

Dirhodium Tetracarboxylates Derived from Adamantylglycine as Chiral Catalysts for Enantioselective C–H Aminations

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Supporting Information

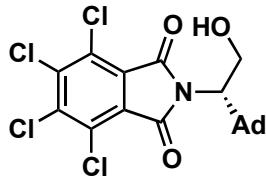
Experimental Procedures S2-S11

Spectral Data S12-S25

General Procedure:

¹H NMR spectra were run at either 400 or 500 MHz, and ¹³C NMR at either 75 or 125 MHz with the sample solvent being CDCl₃ unless otherwise noted. Mass spectral determinations were carried out in GC-MS (EI), LC-MS (ESI) or by Instrument Center, Department of Chemistry, University at Buffalo. IR spectra were obtained using a Perkin Elmer 1760X FT-IR. Optical rotations were measured using a Jasco DIP-370 digital polarimeter. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross GA. Enantiomeric excess was determined by HPLC (UV detection at 254 nm). Analytical TLC was performed on 0.25 mm E. Merck silica gel (60F-254) plates using UV light.

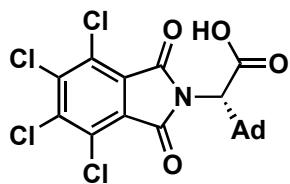
Glassware was dried in oven overnight then flame or heat-gun dried prior to use. Reactions were conducted under argon atmosphere. Column chromatography was carried out on Merck silica gel 60 (230-400 mesh). Solvents THF, Et₂O, CH₃CN, CH₂Cl₂ and toluene were dried by solvent purifier.



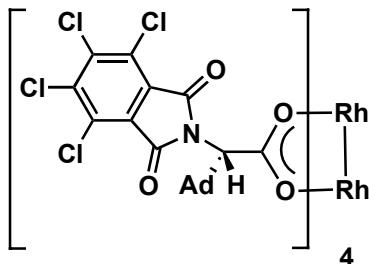
2-((S)-1-Adamantyl-2-hydroxyethyl)4,5,6,7-tetrachloroisindoline-1,3-dione:

Tetrachlorophthalic anhydride (0.76 g, 5.12 mmol, 1.0 equiv.) was added to a solution of (S)-2-amino-2-adamantylethanol (1.0 g, 5.12 mmol, 1.0 equiv.) in DMF (6 mL) and heated at 140 °C for 12 h. After cooling, the reaction mixture was poured into water, and the product precipitated out as a white solid. The crystals were filtered and vacuum dried to give the product (1.9 g, 80% yield) as a white sticky solid. R_f = 0.35 (3:1

hexane/EtOAc); $[\alpha]_D^{25} -4.5^\circ$ (c 0.22, CHCl₃); IR (neat) 3273, 2903, 2849, 1641, 1543, 1401, 1343, 1266, 1132 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 4.53 (t, J = 13.5 Hz, 1H), 4.04 (dd, J = 5.5, 13.5 Hz, 1H), 3.98 (dd, J = 5.5, 13.5 Hz, 1H), 1.98 (bs, 3H), 1.71-1.60 (m, 13 H); ¹³C NMR (125 MHz, CDCl₃) δ 165.1, 129.7, 127.4, 127.3, 64.4, 57.5, 40.1, 37.1, 36.7, 28.3; HRMS (ESI) m/z Calcd for [C₂₀H₂₀Cl₄NO₃]⁺ [(M+H)⁺]: 462.0197. Found: 462.0201.



(S)-Adamantan-1-yl-(4,5,6,7-tetrachloro-1,3-dioxo-1,3-dihydro-isoindol-2-yl)-acetic acid: NaIO₄ (3.4 g, 16.0 mmol, 4.1 eq) in water (25 mL) was added to a stirring solution of 2-((S)-1-adamantyl-2-hydroxyethyl) 4,5,6,7-tetrachloroisooindoline-1,3-dione (1.8 g, 3.9 mmol) in (1:1) EtOAc/CH₃CN (34 mL), and stirred at 23 °C for 10 min. RuCl₃.H₂O (0.02 g, 2.2 mol%) was then added and stirred vigorously for 12 h. The reaction mixture was diluted with DCM and filtered through a pad of celite and charcoal. The filtrate was washed with water and brine and dried over anhydrous MgSO₄, and the solvent was removed *in vacuo*. The resulting residue was dissolved in ether (25 mL) and filtered through a pad of celite and charcoal. The solvent was then concentrated to give the product (1.26 g, 68%) as a white solid. R_f = 0.17 (1:1 hexane/EtOAc); $[\alpha]_D^{25} -14.4^\circ$ (c 0.15, CHCl₃); IR (neat): 2906, 2851, 1723, 1387, 1370, 737 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 4.57 (s, 1H), 1.99 – 1.66 (m, 15H); ¹³C NMR (125 MHz, CDCl₃) δ 170.9, 163.5, 140.5, 130.0, 127.2, 61.2, 39.3, 37.8, 36.5, 28.4; HRMS (EI) m/z Calcd for C₂₀H₁₇Cl₃NO₄³⁷Cl₁: 476.9877. Found: 476.9862.



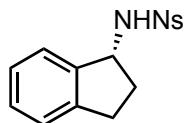
Rh₂(S-TCPTAD)₄ (4b). The following procedure is similar to that reported by Callot.¹ (S)-adamantan-1-yl-(4,5,6,7-tetrachloro-1,3-dioxo-1,3-dihydro-isoindol-2yl)-acetic acid (1.2 g, 2.5 mmol, 6 equiv.) and Rh₂(OAc)₄ (188 mg, 0.42 mmol) were dissolved in dry chlorobenzene (12 mL) in a flask under argon, and stirred at 23 °C for 30 min and then the mixture was heated up to 150 °C and the acetic acid was distilled out as an azeotrope with chlorobenzene for 3 h. Additional 25 mL was added and distilled during the reaction. The mixture was cooled and the solvent was removed *in vacuo*. The residue was subjected to flash chromatography (silica, 1.5:1 hexanes / EtOAc – 1:1 hexanes / EtOAc) to give **4b** (0.55 g, 62%) as a bright green solid. R_f = 0.7 (1:3 hexanes:EtOAc); [α]_D²⁵ +82.6° (c 0.19, CHCl₃); FTIR: 2904, 2850, 1726, 1610, 1370, 1200, 740 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 4.70 (s, 1H), 1.99 – 1.67 (m, 15H); ¹³C NMR (125 MHz, CDCl₃) δ 186.2, 163.4, 162.8, 140.2, 139.8, 130.1, 129.3, 127.3, 62.3, 39.3, 38.4, 36.9, 28.5; HRMS (FAB) calc for [C₈₀H₆₄Cl₁₆N₄O₁₆Rh₂]⁺ ([M+H]⁺) 2102.7522. Found: 2102.7536.

General procedure for the intermolecular C–H amination:

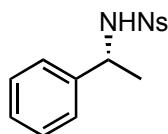
A solution of PhI(OAc)₂ (1.5 equiv.) in trifluorotoluene (10 mL) was added to a solution of substrate (5 equiv.) NsNH₂ (1 equiv.) MgO (2.3 equiv.) and the catalyst (2 mol %) in trifluorotoluene (15 mL) at 23 °C over 0.5 h using a syringe pump. The reaction mixture

¹ Callot, H. J.; Metz, F. *Tetrahedron* **1985**, *41*, 4495.

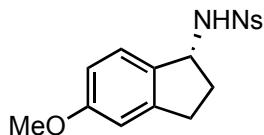
was allowed to stir for 3 h and then filtered to remove the precipitated solids and the filtrate was concentrated. The residue was purified using flash column chromatography.



