Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Stereoselective Synthesis of Chromane Derivatives via a Domino Reaction Catalyzed by Modularly Designed Organocatalysts

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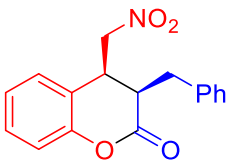
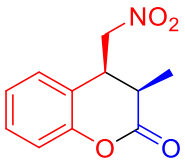
(3*R*,4*S*)-3-Benzyl-4-(nitromethyl)chroman-2-one (4a)[11a,12]



4a

Colorless oil, 28.0 mg, 94% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 4H), 7.29-7.27 (m, 2H), 7.14 – 7.08 (m, 3H), 4.76 (dd, *J* = 12.4, 4.3 Hz, 1H), 4.39 (dd, *J* = 12.5, 10.5 Hz, 1H), 3.69 (dt, *J* = 10.2, 4.9 Hz, 1H), 3.56 (dd, *J* = 14.8, 5.7 Hz, 1H), 3.32 – 3.28 (m, 1H), 2.80 (dd, *J* = 14.8, 9.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 150.9, 136.9, 130.2, 129.2, 128.6, 128.3, 127.3, 125.0, 122.6, 117.4, 75.3, 43.6, 36.6, 32.5. Enantiomeric excess of **4a** was determined by chiral stationary phase HPLC analysis using a ChiralPak AD-H column (95:5 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), minor enantiomer: t_R = 20.2 min, major enantiomer: t_R = 27.5 min.

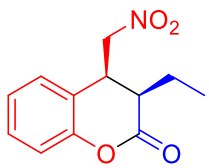
(3*R*,4*S*)-3-Methyl-4-(nitromethyl)chroman-2-one (4b)[12]



4b

Colorless oil, 19.1 mg, 86% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (ddd, *J* = 8.0, 7.0, 2.2 Hz, 1H), 7.21 – 7.12 (m, 3H), 4.68 (dd, *J* = 12.6, 5.2 Hz, 1H), 4.36 (dd, *J* = 12.6, 9.8 Hz, 1H), 3.86 (dt, *J* = 10.2, 5.4 Hz, 1H), 3.16 (dd, *J* = 7.1, 5.6 Hz, 1H), 1.44 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 151.0, 130.2, 128.0, 125.0, 122.5, 117.5, 75.5, 39.4, 36.8, 12.2. Enantiomeric excess of **4b** was determined by chiral stationary phase HPLC analysis using a ChiralPak OD-H column (90:10 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), major enantiomer: t_R = 27.0 min, minor enantiomer: t_R = 30.7 min.

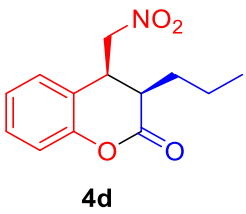
(3*R*,4*S*)-3-Ethyl-4-(nitromethyl)chroman-2-one (4c)[11a,12]



4c

Colorless oil, 22.8 mg, 97% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 1H), 7.20 – 7.11 (m, 3H), 4.62 (dd, *J* = 12.5, 4.8 Hz, 1H), 4.32 (dd, *J* = 12.5, 10.4 Hz, 1H), 3.92 (dt, *J* = 10.3, 5.1 Hz, 1H), 2.86 (td, *J* = 7.3, 5.4 Hz, 1H), 2.13 (dt, *J* = 14.6, 7.3 Hz, 1H), 1.59 (dt, *J* = 14.5, 7.3 Hz, 1H), 1.17 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 150.9, 130.2, 128.1, 124.9, 122.7, 117.4, 75.4, 43.3, 37.4, 20.0, 11.9. Enantiomeric excess of **4c** was determined by chiral stationary phase HPLC analysis using a ChiralPak OD-H column (90:10 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), major enantiomer: t_R = 19.9 min, minor enantiomer: t_R = 22.5 min.

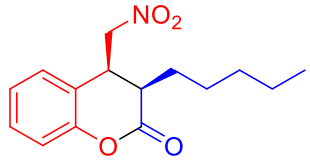
(3*R*,4*S*)-4-(Nitromethyl)-3-propylchroman-2-one (4d)[12]



4d

Colorless oil, 20.8. mg, 83% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (td, *J* = 7.8, 1.8 Hz, 1H), 7.20 – 7.12 (m, 3H), 4.63 (dd, *J* = 12.5, 4.7 Hz, 1H), 4.33 (dd, *J* = 12.5, 10.5 Hz, 1H), 3.89 (dt, *J* = 10.4, 5.1 Hz, 1H), 2.95 (q, *J* = 6.7 Hz, 1H), 2.05 (tdd, *J* = 11.5, 9.6, 5.6 Hz, 1H), 1.61 – 1.51 (m, 3H), 1.03 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 150.9, 130.2, 128.1, 125.0, 122.7, 117.4, 75.5, 41.4, 37.7, 28.7, 20.5, 13.8. Enantiomeric excess of **4d** was determined by chiral stationary phase HPLC analysis using a ChiralPak AD-H column (95:5 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), minor enantiomer: t_R = 10.5 min, major enantiomer: t_R = 13.4 min.

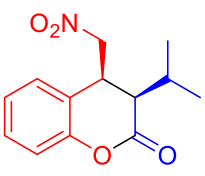
(3*R*,4*S*)-4-(Nitromethyl)-3-pentylchroman-2-one (4e)[11a]



4e

Colorless oil, 25.0 mg, 90% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (td, *J* = 7.8, 1.8 Hz, 1H), 7.20 – 7.12 (m, 3H), 4.62 (dd, *J* = 12.5, 4.7 Hz, 1H), 4.33 (dd, *J* = 12.5, 10.5 Hz, 1H), 3.89 (dt, *J* = 10.4, 5.0 Hz, 1H), 2.93 (td, *J* = 6.8, 5.3 Hz, 1H), 2.10 – 2.05 (m, 1H), 1.53 (dtd, *J* = 14.1, 7.2, 4.4 Hz, 3H), 1.39 – 1.36 (m, 4H), 0.95 – 0.92 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 150.9, 130.2, 128.1, 124.9, 122.7, 117.4, 75.5, 41.7, 37.7, 31.5, 27.0, 26.6, 22.4, 14.0. Enantiomeric excess of **4e** was determined by chiral stationary phase HPLC analysis using a ChiralPak IC column (90:10 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), minor enantiomer: t_R = 22.2 min, major enantiomer: t_R = 49.5 min.

(3*R*,4S)-3-Isopropyl-4-(nitromethyl)chroman-2-one (4f)[12]

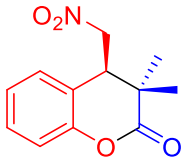


4f

Colorless oil, 22.8. mg, 91% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (td, *J* = 7.8, 1.7 Hz, 1H), 7.19 – 7.11 (m, 3H), 4.60 (dd, *J* = 12.5, 3.8 Hz, 1H), 4.29 (t, *J* = 12.0 Hz, 1H), 3.97 (dt, *J* = 11.5, 4.4 Hz, 1H), 2.58 (dd, *J* = 10.2, 5.0 Hz, 1H), 2.19-2.12 (m, 1H), 1.24 (d, *J* = 6.3 Hz, 3H), 1.17 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 150.9, 130.2, 128.2, 124.8, 123.3, 117.2, 75.3, 48.3, 36.9, 25.6, 23.1, 19.6. Enantiomeric excess of **4f** was determined by chiral

stationary phase HPLC analysis using a ChiralPak AD-H column (95:5 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), minor enantiomer: t_R = 10.0 min, major enantiomer: t_R = 11.4 min.

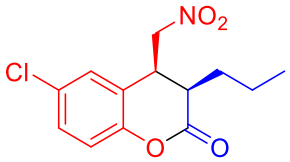
(*R*)-3,3-Dimethyl-4-(nitromethyl)chroman-2-one (4g)[11a]



4g

Colorless oil, 16.3 mg, 69% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (ddd, *J* = 8.2, 6.3, 2.8 Hz, 1H), 7.18 – 7.10 (m, 3H), 4.75 (dd, *J* = 12.5, 5.2 Hz, 1H), 4.36 (dd, *J* = 12.5, 9.7 Hz, 1H), 3.54 (dd, *J* = 9.7, 5.2 Hz, 1H), 1.45 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 150.5, 130.1, 128.7, 125.2, 121.0, 116.9, 45.7, 39.9, 25.5, 21.8. Enantiomeric excess of **4g** was determined by chiral stationary phase HPLC analysis using a ChiralPak OD-H column (95:5 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), major enantiomer: t_R = 20.3 min, minor enantiomer: t_R = 25.8 min.

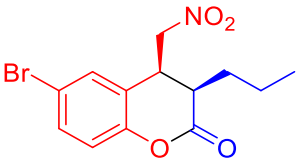
(3*R*,4*S*)-6-Chloro-4-(nitromethyl)-3-propylchroman-2-one (4h)



4h

Colorless oil, 21.0 mg, 74% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.20 (d, *J* = 2.5 Hz, 1H), 7.07 (d, *J* = 8.7 Hz, 1H), 4.62 (dd, *J* = 12.8, 4.7 Hz, 1H), 4.33 (dd, *J* = 12.8, 10.3 Hz, 1H), 3.86 (dt, *J* = 10.2, 5.0 Hz, 1H), 2.91 (td, *J* = 6.9, 5.3 Hz, 1H), 2.07 – 1.99 (m, 1H), 1.60 – 1.51 (m, 3H), 1.03 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 149.4, 130.2, 130.1, 128.0, 124.3, 118.8, 75.0, 41.1, 37.4, 28.6, 20.5, 13.8. ν_{max} (neat, cm^{-1}): 1770, 1556, 1482, 1417, 1377, 1153, 1229,1150, 1099. HRMS (ESI): *m/z* calcd for $C_{13}H_{14}ClNO_4$ $[M + H]^+$: 284.0684; found 284.0691. Enantiomeric excess of **4h** was determined by chiral stationary phase HPLC analysis using a ChiralPak OD-H column (95:5 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), minor enantiomer: t_R = 30.4 min, major enantiomer: t_R = 35.7 min.

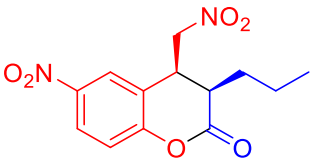
(3*R*,4*S*)-6-Bromo-4-(nitromethyl)-3-propylchroman-2-one (4i)



4i

Colorless oil, 24.0 mg, 73% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.35 (d, *J* = 2.3 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 1H), 4.62 (dd, *J* = 12.9, 4.7 Hz, 1H), 4.33 (dd, *J* = 12.9, 10.3 Hz, 1H), 3.88 – 3.85 (m, 1H), 2.92 – 2.90 (m, 1H), 2.05 – 2.03 (m, 1H), 1.56 – 1.51 (m, 3H), 1.03 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 150.0, 133.2, 130.9, 124.7, 119.1, 117.5, 75.0, 41.1, 37.3, 28.6, 20.5, 13.8. ν_{max} (neat, cm^{-1}): 1701, 1558, 1496, 1272, 1111, 829. HRMS (ESI): *m/z* $[M + H]^+$ calcd. for $C_{13}H_{14}BrNO_4$: 328.0179; found 328.0188. Enantiomeric excess of **4i** was determined by chiral stationary phase HPLC analysis using a ChiralPak OD-H column (97:3 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), minor enantiomer: t_R = 45.8 min, major enantiomer: t_R = 60.4 min.

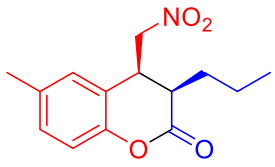
(3*R*,4*S*)-6-Nitro-4-(nitromethyl)-3-propylchroman-2-one (4j)



4j

Colorless oil, 20.0 mg, 68% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 – 8.23 (m, 2H), 7.28 (d, *J* = 8.9 Hz, 2H), 4.61 – 4.51 (m, 2H), 3.87 (td, *J* = 7.6, 1.6 Hz, 1H), 3.01 (ddd, *J* = 8.2, 6.6, 1.7 Hz, 1H), 2.99 – 2.06 (m, 1H), 1.59 – 1.44 (m, 3H), 0.95 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 155.2, 126.1, 125.3, 120.1, 118.3, 77.4, 41.9, 39.2, 32.3, 20.0, 13.4. ν_{max} (neat, cm^{-1}): 1778, 1703, 1622, 1553, 1338, 1288, 1127,1089, 936. HRMS (ESI): *m/z* calcd for $C_{13}H_{14}N_2O_6$ $[M + H]^+$: 295.0925; found 295.0933. Enantiomeric excess of **4j** was determined by chiral stationary phase HPLC analysis using a ChiralPak AD-H column (95:5 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), major enantiomer: t_R = 27.6 min, minor enantiomer: t_R = 34.2 min.

(3*R*,4*S*)-6-Methyl-4-(nitromethyl)-3-propylchroman-2-one (4k)

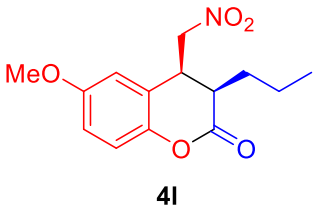


4k

Colorless oil, 17.9 mg, 68% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.06 – 6.89 (m, 2H), 4.61 (dd, *J* = 12.5, 4.7 Hz, 1H), 4.32 (dd, *J* = 12.5, 10.3 Hz, 1H), 3.83 (dt, *J* = 10.3, 5.1 Hz, 1H), 2.93 – 2.90 (m, 1H), 2.33 (s, 3H), 2.06 – 2.03 (m, 1H), 1.58 – 1.50 (m, 3H), 1.02 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 148.7, 134.7, 130.6, 128.3, 122.4, 117.1, 75.6, 41.5, 37.7, 28.7, 20.7, 20.5, 13.8. ν_{max} (neat, cm^{-1}): 1765, 1553, 1496, 1464, 1254, 1146, 1101, 913. HRMS (ESI): *m/z* calcd for $C_{14}H_{17}NO_4$

[M + H]$^+$: 264.1230; found 264.1234. Enantiomeric excess of **4k** was determined by chiral stationary phase HPLC analysis using a ChiralPak OD-H column (95:5 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), minor enantiomer: t_R = 15.3 min, major enantiomer: t_R = 17.2 min.

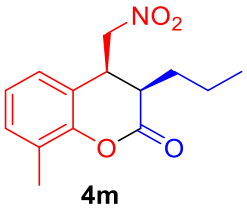
(3*R*,4*S*)-6-Methoxy-4-(nitromethyl)-3-propylchroman-2-one (4l)



4l

Colorless oil, 20.1 mg, 72% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.9 Hz, 1H), 6.89 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.70 (d, *J* = 2.9 Hz, 1H), 4.61 (dd, *J* = 12.6, 4.7 Hz, 1H), 4.33 (dd, *J* = 12.6, 10.5 Hz, 1H), 3.86 – 3.82 (m, 1H), 3.80 (s, 3H), 2.91 (td, *J* = 7.0, 5.4 Hz, 1H), 2.08 – 2.02 (m, 1H), 1.57 – 1.47 (m, 3H), 1.03 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 156.4, 144.6, 123.6, 118.2, 115.3, 112.9, 75.4, 55.7, 41.4, 37.9, 28.7, 20.5, 13.8. ν_{max} (neat, cm^{-1}): 1763, 1556, 1496, 1378, 1209, 1151, 1034, 871. HRMS (ESI): *m/z* calcd for $C_{14}H_{17}NO_5$ [M + H]$^+$: 280.1179; found 280.1184. Enantiomeric excess of **4l** was determined by chiral stationary phase HPLC analysis using a ChiralPak OD-H column (98:2 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), major enantiomer: t_R = 62.5 min, minor enantiomer: t_R = 72.7 min.

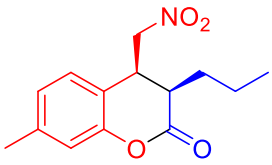
(3*R*,4*S*)-8-Methyl-4-(nitromethyl)-3-propylchroman-2-one (4m)



4m

Colorless oil, 17.1 mg, 65% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (ddd, *J* = 7.4, 1.8, 0.8 Hz, 1H), 7.05 – 6.99 (m, 2H), 4.61 (dd, *J* = 12.4, 4.7 Hz, 1H), 4.31 (dd, *J* = 12.3, 10.5 Hz, 1H), 3.87 – 3.85 (m, 1H), 2.93 (td, *J* = 6.9, 5.3 Hz, 1H), 2.34 (s, 3H), 2.09 – 2.02 (m, 1H), 1.59 – 1.52 (m, 3H), 1.03 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 149.1, 131.7, 126.8, 125.5, 124.5, 122.5, 75.6, 41.4, 38.0, 28.7, 20.6, 15.7, 13.8. ν_{max} (neat, cm^{-1}): 1763, 1552, 1468, 1431, 1377, 1267, 1195,1110, 994. HRMS (ESI): *m/z* calcd for $C_{14}H_{17}NO_4$ [M + H]$^+$: 264.1230; found 264.1238. Enantiomeric excess of **4m** was determined by chiral stationary phase HPLC analysis using a ChiralPak IC column (90:10 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), minor enantiomer: t_R = 12.9 min, major enantiomer: t_R = 30.1 min.

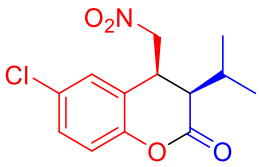
(3*R*,4*S*)-7-Methyl-4-(nitromethyl)-3-propylchroman-2-one (4n)



4n

Colorless oil, 22.9 mg, 87% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.6 Hz, 1H), 6.96 – 6.93 (m, 2H), 4.60 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.30 (dd, *J* = 12.4, 10.5 Hz, 1H), 3.84 (dt, *J* = 10.4, 5.0 Hz, 1H), 2.92 (td, *J* = 7.0, 5.5 Hz, 1H), 2.37 (s, 3H), 2.05 – 2.03 (m, 1H), 1.56 – 1.50 (m, 3H), 1.02 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 150.7, 140.7, 127.7, 125.7, 119.5, 117.8, 75.7, 41.6, 37.4, 28.7, 21.2, 20.5, 13.8. ν_{max} (neat, cm^{-1}): 1761, 1625, 1583, 1551, 1455, 1377, 1247, 1195,1100, 989. HRMS (ESI): *m/z* calcd for $C_{14}H_{17}NO_4$ $[M + H]^+$: 264.1230; found 264.1238. Enantiomeric excess of **4n** was determined by chiral stationary phase HPLC analysis using a ChiralPak AD-H column (95:5 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), minor enantiomer: t_R = 11.4 min, major enantiomer: t_R = 14.0 min.

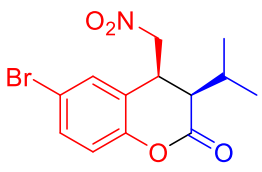
(3*R*,4*S*)-6-Chloro-3-isopropyl-4-(nitromethyl)chroman-2-one (4o)



4o

Colorless oil, 21.0 mg, 74% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.20 (d, *J* = 2.5 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 1H), 4.59 (dd, *J* = 12.8, 3.8 Hz, 1H), 4.29 (dd, *J* = 12.7, 11.4 Hz, 1H), 3.95 (ddd, *J* = 11.4, 5.0, 3.8 Hz, 1H), 2.53 (dd, *J* = 10.1, 5.0 Hz, 1H), 2.21-2.09 (m, 1H), 1.24 (d, *J* = 6.3 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 149.5, 130.2, 129.9, 128.2, 124.9, 118.5, 74.8, 48.0, 36.6, 25.6, 23.0, 19.5. ν_{max} (neat, cm^{-1}): 1705, 1498, 1281, 1081, 947, 783. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{13}H_{14}ClNO_4$: 284.0684; found 284.0693. Enantiomeric excess of **4o** was determined by chiral stationary phase HPLC analysis using a ChiralPak OD-H column (95:5 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), minor enantiomer: t_R = 19.4 min, major enantiomer: t_R = 32.5 min.

