Mechanistic Insights on the Magnesium(II) Ion-Activated Reduction of Methyl Benzoylformate with Chelated NADH Peptide β-Lactam Models

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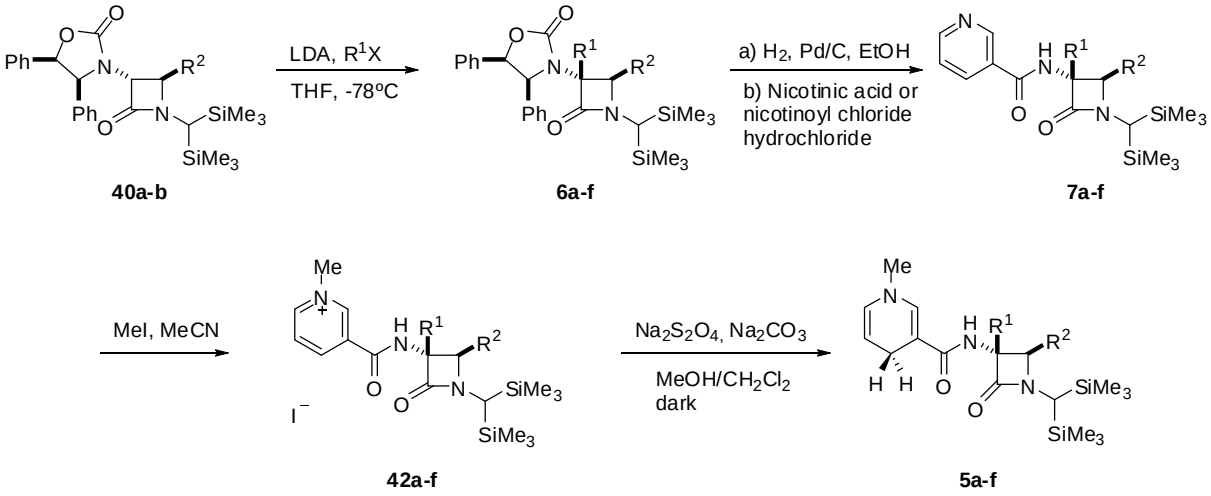
SUPPORTING INFORMATION

1.-Preparation Details and Physical and Spectroscopic Data of Compounds 6a and 6c-d, 7a-f, 42a-f, 5a-f, 43-44, and 8.

1.1 General. All reactions were carried out under an atmosphere of nitrogen or argon in oven or flame-dried glassware with magnetic stirring. Solvents were distilled prior to use. Tetrahydrofuran (THF) was distilled from sodium metal/benzophenone ketyl. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride. Dichloromethane, methanol, water, and deuterated acetonitrile (CD_3CN) used for preparation of NADH models and for biomimetic reductions were deoxygenated by nitrogen bubbling for 2-3 hrs or by freeze-pump-thaw techniques. Magnesium perchlorate was dried by heating under vacuum for 24 h, and then deoxygenated using standard Schlenk techniques. Purification of reaction products was carried out by flash chromatography using silicagel (230-400 mesh). Analytical thin layer chromatography was performed on 0.25 mm silica gel plates. Visualization was accomplished with UV light and phosphomolybdic acid-ammonium cerium (IV) nitratesulfuric acid-water reagent, followed by heating. Melting points are uncorrected. Infrared spectra were recorded over KBr pellets. NMR spectra were recorded at frequencies of 200, 300, and 500 MHz for ^{1}H and 50, 75, and 125 MHz respectively for ^{13}C, at room temperature unless otherwise stated. Chemical shifts are reported in ppm relative to the central line of CD_2Cl_2 (5.33 ppm), $CDCl_3$ (7.28 ppm), and CD_3CN (1.94 ppm) for ^{1}H NMR, and to the central line of CD_2Cl_2 (54.0 ppm), $CDCl_3$ (77.0 ppm) and CD_3CN (1.39 ppm) for ^{13}C NMR. ^{1}H, ^{13}C, and ROESY spectra were processed using MestReNova 5.2.4 software. Combustion analyses were performed on a

elemental analyzer. Enantiomeric excesses were determined by analytical high performance liquid chromatography (HPLC) on a chromatographs equipped with a diode array UV detector or Dual λ absorbance detector using chiral columns with flow rates of 0.7 mL/min and 0.5 mL/min (mobile phase hexane – isopropanol).Optical rotations were measured at 25 ±0.2 °C in methylene chloride unless otherwise stated. Mass spectra were obtained on a Finnigan GCQ mass spectrometer (70 eV) using GC-MS coupling (column: fused silica gel, 15 m, 0.25mm, 0.25 nm phase SPB-5).



Preparation Details and Physical and Spectroscopic Data:

Preparation and physical data of compound **6b**[1] and **6e-f** were previously described[2].

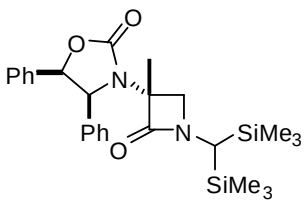
The α-amino-β-lactams obtained by the hydrogenolytic cleavage of the 4,5-diphenyl-oxazolidinyl group were used in the next step without any purification. In the case of α-(2-methylnaphtyl)-β-lactams **6d** and **6f** a partial hydrogenation of the naphthyl moiety was observed and the corresponding 5,6,7,8-tetrahydronaphthyl derivatives were obtained.

[1] Palomo, C. Aizpurua, J. M. Benito, A. Cuerdo, L., Fratila, R. M.; Miranda, J. I.; Linden, A., *J. Org. Chem.*, **2006**, *71*, 6368-6373.

[2] Palomo, C., Aizpurua, J. M., Ganboa, I., Benito, A., Cuerdo, L., Fratila, R. M., Jimenez, A., Loinaz, I., Miranda, J. I., Pytlewska, K. R., Micle, A., Linden, A., *Org. Lett.*, **2004**, *6*, 4443-4446.

1.2 General Procedure for the α-Alkylation of (3*S*)-1-[Bis(trimethylsilyl)methyl]-3-[(4*S*,5*R*)-4,5-diphenyl-2-oxo-oxazolidin-3-yl]-azetidin-2-one 40a. To a suspension of 1,10-phenanthroline (0.3 mg, indicator) in anhydrous THF (50 mL) cooled to –78ºC under nitrogen atmosphere 2.5M n-BuLi was added drop-wise until dark red color was observed (usually 2 or 3 drops). Dry diisopropylamine (10.32 mmol, 1.5 mL) and 2.5M n-BuLi (10.32 mmol, 4.1 mL) were added and the mixture was stirred at –78ºC for 10min. A solution of the corresponding β-lactam **40a** (9.38 mmol) in anhydrous THF (40 mL) was added drop-wise during 2 min, and the stirring was continued for 30 min at –78ºC. Freshly distilled alkyl halide (5 equivalents, 46.9 mmol) was added, and stirring was continued for 24 hours, allowing the temperature to reach 20ºC by consumption of the bath. The reaction mixture was taken up over CH_2Cl_2 (50 mL), washed successively with saturated aqueous NH_4Cl (50 mL), 1M HCl (50 mL), saturated aqueous $NaHCO_3$ (50 mL) and H_2O (2 x 25 mL), dried ($MgSO_4$) and evaporated under reduced pressure. The products were purified by column chromatography (silicagel-60, eluent: hexanes/EtOAc).

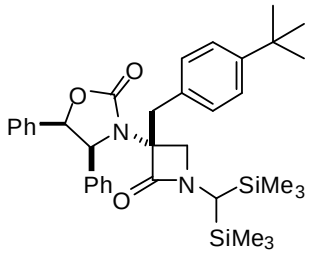
(3*R*)-3-methyl-1-[bis(trimethylsilyl)methyl]-[(4*S*,5*R*)-4,5-diphenyl-2-oxo-oxazolidin-3-yl]-azetidin-2-one (6a):



6a

The general procedure was followed from **40a** (5 mmol, 2.33 g), LDA (1.5 eq.), and methyl iodide (5 eq., 25 mmol, 4.73 mL). The reaction mixture was allowed to warm at room temperature overnight. Eluent: hexanes, then hexanes/ EtOAc: 3/1. Yield: 154 g (64%); white solid; mp: 142ºC; $[\alpha]_D^{25}$ = -48 (c= 1.0, CH_2Cl_2); IR(cm^{-1}, KBr): 1750.3 (C=O); 846.0 (C-Si). MS (TOF, CI) m/z: 481.2(100), 482.2(38), 466.2(16), 465.2(39), 279.1(20). ^{1}H-NMR (δ, ppm, $CDCl_3$): 7.05-7.11 (m, 10H), 5.90 (d, 1H, *J*= 7.4Hz), 5.25 (d, 1H, *J*= 7.4Hz), 3.89 (d, 1H, *J*= 5.7Hz), 3.28 (d, 1H, *J*= 5.7Hz), 2.75 (s, 1H), 1.31 (s, 3H), 0.21 (s, 9H), 0.15 (s, 9H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 166.7, 156.8, 136.1, 134.2, 128.7, 128.6, 128.5, 128.3, 128.12, 126.2, 81.2, 67.2, 66.4, 57.6, 37.5, 19.8, 0.25, 0.23. HRMS (*m/z*): 481.2350; $C_{26}H_{37}N_2O_3Si_2$ requires 481.2343.

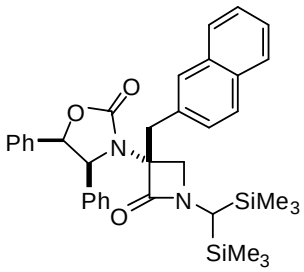
(3*R*)-(4-*tert*-Butyl-benzyl)-1-[bis(trimethylsilyl)methyl]-[(4*S*,5*R*)-4,5-diphenyl-2-oxo-oxazolidin-3-yl]-azetidin-2-one (6c):



6c

The general procedure was followed from **40a** (5 mmol, 2.33 g), LDA (1.5 eq.), and 4-*tert*-butyl benzyl bromide (3 eq., 15 mmol, 2.84 mL). The reaction mixture was allowed to warm at room temperature overnight. Eluent: hexanes, then hexanes/ EtOAc: 5/1. Yield: 1.96 g (64%); white solid; mp: 223ºC; $[\alpha]_D^{25}$ = -2.35 (c= 1.0, CH_2Cl_2); IR(cm^{-1}, KBr): 1739.3 (C=O); 1731.7 (C=O); 1252.6 (^{t}Bu); 836.0 (C-Si). HPLC-MS, MeOH/HCOOH m/z (Ion Source Type: ESI, positive polarity): MS+1: 613.5, MS2 (613.5): 597.3, 567.3, 366.2, 188.0. ^{1}H-NMR (δ, ppm, $CDCl_3$): 7.25-7.04 (m, 14H), 5.91 (d, 1H, *J*= 7.3Hz), 5.45 (d, 1H, *J*= 7.3Hz), 3.59 (d, 1H, *J*= 6.4Hz), 3.49 (d, 1H, *J*= 6.4Hz), 2.93 (d, 1H, *J*= 13.7Hz), 2.57 (s, 1H), 2.34 (d, 1H, *J*= 13.7Hz), 1.24 (s, 9H), 0.04 (s, 9H), -0.15 (s, 9H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 164.4, 156.7, 149.8, 135.6, 133.9, 131.8, 128.9, 128.5, 128.1, 125.7, 81.2, 72.4, 65.3, 52.3, 37.5, 36.7, 34.4, 31.3, -0.4, -0.6. Anal. Calcd. For $C_{36}H_{48}N_2O_3Si_2$ (612.95): C, 70.54; H, 7.89; N, 4.57. Found: C, 70.60; H, 7.83; N, 4.59.

(3*R*)-3-[(2-Naphthyl)-methyl]-1-[bis(trimethylsilyl)methyl]-3-[(4S,5*R*)-4,5-diphenyl-2-oxo-oxazolidin-3-yl]-azetidin-2-one (6d):



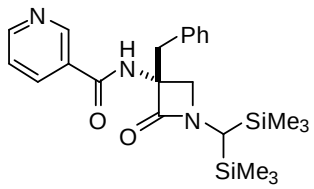
6d

The general procedure was followed from **40a** (5 mmol, 2.33 g), LDA (1.2 eq.), and 2-bromomethyl-naphthalene (1.6 eq., 8 mmol, 1.85 g). After the addition of the bromide the CO_2/acetone bath was replaced by an ice-salt bath and the reaction mixture was stirred at 0ºC for 2 h and then allowed to warm at room temperature overnight. Eluent: hexanes, then hexanes/ EtOAc: 6/1. Yield: 2.33 g (77%); white powder; mp: 235-236ºC; $[\alpha]_D^{25}$ = +15.25 (c= 1.0, CH_2Cl_2); IR(cm^{-1}, KBr): 1736.5 (C=O); 1702.8 (C=O); 820.0 (C-Si). HPLC-MS, MeOH/HCOOH m/z (Ion Source Type: ESI, positive polarity): MS+1: 607.3, MS2 (607.4): 591.3, 188.0, MS3 (591.0): 561.2, 450.2, 379.2, 262.1, 188.0. ^{1}H-NMR (δ, ppm, $CDCl_3$): 7.74-7.68 (m, 3H), 7.58 (s, 1H), 7.42 (m, 2H), 7.30-7.28 (m, 2H), 7.23 (d, 1H, *J*= 8.4Hz), 7.17-7.10 (m, 8H), 5.93 (d, 1H, *J*= 7.3Hz), 5.47 (d, 1H, *J*= 7.3Hz), 3.62 (d, 1H, *J*= 6.5Hz), 3.54 (d, 1H, *J*= 6.5Hz), 3.15 (d, 1H, *J*= 13.7Hz), 2.58

(d, 1H, *J*= 13.7Hz), 2.48 (s, 1H), -0.06 (s, 9H), -0.31 (s, 9H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 164.4, 156.9, 135.7, 134.09, 133.7, 132.7, 132.5, 129.4, 129.3, 128.9, 128.7, 128.4, 128.1, 127.8, 127.6, 127.5, 126.1, 125.8, 81.4, 72.4, 65.5, 52.8, 37.9, 37.7, -0.4, -0.7. Anal. Calcd. For $C_{36}H_{42}N_2O_3Si_2$ (612.95): C, 71.24; H, 6.98; N, 4.62. Found: C, 69.22; H, 6.623; N, 4.61.

1.3 General Procedures for the Preparation of Nicotinamides 7a-f

1.3.1 Preparation of (3*R*)-3-Benzyl-1-[bis(trimethylsilyl)methyl]-3-nicotinamido-azetidin-2-one (7b) (COUPLING METHOD A).



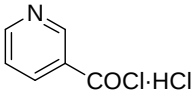
7b

A solution of the corresponding amine (2.2 mmol) in dry CH_2Cl_2 (25 mL) under nitrogen atmosphere was cooled to 0ºC. Then, nicotinic acid (1.5 eq, 3.3 mmol), NEt_3 (1.5 eq, 3.3 mmol,), HOBt (1.5 eq, 3.3 mmol), and EDC·HCl (1.5 eq, 3.3 mmol) were added. The stirring was continued for an hour at 0ºC, and for 24 h at room temperature. After that time, CH_2Cl_2 (10 mL) was added and the solution was washed with 1M aq. $KHSO_4$ (20 mL) and H_2O (20 mL). The organic phase was decanted and dried over $MgSO_4$. The solvents were evaporated under reduced pressure and the crude was purified by flash column chromatography (eluent EtOAc). Yield: 3.82 g (87%); white solid; mp: 113ºC; $[\alpha]_D^{25}$ = -25.6 (c= 1.0, CH_2Cl_2); IR(cm^{-1}, KBr): 1726 (C=O); 1650 (C=O); 847.8 (C-Si). HPLC-MS, MeOH/HCOOH m/z (Ion Source Type: ESI, positive polarity): MS+1: 440.2, MS2 (440.2): 253.0, 188.0, MS3 (188.0): 172.0, 114.1. ^{1}H-NMR (δ, ppm, $CDCl_3$): 9.11 (bs, 1H), 8.85 (bs, 1H); 8.72 (d, 1H, *J*= 3.9Hz), 8.24 (dt, 1H, J_1= 1.9Hz, J_2= 1.9Hz, J_3= 7.9Hz), 7.33 (dd, 1H, J_1= 4.6Hz, J_2= 7.9Hz), 7.08 (m, 5H), 3.57 (s, 2H), 3.31 (d, 1H, *J*= 13.6Hz), 3.13 (d, 1H, *J*= 13.8Hz), 2.52 (s, 1H), 0.00 (s, 9H), -0.04 (s, 9H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 166.3, 166.1, 152.0, 149.1, 135.2, 135.1, 130.4, 129.8, 128.4, 127.0, 123.14, 69.0, 54.3, 38.2, 37.8, -0.4, -0.5. Anal. Calcd. For $C_{23}H_{33}N_3O_2Si_2$ (439.71): C, 62.83; H, 7.56; N, 9.56. Found: C, 62.86; H, 7.72; N, 9.78.

1.3.2 General Procedure for the Preparation of (3*R*)-3-alkyl-1-[bis(trimethylsilyl)methyl]-3-nicotinamido-azetidin-2-ones 7a and 7c-f (COUPLING METHOD B):

To a solution of the nicotinoyl chloride hydrochloride **41** (3.6 mmol, 0.64 g) in 40 mL of dry CH_3CN cooled to -5ºC under nitrogen atmosphere, N,N-diisopropylethylamine (DIPEA) (24 mmol, 4.2 mL), and a solution of the corresponding α-amino-β-lactam (3 mmol) in 10 mL CH_3CN were added. The reaction mixture was stirred for 1 hour at 0ºC, then at room temperature (5 to 18 hours, monitored by ^{1}-H NMR). After that time, CH_2Cl_2 (20 mL) was added and the solution was washed with NaOH 0.1 M (20 mL), NH_4Cl (20 mL) and H_2O (20 mL). The organic phase was decanted and dried over $MgSO_4$. The solvents were evaporated under reduced pressure and the crude was purified by flash chromatography, eluent: EtOAc.

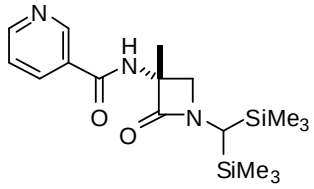
Nicotinoyl chloride hydrochloride 41:



41

To a suspension of nicotinic acid (1 mmol, 0.124 g) in dry dichlorometane (10 mL) under nitrogen, three drops of dry DMF and oxalyl chloride (1.2 eq., 1.2 mmol, 0.103 mL) were added drop-wise. The nitrogen balloon was replaced by a dessicator and the reaction mixture was stirred at room temperature for 2 hours. After that time, solvents were evaporated carefully under a nitrogen atmosphere to afford quantitatively the acid chloride **41**.

(3*R*)-3-methyl-1-[bis(trimethylsilyl)methyl]-3-nicotinamido-azetidin-2-one (7a):

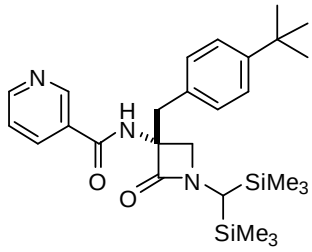


7a

The general procedure was followed (Coupling Method B) from the corresponding α-amino-β-lactam (0.25 mmol, 0.06 g), nicotinoyl chloride hydrochloride (0.42 mmol, 0.035 g), and N,N-diisopropylethylamine (1.84 mmol, 0.32 mL). Yield: 0.458 g (62%); white solid; mp: 123-124ºC; $[\alpha]_D^{25}$ = -35 (c= 0.5, CH_2Cl_2); IR(cm^{-1}, KBr): 1752.4 (C=O); 1667.2 (C=O); 1250.4 (^{t}Bu); 850.1 (C-Si). MS (TOF, CI) m/z: 364.2(100), 349.2(19), 348.2(75), 189.1(15), 188.1(88), 162.1(34). ^{1}H-NMR (δ, ppm, $CDCl_3$): 9.10 (d, 1H, *J*=1.7Hz), 8.72 (dd, 1H, J_1= 1.5Hz, J_2= 3.3Hz), 8.17 (dt, 1H, J_1= 1.8Hz, J_2= 4.8Hz, J_3= 7.9Hz), 7.92 (bs, 1H) 7.36 (dd, 1H, J_1= 4.8Hz, J_2= 7.8Hz), 3.76 (d, 1H, *J*= 6.0Hz), 3.52 (d, 1H, *J*= 6.0Hz), 2.74 (s, 1H), 1.70 (s, 3H), 0.01 (s, 9H), -0.04 (s, 9H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 168.0, 166.1, 152.7, 149.2, 135.4,

130.0, 123.6, 65.3, 57.8, 37.7, 20.2, 0.2, 0.1. HRMS (*m/z*): 364.1864; C_{17} H_{30} N_3 O_2 Si_2 requires 364.1877.

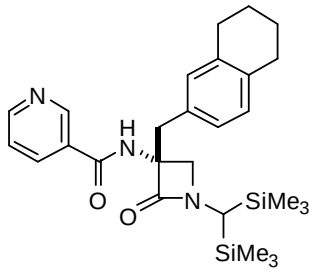
(3*R*)-3-(4-*tert*-Butyl-benzyl)-1-[bis(trimethylsilyl)methyl]-3-nicotinamido-azetidin-2-one (7c):



7c

The general procedure was followed (Coupling Method B) from the corresponding α-amino-β-lactam (1.49 mmol, 0.58 g), nicotinoyl chloride hydrochloride (1.79 mmol, 032 g), and N,N-diisopropylethylamine (11.9 mmol, 2.16 mL). Yield: 0.458 g (62%); white solid; mp: 157-158ºC; $[\alpha]_D^{25}$ = -14.6 (c= 0.5, CH_2Cl_2); IR(cm^{-1}, KBr): 1723.4 (C=O); 1659.7 (C=O); 1246.0 (^{t}Bu); 842.0 (C-Si). HPLC-MS, MeOH/HCOOH m/z (Ion Source Type: ESI, positive polarity): MS+1: 496.4, MS2 (496.4): 480.2, 309.2, 188.1, MS3 (309.2): 253.0, 174.9. ^{1}H-NMR (δ, ppm, $CDCl_3$): 9.10 (d, 1H, *J*=1.8Hz), 8.76 (dd, 1H, J_1= 1.8Hz, J_2= 4.8Hz), 8.38 (bs, 1H), 8.21(dt, 1H, J_1= 1.8Hz, J_2= 4.8Hz, J_3= 7.9Hz), 7.38 (dd, 1H, J_1= 4.8Hz, J_2= 7.9Hz), 7.15 (d, 2H, *J*=8.2Hz), 7.10 (d, 2H, *J*=8.2Hz), 3.60 (d, 1H, *J*= 6.4Hz), 3.58 (d, 1H, *J*= 6.4Hz), 3.37 (d, 1H, *J*= 13.7Hz), 3.13 (d, 1H, *J*= 13.7Hz), 2.55 (s, 1H), 1.25 (s, 9H), 0.01 (s, 9H), -0.04 (s, 9H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 166.6, 166.3, 152.5, 150.1, 149.4, 135.4, 132.3, 130.4, 130.1, 125.8, 123.5, 69.5, 54.2, 38.1, 37.9, 34.6, 31.5, -0.1. Anal. Calcd. For $C_{27}H_{41}N_3O_2Si_2$ (495.80): C, 65.41; H, 8.34; N, 8.48. Found: C, 65.34; H, 8.47; N, 8.85.

(3*R*)-3-[(5,6,7,8-Tetrahydronaphthalen-2-yl)methyl]-1-[bis(trimethylsilyl)methyl]-3-nicotinamido-azetidin-2-one (7d):

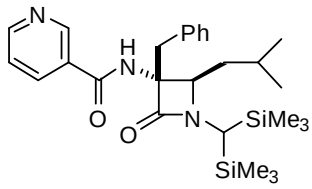


7d

The general procedure was followed (Coupling Method B) from the corresponding α-amino-β-lactam (2.1 mmol, 0.815 g), nicotinoyl chloride hydrochloride (2.52 mmol, 0.45 g), and N,N-diisopropylethylamine (16.8 mmol, 3 mL). Yield: 0.602 g (60%); white solid; mp: 184ºC; $[\alpha]_D^{25}$ = -22.4 (c= 0.5, CH_2Cl_2); IR(cm^{-1}, KBr): 1720.0 (C=O); 1650.9 (C=O); 845.6 (C-Si). HPLC-MS, MeOH/HCOOH m/z (Ion Source Type: ESI, positive polarity): MS+1: 494.5, MS2 (49.5): 307.1, 188.1, MS3 (307.0): 279.1, 174.9, 106.1. ^{1}H-NMR (δ, ppm,

$CDCl_3$): 9.02 (s, 1H), 8.75 (d, 1H, *J*= 3.5Hz), 8.14 (bs, 1H), 7.61(bs, 1H), 7.37 (m, 1H), 6.96-6.90 (m, 3H), 3.64 (d, 1H, *J*= 6.2Hz), 3.62(d, 1H, *J*= 6.2Hz), 3.29 (d, 1H, *J*= 13.7Hz), 3.16 (d, 1H, *J*= 13.7Hz), 2.68 (m, 4H), 2.61 (s, 1H), 1.74 (m, 4H), 0.05 (s, 9H), -0.01 (s, 9H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 166.5, 165.8, 152.4, 148.7, 131.0, 129.8, 129.4, 127.6, 127.3, 123.3, 69.0, 54.0, 38.1, 37.6, 29.3, 29.1, 23.2, -0.3, -0.4. Anal. Calcd. For $C_{27}H_{39}N_3O_2Si_2$ (493.79): C, 65.67; H, 7.96; N, 8.51. Found: C, 65.37; H, 7.99; N, 8.62.

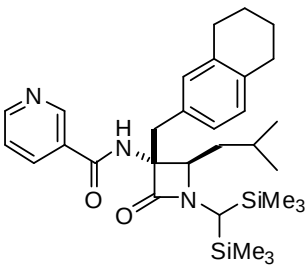
(3*R*,4*R*)-3-Benzyl-1-[bis(trimethylsilyl)methyl]-4-isobutyl-3-nicotinamido-azetidin-2-one (7e):



7e

The general procedure was followed (Coupling Method B) from the corresponding α-amino-β-lactam (3 mmol, 1.18 g), nicotinoyl chloride hydrochloride (3.6 mmol, 0.641 g), and N,N-diisopropylethylamine (24 mmol, 4.2 mL). Yield: 1.04 g (70%); yellowish oil; $[\alpha]_D^{25}$ = +17.2 (c= 1.0, CH_2Cl_2); IR(cm^{-1}, KBr): 1731.5 (C=O); 1666.9 (C=O); 847.7 (C-Si). HPLC-MS, MeOH/HCOOH m/z (Ion Source Type: ESI, positive polarity): MS+1: 496.3, MS2 (496.3): 480.2, 373.3, 293.1, 244.1, MS3 (244.1): 228.1, 161.0. ^{1}H-NMR (δ, ppm, $CDCl_3$): 8.72-8.68 (m, 2H), 7.83 (d, 1H, *J*= 7.8Hz), 7.29-7.18 (m, 6H), 6.50 (bs, 1H), 3.94 (m, 1H), 3.50 (d, 1H, *J*= 13.7Hz), 3.08 (d, 1H, *J*= 13.7Hz), 2.18 (m, 1H), 1.82 (m, 1H), 1.68 (s, 1H), 1.58 (m, 1H), 1.07 (m, 6H), 0.26 (s, 9H), 0.16 (s, 9H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 166.9, 165.8, 152.5, 148.3, 135.5, 134.7, 130.5, 129.9, 126.9, 123.4, 68.1, 64.8, 64.6, 38.1, 37.4, 35.1, 29.7, 25.4, 23.0, 0.1. Anal. Calcd. For $C_{27}H_{41}N_3O_2Si_2$ (495.80): C, 65.41; H, 8.34; N, 8.48. Found: C, 65.23; H, 8.37; N, 8.16.

(3*R*,4*R*)-3-[(5,6,7,8-Tetrahydronaphthalen-2-yl)methyl]-4-isobutyl-1-[bis(trimethylsilyl)methyl]-3-nicotinamido-azetidin-2-one (7f):



7f

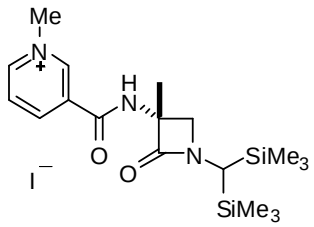
The general procedure was followed (Coupling Method B) from the corresponding α-amino-β-lactam (1.8 mmol, 0.8 g), nicotinoyl chloride hydrochloride (2.15 mmol, 0.384 g), and N,N-diisopropylethylamine (14.3 mmol, 2.6 mL). Yield: 0.72 g, (73%); oil; $[\alpha]_D^{25}$ = +7.4 (c= 1.0, CH_2Cl_2); IR(cm^{-1}, KBr): 1745.5 (C=O); 1666.7 (C=O); 854.0 (C-Si). HPLC-MS, MeOH/HCOOH m/z (Ion Source Type: ESI, positive polarity): MS+1: 550.3, MS2 (550.3): 534.3, 427.2, 349.13, 244.1,

MS3 (534.3): 448.2, 412.2, 347.2, 291.1, 225.1, 183.0. ^{1}H-NMR (δ, ppm, $CDCl_3$): 8.78 (s, 1H), 8.71 (d, 1H, *J*= 1.9Hz), 7.88 (d, 1H, *J*= 7.9Hz), 7.33 (m, 1H), 7.02 (d, 1H, *J*= 7.5Hz), 6.93 (d, 1H, *J*= 7.7Hz), 6.68 (s, 1H), 6.59 (bs, 1H), 3.96 (m, 1H), 3.40 (d, 1H, *J*= 13.7Hz), 3.00 (d, 1H, *J*= 13.7Hz), 2.68 (m, 4H), 2.49 (s, 1H), 2.14 (m, 2H), 1.81 (m, 1H), 1.72 (m, 4H), 1.58 (m, 1H), 1.07 (m, 6H), 0.25 (s, 9H), 0.16 (s, 9H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 166.8, 165.8, 152.2, 148.1, 136.8, 135.7, 134.9, 132.2, 131.1, 129.1, 127.5, 123.4, 68.1, 64.4, 38.1, 37.3, 34.6, 29.0, 25.4, 22.9, 0.1. Anal. Calcd. For $C_{31}H_{47}N_3O_2Si_2$ (549.89): C, 67.71; H, 8.61; N, 7.64. Found: C, 67.41; H, 8.54; N, 7.39.

1.4. General Procedure for the Preparation of Pyridinium Iodides 42a-f [3].

To a solution of the corresponding nicotinamide (1.00 mmol) in CH_3CN (10 mL) under N_2 atmosphere, methyl iodide (6 mL) was added. The reaction mixture was stirred at 50ºC for 2-24 h. After that time, the solvents were evaporated and the residue was dried under vacuum to afford the pyridinium iodide as a hydroscopic solid which was used without further purification.

N-[(3*R*)-3-methyl-1-(bis(trimethylsilyl)methyl)-2-oxoazetidin-3-yl)-1-methylpyridinium]-3-carboxamide iodide (42a):

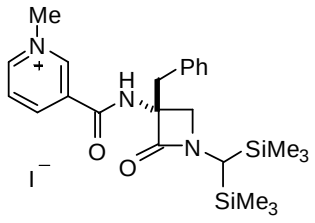


42a

The general procedure was followed (reaction time: 24 h) from **7a** (0.6 mmol, 0.217 g). Yield: 0.303 g (100%); yellow oil; $[\alpha]_D^{25}$ = + 33 (c= 1.0, CH_2Cl_2); IR(cm^{-1}, KBr): 1738.2 (C=O); 1678.0 (C=O); 846.9 (C-Si). MS (TOF, CI) m/z: 364.2(100), 349.2(21), 348.2(73), 189.1(18), 188.1(95), 162.1(41). ^{1}H-NMR (δ, ppm, $CDCl_3$): 9.73 (s, 1H); 9.20 (d, 1H, *J*= 5.9Hz); 8.93 (d, 1H, *J*= 8.0Hz); 8.53 (s, 1H); 8.16 (dd, 1H, J_1= 6.3Hz, J_2= 7.7Hz); 4.57 (s, 3H); 3.95 (d, 1H, *J*= 5.1Hz); 3.29 (d, 1H, *J*= 5.1Hz); 2.75 (s, 1H); 1.81 (s, 3H); 0.20 (s, 9H); 0.18 (s, 9H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 168.39, 160.95, 147.17, 144.92, 133.38, 128.09, 64.66, 56.05, 49.59, 37.19, 21.27, 0.09. HRMS (*m/z*): 364.1881; $C_{17}H_{30}N_3O_2Si_2$ requires 364.1877.

[3] Kanomata, N., Nakata, T., *J. Am. Chem. Soc.*, **2000**, *122*, 4563-4568.

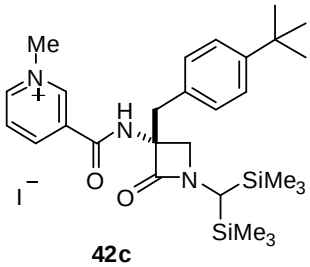
N-[(3*R*)-3-Benzyl-1-(bis(trimethylsilyl)methyl)-2-oxoazetidin-3-yl)-1-methylpyridinium]-3-carboxamide iodide (42b):



42b

The general procedure was followed (reaction time: 24 h) from **7b** (0.6 mmol, 0.246 g). Yield: 0.348 g (100%); yellow solid; mp: 104-105ºC; $[\alpha]_D^{25}$ = + 2.9 (c= 1.0, CH_2Cl_2); IR(cm^{-1}, KBr): 1736.4 (C=O); 1675.4 (C=O); 842.0 (C-Si). HPLC-MS, MeCN/NH_3 m/z (Ion Source Type: ESI, negative polarity): MS-1: 580.4, MS2(470.0): 439.3, 266.1, 224.1, 134.1; MS3(439.3): 423.1, 336.0, 264.0. ^{1}H-NMR (δ, ppm, $CDCl_3$): 9.55 (s, 1H); 9.02 (d, 1H, *J*= 6.0Hz); 8.80 (d, 1H, *J*= 8.0Hz); 8.77 (s, 1H); 7.99 (dd, 1H, J_1= 6.0Hz, J_2= 8.0Hz); 7.46-7.24 (m, 5H); 4.50 (s, 3H); 3.93 (d, 1H, *J*= 5.9Hz); 3.57 (d, 1H, *J*= 14.2Hz); 3.52 (d, 1H, *J*= 5.9Hz); 3.43 (d, 1H, *J*= 14.2Hz); 2.72 (s, 1H); 0.13 (s, 9H); 0.06 (s, 9H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 166.4, 161.4, 147.5, 144.9, 144.4, 135.1, 133.6, 130.6, 128.7, 128.4, 128.3, 127.3, 69.4, 53.7, 49.97, 38.8, 371.8, 0.0, -0.2. Anal. Calcd. For $C_{24}H_{36}IN_3O_2Si_2$ (581.64): C, 49.56; H, 6.24; N, 7.22. Found: C, 49.85; H, 6.08; N, 7.54.

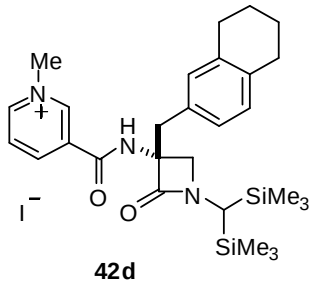
N-[(3*R*)-3-(4-*tert*-Butyl-benzyl)-1-(bis(trimethylsilyl)methyl)-2-oxoazetidin-3-yl)-1-methylpyridinium]-3-carboxamide iodide (42c):



42c

The general procedure was followed (reaction time: 24 h) from **7c** (1.8 mmol, 0.892 g). Yield: 1.03 g (90%); yellow solid; mp: 208ºC; $[\alpha]_D^{25}$ = - 23.2 (c= 1.0, EtOH); IR(cm^{-1}, KBr): 1731.3 (C=O); 1678.2 (C=O); 1252.0 (^{t}Bu); 848.0 (C-Si). HPLC-MS, MeOH/HCOOH m/z (Ion Source Type: ESI, negative polarity): MS-1: 636.4, MS2(554.6): 510.2, MS3(510.2): 323.2, 279.1, 161.0. ^{1}H-NMR (δ, ppm, $CDCl_3$): 9.65 (s, 1H); 9.18 (d, 1H, *J*= 5.9Hz); 8.86-8.83 (m, 2H); 8.04 (m, 1H); 7.35 (d, 2H, *J*= 8.4Hz); 7.33 (d, 2H, *J*= 8.4Hz); 4.57 (s, 3H); 3.87 (d, 1H, *J*= 5.9Hz); 3.51-3.48 (m, 2H); 3.37 (d, 1H, *J*= 14.0Hz); 2.68 (s, 1H); 1.29 (s, 9H); 0.09 (s, 9H); -0.01 (s, 9H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 166.0, 161.4, 149.8, 147.7, 149.9, 144.5, 133.4, 131.8, 130.3, 128.0, 125.6, 69.8, 52.7, 49.5, 38.0, 37.4, 34.4, 31.3, -0.1, -0.3. Anal. Calcd. For $C_{28}H_{44}IN_3O_2Si_2$ (637.74): C, 52.73; H, 6.95; N, 6.59. Found: C, 52.72; H, 6.86; N, 6.63.

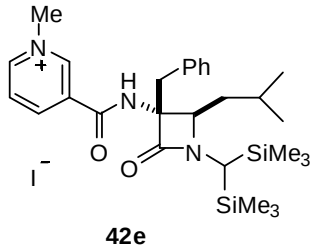
N-{(3*R*)-3-[(5,6,7,8-tetrahydronaphthalen-2-yl)methyl]-1-[bis(trimethylsilyl)methyl]-2-oxoazetidin-3-yl)-1-methylpyridinium}-3-carboxamide iodide (42d):



42d

The general procedure was followed (reaction time: 20 h) from **7d** (0.58 mmol, 0.287 g). Yield: 0.37 g (100%); yellow solid; mp: 116-117ºC; $[\alpha]_D^{25}$ = - 0.49 (c= 1.0, CH_2Cl_2); IR(cm^{-1}, KBr): 1736.0 (C=O); 1672.0 (C=O); 841.0 (C-Si). HPLC-MS, MeOH/HCOOH m/z (Ion Source Type: ESI, negative polarity): MS-1: 634.5, MS2(634.5): 492.9, 300.0. ^{1}H-NMR (δ, ppm, $CDCl_3$): 9.62 (s, 1H); 9.04 (d, 1H, *J*= 5.9Hz); 8.84 (d, 1H, *J*= 8.0Hz); 8.81 (s, 1H); 8.02 (m, 1H); 7.13-6.98 (m, 3H); 4.55 (s, 3H); 3.90 (d, 1H, *J*= 5.9Hz); 3.52 (d, 1H, *J*= 5.9Hz); 3.43 (d, 1H, *J*= 14.0Hz); 3.34 (d, 1H, *J*= 14.0Hz); 2.71 (m, 4H); 2.69 (s, 1H); 1.76 (m, 4H); 0.11 (s, 9H); 0.02 (s, 9H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 166.3, 161.4, 147.5, 144.6, 137.4, 136.3, 133.8, 131.9, 129.5, 128.2, 127.8, 69.9, 53.1, 49.8, 38.3, 37.7, 29.5, 29.2, 23.3, 23.2, 0.0, -0.2. Anal. Calcd. For $C_{28}H_{42}IN_3O_2Si_2$ (635.73): C, 52.90; H, 6.66; N, 6.61. Found: C, 53.21; H, 6.41; N, 6.59.