(R)-N-Indan-1-yl-4-nitro-benzenesulfonamide (5). ^1H NMR (CDCl_3 , 400 MHz) δ 8.38 (d, $J = 8.8$ Hz, 2H), 8.12 (d, $J = 8.8$ Hz, 2H), 7.15-7.26 (m, 3H), 7.09 (d, $J = 7.2$ Hz, 1H), 4.93-4.89 (m, 2H), 2.97-2.90 (m, 1H), 2.85-2.76 (m, 1H), 2.35-2.42 (m, 1H), 1.76-1.82(m, 1H); $[\alpha]_D^{25} +16.4^\circ$ (c 0.68, CHCl_3 , 94 % ee). Lit. $[\alpha]_D +22.7^\circ$ (c 1.30, CHCl_3);² HPLC analysis: 94 % ee. Chiralcel AD-H, 25.0 % *i*-PrOH, 0.8 mL/min, 12.6 min (major), 18.3 (minor). The NMR data are consistent with the published data.³



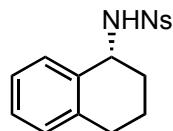
(R)-N-(1-Phenyl-ethyl)- 4-nitro-benzenesulfonamide (7a). ^1H NMR (CDCl_3 , 500 MHz) δ 8.40 (d, $J = 8.5$ Hz, 2H), 8.12 (d, $J = 8.5$ Hz, 2H), 7.18-7.15 (m, 2H), 7.10-7.06 (m, 2H), 6.95 (d, $J = 7.5$ Hz, 1H), 4.84 (d, $J = 8.0$ Hz, 1H), 4.58- 4.55 (m, 1H), 2.77-2.69 (m, 3H); $[\alpha]_D^{25} +11.6^\circ$ (c 0.73, CHCl_3). Lit $[\alpha]_D +6.23^\circ$ (c 0.80, CHCl_3);² HPLC analysis: 74 % ee. Chiralcel OD-H, 1.0 % *i*-PrOH, 0.7 mL/min, 5.8 min (major), 11.1 min (minor). The NMR data are consistent with the published data.³



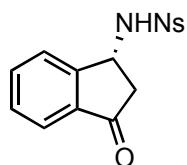
² Yamawaki, M.; Tsutsui, h.; Kitagaki, S.; Anada, M.; Hashimoto. S. *Tetrahedron Lett.* **2002**, *42*, 9561.

³ Nageli, I.; Baud, C.; Bernardinelli, G.; Jacquier, Y.; Moran, M.; Muller, P. *Helv. Chim. Acta* **1997**, *80*, 1087.

(R)-N-(5-Methoxy-indan-1-yl)-4-nitrobenzenesulfonamide (7b). white solid; mp = 95-98 °C; R_f = 0.40 (2:1 hexanes:EtOAc); [α]_D²⁵ +44.9° (c 0.12, acetone); FTIR: 3286, 2946, 1607, 1530, 1493, 1434, 1349, 1164, 1093, 1029, 851, 736, 643, 619 cm⁻¹; ¹H NMR (D₂O, 500 MHz) δ 8.38 (d, J = 7.0 Hz, 2H), 8.12 (d, J = 7.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 1H), 6.70 (m, 2H), 4.86 (s, 2H), 3.77 (s, 3H), 2.89 (m, 1H), 2.77(m, 1H), 2.36 (m, 1H), 1.79 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 160.1, 157.1, 147.2, 145.3, 133.0 128.1, 125.1, 124.6, 103.1, 100.4, 58.8, 55.9, 35.5, 30.1; HRMS (EI) m/z calc for [C₁₆H₁₆N₂O₅S]⁺ [(M)⁺]: 348.0774. Found: 348.0779; HPLC analysis: Chiralcel AD-H, 25.0 % ipa, 0.7 mL/min, 24.0 min (major), 26.3 min (minor).

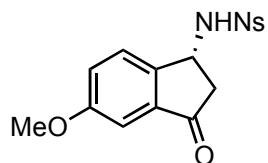


(R)-N-(1,2,3,4-Tetrahydronaphthalene-1-yl)-4-nitrobenzenesulfonamide (7c). ¹H NMR (CDCl₃, 400 MHz) δ 8.40 (d, J = 8.8 Hz, 2H), 8.12 (d, J = 8.8 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 7.10-7.05 (m, 2H), 6.95 (d, J = 7.2 Hz, 1H), 4.83 (d, J = 7.6 Hz, 1H), 4.58-4.55 (m, 1H), 2.81-2.66 (m, 2H), 1.88-1.71(m, 4H); [α]_D²⁵ +34.1° (c 0.64, CHCl₃, 73 % ee), Lit.[α]_D 44.3°(c 1.40, CHCl₃);² HPLC analysis: 73 % ee. Chiralcel AD-H, 25.0 % i-PrOH, 0.7 mL/min, 12.9 min (major), 19.6 min (minor). The NMR data are consistent with the published data.³

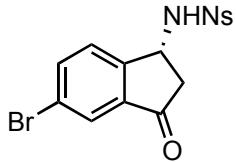


(R)-N-(3-Oxo-indan-1-yl)-4-nitrobenzenesulfonamide (7d). yellow solid, mp = 198-200 °C ; R_f = 0.40 (2:1 hexanes:EtOAc); [α]_D²⁵ -10.5° (c 0.19, acetone, 76 % ee); FTIR:

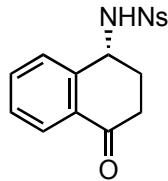
2966, 2906, 2854, 1707, 1530, 1349, 1259, 1166, 1067, 854, 736 cm^{-1} ; ^1H NMR (DMSO, 500 MHz) δ 8.73 (d, $J = 8.5$ Hz, 1H), 8.47 (d, $J = 9.0$ Hz, 2H), 8.13 (d, $J = 9.0$ Hz, 2H), 7.74 (t, $J = 7.5$ Hz, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.54 (m, 2H), 5.10 (m, 1H), 2.80 (dd, $J = 19.0, 8.0$ Hz, 1H), 2.20 (dd, $J = 19.0, 3.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 202.0 (C), 153.2 (C), 149.7 (C), 136.0 (CH), 135.5 (C), 129.2 (CH), 128.1 (CH), 126.2 (CH), 124.8 (CH), 122.5 (CH), 50.9 (CH), 43.8 (CH); Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_5\text{S}$: C, 54.21; H, 3.64; N, 8.43. Found: C, 54.40; H, 3.55; N, 8.39; HPLC analysis: 76 % ee. Chiralcel OJ, 5% *i*-PrOH, 0.8 mL/min, 5.4 min (minor), 7.1 min (major).



(*R*)-*N*-(5-Methoxy-3-oxo-indan-1-yl)-4-nitrobenzenesulfonamide (7e). yellow solid, mp = 165-167 °C; R_f = 0.37 (2:1 Hex:EtOAc); $[\alpha]_D^{25}$ -20.9° (c 0.45, acetone, 74 % ee); FTIR: 3305, 1711, 1692, 1527, 1493, 1350, 1285, 1155, 1089, 855, 740, 669, 616 cm^{-1} ; ^1H NMR (DMSO, 500 MHz) δ 8.66 (d, $J = 8.5$ Hz, 1H), 8.47 (d, $J = 8.5$ Hz, 2H), 8.09 (d, $J = 8.5$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.28 (dd, $J = 2.5, 8.5$ Hz, 1H), 7.06 (s, 1H), 5.00 (m, 1H), 3.79 (s, 3H), 2.80 (dd, $J = 18.5, 7.0$ Hz, 1H), 2.20 (dd, $J = 18.5, 3.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 201.8 (C), 160.3 (C), 149.7 (C), 146.9 (C), 145.7 (C), 137.5 (C), 128.1 (CH), 127.2 (CH), 124.8 (CH), 123.7 (CH), 104.4 (CH), 55.7 (CH₃), 50.5 (CH), 44.4 (CH₂); HRMS (ESI) m/z calc for $[\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_6\text{SNa}]^+$ ($\text{M}+\text{Na}$)⁺ 385.0465. Found: 385.0460; HPLC analysis: 74 % ee: Chiralcel OJ, 5.0 % *i*-PrOH, 0.8 mL/min, 6.9 min (major), 12.4 min (minor).

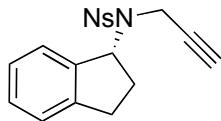


(R)-N-(5-Bromo-3-oxo-indan-1-yl)-4-nitrobenzenesulfonamide (7f). yellow sticky solid; $R_f = 0.47$ (2:1 Hex:EtOAc); $[\alpha]_D^{25} -6.25^\circ$ (c 0.32, acetone, 73 % ee); FTIR: 3419, 2360, 2325, 1653, 1023, 762 cm^{-1} ; ^1H NMR (DMSO, 500 MHz) δ 8.76 (bs, 1H), 8.46 (d, $J = 8.5$ Hz, 2H), 8.11 (d, $J = 8.5$ Hz, 2H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.78 (s, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 5.06 (bs, 1H), 2.83 (dd, $J = 7.5, 18.5$ Hz, 1H), 2.20 (dd, $J = 3.0, 18.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl₃) δ 200.6, 152.1, 149.7, 146.6, 138.0, 137.8, 128.4, 128.1, 125.0, 124.7, 122.7, 50.7, 43.9; HRMS (EI) m/z calc for [C₁₅H₁₁BrN₂O₅S]⁺ (M⁺): 409.9567. Found: 409.9576; HPLC analysis: 73 % ee. Chiralcel OJ, 5.0 % *i*-PrOH, 0.8 mL/min, 5.4 min (major), 7.1 min (minor).