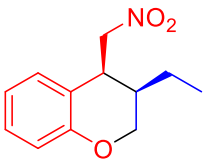
(3*R*,4*S*)-6-Bromo-3-isopropyl-4-(nitromethyl)chroman-2-one (4p)



4p

Colorless oil, 24.0 mg, 73% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.35 (d, *J* = 2.4 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 1H), 4.59 (dd, *J* = 12.8, 3.8 Hz, 1H), 4.29 (dd, *J* = 12.8, 11.4 Hz, 1H), 3.95 (ddd, *J* = 11.4, 5.0, 3.8 Hz, 1H), 2.53 (dd, *J* = 10.1, 5.0 Hz, 1H), 2.15 (dt, *J* = 10.1, 6.6 Hz, 1H), 1.24 (d, *J* = 6.3 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 150.0, 133.2, 131.0, 125.3, 118.9, 117.3, 74.8, 48.0, 36.5, 25.6, 23.0, 19.5. ν_{max} (neat, cm^{-1}): 1769, 1552, 1476, 1374, 1318, 1263, 1183,1097, 972. HRMS (ESI): *m/z* calcd for $C_{13}H_{14}BrNO_4$ $[M + H]^+$: 328.0179; found 328.0189. Enantiomeric excess of **4p** was determined by chiral stationary phase HPLC analysis using a ChiralPak OD-H column (95:5 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), minor enantiomer: t_R = 20.0 min, major enantiomer: t_R = 34.5 min.

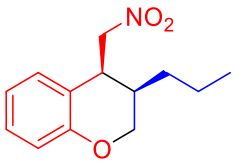
(3*R*,4*S*)-3-Ethyl-4-(nitromethyl)chromane (5a)[10b,12]



5a

Colorless oil, 19.9 mg, 90% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.02 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.90 – 6.85 (m, 2H), 4.66 – 4.62 (m, 1H), 4.52 – 4.51 (m, 1H), 4.24 (ddd, *J* = 11.3, 3.6, 1.2 Hz, 1H), 3.92 (dd, *J* = 11.3, 10.1 Hz, 1H), 3.84 (q, *J* = 6.6 Hz, 1H), 2.17 (dtd, *J* = 6.4, 3.4, 1.6 Hz, 1H), 1.47 – 1.37 (m, 2H), 1.10 – 1.02 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 129.1, 128.7, 120.7, 117.1, 77.5, 66.2, 36.9, 36.4, 20.1, 11.6. Enantiomeric excess of **5a** was determined by chiral stationary phase HPLC analysis using a ChiralPak IB column (95:5 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), major enantiomer: t_R = 9.5 min, minor enantiomer: t_R = 20.4 min.

(3*R*,4*S*)-4-(Nitromethyl)-3-propylchromane (5b)

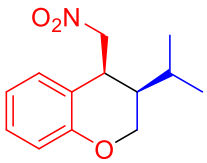


5b

Colorless oil, 22.1 mg, 94% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 1H), 7.01 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.93 – 6.78 (m, 2H), 4.65 (dd, *J* = 12.3, 6.6 Hz, 1H), 4.53 (dd, *J* = 12.3, 7.7 Hz, 1H), 4.22 (ddd, *J* = 11.4, 3.7, 1.3 Hz, 1H), 3.91 (dd, *J* = 11.4, 10.1 Hz, 1H), 3.81 (q, *J* = 6.7 Hz, 1H), 2.32 – 2.23 (m, 1H), 1.52 – 1.28 (m, 4H), 0.99 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 129.1, 128.7, 120.9, 120.7, 117.1, 77.6, 66.5, 37.1, 34.3, 29.2, 20.2, 14.1. ν_{max} (neat, cm^{-1}): 1583, 1552, 1490, 1454, 1377, 1258, 1119,1049, 756.

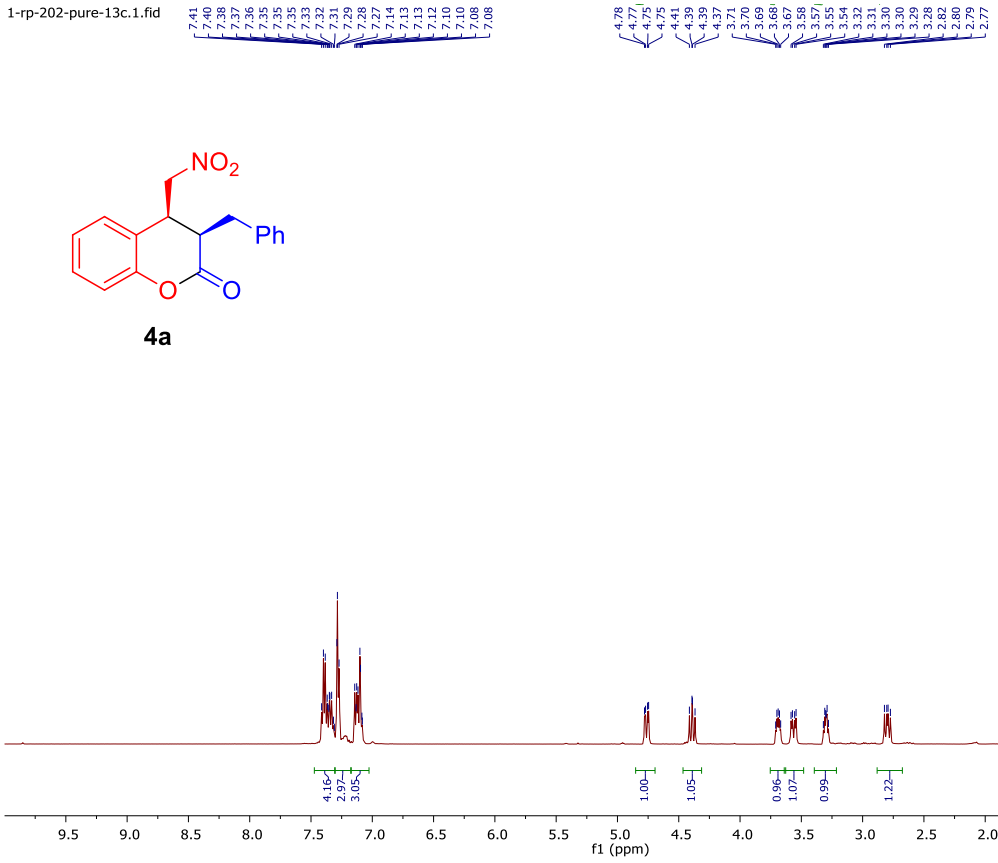
HRMS (ESI): *m/z* calcd for $C_{13}H_{17}NNaO_3$ $[M + Na]^+$: 258.1101; found 258.1112. Enantiomeric excess of **5b** was determined by chiral stationary phase HPLC analysis using a ChiralPak OD-H column (90:10 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), major enantiomer: t_R = 9.3 min, minor enantiomer: t_R = 26.0 min.

(3*R*,4*S*)-3-Isopropyl-4-(nitromethyl)chromane (5c)



5c

Colorless oil, 17.0 mg, 72% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.18 (m, 1H), 6.97 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.86 – 6.83 (m, 2H), 4.64 (dd, *J* = 11.7, 4.3 Hz, 1H), 4.46 – 4.41 (m, 2H), 3.83 – 3.77 (m, 2H), 1.94 (ddt, *J* = 12.1, 10.5, 4.3 Hz, 1H), 1.56-1.49 (m, 1H), 1.17 (d, *J* = 6.6 Hz, 3H), 1.07 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 129.4, 129.2, 121.7, 120.5, 116.8, 77.6, 65.5, 42.0, 35.9, 26.4, 21.1, 20.5. ν_{max} (neat, cm^{-1}): 1606, 1583, 1549, 1490, 1332, 1272, 1153,1068, 1013, 900. HRMS (ESI): *m/z* calcd for $C_{13}H_{17}NO_3$[M + H]$^+$: 236.1281; found 236.1287. Enantiomeric excess of **5c** was determined by chiral stationary phase HPLC analysis using a ChiralPak IB column (95:5 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm), major enantiomer: t_R = 8.1 min, minor enantiomer: t_R = 13.5 min.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2.79
2.77
NO2
Ph
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O
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2.97
3.05
1.00
1.05
0.96
1.07
0.99
1.22
9.5
9.0
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7.5
7.0
6.5
6.0
5.5
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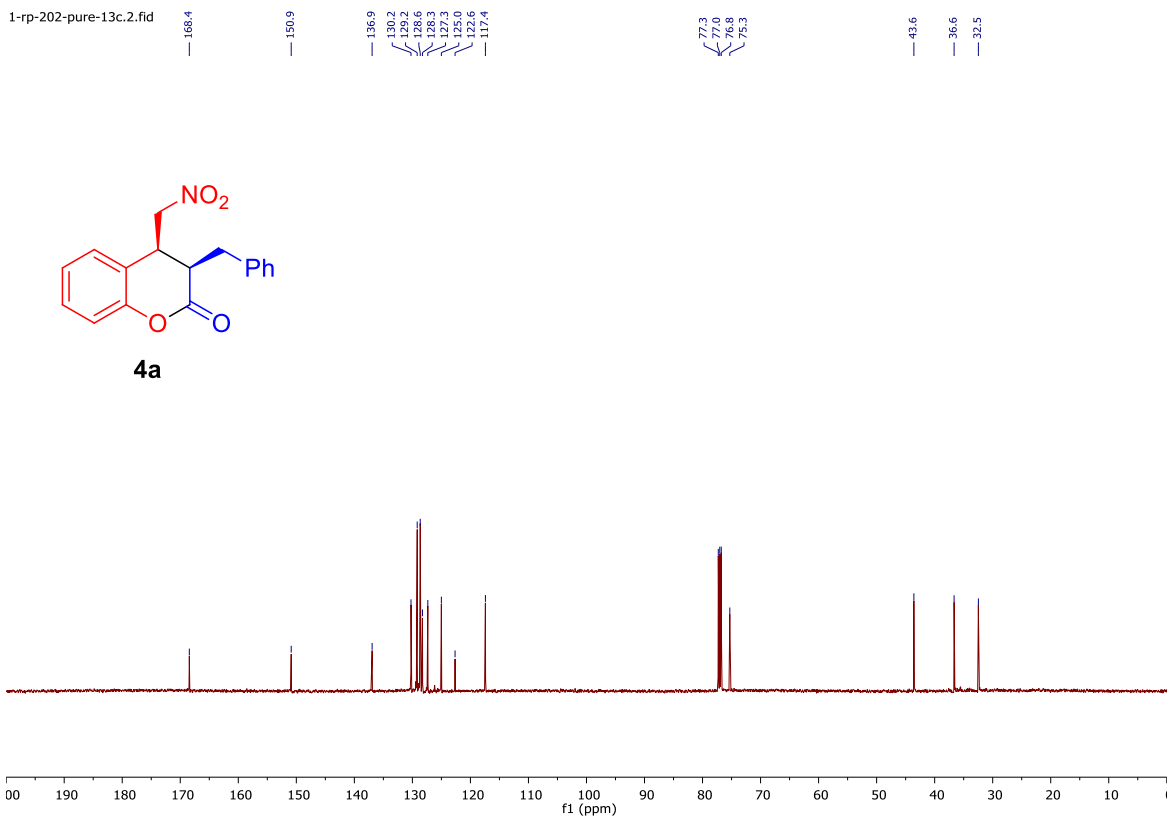
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)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77.0
76.8
75.3
43.6
36.6
32.5
NO2
Ph
O
O
4a
00
190
180
170
160
150
140
130
120
110
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90
80
70
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50
40
30
20
10
f1 (ppm)

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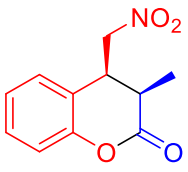

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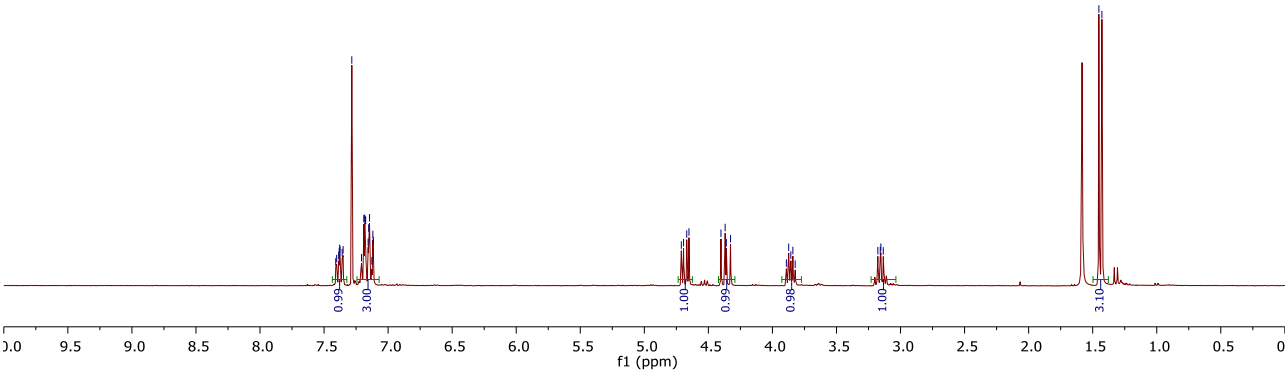

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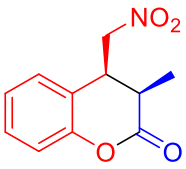

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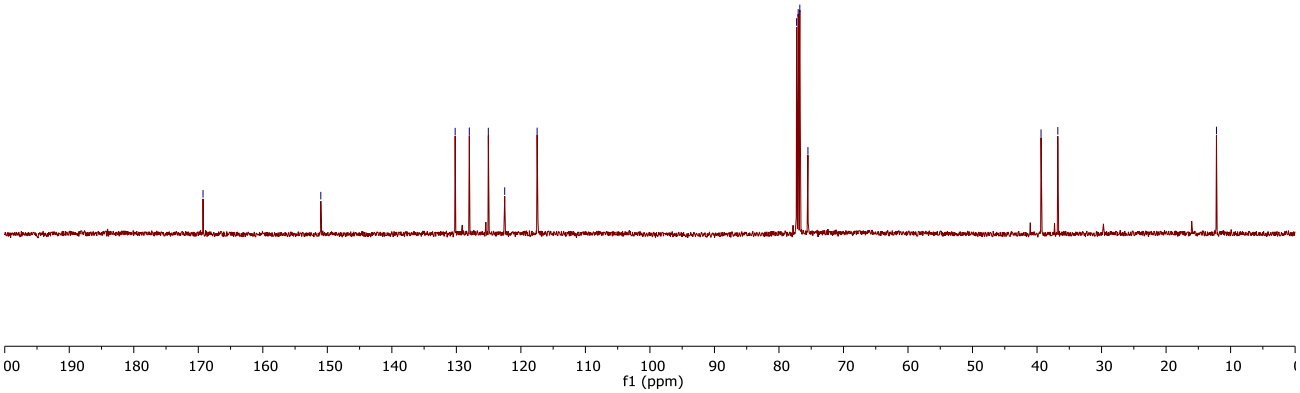

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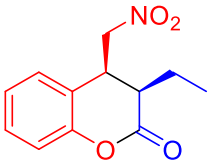

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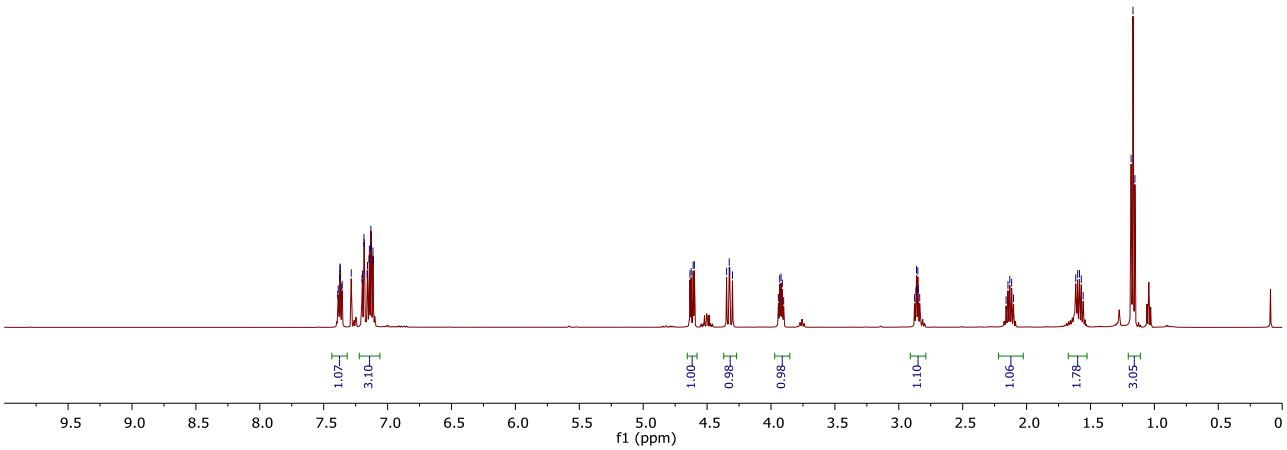

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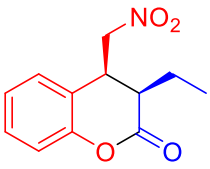

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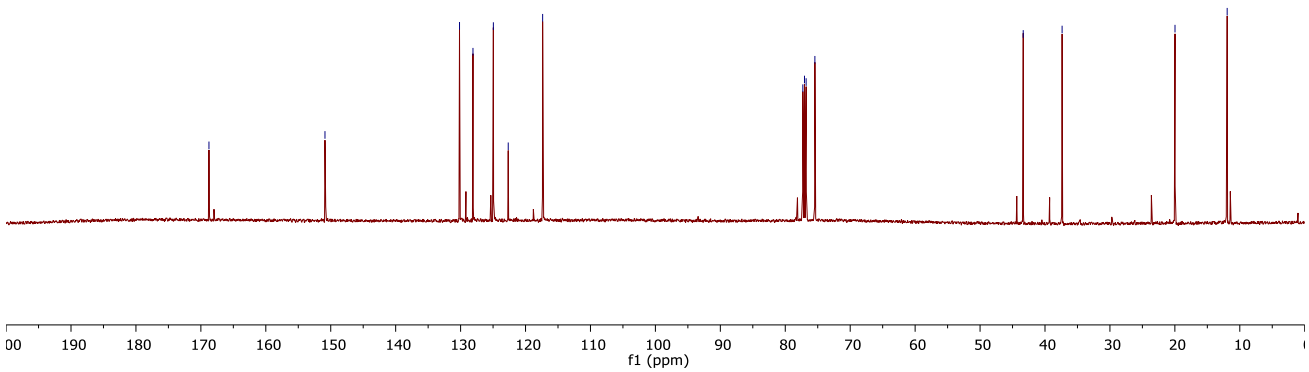

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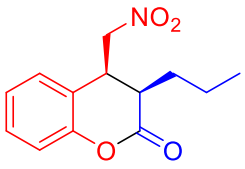

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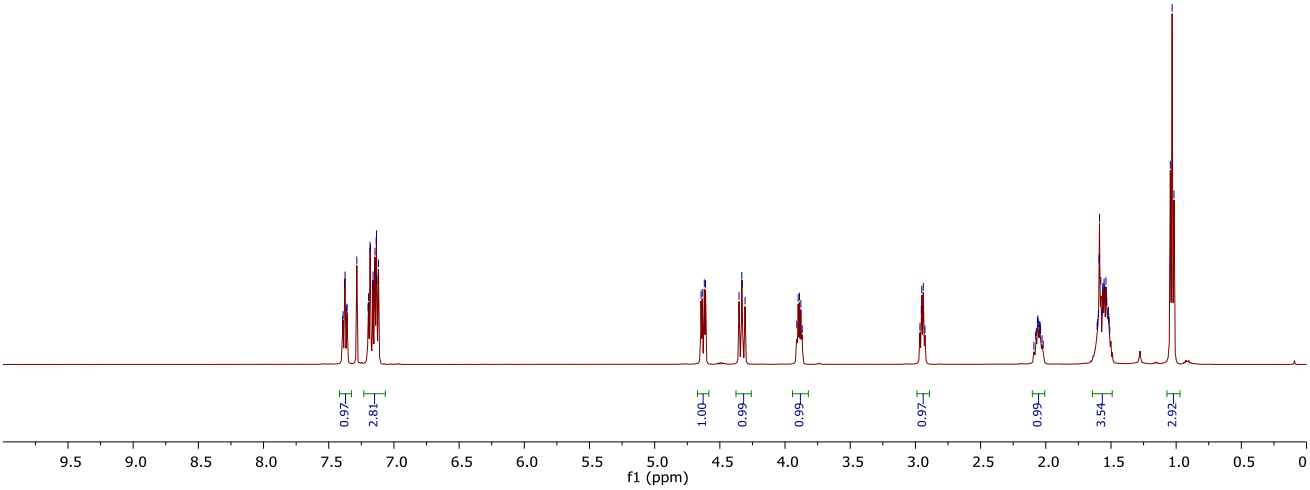

