Electronic Supplementary Material (ESI) for Chemical Science.


# Supplementary Information

**Visible Light Activated BINOL-derived Chiroptical Switches based on Boron Integrated Hydrazone Complexes**

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# S1 General Synthetic Procedures

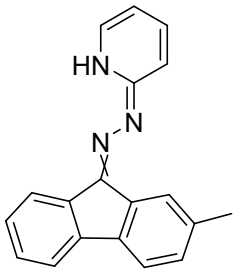
All reactions involving air sensitive reagents were performed under a $N_2$ atmosphere. Reagents were purchased from Sigma Aldrich, Acros or TCI Europe and used as received. Solvents were reagent-grade and used without prior water removal unless otherwise indicated. Anhydrous THF was obtained from a solvent purification system (MBraun SPS-800). Flash column chromatography was performed on silica gel (Merck, type 9385, 230–400 mesh) or on a Büchi Reveleris purification system using Büchi silica cartridges. Thin layer chromatography (TLC) was carried out on aluminium sheets coated with silica gel 60 F254 (Merck). Compounds were visualised with a UV lamp (254 nm) and/or by staining with KMnO4 or Cerium Ammonium Molybdate.

$^{1}$H and $^{13}$C NMR spectra were recorded on a Varian Mercury-Plus 400 or a Bruker Avance 600 NMR spectrometer at 298 K unless otherwise indicated. PSS studies were performed on a Varian Unity Plus 500 NMR spectrometer. Chemical shifts are given in parts per million (ppm) relative to the residual solvent signal (for $CDCl_3$ δ 7.26 for 1H, δ 77.16 for 13C and for $CD_2C_{l2}$ δ 5.32 for 1H, δ 53.84 for 13C). Multiplets in $^{1}$H NMR spectra are designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), br (broad). High resolution mass spectrometry (ESI+) was performed on an LTQ Orbitrap XL spectrometer. UV-Vis and CD spectra were recorded on a JASCO 810 CD spectrometer. For a typical CD irradiation experiment, the quartz cuvette was irradiated *ex-situ* from the side using a fiber coupled-LED M455F3 system from Thorlabs. In the case of thermal equilibration, the cuvette was placed in the dark at 293 K.

# S2 Preparation and Characterization of compounds

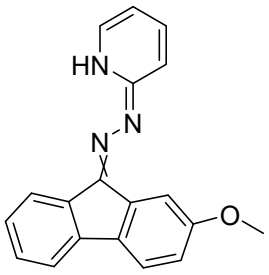
## Synthetic Procedures

2-((2-methyl-9H-fluoren-9-ylidene)hydrazineylidene)-1,2-dihydropyridine **L1**



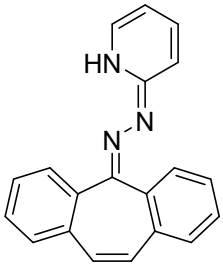

2-Methyl-9*H*-fluoren-9-one (0.200 g, 1.0 mmol, 1.0 eq) and 2-hydrazinopyridine (0.273 g, 2.5 mmol, 2.5 eq) were dissolved in 4 mL of EtOH. The mixture was heated at reflux overnight, after which the solution was allowed to reach room temperature. Subsequently, the mixture was stored in the freezer over night. The resulting crystals were filtered off to obtain the title compound as an orange solid (0.220, 75%).
$^{1}$H NMR (600 MHz, $CD_2Cl_2$) δ 9.40 (br, 2H), 8.27 – 8.21 (m, 2H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.91 – 7.85 (m, 3H), 7.79 – 7.56 (m, 8H), 7.47 (td, *J* = 7.5, 1.0 Hz, 1H), 7.41 – 7.29 (m, 4H), 7.21 (ddd, *J* = 7.7, 1.6, 0.8 Hz, 1H), 6.97 – 6.90 (m, 2H), 2.50 (m, *J* = 0.8 Hz, 6H).
$^{13}$C NMR (151 MHz, $CD_2Cl_2$) δ 156.8, 156.8, 147.7, 147.6, 141.6, 138.9, 138.6, 138.32, 138.3, 138.1, 138.1, 137.9, 137.7, 136.0, 130.7, 130.3, 130.0, 129.9, 129.6, 128.6, 127.4, 127.3, 125.8, 125.0, 121.4, 120.8, 120.4, 120.33, 119.5, 119.33, 117.2, 107.6, 107.5, 53.79, 53.6, 53.4, 53.3, 53.1, 21.5, 21.4.
HRMS (ESI+, m/z) calcd for $C_{19}H_{15}N_3$ [M+H$^+$]= 286.1339, found 286.1321.

2-((2-methoxy-9H-fluoren-9-ylidene)hydrazineylidene)-1,2-dihydropyridine **L2**




2-Methoxy-9*H*-fluoren-9-one[1] (0.60 g, 2.9 mmol, 1.0 eq) and 2-hydrazinopyridine (0.93 g, 8.6 mmol, 3.0 eq) were dissolved in 15 mL of EtOH. The mixture was heated at reflux overnight, after which the solvent was removed in vacuo. The resulting solid was recrystallized from EtOH to provide the title compound as an orange solid (0.385 g, 44%)
$^{1}$H NMR (600 MHz, $CD_2Cl_2$) δ 9.39 (br, 1H), 8.26 (d, *J* = 4.9, 1.9, 0.9 Hz, 1H), 8.03 (dt, *J* = 7.6, 0.9 Hz, 1H), 7.78 (ddd, *J* = 8.4, 7.2, 1.9 Hz, 1H), 7.72 (dt, *J* = 7.6, 0.9 Hz, 1H), 7.67 (dt, *J* = 8.4, 1.0 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.36 (td, *J* = 7.6, 1.0 Hz, 1H), 6.99 – 6.93 (m, 2H), 3.95 (s, 3H).
$^{13}$C NMR (151 MHz, $CD_2Cl_2$) δ 160.3, 156.7, 147.9, 141.6, 141.4, 139.5, 138.2, 131.6, 130.0, 129.9, 126.7, 126.6, 124.9, 120.7, 120.6, 119.9, 117.3, 115.3, 114.1, 107.5, 105.6, 55.6.
HRMS (ESI+, m/z) calcd for $C_{19}H_{15}N_3O$ [M+H$^+$]= 302.1288, found 302.1283.

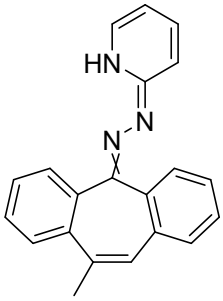
2-((5*H*-dibenzo[a,d][7]annulen-5-ylidene)hydrazineylidene)-1,2-dihydropyridine **L3**



5*H*-dibenzo[a,d][7]annulene-5-thione[2] (0.400 g, 1.80 mmol, 1.0 eq) and 2-hydrazinopyridine (0.295 g, 1.95 mmol, 1.5 eq) were dissolved in anhydrous THF and the mixture was stirred for 45 min at 50 °C. Hereafter, the volatiles were removed under reduced pressure. The crude solid was purified by column chromatography ($SiO_2$; Pentane:EtOAc 7/3) to obtain the title compound as white solid (0.425 g, 80%).

$^1$H NMR (600 MHz, $CD_2Cl_2$) δ 8.62 (br, 1H), 8.05 (ddd, *J* = 5.0, 2.0, 0.9 Hz, 1H), 7.71 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.60 – 7.53 (m, 4H), 7.52 – 7.46 (m, 2H), 7.45 – 7.36 (m, 2H), 7.34 – 7.31 (m, 1H), 6.95 (s, 2H), 6.75 (ddd, *J* = 7.2, 5.0, 1.1 Hz, 1H).
$^{13}$C NMR (151 MHz, $CD_2Cl_2$) δ 156.9, 147.7, 144.8, 139.2, 137.8, 135.2, 134.3, 131.5, 130.6, 130.4, 130.2, 129.1, 128.9, 128.8, 128.7, 128.1, 127.7, 127.0, 115.7, 107.3.
HRMS (ESI+, m/z) calcd for $C_{20}H_{15}N_3$ [M+H$^+$]= 298.1339, found 298.1341.

2-((10-methyl-5H-dibenzo[a,d][7]annulen-5-yilidne)hydrazineylidene)-1,2-dihydropyridine **L4**

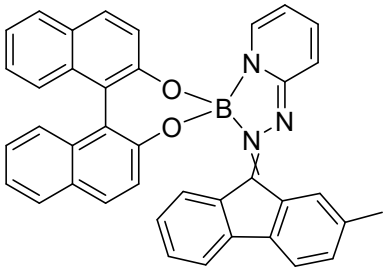


10-methyl-5*H*-dibenzo[a,d][7]annulen-5-one[3] (0.604, 2.74 mmol, 1.0 eq) and Lawesson's reagent (1.66 g, 4.11 mmol, 1.5 eq) were dissolved in 27 mL of anhydrous toluene. The mixture was heated at reflux overnight, whereafter the organic volatiles were removed in *vacuo*. The crude solid was purified by flash column chromatography ($SiO_2$; Pentane:$CH_2Cl_2$ 95/5) to obtain the thioketone as dark green solid (0.525 g, 81%), which was used immediately in the next reaction.
The thioketone (0.525 g, 2.22 mmol, 1.0 eq) and 2-hydrazinopyridine (0.364 g, 3.33 mmol, 1.5 eq) were dissolved in 20 mL of anhydrous THF and the mixture was stirred for 1 h at at 50 °C. Next, the mixture was allowed to cool down to room temperature and the solvent was removed under reduced pressure. The resulting crude solid was purified by column chromatography (SiO2; Pentane:EtOAc 7/3) to obtain the title compound as white solid (0.575 g, 83%).
$^1$H NMR (400 MHz, DMSO-d6) δ 8.91 (d, J = 3.4 Hz, 2H), 8.04 (ddd, J = 4.9, 1.9, 0.9 Hz, 2H), 7.78 – 7.74 (m, 1H), 7.66 – 7.31 (m, 21H), 7.20 – 7.15 (m, 2H), 7.03 – 6.92 (m, 3H), 6.81 – 6.74 (m, 3H), 2.38 (dd, J = 11.0, 1.4 Hz, 6H).
$^{13}$C NMR (151 MHz, $CD_2Cl_2$) δ 156.9, 156.8, 147.5, 145.8, 145.7, 140.0, 139.0, 137.9, 137.3, 136.4, 136.1, 135.4, 134.7, 132.2, 131.5, 131.2, 130.2, 129.8, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.4, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 127.0, 126.7, 126.5, 126.2, 126.0, 115.6, 107.4, 25.0, 24.4.
HRMS (ESI+, m/z) calcd for $C_{21}H_{17}N_3$ [M+H$^+$]= 312.1495, found 312.1489.

**General procedure demethylative direct borylation methodology.**

(R)-2,2'-dimethoxy-1,1'-binaphthalene (1.0 eq) was dissolved in anhydrous $CH_2Cl_2$ (0.1 M). The colorless solution was cooled down to 0 °C and $BBr_3$ (1.3 eq, 1.0 M in $CH_2Cl_2$) was added dropwise. The solution was stirred for 5 more min at 0 °C, after which the mixture was stirred for 3 h at room temperature. In parallel, a solution of hydrazone (1.3 eq) and DBU (1.5 eq) in anhydrous $CH_2Cl_2$ (0.1 M) was prepared. This solution was added dropwise to the ice-cooled mixture containing the boron intermediate. Subsequently, the deep red mixture was stirred for 5 more minutes at 0 °C, before it was allowed to stir at room temperature overnight. Subsequently, the reaction mixture was poured onto a plug of Silica (3 cm) or basic alumina (3 cm) and washed with toluene or $CH_2Cl_2$ until the filtrate appeared to be colorless. The organic volatiles were remove under reduced pressure. The crude products were purified by column chromatography to provide the highly colored boron complexes.

Complex **1**




The general procedure was followed using 80 mg of (R)-2,2'-dimethoxy-1,1'-binaphthalene (0.25 mmol) and 93 mg of hydrazone ligand **L1** (0.33 mmol). The product was purified by column chromatography (SiO2; Toluene: Pentane 9/1) and obtained as a dark red, lustrous solid (28 mg, 19%) as a *trans-cis* mixture (1 : 0.63).

$^1$H NMR (600 MHz, $CD_2C_{l2}$) δ 9.24 (d, *J* = 7.8 Hz, 1H), 9.10 (s, 1H), (8.01 (m, *J* = 8.2, 1.7 Hz, 3H), 7.98 (dd, *J* = 11.4, 8.8 Hz, 3H), 7.89 – 7.82 (m, 4H), 7.62 (dd, *J* = 20.9, 8.2 Hz, 3H), 7.56 – 7.15 (m, 33H), 6.99 (dd, *J* = 10.6, 8.8 Hz, 3H), 6.83 – 6.77 (m, 2H), 6.24 (dt, *J* = 6.2, 1.3 Hz, 1H), 6.11 – 6.05 (m, 1H), 5.40 (t, *J* = 20 Hz, 1H), 2.52 (s, *J* = 5.7, 2H), 0.82 (s, 3H).

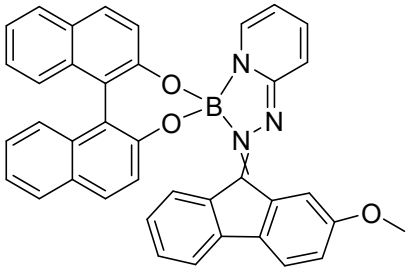
$^{13}$C NMR (151 MHz, $CD_2Cl_2$) δ 160.2, 154.9, 153.5, 153.1, 149.6, 141.4, 141.1, 141.1, 140.7, 138.6, 138.4, 138.4, 137.8, 136.7, 136.6, 134.1, 133.9, 133.6, 133.5, 133.4, 133.4, 132.5, 132.3, 132.0, 131.7, 131.6, 131.4, 130.9, 130.8, 130.8, 130.5, 130.4, 129.8, 129.7, 129.4, 129.0, 128.3, 128.3, 128.2, 128.1, 128.0, 127.8, 127.3, 127.2, 127.1, 126.9, 126.5, 125.9, 125.8, 125.7, 125.5, 125.5, 124.3, 124.2, 123.6, 123.5, 123.3, 123.1, 122.7, 122.6, 122.4, 122.3, 120.2, 119.6, 119.1, 119.0, 119.0, 118.7, 113.2, 113.1, 110.2, 110.1, 21.7, 19.5.

HRMS (ESI+, m/z) calcd for $C_{39}H_{26}N_3O_2$ [M+H$^+$]= 580.2191, found 580.2178.

UV-Vis: see figure 1, p. 17.

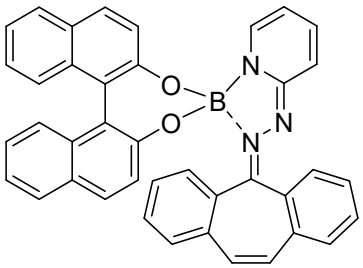
CD: see figure 5, p. 19.

Complex **2**



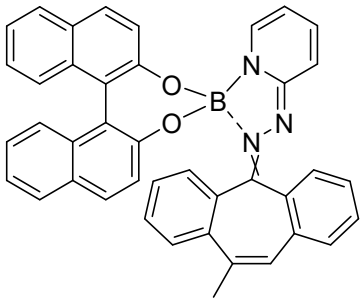
The general procedure was followed using 80 mg of (R)-2,2'-dimethoxy-1,1'-binaphthalene (0.25 mmol) and 98 mg of hydrazone ligand **L2** (0.33 mmol). The product was purified by column chromatography (SiO2; $CH_2Cl_2$ : Pentane 4/1) and yielded a deep red solid (30 mg, 20%) as a *trans-cis* mixture (1 : 0.22).
$^1$H NMR (600 MHz, $CD_2Cl_2$): δ 9.17 (dt, *J* = 7.8, 0.9 Hz, 1H), 8.04 – 7.93 (m, 2H), 7.81 – 7.77 (m, 1H), 7.70 (d, *J* = 2.3 Hz, 1H), 7.56 – 7.27 (m, 13H), 7.02 (dt, *J* = 8.9, 1.0 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 1H), 6.44 – 6.36 (m, 2H), 6.13 (ddd, *J* = 7.0, 6.3, 1.1 Hz, 1H), 2.77 (s, 3H).
$^{13}$C NMR (151 MHz, $CD_2Cl_2$): δ 159.3, 154.9, 153.3, 141.5, 141.2, 136.7, 134.0, 133.6, 133.4, 133.3, 133.3, 131.8, 131.6, 130.8, 130.5, 129.7, 129.6, 128.2, 127.9, 127.3, 127.0, 126.9, 126.5, 125.7, 125.2, 124.3, 123.4, 123.2, 122.4, 119.8, 118.6, 115.4, 113.5, 113.2, 110.3, 54.5.
HRMS (ESI+, m/z) calcd for $C_{39}H_{26}N_3O_3$ [M+H$^+$]= 596.2140, found 596.2122.
UV-Vis: see figure 2, p. 17.
CD: see figure 6, p. 19.

Complex **3**



The general procedure was followed using 400 mg of (R)-2,2'-dimethoxy-1,1'-binaphthalene (1.27 mmol) and 490 mg of hydrazone ligand **L3** (1.65 mmol). The product was purified by column chromatography (SiO2; Pentane: Acetone 4/1) and yielded a bright yellow solid (52 mg, 22%).
$^1$H NMR (600 MHz, $CD_2Cl_2$): δ 7.94 – 7.87 (m, 2H), 7.85 – 7.79 (m, 2H), 7.69 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.48 – 7.42 (m, 2H), 7.37 (dtd, *J* = 7.8, 6.4, 1.2 Hz, 2H), 7.31 – 7.24 (m, 2H), 7.20 – 7.06 (m, 6H), 7.02 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.60 – 6.54 (m, 2H), 6.52 (td, *J* = 7.5, 1.3 Hz, 1H), 6.30 (dt, *J* = 6.3, 1.3 Hz, 1H), 6.15 (td, *J* = 7.5, 1.3 Hz, 1H), 5.89 (td, *J* = 6.5, 1.0 Hz, 1H).
$^{13}$C NMR (151 MHz, $CD_2Cl_2$): δ 160.5, 154.1, 153.8, 153.2, 140.2, 135.8, 134.0, 133.9, 133.2, 133.0, 132.8, 131.5, 131.1, 130.6, 130.0, 129.9, 129.6, 129.5, 129.4, 128.7, 128.6, 128.6, 128.1, 128.1, 128.0, 127.7, 127.5, 126.9, 126.6, 126.1, 125.4, 124.9, 123.8, 123.1, 122.9, 122.2, 122.0, 119.0, 111.9, 107.7.
HRMS (ESI+, m/z) calcd for $C_{40}H_{26}N_3O_2$ [M+H$^+$]= 592.2191, found 592.2194.
UV-Vis: see figure 3, p. 18.
CD: see figure 7, p. 20.

Complex **4**

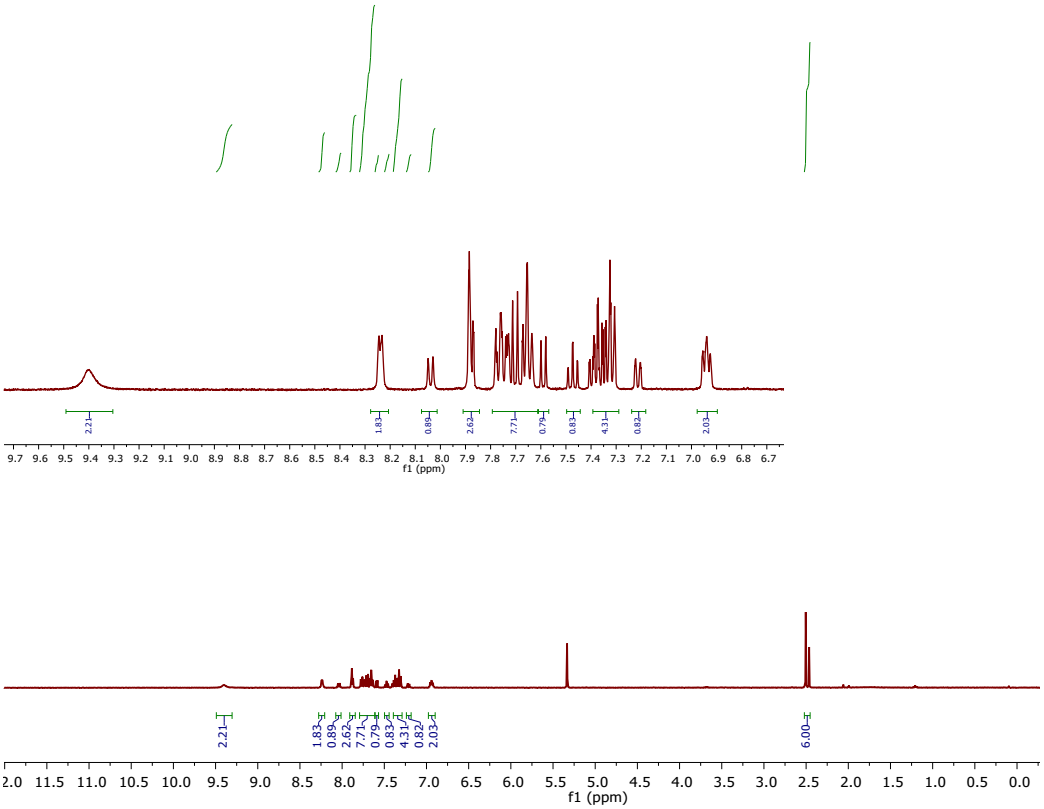



The general procedure was followed using 400 mg of (R)-2,2'-dimethoxy-1,1'-binaphthalene (0.25 mmol) and 514 mg of hydrazone ligand **L4** (1.65 mmol). The product was purified by column chromatography (SiO2; Pentane: Acetone 4/1) and yielded a bright yellow solid (11 mg, 13%).
$^{1}$H NMR (400 MHz, $CD_2Cl_2$) δ 7.93 – 7.84 (m, 4H), 7.81 – 7.55 (m, 7H), 7.47 – 7.31 (m, 11H), 7.30 – 6.95 (m, 16H), 6.71 – 6.60 (m, 1H), 6.60 – 6.48 (m, 4H), 6.41 (d, *J* = 8.7 Hz, 1H), 6.23 (dd, *J* = 22.8, 6.3 Hz, 2H), 5.97 (t, *J* = 7.5 Hz, 2H), 5.90 – 5.81 (m, 2H), 2.64 (d, *J* = 1.4 Hz, 2H), 2.51 (d, *J* = 1.4 Hz, 3H).
$^{13}$C NMR (151 MHz, $CD_2Cl_2$) δ 160.5, 154.9, 153.9, 153.9, 153.3, 153.3, 152.8, 140.2, 140.2, 136.9, 136.4, 136.2, 135.8, 135.7, 135.4, 134.9, 134.5, 133.6, 133.2, 133.2, 133.2, 132.9, 132.9, 132.0, 131.3, 130.7, 130.6, 129.6, 129.6, 129.5, 129.5, 129.5, 129.5, 129.4, 129.3, 129.2, 129.0, 128.8, 128.7, 128.6, 128.6, 128.4, 128.4, 128.2, 128.1, 128.0, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5, 127.3, 126.9, 126.9, 126.8, 126.7, 126.6, 126.6, 126.4, 125.7, 125.8, 125.4, 125.4, 124.9, 124.8, 124.1, 123.9, 123.9, 123.8, 123.1, 123.0, 122.4, 122.3, 121.8, 121.7, 119.0, 118.9, 117.7, 115.6, 111.8, 111.8, 111.2, 107.6, 107.48, 24.4, 23.9.
HRMS (ESI+, m/z) calcd for $C_{41}H_{28}N_3O_2$ [M+H$^+$]= 606.2347, found 606.2339.
UV-Vis: see figure 4, p. 18.
CD: see figure 8, p. 20.

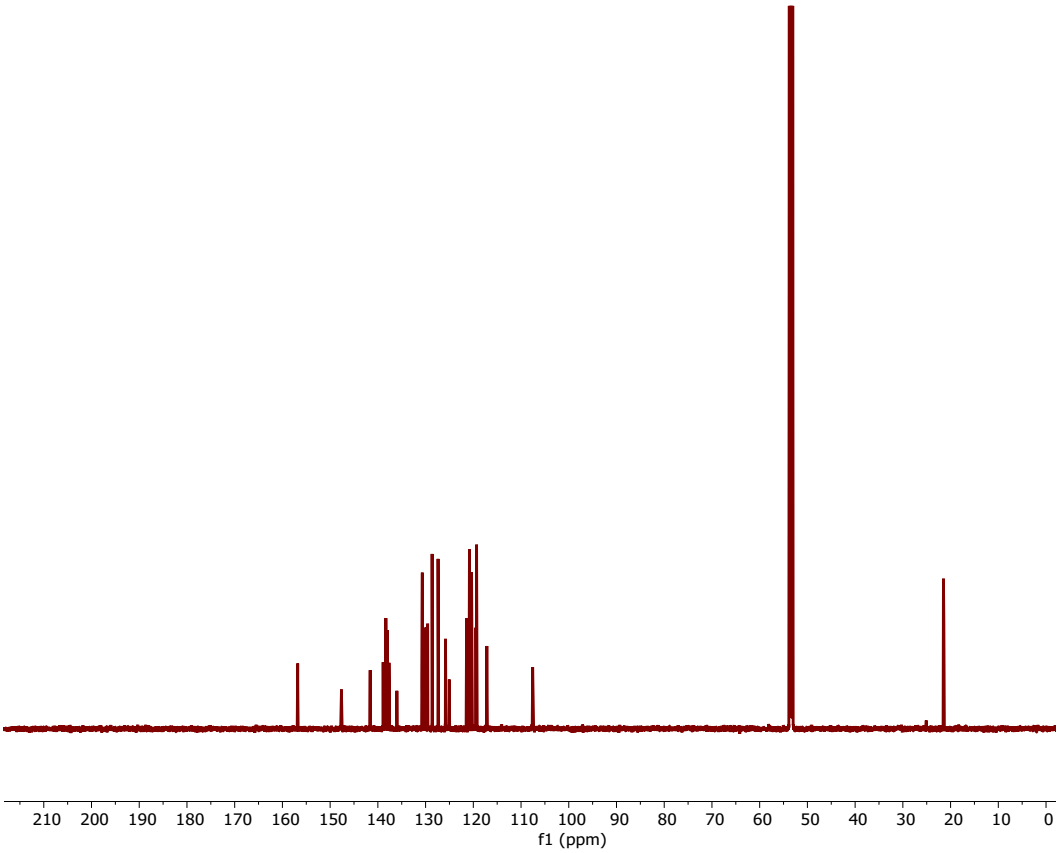
NMR spectra

2-((2-methyl-9H-fluoren-9-ylidene)hydrazineylidene)-1,2-dihydropyridine **L1** ($CD_2Cl_2$)

$^1$H NMR

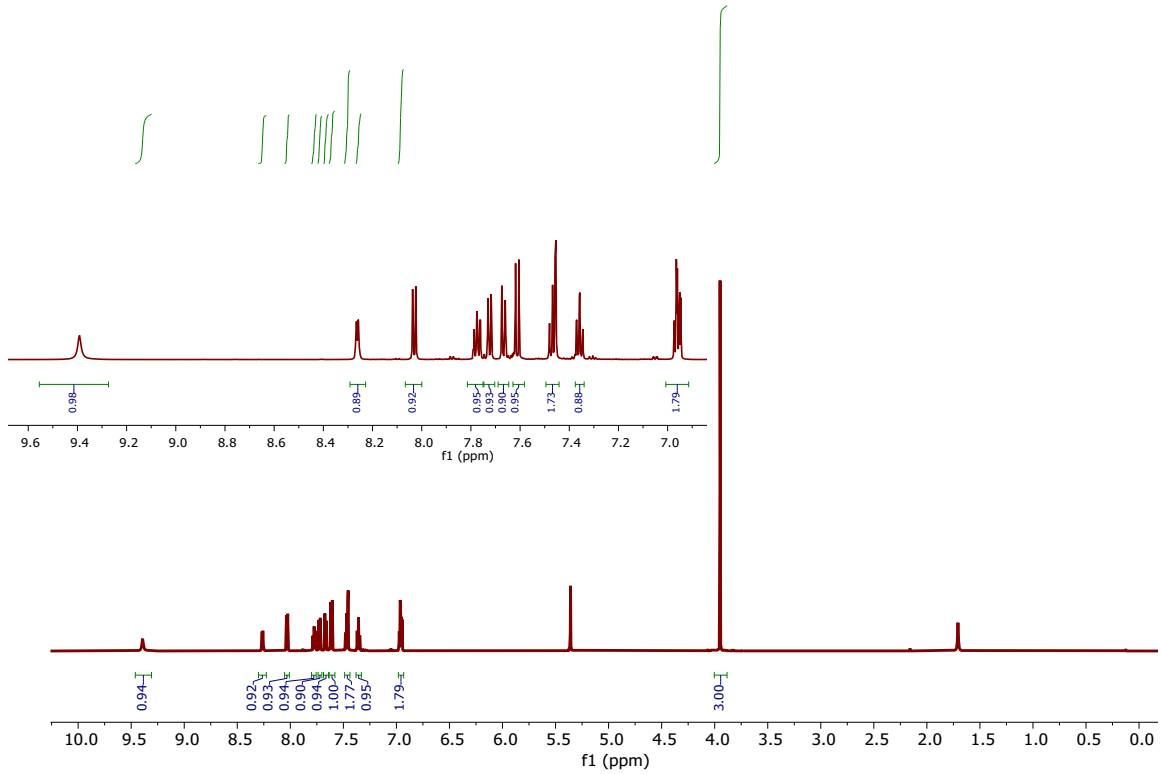



$^{13}$C NMR

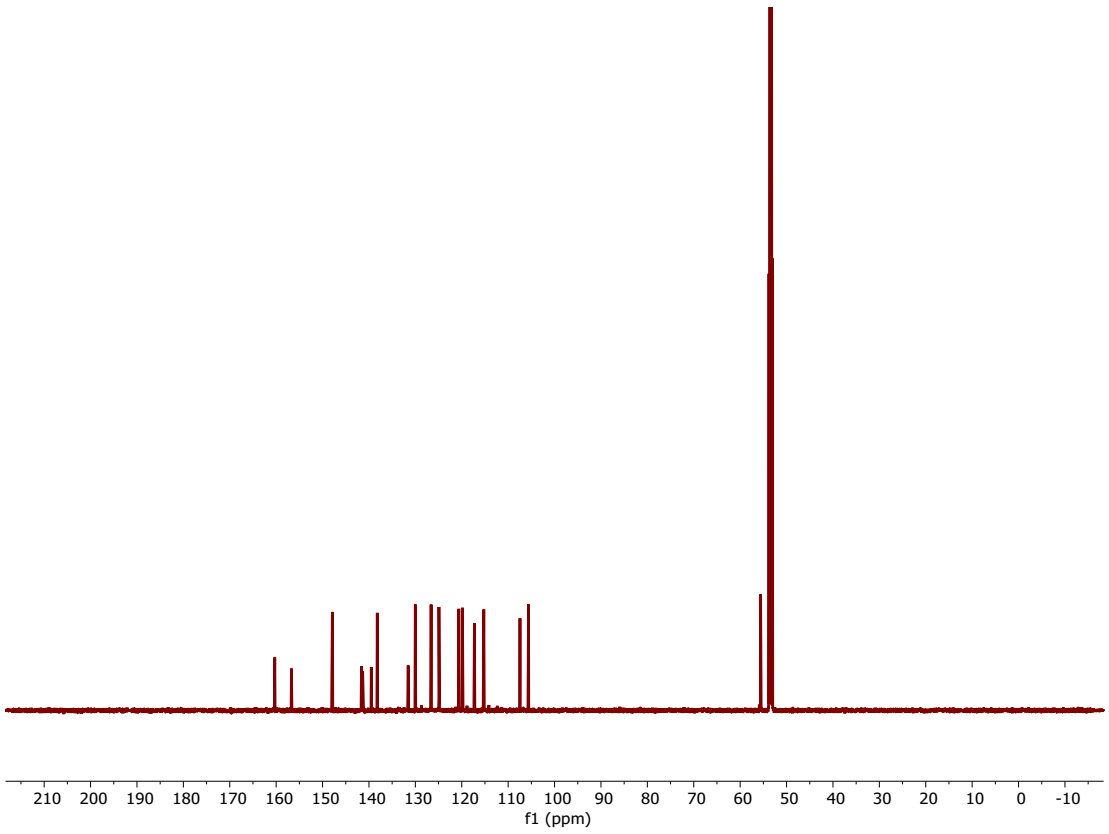


2-((2-methoxy-9H-fluoren-9-ylidene)hydrazineylidene)-1,2-dihydropyridine **L2** ($CD_2Cl_2$)

