New Approach to the Preparation of Bicyclo Octane Derivatives via the Enantioselective Cascade Reaction Catalyzed by Chiral Diamine-$Ni(OAc)_2$ Complex

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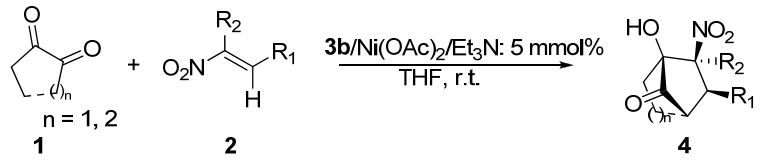
1. General Methods:

All reactions were monitored by thin layer chromatography (TLC), column chromatography purifications were carried out using silica gel. All of substrates were prepared according to the literature. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian instrument (300 MHz and 75 MHz, respectively) using tetramethylsilane as internal reference. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, hept = heptet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). IR spectra were recorded on a FTIR spectrometer. Optical rotations were reported as follows: $[\alpha]_D^{20}$ (c: g/100 mL, in solvent). HR-MS was measured with an APEX II 47e mass spectrometer. The ee value determination was carried out using chiral HPLC with Daicel Chiracel AD-H, IA, OJ-H, AS column on Waters with a 996 UV-detector.

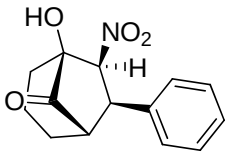
2. General Procedure for the Synthesis of 4:



Reaction conditions: 0.5 mL solvent, 1,2-cyclohexadione **1** (0.75 mmol), nitroalkane **2** (0.5 mmol), 5 mol% catalyst (**3b**/Ni(OAc)$_2$/EtN_3 = 1:1:1) at RT. After the reaction was complete (as determined by TLC); the reaction mixture was concentrated, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 5:1) to afford the product **4**.

3. Spectral Data for the Products 4.

(1S,5S,6R,7S)-1-hydroxy-7-nitro-6-phenylbicyclo[3.2.1]octan-8-one (4a)



4a

Following the general procedure, **4a** was isolated by column chromatography using silica gel as a single diastereoisomer in 98% yield (diastereomeric ratio = 10:1).

White solid. m.p. 143-150 ℃.

H NMR (300 MHz, $CDCl_3$): δ 7.37-7.28 (m, 3H), 7.17-7.14 (m, 2H), 4.77 (d, *J* = 5.7 Hz, 1H), 4.18 (d, *J* = 6 Hz, 1H), 3.28 (s, 1H), 2.81 (d, *J* = 2.1 Hz, 1H), 2.43-2.32 (m, 2H), 2.19-2.05 (m, 1H), 2.01-1.93 (m, 2H), 1.83-1.76 (m, 1H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 212.5, 142.3, 129.4, 127.9, 126.8, 93.7, 81.6, 51.6, 43.9, 39.9, 36.1, 18.0;

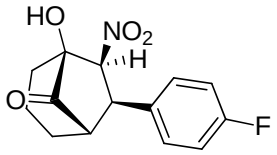
IR ($CHCl_3$): 3444, 2952, 1763, 1549, 1451, 1370, 1334, 1137, 754, 701, 678 cm^{-1};

HRMS (ESI): $C_{14}H_{15}NO_4$+NH_4, Calc: 279.1339, Found: 279.1335;

$[\alpha]_D^{rt}$ = +16 (c = 1.0 in $CHCl_3$);

HPLC: DAICEL CHIRALCEL OJ-H, *n*-hexane/ *i*-PrOH =90/10, flow rate = 1.0 mL/min, retention time: t_{major} = 17.4, t_{minor} = 22.6, 98% ee.

(1S,5S,6R,7S)-6-(4-fluorophenyl)-1-hydroxy-7-nitrobicyclo[3.2.1]octan-8-one (4b)



4b

Following the general procedure, **4b** was isolated by column chromatography using silica gel as a single diastereoisomer in 98% yield (diastereomeric ratio = 50:1).

Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16-7.12 (m, 2H), 7.06-7.01 (m, 2H), 4.71 (d, *J* = 6 Hz, 1H), 4.17 (d, *J* = 6 Hz, 1H), 3.27 (s, 1H), 2.78 (s, 1H), 2.44-2.32 (m, 2H), 2.17-2.08 (m, 1H), 2.01-1.90 (m, 2H), 1.79-1.72 (m, 1H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 212.3, 138.2 (J_{C-F} = 3.75 Hz), 128.4 (J_{C-F} = 8.25 Hz), 116.3(J_{C-F} = 21.75 Hz), 93.7, 81.6, 51.7, 43.3, 39.8, 36.0, 17.9;

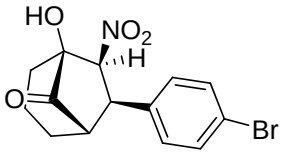
IR ($CHCl_3$): 3444, 2954, 2927, 1763, 1550, 1511, 1452, 1370, 1335, 1231, 1138, 1100, 930, 835, 803, 672 cm^{-1};

HRMS (ESI): $C_{14}H_{14}NFO_4$+NH_4, Calc: 297.1245, Found: 297.1242;

$[\alpha]_D^{rt}$ = +9 (c = 1.0 in $CHCl_3$);

HPLC: DAICEL CHIRALCEL OJ-H, *n*-hexane/ *i*-PrOH =95/5, flow rate = 1.0 mL/min, retention time: t_{major} = 60.6, t_{minor} = 70.2, >99% ee.

(1S,5S,6R,7S)-6-(4-bromophenyl)-1-hydroxy-7-nitrobicyclo[3.2.1]octan-8-one (4c)



4c

Following the general procedure, **4a** was isolated by column chromatography using silica gel as a single diastereoisomer in 77% yield (diastereomeric ratio = 40:1).

White solid. m.p. 148-152 ℃.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50-7.45 (m, 2H), 7.06-7.02 (m, 2H), 4.70 (d, *J* = 6 Hz, 1H), 4.14 (d, *J* = 5.7 Hz, 1H), 3.24 (s, 1H), 2.79-2.76 (m, 1H), 2.45-2.30 (m, 2H), 2.18-2.07 (m, 1H), 2.03-1.86 (m, 2H), 1.81-1.72 (m, 1H);

^{13}C NMR (75 MHz, CDCl3): δ 212.1, 141.2, 132.5, 128.5, 121.9, 93.3, 81.5, 51.5, 43.4, 39.8, 36.0, 17.9;

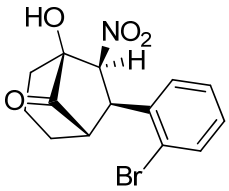
IR ($CHCl_3$): 3429, 2925, 1763, 1549, 1490, 1371, 1138, 1074, 1010, 825, 732 cm^{-1};

HRMS (ESI): $C_{14}H_{14}NBrO_4$+NH_4, Calc: 357.0444, Found: 357.0439;

$[\alpha]_D^{rt}$ = +12 (c = 1.0 in $CHCl_3$);

HPLC: DAICEL CHIRALCEL OJ-H, *n*-hexane/ *i*-PrOH =90/10, flow rate = 1.0 mL/min, retention time: t_{minor} = 17.3, t_{major} = 22.4, 97% ee.

(1S,5S,6R,7S)-6-(2-bromophenyl)-1-hydroxy-7-nitrobicyclo[3.2.1]octan-8-one (4d)



4d

Following the general procedure, **4d** was isolated by column chromatography using silica gel as both diastereoisomer in 99% yield (diastereomeric ratio = 5:4).

White solid. m.p. 139-144 ℃.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62-7.59 (m, 1H), 7.34-7.29 (m, 1H), 7.18-7.13 (m, 1H), 7.02-6.99 (m, 1H), 5.09 (d, *J* = 6.3 Hz, 1H), 4.80 (d, *J* = 6.6 Hz, 1H), 3.31 (s, 1H), 2.63 (d, *J* = 3.9 Hz, 1H), 2.52-2.42 (m, 2H), 2.18-1.99 (m, 3H), 1.83-1.76 (m, 1H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 212.4, 140.7, 133.7, 129.4, 128.6, 128.2, 123.7, 91.8, 81.8, 52.5, 43.1, 40.4, 36.4, 17.9;

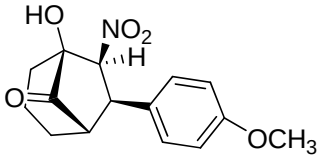
IR ($CHCl_3$): 3428, 2928, 1763, 1551, 1471, 1445, 1369, 1139, 1027, 929, 753 cm^{-1};

HRMS (ESI): $C_{14}H_{14}NBrO_4$+NH_4, Calc: 357.0444, Found: 357.0434;

$[\alpha]_D^{rt}$ = -14 (c = 1.0 in $CHCl_3$);

HPLC: DAICEL CHIRALCEL OJ-H, *n*-hexane/ *i*-PrOH =90/10, flow rate = 1.0 mL/min, retention time: t_{major} = 28.7, t_{minor} = 34.1, 90% ee, t_{major} = 58.5, t_{minor} = 79.4, 91% ee

(1S,5S,6R,7S)-1-hydroxy-6-(4-methoxyphenyl)-7-nitrobicyclo[3.2.1]octan-8-one (4e)



4e

Following the general procedure, **4e** was isolated by column chromatography using silica gel as a single diastereoisomer in 74% yield (diastereomeric ratio = 50:1).

Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10-7.05 (m, 2H), 6.88-6.83 (m, 2H), 4.73 (d, *J* = 5.7 Hz, 1H), 4.13 (d, *J* = 5.7 Hz, 1H), 3.79 (s, 3H), 3.27 (s, 1H), 2.77 (d, *J* = 2.7 Hz, 1H), 2.42-2.32 (m, 2H), 2.16-2.04 (m, 1H), 2.02-1.92 (m, 2H), 1.77-1.75 (m, 1H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 212.6, 159.1, 134.5, 127.8, 114.7, 94.1, 81.6, 55.3, 51.8, 43.2, 39.8, 36.0, 17.9;

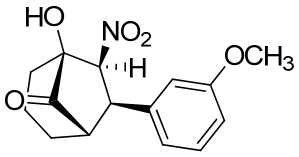
IR ($CHCl_3$): 3439, 2925, 1762, 1612, 1549, 1515, 1457, 1070, 1253, 1182, 1030, 831 cm^{-1};

HRMS (ESI): $C_{15}H_{17}NO_4$+NH_4, Calc: 309.1445, Found: 309.1447;

$[\alpha]_D^{rt}$ = +10 (c = 1.0 in $CHCl_3$);

HPLC: DAICEL CHIRALCEL AD-H, *n*-hexane/ *i*-PrOH =80/20, flow rate = 1.0 mL/min, retention time: t_{major} = 56.7, t_{minor} = 65.4, 98% ee.

(1S,5S,6R,7S)-1-hydroxy-6-(3-methoxyphenyl)-7-nitrobicyclo[3.2.1]octan-8-one (4f)



4f

Following the general procedure, **4f** was isolated by column chromatography using silica gel as a single diastereoisomer in 98% yield (diastereomeric ratio = 50:1).

White solid. m.p. 144-149 ℃.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (t, *J* = 8.1 Hz, 1H), 6.83-6.79 (m, 1H), 6.72-6.70 (m, 2H), 4.78 (d, *J* = 6 Hz, 1H), 4.15 (d, *J* = 6 Hz, 1H), 3.79 (s, 3H), 3.27 (s, 1H), 2.81 (d, *J* = 2.4 Hz, 1H), 2.43-2.32 (m, 2H), 2.17-2.05 (m, 1H), 2.00-1.91 (m, 2H), 1.80-1.73 (m, 1H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 212.4, 160.2, 143.8, 130.6, 118.7, 112.9, 112.8, 93.5, 81.6, 55.3, 51.5, 43.9, 39.8, 36.0, 17.9;

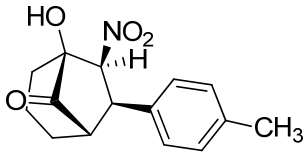
IR ($CHCl_3$): 3439, 2937, 1763, 1602, 1549, 1454, 1370, 1267, 1050, 783, 699 cm^{-1};

HRMS (ESI): $C_{15}H_{17}NO_4$+NH_4, Calc: 309.1445, Found: 309.1451;

$[\alpha]_D^{rt}$ = +10 (c = 1.0 in $CHCl_3$);

HPLC: DAICEL CHIRALCEL AD-H, *n*-hexane/ *i*-PrOH =80/20, flow rate = 1.0 mL/min, retention time: t_{major} = 33.6, t_{minor} = 45.2, 98% ee.

(1S,5S,6R,7S)-1-hydroxy-7-nitro-6-p-tolylbicyclo[3.2.1]octan-8-one (4g)



4g

Following the general procedure, **4g** was isolated by column chromatography using silica gel as a single diastereoisomer in 80% yield (diastereomeric ratio = 6:1).

Yellow solid. m.p. 135-143 ℃.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.14 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.1 Hz, 2H), 4.75 (d, J = 5.9 Hz, 1H), 4.14 (d, J = 5.9 Hz, 1H), 3.34 (s, 1H), 2.78 (d, J = 2.5 Hz, 1H), 2.43-2.35 (m, 2H), 2.32 (s, 3H), 2.17-1.92 (m, 3H), 1.77-1.73 (m, 1H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 212.7, 139.3, 137.6, 130.0, 126.6, 93.8, 81.6, 51.7, 43.5, 39.8, 36.0, 21.0, 17.9;

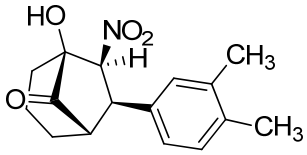
IR ($CHCl_3$): 3358, 2929, 2860, 2024, 1754, 1550, 1369, 1234, 1135, 1057, 930, 814, 672, 572, 513 cm^{-1};

HRMS (ESI): $C_{15}H_{17}NO_4$+Na, Calc: 298.1050, Found: 298.1055;

$[\alpha]_D^{rt}$ = +20 (c = 1.0 in $CHCl_3$);

HPLC: DAICEL CHIRALCEL IA, *n*-hexane/ *i*-PrOH =90/10, flow rate = 1.0 mL/min, retention time: t_{major} = 20.4, t_{minor} = 30.0, >99% ee.

(1S,5S,6R,7S)-6-(3,4-dimethylphenyl)-1-hydroxy-7-nitrobicyclo[3.2.1]octan-8-one (4h)



4h

Following the general procedure, **4h** was isolated by column chromatography using silica gel as both diastereoisomer in 91% yield (diastereomeric ratio = 7:1).

Yellow solid. m.p. 123-126 ℃.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08 (d, J = 7.7 Hz, 1H), 6.91-6.86 (m, 2H), 4.78 (d, J = 5.9 Hz, 1H), 4.11 (d, J = 5.9 Hz, 1H), 3.42 (s, 1H), 2.76 (d, J = 2.8 Hz, 1H), 2.41-2.31 (m, 2H), 2.22 (s, 6H), 2.11-1.93 (m, 3H), 1.81-1.74 (m, 1H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 212.9, 139.9, 137.8, 136.3, 130.5, 127.8, 124.1, 93.8, 81.7, 51.8, 43.5, 39.8, 36.1, 19.8, 19.4, 17.9;

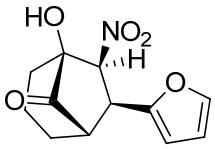
IR ($CHCl_3$): 3381, 2924, 2855, 2023, 1758, 1546, 1455, 1371, 1232, 1135, 1058, 933, 801, 715, 668 cm^{-1};

HRMS (ESI): $C_{15}H_{17}NO_4$+Na, Calc: 312.1206, Found: 312.1217;

$[\alpha]_D^{rt}$ = +12 (c = 1.0 in $CHCl_3$);

HPLC: DAICEL CHIRALCEL IA, *n*-hexane/ *i*-PrOH =90/10, flow rate = 1.0 mL/min, retention time: t_{major} = 13.0, t_{minor} = 20.6, >97% ee.

(1S,5S,6S,7S)-6-(furan-2-yl)-1-hydroxy-7-nitrobicyclo[3.2.1]octan-8-one (4i)



4i

Following the general procedure, **4i** was isolated by column chromatography using silica gel as both diastereoisomer in 70% yield (diastereomeric ratio = 30:1).

Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (d, *J* = 1.2 Hz, 1H), 6.31-6.30 (m, 1H), 6.19 (d, *J* = 3.3 Hz, 1H), 4.94 (d, *J* = 6 Hz, 1H), 4.30 (d, *J* = 5.7 Hz, 1H), 3.28 (s, 1H), 2.83 (d, *J* = 2.4 Hz, 1H), 2.43-2.29 (m, 2H), 2.15-2.05 (m, 1H), 2.02-1.86 (m, 2H), 1.78-1.70 (m, 1H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 211.1, 152.7, 143.1, 110.5, 106.5, 90.2, 81.2, 49.5, 39.8, 37.8, 35.5, 17.9;

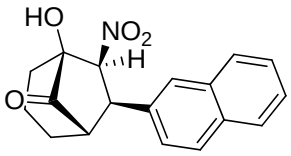
IR ($CHCl_3$): 3431, 2926, 1766, 1551, 1453, 1371, 1335, 1141, 1070, 934, 743 cm^{-1};

HRMS (ESI): $C_{12}H_{13}NO_5$+NH_4, Calc: 269.1132, Found: 269.1138;

$[\alpha]_D^{rt}$ = +48 (c = 1.0 in $CHCl_3$);

HPLC: DAICEL CHIRALCEL OJ-H, *n*-hexane/ *i*-PrOH =95/5, flow rate = 1.0 mL/min, retention time: t_{major} = 33.5, t_{minor} = 40.0, >99% ee.

