Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Planar Chiral [2.2]Paracyclophane-based Bis(thiourea) Catalyst: Application to Asymmetric Henry Reaction

Shinji Kitagaki,*[,†] Takahiro Ueda, Chisato Mukai

Division of Pharmaceutical Sciences, Graduate School of Medical Sciences, Kanazawa University

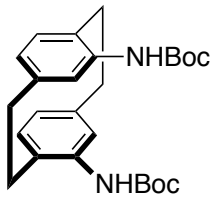
Kakuma-machi, Kanazawa, 920-1192, Japan

† Current address: Faculty of Pharmacy, Meijo University, 150 Yagotoyama, Tempaku-ku, Nagoya 468-8503, Japan.

Table of Contents.

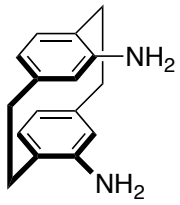
General Experimental Details. Melting points were measured with YANAGIMOTO micro melting point apparatus, and were uncorrected. Optical rotations were measured on a JASCO P-2200. IR spectra were measured with a SHIMADZU FTIR-8700 spectrometer for samples in $CHCl_3$. ^1H NMR spectra were measured with a JEOL JNM-ECS400 or JNM-ECA600 spectrometers for samples in $CDCl_3$. Tetramethylsilane (0.00 ppm) was used as an internal standard. ^{13}C NMR spectra were measured with JNM-ECS400 or JNM-ECA600 spectrometers for samples in $CDCl_3$. $CDCl_3$ (77.00 ppm) was used as an internal standard. High resolution mass spectra were measured in direct analysis in real time with TOF analyzer, a JEOL JMS-T100TD, or JMS-SX102A. Commercially available reagents were used throughout without purification unless otherwise stated. *i*-Pr_2NEt was distilled from calcium hydride under a nitrogen atmosphere. Silica gel (silica gel 60N, 40-50 mm, Kanto Chemical) was used for chromatography. All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Organic extracts were dried over anhydrous Na_2SO_4. Experimental details and the spectroscopic data of compounds **2** and **13** have been described in reference 1. Bromocyclophanol (R_p)-**7** was prepared according to Rozenberg's procedure.[2]

(R_p)-(–)-4,12-Bis[(*N-tert*-butoxycarbonyl)amino][2.2]-paracyclophane [(R_p)-3].



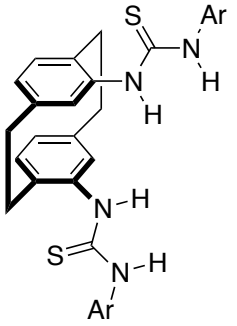
To an oven-dried screw cap tube equipped with a magnetic stirring bar were added (R_p)-**2** (20.0 mg, 4.59 x 10^{-2} mmol), *N-ter*t-butyl carbamate (32.3 mg, 0.275 mmol), JohnPhos (2.7 mg, 9.2 x 10^{-3} mmol), $Pd_2(dba)_3$ (4.2 mg, 4.6 x 10^{-3} mmol), NaOPh (15.7 mg, 0.135 mmol) and toluene (0.1 mL). After flushing with argon, the tube was capped and stirred for 18 h at 85 °C. The reaction mixture was cooled, diluted with CH_2Cl_2, quenched by addition of saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was washed with brine, dried and concentrated to dryness. The residue was chromatographed with hexane-EtOAc (20:1) to afford (R_p)-**3** as a white solid (12.6 mg, 63%). Mp 187-188 °C; $[\alpha]_D^{26}$ –36.2 (*c* 1.00, $CHCl_3$); IR ν_{max}/cm^{-1} 3441, 3335, 1715, 1516; ^1H NMR (600 MHz) δ 7.06 (brs, 1H), 6.71 (brs, 1H), 6.48 (d, *J* = 7.9 Hz, 2H), 6.35 (dd, *J* = 7.9, 1.7 Hz, 2H), 3.31-3.27 (m, 2H), 3.04 (dd, *J* = 11.5, 11.2 Hz, 2H), 2.96-2.91 (m, 2H), 2.75-2.71 (m, 2H), 1.55 (s, 18H); ^{13}C NMR (150 MHz, 55 °C) δ 153.7, 140.6, 136.7, 135.3, 132.0, 129.2, 123.1, 80.1, 33.4, 33.1, 28.5; MS (DART) *m/z* 439 (32.3, M^++1); HRMS (DART) calcd for $C_{26}H_{35}N_2O_4$ 439.2597, found 439.2599.

(R_p)-(+)-4,12-Diamino[2.2]paracyclophane [(R_p)-4].[3]



To a solution of (R_p)-**3** (43.6 mg, 9.95 x 10^{-2} mmol) in CH_2Cl_2 (1.0 mL) was added TFA (0.08 mL, 1 mmol) at room temperature. The reaction mixture was stirred for 26 h, quenched by addition of saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane-EtOAc (2:1) to afford (R_p)-**4** (21.7 mg, 92%) as a brown solid. Mp 189-191 °C; $[\alpha]_D^{28}$ +95.4 (*c* 1.00, $CHCl_3$); IR ν_{max}/cm^{-1} 3468, 3387, 1616; ^{1}H NMR (600 MHz) δ 6.35 (d, *J* = 7.6 Hz, 2H), 6.19 (d, *J* = 1.4 Hz, 2H), 6.04 (dd, *J* = 7.6, 1.4 Hz, 2H), 3.37 (brs, 4H), 3.05-3.01 (m, 2H), 2.92-2.89 (m, 4H), 2.64-2.59 (m, 2H); ^{13}C NMR (150 MHz) δ 144.5, 141.1, 135.1, 124.0, 123.0, 116.3, 32.7, 32.0; MS (DART) *m/z* 239 (57.9, M^++1); HRMS (DART) calcd for $C_{16}H_{19}N_2$ 239.1548, found 239.1545.

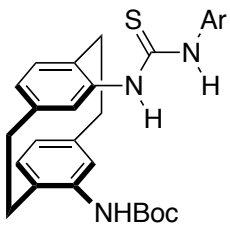
(R_p)-(–)-4,12-Bis{*N'*-[3,5-bis(trifluoromethyl)phenyl]thioureido}-[2.2]paracyclophane [(R_p)-1].



Ar=3,5-$(CF_3)_2C_6H_3$

To a solution of (R_p)-**3** (21.7 mg, 9.11 x 10^{-2} mmol) in THF (1.8 mL) was added 3,5-bis(trifluoromethyl)phenyl isothiocyanate (0.16 mL, 0.91 mmol) at 0 °C. The reaction mixture was stirred for 1 d at the same temperature and concentrated to dryness. The residue was chromatographed with hexane-EtOAc (6:1) to afford (R_p)-**1** (52.4 mg, 74%) as a white solid. Mp 129-130 °C; $[\alpha]_D^{26}$ –26.3 (*c* 1.00, $CHCl_3$); IR ν_{max}/cm^{-1} 3342, 1529, 1279, 1182, 1142; ^{1}H NMR (600 MHz) δ 9.20 (brs, 2H), 8.13 (brs, 2H), 7.89 (s, 4H), 7.64 (s, 2H), 6.71 (d, *J* = 7.3 Hz, 4H), 6.64 (d, *J* = 7.3 Hz, 2H), 3.35-3.30 (m, 2H), 3.19-3.03 (m, 4H), 2.92-2.84 (m, 2H); ^{13}C NMR (150 MHz) δ 178.8, 142.6, 139.1, 136.6, 135.0, 134.7, 133.0, 132.2 (q, $J_{C\text{-}F}$ = 33.5 Hz), 125.3, 124.7, 123.7 (q, $J_{C\text{-}F}$ = 272.7 Hz), 119.6, 33.6, 33.1; MS (EI) *m/z* 781 (63.5, M^+); HRMS calcd for $C_{34}H_{25}F_{12}N_4S_2$ 781.1329, found 781.1321.

(R_p)-(–)-*N*-[12-(*N*-*tert*-Butoxycarbonyl)amino[2.2]paracyclophan-4-yl]-*N'*-[3,5-bis(trifluoromethyl)phenyl]thiourea [(R_p)-8].

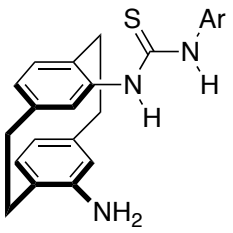


To a solution of (R_p)-**3** (30.0 mg, 6.84 x 10^{-2} mmol) in CH_2Cl_2 (0.7 mL) was added TFA (0.01 mL, 0.3 mmol) at room temperature. The reaction mixture was stirred for 2.5 h, quenched by addition of

saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane-EtOAc (6:1) to afford (R_p)-(–)-12-amino-4-(*N*-*tert*-butoxycarbonyl)amino[2.2]-paracyclophane (16.8 mg, 73%) as a white solid. Mp 157-159 °C; $[\alpha]_D^{27}$ –90.3 (*c* 0.90, $CHCl_3$); IR ν_{max}/cm^{-1} 3443, 3348, 1720, 1518; ^{1}H NMR (600 MHz) δ 7.54 (s, 1H), 6.49 (d, *J* = 7.7 Hz, 1H), 6.32 (d, *J* = 7.7 Hz, 1H), 6.26 (dd, *J* = 7.7, 1.7 Hz, 2H), 6.06 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.75 (d, *J* = 1.7 Hz, 1H), 3.86 (brs, 2H), 3.19-3.12 (m, 2H) 3.08-3.04 (m, 2H), 2.99 (dd, *J* = 12.0, 11.2 Hz, 1H), 2.84-2.79 (m, 1H), 2.73-2.61 (m, 2H), 1.56 (s, 9H); ^{13}C NMR (150 MHz, 55 °C) δ 153.4, 146.4, 140.9, 140.5, 136.7, 135.6, 134.9, 128.4, 124.2, 122.6, 119.1, 118.7, 80.4, 33.4, 32.6, 32.3, 28.4; MS (DART) *m/z* 339 (14.25, M^++1); HRMS (DART) calcd for $C_{21}H_{27}N_2O_2$ 339.2073, found 339.2078.

To a solution of the above amine (5.6 mg, 1.7 x 10^{-2} mmol) in THF (0.4 mL) was added 3,5-bis(trifluoromethyl)phenyl isothiocyanate (9.0 μL, 4.9 x 10^{-2} mmol) at 0 °C. The reaction mixture was stirred for 11.5 h at room temperature and concentrated to dryness. The residue was chromatographed with hexane-acetone (5:1) to afford (R_p)-**8** (8.5 mg, 82%) as a white solid. Mp 105-107 °C; $[\alpha]_D^{26}$ –63.5 (*c* 0.83, $CHCl_3$); IR ν_{max}/cm^{-1} 3439, 3344, 1715, 1518, 1279, 1180, 1143; ^{1}H NMR (600 MHz, 55 °C) δ 9.47 (s, 1H), 8.00 (s, 2H), 7.74 (s, 1H), 7.62, (s, 1H), 7.34 (s, 1H), 6.65 (d, *J* = 7.9 Hz, 2H), 6.55 (d, *J* = 7.9 Hz, 1H), 6.50 (d, *J* = 7.9 Hz, 1H), 6.39 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.29 (d, *J* = 8.2 Hz, 2H), 3.37-3.33 (m, 1H), 3.22 (dd, *J* = 14.1, 10.0 Hz, 1H), 3.15-3.06 (m, 3H), 3.02-2.97 (m, 1H), 2.87-2.78 (m, 2H), 1.57 (s, 9H); ^{13}C NMR (150 MHz, DMSO-d_6, 60 °C) δ 179.6, 153.2, 141.7, 140.6, 139.8, 136.5, 136.3, 135.9, 135.1, 133.0, 131.0, 129.9 (q, $J_{C\text{-}F}$ = 32.6 Hz), 128.7, 125.2, 123.3, 123.0 (q, $J_{C\text{-}F}$ = 272.7 Hz), 122.4, 116.7, 78.9, 33.2, 32.9, 32.3, 28.0; MS (DART) *m/z* 610 (100.0, M^++1); HRMS (DART) calcd for $C_{30}H_{30}F_6N_3O_2S$ 610.1963, found 610.1948.

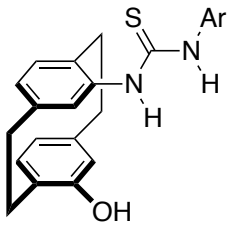
(R_p)-(–)-*N*-(12-Amino[2.2]paracyclophan-4-yl)-*N'*-[3,5-bis-(trifluoromethyl)phenyl]thiourea [(R_p)-9].



To a solution of (R_p)-**4** (10.0 mg, 4.20 x 10^{-2} mmol) in CH_2Cl_2 (0.4 mL) was added 3,5-bis(trifluoromethyl)phenyl isothiocyanate (9.0 μL, 4.9 x 10^{-2} mmol) at 0 °C. The reaction mixture was stirred for 2.5 h at room temperature and concentrated to dryness. The residue was chromatographed with hexane-EtOAc (4:1) to afford (R_p)-**9** (17.5 mg, 78%) as a white solid. Mp 99-101 °C; $[\alpha]_D^{26}$

–57.1 (*c* 1.00, $CHCl_3$); IR ν_{max}/cm^{-1} 3394, 3339, 1620, 1279, 1182, 1142; ^1H NMR (600 MHz) δ 8.35 (s, 1H), 7.97 (s, 2H), 7.92 (s, 1H), 7.68 (s, 1H), 7.01 (s, 1H), 6.74 (dd, J = 7.9 Hz, 1H), 6.55 (dd, J = 7.9, 1.5 Hz, 1H), 6.38 (d, J = 7.7 Hz, 1H), 6.16 (dd, J = 7.7, 1.7 Hz, 1H), 5.86 (d, J = 1.7 Hz, 1H), 3.66 (brs, 2H), 3.21-3.16 (m, 1H), 3.13-3.05 (m, 3H), 2.99-2.92 (m, 2H), 2.85-2.80 (m, 1H), 2.74-2.67 (m, 1H); ^{13}C NMR (150 MHz) δ 179.3, 145.3, 142.9, 140.9, 139.7, 135.8, 135.3, 134.7, 133.9, 133.6, 131.8 (q, $J_{C\text{-}F}$ = 34.0 Hz), 125.0, 124.4, 124.4, 122.9 (q, $J_{C\text{-}F}$ = 273.1 Hz), 122.6, 119.4, 117.2, 34.0, 32.6, 32.1, 31.9; MS (DART) *m/z* 510 (37.2, M^++1); HRMS (DART) calcd for $C_{25}H_{22}F_6N_3S$ 510.1439, found 510.1426.

(R_p)-(–)-*N*-(12-Hydroxy[2.2]paracyclophan-4-yl)-*N'*-[3,5-bis-(trifluoromethyl)phenyl]thiourea [(R_p)-10].[4]

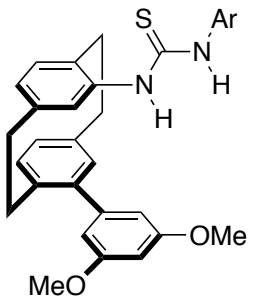


To an oven-dried screw cap tube equipped with a magnetic stirring bar were added (R_p)-4-bromo-12-hydroxy[2.2]paracyclophane (20.0 mg, 6.60 x 10^{-2} mmol), *N-tert*-butyl carbamate (9.3 mg, 7.9 x 10^{-2} mmol), JohnPhos (3.9 mg, 1.3 x 10^{-2} mmol), $Pd_2(dba)_3$ (6.0 mg, 6.6 x 10^{-3} mmol), NaOPh (11.5 mg, 9.91 x 10^{-2} mmol), and toluene (0.15 mL). After flushing with argon, the tube was capped and stirred for 18 h at 85 °C. The reaction mixture was cooled, diluted with CH_2Cl_2, quenched by addition of saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was washed with 10% aqueous NaOH, water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane-EtOAc (20:1) to afford (R_p)-12-(*N-tert*-butoxycarbonyl)amino-4-hydroxy[2.2]paracyclophane (13.7 mg, 61%) as a white solid.

To a solution of the above carbamate (13.7 mg, 4.04 x 10^{-2} mmol) in CH_2Cl_2 (0.4 mL) was added TFA (0.03 mL, 0.39 mmol) at room temperature. The reaction mixture was stirred for 18 h, quenched by addition of saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was washed with water and brine, dried and concentrated to leave the crude (R_p)-12-amino-4-hydroxy[2.2]paracyclophane (9.2 mg) as a yellow solid. To a solution of the crude amine in CH_2Cl_2 (0.75 mL) was added 3,5-bis(trifluoromethyl)phenyl isothiocyanate (20 μL, 0.11 mmol) at 0 °C. The reaction mixture was stirred for 18 h at room temperature and concentrated to dryness. The residue was chromatographed with hexane-EtOAc (10:1) to afford (R_p)-**10** (14.4 mg, 70% for 2 steps) as a white solid. Mp 124-126 °C; $[\alpha]_D^{23}$ –32.1 (*c* 0.20, toluene) [lit.,[4] $[\alpha]_D^{20}$ +35.2 (*c* 0.75, toluene) for (S_p)-**10**];

^{1}H NMR (600 MHz) δ 10.03 (s, 1H), 7.99 (s, 1H), 7.89 (d, J = 7.8 Hz, 2H), 7.75 (s, 1H), 6.84 (dd, J = 16.0, 1.4 Hz, 1H), 6.70 (d, J = 7.8 Hz, 2H), 6.54 (d, J = 7.8 Hz, 1H), 6.49 (d, J = 7.8 Hz, 1H), 6.28 (dd, J = 7.8, 1.6 Hz, 2H), 5.99 (dd, J = 21.2, 1.6 Hz, 1H), 3.41-3.35 (m, 1H), 3.27-3.20 (m, 1H), 3.12-2.98 (m, 4H), 2.94-2.86 (m, 1H), 2.64-2.56 (m, 1H).

(R_p)-(+)-*N*-{12-(3,5-Dimethoxyphenyl)[2.2]paracyclophan-4-yl}-*N'*-[3,5-bis(trifluoromethyl)phenyl]thiourea [(R_p)-11].



To a solution of (R_p)-4-amino-12-(3,5-dimethoxyphenyl)[2.2]-paracyclophane[1] (5.5 mg, 1.3 x 10^{-2} mmol) in THF (0.3 mL) was added 3,5-bis(trifluoromethyl)phenyl isothiocyanate (8.0 μL, 4.1 x 10^{-2} mmol) at 0 °C. The reaction mixture was stirred for 41 h at room temperature and concentrated to dryness. The residue was chromatographed on alumina with hexane-EtOAc (10:1) to afford (R_p)-**11** (5.4 mg, 66%) as a white solid. Mp 80-82 °C; $[\alpha]_D^{20}$ +135.7 (*c* 0.48, $CHCl_3$); IR ν_{max}/cm^{-1} 3402, 3348, 1278, 1182, 1142; ^{1}H NMR (600 MHz) δ 7.97 (s, 2H), 7.66 (s, 1H), 7.62 (s, 1H), 7.58 (s, 1H), 6.96 (d, J = 1.7 Hz, 1H), 6.81 (d, J = 7.9 Hz, 1H), 6.77 (dd, J = 7.9, 1.7 Hz, 1H), 6.69 (d, J = 7.9 Hz, 1H), 6.56 (d, J = 2.2 Hz, 2H), 6.52-6.49 (m, 2H), 6.42 (d, J = 1.4 Hz, 1H), 3.90 (s, 6H), 3.59-3.53 (m, 1H), 3.39-3.35 (m, 1H), 3.32-3.28 (m, 1H), 3.10 (ddd, J = 13.4, 10.0, 6.9 Hz, 1H), 2.99-2.89 (m, 3H), 2.70-2.65 (m, 1H); ^{13}C NMR (150 MHz) δ 179.2, 161.1, 143.4, 142.2, 141.8, 139.7, 139.1, 136.9, 136.3, 136.0, 135.4, 133.4, 133.0, 132.7, 131.8 (q, $J_{C\text{-}F}$ = 34.0 Hz), 128.3, 127.4, 124.4, 122.4 (q, $J_{C\text{-}F}$ = 273.1 Hz), 119.3, 107.2, 99.5, 55.6, 34.0, 33.9, 33.3, 32.6; MS (EI) 630 (15.3, M^+); HRMS (EI) calcd for $C_{33}H_{28}F_6N_2O_2S$ 630.1776, found 630.1778.

Typical Procedure for Henry Reaction (Table 2, Entry 1).

To a solution of aldehyde **5a** (15.1 mg, 0.100 mmol), (R_p)-**1** (3.9 mg, 5.0 x 10^{-3} mmol) and *i*-Pr_2NEt (3.4 μL, 2.0 x 10^{-2} mmol) in THF (0.1 mL) was added nitromethane (**6a**) (54 μL, 1.0 mmol) at –25 °C. After being stirred for 3 h at the same temperature, the reaction mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with EtOAc. The extract was washed with brine, dried and concentrated to dryness. The residue was purified by flash chromatography on silica gel with hexane-EtOAc (3:1) to afford **7a** (17.8 mg, 84%) as a yellow solid.

(*R*)-2-Nitro-1-(4-nitrophenyl)ethanol (7a).

$[\alpha]_D^{27}$ –31.1 (*c* 0.87, $CHCl_3$) {lit.,[5] $[\alpha]_D^{24}$ –30.4 (*c* 0.53, $CHCl_3$) for 88% ee}; ^{1}H NMR (600 MHz) δ 8.28-8.26 (m, 2H), 7.65-7.62 (m, 2H), 5.63-5.60 (m, 1H), 4.63-4.56 (m, 2H), 3.18 (d, *J* = 4.0 Hz, 1H); ^{13}C NMR (150 MHz) δ 148.1, 144.9, 126.9, 124.2, 80.6, 69.9; HPLC: OD-H column; λ = 254 nm; eluent: hexane/isopropanol = 85/15; flow rate: 0.8 mL/min; t_R = 22.3 min (major), t_R = 28.0 min (minor); ee = 97%.

(*R*)-1-(4-Chlorophenyl)-2-nitroethanol (7b).

$[\alpha]_D^{26}$ –41.6 (*c* 0.32, $CHCl_3$) {lit.,[5] $[\alpha]_D^{22}$ –38.8 (*c* 0.55, $CHCl_3$) for 90% ee}; ^{1}H NMR (600 MHz) δ 7.39-7.35 (m, 4H), 5.46 (dd, *J* = 9.5, 2.9 Hz, 1H), 4.57 (dd, *J* = 13.4, 9.5 Hz, 1H), 4.51 (dd, *J* = 13.4, 2.9 Hz, 1H), 2.90 (s, 1H); ^{13}C NMR (150 MHz) δ 136.5, 134.9, 129.2, 127.3, 80.9, 70.3; HPLC: OD-H column; λ = 254 nm; eluent: hexane/isopropanol = 85/15; flow rate: 0.8 mL/min; t_R = 12.8 min (major), t_R = 15.7 min (minor); ee = 95%.

(*R*)-2-Nitro-1-phenylethanol (7c).

$[\alpha]_D^{26}$ –33.3 (*c* 0.26, $CHCl_3$) {lit.,[6] $[\alpha]_D^{23}$ –37.0 (*c* 3.55, $CHCl_3$) for 87% ee}; ^{1}H NMR (600 MHz) δ 7.44-7.35 (m, 5H), 5.47 (dt, *J* = 9.6, 2.9 Hz, 1H), 4.61 (dd, *J* = 13.4, 3.6 Hz, 1H), 4.52 (dd, *J* = 13.4, 2.9 Hz, 1H), 2.83 (d, *J* = 3.3 Hz, 1H); ^{13}C NMR (150 MHz) δ 138.0, 129.0, 129.0, 125.9, 81.2, 71.0; HPLC: OD-H column; λ = 254 nm; eluent: hexane/isopropanol = 85/15; flow rate: 0.8 mL/min; t_R = 14.0 min (major), t_R = 17.4 min (minor); ee = 90%.

(*R*)-1-(4-Methoxyphenyl)-2-nitroethanol (7d).

$[\alpha]_D^{26}$ –34.4 (*c* 0.65, $CHCl_3$) {lit.,[6] $[\alpha]_D^{23}$ –35.5 (*c* 4.70, $CHCl_3$) for 76% ee}; ^{1}H NMR (600 MHz) δ 7.33-7.31 (m, 2H), 6.94-6.91 (m, 2H), 5.41 (d, *J* = 9.8 Hz, 1H), 4.60 (dd, *J* = 13.2, 9.8 Hz, 1H), 4.50 (dd, *J* = 13.2, 3.1 Hz, 1H), 3.81 (s, 3H), 2.71 (d, *J* = 2.6 Hz, 1H); ^{13}C NMR (150 MHz) δ 160.0, 130.0, 127.2, 114.4, 81.2, 71.0, 55.3; HPLC: OD-H column; λ = 254 nm; eluent: hexane/isopropanol = 85/15; flow rate: 0.8 mL/min; t_R = 18.2 min (major), t_R = 22.1 min (minor); ee = 86%.

(*R*)-2-Nitro-1-(3-nitrophenyl)ethanol (7e).

$[\alpha]_D^{26}$ –27.4 (*c* 0.87, CH_2Cl_2) {lit.,[7] $[\alpha]_D^{24}$ –27.4 (*c* 1.74, CH_2Cl_2) for 89% ee}; ^{1}H NMR (600 MHz) δ 8.33 (t, *J* = 1.7 Hz, 1H), 8.24-8.22 (m, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.62 (t, *J* = 7.9 Hz, 1H), 5.62 (dd, *J* = 8.8, 3.3 Hz, 1H), 4.66-4.59 (m, 2H), 3.26 (s, 1H); ^{13}C NMR (150 MHz) δ 148.5, 140.1, 132.0, 130.1, 123.8, 121.1, 80.6, 69.8; HPLC: OD-H column; λ = 254 nm; eluent: hexane/isopropanol = 90/10; flow rate: 0.8 mL/min; t_R = 34.1 min (major), t_R = 39.1 min (minor); ee = 96%.

(*R*)-2-Nitro-1-(2-nitrophenyl)ethanol (7f).

$[\alpha]_D^{20}$ +232.5 (*c* 0.75, CH_2Cl_2) {lit.,[8] $[\alpha]_D^{21}$ +227.1 (*c* 1.00, CH_2Cl_2) for 89% ee}; ^{1}H NMR (600 MHz) δ 8.09 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.77-7.74 (m, 1H), 7.57-7.55 (m, 1H), 6.05 (dd, *J* = 7.0, 2.2 Hz, 1H), 4.87 (dd, *J* = 13.7, 2.2 Hz, 1H), 4.56 (dd, *J* = 13.7, 9.1 Hz, 1H), 3.29 (s, 1H); ^{13}C NMR (150 MHz) δ 147.1, 134.4, 134.0, 129.7, 128.7, 125.0, 80.0, 66.8; HPLC: OD-H column; λ = 254 nm; eluent: hexane/isopropanol = 95/5; flow rate: 0.7 mL/min; t_R = 45.4 min (major), t_R = 51.4 min (minor); ee = 94%.

