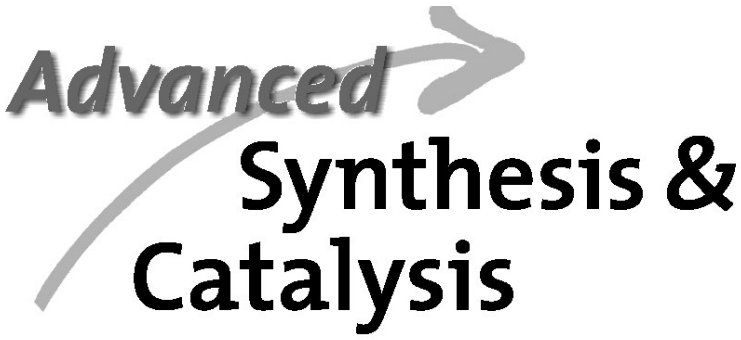

Supporting Information

Rhodium Catalyzed Asymmetric Intramolecular Cyclopropanation of Substituted Allylic Cyanodiazoacetates

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Supporting information

Caution: Although we have not experienced any complications in handling cyanodiazoacetates, extreme care should be taken when manipulating them due to their potential explosive nature.

Experimental

Unless stated otherwise, all compounds were purchased from commercial suppliers (Aldrich, Strem and Alfa Aesar) and used without further purification. Anhydrous solvents were obtained either by filtration through drying columns (THF, DCM, Et_2O, CH_3CN, DMF, hexane and toluene) on a GlassContour system (Irvine, CA), or by distillation over calcium hydride(pyridine, triethylamine and TMSCl). All reactions were carried out using standard Schlenk techniques under a dry argon atmosphere unless otherwise stated. All reported yields are of isolated pure material obtained from an average of at least two runs. Analytical thin layer chromatography (TLC) was performed using EM Reagent 0.25 mm silica gel 60-F plates. Visualization of the developed chromatography was performed by UV absorbance, aqueous cerium molybdate, iodine, or aqueous potassium permanganate. Flash chromatography was performed using Silicycle, Ultra Pure Silica Gel 60 Å (230-400 mesh) with the indicated solvent system. ^{1}H NMR and ^{19}F NMR spectra were recorded in deuterated chloroform, unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (400, 400, 300 and 300 MHz respectively) at ambient temperatures. Chemical shifts are reported in ppm on the δ scale from an internal standard of residual chloroform (7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet), and coupling constant in Hz, integration. ^{13}C NMR spectra were recorded in deuterated chloroform, unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (100, 100, 75 and 75 MHz respectively) with complete proton decoupling. Chemical shifts are reported in ppm from the central peak

of deuterated chloroform (77.23 ppm) on the δ scale. IR spectra were recorded as a thin film on a Perkin Elmer Model 2000 FTIR instrument. Low resolution mass spectra were performed on an Agilent 1100 Series LC/MSD system equipped with an APCI mass detector with simultaneous diode array UV detection. GC analysis was performed on a Hewlett-Packard 1100 gas chromatograph fitted with Chiraldex Cyclodex gamma or beta capillary columns. SFC (super fluid chromatography) was performed on Berber instrument equipped with chiral stationary phase and a diode array UV detector. Data are reported as follows: (column type, modified, flow rate: rentention time (t_r)). Optical rotations were determined with a Perkin-Elmer 341 polarimeter at 589 nm. Data are reported as follows: $[\alpha]_{\lambda}^{temp}$, Concentration (*c* in g/100 mL), and solvent. Elemental analyses were performed by the Laboratoire d'analyse élémentaire de l'Université de Montréal. Melting points are uncorrected.

Synthesis of 4'-Fluoro-benzyl 2-oxaazetidine-4(*S*)-carboxylate (23)

The title compound was synthesized according the procedure described in literature.[1]

Light yellow solid (yield, 30%): R_f 0.51 (60% ethyl acetate/ hexane); mp 67-68 ^oC.

^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (m, 2H, ArH), 7.03 (m, 2H, ArH), 6.73 (br, 1H, NH), 5.14 (s, 2H, CH_2Ar), 4.17 (dd, *J* = 5.82 Hz, *J* = 2.67 Hz, 1H, CH), 3.29 (dddd, *J* = 1.46 Hz, 1H, CH_2), 3.01 (dt, *J* = 14.89 Hz, 1H, CH_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1 (C=O), 164.6 (C=O), 131.0 (Ar), 116.0 (Ar), 115.7 (Ar), 66.8 (CH_2Ar), 47.4 (CHCOO), 43.6 (CH_2CH); ^{13}F NMR (300 MHz, $CDCl_3$) δ -115.57 (s).

IR (film) 3218, 1715 (C=O), 1602 (C=O), 1515, 1343, 1225, 1059, 828 cm^{-1}.

MS(APCI-) Calcd. for $C_{11}H_{10}FNO_3$: 223.1. Found: $[M-1]^+$ 222.1.

Anal. Calcd. for $C_{11}H_{10}FNO_3$: C, 59.19; H, 4.52; N, 6.28. Found: C, 59.10; H, 4.78; N, 6.10.

$[\alpha]_D^{20}$ -37.3 (*c* 0.409, $CHCl_3$).

(1*R*,5*S*)-3-Oxa-bicyclo[3.1.0]hexan-2-one-1-carbonitrile (1c)

White solid (yield, 76%): R_f 0.18 (40% ethyal acetate/ hexane); mp 94-95 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 4.50 (dd, *J* = 9.70 Hz, *J* = 4.70 Hz, 1H, CH_2O), 4.27 (d, *J* = 9.70 Hz, 1H, CH_2O), 2.99 (m, 1H, CH), 1.99 (q, 1H, CH_2), 1.58 (q, 1H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8 (C=O), 115.0 (CN), 68.3 (CH_2O), 26.6 (CH), 20.6 (CH_2), 17.1 (CCN).

IR (film) 2921, 2250 (CN), 1781 (C=O), 1385, 1295, 1115, 990 cm^{-1}.

Anal. Calcd. for $C_6H_5NO_2$: C, 58.54; H, 4.09; N, 11.38. Found: C, 58.16; H, 4.04; N, 11.38.

Enantiomeric excess: 85%, GC analysis (Chiralcel cyclodex beta, 140 ^oC, t_r[(1*R*)-**1c**] =18.4 min, t_r[(1*S*)-**1c**] =18.8 min. After one recrystalization with solvent of 70% ethyl acetate/hexane, e.e. › 99% (57% yield, 0.09 mmol, 11 mg).

$[\alpha]_D^{20}$ +170.8 (*c* 0.258, $CHCl_3$).

(1*R*,5*S*)-6,6-Dimethyl-3-oxa-bicyclo[3.1.0]hexan-2-one-1-carbonitrile (2c) as a white solid (57%) R_f 0.56 (40% ethyl acetate/hexane); mp 77 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 4.52 (dd, *J* = 10.25 Hz, *J* = 5.43 Hz, 1H, CH_2O), 4.22 (d, *J* = 10.25 Hz, 1H, CH_2O), 2.73 (d, *J* = 5.39 Hz, 1H, CH), 1.46 (s, 3H, CH_3), 1.31 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0 (C=O), 114.7 (CN), 65.7 (CH_2O), 37.9 (CH), 32.3 (CCN), 28.6

($C(CH_3)_2$), 23.6 (CH_3); 14.9 (CH_3).

IR (film) 2974, 2244 (CN), 1760 (C=O), 1457, 1363, 1081, 998 cm^{-1}.

Anal. Calcd. for $C_8H_9NO_2$: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.26; H, 6.07; N, 9.28.

Enantiomeric excess: 56%, GC analysis (Chiralcel cyclodex beta, 140 ^oC, t_r[(1*R*,5*S*)-**2c**] = 15.0 min, t_r[(1*S*,5*R*)-**2c**] = 15.4 min.

$[\alpha]_D^{20}$ +78.6 (*c* 0.192, $CHCl_3$).

[1*R*-(1a,5a,6a)]-6–Ethyl-3-oxa-bicyclo[3.1.0]hexan-2-one-1-carbonitrile (3c) as a brown oil (66%): R_f 0.28 (40% ethyl acetate/hexane).

^1H NMR (400 MHz, $CDCl_3$) δ 4.55 (dd, *J* = 10.2 Hz, *J* = 5.38 Hz, 1H, CH_2O), 4.19 (d, *J* = 10.3 Hz, 1H, CH_2O), 3.02 (m, 1H, $CHCH_2O$), 2.10 (q, 1H, $CHCH_2CH_3$), 1.53 (m, 2H, CH_2CH_3), 1.13 (t, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5 (C=O), 115.7 (CN), 65.1 (CH_2O), 34.1 ($CHCH_2O$), 31.5 ($CHCH_2CH_3$), 21.9 (CCN), 16.5 (CH_2CH_3), 12.9 (CH_3).

IR (film) 2972, 2246 (CN), 1768 (C=O), 1465, 1374, 1084, 990 cm^{-1}.

Anal. Calcd. for $C_8H_9NO_2$: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.27; H, 6.17; N, 9.24.

[1*R*-(1a,5a,**6**b**)]-6-Phenyl-3-oxa-bicyclo[3.1.0]hexan-2-one-1-carbonitrile (4c)** as a yellow oil (49%): R_f 0.1 (40% ethyl acetate/hexane).

^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (m, 3H, ArH), 7.27 (m, 2H, ArH), 4.62 (dd, *J* = 9.68 Hz, *J* = 4.76 Hz,1H, CH_2O), 4.44 (d, *J* = 9.66 Hz, 1H, CH_2O), 3.36 (t, 1H, ArCH), 2.94 (d, *J* = 5.48 Hz, 1H, $CHCH_2O$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2 (C=O), 130.8 (C_6H_5), 129.4 (C_6H_5), 128.0 (C_6H_5), 113.0 (CN), 68.5 (CH_2O), 36.6 (C_6H_5CH), 30.6 ($CHCH_2O$), 26.2 (CCN).

IR (film) 3069, 2247 (CN), 1767 (C=O), 1501, 1374, 1073, 1000 cm^{-1}.

MS(APCI-) Calcd. for $C_{12}H_9NO_2[M-1]^+$:198.06. Found: 198.05.

Enantiomeric excess: 35%, SFC analysis (Chiralcel Chiralcel OD 4.6x250mm, 15% MeOH, flow, 2.0 mL/min) t_r[(1*R*)-**4c**] = 9.8 min, t_r[(1*S*)-**4c**] = 10.2 min.

$[\alpha]_D^{20}$ +67 (*c* 0.067, $CHCl_3$).

[1*S*-(1a,5a,6b)]-6-Carbethoxy-3-oxa-bicyclo[3.1.0]hexan-2-one-1-carbonitrile (5c) as a yellow solid (90%): R_f 0.049 (20% ethyl acetate/hexane); mp 82 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 4.57 (dd, *J* = 10.12 Hz, *J* = 4.48Hz, 1H, CH_2O), 4.36 (d, *J* = 10.12 Hz, 1H, CH_2O), 4.29 (q, 2H, CH_2CH_3), 3.38 (t, 1H, CHC=O), 2.47 (d, *J* = 4.7 Hz, 1H, $CHCH_2O$), 1.33 (t, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9 (NCCC=O, 165.4 ($COOCH_2CH_3$), 111.9 (CN), 68.0 (CH_2O), 63.2 ($COOCH_2$), 31.1 (CHCOO), 31.0 ($CHCH_2O$), 24.1 (CCN), 14.2 (CH_3).

IR (film) 2938, 2258 (CN), 1781 (C=O), 1420, 1380, 1191 cm^{-1}.

Anal. Calcd. for $C_9H_9NO_4$: C, 55.39; H, 4.65; N, 7.18. Found: C, 55.23; H, 4.60; N, 7.03.

Enantiomeric excess: 80%, GC analysis (Chiralcel cyclodex gamma, 200 ^oC, t_r[(1*S*)-**5c**] = 8.9 min, t_r[(1*R*)-**5c**] = 9.0min.

$[\alpha]_D^{20}$ +92.8 (*c* 0.15, $CHCl_3$).

[1*S*-(1a,5a,6b)]-6-Chloro-3-oxa-bicyclo[3.1.0]hexan-2-one-1-carbonitrile (6c) as a white solid (81%): R_f 0.21 (30% ethyl acetate/hexane); mp 94- 95 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 4.52 (dd, *J* = 9.99 Hz, *J* = 5.0 Hz, 1H, CH_2O), 4.41 (d, *J* = 10.05 Hz, 1H,

CH_2O), 3.59 (d, *J* = 3.45 Hz, 1H, HCCl), 3.17 (t, 1H, $CHCH_2O$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7 (C=O), 111.8 (CN), 67.9 (CH_2O), 38.6 (HCCl), 34.4 ($CHCH_2O$), 26.3 (CCN).

IR (film) 2257 (CN), 1769 (C=O), 1469, 1307, 1198, 1076, 947 cm^{-1}.

Anal. Calcd. for $C_6H_4ClNO_2$: C, 45.74; H, 2.56; N, 8.89. Found: C, 45.93; H, 2.48; N, 8.60.

[1*S*-(1a**,5**a**,6**b**)]-6-Bromo-3-oxa-bicyclo[3.1.0]hexan-2-one-1-carbonitrile (7c)** as a white solid (57%): R_f 0.17 (30% ethyl acetate/hexane); mp 93-94 °C.

^1H NMR (400 MHz, $CDCl_3$) δ 4.51 (dd, *J* = 10.01 Hz, *J* = 4.92 Hz, 1H, CH_2O), 4.43 (d, *J* = 10.00 Hz, 1H, CH_2O), 3.42 (d, *J* = 9.34 Hz, 1H, CHBr), 3.19 (t, 1H, $CHCH_2O$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7 (C=O), 112.6 (CN), 68.2 (CH_2O), 34.9 (CHBr), 25.9 ($CHCH_2O$), 23.6 (CCN).

IR (film) 3074, 2252 (CN), 1779 (C=O), 1470, 1291, 1097, 950 cm^{-1}.

