Electronic Supplementary Information for Dalton Transactions

Supplementary Information for

A Zirconium Bis(amidate) Complex Exhibiting Improved Aminoalkene Cyclohydroamination Activity

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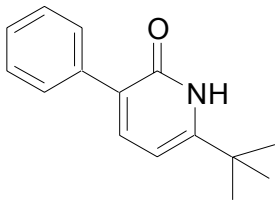
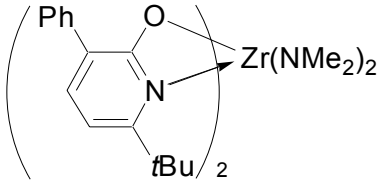
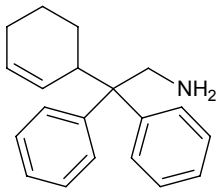
General. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker 300 MHz or 400 MHz Avance spectrometer at ambient temperature and chemical shifts are given relative to residual solvent. GCMS spectra were recorded on an Agilent series 6890 GC system with a 5973 Mass Selective Detector. Single crystal X-ray structure determinations, MS, and elemental analyses determinations were performed at the Department of Chemistry, University of British Columbia. All reactions were carried out using standard Schlenk line and glovebox techniques under an atmosphere of nitrogen, unless described otherwise. $Ti(NMe_2)_4$ and $Zr(NMe_2)_4$ were purchased from Strem and used as received. d_8-Toluene was degassed and dried over molecular sieves. Amino alkenes 2,2-diphenyl-4-pentenylamine,[1] 2,2-diphenyl-5-hexenylamine,[2] 2,2,5-triphenyl-4-pentenylamine,[2,3] 2,2-diphenyl-4-hexenylamine,[2] 2,2-dimethyl-4-pentenylamine,[3] and 1-methyl-4-pentenylamine[4] were prepared as described in the literature with some modification from commercially available starting materials purchased from Aldrich. Amino alkene substrates were dried over CaH or 4Å molecular sieves and degassed prior to use. Heterocyclic products 2-methyl-4,4-diphenylpyrrolidine,[1] 2-methyl-5,5-diphenylpiperidine,[5] 2-methyl-4,4-dimethylpyrrolidine,[3] 2-benzyl-4,4-diphenyl-pyrrolidine,[6] 2,5-dimethylpyrrolidine[7] and (+/-)-(S,S)-3, 3-diphenyl-1-(*p*-toluenesulfonyl)-octahydro-indole[8] are known compounds. The 6-*tert*-butyl-3-phenyl-2-pyridone proligand was prepared as described in the literature[9] and was heated to 80 ^{o}C under vacuum for at least three days prior to use. **2-**Cyclohex-2-enyl-2,2-diphenyl-ethylamine was prepared using modified literature procedures[10] from commercially available starting materials with full characterization data provided below. 1,3,5-Trimethoxybenzene purchased from Aldrich, was used as an internal standard and was sublimed under vacuum prior to use.



6-tert-Butyl-3-phenyl-2-pyridone.[9] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.38 (9H, s, -(C*H*$_3$)$_3$), 6.19 (1H, d, J = 7.4 Hz, C5-*H*), 7.24 – 7.41 (3H, m, Ar-*H*), 7.55 (1H, d, J = 7.4 Hz, C4-*H*), 7.78 – 7.81 (2H, m, Ar-*H*), 12.00 (1H, br s, N*H*); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 28.9, 34.8, 101.8, 127.2, 127.7, 127.9, 128.3, 136.6, 139.1, 156.2, 163.5; MS (EI): *m/z* 227 (M^+).



