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A Clear-Cut Example of Selective Bpin-Bdan Activation and Precise Bdan Transfer on Boron Conjugate Addition

Jessica Cid, Jorge J. Carbó* and Elena Fernández*[a]

Dedication ((optional))

The Lewis acidity of the boron atom is the key factor governing the reactivity of organoboron compounds. The vacant p-orbital of the boron atom can be partially filled with the electron lone pair of adjacent atoms, tuning the Lewis acid property. Nitrogen atoms donate their lone pair of electrons thus lowering the acidity significantly in comparison with that of the corresponding oxygen atoms of boronic acids and their esters.[1] Diamines, which form cyclic diaminoboranes, increase the overall stability on the boryl species reducing the reactivity.[2] Interestingly, organoboranes with C-Bdan moieties (dan=1,8-diaminonaphthalene) are particularly easy to handle since the dan moiety act as a masking group on B.[3-5] So far Bpin moieties have been exclusively transferred from symmetric B_2pin_2 (**1**) reagent to unsaturated substrates, but the pinacol substituent on B does not mask the B atom towards further interactions. In that context, the interest of generating C_β-Bdan enoates (**2**) was justified because they have served as intermediates towards the copper mediated asymmetric conjugate borylation (Scheme 1, *pathway b*)[6] or alkylation (Scheme 1, *pathway c*)[7] with total efficiency. However, nowdays the synthesis of C_β-Bdan enoates requires a multistep synthetic methodology (Scheme 1, *pathway a*).[8] We became interested in developing a method to access directly to chiral alkylboronate derivatives containing the Bdan moiety, from commercialy accessible α,β-unsaturated esters and ketones, following a catalytic β-boration reaction (Scheme 1, *pathway* d).[9] Towards this new strategy we envisaged the activation of the mixed diboron reagent Bpin-Bdan (**3**), with an alkoxide.[10] To the best of our knowledge there is only one example in the literature in which Bpin-Bdan has been used to diborate alkynes in a regioselective manner, and it was required the activation of the diboron by transition metal complexes.[11]

[a] Ms Jessica Cid, Dr. Jorge J. Carbó, Dr. Elena Fernández
Department Química Física i Inorgànica
University Rovira i Virgili
C/Marcel·li Domingo s/n
Fax: (+) 34 977 559563
E-mail: maraielena.fernandez@urv.cat, j.carbo@urv.cat

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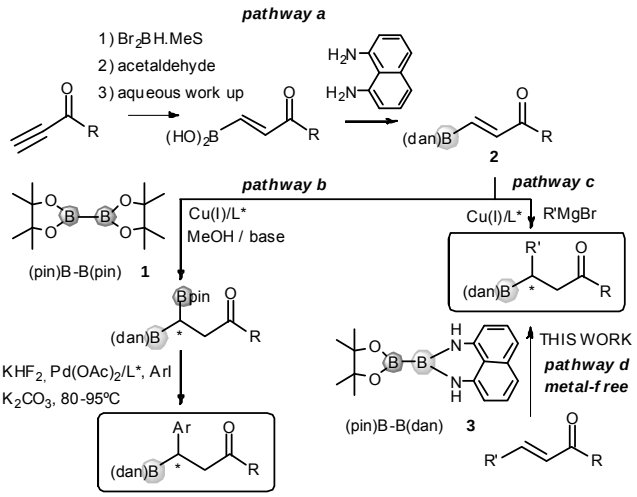


Scheme 1. Synthesis of C_β-Bdan carbonyl compounds

Initially, we computationally explored the potential reactivity of the Bpin-Bdan reagent. Previous DFT studies by Bo et al. have already demonstrated the nucleophilic character of B(sp^2) moiety of MeO^-→Bpin-Bpin adducts.[10b,12] Subsequently, a tendency map was constructed based on DFT calculations and NBO analysis of ground-state structures in order to establish a gradient in the nucleophilic character of trivalent boron moieties.[13a] Structure-Activity Relationships (SAR) approaches can be used to screen large and varied dataset of compounds in homogeneous catalysis.[14] The boron p/s ratio in the M-B σ-bond was considered an indicator of the intrinsic nucleophilicity of the boryl fragment, based on a previous work of Lin and Marder.[13b] For diboron reagents that are activated with Lewis bases, the p/s ratio of the B(sp^2) atom is relatively low with respect to the corresponding fragment bonded to Pt (Figure 1). This indicated the greater polarizability of the B(sp^2) moiety in the B-B bond, and consequently, its propensity to react with soft electrophiles. Moreover, the MeO^- ion induced greater polarization of the B-B bond than the nitrogen- and carbon-donor Lewis bases.[13a] Thus, we initially calculated the p/s ratio of the B atom, from the Bdan(sp^2) moiety, in the MeO^-→Bpin-Bdan adduct in other to

evaluate the potential of Bdan as a nucleophilic boryl moiety.[15] The computed p/s value, 1.15, is within the range (1.03 – 1.19) of other tested diboron compounds activated with Lewis bases (Figure 1).[13a]

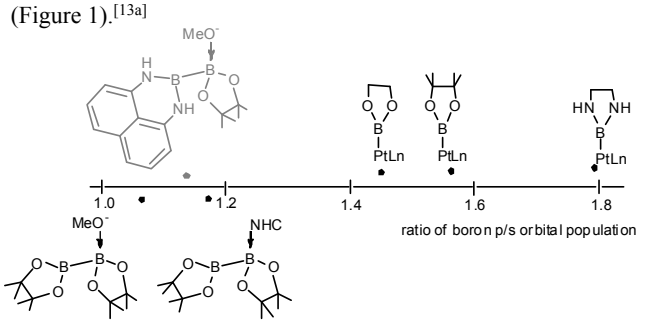


Figure 1. Relative distribution of p/s ratio of the orbital population of *B* in *B*-Pt(PMe$_3$)$_2$Cl moieties and Lewis acid-base adducts

Although the tendency map identifies Bdan as a potential nucleophilic boryl moiety,[13a] its semi-quantitative nature does not allow discerning whether the Bdan moiety is more or less reactive than the Bpin moiety. Therefore, we performed a more detailed DFT study in order to compare the reactivity of both adducts (Figure 2).[15] Using the CH_2CHCHO substrate as the simplest model of α,β-unsaturated carbonyl compound, we located the transition states (TSs) corresponding to the nucleophilic attack of the Bpin(sp^2) and Bdan(sp^2) moieties at the β-carbon of the olefinic group. The computed energy barrier for the Bdan group (+12.0 kcal.mol^{-1}) is higher than that for the Bpin moiety, +4.2 kcal.mol^{-1}, indicating that the Bdan(sp^2) has a lower nucleophilic character than Bpin(sp^2). However, due to the π-donation from nitrogen lone pair to boron empty orbital, the acidity of boron is weakened and has less tendency to add the alkoxide. The MeO$^-$→Bpin-Bdan adduct is 7.4 kcal.mol^{-1} lower in energy than MeO$^-$→Bdan-Bpin. In this scenario, the 1,8-diaminonaphtalene group might protect the boron from alkoxide attack forming preferentially the MeO$^-$→Bpin-Bdan reagent, which only needs to overcome a modest energy barrier to realese Bdan as a nucleophile.[16]

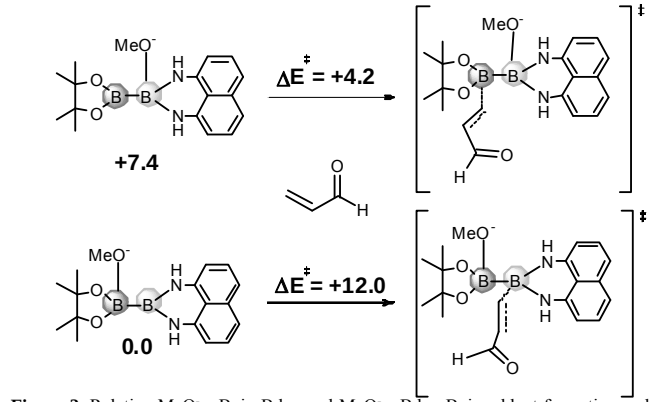
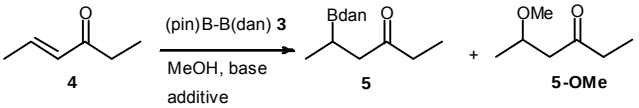


Figure 2. Relative MeO$^-$→Bpin-Bdan and MeO$^-$→Bdan-Bpin adduct formation and relative reactivity with CH_2CHCHO. Electronic energies in kcal.mol^{-1}

These results prompted us to use the Bpin-Bdan reagent in the organocatalyic β-boration reation of α,β-unsaturated carbonyl compounds. We adapted the synthetic protocol from Suginome's method,[11] by mixing tetrakis(dimethylamino)diboron, $B_2(NMe_2)_4$,[17] with 1,8-diaminonaphthalene and pinacol in a 1:1:1 ratio. In the presence of a base and MeOH, some spectroscopic evidences demonstrated the formation of the Lewis acid-base adduct [RO$^-$→Bpin-Bdan]. The original ^{11}B NMR spectra of the mixed diboron reagent Bpin-Bdan, in MeOH as solvent, shows signals at 28.5 and 25.2 ppm due to the sp^2 Bpin and sp^2 Bdan fragments, respectively. After the addition of 1 eq of NaO*t*Bu, one of the signals completely shifted to higher fields (1.59 ppm), with one signal remaining at low field (33.2 ppm). The new signal might correspond to the sp^3 Bpin moiety of the adduct [RO$^-$→Bpin-Bdan] in agreement with previous spectroscopic evidences of [RO$^-$→Bpin-Bpin].[10] This finding is also in agreement with the DFT calculations that suggested the preferred formation of the lewis acid-base adduct [MeO$^-$→Bpin-Bdan].

With the aim of activating organocatalytically Bpin-Bdan (**3**) and selectively transfer the Bdan moiety to activated olefins, we first attempted to find the optimal conditions for the β-boration of 4-hexen-3-one with Bpin-Bdan (Table 1). When the reaction was carried out in MeOH as solvent at 70ºC, no β-borated product was observed. The sole addition of 9 mol% of NaOtBu favoured the formation of 5-methoxy-hexan-3-one (**5-OMe**) as the only product, with a conversion of 72% (Table 1, entry 1). It seemed that the MeOH-base interaction provided the methoxy group that attacked directly to the substrate instead of activating Bpin-Bdan. However, when no base was present in the reaction media and PCy_3 was added as additive (6 mol%), the substrate was totally transformed into the β-borated product **5** with exclusive formation of the C_β-Bdan bond, (Table 1, entry 2).

Table 1 Optimization of reaction conditions for the organocatalytic β-boration of 4-hexen-3-one (**4**) with Bpin-Bdan (**3**).[a]



Entry	Additive	Base	Conv (%)[b]	C_β-B(dan) (**5**) (%)[c]	C_β-OMe (**5-OMe**)(%)[c]
1	---	NaO^{t}Bu	72	---	99
2	PCy_3	---	99	99	---
3	PCy_3	NaO^{t}Bu	99	99	---
4[d]	PCy_3	NaO^{t}Bu	23	99	---
5	PPh_3	NaO^{t}Bu	99	60	40
6	PPh_3	---	70	99	---

[a] Reaction conditions: substrate (0.25 mmol), Bpin-Bdan (0.275 mmol), base (9 mol%), PR3 (6 mol%), MeOH (2 mL), 70ºC, 16h. [b]Conversion calculated by G.C-MS from an average of two reactions. [c]Selectivity calculated by 1H NMR [d]25ºC

The use of phosphines to assist the organocatalytic β-boration reaction of α,β-unsaturated carbonyl compounds was already demonstrated.[18] The presence of base and phosphine as additive resulted beneficial (Table 1, entry 3), and the reaction was observed even at 25ºC (Table 1, entry 4). The nature of the phosphine is also important. When PPh_3 was involved in the reaction together with NaOtBu as base, selectivity towards the β-borated product decreased to 60% with the generation of 5-methoxy-hexan-3-one (**5-OMe**) as byproduct (Table 1, entry 5).

But once again, when no base was present and PPh_3 assisted the reaction, the β-borated product was exclusively formed, but with lower conversion (Table 1, entry 6). Importantly, the activation of Bpin-Bdan (**3**) with the alkoxide exclusively renders C_β-Bdan formation as no C_β-Bpin product has been detected. The scope of substrates was also a subject of study. Under optimized reaction conditions, we were able to generalize the selective transfer of the Bdan moiety to a variety of α,β-unsaturated ketones and esters (Figure 3).

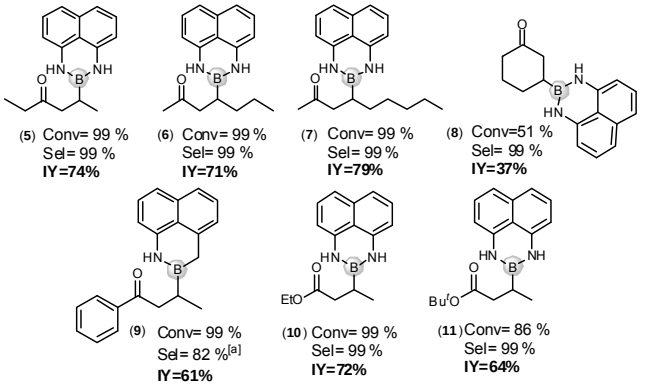
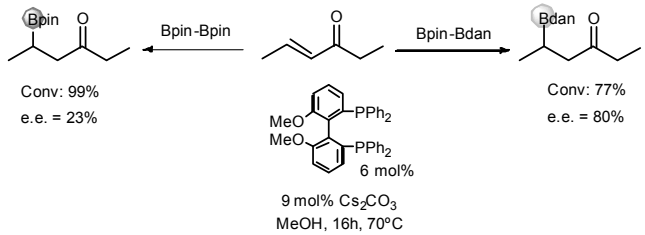


Figure 3. Substrate scope of selective organocatalytic β-boration of α,β-unsaturated carbonyl compounds with Bpin-Bdan under the conditions listed in Table 1 and PCy_3 as additive. IY=isolated yield. [a]18% of β-methoxy byproduct was observed

We recently pointed out that chiral phosphines can assist the asymmetric organocatalytic β-boration of α,β-unsaturated carbonyl compounds with B_2pin_2.[10a] In the present study, we explored this possibility and conducted a parallel β-boration of model substrate **4**, with B_2pin_2 and Bpin-Bdan in the presence of (*R*)-(+)-MeO-BIPHEP diphosphine (*R*)-(+)-(6,6′-Dimethoxybiphenyl-2,2′-diyl)bis(diphenylphosphine**)**. Scheme 2 shows that the asymmetric induction in the organocatalytic C_β-Bdan formation is much higher (e.e=80%) than that observed in the formation of the C_β-Bpin bond (e.e=23%). Other chiral phosphines such as Josiphos type ligands provided similar results to the β-boration with B_2pin_2.



Scheme 2. Comparative asymmetric β-boration of **4** with B_2pin_2 and Bpin-Bdan assisted by (*R*)-(+)-MeO-BIPHEP diphosphine

To get more insight into the selective addition of Bdan moiety in the presence of phosphines as additive, we performed a systematic DFT study using PMe_3 and CH_2CHCHO as model phosphine and substrate, respectively. First of all, DFT studies related to the plausible interaction of PMe_3 with Bpin-Bdan, demonstrated the lack of stability of the corresponding [PMe_3→Bpin-Bdan] adduct. Similar conclusion was observed from the spectroscopic studies carried out in ^{11}B NMR and ^{31}P NMR by mixing Bpin-Bdan and PMe_3. Recently, Bo and co-workers had computationally characterized the role of the phosphine in the organocatalytic β-boration of α,β-unsaturated ketones and esters with Bpin-Bpin reagent.[18] In that previous study, the role of the phosphine was associated with the preactivation of the substrate, by forming a phosphonium salt. Following previous proposal,[18] we suggest a catalytic cycle that starts with the plausible phosphine attack to the electrophilic carbon of the α,β–unsaturated carbonyl compound yielding the zwitterionic phosphonium enolate, species **B** in Figure 4. In the presence of an excess of methanol, a MeOH molecule might be H-bonded to the α-carbon of **B** intermediate, species **C** in Figure 4. This species may act as a Brönsted base deprotonating directly the MeOH molecule; however, the process is computed to be thermodynamically disfavoured by 5.1 kcal.mol^{-1}. From **C**, two ion pairs can be also formed by the interaction with Bpin-Bdan: the [α-H,β-PMe_3-propionaldehyde]$^+$[MeO^-→Bdan-Bpin], **Da**, (Figure 4, *mechanism a*) and the [α-H,β-PMe_3-propionaldehyde]$^+$[MeO^-→Bpin-Bdan], **Db**, (Figure 4, *mechanism b*). The corresponding energies associated to the formation of the ion-pair **Da** (+5.6 kcal.mol^{-1}) and **Db** (-7.5 kcal.mol^{-1}), clearly shows the favoured formation of the ion-pair **Db**, in which Bpin moiety acts as the preferred Lewis acid. Moreover, the energy barrier to reach the ion pair **Db** is significantly lower than that calculated to reach the ion pair **Da**, 4.0 and 13.9 kcal.mol^{-1}, respectively. These results are coherent with previous experimental findings in which quantitative formation of phosphonium species required the presence of the diboron reagent,[18] and indicate that the Bdan moiety is not as good Lewis acid as Bpin moiety.