Anal. Calcd. for $C_6H_4BrNO_2$: C, 35.67; H, 2.00; N, 6.93. Found: C, 36.00; H, 1.87; N, 6.73.

Enantiomeric excess: 82%, GC analysis (Chiralcel cyclodex gamma, 175 °C, t_r[(1*R*)-**7c**] = 18.8 min, t_r[(1*S*)-**7c**] = 19.4 min.

$[\alpha]_D^{20}$ +65.2 (*c* 0.175, $CHCl_3$).

[1*S*-(1a**,5**a**,6**b**)]-6-Iodo-3-oxa-bicyclo[3.1.0]hexan-2-one-1-carbonitrile (8c)** as a white solid (33%) R_f 0.39 (40% ethyl acetate/hexane); mp 97-98 °C.

^1H NMR (300 MHz, $CDCl_3$) δ 4.41 (m, 2H, CH_2O), 3.08 (m, 2H, $CHCH_2O$, CHI).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6 (C=O), 113.8 (CN), 68.5 (CH_2O), 36.5 ($CHCH_2O$), 26.0 (CCN), -11.3 (CHI).

IR (film) 3068, 2248 (CN), 1773 (C=O), 1467, 1387, 1273, 1094, 996 cm^{-1}.

Anal. Calcd. for $C_6H_4INO_2$: C, 28.94; H, 1.62; N, 5.63. Found: C, 29.40; H, 1.58; N, 5.32.

Enantiomeric excess: 75%, GC analysis (Chiralcel cyclodex gamma, 175 °C, t_r[(1*R*)-**8c**] = 32.5 min, t_r[(1*S*)-**8c**] = 33.6 min.

$[\alpha]_D^{20}$ +52 (*c* 0.1, $CHCl_3$).

[1*S*-(1a**,5**a**,6**a**)]-6-Chloro-3-oxa-bicyclo[3.1.0]hexan-2-one-1-carbonitrile (9c)** as a white solid (62%): R_f 0.24 (40% ethyl acetate/hexane); mp 94-95 °C.

^1H NMR (400 MHz, $CDCl_3$) δ 4.69 (dd, *J* = 10.29 Hz, *J* = 5.28 Hz, 1H, CH_2O), 4.42 (dd, *J* = 10.28 Hz, *J* = 0.69 Hz, 1H, CH_2O), 4.20 (d, *J* = 7.24 Hz, 1H, CHCl), 3.29 (m, 1H, $CHCH_2O$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8 (C=O), 113.2 (CN), 64.7 (CH_2O), 40.8 (CHCl), 32.8 ($CHCH_2O$), 25.7 (CCN).

IR (film) 3075, 2253 (CN), 1766 (C=O), 1472, 1396, 1109, 996 cm^{-1}.

Anal. Calcd. for $C_6H_4BrNO_2$: C, 45.74; H, 2.56; N, 8.89. Found: C, 45.56; H, 2.44; N, 8.66.

Enantiomeric excess: 77%, GC analysis (Chiralcel cyclodex beta, 115 °C, t_r[(1*R*)-**9c**] = 164.2 min, t_r[(1*S*)-**9c**] = 167.4 min.

$[\alpha]_D^{20}$ -15.7 (*c* 0.108, $CHCl_3$).

[(1*S*-(1a**,5**a**,6**a**)]-6-Bromo-3-oxa-bicyclo[3.1.0]hexan-2-one-1-carbonitrile (10c)** as a white solid (75%): R_f 0.17 (30% ethyl acetate/hexane); mp 93-94 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.71 (dd, *J* = 10.25 Hz, *J* = 5.24 Hz, 1H, CH_2O), 4.33 (d, *J* = 9.07 Hz, 1H, CH_2O), 4.13 (d, *J* = 7.67 Hz, 1H, CHBr), 3.29 (m, 1H, $CHCH_2O$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1(C=O), 113.4 (CN), 65.9 (CH_2O), 32.2 (CHBr), 28.0 ($CHCH_2O$), 25.2 (CCN).

IR (film) 3082, 2247 (CN), 1770 (C=O), 1465, 1348, 1092, 993 cm^{-1}.

Anal. Calcd. for $C_6H_4BrNO_2$: C, 35.67; H, 2.00; N, 6.93. Found: C, 35.75; H, 1.90; N, 6.75.

Enantiomeric excess: 91%, GC analysis (Chiralcel cyclodex beta, 154 °C, t_r[(1*S*)-**10c**] = 40.2 min, t_r[(1*R*)-**10c**] = 40.9 min.

$[\alpha]_D^{20}$ -43.6 (*c* 0.183, $CHCl_3$).

[1*S*-(1a,5a,6a)]-6-Iodo-3-oxa-bicyclo[3.1.0]hexan-2-one-1-carbonitrile (11c) as a white solid (63%): R_f 0.30 (40% ethyl acetate/hexane); mp 97-98 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.73 (dd, *J* = 10.33 Hz, *J* = 5.04 Hz, 1H, CH_2O), 4.12 (d, *J* = 10.25 Hz, 1H, CH_2O), 3.87 (d, *J* = 7.77 Hz, 1H, $CHCH_2O$), 3.08 (q, 1H, CHI).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8 (C=O), 113.6 (CN), 68.0 (CH_2O), 31.4 ($CHCH_2O$), 24.7 (CCN), -3.8 (CHI).

IR (film) 3063, 2247 (CN), 1766 (C=O), 1459, 1394, 1092, 989 cm^{-1}.

Anal. Calcd. for $C_6H_4INO_2$: C, 28.94; H, 1.62; N, 5.63. Found: C, 28.98; H, 1.49; N, 5.50.

Enantiomeric excess: 86%, GC analysis (Chiralcel cyclodex beta, 170 °C, t_r[(1*R*)-**11c**] = 36.1 min, t_r[(1*S*)-**11c**] = 37.3 min.

$[\alpha]_D^{20}$ -79.5 (*c* 0.092, $CHCl_3$).

(1*S*,5*S*)-6,6-Dibromo-3-oxa-bicyclo[3.1.0]hexan-2-one-1-carbonitrile (12c) as a yellow solid (69%): R_f 0.29 (30% ethyl acetate/hexane); mp 105-106 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.64 (dd, *J* = 10.58 Hz, *J* = 5.51 Hz, 1H, CH_2O), 4.40 (d, *J* = 10.58 Hz, 1H, CH_2O), 3.50 (dd, *J* = 5.49 Hz *J* = 0.85 Hz, 1H, $CHCH_2O$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (C=O), 112.3 (CN), 67.4 (CH_2O), 42.8 ($CHCH_2O$), 35.7 (CBr_2), 24.2 (CCN).

IR (film) 3068, 2253 (CN), 1770 (C=O), 1458, 1394, 1111, 964 cm^{-1}.

Anal. Calcd. for $C_6H_3Br_2NO_2$: C, 25.65; H, 1.08; N, 4.99. Found: C, 25.95; H, 1.00; N, 4.90.

Enantiomeric excess: 62%, GC analysis (Chiralcel cyclodex gamma, 185 °C, t_r[(1*S*)-**12c**] = 22.6 min, t_r[(1*R*)-**12c**] = 23.0 min.

$[\alpha]_D^{20}$ -8.6 (*c* 0.192, $CHCl_3$).

(1*S*,5*S*)-6,6-Diiodo-3-oxa-bicyclo[3.1.0]hexan-2-one-1-carbonitrile (13c) as a light yellow solid (55%): R_f 0.32 (30% ethyl acetate/hexane); mp 135- 136 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.53 (dd, *J* = 10.61 Hz, *J* = 5.38 Hz, 1H, CH_2O), 4.10 (dd, *J* = 10.60 Hz, *J* = 0.81 Hz, 1H, CH_2O), 3.35 (dd, *J* = 5.3 Hz, *J* = 0.81 Hz, 1H $CHCH_2O$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9 (C=O), 114.4 (CN), 70.0 (CH_2O), 44.2 (CH), 36.1 (CCN), -66.9 (CI_2).

IR (film) 3065, 2248 (CN), 1755 (C=O), 1457, 1382, 1102, 962 cm^{-1}.

MS(APCI-) Calcd. for $C_6H_3I_2NO_2[M-1]^+$: 373.8. Found: 373.8.

Enantiomeric excess: 47%, SFC analysis (Chiralcel OJ 4.6x 250 mm, 8.0 % MeOH. Flow: 2.0 mL/min; t_r[(1*R*)-**13c**] = 21.5 min, t_r[(1*S*)-**13c**] = 24.6 min.

$[\alpha]_D^{20}$ -16 (*c* 0.1, $CHCl_3$).

6,6-Fluoro,bromo-3-oxa-bicyclo[3.1.0]hexan-2-one-1-carbonitrile (14c) as a light yellow oil (38%): R_f 0.19 (30% ethyl acetate/hexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6α, 4.71 (m, 1H, CH_2O), 4.41 (d, *J* = 10.44 Hz, 1H, CH_2O), 3.54 (dd, *J* = 14.03 Hz, *J* = 5.73 Hz, 1H, $CHCH_2O$); 6β, 4.63 (m, 2H, CH_2O), 3.54 (m, 1H, $CHCH_2O$). ^{13}F NMR ($CDCl_3$, 300 MHz) δ 6α, -128.11 (dd, $J^{F\text{-}H}$ = 14.10 Hz, $J^{F\text{-}H}$= 2.37 Hz, 1H, CH_2O); 6β, -149.5 (d, $J^{F\text{-}H}$ = 1.73 Hz)

^{13}C NMR (100 MHz, $CDCl_3$) δ 6α 163.1 (C=O), 109.6 (CN), 78.5 (C-CBrF), 66.4(CH_2O), 36.9 (CH), 31.4 (CCN); δ 6β 163.1 (C=O), 109.6 (CN), 81.6 (C-CBrF), 64.7 (CH_2O), 41.0 (CH), 31.4 (CCN).

IR (film) 3069, 2257 (CN), 1784 (C=O), 1404, 1354, 1277, 1078, 962 cm^{-1}.

Anal. Calcd. for $C_6H_3BrFNO_2$: C, 32.76; H, 1.37; N, 6.37. Found C, 33.15; H, 1.08; N, 6.44.

General Experimental Procedure for Diazo Transfer.[2]

To a stirred solution of *E*-3-carbethoxyallylic cyanoacetate (100mg, 0.88 mmol) in acetonitrile (2.0 mL) cooled to 0 °C was added triflyl azide (1.6 mL, 1.0M in hexane, 1.5 equiv). Distilled pyridine (0.14 mL, 1.76 mmol, 2.0 equiv) was added slowly dropwise. The reaction mixture was allowed to stir for 14 h, warming to room temperature, and then concentrated under reduced pressure. Purified on silica gel ($CHCl_3$) afforded **(*E*)-3-Carbethoxyallylic α-cyano-α-diazoacetate** as a yellow solid (**5b**) (97 mg, 76%): R_f 0.13 ($CHCl_3$); mp 35 °C.

^{1}H NMR (300MHz, $CDCl_3$) δ 6.86 (dt, *J* = 15.77 Hz, 1H, =CHCOO), 6.00 (dt, *J* = 15.77 Hz, 1H, CH=CHCOO), 4.88 (dd, *J* = 4.82 Hz, *J* = 1.89 Hz, 2H, $CNCH_2$), 4.16 (q, 2H, CH_2CH_3), 1.25 (t, 3H, CH_3).

^{13}C NMR (75MHz, $CDCl_3$) δ 165.4 (=CHCOO), 160.9 ($CNCH_2COO$), 139.3 (=CHCOO), 123.4 (CH=CHCOO), 107.0 (CN), 64.8 ($CNCH_2$), 60.8 (CH_2CH_3), 14.2 (CH_3).

IR (film): 2984, 2230 (CN), 2137 (CN_2), 1719 (CO), 1665 (CO), 1446, 1384, 1368, 1255, 1129, 1035, 966 cm^{-1}.

Anal. Calcd. for $C_9H_9N_3O_4$: C, 48.43; H, 4.06; N, 18.83. Found: C, 48.48; H, 4.14; N, 18.5.

For the synthesis of compound (**1b**) and (**3b**), see reference.[2]

3-Methyl-2-bute-2-enyl α-cyano-α-diazoacetate (**2b**) R_f 0.59 ($CHCl_3$).

^{1}H NMR (400MHz, $CDCl_3$) δ 5.32 (t, 1H, CH), 4.73 (d, *J* = 7.39Hz, 2H, CH_2), 1.72 (d, *J* = 15.94 Hz, 3H, CH_3).

^{13}C NMR (100MHz, $CDCl_3$) δ 161.5 (CO), 141.5 (=$C(CH_3)_2$), 117.5 (CH=), 107.6 (CN), 64.2 (OCH_2), 26.0 (CH_3), 18.3 (CH_3).

IR (film): 2976, 2229, 2138, 1718, 1447, 1383, 1268, 1136, 912 cm^{-1}.

Anal. Calcd. for $C_8H_9N_3O_2$: C, 53.63; H, 5.06; N, 23.45. Found: C, 53.68; H, 5.12; N, 23.26.

(*E*)-3-Phenylallylic α-cyano-α-diazoacetate (**4b**) R_f 0.74($CHCl_3$).

^{1}H NMR (400MHz, $CDCl_3$) δ 7.41 (m, 2H, ArH), 7.34 (m, 3H, ArH), 6.71 (d, *J* = 15.86 Hz, 1H, =CHAr), 6.29 (m, 1H, C=$CHCH_2$), 4.92 (dd, *J* = 6.72 Hz, *J* = 1.18 Hz 2H, CH_2).

^{13}C NMR (100MHz, $CDCl_3$) δ 161.2 (CO), 136.1 (Ar), 135.7 (CN_2), 128.8 (Ar), 128.4 (=CAr), 126.9 (Ar), 121.5 (CH_2C=), 107.4 (CN), 67.7 (CH_2).

IR (film): 2942, 2227 (CN), 2169 (CN_2), 1689 (CO), 1386, 1135, 972cm^{-1}.