$^1$H NMR

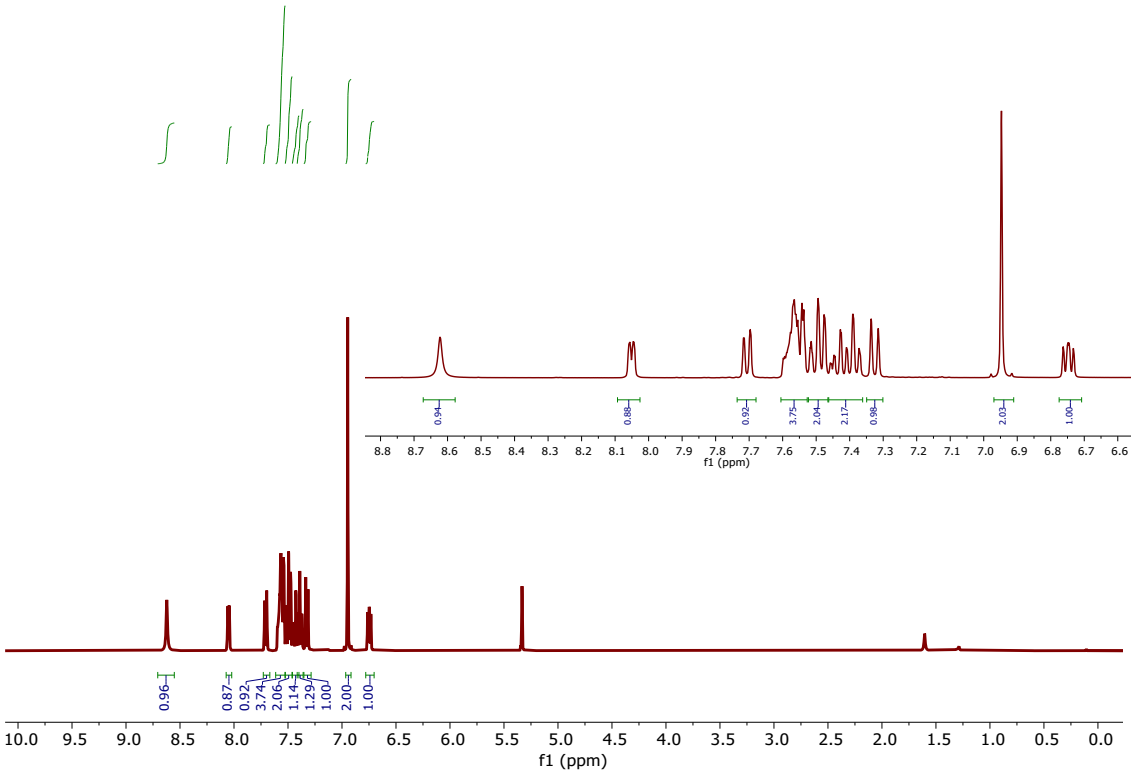



$^{13}$C NMR

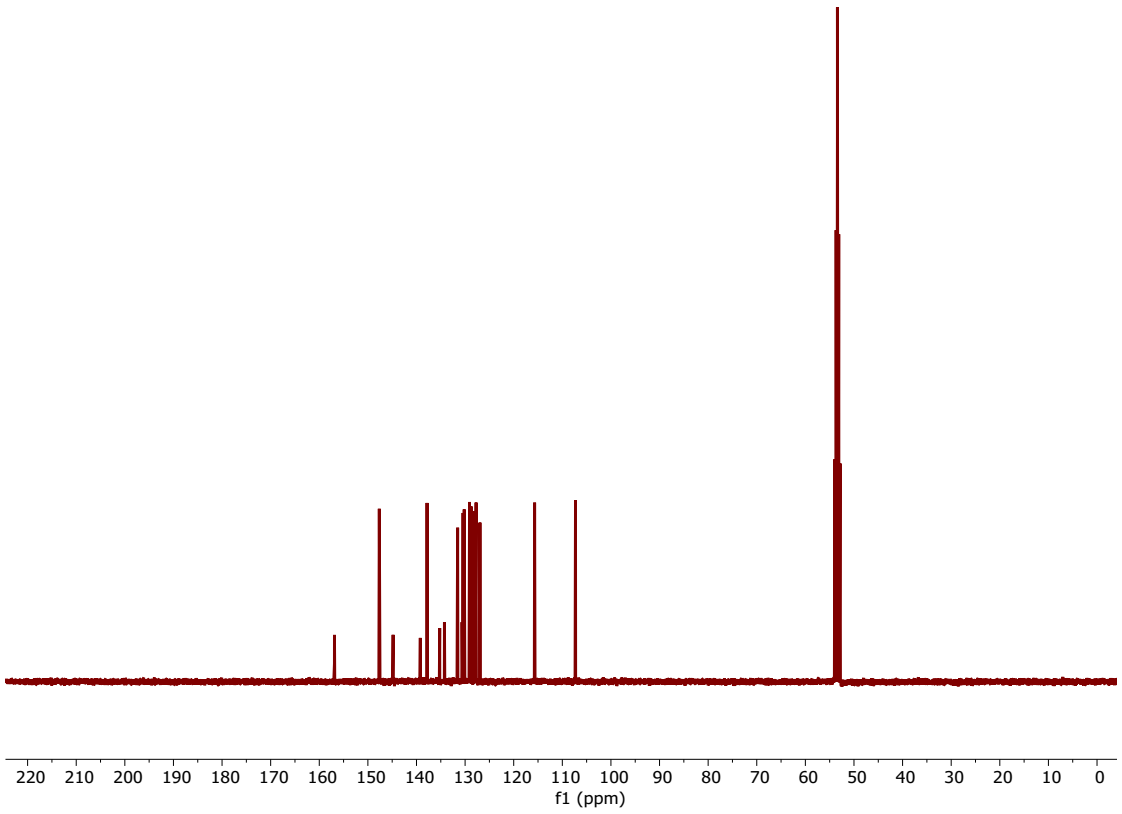


2-((5*H*-dibenzo[a,d][7]annulen-5-ylidene)hydrazineylidene)-1,2-dihydropyridine **L3** ($CD_2Cl_2$)

$^1$H NMR

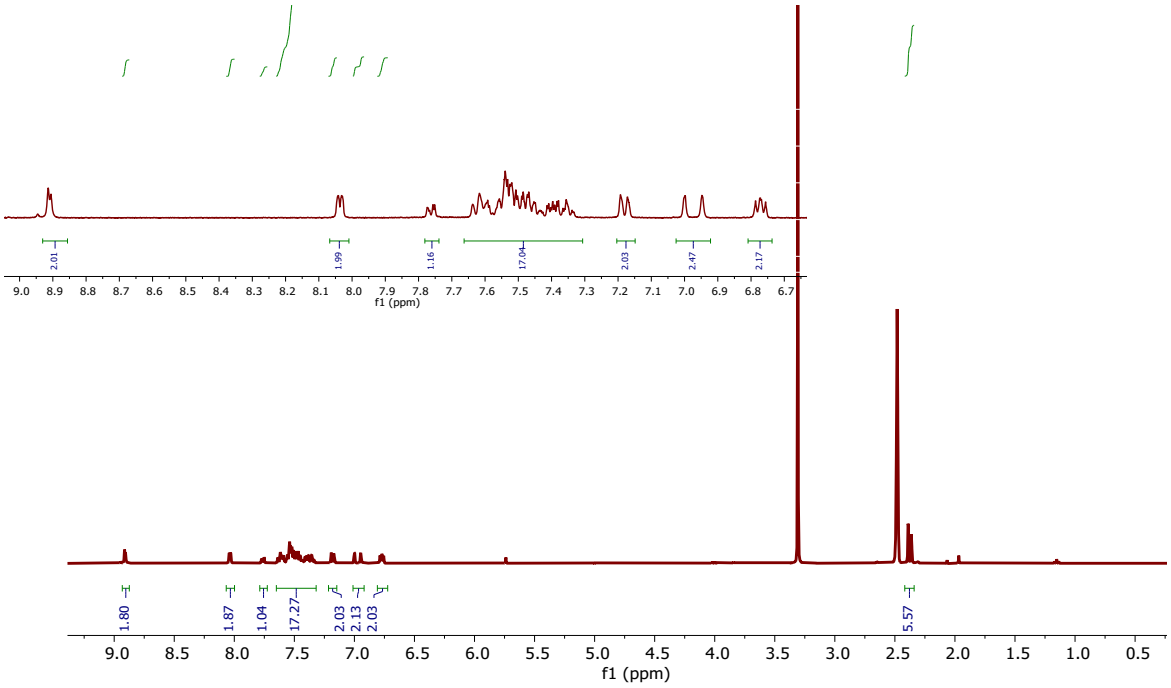



$^{13}$C NMR

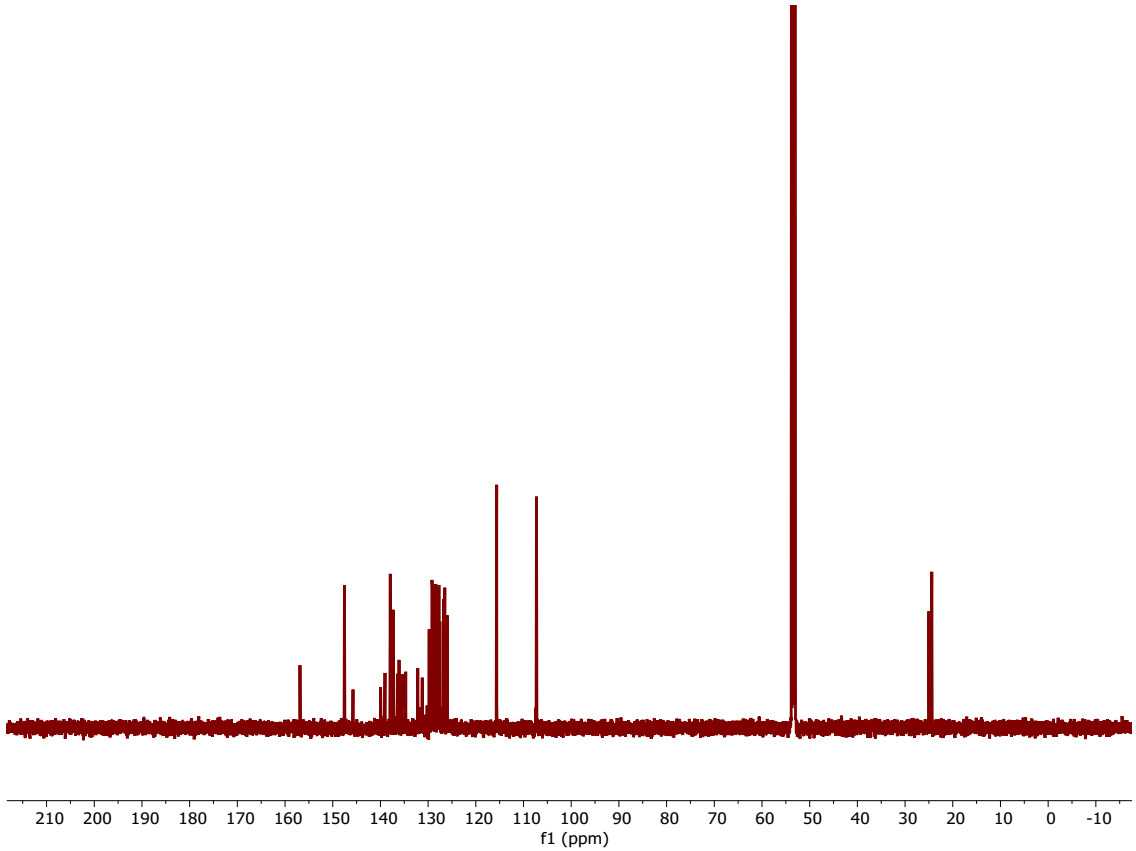


2-((10-methyl-5H-dibenzo[a,d][7]annulen-5-yilidne)hydrazineylidene)-1,2-dihydropyridine **L4** (DMSO-d6)

$^{1}$H NMR

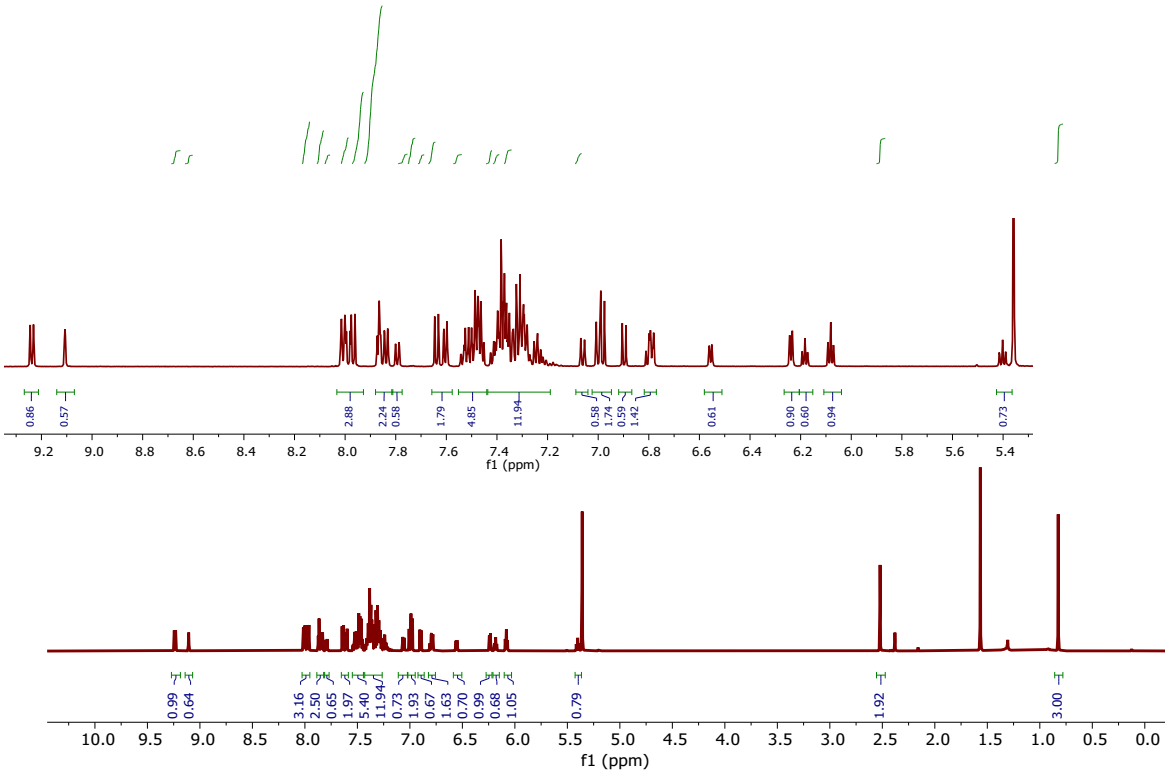



$^{13}$C

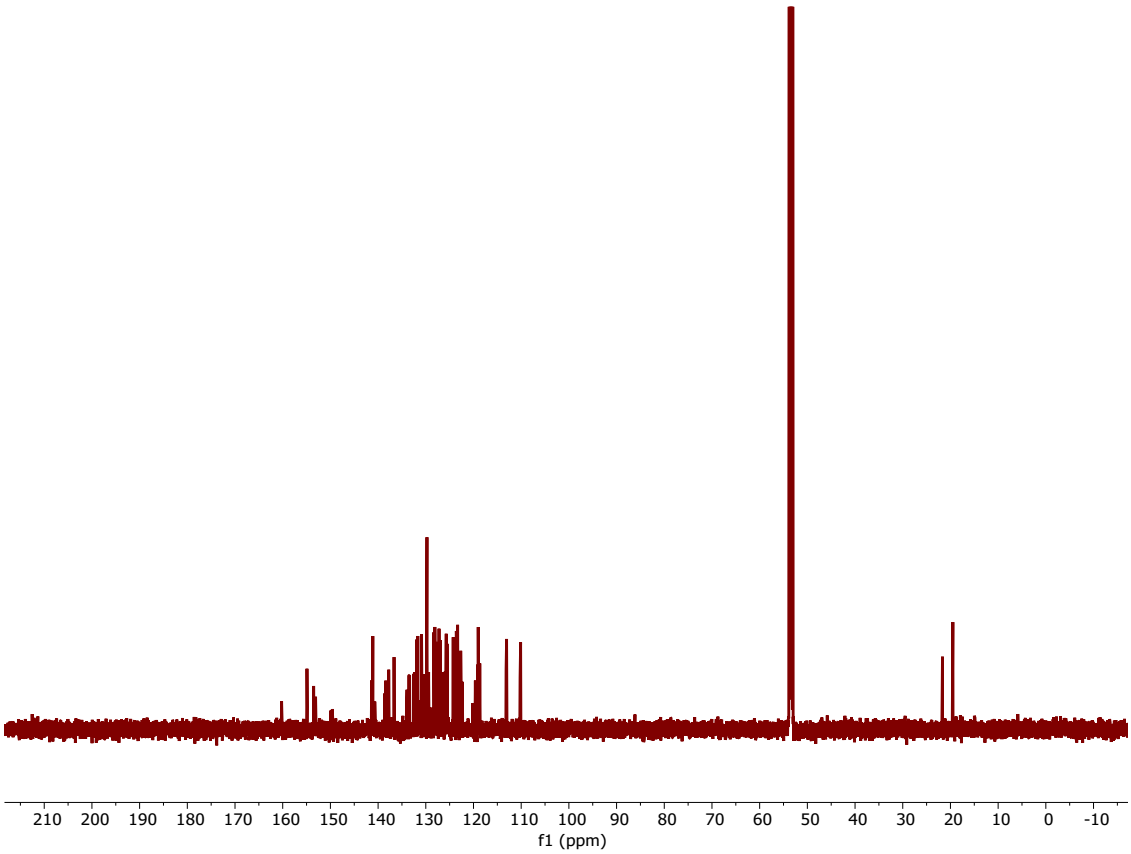


Complex **1** ($CD_2Cl_2$)

$^1$H NMR

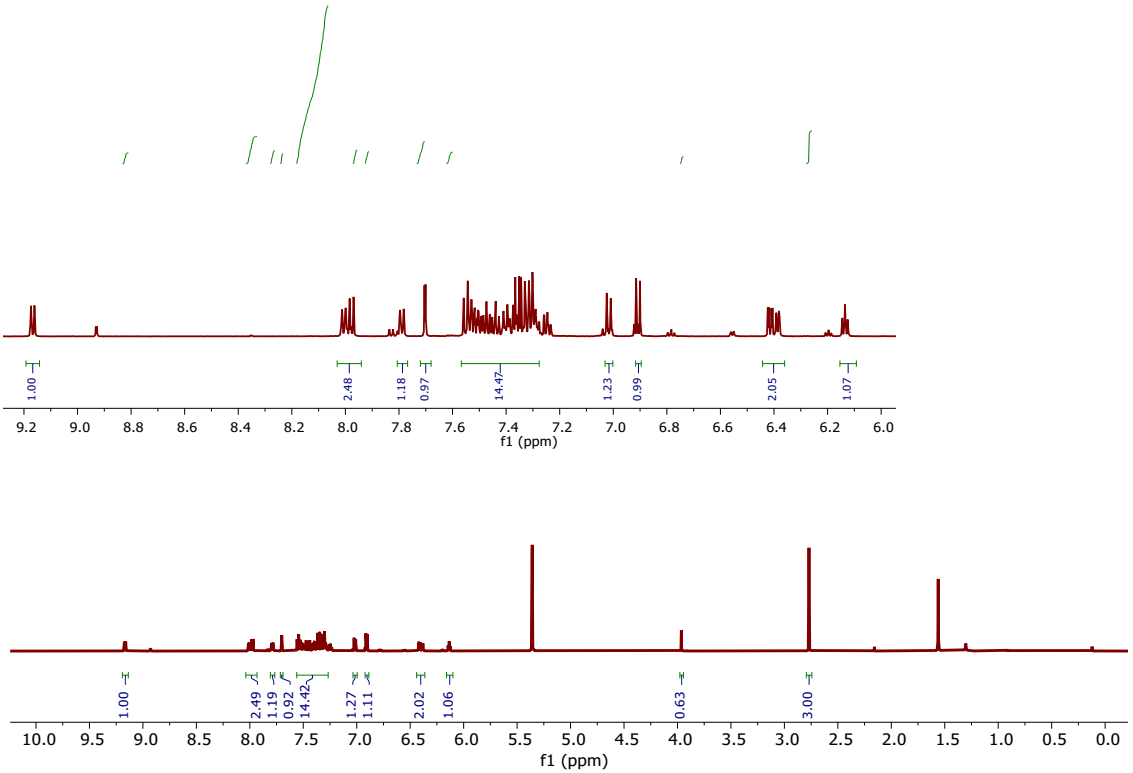



$^{13}$C NMR

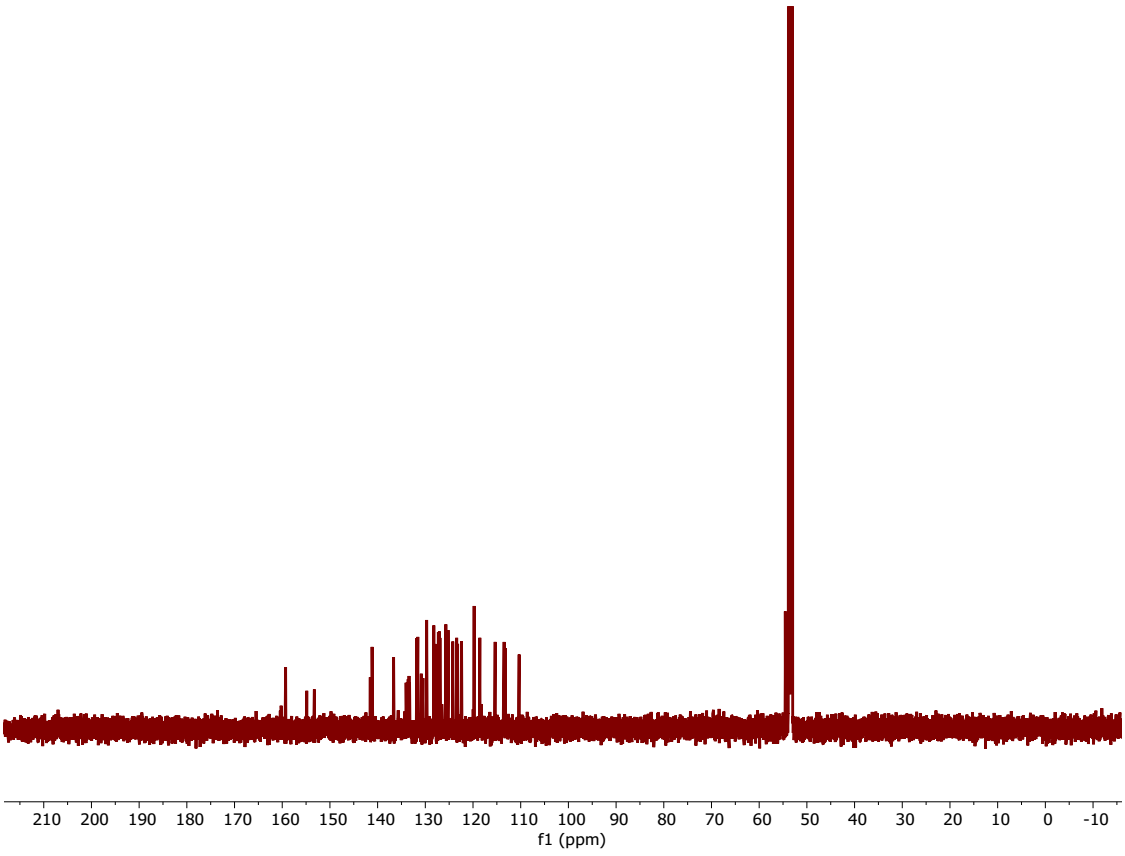


Complex **2** ($CD_2Cl_2$)

$^1$H NMR

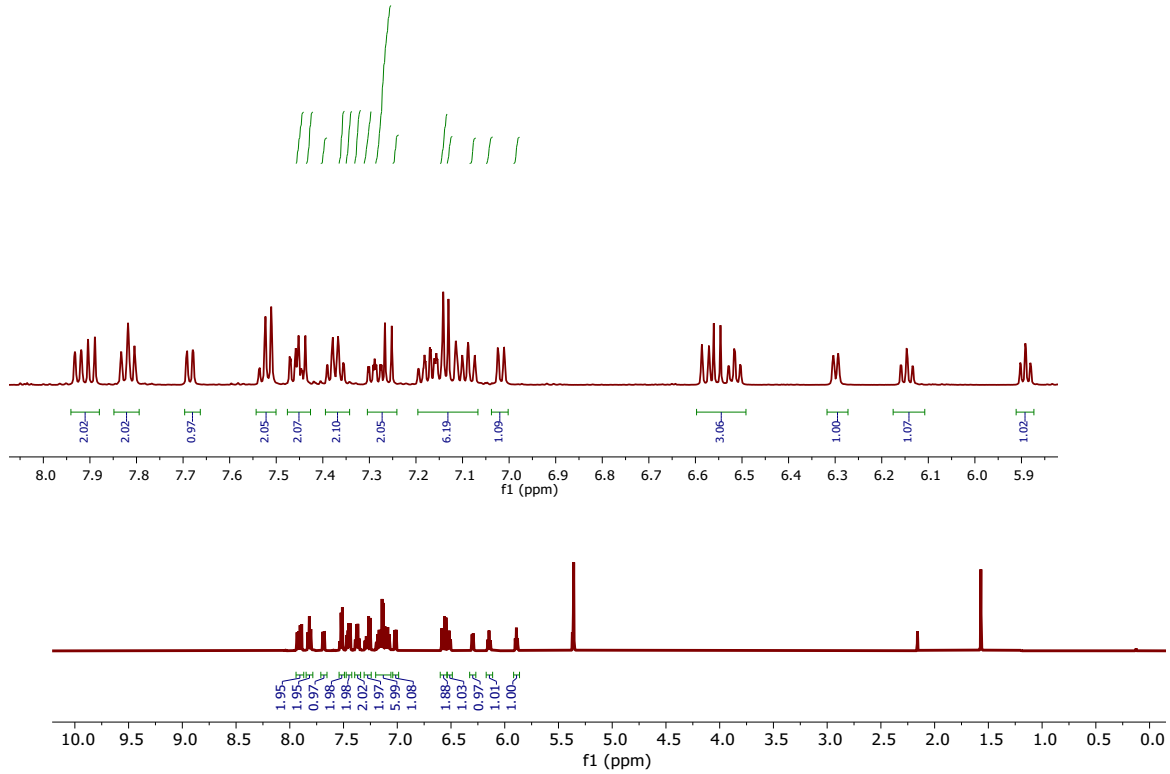



$^{13}$C NMR

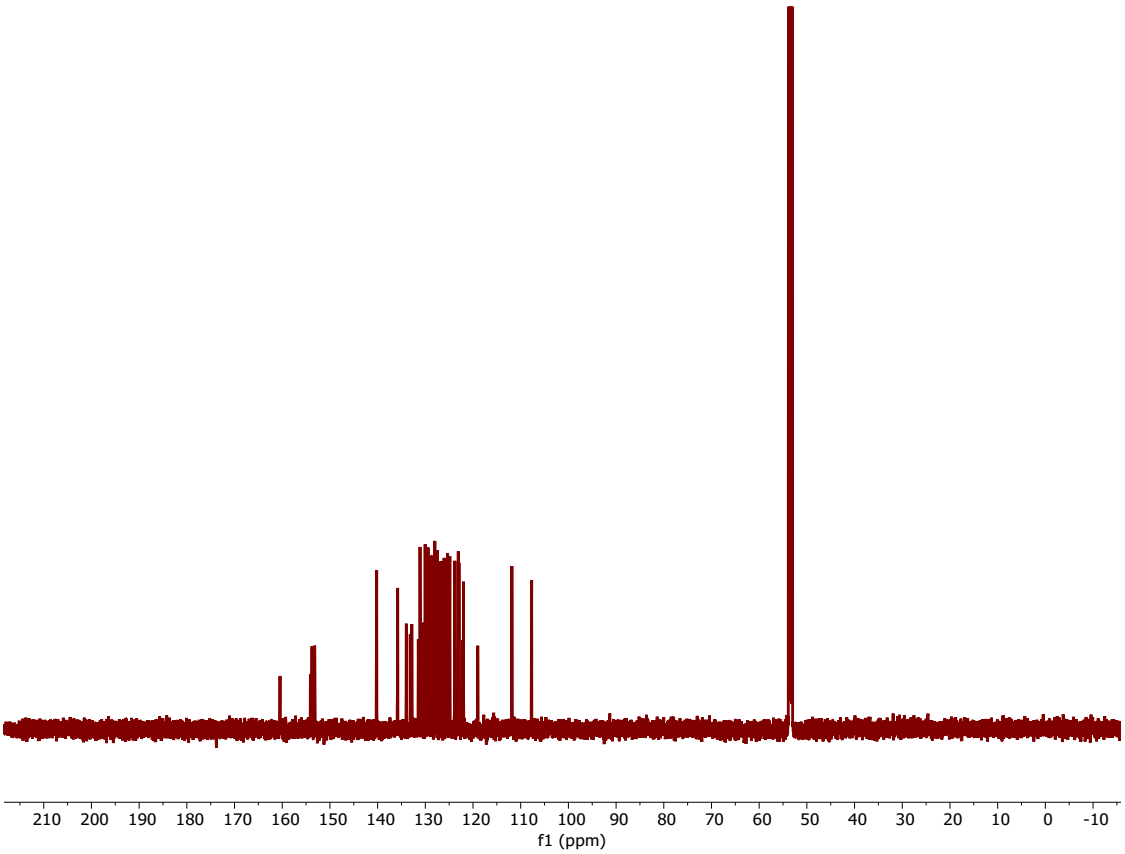


Complex **3** ($CD_2Cl_2$)

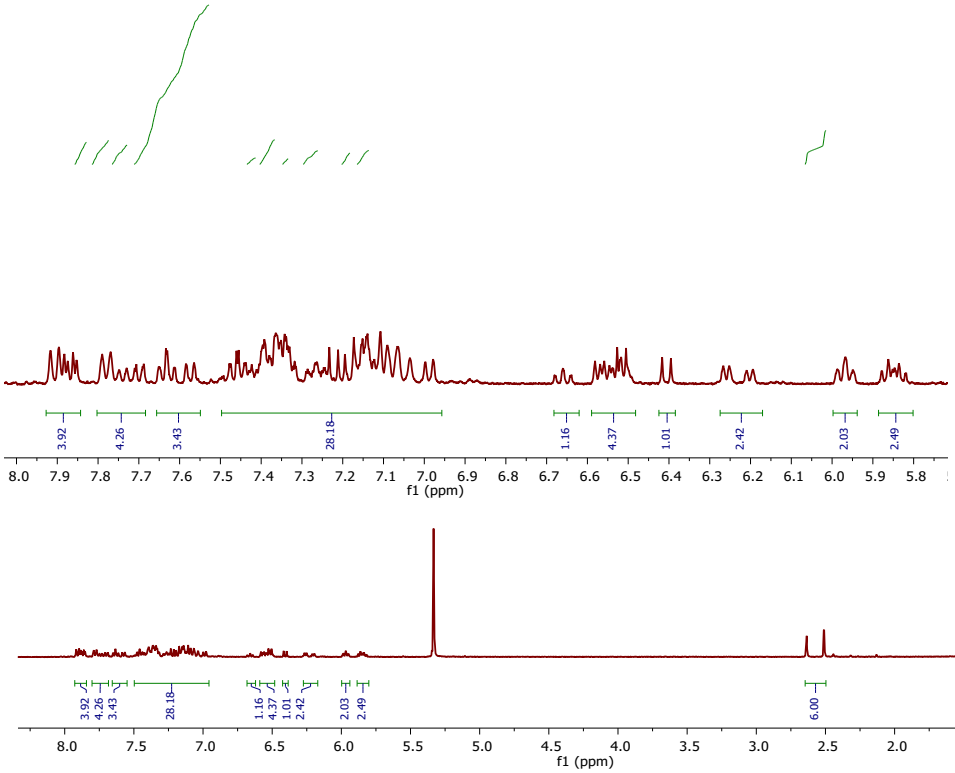
$^1$H NMR



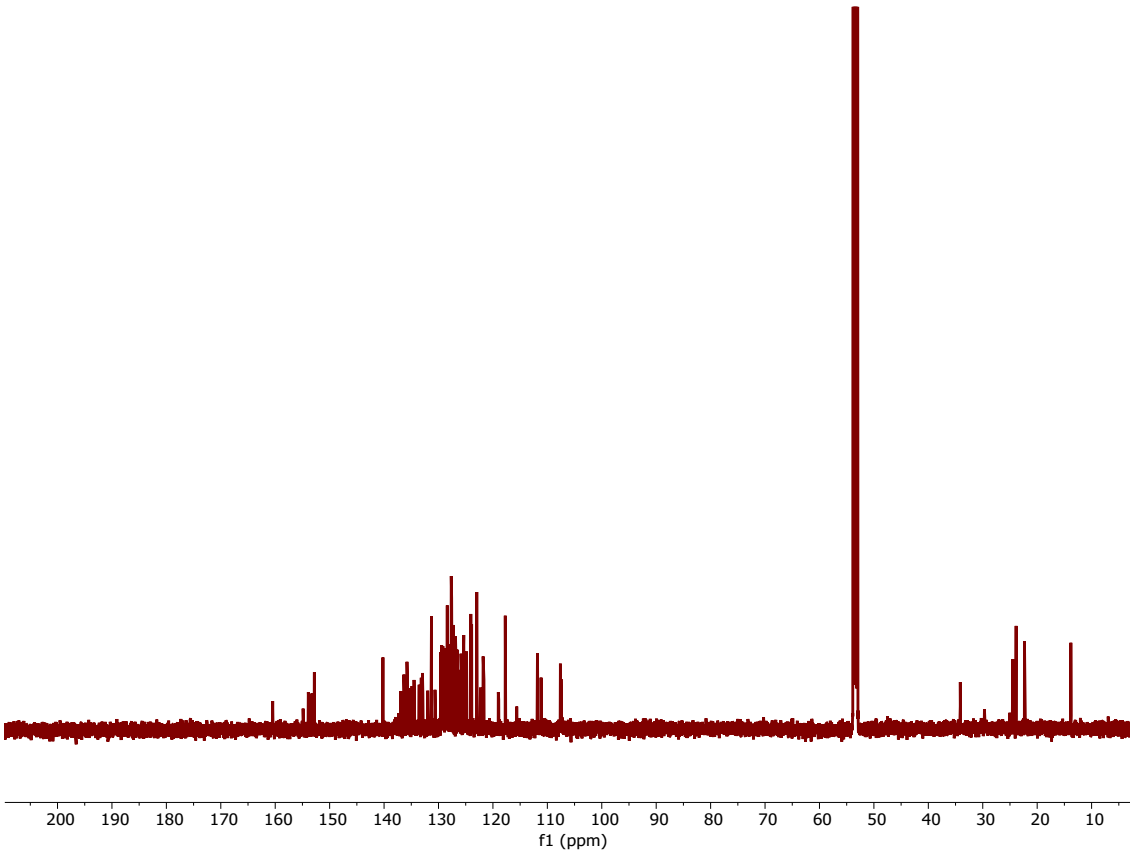

$^{13}$C NMR



Complex **4** ($CD_2Cl_2$)




