Supporting information for:

Chiral Monophosphites Derived from Carbohydrate: Conformational Effect in Catalytic Asymmetric Hydrogenation

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CONTENTS

General Procedures: All reactions and manipulations were performed in a nitrogen-filled glovebox or using standard Schlenk-type techniques. Melting points were determined using a Metter FP5 melting apparatus in open capillaries and are uncorrected. Optical rotations were measured on a JASCO, P-1020 high sensitive polarimeter. ^{1}H NMR and ^{13}C NMR spectra were obtained on BRUKER DRX 400 spectrometers with TMS as an internal standard, ^{31}P NMR spectra were recorded with 85% H_3PO_4 as an external standard. High resolution mass spectra were recorded on Applied Biosystems Mariner System 5303. Enantiomeric excess (ee) were determined by GC analysis on an Agilent HP-4890 or 6890 GC instrument with FID as detector.

Materials: All solvents were dried and degassed by standard methods and stored under nitrogen. dimethyl itaconate was purchased from Acros. enamides, and chiral alcohols **7-10** derived from D-fructose and D-glucose were known compounds which were synthesized according to the literature procedure.[1] All other chemicals obtained commercially.

(A). Preparation and Physical data of ligands 3-6

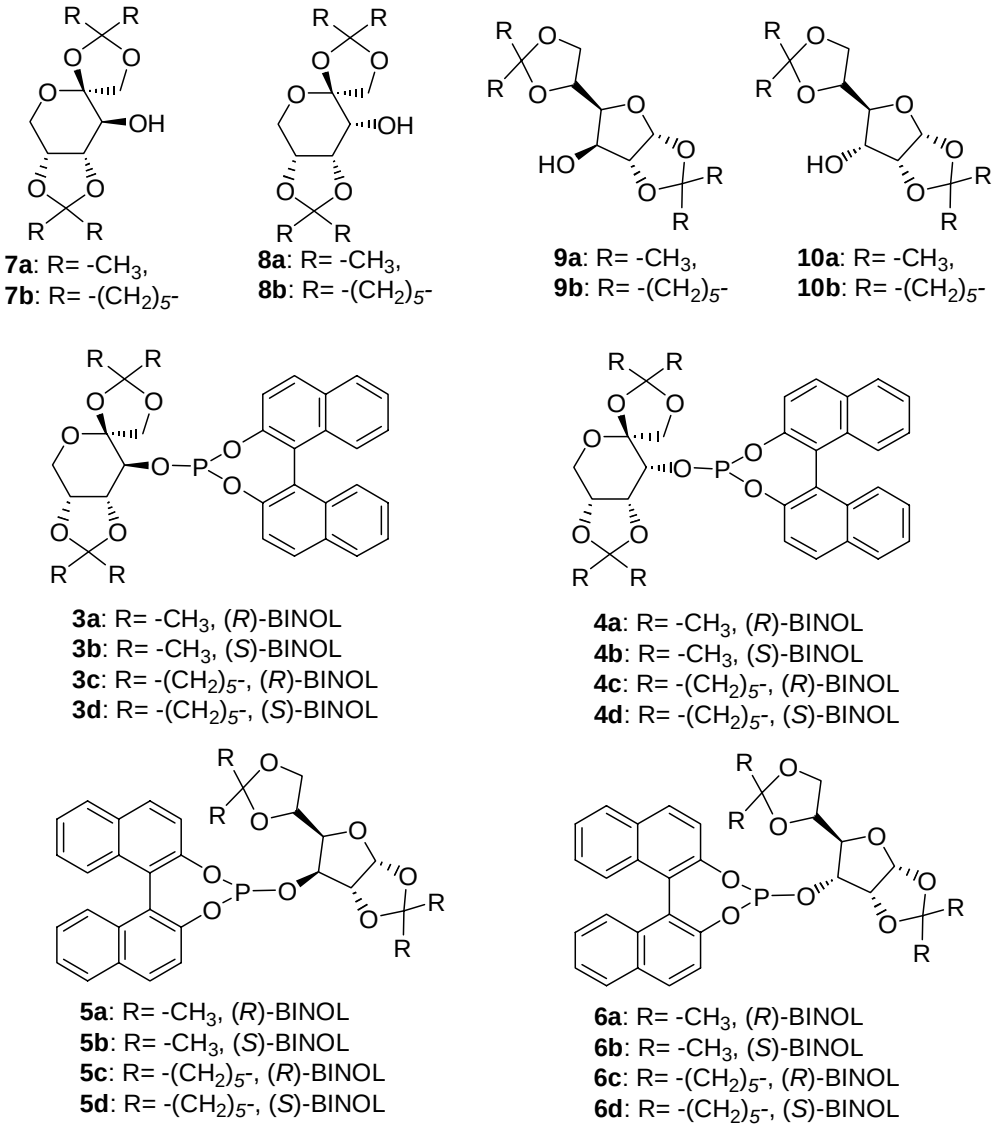
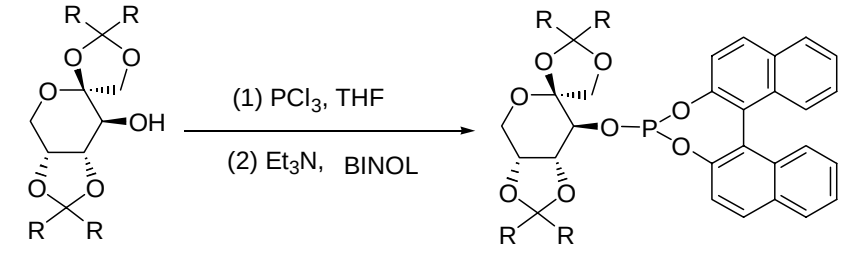


Fig. 1. Structure of chiral alcohols and ligands 3-6

General procedure for synthesis of the ligands 3-6



Scheme 1. The synthesis route of monophosphite ligands

To a stirred solution of **7** (1.5 mmol) in THF (5 mL) was slowly added PCl_3 (132 μL, 1.5

mmol) as a solution in THF (4 mL) and the resulting mixture was stirred for 1 h at room temperature. The reaction mixture was then cooled to –10 ^{o}C and Et_3N (1.07 mL, 4.5 mmol) was slowly added. The reaction mixture was allowed to warm to room temperature, maintained under these conditions for 0.25 h, and then cooled to 0 ^{o}C, solid BINOL was added and the resulting mixture was allowed to warm to room temperature and stirred overnight prior to dilution with diethyl ether. The solid were removed by filtration through a pad of Celite, the solvent was removed in *vacuo* and the residue was purified by flash chromatography (EtOAc / hexane: 1 / 20~1 / 10)), furnished the title ligands as white foam in 75-90% yields.

The above procedure was followed using **7a** and R-BINOL. After workup, it gave **3a.** mp 121-122 ^{o}C; $[\alpha]_D^{12}$ = -430.54 (*c* 1.06, THF); ^{1}H NMR (DMSO-d^6): δ 1.27 (s, 3H), 1.34 (s, 3H), 1.43 (s, 3H), 1.53 (s, 3H), 3.99 (m, 3H), 4.09 (t, *J* = 6.4 Hz, 1H), 4.24 (d, *J* = 9.2 Hz, 1H), 4.30 (t, *J* = 4.8 Hz 1H), 4.43 (t, *J* = 8.4 Hz 1H), 7.21-7.24 (m, 2H), 7.34-7.36 (m, 2H), 7.47-7.57 (m, 4H), 8.05-8.10 (m, 3H), 8.17 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (DMSO-d^6): δ 26.15, 27.87, 59.96, 71.44, 73.35, 73.94, 74.11, 75.16, 103.74, 108.88, 111.62, 121.67, 122.00, 122.26, 123.56, 125.13, 125.37, 125.89, 126.01, 126.60, 126.78, 128.57, 128.71, 129.95, 130.75, 130.87, 131.20, 131.71, 132.02, 146.79, 147.36; ^{31}P NMR (DMSO-d^6): δ 159.37; HRMS (APCI) calcd for $C_{32}H_{32}O_8P$ (M^++1): 575.1829, found: 575.1850.

The above procedure was followed using **7a** and S-BINOL. After workup, it gave **3b.** mp 107-108 ^{o}C; $[\alpha]_D^{12}$ = +196.98 (*c* 1.20, THF); ^{1}H NMR (DMSO-d^6): δ 0.90 (s, 3H), 1.33 (s, 3H), 1.39 (s, 3H), 1.51 (s, 3H), 3.84 (d, *J* = 9.2 Hz , 1H), 3.95-3.99 (m, 3H), 4.27-4.37 (m, 3H), 7.21-7.23 (m, 2H), 7.33-7.35 (m, 2H), 7.51-7.54 (m, 3H), 7.61 (d, *J* = 8.8 Hz, 1H), 8.04-8.17 (m, 4H); ^{13}C NMR (DMSO-d^6): δ 25.19, 26.37, 26.60, 27.92, 59.61, 70.54, 73.16, 73.31, 73.43, 75.51, 103.54, 108.92, 111.69, 121.70, 122.04, 123.50, 125.08, 125.31,125.87, 126.02, 126.49, 126.72, 128.54, 128.69, 129.99, 130.76, 131.17, 131.64, 132.07, 146.96, 147.36; ^{31}P NMR (DMSO-d^6): δ 158.48; HRMS (APCI) calcd for $C_{32}H_{32}O_8P$ (M^++1): 575.1829, found: 575.1841□

The above procedure was followed using **7b** and R-BINOL. After workup, it gave **3c.** mp 135-136 ^{o}C; $[\alpha]_D^{25}$ = -382.45 (*c* 1.08, THF); ^{1}H NMR (DMSO-d^6): δ 1.24-1.75 (m, 20H), 3.97-4.04 (m, 3H), 4.10 (t, *J* = 6.4 Hz, 1H), 4.23 (d, *J* = 9.2 Hz, 1H), 4.30 (d, *J* = 4.4 Hz, 1H), 4.42 (t, *J* = 8.4

Hz, 1H), 7.21-7.24 (m, 2H), 7.33-7.38 (m, 2H), 7.46-7.53 (m, 4H), 8.05-8.09 (m, 3H), 8.18 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (DMSO-d^6): δ 23.32, 23.56, 23.68, 24.40, 24.54, 35.05, 35.16, 35.47, 37.32, 60.25, 71.06, 73.03, 74.25, 74.43, 74.80, 403.34, 109.45, 112.20, 121.49, 122.01, 122.32, 123.62, 125.14, 125.38, 125.89, 126.02, 126.62, 126.81, 128.59, 128.73, 129.76, 130.77, 130.95, 131.19, 131.73, 132.06, 146.83, 147.41; ^{31}P NMR (DMSO-d^6): δ 159.55; HRMS (APCI) calcd for $C_{38}H_{40}O_8P$ (M^++1): 655.2455, found: 655.2508.

The above procedure was followed using **7b** and S-BINOL. After workup, it gave **3d.** mp 153-154 ^{o}C; $[\alpha]_D^{25}$ = +196.98 (*c* 1.20, THF); ^{1}H NMR (DMSO-d^6): δ 1.07-1.69 (m, 20H), 3.83-4.00 (m, 4H), 4.30-4.32 (m, 2H), 4.38 (m, 1H), 7.21-7.22 (m, 2H), 7.32-7.36 (m, 2H), 7.47-7.62 (m, 4H), 8.05-8.17 (m, 4H); ^{13}C NMR (DMSO-d^6): δ 22.10, 22.54, 22.97, 23.38, 23.50, 24.28, 24.45, 34.29, 35.28, 36.05, 37.42, 59.78, 70.16, 73.14, 73.32, 73.47, 75.19, 103.19, 109.48, 112.17, 121.71, 121.96, 122.11, 123.52, 125.07, 125.32, 125.87, 126.01, 126.50, 126.73, 128.55, 128.70, 130.04, 130.77, 131.17, 131.67, 132.08, 146.99, 147.41; ^{31}P NMR (DMSO-d^6): δ 158.47; HRMS (APCI) calcd for $C_{38}H_{40}O_8P$ (M^++1): 655.2455, found: 655.2481□

The above procedure was followed using **8a** and R-BINOL. After workup, it gave **4a.** mp 120-121 ^{o}C; $[\alpha]_D^{25}$ = -360.71 (*c* 1.20, THF); ^{1}H NMR (DMSO-d^6): δ 1.27 (s, 3H), 1.33 (s, 3H), 1.40 (s, 3H), 1.46 (s, 3H), 3.57 (d, *J* = 13.2 Hz, 1H), 3.67 (d, *J* = 9.2 Hz, 1H), 3.82 (d, *J* = 13.2 Hz, 1H), 4.04 (d, *J* = 9.2 Hz, 1H), 4.40 (d, *J* = 7.6 Hz, 1H), 4.72 (d, *J* = 8.0 Hz, 1H), 4.91 (d, *J* = 10.4 Hz, 1H), 7.20-7.22 (m, 2H), 7.34-7.38 (m, 2H), 7.49-7.58 (m, 4H), 8.08-8.19 (m, 4H); ^{13}C NMR (DMSO-d^6): δ 24.60, 25.86, 26.06, 26.27, 62.59, 70.55, 71.09, 71.26, 73.40, 73.78, 104.70, 108.69, 109.02, 121.45, 121.98, 125.22, 125.47, 125.85, 126.01, 126.68, 126.85, 128.64, 128.72, 130.09, 130.86, 131.01, 131.26, 131.80, 132.03, 146.59, 147.08; ^{31}P NMR (DMSO-d^6): δ 157.75; HRMS (APCI) calcd for $C_{32}H_{32}O_8P$ (M^++1): 575.1829, found: 575.1786□

The above procedure was followed using **8a** and S-BINOL. After workup, it gave **4b.** mp 147-148 ^{o}C; $[\alpha]_D^{25}$ = +201.12 (*c* 0.89, THF); ^{1}H NMR (DMSO-d^6): δ 1.23 (s, 3H), 1.32 (s, 3H), 1.48 (s, 3H), 1.58 (s, 3H), 3.58 (d, *J* = 13.2 Hz, 1H), 3.82-3.85 (m, *2*H), 4.32-4.36 (m, 2H), 4.42-4.44 (m, 1H), 4.92 (m, 1H), 7.23-7.25 (m, 2H), 7.34-7.36 (m, 2H), 7.50-7.52 (m, 2H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 8.07-8.20 (m, 4H); ^{13}C NMR (DMSO-d^6): δ 24.49, 25.44,

25.98, 26.06, 62.65, 70.90, 72.82, 73.03, 73.51, 73.87, 105.07, 108.86, 109.07, 121.46, 122.04, 123.43, 125.24, 125.40, 125.88, 126.00, 126.65, 126.80, 128.57, 128.69, 130.27, 130.81, 130.92, 131.20, 131.75, 132.04, 146.69, 147.75; ^{31}P NMR (DMSO-d^6): δ 160.52; HRMS (APCI) calcd for $C_{32}H_{32}O_8P$ (M^++1): 575.1829, found: 575.1797□

The above procedure was followed using **8b** and R-BINOL. After workup, it gave **4c.** mp 134-135 ^{o}C; $[\alpha]_D^{25}$ = -325.42 (*c* 1.05, THF); ^{1}H NMR (DMSO-d^6): δ 1.35-1.72 (m, 20H), 3.57 (d, *J* = 13.2 Hz, 1H), 3.67 (d, *J* = 9.2 Hz, 1H), 3.84 (d, *J* = 12.8 Hz, 1H), 4.00 (t, *J* = 9.2 Hz, 1H), 4.41 (d, *J* = 7.6 Hz, 1H), 4.72 (d, *J* = 8.0 Hz, 1H), 4.94 (d, *J* = 10.4 Hz, 1H), 7.20-7.24 (m, 2H), 7.34-7.37 (m, 2H), 7.48-7.57 (m, 4H), 8.08 (m, 3H), 8.17-8.20 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (DMSO-d^6): δ 23.24, 23.36, 23.50, 24.56, 33.77, 35.21, 35.33, 35.52, 62.69, 70.06, 71.10, 71.29, 73.13, 73.53, 104.18, 109.29, 109.67, 121.37, 121.99, 122.08, 123.52, 125.23, 125.48, 125.84, 126.01, 126.68, 126.86, 128.66, 128.72, 129.98, 130.87, 131.05, 131.26, 131.79, 132.04, 146.54, 147.10; ^{31}P NMR (DMSO-d^6): δ 153.43; HRMS (APCI) calcd for $C_{38}H_{40}O_8P$ (M^++1): 655.2455, found: 655.2434□

The above procedure was followed using **8b** and S-BINOL. After workup, it gave **4d.** mp 143-144 ^{o}C; $[\alpha]_D^{25}$ = +151.82 (*c* 1.23, THF); ^{1}H NMR (DMSO-d^6): δ 1.33-1.85 (m, 20H), 3.58 (d, *J* = 13.2 Hz, 1H), 3.79-3.85 (m, 2H), 4.29-4.41 (m, 3H), 4.91 (d, *J* = 8.4 Hz, 1H), 7.21-7.23 (m, 2H), 7.34-7.38 (m, 2H), 7.51 (m, 2H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 8.06-8.10 (m, 2H), 8.14 (d, *J* = 9.2 Hz, 1H), 8.17 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (DMSO-d^6): δ 23.19, 23.34, 23.50, 24.56, 33.78, 34.56, 35.01, 35.48, 62.77, 70.58, 72.96, 73.18, 73.69, 104.72, 109.62, 109.72, 121.32, 121.49, 125.23, 125.42, 125.90, 126.01, 126.65, 126.78, 128.60, 128.67, 130.33, 130.80, 130.92, 131.21, 131.74, 132.02, 146.63; ^{31}P NMR (DMSO-d^6): δ 154.91; HRMS (APCI) calcd for $C_{38}H_{40}O_8P$ (M^++1): 655.2455, found: 655.2470□

The above procedure was followed using **9a** and R-BINOL. After workup, it gave **5a.** mp 113-114 ^{o}C; $[\alpha]_D^{25}$ = -303.13 (*c* 1.14, THF); ^{1}H NMR (DMSO-d^6): δ 1.28 (s, 3H), 1.33 (s, 3H), 1.38 (s, 3H), 1.42 (s, 3H), 3.74-3.77 (m, 1H), 3.96-4.02 (m, 2H), 4.15-4.18 (m, 1H), 4.69 (d, *J* = 9.6 Hz, 1H), 4.81 (d, *J* = 3.6 Hz, 1H), 5.80 (d, *J* = 3.2 Hz, 1H), 7.21-7.23 (m, 2H), 7.34-7.37 (m, 2H), 7.49-7.53 (m, 2H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 8.08-8.21 (m, 4H); ^{13}C NMR (DMSO-d^6): δ 25.33, 26.09, 26.54, 26.66, 66.41, 71.72, 77.69, 77.82, 80.12, 83.68, 104.53, 108.62,

111.59, 121.55, 121.85, 125.25, 125.51, 125.98, 126.05, 126.69, 126.86, 128.68, 128.74, 130.40, 130.77, 131.06, 131.28, 131.64, 131.99, 146.52, 147.66; ^{31}P NMR (DMSO-d^6): δ 147.75; HRMS (APCI) calcd for $C_{32}H_{32}O_8P$ (M^++1): 575.1829, found: 575.1802□

The above procedure was followed using **9a** and S-BINOL. After workup, it gave **5b.** mp 107-108 ^{o}C; $[\alpha]_D^{25}$ = +291.92 (*c* 1.11, THF); ^{1}H NMR (DMSO-d^6): δ 1.20 (s, 3H), 1.38 (s, 3H), 1.39 (s, 3H), 1.42 (s, 3H), 3.80-3.83 (m, 1H), 3.96-4.00 (m, 1H), 4.08-4.10 (m, 1H), 4.22-4.25 (m, 1H), 4.59 (d, *J* = 3.6 Hz, 1H), 4.79-4.82 (m, 1H), 5.82 (d, *J* = 3.6 Hz, 1H), 7.20-7.22 (m, 2H), 7.35-7.36 (m, 2H), 7.49-7.52 (m, 2H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 8.08-8.21 (m, 4H); ^{13}C NMR (DMSO-d^6): δ 25.20, 25.86, 26.43, 26.55, 66.21, 71.88, 77.16, 77.31, 80.18, 83.74, 104.54, 108.57, 111.40, 121.56, 121.64, 121.95, 123.35, 125.30, 125.49, 125.95, 126.75, 126.87, 128.66, 128.74, 130.30, 130.82, 131.03, 131.28, 131.74, 132.00, 146.65, 147.25; ^{31}P NMR (DMSO-d^6): δ 152.58; HRMS (APCI) calcd for $C_{32}H_{32}O_8P$ (M^++1): 575.1829, found: 575.1795□

The above procedure was followed using **9b** and R-BINOL. After workup, it gave **5c.** mp 121-122 ^{o}C; $[\alpha]_D^{25}$ = -267.67 (*c* 1.13, THF); ^{1}H NMR (DMSO-d^6): δ 1.33-1.59 (m, 20H), 3.74 (m, 1H), 3.97-4.12 (m, 3H), 4.79 (m, 2H), 5.85 (d, *J* = 3.6 Hz, 1H), 7.22-7.24 (m, 2H), 7.35-7.37 (m, 2H), 7.50-7.54 (m, 3H), 7.65 (d, *J* = 8.4 Hz, 1H), 8.08–8.15 (m, 3H), 8.18 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (DMSO-d^6): δ 22.39, 23.22, 23.58, 24.30, 24.65, 32.39, 33.47, 34.46, 35.17, 35.43, 35.91, 36.03, 66.34, 71.43, 77.77, 77.94, 80.40, 83.29, 104.31, 105.33, 109.10, 112.13, 121.38, 121.73, 121.86, 123.53, 125.22, 125.49, 125.91, 126.04, 126.67, 126.85, 128.67, 130.36, 130.79, 131.03, 131.25, 131.70, 132.02, 146.58, 147.47; ^{31}P NMR (DMSO-d^6): δ 149.34; HRMS (APCI) calcd for $C_{38}H_{40}O_8P$ (M^++1): 655.2455, found: 655.2463□

The above procedure was followed using **9b** and S-BINOL. After workup, it gave **5d.** mp 118-119 ^{o}C; $[\alpha]_D^{25}$ = +262.74 (*c* 1.08, THF); ^{1}H NMR (DMSO-d^6): δ 1.33-1.68 (m, 20H), 3.81-3.83 (m, 1H), 4.01-4.06 (m, 2H), 4.25-4.27 (m, 1H), 4.57 (m, 1H), 4.71 (d, *J* = 9.6 Hz, 1H), 5.87 (d, *J* = 3.6 Hz, 1H), 7.20-7.22 (m, 2H), 7.33-7.36 (m, 2H), 7.50-7.52 (m, 2H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 8.06–8.10 (m, 2H), 8.13 (d, *J* = 8.8 Hz, 1H), 8.18 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (DMSO-d^6): δ 23.19, 23.43, 23.51, 23.62, 24.31, 24.63, 34.34, 34.91, 35.74, 35.99, 66.18, 71.63, 77.49, 77.64, 80.33, 83.36, 104.28, 109.04, 111.81, 121.53, 121.92, 125.25, 125.44, 125.97,

126.70, 126.81, 128.60, 128.72, 130.38, 130.79, 131.00, 131.26, 131.77, 132.01, 146.69; ^{31}P NMR (DMSO-d^6): δ 149.05; HRMS (APCI) calcd for $C_{38}H_{40}O_8P$ (M^++1): 655.2455, found: 655.2507□

The above procedure was followed using **10a** and R-BINOL. After workup, it gave **6a.** mp 76-77 ^{o}C; $[\alpha]_D^{25}$ = -248.68 (*c* 0.98, THF); ^{1}H NMR (DMSO-d^6): δ 1.28 (s, 3H), 1.30 (s, 3H), 1.33 (s, 3H), 1.44 (s, 3H), 3.74-3.78 (m, 1H), 3.98-4.08 (m, 2H), 4.20-4.23 (m, 1H), 4.53-4.60 (m, 2H), 5.73 (d, *J* = 3.6 Hz, 1H), 7.19-7.21 (m, 2H), 7.34-7.38 (m, 2H), 7.49-7.51 (m, 3H), 7.60 (d, *J* = 8.8 Hz, 1H), 8.07-8.19 (m, 4H); ^{13}C NMR (DMSO-d^6): δ 25.00, 26.15, 26.54, 26.63, 64.67, 73.88, 73.98, 74.71, 78.11, 78.44, 103.54, 108.89, 112.49, 121.62, 121.73, 121.88, 123.41, 125.21, 125.42, 125.90, 125.99, 126.67, 126.81, 128.61, 128.70, 130.12, 130.77, 130.95, 131.22, 131.77, 132.01, 146.70, 147.37; ^{31}P NMR (DMSO-d^6): δ 148.81; HRMS (APCI) calcd for $C_{32}H_{32}O_8P$ (M^++1): 575.1829, found: 575.1786□

The above procedure was followed using **10a** and S-BINOL. After workup, it gave **6b.** mp 111-112 ^{o}C; $[\alpha]_D^{25}$ = +318.37 (*c* 1.15, THF); ^{1}H NMR (DMSO-d^6): δ 1.33 (s, 3H), 1.37 (s, 3H), 1.38 (s, 3H), 1.46 (s, 3H), 3.73-3.76 (m, 1H), 3.96-4.01 (m, 2H), 4.17 (t, *J* = 5.6 Hz, 1H), 4.55-4.59 (m, 1H), 4.81 (t, *J* = 4.2 Hz, 1H), 5.75 (d, *J* = 3.2 Hz, 1H), 7.20-7.24 (m, 2H), 7.33-7.36 (m, 2H), 7.48-7.58 (m, 4H), 8.06-8.19 (m, 4H); ^{13}C NMR (DMSO-d^6): δ 25.17, 26.28, 26.54, 26.60, 65.11, 74.14, 74.30, 74.82, 77.41, 78.54, 103.44, 109.01, 112.29, 121.58, 121.84, 122.35, 123.56, 125.13, 125.43, 125.87, 126.05, 126.54, 126.80, 128.59, 128.71, 129.89, 130.93, 131.24, 131.67, 132.02, 146.71, 147.51; ^{31}P NMR (DMSO-d^6): δ 151.85; HRMS (APCI) calcd for $C_{32}H_{32}O_8P$ (M^++1): 575.1829, found: 575.1864□

The above procedure was followed using **10b** and R-BINOL. After workup, it gave **6c.** mp 110-111 ^{o}C; $[\alpha]_D^{25}$ = -192.45 (*c* 1.00, THF); ^{1}H NMR (DMSO-d^6): δ 1.31-1.68 (m, 20H), 3.70-3.74 (m, 1H), 3.97-4.00 (m, 1H), 4.07-4.10 (m, 1H), 4.14-4.17 (m, 1H), 4.52-4.54 (m, 1H), 4.60 (t, *J* = 4.0 Hz, 1H), 5.75 (d, *J* = 3.6 Hz, 1H), 7.20-7.22 (m, 2H), 7.34-7.37 (m, 2H), 7.49-7.56 (m, 4H), 8.07–8.13 (m, 3H), 8.18 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (DMSO-d^6): δ 23.38, 24.32, 24.61, 34.20, 35.54, 35.83, 64.83, 74.71, 78.03, 78.25, 103.32, 109.42, 113.12, 121.52, 121.80, 122.00, 123.40, 125.15, 125.37, 125.89, 126.00, 126.61, 126.78, 128.61, 128.69, 130.07, 130.77, 130.92, 131.16, 131.77, 132.03, 146.90, 147.44; ^{31}P NMR (DMSO-d^6): δ 148.71; HRMS (APCI) calcd for

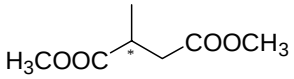
$C_{38}H_{40}O_8P$ (M^++1): 655.2455, found: 655.2395

The above procedure was followed using **10b** and S-BINOL. After workup, it gave **6d.** mp 131-132 ^oC; $[\alpha]_D^{25}$ = +358.48 (*c* 1.00, THF); ^1H NMR (DMSO-d^6): δ 1.37-1.65 (m, 20H), 3.70-3.74 (m, 1H), 3.92-3.95 (m, 1H), 3.98-4.02 (m, 1H), 4.15-4.18 (m, 1H), 4.60-4.66 (m, 1H), 4.82 (t, *J* = 4.0 Hz, 1H), 5.77 (d, *J* = 3.6 Hz, 1H), 7.20-7.25 (m, 2H), 7.33-7.39 (m, 2H), 7.48-7.57 (m, 4H), 8.07–8.09 (m, 3H), 8.18 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (DMSO-d^6): δ 23.46, 24.38, 24.71, 34.38, 35.63, 35.83, 65.25, 74.51, 74.70, 77.41, 78.18, 103.09, 109.55, 112.88, 121.33, 121.94, 122.46, 123.59, 125.15, 125.44, 125.83, 126.05, 126.57, 126.84, 128.60, 128.72, 129.75, 130.99, 131.21, 131.68, 132.05, 146.75, 147.48; ^{31}P NMR (DMSO-d^6): δ 153.48; HRMS (APCI) calcd for $C_{38}H_{40}O_8P$ (M^++1): 655.2455, found: 655.2416

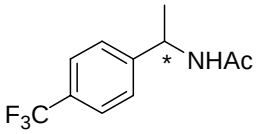
(B) General procedure for asymmetric hydrogenation

In a nitrogen-filled glovebox, to a solution of $[Rh(COD)_2]BF_4$ (2.0 mg, 0.005 mmol) in anhydrous and degassed CH_2Cl_2 (1 mL) was added ligand (0.011 mmol). After stirring the mixture for 30 min, a substrate (0.5 mmol) dissolved in CH_2Cl_2 (1 mL) was added. The reaction mixture was transferred to a Parr stainless autoclave. The autoclave was purged three times with hydrogen and the pressure was set to 1.2 or 10 atm, the hydrogenation was performed at room temperature for 12 h. After carefully releasing the hydrogen, the reaction mixture was passed through a short silica-gel plug to remove the catalyst. The resulting solution was used directly for chiral GC to measure enantiomeric excesses.

