Supporting Information

Titanocene(III) Chloride-Mediated Reductions of Oxazines, Hydroxamic Acids, and *N*-Hydroxy Carbamates

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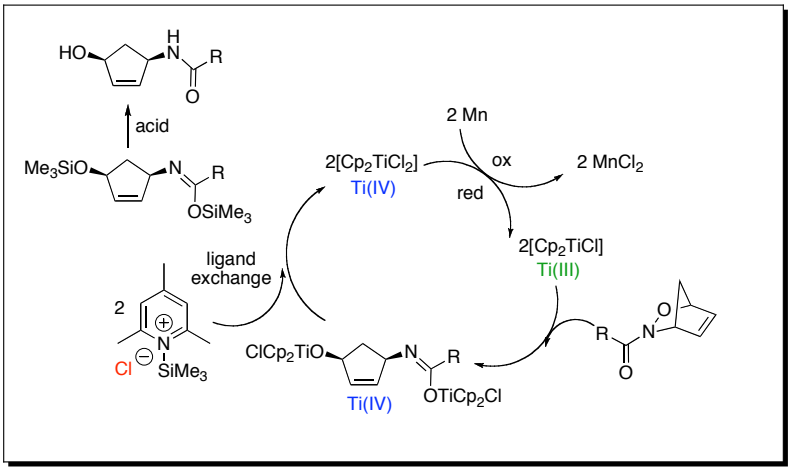
General Experimental: Commercially available reagents and anhydrous solvents were used without further purification unless otherwise specified. Tetrahydrofuran (THF) was distilled from sodium and benzophenone and was thoroughly degassed (dry Argon) with a gas dispersion tube for 45 min prior to use. Diphenylphosphino-polystyrene (PS-PPh_3) was purchased from Biotage. Reactions were monitored by thin-layer chromatography (TLC) on silica gel 60 F254 (0.2 mm) precoated aluminum foil and visualized with an ethanolic solution of $KMnO_4$. Flash chromatography was performed with silica gel 60 (230–400 mesh). ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature with the residual solvent peaks as internal standards. The line positions of multiplets are given in ppm (δ) and the coupling constants (*J*) are given as absolute values in Hertz. Infrared spectra were recorded by a FT-IR spectrometer and reported as cm^{-1}. All melting points were recorded uncorrected. High-resolution mass spectra (HRMS) data were obtained as specified.

Proposed Catalytic Cycles for Cp_2TiCl-Mediated N-O Bond Reductions:



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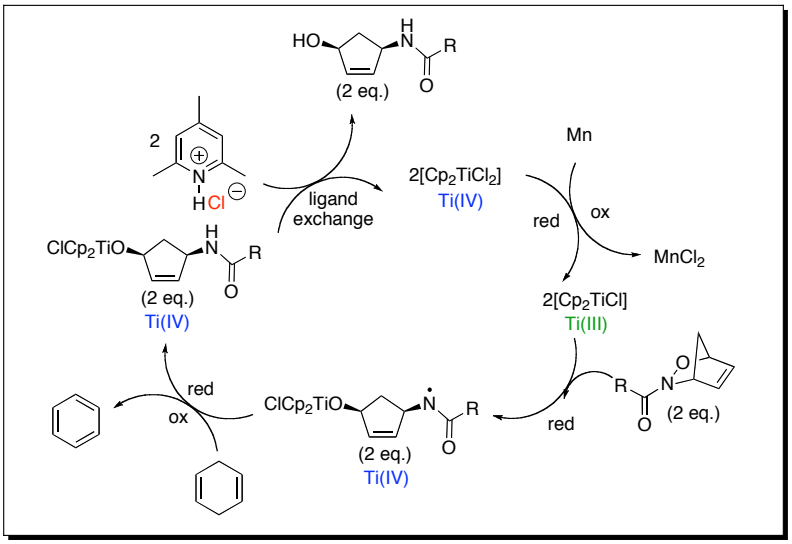

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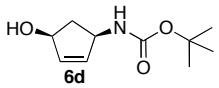
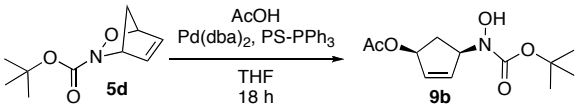
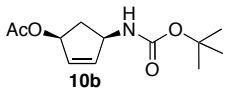