(*R*)-2-Nitro-1-pyridin-3-yl-ethanol (7g).

$[\alpha]_D^{26}$ –52.3 (*c* 0.34, CH_2Cl_2) {lit.,[9] $[\alpha]_D^{25}$ +37.6 (*c* 1.04, CH_2Cl_2) for (*S*)-**7g**, 86% ee}; ^{1}H NMR (600 MHz) δ 8.56 (d, *J* = 2.1 Hz, 1H), 8.52 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.82 (dt, *J* = 7.9, 1.7 Hz, 1H), 7.37 (dd, *J* = 7.9, 4.8 Hz, 1H), 5.53 (dd, *J* = 9.6, 3.1 Hz, 1H), 4.95 (brs, 1H), 4.64 (dd, *J* = 13.2, 9.6 Hz, 1H), 4.56 (dd, *J* = 13.2, 3.1 Hz, 1H); ^{13}C NMR (150 MHz) δ 149.7, 147.3, 134.6, 134.2, 124.0, 81.0, 68.6; HPLC: OD-H column; λ = 254 nm; eluent: hexane/isopropanol = 75/25; flow rate: 0.8 mL/min; t_R = 15.6 min (major), t_R = 30.1 min (minor); ee = 91%.

(*R*)-1-Naphtalen-1-yl-2-nitroethanol (7h).

$[\alpha]_D^{28}$ –25.8 (*c* 0.88, $CHCl_3$) {lit.,[5] $[\alpha]_D^{22}$ –24.7 (*c* 0.58, $CHCl_3$) for 93% ee}; ^{1}H NMR (600 MHz) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.60-7.50 (m, 3H), 6.25 (d, *J* = 9.1 Hz, 1H), 4.70-4.63 (m, 2H), 2.89 (d, *J* = 2.9 Hz, 1H); ^{13}C NMR (150 MHz) δ 133.7, 133.5, 129.5, 129.4, 129.3, 127.1, 126.1, 125.5, 123.4, 121.8, 80.8, 68.3; HPLC: OD-H column; λ = 254 nm; eluent: hexane/isopropanol = 85/15; flow rate: 0.8 mL/min; t_R = 16.0 min (major), t_R = 24.8 min (minor); ee = 91%.

(*R*)-1-Nitro-4-phenylbutan-2-ol (7i).

$[\alpha]_D^{24}$ +9.6 (*c* 0.73, $CHCl_3$) {lit.,[10] $[\alpha]_D^{22}$ +14.2 (*c* 1.00, $CHCl_3$) for 85% ee}; ^{1}H NMR (600 MHz) δ 7.32-7.29 (m, 2H), 7.25-7.19 (m, 3H), 4.46-4.27 (m, 3H), 2.88-2.82 (m, 1H), 2.78-2.71 (m, 1H), 2.65 (brs, 1H), 1.92-1.74 (m, 2H); ^{13}C NMR (150 MHz) δ 140.9, 128.9, 128.7, 126.6, 80.8, 68.0, 35.4, 31.6; HPLC: AD-H column; λ = 254 nm; eluent: hexane/isopropanol = 90/10; flow rate: 0.6 mL/min; t_R = 19.8 min (major), t_R = 25.3 min (minor); ee = 68%.

2-Nitro-1-(4-nitrophenyl)propan-1-ol (7j).

Diastereomer ratio was determined by ^{1}H NMR. Preferred configuration was determined by comparison of elution order of HPLC using the reported value.[11] ^{1}H NMR (600 MHz) δ 8.28-8.25 (m, 2H) (*syn*/*anti*), 7.61-7.59 (m, 2H) (*syn*/*anti*), 5.57 (d, *J* = 3.3 Hz, 0.6H) (*anti*), 5.21 (d, *J* = 8.2 Hz, 0.4H) (*syn*), 4.78-4.70 (m, 1H) (*syn*/*anti*), 3.04 (d, *J* = 3.4 Hz, 0.6H) (*anti*), 2.98 (d, *J* = 3.8 Hz, 0.4H) (*syn*), 1.50 (d, *J* = 6.8 Hz, 1.8H) (*anti*), 1.40 (d, *J* = 6.8 Hz, 1.2H) (*syn*); ^{13}C NMR (150 MHz) δ 148.3 (*syn*), 147.9 (*anti*), 145.4 (*anti*), 145.2 (*syn*), 127.9 (*syn*), 127.0 (*anti*), 124.1 (*syn*), 123.9 (*anti*), 87.7 (*syn*), 86.7 (*anti*), 75.0 (*syn*), 72.8 (*anti*), 16.2 (*syn*), 11.8 (*anti*); HPLC: AS-H column; λ = 254 nm; eluent: hexane/isopropanol = 90/10; flow rate: 1.0 mL/min; t_R = 35.9 min (*anti*), t_R = 44.2 min (*syn* minor: 1*S*,2*S*), t_R = 51.1 min (*syn* major: 1*R*,2*R*); ee_{syn} = 89%: OJ-H column; λ = 254 nm; eluent: hexane/isopropanol = 85/15; flow rate: 0.7 mL/min; t_R = 40.2 min (*anti* minor: 1*S*,2*R*), t_R = 43.3 min (*anti* major: 1*R*,2*S*), t_R = 63.8 min (*syn*); ee_{anti} = 93%.

2-Nitro-1-(4-nitrophenyl)butan-1-ol (7k).

Diastereomer ratio was determined by ^{1}H NMR. Preferred configuration was determined by

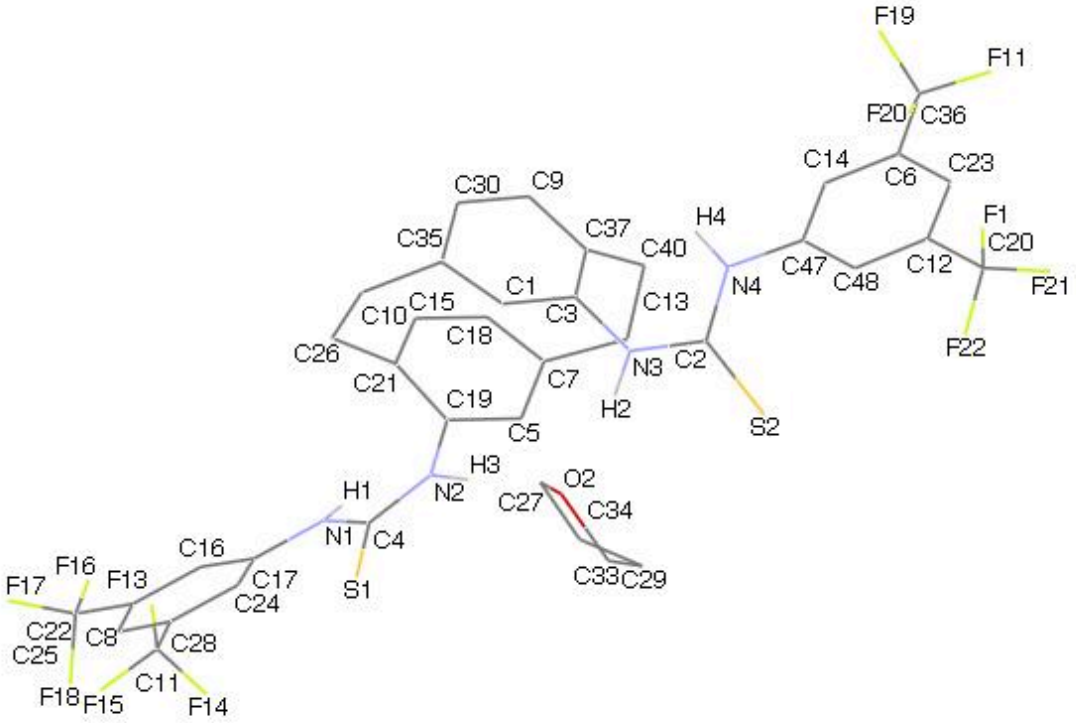
comparison of elution order of HPLC using the reported value.[12] ^{1}H NMR (600 MHz) δ 8.28-8.23 (m, 2H) (*syn*/*anti*), 7.60-7.58 (m, 2H) (*syn*/*anti*), 5.34 (d, J = 4.5 Hz, 0.4H) (*anti*), 5.19 (d, J = 8.4 Hz, 0.6H) (*syn*), 4.64-4.57 (m, 1H) (*syn*/*anti*), 3.05 (brs, 0.4H) (*anti*), 2.96 (brs, 0.6H) (*syn*), 2.23-2.15 (m, 0.4H) (*anti*), 1.97-1.90 (m, 0.6H) (*syn*), 1.87-1.80 (m, 0.4H) (*anti*), 1.53-1.46 (m, 0.6H) (*syn*), 0.96-0.91 (m, 3H) (*syn*/*anti*); ^{13}C NMR (150 MHz) δ 148.2 (*syn*), 148.0 (*anti*), 145.5 (*syn*), 145.4 (*anti*), 127.8 (*syn*), 127.2 (*anti*), 124.1 (*syn*), 123.9 (*anti*), 94.5 (*syn*), 94.1 (*anti*), 74.3 (*syn*), 73.2 (*anti*), 23.8 (*syn*), 21.1 (*anti*), 10.3 (*anti*), 10.1 (*syn*); HPLC: AD-H column; λ = 254 nm; eluent: hexane/isopropanol = 90/10; flow rate: 1.0 mL/min; t_R = 13.6 min (*anti*), t_R = 21.1 min (*syn* major: 1*R*,2*R*), t_R = 33.4 min (*syn* minor: 1*S*,2*S*); ee_{syn} = 87%: OD-H column; λ = 254 nm; eluent: hexane/isopropanol = 90/10; flow rate: 1.0 mL/min; t_R = 13.5 min (*anti* major: 1*R*,2*S*), t_R = 15.0 min (*anti* minor: 1*R*,2*S*), t_R = 18.6 min (*syn*); ee_{anti} = 91%.

1-(4-Chlorophenyl)-2-nitropropan-1-ol (7l).

Diastereomer ratio was determined by ^{1}H NMR. Preferred configuration was determined by comparison of elution order of HPLC using the reported value.[11] ^{1}H NMR (600 MHz) δ 7.39-7.31 (m, 4H) (*syn*/*anti*), 5.38 (s, 0.6H) (*anti*), 5.03 (d, J = 8.8 Hz, 0.4H) (*syn*), 4.75-4.64 (m, 1H) (*syn*/*anti*), 2.82 (d, J = 2.7 Hz, 0.6H) (*anti*), 2.72 (s, 0.4H) (*syn*), 1.50 (d, J = 7.0 Hz, 1.8H) (*anti*), 1.33 (d, J = 7.0 Hz, 1.2H) (*syn*); ^{13}C NMR (150 MHz) δ 136.8 (*anti*), 136.7 (*syn*), 135.1 (*syn*), 134.4 (*anti*), 129.2 (*syn*), 128.9 (*anti*), 128.2 (*syn*), 127.3 (*anti*), 88.1 (*syn*), 87.1 (*anti*), 75.5 (*syn*), 73.2 (*anti*), 16.4 (*syn*), 12.0 (*anti*); HPLC: AD-H column; λ = 254 nm; eluent: hexane/isopropanol = 97/3; flow rate: 1.0 mL/min; t_R = 25.6 min (*anti* minor: 1*S*,2*R*), t_R = 27.0 min (*anti* major: 1*R*,2*S*); ee_{anti} = 91%; t_R = 37.3 min (*syn* major: 1*R*,2*R*), t_R = 42.5 min (*syn* minor: 1*S*,2*S*); ee_{syn} = 89%.

X-ray Crystallographic Analysis.

Crystal of *rac*-**1** was obtained from THF-hexane solution. CCDC 912711 contains the supplementary crystallographic data.



References

1. S. Kitagaki, Y. Ohta, S. Tomonaga, R. Takahashi, C. Mukai, *Tetrahedron: Asymmetry* **2011**, *22*, 986.

2. R. Zhuravsky, Z. Starikova, E. Vorontsov, V. Rozenberg, *Tetrahedron: Asymmetry* **2008**, *19*, 216.

3. B. Qu, Y. Ma, Q. Ma, X. Liu, F. He, C. Song, *J. Org. Chem.* **2009**, *74*, 6867-6869.

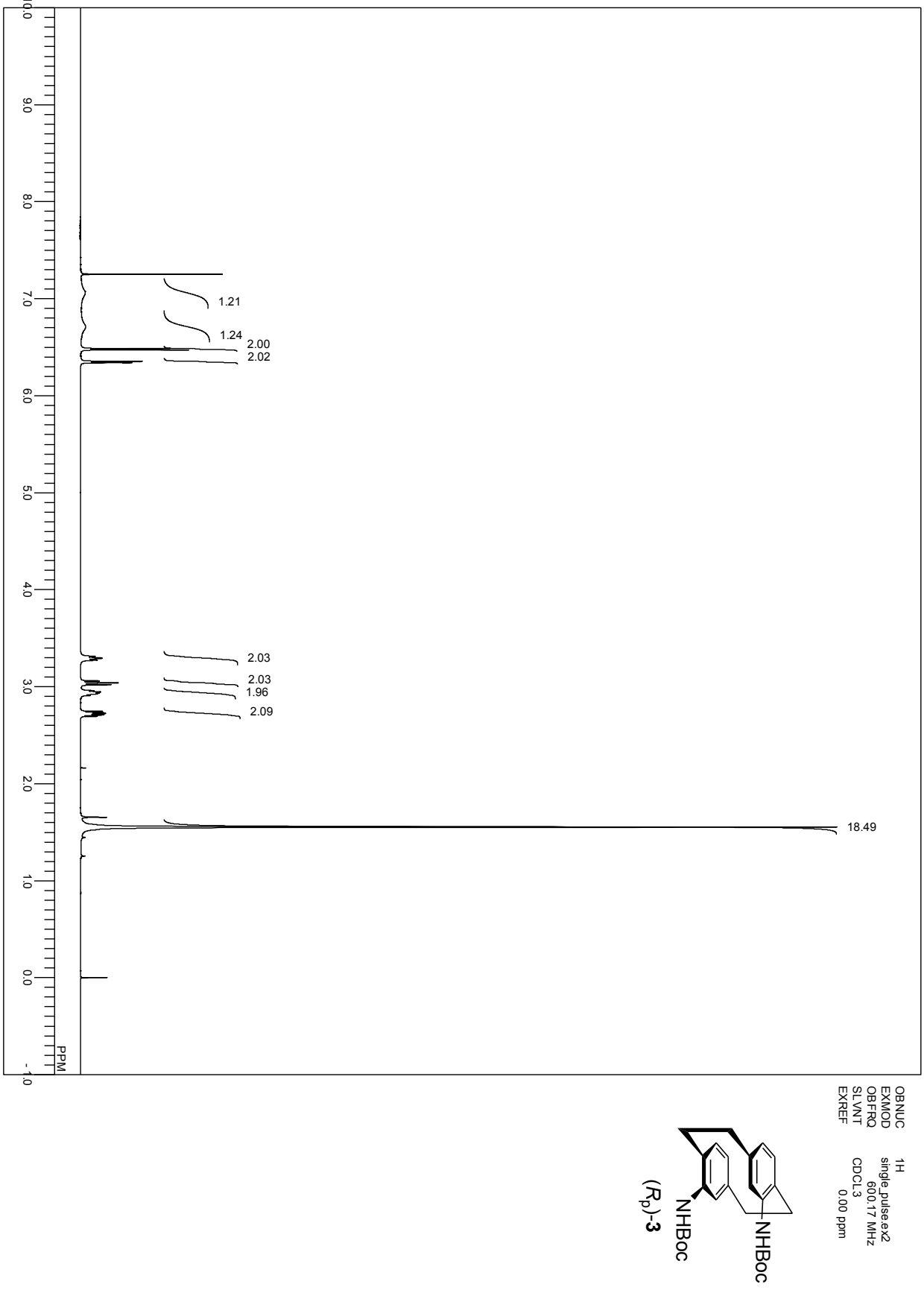
4. J. F. Schneider, F. C. Falk, R. Fröhlich, J. Paradies, *Eur. J. Org. Chem.* **2010**, 2265-2269.

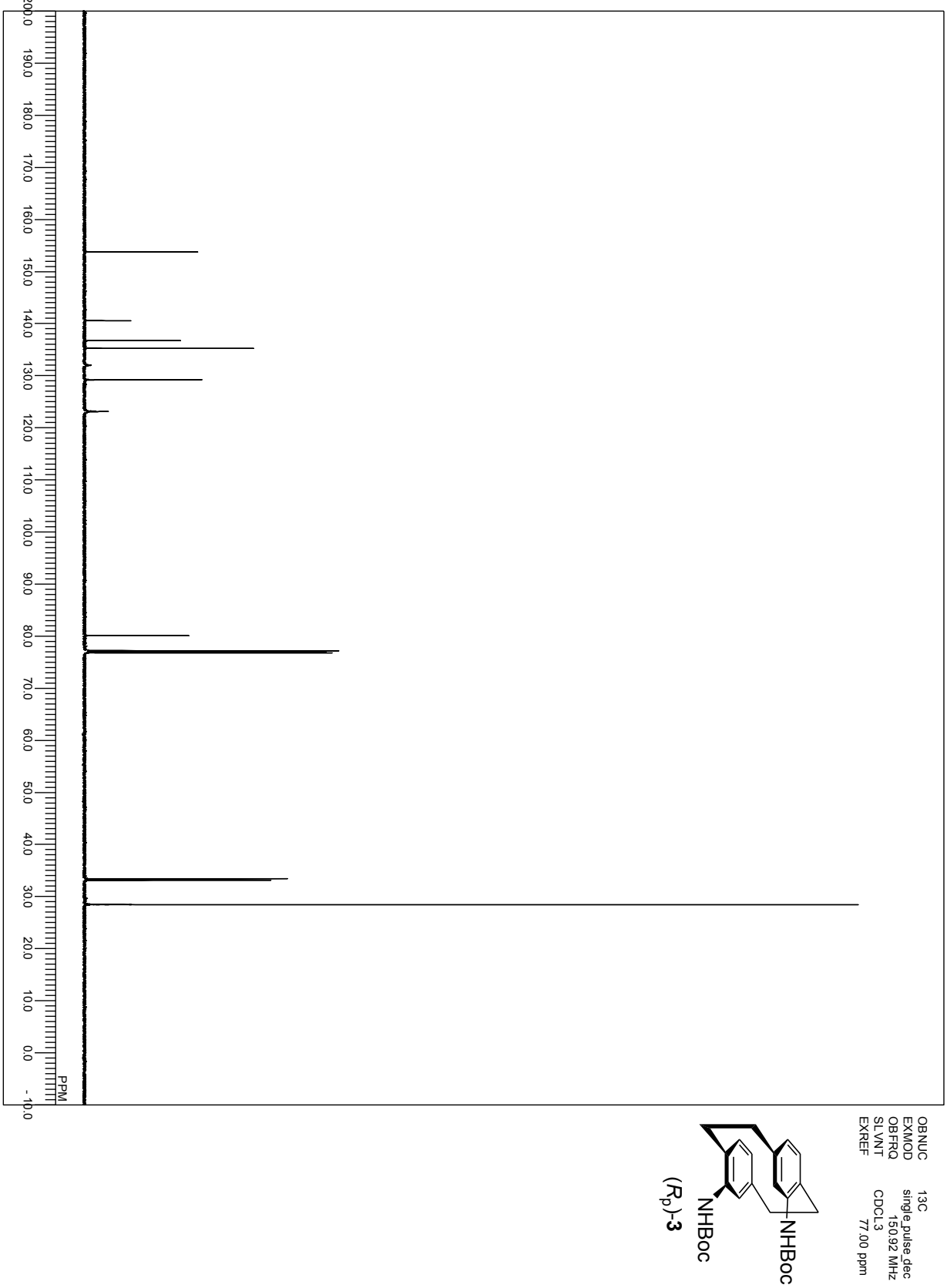
5. M. Steurer, C. Bolm, *J. Org. Chem.* **2010**, *75*, 3301-3310.

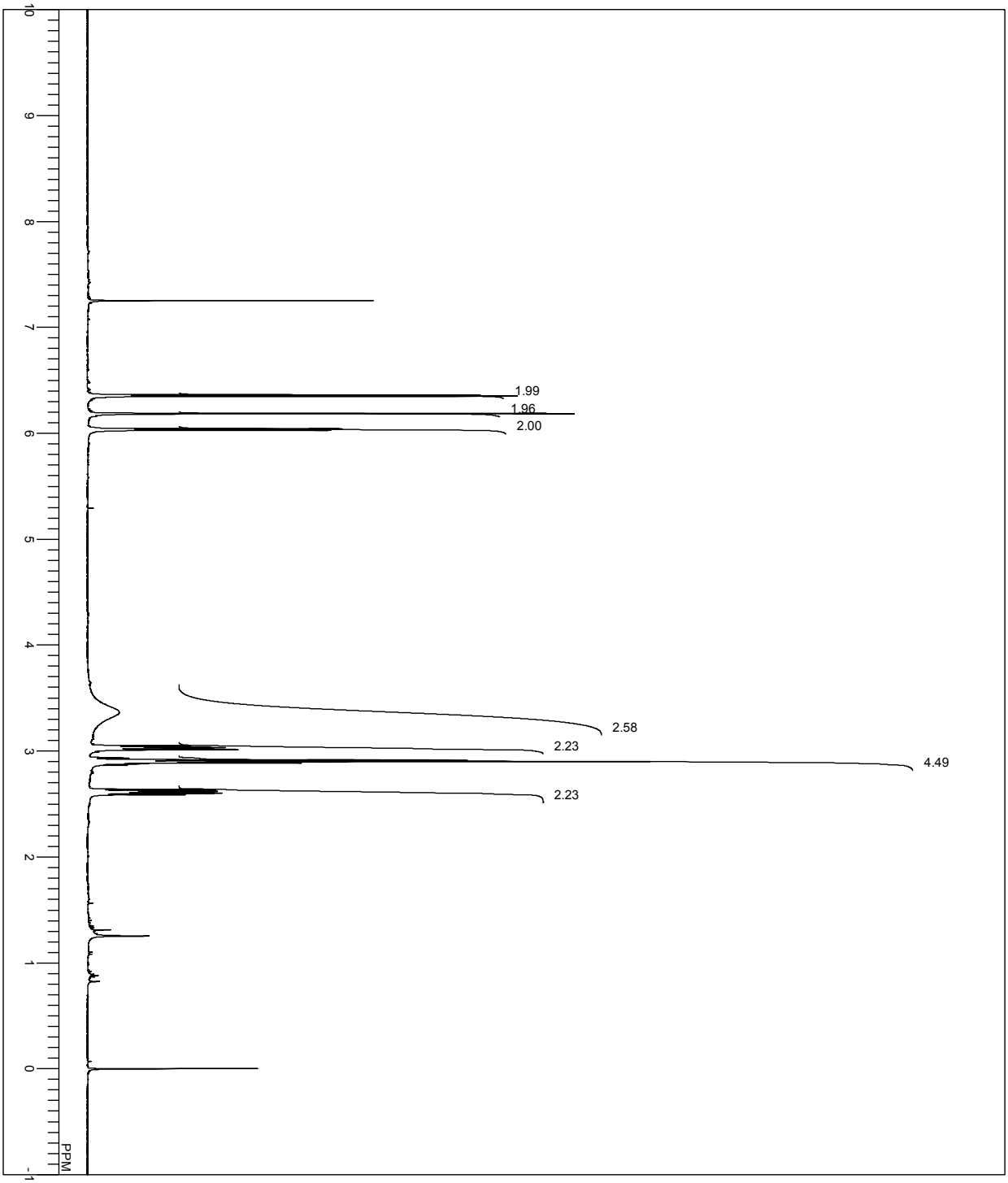
6. A. Bulut, A. Aslan, Ö. Dogan, *J. Org. Chem.* **2008**, *73*, 7373-7375.

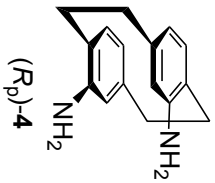
7. K. Dhahagani, J. Rajesh, R. Kannan, G. Rajagopal, *Tetrahedron: Asymmetry* **2011**, *22*,

857-865.
8. D. A. Evans, D. Seidel, M. Rueping, H. W. Lam, J. T. Shaw, C. W. Downey, *J. Am. Chem. Soc.* **2003**, *125*, 12692-12693.
9. T. Marcelli, R. N. S. van der Haas, J. H. van Maarseveen, H. Hiemstra, *Angew. Chem. Int. Ed.* **2006**, *45*, 929-931.
10. M. Rachwalski, S. Leśniak, E. Sznajder, P. Kiełbasiński, *Tetrahedron: Asymmetry* **2009**, *20*, 1547-1549.
11. M. Breuning, D. Hein, M. Steiner, V. H. Gessner, C. Strohmann, *Chem. Eur. J.* **2009**, *15*, 12764-12769.
12. R. Kowalczyk, J. Skarżewski, *Tetrahedron: Asymmetry* **2009**, *20*, 2467-2473.