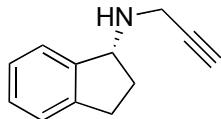


(R)-N-(4-Oxo-1,2,3,4-tetrahydronaphthalene-1-yl)-4-nitrobenzenesulfonamide (7g). $R_f = 0.40$ (2:1 hexanes:EtOAc); $[\alpha]_D^{25} -13.4^\circ$ (c 1.02, acetone, 78 % ee); FTIR: 2966, 2906, 2854, 1707, 1530, 1349, 1259, 1166, 1067, 854, 736 cm^{-1} ; ^1H NMR (DMSO, 300 MHz) δ 8.75 (d, $J = 8.7$ Hz, 1H), 8.44 (d, $J = 8.7$ Hz, 2H), 8.14 (d, $J = 8.7$ Hz, 2H), 7.84 (d, $J = 7.8$ Hz, 1H), 7.61 (t, $J = 7.8$ Hz, 1H), 7.43 (t, $J = 7.5$ Hz, 1H), 7.34 (d, $J = 7.8$ Hz, 1H), 4.78 (m, 1H), 2.61 (m, 2H), 1.93 (m, 2H); ^{13}C NMR (125 MHz, DMSO) δ 196.1, 149.6, 147.4, 143.1, 133.8, 131.5, 128.1, 127.9, 127.7, 126.3, 124.7, 51.2, 35.2, 29.5; HRMS (EI) m/z calc for [C₁₆H₁₄N₂O₅S]⁺ (M⁺): 346.0623. Found: 346.0634; HPLC

analysis: 78 % ee. Chiralcel OJ, 5.0 % *i*-Propanol, 0.8 mL/min, 15.4 min (minor), 18.1 min (major).



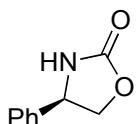
(*R*)-Indan-1-yl-4-nitro-N-prop-2-ynyl-benzenesulfonamide (8). light yellow solid, mp = 102-105 °C; R_f = 0.40 (5:1 hexanes:EtOAc); [α]_D²⁵ -12.3° (c 1.17, CHCl₃); FTIR: 3281, 3101, 2946, 1528, 1348, 1158, 1093, 855, 737, 684 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 8.40 (d, J = 7.0 Hz, 2H), 8.22 (d, J = 7.0 Hz, 2H), 7.29-7.15 (m, 4H), 5.61 (t, J = 7.5 Hz, 1H), 4.28 (dd, J = 19.0, 2.5 Hz, 1H), 3.60 (dd, J = 19.0, 2.5 Hz, 1H), 3.04 (m, 1H), 2.83 (m, 1H), 2.23 (m, 2H), 2.12 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 149.9 (C), 146.5 (C), 143.6 (C), 138.8 (C), 128.9 (CH), 128.8 (CH), 127.1 (CH), 125.1 (CH), 124.5 (CH), 124.1 (CH), 78.9 (C), 72.9 (C), 63.8 (CH), 32.8 (CH₂), 30.1 (CH₂), 29.1 (CH₂); HRMS (EI) *m/z* calc for [C₁₈H₁₆N₂O₄S]⁺ (M⁺): 356.0825. Found: 356.0819.



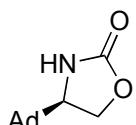
(*R*)-Indan-1-yl-prop-2-ynyl-amine (9). solid, mp = 148 °C R_f = 0.33 (3:1 hexanes:EtOAc); [α]_D²⁵ +18.8° (c 1.7, CHCl₃); FTIR: 3281, 2929, 2848, 1456, 1349, 1161, 1088, 649 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.57-7.54(m, 1H), 7.46-7.39 (m, 3H), 4.62 (t, J = 10Hz, 1H), 3.73 (s, 2H), 3.25 (m, 1H), 3.06 (m, 1H), 2.62 (m, 1H), 2.46 (s, 1H), 2.12 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 144.5 (C), 143.8 (C), 127.6 (CH), 126.2 (CH), 124.8 (CH), 124.2 (CH), 82.5 (C), 71.3 (C), 61.9 (CH), 36.1 (CH₂), 33.3 (CH₂), 30.4 (CH₂); HRMS (ESI) *m/z* calc for [C₁₂H₁₃NNa]⁺ ([M+Na]⁺): 194.0946. Found: 194.0932.

General Procedure for Intramolecular C–H Amination:

To a solution of *N*-tosyloxycarbamate (0.5 mmol) in dichloromethane (10.0 mL), were added K₂CO₃ (1.5 mmol, 3 equiv.) and Rh₂(S-TCPTAD)₄ (0.01 mmol). The resulting suspension was stirred at 23 °C for 4 h. The mixture was filtered to remove the precipitate and the solvent was removed under vacuum. The crude reaction mixture was then purified by flash chromatography.



(R)-4-Phenylloxazolidin-2-one (11a). ¹H NMR (400 MHz, CDCl₃) δ 7.42–7.32 (m, 5H), 6.11 (bs, 1H), 4.95 (t, *J* = 7.6 Hz, 1H), 4.72 (t, *J* = 8.8 Hz, 1H), 4.17 (dd, *J* = 8.8, 7.6 Hz, 1H); [α]_D²⁵ -40.8° (*c* 0.86, CHCl₃, 82 % ee) Lit. [α]_D for (R)-4-phenyloxazolidin-2-one:⁴ -57.7° (*c* 1.00, CHCl₃); HPLC analysis. 82 % ee. Chiralcel OD-H, 7 % *i*-PrOH, 0.9 mL/min, 14.0 min (major), 17.2 min (minor). The NMR data are consistent with the published data.⁵

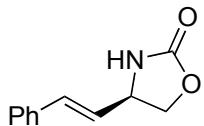


(R)-4-Adamantyloxazolidin-2-one (11b). ¹H NMR (500 MHz, CDCl₃) δ 5.62 (bs, 1H), 4.30 (d, *J* = 7.5 Hz, 2H), 3.40 (t, *J* = 7.2 Hz, 1H), 2.03 (s, 3H), 1.77–1.51 (m, 12H); [α]_D²⁵ -12.5 (*c* 0.62, CHCl₃, 78 % ee); lit. [α]_D for (S)-4-adamantyloxazolidin-2-one⁶: +8.1 (*c* 0.78, CHCl₃); HPLC analysis. 78 % ee. Chiralcel OD-H, 0.9 mL/min, 7 % *i*-PrOH, 13.1 min (minor), 24.7 min (major). The NMR data are consistent with the published data.⁵

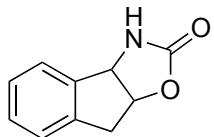
⁴ Evans, D. A.; Sjogren, E. B. *Tetrahedron Lett.* **1985**, *26*, 3783.

⁵ (a) Espino, C.G.; Du Bois, J. *Angew. Chem. Int. Ed.* **2001**, *40*, 598. (b) Lebel, H.; Huard, K.; Lectard, S. *J. Am. Chem. Soc.* **2005**, *127*, 14198.

⁶ Takacs, J. M.; Jaber, M. R.; Vellekoop, A. S. *J. Org. Chem.* **1998**, *63*, 2742.



