group (**1r**) are performed with **[Co(P5)]** vs. **[Co(P4)]** (cf. Fig. 3A and 3B).

(4) We tested the conformational preference in absence of a bridge (Scheme S4), since we hypothesized that it is very likely that the herein identified least strained conformation will also play a significant role in the real systems with the bridge (Schemes S2 and S3). This is sought to further support the finally proposed stereochemical model.

3. Various conformers for HAA transition states after optimization with M06L/LANL2DZ

With the [Co(P4)]$_{model}$ system. The conformer distributions for various HAA modes with **[Co(P4)]$_{model}$** at the ωB97XD/Def2TZVPP$_{benzene(SMD)}$//M06L/LANL2DZ are shown in Fig. S10-1 (left side). Modes **A1–B1** lead to generation of the major enantiomer with **[Co(P4)]$_{model}$**, whereby **A1** and **A2** are used to denote conformations wherein both aryl-containing moieties are on one side of the bridge (i.e. nearby-the-bridge) and **B1** is applied to conformations wherein phenyl ring **A** is behind and phenyl ring **B** is in front of the bridge (i.e., underneath-the-bridge; Scheme S2). The nomenclature for HAA modes, which lead to the corresponding minor enantiomer is **C1** and **C2** (aryl rings on same side) and **D1** (aryl rings on opposite sides). Qualitatively very similar results to ωB97XD are obtained with other investigated density functionals [M06 (Fig. S10-2), MN12SX (Fig. S10-3) and M06L (Fig. S10-4)]. For images of the most stable conformers for each mode, see Fig. S11-1. We find that mode **D1** emerges as the most favored pathway with **[Co(P4)]$_{model}$** (1.2 kcal/mol lower in energy than mode **A1**, Fig. S10-1).

With the [Co(P5)]$_{model}$ system. In case of the larger **[Co(P5)]$_{model}$** system the energy difference between modes **D1** and **A1** is larger (3.6 kcal/mol in favor of **D1**, Fig. S10-1, right side). Qualitatively very similar results to ωB97XD are obtained with other investigated density functionals [M06 (Fig. S10-2), MN12SX (Fig. S10-3) and M06L (Fig. S10-4)]. For images of the most stable conformers for each mode, see Figs. S12-1/S12-2.