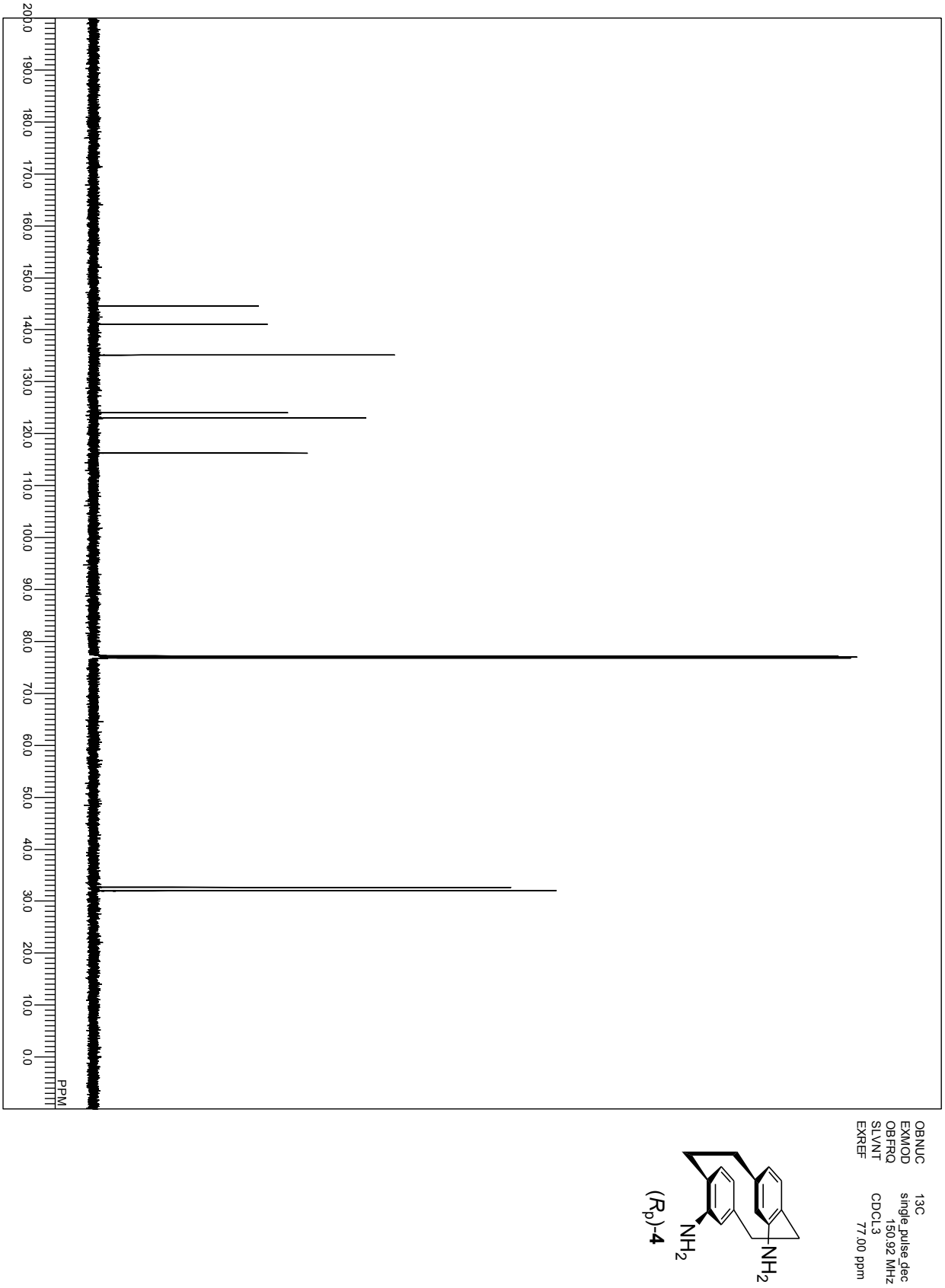

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
PPM
1.21
1.24
2.00
2.02
2.03
2.03
1.96
2.09
18.49
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
SLVNT CDCL3
EXREF 0.00 ppm
NHBoc
NHBoc
(Rp)-3

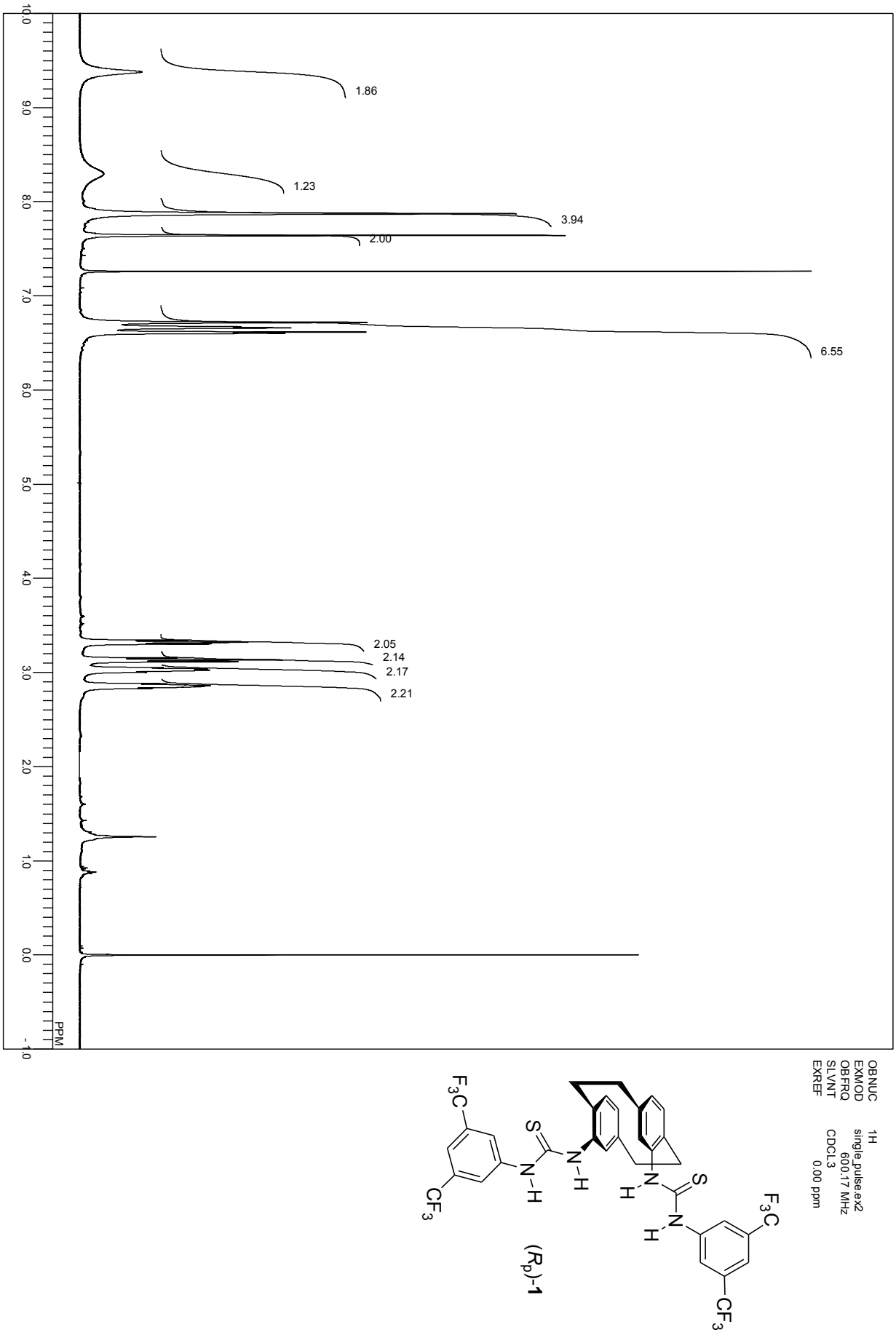

OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
SLVNT CDCL3
EXREF 77.00 ppm
NHBoc
NHBoc
(Rp)-3
PPM
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0





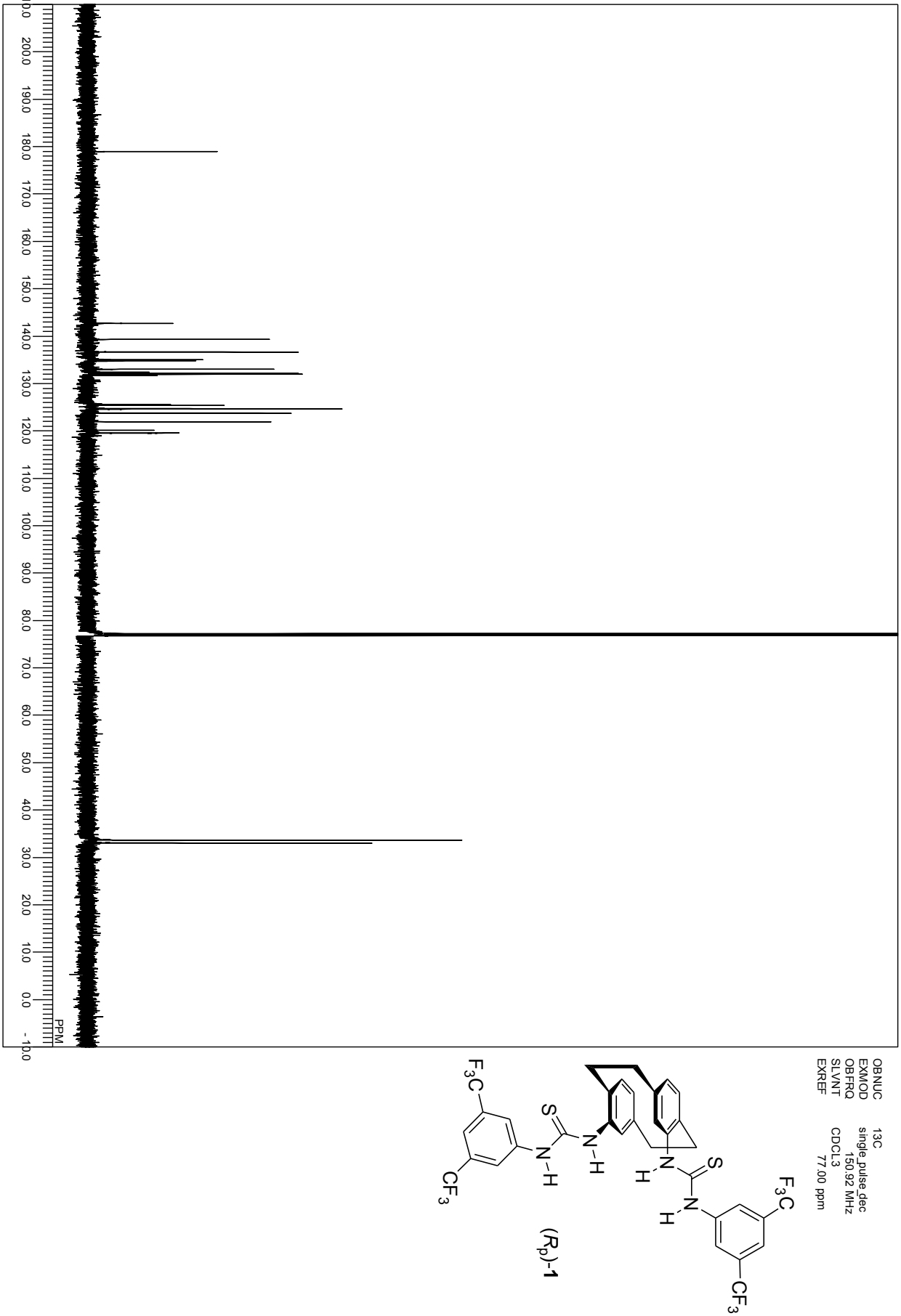
(R_p)-**4**

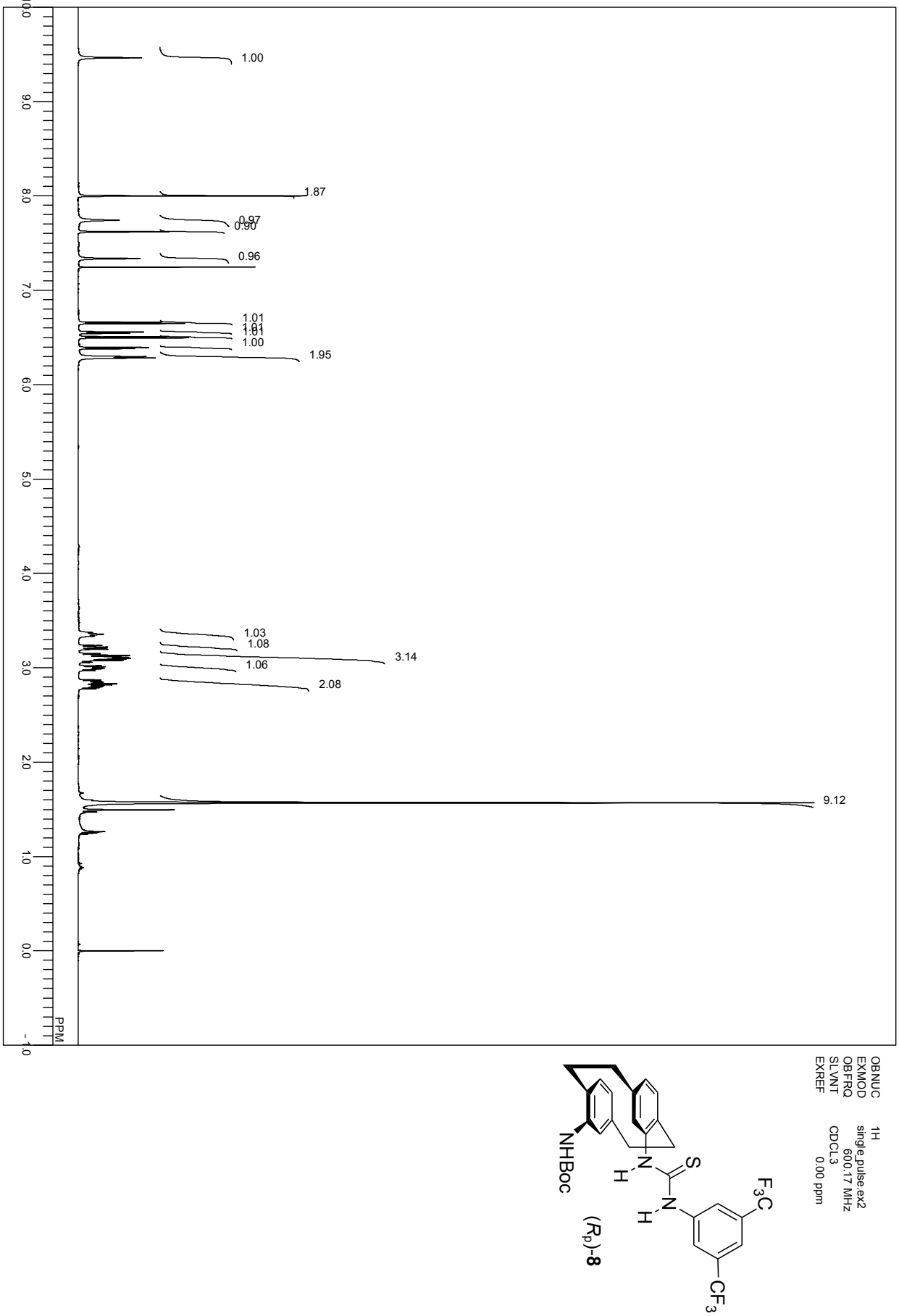

200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
PPM
OBNUC 13C
EXMOD single_pulse.dec
OBFRQ 150.92 MHz
SLVNT CDCL3
EXREF 77.00 ppm
NH2
NH2
(Rp)-4

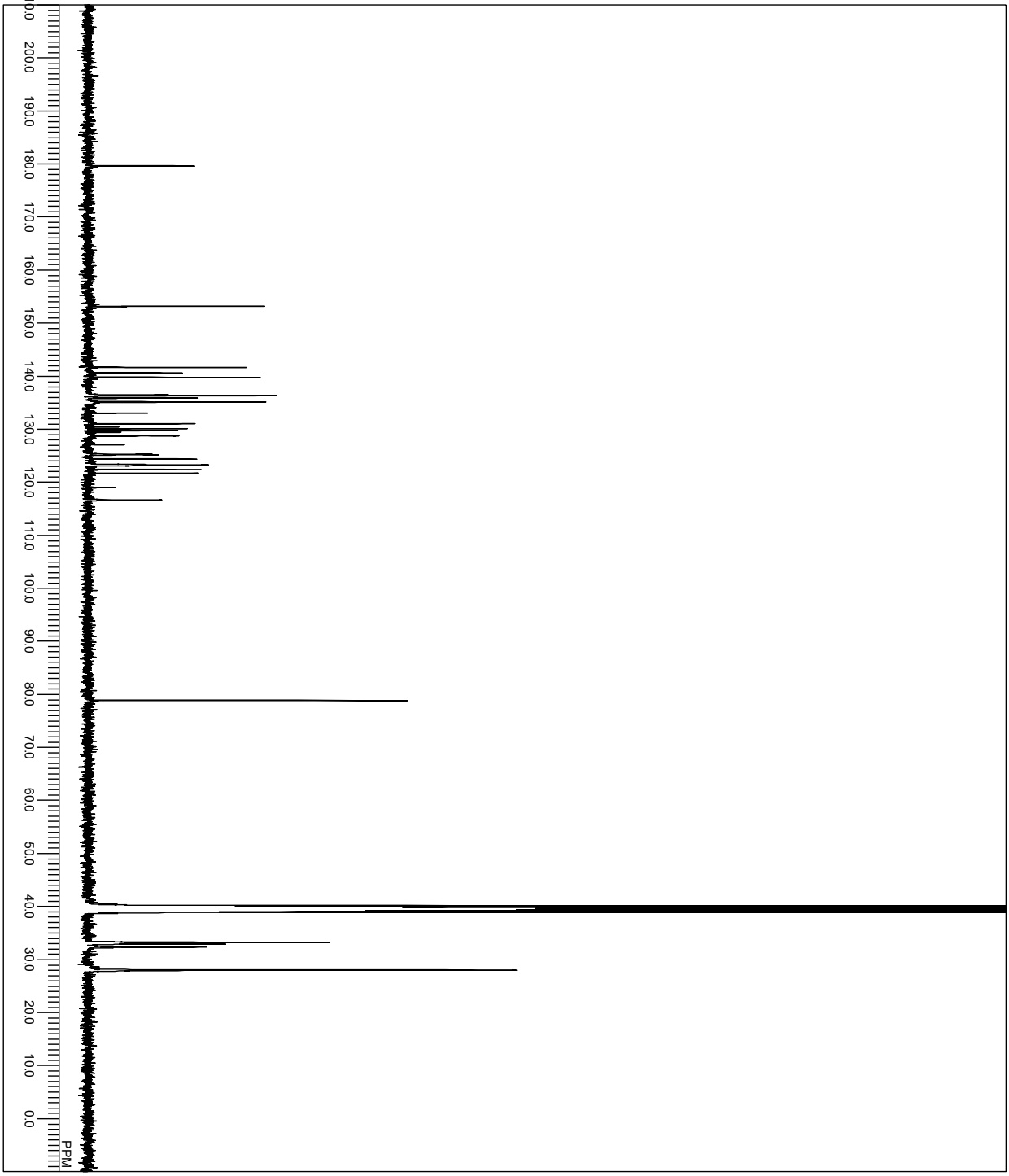

1.86
1.23
3.94
2.00
6.55
2.05
2.14
2.17
2.21
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
- 1.0
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
SLVNT CDCL3
EXREF 0.00 ppm

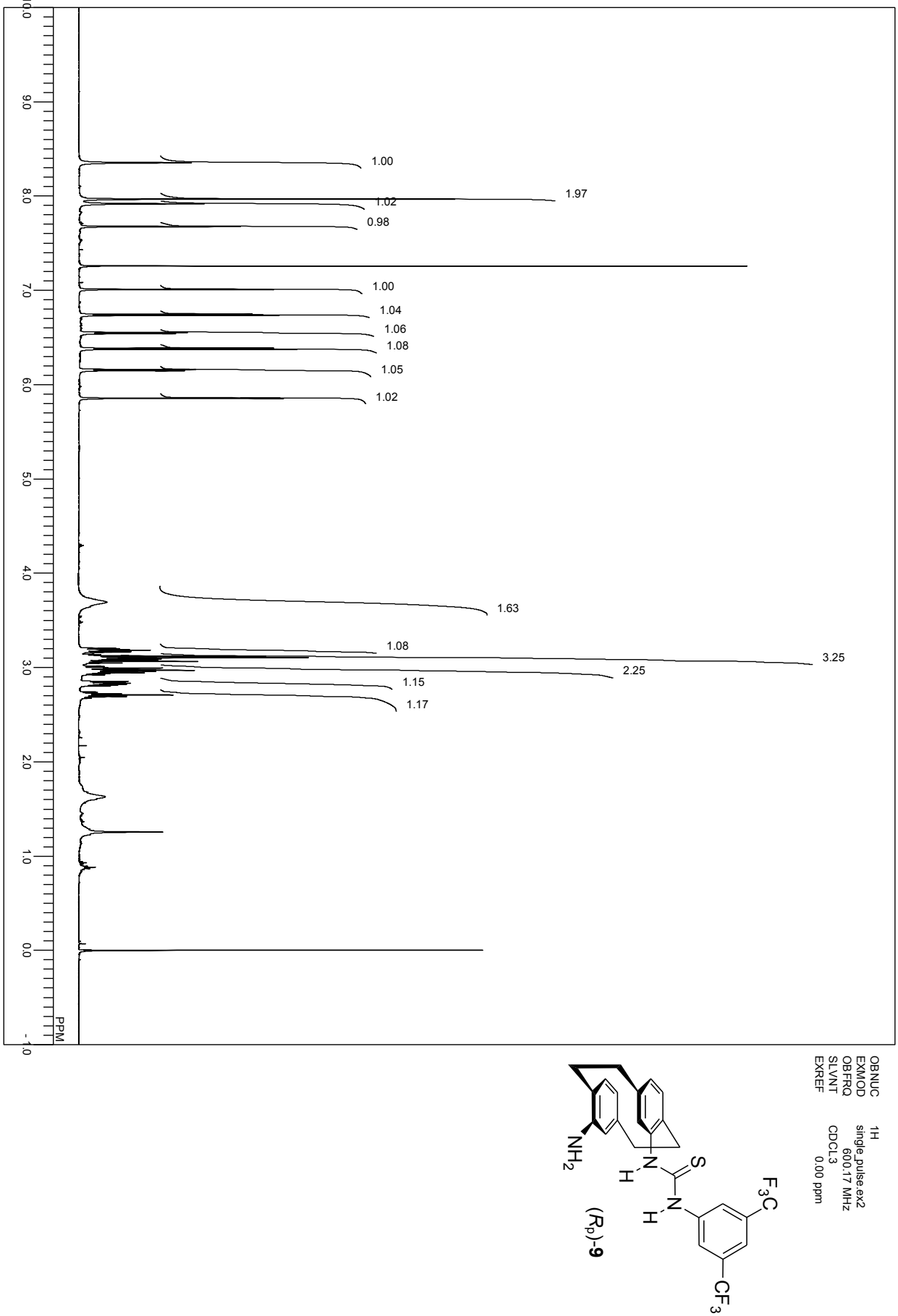
F3C
CF3
S
N–H
N–H
N
H
S
N
H
F3C
CF3

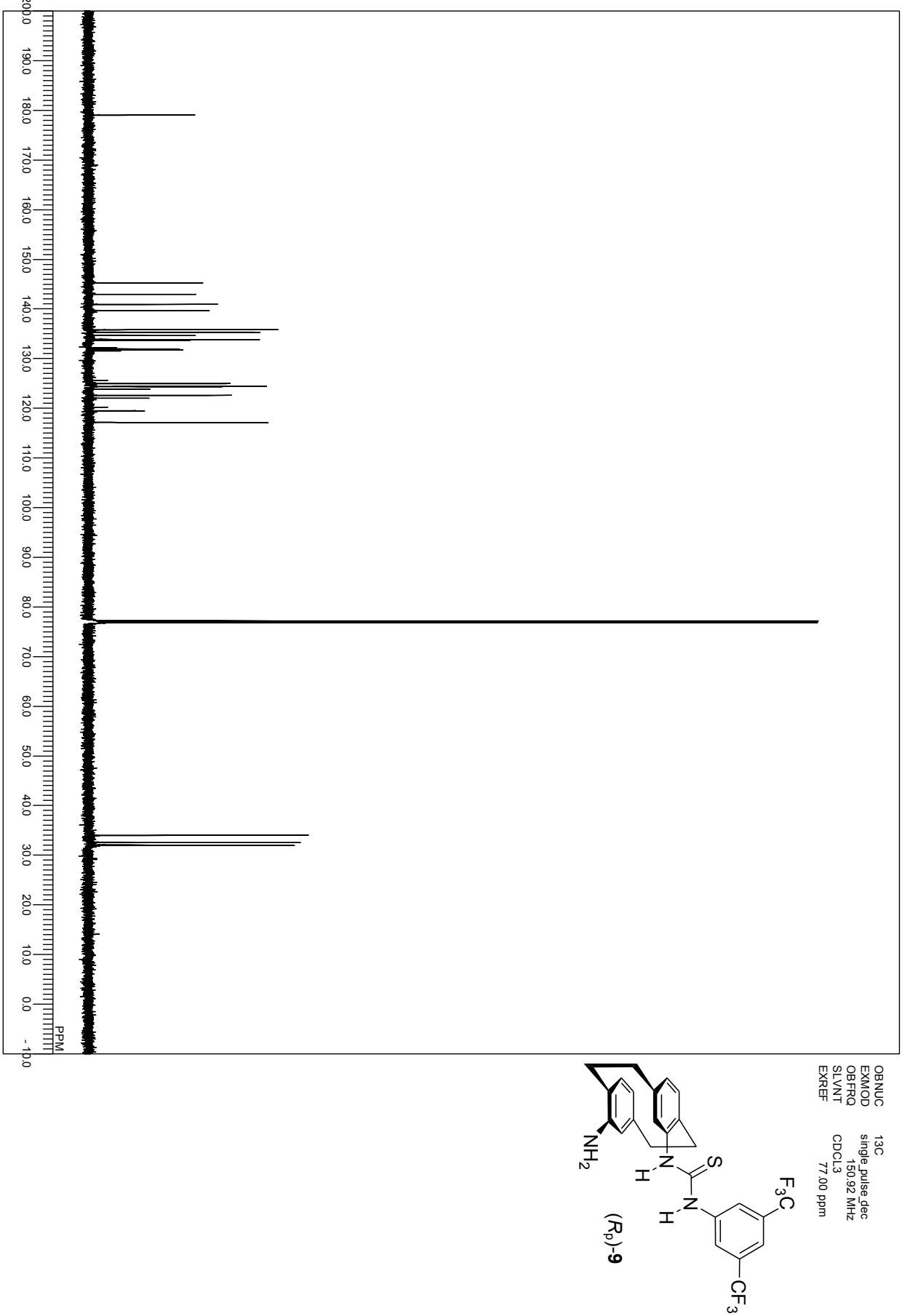
(R_p)-**1**

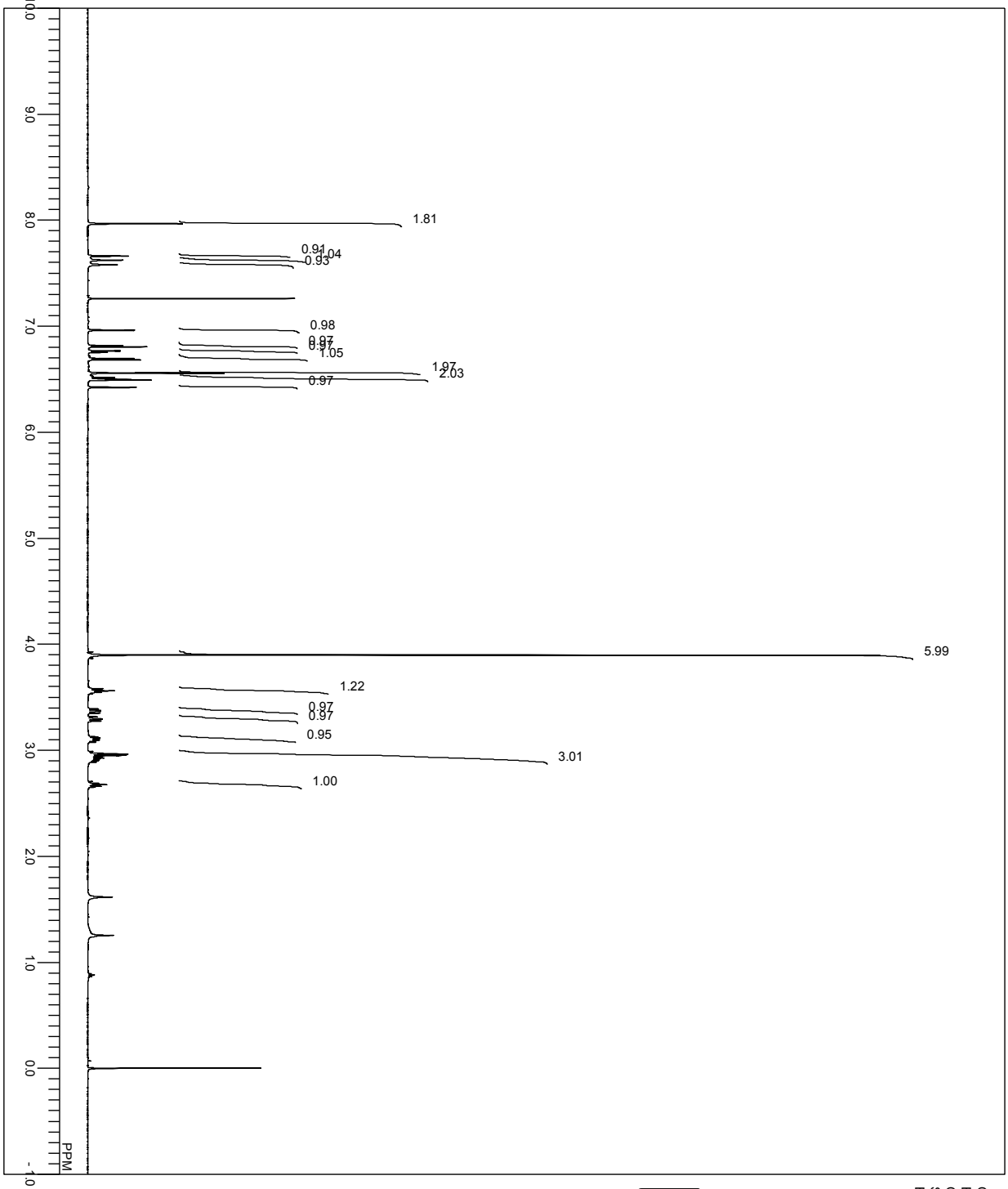

OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
SLVNT CDCL3
EXREF 77.00 ppm
PPM
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
F3C
CF3
S
N–H
N–H
N
H
S
N
H
F3C
CF3
(Rp)-1

