Supporting Information

Highly efficient asymmetric Michael addition of aldehyde to nitroolefin using perhydroindolic acid as a chiral organocatalyst

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CONTENTS

1. General

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian MERCURY plus-400 spectrometer with TMS as an internal standard. HRMS was performed on the Analysis Center of Shanghai Jiao Tong University. The enantioselectivity was measured by high performance liquid chromatography (HPLC) using Daicel Chiralcel AD-H, OD-H, AS-H, OJ-H and OZ-H column with hexane/2-propyl alcohol as eluent. Column chromatography was performed using 100-200 mesh silica gel. All commercially available substrates were used as received. Nitroolefins were prepared according to the literature procedures.[1]

2. General Procedure for the Michael addition reaction

The catalyst **1d** (1.69 mg, 0.01 mmol), DIPEA (1.75 μL, 0.01 mmol) and aldehyde (2 mmol) were dissolved in DCM (1 mL) at 0 ℃. The solution was stirred for 5 min, and then appropriate nitroolefin (0.2 mmol) was added. The reaction mixture was then stirred at 0 ℃ until the complete consumption of nitroolefin (monitored by TLC). The solvent was evaporated and the residue was purified by flash column silica-gel chromatography (PE / EA = 8 / 1) to provide the corresponding Michael adducts. Diastereoselectivity were measured by ^{1}H NMR analysis of the crude product directly. The enantiomeric excess (ee) was determined by HPLC analysis of pure product. The absolute configurations of the products were determined by comparing with preciously reported literature data.[2,3]

3. Characterization Data of Michael adducts

(2*R*,3*S*)-2-ethyl-4-nitro-3-phenylbutanal (6aa)[2b]

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71 (d, J = 2.5 Hz, 1H), 7.38 – 7.14 (m, 5H), 4.75 – 4.58 (m, 2H), 3.83 – 3.74 (m, 1H), 2.72 – 2.63 (m, 1H), 1.55 – 1.45 (m, 2H), 0.83 (t, J = 7.5

Hz, 3H). HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel OD-H), Hex: *i*-PrOH 91:9, UV 230 nm, 0.9ml/min, syn: t_R= 32.96 min (major) and t_R= 24.73 min (minor).

(2*R*,3*S*)-2-methyl-4-nitro-3-phenylbutanal (6ba)[2b]

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (d, J = 1.8 Hz, 1H), 7.37 – 7.12 (m, 5H), 4.83 – 4.75 (m, 1H), 4.72 – 4.64 (m, 1H), 3.86 – 3.74 (m, 1H), 2.85 – 2.70 (m,1H), 0.99 (d, J = 7.2 Hz, 3H). HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel OD-H), Hex: *i*-PrOH 90:10, UV 210 nm, 0.8ml/min, syn: t_R= 48.66 min (major) and t_R= 31.92 min (minor).

(2*R*,3*S*)-2-isopropyl-4-nitro-3-phenylbutanal (6ca)[2b]

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.92 (d, J = 2.4 Hz, 1H), 7.38 – 7.25 (m, 3H), 7.21 – 7.15 (m, 2H), 4.70 – 4.63 (m, 1H), 4.61 – 4.53 (m, 1H), 3.94 – 3.85 (m, 1H), 2.80 – 2.74 (m, 1H), 1.77 – 1.66 (m, 1H), 1.09 (d, J = 7.2 Hz, 3H), 0.88 (d, J = 7.0 Hz, 3H). HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel OD-H), Hex: *i*-PrOH 95:5, UV 210 nm, 0.8ml/min, syn: t_R= 27.20 min (major) and t_R= 25.67 min (minor).

(*R*)-2-((*S*)-2-nitro-1-phenylethyl)hexanal (**6ea**)[2b]

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (d, J = 2.7 Hz, 1H), 7.44 – 7.15 (m, 5H), 4.84 – 4.57 (m, 2H), 3.86 – 3.72 (m, 1H), 2.81 – 2.63 (m, 1H), 1.52 – 1.07 (m, 6H), 0.78 (t, J = 6.8

Hz, 3H). HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel OD-H), Hex: *i*-PrOH 90:10, UV 210 nm, 0.8 ml/min, syn: t_R= 28.48 min (major) and t_R= 21.13 min (minor).

(2*R*,3*S*)-3-(4-chlorophenyl)-2-methyl-4-nitrobutanal (6bb)[2b]

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.69 (d, J = 1.5 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.15 – 7.09 (m, 2H), 4.82 – 4.73 (m, 1H), 4.68 – 4.59 (m, 1H), 3.83 – 3.75 (m, 1H), 2.81 – 2.70 (m, 1H), 1.00 (d, J = 7.2 Hz, 3H). HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: *i*-PrOH 97:3, UV 210 nm, 0.9 ml/min, syn: t_R= 24.16 min (major) and t_R= 33.93 min (minor).

(2*R*,3*S*)-3-(3-chlorophenyl)-2-methyl-4-nitrobutanal (6bc)[3a]

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, J = 1.5 Hz, 1H), 7.32 – 6.97 (m, 4H), 4.84 – 4.75 (m, 1H), 4.69 – 4.61 (m, 1H), 3.82 – 3.74 (m, 1H), 2.82 – 2.70 (m, 1H), 1.01 (d, J = 7.3 Hz, 3H). HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel OZ-H), Hex: *i*-PrOH 90:10, UV 210 nm, 0.8 ml/min, syn: t_R= 35.05 min (major) and t_R= 29.42 min (minor).