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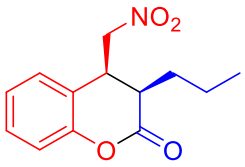

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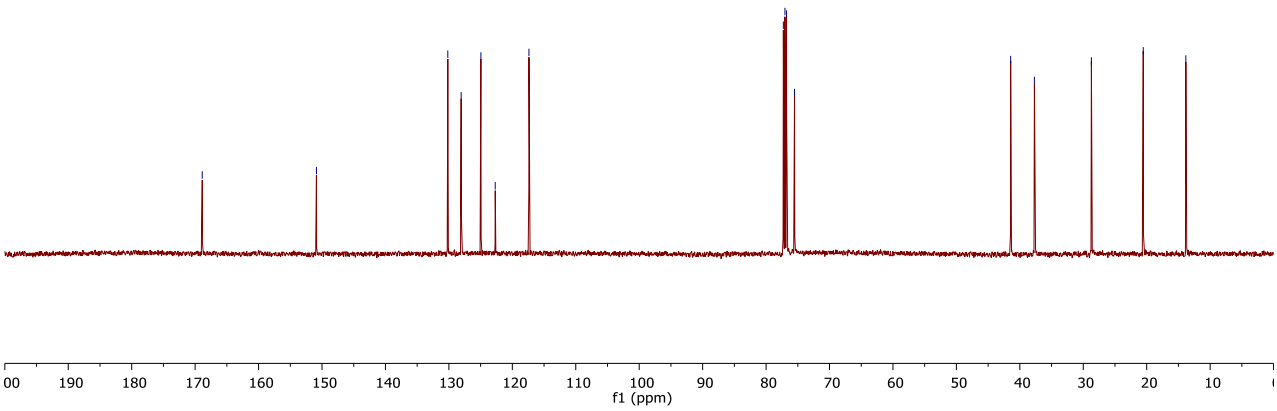

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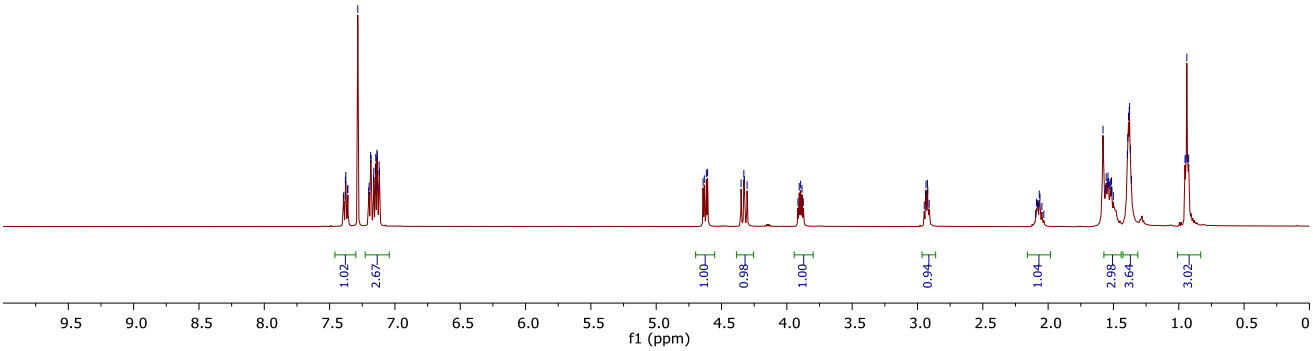

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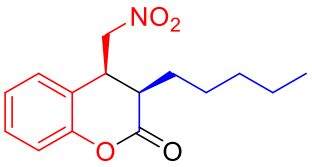

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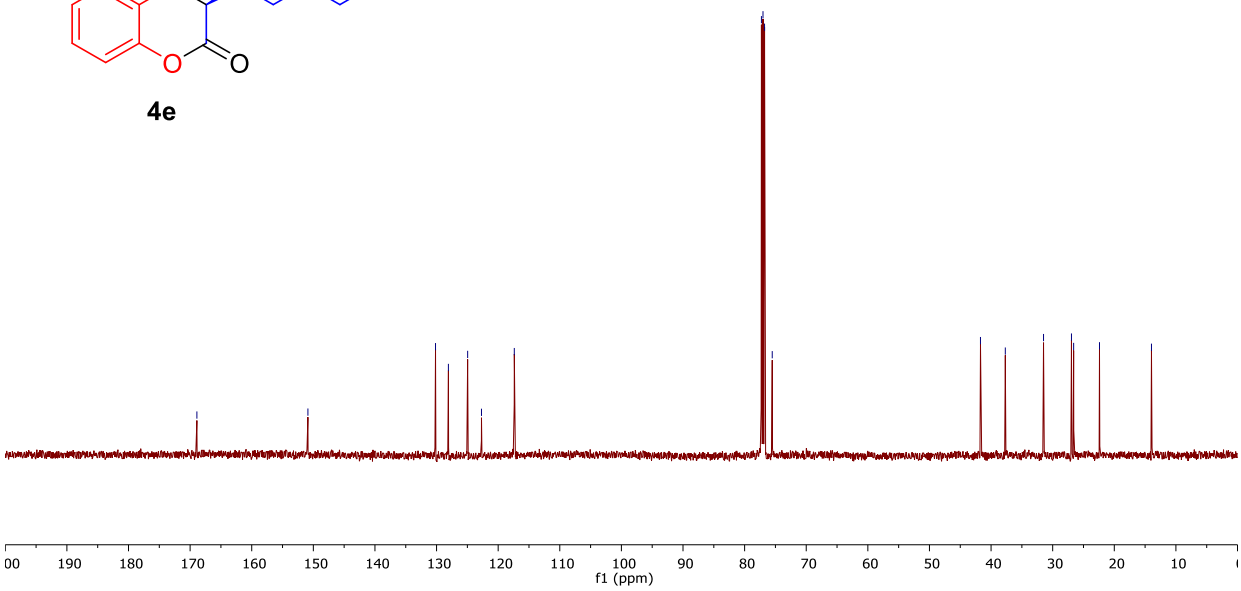

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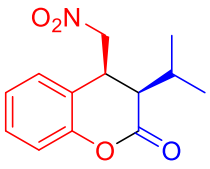

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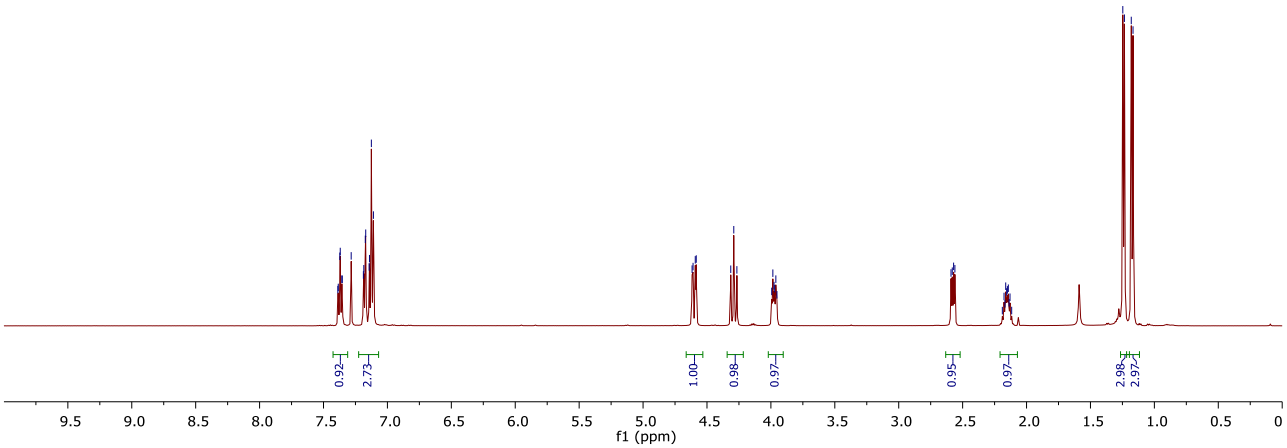

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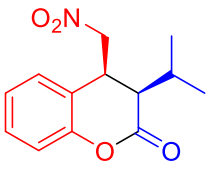

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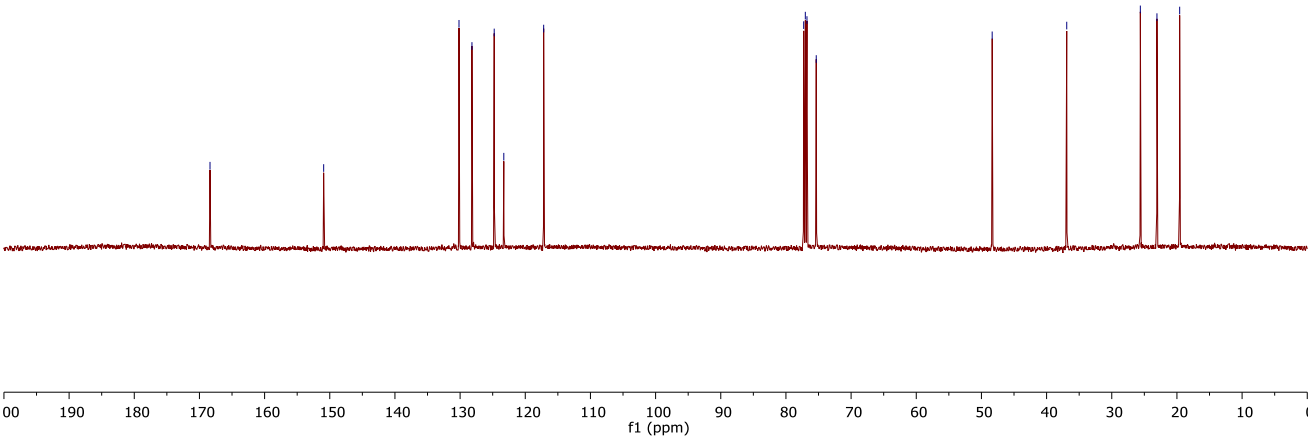

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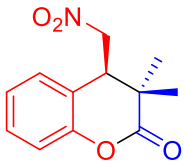
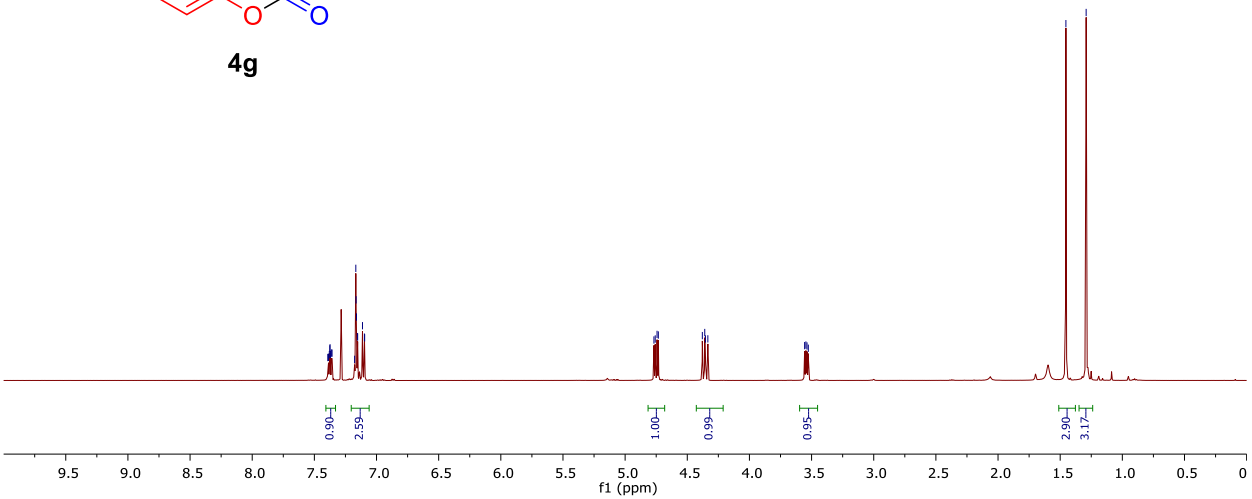


4g



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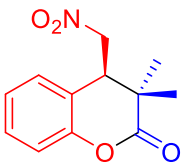

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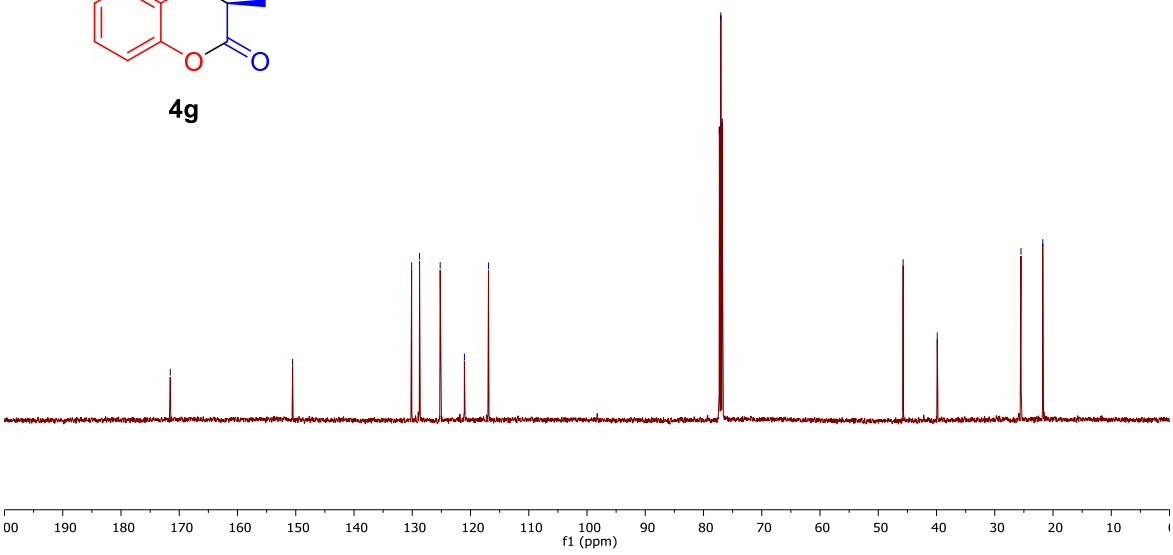

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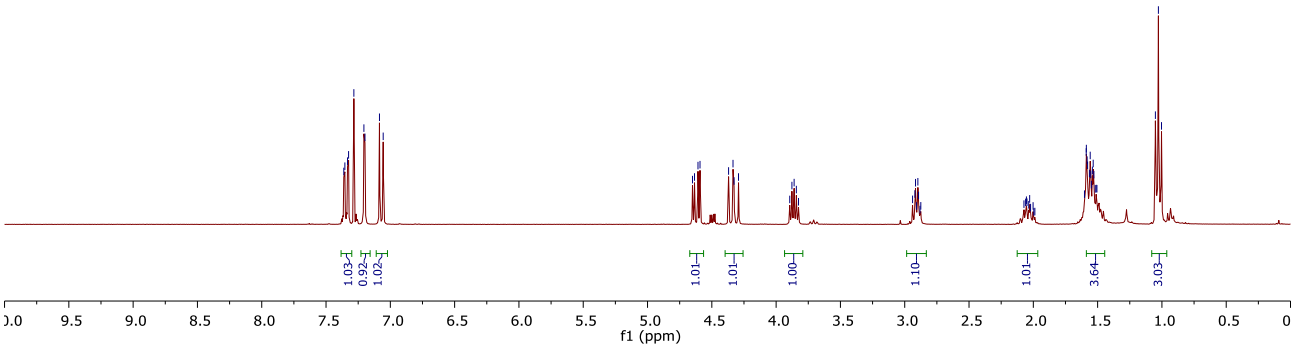
4h



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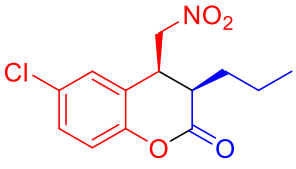

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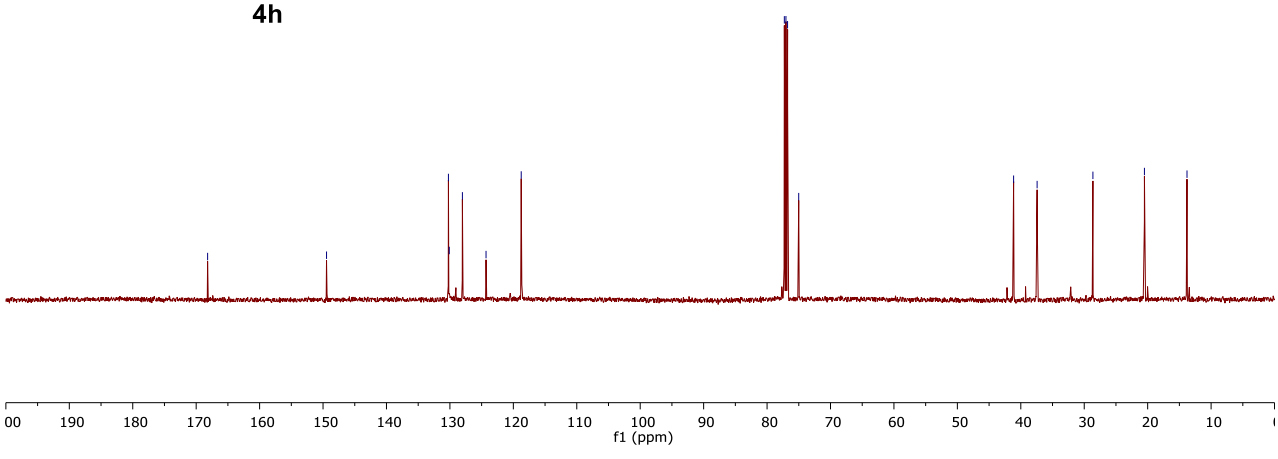

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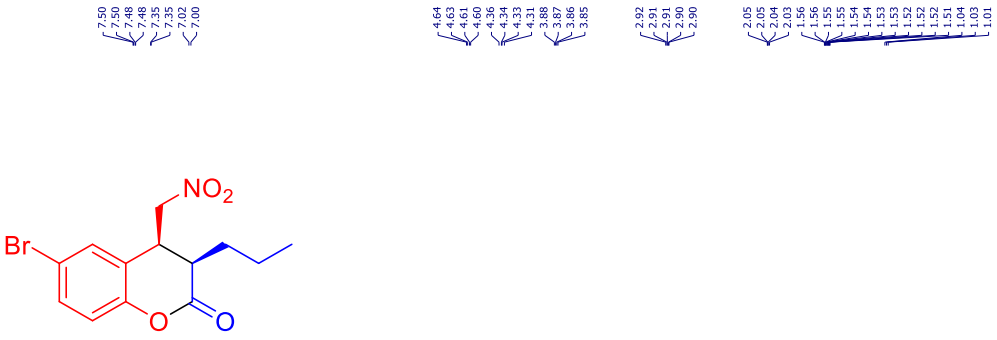

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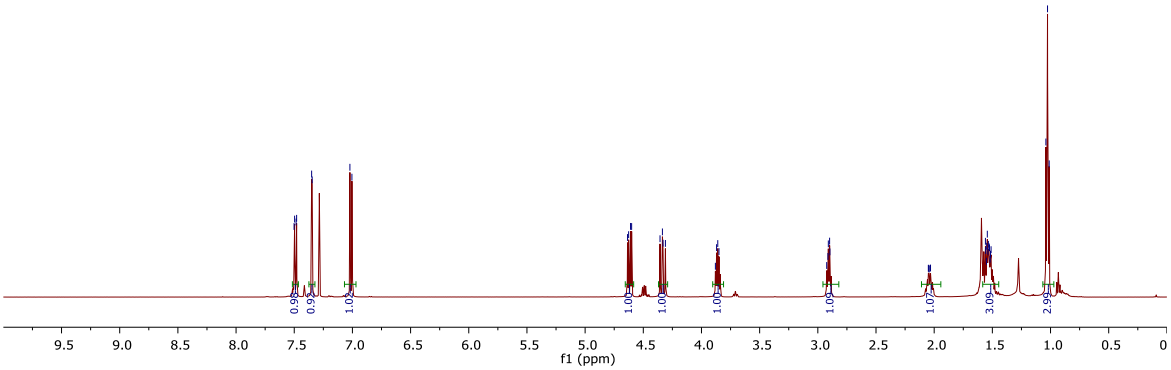