Initial analysis of the results. The above energies are only in agreement with the experimentally observed trend for the system with the 8-carbon bridge (**[Co(P5)]$_{model}$**), however, mode **A1**, which leads to formation of the correct enantiomer with **[Co(P4)]$_{model}$** is energetically disfavored by 1.2 kcal/mol relative to **D1** (Fig. S10-1). We initially thought such discrepancy might either be attributed to the computational uncertainty associated with the DFT method and/or the uncertainty arising from the high conformational flexibility. It has to be stated at this point that reinvestigation of modes **A1** and **D1** at the higher M06L/Def2TZVPP$_{benzene(SMD)}$//M06L/Def2SVP$_{benzene(SMD)}$ level (data not shown) did not lead to a significant qualitative as well as quantitative change in the computed preference. ***Alternatively, a more intriguing mechanistic scenario***, which would nonetheless be in agreement with the seemingly inconsistent computational results, is proposed below (see Scheme S5; cf. Fig. 4B) and the following mechanistic investigations are provided in support of the latter hypothesis (see next paragraph).
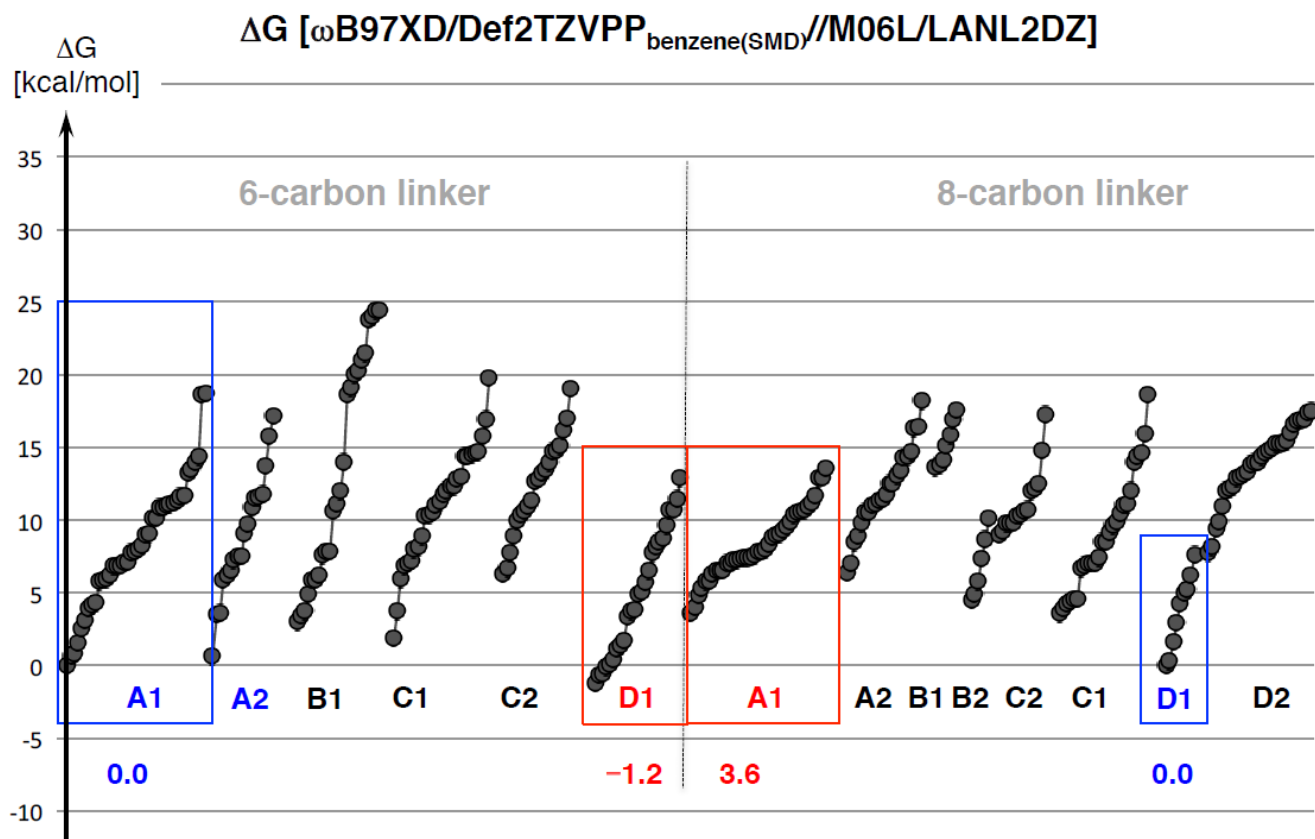
Fig. S10-1. Conformer distribution (ΔG in kcal/mol at the ωB97XD/Def2TZVPP$_{\text{benzene(SMD)}}$//M06L/LANL2DZ level) for HAA transition states with **[Co(P4)]$_{\text{model}}$** (left) and **[Co(P5)]$_{\text{model}}$** (right); for the corresponding mode of additions **A1−D2**, see Schemes S2−S3.
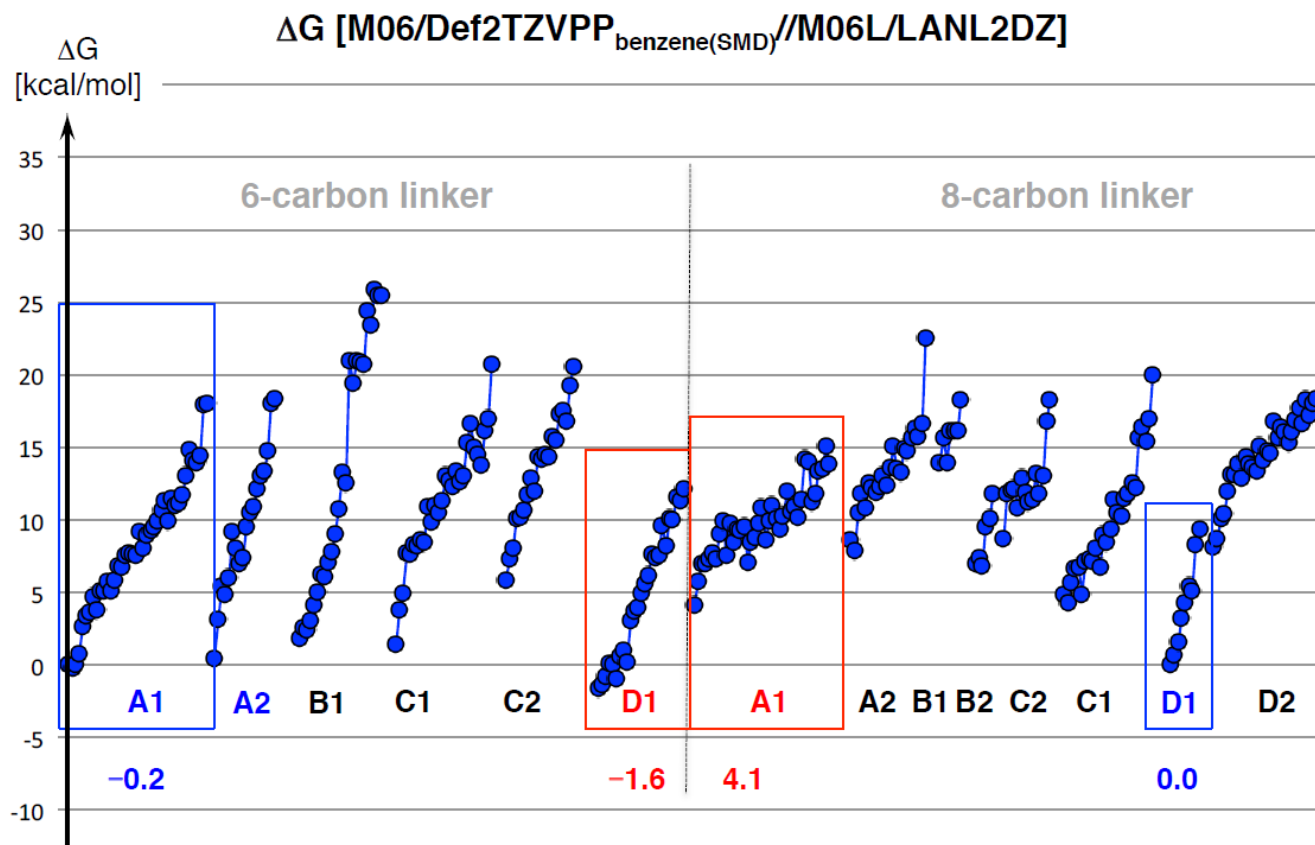
Fig. S10-2. Conformer distribution (ΔG in kcal/mol at the M06/Def2TZVPP$_{benzene(SMD)}$//M06L/LANL2DZ level) for HAA transition states with **[Co(P4)]$_{model}$** (left) and **[Co(P5)]$_{model}$** (right); for the corresponding mode of additions **A1−D2**, see Schemes S2−S3.
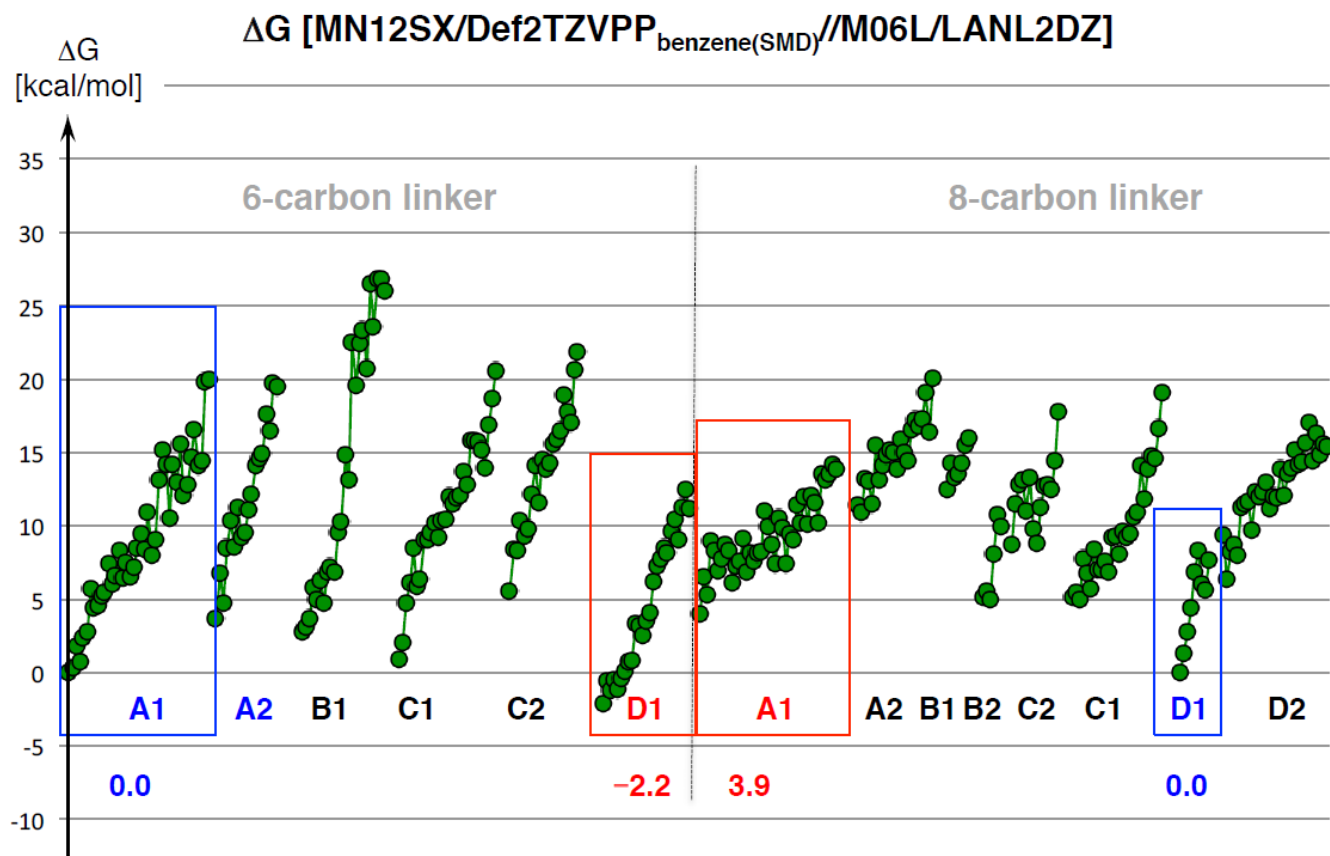
Fig. S10-3. Conformer distribution (ΔG in kcal/mol at the MN12SX/Def2TZVPP$_{benzene(SMD)}$//M06L/LANL2DZ level) for HAA transition states with **[Co(P4)]$_{model}$** (left) and **[Co(P5)]$_{model}$** (right); for the corresponding mode of additions **A1−D2**, see Schemes S2−S3.
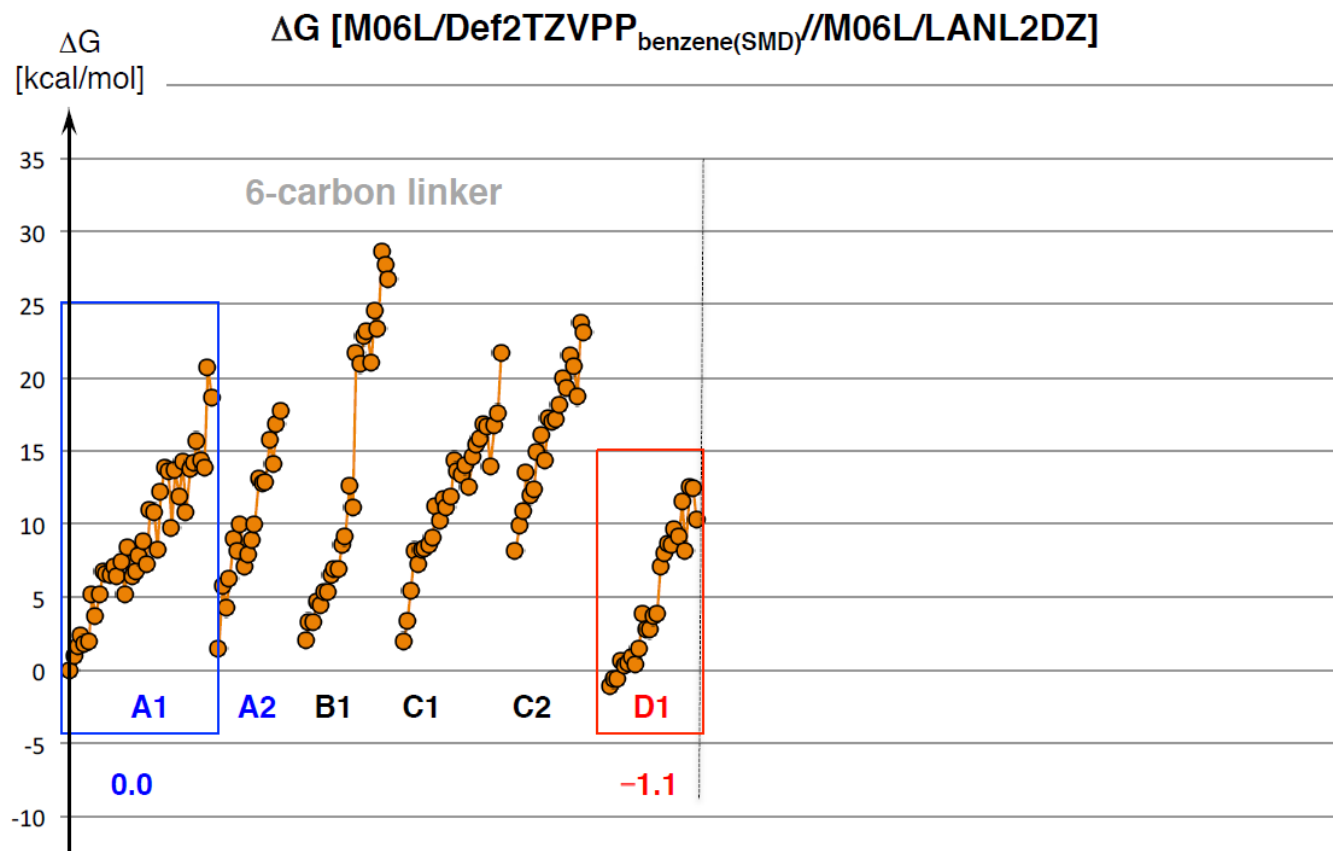
Fig. S10-4. Conformer distribution (ΔG in kcal/mol at the M06L/Def2TZVPP$_{benzene(SMD)}$// M06L/LANL2DZ level) for HAA transition states with **[Co(P4)]$_{model}$**; for the corresponding mode of additions **A1−D1**, see Scheme S2.