(2*R*,3*S*)-3-(4-fluorophenyl)-2-methyl-4-nitrobutanal (6bd)[3b]

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (d, J = 1.5 Hz, 1H), 7.22 – 7.11 (m, 2H), 7.07 – 6.99 (m, 2H), 4.83 – 4.73 (m, 1H), 4.68 – 4.59 (dd, J = 12.7, 9.6 Hz, 1H), 3.85 – 3.75 (m, 1H), 2.84 – 2.66 (m, 1H), 1.00 (d, J = 7.4 Hz, 3H). HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: *i*-PrOH 97:3, UV 210 nm, 0.9 ml/min, syn: t_R= 22.99 min (major) and t_R= 30.86 min (minor).

(2*R*,3*S*)-2-methyl-4-nitro-3-(4-(trifluoromethyl)phenyl)butanal (6be)[3d]

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (d, J = 1.4 Hz, 1H), 7.61 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 4.87 – 4.79 (m, 1H), 4.75 – 4.65 (m, 1H), 3.96 – 3.84 (m, 1H), 2.90 – 2.75 (m, 1H), 1.00 (d, J = 7.4 Hz, 3H). HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: *i*-PrOH 90:10, UV 210 nm, 0.8 ml/min, syn: t_R= 11.83 min (major) and t_R= 15.00 min (minor).

(2*R*,3*S*)-3-(4-methoxyphenyl)-2-methyl-4-nitrobutanal (6bf)[2b]

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.69 (d, J = 1.7 Hz, 1H), 7.17 – 6.97 (m, 2H), 6.95 – 6.77 (m, 2H), 4.82 – 4.70 (m, 1H), 4.67 – 4.58 (m, 1H), 3.77 (s, 3H), 3.76 – 3.71 (m, 1H), 2.81 – 2.63 (m, 1H), 0.98 (d, J = 7.3 Hz, 3H). HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AS-H), Hex: *i*-PrOH 85:15, UV 210 nm, 0.8 ml/min, syn: t_R= 45.56 min (major) and t_R= 35.23 min (minor).

(2*R*,3*S*)-3-(3-methoxyphenyl)-2-methyl-4-nitrobutanal (6bg)

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.69 (d, J = 1.6 Hz, 1H), 7.27 – 7.21 (m, 1H), 6.83 – 6.67 (m, 3H), 4.80 – 4.73 (m, 1H), 4.69 – 4.62 (m, 1H), 3.78 (s, 3H), 3.84 – 3.72 (m, 1H), 2.83 – 2.69 (m, 1H), 1.00 (d, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.4, 160.1, 138.4, 130.3, 120.3, 114.6, 113.1, 78.2, 55.4, 48.6, 44.2, 12.3. HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel OZ-H), Hex: *i*-PrOH 90:10, UV 210 nm, 0.8 ml/min, syn: t_R= 40.98 min (major) and t_R= 35.47 min (minor). HRMS (ESI-TOF) Calcd. For $C_{12}H_{15}NO_4$ [M-H] 236.0923, Found: 236.0938. IR(v/cm^{-1}): 2970, 2939, 2888, 2839, 2729, 1724, 1601, 1552, 1491, 1456, 1382, 1263, 1161, 1045, 785, 702.

(2*R*,3*S*)-3-(2-methoxyphenyl)-2-methyl-4-nitrobutanal (6bh)[2b]

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, J = 1.8 Hz, 1H), 7.31 – 7.23 (m, 1H), 7.07 (dd, J = 7.5, 1.7 Hz, 1H), 6.96 – 6.83 (m, 2H), 4.90 – 4.81 (m, 1H), 4.77 – 4.70 (m, 1H), 4.10 – 3.96 (m, 1H), 3.83 (s, 3H), 3.09 – 2.91 (m, 1H), 0.93 (d, J = 7.3 Hz, 3H). HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AS-H), Hex: *i*-PrOH 98:2, UV 210 nm, 0.95 ml/min, syn: t_R= 45.50 min (major) and t_R= 43.61 min (minor).

(2*R*,3*S*)-2-methyl-4-nitro-3-o-tolylbutanal (6bi)[3c]

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.72 (d, J = 2.0 Hz, 1H), 7.23 – 7.08 (m, 4H), 4.83 – 4.61 (m, 2H), 4.22 – 4.03 (m, 1H), 2.82 – 2.71 (m, 1H), 2.38 (s, 3H), 0.96 (d, J = 7.3 Hz, 3H). HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AS-H), Hex: *i*-PrOH 95:5, UV 210 nm, 0.9 ml/min, syn: t_R= 23.11 min (major) and t_R= 24.89 min (minor).

(2*R*,3*S*)-3-(3,4-dimethoxyphenyl)-2-methyl-4-nitrobutanal (6bj)

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (d, J = 1.9 Hz, 1H), 6.86 – 6.62 (m, 3H), 4.84 – 4.72 (m, 1H), 4.69 – 4.61 (m, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.79 – 3.70 (m, 1H), 2.82 – 2.68 (m, 1H), 1.02 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 202.6, 149.4, 148.9, 129.0, 120.3, 111.6, 111.3, 78.5, 56.1, 56.0, 48.8, 43.9, 12.3. HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel OJ-H), Hex: *i*-PrOH 75:25, UV 210 nm, 0.6 ml/min, syn: t_R= 80.56 min (major) and t_R= 122.64 min (minor). HRMS (ESI-TOF) Calcd. For $C_{13}H_{17}NO_5$ [M-H] 266.1028, Found: 266.1040. IR(v/cm^{-1}): 2968, 2937, 2888, 2839, 1722, 1592, 1552, 1518, 1463, 1381, 1263, 1145, 1026,980, 901, 810, 768.