$^{13}C$ NMR



# S3 UV-VIS spectroscopy

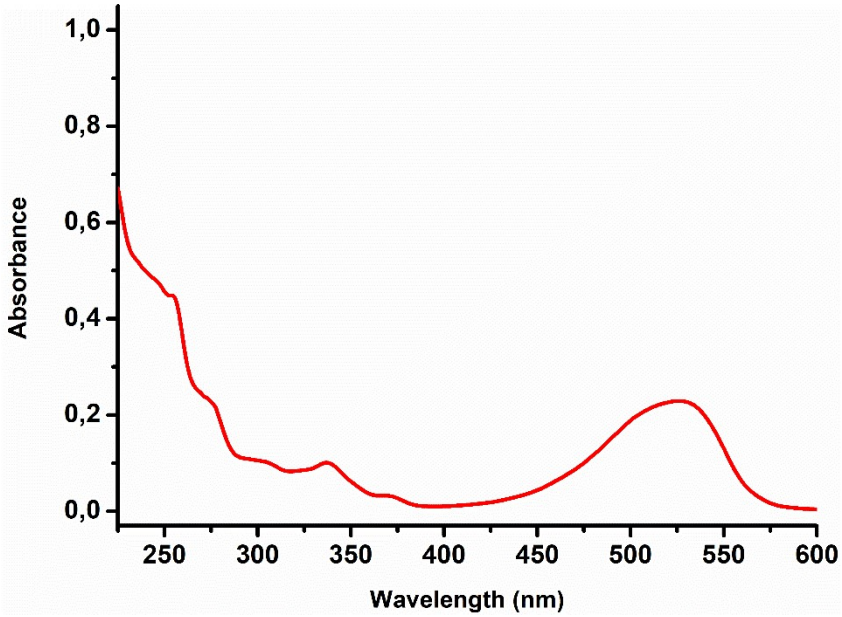



Figure 1: UV-Vis spectrum **1** ($CH_3CN$, 298 K, 3 x $10^{-5}$ M)

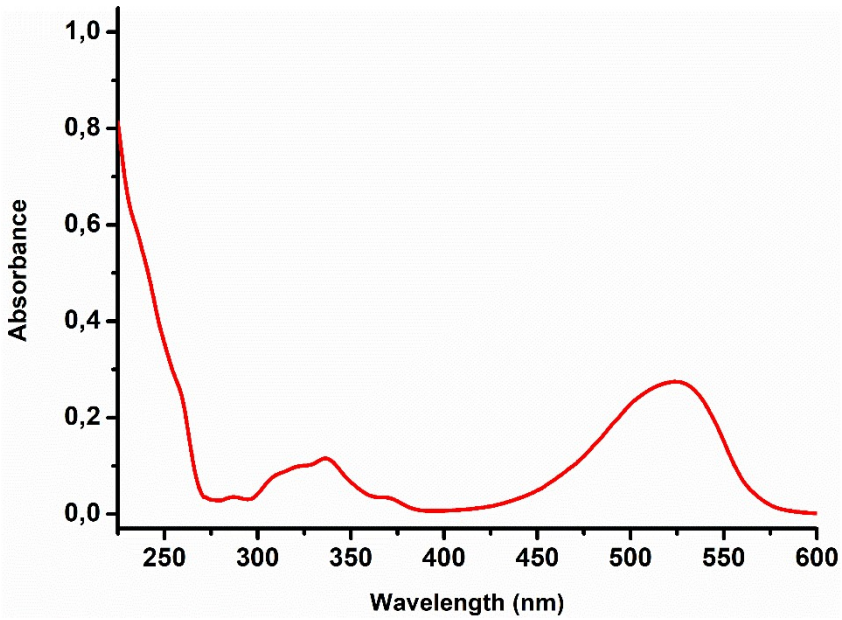



Figure 2: UV-Vis spectrum **2** ($CH_3CN$, 298 K, 3 x $10^{-5}$ M)

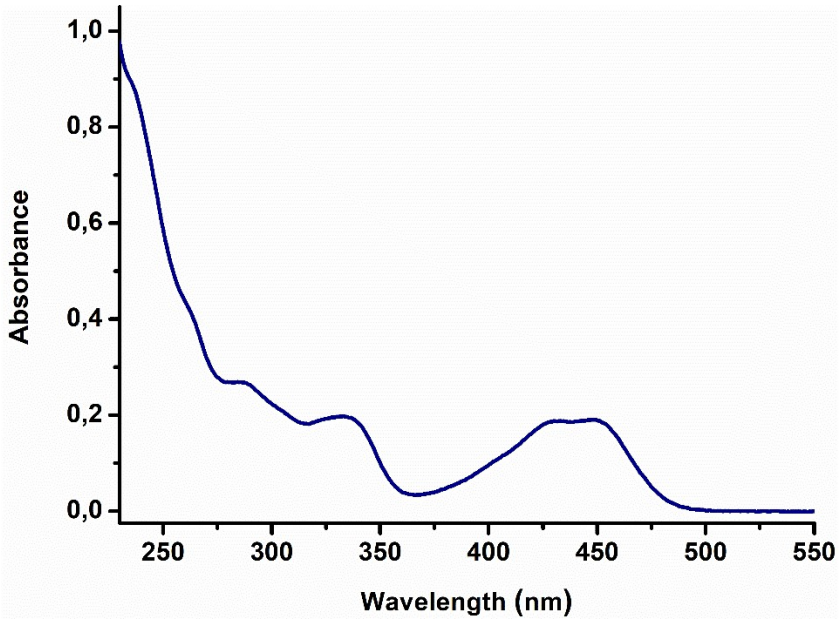


Figure 3: UV-Vis spectrum **3** ($CH_3CN$, 298 K, 3 x $10^{-5}$ M)

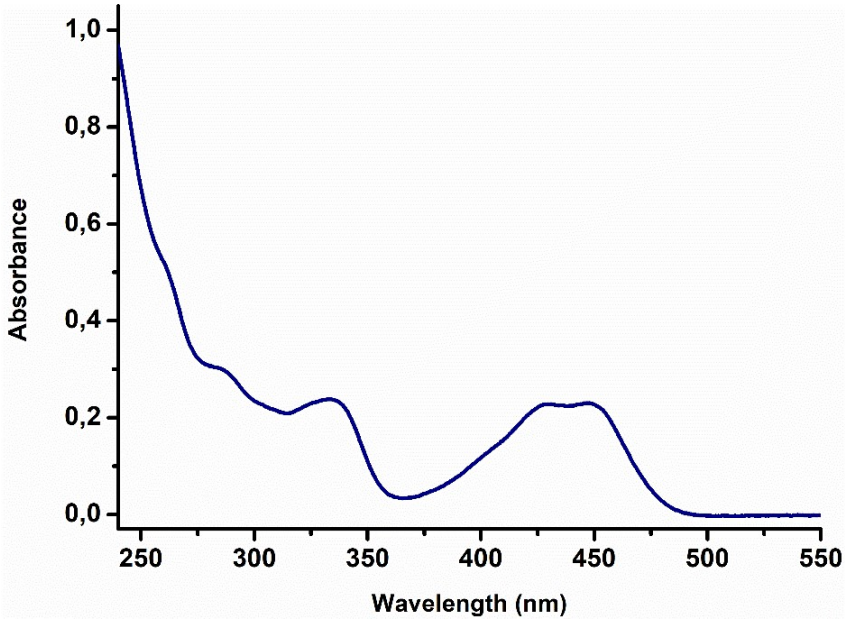


Figure 4: UV-Vis spectrum **4** ($CH_3CN$, 298 K, 3 x $10^{-5}$ M)

# S4 CD spectroscopy

For a typical experiment, a solution of a complex (c = $10^{-5}$ M) in $CH_3CN$ was prepared in the dark and transferred into a quart cuvette. In case of a photoirradiation experiment, the cuvette was irradiated *ex-situ* from the side using a fiber coupled-LED M455F3 system from Thorlabs. In the case of thermal equilibration, the cuvette was placed in the dark at 293 K.

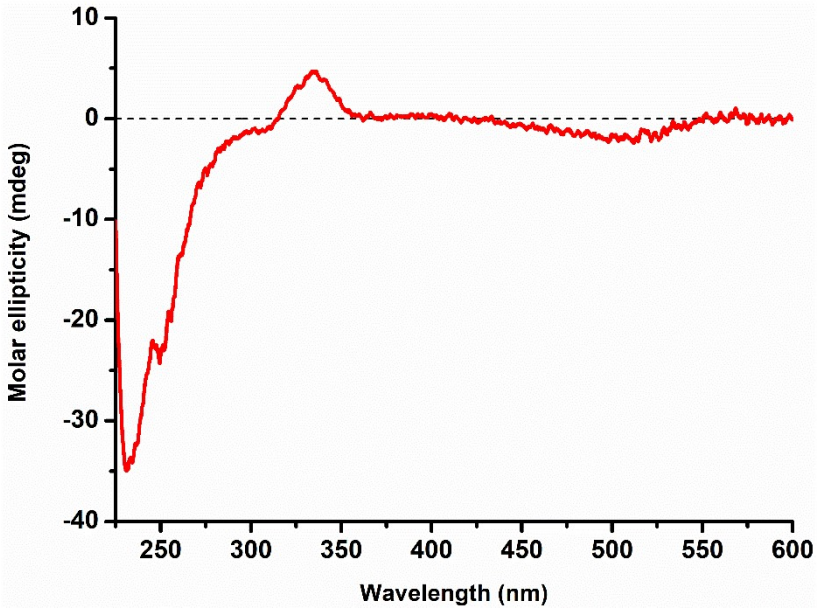



Figure 5: CD spectra of **1** ($CH_3CN$, 298 K, $10^{-5}$ M)

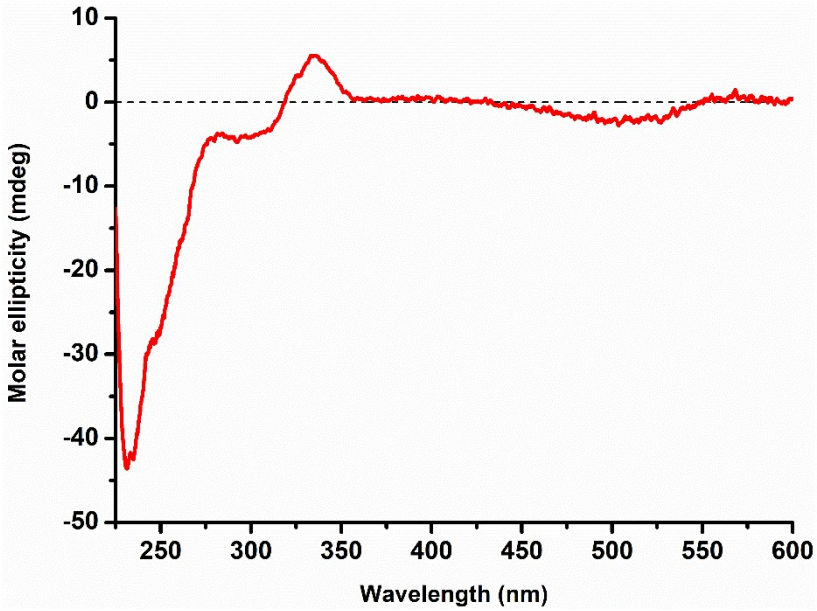



Figure 6: CD spectra of **2** ($CH_3CN$, 298 K, $10^{-5}$ M)

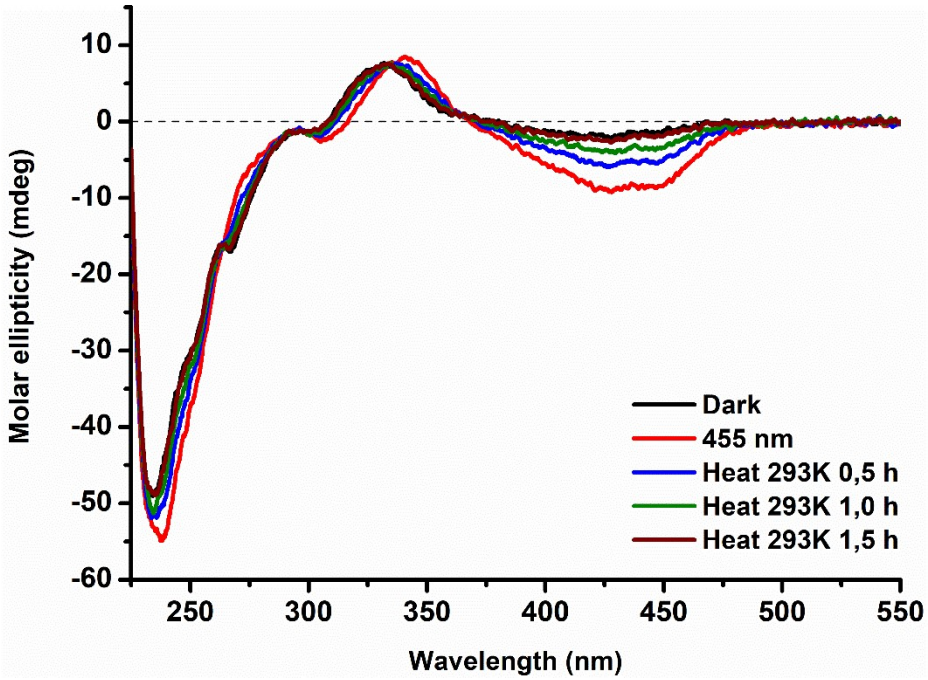



Figure 7: CD spectra of **3** before irradiation, irradiated during the indicated period (455 nm) and after thermal equilibration ($CH_3CN$, 298 K, $10^{-5}$ M)

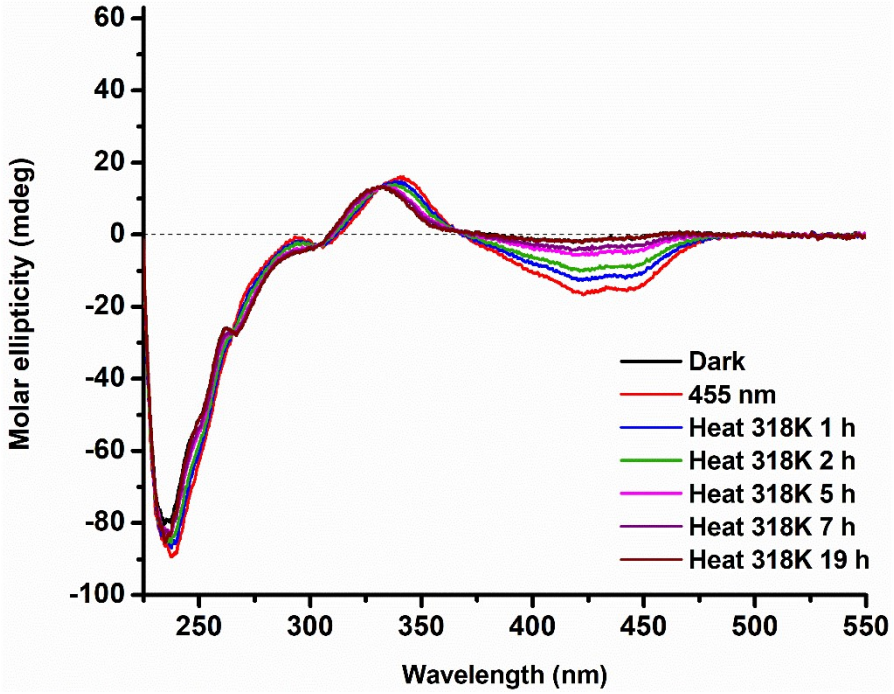
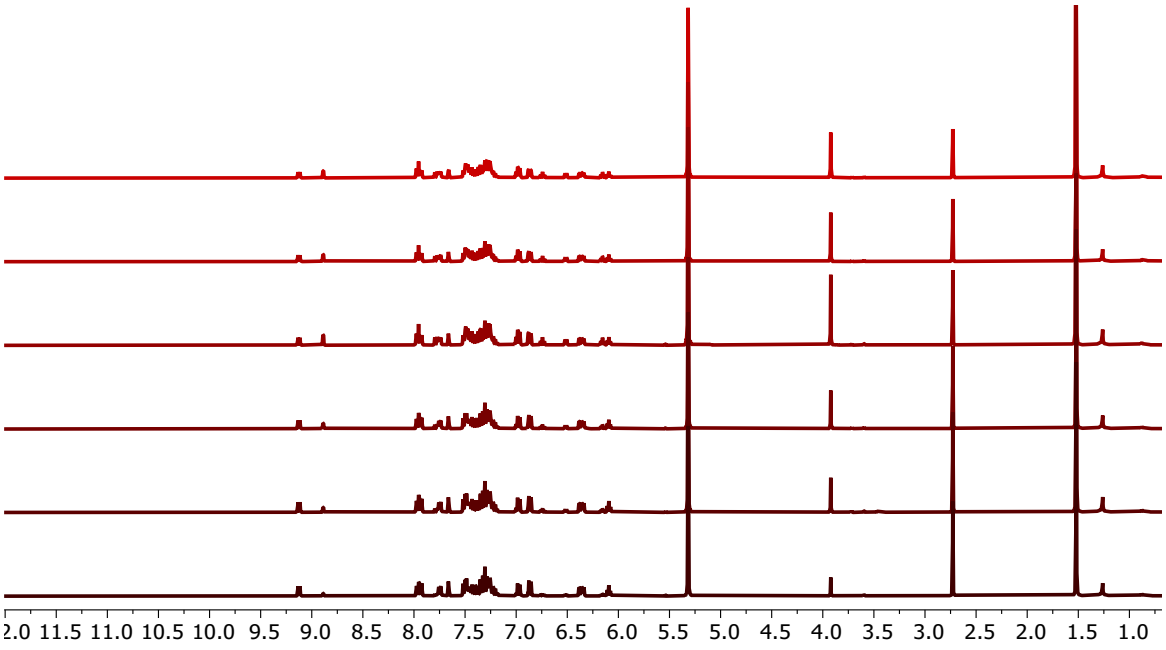



Figure 8: CD spectra of **4** before irradiation, irradiated during indicated period (455 nm) and after heating at 343K ($CH_3CN$, 298 K, $10^{-5}$ M)

# S5 $^{1}$H NMR Irradiation Studies, PSS Determination & Kinetic Studies

For the irradiation of complex **2**, a solution in $CD_2Cl_2$ ( c = 3 x $10^{-3}$ M) was prepared in the dark and transferred into a NMR tube. The NMR tube was placed in the dark and irradiated *ex-situ* from the side at 298 K using a fiber coupled-LED M528F3 system from Thorlabs. $^{1}$H spectra were recorded at the indicated time frames on a Varian Unity Plus 500 MHz NMR spectrometer. Irradiation continued until no further *cis-trans* ratio changes in the spectrum appeared. After PSS was reached, the NMR tube was covered with aluminium foil and stored at 298 K for 24 h.



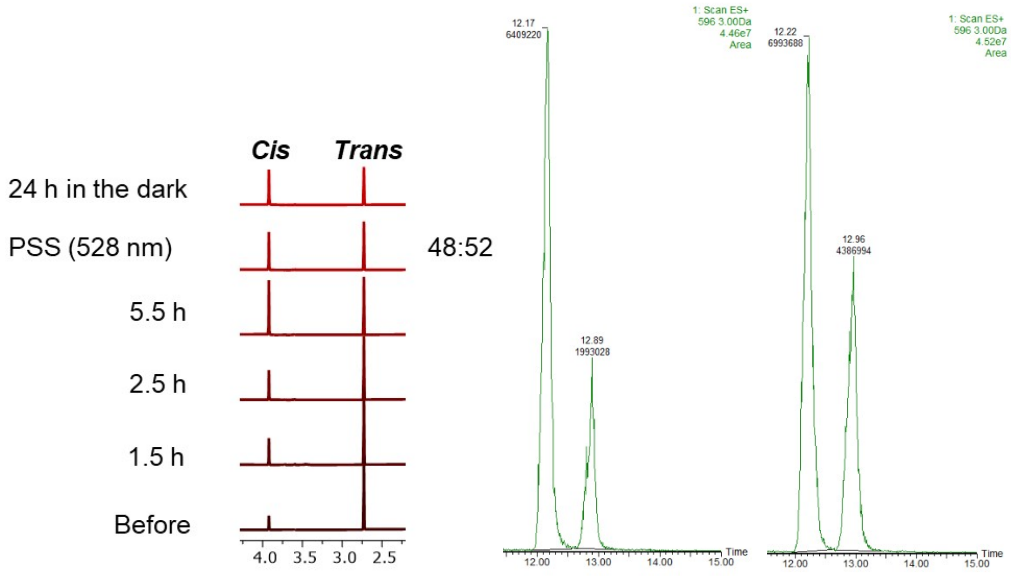




Figure 9: Photoisomerization of **2** using 528 nm over time until PSS (48:52) is reached ($CD_2Cl_2$, 298 K, 400 MHz): full spectrum, close-up of methoxy resonances and LC-MS chromatograms before irradiation (left) and at PSS (right) (Acquity HSS T3 1.8 µm, 2.1x150 mm column, 0.3 mL/min, gradient $H_2O$ + 0.1% Formic Acid / $CH_3CN$ + 0.1% Formic Acid)

For the irradiation of complex **3**, a solution in $CD_3CN$ ( c = 3.5 x $10^{-3}$ M) was prepared in the dark and transferred into a NMR tube which and subsequently equipped with a glass optic fibre via a Wilmad© coaxial insert for *in-situ* irradiation. The NMR tube was placed in Varian Unity Plus 500 MHz NMR spectrometer and cooled to 273 K. Irradiation at this temperature with a fiber coupled-LED M455F3 system from Thorlabs took place until no further changes appeared in the $^1H$ spectrum (90 min), meaning PSS (80:20) was reached. Allowing the sample to reach 298 K and thermally equilibrate, gave full recovery of the $^1H$ NMR spectrum recorded at 298 K.

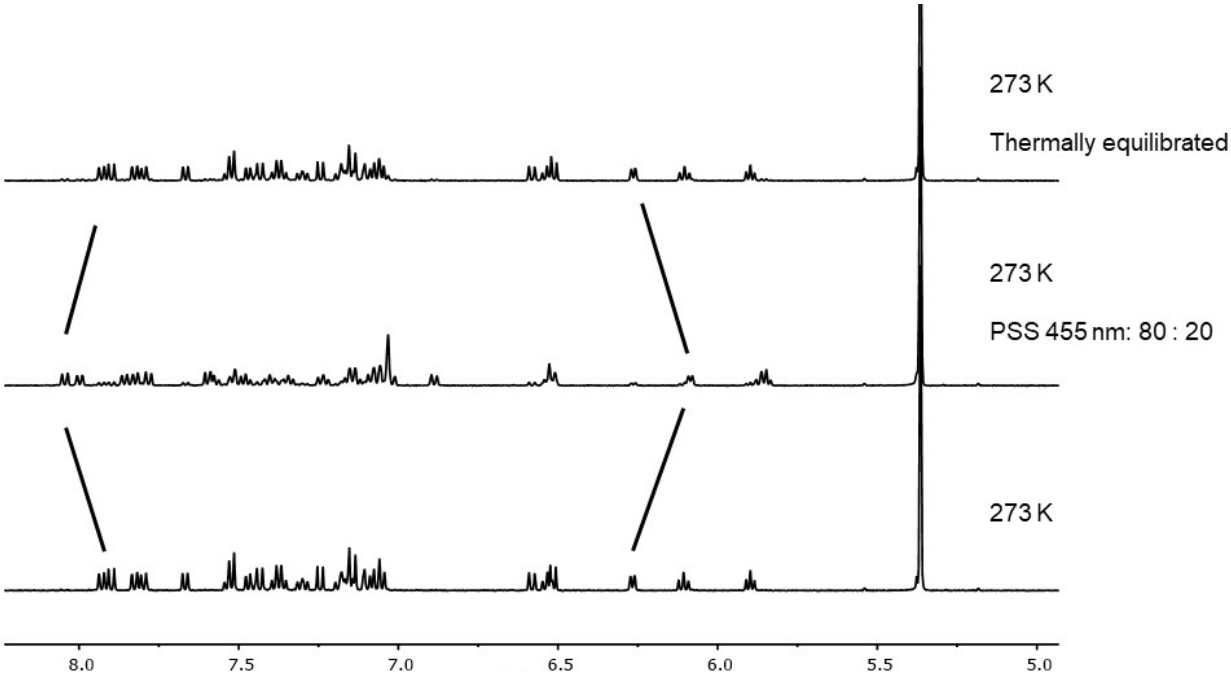



Figure 10: Photoisomerization of **3** using 455 nm until PSS (80:20) is reached ($CD_2Cl_2$, 273 K, 500 MHz)

## Kinetic Studies

A solution of a complex **3** or **4** (c = $10^{-5}$ M) in $CH_3CN$ was prepared in the dark and transferred into a quartz cuvette. The cuvette was irradiated at 455 nm *ex-situ* from the side using a fiber coupled-LED M455F3 system from Thorlabs until the PSS was reached (10 min). The thermal isomerization process was monitored by assessing the change in molar ellipticity at 430 nm as a function of time (1 h or 10 min intervals).

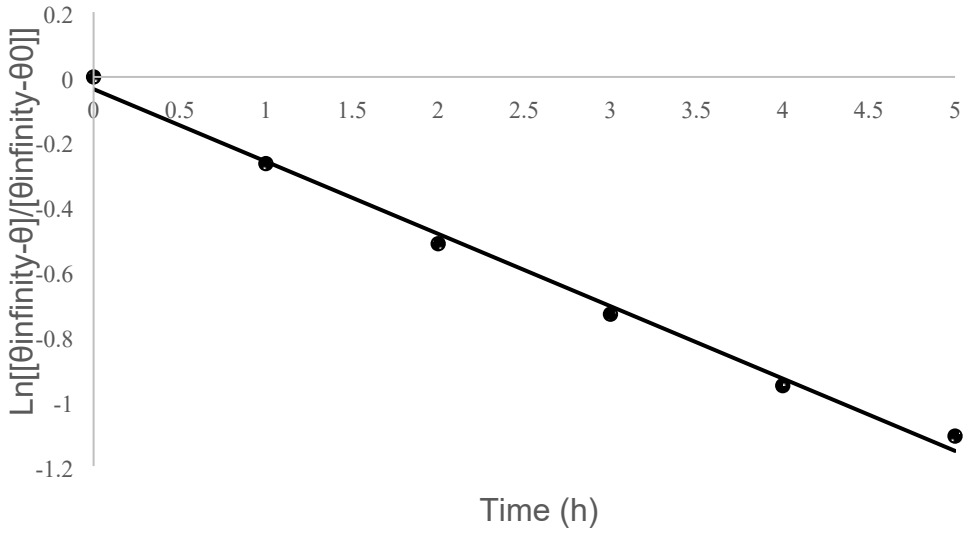



Figure 11: Plot of $Ln[[\theta_{infinity}-\theta]/[\theta_{infinity}-\theta_0]]$ versus time (h) showing first-order decay of **4** in $CH_3CN$ at 318 K starting from PSS. $\theta_{infinity}$ and $\theta_0$ stand for the molar ellipticity at the end of the thermal relaxation and at the start, respectively. The half-life ($t_{1/2}$) of the metastable → stable isomerization was calculated to be 3.1 h.

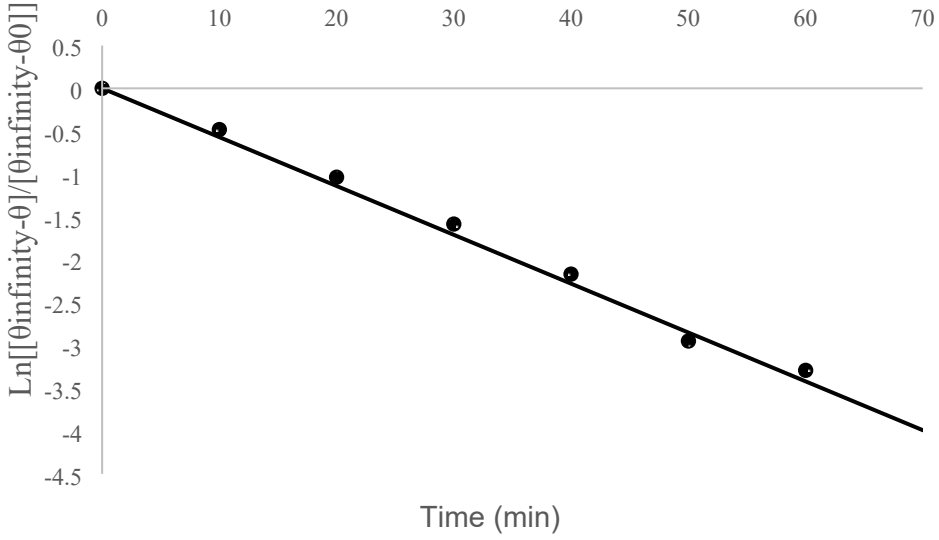



Figure 12: Plot of $Ln[[\theta_{infinity}-\theta]/[\theta_{infinity}-\theta_0]]$ versus time (h) showing first-order decay of **3** in $CH_3CN$ at 293 K starting from PSS. $\theta_{infinity}$ and $\theta_0$ stand for the molar ellipticity at the end of the thermal relaxation and at the start, respectively. The half-life ($t_{1/2}$) of the metastable → stable isomerization was calculated to be 12 min.

# S6 Single-Crystal X-ray Diffraction

Single-crystals were mounted on a cryoloop and placed in the nitrogen stream (100 K) of a Bruker-AXS D8 Venture diffractometer. Data collection and processing was carried out using the Bruker APEX3 software suite.[4,5] A multi-scan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*).[6] The structures were solved using *SHELXT*[7] and refinement was performed using *SHELXL*.[8] The hydrogen atoms were generated by geometrical considerations, constrained by idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Crystals of complexes **1** and **3** had been prepared from chiral material containing (*R*)-BINOL, whose absolute configuration therefore did not have to be determined using anomalous dispersion effects. No A- or B-level alerts were raised by CheckCIF for the fully refined structures. Crystal structures are available free of charge at the CCDC (complex **1**: 2181178, complex **3**: 2181177).

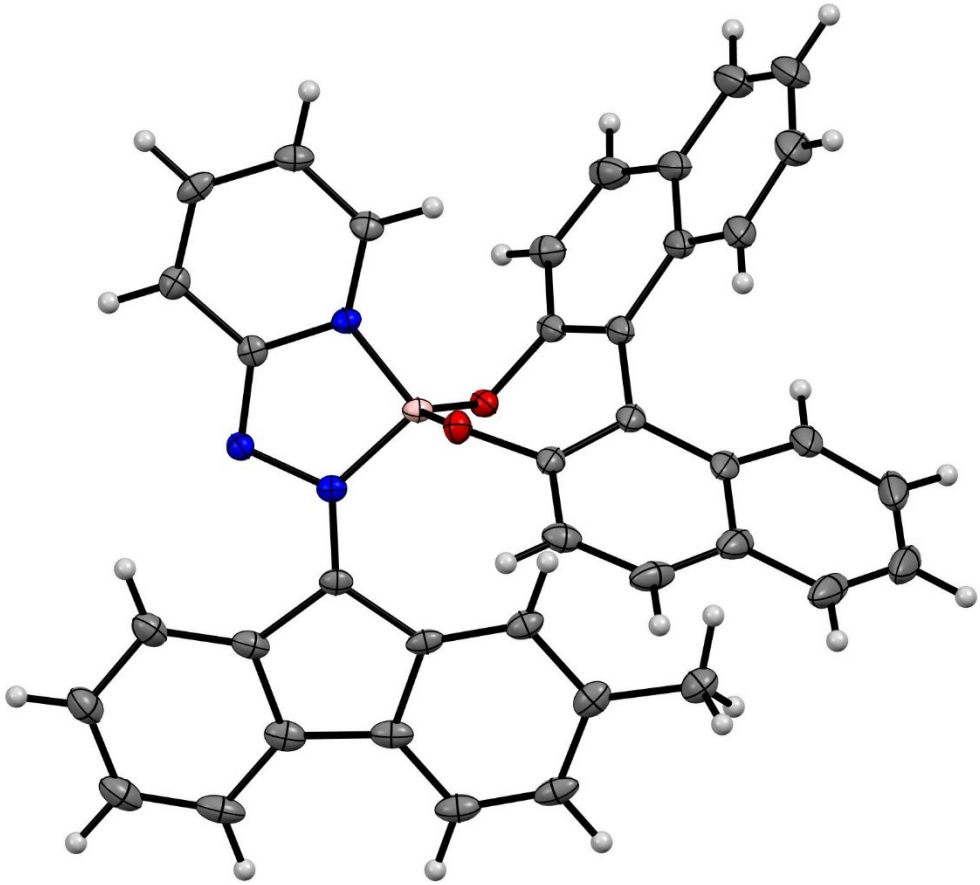


Figure 13: ORTEP image (ellipsoid at 50% probability) of complex **1**. $CH_2Cl_2$ molecule was omitted for the sake of clarity.

| | |
|---|---|
| Name | Complex **1** |
| Formula | $C_{40}H_{28}BCl_2N_3O_2$ |
| Molecular Weight | 664.36 |
| Crystal System | monoclinic |
| T [K] | 100(2) |
| Space Group | *P* $2_1$ |
| a [Å] | 13.3750(4) |
| b [Å] | 6.5182(2) |
| c [Å] | 18.2995(6) |
| α [°] | 90 |
| β [°] | 98.2810(10) |
| γ [°] | 90 |
| V [Å$^3$] | 1578.73(9) |
| Z | 2 |
| Dcalc [g·cm$^{-3}$] | 1.398 |
| Radiation [Å] | Cu $K_\alpha$ 1.54178 |
| F(000) | 688 |
| $h_{min}$, $h_{max}$ | –16, 16 |
| $k_{min}$, $k_{max}$ | –8, 8 |
| $l_{min}$, $l_{max}$ | –22, 22 |
| μ [mm$^{-1}$] | 2.187 |
| Crystal Size [mm] | 0.16 x 0.14 x 0.08 |
| Colour, Shape | Clear dark red block |
| Rint | 0.0366 |
| $\theta_{min}$, $\theta_{max}$ [°] | 2.440, 74.389 |
| Total Reflections (before merge) | 31206 |
| Data (I>3 x sigma(I)) [Reflections,Parameters,Restraints] | 6297, 452, 16 |
| S (=GooF) | 1.061 |
| Min. Residual Density [e/Å$^3$] | –0.573 |
| Max. Residual Density [e/Å$^3$] | 0.456 |
| Threshold Expression | I>2sigma(I) |
| R1 | 0.0490 |
| wR2 | 0.1302 |
| Flack X | 0.081(7) |