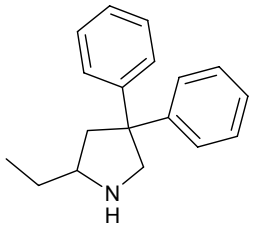
Bis(6-*tert*-butyl-3-phenyl-2-pyridonate) zirconium bis(dimethylamido) complex 1. All metal complex synthesis reactions were carried out in a glovebox unless otherwise stated. To a small screw capped vial containing a magnetic stir bar was added 6-*tert*-butyl-3-phenyl-2-pyridone (0.850 g, 3.7 mmol), benzene (3 ml), and tetrakis(dimethylamido)zirconium (0.500 g, 1.9 mmol in 2ml of benzene). The mixture was then stirred at room temperature for 20 h. The solvents were then removed under reduced pressure to afford the analytically pure bis(6-*tert*-butyl-3-phenyl-2-pyridonato)zirconium-bis(dimethylamido) complex **1** as a pale yellow microcrystalline solid. Yield: > 98%. Crystals suitable for X-ray crystallography were obtained from a saturated solution of the complex in benzene/pentanes. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.26 (18H, s, -C(C*H*$_3$)$_3$), 3.26 (12H, s, Zr-(N(C*H*$_3$)$_2$)$_2$), 6.57 (2H, d, J= 8 Hz, Ar-H), 7.25 (2H, m, Ar-H), 7.44 (4H, m, Ar-H), 7.55 (2H, d, J= 8 Hz, Ar-H), 8.07 (4H, m, Ar-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 29.7, 36.3, 42.6, 110.1, 121.1, 128.4, 128.9, 137.2, 140.4, 165.3; MS (EI): *m/z* 631 (M^+), 587 (M-NMe_2), 543 (M-2NMe_2); Anal. Calcd for $C_{34}H_{44}N_4O_2Zr$: C, 64.62; H, 7.02; N, 8.87. Found: C, 64.71; H, 7.18; N, 9.07.



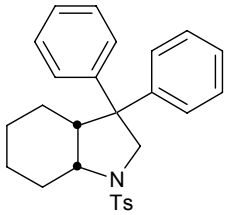
2-(Cyclohex-2-enyl)-2,2-diphenyl-ethylamine.[10] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.77 (2H, br s, -N*H*$_2$), 0.9 – 1.1 (1H, m, -CH_2-CH*H*-CH-CH=CH-), 1.5 – 1.6 (2H, m, -

CH_2-C*H*$_2$-CH_2-), 1.6 – 1.8 (1H, m, -CH=CH-CH*H*-CH_2-), 1.8 – 2.0 (2H, m, -CH=CH-C*H*H-CH_2-, -CH_2-C*H*H-CH-CH=CH-), 3.2 – 3.4 (2H, m, -CH=CH-C*H*-, -Ph_2C-CH*H*-NH_2), 3.45 (1H, d, J = 13.2 Hz, -Ph_2C-C*H*H-NH_2), 5.5 – 5.7 (1H, m, -CH=C*H*-), 5.8 – 5.9 (1H, m, -C*H*=CH-), 7.1 – 7.4 (10H, m, Ar*H*); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 22.59, 24.97, 25.18, 39.77, 49.65, 56.74, 126.15, 126.20, 127.50, 127.92, 129.07, 129.38, 129.76, 129.90, 142.80, 144.80; MS (EI): *m/z* 276 (M-H$^+$). Anal. Calcd for $C_{20}H_{23}N$: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.39; H, 8.39; N, 5.04.

General procedure for NMR-tube scale intramolecular amino alkene hydroamination. All NMR-tube scale reactions were prepared in an N_2-filled glove box. A J. Young NMR-tube equipped with a Teflon screw cap would be charged with the internal standard (1,3,5-trimethoxybenzene) (0.5 mmol), the catalyst (0.025 mmol), and the amino alkene (0.5 mmol) dissolved in either d_6-benzene (~1 ml), d_{10}-xylenes (~1 ml) or d_8-toluene (~1 ml). The tube would then be sealed, heated to, and maintained at, the appropriate temperature for the stated duration of time. The conversion and yield were determined by comparing the integration of the internal standard with a well resolved signal for the cyclic product.



2-Ethyl-4,4-diphenyl-pyrrolidine. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.97 (3H, t, J = 7.4 Hz, -CH_2-C*H*$_3$), 1.49 – 1.70 (2H, m, -CH-C*H*$_2$-CH_3), 2.10 (1H, dd, J = 9.6, 12.7 Hz, Ph_2C-C*H*H-CH(Et)-NH-), 2.77 (1H, dd, J = 9.6, 12.6 Hz, Ph_2C-CH*H*-CH(Et)-NH-), 3.15 – 3.24 (1H, m, -CH_2-C*H*(Et)-NH-), 3.34 (1H, br s, -N*H*-), 3.47 (1H, d, J = 11.5 Hz, Ph_2C-CH*H*-NH-), 3.80 (1H, d, J = 11.5 Hz, Ph_2C-C*H*H-NH-), 7.15 – 7.40 (10H, m, Ar*H*); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 12.6, 30.5, 45.7, 57.4, 58.0, 60.7, 127.2, 127.9, 128.0, 129.4, 129.5, 147.4, 148.2; HRMS Calcd for $C_{18}H_{21}N$ [M$^+$]: 251.16740; Found: 251.16720.