(1S,5S,6R,7S)-1-hydroxy-6-(naphthalen-2-yl)-7-nitrobicyclo[3.2.1]octan-8-one (4j)



4j

Following the general procedure, **4j** was isolated by column chromatography using silica gel as both diastereoisomer in 99% yield (diastereomeric ratio = 8:1).

Yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85-7.79 (m, 3H), 7.65 (s, 1H), 7.53-7.46 (m, 2H), 7.23-7.20 (m, 1H), 4.87 (d, *J* = 5.7 Hz, 1H), 4.36 (d, *J* = 6 Hz, 1H), 3.32 (s, 1H), 2.92 (d, *J* = 2.4 Hz, 1H), 2.46-2.37 (m, 2H), 2.21-2.01 (m, 3H), 1.86-1.75 (m, 1H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 212.5, 139.3, 133.3, 132.6, 129.7, 127.8, 127.7, 126.8, 126.4, 125.7, 124.2, 93.5, 81.7, 51.6, 44.1, 39.9, 36.1, 18.0;

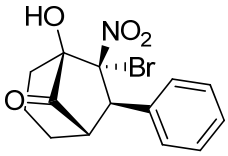
IR ($CHCl_3$): 3433, 2928, 1762, 1548, 1451, 1369, 1237, 1136, 1056, 818, 734, 478 cm^{-1};

HRMS (ESI): $C_{18}H_{17}NO_4$+NH_4, Calc: 329.1496, Found: 329.1492;

$[\alpha]_D^{rt}$ = +11 (c = 1.0 in $CHCl_3$);

HPLC: DAICEL CHIRALCEL OJ-H, *n*-hexane/ *i*-PrOH =90/10, flow rate = 1.0 mL/min, retention time: t_{major} = 52.3, t_{minor} = 69.6, 92% ee.

(1R,5S,6R,7R)-7-bromo-1-hydroxy-7-nitro-6-phenylbicyclo[3.2.1]octan-8-one (4k)



4k

Following the general procedure, **4k** was isolated by column chromatography using silica gel as both diastereoisomer in 99% yield (diastereomeric ratio = 20:1).

Yellow solid. m.p. 178-188 ℃.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.28 (m, 5H), 4.23 (d, *J* = 1.5 Hz, 1H), 3.28 (s, 1H), 3.25-3.23 (m, 1H), 2.60-2.55 (m, 1H), 2.27-2.11 (m, 4H), 1.88-1.79 (m, 1H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 210.8, 134.5, 128.8, 128.6, 128.5, 108.2, 85.2, 57.2, 48.7, 43.9, 36.6, 17.4;

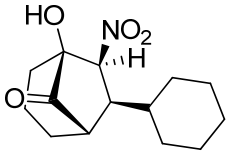
IR ($CHCl_3$): 3394, 2957, 1767, 1568, 1447, 1343, 1151, 1087, 1075, 1028, 918, 742, 730, 700 cm^{-1};

HRMS (ESI): $C_{14}H_{14}NBrO_4$+NH_4, Calc: 357.0444, Found: 357.0439;

$[\alpha]_D^{rt}$ = +8 (c = 1.0 in $CHCl_3$);

HPLC: DAICEL CHIRALCEL AD-H, *n*-hexane/ *i*-PrOH =90/10, flow rate = 1.0 mL/min, retention time: t_{minor} = 21.1, t_{major} = 24.4, 82% ee.

(1S,5S,6S,7S)-6-cyclohexyl-1-hydroxy-7-nitrobicyclo[3.2.1]octan-8-one (4l)



4l

Following the general procedure, **4i** was isolated by column chromatography using silica gel as both diastereoisomer in 51% yield (diastereomeric ratio = 8:1).

Yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.62 (d, *J* = 6.3 Hz, 1H), 3.18 (s, 1H), 2.85 (t, *J* = 6.6 Hz, 1H), 2.56 (d, *J* = 3.9 Hz, 1H), 2.30-2.25 (m, 1H), 2.17-2.03 (m, 2H), 1.96-1.86 (m, 2H), 1.78-1.60 (m, 6H), 1.43-1.31 (m, 1H), 1.25-1.14 (m, 3H), 1.00- 0.85 (m, 2H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 213.1, 89.5, 81.5, 47.1, 43.9, 41.7, 39.9, 36.1, 29.8, 29.3, 26.1, 25.9, 17.9;

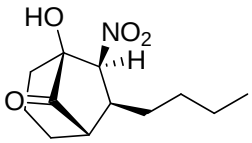
IR ($CHCl_3$): 3429, 2927, 2854, 1763, 1548, 1449, 1369, 1335, 1238, 1137, 1052, 932, 687 cm^{-1};

HRMS (ESI): $C_{14}H_{21}NO_4$+NH_4, Calc: 285.1809, Found: 285.1817;

$[\alpha]_D^{rt}$ = +52 (c = 1.0 in $CHCl_3$);

HPLC: DAICEL CHIRALCEL OJ-H, *n*-hexane/ *i*-PrOH =90/10, flow rate = 1.0 mL/min, retention time: t_{minor} = 12.6, t_{major} = 16.5, 97% ee.

(1S,5S,6S,7S)-6-butyl-1-hydroxy-7-nitrobicyclo[3.2.1]octan-8-one (4m)



4m

Following the general procedure, **4m** was isolated by column chromatography using silica gel as both diastereoisomer in 87% yield (diastereomeric ratio = 43:1).

Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.4 (d, *J* = 5.4 Hz, 1H), 3.15 (s, 1H), 2.95 (q, *J* = 7.5, 13.5 Hz, 1H), 2.42-2.40 (m, 1H), 2.37-2.33 (m, 1H), 2.21-2.13 (m, 1H), 2.07-1.96 (m, 1H), 1.90-1.85 (m, 2H), 1.71-1.63 (m, 1H), 1.53-1.43 (m, 2H), 1.39-1.29 (m, 4H), 0.90 (t, *J* = 6.6 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 212.5, 92.0, 81.4, 49.6, 39.8, 38.6, 35.7, 35.5, 28.6, 22.3, 18.1, 13.8;

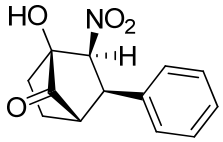
IR ($CHCl_3$): 3426, 2956, 2929, 2862, 1764, 1548, 1453, 1371, 1337, 1239, 1145, 1095, 1055, 678 cm^{-1} ;

HRMS (ESI): $C_{12}H_{19}NO_4$+NH_4, Calc: 259.1652, Found: 259.1648;

$[\alpha]_D^{rt}$ = +41 (c = 1.0 in $CHCl_3$);

HPLC: DAICEL CHIRALCEL OJ-H, *n*-hexane/ *i*-PrOH =90/10, flow rate = 1.0 mL/min, retention time: t_{minor} = 12.1, t_{major} = 15.7, 97% ee.

(1S,2S,3R,4S)-1-hydroxy-2-nitro-3-phenylbicyclo[2.2.1]heptan-7-one (4n)



4n

Following the general procedure, **4n** was isolated by column chromatography using silica gel as both diastereoisomer in 67% yield (diastereomeric ratio = 10:1).

White solid. m.p. 170-175 ℃.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.26 (m, 5H), 6.57 (s, 1H), 5.31 (dd, J = 13.8, 8.5 Hz, 1H), 4.92 (dd, J = 13.8, 7.4 Hz, 1H), 4.49 (t, J = 8.0 Hz, 1H), 2.50- 2.35 (m, 4H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 203.3, 148.9, 141.8, 136.7, 129.3, 128.3, 127.9, 76.5, 45.4, 31.7, 24.7;

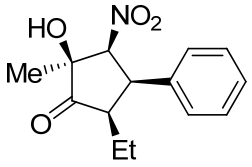
IR ($CHCl_3$): 3313, 2919, 1696, 1655, 1546, 1407, 1348, 1304, 1230, 1220, 910, 758, 683 cm^{-1};

HRMS (ESI): $C_{14}H_{21}NO_4$+Na, Calc: 270.0737, Found: 270.0741;

$[\alpha]_D^{rt}$ = +75 (c = 1.0 in $CHCl_3$);

HPLC: DAICEL CHIRALCEL IA, *n*-hexane/ *i*-PrOH =90/10, flow rate = 1.0 mL/min, retention time: t_{minor} = 24.0, t_{major} = 28.9, 50% ee.

(2S,3S,4R,5R)-5-ethyl-2-hydroxy-2-methyl-3-nitro-4-phenylcyclopentanone (4o)



4o

Following the general procedure, **4o** was isolated by column chromatography using silica gel as both diastereoisomer in 86% yield (diastereomeric ratio = 4:1).

White solid. m.p. 164-169 ℃.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41-7.31 (m, 5H), 4.86 (d, J = 10.5 Hz, 1H), 4.00 (t, J = 10.8 Hz, 1H), 2.71 (s, 1H), 2.66-2.58 (m, 1H), 1.74 (m, 3H), 1.61 (s, 3H), 0.89 (t, J = 7.5 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 210.7, 137.5, 129.2, 128.1, 127.5 93.8 76.1 53.7, 46.3, 21.8, 20.9, 10.8;

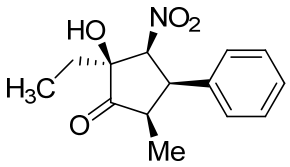
IR ($CHCl_3$): 3305,3031, 2920, 2024, 1688, 1653, 1548, 1409, 1377, 1351, 1126, 914, 763, 698, 642 cm^{-1};

HRMS (ESI): $C_{14}H_{21}NO_4$+Na, Calc: 286.1050, Found: 286.1055;

$[\alpha]_D^{rt}$ = +54 (c = 1.0 in $CHCl_3$);

HPLC: DAICEL CHIRALCEL IA, *n*-hexane/ *i*-PrOH =90/10, flow rate = 1.0 mL/min, retention time: t_{minor} = 11.4, t_{major} = 23.5, 90% ee.

(2S,3S,4R,5R)-2-ethyl-2-hydroxy-5-methyl-3-nitro-4-phenylcyclopentanone (4p)



4p

Following the general procedure, **4p** was isolated by column chromatography using silica gel as both diastereoisomer in 91% yield (diastereomeric ratio = 29:1).

White solid. m.p. 166-170 ℃.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.30 (m, 5H), 5.05 (d, J = 9.6 Hz, 1H), 3.79 (dd, J = 12.4, 9.6 Hz, 1H), 2.72 (s, 1H), 2.62 (dq, J = 13.4, 6.7 Hz, 1H), 2.05-1.91 (m, 2H), 1.20 (d, J = 6.7 Hz, 3H), 1.03 (t, J = 7.4 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 211.8, 137.2, 129.3, 128.2, 127.3, 90.7, 79.2, 49.1, 47.8, 28.9, 12.2, 7.7;

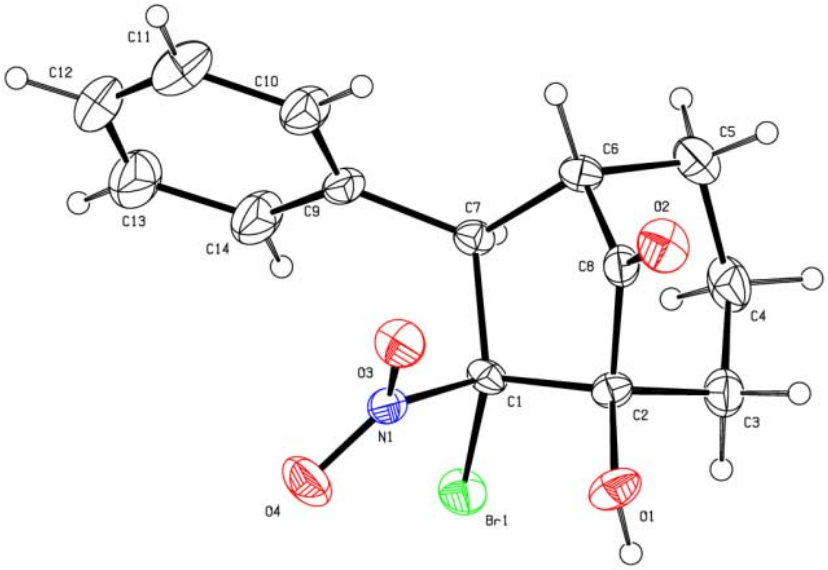
IR ($CHCl_3$): 3499, 2979, 2361, 2022, 1754, 1555, 1457, 1379, 1306, 1116, 753, 699,495 cm^{-1};

HRMS (ESI): $C_{14}H_{21}NO_4$+Na, Calc: 286.1055, Found: 286.1049;

$[\alpha]_D^{rt}$ = +111 (c = 1.0 in $CHCl_3$);

HPLC: DAICEL CHIRALCEL AS, *n*-hexane/ *i*-PrOH =90/10, flow rate = 1.0 mL/min, retention time: t_{minor} = 14.3, t_{major} = 19.2, 97% ee.

4. X-ray Structure of the adduct 4k.



Bond precision: C-C = 0.0069 A Wavelength=0.71073

Cell: a=6.9084(19) b=14.098(4) c=14.210(4)

alpha=90 beta=90 gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	1384.0(7)	1384.0(7)
Space group	P 21 21 21	P2(1)2(1)2(
Hall group	P 2ac 2ab	?
Moiety formula	C14 H14 Br N O4	?
Sum formula	C14 H14 Br N O4	C14 H14 Br N O4
Mr	340.16	340.17

Dx,g cm-3	1.633	1.633
Z	4	4
Mu (mm-1)	2.982	2.983
F000	688.0	688.0
F000'	687.19	
h,k,lmax	8,17,17	8,17,17
Nref	1504[2570]	2550
Tmin,Tmax	0.479,0.519	0.523,0.560
Tmin'	0.470	

Correction method= MULTI-SCAN

Data completeness= 1.70/0.99 Theta(max)= 25.500

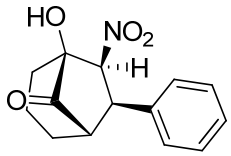
R(reflections)= 0.0368(2002) wR2(reflections)= 0.0727(2550)

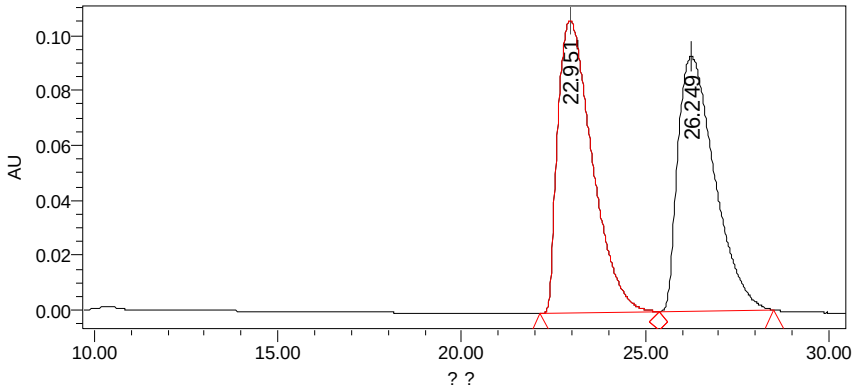
S = 0.982 Npar= 182

5. HPLC spectra for compounds 4

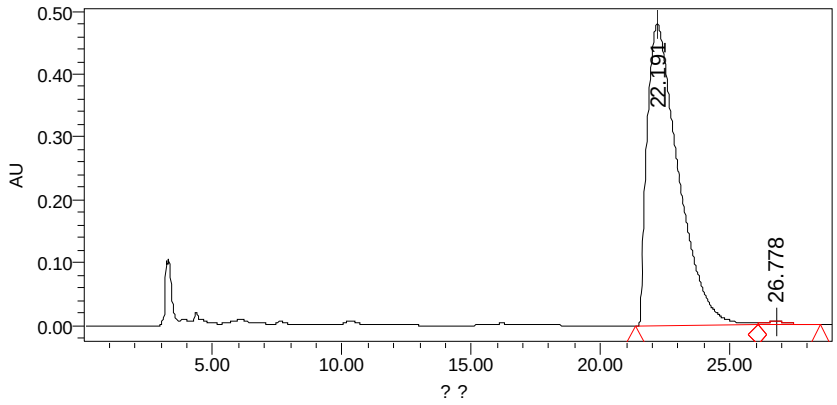
(1S,5S,6R,7S)-1-hydroxy-7-nitro-6-phenylbicyclo[3.2.1]octan-8-one (4a)

Chiralpak OJ-H column, *n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min.