Mode A1 **Mode A2**

Mode B1 **Mode C1**

Mode C2 **Mode D1**
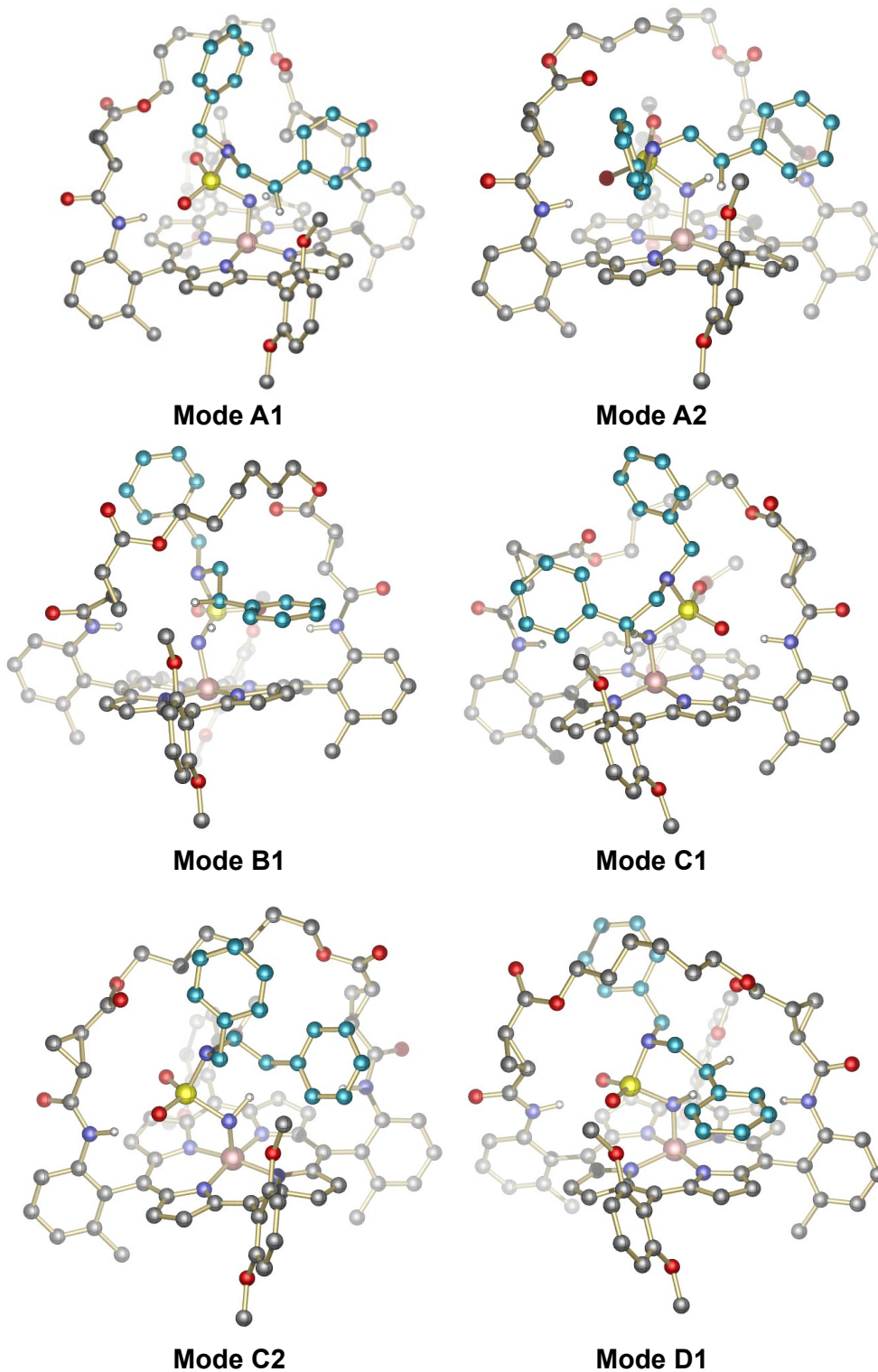
Fig. S11-1. Lowest free energy conformers for various HAA modes with **[Co(P4)]$_{model}$** at the ωB97XD/Def2TZVPP$_{benzene(SMD)}$//M06L/LANL2DZ level (Fig. S10-1, Scheme S2); ball and stick model, most hydrogen atoms have been omitted for clarity.

Front view:
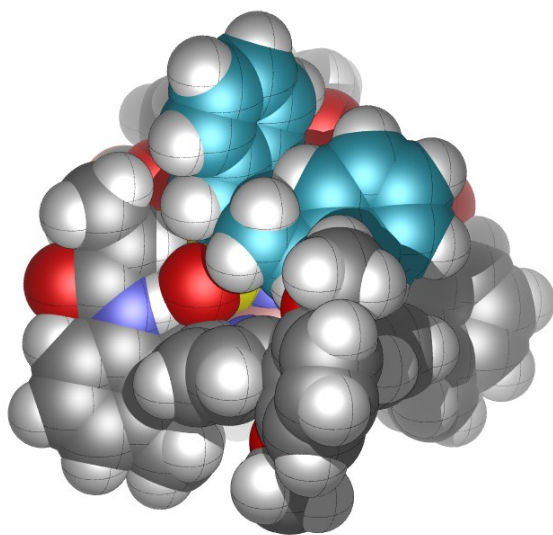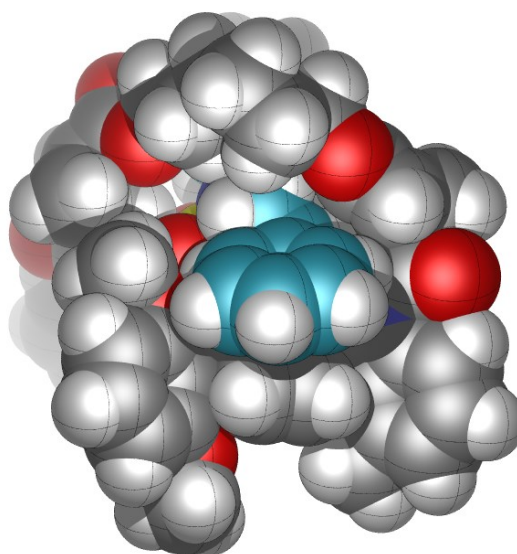
Mode A1_C6   Mode D1_C6

Side view:
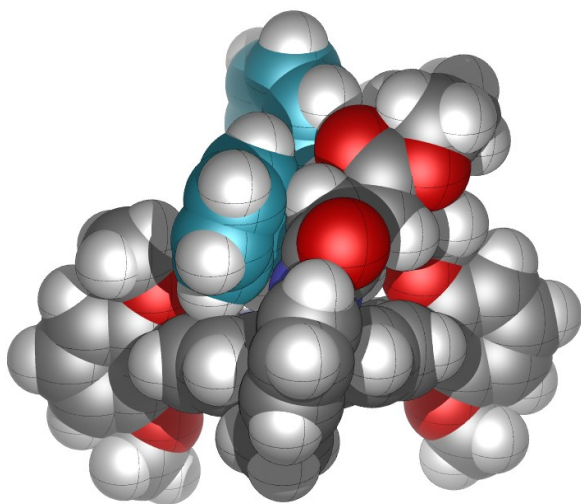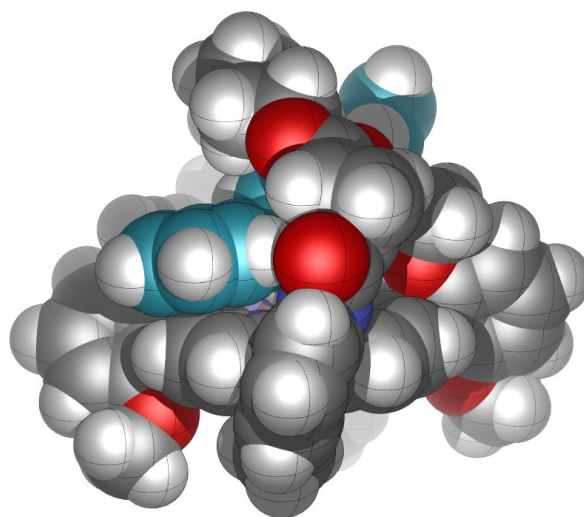
Mode A1_C6   Mode D1_C6

Fig. S11-2. Lowest free energy conformers for HAA modes **A1** and **D1** with **[Co(P4)]**$_{model}$ at the ωB97XD/Def2TZVPP$_{benzene(SMD)}$//M06L/LANL2DZ level (Fig. S10-1, Scheme S2); space filling model.