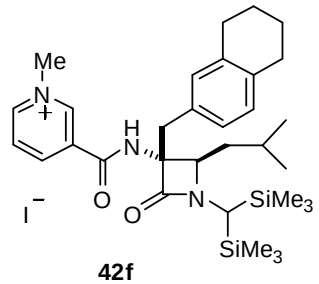
N-[(3*R*,*4*R)-3-Benzyl-1-(bis(trimethylsilyl)methyl)-4-isobutyl-2-oxoazetidin-3-yl)-1-methylpyridinium]-3-carboxamide iodide (42e):



42e

The general procedure was followed (reaction time: 18 h) from **7e** (1.38 mmol, 0.684 g). Yield: 0.88 g (100%); yellow solid; mp: 88-89ºC; $[\alpha]_D^{25}$ = + 2.25 (c= 1.0, MeOH); IR(cm^{-1}, KBr): 1738.0 (C=O); 1681.5 (C=O); 842.0 (C-Si). HPLC-MS, MeOH/HCOOH m/z (Ion Source Type: ESI, negative polarity): MS-1: 636.2, MS2(510.4): 267.1, 239.0, 148.0, 94.2. ^{1}H-NMR (δ, ppm, $CDCl_3$): 8.94-8.91 (m, 2H); 8.52 (d, 1H, *J*= 8.0Hz); 8.26 (s, 1H); 7.78 (dd, 1H, J_1= 6.2Hz, J_2= 8.0Hz); 7.67 (m, 2H); 7.32 (m, 3H); 4.31 (s, 3H); 3.94 (dd, 1H, J_1= 4.9Hz, J_2= 8.2Hz); 3.58 (d, 1H, *J*= 14.1Hz); 3.12 (d, 1H, *J*= 14.1Hz); 2.01 (m, 1H); 1.83 (s, 1H); 1.66 (m, 1H); 1.54 (m, 1H); 1.04 (d, 3H, *J*= 6.6Hz); 1.00 (d, 3H, *J*= 6.6Hz); 0.26 (s, 9H); 0.21 (s, 9H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 166.4, 161.0, 147.4, 144.7, 135.7, 133.4, 131.3, 128.3, 127.0, 68.2, 64.3, 49.6, 36.8, 35.7, 25.4, 23.4, 23.0, 0.3. Anal. Calcd. For $C_{28}H_{44}IN_3O_2Si_2$ (637.74): C, 52.73; H, 6.95; N, 6.59. Found: C, 52.51; H, 6.54; N, 6.42.

N-{(3*R*,4*R*)-3-[(5,6,7,8-tetrahydronaphthalen-2-yl)methyl]-1-[bis(trimethylsilyl)methyl]-4-isobutyl-2-oxoazetidin-3-yl)-1-methylpyridinium}-3-carboxamide iodide (42f):



42f

The general procedure was followed (reaction time: 20 h) from **7f** (1 mmol, 0.55 g). Yield: 0.69 g (98%); yellow solid; mp: 113-114ºC; $[\alpha]_D^{25}$ = + 0.26 (c= 1.0, CH_2Cl_2); IR(cm^{-1}, KBr): 1731.6 (C=O); 1673.0 (C=O); 842.0 (C-Si). HPLC-MS, MeOH/HCOOH m/z (Ion Source Type: ESI, negative polarity): MS-1: 690.4, MS2(690.4): 548.2. ^{1}H-NMR (δ, ppm, $CDCl_3$): 9.02 (d, 1H, *J*= 5.9Hz); 8.93 (s, 1H); 8.52 (d, 1H, *J* = 8.1Hz); 8.18 (s, 1H); 7.80 (m, 1H); 7.34 (m, 2H); 6.98 (d, 1H, *J*= 8.3Hz), 4.36 (s, 3H); 3.96 (m, 1H); 3.46 (d, 1H, *J*= 14.1Hz); 3.06 (d, 1H, *J*= 14.1Hz); 2.76 (bs, 4H); 2.36 (s, 1H); 2.06 (m, 1H); 1.77 (m, 4H); 1.68 (m, 1H); 1.55 (m, 1H); 1.04 (d, 3H, *J*= 6.6Hz); 1.01 (d, 3H, *J*= 6.6Hz); 0.25 (s, 9H); 0.21 (s, 9H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 166.6, 160.9, 147.6, 144.6, 144.1, 136.9, 135.8, 133.7, 132.4, 131.8, 129.0, 128.1, 68.3, 64.2, 49.8, 37.0, 35.4, 29.5, 29.2, 25.5, 23.3, 23.0, 0.4. Anal. Calcd. For $C_{32}H_{50}IN_3O_2Si_2$ (691.83): C, 55.55; H, 7.28; N, 6.07. Found: C, 55.12; H, 6.81; N, 6.06.

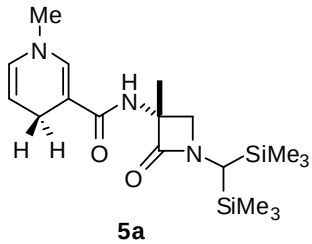
1.5 General Procedure for the Reduction of Pyridinium Iodides 42a-f[3].

To a solution of the corresponding pyridinium salt (0.5 mmol) in 12 mL of deoxygenated CH_2Cl_2/MeOH (3/1) a deoxygenated solution of $Na_2S_2O_4$ (10.0 mmol) in 0.5M aqueous Na_2CO_3[4] (12.5 mL) was added and the mixture was vigorously stirred under nitrogen in the dark for 16 h (soon the colour of the solution turned from orange to yellow). The organic layer was separated, the aqueous phase was extracted with CH_2Cl_2 (deoxygenated; 10 mL x 2) and the combined organic phase was dried ($MgSO_4$) and concentrated *in vacuo* to give the crude corresponding dihydropyridine which was used in the following reaction without further purification. These compounds can be kept for 24-48 hours at -30ºC without oxidation or decomposition. 1,4-Dihydronicotinamides **5a-f** were found to be light and air sensitive. Any attempt to purify these compounds either by preparative HPLC, preparative thin layer chromatography or crystallization has failed, leading to decomposition of the products. Due

[4] However, the use of 0.5M aqueous $KHCO_3$ (pH<8.5) instead of Na_2CO_3 considerably reduced the reaction times (2-4 h) and provided a cleaner spectrum of the reaction crude.

to this enhanced instability, we always prepared the NADH models just before using in the biomimetic reductions.

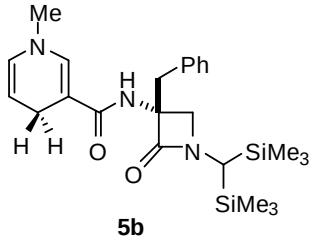
(3*R*)-3-methyl-1-[bis(trimethylsilyl)methyl]-3-(N-methyl-dihydronicotinamido)-azetidin-2-one (5a):



5a

The general procedure was followed from **42a** (0.5 mmol, 0.252 g). Yield: 0.159 g (84%); orange solid; ^{1}H-NMR (δ, ppm, $CDCl_3$): 6.95 (s, 1H); 5.79 (s, 1H,); 5.67 (d, 1H, J_1= 8.1Hz); 4.72 (m, 1H); 3.66 (d, 1H, *J*= 6.0Hz); 3.44 (d, 1H, *J*= 6.0Hz); 3.08 (bs, 1H); 2.93 (s, 3H); 2.76 (bs, 1H); 1.61 (s, 3H); 0.13 (s, 18H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 168.80, 168.31, 140.29, 130.15, 103.07, 65.03, 57.73, 41.16, 36.80, 30.15, 22.67, 20.42, 0.17, 0.12.

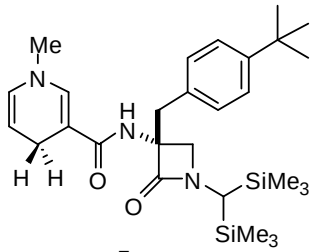
(3*R*)-3-Benzyl-1-[bis(trimethylsilyl)methyl]-3-(N-methyl-dihydronicotinamido)-azetidin-2-one (5b):



5b

The general procedure was followed from **42b** (0.5 mmol, 0.291 g). Yield: 0.145 g (64%); orange solid; ^{1}H-NMR (δ, ppm, CD_2Cl_2): 7.33-7.15 (m, 5H); 6.90 (d, 1H, *J*= 1.5Hz); 5.72 (dq, 1H, J_1= 8.9Hz, J_2= 1.8Hz, J_3= 1.5Hz, J_4= 1.5Hz); 5.63 (s, 1H); 4.70 (dt, 1H, J_1= 7.9Hz, J_2= 3.4Hz); 3.60 (d, 1H, *J*= 5.9Hz); 3.49 (d, 1H, *J*= 5.9Hz); 3.25 (m, 2H); 2.98 (dm, 2H); 2.94 (s, 3H); 2.60 (s, 1H); 0.09 (s, 9H); 0.04 (s, 9H). ^{13}C-NMR (δ, ppm, CD_2Cl_2): 167.6, 167.5, 139.6, 136.3, 130.6, 130.0, 128.6, 127.1, 124.1, 115.6, 102.5, 99.0, 68.3, 55.1, 40.7, 39.3, 37.3, 22.3, -0.4.

(3*R*)-3-(4-*tert*-Butyl-benzyl)-1-[bis(trimethylsilyl)methyl]-3-(N-methyl-dihydronicotinamido)-azetidin-2-one (5c):

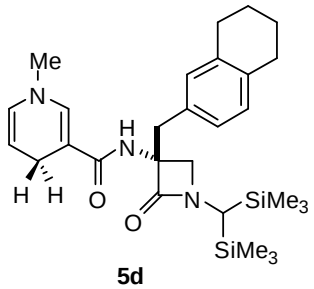


5c

The general procedure was followed from **42c** (0.5 mmol, 0.319 g). Yield: 0.163 g (64%); oil; ^{1}H-NMR (δ, ppm, CD_2Cl_2): 7.35 (d, 2H, *J*= 7.4Hz); 7.21 (d, 1H, *J*= 7.4Hz); 6.91 (s, 1H); 5.75 (d, 1H, *J*= 7.8Hz); 4.71 (m, 1H); 3.56 (d, 1H, *J*= 5.8Hz); 3.49 (d, 1H, *J*= 5.8Hz); 3.23 (d, 1H, *J*= 13.7Hz); 3.13 (d, 1H, *J*= 13.7Hz); 3.02

(bs, 2H); 2.94 (s, 3H); 2.58 (s, 1H); 1.324 (s, 9H); 0.07 (s, 9H); 0.0 (s, 9H). ^{13}C-NMR (δ, ppm, CD_2Cl_2): 167.0, 166.9, 149.2, 138.9, 132.5, 129.7, 129.4, 125.1, 101.9, 98.5, 68.0, 53.9, 40.1, 37.9, 36.6, 33.9, 30.7, 21.8, -0.9, -1.0.

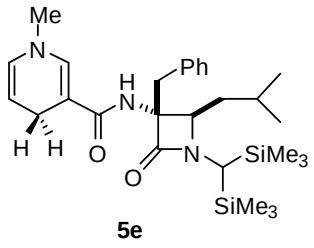
(3*R*)-3-[(5,6,7,8-Tetrahydronaphthalen-2-ylmethyl]-1-[bis(trimethylsilyl)methyl]-3-(N-methyl-dihydronicotinamido)-azetidin-2-one (5d):



5d

The general procedure was followed from **42d** (0.5 mmol, 0.319 g). Yield: 0.165 g (65%); oil; ^{1}H-NMR (δ, ppm, CD_2Cl_2): 6.95-6.94 (m, 3H); 6.91 (s, 1H); 6.86 (d, 1H, *J*= 1.5Hz); 5.68 (dq, 1H, J_1= 7.9Hz, J_2= 1.5Hz, J_3= 1.5Hz, J_4= 1.51Hz); 5.62 (s, 1H); 4.68 (m, 1H); 3.54 (d, 1H, *J*= 5.8Hz); 3.46 (d, 1H, *J*= 5.8Hz); 3.11 (d, 1H, *J*= 13.6Hz); 3.09 (d, 1H, *J*= 13.6Hz); 2.98 (m, 2H); 2.90 (s, 3H); 2.70 (m, 4H); 2.55 (s, 1H); 1.76 (m, 4H); 0.04 (s, 9H); -0.01 (s, 9H). ^{13}C-NMR (δ, ppm, CD_2Cl_2): 166.7, 164.7, 138.3, 136.1, 134.8, 131.8, 130.0, 129.9, 128.1, 126.6, 101.2, 97.8, 67.2, 53.4, 39.5, 37.6, 35.9, 30.9, 28.7, 28.3, 28.0, 22.2, -1.6.

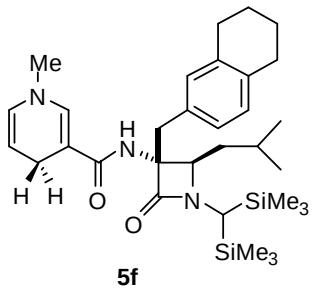
(3*R*,4*R*)-3-Benzyl-4-isobutyl-1-[bis(trimethylsilyl)methyl]-3-(N-methyl-dihydronicotinamido)-azetidin-2-one (5e):



5e

The general procedure was followed from **42e** (0.5 mmol, 0.319 g). Yield: 0.22 g (87%); oil; ^{1}H-NMR (δ, ppm, CD_2Cl_2): 7.27-7.21 (m, 5H); 6.80 (d, 1H, *J*= 1.3Hz); 5.64 (dq, 1H, J_1= 8.9Hz, J_2= 1.8Hz, J_3= 1.5Hz, J_4= 1.51Hz); 5.63 (s, 1H); 4.60 (m, 1H); 3.82 (m, 1H); 3.35 (d, 1H, *J*= 13.6Hz); 2.92 (d, 1H, *J*= 13.6Hz); 2.88 (s, 2H); 2.82 (m, 2H); 2.75 (s, 1H); 2.10 (m, 2H); 1.71 (m, 1H); 1.51 (m, 1H); 1.00 (m, 6H); 0.20 (s, 9H); 0.12 (s, 9H). ^{13}C-NMR (δ, ppm, CD_3CN): 168.5, 168.3, 140.0, 138.0, 137.6, 131.7, 131.6, 131.2, 129.0, 127.6, 102.8, 100.1, 68.6, 65.3, 55.4, 41.0, 38.2, 37.2, 36.7, 26.3, 23.5, 23.3, 22.9, 0.5.

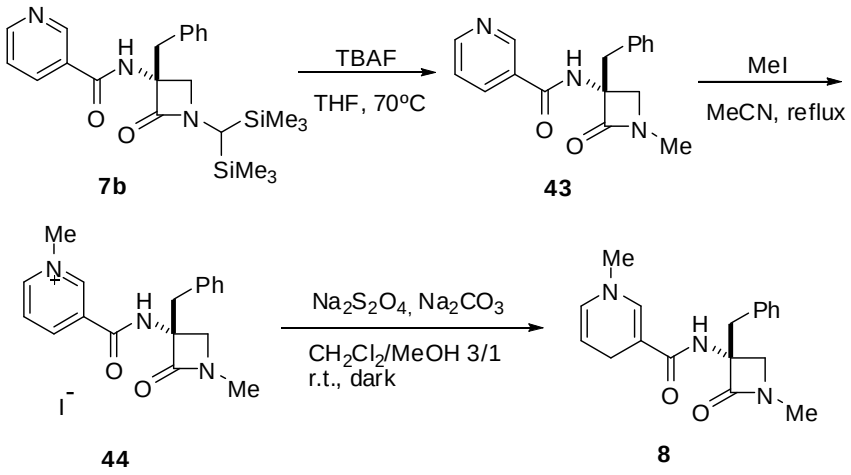
(3*R*,4*R*)-3-(5,6,7,8-Tetrahydronaphthalen-2-yl)methyl]-4-isobutyl-1-[bis(trimethylsilyl)methyl]-3-(N-methyl-dihydronicotinamido)-azetidin-2-one (5f):



5f

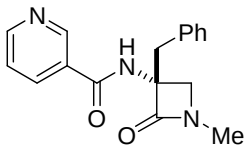
The general procedure was followed from **42f** (0.5 mmol, 0.346 g). Yield: 0.167 g (5%); oil; ^{1}H-NMR (δ, ppm, CD_2Cl_2): 6.97-6.84 (m, 3H); 6.84 (d, 1H, *J*= 1.4Hz); 5.69 (dq, 1H, J_1= 7.9Hz, J_2= 1.3Hz, J_3= 1.3Hz, J_4= 1.3Hz); 5.38 (s, 1H); 4.66 (m, 1H); 3.87 (m, 1H); 3.26 (d, 1H, *J*= 13.7Hz); 2.92 (s, 3H); 2.85 (d, 1H, *J*= 13.7Hz); 2.83 (m, 2H); 2.74 (m, 5H); 2.09 (m, 2H); 1.71 (m, 1H); 1.62 (m, 4H); 1.54 (m, 1H); 1.03 (m, 6H); 0.23 (s, 9H); 0.16 (s, 9H). ^{13}C-NMR (δ, ppm, CD_2Cl_2): 167.9, 166.1, 139.3, 136.6, 135.6, 133.4, 131.4, 130.1, 128.8, 117.1, 110.1, 102.4, 99.4, 67.9, 64.6, 47.9, 40.7, 38.1, 36.9, 35.2, 29.9, 29.6, 29.2, 25.6, 23.6, 22.9, 0.08.

1.6 Preparation of (3*R*)-3-Benzyl-1-Methyl-3-(N-methyldihydronicotinamido)-azetidin-2-one 8



7b **43** **44** **8**

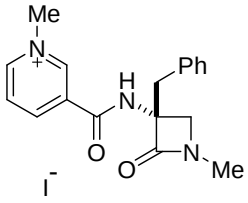
(3*R*)-3-Benzyl-1-methyl-3-nicotinamido-azetidin-2-one (43):



43

To a refluxing solution of the bis(trimethylsilyl)-methyl-nicotinamide **7b** (1 mmol, 0.44 g) in 30 mL dry THF under nitrogen 4 mL of an 1M TBAF solution in THF[5] were added drop-wise and the mixture was stirred at reflux for 1h (complete consumption of starting material was checked by ^{1}H-NMR). The solvent was evaporated under reduced pressure and the crude was dissolved in CH_2Cl_2 and the excess of TBAF was removed by flash chromatography (fluent CH_2Cl_2). Yield: 0.186 (64%); oil; $[\alpha]_D^{25}$ = + 2.05 (c= 1.0, CH_2Cl_2); IR(cm^{-1}, KBr): 3450; 1734.0 (C=O); 1659.0 (C=O). HPLC-MS, MeOH/HCOOH m/z (Ion Source Type: ESI, positive polarity): MS+1: 296.1, MS2(296.1): 253.0, MS3(253.0): 225.0, 174.9; 134.0; 106.0. ^{1}H-NMR (δ, ppm, $CDCl_3$): 9.00 (bs, 1H); 8.69 (d, 1H, *J*= 3.7Hz); 8.13 (d, 1H, *J*= 7.9Hz); 7.68 (bs, 1H); 7.37 8m, 1H); 3.71 (d, 1H, *J*= 5.9 Hz); 3.47 (d, 1H, *J*= 5.9 Hz); 2.74 (s, 3H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 168.1, 166.0, 152.5, 149.1, 135.9, 135.1, 130.3, 129.7, 128.7, 127.5, 123.6, 69.0, 53.0, 38.8, 28.5. Anal. Calcd. For $C_{17}H_{17}N_3O_2$ (295.34): C, 69.14; H, 5.80; N, 14.23. Found: C, 70.60; H, 5.82; N, 14.21.

N-[(3*R*)-3-Benzyl-1-methyl)-2-oxoazetidin-3-yl)-1-methylpyridinium]-3-carboxamide iodide (44):

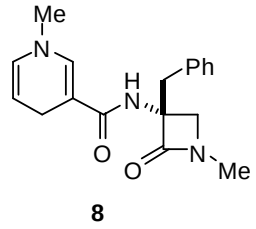


44

The general procedure (page 10) was followed (reaction time: 4 h) from **43** (0.6 mmol, 0.264 g). Yield: 0.256 g (98%); yellow oil; IR(cm^{-1}, KBr): 1742.2 (C=O); 1668.2 (C=O). HPLC-MS, MeOH/HCOOH m/z (Ion Source Type: ESI, negative polarity): MS-1: 436.7; ^{1}H-NMR (δ, ppm, $CDCl_3$): 9.96 (bs, 1H); 8.91 (m, 1H); 8.83 (s, 1H); 8.09 (m, 1H); 7.36-7.29 (d, 2H, *J*= 7.3Hz); 4.59 (s, 3H); 3.71 (d, 1H, *J*= 5.4Hz); 3.51 (s, 2H); 3.25 (d, 1H, *J*= 5.4Hz); 2.59 (s, 3H) . ^{13}C-NMR (δ, ppm, $CDCl_3$): 167.8, 161.7, 147.4, 145.3, 144.9, 134.2, 133.1, 130.5, 128.5, 128.4, 127.5, 69.7, 51.3, 49.9, 38.7, 28.3. Anal. Calcd. For $C_{18}H_{20}IN_3O_2$ (437.27): C, 49.44; H, 4.61; N, 9.61. Found: C, 50.90; H, 4.72; N, 8.57.

[5] Tetrabutylammonium fluoride solution (1M in THF, containing 5% water, available from Acros Organics), was dried over molecular sieves for 48h prior to use.

(3*R*)-3-Benzyl-1-Methyl-3-(N-methyldihydronicotinamido)-azetidin-2-one 8:



8

The general procedure (page 13) was followed from **44** (0.45 mmol, 0.190 g). Yield: 0.108 g, (82%); yellow oil; ^{1}H-NMR (δ, ppm, CD_2Cl_2): 7.26-7.18 (m, 5H); 6.79 (s, 1H); 5.60 (dd, 1H, J_1= 8.0Hz, J_2= 1.6Hz); 4.59 (dt, 1H, J_1= 7.8Hz, J_2= 3.4Hz, J_3= 3.4Hz); 3.53 (d, 1H, *J*= 5.2Hz); 3.26 (d, 1H, *J*= 5.2Hz); 3.14 (d, 1H, *J*= 13.9Hz); 3.07 (d, 1H, *J*= 13.9Hz); 2.92-2.88 (m, 1H); 2.82 (s, 3H); 2.82-2.80 (m, 1H); 2.64 (s, 3H). ^{13}C-NMR (δ, ppm, CD_2Cl_2): 169.4, 167.6, 140.1, 136.3, 130.3, 129.06, 127.86, 102.7, 98.8, 68.5, 41.1, 40.0, 28.5, 22.5.

1.7 General Procedure for the Biomimetic Reduction of Methyl Benzoylformate with the NADH models 8 and 5a-f.

All reactions were conducted in the dark, under a nitrogen atmosphere, at room temperature, in sealed NMR tubes or flasks.

In a typical run, a solution of the NADH model (0.103 mmol, 1.1 eq.), $Mg(ClO_4)_2$ (0.103 mmol, 1.1 eq., 23.0 mg), and methyl benzoylformate (0.093 mmol) in 0.7 mL of deoxygenated CD_3CN was prepared in a dried NMR tube in the dark and the reaction was followed by ^{1}H-NMR. After complete consumption of the NADH model, H_2O was added and the aqueous layer was extracted with CH_2Cl_2 (4 x 2 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude reaction mixture was submitted to the HPLC analysis although in some cases the resulting mandelate was isolated by preparative thin layer chromatography (eluent: Hexanes/EtOAc). Enantiomeric excesses were determined by HPLC using chiral stationary phases (Chiralcel OD) and Hexanes/Isopropanol as mobile phase. Reaction conditions, yields, and HPLC conditions are given in **Table S1**.

Table S1.

Entry	NADH Model	Reaction Conditions	Yield (%)	Major enantiomer	Ee (%)	HPLC Conditions
1	**8**	CD_3CN, $Mg(ClO_4)_2$, r.t., 16h	60 (NMR)	S	60	Chiralcel OD, Hex/iPrOH 80/20 Flow rate 0.5 mL/min
2	**5a**	CD_3CN, $Mg(ClO_4)_2$, r.t., 14h	95 (NMR)	S	73	Chiralcel ODH, Hex/iPrOH 85/15 Flow rate 1 mL/min
3	**5b**	CD_3CN, $Mg(ClO_4)_2$, r.t., 14h	66 (NMR)	S	78	Chiralcel OD, Hex/iPrOH 80/20 Flow rate 0.7 mL/min
4	**5d**	CD_3CN, $Mg(ClO_4)_2$, r.t., 18h	100 (NMR)	S	82	Chiralcel OD, Hex/iPrOH 80/20 Flow rate 0.7 mL/min
5	**5d**	CD_3CN, $Mg(ClO_4)_2$, r.t., 14h	100 (NMR)	S	90	Chiralcel OD, Hex/iPrOH 80/20 Flow rate 0.7 mL/min
6	**5e**	CD_3CN, $Mg(ClO_4)_2$, r.t., 16h	50 (NMR)	S	90	Chiralcel OD, Hex/iPrOH 80/20 Flow rate 0.7 mL/min
7	**5f**	CD_3CN, $Mg(ClO_4)_2$, r.t., 18h	94 (NMR)	S	90	Chiralcel OD, Hex/iPrOH 80/20 Flow rate 0.7 mL/min

2.-Selected HPLC Chromatograms

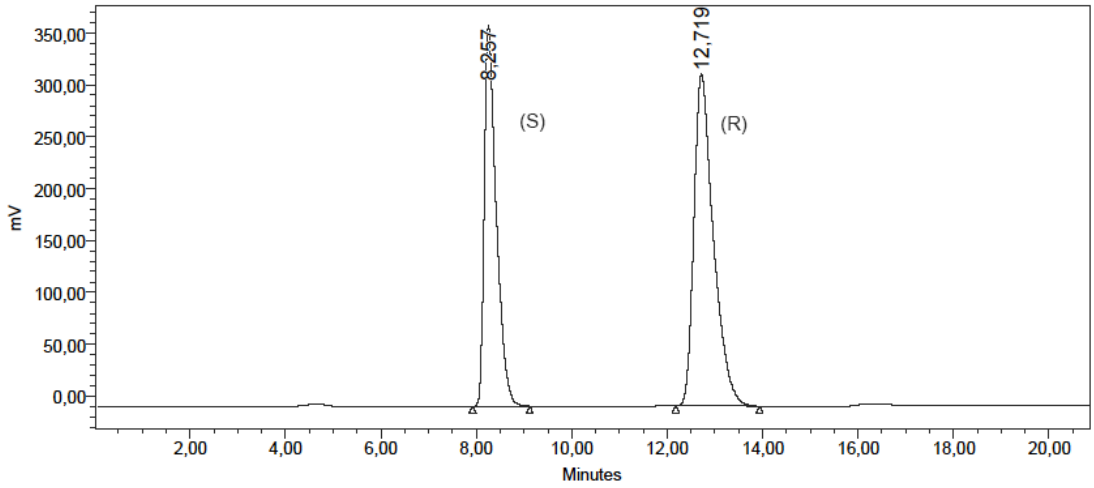
Empower software

Injection Summary Report

Reported by User: USUARIO GENERAL (HPLC) Project Name: Raluca

SAMPLE INFORMATION

Sample Name:	(R) + (S) mm ODv 19.02.04	Acquired By:	HPLC
Sample Type:	Unknown	Date Acquired:	19/02/2004 16:56:10
Vial:	1	Acq. Method Set:	raluca
Injection #:	1	Date Processed:	19/02/2004 17:20:32
Injection Volume:	10,00 ul	Processing Method:	RS mm ODv 190204 254
Run Time:	200,0 Minutes	Channel Name:	Satin Ch 2
Sample Set Name:		Proc. Chnl. Descr.:	254



Channel Satin Ch 2; Processed Channel: 254; Result Id: 1489; Processing Method: RS mm ODv 190204 254

Processed Channel Descr.: 254

	Processed Channel Descr.	RT	Area	% Area	Height
1	254	8,257	6373814	41,24	367801
2	254	12,719	9080500	58,76	320177

Figure S1. HPLC chromatogram of racemic methyl mandelate. Conditions: CHIRALCEL OD column; mobile phase: Hex/iPrOH 80/20; flow rate 0.7 mL/min.

```
RA449 TLC fr.1
Chiralcel OD nueva
Hex/iPrOH 80/20
0.7 mL/min
5.05.05

=====================================================================
Injection Date  : 04/01/1980 18:12:02 PM
Sample Name     : RA449TLC1                          Vial :   -
Acq. Operator   : raluca
Acq. Method     : C:\HPCHEM\1\METHODS\RAQUEL.M
Last changed    : 04/01/1980 16:08:02 PM by raluca
                  (modified after loading)
Analysis Method : E:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 29/05/1905 12:52:23 PM
                  (modified after loading)
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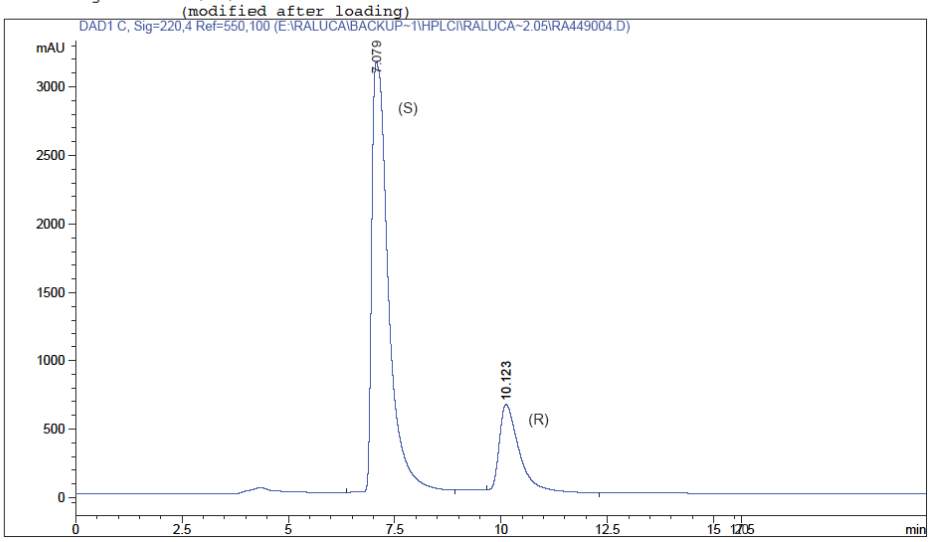


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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: DAD1 C, Sig=220,4 Ref=550,100
 Results obtained with standard integrator!

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.079 VV    0.3663 8.70902e4  3149.71875  79.9337
   2  10.123 VV    0.5006 2.18628e4   649.12970  20.0663

Totals :                  1.08953e5  3798.84845

=====================================================================
                        *** End of Report ***
```
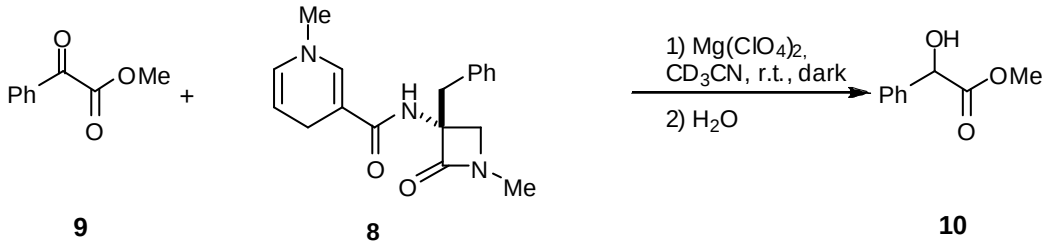



9 **8** **10**

Figure S2. HPLC chromatogram of crude methyl mandelate obtained from the reduction of methyl benzoylformate with NADH model **8**. Conditions: CHIRALCEL OD column; mobile phase: Hex/iPrOH 80/20; flow rate 0.7 mL/min.

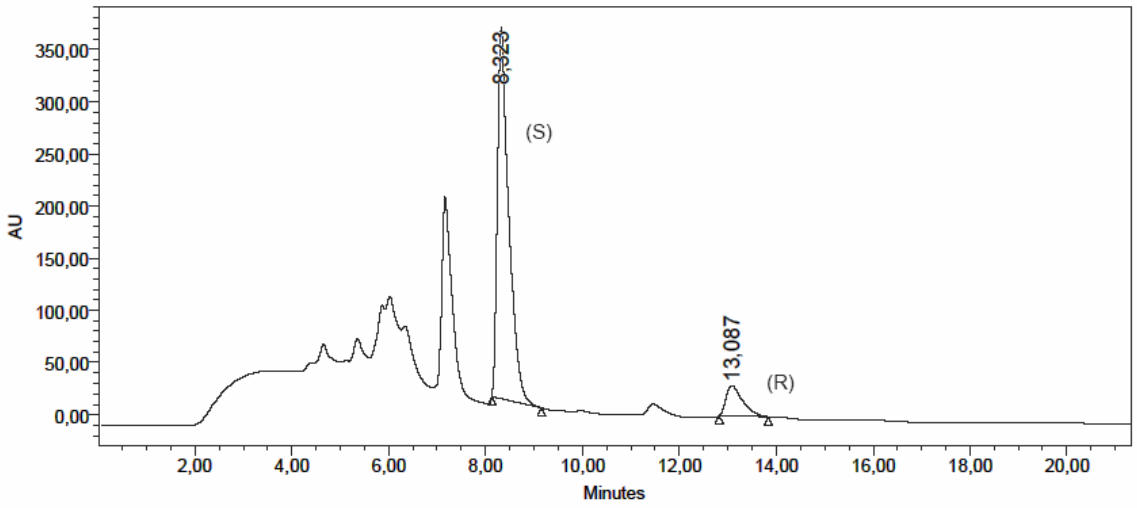
Empower software

Injection Summary Report

Reported by User: USUARIO GENERAL (HPLC) Project Name: Raluca

SAMPLE INFORMATION

Sample Name:	Ra 114 OD vieja hex/iPrOH 80/20	Acquired By:	HPLC
Sample Type:	Unknown	Date Acquired:	26/06/2003 18:53:07
Vial:	1	Acq. Method Set:	Raluca1
Injection #:	5	Date Processed:	14/02/2005 15:48:39
Injection Volume:	10,00 ul	Processing Method:	superralu
Run Time:	120,0 Minutes	Channel Name:	Satin Ch 1
Sample Set Name:		Proc. Chnl. Descr.:	254



Channel Satin Ch 1; Processed Channel: 254; Result Id: 1647; Processing Method: superralu

Processed Channel Descr.: 254

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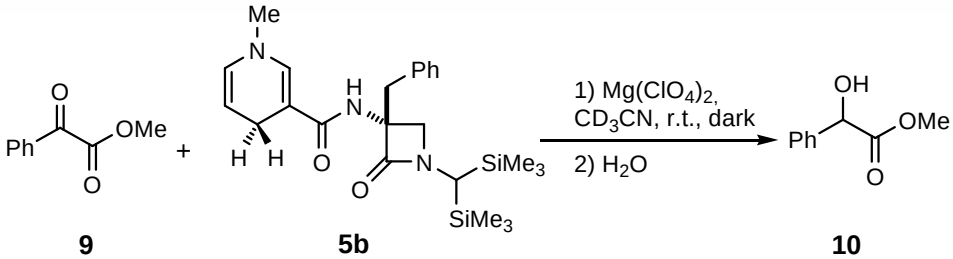
1	254	8,323	5856812	89,38	357103
2	254	13,087	695994	10,62	29412



9 **5b** **10**

Figure S3. HPLC chromatogram of crude methyl mandelate obtained from the reduction of methyl benzoylformate with NADH model **5b**. Conditions: CHIRALCEL OD column; mobile phase: Hex/iPrOH 80/20; flow rate 0.7 mL/min.

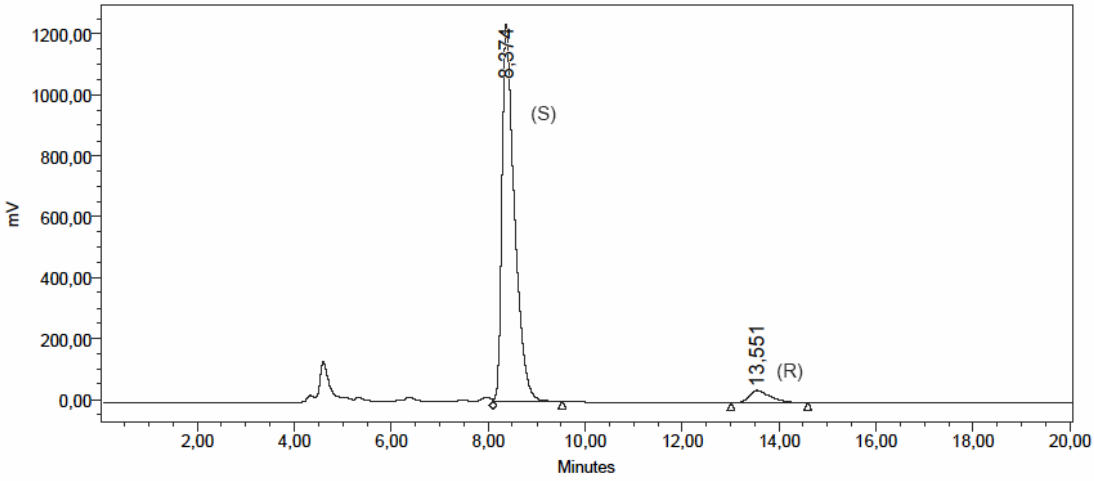
Empower software

Injection Summary Report

Reported by User: USUARIO GENERAL (HPLC) Project Name: Raluca

SAMPLE INFORMATION

Sample Name:	RA200_2 ODv 4.03.04	Acquired By:	HPLC
Sample Type:	Unknown	Date Acquired:	04/03/2004 9:24:20
Vial:	1	Acq. Method Set:	raluca
Injection #:	1	Date Processed:	17/02/2005 18:07:46
Injection Volume:	10,00 ul	Processing Method:	RA200_1 254nm
Run Time:	200,0 Minutes	Channel Name:	Satin Ch 2
Sample Set Name:		Proc. Chnl. Descr.:	254



Channel Satin Ch 2; Processed Channel: 254; Result Id: 1663; Processing Method: RA200_1 254nm

Processed Channel Descr.: 254

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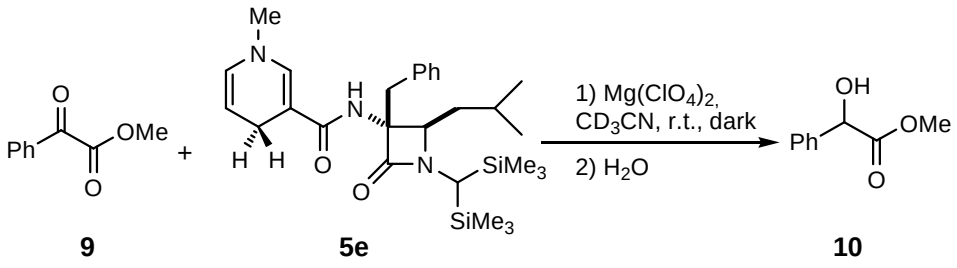
2	254	13,551	1184971	5,07	40493



9 **5e** **10**

Figure S4. HPLC chromatogram of crude methyl mandelate obtained from the reduction of methyl benzoylformate with NADH model **5e**. Conditions: CHIRALCEL OD column; mobile phase: Hex/iPrOH 80/20; flow rate 0.7 mL/min.