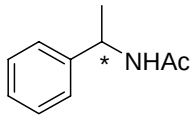
(C) GC Conditions for Determination of enantiomeric excesses of hydrogenation products



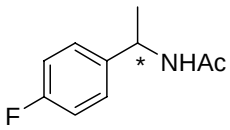
The ee's were determined by GC analysis using a Supelco γ-DEX 225 column, 30m x 0.25mm. Oven temperature is 80 ^oC. t(S)=14.4, t(R)=15.3. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.[2]



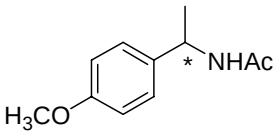
The ee's were determined by GC analysis using a Supelco Chiral select 1000 column, 30m x 0.25mm. Oven temperature is 150 ^{o}C. t(S)=9.7, t(R)=10.3. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.[3]



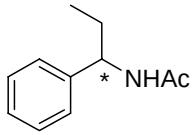
The ee's were determined by GC analysis using a Supelco Chiral select 1000 column, 30m x 0.25mm. Oven temperature is 130 ^{o}C. t(S)=16.7, t(R)=18.3. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.[3]



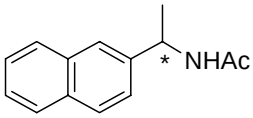
The ee's were determined by GC analysis using a Supelco Chiral select 1000 column, 30m x 0.25mm. Oven temperature is 140 ^{o}C. t(S)=12.9, t(R)=13.6. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.[3]



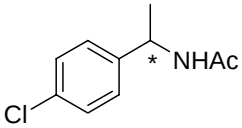
The ee's were determined by GC analysis using a Supelco Chiral select 1000 column, 30m x 0.25mm. Oven temperature is 140 ^{o}C. t(S)=45.0, t(R)=46.9. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.[3]



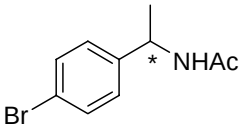
The ee's were determined by GC analysis using a Supelco Chiral select 1000 column, 30m x 0.25mm. Oven temperature is 130 ^{o}C. t(S)=20.9, t(R)=22.0. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.[3]



The ee's were determined by GC analysis using a Chrompack chiral fused silica 25m x 0.25mm Chirasil-L-Val column. Oven temperature is 170 ^{o}C. t(S)=22.4, t(R)=24.0. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.[3]



The ee's were determined by GC analysis using a Supleco Chiral select 1000 column, 30m x 0.25mm. Oven temperature is 150 ^{o}C. t(S)=24.80, t(R)=25.50. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.[3]



The ee's were determined by GC analysis using a Supelco Chiral select 1000 column, 30m x 0.25mm. Oven temperature is 150 ^{o}C. t(S)=43.2, t(R)=45.1. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.[3]

References

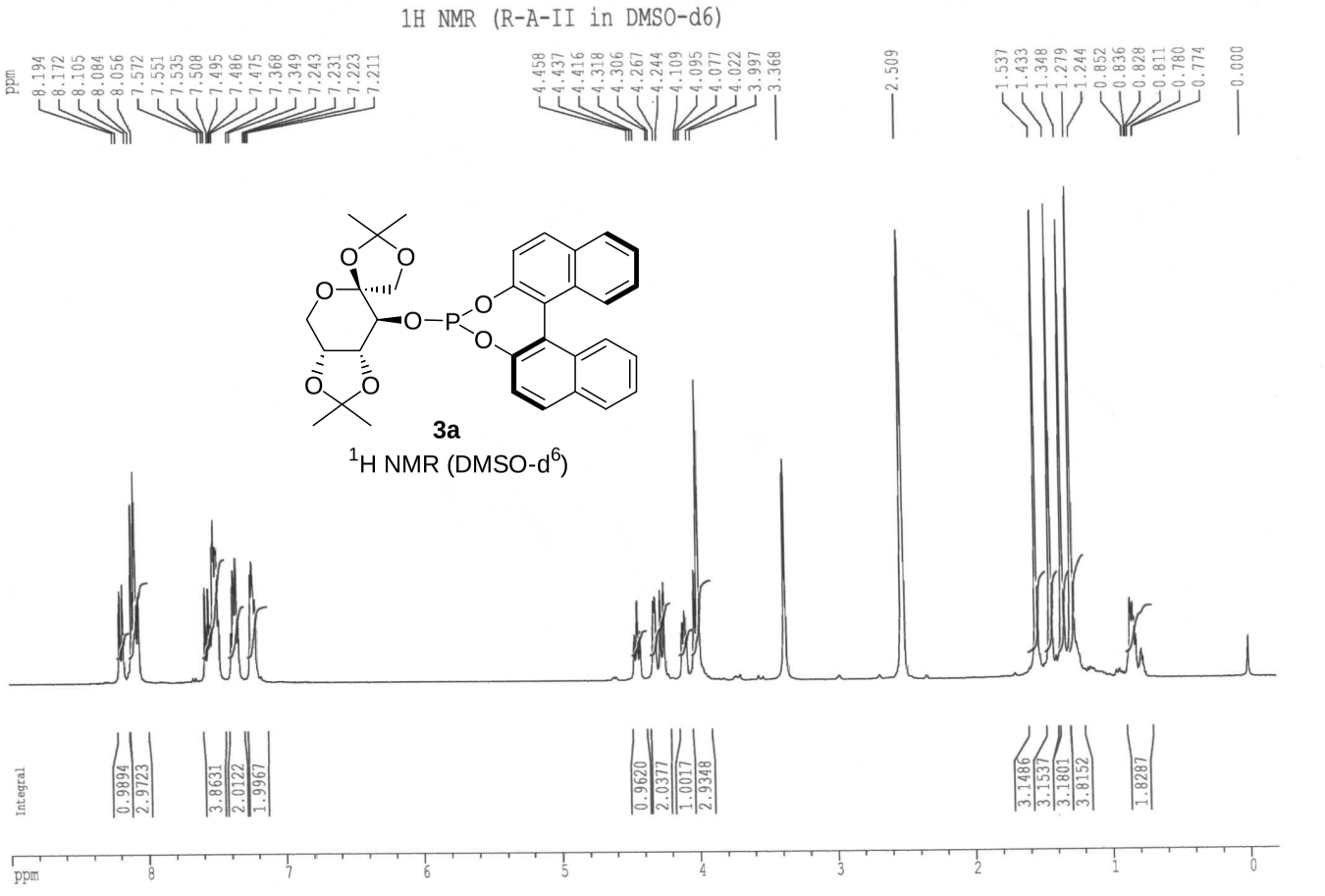
(1) (a) Burk, M. J.; Casy, G.; Johnson, N. B. *J. Org. Chem.* **1998**, *63*, 6084. (b) Zhang,

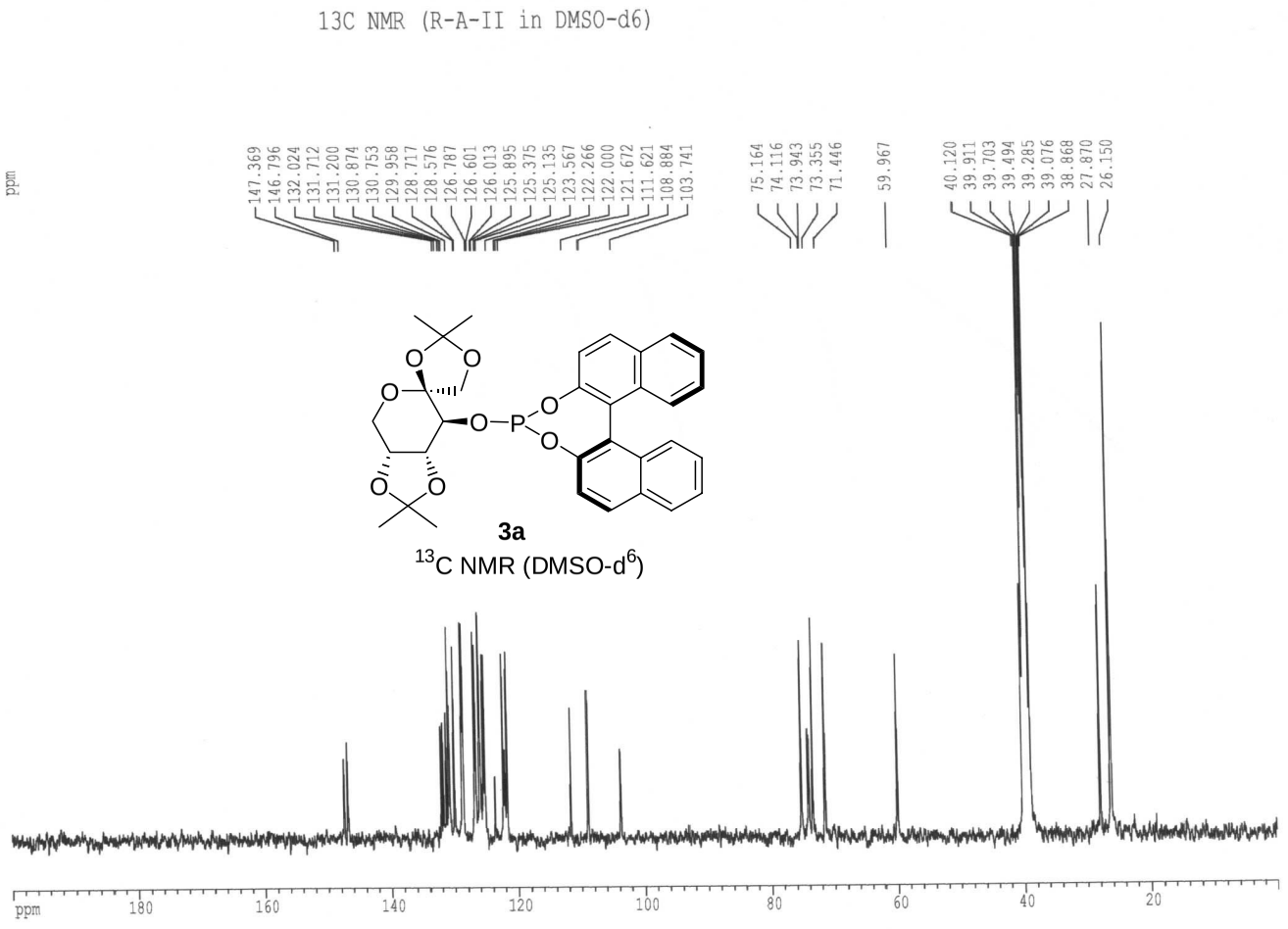
Z.; Zhu, G.; Jiang, Q.; Xiao, D.; Zhang, X. *J. Org. Chem.* **1999**, *64*, 1774. (c) Hockett, R. C.; Miller, R. E.; Scattergood, A. *J. Am. Chem. Soc*. **1949**, *71*, 3072; (d) James, K.; Tatchell, A. R.; Ray, P. K. *J. Chem. Soc.(C)*, **1967**, 2681; (e) Singh, P. P.; Gharia, M. M.; Dasgupta, F.; Srivastava, H. C. *Tetrahedron Lett*. **1977**, 439; (h) Wang, Z. X.; Tu, Y.; Frohn, M.; Zhang, J. R.; Shi, Y. *J. Am. Chem. Soc*. **1997**, *119*, 11224.

(2) Berens, U.; Burk, M. J.; Gerlach, A.; Hems, W. *Angew. Chem. Int. Ed.* **2000,** *39*, 1981.

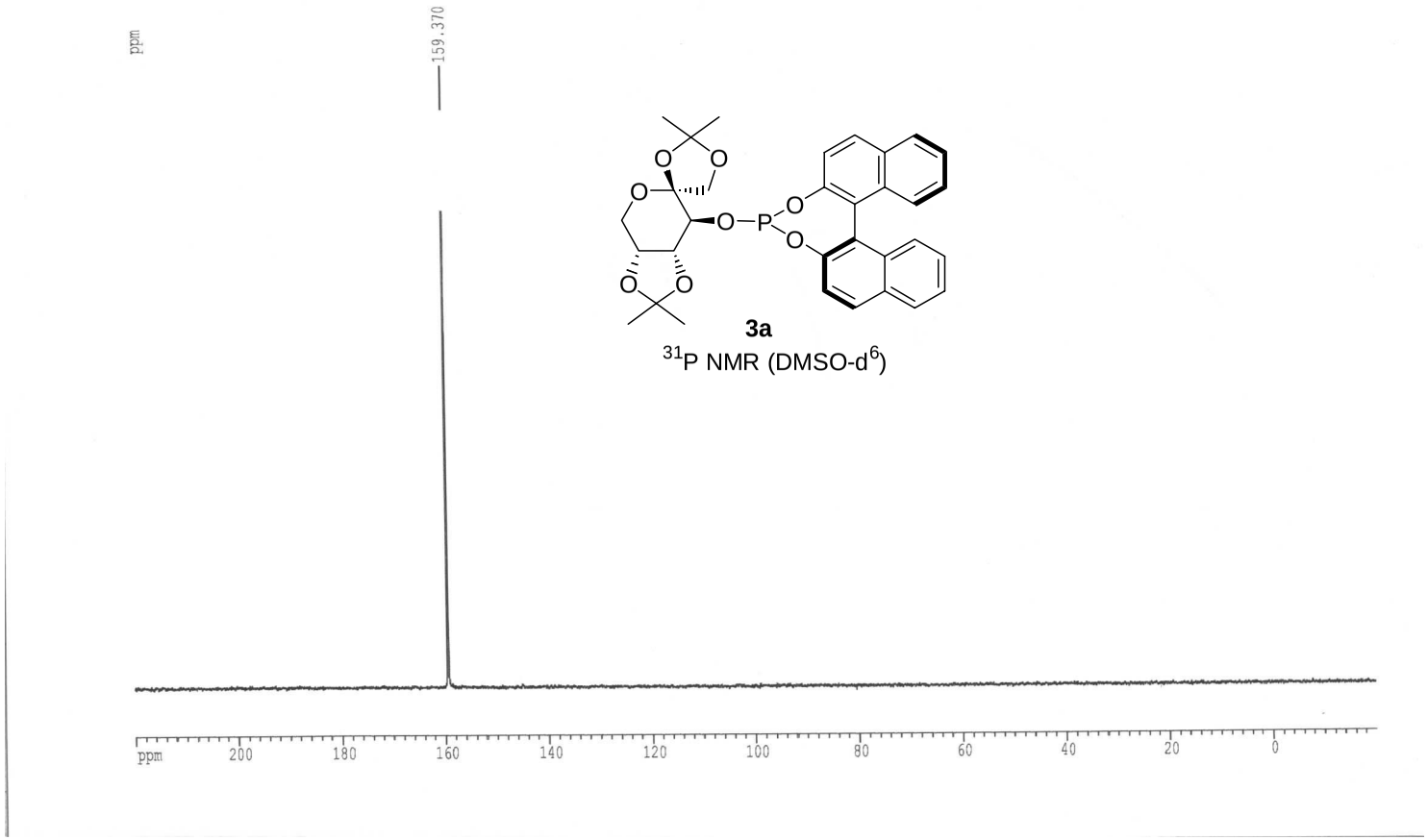
(3) (a)Burk, M. J.; Wang, Y. M.; Lee, J. R.; *J. Am. Chem. Soc.* **1996**, *118*, 5142. (b) Zhu, G.; Casalnuovo, A. L.; Zhang, X. *J. Org. Chem.* **1998**, *63*, 8100.

(D) NMR for monophosphite ligands 3-6


1H NMR (R-A-II in DMSO-d6)
ppm
8.194
8.172
8.105
8.084
8.056
7.572
7.551
7.535
7.508
7.495
7.486
7.475
7.368
7.349
7.243
7.231
7.223
7.211
4.458
4.437
4.416
4.318
4.306
4.267
4.244
4.109
4.095
4.077
4.022
3.997
3.368
2.509
1.537
1.433
1.348
1.279
1.244
0.852
0.836
0.828
0.811
0.780
0.774
0.000
3a
1H NMR (DMSO-d6)
Integral
0.9894
2.9723
3.8631
2.0122
1.9967
0.9620
2.0377
1.0017
2.9348
3.1486
3.1537
3.1801
3.8152
1.8287
ppm
8
7
6
5
4
3
2
1
0

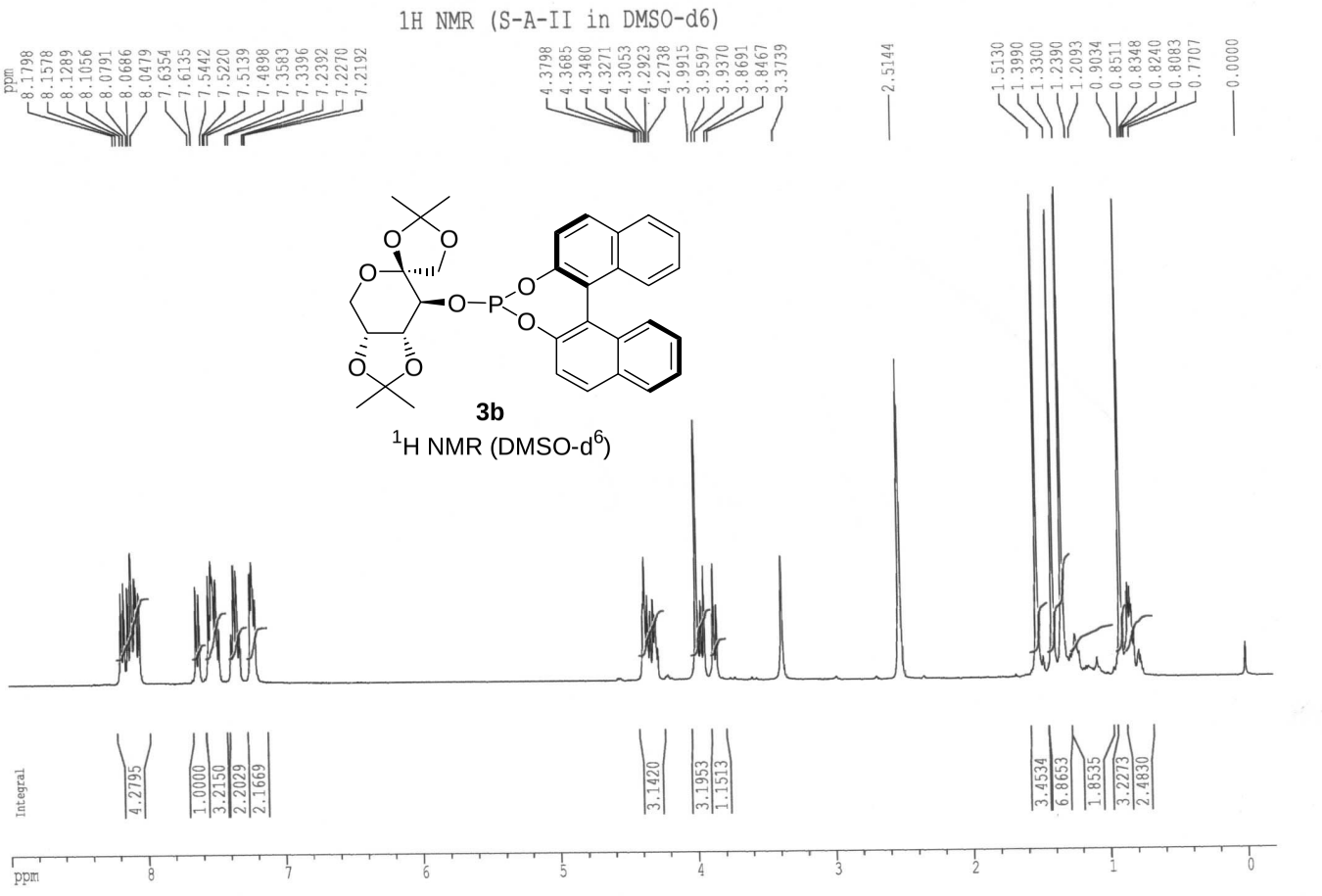

13C NMR (R-A-II in DMSO-d6)
ppm
147.369
146.796
132.024
131.712
131.200
130.874
130.753
129.958
128.717
128.576
126.787
126.601
126.013
125.895
125.375
125.135
123.567
122.266
122.000
121.672
111.621
108.884
103.741
75.164
74.116
73.943
73.355
71.446
59.967
40.120
39.911
39.703
39.494
39.285
39.076
38.868
27.870
26.150
O
O
O
O
O
P
O
O
O
O
3a
13C NMR (DMSO-d6)
ppm
180
160
140
120
100
80
60
40
20

31P NMR (R-A-II in DMSO-d6)



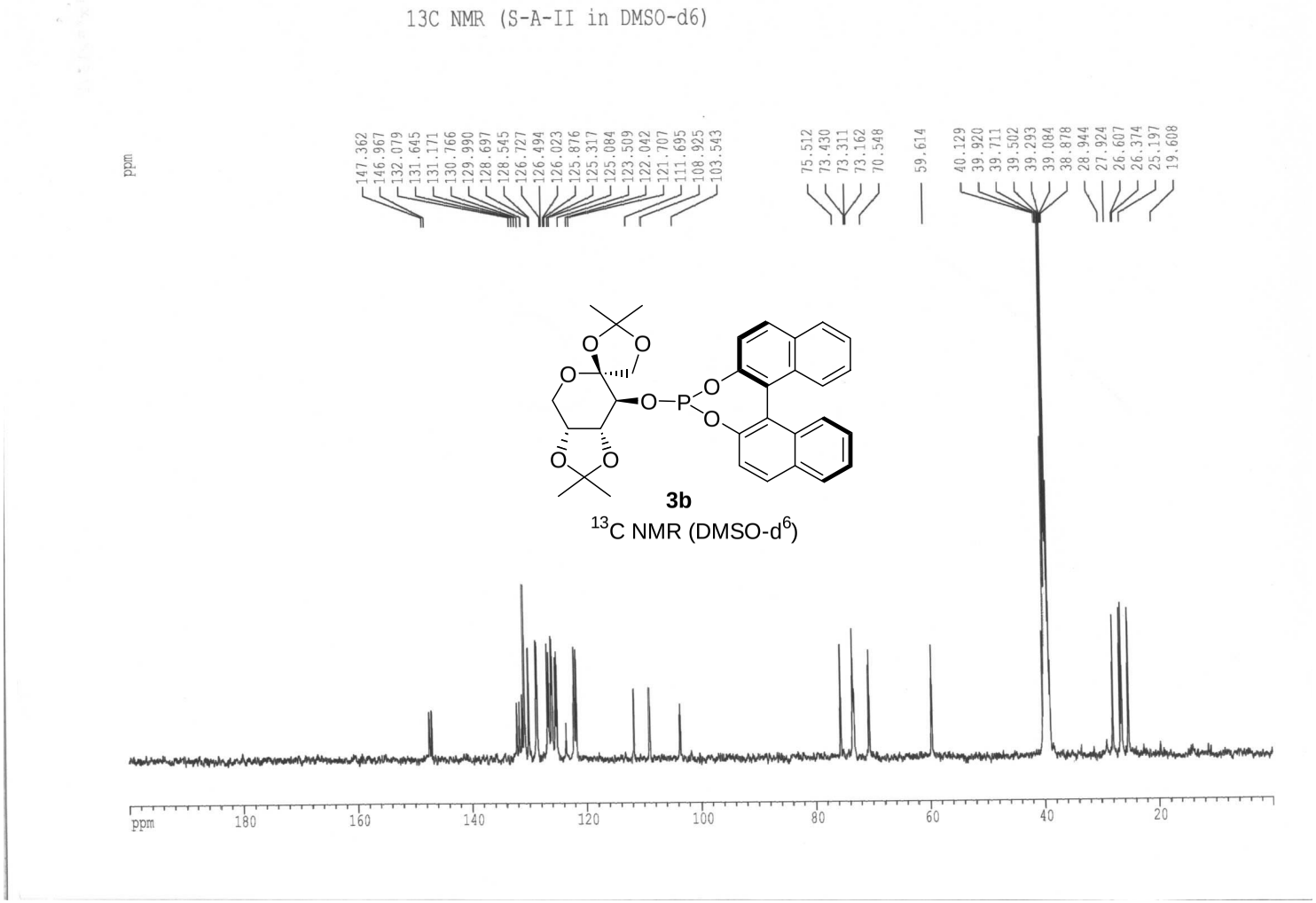
3a

^{31}P NMR (DMSO-d^{6})