(±)cis-*Z*-*tert*-Butyl-4-hydroxycyclopent-2-enylcarbamate 6d. Prepared according to General Procedure A and B. Crude material was purified by silica gel chromatography (30% EtOAc/hexanes to 50% EtOAc/hexanes) to afford product as white solids (79% and 71%, respectively). Spectral data is consistent with previously reported data.[1]

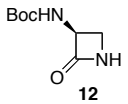


(±)cis-*Z*-4-(*tert*-Butoxycarbonyl(hydroxy)amino)cyclopent-2-enyl acetate 9b. A clean flame-dried 25 mL round bottom flask equipped with a stir bar was evacuated and purged with Ar. A THF solution (5 mL) of Boc cycloadduct **5d** (100 mg, 0.51 mmol), $Pd(dba)_2$ (29 mg, 0.05 mmol), and diphenylphosphino-polystyrene ($PS\text{-}PPh_3$) (88 mg, 0.15 mmol) was charged with acetic acid (0.145 mL, 2.54 mmol) and stirred at rt under Ar for 18 h. The reaction mixture was filtered through a Whatman Glass Microfiber Filter (Type GF/F) and the palladium/resin mixture was washed with CH_2Cl_2. The filtrate was added sat. $NaHCO_3$ (3 mL) and the CH_2Cl_2 layer was removed. The aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organics were washed with brine (15 mL), dried over Na_2SO_4, filtered and concentrated to an oil. The resultant residue was purified by silica gel chromatography (2% MeOH/CH_2Cl_2) to afford **9b** as a tan oil (83 mg, 64%). ^{1}H NMR (600 MHz, MeOH-d_4) δ 1.49 (s, 9H), 1.86 (ddd, 1H, *J*= 13.8 Hz, 5.9 Hz, 5.3 Hz,), 2.03 (s, 3H), 2.6 (ddd, 1H, *J*= 13.8 Hz, 7.9 Hz, 7.8 Hz), 5.09 (ddddd, 1H, *J*= 8.0 Hz, 6.9 Hz, 1.9 Hz, 1.9 Hz, 1.9 Hz), 5.50–5.53 (m, 2H), 5.92 (ddd, 1H, *J*= 5.7 Hz, 2.0 Hz, 1.2 Hz), 5.94 (ddd, 1H, *J*= 5.6 Hz, 2.0 Hz, 2.0 Hz); ^{13}C NMR (150 MHz, MeOH-d_4) δ 21.1, 28.7, 34.3, 64.1, 79.1, 82.6, 133.6, 136.3, 158.3, 172.8; IR (thin film, cm^{-1}) 3390, 2978, 2140, 1732, 1694, 1479; HRMS (FAB) *m/z* (M+H): calcd for $C_{12}H_{19}NO_5^+$, 258.1341; found, 258.1356.



10b

(±)-*cis*-*Z*-4-(*tert*-Butoxycarbonylamino)cyclopent-2-enyl acetate 10b. Prepared according to General Procedure A and C. Crude material was purified by silica gel chromatography (50% EtOAc/hexanes to 70% EtOAc/hexanes) to afford product as white solids (73% and 44%, respectively). Spectral data is consistent with previously reported data.[2]



12

(*S*)-*tert*-Butyl 2-oxoazetidin-3-ylcarbamate 12. Prepared according to General Procedure A. Crude material was purified by silica gel chromatography (75% EtOAc/hexanes) to afford product as white solids (80%). Spectral data is consistent with previously reported data.[3]