3.-^{1}H and ^{13}C NMR Spectra of Compounds 6a, 6b-c, 7a-f, 41a-f, 5a-f, 42-43, and 8

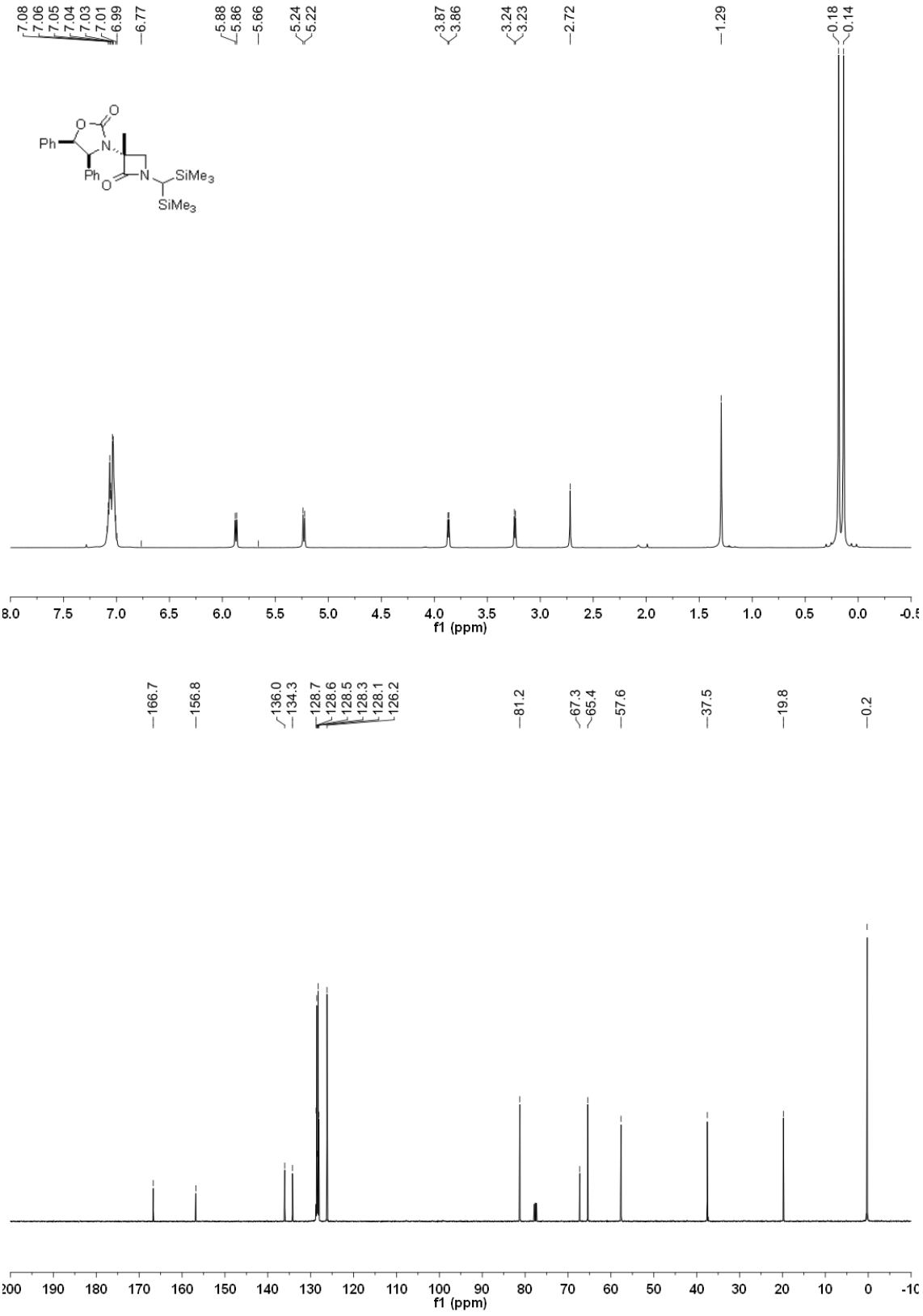


Figure S5. ^{1}H and ^{13}C NMR spectra for compound **6a** ($CDCl_3$).

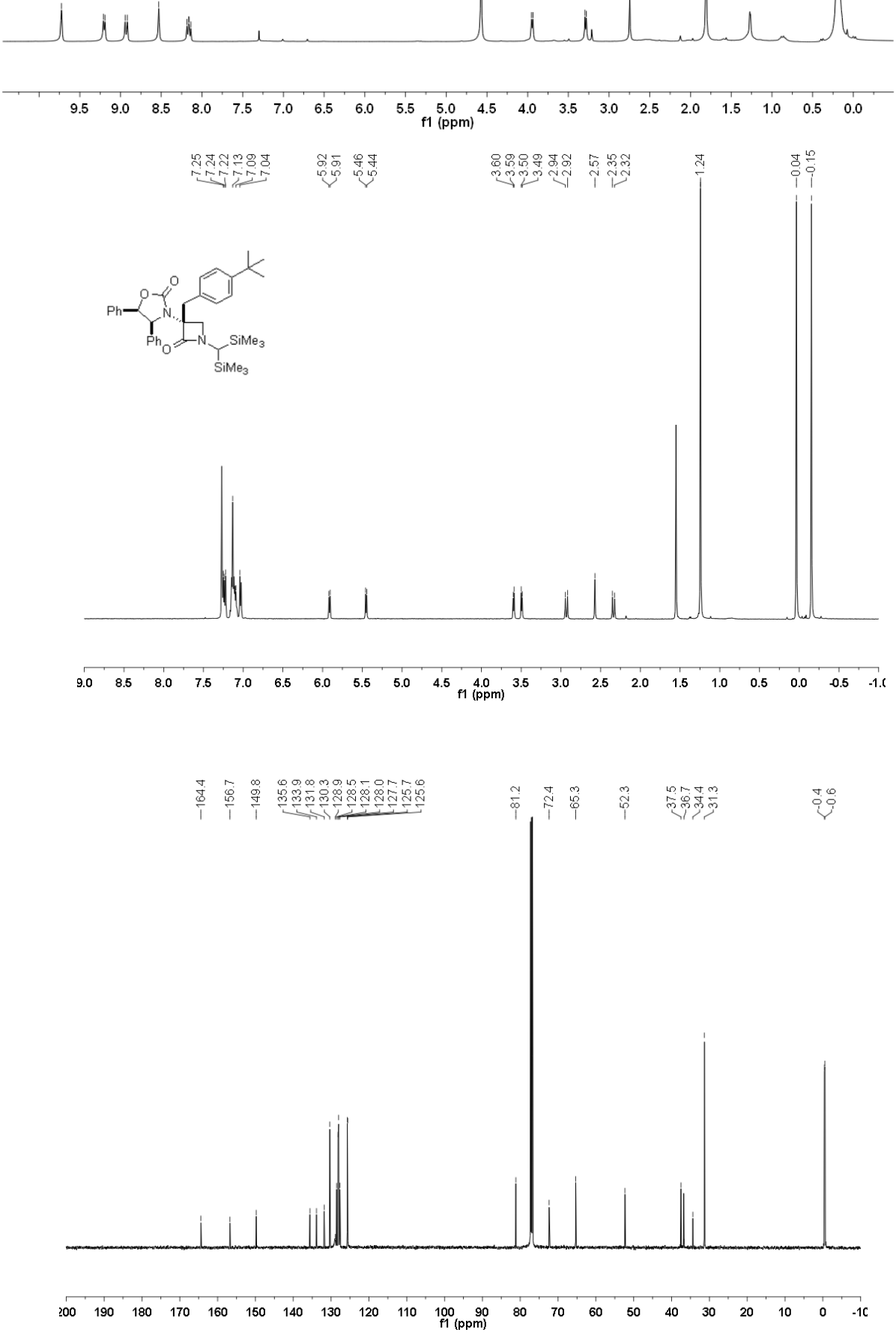


Figure S6. ^{1}H and ^{13}C NMR spectra for compound **6c** ($CDCl_3$).

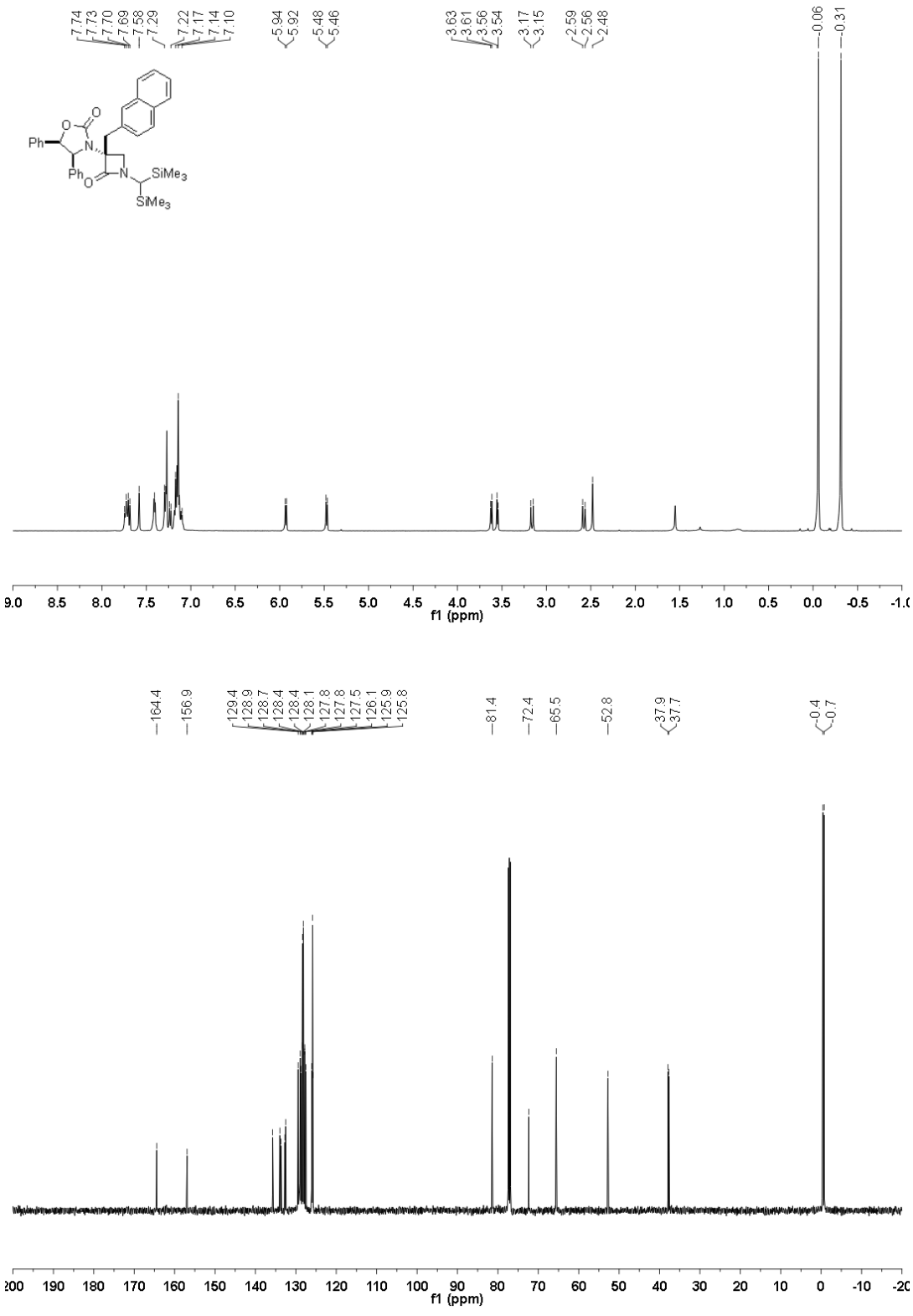


Figure S7. ^{1}H and ^{13}C NMR spectra for compound **6d** ($CDCl_3$).

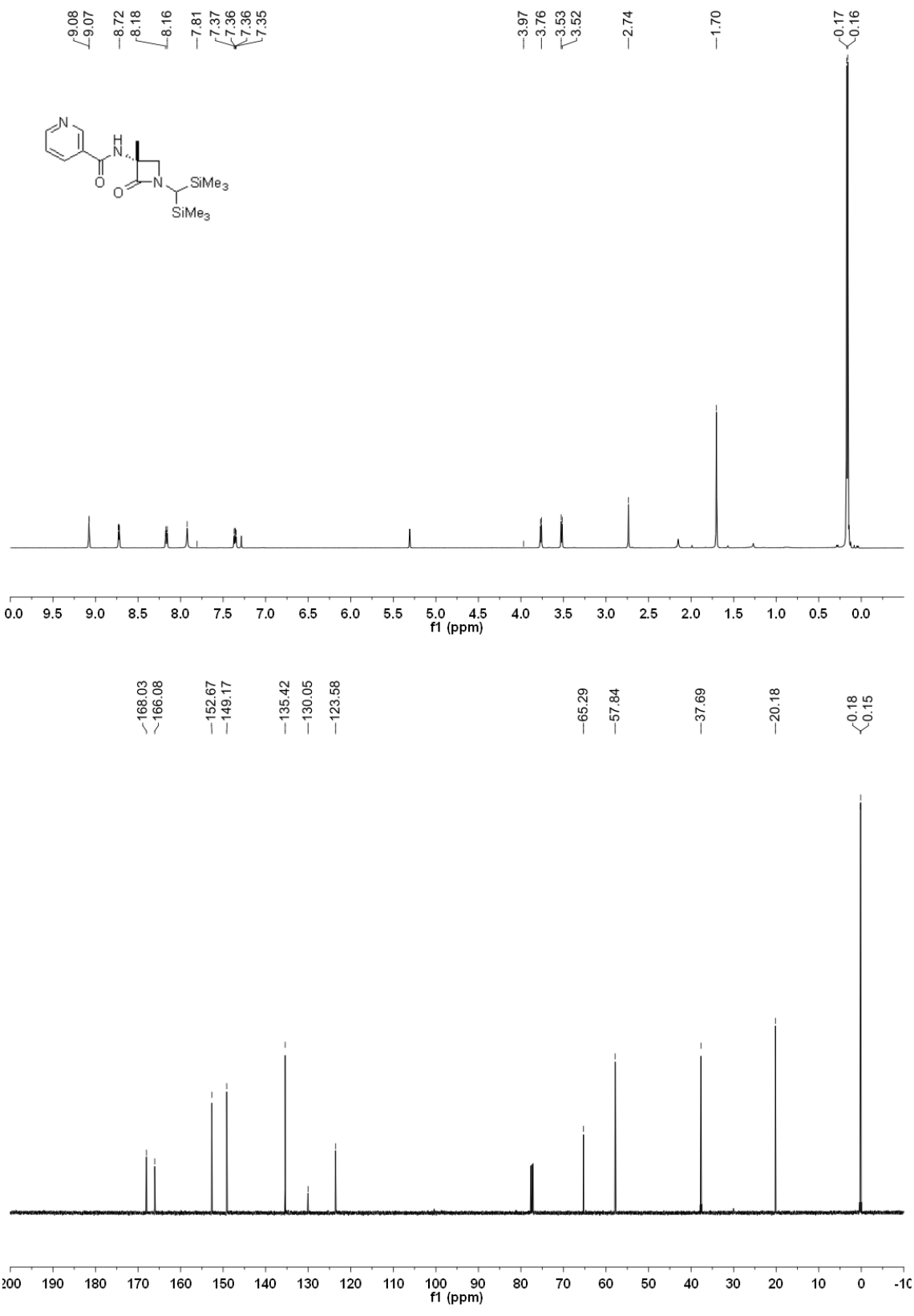


Figure S8. ^{1}H and ^{13}C NMR spectra for compound **7a** ($CDCl_3$).

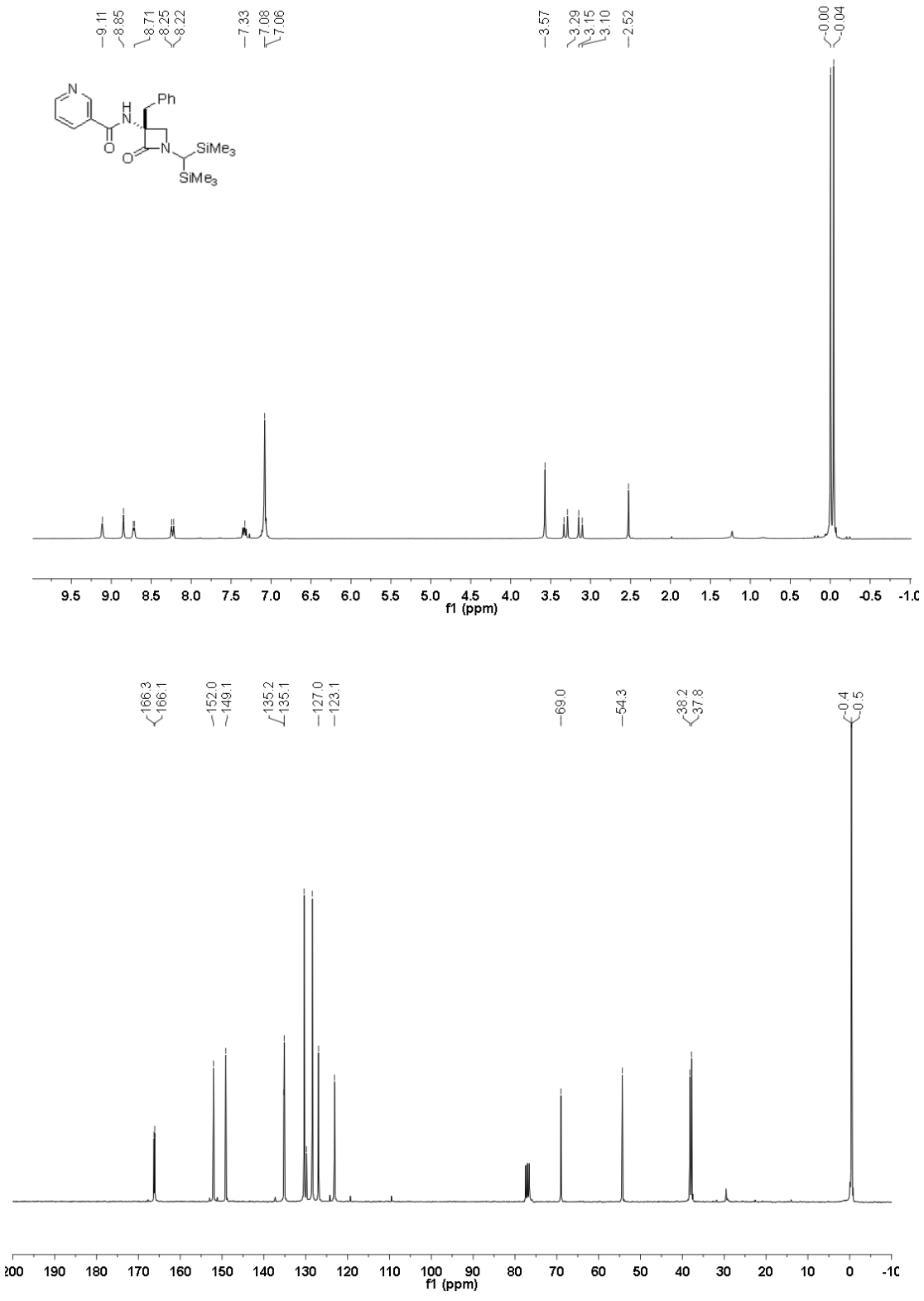


Figure S9. ^{1}H and ^{13}C NMR spectra for compound **7b** ($CDCl_3$).

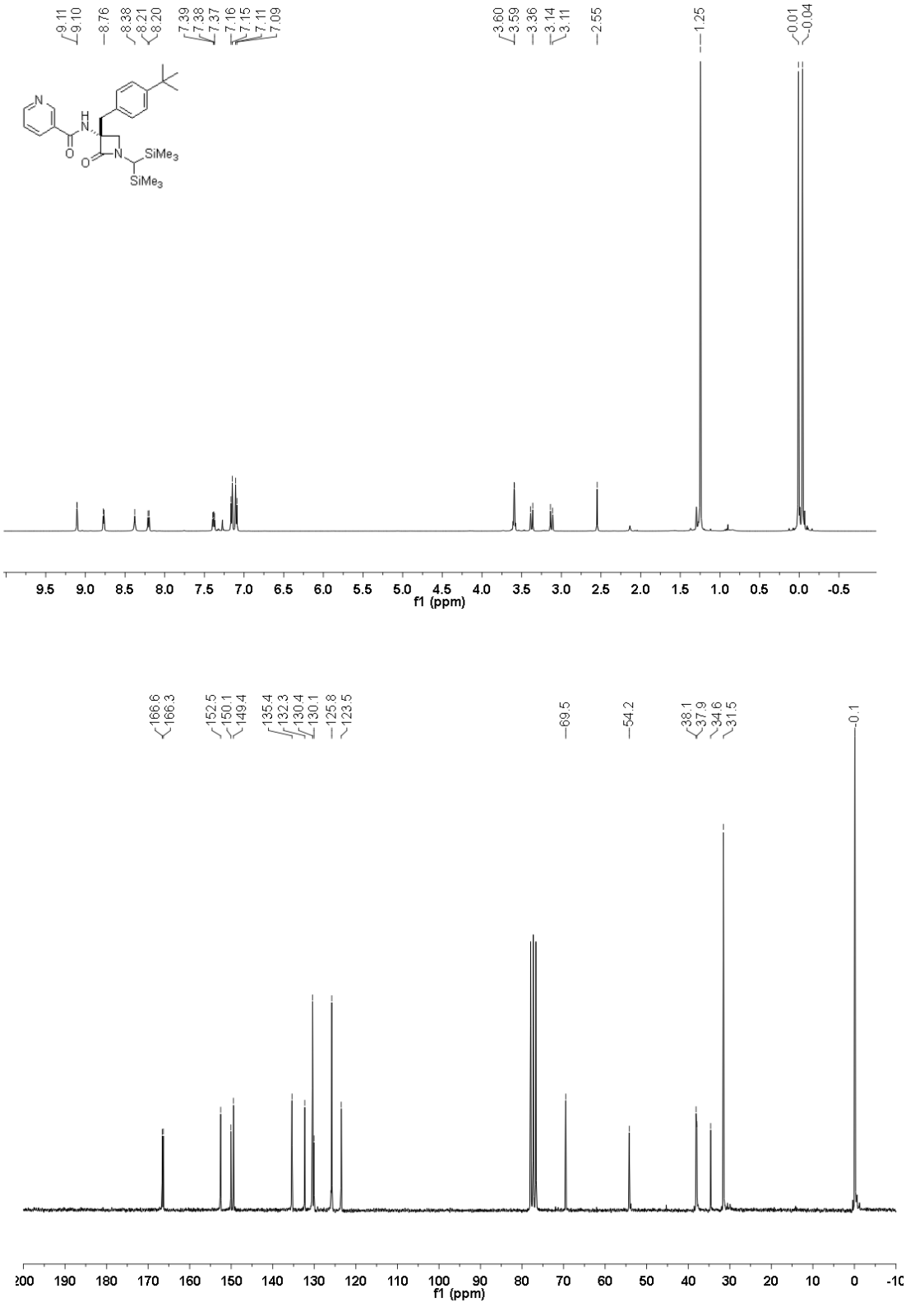


Figure S10. ^{1}H and ^{13}C NMR spectra for compound **7c** ($CDCl_3$).

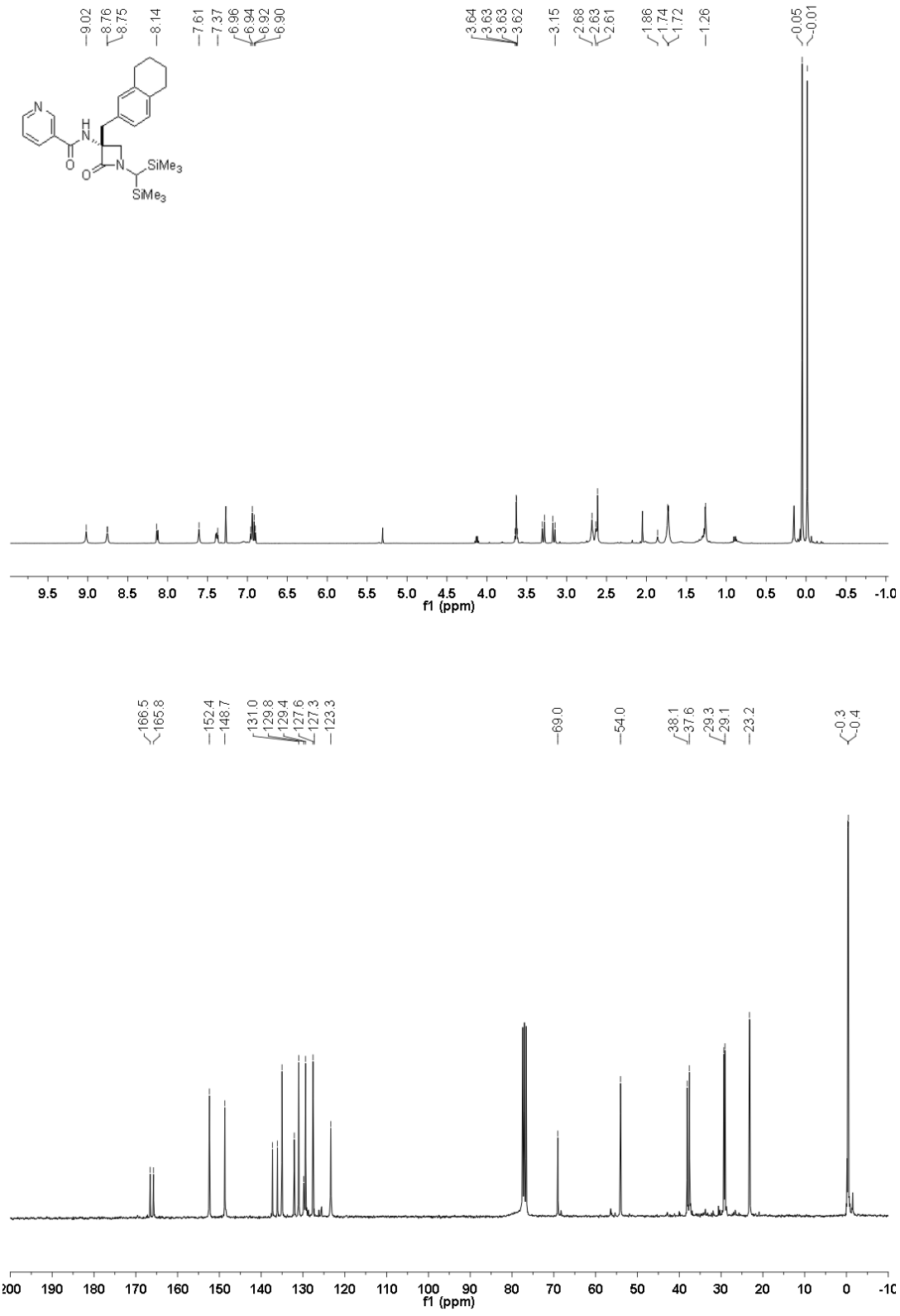


Figure S11. ^{1}H and ^{13}C NMR spectra for compound **7d** ($CDCl_3$).

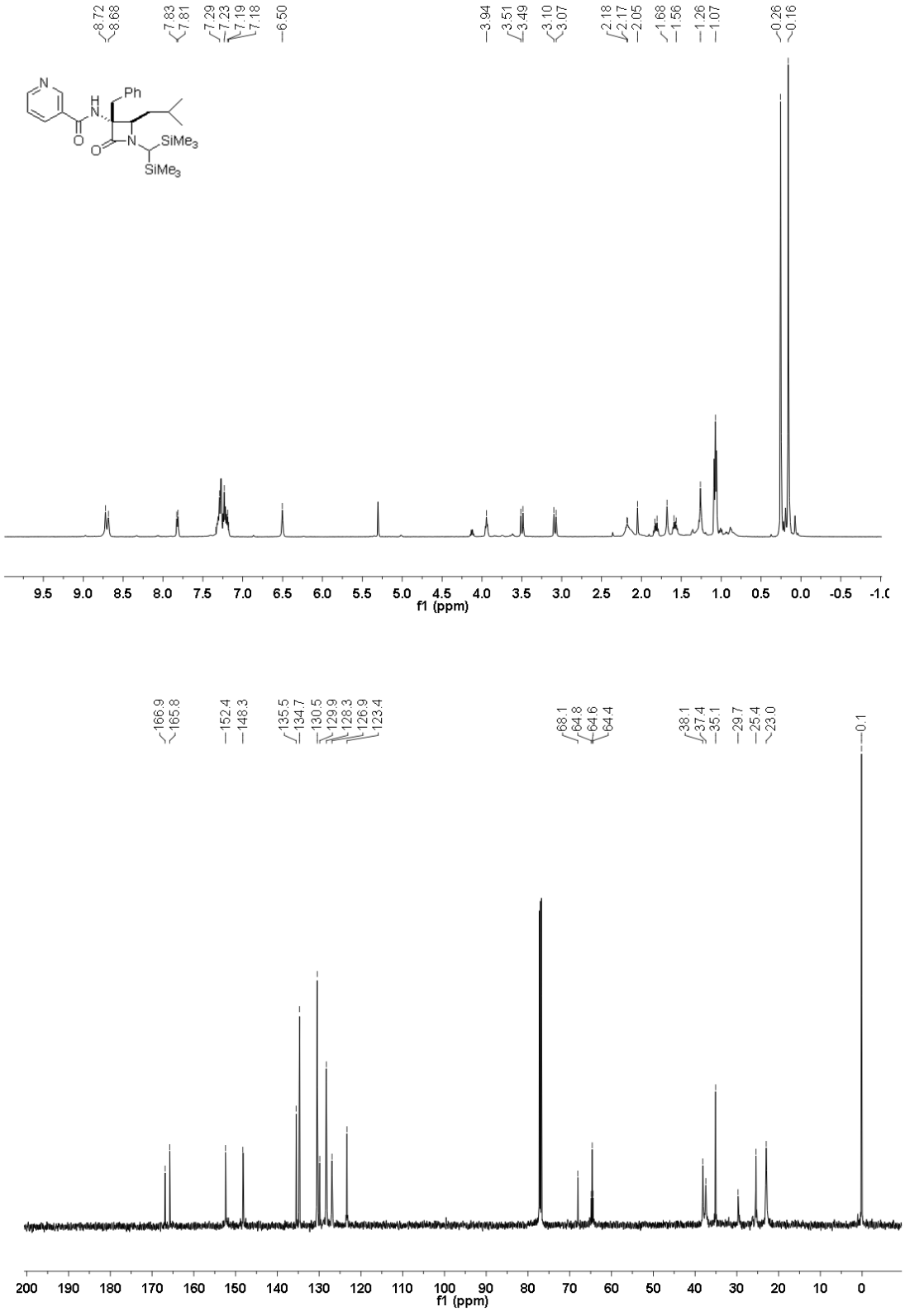


Figure S12. ^{1}H and ^{13}C NMR spectra for compound **7e** ($CDCl_3$).

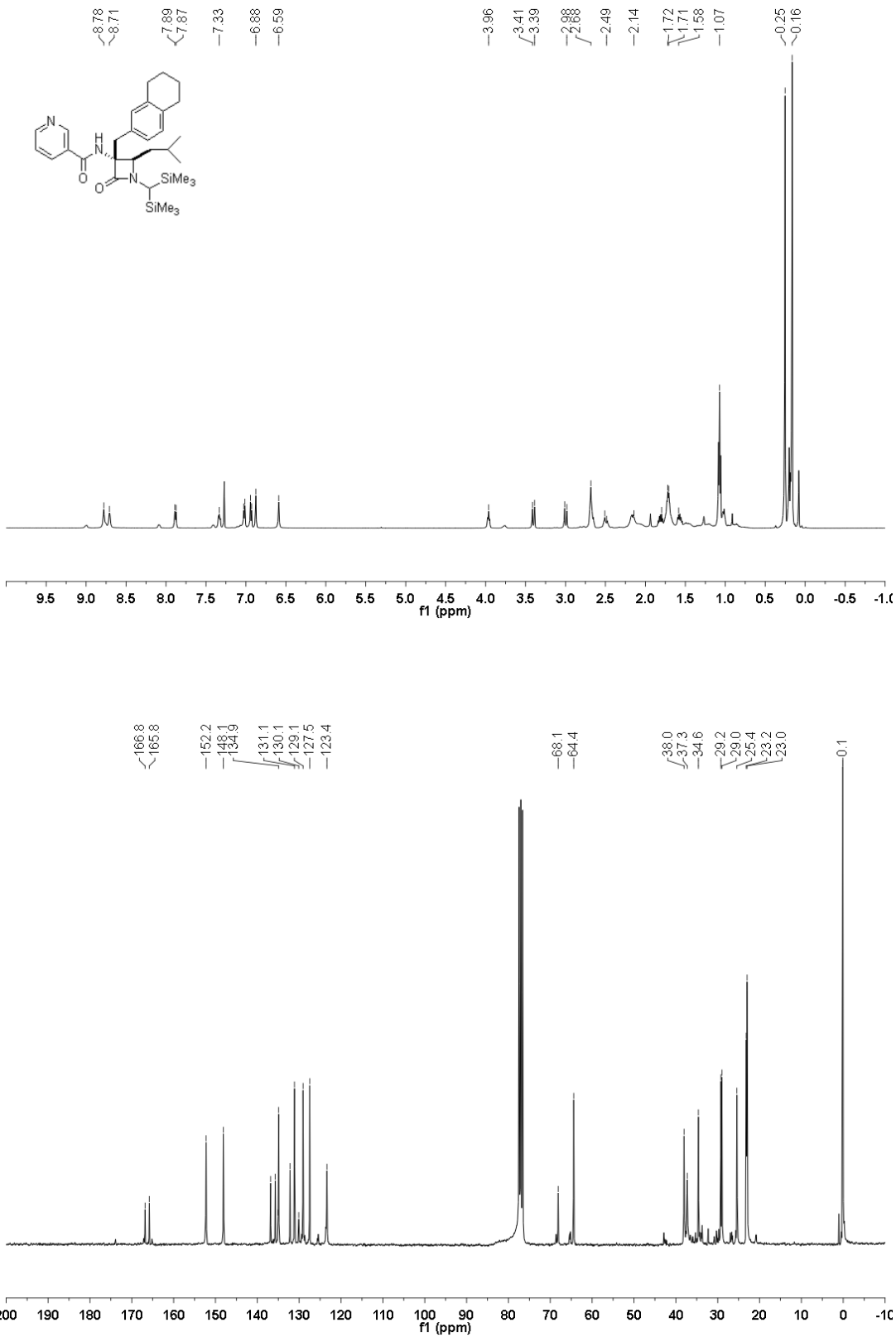


Figure S13. ^{1}H and ^{13}C NMR spectra for compound **7f** ($CDCl_3$).

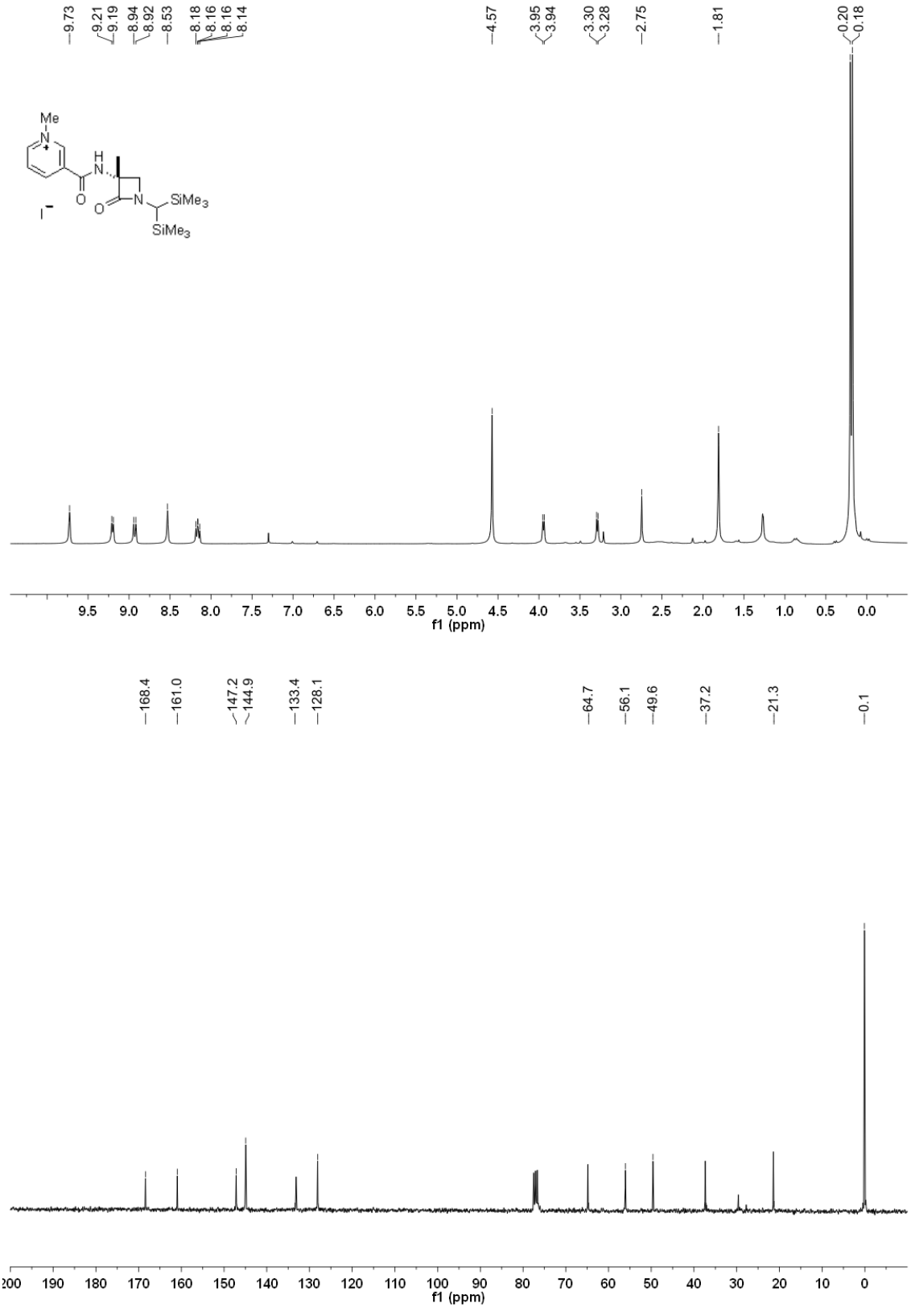


Figure S14. ^{1}H and ^{13}C NMR spectra for compound **42a** ($CDCl_3$).

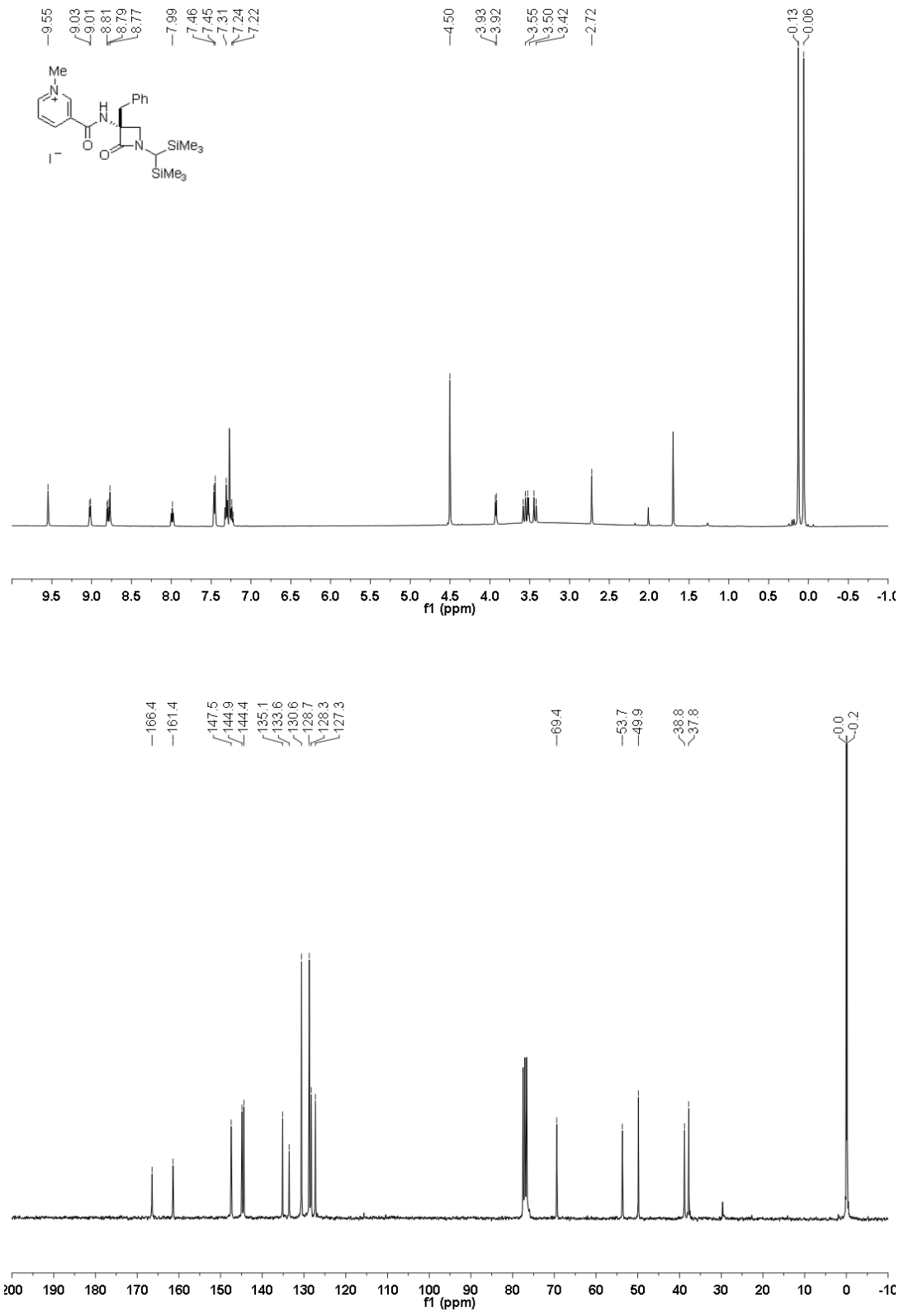


Figure S15. ^{1}H and ^{13}C NMR spectra for compound **42b** ($CDCl_3$).

