**Supporting Information**

**for**

# Ligand-controlled β-selective C($sp^3$)–H Arylation of *N*-Boc-piperidines

**CHEMICAL SCIENCE**

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# GENERAL CONSIDERATIONS

Reactions involving air-sensitive compounds were performed under an oxygen-free atmosphere of argon with rigorous exclusion of moisture from reagents and glassware using standard techniques. Commercially available reagents were used without further purification unless otherwise stated. Phosphines and palladium sources were stored in a glove box. Anhydrous solvents and amines were obtained by distillation over calcium hydride ($Et_3N$, TMEDA, DCM), or sodium / benzophenone ($Et_2O$, THF, toluene), DMF (99.5% extra dry, stored over 4 Å molecular sieves), and zinc chloride solution (0.5 M or 0.7M in THF) were purchased from Sigma Aldrich or Acros Organic. Synthesis, $^1H$ and $^{13}C$ NMR data for compounds **1e**,[1] **L4**,[2] **L5**,[2] **L6**,[3] **2g**,[4] **2h**,[5] **2i**,[6] **2j**,[6] **2k**,[6] **2m**,[4] **4**,[7] **11a**[8] were identical to those described in the literature.

Flash column chromatography and preparative thin-layer chromatography were performed using normal phase silica gel (40-63 µm, and 1000 µm respectively) according to the method described by Still[9]. Products were eluted with mixture of solvents (volume/volume) and were visualized with U.V. light (254 nm) and developed with $KMnO_4$ (solution of : potassium permanganate (1.5g), potassium carbonate (10g) and NaOH 10% (1.25 mL) in water (200 mL)) or diiode.

GC/MS analyses were performed on a Shimadzu QP2010 GC/MS apparatus, with injection on a DB-5ms column lined with a mass (EI 0.7 kV) detection system. High-resolution mass spectra were measured on a Thermofinnigan mat 95xL under electrospray ionization (ESI) or electronic impact (EI) mode.

Melting points were obtained on a Buchi melting point B-540 apparatus.

Infrared spectra were taken on a Perkin Elmer Spectrum One FTIR and are reported in reciprocal centimetres ($cm^{-1}$).

Nuclear magnetic resonance spectra ($^1H$, $^{13}C$, $^{19}F$ and $^{31}P$) were recorded either on a Bruker ALS 300, DRX 300 or DRX 400 spectrometer (300, 300 and 400 MHz respectively) in deuterated chloroform (residual peaks $^1H$ δ 7.26 ppm, $^{13}C$ δ 77.16 ppm) unless otherwise noted. The corresponding chemical shifts are reported relative to the chemical shift of the residual solvent for $^1H$ and $^{13}C$ NMR. $^{19}F$ NMR and $^{31}P$ NMR spectra are calibrated with an external reference and recorded with complete proton decoupling. Data are reported as follows: chemical shift in parts per million (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, and br = broad), integration value, coupling constant in Hz if applicable.

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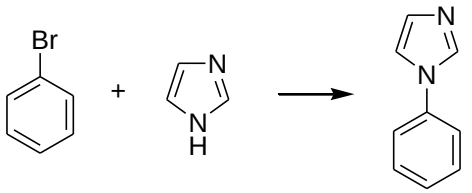
[1] Beak, P.; Zajdel, W.J. *J. Am. Chem. Soc.* **1984**, *106*, 1010
[2] Aspin,S.; Goutierre, A-S.; Larini, P.; Jazzar, R.; Baudoin, O. *Angew. Chem. Int. Ed.* **2012**, *51*, 10808
[3] Pingen, D.; Muller, C.; Vogt D. *Angew. Chem. Int. Ed.* **2010**, *49*, 8130
[4] Beng. T.K.; Gawley, R.E. *Org. Lett.* **2011**, *13*, 394
[5] PCT Int. Appl. WO 2005082367, **2005**
[6] Coldham, I.; Leoroni, D. *Org. Lett*. **2008**, *10*, 3923
[7] Coldham, I.; Leonori, D. *J. Org. Chem.* **2010**, *75*, 4069
[8] Dieter, R.K.; Li, SJ. *J. Org. Chem.* **1997**, *62*, 7726
[9] Still, W. C.; Khan, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

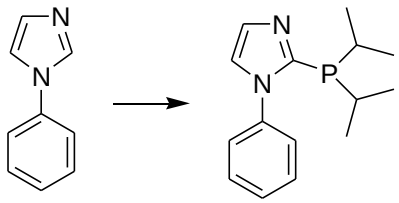
# Synthesis of ligands

## 1-phenylimidazole




CuI (699 mg, 3.67 mmol, 0.1 equiv.), 1,10-phenanthroline (1.45 g, 8.08 mmol, 0.22 equiv.), and 50 mL of dimethylformamide were added to a three-necked flask. This mixture was refluxed at 120 °C for 15 min, then cooled to room temperature. Imidazole (5 g, 73.45 mmol, 2.0 equiv.), KO*t*-Bu (8.24 g, 73.45 mmol, 2.0 equiv.), bromobenzene (3.87 mL, 36.72 mmol, 1.0 equiv.) and 18-crown-6 (970 mg, 3.67 mmol, 0.1 equiv.) were added. The mixture was refluxed at 130 °C for 72 hours and cooled to room temperature. The reaction mixture was extracted with dichloromethane. $NH_4Cl$ (100 mL) was added and extracted with ethyl acetate (3 x 50 mL). The organic phase was washed with brine (3 x 150 mL), dried over $MgSO_4$, filtered, and evaporated. The crude product was distilled under reduced pressure to give 3.41 g (64 %) as a yellow oil: bp 115°C/0.1 mBar.
According to the data of Sigma-Aldrich.[10]
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 7.20-7.21 (t, *J* = 1.0 Hz, 1H), 7.28-7.29 (t, *J* = 1.3 Hz, 1H), 7.37-7.41 (m, 3H), 7.46-7.51 (m, 2H), 7.86 (br s, 1H).

## 2-(diisopropylphosphanyl)-1-phenylimidazole (L7)




This Phosphine ligand was synthesized following the procedure of Baudoin *et al*.19
In a three-necked flask, 1-phenylimidazole (500 mg, 3.47 mmol, 1.0 equiv.) was dissolved in 5 mL of anhydrous THF under argon containing TMEDA (0.58 mL, 3.81 mmol, 1.1 equiv.), and cooled to -30 °C. *n*-BuLi (1.73 mL, 3.81 mmol, 1.1 equiv., 2.21 M in hexane) was slowly added and the reaction mixture was stirred at -30 °C for 30 min. Chlorodiisopropylphosphine (0.61 mL, 3.81 mmol, 1.1 equiv.) was then added dropwise at -30 °C. The reaction mixture was warmed to room temperature and then stirred at 50 °C for 2 h 30. After cooling in an ice bath, degassed water was added and the organic phase was separated. The aqueous layer was extracted with ethyl acetate and the combined organic layers were dried over $MgSO_4$, then concentrated under vacuum. Purification of the crude on silica gel (elution with Cyhex / EtOAc: 90 / 10) gived 157 mg (17 % yield) of the desired phosphine as a white solid.

[10] Charaterization data in accordance with the commercially available compound (Sigma-Aldrich)

**$^{1}$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 0.96-1.00 (dd, *J* = 6.9 Hz, 4.1 Hz, 6H), 1.01-1.03 (dd, *J* = 6.6, 0.7 Hz, 6H), 2.22-2.37 (2 x sept, *J* = 7.1, 6.8, 1.6 Hz, 2H), 7.18-7.19 (m, 1H), 7.30-7.32 (m, 1H), 7.33-7.35 (m, 2H), 7.42-7.49 (m, 3H).
**$^{13}$C-{$^{1}$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 19.6, 19.7, 19.9, 20.1, 24.9, 25.0, 117.7, 123.4, 127.0, 127.4 (d, *J* = 3.8 Hz),128.4, 128.6, 129.1, 130.5, 147.4.
**$^{31}$P-{$^{1}$H} NMR (121 MHz, $CDCl_3$, 293 K) δ** -13.7.

**IR (neat) ν** : 1150, 1187, 1496, 1596

**HRMS (ESI) m/z:** calculated for $C_{15}H_{22}N_2P$ ([M+H]$^+$): 261.1515; found 261.1509.

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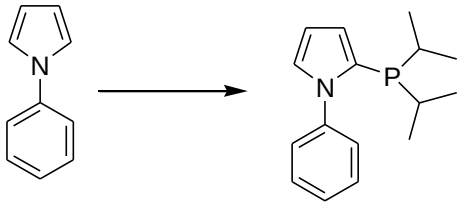
**2-(diisopropylphosphanyl)-1-phenylpyrrole (L8)**

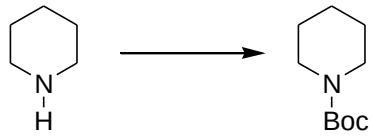



This Phosphine ligand was synthesized following the procedure of D. Vogt *et al*.[11]
In a 3-neck round-bottom Schlenk flask, 1-phenylpyrrole (500 mg, 3.5 mmol, 1 equiv.) was dissolved in dry degassed hexane (6 mL). To this, TMEDA (0.78 mL, 5.25 mmol, 1.5 equiv.) was added followed by a 2.5 M solution of BuLi in hexane (1.4 mL, 3.5 mmol, 1 equiv.). The mixture was refluxed during 3H. Chlorodiisopropylphosphine (0.56 mL, 3.5 mmol, 1 equiv.) was then added dropwise at reflux temperature. After addition, the mixture was refluxed for an additional hour and cooled to room temperature. Degassed water was added to quench the reaction. The layers were separated and the aqueous layer was extracted twice with hexane (2 x 10 mL). All hexane fractions were combined, dried over $MgSO_4$ and filtered. The solvents were evaporated and the Phosphine was recrystallized from methanol to give pure ligand as a white powder (65%, 587 mg).
**$^{1}$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 0.89-1.03 (2x dd, *J* = 11.8 Hz, 7.0 Hz, 12 H), 1.91-2.05 (sept, *J* = 7.0, 6.5 Hz, 2H), 6.37 (t, *J* = 3.2 Hz, 1H), 6.54 (dd, *J* = 3.8, 1.6 Hz, 1H), 6.99 (q, *J* = 4.0, 2.4 Hz, 1H) 7.31-7.49 (m, 5H).
**$^{31}$P-{$^{1}$H} NMR (121 MHz, $CDCl_3$, 293 K ) δ:** -17.5 ($^{1}J_{P\text{-}Se}$ = 713.5 Hz).

[11] Pingen,D.; Müller, C.;Vogt, D. *Angew. Chem. Int. Ed.* **2010**, *49*, 8130 –8133

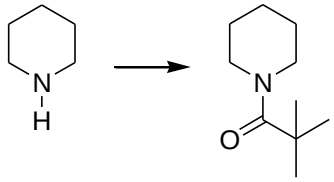
# Synthesis of subtrates

## *Tert*-butyl piperidine-1-carboxylate (1a)



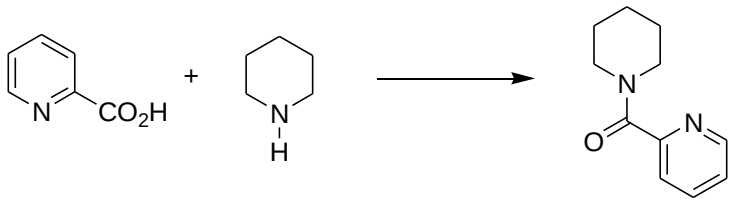

A solution of piperidine (5g, 59 mmol, 1 equiv.) and triethylamine (8.2 mL, 59 mmol, 1 equiv.) in 20 mL of THF was cooled to 0°C, and di-*tert*-butyl dicarbonate (12.8 g, 59 mmol, 1 equiv.) was added portionwise. The mixture was stirred for 10 min, warmed to room temperature, and then stirred for 2 hours. The mixture was diluted with 25 mL of water, and extracted with ethyl acetate (2 x 25 mL). The organic layers were dried over $MgSO_4$ and then concentrated to give a crude product which was distilled under reduced pressure to give 9.85 g (90.5 %) of **1a** as colorless oil: bp 65 °C/1 Torr.
According to P. Beak *et al*.[12]
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.43 (s, 9H), 1.47-1.54 (m, 6H), 3.31-3.35 (br t, 4 H).

## 1-(2,2-Dimethylpropanoyl)piperidine (1b)




A solution of piperidine (1g, 11.7 mmol, 1 equiv.) and triethylamine (1.63 mL, 11.7 mmol, 1 equiv.) in 15 mL of anhydrous diethylether was cooled to 0°C, and trimethylacetyl chloride (1.45 mL, 11.7 mmol, 1 equiv.) was slowly added. The mixture was stirred for 10 min, warmed to room temperature, and then stirred for 3 hours. The mixture was diluted with 5 mL of water, and extracted with diethylether (2 x 20 mL). The organic layers were dried over $MgSO_4$ and then concentrated to give a crude product which was distilled under reduced pressure to give 1.12 g (56 %) of **1b** as a colorless oil: bp 102°C/0.1 mBar.
According to J-M. Gaudin *et al*.[13]
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.28 (s, 9H), 1.50-1.57 (m, 4H), 1.60-1.65 (m, 2H), 3.54-3.57 (br t, 4 H).

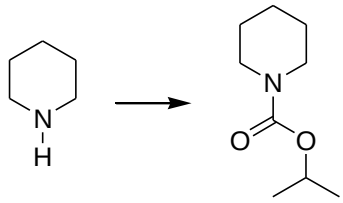
## *N*-(2-Pyridinylcarbonyl)piperidine (1c)




[12] Beak, P.; Lee. W.K. *J. Org. Chem*. **1993**, *58*, 1109
[13] Gaudin, J-M.; Lander, T.; Nikolaenko, O.; *Chemistry & Biodiversity*, **5**, *4*, 617

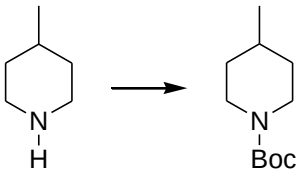
2-Pyridinecarboxylic acid (1 g, 8.12 mmol, 1 equiv.) was refluxed during 1.5 hour in 10 mL of thionylchloride. After warming to room temperature, the excess of thionylchloride was concentrated under reduce pressure. The corresponding oil was co-evaporated with 2 x 20 mL of dichloromethane. Picolinoyl Chloride was solubized on 2 mL of anhydrous dichloromethane, and was added slowly to a solution of piperidine (0.88 mL, 8.9 mmol, 1.1 equiv.) and triethylamine (1.24 mL, 8.9 mmol, 1.1 equiv.) in 5 mL of anhydrous dichloromethane at 0°C. The mixture was stirred for 10 min, warmed to room temperature, and then stirred for 1 hour. The mixture was diluted with 5 mL of water, and extracted with dichloromethane (2 x 10 mL). The organic layers were dried over $MgSO_4$ and then concentrated to give a crude product which was purified by silica gel column chromatography eluting with cyclohexane / ethyl acetate (50 / 50 to 25 / 75) to give 655 g (42 %) of **1c** as a beige powder.
According to Q.L Luo *et al*.[14]
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.53 (br.s, 2H), 1.65 (br.s, 4H), 3.38 (br.s, 2H), 3.70 (br.s, 2 H), 7.28 (t, *J* = 6.1 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 8.53 (d, *J* = 3.9 Hz, 1H).

## ***I*sopropyl piperidine-1-carboxylate (1d)**




Isopropyl chloroformate (10.1 mL, 11 mmol, 1 equiv.) (1M in toluene) was slowly added to a solution of piperidine (1 mL, 11 mmol, 1 equiv.) in 10 mL of anhydrous dichloromethane at 0°C containing potassium carbonate (1.4 g, 11 mmol, 1 equiv.) under argon. After complete addition the reaction mixture was heated at 45°C for 4 hours. After cooled to room temperature, 10 mL of water was added, and extracted with dichloromethane (3 x 15 mL), dried over $MgSO_4$ and then concentrated to give a crude product which was distilled under reduced pressure to give 1.55 g (89 %) of **1d** as a colorless oil: bp 62°C/0.1 mBar.
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.16-1.18 (d, *J* = 6.3 Hz, 6H), 1.41-1.56 (m, 6H), 3.31-3.35 (t, *J* = 5.6 Hz, 4H), 4.78-4.91 (sept, 1H).
**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 22.3, 24.5, 25.7, 44.6, 68.2, 155.3.
**IR (neat) ν:** 1023, 1147, 1688
**MS (EI) m/z** 171($M^{+\cdot}$)

## ***Tert*-butyl 4-methylpiperidine-1-carboxylate (5a)**




A solution of 4-Methylpiperidine (2 mL, 16.94 mmol, 1 equiv.) and triethylamine (2.36 mL, 16.94 mmol, 1 equiv.) in 10 mL of THF was cooled to 0°C, and di-*tert*-butyl dicarbonate (3.70

[14] Luo, Q.L.; Lv, L.; Li, Y.; Tan, J-P.; Nan, W.; Hui, Q. *Eur. J. Org. Chem.* **2011**, 6916

g, 16.94 mmol, 1 equiv.) was added portionwise. The mixture was stirred for 10 min, warmed to room temperature, and then stirred for 4 hours. The mixture was diluted with 10 mL of water, and extracted with ethyl acetate (2 x 15 mL). The organic layers were dried over $MgSO_4$ and then concentrated to give a crude product which was distilled under reduced pressure to give 2.7 g (80 %) of **5a** as a colorless oil: bp 70°C/0.1 mBar.

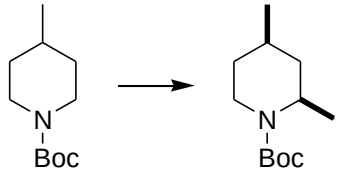
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 0.92-0.94 (d, *J* = 6.4 Hz, 3H), 1.00-1.14 (m, 2H), 1.45 (s, 9H), 1.56 (m, 1H), 1.62 (br, 2H), 2.63-2.71 (t, *J* = 12.6 Hz, 2H), 4.06-4.03 (m, 2H)

**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 21.9, 28.5, 31.0, 34.1, 44.1, 79.1, 155.0.

**IR (neat) ν:** 1238, 1689

**MS (EI) m/z** 199($M^{+\cdot}$)

## *Tert*-butyl 2,4-dimethylpiperidine-1-carboxylate (5b)




In a Schlenk-tube under argon, a solution of *tert*-butyl 4-methylpiperidine-1-carboxylate (1.5 g, 7.53 mmol, 1equiv.) and TMEDA (1.36 mL, 9.03 mmol, 1.2 equiv.) in 15 mL of anhydrous diethylether was cooled to -78 °C and s-BuLi (1.1 M in hexanes) (8.2 mL, 9.03 mmol, 1.2 equiv.) was slowly added via syringe. The reaction mixture was stirred for 3 hours at this temperature before dimethylsulfate (0.79 mL, 8.28 mmol, 1.1 equiv.) was added. The reaction mixture was stirred for 1 hour at -78 °C and then was warmed to room temperature and stirred for 1 hour. The reaction mixture was quenched with 7.5 ml of $NH_4Cl$ sat, extracted with ethyl acetate (2 x 10 mL), washed with brine (10 mL). The organic layers were dried over $MgSO_4$ and then concentrated to give a crude product which was distilled under reduced pressure to give 816 mg (51 %) of **5b** as a colorless oil: bp 80 °C/0.1 mBar.

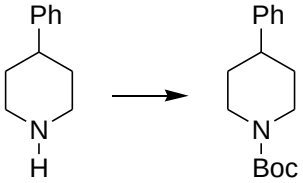
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 0.95-0.98 (d, *J* = 6.8 Hz, 3H), 1.05-1.13 (m, 2H), 1.15-1.18 (d, *J* = 6.5 Hz, 3H), 1.45 (s, 9H), 1.60-1.74 (m, 2H), 1.80-1.90 (m, 1H), 3.01-3.11 (ddd, *J* = 13.8, 10.1, 5.7 Hz, 1H), 3.62-3.70 (ddd, *J* = 13.9, 7.0, 3.4 Hz, 1H), 3.82-3.94 (m, 1H).

**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 20.1, 21.7, 26.6, 28.6, 31.4, 37.1, 38.0, 49.3, 79.0, 155.5.

**IR (neat) ν:** 1037, 1245, 1687

**MS (EI) m/z** 213 ($M^{+\cdot}$)

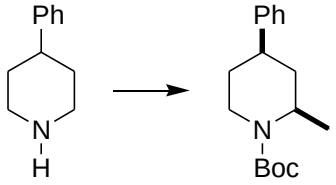
## *Tert*-butyl 4-phenylpiperidine-1-carboxylate




A solution of 4-phenylpiperidine (1 g, 6.20 mmol, 1 equiv.) and triethylamine (0.86 mL, 6.20 mmol, 1 equiv.) in 5 mL of THF was cooled to 0°C, and di-*tert*-butyl dicarbonate (1.33 g, 6.20 mmol, 1 equiv.) was added portionwise. The mixture was stirred for 10 min, warmed to room temperature, and then stirred for 22 hours. The mixture was diluted with 10 mL of

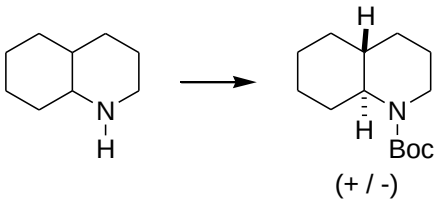
water, and extracted with ethyl acetate (2 x 15 mL). The organic layers were dried over $MgSO_4$ and then concentrated to give a crude product which was distilled under reduced pressure to give 1.22 g (75 %) of desired product as a colorless oil: bp 152 °C/0.1 mBar.
According to X. Hu et *al.*[15]
**$^1$H NMR (400 MHz, $CDCl_3$, 293 K) δ:** 1.49 (s, 9H), 1.62 (qd, *J* = 12.6, 3.5 Hz, 2H), 1.82 (m, 2H), 2.63 (m, 1H), 2.81 (m, 2H), 4.24 (m, 2H), 7.21 (m, 3H), 7.31 (m, 2H).

## *Tert*-butyl *cis*-2-methyl-4-phenylpiperidine-1-carboxylate (5c)




In a Schlenk-tube under argon, a solution of *tert*-butyl 4-phenylpiperidine-1-carboxylate (700 mg, 2.68 mmol, 1 equiv.) and TMEDA (485 µL, 3.21 mmol, 1.2 equiv.) in anhydrous diethylether was cooled to -78 °C and s-BuLi (1.2 M in hexanes) (2.68 mL, 3.21 mmol, 1.2 equiv.) was slowly added via syringe. The reaction mixture was stirred for 4 hours at this temperature before dimethylsulfate (0.28 mL, 2.95 mmol, 1.1 equiv.) was added. The reaction mixture was stirred for 30 min at -78 °C and then was slowly allowed to warm to room temperature and stirred for 1 hour. The reaction mixture was quenched with 7.5 mL of $NH_4Cl$ sat, extracted with ethyl acetate (2 x 10 mL), washed with brine (10 mL). The organic layers were dried over $MgSO_4$ and then concentrated to give a crude product which was distilled under reduced pressure to give 434 mg (59 %) of **5c** as a colorless oil: bp 147 °C/0.1 mBar.
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.19-1.21 (d, *J* = 6.3 Hz, 3H), 1.49 (s, 9H), 1.57-1.63 (m, 2H), 1.87-1.95 (ddd, *J* = 13.3, 6.2, 1.1 Hz, 1H), 2.10-2.23 (m, 1H), 2.70-2.82 (m, 1H), 3.20-3.30 (ddd, *J* = 13.9, 9.7, 6.4 Hz, 1H), 3.76-3.85 (ddd, *J* = 13.3, 7.6, 3.1 Hz, 1H), 3.92-4.02 (m, 1H), 7.18-7.22 (m, 3H), 7.28-7.33 (m, 2H).
**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 20.0, 28.6, 31.4, 37.2, 37.7, 38.1, 50.2, 79.3, 126.2, 126.9, 128.6, 146.2, 155.5.
**IR (neat) ν:** 1047, 1247, 1685
**MS (EI) m/z** 275 ($M^{+\cdot}$)

## *Tert*-butyl *trans*-decahydroquinoline-1-carboxylate (9)

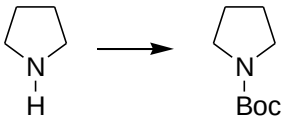



A solution of *cis*- and *trans*-decahydroquinoline mixture (2 g, 14.36 mmol, 1 equiv.) and triethylamine (2 mL, 14.36 mmol, 1 equiv.) in 20 mL of THF was cooled to 0°C, and di-*tert*-butyl dicarbonate (3.13 g, 14.36 mmol, 1 equiv.) was added portionwise. The mixture was

[15] Vechorkin, O.; Proust, V.; Hu, X. *J. Am. Chem. Soc.* **2009**, *131*, 9756

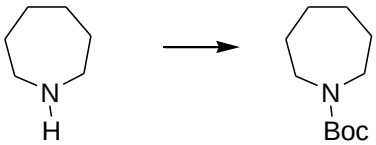
stirred for 10 min, warmed to room temperature, and then stirred for 72 hours. The mixture was diluted with 25 mL of water, and extracted with ethyl acetate (2 x 25 mL). The organic layers were dried over $MgSO_4$ and then concentrated to give a crude product which was distilled under reduced pressure to give 1.77 g (51 %) of **9** as colorless oil: bp 150 °C/1 mmHg.
According to A. I. Meyers *et al*.[16]
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 0.90-1.90 (m, 12H), 1.45 (s**,** 9H), 2.08 (m, 1H), 2.97-3.06 (ddd, *J* = 10.6, 10.6, 3.1 Hz, 1H), 3.12-3.22(ddd, *J* = 10.6, 10.6, 5.0 Hz, 1H), 3.57-3.64 (ddd, *J* = 10.6, 6.5, 2.8 Hz, 1H).

## ***Tert*-butyl pyrrolidine-1-carboxylate**




A solution of pyrrolidine (2.5 mL, 30 mmol, 1 equiv.) and triethylamine (4.25 mL, 30 mmol, 1 equiv.) in 10 mL of THF was cooled to 0°C, and di-*tert*-butyl dicarbonate (6.64 g, 30 mmol, 1 equiv.) was added portionwise. The mixture was stirred for 10 min, warmed to room temperature, and then stirred for 72 hours. The mixture was diluted with 15 mL of HCl 1N, and extracted with ethyl acetate (2 x 25 mL). The organic layers were dried over $MgSO_4$ and then concentrated to give a crude product which was distilled under reduced pressure to give 3.6 g (69 %) of *tert*-butyl pyrrolidine-1-carboxylate as a colorless oil: bp 70-75 °C/0.5 mmHg.
According to R.K. Dieter *et al*.19
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.46 (s, 9H), 1.84 (m, 4H), 3.30 (m, 4 H).

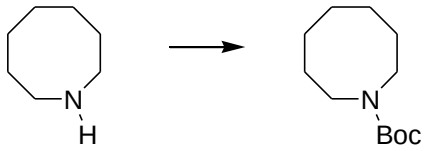
## ***Tert*-butyl perhydroazepine-1-carboxylate**




A solution of azepane (1g, 10 mmol, 1equiv.) and triethylamine (1.4, 10 mmol, 1 equiv.) in 5 mL of THF was cooled to 0°C, and di-*tert*-butyl dicarbonate (2.2 g, 10 mmol, 1 equiv.) was added portionwise. The mixture was stirred for 10 min, warmed to room temperature, and then stirred for 4 hours. The mixture was diluted with 10 mL of water, and extracted with ethyl acetate (2 x 15 mL). The organic layers were dried over $MgSO_4$ and then concentrated to give a crude product which was distilled under reduced pressure to give 1.23 g (62 %) of *tert*-butyl perhydroazepine-1-carboxylate as a colorless oil: bp 110-115 °C/0.5 mmHg.
According to P. Beak *et al*.19
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.46 (s, 9H), 1.52-1.59 (br, 4H), 1.65-1.67 (br, 4H), 3.29-3.41 (m, 4 H).

[16] Meyers, A.I.; Milot, G. *J. Am. Chem. Soc.* **1993**, *115*, 6652

## ***Tert*-butyl azocane-1-carboxylate**




A solution of azocane (1g, 8.83 mmol, 1 equiv.) and triethylamine (1.23, 8.83 mmol, 1 equiv.) in 5 mL of THF was cooled to 0°C, and di-*tert*-butyl dicarbonate (1.93 g, 8.83 mmol, 1 equiv.) was added portionwise. The mixture was stirred for 10 min, warmed to room temperature, and then stirred for 24 hours. The mixture was diluted with 10 mL of water, and extracted with ethyl acetate (2 x 15 mL). The organic layers were dried over $MgSO_4$ and then concentrated to give a crude product which was distilled under reduced pressure to give 1.41 g (75 %) of *tert*-butyl azocane-1-carboxylate as a colorless oil: bp 95 °C/ 0.1 mBar.

**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.46 (s, 9H), 1.52 (br m, 6H), 1.62-1.70 (m, 4H), 3.25-3.29 (t, *J* = 6.0 Hz, 2H), 3.31-3.36 (t, *J* = 6.0 Hz, 2H ).

**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 25.0, 26.2, 26.3, 27.2, 27.6, 28.7, 47.5, 48.0, 79.0, 155.6.

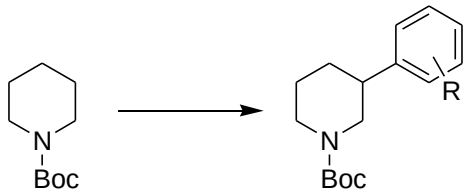
**IR (neat) ν:** 1051, 1687

**MS (EI) m/z** 213($M^{+\cdot}$)

# β-Arylation of Boc-piperidines

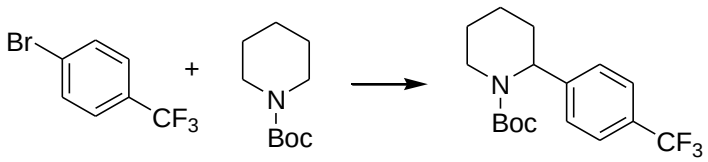
## Arylation of unsubstituted piperidine

**General procedure A for arylation reactions of *tert*-butyl piperidine-1-carboxylate:**




In a Schlenk-tube under argon, a solution of *tert*-butyl piperidine-1-carboxylate **1a** (92.6 mg, 0.5 mmol, 1 equiv.) and TMEDA (90 μL, 0.6 mmol, 1.2 equiv.) in anhydrous diethylether (1 mL) was cooled to -78 °C and s-BuLi (1,4 M in cyclohexane) (0.43 mL, 0.6 mmol, 1.2 equiv.) was slowly added via syringe. The reaction mixture was stirred for 3 h at this temperature before a solution of $ZnCl_2$ (0.5 or 0.7 M in THF) (1.2 or 0.85 mL, 0.6 mmol, 1.2 equiv.) was added. The reaction mixture was stirred for 30 min at -78 °C and was then allowed to warm to room temperature and stirred for 1 hour. Solvents were removed in vaccuo. Meanwhile, a solution of $Pd_2(dba)_3.CHCl_3$ (12.9 mg, 0.025 mmol, 2.5 mol%) and ligand (0.05 mmol, 5 mol%) was prepared in 1.5 mL of anhydrous toluene and allowed to stirred for 15 min at room temperature. The catalyst solution was added to the piperidinylzinc reagent followed by the arylbromide (0.35 mmol, 0.7 eq). This mixture was heated to 60°C for 17 hours. $NH_4Cl$ sat. aq. solution (2 mL) was added, and aqueous layer was extracted with EtOAc (2 x 5 mL). The combined organic layers were dried over $MgSO_4$. The solvents were evaporated and the residue was subjected to column chromatography yielding the β-arylated product.

***Tert*-butyl 2-[4-(trifluoromethyl)phenyl]piperidine-1-carboxylate (2a)**




The above compound was prepared according to general procedure **A** from 4-bromobenzotrifluoride and *tert*-butyl piperidine-1-carboxylate (**1a**) and Sphos as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived 77 mg (67 %) of the desired compound as a colorless oil.

Selectivity α/β: 96 : 4 (determined from GCMS of crude)

**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.31-1.37 (m, 1H), 1.45 (s, 9H), 1.52-1.64 (m, 3H), 1.86-1.98 (m, 1H), 2.26-2.31 (br d, 1H), 2.69-2.79 (dt, *J* = 13.7, 4.1 Hz, 1H), 4.05-4.09 (br d, 1H), 5.43 (br s, 1H), 7.31-7.34 (d, *J* = 8.0 Hz, 2H), 7.57-7.60 (d, *J* = 8.1 Hz, 2H).

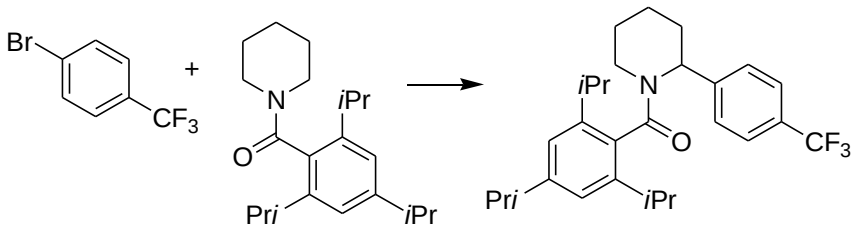
**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 19.4, 25.4, 28.3, 28.5, 40.4, 53.3, 80.0, 122.5, 125.5 (q, *J* = 3.7 Hz), 126.1, 127.0, 128.2 (q, *J* = 32.4 Hz), 145.1, 155.7.

**$^{19}$F-{$^1$H} NMR (282 MHz, $CDCl_3$, 293 K) δ:** -62.4.

**IR (neat) ν :** 1067, 1687

**HRMS (ESI) m/z:** calculated for $C_{17}H_{22}F_3NNaO_2$ ($[M+Na]^+$): 352.1495; found 352.1495.

## (2-[4-(trifluoromethyl)phenyl]piperidin-1-yl)(2,4,6-triisopropylphenyl)methanone (2e)




The above compound was prepared according to general procedure **A** from 4-bromobenzotrifluoride and (2,4,6-triisopropylphenyl)(piperidin-1-yl)methanone (**1e**) and Davephos as ligand. Purification on silica gel (elution with dichloromethane) gived 109.3 mg (68 %) of the desired compound as a white solid.

Selectivity $\alpha/\beta$: 96 : 4 (determined from GCMS of crude)

**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.20-1.33 (m**,** 18H), 1.43-1.52 (m, 2H), 1.57-1.67 (m, 1H) 1.73-1.77 (m, 1H) 1.96-2.08 (m, 1H), 2.43-2.47 (br d, 1H), 2.85-3.03 (m, 4H), 3.42-3.46 (br d, 1H), 6.30-6.31 (d, *J* = 4.3 Hz, 1H), 7.00-7.04 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.53-7.56 (d, *J* = 7.8 Hz, 2H), 7.62-7.65 (d, *J* = 8.2 Hz, 2H).

**$^{13}$C-{$^1$H} NMR (100 MHz, $CDCl_3$, 293 K) δ:** 19.8, 23.5, 23.8, 24.1, 24.8, 25.9, 26.0, 28.1, 31.1, 31.2, 31.4, 34.4, 43.7, 50.3, 121.3, 121.4, 123.0, 125.5 (q, *J* = 3.8 Hz), 127.3, 127.7, 128.7 (q, *J* = 32.1 Hz), 131.8, 144.2, 144.4, 144.5, 149.5, 171.1.

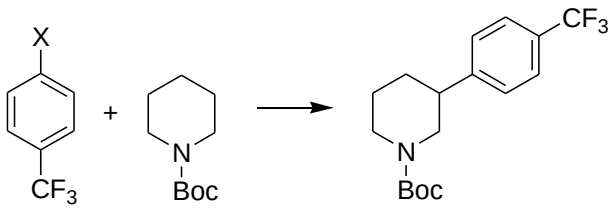
**$^{19}$F-{$^1$H} NMR (282 MHz, $CDCl_3$, 293 K) δ:** -62.4.

**IR (neat) ν :** 1167, 1271, 1614

**HRMS (ESI) m/z:** calculated for $C_{28}H_{36}F_3NNaO$ ($[M+Na]^+$): 482.2641; found 482.2635.

**Mp** = 144-146 °C.

## *Tert*-butyl 3-[4-(trifluoromethyl)phenyl]piperidine-1-carboxylate (3a)




X = Cl, Br, I, OTf

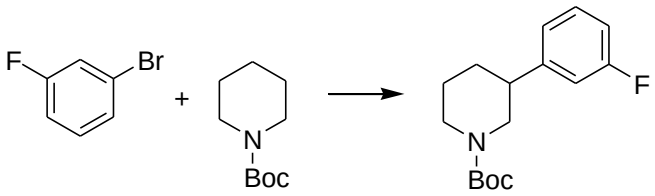
The above compound was prepared according to general procedure **A** from 4-halogenobenzotrifluoride or 4-(trifluoromethyl)phenyl trifluoromethansulfonate and *tert*-butyl piperidine-1-carboxylate (**1a**) using **L**[8] as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived of the desired compound as a white solid.

| X | Mass (mg) | Yield (%) | Selectivity $\beta/\alpha^*$ |
|---|---|---|---|
| Cl | 63.6 | 55 | 89 : 11 |
| Br | 68 | 59 | 91 : 9 |
| I | 62.4 | 54 | 89 : 11 |
| OTf | 65.3 | 57 | 9 : 1 |

* determined from GCMS of crude

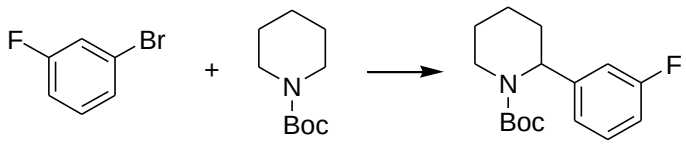
**$^{1}$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.47 (s**,** 9H), 1.59-1.66 (m, 2H), 1.75-1.79 (m, 1H), 2.00-2.03 (m, 1H), 2.73-2.79 (m, 3H), 4.13-4.16 (m, 2H), 7.32-7.35 (d, *J* = 8.1 Hz, 2H), 7.55-7.58 (d, *J* = 8.1 Hz, 2H).
**$^{13}$C-{$^{1}$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 25.4, 28.6, 31.7, 42.5, 44.3, 50.3, 79.8, 122.5, 125.5 (q, *J* = 3.7 Hz), 126.1, 127.6, 128.4 (q, *J* = 32.1 Hz), 147.7, 154.9.
**$^{19}$F-{$^{1}$H} NMR (282 MHz, $CDCl_3$, 293 K) δ:** -62.4.
**IR (neat) ν :** 1261, 1689
**HRMS (ESI) m/z:** calculated for $C_{17}H_{22}F_3NNaO_2$ ($[M+Na]^+$): 352.1495; found 352.1510.
**Mp** = 84 °C.

## *Tert*-butyl 3-(3-fluorophenyl)piperidine-1-carboxylate (3f)




The above compound was prepared according to general procedure **A** from 3-bromo-fluorobenzene and *tert*-butyl piperidine-1-carboxylate (**1a**) using **L$^{8}$** as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived 61.2 mg (63 %) of the desired compound as a yellow solid.
Selectivity β/α: 9 : 1 (determined from GCMS of crude)
**$^{1}$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.46 (s**,** 9H), 1.53-1.58 (m, 2H), 1.73-1.76 (m, 1H), 1.99-2.02 (m, 1H), 2.63-2.77 (m, 3H), 4.11-4.14 (m, 2H), 6.87-6.93 (m, 2H), 6.98-7.01 (d, *J* = 7.7 Hz, 1H), 7.22-7.29 (q, *J* = 6.6, 7.8 Hz, 1H).
**$^{13}$C-{$^{1}$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 25.4, 28.5, 31.7, 42.3, 44.3, 50.5, 79.6, 113.3 (d, *J* = 21 Hz), 113.9 (d, *J* = 21 Hz), 122.9 (d, *J* = 2.25 Hz), 129.9 (d, *J* = 8.25 Hz), 146.2 (d, *J* = 6.75 Hz), 154.9, 161.4 (d, *J* = 243.75 Hz).
**$^{19}$F-{$^{1}$H} NMR (282 MHz, $CDCl_3$, 293 K) δ:** -113.3.
**IR (neat) ν :** 1029, 1245, 1686
**HRMS (ESI) m/z:** calculated for $C_{16}H_{22}FNNaO_2$ ($[M+Na]^+$): 302.1527; found 302.1527.
**Mp** = 60 °C.

## *Tert*-butyl 2-(3-fluorophenyl)piperidine-1-carboxylate (2f)




The above compound was prepared according to general procedure **A** from 3-bromo-fluorobenzene and *tert*-butyl piperidine-1-carboxylate (**1a**) using **L$^{8}$** as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived the desired compound as a yellow oil.
Selectivity β/α: 9 : 1 (determined from GCMS of crude)
**$^{1}$H NMR (400 MHz, $CDCl_3$, 293 K) δ:** 1.36-1.43 (m, 1H), 1.46 (s**,** 9H), 1.49-1.63 (m, 3H), 1.83-1.93 (m, 1H), 2.21-2.28 (d m, *J* = 14.2 Hz, 1H), 2.71-2.78 (dd, *J* = 12.1, 3.7 Hz, 1H), 4.03-4.07

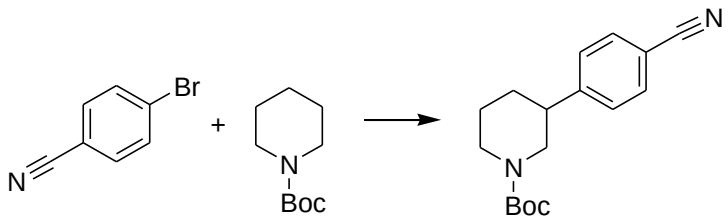
(br d, *J* = 13.6 Hz, 1H), 5.38-5.39 (br d, *J* = 4.0 Hz, 1H), 6.89-6.94 (m, 2H), 6.98-7.00 (d m, *J* = 7.8 Hz, 1H), 7.27-7.33 (ddd, *J* = 8.9, 7.9, 3.4 Hz, 1H).

**$^{13}$C-{$^{1}$H} NMR (100.6 MHz, $CDCl_3$, 293 K) δ:** 19.5, 25.5, 28.3, 28.6, 40.3, 53.2, 79.9, 113.3 (d, *J* = 21.1 Hz), 113.6 (d, *J* = 22 Hz), 122.2 (d, *J* = 2.5 Hz), 130.1 (d, *J* = 8.1 Hz), 143.6 (d, *J* = 6.4 Hz), 155.7, 162.3 (d, *J* = 243.6 Hz).

**$^{19}$F-{$^{1}$H} NMR (376 MHz, $CDCl_3$, 293 K) δ:** -113.2.

**HRMS (ESI) m/z:** calculated for $C_{16}H_{22}FNNaO_2$ ($[M+Na]^+$): 302.1527; found 302.1527.

## *Tert*-butyl 3-(4-cyanophenyl)piperidine-1-carboxylate (3g)




The above compound was prepared according to general procedure **A** from 4-bromobenzonitrile and *tert*-butyl piperidine-1-carboxylate (**1a**) using **L$^8$** as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 90 / 10) gived 51.4 mg (51 %) of the desired compound as a yellow oil.

Selectivity β/α: 85 : 15 (determined from GCMS of crude)

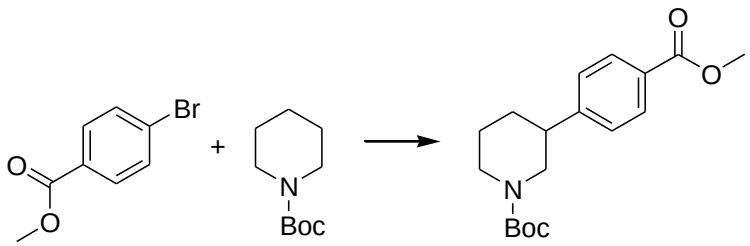
**$^{1}$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.45 (s**,** 9H), 1.53-1.63 (m, 2H), 1.73-1.76 (m, 1H), 1.98-2.01 (m, 1H), 2.71-2.74 (m, 3H), 4.09-4.13 (m, 2H), 7.30-7.33 (d, *J* = 8.3 Hz, 2H), 7.57-7.60 (d, *J* = 8.2 Hz, 2H).

**$^{13}$C-{$^{1}$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 25.2, 28.5, 31.5, 42.6, 44.2, 49.9, 79.8, 110.5, 118.9, 128.0, 132.4, 149.0, 154.8.

**IR (neat) ν :** 1254, 1689, 2226

**HRMS (ESI) m/z:** calculated for $C_{17}H_{22}N_2NaO_2$ ($[M+Na]^+$): 309.1573; found 309.1583.

## *Tert*-butyl 3-(4-(methoxycarbonyl)phenyl)piperidine-1-carboxylate (3h)



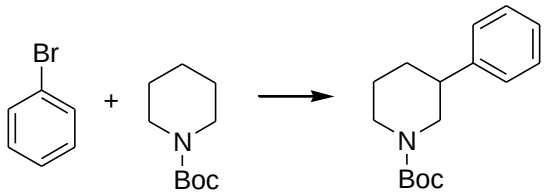

The above compound was prepared according to general procedure **A** from methyl 4-bromobenzoate and *tert*-butyl piperidine-1-carboxylate (**1a**) using **L$^8$** as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 90 / 10) gived 64.1 mg (57 %) of the desired compound as a white solid.

Selectivity β/α: 82 : 18 (determined from GCMS of crude)

**$^{1}$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.46 (s**,** 9H), 1.58-1.66 (m, 2H), 1.73-1.77 (m, 1H), 1.99-2.03 (m, 1H), 2.72-2.78 (m, 3H), 3.89 (s, 3H), 4.13-4.15 (m, 2H), 7.27-7.30 (d, *J* = 8.4 Hz, 2H), 7.96-7.98 (d, *J* = 8.3 Hz, 2H).

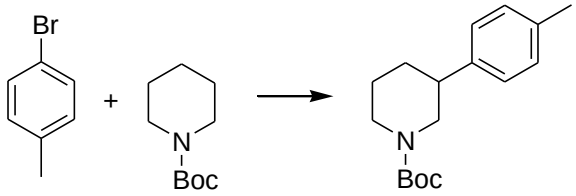
**$^{13}$C-{$^{1}$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 25.3, 28.5, 31.6, 42.6, 44.3, 50.2, 52.1, 79.6, 127.2, 128.6, 129.9, 148.9, 154.8, 167.0.
**IR (neat) ν :** 1018, 1264, 1688, 1717
**HRMS (ESI) m/z:** calculated for $C_{18}H_{25}NNaO_4$ ($[M+Na]^+$): 342.1676; found 342.1670.
**Mp** = 58 °C.

## *Tert*-butyl 3-phenylpiperidine-1-carboxylate (3i)



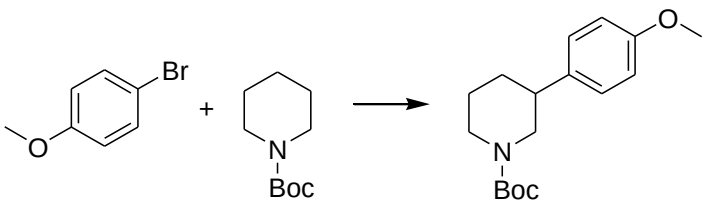

The above compound was prepared according to general procedure **A** from bromobenzene and *tert*-butyl piperidine-1-carboxylate (**1a**) using **L$^8$** as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived 40.8 mg (45 %) of the desired compound as a white solid.
Selectivity β/α: 9 : 1 (determined from GCMS of crude)
**$^{1}$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.46 (s, 9H), 1.58-1.65 (m, 2H), 1.73-1.76 (m, 1H), 1.99-2.03 (m, 1H), 2.69-2.76 (m, 3H), 4.13-4.17 (m, 2H), 7.21-7.33 (m, 5H).
**$^{13}$C-{$^{1}$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 25.6, 28.6, 31.9, 42.7, 44.5, 50.8, 79.5, 126.7, 127.2, 128.6, 143.7, 154.9.
Selectivity β/α: 9 : 1
**IR (neat) ν :** 1253,1694
**HRMS (ESI) m/z:** calculated for $C_{16}H_{23}NNaO_2$ ($[M+Na]^+$): 284.1621; found 284.1621.
**Mp** = 72-74 °C.

## *Tert*-butyl 3-(4-tosyl)piperidine-1-carboxylate (3j)




The above compound was prepared according to general procedure **A** from 4-bromotoluene and *tert*-butyl piperidine-1-carboxylate (**1a**) using **L$^8$** as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 98 / 2) gived 67.5 mg (70 %) of the desired compound as a yellow solid.
Selectivity β/α: 82 : 18 (determined from GCMS of crude)
**$^{1}$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.47 (s, 9H), 1.54-1.64 (m, 2H), 1.74-1.77 (m, 1H), 1.99-2.02 (m, 1H), 2.33 (s, 3H), 2.60-2.76 (m, 3H), 4.10 (bm, 2H), 7.13 (s, 4H).
**$^{13}$C-{$^{1}$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 21.1, 25.6, 28.6, 32.0, 42.2, 44.3, 50.8, 79.5, 127.7, 129.3, 136.2, 140.7, 154.9.
**IR (neat) ν :** 1029, 1254, 1686
**HRMS (ESI) m/z:** calculated for $C_{17}H_{25}NNaO_2$ ($[M+Na]^+$): 298.1778; found 298.1771.
**Mp** = 54-56 °C.

## *Tert*-butyl 3-(4-methoxyphenyl)piperidine-1-carboxylate (3k)




The above compound was prepared according to general procedure **A** from 4-bromoanisole and *tert*-butyl piperidine-1-carboxylate (**1a**) using **L**[8] as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 90 / 10) gived 56.5 mg (55 %) of the desired compound as an oil.