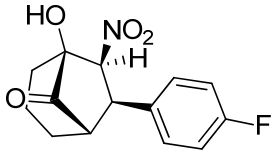
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		22.951	6920093	51.45	106323	Bb			Unknown	
2		26.249	6529291	48.55	92835	bb			Unknown	

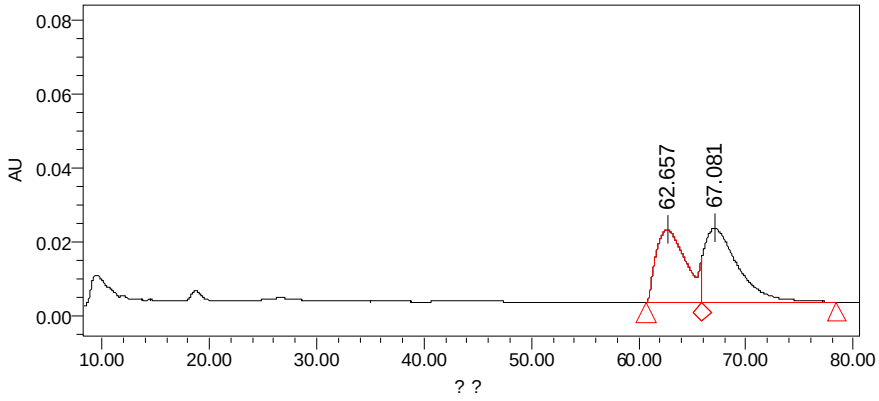


	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		22.191	40423993	99.01	480418	BV			Unknown	
2		26.778	404884	0.99	5944	Vb			Unknown	

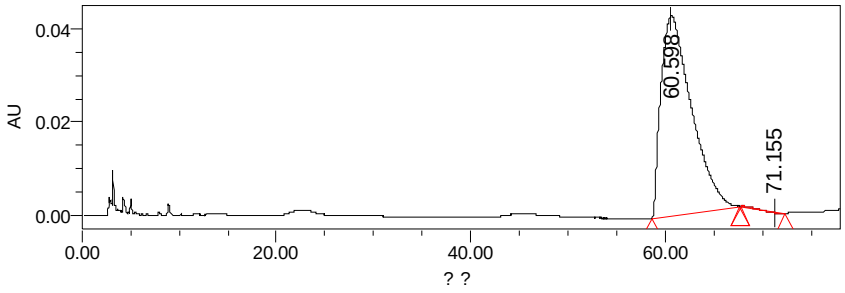
(1S,5S,6R,7S)-6-(4-fluorophenyl)-1-hydroxy-7-nitrobicyclo[3.2.1]octan-8-one (4b)

Chiralpak OJ-H column, *n*-hexane/ *i*-PrOH = 95/5, flow rate = 1.0 mL/min.





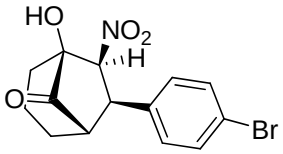
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		62.641	3514889	49.34	19193	Bv			Unknown	
2		67.087	3608880	50.66	18601	Vb			Unknown	

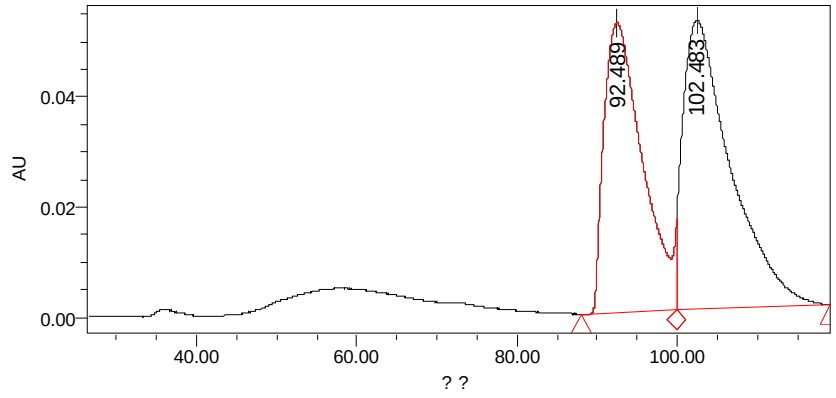


	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		60.598	9347996	99.52	42778	Bb			Unknown	
2		71.155	44997	0.48	-304	Bb			Unknown	

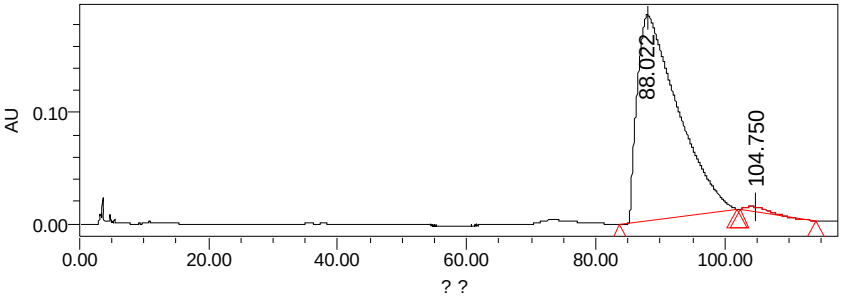
(1S,5S,6R,7S)-6-(4-bromophenyl)-1-hydroxy-7-nitrobicyclo[3.2.1]octan-8-one (4c)

Chiralpak OJ-H column, *n*-hexane/ *i*-PrOH = 95/5, flow rate = 1.0 mL/min.





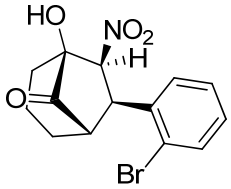
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		92.489	18553751	48.52	52384	bv			Unknown	
2		102.483	19688644	51.48	51769	vb			Unknown	

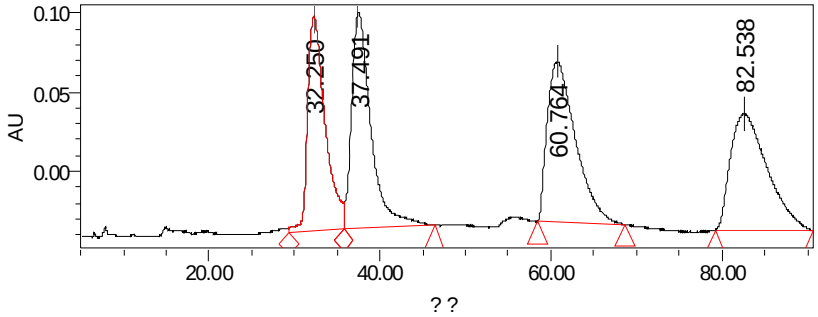


	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		88.022	80956847	98.70	184681	bb			Unknown	
2		104.750	1064439	1.30	4091	bb			Unknown	

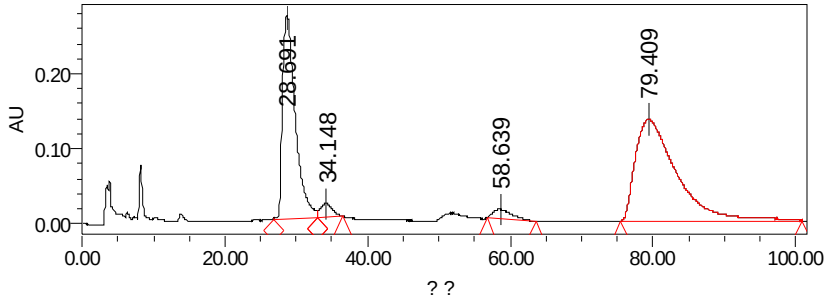
(1S,5S,6R,7S)-6-(2-bromophenyl)-1-hydroxy-7-nitrobicyclo[3.2.1]octan-8-one (4d)

Chiralpak OJ column, *n*-hexane/ *i*-PrOH = 9/1, flow rate = 1.0 mL/min.





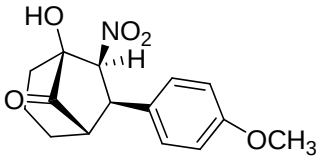
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		32.225	23486449	22.69	171354	VV			Unknown	
2		37.536	24193889	23.37	170864	VV			Unknown	
3		60.667	27934147	26.99	124611	BB			Unknown	
4		82.629	27891928	26.95	91866	bb			Unknown	

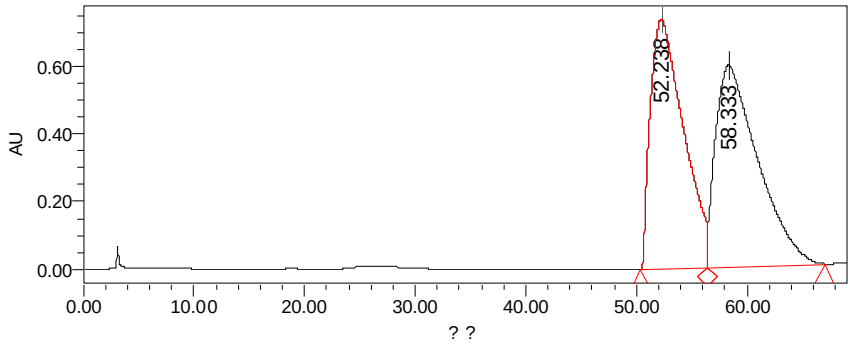


	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		28.692	47762483	94.91	373577	bv			Unknown	
2		34.108	2559270	5.09	26273	vb			Unknown	
3		58.497	3508154	4.57	18140	bb			Unknown	
4		79.435	73318690	95.43	181568	bb			Unknown	

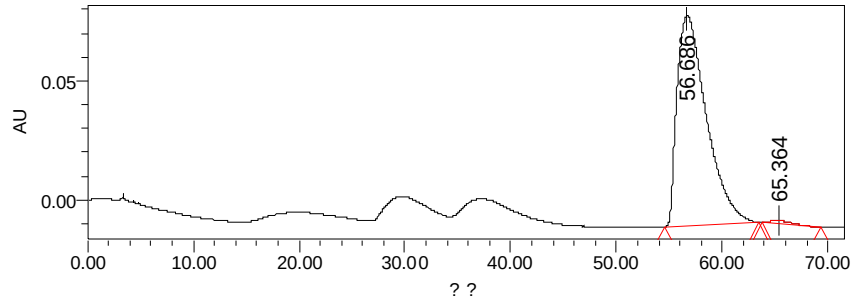
(1S,5S,6R,7S)-1-hydroxy-6-(4-methoxyphenyl)-7-nitrobicyclo[3.2.1]octan-8-one (4e)

Chiralpak OJ-H column, *n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min.





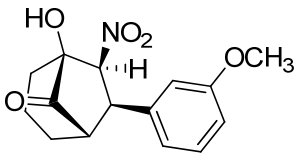
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		52.238	153545387	49.20	739609	BV			Unknown	
2		58.333	158549454	50.80	596490	VB			Unknown	

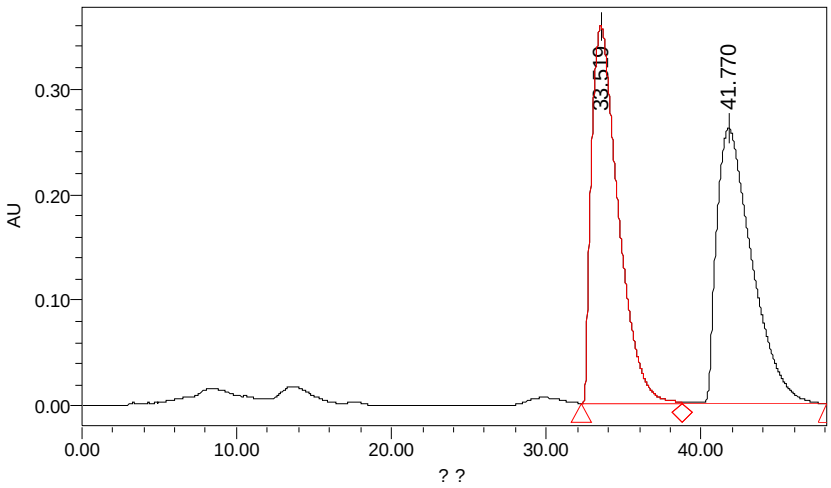


	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		56.686	17057148	98.88	88039	Bb			Unknown	
2		65.364	193774	1.12	1439	Bb			Unknown	

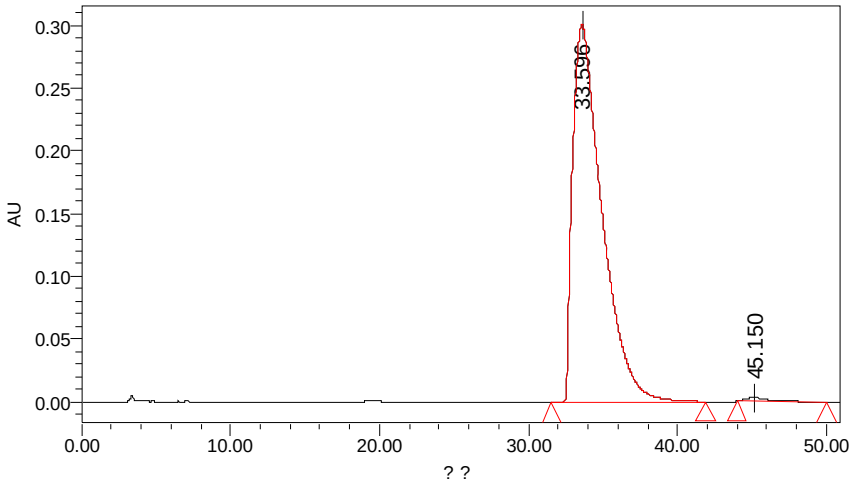
(1S,5S,6R,7S)-1-hydroxy-6-(3-methoxyphenyl)-7-nitrobicyclo[3.2.1]octan-8-one (4f)

Chiralpak OJ-H column, *n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min.





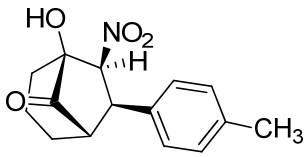
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		33.519	42917814	50.97	356235	bv			Unknown	
2		41.770	41277924	49.03	260263	vb			Unknown	

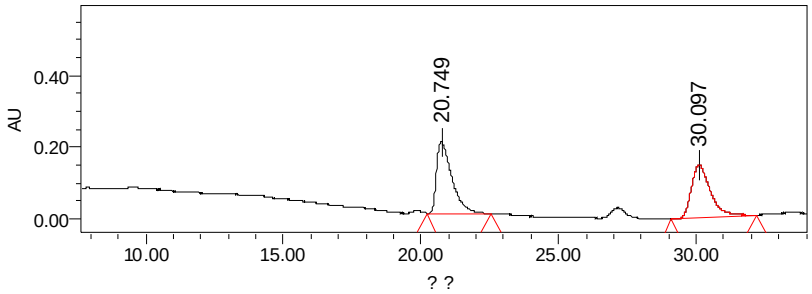


	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		33.596	41391997	99.12	301316	bb			Unknown	
2		45.150	369120	0.88	2884	BB			Unknown	

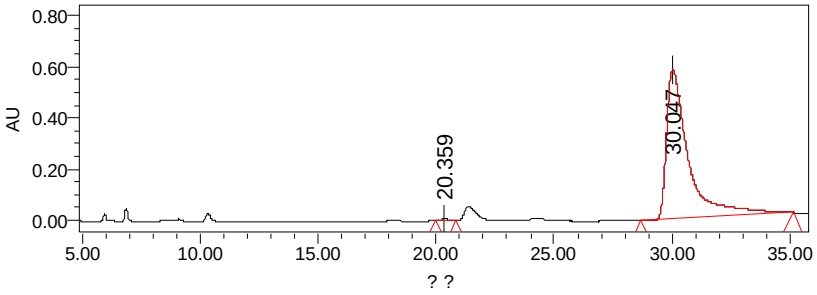
(1S,5S,6R,7S)-1-hydroxy-7-nitro-6-p-tolylbicyclo[3.2.1]octan-8-one (4g)

Chiralpak IA column, *n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min.





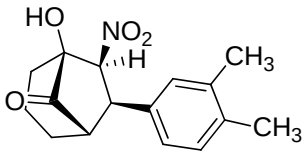
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		20.749	7730685	51.77	198862	bb			Unknown	
2		30.097	7202149	48.23	148250	bb			Unknown	

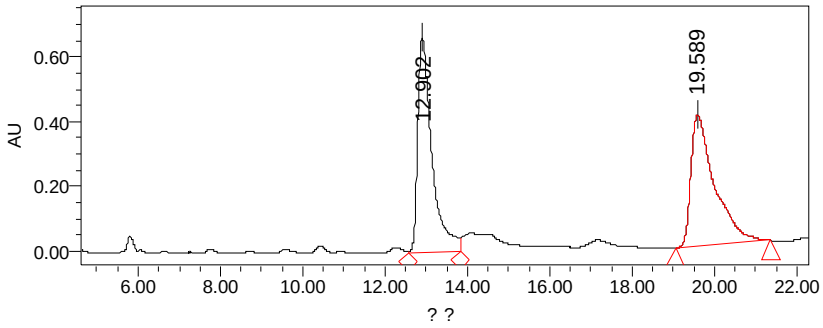


	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		20.359	189463	0.49	7398	bb			Unknown	
2		30.047	38180741	99.51	585148	bb			Unknown	

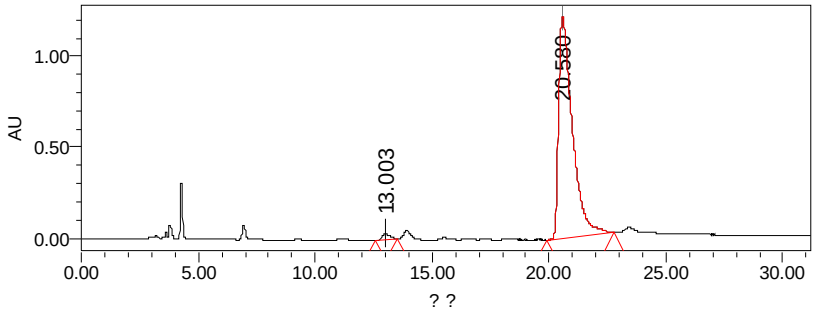
(1S,5S,6R,7S)-6-(3,4-dimethylphenyl)-1-hydroxy-7-nitrobicyclo[3.2.1]octan-8-one (4h)

Chiralpak IA column, *n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min.