(2*R*,3*S*)-2-methyl-3-(naphthalen-1-yl)-4-nitrobutanal (6bk)[2b]

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (d, J = 1.8 Hz, 1H), 8.24 – 8.05 (m, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.63 – 7.33 (m, 4H), 5.00 – 4.82 (m, 3H), 3.10 – 2.92 (m, 1H), 0.99 (d, J = 7.3 Hz, 3H). HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AS-H), Hex: *i*-PrOH 90:10, UV 210 nm, 0.8 ml/min, syn: t_R= 37.14 min (major) and t_R= 39.39 min (minor).

(2*R*,3*S*)-2-methyl-3-(naphthalen-2-yl)-4-nitrobutanal (6bl)[3a]

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (d, J = 1.6 Hz, 1H), 7.86 – 7.78 (m, 3H), 7.68 – 7.61 (m, 1H), 7.53 – 7.45 (m, 2H), 7.35 – 7.24 (m, 1H), 4.91 – 4.84 (m, 1H), 4.82 – 4.73 (m, 1H), 4.04 – 3.92 (m, 1H), 2.93 – 2.82 (m, 1H), 1.02 (d, J = 7.3 Hz, 3H). HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AS-H), Hex: *i*-PrOH 90:10, UV 210 nm, 0.8 ml/min, syn: t_R= 34.53 min (major) and t_R= 41.53 min (minor).

(2*R*,3*R*)-3-(furan-2-yl)-2-methyl-4-nitrobutanal (6bm)[2b]

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (d, J = 1.0 Hz, 1H), 7.44 – 7.30 (m, 1H), 6.32 – 6.28 (m, 1H), 6.21 – 6.16 (m, 1H), 4.78 – 4.66 (m, 2H), 4.13 – 4.03 (m, 1H), 2.87–2.75 (m, 1H), 1.06 (d, J = 7.3 Hz, 3H). HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AS-H), Hex: *i*-PrOH 90:10, UV 210 nm, 0.8 ml/min, syn: t_R= 24.77 min (major) and t_R= 22.84 min (minor).

(2*R*,3*R*)-2-methyl-4-nitro-3-(thiophen-2-yl)butanal (6bn)[2b]

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (d, J = 1.2 Hz, 1H), 7.25 – 7.21 (m, 1H), 6.97 – 6.87 (m, 2H), 4.83 – 4.64 (m, 2H), 4.27 – 4.12 (m, 1H), 2.90 – 2.68 (m, 1H), 1.12 (d, J = 7.3 Hz, 3H). HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel OZ-H), Hex: *i*-PrOH 98:2, UV 230 nm, 0.95 ml/min, syn: t_R= 84.95 min (major) and t_R= 57.26 min (minor).

(2*R*,3*S*)-2-methyl-4-nitro-3-(pyridin-3-yl)butanal (6bo)

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (d, J = 1.4 Hz. 1H), 8.56 – 8.45 (m, 2H), 7.54 – 7.50 (m, 1H), 7.33 – 7.22 (m, 1H), 4.84 – 4.79 (m, 1H), 4.73 – 4.65 (m, 1H), 3.90 – 3.80 (m, 1H), 2.91 – 2.77 (m, 1H), 1.01 (d, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 149.9, 149.7, 135.7, 132.8, 124.0, 77.6, 48.1, 41.7, 12.4. HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel OZ-H), Hex: *i*-PrOH 75:25, UV 210 nm, 0.6 ml/min, syn: t_R= 49.58 min (major) and t_R= 61.62 min (minor). HRMS (ESI-TOF) Calcd. For $C_{10}H_{12}N_2O_3$ [M+H] 209.0926, Found: 209.0925. IR(v/cm^{-1}): 3035, 2974, 2935, 2881, 2854, 2730, 1724, 1576, 1556, 1381, 1025, 814, 717.

(2*R*,3*S*)-3-(4-chlorophenyl)-2-isopropyl-4-nitrobutanal (6cb)

White solid (melting point: 78.2-80.0℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (d, J = 2.2 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.16 – 7.08 (m, 2H), 4.71 – 4.62 (m, 1H), 4.58 – 4.47 (m, 1H), 3.92 – 3.83 (m, 1H), 2.78 – 2.70 (m, 1H), 1.76 – 1.64 (m, 1H), 1.10 (d, J = 7.2 Hz, 3H), 0.86 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.2, 135.8, 134.2, 129.6, 129.5, 78.9, 58.7, 41.5, 28.1, 21.8, 17.1. HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel OJ-H), Hex: *i*-PrOH 85:15, UV 210 nm, 0.7 ml/min, syn : t_R= 28.95 min (major) and t_R= 26.76 min (minor). HRMS (ESI-TOF) Calcd. For $C_{13}H_{16}ClNO_3$ [M-H] 268.0740, Found: 268.0728. IR(v/cm^{-1}): 3029, 2964, 2934, 2875, 2845, 2742, 1716, 1554, 1492, 1468, 1379, 1087, 1013, 831, 721.

