Enantioselective Thiolysis and Aminolysis of Cyclic Anhydrides Using a Chiral-Diamine-Derived Thiourea Catalyst

Jae Ho Shim, Sung Joo Park, Byung Kook Ahn, Ji Yeon Lee, Hyeon Soo Kim and Deok-Chan Ha**

Department of Anatomy, Korea University College of Medicine, 46, Gaeunsa 2-gil, Seongbuk-gu, Seoul, 02842, Republic of Korea

E-mail: shimjh3000@korea.ac.kr

Department of Chemistry, Korea University , 145 Anam-ro Seongbuk-gu , Seoul 02841, Korea

E-mail: dechha@korea.ac.kr

Supporting Information

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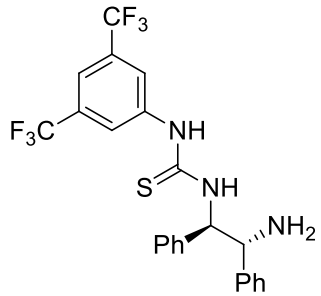
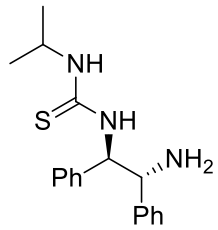
1. Compound Characterization Data

1-[(1*R*,2*R*)-2-Amino-1,2-diphenylethyl]-3-[3,5-bis(trifluoromethyl)phenyl]thiourea(1a)



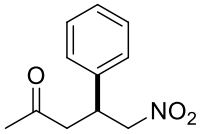
[α]$_D^{25}$ +13.5 (*c* 1.0, CH_3Cl); ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.25 (s, 2H), 7.78 (s, 1H),7.32~7.15 (m, 13H), 5.99 (d, *J* = 3 Hz, 1H), 4.77 (d, *J* = 3 Hz, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-*d6*) δ 180.51, 143.26, 142.48, 130.82, 130.56, 128.51, 128.29 127.66, 127.55, 127.38, 124.78, 122.62, 121.34, 116.08, 63.66, 59.94 ppm; IR (KBr) 3305, 3032, 2963, 1652,1601, 1557, 1383, 1277, 1262, 803, 700 cm^{-1}; HRMS (FAB+) for $C_{23}H_{19}F_6N_3S$ $[M+H]^+$ Calcd: 484.1282, Found: 484.1254;

1-[(1*R*,2R)-2-Amino-1,2-diphenylethyl]-3-isopropylthiourea (1b)



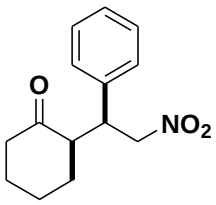
[α]$_D^{25}$ +62.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37~7.21 (m, 11H), 6.04 (br s, 1H), 5.09(br s, 1H), 4.30 (s, 1H), 4.15 (br s, 1H), 1.73 (s, 2H), 1.09~1.03 (m, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.68, 142.06, 129.00, 128.75, 127.88, 126.91,64.12, 60.55, 46.39, 22.70 ppm; IR (KBr) 3335, 2966, 1527, 1326, 1273, 966, 695, 514 cm^{-1}; HRMS (ESI+) for $C_{18}H_{23}N_3S$ $[M+H]^+$ Calcd: 314.1691, Found: 314.1627;

(*S*)-5-Nitro-4-phenylpentan-2-one (2a)[1]



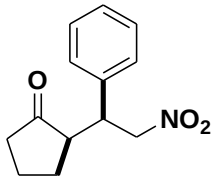
$[\alpha]_D^{20}$ +4.5 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35~7.21 (m, 5H), 4.72~4.67 (dd, *J* = 12.3, 7.0 Hz, 1H), 4.63~4.58 (dd, *J* = 12.3, 7.6 Hz, 1H), 4.05~3.98 (m, 1H), 2.92 (d, *J* = 7.0 Hz, 2H), 2.13 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.67, 138.99, 129.30, 128.14, 127.59, 79.67, 46.33, 39.23, 30.65 ppm; IR (KBr) 3064, 3035, 2968, 2948, 2919, 2902, 1714, 1548, 1384, 1361, 1163, 758, 696, 548 cm^{-1}; LRMS (FAB^+) for $C_{11}H_{13}NO_3$ $[M+H]^+$ Calcd: 208, Found: 208; HPLC [Chiralcel AD-H, hexane/ 2-propanol = 4/96, flow rate = 1.0 mL/min, λ = 254 nm, retention times: (major) 28.2 min, (minor) 38.3 min];

(*R*)-2-[(*S*)-2-Nitro-1-phenylethyl]cyclohexanone (2b)[1,3]



$[\alpha]_D^{26}$ +37.5 (*c* 0.100, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.34-7.23 (m, 3H), 7.16 (d, *J* = 7 Hz, 2H), 4.95 (dd, *J* = 12, 5 Hz, 1H), 4.63 (dd, *J* = 12, 10 Hz, 1H), 3.76 (dt, *J* = 10, 5 Hz, 1H), 2.68 (m, *J* = 11, 9, 8 Hz, 1H), 2.49-2.33 (m, 2H), 2.10-2.04 (m, 1H), 1.79-1.52 (m, 4H), 1.52-1.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 211.9, 137.6, 128.8, 128.1, 127.7, 78.8, 52.4, 43.8, 42.7, 33.1, 28.5, 24.9, IR(KBr) 3855.1, 3650.7, 3448.2, 2921.1, 1700.9, 1552.4, 1382.7, 1243.9, 1130.1, 696.2, 561.2 cm^{-1}; LRMS(FAB+) for $C_{14}H_{17}NO_3$[M+H]+ Calcd:247, Found: 247; chiral-phase HPLC, AS-H column (*i*-PrOH/hexane = 20:80), 254 nm, flow rate = 0.5 ml/min, t_r (major) = 19.74 min, t_r (minor) = 27.57 min.

(*R*)-2-[(*S*)-2-Nitro-1-phenylethyl]cyclopentanone(2c)[1]

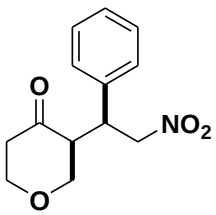


$[\alpha]_D^{23}$ +12.1(*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.34-7.23 (m, 3H), 7.20-7.15 (m, 2H), 5.37-5.30 (m, 1H), 4.71 (dd, *J* = 13, 10 Hz, 1H), 3.76-3.65 (m, 1H), 2.44-2.31 (m, 2H), 2.19-2.06 (m, 1H) , 1.94-1.83 (m, 2H), 1.76-1.66 (m, 1H), 1.55-1.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 218.5, 137.6, 128.8, 127.9, 78.2, 50.4, 44.1, 38.6, 28.3, 20.2,

IR (KBr) 3363.4, 2921.7, 1731.8, 1552.4, 1378.9, 1124.3 cm^{-1}; LRMS(FAB+) for

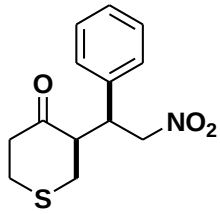
$C_{13}H_{15}NO_3$[M+H]+ Calcd: 234, Found: 234; chiral-phase HPLC, AS-H column (*i*-PrOH/hexane = 20:80), 254 nm, flow rate = 0.5 ml/min, t_r (major) = 22.74 min, t_r (minor) = 30.47 min.

(*S*)-3-[(*S*)-2-Nitro-1-phenylethyl]tetrahydropyran-4-one (2d)[3]



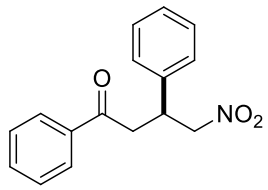
$[\alpha]_D^{23}$ +14.4 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.37-7.26 (m, 3H), 7.21-7.16 (m, 2H), 4.96 (dd, *J* = 12, 5 Hz, 1H), 4.64 (dd, *J* = 12, 10 Hz, 1H), 4.20-4.10 (m, 1H), 3.87-3.68 (m, 2H), 3.70 (dd, *J* = 11, 5 Hz, 1H), 3.27 (dd, *J* = 11, 10 Hz, 1H), 2.93-2.83 (m, 1H), 2.73-2.61 (m, 1H), 2.60-2.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 207.4, 136.1, 128.9, 127.8, 78.6, 71.5, 68.9, 53.2, 42.9, 41.2, 29.6; IR (KBr) 3278.5, 2923.7, 2291.1, 1735.7, 1457.9, 1243.9, 1087.7 cm^{-1}; chiral-phase HPLC, AS-H column (*i*-PrOH/hexane = 50:50), 254 nm, flow rate = 0.5 ml/min, t_r (major) = 19.29 min, t_r (minor) = 25.53 min.

(*R*)-3-[(*S*)-2-Nitro-1-phenylethyl]tetrahydrothiopyran-4-one (2e)[3]



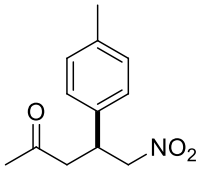
[α]$_D^{23}$ +21.9 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.37-7.26 (m, 3H), 7.21-7.16 (m, 2H), 4.96 (dd, *J* = 12, 5 Hz, 1H), 4.64 (dd, *J* = 12, 10 Hz, 1H), 4.20-4.10 (m, 1H), 3.87-3.68 (m, 2H), 3.70 (dd, *J* = 11, 5 Hz, 1H), 3.27 (dd, J = 11, 10 Hz, 1H), 2.93-2.83 (m, 1H), 2.73-2.61 (m, 1H), 2.60-2.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 209.5, 136.5, 129.3, 128.3, 128.2, 78.6, 55.0, 44.6, 53.5, 35.1, 31.6; IR (KBr) 3367.2, 1646.9, 1376.9, 1093.4 cm^{-1}; chiral-phase HPLC, AS-H column (*i*-PrOH/hexane = 50:50), 254 nm, flow rate = 0.5 ml/min, t_r (major) = 18.40 min, t_r (minor) = 26.84 min.

(*S*)-4-Nitro-1,3-diphenyl-butan-1-one (2f)



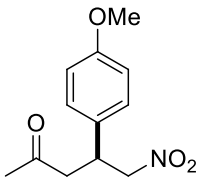
[α]$_D^{20}$ –18.5 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.91~7.92 (m, 2H), 7.59~7.26 (m, 8H), 4.85~4.81 (dd, *J* = 12.5, 6.7 Hz, 1H), 4.71~4.67 (dd, *J* = 12.5, 7.8 Hz, 1H), 4.26~4.20 (m, 1H), 3.51~3.46 (dd, *J* = 17.7, 6.4 Hz, 1H), 3.45~3.40 (dd, *J* = 17.7, 7.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.87, 139.15, 136.39, 133.60, 129.09, 128.77, 128.04, 127.90, 127.48, 79.58, 41.54, 39.30 ppm; IR (KBr) 3058, 3029, 2920, 1687, 1544, 1440, 1367, 1268, 1224, 1084, 988, 764, 703, 623, 559 cm^{-1}; LRMS (ESI^+) for $C_{16}H_{15}NO_3$ $[M+Na]^+$ Calcd: 292.1, Found: 292.1; HPLC [Chiralcel AD-H, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention times: (major) 12.8 min, (minor) 17.4 min];

(*S*)-5-Nitro-4-(p-tolyl)pentan-2-one (3a) [7]



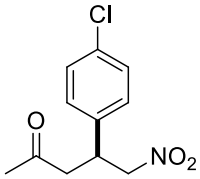
$[\alpha]_D^{20}$ +4.7 (*c* 1.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.13~7.08 (m, 4H), 4.68~4.64 (dd, *J* = 12.3, 6.9 Hz, 1H), 4.58~4.54 (dd, *J* = 12.1, 7.7 Hz, 1H), 3.99~3.93 (m, 1H), 2.89 (d, *J* = 7.7 Hz, 1H), 2.31 (s, 3H), 2.10 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.57, 137.62, 135.76, 129.74, 127.24, 79.63, 46.22, 38.76, 30.41, 21.05 ppm; IR (KBr) 3056, 3029, 2976, 2944, 2924, 1717, 1551, 1378, 1365, 1163, 816, 544 cm^{-1}; LRMS (ESI^+) for $C_{12}H_{15}NO_3$ $[M+Na]^+$ Calcd: 244.1, Found: 244.2; HPLC [Chiralcel AS-H, hexane/2-pro panol = 80/20, flow rate = 1.0 mL/min, λ = 213 nm, retention times: (major) 13.1 min, (minor) 20.4 min];

(*S*)-4-(4-Methoxyphenyl)-5-nitropentan-2-one (3b) [7]



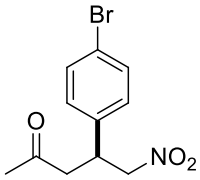
$[\alpha]_D^{20}$ –5.7 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.67~4.63 (dd, *J* = 12.3, 6.8 Hz, 1H), 4.57~4.53 (dd, *J* = 12.3, 7.8 Hz, 1H), 3.98~3.92 (m, 1H), 3.78 (s, 3H), 2.88 (d, *J* = 7.0, 2H), 2.11 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.55, 159.13, 130.67, 128.45, 114.44, 79.73, 55.26, 46.29, 38.42, 30.43 ppm; IR (KBr) 3028, 3002, 2960, 2901, 1715, 1550, 1517, 1260, 1180, 1033, 813,544cm^{-1}; LRMS (ESI^+) for $C_{12}H_{15}NO_4$ $[M+Na]^+$ Calcd: 260.1, Found: 260.1; HPLC [Chiralcel AS-H, hexane/2-propanol = 80/20, flow rate = 1.4 mL/min, λ = 213 nm, retention times: (major) 16.2 min, (minor) 37.9 min];

(*S*)-4-(4-Chlorophenyl)-5-nitropentan-2-one (3c) [7]



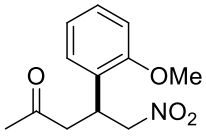
[α]$_D^{20}$ –2.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32~7.29 (m, 2H), 7.17~7.15 (m, 2H), 4.70~4.66 (dd, *J* = 12.4, 6.7 Hz, 1H), 4.59~4.55 (dd, *J* = 12.4, 7.9 Hz, 1H), 4.02~3.96 (m, 1H), 2.94~2.90 (dd, *J* = 18.5, 7.0 Hz, 1H), 2.89~2.85 (dd, *J* = 19.0, 7.0 Hz, 1H), 2.12 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.03, 137.35, 133.79, 129.26, 128.82, 79.19, 45.97, 38.40, 30.39 ppm; LRMS (ESI^+) for $C_{11}H_{12}ClNO_3$ $[M+Na]^+$ Calcd: 264.0, Found: 264.1; HPLC [Chiralcel AD-H, hexane/2-propanol = 5/95, flow rate = 1.0 mL/min, λ = 254 nm, retention times: (major) 14.1 min, (minor) 21.9 min]; R_f (SiO_2, EtOAc/*n*-hexane = 1/5) = 0.22

(*S*)-4-(4-Bromophenyl)-5-nitropentan-2-one (3d) [7]



[α]$_D^{20}$ –0.6 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.0 Hz, 2H), 7.10 (d, *J* = 7.0 Hz, 2H), 4.69~4.66 (dd, *J* = 12.5, 6.5 Hz, 1H), 4.59~4.55 (dd, *J* = 12.7, 7.5 Hz, 1H), 4.0~3.95 (m, 1H), 2.88 (d, *J* = 7.5 Hz, 2H), 2.12 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.04, 137.91, 132.20, 129.18, 121.85, 79.10, 45.91, 38.46, 30.38 ppm; LRMS (ESI^+) for $C_{11}H_{12}BrNO_3$ $[M+Na]^+$ Calcd: 308.0, Found: 308.0; HPLC [Chiralcel AD-H, hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 210 nm, retention times: (major) 10.9 min, (minor) 12.5 min];

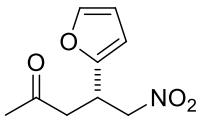
(*S*)-4-(2-Methoxyphenyl)-5-nitropentan-2-one (3e) [7]



[α]$_D^{20}$ +16.4 (*c* 1.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26~7.23 (m, 1H), 7.15~7.13

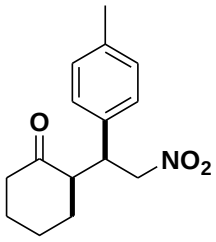
(m, 1H), 6.92~6.87 (m, 2H), 4.76~4.69 (m, 2H), 4.25~4.19 (m, 1H), 3.86 (s, 3H), 3.05~3.0 (dd, *J* = 18.0, 7.5 Hz, 1H), 2.98~2.93 (dd, *J* = 18.0, 7.0 Hz, 1H), 2.13 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.16, 157.09, 129.31, 129.01, 126.44, 120.94, 110.99, 77.85, 55.35, 44.52, 35.33, 30.25 ppm; LRMS(ESI$^+$) for $C_{12}H_{15}NO_4$[M+Na]$^+$Calcd: 260.1, Found: 260.1; HPLC [Chiralcel AD-H, hexane/2-propanol = 5/95, flow rate = 1.0 mL/min, λ = 254 nm, retention times: (major) 14.1 min, (minor) 21.9 min];

(*S*)-4-(Furan-2-yl)-5-nitropentan-2-one (3f)[7]



[α]$_D^{20}$ –8.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34~7.33 (dd, *J* = 1.8, 0.7 Hz, 1H), 6.30~6.29 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.14 (d, *J* = 3.2 Hz, 1H), 4.71~4.68 (dd, *J* = 12.6, 6.6 Hz, 1H), 4.67~4.64 (dd, *J* = 12.6, 6.6 Hz, 1H), 4.13~4.07 (m, 1H), 3.00~2.95 (dd, *J* = 16.7, 5.2 Hz, 1H), 2.93~2.87 (dd, *J* = 16.7, 6.0 Hz, 1H), 2.18 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.11, 151.69, 142.31, 110.50, 107.10, 77.07, 43.49, 32.89, 30.22 ppm; IR (flim) 3151, 3124, 2920, 1714, 1552, 1430, 1377, 1165, 1015, 741 cm^{-1}; LRMS (ESI$^+$) for $C_9H_{11}NO_4$ [M+Na]$^+$ Calcd: 220.1, Found: 220.1; HPLC [Chiralcel AD-H, hexane/2-pro panol = 94/6, flow rate = 1.0 mL/min, λ = 213 nm, retention times: (major) 10.5 min, (minor) 11.6 min];

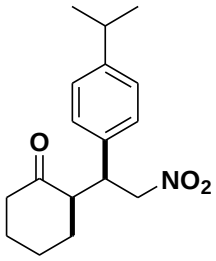
(*R*)-2-[(*S*)-1-(3-Methylphenyl)-2-nitroethyl]cyclohexanone(4a)[2]



[α]$_D^{23}$ +10.8 (*c* 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.12 (d, *J* = 8 Hz, 2H), 7.04 (d, *J* = 8 Hz, 2H), 4.91 (dd, *J* = 12, 5 Hz, 1H), 4.60 (dd, *J* = 12, 10 Hz, 1H), 3.72 (dt, *J* =

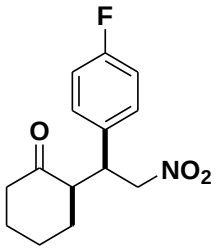
10, 5 Hz, 1H), 2.71-2.62 (m, 1H), 2.50-2.37 (m, 2H), 2.10 (s, 3H), 2.08 (m, 1H), 1.81-1.53 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.0, 137.4, 134.5, 129.5, 127.9, 78.9, 52.5, 43.5, 42.7, 33.1, 28.5, 24.9, 21.0; IR (KBr) 3286.2, 2925.6, 1704.8, 1552.4, 13789, 1130.1, 819.6 cm^{-1}; LRMS(FAB+) for $C_{15}H_{19}NO_3$ [M+H]+ Calcd: 262, Found: 262
chiral-phase HPLC, AD-H column (*i*-PrOH/hexane = 5:95), 254 nm, flow rate = 1 ml/min, t_r (major) = 10.54 min, t_r (minor) = 12.98 min.

(*R*)-2-[(*S*)-1-(4-Isopropylphenyl)-2-nitroethyl]cyclohexanone (4b)[4]



$[\alpha]_D^{23}$ +16.9 (*c* 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.16 (d, *J* = 8 Hz, 2H), 7.07 (d, *J* = 8 Hz, 2H), 4.91 (dd, *J* = 12, 4 Hz, 1H), 4.62 (dd, *J* = 12, 10 Hz, 1H), 3.76-3.70 (m, 1H), 2.88-2.85 (m, 1H), 2.71-2.65 (m, 1H), 2.49-2.38 (m, 2H), 2.09-2.04 (m, 1H), 1.81-1.58 (m, 5H), 1.22 (d, *J* = 7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 212.2, 148.2, 134.8, 127.9, 126.9, 78.9, 52.5, 43.4, 33.6, 29.6, 28.5, 24.9, 23.8; IR (KBr) 3853.2, 3357.6, 2925.6, 2345.1, 1706.7, 1552.4, 1378.9, 1089.6 cm^{-1}, chiral-phase HPLC, AD-H column (*i*-PrOH/hexane = 3:97), 254 nm, flow rate = 1 ml/min, t_r (major) = 10.19 min, t_r (minor) = 12.15 min.

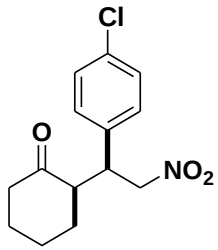
(*R*)-2-[(*S*)-1-(4-Fluorophenyl)-2-nitroethyl]cyclohexanone(4c)2



$[\alpha]_D^{23}$ +29.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.14-7.17 (m, 2H), 7.03-6.99

(m, 2H), 4.95 (dd, *J* = 8, 5 Hz, 1H), 4.59 (dd, *J* = 12, 10 Hz, 1H), 3.80-3.74 (m, 1H), 2.67-2.65 (m, 1H), 2.49-2.32 (m, 2H), 2.12-2.04 (m, 1H), 1.81-1.56 (m, 4H), 1.26-1.20 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 211.6, 163.3, 160.8, 133.3, 129.7, 115.9, 78.8, 52.5, 43.2, 42.7, 33.1, 28.4, 25.0; IR (KBr) 3266.9, 2923.7, 2279.5, 1708.7, 1550.5, 1376.9, 1093.4, 853.0 cm^{-1}; LRMS(FAB+) for $C_{14}H_{16}FNO_3$ [M+H]+ Calcd: 266, Found: 266; chiral-phase HPLC, AS-H column (*i*-PrOH/hexane = 10:90), 254 nm, flow rate = 1 ml/min, t_r (major) = 17.62 min, t_r (minor) = 23.07 min.

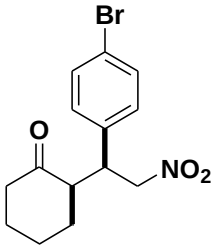
(*R*)-2-[(*S*)-1-(4-Chlorophenyl)-2-nitroethyl]cyclohexanone (4d)[2]



$[\alpha]_D^{23}$ +24.6 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.31 (d, *J* = 8 Hz, 2H), 7.13 (d, *J* = 8 Hz, 2H), 4.96 (dd, *J* = 12, 4 Hz, 1H), 4.62 (dd, *J* = 12, 10 Hz, 1H), 3.78 (dt, *J* = 10, 4 Hz, 1H), 2.69-2.60 (m, 1H), 2.51-2.34 (m, 2H), 2.15-2.05 (m, 1H), 1.83-1.52 (m, 4H), 1.28-1.23 (m, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) 211.6, 136.3, 133.7, 129.6, 129.2, 78.6, 52.4, 43.4, 42.8, 33.2, 28.5, 25.1; IR (KBr) 3252.2, 2897.7, 1721.7, 1555.0, 1087.5 cm^{-1};

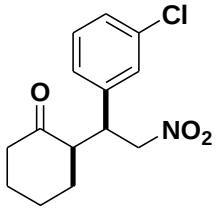
chiral-phase HPLC, AS-H column (*i*-PrOH/hexane = 10:90), 254 nm, flow rate = 1 ml/min, t_r (major) = 14.96 min, t_r (minor) = 21.15 min.

(*R*)-2-[(*S*)-1-(4-Bromophenyl)-2-nitroethyl]cyclohexanone(4e)[1,2]



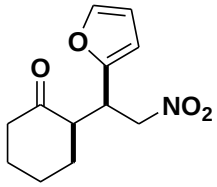
$[\alpha]_D^{25}$ +16.4 (*c* 0.80, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.46 (d, *J* = 8 Hz, 2H), 7.06 (d, *J* = 8 Hz, 2H), 4.93 (dd, *J* = 12, 4 Hz, 1H), 4.60 (dd, *J* = 12, 10 Hz, 1H), 3.75 (dt, *J* = 10, 4 Hz, 1H), 2.69-2.60 (m, 1H), 2.51-2.32 (m, 2H), 2.15-2.05 (m, 1H), 1.85-1.58 (m, 4H), 1.30-1.16 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 211.4, 136.7, 132.0, 129.8, 121.7, 78.4, 52.3, 43.4, 42.7, 33.1, 28.4, 25.0; IR (KBr) 3373.0, 2927.5, 1706.7, 1550.5, 1376.9, 1087.7, 827.3 cm^{-1}; LRMS(FAB+) for $C_{14}H_{16}BrNO_3$ [M+H]+ Calcd: 326, Found: 326; chiral-phase HPLC, AS-H column (*i*-PrOH/hexane = 10:90), 254 nm, flow rate = 0.5 ml/min, t_r (major) = 20.22 min, t_r (minor) = 29.08 min.

(*R*)-2-[(*S*)-1-(3-Chlorophenyl)-2-nitroethyl]cyclohexanone(4f)[2]



$[\alpha]_D^{23}$ +17.2 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.26-7.24 (m, 2H), 7.17 (s, 1H), 7.09-7.06 (m, 1H), 4.94 (dd, *J* = 13, 4 Hz, 1H), 4.61 (d, *J* = 13, 10 Hz, 1H), 3.75 (dt, *J* = 10, 4 Hz, 1H), 2.69-2.64 (m, 1H), 2.62-2.34 (m, 2H), 2.13-2.07 (m, 1H), 1.82-1.57 (m, 4H), 1.23-1.19 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 211.4, 139.8, 134.7, 130.1, 128.2, 128.0, 126.4, 78.3, 52.2, 43.6, 42.7, 33.2, 28.4, 25.0; IR (KBr) 3284.3, 2929.4, 2362.4, 1706.7, 1552.4, 1378.9, 1130.1, 794.5 cm^{-1}; chiral-phase HPLC, AS-H column (*i*-PrOH/hexane = 10:90), 254 nm, flow rate = 1 ml/min, t_r (major) = 16.09 min, t_r (minor) = 22.16 min.

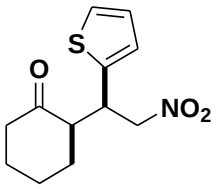
(*R*)-2-[(*R*)-1-(Furan-2-yl)-2-nitroethyl]cyclohexanone(4g)[1]



$[\alpha]_D^{23}$ +12.4 (*c* 2.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.35 (m, 1H), 6.28 (dd, *J* = 3, 2 Hz, 1H), 6.18 (d, *J* = 3 Hz, 1H), 4.83-4.63 (m, 2H), 3.97 (dt, *J* = 10, 5 Hz, 1H), 2.80-

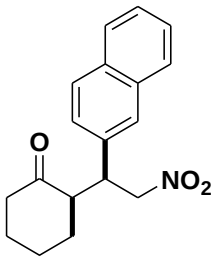
2.71 (m, 1H), 2.50-2.31 (m, 2H), 2.14-2.04 (m, 1H), 1.88-1.56 (m, 4H), 1.35-1.21 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 211.0, 150.9, 142.3, 110.3, 109.0, 77.1, 51.1, 42.6, 37.6, 32.5, 28.2, 25.1; IR (KBr) 3392., 2941.0, 1706.7, 1552.4, 1430.9, 1376.9, 1130.1, 1014.4, 916.0, 740.5 cm^{-1}; HRMS(FAB+) for $C_{12}H_{15}NO_4$ [M+H]+ Calcd: 238.1079, Found: 238.1080; chiral-phase HPLC, AD-H column (*i*-PrOH/hexane = 5:95), 254 nm, flow rate = 0.7 ml/min, t_r (minor) = 26.50 min, t_r (major) = 33.60 min.

(*R*)-2-[(*S*)-1-Thien-2-yl-2-nitroethyl]cyclohexanone(4h)[1]



$[\alpha]_D^{23}$ +20.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.22-7.21 (m, 1H), 6.93 (dd, *J* = 5, 3 Hz, 1H), 6.88-6.87 (m, 1H), 4.89 (dd, *J* = 12, 5 Hz, 1H), 4.65 (dd, *J* = 12, 9 Hz, 1H), 4.13 (dt, *J* = 9, 5 Hz, 1H), 2.73-2.64 (m, 1H), 2.50-2.32 (m, 2H), 2.14-2.06 (m, 1H), 1.95-1.82 (m, 2H), 1.69-1.58 (m, 2H), 1.39-1.29 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 211.1, 140.4, 126.8, 126.5, 124.9, 79.1, 53.2, 42.5, 39.3, 32.7, 28.2, 25.0; IR (KBr) 3392.3, 3110.7, 2939.1, 2285.3, 1704.8, 1552.4, 1378.9, 1253.5, 1128.2, 850.4, 705.8 cm^{-1}; HRMS(FAB+) for $C_{12}H_{15}NO_3S$ $[M+H]^+$ Calcd: 254.0851, Found: 254.0853; chiral-phase HPLC, AS-H column (*i*-PrOH/hexane = 4:96), 254 nm, flow rate = 0.5 ml/min, t_r (minor) = 29.95 min, t_r (major) = 35.16 min.

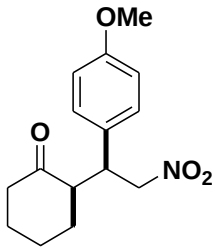
(*R*)-2-[(*S*)-1-Naphthalen-2-yl-2-nitroethyl]cyclohexanone(4i)[5]



$[\alpha]_D^{23}$ +15.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.84-7.78 (m, 3H), 7.64 (s, 1H), 7.50-7.46 (m, 2H), 7.29 (dd, *J* = 11, 2 Hz, 1H), 5.03 (dd, *J* = 12, 4 Hz, 1H), 4.74

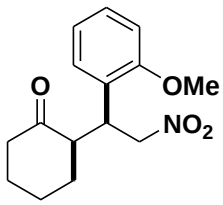
(dd, *J* = 12, 10 Hz, 1H), 3.95 (dt, *J* = 10, 4 Hz, 1H), 2.83-2.74 (m, 1H), 2.54-2.36 (m, 2H), 2.11-2.04 (m, 1H), 1.79-1.62 (m, 4H), 1.32-1.29 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 211.8, 135.0, 133.2, 128.8, 127.7, 126.4, 126.1, 125.1, 78.8, 52.4, 44.0, 42.7, 33.3, 28.5, 25.0; IR (KBr) 3376.9, 2923.7, 1700.9, 1550.5, 1382.7, 1091.5, 825.4 cm^{-1}; LRMS(FAB+) for $C_{18}H_{19}NO_3$ [M]+ Calcd: 297, Found: 297; chiral-phase HPLC, AS-H column (*i*-PrOH/hexane = 50:50), 254 nm, flow rate = 0.7 ml/min, t_r (major) = 9.14 min, t_r (minor) = 13.12 min.

(*R*)-2-[(*S*)-1-(4-Methoxyphenyl)-2-nitroethyl]cyclohexanone(4j)[5]



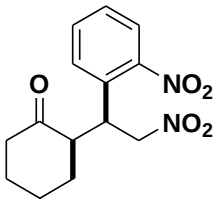
$[\alpha]_D^{23}$ +10.8 (*c* 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.08 (d, *J* = 9 Hz, 2H), 6.85 (d, *J* = 9 Hz, 2H), 4.91 (dd, *J* = 12, 4 Hz, 1H), 4.58 (dd, *J* = 12, 10 Hz, 1H), 3.78 (s, 3H), 3.71 (dt, *J* = 10, 4 Hz, 1H), 2.69-2.60 (m, 1H), 2.52-2.32 (m, 2H), 2.13-2.03 (m, 1H), 1.83-1.51 (m, 4H), 1.30-1.16 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 212.2, 15809, 129.4, 129.1, 114.2, 79.0, 55.1, 52.6, 43.1, 42.7, 33.1, 28.5, 24.9; IR (KBr) 3380.7, 2950.7, 2360.5, 1700.9, 1552.4, 1388.5, 1255.4, 1089.6, 831.2 cm^{-1}; HRMS(FAB+) for $C_{15}H_{19}NO_4$ [M]+ Calcd: 278.1392, Found: 278.1390; chiral-phase HPLC, AD-H column (*i*-PrOH/hexane = 20:80), 254 nm, flow rate = 0.5 ml/min, t_r (major) = 18.59 min, t_r (minor) = 23.72 min.