3b

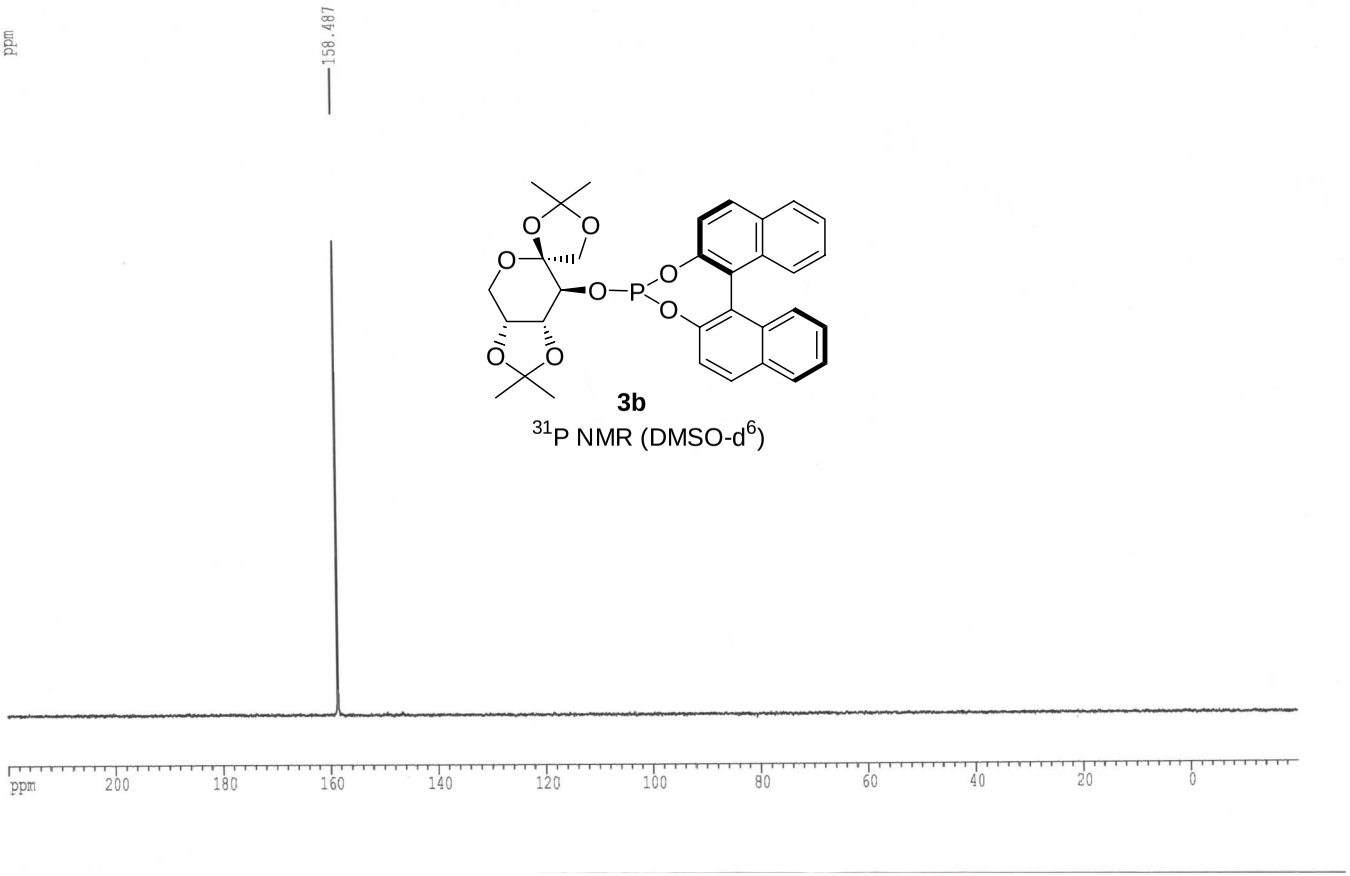
^{1}H NMR (DMSO-d^6)



3b

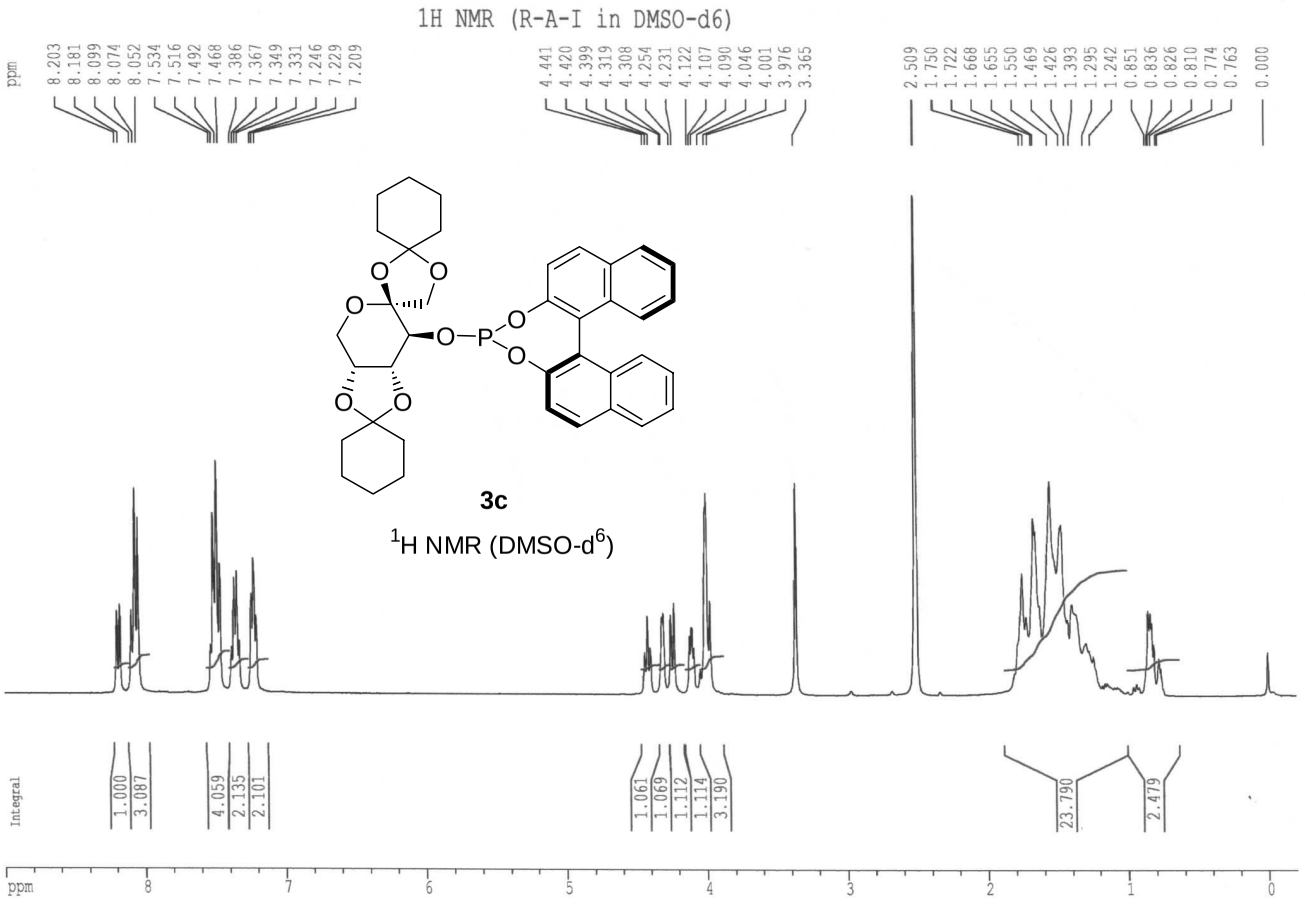
^{13}C NMR (DMSO-d^6)

31P NMR (S-A-II in DMSO-d6)



3b

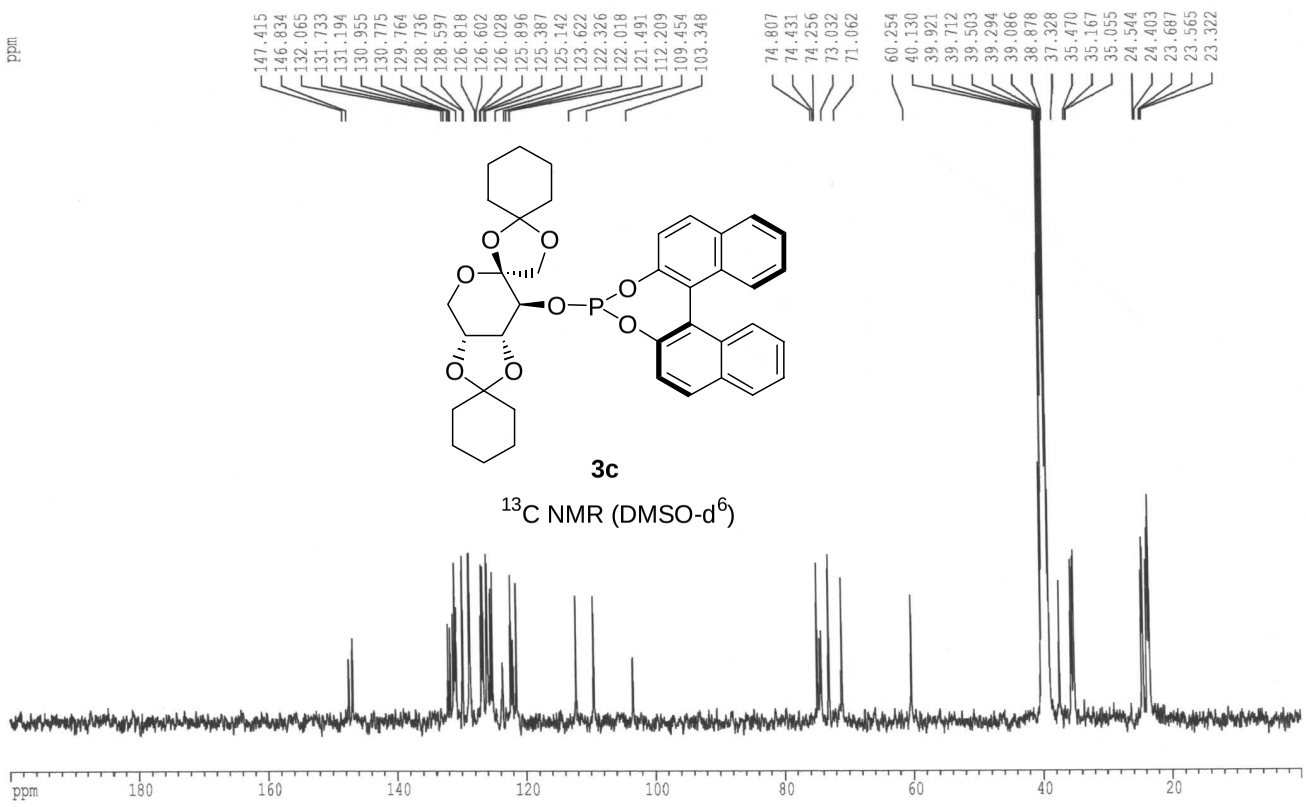
^{31}P NMR (DMSO-d^{6})



3c

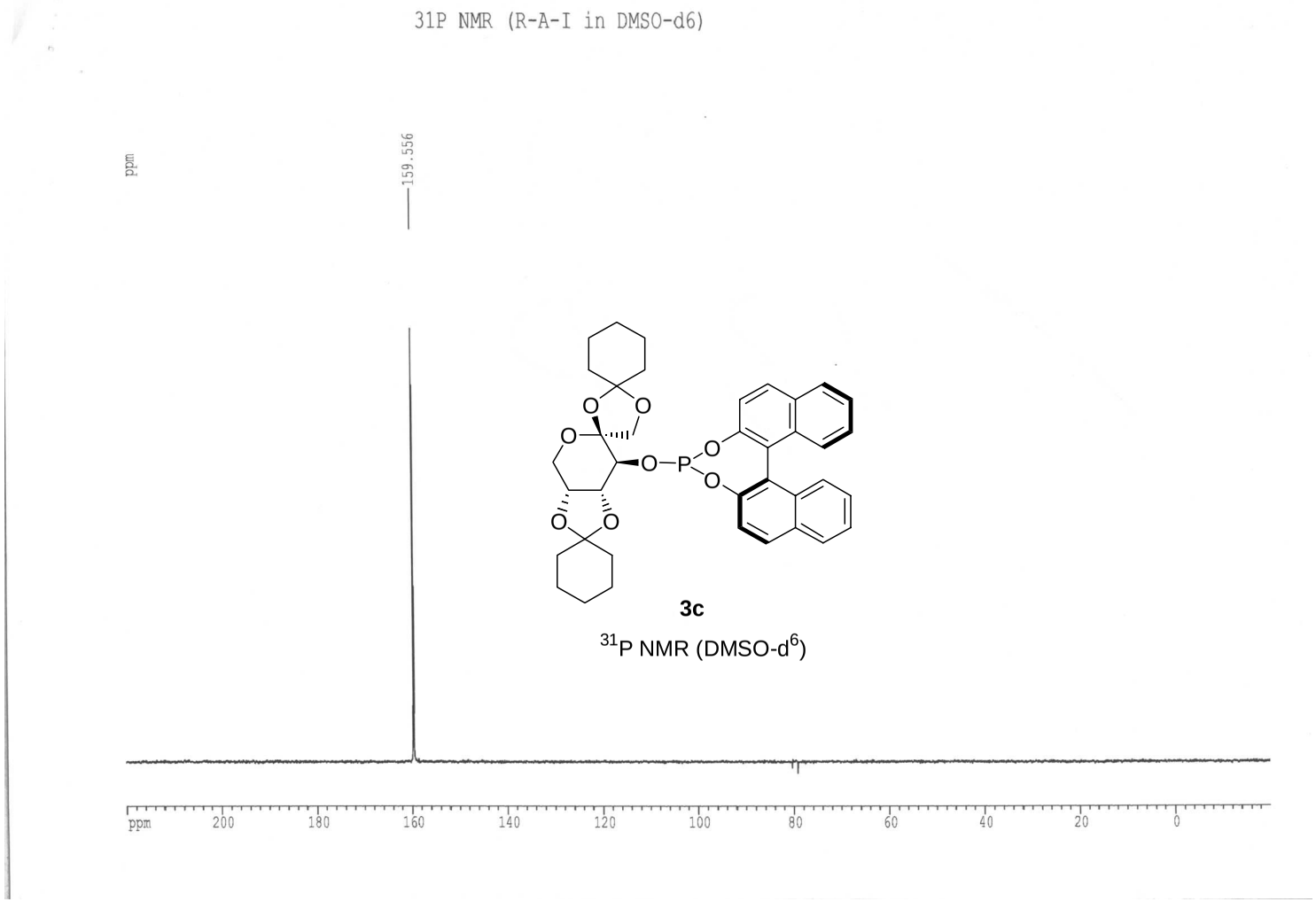
^{1}H NMR (DMSO-d^{6})

13C NMR (R-A-I in DMSO-d6)



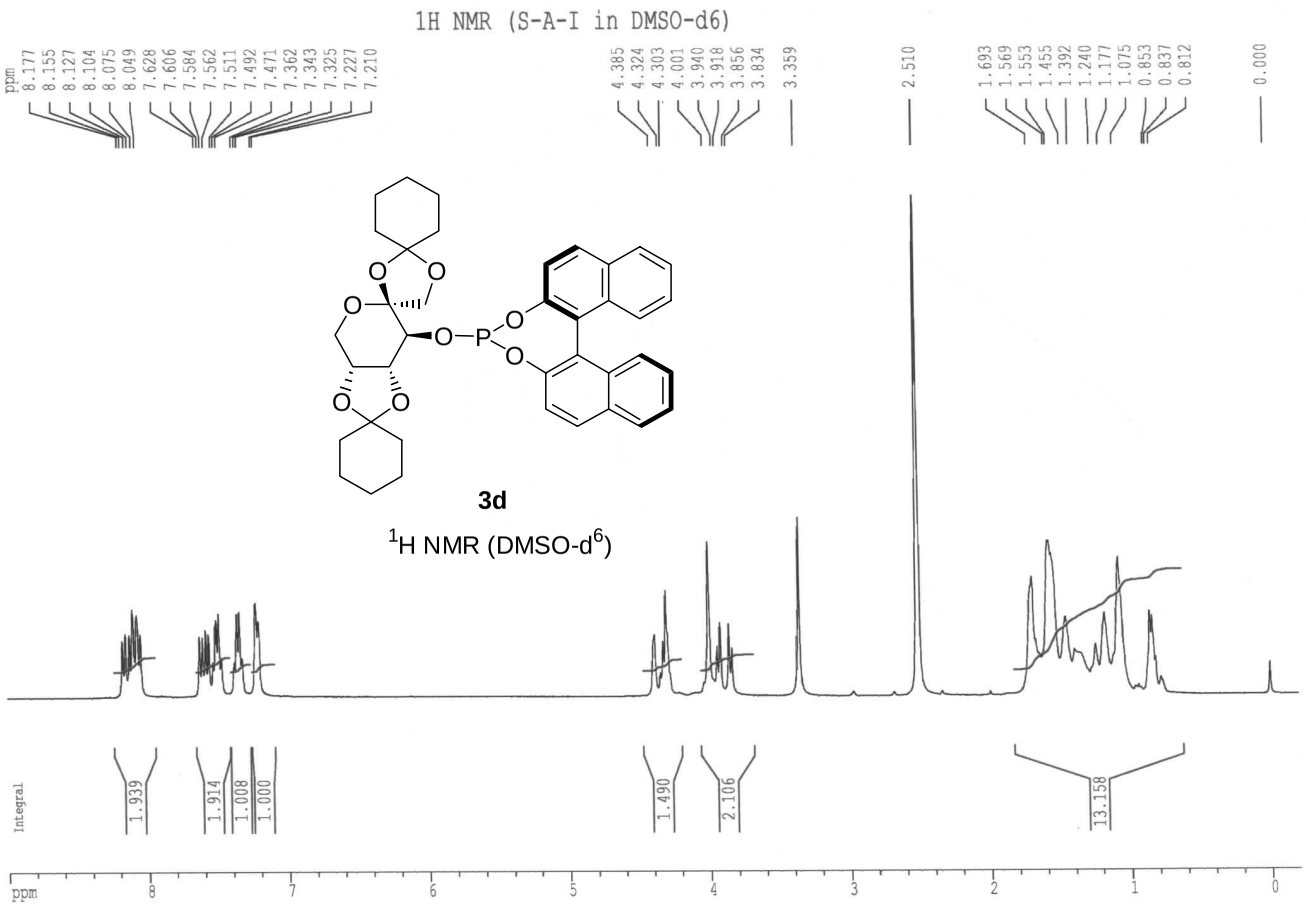
3c

^{13}C NMR (DMSO-d^{6})

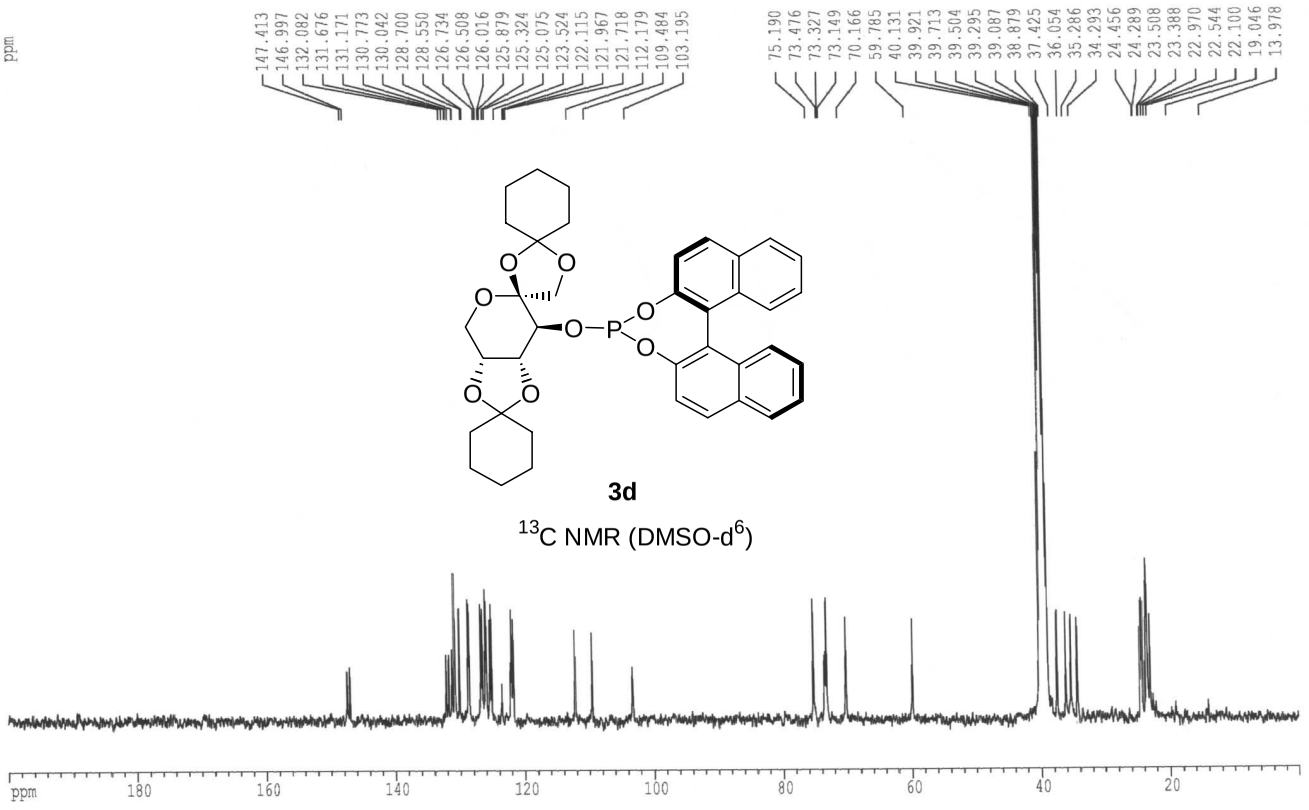


3c

^{31}P NMR (DMSO-d^{6})

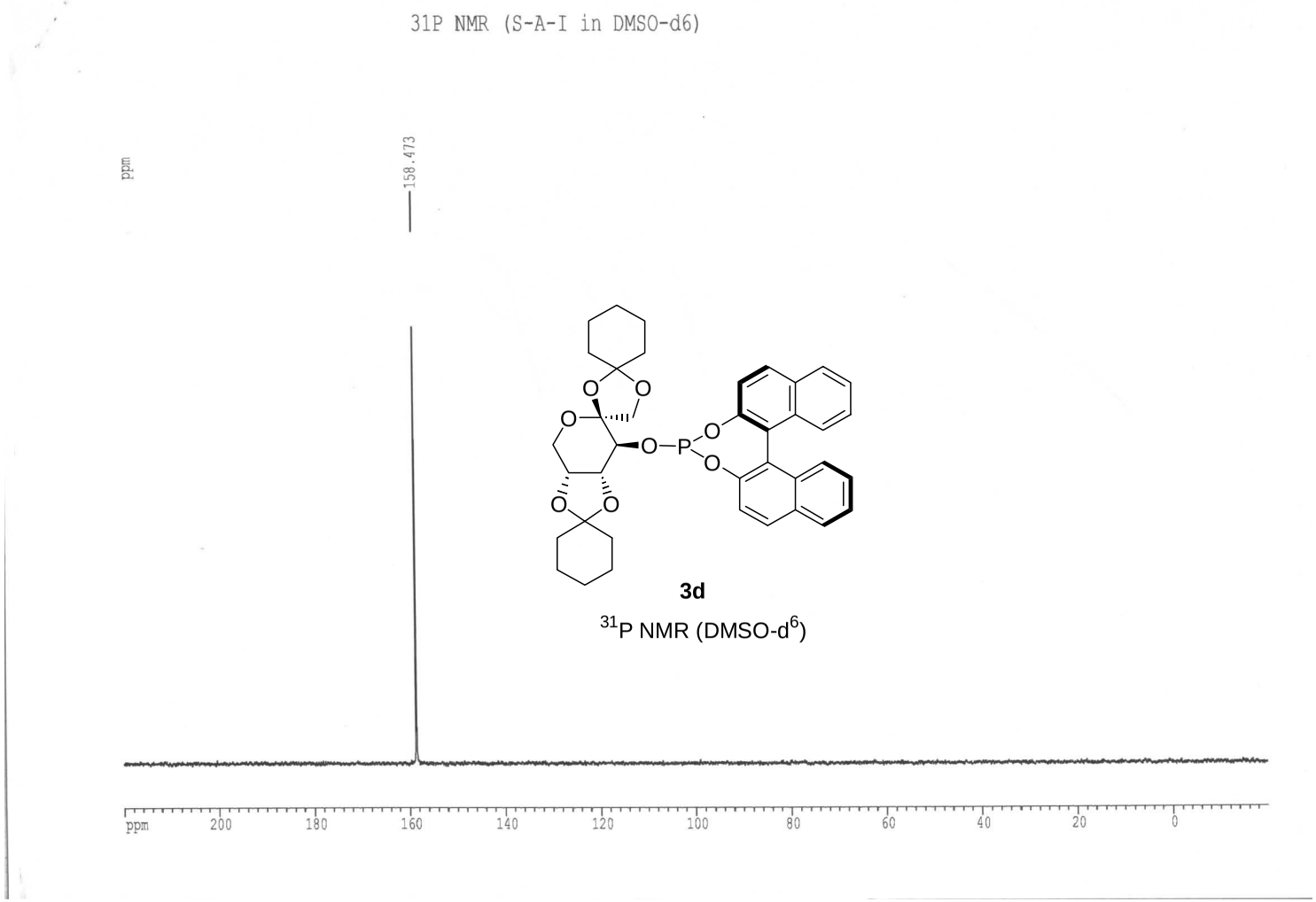

1H NMR (S-A-I in DMSO-d6)
ppm
8.177
8.155
8.127
8.104
8.075
8.049
7.628
7.606
7.584
7.562
7.511
7.492
7.471
7.362
7.343
7.325
7.227
7.210
4.385
4.324
4.303
4.001
3.940
3.918
3.856
3.834
3.359
2.510
1.693
1.569
1.553
1.455
1.392
1.240
1.177
1.075
0.853
0.837
0.812
0.000
3d
1H NMR (DMSO-d6)
Integral
1.939
1.914
1.008
1.000
1.490
2.106
13.158
ppm
8
7
6
5
4
3
2
1
0

13C NMR (S-A-I in DMSO-d6)



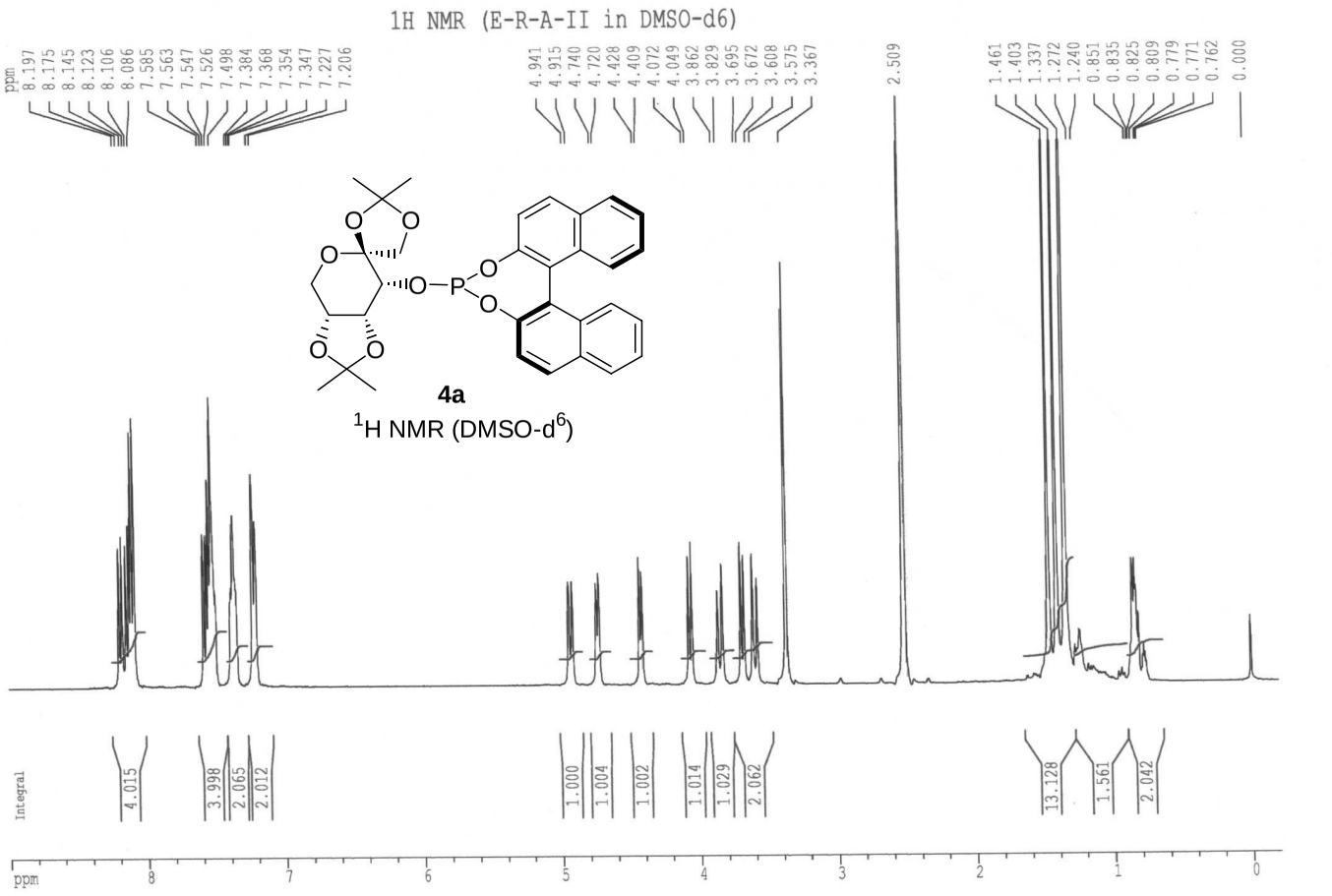
3d

^{13}C NMR (DMSO-d^{6})