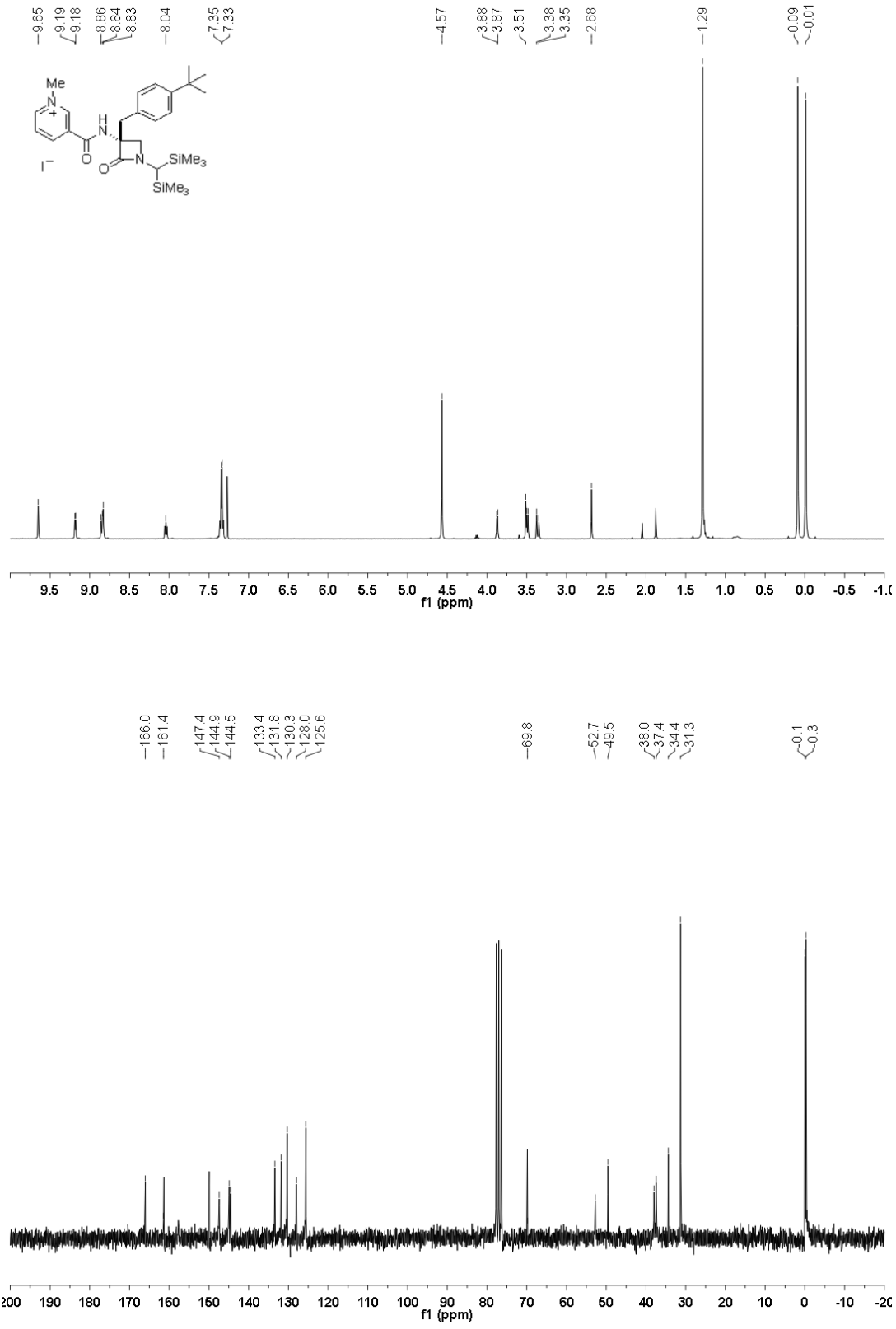


Figure S16. ^{1}H and ^{13}C NMR spectra for compound **42c** ($CDCl_3$).

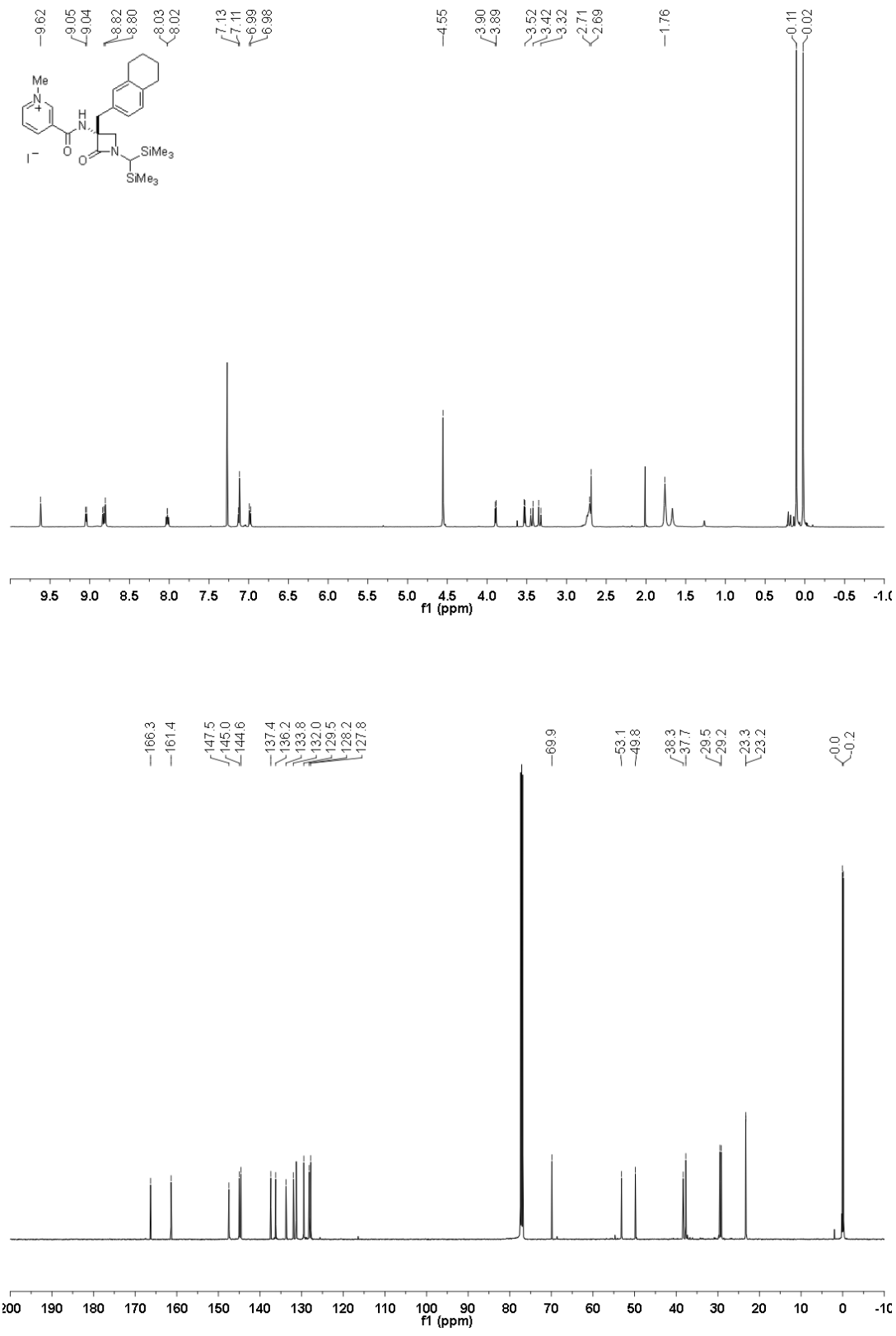


Figure S17. ^{1}H and ^{13}C NMR spectra for compound **42d** ($CDCl_3$).

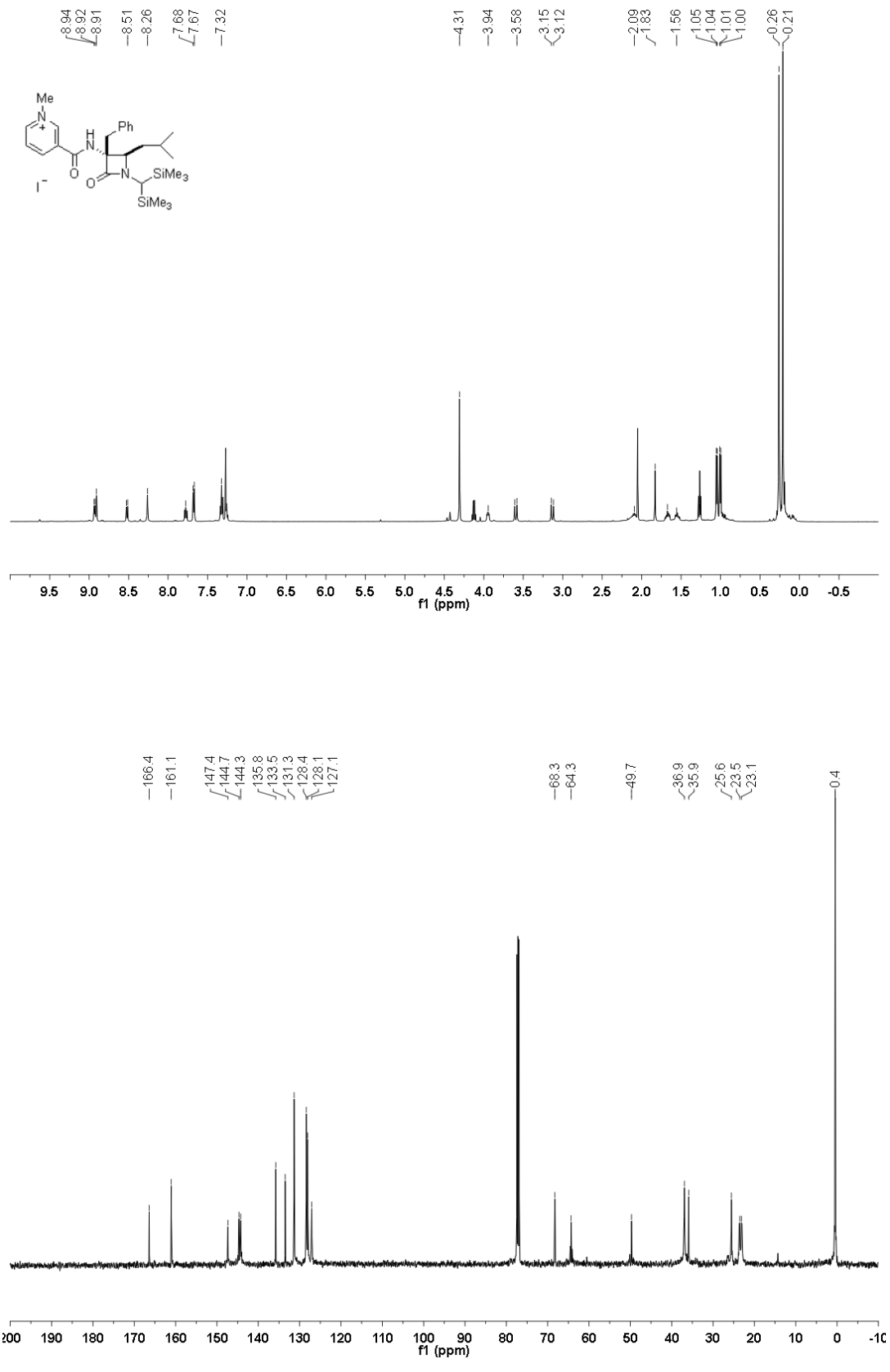


Figure S18. ^{1}H and ^{13}C NMR spectra for compound **42e** ($CDCl_3$).

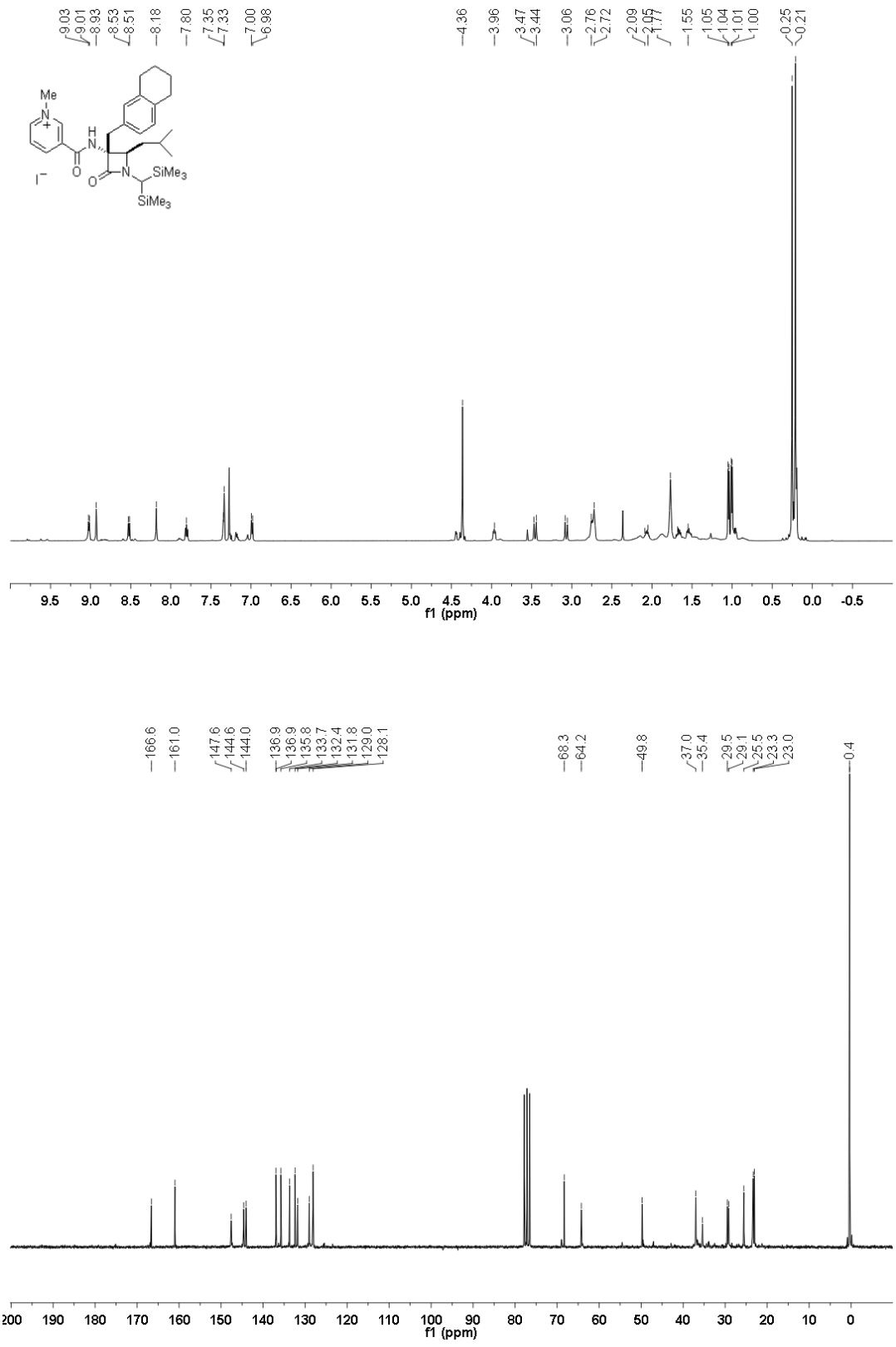


Figure S19. ^{1}H and ^{13}C NMR spectra for compound **42f** ($CDCl_3$).

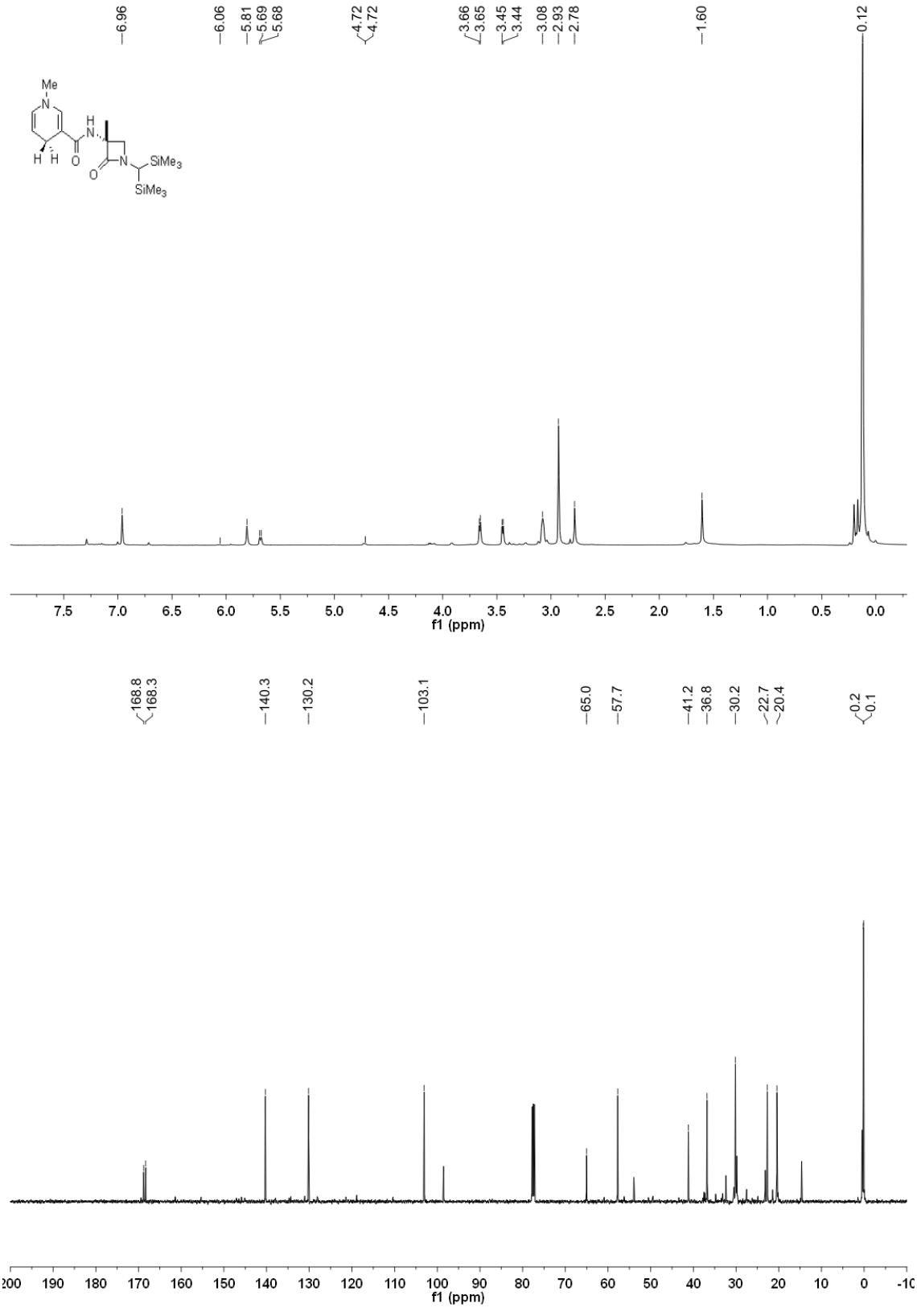


Figure S20. ^{1}H and ^{13}C NMR spectra for compound **5a** ($CDCl_3$).

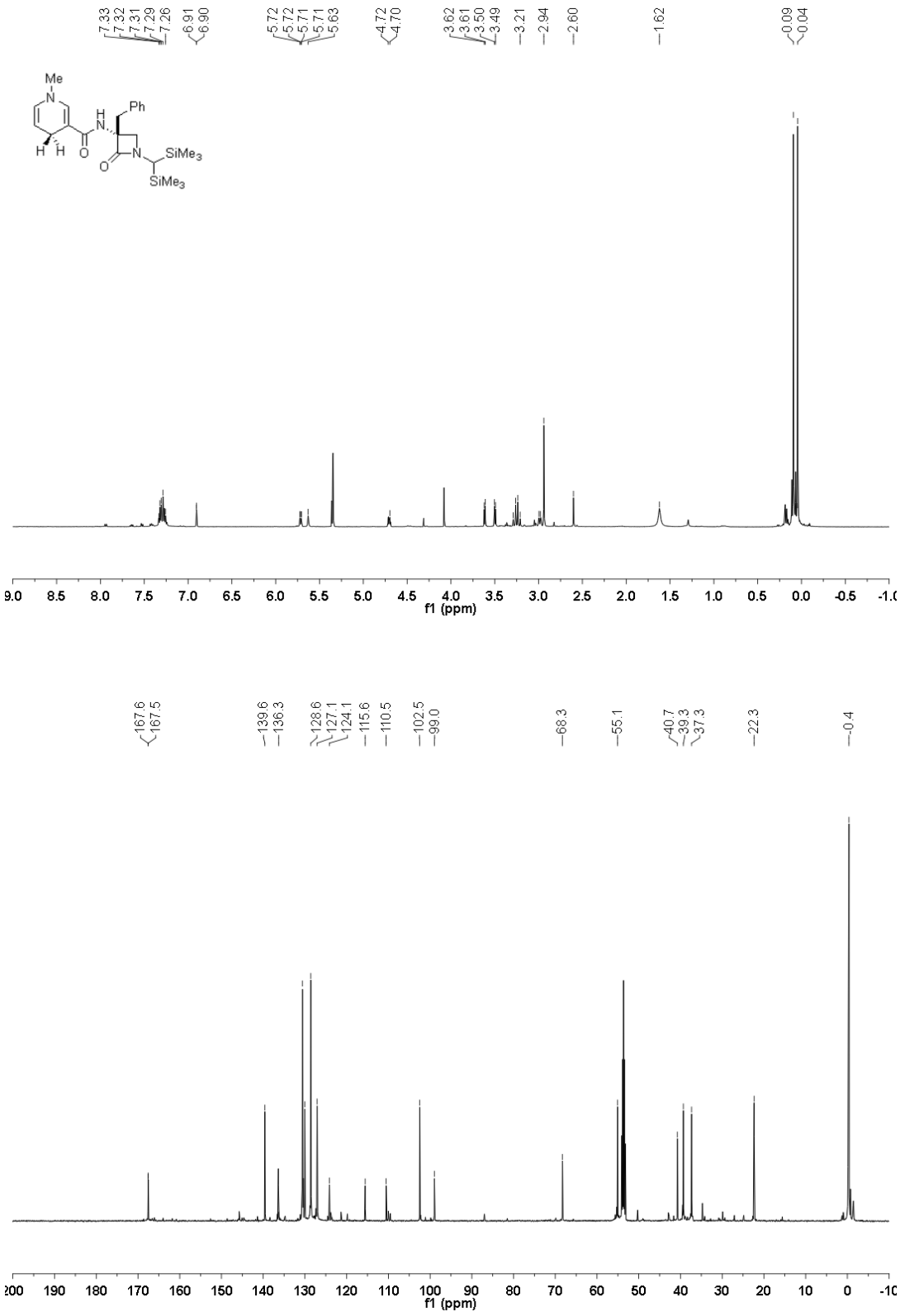


Figure S21. ^{1}H and ^{13}C NMR spectra for compound **5b** (CD_2Cl_2).

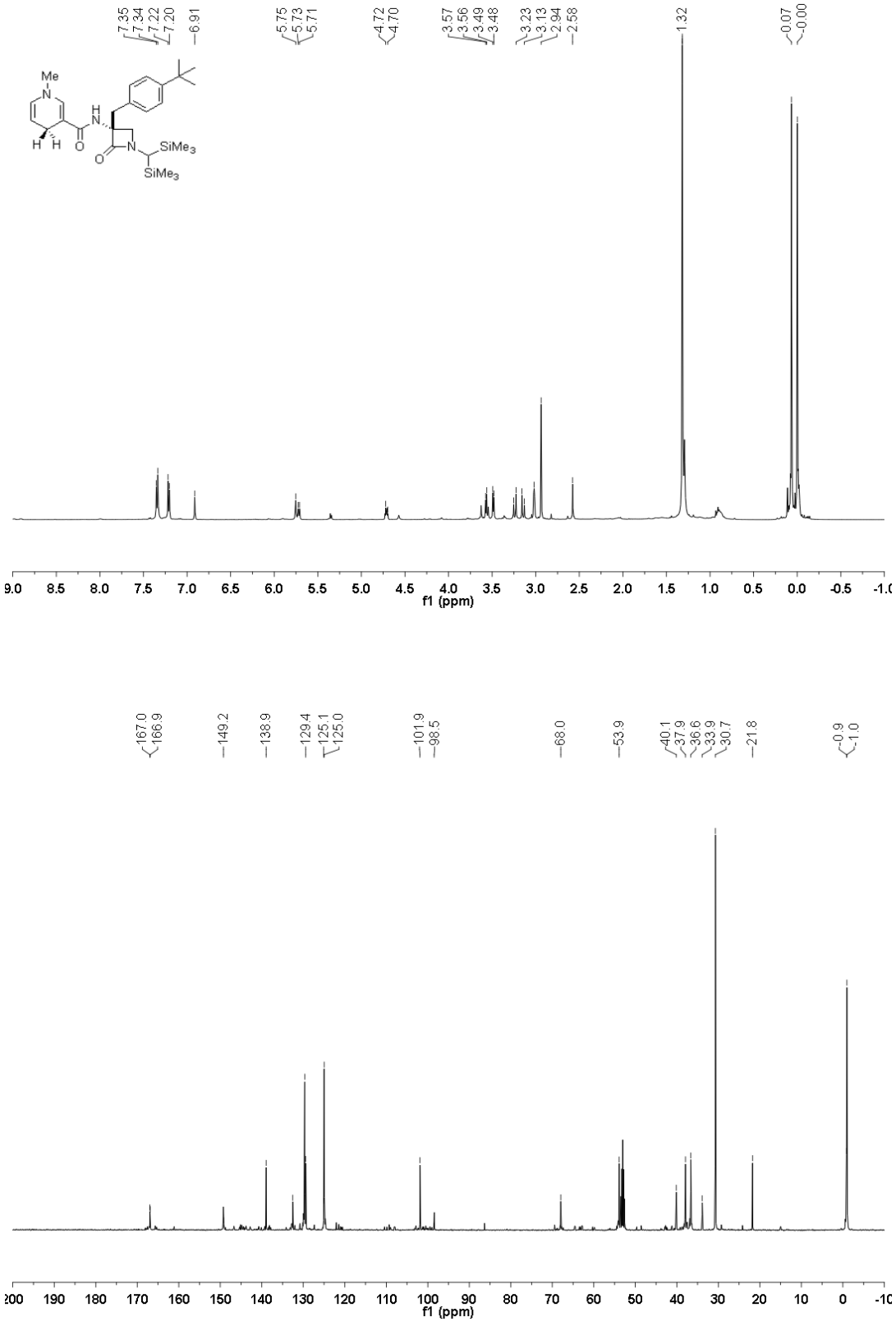


Figure S22. ^{1}H and ^{13}C NMR spectra for compound **5c** (CD_2Cl_2).

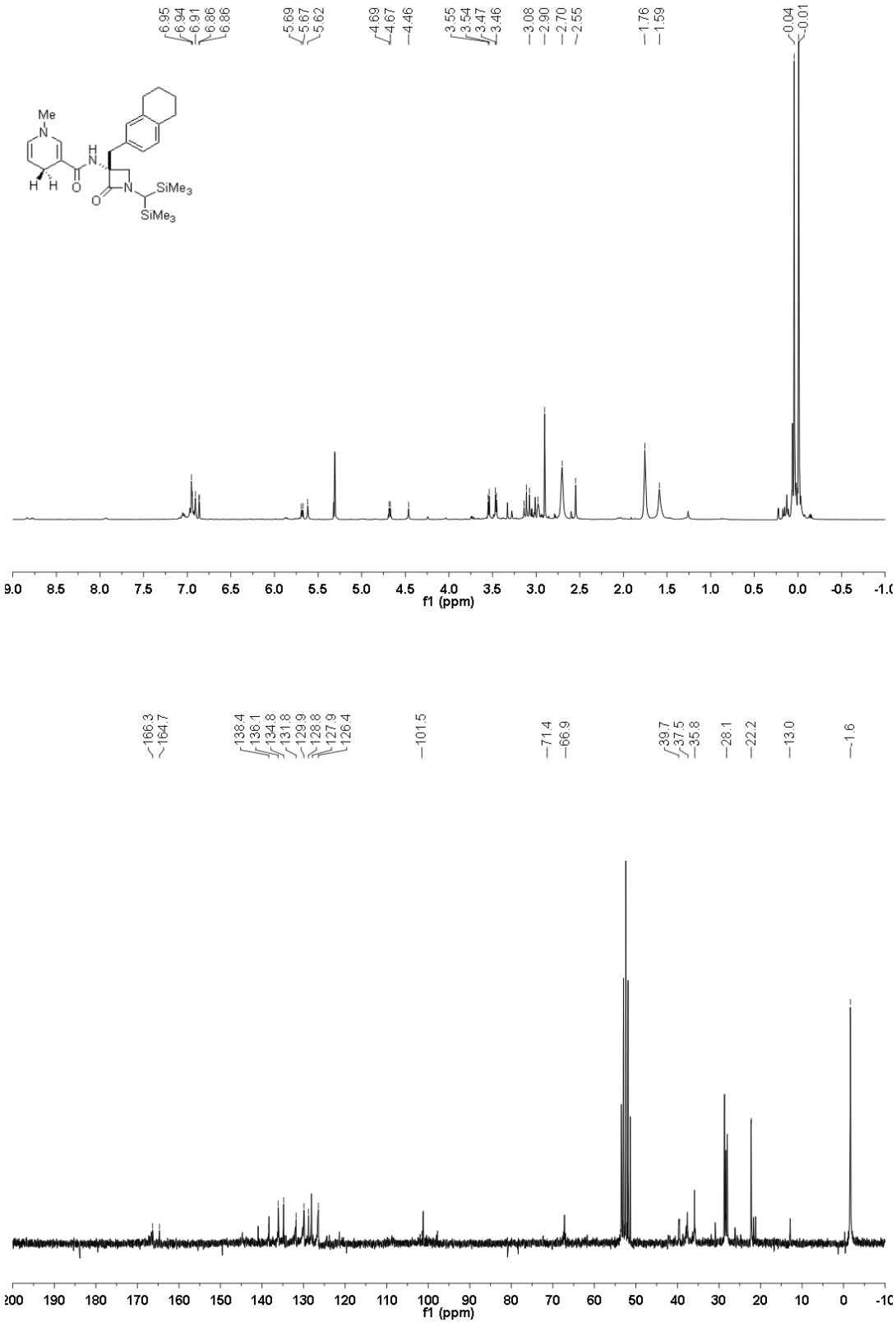


Figure S23. ^{1}H and ^{13}C NMR spectra for compound **5d** (CD_2Cl_2).

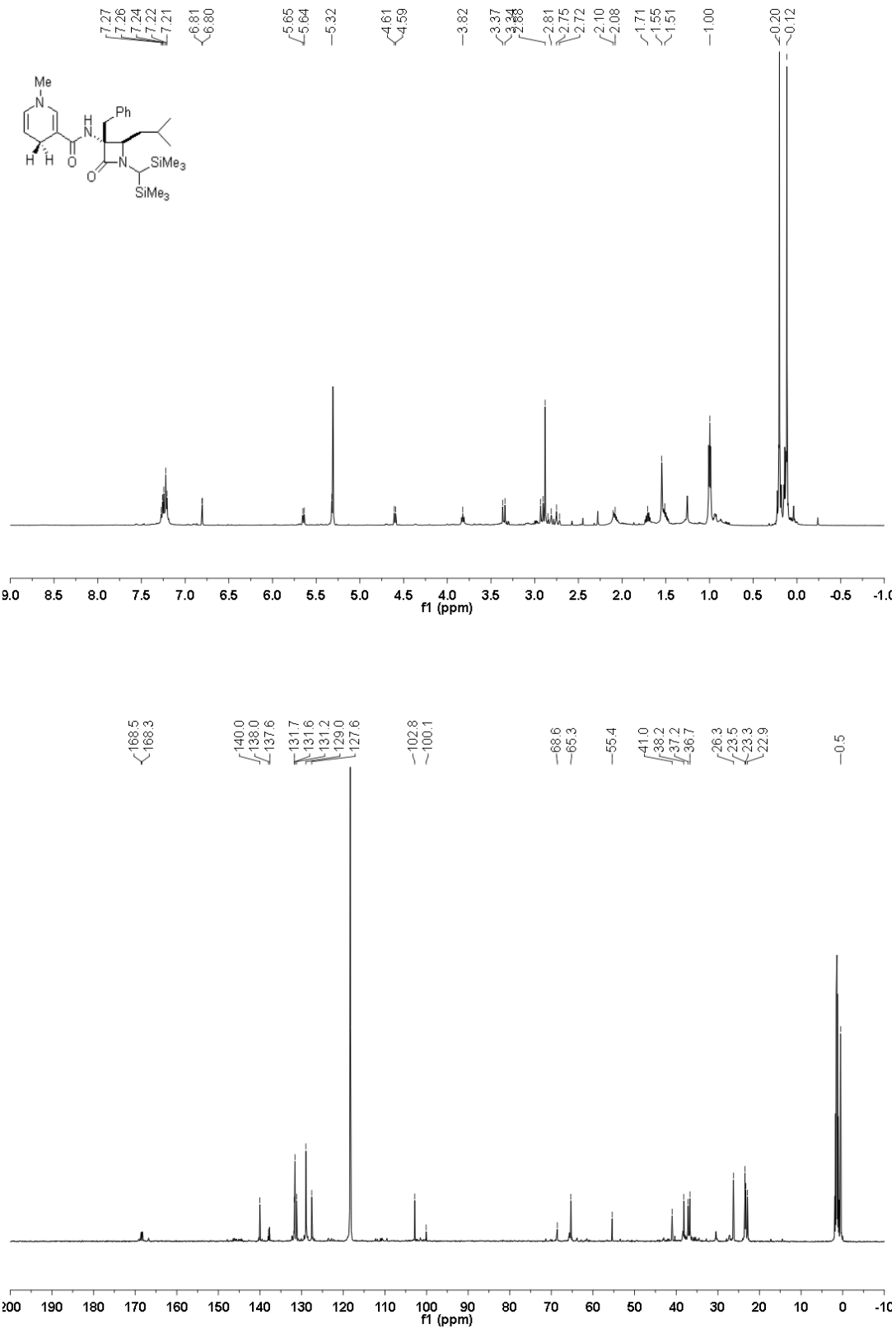


Figure S24. ^{1}H ($CDCl_3$) and ^{13}C NMR (CD_3CN)spectra for compound **5e**.

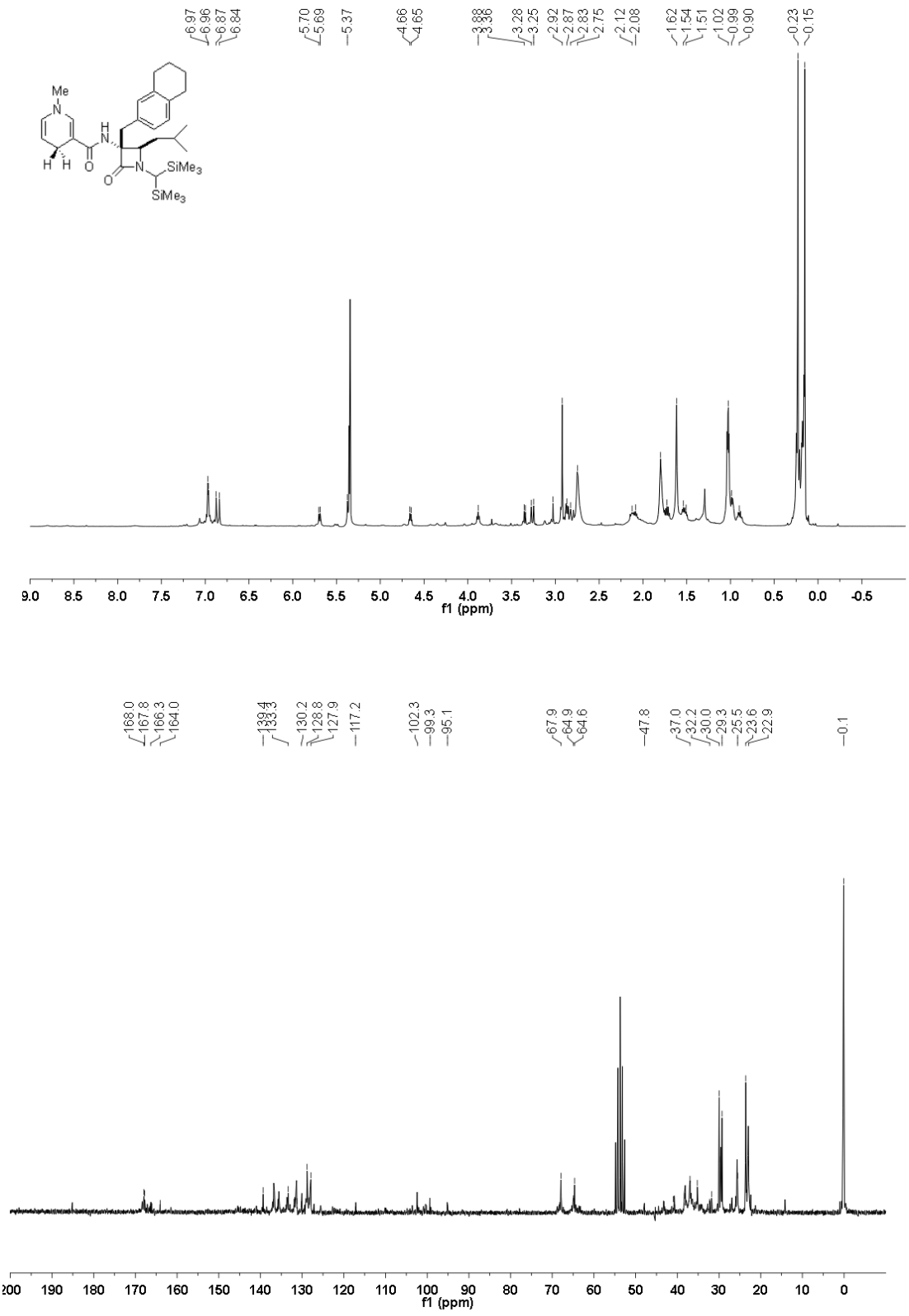


Figure S25. ^{1}H and ^{13}C NMR spectra for compound **5f** (CD_2Cl_2).