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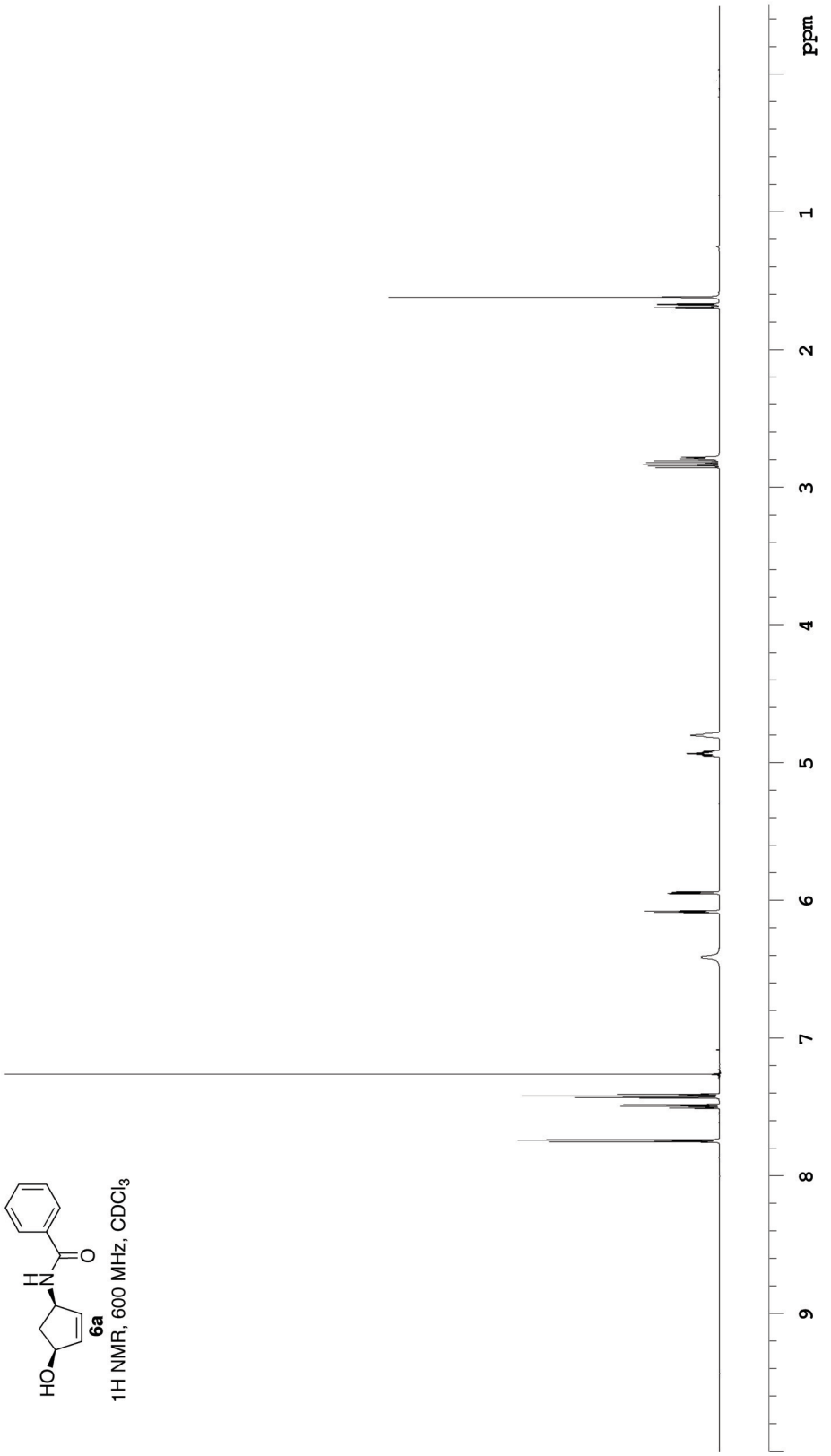
[1] Zhang, D.; Süling, C.; Miller, M. J. *J. Org. Chem.* **1998**, *63*, 885−888.

[2] Zhang, D.; Miller, M. J. *J. Org. Chem.* **1998**, *63*, 755−759.