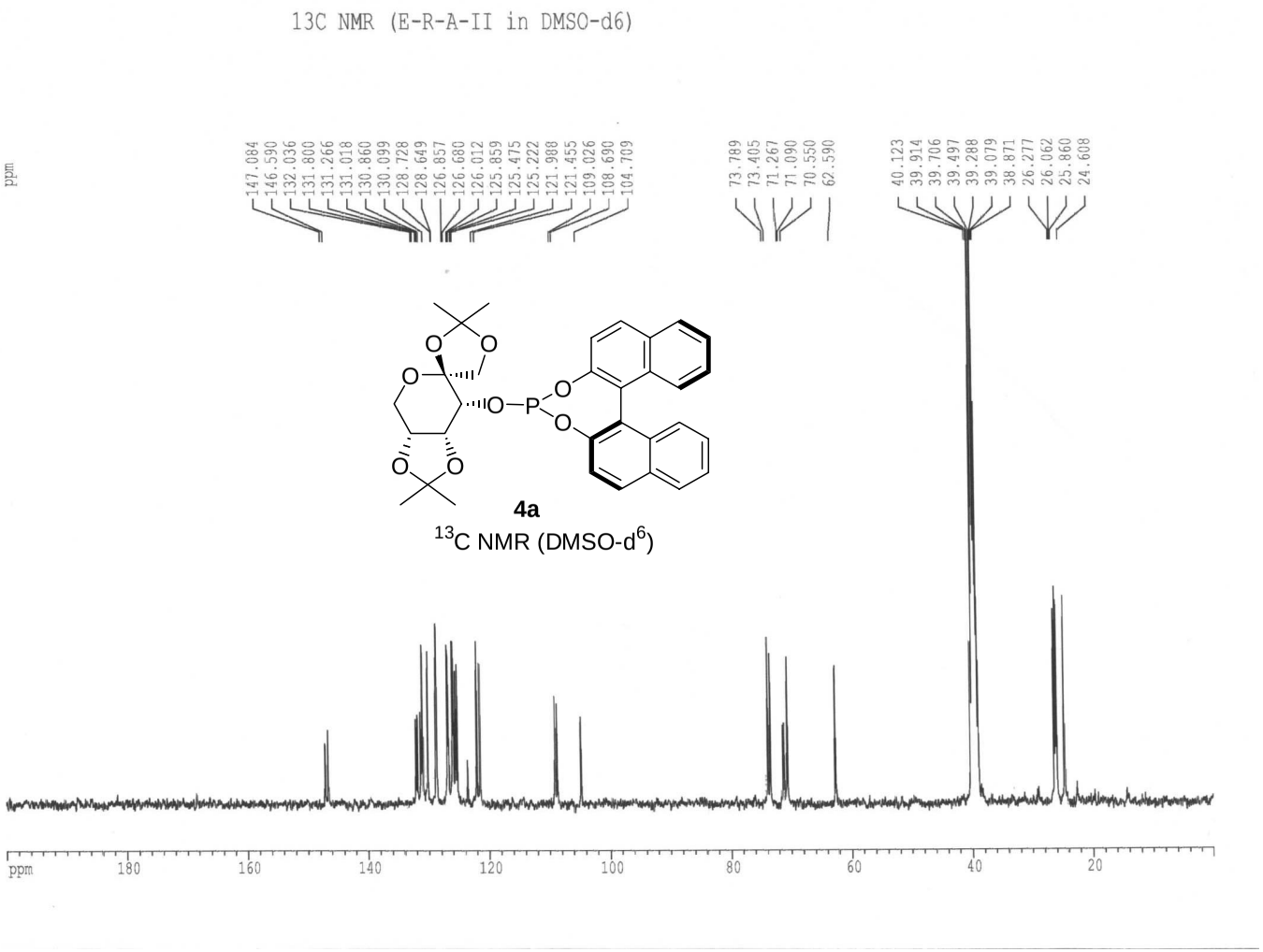
3d

^{31}P NMR (DMSO-d^{6})

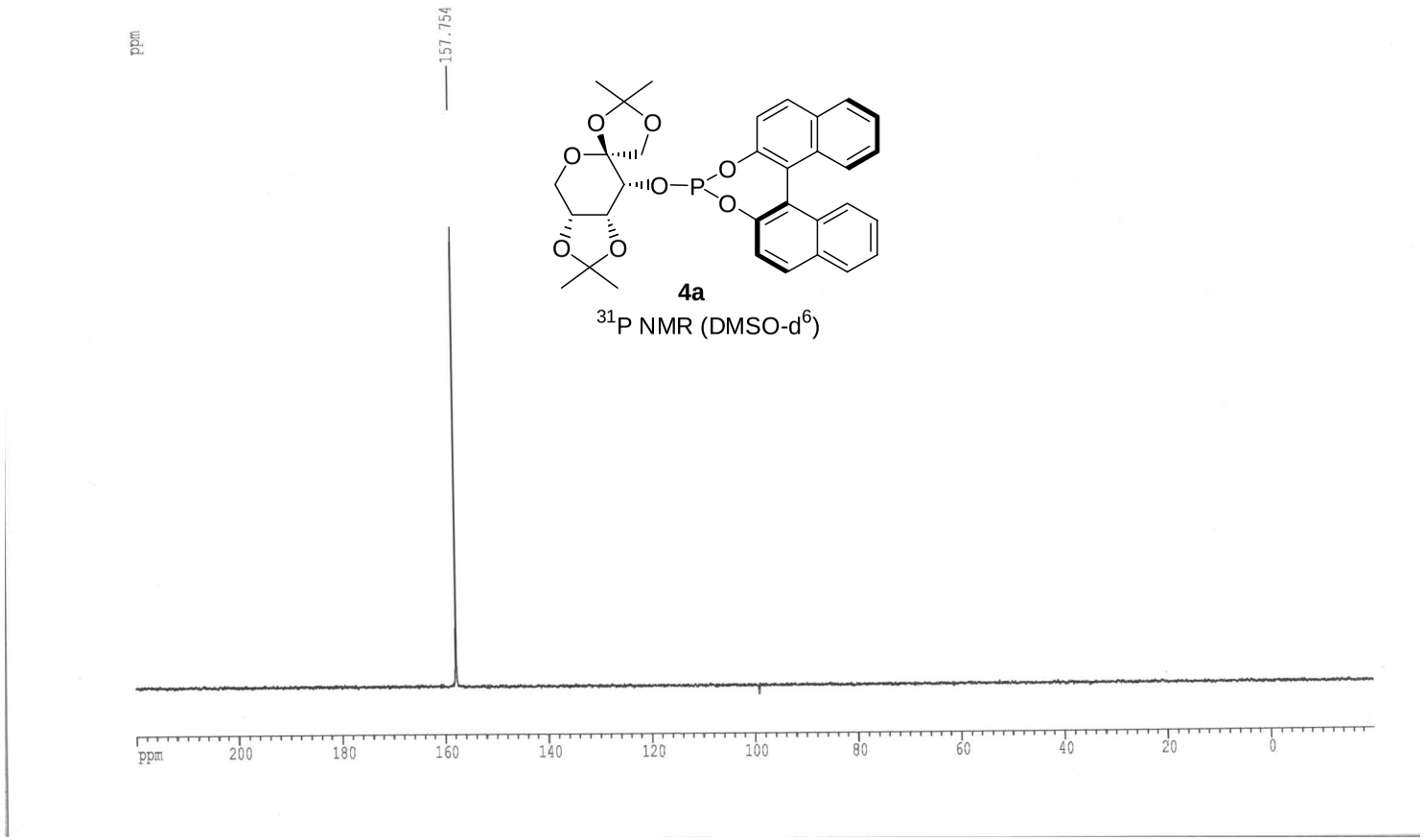


4a

^{1}H NMR (DMSO-d^6)

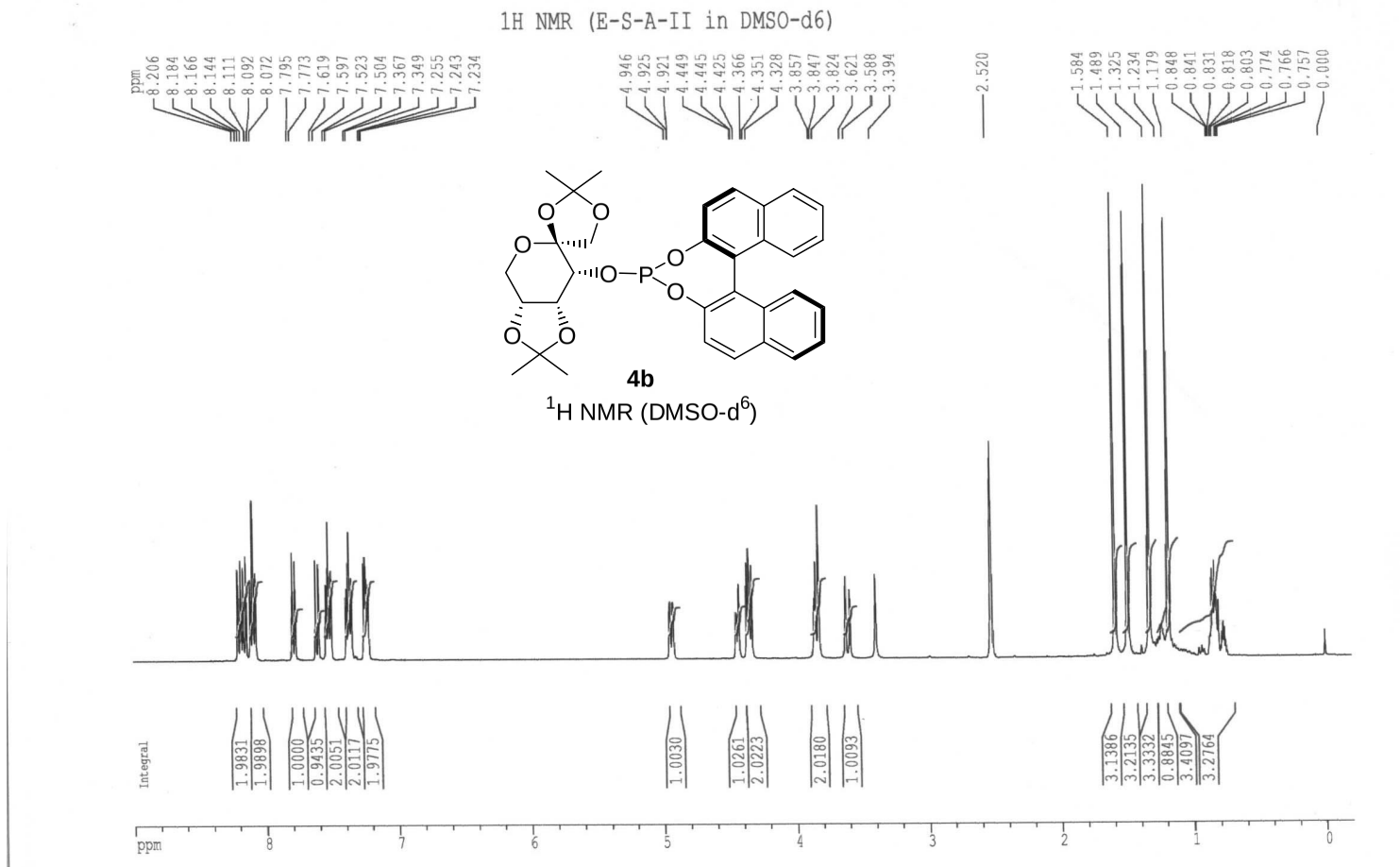

13C NMR (E-R-A-II in DMSO-d6)
ppm
147.084
146.590
132.036
131.800
131.266
131.018
130.860
130.099
128.728
128.649
126.857
126.680
126.012
125.859
125.475
125.222
121.988
121.455
109.026
108.690
104.709
73.789
73.405
71.267
71.090
70.550
62.590
40.123
39.914
39.706
39.497
39.288
39.079
38.871
26.277
26.062
25.860
24.608
O
O
O
O
O—P
O
O
O
4a
13C NMR (DMSO-d6)
ppm
180
160
140
120
100
80
60
40
20

31P NMR (E-R-A-II in DMSO-d6)



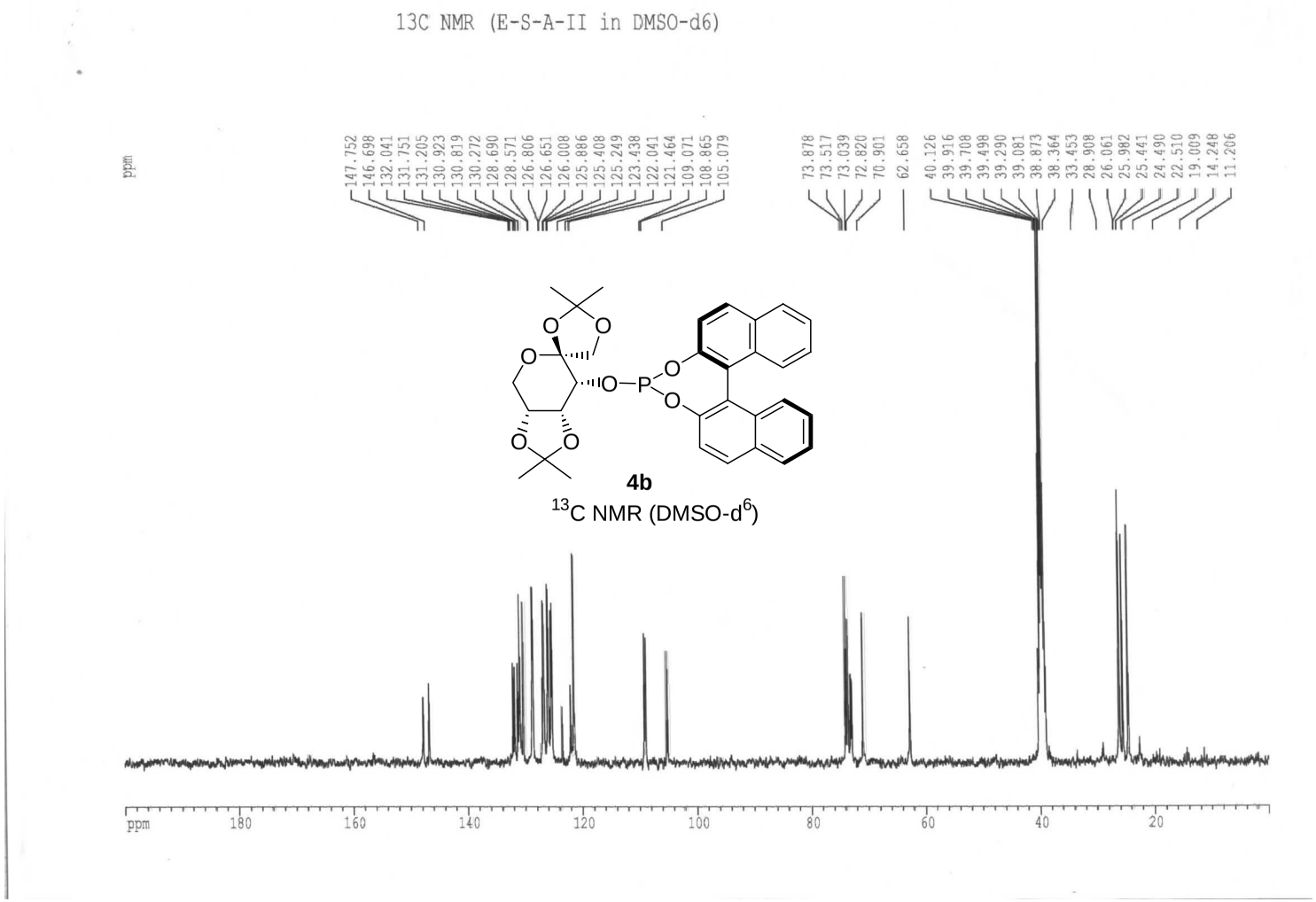
4a

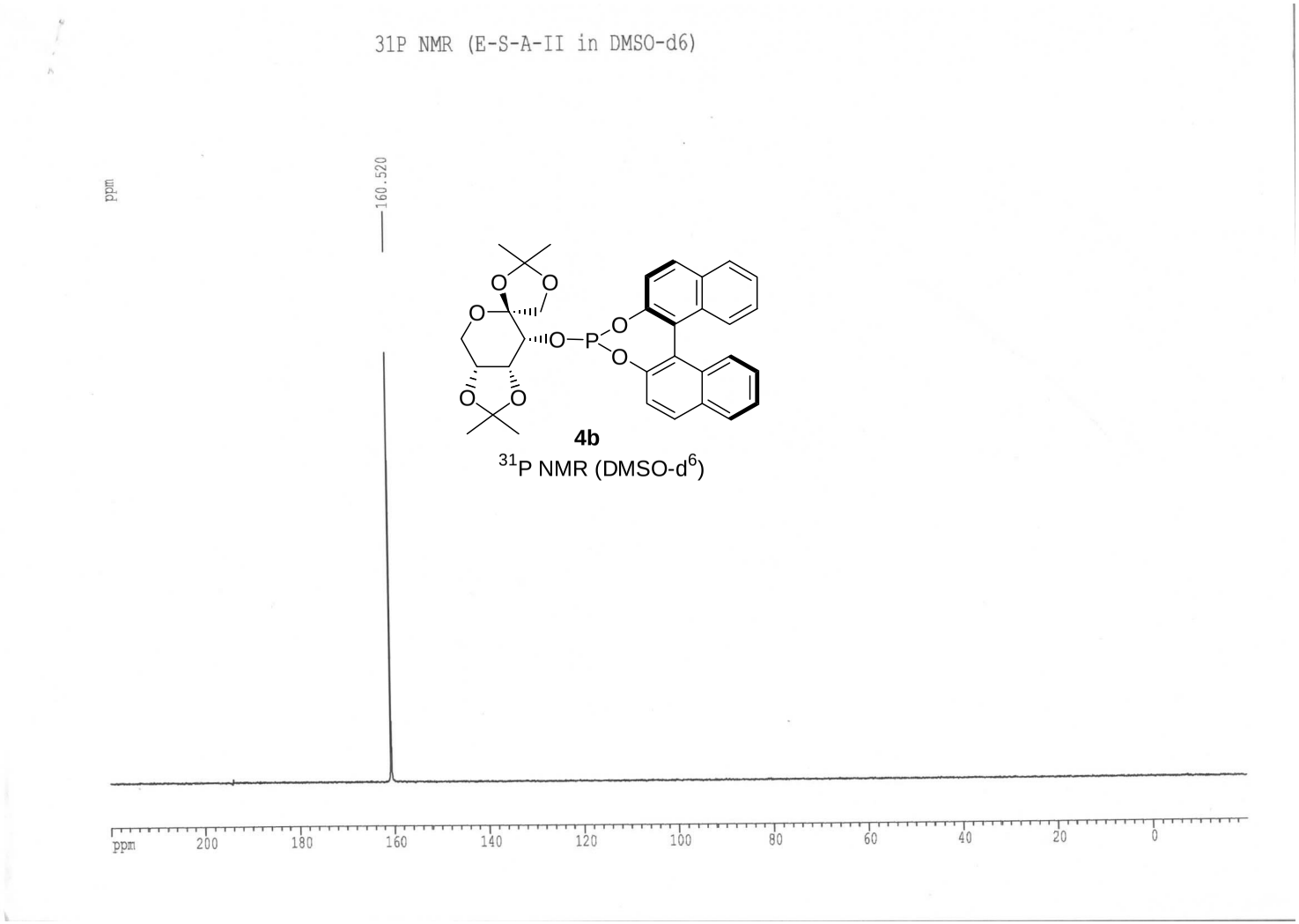
^{31}P NMR (DMSO-d^{6})



4b

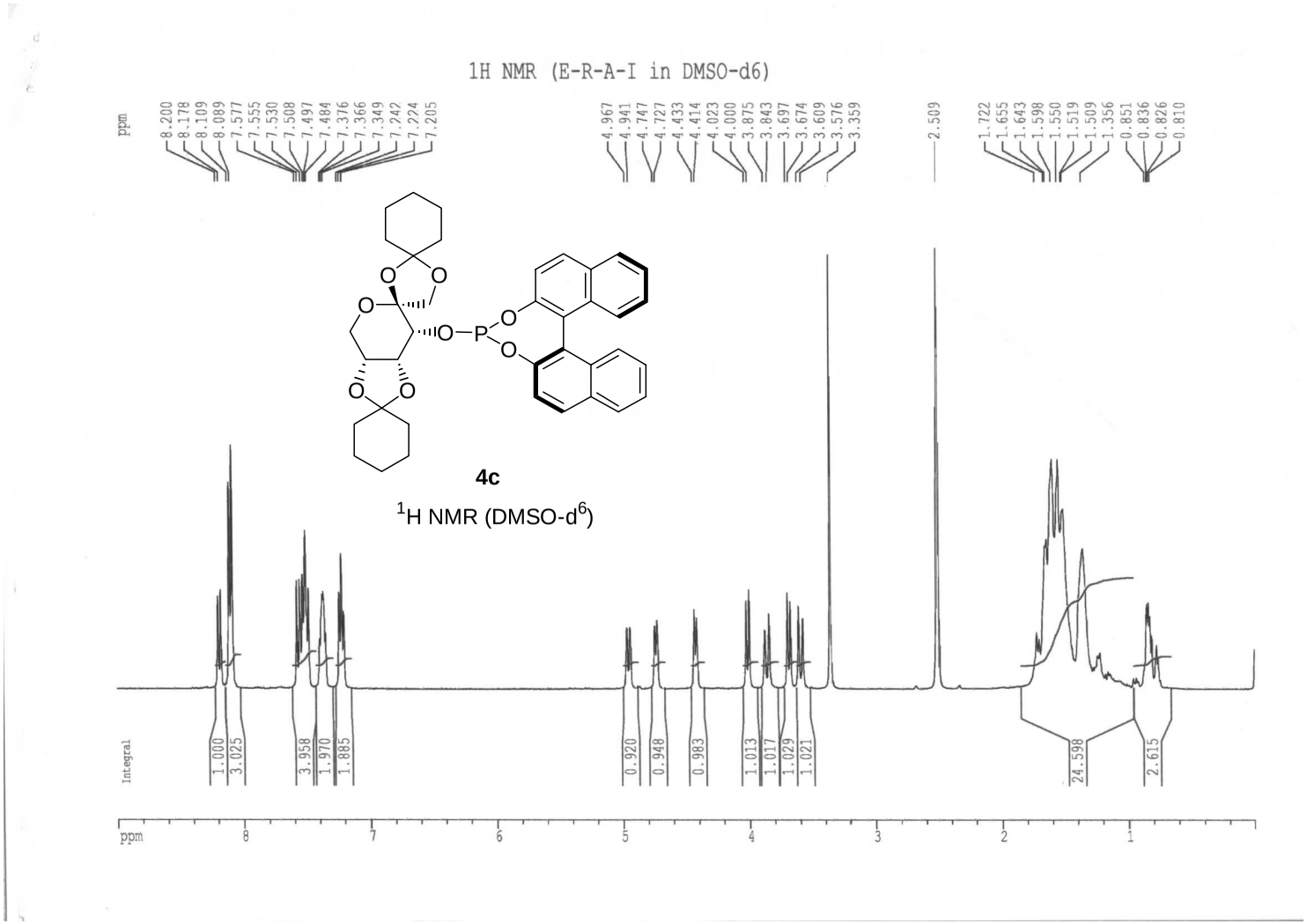
^{1}H NMR (DMSO-d^{6})


13C NMR (E-S-A-II in DMSO-d6)
ppm
147.752
146.698
132.041
131.751
131.205
130.923
130.819
130.272
128.690
128.571
126.806
126.651
126.008
125.886
125.408
125.249
123.438
122.041
121.464
109.071
108.865
105.079
73.878
73.517
73.039
72.820
70.901
62.658
40.126
39.916
39.708
39.498
39.290
39.081
38.873
38.364
33.453
28.908
26.061
25.982
25.441
24.490
22.510
19.009
14.248
11.206
O
O
O
O
O
O
O
P
O
4b
13C NMR (DMSO-d6)
ppm
180
160
140
120
100
80
60
40
20



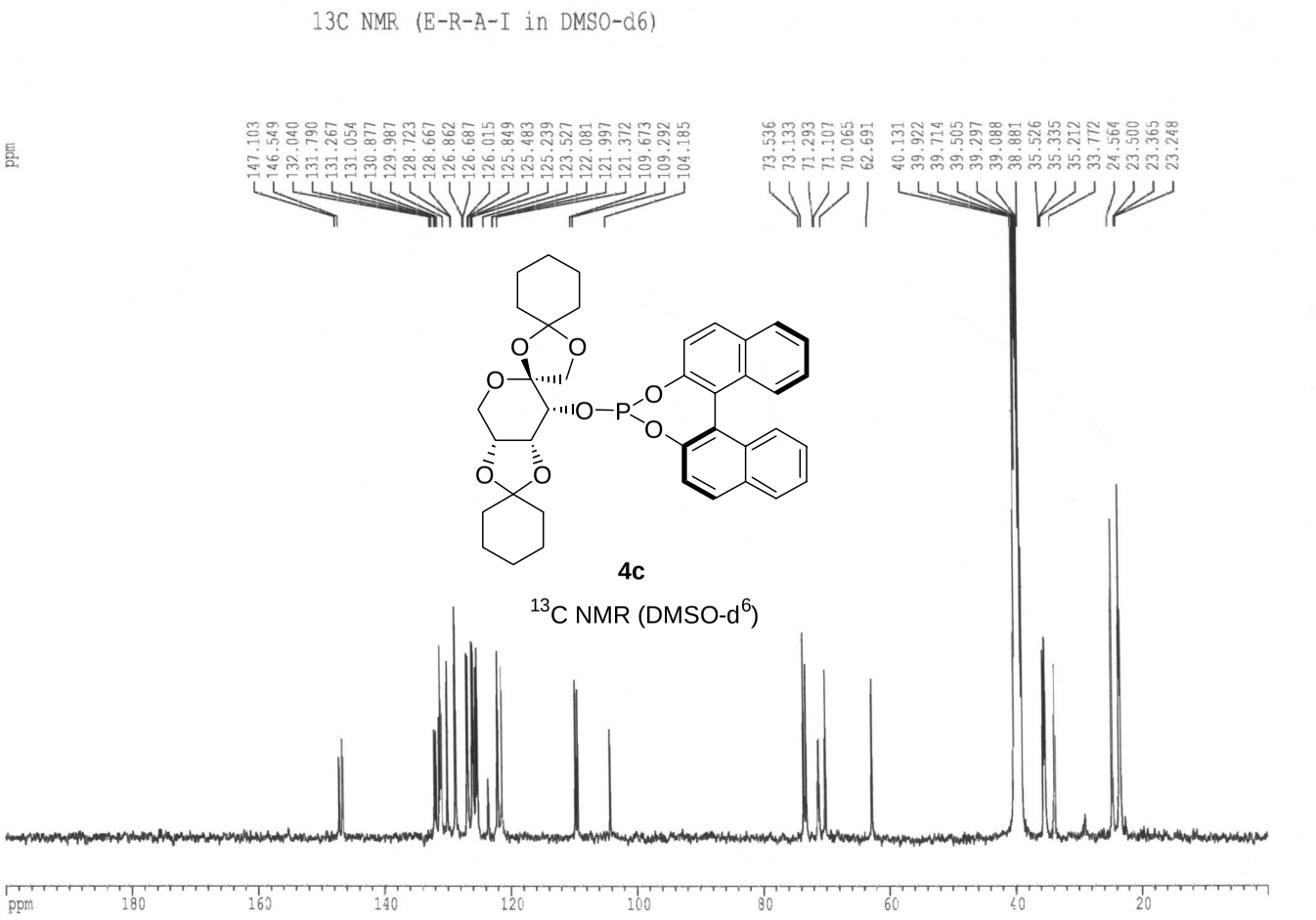
4b

^{31}P NMR (DMSO-d^{6})