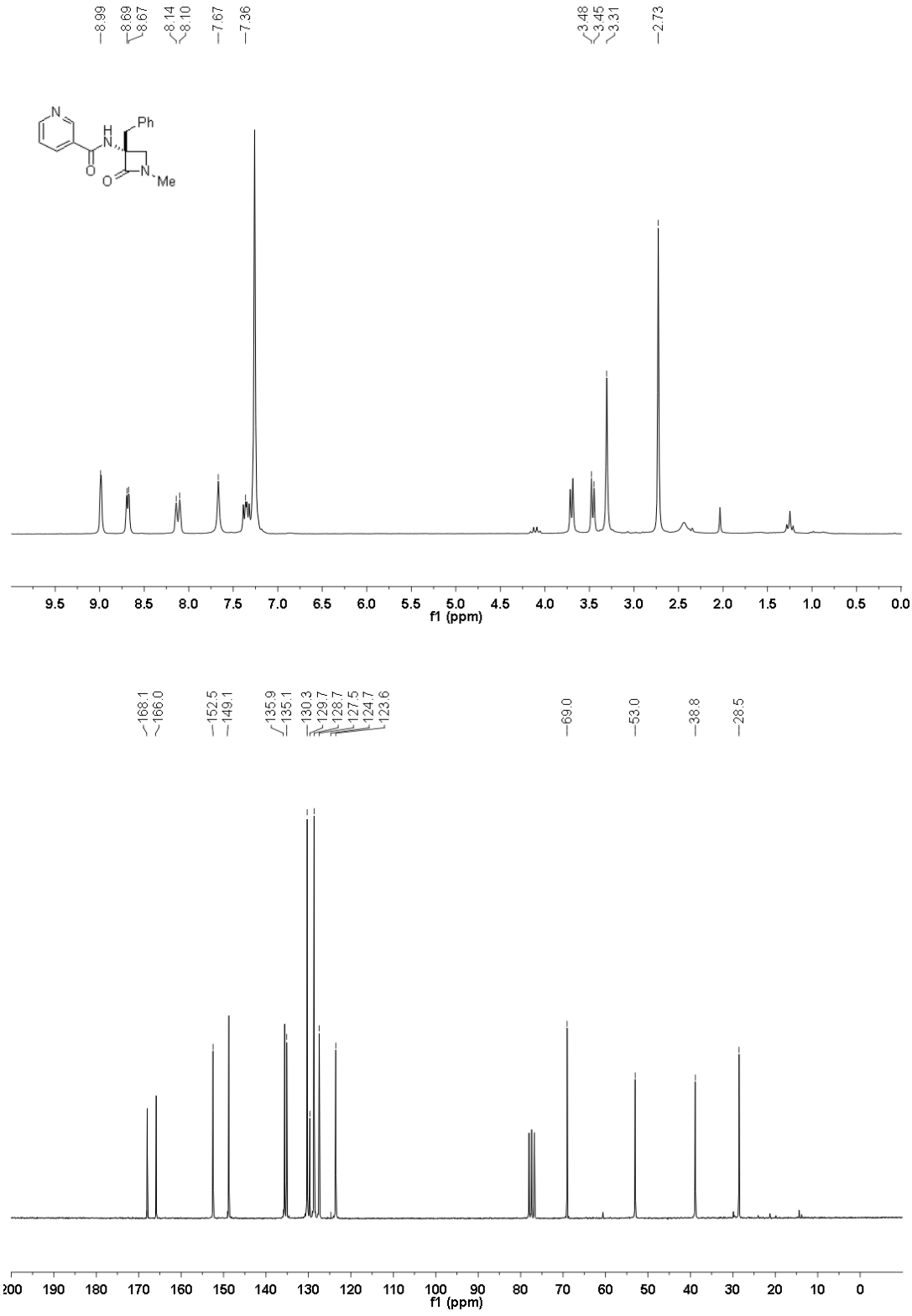


Figure S26. ^{1}H and ^{13}C NMR spectra for compound **43** ($CDCl_3$).

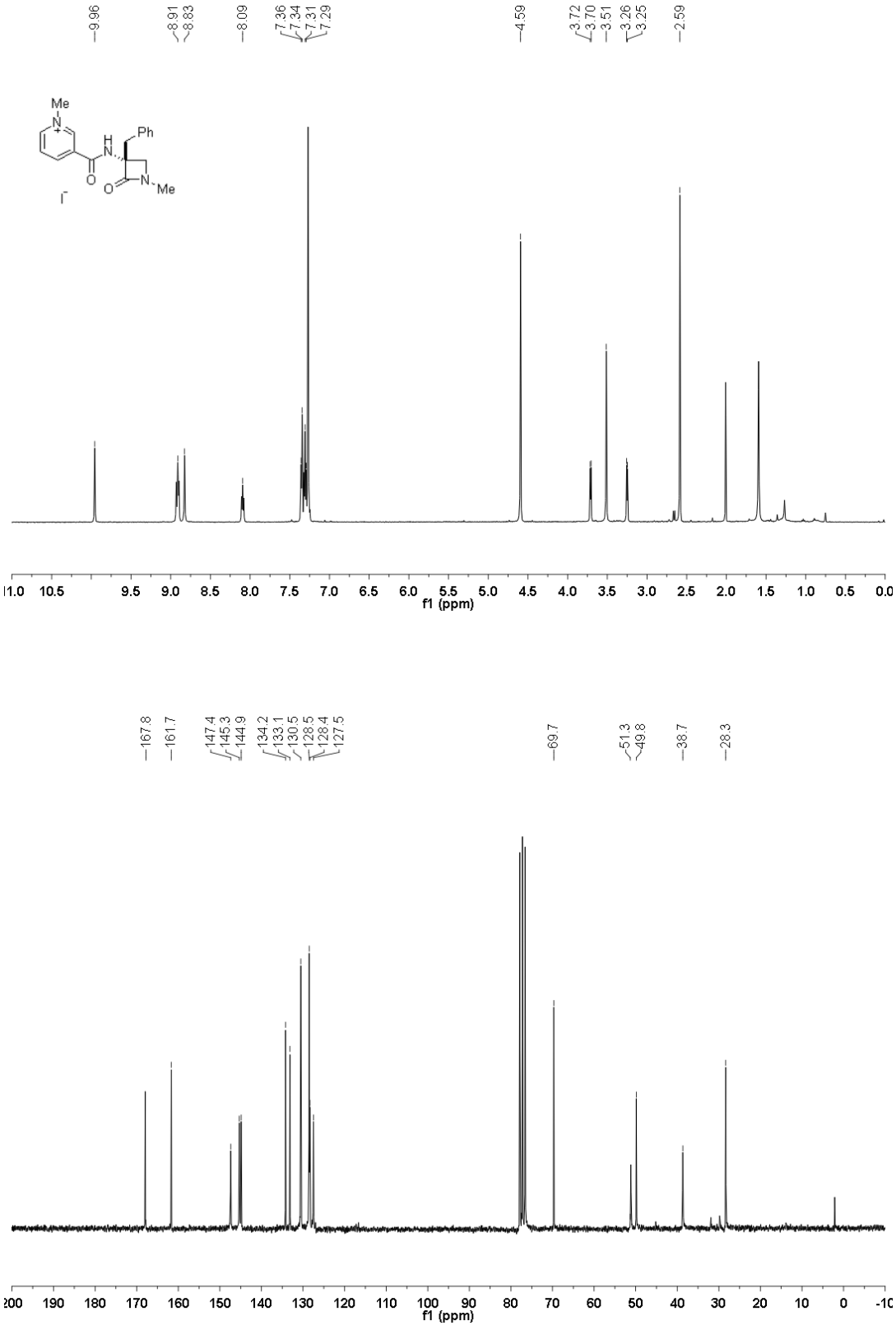


Figure S27. ^{1}H and ^{13}C NMR spectra for compound **44** ($CDCl_3$).

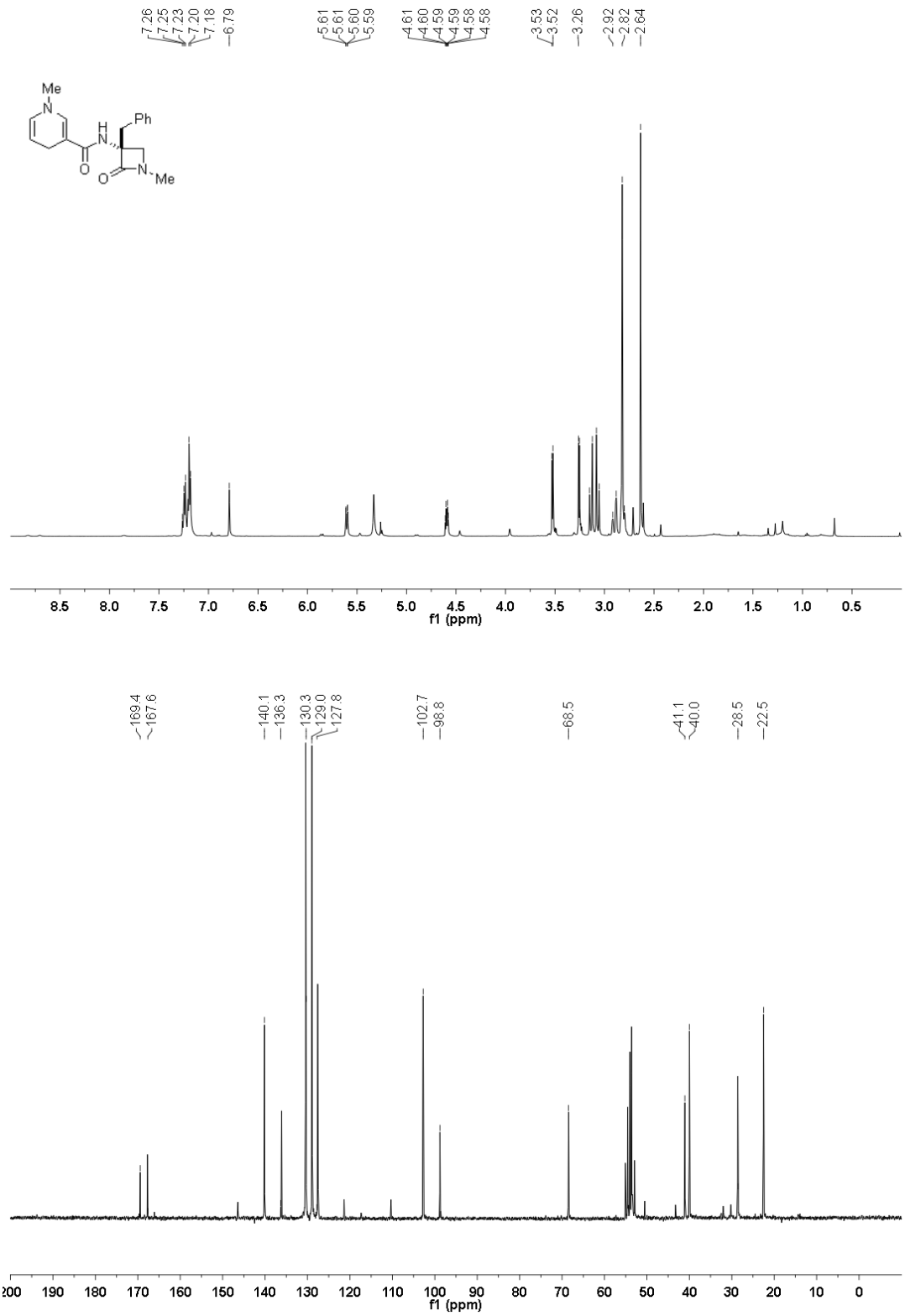


Figure S28. ^{1}H and ^{13}C NMR spectra for compound **8** (CD_2Cl_2).

4.-NMR Complexation Studies

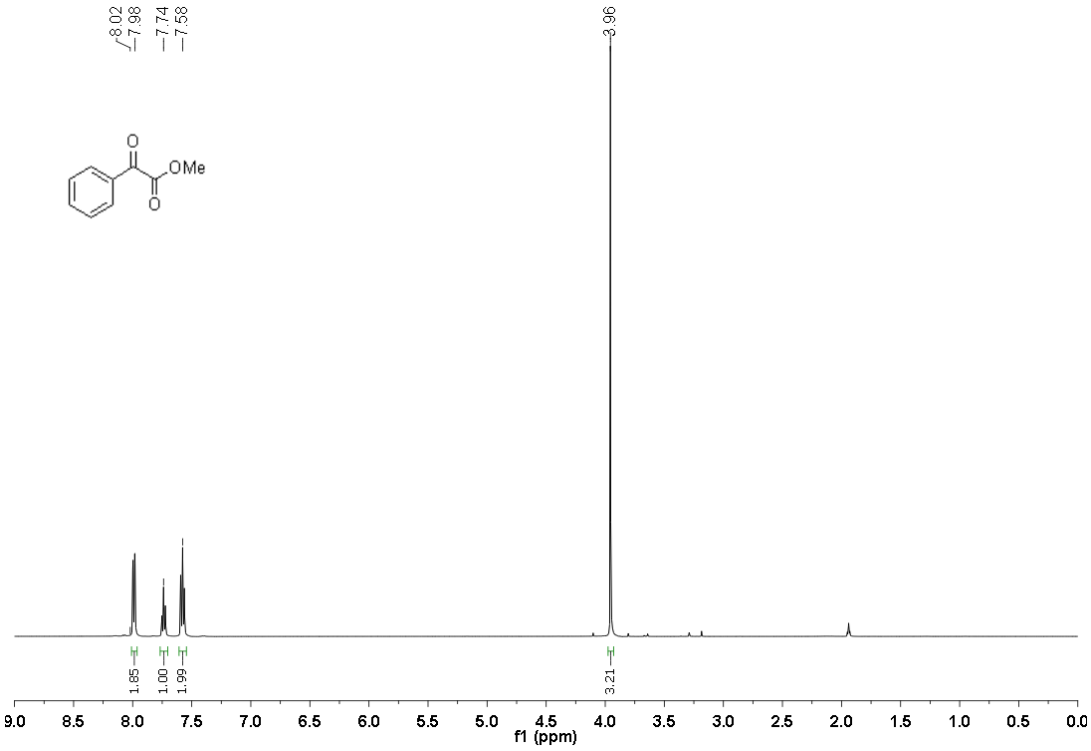


Figure S29. ^{1}H-NMR spectrum of methyl benzoylformate (CD_3CN, 500 MHz, r.t.)

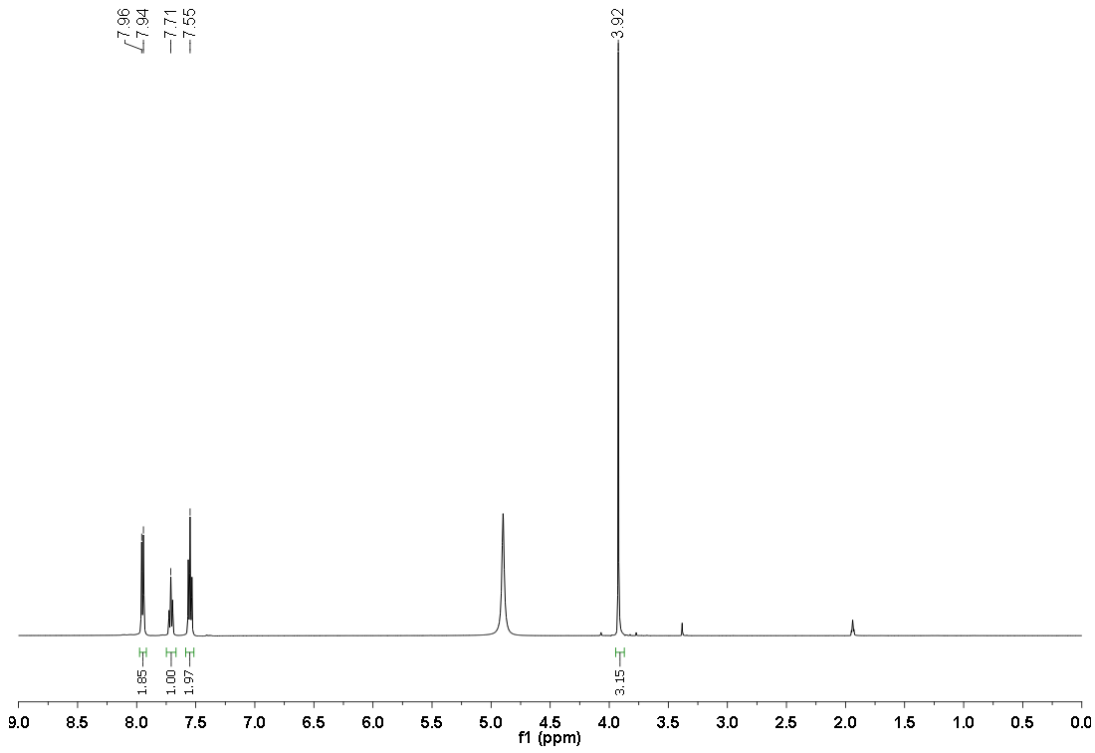


Figure S30. ^{1}H-NMR spectrum of methyl benzoylformate in the presence of 1 eq $Mg(ClO_4)_2$ (CD_3CN, 500 MHz, r.t.)

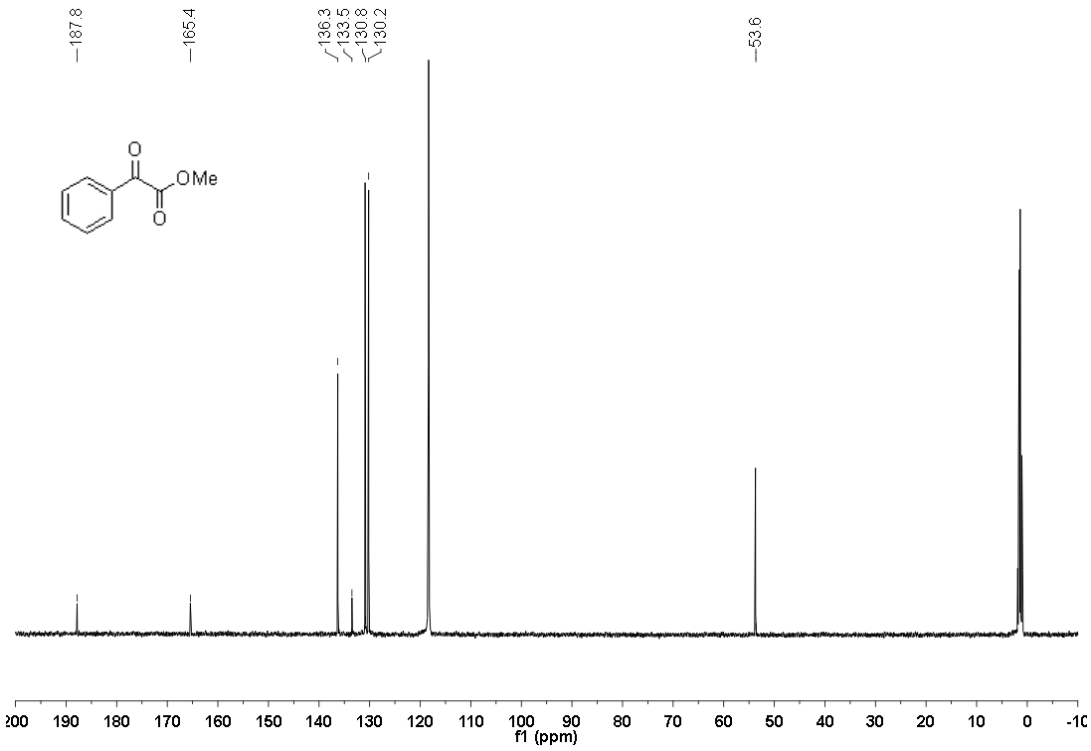


Figure S31. ^{13}C-NMR spectrum of methyl benzoylformate (CD_3CN, 125 MHz, r.t.)

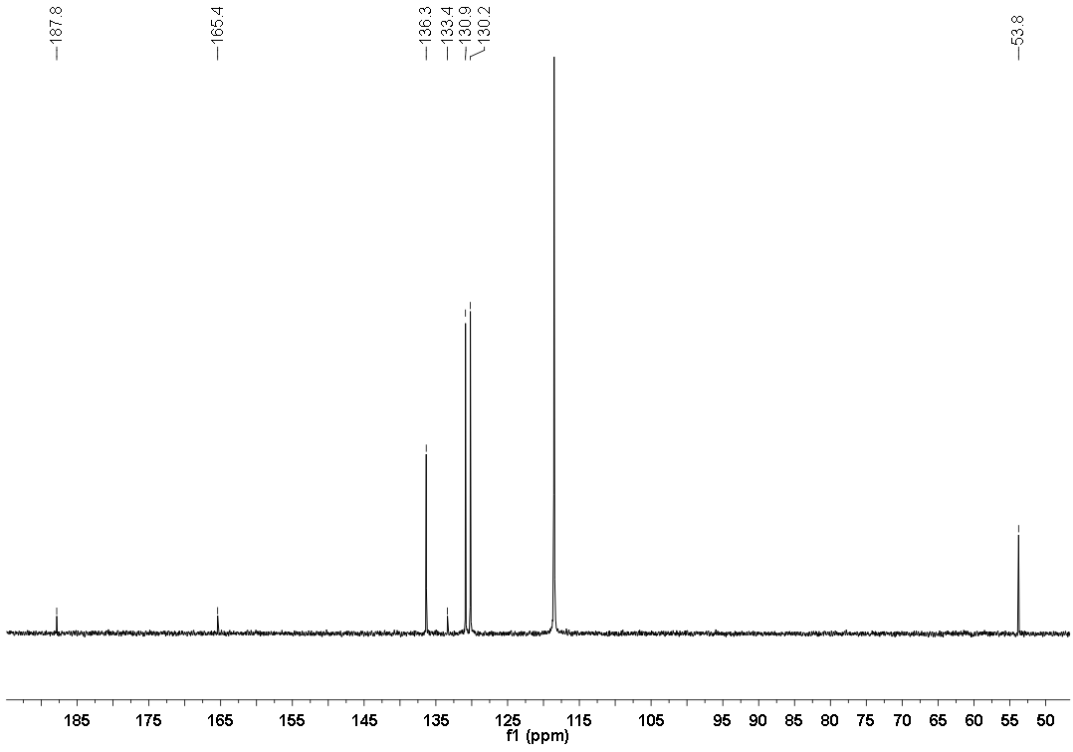


Figure S32. ^{13}C-NMR spectrum of methyl benzoylformate in the presence of 1 eq $Mg(ClO_4)_2$ (CD_3CN, 125 MHz, r.t.)

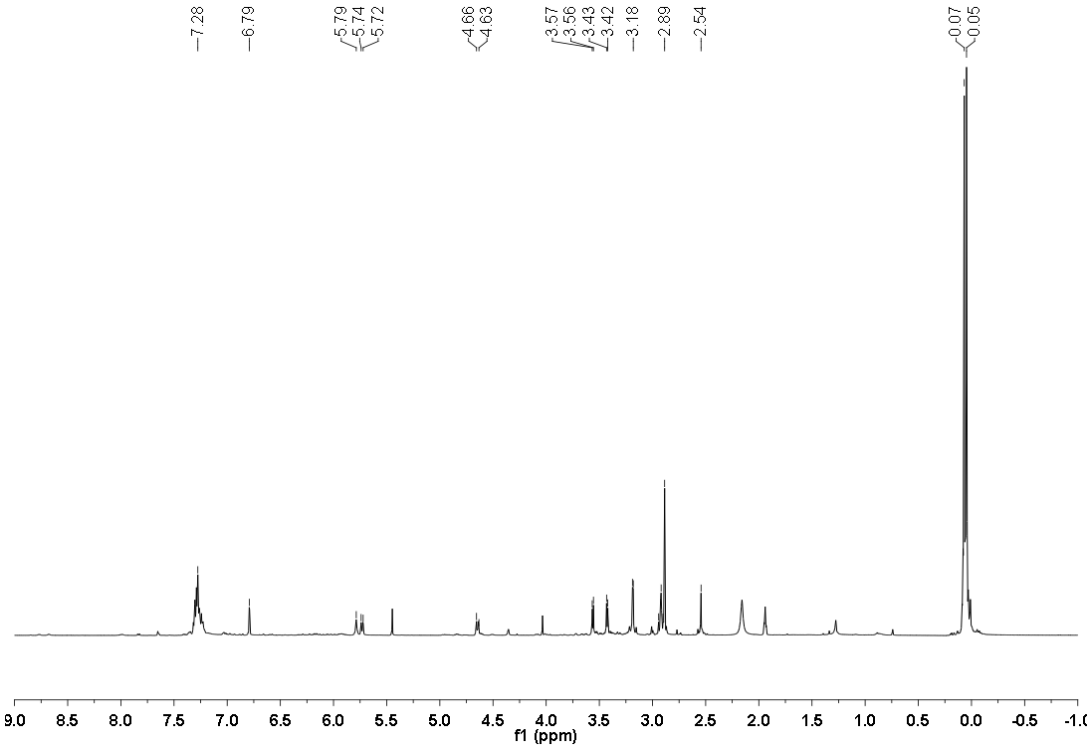


Figure S33. ^{1}H-NMR spectrum of model **5b** (CD_3CN, 500 MHz, r.t.)

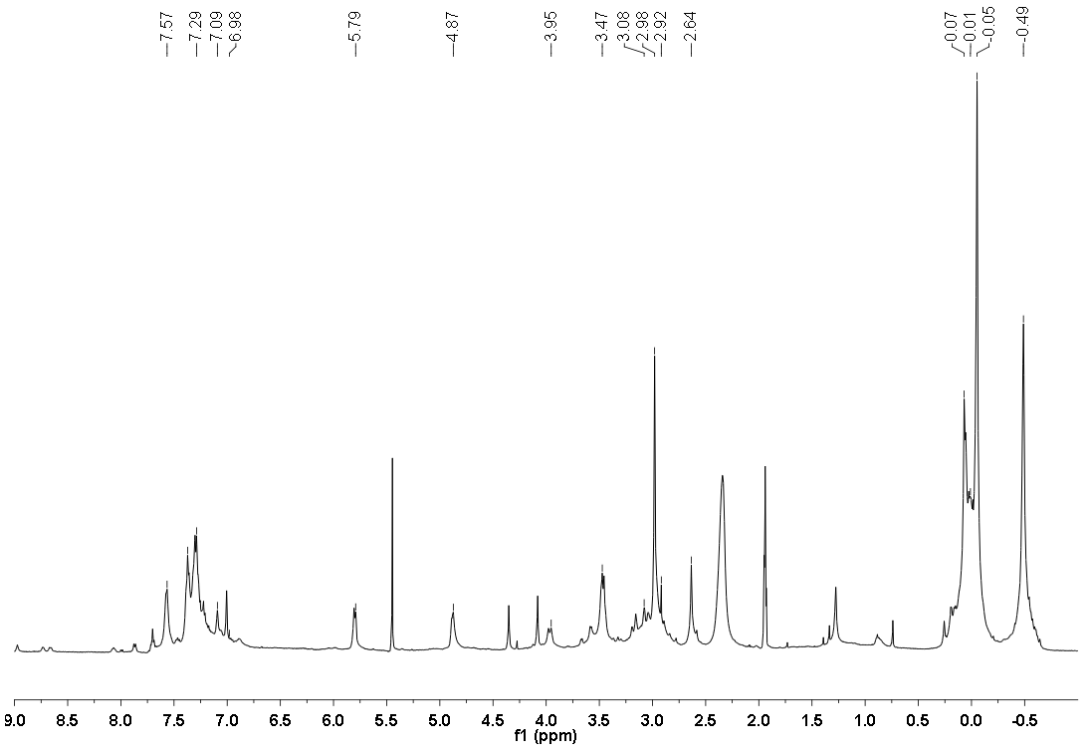


Figure S34. ^{1}H-NMR spectrum of model **5b** in the presence of 1 eq $Mg(ClO_4)_2$ (CD_3CN, 500 MHz, r.t.)

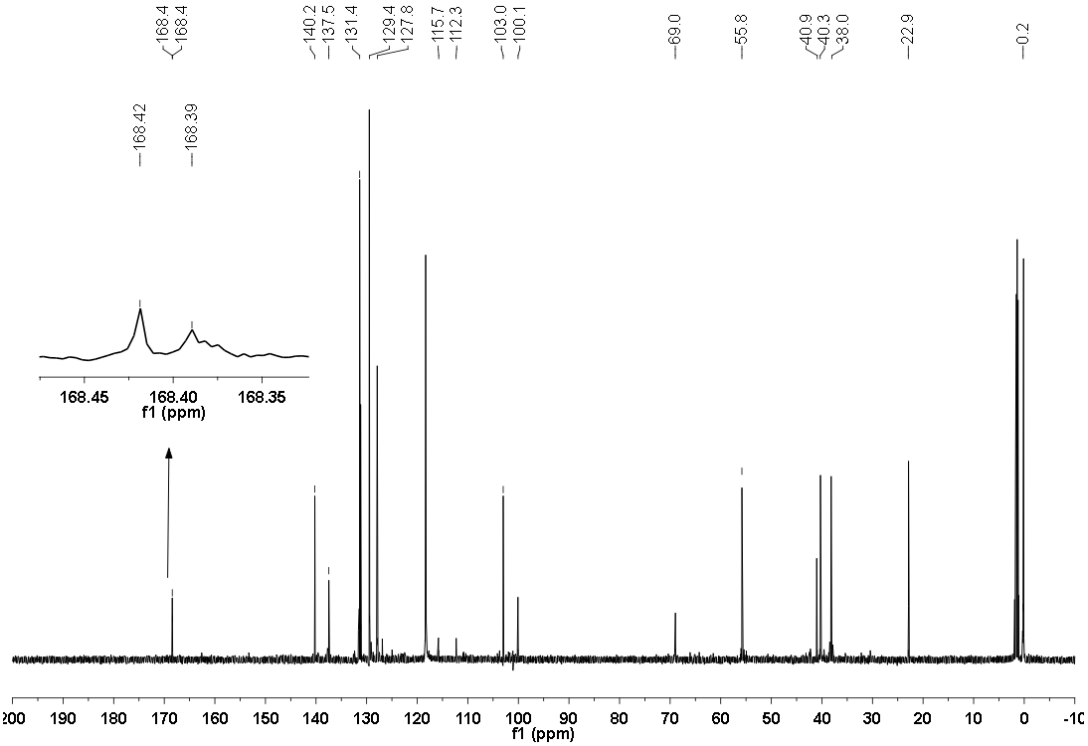


Figure S35. ^{13}C-NMR spectrum of model **5b** (CD_3CN, 125 MHz, r.t.)

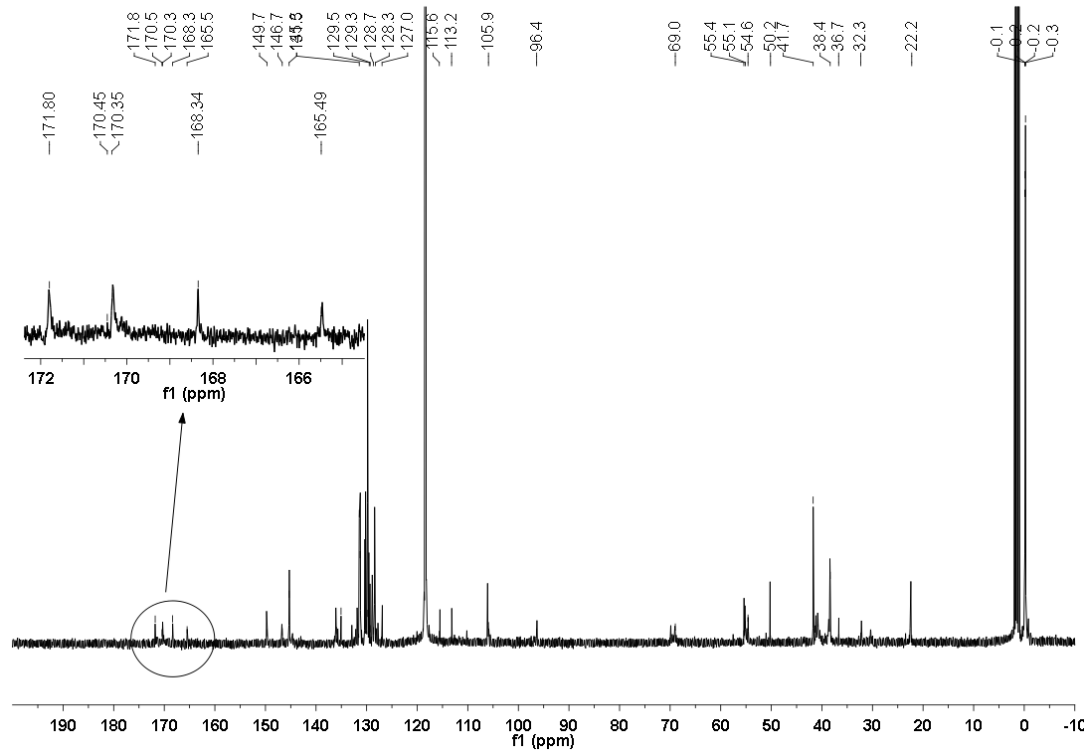


Figure S36. ^{13}C-NMR spectrum of model **5b** in the presence of 1 eq $Mg(ClO_4)_2$ (CD_3CN, 125 MHz, r.t.)

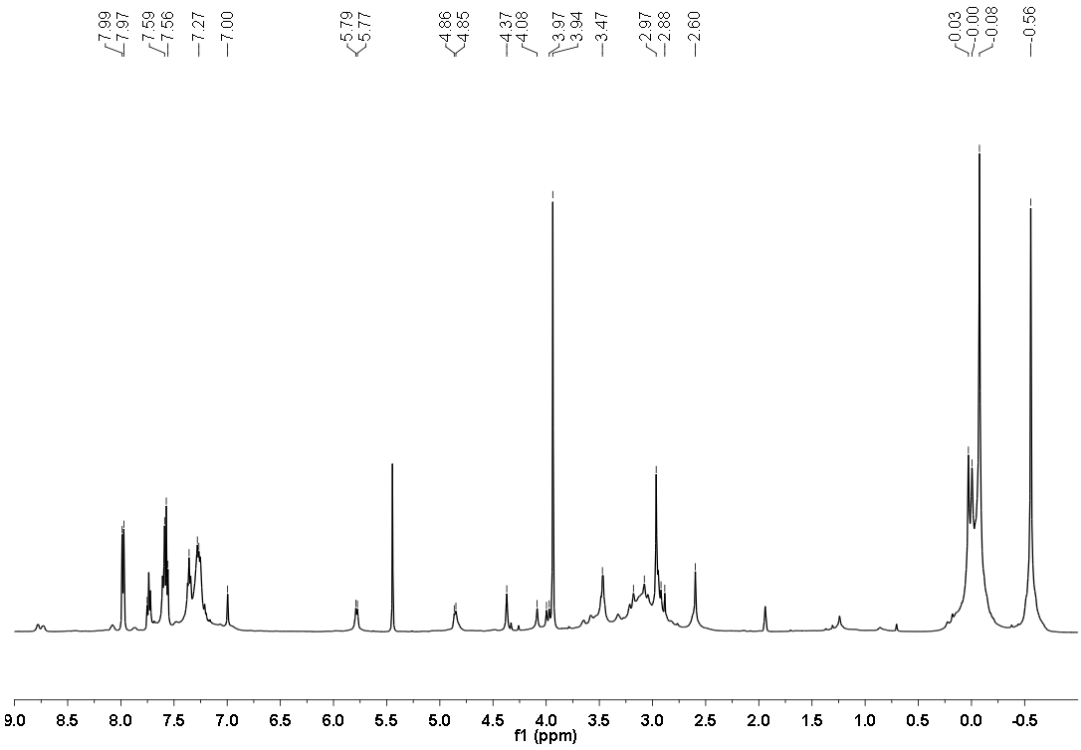


Figure S37. ^{1}H-NMR spectrum of the equimolar ternary mixture **5b**/**9**/ $Mg(ClO_4)_2$ (CD_3CN, 500 MHz, 273K)

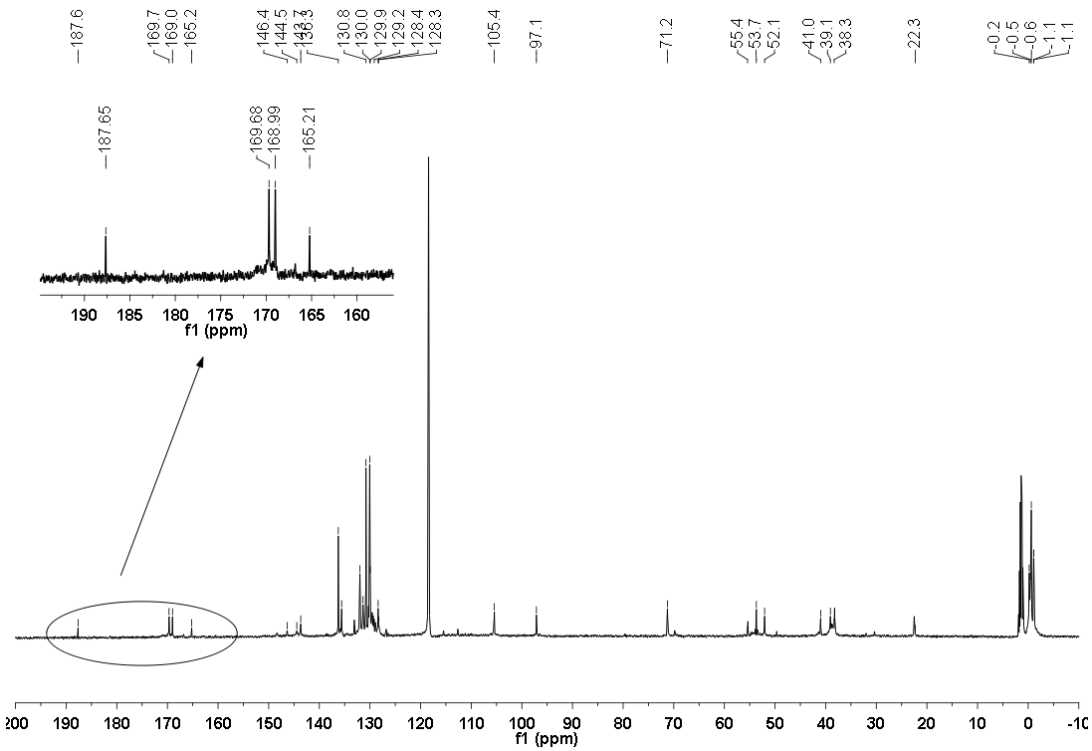


Figure S38. ^{13}C-NMR spectrum of the equimolar ternary mixture **5b**/**9**/ $Mg(ClO_4)_2$ (CD_3CN, 125 MHz, 273K)

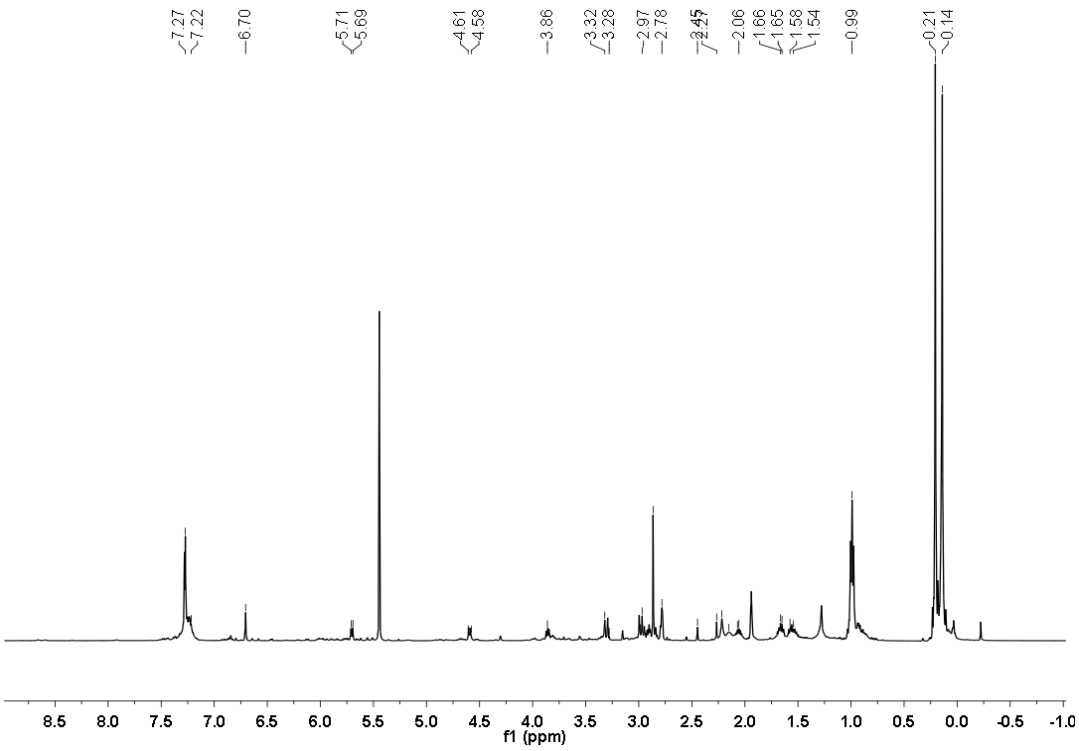


Figure S39. ^{1}H-NMR spectrum of model **5e** (CD_3CN, 500 MHz, r.t.)