[3] Mattingly, P. G.; Miller, M. J. *J. Org. Chem.* **1980**, *45*, 410−415.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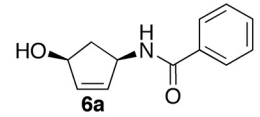
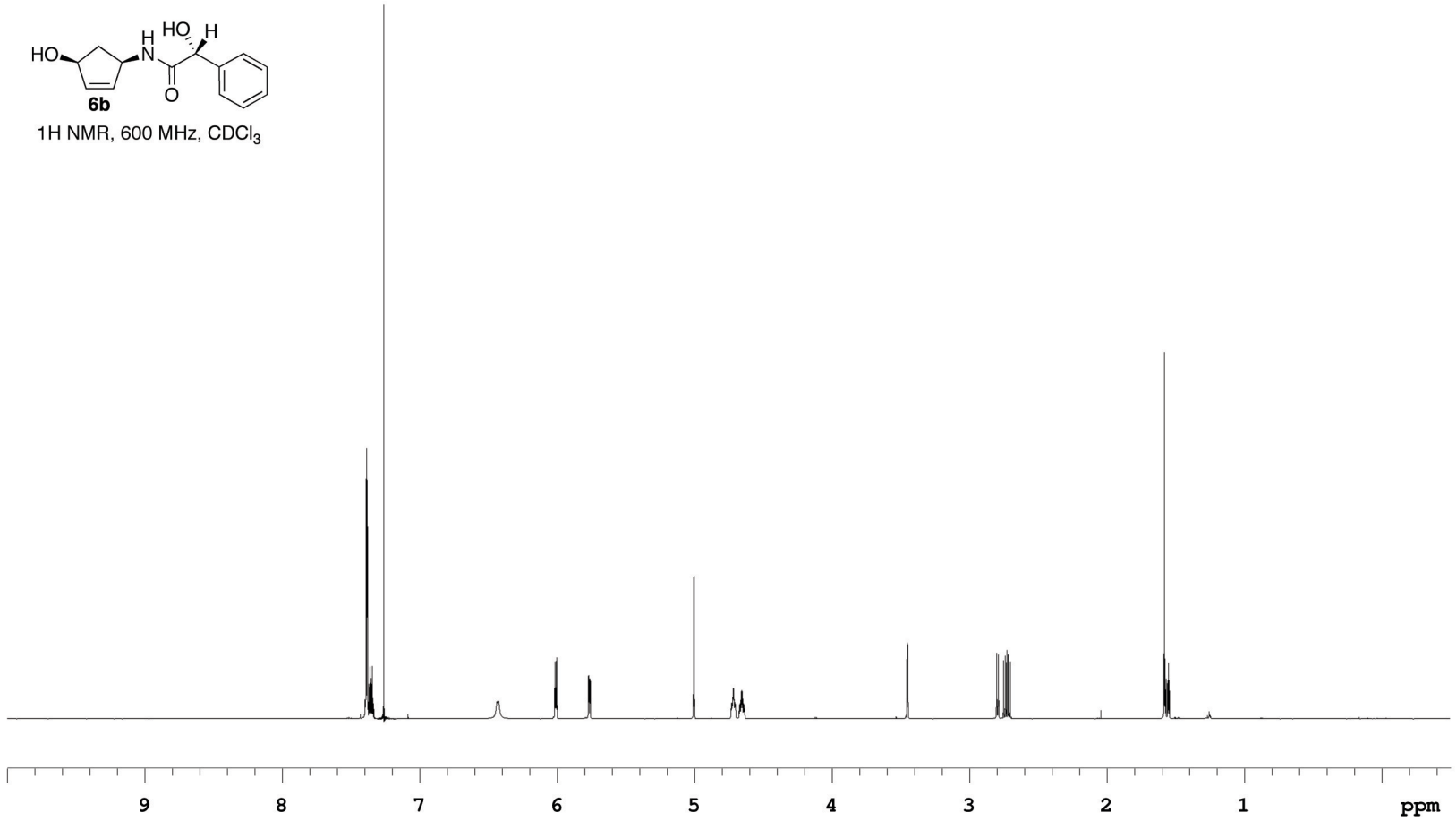
H
N
O
6a
1H NMR, 600 MHz, CDCl3
ppm
1
2
3
4
5
6
7
8
9