Mode A1

Mode A2

Mode B1

Mode B2
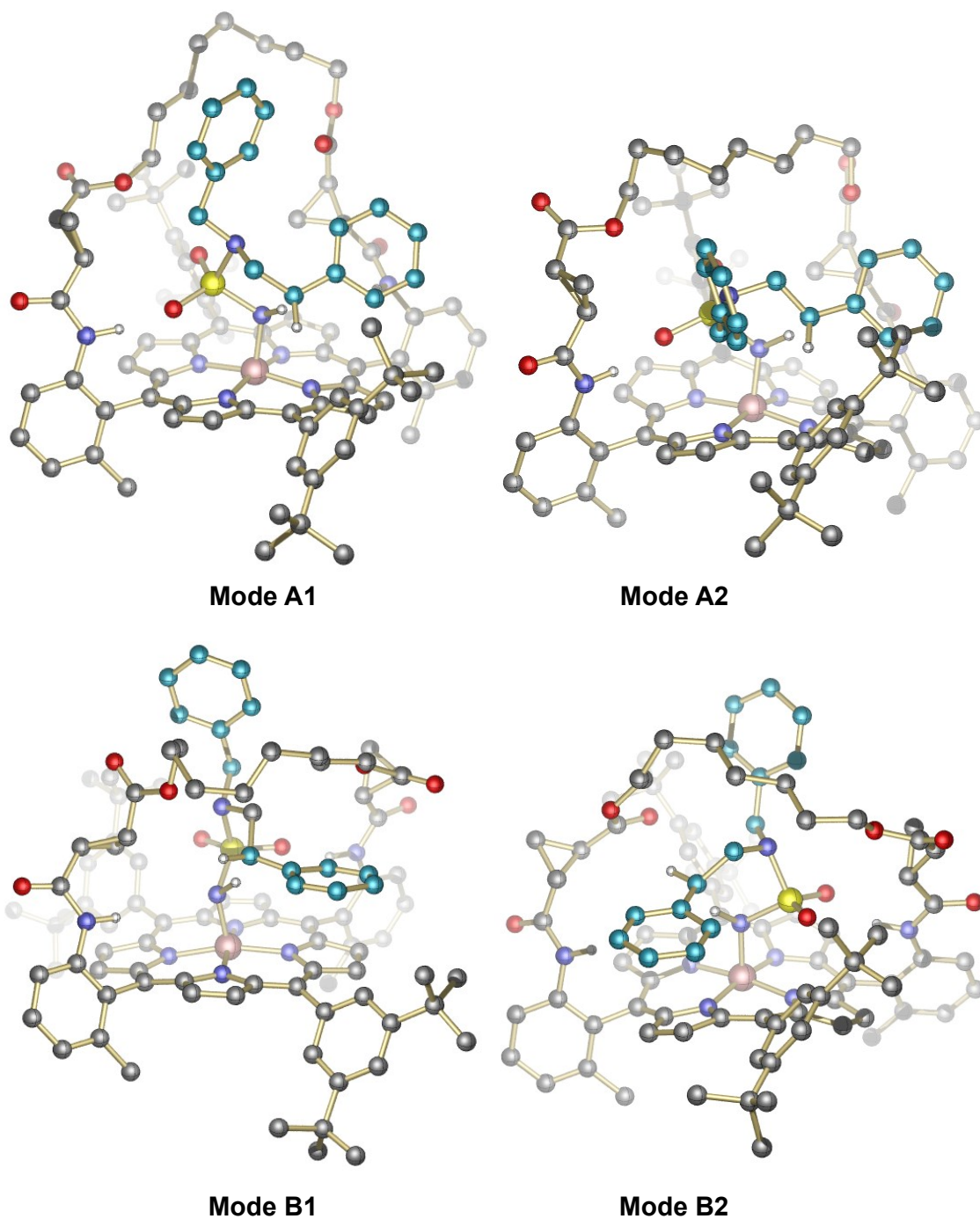
Fig. S12-1. Lowest free energy conformers for various HAA modes with **[Co(P5)]$_{model}$** at the ωB97XD/Def2TZVPP$_{benzene(SMD)}$//M06L/LANL2DZ level (Fig. S10-1, Scheme S3); ball and stick model, most hydrogen atoms have been omitted for clarity.

Mode C1   **Mode C2**

Mode D1   **Mode D2**
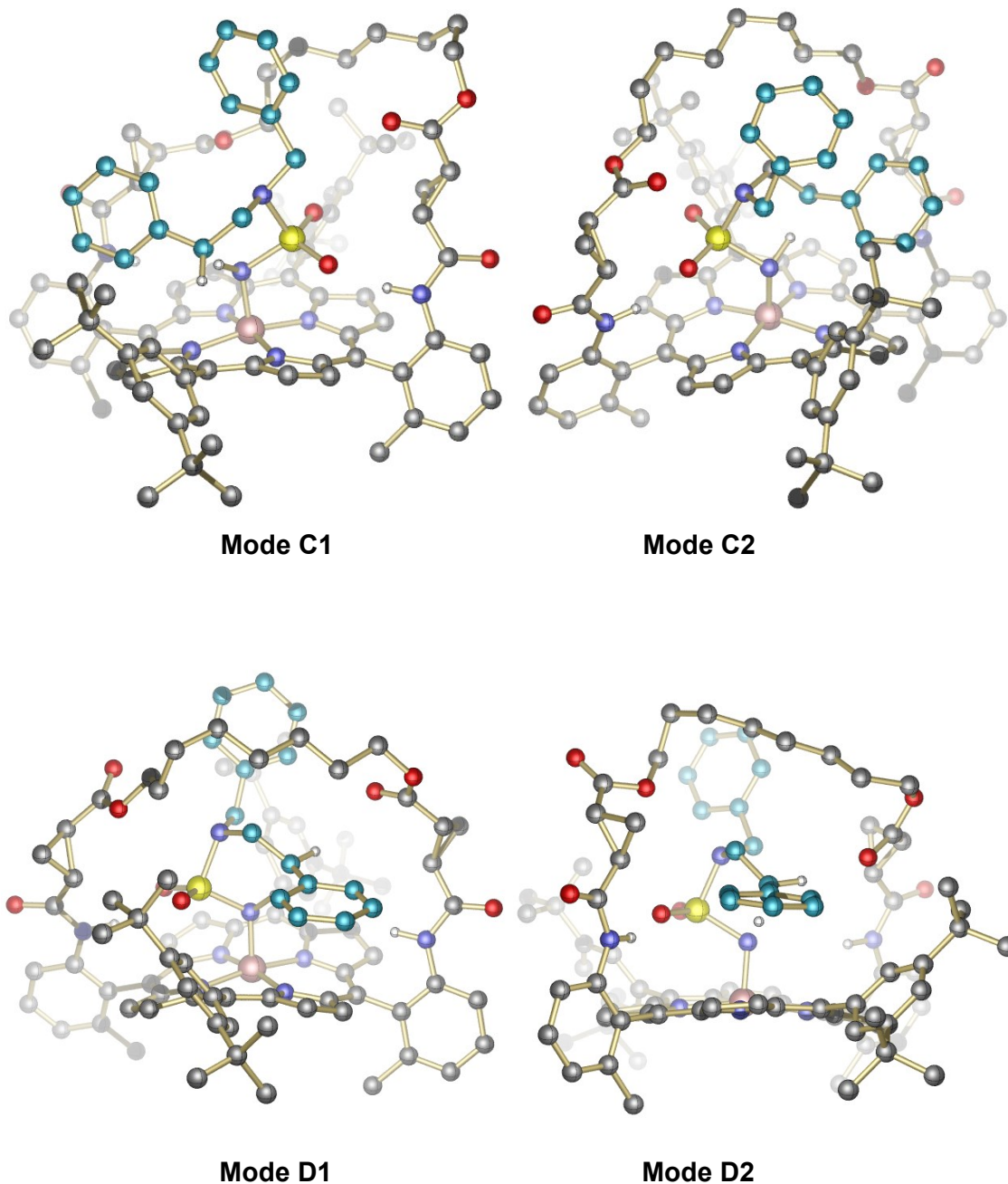
Fig. S12-2. Lowest free energy conformers for various HAA modes with **[Co(P5)]$_{model}$** at the ωB97XD/Def2TZVPP$_{benzene(SMD)}$//M06L/LANL2DZ level (Fig. S10-1, Scheme S3); ball and stick model, most hydrogen atoms have been omitted for clarity.