(2*R*,3*S*)-2-isopropyl-3-(2-methoxyphenyl)-4-nitrobutanal (6cc)

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.91 (d, J = 2.4 Hz, 1H), 7.30 – 7.23 (m, 1H), 7.11 (dd, J = 7.4, 1.7 Hz, 1H), 6.94 – 6.83 (m, 2H), 4.83 – 4.75 (m, 1H), 4.61 – 4.54 (m, 1H), 4.17 – 4.07 (m, 1H), 3.85 (s, 3H), 3.08 – 3.02 (m, 1H), 1.74 – 1.63 (m, 1H), 1.10 (d, J = 7.2 Hz, 3H), 0.84 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.1, 157.7, 130.9, 129.4, 124.8, 121.2, 111.4, 77.5, 57.1, 55.5, 39.4, 28.4, 21.9, 17.3. HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel OJ-H), Hex: *i*-PrOH 96:4, UV 210 nm, 0.8 ml/min, syn : t_R= 37.63 min (major) and t_R= 31.79 min (minor). HRMS (ESI-TOF) Calcd. For $C_{14}H_{19}NO_4$ [M-H] 264.1236, Found: 264.1221. IR(v/cm^{-1}): 2964, 2942, 2875, 2840, 2741, 1716, 1601, 1587, 1552, 1494, 1464, 1381, 1246, 1124, 1026, 756.

References

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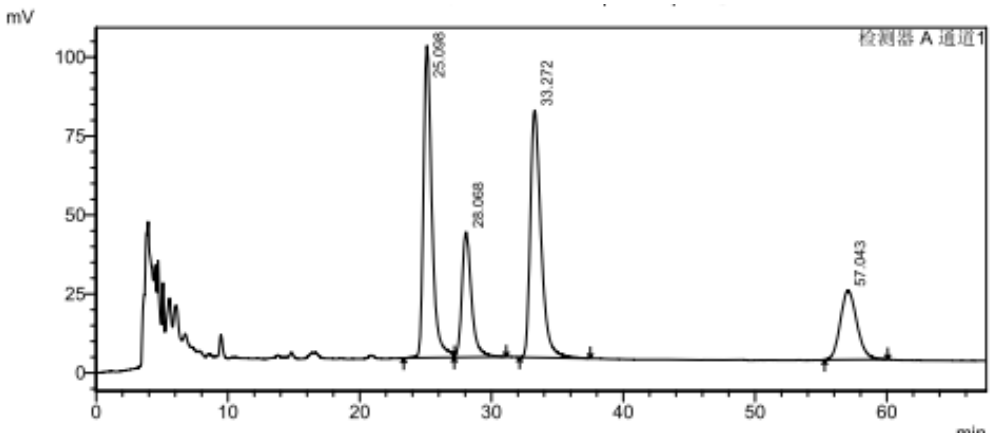
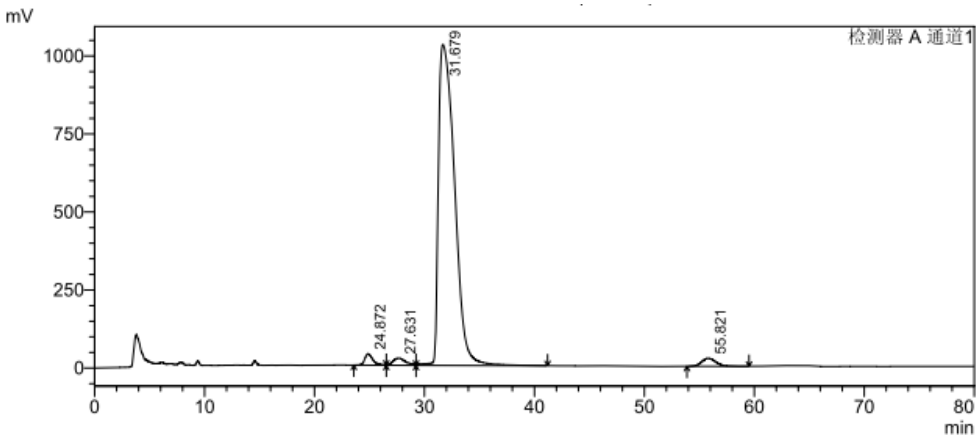
4. HPLC Spectra

Figure 1. Racemic product of (*E*)-(2-nitrovinyl)benzene with butyraldehyde: Using a Chiral OD-H column, Hex: *i*-PrOH 91:9, UV 230 nm, 0.9ml/min, syn: t_R= 32.96 min (major) and t_R= 24.73 min (minor).



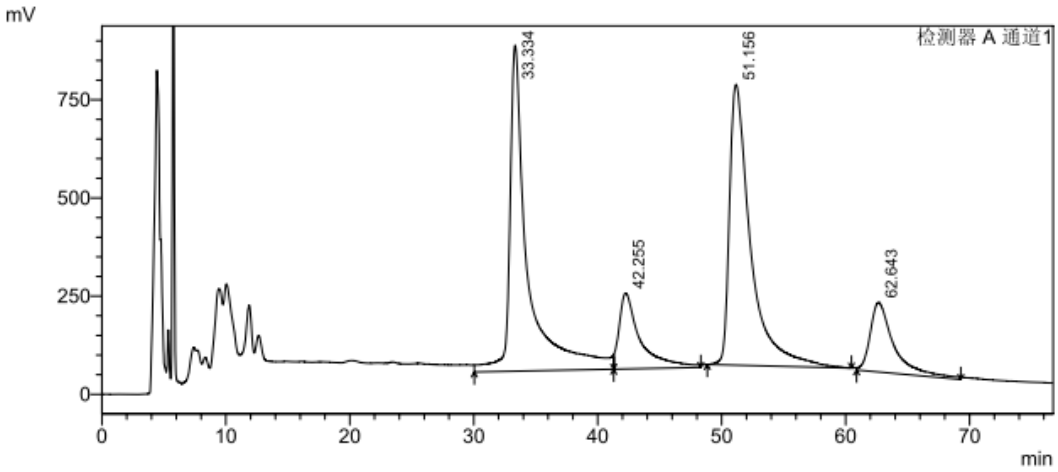
Peak	Retention Time/min	Area %
1	25.098	34.507
2	28.068	15.689
3	33.272	34.727
4	57.043	15.076

Figure 2. Enantioselective product of (*E*)-(2-nitrovinyl)benzene with butyraldehyde.