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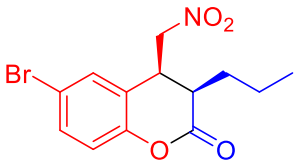
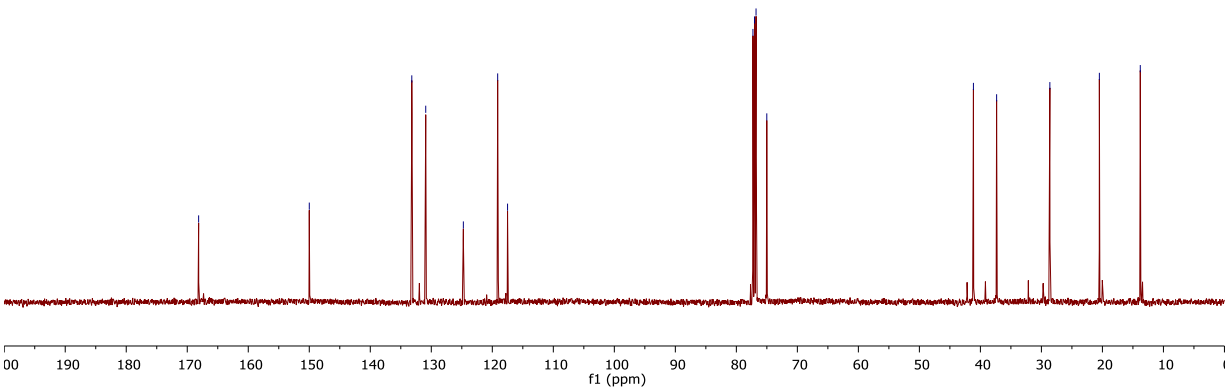
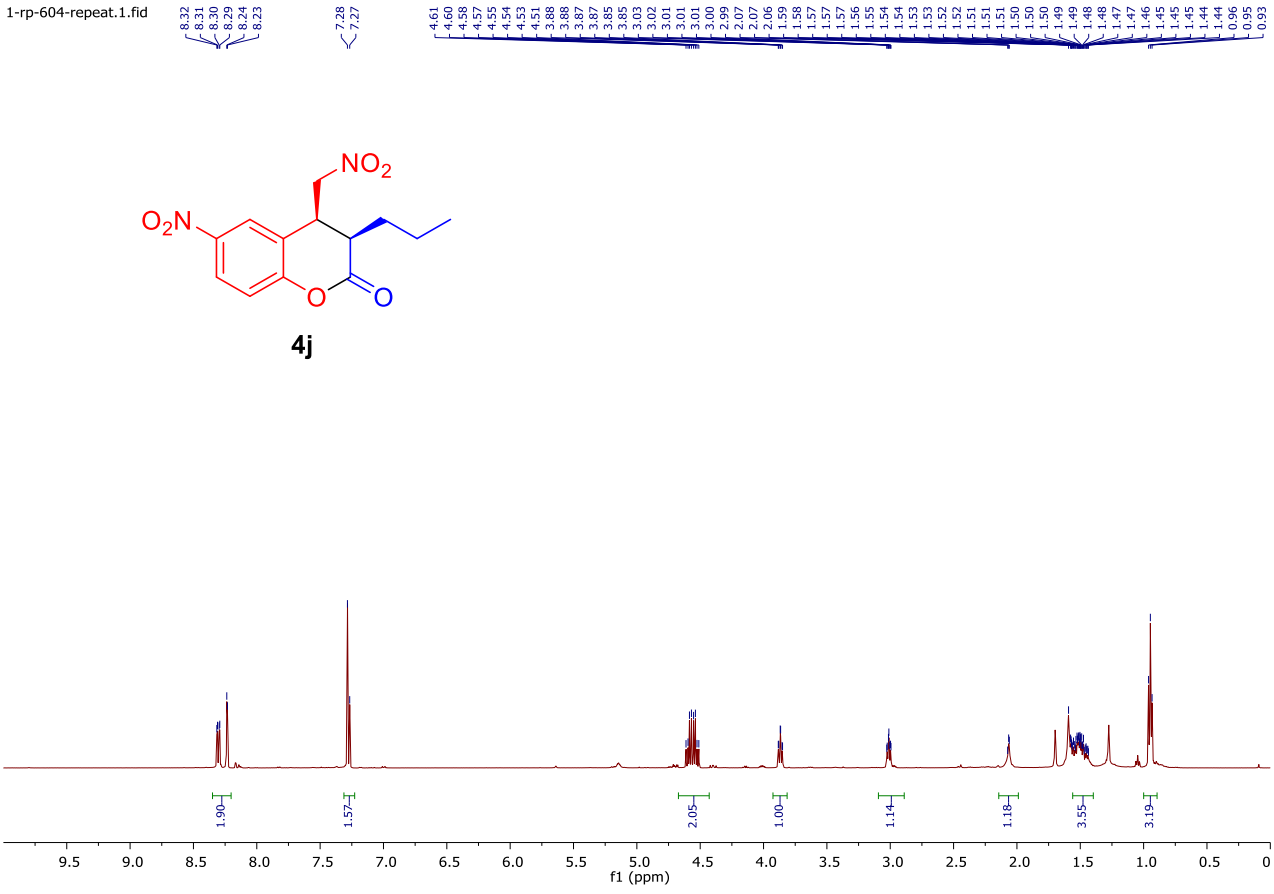


4i

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3.88
3.88
3.87
3.87
3.85
3.85
3.03
3.02
3.01
3.01
3.01
3.00
2.99
2.07
2.07
2.06
1.59
1.58
1.57
1.57
1.57
1.56
1.55
1.54
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1.51
1.51
1.50
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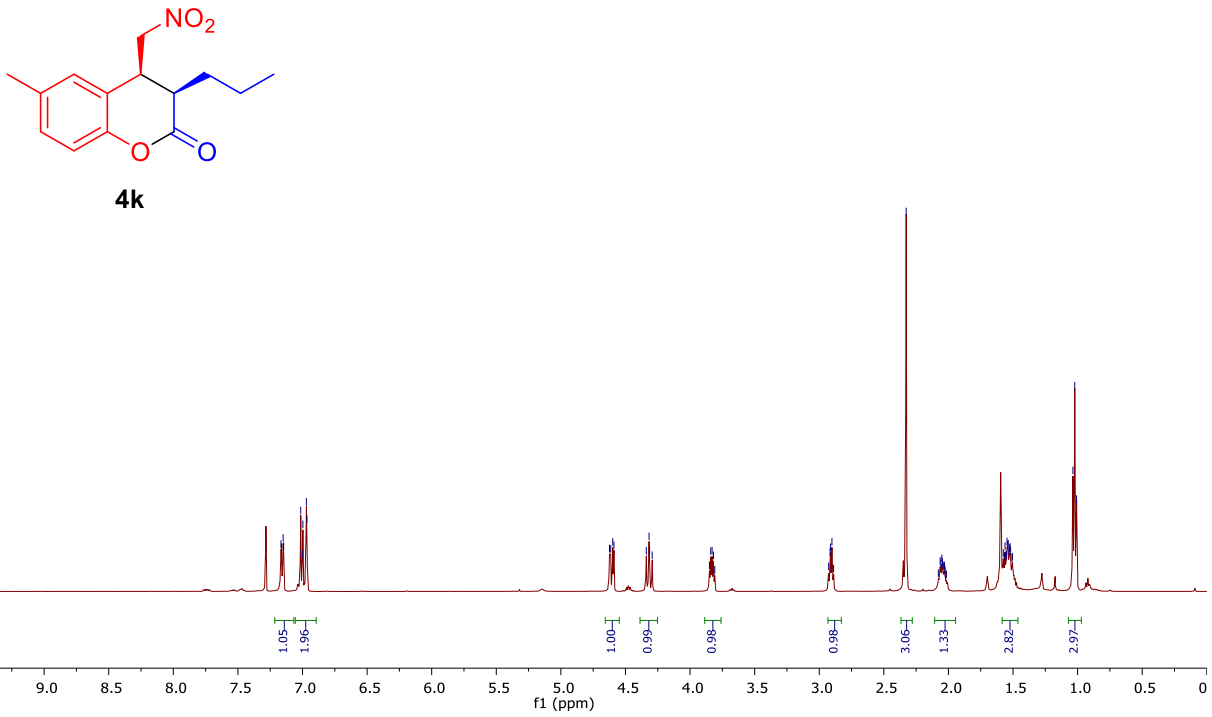
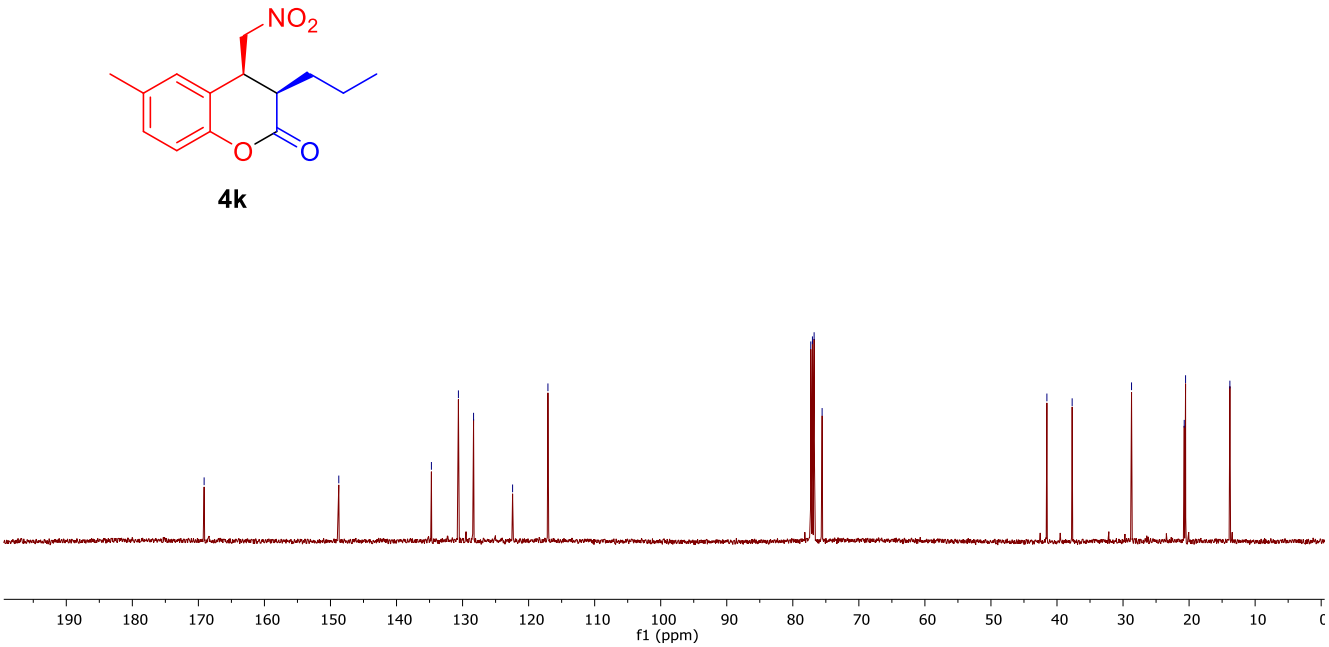
1.49
1.48
1.48
1.47
1.47
1.46
1.45
1.45
1.45
1.44
1.44
0.96
0.95
0.93
NO2
O2N
O
O
4j
1.90
1.57
2.05
1.00
1.14
1.18
3.55
3.19
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)
1-rp-604-repeat.2.fid
166.2
155.3
126.1
125.3
120.1
118.3
77.4
77.3
77.0
76.8
41.9
39.2
32.3
20.0
13.4
NO2
O2N
O
O
4j
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

1-RP-519-REPEAT-PURE-1.2.fid



4k

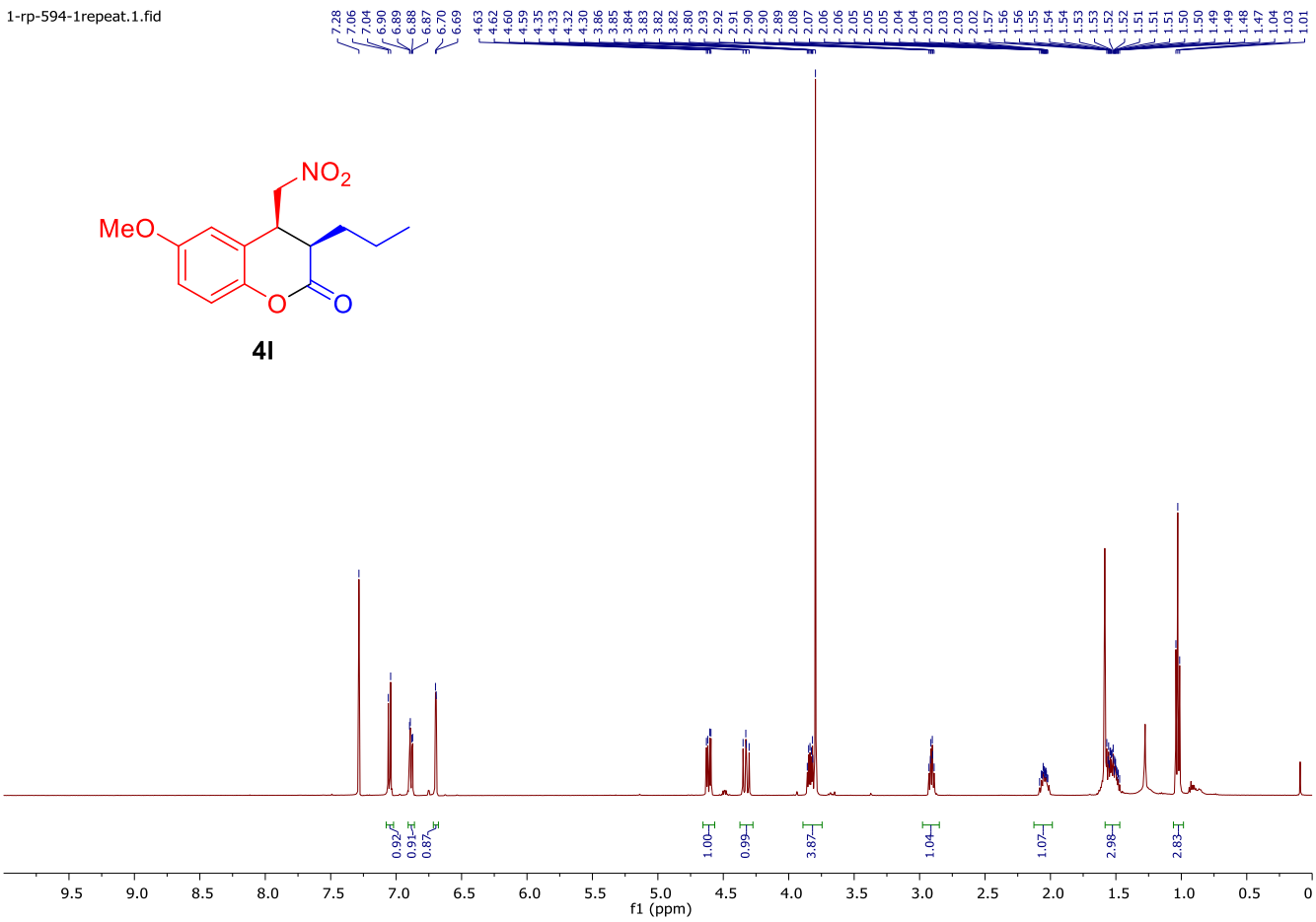
1-RP-519-REPEAT-PURE-1.1.fid



4k

1-rp-594-1repeat.1.fid

4l



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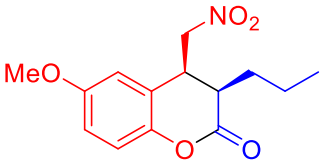
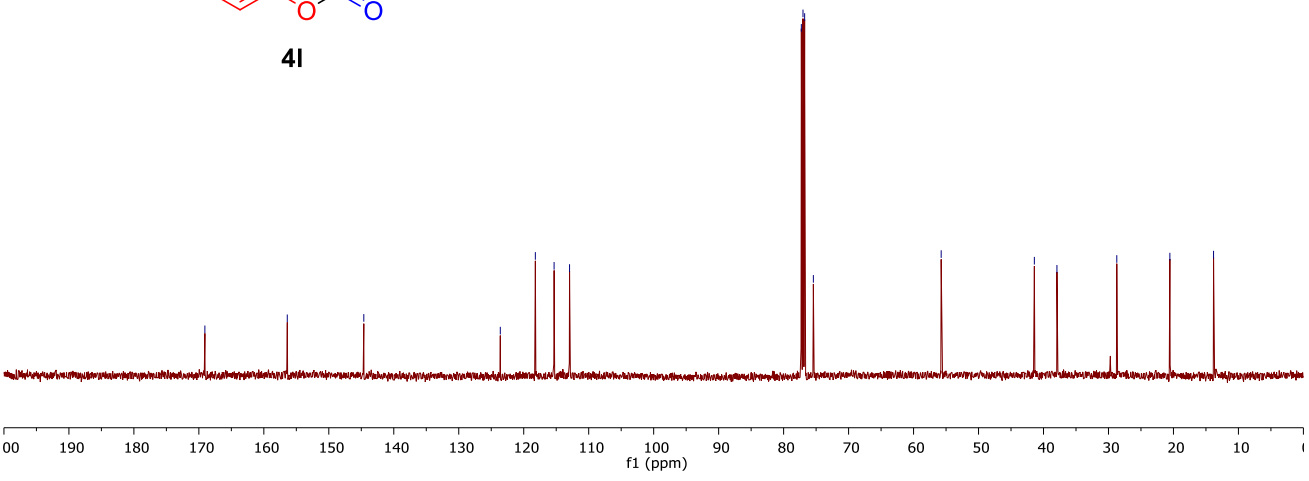


4l



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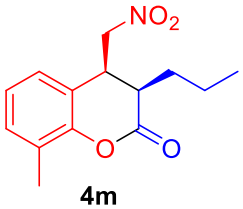

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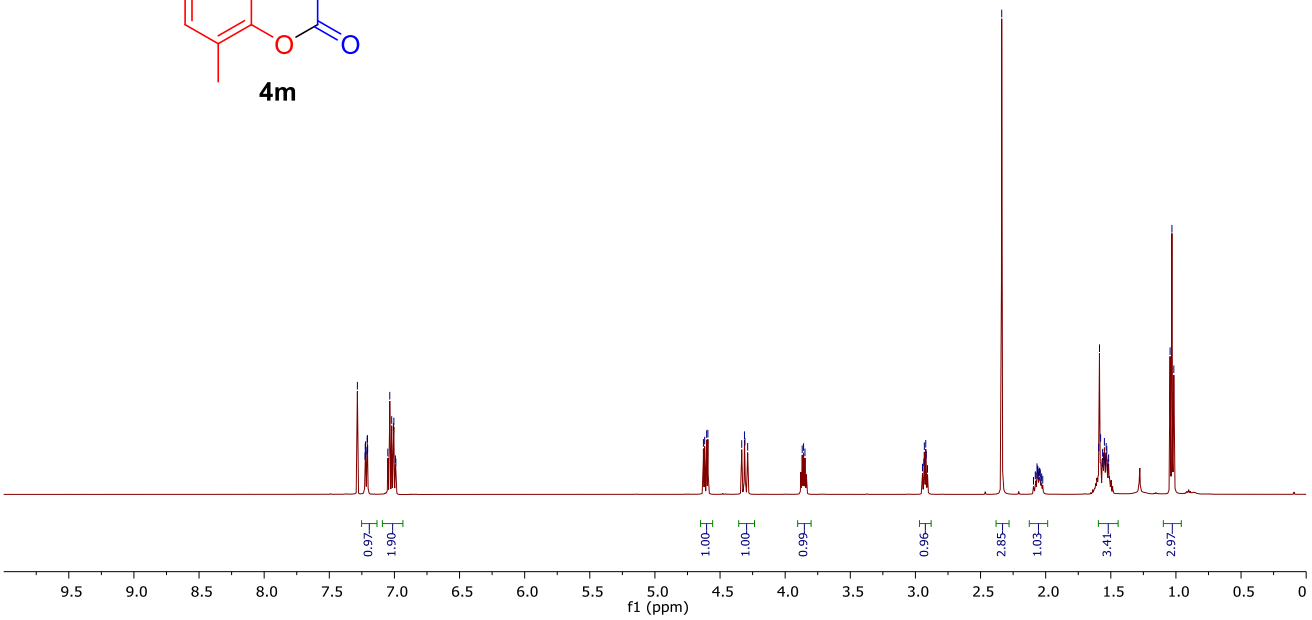