Anal. Calcd. for (%) $C_{12}H_9N_3O_2$: C, 63.43; H, 3.99; N, 18.49. Found: C, 63.18; H, 3.95; N, 18.37.

(*E*)-3-Chloro-2-propenyl α-cyano–α-diazoacetate (**6b**) R_f 0.34 ($CHCl_3$).

^{1}H NMR (400MHz, $CDCl_3$) δ 6.42 (dt, *J* = 13.37 Hz, 1H, =CHCl), 6.08 (dt, *J* = 13.37 Hz, 1H, =$CHCH_2$), 4.74 (dd, *J* = 7.05 Hz, *J* = 1.21 Hz, 2H, CH_2).

^{13}C NMR (100MHz, $CDCl_3$) δ 161.2 (CO), 126.3 (=CHCl), 125.9 (=$CHCH_2$), 107.1 (CN), 64.8 (CH_2).

IR (film): 3073, 2230 (CN), 2132 (CN_2), 1713 (CO), 1448, 1378, 1321, 1295, 1242, 1124, 938 cm^{-1}.

Anal. Calcd. for $C_6H_4ClN_3O_2$: C, 38.83; H, 2.17; N, 22.64. Found: C, 38.93; H, 2.16; N, 22.35.

(*E*)-3-Bromo allylic α-cyano-α-diazoacetate (**7b**) R_f 0.37 ($CHCl_3$).

^{1}H NMR (400MHz, $CDCl_3$) δ 6.53 (dt, *J* = 13.73 Hz, 1H, =CHBr), 6.31 (m, 1H, CH=), 4.68 (dd, *J* = 6.76 Hz, *J* = 1.10 Hz, 2H, CH_2).

^{13}C NMR (100MHz, $CDCl_3$) δ 161.0 (CO), 130.2 (=CHBr), 113.1 (CH=), 107.1 (CN), 66.0 (CH_2).

IR (film): 3071, 2229 (CN), 2131 (CN_2), 1712 (CO), 1446, 1377, 1319, 1241, 1123, 938 cm^{-1}.

Anal. Calcd. for $C_6H_4BrN_3O_2$: C, 31.33; H, 1.75; N, 18.27. Found: C, 31.39; H, 1.74; N, 17.88.

(*E*)-3-Iodo-2-propenyl α-cyano-α-diazoacetate (**8b**) R_f 0.39 ($CHCl_3$).

^{1}H NMR (300MHz, $CDCl_3$) δ 6.62 (m, 2H, CH=CHI), 4.65 (d, *J* = 5.00 Hz, 2H, CH_2).

^{13}C NMR (75MHz, $CDCl_3$) δ 160.9 (CO), 138.1 (=CHI), 107.1 (CN), 83.6 (CH=), 67.9 (CH_2).

IR (film): 3058, 2950, 2229 (CN), 2132 (CN_2), 1713 (CO), 1443, 1376, 1318, 1264, 1127, 943 cm^{-1}.

Anal. Calcd. for (%) $C_6H_4IN_3O_2$: C, 26.01; H, 1.46; N, 15.17. Found: C, 26.26; H, 1.40; N, 14.82.

(*Z*)-3-Chloro-2-propenyl α-cyano-α-diazoacetate (**9b**) R_f 0.39 ($CHCl_3$).

^{1}H NMR (300MHz, $CDCl_3$) δ 6.31 (dt, *J* = 7.34 Hz, 1H, =CHCl), 5.96 (m, 1H, CH=), 4.97 (dd, *J* = 6.40 Hz, *J* = 1.51 Hz, 2H, CH_2).

^{13}C NMR (100MHz, $CDCl_3$) δ 161.2 (CO), 124.8 (=CHCl), 123.7 (CH=), 107.2 (CN), 62.3 (CH_2).

IR (film): 3091, 2231 (CN), 2144 (CN_2), 1724 (CO), 1446, 1383, 1331, 1291, 1136, 956 cm^{-1}.

Anal. Calcd. for $C_6H_4ClN_3O_2$: C, 38.83; H, 2.17; N, 22.64. Found: C, 39.02; H, 2.14; N, 22.35.

(*Z*)-3-Bromo-2-propenyl α-cyano-α-diazoacetate (**10b**) R_f 0.52 ($CHCl_3$).

^{1}H NMR (400MHz, $CDCl_3$) δ 6.48 (dt, *J* = 7.39 Hz, 1H, CHBr), 6.33 (m, 1H, CH), 4.94 (dd, *J* = 6.13 Hz, 2H, CH_2).

^{13}C NMR (75MHz, $CDCl_3$) δ 161.1 (CO), 128.0 (=CHBr), 112.7 (CH=), 107.2 (CN), 64.6 (CH_2).

IR (film): 2230 (CN), 2134 (CO), 1716 (CO), 1441, 1378, 1324, 1265, 1127, 956 cm^{-1}.

Anal. Calcd. for $C_6H_4BrN_3O_2$: C, 31.33; H, 1.75; N, 18.27. Found: C, 31.49; H, 1.70; N, 17.86.

(*Z*)-3-Iodo-2-propenyl α-cyano-α-diazoacetate (**11b**) R_f 0.39 ($CHCl_3$).

^{1}H NMR (300MHz, $CDCl_3$) δ 6.61 (dd, *J* = 7.96 Hz, *J* = 1.40 Hz, 1H, CHI), 6.49 (m, 1H, CH), 4.84 (dd, *J* = 5.92 Hz, *J* = 1.42 Hz, 2H, CH_2).

^{13}C NMR (75MHz, $CDCl_3$) δ 161.2 (CO), 134.2 (=CHI), 107.1 (CN), 86.9 (CH=), 69.3 (CH_2).

IR (film): 2933, 2229 (CN), 2132 (CN_2), 1713 (CO), 1442, 1374, 1321, 1263, 1124, 955 cm^{-1}.

Anal Calcd. for (%) $C_6H_4IN_3O_2$: C, 26.01; H, 1.46; N, 15.17. Found: C, 26.33; H, 1.42; N, 15.08.

3,3-Dibromo-2-propenyl α-cyano–α-diazoacetate (**12b**) R_f 0.34 ($CHCl_3$).

^{1}H NMR (300MHz, $CDCl_3$) δ 6.63 (t, 1H, CH), 4.76 (d, *J* = 6.63 Hz, 2H, CH_2).

^{13}C NMR (100MHz, $CDCl_3$) δ 161.1 (CO), 131.2 (CH=), 107.0 (CN), 96.3 (=CBr_2), 65.9 (CH_2).

IR (film): 3043, 2945, 2230 (CN), 2136 (CN_2), 1717 (CO), 1442, 1377, 1321, 1262, 1130, 947 cm^{-1}.

Anal Calcd. for (%) $C_6H_3Br_2N_3O_2$: C, 23.33; H, 0.98; N, 13.60. Found: C, 23.48; H, 0.89; N, 13.27.

3,3-Diiodo-2-propenyl α-cyano-α-diazoacetate (**13b**) R_f 0.38 ($CHCl_3$).

^{1}H NMR (300MHz, $CDCl_3$) δ 7.26 (t, 1H, CH), 4.55 (d, *J* = 6.21 Hz, 2H, CH_2).

^{13}C NMR (75MHz, $CDCl_3$) δ 144.7 (CO), 144.7 (CH=), 107.0 (CN), 71.4 (CH_2), 18.0 (=CI_2).

IR (film): 3019, 2228 (CN), 2131 (CN_2), 1713 (CO), 1371, 1318, 1240, 1122, 950 cm^{-1}.

Anal Calcd. for (%) $C_6H_3I_2N_3O_2$: C, 17.89; H, 0.75; N, 10.43. Found: C, 18.26; H, 0.72; N, 10.32.

3,3-Fluoro,bromo-2-propenyl α-cyano-α-diazoacetate (**14b**) R_f 0.2 ($CHCl_3$).

^{1}H NMR (300MHz, $CDCl_3$) δ (*Z*) 5.77 (dt, $J^{F\text{-}H}$ = 11.06 Hz, 1H, CH=), (*E*) 5.36 (dt, $J^{F\text{-}H}$ = 28.67 Hz, 1H, CH=), 4.76 (dt, *J* = 7.64 Hz, 2H, CH_2). ^{13}F NMR ($CDCl_3$, 300MHz): δ (*Z*) -67.0 (dd, $J^{F\text{-}H}$ = 28.62 Hz, $J^{F\text{-}H}$ = 2.36 Hz), (*E*) -62.5 (d, $J^{F\text{-}H}$ = 10.36 Hz)

^{13}C NMR (75MHz, $CDCl_3$) δ (*Z*): 161.2 (CO) , 141.2 (d, *J* = 322.16 Hz, =CBrF), 107.1 (CN), 104.9 (d, *J* = 20.86 Hz, CH=) , 63.9 (d, *J* = 8.74 Hz, CH_2O); δ (*E*): 161.2 (CO) , 138.3 (d, *J* = 327.38 Hz, =CBrF), 107.1 (CN), 1.6.6 (d, *J* = 10.53 Hz, CH=) , 59.9 (d, *J* = 4.25 Hz, CH_2O).

IR (film): 2967, 2230 (CN), 2134 (CN_2), 1717 (CO), 1384, 1324, 1242, 1130, 936 cm^{-1}.

Anal Calcd. for $C_6H_3BrFN_3O_2$: C, 29.06; H, 1.22; N, 16.94. Found: C, 29.42; H, 0.91; N, 16.9.

For the synthesis of α-cyanoesters, see reference.[3]

For **allylic α-cyanoacetate** (**1a**) and (***Z*)-pent-2-enyl α-cyanoacetate** (**3a**) see reference.[2]

3-Methyl-2-butenyl α-cyanoacetate (**2a**), R_f 0.32 (20% ethyl acetate/hexane).

^{1}H NMR (400MHz, $CDCl_3$) δ 5.34 (t, 1H, CH), 4.67 (d, *J* = 7.37 Hz, 2H, CH_2), 3.44 (d, *J* = 1.00 Hz, 2H, CH_2), 1.73 (d, *J* = 17.38 Hz, 6H, CH_3).

^{13}C NMR (100MHz, $CDCl_3$) δ 163.1 (CO), 141.1 (=CCH_3), 117.3 (CH=), 113.3 (CN), 63.7 (CH_2O), 25.9 (CH_3), 24.9 (CH_2CN), 18.2 (CH_3).

IR (film): 2934, 2265 (CN), 1746 (CO), 1447, 1346, 1183, 988 cm^{-1}.

Anal. Calcd. for $C_8H_{11}NO_2$: C, 62.73; H, 7.24; N, 9.14. Found: C, 62.30; H, 7.29; N, 9.09.

(*E*)-3-Phenylallylic α-cyanoacetate (**4a**),[4] R_f 0.65 (20% ethyl acetate/hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 5H, ArH), 6.72 (d, *J* = 15.80 Hz, 1H, CH), 6.29 (dt, *J* = 15.86 Hz, 1H, CH), 4.86 (dd, *J* = 6.69 Hz, *J* = 0.99 Hz, 2H, CH_2), 3.50 (s, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (CO), 136.2 (=CHAr), 135.9 (C), 128.9 (Ar), 128.7 (Ar), 127.0 (Ar), 121.5 (CH=), 113.1 (CN), 67.6 (CH_2O), 25.0 (CH_2).

IR (film) 2959, 2267, 1739, 1495, 1445, 1382, 1341, 1177, 969, 742, 690 cm^{-1}.

Anal. Calcd. for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.74; H, 5.51; N, 6.84.

(*E*)-3-Carbethoxyallylic α-cyanoacetate (**5a**),[5] R_f 0.33 (30% ethyl acetate/hexane).

^{1}H NMR (400MHz, $CDCl_3$) δ 6.87 (dt, *J* = 15.78 Hz, 1H, $CHCOOCH_2CH_3$), 6.02 (dt, *J* = 15.78 Hz, 1H, CH=), 4.82 (dd, *J* = 4.84 Hz, *J* = 1.88 Hz, 2H, $CNCH_2$), 4.16 (q, 2H, CH_2CH_3), 3.55 (s, 2H, CH_2O), 1.24 (t, 3H, CH_3).

^{13}C NMR (100MHz, $CDCl_3$) δ 165.5 (CO), 162.7 (CO), 139.3 (=CHCOOEt), 123.4 (CH=), 112.9 (CN), 64.7 (CH_2O), 60.9 (CH_2CH_3), 24.7 ($CNCH_2$), 14.2 (CH_3).

IR (film): 2983, 2266 (CN), 1752 (CO), 1713 (CO), 1666, 1447, 1338, 1261, 1174, 1034, 968 cm^{-1}.

Anal. Calcd. for $C_9H_{11}NO_4$: C, 54.82; Hm 5.62; N, 7.10. Found: C, 54.97; H, 5.77; N, 7.08.

(*E*)-3-Chloro-2-propenyl α-cyanoacetate (**6a**) R_f 0.32 (20% ethyl acetate/hexane).

^{1}H NMR (300MHz, $CDCl_3$) δ 6.38 (dd, *J* = 13.36 Hz, *J* = 1.09 Hz, 1H, CH), 6.02 (m, 1H, CH), 4.63 (dd, *J* = 6.70 Hz, *J* = 1.13 Hz, 2H, CH_2), 3.50 (s, 2H, CH_2O).

^{13}C NMR (75MHz, $CDCl_3$) δ 162.9 (CO), 126.2 (=CHCl), 125.0 (CH=), 113.2 (CN), 64.3 (CH_2O), 24.7 ($CNCH_2$).

IR (film): 2934, 2266 (CN), 1746 (CO), 1641, 1450, 1379, 1334, 1179, 935 cm^{-1}.

Anal. Calcd. for $C_6H_6ClNO_2$: C, 45.16; H, 3.79; N, 8.78. Found: C, 44.80; H, 3.71; N, 8.68.

(*E*)-3-Bromo-2-propenyl α-cyanoacetate (**7a**) R_f 0.35 (20% ethyl acetate/hexane).