(+/-)

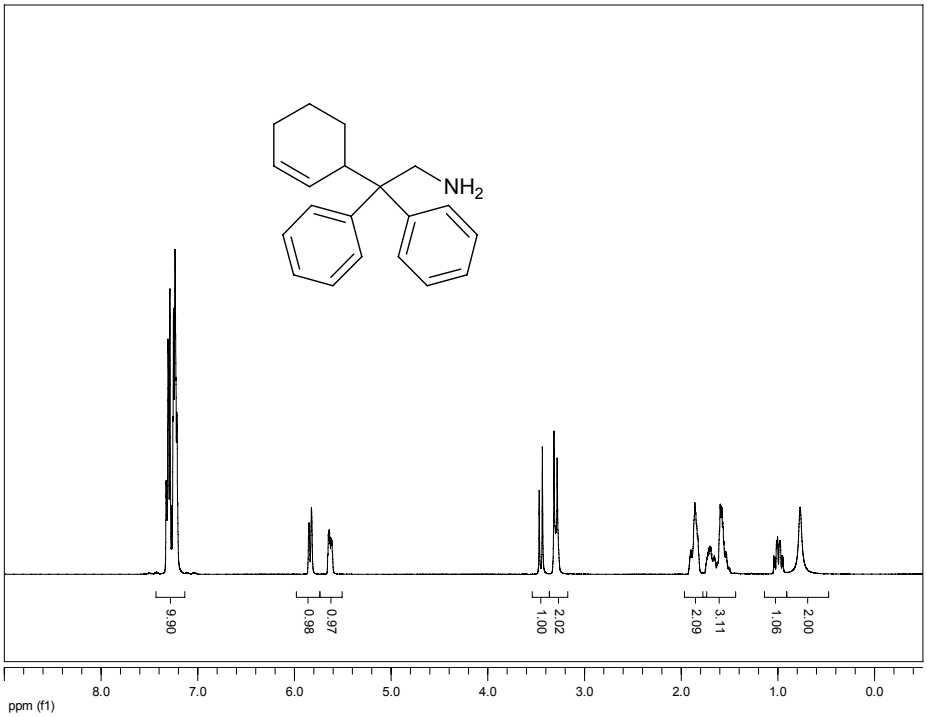
(+/-)-(S,S)-3,3-Diphenyl-1-(*p*-toluenesulfonyl)-octahydro-indole.[8] The hydro-amination reaction was prepared in an N_2-filled glovebox. A J. Young NMR-tube equipped with a Teflon screw cap was charged with a solution of the precatalyst (0.032 g, 0.05 mmol) and 2-(cyclohex-2-enyl)-2,2-diphenyl-ethylamine (0.069 g, 0.25 mmol)