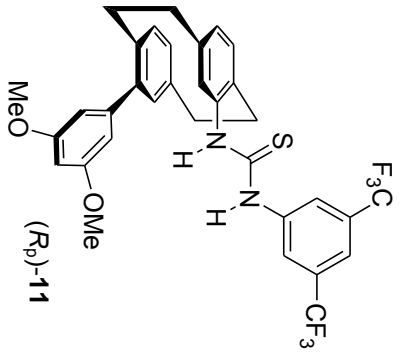

1.00
1.87
0.97
0.90
0.96
1.01
1.01
1.01
1.00
1.95
1.03
1.08
3.14
1.06
2.08
9.12
PPM
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
SLVNT CDCL3
EXREF 0.00 ppm
NHBoc
N
H
S
N
H
F3C
CF3
(Rp)-8


PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
SLVNT DMSO
EXREF 39.52 ppm
NHBoc
H
N
S
H
N
F3C
CF3
(Rp)-8

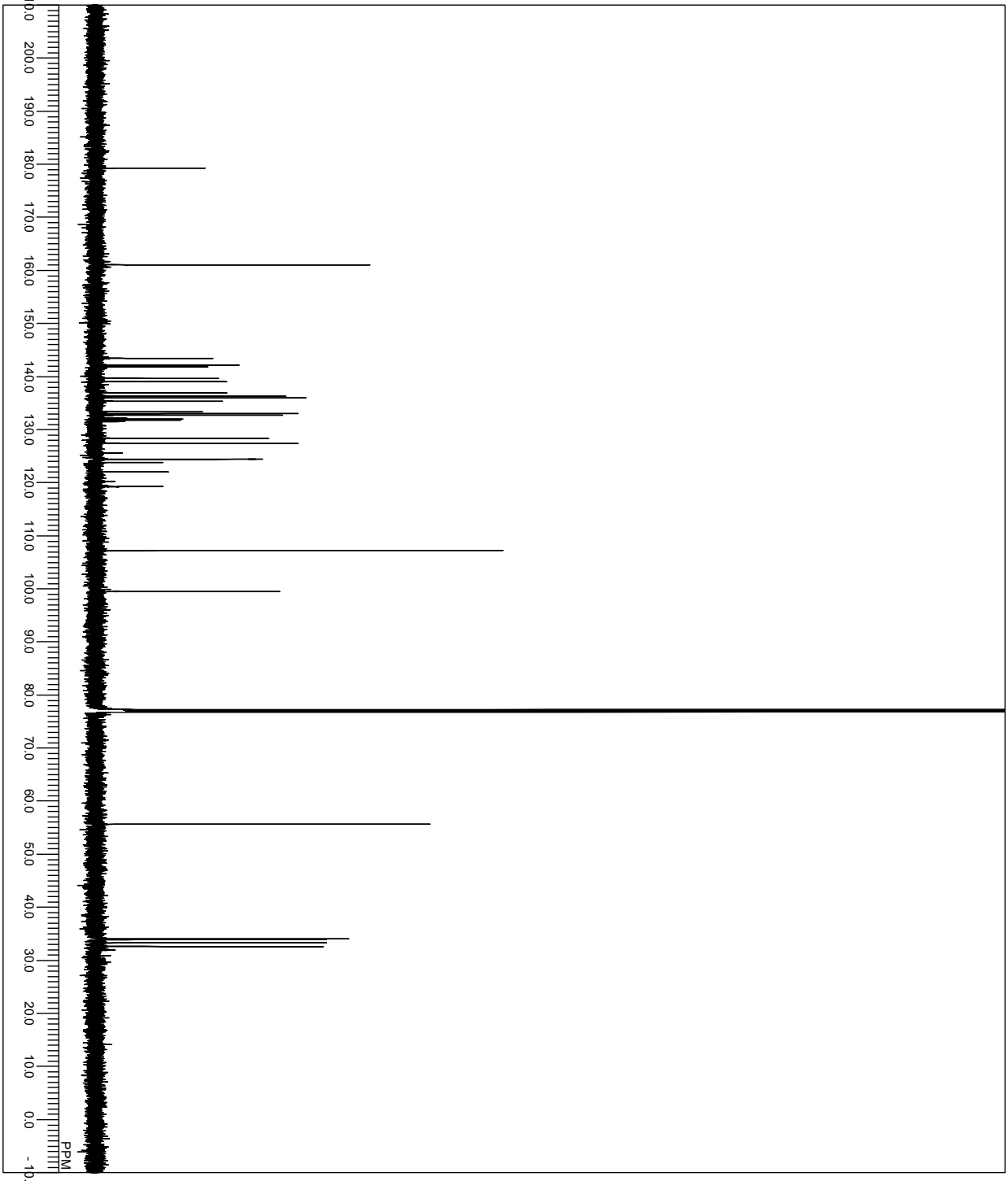

1.00
1.97
1.02
0.98
1.00
1.04
1.06
1.08
1.05
1.02
1.63
1.08
3.25
2.25
1.15
1.17
PPM
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
SLVNT CDCL3
EXREF 0.00 ppm
NH2
S
N
H
N
H
F3C
CF3
(Rp)-9

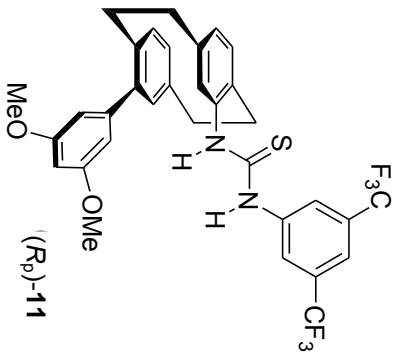

OBNUC 13C
EXMOD single_pulse.dec
OBFRQ 150.92 MHz
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
NH2
H
N
S
N
H
F3C
CF3
(Rp)-9


10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
- 1.0
PPM
1.81
0.91
1.04
0.93
0.98
0.97
0.97
1.05
1.97
2.03
0.97
5.99
1.22
0.97
0.97
0.95
3.01
1.00
OBNUC
EXMOD
OBFRQ
SLVNT
EXREF
1H
single_pulse.ex2
600.17 MHz
CDCL3
0.00 ppm

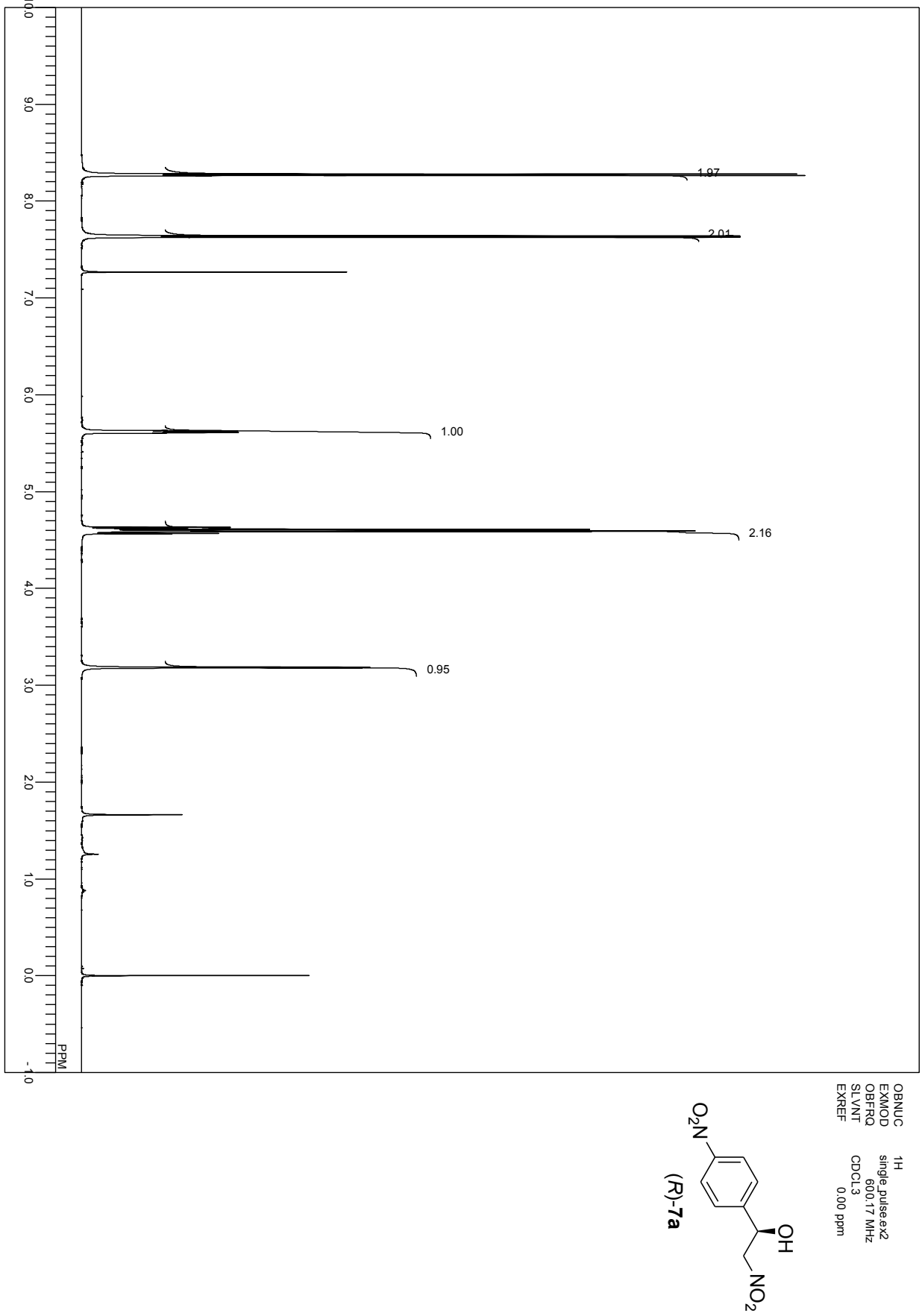

MeO
OMe
N
H
S
N
H
F3C
CF3

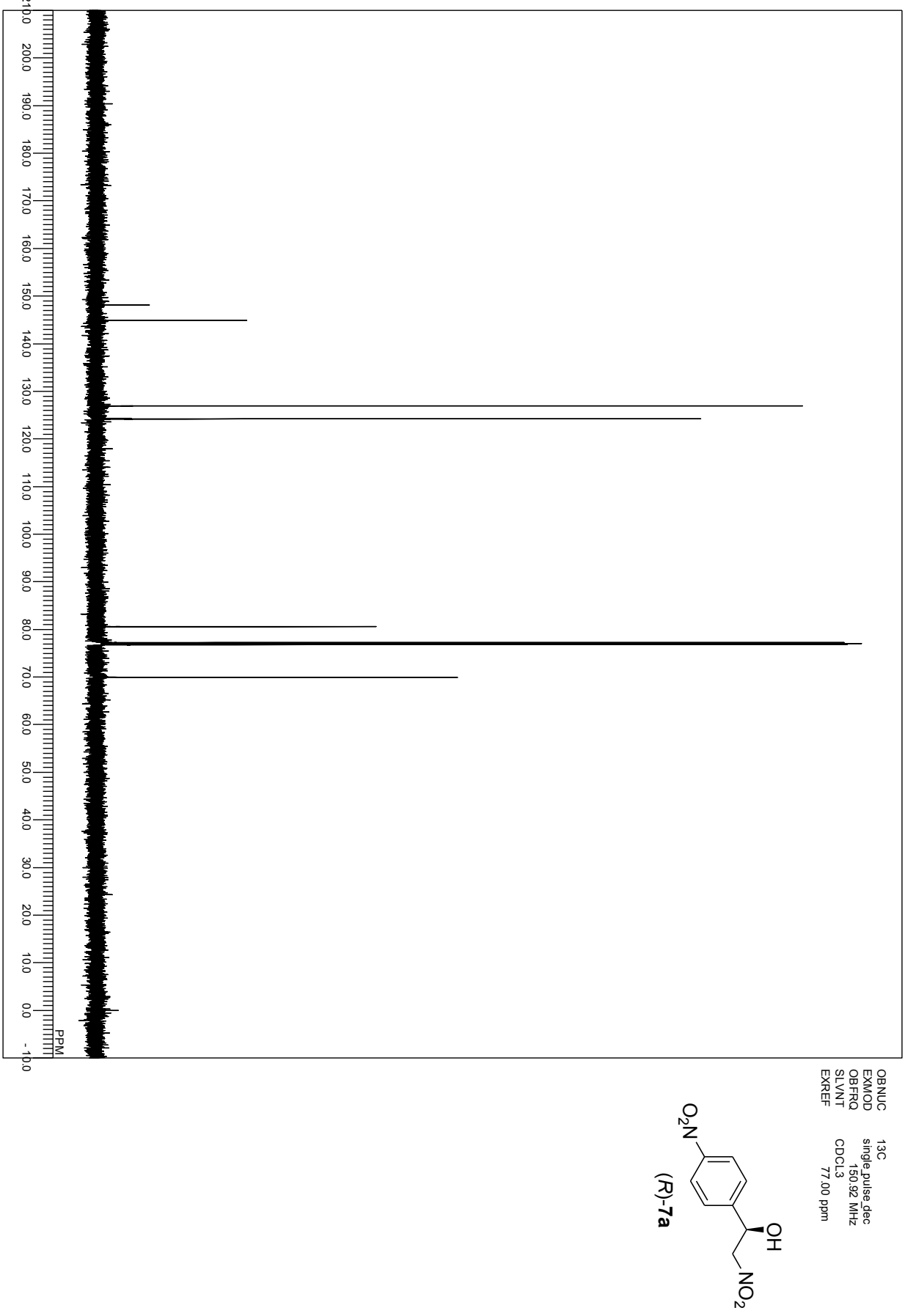
(R_p)-**11**


PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
SLVNT CDCL3
EXREF 77.00 ppm

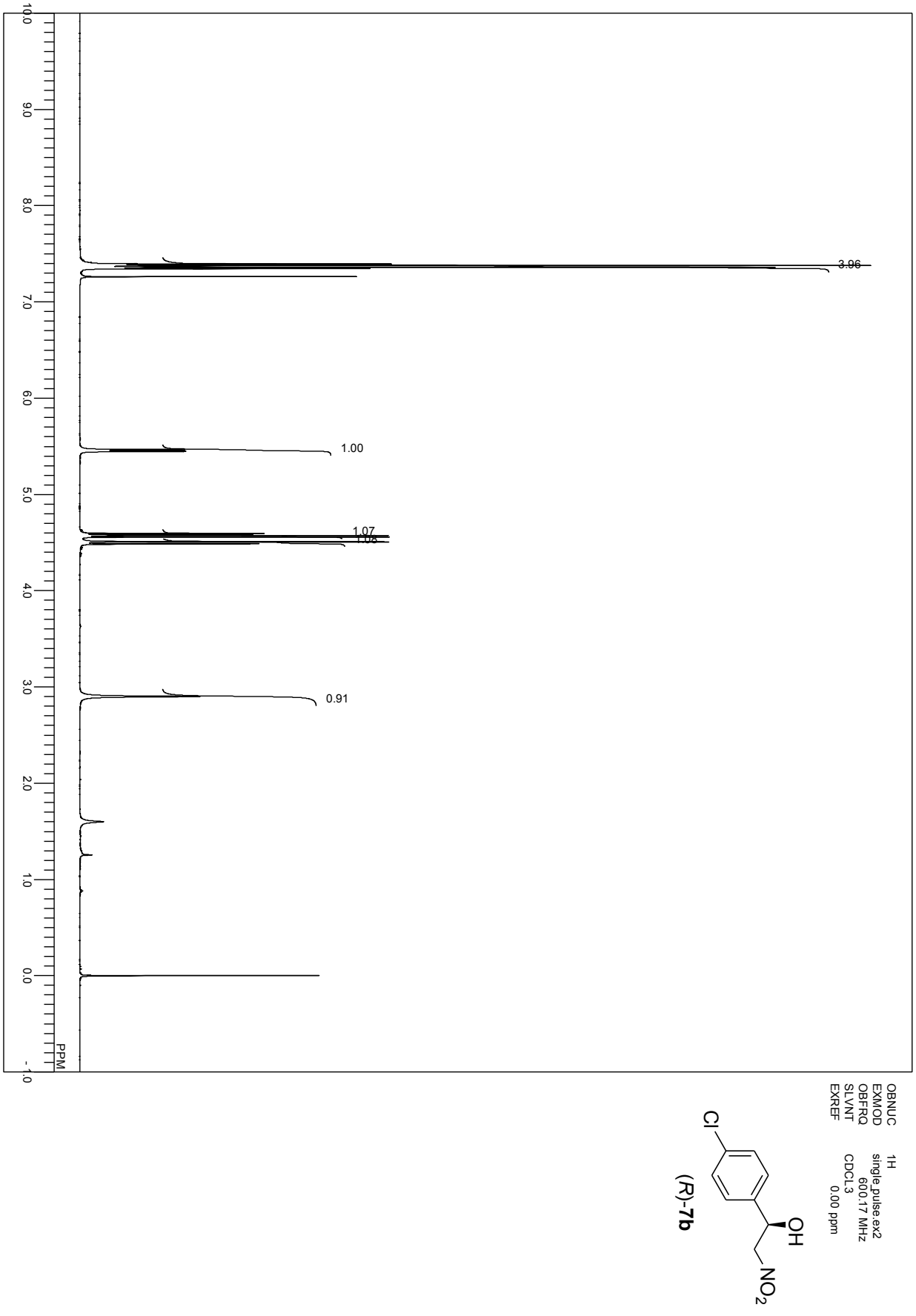

MeO
OMe
N
H
S
N
H
F3C
CF3

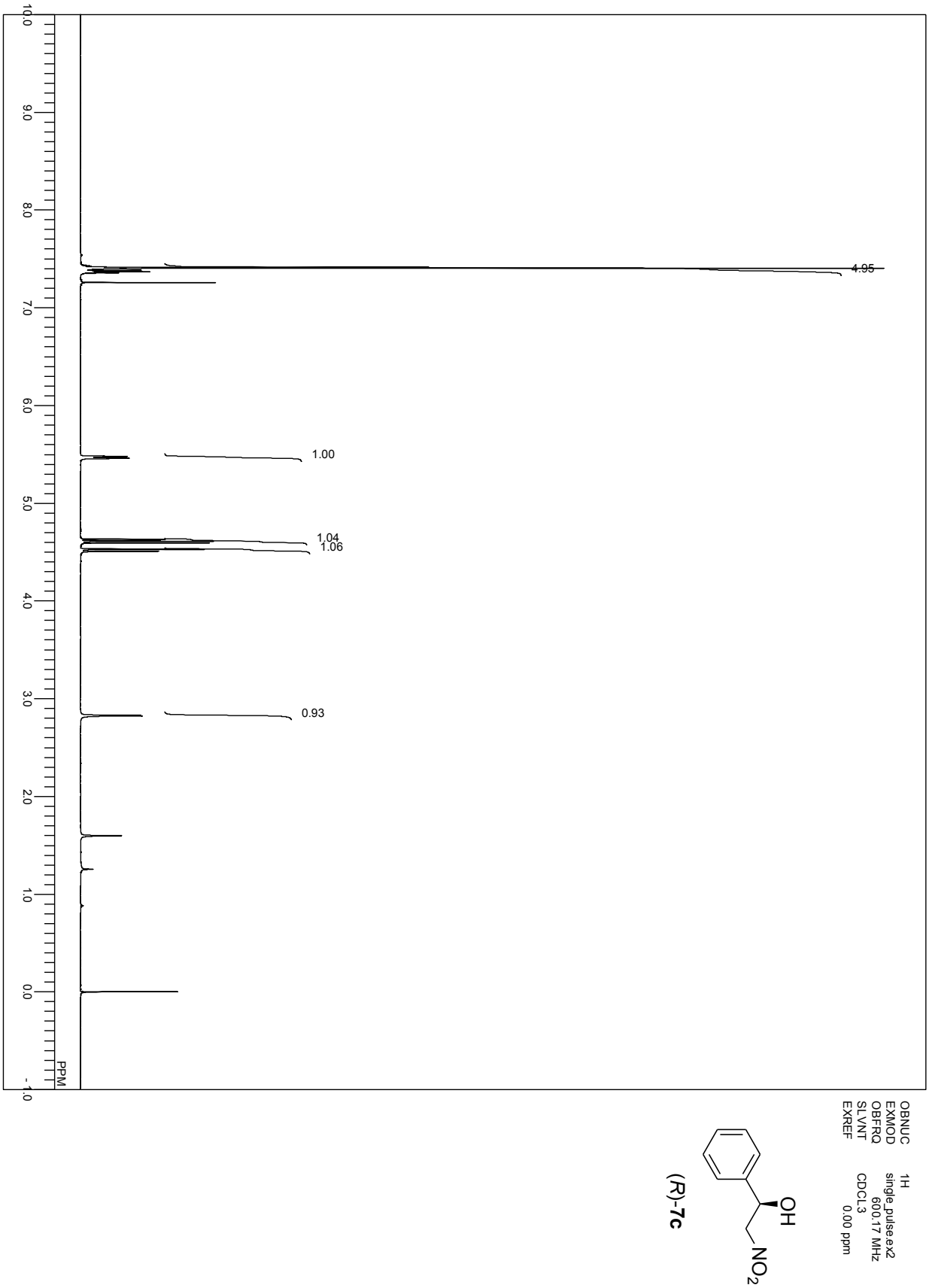
(*R*$_p$)-**11**

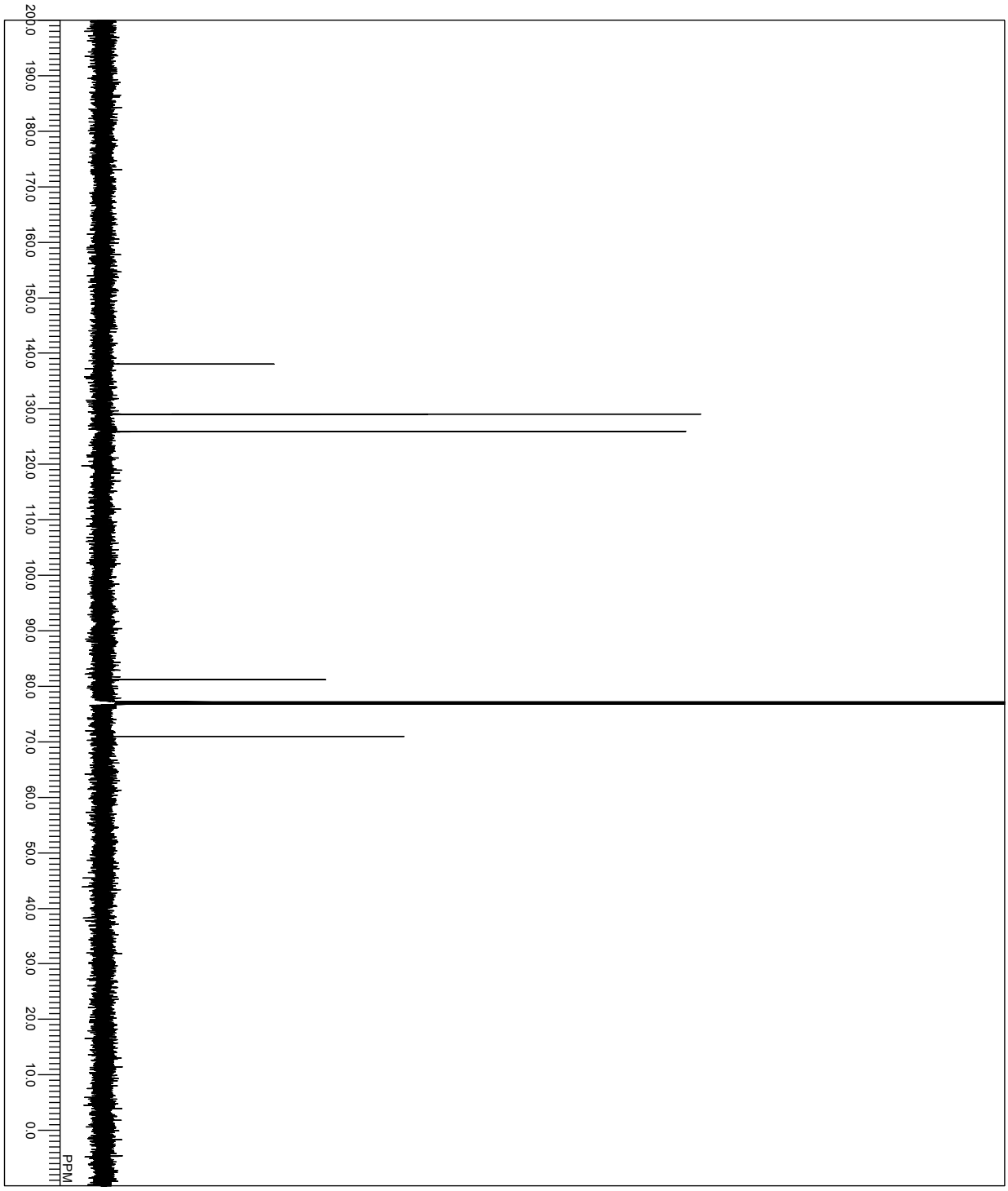

1.97
2.01
1.00
2.16
0.95
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
OBNUC
EXMOD
OBFRQ
SLVNT
EXREF
1H
single_pulse.ex2
600.17 MHz
CDCL3
0.00 ppm
O2N
OH
NO2
(R)-7a


OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
SLVNT CDCL3
EXREF 77.00 ppm
PPM
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
O2N
OH
NO2

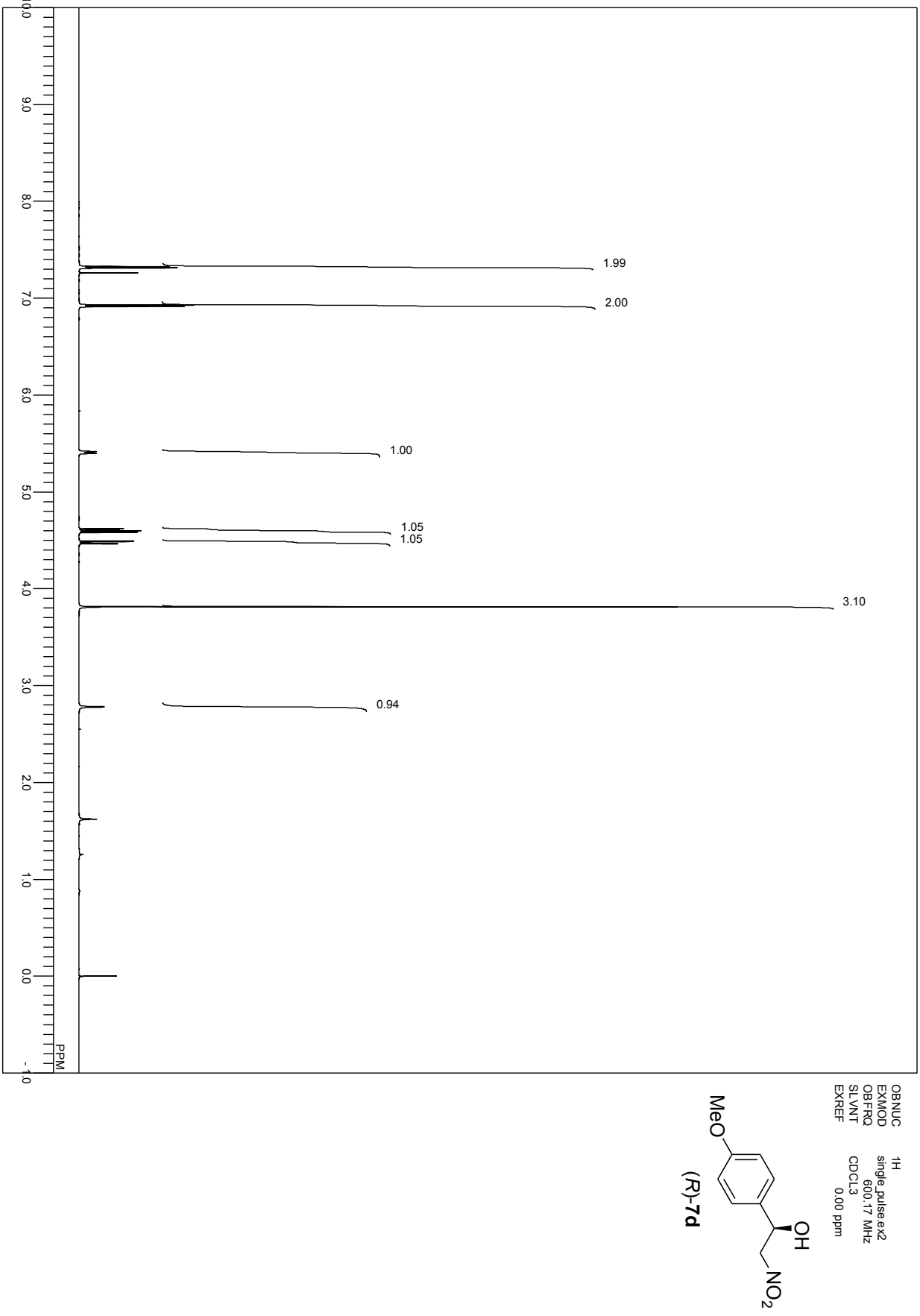
(*R*)-**7a**

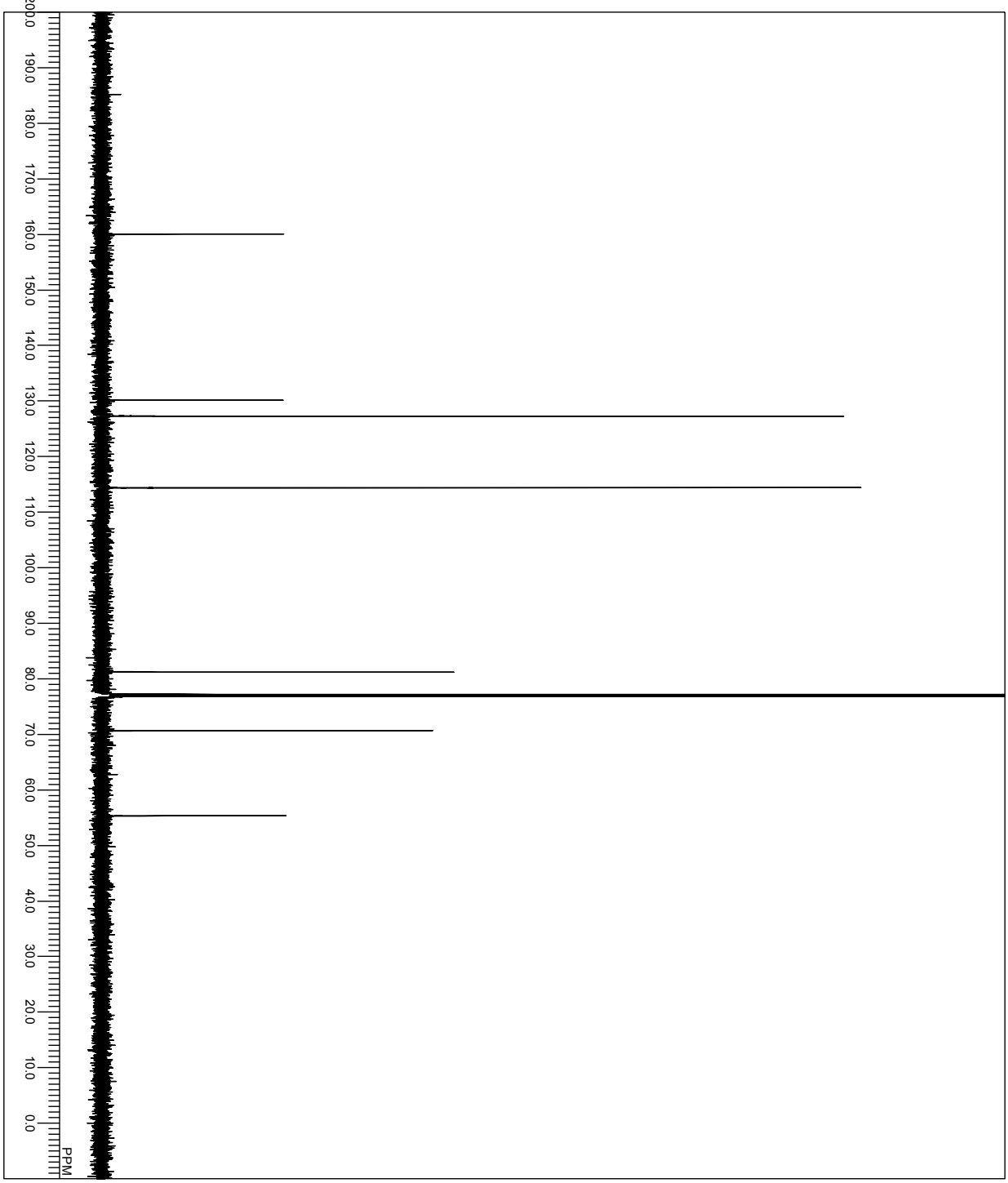

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
- 1.0
PPM
3.96
1.00
1.07
1.08
0.91
OBNUC
EXMOD
OBFRQ
SLVNT
EXREF
1H
single_pulse.ex2
600.17 MHz
CDCL3
0.00 ppm
Cl
OH
NO2
(R)-7b

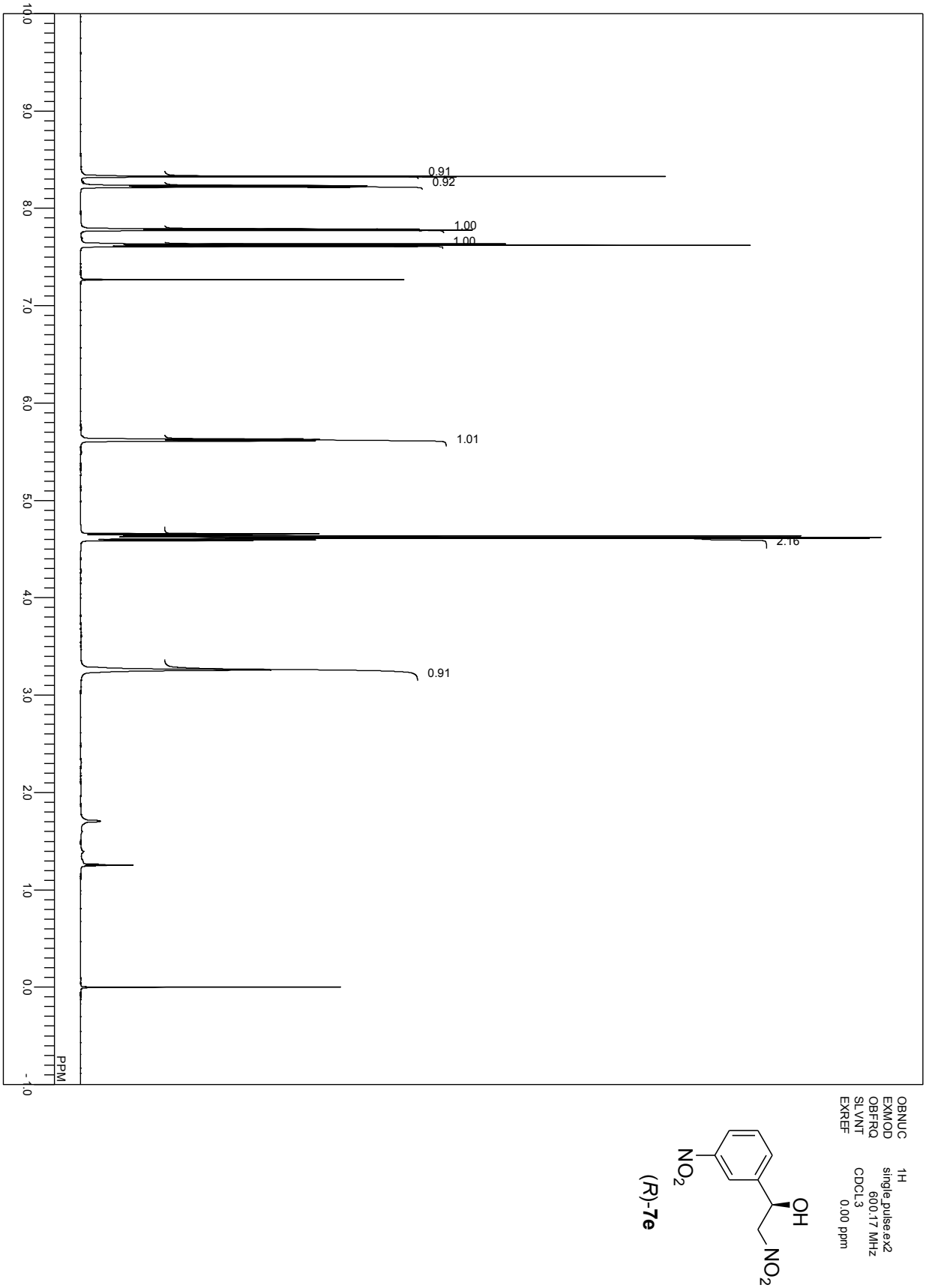

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
PPM
4.95
1.00
1.04
1.06
0.93
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
SLVNT CDCL3
EXREF 0.00 ppm
OH
NO2
(R)-7c

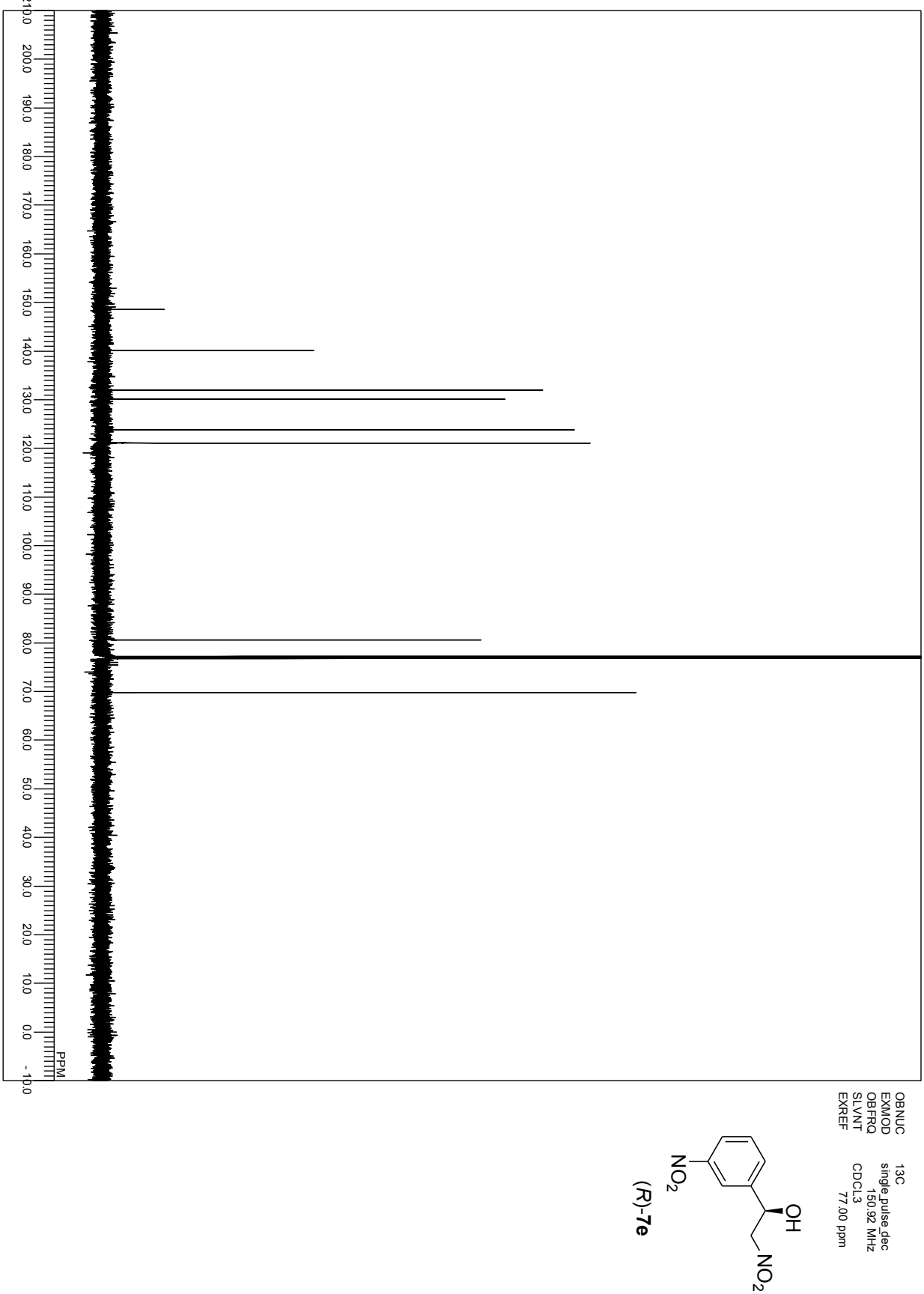

200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
PPM
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
SLVNT CDCL3
EXREF 77.00 ppm
OH
NO2

(*R*)-**7c**

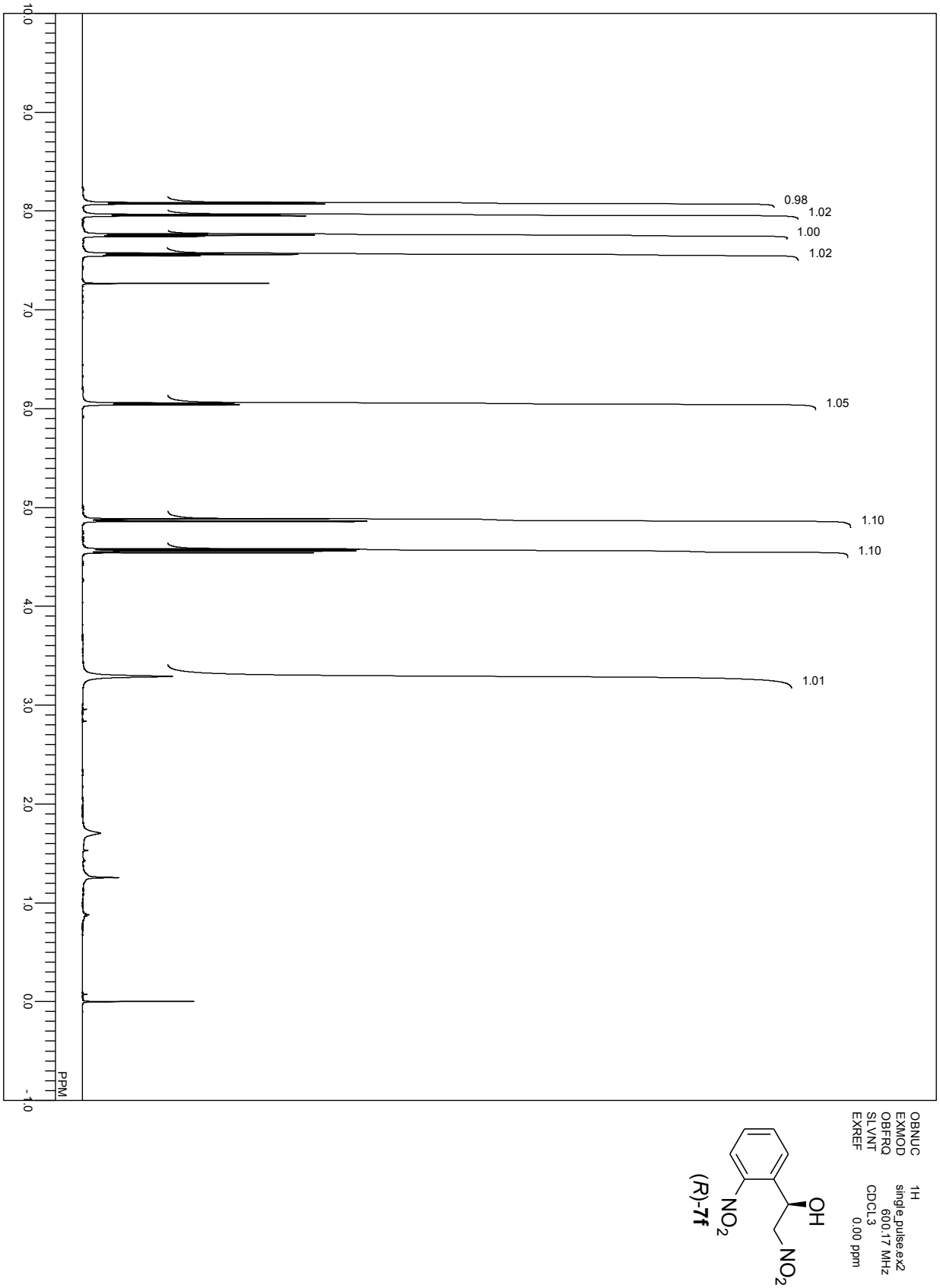

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
PPM
1.99
2.00
1.00
1.05
1.05
3.10
0.94
OBNUC
EXMOD
OBFRQ
SLVNT
EXREF
1H
single_pulse.ex2
600.17 MHz
CDCL3
0.00 ppm
MeO
OH
NO2
(R)-7d

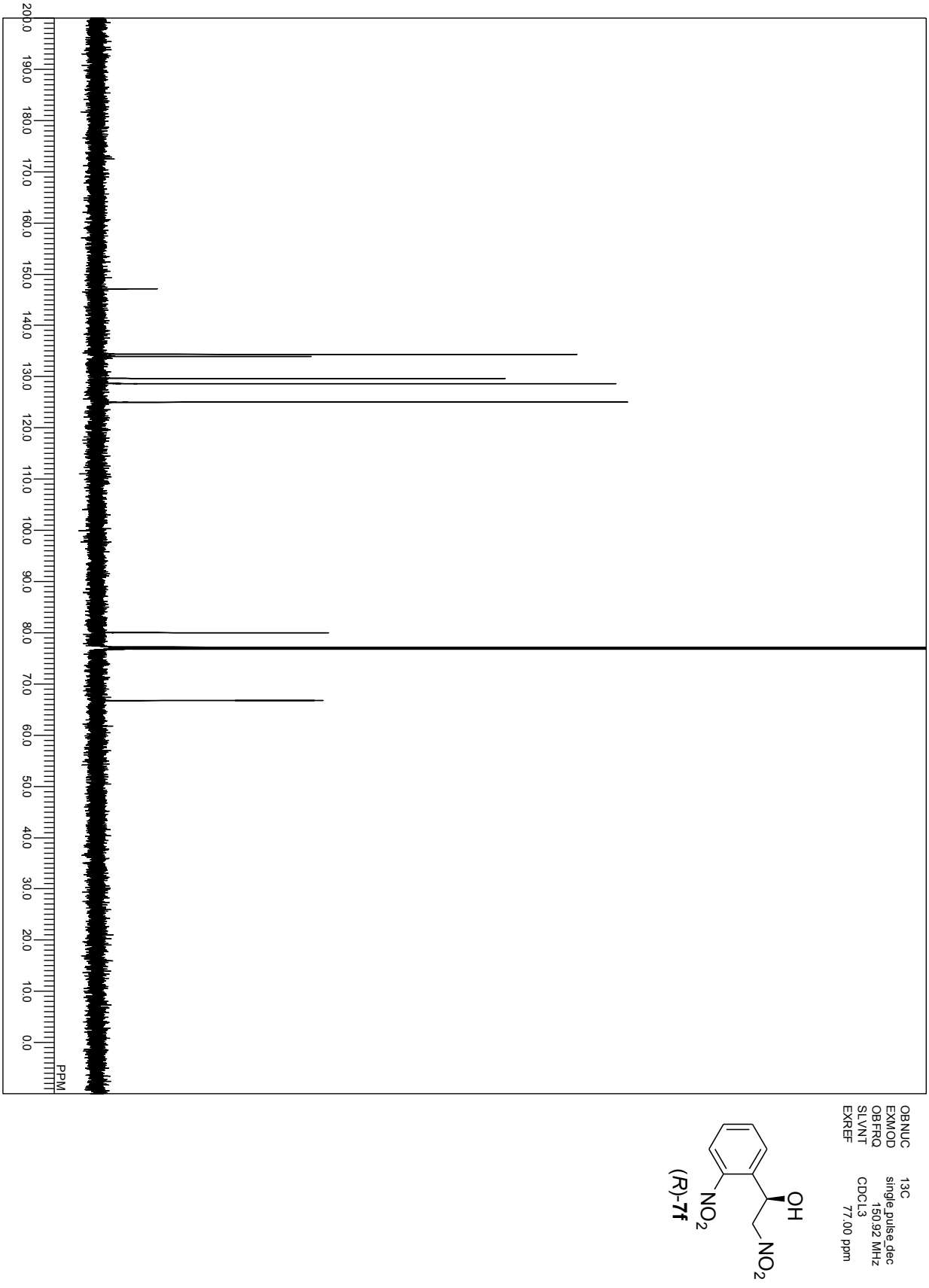

OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
SLVNT CDCL3
EXREF 77.00 ppm
MeO
OH
NO2
(R)-7d
PPM
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0