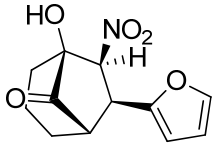
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		12.902	15815489	49.46	662085	VV			Unknown	
2		19.589	16163115	50.54	405338	bb			Unknown	

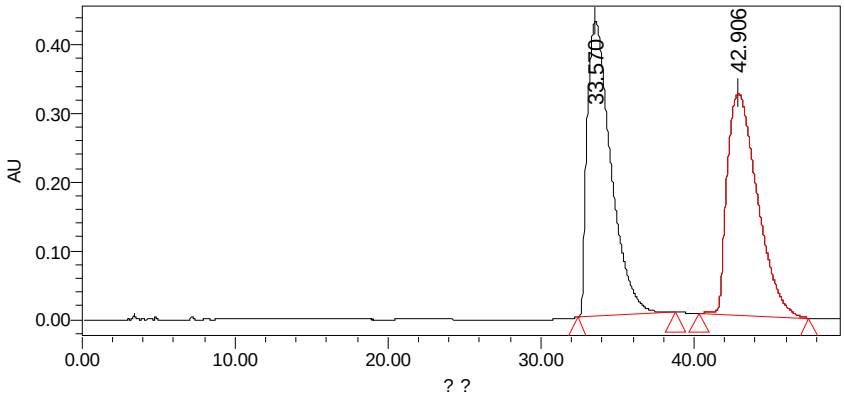


	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		13.003	669445	1.34	31585	bb			Unknown	
2		20.580	49364489	98.66	1216835	bb			Unknown	

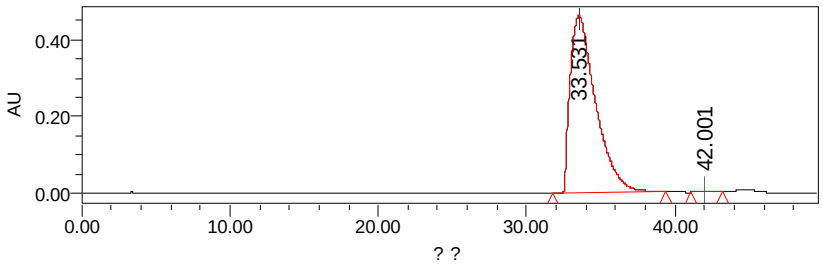
(1S,5S,6S,7S)-6-(furan-2-yl)-1-hydroxy-7-nitrobicyclo[3.2.1]octan-8-one (4i)

Chiralpak OJ-H column, *n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min.





	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		33.570	46663523	51.33	430411	Bb			Unknown	
2		42.906	44242430	48.67	322470	bB			Unknown	

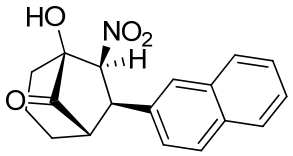


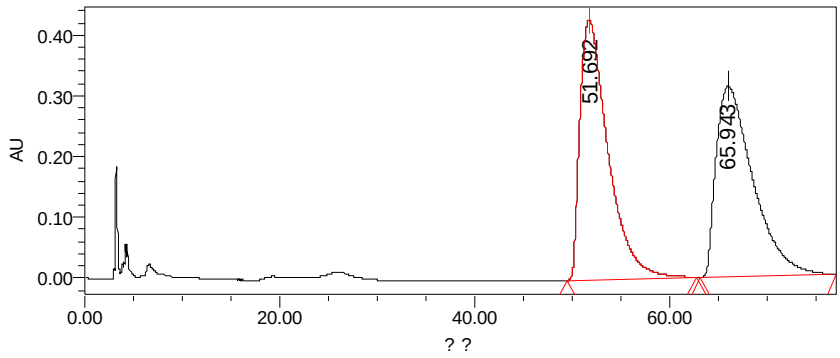
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes

1		33.531	55305683	99.62	462162	Bb			Unknown	
2		42.001	209364	0.38	2994	Bb			Unknown	

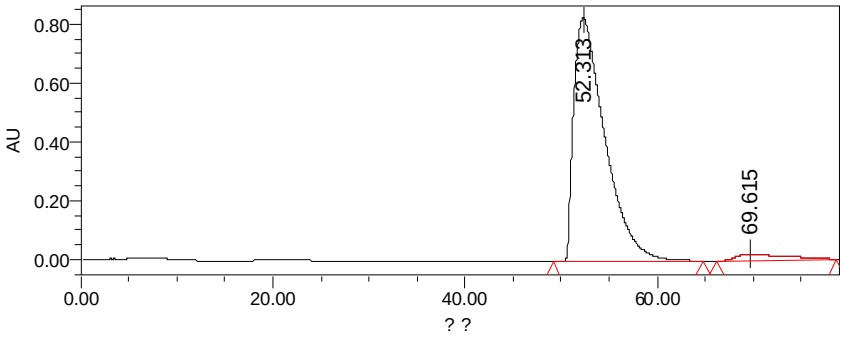
(R)-dimethyl 2-(1-(2-chlorophenyl)-3-oxo-3-phenylpropyl)malonate (3ag)

Chiralpak OJ-H column, *n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min.





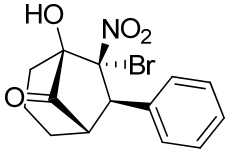
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		51.692	85845008	50.92	427632	Bb			Unknown	
2		65.943	82756537	49.08	314022	Bb			Unknown	

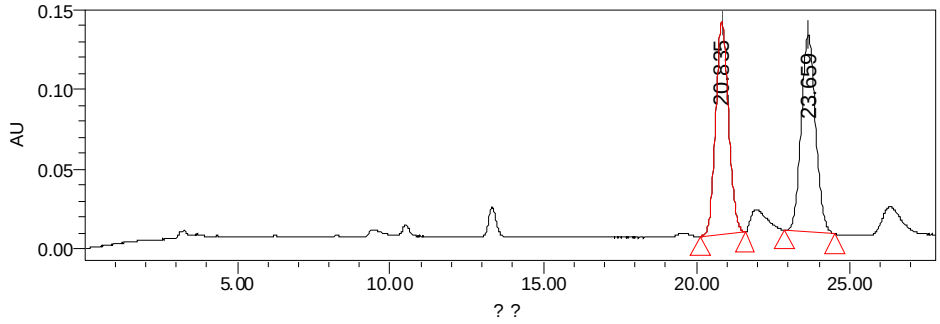


	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		52.313	188034638	96.12	829338	Bb			Unknown	
2		69.615	7596363	3.88	21269	Bb			Unknown	

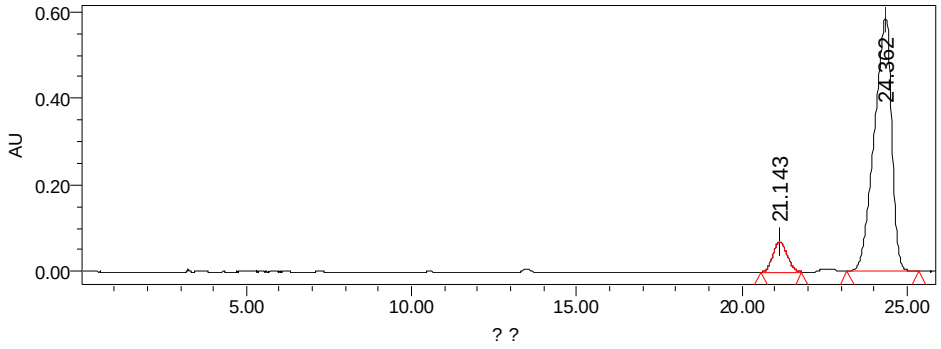
(1R,5S,6R,7R)-7-bromo-1-hydroxy-7-nitro-6-phenylbicyclo[3.2.1]octan-8-one (4k)

Chiralpak AD-H column, *n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min.





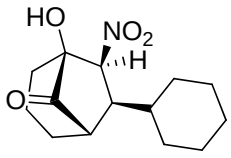
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		20.835	3904741	49.10	133867	Bb			Unknown	
2		23.659	4048402	50.90	124192	Bb			Unknown	

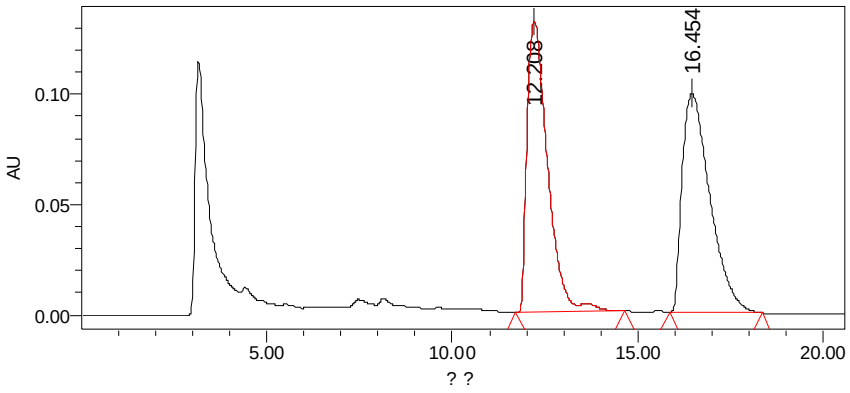


	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		21.143	2104251	8.87	70847	Bb			Unknown	
2		24.362	21605709	91.13	586066	Bb			Unknown	

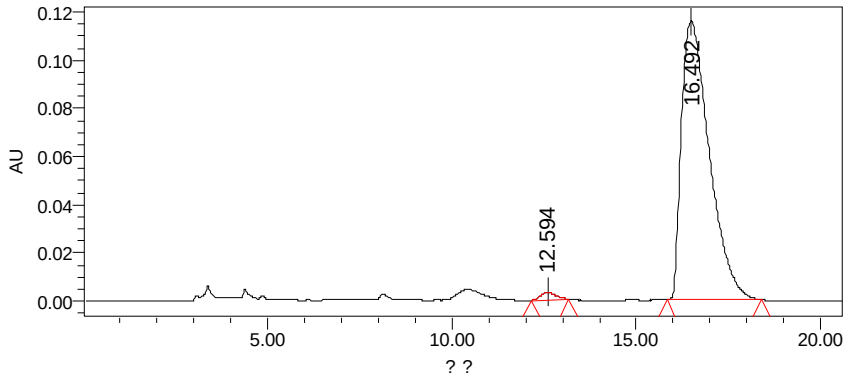
(1S,5S,6S,7S)-6-cyclohexyl-1-hydroxy-7-nitrobicyclo[3.2.1]octan-8-one (4l)

Chiralpak OJ-H column, *n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min.





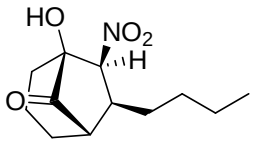
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		12.208	6400729	49.26	165546	Bb			Unknown	
2		16.455	6592990	50.74	124812	Bb			Unknown	

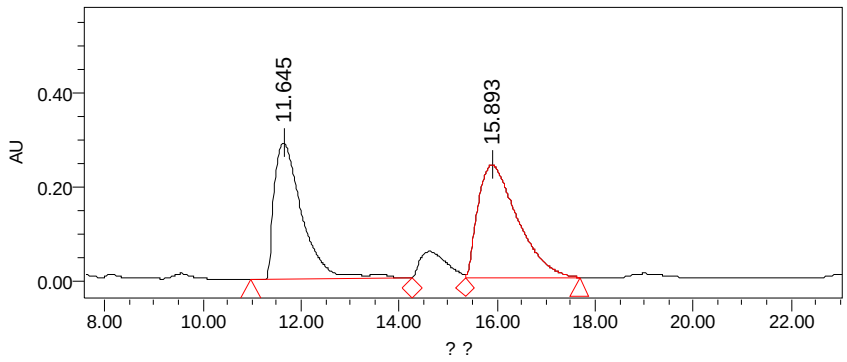


	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		12.594	88778	1.44	3081	BB			Unknown	
2		16.492	6078857	98.56	115844	BB			Unknown	

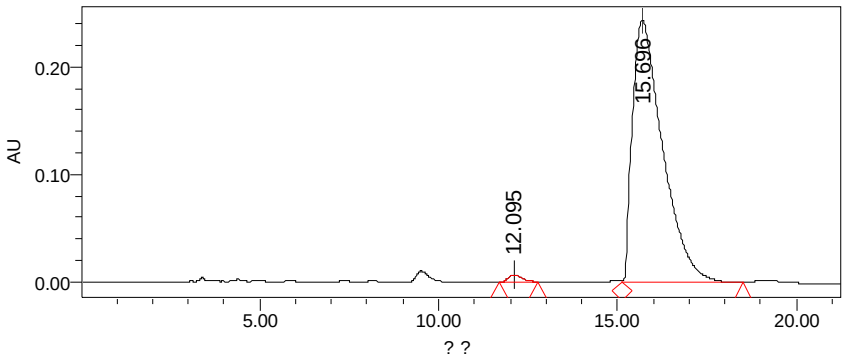
(1S,5S,6S,7S)-6-butyl-1-hydroxy-7-nitrobicyclo[3.2.1]octan-8-one (4m)

Chiralpak OJ-H column, *n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min.





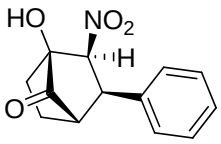
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		11.645	11070118	49.39	288643	Bv			Unknown	
2		15.893	11343944	50.61	229487	Vb			Unknown	

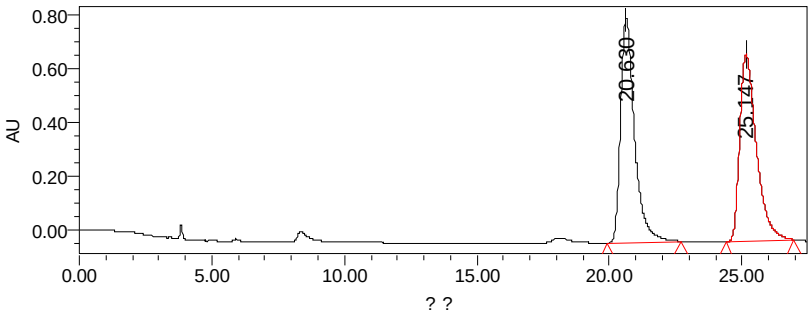


	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		12.095	178354	1.23	6805	BB			Unknown	
2		15.696	14360632	98.77	243807	Bb			Unknown	

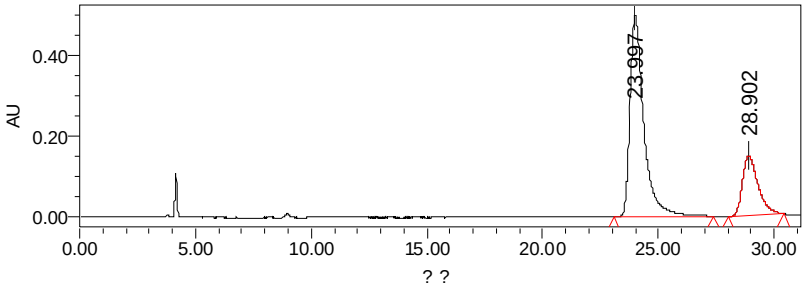
(1S,2S,3R,4S)-1-hydroxy-2-nitro-3-phenylbicyclo[2.2.1]heptan-7-one (4n)

Chiralpak IA column, *n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min.





	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		20.630	30380714	50.06	830435	bb			Unknown	
2		25.147	30312884	49.94	692230	bb			Unknown	

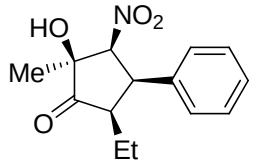


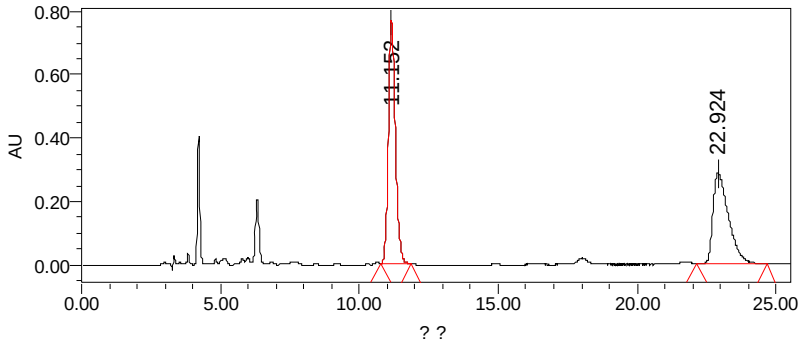
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		23.997	20895370	75.15	499893	bb			Unknown	

2		28.902	6909843	24.85	147620	bb			Unknown	

(2S,3S,4R,5R)-5-ethyl-2-hydroxy-2-methyl-3-nitro-4-phenylcyclopentanone (4o)

Chiralpak IA column, *n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min.