Selectivity β/α: 88 : 12 (determined from GCMS of crude)

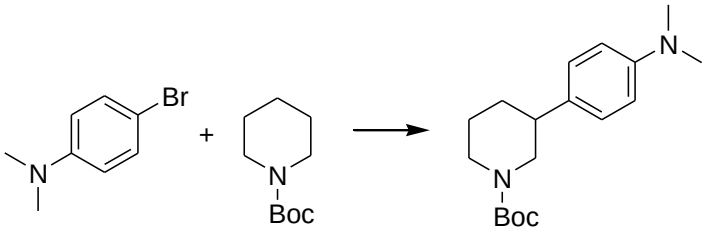
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.47 (s**,** 9H), 1.57-1.60 (m, 2H), 1.73-1.83 (m, 1H), 1.97-2.00 (m, 1H), 2.62-2.71 (m, 3H), 3.79 (s, 3H), 4.11-4.15 (m, 2H), 6.84-6.87 (d, *J* = 8.6 Hz, 2H), 7.13-7.16 (d, *J* = 8.7 Hz, 2H).

**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 25.6, 28.6, 32.0, 41.8, 44.3, 51.1, 55.3, 79.5, 114.0, 128.1, 135.8, 154.9, 158.3.

**IR (neat) ν :** 1034, 1243, 1685

**HRMS (ESI) m/z:** calculated for $C_{17}H_{25}NNaO_3$ ($[M+Na]^+$): 314.1727; found 314.1720.

## *Tert*-butyl 3-(4-(dimethylamino)phenyl)piperidine-1-carboxylate (3l)




The above compound was prepared according to general procedure **A** from 4-bromo-*N,N*-dimethylaniline and *tert*-butyl piperidine-1-carboxylate (**1a**) using **L**[8] as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived 51.2 mg (48 %) of the desired compound as a white solid.

Selectivity β/α: 78 : 22 (determined from GCMS of crude)

**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.47 (s**,** 9H), 1.57-1.60 (m, 2H), 1.74-1.76 (m, 1H), 1.97-2.00 (m, 1H), 2.55-2.74 (m, 3H), 2.93 (s, 6H), 4.14-4.17 (m, 2H), 6.70-6.73 (d, *J* = 8.4 Hz, 2H), 7.10-7.13 (d, *J* = 8.4 Hz, 2H).

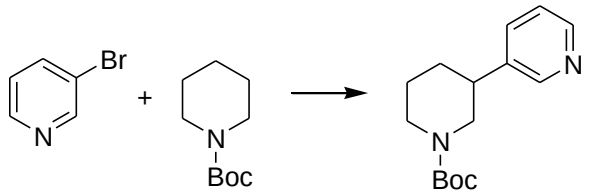
**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 25.7, 28.6, 32.1, 40.9, 41.7, 44.0, 51.1, 79.4, 112.9, 127.8, 131.8, 149.5, 155.0.

**IR (neat) ν :** 1264, 1684

**HRMS (ESI) m/z:** calculated for $C_{18}H_{29}N_2O_2$ ($[M+H]^+$): 305.2224; found 305.2222.

**Mp** = 96-98 °C.

## *Tert*-butyl 3-(pyridin-3-yl)piperidine-1-carboxylate (3m)




The above compound was prepared according to general procedure **A** from 3-bromopyridine and *tert*-butyl piperidine-1-carboxylate (**1a**) using **L**[8] as ligand at 80°C for 17 hours. Purification on silica gel (elution with $CH_2Cl_2$ / MeOH: 98.5 / 1.5) gived 57.3 mg (62 %) of the desired compound as an oil.

Selectivity β/α: 91 : 9 (determined from GCMS of crude)

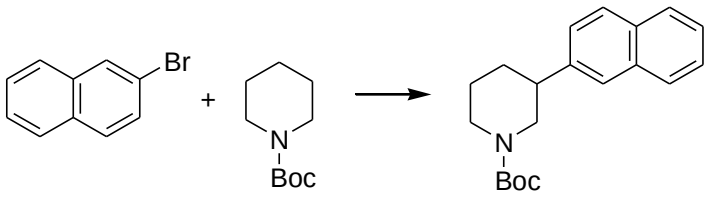
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.44 (s**,** 9H), 1.53-1.64 (m, 2H), 1.73-1.77 (m, 1H), 1.98-2.01 (m, 1H), 2.70-2.78 (m, 3H), 4.10-4.13 (m, 2H), 7.19-7.21 (m, 1H), 7.50-7.53 (m, 1H), 8.44-8.48 (m, 2H).

**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 25.3, 28.5, 31.5, 40.1, 44.2, 50.2, 79.8, 123.5, 134.5, 138.8, 148.2, 149.1, 154.8.

**IR (neat) ν :** 1024, 1256, 1684

**HRMS (ESI) m/z:** calculated for $C_{15}H_{23}N_2O_2$ ($[M+H]^+$): 263.1754; found 263.1763.

## *Tert*-butyl 3-(2-naphtyl)piperidine-1-carboxylate (3n)




The above compound was prepared according to general procedure **A** from 4-bromoanisole and *tert*-butyl piperidine-1-carboxylate (**1a**) using **L**[8] as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 98 / 2) gived 66.7 mg (61 %) of the desired compound as a white solid.

Selectivity β/α: 71 : 29 (determined from GCMS of crude)

**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.50 (s**,** 9H), 1.62-1.84 (m, 3H), 2.10-2.13 (m, 1H), 2.76-2.87 (m, 3H), 4.22 (m, 2H), 7.37-7.41 (dd, *J* = 8.7, 1.3 Hz, 1H), 7.44-7.48 (m, 2H), 7.68 (s, 1H), 7.79-7.83 (m, 3H).

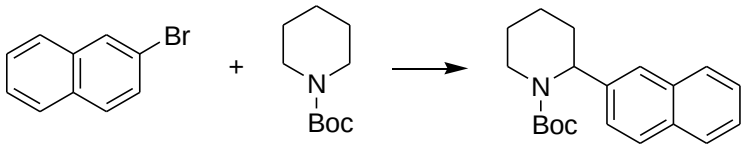
**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 25.6, 28.6, 31.8, 42.7, 44.3, 50.7, 79.6, 125.3, 125.6, 126.0, 126.1, 127.6, 127.7, 128.1, 132.5, 133.6, 141.1, 155.0.

**IR (neat) ν :** 1028, 1265, 1690

**HRMS (ESI) m/z:** calculated for $C_{20}H_{25}NNaO_2$ ($[M+Na]^+$): 334.1778; found 334.1770.

**Mp** = 72-74 °C.

## *Tert*-butyl 2-(2-naphtyl)piperidine-1-carboxylate (2n)



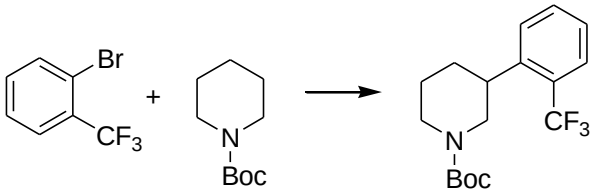

The above compound was prepared according to general procedure **A** from 4-bromoanisole and *tert*-butyl piperidine-1-carboxylate (**1a**) using **L**[8] as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 98 / 2) gived 11.3 mg (10.3 %) of the desired compound as a white solid.

**$^1$H NMR (400 MHz, $CDCl_3$, 293 K) δ:** 1.48 (s**,** 9H), 1.52-1.59 (m, 3H), 1.63-1.67 (m, 1H), 1.92-2.01 (m, 1H), 2.41-2.47 (br m, *J* = 14.2 Hz 1H), 2.79-2.87 (m, 1H), 4.08-4.12 (br d, *J* = 13.4 Hz , 1H), 5.56-5.57 (br d, *J* = 3.6 Hz, 1H), 7.35-7.38 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.43-7.49 (m, 2H), 7.64 (s, 1H), 7.79-7.83 (m, 3H).

**$^{13}$C-{$^1$H} NMR (100.6 MHz, $CDCl_3$, 293 K) δ:** 19.6, 25.6, 28.3, 28.6, 28.8, 40.4, 53.6, 79.8, 125.1, 125.3, 125.7, 126.2, 127.6, 128.0, 128.4, 132.3, 133.6, 138.1, 155.9.

**HRMS (ESI) m/z:** calculated for $C_{20}H_{25}NNaO_2$ ($[M+Na]^+$): 334.1778; found 334.1778.

## *Tert*-butyl 3-[2-(trifluoromethyl)phenyl]piperidine-1-carboxylate (3o)




The above compound was prepared according to general procedure **A** from 2-bromo-benzotrifluoride and *tert*-butyl piperidine-1-carboxylate (**1a**) using Davephos as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived 71.7 mg (62 %) of the desired compound as an oil.

Selectivity β/α: 97 : 3 (determined from GCMS of crude)

**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.44 (s**,** 9H), 1.63-1.77 (m, 3H), 1.95-1.99 (m, 1H), 2.68-2.79 (m, 2H), 3.03-3.10 (m, 1H), 4.14-4.26 (m, 2H), 7.28-7.33 (t, *J* = 7.5 Hz, 1H), 7.40-7.42 (d, *J* = 7.7 Hz, 1H), 7.48-7.53 (t, *J* = 7.5 Hz, 1H), 7.63-7.65 (d, *J* = 7.8 Hz, 1H).

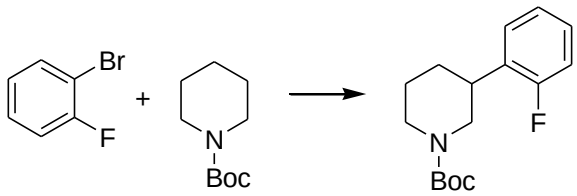
**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 25.5, 28.5, 32.3, 38.8, 44.1, 51.2, 79.7, 126.0 (q, *J* = 6.1 Hz), 126.6, 127.9, 128.0 (q, *J* = 29.1 Hz), 132.0, 142.6, 154.8.

**$^{19}$F-{$^1$H} NMR (282 MHz, $CDCl_3$, 293 K) δ:** -59.0.

**IR (neat) ν :** 1034, 1264, 1688

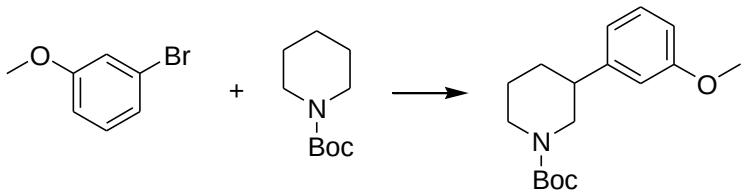
**HRMS (ESI) m/z:** calculated for $C_{17}H_{22}F_3NNaO_2$ ($[M+Na]^+$): 352.1495; found 352.1492.

## *Tert*-butyl 3-(3-fluorophenyl)piperidine-1-carboxylate (3p)




The above compound was prepared according to general procedure **A** from 2-bromo-fluorobenzene and *tert*-butyl piperidine-1-carboxylate (**1a**) using Davephos as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived 66.8 mg (68 %) of the desired compound as a yellow solid.
Selectivity β/α: 92 : 8 (determined from GCMS of crude)
**$^{1}$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.46 (s**,** 9H), 1.57-1.77 (m, 3H), 1.95-2.00 (m, 1H), 2.70-2.85 (m, 2H), 2.94-3.03 (m, 1H), 4.16 (m, 2H), 6.99-7.11 (m, 2H), 7.16-7.23 (m, 2H).
**$^{13}$C-{$^{1}$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 25.5, 28.6, 30.6, 36.2, 44.3, 49.8, 79.6, 115.5 (d, *J* = 22.5 Hz), 124.2 (d, *J* = 3.75 Hz), 128.0 (d, *J* = 8.1 Hz), 128.1 (d, *J* = 2.6 Hz), 130.3 (d, *J* = 14.5 Hz), 154.9, 159.3 (d, *J* = 244.5 Hz).
**$^{19}$F-{$^{1}$H} NMR (282 MHz, $CDCl_3$, 293 K) δ:** -119.4.
**IR (neat) ν :** 1225, 1689
**HRMS (ESI) m/z:** calculated for $C_{16}H_{22}FNNaO_2$ ($[M+Na]^+$): 302.1527; found 302.1529.
**Mp** = 76 °C.

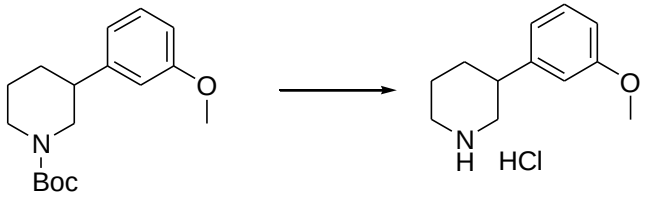
## *Tert*-butyl 3-(3-methoxyphenyl)piperidine-1-carboxylate (3q)




The above compound was prepared according to general procedure **A** from 2-bromo-fluorobenzene (1.31 g, 7 mmol) and *tert*-butyl piperidine-1-carboxylate (**1a**) (1.85g, 10 mmol) using **L**[8] as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived 1.45 g 1.45 g (71 %) of the desired compound as a pale yellow oil.
Selectivity β/α: 86 : 14 (determined from GCMS of crude)
According to J. Bosch et al.[17]
**$^{1}$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.46 (s, 9H), 1.59 (m, 2H), 1.75 (m, 1H), 2.02 (m, 1H), 2.60-2.76 (m, 2H), 2.74 (t, *J* = 11.5 Hz, 1H), 3.80 (s, 3H), 4.17 (m, 2H), 6.78 (m, 3H), 7.23 (dd, *J* = 8.3, 7.1 Hz, 1H).

[17] Amat, M.; Canto, M.; Llor, N.; Escolano, C.; Molins, E.; Espinosa,E.; Bosch, J. *J. Org. Chem*. **2002**, *67*, 5343

**3-(3-methoxyphenyl)piperidine hydrochloride (3r)**

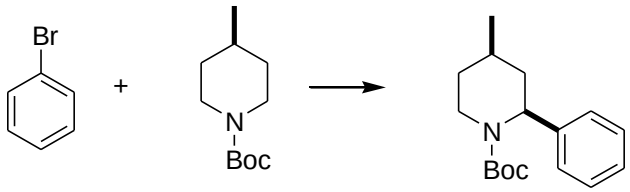



To a solution of *tert*-butyl 3-(3-methoxyphenyl)piperidine-1-carboxylate (1.45 g, 1 equiv.) in diethylether (15 mL) was added trifluoroacetic acid (14.5 mL; 40 equiv.) at 0 °C. The reaction mixture was stirred for 4 h at 20°C, then cooled to 0 °C and carefully neutralized using NaHCO3 sat. aq. solution. The resulting mixture was extracted with dichloromethane (3 x 30 mL). The combined organic phases were washed with NaOH 10%, extracted with HCl 1N (3x25 mL) and the acidic layer was evaporated via rotary evaporation with toluene and gived 992 mg (91 %) of desired product as a white powder.
According to J. Bosch et *al.*[17] and H. Wikstrom et *al.*[18]
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.58-1.70 (m, 1H), 1.97-2.12 (m, 3H), 2.88 (br m, 2H), 3.16-3.24 (br t, *J* = 13.1 Hz, 1H), 3.51-3.55 (br d, *j* = 10.0 Hz, 2H),3.79 (s, 3H), 6.72-6.81 (m, 3H), 7.21-7.24 (d, *J* = 8.0 Hz, 1H), 9.69 (br s, 1H), 9.87 (br s, 1H).

[18] Wikstrom, H.; Sanchez, D.; Lindberg, P.; Hacksell, U.; Arvidsson, L-E.; Johansson, A.M. Thorberg, S-O.; Lars, J.; Nilsson, G.; Svensson, K.; Hjorth, S.; Clark, D.; Carlssone A. *J. Med. Chem.* **1984**, *27*, 1031

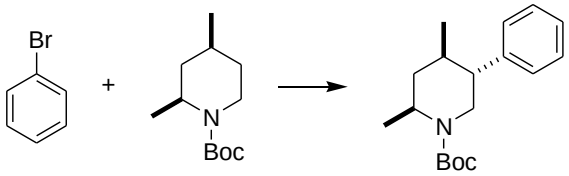
## Arylation of 4- or 2,4-(Di)substitutedpiperidine

### *Tert*-butyl 2-phenyl-4-methylpiperidine-1-carboxylate (6a)



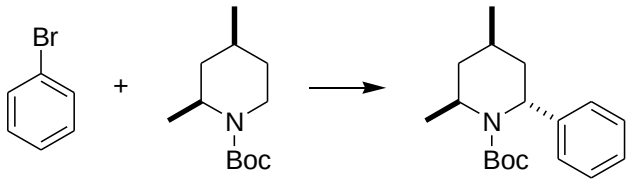

The above compound was prepared according to general procedure **A** from bromobenzene and *tert*-butyl 4-methylpiperidine-1-carboxylate (**5a**) (99.6 mg, 0.5 mmol, 1 equiv.) using **L**[8] as ligand at 80 °C. Purification on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived 30.6 mg (32 %) of the desired compound as a yellow oil.
Selectivity $\alpha/\beta$: > 98 : 2 (determined from GCMS of crude)
d.r. > 95 : 5
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 0.89-0.92 (d, *J* = 6.7 Hz, 3H), 1.28 (s, 9H), 1.44-1.61 (m, 2H), 1.75-1.87 (m, 1H), 1.93-2.04 (m, 2H), 3.25-3.35 (ddd, *J* = 13.7, 10.5, 5.6 Hz, 1H), 3.92-4.00 (ddd, *J* = 13.6, 6.9, 3.2 Hz, 1H), 4.79-4.85 (dd, *J* = 9.9, 6.3 Hz, 1H), 7.17-7.21 (m, 3H), 7.26-7.32 (m, 2H).
**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 21.7, 26.7, 28.4, 31.2, 32.5, 35.6, 57.0, 79.5, 125.3, 126.4, 128.4, 143.8, 144.9.
**IR (neat) ν :** 1144, 1685
**HRMS (ESI) m/z:** calculated for $C_{17}H_{25}NNaO_2$ ($[M+Na]^+$): 298.1778; found 298.1784.

### *Tert*-butyl 2,4-dimethyl-5-phenylpiperidine-1-carboxylate (7a)



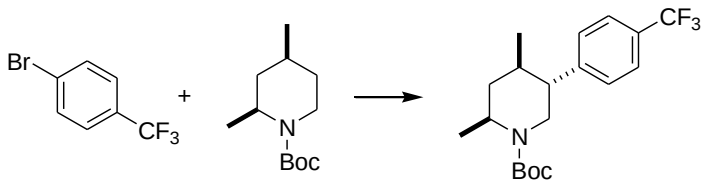

The above compound was prepared according to general procedure **A** from bromobenzene and *tert*-butyl 2,4-dimethylpiperidine-1-carboxylate (**5b**) (106.7 mg, 0.5 mmol, 1 equiv.) using **L**[8] as ligand at 80 °C. Purification on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived 76.9 mg (76 %) of the desired compound as a yellow oil.
Selectivity $\beta/\alpha$: > 98 : 2 (determined from GCMS of crude)
d.r. > 95 : 5
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 0.85-0.87 (d, *J* = 6.5 Hz, 3H), 1.23-1.25 (d, *J* = 6.4 Hz, 3H), 1.40 (s**,** 9H), 1.70-1.85 (m, 3H), 2.28-2.35 (ddd, *J* = 9.7, 6.5, 3.5 Hz, 1H), 3.43-3.50 (dd, *J* = 14, 6.6 Hz, 1H), 3.63-3.69 (dd, *J* = 14, 3.5 Hz, 1H), 3.88-4.01 (m, 1H), 7.17-7.21 (m, 3H), 7.24-7.27 (m, 2H).
**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 19.8**, 20.2, 28.6, 34.8, 38.7, 45.5, 50.2, 50.6, 79.2, 126.4, 127.8, 128.4, 145.5, 155.2.**
**IR (neat) ν :** 1018, 1246, 1685
**HRMS (ESI) m/z:** calculated for $C_{18}H_{27}NNaO_2$ ($[M+Na]^+$): 312.1934, found 312.1918.

## *Tert*-butyl 2,4-dimethyl-6-phenylpiperidine-1-carboxylate



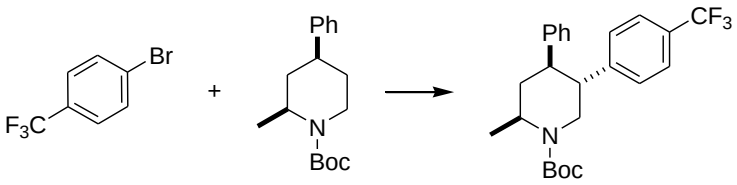

The above compound was prepared according to general procedure **A** from bromobenzene and *tert*-butyl 2,4-dimethylpiperidine-1-carboxylate (**5b**) (106.7 mg, 0.5 mmol, 1 equiv.) using Ruphos as ligand at 80°C. Purification on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived 40 mg (39 %) of the desired compound as a yellow oil.
Selectivity α/β: 60 : 40 (determined from GCMS of crude)
d.r. > 95 : 5
**$^{1}$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 0.93-0.95 (d, *J* = 6.5 Hz, 3H), 1.32 (s, 9H), 1.38-1.40 (d, *J* = 6.8 Hz, 3H), 1.60-1.82 (m, 3H), 1.86-1.95 (m, 1H), 2.09-2.14 (br d, 1H), 3.82-3.88 (q, *J* = 5.9 Hz, 1H), 5.24 (br s, 1H), 7.16-7.32 (m, 5H).
**$^{13}$C-{$^{1}$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 23.0, **23.3, 23.4, 28.4, 36.4, 38.1, 48.6, 56.4, 79.4, 126.0, 126.2, 128.3, 143.7, 156.2.**
**IR (neat) ν :** 1030, 1250, 1687
**HRMS (ESI) m/z:** calculated for $C_{18}H_{27}NNaO_2$ ([M+Na]$^{+}$): 312.1934, found 312.1921.

## *Tert*-butyl 2,4-dimethyl-5-[4-(trifluoromethyl)phenyl]piperidine-1-carboxylate (7b)



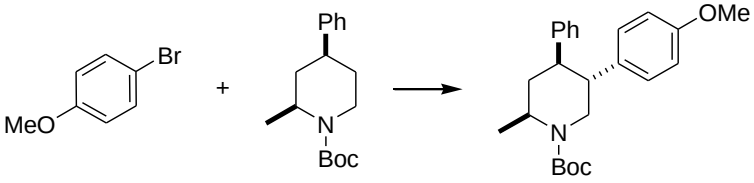

The above compound was prepared according to general procedure **A** from 4-bromobenzotrifluoride and *tert*-butyl 2,4-dimethylpiperidine-1-carboxylate (**5b**) (106.7 mg, 0.5 mmol, 1 equiv.) using **L$^{8}$** as ligand at 80°C. Purification on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived 64.1 mg (51 %) of the desired compound as a yellow oil.
Selectivity β/α: >98 : 2 (determined from GCMS of crude)
d.r. > 95 : 5
**$^{1}$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 0.86-0.88 (d, *J* = 6.5 Hz, 3H), 1.22-1.24 (d, *J* = 6.3 Hz, 3H), 1.41 (s, 9H), 1.67-1.85 (m, 3H), 2.28-2.35 (ddd, *J* = 9.5, 6.8, 2.9 Hz, 1H), 3.40-3.48 (dd, *J* = 14.2, 6.7 Hz, 1H), 3.68-3.74 (dd, *J* = 14.2, 2.9 Hz, 1H), 3.92-4.04 (m, 1H), 7.29-7.32 (d, *J* = 7.8 Hz, 2H), 7.51-7.54 (d, *J* = 8 Hz, 2H).
**$^{13}$C-{$^{1}$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 19.6, 20.0, 28.5, 34.8, 38.4, 44.5, 50.1, 60.4, 79.5, 122.6, 125.3 (q, *J* = 3.8 Hz), 126.2, 128.1, 128.2 (q, *J* = 32.6 Hz), 149.8, 155.1.
**$^{19}$F-{$^{1}$H} NMR (376 MHz, $CDCl_3$, 293 K) δ:** -62.36.
**IR (neat) ν :** 1017, 1248, 1685
**HRMS (ESI) m/z:** calculated for $C_{19}H_{26}F_3NNaO_2$ ([M+Na]$^{+}$): 380.1808; found 380.1798.

## *Tert*-butyl 2-methyl-4-phenyl-5-[4-(trifluoromethyl)phenyl]piperidine-1-carboxylate (8a)




The above compound was prepared according to general procedure **A** from 4-bromobenzotrifluoride and *tert*-butyl 2-methyl-4-phenylpiperidine-1-carboxylate (**5c**) (137.7 mg, 0.5 mmol, 1 equiv.) using **L**[8] as ligand at 80°C. Purification on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived 83 mg (57 %) of the desired compound as a colorless solid.
Selectivity β/α: > 98 : 2 (determined from GCMS of crude)
d.r. > 95 : 5
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.27-1.29 (d, *J* = 6 Hz, 3H), 1.45 (s, 9H), 1.72-1.85 (q, *J* = 11,7 Hz, 1H), 1.96-2.02 (m, 1H), 2.76-2.85 (dt, *J* = 12.6, 2.2 Hz ,1H), 2.96-3.02 (bt, *J* = 8.2 Hz, 1H), 3.57-3.64 (dd, *J* = 14.3, 6.8 Hz, 1H), 3.93-3.98 (dd, *J* = 14.5, 1.6 Hz, 1H), 4.06-4.18 (m, 1H), 6.95-6.98 (d, *J* = 6.8 Hz, 2H), 7.11-7.19 (m, 5H), 7.40-7.43 (d, *J* = 8 Hz, 2H).
**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 19.4, 28.6, 37.5, 43.9, 46.8, 49.7, 50.4, 79.7, 122.6, 125.1 (q, *J* = 2.8 Hz), 126.2, 126.6, 127.5, 128.0, 128.1 (q, *J* = 32.0 Hz), 128.5, 143.8, 150.0, 155.1.
**$^{19}$F-{$^1$H} NMR (282 MHz, $CDCl_3$, 293 K) δ:** -62.4.
**IR (neat) ν :** 1068, 1678
**HRMS (ESI) m/z:** calculated for $C_{24}H_{28}F_3NNaO_2$ ($[M+Na]^+$): 442.1964; found 442.1953.

## *Tert*-butyl 2-methyl-4-phenyl-5-[4-(methoxy)phenyl]piperidine-1-carboxylate (8b)



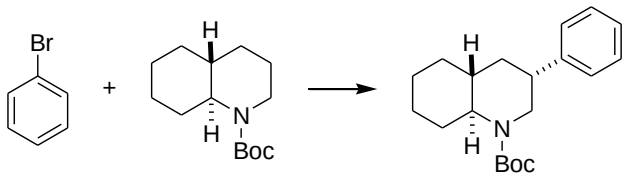

The above compound was prepared according to general procedure **A** from 4-bromoanisole and *tert*-butyl 2-methyl-4-phenylpiperidine-1-carboxylate (**5c**) (137.7 mg, 0.5 mmol, 1 equiv.) using **L**[8] as ligand at 80°C. Purification on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived 81.3 mg (61%) of the desired compound as a pale yellow oil.
Selectivity β/α: > 98 : 2 (determined from GCMS of crude)
d.r. > 95 : 5
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.27-1.29 (d, *J* = 6.2 Hz, 3H), 1.46 (s, 9H), 1.70-1.82 (q, *J* = 12.2 Hz, 1H), 1.92-2.00 (ddd, *J* = 13.7, 6.1, 2.7 Hz, 1H), 2.75-2.89 (m, 2H), 3.57-3.64 (dd, *J* = 14.1, 6.2 Hz, 1H), 3.71 (s, 3H), 3.84-3.90 (dd, *J* = 14.0, 1.8 Hz, 1H), 4.01-4.13 (m, 1H), 6.68-6.71 (d, *J* = 8.6 Hz, 2H), 6.92-6.95 (d, *J* = 8.6 Hz, 2H), 6.99-6.96 (d, *J* = 6.9 Hz, 2H), 7.11-7.20 (m, 3H).
**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 19.6, 28.6, 37.8, 45.0, 47.0, 48.9, 50.6, 55.2, 79.4, 113.6, 126.3, 127.5, 128.3, 128.6, 137.0, 144.6, 155.2, 158.0.
**IR (neat) ν :** 1027, 1243, 1682
**HRMS (ESI) m/z:** calculated for $C_{24}H_{31}NNaO_3$ ($[M+Na]^+$): 404.2196; found 404.2187.

# Arylation of *Trans*-decahydroquinoline

**General procedure B for arylation reactions of *tert*-butyl *trans*-decahydroquinoline-1-carboxylate:**

In a Schlenk-tube under argon, a solution of *tert*-butyl *trans*-decahydroquinoline-1-carboxylate (**9**) (119.7 mg, 0.5 mmol, 1 equiv.) and TMEDA (90 μL, 0.6 mmol, 1.2 equiv.) in anhydrous diethylether (1 mL) was cooled to -78 °C and s-BuLi (1,4 M in cyclohexane) (0.43 mL, 0.6 mmol, 1.2equiv.) was slowly added via syringe. The reaction mixture was stirred for 3 h at this temperature before a solution of $ZnCl_2$ (0.5 M in THF) (1.2 mL, 0.6 mmol, 1.2 equiv.) was added. The reaction mixture was stirred for 30 min at -78 °C and was then allowed to warm to room temperature and stirred for 1 hour. Solvents were removed in vaccuo. Meanwhile, a solution of $Pd_2(dba)_3.CHCl_3$ (12.9 mg, 0.025 mmol, 2.5 mol%) and ligand (0.05 mmol, 5 mol%) was prepared in 1.5 mL of anhydrous toluene and allowed to stirred for 15 min at room temperature. The catalyst solution was added to the piperidinylzinc reagent followed by the arylbromide (0.35 mmol, 0.7 eq). This mixture was heated to 80°C for 17 h. $NH_4Cl$ sat. aq. solution (2 mL) was added, and aqueous layer was extracted with EtOAc (2 x 5 mL). The combined organic layers were dried over $MgSO_4$. The solvents were evaporated and the residue was subjected to column chromatography yielding the β-arylated product.

**_Tert_-butyl _trans_-octahydro-3-phenylquinoline-1(2H)-carboxylate (10a)**




The above compound was prepared according to general procedure **B** from bromobenzene, and *tert*-butyl *trans*-decahydroquinoline-1-carboxylate (**9**) using **L**[8] as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 90 / 10) gived 62.6 mg (57 %) of the desired compound as a colorless solid.

Selectivity β/α: 96 : 4 (determined from $^1$H NMR of crude)

d.r. > 95 : 5

**$^1$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.02-1.14 (m, 1H), 1.25-1.35 (m, 3H), 1.39 (s, 9H), 1.57-1.82 (m, 5H), 1.94-2.01 (ddd, *J* = 13.1, 7.1, 3.0 Hz, 1H), 2.15-2.20 (bd, 1H), 2.89-2.99 (m, 1H), 2.99-3.08 (dt, *J* = 11.1, 3.3 Hz, 1H), 3.34-3.40 (dd, *J* = 13.6, 5.6 Hz, 1H), 3.73-3.79 (dd, *J* = 13.7, 5.2 Hz, 1H), 7.16-7.21 (m, 3H), 7.26-7.31 (m, 2H).

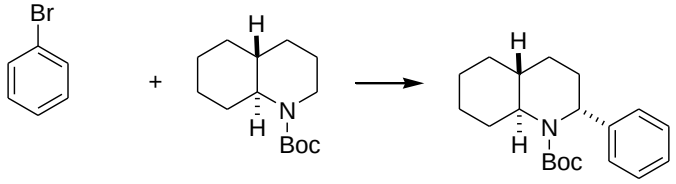
**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 26.1, 26.2, 28.6, 31.3, 33.4, 37.9, 39.2, 42.2, 48.8, 63.1, 79.2, 126.4, 127.1, 128.6, 145.4, 155.4.

**IR (neat) ν :** 1242, 1681

**HRMS (ESI) m/z:** calculated for $C_{20}H_{29}NNaO_2$ ($[M+Na]^+$): 338.2091; found 338.2091.

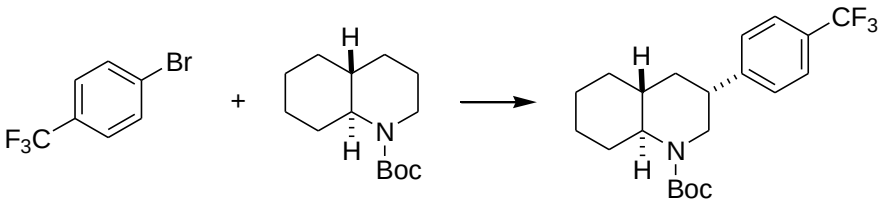
**Mp:** 76°C

## *Tert*-butyl *trans*-octahydro-2-phenylquinoline-1(2H)-carboxylate



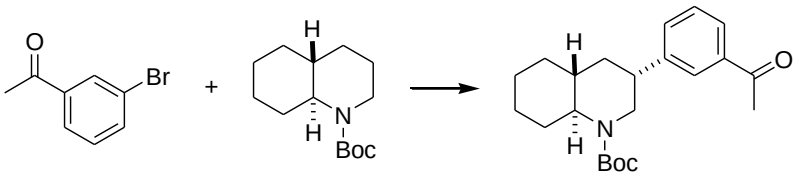

The above compound was prepared according to general procedure **B** from bromobenzene and *tert*-butyl *trans*-decahydroquinoline-1-carboxylate (**9**) using Ruphos as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived 67.8 mg (61 %) of the desired compound as a yellow oil.
Selectivity $\alpha/\beta$: 93 : 7 (determined from $^{1}$H NMR of crude)
d.r. > 95 : 5
**$^{1}$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 0.83-0.95 (m, 1H), 1.04-1.09 (m, 1H), 1.21-1.28 (m, 2H) 1.39 (s**,** 9H), 1.51-1.64 (m, 4H), 1.71-1.76 (m, 1H), 1.90-2.02 (m, 1H), 2.11-2.20 (m, 3H), 2.70-2.78 (dt, *J* = 10.2, 5.2 Hz, 1H), 5.44-5.47(dd, *J* = 5.3, 2.6 Hz, 1H), 7.19-7.36 (m, 5H).
**$^{13}$C-{$^{1}$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 25.9, 26.8, 27.7, 28.0, 28.6, 31.6, 33.7, 40.3, 57.5, 59.8, 79.5, 126.3, 126.5, 128.6, 142.0, 156.6.
**IR (neat) ν :** 1240, 1698
**HRMS (ESI) m/z:** calculated for $C_{20}H_{29}NNaO_2$ ($[M+Na]^+$): 383.2611; found 383.2617.

## *Tert*-butyl *trans*-octahydro-3-[4-(trifluoromethyl)phenyl]quinoline-1(2H)-carboxylate (10b)




The above compound was prepared according to general procedure **B** from 4-bromobenzotrifluoride and *tert*-butyl *trans*-decahydroquinoline-1-carboxylate (**9**) using **L**[8] as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 90 / 10) gived 74 mg (55 %) of the desired compound as a yellow oil.
Selectivity $\beta/\alpha$: 95 : 5(determined from $^{1}$H NMR of crude)
d.r. > 95 : 5
**$^{1}$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.06-1.17 (m, 1H), 1.24-1.34 (m, 3H), 1.38 (s**,** 9H), 1.54-1.82 (m, 5H), 1.95-2.03 (ddd, *J* = 13.1, 7.5, 2.9 Hz, 1H), 2.16-2.20 (bd, 1H), 2.98-3.12 (m, 2H), 3.43-3.50 (dd, *J* = 13.8, 4.7 Hz, 1H), 3.67-3.74 (dd, *J* = 13.8, 5.4 Hz, 1H), 7.29-7.32 (d, *J* = 8.1 Hz, 2H), 7.51-7.54 (d, *J* = 8.1 Hz, 2H).
**$^{13}$C-{$^{1}$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 26.0, 26.1, 28.5, 31.3, 33.2, 37.3, 39.1, 42.0, 47.4, 62.8, 79.5, 122.6, 125.4 (q, *J* = 3.8 Hz), 126.2, 127.5, 128.1 (q, *J* = 32.7 Hz), 149.7, 155.3.
**$^{19}$F-{$^{1}$H} NMR (282 MHz, $CDCl_3$, 293 K) δ:** -62.4.
**IR (neat) ν :** 1244, 1684
**HRMS (ESI) m/z:** calculated for $C_{21}H_{28}F_3NNaO_2$ ($[M+Na]^+$): 406.1964; found 406.1955.

## *Tert*-butyl *trans*-3-(3-acetylphenyl)-octahydroquinoline-1(2H)-carboxylate (10c)




The above compound was prepared according to general procedure **B** from 3-bromoacetophenone and *tert*-butyl *trans*-decahydroquinoline-1-carboxylate (**9**) using **L**[8] as ligand. Purification on silica gel (elution with Cyhex / EtOAc: 90 / 10) gived 53.8 mg (43 %) of the desired compound as a colorless oil.

Selectivity $\beta/\alpha$: 95 : 5 (determined from $^{1}$H NMR of crude)

d.r. > 95 : 5

**$^{1}$H NMR (300 MHz, $CDCl_3$, 293 K) δ:** 1.06-1.31 (m, 4H), 1.38 (s, 9H), 1.57-1.81 (m, 5H), 1.96-2.03 (ddd, *J* = 13.1, 7.3, 2.8 Hz, 1H), 2.15-2.19 (bd, 1H), 2.58 (s, 3H), 3.00-3.10 (m, 2H), 3.42-3.48 (dd, *J* = 13.8, 5.1 Hz, 1H), 3.70-3.76 (dd, *J* = 13.8, 5.3 Hz, 1H), 7.34-7.42 (m, 2H), 7.76-7.80 (m, 2H).

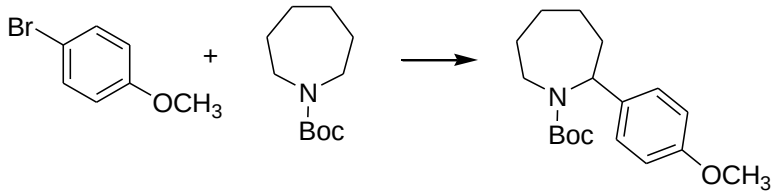
**$^{13}$C-{$^{1}$H} NMR (75 MHz, $CDCl_3$, 293 K) δ:** 26.0, 26.1, 28.5, 31.3, 33.3, 37.7, 39.2, 42.1, 47.8, 63.0, 79.4, 126.5, 126.9, 128.8, 132.0, 137.4, 146.1, 155.3, 198.4.

**IR (neat) ν :** 1267, 1680

**HRMS (ESI) m/z:** calculated for $C_{22}H_{31}NNaO_3$ ($[M+Na]^+$): 380.2196, found 380.2182.

## Arylation of Perhydroazepine and azocane

### *Tert*-butyl 2-[(4-methoxy)phenyl]perhydroazepine-1-carboxylate (11b)




In a Schlenk-tube under argon, a solution of *tert*-butyl perhydroazepine-1-carboxylate (99.6 mg, 0.5 mmol, 1 equiv.) and TMEDA (90 μL, 0.6 mmol, 1.2 equiv.) in anhydrous diethylether (1 mL) was cooled to -78 °C and s-BuLi (1,4 M in cyclohexane) (0.43 mL, 0.6 mmol, 1.2equiv.) was slowly added via syringe. The reaction mixture was stirred for 2 h at this temperature before a solution of $ZnCl_2$ (0.5 M in THF) (1.2, 0.6 mmol, 1.2 equiv.) was added. The reaction mixture was stirred for 30 min at -78 °C and was then allowed to warm to room temperature and stirred for 1 hour. Solvents were removed in vaccuo. Meanwhile, a solution of $Pd_2(dba)_3.CHCl_3$ (12.9 mg, 0.025 mmol, 2.5 mol%) and **L**[8] (6.5 mg, 0.05 mmol, 5 mol%) was prepared in 1.5 mL of anhydrous toluene and allowed to stirred for 15 min at room temperature. The catalyst solution was added to the piperidinylzinc reagent followed by the 4-bromoanisole (44 μL, 0.35 mmol, 0.7 eq). This mixture was heated to 80°C for 17 h. $NH_4Cl$ sat. aq. solution (2 mL) was added, and aqueous layer was extracted with EtOAc (2 x 5 mL). The combined organic layers were dried over $MgSO_4$. The solvents were evaporated and the residue was subjected to column chromatography on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived 38 mg (36 %) of the desired compound as a yellow oil.

Selectivity α/β: 95 : 5 (determined from GCMS of crude)

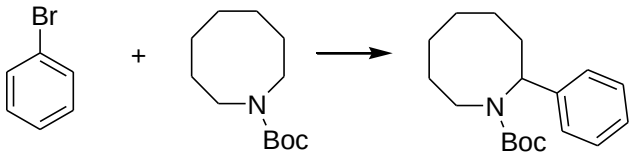
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K, rotamers) δ:** 1.18-1.30 (m, 2H), 1.33(s, 4.5H),1.47 (s, 4.5H) 1.56-1.75 (m, 3H), 1.80-1.92 (m, 2H), 2.18-2.39 (m, 1H), 2.82-2.98 (m, 1H), 3.77 (s, 1.5H), 3.79 (s, 1.5H), 3.79-3.83 (br d, 0.5H), 4.04-4.01 (br d, 0.5 H), 4.85-4.91 (dd, *J* = 12.1, 5.9,Hz, 0.5H), 5.12-5.18 (dd, *J* = 11.7, 6.4 Hz, 0.5H), 6.81-6.85 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.09-7.18 (dd, *J* = 17.5, 8.6 Hz, 2H).

**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K, rotamers) δ:** 25.6, 26.4, 28.5, 28.7, 29.5, 29.7, 29.8, 35.5, 36.5, 43.0, 43.2, 55.4, 57.3, 57.4, 57.7, 59.7, 79.3, 79.5, 133.7, 113.9, 126.8, 127.1, 136.0, 137.0, 154.7, 156.0, 158.3.

**IR (neat) ν :** 1034, 1245, 1683

**HRMS (ESI) m/z:** calculated for $C_{18}H_{27}NNaO_3$ ($[M+Na]^+$): 328.1883; found 328.1874.

### *Tert*-butyl 2-phenylazocane-1-carboxylate (11c)




In a Schlenk-tube under argon, a solution of *tert*-butyl azocane-1-carboxylate (106.7 mg, 0.5 mmol, 1equiv.) and TMEDA (90 μL, 0.6 mmol, 1.2 equiv.) in anhydrous diethylether (1 mL) was cooled to -78 °C and s-BuLi (1,4 M in cyclohexane) (0.43 mL, 0.6 mmol, 1.2equiv.) was slowly added via syringe. The reaction mixture was stirred for 2 h at this temperature before

a solution of $ZnCl_2$ (0.5 M in THF) (1.2, 0.6 mmol, 1.2 equiv.) was added. The reaction mixture was stirred for 30 min at -78 °C and was then allowed to warm to room temperature and stirred for 1 hour. Solvents were removed in vacuo. Meanwhile, a solution of $Pd_2(dba)_3.CHCl_3$ (12.9 mg, 0.025 mmol, 2.5 mol%) and **L**[8] (6.5 mg, 0.05 mmol, 5 mol%) was prepared in 1.5 mL of anhydrous toluene and allowed to stirred for 15 min at room temperature. The catalyst solution was added to the piperidinylzinc reagent followed by the bromobenzene (39 μL, 0.35 mmol, 0.7 eq). This mixture was heated to 80°C for 17 h. $NH_4Cl$ sat. aq. solution (2 mL) was added, and aqueous layer was extracted with EtOAc (2 x 5 mL). The combined organic layers were dried over $MgSO_4$. The solvents were evaporated and the residue was subjected to column chromatography on silica gel (elution with Cyhex / EtOAc: 95 / 5) gived 32.4 mg (32 %) of the desired compound as a yellow oil.

Selectivity α/β: > 98 : 2 determined from GCMS of crude)

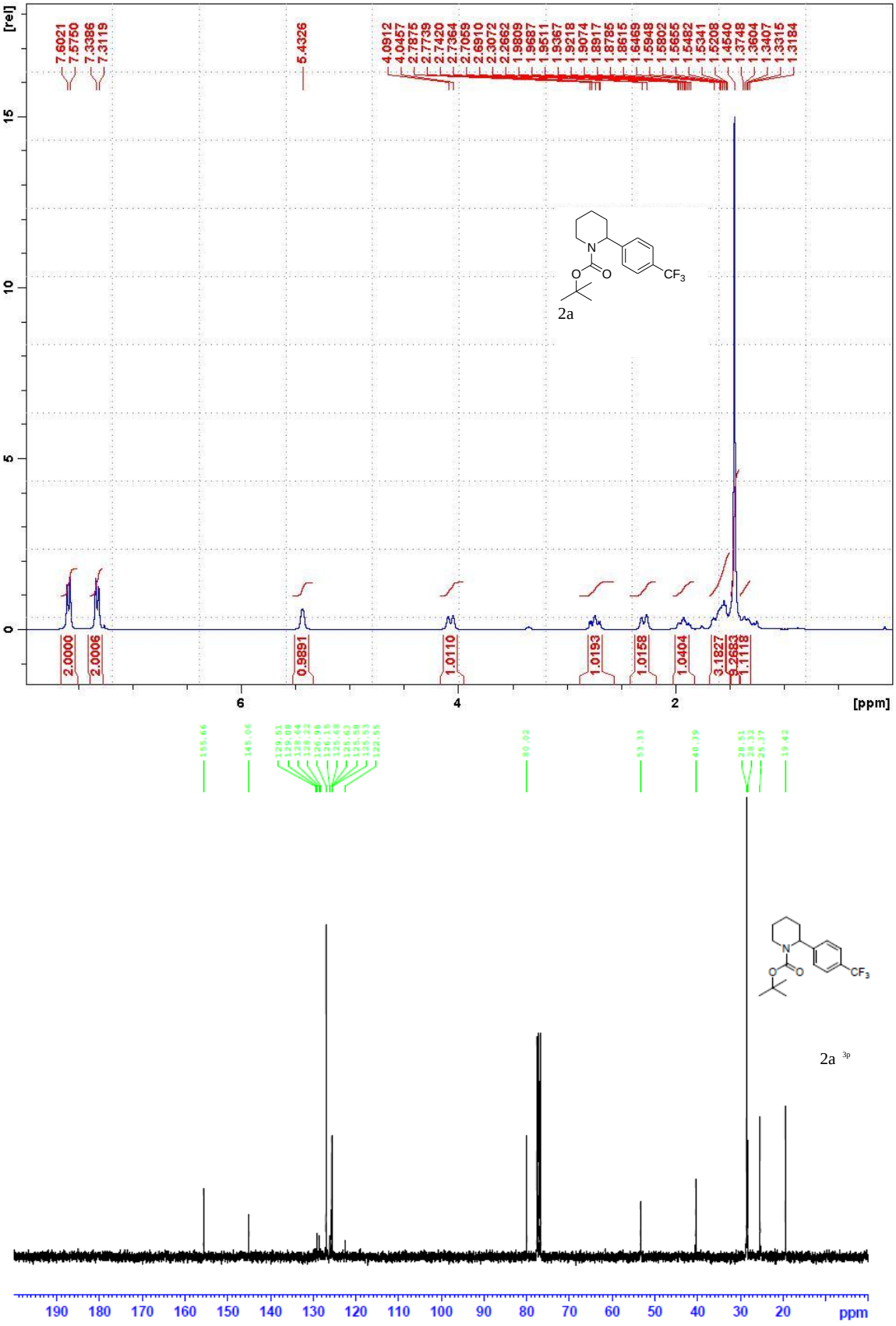
**$^1$H NMR (300 MHz, $CDCl_3$, 293 K, rotamers) δ:** 1.37 (s, 3.5H), 1.48 (s, 5.5H), 1.53-1.77 (m, 7H), 1.90-2.02 (m, 3H), 2.88-2.98 (m, 0.6H), 3.03-3.12 (br t, 0.4H), 3.48-3.56 (dq, *J* = 14.6, 2.3 Hz, 0.6H), 3.61-3.68 (dt, *J* = 13.9, 3.4 Hz, 0.4 H), 4.94-4.99 (dd, *J* = 11.5, 4.2 Hz, 0.4H), 5.24-5.29 (t, *J* = 7.8 Hz, 0.6H), 7.20-7.32 (m, 5H).