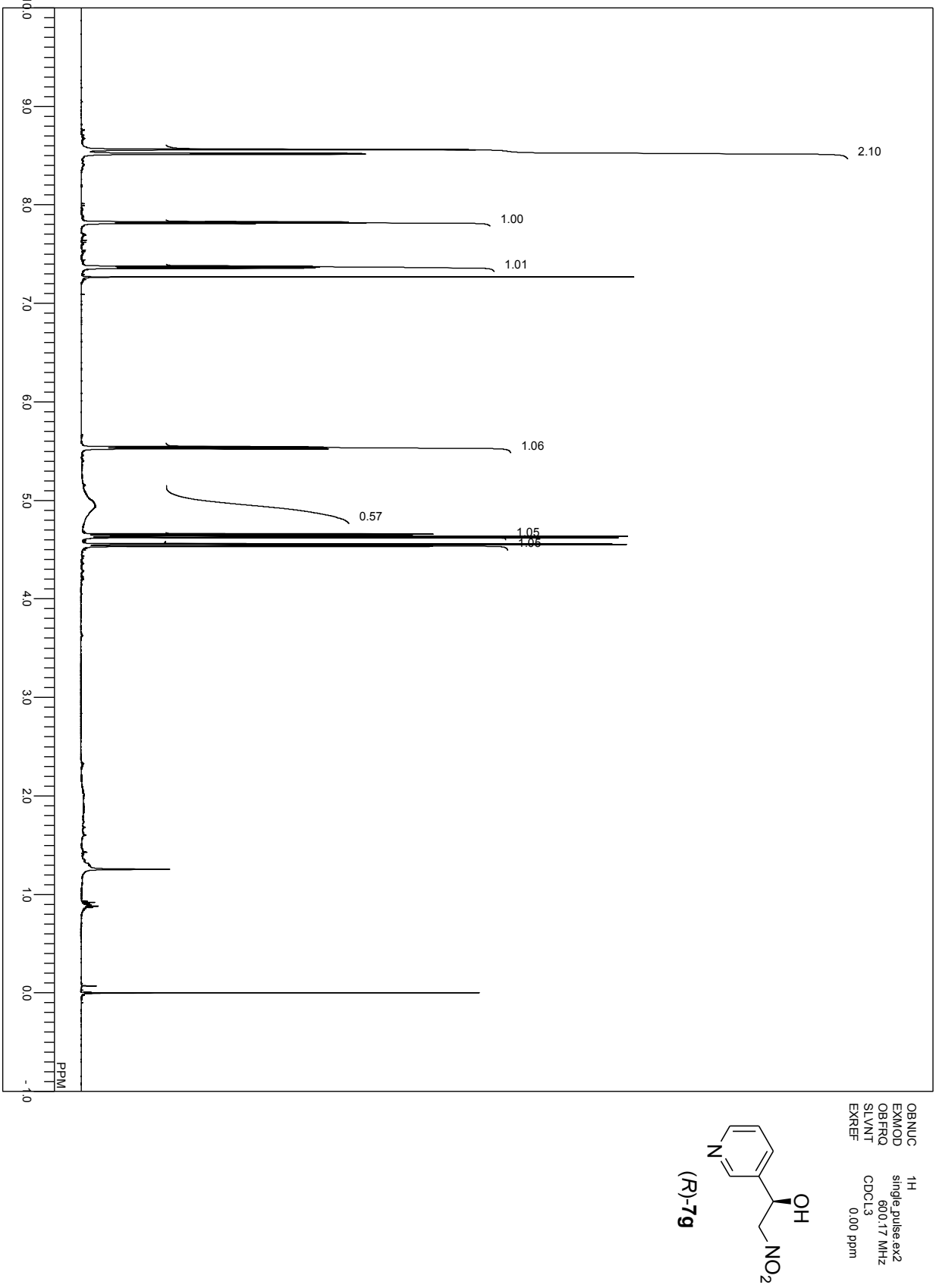

0.91
0.92
1.00
1.00
1.01
2.16
0.91
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
SLVNT CDCL3
EXREF 0.00 ppm
NO2
OH
NO2
(R)-7e

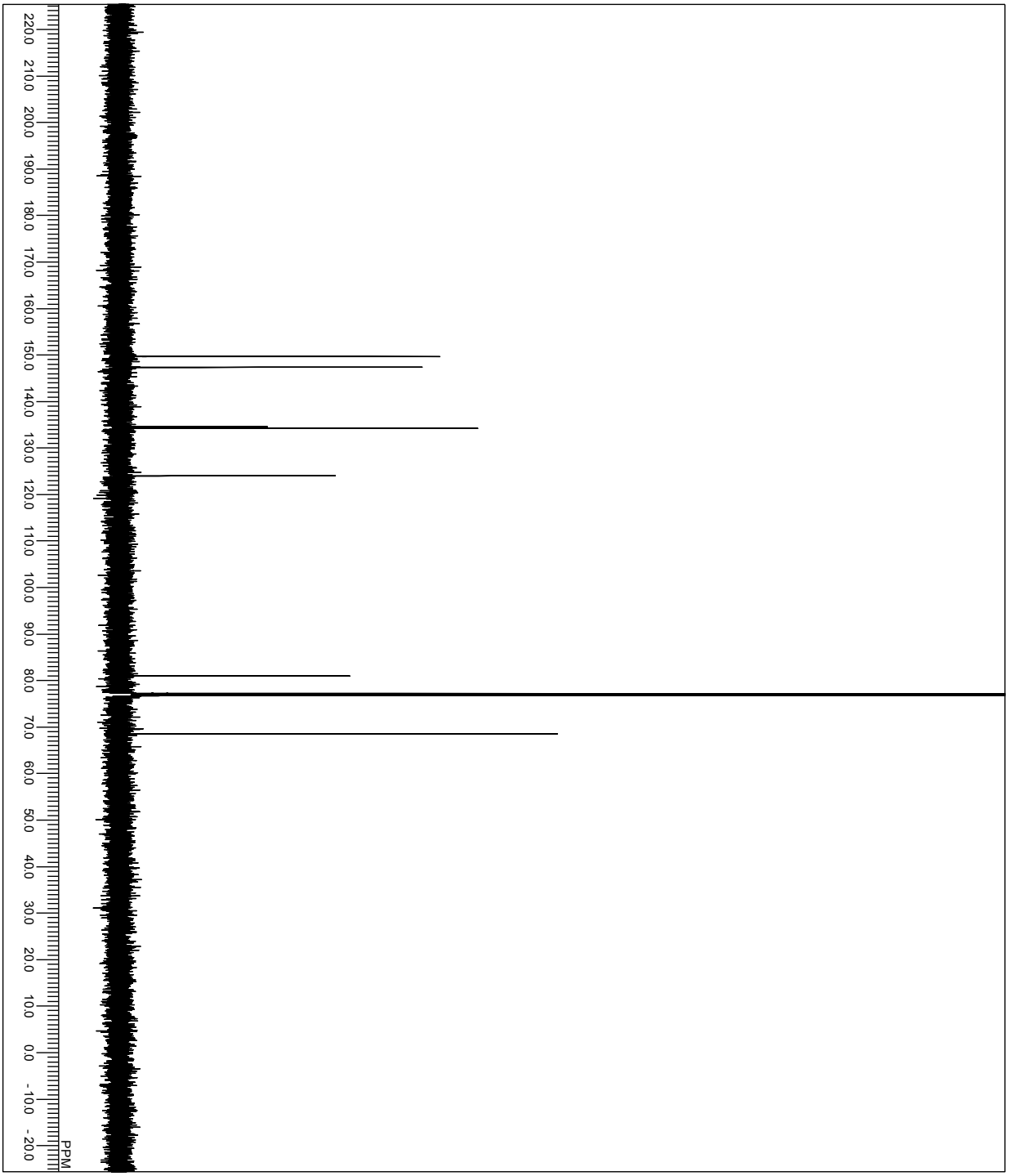

OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
SLVNT CDCL3
EXREF 77.00 ppm
PPM
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
OH
NO2
NO2

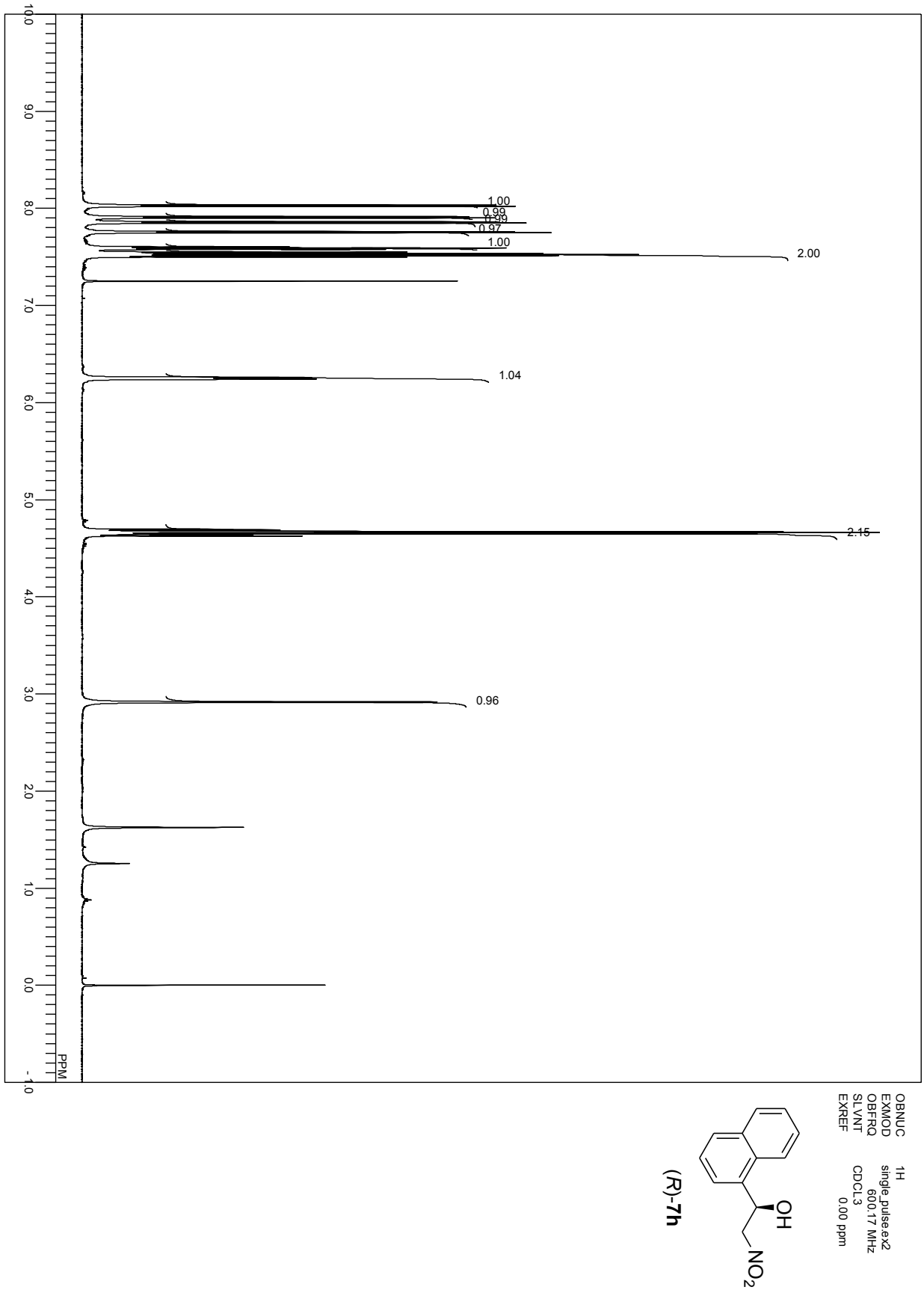
(*R*)-**7e**

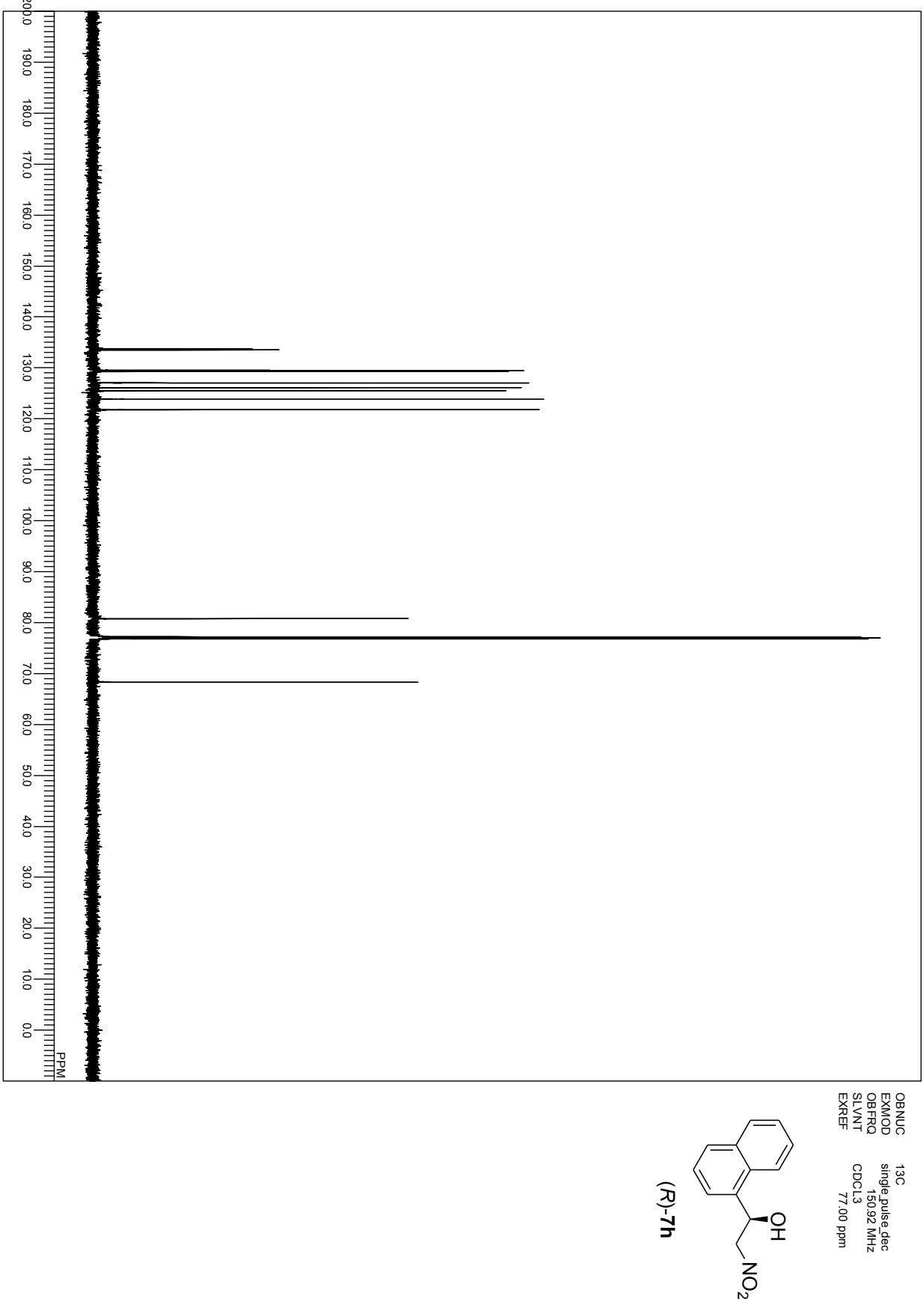

0.98
1.02
1.00
1.02
1.05
1.10
1.10
1.01
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
SLVNT CDCL3
EXREF 0.00 ppm
(R)-7f
NO2
OH
NO2

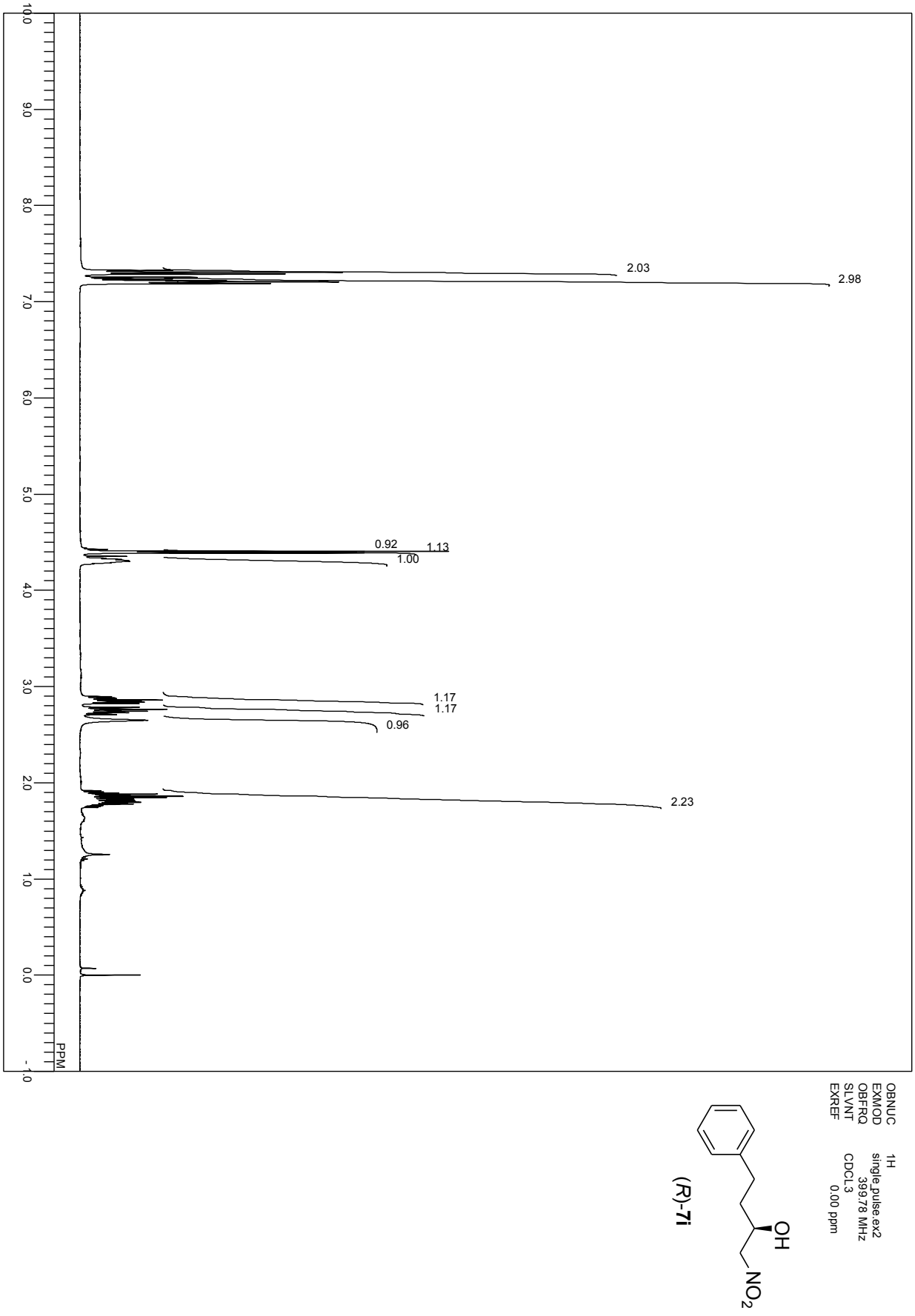

200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
PPM
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
SLVNT CDCl3
EXREF 77.00 ppm
OH
NO2
NO2
(R)-7f

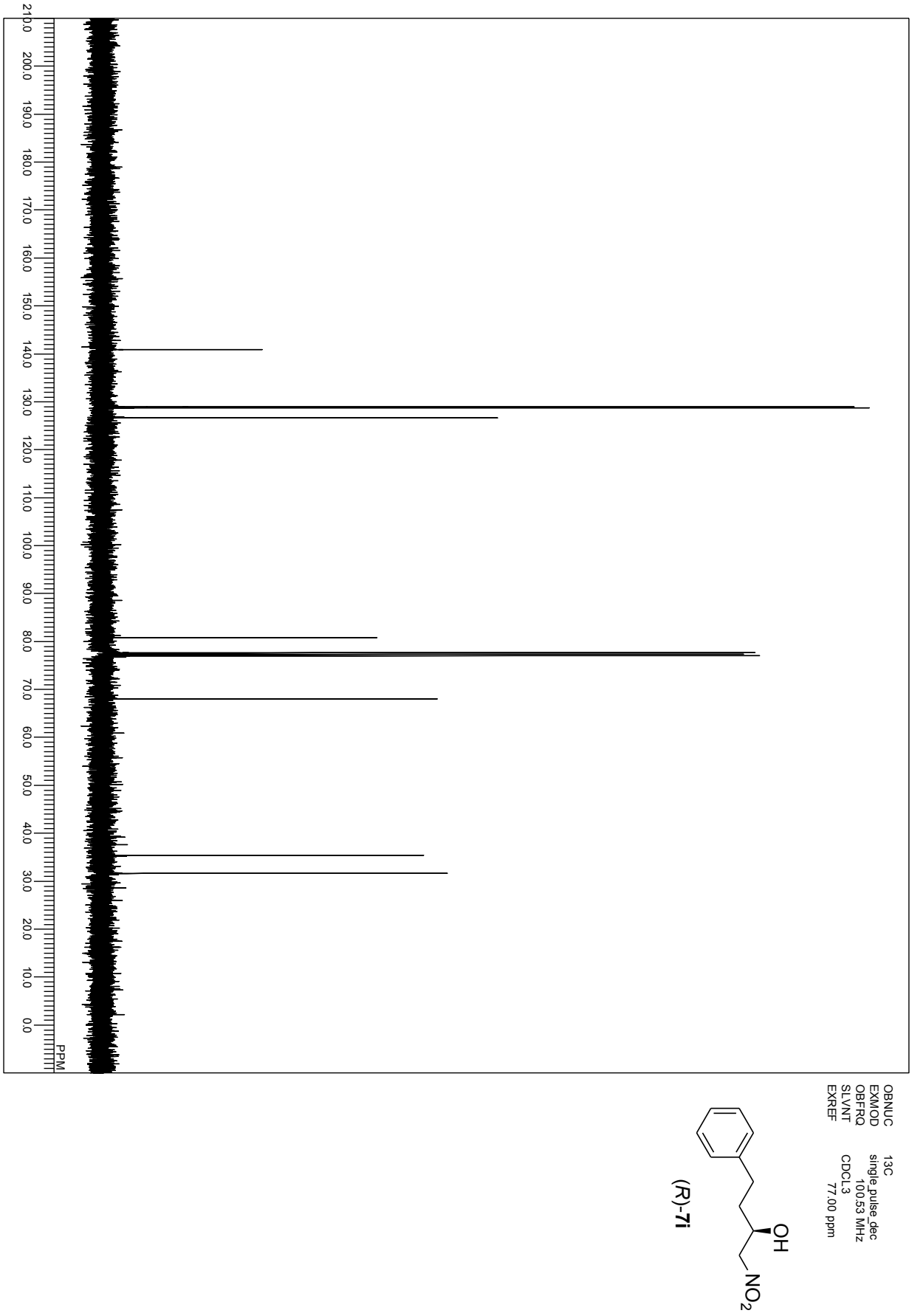


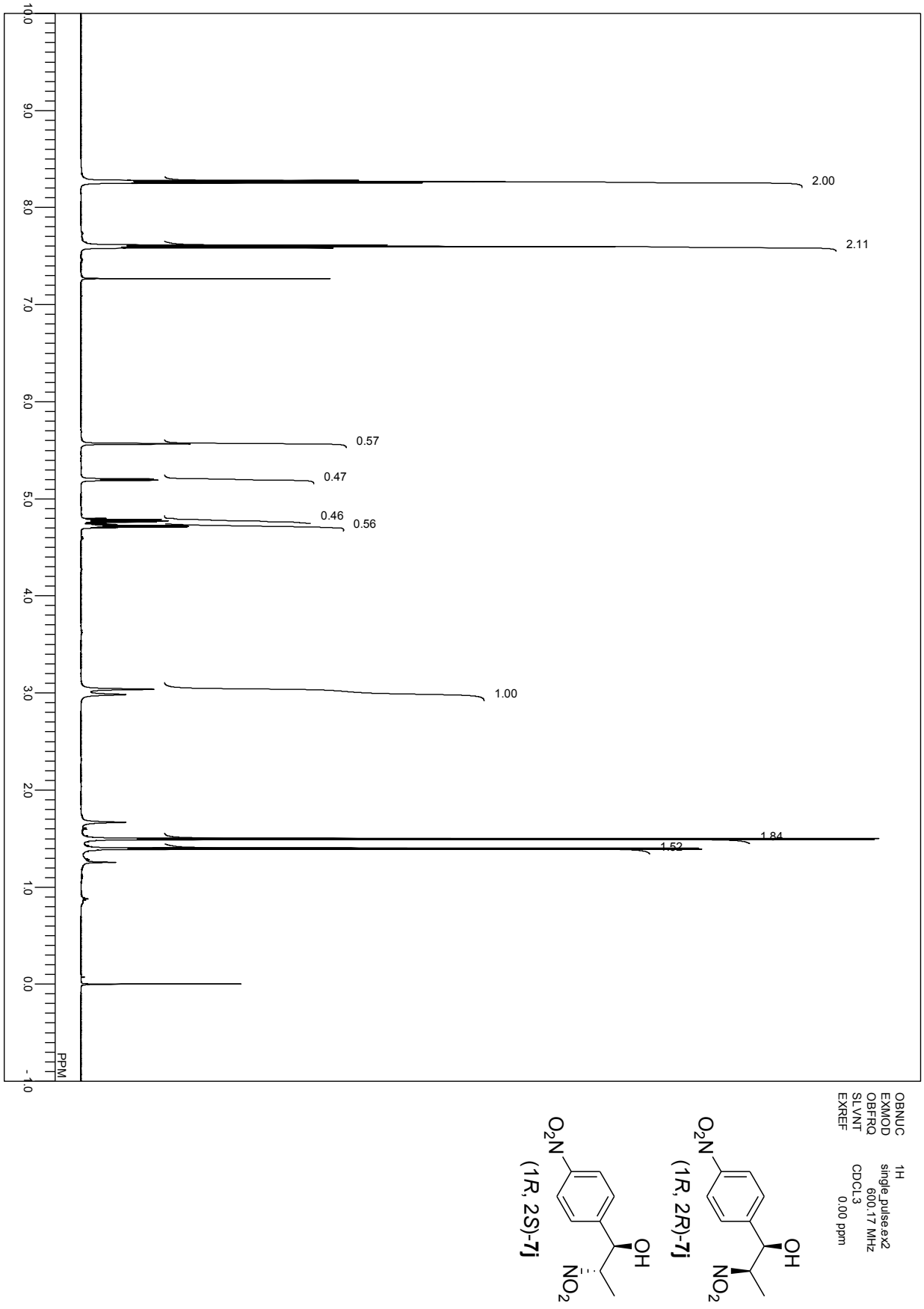

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
PPM
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
SLVNT CDCL3
EXREF 77.00 ppm
N
OH
NO2
(R)-7g