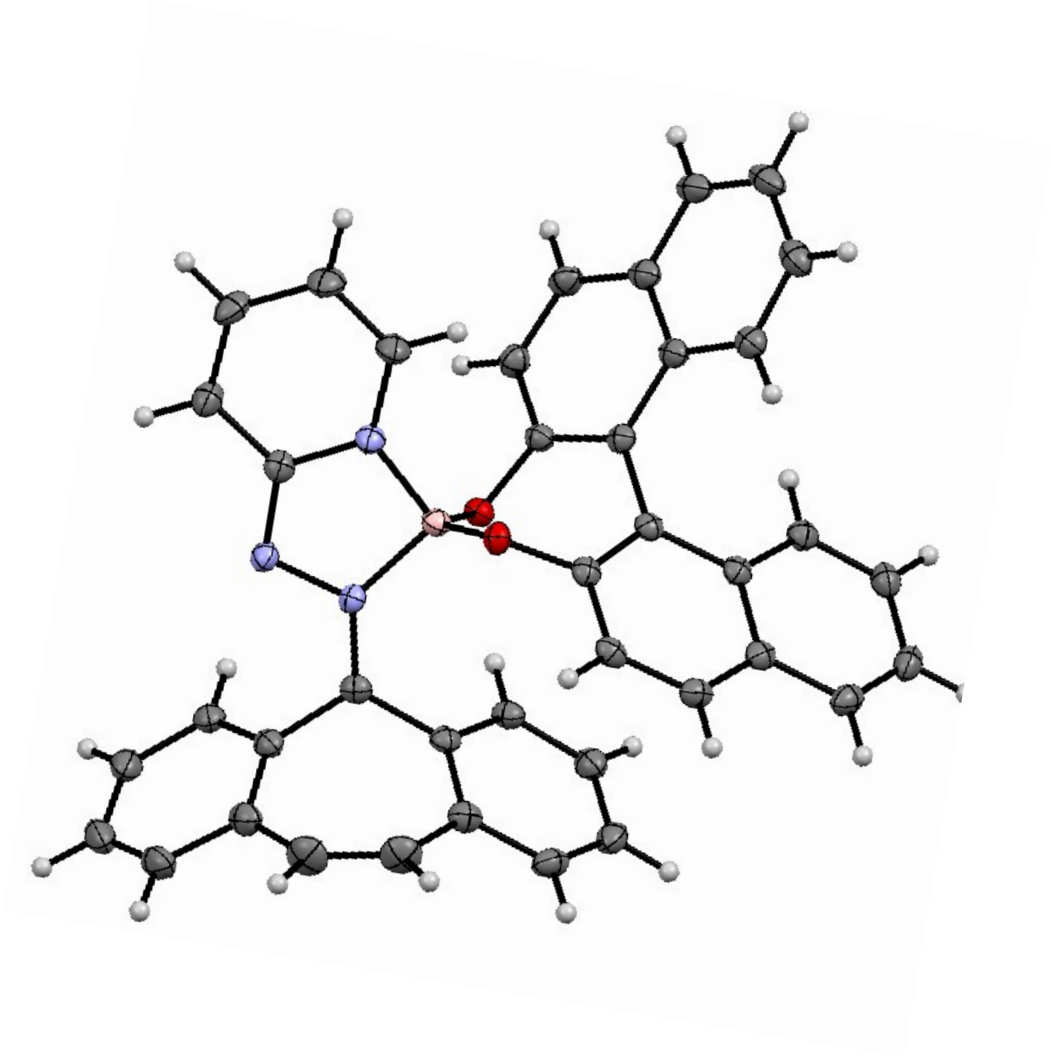


Figure 14: ORTEP image (ellipsoid at 50% probability) of complex **3**

| | |
|---|---|
| Name | Complex **3** |
| Formula | $C_{40}H_{26}BN_3O_2$ |
| Molecular Weight | 591.45 |
| Crystal System | orthorhombic |
| T [K] | 100(2) |
| Space Group | *P* $2_12_12_1$ |
| a [Å] | 9.9788(3) |
| b [Å] | 15.3329(5) |
| c [Å] | 19.7187(6) |
| α [°] | 90 |
| β [°] | 90 |
| γ [°] | 90 |
| V [Å$^3$] | 3017.04(16) |
| Z | 4 |
| Dcalc [g·cm$^{-3}$] | 1.302 |
| Radiation [Å] | Cu $K_\alpha$ 1.54178 |
| F(000) | 1232 |
| $h_{min}$, $h_{max}$ | –12, 12 |
| $k_{min}$, $k_{max}$ | –18, 17 |
| $l_{min}$, $l_{max}$ | –24, 24 |
| μ [mm$^{-1}$] | 0.634 |
| Crystal Size [mm] | 0.282 x 0.235 x 0.113 |
| Colour, Shape | Bright yellow block |
| Rint | 0.0286 |
| θmin, θmax [°] | 4.484, 72.204 |
| Total Reflections (before merge) | 32344 |
| Data (I>3 x sigma(I)) [Reflections,Parameters,Restraints] | 5879, 415, 150 |
| S (=GooF) | 1.069 |
| Min. Residual Density [e/Å$^3$] | –0.162 |
| Max. Residual Density [e/Å$^3$] | 0.168 |
| Threshold Expression | I>2sigma(I) |
| R1 | 0.0295 |
| wR2 | 0.0697 |
| Flack X | -0.01(8) |

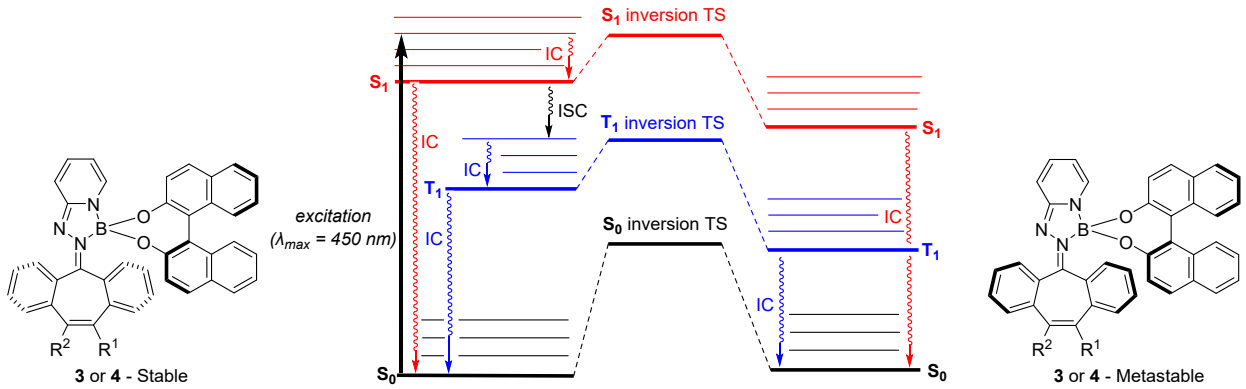
# S7 DFT calculations

## S7.1 Overview of Methods and Results

All computational input files were prepared in GaussView 6.0 on a local Windows 10 terminal. Input files were then transferred to the Rijksuniversiteit Groningen Peregrine HPC cluster where DFT or TD-DFT calculations were carried out using the Gaussian 16 (g16) suite of programs.

The DFT or TD-DFT thermochemistry of inversion for $S_0$ ground state and both $S_1$ and $T_1$ excited states of both stable and metastable states of **3**, in addition to transition states leading between each stable and metastable state, was examined at the MN15/Def2SVP/SMD=MeCN level. Geometry optimization to either ground state $S_0$ or excited state $S_1$ or $T_1$ minima of stable (S), metastable (M) structures or inversion transition states (TS) using the g16 *opt* command at the MN15 functional and Def2SVP basis set level of theory with implicit solvation using the Solvation Model based on Density (SMD = water).[9,10,11] Transition state geometry inputs were the result of rational guess based on steric clashes expected during the stereochemical inversion event, or were the result of potential energy surface relaxed coordinate scans using the g16 *scan* command at the MN15/Def2SVP/SMD=MeCN level. Intrinsic reaction coordinate (IRC)iv calculations were carried out on the transition state structures to verify that they connected to the associated reactant and product minima structures.

After optimization, frequency DFT calculations of all obtained optimized structures were carried out using the g16 *freq* command at the MN15/Def2SVP/SMD=MeCN level, to confirm that minima structures had zero imaginary frequencies and that transition states had a single imaginary frequency. All shown free energies (*Table 1*) are ZPE and thermally corrected and were obtained from the frequency calculations. All shown free energies are reported in kcal/mol, at 298.15 K and 1 atm.




ZPE-corrected free energies of structures optimized at the MN15/Def2SVP/SMD=MeCN level, all values in kcal/mol

Compound **3** ($R^1 = R^2 = H$)

| | stable state | transition state | metastable state | $\Delta G^{\ddagger}_{inv.}$ |
|---|---|---|---|---|
| singlet $S_0$ state | 0.0 | +27.9 | +2.8 | 27.9 |
| singlet $S_1$ state | +59.1 | +64.3 | +48.9 | 5.2 |
| triplet $T_1$ state | +38.3 | +43.5 | +27.6 | 5.5 |

Compound ***(Z)*-4** ($R^1 = CH_3$, $R^2 = H$)

| | stable state | transition state | metastable state | $\Delta G^{\ddagger}_{inv.}$ |
|---|---|---|---|---|
| singlet $S_0$ state | 0.0 | +31.0 | +2.8 | 31.0 |
| singlet $S_1$ state | +59.5 | +65.0 | +51.2 | 5.5 |
| triplet $T_1$ state | +38.9 | +44.4 | +29.8 | 5.6 |

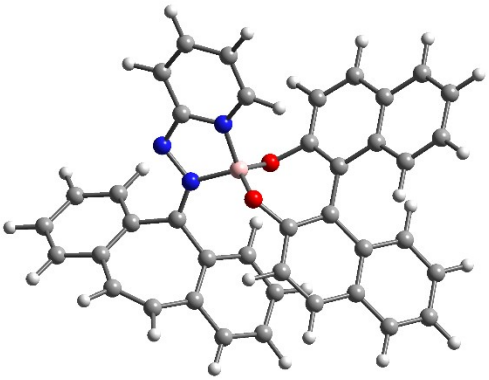
Compound ***(E)*-4** ($R^1 = H$, $R^2 = CH_3$)

| | stable state | transition state | metastable state | $\Delta G^{\ddagger}_{inv.}$ |
|---|---|---|---|---|
| singlet $S_0$ state | 0.0 | +29.8 | +2.7 | 29.8 |
| singlet $S_1$ state | +59.4 | +65.4 | +55.2 | 5.2 |
| triplet $T_1$ state | +38.6 | +44.1 | +28.5 | 5.5 |

Table 1. The ground state $S_0$ or excited state $S_1$ or $T_1$ free energies of stable (S), metastable (M) structures or inversion transition states (TS) for compounds **3** and **4** as calculated by DFT (obtained at the MN15/Def2SVP/SMD=MeCN level of theory).

## S7.2 Optimized Geometries and XYZ Coordinates

**Compound 3 - Stable ($S_0$)** optimized geometry (# opt=calcfc scrf=(smd,solvent=MeCN) def2svp mn15)



EE + Thermal Free Energy Correction: -1875.361596 Ha (+0.0 kcal/mol)

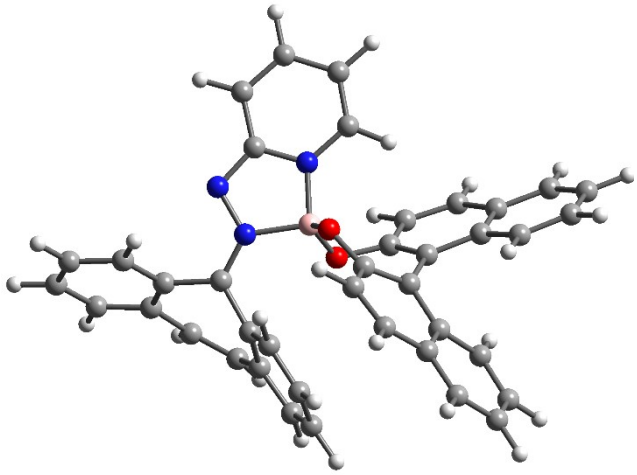
0 1

| | | | |
|---|---|---|---|
| N | -2.06381100 | 0.96918400 | 0.05213600 |
| C | -2.79200800 | -0.08964900 | 0.27968600 |
| C | -2.20360000 | -1.44175600 | 0.40427200 |
| C | -2.66087800 | -2.49244300 | -0.42836400 |
| C | -3.70094100 | -2.33657000 | -1.44927200 |
| C | -4.78059000 | -1.52461000 | -1.41433400 |
| C | -5.17191600 | -0.61266400 | -0.33763400 |
| C | -4.25121800 | 0.04274800 | 0.50647700 |
| C | -6.54786400 | -0.38472600 | -0.12779700 |
| C | -6.99706200 | 0.40616600 | 0.92246900 |
| C | -6.07375800 | 1.01441000 | 1.78377200 |
| C | -4.71159400 | 0.84596200 | 1.56326800 |
| C | -1.23343200 | -1.70333000 | 1.38675700 |
| C | -0.69428400 | -2.97970100 | 1.53525200 |
| C | -1.11778500 | -4.01511300 | 0.69582300 |
| C | -2.07965200 | -3.76545700 | -0.27815600 |
| N | -2.65428600 | 2.20212800 | -0.01696000 |
| C | -1.74086000 | 3.06732100 | -0.45286400 |
| N | -0.49738800 | 2.55601500 | -0.68748100 |
| C | 0.51631000 | 3.29997600 | -1.19334700 |
| C | 0.33846900 | 4.63383000 | -1.46547800 |
| C | -0.93599300 | 5.20712700 | -1.20360800 |
| C | -1.97013300 | 4.44960400 | -0.70673300 |
| B | -0.46689600 | 1.06944700 | -0.21201900 |
| O | 0.18871900 | 0.92282300 | 1.06309800 |
| O | 0.03018000 | 0.24164000 | -1.26599000 |

| | | | |
|---|---|---|---|
| C | 1.50269000 | 1.27549000 | 1.03252400 |
| C | 1.89022600 | 2.46570900 | 1.70089600 |
| C | 3.18552900 | 2.91051500 | 1.61673700 |
| C | 4.13804800 | 2.20921800 | 0.82506100 |
| C | 3.74965400 | 1.00586800 | 0.15667800 |
| C | 2.41203900 | 0.50006800 | 0.32652100 |
| C | 5.46373100 | 2.70389600 | 0.67157900 |
| C | 6.37237300 | 2.05726700 | -0.13474000 |
| C | 5.98035600 | 0.88755300 | -0.83263200 |
| C | 4.70862600 | 0.37635300 | -0.68989800 |
| C | 1.96513500 | -0.78725200 | -0.27131900 |
| C | 2.67118600 | -2.01753300 | -0.02405500 |
| C | 2.31516200 | -3.19952400 | -0.74405200 |
| C | 1.23978000 | -3.14636800 | -1.67457600 |
| C | 0.50502000 | -1.99867200 | -1.82005200 |
| C | 0.83499500 | -0.82858100 | -1.08435400 |
| C | 3.70796000 | -2.12116300 | 0.94917400 |
| C | 4.36366300 | -3.31299400 | 1.17248700 |
| C | 4.02774300 | -4.47320800 | 0.43121600 |
| C | 3.01934300 | -4.41214600 | -0.50419800 |
| H | -3.63558800 | -3.04462000 | -2.28197900 |
| H | -5.51243900 | -1.62889600 | -2.22179400 |
| H | -7.26372700 | -0.86309700 | -0.80132200 |
| H | -8.06867000 | 0.55289700 | 1.07482300 |
| H | -6.41926400 | 1.63590000 | 2.61262800 |
| H | -3.98184700 | 1.34830800 | 2.20144300 |
| H | -0.91014300 | -0.89201600 | 2.03838200 |
| H | 0.05945000 | -3.16375900 | 2.30436200 |
| H | -0.69172000 | -5.01587600 | 0.79860600 |
| H | -2.40907300 | -4.56904900 | -0.94214600 |
| H | 1.45955100 | 2.77462100 | -1.36636100 |
| H | 1.15547800 | 5.22713800 | -1.87445300 |
| H | -1.09831100 | 6.26790100 | -1.40933800 |
| H | -2.95992600 | 4.86283600 | -0.51125000 |
| H | 1.12885100 | 3.00919600 | 2.26498700 |
| H | 3.49810300 | 3.82293500 | 2.13108100 |
| H | 5.73809400 | 3.61890800 | 1.20366300 |
| H | 7.38609900 | 2.44724600 | -0.25010500 |
| H | 6.69179300 | 0.38948400 | -1.49553800 |
| H | 4.42091200 | -0.51728200 | -1.24638100 |
| H | 0.98494900 | -4.04727000 | -2.23921500 |
| H | -0.35590900 | -1.94791300 | -2.49035200 |
| H | 3.97161900 | -1.24163300 | 1.53977500 |
| H | 5.14595400 | -3.36499000 | 1.93352700 |
| H | 4.55900000 | -5.41009700 | 0.61316600 |

| | | | |
|---|---|---|---|
| H | 2.73160200 | -5.29885100 | -1.07594800 |

**Compound 3 - Metastable ($S_0$)** optimized geometry (# opt=calcfc scrf=(smd,solvent=MeCN) def2svp mn15)



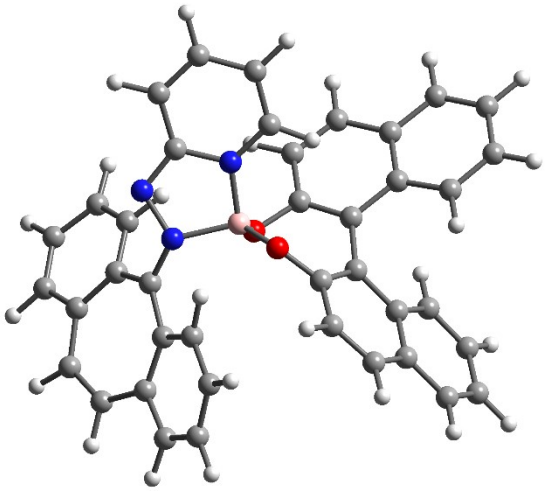
EE + Thermal Free Energy Correction: -1875.357169 Ha (+2.8 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | -2.22124100 | 0.61042400 | -0.59676600 |
| C | -2.81586400 | -0.46243700 | -0.15543400 |
| C | -2.03410500 | -1.66097000 | 0.21038000 |
| C | -2.02369900 | -2.11362900 | 1.55037600 |
| C | -2.86048600 | -1.54183500 | 2.60567500 |
| C | -4.07480100 | -0.95901800 | 2.48077400 |
| C | -4.85587500 | -0.73212800 | 1.26182500 |
| C | -4.28674100 | -0.52212900 | -0.01328600 |
| C | -6.26163500 | -0.70543600 | 1.37143900 |
| C | -7.07169300 | -0.54018700 | 0.25435600 |
| C | -6.49359400 | -0.36856300 | -1.01047000 |
| C | -5.10889000 | -0.34350300 | -1.13723300 |
| C | -1.28060300 | -2.32502600 | -0.76443300 |
| C | -0.47390900 | -3.40911000 | -0.42035100 |
| C | -0.39661500 | -3.81826200 | 0.91408800 |
| C | -1.16117200 | -3.17341900 | 1.88354800 |
| N | -2.95630600 | 1.71187800 | -0.93794000 |
| C | -2.11799200 | 2.74272400 | -1.01943500 |
| N | -0.80139200 | 2.46995900 | -0.77931600 |
| C | 0.16810500 | 3.41152100 | -0.90151800 |
| C | -0.14704500 | 4.71124000 | -1.20796400 |
| C | -1.51438400 | 5.03809900 | -1.42280200 |
| C | -2.49459500 | 4.07928300 | -1.33865900 |
| B | -0.62644800 | 0.92977600 | -0.55318000 |
| O | -0.17123500 | 0.53513100 | 0.74621600 |
| O | 0.14531900 | 0.43899100 | -1.66308100 |
| C | 1.05955100 | 1.01310300 | 1.06958100 |

| | | | |
|---|---|---|---|
| C | 1.13881400 | 2.01235100 | 2.07436200 |
| C | 2.34442000 | 2.59609000 | 2.37007200 |
| C | 3.51454100 | 2.23925400 | 1.64236500 |
| C | 3.43634900 | 1.22815000 | 0.63369200 |
| C | 2.18390800 | 0.55512500 | 0.39775200 |
| C | 4.75340000 | 2.89421300 | 1.89056700 |
| C | 5.87544700 | 2.59141800 | 1.15349200 |
| C | 5.79329200 | 1.62297000 | 0.12224700 |
| C | 4.61108200 | 0.96055300 | -0.12875500 |
| C | 2.05937100 | -0.55526900 | -0.58535500 |
| C | 2.92180000 | -1.70834600 | -0.52591900 |
| C | 2.93650400 | -2.64652200 | -1.60321800 |
| C | 2.06743100 | -2.43987700 | -2.71221900 |
| C | 1.16622400 | -1.40865900 | -2.69902000 |
| C | 1.11398400 | -0.49732600 | -1.60623600 |
| C | 3.75925200 | -1.97450700 | 0.59641800 |
| C | 4.57376900 | -3.08629900 | 0.63417200 |
| C | 4.60768800 | -3.99492100 | -0.45237900 |
| C | 3.79972700 | -3.77526600 | -1.54570800 |
| H | -2.49425600 | -1.71050500 | 3.62344400 |
| H | -4.59754800 | -0.70170300 | 3.40774000 |
| H | -6.70916100 | -0.83375800 | 2.36050300 |
| H | -8.15830800 | -0.54039500 | 0.36509200 |
| H | -7.12461500 | -0.23478300 | -1.89165400 |
| H | -4.64401600 | -0.17198600 | -2.11027300 |
| H | -1.33056100 | -1.97789800 | -1.79880900 |
| H | 0.10787300 | -3.92031800 | -1.19032700 |
| H | 0.25375600 | -4.64908200 | 1.19670600 |
| H | -1.11321400 | -3.49910200 | 2.92599300 |
| H | 1.19494400 | 3.07123100 | -0.74372200 |
| H | 0.63698900 | 5.46310900 | -1.29074400 |
| H | -1.78773300 | 6.06703200 | -1.66852700 |
| H | -3.54808700 | 4.29808400 | -1.51466400 |
| H | 0.21771400 | 2.29750000 | 2.58738900 |
| H | 2.42005200 | 3.36223700 | 3.14602800 |
| H | 4.78721900 | 3.65368700 | 2.67654200 |
| H | 6.82074500 | 3.10282500 | 1.34821000 |
| H | 6.67474500 | 1.40309800 | -0.48469000 |
| H | 4.56540800 | 0.22972200 | -0.93765700 |
| H | 2.10672700 | -3.13746400 | -3.55296800 |
| H | 0.45452300 | -1.25772900 | -3.51404500 |
| H | 3.73810200 | -1.29129400 | 1.44788000 |
| H | 5.19475400 | -3.27145400 | 1.51390500 |
| H | 5.26280200 | -4.86809400 | -0.41396300 |
| H | 3.79753800 | -4.47133300 | -2.38912500 |

**Compound 3 – Inv. TS ($S_0$)** optimized geometry (# opt=calcfc,ts,noeigentest scrf=(smd,solvent=MeCN) def2svp mn15)



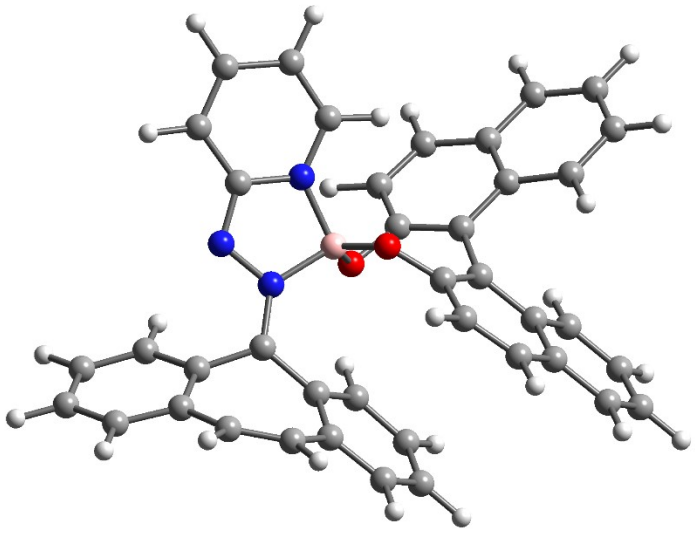
EE + Thermal Free Energy Correction: -1875.317193 Ha (+27.9 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | -2.09851600 | -0.71256400 | 0.95573200 |
| C | -2.89100800 | 0.09081500 | 0.21755800 |
| C | -2.89116100 | 1.50954600 | 0.60561900 |
| C | -3.62935800 | 2.56587700 | -0.01838000 |
| C | -4.73608500 | 2.43261400 | -0.94717700 |
| C | -5.29556500 | 1.33563800 | -1.50028800 |
| C | -4.79100500 | -0.02108000 | -1.56236200 |
| C | -3.64235500 | -0.53433500 | -0.89551900 |
| C | -5.45100900 | -0.83138000 | -2.51877900 |
| C | -4.95122700 | -2.05547600 | -2.92417600 |
| C | -3.72694900 | -2.48880000 | -2.39553900 |
| C | -3.10769100 | -1.74686600 | -1.40527000 |
| C | -2.18411200 | 1.84804700 | 1.78763800 |
| C | -2.05050600 | 3.15392500 | 2.23712100 |
| C | -2.63551800 | 4.20150300 | 1.51968100 |
| C | -3.43057700 | 3.89167500 | 0.42820500 |
| N | -2.52920100 | -1.99013500 | 1.21999400 |
| C | -1.50038000 | -2.71897600 | 1.61197000 |
| N | -0.28356100 | -2.09105000 | 1.56298200 |
| C | 0.85456300 | -2.67322400 | 2.02102000 |
| C | 0.84080600 | -3.95468000 | 2.50653100 |
| C | -0.40287200 | -4.65522300 | 2.53203400 |
| C | -1.56056900 | -4.06197200 | 2.09870500 |
| B | -0.45115300 | -0.68272700 | 0.94174000 |
| O | -0.17452100 | -0.63505900 | -0.48250800 |
| O | 0.32500300 | 0.24504900 | 1.71040800 |
| C | 1.06252400 | -1.11072500 | -0.78303100 |
| C | 1.16239300 | -2.38706200 | -1.39603600 |

| | | | |
|---|---|---|---|
| C | 2.39505200 | -2.94745000 | -1.61637900 |
| C | 3.57806700 | -2.27658500 | -1.19391700 |
| C | 3.47775200 | -0.98959500 | -0.57825200 |
| C | 2.18358300 | -0.37358400 | -0.43497300 |
| C | 4.85517800 | -2.88399600 | -1.35178800 |
| C | 5.99594900 | -2.26602300 | -0.89207700 |
| C | 5.89734400 | -1.01179400 | -0.24002900 |
| C | 4.67569700 | -0.39174200 | -0.08900800 |
| C | 2.00257300 | 0.98797600 | 0.13363400 |
| C | 2.71376000 | 2.11922300 | -0.40584700 |
| C | 2.67891900 | 3.37608800 | 0.27140200 |
| C | 1.91587900 | 3.49219400 | 1.46665300 |
| C | 1.16038500 | 2.43835500 | 1.90989100 |
| C | 1.14507300 | 1.19841800 | 1.21209700 |
| C | 3.44368500 | 2.04558200 | -1.62830700 |
| C | 4.11681100 | 3.13993900 | -2.12743200 |
| C | 4.10799400 | 4.37373900 | -1.43051000 |
| C | 3.39732000 | 4.48454800 | -0.25656400 |
| H | -5.23772800 | 3.38115700 | -1.15939200 |
| H | -6.19727200 | 1.50296900 | -2.09623800 |
| H | -6.36067100 | -0.43583600 | -2.97675700 |
| H | -5.47926600 | -2.64809200 | -3.67418500 |
| H | -3.25972900 | -3.40828700 | -2.75377100 |
| H | -2.15500000 | -2.10107500 | -1.01874900 |
| H | -1.75367400 | 1.04954200 | 2.38732300 |
| H | -1.51281000 | 3.35392300 | 3.16559700 |
| H | -2.52699500 | 5.23689400 | 1.84877400 |
| H | -3.97822800 | 4.68570000 | -0.08486000 |
| H | 1.75978400 | -2.06273500 | 1.96271700 |
| H | 1.76031300 | -4.42053900 | 2.85935700 |
| H | -0.43143400 | -5.68031300 | 2.90912600 |
| H | -2.52547900 | -4.56941400 | 2.12065000 |
| H | 0.23678900 | -2.90062800 | -1.66892400 |
| H | 2.48761800 | -3.92734300 | -2.09178200 |
| H | 4.90554000 | -3.86201800 | -1.83816400 |
| H | 6.97115900 | -2.74272200 | -1.01359800 |
| H | 6.79793700 | -0.53406400 | 0.15288700 |
| H | 4.61845100 | 0.56723300 | 0.42860700 |
| H | 1.92635400 | 4.43881600 | 2.01320300 |
| H | 0.56200900 | 2.50930000 | 2.81843700 |
| H | 3.45134500 | 1.10740900 | -2.18647200 |
| H | 4.65742700 | 3.05658500 | -3.07325100 |
| H | 4.65197200 | 5.23163000 | -1.83203400 |
| H | 3.36227600 | 5.43106200 | 0.28992800 |

**Compound 3 - Stable ($S_1$)** optimized geometry (# opt=calcfc td=(root=1) scrf=(smd,solvent=MeCN) def2svp mn15)



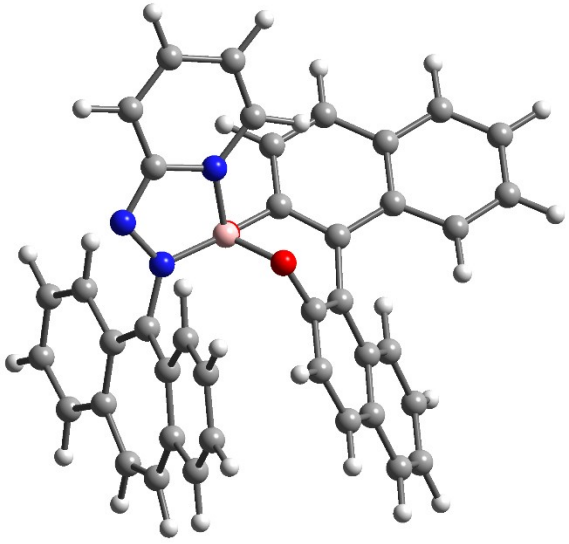
EE + Thermal Free Energy Correction: -1875.267402 Ha (+59.1 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | -2.02018600 | 0.95424600 | 0.07898300 |
| C | -2.82973500 | -0.16797700 | 0.21784100 |
| C | -2.22921500 | -1.49309400 | 0.34862400 |
| C | -2.75558600 | -2.64902800 | -0.30245900 |
| C | -3.93263100 | -2.63933000 | -1.16359900 |
| C | -5.01845600 | -1.83650400 | -1.07695600 |
| C | -5.27191800 | -0.75843800 | -0.13094600 |
| C | -4.24296100 | 0.03120900 | 0.47223700 |
| C | -6.61781400 | -0.43919200 | 0.12839500 |
| C | -6.97984800 | 0.58263900 | 0.99978700 |
| C | -5.97449400 | 1.33401300 | 1.62831800 |
| C | -4.64105300 | 1.07357000 | 1.35895600 |
| C | -1.11246600 | -1.66557100 | 1.20106500 |
| C | -0.52648200 | -2.91004800 | 1.40012800 |
| C | -1.01432600 | -4.03255100 | 0.72018000 |
| C | -2.10716100 | -3.88620700 | -0.12873200 |
| N | -2.69512300 | 2.08408500 | -0.26215700 |
| C | -1.83277800 | 3.03865800 | -0.60162300 |
| N | -0.52338100 | 2.61616900 | -0.60442000 |
| C | 0.46460300 | 3.42477800 | -1.02795000 |
| C | 0.19627800 | 4.73139500 | -1.40423700 |
| C | -1.13795200 | 5.20613500 | -1.36492600 |
| C | -2.16161000 | 4.36152600 | -0.97430900 |
| B | -0.45420500 | 1.11945700 | -0.13971400 |
| O | 0.26533800 | 0.97439800 | 1.10919800 |
| O | 0.09414000 | 0.35495800 | -1.23714800 |
| C | 1.58329000 | 1.29549100 | 1.06435800 |

| | | | |
|---|---|---|---|
| C | 2.00498300 | 2.45541900 | 1.76736400 |
| C | 3.30948900 | 2.87347000 | 1.69161800 |
| C | 4.24263400 | 2.17541200 | 0.87455500 |
| C | 3.82309400 | 1.00123700 | 0.17366400 |
| C | 2.47545500 | 0.51979600 | 0.33422600 |
| C | 5.57903100 | 2.64308600 | 0.73026900 |
| C | 6.47006500 | 1.99849200 | -0.09717200 |
| C | 6.04838100 | 0.85831300 | -0.82596600 |
| C | 4.76527200 | 0.37347000 | -0.69316700 |
| C | 2.00491300 | -0.74468700 | -0.29358100 |
| C | 2.68171900 | -1.99705900 | -0.08008900 |
| C | 2.28738400 | -3.15382200 | -0.82161100 |
| C | 1.20427900 | -3.05422100 | -1.74074700 |
| C | 0.49965600 | -1.88476200 | -1.85602100 |
| C | 0.86843900 | -0.73916500 | -1.09777100 |
| C | 3.72109100 | -2.15014000 | 0.88377800 |
| C | 4.34300400 | -3.36493000 | 1.07960800 |
| C | 3.96902400 | -4.49978300 | 0.31787400 |
| C | 2.95759800 | -4.39037600 | -0.61030000 |
| H | -3.98245700 | -3.46389300 | -1.88235700 |
| H | -5.86073000 | -2.07388100 | -1.73525400 |
| H | -7.39007400 | -1.02415800 | -0.37850700 |
| H | -8.03366100 | 0.79426700 | 1.19286700 |
| H | -6.23842600 | 2.12766300 | 2.33122400 |
| H | -3.86418200 | 1.65123600 | 1.86208900 |
| H | -0.72643700 | -0.80134200 | 1.73872000 |
| H | 0.32250100 | -3.00251700 | 2.08256700 |
| H | -0.54280000 | -5.00954700 | 0.84913100 |
| H | -2.49861000 | -4.75111200 | -0.67107000 |
| H | 1.47030600 | 2.99860900 | -1.06787600 |
| H | 1.01287200 | 5.37177600 | -1.73799400 |
| H | -1.35903100 | 6.23328900 | -1.66082700 |
| H | -3.20651500 | 4.67247700 | -0.95142900 |
| H | 1.25941300 | 2.99711600 | 2.35382900 |
| H | 3.64475300 | 3.76167000 | 2.23340400 |
| H | 5.87642800 | 3.53588900 | 1.28719100 |
| H | 7.49236000 | 2.36767800 | -0.20511800 |
| H | 6.74595400 | 0.36216400 | -1.50489000 |
| H | 4.45513500 | -0.49741800 | -1.27319300 |
| H | 0.92118800 | -3.93719500 | -2.32016000 |
| H | -0.36654700 | -1.79628700 | -2.51603900 |
| H | 4.01356200 | -1.29035400 | 1.48973200 |
| H | 5.12782100 | -3.45481200 | 1.83450600 |
| H | 4.47344400 | -5.45530100 | 0.47799500 |
| H | 2.64061800 | -5.25697500 | -1.19729400 |