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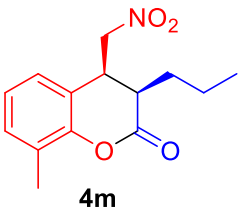
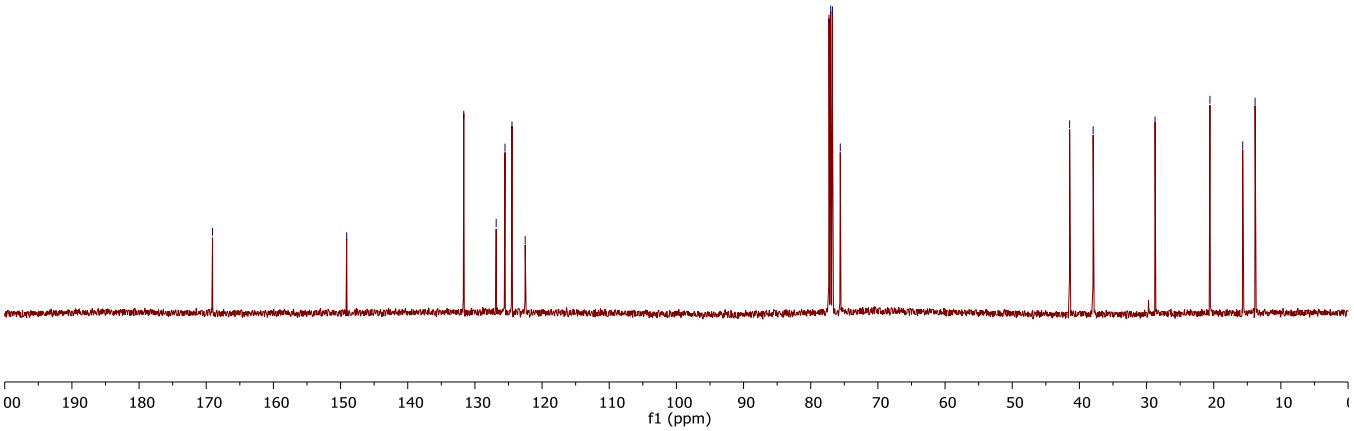


4m



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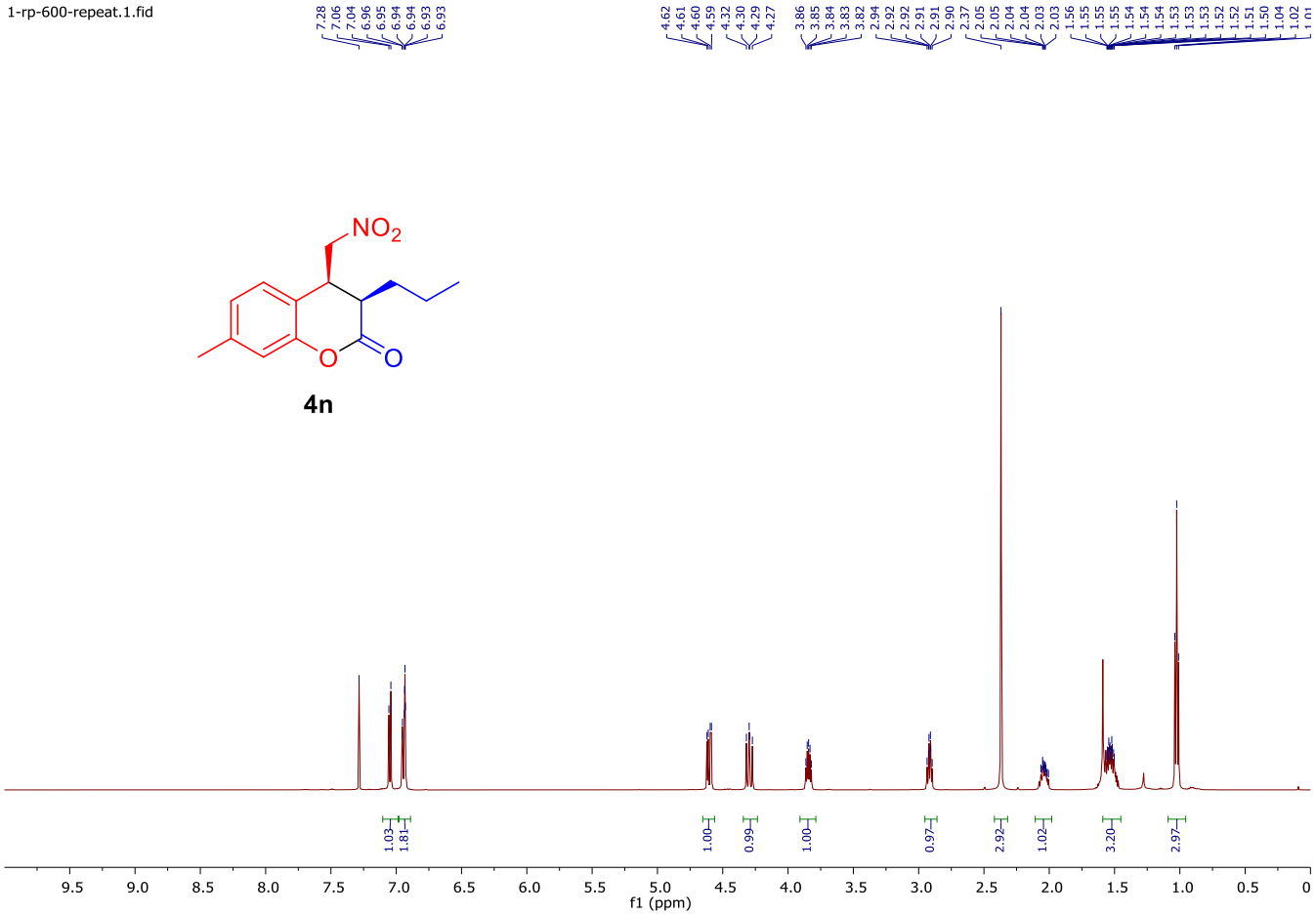
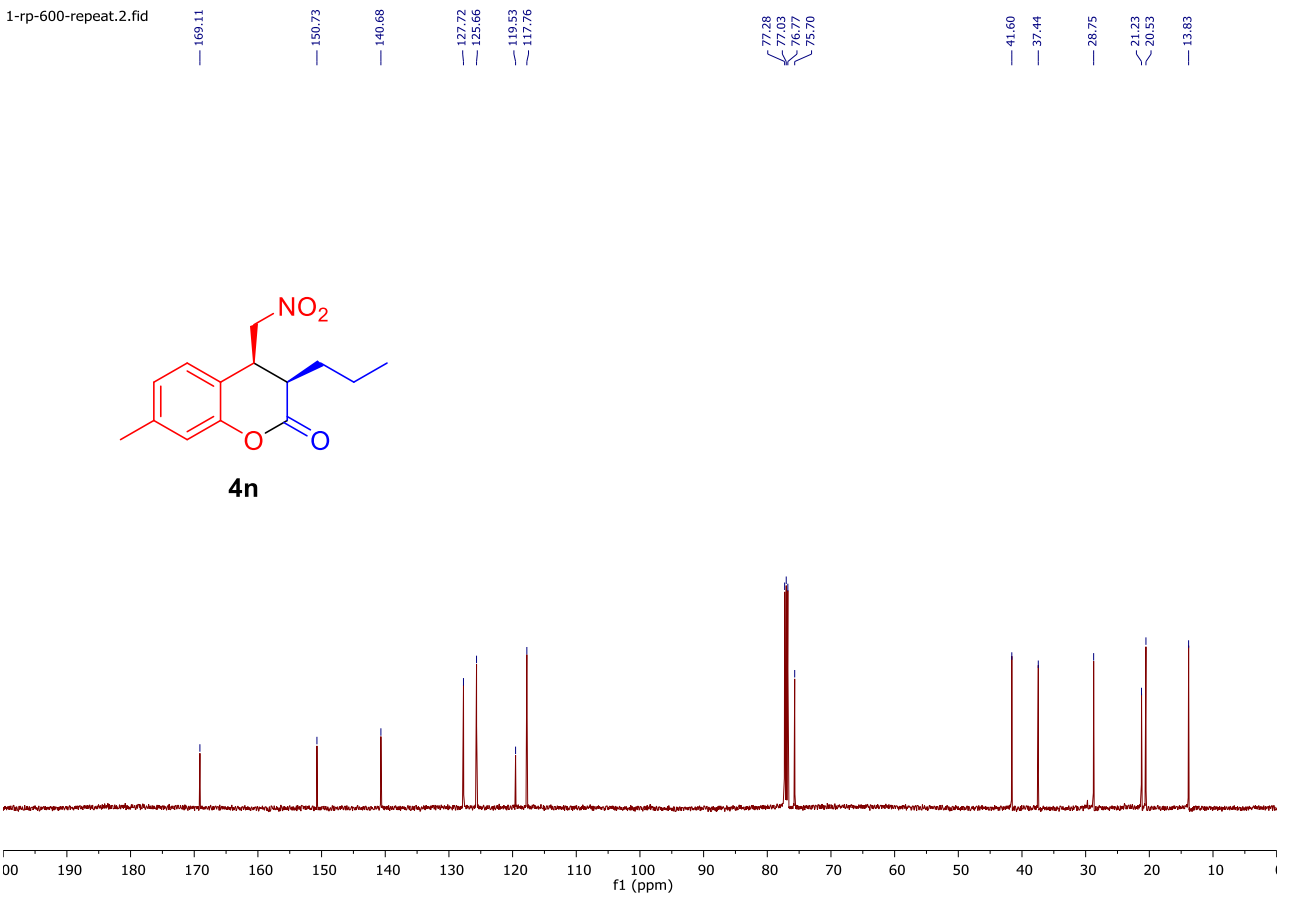


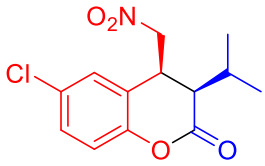
4n

1-rp-600-repeat.2.fid

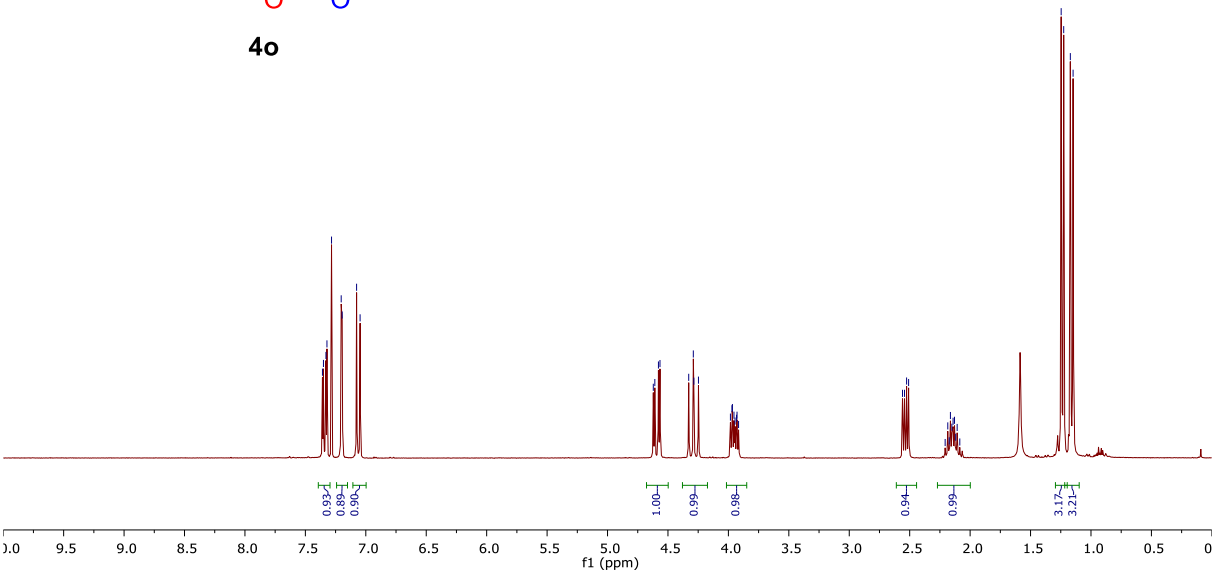


4n

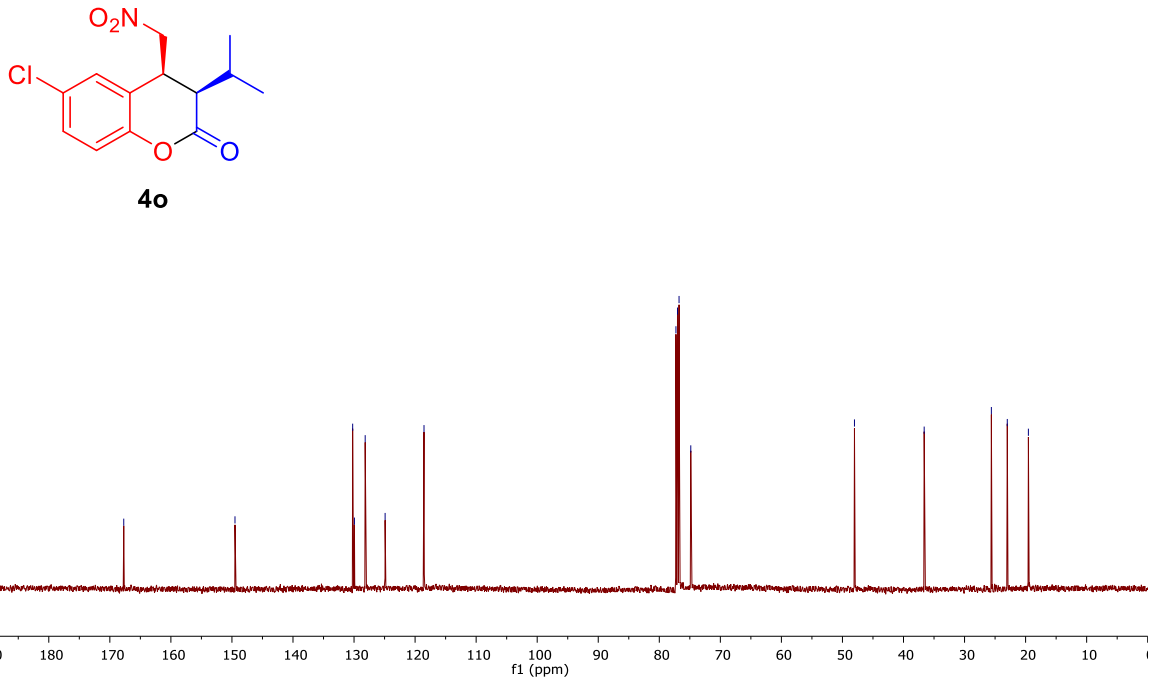
1-rp-486-pure-pure-1.1.fid



4o



1-rp-486-pure.1.fid



4o

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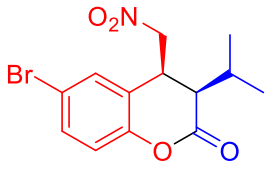

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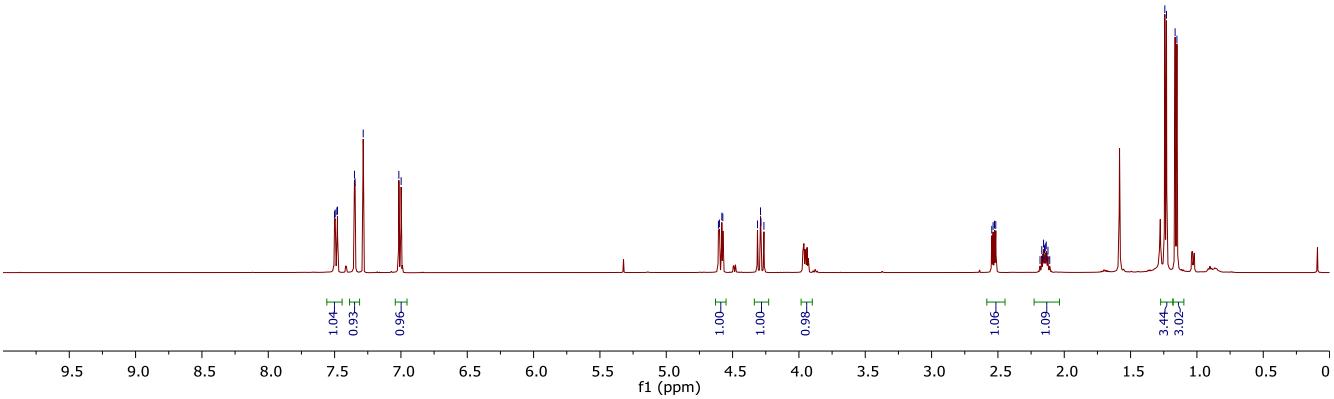