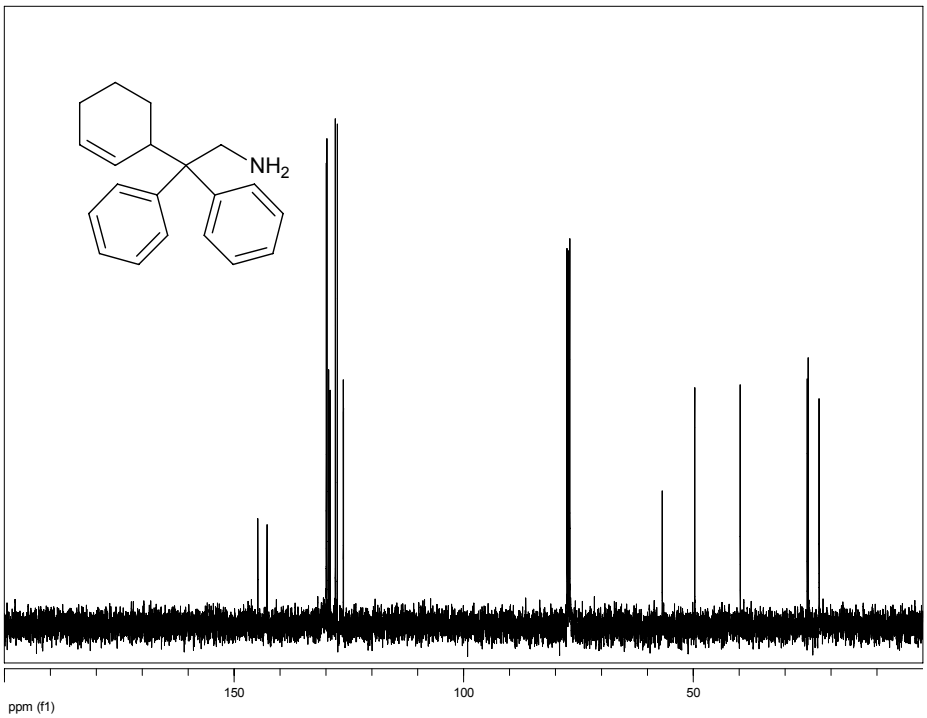
dissolved in d_8-toluene (~ 1 ml). The NMR-tube was then sealed and heated to 145 ^{o}C for 168 hours. Following this the solution was concentrated under reduced pressure and the crude hydroamination mixture was transferred to a small round bottomed flask containing TsCl (1.3 eq) and NEt_3 (3.3 eq), dissolved in CH_2Cl_2 (2-3 ml). This mixture was then stirred over night at room temperature. Following aqueous workup, purification by column chromatography (36:1 hexanes/EtOAc, SiO_2) afforded 0.056 g (52%) of the analytically pure (+/-)-(S,S)-3, 3-diphenyl-1-(*p*-toluenesulfonyl)-octahydro-indole as a colorless foam. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.10 – 1.30 (2H, m), 1.40 – 1.65 (5H, m), 2.32 (3H, s), 2.40 – 2.60 (1H, m), 2.90 – 3.0 (1H, m), 3.70 – 3.80 (1H, m), 4.25 (1H, d, J = 11 Hz), 4.48 (1H, d, J = 11 Hz), 6.90 – 7.60 (14H, m, Ar*H*); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 21.1, 22.4, 25.4, 26.4, 29.7, 45.2, 56.4, 59.1, 60.0, 126.6, 127.0, 127.6, 128.0, 128.5, 129.3, 129.5, 130.2, 135.3, 143.7, 144.8, 146.1; MS (ESI): *m/z* 454 ($M + Na^+$). Anal. Calcd for $C_{27}H_{29}NO_2S$: C, 75.14; H, 6.77; N, 3.25. Found: C, 75.04; H, 6.84; N, 3.20.

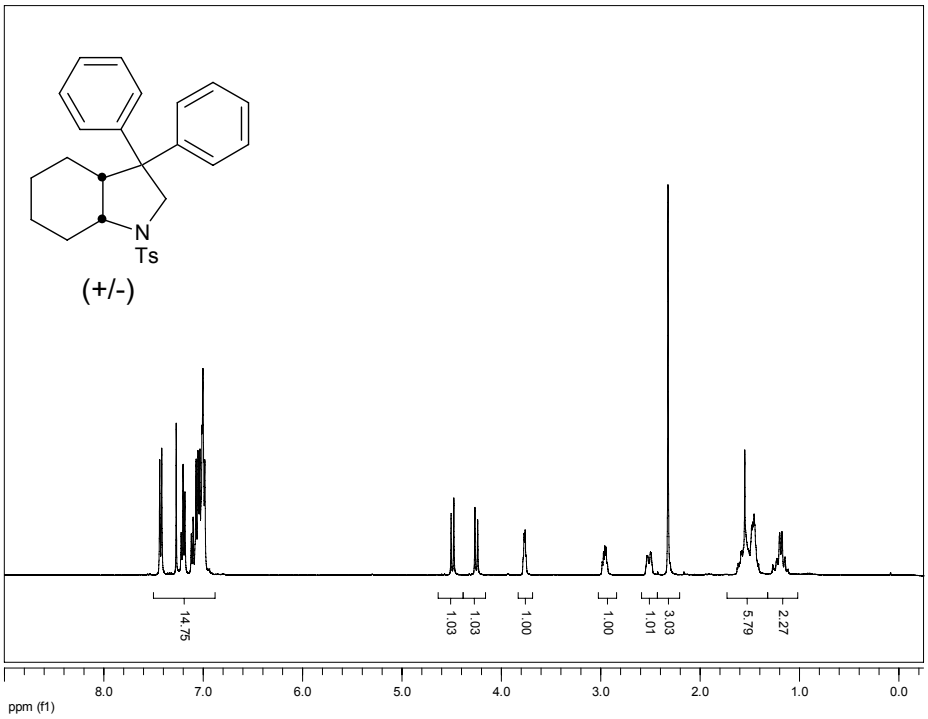
Table 1. Crystallographic parameters for complex **1**.