(*R*)-2-[(*S*)-1-(2-Methoxyphenyl)-2-nitroethyl]cyclohexanone(4k)[2]



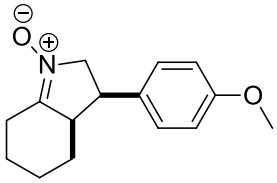
[α]$_D^{23}$ +7.2 (*c* 0.10, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.28-7.22 (m, 1H), 7.09 (dd, *J* = 7, 2 Hz, 1H), 6.91-6.86 (m 2H), 4.84 (dd, *J* = 10, 5 Hz, 1H), 4.00-3.90 (m, 1H), 3.84 (s, 3H), 2.99 (dt, *J* = 10, 5 Hz, 1H), 2.50-2.34 (m, 2H), 2.10-2.04 (m, 1H), 1.80-1.54 (m, 4H), 1.12-1.18 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 212.5, 157.5, 130.9, 128.8, 125.2, 120.8, 110.9, 76.6, 55.3, 50.5, 42.6, 33.2, 28.5, 25.1; IR (KBr) 3293.9, 2935.2, 2345.1, 1706.7, 1550.5, 1378.9, 1245.8, 1122.4, 755.9 cm^{-1}; HRMS(FAB+) for $C_{15}H_{19}NO_4$ [M+H]+ Calcd: 278.1392, Found: 278.1390; chiral-phase HPLC, AS-H column (*i*-PrOH/hexane = 10:90), 254 nm, flow rate = 0.5 ml/min, t_r (major) = 26.35 min, t_r (minor) = 36.10 min.

(*R*)-2-[(*S*)-2-Nitro-1-(2-nitrophenyl)ethyl)cyclohexanone(4l)[5]



[α]$_D^{23}$ +9.8 (*c* 0.80, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.83 (dd, *J* = 8, 2 Hz, 1H), 7.64-7.58 (m, 1H), 7.49-7.41 (m, 2H), 4.98-4.83 (m, 2H), 4.38 (dt, *J* = 9, 4 Hz, 1H), 2.98-2.87 (m, 1H), 2.50-2.34 (m, 2H), 2.17-2.07 (m, 1H), 1.85-1.61 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) 211.1, 150.7, 133.1, 132.8, 129.1, 128.6, 124.9, 77.6, 52.1, 42.8, 38.6, 33.2, 28.3, 25.3; IR (film) 2944, 2864, 1707, 1552, 1527, 1358, 855, 781 cm^{-1}; HRMS(FAB+) for $C_{14}H_{16}N_2O_5$ [M+H]+ Calcd: 293.1137, Found: 293.1141; chiral-phase HPLC, AD-H column (*i*-PrOH/hexane = 15:85), 254 nm, flow rate = 1 ml/min, t_r (major) = 14.45 min, t_r (minor) = 22.22 min.

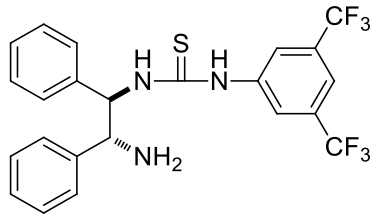
(3R,3aS)-3-(4-Methoxyphenyl)-3,3a,4,5,6,7-hexahydro-2H-indole-1-Oxide(5a)[8]



^{1}H NMR (500MHz, CDCl3): 7.16 (d, 2H, *J* = 8.7, Ar*H*), 6.89 (d, 2H, *J* = 8.7, Ar*H*),

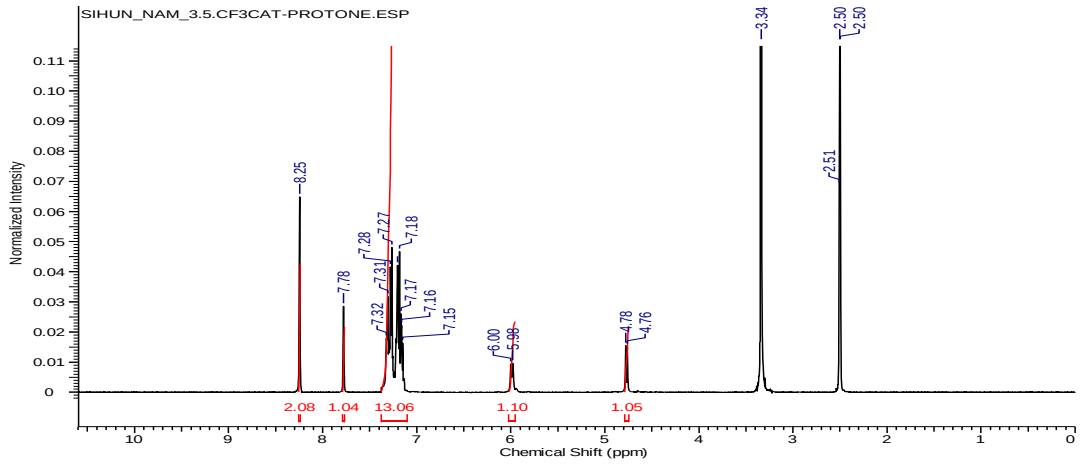
4.27-4.24 (br m, 1H, NC*H*2), 4.15-4.10 (br m, 1H, NC*H*2), 3.81 (s, 3H, OC*H*3), 3.25-3.15 (m, 2H, ArC*H*, NCC*H*2), 2.8-2.7 (ArCHC*H*), 2.12-1.84 (m, 3H, C*H*2), 1.85 (br d, 1H, *J* = 12.8, C*H*2), 1.45-1.18 (m, 4H, C*H*2); ^{13}C NMR (125 MHz, CDCl3): δ 158.9, 148.6, 131.7, 128.3, 114.4, 68.4, 55.3, 50.6, 45.3, 32.3, 24.3, 23.8, 23.5; LRMS(ESI$^+$): *m*/*z* 246.1 (M+H);

2. Copy of HPLC, NMR and MASS Spectra

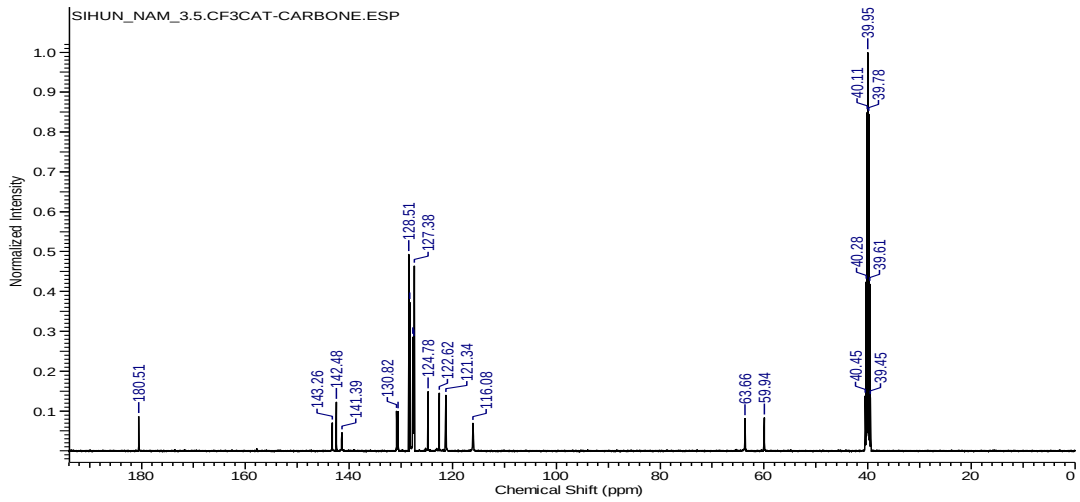


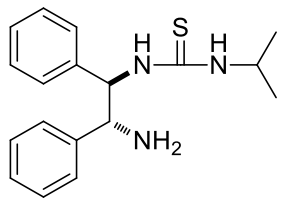
1a

^{1}H NMR



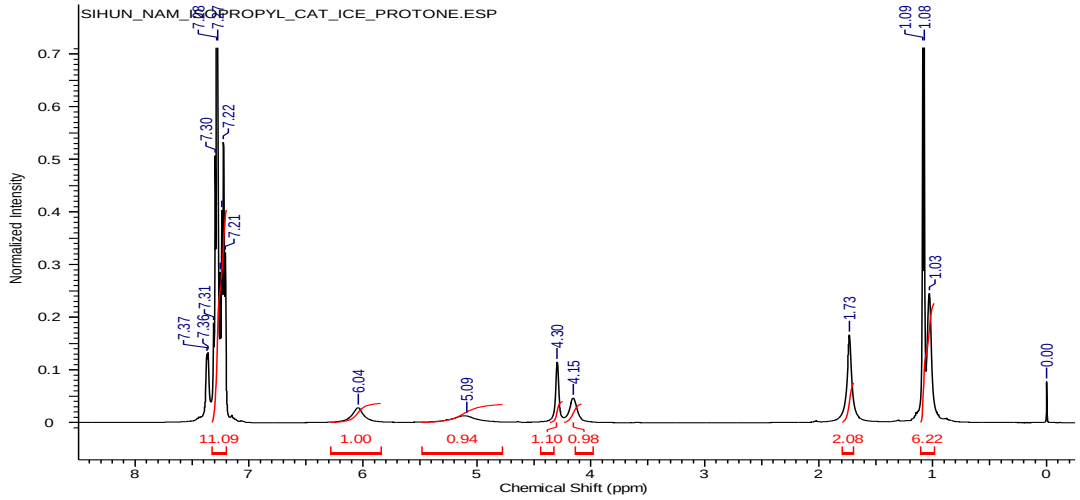
^{13}C NMR



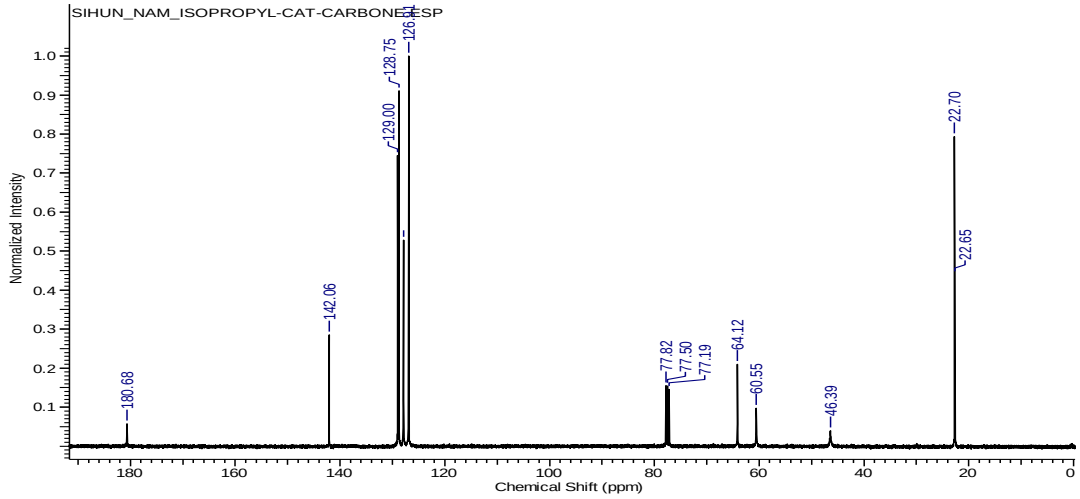


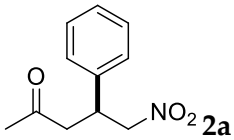
1b

^{1}H NMR



^{13}C NMR

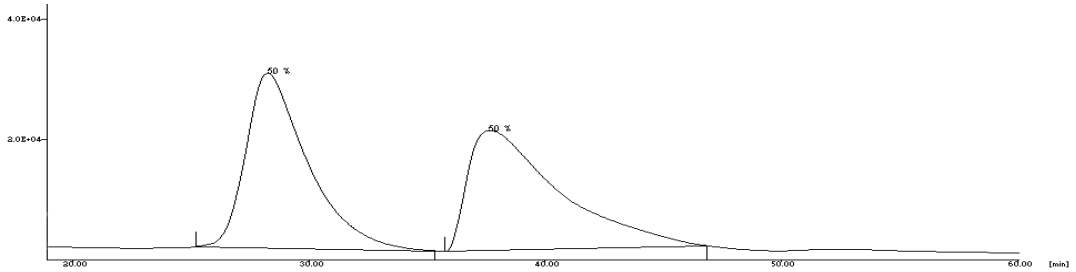




2a

LC data

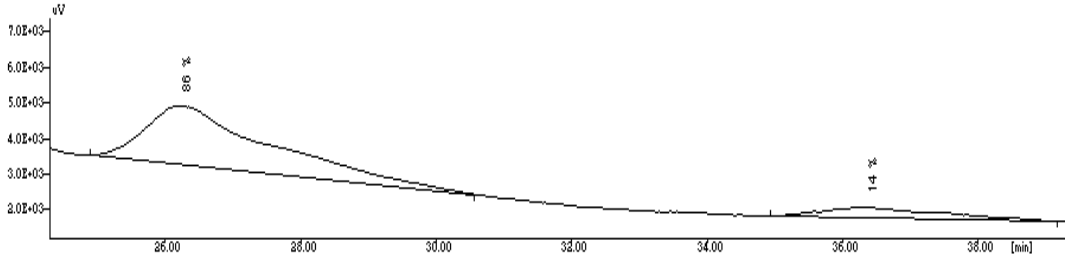
Racemic



#	Name	RT	Area[uV.Sec]	Quantity
1		28.258	5183575.750	0.000
2		37.650	5252568.500	0.000

Total Area of Peak = 10436144.250 [uV.Sec]

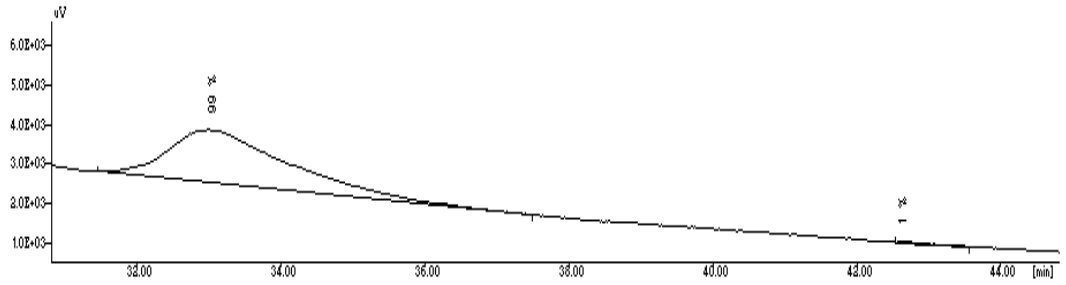
Asymmetric-Table 1-1



#	Name	RT	Area[uV.Sec]	Quantity
1		26.217	211984.571	0.000
2		36.350	35605.786	0.000

Total Area of Peak = 247590.358 [uV.Sec]

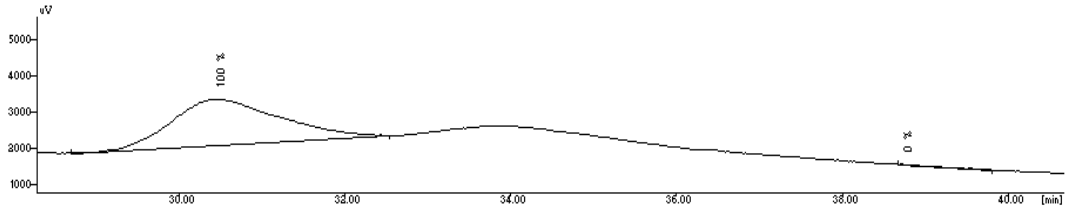
Asymmetric-Table 1-2



#	Name	RT	Area[uV.Sec]	Quantity
1		32.967	156709.400	0.000
2		42.558	1078.585	0.000

Total Area of Peak = 157787.985 [uV.Sec]

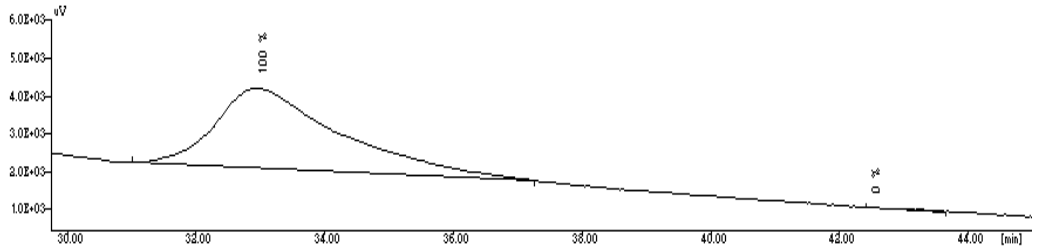
Asymmetric-Table 1-3



#	Name	RT	Area[uV.Sec]	Quantity
1		30.425	112143.125	0.000
2		38.708	225.803	0.000

Total Area of Peak = 112368.928 [uV.Sec]

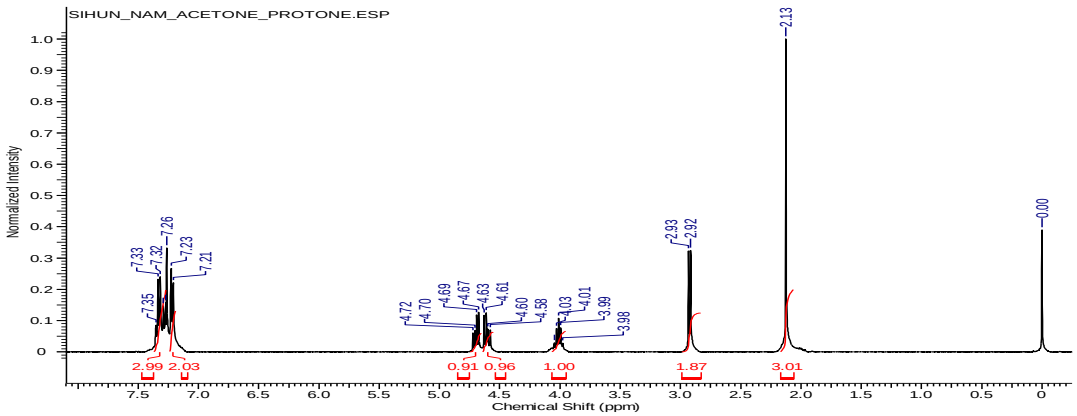
Asymmetric-Table 1-4



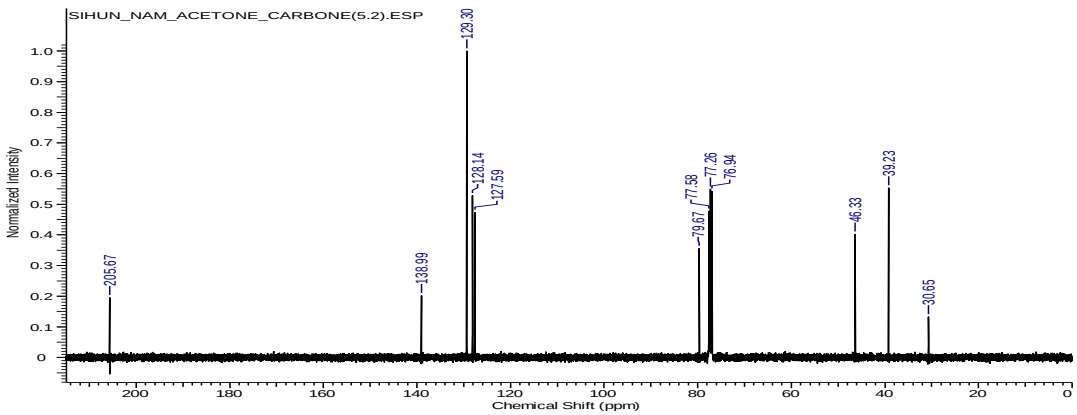
#	Name	RT	Area[uV.Sec]	Quantity
1		32.942	281123.989	0.000
2		42.458	664.608	0.000

Total Area of Peak = 281788.597 [uV.Sec]

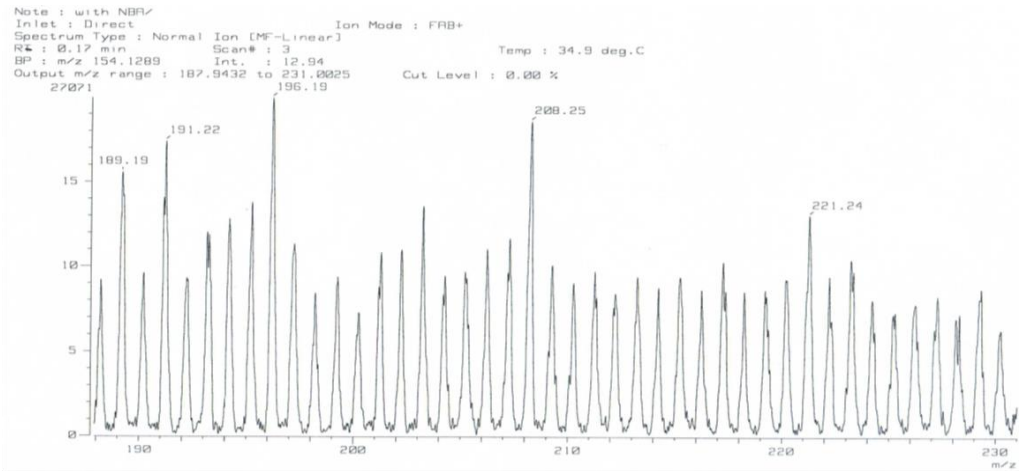
^{1}H NMR

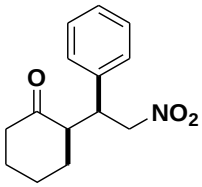


^{13}C NMR



Mass

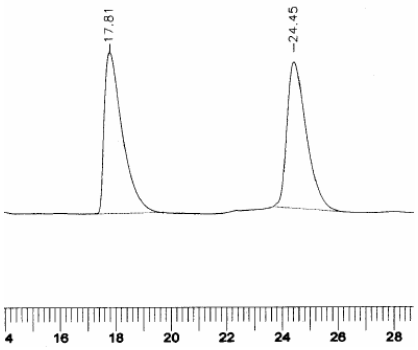


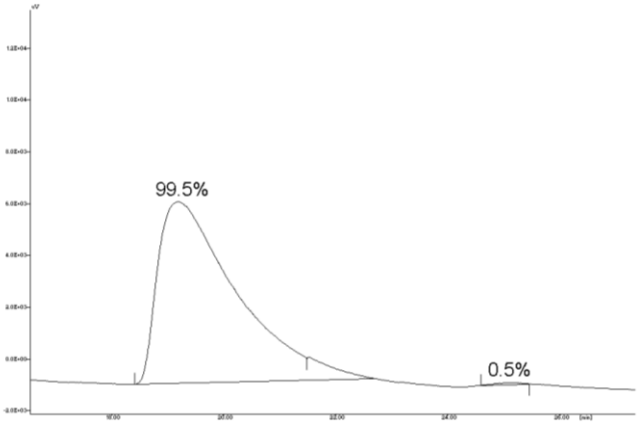


2b

LC data

racemic

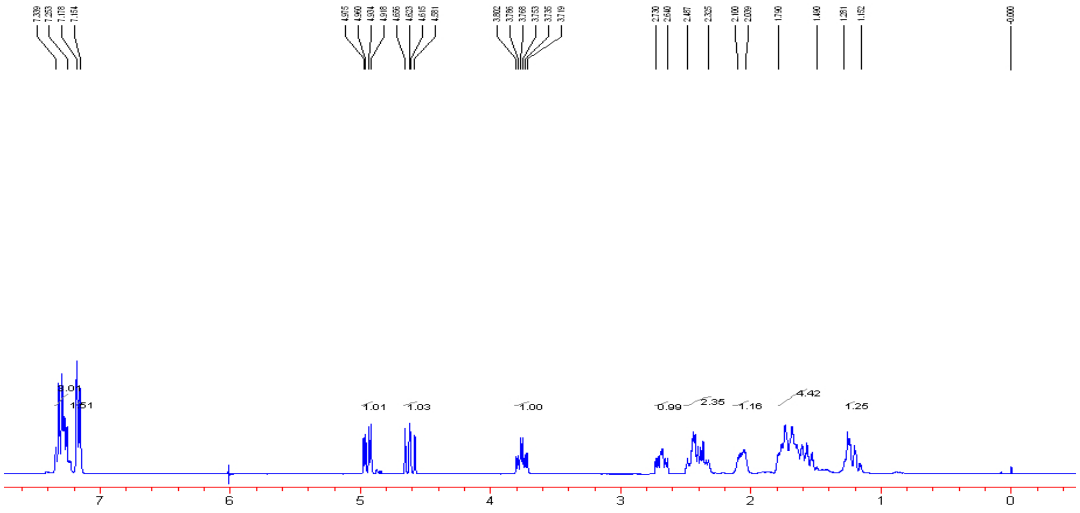




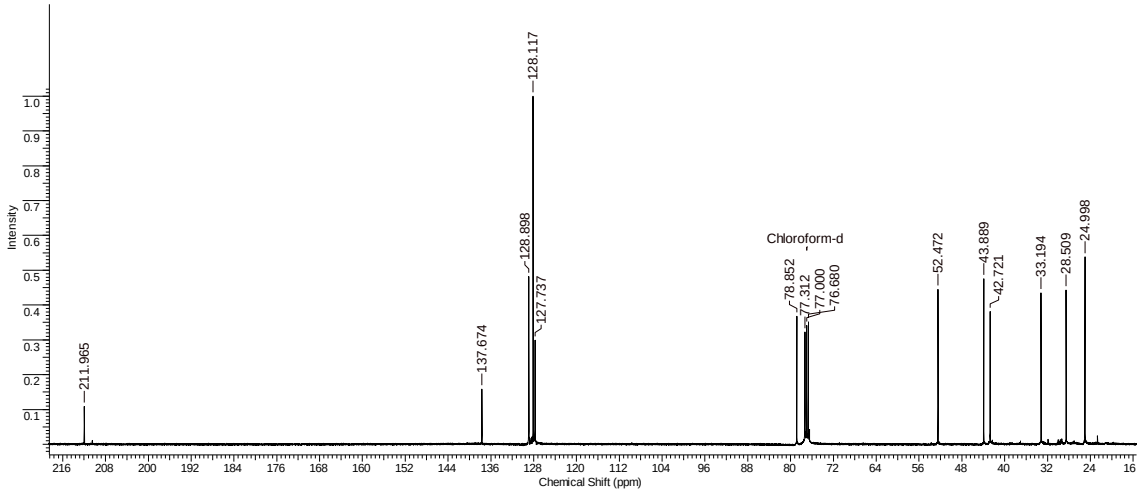
#	Name	RT	Area[uV.Sec]	Quantity
1		19.175	652364.119	0.000
2		25.075	2319.500	0.000

Total Area of Peak = 654683.619 [uV.Sec]

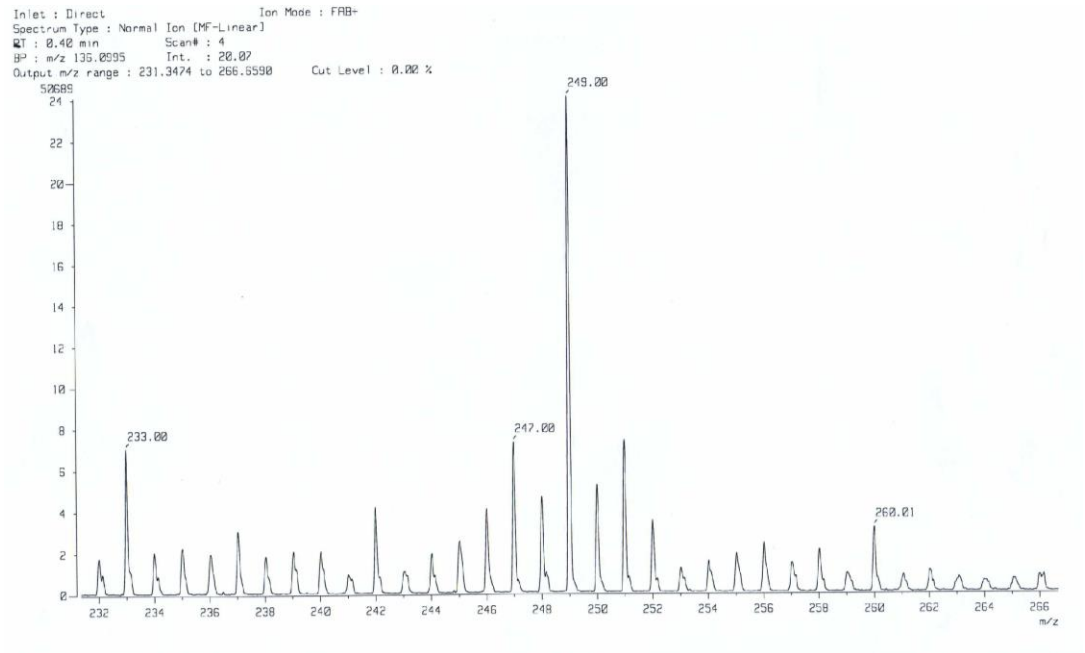
^{1}H NMR

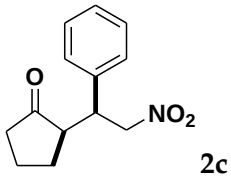

7.339
7.253
7.178
7.154
4.975
4.960
4.934
4.918
4.656
4.623
4.615
4.581
3.802
3.786
3.768
3.753
3.735
3.719
2.378
2.340
2.487
2.325
2.100
2.039
1.790
1.460
1.281
1.182
0.000
8.00
1.51
1.01
1.03
1.00
0.99
2.35
1.16
4.42
1.25
7
6
5
4
3
2
1
0

^{13}C NMR


Intensity
Chemical Shift (ppm)
211.965
137.674
128.898
128.117
127.737
Chloroform-d
78.852
77.312
77.000
76.680
52.472
43.889
42.721
33.194
28.509
24.998

Mass

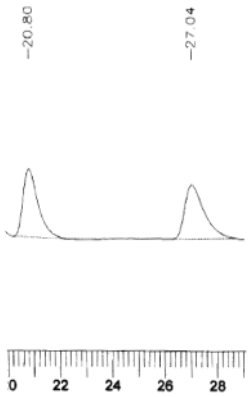

Inlet : Direct
Ion Mode : FAB+
Spectrum Type : Normal Ion (MF-Linear)
RT : 0.40 min
Scan# : 4
BP : m/z 135.0995
Int. : 20.07
Output m/z range : 231.3474 to 266.6590
Cut Level : 0.00 %
52689
249.00
233.00
247.00
260.01
m/z