In the next step, it has been suggested that the enhanced nucleophilic sp^2 boryl unit in the ion-pairs **Da** and **Db** might transfer the Bpin moiety or the Bdan moiety, respectively, to the β-carbon of another molecule of substrate through the transition state $\mathbf{TS_{D\text{-}E}}$. For both types of boryl units the process is strongly exothermic, -51.5 kcal.mol^{-1} for Bpin release in *mechanism a* and -41.9 kcal.mol^{-1} for Bdan release in *mechanism b*. As it was found for the free anionic adducts depicted in the Figure 2, the activated Bpin(sp^2) moiety is more reactive than the Bdan(sp^2) one ($\Delta E^{\neq}$ = 13.0 and 25.3 kcal.mol^{-1}, respectively). However, if we look at the overall catalytic cycle, the transition state $\mathbf{TS_{D\text{-}E}}$ is the most energetically demanding, and this is higher in energy for Bpin release ($\mathbf{TSa_{D\text{-}E}}$) than for Bdan release ($\mathbf{TSb_{D\text{-}E}}$) by ~ 1 kcal.mol^{-1}. Thus, the computed overall catalytic cycle explains the observed selectivity from both the thermodynamic and the kinetic point of view. Thermodynamically, the deprotontation of methanol requires the enhanced Lewis acidity of Bpin moiety in Bpin-Bdan by forming the [MeO^-→Bpin-Bdan] adduct. Kinetically, the overall energy barrier to transfer Bdan moiety from the ion pair to acrylaldehyde is somewhat lower than that for the Bpin transfer.

In summary, we have been able to demostrate a new activation of B(pin)-B(dan) in the absence of any metal complex. With the assistance of DFT calculations and spectroscopic studies it was possible to postulate the exclusive formation of the Lewis acid-base adduct [RO^-→B(pin)-B(dan)]. This activated intermediate reacts with α,β-unsaturated carbonyl compounds to give exclusively the C_β-Bdan carbonyl compound with high yields. In addition to the unprecedented conjugate Bdan addition to α,β-unsaturated ketones and esters, the presence of chiral diphosphine as additive assisted the asymmetric induction in a more efficient way than the analogue borylation with B_2pin_2 The new synthetic platform opens a non existing methodology to prepare selectively

Cβ-Bdan carbonyl compounds in a selective straightforward pathway.

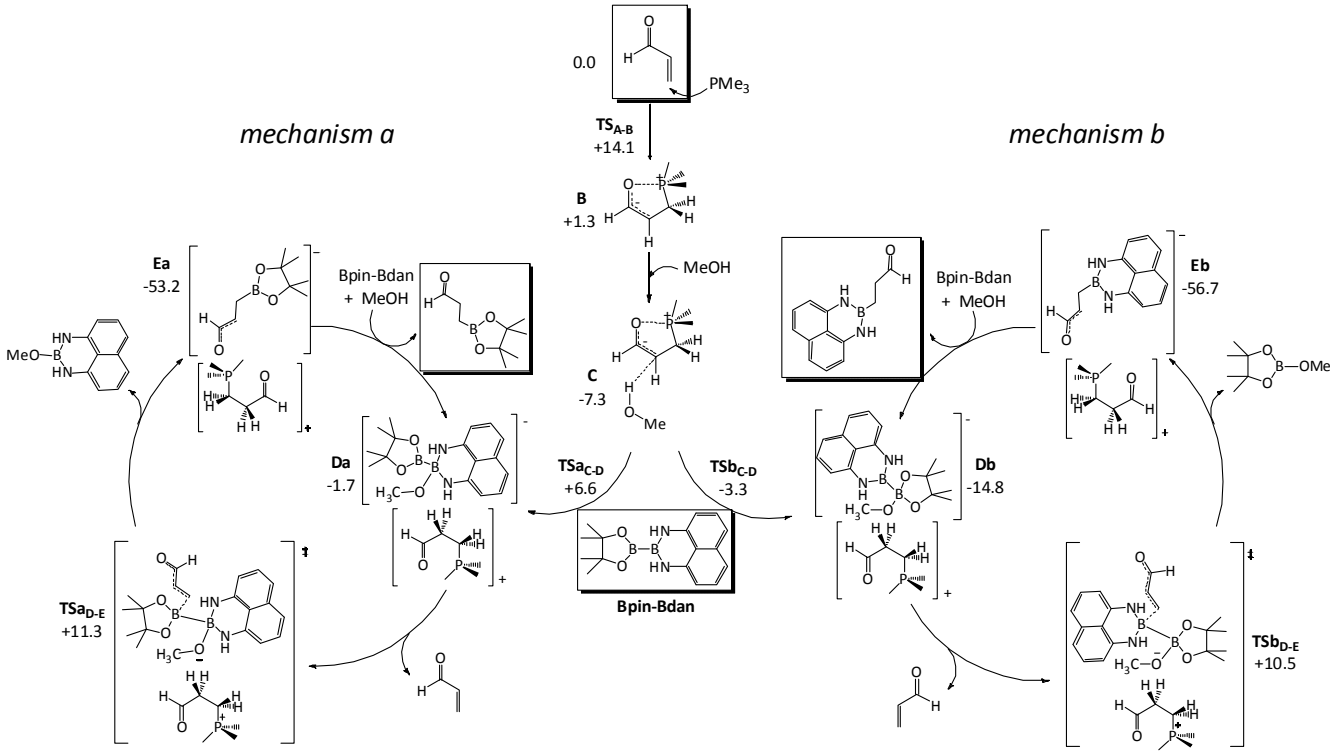


Figure 4. Suggested catalytic cycle for β-boration of acrylaldehyde with Bpin-Bdan diboron reagent in the presence of MeOH and PMe_3. Mechanism ***a*** depicts the Cβ-Bpin formation and mechanism ***b*** illustrates the Cβ-Bdan formation. Electronic energies in kcal.mol^{-1}.

Acknowledgements

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Keywords: Boration • Nucleophilic boron • DFT • diboron

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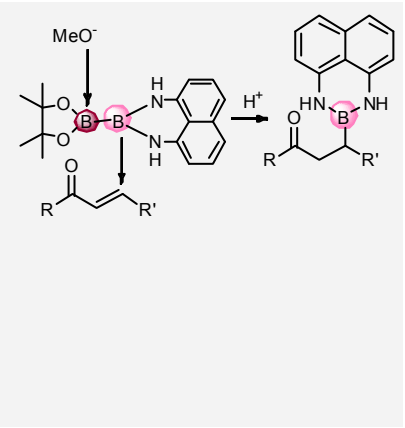
A Clear-Cut Example of Selective Bpin-Bdan Activation and Precise Bdan Transfer on Boron Conjugate Addition



The hypothesis of activating the non symmetrical Bpin-Bdan diboron reagent with an alkoxide unit, made us postulate a double possible adduct formation, MeO^-→Bpin-Bdan or MeO^-→Bdan-Bpin, but experimental and theoretical evidences confirmed the preference of MeO^-→Bpin interaction and therefore the selective formation of C-Bdan bond when reacting with activated C=C

Supporting information

A Clear-Cut Example of Selective Bpin-Bdan Activation and Precise Bdan Transfer on Boron Conjugate Addition

Jessica Cid, Jorge J. Carbó and Elena Fernández**

Universidad Rovira i Virgili, C/ Marcel·lí i Domingo s/n. 43005 Tarragona, Spain

j.carbo@urv.cat, mariaelena.fernandez@urv.cat

Contents

1. Intrumentation and chemicals

All reactions and manipulations were carried out under a nitrogen atmosphere by using Schlenk-type techniques. The solvents were distilled over dehydrating reagents and were deoxygenated before use. Bpin-Bdan was synthetized as previously reported[1] Bis(pinacolato)diboron was used as purchased from Allychem. Ligands PPh_3, PCy_3 and (R)-(+)-MeO-BIPHEP were used as purchased from STREM. Substrates, 4-hexen-3-one and 3-heptene-2-one were used as purchased from Alfa Aesar. Substrates, 3-nonen-2-one, trans-1-phenyl-2-buten-1-one, 2-cyclohexen-1-one, ethyl crotonate and tert-butyl crotonate were used as purchased from Sigma Aldrich.
All other materials were purchased directly from standard chemical suppliers and used without further purification, unless stated otherwise.

Deuterated chloroform ($CDCl_3$) was used as solvent for routine NMR measurements. NMR spectra were obtained on either a Varian Gemini 300 or a Varian Mercury 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane, references to the chemical shifts of residual solvent resonances. ^{11}B NMR chemical shifts are reported in ppm (δ) relative to $BF_3(CH_3)_2O$. Coupling constants (*J*) are given in Hz, and the multiplicity of the NMR signals is described as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m).
HPLC-TOF was equipped with chiral column Chiracel OD-H. Electron impact (EI) (70 Ev) and chemical ionization (CI) were recorded with a Kratos MS50 or a Finnigan MAT 95S spectrometer. Accurate mass determinations were carried out on a Kratos Concept IS spectrometer.

2. Experimental procedure for the organocatalytic β-boration of α,β-unsaturated compounds

2.1 General procedure for the β-boration of α,β-unsaturated carbonyl compounds

The phosphine, (0.015 mmol), sodium tert-butoxide (2.2 mg, 0.023 mmols) and Bpin-Bdan (81 mg, 0.275 mmol) were transferred into an oven-dried Schlenk tube under nitrogen. MeOH (2 mL) was added. The substrate (0.25 mmol) was added, and the reaction mixture was stirred at 70 ^{o}C oil bath temperature for 16 hours. The reaction mixture was cooled to room temperature. An aliquot of 0.2 mL was gently concentrated on a rotary evaporator at room temperature and analysed by ^{1}H-NMR to determine the conversion. The sample was combined with the rest of the reaction mixture, all the volatiles were removed in vacuum and the crude product was purified by column chromatography.

2.2 General procedure for the chiral β-boration of α,β-unsaturated carbonyl compounds

The chiral phosphine, (R)-(+)-MeO-BIPHEP (8.7 mg, 0.015 mmol), cesium carbonate (7.3 mg, 0.023 mmols) and Bpin-Bdan (81 mg, 0.275 mmol) were transferred into an oven-dried Schlenk tube under nitrogen. THF (2 mL) and MeOH (51 μl, 1.25mmol) were added. The mixture was stirred 10 minutes at room temperature to dissolve the phosphine and the borane reagent completely. The substrate (0.25 mmol) was added, and the reaction mixture was stirred at 70 ^{o}C oil bath temperature for 16 hours. The reaction mixture was cooled to room temperature. An aliquot of 0.2 mL was gently concentrated on a rotary esvaporator at room temperature and analysed by ^{1}H-NMR to determine the conversion. The sample was combined with the rest of the reaction mixture, all the volatiles were removed in vacuum and the crude product was purified by column chromatography.

3. Characterization of the pure organoboron compounds

3.1 5-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)hexan-3-one (5): Flash column chromatography (petroleum ether/EtOAc = 4:1) yielded **5** (74 % yield) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.09 (dd, *J*=8.0, 7.6 Hz, 2H), 7.00 (dd, *J*=8, 1.2 Hz, 2H), 6.30 (dd, *J*=7.2, 1.2 Hz, 2H), 5.74 (br s, 2H), 2.57 (d, *J*=6.8 Hz, 1H), 2.47 (dd, *J*=16, 7.2 Hz, 1H), 2.43 (q, *J*=7.6 Hz, 2H), 1.57 (m, 1H), 1.06 (t, *J*=7.2 Hz, 3H), 1.04 (d, *J*=7.2 Hz, 3H); ^{13}C {^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 212.6, 141.4, 136.5, 127.8, 119.9, 117.7, 105.9, 47.1, 36.5, 16.6, 8.1; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 32.5; MS (70 eV) *m/z* : 267.16 [M^{+}]

3.2 4-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)heptan-2-one (6): Flash column chromatography (petroleum ether/EtOAc = 4:1) yielded **6** (71 % yield) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.09 (dd, *J*=8.4, 7.2 Hz, 2H), 7.00 (dd, *J*=7.2, 1.2 Hz, 2H), 6.31 (dd, *J*=6.8, 1.2 Hz, 2H), 5.73 (br s, 2H), 2.57 (d, *J*=6.8 Hz, 2H), 2.15 (s, 3H), 1.40-1.24 (m, 5H), 0.91 (t, *J*=7.2 Hz, 3H); ^{13}C {^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 209.6, 141.3, 136.5, 127.7, 119.8, 117.6, 105.8, 46.6, 34.2, 30.4, 25.3, 22.4, 14.5; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 32.6 ; MS (70 eV) *m/z* : 281.18 [M^+].

3.3 4-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)nonan-2-one (7): Flash column chromatography (petroleum ether/EtOAc = 8:1) yielded **7** (79 % yield) as a yellow oil.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.08 (dd, *J*=7.6, 7.2 Hz, 2H), 6.99 (d, *J*=8 Hz, 2H), 6.31 (d, *J*=7.6 Hz, 2H), 5.72 (br s, 2H), 2.57 (d, *J*=6.4 Hz, 2H), 2.15 (s, 3H), 1.45-1.27 (m, 9H), 0.87 (t, *J*=6.4 Hz, 3H); ^{13}C {^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 209.6, 141.3, 136.4, 127.7, 119.8, 117.6, 105.8, 46.6, 32.2, 31.9, 30.4, 28.9, 22.7, 14,3; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 32.5; MS (70 eV) *m/z* : 309.21 [M^+].

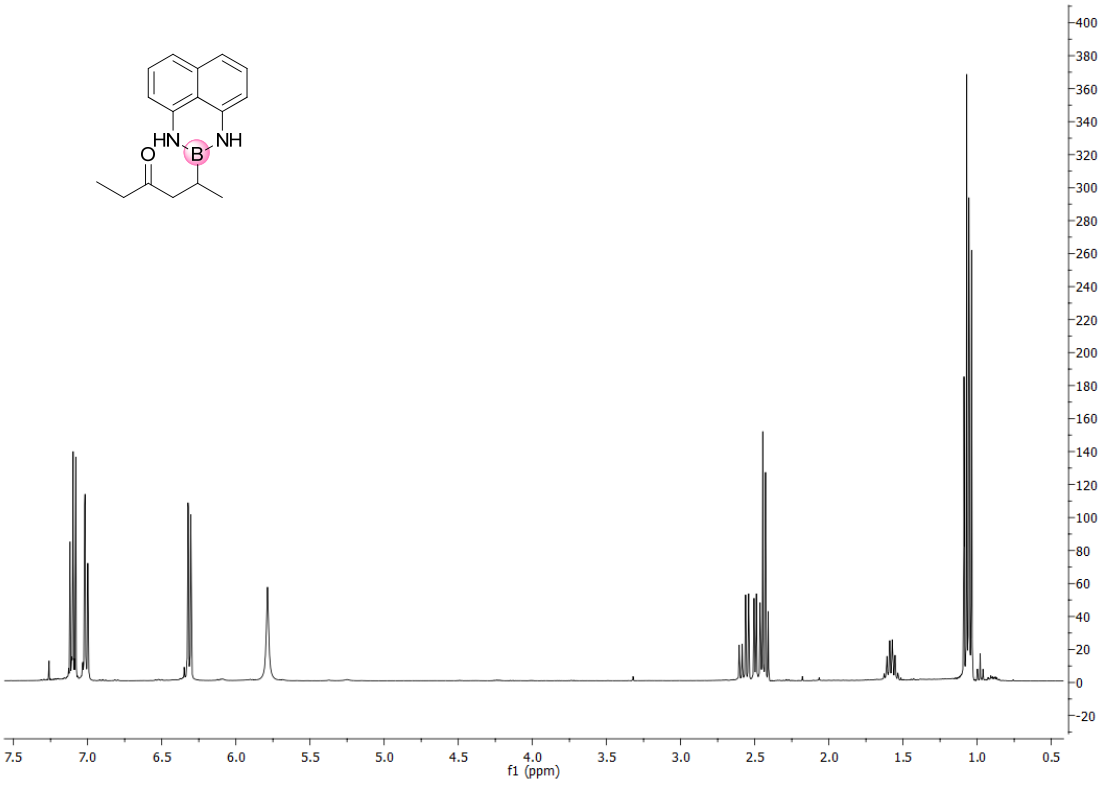
3.4 3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)cyclohexanone (8): Flash column chromatography (petroleum ether/EtOAc = 4:1) yielded **8** (37 % yield) as a yellow oil.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.08 (dd, *J*=8.4, 7.2 Hz, 2H), 6.99 (d, *J*=8 Hz, 2H), 6.30 (d, *J*=7.2 Hz, 2H), 5.68 (br s, 2H), 2.44-2.24 (m, 4H), 2.11-2.06 (m, 1H), 1.92-1.87 (m, 1H), 1.80-1.76 (m, 1H), 1.64-1.59 8m, 1H), 1.50-1.46 (m, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 212.6, 140.8, 127.7, 119.8, 117.9, 106.0, 43.7, 42.1, 28.6, 27.6; ^{11}B NMR (128.3 MHz, $CDCl_3$) 31.7 δ ; MS (70 eV) *m/z* : 265.15 [M^+].

3.5 3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-1-phenylbutan-1-one (9): Flash column chromatography (petroleum ether/EtOAc = 8:1) yielded **9** (61 % yield) as a yellow oil.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, *J*=7.2 Hz, 2H), 7.56 (t, *J*=7.6 Hz, 1H), 7.46 (t, *J*=7.6 Hz, 2H), 7.08 (dd, *J*=8.4, 7.2 Hz, 2H), 6.98 (d, *J*=8.4 Hz, 2H), 6.31 (d, *J*=7.2 Hz, 2H), 5.80 (br s, 2H), 3.16 (dd, *J*=17.6, 8 Hz, 1H), 3.08 (dd, *J*=17.6, 6 Hz, 1H), 1.76 (m, 1H), ,1.14 (d, *J*=7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 200.7, 141.3, 137.1, 136.5, 133.3, 128.8, 128.2, 127.7, 119.8, 117.6, 105.9, 43.4, 25.3, 16.8; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 32.3; MS (70 eV) *m/z* : 275.18 [M^+].