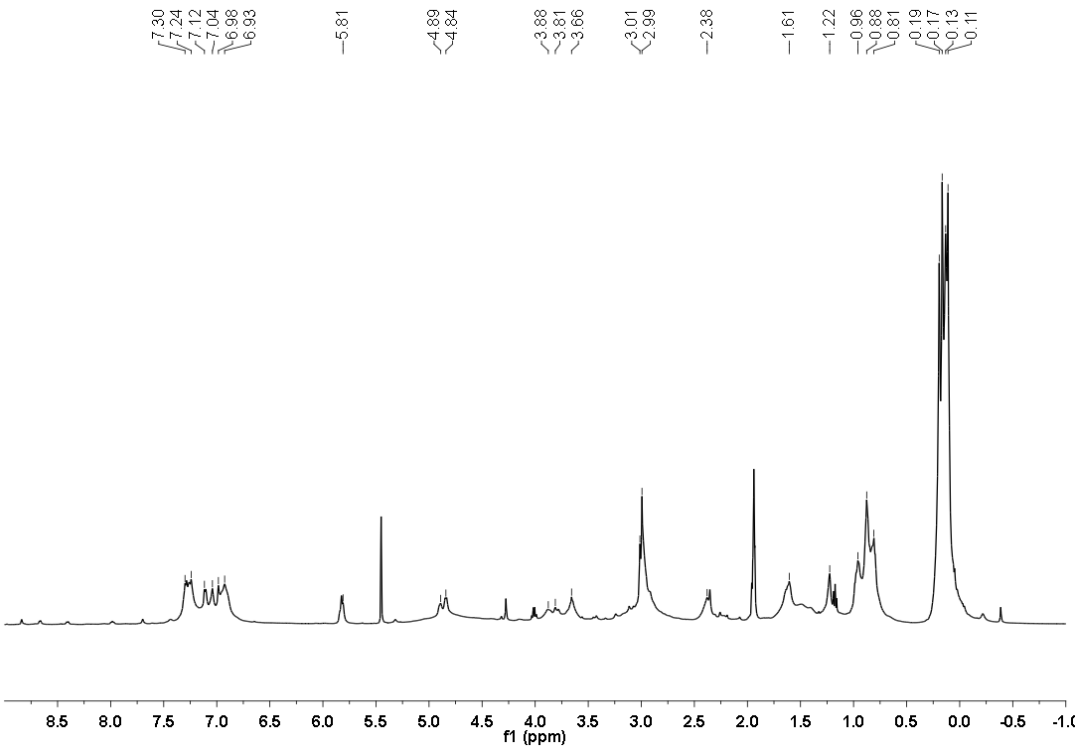


Figure S40. ^{1}H-NMR spectrum of model **5e** in the presence of 1 eq $Mg(ClO_4)_2$ (CD_3CN, 500 MHz, r.t.)

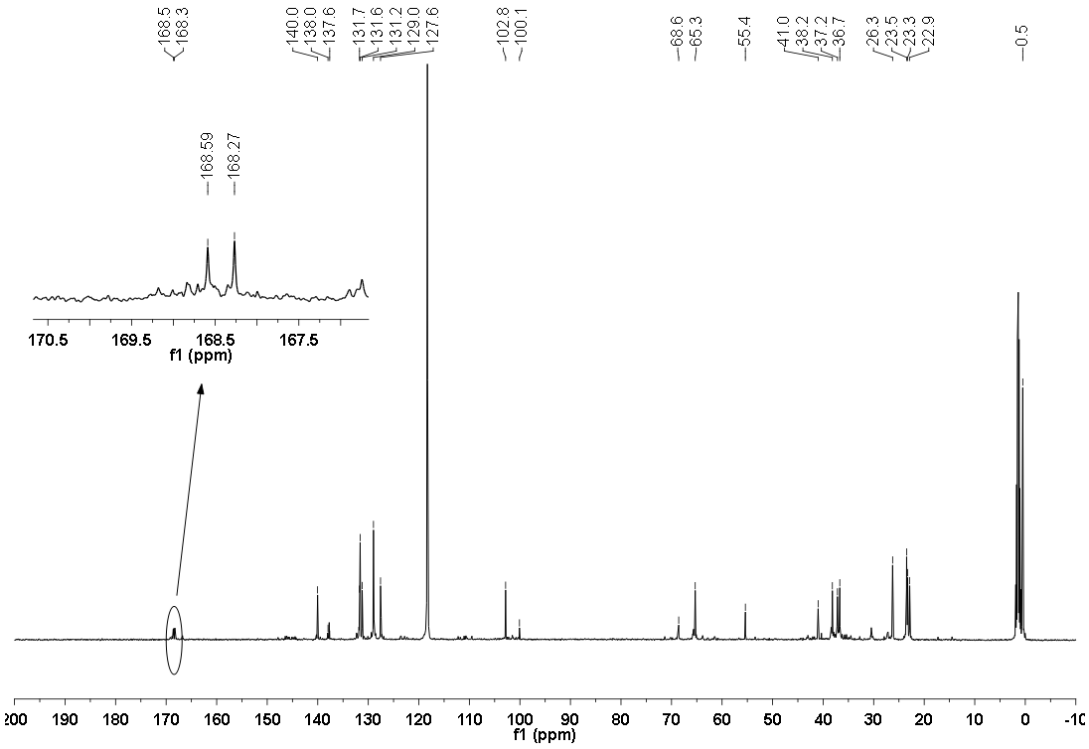


Figure S41. ^{13}C-NMR spectrum of model **5e** (CD_3CN, 125 MHz, r.t.)

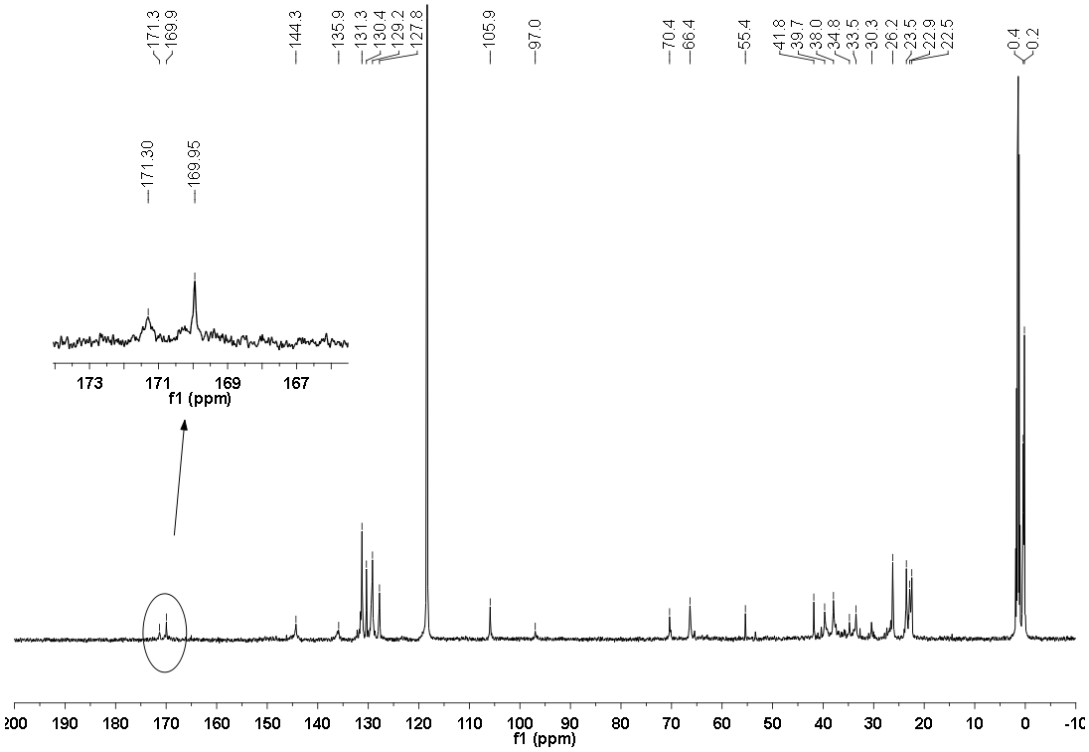


Figure S42. ^{13}C-NMR spectrum of model **5e** in the presence of 1 eq $Mg(ClO_4)_2$ (CD_3CN, 125 MHz, r.t.)

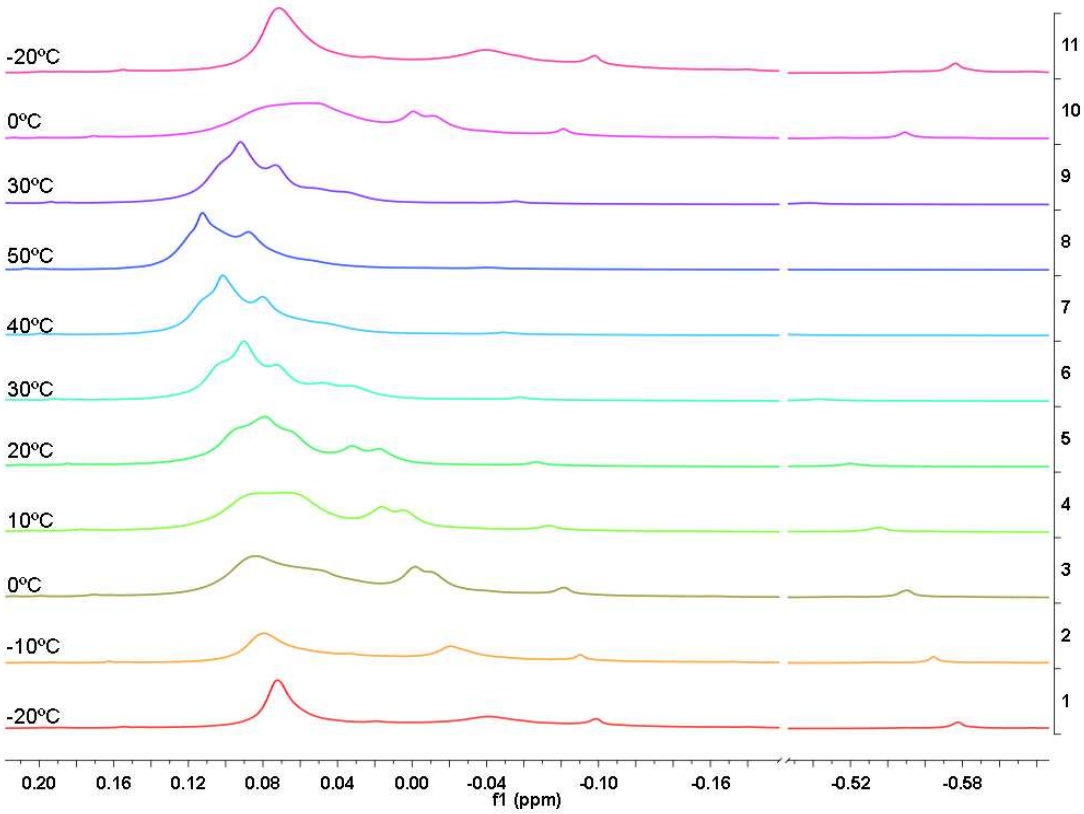


Figure S43. Extensions of the ^{1}H-NMR spectrum of binary mixture **5b**/ $Mg(ClO_4)_2$ recorded at temperatures between -20 and 50ºC (CD_3CN, 500 MHz)

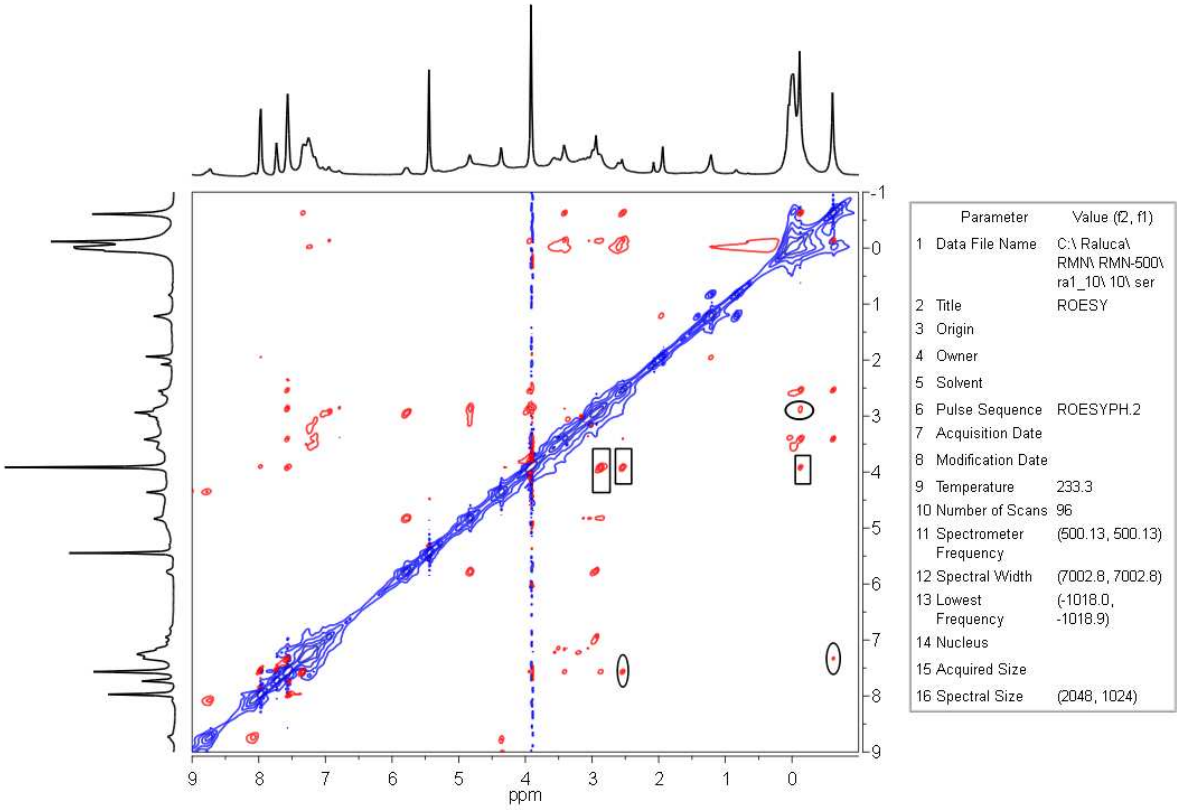


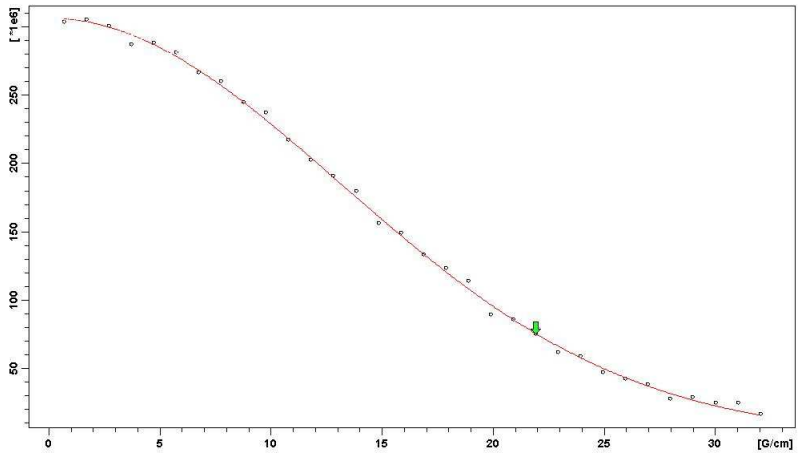
Figure S44. ROESY spectrum of the equimolar ternary mixture **5b**/**9**/ $Mg(ClO_4)_2$ (CD_3CN, 500 MHz, 500ms, 233K).

5.- Diffusion Experiments

For DOSY experiments, the standard Bruker protocol was used in a 500 MHz AVANCE spectrometer equipped with a z-gradient probe. 32 1D 1H spectra were collected with gradient durations specified below. The ledbpg2s pulse sequence, with stimulated echo, longitudinal eddy current compensation, bipolar gradient pulses, and two spoil gradients, was run with a linear gradient (53.5 G cm^{-1}) stepped between 2% and 95%. The 1D ^{1}H spectra were processed and automatically baseline corrected. The diffusion dimension, zero-filled to 1 k, was exponentially fitted according to pre set windows for the diffusion dimension. Diffusion data were processed using Bruker TOPSPIN 1.3 software.

Dataset : d:/NMR_Spectra/data/500/nmr/ra1_88c/10/pdata/1/ct1t2.txt
AREA fit : Diffusion : Variable Gradient :
I=I[0]*exp(-D*SQR(2*PI*gamma*Gi*LD)*(BD-LD/3)*1e4)
32 points for Integral 1, Integral Region from 4.727 to 4.629 ppm
Converged after 33 iterations!
Results Comp. 1

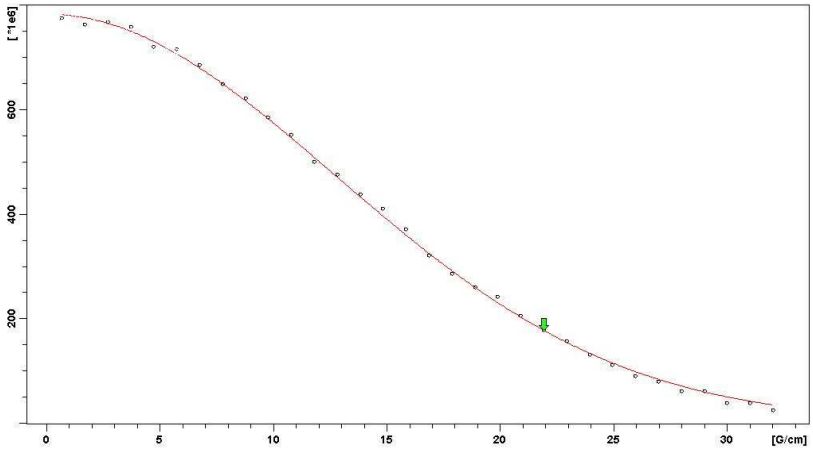
I[0] = 1.003e+000
Diff Con. = 1.424e-009 m2/s
Gamma = 4.258e+003 Hz/G
Little Delta = 1.700m
Big Delta = 99.950m



DOSY parameters and diffusion decay curve for the NADH model **5b** (CD_3CN, 500 MHz, 293K).

Dataset : d:/NMR_Spectra/data/500/nmr/ra1_88c/12/pdata/1/ct1t2.txt
AREA fit : Diffusion Variable Gradient :
I=I[0]*exp(-D*SQR(2*PI*gamma*Gi*LD)*(BD-LD/3)*1e4)
32 points for Integral 1, Integral Region from 4.980 to 4.854 ppm
Converged after 28 iterations!
Results Comp. 1

I[0] = 1.011e+000
Diff Con. = 0.9938e-009 m2/s
Gamma = 4.258e+003 Hz/G
Little Delta = 2.100m
Big Delta = 99.950m

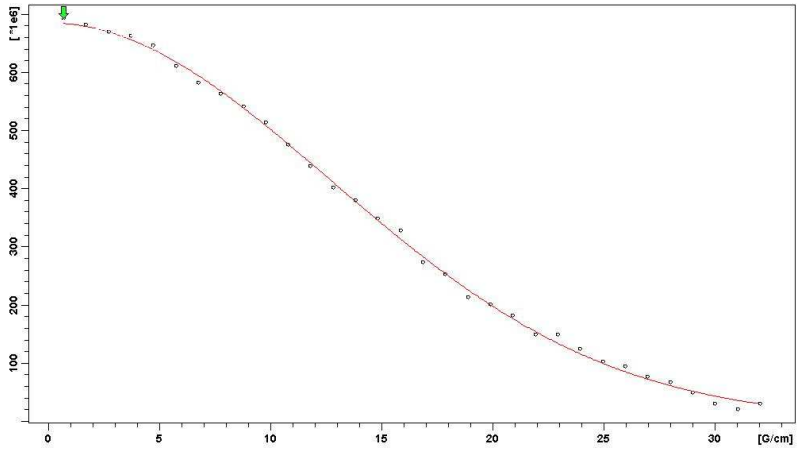


DOSY parameters and diffusion decay curve for the NADH model **5b** in the binary complex **5b**/$Mg(ClO_4)_2$ (CD_3CN, 500 MHz, 293K).

Dataset : d:/NMR_Spectra/data/500/nmr/ra1_88c/14/pdata/1/ct1t2.txt
AREA fit : Diffusion : Variable Gradient :
I=I[0]*exp(-D*SQR(2*PI*gamma*Gi*LD)*(BD-LD/3)*1e4)
32 points for Integral 1, Integral Region from 4.993 to 4.822 ppm
Converged after 38 iterations!

Results Comp. 1

I[0] = 3.557e-001
Diff Con. = 1.102e-009 m2/s
Gamma = 4.258e+003 Hz/G
Little Delta = 2.000m
Big Delta = 99.950m



DOSY parameters and diffusion decay curve for the NADH model **5b** in the ternary complex **5b**/**9**/$Mg(ClO_4)_2$ (CD_3CN, 500 MHz, 293K).

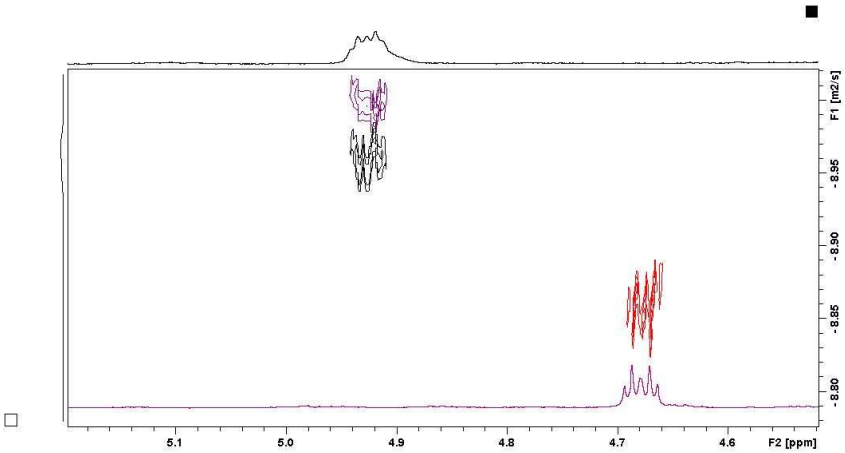


Figure S45. DOSY experiment for compound **5a**. Red: Free **5b**; Magenta: Binary system **5a**/Mg^{2+}; Black: ternary mixture **5b**/**9**/$Mg(ClO_4)_2$ (CD_3CN, 500MHz, 293K).

6.- Computational Methods

6.1. Complete Reference 22 in the Article:

Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, J.A. Jr.; Vreven, T.; Kudin, K.N.; Burant, J.C.; Millam, J.M.; Iyengar, S.S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G.A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J.E.; Hratchian, H.P.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Ayala, P.Y.; Morokuma, K.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Zakrzewski, V.G.; Dapprich, S.; Daniels, A.D.; Strain, M.C.; Farkas, O.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Ortiz, J.V.; Cui, Q.; Baboul, A.G.; Clifford, S.; Cioslowski, J.; Stefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Challacombe, M.; Gill, P.M.W.; Johnson, B.; Chen, W.; Wong, M.W.; Gonzalez, C.; Pople, J.A. Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford CT, **2004**.

6.2. General Information

Computational Analysis. To study the reaction mechanism and to ascertain the origin of the stereoselectivity observed for the reduction of methyl benzoylformate **9** with NADH β-lactam peptidomimetics **5**, we selected first the model structure **11** (see Text). The flexible benzylic moieties in compounds **5a-f** and the bulky $CH(SiMe_3)_2$ were replaced by the less demanding and more rigid two methyl groups to shorten the computational time and limit the conformational energy.

For the initial model studies, all structures were optimized using the functional B3LYP[5] and the 6-31G* basis sets as implemented in Gaussian 03[6]. All energy minima and transition structures were characterized by frequency analysis. The energies reported in this work include zero-point vibrational energy corrections (ZPVE) and are not scaled. The stationary points were characterized by frequency calculations in order to verify that they have the right number of negative eigenvalues. The intrinsic reaction coordinates (IRC)[7] were followed to

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[5](a) Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B* **1988**, *37*, 785-789. (b) Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. (c) Kohn, W.; Becke, A.D.; Parr, R.G. *J. Phys. Chem.* **1996**, *100*, 12974-12980.

[6] For full reference, see paragraph 6.1.

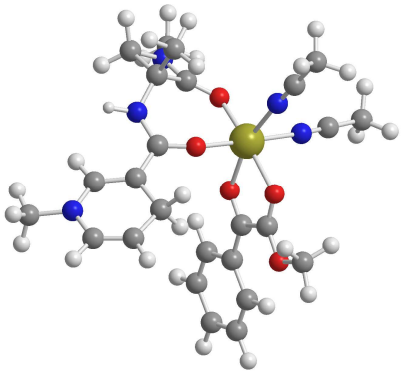
[7] Gonzalez, C.; Schlegel, H.B. *J. Phys. Chem.* **1990**, *94*, 5523-5527.

verify the energy profiles connecting each transition structure to the correct associated local minima. Single-point calculations with the self-consistent reaction field (SCRF) based on the IEF-PCM[8] solvation model (MeCN, ε = 36.64) were carried out at B3LYP/6-311++G** level on the previously optimized most relevant structures.

6.3 Cartesian Coordinates of Ternary Complexes 16-19, 16A-19A and Transition States 26-33, 26A-33A

[8] (a) Cancès, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032-3047. (b) Tomasi, J.; Mennucci, B.; Cancès, E. *J. Mol. Struct. (Theochem)* **1999**, *464*, 211-226.

16



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5	6	0	1.755589	1.291389	0.196216
6	6	0	1.333024	2.610145	0.603060
7	6	0	1.744008	3.745123	-0.056009
8	6	0	-1.062717	-4.528485	-0.301596
9	6	0	1.807629	6.178550	-0.444520
10	6	0	2.719391	-3.624497	3.958949
11	6	0	2.013900	-2.990329	2.853251
12	6	0	0.653578	5.170948	1.499295
13	6	0	0.165845	4.136752	2.189084
14	6	0	0.352110	2.700132	1.764889
15	6	0	4.083583	-0.164320	-2.420453
16	6	0	-2.347122	-0.301031	-0.184443
17	6	0	-2.274977	-0.552882	1.350755
18	6	0	-3.480168	0.253781	-0.908055
19	6	0	-1.598852	-5.832928	-0.667819
20	6	0	-3.189814	-0.376086	3.529266
21	6	0	-5.563521	1.283478	-2.474043
22	6	0	-3.306999	0.450570	-2.301770
23	6	0	-4.724202	0.581107	-0.317801
24	6	0	-5.752095	1.090290	-1.102302
25	6	0	-4.337614	0.962304	-3.072713
26	1	0	0.708691	2.095970	2.611247
27	1	0	-0.621848	2.256563	1.492654
28	1	0	-2.274077	-5.731989	-1.523274

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33	1	0	3.409863	1.930839	-0.801630
34	1	0	2.075877	-2.633955	-3.877013
35	1	0	3.821997	-2.544145	-4.236757
36	1	0	2.718971	-1.286883	-4.855733
37	1	0	3.705280	-0.804654	1.041590
38	1	0	5.100577	0.043364	0.341799
39	1	0	2.034292	-4.272068	4.515095
40	1	0	3.115770	-2.861114	4.635763
41	1	0	3.548285	-4.228408	3.576547
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43	1	0	-3.141621	-1.449174	3.719867
44	1	0	-4.101767	0.056354	3.934815
45	1	0	-6.372228	1.682617	-3.079298
46	1	0	-2.354720	0.195288	-2.752514
47	1	0	-4.888136	0.434106	0.739906
48	1	0	-6.705091	1.336338	-0.645093
49	1	0	-4.196703	1.112428	-4.138393
50	1	0	2.354153	3.697092	-0.953415
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65	8	0	-1.274162	-1.111485	1.792412
66	12	0	0.296806	-1.522311	0.382689
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E(RB+HF-LYP) = -1821.01033572
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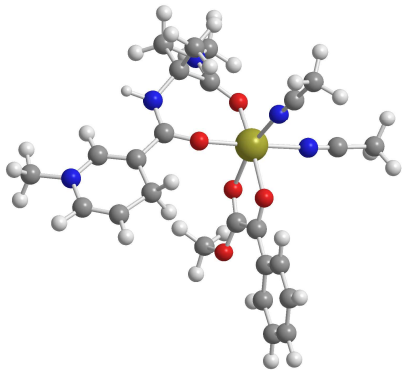
17



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8	8	0	1.694129	-2.249952	-0.671557
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10	6	0	0.101319	-3.143580	4.665431
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13	7	0	-1.041473	-3.324565	-0.383178
14	6	0	0.118190	-2.640803	3.298206
15	7	0	0.131820	-2.241148	2.213224
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21	6	0	-3.861487	0.549209	-0.035479
22	8	0	-2.293491	0.680569	-2.614008
23	6	0	-1.553898	0.714457	-3.872757
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30	6	0	2.574434	3.415690	0.023922
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33	6	0	1.188349	5.213973	0.723536
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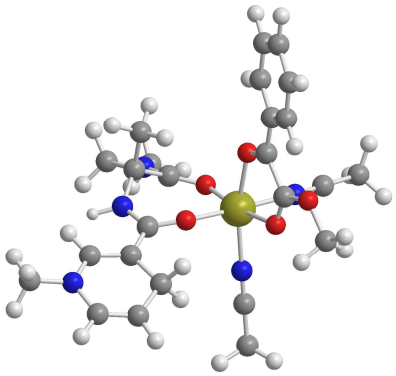
18



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53	7	0	-2.120910	2.586897	1.120464
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62	7	0	2.480081	0.351556	-1.560890
63	1	0	3.415764	0.219625	-1.917186
64	6	0	0.568452	0.120506	-3.152952
65	1	0	-0.027518	-0.445615	-2.433499
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67	1	0	1.125802	-0.582981	-3.780107

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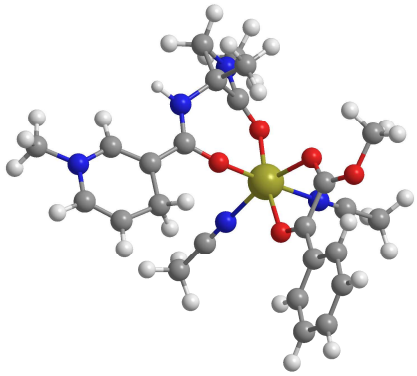
19



Standard orientation:

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6	7	0	-3.244048	-3.270790	-0.624316
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8	8	0	-1.143581	-2.604644	0.165289
9	8	0	-0.910355	0.230672	-0.268811
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11	6	0	2.167224	-3.667278	1.801174
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15	8	0	1.403203	-1.370935	-1.304714
16	6	0	2.713436	0.317707	-0.232313
17	6	0	2.405732	-0.666329	-1.397545
18	6	0	3.788671	1.294901	-0.208581
19	8	0	3.255507	-0.718582	-2.389973
20	6	0	2.992059	-1.675712	-3.461029
21	6	0	5.797406	3.234684	0.009699
22	6	0	4.019129	1.959220	1.022651
23	6	0	4.581567	1.632038	-1.331331
24	6	0	5.573073	2.598585	-1.215043
25	6	0	5.017998	2.912812	1.129317
26	6	0	-2.375859	2.060335	-0.207113
27	6	0	-3.658265	2.555364	-0.258582
28	7	0	-3.981269	3.838615	-0.004222
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33	7	0	-0.367514	-0.747034	2.586281
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35	6	0	-1.097097	-0.225437	5.040553
36	1	0	-2.785409	-4.831470	0.658042
37	1	0	-3.749073	-5.302575	-0.768168
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39	6	0	-3.951091	-2.424768	-1.600498
40	1	0	-0.951955	-0.925906	-2.733574
41	1	0	-2.472763	-0.910750	-3.655254
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44	1	0	3.808547	-4.394802	2.891988
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51	1	0	4.417006	1.152704	-2.285787
52	1	0	6.174519	2.858255	-2.080238
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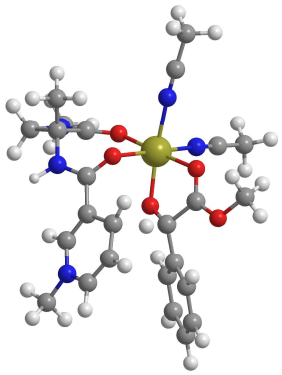
62	1	0	-1.799633	0.613617	5.052372
63	1	0	-0.220417	0.035794	5.641513
64	1	0	-1.581779	-1.102692	5.480378
65	1	0	-4.142425	-2.923626	-2.554961
66	1	0	-4.873309	-1.990417	-1.201949
67	1	0	-1.697731	-2.453826	-3.247758

E(RB+HF-LYP) = -1821.01119670

Sum of electronic and thermal Enthalpies= -1820.431789

Sum of electronic and thermal Free Energies= -1820.553233

TS26



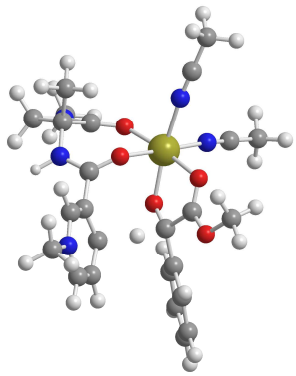
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.921574	-2.334331	3.072883
2	6	0	2.763084	-2.545963	-0.278441
3	6	0	3.665559	-2.352800	-1.495808
4	6	0	2.907849	-1.514649	0.874201
5	6	0	0.576571	-1.736656	-1.077353
6	6	0	-0.891976	-1.940649	-1.156609
7	6	0	-1.552031	-2.876844	-0.386197
8	6	0	1.896697	3.236843	2.400636
9	6	0	-3.584492	-4.011598	0.425480
10	6	0	4.944663	2.838519	-2.645107
11	6	0	3.893814	2.223964	-1.844574
12	6	0	-3.628943	-2.343082	-1.380145
13	6	0	-3.051691	-1.378584	-2.149542
14	6	0	-1.671740	-1.033482	-1.960893
15	6	0	3.303153	-3.561021	0.784274
16	6	0	-1.488861	0.924244	-0.052298
17	6	0	-1.045804	2.150423	-0.883978
18	6	0	-2.836036	0.950163	0.632867
19	6	0	2.082502	4.212708	3.466460
20	6	0	-1.586035	4.016970	-2.241306
21	6	0	-5.291247	0.913506	1.992897
22	6	0	-2.893103	0.589470	1.988572
23	6	0	-4.028702	1.266037	-0.041428
24	6	0	-5.246163	1.252247	0.638765
25	6	0	-4.111690	0.580573	2.664675
26	1	0	-1.153647	-0.482101	-2.742416
27	1	0	-1.722003	0.167757	-1.057732
28	1	0	1.322558	4.067804	4.240643
29	1	0	1.992302	5.226667	3.064518
30	1	0	3.074335	4.093573	3.913488
31	1	0	4.248108	-4.045790	0.524196

32	1	0	2.583321	-4.306876	1.140352
33	1	0	0.978309	-3.691966	-0.588136
34	1	0	3.831184	-1.297412	3.401558
35	1	0	4.969499	-2.644690	3.128873
36	1	0	3.321591	-2.976368	3.725893
37	1	0	3.343981	-1.489735	-2.080421
38	1	0	3.631944	-3.244156	-2.131173
39	1	0	4.773318	3.917103	-2.717654
40	1	0	4.945891	2.410491	-3.652411
41	1	0	5.920250	2.663526	-2.180998
42	1	0	-0.975877	3.678466	-3.080538
43	1	0	-1.022292	4.719259	-1.625476
44	1	0	-2.517096	4.462302	-2.586110
45	1	0	-6.239473	0.913204	2.522492
46	1	0	-1.970502	0.338185	2.500089
47	1	0	-4.007986	1.544459	-1.089525
48	1	0	-6.159714	1.512756	0.112162
49	1	0	-4.141652	0.323415	3.719794
50	1	0	-1.041643	-3.502939	0.336161
51	1	0	-4.138255	-3.457617	1.188242
52	1	0	-2.851004	-4.659092	0.906378
53	1	0	-4.273146	-4.625517	-0.158757
54	1	0	-4.677411	-2.606786	-1.450442
55	1	0	-3.657176	-0.850559	-2.876934
56	7	0	3.444478	-2.418460	1.704057
57	7	0	1.348008	-2.750949	-0.615267
58	7	0	3.058550	1.738748	-1.209446
59	7	0	-2.890152	-3.065610	-0.470075
60	7	0	1.749135	2.462373	1.555264
61	8	0	2.617074	-0.325450	1.040883
62	8	0	1.083420	-0.645489	-1.410954
63	8	0	-0.481142	0.410306	0.612692
64	8	0	-1.991682	2.875279	-1.433909
65	8	0	0.158377	2.367982	-1.043128
66	12	0	1.380883	0.971812	-0.016142
67	1	0	4.701496	-2.198873	-1.177012

E(RB+HF-LYP) = -1820.97560606
Sum of electronic and thermal Enthalpies= -1820.400229
Sum of electronic and thermal Free Energies= -1820.518232
HF (B3LYP/6-311++G**//B3LYP/6-31G* in MeCN) = -1821.612262
Frequency: 634.2i

TS27



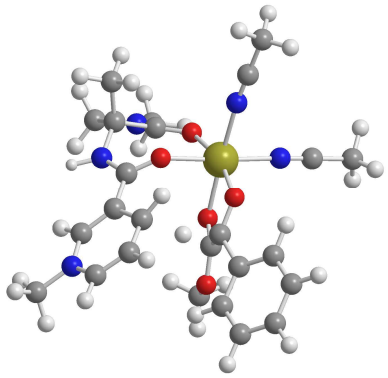
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.948784	-0.556252	-3.770075
2	6	0	-2.617045	-2.383727	-1.032070
3	6	0	-3.476704	-2.866567	0.135362
4	6	0	-2.865350	-0.914591	-1.483661
5	6	0	-0.404977	-2.059018	0.024780
6	6	0	1.058356	-2.406449	0.031033
7	6	0	1.544472	-3.441059	0.784773
8	6	0	-2.272473	4.069872	-0.119578
9	6	0	3.385960	-4.854169	1.640431
10	6	0	-4.548257	0.841761	4.083480
11	6	0	-3.613930	0.796501	2.966469
12	6	0	3.762999	-2.938642	0.144165
13	6	0	3.347089	-1.893695	-0.626900
14	6	0	1.962071	-1.499188	-0.648707
15	6	0	-3.159542	-2.740270	-2.455633
16	6	0	1.416050	1.054038	-0.067373
17	6	0	1.228674	1.299581	1.448271
18	6	0	2.577983	1.708048	-0.776035
19	6	0	-2.595867	5.459478	-0.413734
20	6	0	2.145644	1.617920	3.608745
21	6	0	4.663787	2.888010	-2.236142
22	6	0	2.323648	2.317960	-2.015179
23	6	0	3.896420	1.677064	-0.284979
24	6	0	4.928389	2.268310	-1.011679
25	6	0	3.359637	2.909998	-2.735197
26	1	0	1.849653	-0.203463	-0.007294
27	1	0	-4.526989	-2.609598	-0.034498
28	1	0	-2.033640	5.794249	-1.291053
29	1	0	-2.333675	6.092337	0.439855
30	1	0	-3.666675	5.559342	-0.616643
31	1	0	-4.076009	-3.337018	-2.465636
32	1	0	-2.428346	-3.162586	-3.154247