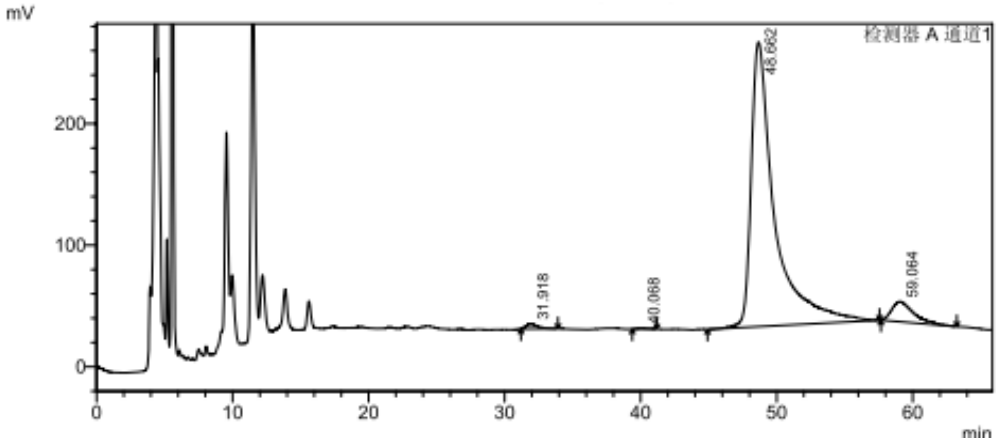
Peak	Retention Time/min	Area %
1	24.872	1.691
2	27.631	1.655
3	31.679	94.578
4	55.821	2.007

Figure 3. Racemic product of (*E*)-(2-nitrovinyl)benzene with propyl aldehyde: using Chiral OD-H column, Hex: *i*-PrOH 90:10, UV 210 nm, 0.8ml/min.



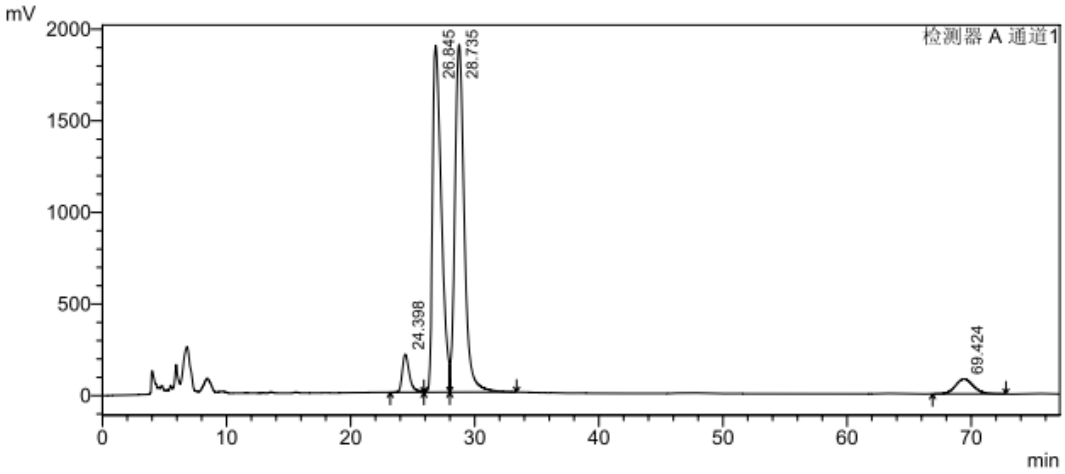
Peak	Retention Time/min	Area %
1	33.334	38.818
2	42.255	10.687
3	51.156	39.536
4	62.643	10.959

Figure 4. Enantioselective product of (*E*)-(2-nitrovinyl)benzene with propionaldehyde



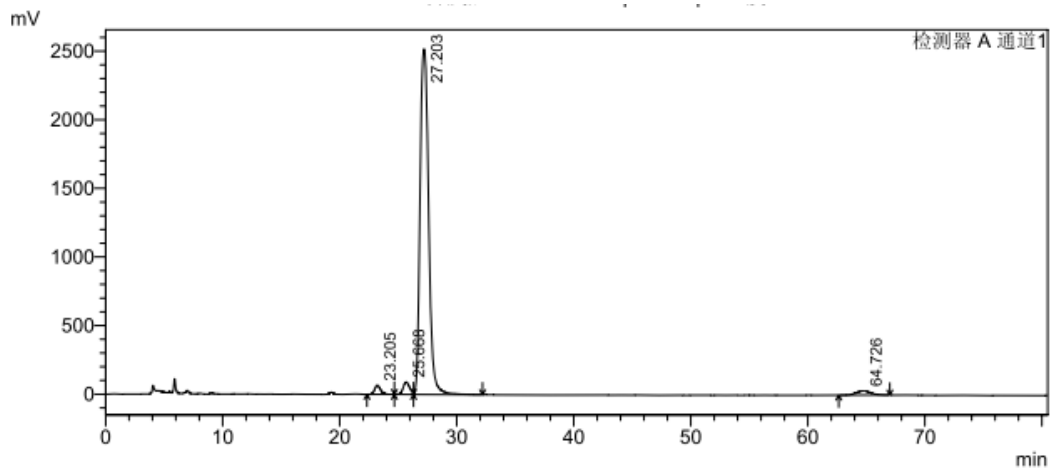
Peak	Retention Time/min	Area %
1	31.918	0.815
2	40.068	0.173
3	48.662	92.822
4	59.064	6.189