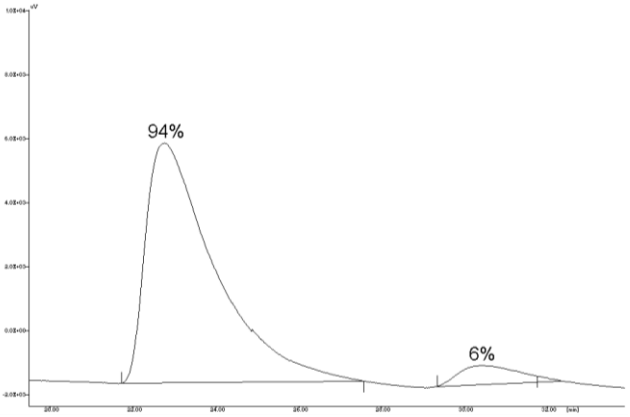


2c

LC data

racemic

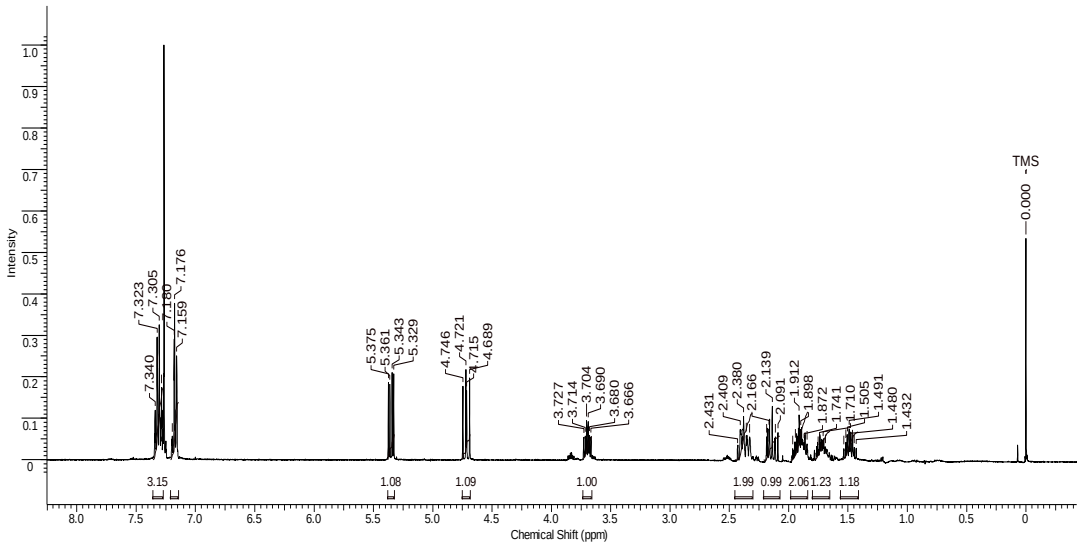




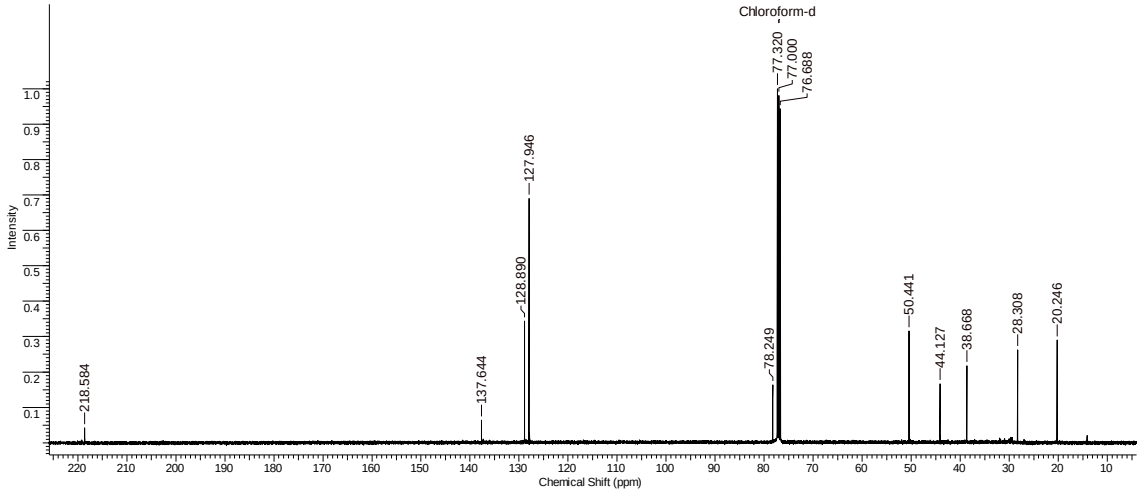
#	Name	RT	Area[uV.Sec]	Quantity
1		22.742	861745.000	0.000
2		30.475	55642.856	0.000

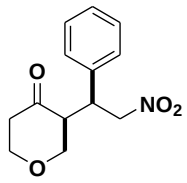
Total Area of Peak = 917387.856 [uV.Sec]

^{1}H NMR



^{13}C NMR

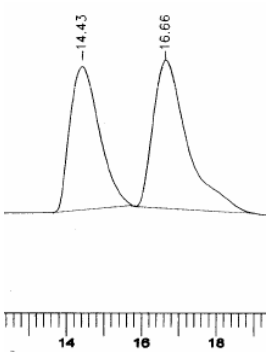

Chloroform-d
77.320
77.000
76.688
127.946
128.890
137.644
218.584
78.249
50.441
44.127
38.668
28.308
20.246
Intensity
Chemical Shift (ppm)

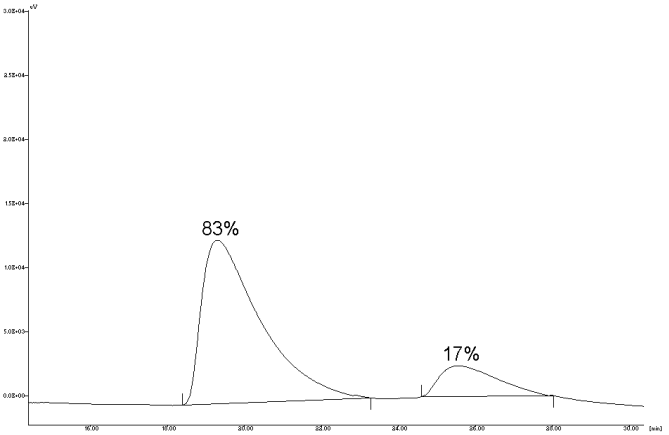


2d

LC data

racemic

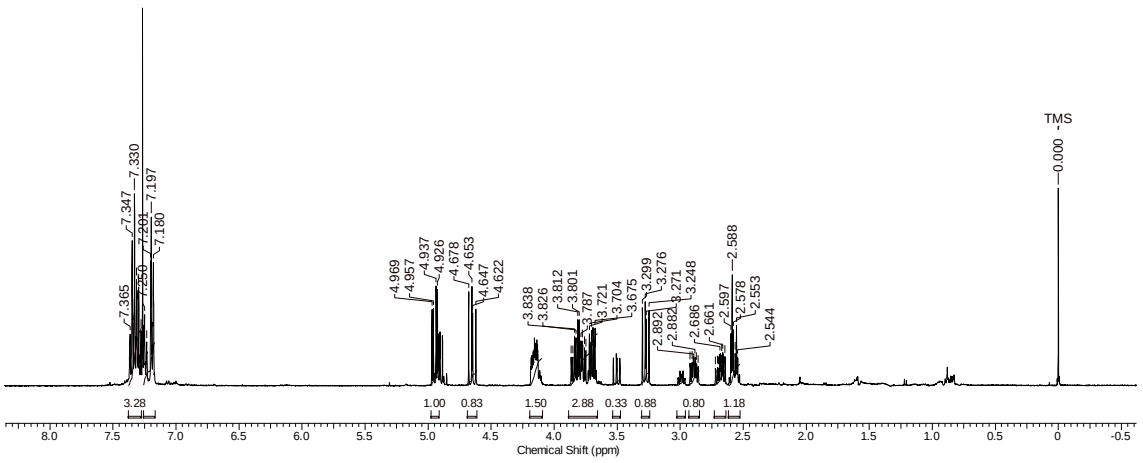




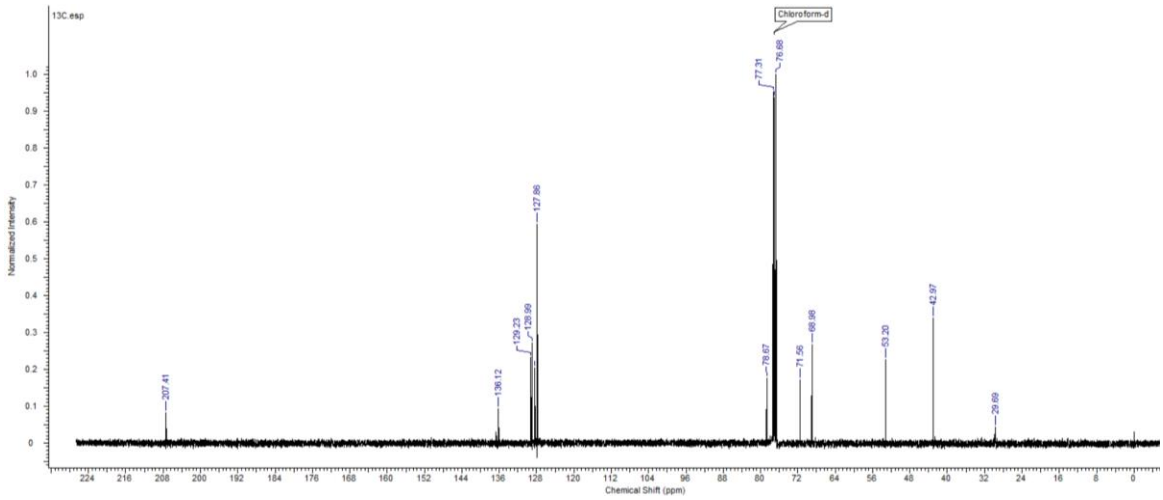
#	Name	RT	Area[uV.Sec]	Quantity
1		19.292	1416102.812	0.000
2		25.533	384599.179	0.000

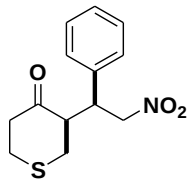
Total Area of Peak = 1800701.991 [uV.Sec]

^{1}H NMR



^{13}C NMR

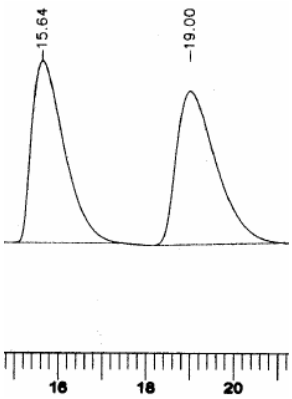

13C.esp
Chloroform-d
77.31
76.68
127.86
129.23
129.99
136.12
207.41
78.67
71.56
68.98
53.20
42.97
29.69
Normalized Intensity
Chemical Shift (ppm)

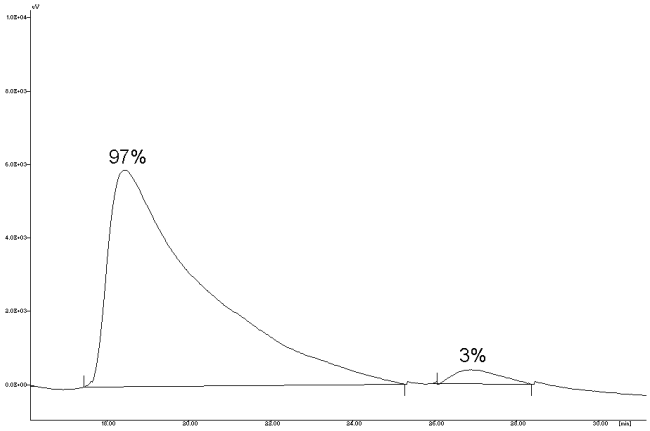


2e

LC data

racemic

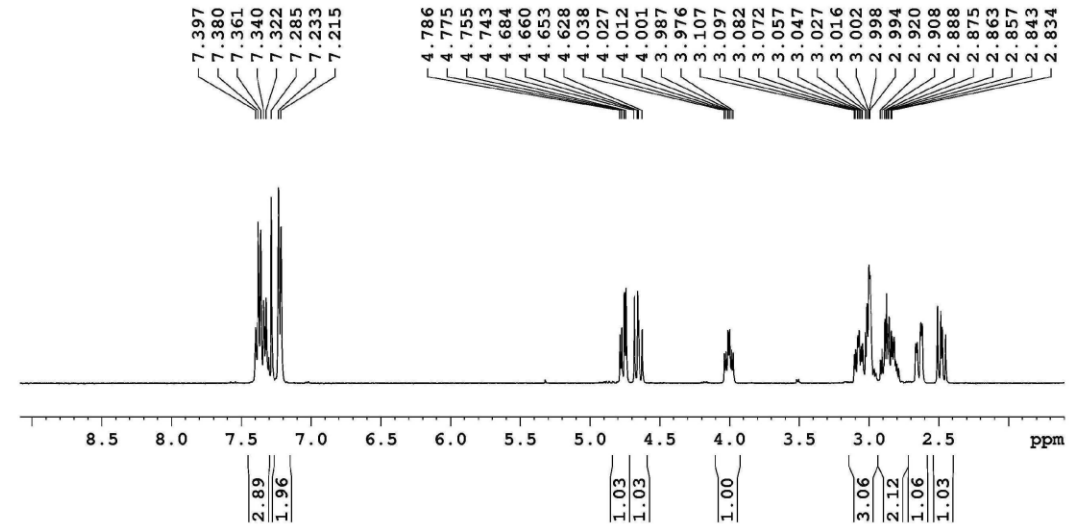




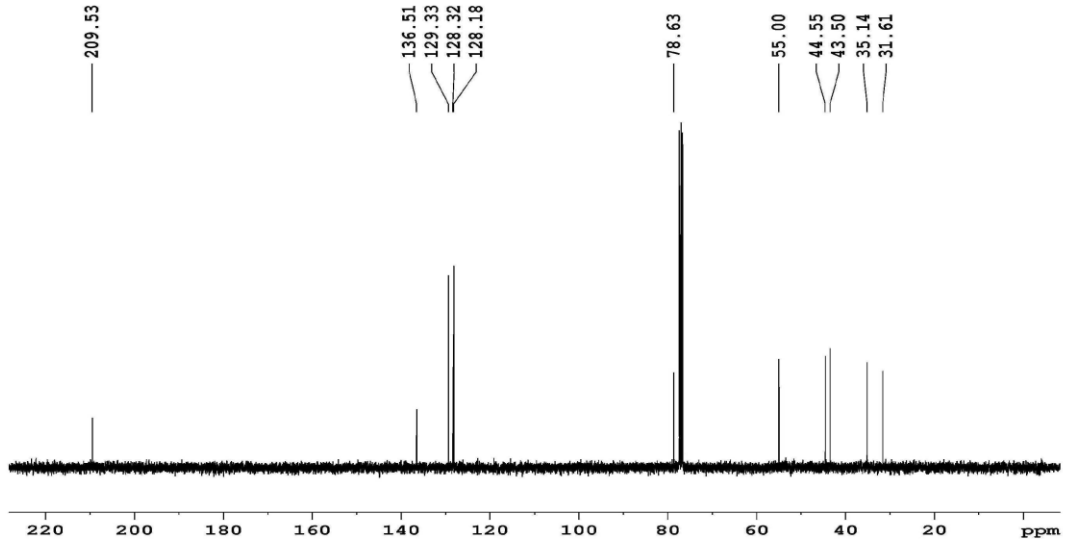
#	Name	RT	Area[uV.Sec]	Quantity
1		18.408	944894.000	0.000
2		26.842	29752.344	0.000

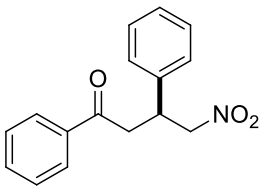
Total Area of Peak = 974646.344 [uV.Sec]

^{1}H NMR


7.397
7.380
7.361
7.340
7.322
7.285
7.233
7.215
4.786
4.775
4.755
4.743
4.684
4.660
4.653
4.628
4.038
4.027
4.012
4.001
3.987
3.976
3.107
3.097
3.082
3.072
3.057
3.047
3.027
3.016
3.002
2.998
2.994
2.920
2.908
2.888
2.875
2.863
2.857
2.843
2.834
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
ppm
2.89
1.96
1.03
1.03
1.00
3.06
2.12
1.06
1.03

^{13}C NMR

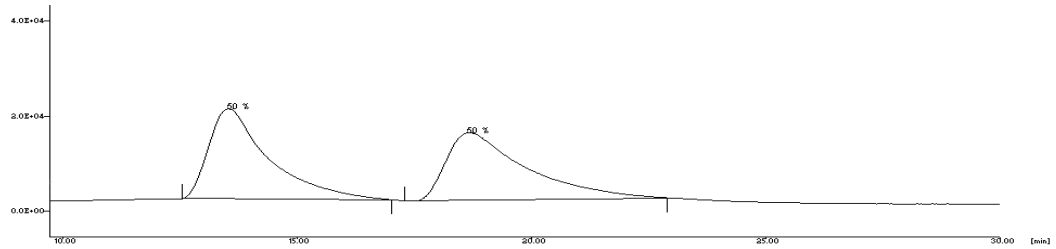

209.53
136.51
129.33
128.32
128.18
78.63
55.00
44.55
43.50
35.14
31.61
220
200
180
160
140
120
100
80
60
40
20
ppm



2f

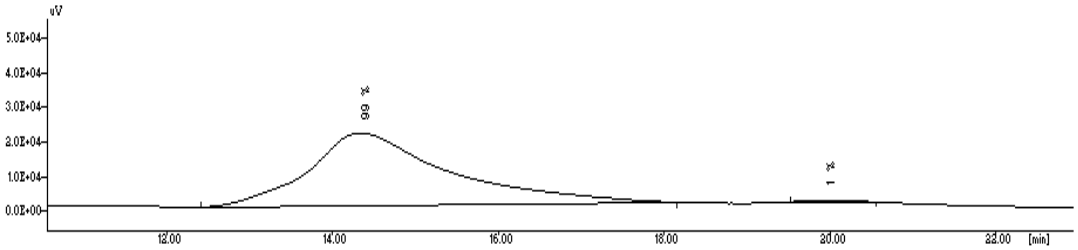
LC data

racemic



#	Name	RT	Area[uV.Sec]	Quantity
1		13.533	1654427.500	0.000
2		18.650	1636835.605	0.000

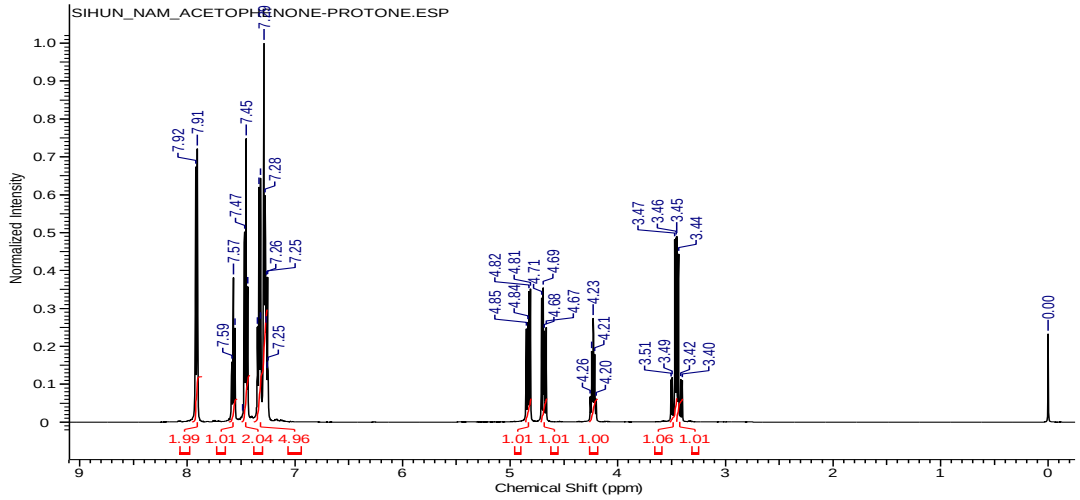
Total Area of Peak = 3291263.105 [uV.Sec]



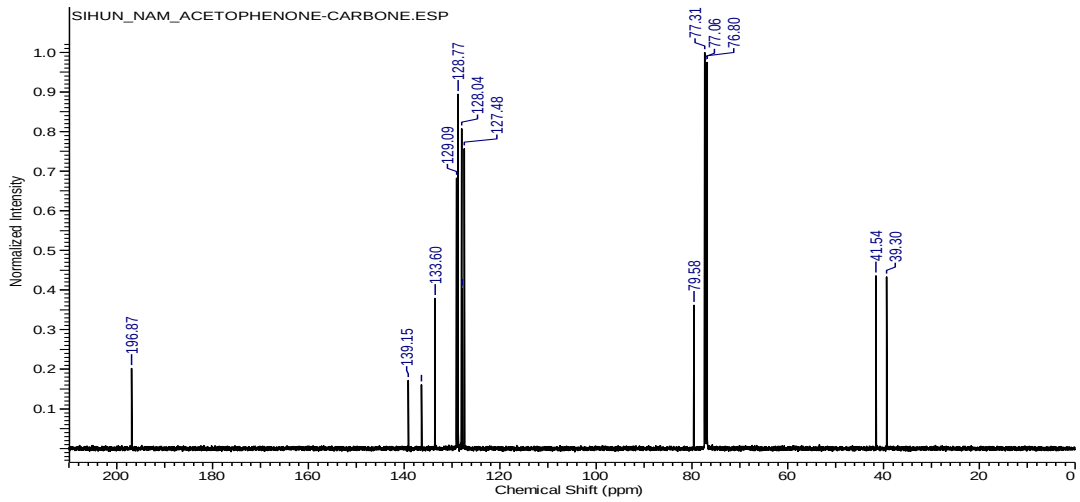
#	Name	RT	Area[uV.Sec]	Quantity
1		14.317	2519443.881	0.000
2		19.933	15846.500	0.000

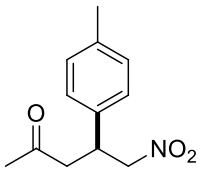
Total Area of Peak = 2535290.381 [uV.Sec]

^{1}H NMR



^{13}C NMR

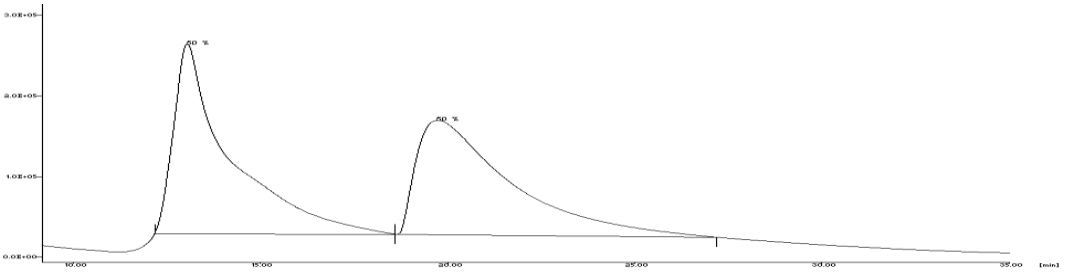




3a

LC data

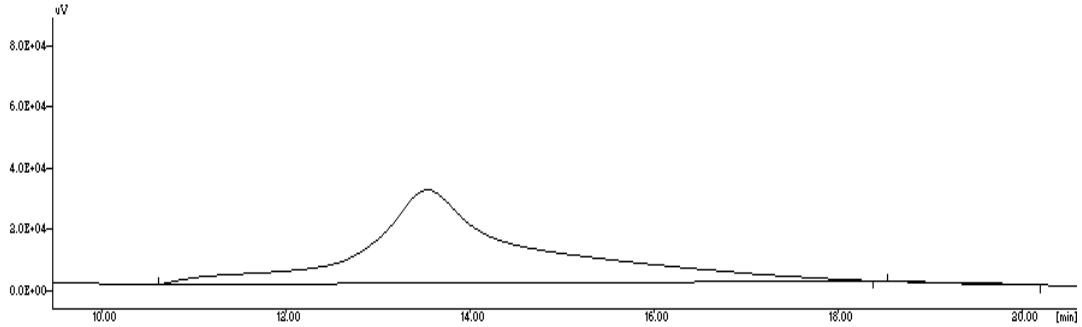
Racemic



#	Name	RT	Area[uV.Sec]	Quantity
1		13.025	24260518.000	0.000
2		19.725	24470144.676	0.000

Total Area of Peak = 48730662.676 [uV.Sec]

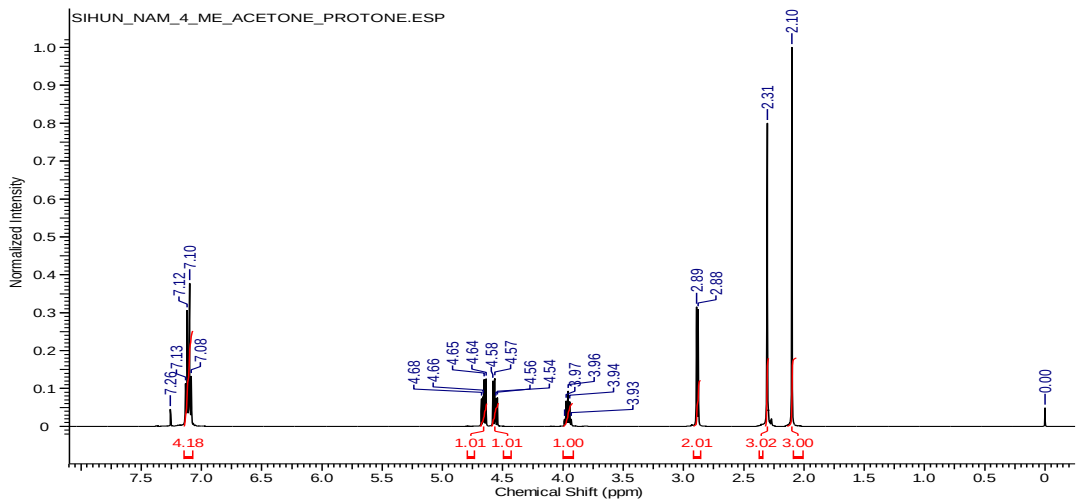
Asymmetric



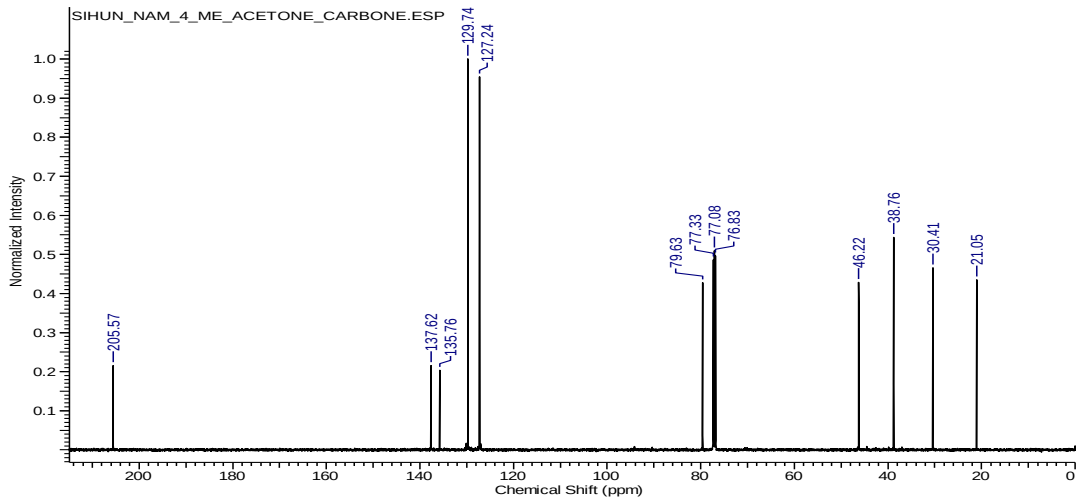
#	Name	RT	Area[uV.Sec]	Quantity
1		13.533	3641381.500	0.000
2		19.967	8063.435	0.000

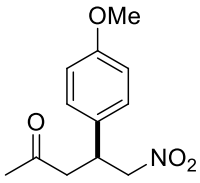
Total Area of Peak = 3649444.935 [uV.Sec]

^{1}H NMR



^{13}C NMR

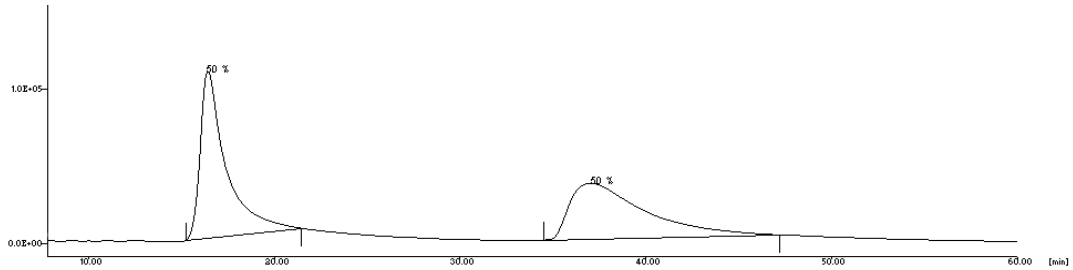




3b

LC data

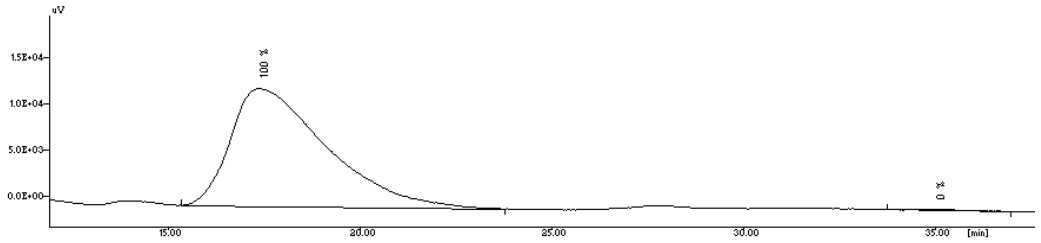
Racemic



#	Name	RT	Area[uV.Sec]	Quantity
1		16.408	10185777.000	0.000
2		37.042	10015080.836	0.000

Total Area of Peak = 20200857.836 [uV.Sec]

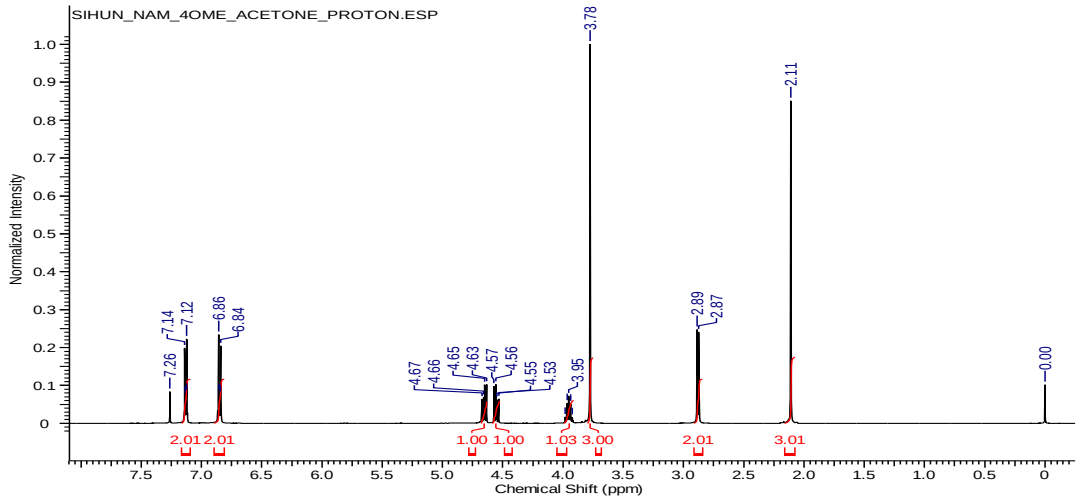
Asymmetric



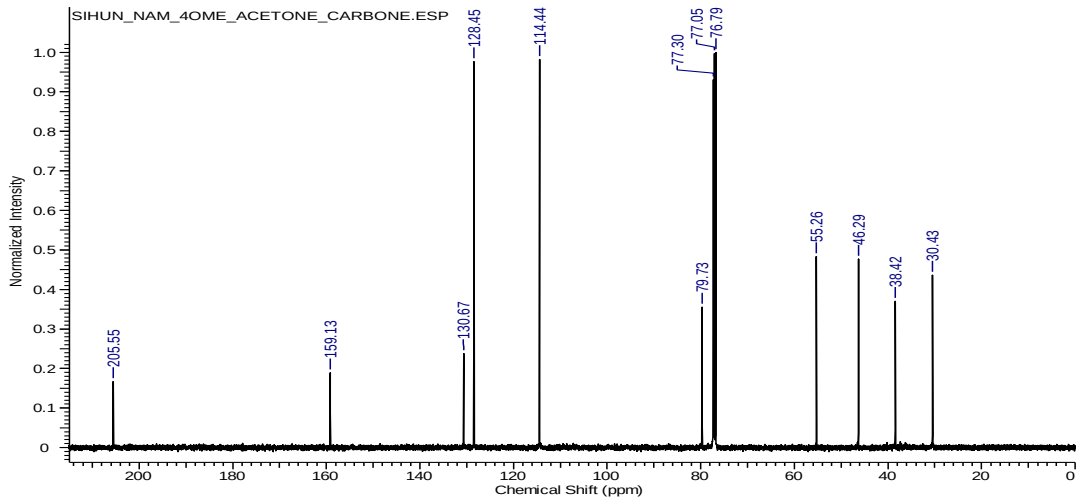
#	Name	RT	Area[uV.Sec]	Quantity
1		16.225	2571746.500	0.000
2		37.917	240342.093	0.000