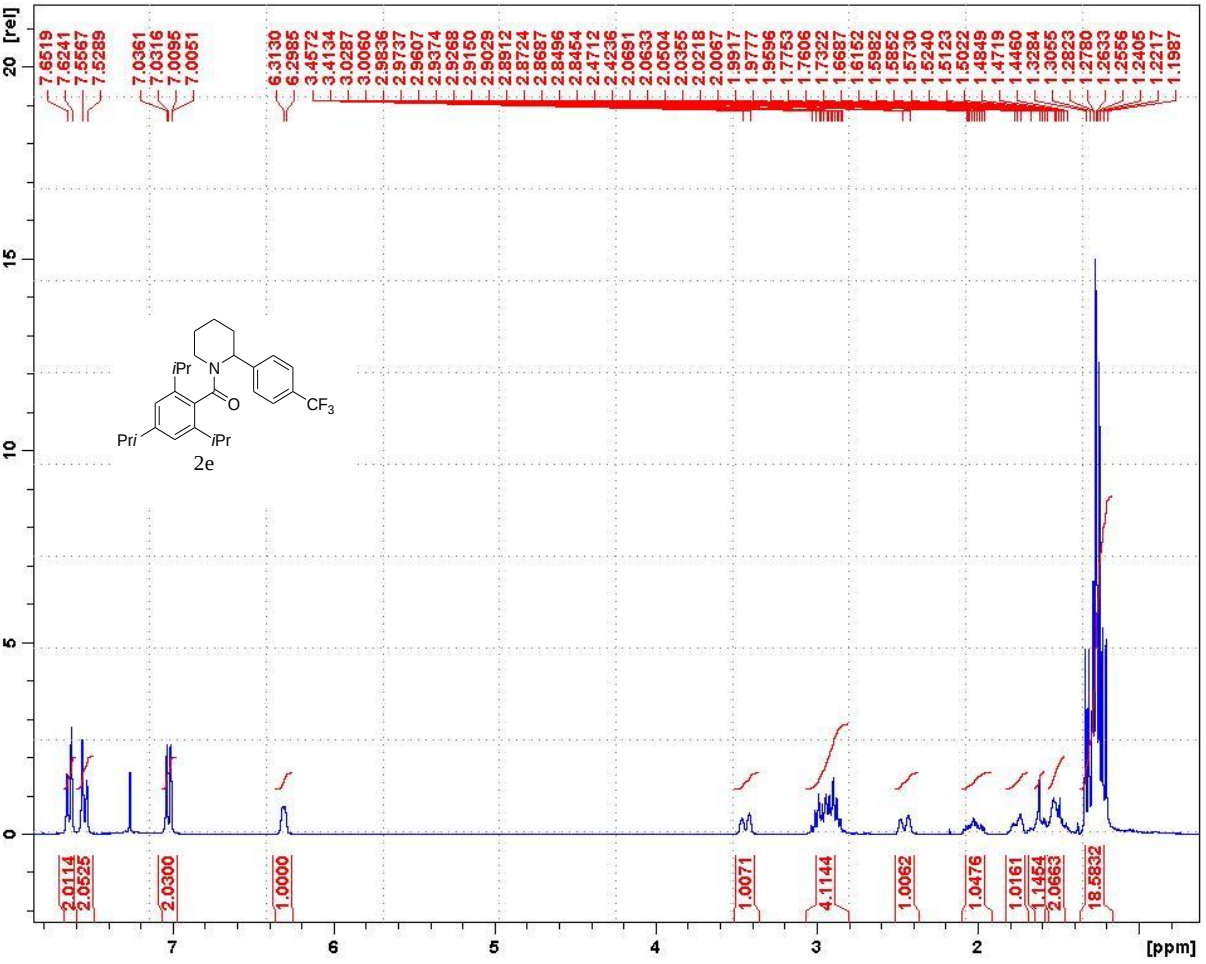
**$^{13}$C-{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K, rotamers) δ:** 24.5, 25.1, 26.4, 26.6, 27.2, 28.1, 28.6, 28.7, 29.6, 30.6, 42.5, 58.1, 59.6, 79.4, 79.5, 126.1, 126.4, 126.7, 126.8, 128.4, 128.5, 143.5, 144.1, 155.7, 156.4 .

**IR (neat) ν :** 1025, 1252, 1684

**HRMS (ESI) m/z:** calculated for $C_{18}H_{27}NNaO_2$ ($[M+Na]^+$): 312.1934; found 312.1936.

# NMR Spectra of target compounds

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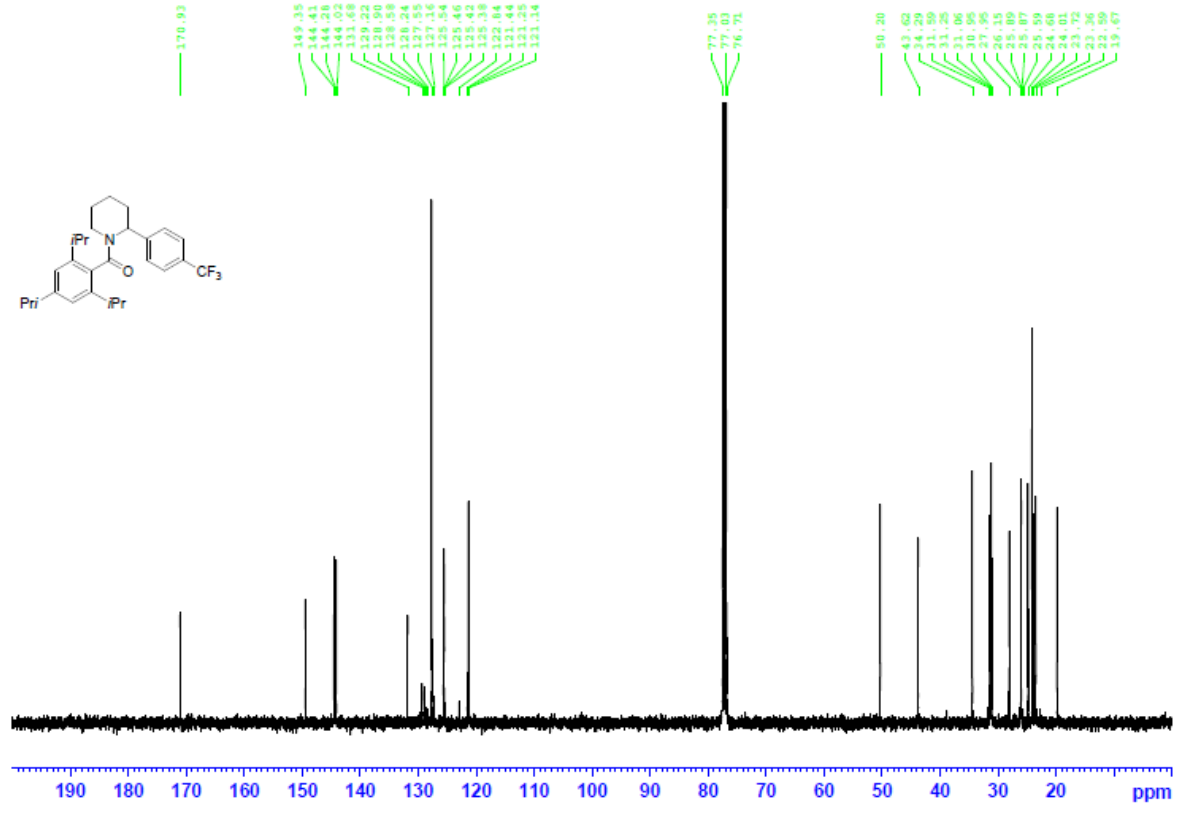
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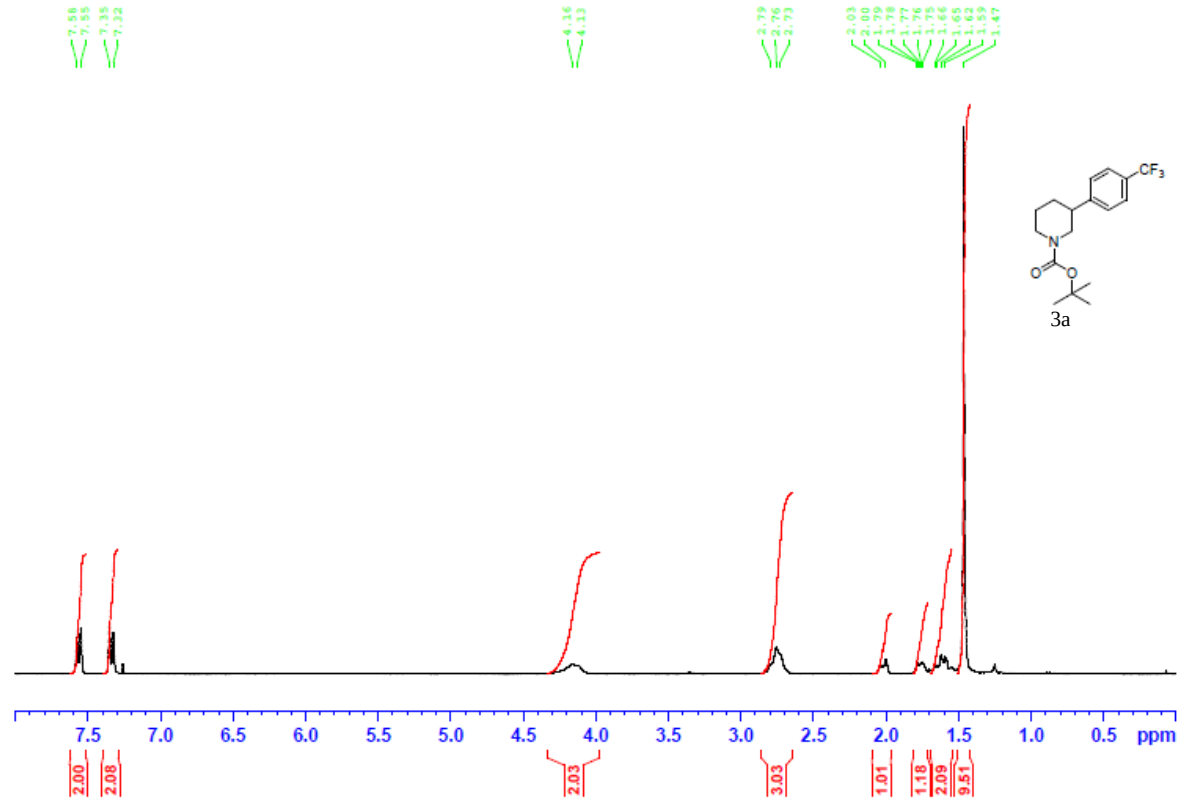
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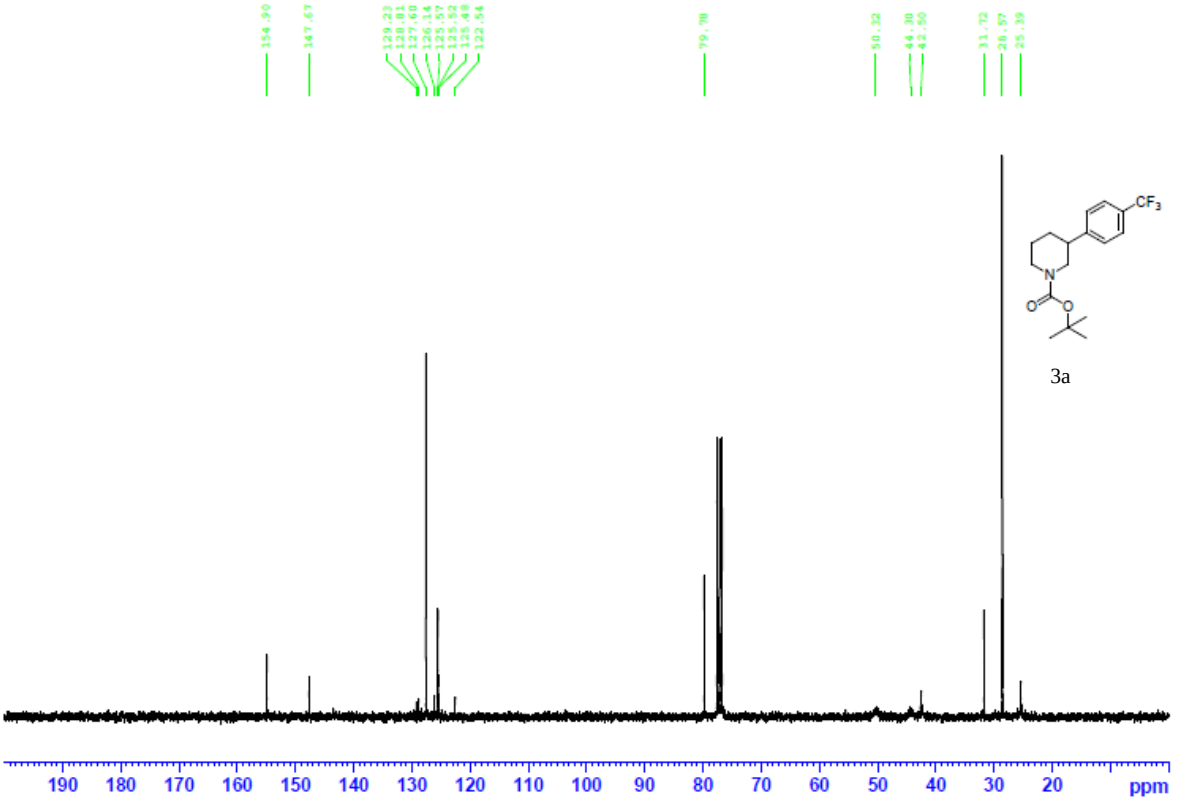
3a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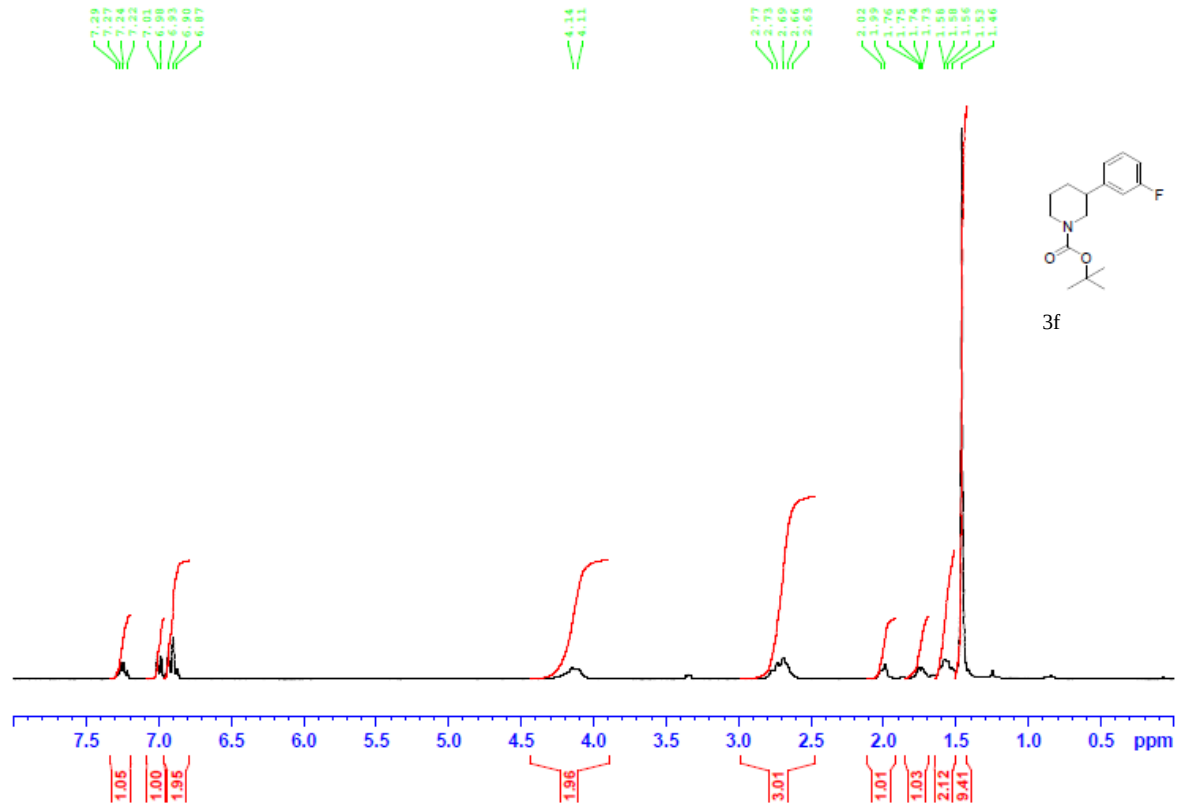
3a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O
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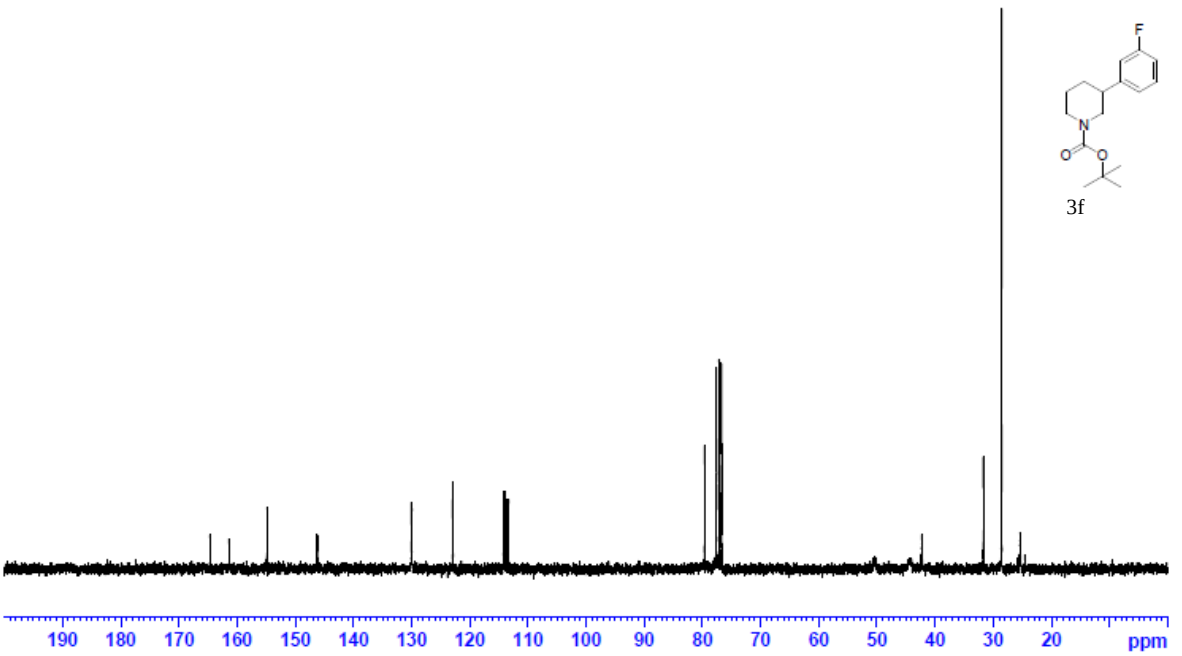
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O
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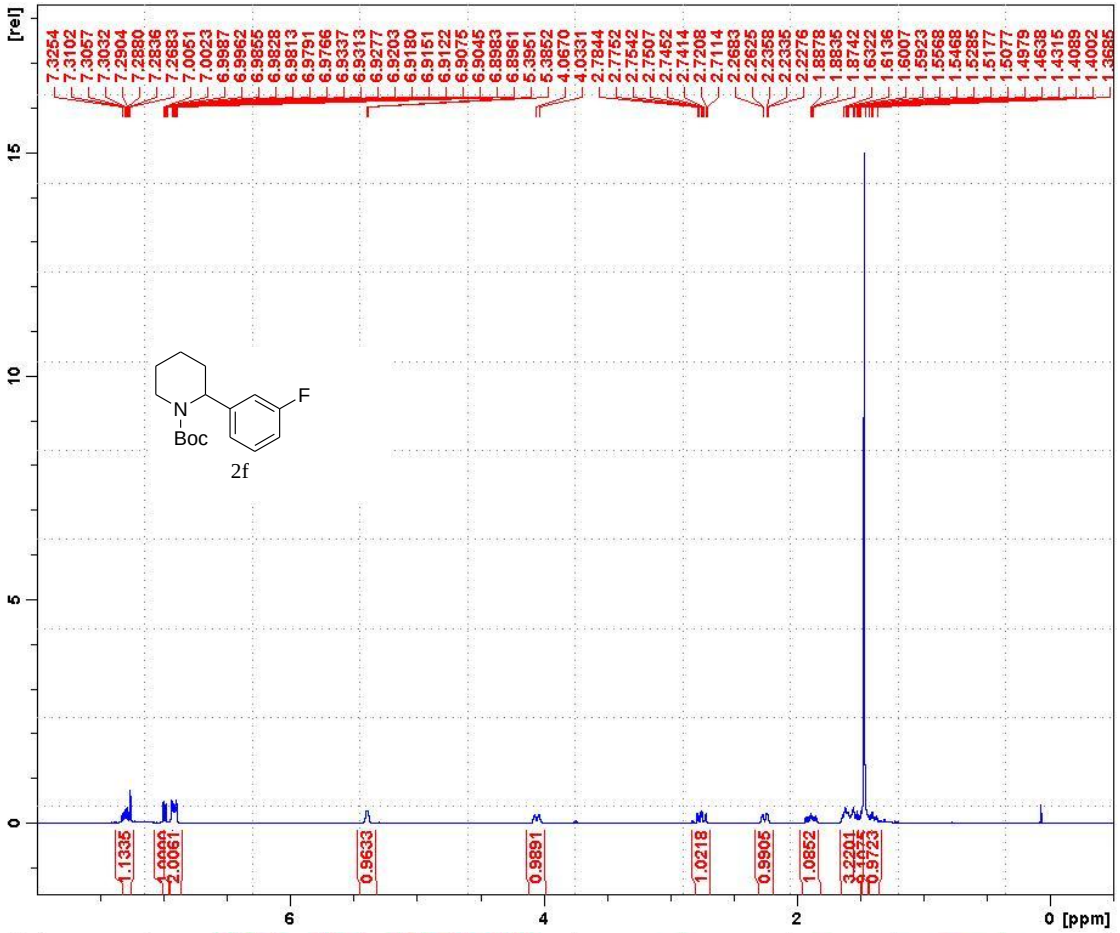
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Boc
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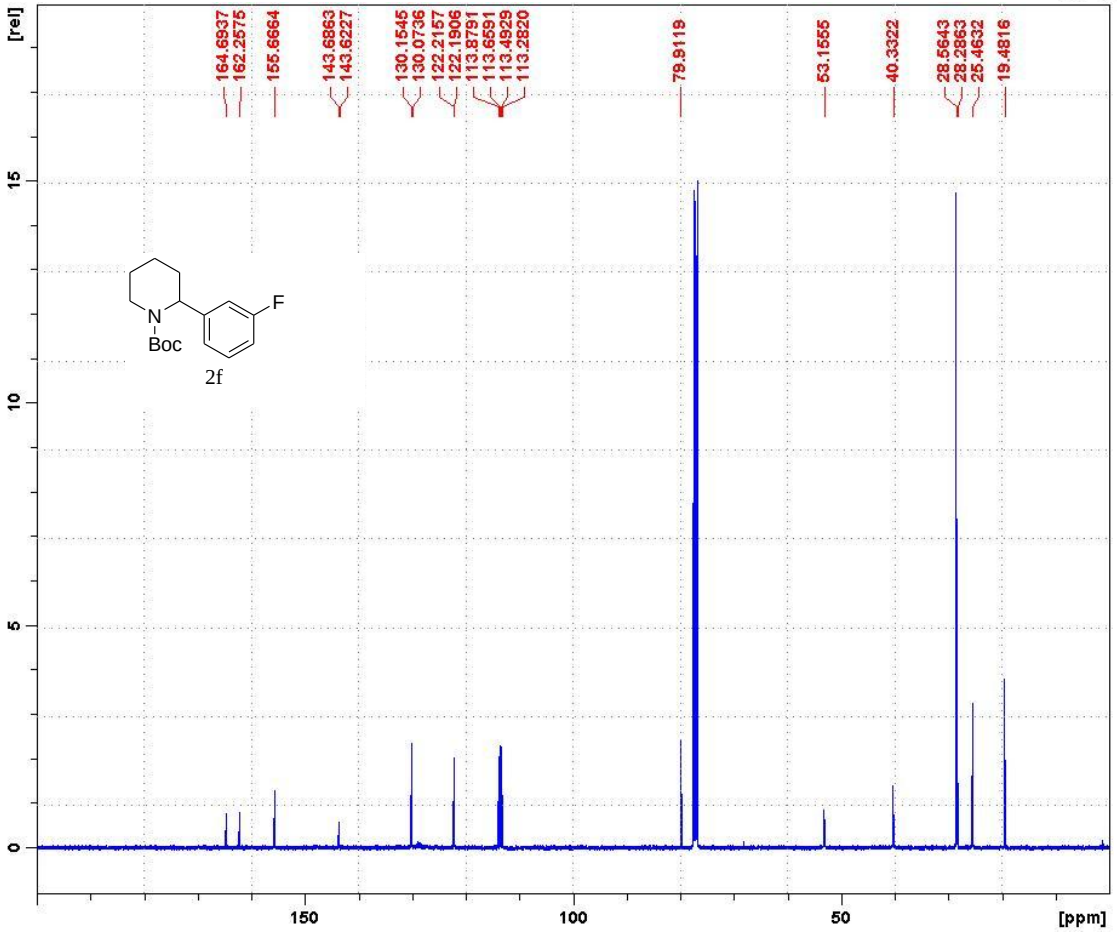
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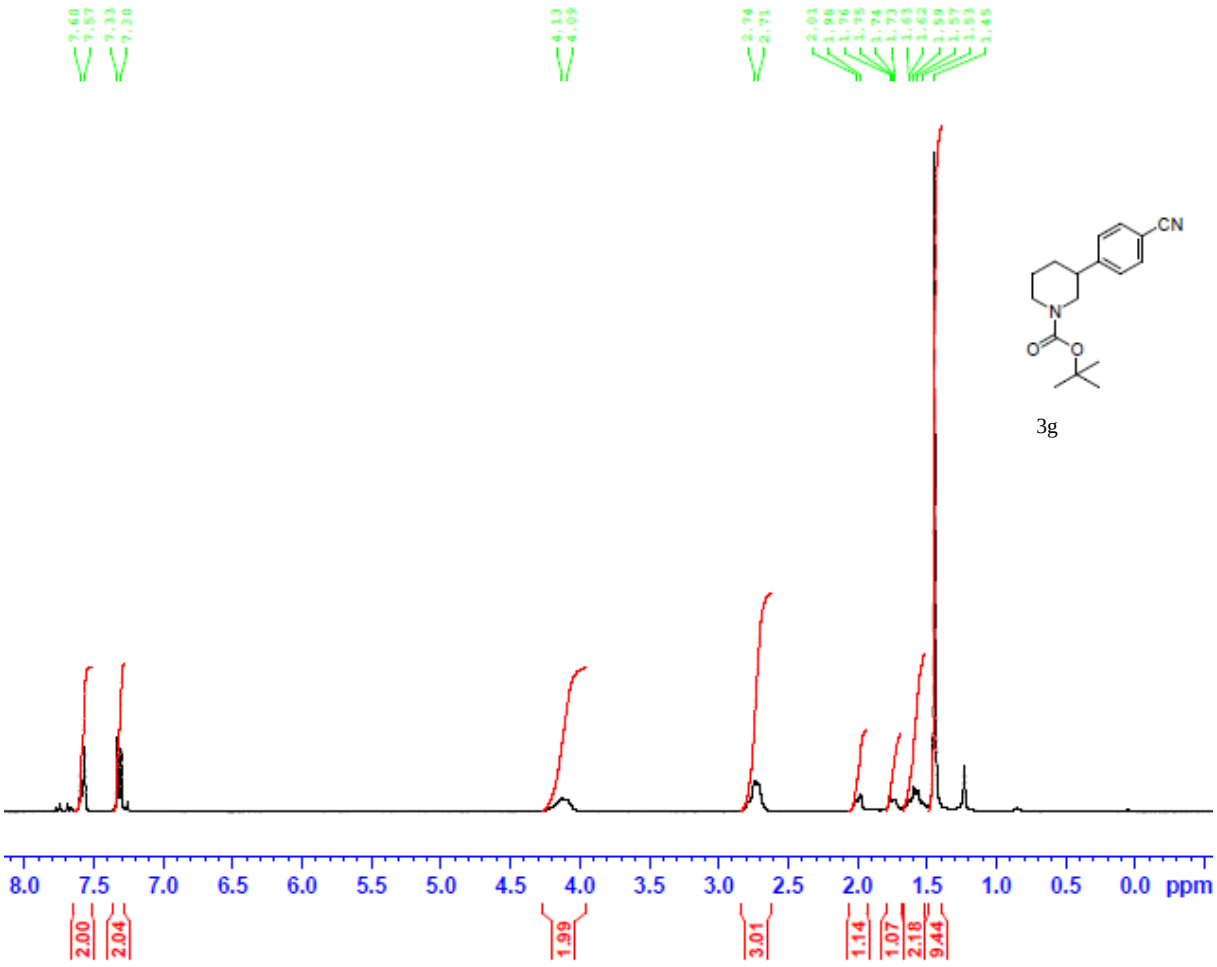


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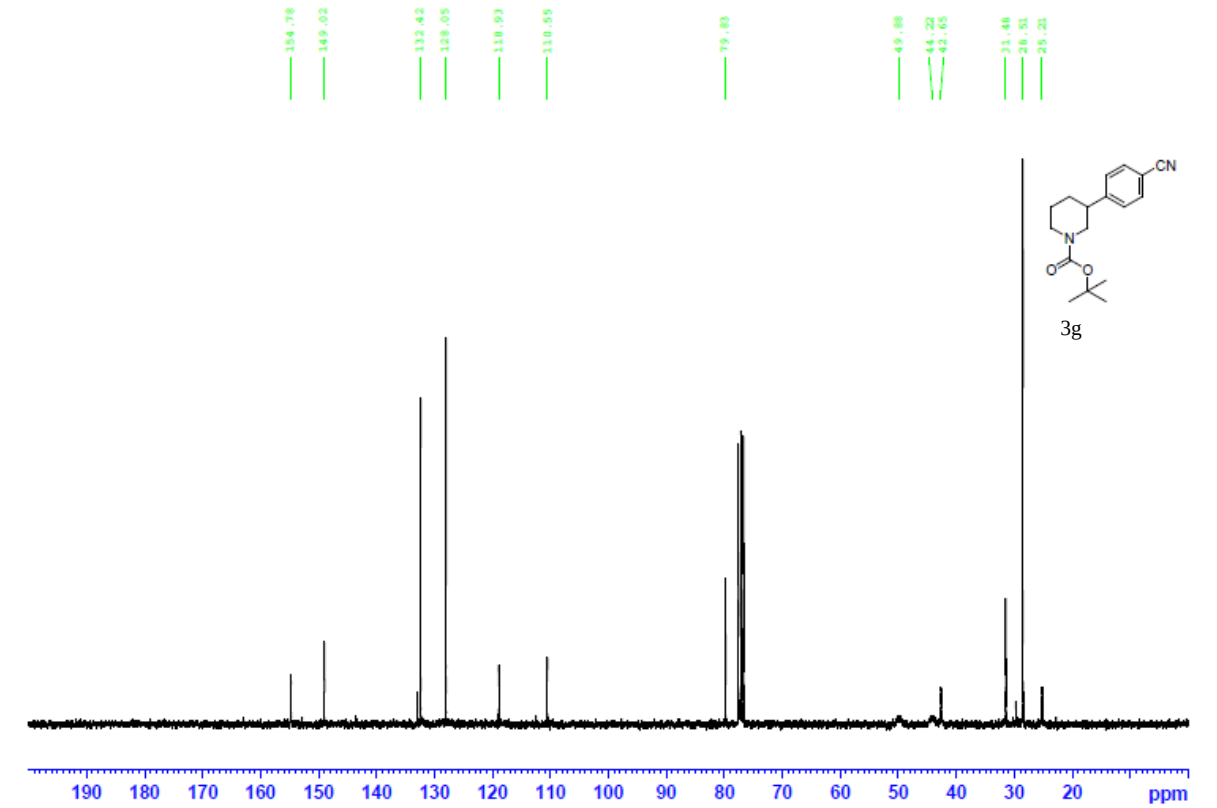


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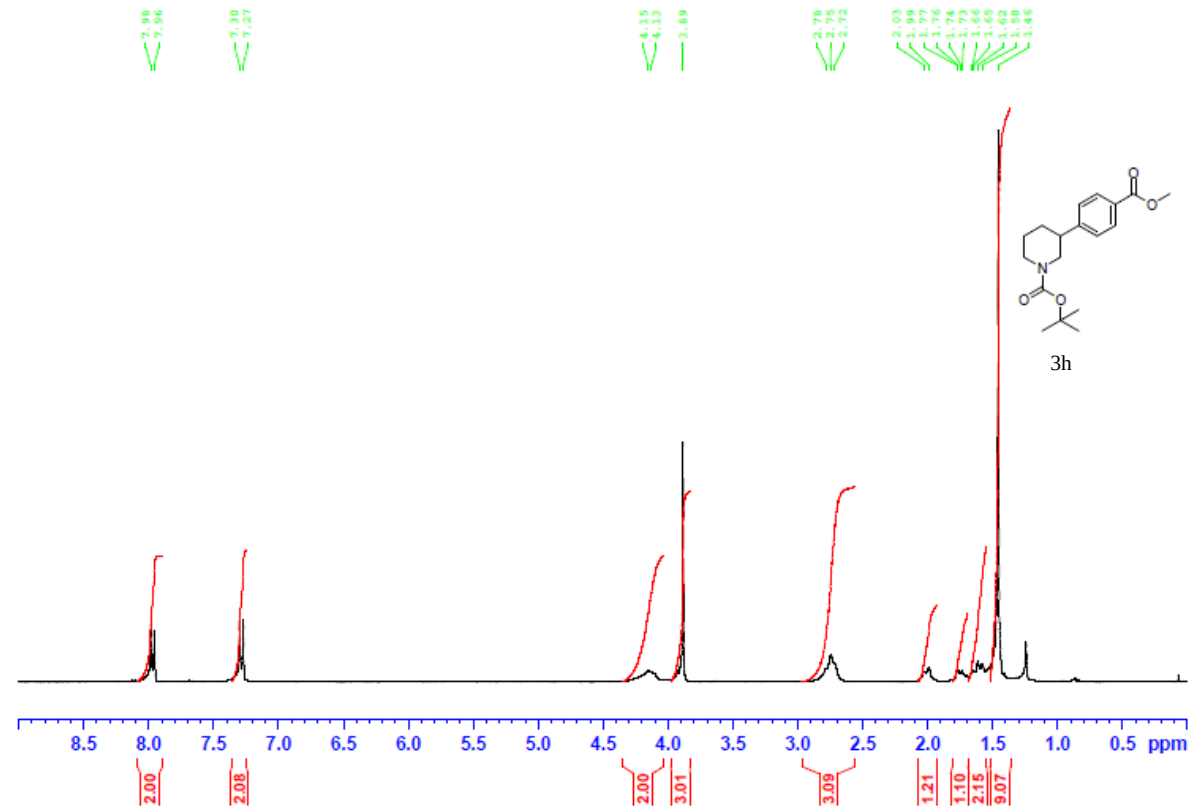
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1.76
1.74
1.73
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1.62
1.58
1.46
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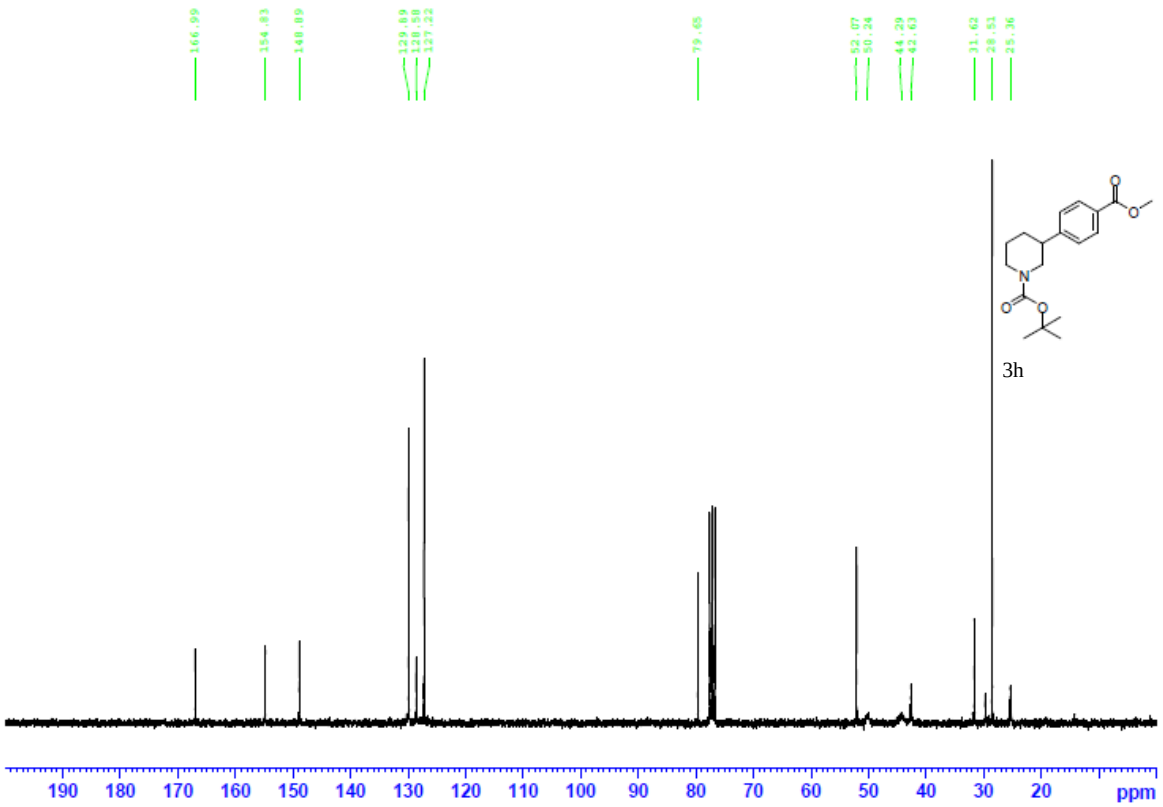
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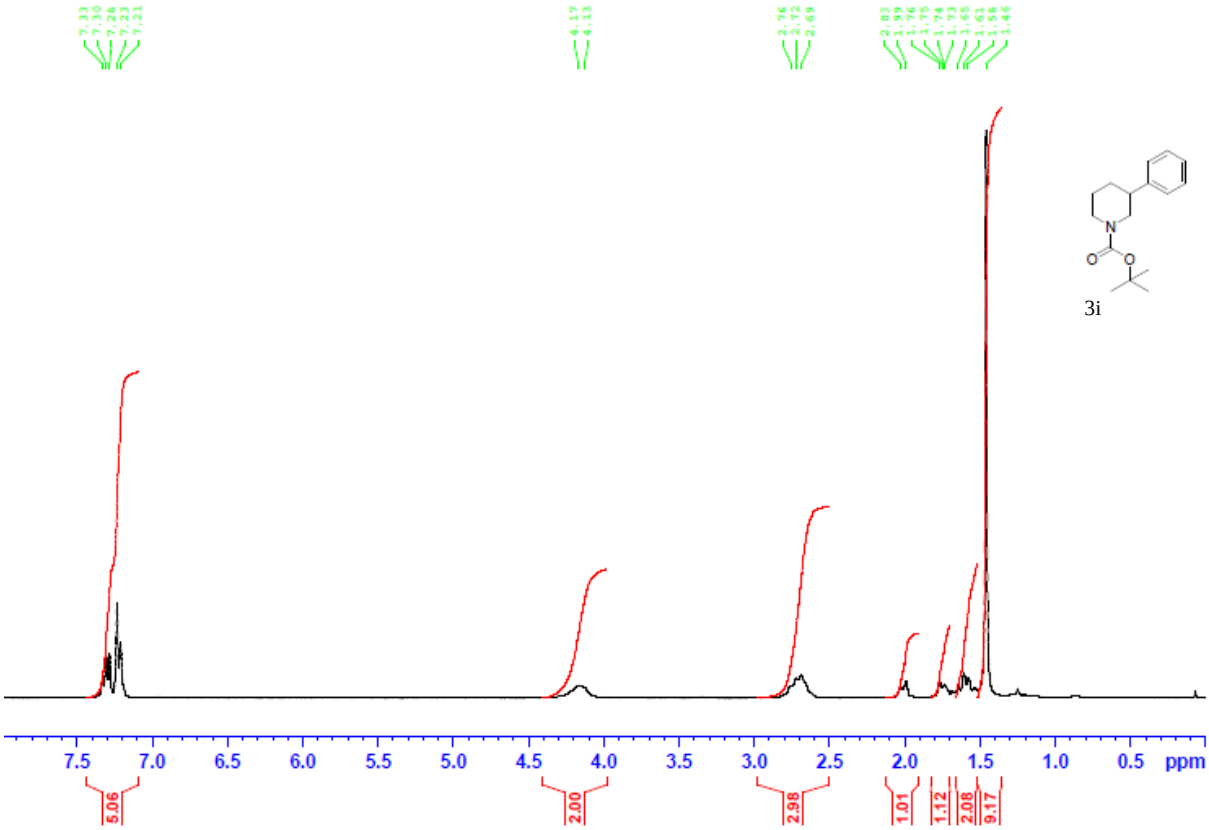
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2.72
2.69
2.03
1.99
1.76
1.75
1.74
1.73
1.65
1.61
1.56
1.46
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5.0
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4.0
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2.08
9.17

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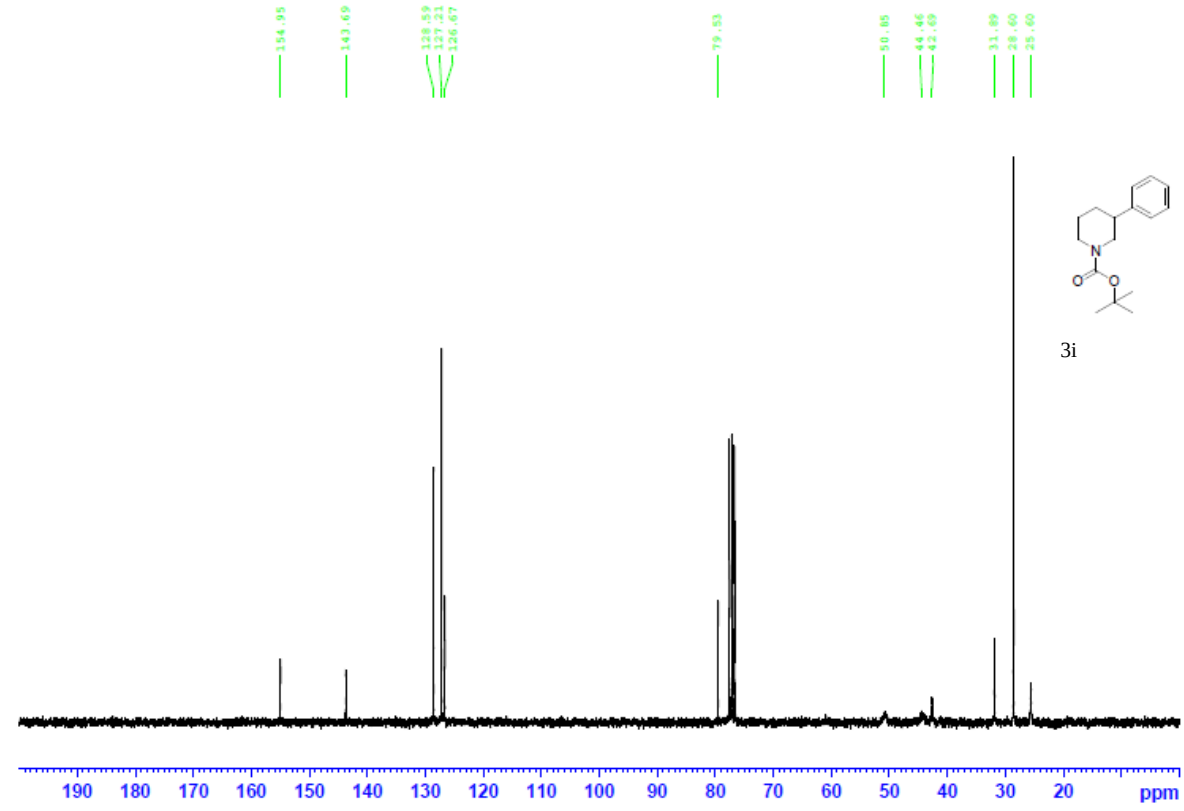
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28.60
25.60
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150
140
130
120
110
100
90
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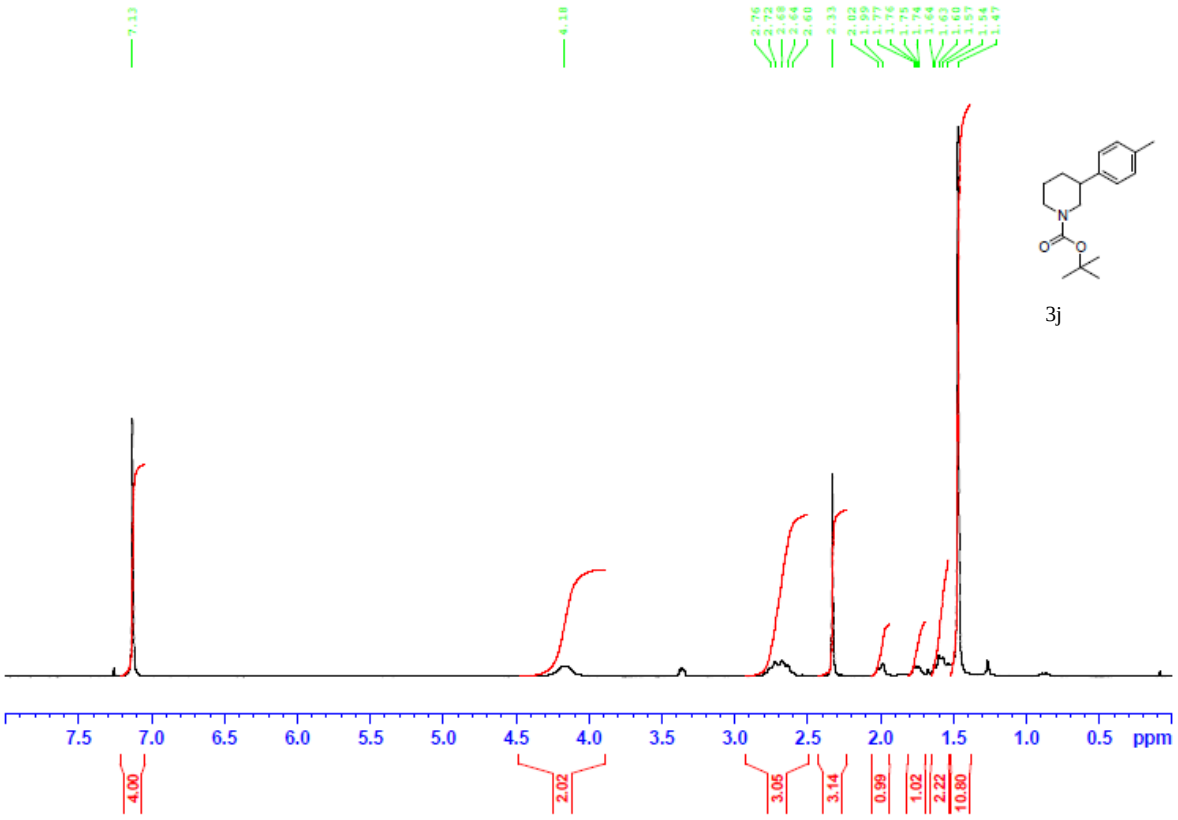
70
60
50
40
30
20
ppm