**Compound 3 - Metastable ($S_1$)** optimized geometry (# opt=calcfc td=(root=1) scrf=(smd,solvent=MeCN) def2svp mn15)



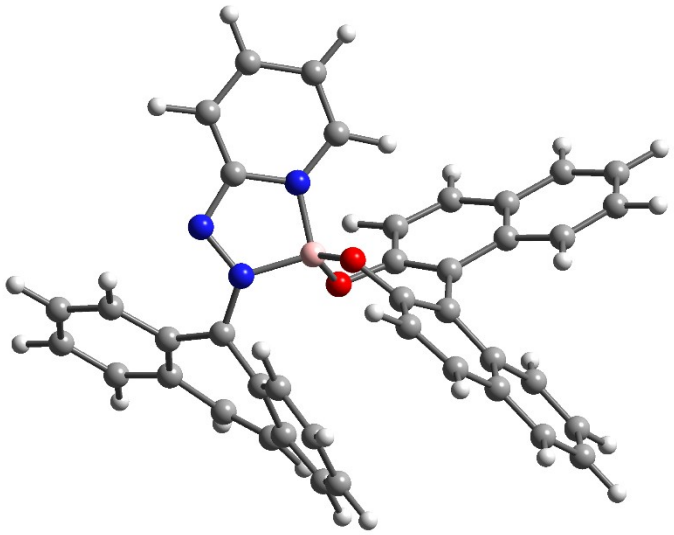
EE + Thermal Free Energy Correction: -1875.283652 Ha (+48.9 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | -1.85604000 | 1.47298800 | -0.04391900 |
| C | -2.64100700 | 0.36930200 | 0.27745200 |
| C | -2.76791300 | 0.09344700 | 1.68598200 |
| C | -3.21889300 | -1.13263500 | 2.28502600 |
| C | -3.59911100 | -2.32906300 | 1.58162100 |
| C | -3.78616300 | -2.55703400 | 0.25460400 |
| C | -3.70442600 | -1.66720000 | -0.87249600 |
| C | -3.21156600 | -0.31643500 | -0.85654000 |
| C | -4.11683600 | -2.22751500 | -2.10511200 |
| C | -4.11534000 | -1.50599700 | -3.28467700 |
| C | -3.68966400 | -0.16505800 | -3.26750200 |
| C | -3.23596000 | 0.40246800 | -2.09451100 |
| C | -2.39155400 | 1.15396800 | 2.56130200 |
| C | -2.49021500 | 1.04542500 | 3.93634400 |
| C | -2.92119300 | -0.15986400 | 4.51421700 |
| C | -3.26196200 | -1.22375900 | 3.69449300 |
| N | -2.41441900 | 2.71718000 | -0.15912700 |
| C | -1.43538700 | 3.54059700 | -0.51225300 |
| N | -0.20389800 | 2.93773800 | -0.66511100 |
| C | 0.88472600 | 3.62808200 | -1.08642000 |
| C | 0.81112900 | 4.97386800 | -1.34571900 |
| C | -0.44216800 | 5.63524300 | -1.16702600 |
| C | -1.55374300 | 4.94195000 | -0.76087600 |
| B | -0.32844200 | 1.43323400 | -0.29135000 |
| O | 0.35034300 | 1.06188600 | 0.94571100 |
| O | 0.10910400 | 0.61737100 | -1.41608600 |
| C | 1.70159900 | 1.02531500 | 0.89272400 |

| | | | |
|---|---|---|---|
| C | 2.43329600 | 2.03550900 | 1.57434000 |
| C | 3.80352400 | 2.06621800 | 1.50303000 |
| C | 4.50725400 | 1.11250200 | 0.71460100 |
| C | 3.77623800 | 0.09168000 | 0.02967100 |
| C | 2.34804300 | 0.02213900 | 0.17883400 |
| C | 5.92270700 | 1.17492000 | 0.58060200 |
| C | 6.59926400 | 0.28292400 | -0.22019700 |
| C | 5.87566000 | -0.70655100 | -0.93232000 |
| C | 4.50620100 | -0.79969500 | -0.81030000 |
| C | 1.51770000 | -1.04820300 | -0.43244900 |
| C | 1.75829500 | -2.44572100 | -0.19152100 |
| C | 0.97848900 | -3.42757200 | -0.87832300 |
| C | -0.04748500 | -3.00038500 | -1.76734200 |
| C | -0.31651000 | -1.66516700 | -1.93029900 |
| C | 0.44077800 | -0.68038300 | -1.23585700 |
| C | 2.73169100 | -2.90642000 | 0.74305700 |
| C | 2.94103300 | -4.25236200 | 0.95339900 |
| C | 2.19077900 | -5.22081000 | 0.24045400 |
| C | 1.22614000 | -4.81013100 | -0.65173700 |
| H | -3.78739700 | -3.18372100 | 2.23770600 |
| H | -4.09342500 | -3.57309700 | -0.00943100 |
| H | -4.45486600 | -3.26617700 | -2.10268900 |
| H | -4.45670000 | -1.96802600 | -4.21301500 |
| H | -3.71011500 | 0.43107700 | -4.18191200 |
| H | -2.91179600 | 1.44149400 | -2.09859400 |
| H | -2.03187300 | 2.08323300 | 2.12223700 |
| H | -2.21456900 | 1.89230000 | 4.56763500 |
| H | -2.97817300 | -0.26394800 | 5.59969300 |
| H | -3.57885300 | -2.17241800 | 4.13328400 |
| H | 1.80406200 | 3.04890300 | -1.20623000 |
| H | 1.69478500 | 5.51762000 | -1.67863500 |
| H | -0.51599100 | 6.70731300 | -1.36362400 |
| H | -2.52515600 | 5.41907800 | -0.62609700 |
| H | 1.87044200 | 2.77747700 | 2.14569800 |
| H | 4.37334800 | 2.83655700 | 2.02937800 |
| H | 6.45911500 | 1.95822300 | 1.12340900 |
| H | 7.68538600 | 0.34197900 | -0.32014900 |
| H | 6.40847700 | -1.39817000 | -1.58929100 |
| H | 3.96279600 | -1.55886300 | -1.37607100 |
| H | -0.63138100 | -3.75473900 | -2.30213100 |
| H | -1.11705100 | -1.32168200 | -2.58930000 |
| H | 3.30865900 | -2.17488000 | 1.31199100 |
| H | 3.68846900 | -4.57605000 | 1.68170800 |
| H | 2.37121700 | -6.28460600 | 0.41063900 |
| H | 0.62302400 | -5.54002900 | -1.19900900 |

**Compound 3 – Inv. TS ($S_1$)** optimized geometry (# opt=calcfc,ts,noeigentest td=(root=1) scrf=(smd,solvent=MeCN) def2svp mn15)



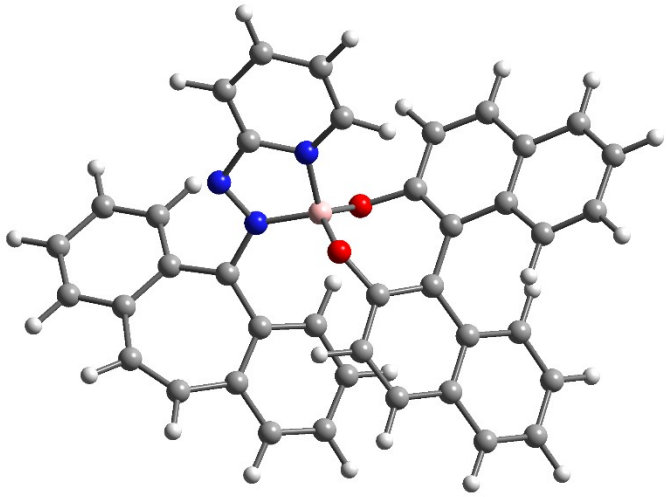
EE + Thermal Free Energy Correction: -1875.259156 Ha (+64.3 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | -2.27219200 | 0.25876000 | -1.05686000 |
| C | -2.75264800 | -0.79871000 | -0.28709600 |
| C | -4.01680200 | -0.70784200 | 0.43868800 |
| C | -4.15830200 | -1.12597600 | 1.79848400 |
| C | -3.10344100 | -1.71697600 | 2.60815700 |
| C | -2.00343300 | -2.40798900 | 2.22024400 |
| C | -1.54673700 | -2.72067000 | 0.88119000 |
| C | -1.89665400 | -1.96272700 | -0.28174400 |
| C | -0.64634700 | -3.79652100 | 0.74920300 |
| C | -0.14650300 | -4.19130400 | -0.48516100 |
| C | -0.51701700 | -3.47075900 | -1.63268600 |
| C | -1.33601300 | -2.35863600 | -1.52432000 |
| C | -5.16192200 | -0.17184500 | -0.20343100 |
| C | -6.37533800 | -0.02659600 | 0.45671000 |
| C | -6.49574200 | -0.39050400 | 1.80473300 |
| C | -5.39238900 | -0.92707700 | 2.45375600 |
| N | -3.09382300 | 1.21500600 | -1.53306500 |
| C | -2.42875500 | 2.36913300 | -1.59443300 |
| N | -1.11771300 | 2.27989700 | -1.17493700 |
| C | -0.31242300 | 3.35811000 | -1.17270800 |
| C | -0.78659300 | 4.59868800 | -1.56350900 |
| C | -2.13201000 | 4.72005100 | -1.99647000 |
| C | -2.95473200 | 3.61018900 | -2.02485900 |
| B | -0.78290300 | 0.78197000 | -0.84296100 |
| O | -0.42125800 | 0.50195500 | 0.52430100 |
| O | 0.21439900 | 0.37881600 | -1.81615000 |
| C | 0.69759200 | 1.12289900 | 0.97070800 |

| | | | |
|---|---|---|---|
| C | 0.54182000 | 2.15297100 | 1.93647000 |
| C | 1.63070100 | 2.86995300 | 2.36225100 |
| C | 2.91770600 | 2.62088800 | 1.80703100 |
| C | 3.07767300 | 1.57984900 | 0.83888700 |
| C | 1.94369200 | 0.76876900 | 0.47225300 |
| C | 4.03850000 | 3.41197800 | 2.18533300 |
| C | 5.27329100 | 3.21344200 | 1.61074100 |
| C | 5.42801300 | 2.21504000 | 0.61716500 |
| C | 4.36411100 | 1.42218200 | 0.24421900 |
| C | 2.06496800 | -0.37556000 | -0.47003900 |
| C | 3.04062900 | -1.41600500 | -0.26572600 |
| C | 3.31575700 | -2.35228800 | -1.30913600 |
| C | 2.59110300 | -2.25556100 | -2.53070100 |
| C | 1.57603000 | -1.34505700 | -2.66075700 |
| C | 1.26034500 | -0.44109700 | -1.60663100 |
| C | 3.74597600 | -1.56660400 | 0.96365300 |
| C | 4.67565300 | -2.56980900 | 1.13764400 |
| C | 4.96444200 | -3.47730500 | 0.08843700 |
| C | 4.29229700 | -3.36671500 | -1.10851300 |
| H | -3.29397800 | -1.67806600 | 3.68551200 |
| H | -1.41032400 | -2.86414100 | 3.01961000 |
| H | -0.35301400 | -4.33351100 | 1.65533800 |
| H | 0.53016400 | -5.04525400 | -0.56037500 |
| H | -0.14157100 | -3.77106700 | -2.61298000 |
| H | -1.59316600 | -1.77965900 | -2.41445800 |
| H | -5.09024100 | 0.11300500 | -1.25040400 |
| H | -7.23590800 | 0.37375400 | -0.08440100 |
| H | -7.44038500 | -0.25828700 | 2.33626900 |
| H | -5.46355100 | -1.21464300 | 3.50607700 |
| H | 0.72574600 | 3.19772100 | -0.86868800 |
| H | -0.11652800 | 5.45856600 | -1.55532600 |
| H | -2.51473100 | 5.69156700 | -2.31518200 |
| H | -3.99286300 | 3.65653500 | -2.35604300 |
| H | -0.46357000 | 2.35024100 | 2.31518300 |
| H | 1.52342300 | 3.65975800 | 3.11031700 |
| H | 3.88977900 | 4.19130800 | 2.93782700 |
| H | 6.12656400 | 3.82906800 | 1.90396100 |
| H | 6.39914000 | 2.07645500 | 0.13606000 |
| H | 4.50151700 | 0.67083300 | -0.53482600 |
| H | 2.82936300 | -2.94644900 | -3.34381800 |
| H | 0.96607600 | -1.29253800 | -3.56568400 |
| H | 3.52778000 | -0.88275700 | 1.78667000 |
| H | 5.19021000 | -2.66974900 | 2.09636700 |
| H | 5.70780600 | -4.26396400 | 0.23583900 |
| H | 4.48873900 | -4.06443300 | -1.92744100 |

**Compound 3 - Stable ($T_1$)** optimized geometry (# opt=calcfc scrf=(smd,solvent=MeCN) def2svp mn15)



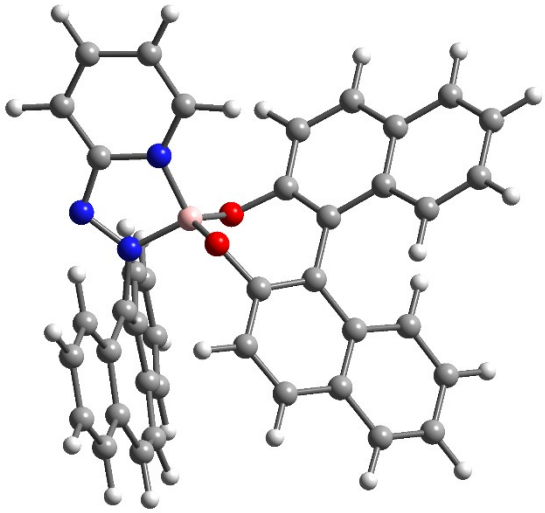
EE + Thermal Free Energy Correction: -1875.300587 Ha (+38.3 kcal/mol)

0 3

| | | | |
|---|---|---|---|
| N | -1.99662700 | 0.98807700 | 0.02277900 |
| C | -2.83151900 | -0.16717800 | 0.16984600 |
| C | -2.23818800 | -1.49860400 | 0.28878200 |
| C | -2.79998100 | -2.62914600 | -0.36647700 |
| C | -4.00543800 | -2.57091800 | -1.19557700 |
| C | -5.07336400 | -1.75757200 | -1.04610800 |
| C | -5.28279700 | -0.70739400 | -0.04849500 |
| C | -4.22653100 | 0.05385200 | 0.52533700 |
| C | -6.61164500 | -0.40354600 | 0.30322200 |
| C | -6.91786500 | 0.58801000 | 1.22965200 |
| C | -5.87773600 | 1.32236200 | 1.81597000 |
| C | -4.56056500 | 1.06615000 | 1.45926300 |
| C | -1.11762900 | -1.70228400 | 1.12475100 |
| C | -0.55176600 | -2.96234100 | 1.29622900 |
| C | -1.07556700 | -4.06303300 | 0.61019100 |
| C | -2.18030200 | -3.88353400 | -0.21814900 |
| N | -2.67106000 | 2.07269200 | -0.37842500 |
| C | -1.80313400 | 3.04666000 | -0.71589000 |
| N | -0.50052300 | 2.65714300 | -0.65131100 |
| C | 0.49605900 | 3.47476200 | -1.02814000 |
| C | 0.21975400 | 4.76843400 | -1.44262700 |
| C | -1.12039900 | 5.20577700 | -1.48576300 |
| C | -2.14731500 | 4.34685000 | -1.13158800 |
| B | -0.43771900 | 1.14559600 | -0.16793600 |
| O | 0.25973000 | 1.00643000 | 1.08605300 |
| O | 0.12700600 | 0.40057600 | -1.26749400 |
| C | 1.58610100 | 1.30031800 | 1.06676500 |
| C | 2.01521700 | 2.44471500 | 1.79007700 |

| | | | |
|---|---|---|---|
| C | 3.32892700 | 2.83753700 | 1.74625500 |
| C | 4.26526700 | 2.12877600 | 0.94225800 |
| C | 3.83756700 | 0.97007900 | 0.22119200 |
| C | 2.47759000 | 0.51305600 | 0.34881800 |
| C | 5.61331200 | 2.57136400 | 0.83046600 |
| C | 6.50851300 | 1.91732500 | 0.01510800 |
| C | 6.07974600 | 0.79310900 | -0.73399500 |
| C | 4.78496900 | 0.33237000 | -0.63246700 |
| C | 2.00004000 | -0.73840800 | -0.29969000 |
| C | 2.65242100 | -2.00365400 | -0.08429600 |
| C | 2.25640800 | -3.14582700 | -0.84674200 |
| C | 1.19476900 | -3.02024900 | -1.78758100 |
| C | 0.51008800 | -1.83931400 | -1.90487400 |
| C | 0.88169900 | -0.70808300 | -1.12701600 |
| C | 3.66528700 | -2.18365600 | 0.90248700 |
| C | 4.26065500 | -3.41127400 | 1.10179400 |
| C | 3.88547000 | -4.53208900 | 0.32037300 |
| C | 2.89960600 | -4.39583800 | -0.63159200 |
| H | -4.08541100 | -3.36335900 | -1.94743100 |
| H | -5.93719400 | -1.95195500 | -1.69090200 |
| H | -7.41460500 | -0.97127000 | -0.17506400 |
| H | -7.95802200 | 0.79437700 | 1.49076100 |
| H | -6.09838000 | 2.10240300 | 2.54839300 |
| H | -3.75347100 | 1.64340000 | 1.91437200 |
| H | -0.70067500 | -0.85050000 | 1.66094800 |
| H | 0.31016200 | -3.08192000 | 1.95798500 |
| H | -0.62288200 | -5.05154500 | 0.71789700 |
| H | -2.60115800 | -4.73449400 | -0.76085400 |
| H | 1.50944900 | 3.06771300 | -1.00211100 |
| H | 1.03739000 | 5.42429200 | -1.74074200 |
| H | -1.34891200 | 6.22166400 | -1.81352300 |
| H | -3.19811900 | 4.63427100 | -1.16907000 |
| H | 1.26804600 | 2.99503200 | 2.36634400 |
| H | 3.66983600 | 3.71354800 | 2.30407100 |
| H | 5.91641800 | 3.45272500 | 1.40229400 |
| H | 7.53984800 | 2.26725900 | -0.06807400 |
| H | 6.78131500 | 0.29009200 | -1.40367300 |
| H | 4.47004600 | -0.52631100 | -1.22784400 |
| H | 0.91037800 | -3.89309200 | -2.38149000 |
| H | -0.34138000 | -1.73100500 | -2.58082400 |
| H | 3.95786600 | -1.33490000 | 1.52378100 |
| H | 5.02493800 | -3.52205100 | 1.87475800 |
| H | 4.36869300 | -5.49797700 | 0.48362000 |
| H | 2.58164300 | -5.25120900 | -1.23433000 |

**Compound 3 - Metastable ($T_1$)** optimized geometry (# opt=calcfc scrf=(smd,solvent=MeCN) def2svp mn15)



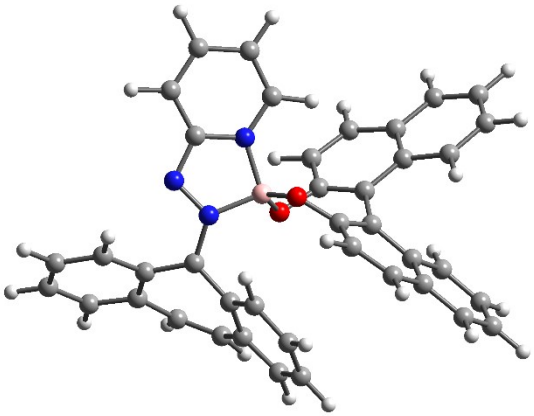
EE + Thermal Free Energy Correction: -1875.317659 Ha (+27.6 kcal/mol)

0 3

| | | | |
|---|---|---|---|
| N | -1.81790600 | 1.52631900 | 0.04261800 |
| C | -2.62025200 | 0.38160700 | 0.31240800 |
| C | -2.72463300 | 0.03175000 | 1.71380200 |
| C | -3.18842400 | -1.21906100 | 2.23490900 |
| C | -3.58542600 | -2.37345600 | 1.44107100 |
| C | -3.79636700 | -2.51199500 | 0.11462200 |
| C | -3.72163600 | -1.54676000 | -0.97272600 |
| C | -3.20587200 | -0.21497600 | -0.87253700 |
| C | -4.16300700 | -2.02036500 | -2.22290300 |
| C | -4.14996100 | -1.23522500 | -3.37086400 |
| C | -3.67898300 | 0.07910400 | -3.27657200 |
| C | -3.21533300 | 0.56621300 | -2.06253600 |
| C | -2.32047600 | 1.01126400 | 2.66406800 |
| C | -2.38875800 | 0.79918500 | 4.03323800 |
| C | -2.85125300 | -0.42370700 | 4.53255300 |
| C | -3.23214600 | -1.40928600 | 3.62917600 |
| N | -2.34303700 | 2.74155900 | 0.00458400 |
| C | -1.35583900 | 3.60152800 | -0.36391500 |
| N | -0.15669000 | 2.99634000 | -0.59898100 |
| C | 0.91879100 | 3.68774200 | -1.01901900 |
| C | 0.84088500 | 5.05572400 | -1.20338700 |
| C | -0.38457400 | 5.70852500 | -0.94828800 |
| C | -1.49290600 | 4.99194300 | -0.53093600 |
| B | -0.28596300 | 1.46103500 | -0.25169800 |
| O | 0.39964300 | 1.09911200 | 0.96604800 |
| O | 0.10500400 | 0.67934800 | -1.39706200 |
| C | 1.75206900 | 1.01863600 | 0.88519200 |

| | | | |
|---|---|---|---|
| C | 2.52533300 | 2.00318900 | 1.55584400 |
| C | 3.89464300 | 1.98759900 | 1.46040400 |
| C | 4.55194300 | 1.01205900 | 0.65911000 |
| C | 3.77601700 | 0.01870500 | -0.01646600 |
| C | 2.34903000 | -0.00218800 | 0.15620400 |
| C | 5.96655400 | 1.02582800 | 0.50284300 |
| C | 6.59855300 | 0.11266800 | -0.31016600 |
| C | 5.83021700 | -0.84951400 | -1.01277800 |
| C | 4.46053700 | -0.89556000 | -0.86968000 |
| C | 1.47358600 | -1.04058200 | -0.44857000 |
| C | 1.67140000 | -2.44651900 | -0.21981100 |
| C | 0.85701600 | -3.39648100 | -0.91083200 |
| C | -0.15693600 | -2.92984700 | -1.79338200 |
| C | -0.38667800 | -1.58548400 | -1.94344700 |
| C | 0.40308400 | -0.63526000 | -1.24024300 |
| C | 2.63449600 | -2.94430500 | 0.70613100 |
| C | 2.80028800 | -4.29769800 | 0.90618100 |
| C | 2.01501400 | -5.23575000 | 0.19007100 |
| C | 1.06051700 | -4.78810600 | -0.69495800 |
| H | -3.75806400 | -3.27195200 | 2.04184100 |
| H | -4.11339700 | -3.50767700 | -0.21143000 |
| H | -4.52663200 | -3.04982900 | -2.27566900 |
| H | -4.50328900 | -1.63850800 | -4.32185600 |
| H | -3.66550900 | 0.72774200 | -4.15526200 |
| H | -2.85196000 | 1.59152900 | -2.02825400 |
| H | -1.95575000 | 1.97297900 | 2.30783500 |
| H | -2.07503000 | 1.59279200 | 4.71503400 |
| H | -2.90390400 | -0.60741400 | 5.60745500 |
| H | -3.57627800 | -2.37871300 | 3.99882000 |
| H | 1.82804600 | 3.11147700 | -1.20680400 |
| H | 1.71561000 | 5.60868000 | -1.54477400 |
| H | -0.46070200 | 6.78860100 | -1.08954000 |
| H | -2.45753600 | 5.46090700 | -0.33601100 |
| H | 1.99766000 | 2.76170500 | 2.13878700 |
| H | 4.49901100 | 2.73691800 | 1.97827600 |
| H | 6.53845900 | 1.78856300 | 1.03849400 |
| H | 7.68435500 | 0.13400100 | -0.42705900 |
| H | 6.32859700 | -1.55760000 | -1.67908800 |
| H | 3.88238100 | -1.63400900 | -1.42822800 |
| H | -0.76524100 | -3.66074800 | -2.33342000 |
| H | -1.17802100 | -1.21168800 | -2.59681700 |
| H | 3.23783100 | -2.23575000 | 1.27687200 |
| H | 3.53983100 | -4.65117300 | 1.62861900 |
| H | 2.16101300 | -6.30599400 | 0.35268000 |
| H | 0.43151800 | -5.49409700 | -1.24429900 |

**Compound 3 – Inv. TS ($T_1$)** optimized geometry (# opt=calcfc,ts,noeigentest scrf=(smd,solvent=MeCN) def2svp mn15)



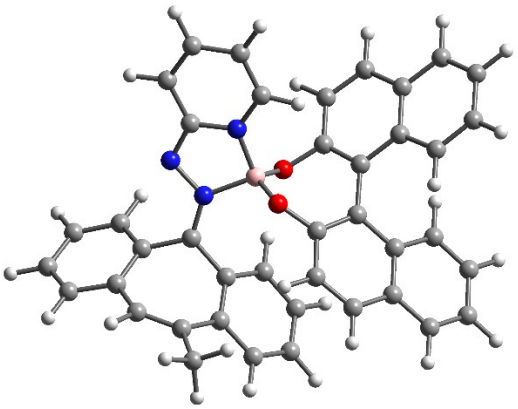
EE + Thermal Free Energy Correction: -1875.292306 Ha (+43.5 kcal/mol)

0 3

| | | | |
|---|---|---|---|
| N | -2.20313900 | 0.48122100 | -0.93117400 |
| C | -2.82100500 | -0.60547800 | -0.22772800 |
| C | -4.18602500 | -0.50342700 | 0.28793400 |
| C | -4.51854400 | -0.90545700 | 1.61134600 |
| C | -3.56287300 | -1.48001000 | 2.56025300 |
| C | -2.46021200 | -2.21662700 | 2.30402100 |
| C | -1.89952500 | -2.60586300 | 1.01157800 |
| C | -2.05608500 | -1.83848300 | -0.17805000 |
| C | -1.10861600 | -3.76735100 | 0.97236100 |
| C | -0.52325100 | -4.21761600 | -0.20821600 |
| C | -0.69570700 | -3.47509800 | -1.38211700 |
| C | -1.42324700 | -2.29013800 | -1.35742400 |
| C | -5.22646200 | -0.01389100 | -0.53789400 |
| C | -6.53018000 | 0.11592000 | -0.07273100 |
| C | -6.84184600 | -0.23090800 | 1.24723400 |
| C | -5.83898400 | -0.73235100 | 2.06957400 |
| N | -2.95806300 | 1.53875100 | -1.22786600 |
| C | -2.17375100 | 2.62973200 | -1.34283900 |
| N | -0.86306600 | 2.39111800 | -1.05507000 |
| C | 0.05960800 | 3.36424700 | -1.12355400 |
| C | -0.30936500 | 4.65659600 | -1.46232500 |
| C | -1.66253700 | 4.93112300 | -1.75264900 |
| C | -2.60752100 | 3.92053800 | -1.70181300 |
| B | -0.67744700 | 0.84031700 | -0.75128800 |
| O | -0.30578900 | 0.52682800 | 0.60111600 |
| O | 0.24666000 | 0.37460200 | -1.76240400 |
| C | 0.86398600 | 1.07839100 | 1.01377600 |
| C | 0.79955700 | 2.11581900 | 1.98114900 |
| C | 1.94143700 | 2.77048300 | 2.36684900 |
| C | 3.19191000 | 2.44893100 | 1.76779700 |

| | | | |
|---|---|---|---|
| C | 3.25913600 | 1.40118200 | 0.79629700 |
| C | 2.06890000 | 0.65555000 | 0.47064600 |
| C | 4.36790300 | 3.17569200 | 2.10569100 |
| C | 5.56841200 | 2.90857700 | 1.48812900 |
| C | 5.63194000 | 1.90347300 | 0.49127800 |
| C | 4.51294700 | 1.17144900 | 0.15713400 |
| C | 2.09280500 | -0.49022600 | -0.47772300 |
| C | 3.00898900 | -1.58803100 | -0.30334500 |
| C | 3.18642900 | -2.54348700 | -1.35065200 |
| C | 2.42645900 | -2.40502600 | -2.54649600 |
| C | 1.46859600 | -1.43093600 | -2.64730000 |
| C | 1.24936100 | -0.50625900 | -1.58712600 |
| C | 3.74801900 | -1.77798500 | 0.90054300 |
| C | 4.62029300 | -2.83555200 | 1.04566600 |
| C | 4.81360800 | -3.76282000 | -0.00832800 |
| C | 4.10554200 | -3.61547500 | -1.18019700 |
| H | -3.85276300 | -1.37875100 | 3.61145300 |
| H | -1.94827700 | -2.65242900 | 3.16864600 |
| H | -0.96145700 | -4.32383000 | 1.90209600 |
| H | 0.07012100 | -5.13443900 | -0.21431400 |
| H | -0.24440800 | -3.81258400 | -2.31719600 |
| H | -1.52837000 | -1.69365500 | -2.26757900 |
| H | -4.99527700 | 0.25686300 | -1.56718800 |
| H | -7.30716100 | 0.49117100 | -0.74287600 |
| H | -7.85935900 | -0.11567000 | 1.62696300 |
| H | -6.06705800 | -1.01063900 | 3.10221500 |
| H | 1.09339100 | 3.08158700 | -0.90845800 |
| H | 0.44794700 | 5.43887600 | -1.50940200 |
| H | -1.96361600 | 5.94459000 | -2.02462000 |
| H | -3.66132700 | 4.08535800 | -1.92704200 |
| H | -0.17913600 | 2.37020700 | 2.39407100 |
| H | 1.90513000 | 3.56549800 | 3.11617800 |
| H | 4.28937700 | 3.96157000 | 2.86194500 |
| H | 6.46472100 | 3.47506300 | 1.75036200 |
| H | 6.57639400 | 1.71060700 | -0.02306000 |
| H | 4.58101000 | 0.41311700 | -0.62431300 |
| H | 2.59076300 | -3.11341100 | -3.36286000 |
| H | 0.83244100 | -1.34172800 | -3.53114700 |
| H | 3.60292300 | -1.07961300 | 1.72737800 |
| H | 5.16288600 | -2.96380900 | 1.98536300 |
| H | 5.51251300 | -4.59298600 | 0.11611000 |
| H | 4.22812000 | -4.32684500 | -2.00170800 |

**Compound *(Z)*-4 - Stable ($S_0$)** optimized geometry (# opt=calcfc scrf=(smd,solvent=MeCN) def2svp mn15)



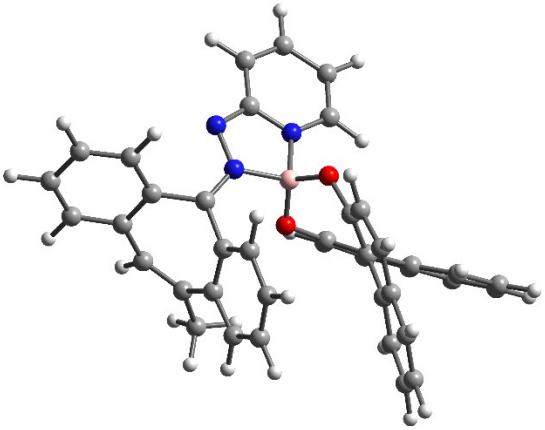
EE + Thermal Free Energy Correction: -1914.564643 Ha (+0.0 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | 1.90277200 | 1.18943400 | -0.13274700 |
| C | 2.68346500 | 0.18117200 | -0.40351900 |
| C | 2.17405000 | -1.19967800 | -0.55798400 |
| C | 2.69736400 | -2.25410100 | 0.23085600 |
| C | 3.69189100 | -2.04900700 | 1.30992200 |
| C | 4.71873200 | -1.16659900 | 1.24012700 |
| C | 5.07756800 | -0.26370600 | 0.14338200 |
| C | 4.12537900 | 0.38644700 | -0.66683800 |
| C | 6.44192200 | 0.00270000 | -0.09217200 |
| C | 6.84592500 | 0.82806800 | -1.13500400 |
| C | 5.88923300 | 1.43624900 | -1.95929900 |
| C | 4.53675200 | 1.22826500 | -1.71298500 |
| C | 1.22236600 | -1.47069000 | -1.55584600 |
| C | 0.76523100 | -2.76813700 | -1.77494900 |
| C | 1.26702500 | -3.81404400 | -0.99655500 |
| C | 2.20782500 | -3.55288100 | -0.00370100 |
| N | 2.41937200 | 2.45512200 | -0.05280400 |
| C | 1.47138800 | 3.24794900 | 0.44328800 |
| N | 0.27279100 | 2.65152200 | 0.71070600 |
| C | -0.76532200 | 3.31418600 | 1.27601500 |
| C | -0.66173500 | 4.64867200 | 1.58142400 |
| C | 0.56220300 | 5.30995500 | 1.28761800 |
| C | 1.62169000 | 4.63504500 | 0.72879200 |
| B | 0.31351300 | 1.18472600 | 0.17915200 |
| O | -0.36869200 | 1.05041900 | -1.08367200 |
| O | -0.10495600 | 0.28665500 | 1.20928500 |
| C | -1.70086300 | 1.31570200 | -1.00437000 |
| C | -2.18266900 | 2.50591300 | -1.60848700 |
| C | -3.50196300 | 2.85882600 | -1.47518900 |
| C | -4.38612700 | 2.06085000 | -0.69583900 |

| | | | |
|---|---|---|---|
| C | -3.90242800 | 0.85827100 | -0.09133400 |
| C | -2.53904100 | 0.45177900 | -0.31320300 |
| C | -5.73780100 | 2.45717600 | -0.49193600 |
| C | -6.58160400 | 1.71514800 | 0.30261900 |
| C | -6.09575800 | 0.54498400 | 0.93791400 |
| C | -4.79645500 | 0.12817900 | 0.74542700 |
| C | -1.99210000 | -0.82753300 | 0.21422900 |
| C | -2.61905200 | -2.09122700 | -0.07439400 |
| C | -2.16277100 | -3.27769100 | 0.57848700 |
| C | -1.06770500 | -3.19308200 | 1.48353100 |
| C | -0.41087400 | -2.00447700 | 1.66703900 |
| C | -0.84048600 | -0.82737500 | 0.99712000 |
| C | -3.67270400 | -2.22154500 | -1.02591800 |
| C | -4.25166500 | -3.44441400 | -1.28993100 |
| C | -3.81680600 | -4.61145600 | -0.61381500 |
| C | -2.78893700 | -4.52387600 | 0.29805800 |
| H | 5.43655400 | -1.18388900 | 2.06824100 |
| H | 7.18586300 | -0.46796800 | 0.55597900 |
| H | 7.90990900 | 1.00428700 | -1.30857300 |
| H | 6.20123000 | 2.08661000 | -2.77923200 |
| H | 3.77882900 | 1.72576200 | -2.32146800 |
| H | 0.84953900 | -0.64701400 | -2.16441800 |
| H | 0.02337900 | -2.96010200 | -2.55349300 |
| H | 0.91906200 | -4.83704800 | -1.15782000 |
| H | 2.58148100 | -4.38074900 | 0.60128800 |
| H | -1.66551200 | 2.72381400 | 1.46786000 |
| H | -1.49742800 | 5.17648000 | 2.03942900 |
| H | 0.66487800 | 6.37304300 | 1.51834800 |
| H | 2.57408400 | 5.11737800 | 0.50744800 |
| H | -1.47343100 | 3.12309400 | -2.16472000 |
| H | -3.88679600 | 3.76999800 | -1.94032600 |
| H | -6.08586900 | 3.37396000 | -0.97565900 |
| H | -7.61613100 | 2.02983600 | 0.45677900 |
| H | -6.75636300 | -0.02939400 | 1.59164500 |
| H | -4.43616700 | -0.76794400 | 1.25356800 |
| H | -0.73486000 | -4.09938300 | 1.99681900 |
| H | 0.46374200 | -1.92454000 | 2.31684000 |
| H | -4.01204600 | -1.33610000 | -1.56691600 |
| H | -5.04956600 | -3.51536400 | -2.03301700 |
| H | -4.28807800 | -5.57348100 | -0.82716300 |
| H | -2.42514200 | -5.41389700 | 0.81905400 |
| C | 3.59161200 | -2.96111700 | 2.50562200 |
| H | 3.89213400 | -3.99157800 | 2.25583500 |
| H | 4.24600700 | -2.61252100 | 3.31601500 |
| H | 2.55722900 | -3.01342900 | 2.88166000 |