Front view:
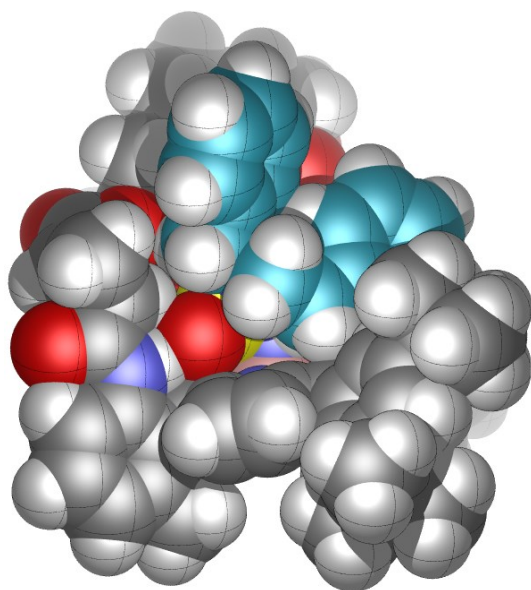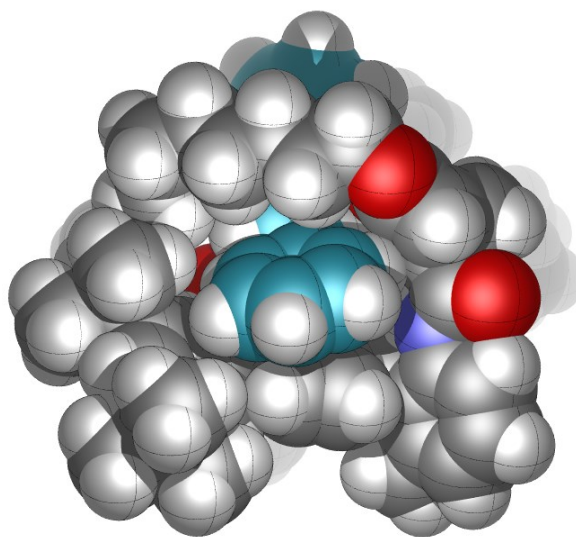
Mode A1_C8   **Mode D1_C8**

Side view:
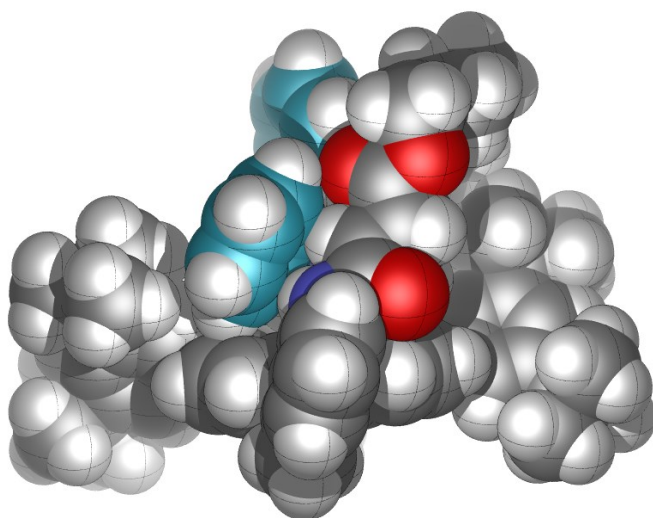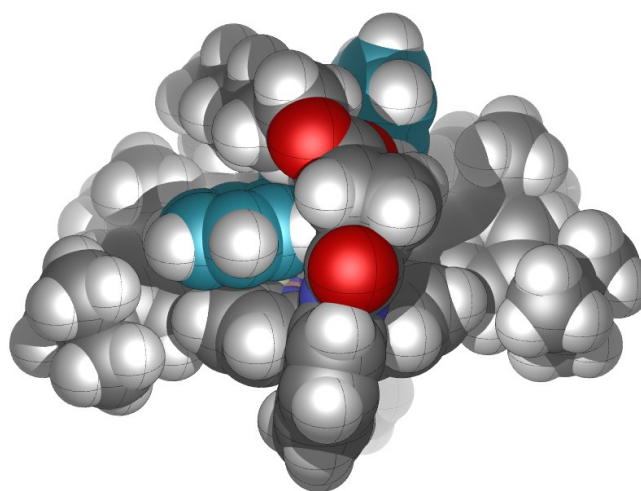
Mode A1_C8   **Mode D1_C8**

Fig. S12-3. Lowest free energy conformers for HAA modes **A1** and **D1** with **[Co(P5)]$_{model}$** at the ωB97XD/Def2TZVPP$_{benzene(SMD)}$//M06L/LANL2DZ level (Fig. S10-1, Scheme S3); space filling model.

4. Energetically most stable HAA transition state in model system without a bridge

The experimentally obtained results with isotopically labeled substrates clearly indicate that HAA is stereochemistry determining (cf. Fig. 4A). In contrast, the DFT results suggest that it is likely not the energetically most stable HAA transition state that is relevant to the outcome of the reaction (Fig. S10-1). Additional calculations on a model system without a bridge have been performed to shed light onto possible reasons (**[Co]**$_{model01}$; Scheme S4).

Scheme S4. Investigated transition state conformations for HAA with **[Co]**$_{model01}$