3i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6.5
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5.5
5.0
4.5
4.0
3.5
3.0
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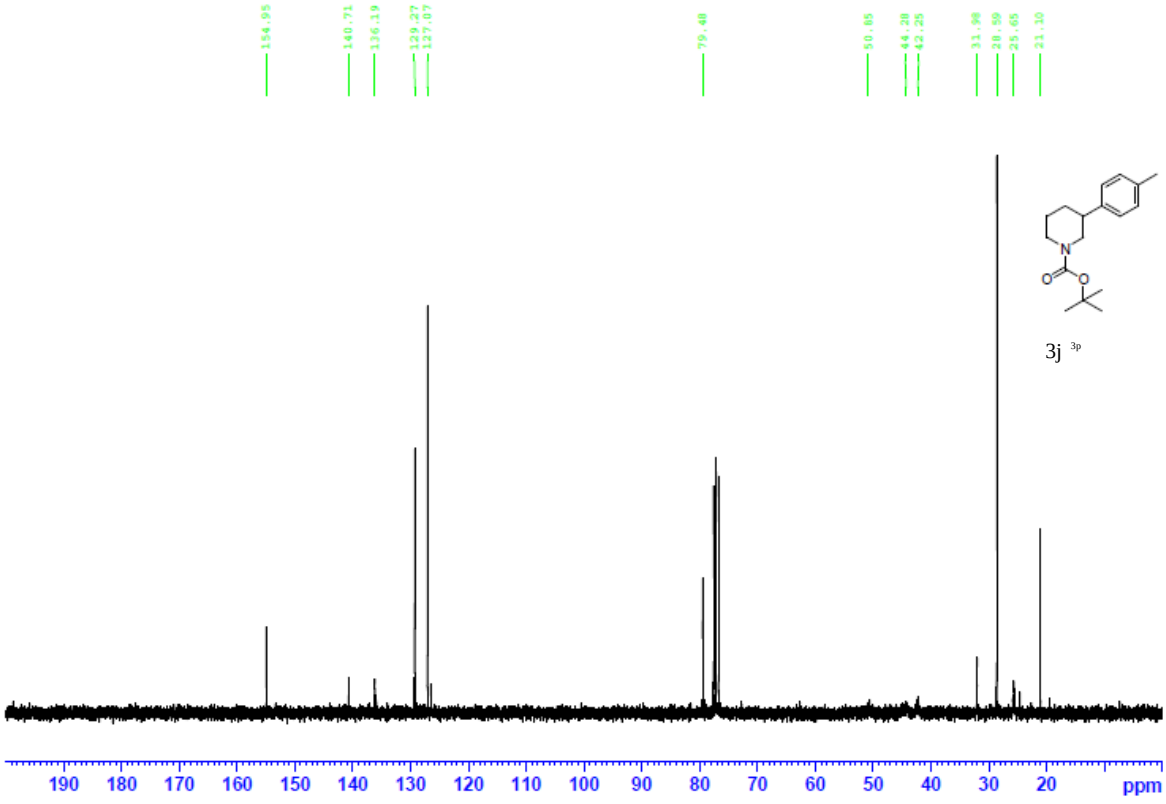
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21.10
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50
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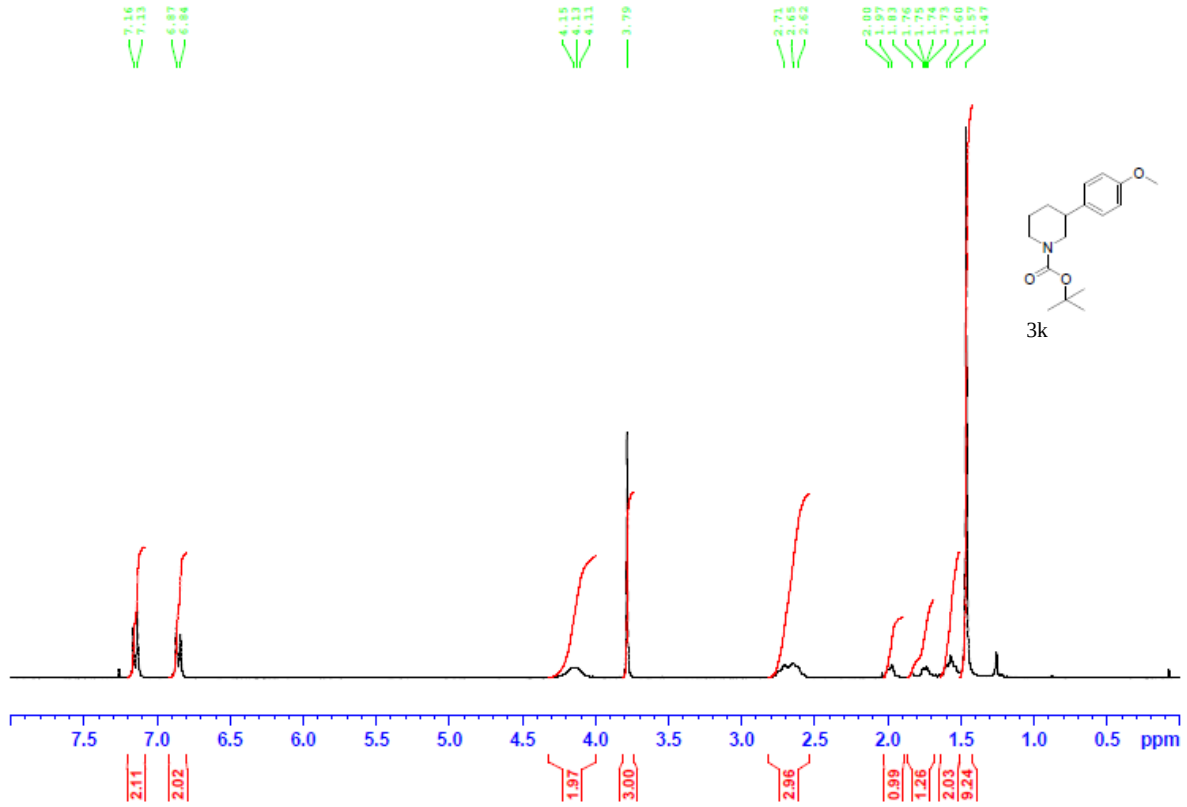
20
ppm

3j [3p]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2.62
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1.83
1.76
1.75
1.74
1.73
1.60
1.57
1.47
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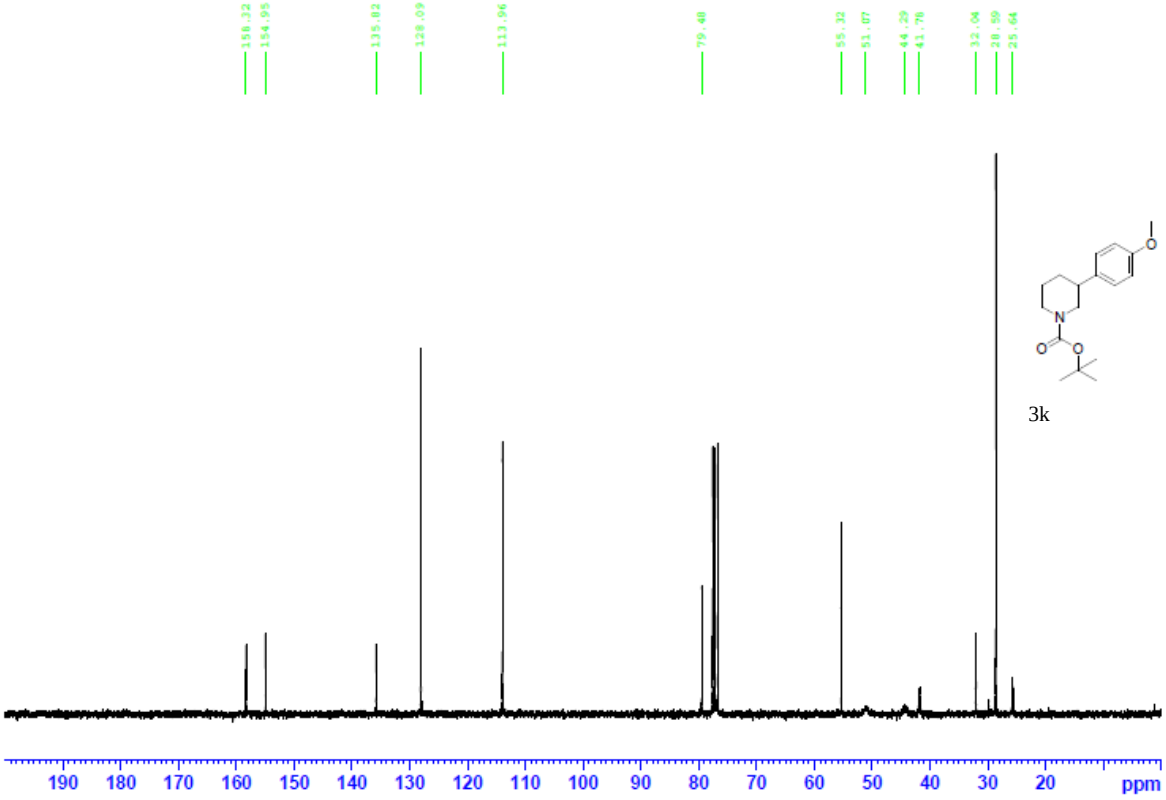
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120
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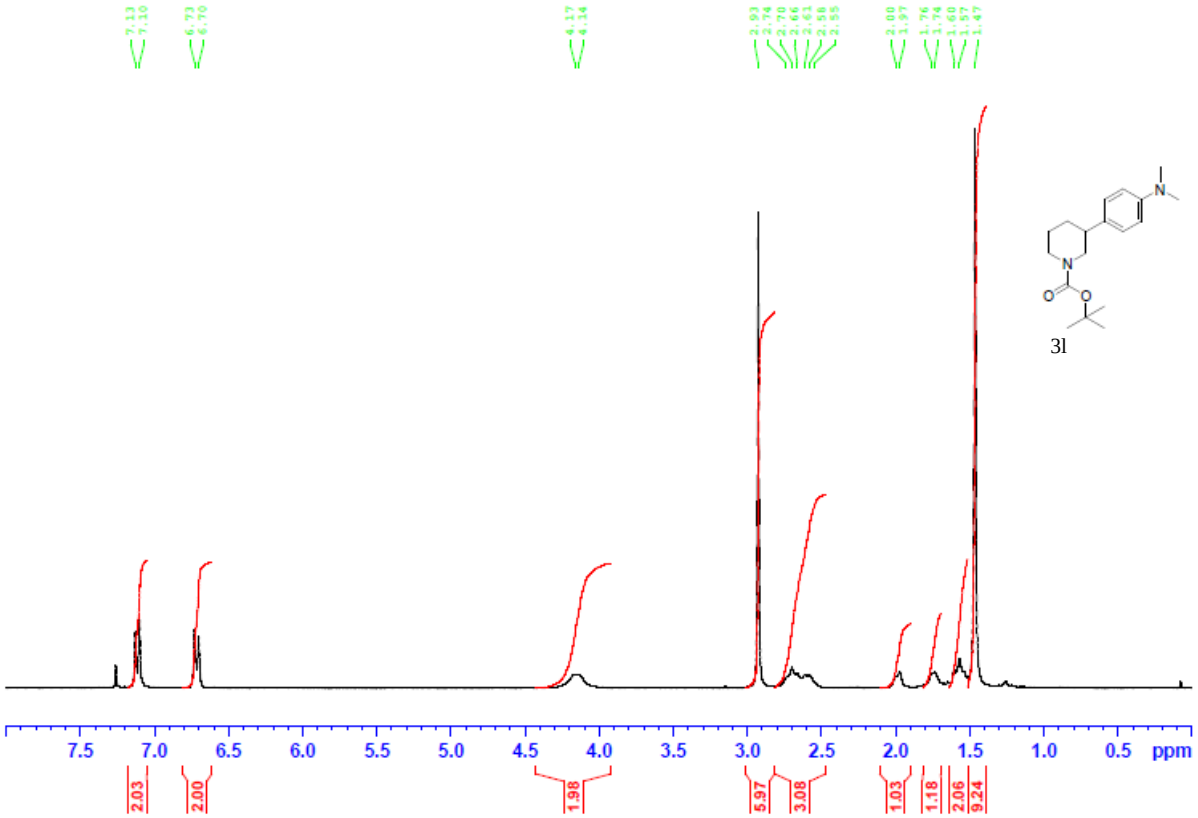
20
ppm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5.0
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9.24

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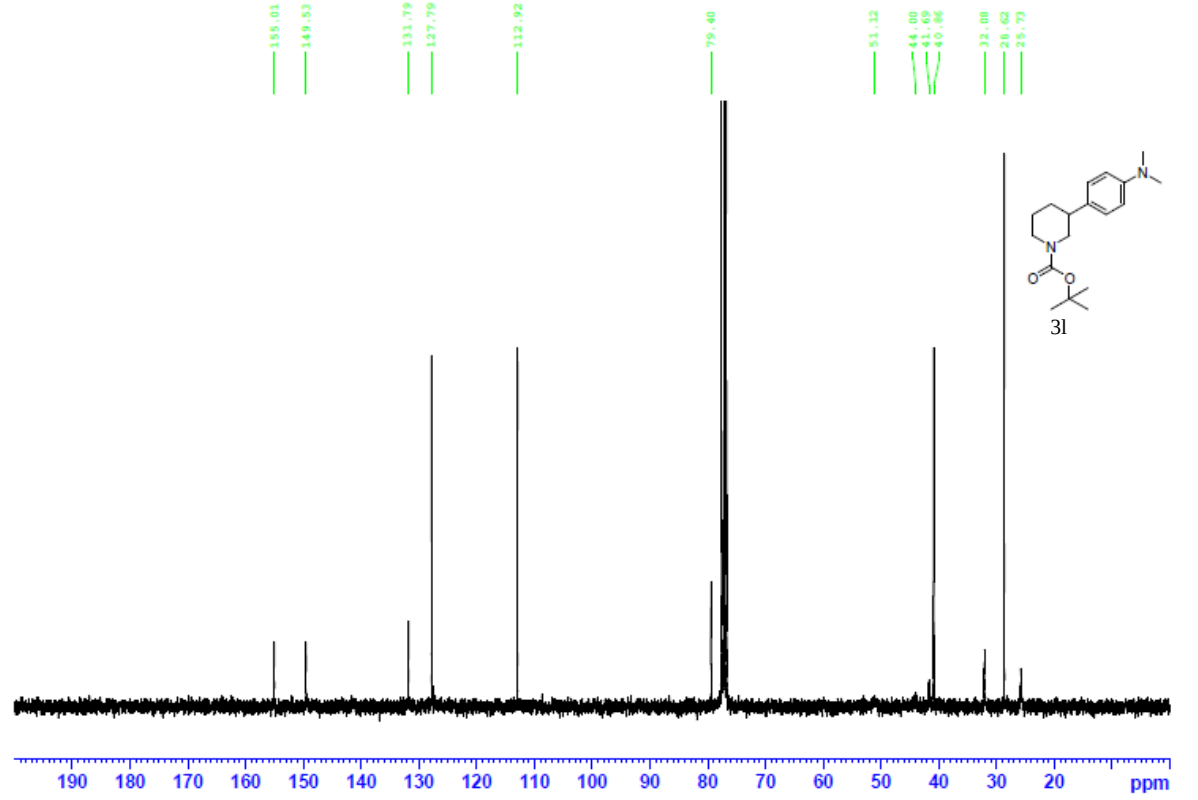
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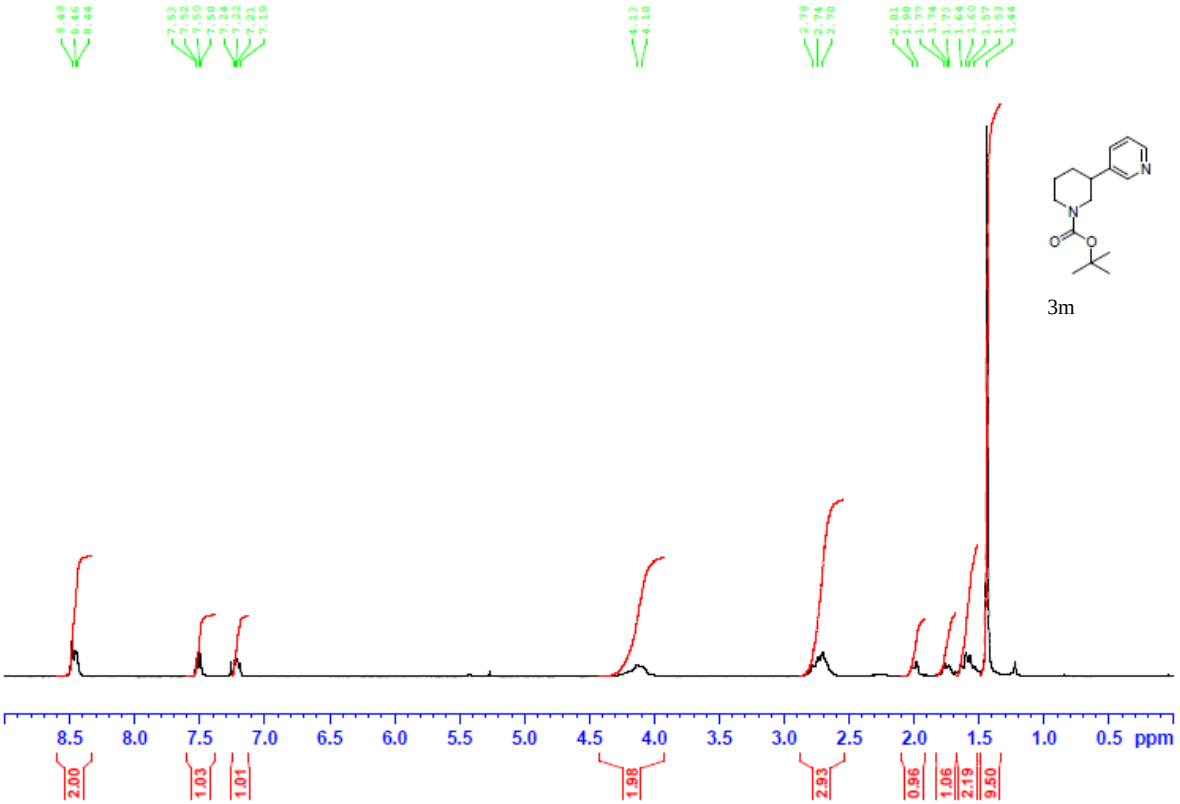
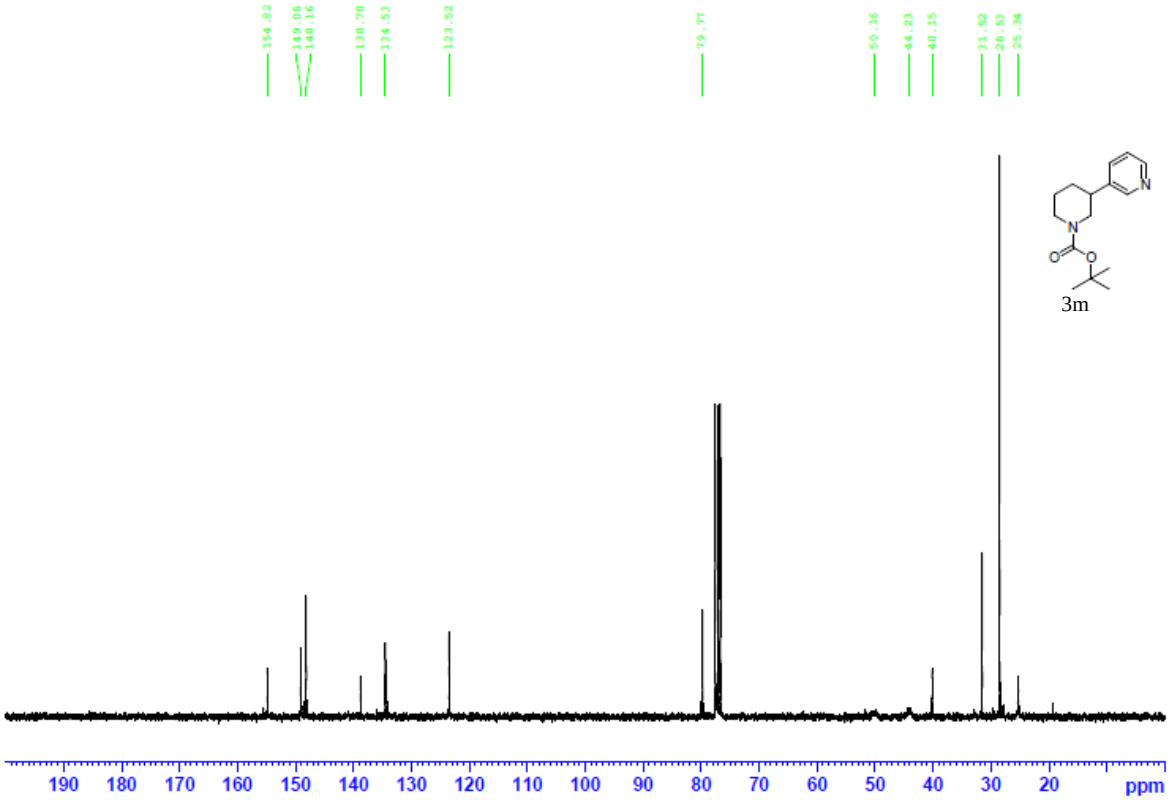
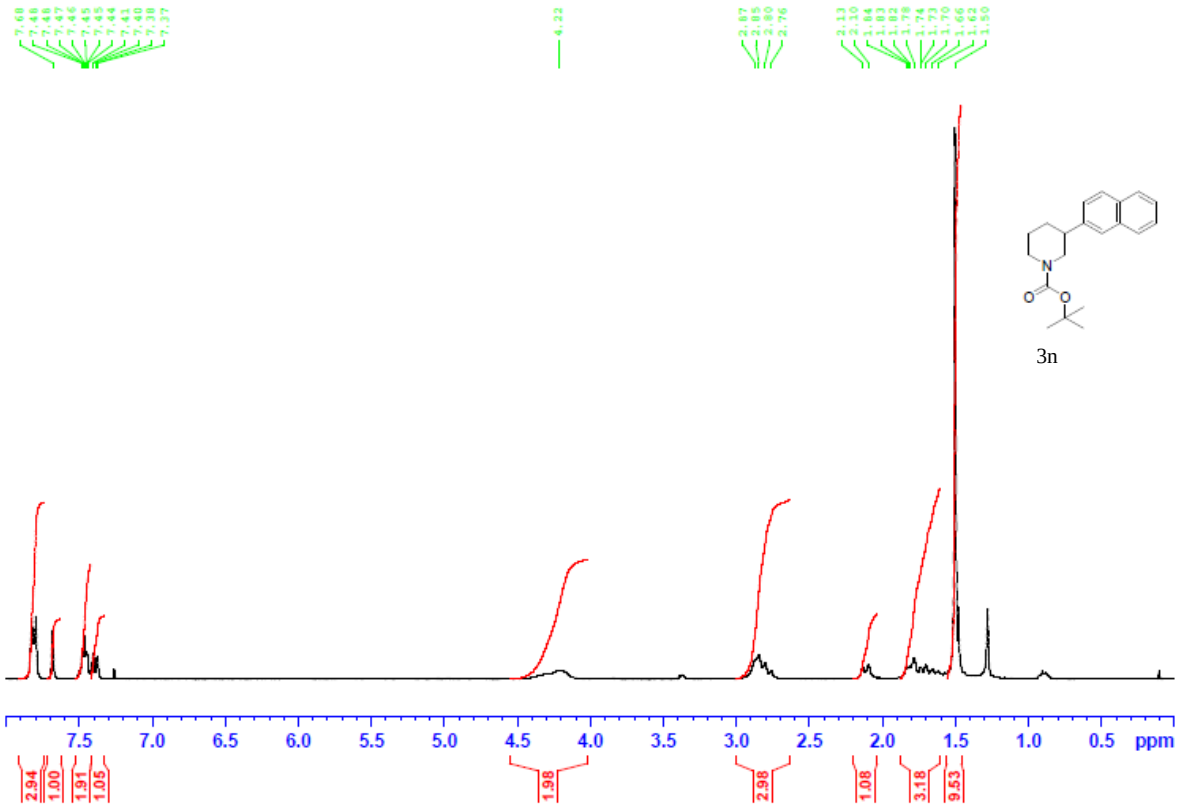
ppm

3l

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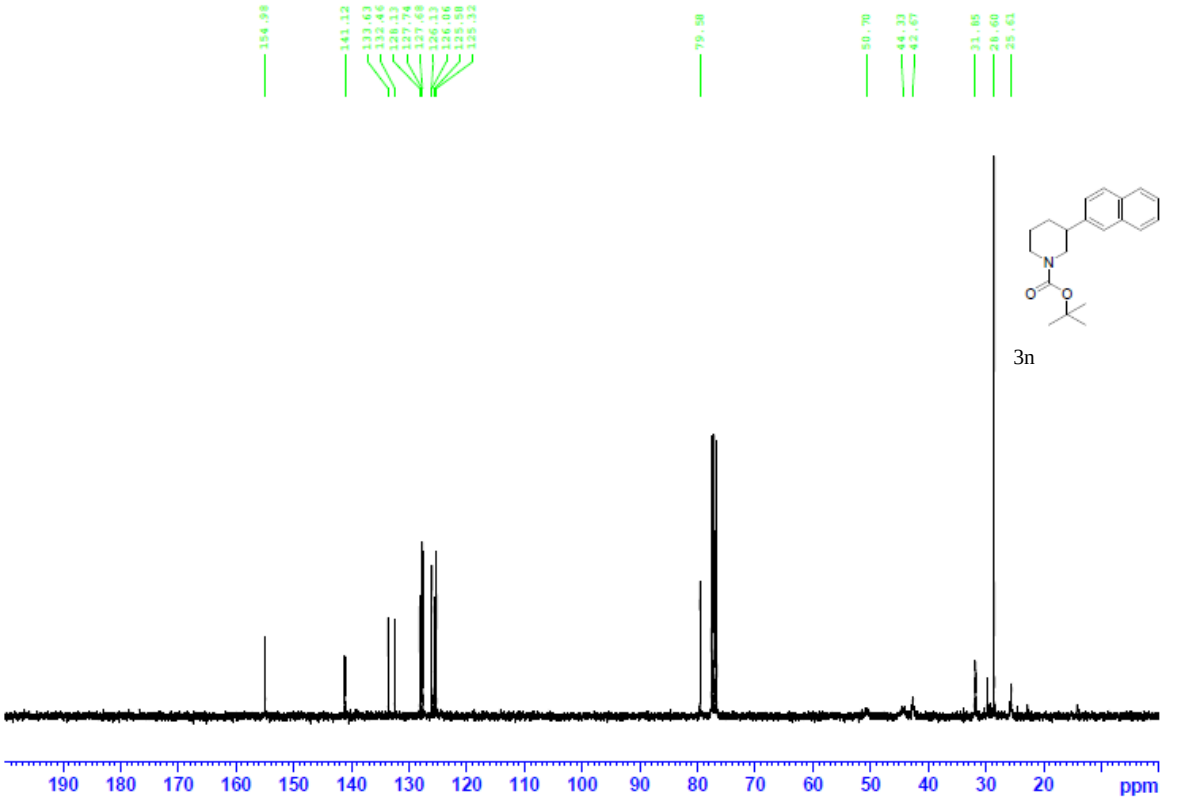
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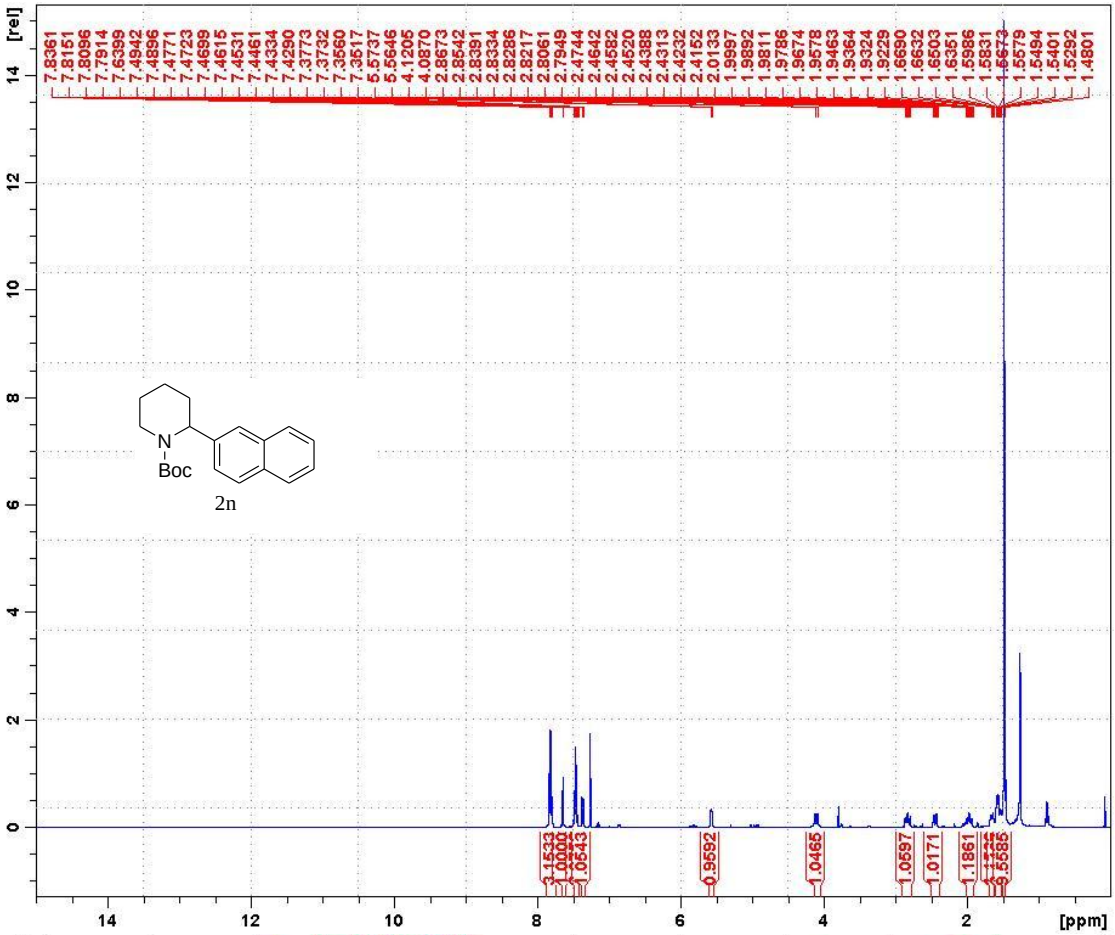


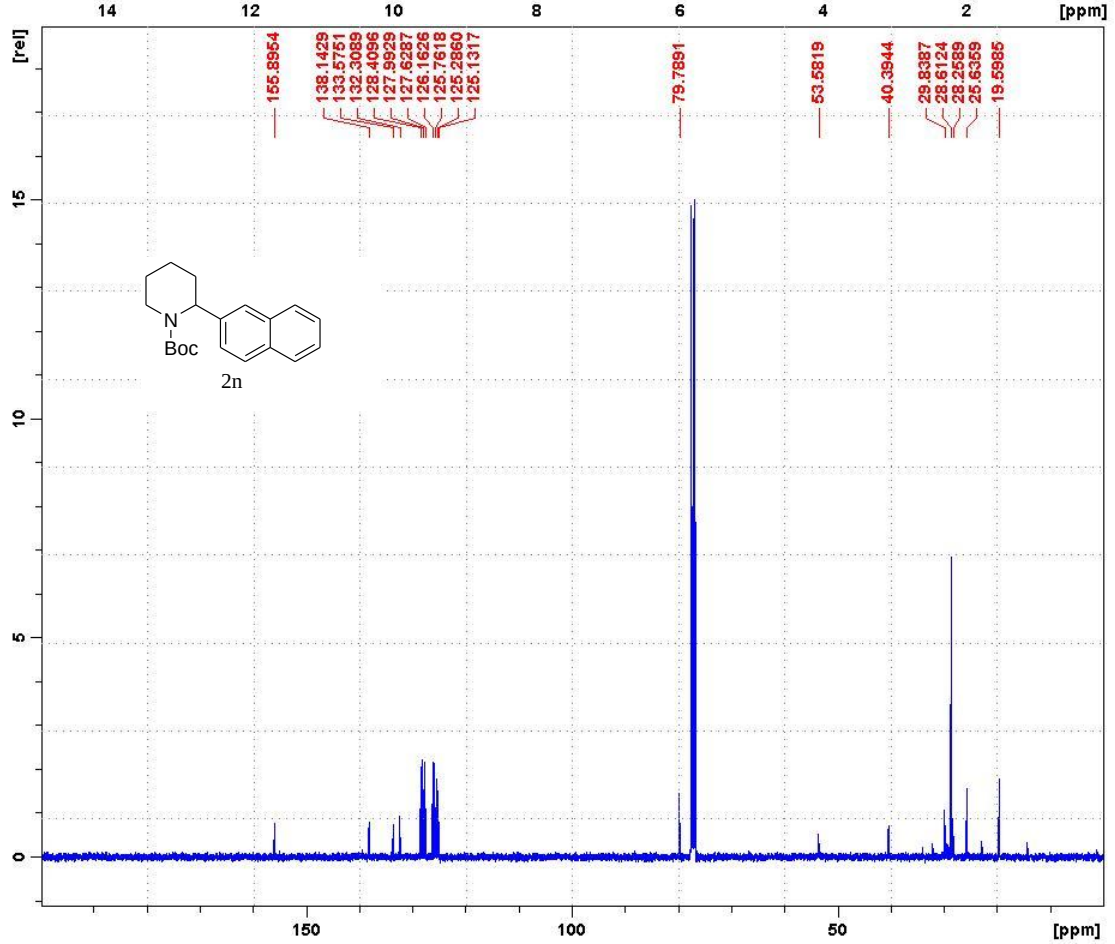

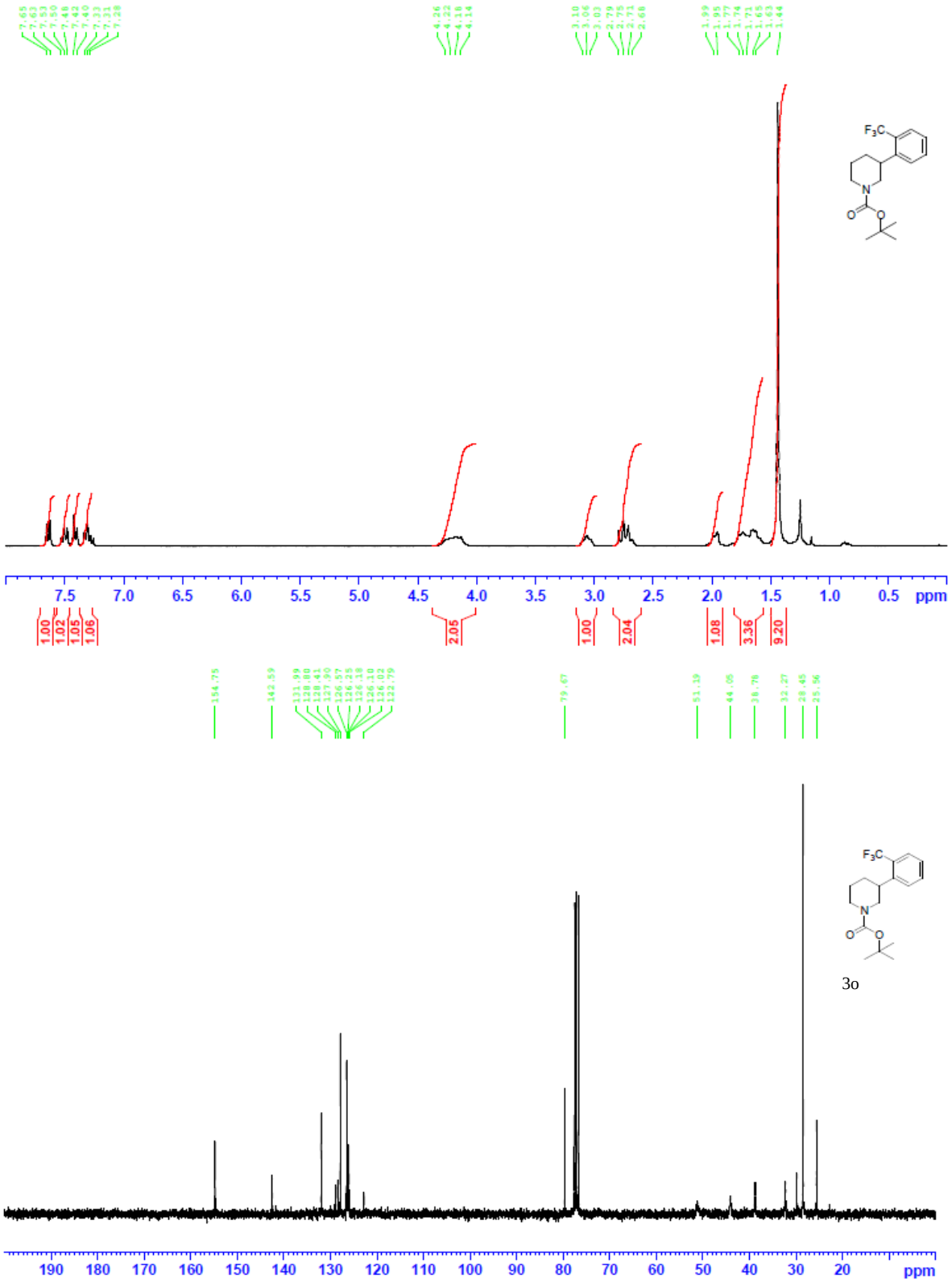
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3.03
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2.75
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1.63
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F3C
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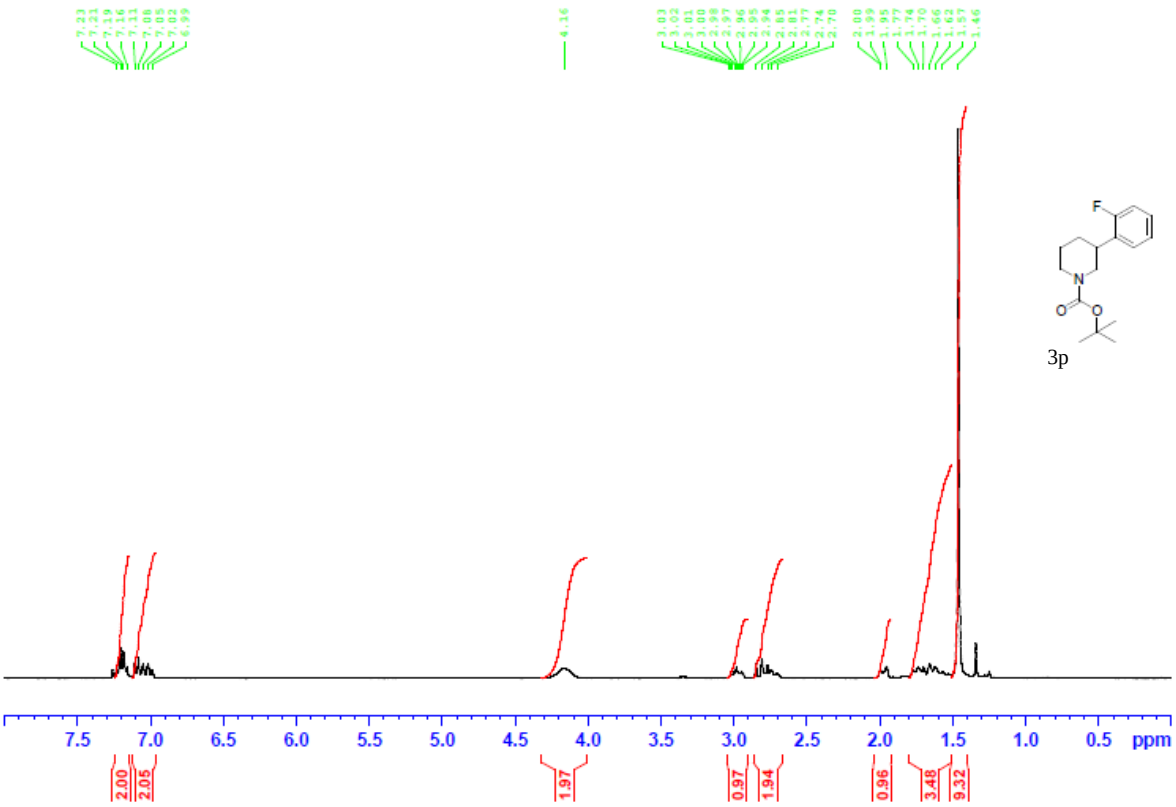
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1.46
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N
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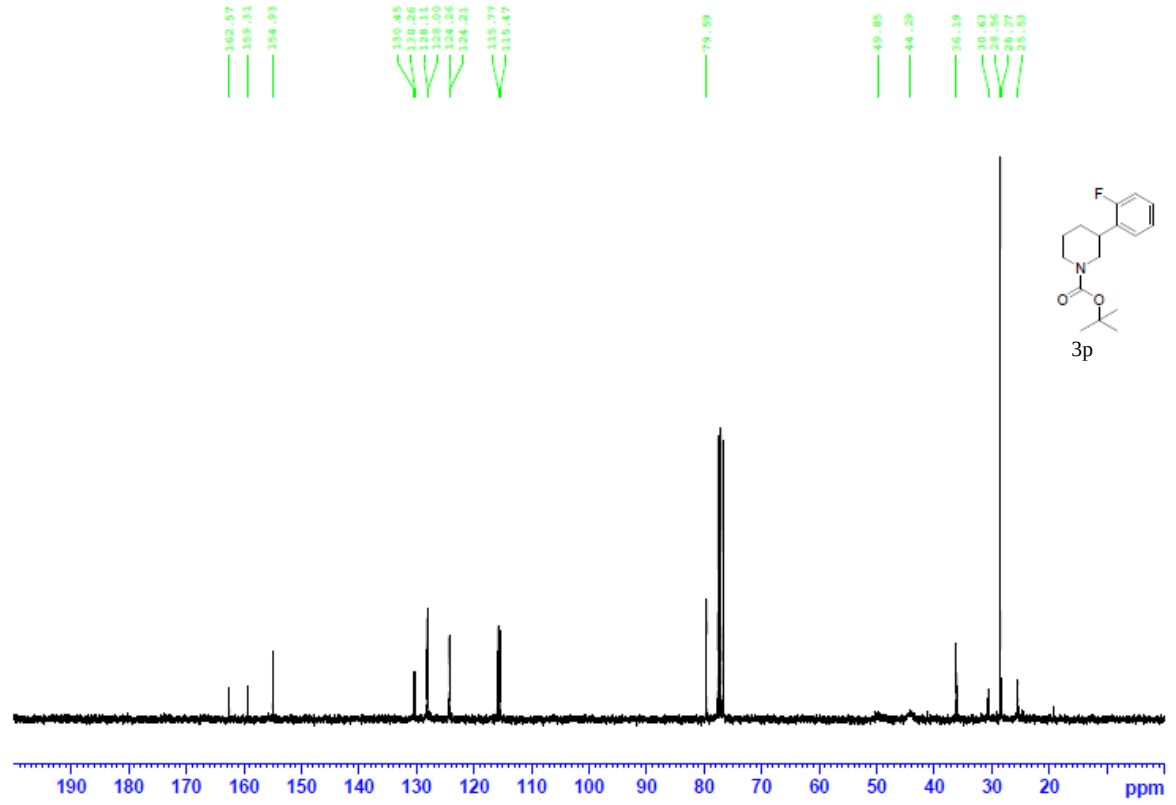
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28.56
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O
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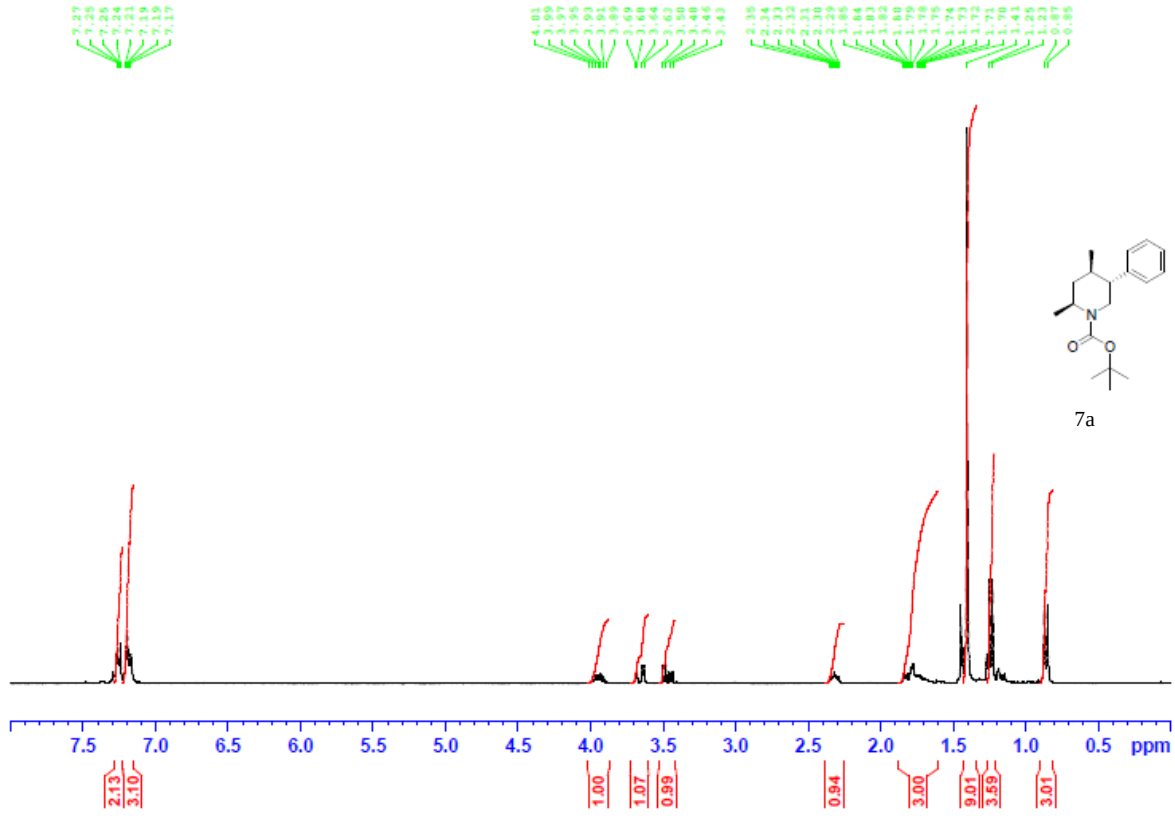
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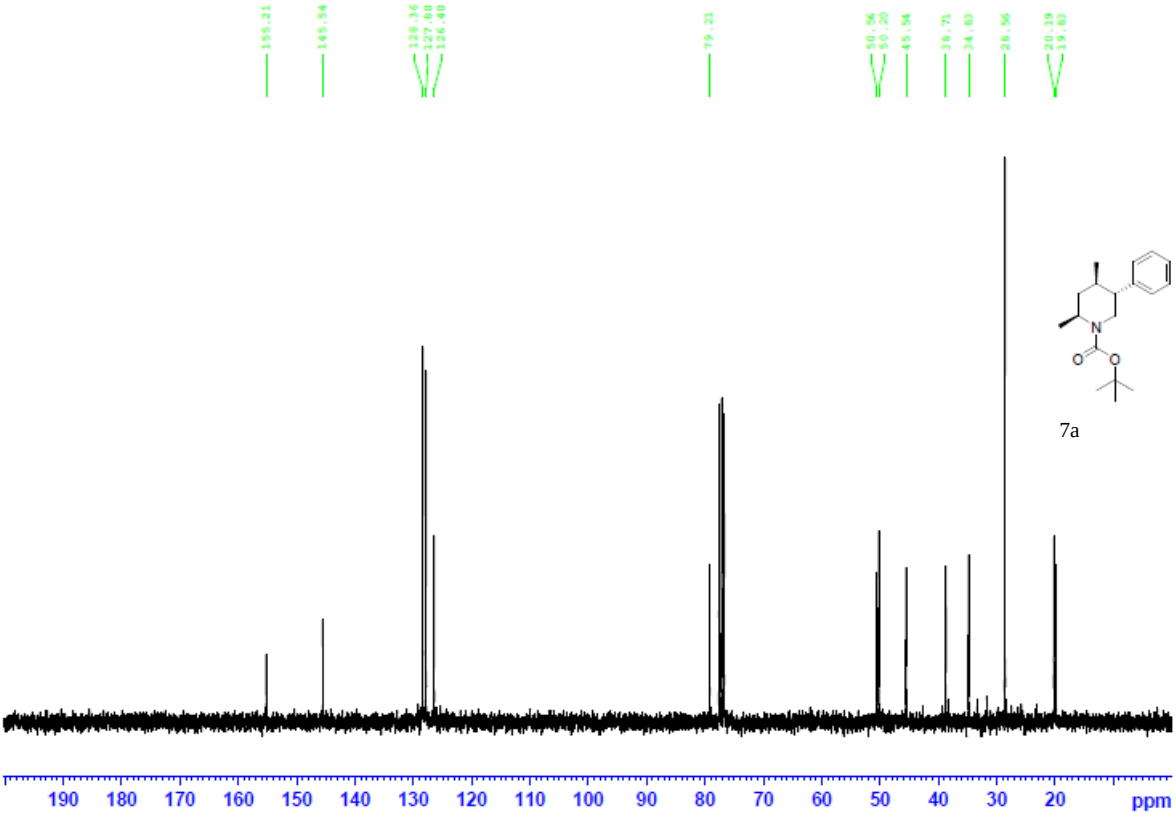
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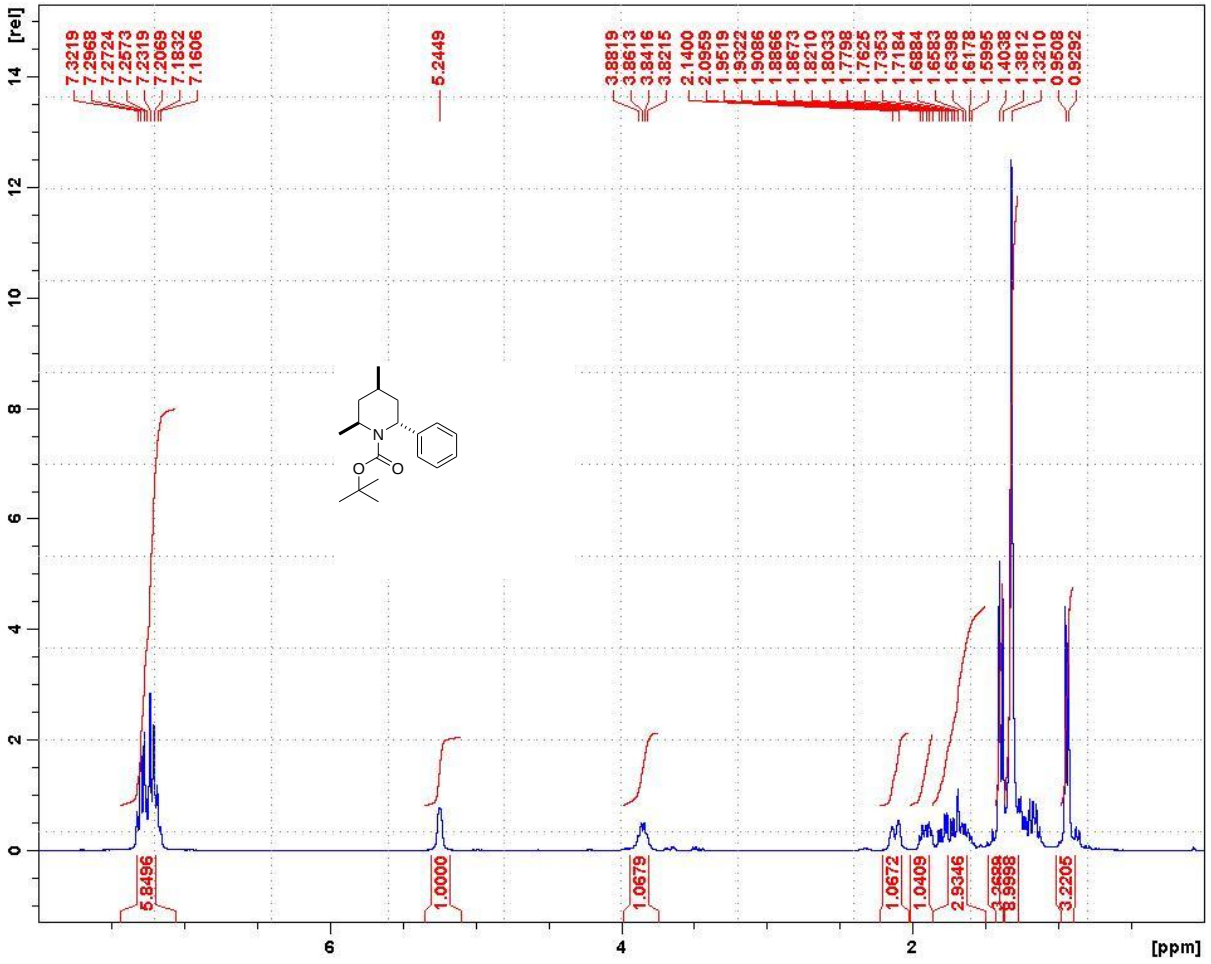
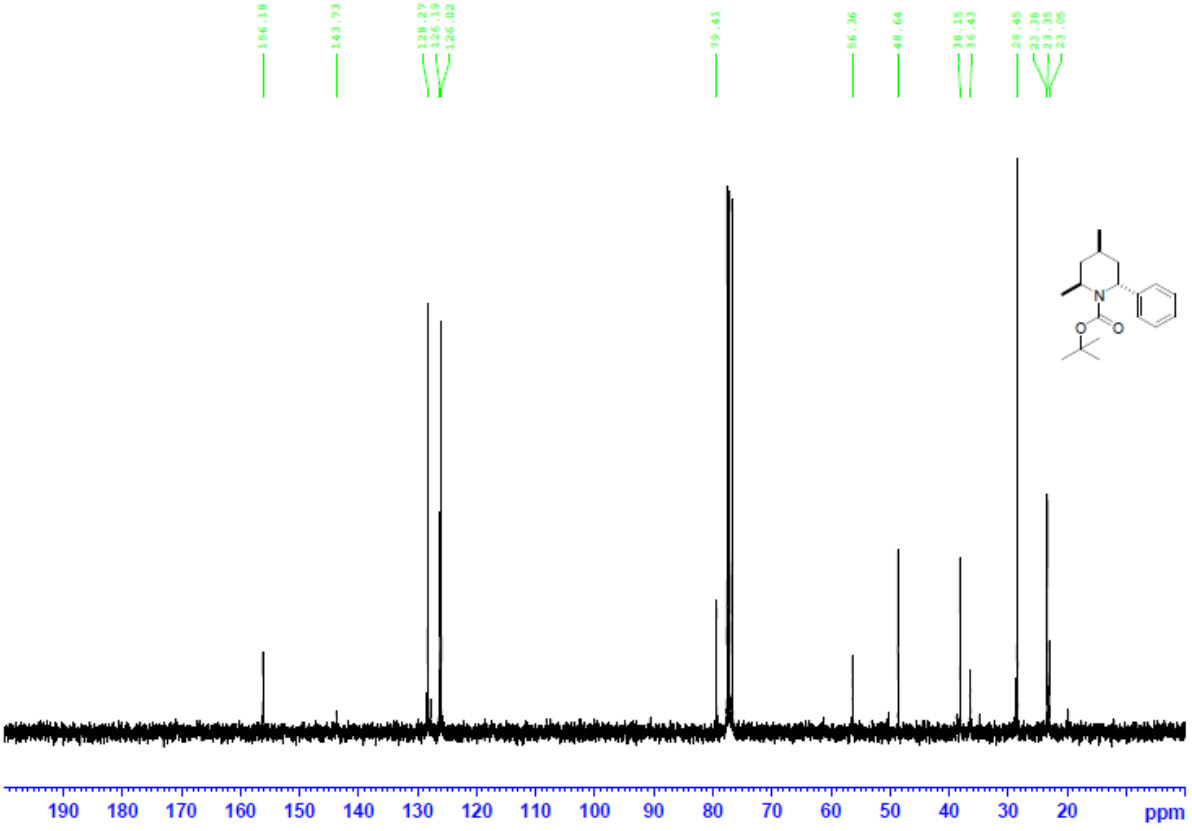
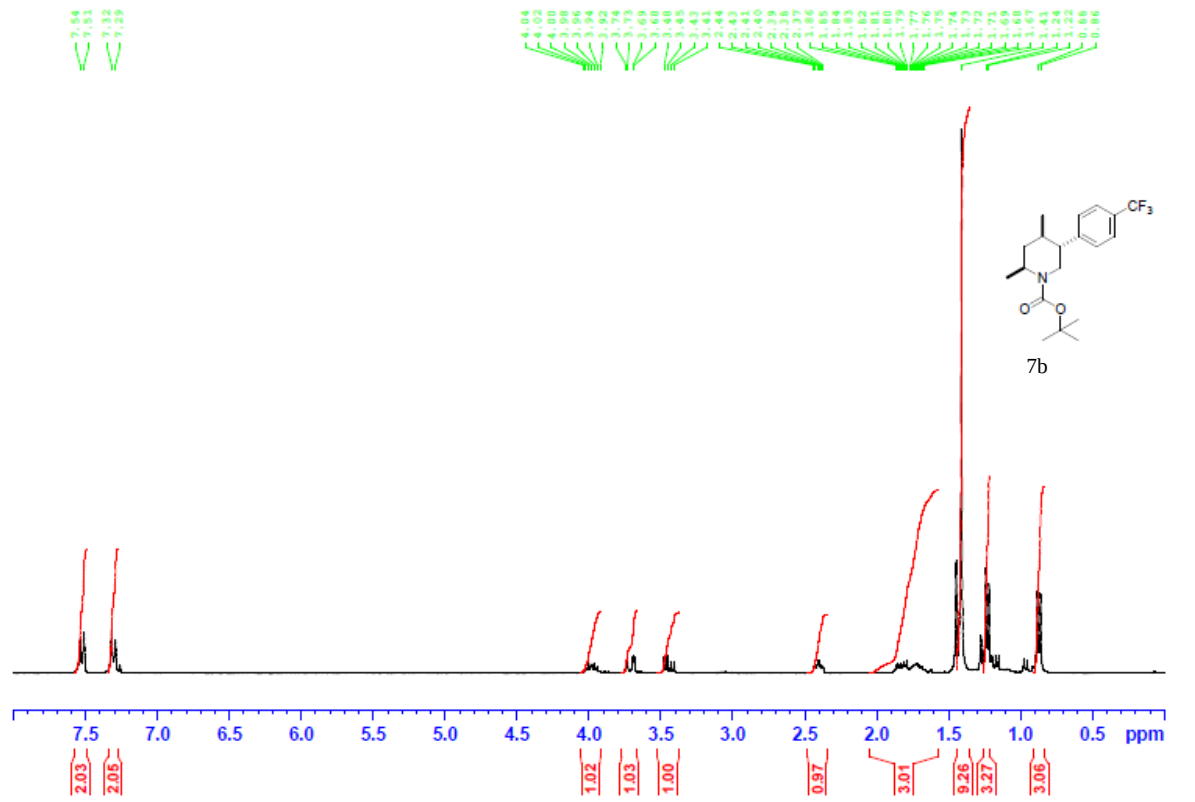
ppm