**Compound (*Z*)-4 - Metastable ($S_0$)** optimized geometry (# opt=calcfc scrf=(smd,solvent=MeCN) def2svp mn15)



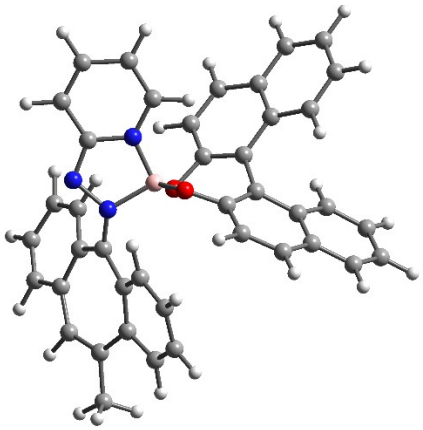
EE + Thermal Free Energy Correction: -1914.560181 Ha (+2.8 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | -2.20920700 | 0.63378200 | -0.79131500 |
| C | -2.65264300 | -0.50840600 | -0.36091300 |
| C | -1.74406200 | -1.63525900 | -0.05627300 |
| C | -1.48219200 | -1.95745700 | 1.29438900 |
| C | -2.13195800 | -1.23721000 | 2.41250000 |
| C | -3.41913700 | -0.80563200 | 2.38604900 |
| C | -4.41403200 | -0.88285100 | 1.30679500 |
| C | -4.08038600 | -0.73181000 | -0.05627200 |
| C | -5.77559900 | -1.03354600 | 1.63590900 |
| C | -6.75358000 | -1.08662400 | 0.64754500 |
| C | -6.40030900 | -0.95712500 | -0.70201600 |
| C | -5.06613200 | -0.76553700 | -1.05093900 |
| C | -1.17638800 | -2.37938700 | -1.09553500 |
| C | -0.31152200 | -3.43691200 | -0.81265500 |
| C | 0.01525200 | -3.72154100 | 0.51434200 |
| C | -0.55534300 | -2.98248000 | 1.55144000 |
| N | -3.07737500 | 1.65455300 | -1.06615600 |
| C | -2.35870500 | 2.77371900 | -1.14149100 |
| N | -1.01268600 | 2.63963800 | -0.94966000 |
| C | -0.15327000 | 3.68387000 | -1.04101900 |
| C | -0.61396600 | 4.95286700 | -1.28690000 |
| C | -2.01315900 | 5.13431200 | -1.46652600 |
| C | -2.88313800 | 4.07241700 | -1.40271700 |
| B | -0.66239900 | 1.13299000 | -0.74223000 |
| O | -0.20908500 | 0.78065000 | 0.57017800 |
| O | 0.19249700 | 0.75220200 | -1.83030500 |
| C | 1.03345000 | 1.19344000 | 0.92376900 |
| C | 1.13758000 | 2.15859800 | 1.96032400 |
| C | 2.36679500 | 2.64256100 | 2.32971300 |
| C | 3.54183500 | 2.21975100 | 1.64672200 |

| | | | |
|---|---|---|---|
| C | 3.43848700 | 1.24937300 | 0.60094800 |
| C | 2.15328300 | 0.67830800 | 0.28593100 |
| C | 4.81201300 | 2.77022900 | 1.97610500 |
| C | 5.94383600 | 2.40666600 | 1.28255000 |
| C | 5.84116800 | 1.47945200 | 0.21604300 |
| C | 4.62679000 | 0.91680600 | -0.11328700 |
| C | 1.99948300 | -0.39496900 | -0.73320700 |
| C | 2.78013300 | -1.60392100 | -0.68029100 |
| C | 2.78879800 | -2.49645200 | -1.79521800 |
| C | 2.00056700 | -2.18376000 | -2.93887800 |
| C | 1.15672800 | -1.10452100 | -2.91974600 |
| C | 1.10354200 | -0.24397300 | -1.78783000 |
| C | 3.51767600 | -1.97861000 | 0.48001900 |
| C | 4.22259100 | -3.16247500 | 0.52653600 |
| C | 4.24734400 | -4.03278500 | -0.59183400 |
| C | 3.54373300 | -3.69990300 | -1.72820400 |
| H | -3.80784600 | -0.38416000 | 3.32045400 |
| H | -6.05506200 | -1.11709600 | 2.68957100 |
| H | -7.80092900 | -1.22096500 | 0.92725600 |
| H | -7.16869600 | -0.98796600 | -1.47748700 |
| H | -4.77591200 | -0.62862800 | -2.09498000 |
| H | -1.41466100 | -2.11918600 | -2.12969100 |
| H | 0.12437200 | -4.01890600 | -1.62710000 |
| H | 0.71880800 | -4.52570100 | 0.74516100 |
| H | -0.29615500 | -3.22718600 | 2.58309400 |
| H | 0.90583600 | 3.44829800 | -0.90698300 |
| H | 0.08008900 | 5.79043700 | -1.34699900 |
| H | -2.40196500 | 6.13593500 | -1.66519300 |
| H | -3.95791100 | 4.18430800 | -1.54789700 |
| H | 0.21630400 | 2.49227800 | 2.44327900 |
| H | 2.46047600 | 3.37763900 | 3.13327200 |
| H | 4.86314500 | 3.50001700 | 2.78883400 |
| H | 6.91365800 | 2.83865400 | 1.53918900 |
| H | 6.73279900 | 1.21227700 | -0.35609100 |
| H | 4.56826200 | 0.21687900 | -0.94822100 |
| H | 2.04073400 | -2.84707600 | -3.80697100 |
| H | 0.49375400 | -0.87799800 | -3.75781500 |
| H | 3.49753000 | -1.32515400 | 1.35482500 |
| H | 4.76311500 | -3.43503600 | 1.43612700 |
| H | 4.81502000 | -4.96480800 | -0.54542500 |
| H | 3.53841900 | -4.36364500 | -2.59733600 |
| C | -1.32047900 | -1.06280300 | 3.66795800 |
| H | -1.85060800 | -0.43102100 | 4.39351500 |
| H | -1.10558800 | -2.02703800 | 4.15576800 |
| H | -0.34793000 | -0.59725700 | 3.43691300 |

**Compound (*Z*)-4 – Inv. TS ($S_0$)** optimized geometry (# opt=calcfc,ts,noeigentest scrf=(smd,solvent=MeCN) def2svp mn15)



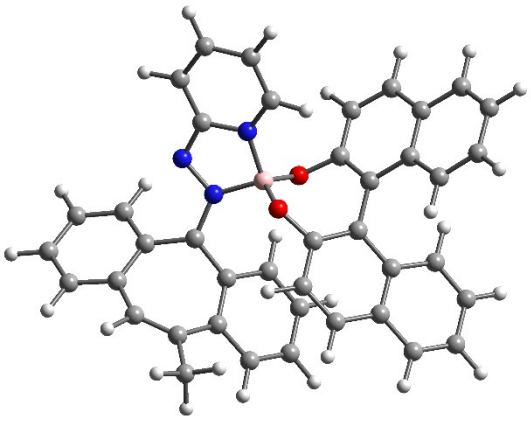
EE + Thermal Free Energy Correction: -1914.515280 Ha (+31.0 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | -1.86967300 | -0.98694600 | 1.06144300 |
| C | -2.75113800 | -0.25898800 | 0.34225200 |
| C | -2.83900700 | 1.16309600 | 0.69695600 |
| C | -3.60286900 | 2.19254200 | 0.04309300 |
| C | -4.76834000 | 2.00110400 | -0.83369500 |
| C | -5.25600900 | 0.81675000 | -1.28855900 |
| C | -4.67809100 | -0.50775900 | -1.35244800 |
| C | -3.48231100 | -0.95291600 | -0.73066400 |
| C | -5.33242600 | -1.36973500 | -2.26979000 |
| C | -4.77940800 | -2.56788000 | -2.68082200 |
| C | -3.50996900 | -2.92669600 | -2.20052000 |
| C | -2.89482500 | -2.13941700 | -1.24520700 |
| C | -2.13488100 | 1.53625800 | 1.87182400 |
| C | -1.98905500 | 2.85302500 | 2.28108500 |
| C | -2.54282500 | 3.87112100 | 1.50470400 |
| C | -3.35072900 | 3.52830100 | 0.42996000 |
| N | -2.19713600 | -2.28794000 | 1.36639400 |
| C | -1.09354000 | -2.94631900 | 1.66554600 |
| N | 0.07142500 | -2.23998900 | 1.51175600 |
| C | 1.27930300 | -2.74733300 | 1.87128700 |
| C | 1.39112000 | -4.02645500 | 2.34933300 |
| C | 0.20233500 | -4.80696700 | 2.47949800 |
| C | -1.02386100 | -4.29004700 | 2.15085700 |
| B | -0.24285900 | -0.82203800 | 0.96421800 |
| O | -0.03179700 | -0.67127800 | -0.46421300 |
| O | 0.48518300 | 0.12847200 | 1.75679300 |
| C | 1.22123500 | -1.03411100 | -0.84258600 |
| C | 1.38212400 | -2.26036000 | -1.53934700 |
| C | 2.63932700 | -2.71885100 | -1.84052700 |
| C | 3.79057400 | -1.99448000 | -1.41886800 |

| | | | |
|---|---|---|---|
| C | 3.62895500 | -0.75769100 | -0.71904500 |
| C | 2.30306000 | -0.24155500 | -0.49094600 |
| C | 5.09768400 | -2.50252200 | -1.65991100 |
| C | 6.21237100 | -1.83819700 | -1.20087300 |
| C | 6.05640100 | -0.63709100 | -0.46554800 |
| C | 4.80336300 | -0.11183900 | -0.23341800 |
| C | 2.05837600 | 1.06618800 | 0.17290700 |
| C | 2.67950200 | 2.27277400 | -0.31320300 |
| C | 2.60301900 | 3.47642800 | 0.45190500 |
| C | 1.88778400 | 3.46529700 | 1.68176200 |
| C | 1.21172300 | 2.34136200 | 2.07720700 |
| C | 1.23375500 | 1.15295500 | 1.29397000 |
| C | 3.35896800 | 2.32715800 | -1.56537000 |
| C | 3.94553200 | 3.49183600 | -2.01232800 |
| C | 3.89657300 | 4.67250500 | -1.23024300 |
| C | 3.23287100 | 4.65948900 | -0.02411000 |
| H | -6.19917000 | 0.88648400 | -1.83863700 |
| H | -6.28264300 | -1.03500500 | -2.69256600 |
| H | -5.30377800 | -3.19980800 | -3.40078900 |
| H | -3.00789900 | -3.82302900 | -2.56999900 |
| H | -1.90817500 | -2.43122300 | -0.89219500 |
| H | -1.71182800 | 0.75000200 | 2.49295700 |
| H | -1.46052300 | 3.08216000 | 3.20740200 |
| H | -2.40856400 | 4.92103500 | 1.77300000 |
| H | -3.85232500 | 4.33296800 | -0.10392600 |
| H | 2.13566300 | -2.07963200 | 1.74292600 |
| H | 2.36615800 | -4.43030200 | 2.61998400 |
| H | 0.27304900 | -5.83113200 | 2.85361500 |
| H | -1.94886800 | -4.85809300 | 2.25496000 |
| H | 0.48214100 | -2.81860100 | -1.80983000 |
| H | 2.77821600 | -3.65910400 | -2.38039200 |
| H | 5.19303100 | -3.44288600 | -2.20970400 |
| H | 7.21144000 | -2.23899200 | -1.38599200 |
| H | 6.93799200 | -0.12485200 | -0.07299800 |
| H | 4.70392200 | 0.80676800 | 0.34710600 |
| H | 1.86956900 | 4.37119800 | 2.29329300 |
| H | 0.64742100 | 2.31390100 | 3.00993400 |
| H | 3.39630000 | 1.43144200 | -2.18843300 |
| H | 4.44824400 | 3.50575100 | -2.98232600 |
| H | 4.37244800 | 5.58691000 | -1.59148600 |
| H | 3.16770700 | 5.56258100 | 0.58911100 |
| C | -5.58070400 | 3.22296400 | -1.19343300 |
| H | -5.93050700 | 3.76503600 | -0.30124000 |
| H | -4.99260300 | 3.93628100 | -1.79252700 |
| H | -6.45732000 | 2.93324600 | -1.78625000 |

**Compound (*Z*)-4 - Stable ($S_1$)** optimized geometry (# opt=calcfc td=(root=1) scrf=(smd,solvent=MeCN) def2svp mn15)



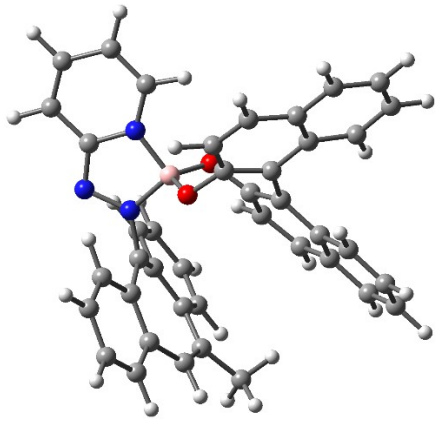
EE + Thermal Free Energy Correction: -1914.469852 Ha (+59.5 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | -1.84722000 | -1.24801500 | -0.32880400 |
| C | -2.72686900 | -0.17588600 | -0.39749100 |
| C | -2.19321300 | 1.15749000 | -0.62526500 |
| C | -2.69126900 | 2.33985800 | 0.00782200 |
| C | -3.66896800 | 2.31286200 | 1.10975000 |
| C | -4.70249400 | 1.43564200 | 1.18993600 |
| C | -5.09264900 | 0.38624900 | 0.25628400 |
| C | -4.16150100 | -0.40043400 | -0.48447200 |
| C | -6.46591900 | 0.08558400 | 0.16760600 |
| C | -6.94665300 | -0.91150400 | -0.67276600 |
| C | -6.03777200 | -1.65409400 | -1.44254500 |
| C | -4.67665600 | -1.41305600 | -1.33844000 |
| C | -1.15862400 | 1.29957400 | -1.58603500 |
| C | -0.64578700 | 2.54016700 | -1.93571800 |
| C | -1.14627900 | 3.69825800 | -1.32667600 |
| C | -2.14195100 | 3.58164500 | -0.36136700 |
| N | -2.40896200 | -2.46715200 | -0.14709900 |
| C | -1.49452000 | -3.32058800 | 0.30831900 |
| N | -0.26283900 | -2.74006000 | 0.52086900 |
| C | 0.73869600 | -3.42834500 | 1.09586200 |
| C | 0.57782500 | -4.76469700 | 1.42930600 |
| C | -0.66171800 | -5.40144200 | 1.17144300 |
| C | -1.70677500 | -4.68281400 | 0.61688100 |
| B | -0.29202000 | -1.25953300 | 0.01456300 |
| O | 0.50167800 | -1.10428200 | -1.19097100 |
| O | 0.10603000 | -0.40026800 | 1.10181400 |
| C | 1.83025600 | -1.32714200 | -1.03177600 |
| C | 2.38784300 | -2.49068700 | -1.62582500 |
| C | 3.70956900 | -2.80184900 | -1.42764800 |
| C | 4.52393800 | -1.98763600 | -0.59114700 |

| | | | |
|---|---|---|---|
| C | 3.96706100 | -0.81128600 | 0.00218500 |
| C | 2.60458500 | -0.44734300 | -0.28572000 |
| C | 5.87616500 | -2.34011500 | -0.32125200 |
| C | 6.65119500 | -1.58069200 | 0.52542000 |
| C | 6.09237400 | -0.43645100 | 1.14799100 |
| C | 4.79093000 | -0.06229100 | 0.89291700 |
| C | 1.98903100 | 0.80581300 | 0.22790000 |
| C | 2.57695800 | 2.09702900 | -0.01435700 |
| C | 2.03168900 | 3.25698500 | 0.61886600 |
| C | 0.89280000 | 3.11677000 | 1.46166500 |
| C | 0.28145800 | 1.89851400 | 1.60248500 |
| C | 0.79906300 | 0.74714300 | 0.94782500 |
| C | 3.67670800 | 2.28188900 | -0.90268200 |
| C | 4.21410800 | 3.53147500 | -1.12680200 |
| C | 3.68830100 | 4.67268000 | -0.47152400 |
| C | 2.61565200 | 4.53190900 | 0.38034000 |
| H | -5.40760600 | 1.59176900 | 2.01461000 |
| H | -7.16027000 | 0.66628800 | 0.78098600 |
| H | -8.01867700 | -1.11064400 | -0.73486000 |
| H | -6.39823400 | -2.42582900 | -2.12679800 |
| H | -3.97805900 | -1.99081400 | -1.94345400 |
| H | -0.79041500 | 0.40665200 | -2.08835400 |
| H | 0.13756500 | 2.60703100 | -2.69501600 |
| H | -0.75274700 | 4.68195500 | -1.59262100 |
| H | -2.50686300 | 4.48551000 | 0.12923400 |
| H | 1.66747400 | -2.88269400 | 1.28371400 |
| H | 1.40458000 | -5.30589800 | 1.88966900 |
| H | -0.79644600 | -6.45419700 | 1.42638400 |
| H | -2.68662300 | -5.12165700 | 0.42522600 |
| H | 1.73206800 | -3.12134600 | -2.23054200 |
| H | 4.14915300 | -3.69170500 | -1.88565300 |
| H | 6.28118100 | -3.23738000 | -0.79725100 |
| H | 7.68670900 | -1.86182700 | 0.72968900 |
| H | 6.69779200 | 0.15154400 | 1.84186400 |
| H | 4.37350900 | 0.81417900 | 1.39163800 |
| H | 0.49147900 | 4.00371900 | 1.96030300 |
| H | -0.62267500 | 1.77316000 | 2.20350200 |
| H | 4.08619400 | 1.41629700 | -1.42714100 |
| H | 5.04937000 | 3.64369500 | -1.82220200 |
| H | 4.12647400 | 5.65668300 | -0.65282900 |
| H | 2.18321400 | 5.40088600 | 0.88420000 |
| C | -3.55422800 | 3.39168100 | 2.15545400 |
| H | -3.86977800 | 4.37232800 | 1.76329600 |
| H | -4.18877200 | 3.16176400 | 3.02198300 |
| H | -2.51215500 | 3.50598900 | 2.49559600 |

**Compound (*Z*)-4 - Metastable ($S_1$)** optimized geometry (# opt=calcfc td=(root=1) scrf=(smd,solvent=MeCN) def2svp mn15)



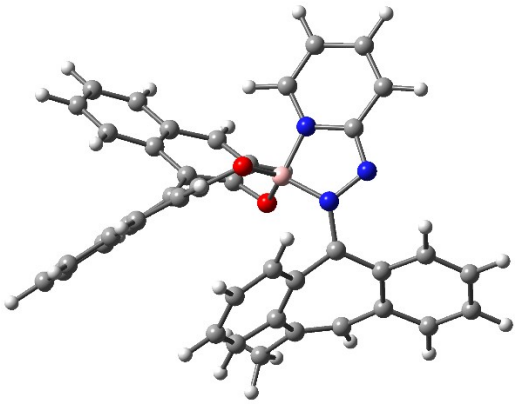
EE + Thermal Free Energy Correction: -1914.483075 Ha (+51.2 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | -1.55515400 | 1.82218700 | -0.07388600 |
| C | -2.39803600 | 0.77795500 | 0.29805900 |
| C | -2.54473600 | 0.59100800 | 1.71284100 |
| C | -3.04709000 | -0.59066200 | 2.33950900 |
| C | -3.31633800 | -1.84807200 | 1.68544600 |
| C | -3.45212200 | -2.21274900 | 0.37767200 |
| C | -3.48502100 | -1.30887400 | -0.77225200 |
| C | -3.04862400 | 0.05754500 | -0.77815200 |
| C | -3.94921700 | -1.84879400 | -1.99538200 |
| C | -4.03783200 | -1.10454000 | -3.16093400 |
| C | -3.65938200 | 0.24492000 | -3.15565700 |
| C | -3.16948300 | 0.80076800 | -1.98962200 |
| C | -2.15370900 | 1.68240000 | 2.54275000 |
| C | -2.33075100 | 1.65438000 | 3.91250800 |
| C | -2.85449600 | 0.50222500 | 4.52412000 |
| C | -3.17892700 | -0.59812900 | 3.74765700 |
| N | -2.01915300 | 3.10162200 | -0.25660500 |
| C | -0.97177300 | 3.83092000 | -0.62427200 |
| N | 0.21233200 | 3.13713900 | -0.71634900 |
| C | 1.36480500 | 3.72715100 | -1.11685400 |
| C | 1.40640900 | 5.06487900 | -1.41885100 |
| C | 0.20190300 | 5.81997500 | -1.31108700 |
| C | -0.97332800 | 5.22612800 | -0.92478600 |
| B | -0.04243700 | 1.64777200 | -0.34279800 |
| O | 0.59665100 | 1.20607400 | 0.89243900 |
| O | 0.34183300 | 0.80698800 | -1.47344400 |
| C | 1.92188500 | 0.94577500 | 0.85792500 |
| C | 2.80067000 | 1.82818800 | 1.54397100 |
| C | 4.15672800 | 1.61985300 | 1.51311100 |
| C | 4.70479000 | 0.54183300 | 0.76234300 |

| | | | |
|---|---|---|---|
| C | 3.82587000 | -0.34917100 | 0.06988500 |
| C | 2.40367300 | -0.16608300 | 0.17688500 |
| C | 6.11263200 | 0.35576900 | 0.67010400 |
| C | 6.64599600 | -0.65395700 | -0.09845300 |
| C | 5.78102700 | -1.51524200 | -0.81917000 |
| C | 4.41328100 | -1.36792900 | -0.73654500 |
| C | 1.41996700 | -1.07750600 | -0.46352500 |
| C | 1.40945300 | -2.49584400 | -0.22857400 |
| C | 0.52062400 | -3.33158300 | -0.97347900 |
| C | -0.35522800 | -2.73603400 | -1.92390500 |
| C | -0.39494300 | -1.37316200 | -2.07531900 |
| C | 0.46029100 | -0.52990600 | -1.31318500 |
| C | 2.23527700 | -3.11477900 | 0.75524200 |
| C | 2.20023200 | -4.47646700 | 0.96489900 |
| C | 1.33892400 | -5.30347300 | 0.20079400 |
| C | 0.51481300 | -4.73599100 | -0.74500000 |
| H | -3.43106400 | -2.67028000 | 2.39910900 |
| H | -4.26411300 | -2.89052200 | -2.02855500 |
| H | -4.41505300 | -1.57106200 | -4.07340700 |
| H | -3.75517300 | 0.85472100 | -4.05603200 |
| H | -2.90080900 | 1.85568700 | -1.97158300 |
| H | -1.74286500 | 2.57194700 | 2.06710700 |
| H | -2.05361700 | 2.52073700 | 4.51622200 |
| H | -2.98531400 | 0.46479800 | 5.60758700 |
| H | -3.54239400 | -1.51204500 | 4.22297400 |
| H | 2.23897500 | 3.07437700 | -1.18493600 |
| H | 2.33912100 | 5.52944200 | -1.73699700 |
| H | 0.21598100 | 6.88690300 | -1.54527600 |
| H | -1.90958600 | 5.77925100 | -0.84289000 |
| H | 2.36005200 | 2.66647400 | 2.08883100 |
| H | 4.83753600 | 2.29000100 | 2.04470100 |
| H | 6.76165600 | 1.04415100 | 1.21858900 |
| H | 7.72817500 | -0.78574500 | -0.16656900 |
| H | 6.20310400 | -2.29970300 | -1.45189700 |
| H | 3.76311000 | -2.03089100 | -1.31026600 |
| H | -1.01390000 | -3.38069400 | -2.51347500 |
| H | -1.08696300 | -0.89661400 | -2.77338900 |
| H | 2.89372000 | -2.49035400 | 1.36241200 |
| H | 2.83741900 | -4.92230900 | 1.73240600 |
| H | 1.32448600 | -6.38210700 | 0.37254000 |
| H | -0.16854300 | -5.35318000 | -1.33555700 |
| C | -3.66034300 | -3.68425900 | 0.11907000 |
| H | -3.46920600 | -4.26319200 | 1.03146700 |
| H | -4.68913700 | -3.90169900 | -0.21108600 |
| H | -2.98467600 | -4.04890200 | -0.67083900 |

**Compound (*Z*)-4 – Inv. TS ($S_1$)** optimized geometry (# opt=calcfc,ts,noeigentest td=(root=1) scrf=(smd,solvent=MeCN) def2svp mn15)



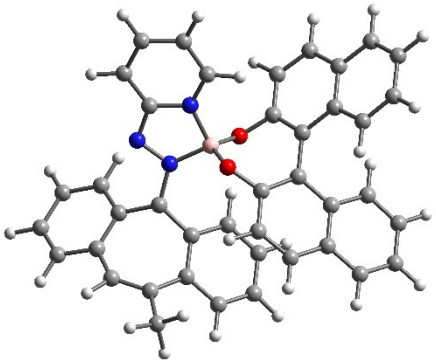
EE + Thermal Free Energy Correction: -1914.461117 Ha (+65.0 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | -2.22298500 | 0.57129400 | -1.08211500 |
| C | -2.74979900 | -0.52774100 | -0.41434800 |
| C | -4.04568400 | -0.51301400 | 0.23789800 |
| C | -4.22979600 | -1.08838300 | 1.53379000 |
| C | -3.16129700 | -1.64628700 | 2.35019500 |
| C | -2.01427400 | -2.28982200 | 2.00025300 |
| C | -1.61002600 | -2.57603800 | 0.61792000 |
| C | -1.93363000 | -1.72555900 | -0.48471000 |
| C | -0.79411100 | -3.69879100 | 0.37612000 |
| C | -0.35389900 | -4.03632100 | -0.89954200 |
| C | -0.68612400 | -3.20985300 | -1.98129100 |
| C | -1.42602700 | -2.05797800 | -1.76609400 |
| C | -5.17569200 | 0.07184600 | -0.39413900 |
| C | -6.42277300 | 0.08841400 | 0.21290800 |
| C | -6.59484900 | -0.45251100 | 1.49665200 |
| C | -5.50231600 | -1.01819700 | 2.13932400 |
| N | -3.01190900 | 1.61894200 | -1.39857200 |
| C | -2.27932400 | 2.73223600 | -1.39668500 |
| N | -0.95354100 | 2.52356400 | -1.07681300 |
| C | -0.08011200 | 3.54559900 | -1.02712000 |
| C | -0.49351900 | 4.84443600 | -1.27196400 |
| C | -1.85156300 | 5.08869900 | -1.60093500 |
| C | -2.74695400 | 4.03796600 | -1.67487100 |
| B | -0.70247700 | 0.99075800 | -0.86037200 |
| O | -0.35342100 | 0.60475300 | 0.48676200 |
| O | 0.27140800 | 0.59789800 | -1.85980200 |
| C | 0.79782700 | 1.13283600 | 0.96725200 |
| C | 0.70244900 | 2.10951300 | 1.99453700 |
| C | 1.83227200 | 2.72985300 | 2.46341900 |
| C | 3.10324900 | 2.43759900 | 1.89245800 |

| | | | |
|---|---|---|---|
| C | 3.20190100 | 1.45211700 | 0.86014400 |
| C | 2.02118300 | 0.73704600 | 0.44506200 |
| C | 4.26921300 | 3.13341800 | 2.31831600 |
| C | 5.49085900 | 2.89721600 | 1.72996200 |
| C | 5.58684100 | 1.95603400 | 0.67506000 |
| C | 4.47780400 | 1.25363000 | 0.25511600 |
| C | 2.07300500 | -0.34956400 | -0.56863300 |
| C | 2.98259400 | -1.45819100 | -0.43214500 |
| C | 3.20739200 | -2.33816400 | -1.53496400 |
| C | 2.49562900 | -2.11728600 | -2.74795400 |
| C | 1.53594900 | -1.14208300 | -2.81774400 |
| C | 1.26903100 | -0.29275100 | -1.70623200 |
| C | 3.66874600 | -1.73220700 | 0.78671200 |
| C | 4.53659800 | -2.79796900 | 0.89555300 |
| C | 4.77906900 | -3.64823500 | -0.21181300 |
| C | 4.12168500 | -3.41928100 | -1.40023400 |
| H | -3.36948900 | -1.60608700 | 3.42571400 |
| H | -0.51262000 | -4.33837100 | 1.21372900 |
| H | 0.25100500 | -4.93310800 | -1.05039000 |
| H | -0.35008200 | -3.45843100 | -2.98997300 |
| H | -1.66436500 | -1.39666100 | -2.60252800 |
| H | -5.06031300 | 0.48929000 | -1.39194400 |
| H | -7.27244700 | 0.52488200 | -0.31751800 |
| H | -7.57077500 | -0.42528400 | 1.98580600 |
| H | -5.61153300 | -1.42306900 | 3.14912800 |
| H | 0.96012500 | 3.29293400 | -0.80383800 |
| H | 0.23143000 | 5.65751500 | -1.22841800 |
| H | -2.18723600 | 6.10783000 | -1.80213800 |
| H | -3.79819700 | 4.17834400 | -1.92946100 |
| H | -0.28973600 | 2.34396300 | 2.38667800 |
| H | 1.77161000 | 3.47644300 | 3.25958500 |
| H | 4.16624300 | 3.87104400 | 3.11898200 |
| H | 6.37924000 | 3.44033000 | 2.05989700 |
| H | 6.54885100 | 1.78937300 | 0.18460900 |
| H | 4.57118700 | 0.54514000 | -0.56935100 |
| H | 2.69683700 | -2.76532200 | -3.60520300 |
| H | 0.93417700 | -0.99403000 | -3.71754900 |
| H | 3.48542700 | -1.09311300 | 1.65308400 |
| H | 5.03798300 | -2.99221000 | 1.84676700 |
| H | 5.47461600 | -4.48498500 | -0.11575900 |
| H | 4.28217100 | -4.07135200 | -2.26338500 |
| C | -1.14583200 | -2.83711500 | 3.10273100 |
| H | -1.44407100 | -2.42087800 | 4.07407600 |
| H | -1.22207300 | -3.93445100 | 3.17306600 |
| H | -0.08459000 | -2.60203700 | 2.92524200 |

**Compound (*Z*)-4 - Stable ($T_1$)** optimized geometry (# opt=calcfc scrf=(smd,solvent=MeCN) def2svp mn15)



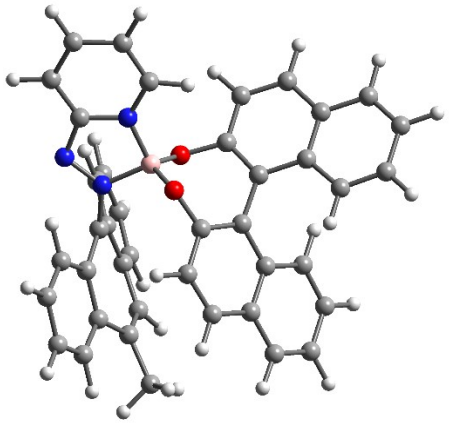
EE + Thermal Free Energy Correction: -1914.502722 Ha (+38.9 kcal/mol)