3.6 ethyl 3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)butanoate (10): Flash column chromatography (petroleum ether/EtOAc = 4:1) yielded **10** (72 % yield) as a yellow oil.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.10 (dd, *J*=8.0, 7.6 Hz, 2H), 7.01 (dd, *J*=8, 1.2 Hz, 2H), 6.31 (dd, *J*=7.6, 1.2 Hz, 2H), 5.80 (br s, 2H), 4.15 (q, J=7.2 Hz, 2H), 2.46 (dd, *J*=15.6, 7.6 Hz, 1H), 2.37 (dd, *J*=15.6, 6.8 Hz, 1H), 1.57 (m, 1H), 1.26 (t, *J*=7.2 Hz, 3H), 1.10 (d, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 174.1, 141.2, 136.4, 127.7, 119.8, 117.7, 105.9, 60.7, 38.7, 25.3, 16.5, 14.4 ; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 32.6; MS (70 eV) *m/z* : 283.16 [M^+].

3.7 tert-butyl 3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)butanoate (11): Flash column chromatography (petroleum ether/EtOAc = 4:1) yielded **11** (64 % yield) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.10 (dd, *J*=8.0, 7.2 Hz, 2H), 7.01 (d, *J*=8 Hz, 2H), 6.31 (d, *J*=7.6 Hz, 2H), 5.80 (br s, 2H), 2.37 (dd, *J*=15.6, 8 Hz, 1H), 2.30 (dd, *J*=15.6, 7.2 Hz, 1H), 1.57 (m, 1H), 1.46 (s, 9H), 1.09 (d, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 173.5, 141.3, 136.4, 127.7, 119.8, 117.6, 105.8, 80.7, 39.9, 28.3, 16.4; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 35.5; MS (70 eV) *m/z* : 293.19 [M^+].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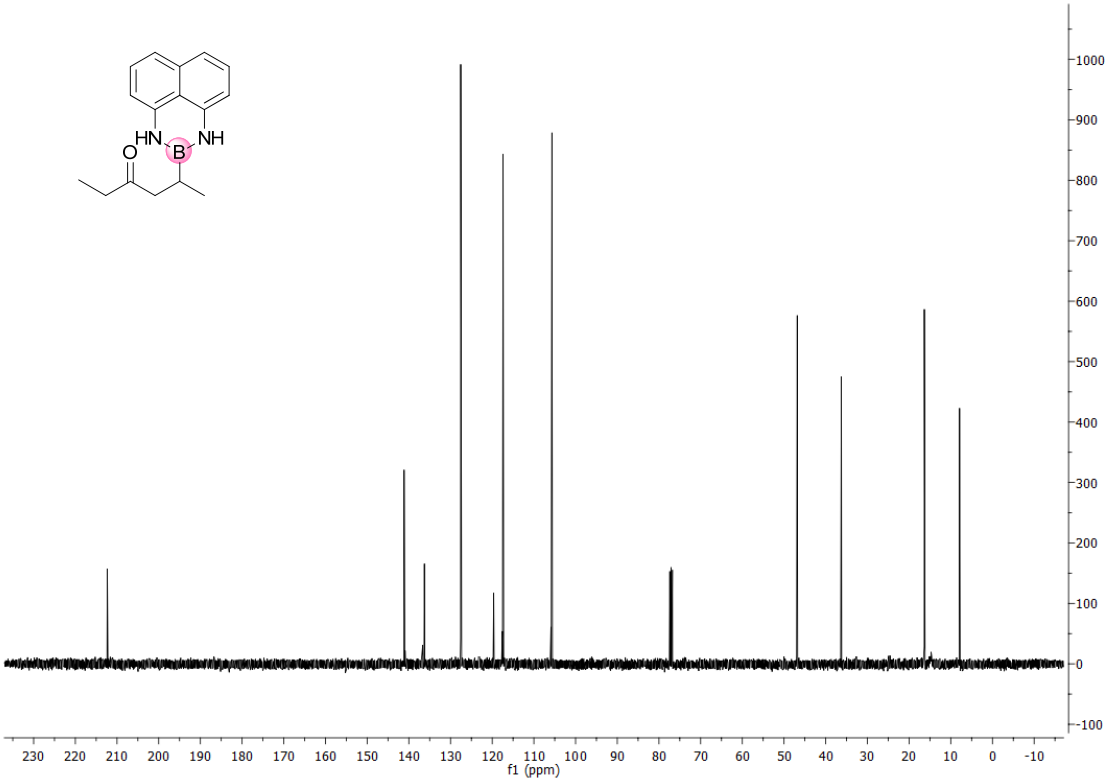
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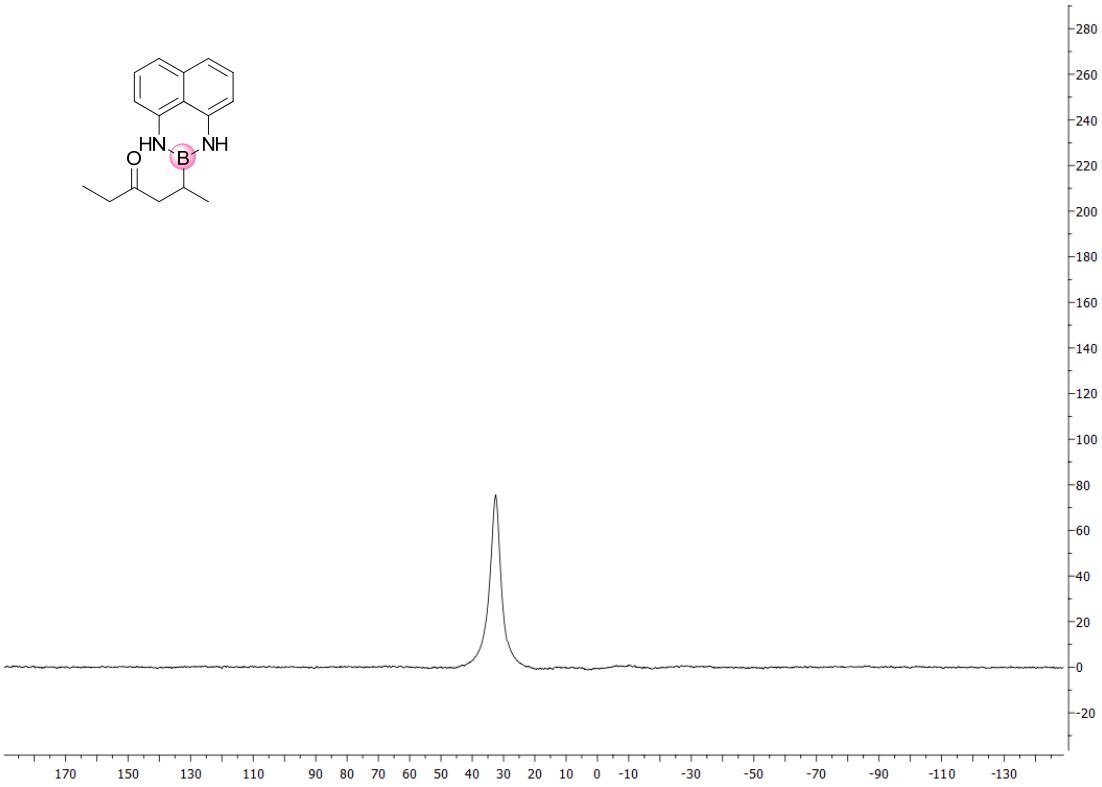
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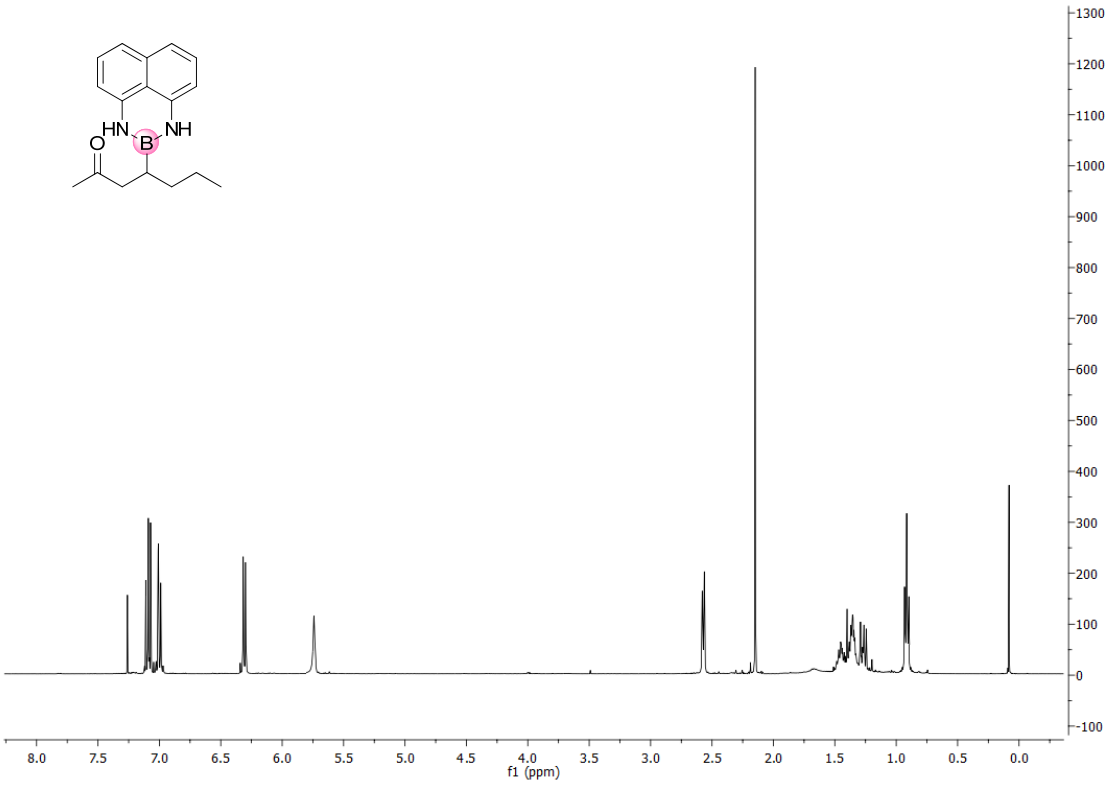
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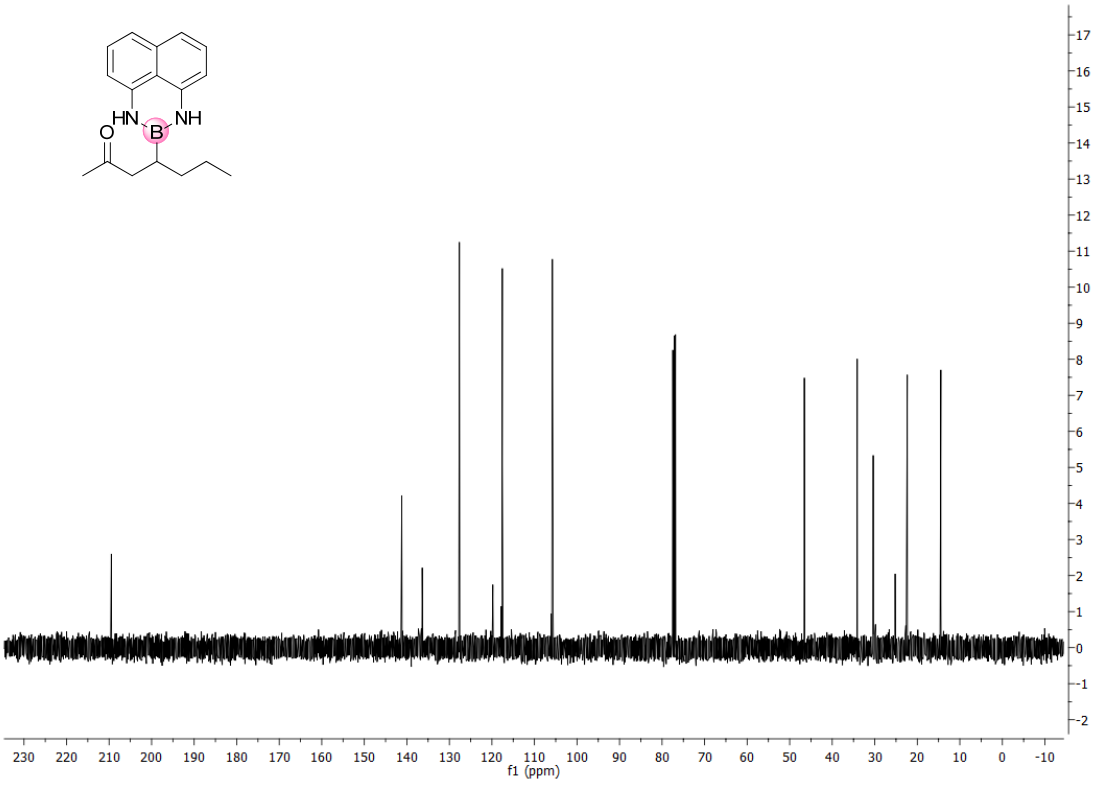
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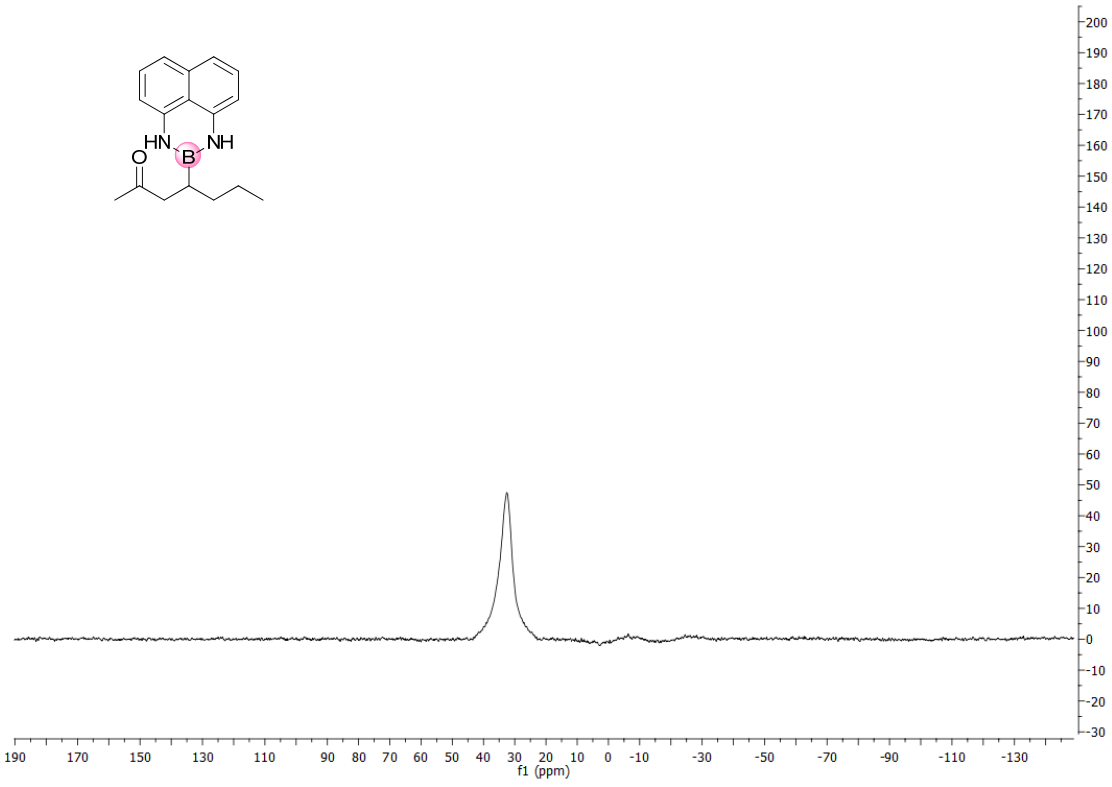
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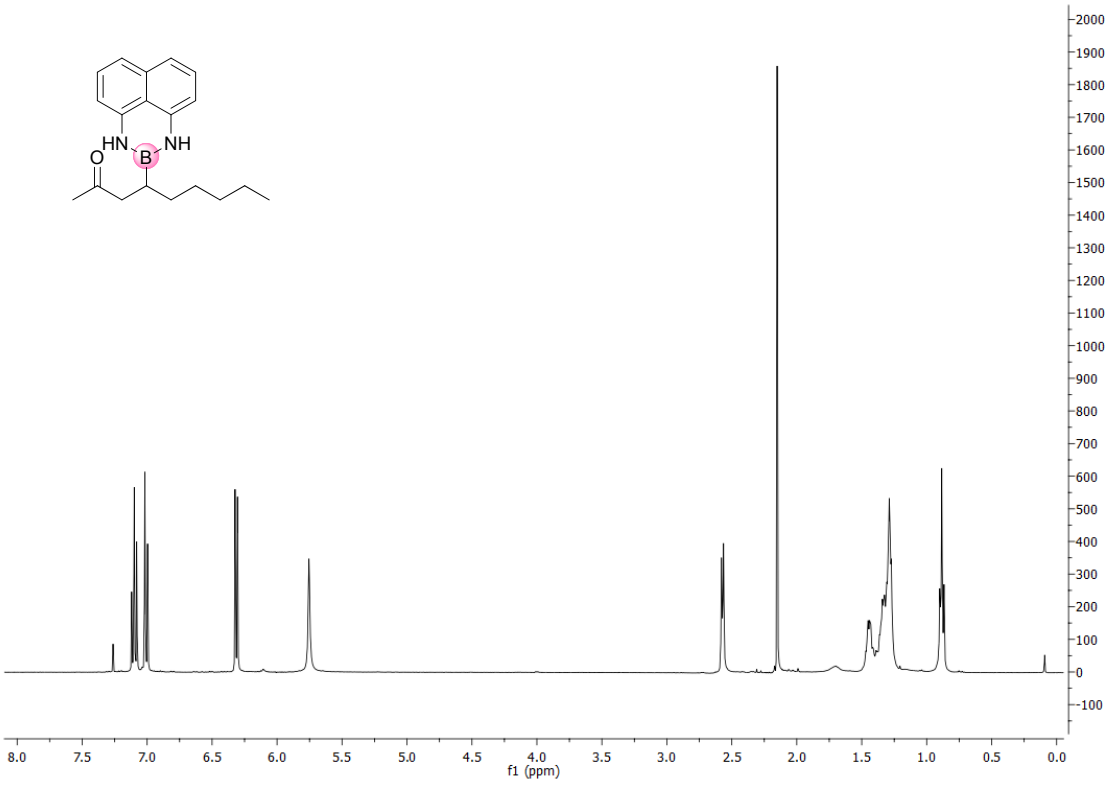
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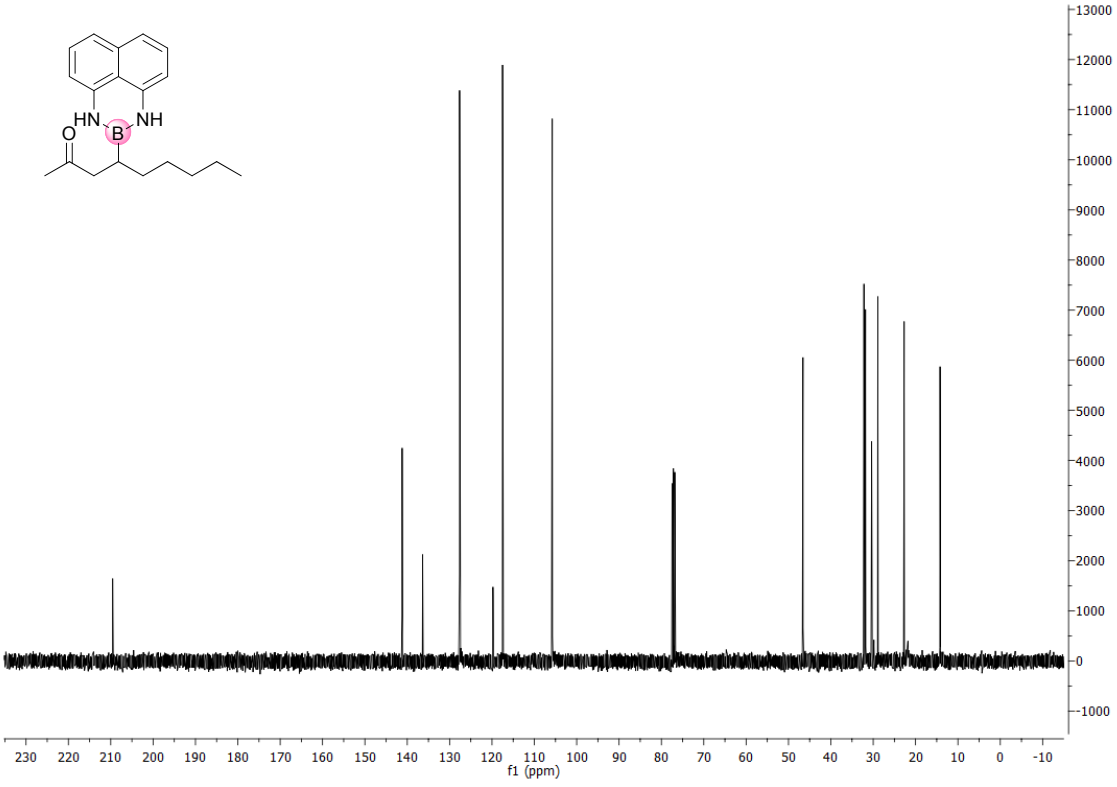
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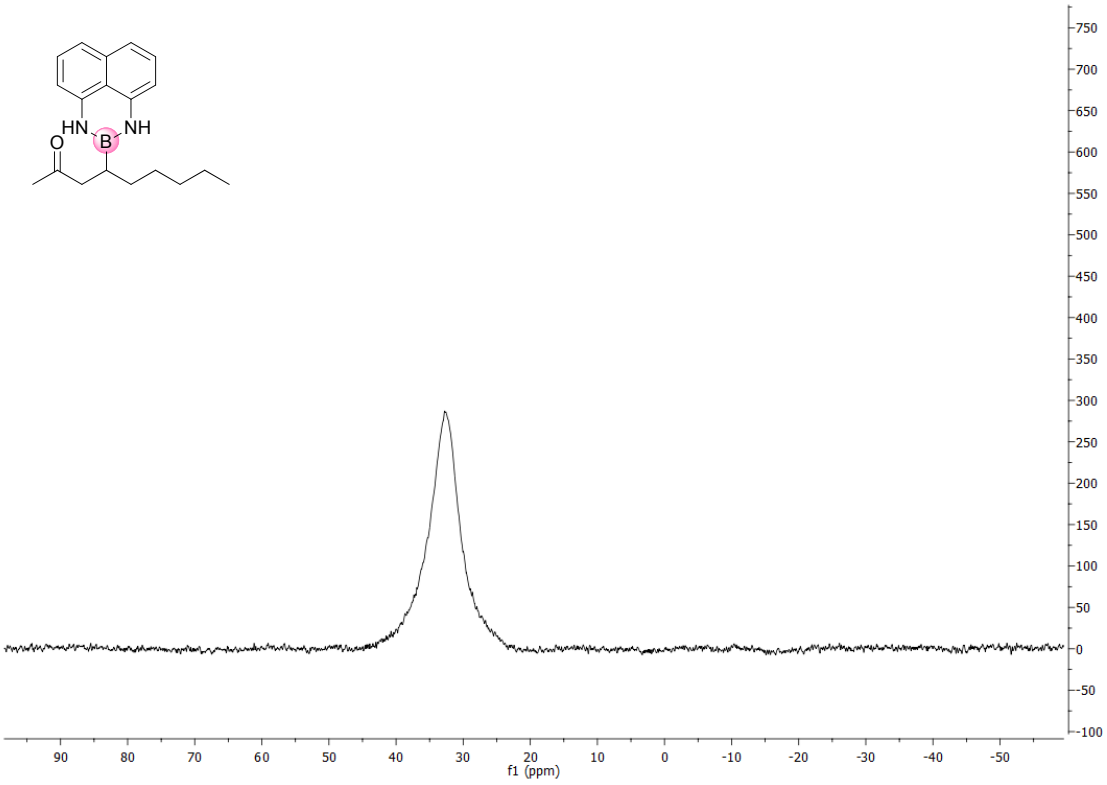
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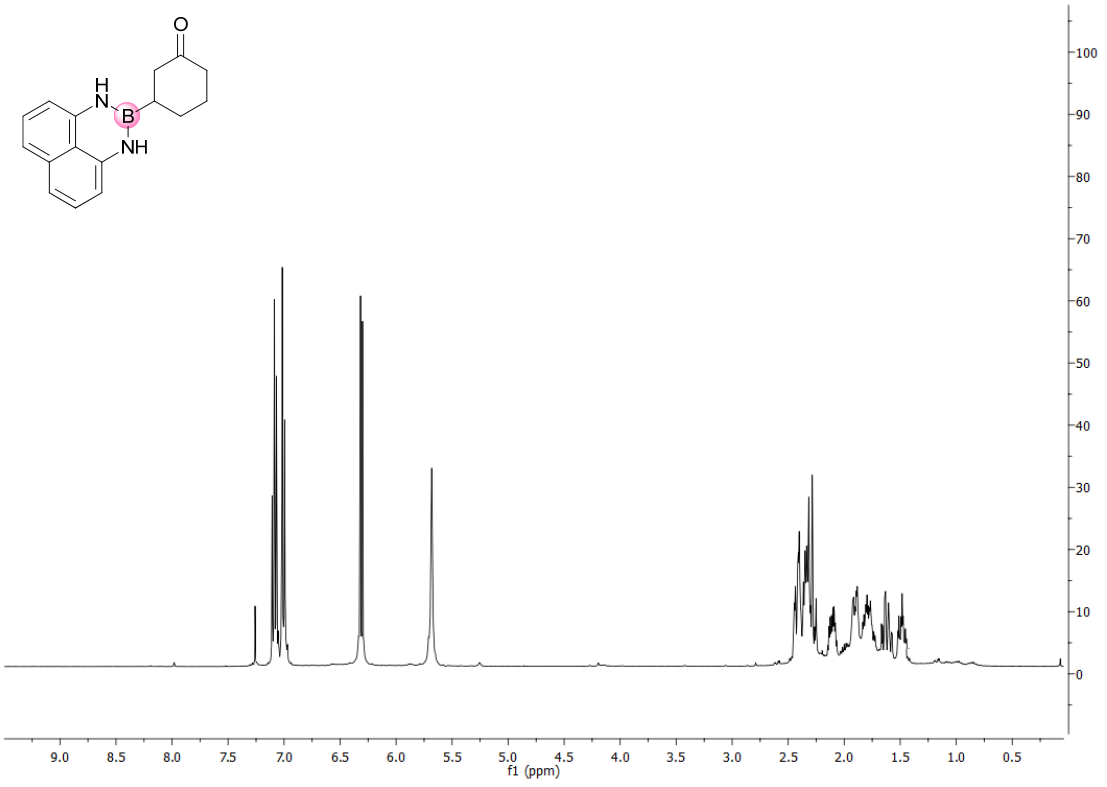
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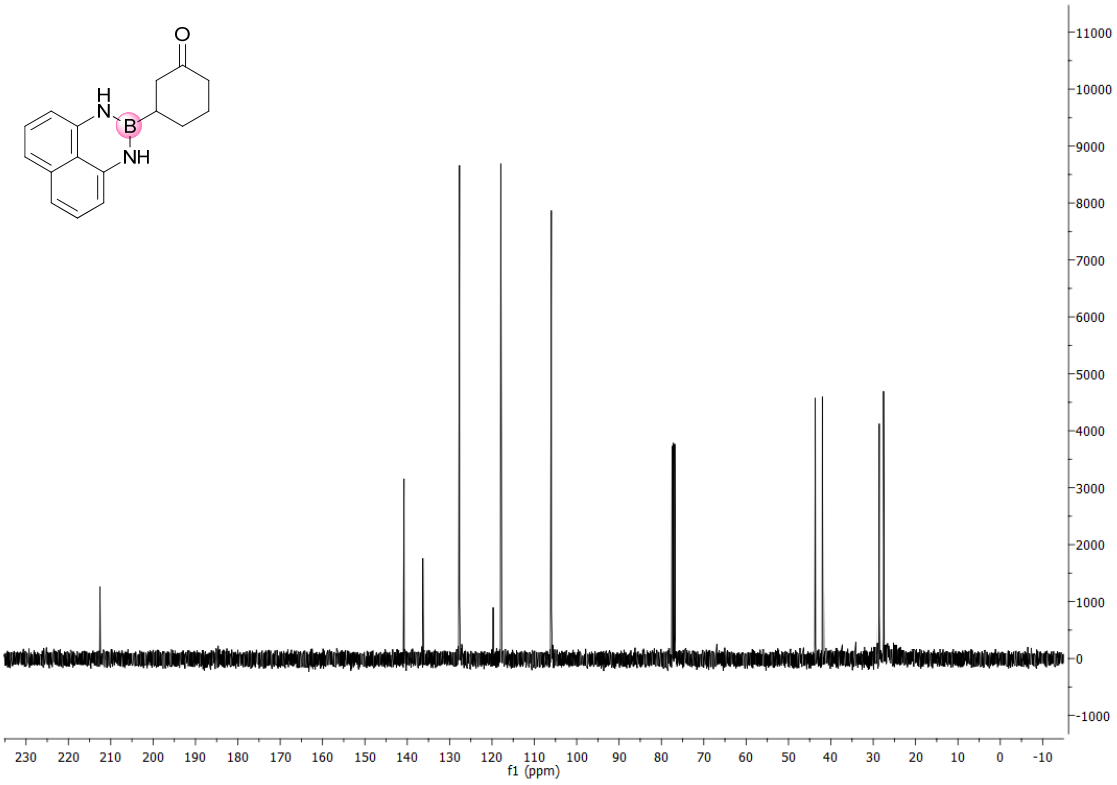