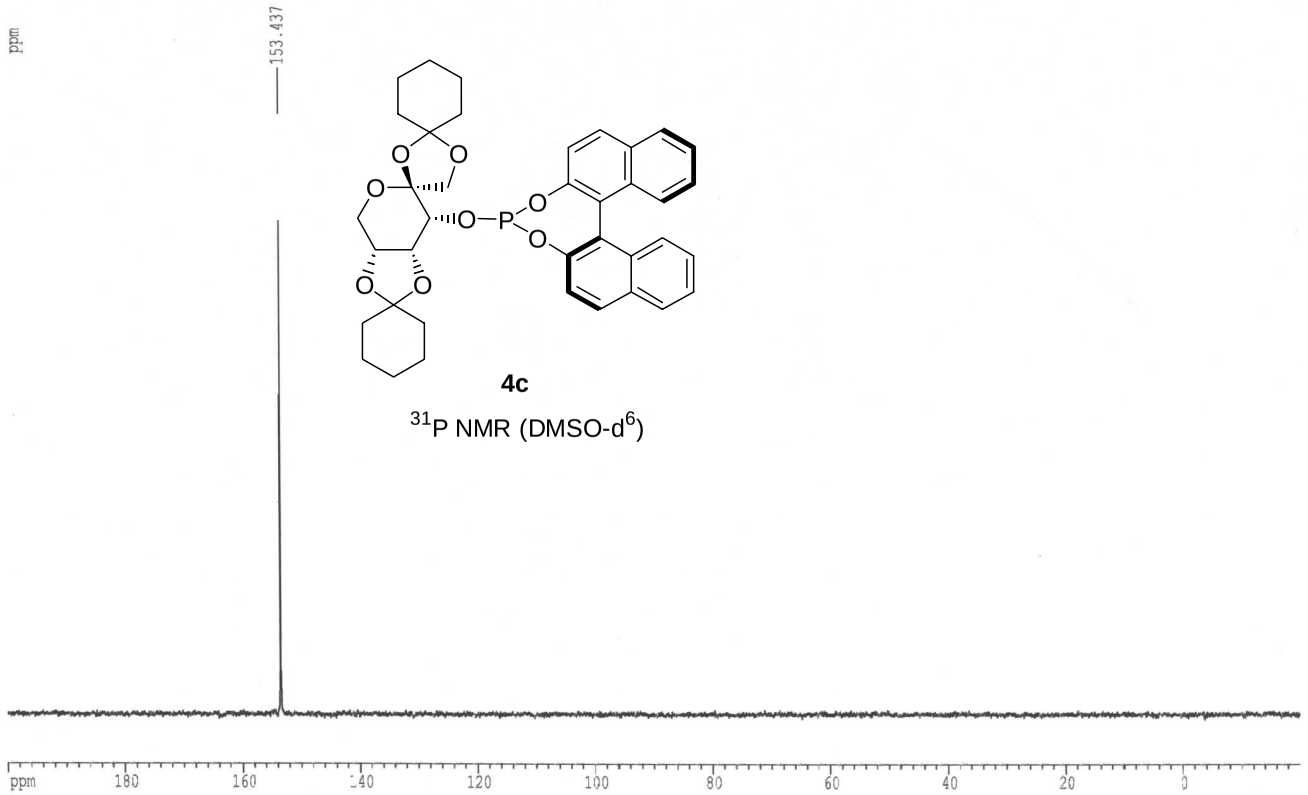


4c

^{1}H NMR (DMSO-d^{6})

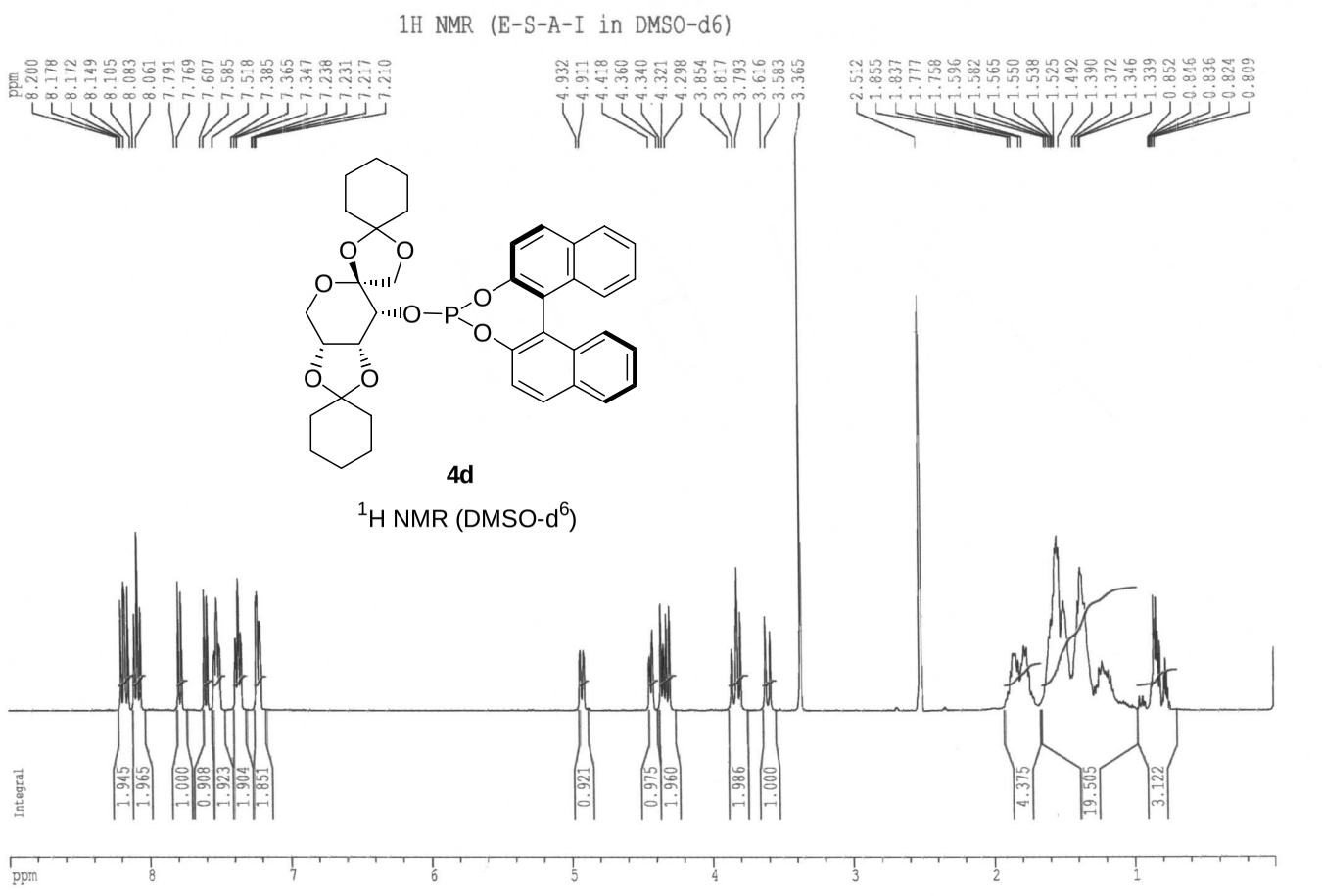

13C NMR (E-R-A-I in DMSO-d6)
ppm
147.103
146.549
132.040
131.790
131.267
131.054
130.877
129.987
128.723
128.667
126.862
126.687
126.015
125.849
125.483
125.239
123.527
122.081
121.997
121.372
109.673
109.292
104.185
73.536
73.133
71.293
71.107
70.065
62.691
40.131
39.922
39.714
39.505
39.297
39.088
38.881
35.526
35.335
35.212
33.772
24.564
23.500
23.365
23.248
O
O
O
O
O
O
O
O
P
4c
13C NMR (DMSO-d6)
ppm
180
160
140
120
100
80
60
40
20

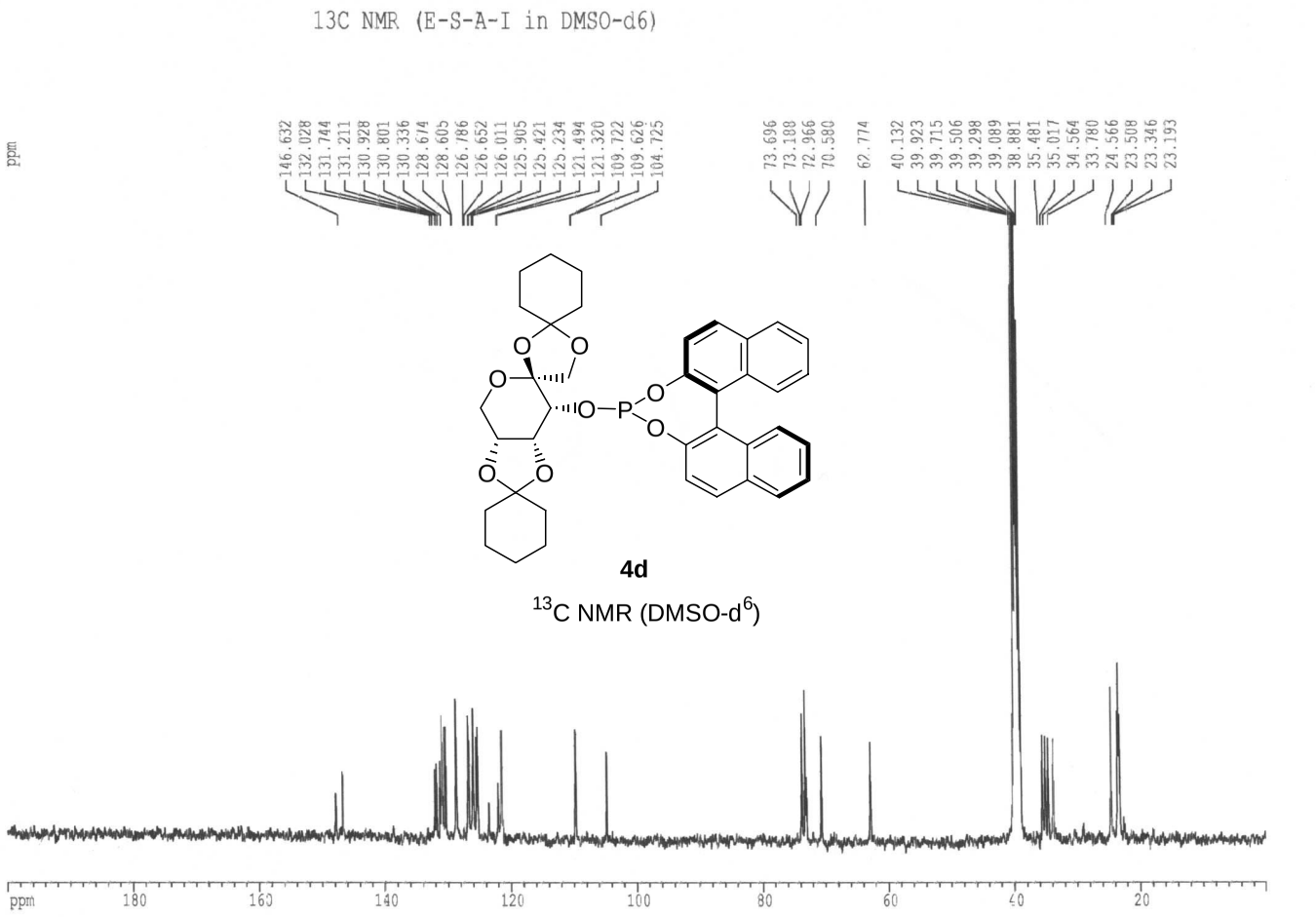
31P NMR (E-R-A-I in DMSO-d6)



4c

^{31}P NMR (DMSO-d^{6})

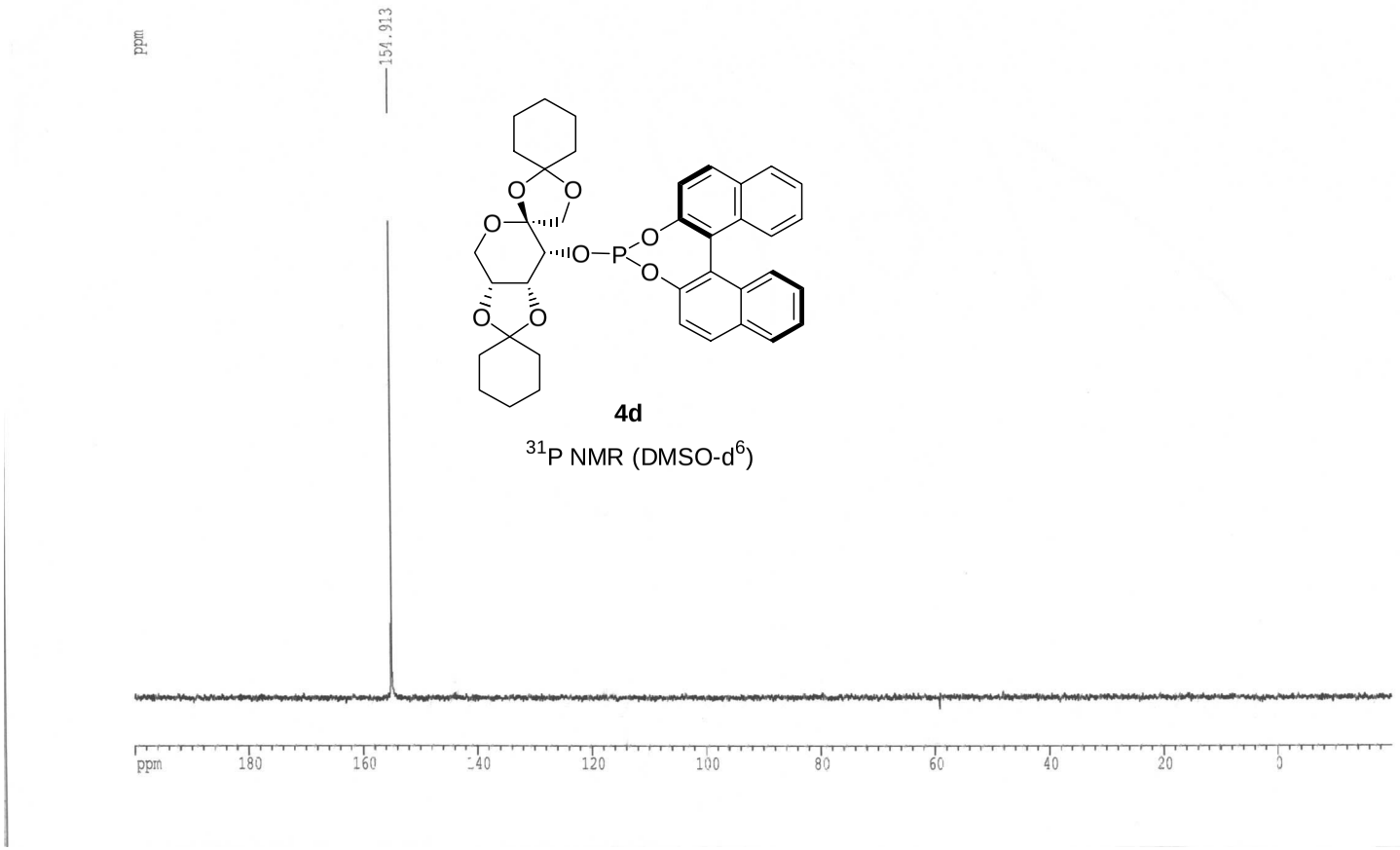

1H NMR (E-S-A-I in DMSO-d6)
ppm
8.200
8.178
8.172
8.149
8.105
8.083
8.061
7.791
7.769
7.607
7.585
7.518
7.385
7.365
7.347
7.238
7.231
7.217
7.210
4.932
4.911
4.418
4.360
4.340
4.321
4.298
3.854
3.817
3.793
3.616
3.583
3.365
2.512
1.855
1.837
1.777
1.758
1.596
1.582
1.565
1.550
1.538
1.525
1.492
1.390
1.372
1.346
1.339
0.852
0.846
0.836
0.824
0.809
O
O
O
O
O
O
O
P
O
O
4d
1H NMR (DMSO-d6)
Integral
1.945
1.965
1.000
0.908
1.923
1.904
1.851
0.921
0.975
1.960
1.986
1.000
4.375
19.505
3.122
ppm
8
7
6
5
4
3
2
1



4d

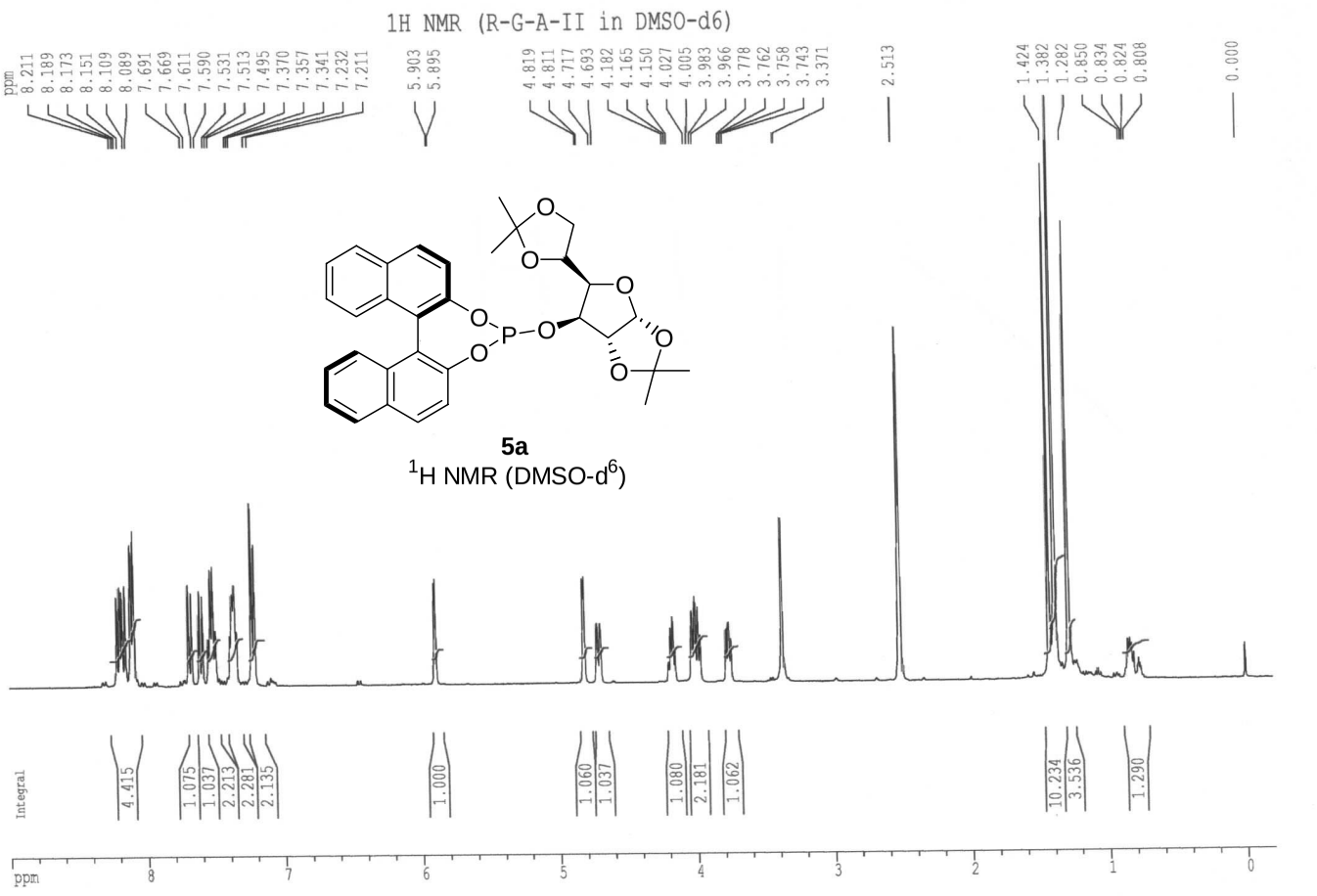
^{13}C NMR (DMSO-d^{6})

31P NMR (E-S-A-I in DMSO-d6)



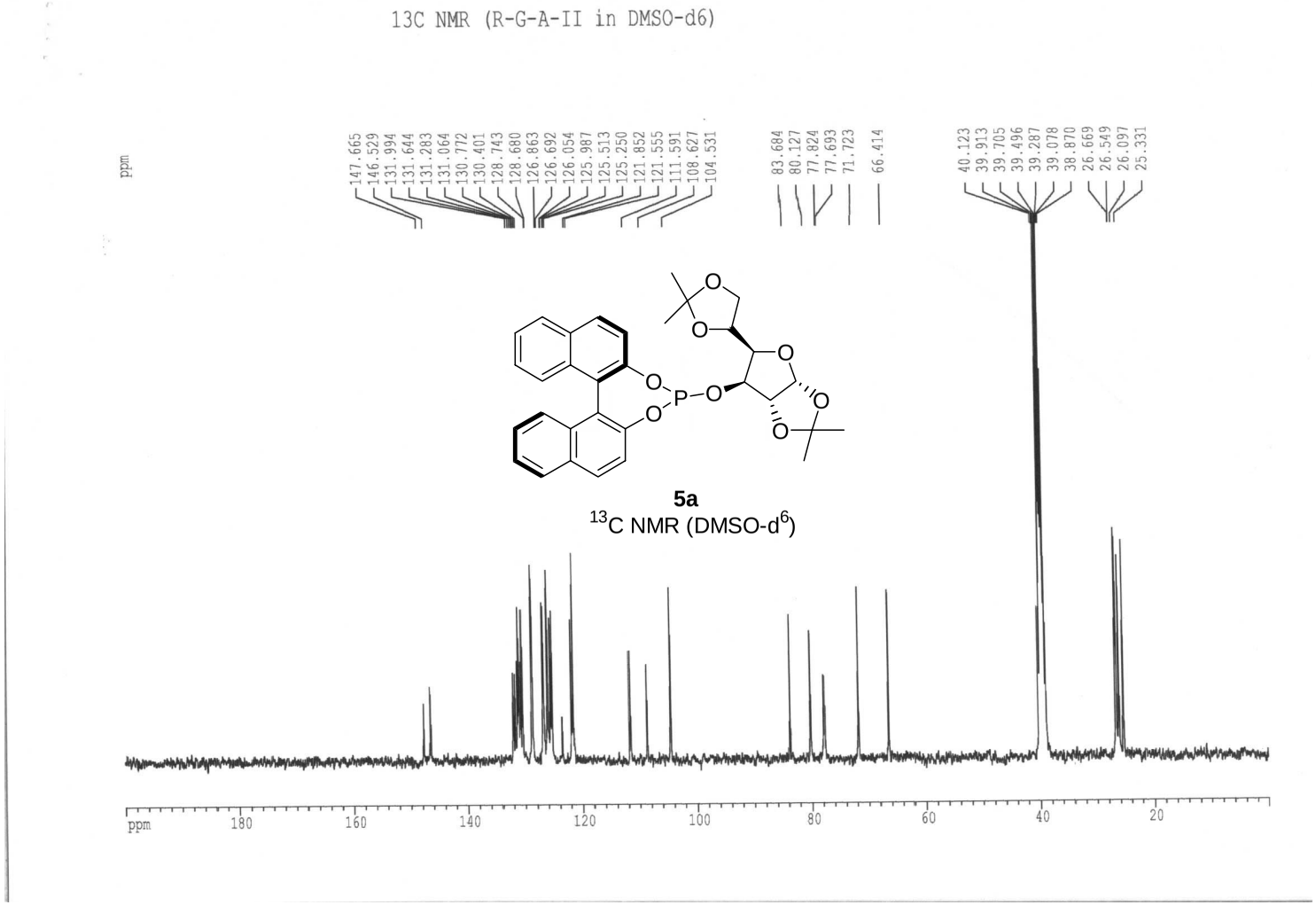
4d

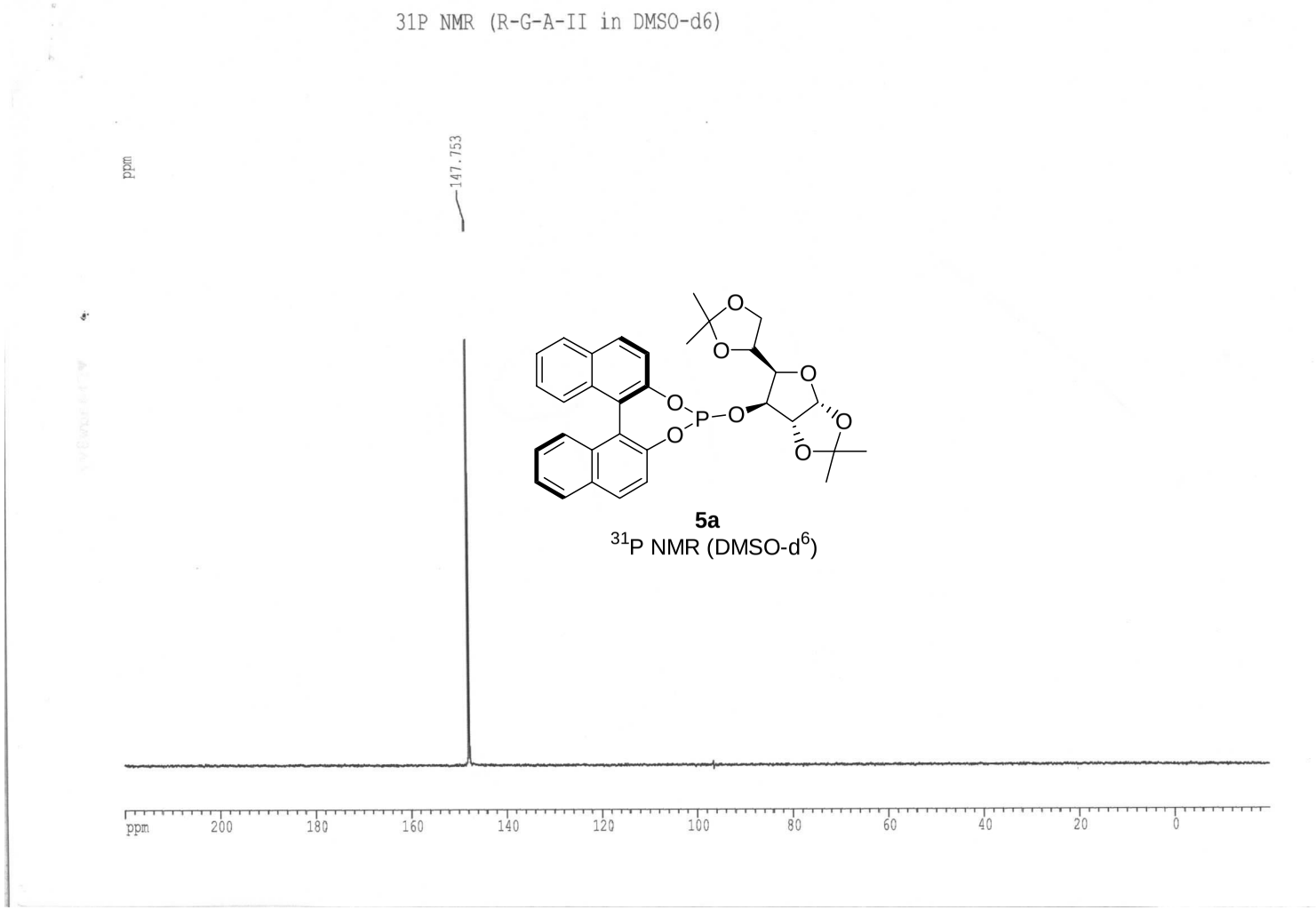
^{31}P NMR (DMSO-d^{6})