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3.43
3.41
2.44
2.43
2.41
2.40
2.39
2.38
2.37
1.86
1.85
1.84
1.83
1.82
1.81
1.80
1.79
1.77
1.76
1.75
1.74
1.73
1.72
1.71
1.69
1.68
1.67
1.41
1.24
1.22
0.88
0.86
CF3
N
O
O
7b
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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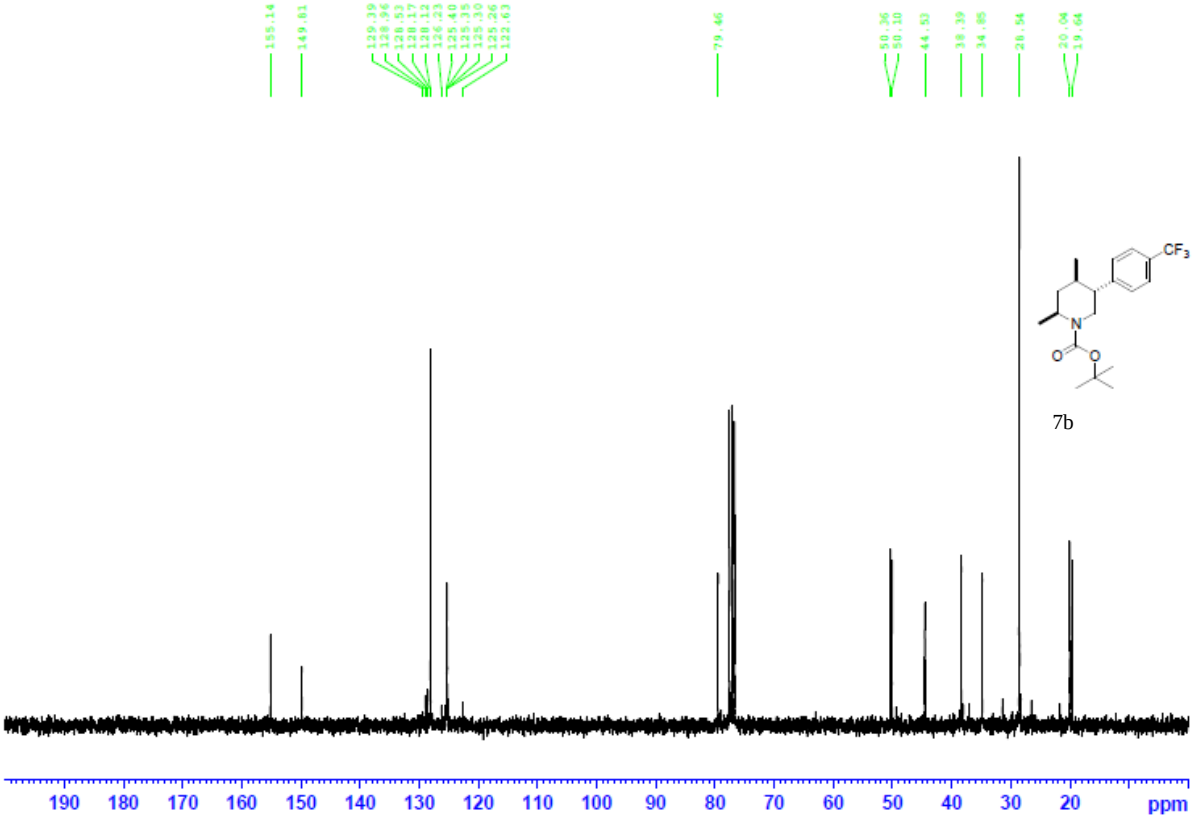
2.05
1.02
1.03
1.00
0.97
3.01
9.26
3.27
3.06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126.23
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125.35
125.30
125.26
122.63
79.46
50.36
50.10
44.53
38.39
34.85
28.54
20.04
19.64
CF3
N
O
O
7b
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160
150
140
130
120
110
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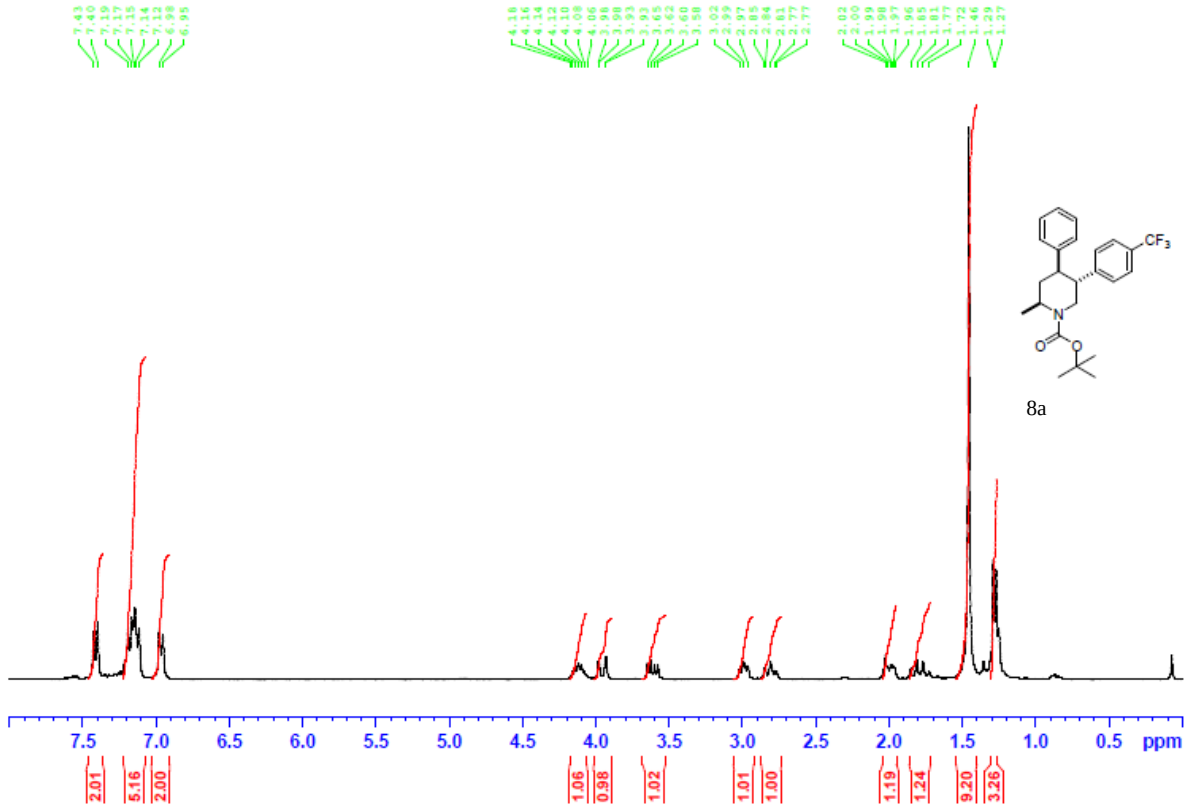
50
40
30
20
ppm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4.16
4.14
4.12
4.10
4.08
4.06
3.96
3.95
3.93
3.92
3.62
3.60
3.58
3.02
2.99
2.97
2.85
2.84
2.81
2.77
2.77
2.02
2.00
1.99
1.98
1.97
1.96
1.85
1.81
1.77
1.72
1.46
1.29
1.27
CF3
N
O
O
8a
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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1.02
1.01
1.00
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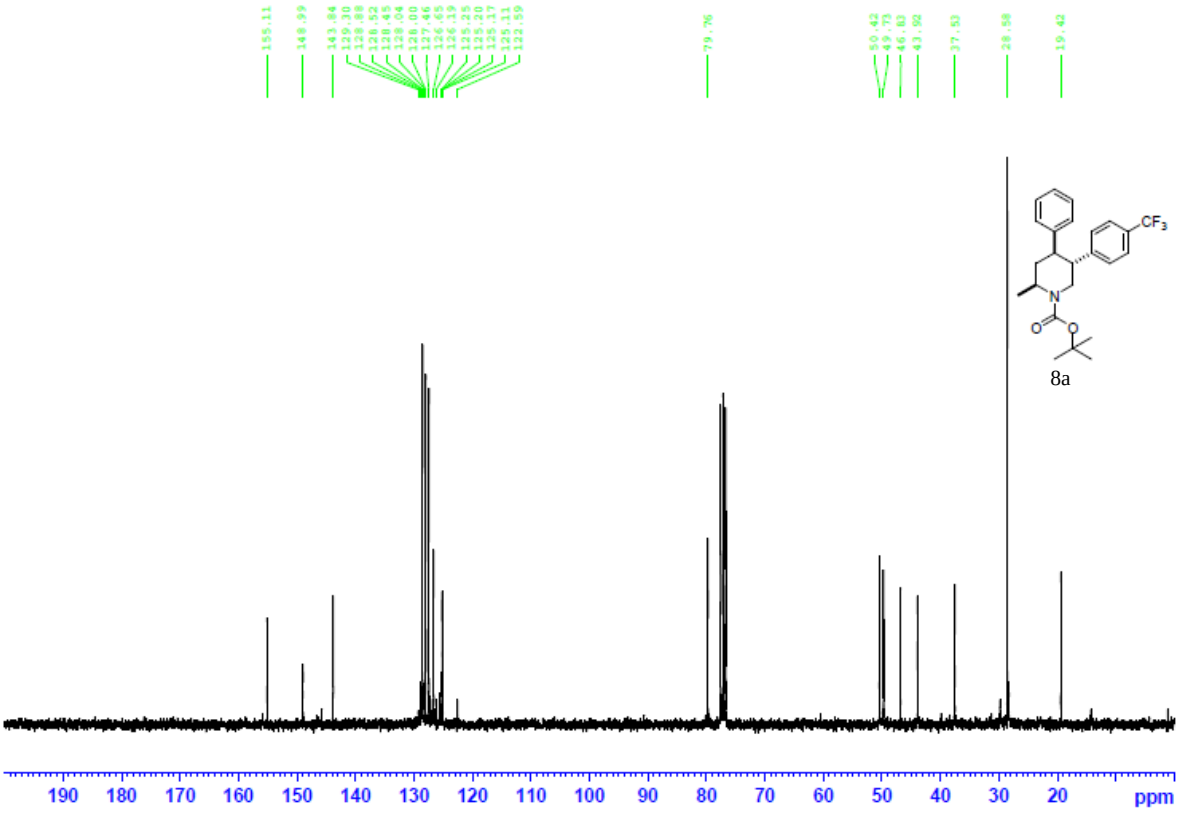
1.24
9.20
3.26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127.46
126.65
126.39
125.25
125.20
125.17
125.11
122.59
79.76
50.42
49.73
46.83
43.92
37.53
28.58
19.42
CF3
N
O
O
8a
190
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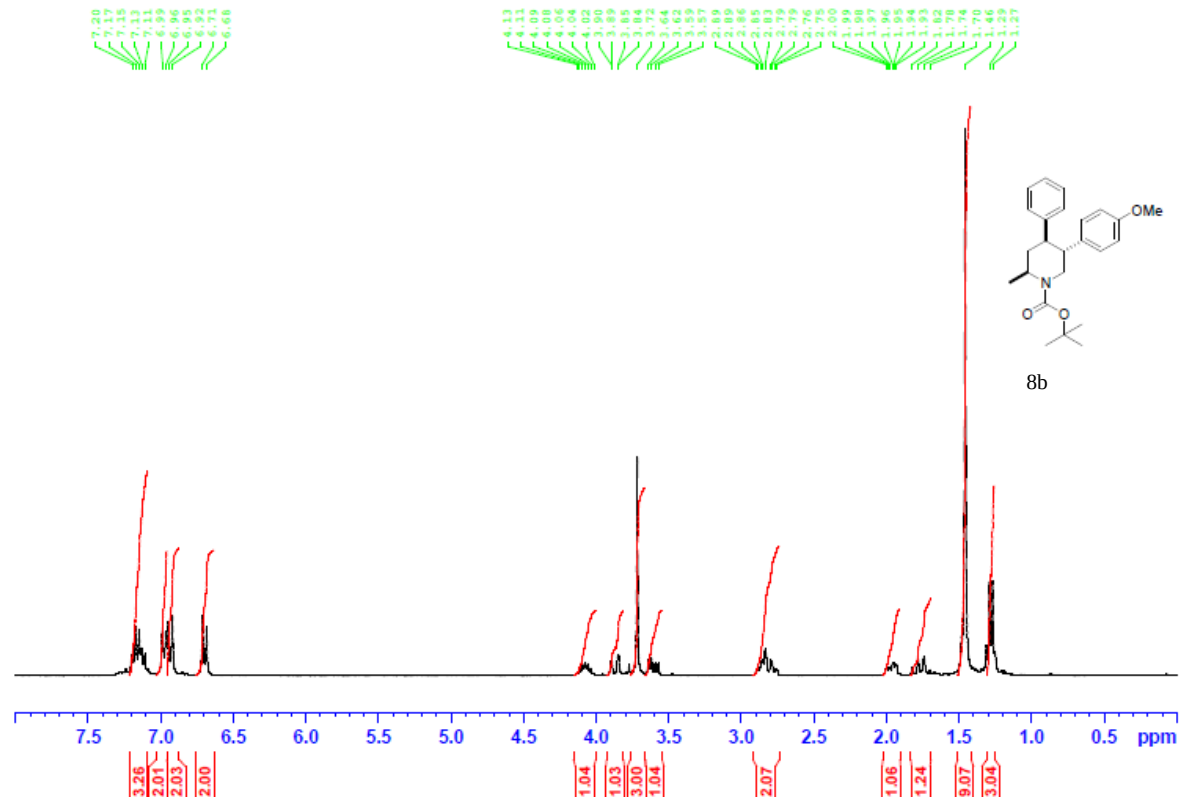
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


OMe
8b
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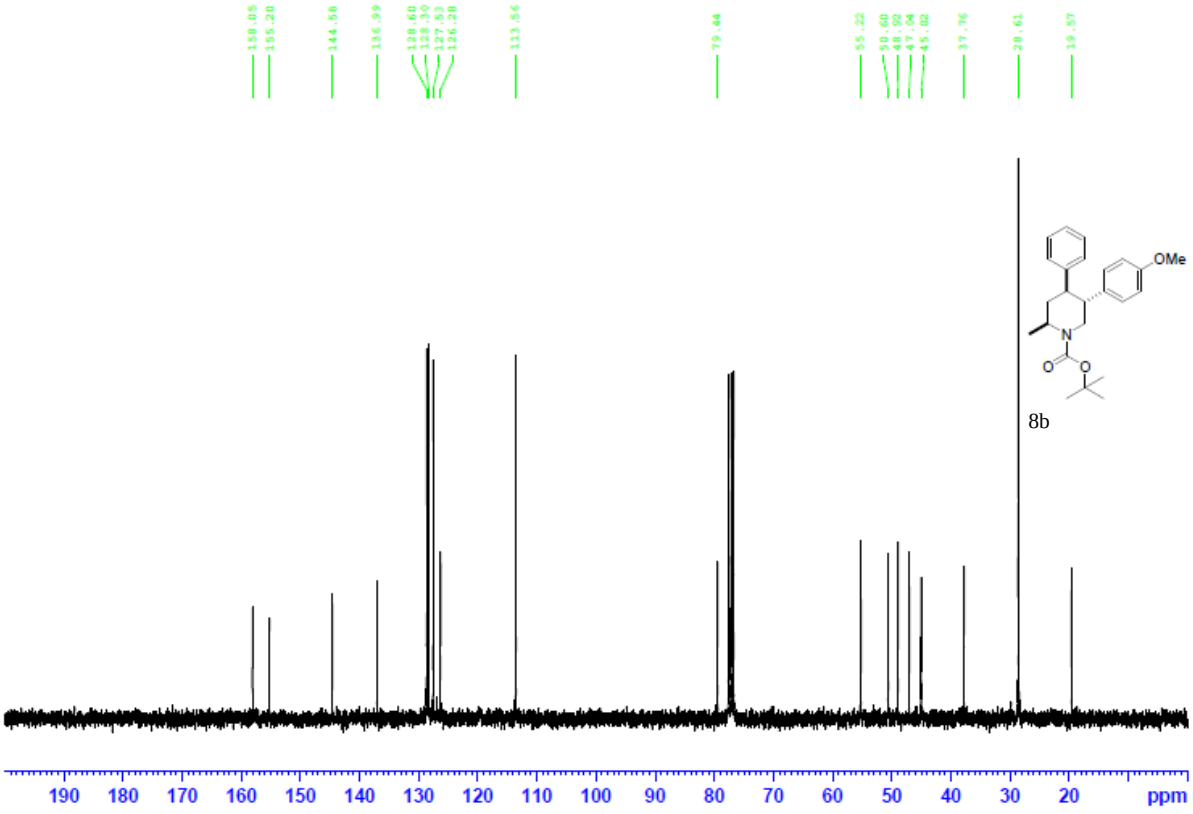
OMe
8b
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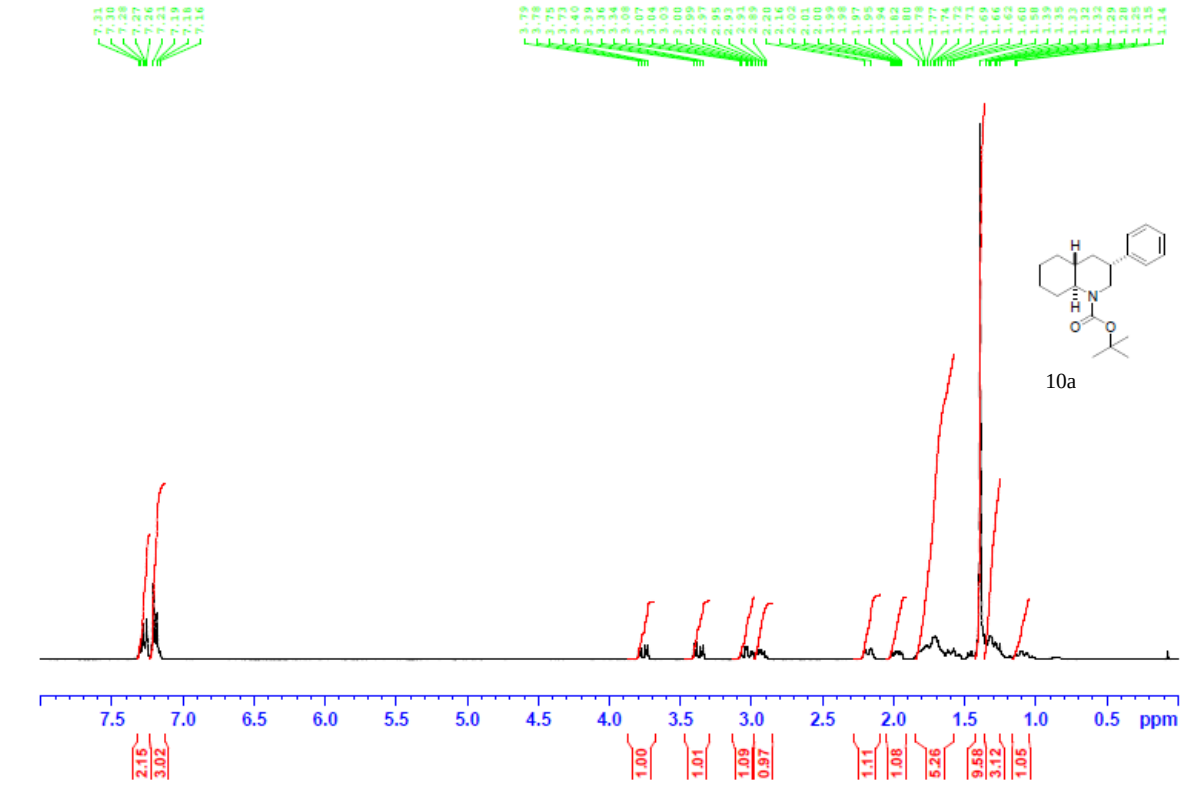
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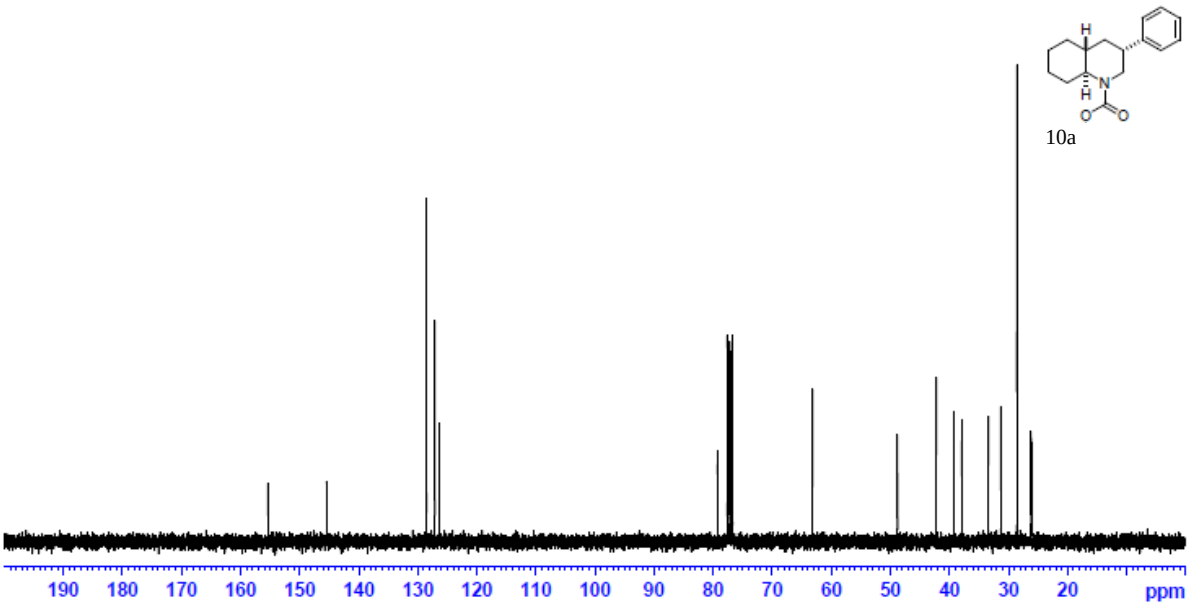
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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190
180
170
160
150
140
130
120
110
100
90
80
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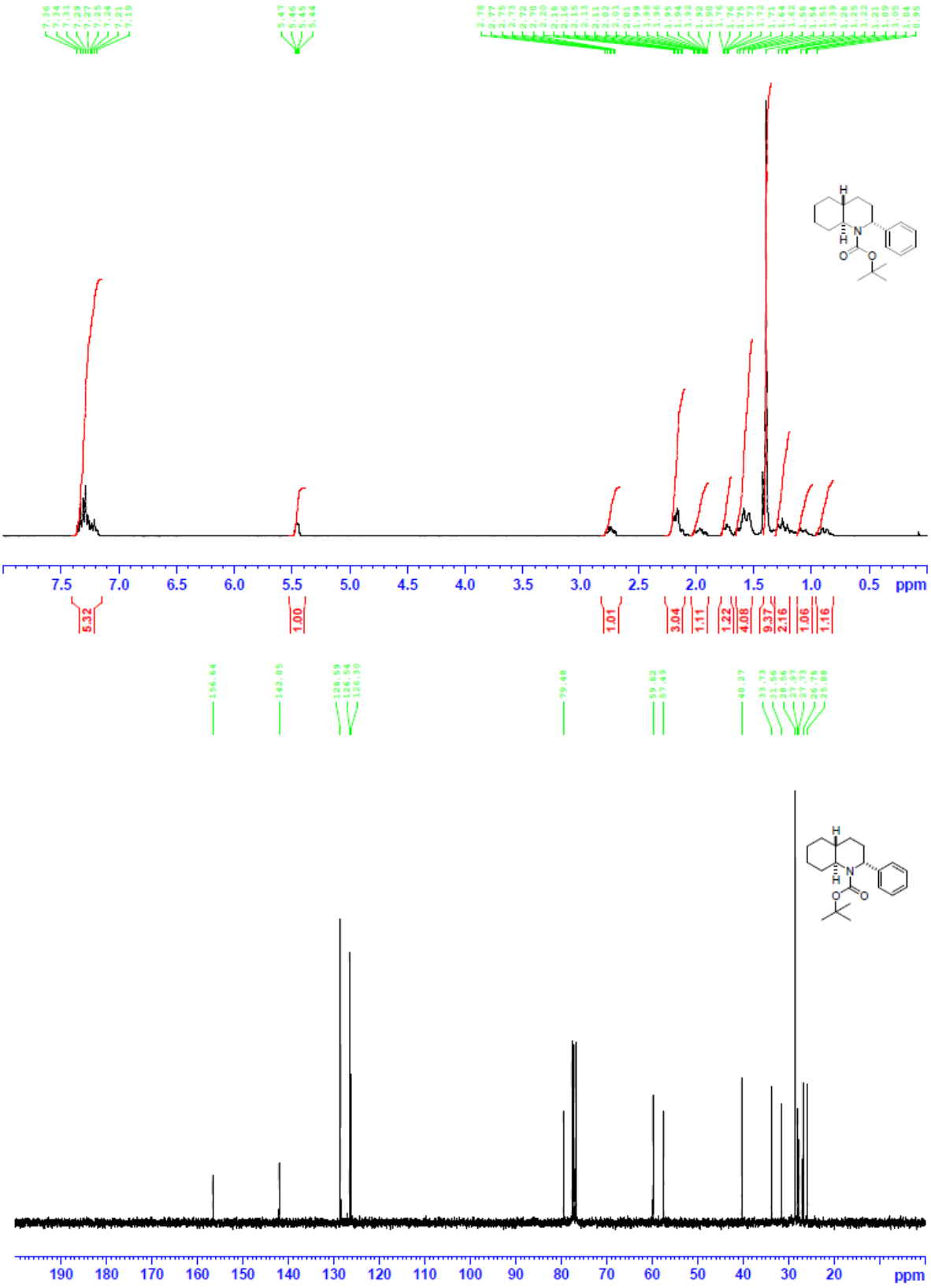
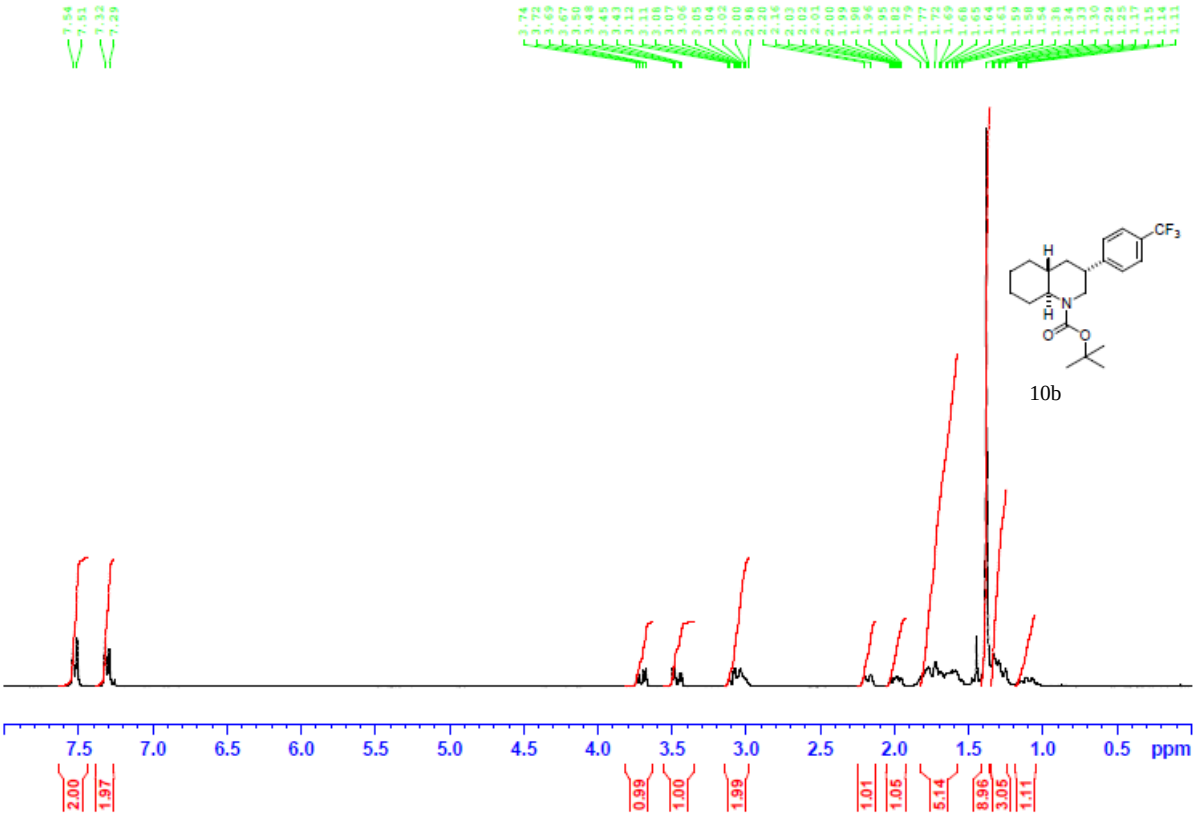
60
50
40
30
20
ppm

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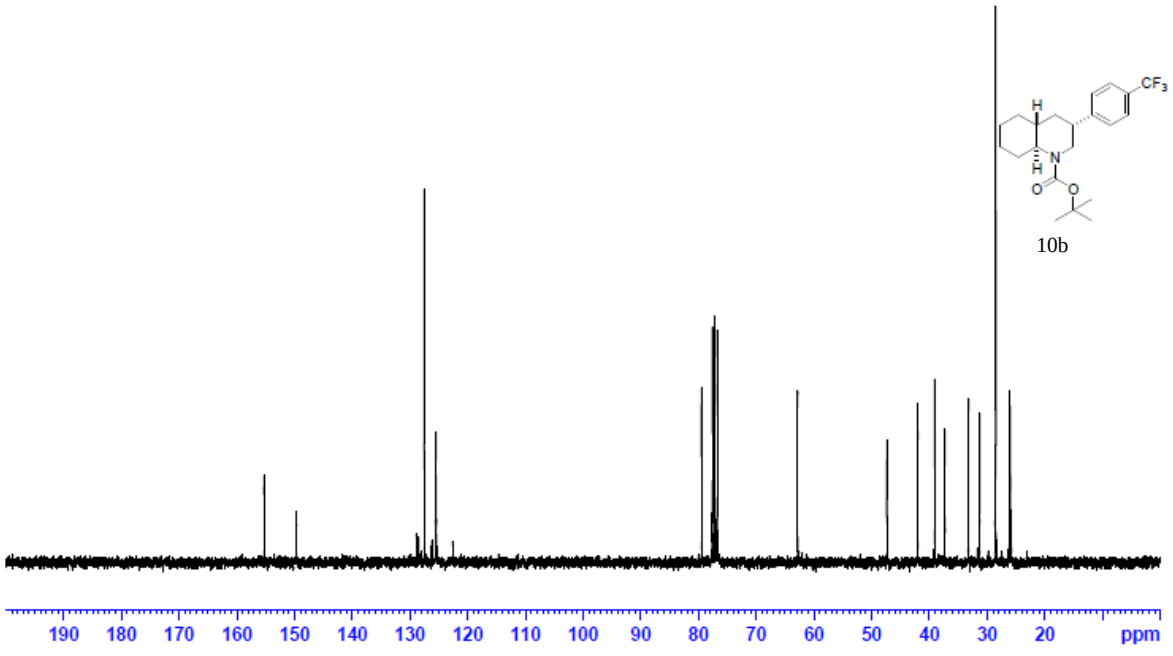
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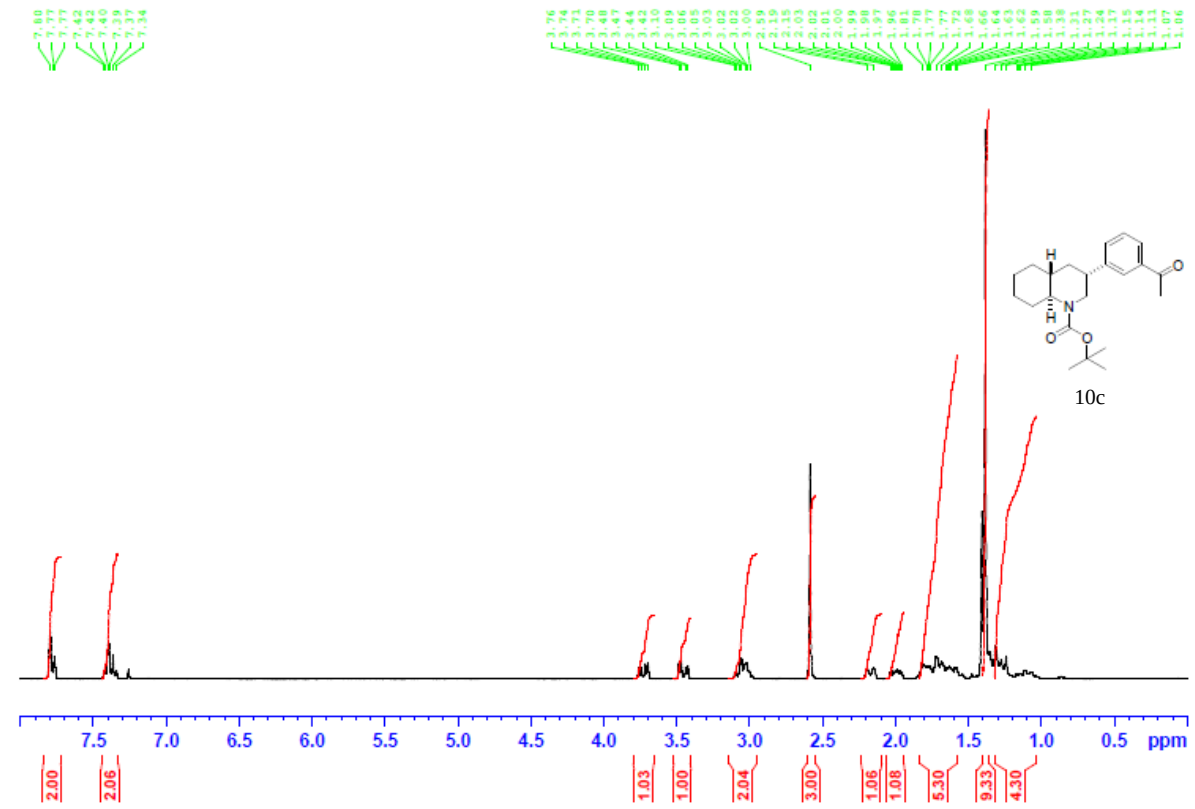
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5.5
5.0
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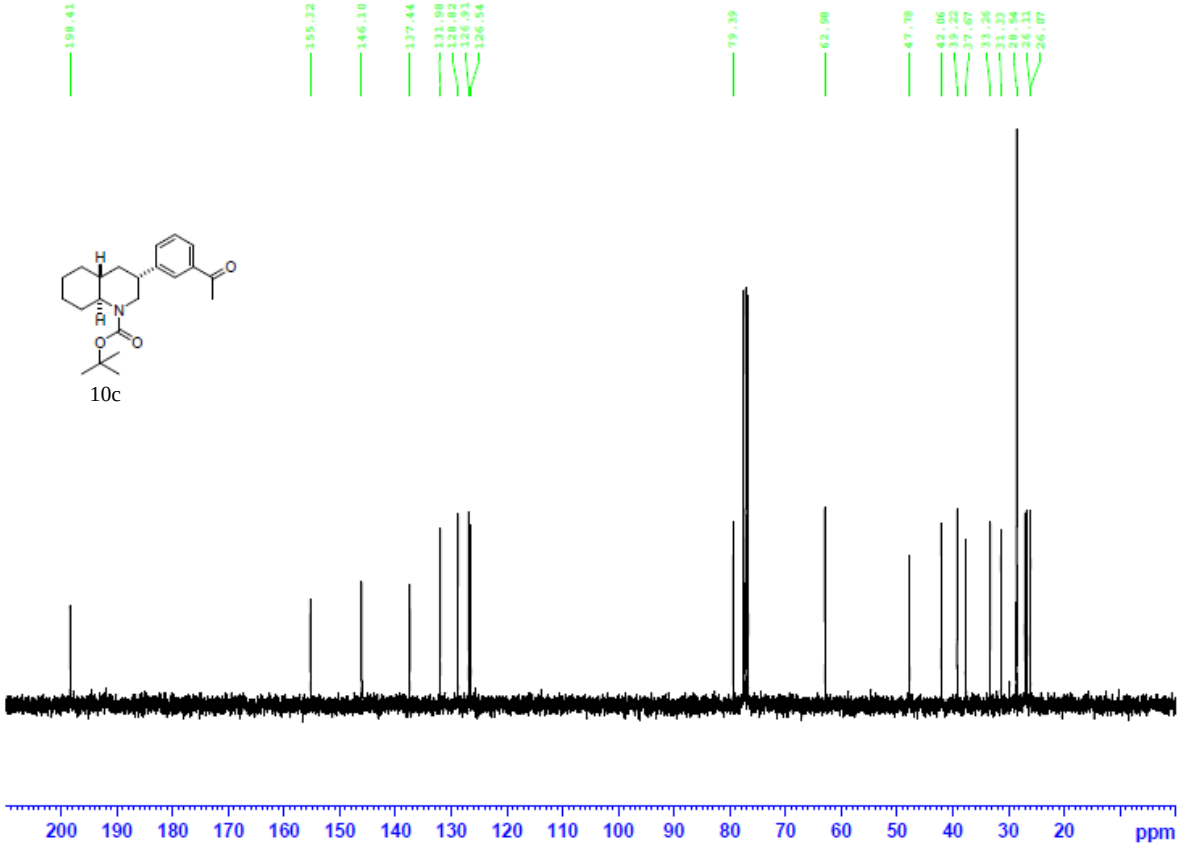
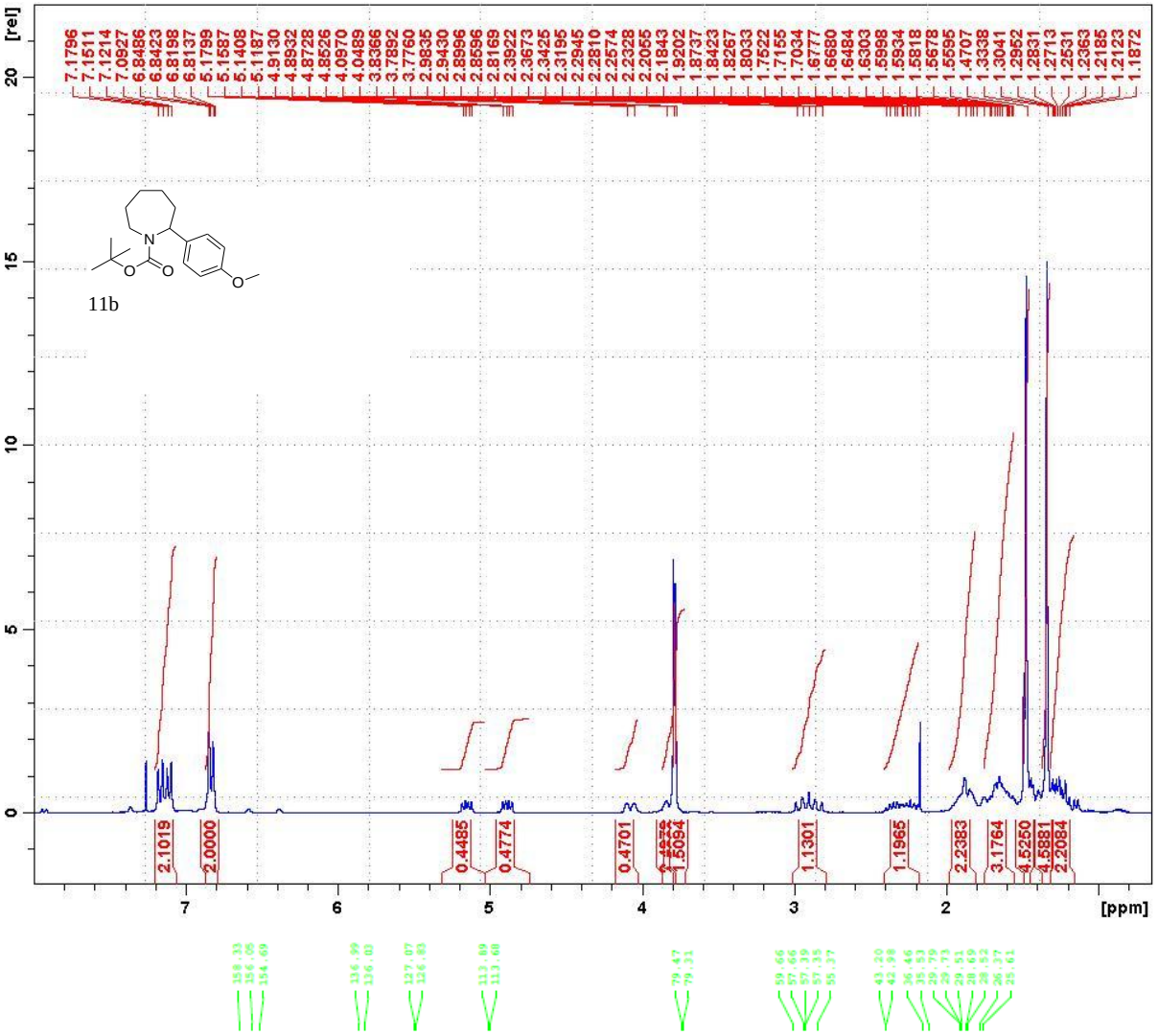
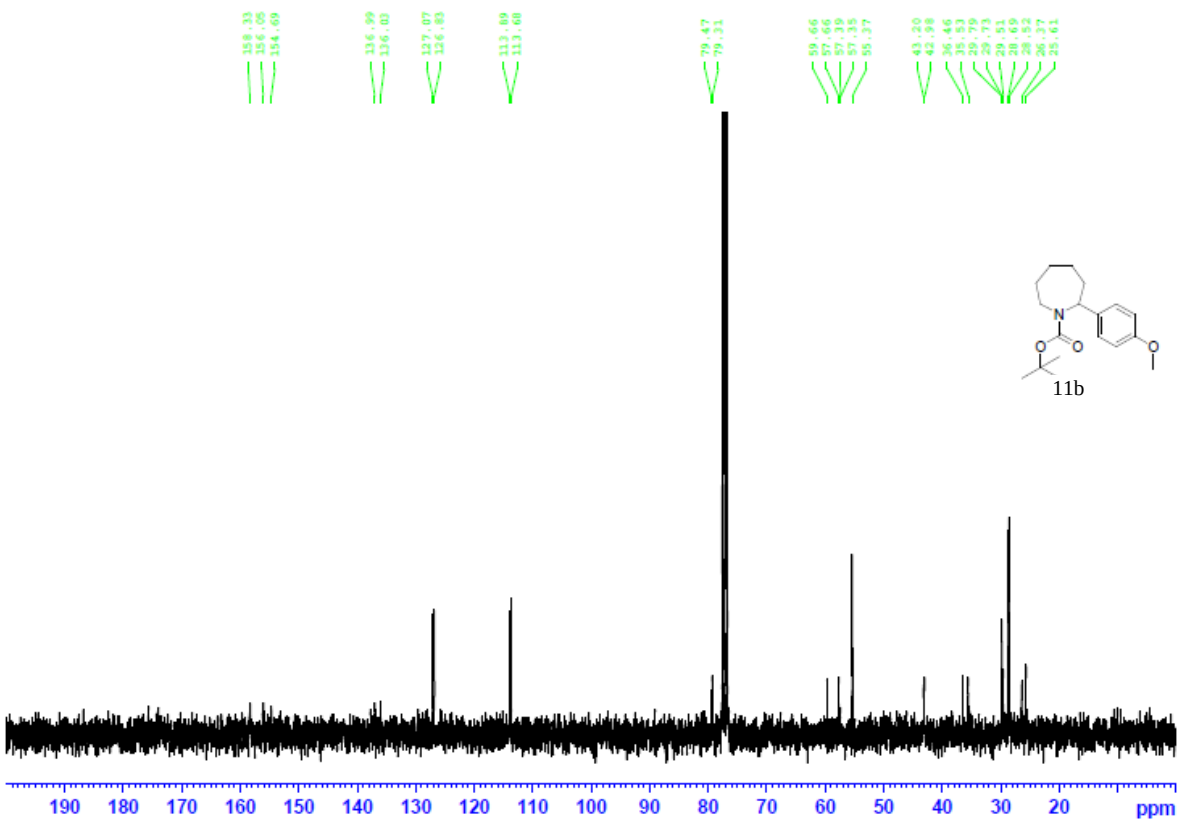
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.06
1.03
1.00
2.04
3.00
1.06
1.08
5.30
9.33
4.30