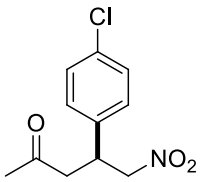
Total Area of Peak = 2812088.593 [uV.Sec]

^{1}H NMR



^{13}C NMR

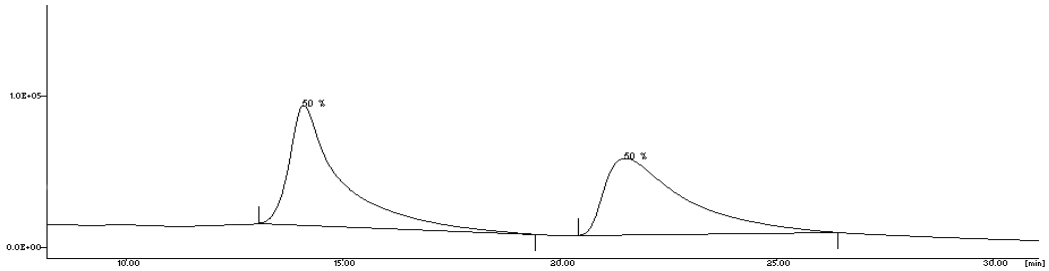




3c

LC data

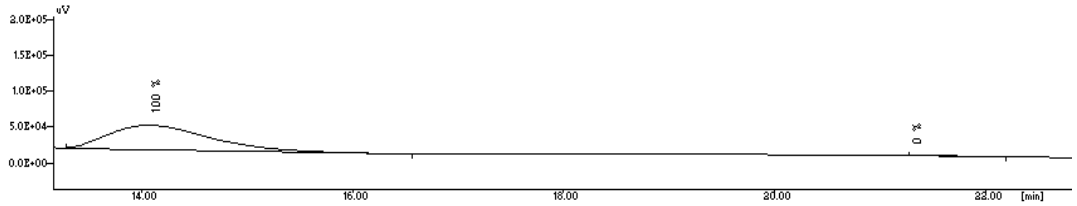
Racemic



#	Name	RT	Area[uV.Sec]	Quantity
1		14.083	6386737.559	0.000
2		21.508	6393443.750	0.000

Total Area of Peak = 12780181.309 [uV.Sec]

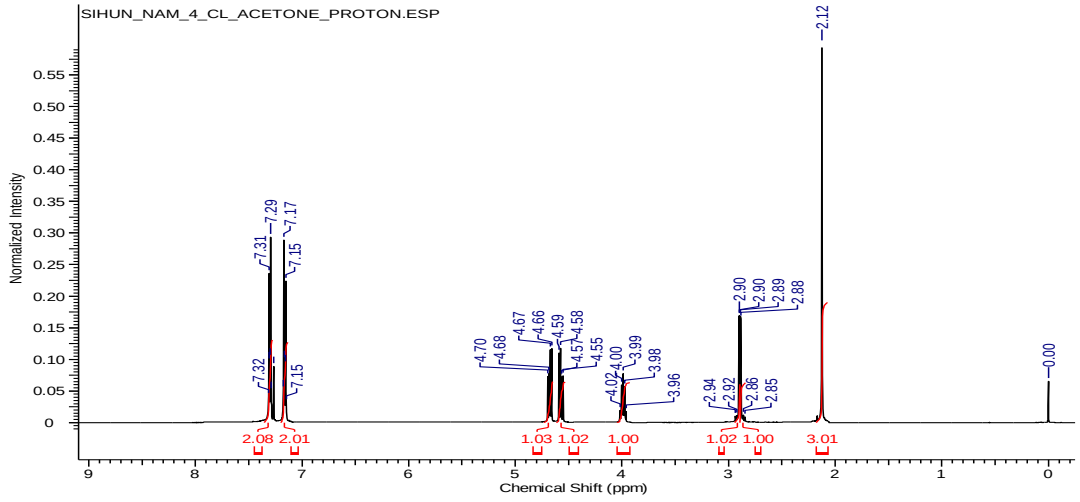
Asymmetric



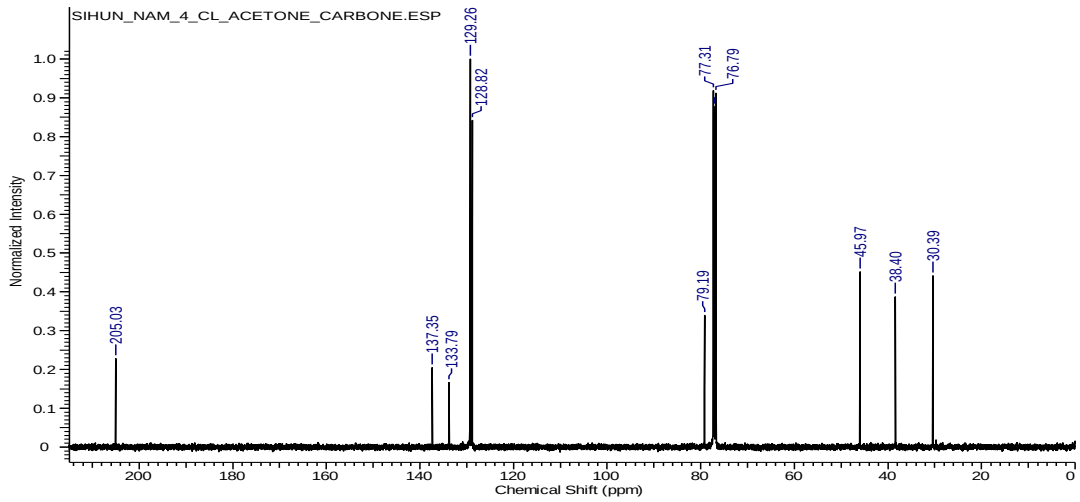
#	Name	RT	Area[uV.Sec]	Quantity
1		14.067	2183761.912	0.000
2		21.283	8401.000	0.000

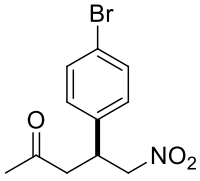
Total Area of Peak = 2192162.912 [uV.Sec]

^{1}H NMR



^{13}C NMR

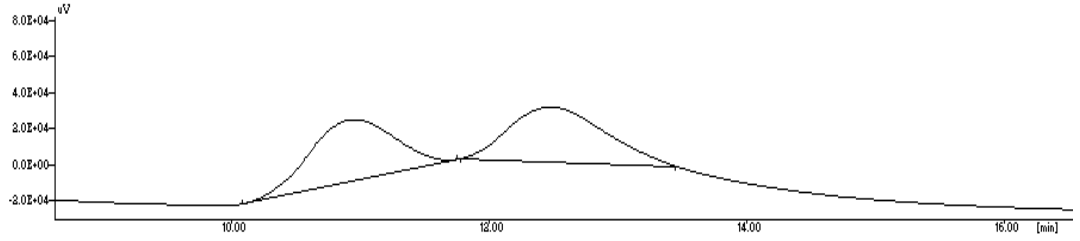




3d

LC data

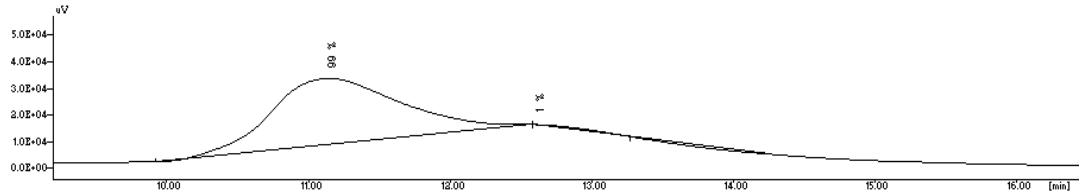
Racemic



#	Name	RT	Area[uV.Sec]	Quantity
1		10.950	1547389.355	0.000
2		12.475	1569378.500	0.000

Total Area of Peak = 3116767.855 [uV.Sec]

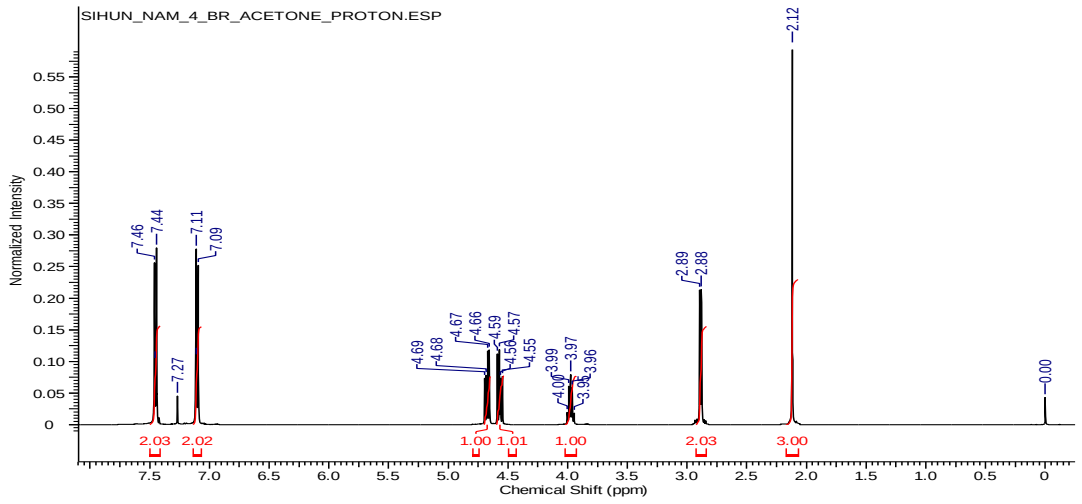
Asymmetric



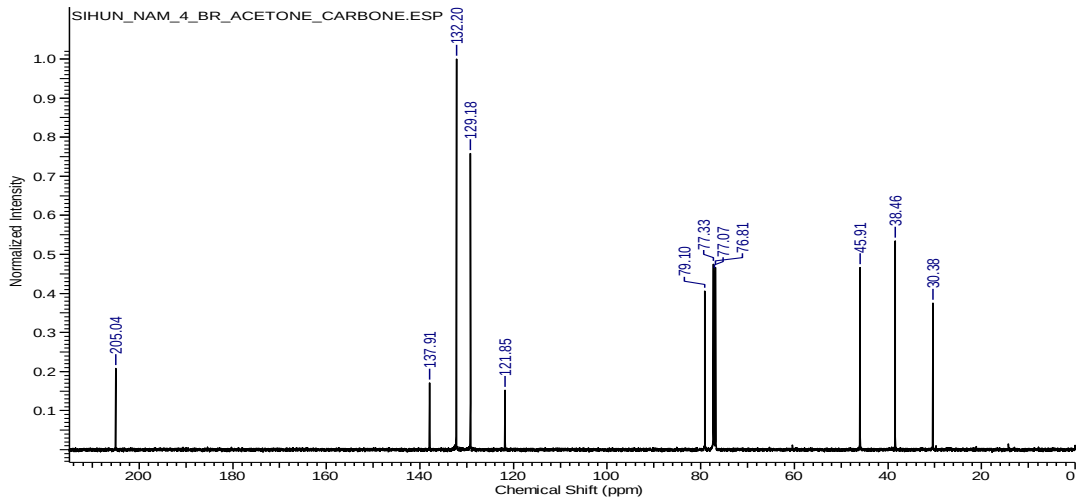
#	Name	RT	Area[uV.Sec]	Quantity
1		11.125	1576694.008	0.000
2		12.592	18015.470	0.000

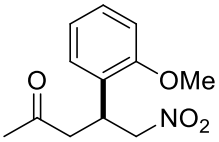
Total Area of Peak = 1594709.478 [uV.Sec]

^{1}H NMR



^{13}C NMR

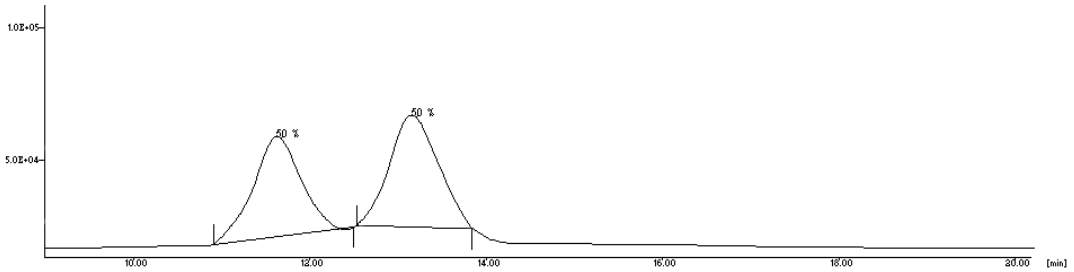




3e

LC data

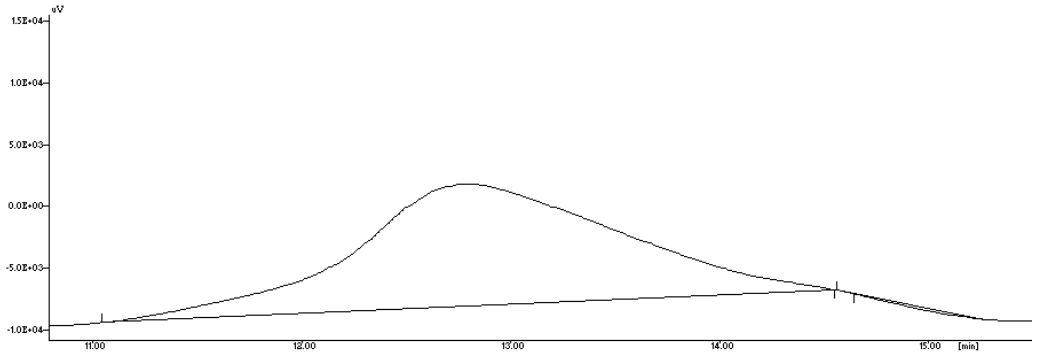
Racemic



#	Name	RT	Area[uV.Sec]	Quantity
1		11.633	1399275.110	0.000
2		13.167	1413026.250	0.000

Total Area of Peak = 2812301.360 [uV.Sec]

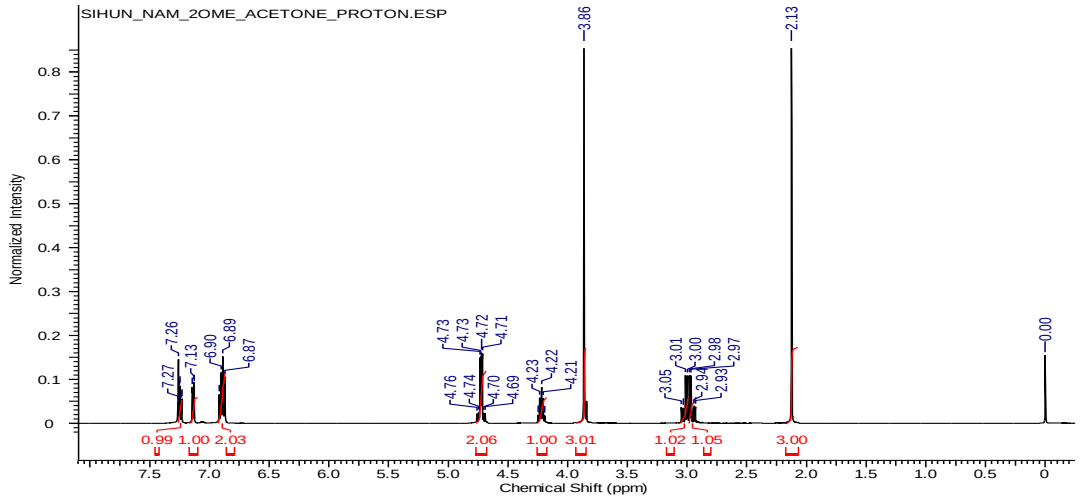
Asymmetric



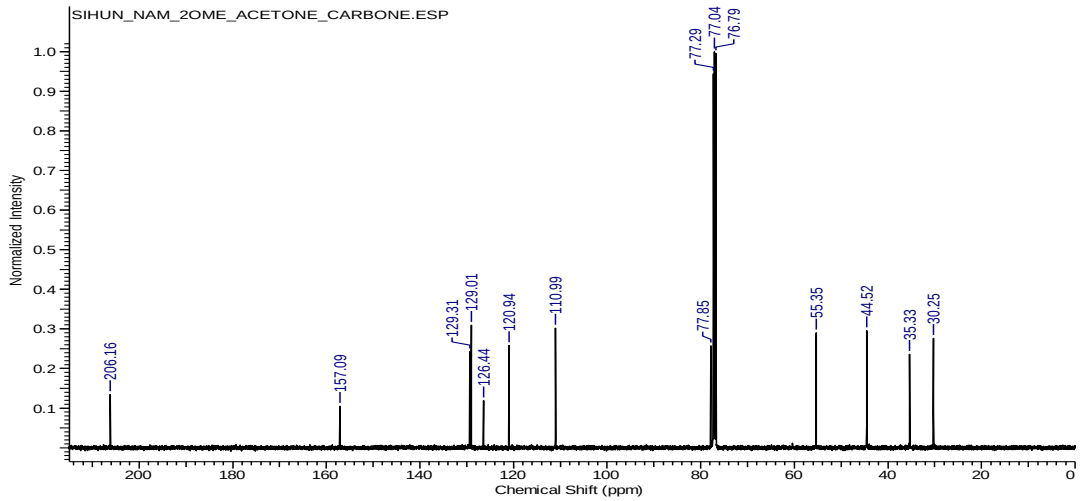
#	Name	RT	Area[uV.Sec]	Quantity
1		12.808	869024.000	0.000
2		14.567	116.706	0.000

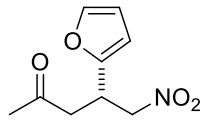
Total Area of Peak = 869140.706 [uV.Sec]

^{1}H NMR


SIHUN_NAM_2OME_ACETONE_PROTON.ESP
Normalized Intensity
Chemical Shift (ppm)
7.27
7.26
7.13
6.90
6.89
6.87
4.76
4.74
4.73
4.73
4.72
4.71
4.70
4.69
4.23
4.22
4.21
3.86
3.05
3.01
3.00
2.98
2.97
2.94
2.93
2.13
0.00
0.99
1.00
2.03
2.06
1.00
3.01
1.02
1.05
3.00

^{13}C NMR

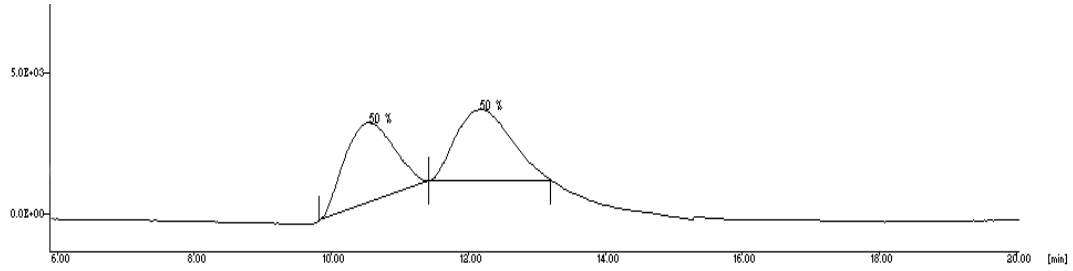

SIHUN_NAM_2OME_ACETONE_CARBONE.ESP
Normalized Intensity
Chemical Shift (ppm)
206.16
157.09
129.31
129.01
126.44
120.94
110.99
77.29
77.04
76.79
77.85
55.35
44.52
35.33
30.25


O
O
NO2

3f

LC data

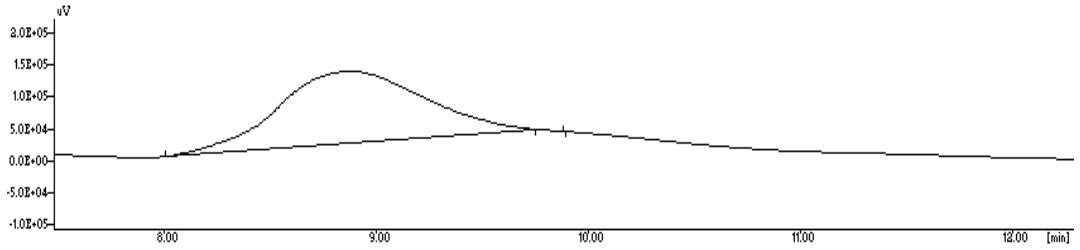
Racemic



#	Name	RT	Area[uV.Sec]	Quantity
1		10.558	137952.844	0.000
2		12.175	137374.276	0.000

Total Area of Peak = 275327.120 [uV.Sec]

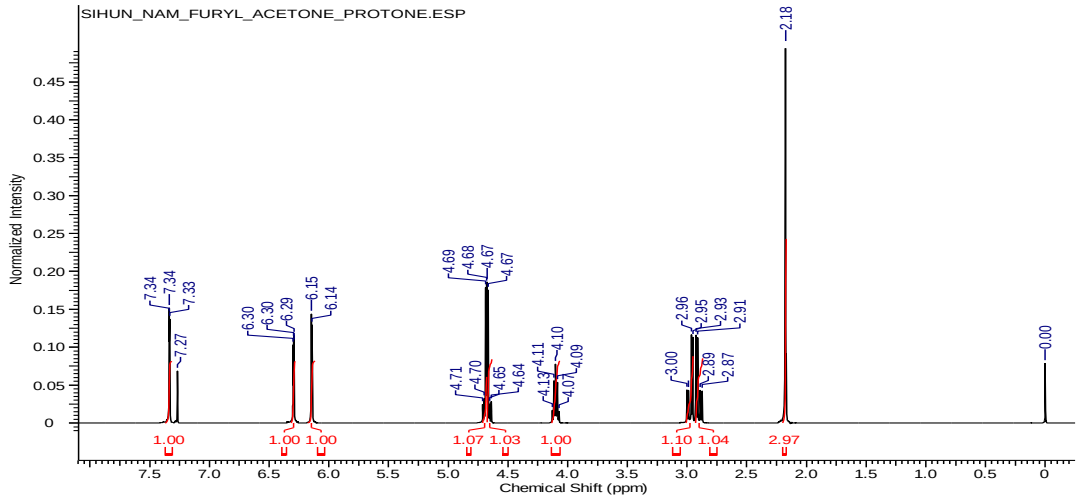
Asymmetric



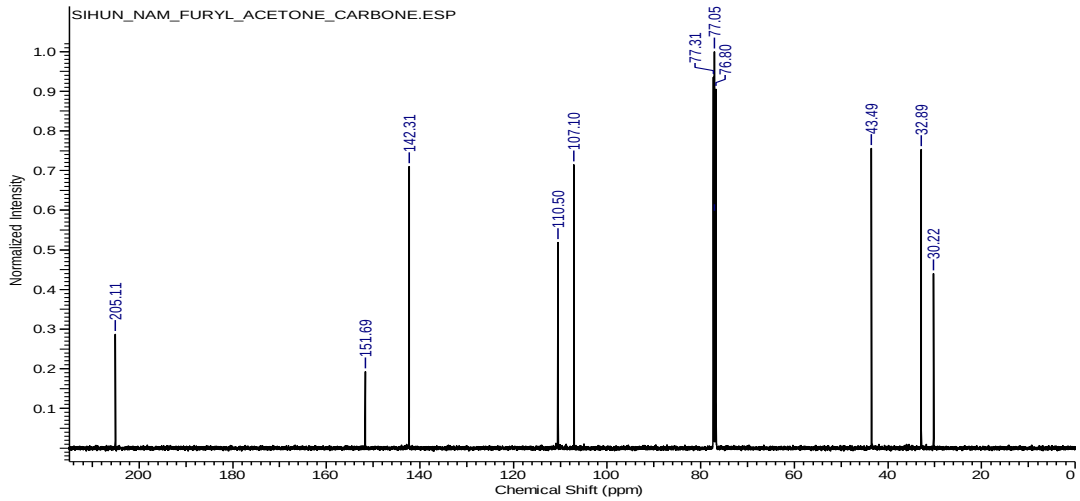
#	Name	RT	Area[uV.Sec]	Quantity
1		8.875	5325457.500	0.000
2		9.867	22870.000	0.000

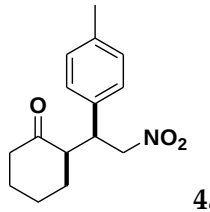
Total Area of Peak = 5348327.500 [uV.Sec]

^{1}H NMR


SIHUN_NAM_FURYL_ACETONE_PROTONE.ESP
Normalized Intensity
Chemical Shift (ppm)
7.34
7.34
7.33
7.27
6.30
6.30
6.29
6.15
6.14
4.69
4.68
4.67
4.67
4.71
4.70
4.65
4.64
4.13
4.11
4.10
4.09
4.01
3.00
2.96
2.95
2.93
2.91
2.89
2.87
2.18
0.00
1.00
1.00
1.00
1.07
1.03
1.00
1.10
1.04
2.97

^{13}C NMR

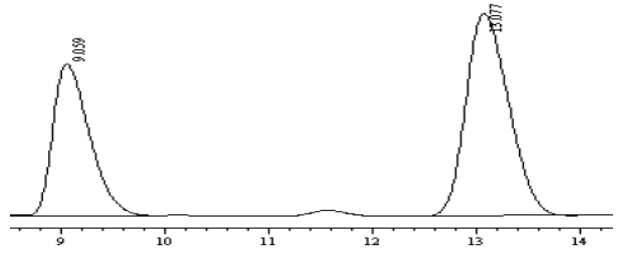

SIHUN_NAM_FURYL_ACETONE_CARBONE.ESP
Normalized Intensity
Chemical Shift (ppm)
205.11
151.69
142.31
110.50
107.10
77.31
77.05
76.80
43.49
32.89
30.22

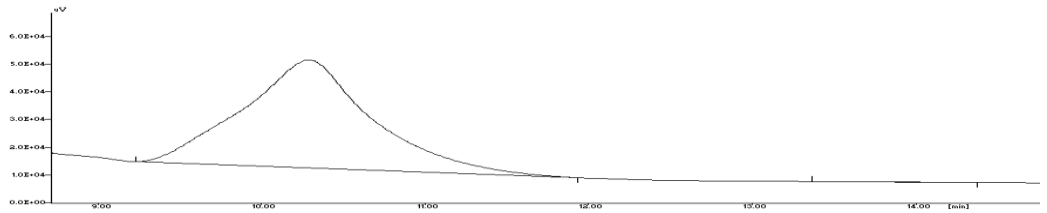

O
NO2

4a

LC data

racemic

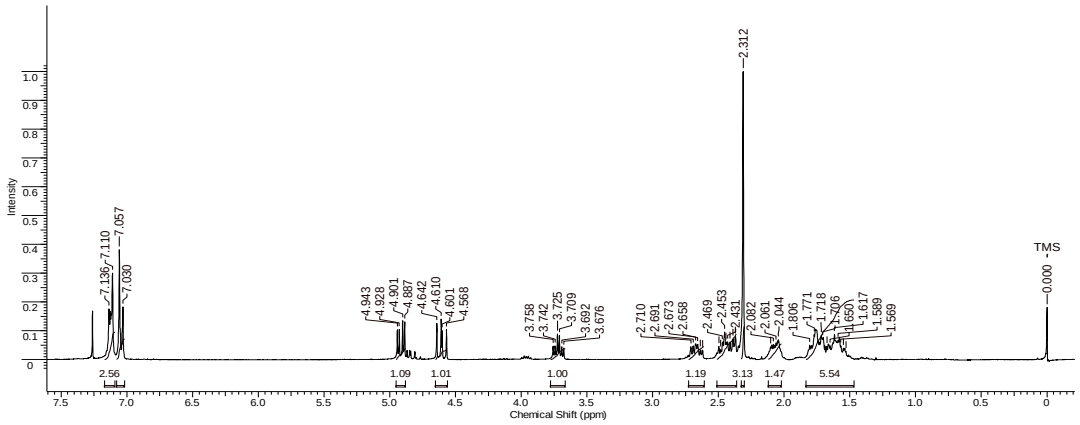




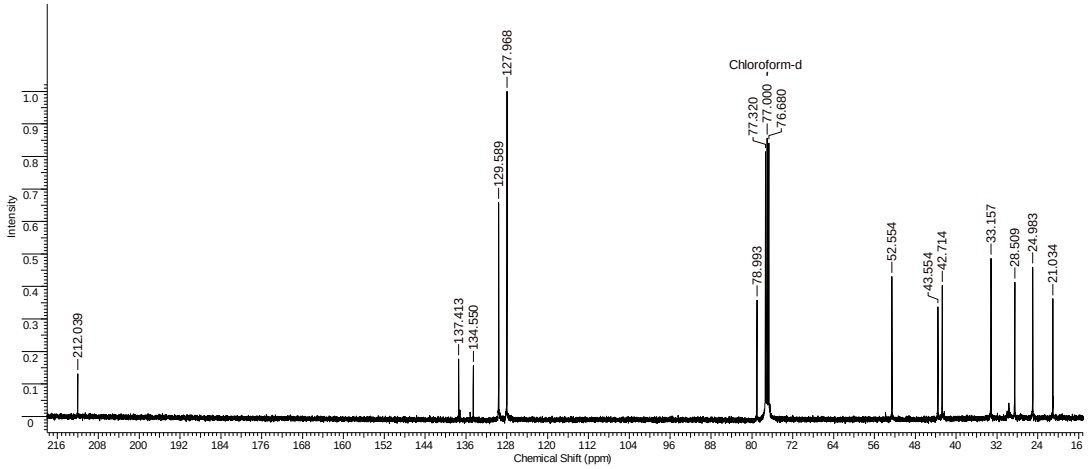
#	Name	RT	Area[uV.Sec]	Quantity
1		10.292	2131081.750	0.000
2		13.383	1543.000	0.000

Total Area of Peak = 2132624.750 [uV.Sec]

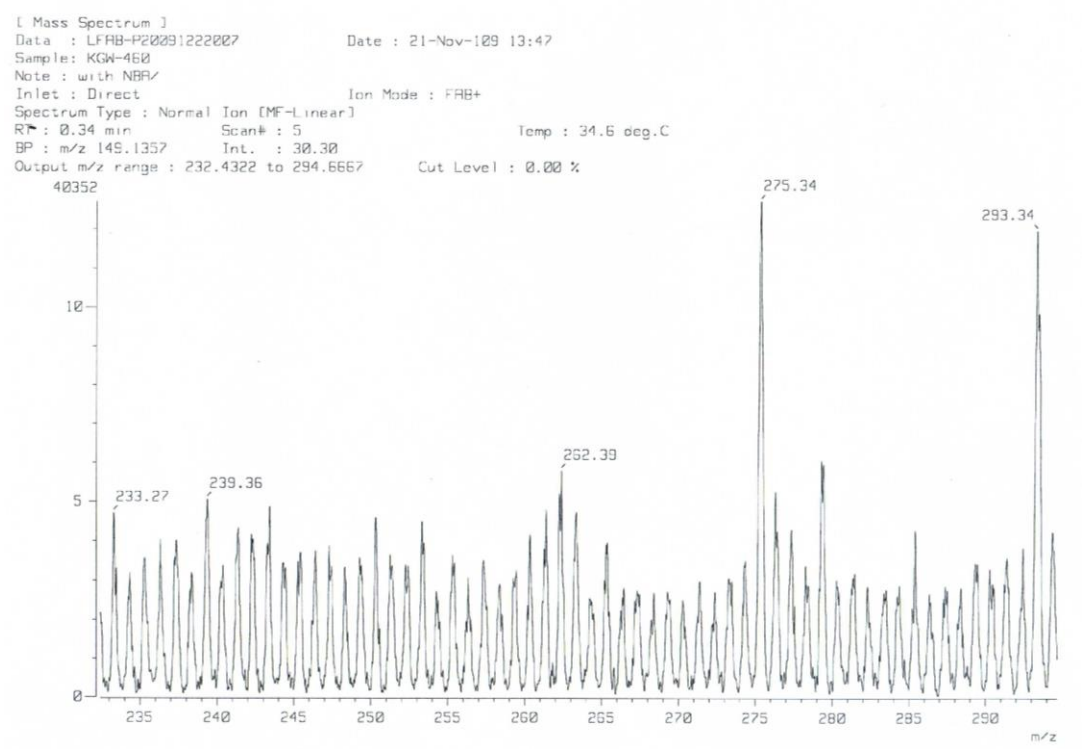
^{1}H NMR

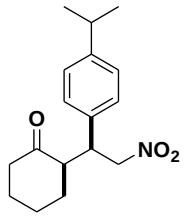


^{13}C NMR


Chloroform-d
127.968
129.589
77.320
77.000
76.680
78.993
137.413
134.550
212.039
52.554
43.554
42.714
33.157
28.509
24.983
21.034
Intensity
Chemical Shift (ppm)