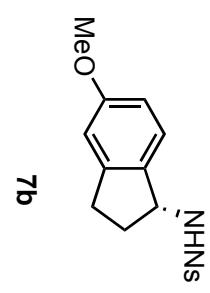
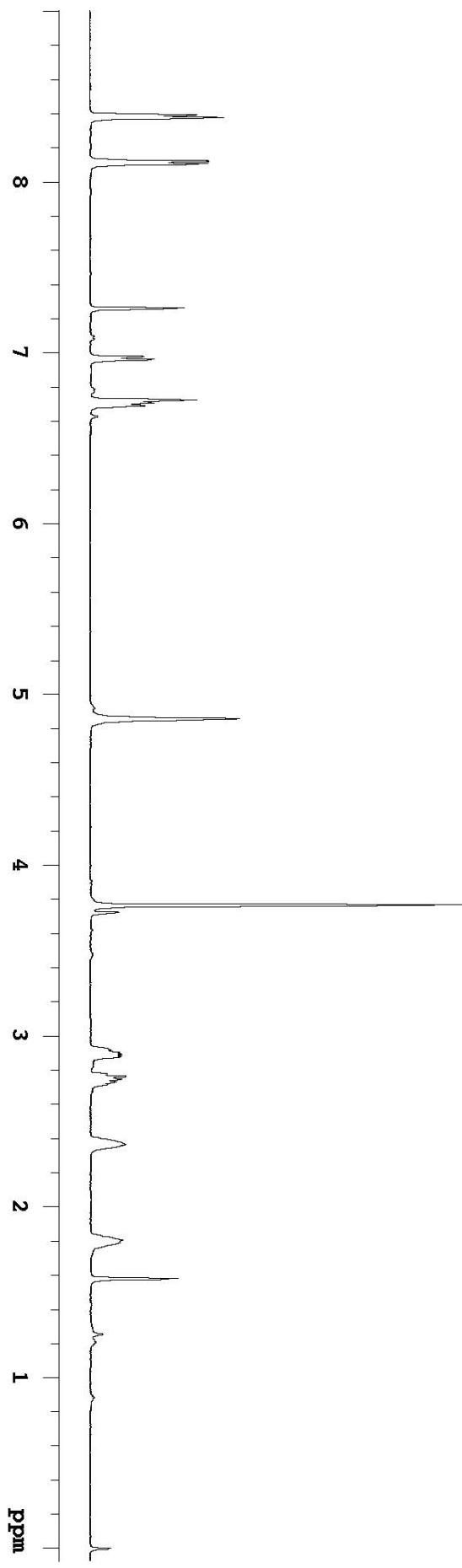
(R)-4-Styryloxazolidin-2-one (11c). ^1H NMR (500 MHz, CDCl_3) δ 7.39- 7.30 (m, 5H), 6.62 (d, $J = 16.0$ Hz, 1H), 6.14 (dd, $J = 16.0, 8.0$ Hz, 1H), 5.09 (bs, 1H), 4.63- 4.54 (m, 2H), 4.16 (m, 1H); $[\alpha]_D^{25} +22.5^\circ$ (c 0.26, CHCl_3), Lit. $[\alpha]_D$ for (R)-4-styryloxazolidin-2-one:⁷ $+19.3$ (c 1.945, CHCl_3); HPLC analysis. 79 % ee. Chiralcel OD-H, 10.0 % *i*-PrOH, 0.9 mL/min, 8.5 min (minor), 15.3 min (major). The NMR data are consistent with the published data.⁵

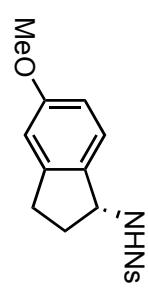


(4*R*,5*S*)-Indano[1,2-*d*]oxazolidin-2-one (11d). ^1H NMR (500 MHz, CDCl_3) δ 7.33-7.26 (m, 4H), 6.87 (bs, 1H), 5.43-5.40 (m, 1H), 5.17 (d, $J = 7.0$, 1H), 3.44-3.34 (m, 2H); $[\alpha]_D^{25} +12.1^\circ$ (c 0.36, CHCl_3 , 43 % ee); Lit. $[\alpha]_D$ for (4*R*,5*S*)-indano[1,2-*d*]oxazolidin-2-one:⁸ $+76.9$ (c 1.2, CHCl_3); HPLC analysis. 43 % ee. Chiralcel AD-H, 7% *i*-PrOH, 0.9 mL/min, 17.0 min (major), 29.0 min (minor). The NMR data are consistent with the published data.⁵

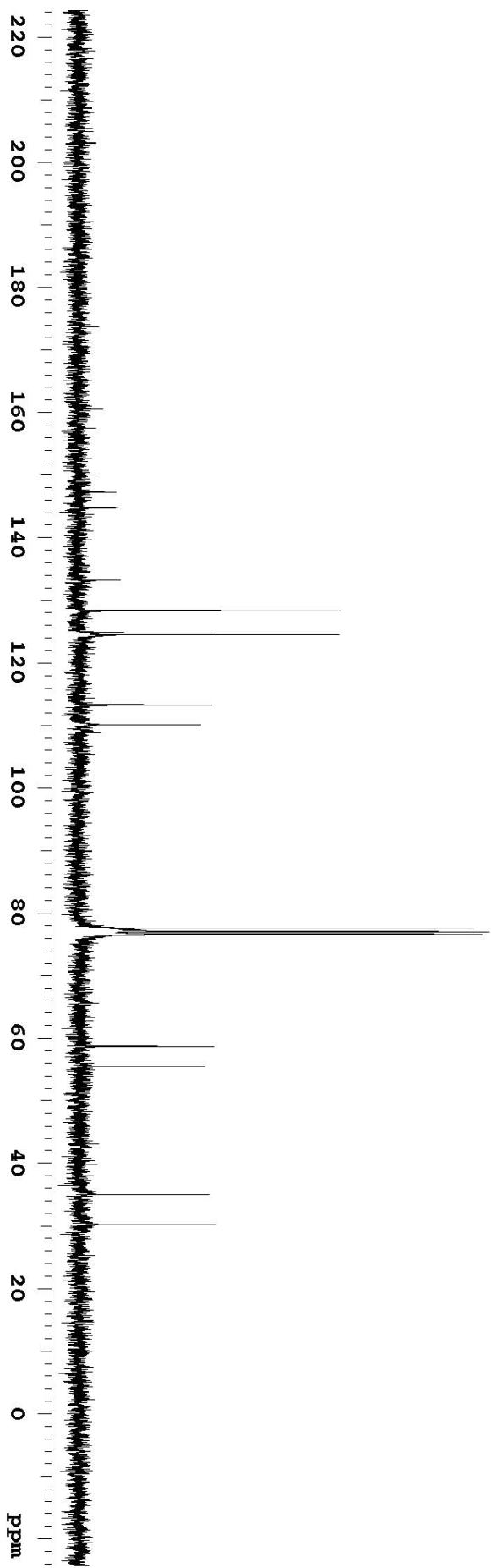
⁷ Sibi, M.P.; Rutherford, D.; Renhowe, P. A.; Li, B. *J. Am. Chem. Soc.* **1999**, *121*, 7509.

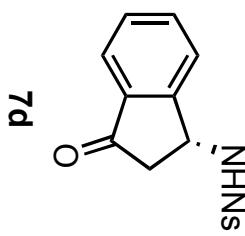
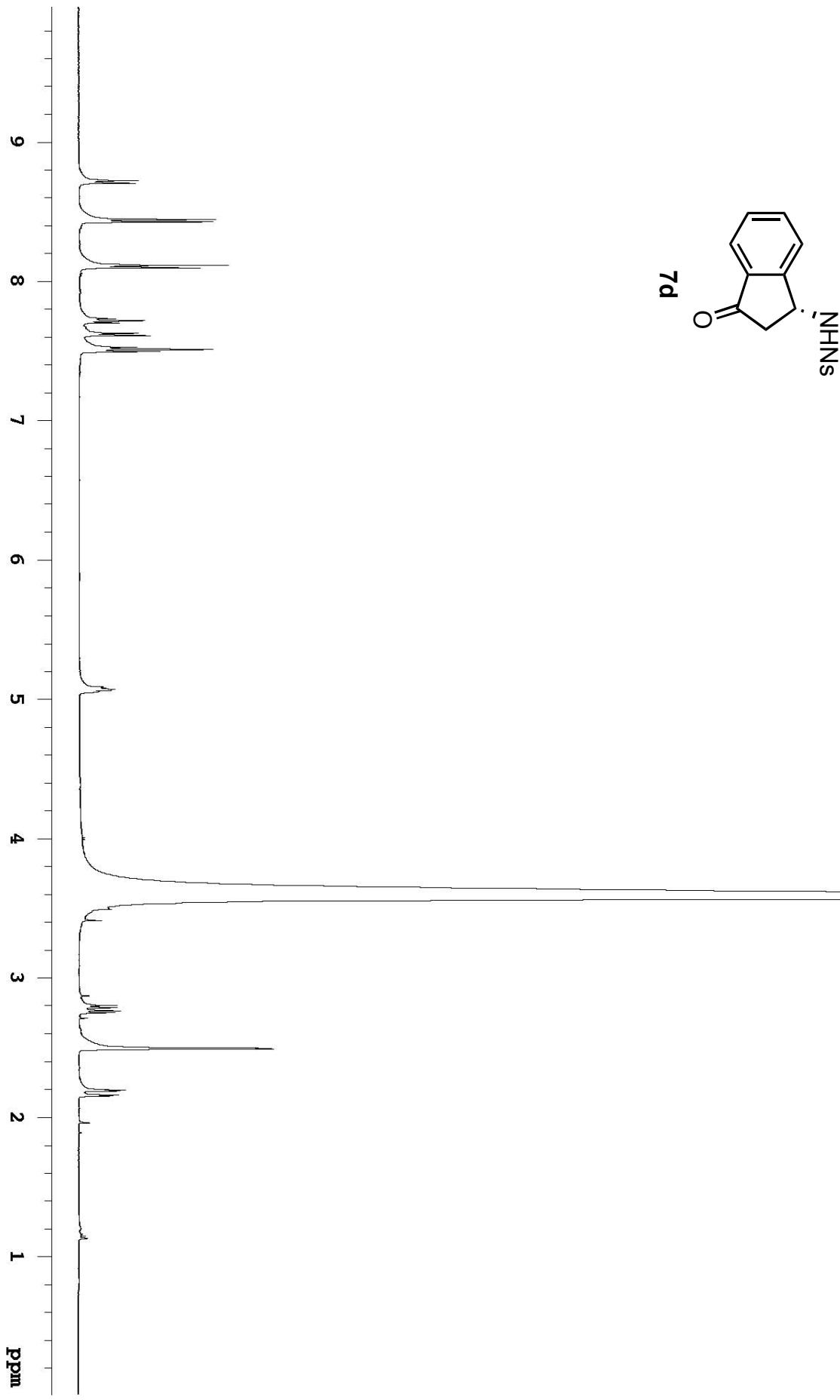
⁸ Ghosh, A. K.; Kincaid, J. F.; Haske, M. G. *Synthesis*, **1997**, *5*, 541.