33	1	0	-0.781531	-3.432575	-1.427010
34	1	0	-3.921901	0.505580	-3.518876
35	1	0	-4.984685	-0.864646	-3.942293
36	1	0	-3.365373	-0.730317	-4.679680
37	1	0	-3.151872	-2.400724	1.068413
38	1	0	-3.401078	-3.954267	0.235251
39	1	0	-4.295396	1.676658	4.744575
40	1	0	-4.496741	-0.090966	4.653645
41	1	0	-5.568801	0.978035	3.712259
42	1	0	1.548347	0.824403	4.061252
43	1	0	1.656709	2.582969	3.750556
44	1	0	3.155456	1.631046	4.014210
45	1	0	5.470357	3.351197	-2.796716
46	1	0	1.307479	2.328472	-2.392878
47	1	0	4.115681	1.205242	0.665934
48	1	0	5.941310	2.248909	-0.620182
49	1	0	3.149478	3.390889	-3.686134
50	1	0	0.896814	-4.107934	1.343243
51	1	0	3.789371	-5.614651	0.965952
52	1	0	2.569278	-5.283792	2.220677
53	1	0	4.168621	-4.518197	2.324475
54	1	0	4.802311	-3.241584	0.203438
55	1	0	4.076434	-1.339466	-1.206219
56	7	0	-1.192598	-2.704094	-0.855745
57	7	0	-2.871983	0.764332	2.080502
58	7	0	-3.381383	-1.298241	-2.658082
59	7	0	-2.014722	2.967327	0.112982
60	7	0	2.880178	-3.706127	0.864357
61	8	0	-2.694183	0.206871	-0.996006
62	8	0	-0.831742	-1.163268	0.770651
63	8	0	0.266860	1.024374	-0.686343
64	8	0	2.313866	1.359114	2.186792
65	8	0	0.088880	1.402004	1.907852
66	12	0	-1.393381	0.899399	0.463512
67	1	0	1.580583	-0.994974	-1.541581

E(RB+HF-LYP) = -1820.96835110
Sum of electronic and thermal Enthalpies= -1820.392965
Sum of electronic and thermal Free Energies= -1820.512676
Frequency: 897.8i

TS28



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.965006	-0.981958	-2.494018
2	6	0	-3.192361	-2.024934	0.398913
3	6	0	-3.788569	-1.872492	1.799009
4	6	0	-3.352804	-0.773849	-0.523947
5	6	0	-0.781824	-1.826274	0.805341
6	6	0	4.162564	0.648291	-0.553879
7	6	0	5.468399	1.124677	-0.450643
8	6	0	4.668676	3.067352	0.745447
9	6	0	0.606496	-2.361514	0.844403
10	6	0	-2.761759	3.331803	4.183088
11	6	0	-1.974544	5.400040	-2.099364
12	6	0	-1.761439	4.132136	-1.414404
13	6	0	0.987134	-3.572263	0.306864
14	6	0	-2.337354	2.653412	2.965780
15	6	0	-4.128891	-2.713812	-0.647617
16	6	0	2.661211	-5.316468	-0.206331
17	6	0	3.226851	-3.245738	0.991798
18	6	0	2.926956	-2.027954	1.528303
19	6	0	1.662447	0.901282	-0.063870
20	6	0	1.068575	0.482985	-1.436992
21	6	0	3.094418	1.386978	-0.015713
22	6	0	1.609729	-1.483801	1.398421
23	6	0	1.356072	-0.236988	-3.675530
24	6	0	5.724782	2.336304	0.196407
25	6	0	3.361931	2.592627	0.648838
26	1	0	6.287251	0.553422	-0.878530
27	1	0	4.864334	4.009061	1.249984
28	1	0	0.293713	-4.244215	-0.186039
29	1	0	1.785183	-5.797949	-0.640738
30	1	0	3.067015	-5.953395	0.583610
31	1	0	3.414162	-5.169330	-0.984437
32	1	0	3.703273	-1.467226	2.035705

33	1	0	1.278104	-0.703086	2.081176
34	1	0	-3.664436	-3.495783	-1.258657
35	1	0	-5.087122	-3.063237	-0.252192
36	1	0	-6.037826	-1.095523	-2.308649
37	1	0	-4.688386	-1.572388	-3.373248
38	1	0	-3.175930	-1.200622	2.404168
39	1	0	-3.844476	-2.846950	2.296030
40	1	0	-4.736878	0.069874	-2.675428
41	1	0	-1.751385	-3.598476	0.410714
42	1	0	-3.811788	3.628939	4.099585
43	1	0	-2.149298	4.224984	4.341669
44	1	0	-2.646040	2.664827	5.043011
45	1	0	-1.926509	5.251915	-3.182654
46	1	0	-1.202595	6.117176	-1.803137
47	1	0	-2.957350	5.804867	-1.838576
48	1	0	4.215125	-3.687267	1.049054
49	1	0	0.804275	0.612989	-4.079797
50	1	0	0.692993	-1.099508	-3.582244
51	1	0	2.218779	-0.470372	-4.296674
52	1	0	6.742526	2.707518	0.272205
53	1	0	2.534712	3.146305	1.078320
54	1	0	3.975292	-0.288610	-1.068702
55	7	0	-4.204915	-1.415474	-1.335408
56	7	0	-1.831947	-2.589209	0.419370
57	7	0	-1.591443	3.127025	-0.869510
58	7	0	2.269995	-4.010284	0.362090
59	7	0	-1.998592	2.117844	1.998988
60	8	0	-2.936337	0.387855	-0.546176
61	8	0	-0.953532	-0.633677	1.105418
62	8	0	0.770820	1.569078	0.630195
63	8	0	-0.156996	0.482328	-1.584083
64	8	0	1.908453	0.109553	-2.377025
65	12	0	-1.163910	1.253461	0.173381
66	1	0	1.760429	-0.267743	0.406086
67	1	0	-4.801316	-1.461179	1.740649

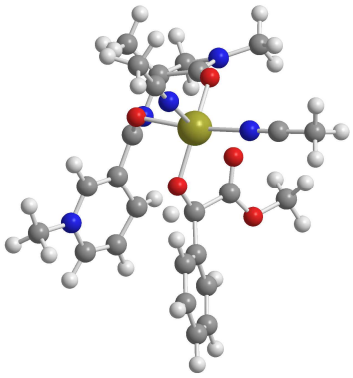
E(RB+HF-LYP) = -1820.96853033

Sum of electronic and thermal Enthalpies= -1820.394281

Sum of electronic and thermal Free Energies= -1820.509898

Frequency: 535.6i

TS29



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.772262	0.479281	-2.634627
2	6	0	-3.061832	-2.034131	-0.805716
3	6	0	-3.815078	-2.864816	0.236156
4	6	0	-3.341161	-0.501171	-0.759855
5	6	0	-0.806295	-2.016289	0.144920
6	6	0	3.740566	0.937545	-1.610669
7	6	0	5.080025	1.311564	-1.523020
8	6	0	4.803190	1.771794	0.834702
9	6	0	0.646333	-2.329964	0.051727
10	6	0	-2.307244	0.952613	5.466398
11	6	0	-1.468012	5.551754	1.039072
12	6	0	-1.364512	4.100564	0.963721
13	6	0	1.286914	-2.706810	1.213088
14	6	0	-1.922314	0.897219	4.062595
15	6	0	-3.776629	-1.956948	-2.194408
16	6	0	3.267126	-3.427396	2.490759
17	6	0	3.343179	-2.962486	0.076836
18	6	0	2.793849	-2.548909	-1.095703
19	6	0	1.468319	0.580831	-0.501197
20	6	0	0.518207	1.131038	-1.576993
21	6	0	2.914488	0.990582	-0.474068
22	6	0	1.431920	-2.065106	-1.131995
23	6	0	0.165576	2.034693	-3.740550
24	6	0	5.613914	1.733457	-0.302559
25	6	0	3.464558	1.393915	0.753633
26	1	0	5.708135	1.275640	-2.408209
27	1	0	5.214546	2.101489	1.784442
28	1	0	0.744906	-2.799631	2.146422
29	1	0	2.522869	-3.510580	3.282485
30	1	0	4.015178	-2.682233	2.773703
31	1	0	3.748961	-4.397642	2.347540

32	1	0	3.401031	-2.546932	-1.993112
33	1	0	1.559526	-0.639636	-1.046504
34	1	0	-3.131361	-2.093615	-3.069501
35	1	0	-4.676092	-2.571529	-2.289164
36	1	0	-5.821899	0.188928	-2.742877
37	1	0	-4.334855	0.618751	-3.628440
38	1	0	-3.398601	-2.703363	1.231591
39	1	0	-3.747436	-3.929091	-0.013489
40	1	0	-4.709495	1.413597	-2.073960
41	1	0	-1.312077	-3.027081	-1.570700
42	1	0	-3.250503	1.497854	5.571719
43	1	0	-1.532805	1.464309	6.046366
44	1	0	-2.436969	-0.060760	5.858773
45	1	0	-1.734056	5.959431	0.058870
46	1	0	-0.510560	5.977778	1.355053
47	1	0	-2.239917	5.833321	1.762154
48	1	0	4.370716	-3.296317	0.159755
49	1	0	-0.401438	2.881317	-3.350667
50	1	0	-0.515831	1.247185	-4.068836
51	1	0	0.821050	2.344910	-4.551975
52	1	0	6.656616	2.030276	-0.239014
53	1	0	2.826364	1.420257	1.630171
54	1	0	3.337794	0.617245	-2.565828
55	1	0	-4.872948	-2.584513	0.251970
56	7	0	-1.627556	-2.362964	-0.873101
57	7	0	-1.282775	2.948696	0.905934
58	7	0	2.602838	-3.013692	1.240412
59	7	0	-4.042632	-0.537985	-1.899899
60	7	0	-1.619150	0.854903	2.947970
61	8	0	-3.056081	0.438006	-0.006679
62	8	0	-1.260246	-1.392961	1.126197
63	8	0	0.841841	0.425106	0.633129
64	8	0	-0.693601	1.135279	-1.348960
65	8	0	1.054618	1.521637	-2.712259
66	12	0	-1.163233	0.755465	0.814890
67	1	0	0.933682	-2.051101	-2.101555

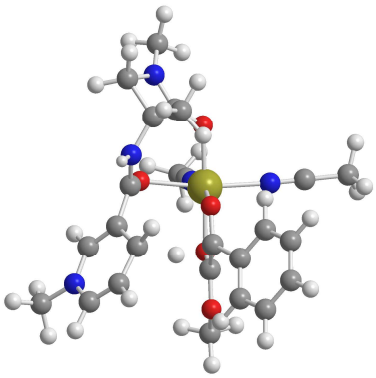
E(RB+HF-LYP) = -1820.96185729

Sum of electronic and thermal Enthalpies= -1820.386764

Sum of electronic and thermal Free Energies= -1820.504962

Frequency: 879.4i

TS30



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.463047	-0.378755	-1.738862
2	6	0	2.052699	-0.803457	-2.594823
3	6	0	2.940505	-0.050436	-1.566931
4	6	0	0.652742	-1.788614	-0.765989
5	6	0	-0.689776	-2.381285	-0.474903
6	6	0	-0.761395	-3.388419	0.457040
7	6	0	1.473395	3.956435	1.250912
8	6	0	-1.971216	-5.136287	1.710193
9	6	0	4.267179	-0.111442	4.382456
10	6	0	3.355458	0.105364	3.267119
11	6	0	-3.104188	-3.559410	0.195310
12	6	0	-3.119309	-2.531870	-0.696843
13	6	0	-1.912768	-1.791807	-0.988519
14	6	0	3.398435	-1.501388	-3.003946
15	6	0	-1.547460	0.694519	-0.053196
16	6	0	-1.503827	0.524252	1.483943
17	6	0	-2.630738	1.532140	-0.677666
18	6	0	1.577662	5.399777	1.418356
19	6	0	-2.622781	0.302117	3.561625
20	6	0	-4.566353	3.101658	-1.963995
21	6	0	-2.254863	2.458422	-1.664551
22	6	0	-3.992425	1.387629	-0.354570
23	6	0	-4.950046	2.171128	-0.993903
24	6	0	-3.217267	3.242799	-2.296875
25	6	0	1.468592	0.132503	-3.657319
26	1	0	0.728448	5.893351	0.935563
27	1	0	1.579784	5.653996	2.482876
28	1	0	2.505390	5.760467	0.963207

29	1	0	3.472024	-2.557574	-2.730395
30	1	0	3.716338	-1.346917	-4.039349
31	1	0	5.527874	0.398628	-0.975225
32	1	0	5.925429	-1.298444	-1.367014
33	1	0	5.993688	-0.049472	-2.637908
34	1	0	3.725957	-0.020879	5.329428
35	1	0	4.707068	-1.111427	4.316882
36	1	0	5.069133	0.633026	4.358276
37	1	0	-2.082820	-0.603246	3.844511
38	1	0	-2.137076	1.177792	3.994795
39	1	0	-3.667374	0.248834	3.861872
40	1	0	-5.316366	3.712163	-2.457912
41	1	0	-1.204692	2.560801	-1.914392
42	1	0	-4.304346	0.669928	0.395886
43	1	0	-5.998615	2.056506	-0.735838
44	1	0	-2.915734	3.965208	-3.049735
45	1	0	0.130294	-3.785376	0.928754
46	1	0	-2.138194	-6.055241	1.140845
47	1	0	-1.020175	-5.205360	2.238447
48	1	0	-2.774430	-5.006077	2.438414
49	1	0	-3.993280	-4.123009	0.453930
50	1	0	-4.055165	-2.252962	-1.167543
51	1	0	1.032248	-0.443640	-4.481998
52	1	0	0.323381	-1.989676	-2.751205
53	1	0	-1.987400	-0.545546	-0.330902
54	1	0	0.694370	0.761277	-3.208947
55	1	0	2.247431	0.775555	-4.077225
56	7	0	2.632634	0.279567	2.382305
57	7	0	0.990398	-1.655014	-2.064918
58	7	0	4.061561	-0.605612	-2.038677
59	7	0	1.392488	2.810982	1.116709
60	7	0	-1.938240	-3.974534	0.800962
61	8	0	1.408139	-1.455366	0.171435
62	8	0	-0.339745	0.769555	-0.540160
63	8	0	-2.653364	0.427584	2.111626
64	8	0	2.753184	0.813982	-0.700770
65	8	0	-0.409489	0.446244	2.048038
66	12	0	1.267706	0.655966	0.723686
67	1	0	-1.869170	-1.261435	-1.942730

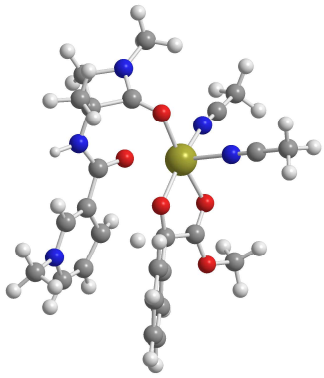
E(RB+HF-LYP) = -1820.96782449

Sum of electronic and thermal Enthalpies= -1820.392565

Sum of electronic and thermal Free Energies= -1820.510571

Frequency: 903.6i

TS31



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.414470	-1.346660	-0.103654
2	6	0	2.330533	-2.926876	0.612981
3	6	0	3.008590	-1.542572	0.726852
4	6	0	0.478177	-1.893069	-0.704081
5	6	0	-0.984722	-1.931718	-0.960154
6	6	0	-1.853026	-2.711915	-0.221619
7	6	0	1.881598	2.994380	2.693559
8	6	0	-4.094988	-3.522937	0.389082
9	6	0	4.895479	2.795252	-2.499522
10	6	0	3.902823	2.116368	-1.676355
11	6	0	-3.690981	-2.090434	-1.571249
12	6	0	-2.906126	-1.264976	-2.317427
13	6	0	-1.542362	-1.023444	-1.933351
14	6	0	3.605608	-3.304067	-0.225874
15	6	0	-1.452878	0.966381	-0.082754
16	6	0	-0.887377	2.168411	-0.864806
17	6	0	-2.856112	1.019742	0.468805
18	6	0	2.061261	3.877662	3.837904
19	6	0	-1.223225	4.095524	-2.203473
20	6	0	-5.433800	1.006352	1.580871
21	6	0	-3.057943	0.596810	1.793215
22	6	0	-3.966166	1.411500	-0.300765
23	6	0	-5.244574	1.409442	0.257198
24	6	0	-4.337333	0.598531	2.346407
25	1	0	-0.858855	-0.594211	-2.663198
26	1	0	1.107346	4.012763	4.357224
27	1	0	2.426600	4.853691	3.503707
28	1	0	2.787032	3.443281	4.532484
29	1	0	3.429199	-3.403247	-1.300355

30	1	0	4.198761	-4.141949	0.151232
31	1	0	5.407530	-0.360407	0.364076
32	1	0	5.584905	-1.244360	-1.180375
33	1	0	6.220087	-1.947857	0.329122
34	1	0	4.559538	3.813283	-2.720377
35	1	0	5.033903	2.255282	-3.441429
36	1	0	5.852686	2.845025	-1.971214
37	1	0	-0.604784	3.729309	-3.024850
38	1	0	-0.635974	4.738879	-1.546607
39	1	0	-2.102090	4.617836	-2.576029
40	1	0	-6.429010	1.016534	2.015765
41	1	0	-2.198045	0.292183	2.379519
42	1	0	-3.833353	1.736931	-1.326586
43	1	0	-6.092883	1.729272	-0.340907
44	1	0	-4.478980	0.296052	3.380253
45	1	0	-1.532241	-3.306148	0.625955
46	1	0	-4.581890	-2.828957	1.079811
47	1	0	-3.531907	-4.267974	0.952286
48	1	0	-4.846712	-4.030489	-0.217994
49	1	0	-4.738305	-2.265307	-1.785507
50	1	0	-3.334132	-0.759876	-3.175603
51	7	0	3.112743	1.581119	-1.023296
52	7	0	4.132779	-1.976407	0.146130
53	7	0	1.739357	2.291695	1.786719
54	7	0	-3.177066	-2.777080	-0.494253
55	8	0	2.676487	-0.449002	1.203299
56	8	0	1.173360	-0.932618	-1.101011
57	8	0	-0.530790	0.402885	0.658369
58	8	0	-1.749031	2.970641	-1.443219
59	8	0	0.336668	2.299117	-0.955804
60	12	0	1.407985	0.846799	0.178464
61	1	0	-1.614624	0.212287	-1.129317
62	7	0	1.027109	-2.935063	-0.032566
63	1	0	0.458637	-3.754339	0.136959
64	6	0	2.236496	-3.655389	1.957274
65	1	0	1.527082	-3.149710	2.619384
66	1	0	3.211620	-3.677412	2.451236
67	1	0	1.914508	-4.693775	1.813177

E(RB+HF-LYP) = -1820.97058838

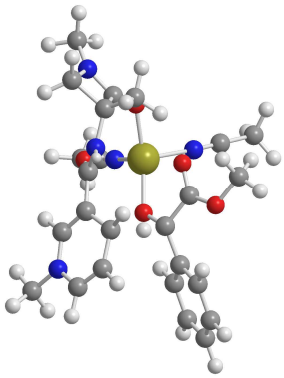
Sum of electronic and thermal Enthalpies= -1820.395166

Sum of electronic and thermal Free Energies= -1820.512335

HF (B3LYP/6-311++G**//B3LYP/6-31G* in MeCN) = -1821.606361

Frequency: 746.8i

TS32



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.764538	-0.735706	0.205943
2	6	0	2.846597	-1.527498	-1.643782
3	6	0	3.405994	-0.419476	-0.704671
4	6	0	0.939195	-1.892328	-0.089680
5	6	0	-3.998350	0.672914	-1.295014
6	6	0	-5.336512	0.970077	-1.045250
7	6	0	-4.796102	1.504701	1.250242
8	6	0	-0.475619	-2.329894	0.059788
9	6	0	2.274064	1.380373	5.126874
10	6	0	1.289553	5.739670	0.386439
11	6	0	1.213227	4.285940	0.437292
12	6	0	-0.880340	-2.727287	1.316698
13	6	0	1.917717	1.232066	3.722109
14	6	0	4.146856	-2.304982	-1.222533
15	6	0	-2.547923	-3.575512	2.920075
16	6	0	-3.070407	-3.173191	0.550751
17	6	0	-2.760137	-2.756669	-0.704822
18	6	0	-1.588175	0.477268	-0.473827
19	6	0	-0.816239	1.039429	-1.679964
20	6	0	-3.041283	0.803466	-0.272814
21	6	0	-1.463956	-2.179114	-0.985990
22	6	0	-0.793277	1.856915	-3.908378
23	6	0	-5.738583	1.390566	0.225289
24	6	0	-3.457454	1.204242	1.007394
25	6	0	2.824598	-1.103365	-3.114490
26	1	0	-5.105121	1.832717	2.238545
27	1	0	-0.181592	-2.749792	2.144108
28	1	0	-1.674331	-3.588900	3.571511
29	1	0	-3.291127	-2.882672	3.323350

30	1	0	-2.971876	-4.581309	2.868576
31	1	0	-3.508314	-2.827322	-1.485403
32	1	0	-1.677071	-0.776442	-0.951736
33	1	0	4.816912	-2.594608	-2.037121
34	1	0	3.975287	-3.146290	-0.545058
35	1	0	5.911179	-1.422607	1.045636
36	1	0	6.630544	-0.793605	-0.460520
37	1	0	5.663677	0.284508	0.580906
38	1	0	3.087793	2.105091	5.230249
39	1	0	1.408510	1.733880	5.695966
40	1	0	2.600900	0.418418	5.533762
41	1	0	2.010257	6.047107	-0.377863
42	1	0	0.307805	6.156859	0.141160
43	1	0	1.610456	6.131500	1.356640
44	1	0	-4.040319	-3.579136	0.812697
45	1	0	-0.222098	2.737362	-3.611532
46	1	0	-0.124503	1.096075	-4.316099
47	1	0	-1.568333	2.115849	-4.626991
48	1	0	-6.781425	1.627017	0.414731
49	1	0	-2.717839	1.289663	1.795968
50	1	0	-3.700265	0.350656	-2.287029
51	1	0	1.081635	-2.644620	-1.989198
52	1	0	-6.066907	0.874688	-1.843194
53	1	0	2.070342	-0.327532	-3.272461
54	1	0	3.797794	-0.704130	-3.413038
55	1	0	2.604194	-1.960458	-3.762070
56	7	0	1.154241	3.131883	0.477043
57	7	0	-2.141560	-3.138610	1.571312
58	7	0	4.553279	-1.076328	-0.516710
59	7	0	1.635946	1.116761	2.607053
60	7	0	1.552247	-2.094769	-1.280443
61	8	0	1.528070	-1.304310	0.839479
62	8	0	-0.812519	0.401434	0.573741
63	8	0	0.409665	1.155559	-1.594873
64	8	0	3.017172	0.691218	-0.312232
65	8	0	-1.507982	1.320708	-2.760416
66	12	0	1.141109	0.940163	0.489493
67	1	0	-1.141662	-2.188988	-2.027870

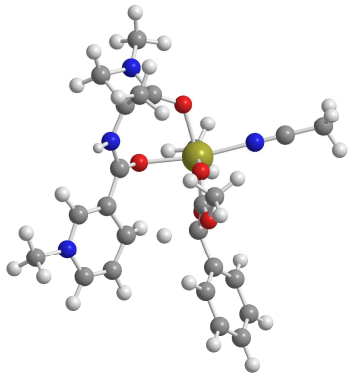
Sum of electronic and thermal Enthalpies= -1820.389752

Sum of electronic and thermal Free Energies= -1820.507837

E(RB+HF-LYP) = -1820.96495894

Frequency: 890.9i

TS33



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.723163	0.768227	0.548816
2	6	0	-2.808273	2.094788	-0.964067
3	6	0	-3.377580	0.738400	-0.449104
4	6	0	-0.742530	1.873487	0.438648
5	6	0	4.136117	-0.796151	-0.619611
6	6	0	5.418163	-1.323985	-0.481813
7	6	0	4.534841	-3.132303	0.859244
8	6	0	0.638435	2.365586	0.731027
9	6	0	-2.663540	-2.986574	4.353085
10	6	0	-2.011180	-5.431193	-1.928601
11	6	0	-1.778797	-4.140610	-1.294311
12	6	0	1.070442	3.648259	0.480434
13	6	0	-2.285295	-2.408416	3.070599
14	6	0	-4.094862	2.702488	-0.299042
15	6	0	2.758932	5.452842	0.555111
16	6	0	3.202070	3.183512	1.390352
17	6	0	2.839785	1.903452	1.686909
18	6	0	1.633012	-0.900341	-0.112652
19	6	0	1.044455	-0.546356	-1.500382
20	6	0	3.037618	-1.442674	-0.026555
21	6	0	1.548606	1.402744	1.312363
22	6	0	1.353554	-0.015251	-3.791196
23	6	0	5.620519	-2.494771	0.254203
24	6	0	3.251320	-2.605506	0.728936
25	1	0	6.261014	-0.823587	-0.949623
26	1	0	4.689251	-4.040912	1.433816
27	1	0	0.424419	4.421122	0.078691
28	1	0	1.964009	5.996504	0.044596
29	1	0	2.970285	5.937679	1.511745

30	1	0	3.655998	5.461382	-0.068516
31	1	0	3.544439	1.260357	2.201498
32	1	0	1.106938	0.577843	1.877106
33	1	0	-4.778082	3.222876	-0.977091
34	1	0	-3.911342	3.301525	0.597436
35	1	0	-5.887453	1.143659	1.563623
36	1	0	-6.575376	1.047210	-0.079015
37	1	0	-5.630193	-0.319172	0.570695
38	1	0	-3.628067	-3.496112	4.264411
39	1	0	-1.906043	-3.709789	4.671145
40	1	0	-2.743382	-2.199191	5.108988
41	1	0	-2.137619	-5.299084	-3.007668
42	1	0	-1.159789	-6.094531	-1.746905
43	1	0	-2.915918	-5.890572	-1.518398
44	1	0	4.172828	3.593393	1.644828
45	1	0	0.721915	-0.842324	-4.118648
46	1	0	0.774517	0.910308	-3.765797
47	1	0	2.224549	0.088521	-4.435339
48	1	0	6.620393	-2.905918	0.356866
49	1	0	2.401418	-3.086323	1.200067
50	1	0	3.991092	0.111802	-1.196427
51	7	0	-1.594391	-3.116927	-0.789978
52	7	0	2.328757	4.058852	0.785083
53	7	0	-4.496301	1.317641	0.001514
54	7	0	-1.982958	-1.951867	2.052730
55	8	0	-3.040263	-0.449382	-0.510785
56	8	0	-1.132945	0.829516	0.988375
57	8	0	0.716563	-1.440554	0.650514
58	8	0	-0.183072	-0.482661	-1.631630
59	8	0	1.892165	-0.300098	-2.471986
60	12	0	-1.218264	-1.184241	0.159756
61	1	0	1.794903	0.322163	0.289980
62	6	0	-2.792182	2.162612	-2.493846
63	1	0	-2.033899	1.481219	-2.890281
64	1	0	-3.764231	1.873640	-2.903338
65	1	0	-2.577337	3.181658	-2.837938
66	7	0	-1.517253	2.547864	-0.443816
67	1	0	-1.097436	3.308426	-0.963505

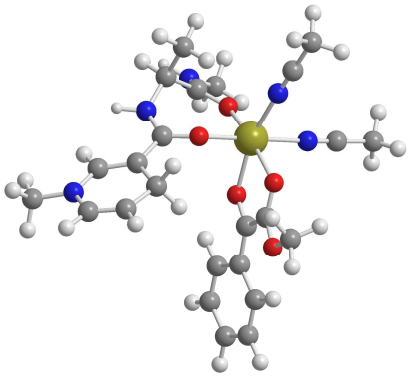
Sum of electronic and thermal Enthalpies= -1820.390923

Sum of electronic and thermal Free Energies= -1820.510507

E(RB+HF-LYP) = -1820.96608109

Frequency: 784.5i

16A



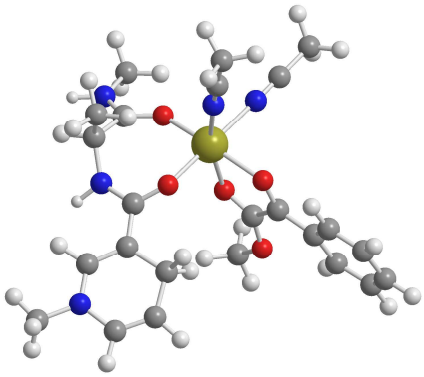
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.932310	-1.305547	-4.074268
2	6	0	-0.997450	-3.284855	-1.409476
3	6	0	-1.785645	-3.933116	-0.259435
4	6	0	-1.778663	-2.113159	-2.033066
5	6	0	0.779778	-2.116812	-0.015680
6	6	0	2.168721	-2.074750	0.387744
7	6	0	3.177199	-2.644819	-0.352309
8	6	0	-4.094803	2.035386	-0.304252
9	6	0	5.527007	-3.229366	-0.817962
10	6	0	-4.352559	-2.057141	3.713991
11	6	0	-3.528320	-1.491871	2.654199
12	6	0	4.824936	-2.110854	1.273902
13	6	0	3.932497	-1.498665	2.055905
14	6	0	2.484749	-1.315983	1.671309
15	6	0	0.314965	2.154153	-0.029028
16	6	0	0.009044	2.033111	1.491287
17	6	0	1.153749	3.168493	-0.647218
18	6	0	-5.204648	2.934781	-0.592244
19	6	0	0.432777	2.640963	3.742077
20	6	0	2.704102	5.060094	-2.012984
21	6	0	1.429908	3.012466	-2.028801
22	6	0	1.665755	4.298536	0.033245
23	6	0	2.430957	5.233998	-0.652973
24	6	0	2.202387	3.946124	-2.699916
25	1	0	1.828787	-1.656299	2.485119
26	1	0	2.256357	-0.241518	1.558123
27	1	0	-4.916500	3.646224	-1.372476
28	1	0	-5.481817	3.488499	0.310238
29	1	0	-6.070133	2.360071	-0.936723

30	1	0	1.065675	-3.586047	-1.379953
31	1	0	-3.134355	-0.445960	-3.437392
32	1	0	-3.876011	-1.759157	-4.390857
33	1	0	-2.372813	-0.984889	-4.957542
34	1	0	-1.907846	-3.246814	0.578218
35	1	0	-1.252707	-4.822843	0.088719
36	1	0	-4.821250	-1.253654	4.290783
37	1	0	-3.733884	-2.662377	4.384057
38	1	0	-5.135090	-2.689000	3.282211
39	1	0	0.605601	1.606802	4.042571
40	1	0	-0.598940	2.930150	3.947776
41	1	0	1.135527	3.316969	4.224087
42	1	0	3.306408	5.793783	-2.540764
43	1	0	1.031442	2.148528	-2.548635
44	1	0	1.459269	4.449769	1.083258
45	1	0	2.815549	6.102617	-0.128241
46	1	0	2.416602	3.816829	-3.756095
47	1	0	2.994233	-3.110384	-1.316545
48	1	0	6.242172	-2.454745	-1.113746
49	1	0	5.084153	-3.660744	-1.717379
50	1	0	6.059424	-4.017462	-0.276084
51	1	0	5.866495	-2.236793	1.545340
52	1	0	4.264691	-1.109609	3.013103
53	1	0	-2.775220	-4.244369	-0.610879
54	7	0	0.383419	-2.913143	-1.062477
55	7	0	-2.872418	-1.045896	1.812712
56	7	0	-3.215258	1.320116	-0.076457
57	7	0	4.472760	-2.661102	0.022824
58	8	0	-2.099799	-1.092513	-1.386314
59	8	0	-0.070190	-1.419652	0.609490
60	8	0	-0.254911	1.264010	-0.679702
61	8	0	0.699222	2.781572	2.312548
62	8	0	-0.839620	1.218242	1.843107
63	12	0	-1.569957	-0.115174	0.312679
64	1	0	-0.877258	-4.040518	-2.192178
65	7	0	-2.144691	-2.270760	-3.308513
66	1	0	-1.868159	-3.119760	-3.784188

E(RB+HF-LYP) = -1782.92460380
Sum of electronic and thermal Enthalpies= -1782.349648
Sum of electronic and thermal Free Energies= -1782.474985
HF (B3LYP/6-311++G**//B3LYP/6-31G* in MeCN) = -1783.550159

17A



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.271024	4.492690	-2.420552
2	6	0	-3.428051	1.698252	-0.046447
3	6	0	-3.433626	2.019651	1.456414
4	6	0	-2.454480	2.622035	-0.802533
5	6	0	-2.217839	-0.530112	0.185218
6	6	0	4.246462	-2.090154	-0.963532
7	6	0	5.332952	-2.887777	-0.625292
8	6	0	4.953223	-2.438121	1.731796
9	6	0	-1.552081	-4.294601	0.349975
10	6	0	0.354021	2.874647	4.805751
11	6	0	3.401605	4.916977	-0.697934
12	6	0	2.447627	3.847295	-0.434347
13	6	0	-2.415568	-1.959262	0.219799
14	6	0	0.277319	2.468613	3.408843
15	6	0	-3.671561	-2.516998	0.156699
16	6	0	-1.188115	-2.832758	0.445437
17	6	0	-5.262202	-4.398766	0.212376
18	6	0	-2.809631	-4.728984	0.236555
19	6	0	2.366091	-0.571422	-0.197873
20	6	0	1.640737	-0.390213	-1.562275
21	6	0	3.498462	-1.448372	0.051869
22	6	0	1.290479	-1.023664	-3.818571
23	6	0	5.685043	-3.067858	0.715870
24	6	0	3.875812	-1.630578	1.406168
25	1	0	-5.389763	-5.127896	-0.593623
26	1	0	-3.073027	-5.778783	0.182579
27	1	0	-0.753315	-5.028342	0.389218
28	1	0	-0.726313	-2.613975	1.420962
29	1	0	-0.407535	-2.592246	-0.294449

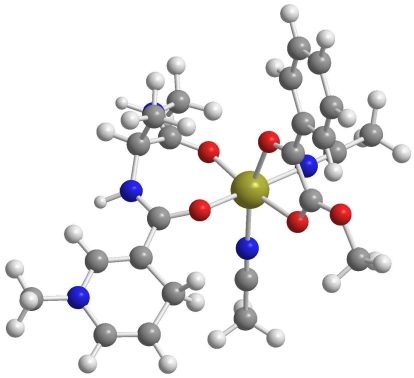
30	1	0	-3.670957	3.076878	1.613783
31	1	0	-5.453427	-4.890688	1.171965
32	1	0	-1.214242	4.401326	-2.175030
33	1	0	-2.622249	5.497640	-2.169955
34	1	0	-2.415577	4.316918	-3.490426
35	1	0	-2.467475	1.804773	1.913588
36	1	0	-4.200473	1.418421	1.953143
37	1	0	-3.929476	-0.182095	-0.858744
38	1	0	-0.175349	3.821760	4.949746
39	1	0	1.400491	3.003177	5.099578
40	1	0	-0.102799	2.109517	5.441292
41	1	0	3.555105	5.024706	-1.776236
42	1	0	4.360545	4.687903	-0.222642
43	1	0	3.022338	5.862007	-0.296588
44	1	0	1.451852	-0.015646	-4.203435
45	1	0	0.225845	-1.207720	-3.668156
46	1	0	1.732117	-1.772081	-4.472823
47	1	0	6.531660	-3.698294	0.971637
48	1	0	3.300813	-1.137153	2.181568
49	1	0	3.989811	-1.956627	-2.004881
50	1	0	5.909058	-3.371170	-1.407731
51	1	0	5.230134	-2.582347	2.771290
52	1	0	-4.566108	-1.902363	0.115677
53	1	0	-5.989151	-3.596082	0.076513
54	7	0	-3.193418	0.280018	-0.345717
55	7	0	1.690113	2.999494	-0.223290
56	7	0	0.213988	2.144577	2.300638
57	7	0	-3.908492	-3.843615	0.177022
58	8	0	-1.219084	2.591188	-0.615232
59	8	0	1.849963	0.127741	0.687791
60	8	0	0.755649	0.458048	-1.634601
61	8	0	-1.139633	-0.031688	0.618902
62	8	0	1.992081	-1.176751	-2.547288
63	12	0	0.204220	1.414376	0.230408
64	1	0	-4.433882	1.895920	-0.431014
65	7	0	-3.010571	3.497531	-1.644969
66	1	0	-4.016364	3.482579	-1.754556

E(RB+HF-LYP) = -1782.92612538

Sum of electronic and thermal Enthalpies= -1782.353093

Sum of electronic and thermal Free Energies= -1782.473547

18A



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.343209	4.673145	-2.737217
2	6	0	1.485827	1.003321	-2.693570
3	6	0	0.809313	2.296611	-2.201280
4	6	0	2.138655	-0.288625	-0.599430
5	6	0	3.146684	-1.146658	-0.027366
6	6	0	4.229346	-1.578314	-0.758348
7	6	0	-2.793145	3.409322	1.176222
8	6	0	6.291496	-2.886504	-1.090894
9	6	0	2.432202	3.334165	3.664551
10	6	0	1.586739	2.680782	2.673980
11	6	0	5.165984	-2.712751	1.106919
12	6	0	4.134175	-2.391280	1.891364
13	6	0	2.915324	-1.654398	1.390109
14	6	0	-2.464672	-0.923188	0.117033
15	6	0	-2.031821	-0.923831	1.610697
16	6	0	-3.405382	-1.848168	-0.491730
17	6	0	-3.834205	4.385898	1.469991
18	6	0	-2.260239	-1.728438	3.827669
19	6	0	-5.188167	-3.543738	-1.829696
20	6	0	-3.863344	-1.529034	-1.794971
21	6	0	-3.854012	-3.041413	0.122803
22	6	0	-4.733991	-3.879765	-0.550777
23	6	0	-4.751778	-2.365352	-2.450669
24	6	0	0.435995	-0.012573	-3.174876
25	1	0	-4.619490	4.334246	0.709306
26	1	0	-4.274266	4.180653	2.450860
27	1	0	-3.409490	5.394616	1.475267
28	1	0	-0.349541	4.574404	-1.902887
29	1	0	1.111337	5.411874	-2.488874

30	1	0	-0.197682	5.002445	-3.628278
31	1	0	2.016607	3.184369	4.665959
32	1	0	3.441683	2.912705	3.631350
33	1	0	2.487401	4.407708	3.458730
34	1	0	-1.200386	-1.968611	3.923223
35	1	0	-2.465507	-0.738790	4.238181
36	1	0	-2.882438	-2.486933	4.297449
37	1	0	-5.882827	-4.200288	-2.345437
38	1	0	-3.519147	-0.613695	-2.263233
39	1	0	-3.507237	-3.316865	1.108645
40	1	0	-5.068596	-4.798165	-0.079301
41	1	0	-5.109917	-2.108441	-3.442510
42	1	0	4.342671	-1.331313	-1.810072
43	1	0	6.209878	-3.974727	-1.182924
44	1	0	6.236603	-2.443614	-2.086955
45	1	0	7.261465	-2.638198	-0.649197
46	1	0	6.033931	-3.257894	1.458964
47	1	0	4.165946	-2.688505	2.934799
48	1	0	0.943460	-0.894522	-3.576143
49	1	0	2.029585	-2.308920	1.431483
50	1	0	3.407009	0.526205	-1.967131
51	1	0	2.673962	-0.815368	2.059319
52	1	0	-0.228858	-0.322131	-2.368171
53	1	0	-0.167856	0.428926	-3.974355
54	7	0	0.914340	2.162586	1.888932
55	7	0	2.432780	0.462594	-1.711495
56	7	0	-1.967120	2.634848	0.941659
57	7	0	5.210736	-2.355708	-0.259250
58	8	0	-1.923636	0.000118	-0.513799
59	8	0	-2.638619	-1.754979	2.417521
60	8	0	0.129216	2.343506	-1.153474
61	8	0	0.995528	-0.210232	-0.062500
62	8	0	-1.176175	-0.115867	1.962190
63	12	0	-0.385343	1.168395	0.423188
64	1	0	2.108178	1.266239	-3.555334
65	7	0	0.954407	3.368284	-2.986557
66	1	0	1.525952	3.277970	-3.816598