Mass

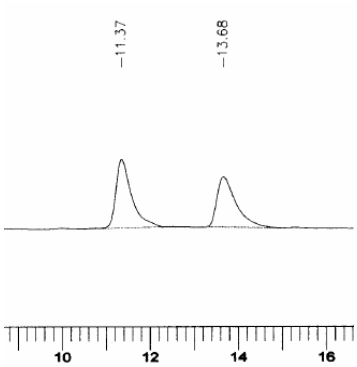

[Mass Spectrum]
Data : LFAB-P2009122007 Date : 21-Nov-109 13:47
Sample: KGW-460
Note : with NBA/
Inlet : Direct Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.34 min Scan# : 5 Temp : 34.6 deg.C
BP : m/z 149.1357 Int. : 30.30
Output m/z range : 232.4322 to 294.6667 Cut Level : 0.00 %
40352
275.34
293.34
262.39
239.36
233.27
m/z

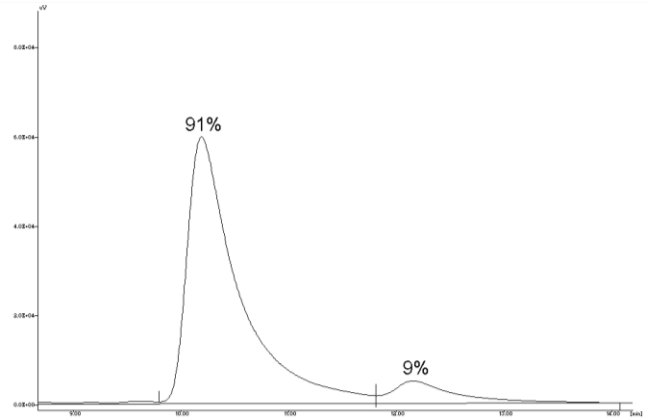


4b

LC data

racemic

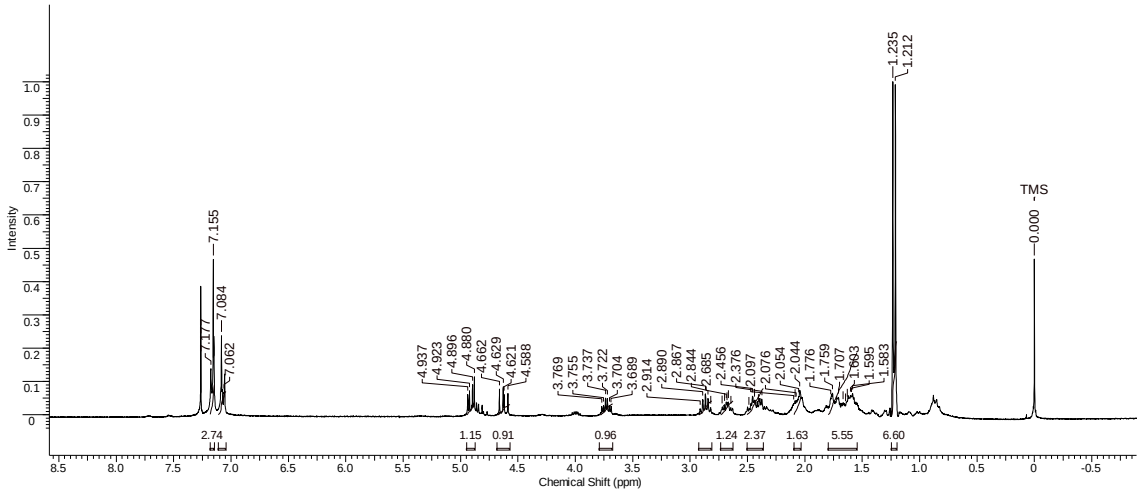




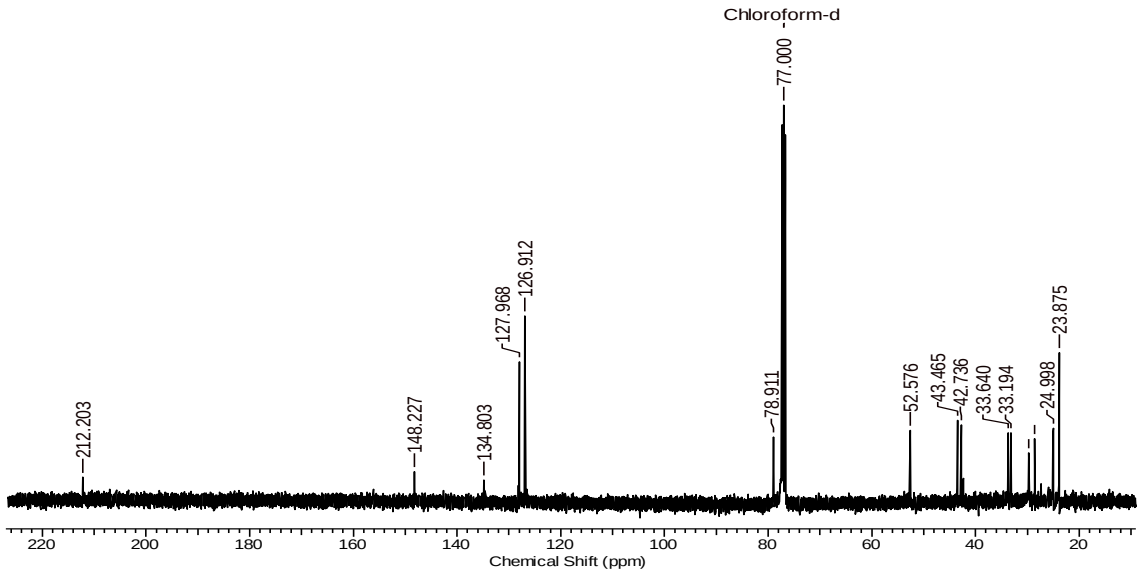
#	Name	RT	Area[uV.Sec]	Quantity
1		10.192	2000388.414	0.000
2		12.158	207832.166	0.000

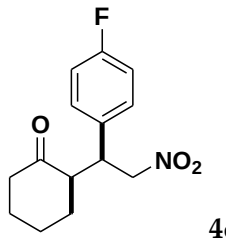
Total Area of Peak = 2208220.581 [uV.Sec]

^{1}H NMR



^{13}C NMR

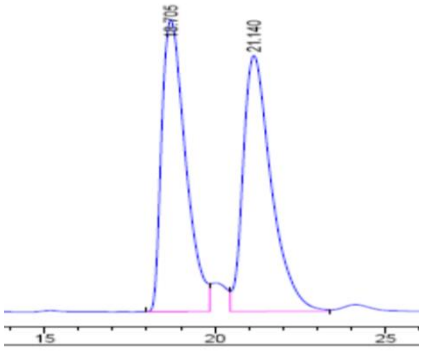

Chloroform-d
77.000
212.203
148.227
134.803
127.968
126.912
78.911
52.576
43.465
42.736
33.640
33.194
24.998
23.875
220
200
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

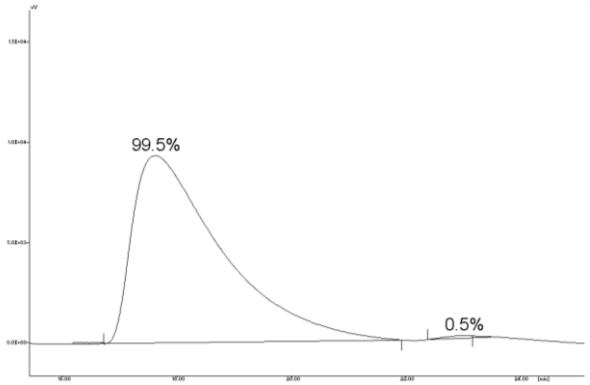


4c

LC data

racemic

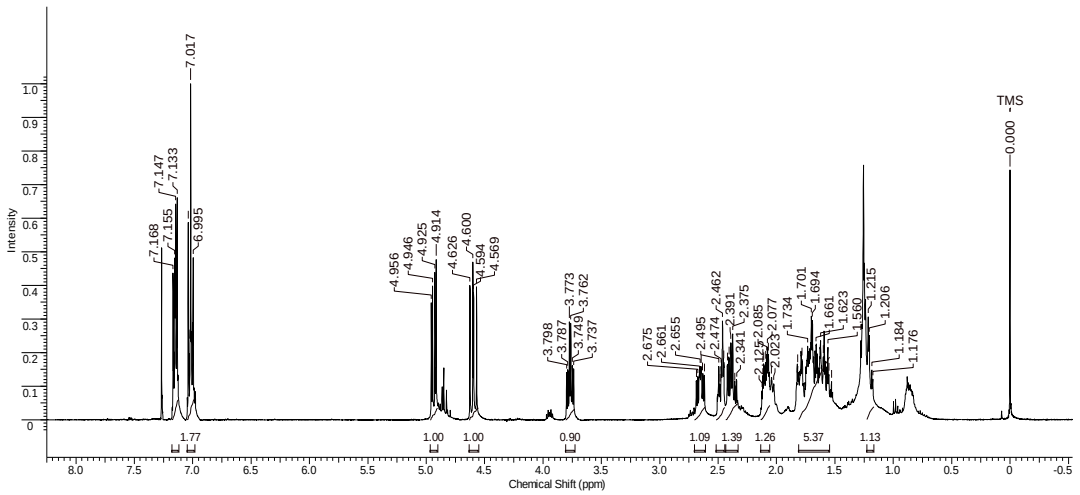




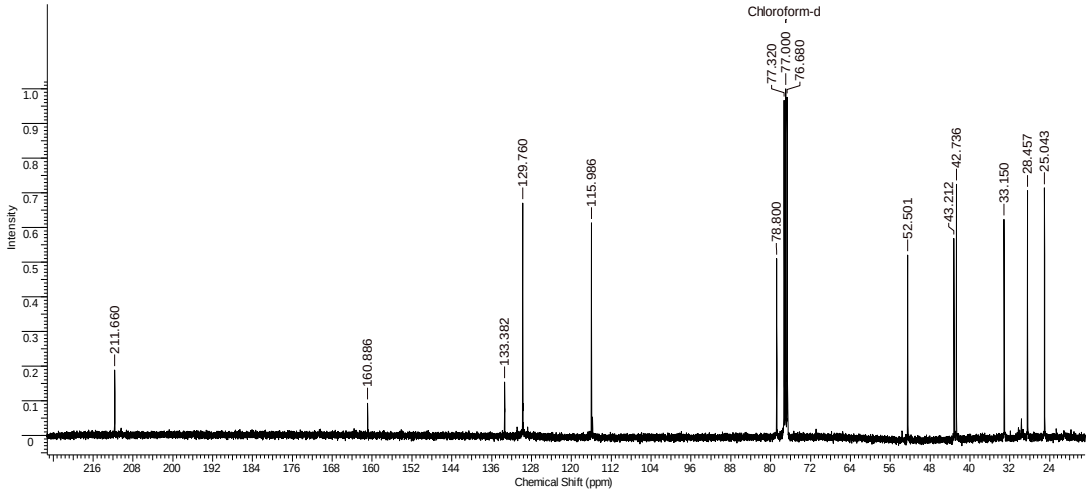
#	Name	RT	Area[uV.Sec]	Quantity
1		19.292	1416102.812	0.000
2		25.533	384599.179	0.000

Total Area of Peak = 1800701.991 [uV.Sec]

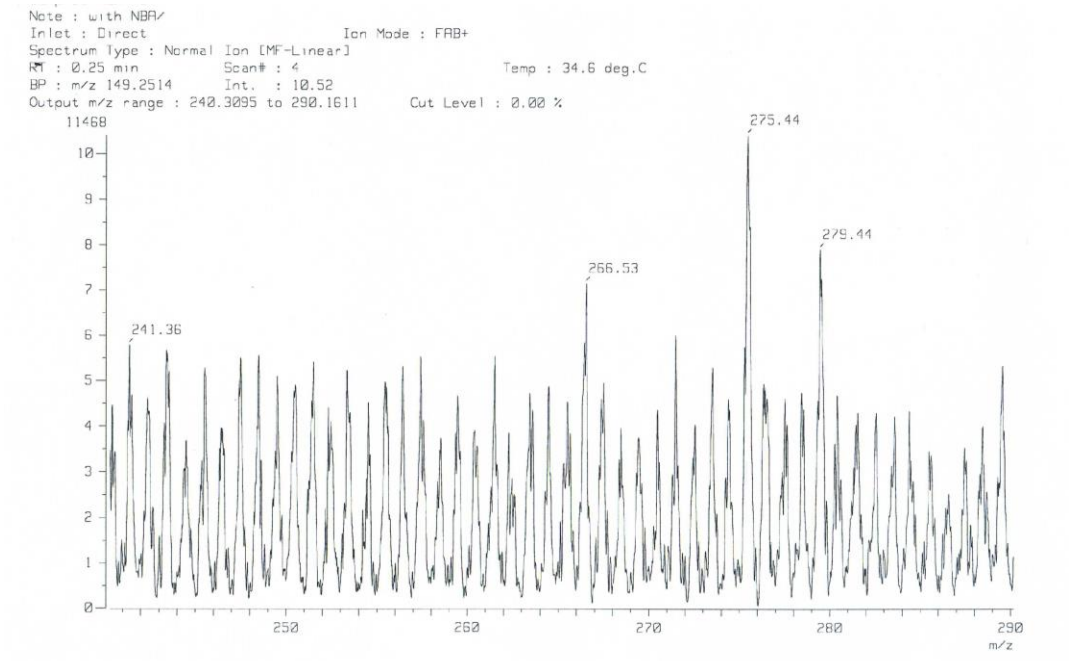
^{1}H NMR

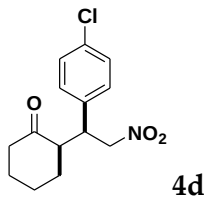


^{13}C NMR


Chloroform-d
77.320
77.000
76.680
129.760
115.986
78.800
52.501
43.212
42.736
33.150
28.457
25.043
211.660
160.886
133.382
Intensity
Chemical Shift (ppm)

Mass

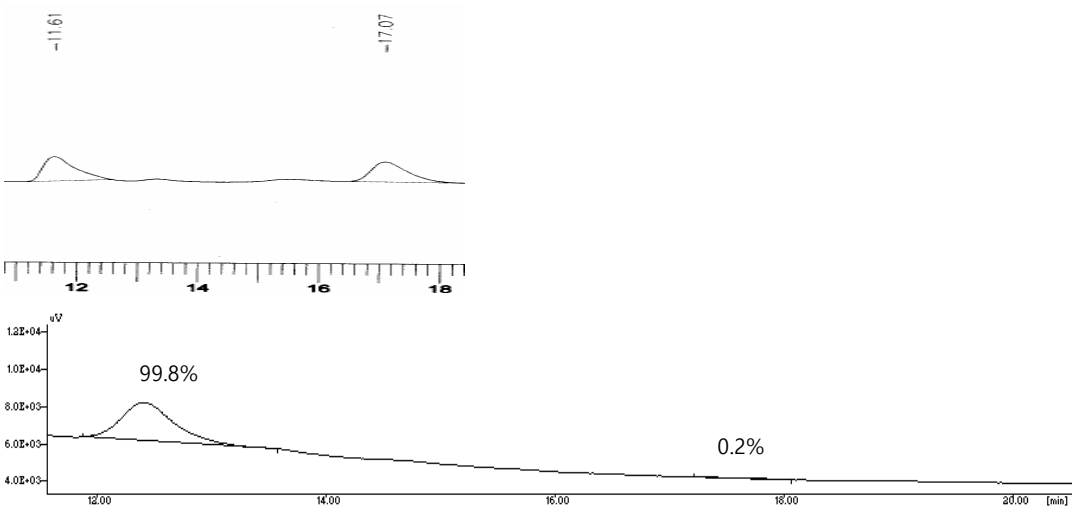

Note : with NBA
Inlet : Direct
Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.25 min
Scan# : 4
Temp : 34.6 deg.C
BP : m/z 149.2514
Int. : 10.52
Output m/z range : 240.3095 to 290.1611
Cut Level : 0.00 %
11468
275.44
279.44
266.53
241.36
m/z



4d

LC data

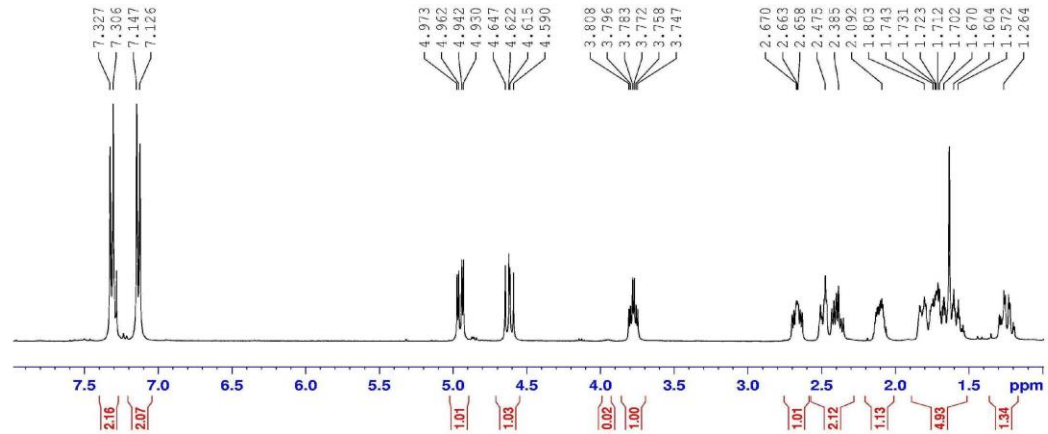
racemic



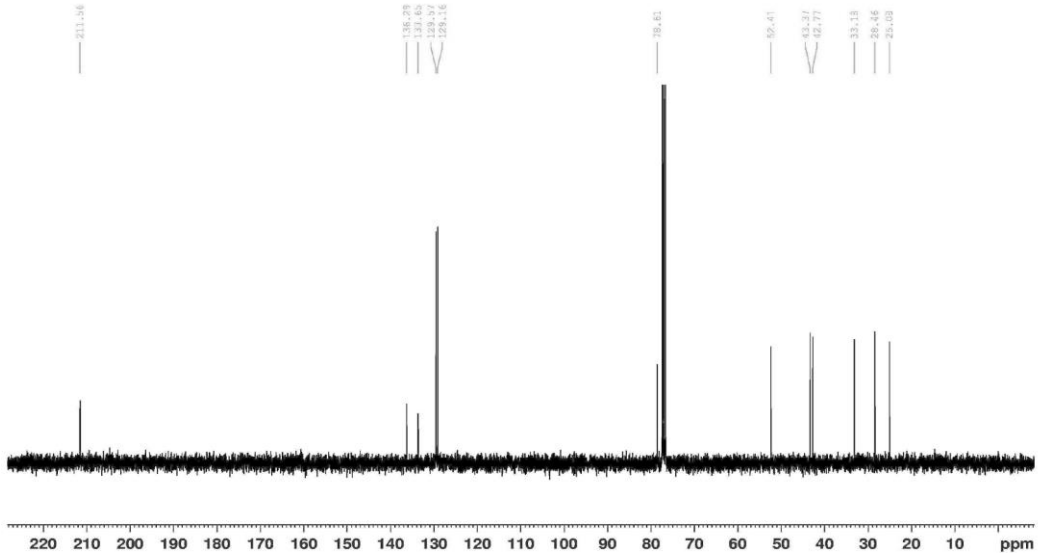
#	Name	RT	Area[uV.Sec]	Quantity
1		12.392	65651.549	0.000
2		17.242	158.500	0.000

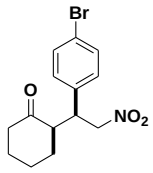
Total Area of Peak = 65810.049 [uV.Sec]

^{1}H NMR



^{13}C NMR

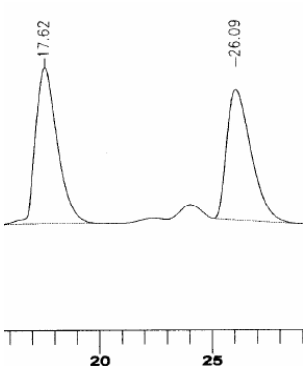

211.96
136.29
131.46
129.97
129.16
78.61
59.41
43.37
42.77
33.13
28.46
25.09
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

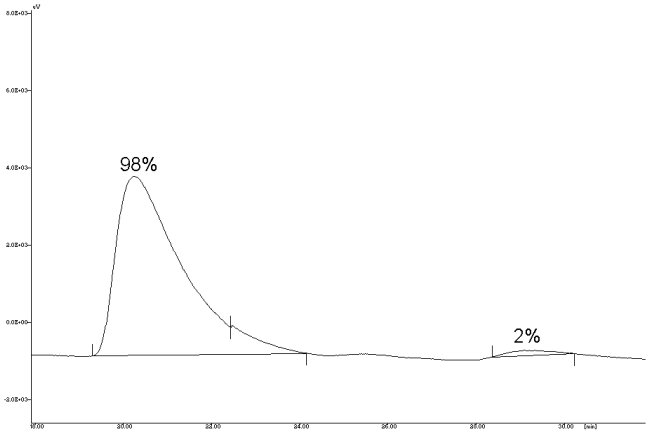


4e

LC data

racemic

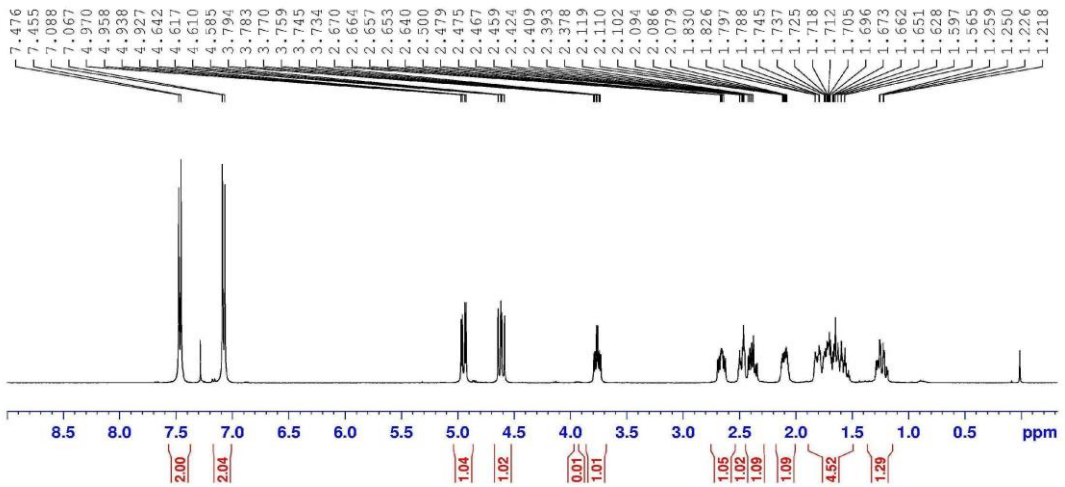




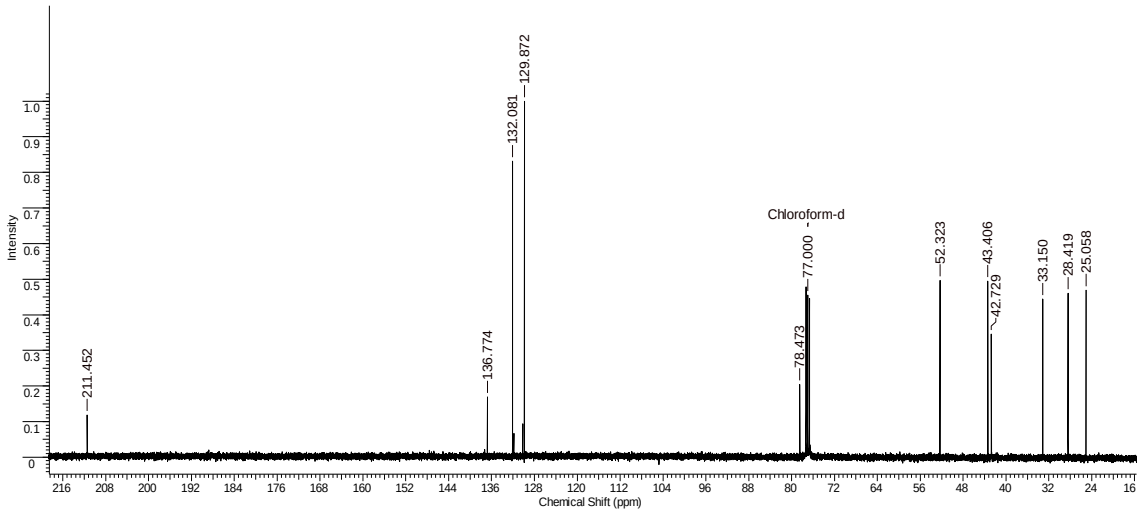
#	Name	RT	Area[uV.Sec]	Quantity
1		20.225	450132.882	0.000
2		29.083	9549.000	0.000

Total Area of Peak = 459681.882 [uV.Sec]

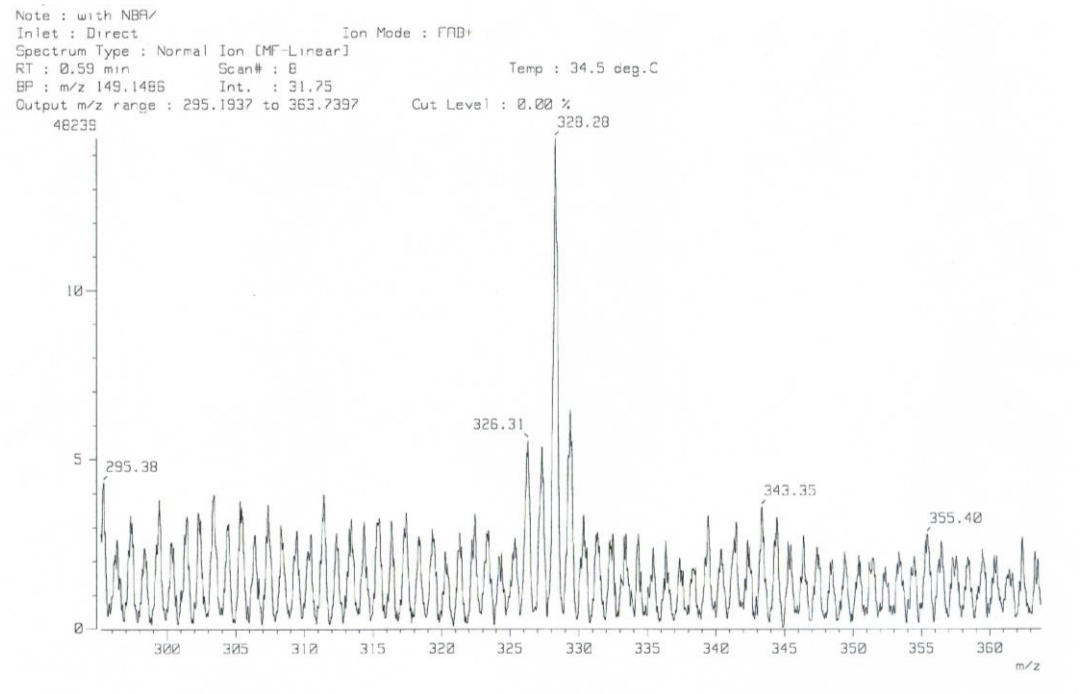
^{1}H NMR

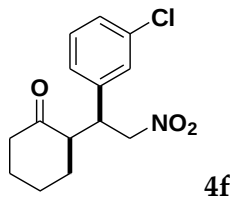


^{13}C NMR


Intensity
Chemical Shift (ppm)
Chloroform-d
211.452
136.774
132.081
129.872
78.473
77.000
52.323
43.406
42.729
33.150
28.419
25.058

Mass

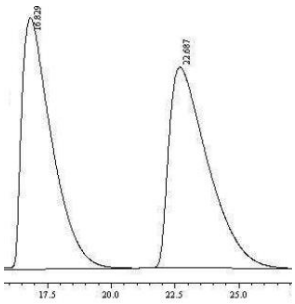

Note : with NBA/
Inlet : Direct
Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.59 min
Scan# : 8
Temp : 34.5 deg.C
BP : m/z 149.1486
Int. : 31.75
Output m/z range : 295.1937 to 363.7397
Cut Level : 0.00 %
48239
328.28
326.31
295.38
343.35
355.40
m/z

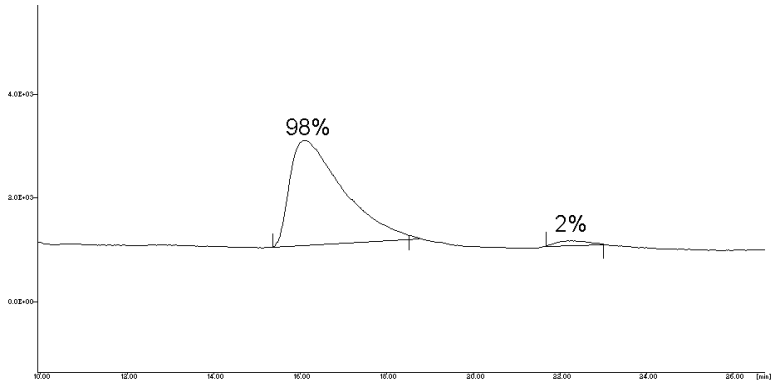


4f

LC data

Racemic

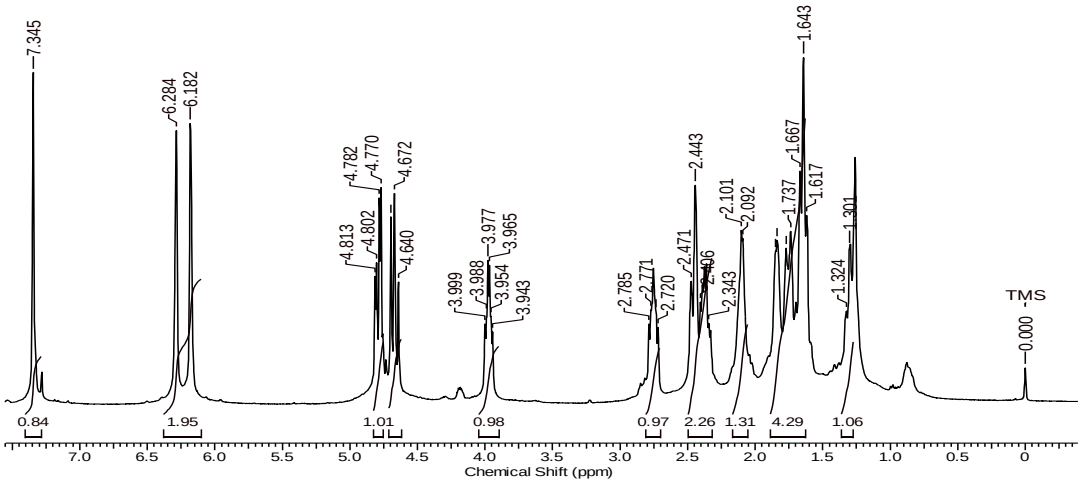




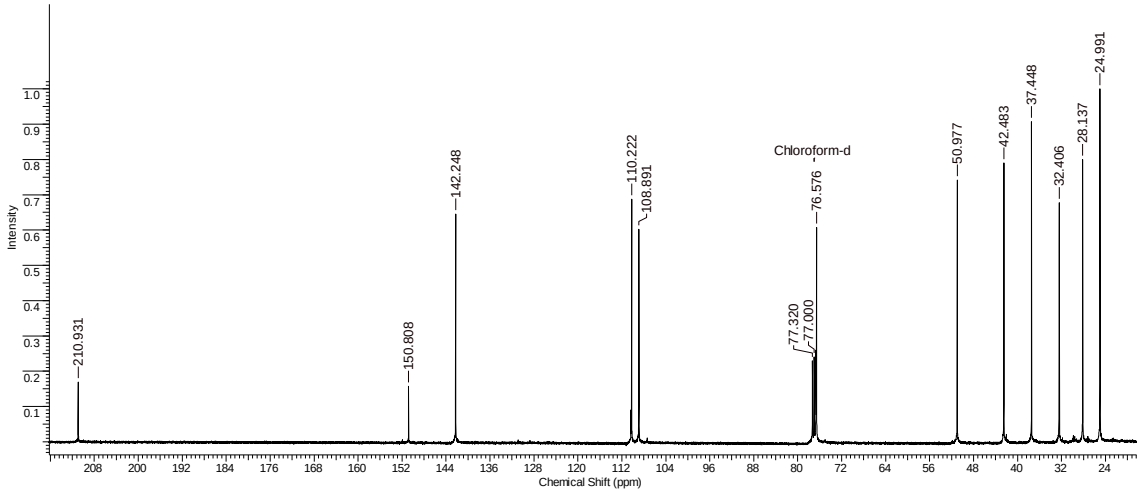
#	Name	RT	Area[uV.Sec]	Quantity
1		16.092	171111.478	0.000
2		22.167	4330.250	0.000