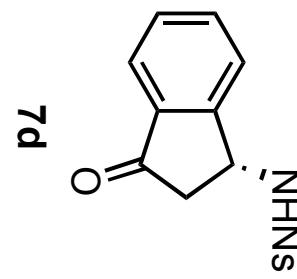
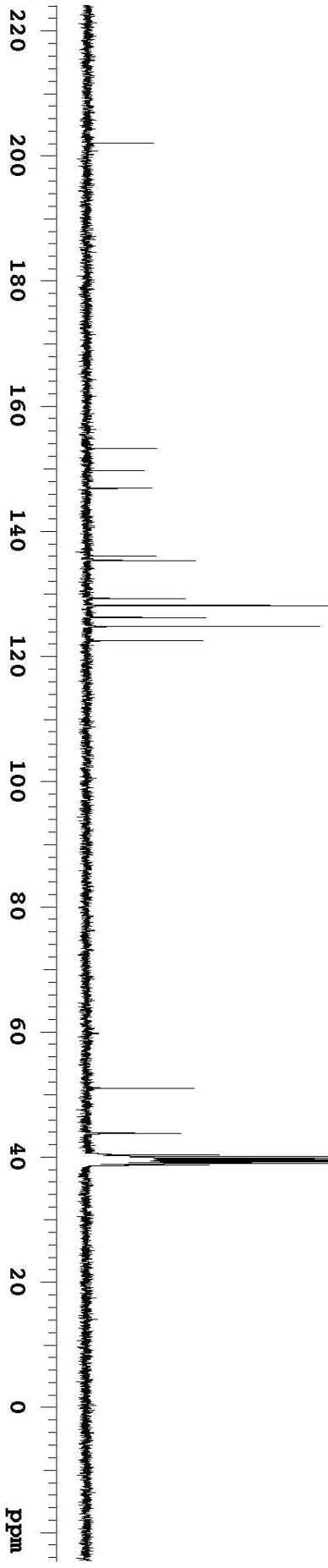


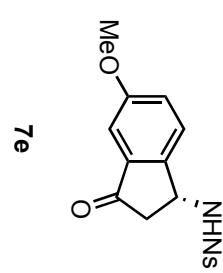
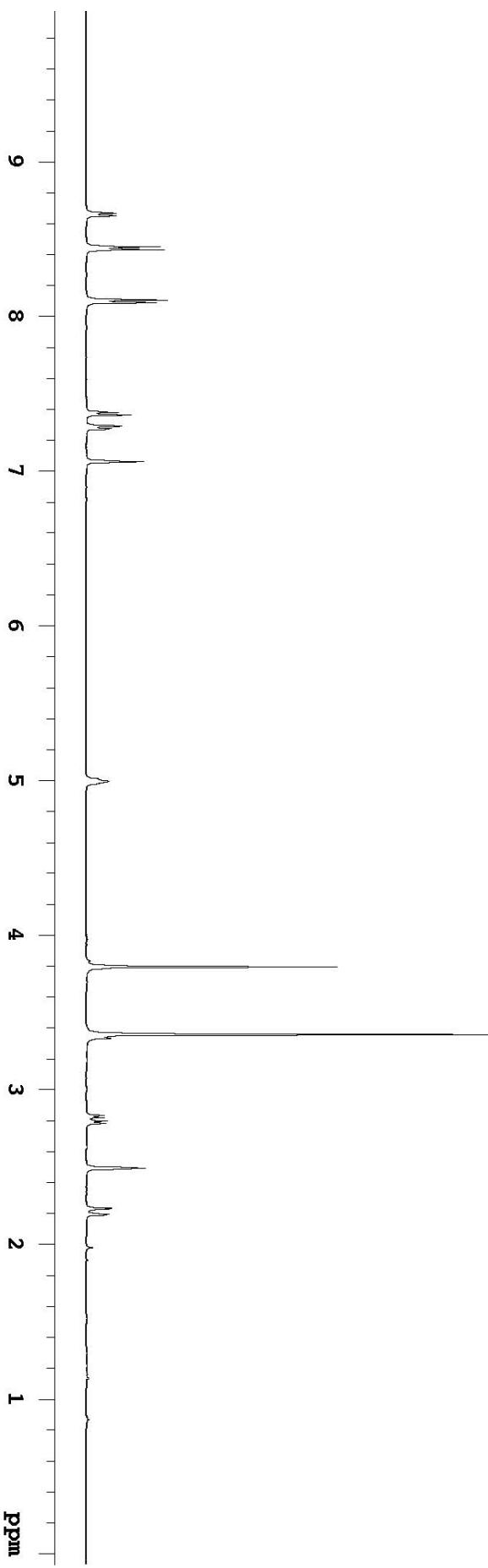


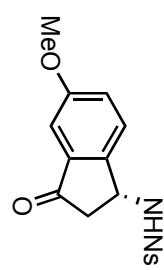
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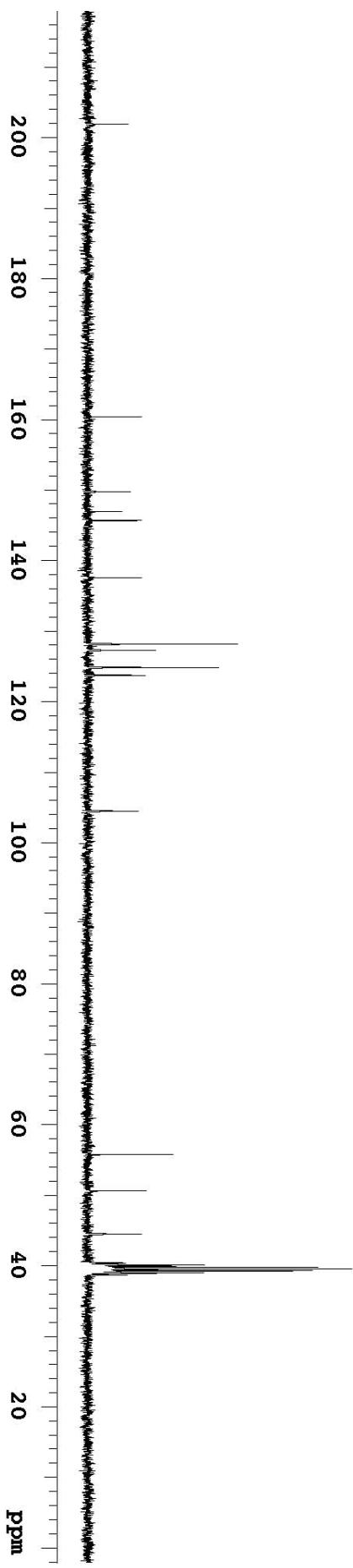