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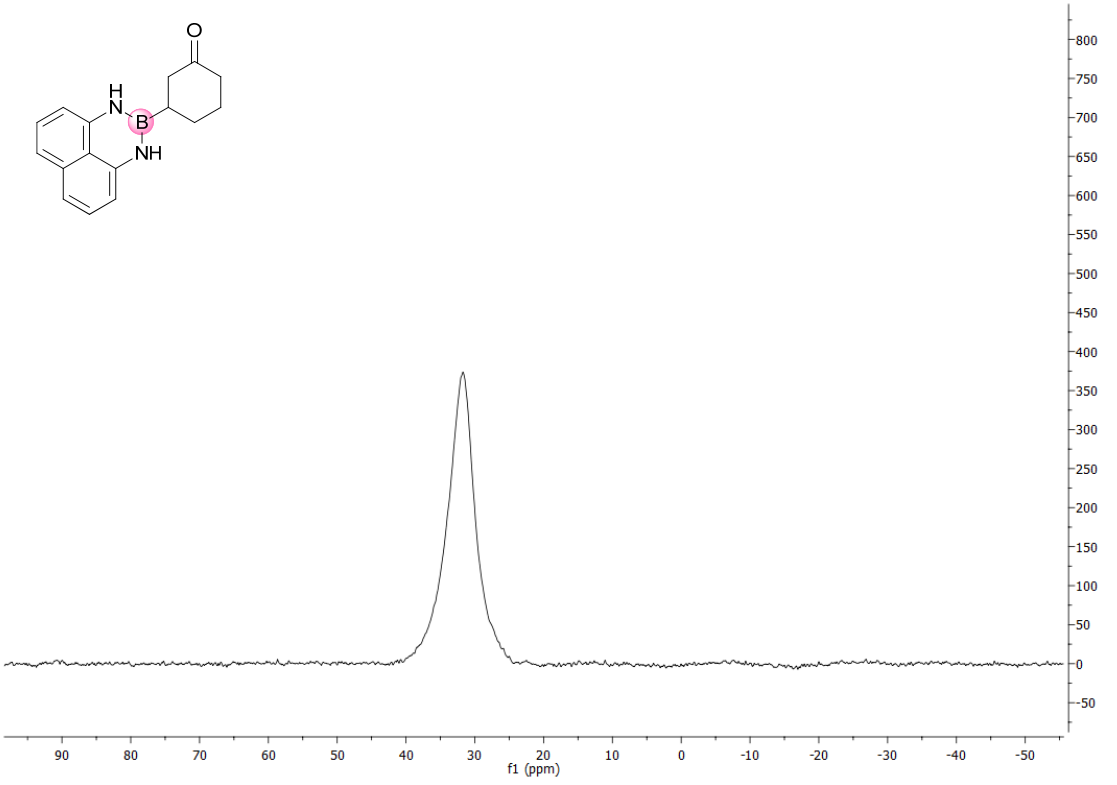
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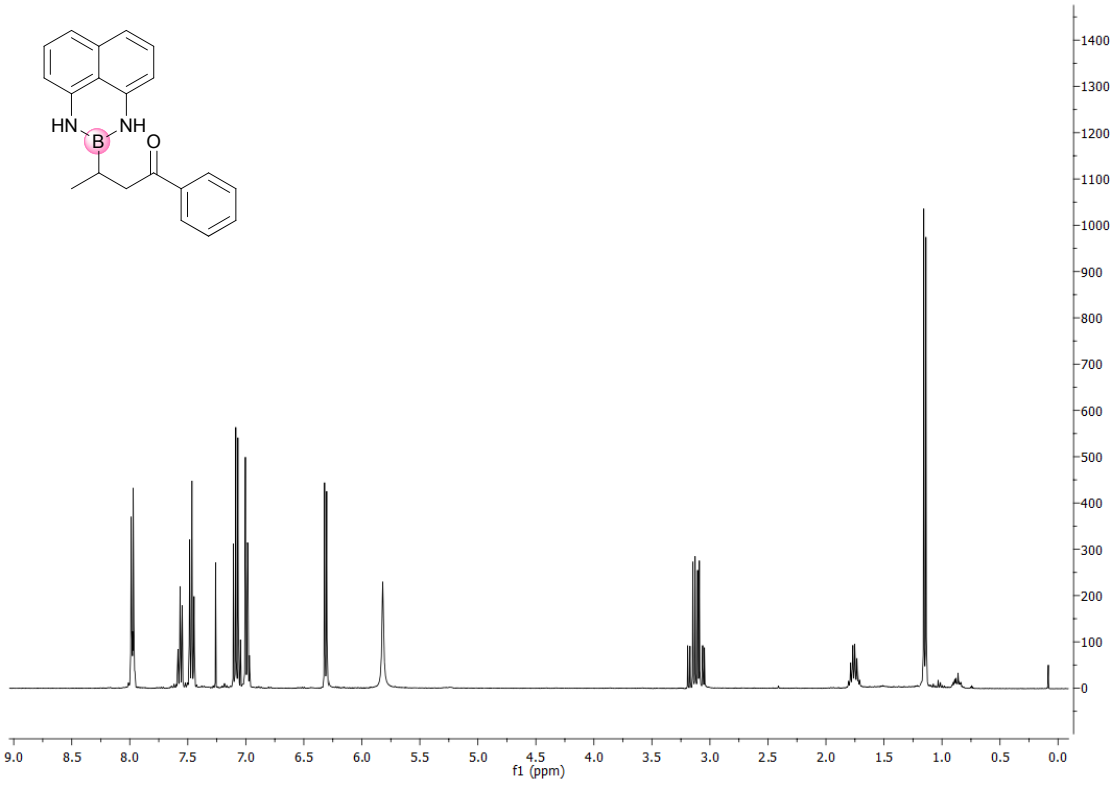
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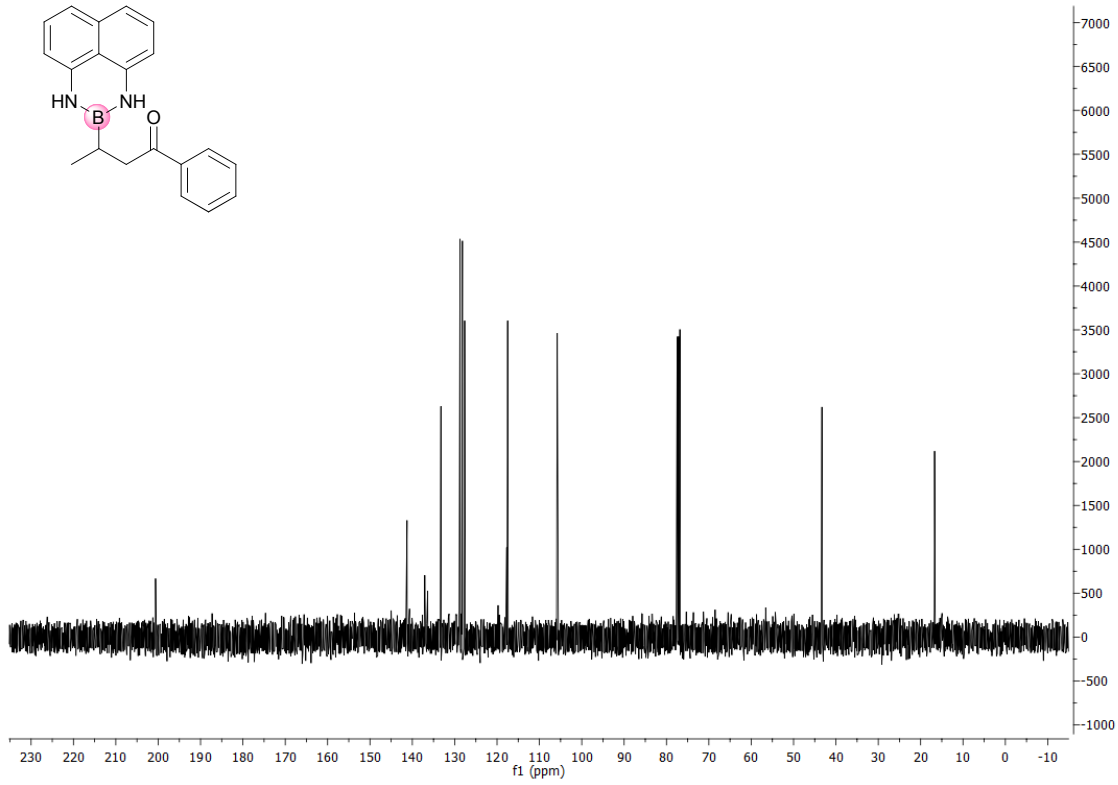
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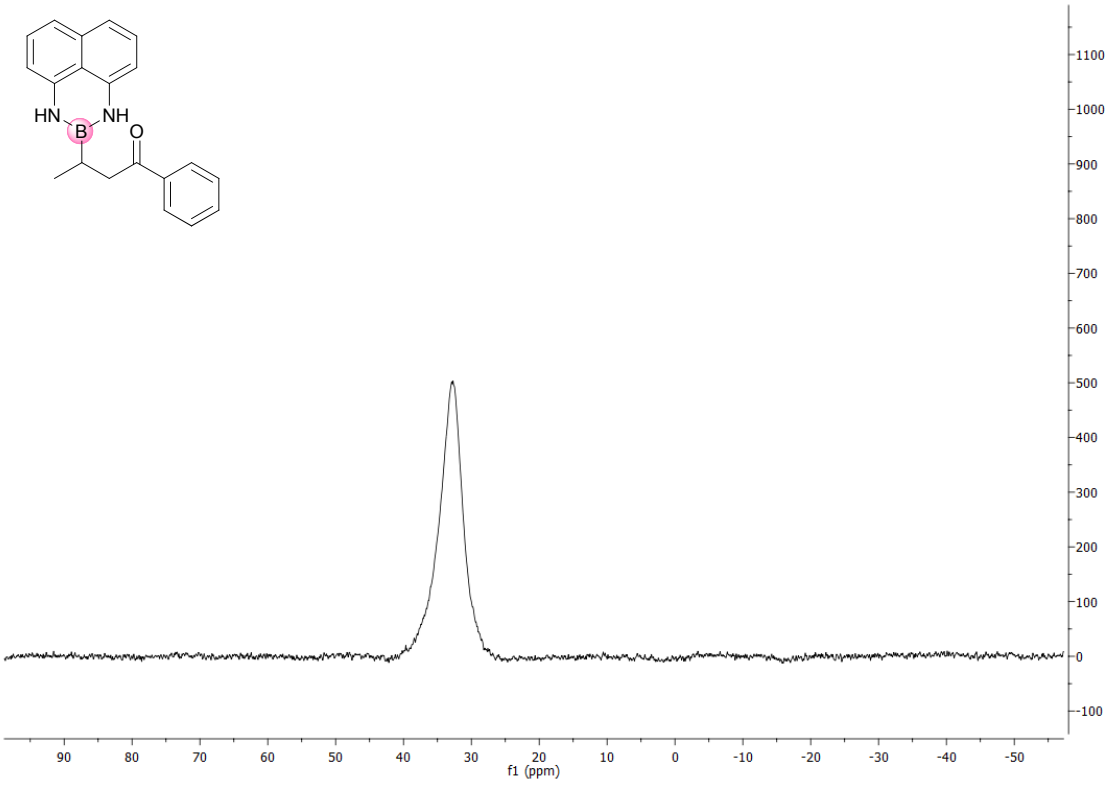
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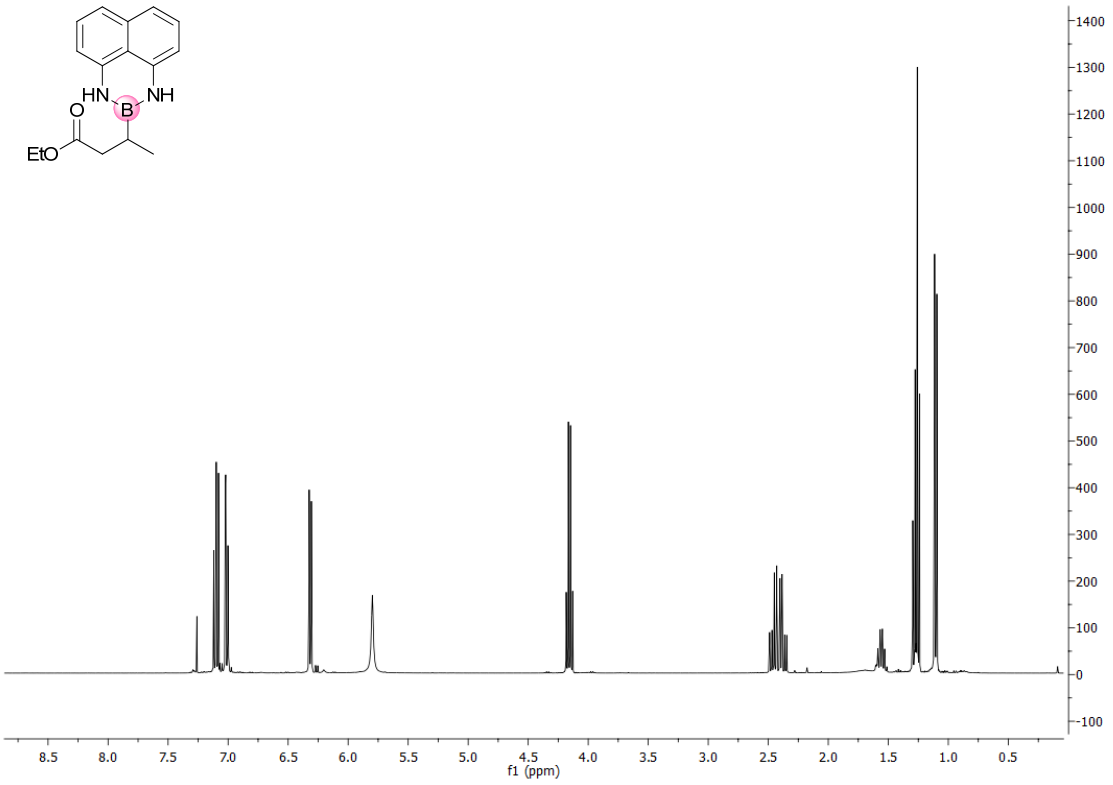
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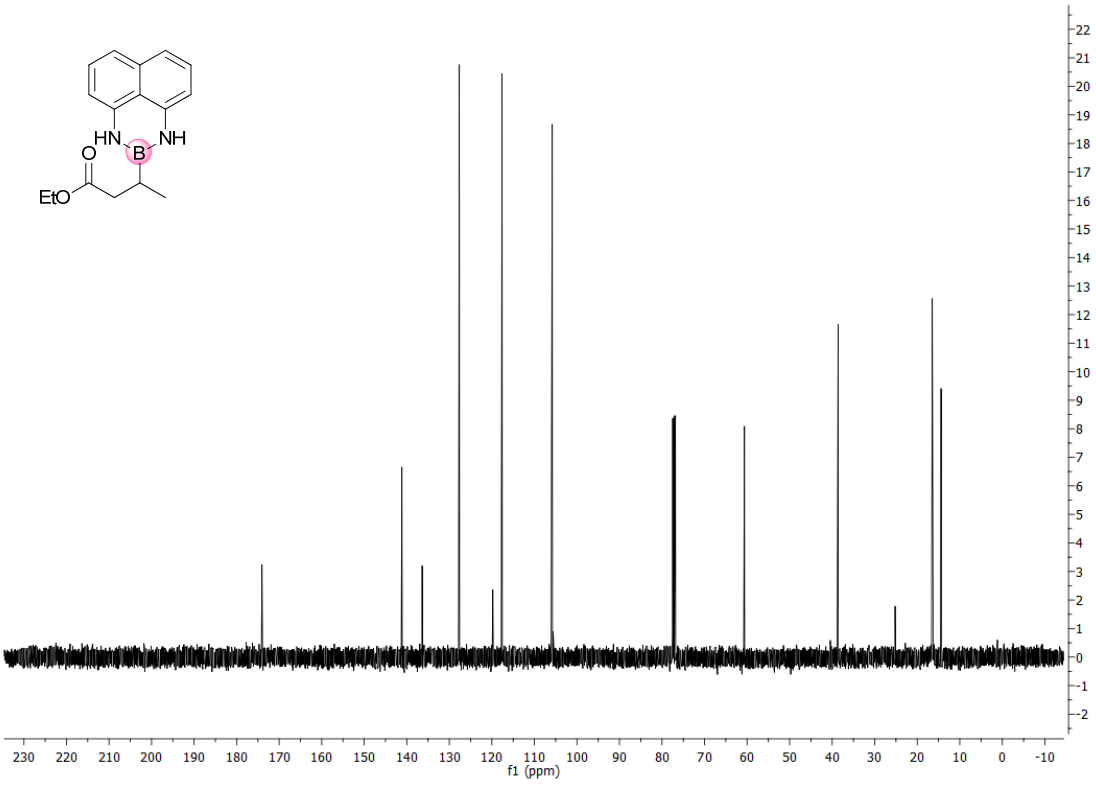
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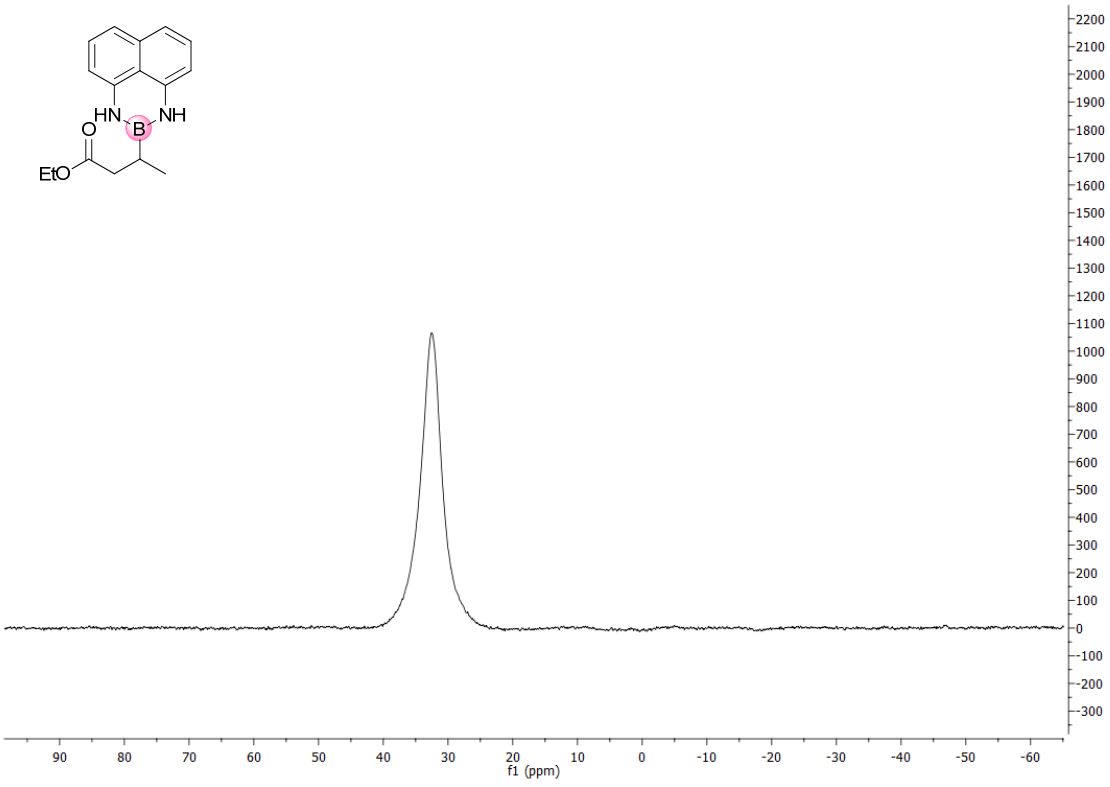
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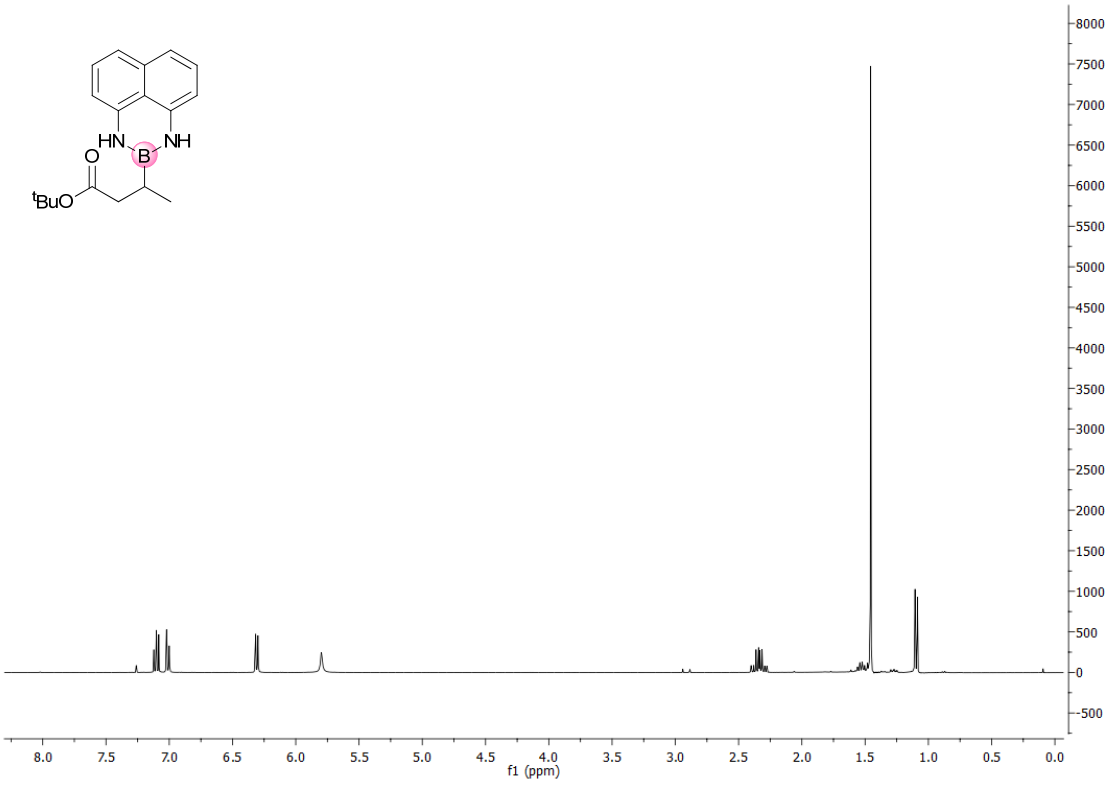
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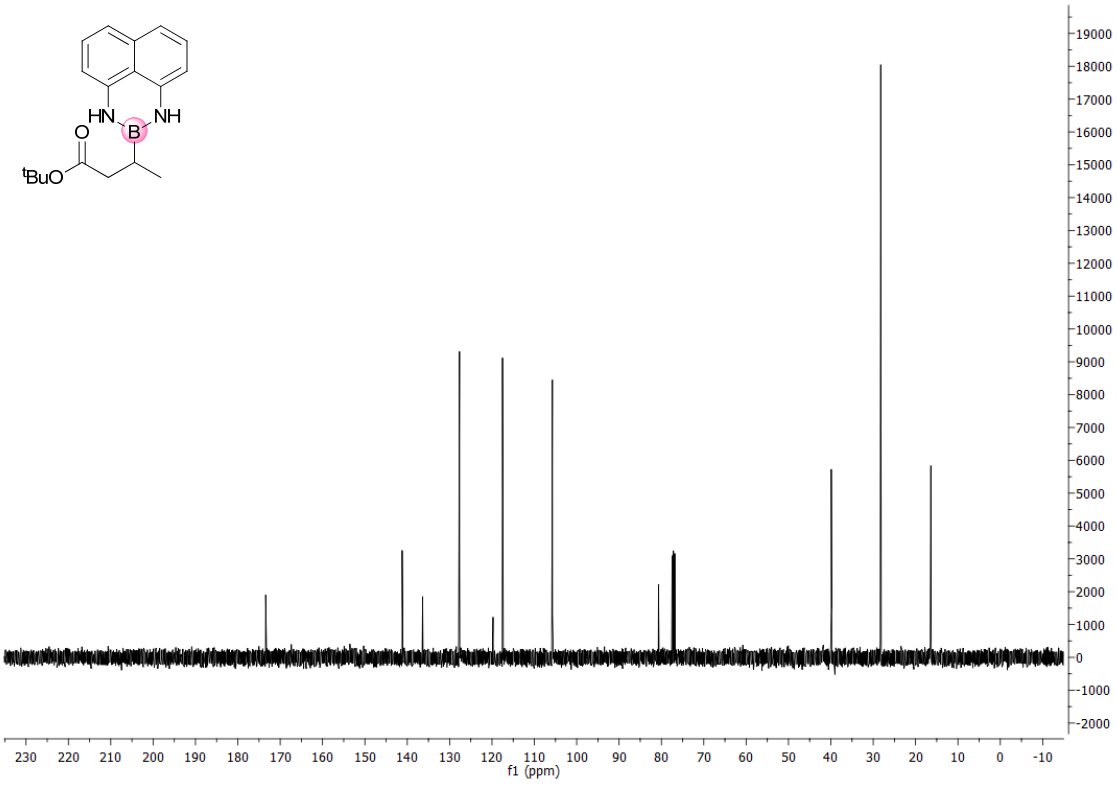
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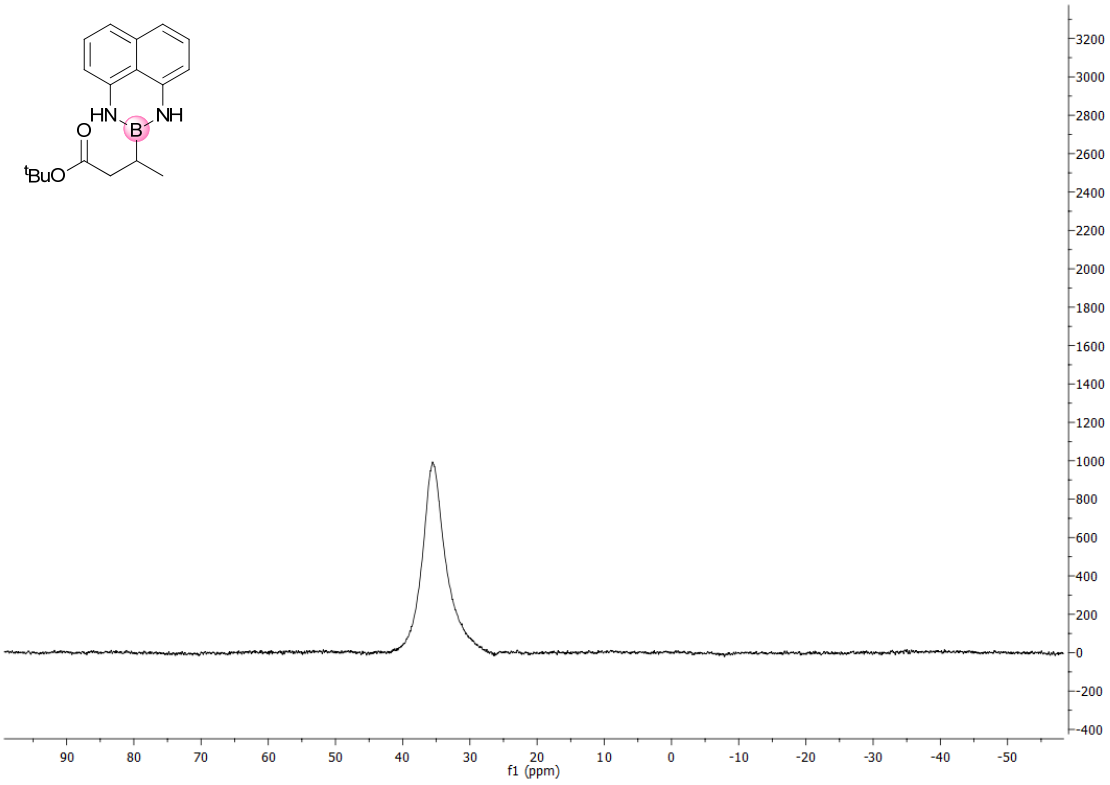
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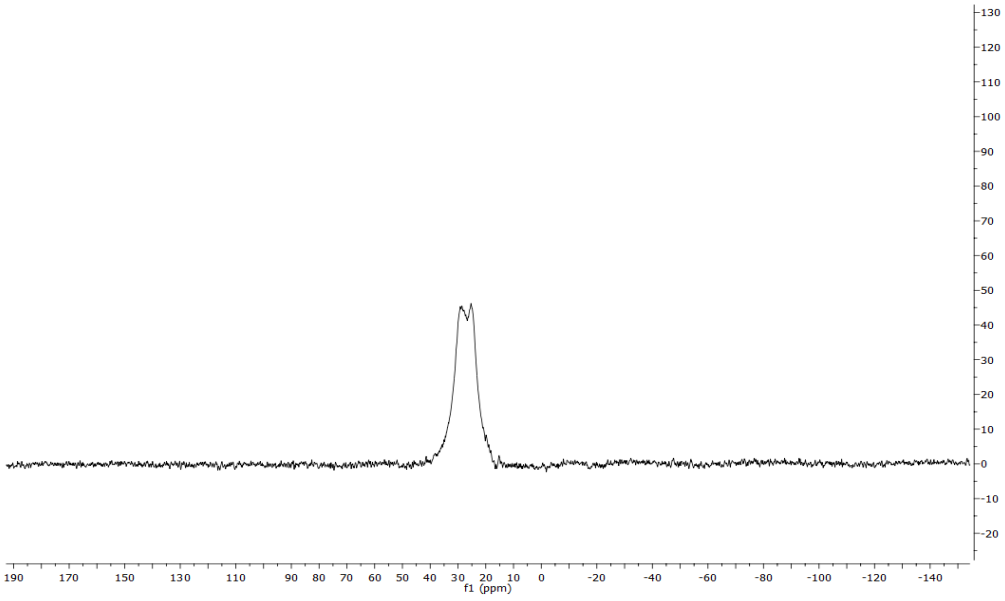
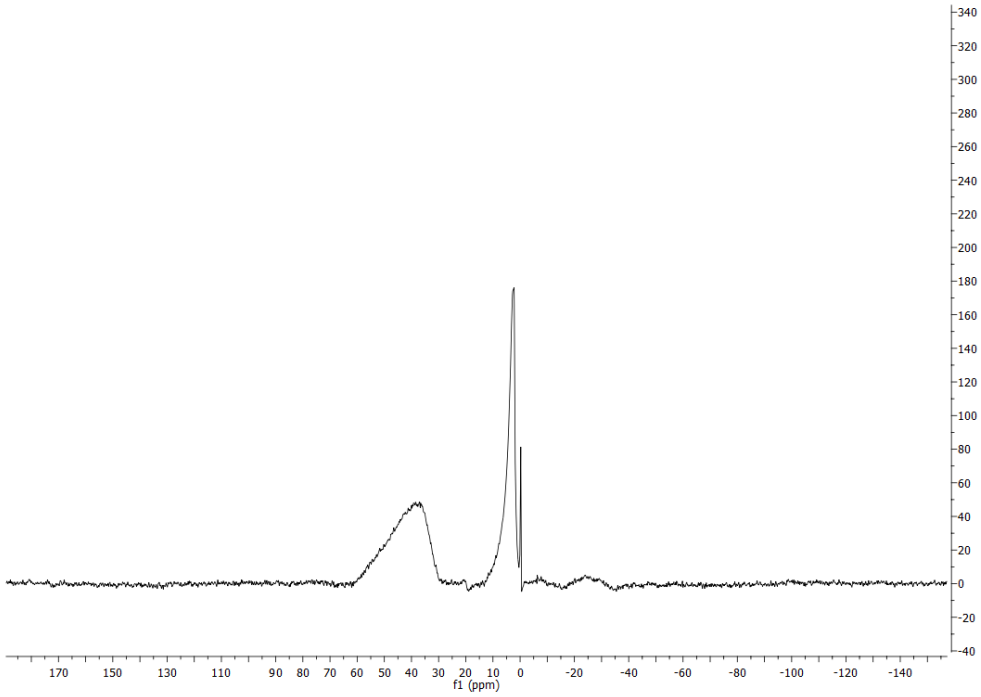
4. NMR spectroscopic study