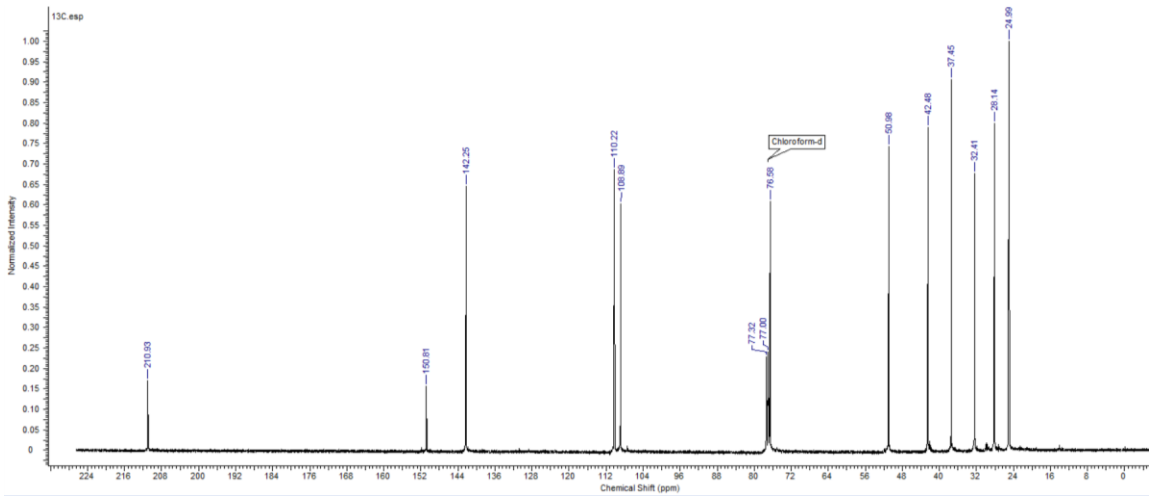
Total Area of Peak = 175441.728 [uV.Sec]

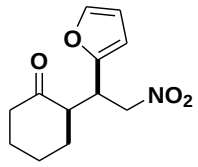
^{1}H NMR



^{13}C NMR


Intensity
Chemical Shift (ppm)
210.931
150.808
142.248
110.222
108.891
77.320
77.000
76.576
Chloroform-d
50.977
42.483
37.448
32.406
28.137
24.991

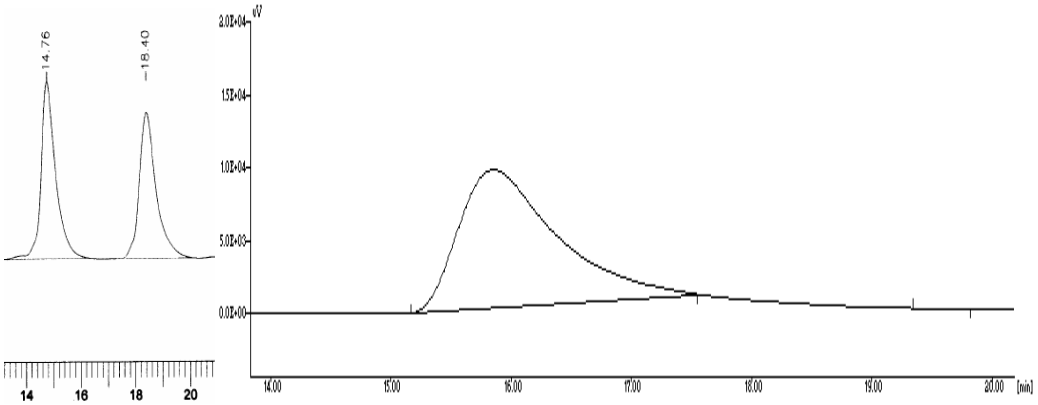

13C.esp
Normalized Intensity
Chemical Shift (ppm)
210.93
150.81
142.25
110.22
108.89
77.32
77.00
76.58
Chloroform-d
50.98
42.48
37.45
32.41
28.14
24.99



4g

LC data

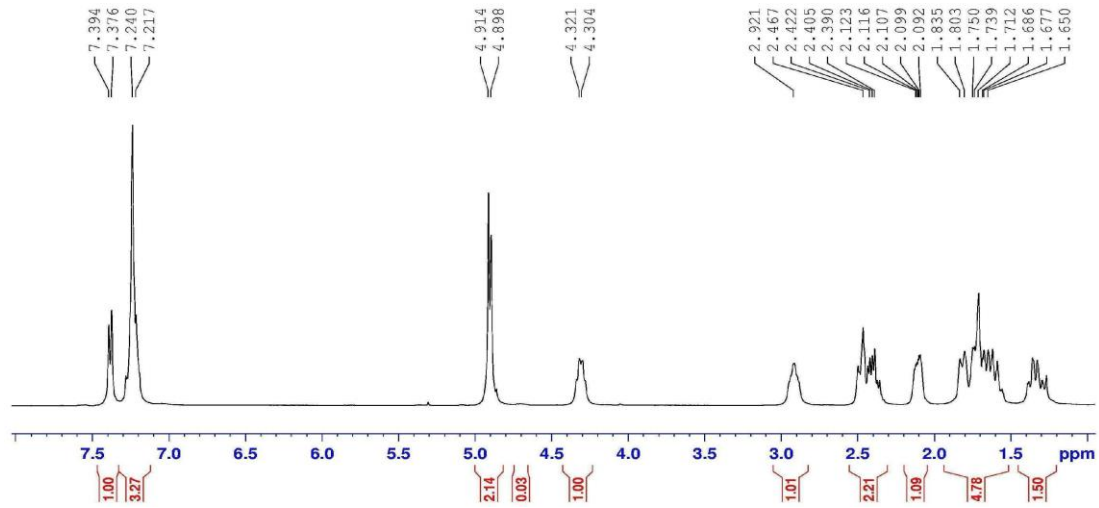
racemic



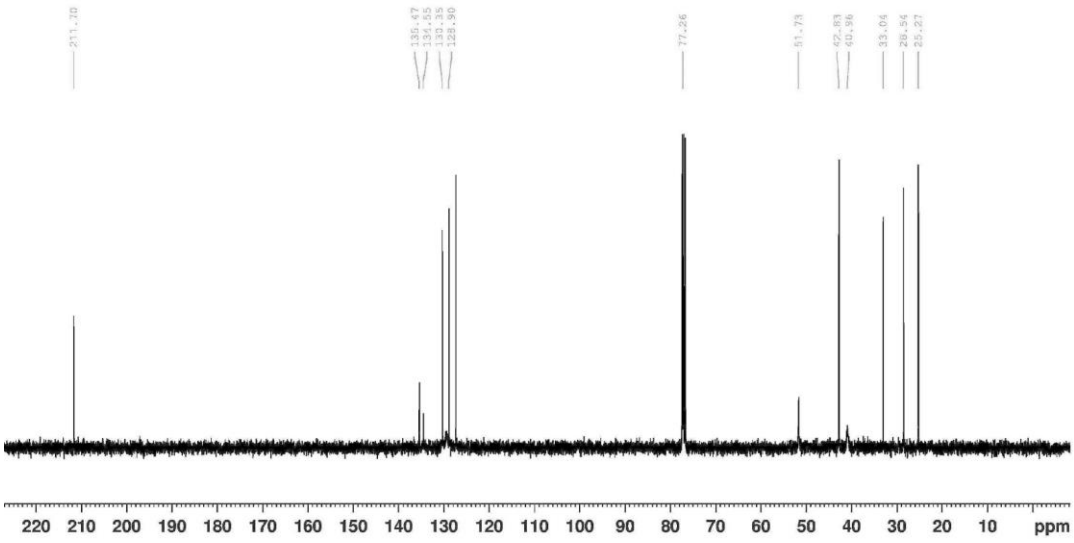
#	Name	RT	Area[uV.Sec]	Quantity
1		15.867	538192.000	0.000
2		19.392	69.500	0.000

Total Area of Peak = 538261.500 [uV.Sec]

^{1}H NMR

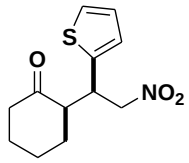


^{13}C NMR



Mass

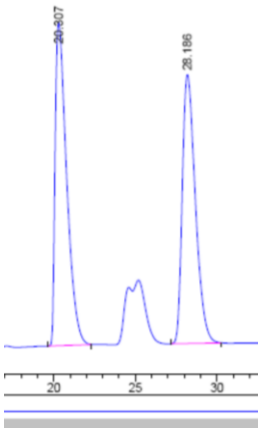
```
[ Elemental Composition ]
Data  : HFAB-POS-091223020              Date : 23-Dec-2009 17:05
Sample: KGW-468
Note :
Inlet : Direct                          Ion Mode : FAB+
RT : 2.17 min                           Scan#: 27
Elements : C 12/0, H 16/0, O 4/0, N 1/0
Mass Tolerance       : 10mmu
Unsaturation (U.S.) : 0.0 - 100.0

Observed m/z   Int%
  238.1080      12.7
Estimated m/z  Error[ppm]  U.S.     C     H     O     N
  238.1079       +0.1       5.5    12    16     4     1
```

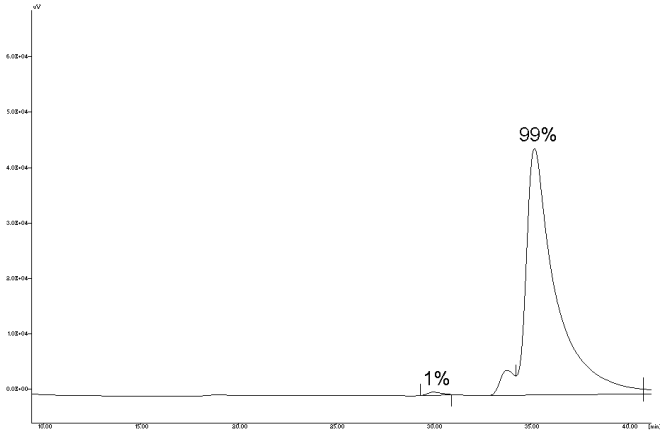


4h

LC data

racemic

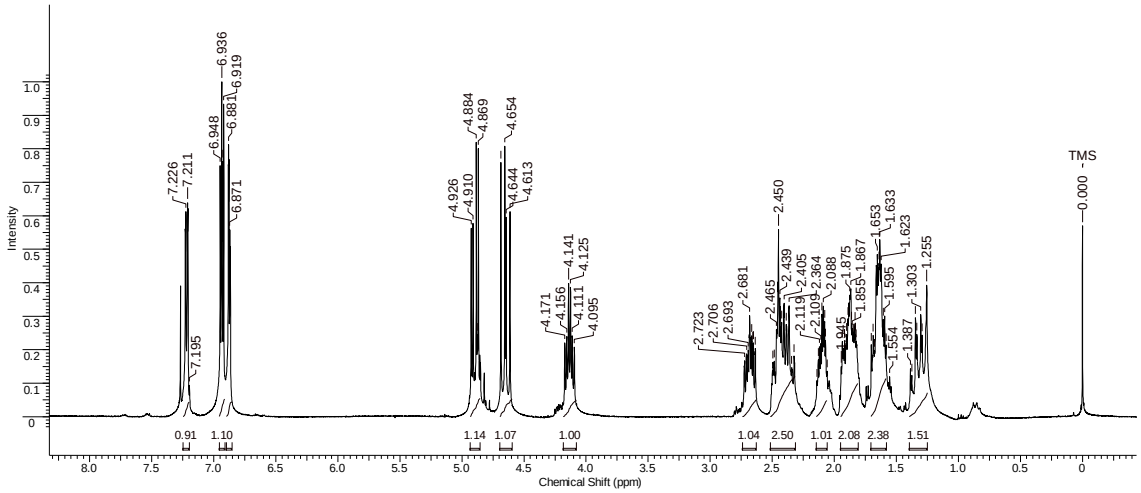




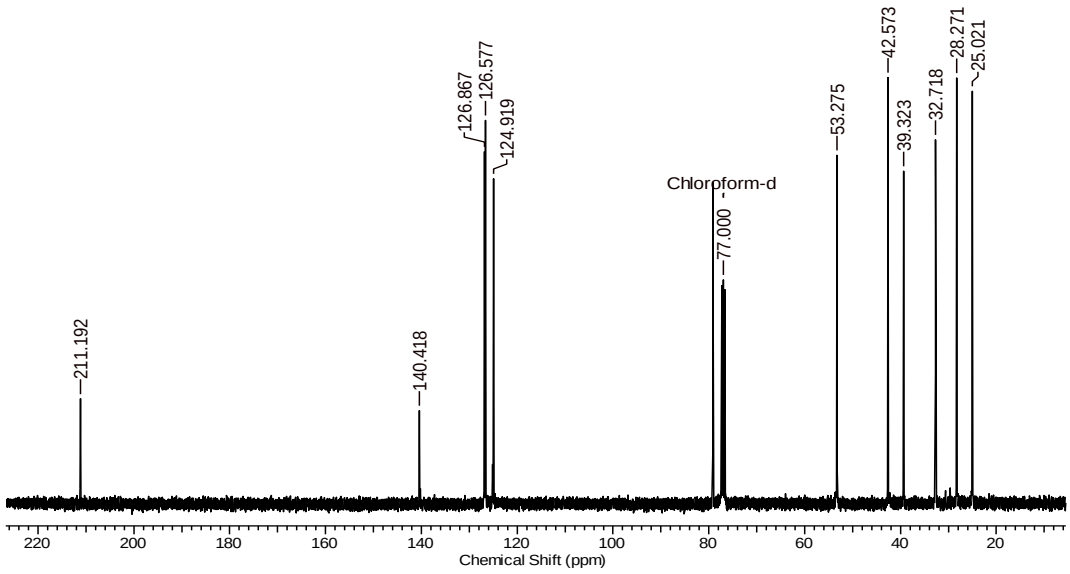
#	Name	RT	Area[uV.Sec]	Quantity
1		29.958	33101.830	0.000
2		35.167	4566167.050	0.000

Total Area of Peak = 4599268.880 [uV.Sec]

^{1}H NMR



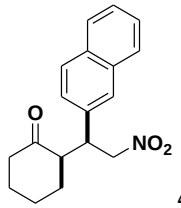
^{13}C NMR



Mass

[Elemental Composition]
Data : HFAB-POS-091223021 Date : 23-Dec-2009 17:16
Sample: KGW-471
Note :
Inlet : Direct Ion Mode : FAB+
RT : 2.09 min Scan#: 26
Elements : C 12/0, H 16/0, O 3/0, N 1/0, S 1/0
Mass Tolerance : 10mmu
Unsaturation (U.S.) : 0.0 - 100.0

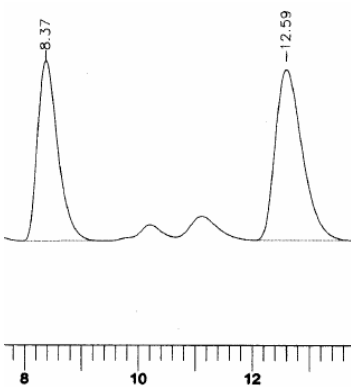
Observed m/z	Int%						
254.0853	19.3						
Estimated m/z	Error[ppm]	U.S.	C	H	O	N	S
254.0851	+0.9	6.5	12	16	3	1	1

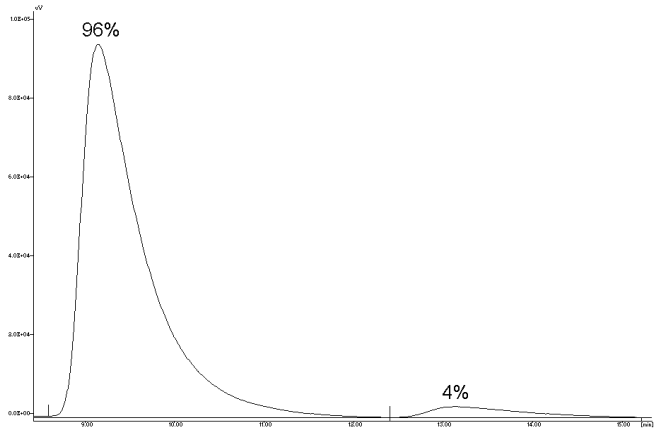


4i

LC data

racemic

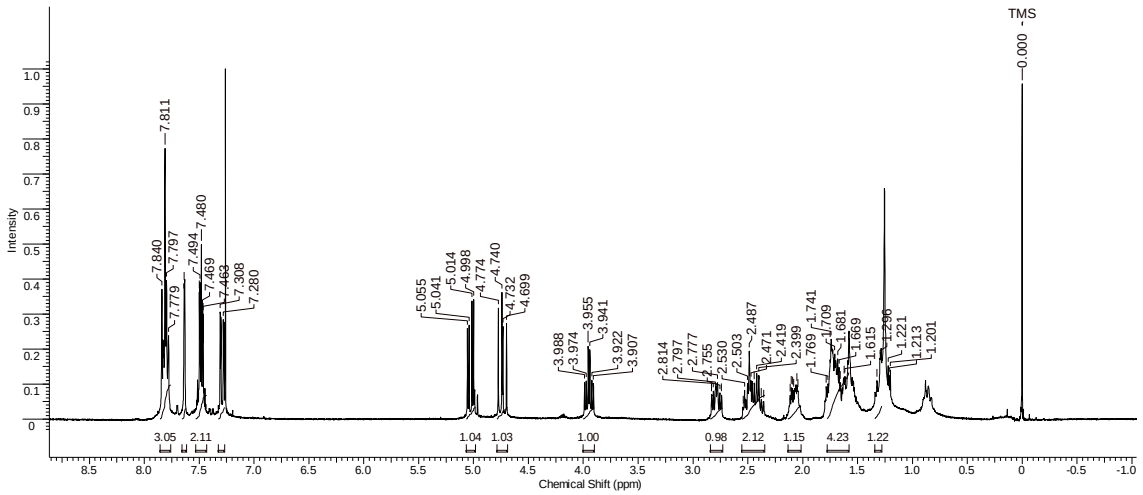




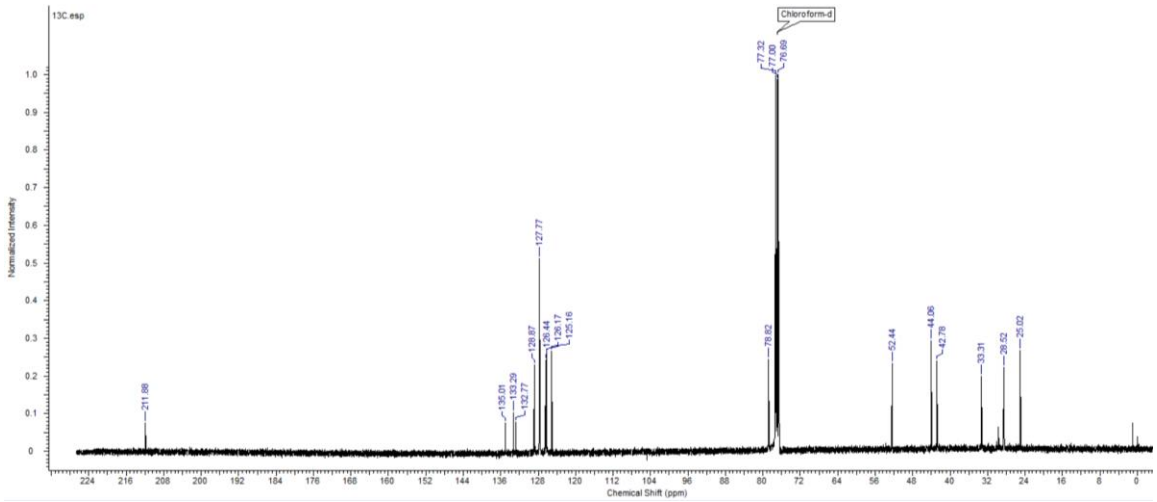
#	Name	RT	Area[uV.Sec]	Quantity
1		9.142	4540475.150	0.000
2		13.117	193295.000	0.000

Total Area of Peak = 4733770.150 [uV.Sec]

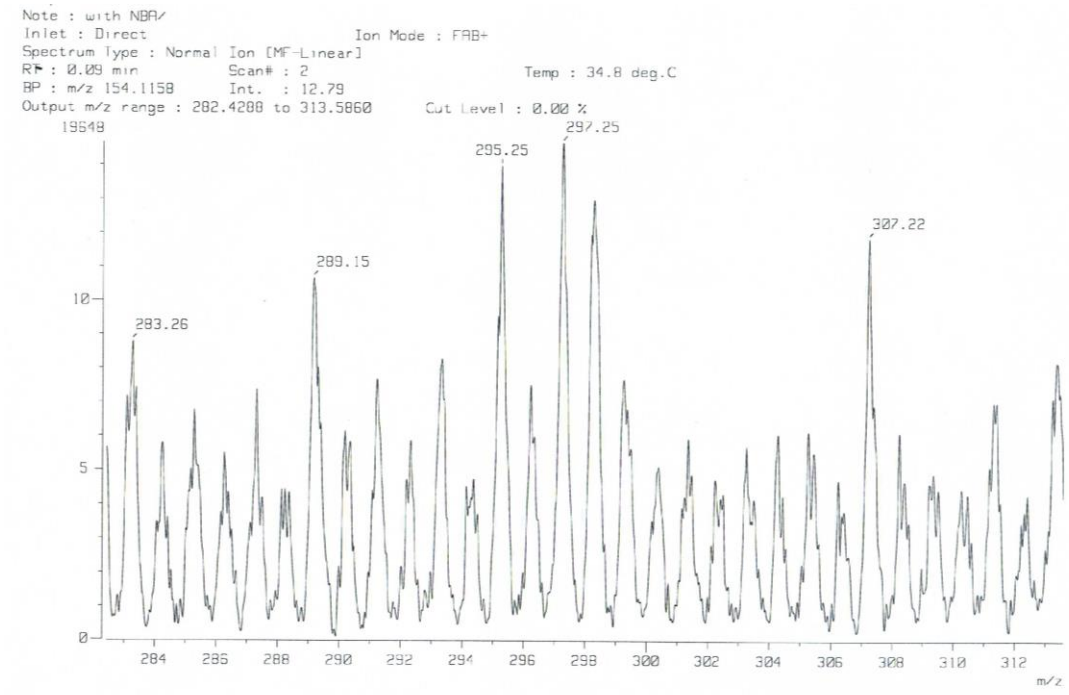
^{1}H NMR

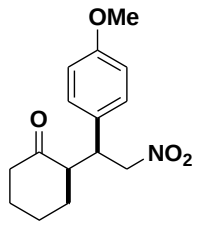


^{13}C NMR


13C.esp
Chloroform-d
77.32
77.00
76.69
127.77
129.87
126.44
126.17
125.16
136.01
133.29
132.77
211.88
79.82
52.44
44.06
42.78
33.31
28.52
25.02
Normalized Intensity
Chemical Shift (ppm)

Mass

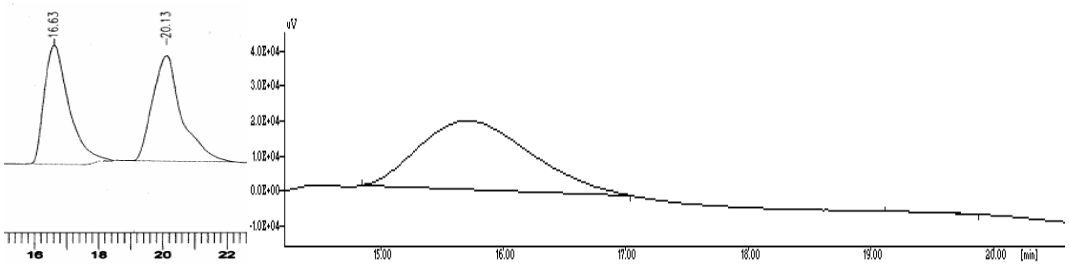

Note : with NBA/
Inlet : Direct
Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.09 min
Scan# : 2
Temp : 34.8 deg.C
BP : m/z 154.1158
Int. : 12.79
Output m/z range : 282.4288 to 313.5860
Cut Level : 0.00 %
19548
297.25
295.25
307.22
289.15
283.26
m/z



4j

LC data

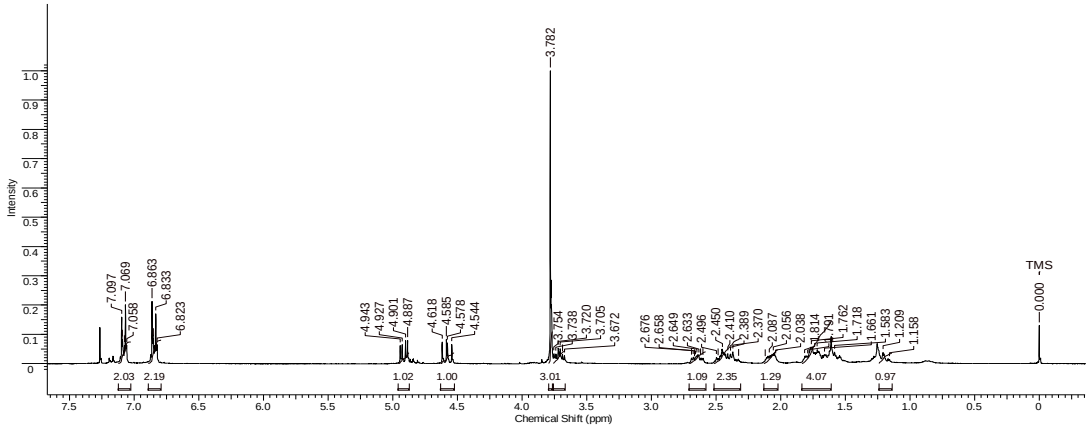
racemic



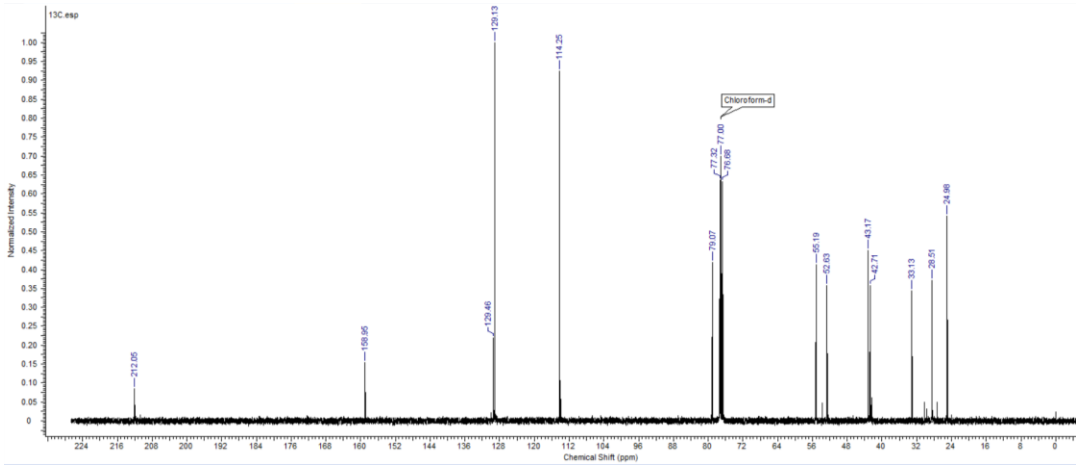
#	Name	RT	Area[uV.Sec]	Quantity
1		15.717	1241067.250	0.000
2		19.142	7222.000	0.000

Total Area of Peak = 1248289.250 [uV.Sec]

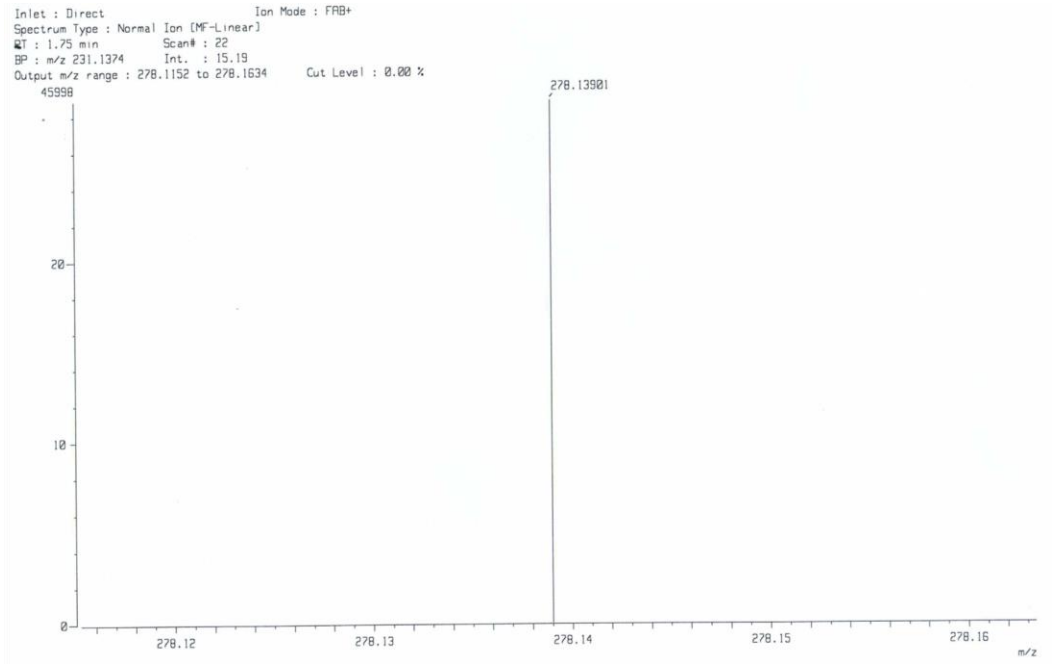
^{1}H NMR

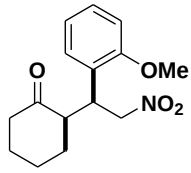


^{13}C NMR


13C.esp
Chloroform-d
Chemical Shift (ppm)
Normalized Intensity

Mass

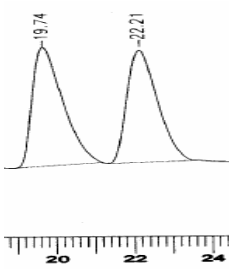

Inlet : Direct
Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 1.75 min
Scan# : 22
BP : m/z 231.1374
Int. : 15.19
Output m/z range : 278.1152 to 278.1634
Cut Level : 0.00 %
45998
278.13901
m/z