Figure 5. Racemic product of (*E*)-(2-nitrovinyl)benzene with isovaleraldehyde: Using Chiral OD-H column, Hex: *i*-PrOH 95:5, UV 210 nm, 0.8ml/min, syn: t_R= 27.20 min (major) and t_R= 25.67 min (minor).



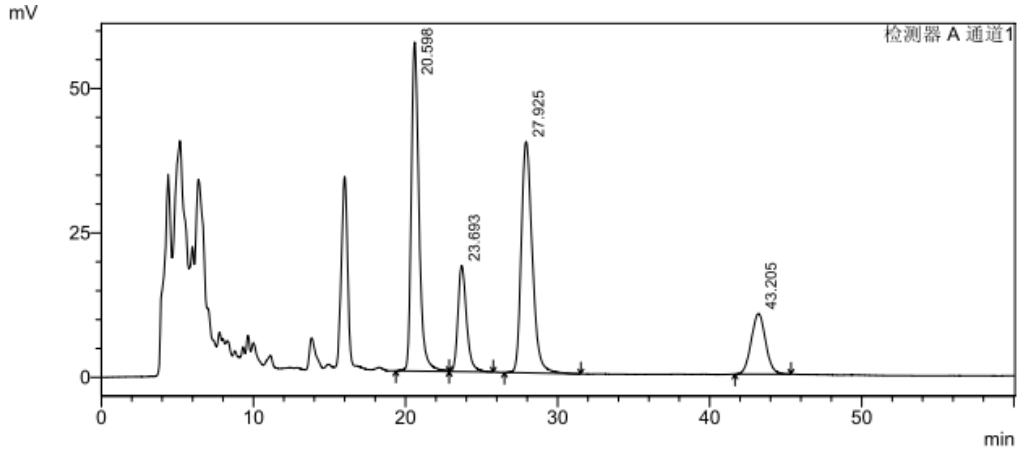
Peak	Retention Time/min	Area %
1	24.398	5.420
2	26.845	44.491
3	28.735	44.633
4	69.424	5.456

Figure 6. Enantioselective product of (*E*)-(2-nitrovinyl)benzene with isovaleraldehyde



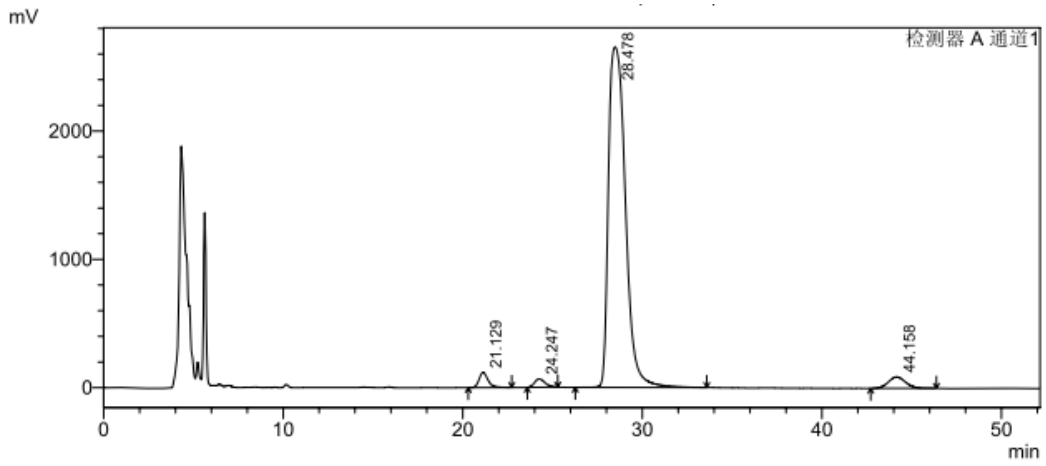
Peak	Retention Time/min	Area %
1	23.205	1.676
2	25.668	2.609
3	27.203	93.732
4	64.726	1.983

Figure 7. Racemic product of (*E*)-(2-nitrovinyl)benzene and *n*-hexyl aldehyde: Using Chiral OD-H column, Hex: *i*-PrOH 90:10, UV 210 nm, 0.8 ml/min.