^{1}H NMR (300MHz, $CDCl_3$) δ 6.55 (dt, *J* = 13.72 Hz, 1H, CH), 6.33 (m, 1H, CH), 4.65 (dd, *J* = 6.81 Hz, *J* = 1.23 Hz, 2H, CH_2), 3.50 (s, 2H, CH_2).

^{13}C NMR (100MHz, $CDCl_3$) δ 162.8 (CO), 130.2 (=CHBr), 113.1 (CH=), 112.6 (CN), 65.6 (CH_2O), 24.7 ($CNCH_2$).

IR (film): 2931, 2267 (CN), 1747 (CO), 1626, 1448, 1335, 1250, 1178, 934 cm^{-1}.

Anal. Calcd. for $C_6H_6BrNO_2$: C, 35.32; H, 2.96; N, 6.87. Found: C, 35.49; H, 2.88; N, 6.68.

(*E*)-3-Iodo-2-propenyl α-cyanoacetate (**8a**) R_f 0.31 (20% ethyl acetate/hexane).

^{1}H NMR (300MHz, $CDCl_3$) δ 6.64 (m, 2H, CH), 4.60 (d, *J* = 5.02 Hz, 2H, CH_2), 3.50 (s, 2H, CH_2).

^{13}C NMR (75MHz, $CDCl_3$) δ 162.6 (CO), 138.1 (=CHI), 112.9 (CN), 83.5 (CH=), 67.9 (CH_2O), 24.8 ($CNCH_2$).

IR (film): 3058, 2968, 2263, 1733, 1614, 1453, 1376, 1334, 1188, 937cm^{-1}.

Anal. Calcd. for $C_6H_6INO_2$: C, 28.71; H, 2.41; N, 5.58. Found: C, 29.13; H, 2.29; N, 5.39.

(*Z*)-3-Chloro-2-propenyl α-cyanoacetate (**9a**) R_f 0.22 (20% ethyl acetate/hexane).

^{1}H NMR (300MHz, $CDCl_3$) δ 6.30 (dt, *J* = 7.34 Hz, 1H, CH), 5.95 (q, 1H, CH), 4.89 (dd, *J* = 6.4 Hz, 2H, CH_2), 3.50 (s, 2H, CH_2).

^{13}C NMR (75MHz, $CDCl_3$) δ 162.9 (CO), 124.7 (=CHCl), 123.6 (CH=), 113.0 (CN), 62.0 (CH_2O), 24.8 ($CNCH_2$).

IR (film): 2933, 2264, 1752, 1637, 1447, 1382, 1342, 1272, 1183, 631 cm^{-1}.

Anal. Calcd. for $C_6H_6ClNO_2$: C, 45.16; H, 3.79; N, 8.78. Found: C, 44.86; H, 3.78; N, 8.67.

(*Z*)-3-Bromo-2-propenyl α-cyanoacetate (**10a**) R_f 0.25 (20% ethyl acetate/hexane).

^{1}H NMR (300MHz, $CDCl_3$) δ 6.45 (dt, *J* = 7.37 Hz, 1H, CH), 6.30 (m, 1H, CH), 4.83 (dd, *J* = 6.12 Hz, *J* = 0.96 Hz, 2H, CH_2), 3.50 (s, 2H, CH_2).

^{13}C NMR (75MHz, $CDCl_3$) δ 162.9 (CO), 128.0 (=CHCl), 113.0 (CN), 112.7 (CH=), 64.4 (CH_2O), 24.7 ($CNCH_2$).

IR (film): 2931, 2264 (CN), 1748 (CO), 1628, 1449, 1378, 1337, 1266, 1180, 999 cm^{-1}.

Anal. Calcd. for $C_6H_6BrNO_2$: C, 35.32; H, 2.96; N, 6.87. Found: C, 35.61; H, 3.07; N, 6.94.

(*Z*)-3-Iodo-2-propenyl α-cyanoacetate (**11a**) R_f 0.32 (20% ethyl acetate/hexane).

^{1}H NMR (300MHz, $CDCl_3$) δ 6.59 (dt, *J* = 7.95 Hz, 1H, CH), 6.46 (m, 1H, CH), 4.75 (dd, *J* = 5.92 Hz, *J* = 1.39 Hz, 2H, CH_2), 3.51 (s, 2H, CH_2).

^{13}C NMR (75MHz, $CDCl_3$) δ 162.9 (CO), 134.2 (=CHI), 113.0 (CN), 86.8 (CH=), 69.0 (CH_2O), 24.7 ($CNCH_2$).

IR (film): 2931, 2263 (CN), 1751 (CO), 1616, 1446, 1375, 1335, 1179, 995 cm^{-1}.

Anal. Calcd. for $C_6H_6INO_2$: C, 28.71; H, 2.41; N, 5.58. Found: C, 29.02; H, 2.38; N, 5.50.

3,3-Dibromo 2-propenyl α-cyanoacetate (**12a**) R_f 0.31 (20% ethyl acetate/hexane).

^{1}H NMR (400MHz, $CDCl_3$) δ 6.60 (t, 1H, CH), 4.64 (d, *J* = 6.62 Hz, 2H, CH_2), 3.52 (s, 2H, CH_2).

^{13}C NMR (100MHz, $CDCl_3$) δ 162.8 (CO), 131.2 (CH=), 113.0 (CN), 95.7 (C=), 65.5 (CH_2O), 24.6 ($CNCH_2$).

IR (film): 2961, 2256 (CN), 1734 (CO), 1452, 1371, 1278, 1243, 984 cm^{-1}.

Anal. Calcd. for $C_6H_5Br_2NO_2$: C, 25.47; H, 1.78; N, 4.95. Found: C, 25.52; H, 1.66; N, 4.75.

3,3- Diiodo 2-propenyl α-cyanoacetate (**13a**) R_f 0.45 (20% ethyl acetate/hexane).

^{1}H NMR (300MHz, $CDCl_3$) δ 7.26 (t, 1H, CH), 4.48 (d, *J* = 6.23 Hz, 2H, CH_2), 3.51 (s, 2H, CH_2).

^{13}C NMR (75MHz, $CDCl_3$) δ 162.7 (CO), 144.7 (CH=), 112.8 (CN), 71.2 (CH_2O), 24.7 ($CNCH_2$), 18.0 ($=CI_2$).

IR (film): 2926, 2264 (CN), 1744 (CO), 1595, 1442, 1372, 1330, 1174, 1003 cm^{-1}.

Anal. Calcd. for $C_6H_5I_2NO_2$: C, 19.12; H, 1.34; N, 3.72. Found: C, 19.57; H, 1.15; N, 3.68.

3,3-Fluoro,bromo-2-propenyl α-cyanodiazoacetate(**14a**) R_f 0.26 (20% ethyl acetate/hexane).

^{1}H NMR (300MHz, $CDCl_3$) δ (*Z*) 5.80 (dt, J^{F-H} = 11.09 Hz, 1H, CH=), (*E*) 5.38 (dt, J^{F-H} = 28.77 Hz, 1H, CH=), 4.73 (dt, *J* = 7.65 Hz, 2H, CH_2O), 3.49 (d, *J* = 1.67 Hz, 2H, CH_2CN); ^{13}F NMR (300MHz, $CDCl_3$) δ (*Z*) -67.4 (m), (*E*) -62.9 (d, J = 11.04 Hz).

^{13}C NMR ($CDCl_3$, 75MHz) δ (*Z*) 162.9 (CO), 112.9 (=CBrF), 106.4 (d, *J* = 10.50 Hz, CH=), 104.6 (CN) , 59.6 (d, *J* = 4.2 Hz, CH_2O), 24.7 (CH_2CN); δ (*E*) 162.9 (CO) , 112.9 (=CBrF), 104.9 (CH=), 104.6 (CN), 63.2 (d, *J* = 8.5 Hz, CH_2O) , 24.7 (CH_2CN).

IR (film): 2932, 2267 (CN), 1750 (CO), 1384, 1337, 1243, 1179, 992 cm^{-1}.

Anal Calcd. for $C_6H_5BrFNO_2$: C, 32.46; H, 2.27; N, 6.31. Found: C, 32.37; H, 2.24; N, 6.2

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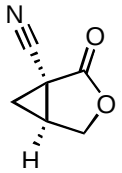

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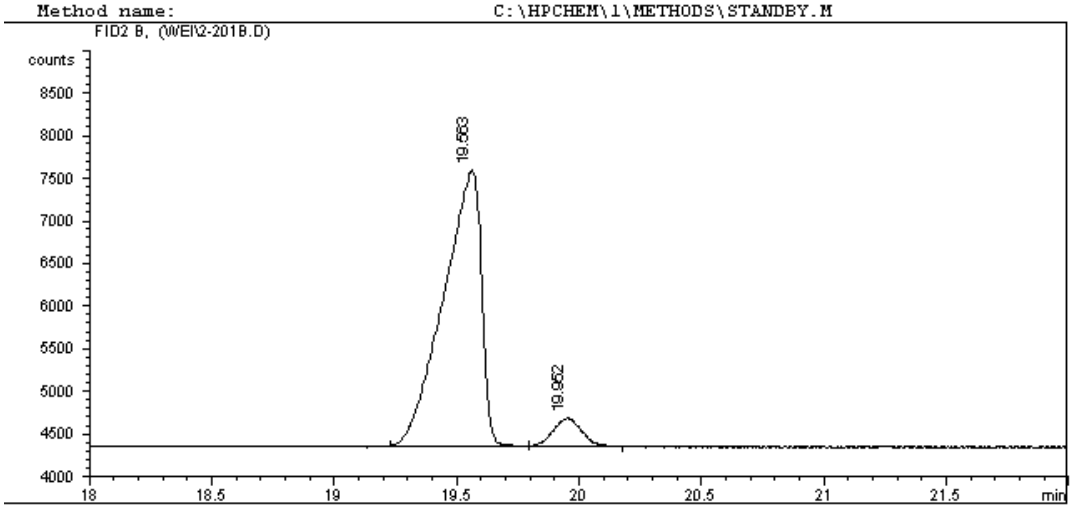

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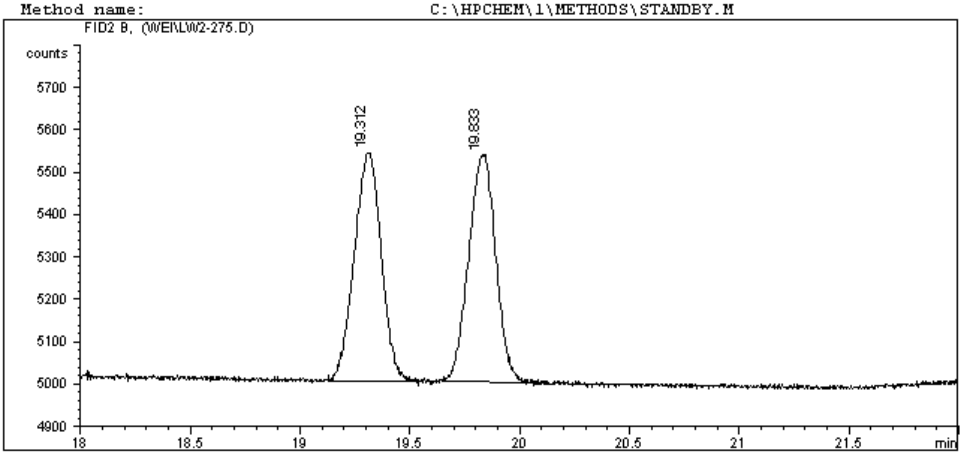
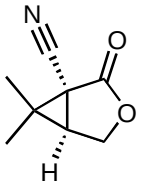
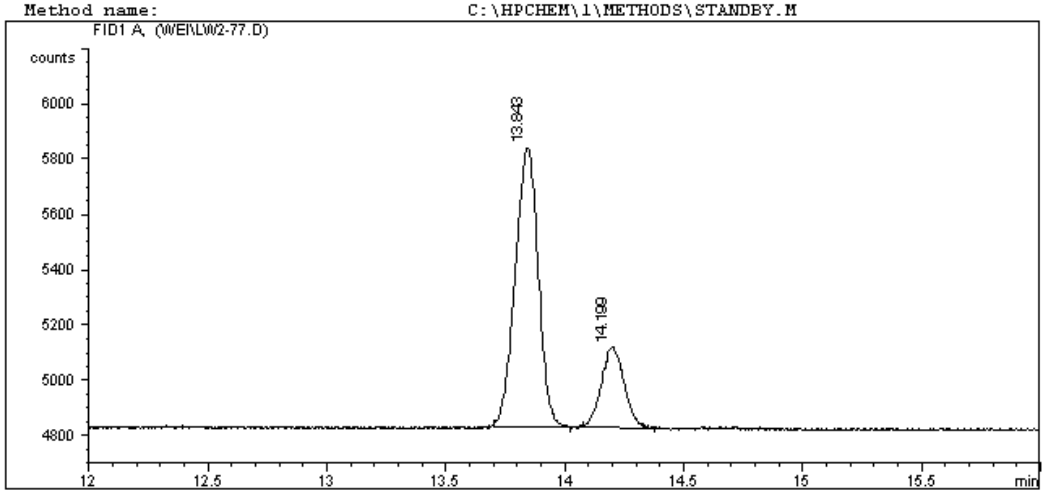


Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
19.31	4632.3	538.1	50.1	0.109	1.083
19.83	4607.5	534.6	49.9	0.105	1.054