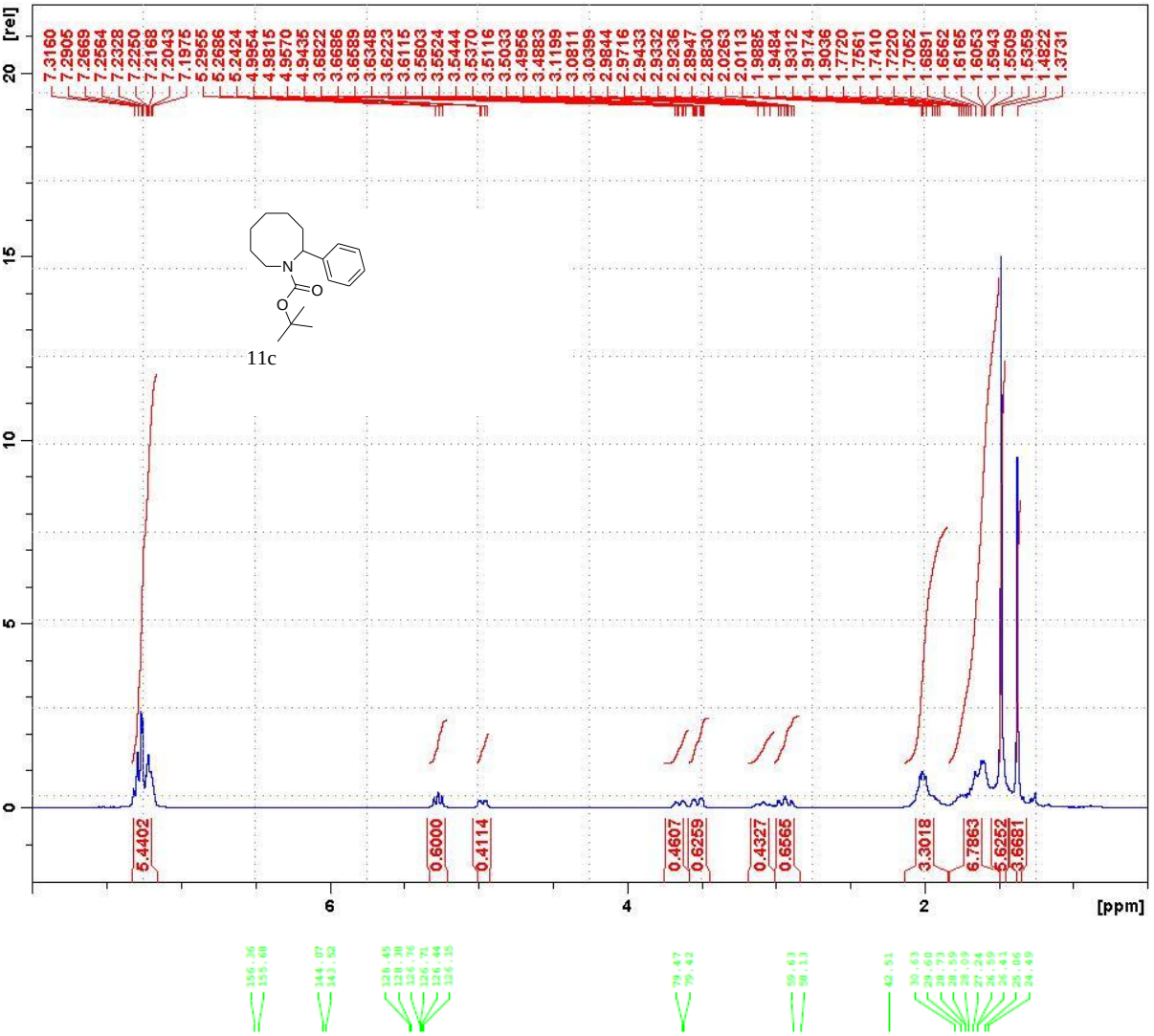

10c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm




11b




11b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7.2043
7.1975
5.2955
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5.2424
4.9954
4.9815
4.9570
4.9435
3.6822
3.6686
3.6589
3.6348
3.6223
3.6115
3.5603
3.5524
3.5444
3.5370
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3.5033
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3.4883
3.1199
3.0811
3.0399
2.9844
2.9716
2.9433
2.9332
2.9236
2.8847
2.8830
2.0263
2.0113
1.9885
1.9484
1.9312
1.9174
1.9036
1.7720
1.7561
1.7410
1.7220
1.7052
1.6891
1.6562
1.6165
1.6053
1.5943
1.5509
1.5359
1.4822
1.3731
11c
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0.6000
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0.6259
0.4327
0.6565
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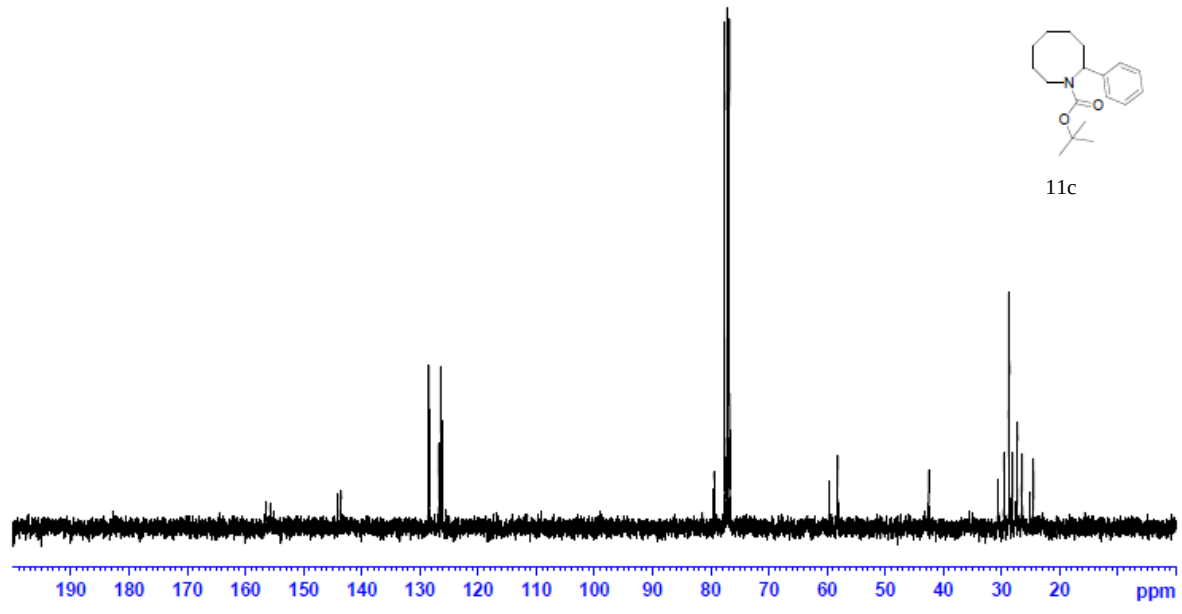
6.7863
5.6252
3.6681
[ppm]


11c
ppm

**Part 2: Computational Details.**

All calculations were performed with the Gaussian09 package[19] of programs with the hybrid B3PW91 functional.[20,21] The Pd atom was represented by the relativistic effective core potential (RECP) from the Stuttgart group and the associated basis set augmented by a f polarization function ($\alpha$ = 1.472).[22] The remaining atoms (C, H, N, O) were represented by a 6-31G(d,p) basis set.[23] The P atom was represented by RECP from the Stuttgart group and the associated basis set,[24] augmented by a d polarization function.[25] Full optimization of geometry was performed without any symmetry constraint, followed by analytical computation of the Hessian matrix to identify the nature of the located extrema as minima or transition states. Connection between reactant and product through a given transition state was checked by optimization of slightly altered geometries of the transition state along the two directions of the transition state vector associated to the imaginary frequency. PCM calculations[26] (solvent=toluene) have been performed on the gas phase optimized geometry. The basis set for Pd and P was the same, whereas a 6-311+G(d,p) basis set was used for all the remaining atoms. All energies given in the text are Gibbs free energies G (T = 298 K, P = 1 atm) defined as the sum of the PCM electronic energy and the gas phase Gibbs free energy correction.

[19] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

[20] Becke, A. D. J. Chem. Phys. 1993, 98, 5648.

[21] Perdew, J. P.; Wang, Y. Phys. Rev. B 1992, 45, 13244.

[22] Andrae, D.; Haussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. Theor. Chim. Acta 1990, 77, 123.

[23] Hariharan, P. C.; Pople, J. A. Theor. Chim. Acta 1973, 28, 213.

[24] Bergner, A.; Dolg, M.; Kuchle, W.; Stoll, H.; Preuss, H. Mol. Phys. 1993, 30, 1431.

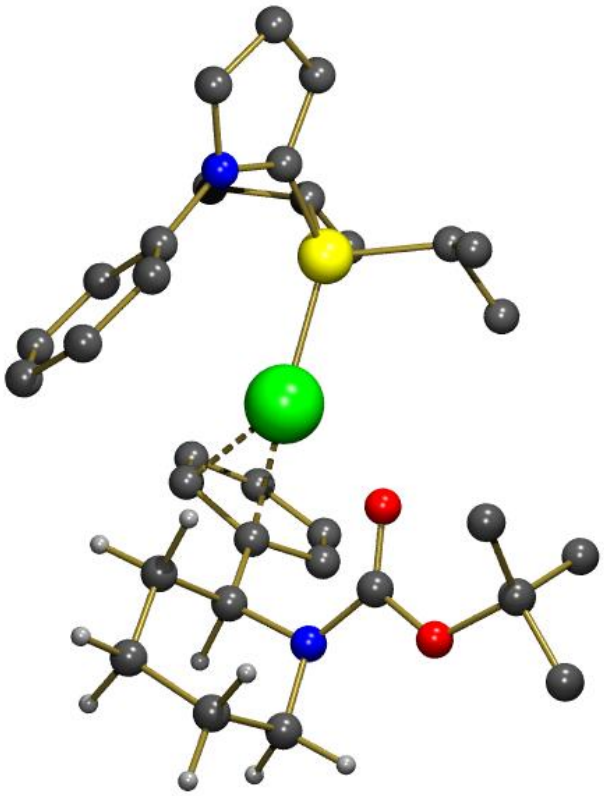
[25] Hollwarth, A.; Bohme, H.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Kohler, K. F.; Stagmann, R.; Veldkamp, A.; Frenking, G. Chem. Phys. Lett. 1993, 203, 237.

[26] Tomasi, J.; Mennucci, B.; Cammi, R. Chem. Rev. 2005, 105, 2999.

**Images (hydrogens of the piperidine are shown while the others have been omitted for clarity), Gas Phase Electronic Energy, PCM Electronic Energy and Gas Phase Gibbs Free Energy corrections (a.u.), and Cartesian Coordinates (Å) of all the Structures Mentioned in the Text.**

**Reaction mechanism:**

**2i**



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PCM: E(RB3PW91) = -1640.87496044
Gibbs: 0.636927

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C,0,-3.5082795729,1.0747488476,2.7751975214
C,0,-4.5964896532,0.5154466924,1.8513658159
C,0,-4.6089297315,1.2410308165,0.5027663418
Pd,0,0.4856040043,0.8885518369,-0.174274607
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C,0,-2.8684112341,0.099944399,-0.7918896191
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C,0,-3.1308780855,-2.8718570644,-1.307555762
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C,0,-1.188483801,2.9647900735,-1.2781985274
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C,0,0.7492805433,4.3968335258,-1.0058107613
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C,0,0.1012909029,2.8753452785,0.7866190765
P,0,2.394747936,-0.2739233899,-0.7237382283
C,0,3.209486263,-1.5964546624,0.2819688937
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C,0,4.2675591555,-2.3996541061,-0.1219261751
C,0,1.8183379927,-1.5767610188,2.4174604994
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C,0,1.3753188432,-0.4068359153,-3.3712460851
C,0,3.9465458464,0.7732265093,-1.0532472979
C,0,4.4269552693,1.3785198742,0.2668572753
C,0,1.3635014269,-2.5313312682,-2.0532401891
C,0,3.7014675952,1.8704269225,-2.0889919141
C,0,-5.2397539494,-2.1139082915,-2.4369752866
C,0,-3.0238547876,-1.4310013109,-3.3947520053
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H,0,-0.4820660713,4.3048059555,-2.7860522657
H,0,1.4056178486,5.1692343452,-1.3967615941
H,0,3.1340033985,-1.4994568769,-2.7354702836
H,0,4.7170817967,0.0844225921,-1.4242450077
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H,0,1.9121309361,-3.2059420446,-1.3919058552
H,0,0.4016122949,-0.1078167759,-2.9678899759
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H,0,2.8037647444,2.4481108228,-1.8420190291
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H,0,1.1590917184,-3.0640556229,-2.9901042624
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H,0,-5.8044852889,-2.3058140962,-1.5198033883
H,0,-5.7281439839,-1.2995399037,-2.9801561093
H,0,-3.4976206015,-0.5947688737,-3.9184742142
H,0,-1.9874527577,-1.1723750115,-3.1784883027
H,0,-3.0394237242,-2.3004057277,-4.059973206
H,0,-3.6854026745,-3.0486299927,-0.3802933282
H,0,-3.1400736802,-3.7990013164,-1.8894204615
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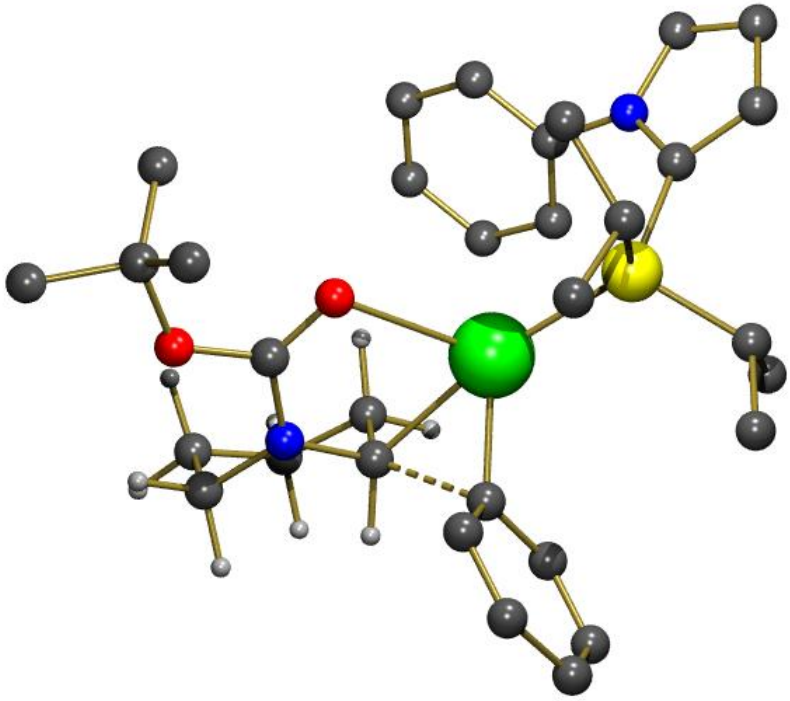
**TS-Ia-alpha**



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C,0,-3.0150740103,1.5706356179,2.7344540635
C,0,-4.2280312861,1.132632253,1.9057365095
C,0,-4.0954845859,1.5602670964,0.4403991015
Pd,0,0.2249733234,0.5439643274,0.0820623787
O,0,-1.6972195072,-0.763794352,-0.9011619482
C,0,-2.7425040702,-0.1491488419,-0.7028807145
O,0,-3.9581226499,-0.589587398,-1.0883765446
C,0,-4.1143249448,-1.8444468063,-1.8249834687
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N,0,2.8574786973,-2.2762892539,1.4843519297
C,0,3.7884962378,-3.2505103265,1.7632807556
C,0,4.8356120357,-3.1279783272,0.8806258805
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C,0,-0.2047042747,-3.0799101316,3.4071220621
C,0,-0.3761814939,-1.9138172098,4.1515743458
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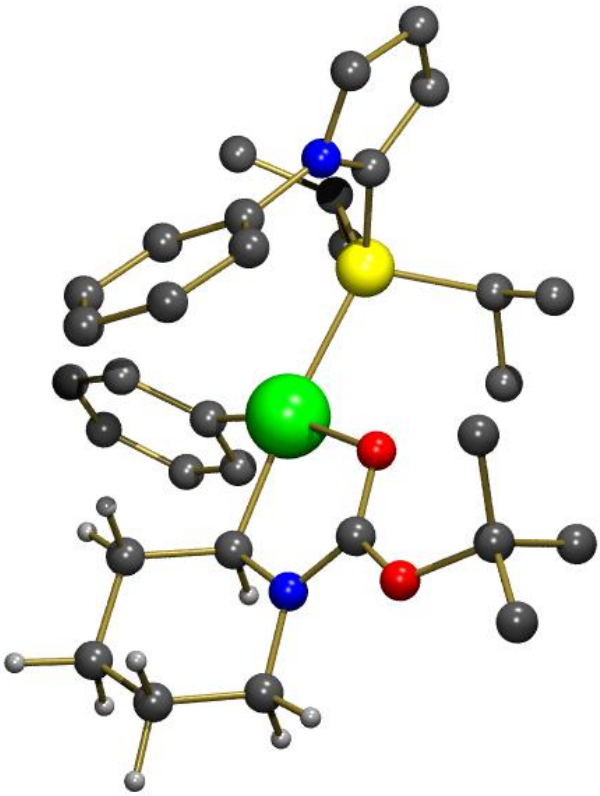
**Ia**



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C,0,2.2574846014,0.7279002782,-2.5231666596
C,0,3.700467478,0.6682257548,-3.0437461119
C,0,4.4991463817,-0.4138171913,-2.3160197206
C,0,4.4156780081,-0.2213661475,-0.8022716378
Pd,0,0.3348181848,0.8459424351,-0.1282661076
O,0,1.2678564894,-0.858094418,0.8860134443
C,0,2.4610405536,-0.9675626633,0.5114965417
O,0,3.2808898824,-1.9331617762,0.9534896909
C,0,2.9869852809,-2.7586605359,2.1255033304
C,0,1.7333420706,-3.6009483422,1.9037660659
C,0,-0.0682960778,2.5302882769,-1.120600641
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C,0,-0.9983743701,3.7499555844,-3.0315467008
C,0,-0.7615798611,2.5566725321,-2.3434383358
P,0,-1.7562648836,0.76014103,1.0960599661
C,0,-2.7644149857,-0.7854764604,1.0846148108
N,0,-2.5902847854,-1.9127949001,0.2862511278
C,0,-3.5058649888,-2.8708765884,0.6563017406
C,0,-4.2736942808,-2.3823932692,1.6866345926
C,0,-3.8088276617,-1.0751741084,1.9534248479
C,0,-1.7277866461,-2.1184672487,-0.826799093
C,0,-0.9873536105,-3.3010760146,-0.8958732992
C,0,-0.2202974556,-3.576431008,-2.0248564547
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C,0,-3.1952684156,1.9816453257,0.8667200846
C,0,-3.826061823,1.8284159528,-0.5172585226
C,0,-0.9293131044,-0.359271304,3.5840429216
C,0,-2.8315358364,3.4382535216,1.1534455597
C,0,4.2203686352,-3.655232533,2.2115312299
C,0,2.8855172946,-1.8671389516,3.3599173944
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H,0,-0.7220357035,5.8916797955,-3.052086105
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H,0,-3.9303438165,1.6529031743,1.6137119115
H,0,-0.0851200301,-0.780473229,3.0305038669
H,0,-1.7282032033,-1.1031958628,3.5995856507
H,0,0.6569908583,1.6864182153,2.7173710859
H,0,-0.5374865524,2.9793382052,2.669290621

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H,0,4.1331484664,-4.3303735745,3.0677471715
H,0,4.323006797,-4.2578001658,1.3044047147
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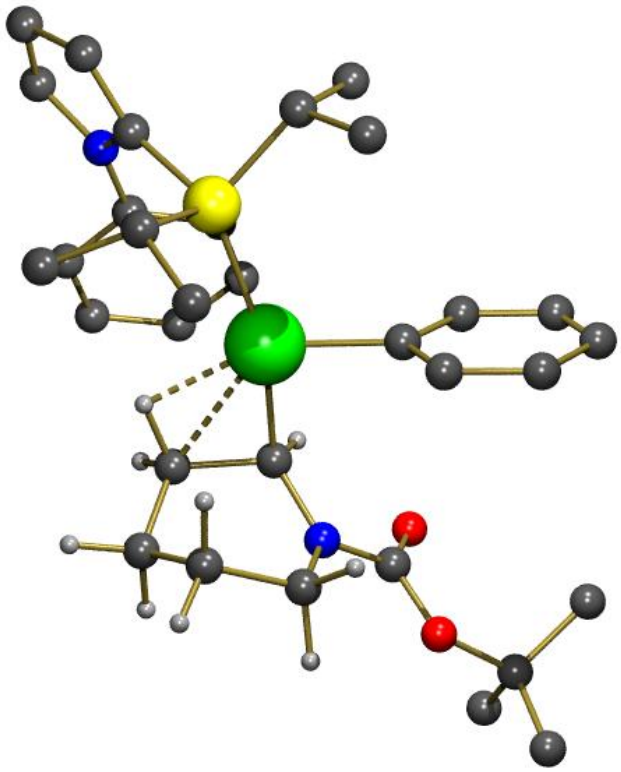
**Ib**



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PCM: E(RB3PW91) = -1640.84440700
Gibbs: 0.634637

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C,0,1.9899297631,2.5150617784,-2.4502207765
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C,0,0.8468433313,1.4995611826,-0.5407217264
Pd,0,-0.3348359955,0.0757324797,0.276958633
H,0,1.1925181432,2.5294388138,1.3308551069
H,0,5.1164087366,-0.0677747677,-2.2344478799
H,0,3.1715585802,4.2786657611,-2.0547335154
P,0,-2.4660360054,1.196539702,0.5094587989
C,0,-2.9069339162,1.5351193038,2.3251843942
C,0,-2.7990878298,2.8427722561,-0.3726659672
C,0,-3.3402007292,0.2445692521,3.0230806929
C,0,-1.7146610015,2.1502733719,3.0639583318
H,0,-3.7460917214,2.2441869885,2.3248314484

C,0,-1.9735261699,4.0170390617,0.1516212722
C,0,-2.586442558,2.649148584,-1.8749914336
H,0,-3.862576681,3.0484926567,-0.1937713414
C,0,-2.9738807564,-1.7807036508,-1.1256546084
H,0,-2.5429214968,-0.5074887262,2.9753860689
H,0,-4.2409941908,-0.1837583273,2.5781736495
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H,0,-1.5405893344,2.4088828302,-2.091504289
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C,0,-1.0507726538,-2.1473426247,-2.5377327319
H,0,-2.0373978101,-0.2420352946,-2.3059495455
H,0,-2.0163042728,-5.0408217982,-1.0391074936
C,0,-1.0496429015,-3.4988534169,-2.1974361375
H,0,-0.3060917269,-1.7584048948,-3.2255638824
H,0,-0.3040540889,-4.1654503863,-2.6205840116
H,0,0.7803169311,0.7512584216,-2.5683476154
N,0,-4.0307281787,-0.9539693851,-0.6513540546
C,0,-3.9754456999,0.3036708515,-0.0560910645
C,0,-5.3475910763,-1.3141426247,-0.8193444884
C,0,-5.2899679237,0.7063412873,0.1398981105
C,0,-6.1508125588,-0.3069764971,-0.3387007092
H,0,-5.5939260394,-2.2419076161,-1.3147483623
H,0,-5.5932853262,1.6336536744,0.607728495
H,0,-7.232013723,-0.299549997,-0.3427169237
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H,0,-3.5408024916,0.441961631,4.0827442888
H,0,2.2154648631,2.5030176031,-3.5146785603
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O,0,4.6890947755,-0.669803746,0.4372173264
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H,0,7.9324387749,-0.0333812379,0.2737406353
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H,0,6.9874859164,-0.7654616179,1.5863369787
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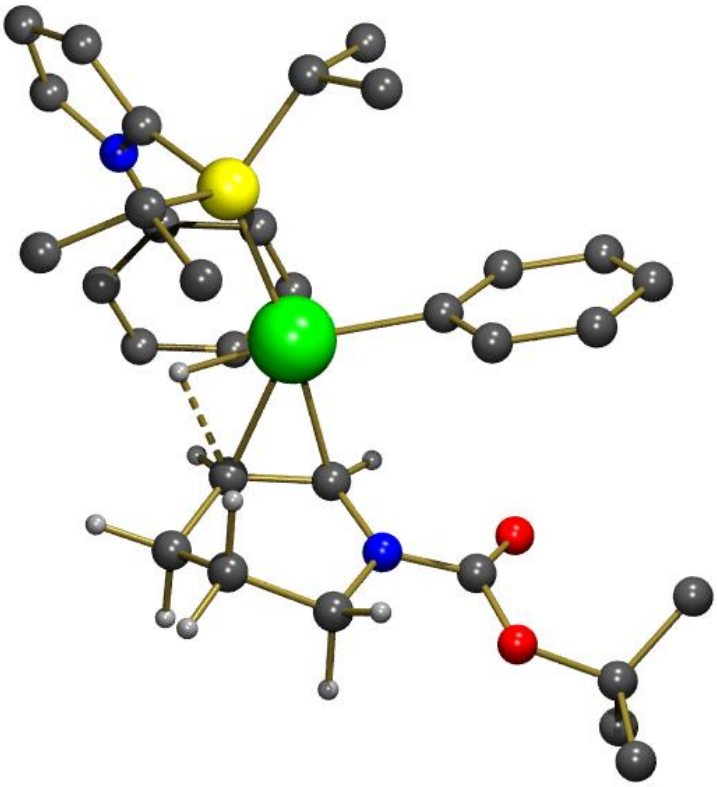
**TS-Ib-IIa**



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PCM: E(RB3PW91) = -1640.82707225
Gibbs: 0.632024

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C,0,0.7123722238,1.258038774,-0.8217780319
Pd,0,-0.3902930641,-0.1293706487,0.2795544863
H,0,1.4762582123,2.2473949726,0.9453902805
H,0,5.1543072549,0.7966492618,-1.7386891137
H,0,2.8744104445,3.9306524752,-2.7463901002
P,0,-2.4037538807,1.0420217468,0.4311188408
C,0,-2.7858647621,1.5110174325,2.2302323049
C,0,-2.770840444,2.6458034531,-0.5144131008
C,0,-3.2994781533,0.3176108718,3.0354602669
C,0,-1.5398992087,2.097072657,2.9001798746
H,0,-3.570517576,2.2789357693,2.1824060973
C,0,-1.8929255582,3.8315559751,-0.1141313981
C,0,-2.7031056808,2.395029133,-2.0209221775
H,0,-3.8125176676,2.8722235525,-0.2486439146
C,0,-2.9775275963,-2.0032798047,-1.0960009861
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H,0,-4.2419385821,-0.0716653983,2.6447460945
H,0,-0.7622970821,1.3306930226,2.9784985646
H,0,-1.1109480039,2.9398612858,2.3551978477
H,0,-0.8302895588,3.6111116749,-0.2498189256
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H,0,-1.6802601446,2.1608452682,-2.3297764077
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C,0,-2.048507218,-1.5396854653,-2.0306508324
C,0,-2.0180485389,-4.2164698579,-1.2351220831
C,0,-1.1040288718,-2.4194363497,-2.5588153697
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C,0,-6.1115469781,-0.4810901986,-0.2354994744
H,0,-5.6023486884,-2.4500263262,-1.1683365335
H,0,-5.5062131785,1.4846996262,0.6267305917
H,0,-7.1920224337,-0.4657718428,-0.1995162277
H,0,-3.6761609293,-3.6853329451,0.0445546983

H,0,-3.0163316388,3.2977198816,-2.5586277867
H,0,-2.1383745086,4.6900186892,-0.7508437118
H,0,-1.7849062442,2.436915386,3.9135626875
H,0,-3.4566146861,0.6159392225,4.0788126771
H,0,1.5807065721,2.2144714068,-4.0030314178
C,0,1.3679233063,-1.434981496,0.277026471
C,0,0.3748224058,-2.10554712,1.0355291607
C,0,0.641565664,-2.3079643374,2.5118086958
C,0,1.3949027893,-1.1009269116,3.0599206927
C,0,2.7160536955,-0.8837043194,2.329790551
H,0,-0.2876583131,-2.4744928974,3.0654699973
H,0,-0.1743372933,-2.8871288764,0.5174676169
H,0,1.507014115,-1.661253235,-0.7729734828
H,0,0.7577990747,-0.215651075,2.943683655
H,0,1.6069611169,-1.2157622352,4.1282657736
H,0,3.1357493248,0.0927835483,2.5865658179
H,0,3.445566726,-1.6374731697,2.654906232
H,0,1.2540899814,-3.2146629668,2.6283813869
N,0,2.5627269224,-0.9729174549,0.8754532346
C,0,3.6346367835,-0.7478772503,0.0391927358
O,0,3.6151828803,-0.940831729,-1.1644252062
O,0,4.6955659787,-0.3228918313,0.756744062
C,0,5.9683654309,-0.0294516226,0.0987037346
C,0,6.8486262494,0.4184423815,1.2630991649
H,0,7.8496061603,0.6704757776,0.9007775257
H,0,6.4237571136,1.3016123888,1.749060239
H,0,6.9396322033,-0.3772197373,2.0086104589
C,0,6.5311337171,-1.2962020198,-0.5443112518
H,0,6.6124465238,-2.0968438298,0.1981806037
H,0,5.8937106037,-1.6332395506,-1.3624788122
H,0,7.5332983376,-1.094029892,-0.9361530157
C,0,5.793622372,1.1030297215,-0.9106697908
H,0,5.3419655896,1.974964463,-0.428885629
H,0,6.7729866992,1.3955968399,-1.3037803108
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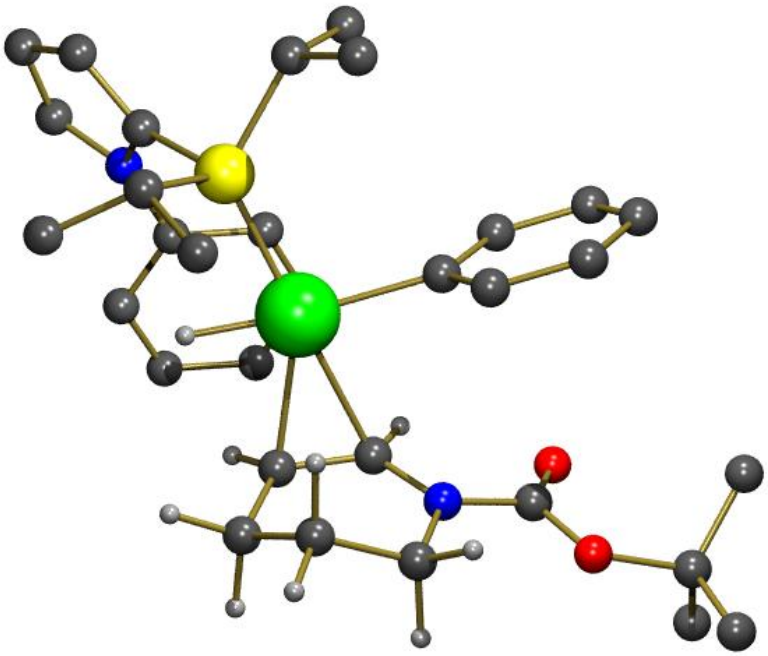
**IIa**



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Gibbs: 0.632523

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C,0,-2.7437679844,-3.2134297554,-1.0398253283
C,0,-1.9023343311,-2.5878244947,-1.9586205584
C,0,-0.9854136515,-1.6235450363,-1.5311865974
C,0,-0.8664489927,-1.2406801345,-0.183673523
Pd,0,0.5115602278,0.1630485109,0.5622577671
H,0,-1.7044149967,-1.626876597,1.7748034679
H,0,-5.0183261286,-0.5835711971,-2.2017556682
H,0,-3.453202774,-3.9698546983,-1.3662128633
P,0,2.2562282735,-1.2453540309,1.0108732327
C,0,2.6492523704,-1.2660770177,2.868970187
C,0,2.2981162182,-3.0882734335,0.5670946733
C,0,3.4917500519,-0.0706384424,3.3109999826
C,0,1.3498054324,-1.3198704662,3.677032451
H,0,3.2212655119,-2.1900775578,3.0326561389

C,0,1.2561660048,-3.9296976031,1.3029582466
C,0,2.2062718027,-3.2848648291,-0.9459097564
H,0,3.2986202917,-3.4031489988,0.894802861
C,0,3.1971136825,1.1453478733,-1.2924427384
H,0,2.9738619169,0.8686695179,3.0886576335
H,0,4.4670085179,-0.0460244472,2.8207463961
H,0,0.7885897681,-0.3906157747,3.534456187
H,0,0.6960242943,-2.1473109656,3.3918325735
H,0,0.2399849919,-3.5901265858,1.0841981583
H,0,1.4045784386,-3.9216011639,2.3864674208
H,0,1.2218341084,-2.9910064317,-1.3210136793
H,0,2.9773289723,-2.7171730417,-1.4760511298
C,0,3.37979734,2.5277485181,-1.2132338323
C,0,2.1876903579,0.615435099,-2.0993392483
C,0,2.5562856364,3.3792157911,-1.9462800272
C,0,1.3630243601,1.4752206998,-2.8244013326
H,0,2.0730001891,-0.460030919,-2.1804252557
H,0,2.7050631295,4.4536429021,-1.8848869837
C,0,1.5448765168,2.8557294569,-2.752469497
H,0,0.5814595095,1.0603419881,-3.4541175592
H,0,0.9040753709,3.5196558051,-3.3253815723
H,0,-0.3544072886,-1.1509761073,-2.2827735826
N,0,4.1113094035,0.2918111251,-0.6121788019
C,0,3.861210181,-0.7673234804,0.2537232204
C,0,5.4640301278,0.3708979837,-0.8445124797
C,0,5.0922106996,-1.3400832403,0.5475838459
C,0,6.0984831913,-0.6248033384,-0.1394142251
H,0,5.848682384,1.1069071418,-1.5354027844
H,0,5.2467080805,-2.1732472279,1.2204070645
H,0,7.1621758784,-0.8180295884,-0.1280127442
H,0,4.1599089277,2.9244295991,-0.5705785919
H,0,2.3531589498,-4.3442572625,-1.1875797677
H,0,1.3373479115,-4.9728236709,0.9745706665
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H,0,-1.9612716783,-2.8475641681,-3.0139798824
C,0,-1.2685570941,1.6499097639,-0.0301982802
C,0,-0.2977474144,2.2765693083,0.7294295281
C,0,-0.6245576878,2.6972379527,2.1411503051
C,0,-1.664984636,1.7464236116,2.7290680241
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H,0,0.4948458745,2.7930508987,0.1991860703
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H,0,-1.9803898398,2.0704875116,3.7267588066
H,0,-3.5593218517,0.8481798507,2.1915076739
H,0,-3.4789762988,2.5849265013,1.903264869
H,0,-1.0230468753,3.7236375459,2.1270491399
N,0,-2.5541452542,1.392793509,0.4442096787

C,0,-3.5258402998,1.0900497708,-0.4951545493
O,0,-3.3119741244,1.017386896,-1.6916507415
O,0,-4.7169608197,0.9388186939,0.1100715569
C,0,-5.9239086926,0.6683713706,-0.6753129394
C,0,-7.0019615335,0.5652912742,0.4006531964
H,0,-7.9748099749,0.373864701,-0.0615245937
H,0,-6.7803330884,-0.2530287843,1.0919117828
H,0,-7.0676468916,1.4951845611,0.9733897949
C,0,-6.2064381977,1.84094301,-1.6127845882
H,0,-6.2721815687,2.7758403763,-1.0468153715
H,0,-5.4221653095,1.9338297946,-2.3650688791
H,0,-7.1640968062,1.6825236145,-2.1188735293
C,0,-5.7818652785,-0.6526995547,-1.4269023612
H,0,-5.5022407342,-1.4540547321,-0.7374723189
H,0,-6.739941055,-0.9119715482,-1.8896107702
H,0,-3.3138205427,-3.3237496886,1.0368513174
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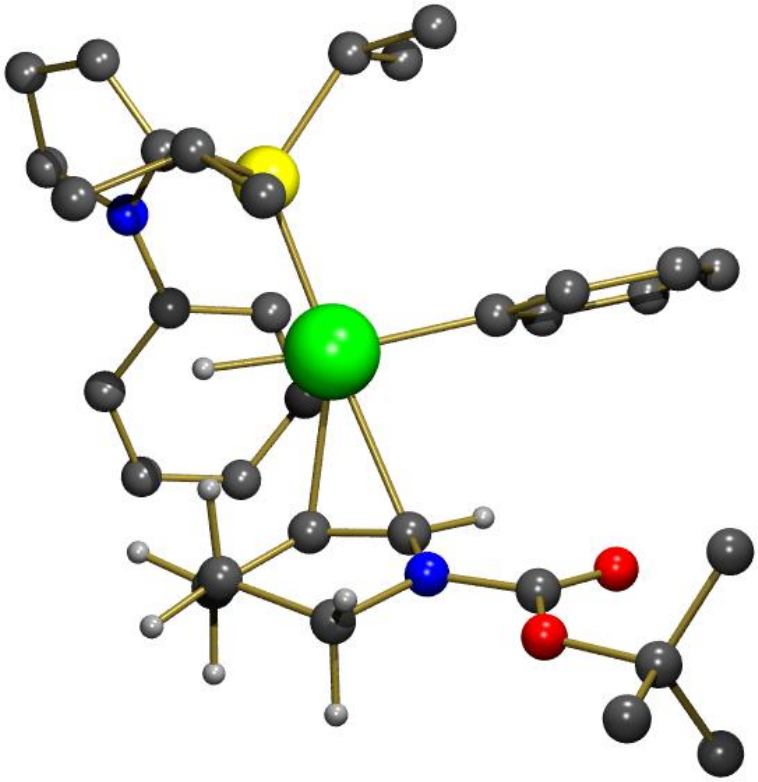
**TS-IIa-IIb**



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PCM: E(RB3PW91) = -1640.83018290
Gibbs: 0.634396

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C,0,-1.9023938061,-2.134176188,-3.7626358494
C,0,-1.0682761884,-1.0466061714,-4.0128855385
C,0,-0.4202195993,-0.3994934779,-2.9556009289
C,0,-0.5731223461,-0.8044434811,-1.6168687738
Pd,0,0.3781907331,0.1956639098,-0.0307263401
H,0,-1.6117815733,-2.2435042971,-0.382159211
H,0,-5.3488938462,-1.7961931282,-0.584997607
H,0,-2.4085671276,-2.6417018577,-4.5799961941
P,0,2.1635880666,-1.1955517548,0.2355008003
C,0,2.1385848529,-1.9647020207,1.9710968803
C,0,2.5509697765,-2.6854441827,-0.8753726826
C,0,2.6698427647,-1.0196557705,3.0482592953
C,0,0.71733581,-2.4174419793,2.3220837939
H,0,2.7962654259,-2.8430318834,1.9085510251
C,0,1.5409872162,-3.8279578807,-0.7799192729
C,0,2.7456606072,-2.2340403939,-2.322432567
H,0,3.5174390247,-3.0406645512,-0.4919524029
C,0,3.3085073118,1.9462157016,-0.700542087
H,0,2.0703949924,-0.1040326932,3.0857287279
H,0,3.7106016209,-0.7374344817,2.8758446983
H,0,0.0525182391,-1.5493532058,2.3876409704
H,0,0.2893120187,-3.1024662322,1.5869641146
H,0,0.5397610081,-3.5014033537,-1.0730036502
H,0,1.4939642163,-4.2619320691,0.222879735
H,0,1.8136197724,-1.8416459433,-2.7397109511
H,0,3.5253711735,-1.4701854696,-2.4043398404
C,0,3.2743207563,3.1956808476,-0.0771906849
C,0,2.6414155333,1.7477237122,-1.9111479826
C,0,2.5829687775,4.249175022,-0.6705275002
C,0,1.949291694,2.8068412748,-2.4967678489
H,0,2.6895453888,0.7816926851,-2.4013993071
H,0,2.5635566361,5.2201305308,-0.183650569
C,0,1.9201463646,4.0587414985,-1.8830858284
H,0,1.4420150518,2.6534673988,-3.4447550483
H,0,1.388056565,4.8825041395,-2.3502023986
H,0,0.2229373177,0.448184631,-3.1905592984
N,0,4.1241577023,0.9225583876,-0.138683439
C,0,3.819233074,-0.3995968989,0.1656932363
C,0,5.4705140152,1.1276904986,0.0544259181
C,0,5.0100029612,-1.0033516715,0.5498606363
C,0,6.0458221588,-0.0450654038,0.4831625918
H,0,5.9070535509,2.0869806612,-0.1825082528
H,0,5.109564158,-2.0285550077,0.8811991396
H,0,7.0915532438,-0.1943605762,0.7134933614
H,0,3.786944579,3.3294012332,0.8705367134

H,0,3.0572373473,-3.0877353879,-2.9358596964
H,0,1.8416806567,-4.630526603,-1.4642251237
H,0,0.717756195,-2.9236279221,3.2950390343
H,0,2.6034428182,-1.508298329,4.0277892776
H,0,-0.9199417453,-0.6987033543,-5.0338577693
C,0,-1.7615828129,1.3887516313,-0.0404033356
C,0,-0.6925288531,2.1767045254,0.326844771
C,0,-0.6361211231,2.7550423481,1.719210807
C,0,-1.2654459655,1.7780058948,2.7057013876
C,0,-2.6726282595,1.3736458917,2.2804005437
H,0,0.3946212999,2.980273088,2.0022923482
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H,0,-3.033096889,0.5444635132,2.8914409463
H,0,-3.3664031499,2.2113746919,2.4340685711
H,0,-1.1922191522,3.7059178176,1.7309307888
N,0,-2.7332154684,0.9699725264,0.8673731401
C,0,-3.8847671629,0.3908813016,0.3458825875
O,0,-4.0759615197,0.213414854,-0.8406331599
O,0,-4.7367655022,0.087147726,1.3418377174
C,0,-6.0304298812,-0.5367953365,1.0479713258
C,0,-6.6467386567,-0.6917780918,2.4358412681
H,0,-7.63310111,-1.1579278085,2.3566922689
H,0,-6.0167158692,-1.3212330904,3.0711190734
H,0,-6.7623526885,0.2826905133,2.9195398752
C,0,-6.8787356581,0.3930583096,0.1823492384
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H,0,-6.4403719542,0.5148459475,-0.8086291963
H,0,-7.884414357,-0.0259193653,0.0756737059
C,0,-5.8153897646,-1.9004619573,0.3951654968
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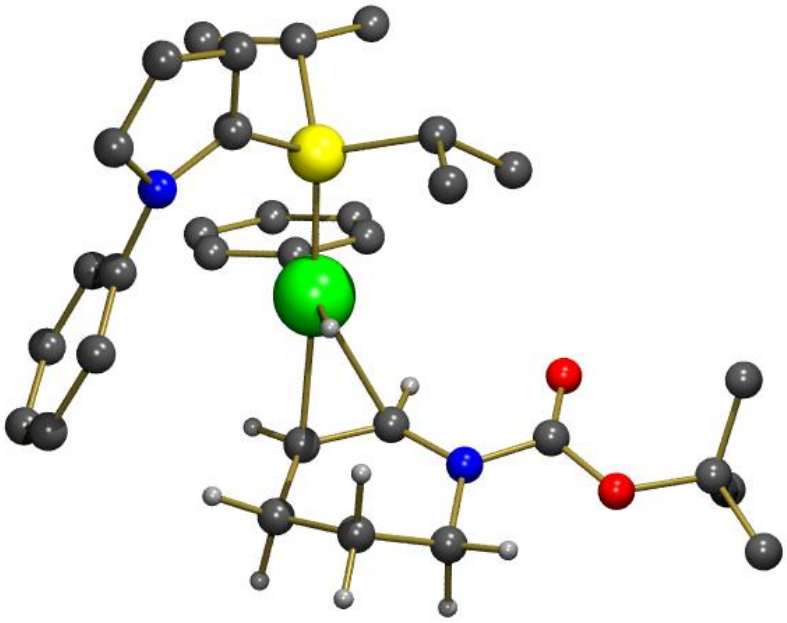
**IIb**



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Gibbs: 0.632987

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C,0,-0.2985706677,4.9926982902,-1.7913506095
C,0,-1.2853496599,4.1201721678,-2.2472462517
C,0,-1.308979927,2.7935983383,-1.8051122374
C,0,-0.3601698385,2.2781433501,-0.9008412472
Pd,0,-0.3146004962,0.239865709,-0.3724442739
H,0,1.4002125734,2.8545538458,0.2239781346
H,0,1.4424745115,5.1828124061,-0.5358223832
H,0,-0.2752915713,6.0255047742,-2.1300801726
P,0,-1.5115636532,0.2726593646,1.5781864282
C,0,-0.3980644751,-0.3102577927,3.0009701549
C,0,-2.3154847706,1.8377533099,2.2843541506
C,0,-0.2839465214,-1.8326084501,3.072244233
C,0,0.9924206344,0.3169687401,2.8671065839
H,0,-0.8804298196,0.0597720784,3.9167659444

C,0,-1.3169813764,2.930456533,2.6622955553
C,0,-3.3783643803,2.3669818965,1.3216514069
H,0,-2.8181133581,1.4855169599,3.1956250889
C,0,-3.3386992621,-1.6621735874,-0.6652281102
H,0,0.1120108529,-2.2287664558,2.1313614968
H,0,-1.2448129162,-2.3133132146,3.2675012711
H,0,1.4969368279,-0.0671051022,1.9758124328
H,0,0.9694330536,1.4048750134,2.779996897
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H,0,-2.9242799944,2.6951109108,0.3816945244
H,0,-4.1436819187,1.6138316738,1.1083066085
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C,0,-3.3828004473,-0.486269187,-1.4171593214
C,0,-3.1405159592,-2.9575858456,-2.6943363675
C,0,-3.304581246,-0.5552888695,-2.8073562442
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C,0,-3.1930497777,-1.7868541699,-3.4508663269
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C,0,-2.9646623479,-0.8437266194,1.7217635816
C,0,-4.5381757859,-2.4029054734,1.3160433941
C,0,-3.6226436499,-1.1314553542,2.9106346951
C,0,-4.6083820268,-2.1114007107,2.6572177233
H,0,-5.1451353686,-3.0488717495,0.698932402
H,0,-3.3861894297,-0.6963709809,3.8727718936
H,0,-5.2965821089,-2.5470020091,3.3682007709
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H,0,-2.0394677355,4.4714593693,-2.9497252986
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C,0,0.7311979231,-0.2687215531,-2.3371300394
C,0,0.6389400051,-1.6904535409,-2.823619843
C,0,1.4559007241,-2.6310302158,-1.9426177011
C,0,2.8472599115,-2.0737402599,-1.6626552725
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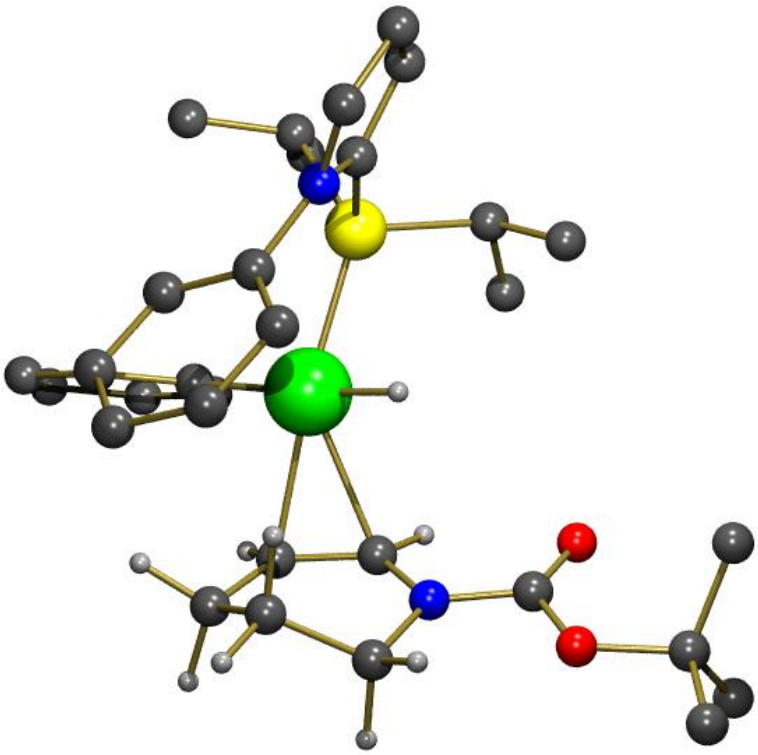
H,0,3.3833164762,-2.7063839206,-0.9563095429
H,0,3.4401838451,-2.0355765444,-2.5877205516
H,0,1.0108818903,-1.7249025314,-3.8595940575
N,0,2.7674693282,-0.7209245956,-1.0955522236