^{11}B NMR of BpinBdan with MeOH as a solvent.

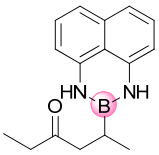


^{11}B NMR of BpinBdan with MeOH as a solvent with 1 eq. of NaO^{t}Bu.



5. Analysis of the enantiomeric excess of boronate esters (HPLC-TOF).

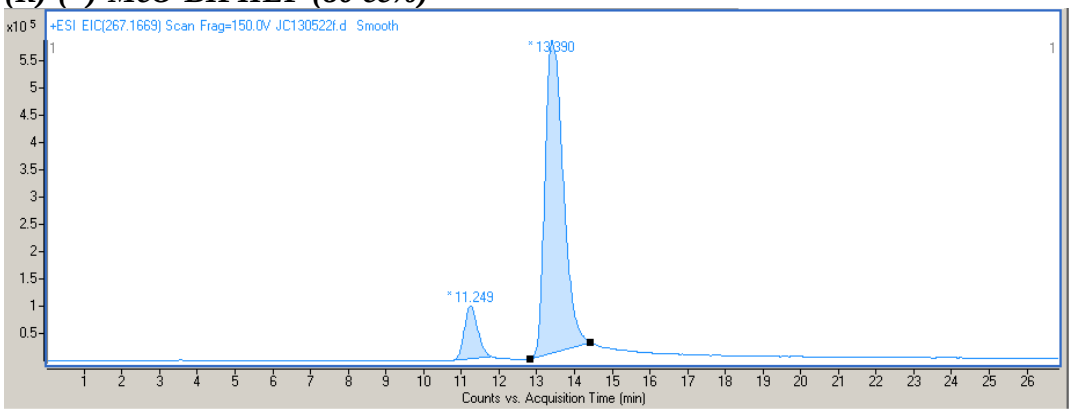
The racemic mixture of **boronate esters** obtained from the β-boration of 4-hexen-3-one were analyzed by chiral HPLC-TOF to optimize the separation of the enantiomers, and to determine their retention times. The enantiomeric excesses of the products obtained in the asymmetric borylation were also analysed by HPLC-TOF.

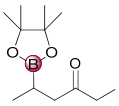


5-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)hexan-3-one (5)

Conditions: OD-H column, 25 °C, flow = 1 ml/min, hexane/isopropanol = 80/20 (v/v).

(R)-(+)-MeO-BIPHEP (80 ee%)

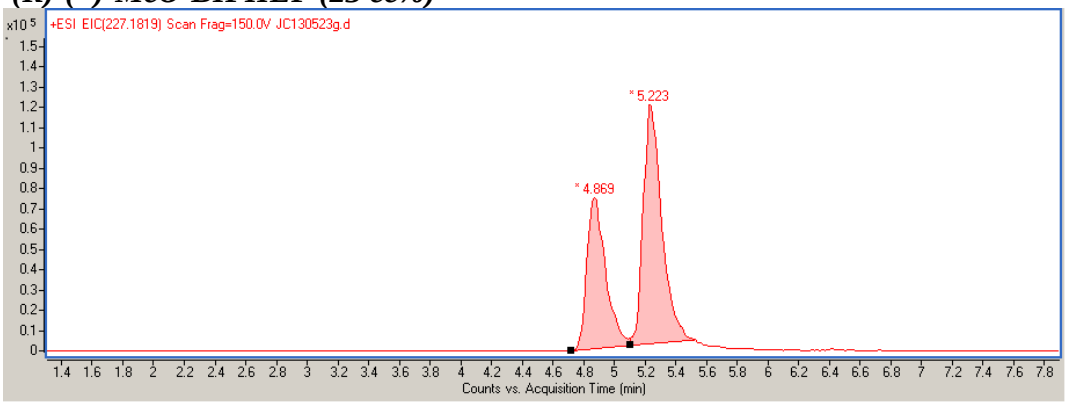




5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-3-one

Conditions: OD-H column, 25 °C, flow = 1 ml/min, hexane/isopropanol = 99.9/0.5 (v/v).

(R)-(+)-MeO-BIPHEP (23 ee%)



6. Computational details

All calculations were performed using the Gaussian09 series of programs.[2] Calculations were performed within the framework of density functional theory (DFT)[3] using the B3LYP functional.[4] All the atoms were represented by means of the 6-31G(d,p) basis set.[5] All geometry optimizations were full, with no restrictions. All stationary points located in the potential energy hypersurface were characterized as minima or transition states by vibrational analysis. Transition states had one and only one imaginary frequency, whose normal mode corresponded to the expected motion. The bonding situation of the molecules as well as the fragment charges, has been analyzed using the NBO method.[6]

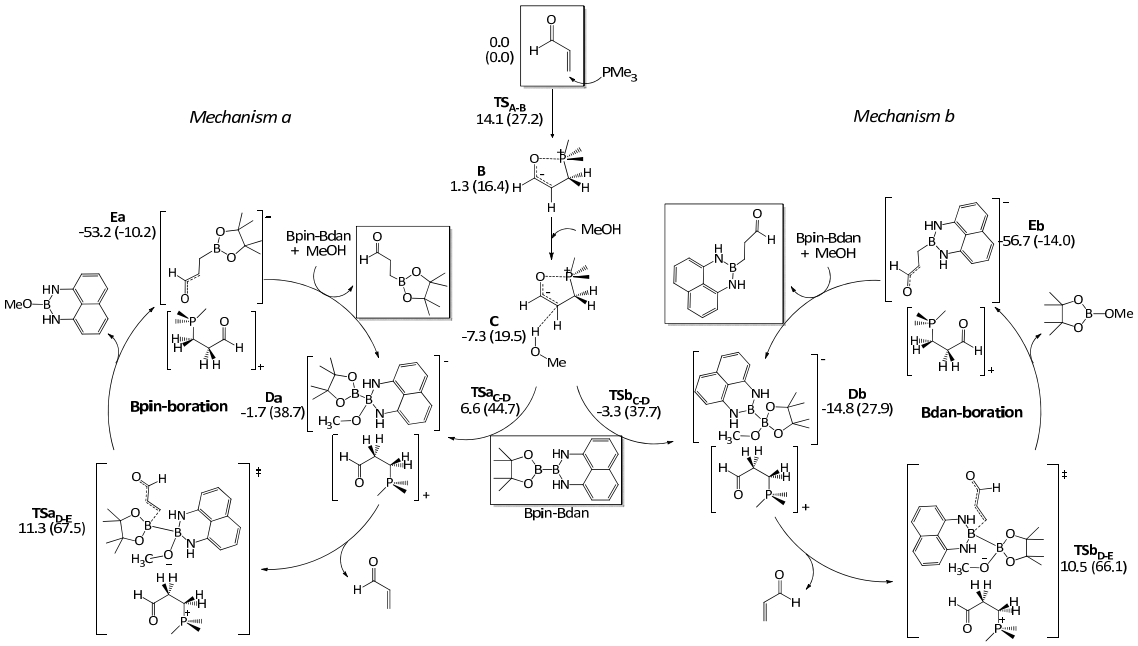
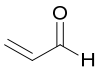


Figure S1. Suggested catalytic cycle for the β-boration of acrylaldehyde with Bpin-Bdan diboron reagent in the presence of MeOH an PMe_3. *Mechanism a* depicts Cβ-Bpin formation and *mechanism b* illustrates the Cβ-Bdan formation. Electronic energies and Gibbs free energies (in parenthesis) in kcal.mol^{-1}.

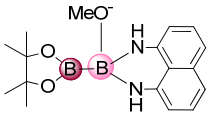
In the main text we discussed the energy profile using the values of electronic energies. The vibrational analysis gave also access to Gibbs free energies that are collected in Figure S1 (in parenthesis). As previously found,[7] we must note that the assembly of four molecular entities implies an entropic cost, which is apparently overestimated by calculations (ΔG values in Figure S1). For example, note the exaggerated accumulated value for **TS_{D-E}**. Solvent effects introduced through continuous solvent models does not take into account the entropy gain/loss due to solvent reorganization, a component that can partly compensate the entropy loss of merging two species. Formation of the final β-borated product largely overcomes the costs of the formation of these species.