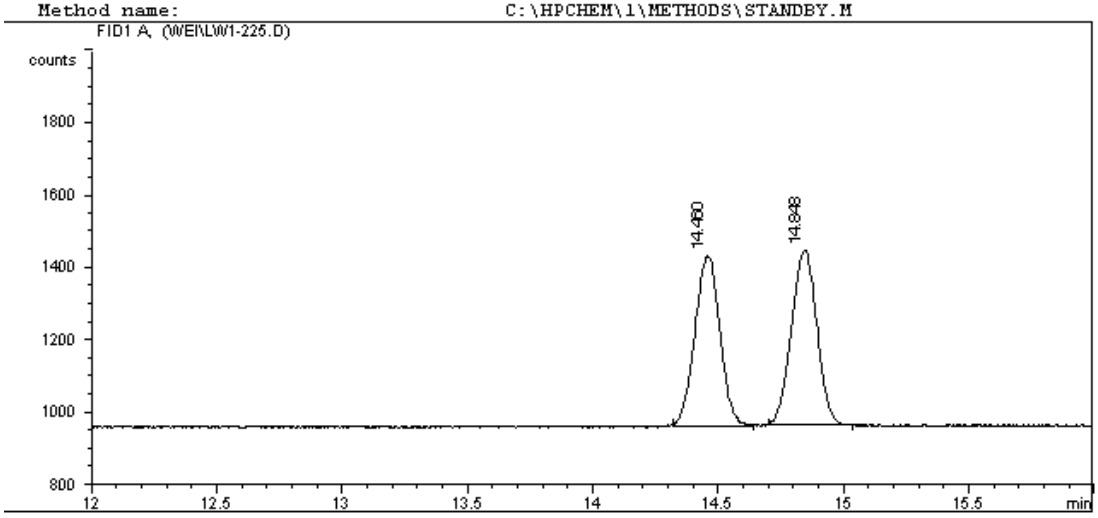
Data File name: C:\HPCHEM\1\DATA\WEI\LW2-77.D
Method name: C:\HPCHEM\1\METHODS\STANDBY.M



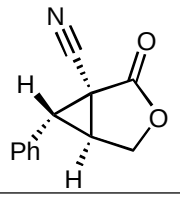
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
13.84	6827.4	1011.7	77.9	0.094	1.088
14.20	1933.1	288.0	22.1	0.080	0.855

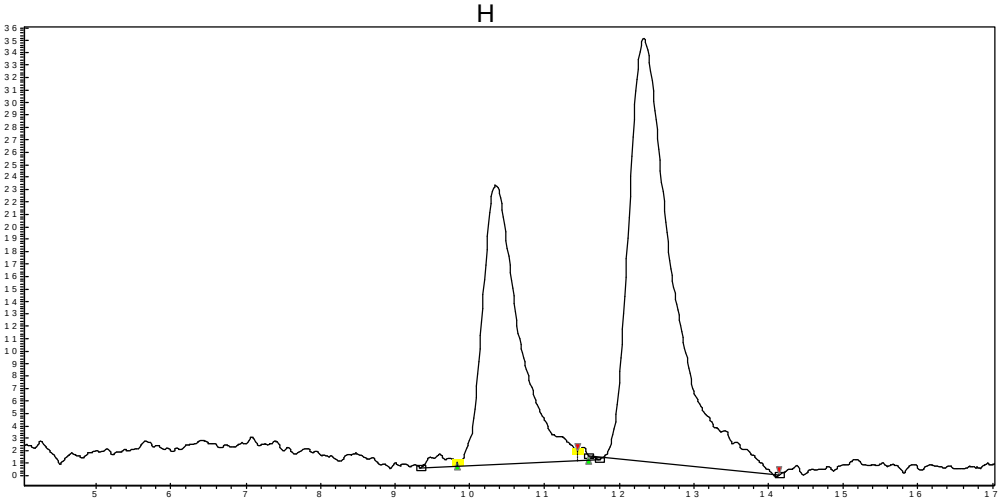
Racemate

Data File name: C:\HPCHEM\1\DATA\WEI\LW1-225.D
Method name: C:\HPCHEM\1\METHODS\STANDBY.M



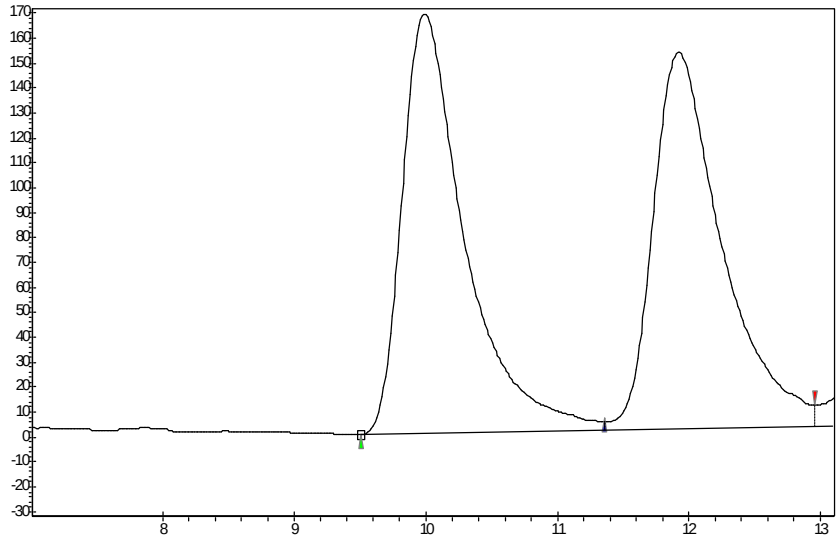
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
14.46	3269.2	469.8	48.8	0.098	1.055
14.85	3427.7	483.1	51.2	0.087	1.142



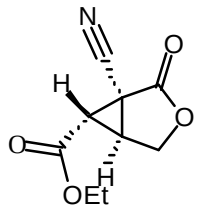


Name	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	9.84	10.35	11.44	35.85	22.4	12.9	35.847
2	11.6	12.33	14.15	64.15	34	23.1	64.153
Total				100	56.4	36	100

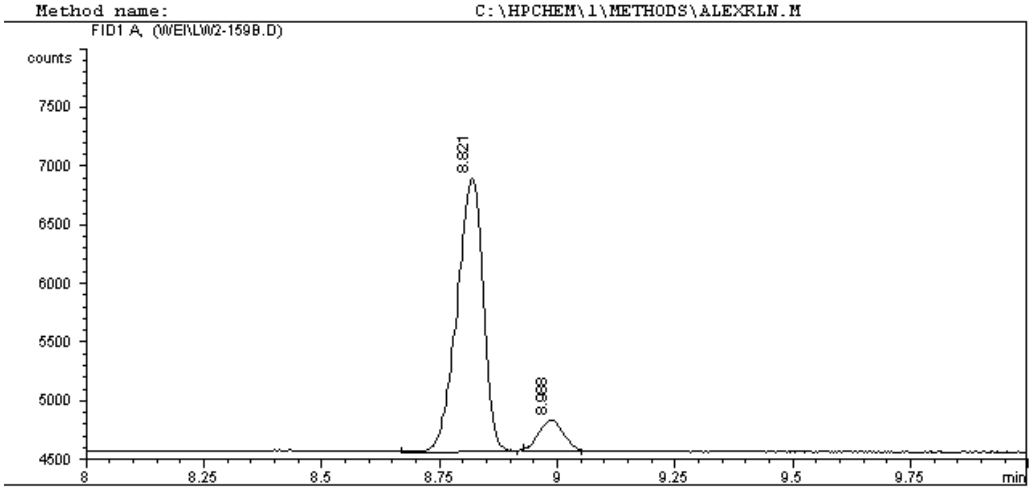
Racemate



Name	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	9.51	9.99	11.36	50.42	168	93.1	50.42
2	11.36	11.92	12.96	49.58	151	91.6	49.58
Total				100	319	184.7	100



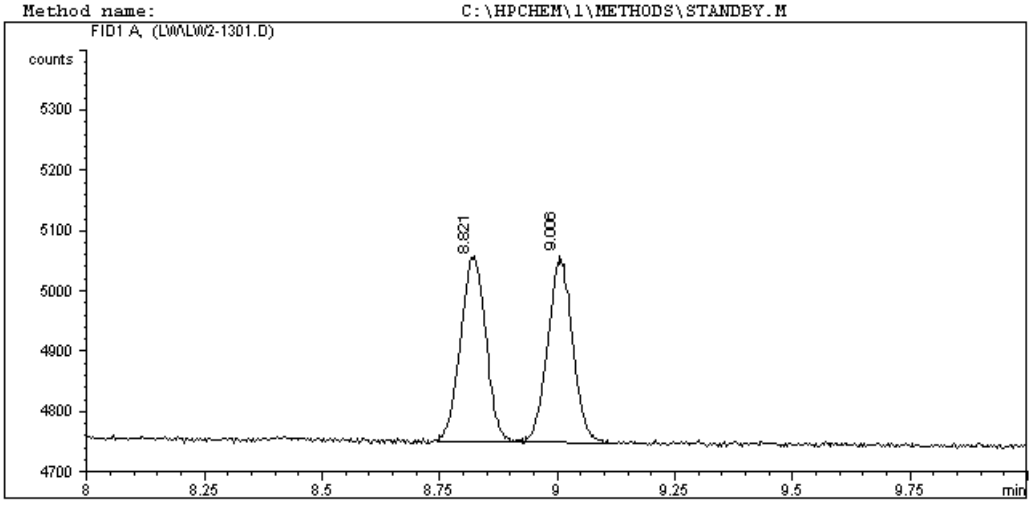
Data File name: C:\HPCHEM\1\DATA\WEI\LW2-159B.D
Method name: C:\HPCHEM\1\METHODS\ALEXRLN.M



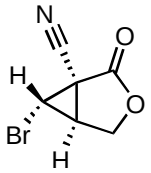
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
8.82	9066.5	2331.8	90.7	0.065	1.410
8.99	932.4	261.9	9.3	0.059	0.990

Racemate

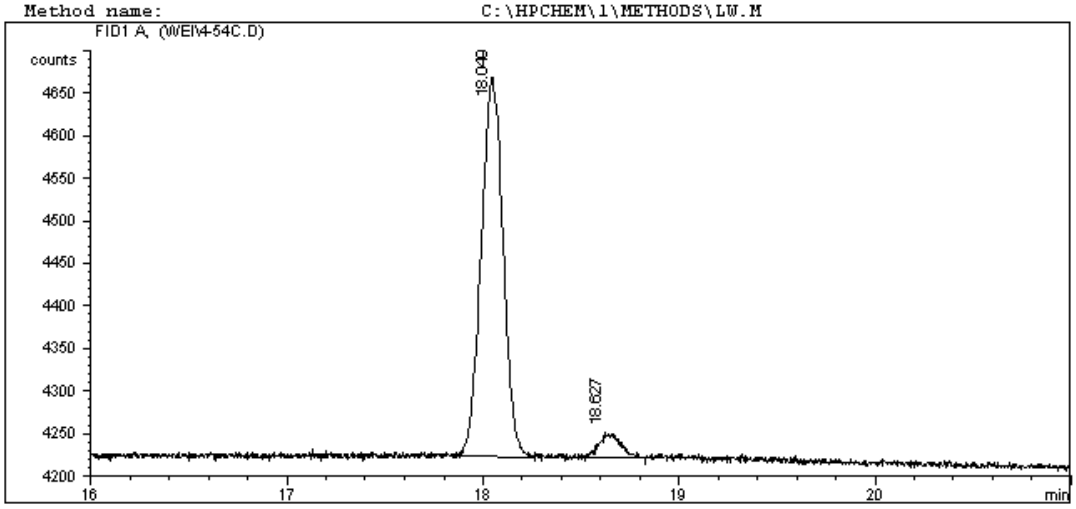
Data File name: C:\HPCHEM\1\DATA\LW\LW2-1301.D
Method name: C:\HPCHEM\1\METHODS\STANDBY.M



Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
8.82	1144.0	302.8	49.9	0.058	0.933
9.01	1147.8	309.1	50.1	0.052	0.949



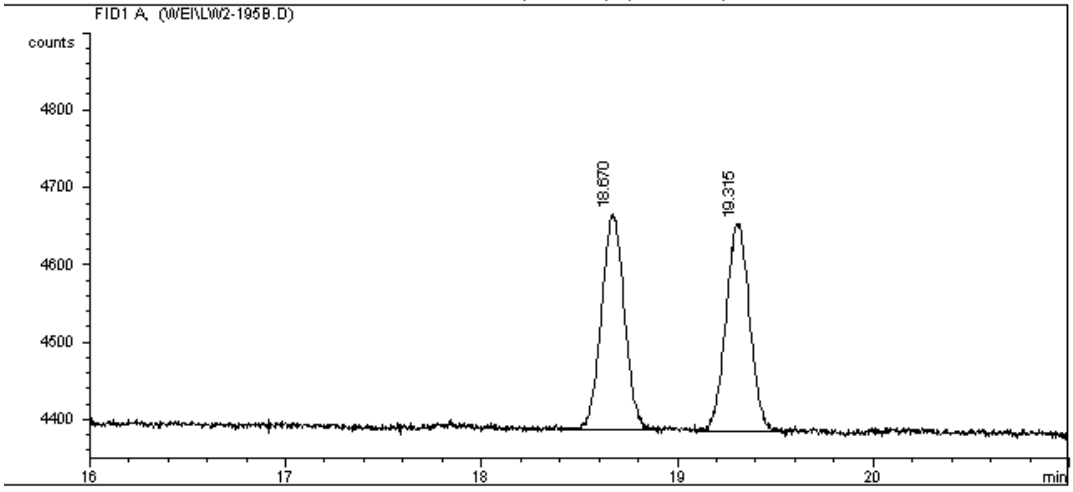
Data File name: C:\HPCHEM\1\DATA\WEI\4-54C.D
Method name: C:\HPCHEM\1\METHODS\LW.M



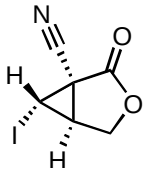
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
18.05	3448.4	444.7	93.7	0.129	1.069
18.63	232.2	30.9	6.3	0.125	0.515