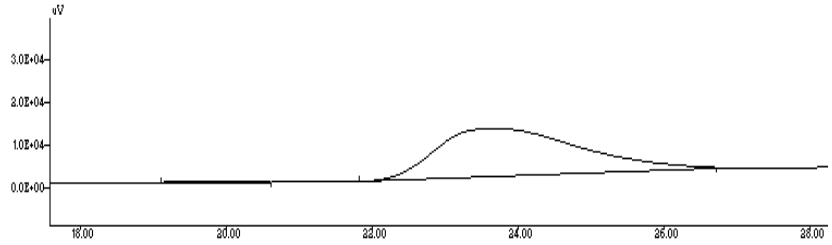


4k

LC data

racemic

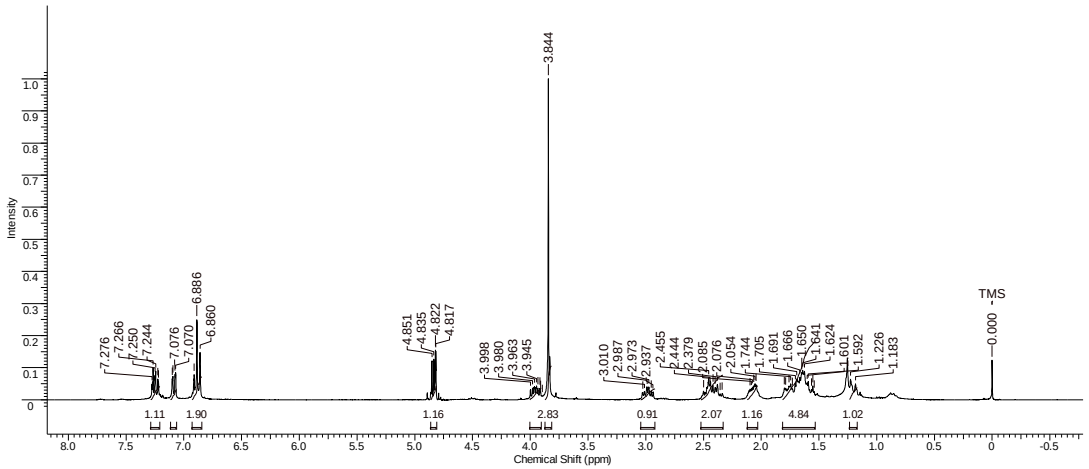




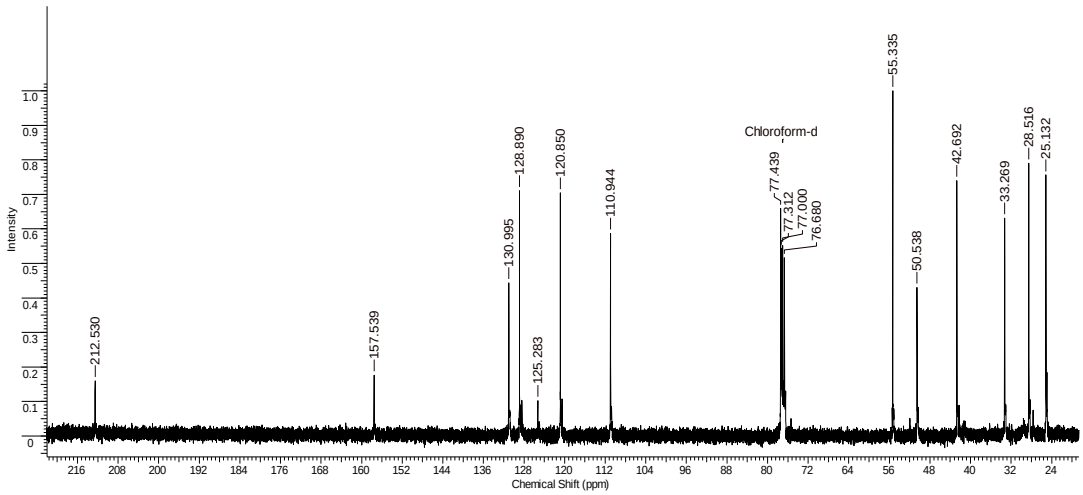
#	Name	RT	Area[uV.Sec]	Quantity
1		19.758	4042.809	0.000
2		23.683	1513756.491	0.000

Total Area of Peak = 1517799.300 [uV.Sec]

^{1}H NMR

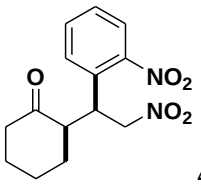


^{13}C NMR



Mass

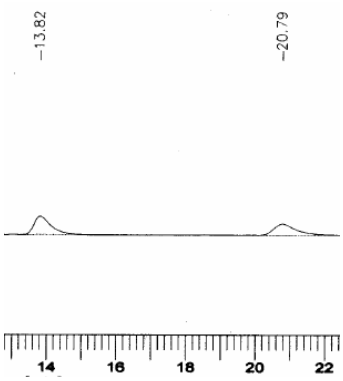
```
[ Elemental Composition ]
Data  : HFAB-POS-091229002              Date : 29-Dec-2009 17:56
Sample: 465
Note :
Inlet : Direct                          Ion Mode : FAB+
RT : 1.75 min                           Scan#: 22
Elements : C 15/0, H 20/0, O 4/0, N 1/0
Mass Tolerance      : 10mmu
Unsaturation (U.S.) : 0.0 - 100.0

Observed m/z   Int%
  278.1390      28.9
Estimated m/z  Error[ppm]  U.S.     C     H     O     N
  278.1392       -0.8       6.5    15    20     4     1
```

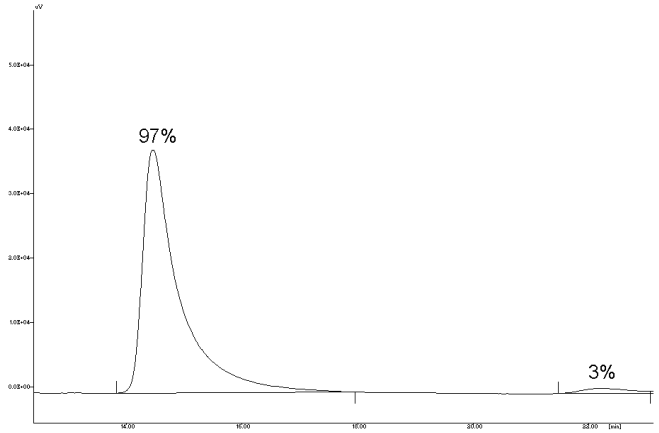


4l

LC data

racemic

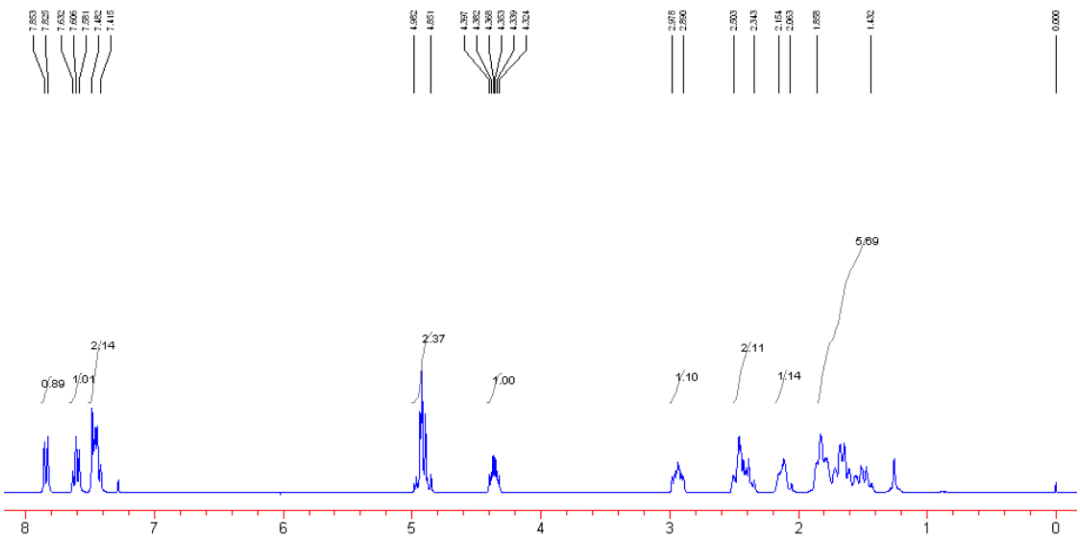




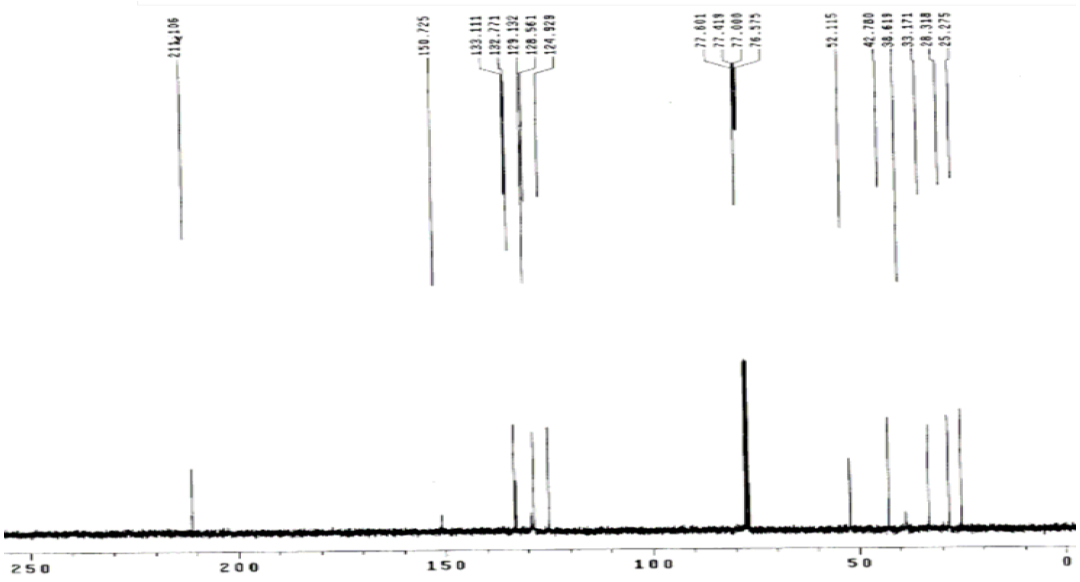
#	Name	RT	Area[uV.Sec]	Quantity
1		14.450	1631400.500	0.000
2		22.225	43091.037	0.000

Total Area of Peak = 1674491.537 [uV.Sec]

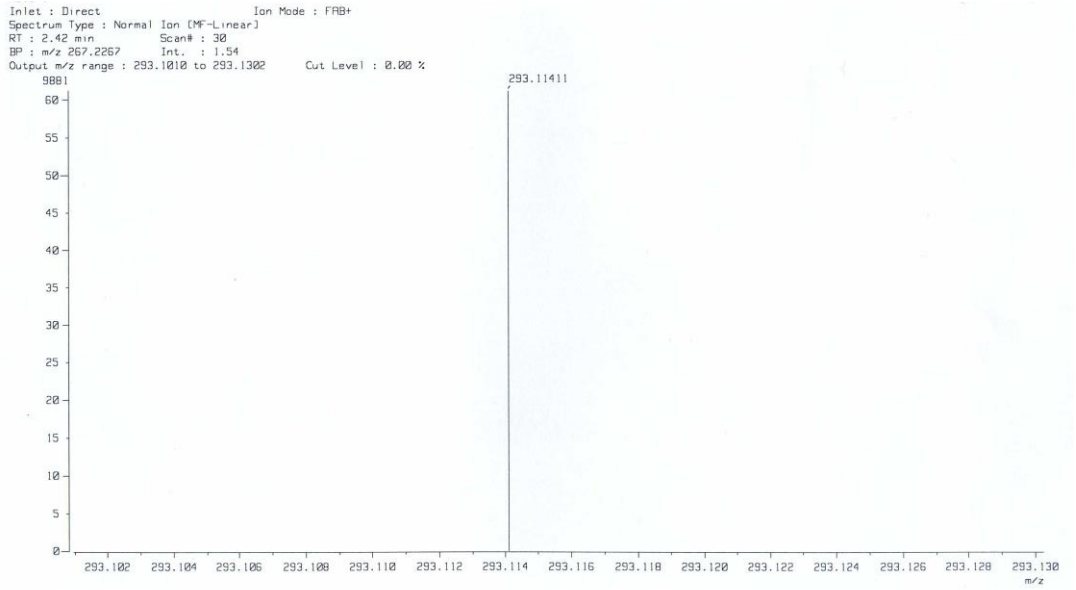
^{1}H NMR

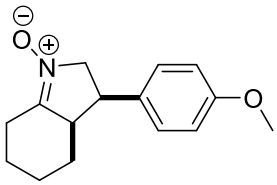

0.89
1.01
2.14
2.37
1.00
1.10
2.11
1.14
5.69
8
7
6
5
4
3
2
1
0

^{13}C NMR


250
200
150
100
50
0

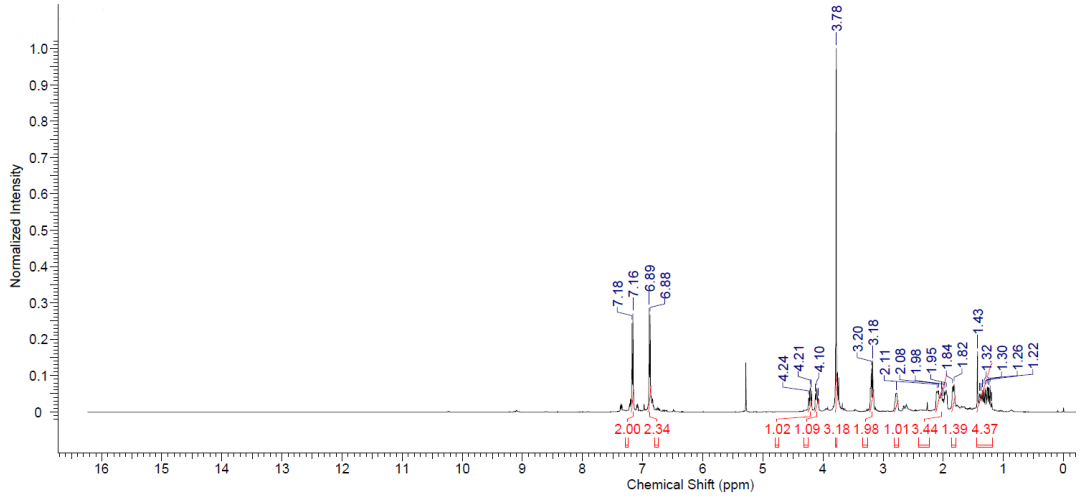
Mass


Inlet : Direct
Ion Mode : FAB+
Spectrum Type : Normal Ion (MF-Linear)
RT : 2.42 min
Scan# : 30
BP : m/z 267.2267
Int. : 1.54
Output m/z range : 293.1010 to 293.1302
Cut Level : 0.00 %
9881
293.11411
60
55
50
45
40
35
30
25
20
15
10
5
0
293.102
293.104
293.106
293.108
293.110
293.112
293.114
293.116
293.118
293.120
293.122
293.124
293.126
293.128
293.130
m/z

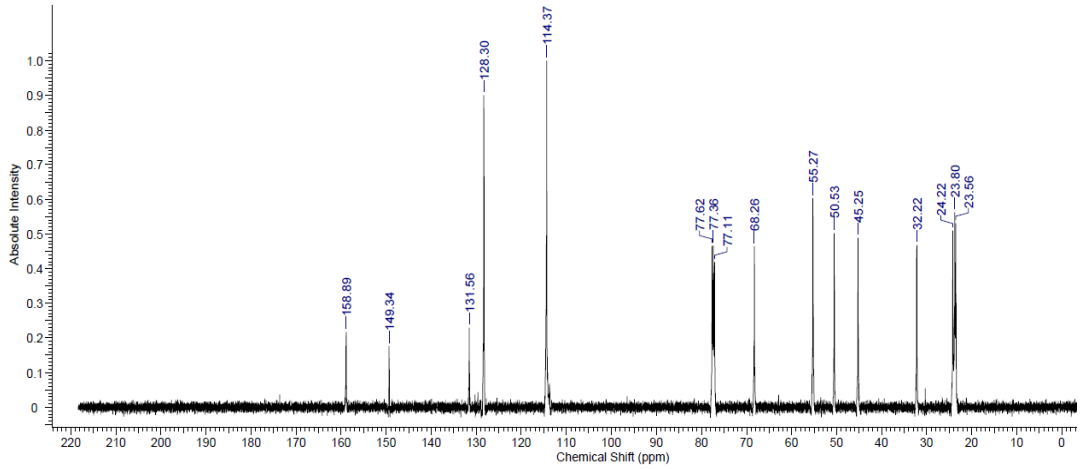


5a

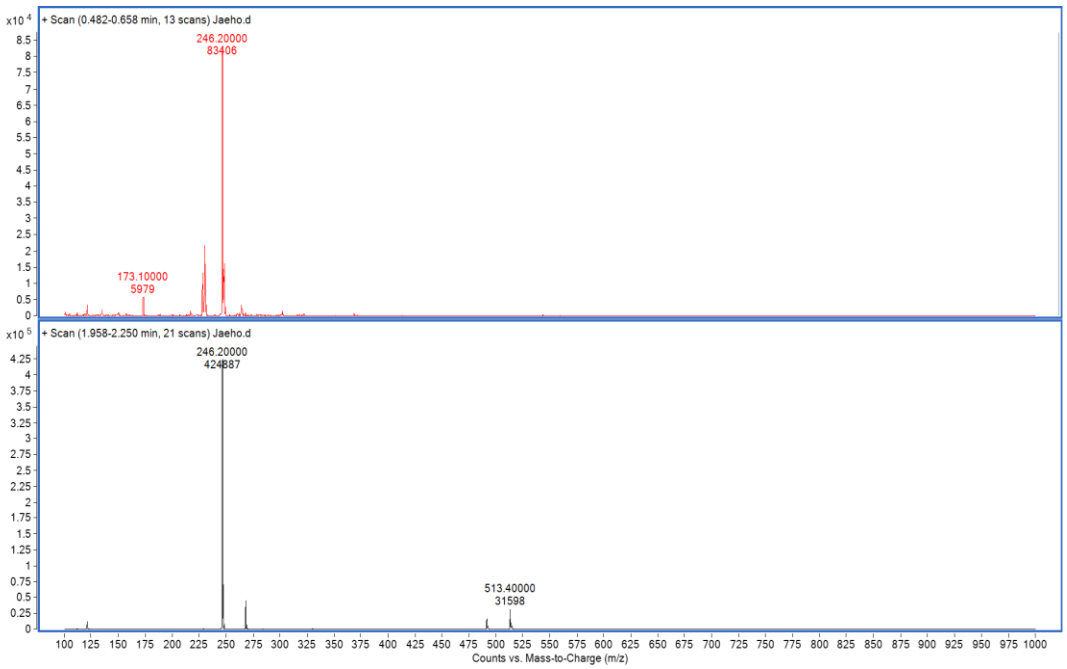
^{1}H NMR


Normalized Intensity
Chemical Shift (ppm)
7.18
7.16
6.89
6.88
3.78
4.24
4.21
4.10
3.20
3.18
2.11
2.08
1.98
1.95
1.84
1.82
1.43
1.32
1.30
1.26
1.22
2.00 2.34
1.02 1.09 3.18 1.98 1.01 3.44 1.39 4.37

^{13}C NMR

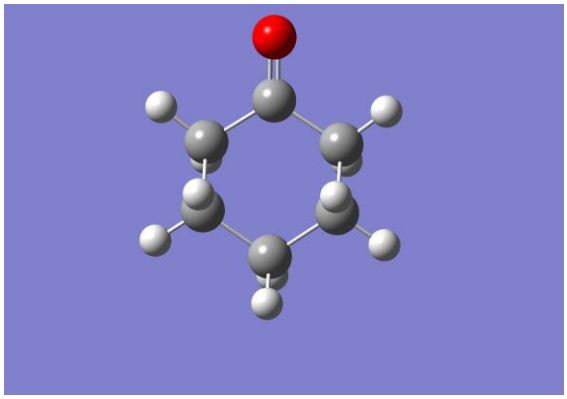

Absolute Intensity
Chemical Shift (ppm)
158.89
149.34
131.56
128.30
114.37
77.62
77.36
77.11
68.26
55.27
50.53
45.25
32.22
24.22
23.80
23.56

Mass



3. DFT Calculations for all Calculated Structures

Cyclohexanone(1)



Calculation Type = FREQ

Calculation Method = RB3LYP

Basis Set = 6-31G(d,p)

Charge = 0

Spin = Singlet

Solvation = None

E(RB3LYP) = -308.19901 Hartree

RMS Gradient Norm = 4.33e-07 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 2.9299941 Debye

Polarizability = 58.174667 a.u.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -308.19901 Hartree

Zero-point Energy Correction = 0.152576 Hartree

Thermal Correction to Energy = 0.158986 Hartree

Thermal Correction to Enthalpy = 0.15993 Hartree

Thermal Correction to Free Energy = 0.122297 Hartree

EE + Zero-point Energy = -308.04644 Hartree

EE + Thermal Energy Correction = -308.04003 Hartree

EE + Thermal Enthalpy Correction = -308.03908 Hartree

EE + Thermal Free Energy Correction = -308.07671 Hartree

E (Thermal) = 99.765 kcal/mol

Heat Capacity (Cv) = 24.548 cal/mol-kelvin

Entropy (S) = 79.206 cal/mol-kelvin

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C 0.18374 0.52474 1.27566

H -0.36284 0.92151 2.1354

H 1.22462 0.87608 1.3211

C -0.4527 1.07025 0.

C 0.18374 0.52474 -1.27566

H -0.36284 0.92151 -2.1354

H 1.22462 0.87608 -1.3211

C 0.18374 -1.02885 -1.26798

H 0.68647 -1.39851 -2.16899

H -0.85312 -1.38766 -1.29413

C 0.87835 -1.5703 0.

H 0.85701 -2.66668 0.

H 1.93168 -1.2576 0.

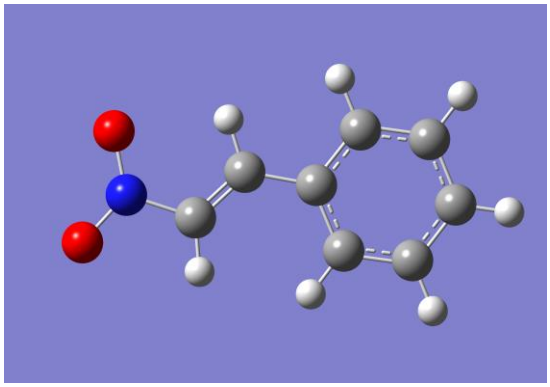
C 0.18374 -1.02885 1.26798

H 0.68647 -1.39851 2.16899

H -0.85312 -1.38766 1.29413

O -1.39283 1.86889 0.

Nitrostyrene(2)



Calculation Type = FREQ

Calculation Method = RB3LYP

Basis Set = 6-31G(d,p)

Charge = 0

Spin = Singlet

Solvation = None

E(RB3LYP) = -511.28944 Hartree

RMS Gradient Norm = 1.82e-07 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 5.5830437 Debye

Polarizability = 97.879667 a.u.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -511.28944 Hartree

Zero-point Energy Correction = 0.136109 Hartree

Thermal Correction to Energy = 0.145175 Hartree

Thermal Correction to Enthalpy = 0.14612 Hartree

Thermal Correction to Free Energy = 0.100523 Hartree

EE + Zero-point Energy = -511.15333 Hartree

EE + Thermal Energy Correction = -511.14426 Hartree

EE + Thermal Enthalpy Correction = -511.14332 Hartree

EE + Thermal Free Energy Correction = -511.18892 Hartree

E (Thermal) = 91.099 kcal/mol

Heat Capacity (Cv) = 33.914 cal/mol-kelvin

Entropy (S) = 95.966 cal/mol-kelvin

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

O -3.86266 0.96927 -0.00009

O -3.23122 -1.23618 0.00009

N -2.98363 0.02854 -0.00001

C -1.60198 0.47697 -0.00004

C -0.61631 -0.42547 0.00003

H -1.52012 1.55148 -0.00013

C 1.36347 1.13408 0.00006

C 0.81932 -0.166 0.00002

C 1.69946 -1.26498 -0.00004

C 3.07945 -1.07331 -0.00006

C 3.60403 0.2208 -0.00002

C 2.74107 1.32312 0.00004

H 0.70517 1.99468 0.00013

H 1.29026 -2.26934 -0.00006

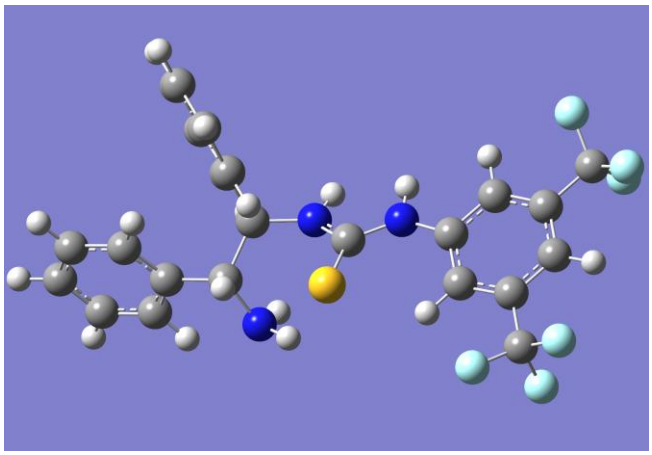
H 3.74341 -1.92936 -0.0001

H 4.67686 0.37262 -0.00004

H 3.14696 2.3277 0.00008

H -0.93714 -1.46361 0.0001

Cat(3)



Calculation Type = FREQ

Calculation Method = RB3LYP

Basis Set = 6-31G(d,p)

Charge = 0

Spin = Singlet

Solvation = None

E(RB3LYP) = -2038.4288 Hartree

RMS Gradient Norm = 2.27e-07 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 6.5837473 Debye

Polarizability = 260.52867 a.u.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -2038.4288 Hartree

Zero-point Energy Correction = 0.390127 Hartree

Thermal Correction to Energy = 0.419217 Hartree

Thermal Correction to Enthalpy = 0.420161 Hartree

Thermal Correction to Free Energy = 0.324789 Hartree

EE + Zero-point Energy = -2038.0387 Hartree

EE + Thermal Energy Correction = -2038.0096 Hartree

EE + Thermal Enthalpy Correction = -2038.0086 Hartree

EE + Thermal Free Energy Correction = -2038.104 Hartree

E (Thermal) = 263.062 kcal/mol

Heat Capacity (Cv) = 110.826 cal/mol-kelvin

Entropy (S) = 200.727 cal/mol-kelvin

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C 5.74711 -0.78311 -2.1758

C 5.29937 -0.43973 -0.88738

C 6.15799 -0.65119 0.19986

C 7.42543 -1.21562 0.00722

C 7.8571 -1.56314 -1.27378

C 7.0129 -1.33702 -2.36849

H 5.08006 -0.63131 -3.01763

H 5.86139 -0.36951 1.20179

H 8.0742 -1.37641 0.86262

H 8.8399 -1.99868 -1.4214

H 7.34017 -1.59788 -3.37019

C 4.05814 1.24168 1.63874

C 4.26162 0.87367 2.97981

C 4.89927 1.74024 3.86985

C 5.33905 2.99336 3.42846

C 5.13185 3.37049 2.09892

C 4.49141 2.50311 1.20716

H 3.92382 -0.10157 3.3244

H 5.05481 1.43991 4.90118

H 5.83854 3.66844 4.11552

H 5.46497 4.34327 1.75252

H 4.32106 2.82013 0.18579

C 3.90344 0.18845 -0.75592

C 3.3613 0.23871 0.71698

N 1.88773 0.40798 0.77769

N 2.92716 -0.42731 -1.68088

H 3.51456 -0.75581 1.15031

H 3.97185 1.22284 -1.10368

H 1.37675 -0.40705 1.13937

C 1.10299 1.38213 0.24395

C -1.67223 2.53293 -0.85512

C -2.98896 2.8615 -1.19717

C -4.09174 2.37543 -0.49682

C -3.84297 1.54371 0.59826

C -2.54883 1.22897 0.97977

C -1.43719 1.69827 0.24881

H -5.09866 2.65325 -0.78084

H -2.37739 0.60988 1.84758

N -0.1959 1.25192 0.72118

S 1.61523 2.58787 -0.89578

H -0.27597 0.63505 1.54775

F -6.01962 1.7715 1.60881

F -4.56388 0.30088 2.52336

F -5.55108 -0.15891 0.58918

F -3.32184 2.91209 -3.57734

F -4.4125 4.41224 -2.33724

F -2.19318 4.59691 -2.64858

C -4.97355 0.91138 1.33209

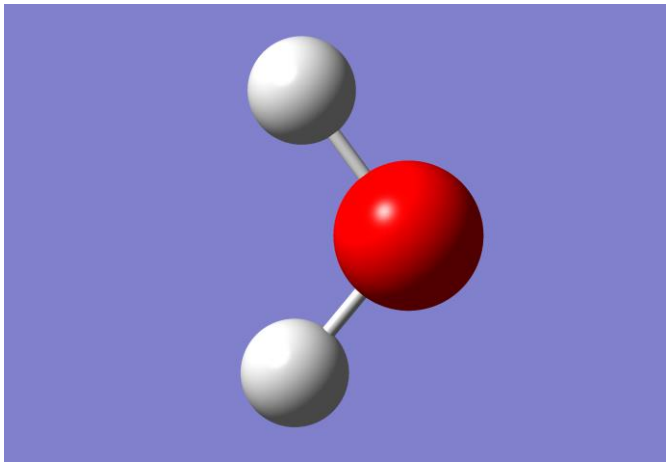
C -3.22171 3.6913 -2.41806

H 2.08747 0.1157 -1.68913

H -0.84013 2.93988 -1.41126

H 2.71994 -1.35698 -1.37631

H_2O



Calculation Type = FREQ

Calculation Method = RB3LYP

Basis Set = 6-31G(d,p)

Charge = 0

Spin = Singlet

Solvation = None

E(RB3LYP) = -75.973965 Hartree

RMS Gradient Norm = 0.000115305 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 2.2397 Debye

Polarizability = 4.2726667 a.u.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -75.973965 Hartree

Zero-point Energy Correction = 0.019746 Hartree

Thermal Correction to Energy = 0.022581 Hartree

Thermal Correction to Enthalpy = 0.023525 Hartree

Thermal Correction to Free Energy = 0.002 Hartree

EE + Zero-point Energy = -75.954218 Hartree

EE + Thermal Energy Correction = -75.951384 Hartree

EE + Thermal Enthalpy Correction = -75.95044 Hartree

EE + Thermal Free Energy Correction = -75.971965 Hartree

E (Thermal) = 14.17 kcal/mol

Heat Capacity (Cv) = 5.999 cal/mol-kelvin

Entropy (S) = 45.304 cal/mol-kelvin

Symbolic Z-matrix:

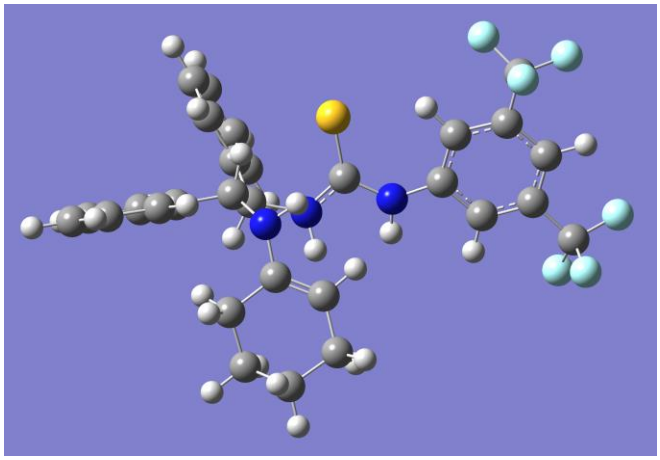
Charge = 0 Multiplicity = 1

O -0.0579 2.33917 -0.16269

H 0.9021 2.33917 -0.16269

H -0.37836 3.24411 -0.16269

IM



Calculation Type = FREQ

Calculation Method = RB3LYP

Basis Set = 6-31G(d,p)