C,0,3.7550301732,-0.1962072615,-0.2749412701
O,0,3.7178523967,0.9332124611,0.1788561128
O,0,4.7299117322,-1.0983777938,-0.0771034648
C,0,5.8906845446,-0.776681508,0.7609437639
C,0,6.7054192681,-2.0660804923,0.7054895393
H,0,7.6194289619,-1.9556582853,1.2960379963
H,0,6.1315658322,-2.9049697927,1.1101130691
H,0,6.9856178796,-2.3026496746,-0.3250655868
C,0,6.6710793017,0.3829225319,0.1454687038
H,0,6.9361293624,0.1552762542,-0.8918566131
H,0,6.0885499336,1.3045782473,0.1691638907
H,0,7.598476999,0.5366565097,0.7062807335
C,0,5.4423416125,-0.4808125015,2.1901261837
H,0,4.8479544584,-1.3117760048,2.5826657527
H,0,6.3226833335,-0.361659007,2.8298133173
H,0,4.8492506306,0.4331143266,2.2341908707
H,0,-0.2789288138,-1.3180078265,0.0387642977

**TS-IIb-IIc**



GP: E(RB3PW91) = -1640.49263833
PCM: E(RB3PW91) = -1640.82960669
Gibbs: 0.634452

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C,0,1.862996399,5.0117301036,0.7417447276
C,0,2.8530475501,4.8745466231,1.7138909164
C,0,3.1344967859,3.6039499647,2.2129476241
C,0,2.4357318746,2.4899496425,1.7369557428
C,0,1.434327671,2.5868507876,0.752756154
Pd,0,0.271435809,0.9394301226,0.140329916
H,0,0.4012764126,4.0382051777,-0.4792018189
H,0,1.626167005,5.9963851081,0.3423351101
H,0,3.3940220059,5.7441221747,2.0785824247
P,0,1.4578613696,0.2496333002,-1.6860642822
C,0,0.3286613539,0.3278089526,-3.2106898211
C,0,3.0267399266,1.1283370681,-2.2915389225
C,0,-0.5651159041,-0.9031746883,-3.356388395
C,0,-0.5371413859,1.5918261774,-3.1663301762
H,0,1.0152635834,0.3822878051,-4.0674953008
C,0,2.8031749104,2.5758692804,-2.7248076698
C,0,4.1344099558,1.0260827591,-1.2440065527
H,0,3.3250684303,0.5395283406,-3.1696984211
C,0,1.8486707278,-2.3533288807,0.6250286896
H,0,-1.2151534975,-1.0060283067,-2.4820664601
H,0,0.0067472444,-1.8255029957,-3.4767477846
H,0,-1.289162054,1.4972452659,-2.37714426
H,0,0.0359475371,2.503894124,-2.9837452289
H,0,2.413913442,3.1808614317,-1.9018313978
H,0,2.1224879506,2.6568353163,-3.5767072764
H,0,3.8635824267,1.5716111847,-0.3351019773
H,0,4.3532811399,-0.0151095807,-0.9869054513
C,0,1.0824958744,-3.3554015554,1.2280450942
C,0,2.4395438581,-1.3596830564,1.4087502054
C,0,0.940486941,-3.3854410768,2.612861212
C,0,2.2797267702,-1.3901952442,2.7935002864
H,0,3.0495739729,-0.59488347,0.9416279671
H,0,0.3545079447,-4.1753694735,3.074270956
C,0,1.5437003093,-2.4062772016,3.401263593
H,0,2.7553753502,-0.6250117931,3.4000719699
H,0,1.4402216229,-2.4335311932,4.482109801
H,0,2.6824706449,1.5150911373,2.1557838619
N,0,2.1128113402,-2.4490030671,-0.7690504552
C,0,2.1019088931,-1.4723886899,-1.7596748306
C,0,2.5933212625,-3.623164565,-1.305209919
C,0,2.5843234272,-2.0736155963,-2.9150210209
C,0,2.890545045,-3.4231376671,-2.6312542357
H,0,2.7327822396,-4.4863232704,-0.6712928197
H,0,2.6716497172,-1.588859321,-3.8783304369
H,0,3.2908231922,-4.1610515087,-3.3125024256

H,0,0.607959464,-4.108010283,0.6058484339
H,0,5.0576182205,1.4677627527,-1.6374111806
H,0,3.7609793298,3.0118424134,-3.0335382424
H,0,-1.0650867482,1.7091797835,-4.1204050195
H,0,-1.2081847393,-0.7794035731,-4.2359609868
H,0,3.9008938238,3.4779515077,2.9760302001
C,0,-1.9904554873,1.2785874395,0.8691725873
C,0,-1.1075862968,1.7243398582,1.8296223505
C,0,-0.9668120382,1.0031406224,3.1433381891
C,0,-1.5090219783,-0.4197980624,3.0346802147
C,0,-2.8929563144,-0.4370577727,2.3942580543
H,0,0.0824919783,0.9954658345,3.4575950429
H,0,-0.7744393215,2.7531140313,1.7705377679
H,0,-2.2424274261,1.8733251836,-0.001790294
H,0,-0.8273029233,-1.0249554297,2.4288079994
H,0,-1.5732249162,-0.8896260824,4.0219067125
H,0,-3.2472774532,-1.4588948586,2.2622529922
H,0,-3.6191608894,0.0852721215,3.033776247
H,0,-1.5159751507,1.5620194118,3.9161993296
N,0,-2.8608498232,0.2091478104,1.0784335293
C,0,-3.7018634816,-0.1422755997,0.0420245671
O,0,-3.6690279172,0.3880499364,-1.0558663179
O,0,-4.5461603038,-1.1155227697,0.4266592504
C,0,-5.5580822392,-1.6376831789,-0.4966957538
C,0,-6.2654422134,-2.6923485668,0.3503073848
H,0,-7.0666212839,-3.1612343696,-0.2281677419
H,0,-5.5643272391,-3.4714545206,0.6638277504
H,0,-6.7034884382,-2.2396913229,1.2446591259
C,0,-6.5258034091,-0.5247606044,-0.8930776214
H,0,-6.9623165244,-0.063638903,-0.0014537051
H,0,-6.018714598,0.2430290401,-1.4783718581
H,0,-7.3405145671,-0.9451980675,-1.4911103188
C,0,-4.8847111667,-2.2800178953,-1.7073658332
H,0,-4.1582144211,-3.0318184795,-1.3833211092
H,0,-5.639761896,-2.7804728691,-2.3221291142
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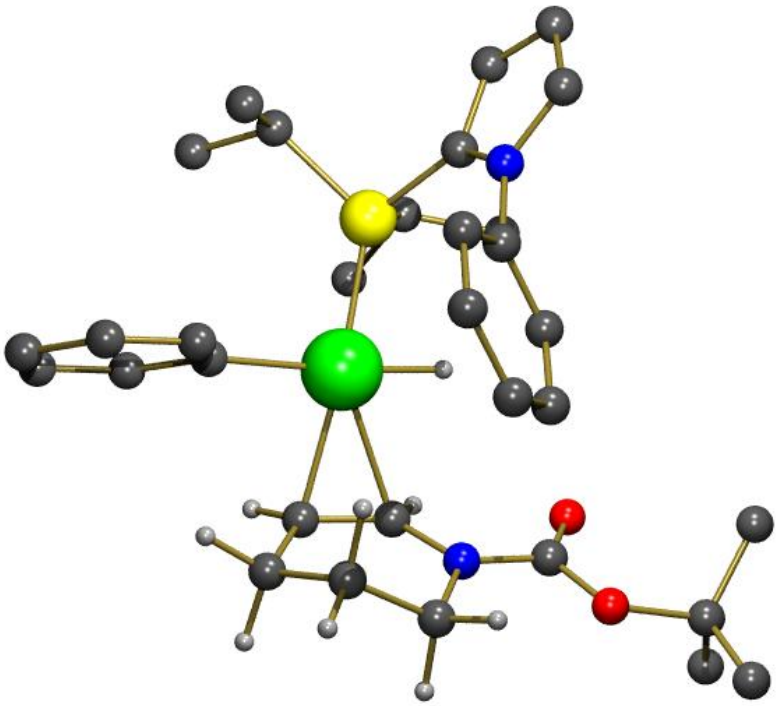
H,0,-0.5420357562,-0.3453200539,-0.3720773893

**IIc**



GP: E(RB3PW91) = -1640.49415744
PCM: E(RB3PW91) = -1640.83101460
Gibbs: 0.633026

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C,0,-3.9486191479,-3.437585998,-0.5008469153
C,0,-4.1929484435,-3.5537279314,0.8670091063
C,0,-3.435403315,-2.7899533415,1.7542781021
C,0,-2.4512096129,-1.9200057941,1.2740650812
C,0,-2.1765397874,-1.7813079088,-0.1004353242
Pd,0,-0.5976386122,-0.5513634263,-0.7281308435
H,0,-2.7876283417,-2.5149852125,-2.042778737
H,0,-4.5289088194,-4.0271060792,-1.2085658256
H,0,-4.960595892,-4.2294815767,1.2358109249
P,0,-1.7269917531,1.4410797773,-0.9246346956
C,0,-1.3428803139,2.1836915564,-2.6301042869
C,0,-3.6239310562,1.540300836,-0.8592442231
C,0,-0.0249607335,2.9579452521,-2.6589615769
C,0,-1.3196732443,1.0889484674,-3.7023581414
H,0,-2.1730456597,2.8740440433,-2.8352819265

C,0,-4.3332461832,0.6851352225,-1.9074846582
C,0,-4.1350964919,1.2354794414,0.5486101935
H,0,-3.8221766999,2.5991517387,-1.0745448623
C,0,-0.121498556,1.7885618744,2.1399515262
H,0,0.8120791918,2.3029045295,-2.393960642
H,0,-0.0256998683,3.8094361125,-1.9757686483
H,0,-0.4701902968,0.4203653735,-3.5299451039
H,0,-2.2244713619,0.4774474842,-3.7218560352
H,0,-4.0808606389,-0.3724980727,-1.7955656429
H,0,-4.1025186094,0.9997730386,-2.928719684
H,0,-3.9485964556,0.1935987745,0.8215067634
H,0,-3.6703772023,1.8832237033,1.2977276153
C,0,1.1312398521,1.34194836,1.7180538917
C,0,-0.6836348217,1.3051008903,3.3226630532
C,0,1.8252238212,0.4174760502,2.4958748301
C,0,0.014329593,0.3759002106,4.0920019249
H,0,-1.6584086459,1.6680035431,3.6342502811
H,0,2.8074213106,0.0853237803,2.1742801838
C,0,1.2720330714,-0.0643576532,3.6825259198
H,0,-0.4227333554,0.003900798,5.0142166409
H,0,1.8223721896,-0.7777510709,4.2896249116
H,0,-1.8841286566,-1.3323175842,1.9952452998
N,0,-0.7835175653,2.8451125418,1.4450075946
C,0,-1.3787887822,2.8620665937,0.190657933
C,0,-0.8687361032,4.0984535728,2.0022283437
C,0,-1.8398714317,4.1579283359,-0.0108676708
C,0,-1.5143053693,4.9353381789,1.1220828376
H,0,-0.4319340277,4.2851641035,2.9725285913
H,0,-2.3662727166,4.502045809,-0.8913907561
H,0,-1.7206016734,5.9854080344,1.2761729702
H,0,1.5572859186,1.7320203974,0.8004071713
H,0,-5.2174159912,1.4073155325,0.5886946558
H,0,-5.4179421598,0.7816453636,-1.7769436548
H,0,-1.1989937757,1.544870747,-4.692420807
H,0,0.1536204236,3.3319553974,-3.6741579495
H,0,-3.6123940575,-2.8682545888,2.8257791344
C,0,1.3934247459,-1.6479439506,-1.3480402452
C,0,0.3608322089,-2.554490177,-1.1591036549
C,0,0.4226953244,-3.5759031525,-0.0530642101
C,0,1.3057758757,-3.0713674207,1.0815008588
C,0,2.6583154608,-2.5998914548,0.5601607257
H,0,-0.5814347769,-3.8057795715,0.3113341058
H,0,-0.2488951237,-2.7886844128,-2.0277059022
H,0,1.5622016409,-1.1505919329,-2.2931831241
H,0,0.8034333328,-2.24194277,1.5921486693
H,0,1.4756200506,-3.8587555897,1.8238795543
H,0,3.2588289336,-2.1734706301,1.3630025208
H,0,3.2206751796,-3.4504850802,0.1484569157
H,0,0.8371786375,-4.5098711374,-0.4630763447
N,0,2.4980842164,-1.5842191765,-0.4874789451

C,0,3.4781687749,-0.6628467191,-0.7918629078
O,0,3.3926615596,0.1281876175,-1.7158513804
O,0,4.5155902044,-0.7668649033,0.0637548038
C,0,5.7214687791,0.0474184825,-0.1265568063
C,0,6.6219022869,-0.4224110128,1.0127089989
H,0,7.5760873699,0.1113041811,0.9792936263
H,0,6.1537713139,-0.2298925602,1.9826552071
H,0,6.8220567747,-1.4947016562,0.9310274734
C,0,6.3555293202,-0.2695615619,-1.4796497289
H,0,6.5403326707,-1.3445491186,-1.5710040874
H,0,5.7122800899,0.0522888847,-2.2993486491
H,0,7.316489006,0.2479693788,-1.5619517093
C,0,5.3891865385,1.5304053575,0.0219513953
H,0,4.9098183181,1.7211283971,0.9873651971
H,0,6.3130335203,2.1164570534,-0.0168877674
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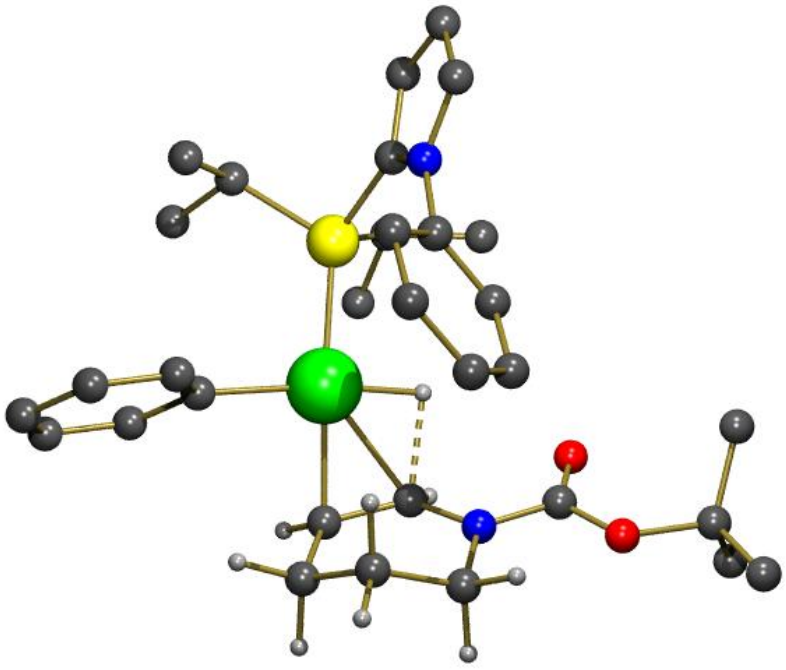
H,0,0.5485898556,0.4964396021,-1.131006144

**TS-IIc-III**



GP: E(RB3PW91) = -1640.49009432

PCM: E(RB3PW91) = -1640.82669860
Gibbs: 0.631629

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C,0,-4.43999271,-3.4818989632,1.0356702511
C,0,-3.6725264,-2.6880436585,1.8872900704
C,0,-2.6534001136,-1.8809698249,1.3726853524
C,0,-2.356391171,-1.8345455056,-0.0035110118
Pd,0,-0.7261004802,-0.7382730538,-0.6808533619
H,0,-2.9506959326,-2.6777272839,-1.9062722227
H,0,-4.7539688948,-4.0780459359,-1.0114113085
H,0,-5.2356092881,-4.1080216261,1.4318161528
P,0,-1.6957671755,1.3861803592,-0.9133266187
C,0,-1.0954695397,2.1519575311,-2.5464975695
C,0,-3.5843280741,1.5392746075,-1.044025196
C,0,0.2773583493,2.809938917,-2.3989981426
C,0,-1.0495138124,1.1096857425,-3.6682093188
H,0,-1.8388579771,2.9212560107,-2.7981866362
C,0,-4.1977230461,0.6510348174,-2.1252953342
C,0,-4.2313757864,1.2778369771,0.316871098
H,0,-3.749151912,2.5914125643,-1.3126804766
C,0,-0.1792373214,1.7195964042,2.191909787
H,0,1.0344245234,2.0737230472,-2.1057229341
H,0,0.271052017,3.6175026548,-1.6637578544
H,0,-0.2771045491,0.3640375576,-3.4558527194
H,0,-1.9925131001,0.5776628433,-3.8082084194
H,0,-3.9433332851,-0.3995431491,-1.9626527259
H,0,-3.8865726402,0.940745813,-3.1322040433
H,0,-4.0660103097,0.2464321855,0.6392334531
H,0,-3.8454521773,1.9522301108,1.086625305
C,0,1.0556871398,1.2778232842,1.7147706668
C,0,-0.6791350507,1.243553027,3.4054212756
C,0,1.79590974,0.3706298271,2.4696771013
C,0,0.0658890404,0.3328254056,4.1520778243
H,0,-1.6437320022,1.5968779017,3.7572006
H,0,2.7659022126,0.0456851224,2.1065547939
C,0,1.3072790036,-0.0998605944,3.6888428891
H,0,-0.3235031343,-0.0329096058,5.0978496184
H,0,1.8941725324,-0.7992109712,4.2775649948
H,0,-2.0802525656,-1.267115949,2.066096185
N,0,-0.8819633699,2.7615664505,1.5199056229
C,0,-1.4212314181,2.7962275635,0.2403606147
C,0,-1.0179777718,3.9997655911,2.1021512019
C,0,-1.8976415331,4.087694605,0.0479287823
C,0,-1.6410081071,4.8437532747,1.2129844339
H,0,-0.619939886,4.1750965727,3.0910306078
H,0,-2.3940880824,4.4423706854,-0.8454107732
H,0,-1.8780342344,5.8849663971,1.3825219669
H,0,1.4368074438,1.6640045904,0.7754679798

H,0,-5.313339835,1.4405219131,0.2439102773
H,0,-5.290348677,0.7367937104,-2.0875352929
H,0,-0.7934544382,1.5982002506,-4.6160610518
H,0,0.5870158421,3.2289282284,-3.3639323693
H,0,-3.8693937207,-2.6929586615,2.9581117151
C,0,1.2746000171,-1.6243718738,-1.3549822081
C,0,0.2526627499,-2.5867693193,-1.1080416708
C,0,0.4090078,-3.6134212429,-0.0110783635
C,0,1.3254933294,-3.0868982646,1.0843961062
C,0,2.6438066282,-2.6012401499,0.4957824942
H,0,-0.5696276558,-3.8830764473,0.3952499525
H,0,-0.2880564372,-2.9172026487,-1.9937555169
H,0,1.4825768761,-1.3180754379,-2.3745937264
H,0,0.833443969,-2.2617034187,1.6116585408
H,0,1.541838206,-3.8675087578,1.8221219055
H,0,3.2853374303,-2.1768772866,1.2676951297
H,0,3.1881639289,-3.4464735774,0.0494929366
H,0,0.8415348293,-4.5316678128,-0.4393006968
N,0,2.4256858897,-1.574955366,-0.5310300267
C,0,3.3595634666,-0.6150811879,-0.8384818517
O,0,3.1930963101,0.2173259949,-1.7173633804
O,0,4.4473626862,-0.7213517714,-0.0493477424
C,0,5.6116988757,0.1466988549,-0.2606200361
C,0,6.5887773416,-0.3443175218,0.8040883294
H,0,7.5208189464,0.2252099869,0.7464598159
H,0,6.1686198347,-0.2163710568,1.8061293522
H,0,6.8203279323,-1.4033499197,0.6580731567
C,0,6.1811435675,-0.0788021924,-1.6598198945
H,0,6.4007005876,-1.1398003495,-1.8152804488
H,0,5.4815612722,0.2564814924,-2.426403261
H,0,7.1159174583,0.4803534768,-1.7673905852
C,0,5.2365312907,1.6069415389,-0.0182358868
H,0,4.799759819,1.7302169505,0.9778475715
H,0,6.1367432433,2.227701993,-0.0698249014
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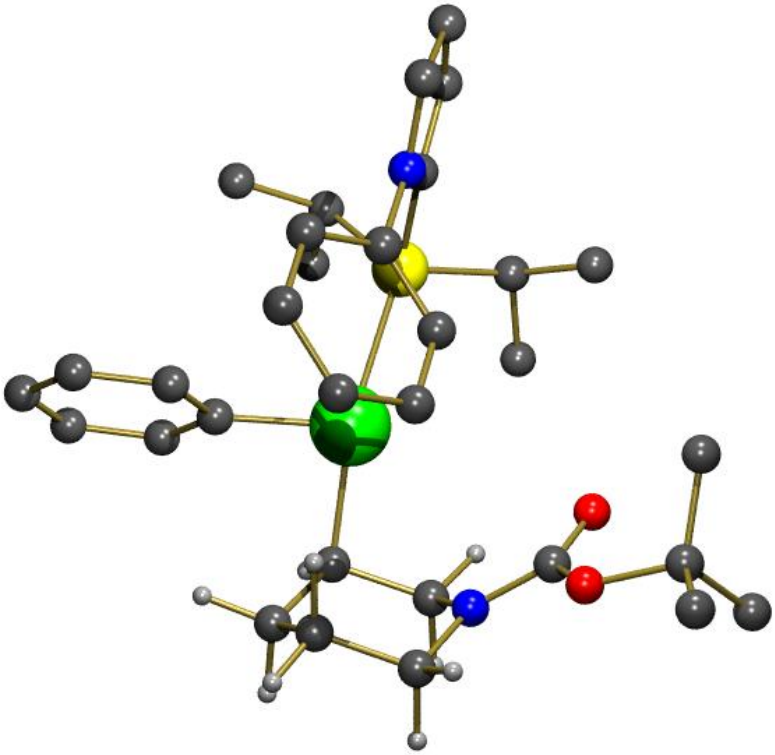
H,0,0.6642500494,-0.0469871106,-1.1698198002

**III**



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PCM: E(RB3PW91) = -1640.84059219
Gibbs: 0.635699

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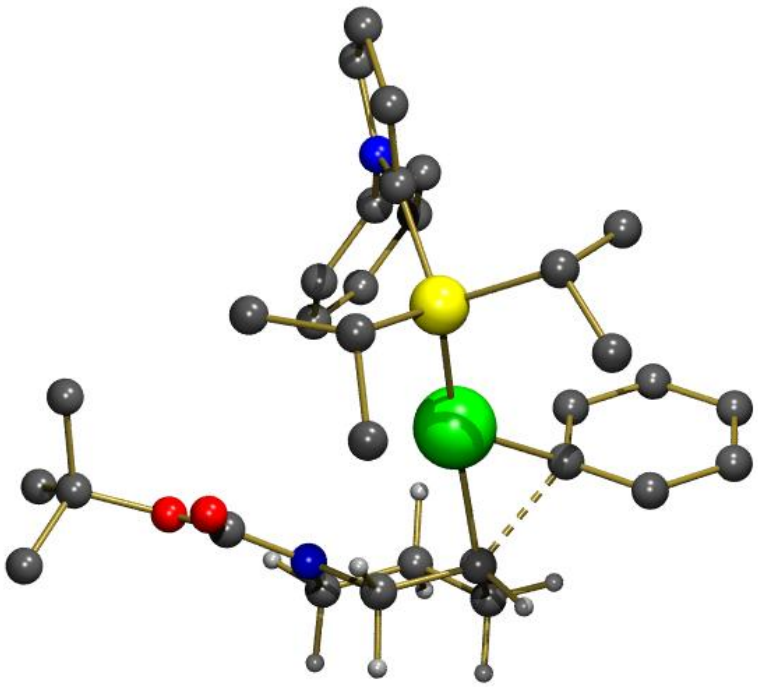
C,0,-4.1067206959,-3.1767515245,0.2882484204
C,0,-4.2076084321,-3.0237023438,1.6699292109
C,0,-3.2524141394,-2.2608447008,2.3414903667
C,0,-2.2105217719,-1.6489214228,1.6403256996
C,0,-2.107518,-1.789725351,0.2484005587
Pd,0,-0.6700359435,-0.8225571404,-0.7092253839
H,0,-2.9949232874,-2.7222572965,-1.4912235684
H,0,-4.8407304783,-3.7732100582,-0.2494943088
H,0,-5.0182381841,-3.4967886488,2.2177967343
P,0,-1.5064890209,1.4752115726,-0.8836147708
C,0,-0.7116723937,2.3023252445,-2.4062508521
C,0,-3.3571117821,1.5796192898,-1.2854718334
C,0,0.5490598617,3.0945187531,-2.0553631493
C,0,-0.377781889,1.2563651846,-3.4761108029
H,0,-1.4735429037,2.9937561912,-2.7927356073

C,0,-3.740575537,0.7216335032,-2.4911830919
C,0,-4.1920411976,1.2145890415,-0.0568816104
H,0,-3.5369674723,2.6341547765,-1.5325248359
C,0,-0.1816701806,1.7206657123,2.2777103051
H,0,1.3347695769,2.4271539007,-1.6855222649
H,0,0.3603298428,3.8707299103,-1.3105569237
H,0,0.4731580973,0.6475788949,-3.1514242803
H,0,-1.2100619244,0.5871451137,-3.7067476225
H,0,-3.4681815328,-0.3265639112,-2.3328806399
H,0,-3.2716290447,1.0673446171,-3.4163038463
H,0,-4.0400830869,0.1710567998,0.2321050835
H,0,-3.9519213255,1.8500295123,0.8000338643
C,0,0.9463374136,1.1453168511,1.6896701124
C,0,-0.5847644866,1.3238948324,3.5562441083
C,0,1.6674210262,0.1763408459,2.3860384211
C,0,0.1480296581,0.3635365457,4.249687863
H,0,-1.4737310815,1.7669861986,3.9948563938
H,0,2.5480393413,-0.259343612,1.9243925966
C,0,1.2751891062,-0.2132752736,3.6662760985
H,0,-0.1690214354,0.0621101925,5.2439892603
H,0,1.8463361572,-0.9625998052,4.2066454409
H,0,-1.4818882264,-1.053197535,2.1825298635
N,0,-0.8863508158,2.7763953819,1.6368273492
C,0,-1.4227225404,2.8354875426,0.3539538263
C,0,-1.1061642867,3.9757884489,2.2724400692
C,0,-1.9770119814,4.1016923577,0.2157097754
C,0,-1.7758990262,4.8181153636,1.4167066848
H,0,-0.7261697718,4.1337827509,3.2711296612
H,0,-2.4811977146,4.4670240591,-0.6689942831
H,0,-2.0758632523,5.834679027,1.6303602021
H,0,1.2756132988,1.4779449365,0.711174037
H,0,-5.2562095201,1.3495250223,-0.2848266106
H,0,-4.8260882723,0.7647518532,-2.6400024705
H,0,-0.0800693973,1.7561557693,-4.4060022916
H,0,0.9399782427,3.5761289687,-2.9597337447
H,0,-3.315122024,-2.1371917525,3.4206227873
C,0,1.3958006294,-2.2962075556,-1.8865187413
C,0,0.0934933773,-2.6783926975,-1.1789781835
C,0,0.3596902244,-3.7588029054,-0.1321447079
C,0,1.4973445708,-3.3761617056,0.8132557494
C,0,2.760648526,-3.0161493411,0.0302753425
H,0,-0.54956422,-3.9773687097,0.4339838694
H,0,-0.6026247818,-3.0701211924,-1.9336090645
H,0,1.7380726558,-3.1412888822,-2.5141523696
H,0,1.1928570525,-2.514783156,1.4192507258
H,0,1.7256768795,-4.2020479055,1.498552862
H,0,3.5605322537,-2.6706506166,0.6831806636
H,0,3.1285296406,-3.9060434649,-0.5057115145
H,0,0.6415570957,-4.6947990818,-0.6474910779
N,0,2.4673778844,-1.9769010911,-0.9491243986

C,0,3.1163727302,-0.7880459115,-1.0485246207
O,0,2.8148429265,0.0966651936,-1.8465907717
O,0,4.1295198384,-0.693634199,-0.1502545546
C,0,5.1525154495,0.3454732323,-0.276423613
C,0,6.1345113074,-0.0189091718,0.8347223441
H,0,6.9687212661,0.6886550686,0.8447548698
H,0,5.6439436717,0.0143311203,1.8121621287
H,0,6.5352463227,-1.0252813536,0.6824152408
C,0,5.8274760733,0.2473204578,-1.6435530102
H,0,6.2189158449,-0.7622553964,-1.8042454701
H,0,5.1252289816,0.4885375166,-2.4429541633
H,0,6.6667407231,0.9485199123,-1.6900285439
C,0,4.5589507575,1.7313062914,-0.0323295112
H,0,4.0413344295,1.7637518985,0.9312187395
H,0,5.3640932918,2.473083503,-0.0062015822
H,0,3.8591035992,1.9987506025,-0.8239473275
H,0,1.2806404131,-1.441892457,-2.5598262786

**TS-III-beta**



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PCM: E(RB3PW91) = -1640.81455808
Gibbs: 0.634961

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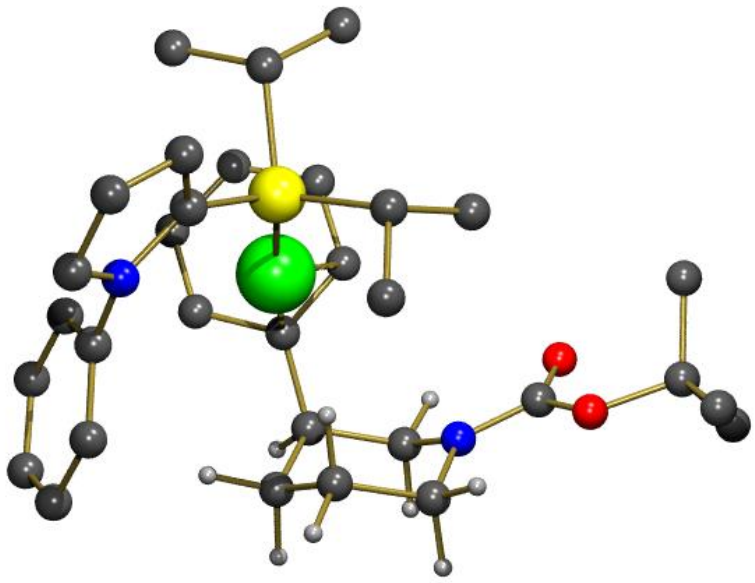
C,0,3.2550851009,3.8960654477,-0.2387503323
C,0,3.2826025182,3.9907289681,1.1526068853
C,0,2.2930150895,3.3439069029,1.8936155106
C,0,1.2852587931,2.6184246824,1.2598000717
C,0,1.2577989235,2.494136578,-0.1453358191
Pd,0,0.5895502948,0.6765478267,-0.7369584464
H,0,2.2500209889,3.1149285028,-1.9652436911
H,0,4.0160107456,4.3950051982,-0.8346931975
H,0,4.0586097126,4.5648760314,1.6510675697
P,0,1.7852440933,-1.3111961132,-0.9401692877
C,0,1.2137391314,-2.4298153623,-2.3670165846
C,0,3.6334643318,-1.0245642118,-1.2657218233
C,0,0.0205420465,-3.2903364338,-1.9437491975
C,0,0.8322494982,-1.6003858449,-3.596515978
H,0,2.063636405,-3.0822318582,-2.6121188333
C,0,3.8993374562,-0.2122749092,-2.5319514642
C,0,4.2469064443,-0.3419255787,-0.0416915912
H,0,4.0761309398,-2.0230027726,-1.3764293648
C,0,0.6704256592,-1.4513737286,2.310428564
H,0,-0.8327802105,-2.6587469663,-1.6718811275
H,0,0.2597095859,-3.9448805906,-1.102561972
H,0,-0.0306838205,-0.9663962577,-3.3680273934
H,0,1.6369160067,-0.9535235192,-3.9513182596
H,0,3.3446508794,0.7320760002,-2.5141742122
H,0,3.6327138051,-0.7558100948,-3.4419863294
H,0,3.8080984734,0.6488555392,0.1138293572
H,0,4.0993736978,-0.9309203859,0.8679557216
C,0,-0.5770627935,-1.1307837918,1.7706057518
C,0,1.0927935718,-0.8575859319,3.5026069594
C,0,-1.4025888175,-0.2266874999,2.4384040152
C,0,0.2585826489,0.0375496608,4.1681465946
H,0,2.0732832148,-1.1027774467,3.8994107289
H,0,-2.3768252387,0.0060134383,2.0205454212
C,0,-0.9921904848,0.353223389,3.6391898254
H,0,0.5896734719,0.4889118944,5.0991961843
H,0,-1.6467002016,1.0452897321,4.16176615
H,0,0.5358837138,2.1154631559,1.8629073169
N,0,1.4917885794,-2.4491021358,1.7162881108
C,0,1.9568782899,-2.5556524589,0.4089163355
C,0,1.9286702638,-3.5346373791,2.4399674728
C,0,2.6909826898,-3.7324787423,0.3459972335
C,0,2.670003837,-4.3494767511,1.6173928152
H,0,1.6339763199,-3.6473842973,3.473103787
H,0,3.1960857445,-4.1031809029,-0.5361569886
H,0,3.1329146557,-5.2851995296,1.8990452288
H,0,-0.9101144439,-1.6135958582,0.8584299282

H,0,5.3264346513,-0.2165599814,-0.188375338
H,0,4.9672607203,0.0286754219,-2.597657834
H,0,0.5493158718,-2.267144826,-4.4201900777
H,0,-0.2960846582,-3.9189107942,-2.7848236467
H,0,2.3022222352,3.4018705869,2.9797811831
C,0,-1.6052385286,1.8117370113,-1.7469465545
C,0,-0.4422773046,2.6605530842,-1.1548972525
C,0,-1.0896452667,3.8008682186,-0.3553637487
C,0,-2.0898611068,3.2939277262,0.680837988
C,0,-3.186004889,2.4590272082,0.0266585468
H,0,-0.3355549185,4.4374813186,0.113023545
H,0,0.0635197045,3.084518194,-2.0250994608
H,0,-2.103247536,2.4713740334,-2.4857702616
H,0,-1.5760380178,2.6864744029,1.4338904718
H,0,-2.5519525557,4.1395456226,1.2041729296
H,0,-3.8493534509,2.0204066309,0.7701763075
H,0,-3.7987679886,3.1029963155,-0.6271459484
H,0,-1.6346844562,4.4336239483,-1.0762415392
N,0,-2.5978109362,1.3908491365,-0.7720870522
C,0,-3.1363804568,0.1403422695,-0.8850187335
O,0,-2.7440551743,-0.7077043587,-1.6766745254
O,0,-4.140087957,-0.0435966603,0.0065532075
C,0,-4.9716492744,-1.2480786218,-0.0320255911
C,0,-5.9869243244,-0.9852330453,1.0778731369
H,0,-6.6875385291,-1.8221543459,1.1506682437
H,0,-5.4848494682,-0.871630183,2.0433118324
H,0,-6.5566004031,-0.0737984748,0.8740464223
C,0,-5.6714571894,-1.3555646581,-1.3856279001
H,0,-6.229385339,-0.4383847615,-1.5996730661
H,0,-4.9504105122,-1.528891308,-2.1854024901
H,0,-6.3819209519,-2.1880928444,-1.3652665502
C,0,-4.1408266423,-2.4897929454,0.2845336234
H,0,-3.6122937668,-2.3654139345,1.2347215022
H,0,-4.8022558713,-3.3573121218,0.3781892986
H,0,-3.4144862161,-2.6835035551,-0.504926976
H,0,-1.2784617382,0.9245610049,-2.2955198777

**3i**



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PCM: E(RB3PW91) = -1640.88531291
Gibbs: 0.637486

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C,0,0.5919010519,3.4392456865,-0.9777104812
C,0,1.8424564113,3.8577021598,-0.5441731611
C,0,2.2866351478,3.4835427261,0.731963483
C,0,1.4535629635,2.7604378067,1.5791278952
C,0,0.1198664624,2.4124415123,1.212448295
Pd,0,0.7881798172,0.6343727007,0.0371172569
H,0,-1.2898040644,2.5379027951,-0.4457856188
H,0,0.2379576952,3.7045842008,-1.970317503
H,0,2.4774867259,4.4544849222,-1.1926412579
P,0,1.4427101027,-1.0359206955,-1.3866380106
C,0,0.0100427241,-2.0547199332,-2.1115346566
C,0,2.3941200039,-0.4156876152,-2.9096744209
C,0,-0.4050389867,-3.1637230258,-1.1425685072
C,0,-1.1915684949,-1.1600402704,-2.4220075612
H,0,0.3837164315,-2.51006116,-3.0392533663

C,0,1.5681713121,0.5123164582,-3.7990482706
C,0,3.6691829594,0.2808568368,-2.4325442847
H,0,2.6720166757,-1.3071693199,-3.4858313311
C,0,2.9307556174,-2.034971911,1.5624634731
H,0,-0.689084764,-2.7423082023,-0.1711497944
H,0,0.3940884109,-3.8904829126,-0.9795562438
H,0,-1.5835695027,-0.7146769412,-1.5015404363
H,0,-0.9531978977,-0.3398490609,-3.1022345024
H,0,1.1547497703,1.3454860396,-3.2207894436
H,0,0.7439607645,-0.0081041586,-4.2941096866
H,0,3.421419222,1.156688653,-1.8224237463
H,0,4.2967120806,-0.3905604482,-1.8383185014
C,0,2.4339735313,-2.7004192071,2.6862996412
C,0,3.4079322234,-0.7272781498,1.675678691
C,0,2.4394307068,-2.0692311286,3.9280675106
C,0,3.4084529241,-0.1034627484,2.9221288783
H,0,3.8037015081,-0.2212472404,0.8024391001
H,0,2.0602378153,-2.5952520681,4.7996786422
C,0,2.9329081234,-0.7705939955,4.0504173691
H,0,3.7984332587,0.9061403324,3.0089407697
H,0,2.949644044,-0.2824008468,5.0207809721
H,0,1.7813827333,2.5428250704,2.5930683458
N,0,3.039753095,-2.7500173123,0.3374145335
C,0,2.5963664962,-2.4090863835,-0.9370830473
C,0,3.7428524502,-3.9312240054,0.2718069142
C,0,3.0405613908,-3.4133148589,-1.7878987477
C,0,3.761194026,-4.3659845135,-1.0323059254
H,0,4.2108865422,-4.3296794883,1.1602020859
H,0,2.8342638716,-3.4660479235,-2.8487214736
H,0,4.2471614908,-5.2602976245,-1.3975111356
H,0,2.052794673,-3.7114540928,2.5776200223
H,0,4.2610644691,0.6186878191,-3.2918302402
H,0,2.2055205852,0.9331123883,-4.5864161805
H,0,-1.9897648395,-1.7567520955,-2.8815534601
H,0,-1.2771247729,-3.6982631101,-1.5382454154
H,0,3.2745367184,3.7792343989,1.0754575775
C,0,-2.3545589436,2.3316306415,1.9645976128
C,0,-0.8810526028,2.1552345756,2.3482263049
C,0,-0.7113728455,0.8219165776,3.1006204673
C,0,-1.314457887,-0.3488523258,2.3273405869
C,0,-2.77155277,-0.0923394013,1.9509751694
H,0,0.3463960228,0.6289023543,3.3071404486
H,0,-0.6815337905,2.9579396284,3.0729849086
H,0,-2.9265116926,2.4716931818,2.8971527432
H,0,-0.726727996,-0.5042803191,1.4038165181
H,0,-1.2469668547,-1.2704115331,2.9171752262
H,0,-3.1556594604,-0.8826099896,1.3077970082
H,0,-3.3951592337,-0.0706943929,2.861854167
H,0,-1.2159827345,0.9142290459,4.0736419389
N,0,-2.8964846594,1.1822520831,1.2546828614

C,0,-3.7567838011,1.4141743227,0.2160066061
O,0,-3.9404136341,2.52127248,-0.2737965552
O,0,-4.3493542725,0.2746240966,-0.2024002453
C,0,-5.3659514732,0.3093590084,-1.2545015397
C,0,-5.7602303371,-1.1599802006,-1.3829682656
H,0,-6.5344497101,-1.275919796,-2.1471731247
H,0,-4.8968509705,-1.7673630553,-1.669707176
H,0,-6.1503491562,-1.5400783586,-0.4341761344
C,0,-6.5582341213,1.1482990075,-0.7967455165
H,0,-6.9432294825,0.7737587448,0.1571993547
H,0,-6.2742148896,2.1948432485,-0.6798874879
H,0,-7.3615339961,1.0805249581,-1.5373931034
C,0,-4.7722924943,0.8237141891,-2.564610104
H,0,-3.894533396,0.2327362145,-2.842036207
H,0,-5.5145423336,0.7265697276,-3.3638349612
H,0,-4.4812337414,1.8703807924,-2.4750171313
H,0,-2.5165503556,3.2153545052,1.347420407

**Table 2:**

**$L^7$ Ia**

GP: E(RB3PW91) = -1656.57694139
PCM: E(RB3PW91) = -1656.91617375
Gibbs: 0.627548

N,0,-2.3076112931,1.8557912642,-0.4734855644
C,0,-0.9386935655,2.3483928993,-0.19779222
C,0,-0.9588372901,3.1066801874,1.1301146244
C,0,-2.0333349856,4.2028811705,1.1573574455
C,0,-3.4099420423,3.6267378371,0.8231194406
C,0,-3.368953047,2.8587981623,-0.4975613332
Pd,0,0.3322942923,0.7327285338,-0.3450750962
O,0,-1.5775203779,-0.2929781593,-0.6484963866
C,0,-2.5111507522,0.5466843674,-0.6441632455
O,0,-3.7996623227,0.2080408082,-0.7979826112
C,0,-4.229945638,-1.1058859638,-1.2786376978
C,0,-3.8141815585,-2.2070769269,-0.306577373
C,0,1.833505088,2.03976549,-0.193244561
C,0,2.2631261547,2.7544668227,-1.3268521267
C,0,3.2859157059,3.7039475778,-1.2532825905
C,0,3.9093016602,3.977593962,-0.0364893944
C,0,3.4907633802,3.2943389888,1.1040351716
C,0,2.4679062793,2.3451626204,1.0235799856
P,0,1.730955579,-1.2026261097,-0.7154129829
C,0,1.5193741405,-2.708665764,0.349066462
N,0,0.7905630264,-2.8600579051,1.5138400967
C,0,0.9272855453,-4.1778145925,1.8983174404
C,0,1.732472966,-4.7658778791,0.9596327276

C,0,0.0554391992,-1.9138705813,2.2847881399
C,0,-1.2407253581,-2.2390940584,2.6901981085
C,0,-1.9445017024,-1.370877053,3.5203645603
C,0,-1.361994581,-0.1754913439,3.9396835347
C,0,-0.0713829591,0.1475556262,3.5244892045
C,0,0.6439991802,-0.7190539528,2.699888181
C,0,1.365196564,-1.9376279717,-2.425906034
C,0,1.1914966368,-0.8045235289,-3.4432418355
C,0,3.6273289263,-1.2173695123,-0.6783134942
C,0,4.1517359184,-0.8677594806,0.7144983734
C,0,0.1294031847,-2.8372721443,-2.4093735137
C,0,4.271678034,-0.343152995,-1.7532405119
C,0,-5.750326448,-0.9635354178,-1.3011823464
C,0,-3.691259789,-1.3315151514,-2.6884007088
H,0,1.7907894143,2.5695840501,-2.2894045258
H,0,3.592213693,4.2343987375,-2.1528169714
H,0,4.7036873828,4.7169535492,0.0232229621
H,0,2.242228525,-2.543921589,-2.6843627305
H,0,3.8574062578,-2.2709375467,-0.8813201753
H,0,-0.7322868134,-2.3050611211,-1.9954121737
H,0,0.2987699576,-3.7419755995,-1.8227688205
H,0,0.2946645638,-0.2186954977,-3.215321486
H,0,2.0363350507,-0.1114260085,-3.4612494798
H,0,3.9919329416,0.7083854653,-1.6457986931
H,0,4.0138712516,-0.6722648637,-2.7636396469
H,0,3.9302106042,0.1711334362,0.9756916251
H,0,3.7364098577,-1.5260104534,1.4846333468
H,0,1.6612528766,-0.4877063837,2.4051091619
H,0,-2.9500735034,-1.6304326496,3.8389041624
H,0,0.3907066236,1.0742591317,3.8509722528
H,0,-1.9094987212,0.4995074446,4.5910648885
H,0,2.1551973698,1.8412240456,1.9357361977
H,0,0.4779641291,-4.5425560129,2.8093208991
H,0,2.0741480782,-5.791630886,0.9225707263
H,0,-1.6901283071,-3.1666187809,2.3490488516
H,0,5.2410903732,-0.9913786369,0.7372562159
H,0,5.3626868209,-0.4094408822,-1.6626938736
H,0,1.0796374508,-1.2245382304,-4.4504109554
H,0,-0.1194472771,-3.1379408453,-3.4344812606
H,0,3.9584019008,3.5014441962,2.0647249423
H,0,-2.0562236842,4.6985191011,2.136044944
H,0,-1.1430411883,2.3980433866,1.9490134793
H,0,0.0304356647,3.5413760724,1.3000794369
H,0,-0.6948637006,3.0539822782,-1.0073984384
H,0,-3.7310093687,2.9415189486,1.6190759061
H,0,-4.1658481798,4.4187408791,0.7548617137
H,0,-4.3199352958,2.3701828068,-0.709217797
H,0,-3.1523833093,3.5544639438,-1.3218192055
H,0,-1.7777200818,4.9769903849,0.4192278409
H,0,-6.2078155842,-1.8916664088,-1.655795574

H,0,-6.1325987604,-0.7498323041,-0.2988197797
H,0,-6.0537746939,-0.15109514,-1.9677178279
H,0,-4.01904125,-0.5273792187,-3.3545346313
H,0,-2.6013732881,-1.3698907177,-2.6919079303
H,0,-4.0712171147,-2.2785701337,-3.0839845991
H,0,-4.1629940429,-1.969283536,0.7028562144
H,0,-4.2736527893,-3.152596365,-0.612879863
H,0,-2.7315642995,-2.3266188311,-0.2824881136
N,0,2.0914787146,-3.8536440413,0.0095999156

**$L^7$ TS-alpha**

GP: E(RB3PW91) = -1656.52080090
PCM: E(RB3PW91) = -1656.86287175
Gibbs: 0.623133

N,0,2.9570111156,0.5036862646,-0.5699445521
C,0,1.827359989,0.9766364647,-1.3762692327
C,0,1.543720159,-0.0333599612,-2.511084406
C,0,2.8183746152,-0.1726036845,-3.3690286087
C,0,4.0594324594,-0.4819719031,-2.5240595178
C,0,4.2009625527,0.4907345481,-1.3483806459
Pd,0,-0.1205333083,0.541328162,-0.2909519385
O,0,1.7007745651,-0.6140804308,0.9954801688
C,0,2.7869798896,-0.3421361375,0.4886356176
O,0,3.9657883799,-0.8223895242,0.9347251399
C,0,4.0397894832,-1.6777846001,2.1201179811
C,0,3.2813109455,-2.9824757358,1.8828831636
C,0,0.7238777377,2.3711231223,-0.6190117904
C,0,1.3121711861,2.9748565779,0.5105822189
C,0,1.2513392827,4.3556103328,0.6960742486
C,0,0.641995566,5.1786529387,-0.2512007765
C,0,0.094591094,4.5976251812,-1.3979460089
C,0,0.1445762979,3.2199662292,-1.589553064
P,0,-2.2338813582,0.5172109752,0.6525835354
C,0,-3.5247664206,-0.792945588,0.3684799638
N,0,-3.3649422173,-2.031089817,-0.2214834125
C,0,-5.3892264907,-1.8526457123,0.6054342975
C,0,-2.2540277427,-2.5955934479,-0.9135703634
C,0,-1.6803945166,-3.7699684037,-0.422931513
C,0,-0.6725334879,-4.4019861394,-1.147387273
C,0,-0.2417765775,-3.8654324723,-2.3600063023
C,0,-0.8130263935,-2.6870689054,-2.839914894
C,0,-1.8166345523,-2.0433054907,-2.1182765847
C,0,-2.1645170817,0.4011479112,2.5493985602
C,0,-1.0223231938,1.2556455756,3.1035676092
C,0,-3.3811970924,1.9851248969,0.3264403985
C,0,-3.6189838737,2.1000164421,-1.1794577505
C,0,-1.9869681092,-1.0534638749,2.989977416