Racemate

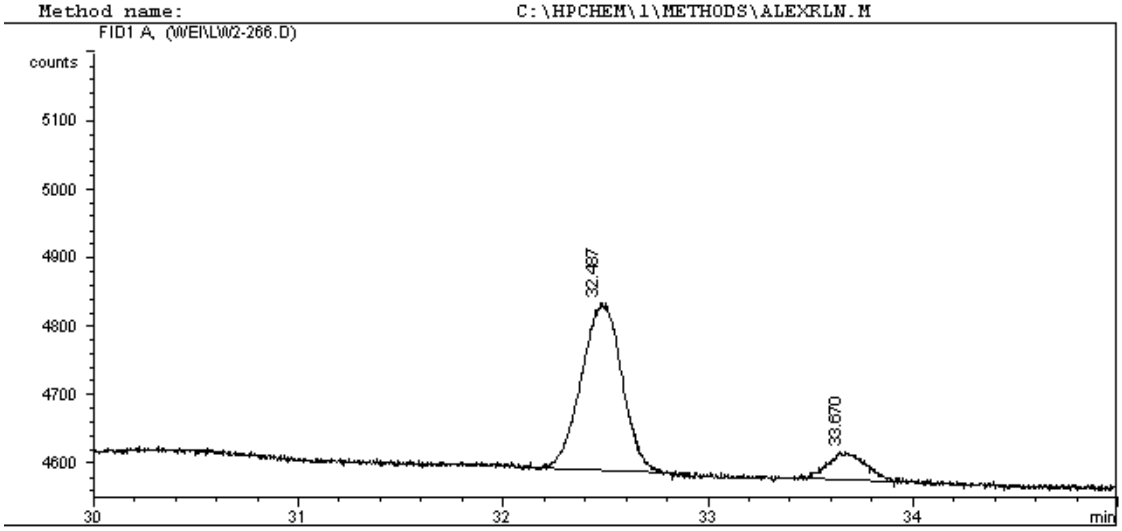
Data File name: C:\HPCHEM\1\DATA\WEI\LW2-195B.D
Method name: C:\HPCHEM\1\METHODS\ALEXRLN.M



Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
18.67	2291.5	280.0	50.2	0.136	0.960
19.32	2273.3	269.0	49.8	0.141	1.183



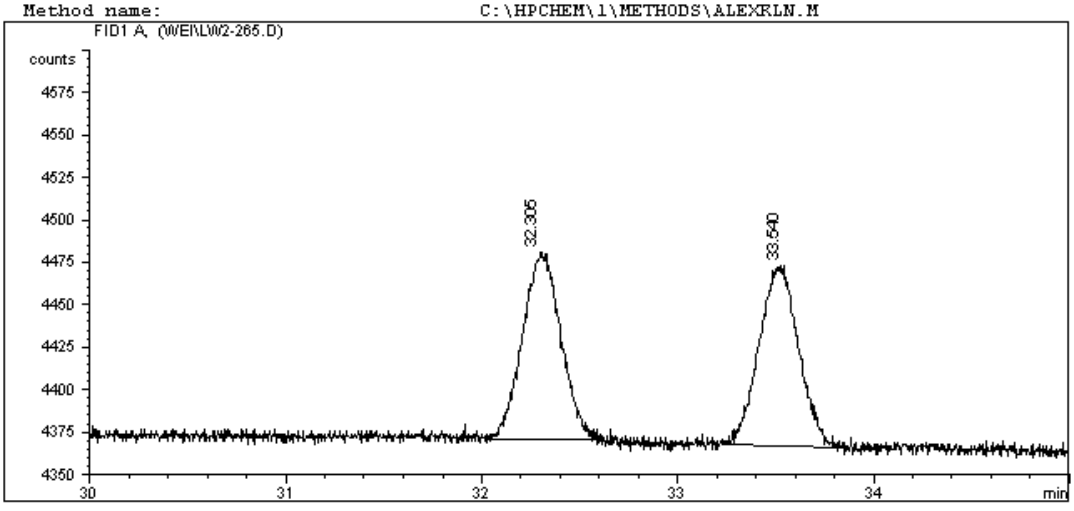
Data File name: C:\HPCHEM\1\DATA\WEI\LW2-266.D
Method name: C:\HPCHEM\1\METHODS\ALEXRLN.M



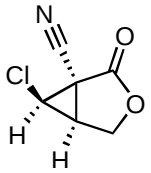
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
32.49	3403.4	246.1	87.5	0.230	1.104
33.67	486.4	38.4	12.5	0.211	0.465

Racemate

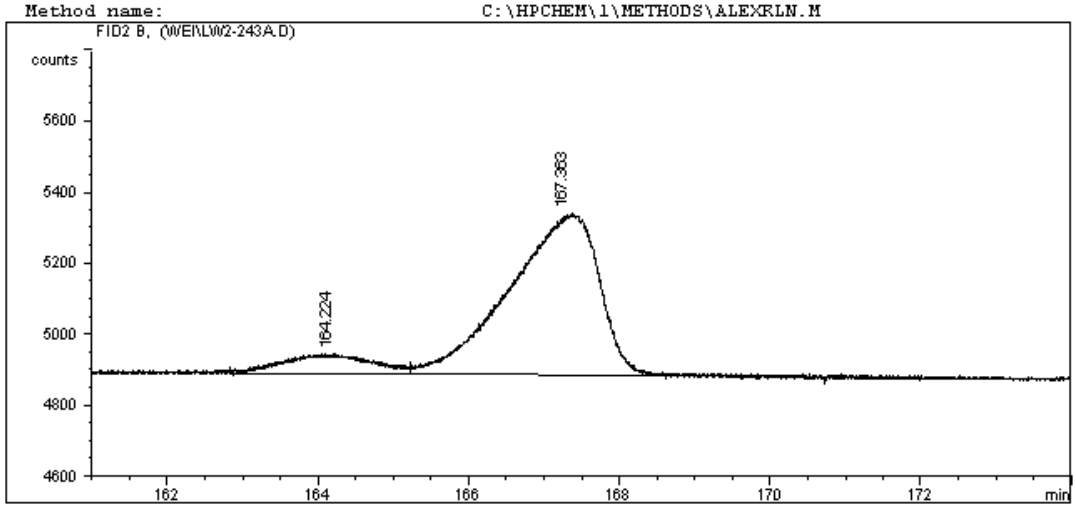
Data File name: C:\HPCHEM\1\DATA\WEI\LW2-265.D
Method name: C:\HPCHEM\1\METHODS\ALEXRLN.M



Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
32.31	1505.9	110.5	50.3	0.227	0.951
33.54	1485.3	106.4	49.7	0.233	1.432



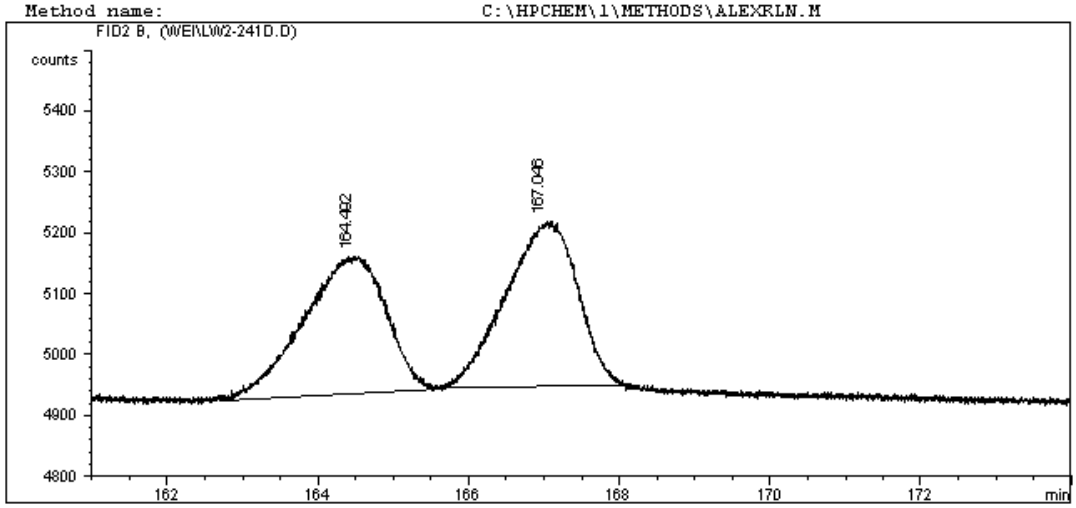
Data File name: C:\HPCHEM\1\DATA\WEI\LW2-243A.D
Method name: C:\HPCHEM\1\METHODS\ALEXRLN.M



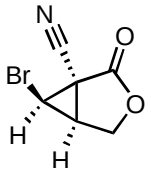
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
164.22	4753.9	57.7	11.2	1.374	
167.36	3756->	457.7	88.8	1.368	2.112

Racemate

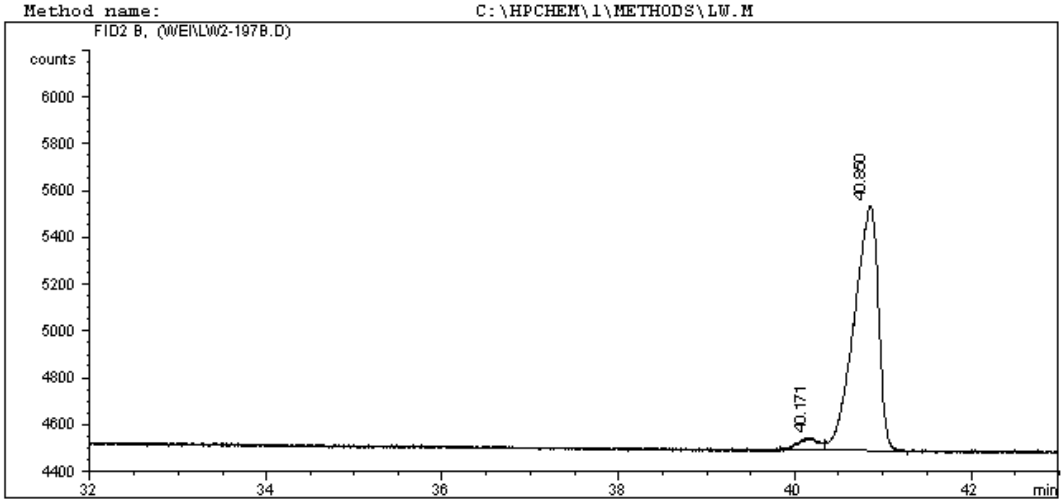
Data File name: C:\HPCHEM\1\DATA\WEI\LW2-241D.D
Method name: C:\HPCHEM\1\METHODS\ALEXRLN.M



Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
164.49	1725->	227.8	49.1	1.262	1.608
167.05	1790->	272.8	50.9	1.094	1.334



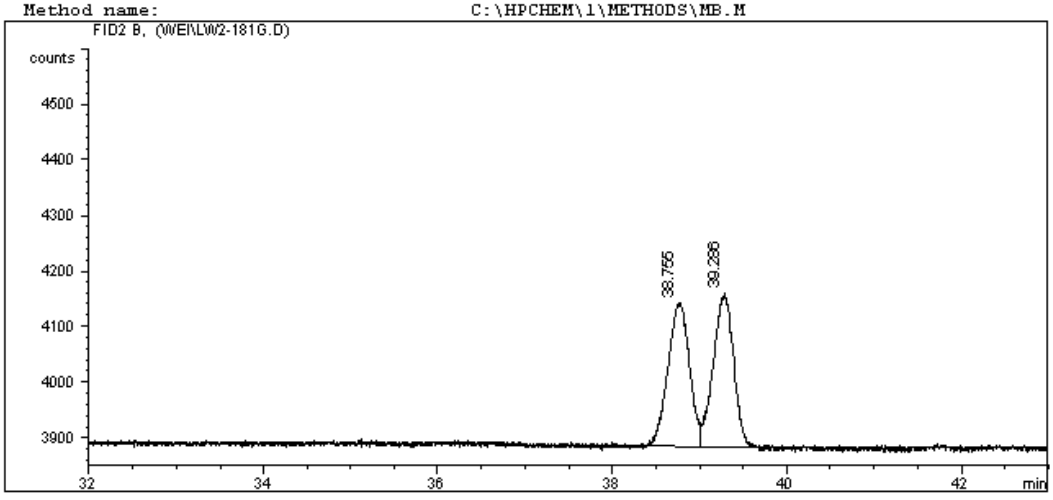
Data File name: C:\HPCHEM\1\DATA\WEI\LW2-197B.D
Method name: C:\HPCHEM\1\METHODS\LW.M



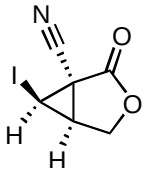
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
40.17	839.3	50.4	4.0	0.278	
40.85	2005->	1042.6	96.0	0.321	1.718

Racemate

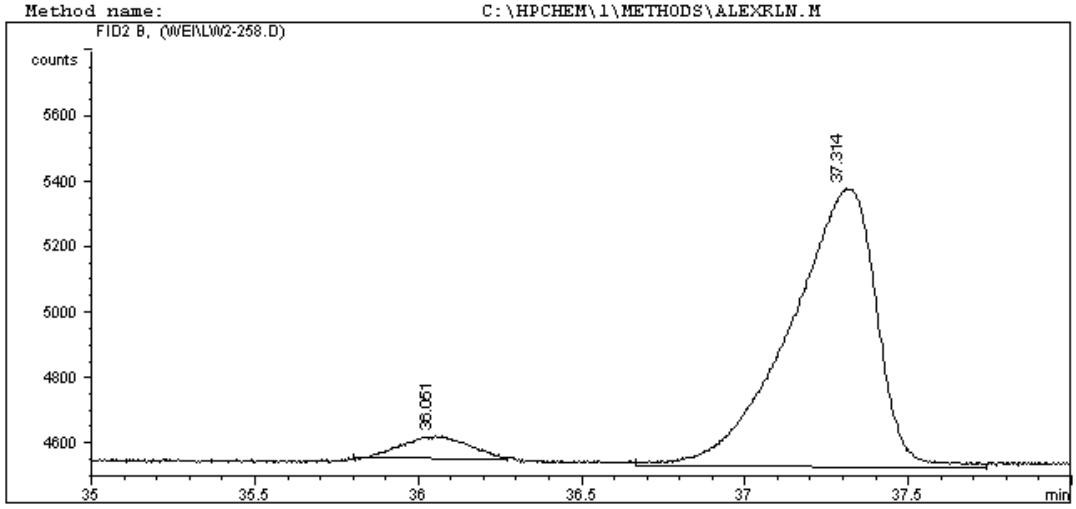
Data File name: C:\HPCHEM\1\DATA\WEI\LW2-181G.D
Method name: C:\HPCHEM\1\METHODS\MB.M



Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
38.76	4451.4	256.8	49.8	0.206	0.904
39.29	4496.0	275.6	50.2	0.192	1.149



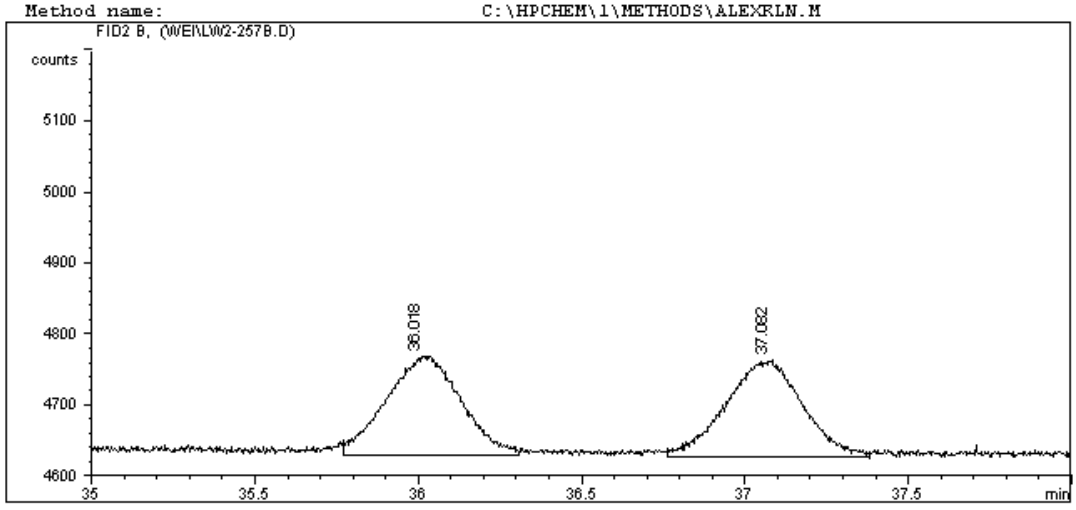
Data File name: C:\HPCHEM\1\DATA\WEI\LW2-258.D
Method name: C:\HPCHEM\1\METHODS\ALEXRLN.M



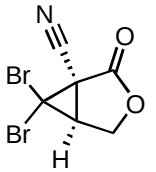
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
36.05	1002.3	69.9	6.0	0.239	0.953
37.31	1564->	853.2	94.0	0.216	1.872

Racemate

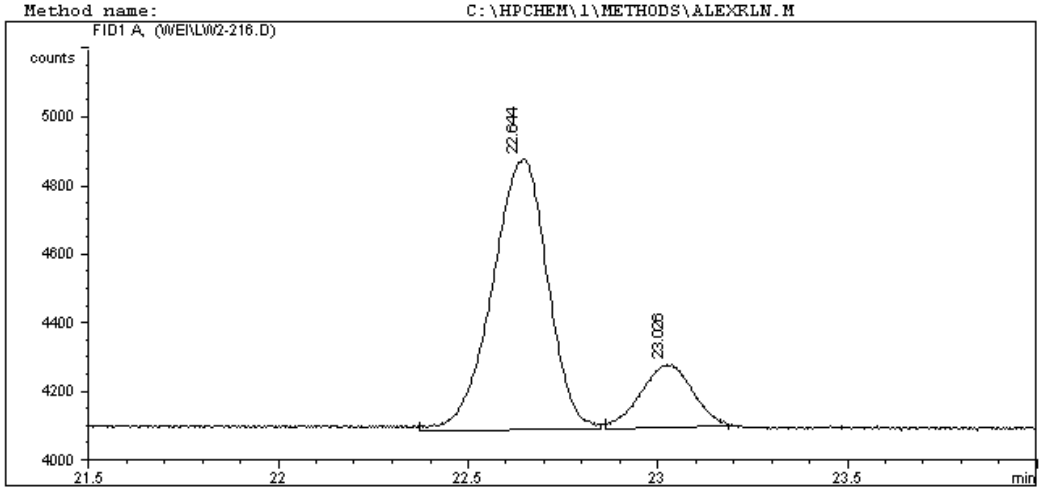
Data File name: C:\HPCHEM\1\DATA\WEI\LW2-257B.D
Method name: C:\HPCHEM\1\METHODS\ALEXRLN.M



Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
36.02	2197.2	138.8	49.9	0.187	1.009
37.08	2203.3	135.9	50.1	0.191	1.358



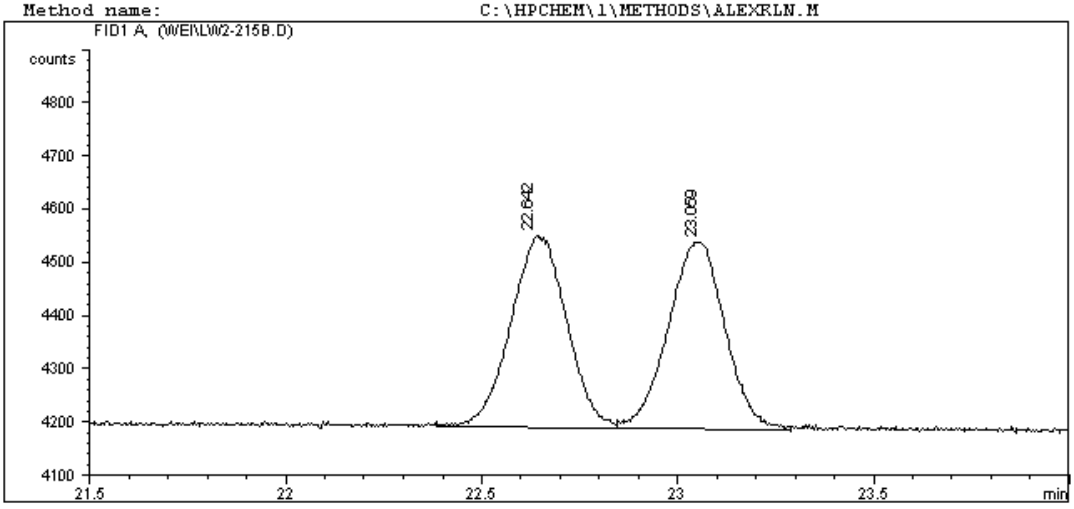
Data File name: C:\HPCHEM\1\DATA\WEI\LW2-216.D
Method name: C:\HPCHEM\1\METHODS\ALEXRLN.M



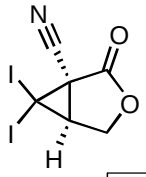
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
22.64	7997.4	789.2	82.1	0.169	1.199
23.03	1748.1	185.5	17.9	0.157	1.049

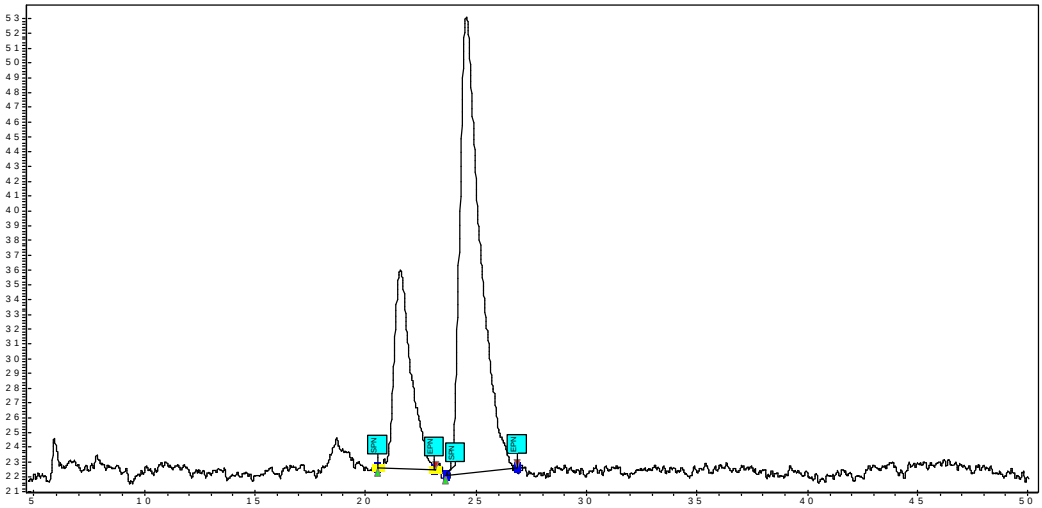
Racemate

Data File name: C:\HPCHEM\1\DATA\WEI\LW2-215B.D
Method name: C:\HPCHEM\1\METHODS\ALEXRLN.M



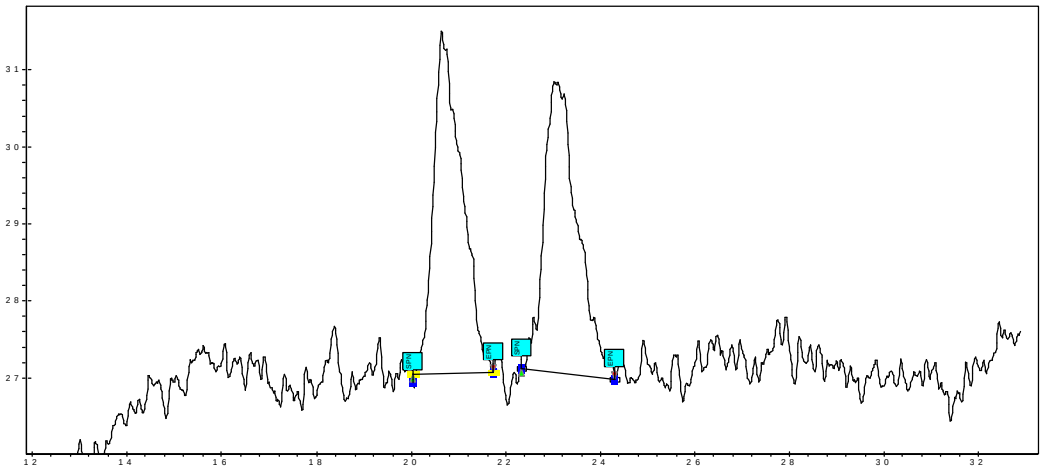
Meas.RT min	Area mAU*sec	Height mAU	Area %	Width min	Symm.
22.64	3595.8	361.7	50.3	0.166	0.913
23.06	3557.6	352.6	49.7	0.168	1.267





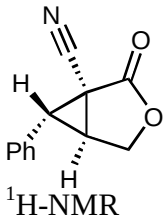
Name	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	20.56	21.59	23.15	26.54	13.4	11.8	26.536
2	23.64	24.57	26.85	73.46	30.8	32.8	73.464
Total				100	44.2	44.7	100

Racemate

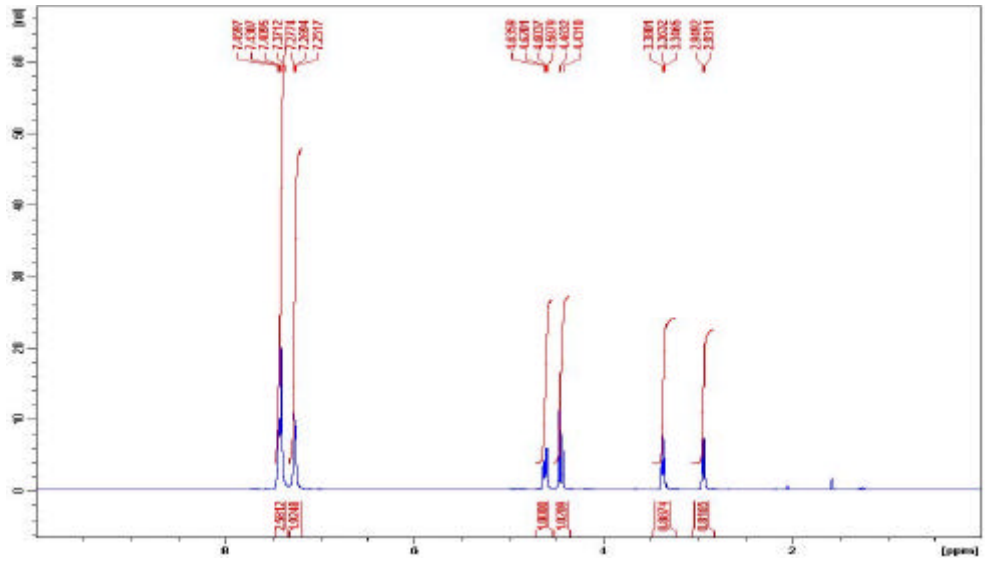


Name	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	20.03	20.64	21.73	49.55	4.5	3.1	49.546
2	22.32	23.11	24.31	50.45	3.8	3.1	50.454
Total				100	8.2	6.2	100