7. Geometries

Figure 2



C	1.208967	1.292384	0.000000
H	2.114629	0.689122	0.000000
H	1.341208	2.369572	0.000000
C	0.000000	0.719599	0.000000
H	-0.919733	1.299533	0.000000
C	-0.147272	-0.748515	0.000000
H	0.815856	-1.309022	0.000000
O	-1.215266	-1.328752	0.000000



C	-4.652484	-2.004599	-0.829784
C	-5.162689	-0.741235	-0.606093
C	-4.301162	0.319075	-0.211518
C	-2.903335	0.048740	-0.053314
C	-2.398528	-1.272858	-0.288741
C	-3.282892	-2.282099	-0.675572
H	-5.834442	1.846812	-0.085534
H	-5.320268	-2.809209	-1.132078
H	-6.224125	-0.540019	-0.727632
C	-4.774246	1.637411	0.032918
C	-2.010680	1.100110	0.341871
H	-2.900291	-3.284039	-0.854985
C	-2.521556	2.379425	0.572205
C	-3.895261	2.631980	0.414917
H	-1.844344	3.174904	0.872339
H	-4.268595	3.637605	0.599662
N	-1.045522	-1.496137	-0.118603
N	-0.674619	0.793004	0.478426
B	-0.071986	-0.499761	0.268035
C	3.171683	1.058804	-0.141177
C	3.521907	-0.281606	-0.904038
B	1.648758	-0.693033	0.449847
O	2.305137	-1.001574	-0.842565
O	2.242047	0.649254	0.842302
C	4.635610	-1.088366	-0.197973
H	4.695040	-2.075147	-0.669944
H	5.620571	-0.609047	-0.276071
H	4.378490	-1.242575	0.851310
C	3.904987	-0.100045	-2.380484
H	4.798218	0.527430	-2.497038
H	4.120911	-1.078909	-2.823483

H	3.086190	0.346553	-2.949496
C	4.365836	1.735807	0.549418
H	5.145412	2.025502	-0.167668
H	4.026775	2.642884	1.063545
H	4.806661	1.074711	1.298584
C	2.483616	2.086148	-1.068008
H	2.086377	2.901278	-0.452051
H	3.165443	2.523241	-1.808607
H	1.646727	1.619578	-1.594501
O	2.028035	-1.736044	1.442319
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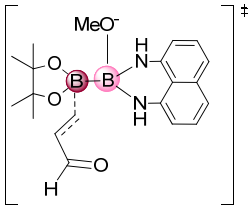
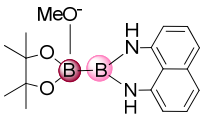
H	1.899511	-2.376785	3.380243
H	2.037346	-0.610406	3.197968
H	0.502237	-1.420086	2.838837
H	-0.041983	1.534754	0.754212
H	-0.732720	-2.441981	-0.287745



C	4.644527	0.353787	2.008374
C	5.122184	-0.452118	0.993705
C	4.245554	-0.904227	-0.029477
C	2.873613	-0.497001	0.005819
C	2.400534	0.341907	1.071332
C	3.297972	0.750670	2.061162
H	5.720666	-2.066009	-1.113304
H	5.321857	0.694686	2.789019
H	6.165974	-0.754200	0.966080
C	4.678213	-1.759418	-1.080762
C	1.965446	-0.960949	-1.002480
H	2.944293	1.388445	2.867460
C	2.431186	-1.811505	-2.006334
C	3.783184	-2.197762	-2.035592
H	1.739901	-2.163826	-2.767992
H	4.124514	-2.855546	-2.832659
N	1.072728	0.700688	1.085615
N	0.651819	-0.547519	-0.934066
B	0.102340	0.371491	0.048179
C	-3.587982	-0.766644	-0.700754
C	-3.949052	0.162824	0.541750
B	-1.679752	-0.261773	0.598069
O	-2.691868	0.717619	0.914000
O	-2.201953	-1.058429	-0.514416
C	-4.505731	-0.627744	1.744958
H	-4.600326	0.058450	2.592585
H	-5.491189	-1.063559	1.541682

H	-3.813198	-1.418050	2.040796
C	-4.909422	1.315372	0.223425
H	-5.888115	0.947604	-0.107780
H	-5.061746	1.914949	1.126821
H	-4.503580	1.974748	-0.546534
C	-4.356867	-2.096856	-0.744224
H	-5.438210	-1.939382	-0.842076
H	-4.021910	-2.681418	-1.607981
H	-4.170651	-2.690855	0.152385
C	-3.763042	-0.065671	-2.060709
H	-3.305880	-0.688627	-2.836782
H	-4.818949	0.079828	-2.316980
H	-3.269628	0.907928	-2.078336
O	-1.282799	-1.018374	1.766228
C	-0.617693	-2.248030	1.629241
H	-0.697287	-2.791580	2.580774
H	-1.057655	-2.867333	0.834706
H	0.451053	-2.120537	1.404858
H	0.012264	-0.960959	-1.600443
H	0.782438	1.250199	1.881707
C	-0.760676	1.914178	-0.806202
C	0.328578	2.644193	-1.305808
H	0.818095	2.350820	-2.231778
C	0.885285	3.756266	-0.597755
H	0.385053	3.955380	0.385292
H	-1.362781	1.351054	-1.511313
H	-1.354273	2.349179	-0.007556
O	1.797823	4.497959	-0.979905



C	-4.149961	-2.198927	-1.138759
C	-4.855194	-1.019059	-0.990829
C	-4.200368	0.141872	-0.491596
C	-2.817137	0.060118	-0.128978
C	-2.102535	-1.182192	-0.277912
C	-2.793523	-2.293335	-0.795176
H	-5.931675	1.445166	-0.624978
H	-4.655205	-3.082513	-1.528635
H	-5.907013	-0.957763	-1.260963
C	-4.879223	1.385222	-0.357042
C	-2.120098	1.231451	0.339979
H	-2.260911	-3.235463	-0.913373
C	-2.837312	2.437952	0.441084
C	-4.195653	2.497546	0.098260
H	-2.321097	3.327689	0.797184
H	-4.719861	3.448137	0.196120
N	-0.782529	-1.231218	0.052532

N	-0.793045	1.146622	0.630518
B	-0.020935	-0.158872	0.863675
C	3.565928	0.983218	-0.477538
C	3.718649	-0.582021	-0.528628
B	1.615397	-0.017162	0.278310
O	2.360899	-1.028558	-0.342028
O	2.385964	1.150166	0.331980
C	4.545864	-1.148002	0.638132
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H	5.612600	-0.915452	0.541114
H	4.185828	-0.758443	1.593986
C	4.242495	-1.147120	-1.850902
H	5.260585	-0.796828	-2.059348
H	4.265554	-2.240237	-1.796409
H	3.598678	-0.869288	-2.687507
C	4.724248	1.733583	0.183838
H	5.659853	1.593754	-0.370973
H	4.500032	2.804837	0.204162
H	4.876546	1.406181	1.214236
C	3.261902	1.607805	-1.849626
H	2.959163	2.648462	-1.700962
H	4.132214	1.591256	-2.515597
H	2.433560	1.088419	-2.338698
O	-0.053038	-0.423163	2.342050
C	0.548068	-1.584953	2.805304
H	0.475527	-1.626857	3.904019
H	0.075311	-2.508014	2.415594
H	1.625504	-1.660711	2.547675
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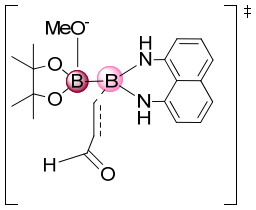
H	-0.388368	1.997717	0.995685



C	3.723555	2.213328	1.013223
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C	4.003463	0.315854	-0.478435
C	2.798724	-0.256169	0.040239
C	2.069467	0.423074	1.075195
C	2.545267	1.656389	1.540753
H	5.645357	0.045455	-1.870100
H	4.068622	3.171699	1.397669
H	5.357819	2.007650	-0.369489
C	4.730384	-0.389417	-1.475917
C	2.330357	-1.523401	-0.455068
H	2.004117	2.168149	2.333607
C	3.090622	-2.184105	-1.429978
C	4.272969	-1.612978	-1.925805
H	2.744488	-3.143316	-1.808940

H	4.835270	-2.151458	-2.687048
N	0.946103	-0.165007	1.598208
N	1.178131	-2.050293	0.052726
B	0.237768	-1.372217	1.008218
C	-2.134400	1.756395	0.346978
C	-1.496636	1.620318	-1.105091
B	-1.133845	-0.342887	0.100819
O	-0.782102	0.369109	-1.043679
O	-1.979523	0.436197	0.908698
C	-0.479951	2.710326	-1.469814
H	-0.081230	2.505094	-2.468100
H	-0.943417	3.703852	-1.487728
H	0.363595	2.722968	-0.777295
C	-2.536985	1.514428	-2.231400
H	-3.060649	2.465080	-2.382309
H	-2.018651	1.259086	-3.161007
H	-3.279792	0.740137	-2.034959
C	-1.377800	2.730291	1.265740
H	-1.498764	3.770728	0.944746
H	-1.778194	2.638395	2.280775
H	-0.309340	2.505514	1.297320
C	-3.627816	2.106047	0.371434
H	-3.970087	2.137524	1.411182
H	-3.815604	3.090075	-0.074223
H	-4.229338	1.361446	-0.152109
O	-0.283572	-2.334273	1.953726
C	-1.034491	-1.882407	3.047490
H	-1.365420	-2.753151	3.629580
H	-0.440931	-1.242377	3.724137
H	-1.923570	-1.308926	2.744838
H	0.428662	0.423906	2.235975
H	0.939316	-2.972177	-0.283176
C	-2.012018	-2.206978	-0.473699
C	-3.154500	-1.823407	-1.158741
C	-4.404146	-1.590335	-0.496261
H	-3.104394	-1.571810	-2.215416
H	-1.146033	-2.531749	-1.041207
H	-2.084696	-2.633062	0.521192
H	-4.398957	-1.852790	0.589627
O	-5.434383	-1.140969	-1.015677

Figure 4

TS_{A-B}

C	-0.492477	2.496787	1.509904
C	0.610948	2.768217	2.369267
C	1.865484	2.207689	2.056398
H	0.508946	3.463267	3.196938
H	-1.475214	2.849445	1.821913
H	-0.530353	1.488052	1.096528
H	2.664697	2.340996	2.818728
O	2.139174	1.602599	0.990650
P	-0.237566	3.406036	-0.431382
C	-1.516589	4.435842	-1.290445
H	-1.766746	5.300082	-0.668627
H	-1.163261	4.791809	-2.264438
H	-2.425300	3.845894	-1.439143
C	1.239400	4.473505	-0.290935
H	2.109655	3.817573	-0.217829
H	1.332978	5.148772	-1.145206
H	1.176881	5.045620	0.639399
C	0.212093	2.080614	-1.615852
H	0.605896	2.483355	-2.553912
H	0.973096	1.479824	-1.108521
H	-0.661838	1.458798	-1.831888

B

C	-1.862448	-1.779989	-0.144598
C	-2.728565	-0.612948	-0.494659
C	-2.042367	0.535628	-0.652720
H	-3.801986	-0.696783	-0.607199
H	-1.888605	-2.600857	-0.876833
H	-2.095431	-2.243681	0.825641
H	-2.509137	1.488793	-0.909509
O	-0.724937	0.557184	-0.497570
P	-0.068528	-1.246319	-0.038398
C	0.932614	-1.060524	-1.578306
H	1.348337	-0.053697	-1.610989
H	1.720231	-1.813275	-1.650033
H	0.255143	-1.159678	-2.430913
C	0.558132	-0.416795	1.487110
H	1.270364	-1.040312	2.031243
H	1.003590	0.539194	1.212797
H	-0.301816	-0.202221	2.127566
C	0.559721	-2.984403	0.403174
H	1.647332	-2.982583	0.535684
H	0.107931	-3.343160	1.334789
H	0.318319	-3.704341	-0.386854

C

C	2.982476	0.115844	0.146668
P	3.021938	-0.987383	1.656407
C	3.289174	-0.657198	-1.100180
C	-0.426556	-2.021439	-1.940014
O	0.282393	-1.251472	-0.987474
H	-0.373677	-1.592266	-2.952408
H	-0.075742	-3.063405	-1.992379
H	-1.477805	-2.035172	-1.637022
H	1.229054	-1.248294	-1.233540
H	1.986614	0.578313	0.148767
C	3.656966	-1.945364	-0.872837
O	3.670629	-2.436403	0.340567
H	3.330487	-0.184735	-2.074143
C	4.632211	-1.352657	2.474568
H	5.424624	-0.880666	1.887363
H	4.659960	-0.966515	3.495694
H	4.806921	-2.427587	2.454945
C	1.638754	-2.161662	1.943954
H	1.126566	-1.944934	2.883872
H	0.941023	-2.043344	1.107230
H	2.023549	-3.180435	1.929135
C	2.452975	0.361542	2.850542
H	3.142222	1.213039	2.839192
H	1.457095	0.726968	2.579697
H	2.405948	-0.022915	3.874843
H	3.697615	0.925831	0.356722
H	3.944999	-2.625229	-1.681408

$TSa_{C\text{-}D}$

B	0.877565	-1.756238	0.128360
C	2.603485	1.815389	0.154735
P	1.682297	3.217963	-0.591671
C	2.328284	1.499790	1.621022
O	1.089116	-3.040314	0.588699
O	1.886088	-1.379517	-0.760912
C	-0.918954	0.899131	2.528768
O	0.034741	0.205573	1.730096
H	-1.456846	0.194923	3.168639
H	-0.387027	1.619351	3.161912
H	-1.650243	1.437275	1.913923
C	2.139864	-3.659816	-0.196018
C	2.914387	-2.411366	-0.769216
C	3.433225	-2.566248	-2.198388
C	2.957895	-4.570028	0.719867
C	1.444480	-4.498422	-1.278522
H	2.161573	-5.062379	-1.883314
H	0.770549	-5.208670	-0.792091
H	0.843858	-3.870797	-1.942460
H	3.796920	-5.021919	0.179766
H	2.321524	-5.378371	1.091243
H	3.348379	-4.028879	1.583493

H	4.169118	-3.374784	-2.263795
H	2.624053	-2.775400	-2.900135
H	3.924242	-1.640840	-2.515581
C	4.045756	-1.927888	0.148484
H	4.415790	-0.963914	-0.213446
H	3.691994	-1.792746	1.174129
H	4.885680	-2.629180	0.161080
H	1.051165	0.815076	1.673612
H	2.365029	0.942096	-0.464737
C	2.225714	2.614546	2.503817
O	1.988298	3.785558	2.142544
H	2.942207	0.677701	1.995434
C	2.581575	4.804251	-0.554243
H	3.563263	4.671556	-1.017877
H	2.019322	5.548535	-1.125709
H	2.692691	5.117259	0.482443
C	-0.039909	3.401365	-0.052989
H	-0.563119	4.070765	-0.741417
H	-0.513355	2.413487	-0.077748
H	-0.048259	3.805287	0.958654
C	1.599611	2.807572	-2.378041
H	2.606422	2.638300	-2.769819
H	1.010144	1.900121	-2.526234
H	1.135798	3.625220	-2.936320
C	-2.280123	0.325087	-0.971641
C	-2.984204	-1.249168	0.824461
C	-3.315482	-0.290938	-0.195007
C	-2.630703	1.166498	-2.027984
C	-4.021284	-1.870772	1.525271
C	-4.688869	-0.006855	-0.489207
C	-3.983336	1.440648	-2.308245
H	-1.846864	1.614720	-2.636338
C	-5.363415	-1.561983	1.245084
H	-3.778119	-2.600260	2.294381
C	-4.994455	0.887015	-1.553048
C	-5.704637	-0.649575	0.267193
H	-4.226476	2.105593	-3.134051
H	-6.145178	-2.059871	1.814290
H	-6.745537	-0.425593	0.051736
H	-6.035762	1.105666	-1.772779
N	-1.661715	-1.543508	1.059587
H	-1.500496	-2.303902	1.704349
N	-0.954487	0.066792	-0.650381
H	-0.313561	0.211130	-1.417700
B	-0.493630	-0.788504	0.508208
H	3.659872	2.063974	-0.038563
H	2.291141	2.390949	3.588480

$TSb_{C\text{-}D}$

B	0.705607	1.310105	0.476152
C	0.789726	-2.535162	0.103826

P	2.421294	-2.566278	-0.743874
C	0.816190	-2.194724	1.586734
C	1.198453	0.818911	3.050255
O	1.445000	0.403082	1.704458
H	0.272148	0.374921	3.439188
H	2.031199	0.506734	3.688716
H	1.117055	1.906185	3.058231
O	1.546576	1.021406	-0.693910
O	0.911113	2.691128	0.809698
C	2.069378	3.176457	0.115956
C	2.091016	2.269519	-1.171516
C	1.157779	2.795344	-2.276936
H	0.156683	2.987928	-1.882975
H	1.074821	2.039011	-3.065041
H	1.535187	3.715118	-2.734949
H	0.919388	4.860618	-0.657358
C	1.868204	4.670970	-0.152435
H	1.853386	5.212435	0.798440
H	2.681296	5.082560	-0.761107
C	3.313760	2.986371	1.003488
H	3.143069	3.492463	1.958640
H	4.211549	3.419641	0.549615
C	3.483014	2.025480	-1.760257
H	3.410069	1.373123	-2.637275
H	4.152770	1.553064	-1.039054
H	3.496292	1.929664	1.210217
H	3.940578	2.965546	-2.087647
H	1.237918	-0.706019	1.659255
H	0.189466	-1.800483	-0.443189
C	1.731775	-2.927731	2.384726
O	2.718743	-3.558896	1.944955
H	-0.178932	-2.055130	2.013859
C	3.039066	-4.263613	-0.983434
H	2.303565	-4.844313	-1.547034
H	3.977413	-4.237738	-1.544572
H	3.192028	-4.702305	0.002735
C	3.707330	-1.512303	-0.017237
H	4.555429	-1.469550	-0.707155
H	3.285982	-0.512192	0.111627
H	4.006614	-1.939847	0.938887
C	2.113672	-1.885969	-2.412739
H	1.307677	-2.438516	-2.903611
H	1.823029	-0.838842	-2.284189
H	3.014508	-1.945429	-3.029534
C	-3.285402	0.470288	1.143050
C	-2.713276	-0.081540	-1.212455
C	-3.668936	-0.005870	-0.150777
C	-4.232483	0.542917	2.156945
C	-3.106611	-0.533241	-2.465645
C	-5.023925	-0.400409	-0.388970
C	-5.563351	0.149484	1.914288
H	-3.940303	0.906604	3.138949
C	-4.443215	-0.919880	-2.691034

H	-2.378256	-0.582775	-3.271474
C	-5.959214	-0.312807	0.677376
C	-5.383607	-0.861315	-1.685199
H	-6.286155	0.215389	2.723356
H	-4.730182	-1.269384	-3.679515
N	-1.404017	0.305414	-0.933204
N	-1.956868	0.848351	1.338579
B	-0.938111	0.806165	0.329474
H	-6.988118	-0.612660	0.500502
H	-6.411127	-1.161850	-1.869070
H	-1.756130	1.227133	2.252761
H	-0.760294	0.296660	-1.712625
H	1.583981	-2.865331	3.483818
H	0.358185	-3.526764	-0.108748