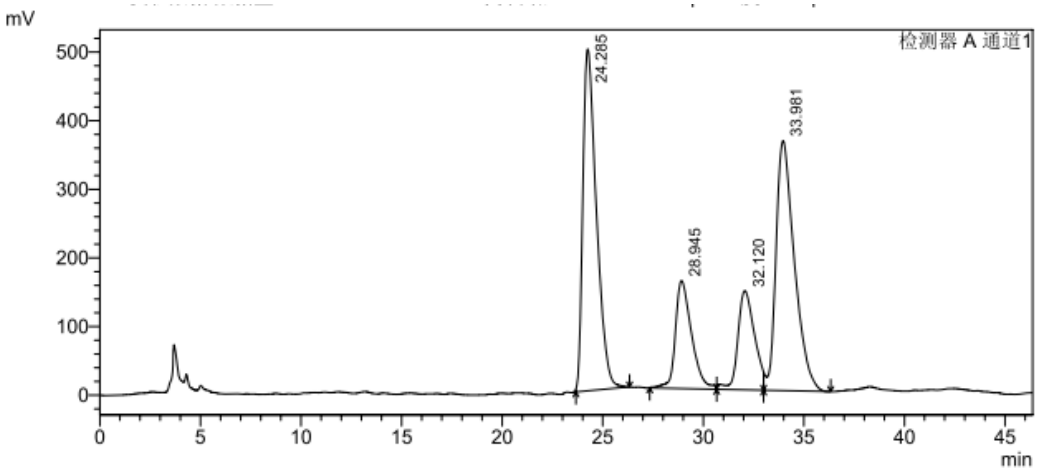
Peak	Retention Time/min	Area %
1	20.598	36.728
2	23.693	13.313
3	27.925	37.214
4	43.205	12.746

Figure 8. Enantioselective product of (*E*)-(2-nitrovinyl)benzene and *n*-hexyl aldehyde



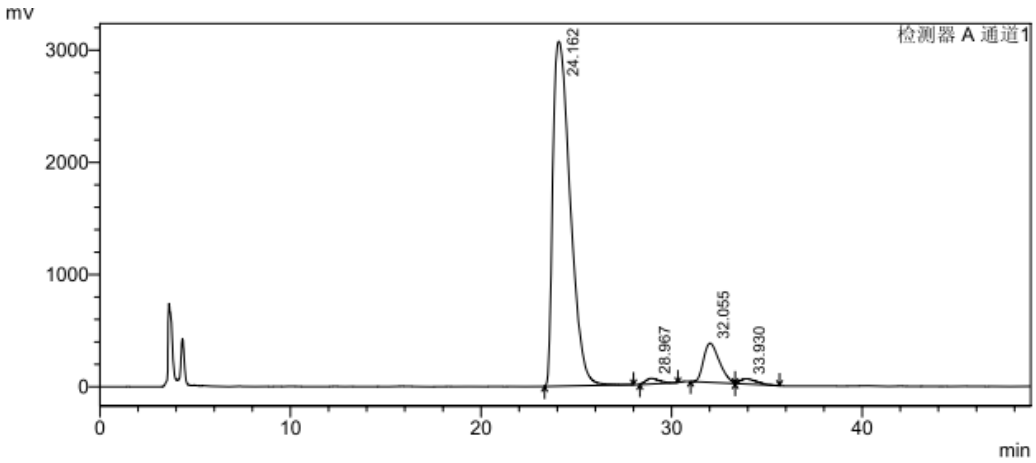
Peak	Retention Time/min	Area %
1	21.129	2.192
2	24.247	1.416
3	28.478	93.210
4	44.158	3.182

Figure 9. Racemic product of (*E*)-1-chloro-4-(2-nitrovinyl)benzene and propyl aldehyde: Chiral AD-H column, Hex: *i*-PrOH 97:3, UV 210 nm, 0.9 ml/min.



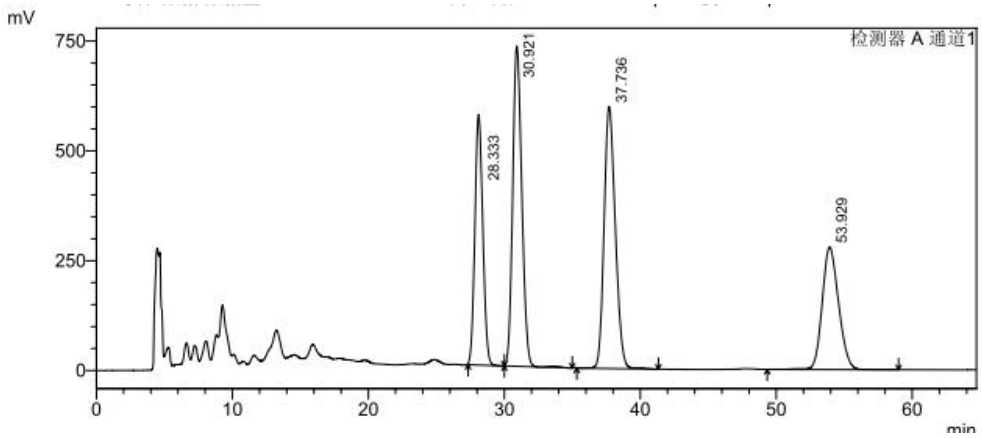
Peak	Retention Time/min	Area %
1	24.285	36.666
2	28.945	13.790
3	32.120	13.015
4	33.981	36.529

Figure 10. Enantioselective product of (*E*)-1-chloro-4-(2-nitrovinyl)benzene and propyl aldehyde.