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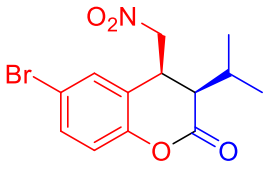
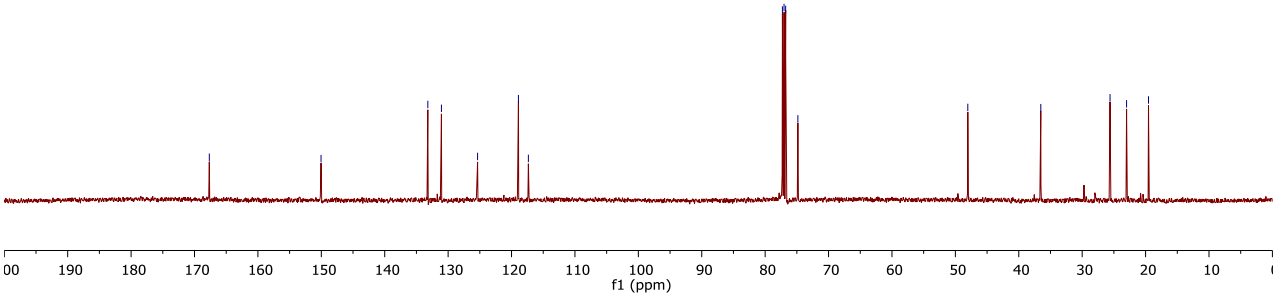
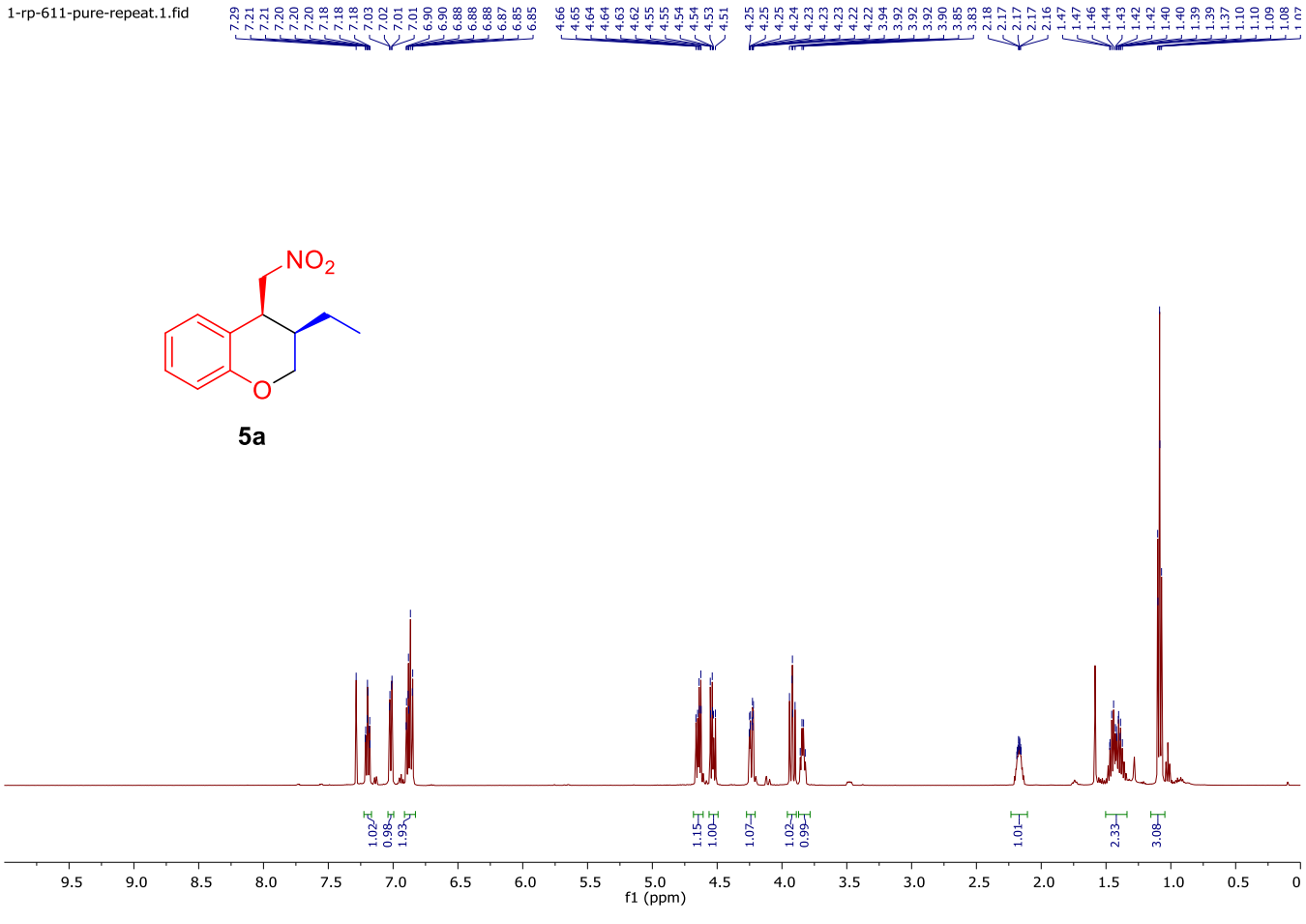
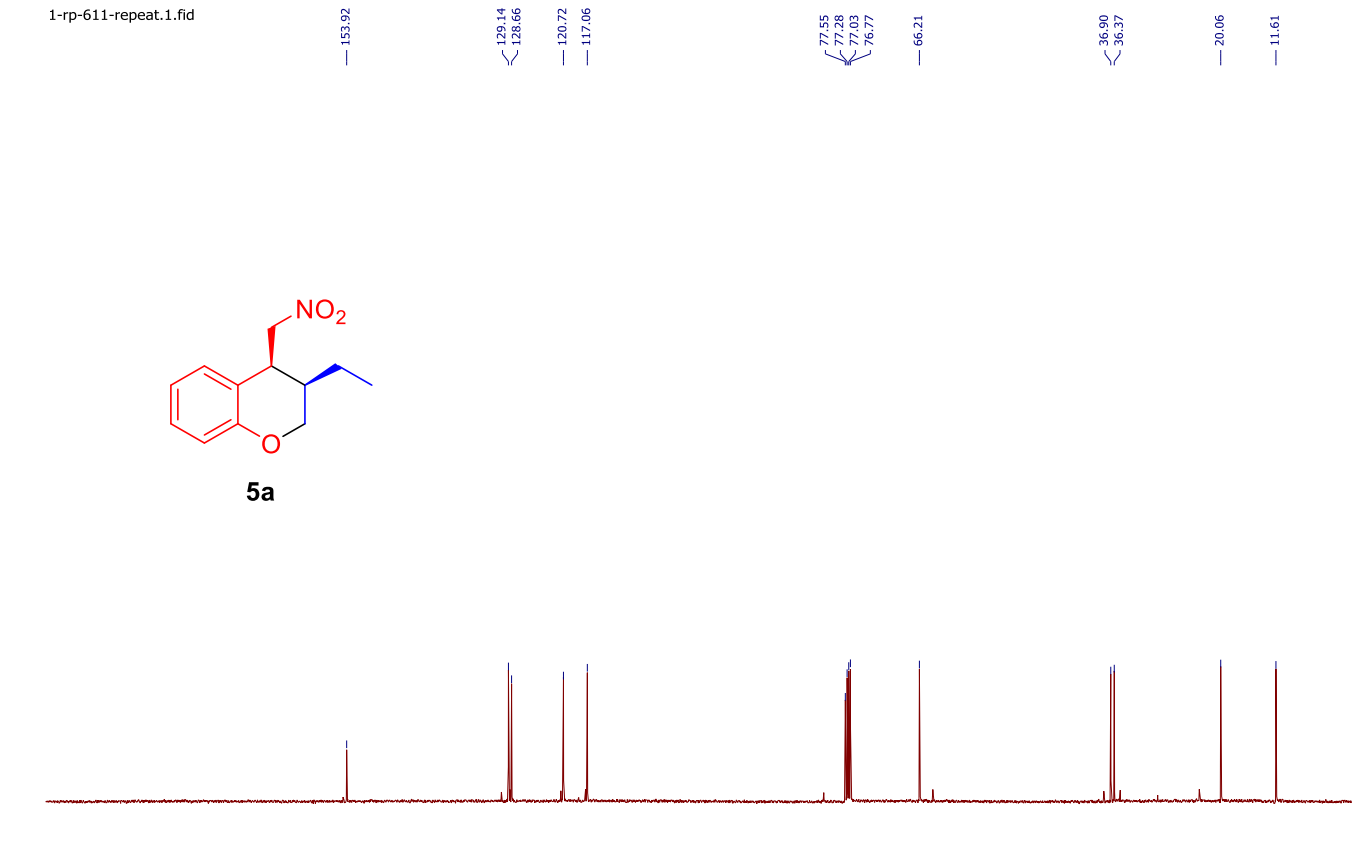


4p




1-rp-611-pure-repeat.1.fid
NO2
O
5a
f1 (ppm)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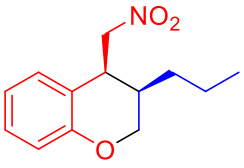
NO2
O
5a
f1 (ppm)



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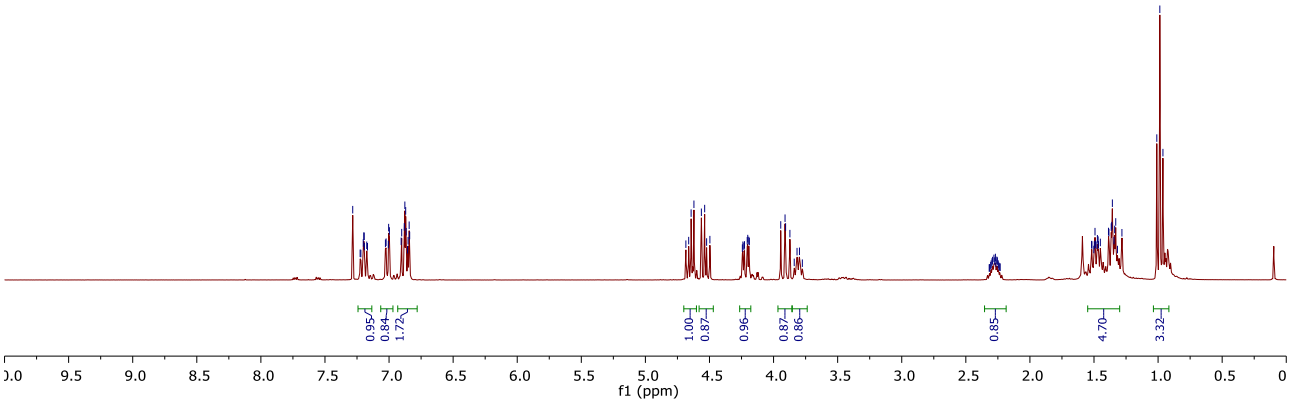

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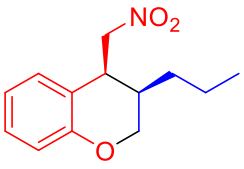

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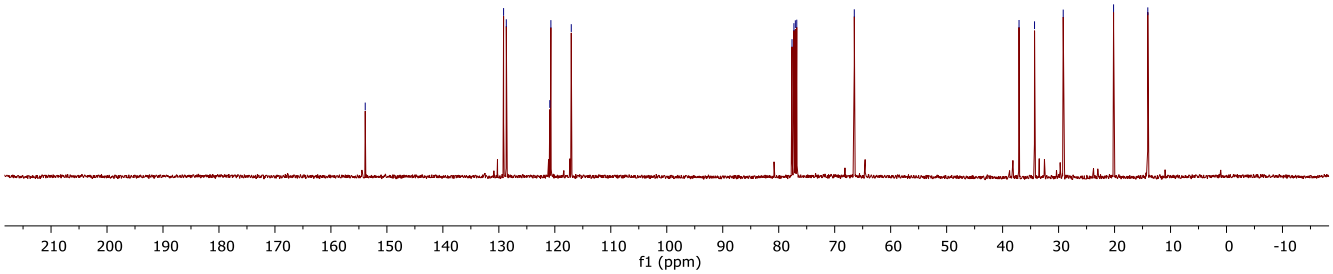
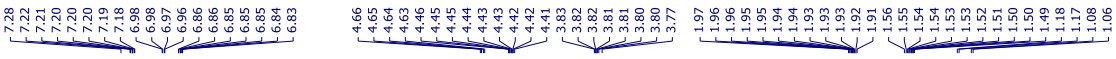
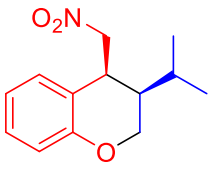


1-rp-613-repeat-1.1.fid





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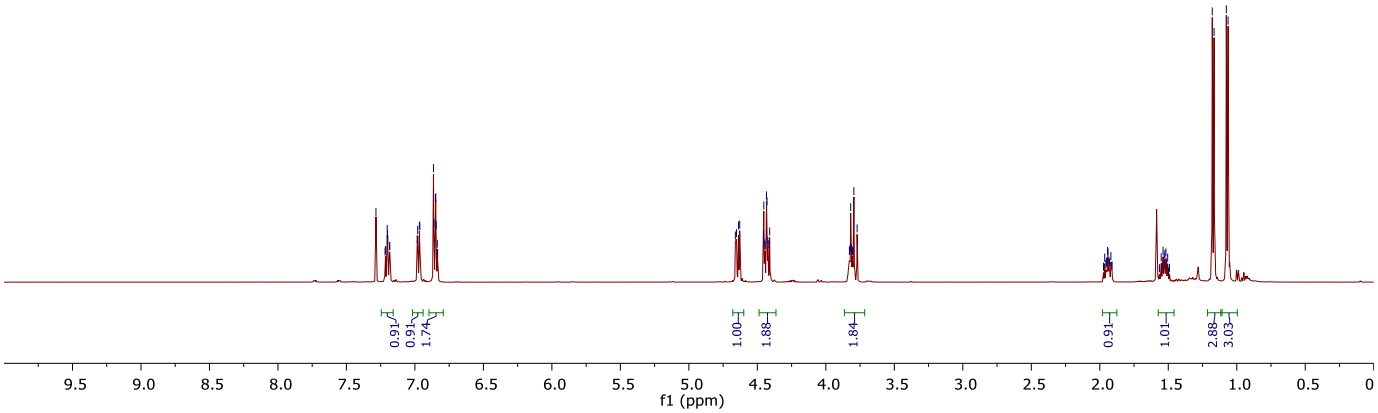

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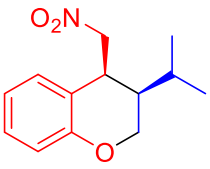
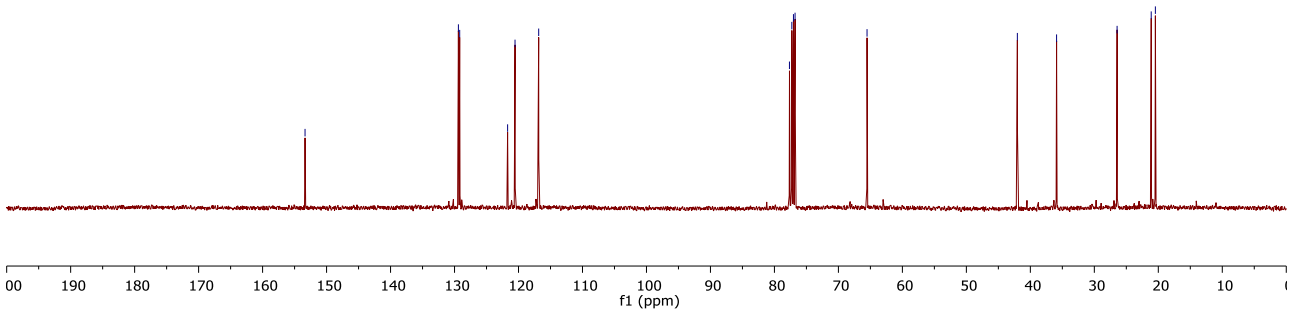


5c



==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-201-rm-5%.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 10 uL
Data File Name	: 1-rp-201-rm-5%.lcd
Method File Name	: ChiralPak AD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 3/20/2018 9:43:40 AM
Data Processed	: 3/20/2018 10:58:45 AM

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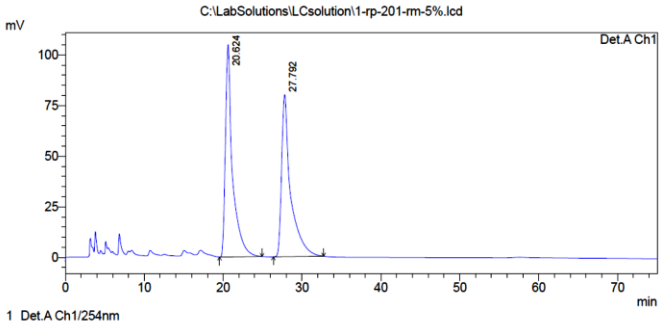

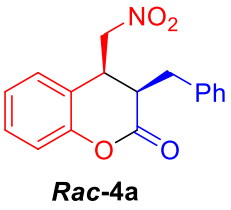

***Rac*-4a**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.624	6560502	104916	50.867	56.718
2	27.792	6336783	80063	49.133	43.282
Total		12897285	184979	100.000	100.000

HPLC of racemic **4a**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-202-chiral-5%.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 10 uL
Data File Name	: 1-rp-202-chiral-5%.lcd
Method File Name	: ChiralPak AD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
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Data Processed	: 3/20/2018 12:39:27 PM

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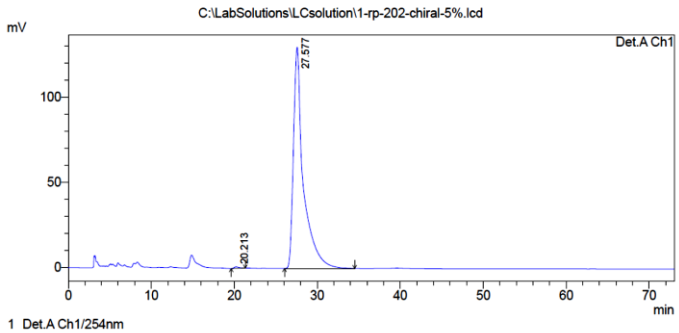

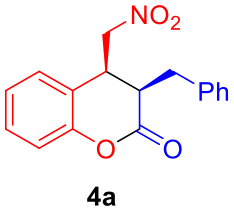

4a

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.213	38315	923	0.356	0.706
2	27.577	10713171	129808	99.644	99.294
Total		10751485	130730	100.000	100.000

HPLC of **4a**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-340-pure-od.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-340-pure-od.lcd
Method File Name	: ChiralCel OD-H-10%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 5/21/2018 1:39:47 PM
Data Processed	: 5/21/2018 2:26:55 PM

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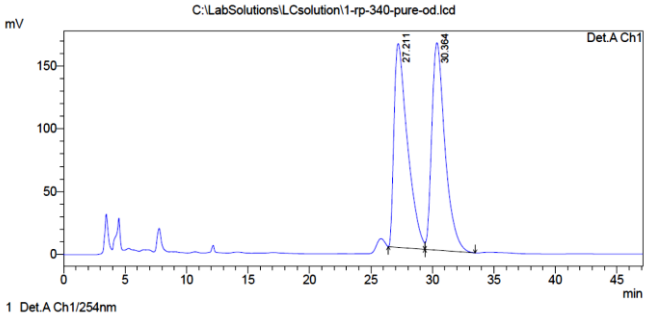

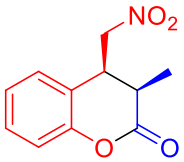

***Rac*-4b**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.211	12317477	162001	49.889	49.552
2	30.364	12372242	164932	50.111	50.448
Total		24689719	326933	100.000	100.000

HPLC of racemic **4b**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-496-pure-1.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-496-pure-1.lcd
Method File Name	: ChiralCel OD-H-10%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 6/9/2018 12:02:52 PM
Data Processed	: 6/9/2018 12:45:59 PM

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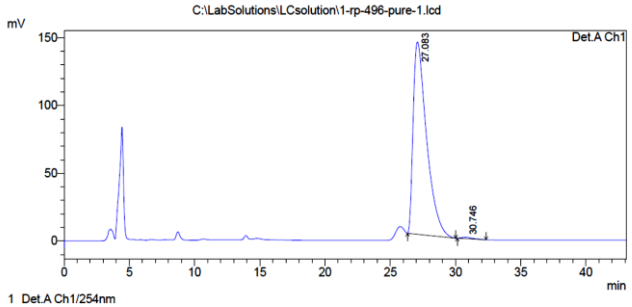

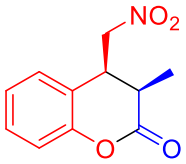

4b

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.083	10148527	142067	99.422	99.282
2	30.746	58987	1027	0.578	0.718
Total		10207514	143094	100.000	100.000

HPLC of **4b**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-461-0d.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-461-0d.lcd
Method File Name	: ChiralCel OD-H-10%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
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Data Processed	: 5/21/2018 11:46:11 AM

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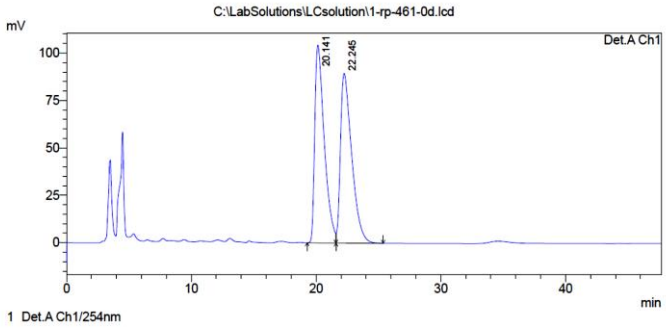

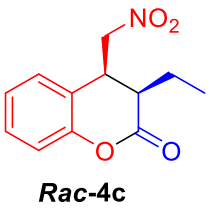

***Rac*-4c**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.141	5524410	104319	49.659	53.818
2	22.245	5600320	89519	50.341	46.182
Total		11124731	193838	100.000	100.000

HPLC of racemic **4c**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-462.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-462.lcd
Method File Name	: ChiralCel OD-H-10%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 5/21/2018 11:51:46 AM
Data Processed	: 5/21/2018 12:29:17 PM

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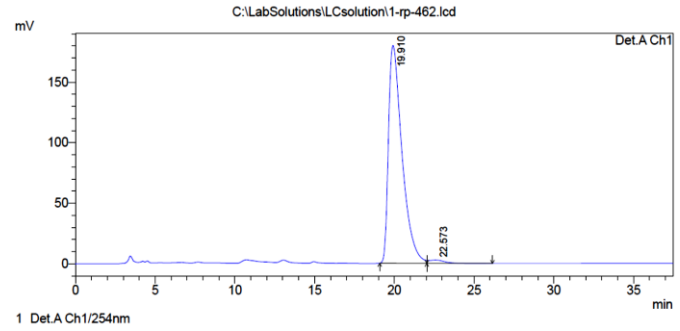

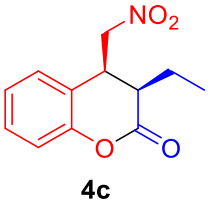

4c

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.910	10614938	180073	98.211	98.507
2	22.573	193371	2730	1.789	1.493
Total		10808309	182803	100.000	100.000

HPLC of **4c**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-394-rm.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-394-rm.lcd
Method File Name	: ChiralPak AD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 4/30/2018 9:20:16 AM
Data Processed	: 4/30/2018 10:13:04 AM