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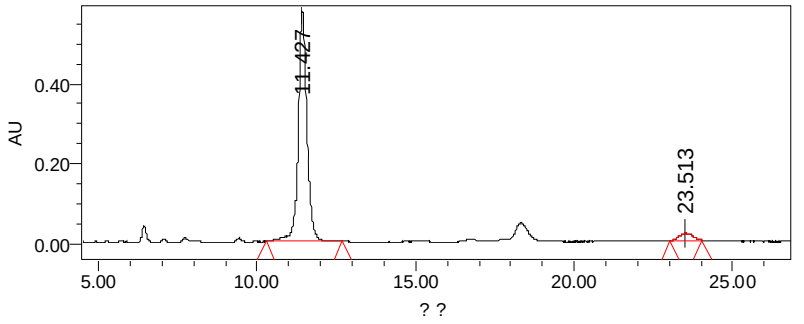
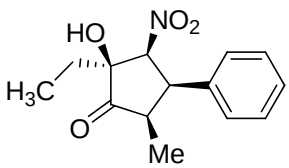
1		11.152	12749739	53.37	752266	bb			Unknown	
2		22.924	11141461	46.63	285381	bb			Unknown	

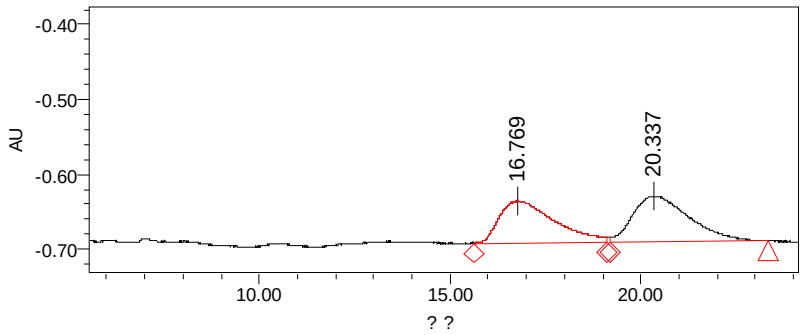


	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		11.427	10970356	95.12	577208	bb			Unknown	
2		23.513	562397	4.88	18756	bb			Unknown	

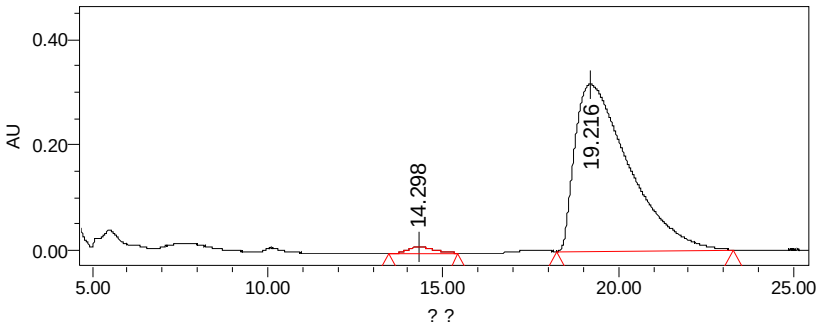
(2S,3S,4R,5R)-2-ethyl-2-hydroxy-5-methyl-3-nitro-4-phenylcyclopentanone (4p)

Chiralpak AS column, *n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min.



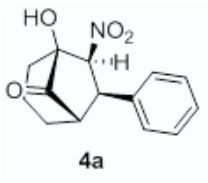


	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		16.769	5696183	47.06	56451	VV			Unknown	
2		20.337	6407758	52.94	61414	VB			Unknown	

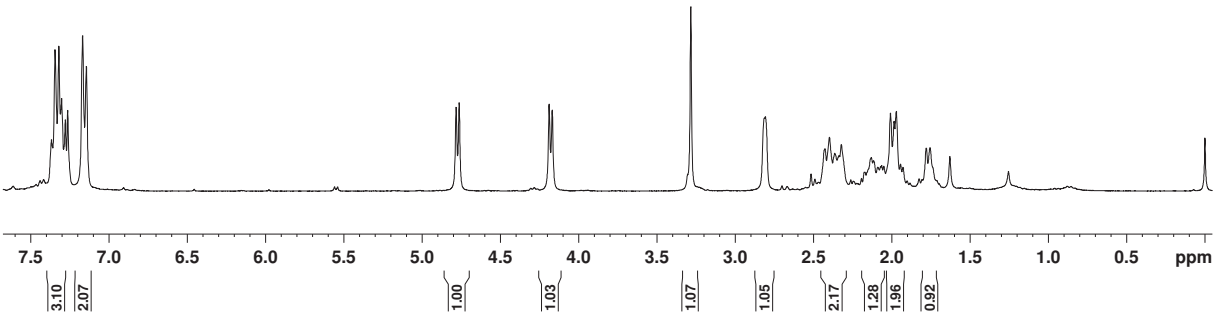


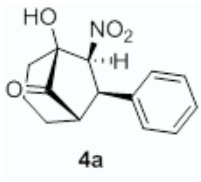
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		14.298	593016	1.72	11966	bb			Unknown	
2		19.216	33891103	98.28	315934	bb			Unknown	

6. Copies of ^{1}H NMR and ^{13}C NMR Spectra



4a





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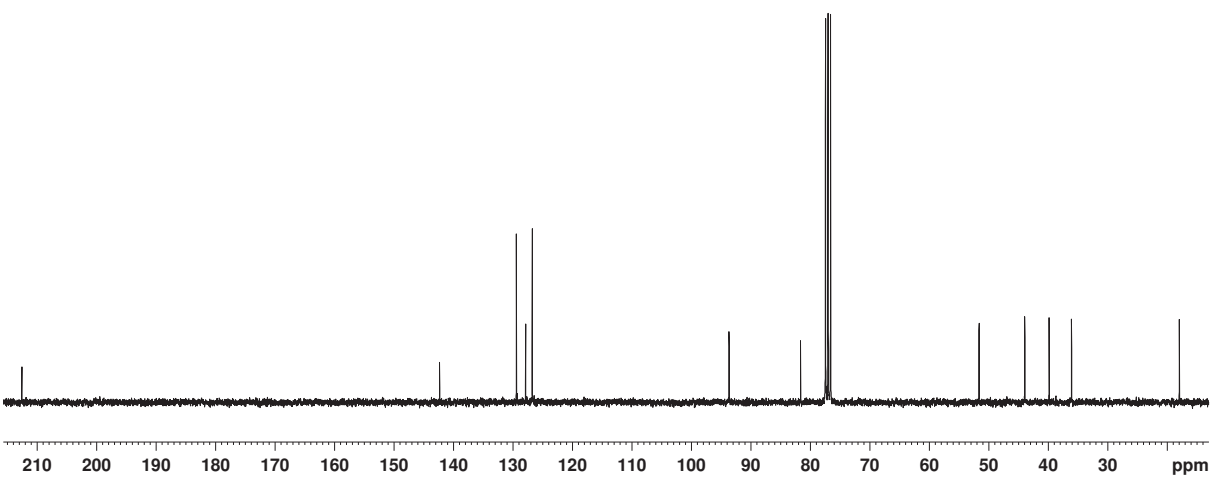


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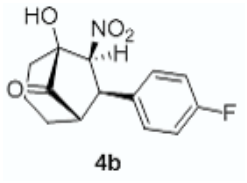
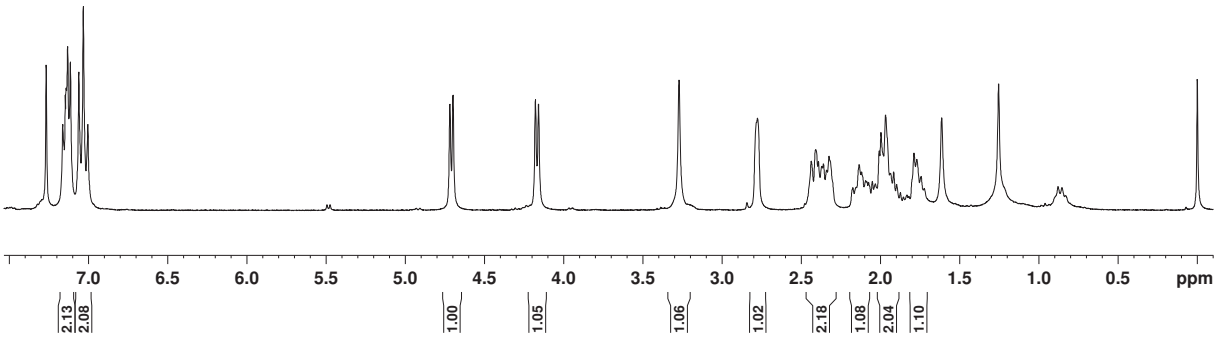

HO
NO2
H
O
F

4b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1.10


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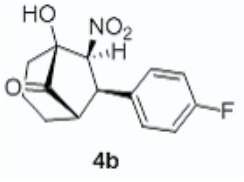
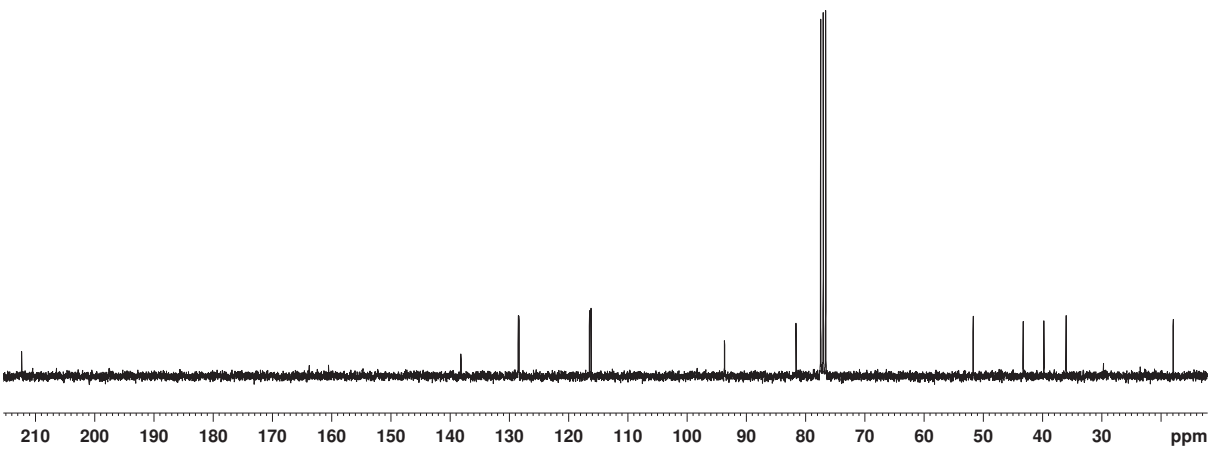

HO
NO2
H
O
F

4b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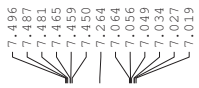

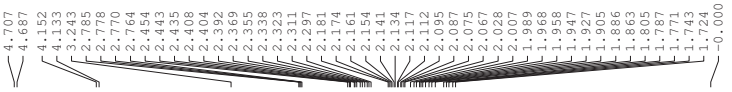

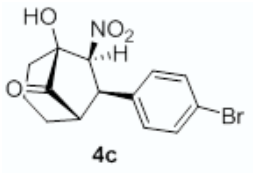

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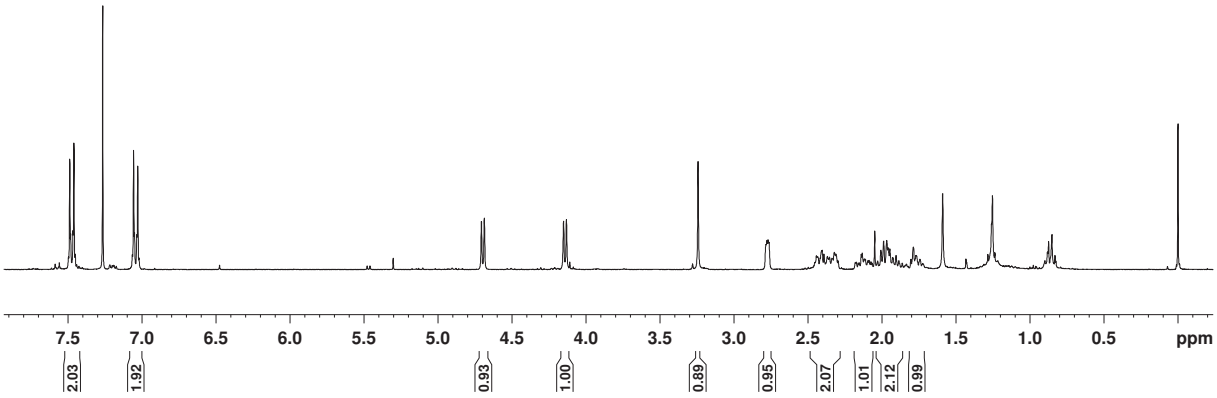

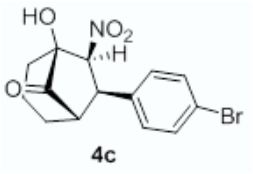

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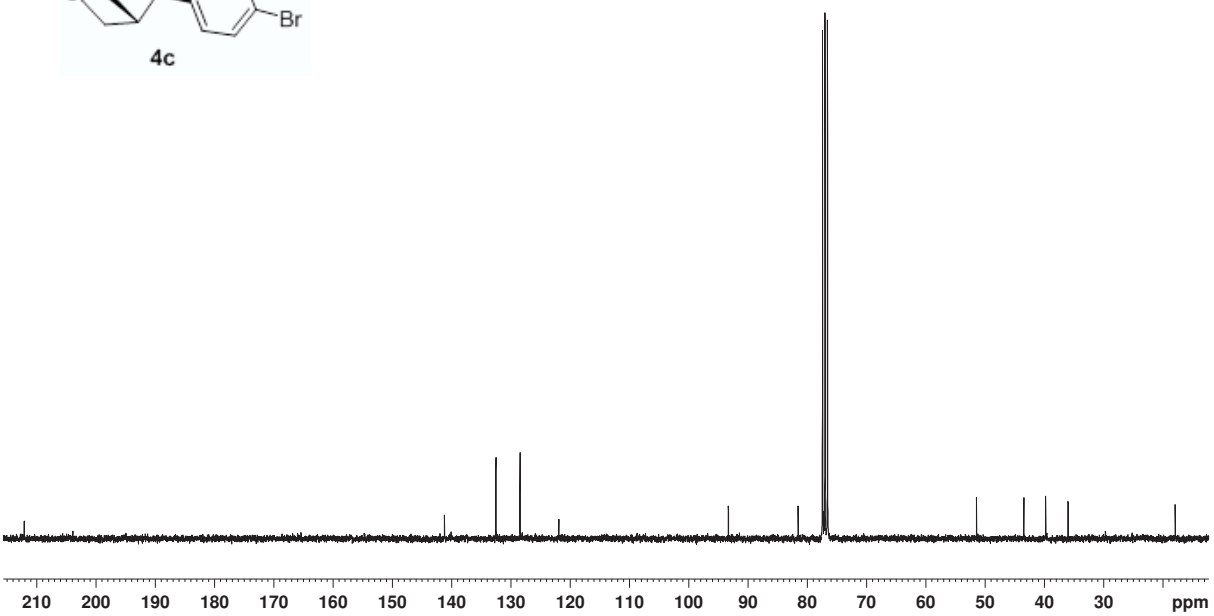

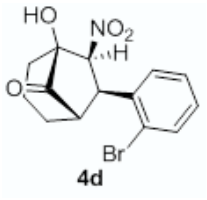

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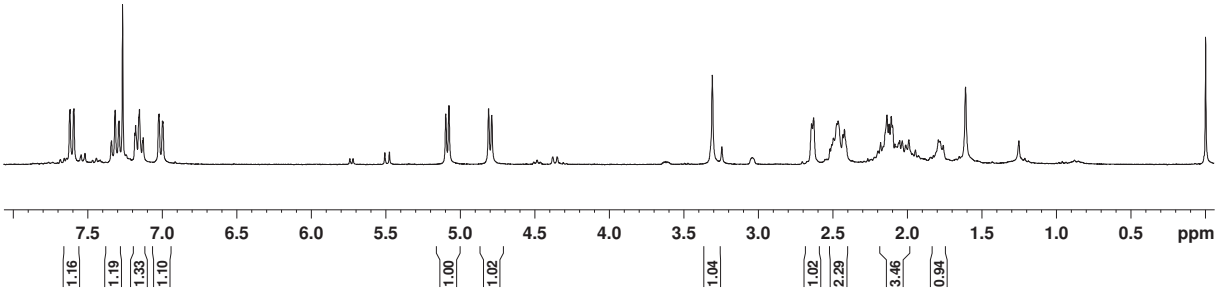

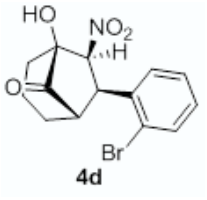

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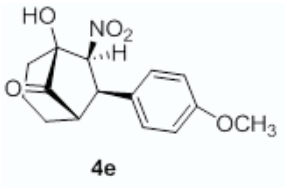

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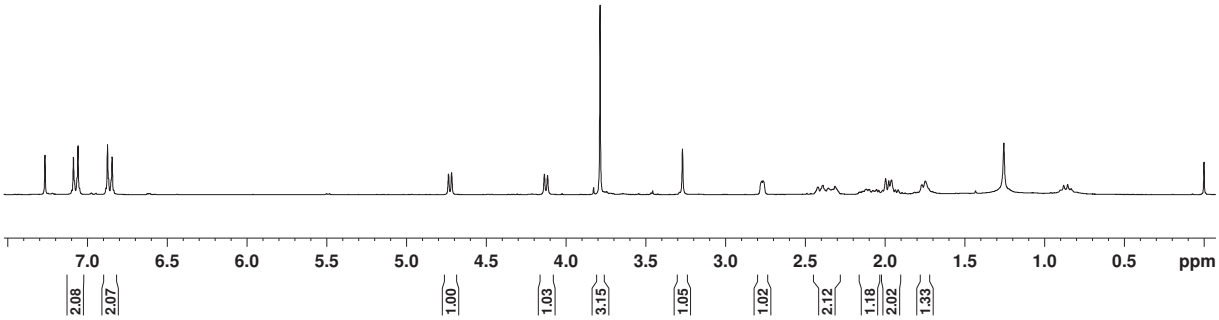