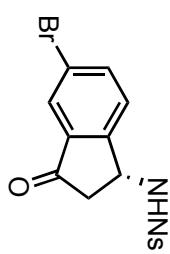
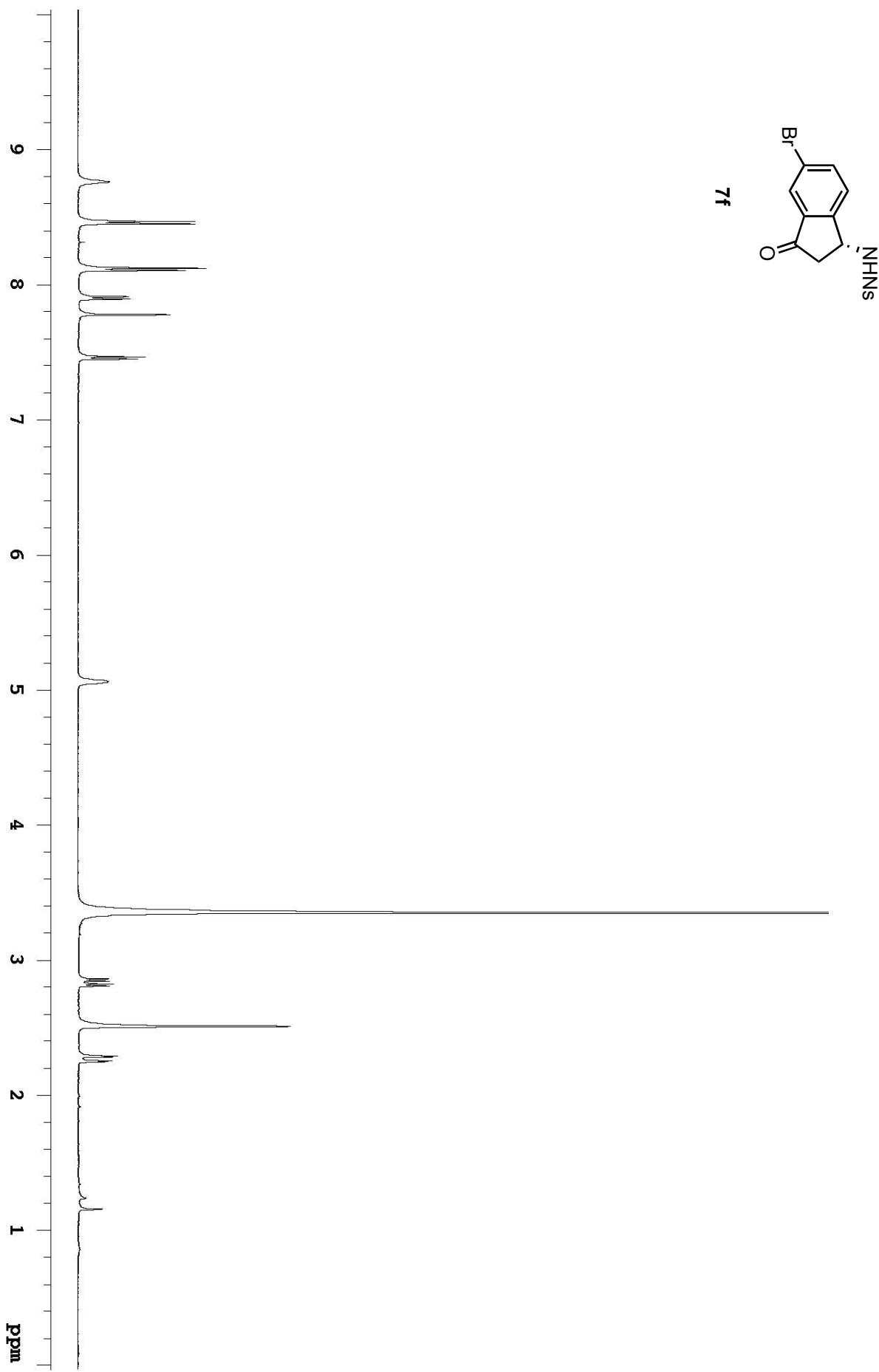


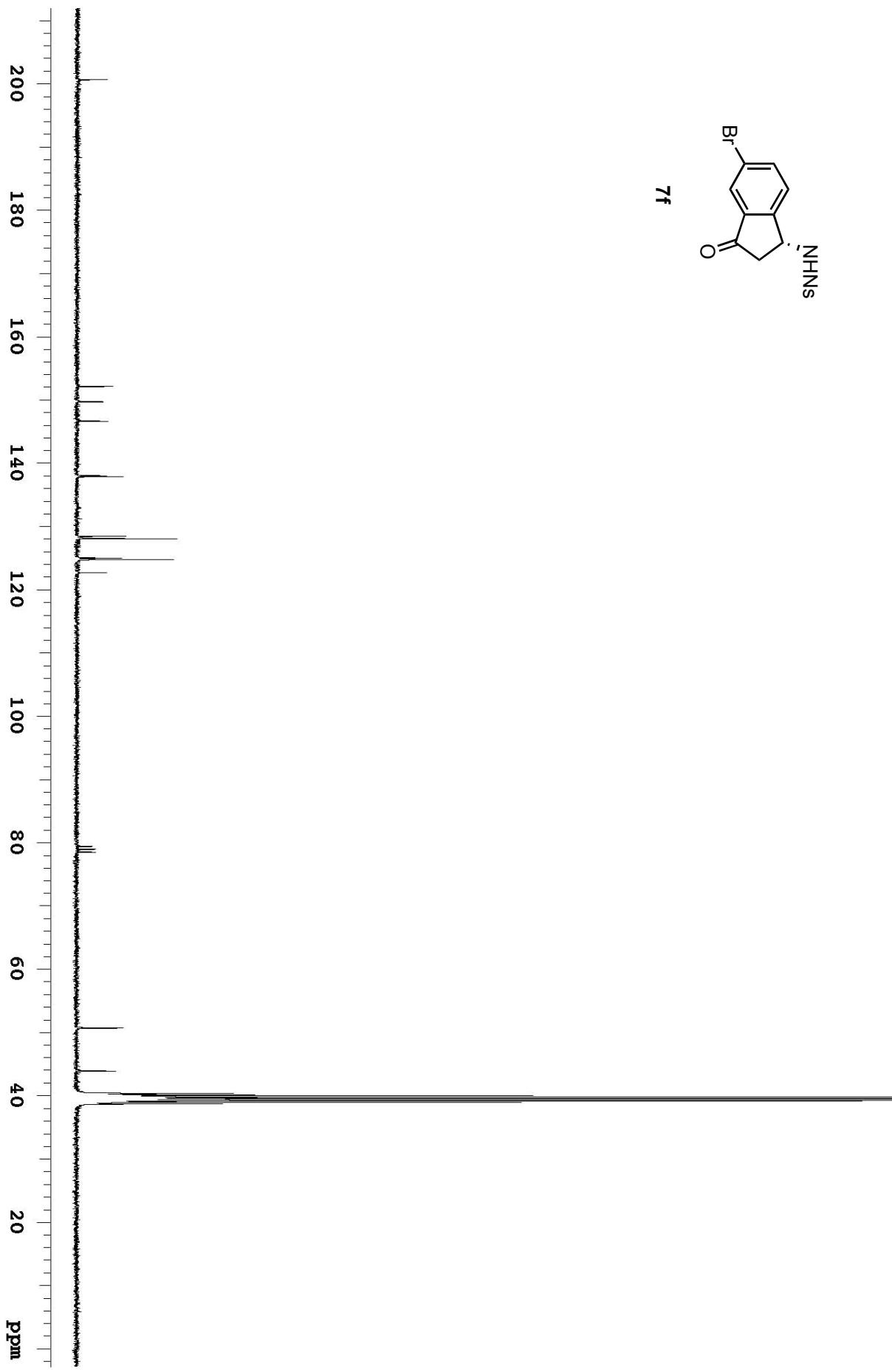
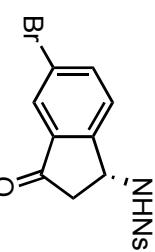