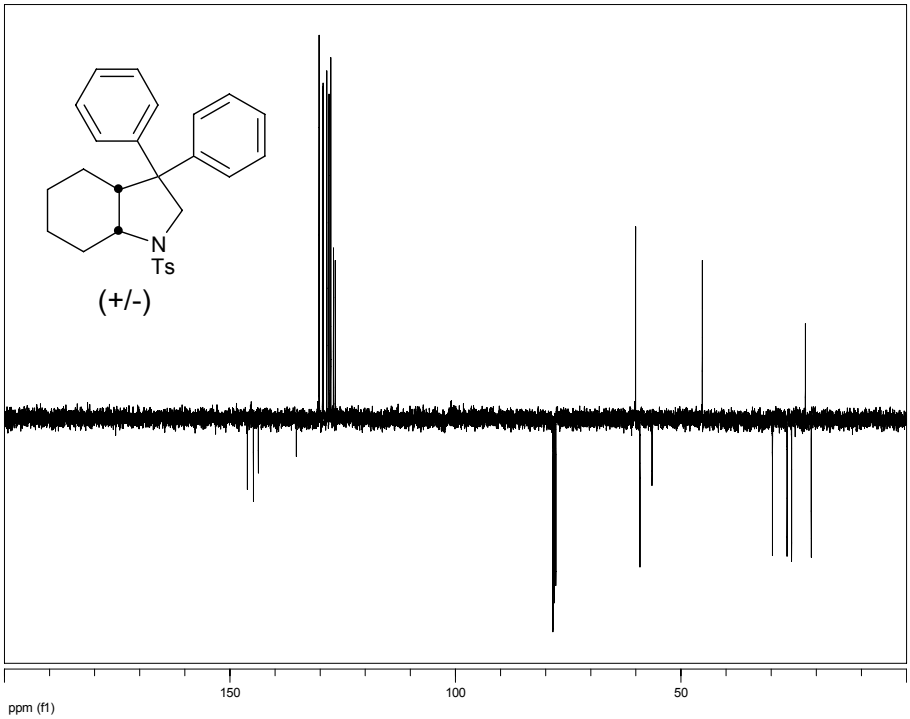
Formula	$C_{34}H_{44}N_4O_2Zr$
formula wt	631.95
cryst dimens, mm	$0.5 \times 0.5 \times 0.5$
temp, K	173
wavelength (Å)	0.71073
cryst syst	Monoclinic
space group	$P2_1/n$
a, Å	13.206(2)
b, Å	17.563(3)
c, Å	13.563(3)
α, deg	90
β, deg	92.226(11)
γ, deg	90
V, $Å^3$	3143.4(9)
Z	4
D_c, Mg/m^3	1.335
abs coeff, mm^{-1}	0.386
F(000)	1328
θ range, deg	1.90 – 34.98
index ranges	$-20 \leq h \leq 19$
	$-27 \leq k \leq 28$
	$-21 \leq l \leq 19$
No. of rflns	53325
No. of indep rflns	13181
No. of data /restraints /params	13181/0/370
goodness of fit on F^2	0.981
final R indices ($I > 2\sigma(I)$)	0.0419,
	0.1020
R indices (all data)	0.0820,
	0.1235