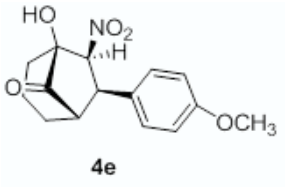

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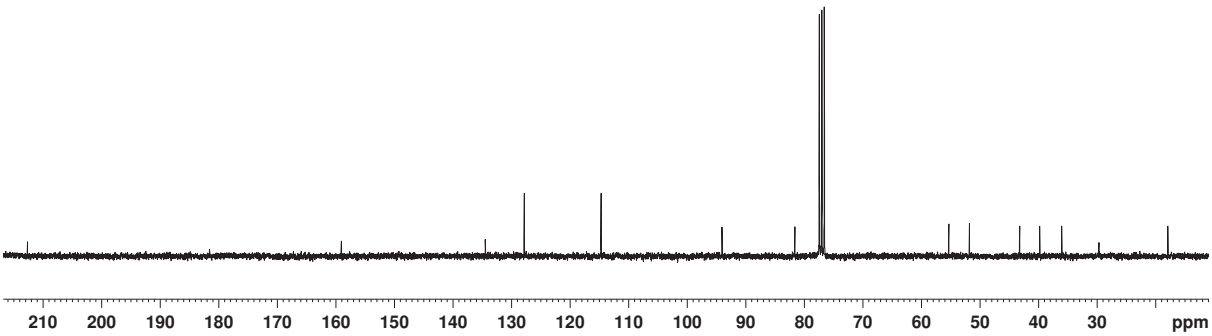

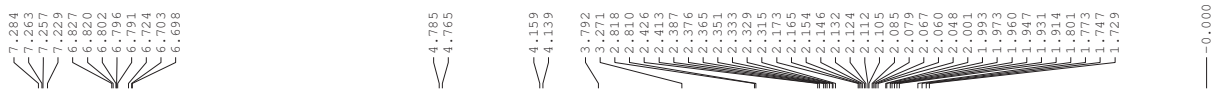

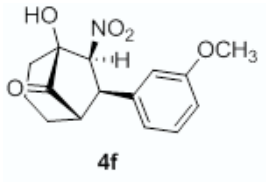

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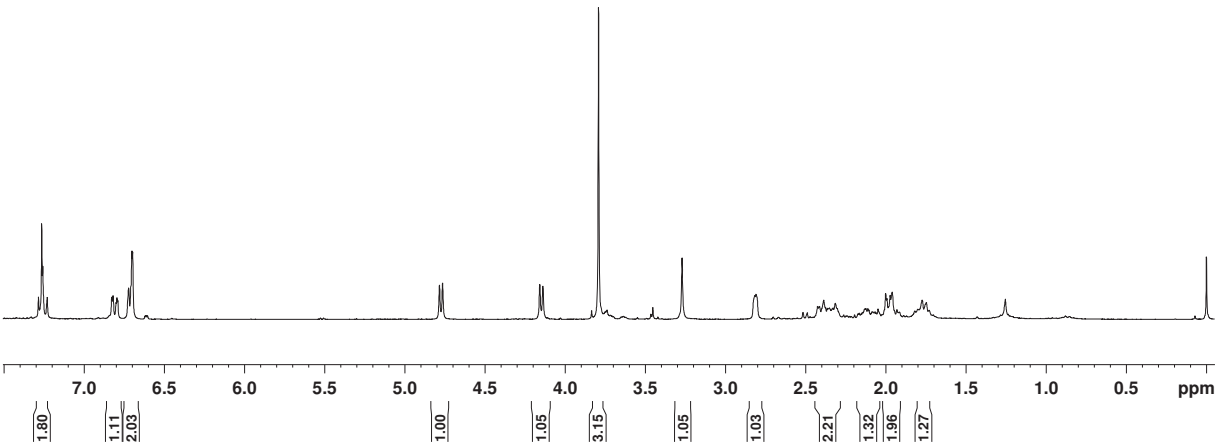

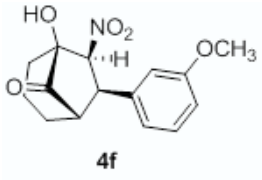

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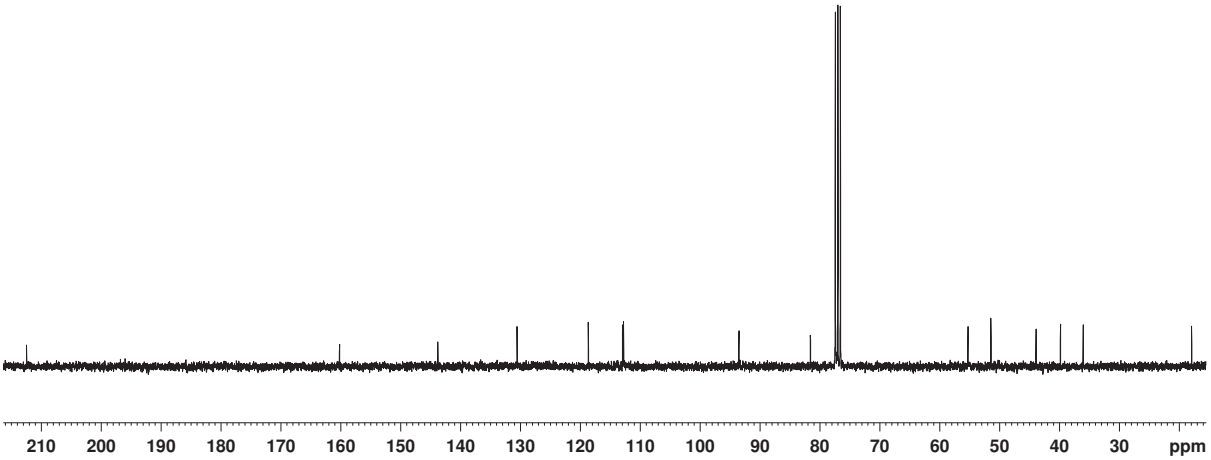

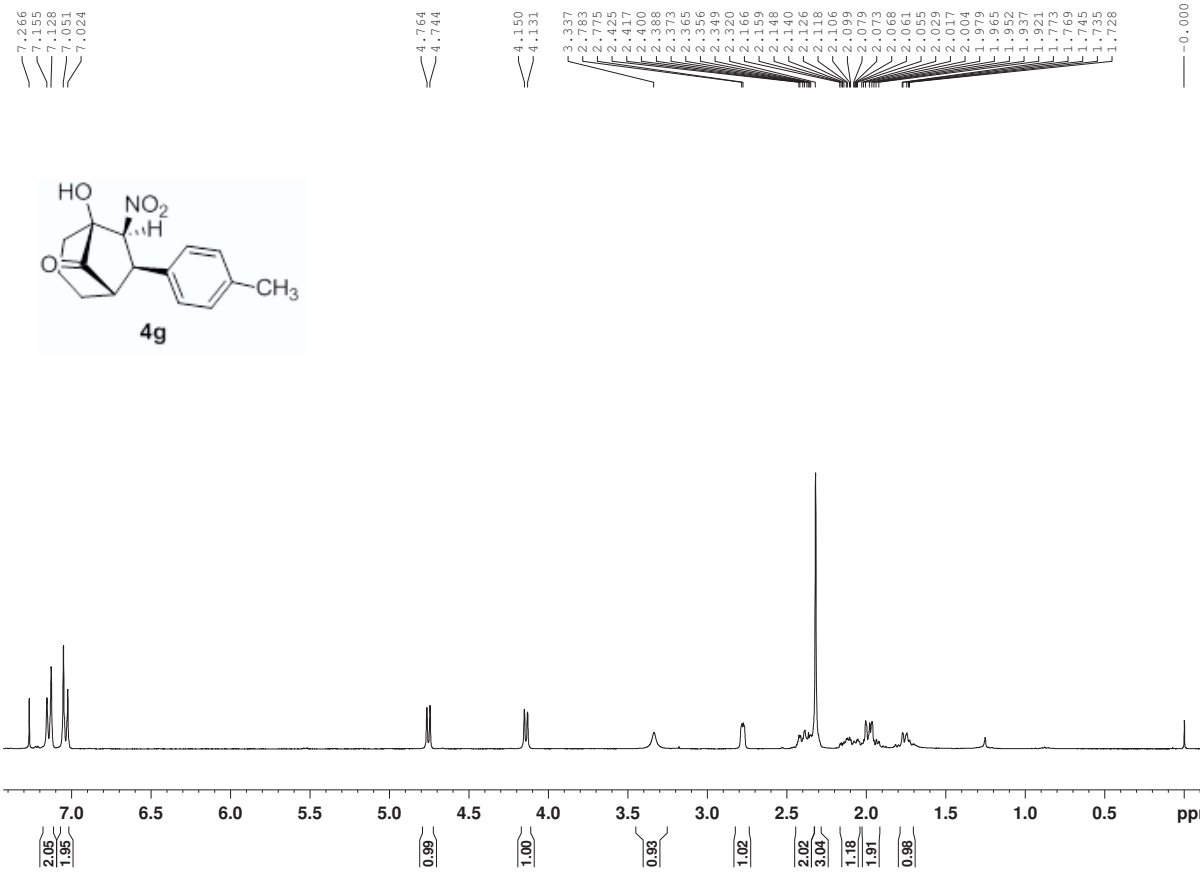

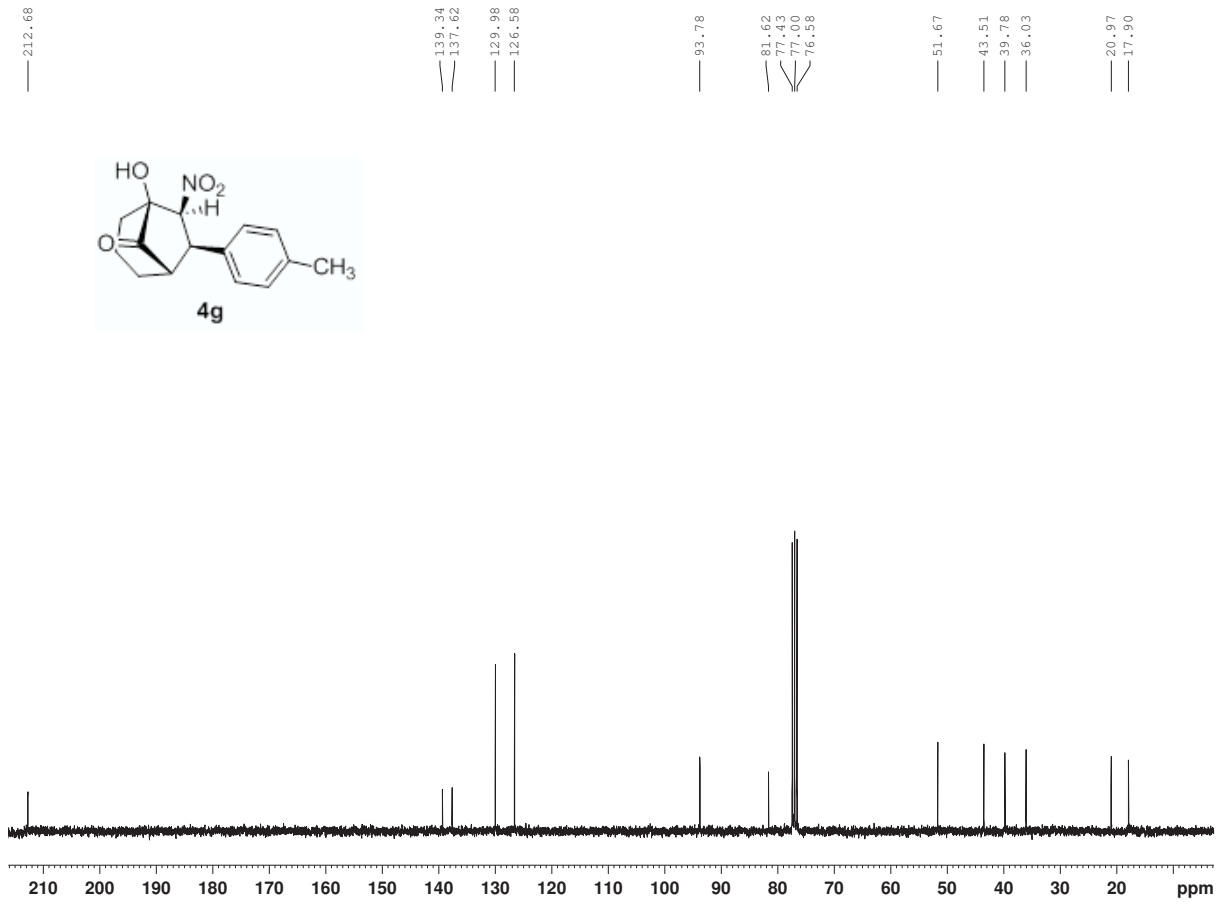

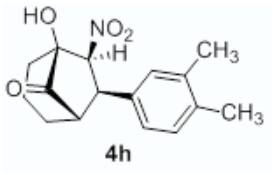

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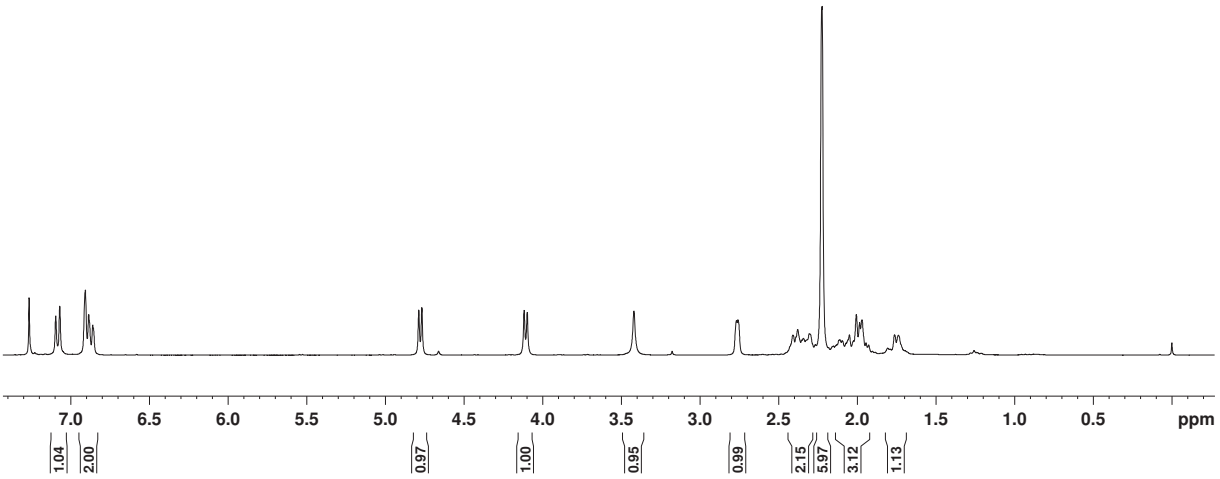

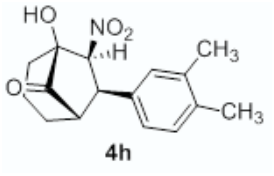

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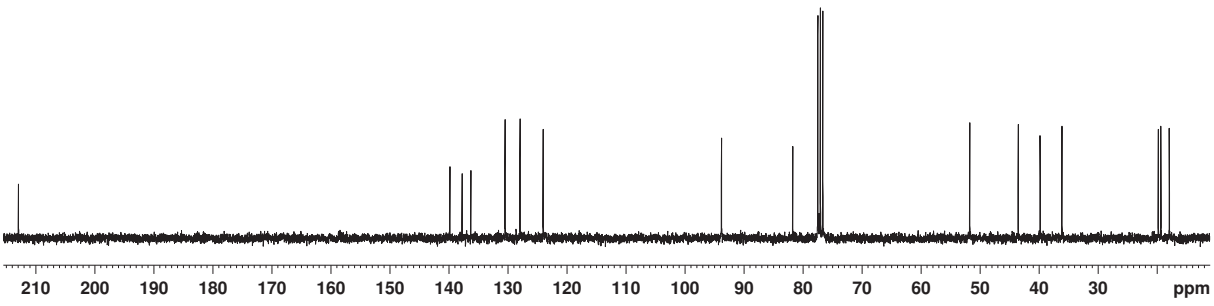

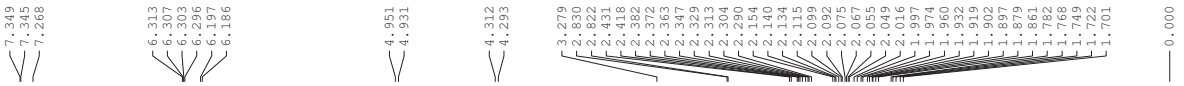
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4.293
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2.830
2.822
2.431
2.418
2.382
2.372
2.363
2.347
2.329
2.313
2.304
2.290
2.154
2.140
2.134
2.115
2.099
2.092
2.075
2.067
2.055
2.049
2.016
1.997
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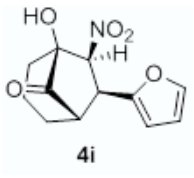
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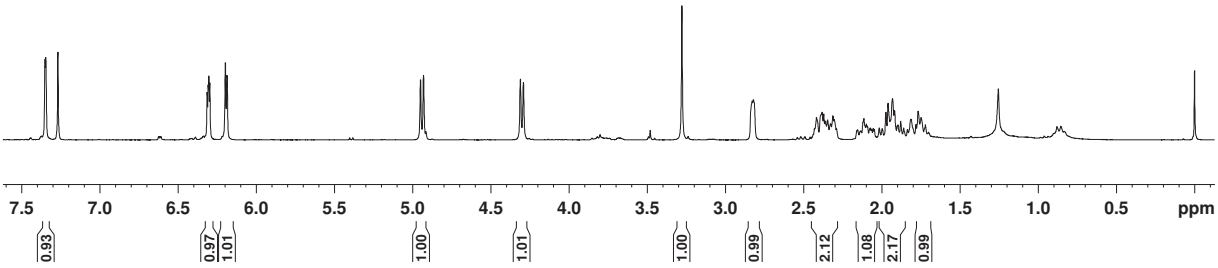
H
O
O