Da

B	0.336481	1.597486	-0.269603
C	3.485860	-1.014324	-0.489086
P	2.862729	-2.088646	0.869691
C	2.981631	-1.290244	-1.911824
O	0.010860	2.904139	-0.584887
O	1.563596	1.581198	0.434448
C	-0.700079	-1.745554	-2.126169
O	0.067346	-0.776770	-1.440875
H	-1.376671	-1.291538	-2.860825
H	-0.022974	-2.428452	-2.664269
H	-1.316937	-2.352180	-1.444890
C	0.862684	3.814631	0.145107
C	2.128048	2.926836	0.432907
C	2.806559	3.178027	1.779067
C	1.113491	5.049964	-0.719832
C	0.098273	4.215750	1.416263
H	0.639555	4.965494	2.002406
H	-0.867295	4.636481	1.124272
H	-0.098673	3.347143	2.050601
H	1.801965	5.746239	-0.228231
H	0.167345	5.572640	-0.885984
H	1.522266	4.783476	-1.696173
H	3.179619	4.205680	1.844308
H	2.123143	3.005826	2.612517
H	3.664596	2.507460	1.897176
C	3.168392	2.984645	-0.695530
H	3.944425	2.232747	-0.518171
H	2.708096	2.779767	-1.665881
H	3.658831	3.961627	-0.744356
H	1.885536	-1.082145	-1.946768
H	3.154849	-0.009081	-0.208968
C	3.237623	-2.669441	-2.420570
O	3.576529	-3.607515	-1.716459
H	3.432466	-0.566421	-2.603579

C	4.122977	-3.303739	1.375861
H	5.039112	-2.788003	1.676276
H	3.748186	-3.884679	2.223019
H	4.329882	-3.961390	0.531140
C	1.307896	-2.930725	0.491104
H	0.884061	-3.336252	1.413793
H	0.623452	-2.195294	0.043569
H	1.499870	-3.738925	-0.215825
C	2.587171	-0.979554	2.288881
H	3.546928	-0.586087	2.636341
H	1.966250	-0.138136	1.964664
H	2.107797	-1.521370	3.108190
C	-2.449992	-0.810018	1.035816
C	-3.263374	0.308152	-1.032128
C	-3.522678	-0.484090	0.139351
C	-2.736206	-1.527373	2.202314
C	-4.342149	0.658638	-1.854429
C	-4.858802	-0.899829	0.445135
C	-4.050466	-1.941525	2.485298
H	-1.927423	-1.766166	2.891749
C	-5.645335	0.233735	-1.549827
H	-4.157550	1.263245	-2.739904
C	-5.093905	-1.648823	1.632252
C	-5.913399	-0.534467	-0.433675
H	-4.240019	-2.503828	3.397604
H	-6.458084	0.519839	-2.214526
H	-6.926377	-0.855120	-0.206437
H	-6.106585	-1.970305	1.860026
N	-1.980787	0.709207	-1.301405
H	-1.900468	1.358095	-2.071053
N	-1.175078	-0.393834	0.727496
H	-0.515704	-0.528615	1.480160
B	-0.717746	0.255396	-0.587823
H	4.579675	-1.056174	-0.431677
H	3.071357	-2.820372	-3.506669

Db

B	1.000877	-1.222476	-0.646567
C	0.282796	2.620123	0.256412
P	2.035469	2.709428	0.814144
C	0.039981	2.512033	-1.253991
C	1.387013	-0.452035	-2.997204
O	1.585964	-0.189955	-1.628501
H	0.354689	-0.225788	-3.326113
H	2.062121	0.176888	-3.594714
H	1.588541	-1.502648	-3.238673
O	1.752716	-0.992172	0.642047
O	1.346370	-2.592759	-1.032558
C	2.526902	-2.990733	-0.345203
C	2.406394	-2.210512	1.020291
C	1.506980	-2.943976	2.033281
H	0.550651	-3.209723	1.575943

H	1.308711	-2.279515	2.882252
H	1.972375	-3.854814	2.424561
H	1.586871	-4.869744	0.242016
C	2.516056	-4.517925	-0.210476
H	2.593410	-4.971180	-1.203905
H	3.360122	-4.877510	0.390044
C	3.769715	-2.569370	-1.156726
H	3.691988	-3.001166	-2.159460
H	4.703071	-2.926737	-0.706563
C	3.748841	-1.881690	1.685062
H	3.583531	-1.361623	2.636031
H	4.362453	-1.240580	1.047842
H	3.813682	-1.483353	-1.261776
H	4.316755	-2.792642	1.905616
H	0.541493	1.596164	-1.625898
H	-0.134444	1.720966	0.721385
C	0.509054	3.680399	-2.060592
O	1.270318	4.539743	-1.648370
H	-1.028551	2.347457	-1.441203
C	2.431326	4.413319	1.326934
H	1.777560	4.711755	2.151124
H	3.470715	4.464890	1.662341
H	2.277639	5.077554	0.475558
C	3.214120	2.154934	-0.443489
H	4.193185	2.027787	0.026950
H	2.857978	1.195203	-0.854690
H	3.278860	2.907509	-1.231240
C	2.185342	1.627667	2.260751
H	1.447219	1.911151	3.016485
H	2.009669	0.599887	1.905242
H	3.188472	1.708741	2.688296
C	-3.103966	-0.765724	-1.145146
C	-2.511167	-0.348068	1.232255
C	-3.488910	-0.416384	0.189209
C	-4.072949	-0.836170	-2.140785
C	-2.905291	-0.025504	2.526305
C	-4.862976	-0.145085	0.485791
C	-5.421651	-0.564246	-1.840173
H	-3.781544	-1.106701	-3.152687
C	-4.260279	0.239011	2.808790
H	-2.161681	0.013963	3.318815
C	-5.817817	-0.224060	-0.563761
C	-5.220853	0.188074	1.821213
H	-6.159861	-0.627564	-2.635711
H	-4.546566	0.486686	3.828007
N	-1.185649	-0.597873	0.891794
N	-1.758438	-1.019050	-1.398175
B	-0.704664	-0.970878	-0.417479
H	-6.861372	-0.018752	-0.342618
H	-6.262740	0.393446	2.050185
H	-1.551803	-1.311071	-2.342607
H	-0.519083	-0.627314	1.652490
H	0.142040	3.717196	-3.107125

H	-0.225544	3.491658	0.683105

$TSa_{D\text{-}E}$

B	0.026741	1.470936	0.252107
C	3.829142	-0.887205	-1.207073
P	3.550459	-1.743496	0.405233
C	2.766547	-1.059301	-2.301138
O	-0.431589	2.783175	0.132181
O	1.439914	1.479612	0.296795
C	-0.679432	0.094304	-3.282015
O	-0.134505	0.363964	-1.997573
H	-1.430240	0.839596	-3.571765
H	0.135747	0.118262	-4.016946
H	-1.161395	-0.893609	-3.319343
C	0.666510	3.711773	0.267903
C	1.903671	2.808257	-0.087783
C	3.177049	3.144541	0.689220
C	0.422095	4.887652	-0.679233
C	0.670930	4.213928	1.720224
H	1.415615	5.000805	1.877440
H	-0.315370	4.624877	1.952510
H	0.873269	3.404855	2.427116
H	1.264401	5.588300	-0.669322
H	-0.471303	5.432083	-0.359630
H	0.259641	4.549409	-1.704184
H	3.492760	4.174163	0.489004
H	3.040009	3.030688	1.766396
H	3.997074	2.488227	0.378488
C	2.202663	2.778661	-1.594004
H	3.006572	2.062098	-1.791800
H	1.323758	2.454790	-2.154384
H	2.535070	3.755311	-1.958346
H	1.783000	-0.648710	-2.001996
H	3.899188	0.174291	-0.958561
C	2.584940	-2.472493	-2.770079
O	3.074498	-3.441909	-2.218411
H	3.048638	-0.450381	-3.171801
C	4.700611	-3.145738	0.563376
H	5.733323	-2.788956	0.523891
H	4.531121	-3.640348	1.523560
H	4.517991	-3.842096	-0.256225
C	1.860240	-2.339241	0.617447
H	1.726685	-2.596257	1.675662
H	1.166413	-1.523849	0.401107
H	1.683074	-3.193099	-0.037986
C	3.926642	-0.547748	1.715377
H	4.983555	-0.269590	1.677606
H	3.296993	0.330705	1.549961
H	3.657227	-0.980017	2.684521
C	-2.614099	-1.644657	-0.104539

C	-3.606991	0.581537	-0.599267
C	-3.750458	-0.771183	-0.140683
C	-2.781047	-2.963449	0.315904
C	-4.728818	1.412531	-0.612388
C	-5.032765	-1.254902	0.271327
C	-4.049653	-3.432152	0.709308
H	-1.921655	-3.630390	0.338413
C	-5.981760	0.929225	-0.195459
H	-4.625169	2.439344	-0.954760
C	-5.153447	-2.606932	0.697034
C	-6.144901	-0.371426	0.235801
H	-4.150157	-4.465315	1.033400
H	-6.836596	1.601223	-0.218495
H	-7.118333	-0.735735	0.551681
H	-6.126997	-2.975549	1.007666
N	-2.368782	1.019544	-1.023077
H	-2.303568	2.018843	-1.162033
N	-1.386840	-1.149072	-0.504332
H	-0.666528	-1.849027	-0.594392
B	-1.093427	0.260730	-0.880850
H	4.810619	-1.214084	-1.567211
H	1.947338	-2.599841	-3.668495
C	-0.812108	0.644785	1.998400
H	-0.487046	1.580317	2.453324
C	-0.262279	-0.529151	2.505886
H	-0.711792	-1.489745	2.270482
C	0.952966	-0.518268	3.244371
H	1.315083	0.498835	3.522112
O	1.637588	-1.511301	3.571308
H	-1.836846	0.651977	1.648504

$TSb_{D\text{-}E}$

B	-1.871005	-0.088663	-0.326946
C	2.496846	-1.578317	-0.368040
P	1.506861	-3.111822	-0.133453
C	2.322285	-0.827025	-1.692400
C	-1.269029	0.189097	-2.692036
O	-1.018207	-0.441613	-1.442608
H	-0.731356	1.141381	-2.769388
H	-0.916450	-0.473890	-3.491958
H	-2.337328	0.378627	-2.830315
O	-1.823258	-1.089950	0.723306
O	-3.236296	0.195853	-0.602602
C	-4.046947	-0.844136	-0.038218
C	-3.168668	-1.357920	1.171238
C	-3.413307	-0.583433	2.476495
H	-3.334823	0.495413	2.326859
H	-2.660373	-0.880775	3.214735
H	-4.398559	-0.800348	2.900490
H	-5.289171	0.600399	1.027136

C	-5.401953	-0.252534	0.355594
H	-5.920187	0.098201	-0.541552
H	-6.036584	-1.001776	0.842083
C	-4.255322	-1.917541	-1.122804
H	-4.706097	-1.442793	-1.998718
H	-4.919598	-2.721968	-0.790303
C	-3.296928	-2.858269	1.457317
H	-2.653743	-3.134237	2.299938
H	-3.005818	-3.460269	0.593889
H	-3.302018	-2.354776	-1.432677
H	-4.324997	-3.121050	1.728919
H	1.273324	-0.520671	-1.824957
H	2.228702	-0.912556	0.456210
C	2.763155	-1.603690	-2.896973
O	3.031359	-2.792833	-2.878053
H	2.882745	0.116331	-1.649852
C	2.629780	-4.546331	-0.134753
H	3.351704	-4.452116	0.681074
H	2.057956	-5.468260	-0.000121
H	3.156677	-4.569654	-1.090594
C	0.216674	-3.360040	-1.381375
H	-0.410314	-4.199840	-1.068333
H	-0.392696	-2.447015	-1.440889
H	0.676511	-3.584300	-2.344675
C	0.696876	-3.002103	1.487606
H	1.412252	-2.656340	2.238423
H	-0.131763	-2.286438	1.402376
H	0.303413	-3.981180	1.774682
C	1.613577	2.323998	-0.245571
C	1.298585	1.036078	1.854035
C	2.162100	1.712272	0.931059
C	2.469429	2.983832	-1.129924
C	1.848586	0.419746	2.979985
C	3.571454	1.766205	1.178332
C	3.850909	3.041058	-0.869802
H	2.056670	3.463629	-2.013090
C	3.238211	0.477546	3.213148
H	1.192379	-0.075003	3.692059
C	4.403195	2.444469	0.247590
C	4.086908	1.127617	2.342048
H	4.493040	3.569872	-1.569772
H	3.641015	0.002557	4.104593
N	-0.053272	0.987669	1.569809
N	0.255110	2.230494	-0.459718
B	-0.697956	1.534874	0.385425
H	5.471794	2.497420	0.434653
H	5.155143	1.168459	2.534723
H	-0.116145	2.823609	-1.194366
H	-0.595733	0.372201	2.160409
H	2.824041	-1.031184	-3.844782
H	3.542992	-1.867799	-0.225303
C	-2.222170	2.629142	0.557590
H	-3.022100	1.982301	0.896654

C	-2.532021	3.470591	-0.541517
H	-3.287067	3.160597	-1.260122
C	-1.858424	4.703504	-0.787853
H	-1.092301	4.962552	-0.010819
O	-2.054917	5.480497	-1.733055
H	-1.718378	3.151283	1.380901

Ea

B	-2.427715	-1.063831	-0.504073
C	-1.382193	-2.107735	-1.042667
C	0.023757	-1.715587	-0.628052
H	-3.040160	2.246473	-1.716115
H	-2.028567	1.847306	-0.321054
H	-3.492755	2.830064	-0.102522
H	-2.566493	1.645372	1.923039
H	-4.315216	1.786534	2.200183
H	-3.375453	0.546298	3.045128
H	-5.838323	1.643473	-0.326543
H	-5.878881	-0.009465	-0.975539
H	-5.292267	1.320412	-1.980038
H	-5.842196	-0.255004	1.541277
H	-4.674538	-1.380218	2.260927
H	-5.136666	-1.558587	0.563317
C	-4.930221	-0.829218	1.351626
C	-5.311749	0.922749	-0.961249
C	-3.751878	0.079662	0.974024
C	-3.881720	0.704476	-0.470242
C	-3.484203	1.080662	2.096859
C	-3.061048	1.988927	-0.653544
O	-2.589143	-0.779290	0.835747
O	-3.257134	-0.309713	-1.302940
H	0.736103	-1.481494	-2.583590
C	0.996487	-1.408515	-1.518097
H	0.208007	-1.676732	0.442662
O	2.257005	-1.024307	-1.331124
H	-1.633885	-3.108129	-0.654886
H	-1.450536	-2.169036	-2.135253
H	2.083592	1.277179	-1.590095
C	2.067501	1.813982	-0.631708
C	3.205040	2.798206	-0.626932
H	1.135620	2.398542	-0.644754
C	2.050040	0.809139	0.526095
O	4.162069	2.765226	0.120825
H	3.123039	3.600183	-1.394868
P	3.265129	-0.598919	0.382947
H	1.062341	0.343101	0.548091
H	2.219635	1.323240	1.475291
C	2.831304	-2.286574	0.985631
C	4.257158	-0.142732	1.930413
C	4.696307	-0.489844	-0.768356
H	2.265154	-2.859189	0.255559

H	2.257875	-2.195958	1.913036
H	3.770567	-2.792159	1.229457
H	3.625606	-0.191983	2.824626
H	4.634369	0.878742	1.834491
H	5.105554	-0.818677	2.082668
H	4.398386	-0.723376	-1.785988
H	5.452338	-1.199249	-0.418885
H	5.119522	0.514371	-0.696324

Eb

C	0.464660	-2.445496	0.535214
C	-0.847163	-1.731045	0.289027
H	-1.415163	-1.690068	2.302160
C	-1.709544	-1.387886	1.282431
H	-1.060601	-1.461875	-0.745081
O	-2.863730	-0.749826	1.236713
H	0.539873	-3.362751	-0.070700
H	0.490138	-2.793732	1.580246
H	-2.410646	1.391696	0.805889
C	-2.689605	1.790813	-0.179718
C	-3.679488	2.906221	0.015515
H	-1.774223	2.231043	-0.600412
C	-3.188119	0.645324	-1.064944
O	-4.840146	2.875653	-0.344706
H	-3.278405	3.801240	0.539929
P	-4.409479	-0.514742	-0.283863
H	-2.335653	0.024005	-1.343159
H	-3.642270	1.042892	-1.976668
C	-4.155759	-2.318998	-0.509534
C	-5.805181	-0.288339	-1.513000
C	-5.345010	0.006125	1.207389
H	-3.100325	-2.579376	-0.427149
H	-4.567138	-2.644984	-1.467652
H	-4.691013	-2.824425	0.298840
H	-5.484427	-0.571095	-2.521151
H	-6.118446	0.758810	-1.528758
H	-6.663857	-0.912142	-1.243707
H	-4.686983	0.063904	2.068822
H	-6.120722	-0.746862	1.378404
H	-5.828968	0.961138	0.996269
C	4.156701	-1.230896	-0.228195
C	2.754364	0.739923	0.360738
C	4.016888	0.176728	-0.010697
C	5.390596	-1.754615	-0.588982
C	2.642173	2.108150	0.568305
C	5.153195	1.032186	-0.168038
C	6.504025	-0.903874	-0.741227
H	5.493175	-2.824411	-0.752876
C	3.767534	2.942267	0.411669
H	1.682310	2.529750	0.855526
C	6.398252	0.455031	-0.538432

C	4.994517	2.427779	0.052681
H	7.460378	-1.336013	-1.023645
H	3.657696	4.010393	0.580214
N	1.673741	-0.126245	0.497720
N	3.026711	-2.036005	-0.067587
B	1.743208	-1.534462	0.305994
H	5.855716	3.079125	-0.065148
H	7.262392	1.102224	-0.657590
H	0.780572	0.280153	0.746794
H	3.172371	-3.022461	-0.229630

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