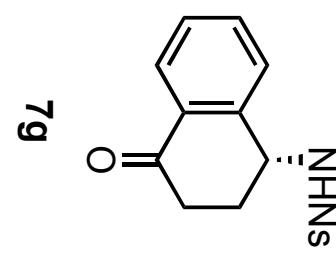
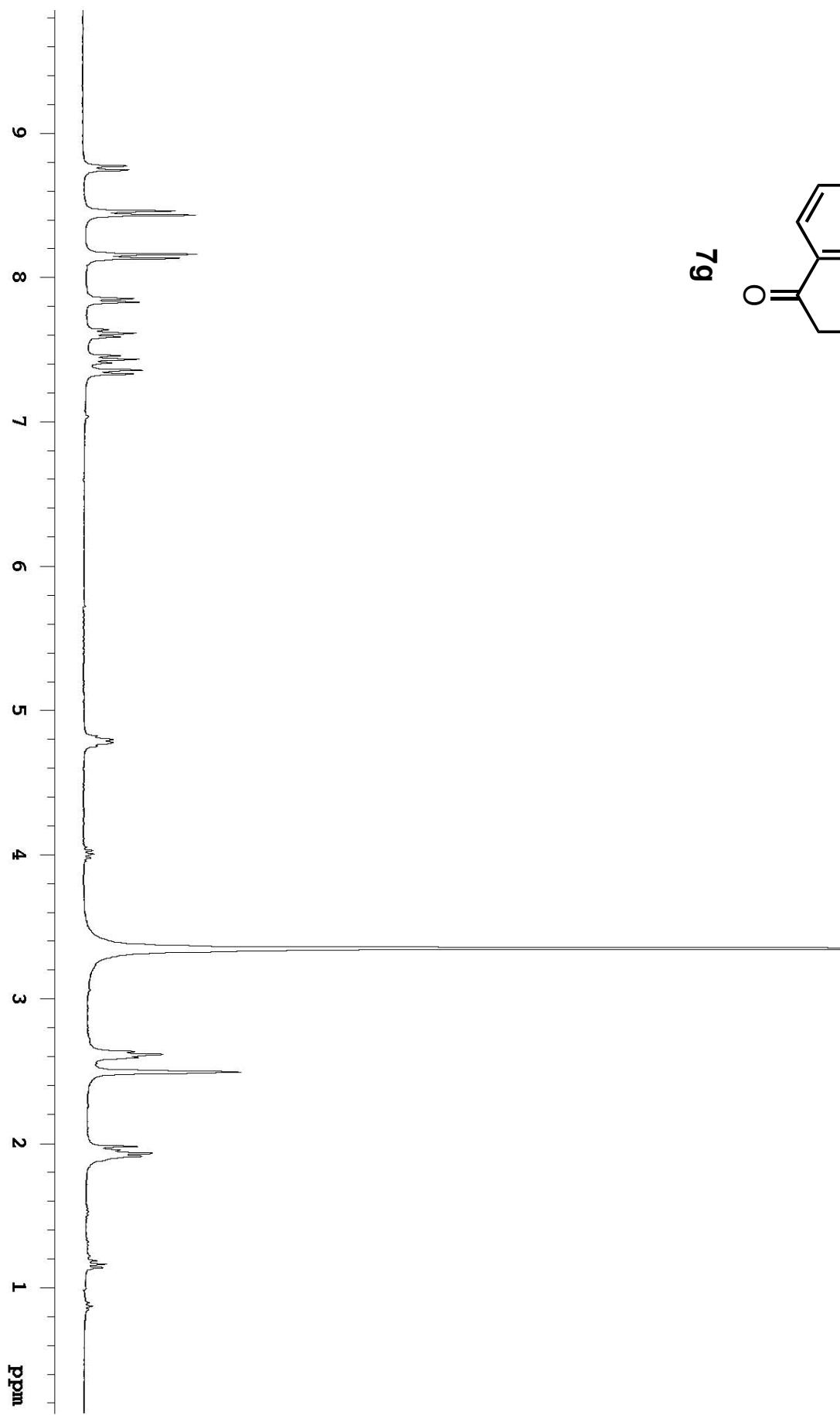


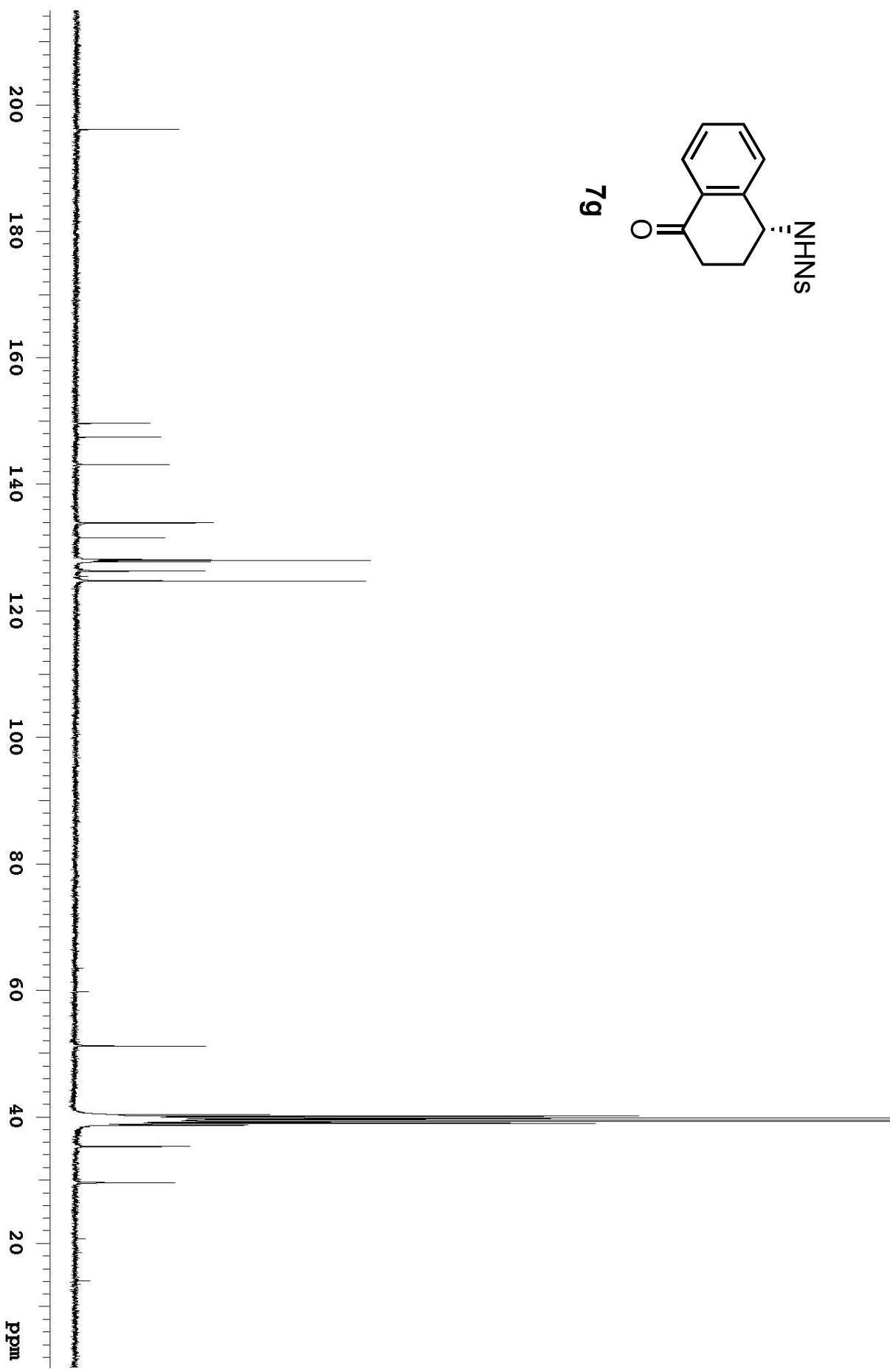
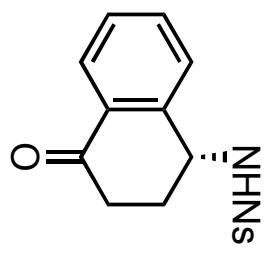
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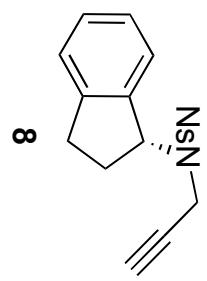
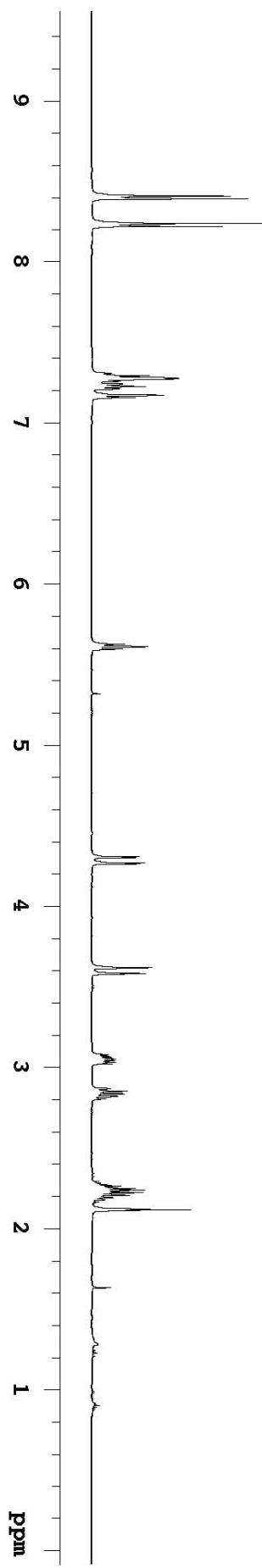