6a

13C NMR, 150 MHz, $CDCl_3$


HO
H
N
HO
H
O
6b
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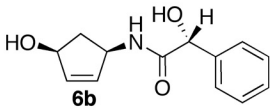
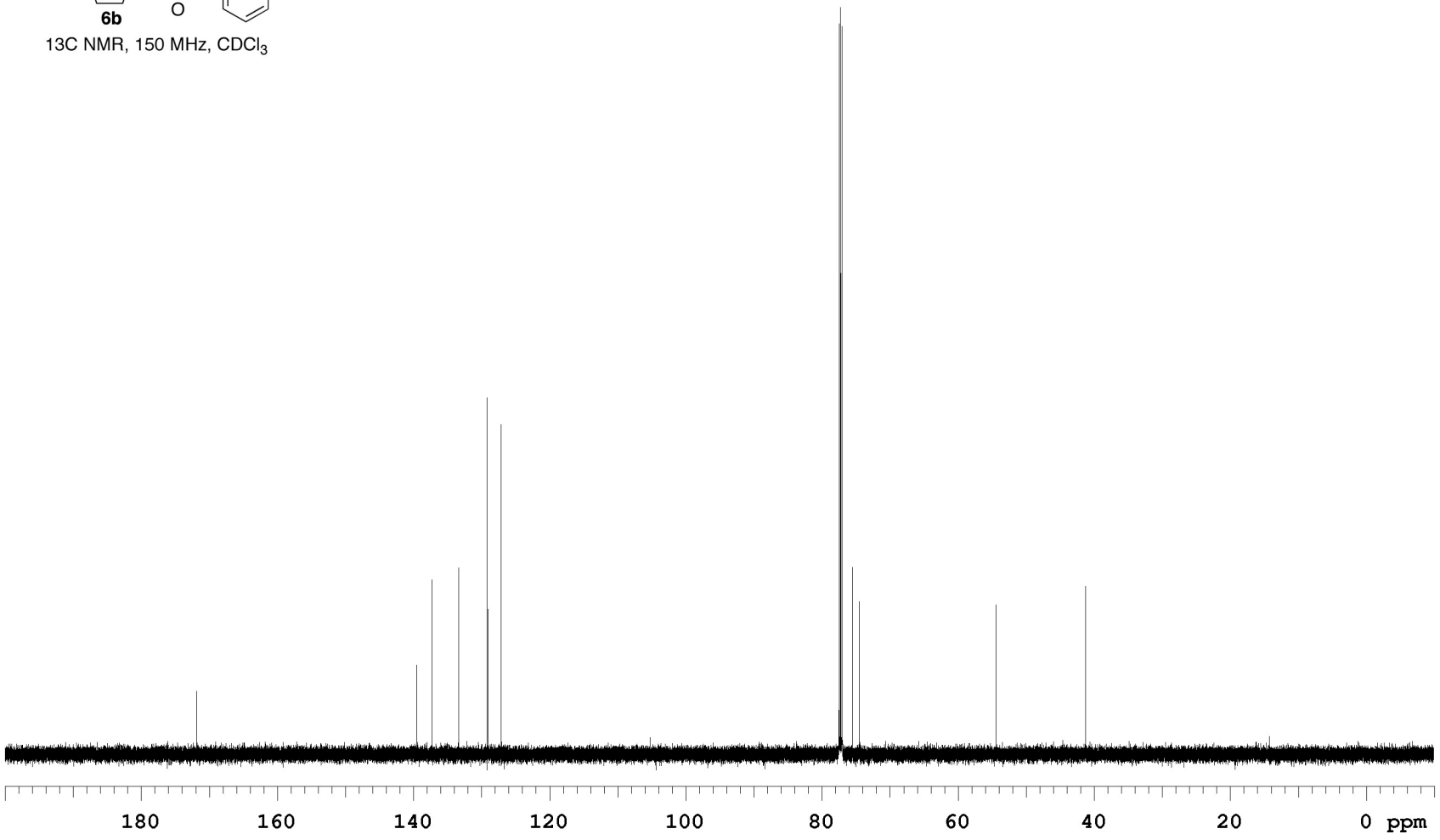
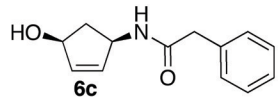
9
8
7
6
5
4
3
2
1
ppm