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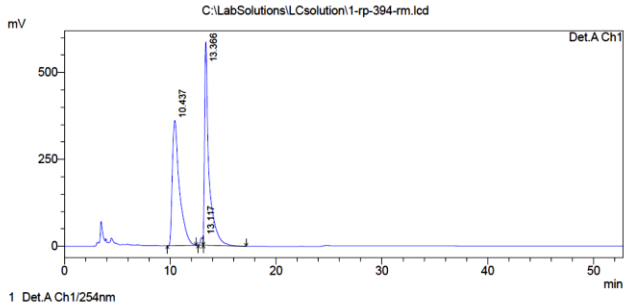

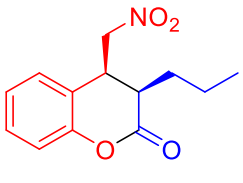

***Rac*-4d**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.437	16921632	360658	49.376	37.182
2	13.117	374017	24086	1.091	2.483
3	13.366	16975484	585232	49.533	60.335
Total		34271133	969976	100.000	100.000

HPLC of racemic **4d**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-395-pure.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-395-pure.lcd
Method File Name	: ChiralPak AD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 4/30/2018 10:23:43 AM
Data Processed	: 4/30/2018 10:46:37 AM

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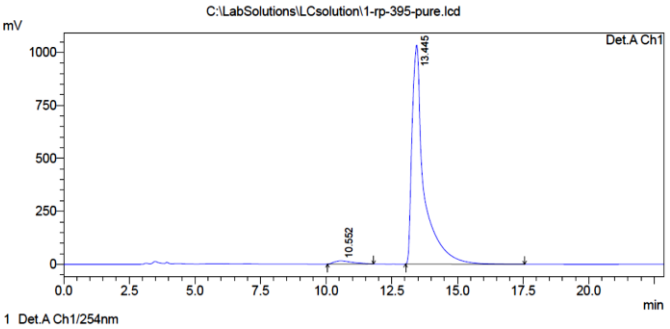

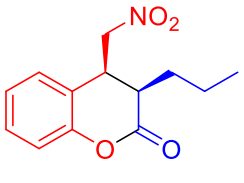

4d

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.552	727473	15341	2.187	1.464
2	13.445	32543555	1032892	97.813	98.536
Total		33271029	1048234	100.000	100.000

HPLC of **4d**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-172-racemic.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 10 uL
Data File Name	: 1-rp-172-racemic.lcd
Method File Name	: ChiralPak IC-10.0%-1.0 mL-254nm-60MINS.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 2/20/2018 12:19:55 PM
Data Processed	: 2/20/2018 1:47:58 PM

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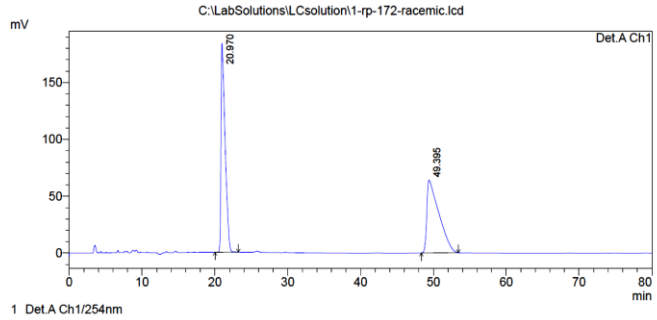

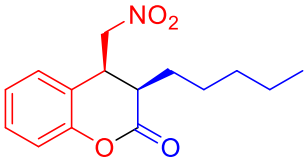

***Rac*-4e**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.970	7131886	183773	49.172	74.138
2	49.395	7372126	64105	50.828	25.862
Total		14504012	247878	100.000	100.000

HPLC of racemic **4e**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-sj-115-10%chiral.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-sj-115-10%chiral.lcd
Method File Name	: ChiralPak IC-10%-1.0 mL-254nm-60mins.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 4/26/2018 12:56:46 PM
Data Processed	: 4/26/2018 2:07:01 PM

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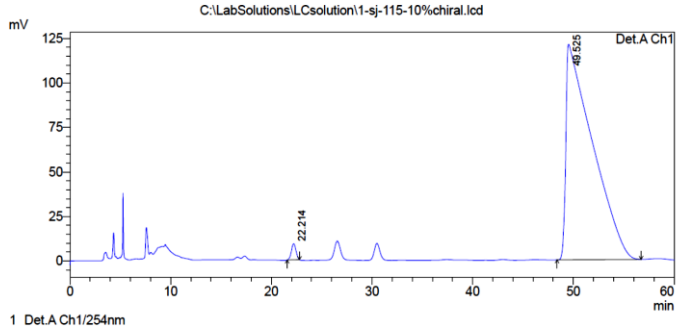

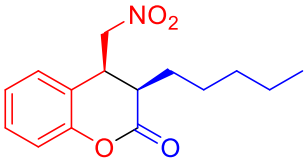

4e

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.214	286827	9048	1.276	6.955
2	49.525	22183712	121032	98.724	93.045
Total		22470539	130079	100.000	100.000

HPLC of **4e**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-354-rm.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-354-rm.lcd
Method File Name	: ChiralPak AD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 4/17/2018 3:53:12 PM
Data Processed	: 4/17/2018 4:11:45 PM

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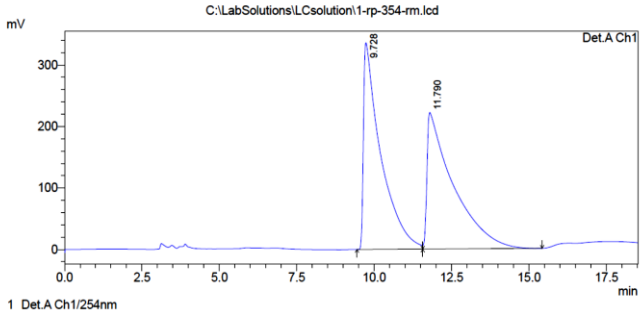

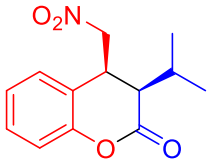

***Rac*-4f**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.728	12949724	336144	49.866	60.206
2	11.790	13019454	222180	50.134	39.794
Total		25969178	558325	100.000	100.000

HPLC of racemic **4f**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-355-pure-chiral.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-355-pure-chiral.lcd
Method File Name	: ChiralPak AD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 4/17/2018 4:13:27 PM
Data Processed	: 4/17/2018 4:31:35 PM

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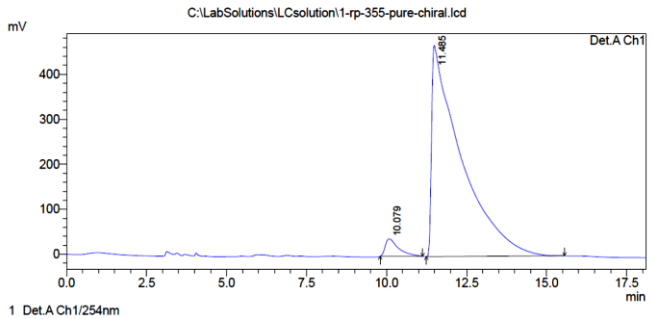

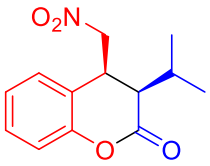

4f

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.079	1122671	38926	3.601	7.659
2	11.485	30051864	469335	96.399	92.341
Total		31174535	508261	100.000	100.000

HPLC of **4f**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-RP-472-OD.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-RP-472-OD.lcd
Method File Name	: ChiralPak OD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 5/23/2018 2:48:34 PM
Data Processed	: 5/23/2018 3:21:19 PM

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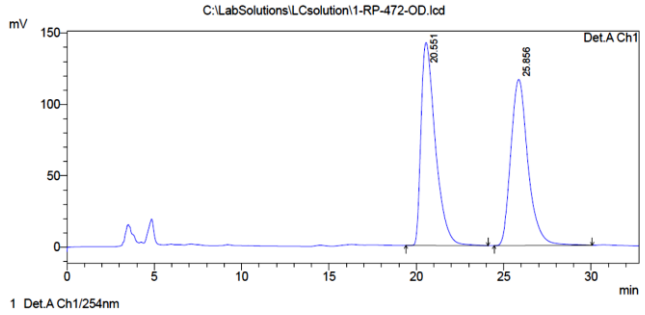

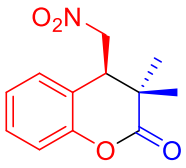

***Rac*-4g**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.551	8108928	142185	50.378	54.979
2	25.856	7987261	116432	49.622	45.021
Total		16096190	258617	100.000	100.000

HPLC of racemic **4g**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-RP-473.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-RP-473.lcd
Method File Name	: ChiralPak OD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 5/23/2018 3:22:22 PM
Data Processed	: 5/23/2018 3:56:43 PM

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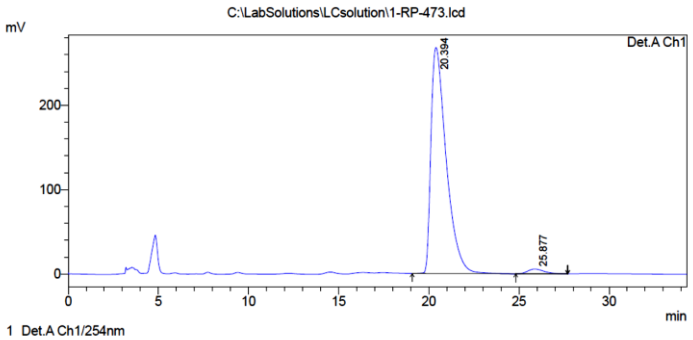

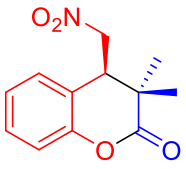

4g

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.394	15786372	268018	97.809	97.925
2	25.877	353603	5678	2.191	2.075
Total		16139974	273696	100.000	100.000

HPLC of **4g**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-RP-492-RM.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-RP-492-RM.lcd
Method File Name	: ChiralPak OD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 5/30/2018 8:55:11 AM
Data Processed	: 5/30/2018 9:49:28 AM

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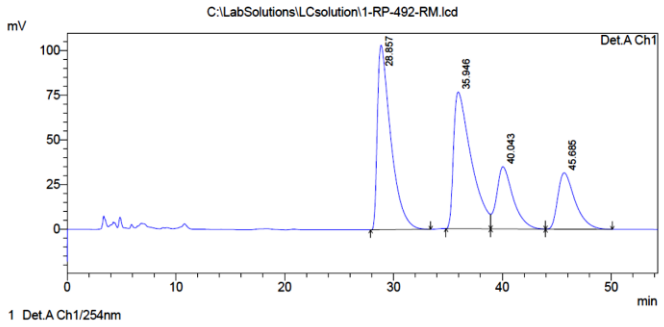

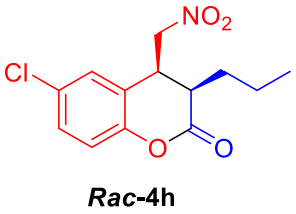

***Rac*-4h**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.857	8851494	103157	35.965	41.969
2	35.946	8604772	76372	34.962	31.072
3	40.043	3681464	34752	14.958	14.139
4	45.685	3473835	31511	14.115	12.820
Total		24611564	245792	100.000	100.000

HPLC of racemic **4h**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-RP-493.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-RP-493.lcd
Method File Name	: ChiralPak OD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 5/30/2018 9:53:48 AM
Data Processed	: 5/30/2018 10:53:41 AM

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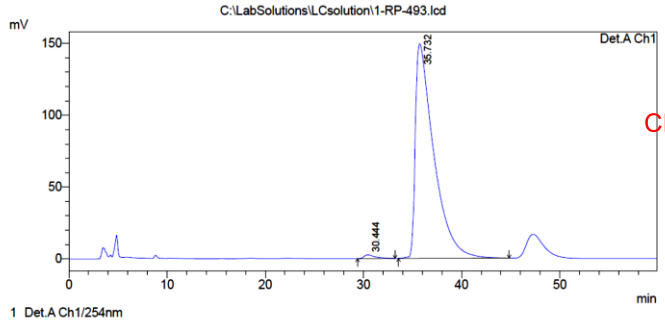

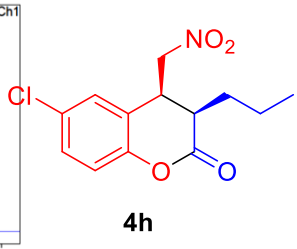

4h

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.444	202908	2564	1.030	1.687
2	35.732	19505569	149400	98.970	98.313
Total		19708477	151964	100.000	100.000

HPLC of **4h**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-618.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-618.lcd
Method File Name	: ChiralPak IC-10%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/9/2018 11:03:38 AM
Data Processed	: 7/9/2018 11:42:44 AM

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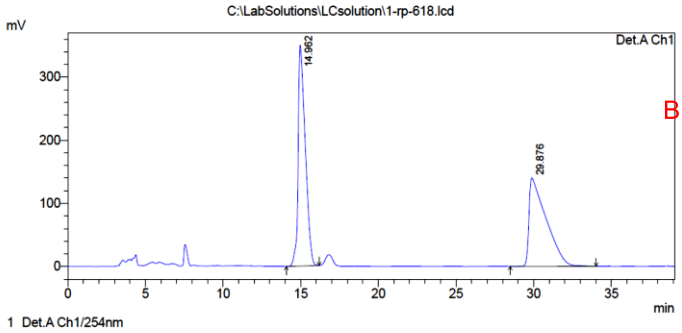

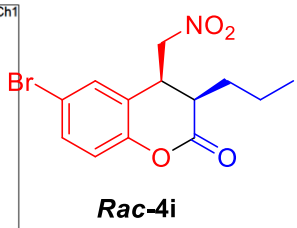

***Rac*-4i**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.962	11157225	349837	50.756	71.382
2	29.876	10825062	140253	49.244	28.618
Total		21982288	490090	100.000	100.000

HPLC of racemic **4i**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-602.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-602.lcd
Method File Name	: ChiralPak IC-10%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/9/2018 11:43:42 AM
Data Processed	: 7/9/2018 12:31:26 PM

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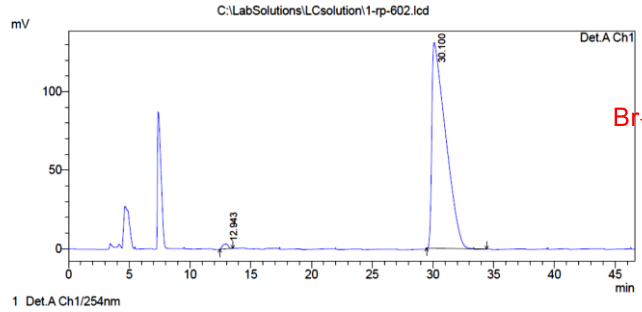

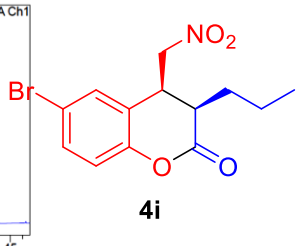

4i

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.943	99329	3122	0.949	2.328
2	30.100	10362704	130991	99.051	97.672
Total		10462033	134113	100.000	100.000

HPLC of **4i**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-RP-603-5% ADH.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-RP-603-5% ADH.lcd
Method File Name	: ChiralPak AD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/5/2018 9:35:31 AM
Data Processed	: 7/5/2018 10:33:05 AM

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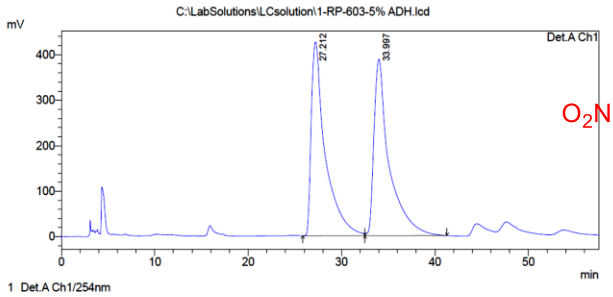

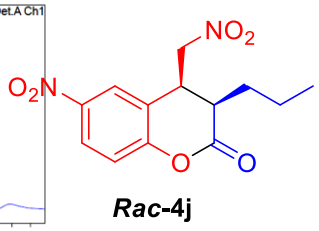

***Rac*-4j**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.212	44348137	426256	50.207	52.337
2	33.997	43981666	388182	49.793	47.663
Total		88329804	814437	100.000	100.000

HPLC of racemic **4j**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-RP-604-5% ADH.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-RP-604-5% ADH.lcd
Method File Name	: ChiralPak AD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/5/2018 10:35:35 AM
Data Processed	: 7/5/2018 11:33:02 AM

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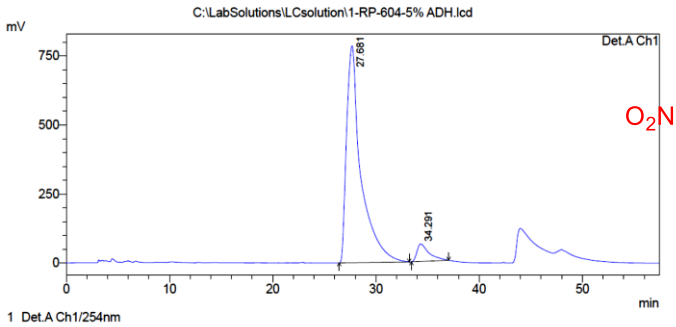

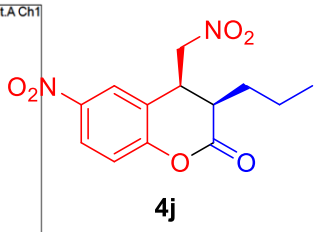

4j

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.681	76094791	785830	93.625	92.533
2	34.291	5181673	63409	6.375	7.467
Total		81276464	849240	100.000	100.000

HPLC of **4j**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-518-repeat-5.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-518-repeat-5.lcd
Method File Name	: ChiralPak OD-H-5%-1.0 mL-254nm-60min.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 6/9/2018 2:32:31 PM
Data Processed	: 6/27/2018 4:55:18 PM

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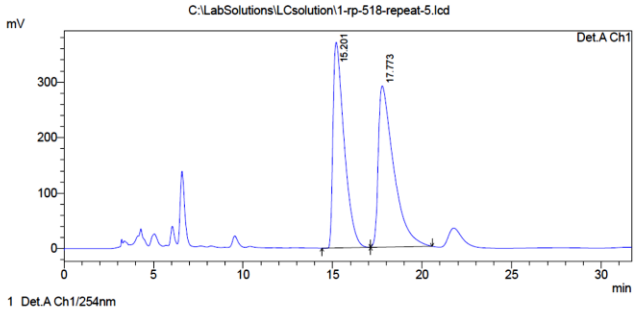

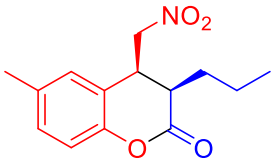

***Rac*-4k**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.201	16038108	370536	47.939	56.064
2	17.773	17417468	290385	52.061	43.936
Total		33455575	660921	100.000	100.000

HPLC of racemic **4k**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-519-5%-odh.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-519-5%-odh.lcd
Method File Name	: ChiralPak OD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 6/27/2018 5:04:39 PM
Data Processed	: 6/27/2018 5:30:08 PM

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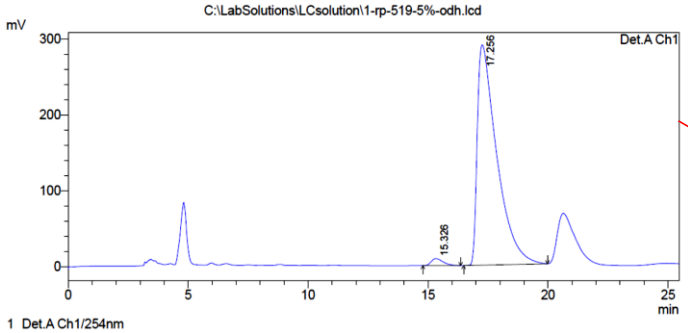
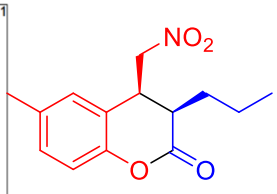




4k

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.326	323795	9361	1.935	3.123
2	17.256	16405787	290371	98.065	96.877
Total		16729582	299732	100.000	100.000