5a

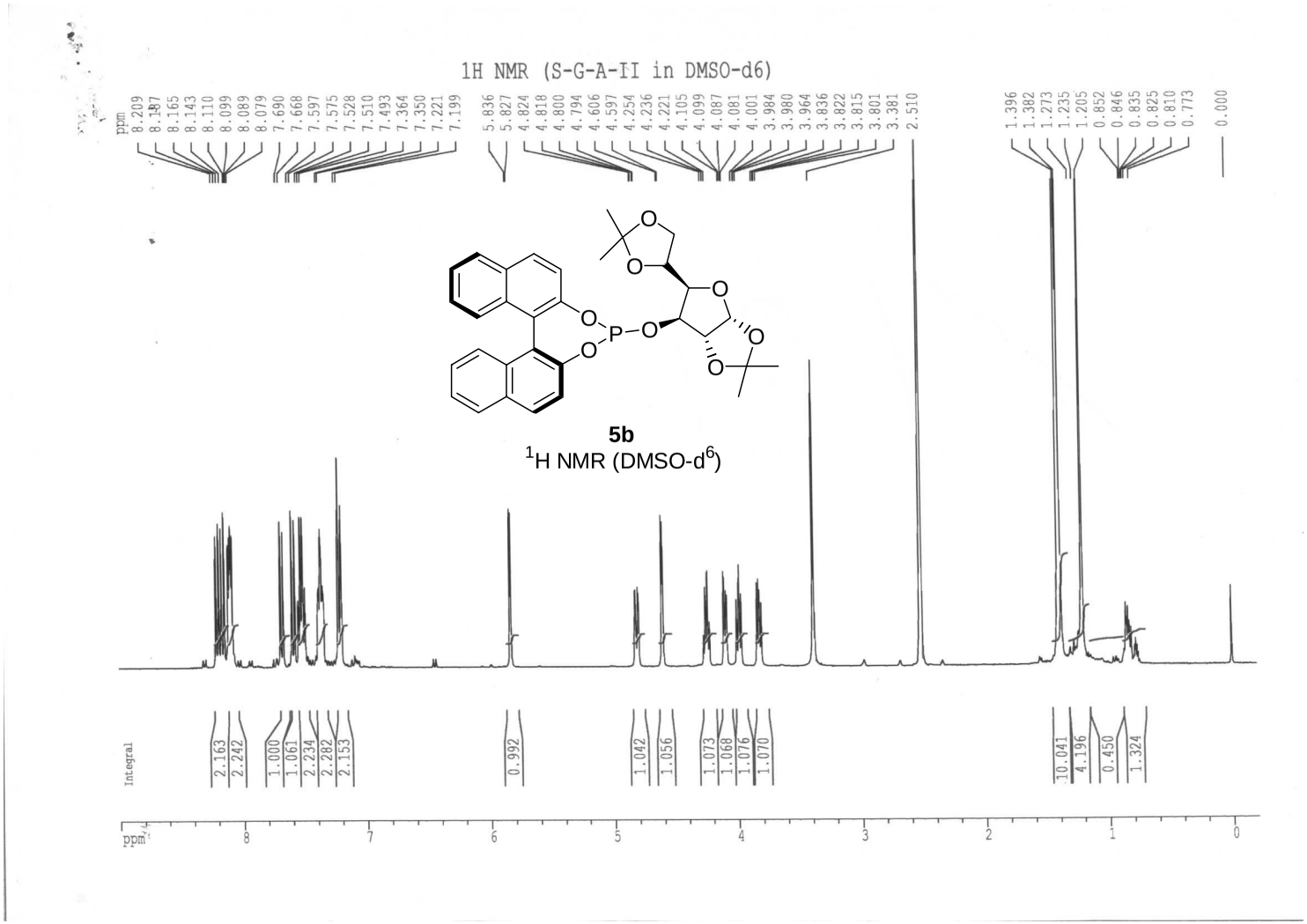
^{1}H NMR (DMSO-d^{6})


13C NMR (R-G-A-II in DMSO-d6)
ppm
147.665
146.529
131.994
131.644
131.283
131.064
130.772
130.401
128.743
128.680
126.863
126.692
126.054
125.987
125.513
125.250
121.852
121.555
111.591
108.627
104.531
83.684
80.127
77.824
77.693
71.723
66.414
40.123
39.913
39.705
39.496
39.287
39.078
38.870
26.669
26.549
26.097
25.331
O
O
O
O
O
P
O
O
O
O
5a
13C NMR (DMSO-d6)
ppm
180
160
140
120
100
80
60
40
20



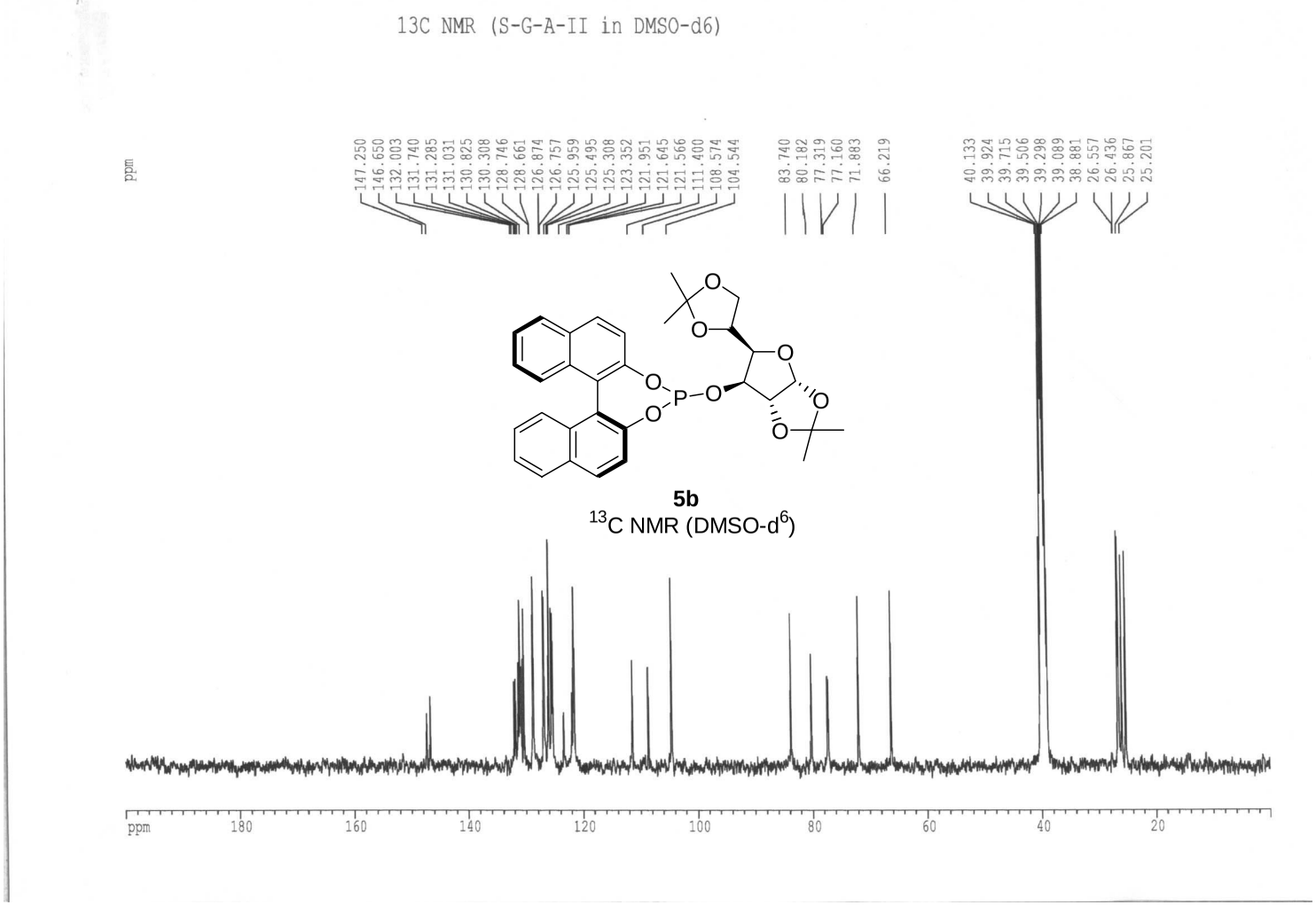
5a

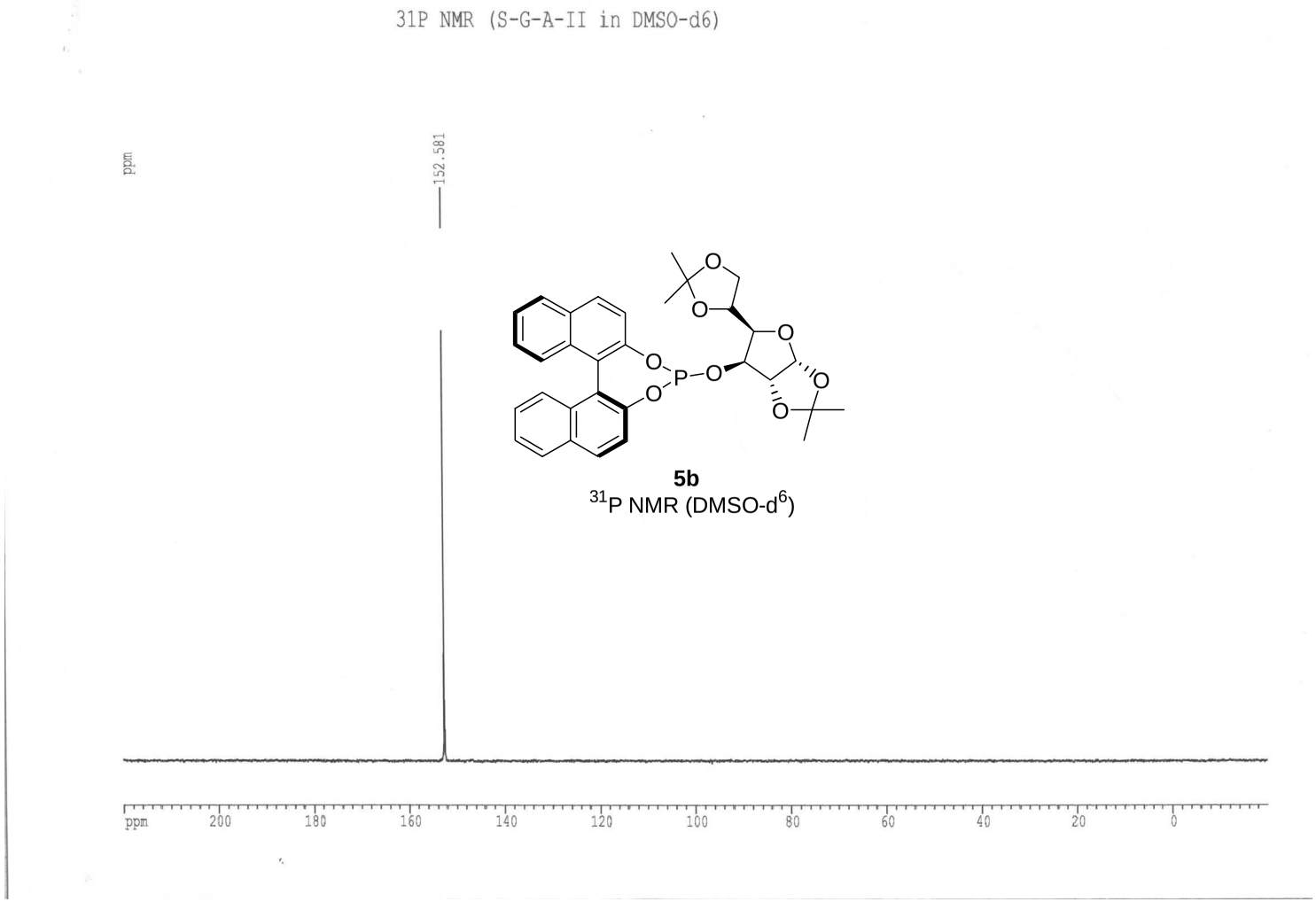
^{31}P NMR (DMSO-d^{6})



5b

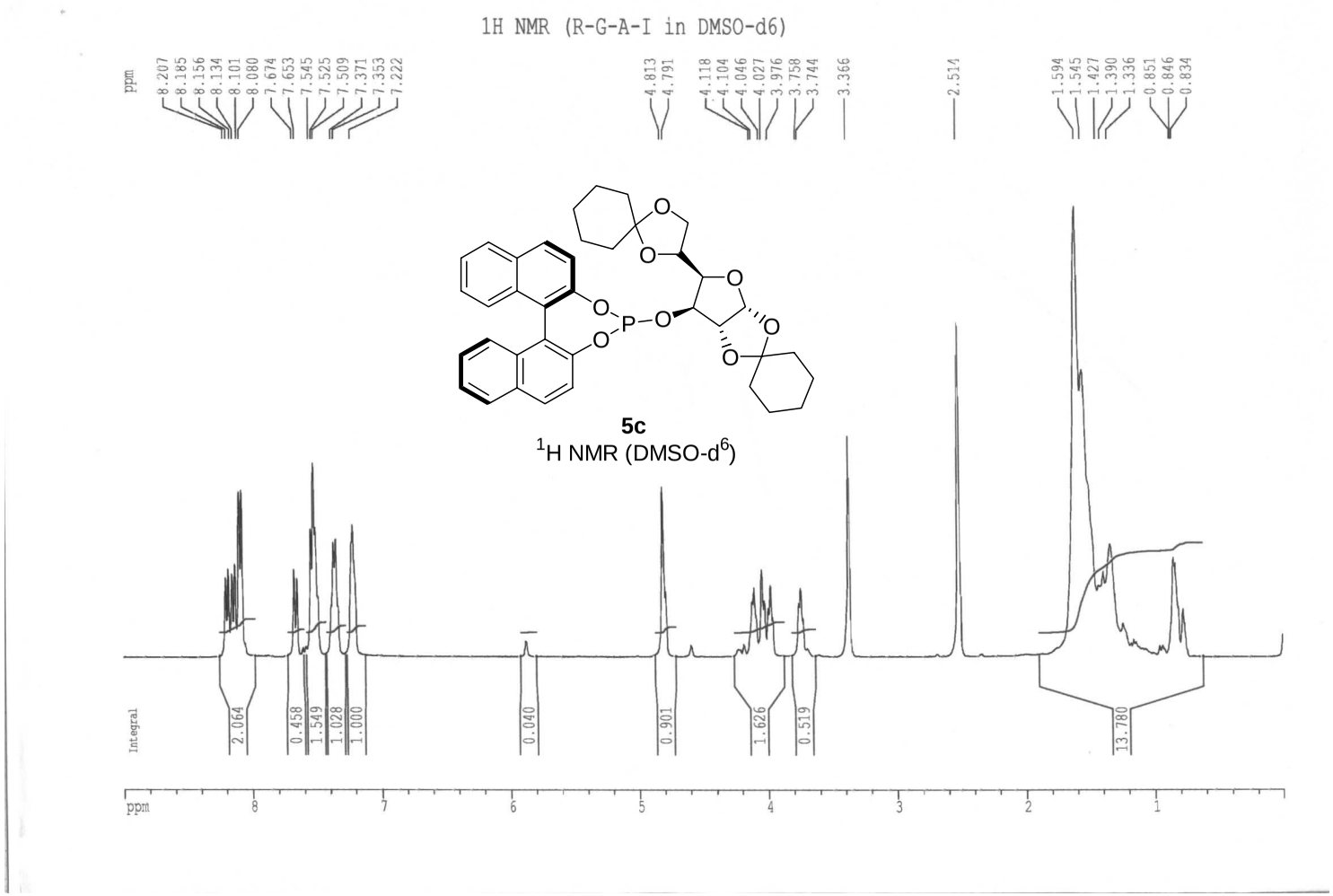
^{1}H NMR (DMSO-d^{6})


13C NMR (S-G-A-II in DMSO-d6)
ppm
147.250
146.650
132.003
131.740
131.285
131.031
130.825
130.308
128.746
128.661
126.874
126.757
125.959
125.495
125.308
123.352
121.951
121.645
121.566
111.400
108.574
104.544
83.740
80.182
77.319
77.160
71.883
66.219
40.133
39.924
39.715
39.506
39.298
39.089
38.881
26.557
26.436
25.867
25.201
O
O
O
O
O
P
O
O
O
O
5b
13C NMR (DMSO-d6)
ppm
180
160
140
120
100
80
60
40
20



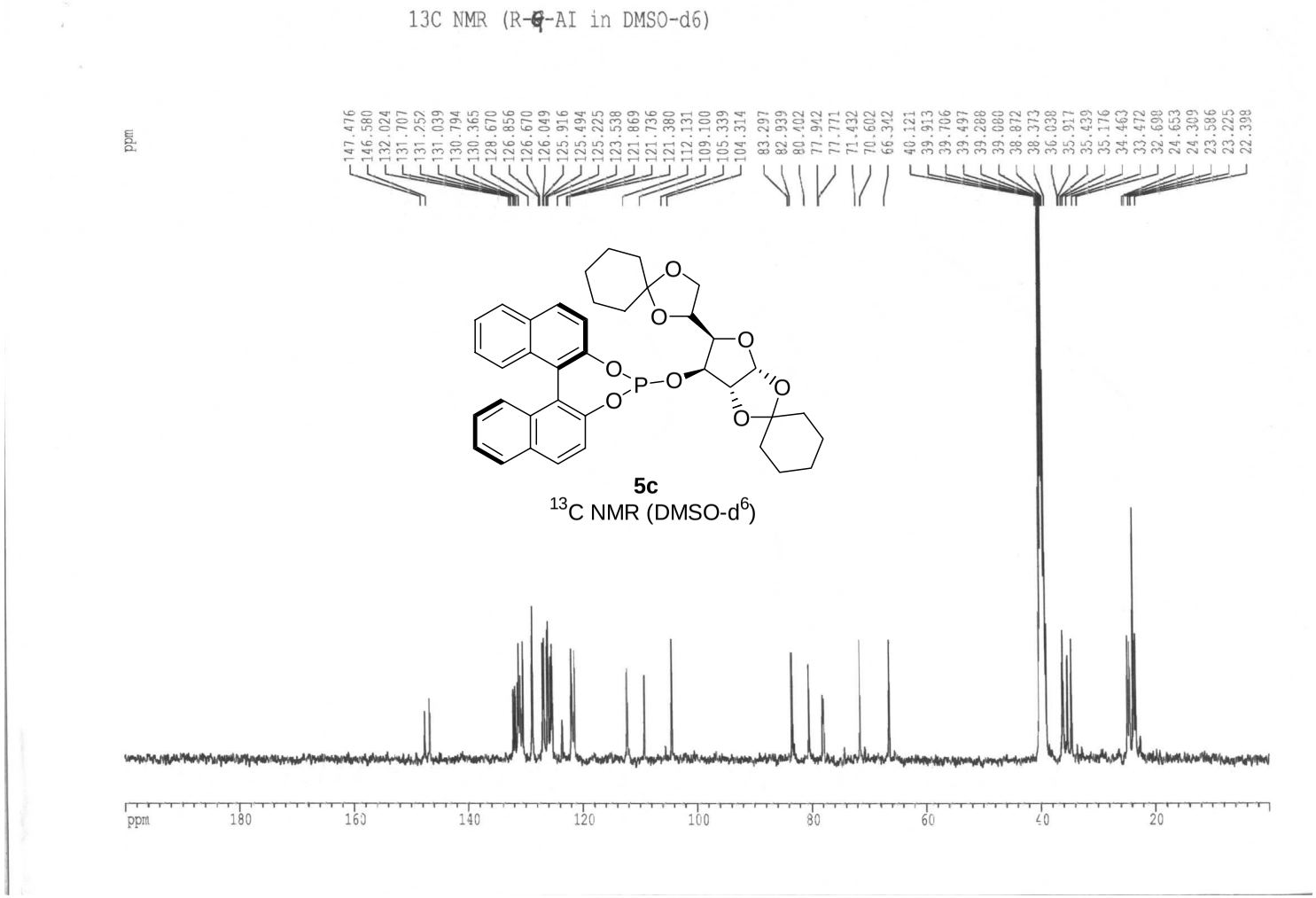
5b

^{31}P NMR (DMSO-d^{6})



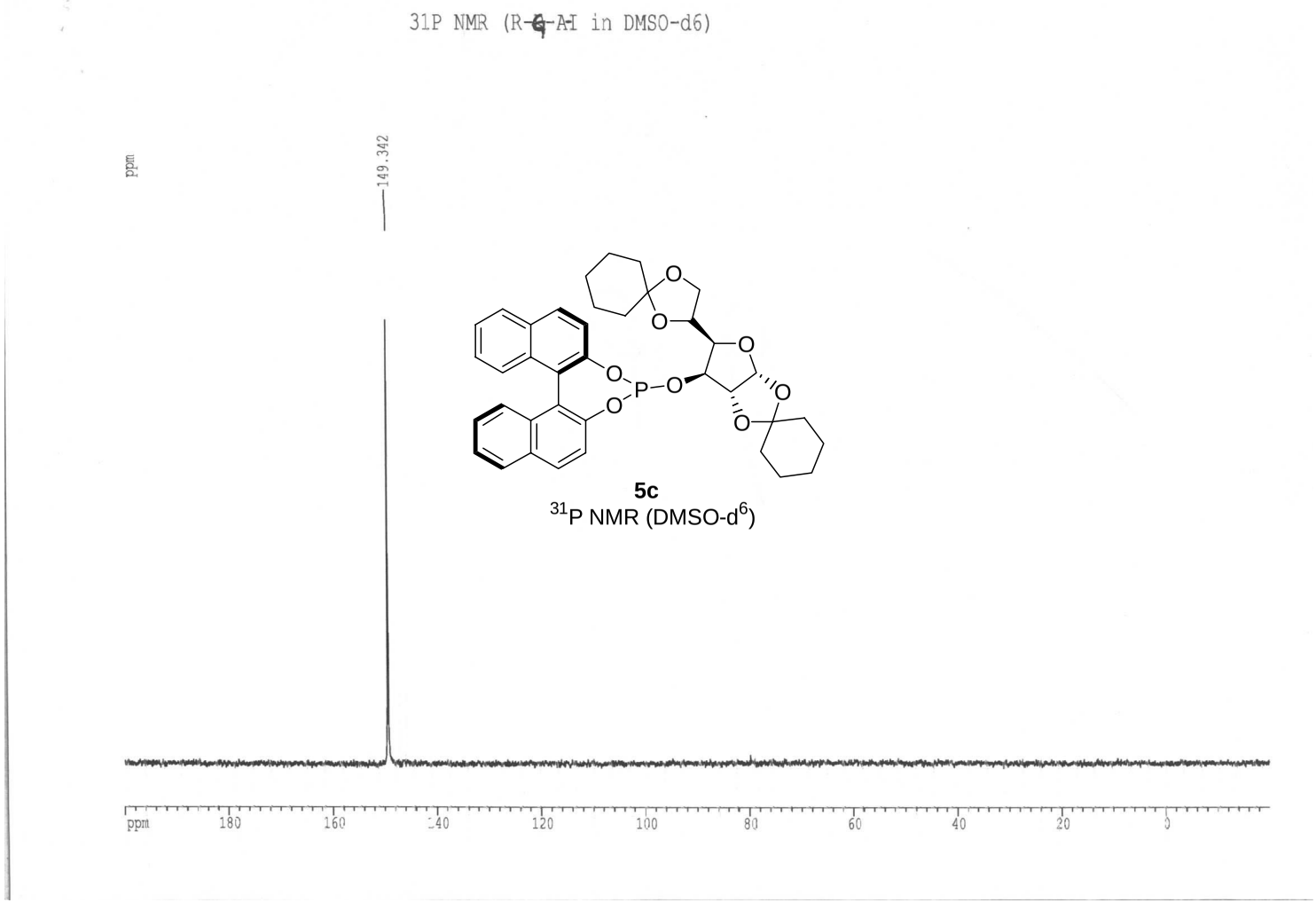
5c

^{1}H NMR (DMSO-d^{6})