Charge = 0

Spin = Singlet

Solvation = None

E(RB3LYP) = -2270.6162 Hartree

RMS Gradient Norm = 5.86e-07 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 6.1827507 Debye

Polarizability = 319.49967 a.u.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -2270.6162 Hartree

Zero-point Energy Correction = 0.518833 Hartree

Thermal Correction to Energy = 0.553307 Hartree

Thermal Correction to Enthalpy = 0.554252 Hartree

Thermal Correction to Free Energy = 0.446535 Hartree

EE + Zero-point Energy = -2270.0974 Hartree

EE + Thermal Energy Correction = -2270.0629 Hartree

EE + Thermal Enthalpy Correction = -2270.0619 Hartree

EE + Thermal Free Energy Correction = -2270.1697 Hartree

E (Thermal) = 347.206 kcal/mol

Heat Capacity (Cv) = 132.447 cal/mol-kelvin

Entropy (S) = 226.71 cal/mol-kelvin

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C 5.62403 -1.10816 -2.13669

C 5.17186 -0.80836 -0.84143

C 5.9567 -1.20195 0.25006

C 7.16002 -1.88727 0.05079

C 7.59811 -2.18247 -1.23931

C 6.82495 -1.78592 -2.3353

H 5.00739 -0.81741 -2.97815

H 5.65192 -0.95812 1.25956

H 7.75331 -2.1841 0.90822

H 8.5313 -2.7122 -1.39189

H 7.15792 -2.00749 -3.34307

C 3.99502 1.03539 1.70308

C 3.51183 1.15176 3.01552

C 4.12082 2.00872 3.92991

C 5.23007 2.76715 3.54585

C 5.71933 2.65735 2.24471

C 5.10729 1.79688 1.32909

H 2.64169 0.57669 3.31102

H 3.73048 2.08725 4.93818

H 5.70496 3.4369 4.2533

H 6.57604 3.24419 1.93435

H 5.50878 1.72536 0.32742

C 3.86123 -0.0248 -0.7011

C 3.2962 0.03469 0.76875

N 1.83058 0.23508 0.79767

N 2.84352 -0.48562 -1.66909

H 3.42452 -0.96527 1.20073

H 4.04575 1.01194 -0.99538

H 1.28108 -0.61035 1.00138

C 1.15812 1.32889 0.34653

C -1.31833 3.12093 -0.58065

C -2.54068 3.68645 -0.94293

C -3.76019 3.15639 -0.53882

C -3.73599 2.00947 0.25124

C -2.53747 1.43432 0.6293

C -1.30114 1.96707 0.21685

H -4.68876 3.63977 -0.80811

H -2.53744 0.56532 1.26751

N -0.17966 1.25612 0.6624

S 1.89931 2.62444 -0.53808

H -0.43371 0.49509 1.31312

F -5.96666 2.24372 1.03079

F -4.79262 0.46289 1.71784

F -5.55434 0.56632 -0.34338

F -2.55251 4.51995 -3.17492

F -3.65324 5.65264 -1.63065

F -1.41592 5.64389 -1.65079

C -5.00088 1.34716 0.66433

C -2.5363 4.87489 -1.84425

C 2.1582 -1.70756 -1.61086

H 2.27989 0.29813 -2.00706

H -0.39278 3.58049 -0.88949

C 0.86547 -1.79356 -2.00995

C 0.10769 -3.08747 -2.19866

H 0.34026 -0.87892 -2.27874

H -0.42382 -3.07062 -3.16026

H -0.66096 -3.17802 -1.41573

C 2.93665 -2.9427 -1.18066

H 3.67747 -3.17471 -1.95657

H 3.50891 -2.72891 -0.27235

C 2.00948 -4.15351 -0.94392

H 2.6184 -5.05465 -0.80932

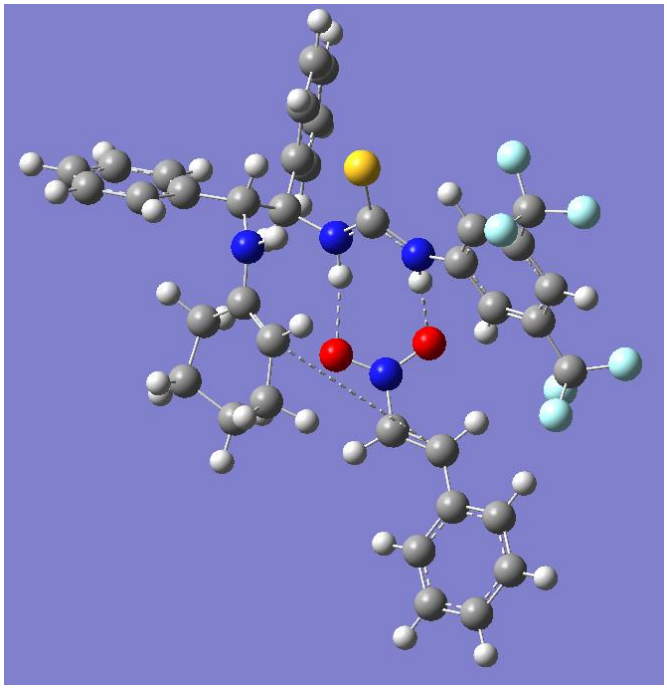
H 1.42729 -3.98382 -0.0324

C 1.04116 -4.31689 -2.13221

H 0.44929 -5.23455 -2.03071

H 1.61802 -4.38944 -3.063

TS1



Calculation Type = FREQ

Calculation Method = RB3LYP

Basis Set = 6-31G(d,p)

Charge = 0

Spin = Singlet

Solvation = None

E(RB3LYP) = -2781.957 Hartree

RMS Gradient Norm = 3.01e-07 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 9.5685843 Debye

Polarizability = 521.921 a.u.

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -2781.957 Hartree

Zero-point Energy Correction = 0.658736 Hartree

Thermal Correction to Energy = 0.703378 Hartree

Thermal Correction to Enthalpy = 0.704323 Hartree

Thermal Correction to Free Energy = 0.574802 Hartree

EE + Zero-point Energy = -2781.2983 Hartree

EE + Thermal Energy Correction = -2781.2536 Hartree

EE + Thermal Enthalpy Correction = -2781.2527 Hartree

EE + Thermal Free Energy Correction = -2781.3822 Hartree

E (Thermal) = 441.377 kcal/mol

Heat Capacity (Cv) = 170.567 cal/mol-kelvin

Entropy (S) = 272.598 cal/mol-kelvin

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C -4.89571 -3.26206 -1.66229

C -4.40239 -2.39198 -0.67775

C -5.26792 -1.99522 0.34946

C -6.58963 -2.45123 0.39055

C -7.06828 -3.3112 -0.59858

C -6.2137 -3.71668 -1.62793

H -4.23855 -3.58009 -2.46349

H -4.91532 -1.34385 1.13619

H -7.24111 -2.13612 1.19742

H -8.09217 -3.6644 -0.56711

H -6.57332 -4.38673 -2.4001

C -2.37548 -2.46835 1.66305

C -2.8264 -2.01831 2.91382

C -2.92246 -2.89179 3.99894

C -2.56676 -4.23356 3.84646

C -2.11112 -4.69055 2.60726

C -2.01344 -3.81678 1.52183

H -3.10847 -0.97741 3.03879

H -3.27396 -2.52759 4.95728

H -2.64269 -4.91537 4.68513

H -1.82925 -5.72928 2.48293

H -1.63605 -4.17288 0.57432

C -2.94418 -1.93874 -0.81728

C -2.28024 -1.47242 0.50895

N -0.86305 -1.01802 0.31879

N -2.80931 -0.93704 -1.92004

H -2.77685 -0.55393 0.81801

H -2.3794 -2.79791 -1.17155

H -0.66466 -0.18515 0.88242

C 0.22201 -1.68351 -0.14219

C 3.269 -2.48012 -0.42555

C 4.63989 -2.59965 -0.58337

C 5.50898 -1.5415 -0.3359

C 4.97195 -0.34059 0.09403

C 3.60076 -0.18215 0.26688

C 2.72986 -1.24545 -0.00587

H 6.57573 -1.65533 -0.46429

H 3.21134 0.76985 0.61076

N 1.36921 -1.0081 0.24706

S 0.17243 -3.03109 -1.23238

H 1.19712 -0.09017 0.65357

F 7.18307 0.46307 0.19971

F 5.7097 1.26282 1.67238

F 5.59035 1.88384 -0.44397

F 5.84295 -3.7783 -2.24838

F 6.15641 -4.35789 -0.13914

F 4.22821 -4.85142 -1.14854

C 5.86564 0.81139 0.37882

C 5.2082 -3.899 -1.02982

C -2.98538 0.46194 -1.75068

C -4.1549 0.93702 -0.90339

H -3.87723 0.86515 0.15699

O -0.58576 1.62948 1.32893

O 1.52485 2.50323 1.19967

N 0.23858 2.6083 1.11691

C -0.31746 3.8797 0.76491

H -1.94254 -1.13129 -2.43408

H 2.60052 -3.29022 -0.62045

C -4.5702 2.38557 -1.20887

C -2.19145 1.33608 -2.39999

C -2.39275 2.83652 -2.4076

C -3.3415 3.30239 -1.28842

H -1.3652 0.96771 -3.00284

H -2.7958 3.14844 -3.38554

H -1.42064 3.3429 -2.30921

H -3.65234 4.34231 -1.46351

H -2.80244 3.29553 -0.32594

H -5.11651 2.43068 -2.1596

H -5.26597 2.73404 -0.43506

H -5.00392 0.26279 -1.04068

C 0.46196 4.96722 0.83677

H 1.48315 4.83433 1.17835

H -1.34908 3.88485 0.44905

C -1.18728 6.65084 -0.06705

C 0.06325 6.33232 0.50706

C 0.97546 7.375 0.76726

C 0.64513 8.69656 0.4748

C -0.59804 8.99745 -0.08694

C -1.51158 7.97058 -0.35899

H -1.89211 5.86203 -0.29427

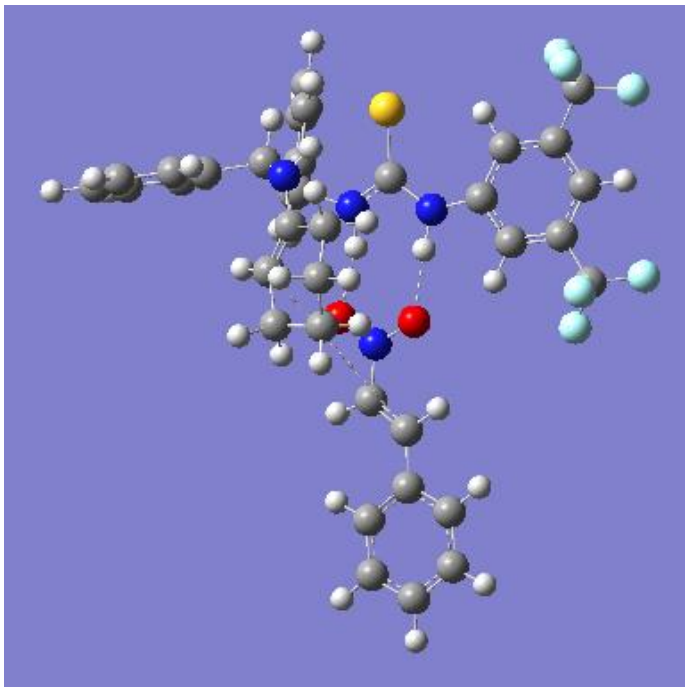
H 1.94126 7.1428 1.20124

H 1.35354 9.48883 0.68148

H -0.85418 10.02431 -0.31666

H -2.47162 8.20345 -0.80228

TS2



Calculation Type = FREQ

Calculation Method = RB3LYP

Basis Set = 6-31G(d,p)

Charge = 0

Spin = Singlet

Solvation = None

E(RB3LYP) = -2781.954 Hartree

RMS Gradient Norm = 1.42e-07 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 12.81188 Debye

Polarizability = 534.43433 a.u.

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -2781.954 Hartree

Zero-point Energy Correction = 0.658255 Hartree

Thermal Correction to Energy = 0.703092 Hartree

Thermal Correction to Enthalpy = 0.704036 Hartree

Thermal Correction to Free Energy = 0.572146 Hartree

EE + Zero-point Energy = -2781.2957 Hartree

EE + Thermal Energy Correction = -2781.2509 Hartree

EE + Thermal Enthalpy Correction = -2781.25 Hartree

EE + Thermal Free Energy Correction = -2781.3819 Hartree

E (Thermal) = 441.197 kcal/mol

Heat Capacity (Cv) = 170.694 cal/mol-kelvin

Entropy (S) = 277.586 cal/mol-kelvin

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C -3.54727 -3.08977 -2.4706

C -3.0741 -2.94251 -1.15742

C -3.91457 -3.29998 -0.09724

C -5.20234 -3.78719 -0.34198

C -5.66294 -3.92698 -1.64955

C -4.8274 -3.5763 -2.71581

H -2.89946 -2.80653 -3.29301

H -3.56663 -3.22007 0.92946

H -5.8396 -4.06233 0.49186

H -6.66006 -4.30906 -1.83996

H -5.17715 -3.68501 -3.73711

C -0.95209 -3.67536 1.10357

C -1.38883 -3.95051 2.40679

C -1.16877 -5.20194 2.98359

C -0.49954 -6.19493 2.25832

C -0.06145 -5.92101 0.96078

C -0.29399 -4.66811 0.38726

H -1.90462 -3.17883 2.97326

H -1.51442 -5.40104 3.99242

H -0.32226 -7.16905 2.70111

H 0.46328 -6.67945 0.38977

H 0.07588 -4.47625 -0.60545

C -1.65272 -2.42146 -0.98653

C -1.18886 -2.30048 0.50172

N -0.03169 -1.39828 0.69867

N -1.41503 -1.24741 -1.82156

H -1.95993 -1.78113 1.09543

H -1.01509 -3.21458 -1.38093

H -0.09614 -0.81993 1.5423

C 1.12037 -1.24767 0.01296

C 4.23504 -0.49961 0.56689

C 5.51525 -0.00871 0.35226

C 5.73151 1.24579 -0.21345

C 4.63108 2.00751 -0.57339

C 3.33817 1.52186 -0.39038

C 3.12839 0.25745 0.16999

H 6.73282 1.63409 -0.34461

H 2.4861 2.12432 -0.68663

N 1.77244 -0.11942 0.45478

S 1.68824 -2.20696 -1.33956

H 1.17247 0.7144 0.70766

F 6.14416 3.68748 -1.28645

F 4.22517 4.33929 -0.37896

F 4.23304 3.47416 -2.39762

F 7.24555 -1.4999 -0.35212

F 7.69442 -0.07253 1.25759

F 6.3493 -1.8108 1.64573

C 4.81494 3.36852 -1.15681

C 6.6913 -0.84869 0.72349

C -2.16125 -0.07235 -1.83199

C -3.25583 0.16103 -1.07793

O -0.6339 0.47426 2.46685

O -0.04265 1.8071 0.72036

N -0.8462 1.5025 1.69228 4

C -2.02281 2.23407 1.95577

H -0.43635 -1.17323 -2.1042

H 4.10599 -1.43303 1.11948

C -4.1464 1.3726 -1.25914

C -1.64932 0.9418 -2.85254

C -2.75732 1.90595 -3.30977

C -3.47805 2.4933 -2.08627

H -1.25052 0.39692 -3.71723

H -3.48105 1.36231 -3.93128

H -2.32492 2.7046 -3.9255

H -4.23184 3.22829 -2.39793

H -2.73881 3.02114 -1.46741

H -5.07594 1.06734 -1.76773

H -4.44833 1.77059 -0.28137

H -3.61235 -0.61683 -0.40559

C -2.44166 3.25466 1.18007

H -1.84236 3.48474 0.3041

H -2.51611 1.87724 2.84722

C -3.91801 5.13296 0.55374

C -3.60489 4.08184 1.44233

C -4.4287 3.88735 2.57441

C -5.5242 4.7094 2.80033

C -5.8211 5.74749 1.90852

C -5.01529 5.95724 0.78813

H -3.29703 5.29445 -0.31929

H -4.20133 3.09186 3.27542

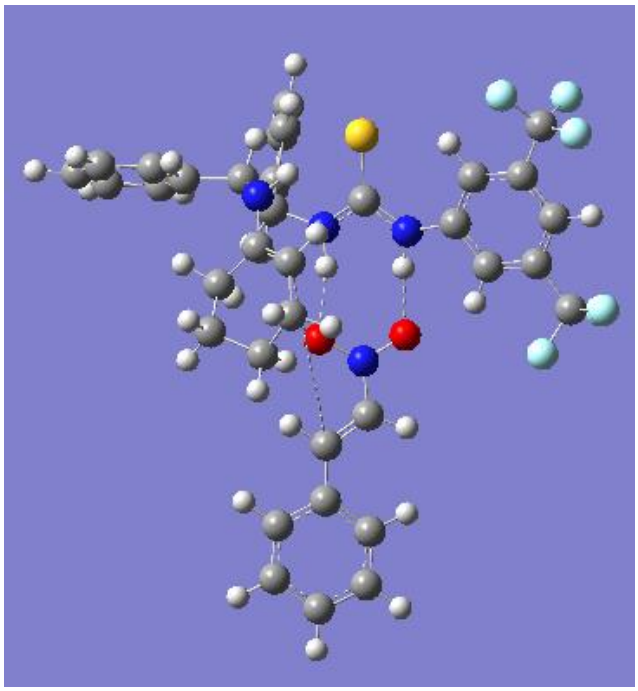
H -6.14919 4.54921 3.67156

H -6.67593 6.38927 2.09046

H -5.24284 6.76169 0.09814

H -0.81537 1.50991 -2.41251

TS3



Calculation Type = FREQ

Calculation Method = RB3LYP

Basis Set = 6-31G(d,p)

Charge = 0

Spin = Singlet

Solvation = None

E(RB3LYP) = -2781.9481 Hartree

RMS Gradient Norm = 2.13e-07 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 14.737711 Debye

Polarizability = 555.66833 a.u.

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -2781.9481 Hartree

Zero-point Energy Correction = 0.657951 Hartree

Thermal Correction to Energy = 0.703004 Hartree

Thermal Correction to Enthalpy = 0.703948 Hartree

Thermal Correction to Free Energy = 0.570412 Hartree

EE + Zero-point Energy = -2781.2901 Hartree

EE + Thermal Energy Correction = -2781.2451 Hartree

EE + Thermal Enthalpy Correction = -2781.2441 Hartree

EE + Thermal Free Energy Correction = -2781.3777 Hartree

E (Thermal) = 441.142 kcal/mol

Heat Capacity (Cv) = 170.76 cal/mol-kelvin

Entropy (S) = 281.05 cal/mol-kelvin

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C -4.67766 -2.90165 -2.04011

C -4.16973 -2.60391 -0.76511

C -5.06697 -2.50402 0.30634

C -6.43943 -2.6807 0.10317

C -6.93497 -2.9659 -1.16846

C -6.04519 -3.07931 -2.24101

H -3.98189 -2.97267 -2.86642

H -4.70088 -2.31316 1.30549

H -7.11736 -2.59942 0.94548

H -7.99902 -3.10278 -1.32347

H -6.41757 -3.30599 -3.23384

C -2.38524 -2.44495 2.01891

C -2.85971 -1.72977 3.13088

C -3.02761 -2.35131 4.36796

C -2.71712 -3.70552 4.51364

C -2.2387 -4.42386 3.41709

C -2.07213 -3.80104 2.17745

H -3.10426 -0.6774 3.02079

H -3.39948 -1.78303 5.21293

H -2.84673 -4.19454 5.47216

H -1.98907 -5.47315 3.52345

H -1.67184 -4.36247 1.34568

C -2.64695 -2.47455 -0.59836

C -2.21841 -1.68674 0.69795

N -0.8655 -1.08192 0.59449

N -1.9957 -1.9514 -1.81434

H -2.87302 -0.81205 0.75784

H -2.24147 -3.48405 -0.49996

H -0.88344 -0.05474 0.6201

C 0.32503 -1.68307 0.35725

C 3.42421 -2.02709 -0.24764

C 4.78997 -1.95739 -0.50607

C 5.51963 -0.79054 -0.32394

C 4.84411 0.33089 0.14487

C 3.4845 0.29199 0.40941

C 2.74227 -0.89099 0.21507

H 6.57109 -0.74677 -0.56768

H 2.98439 1.19208 0.74243

N 1.37158 -0.79889 0.4991

S 0.49555 -3.35807 -0.10152

H 1.11387 0.12143 0.88653

F 6.67584 1.70586 -0.42929

F 6.09355 1.64131 1.69938

F 4.78978 2.69218 0.2615

F 6.58975 -2.88297 -1.72187

F 5.97979 -3.92348 0.12791

F 4.66878 -4.02703 -1.64657

C 5.5973 1.58492 0.41576

C 5.50039 -3.19467 -0.93752

C -2.00368 -0.61497 -2.24551

C -3.199 0.25381 -1.87079

H -3.09011 0.58357 -0.82883

O -1.1866 1.80713 0.45768

O 0.88464 1.85462 1.45903

N -0.16452 2.45101 0.95824

C -0.15409 3.86672 0.99095

C -1.21856 4.56711 0.55121

H 0.7623 4.26372 1.39514

H -1.11391 -2.43924 -1.99191

H 2.8887 -2.94608 -0.4213

C -3.30715 1.50389 -2.77039

C -1.35041 6.01017 0.5193

C -2.55408 6.56125 0.03028

C -2.73423 7.94004 -0.02267

C -1.71613 8.79314 0.41116

C -0.51499 8.2614 0.89831

C -0.3307 6.88593 0.95294

H -3.34134 5.8963 -0.30738

H -3.66271 8.34978 -0.40082

H -1.85413 9.8669 0.37016

H 0.27352 8.9246 1.2324

H 0.60355 6.48699 1.32918

C -0.99099 -0.13121 -3.00284

C -0.93579 1.27008 -3.56607

C -1.93759 2.207 -2.85991

H -0.16108 -0.78904 -3.25117

H -1.16037 1.25616 -4.64557

H 0.08392 1.66732 -3.46665

H -2.01686 3.15768 -3.40035

H -1.57866 2.40376 -1.84195

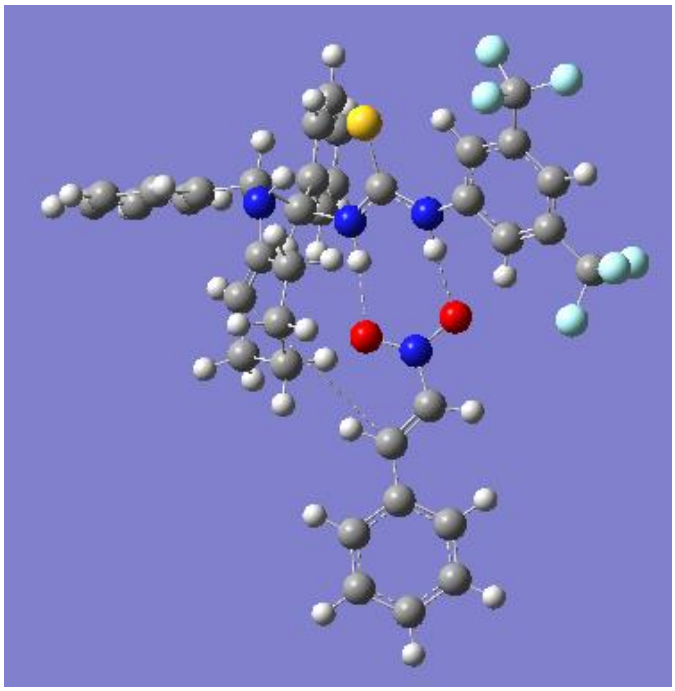
H -3.62924 1.20606 -3.77624

H -4.06911 2.17822 -2.36079

H -2.05947 3.98556 0.18617

H -4.11113 -0.34384 -1.93384

TS4



Calculation Type = FREQ

Calculation Method = RB3LYP

Basis Set = 6-31G(d,p)

Charge = 0

Spin = Singlet

Solvation = None

E(RB3LYP) = -2781.9516 Hartree

RMS Gradient Norm = 2.197e-06 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 14.308442 Debye

Polarizability = 544.00733 a.u.

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -2781.9516 Hartree

Zero-point Energy Correction = 0.657836 Hartree

Thermal Correction to Energy = 0.702898 Hartree

Thermal Correction to Enthalpy = 0.703842 Hartree

Thermal Correction to Free Energy = 0.570008 Hartree

EE + Zero-point Energy = -2781.2937 Hartree

EE + Thermal Energy Correction = -2781.2487 Hartree

EE + Thermal Enthalpy Correction = -2781.2477 Hartree

EE + Thermal Free Energy Correction = -2781.3816 Hartree

E (Thermal) = 441.075 kcal/mol

Heat Capacity (Cv) = 170.741 cal/mol-kelvin

Entropy (S) = 281.679 cal/mol-kelvin

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C -4.27482 -3.9004 -1.37833

C -3.89886 -2.79944 -0.60528

C -4.85499 -2.17101 0.19309

C -6.16455 -2.63346 0.22408

C -6.53279 -3.72995 -0.54804

C -5.58677 -4.36041 -1.34899

H -3.53604 -4.40434 -2.01276

H -4.55132 -1.29673 0.79542

H -6.90499 -2.13263 0.85579

H -7.56434 -4.09548 -0.52538

H -5.87431 -5.22305 -1.95894

C -1.87478 -2.98759 1.70602

C -2.30547 -2.79873 3.02097

C -2.21323 -3.8385 3.93891

C -1.69447 -5.06973 3.55102

C -1.26775 -5.26187 2.24128

C -1.35806 -4.22508 1.3201

H -2.72363 -1.83401 3.33211

H -2.5526 -3.6872 4.96885

H -1.62378 -5.88692 4.27635

H -0.85848 -6.2292 1.93156

H -1.01776 -4.35014 0.27512

C -2.46496 -2.32371 -0.66829

C -1.97737 -1.84743 0.72425

N -0.71268 -1.05065 0.71956

N -2.31279 -1.37891 -1.8059

H -2.74962 -1.10656 1.10131

H -1.80982 -3.20631 -0.94761

H -0.69305 -0.46085 1.52914

C 0.54092 -1.43555 0.2189

C 3.40424 -1.54992 -0.64379

C 4.74263 -1.51114 -1.00481

C 5.60839 -0.54608 -0.48984

C 5.11012 0.39527 0.40448

C 3.77138 0.38252 0.79053

C 2.9192 -0.59532 0.26319

H 6.66323 -0.53988 -0.79418

H 3.40962 1.1428 1.4988

N 1.54806 -0.59418 0.69795

S 0.78883 -2.68573 -0.88571

H 1.29557 0.20368 1.27239

F 7.29863 1.45477 0.59474

F 6.07651 1.45079 2.34784

F 5.59457 2.73841 0.7115

F 5.79826 -1.96306 -3.12483

F 6.36951 -3.22384 -1.49589

F 4.46304 -3.47804 -2.42573

C 6.00846 1.48045 0.99603

C 5.31812 -2.52824 -1.99123

C -2.70463 0.00076 -1.78138

C -3.38109 0.60625 -0.78815

H -3.6515 0.06177 0.13456

O -1.2808 1.86026 2.28886

O 0.76837 1.92224 1.79412

N -0.32256 2.47737 1.86558

C -0.45759 3.86593 1.41529

C -1.58839 4.34536 0.86406

H 0.43116 4.52003 1.51762

H -1.39496 -1.46895 -2.19498

H 2.61418 -2.31114 -1.03599

C -3.87016 2.00668 -0.85486

C -1.6996 5.72236 0.40907

C -2.85652 6.12728 -0.26864

C -2.98323 7.44116 -0.70076

C -1.96242 8.35787 -0.46428

C -0.80676 7.95928 0.20144

C -0.67321 6.64708 0.63473

H -3.65728 5.40199 -0.46726

H -3.88923 7.75584 -1.23028

H -2.06771 9.39375 -0.80513

H -0.00128 8.67924 0.38276

H 0.23869 6.31372 1.15478

C -2.34261 0.73728 -3.04363

C -3.25166 1.93204 -3.27927

C -3.32557 2.79607 -2.0353

H -1.28633 1.06957 -2.97002

H -2.38853 0.06437 -3.92436

H -4.26673 1.58946 -3.56137

H -2.8812 2.52409 -4.13823

H -3.9581 3.68707 -2.21892

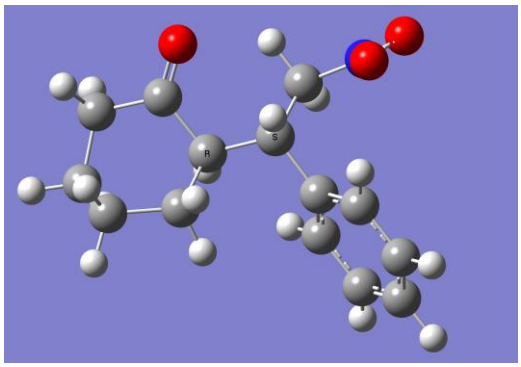
H -2.31808 3.19358 -1.79449

H -4.97829 1.98221 -0.88789

H -3.60661 2.53505 0.09151

H -2.48055 3.69964 0.71278

Product



Calculation Type = FREQ

Calculation Method = RB3LYP

Basis Set = 6-31G(d,p)

Charge = 0

Spin = Singlet

Solvation = None

E(RB3LYP) = -819.51642 Hartree

RMS Gradient Norm = 5.91e-07 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 5.9999245 Debye

Polarizability = 141.44933 a.u.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -819.51642 Hartree

Zero-point Energy Correction = 0.292794 Hartree

Thermal Correction to Energy = 0.309062 Hartree

Thermal Correction to Enthalpy = 0.310006 Hartree

Thermal Correction to Free Energy = 0.246869 Hartree

EE + Zero-point Energy = -819.22362 Hartree

EE + Thermal Energy Correction = -819.20736 Hartree

EE + Thermal Enthalpy Correction = -819.20641 Hartree

EE + Thermal Free Energy Correction = -819.26955 Hartree

E (Thermal) = 193.939 kcal/mol

Heat Capacity (Cv) = 61.819 cal/mol-kelvin

Entropy (S) = 132.882 cal/mol-kelvin

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C 2.43858 0.88172 -0.00108

O -1.85712 2.3288 -1.15887

O -2.36937 3.02426 0.95151

N -1.661 2.38286 0.10719

C -0.42554 1.68178 0.66275

C 1.30818 -0.12515 0.17492

C 1.62572 -1.38366 -0.7082

H 1.27495 -1.18128 -1.72563

H 1.03433 -2.21664 -0.31978

C -0.08373 0.44707 -0.18712

H -0.67692 1.45202 1.69604

C -1.30105 -1.41317 1.07528

C -1.195 -0.59573 -0.05997

C -2.16129 -0.71797 -1.06766

C -3.19452 -1.65044 -0.95438

C -3.28209 -2.46966 0.17236

C -2.3338 -2.34503 1.19052

H -0.57517 -1.3258 1.87716

H -2.11569 -0.05622 -1.92306

H -3.93345 -1.73103 -1.74329

H -4.08393 -3.19341 0.26052

H -2.39949 -2.9705 2.07356

C 3.81093 0.36021 0.43201

H 4.54869 0.7483 -0.27968

H 4.04134 0.81002 1.40893

C 3.86814 -1.18153 0.50163

H 4.91196 -1.51201 0.52455

H 3.38949 -1.54427 1.41948

C 3.13897 -1.75434 -0.73213

H 3.25204 -2.84243 -0.77909

H 3.60931 -1.33611 -1.63117

H 0.3753 2.41863 0.58193

H -0.03975 0.80044 -1.221

O 2.27692 2.02686 -0.44141

H 1.32959 -0.44369 1.22683

4 . Reference

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