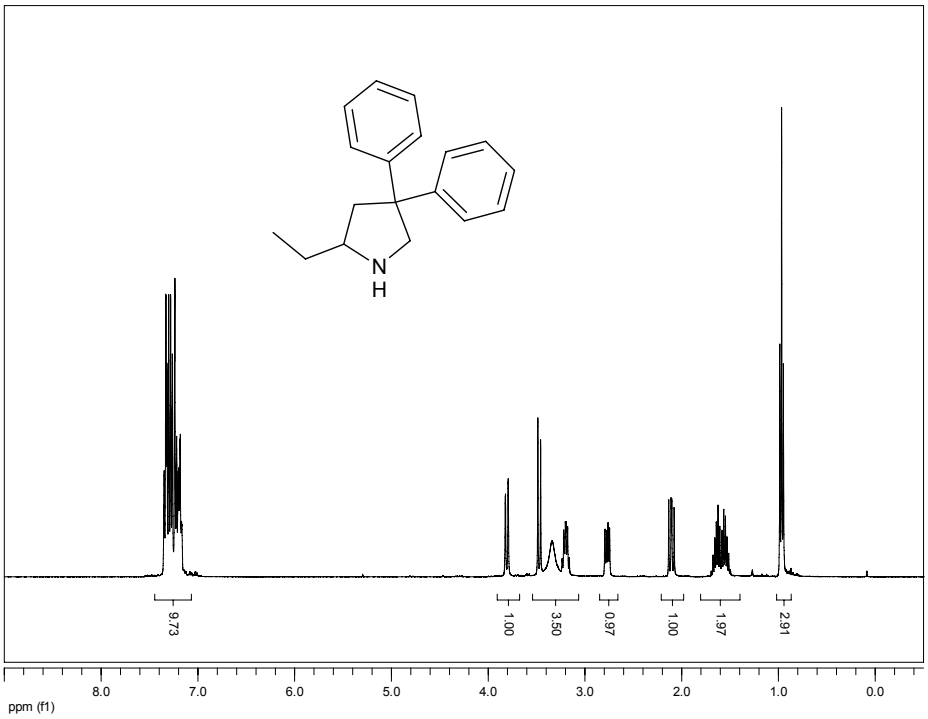
Representative ^{1}H and ^{13}C NMR Spectra are appended.

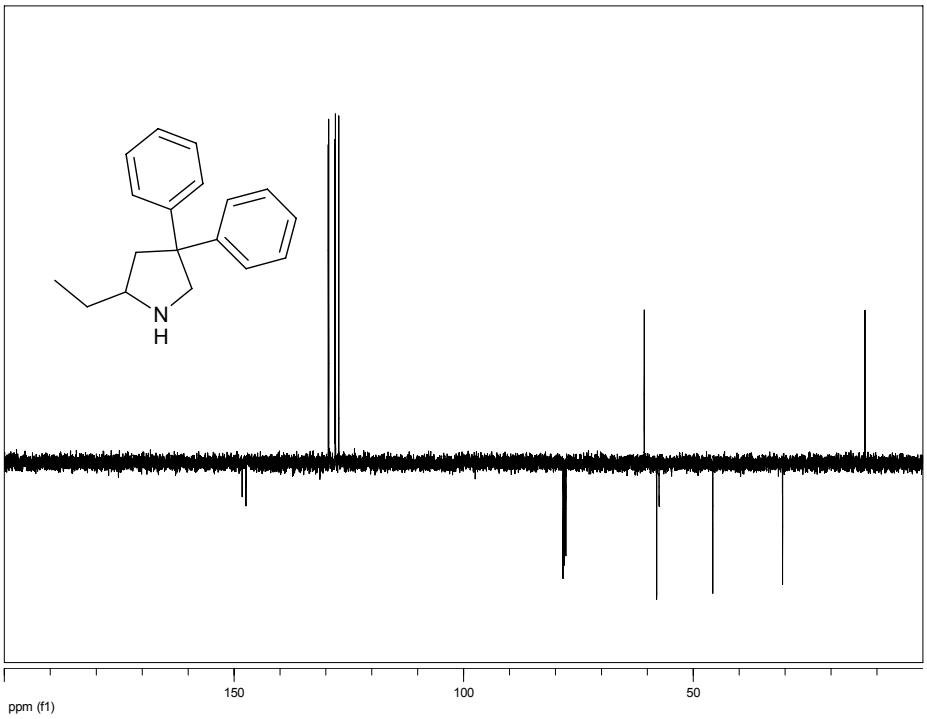












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