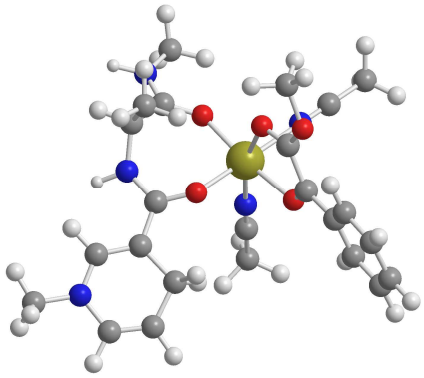
E(RB+HF-LYP) = -1782.92757376

Sum of electronic and thermal Enthalpies= -1782.352567

Sum of electronic and thermal Free Energies= -1782.476979

HF (B3LYP/6-311++G**//B3LYP/6-31G* in MeCN) = -1783.553117

19A



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.019651	5.336302	-0.137034
2	6	0	2.663649	1.843934	-1.608431
3	6	0	1.828297	1.494818	-2.851695
4	6	0	1.970640	2.940177	-0.777024
5	6	0	2.219426	-0.346885	-0.392675
6	6	0	2.787341	-1.628495	-0.056365
7	6	0	4.029032	-2.012001	-0.508873
8	6	0	1.090526	0.856950	4.950290
9	6	0	-2.334113	0.182485	-1.491692
10	6	0	-3.563780	4.493146	1.840756
11	6	0	-2.595476	3.503003	1.387066
12	6	0	5.889285	-3.606577	-0.774746
13	6	0	3.943332	-4.064541	0.684696
14	6	0	2.713131	-3.813308	1.139091
15	6	0	1.915662	-2.597341	0.732879
16	6	0	-2.521366	-0.692308	-0.218837
17	6	0	-3.428408	-1.821219	-0.092122
18	6	0	0.673439	0.978882	3.559555
19	6	0	-2.994182	0.819666	-3.677967
20	6	0	-5.105852	-4.024383	0.330657
21	6	0	-3.604512	-2.354356	1.209596
22	6	0	-4.105018	-2.423381	-1.179382
23	6	0	-4.931549	-3.518920	-0.961142
24	6	0	-4.440668	-3.439099	1.416636
25	1	0	5.752764	-4.483002	-1.416920
26	1	0	4.511477	-4.945318	0.960170
27	1	0	2.257959	-4.525457	1.820062
28	1	0	1.033136	-2.898373	0.145888

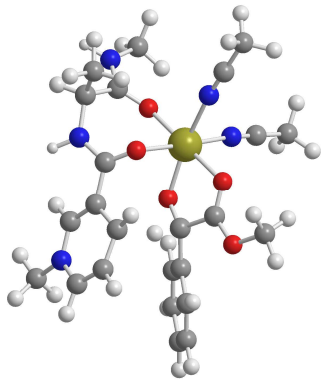
29	1	0	1.501547	-2.098394	1.621426
30	1	0	-3.129797	1.863373	-3.391319
31	1	0	0.238681	0.559170	5.569690
32	1	0	1.475150	1.816125	5.310741
33	1	0	1.666891	2.393662	-3.455662
34	1	0	1.946370	6.156033	-0.856624
35	1	0	2.675868	5.637037	0.685314
36	1	0	1.030644	5.101592	0.253424
37	1	0	0.857786	1.078011	-2.581454
38	1	0	2.371918	0.766262	-3.460072
39	1	0	4.029465	0.545621	-0.662272
40	1	0	-3.141196	5.079029	2.662995
41	1	0	-4.472790	3.994013	2.190806
42	1	0	-3.821651	5.168255	1.018768
43	1	0	-2.005282	0.668721	-4.113371
44	1	0	1.877023	0.101185	5.039934
45	1	0	-3.777940	0.491117	-4.356861
46	1	0	-5.759528	-4.876365	0.493261
47	1	0	-3.082507	-1.893014	2.040261
48	1	0	-3.976640	-2.048107	-2.184601
49	1	0	-5.442617	-3.981745	-1.799206
50	1	0	-4.580352	-3.834973	2.417542
51	1	0	4.610846	-1.385060	-1.178457
52	1	0	6.597897	-3.855442	0.021380
53	1	0	6.304906	-2.793549	-1.372629
54	7	0	3.038265	0.680908	-0.795686
55	7	0	-1.826907	2.717257	1.027806
56	7	0	4.611722	-3.186432	-0.198058
57	7	0	0.340483	1.075620	2.456517
58	8	0	0.907894	2.738656	-0.150581
59	8	0	-1.469030	1.055255	-1.467762
60	8	0	0.971612	-0.161774	-0.291858
61	8	0	-3.139386	-0.030184	-2.499486
62	8	0	-1.806086	-0.295707	0.714702
63	12	0	-0.333210	1.215275	0.369631
64	1	0	3.618118	2.251279	-1.957835
65	7	0	2.548770	4.144888	-0.799758
66	1	0	3.413085	4.250049	-1.315261

E(RB+HF-LYP) = -1782.92730280

Sum of electronic and thermal Enthalpies= -1782.352262

Sum of electronic and thermal Free Energies= -1782.477360

TS26A



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.619534	-2.957297	-0.092419
2	6	0	3.472799	-2.779260	-1.362569
3	6	0	2.993218	-1.925346	0.991997
4	6	0	0.470833	-1.940800	-0.910868
5	6	0	-1.012726	-2.042424	-0.932865
6	6	0	-1.726399	-2.827223	-0.049441
7	6	0	2.105089	2.947316	2.306371
8	6	0	-3.819014	-3.695737	0.917580
9	6	0	5.190841	2.120431	-2.686231
10	6	0	4.107278	1.615121	-1.853391
11	6	0	-3.776689	-2.271408	-1.087298
12	6	0	-3.145694	-1.451882	-1.972336
13	6	0	-1.740712	-1.181152	-1.834558
14	6	0	-1.395963	0.907779	-0.133827
15	6	0	-0.811972	2.016690	-1.036935
16	6	0	-2.746371	1.115000	0.509288
17	6	0	2.307883	3.969393	3.324980
18	6	0	-1.132102	3.816239	-2.546277
19	6	0	-5.219289	1.414149	1.802868
20	6	0	-2.867603	0.849983	1.883048
21	6	0	-3.886219	1.505558	-0.215199
22	6	0	-5.112145	1.658622	0.431986
23	6	0	-4.094183	1.007545	2.525594
24	1	0	4.529941	-2.918975	-1.115593
25	1	0	-2.006133	4.324192	-2.948908
26	1	0	-6.173247	1.543532	2.305678
27	1	0	-1.986173	0.539884	2.433467
28	1	0	-3.815887	1.709324	-1.278148

29	1	0	-5.983515	1.974336	-0.134309
30	1	0	-4.171830	0.823606	3.593526
31	1	0	0.673842	-3.793168	-0.097361
32	1	0	-0.514528	4.503082	-1.965669
33	1	0	3.334177	-1.790928	-1.800012
34	1	0	3.192529	-3.536428	-2.100279
35	1	0	-1.254640	-3.396014	0.743554
36	1	0	-4.278214	-3.009539	1.634626
37	1	0	-3.133569	-4.364109	1.439319
38	1	0	-4.592420	-4.290903	0.428077
39	1	0	5.096335	3.204909	-2.800143
40	1	0	5.149559	1.654369	-3.675691
41	1	0	6.156913	1.894049	-2.224495
42	1	0	-4.841538	-2.468291	-1.118454
43	1	0	-3.723044	-0.976601	-2.756752
44	1	0	-1.197749	-0.780612	-2.688129
45	1	0	1.839130	3.658272	4.263779
46	1	0	1.859611	4.913402	2.999747
47	1	0	3.378128	4.123577	3.493992
48	1	0	-0.541050	3.358577	-3.341598
49	7	0	1.169176	-2.946158	-0.337448
50	7	0	3.245124	1.216496	-1.193973
51	7	0	-3.075558	-2.927831	-0.099848
52	7	0	1.942490	2.136718	1.498102
53	8	0	2.485916	-0.788201	1.036562
54	8	0	1.034031	-0.945320	-1.414684
55	8	0	-0.462552	0.335505	0.585247
56	8	0	0.412058	2.111750	-1.162739
57	8	0	-1.667583	2.782003	-1.672917
58	12	0	1.455962	0.641580	-0.042140
59	1	0	-1.690485	0.093544	-1.098104
60	1	0	2.820803	-3.954809	0.310634
61	7	0	3.917475	-2.326107	1.871240
62	1	0	4.281517	-3.267216	1.790052
63	6	0	4.470365	-1.485135	2.933536
64	1	0	5.508957	-1.221331	2.711215
65	1	0	4.431177	-2.023868	3.883520
66	1	0	3.869386	-0.579550	3.001661

E(RB+HF-LYP) = -1782.89449709

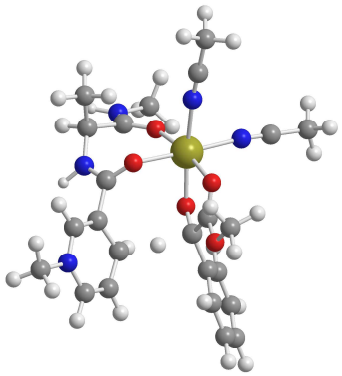
Sum of electronic and thermal Enthalpies= -1782.324389

Sum of electronic and thermal Free Energies= -1782.442696

HF (B3LYP/6-311++G**//B3LYP/6-31G* in MeCN) = -1783.533210

Frequency: 717.0i

TS27A



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.262614	-2.644669	-1.643412
2	6	0	-3.077557	-3.261762	-0.495798
3	6	0	-2.757481	-1.220905	-1.969623
4	6	0	-0.156552	-2.147962	-0.341990
5	6	0	1.344073	-2.296904	-0.331828
6	6	0	1.938616	-3.347664	0.312954
7	6	0	-2.844528	3.520939	0.241574
8	6	0	3.913855	-4.637310	1.045511
9	6	0	-4.771452	-0.513570	3.857107
10	6	0	-3.819441	-0.273838	2.780651
11	6	0	4.092214	-2.502403	-0.169231
12	6	0	3.567378	-1.426178	-0.821092
13	6	0	2.143580	-1.201062	-0.846797
14	6	0	1.216032	1.123261	0.061304
15	6	0	0.956332	1.112568	1.585666
16	6	0	2.269608	2.047379	-0.496487
17	6	0	-3.329625	4.892016	0.154562
18	6	0	1.760037	1.250084	3.809411
19	6	0	4.164977	3.742589	-1.682861
20	6	0	1.945193	2.783226	-1.647922
21	6	0	3.564965	2.154182	0.043112
22	6	0	4.501632	3.000396	-0.547427
23	6	0	2.885322	3.630698	-2.230962
24	1	0	-2.737653	-4.284528	-0.309533
25	1	0	2.746051	1.349736	4.258972
26	1	0	4.897012	4.403830	-2.136967
27	1	0	0.949416	2.686668	-2.065737
28	1	0	3.838851	1.587872	0.925892
29	1	0	5.496236	3.083659	-0.119144

30	1	0	2.619820	4.205331	-3.113590
31	1	0	-0.235340	-3.131998	-2.097496
32	1	0	1.128496	2.102854	4.063473
33	1	0	-4.134222	-3.300756	-0.778514
34	1	0	-2.978314	-2.678089	0.419496
35	1	0	1.366648	-4.155374	0.756430
36	1	0	4.261555	-5.336058	0.278777
37	1	0	3.179951	-5.131997	1.682357
38	1	0	4.757646	-4.320664	1.661532
39	1	0	-4.681291	0.272220	4.613722
40	1	0	-4.571033	-1.482271	4.325336
41	1	0	-5.792036	-0.511790	3.461777
42	1	0	5.159475	-2.682321	-0.107438
43	1	0	4.235484	-0.717302	-1.296368
44	1	0	1.724458	-0.632864	-1.682863
45	1	0	-2.710415	5.462233	-0.544943
46	1	0	-3.282778	5.367076	1.139470
47	1	0	-4.366173	4.901353	-0.196500
48	1	0	1.277426	0.320637	4.116491
49	7	0	-3.063563	-0.081009	1.927343
50	7	0	-2.458007	2.433583	0.310654
51	7	0	3.295089	-3.454434	0.418012
52	7	0	-0.804613	-2.668586	-1.399983
53	8	0	-2.588548	-0.260910	-1.194131
54	8	0	-0.717648	-1.534298	0.580048
55	8	0	0.103722	0.992589	-0.607199
56	8	0	-0.196643	0.972128	2.000432
57	8	0	2.000397	1.230487	2.374386
58	12	0	-1.542825	0.442378	0.431258
59	1	0	1.854513	-0.053914	-0.041895
60	1	0	-2.397521	-3.267864	-2.532267
61	7	0	-3.421501	-1.080604	-3.120298
62	1	0	-3.561991	-1.893787	-3.705187
63	6	0	-4.022448	0.182445	-3.554484
64	1	0	-3.372279	1.006908	-3.259842
65	1	0	-5.008717	0.321267	-3.100104
66	1	0	-4.124113	0.165439	-4.640463

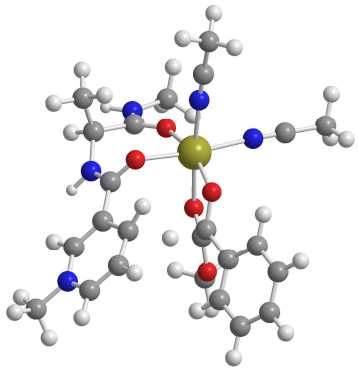
E(RB+HF-LYP) = -1782.88531600

Sum of electronic and thermal Enthalpies= -1782.315295

Sum of electronic and thermal Free Energies= -1782.436008

Frequency: 923.9i

TS28A



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.042465	0.765980	-2.363974
2	6	0	2.822844	2.766579	0.040533
3	6	0	3.402598	2.780291	1.466284
4	6	0	3.345253	1.541427	-0.744372
5	6	0	0.495319	2.061313	0.653775
6	6	0	-3.898878	-1.388752	-0.558737
7	6	0	-5.074872	-2.125876	-0.433830
8	6	0	-3.899581	-3.783968	0.876375
9	6	0	-0.974865	2.342906	0.678710
10	6	0	3.358350	-2.330233	4.352093
11	6	0	2.904424	-4.885936	-1.758465
12	6	0	2.506206	-3.611122	-1.175969
13	6	0	-1.568868	3.479700	0.175351
14	6	0	2.839440	-1.821442	3.089580
15	6	0	-3.520706	4.933263	-0.258917
16	6	0	-3.705316	2.779107	0.909747
17	6	0	-3.188725	1.634358	1.440507
18	6	0	-1.414948	-1.073549	-0.046743
19	6	0	-0.898640	-0.610184	-1.432356
20	6	0	-2.707354	-1.851717	0.025809
21	6	0	-1.801296	1.321603	1.280252
22	6	0	-1.277956	-0.124810	-3.720590
23	6	0	-5.077486	-3.326789	0.280768
24	6	0	-2.722362	-3.047278	0.758724
25	1	0	4.495541	2.809061	1.415518
26	1	0	-1.317677	0.633628	1.973047
27	1	0	-0.508428	-0.821632	-4.056337
28	1	0	-0.868178	0.886111	-3.671636
29	1	0	-2.148082	-0.163468	-4.373175

30	1	0	-5.994122	-3.901624	0.374091
31	1	0	-1.803804	-3.385397	1.224903
32	1	0	0.984681	3.684981	-0.488173
33	1	0	-3.844076	0.953211	1.970903
34	1	0	5.915505	0.407587	-1.808786
35	1	0	5.368328	1.185050	-3.317611
36	1	0	4.362735	-0.067171	-2.541532
37	1	0	3.099146	1.895507	2.025954
38	1	0	3.062616	3.675077	1.995498
39	1	0	-3.907060	-0.460711	-1.121710
40	1	0	-5.989830	-1.766149	-0.895606
41	1	0	-3.899539	-4.715619	1.434647
42	1	0	4.437513	-2.495210	4.274853
43	1	0	2.868850	-3.277697	4.598565
44	1	0	3.163017	-1.610641	5.153214
45	1	0	2.996907	-4.789235	-2.844671
46	1	0	2.152702	-5.648470	-1.531592
47	1	0	3.867729	-5.201270	-1.345650
48	1	0	-1.014411	4.287550	-0.288630
49	1	0	-2.749781	5.554755	-0.714396
50	1	0	-3.990981	5.485459	0.558570
51	1	0	-4.270381	4.680488	-1.012631
52	1	0	-4.752600	3.046505	0.991164
53	7	0	1.349410	2.885446	0.009832
54	7	0	2.187963	-2.601387	-0.711416
55	7	0	-2.906172	3.696393	0.265431
56	7	0	2.424994	-1.419913	2.087932
57	8	0	2.932529	0.382412	-0.558597
58	8	0	0.899287	1.038320	1.233277
59	8	0	-0.413507	-1.476160	0.701014
60	8	0	-1.768456	-0.527662	-2.413647
61	8	0	0.291585	-0.301878	-1.549048
62	12	0	1.420922	-0.781443	0.253841
63	1	0	-1.770249	0.079860	0.342856
64	1	0	3.171312	3.666236	-0.475455
65	7	0	4.333396	1.800653	-1.609234
66	1	0	4.662631	2.752711	-1.701413

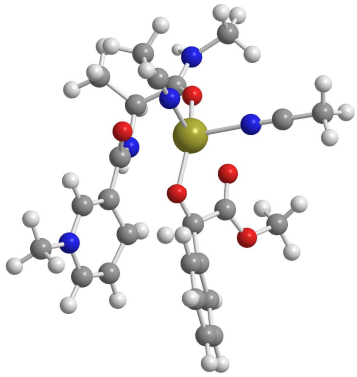
E(RB+HF-LYP) = -1782.88358570

Sum of electronic and thermal Enthalpies= -1782.313746

Sum of electronic and thermal Free Energies= -1782.433989

Frequency: 584.2i

TS29A



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.465562	0.619492	-1.567240
2	6	0	-2.854231	-2.179654	-1.561473
3	6	0	-3.513576	-3.295312	-0.722029
4	6	0	-3.483495	-0.805084	-1.242553
5	6	0	-0.700359	-2.067169	-0.295682
6	6	0	3.779573	1.368193	-1.179000
7	6	0	5.076698	1.771954	-0.868717
8	6	0	4.524739	1.759608	1.485389
9	6	0	0.778605	-2.255396	-0.329482
10	6	0	-2.713553	-0.039939	5.143121
11	6	0	-2.103527	5.194974	1.436018
12	6	0	-1.881085	3.778074	1.179687
13	6	0	1.362453	-2.764225	0.811877
14	6	0	-2.285569	0.145001	3.762958
15	6	0	3.288422	-3.555409	2.127613
16	6	0	3.503175	-2.756548	-0.188396
17	6	0	3.010864	-2.211867	-1.331644
18	6	0	1.430278	0.712927	-0.423754
19	6	0	0.570154	1.395551	-1.498277
20	6	0	2.835922	1.169017	-0.155321
21	6	0	1.627389	-1.793647	-1.406790
22	6	0	0.394677	2.589604	-3.538238
23	6	0	5.451924	1.972931	0.462077
24	6	0	3.228031	1.350810	1.181457
25	1	0	-4.591322	-3.324958	-0.907370
26	1	0	1.204301	-1.683788	-2.406151
27	1	0	-0.207444	3.383905	-3.094511
28	1	0	-0.253397	1.851534	-4.014795
29	1	0	1.112461	2.995750	-4.248213

30	1	0	6.461812	2.294025	0.699576
31	1	0	2.500407	1.183801	1.968184
32	1	0	-0.890806	-2.552228	-2.264576
33	1	0	3.675864	-2.056341	-2.172917
34	1	0	-5.863867	0.616283	-0.548198
35	1	0	-6.292040	0.640198	-2.278015
36	1	0	-4.844818	1.507198	-1.704529
37	1	0	-3.344673	-3.132585	0.343273
38	1	0	-3.094873	-4.264591	-1.007675
39	1	0	3.500649	1.220614	-2.216686
40	1	0	5.795631	1.931889	-1.666767
41	1	0	4.812290	1.917828	2.520872
42	1	0	-3.662520	0.478528	5.312378
43	1	0	-1.959736	0.366153	5.824945
44	1	0	-2.848127	-1.105598	5.352876
45	1	0	-2.427285	5.695063	0.517902
46	1	0	-1.176625	5.659441	1.787150
47	1	0	-2.876340	5.320064	2.200861
48	1	0	0.761366	-3.014632	1.677383
49	1	0	2.495649	-3.817527	2.828059
50	1	0	3.942746	-2.807237	2.582903
51	1	0	3.865127	-4.451819	1.887478
52	1	0	4.540642	-3.047320	-0.074043
53	7	0	-1.703534	2.653489	0.977425
54	7	0	2.688411	-3.007540	0.897003
55	7	0	-1.946716	0.292059	2.667691
56	7	0	-1.384716	-2.184046	-1.461523
57	8	0	-2.977321	0.044269	-0.484282
58	8	0	-1.279388	-1.767554	0.764736
59	8	0	0.695751	0.330791	0.586043
60	8	0	1.200688	1.951558	-2.510217
61	8	0	-0.655761	1.347458	-1.390878
62	12	0	-1.317361	0.517984	0.585519
63	1	0	1.659532	-0.406837	-1.140194
64	1	0	-3.056375	-2.380350	-2.618568
65	7	0	-4.669600	-0.584526	-1.817194
66	1	0	-5.060242	-1.293824	-2.423499

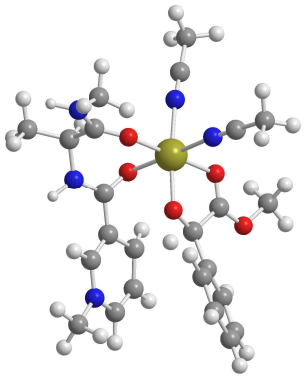
E(RB+HF-LYP) = -1782.88081755

Sum of electronic and thermal Enthalpies= -1782.311102

Sum of electronic and thermal Free Energies= -1782.430305

Frequency: 892.1i

TS30A



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.422103	-0.028790	-1.311339
2	6	0	2.137848	-1.290263	-2.793271
3	6	0	3.047005	-0.486570	-1.847729
4	6	0	0.519535	-1.852045	-0.927238
5	6	0	-0.884323	-2.289635	-0.631981
6	6	0	-1.038788	-3.349404	0.229530
7	6	0	1.879189	3.718755	0.986153
8	6	0	-2.388091	-5.063372	1.383289
9	6	0	4.501517	-0.581429	3.999419
10	6	0	3.590238	-0.274317	2.904921
11	6	0	-3.389153	-3.310276	-0.025565
12	6	0	-3.319653	-2.226062	-0.845115
13	6	0	-2.057838	-1.563247	-1.080191
14	6	0	-1.470880	0.781881	0.020038
15	6	0	-1.307053	0.505552	1.534018
16	6	0	-2.515231	1.755955	-0.455687
17	6	0	2.053679	5.157947	1.130302
18	6	0	-2.246440	0.213823	3.690571
19	6	0	-4.387301	3.572242	-1.485973
20	6	0	-2.149393	2.656514	-1.470184
21	6	0	-3.837916	1.761829	0.023952
22	6	0	-4.763005	2.668740	-0.487867
23	6	0	-3.079122	3.562534	-1.975714
24	6	0	1.882657	-0.445307	-4.056417
25	1	0	-1.440730	-5.251436	1.888655
26	1	0	-4.144572	1.065257	0.795661
27	1	0	-5.780475	2.670671	-0.108351
28	1	0	-2.784262	4.262018	-2.752551
29	1	0	1.273450	-1.005513	-4.774136

30	1	0	1.366747	0.482225	-3.793402
31	1	0	2.827132	-0.198620	-4.548776
32	1	0	0.123286	-1.869287	-2.906918
33	1	0	-1.131640	2.638024	-1.843616
34	1	0	4.980869	0.802341	-0.763456
35	1	0	5.961220	-0.683153	-0.620161
36	1	0	6.120356	0.356455	-2.059516
37	1	0	-0.182712	-3.855369	0.661001
38	1	0	-2.645636	-5.926014	0.761979
39	1	0	-3.166704	-4.907057	2.132913
40	1	0	4.022455	-0.353166	4.956702
41	1	0	4.767457	-1.642855	3.978187
42	1	0	5.413123	0.017245	3.907209
43	1	0	-4.320629	-3.817054	0.199153
44	1	0	-4.228737	-1.838640	-1.290784
45	1	0	-1.969052	-0.950112	-1.980031
46	1	0	1.117020	5.671862	0.892670
47	1	0	2.342181	5.399364	2.158055
48	1	0	2.834881	5.508388	0.448517
49	1	0	-1.744023	-0.739575	3.863236
50	1	0	-1.667087	1.027032	4.130465
51	1	0	-3.260825	0.202396	4.084398
52	1	0	-5.111946	4.278241	-1.880604
53	7	0	0.843969	-1.681541	-2.220492
54	7	0	1.740369	2.576803	0.870076
55	7	0	-2.260518	-3.854655	0.546744
56	7	0	2.866281	-0.029216	2.037790
57	8	0	1.336294	-1.695161	0.007113
58	8	0	-0.308923	0.775600	-0.569513
59	8	0	-2.399467	0.440459	2.261013
60	8	0	-0.175146	0.318136	1.987974
61	8	0	2.629648	0.438644	-1.123281
62	12	0	1.380235	0.441203	0.502529
63	1	0	-2.041701	-0.385491	-0.306736
64	1	0	2.666301	-2.209893	-3.077281
65	7	0	4.347855	-0.769208	-1.970620
66	1	0	4.618996	-1.529753	-2.581286

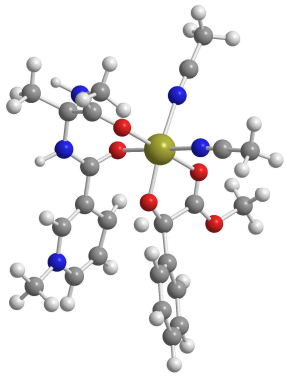
E(RB+HF-LYP) = -1782.88247389

Sum of electronic and thermal Enthalpies= -1782.312726

Sum of electronic and thermal Free Energies= -1782.433097

Frequency: 894.5i

TS31A



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.793869	2.615529	-0.409832
2	6	0	3.091450	1.747735	0.836246
3	6	0	0.547700	1.808766	-1.049470
4	6	0	-0.924379	1.998545	-1.035146
5	6	0	-1.563556	2.858716	-0.165574
6	6	0	2.026876	-3.043740	2.310842
7	6	0	-3.574154	3.889868	0.818327
8	6	0	5.069498	-2.414285	-2.754487
9	6	0	4.018790	-1.861982	-1.909564
10	6	0	-3.673482	2.377750	-1.117721
11	6	0	-3.118065	1.488851	-1.986290
12	6	0	-1.726031	1.146429	-1.881265
13	6	0	-1.431153	-0.897648	-0.117419
14	6	0	-0.914885	-2.059979	-0.994995
15	6	0	-2.772628	-1.028971	0.564317
16	6	0	2.212149	-4.050091	3.348257
17	6	0	-1.345259	-3.882578	-2.447857
18	6	0	-5.222503	-1.187511	1.924694
19	6	0	-2.848349	-0.720038	1.932066
20	6	0	-3.945267	-1.392418	-0.120838
21	6	0	-5.159821	-1.475563	0.559527
22	6	0	-4.063919	-0.807813	2.607970
23	6	0	4.365697	1.480882	2.940147
24	1	0	-2.248760	-4.352704	-2.830929
25	1	0	-6.168118	-1.262111	2.453684
26	1	0	-1.941474	-0.431696	2.452144
27	1	0	-3.910053	-1.629494	-1.178632
28	1	0	-6.057325	-1.770686	0.023771
29	1	0	-4.107266	-0.589908	3.671446

30	1	0	0.944443	3.664107	-0.262608
31	1	0	-0.761303	-4.586488	-1.853043
32	1	0	-1.035056	3.432244	0.587036
33	1	0	-4.076278	3.264811	1.561788
34	1	0	-2.832344	4.518336	1.311741
35	1	0	-4.305116	4.528022	0.317574
36	1	0	4.929000	-3.494388	-2.862480
37	1	0	5.033993	-1.950522	-3.745233
38	1	0	6.050122	-2.226306	-2.306394
39	1	0	-4.726375	2.632864	-1.124512
40	1	0	-3.746216	1.015337	-2.731762
41	1	0	-1.233173	0.685041	-2.734410
42	1	0	1.718113	-3.729814	4.270865
43	1	0	1.779377	-5.002105	3.025406
44	1	0	3.279084	-4.193156	3.545597
45	1	0	-0.736487	-3.478894	-3.258817
46	1	0	3.701183	0.627535	3.065753
47	1	0	4.390997	3.109219	1.572232
48	1	0	5.398443	1.131758	2.845124
49	1	0	4.287275	2.140254	3.808113
50	7	0	3.182336	-1.426590	-1.240536
51	7	0	1.339202	2.772013	-0.528671
52	7	0	3.961849	2.208530	1.735733
53	7	0	-2.905653	3.033937	-0.180673
54	7	0	1.878686	-2.245520	1.487714
55	8	0	-0.457607	-0.343063	0.561533
56	8	0	0.300701	-2.221267	-1.132165
57	8	0	-1.816693	-2.798031	-1.598930
58	8	0	2.521960	0.644447	0.970130
59	8	0	1.042141	0.768983	-1.538578
60	12	0	1.433103	-0.766486	-0.079745
61	1	0	-1.717304	-0.103151	-1.098376
62	1	0	3.110136	2.006154	-1.263651
63	6	0	3.475545	3.982865	-0.480407
64	1	0	4.564917	3.878620	-0.482918
65	1	0	3.203538	4.483579	-1.413814
66	1	0	3.187098	4.636327	0.352177

E(RB+HF-LYP) = -1782.89751880

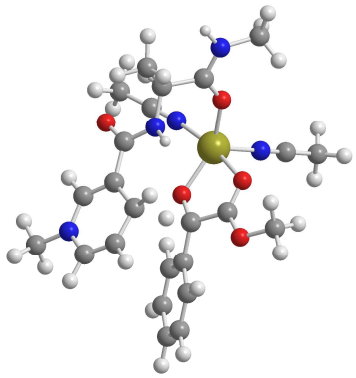
Sum of electronic and thermal Enthalpies= -1782.327558

Sum of electronic and thermal Free Energies= -1782.444852

HF (B3LYP/6-311++G**//B3LYP/6-31G* in MeCN) = -1783.532440

Frequency: 708.1i

TS32A



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.703889	0.257376	-1.494093
2	6	0	2.733533	-2.129116	-0.902009
3	6	0	3.578037	-0.842585	-0.931812
4	6	0	0.422444	-2.349627	-0.065020
5	6	0	-3.584696	1.702489	-0.997624
6	6	0	-4.871479	2.077783	-0.615151
7	6	0	-4.270747	1.798586	1.710648
8	6	0	-1.031562	-2.176998	-0.357218
9	6	0	2.101871	-2.047118	4.175993
10	6	0	2.820813	5.020953	2.476362
11	6	0	2.418052	3.760874	1.869467
12	6	0	-1.886354	-2.762507	0.553124
13	6	0	1.994082	-1.032614	3.139247
14	6	0	-4.108994	-3.404237	1.397541
15	6	0	-3.785252	-2.243235	-0.747260
16	6	0	-3.017258	-1.640182	-1.691821
17	6	0	-1.219664	0.968294	-0.357740
18	6	0	-0.411200	1.750538	-1.407748
19	6	0	-2.620151	1.385999	-0.022319
20	6	0	-1.594326	-1.450235	-1.484050
21	6	0	-0.305502	3.017428	-3.411718
22	6	0	-5.217034	2.131922	0.737094
23	6	0	-2.984511	1.419238	1.335718
24	6	0	3.096660	-3.190329	-1.951524
25	1	0	-1.045107	3.351843	-4.136163
26	1	0	-4.534357	1.845084	2.763340
27	1	0	-6.217742	2.434881	1.030728
28	1	0	-2.240843	1.166675	2.083228
29	1	0	3.005539	-2.807697	-2.974405

30	1	0	4.113122	-3.574212	-1.810199
31	1	0	2.426634	-4.047053	-1.842419
32	1	0	0.968492	-1.485375	-1.858223
33	1	0	0.443148	2.376252	-3.879978
34	1	0	6.083701	0.453738	-0.487252
35	1	0	6.537894	0.024335	-2.156356
36	1	0	5.185130	1.146281	-1.858513
37	1	0	-3.329803	1.674573	-2.050717
38	1	0	-5.604450	2.333051	-1.374682
39	1	0	3.137584	-2.127220	4.520500
40	1	0	1.463391	-1.785978	5.025656
41	1	0	1.781231	-3.007865	3.760372
42	1	0	3.116283	5.731187	1.697601
43	1	0	1.986567	5.441371	3.047001
44	1	0	3.667594	4.855057	3.149908
45	1	0	-1.484634	-3.268701	1.422298
46	1	0	-3.500445	-3.951204	2.117412
47	1	0	-4.680829	-2.630127	1.916647
48	1	0	-4.793015	-4.099673	0.905864
49	1	0	-4.856662	-2.366470	-0.852308
50	1	0	-3.487532	-1.273251	-2.596491
51	1	0	-1.469967	-0.135089	-1.134422
52	1	0	0.176624	3.865452	-2.923661
53	7	0	2.097947	2.759629	1.387742
54	7	0	1.902397	-0.241424	2.301546
55	7	0	-3.227944	-2.783978	0.390640
56	7	0	1.317396	-1.767703	-0.950463
57	8	0	3.155596	0.215220	-0.407393
58	8	0	0.812179	-2.959732	0.927135
59	8	0	-0.451966	0.537736	0.605497
60	8	0	0.815272	1.837859	-1.270969
61	8	0	-1.063337	2.254103	-2.427177
62	12	0	1.511816	0.896501	0.502094
63	1	0	-1.002978	-1.370812	-2.400032
64	1	0	2.876595	-2.557857	0.096976
65	7	0	4.786100	-0.885825	-1.485375
66	1	0	5.099938	-1.751756	-1.900748

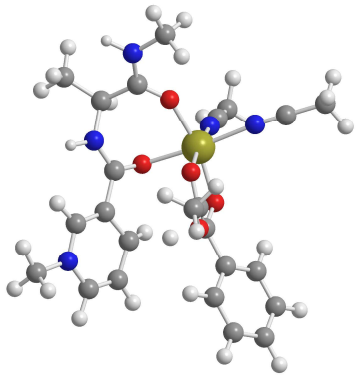
E(RB+HF-LYP) = -1782.88729308

Sum of electronic and thermal Enthalpies= -1782.317542

Sum of electronic and thermal Free Energies= -1782.436073

Frequency: 863.5i

TS33A



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.947096	0.462679	-2.361995
2	6	0	-3.129018	2.250867	0.540205
3	6	0	-3.508347	1.164944	-0.499159
4	6	0	-0.710783	1.898932	0.865847
5	6	0	4.046860	-0.981849	-0.539843
6	6	0	5.295343	-1.593048	-0.439958
7	6	0	4.304248	-3.424129	0.788909
8	6	0	0.710758	2.354855	0.813959
9	6	0	-3.094288	-2.995923	4.226737
10	6	0	-2.337358	-5.084987	-2.047688
11	6	0	-2.079960	-3.820120	-1.371801
12	6	0	1.137703	3.534097	0.242781
13	6	0	-2.629332	-2.356160	3.003395
14	6	0	2.879103	5.187964	-0.342768
15	6	0	3.376081	3.117166	0.883493
16	6	0	3.028637	1.934116	1.466634
17	6	0	1.540983	-0.958767	-0.025366
18	6	0	0.983995	-0.470634	-1.387876
19	6	0	2.911199	-1.595907	0.016182
20	6	0	1.684218	1.453320	1.382745
21	6	0	1.313740	0.190871	-3.638926
22	6	0	5.426983	-2.816818	0.221623
23	6	0	3.054591	-2.814235	0.695381
24	6	0	-4.011701	3.500225	0.569501
25	1	0	2.184561	0.293074	-4.283775
26	1	0	4.403549	-4.374081	1.305997
27	1	0	6.400287	-3.292840	0.295403
28	1	0	2.176874	-3.269344	1.140063
29	1	0	-3.958761	4.071602	-0.365851

30	1	0	-5.056032	3.234612	0.758401
31	1	0	-3.697544	4.158456	1.384642
32	1	0	-1.545257	3.569555	-0.011636
33	1	0	0.790265	1.143017	-3.530808
34	1	0	-5.481009	-0.359356	-1.875984
35	1	0	-5.618105	0.970060	-3.055670
36	1	0	-4.092995	0.056641	-2.907624
37	1	0	3.956227	-0.035138	-1.062875
38	1	0	6.166716	-1.117143	-0.880538
39	1	0	-4.153357	-3.256139	4.134945
40	1	0	-2.517094	-3.907699	4.409943
41	1	0	-2.964895	-2.317152	5.075419
42	1	0	-2.400977	-4.926039	-3.128619
43	1	0	-1.526281	-5.789501	-1.838375
44	1	0	-3.280882	-5.512626	-1.694575
45	1	0	0.468655	4.244016	-0.229995
46	1	0	2.021419	5.689217	-0.791290
47	1	0	3.306019	5.829313	0.432445
48	1	0	3.627305	4.995829	-1.115514
49	1	0	4.385689	3.511059	0.904897
50	1	0	3.787025	1.351692	1.976891
51	1	0	1.326494	0.714386	2.097459
52	1	0	0.630166	-0.566227	-4.026274
53	7	0	-1.873577	-2.818171	-0.833349
54	7	0	-2.257393	-1.850506	2.032746
55	7	0	2.442110	3.909527	0.254781
56	7	0	-1.718420	2.650935	0.373528
57	8	0	-2.931311	0.059663	-0.505061
58	8	0	-0.949972	0.790372	1.377276
59	8	0	0.584567	-1.521755	0.677967
60	8	0	-0.231388	-0.280926	-1.497265
61	8	0	1.842708	-0.236210	-2.355168
62	12	0	-1.309391	-0.997227	0.257901
63	1	0	1.762216	0.193243	0.432298
64	1	0	-3.190700	1.739571	1.506569
65	7	0	-4.483227	1.434910	-1.369117
66	1	0	-4.959536	2.323888	-1.314950

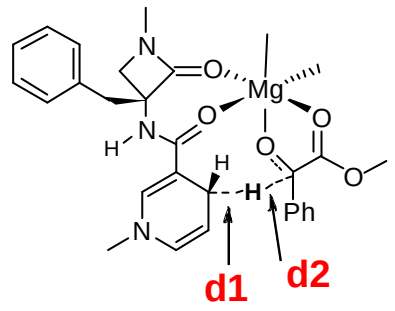
E(RB+HF-LYP) = -1782.88541352

Sum of electronic and thermal Enthalpies= -1782.315700

Sum of electronic and thermal Free Energies= -1782.435429

Frequency: 508.6i

6.4 B3LYP/6-31G* distances (Å) for hydride transfer in Transition States **TS-26-TS-33**



	d1	d2
TS26	1.50	1.28
TS27	1.45	1.33
TS28	1.58	1.26
TS29	1.43	1.34
TS30	1.41	1.34
TS31	1.48	1.30
TS32	1.42	1.34
TS33	1.51	1.30