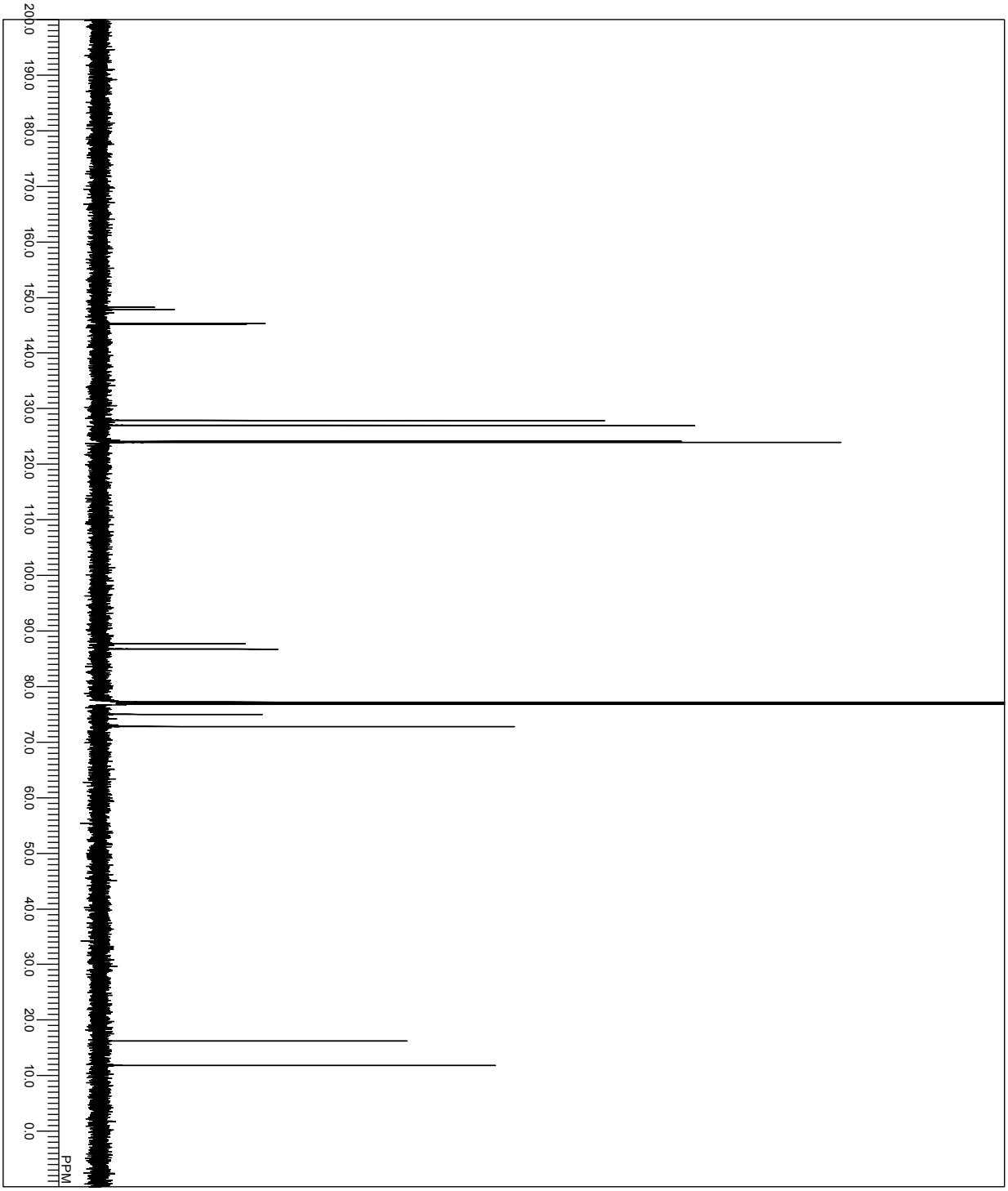

1.00
0.99
0.99
0.97
1.00
2.00
1.04
2.15
0.96
PPM
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
SLVNT CDCL3
EXREF 0.00 ppm
OH
NO2
(R)-7h

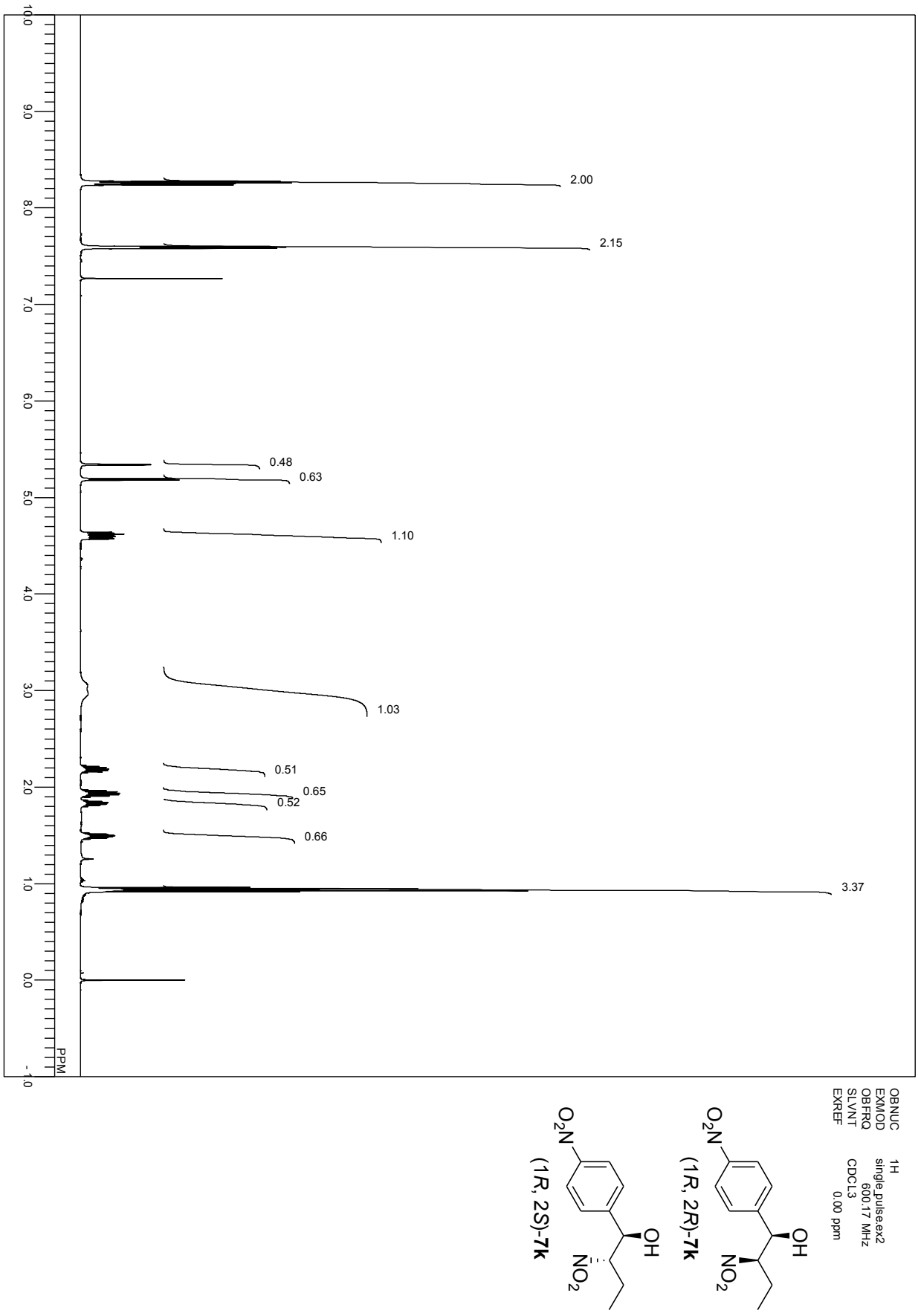

200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
PPM
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
SLVNT CDCL3
EXREF 77.00 ppm
OH
NO2
(R)-7h

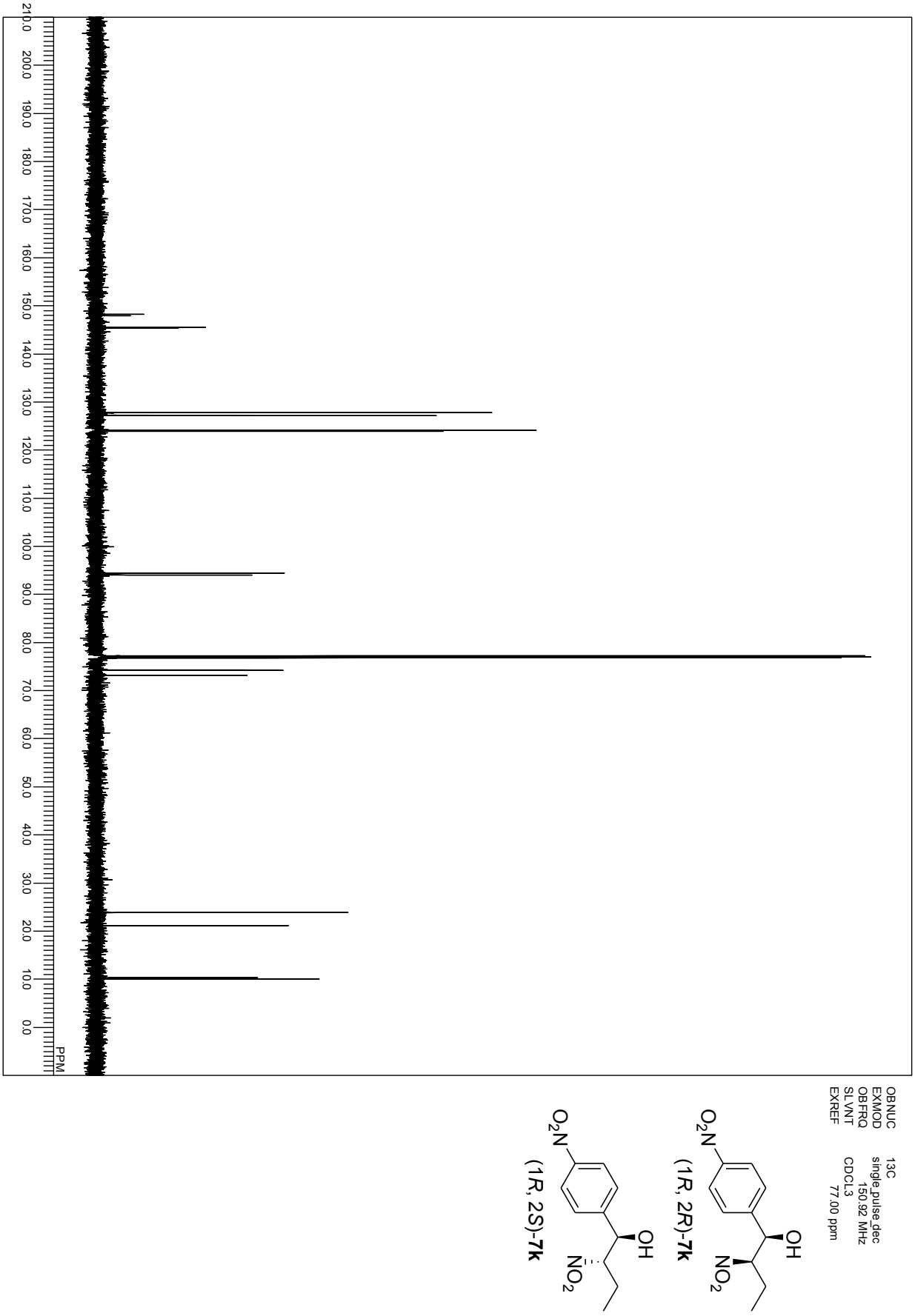

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
- 1.0
PPM
2.03
2.98
0.92
1.13
1.00
1.17
1.17
0.96
2.23
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
SLVNT CDCL3
EXREF 0.00 ppm
(R)-7i
OH
NO2

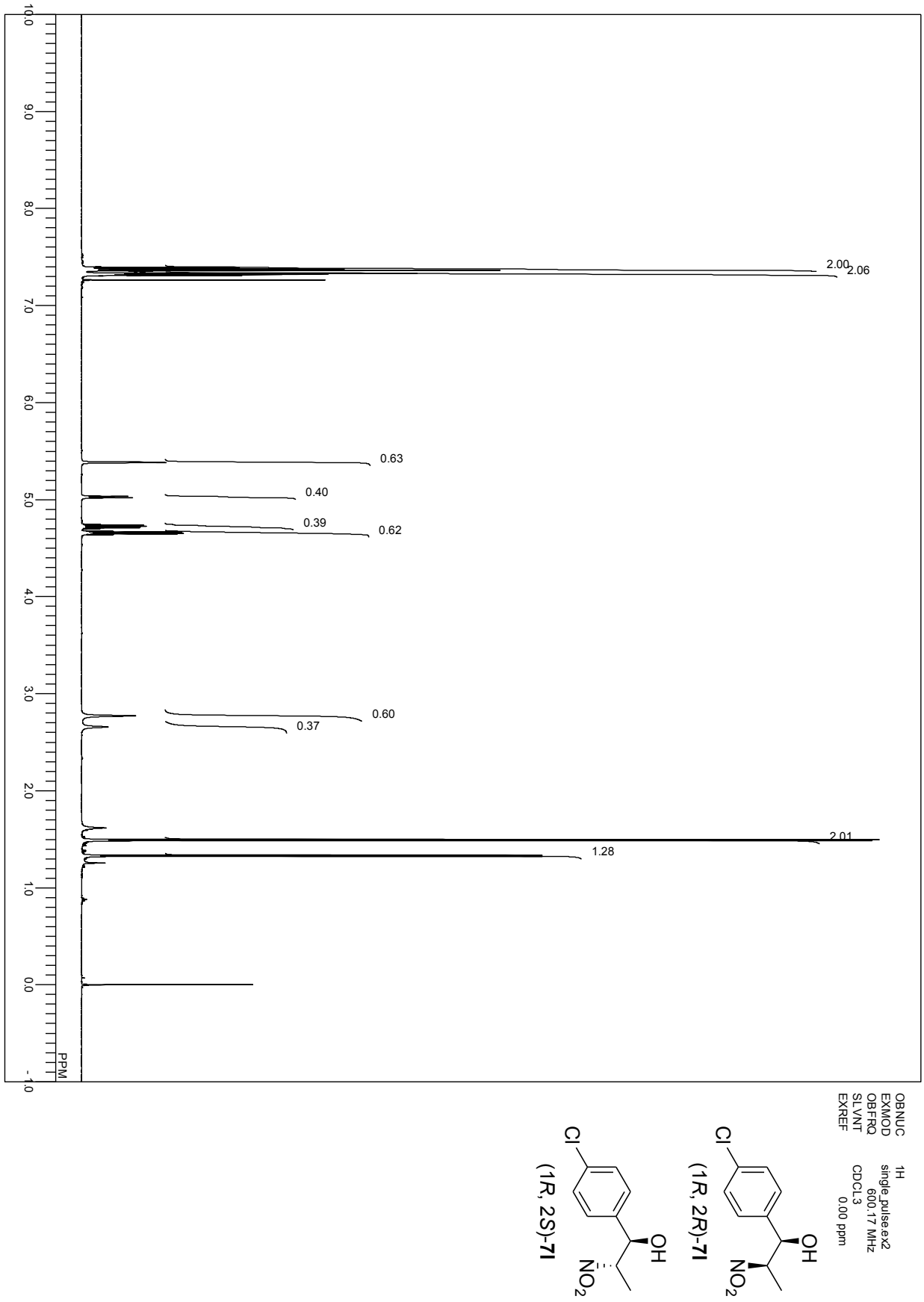

OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
SLVNT CDCL3
EXREF 77.00 ppm
OH
NO2
(R)-7i
PPM
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0

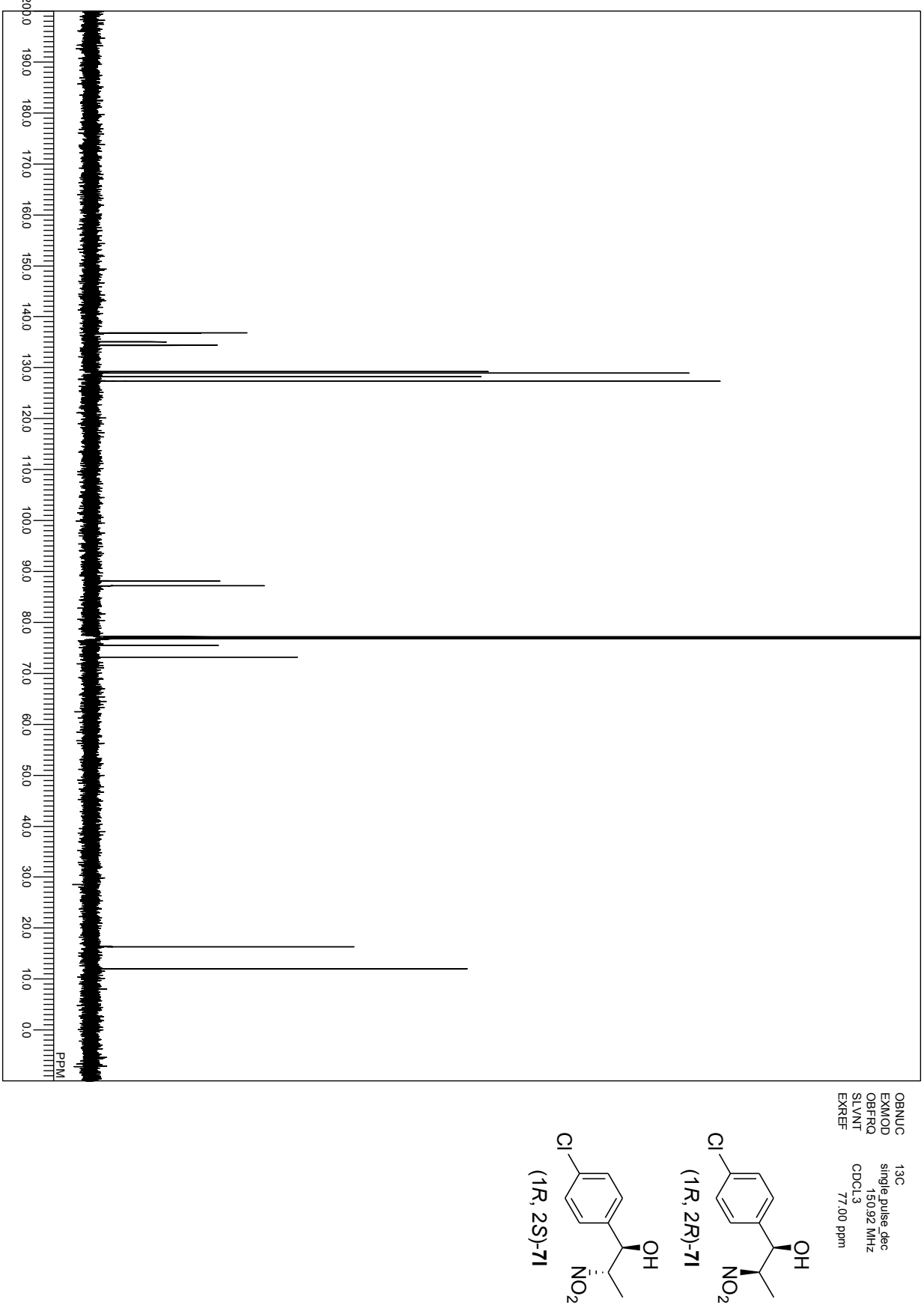

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
- 1.0
PPM
2.00
2.11
0.57
0.47
0.46
0.56
1.00
1.84
1.52
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
SLVNT CDCL3
EXREF 0.00 ppm
O2N
OH
NO2
(1R, 2R)-7j
O2N
OH
NO2
(1R, 2S)-7j


OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
O2N
OH
NO2
(1R, 2R)-7j
O2N
OH
NO2
(1R, 2S)-7j


10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
- 1.0
PPM
2.00
2.15
0.48
0.63
1.10
1.03
0.51
0.65
0.52
0.66
3.37
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
SLVNT CDCL3
EXREF 0.00 ppm
O2N
OH
NO2
(1R, 2R)-7k
O2N
OH
NO2
(1R, 2S)-7k

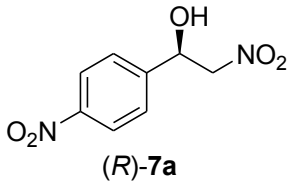

OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
SLVNT CDCL3
EXREF 77.00 ppm
PPM
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
O2N
OH
NO2
(1R, 2R)-7k
(1R, 2S)-7k


10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
PPM
2.00
2.06
0.63
0.40
0.39
0.62
0.60
0.37
2.01
1.28
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
SLVNT CDCL3
EXREF 0.00 ppm
Cl
OH
NO2
(1R, 2R)-7l
Cl
OH
NO2
(1R, 2S)-7l

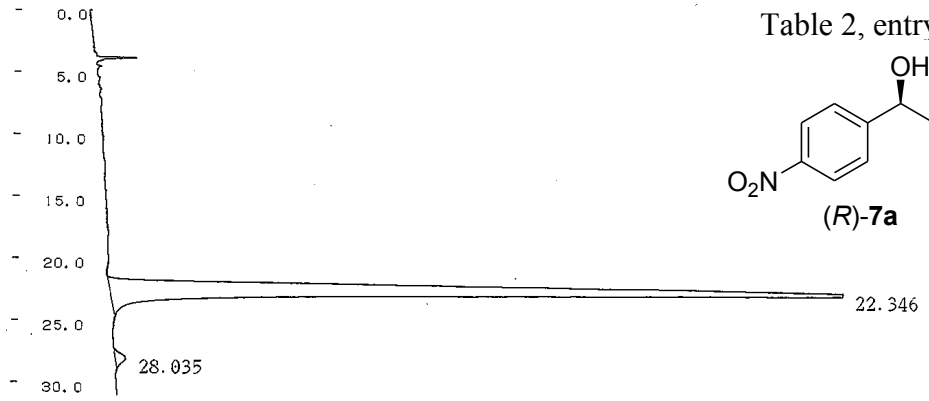

OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
Cl
OH
NO2
(1R, 2R)-7l
Cl
OH
NO2
(1R, 2S)-7l

CHROMATOPAC C-R7A CH=1 REPORT No.=7 ﾌｧｲﾙ=1:@CHRM1.C00 11/11/26 20:19:28

Table 2, entry 1

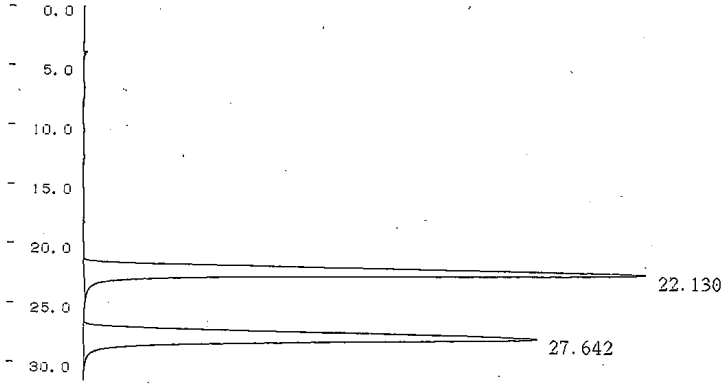


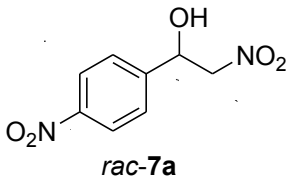
(*R*)-**7a**



** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	22.346	1671661	34066			98.6488	
	2	28.035	22897	441			1.3512	
		TOTAL	1694558	34508			100	





rac-**7a**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	22.13	2209338	47453			50.1937	
	2	27.642	2192286	38346			49.8063	
		TOTAL	4401624	85799			100	

CHROMATOPAC C-R7A CH=1 REPORT No.=5 ｸﾛﾏﾄ=1:@CHRM1.C00 12/09/07 17:03:28

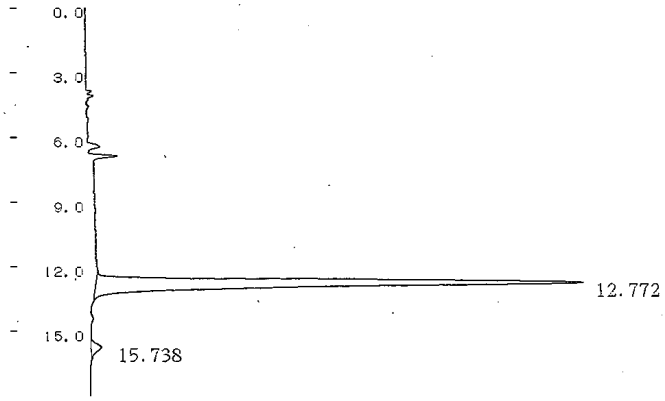
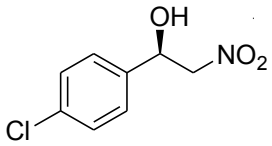


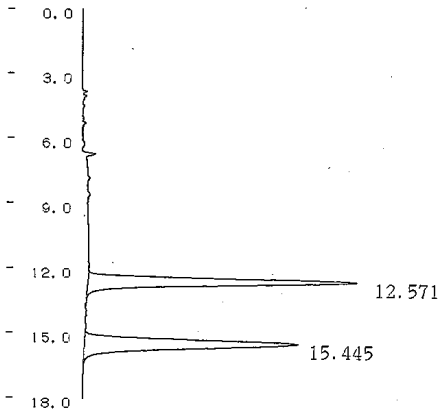
Table 2, entry 2

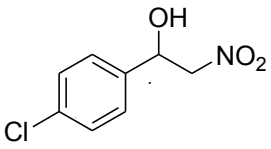


(*R*)-**7b**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	12.772	227098	10280			97.615	
	2	15.738	5549	212			2.385	
		TOTAL	232647	10492			100	





rac-**7b**

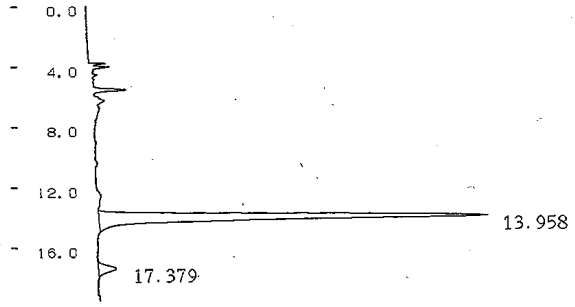
** 定量計算結果 **

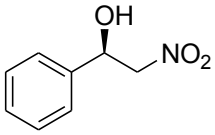
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	12.571	247154	11412			49.9734	
	2	15.445	247417	9074			50.0266	

r2-1

CHROMATOPAC C-R7A CH=1 REPORT No.=8 ｸﾛﾏﾄ=1:@CHRM1.C00 12/03/19 11:22:04

Table 2, entry 3

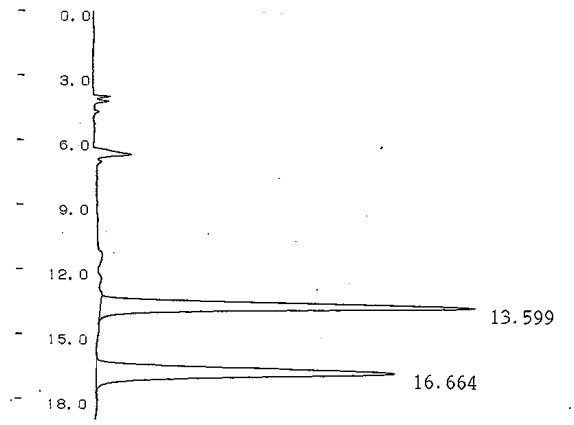


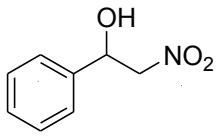


(*R*)-**7c**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	13.958	105881	4097			95.0177	
	2	17.379	5552	189			4.9823	
		TOTAL	111433	4286			100	





rac-**7c**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	13.599	90301	3960			50.2958	
	2	16.664	89238	3167			49.7042	
		TOTAL	179539	7126			100	