4i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0.5
ppm
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0.97
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1.00
1.01
1.00
0.99
2.12
1.08
2.17
0.99


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143.07
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49.48
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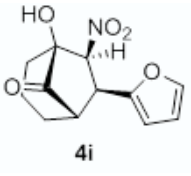
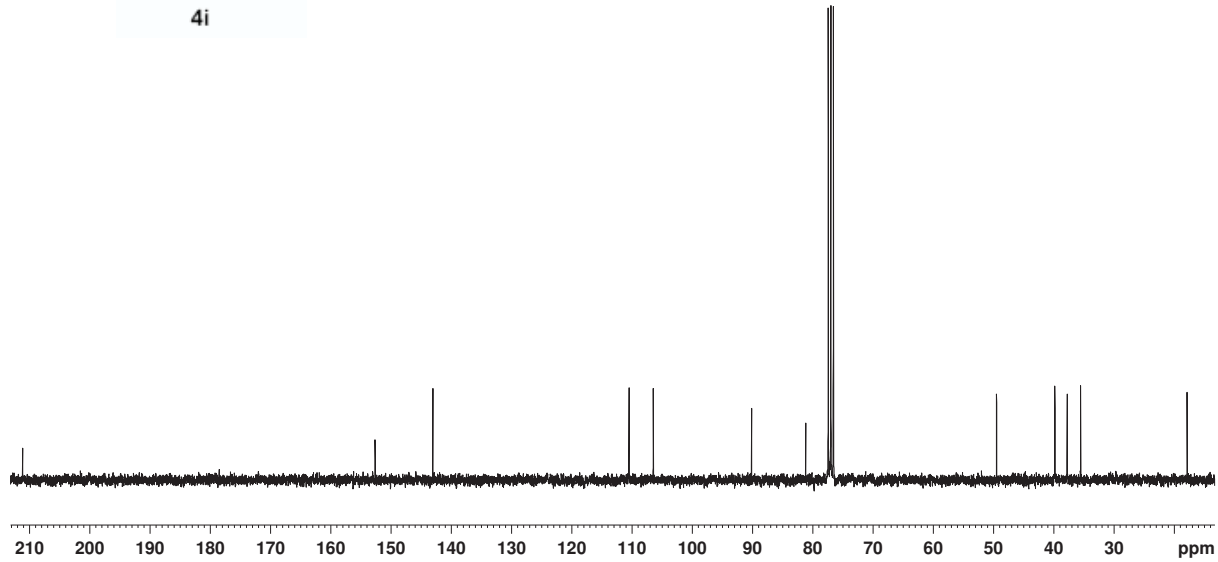
37.76
35.54
17.86


HO
NO2
H
O
O

4i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30
ppm


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7.811
7.803
7.798
7.786
7.648
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7.516
7.510
7.498
7.485
7.479
7.463
7.261
7.229
7.223
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7.195
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4.859
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4.349
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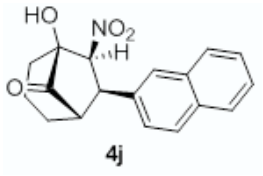
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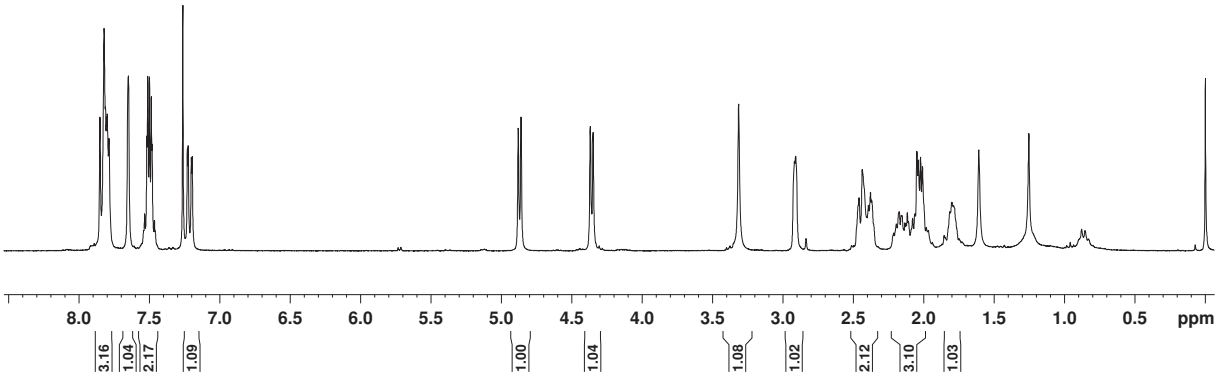
NO2
H
O

4j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1.0
0.5
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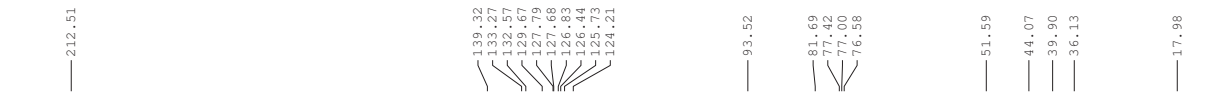
1.04
1.08
1.02
2.12
3.10
1.03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51.59
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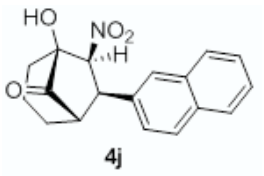
36.13
17.98


HO
NO2
H
O

4j

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50
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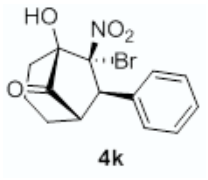
ppm



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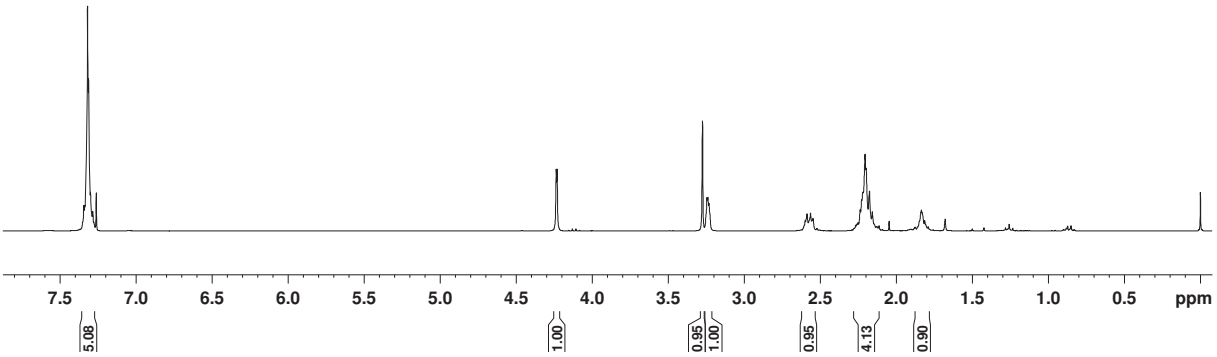

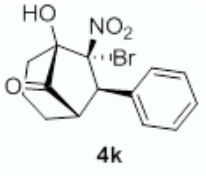

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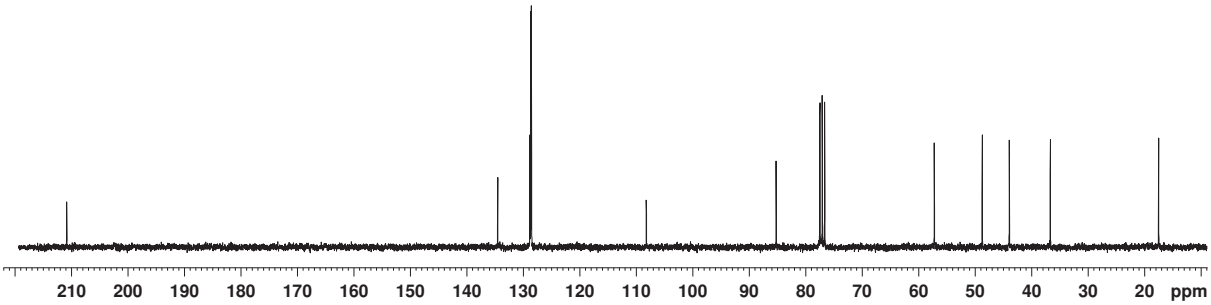

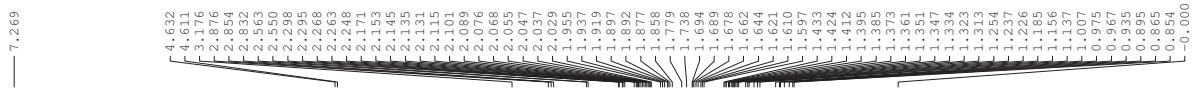

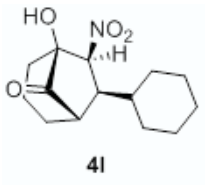

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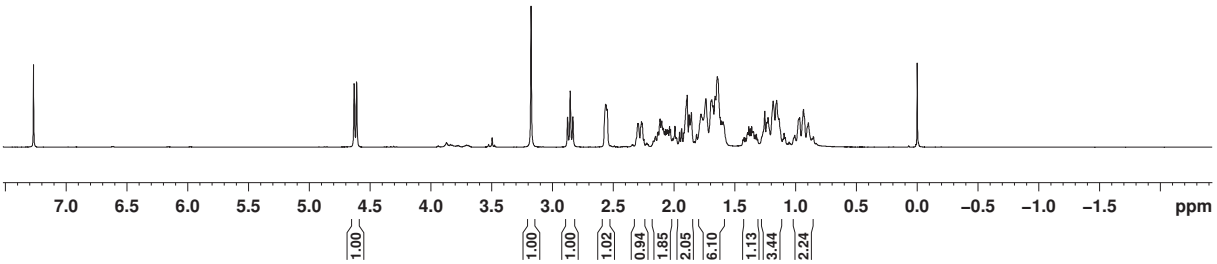

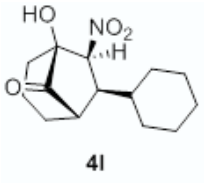

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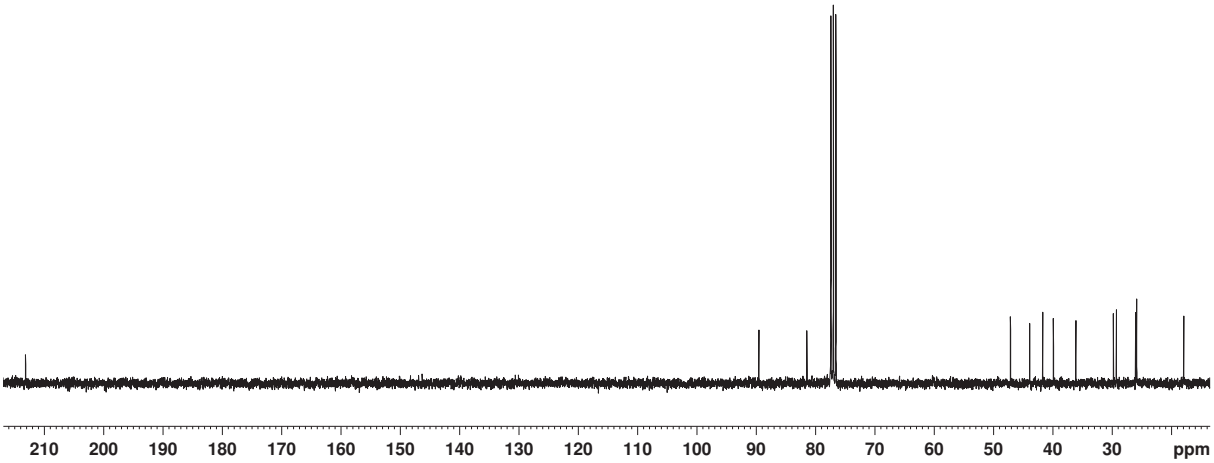