| HAA transition state (Mode E) | HAA transition state (Mode F) | HAA transition state (Mode G) | HAA transition state (Mode H) |
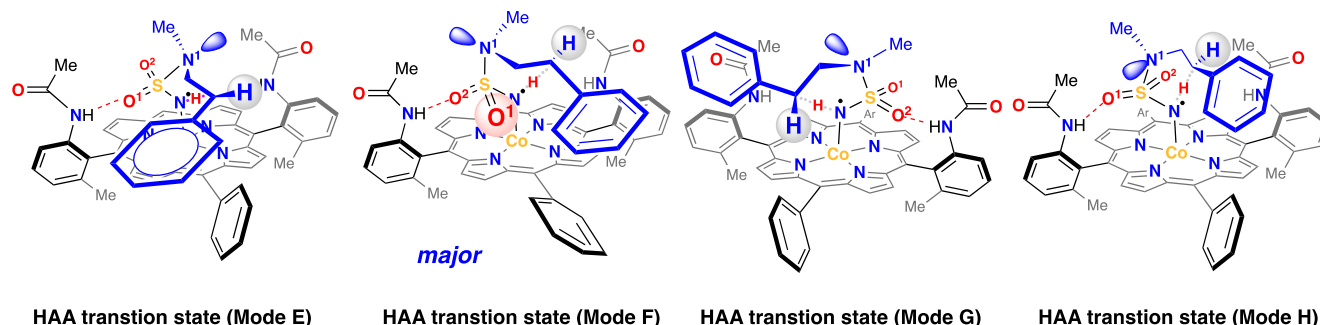
The free energy surfaces and images of computed structures associated with Scheme S4 are shown in Figs. S13-1 and S14-1, respectively. These calculations suggest that mode **F** out of 4 possible modes (**E−H**) is preferred in absence of a bridge (1.8 kcal/mol lower in energy than mode **E** at the ωB97XD/Def2TZVPP$_{benzene(SMD)}$ level; Fig. S14-1). Mode **F** is furthermore the same conformation that is also operative in modes **B2** and **D1** (cf. Schemes S2 and S3). Modes **E** and **F** are distinguished by whether oxygen atom O^1 or O^2 on the substrate engages in an H-bonding interaction with the amide group on the catalyst (Scheme S4). Additionally, the lone pair on N^1 is antiperiplanar with respect to the S−N· bond in **F**, reducing electronic repulsion with the N· radical. The alternative modes **G** and **H**, relevant to modes **A1**, **A2**, **C1** and **C2** in Schemes S2 and S3, are 3.2 and 2.9 kcal/mol above mode **F**, respectively (at the ωB97XD/Def2TZVPP$_{benzene(SMD)}$ level; Fig. S14-1). For instance, mode **G**, relevant to mode **A1**, suffers from steric strain that arises from the close proximity between the phenyl ring on the substrate and the amide moiety on the catalyst.
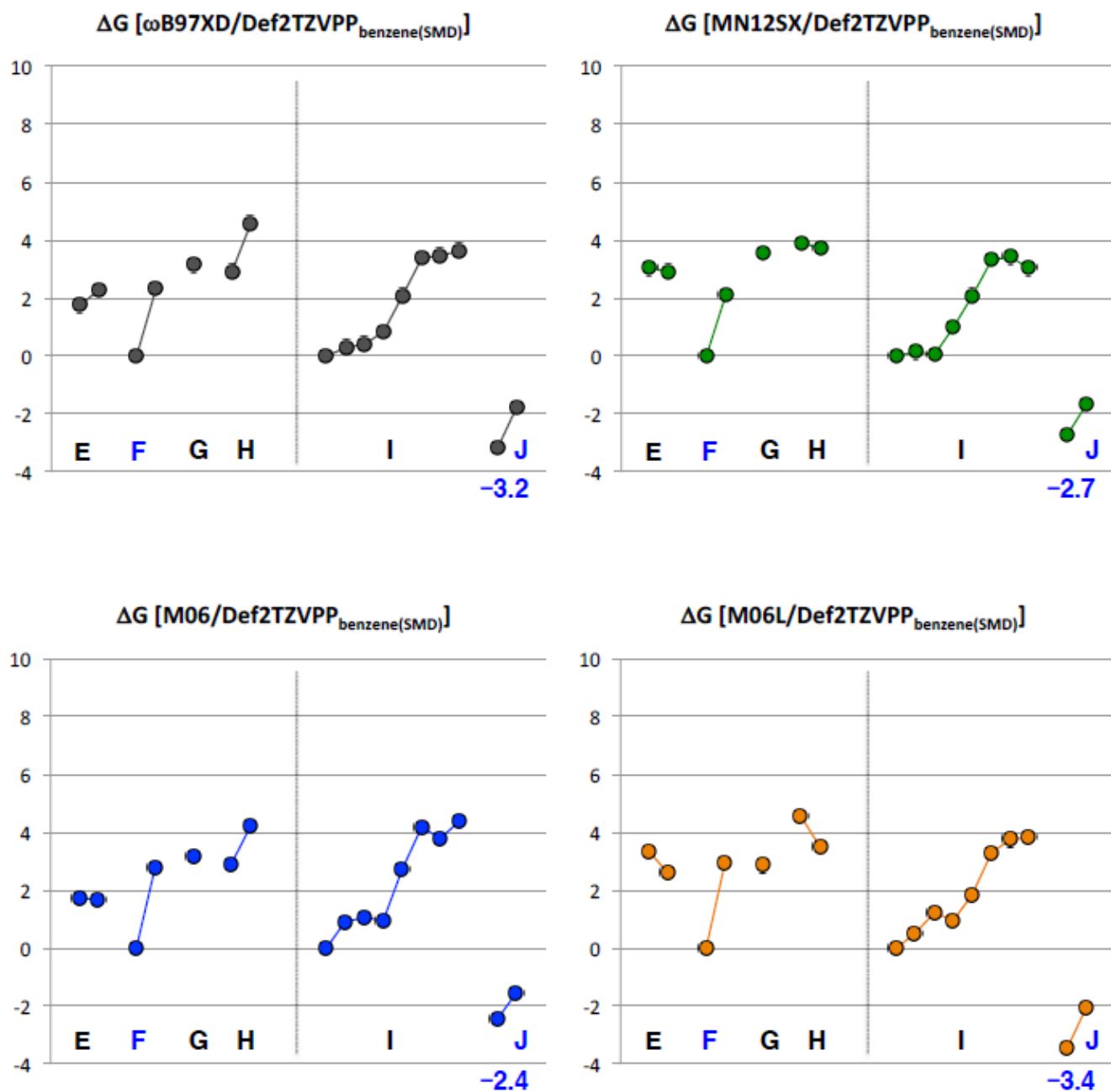
Fig. S13-1. Conformer distribution (ΔG) after geometry optimization with M06L/Def2SVP for HAA transition states with catalyst systems without a bridge $[\text{Co}]_{\text{model01}}$ and $[\text{Co}]_{\text{model02}}$; for the corresponding modes of additions **E-J**, see Schemes S4 and S6 (below).

Mode_E01
(model for Modes B1 and D2)

1.8

Mode_F01
(model for Modes B2 and D1)

favored

0.0

Mode_G01
(model for Modes A1, A2 and C1)

3.2

Mode_H01
(model for Mode C2)

2.9
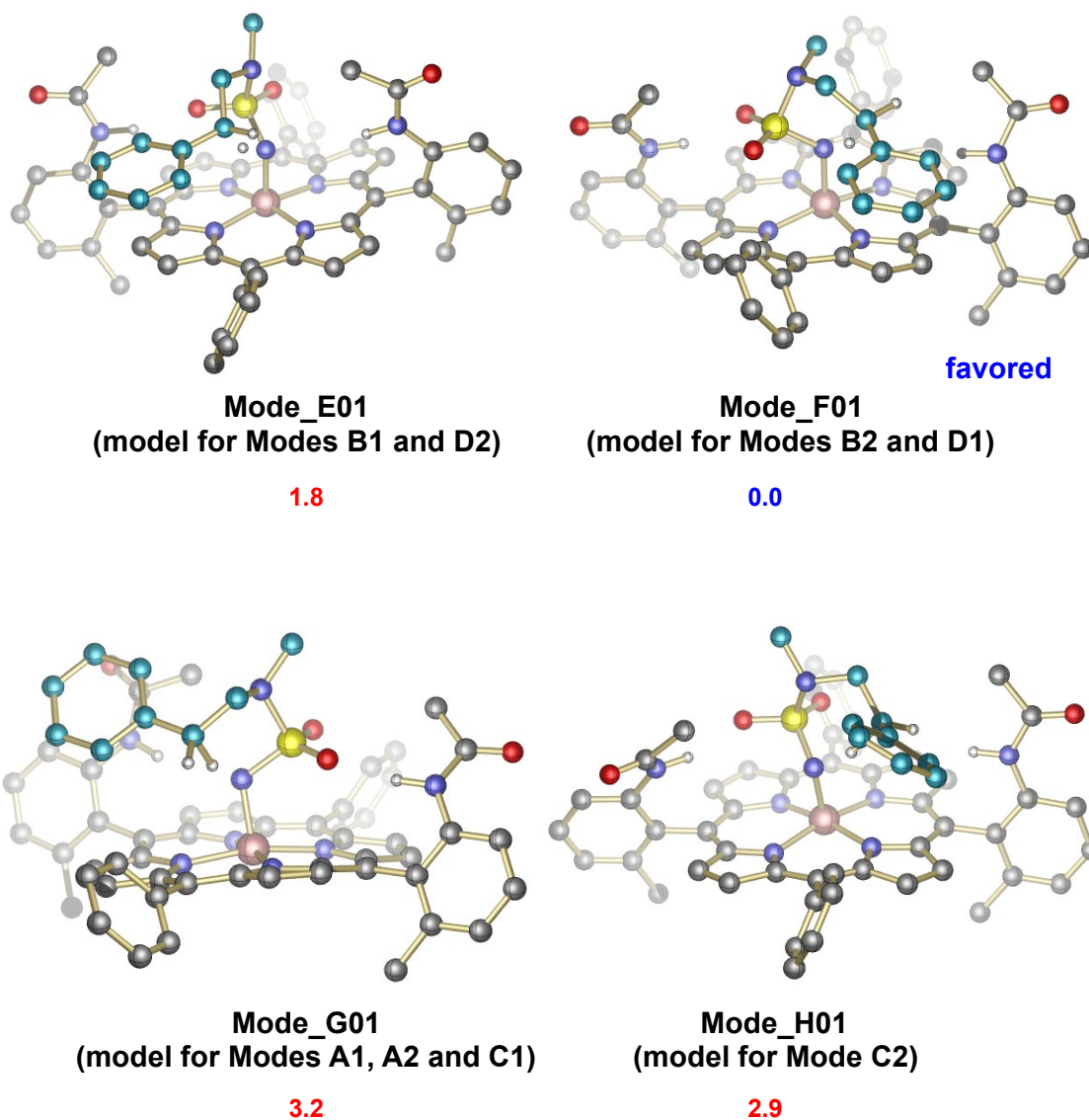
Fig. S14-1. Lowest free energy conformers for various HAA modes (**E-H**) with catalyst systems without a bridge at the ωB97XD/Def2TZVPP$_{benzene(SMD)}$//M06L/Def2SVP level (Fig. S13-1, Scheme S4); ball and stick model, most hydrogen atoms have been omitted for clarity.

# 5. The free energy surface: kinetic vs thermodynamic control (M06L/Def2SVP)

Although mode **D1** (= TS(I)^{under}) "underneath-the-bridge" appears to be the thermodynamically favored pathway for both of the real catalyst systems (**[Co(P4)]** and **[Co(P5)]**), in agreement with the calculations performed on the model system without a bridge (Scheme S4), a more complex mechanism might be operative with **[Co(P4)]**, wherein kinetic control prevails over thermodynamic factors (Scheme S5).