CHROMATOPAC C-R7A CH=1 REPORT No.=2 ﾌｧｲﾙ=1:@CHRM1.C00 12/05/23 13:36:16

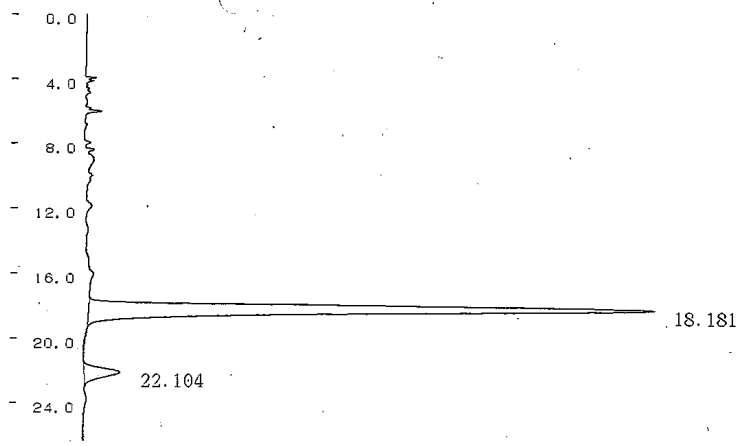
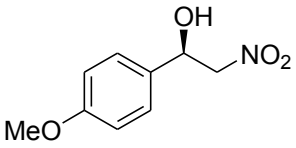


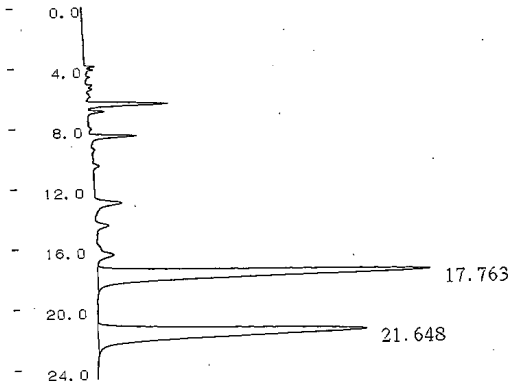
Table 2, entry 4

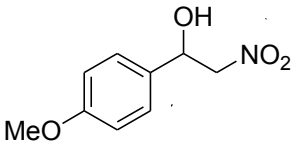


(*R*)-**7d**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	18.181	390023	11928			92.9701	
	2	22.104	29492	764			7.0299	
		TOTAL	419514	12692			100	





rac-**7d**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	17.763	224143	7029			49.9986	
	2	21.648	224155	5697			50.0014	
		TOTAL	448298	12726			100	

CHROMATOPAC C-R7A CH=1 REPORT No.=5 ﾌｧｲﾙ=1:@CHRM1.C00 12/09/20 16:44:30

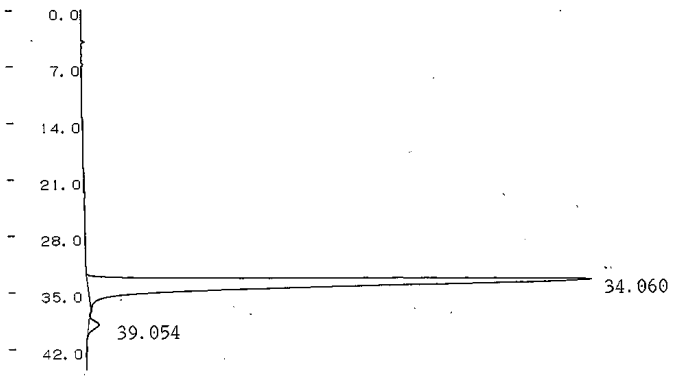
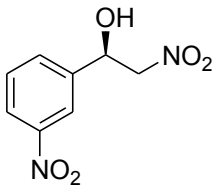


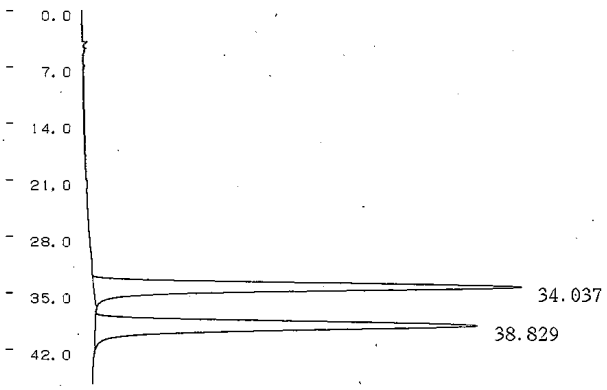
Table 2, entry 5

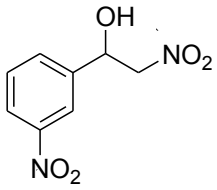


(*R*)-**7e**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	5	34.06	1482257	21276			98.0089	
	6	39.054	30112	430			1.9911	
		TOTAL	1512369	21705			100	





rac-**7e**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	34.037	1261274	18130			50.118	
	2	38.829	1255336	16174			49.882	
		TOTAL	2516609	34305			100	

CHROMATOPAC C-R7A CH=1 REPORT No.=5 ﾌｧｲﾙ=1:@CHRM1.C00 12/08/27 14:12:56

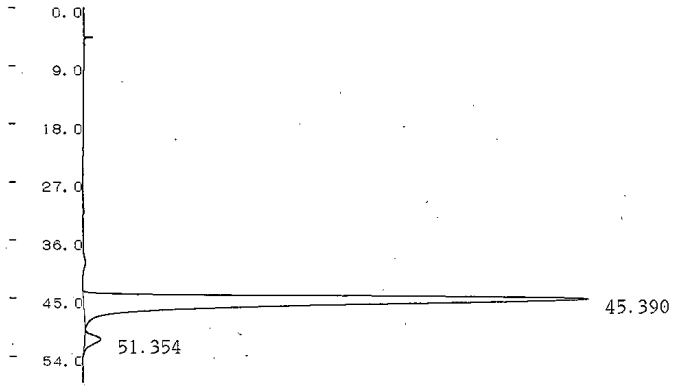
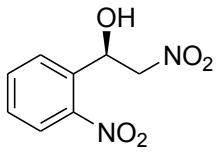


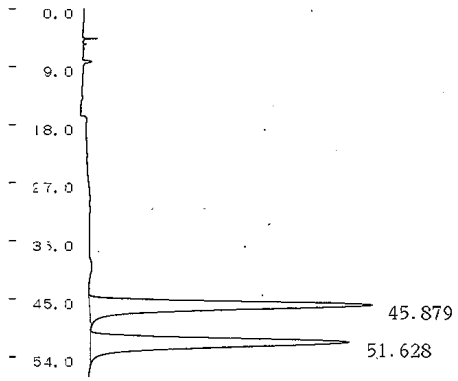
Table 2, entry 6

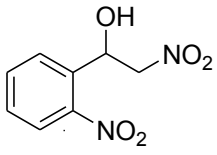


(*R*)-**7f**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	45.39	2007337	21337			96.9196	
	2	51.354	63799	685			3.0804	
		TOTAL	2071137	22022			100	





rac-**7f**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	45.879	532551	5997			50.1968	
	2	51.628	528375	5476			49.8032	
		TOTAL	1060925	11473			100	

CHROMATOPAC C-R7A CH=1 REPORT No.=11 ﾌｧｲﾙ=1:@CHRM1.C00 12/06/28 18:39:26

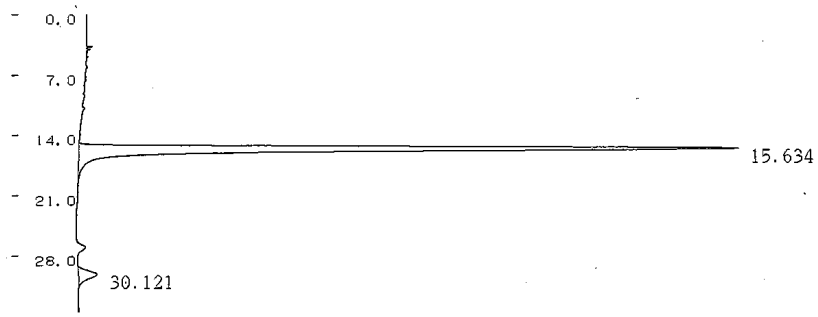
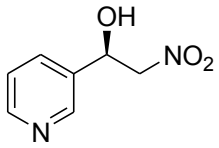


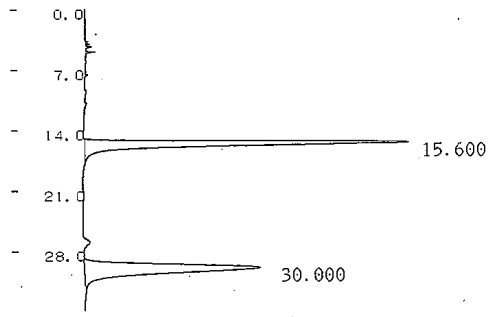
Table 2, entry 7

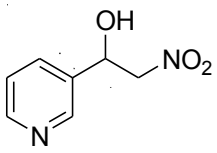


(*R*)-**7g**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	15.634	541615	13929			95.5804	
	2	30.121	25044	395			4.4196	
		TOTAL	566659	14325			100	





rac-**7g**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	15.6	514455	13687	S		50.2417	
	3	30	509504	7488			49.7582	
		TOTAL	1023959	21175			100	

CHROMATOPAC C-R7A CH=1 REPORT No.=4 ﾌﾛｯﾄ=1:@CHRM1.C00 12/08/29 16:30:48

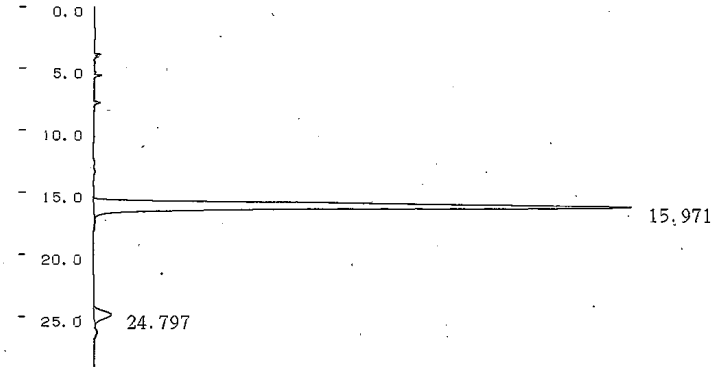
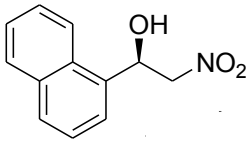


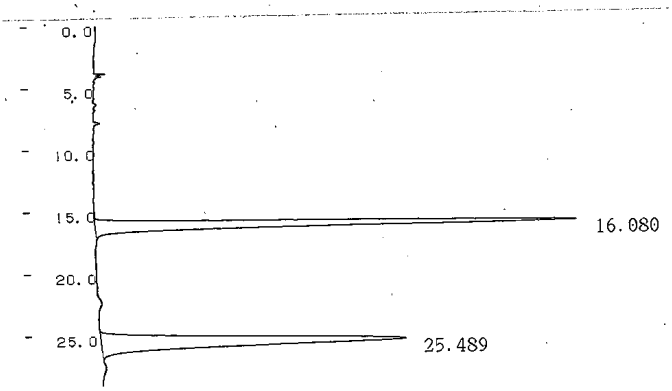
Table 2, entry 8

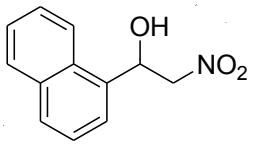


(*R*)-**7h**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	15.971	684250	22669			95.4764	
	2	24.797	32419	733			4.5236	
		TOTAL	716669	23402			100	





rac-**7h**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	16.08	310433	10188			50.0817	
	2	25.489	309420	6471			49.9183	
		TOTAL	619853	16659			100	

CHROMATOPAC C-R7A CH=1 REPORT No.=4 ﾌｧｲﾙ=1:@CHRM1.C00 13/03/07 19:30:14

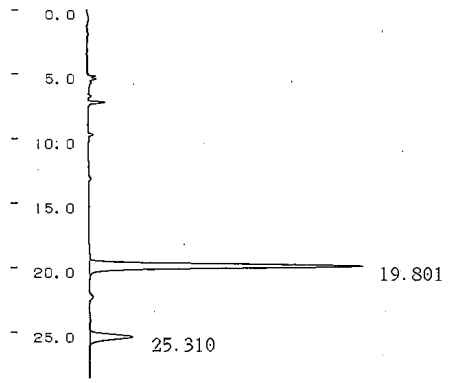
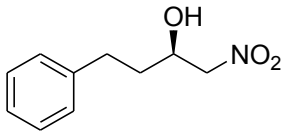


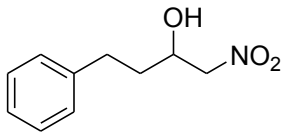
Table 2, entry 9



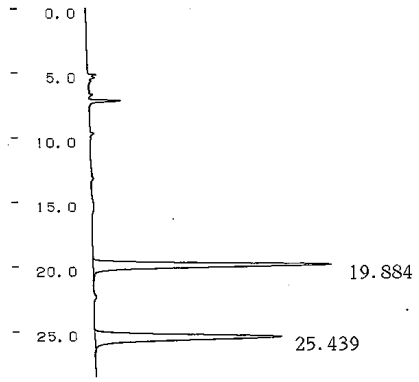
(*R*)-**7i**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	19.801	131220	5777			83.8961	
	2	25.31	25188	912			16.1039	
		TOTAL	156408	6689			100	



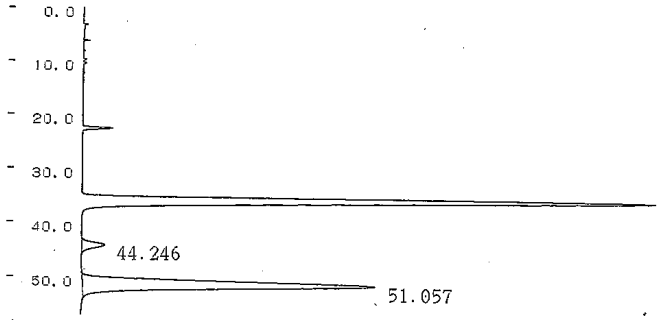
rac-**7i**



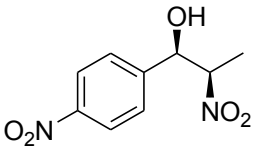
** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	19.884	115492	5052			50.1569	
	2	25.439	114770	3977			49.8431	
		TOTAL	230261	9029			100	

CHROMATOPAC C-R7A CH=1 REPORT No.=9 ﾌｧｲﾙ=1:@CHRM1.C00 12/04/23 19:25:42



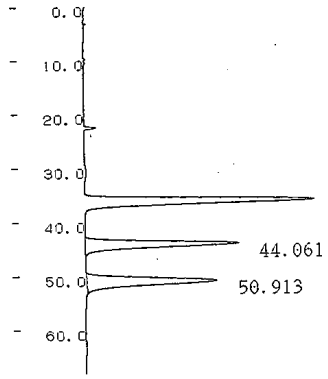
Scheme 2

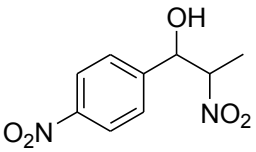


(1*R*, 2*R*)-**7j**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	44.246	69194	966			5.7154	
	2	51.057	1141460	12360			94.2846	
		TOTAL	1210655	13326			100	



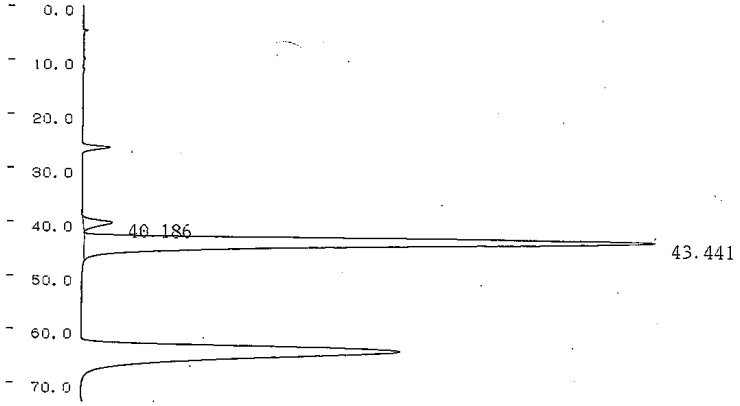


rac-**7j**

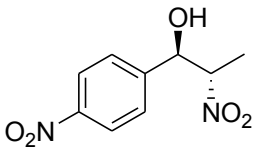
** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	44.061	489433	6541			49.6133	
	2	50.913	497061	5550			50.3867	
		TOTAL	986494	12092			100	

CHROMATOPAC C-R7A CH=1 REPORT No.=9 ﾌｧｲﾙ=1:@CHRM1.C00 12/04/23 13:05:46



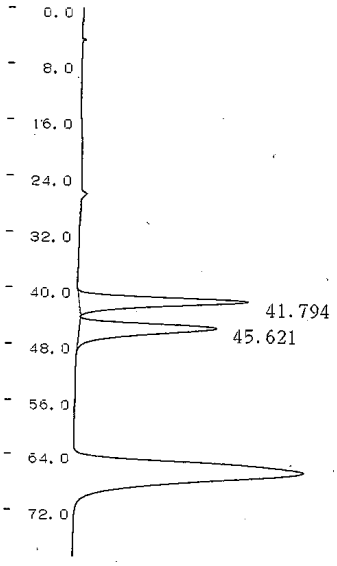
Scheme 2

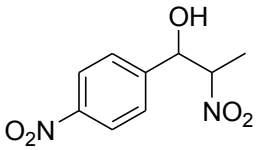


(1*R*, 2*S*)-**7j**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	40.186	95637	1242			3.6061	
	2	43.441	2556466	24098			96.3939	
		TOTAL	2652103	25340			100	



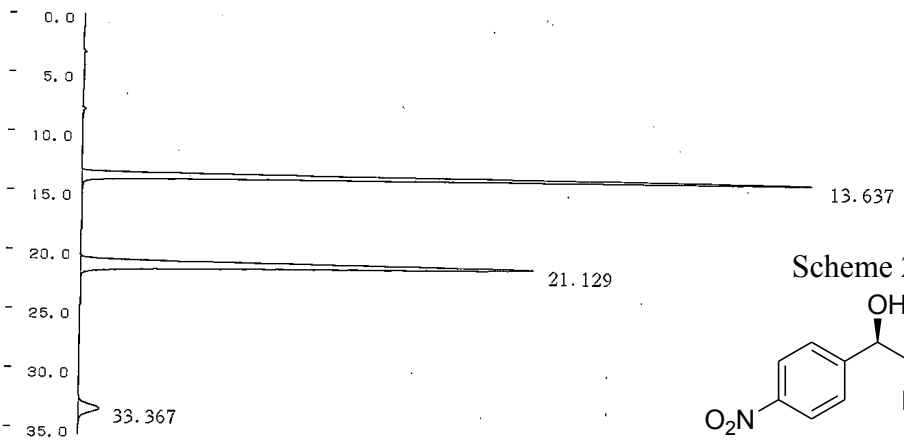


rac-**7j**

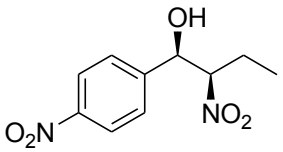
** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	41.794	605919	7211			50.2268	
	2	45.621	600446	5863			49.7732	
		TOTAL	1206364	13074			100	

CHROMATOPAC C-R7A CH=1 REPORT No.=11 ﾌｧｲﾙ=1:@CHRM1.C00 13/03/02 19:49:44



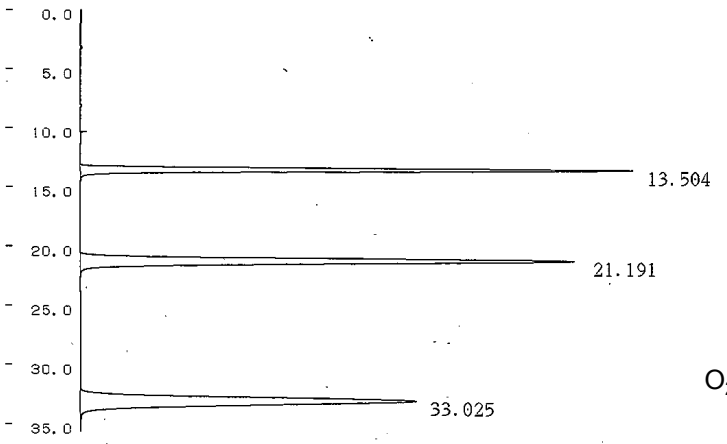
Scheme 2

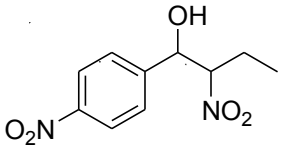


(1*R*, 2*R*)-**7k**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	13.637	1167494	61871			49.3913	
	2	21.129	1116699	38284			47.2424	
	3	33.367	79574	1748			3.3664	
	TOTAL		2363766	101903			100	



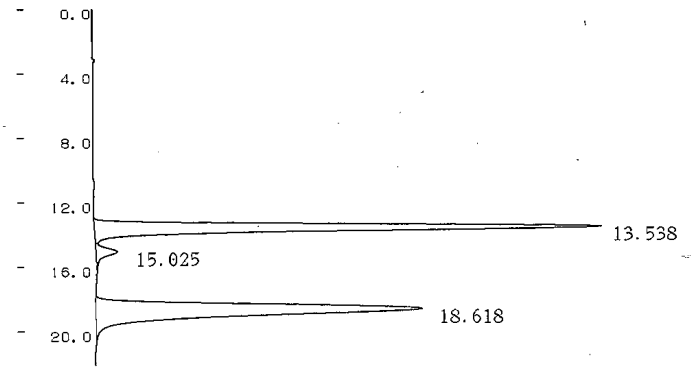


rac-**7k**

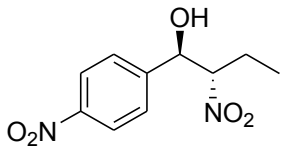
** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	13.504	917997	46860			26.5571	
	2	21.191	1280205	41864			37.0356	
	3	33.025	1258488	28503			36.4073	
	TOTAL		3456690	117227			100	

CHROMATOPAC C-R7A CH=1 REPORT No.=5 ﾌｧｲﾙ=1:@CHRM1.C00 13/03/02 18:05:46



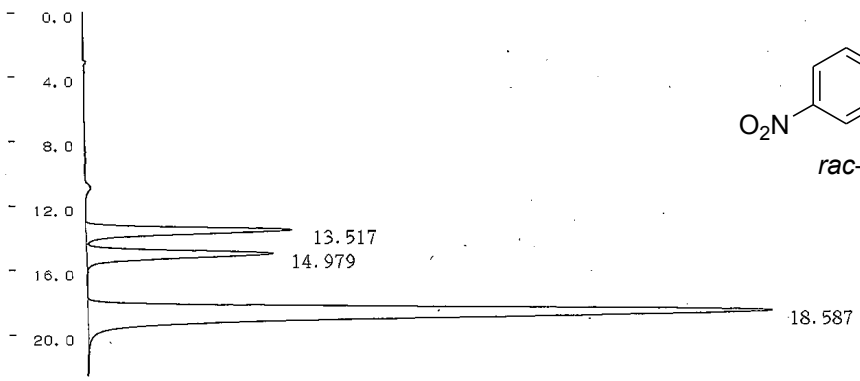
Scheme 2

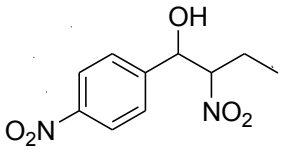


(1*R*, 2*S*)-**7k**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	13.538	1255741	42926			47.9412	
	2	15.025	61170	1797	V		2.3353	
	3	18.618	1302423	27653	S		49.7234	
		TOTAL	2619334	72377			100	





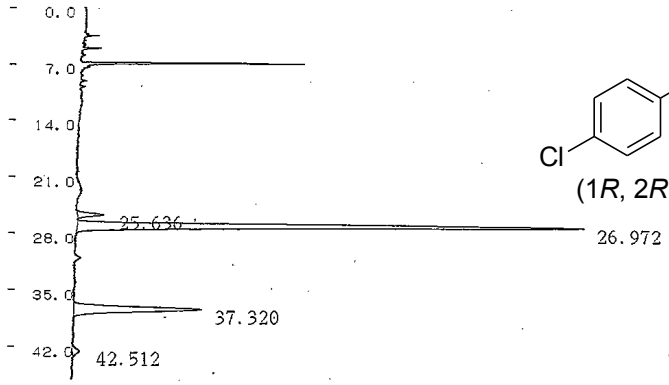
rac-**7k**

** 定量計算結果 **

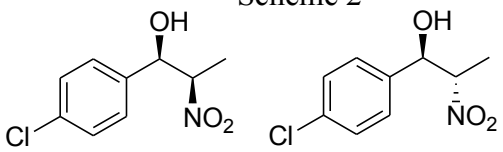
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	13.517	513020	17484			13.7577	
	2	14.979	517785	15875	V		13.8855	
	3	18.587	2698165	58034	S		72.3568	
		TOTAL	3728970	91392			100	

r2-1

CHROMATOPAC C-R7A CH=1 REPORT No.=9 ﾌｧｲﾙ=1:@CHRM1.C00 12/05/15 18:22:36



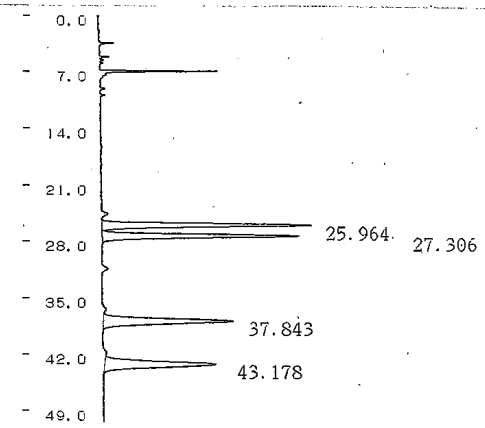
Scheme 2

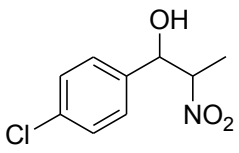


(1*R*, 2*R*)-**7l** (1*R*, 2*S*)-**7l**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	25.636	3882	140			3.3012	
	2	26.972	83287	2674			70.8179	
	3	37.32	28805	681			24.4928	
	4	42.512	1633	40			1.3881	
		TOTAL	117607	3536			100	





rac-**7l**

** 定量計算結果 **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	25.964	66904	2220			26.6168	
	2	27.306	65992	2086	V		26.254	
	3	37.843	59633	1382			23.7244	
	4	43.178	58830	1189			23.4048	
		TOTAL	251359	6876			100	