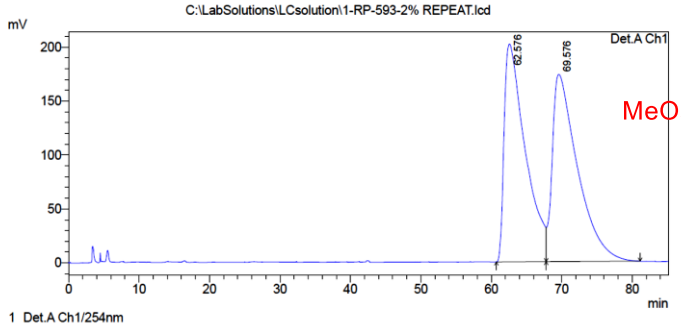
HPLC of **4k**

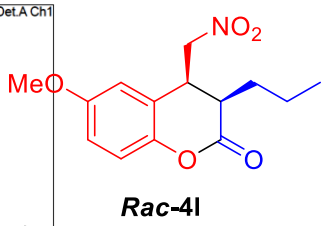
==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-RP-593-2% REPEAT.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-RP-593-2% REPEAT.lcd
Method File Name	: ChiralPak OD-H-2%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/3/2018 10:52:12 AM
Data Processed	: 7/3/2018 12:17:21 PM

<Chromatogram>





***Rac*-4l**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	62.576	41872826	202037	49.173	53.788
2	69.579	43281006	173579	50.827	46.212
Total		85153831	375616	100.000	100.000

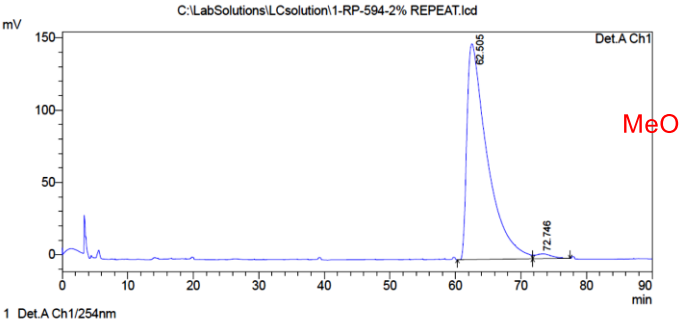
HPLC of racemic **4l**

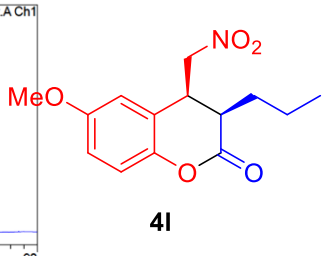
==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-RP-594-2% REPEAT.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-RP-594-2% REPEAT.lcd
Method File Name	: ChiralPak OD-H-2%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/3/2018 12:18:59 PM
Data Processed	: 7/3/2018 2:12:17 PM

<Chromatogram>





4l

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	62.505	32092247	149044	98.248	97.823
2	72.746	572364	3316	1.752	2.177
Total		32664611	152360	100.000	100.000

HPLC of **4l**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-618.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-618.lcd
Method File Name	: ChiralPak IC-10%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/9/2018 11:03:38 AM
Data Processed	: 7/9/2018 11:42:44 AM

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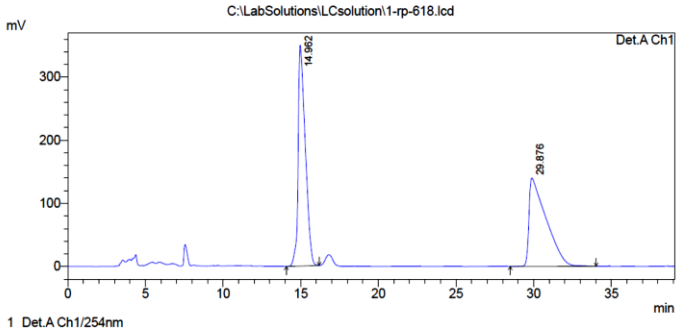

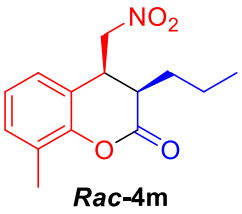

***Rac*-4m**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.962	11157225	349837	50.756	71.382
2	29.876	10825062	140253	49.244	28.618
Total		21982288	490090	100.000	100.000

HPLC of racemic **4m**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-602.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-602.lcd
Method File Name	: ChiralPak IC-10%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/9/2018 11:43:42 AM
Data Processed	: 7/9/2018 12:31:26 PM

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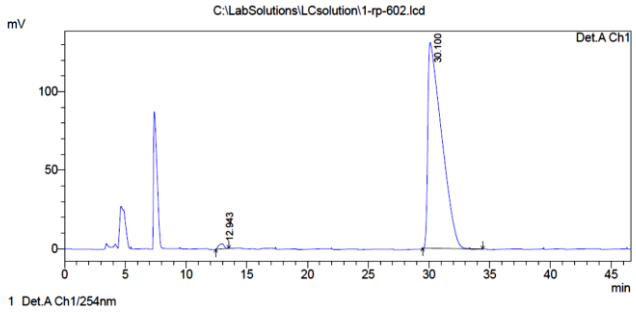

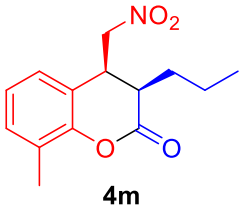

4m

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.943	99329	3122	0.949	2.328
2	30.100	10362704	130991	99.051	97.672
Total		10462033	134113	100.000	100.000

HPLC of **4m**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-599-adh.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-599-adh.lcd
Method File Name	: ChiralPak AD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/3/2018 4:06:53 PM
Data Processed	: 7/3/2018 4:29:31 PM

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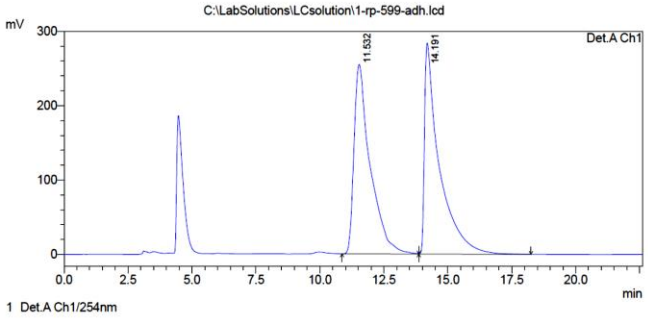

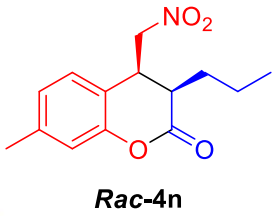

***Rac*-4n**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.532	11224729	254844	49.645	47.314
2	14.191	11385223	283774	50.355	52.686
Total		22609952	538618	100.000	100.000

HPLC of racemic **4n**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-600.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-600.lcd
Method File Name	: ChiralPak AD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/3/2018 4:31:18 PM
Data Processed	: 7/3/2018 4:52:51 PM

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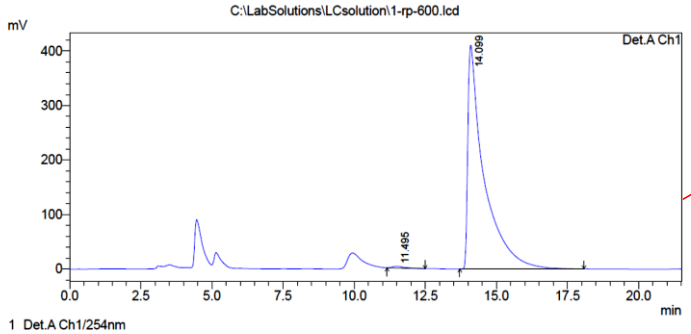
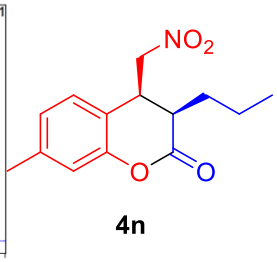




4n

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.495	89380	2952	0.548	0.714
2	14.099	16209677	410359	99.452	99.286
Total		16299057	413311	100.000	100.000

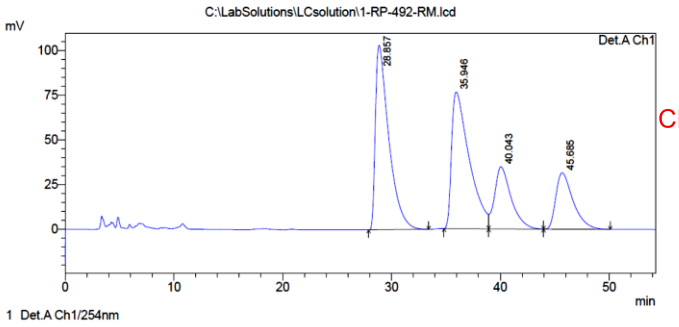
HPLC of **4n**

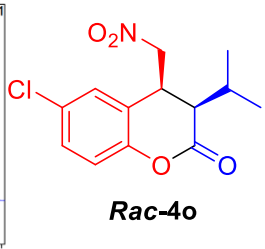
==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-RP-492-RM.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-RP-492-RM.lcd
Method File Name	: ChiralPak OD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 5/30/2018 8:55:11 AM
Data Processed	: 5/30/2018 9:49:28 AM

<Chromatogram>





***Rac*-4o**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.857	8851494	103157	35.965	41.969
2	35.946	8604772	76372	34.962	31.072
3	40.043	3681464	34752	14.958	14.139
4	45.685	3473835	31511	14.115	12.820
Total		24611564	245792	100.000	100.000

HPLC of racemic **4o**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-RP-493.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-RP-493.lcd
Method File Name	: ChiralPak OD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 5/30/2018 9:53:48 AM
Data Processed	: 5/30/2018 10:53:41 AM

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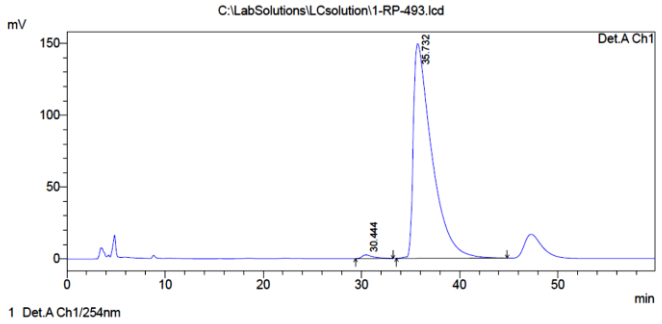

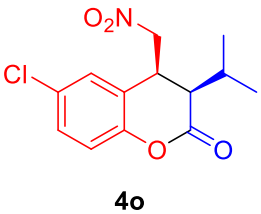

4o

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.444	202908	2564	1.030	1.687
2	35.732	19505569	149400	98.970	98.313
Total		19708477	151964	100.000	100.000

HPLC of **4o**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-585.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-585.lcd
Method File Name	: ChiralPak OD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 6/28/2018 2:15:32 PM
Data Processed	: 6/28/2018 3:25:38 PM

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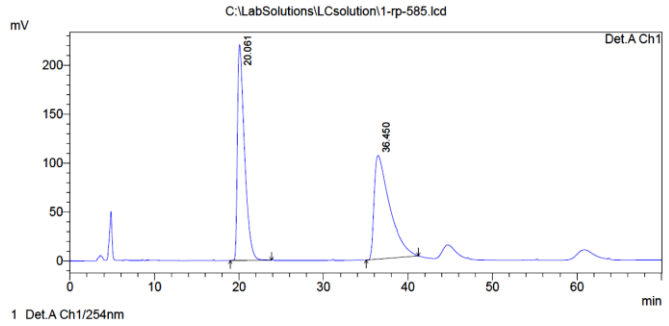

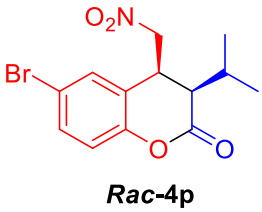

***Rac*-4p**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.061	12867645	220496	48.638	67.585
2	36.450	13588475	105755	51.362	32.415
Total		26456121	326251	100.000	100.000

HPLC of racemic **4p**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-586.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-586.lcd
Method File Name	: ChiralPak OD-H-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 6/28/2018 3:26:02 PM
Data Processed	: 6/28/2018 4:36:58 PM

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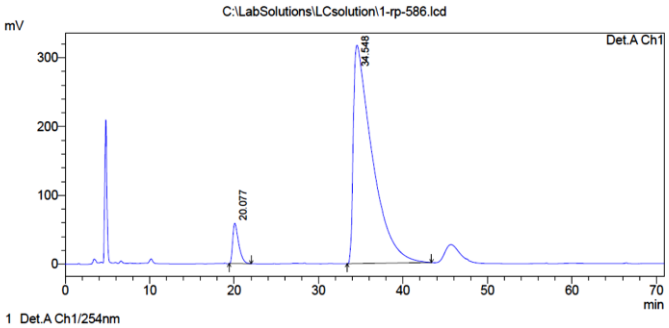
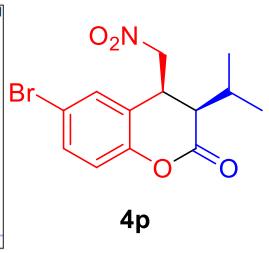




4p

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.077	2871655	58580	5.464	15.585
2	34.548	49685998	317293	94.536	84.415
Total		52557653	375873	100.000	100.000

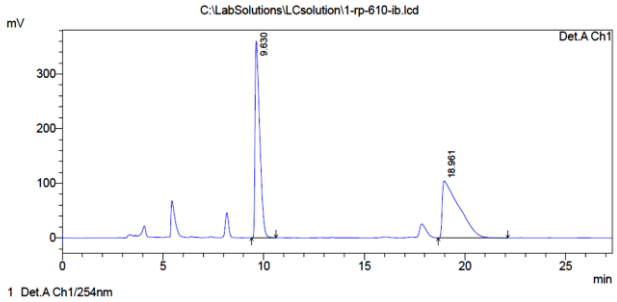
HPLC of **4p**

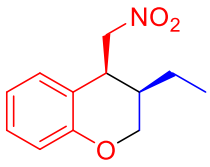
==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-610-ib.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-610-ib.lcd
Method File Name	: ChiralPak IB-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/6/2018 10:02:35 AM
Data Processed	: 7/6/2018 10:29:55 AM

<Chromatogram>





***Rac*-5a**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.630	5810362	359992	49.037	77.507
2	18.961	6038543	104474	50.963	22.493
Total		11848905	464467	100.000	100.000

HPLC of racemic **5a**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-611-ib.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-611-ib.lcd
Method File Name	: ChiralPak IB-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/6/2018 10:30:57 AM
Data Processed	: 7/6/2018 10:59:06 AM

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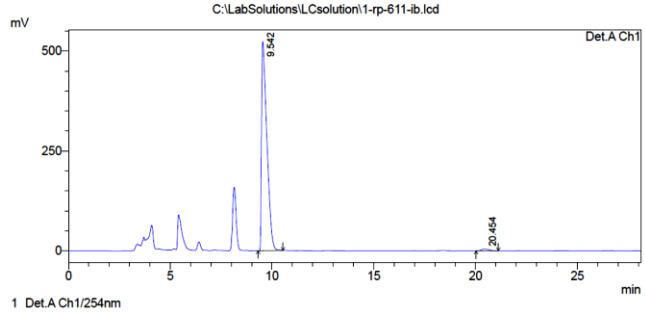
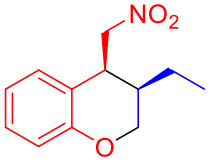




5a

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.542	9570677	523509	98.800	99.138
2	20.454	116248	4554	1.200	0.862
Total		9686925	528063	100.000	100.000

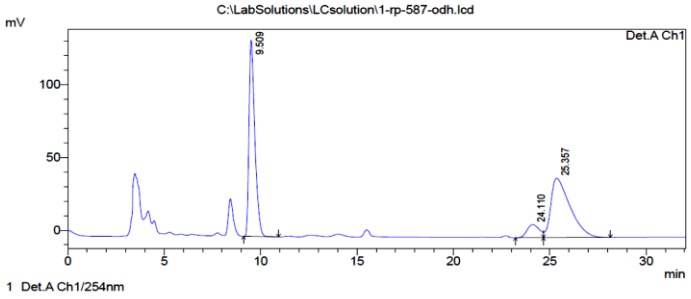
HPLC of **5a**

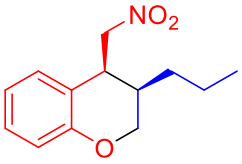
==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-587-odh.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-587-odh.lcd
Method File Name	: ChiralCel OD-H-10%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 6/29/2018 3:18:31 PM
Data Processed	: 6/29/2018 3:50:35 PM

<Chromatogram>





***Rac*-5b**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.509	2839942	134725	46.817	72.984
2	24.110	399956	9056	6.593	4.906
3	25.357	2826158	40814	46.590	22.110
Total		6066055	184595	100.000	100.000

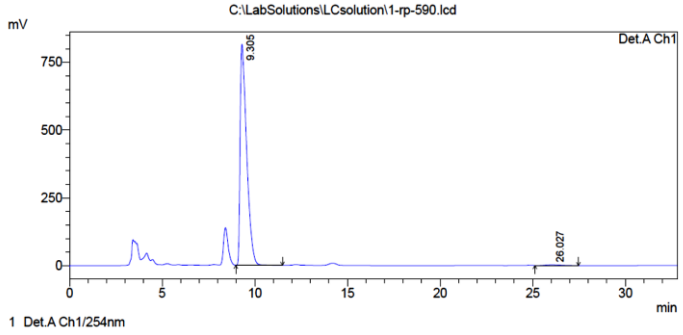
HPLC of racemic **5b**

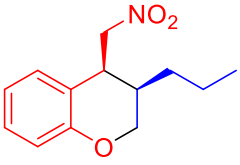
==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-590.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-590.lcd
Method File Name	: ChiralCel OD-H-10%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 6/29/2018 3:53:12 PM
Data Processed	: 6/29/2018 4:26:03 PM

<Chromatogram>





5b

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.305	19962577	815756	99.225	99.640
2	26.027	155970	2951	0.775	0.360
Total		20118547	818707	100.000	100.000

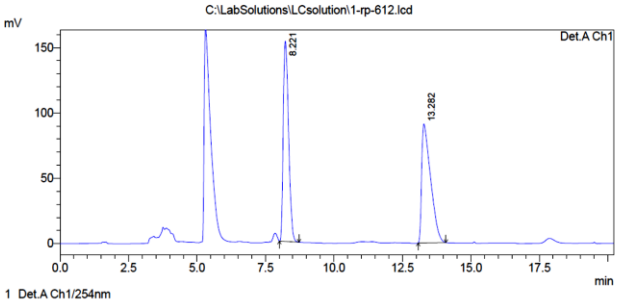
HPLC of **5b**

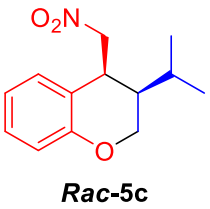
==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-612.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-612.lcd
Method File Name	: ChiralPak IB-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/6/2018 10:59:28 AM
Data Processed	: 7/6/2018 11:19:44 AM

<Chromatogram>





***Rac*-5c**

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.221	2067917	153264	50.034	62.744
2	13.282	2065130	91003	49.966	37.256
Total		4133047	244267	100.000	100.000

HPLC of racemic **5c**

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\1-rp-613.lcd

Acquired by	: Admin
Sample Name	:
Sample ID	:
Vail #	:
Injection Volume	: 1 uL
Data File Name	: 1-rp-613.lcd
Method File Name	: ChiralPak IB-5%-1.0 mL-254nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/6/2018 11:22:25 AM
Data Processed	: 7/6/2018 11:42:46 AM

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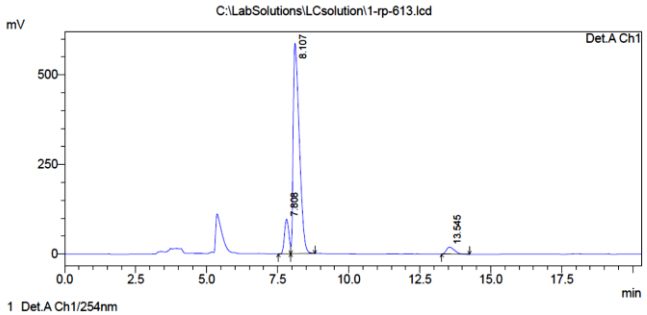

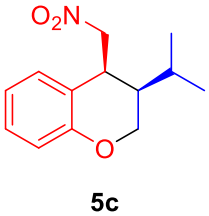

5c

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.808	1034143	96727	10.147	13.766
2	8.107	8776638	586434	86.119	83.460
3	13.545	380568	19492	3.734	2.774
Total		10191350	702654	100.000	100.000

HPLC of **5c**