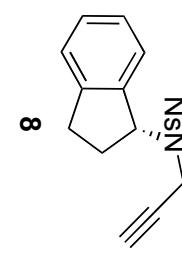
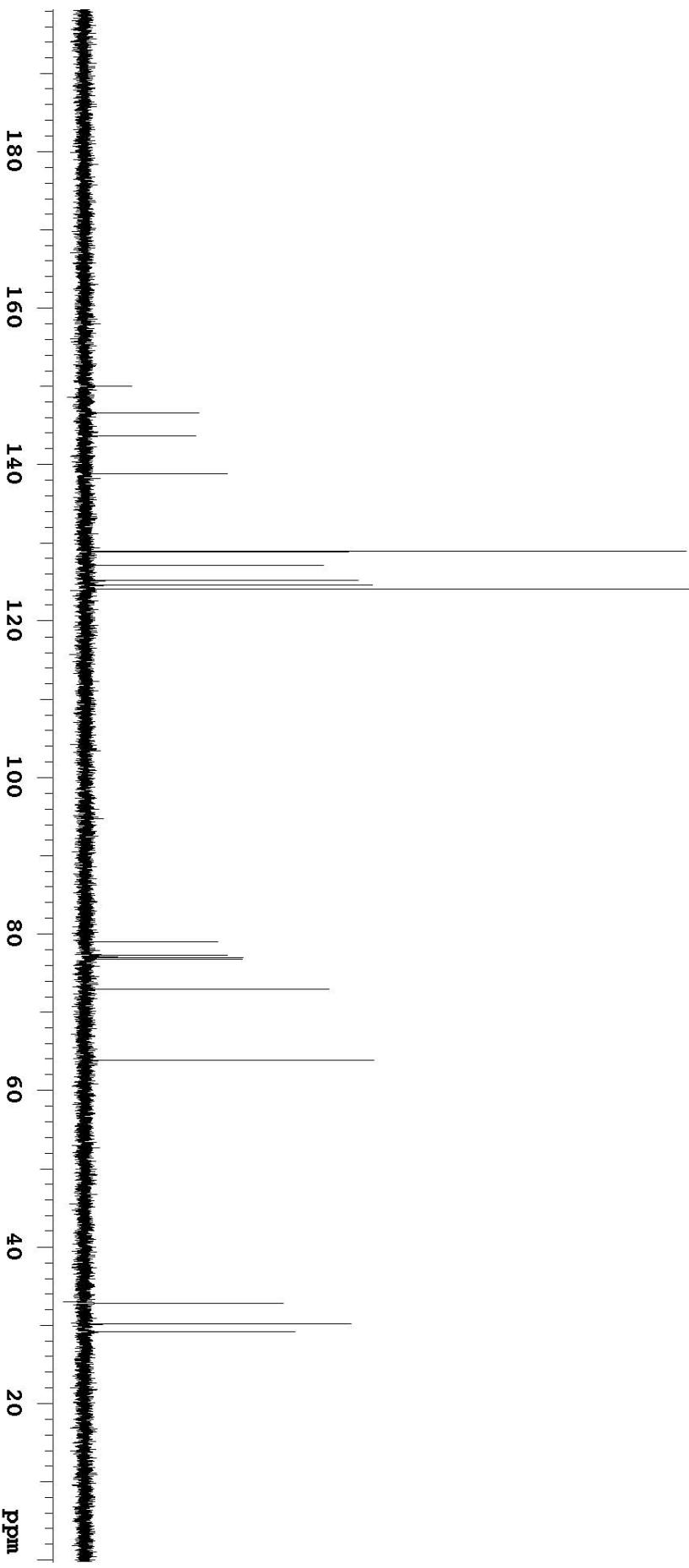


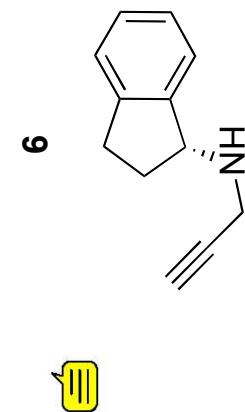
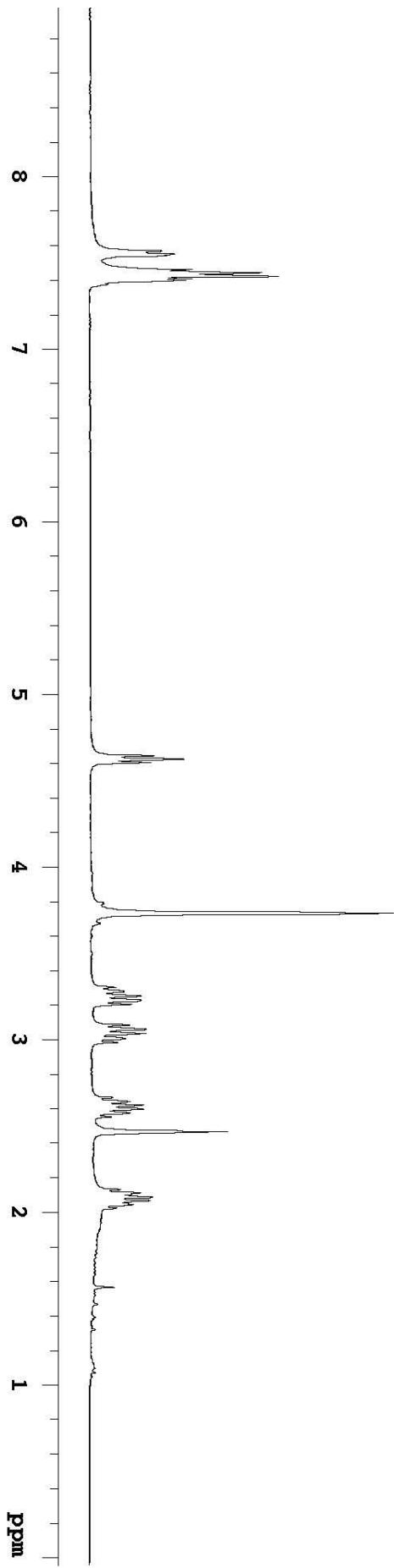




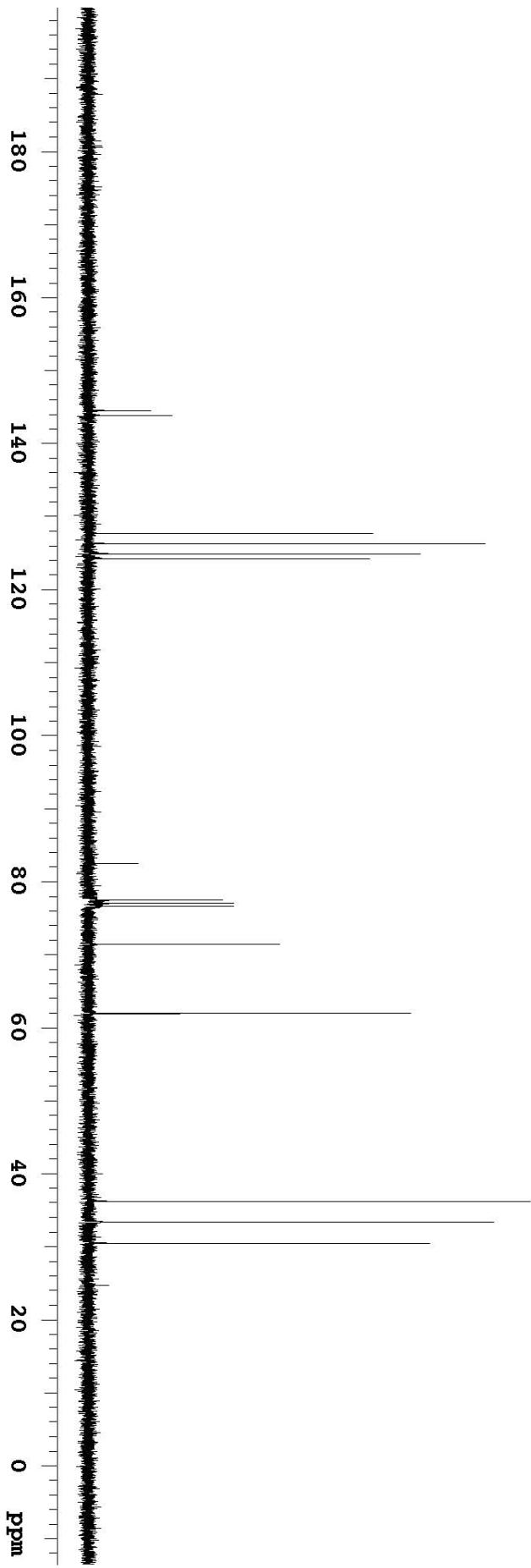








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