6b

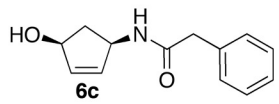
13C NMR, 150 MHz, $CDCl_3$





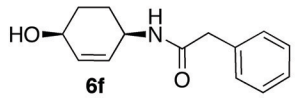
6c

1H NMR, 600 MHz, $CDCl_3$



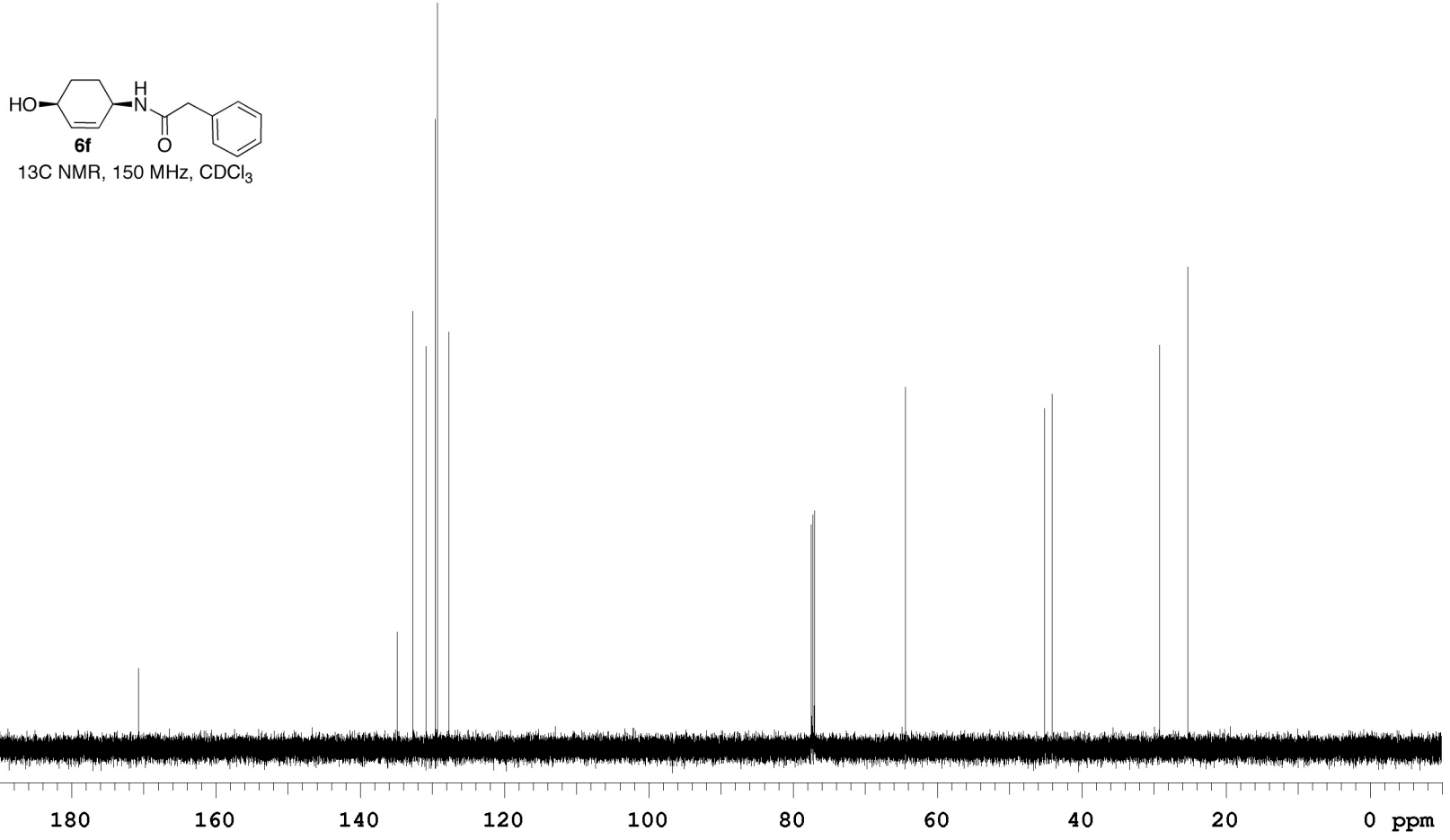
6c

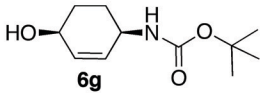
13C NMR, 150 MHz, $CDCl_3$



6f

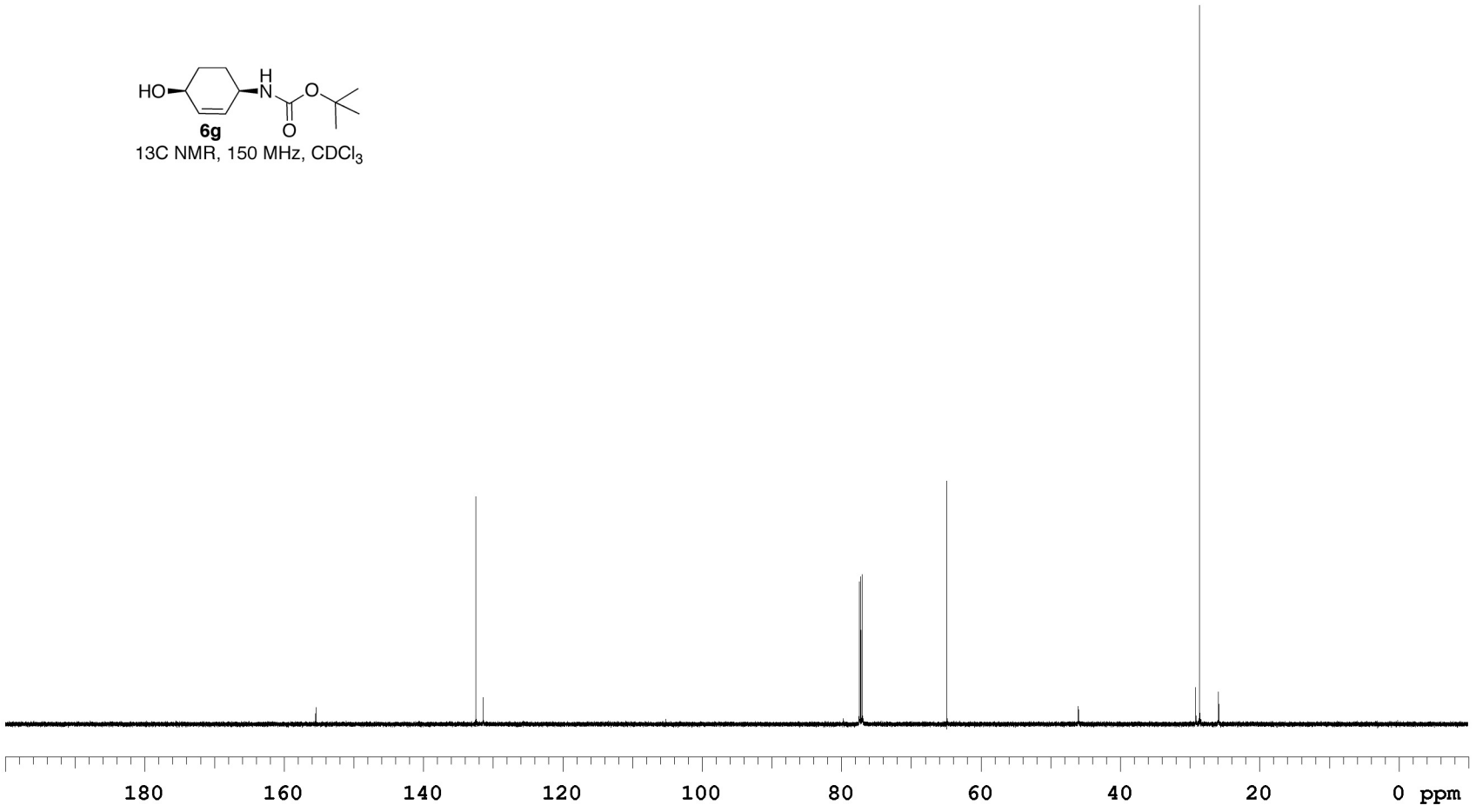
1H NMR, 600 MHz, $CDCl_3$


HO
H
N
O
6f
13C NMR, 150 MHz, CDCl3
180
160
140
120
100
80
60
40
20
0 ppm



6g

1H NMR, 600 MHz, $CDCl_3$


HO
H
N
O
O
6g
13C NMR, 150 MHz, CDCl3
180
160
140
120
100
80
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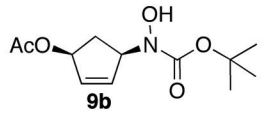
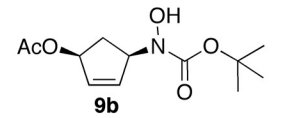
20
0 ppm



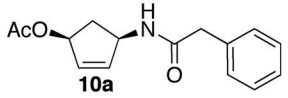
9b

1H NMR, 600 MHz, CD_3OD



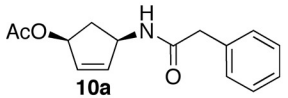
9b

13C NMR, 150 MHz, CD_3OD



10a

1H NMR, 600 MHz, $CDCl_3$



10a

13C NMR, 150 MHz, $CDCl_3$