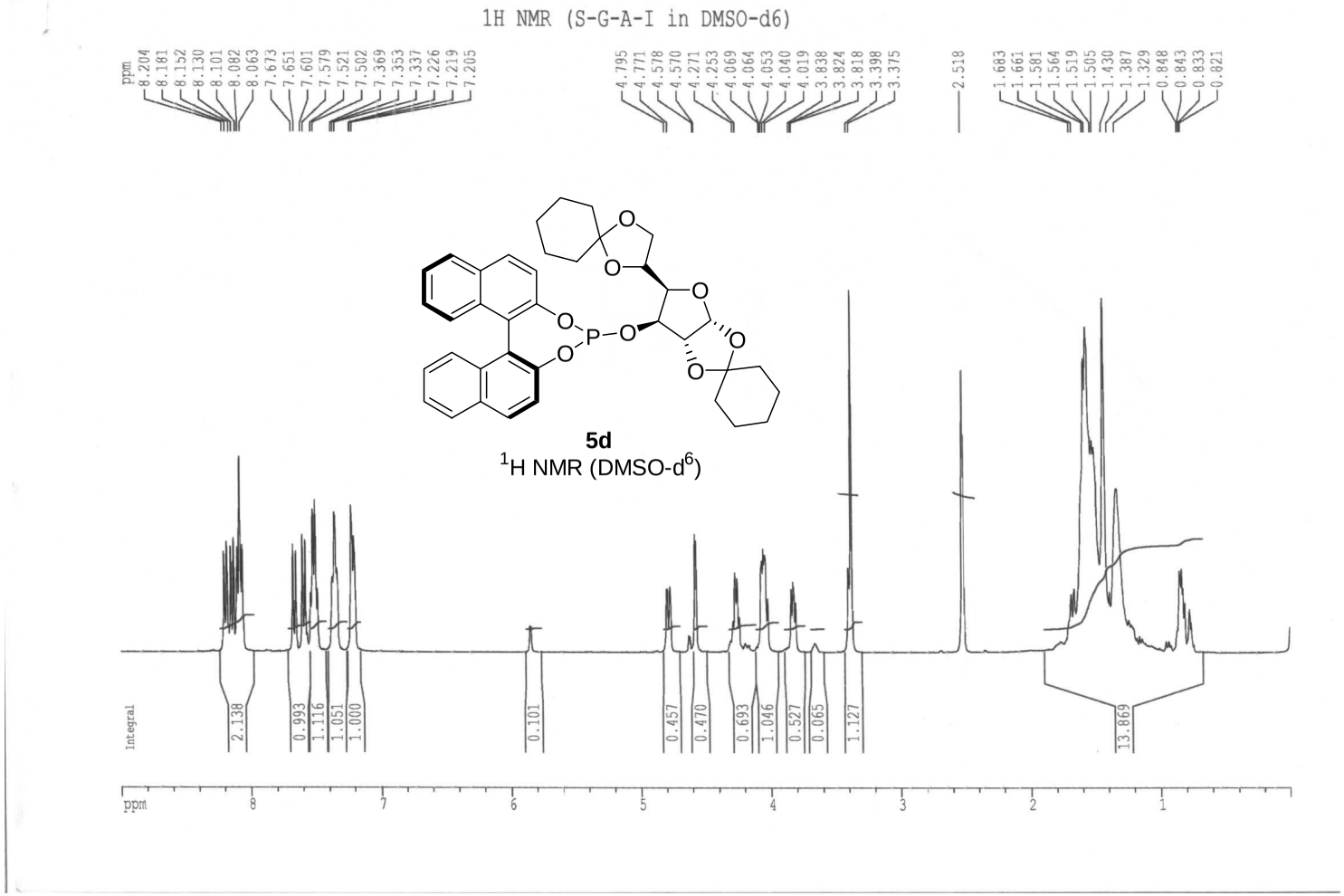
5c

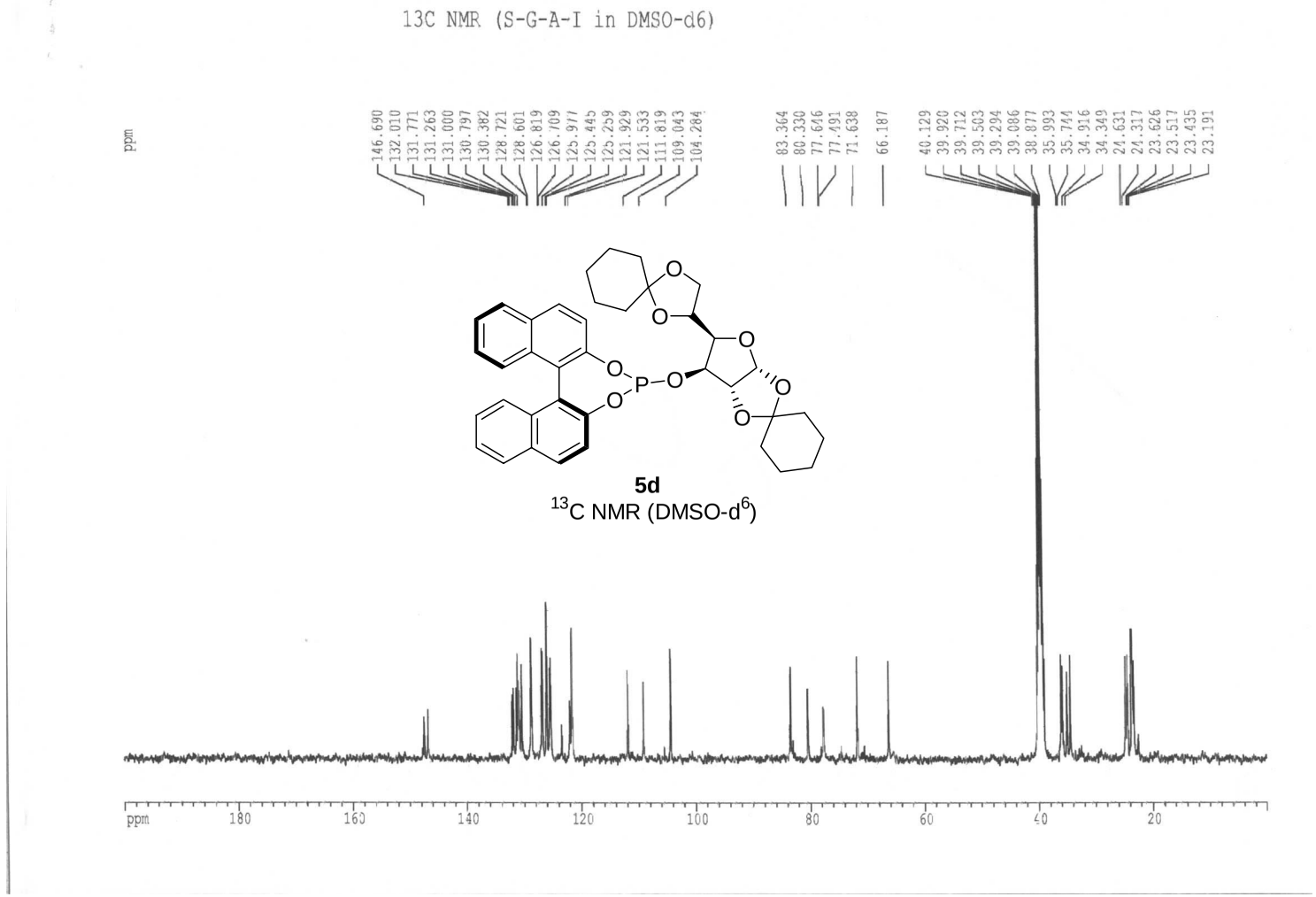
^{13}C NMR (DMSO-d^{6})



5c

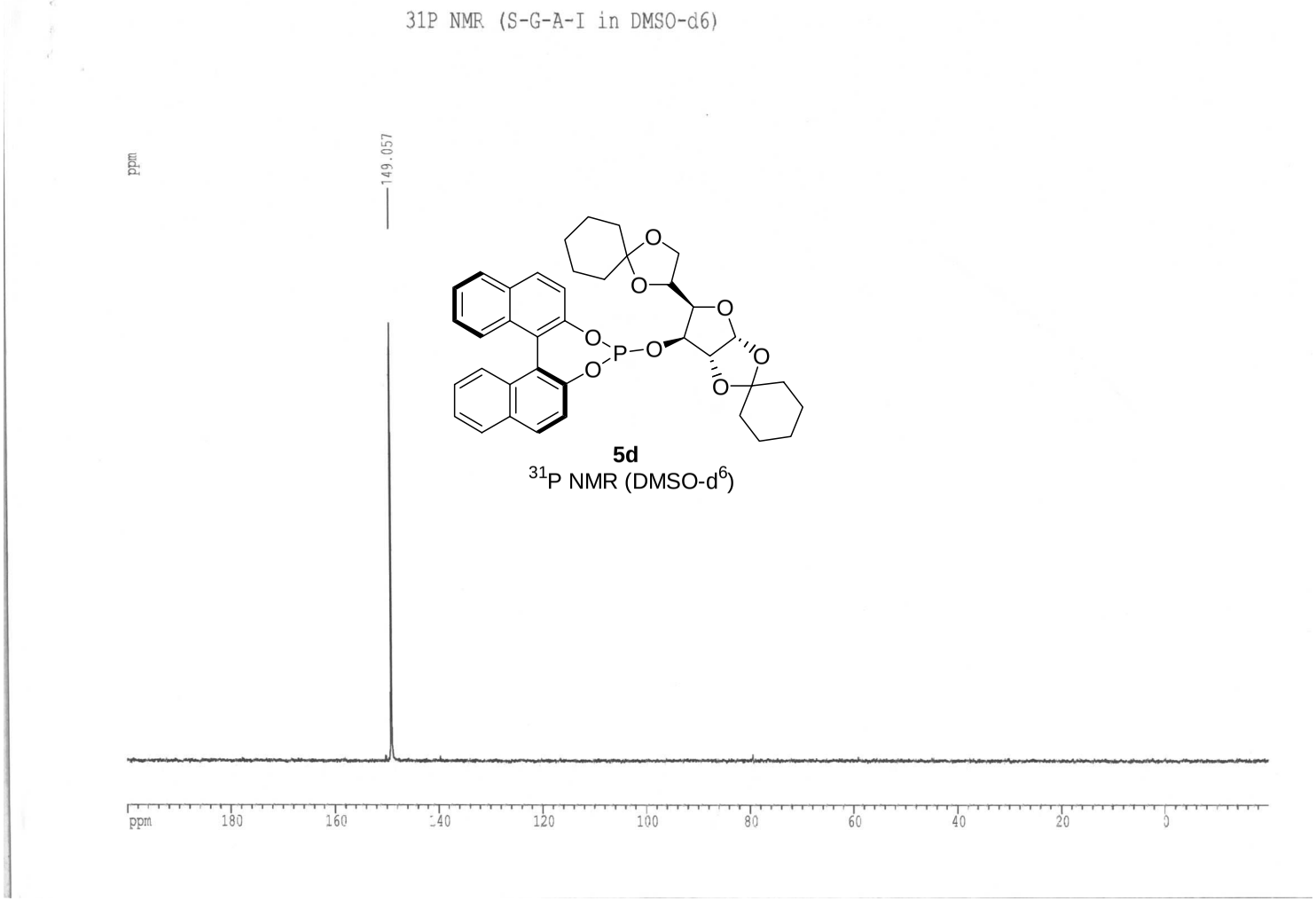
^{31}P NMR (DMSO-d^{6})


1H NMR (S-G-A-I in DMSO-d6)
ppm
8.204
8.181
8.152
8.130
8.101
8.082
8.063
7.673
7.651
7.601
7.579
7.521
7.502
7.369
7.353
7.337
7.226
7.219
7.205
4.795
4.771
4.578
4.570
4.271
4.253
4.069
4.064
4.053
4.040
4.019
3.838
3.824
3.818
3.398
3.375
2.518
1.683
1.661
1.581
1.564
1.519
1.505
1.430
1.387
1.329
0.848
0.843
0.833
0.821
5d
1H NMR (DMSO-d6)
Integral
2.138
0.993
1.116
1.051
1.000
0.101
0.457
0.470
0.693
1.046
0.527
0.065
1.127
13.869
ppm
8
7
6
5
4
3
2
1



5d

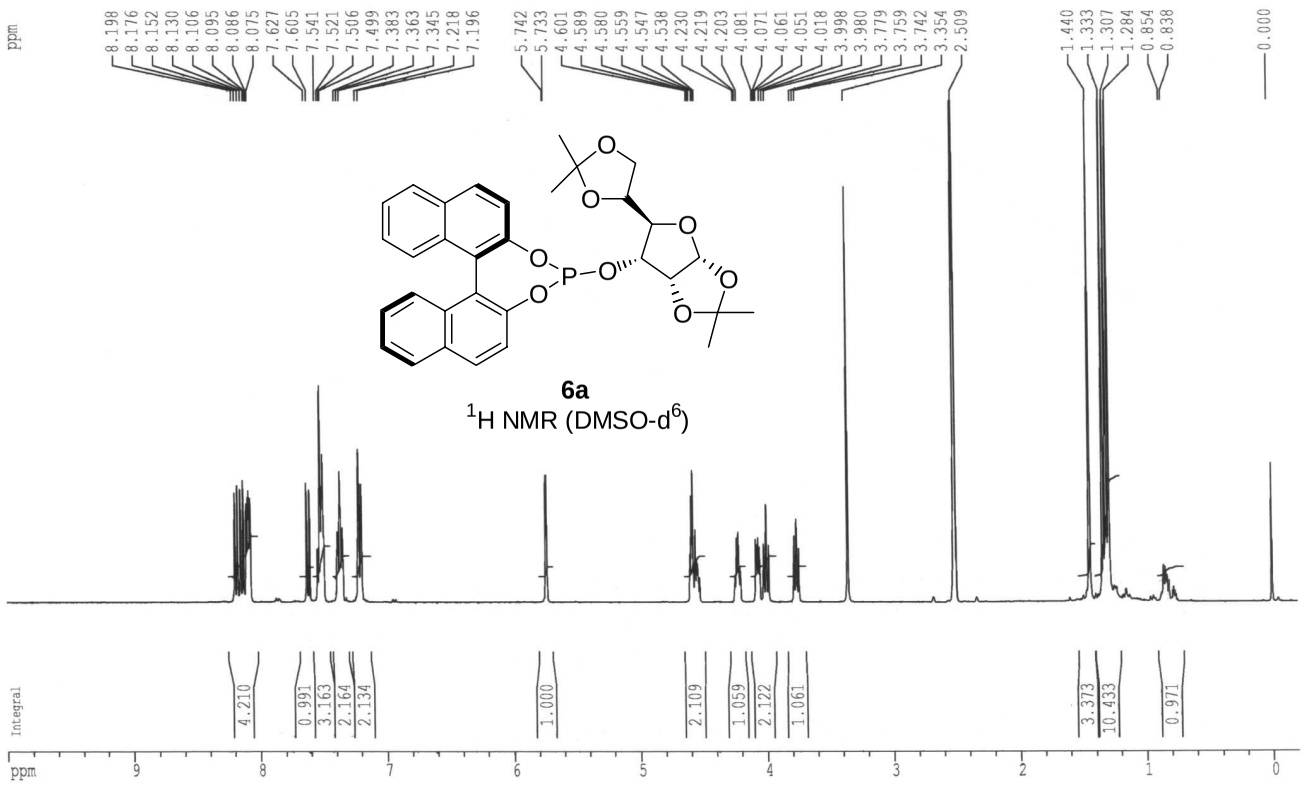
^{13}C NMR (DMSO-d^6)



5d

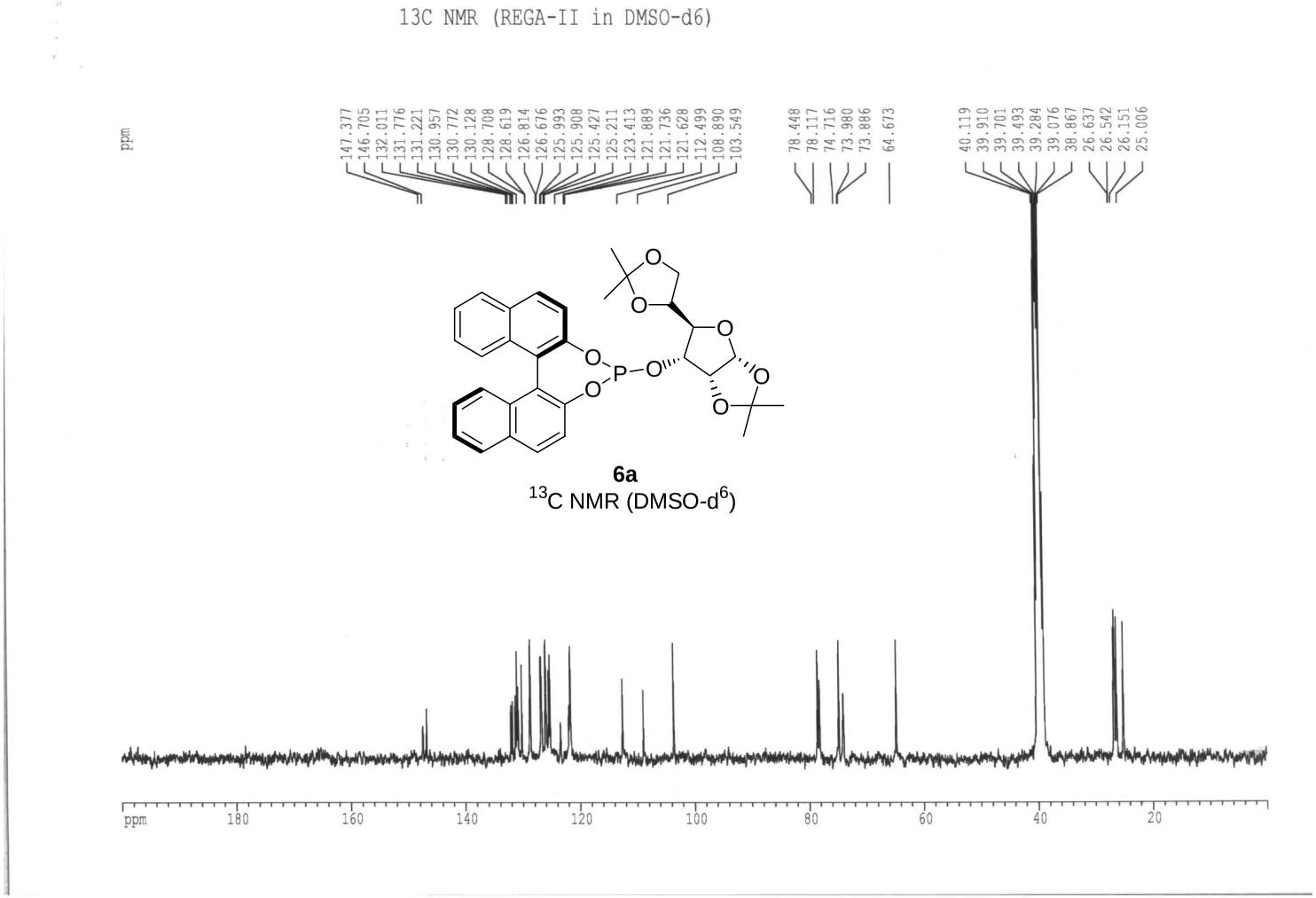
^{31}P NMR (DMSO-d^{6})

1H NMR (REGA-II in DMSO-d6)



6a

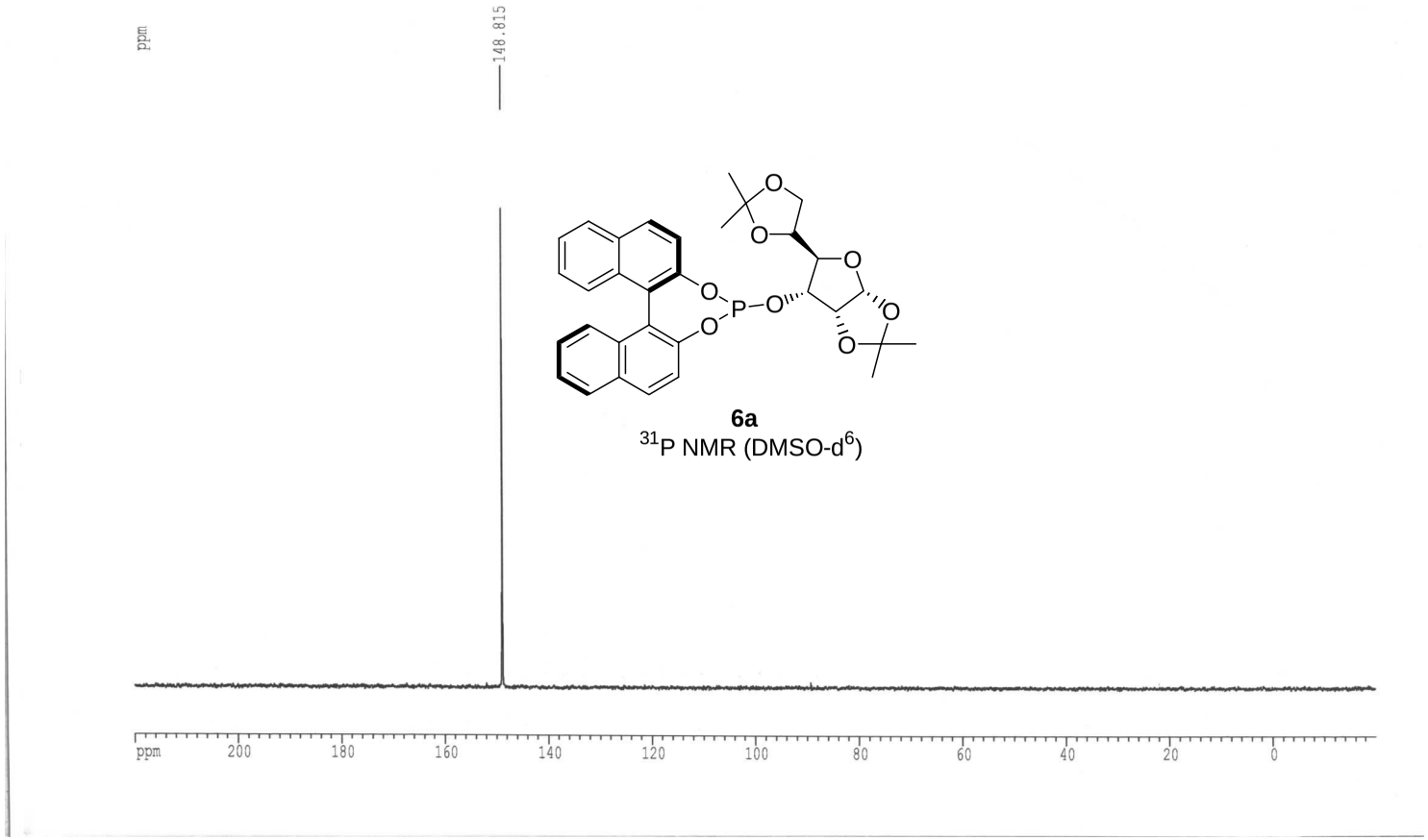
^{1}H NMR (DMSO-d^{6})



6a

^{13}C NMR (DMSO-d^{6})

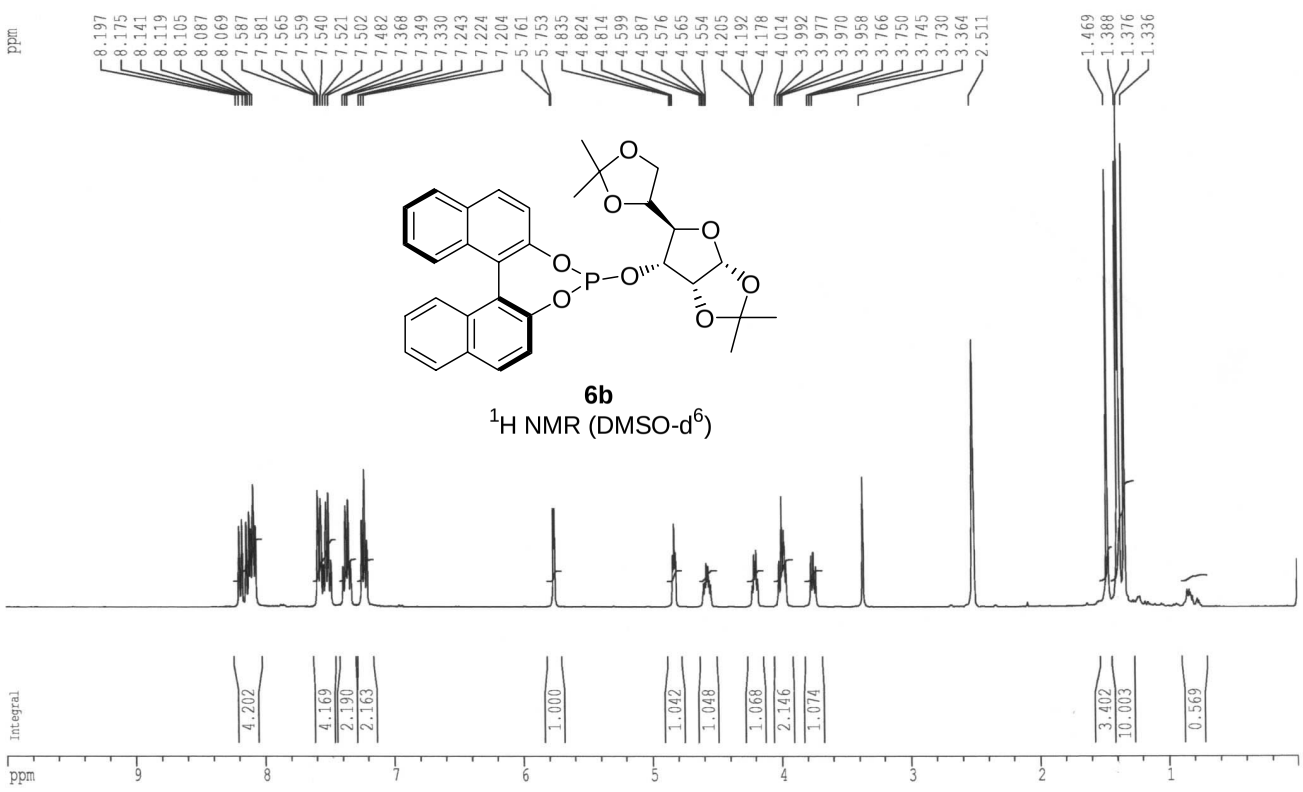
31P NMR (REGA-II in DMSO-d6)



6a

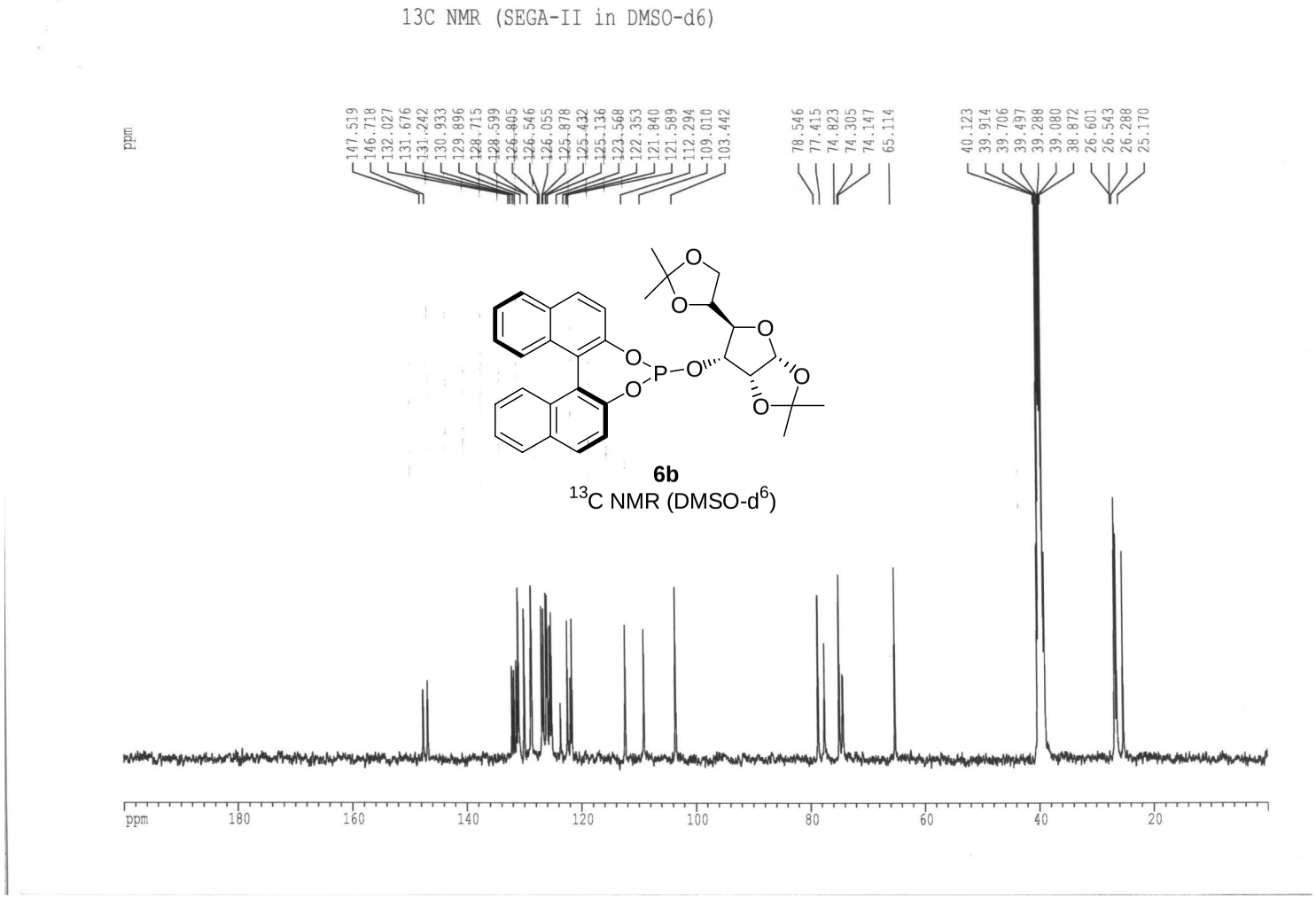
^{31}P NMR (DMSO-d^{6})

1H NMR (SEGA-II in DMSO-d6)