Scheme S5. Proposed rationale for HAA with **[Co(P4)]**$_{model}$ (kinetic control) vs **[Co(P5)]**$_{model}$ (thermodynamic control)
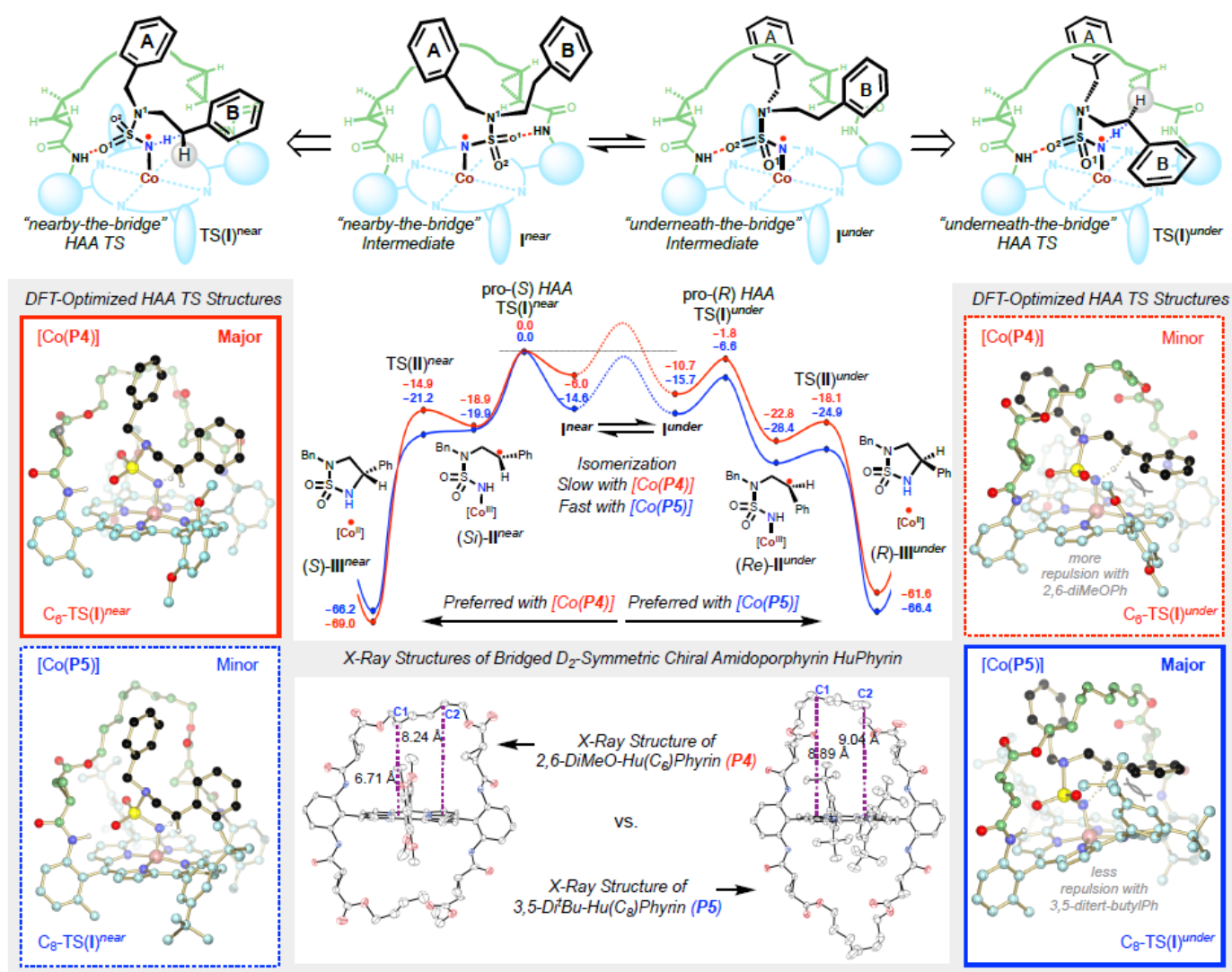
Kinetic control. In case of $[Co(P4)]_{model}$, the energy difference (1.8 kcal/mol) between the most stable mode **D1** (= C_6-TS(**I**)^{under}) and the second most stable mode **A1** (= C_6-TS(**I**)^{near}) is smaller than that with $[Co(P5)]_{model}$ (6.6 kcal/mol). This may be attributed to the reduced available space underneath the bridge as well as a repulsive interaction between O^1 on the substrate and the methoxy group on the catalyst (cf. C_6-TS(**I**)^{under}; right side in Scheme S5). However, the thermodynamically favored mode **D1** (= C_6-TS(**I**)^{under}) may not be kinetically accessible in the smaller $[Co(P4)]_{model}$ system. The following alternative scenario is proposed: It is plausible that the two aryl-containing moieties on the substrate (**A** and **B**) are situated on the same side of the bridge in the initially generated nitrogen-centered radical **I**^{near}. Conformational reorganization (**I**^{near} → **I**^{under}) to access mode **D1** (= TS(**I**)^{under}) may, however, involve a significant kinetic barrier (i.e., it is slow), leaving mode **A1** (= TS(**I**)^{near}) as the only possible choice (*kinetic control*). The exact barrier for such a conformational change (**I**^{near} → **I**^{under}) is difficult to determine with certainty through DFT due to a flat potential energy surface (approximated by dashed line). Nonetheless, comparison of the space-filling images for modes **A1** (= TS(**I**)^{near}) and **D1** (= TS(**I**)^{under}) illustrates the steric demand that may be associated with such a process. That is, phenyl ring **A** is slightly above the top of the bridge in **A1** (see Mode **A1-C$_6$** (= C_6-TS(**I**)^{near}) in Fig. S11-2).

Thermodynamic control. In case of the larger $[Co(P5)]_{model}$ system, the conformational change from (**I**^{near} → **I**^{under}) may not involve a significant barrier. Again, the space-filling images for modes **A1** and **D1** support this proposal (i.e., the phenyl ring **A** is lower than the top of the bridge in **A1**, see Mode **A1-C$_8$** (= C_8-TS(**I**)^{near}) in Fig. S12-3). Therefore, the most stable HAA mode **D1** (= TS(**I**)^{under}) is likely operative in the latter case, leading to the prochiral (*R*) HAA (*thermodynamic control*).

Furthermore, taking into account the above kinetic factors, mode **C1** (cf. Scheme S2) is likely the kinetically accessible pathway through which the minor enantiomer of the product is generated with $[Co(P4)]$ (1.9 kcal/mol above mode **A1**; Fig. S10-1). In both modes, **A1** and **C1**, the two substituents on the substrate (phenyl ring **A** and **B**) are also on the same side of the bridge (Scheme S2).

For a more detailed description of the potential energy surface shown in Scheme S5, see Section 8 below.

6. Rationale regarding enantioselectivity trends based on variations of the substrate

Taking into consideration the above investigations, the following rationale might be given for the experimentally observed trends.

(1) Assuming that the energetic barrier associated with conformational change en route to mode **D1** is a critical factor for enantiodetermination could explain why reactions with substrates containing small moieties (**1i**, **1j** and **1r**) are highly enantioselective when promoted by **[Co(P5)]** (cf. Fig. 3A). That is, the less sterically demanding substrates could possibly facilitate the conformational change that has to occur during transition between modes **A1** and **D1** ($\mathbf{I}^{near} \rightarrow \mathbf{I}^{under}$; cf. Scheme S5). For the same reason, reactions with **1i** and **1j** are only moderately stereoselective when promoted by **[Co(P4)]** (cf. Fig. 3A), likely because the interchange between modes **A1** and **D1** is not completely prohibited. With substrate **1r** bearing the small cyclopropyl group the opposite enantiomer (same sense as with **[Co(P5)]**) is generated, suggesting that $\mathbf{I}^{near} \rightarrow \mathbf{I}^{under}$ isomerization is more facile. It may also be plausible to account for the results with **[Co(P5)]** solely on the basis of mode **D1**. In mode **D1** (Scheme S5) aryl ring **B** is pointing toward the front, which is only possible due to the absence of ortho substituents on the 3,5-di-*tert*-butylaryl ring, a fact that allows the latter aryl moiety to tilt, thereby creating the necessary space to accommodate the substrate.

(2) When reaction of sterically relatively unhindered azide **1r** is catalyzed by [Co(**P5**)], the (*R*)-product is formed with high enantioselectivity (cf. Fig 3B). The same substrate also leads to product (*R*)-**2r** with a small (*R*)-preference (58:42 er) when the reaction is performed with [Co(**P4**)]. Such anomalous (*R*)-selectivity with [Co(**P4**)] agrees well with a thermodynamically more stable but kinetically less accessible "underneath-the-bridge" transition state $C_6\text{-TS}(\mathbf{I})^{under}$ in cases when the substituent on the substrate is small.

(3) Substrates containing additional functional groups with heteroatoms (**1o**, **1p** and **1q**) result in low yields in presence of catalyst **[Co(P4)]** (cf. Fig. 3B). This trend may be rationalized with increased electron-electron repulsion that exists between the substrate's heteroatom and the methoxy group on the catalyst (cf. mode **D1** (= $C_6\text{-TS}(\mathbf{I})^{under}$) in Scheme S5).