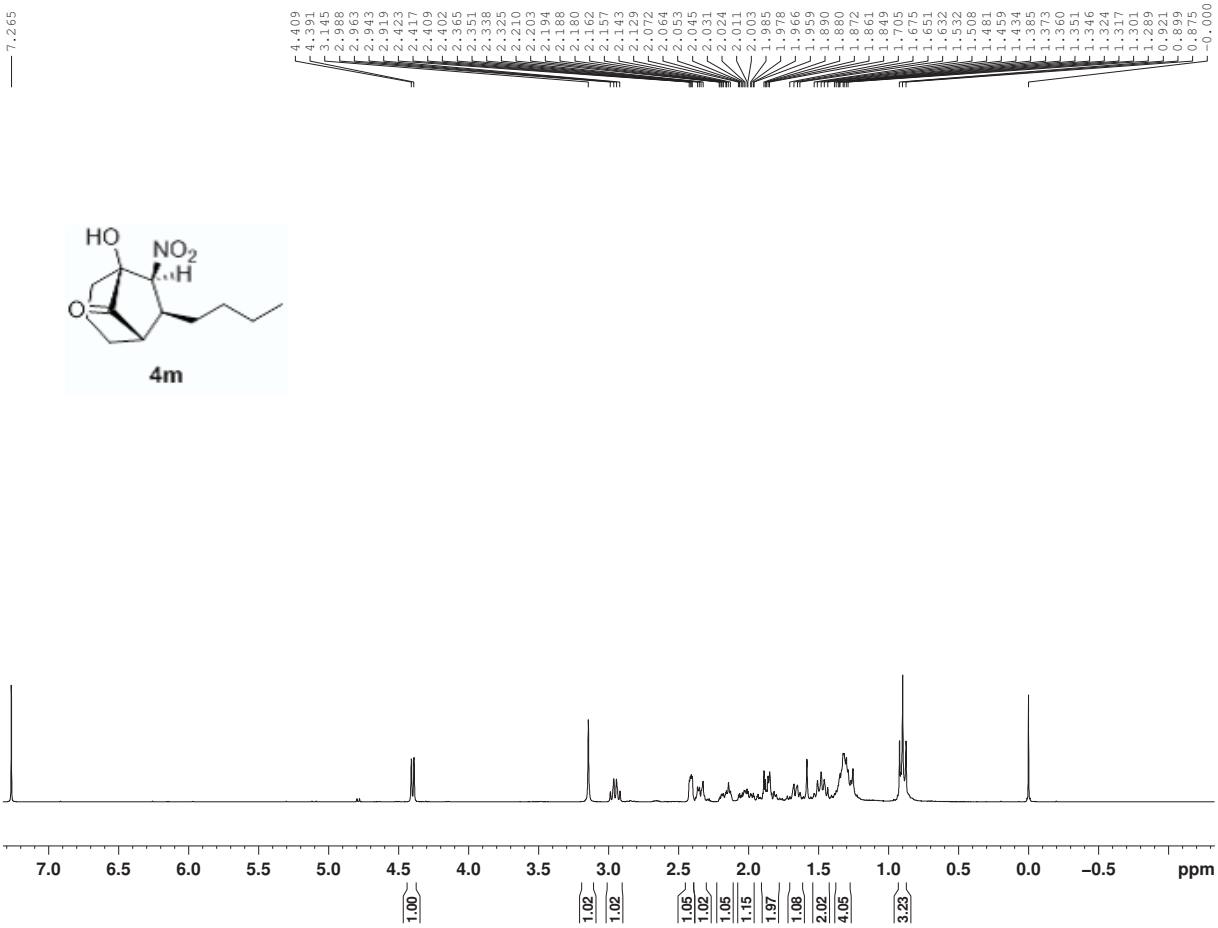
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2.129
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2.045
2.031
2.024
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1.459
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1.385
1.373
1.360
1.351
1.346
1.324
1.317
1.301
1.289
0.921
0.899
0.875
-0.000
HO
NO2
H
O
4m
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6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
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1.0
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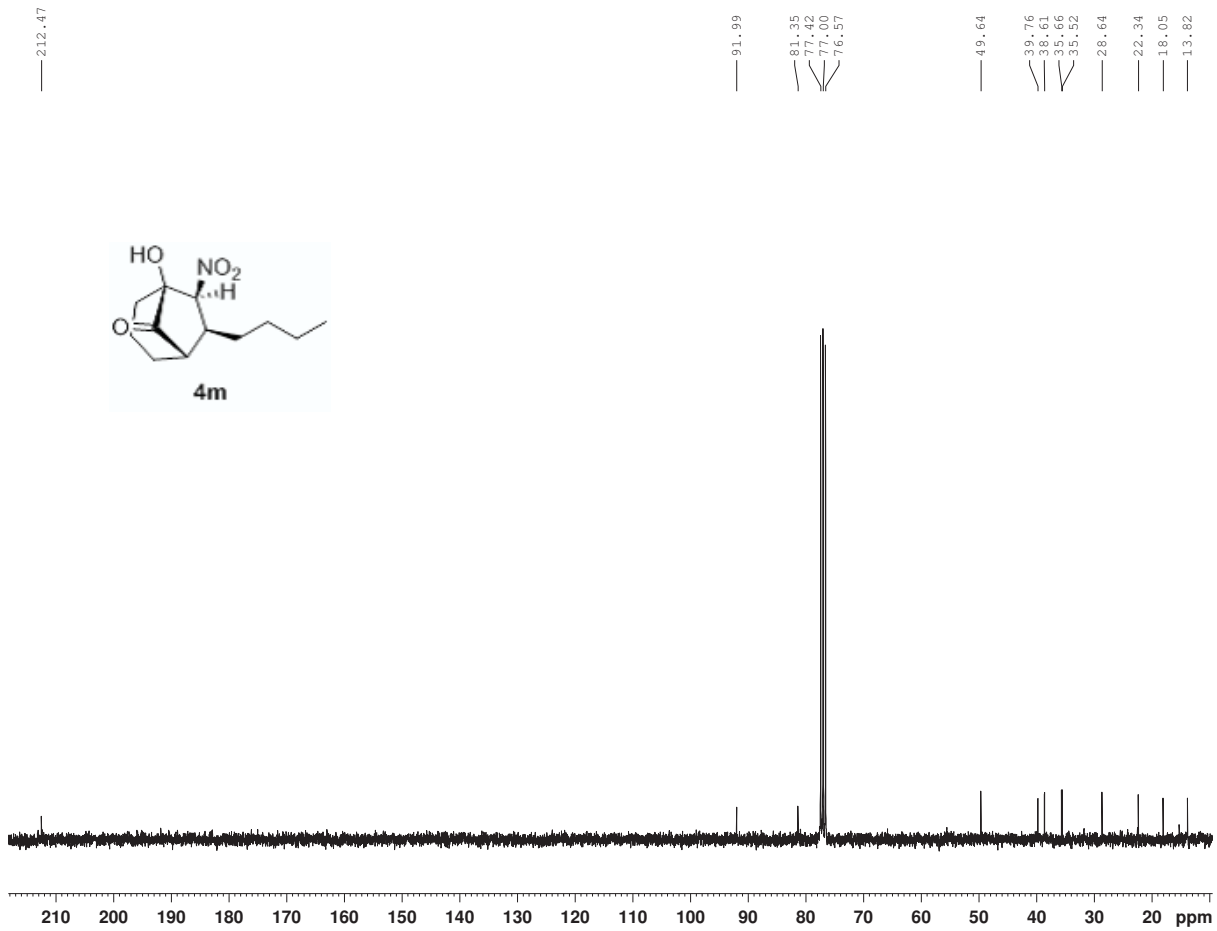
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35.66
35.52
28.64
22.34
18.05
13.82
HO
NO2
H
O
4m
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40
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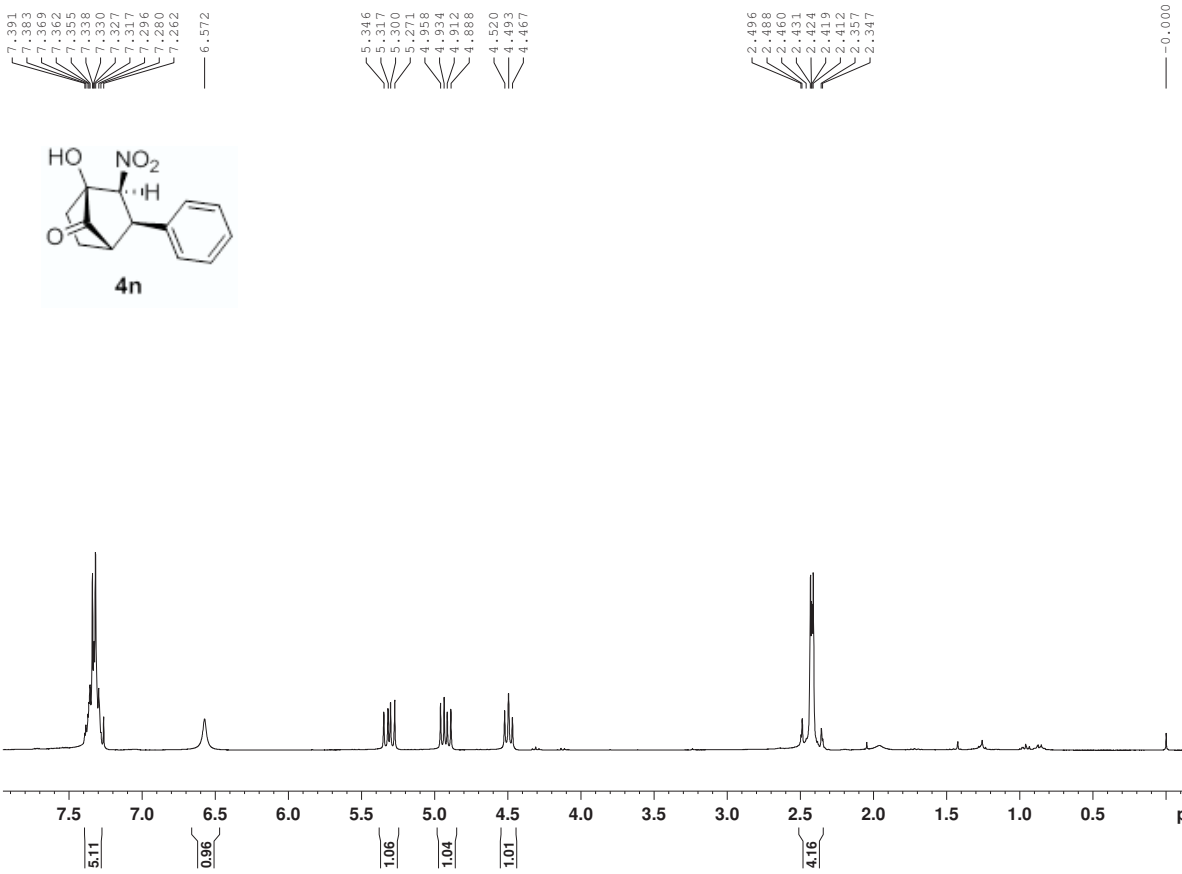
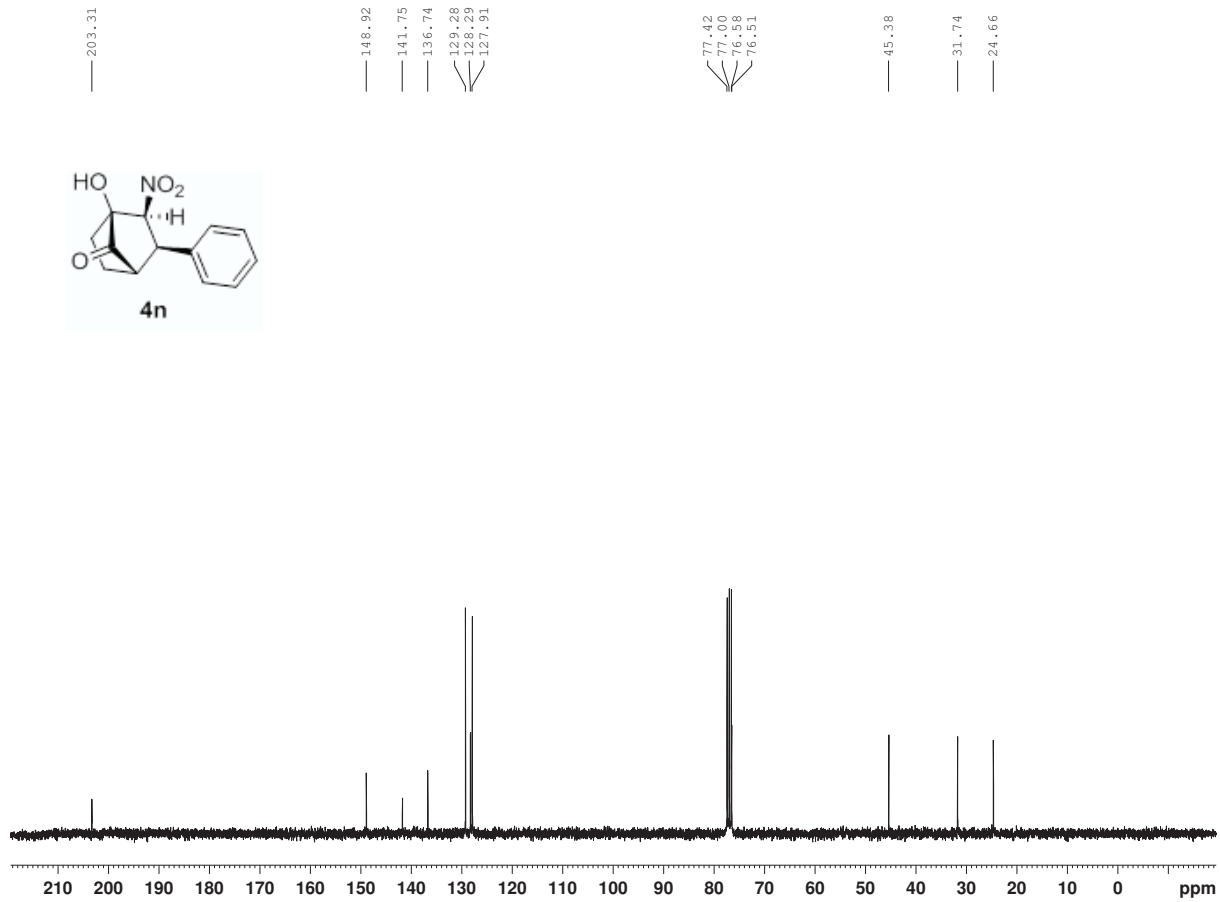
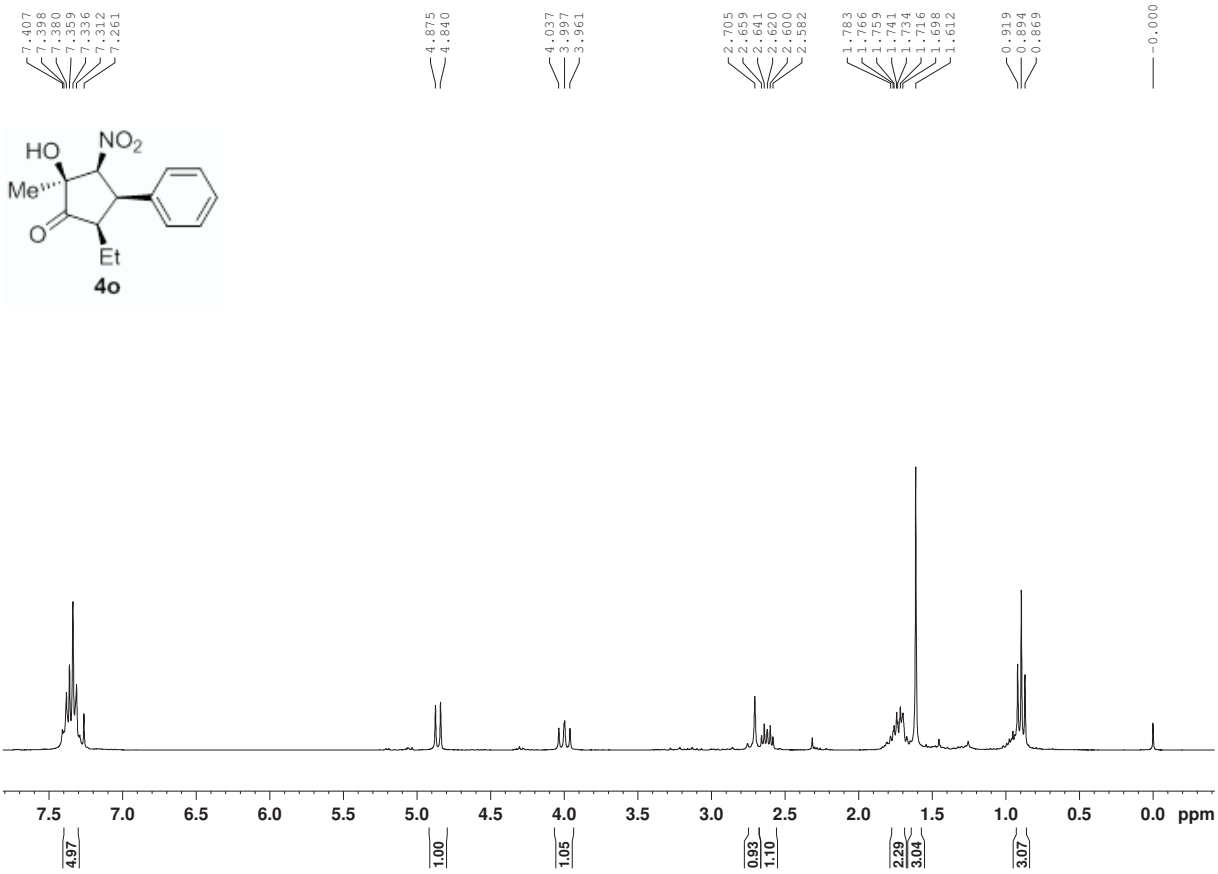
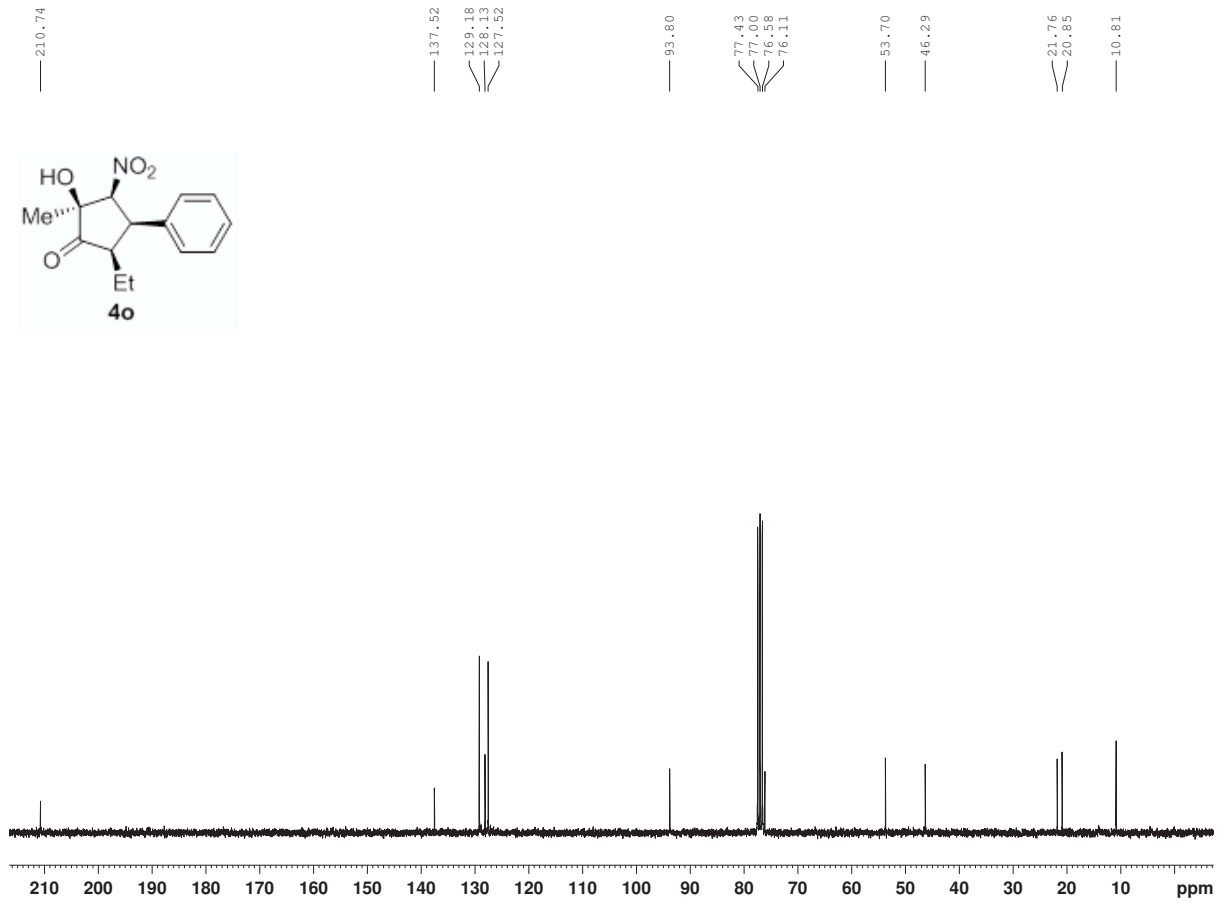
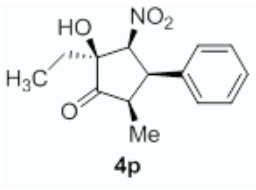
20
ppm











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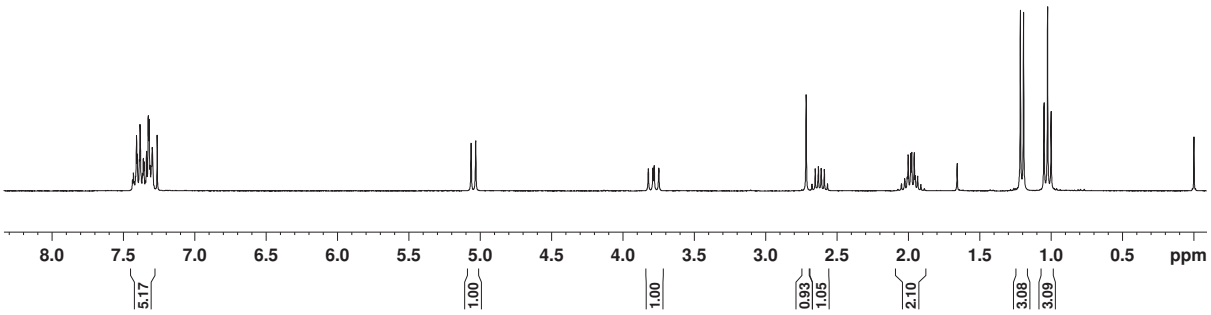

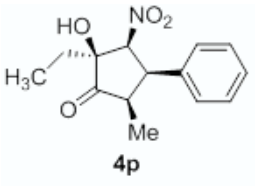

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