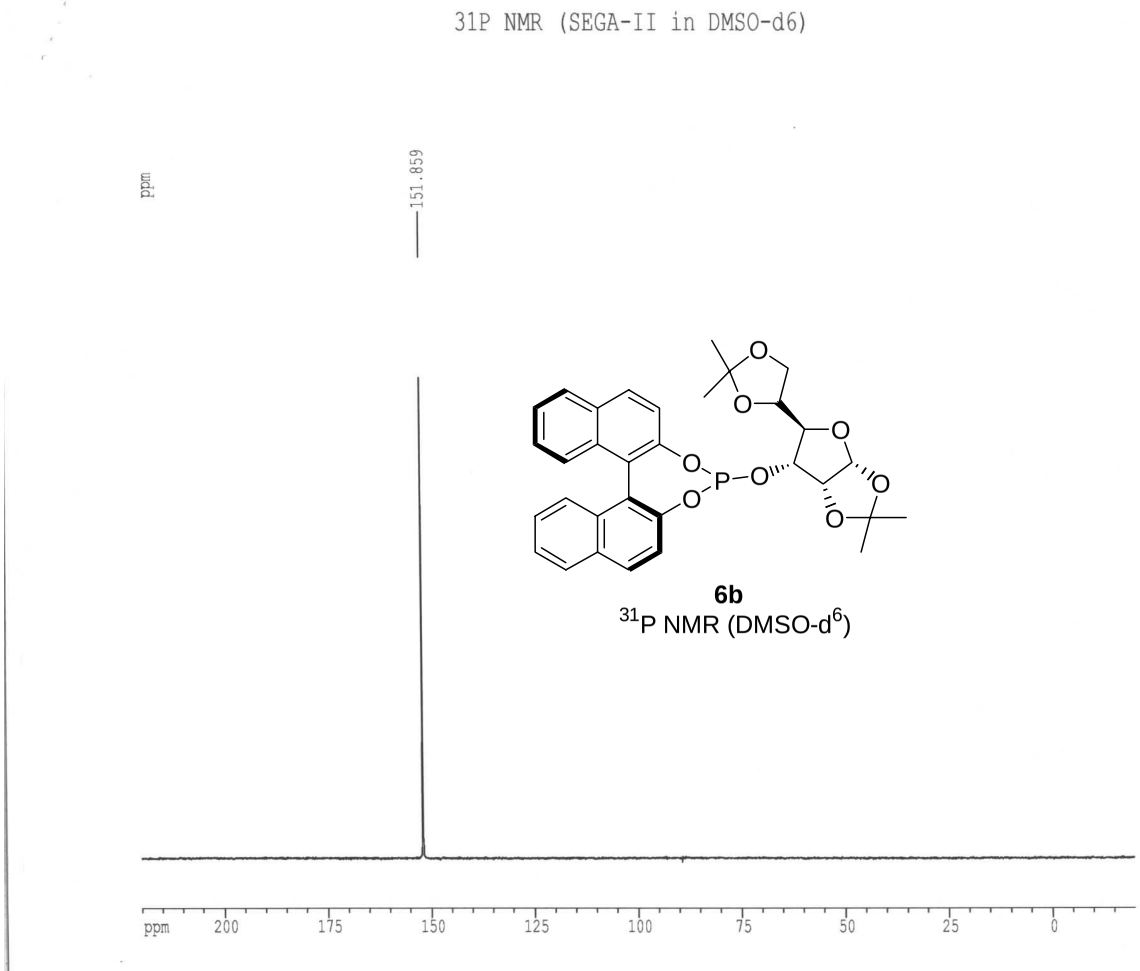
6b

^{1}H NMR (DMSO-d^{6})



6b

^{13}C NMR (DMSO-d^6)



6b

^{31}P NMR (DMSO-d^{6})

```
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EXPNO                      49
PROCNO                      1

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Time                     9.49
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TD                     16384
SOLVENT                 DMSO
NS                       400
DS                         0
SWH                43103.449 Hz
FIDRES              2.630826 Hz
AQ                 0.1901044 sec
RG                      8192
DW                    11.600 usec
DE                    51.00 usec
TE                    300.0 K
d11                0.0300000 sec
PL12                  25.60 dB
CPDPRG2              waltz16
PCPD2                 80.00 usec
SFO2              400.1320000 MHz
NUC2                      1H
PL2                    7.50 dB
D1                 1.00000000 sec
P1                    20.00 usec
DE                    51.00 usec
SFO1              161.9899872 MHz
NUC1                     31P
PL1                    0.00 dB

F2 - Processing parameters
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SF                161.9755436 MHz
WDW                       EM
SSB                        0
LB                     6.00 Hz
GB                         0
PC                     2.00

1D NMR plot parameters
CX                    20.00 cm
F1P                  220.000 ppm
F1                  35634.62 Hz
F2P                  -20.000 ppm
F2                  -3239.51 Hz
PPMCM                12.00000 ppm/cm
HZCM                1943.70667 Hz/cm
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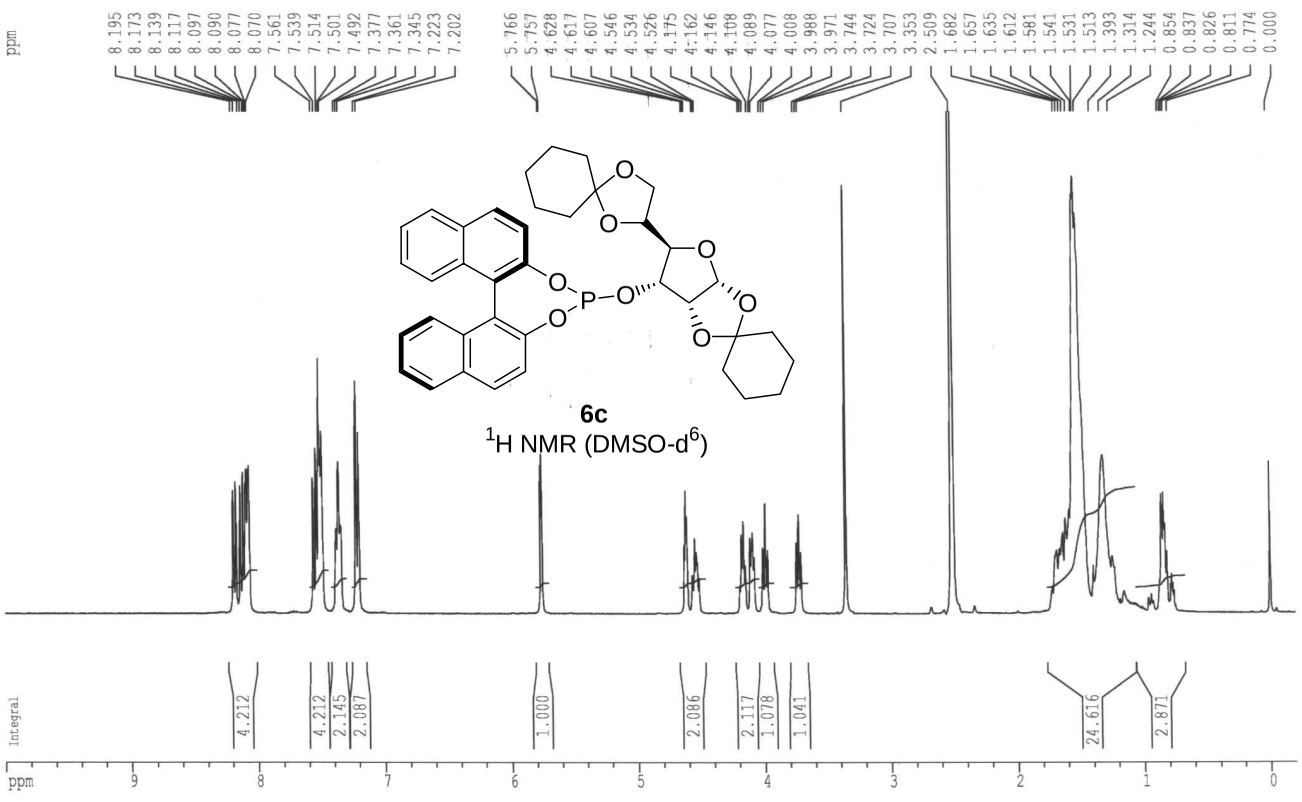
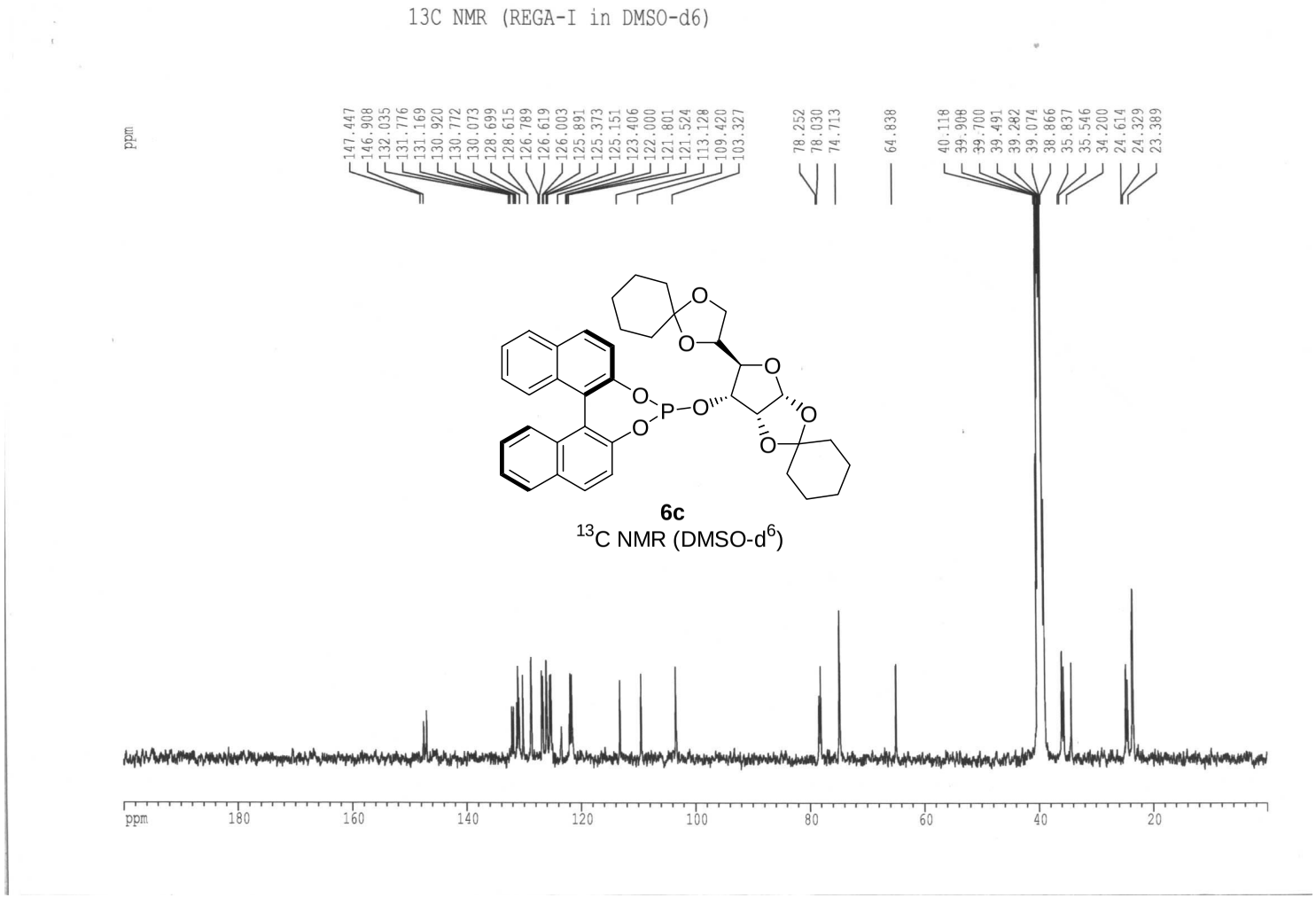
1H NMR (REGA-I in DMSO-d6)



6c

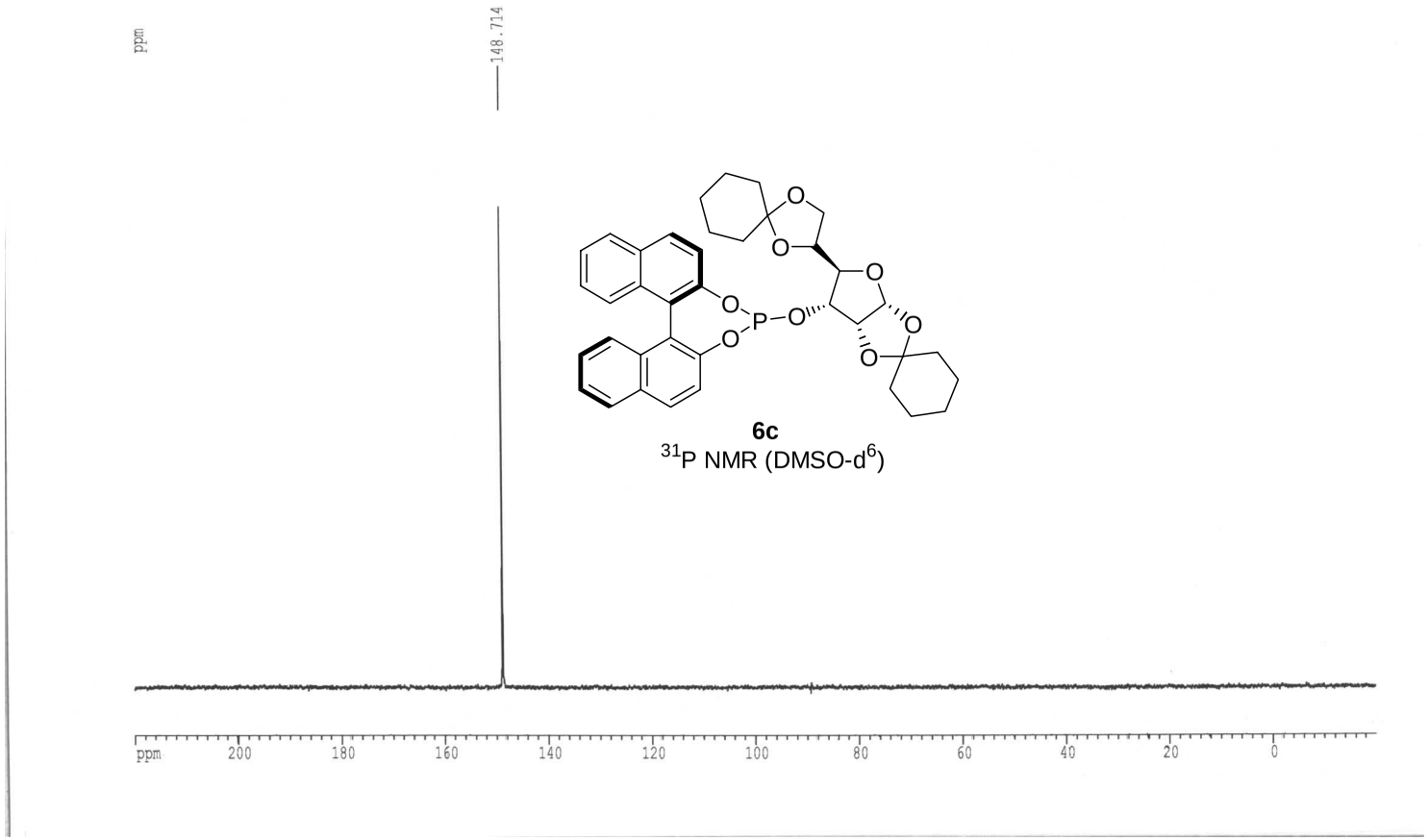
^{1}H NMR (DMSO-d^{6})



6c

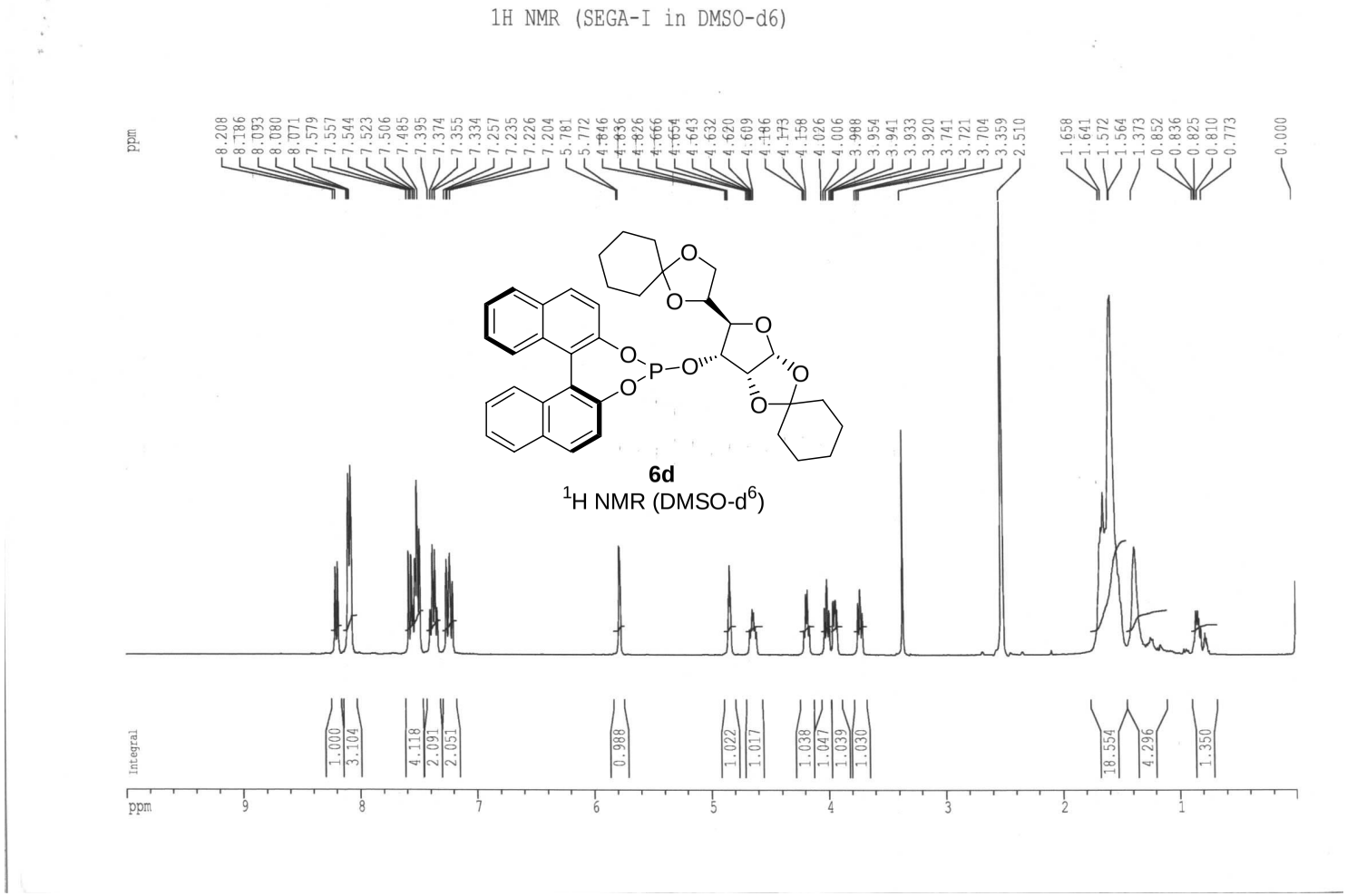
^{13}C NMR (DMSO-d^6)

31P NMR (REGA-I in DMSO-d6)



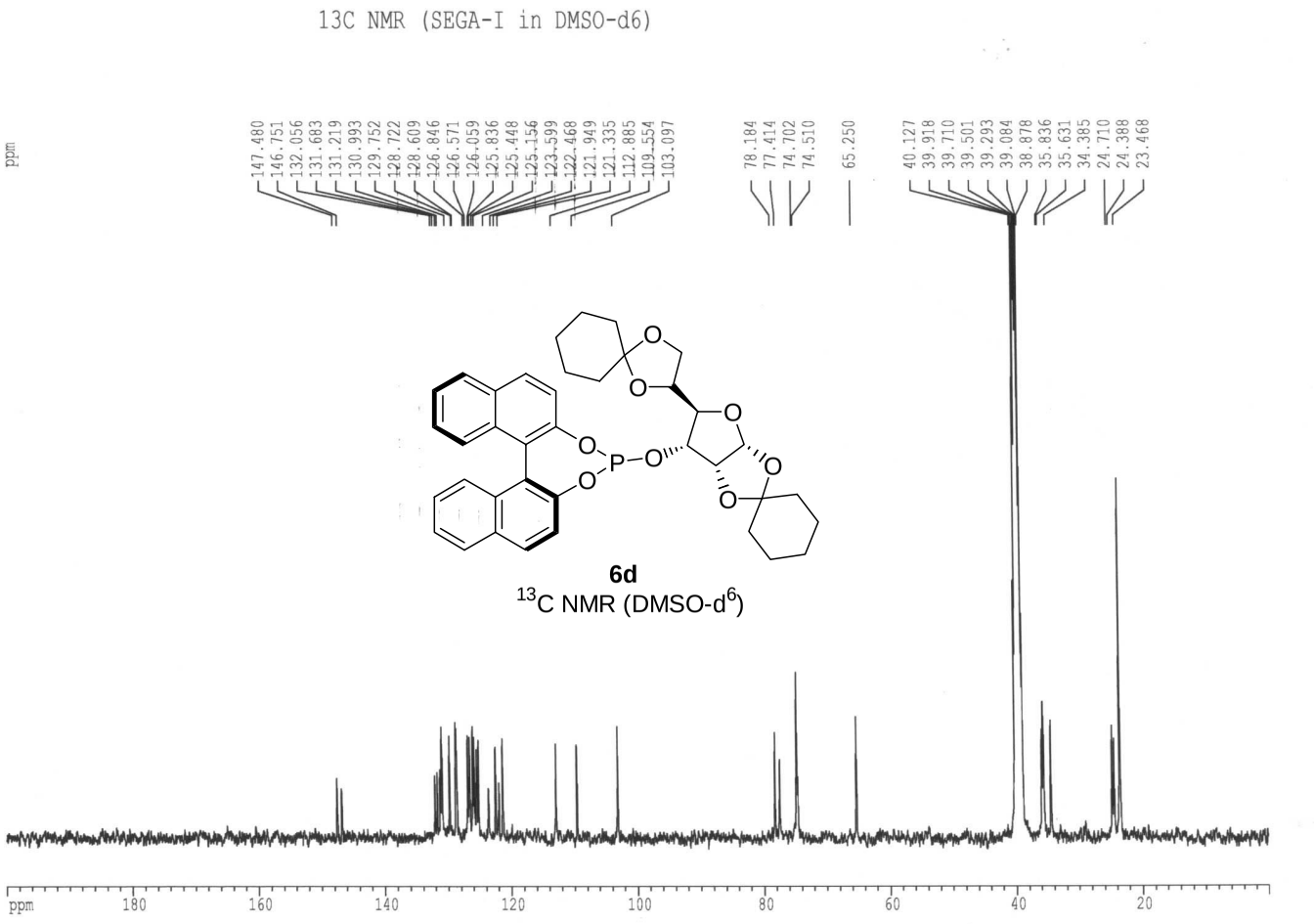
6c

^{31}P NMR (DMSO-d^{6})



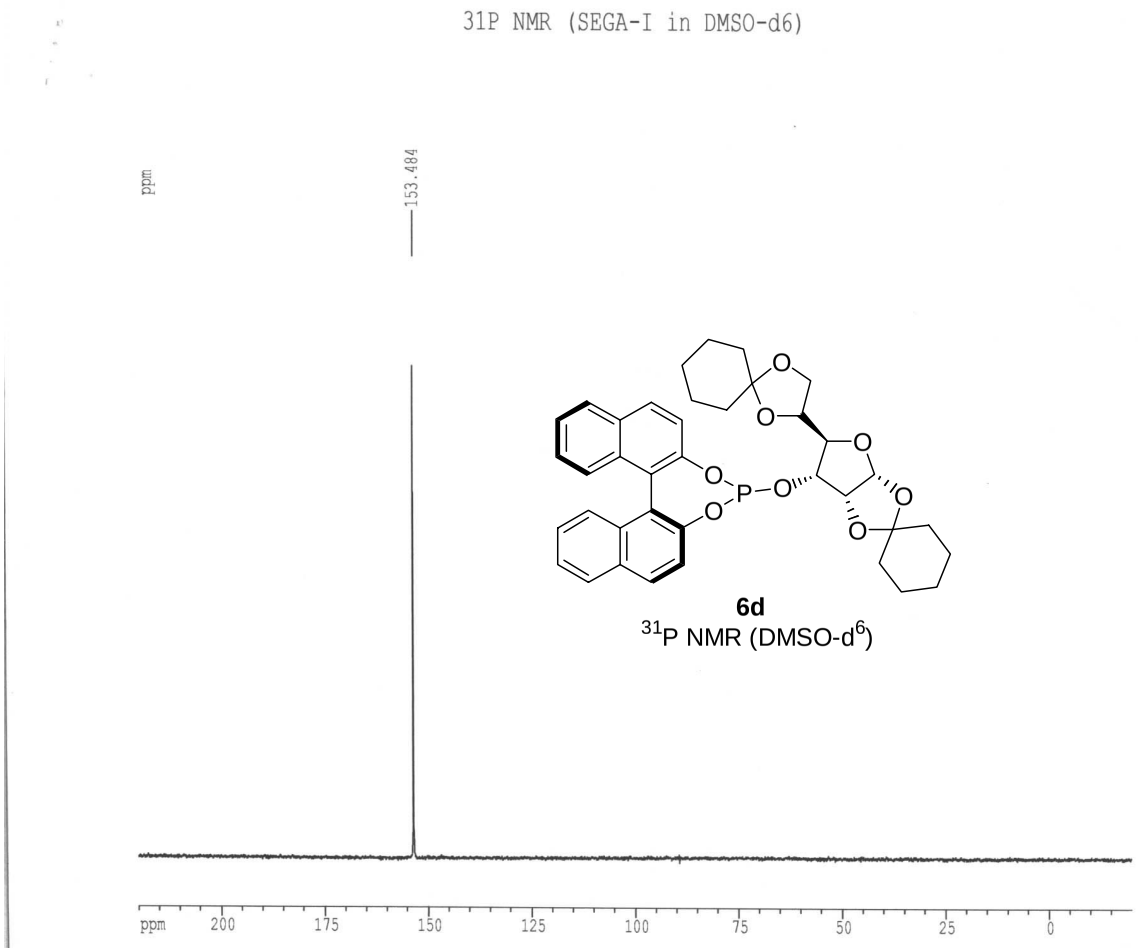
6d

^{1}H NMR (DMSO-d^6)



6d

^{13}C NMR (DMSO-d^6)



6d

^{31}P NMR (DMSO-d^{6})

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Current Data Parameters
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EXPNO                     46
PROCNO                     1

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TD                     16384
SOLVENT                 DMSO
NS                       200
DS                         0
SWH                43103.449 Hz
FIDRES              2.630826 Hz
AQ                  0.1901044 sec
RG                       8192
DW                     11.600 usec
DE                      51.00 usec
TE                      300.0 K
d11                 0.0300000 sec
PL12                    25.60 dB
CPDPRG2                waltz16
PCPD2                   80.00 usec
SFO2               400.1320000 MHz
NUC2                       1H
PL2                     7.50 dB
D1                  1.00000000 sec
P1                      20.00 usec
DE                      51.00 usec
SFO1               161.9899872 MHz
NUC1                      31P
PL1                     0.00 dB

F2 - Processing parameters
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SF                 161.9755436 MHz
WDW                       EM
SSB                        0
LB                      6.00 Hz
GB                         0
PC                      2.00

1D NMR plot parameters
CX                      20.00 cm
F1P                    220.000 ppm
F1                   35634.62 Hz
F2P                    -20.000 ppm
F2                   -3239.51 Hz
PPMCM                 12.00000 ppm/cm
HZCM                1943.70667 Hz/cm
```