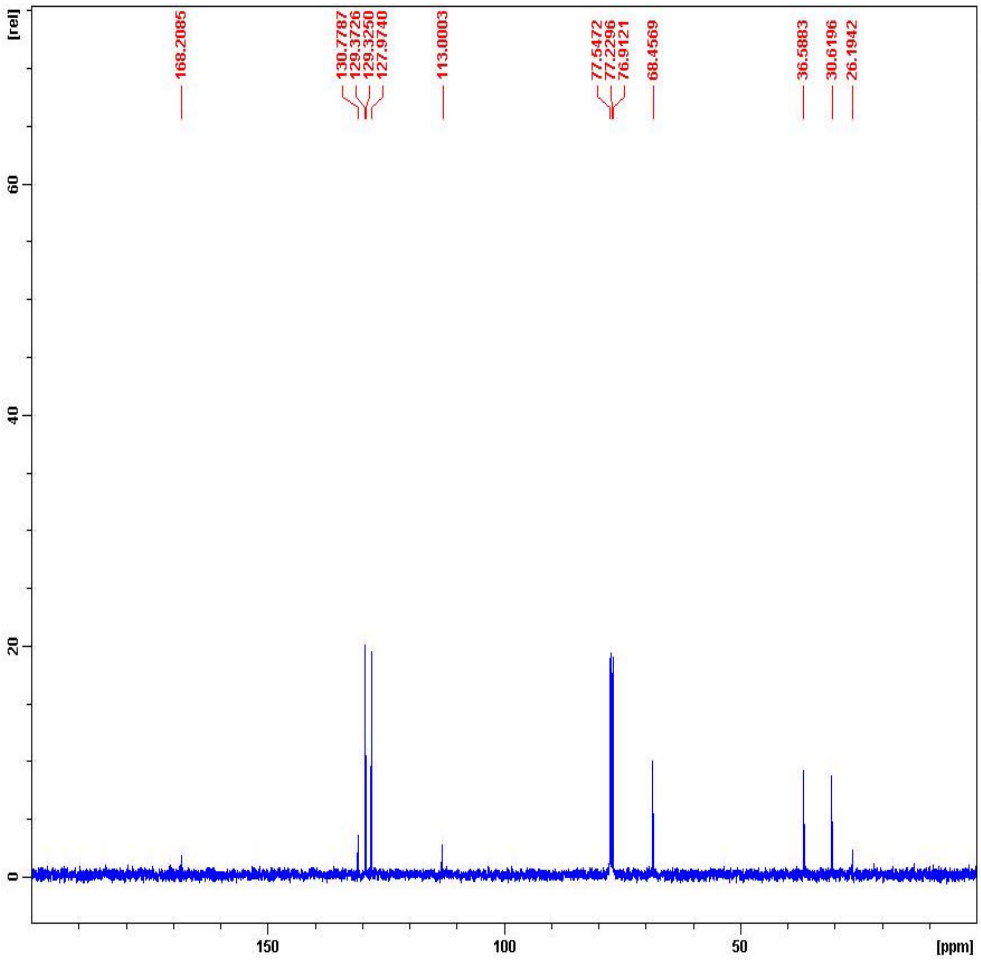
NMR Spectras



^{1}H-NMR



^{13}C-NMR


[rel]
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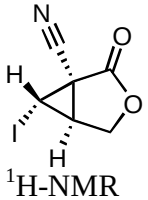
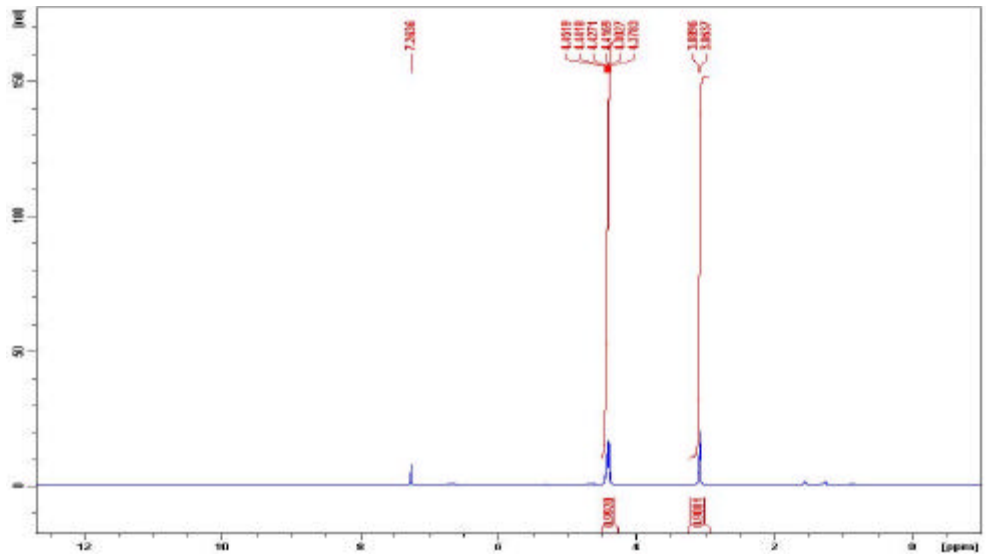
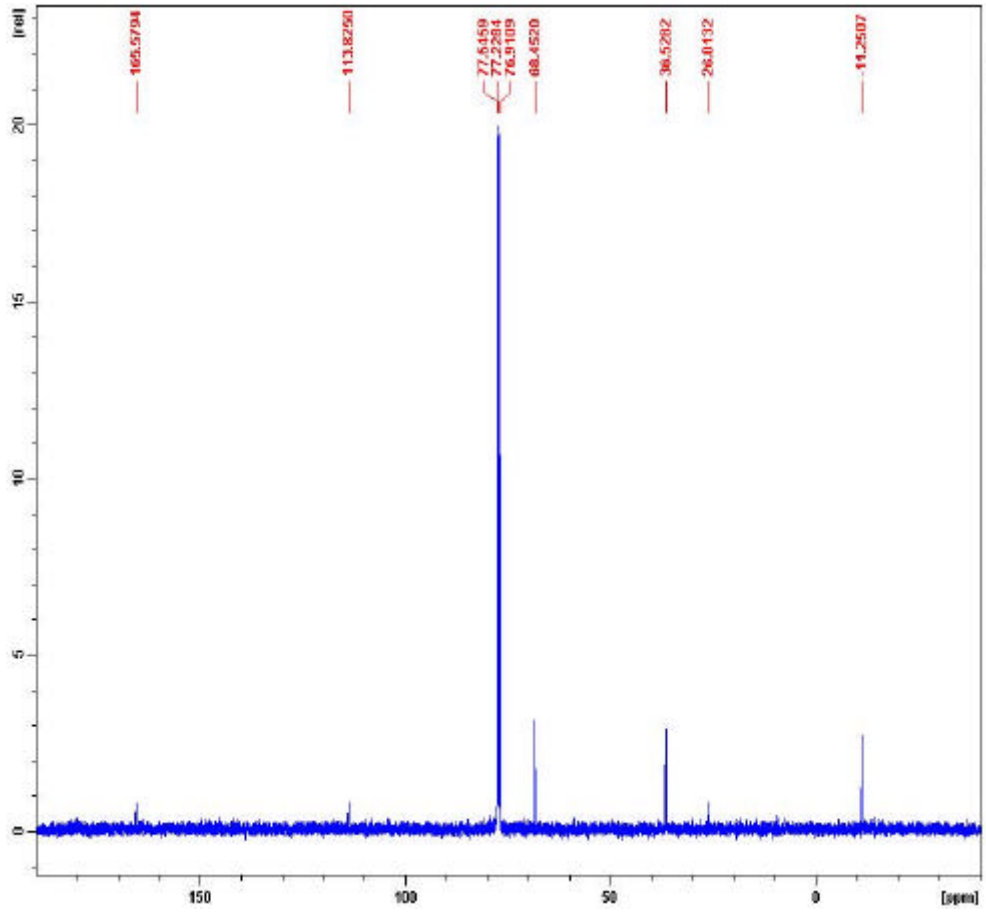
130.7787
129.3726
129.3250
127.9740
113.0003
77.5472
77.2296
76.9121
68.4569
36.5883
30.6196
26.1942
60
40
20
0
150
100
50
[ppm]


N
O
H
O
H

^{1}H-NMR



^{13}C-NMR


165.5794
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77.2284
76.9109
68.4520
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11.2507
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100
50
0
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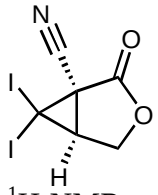
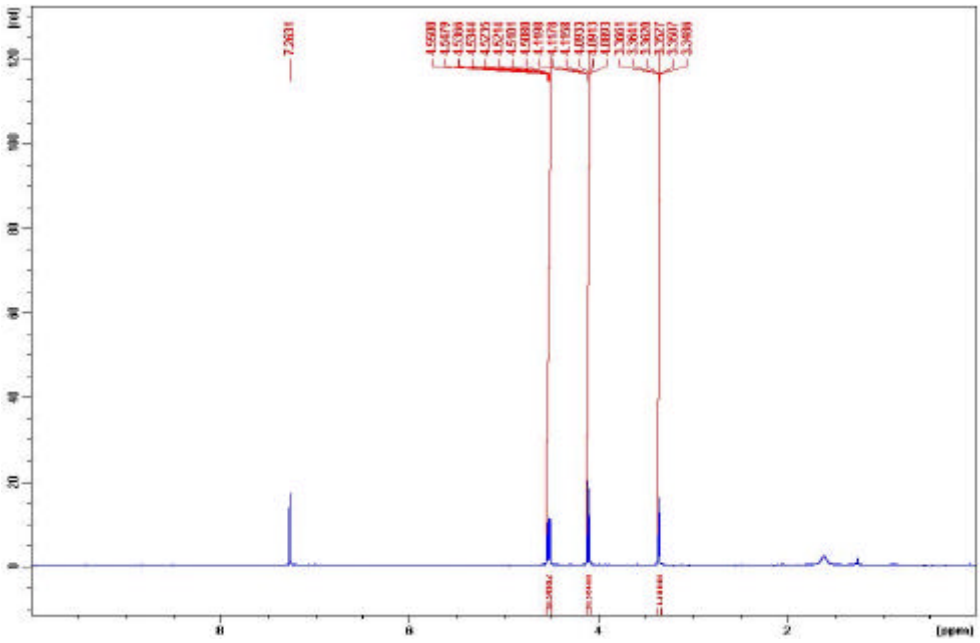
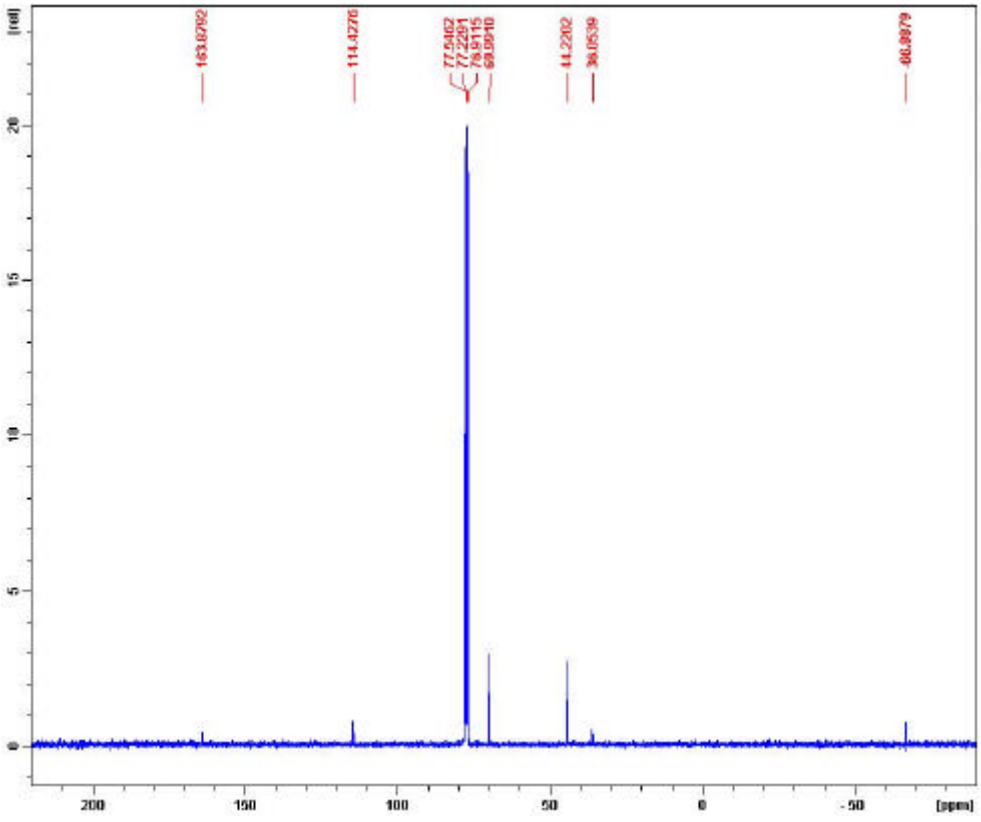
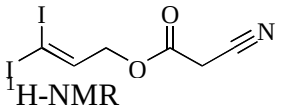


^{1}H-NMR

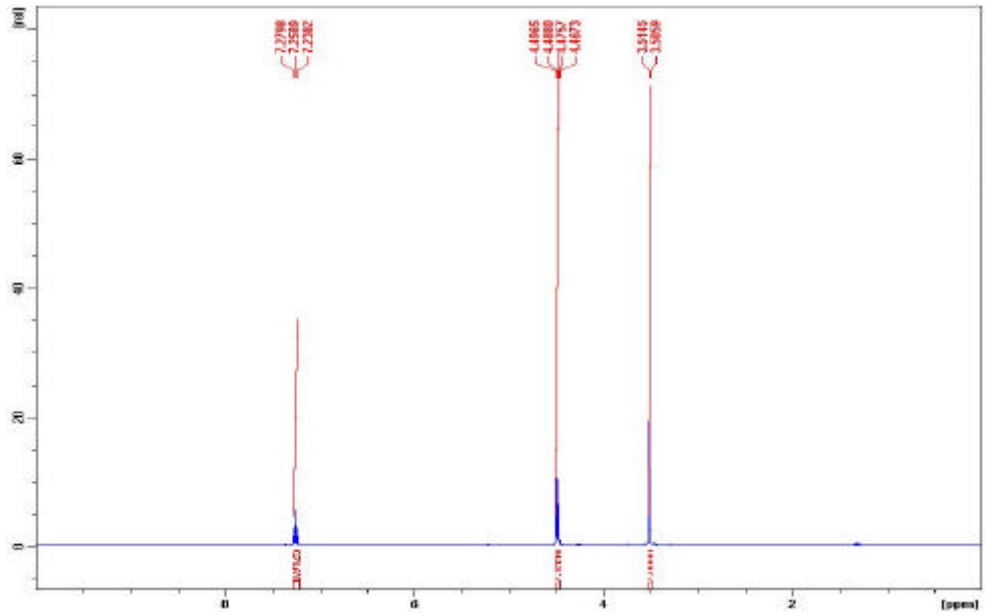


^{13}C-NMR





^{1}H-NMR



^{13}C-NMR