0 3

| | | | |
|---|---|---|---|
| N | -1.81306700 | -1.26017200 | -0.17362700 |
| C | -2.72269700 | -0.16173300 | -0.29994500 |
| C | -2.20985400 | 1.18960000 | -0.50781500 |
| C | -2.79383800 | 2.33020500 | 0.11213500 |
| C | -3.88752600 | 2.23571700 | 1.10520800 |
| C | -4.90659800 | 1.34659900 | 1.02757200 |
| C | -5.15846800 | 0.31173500 | 0.02195900 |
| C | -4.12161000 | -0.44067700 | -0.59221200 |
| C | -6.49725300 | -0.01090400 | -0.26870600 |
| C | -6.82867900 | -1.01255100 | -1.17595200 |
| C | -5.80599300 | -1.73772100 | -1.80326900 |
| C | -4.47759200 | -1.46200500 | -1.50662100 |
| C | -1.14714200 | 1.38554100 | -1.41883000 |
| C | -0.66166500 | 2.65456400 | -1.71622600 |
| C | -1.22654800 | 3.77401000 | -1.09798900 |
| C | -2.26872300 | 3.60016900 | -0.18961800 |
| N | -2.40571400 | -2.40808500 | 0.17650100 |
| C | -1.47468700 | -3.29395100 | 0.58068900 |
| N | -0.21610200 | -2.77579700 | 0.62066000 |
| C | 0.82274500 | -3.49011200 | 1.08230000 |
| C | 0.64393700 | -4.80608000 | 1.48109000 |
| C | -0.64422700 | -5.37626700 | 1.41468400 |
| C | -1.71938600 | -4.62383200 | 0.97206800 |
| B | -0.25755600 | -1.27805700 | 0.09638700 |
| O | 0.48874100 | -1.12965400 | -1.13034000 |
| O | 0.18965300 | -0.44469900 | 1.18443300 |
| C | 1.83030500 | -1.31808100 | -1.03489700 |
| C | 2.38388600 | -2.45528600 | -1.68098100 |
| C | 3.72014800 | -2.73967400 | -1.55454000 |
| C | 4.55571900 | -1.92414000 | -0.74066900 |
| C | 4.00266700 | -0.77269700 | -0.09748100 |

| | | | |
|---|---|---|---|
| C | 2.62007400 | -0.43235400 | -0.31247900 |
| C | 5.92650500 | -2.25189500 | -0.54274100 |
| C | 6.72465400 | -1.49260500 | 0.28214800 |
| C | 6.17174200 | -0.37398700 | 0.95441500 |
| C | 4.85206700 | -0.02351100 | 0.76866900 |
| C | 2.01102300 | 0.80354700 | 0.24954100 |
| C | 2.56963300 | 2.10741700 | 0.00233300 |
| C | 2.03929300 | 3.24773300 | 0.68148700 |
| C | 0.94013100 | 3.07809700 | 1.57099500 |
| C | 0.35072400 | 1.84967000 | 1.71692600 |
| C | 0.85674800 | 0.71698500 | 1.02146400 |
| C | 3.62005400 | 2.32408600 | -0.93668900 |
| C | 4.12664800 | 3.58575700 | -1.16586700 |
| C | 3.61841100 | 4.70716200 | -0.46461500 |
| C | 2.59206400 | 4.53520800 | 0.43730300 |
| H | -5.70254000 | 1.45245900 | 1.77451900 |
| H | -7.28709100 | 0.54725300 | 0.24178400 |
| H | -7.87636500 | -1.23400000 | -1.39097500 |
| H | -6.04891600 | -2.52425200 | -2.52159200 |
| H | -3.68255900 | -2.02886200 | -1.99435000 |
| H | -0.71573600 | 0.51624400 | -1.91383800 |
| H | 0.15702700 | 2.76864000 | -2.43146400 |
| H | -0.85231800 | 4.77722100 | -1.31499500 |
| H | -2.69622900 | 4.47886200 | 0.29661200 |
| H | 1.78920100 | -2.98336800 | 1.13406100 |
| H | 1.49560800 | -5.37731900 | 1.84978900 |
| H | -0.79596200 | -6.41104300 | 1.72752300 |
| H | -2.73550100 | -5.01554000 | 0.92413800 |
| H | 1.71296400 | -3.08800900 | -2.26651000 |
| H | 4.15647700 | -3.60919800 | -2.05283100 |
| H | 6.32700000 | -3.13038800 | -1.05609600 |
| H | 7.77445100 | -1.75464600 | 0.43148400 |
| H | 6.79669200 | 0.21319600 | 1.63143300 |
| H | 4.44065000 | 0.83320000 | 1.30517300 |
| H | 0.55042700 | 3.95098600 | 2.10203800 |
| H | -0.52499900 | 1.70284600 | 2.35404300 |
| H | 4.01493300 | 1.47416300 | -1.49672800 |
| H | 4.92362400 | 3.72266900 | -1.90065700 |
| H | 4.03220900 | 5.70083000 | -0.65031900 |
| H | 2.17215700 | 5.38882500 | 0.97674500 |
| C | -3.89753200 | 3.26589500 | 2.20558100 |
| H | -4.16240400 | 4.26617800 | 1.82599100 |
| H | -4.62958700 | 3.00132500 | 2.98072400 |
| H | -2.90334500 | 3.35742800 | 2.67235100 |

**Compound (*Z*)-4 - Metastable ($T_1$)** optimized geometry (# opt=calcfc scrf=(smd,solvent=MeCN) def2svp mn15)



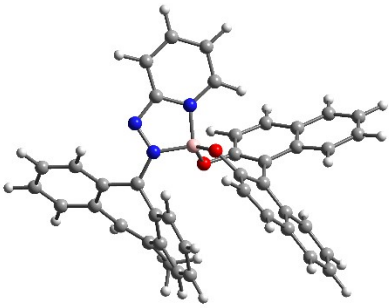
EE + Thermal Free Energy Correction: -1914.517152 Ha (+29.8 kcal/mol)

0 3

| | | | |
|---|---|---|---|
| N | -1.54690200 | 1.84169400 | -0.00701700 |
| C | -2.31432900 | 0.72398300 | 0.42219800 |
| C | -2.27135000 | 0.46311000 | 1.84436100 |
| C | -2.49619500 | -0.81670500 | 2.42848500 |
| C | -2.71002000 | -2.04975300 | 1.68344700 |
| C | -3.14039200 | -2.30334400 | 0.42151700 |
| C | -3.52024700 | -1.30559900 | -0.59998900 |
| C | -3.09478300 | 0.06354100 | -0.60720700 |
| C | -4.26022300 | -1.77263400 | -1.70418600 |
| C | -4.58895300 | -0.97156600 | -2.79427600 |
| C | -4.15588400 | 0.35664000 | -2.81406100 |
| C | -3.42349300 | 0.85088100 | -1.74484400 |
| C | -1.95513300 | 1.53967000 | 2.71550600 |
| C | -1.90389400 | 1.38330600 | 4.09261500 |
| C | -2.13758500 | 0.12508100 | 4.66340300 |
| C | -2.41169500 | -0.95172900 | 3.82846800 |
| N | -2.04146400 | 3.07011800 | -0.05927900 |
| C | -1.04003600 | 3.89622300 | -0.46620900 |
| N | 0.14373500 | 3.25946900 | -0.69088400 |
| C | 1.23772600 | 3.91627400 | -1.11670600 |
| C | 1.19228800 | 5.28130300 | -1.33039000 |
| C | -0.02021500 | 5.96616300 | -1.09763400 |
| C | -1.14560900 | 5.28493500 | -0.66664400 |
| B | -0.02614100 | 1.72963400 | -0.34797700 |
| O | 0.67106300 | 1.32166900 | 0.84393000 |
| O | 0.30537700 | 0.95761500 | -1.52079000 |
| C | 1.98244500 | 0.99627700 | 0.74582800 |
| C | 2.92798800 | 1.82936800 | 1.40133200 |
| C | 4.26883800 | 1.54824000 | 1.32176200 |
| C | 4.73068500 | 0.44458800 | 0.55098100 |

| | | | |
|---|---|---|---|
| C | 3.78229700 | -0.39278800 | -0.11611600 |
| C | 2.37592300 | -0.13351200 | 0.03946600 |
| C | 6.12247400 | 0.18039400 | 0.41531000 |
| C | 6.57427400 | -0.85482500 | -0.37111600 |
| C | 5.64072000 | -1.66216600 | -1.06804300 |
| C | 4.28656300 | -1.43834300 | -0.94409800 |
| C | 1.32992100 | -0.98944500 | -0.58051400 |
| C | 1.25896600 | -2.40945400 | -0.36705400 |
| C | 0.33466900 | -3.19270600 | -1.12560300 |
| C | -0.51559600 | -2.54608000 | -2.06602800 |
| C | -0.51137800 | -1.17919900 | -2.18313100 |
| C | 0.37943700 | -0.39246100 | -1.40400000 |
| C | 2.05942000 | -3.07746600 | 0.60494300 |
| C | 1.95896300 | -4.43812600 | 0.79920200 |
| C | 1.05838400 | -5.21390900 | 0.02636000 |
| C | 0.26387000 | -4.59824400 | -0.91452700 |
| H | -2.52662900 | -2.94107200 | 2.29340800 |
| H | -4.58831400 | -2.81159400 | -1.71681900 |
| H | -5.16886800 | -1.38576300 | -3.62150800 |
| H | -4.39007200 | 1.00865900 | -3.65842400 |
| H | -3.10869700 | 1.89313800 | -1.76903900 |
| H | -1.77062300 | 2.52550300 | 2.28917400 |
| H | -1.67400800 | 2.24356300 | 4.72526800 |
| H | -2.08927000 | -0.01445500 | 5.74530400 |
| H | -2.56069400 | -1.94661200 | 4.25675000 |
| H | 2.13519000 | 3.31463600 | -1.28072600 |
| H | 2.08169500 | 5.80803600 | -1.67529600 |
| H | -0.07145600 | 7.04421100 | -1.26344600 |
| H | -2.09876300 | 5.78097400 | -0.48264300 |
| H | 2.55227700 | 2.68618000 | 1.96541600 |
| H | 5.00283900 | 2.17833100 | 1.83089000 |
| H | 6.82548800 | 0.82893100 | 0.94538500 |
| H | 7.64468400 | -1.04759700 | -0.47197800 |
| H | 5.99846500 | -2.46637100 | -1.71539700 |
| H | 3.58417400 | -2.06107200 | -1.50072100 |
| H | -1.19909900 | -3.15346200 | -2.66636700 |
| H | -1.19544700 | -0.66169200 | -2.86004000 |
| H | 2.74838100 | -2.49125100 | 1.21662800 |
| H | 2.57456300 | -4.92312200 | 1.56049500 |
| H | 0.99244600 | -6.29242100 | 0.18639700 |
| H | -0.44654100 | -5.17625400 | -1.51266900 |
| C | -3.28745200 | -3.75865300 | 0.04400200 |
| H | -2.81692800 | -4.40073500 | 0.80055000 |
| H | -4.34681800 | -4.05381200 | -0.03458100 |
| H | -2.82472000 | -3.97389700 | -0.93183800 |

**Compound (*Z*)-4 – Inv. TS ($T_1$)** optimized geometry (# opt=calcfc,ts,noeigentest scrf=(smd,solvent=MeCN) def2svp mn15)



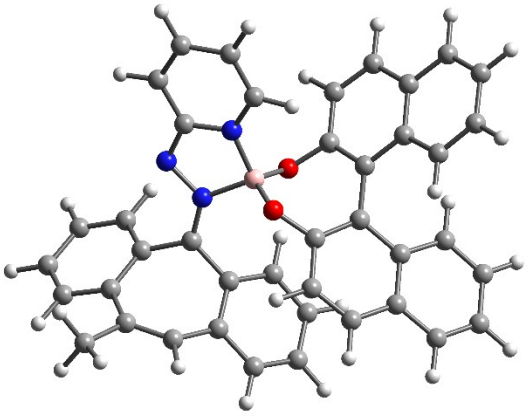
EE + Thermal Free Energy Correction: -1914.493824 Ha (+44.4 kcal/mol)

0 3

| | | | |
|---|---|---|---|
| N | -2.12252100 | 0.73611400 | -0.98081500 |
| C | -2.78509000 | -0.36974900 | -0.35809500 |
| C | -4.16133700 | -0.28625800 | 0.11446800 |
| C | -4.51875800 | -0.81483900 | 1.38451200 |
| C | -3.55821400 | -1.40911100 | 2.31727000 |
| C | -2.45033300 | -2.15087200 | 2.07354700 |
| C | -1.95507200 | -2.50647100 | 0.72617700 |
| C | -2.07848200 | -1.64066900 | -0.39775500 |
| C | -1.25863100 | -3.71708700 | 0.55850400 |
| C | -0.73465500 | -4.10614600 | -0.67277300 |
| C | -0.86446700 | -3.25627300 | -1.77479400 |
| C | -1.50383800 | -2.03074800 | -1.62735100 |
| C | -5.17989500 | 0.28678400 | -0.68507200 |
| C | -6.49523600 | 0.36120300 | -0.24262600 |
| C | -6.83768400 | -0.12542200 | 1.02552400 |
| C | -5.85208600 | -0.69833200 | 1.82217900 |
| N | -2.83450100 | 1.84470400 | -1.18590100 |
| C | -2.00279400 | 2.90529700 | -1.23553700 |
| N | -0.70161800 | 2.58827200 | -0.98206700 |
| C | 0.26471800 | 3.52018200 | -0.99561900 |
| C | -0.04685100 | 4.84819500 | -1.24244700 |
| C | -1.38829600 | 5.20304300 | -1.49763900 |
| C | -2.37923000 | 4.23574300 | -1.50207400 |
| B | -0.58420800 | 1.01588100 | -0.77508000 |
| O | -0.23811300 | 0.60754200 | 0.55977000 |
| O | 0.32850400 | 0.57020600 | -1.80438900 |
| C | 0.95344000 | 1.07730900 | 1.00950700 |
| C | 0.93227200 | 2.06036400 | 2.03400100 |
| C | 2.10219200 | 2.63264400 | 2.46445300 |
| C | 3.34037800 | 2.28370500 | 1.85523700 |
| C | 3.36364000 | 1.29197200 | 0.82470300 |
| C | 2.14085600 | 0.62649600 | 0.45044800 |
| C | 4.54823100 | 2.92998700 | 2.24087200 |

| | | | |
|---|---|---|---|
| C | 5.73870600 | 2.64030400 | 1.61406900 |
| C | 5.76024600 | 1.69332300 | 0.56012200 |
| C | 4.60938200 | 1.03761300 | 0.17917500 |
| C | 2.11505600 | -0.46356500 | -0.56128700 |
| C | 2.97313800 | -1.61480700 | -0.44515800 |
| C | 3.10831500 | -2.51827800 | -1.54357500 |
| C | 2.36323000 | -2.27557000 | -2.73204000 |
| C | 1.45790900 | -1.24884200 | -2.78222200 |
| C | 1.28077900 | -0.37305700 | -1.67380500 |
| C | 3.69451600 | -1.90908700 | 0.74845100 |
| C | 4.51268800 | -3.01522100 | 0.83617100 |
| C | 4.66567700 | -3.89053100 | -0.26762800 |
| C | 3.97185500 | -3.64287100 | -1.43106300 |
| H | -3.84087100 | -1.30068600 | 3.37114500 |
| H | -1.13186700 | -4.38076600 | 1.41534600 |
| H | -0.22034000 | -5.06482600 | -0.76873500 |
| H | -0.45495600 | -3.54231200 | -2.74571500 |
| H | -1.58712700 | -1.35029400 | -2.47902800 |
| H | -4.92183100 | 0.66318300 | -1.67413600 |
| H | -7.25841800 | 0.80116000 | -0.88890100 |
| H | -7.86606300 | -0.05677500 | 1.38699900 |
| H | -6.10395200 | -1.07217300 | 2.81860700 |
| H | 1.28580100 | 3.17556400 | -0.81243500 |
| H | 0.74552000 | 5.59642200 | -1.24615200 |
| H | -1.64443500 | 6.24515900 | -1.69786900 |
| H | -3.42621800 | 4.46373300 | -1.70254600 |
| H | -0.03615600 | 2.34015900 | 2.45466800 |
| H | 2.09899900 | 3.38400100 | 3.25838600 |
| H | 4.50282500 | 3.67323400 | 3.04164700 |
| H | 6.65968700 | 3.14581700 | 1.91290300 |
| H | 6.69787600 | 1.48457800 | 0.03952700 |
| H | 4.64568500 | 0.32328700 | -0.64475600 |
| H | 2.49583000 | -2.94566600 | -3.58564900 |
| H | 0.83352000 | -1.07760800 | -3.66233100 |
| H | 3.57953700 | -1.25204800 | 1.61300600 |
| H | 5.04317000 | -3.22261400 | 1.76863700 |
| H | 5.32195200 | -4.76009100 | -0.18829500 |
| H | 4.06313100 | -4.31254700 | -2.29078700 |
| C | -1.70431700 | -2.73236900 | 3.24784000 |
| H | -2.03783300 | -2.27055400 | 4.18699200 |
| H | -1.86863200 | -3.81869900 | 3.33627900 |
| H | -0.61819200 | -2.58159500 | 3.14501200 |

**Compound *(E)*-4 - Stable ($S_0$)** optimized geometry (# opt=calcfc scrf=(smd,solvent=MeCN) def2svp mn15)



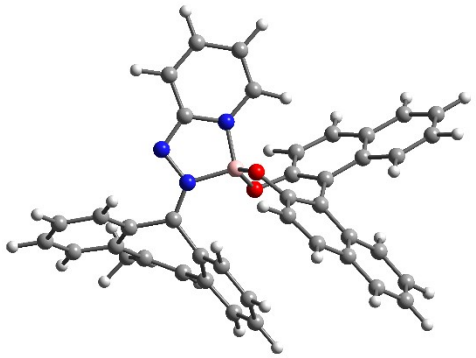
EE + Thermal Free Energy Correction: -1914.564092 Ha (+0.0 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | 1.86144200 | 1.10187600 | -0.15135700 |
| C | 2.61609000 | 0.07435000 | -0.42356600 |
| C | 2.08298500 | -1.29728800 | -0.55858400 |
| C | 2.63349600 | -2.32436300 | 0.24302600 |
| C | 3.66508900 | -2.09521100 | 1.25968800 |
| C | 4.72921700 | -1.25528100 | 1.22654600 |
| C | 5.04686200 | -0.37392700 | 0.08051200 |
| C | 4.05960000 | 0.25252800 | -0.71022600 |
| C | 6.39721900 | -0.12206500 | -0.24132200 |
| C | 6.75287100 | 0.66444400 | -1.33135800 |
| C | 5.76187000 | 1.25317000 | -2.12543800 |
| C | 4.42451600 | 1.05641000 | -1.80317400 |
| C | 1.09642600 | -1.60095600 | -1.51164500 |
| C | 0.63246400 | -2.90632900 | -1.66061600 |
| C | 1.15076000 | -3.92417100 | -0.85263900 |
| C | 2.12835000 | -3.62930700 | 0.09318800 |
| N | 2.40965000 | 2.35403400 | -0.07779900 |
| C | 1.47696900 | 3.17718400 | 0.39737500 |
| N | 0.26109900 | 2.61504600 | 0.66052600 |
| C | -0.76482500 | 3.31213500 | 1.20681500 |
| C | -0.63037900 | 4.64806100 | 1.49318300 |
| C | 0.61271700 | 5.27389600 | 1.20229500 |
| C | 1.66001600 | 4.56395900 | 0.66449200 |
| B | 0.27288600 | 1.13531200 | 0.16399900 |
| O | -0.41639600 | 0.97883100 | -1.09192200 |
| O | -0.15591600 | 0.27271000 | 1.22048400 |
| C | -1.74383900 | 1.26814600 | -1.01517600 |
| C | -2.20796900 | 2.44794700 | -1.65253200 |
| C | -3.52027100 | 2.82755100 | -1.52417300 |
| C | -4.41408600 | 2.06880500 | -0.71719300 |

| | | | |
|---|---|---|---|
| C | -3.94841200 | 0.87632200 | -0.07942300 |
| C | -2.59344700 | 0.43926700 | -0.29552100 |
| C | -5.75744400 | 2.49511400 | -0.51881200 |
| C | -6.60993700 | 1.79248500 | 0.30180800 |
| C | -6.14142000 | 0.63335200 | 0.96949600 |
| C | -4.85078900 | 0.18770400 | 0.78318500 |
| C | -2.06739600 | -0.83416300 | 0.26646400 |
| C | -2.71927300 | -2.09359000 | 0.01724200 |
| C | -2.28328800 | -3.26870800 | 0.70362900 |
| C | -1.18302700 | -3.17854900 | 1.60182200 |
| C | -0.50186000 | -1.99823500 | 1.74717200 |
| C | -0.91227000 | -0.83323200 | 1.04426800 |
| C | -3.77900500 | -2.23176000 | -0.92635800 |
| C | -4.38247500 | -3.45053300 | -1.15173500 |
| C | -3.96776600 | -4.60503200 | -0.44222800 |
| C | -2.93467800 | -4.51024900 | 0.46301400 |
| H | 3.60490500 | -2.77054900 | 2.12124700 |
| H | 7.18362700 | -0.57372800 | 0.36546600 |
| H | 7.80856900 | 0.82122100 | -1.56373800 |
| H | 6.03342600 | 1.87422300 | -2.98162900 |
| H | 3.63768700 | 1.53458800 | -2.39048800 |
| H | 0.70143800 | -0.80116900 | -2.13768600 |
| H | -0.13599700 | -3.12795500 | -2.40482900 |
| H | 0.78431200 | -4.94819200 | -0.95688300 |
| H | 2.52613700 | -4.41976500 | 0.73525400 |
| H | -1.68122500 | 2.74768700 | 1.39983700 |
| H | -1.45686900 | 5.20350800 | 1.93491600 |
| H | 0.74007300 | 6.33739400 | 1.41833800 |
| H | 2.62663300 | 5.01836400 | 0.44573000 |
| H | -1.49092100 | 3.03584600 | -2.22999000 |
| H | -3.89168000 | 3.73097000 | -2.01466900 |
| H | -6.09164100 | 3.40315900 | -1.02812600 |
| H | -7.63784500 | 2.13014800 | 0.45157000 |
| H | -6.80845600 | 0.09086800 | 1.64362400 |
| H | -4.50381300 | -0.69902700 | 1.31644400 |
| H | -0.86675800 | -4.07549000 | 2.14115100 |
| H | 0.37623700 | -1.91613700 | 2.39176100 |
| H | -4.10329000 | -1.35641000 | -1.49247300 |
| H | -5.18453800 | -3.52815200 | -1.88964900 |
| H | -4.45848200 | -5.56364500 | -0.62488600 |
| H | -2.58617500 | -5.39119700 | 1.00927000 |
| C | 5.72065600 | -1.28776400 | 2.36053600 |
| H | 6.65649500 | -1.78925600 | 2.06474100 |
| H | 5.99171200 | -0.27080200 | 2.68389700 |
| H | 5.30927400 | -1.83479000 | 3.21950400 |

**Compound (*E*)-4 - Metastable ($S_0$)** optimized geometry (# opt=calcfc scrf=(smd,solvent=MeCN) def2svp mn15)



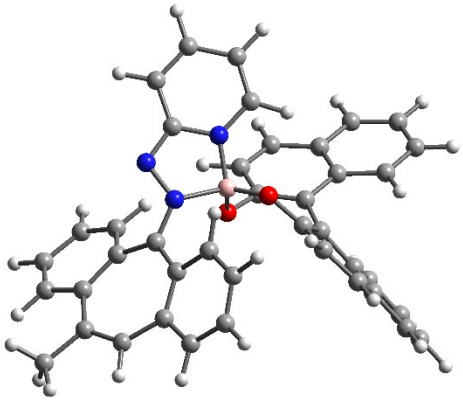
EE + Thermal Free Energy Correction: -1914.559840 Ha (+2.7 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | -2.04604200 | 0.68402300 | -0.76878500 |
| C | -2.67466900 | -0.38617900 | -0.37512100 |
| C | -1.94492500 | -1.61140300 | 0.00034000 |
| C | -2.03511100 | -2.07233900 | 1.33230100 |
| C | -2.87456600 | -1.43627400 | 2.34917100 |
| C | -4.07859800 | -0.82390300 | 2.21351300 |
| C | -4.80033000 | -0.65421600 | 0.93041200 |
| C | -4.15073000 | -0.43667000 | -0.30523200 |
| C | -6.21126200 | -0.66573300 | 0.92559200 |
| C | -6.93941700 | -0.52058000 | -0.25050900 |
| C | -6.27816700 | -0.32500400 | -1.46830200 |
| C | -4.88932800 | -0.27087400 | -1.48754700 |
| C | -1.16717100 | -2.29651000 | -0.93974700 |
| C | -0.43059300 | -3.41859100 | -0.56200900 |
| C | -0.45510700 | -3.84496100 | 0.76956000 |
| C | -1.24435700 | -3.17514100 | 1.70207300 |
| N | -2.74941100 | 1.80538500 | -1.11290700 |
| C | -1.88739400 | 2.81861500 | -1.15837600 |
| N | -0.58382700 | 2.51428100 | -0.88579800 |
| C | 0.40881600 | 3.43571000 | -0.96847200 |
| C | 0.13078700 | 4.74548900 | -1.26786100 |
| C | -1.22274400 | 5.10475700 | -1.51634700 |
| C | -2.22563400 | 4.16702800 | -1.47099000 |
| B | -0.44938000 | 0.97047500 | -0.66016300 |
| O | -0.05856400 | 0.56454700 | 0.65741800 |
| O | 0.35863100 | 0.46431800 | -1.73683300 |
| C | 1.16762400 | 1.01510400 | 1.03308000 |
| C | 1.22741500 | 2.01280400 | 2.04076200 |
| C | 2.43290100 | 2.56775700 | 2.38805500 |
| C | 3.62420000 | 2.18350600 | 1.71035500 |
| C | 3.56532300 | 1.17415800 | 0.69857600 |

| | | | |
|---|---|---|---|
| C | 2.30849500 | 0.53080500 | 0.40953200 |
| C | 4.86616500 | 2.81023000 | 2.01046400 |
| C | 6.01057500 | 2.48277700 | 1.31975000 |
| C | 5.94971800 | 1.51578700 | 0.28566600 |
| C | 4.76459600 | 0.87926300 | -0.01397700 |
| C | 2.19908500 | -0.57670600 | -0.57847900 |
| C | 3.02945900 | -1.75053900 | -0.48195100 |
| C | 3.06823200 | -2.68914300 | -1.55823900 |
| C | 2.25572300 | -2.46004100 | -2.70506700 |
| C | 1.38110400 | -1.40640800 | -2.73112000 |
| C | 1.30118600 | -0.49529700 | -1.63978200 |
| C | 3.81038000 | -2.03658300 | 0.67567700 |
| C | 4.59398800 | -3.16865600 | 0.74862300 |
| C | 4.65250100 | -4.07864900 | -0.33572400 |
| C | 3.89949500 | -3.83915500 | -1.46357100 |
| H | -6.74770700 | -0.81101500 | 1.86457300 |
| H | -8.03065200 | -0.55518100 | -0.21761200 |
| H | -6.84471600 | -0.20160800 | -2.39364700 |
| H | -4.35317900 | -0.08952400 | -2.42161400 |
| H | -1.14504000 | -1.93803000 | -1.97101900 |
| H | 0.17355700 | -3.94816300 | -1.30189900 |
| H | 0.13767700 | -4.70864100 | 1.07922900 |
| H | -1.26909900 | -3.51173900 | 2.74189200 |
| H | 1.42281300 | 3.07053500 | -0.78529300 |
| H | 0.93292900 | 5.48084700 | -1.31966200 |
| H | -1.46668900 | 6.14231700 | -1.75670700 |
| H | -3.26878400 | 4.41133200 | -1.67305100 |
| H | 0.29232600 | 2.32000700 | 2.51420000 |
| H | 2.49348100 | 3.33228500 | 3.16692300 |
| H | 4.88455700 | 3.56888100 | 2.79772400 |
| H | 6.95806700 | 2.97343600 | 1.55330800 |
| H | 6.85041100 | 1.27619300 | -0.28445700 |
| H | 4.73655400 | 0.14881400 | -0.82402900 |
| H | 2.31583100 | -3.15785300 | -3.54440800 |
| H | 0.71158900 | -1.23698200 | -3.57766600 |
| H | 3.76912000 | -1.35256100 | 1.52575200 |
| H | 5.17096700 | -3.36887000 | 1.65463700 |
| H | 5.28299000 | -4.96808100 | -0.26900300 |
| H | 3.91709100 | -4.53517000 | -2.30685200 |
| H | -2.51114900 | -1.56439500 | 3.37521200 |
| C | -4.79545900 | -0.36267300 | 3.45674600 |
| H | -5.20127200 | 0.65325900 | 3.33215500 |
| H | -5.64691600 | -1.01935900 | 3.69889500 |
| H | -4.11666500 | -0.36922200 | 4.32003900 |

**Compound (*E*)-4 – Inv. TS ($S_0$)** optimized geometry (# opt=calcfc,ts,noeigentest scrf=(smd,solvent=MeCN) def2svp mn15)



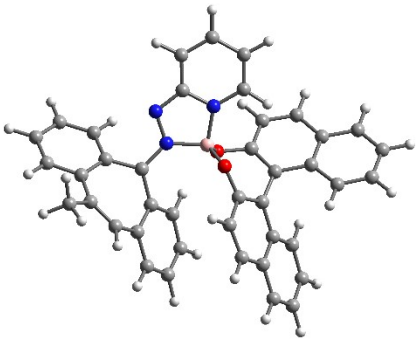
EE + Thermal Free Energy Correction: -1914.516563 (+29.8 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | -1.80871000 | -0.97591000 | 0.99915800 |
| C | -2.71220800 | -0.20014600 | 0.36822200 |
| C | -2.84100100 | 1.15765400 | 0.89891600 |
| C | -3.68906100 | 2.17688200 | 0.37061000 |
| C | -4.81056500 | 2.00689500 | -0.53148900 |
| C | -5.35463100 | 0.92907100 | -1.15496300 |
| C | -4.69690600 | -0.37084100 | -1.34184500 |
| C | -3.45132500 | -0.78604600 | -0.77426100 |
| C | -5.29359800 | -1.22176700 | -2.30596500 |
| C | -4.66034300 | -2.33819300 | -2.82621600 |
| C | -3.35584900 | -2.62872400 | -2.41445500 |
| C | -2.79035200 | -1.87309900 | -1.40380300 |
| C | -2.15961000 | 1.45221100 | 2.10761900 |
| C | -2.14611100 | 2.72106900 | 2.66630400 |
| C | -2.82930400 | 3.76571900 | 2.03358600 |
| C | -3.60526900 | 3.47643500 | 0.92294600 |
| N | -2.07096900 | -2.31526600 | 1.15812100 |
| C | -0.96413500 | -2.92481500 | 1.54151600 |
| N | 0.15892600 | -2.13894100 | 1.57190000 |
| C | 1.35432900 | -2.59054500 | 2.02948100 |
| C | 1.50070200 | -3.88856800 | 2.44399200 |
| C | 0.36196200 | -4.74835200 | 2.38844200 |
| C | -0.85385600 | -4.29106100 | 1.94913600 |
| B | -0.17696300 | -0.75882000 | 0.96293600 |
| O | 0.06768700 | -0.70079700 | -0.47011900 |
| O | 0.50048800 | 0.26431000 | 1.69892800 |
| C | 1.33884900 | -1.06217600 | -0.78583800 |
| C | 1.55121400 | -2.33007900 | -1.38745300 |
| C | 2.82880100 | -2.77596200 | -1.61341800 |
| C | 3.94796100 | -1.99322100 | -1.20963300 |

| | | | |
|---|---|---|---|
| C | 3.73394000 | -0.71313800 | -0.60902600 |
| C | 2.38947700 | -0.21903800 | -0.45932000 |
| C | 5.27463000 | -2.48109200 | -1.37325500 |
| C | 6.35700800 | -1.75266000 | -0.93444400 |
| C | 6.14805500 | -0.50397500 | -0.29803500 |
| C | 4.87526300 | 0.00134100 | -0.14160400 |
| C | 2.08280900 | 1.13038700 | 0.08417500 |
| C | 2.67304100 | 2.31232800 | -0.49224200 |
| C | 2.50937700 | 3.57906600 | 0.14673500 |
| C | 1.73923100 | 3.65224300 | 1.34035100 |
| C | 1.09961900 | 2.53970600 | 1.82063000 |
| C | 1.21351800 | 1.28283400 | 1.16327500 |
| C | 3.40401600 | 2.27879000 | -1.71604500 |
| C | 3.95935200 | 3.42153700 | -2.25048500 |
| C | 3.82378700 | 4.66834900 | -1.59082700 |
| C | 3.10725900 | 4.73994000 | -0.41757100 |
| H | -5.39041600 | 2.92953300 | -0.63180400 |
| H | -6.27878100 | -0.96936200 | -2.69292800 |
| H | -5.16256400 | -2.94930400 | -3.57921400 |
| H | -2.79003900 | -3.44515100 | -2.86738800 |
| H | -1.77741200 | -2.11122400 | -1.08865600 |
| H | -1.65445100 | 0.64519300 | 2.63316900 |
| H | -1.62032500 | 2.89313000 | 3.60781400 |
| H | -2.81184900 | 4.77695100 | 2.44520800 |
| H | -4.23119700 | 4.25621900 | 0.48249700 |
| H | 2.17103600 | -1.86336100 | 2.02917100 |
| H | 2.46508800 | -4.24872600 | 2.80070000 |
| H | 0.46217500 | -5.78870200 | 2.70717900 |
| H | -1.74082000 | -4.92422300 | 1.91026700 |
| H | 0.67540500 | -2.93094900 | -1.64635700 |
| H | 3.00776200 | -3.74836000 | -2.07950500 |
| H | 5.41167100 | -3.45665200 | -1.84773500 |
| H | 7.37132000 | -2.13784900 | -1.06029100 |
| H | 7.00401900 | 0.06157200 | 0.07768200 |
| H | 4.73334300 | 0.95864400 | 0.36277900 |
| H | 1.65005200 | 4.61178000 | 1.85635000 |
| H | 0.49771000 | 2.57874800 | 2.72806400 |
| H | 3.50752000 | 1.33087300 | -2.24732700 |
| H | 4.50404100 | 3.36608100 | -3.19601300 |
| H | 4.27507900 | 5.56545000 | -2.02052900 |
| H | 2.97403300 | 5.69380800 | 0.10031300 |
| C | -6.68566100 | 1.15846200 | -1.82987900 |
| H | -6.61054500 | 1.09767000 | -2.92702300 |
| H | -7.42903500 | 0.40889800 | -1.51692700 |
| H | -7.07459900 | 2.15159400 | -1.57207900 |