C,0,-2.8492757976,3.2919169593,0.9117002014
C,0,5.5386583103,-1.9448010574,2.2394463195
C,0,3.530144851,-0.9251783799,3.3474630999
H,0,1.8049921592,2.3534381111,1.2523251369
H,0,1.690819336,4.7907955448,1.5911247917
H,0,-3.1327479779,0.7700819861,2.9111208174
H,0,-4.322447019,1.7116592043,0.8166707371
H,0,-1.0900963774,-1.4910408333,2.5355867053
H,0,-2.849786935,-1.6719279538,2.730214327
H,0,-0.0594845469,0.866514078,2.757006255
H,0,-1.0797665087,2.3025849618,2.7983756077
H,0,-1.8372351809,3.5155976641,0.5607329224
H,0,-2.8439281829,3.2777347098,2.0050435362
H,0,-2.6856048111,2.3236362443,-1.7063362952
H,0,-4.0404339438,1.1786252662,-1.5946479252
H,0,-2.2797278187,-1.1354841849,-2.4899747668
H,0,-0.2294181239,-5.3173487473,-0.7658248346
H,0,-0.4859419933,-2.2697219692,-3.7874980101
H,0,0.5338932738,-4.3663922447,-2.932226932
H,0,-6.4157260617,-2.0190758344,0.9041307158
H,0,-2.0311790086,-4.1791931805,0.5196307859
H,0,-4.3290347369,2.9099673667,-1.3860778559
H,0,-3.4983647909,4.1205586664,0.6030469193
H,0,-1.0329310311,1.2223586942,4.2004864122
H,0,-1.8602200212,-1.0988572509,4.0785268618
H,0,-0.3787137249,5.2234352455,-2.1515351537
H,0,2.6794005195,-0.9487554333,-4.1319215049
H,0,1.2514167991,-1.0084480192,-2.1058590673
H,0,0.7157553238,0.3201796685,-3.1351617992
H,0,2.2514848767,1.8363806098,-1.8978062757
H,0,3.9890923161,-1.4997116508,-2.11738646
H,0,4.9636148571,-0.4486235004,-3.1443040561
H,0,5.0330366175,0.2190194285,-0.7008517301
H,0,4.3754694891,1.5119198487,-1.7094603751
H,0,2.9788349596,0.7711402009,-3.9099989207
H,0,5.737115426,-2.5849527626,3.1039865688
H,0,5.914667767,-2.4476851738,1.3435121112
H,0,6.0896107329,-1.0085545203,2.3678496389
H,0,4.0643884737,0.0234329862,3.4606429151
H,0,2.4614541588,-0.7238456237,3.2683795899
H,0,3.7104934313,-1.5249815194,4.2453703705
H,0,3.6372505194,-3.4654552192,0.967234009
H,0,3.4613925843,-3.6664328882,2.7185859048
H,0,2.2092742545,-2.8040204746,1.7962249397
H,0,-0.2719499683,2.7897448358,-2.4970692283
H,0,0.6041106718,6.2544242692,-0.1058844323
C,0,-4.5564596165,-2.7087208761,-0.0653489693
H,0,-4.6936094699,-3.698781672,-0.4733056482
N,0,-4.7439299634,-0.6794103737,0.872790356

**$L^7$ TS-beta**

GP: E(RB3PW91) = -1656.52382924
PCM: E(RB3PW91) = -1656.86719061
Gibbs: 0.626555

C,0,0.6758052546,3.5807077176,-0.8006143234
C,0,1.5340282679,4.6105814299,-1.1804762444
C,0,2.7305875326,4.8318677704,-0.4962224161
C,0,3.0555798465,4.0077033991,0.5816034841
C,0,2.2022901727,2.9757924569,0.9710035915
C,0,1.0079738103,2.7210453955,0.2666808146
Pd,0,0.433108601,0.7920579149,0.1122039254
H,0,-0.2557148083,3.4348264639,-1.3412708748
H,0,1.261921954,5.2477315588,-2.0190472859
H,0,3.3933299667,5.6401751146,-0.7914566054
P,0,1.2405276884,-0.716110269,-1.4752654827
C,0,-0.080786406,-1.3710308705,-2.6626950133
C,0,2.6249956507,-0.0555512617,-2.5891670249
C,0,-0.8807885082,-2.4878807028,-1.989134555
C,0,-1.0192999466,-0.2489023907,-3.1126021039
H,0,0.4632454154,-1.7882510876,-3.5186125977
C,0,2.197754322,1.1326160799,-3.448493126
C,0,3.8315313615,0.3043695303,-1.7206800041
H,0,2.8854869815,-0.9064927763,-3.2302325246
C,0,2.1369225705,-2.3798804244,1.4777033943
H,0,-1.3533680646,-2.1303683566,-1.0663725587
H,0,-0.2598101072,-3.3547689982,-1.752258716
H,0,-1.576336407,0.1651743005,-2.265982096
H,0,-0.4974230722,0.5790986463,-3.5959958207
H,0,1.7936809655,1.9464970239,-2.8376295637
H,0,1.454632391,0.8546016416,-4.1998838138
H,0,3.5827178255,1.1052048403,-1.0158973683
H,0,4.2021584187,-0.5595234922,-1.1593029104
C,0,1.4341393897,-3.1472635986,2.4097090529
C,0,2.7335979251,-1.1769386801,1.8605204123
C,0,1.3452999856,-2.7198554309,3.732536621
C,0,2.6362759749,-0.7567794254,3.1859790216
H,0,3.2899641761,-0.5952293495,1.1345524349
H,0,0.8041466655,-3.3229357642,4.4558890489
C,0,1.949921495,-1.5261583114,4.124641527
H,0,3.1169626894,0.1693619677,3.4872692267
H,0,1.889415922,-1.1981899526,5.1583232178
N,0,2.3166290751,-2.8953087347,0.1617577386
C,0,2.0703926401,-2.3279629682,-1.0740491868
C,0,2.8700706369,-4.1374529779,-0.0740891147
C,0,2.9395186184,-4.2679724113,-1.4355768292
H,0,3.1883373708,-4.7704837852,0.7401918409
H,0,3.3242083348,-5.1027594005,-2.0061079049
H,0,0.9661601533,-4.0742569944,2.0918397628

H,0,4.6533100221,0.6576134095,-2.3546926966
H,0,3.0703894978,1.5230324821,-3.9859714271
H,0,-1.7478452151,-0.6454801596,-3.8301660077
H,0,-1.6804890701,-2.8236442859,-2.6599677976
H,0,3.9806233654,4.1703490983,1.1306410009
C,0,-1.9723103714,2.2816879465,0.9088121867
C,0,-0.5451110933,2.3366929819,1.4538445965
C,0,-0.4186244069,1.6215901054,2.8070619369
C,0,-1.0936061294,0.2503604952,2.8181602306
C,0,-2.5272287888,0.3301328145,2.3039908899
H,0,0.6312256936,1.534543686,3.105100256
H,0,-0.3686527423,3.3928114211,1.6537013767
H,0,-2.5927919424,2.977399854,1.506769632
H,0,-0.5238509205,-0.4495308293,2.1920390124
H,0,-1.1036088095,-0.1596768794,3.8352189931
H,0,-2.9725184556,-0.6610390138,2.2368379099
H,0,-3.1385175004,0.9230479111,3.0072407814
H,0,-0.9015644475,2.2568155602,3.5694191314
N,0,-2.5686943667,0.9523197747,0.9848200892
C,0,-3.5298607744,0.6501774933,0.0526990889
O,0,-3.7372140401,1.3206333692,-0.9487863881
O,0,-4.1901262417,-0.4844927863,0.3750519917
C,0,-5.3436423722,-0.9259457684,-0.4086990774
C,0,-5.788930565,-2.1820333605,0.3364323538
H,0,-6.6620952963,-2.6213768385,-0.1549609761
H,0,-4.9879234809,-2.9271300879,0.3482832628
H,0,-6.0564083366,-1.9446824242,1.3703817755
C,0,-6.4382964148,0.1393471975,-0.3698390341
H,0,-6.6902716111,0.3880855939,0.6661482107
H,0,-6.1180696098,1.0453327914,-0.8858299886
H,0,-7.3411501781,-0.2432588105,-0.8564972971
C,0,-4.9277266245,-1.2687400114,-1.8374828788
H,0,-4.1205380068,-2.0070977075,-1.8309482323
H,0,-5.7800107848,-1.7015051857,-2.3718091704
H,0,-4.5901386402,-0.3782042059,-2.3677586105
H,0,-2.033311596,2.6183100212,-0.1263076099
H,0,2.4672498707,2.3577549659,1.8251109498
N,0,2.4423126542,-3.1502924553,-2.0424105149

**$L^1$ Ia**

GP: E(RB3PW91) = -2029.90977810
PCM: E(RB3PW91) = -2030.31747092
Gibbs: 0.854425

N,0,3.5178585303,0.4433732582,-0.6355987786
C,0,2.431028778,1.0912673176,-1.3988339605
C,0,2.5146629805,0.6121841973,-2.850894986
C,0,3.911347745,0.8350570174,-3.4500163977
C,0,4.9971838991,0.2022642664,-2.5779735846

C,0,4.8722103964,0.676559418,-1.1300749478
Pd,0,0.6505677207,0.7300689574,-0.4340388956
O,0,2.0412934969,-0.5739173209,0.765806942
C,0,3.2155690077,-0.3856354577,0.365463189
O,0,4.2844893935,-1.0240337013,0.8772265075
C,0,4.346431489,-1.5191135728,2.2516151579
C,0,3.3982968626,-2.6971578404,2.4482254084
C,0,-0.0339508453,2.1875185103,-1.6159558238
C,0,0.2851211872,3.5284964794,-1.3315408982
C,0,-0.1441114999,4.5762816613,-2.1507704265
C,0,-0.8888217353,4.3124376317,-3.2997420553
C,0,-1.1900373889,2.9885573573,-3.6173697032
C,0,-0.7669761947,1.9451383126,-2.7892971612
P,0,-1.4635619325,0.3608355397,0.8106489896
C,0,-1.8804897554,-1.8732842101,-1.7807544833
C,0,-0.7328899031,-2.6759416595,-1.5614471231
C,0,0.1698088023,-2.8474504271,-2.6229119384
C,0,-0.0654997206,-2.2951319568,-3.8792889495
C,0,-1.2253721262,-1.5656934343,-4.1133583602
C,0,-2.1180949251,-1.3658996298,-3.0627659263
C,0,5.797975857,-1.9780209655,2.3718604832
C,0,4.0627902768,-0.3732267318,3.2181634516
H,0,0.883633053,3.7655570206,-0.454020935
H,0,0.1156705994,5.6012778392,-1.8930809144
H,0,-3.0212632301,-0.7831800905,-3.2248047144
H,0,1.0588032252,-3.4505998545,-2.4747088403
H,0,-1.4308332683,-1.1457068183,-5.0935245198
H,0,0.6511234411,-2.4606401999,-4.6793737492
H,0,-1.7593106256,2.7619530556,-4.5170379677
H,0,3.9623982919,0.4333851181,-4.4698348779
H,0,2.2580103865,-0.4544660764,-2.8992644287
H,0,1.7624391269,1.1431848741,-3.4409276307
H,0,2.6426514067,2.1698552805,-1.3685738001
H,0,4.903917412,-0.8919090291,-2.5984437183
H,0,5.9987159344,0.4468383021,-2.953041958
H,0,5.5857027452,0.1750802497,-0.4767379611
H,0,5.0607279787,1.7586570232,-1.0775961774
H,0,4.0990129722,1.9157876122,-3.5294487466
H,0,5.9819237321,-2.3845151258,3.3706428241
H,0,6.0166666966,-2.756876281,1.6356863579
H,0,6.484032815,-1.1424702395,2.2059650083
H,0,4.7551127875,0.4559748213,3.0422856573
H,0,3.0407379172,-0.007250318,3.1071944129
H,0,4.1951586984,-0.7151025361,4.2492450882
H,0,3.602683005,-3.4740894644,1.7053728764
H,0,3.5503289419,-3.1291567326,3.4427813033
H,0,2.3598406055,-2.3826074794,2.3498235434
H,0,-1.0139636878,0.9244106948,-3.0614680483
H,0,-1.2194642391,5.1245000622,-3.942275673
C,0,-2.9401472014,-1.6746064991,-0.7471675592

C,0,-2.8426105862,-0.8742891215,0.4118297626
C,0,-4.1433807666,-2.3654127143,-0.9938961828
C,0,-3.9259523552,-0.8934092833,1.3103366967
C,0,-5.2131671408,-2.3380983101,-0.1092480372
H,0,-4.2119192571,-2.9555960123,-1.9041241448
C,0,-5.0905701588,-1.6135183537,1.0723695242
H,0,-3.8689708994,-0.3169870466,2.2284249455
H,0,-6.1231974408,-2.8873053678,-0.3344957623
H,0,-5.8983033397,-1.592629893,1.7988256711
C,0,-2.6025683376,1.8880192551,0.9816546941
C,0,-1.8910242659,3.1411538859,1.5084698347
C,0,-3.3496356125,2.1939580486,-0.3253525341
H,0,-3.3509492911,1.596206788,1.7326030544
C,0,-2.8686098859,4.3139933307,1.6635299909
H,0,-1.0911764872,3.420294858,0.8149123026
H,0,-1.4257689506,2.9423032719,2.4784811176
C,0,-4.3281997992,3.3597766721,-0.1468899704
H,0,-2.6251349288,2.4474369547,-1.1057055428
H,0,-3.891603749,1.3059934255,-0.6682967412
C,0,-3.614155481,4.6115894148,0.362711923
H,0,-2.3215243488,5.2013127821,2.0056582845
H,0,-3.5981159008,4.0759617764,2.4521299262
H,0,-4.8293256935,3.5659151418,-1.1004255741
H,0,-5.1166581812,3.0733419342,0.565315892
H,0,-4.3293961901,5.4301380253,0.5115659945
H,0,-2.8965411279,4.9482310908,-0.3974287604
C,0,-1.1544036273,-0.062081137,2.6428379416
C,0,-0.9862184697,-1.5687416832,2.8874694986
C,0,0.0657061992,0.6818693017,3.2096306537
H,0,-2.0483894329,0.2805020331,3.1870152317
C,0,-0.8137277271,-1.869594719,4.3808938873
H,0,-0.1108370735,-1.9202418296,2.3271489052
H,0,-1.8443337068,-2.1224789974,2.4970823323
C,0,0.2381145471,0.3996214338,4.706985049
H,0,0.9516256996,0.3513761341,2.6561192303
H,0,-0.0101098991,1.7606787456,3.0493859592
C,0,0.3578289214,-1.0979435985,4.9904914053
H,0,-0.6788702224,-2.948364178,4.5295346265
H,0,-1.7394930578,-1.5987661096,4.9097472591
H,0,1.1196824694,0.9318941161,5.0855411914
H,0,-0.6259172001,0.8047603176,5.2539058617
H,0,0.4164588995,-1.2810698888,6.0706414372
H,0,1.2963390051,-1.471011942,4.5585064851
N,0,-0.5221821897,-3.3030494171,-0.3079411857
C,0,0.8369350134,-3.7163532028,-0.0199870379
H,0,0.8935230479,-4.001452206,1.0350102262
H,0,1.170351477,-4.5893504186,-0.6114414666
H,0,1.5223600065,-2.8831698822,-0.1809572484
C,0,-1.4633273563,-4.367195444,0.0235650602
H,0,-1.3435289113,-4.6344018038,1.0786528945

H,0,-2.4921189049,-4.0415131359,-0.1248219155
H,0,-1.2939747974,-5.2754222774,-0.5818978574

**$L^1$ TS-alpha**

GP: E(RB3PW91) = -2029.86326528
PCM: E(RB3PW91) = -2030.27246221
Gibbs: 0.851426

N,0,3.3812073937,0.7117488407,-1.0094054809
C,0,2.1193088859,0.9716273558,-1.7045990349
C,0,1.8559575206,-0.1711635707,-2.7133192364
C,0,3.0345015879,-0.216410545,-3.7084381048
C,0,4.3943377805,-0.2840201576,-3.0042819605
C,0,4.5256625942,0.7937318389,-1.9226130705
Pd,0,0.2523680733,0.4293596308,-0.5219848902
O,0,2.4551374775,-0.4391668113,0.7489068988
C,0,3.4361093455,-0.0559470445,0.1170987785
O,0,4.7147267599,-0.318850668,0.4698405243
C,0,5.0375011981,-1.0051658112,1.7188451425
C,0,4.4773220094,-2.4264150753,1.7113084404
C,0,1.0278035601,2.2901454029,-0.8185684796
C,0,1.651447657,2.8798657657,0.2995842204
C,0,1.5640769269,4.2533579308,0.5286217536
C,0,0.8916394305,5.0872919902,-0.3638580324
C,0,0.3030368931,4.5232564484,-1.4995247963
C,0,0.3759256684,3.1533848764,-1.731357583
P,0,-1.7888871398,0.2109246608,0.6028150064
C,0,-2.0692248526,-2.2535532781,-1.7040303786
C,0,-0.9085492108,-2.9802752892,-1.341975698
C,0,0.0213657204,-3.2932577153,-2.3449249214
C,0,-0.1773734839,-2.9120458326,-3.6700050566
C,0,-1.319663879,-2.2037628557,-4.0267130628
C,0,-2.254285866,-1.8903520621,-3.0420870999
C,0,6.5643299227,-1.0345124586,1.6943451357
C,0,4.5361209679,-0.1931922708,2.911355574
H,0,2.1871170709,2.2518701054,1.0039116209
H,0,2.0344708335,4.6738293643,1.4150932076
H,0,-3.154228052,-1.3407712333,-3.3056202418
H,0,0.9075402325,-3.8644752317,-2.0879199586
H,0,-1.4883472662,-1.902155826,-5.0564845264
H,0,0.5596282854,-3.1826011868,-4.4218265868
H,0,-0.2123439925,5.1583167519,-2.2170247979
H,0,2.9186506077,-1.0693722268,-4.3884081318
H,0,1.7607922926,-1.1342143057,-2.2009824495
H,0,0.919560433,-0.0097903762,-3.2562349212
H,0,2.3600923427,1.8248783979,-2.3401026459
H,0,4.5167548664,-1.2643756201,-2.5244204692
H,0,5.2095468012,-0.1819722395,-3.731389117
H,0,5.4500262346,0.6847378208,-1.3578404108

H,0,4.5220042228,1.7954267792,-2.3702111928
H,0,2.9985982151,0.6879087447,-4.333213902
H,0,6.944338622,-1.5305794304,2.5922406509
H,0,6.9260249547,-1.5807310696,0.8180770153
H,0,6.9700642926,-0.0192398566,1.6609455798
H,0,4.9338652913,0.8257746457,2.8711978617
H,0,3.4466142239,-0.1484347603,2.9231030946
H,0,4.880322188,-0.6558304217,3.8419496377
H,0,4.8072183188,-2.9599026431,0.8141096468
H,0,4.8500050165,-2.9710245002,2.5849500979
H,0,3.387793011,-2.4170167907,1.7394333724
H,0,-0.0667743421,2.7394688623,-2.6344479486
H,0,0.8389384879,6.1579887927,-0.1884457703
C,0,-3.1819307657,-1.9868113073,-0.7445146231
C,0,-3.155731263,-1.0558759713,0.3137865148
C,0,-4.3498259361,-2.7449475451,-0.9556061085
C,0,-4.2810275943,-0.9851996401,1.1541563945
C,0,-5.4588273481,-2.6407233162,-0.1255638365
H,0,-4.3629200587,-3.4431289385,-1.7887582065
C,0,-5.4151237668,-1.764605318,0.9553205152
H,0,-4.2763156914,-0.2938213324,1.9922327012
H,0,-6.3420005968,-3.2443270688,-0.3162425965
H,0,-6.2599022306,-1.6768531712,1.6331854287
C,0,-2.9041246229,1.7422529759,0.4273849734
C,0,-2.3064940667,3.0312248333,1.0022727805
C,0,-3.2829299252,1.9271921783,-1.048404887
H,0,-3.8215744376,1.5159831224,0.989278039
C,0,-3.2593495519,4.2176415091,0.8007987237
H,0,-1.3471122825,3.2434473206,0.5161778748
H,0,-2.1071942276,2.9160660543,2.0732017647
C,0,-4.2360899448,3.1112609301,-1.2415474946
H,0,-2.3643374376,2.0950308627,-1.6254483893
H,0,-3.7409538809,1.0108331534,-1.4392103121
C,0,-3.6448455682,4.3994383505,-0.6677917277
H,0,-2.791392425,5.130817298,1.1880537524
H,0,-4.1706427803,4.0566017908,1.3961317643
H,0,-4.4640375715,3.2348655426,-2.3077659138
H,0,-5.1919502654,2.8943565761,-0.742344682
H,0,-4.3534960766,5.2299317191,-0.7770274787
H,0,-2.7474547618,4.6698912573,-1.2401431167
C,0,-1.5549574705,0.0763817207,2.4866949084
C,0,-1.4485830534,-1.3775251717,2.9702865103
C,0,-0.3002441792,0.8507407202,2.9241128281
H,0,-2.4363852543,0.5411067295,2.9560983871
C,0,-1.2485049759,-1.4499165083,4.4884453878
H,0,-0.6011615567,-1.8529014381,2.459126021
H,0,-2.3386379,-1.9471893418,2.6871964099
C,0,-0.1083937595,0.795876054,4.4433721158
H,0,0.5698954972,0.4084058056,2.4217335875
H,0,-0.3405752138,1.8907949825,2.589172177

C,0,-0.029802514,-0.6465734616,4.9448466959
H,0,-1.1547339295,-2.4980165411,4.8000996945
H,0,-2.1467756438,-1.0589374012,4.9889714797
H,0,0.7981797958,1.3474106274,4.7219302543
H,0,-0.9469486828,1.3076978496,4.9385591711
H,0,0.0582323384,-0.6720442077,6.0381789967
H,0,0.8806555312,-1.1154970825,4.54532219
N,0,-0.7077585032,-3.3820429377,0.0040141864
C,0,0.6682279232,-3.5955121088,0.4098787579
H,0,0.6956635799,-3.6907911672,1.5004035611
H,0,1.1210940883,-4.514162682,-0.0070836758
H,0,1.2784989685,-2.7317366848,0.1355564038
C,0,-1.5705479351,-4.4627226398,0.4651993936
H,0,-1.4988361567,-4.5400389315,1.5550721851
H,0,-2.6113750265,-4.2625925686,0.2102977072
H,0,-1.2863240231,-5.438213322,0.0315225087

**$L^1$ TS-beta**

GP: E(RB3PW91) = -2029.86018367
PCM: E(RB3PW91) = -2030.27168181
Gibbs: 0.850796

C,0,1.0615674208,-3.6978527559,0.2334680517
C,0,2.0729465789,-4.6386738223,0.4078814382
C,0,3.1086722582,-4.7546280869,-0.5222035239
C,0,3.1120942656,-3.9118489315,-1.6347645501
C,0,2.1000841476,-2.9708495568,-1.8215433026
C,0,1.0619937178,-2.8239973619,-0.8762192059
Pd,0,0.3243657137,-0.9601994146,-0.6477913822
H,0,0.2596708072,-3.638063863,0.9645498625
H,0,2.049853142,-5.289288887,1.2794529833
H,0,3.891791566,-5.4951696984,-0.3878603151
P,0,1.4513057581,0.5492301538,0.7964085608
C,0,0.8432445078,2.7868695769,-1.6998156587
C,0,-0.5682616969,2.8452908972,-1.7692958497
C,0,1.5702673314,2.4879838882,-2.8564451477
C,0,-1.1895478171,2.5923673142,-2.9999766771
C,0,0.9389416716,2.225858393,-4.0707145582
H,0,2.6546932001,2.4590052383,-2.7937564255
H,0,-2.2714677442,2.6476065846,-3.0698327676
C,0,-0.4489698232,2.2839676607,-4.1391904987
H,0,1.5281505083,1.9886049083,-4.9518458818
H,0,-0.9611625963,2.0988811229,-5.079772127
H,0,3.9066236712,-3.9912711495,-2.373760186
C,0,-2.0037785946,-2.8057400514,-0.8626723988
C,0,-0.7288483465,-2.7107557821,-1.7000609074
C,0,-0.9811752987,-2.1098914703,-3.0881759934
C,0,-1.8655352942,-0.8694034473,-3.0364201306

C,0,-3.1483338034,-1.1311319421,-2.2549626662
H,0,-0.0359214071,-1.8895504257,-3.595465785
H,0,-0.4567030799,-3.7495606818,-1.8785537127
H,0,-2.6025363911,-3.6527626974,-1.2506720329
H,0,-1.3186263161,-0.0449236775,-2.5637120067
H,0,-2.12625419,-0.543918051,-4.0507578777
H,0,-3.7501778178,-0.2269741564,-2.1765303462
H,0,-3.7567985603,-1.8875634423,-2.781662964
H,0,-1.4852369595,-2.8759597777,-3.7017253008
N,0,-2.8362233252,-1.6063108684,-0.9099085943
C,0,-3.6803224686,-1.4127088314,0.1555296781
O,0,-3.5725380528,-1.9993254222,1.2225335441
O,0,-4.6252644124,-0.4843741919,-0.123301341
C,0,-5.720933804,-0.2331009214,0.8121500474
C,0,-6.5564026082,0.8118532961,0.0761230455
H,0,-7.4301457687,1.0840670455,0.6755829504
H,0,-5.9706514797,1.7168763896,-0.1098093916
H,0,-6.9041455593,0.4218142989,-0.8850193474
C,0,-6.529398758,-1.5125821304,1.0234797017
H,0,-6.8737447703,-1.9085842209,0.0627261776
H,0,-5.9307601216,-2.2721800754,1.5278824226
H,0,-7.4100246798,-1.2937853938,1.6358847026
C,0,-5.1913601297,0.3309678288,2.1287701554
H,0,-4.5706624928,1.2128165533,1.94329437
H,0,-6.0314024352,0.6348240048,2.7620271494
H,0,-4.5981206949,-0.4147513019,2.657634579
H,0,-1.7930097089,-3.0261901062,0.1836967
H,0,2.113879416,-2.3440721325,-2.7094237688
N,0,-1.3226074631,3.1601576611,-0.6044552188
C,0,-2.642698893,2.5669496781,-0.5222284695
H,0,-3.0163289373,2.695473158,0.4988923415
H,0,-3.3875804544,3.0238501727,-1.2002060416
H,0,-2.5896770043,1.4959349184,-0.7263324636
C,0,-1.3558472488,4.5762234774,-0.2613893695
H,0,-1.785039196,4.6944045913,0.7392480571
H,0,-0.3476618649,4.9911763567,-0.2440020073
H,0,-1.9655675817,5.1669948968,-0.9688413604
C,0,1.5825790974,3.1978982339,-0.4686276718
C,0,1.7936584375,2.4032548653,0.6750552441
C,0,2.1065036084,4.5044690504,-0.4959800005
C,0,2.4480310766,2.9930074227,1.7719634071
C,0,2.771355452,5.0580990707,0.5907693797
H,0,1.9661314737,5.0924646324,-1.3996551236
C,0,2.9211804675,4.2998765925,1.7484153532
H,0,2.6043071586,2.4099949788,2.6750396332
H,0,3.1594118291,6.0714540297,0.5355527734
H,0,3.4180218847,4.7125552836,2.6222348066
C,0,0.7608696388,0.4098482049,2.559473022
C,0,-0.3729119534,1.4122239432,2.8234378342
C,0,0.2511636383,-1.0138679732,2.8380714975

H,0,1.5898328515,0.6216263479,3.252736989
C,0,-0.8999215111,1.2875690104,4.2580703128
H,0,-1.187495554,1.2137889026,2.1134052062
H,0,-0.0413194676,2.4378832431,2.6357817339
C,0,-0.2511273601,-1.149443689,4.2795727124
H,0,-0.5716704517,-1.2320907086,2.1433630938
H,0,1.0258983438,-1.7577538592,2.6339083055
C,0,-1.3569387361,-0.1365885726,4.5789558431
H,0,-1.7224025597,1.9971483534,4.4125709332
H,0,-0.103803959,1.5802735423,4.9586433704
H,0,-0.6146096533,-2.1701032565,4.4491355897
H,0,0.5871208184,-0.9961643367,4.9755090227
H,0,-1.6728574479,-0.2092494717,5.6269384188
H,0,-2.2349264345,-0.3822742625,3.9665155729
C,0,3.2871848439,0.064513966,0.985465559
C,0,3.5457955634,-1.3103306363,1.6081075718
C,0,3.9815469739,0.1838913898,-0.378241689
H,0,3.7173468191,0.8233421283,1.6540265017
C,0,5.0516362865,-1.5880548784,1.7150983159
H,0,3.0732902773,-2.0894971976,1.0001712109
H,0,3.1013343092,-1.3667855008,2.6077543634
C,0,5.4836780619,-0.0999936108,-0.2708538882
H,0,3.5194573842,-0.5327888725,-1.0695902348
H,0,3.821859086,1.1839644771,-0.7978206305
C,0,5.7489166545,-1.4675071876,0.3598634365
H,0,5.2086908645,-2.5877627436,2.1377067136
H,0,5.5043476834,-0.8753463554,2.4205737332
H,0,5.9440707857,-0.0400377402,-1.264996153
H,0,5.95858732,0.6821196619,0.3395841337
H,0,6.8274472965,-1.6367898331,0.4685725423
H,0,5.3686750705,-2.2530959828,-0.3065417111

**$L^2$ Ia**

GP: E(RB3PW91) = -2124.95474862
PCM: E(RB3PW91) = -2125.39016733
Gibbs: 0.843688

N,0,3.0968205383,-1.5909734318,-0.7929863359
C,0,1.7614973928,-2.2288945627,-0.8224462607
C,0,1.762463134,-3.3876643644,0.1777780112
C,0,2.9246255088,-4.3609981799,-0.0658689915
C,0,4.2657996931,-3.6273970608,-0.0762291752
C,0,4.2361305384,-2.4634354939,-1.0662066483
Pd,0,0.3478777491,-0.7540008688,-0.5409906786
O,0,2.20810806,0.4387181062,-0.2719478297
C,0,3.2011491094,-0.2990634214,-0.4761150091
O,0,4.4733612947,0.1343254392,-0.3581430547

C,0,4.8751118231,1.4951587928,-0.7159459963
C,0,4.400528491,2.4914734893,0.3367063766
C,0,-0.9690310798,-2.1534663894,-1.0749388743
C,0,-1.174403964,-2.4383323931,-2.4375270948
C,0,-2.0526434725,-3.4421556106,-2.855314789
C,0,-2.7427669843,-4.2099656938,-1.9181537816
C,0,-2.5346135682,-3.9633360159,-0.5614273915
C,0,-1.6616289822,-2.9529294831,-0.1487558558
P,0,-1.275924557,1.0698155224,-0.3384968843
C,0,-0.773943319,0.0939697632,2.8739757447
C,0,0.6081167633,0.0678247008,3.123699089
C,0,1.2407058788,-1.102875743,3.5602833871
C,0,0.475109933,-2.2428862708,3.7788450387
C,0,-0.9016960354,-2.2406400914,3.5825165242
C,0,-1.521689048,-1.0656006422,3.1408259216
C,0,6.3993503373,1.4069780041,-0.718983186
C,0,4.352929756,1.8303384336,-2.1092433446
H,0,-0.637249038,-1.8678206072,-3.1927720304
H,0,-2.1891835185,-3.6291986147,-3.9187571151
H,0,2.309154727,-1.1277748021,3.7355562835
H,0,-1.4770914635,-3.1371416053,3.7786613381
H,0,0.9613410082,-3.1527655546,4.1198552338
H,0,-3.0516395992,-4.5657138228,0.1838529436
H,0,2.9313334496,-5.1524313327,0.6942289395
H,0,1.8237730999,-2.9885551202,1.1986233813
H,0,0.8084645681,-3.9167579549,0.1026513174
H,0,1.6458443171,-2.6389857978,-1.8375220222
H,0,4.4847001392,-3.2330132781,0.9252010682
H,0,5.0869931506,-4.3046167853,-0.3419290521
H,0,5.1538249909,-1.8769312406,-1.0287255735
H,0,4.1183940029,-2.8525807889,-2.0883584316
H,0,2.780280248,-4.8591338647,-1.0357469502
H,0,6.8307584989,2.3849851977,-0.9520468057
H,0,6.7677308145,1.0920224966,0.2616260189
H,0,6.7466244501,0.688054888,-1.4666498763
H,0,4.6939334946,1.0872317107,-2.8369262464
H,0,3.2620438155,1.8599650499,-2.1203141435
H,0,4.7277635653,2.8096807328,-2.4220479419
H,0,4.8158283215,2.2320886771,1.3148914128
H,0,4.7484252443,3.4966573696,0.0770421656
H,0,3.3127316882,2.4961462941,0.4061327481
H,0,-1.5099267726,-2.7895241072,0.9149209385
H,0,-3.4210238405,-4.9963551111,-2.239428278
C,0,-1.4643563513,1.3837541589,2.5721579292
C,0,-1.724353206,1.9052553735,1.2890118723
C,0,-1.8905912816,2.1060699245,3.6999348083
C,0,-2.412532459,3.129630043,1.2028669378
C,0,-2.5614446517,3.3160473189,3.5919888882
H,0,-1.6834298475,1.6889453582,4.6814871125
C,0,-2.826985817,3.8333285453,2.3268307087

H,0,-2.628248573,3.5541743344,0.2264291606
H,0,-2.8758054986,3.8479137348,4.4858822956
H,0,-3.3518686223,4.7778751355,2.2118232421
C,0,-3.0557520821,0.9063336303,-1.0022115149
C,0,-3.162383313,0.5925555369,-2.4998341323
C,0,-3.874740508,-0.0911856505,-0.1726886712
H,0,-3.486469843,1.9065898658,-0.8425657448
C,0,-4.6292404443,0.5362694925,-2.9496671114
H,0,-2.6797565065,-0.3691982257,-2.7069669087
H,0,-2.6438815918,1.3532374863,-3.0924083175
C,0,-5.3368953348,-0.1260431823,-0.6308841282
H,0,-3.4405047903,-1.0910820194,-0.2821575401
H,0,-3.8175914301,0.1627682663,0.8899302272
C,0,-5.4447910031,-0.4554225464,-2.1198984672
H,0,-4.67438532,0.2759713826,-4.0144541801
H,0,-5.0750086216,1.5377074988,-2.8547728292
H,0,-5.8925020108,-0.8609948309,-0.0350588755
H,0,-5.8063984605,0.850104778,-0.437982682
H,0,-6.4934940796,-0.4504637681,-2.4424264591
H,0,-5.0631523846,-1.4710915334,-2.2919131843
C,0,-0.6700848324,2.5487715324,-1.3745649505
C,0,0.284243994,3.500881573,-0.6407340081
C,0,0.0083596587,2.0759076802,-2.6722695004
H,0,-1.5759304545,3.1118776902,-1.6504856486
C,0,0.61599213,4.7124449381,-1.5211940382
H,0,1.2005879387,2.9523166986,-0.3907163183
H,0,-0.1446242154,3.8412445714,0.3054884555
C,0,0.3338799657,3.2682561822,-3.5803661511
H,0,0.9277614446,1.5400430016,-2.404400799
H,0,-0.6106448411,1.3538874,-3.2123469393
C,0,1.2105000178,4.3018048424,-2.869918431
H,0,1.3053174641,5.3813096335,-0.9907666556
H,0,-0.3040442582,5.2910551498,-1.6908763106
H,0,0.8269459591,2.9168675915,-4.4953486657
H,0,-0.6052549951,3.7439841642,-3.899007882
H,0,1.3556420259,5.1823855861,-3.5080546656
H,0,2.206680723,3.8718556165,-2.7034894798
C,0,2.6111465605,1.3218836008,3.3273135741
H,0,2.9054649541,2.3631744615,3.1905443663
H,0,2.7545384524,1.0417749917,4.3793764919
H,0,3.2381945235,0.6867415645,2.6911200001
O,0,1.2516430872,1.2510369406,2.9542793872
O,0,-2.8655369616,-0.9439654848,2.9729192604
C,0,-3.6847307669,-2.0533022492,3.2784449179
H,0,-4.7106051206,-1.7237508471,3.1079560097
H,0,-3.4718627988,-2.9081352159,2.6250449338
H,0,-3.5743199755,-2.3608272844,4.326467377

**$L^2$ TS-alpha**

GP: E(RB3PW91) = -2124.90561030
PCM: E(RB3PW91) = -2125.34876623
Gibbs: 0.839994

N,0,3.299808,0.332993,-1.400656
C,0,1.975879,0.442136,-2.01831
C,0,1.586206,-0.921103,-2.635458
C,0,2.657408,-1.313512,-3.673367
C,0,4.076892,-1.252198,-3.100024
C,0,4.342731,0.08491,-2.401118
Pd,0,0.258194,0.299104,-0.53808
O,0,2.56411,-0.122109,0.727211
C,0,3.46882,-0.031459,-0.097234
O,0,4.774116,-0.253803,0.184371
C,0,5.224636,-0.513396,1.548772
C,0,4.619352,-1.812988,2.077014
C,0,0.964297,1.980371,-1.451862
C,0,1.690648,2.866135,-0.630036
C,0,1.602351,4.246705,-0.809018
C,0,0.824664,4.789228,-1.831576
C,0,0.131971,3.92272,-2.681927
C,0,0.205797,2.544632,-2.505542
P,0,-1.642495,0.469858,0.797592
C,0,-1.799058,-2.673394,-0.395512
C,0,-0.641004,-3.287784,0.112222
C,0,0.241711,-3.972885,-0.732987
C,0,-0.045743,-4.047433,-2.092112
C,0,-1.176814,-3.441933,-2.629832
C,0,-2.052483,-2.761312,-1.775207
C,0,6.735098,-0.661122,1.375809
C,0,4.90302,0.679058,2.447569
H,0,2.305077,2.464979,0.169212
H,0,2.15456,4.90408,-0.140469
H,0,1.128645,-4.455517,-0.340815
H,0,-1.375367,-3.514662,-3.692296
H,0,0.630013,-4.588917,-2.748739
H,0,-0.468296,4.324116,-3.495824
H,0,2.450021,-2.31752,-4.063857
H,0,1.507335,-1.698429,-1.867435
H,0,0.608566,-0.857996,-3.123593
H,0,2.16264,1.076283,-2.886524
H,0,4.217856,-2.055873,-2.364851
H,0,4.819394,-1.410735,-3.892045
H,0,5.319209,0.100103,-1.920219
H,0,4.311254,0.910052,-3.124055
H,0,2.586321,-0.624598,-4.527865
H,0,7.206378,-0.859253,2.342975
H,0,6.967559,-1.49042,0.701105
H,0,7.167236,0.253966,0.960565
H,0,5.319972,1.597669,2.022951

H,0,3.825721,0.799898,2.565694
H,0,5.351358,0.527264,3.43472
H,0,4.816782,-2.633512,1.379494
H,0,5.079001,-2.066679,3.037786
H,0,3.542678,-1.711879,2.214475
H,0,-0.322947,1.889211,-3.193848
H,0,0.769777,5.864671,-1.974368
C,0,-2.854842,-2.168131,0.533145
C,0,-2.892581,-0.894002,1.128299
C,0,-3.875097,-3.089528,0.82644
C,0,-3.946882,-0.609337,2.014715
C,0,-4.912092,-2.785188,1.697329
H,0,-3.835684,-4.067345,0.354217
C,0,-4.944507,-1.53193,2.304367
H,0,-3.986331,0.360408,2.503645
H,0,-5.684014,-3.52138,1.904806
H,0,-5.739505,-1.272448,2.998474
C,0,-2.880411,1.791701,0.227536
C,0,-2.344241,3.226133,0.294957
C,0,-3.359942,1.451405,-1.19011
H,0,-3.740148,1.718321,0.908723
C,0,-3.387822,4.230361,-0.212322
H,0,-1.431873,3.308251,-0.308143
H,0,-2.074885,3.485446,1.324584
C,0,-4.403769,2.457079,-1.686344
H,0,-2.489487,1.463247,-1.859417
H,0,-3.7652,0.433862,-1.221068
C,0,-3.870616,3.889212,-1.622693
H,0,-2.96472,5.241982,-0.187546
H,0,-4.249494,4.235295,0.472007
H,0,-4.705704,2.205917,-2.711194
H,0,-5.310019,2.378145,-1.067834
H,0,-4.640022,4.60157,-1.946115
H,0,-3.029423,3.991536,-2.32175
C,0,-1.220537,1.012286,2.572293
C,0,-0.948001,-0.172088,3.512139
C,0,0.002517,1.944378,2.571867
H,0,-2.091364,1.570042,2.952241
C,0,-0.623075,0.309084,4.931387
H,0,-0.100965,-0.746933,3.114111
H,0,-1.800799,-0.856266,3.540289
C,0,0.321371,2.44614,3.984505
H,0,0.858854,1.38385,2.174381
H,0,-0.140198,2.789624,1.892988
C,0,0.555027,1.284291,4.951092
H,0,-0.416809,-0.553689,5.577551
H,0,-1.509735,0.805036,5.353273
H,0,1.201323,3.1009,3.955503
H,0,-0.511792,3.063919,4.351518
H,0,0.727396,1.656686,5.968742

H,0,1.4686,0.749745,4.653881
C,0,0.65666,-3.810256,2.034763
H,0,0.588269,-3.617,3.106186
H,0,0.659891,-4.895089,1.86505
H,0,1.587747,-3.377809,1.649703
O,0,-0.476929,-3.196516,1.456954
O,0,-3.203273,-2.169802,-2.193573
C,0,-3.541876,-2.256717,-3.561529
H,0,-4.495733,-1.738134,-3.668165
H,0,-2.794437,-1.766087,-4.198137
H,0,-3.660805,-3.299267,-3.884621

**$L^2$ TS-beta**

GP: E(RB3PW91) = -2124.90493503
PCM: E(RB3PW91) = -2125.34949322
Gibbs: 0.841897

C,0,1.4480319107,-3.6739938715,-0.2295552607
C,0,2.5789858413,-4.4839724049,-0.2277457653
C,0,3.5899933887,-4.3021385062,-1.1762296686
C,0,3.4452763622,-3.2940056543,-2.128339946
C,0,2.3104965846,-2.4817637464,-2.1424073431
C,0,1.2939634736,-2.6352144679,-1.1768369445
Pd,0,0.3528697207,-0.9422941628,-0.6143274709
H,0,0.6663532108,-3.8473665592,0.5060542068
H,0,2.6708320567,-5.2685457922,0.5202817023
H,0,4.4671956384,-4.942733076,-1.1779861141
P,0,1.2176169484,0.4065243389,1.1181981819
C,0,0.3942217894,2.8449049555,-1.1068871396
C,0,-0.999921337,2.9252387637,-1.2719474091
C,0,1.1948273321,2.6961334214,-2.251720711
C,0,-1.5832641157,2.8574691205,-2.5428387554
C,0,0.6216961865,2.6146992672,-3.5275616314
H,0,-2.656819836,2.927045794,-2.6699960008
C,0,-0.7598953319,2.7085267094,-3.6544140288
H,0,1.2384145269,2.5027562703,-4.4110080957
H,0,-1.2064995018,2.6604506173,-4.6437925427
H,0,4.220650715,-3.136922923,-2.8753049778
C,0,-1.8375587888,-2.7463651448,-1.1529308298
C,0,-0.5247495011,-2.6071713393,-1.9313110241
C,0,-0.7418219311,-1.9500466923,-3.2934393658
C,0,-1.5721003753,-0.678919916,-3.1837710353
C,0,-2.8935162463,-0.9382251676,-2.4696508043
H,0,0.2147969104,-1.7494602302,-3.7862182032
H,0,-0.2364850135,-3.6389690961,-2.1279807634
H,0,-2.419051196,-3.5639069021,-1.6228948435
H,0,-1.0076864233,0.0831092435,-2.6309326634
H,0,-1.7845163867,-0.2670367334,-4.1774803474

H,0,-3.4459741994,-0.009702195,-2.3346659238
H,0,-3.5203357758,-1.6104200877,-3.0820437859
H,0,-1.2713557318,-2.6700690048,-3.9402050762
N,0,-2.6663232563,-1.540411647,-1.1572816145
C,0,-3.5883341084,-1.4439668747,-0.1459546207
O,0,-3.5529438281,-2.1181948469,0.8735463291
O,0,-4.5297006255,-0.5064643607,-0.4162566152
C,0,-5.7234215441,-0.3943964339,0.4218541854
C,0,-6.5432490253,0.6731155265,-0.2995505176
H,0,-7.490384675,0.8349560134,0.2234272099
H,0,-6.0037448664,1.6242290586,-0.3324192938
H,0,-6.7626018973,0.3642256973,-1.3257523609
C,0,-6.4814669742,-1.7217171094,0.4361499208
H,0,-6.7106425057,-2.0399161999,-0.5860352667
H,0,-5.8978053828,-2.5000237881,0.9289061863
H,0,-7.4274728319,-1.5975763662,0.9727977548
C,0,-5.3555331065,0.0690590363,1.8293674925
H,0,-4.7607713123,0.9864889622,1.785765357
H,0,-6.2680183087,0.2817115759,2.3962553348
H,0,-4.7836665916,-0.6973100959,2.35180835
H,0,-1.6729919914,-3.0370224793,-0.1149939216
H,0,2.2223215717,-1.7096134109,-2.9017140831
C,0,-3.1096051295,3.2457732487,-0.2205291382
H,0,-3.4599505821,3.4263538244,0.7969416306
H,0,-3.3909365664,4.0986165601,-0.8522066199
H,0,-3.5802714251,2.3330640177,-0.6057821831
C,0,0.9951054955,3.1859348826,0.2183828105
C,0,1.3337784327,2.2811483099,1.2414795752
C,0,1.1929771396,4.5617533872,0.4313375541
C,0,1.8321801721,2.8070381891,2.4478809603
C,0,1.6964532333,5.0582385593,1.6252612521
H,0,0.9324150528,5.2467850528,-0.3708215828
C,0,2.0111734556,4.1695783861,2.650142099
H,0,2.0838647936,2.1327517689,3.2615801917
H,0,1.8349182512,6.1279882143,1.7564493162
H,0,2.3952747411,4.5312460646,3.6002173641
C,0,0.3482288807,-0.0128416478,2.7544703141
C,0,-0.9174173456,0.8306873711,2.9724195644
C,0,-0.0234214443,-1.5040834123,2.8088899185
H,0,1.059098705,0.202421718,3.567126417
C,0,-1.5965659407,0.4773058221,4.3011389635
H,0,-1.6144033876,0.639126519,2.1447482601
H,0,-0.6839943542,1.8991656134,2.9450079472
C,0,-0.6813672322,-1.8663248927,4.1447595756
H,0,-0.7238596842,-1.7131305771,1.9883379441
H,0,0.8499628741,-2.1385384433,2.6355175637
C,0,-1.9248121991,-1.0136435722,4.3965217726
H,0,-2.5068657936,1.0779251949,4.4215038888
H,0,-0.9297658193,0.7573883651,5.1301092652
H,0,-0.9437586163,-2.9312687036,4.1491811188

H,0,0.0407050387,-1.7189767022,4.9617834446
H,0,-2.361195161,-1.2473229632,5.3755911619
H,0,-2.6799139442,-1.2677522034,3.6412116024
C,0,3.055715464,0.0517596487,1.4648423149
C,0,3.3609540488,-1.3435482138,2.0188565878
C,0,3.8652647081,0.3187273906,0.188883976
H,0,3.3566835705,0.7884231256,2.22239829
C,0,4.8671041468,-1.522087359,2.2539688239
H,0,3.0079366821,-2.1060526969,1.3139000806
H,0,2.8343622728,-1.5066337003,2.9654144023
C,0,5.3678500621,0.1371321141,0.4285479071
H,0,3.5315366988,-0.3843084457,-0.585749748
H,0,3.6568523642,1.3260672695,-0.186445452
C,0,5.6789673673,-1.2524482745,0.9869289728
H,0,5.0618277545,-2.5359786022,2.6246461136
H,0,5.1938296694,-0.8324438258,3.0465769398
H,0,5.9156806864,0.3044218114,-0.5075967182
H,0,5.7207320379,0.9022854292,1.1356961284
H,0,6.7519969275,-1.3534045729,1.1928046127
H,0,5.4265690074,-2.0095250233,0.2320275574
O,0,-1.7074250795,3.1059996984,-0.1265708681
O,0,2.5351394787,2.6794455213,-2.0290431897
C,0,3.3970742305,2.5387372713,-3.1392502633
H,0,4.4103419878,2.5488106035,-2.7355154951
H,0,3.2292121047,1.5899526609,-3.664058398
H,0,3.2837615232,3.3693221328,-3.848054973