(4) Substrates **1s**, **1t** and **1u** carrying bulky units undergo reactions non-selectively with catalyst **[Co(P5)]** (cf. Fig. 3C). It is plausible that the generally favored mode **D1** (cf. $C_8\text{-TS}(\mathbf{I})^{under}$ in Scheme S5) will either be destabilized due to the steric repulsion between the additional bulk and the bridge (with

substrate **1s**) or the bulky group might slow down the conformational change that is required for $\mathbf{I}^{near} \rightarrow$ $\mathbf{I}^{under}$ isomerization (Scheme S5), so that mode **A1** ($= C_8\text{-TS}(\mathbf{I})^{near}$) will become competitive.

7. Kinetic selectivity for HAA leading to 5- or 6-membered ring products

To shed light onto the selective formation of the 5-membered ring product with catalysts **[Co(P4)]** and **[Co(P5)]**, we considered model system **[Co]$_{model02}$** without benzylic hydrogen atoms (Scheme S6) and compared the HAA barriers that would lead to the 5- and 6-membered ring products, respectively. The results indicate that in absence of any possible strain induced by the catalyst bridge and when no benzylic hydrogen atoms are present, HAA through mode **J** is preferred by 3.2 kcal/mol over mode **I**. *For the corresponding free energies and images of computed structures, see Figs. S13-1 and S14-2.* The low strain of the 7-membered ring transition state in **J** permits HAA to occur in an almost linear trajectory from the carbon to the nitrogen atom (167.4°; Fig. S14-2), whereas this angle (among others) is significantly contracted in the 6-membered ring transition state in **I** (156.6°; Fig. S14-2). The strain associated with the 6-membered ring transition state is likely the reason why significant amounts of 6-membered ring product are formed with the non-bridged catalysts (cf. Table S2), albeit generation of the 5-membered ring product is still preferred entropically. That formation of the 5-membered ring product is exclusive with catalysts **[Co(P4)]** and **[Co(P5)]** may be attributed to the steric pressure induced by the bridge which likely facilitates angle contraction and enforces close proximity between the hydrogen atom in β position and the nitrogen-centered radical.

Scheme S6. Investigated transition state conformations for HAA leading to 5- and 6-membered ring products with **[Co]$_{model02}$**

HAA transtion state (Mode I)
leading to 5-membered ring product

HAA transtion state (Mode J)
leading to 6-membered ring product

Mode_I01

(HAA to generate 5-membered ring)

3.2

favored

Mode_J01

(HAA to generate 6-membered ring)

0.0
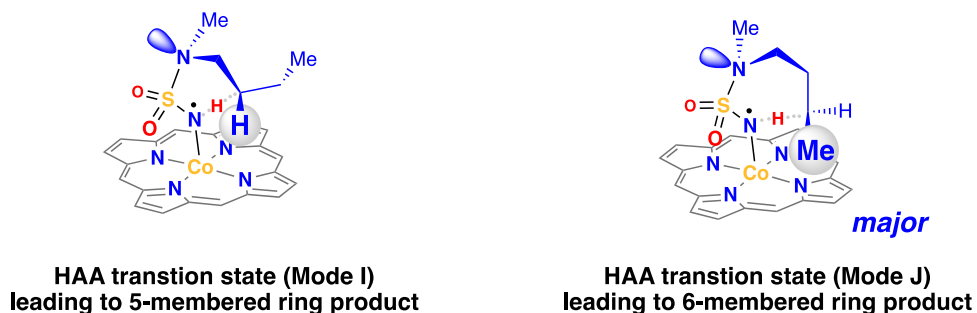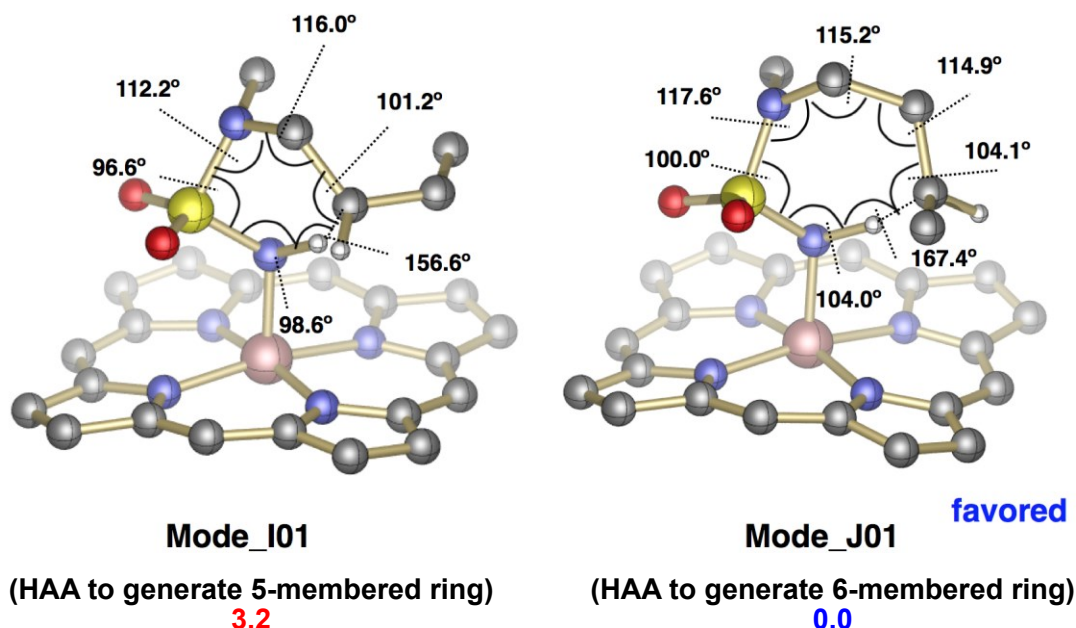
Fig. S14-2. Lowest free energy conformers for various HAA modes (**I–J**) with catalyst systems without a bridge at the ωB97XD/Def2TZVPP$_{benzene(SMD)}$//M06L/Def2SVP level (Fig. S13-1, Scheme S6); ball and stick model, most hydrogen atoms have been omitted for clarity.

8. Captions for movies (SI-C and SI-D) to illustrate the major pathways leading to the enantiodifferentiative HAA and stereoretentive RS by [Co(P4)] and [Co(P5)]:

From the structures generated through the IRC calculations, we created two animations in PyMOL v1.5.0.4. for the most preferred pathways leading to the major enantiomer with **[Co(P4)]** and **[Co(P5)]**, respectively. **They are appended as separate.mp4 files** (See SI-C and SI-D).

SI-C: Animation of **pro-(S)** selective HAA via *"nearby-the-bridge"* transition state and stereoretentive RS with [Co(**P4**)]; duration: 17 seconds. The following time points provide a short description of the animated content; 0:00–0:06 seconds: a 360º rotation of structure **I**^{near} (cf. Scheme S5); 0:06–0:09 seconds: HAA abstraction sequence **I**^{near} → TS(**I**)^{near} → *(Si)*-**II**^{near} (cf. Scheme S5); 0:09–0:11 seconds: conformational adjustment of the bridge performed at the structure of *(Si)*-**II**^{near} (not shown in Scheme S5); 0:11–0:12 seconds: dihedral angle rotation (H–N–Co–N) of the newly generated N–H bond around the N–Co bond [*(Si)*-**II**^{near} → TS(**II**)^{near}; in TS(**II**)^{near} the nitrogen centered singly occupied orbital is of p-character vs sp^3 in *(Si)*-**II**^{near}], followed by radical substitution [TS(**II**)^{near} → [*(S)*-**III**^{near}]; 0:13–0:17 seconds: dissociation of the product (not shown in Scheme S5).

SI-D: Animation of **pro-(*R*)** selective HAA via *"underneath-the-bridge"* transition state and stereoretentive RS with [Co(**P5**)]; duration: 19 seconds. The following time points provide a short description of the animated content; 0:00–0:06 seconds: a 360º rotation of structure $\mathbf{I}^{under}$ (cf. Scheme S5); 0:06–0:09 seconds: HAA abstraction sequence $\mathbf{I}^{under} \rightarrow$ TS(**I**)$^{under} \rightarrow$ *(Re)*-$\mathbf{II}^{under}$ (cf. Scheme S5); 0:09–0:14 seconds: dihedral angle rotation (H−N−Co−N) of the newly generated N−H bond around the N−Co bond [*(Re)*-$\mathbf{II}^{under} \rightarrow$ TS(**II**)^{under}; in TS(**II**)^{under} the nitrogen centered singly occupied orbital is of p-character vs sp^3 in *(Re)*-$\mathbf{II}^{under}$], followed by radical substitution [TS(**II**)$^{under} \rightarrow$ [*(R)*-$\mathbf{III}^{under}$]; 0:14–0:19 seconds: dissociation of the product (not shown in Scheme S5).

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