**Compound (*E*)-4 - Stable ($S_1$)** optimized geometry (# opt=calcfc td=(root=1) scrf=(smd,solvent=MeCN) def2svp mn15)



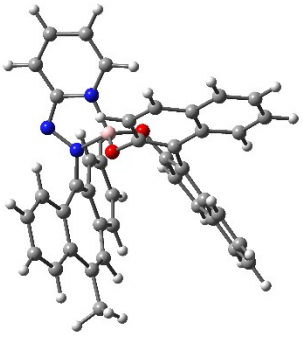
EE + Thermal Free Energy Correction: -1914.469364 Ha (+59.4 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | -1.79128500 | 1.12968700 | 0.18358200 |
| C | -2.64895400 | 0.04895300 | 0.34027400 |
| C | -2.12131200 | -1.29708400 | 0.49345500 |
| C | -2.74527900 | -2.42243100 | -0.12334600 |
| C | -3.88648000 | -2.32306000 | -1.02454600 |
| C | -4.94590100 | -1.47316500 | -0.98597000 |
| C | -5.13353500 | -0.42679000 | 0.03539300 |
| C | -4.05275100 | 0.30395000 | 0.62010800 |
| C | -6.44938200 | -0.06686200 | 0.38566400 |
| C | -6.72757400 | 0.93609200 | 1.30927600 |
| C | -5.66901300 | 1.63750300 | 1.90210600 |
| C | -4.36391500 | 1.33362200 | 1.55310200 |
| C | -0.99849600 | -1.52941200 | 1.32656700 |
| C | -0.50993700 | -2.80962400 | 1.55020400 |
| C | -1.10192100 | -3.90968500 | 0.91369800 |
| C | -2.19300700 | -3.70196300 | 0.07603100 |
| N | -2.41124700 | 2.30024000 | -0.11804300 |
| C | -1.51007200 | 3.19675800 | -0.51129400 |
| N | -0.23160800 | 2.69116200 | -0.58359500 |
| C | 0.78073100 | 3.43318300 | -1.06701500 |
| C | 0.57528700 | 4.75221600 | -1.44007100 |
| C | -0.72190900 | 5.31168800 | -1.33068900 |
| C | -1.77360900 | 4.53622200 | -0.87582800 |
| B | -0.22883400 | 1.20180600 | -0.09541800 |
| O | 0.52430000 | 1.03955600 | 1.13273200 |
| O | 0.23762500 | 0.38550600 | -1.19261200 |
| C | 1.85645500 | 1.27968300 | 1.03464900 |
| C | 2.37229600 | 2.42867800 | 1.69134600 |
| C | 3.69690000 | 2.76222200 | 1.56222300 |
| C | 4.55725100 | 1.98662800 | 0.73523800 |
| C | 4.04256700 | 0.82411700 | 0.07979700 |

| | | | |
|---|---|---|---|
| C | 2.67391800 | 0.43279900 | 0.29613700 |
| C | 5.91464500 | 2.36528300 | 0.53630200 |
| C | 6.73603400 | 1.64503300 | -0.30075400 |
| C | 6.22040900 | 0.51573600 | -0.98472800 |
| C | 4.91466800 | 0.11641100 | -0.79870700 |
| C | 2.10390900 | -0.81388800 | -0.28279100 |
| C | 2.70588500 | -2.10172900 | -0.05764800 |
| C | 2.21294300 | -3.24833300 | -0.75465200 |
| C | 1.10782600 | -3.10109800 | -1.64066400 |
| C | 0.47655500 | -1.89133400 | -1.76512800 |
| C | 0.94411600 | -0.75378600 | -1.05037500 |
| C | 3.76538700 | -2.29800200 | 0.87592900 |
| C | 4.31455800 | -3.54536500 | 1.08395400 |
| C | 3.84305100 | -4.67188500 | 0.36517200 |
| C | 2.80957500 | -4.52012000 | -0.53222000 |
| H | -3.93517900 | -3.12040300 | -1.77556700 |
| H | -7.28231200 | -0.59823800 | -0.07679600 |
| H | -7.76285900 | 1.16867500 | 1.56761800 |
| H | -5.86553900 | 2.41864900 | 2.64012900 |
| H | -3.53888400 | 1.86510300 | 2.02960000 |
| H | -0.53599200 | -0.68198000 | 1.82988800 |
| H | 0.34333400 | -2.95206400 | 2.21858900 |
| H | -0.70705400 | -4.91704900 | 1.06480300 |
| H | -2.65440000 | -4.54762200 | -0.44126900 |
| H | 1.75397300 | 2.94353100 | -1.15568300 |
| H | 1.41115500 | 5.33762500 | -1.82344300 |
| H | -0.89351600 | 6.34938400 | -1.62259600 |
| H | -2.79370200 | 4.91367900 | -0.79759200 |
| H | 1.68204100 | 3.03014900 | 2.28726600 |
| H | 4.10435700 | 3.64105300 | 2.06861300 |
| H | 6.28559300 | 3.25119800 | 1.05907100 |
| H | 7.77524600 | 1.94605900 | -0.45066900 |
| H | 6.86305100 | -0.04058300 | -1.67120600 |
| H | 4.53179100 | -0.74766800 | -1.34445700 |
| H | 0.74864300 | -3.97783400 | -2.18642400 |
| H | -0.40440100 | -1.76341500 | -2.39869600 |
| H | 4.13258300 | -1.44415100 | 1.44875200 |
| H | 5.11727500 | -3.66730000 | 1.81514600 |
| H | 4.29065100 | -5.65383800 | 0.53408900 |
| H | 2.41793300 | -5.37859000 | -1.08510100 |
| C | -6.05956900 | -1.67887000 | -1.97989600 |
| H | -6.94259800 | -2.14080200 | -1.50861000 |
| H | -6.39293500 | -0.72263800 | -2.41188000 |
| H | -5.73462900 | -2.34181600 | -2.79286700 |

**Compound (*E*)-4 - Metastable ($S_1$)** optimized geometry (# opt=calcfc td=(root=1) scrf=(smd,solvent=MeCN) def2svp mn15)



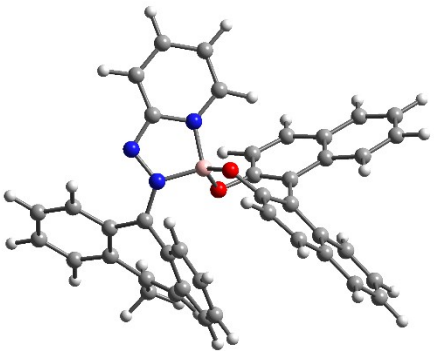
EE + Thermal Free Energy Correction: -1914.476167 Ha (+55.2 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | -1.53801600 | 1.83332200 | -0.07331900 |
| C | -2.43106200 | 0.80098700 | 0.19850000 |
| C | -2.54757200 | 0.42055200 | 1.58871400 |
| C | -3.01748900 | -0.83037400 | 2.12594900 |
| C | -3.49828100 | -1.97758600 | 1.34896500 |
| C | -3.81366400 | -1.98207500 | 0.02052100 |
| C | -3.76768700 | -0.98895300 | -1.02444000 |
| C | -3.12291900 | 0.28353600 | -0.95521200 |
| C | -4.35863500 | -1.38130800 | -2.24849600 |
| C | -4.36513500 | -0.56079500 | -3.36349800 |
| C | -3.74094600 | 0.69760000 | -3.29629500 |
| C | -3.11586500 | 1.09208300 | -2.12938600 |
| C | -2.10996300 | 1.41952800 | 2.50593300 |
| C | -2.14488300 | 1.24546300 | 3.87675500 |
| C | -2.58553800 | 0.02406000 | 4.39700200 |
| C | -2.99634100 | -0.97949800 | 3.52984400 |
| N | -1.90386600 | 3.15530500 | -0.03076700 |
| C | -0.81500000 | 3.85932700 | -0.32245100 |
| N | 0.31439200 | 3.10321700 | -0.55145700 |
| C | 1.49663700 | 3.66649000 | -0.89934000 |
| C | 1.62082000 | 5.02965400 | -1.01366200 |
| C | 0.47582300 | 5.84148900 | -0.76356200 |
| C | -0.73055100 | 5.27816200 | -0.42614500 |
| B | -0.01910200 | 1.59706400 | -0.30187800 |
| O | 0.56311500 | 1.05879200 | 0.91857100 |
| O | 0.32527100 | 0.81672700 | -1.47632600 |
| C | 1.89493000 | 0.81823200 | 0.88350700 |
| C | 2.75625000 | 1.66143100 | 1.63589600 |
| C | 4.11580900 | 1.47723600 | 1.59052600 |
| C | 4.68131400 | 0.46729900 | 0.76180600 |
| C | 3.81784100 | -0.38441300 | 0.00380400 |

| | | | |
|---|---|---|---|
| C | 2.39359400 | -0.23102400 | 0.12049000 |
| C | 6.09197500 | 0.30794000 | 0.66035800 |
| C | 6.64048800 | -0.63757400 | -0.17621600 |
| C | 5.78972500 | -1.45858200 | -0.95849000 |
| C | 4.42001500 | -1.33607000 | -0.87053300 |
| C | 1.41875500 | -1.11309500 | -0.57314200 |
| C | 1.42075100 | -2.54231200 | -0.41403300 |
| C | 0.51644500 | -3.34131200 | -1.18042600 |
| C | -0.39297200 | -2.70122000 | -2.06825500 |
| C | -0.43774100 | -1.33252300 | -2.15247800 |
| C | 0.44314600 | -0.52815500 | -1.37703000 |
| C | 2.27192500 | -3.20857900 | 0.51585800 |
| C | 2.24986200 | -4.58002300 | 0.65004100 |
| C | 1.37666000 | -5.36949600 | -0.13966400 |
| C | 0.52577600 | -4.75625600 | -1.03131000 |
| H | -4.82059900 | -2.37011700 | -2.29943300 |
| H | -4.83987700 | -0.89592500 | -4.28792500 |
| H | -3.73145500 | 1.35733100 | -4.16612100 |
| H | -2.61346300 | 2.05760400 | -2.09864600 |
| H | -1.76181600 | 2.37091100 | 2.10887400 |
| H | -1.82077100 | 2.05258900 | 4.53643200 |
| H | -2.60376100 | -0.15163100 | 5.47449300 |
| H | -3.31579900 | -1.92169400 | 3.96953500 |
| H | 2.32313600 | 2.97561700 | -1.08506300 |
| H | 2.57628400 | 5.47115600 | -1.29575500 |
| H | 0.55964900 | 6.92745400 | -0.84729700 |
| H | -1.62378400 | 5.87457900 | -0.23740200 |
| H | 2.30174000 | 2.45027800 | 2.23985000 |
| H | 4.78596400 | 2.11669800 | 2.17113400 |
| H | 6.73051600 | 0.96398700 | 1.25846800 |
| H | 7.72455300 | -0.74954300 | -0.24967700 |
| H | 6.22462100 | -2.19155400 | -1.64219400 |
| H | 3.77901000 | -1.96678600 | -1.48939400 |
| H | -1.07198800 | -3.31743100 | -2.66422100 |
| H | -1.15235900 | -0.82537200 | -2.80499500 |
| H | 2.94045800 | -2.61503600 | 1.14235300 |
| H | 2.90710100 | -5.06291200 | 1.37713700 |
| H | 1.37340100 | -6.45616300 | -0.02873300 |
| H | -0.16859100 | -5.34462800 | -1.63757300 |
| C | -3.76914600 | -3.26931900 | 2.07856000 |
| H | -2.98454600 | -3.52974400 | 2.80461800 |
| H | -4.72053900 | -3.21770200 | 2.63832600 |
| H | -3.84868500 | -4.10017700 | 1.36305000 |
| H | -4.21045600 | -2.93732100 | -0.34338900 |

**Compound (*E*)-4 – Inv. TS ($S_1$)** optimized geometry (# opt=calcfc,ts,noeigentest td=(root=1) scrf=(smd,solvent=MeCN) def2svp mn15)



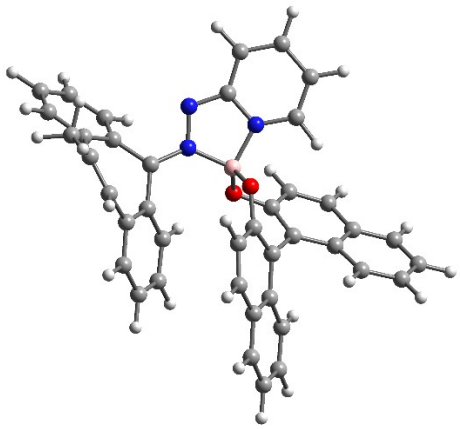
EE + Thermal Free Energy Correction: -1914.459906 Ha (+65.4 kcal/mol)

0 1

| | | | |
|---|---|---|---|
| N | -2.12393400 | 0.53872700 | -1.19871600 |
| C | -2.69114700 | -0.53896400 | -0.52470600 |
| C | -3.95222400 | -0.43006200 | 0.20556700 |
| C | -4.14818400 | -0.94788200 | 1.52496200 |
| C | -3.10359900 | -1.61091200 | 2.32713200 |
| C | -2.08984300 | -2.36794600 | 1.82215000 |
| C | -1.72105100 | -2.66298700 | 0.45259800 |
| C | -1.96443000 | -1.77526300 | -0.64133900 |
| C | -0.97005000 | -3.83355100 | 0.22123200 |
| C | -0.52678200 | -4.18262400 | -1.04754800 |
| C | -0.78552400 | -3.31953400 | -2.12751900 |
| C | -1.44867900 | -2.12302200 | -1.91856200 |
| C | -5.04748400 | 0.20781100 | -0.43095300 |
| C | -6.28219600 | 0.34520100 | 0.18710600 |
| C | -6.46714300 | -0.13762700 | 1.48745700 |
| C | -5.40813700 | -0.76237500 | 2.13414100 |
| N | -2.86199800 | 1.59384000 | -1.59394400 |
| C | -2.09140100 | 2.68164100 | -1.61056600 |
| N | -0.78763500 | 2.44618200 | -1.22726500 |
| C | 0.11749400 | 3.44172300 | -1.18865200 |
| C | -0.24137700 | 4.73980500 | -1.50836500 |
| C | -1.57699800 | 5.01122900 | -1.90223800 |
| C | -2.50350900 | 3.98798400 | -1.96514000 |
| B | -0.60025000 | 0.91565600 | -0.93272400 |
| O | -0.31357600 | 0.57785500 | 0.44271100 |
| O | 0.39198200 | 0.43476000 | -1.87296800 |
| C | 0.82550700 | 1.12126100 | 0.93653700 |
| C | 0.70390800 | 2.15699200 | 1.90109200 |
| C | 1.82195600 | 2.80209800 | 2.36483600 |
| C | 3.10793500 | 2.47315100 | 1.85021900 |
| C | 3.23329600 | 1.42539800 | 0.88427800 |
| C | 2.06236200 | 0.69003700 | 0.47765000 |

| | | | |
|---|---|---|---|
| C | 4.26350300 | 3.19218200 | 2.26593000 |
| C | 5.50095100 | 2.91736800 | 1.72980900 |
| C | 5.62463300 | 1.91137300 | 0.73944600 |
| C | 4.52577700 | 1.18638400 | 0.33135300 |
| C | 2.13554700 | -0.45708700 | -0.46553600 |
| C | 3.02780300 | -1.56375800 | -0.23122000 |
| C | 3.26084100 | -2.52439600 | -1.26253400 |
| C | 2.57773200 | -2.38240100 | -2.50316900 |
| C | 1.64040300 | -1.39678700 | -2.66671600 |
| C | 1.36327700 | -0.46487400 | -1.62639600 |
| C | 3.68946700 | -1.75679900 | 1.01647100 |
| C | 4.54217700 | -2.82127500 | 1.21802900 |
| C | 4.79202700 | -3.75333700 | 0.18036700 |
| C | 4.15805800 | -3.60384900 | -1.03297700 |
| H | -1.47933200 | -2.89555100 | 2.56435000 |
| H | -0.74659300 | -4.47843100 | 1.07548600 |
| H | 0.02822100 | -5.11050500 | -1.20183900 |
| H | -0.44049000 | -3.57960100 | -3.13063900 |
| H | -1.62324200 | -1.43671900 | -2.75046200 |
| H | -4.91699200 | 0.57442500 | -1.44654900 |
| H | -7.10491100 | 0.82350300 | -0.34939200 |
| H | -7.42963800 | -0.02991800 | 1.99194400 |
| H | -5.56262900 | -1.13172200 | 3.14834200 |
| H | 1.13904800 | 3.16731800 | -0.91131100 |
| H | 0.50847200 | 5.53037400 | -1.47321100 |
| H | -1.87004800 | 6.02996800 | -2.16347700 |
| H | -3.53857000 | 4.15011700 | -2.26850100 |
| H | -0.29860200 | 2.41876200 | 2.24697300 |
| H | 1.74084600 | 3.59635400 | 3.11152000 |
| H | 4.13987200 | 3.97863400 | 3.01557900 |
| H | 6.38122500 | 3.47856600 | 2.05108700 |
| H | 6.60015400 | 1.71232100 | 0.28943400 |
| H | 4.64040100 | 0.42691200 | -0.44362800 |
| H | 2.78561200 | -3.09401000 | -3.30671300 |
| H | 1.06629100 | -1.30085200 | -3.59096900 |
| H | 3.49954800 | -1.05482300 | 1.83107300 |
| H | 5.02494400 | -2.95087900 | 2.18965200 |
| H | 5.47497300 | -4.58887100 | 0.34957500 |
| H | 4.32451500 | -4.31895300 | -1.84348500 |
| C | -3.24065900 | -1.54829600 | 3.82747200 |
| H | -3.44817100 | -0.52231300 | 4.16833900 |
| H | -4.06974900 | -2.17862200 | 4.18879300 |
| H | -2.32162600 | -1.90212900 | 4.31299600 |

**Compound (*E*)-4 - Stable ($T_1$)** optimized geometry (# opt=calcfc scrf=(smd,solvent=MeCN) def2svp mn15)



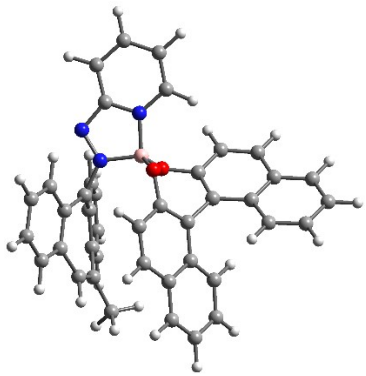
EE + Thermal Free Energy Correction: -1914.502556 Ha (+38.6 kcal/mol)

0 3

| | | | |
|---|---|---|---|
| N | -1.76884500 | 1.15726600 | 0.12961800 |
| C | -2.65230400 | 0.04218000 | 0.28570900 |
| C | -2.12472700 | -1.30791800 | 0.44299200 |
| C | -2.76716900 | -2.41214200 | -0.17922200 |
| C | -3.93187400 | -2.27316200 | -1.05587400 |
| C | -4.98191100 | -1.42197000 | -0.95582500 |
| C | -5.13485500 | -0.40215700 | 0.10644300 |
| C | -4.03598600 | 0.31278900 | 0.66033400 |
| C | -6.43377900 | -0.06576500 | 0.53558400 |
| C | -6.66669100 | 0.91093100 | 1.49956900 |
| C | -5.58416200 | 1.60635300 | 2.05106600 |
| C | -4.29484700 | 1.31438200 | 1.62845500 |
| C | -1.01060700 | -1.55832100 | 1.27567100 |
| C | -0.53185000 | -2.84869900 | 1.47980700 |
| C | -1.14025100 | -3.93087100 | 0.83320600 |
| C | -2.23613000 | -3.70175500 | 0.00496800 |
| N | -2.39611100 | 2.28155000 | -0.23706800 |
| C | -1.48822000 | 3.20190300 | -0.61704000 |
| N | -0.21014600 | 2.73244000 | -0.61930500 |
| C | 0.81442000 | 3.48831700 | -1.04573200 |
| C | 0.59767100 | 4.79789300 | -1.44603600 |
| C | -0.71322300 | 5.31732200 | -1.42019600 |
| C | -1.77189300 | 4.52231400 | -1.01395100 |
| B | -0.21282000 | 1.22493900 | -0.12105900 |
| O | 0.52173100 | 1.06564100 | 1.11024900 |
| O | 0.27075200 | 0.43246300 | -1.22533100 |
| C | 1.86133800 | 1.27930300 | 1.03744800 |
| C | 2.38481000 | 2.40903100 | 1.72063000 |
| C | 3.71763200 | 2.71939300 | 1.62296600 |
| C | 4.57988600 | 1.93905000 | 0.80255000 |

| | | | |
|---|---|---|---|
| C | 4.05708400 | 0.79534100 | 0.12136700 |
| C | 2.67737900 | 0.42576600 | 0.30543200 |
| C | 5.94767200 | 2.29514500 | 0.63548900 |
| C | 6.77196000 | 1.57115500 | -0.19538400 |
| C | 6.24921300 | 0.46119200 | -0.90507600 |
| C | 4.93304700 | 0.08355500 | -0.74985200 |
| C | 2.10030600 | -0.80623900 | -0.29765500 |
| C | 2.67840200 | -2.10590300 | -0.07501600 |
| C | 2.18030600 | -3.23688100 | -0.79301500 |
| C | 1.09246100 | -3.06387500 | -1.69568000 |
| C | 0.48153500 | -1.84353700 | -1.81781900 |
| C | 0.95627900 | -0.72105300 | -1.08469800 |
| C | 3.71533200 | -2.32898500 | 0.87735900 |
| C | 4.23858200 | -3.58775200 | 1.08443600 |
| C | 3.76264600 | -4.69900000 | 0.34536100 |
| C | 2.75057800 | -4.52073000 | -0.57145600 |
| H | -3.99828200 | -3.03537000 | -1.84147100 |
| H | -7.28710800 | -0.59098700 | 0.10337800 |
| H | -7.68835900 | 1.13248700 | 1.81565500 |
| H | -5.74722700 | 2.37591000 | 2.80916000 |
| H | -3.44799500 | 1.85098100 | 2.06031000 |
| H | -0.53222400 | -0.72000900 | 1.78114000 |
| H | 0.32682100 | -3.00959900 | 2.13704800 |
| H | -0.75626000 | -4.94471800 | 0.96905000 |
| H | -2.71378500 | -4.53772300 | -0.51366800 |
| H | 1.80099200 | 3.01981300 | -1.06914100 |
| H | 1.43792900 | 5.40322700 | -1.78537600 |
| H | -0.89485000 | 6.34655300 | -1.73540600 |
| H | -2.80335800 | 4.87434300 | -0.99705300 |
| H | 1.69374400 | 3.01484200 | 2.31114500 |
| H | 4.13087100 | 3.58325700 | 2.14995500 |
| H | 6.32429500 | 3.16694000 | 1.17754900 |
| H | 7.81925800 | 1.85478000 | -0.32095200 |
| H | 6.89482800 | -0.09742600 | -1.58686500 |
| H | 4.54529700 | -0.76568700 | -1.31506600 |
| H | 0.72856400 | -3.92965900 | -2.25556500 |
| H | -0.38717700 | -1.69587300 | -2.46377600 |
| H | 4.08532000 | -1.48728400 | 1.46613400 |
| H | 5.02396400 | -3.73033400 | 1.83055300 |
| H | 4.18957400 | -5.69019200 | 0.51377700 |
| H | 2.35528300 | -5.36707600 | -1.14021200 |
| C | -6.12477800 | -1.57171700 | -1.92804300 |
| H | -7.00705400 | -2.02808400 | -1.45020200 |
| H | -6.44675200 | -0.59531200 | -2.32250600 |
| H | -5.83606400 | -2.21541400 | -2.76999000 |

**Compound (*E*)-4 - Metastable ($T_1$)** optimized geometry (# opt=calcfc scrf=(smd,solvent=MeCN) def2svp mn15)



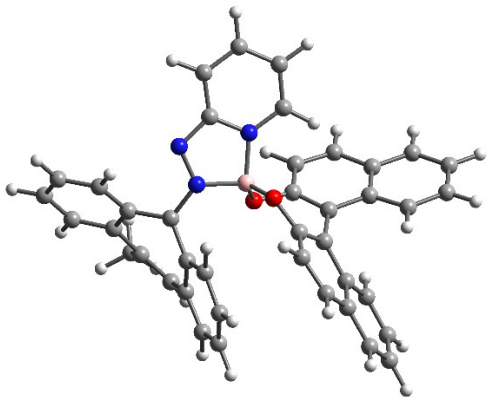
EE + Thermal Free Energy Correction: -1914.518640 Ha (+28.5 kcal/mol)

0 3

| | | | |
|---|---|---|---|
| N | -1.85528100 | 1.58489200 | 0.04937200 |
| C | -2.41092200 | 0.32364300 | 0.39420100 |
| C | -2.22988700 | -0.07871100 | 1.78040000 |
| C | -2.09948000 | -1.42169400 | 2.24997400 |
| C | -2.04969000 | -2.61045700 | 1.37371400 |
| C | -2.59773500 | -2.71705400 | 0.13746700 |
| C | -3.29183200 | -1.76773600 | -0.72418000 |
| C | -3.14854100 | -0.35121700 | -0.64734500 |
| C | -3.99502400 | -2.32018100 | -1.81147600 |
| C | -4.56416400 | -1.53262600 | -2.80693900 |
| C | -4.41051900 | -0.14120300 | -2.74404800 |
| C | -3.70884500 | 0.43120600 | -1.69232000 |
| C | -2.15088400 | 0.97073700 | 2.73273300 |
| C | -1.99904900 | 0.73432700 | 4.09061900 |
| C | -1.89121300 | -0.58122500 | 4.55145700 |
| C | -1.92590200 | -1.62627700 | 3.63356600 |
| N | -2.54572600 | 2.71551700 | 0.08723100 |
| C | -1.69944800 | 3.72105500 | -0.26506300 |
| N | -0.43067300 | 3.30497900 | -0.53824300 |
| C | 0.53573600 | 4.16137600 | -0.91524100 |
| C | 0.26431900 | 5.51202900 | -1.02993500 |
| C | -1.04130400 | 5.96984800 | -0.74856100 |
| C | -2.03408600 | 5.08396900 | -0.36625800 |
| B | -0.34057100 | 1.74938500 | -0.29919400 |
| O | 0.42914000 | 1.38971500 | 0.86316100 |
| O | 0.09863500 | 1.11590000 | -1.51868200 |
| C | 1.77112200 | 1.25402500 | 0.74265900 |
| C | 2.59998300 | 2.17133400 | 1.44237000 |
| C | 3.96591600 | 2.08099700 | 1.34642800 |
| C | 4.56775800 | 1.09408700 | 0.51608900 |
| C | 3.73677200 | 0.17247800 | -0.19509200 |

| | | | |
|---|---|---|---|
| C | 2.30930100 | 0.22881000 | -0.02506900 |
| C | 5.98140400 | 1.02999300 | 0.36501200 |
| C | 6.56373200 | 0.11005400 | -0.47699500 |
| C | 5.74321800 | -0.77840500 | -1.21603900 |
| C | 4.37224900 | -0.74829000 | -1.07915700 |
| C | 1.38633700 | -0.72471600 | -0.69586900 |
| C | 1.51461900 | -2.15134800 | -0.57147800 |
| C | 0.71213800 | -3.00683100 | -1.38822400 |
| C | -0.22575700 | -2.42778100 | -2.28856100 |
| C | -0.41622300 | -1.06935000 | -2.31685800 |
| C | 0.36020000 | -0.21582900 | -1.48719900 |
| C | 2.39494000 | -2.76002100 | 0.37009200 |
| C | 2.48669300 | -4.13140100 | 0.47852000 |
| C | 1.71018700 | -4.97530700 | -0.35492600 |
| C | 0.84055000 | -4.41880200 | -1.26652200 |
| H | -2.50881000 | -3.70835900 | -0.32251100 |
| H | -4.06613400 | -3.40958500 | -1.87529800 |
| H | -5.10494900 | -1.99654300 | -3.63436800 |
| H | -4.83600400 | 0.49784700 | -3.52103400 |
| H | -3.60104500 | 1.51525800 | -1.65445800 |
| H | -2.24076900 | 1.99943200 | 2.38293700 |
| H | -1.96301100 | 1.57446900 | 4.78767600 |
| H | -1.76784000 | -0.79314000 | 5.61555000 |
| H | -1.81591000 | -2.64449700 | 4.00704500 |
| H | 1.51829700 | 3.72886700 | -1.12017600 |
| H | 1.05134700 | 6.20095900 | -1.33544800 |
| H | -1.27074900 | 7.03382500 | -0.83591200 |
| H | -3.05321000 | 5.40202300 | -0.14592600 |
| H | 2.11562300 | 2.93638500 | 2.05355200 |
| H | 4.61114600 | 2.77704200 | 1.88883300 |
| H | 6.59379300 | 1.73893600 | 0.92905500 |
| H | 7.64953400 | 0.07121500 | -0.58922600 |
| H | 6.20165000 | -1.49016100 | -1.90671300 |
| H | 3.75704700 | -1.42978900 | -1.66903000 |
| H | -0.82594300 | -3.08673900 | -2.92246600 |
| H | -1.17461000 | -0.61116800 | -2.95684000 |
| H | 2.99171400 | -2.12224300 | 1.02562400 |
| H | 3.16074800 | -4.57213200 | 1.21687800 |
| H | 1.79699800 | -6.06038900 | -0.26395000 |
| H | 0.22093900 | -5.05189900 | -1.90809400 |
| C | -1.36075000 | -3.83564300 | 1.92384500 |
| H | -0.36023800 | -3.58613300 | 2.31398900 |
| H | -1.92224300 | -4.29136200 | 2.75555400 |
| H | -1.25044700 | -4.59885700 | 1.14165000 |

**Compound (*E*)-4 – Inv. TS ($T_1$)** optimized geometry (# opt=calcfc,ts,noeigentest scrf=(smd,solvent=MeCN) def2svp mn15)



EE + Thermal Free Energy Correction: -1914.493822 Ha (+44.1 kcal/mol)

0 3

| | | | |
|---|---|---|---|
| N | -2.03465100 | 0.65347700 | -1.08803600 |
| C | -2.70906100 | -0.43859600 | -0.45343500 |
| C | -4.08536300 | -0.32450900 | 0.03048500 |
| C | -4.47795200 | -0.77440300 | 1.32254500 |
| C | -3.53796200 | -1.35634200 | 2.30870500 |
| C | -2.47053600 | -2.13013200 | 1.99315500 |
| C | -1.95315700 | -2.53919600 | 0.68797400 |
| C | -2.02105500 | -1.71297800 | -0.46774300 |
| C | -1.25608800 | -3.75736100 | 0.60789600 |
| C | -0.68129900 | -4.19538200 | -0.58291300 |
| C | -0.76163900 | -3.38606300 | -1.72299400 |
| C | -1.39602500 | -2.15077400 | -1.65613300 |
| C | -5.07625900 | 0.20572700 | -0.83008900 |
| C | -6.40352100 | 0.32223400 | -0.43641700 |
| C | -6.78313200 | -0.08747800 | 0.84541700 |
| C | -5.82621900 | -0.62089300 | 1.70314500 |
| N | -2.73965900 | 1.75049800 | -1.36269400 |
| C | -1.90726600 | 2.81011400 | -1.42449500 |
| N | -0.61450600 | 2.50556500 | -1.11762400 |
| C | 0.35022600 | 3.43938600 | -1.13300200 |
| C | 0.04480800 | 4.75691000 | -1.43640500 |
| C | -1.28839800 | 5.09907100 | -1.74636000 |
| C | -2.27691700 | 4.12945800 | -1.74919900 |
| B | -0.50360500 | 0.94257000 | -0.84559600 |
| O | -0.19970400 | 0.58669900 | 0.51434100 |
| O | 0.44006000 | 0.45530700 | -1.82729300 |
| C | 0.97688300 | 1.07727700 | 0.98109600 |
| C | 0.92307300 | 2.10240900 | 1.96223800 |
| C | 2.07844300 | 2.69578700 | 2.40325900 |
| C | 3.33520900 | 2.32450400 | 1.84767300 |

| | | | |
|---|---|---|---|
| C | 3.39151800 | 1.28985800 | 0.86159600 |
| C | 2.18145900 | 0.60667500 | 0.47791300 |
| C | 4.52973300 | 2.98969200 | 2.24250800 |
| C | 5.73957400 | 2.67592100 | 1.66650600 |
| C | 5.79503100 | 1.68445900 | 0.65556100 |
| C | 4.65717600 | 1.01073800 | 0.26701600 |
| C | 2.18761000 | -0.52423400 | -0.48818700 |
| C | 3.04201400 | -1.66810500 | -0.29777500 |
| C | 3.21106300 | -2.61653800 | -1.35280400 |
| C | 2.50239500 | -2.42463700 | -2.57243800 |
| C | 1.59899100 | -1.40201100 | -2.69337000 |
| C | 1.38754300 | -0.48106000 | -1.62841300 |
| C | 3.72642300 | -1.91066800 | 0.92869600 |
| C | 4.54148100 | -3.01094500 | 1.08819500 |
| C | 4.72868000 | -3.93144400 | 0.02715800 |
| C | 4.07109200 | -3.73398800 | -1.16656000 |
| H | -1.93489700 | -2.57550200 | 2.83998100 |
| H | -1.17004700 | -4.36659600 | 1.51195700 |
| H | -0.16205200 | -5.15543400 | -0.62188900 |
| H | -0.30979200 | -3.71281100 | -2.66188300 |
| H | -1.43337200 | -1.50273300 | -2.53583100 |
| H | -4.78413200 | 0.51482600 | -1.83292900 |
| H | -7.14221200 | 0.72859100 | -1.13117700 |
| H | -7.82067200 | 0.00338100 | 1.17433800 |
| H | -6.13490600 | -0.93978700 | 2.69985500 |
| H | 1.36547900 | 3.10495100 | -0.90449300 |
| H | 0.83581400 | 5.50657800 | -1.44118800 |
| H | -1.53962800 | 6.13288800 | -1.99095300 |
| H | -3.31731100 | 4.34730200 | -1.99101700 |
| H | -0.05807300 | 2.39738700 | 2.34094700 |
| H | 2.04991600 | 3.48041500 | 3.16380900 |
| H | 4.45844300 | 3.76659600 | 3.00870400 |
| H | 6.65029200 | 3.19580200 | 1.97205800 |
| H | 6.74870700 | 1.45553400 | 0.17407200 |
| H | 4.71999200 | 0.26187900 | -0.52397900 |
| H | 2.66100900 | -3.12953300 | -3.39296000 |
| H | 1.00237300 | -1.26863900 | -3.59888800 |
| H | 3.58455200 | -1.21798200 | 1.76080500 |
| H | 5.04294800 | -3.17834900 | 2.04443800 |
| H | 5.38227400 | -4.79598200 | 0.16321500 |
| H | 4.18929900 | -4.43908700 | -1.99408000 |
| C | -3.86949000 | -1.15928600 | 3.76695400 |
| H | -4.10544700 | -0.10608800 | 3.98571900 |
| H | -4.74838700 | -1.75157800 | 4.06956500 |
| H | -3.02780400 | -1.47087000 | 4.40013800 |

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