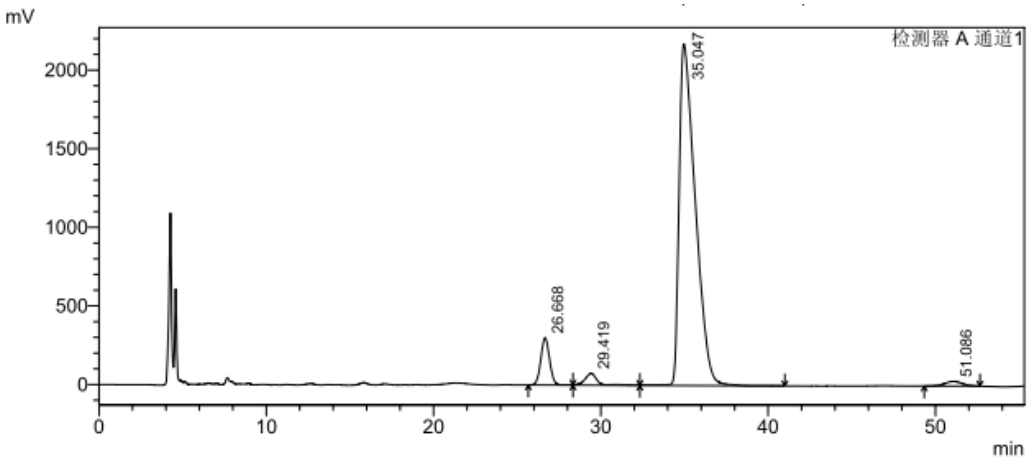
Peak	Retention Time/min	Area %
1	24.162	88.407
2	28.967	1.161
3	32.055	9.140
4	33.930	1.291

Figure 11. Racemic product of (*E*)-1-chloro-3-(2-nitrovinyl)benzene and propyl aldehyde: Chiral OZ-H column, Hex: *i*-PrOH 90:10, UV 210 nm, 0.8 ml/min.



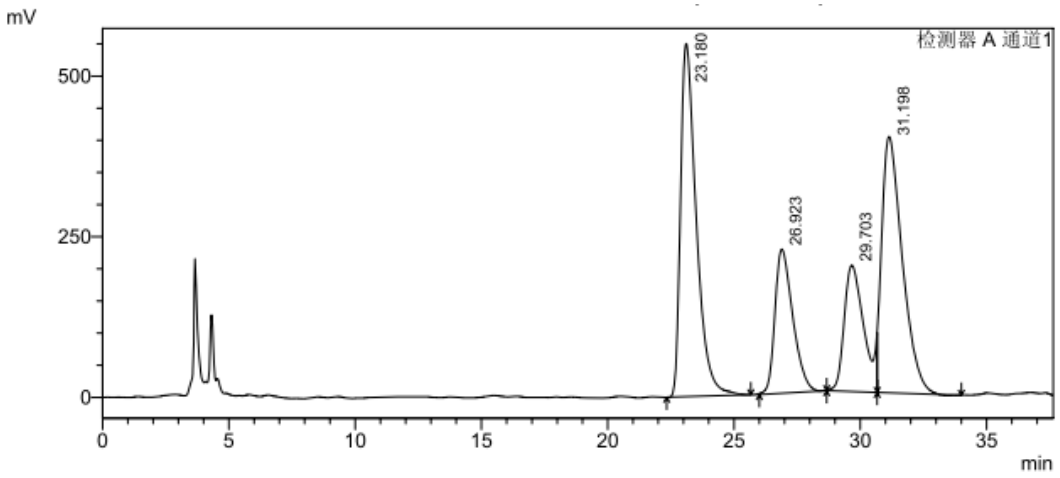
Peak	Retention Time/min	Area %
1	28.333	20.165
2	30.921	29.603
3	37.736	29.877
4	53.929	20.356

Figure 12. Enantioselective product of (*E*)-1-chloro-3-(2-nitrovinyl)benzene and propyl aldehyde.



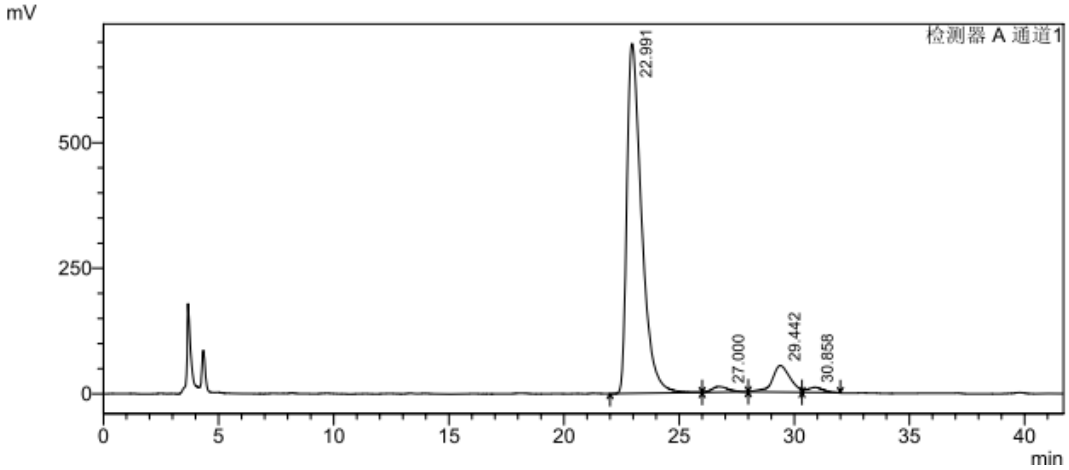
Peak	Retention Time/min	Area %
1	26.668	6.775
2	29.419	2.392
3	35.047	89.544
4	51.086	1.289

Figure 13. Racemic product of (*E*)-1-fluoro-4-(2-nitrovinyl)benzene and propyl aldehyde: Using Chiral AD-H column, Hex: *i*-PrOH 97:3, UV 210 nm, 0.9 ml/min.



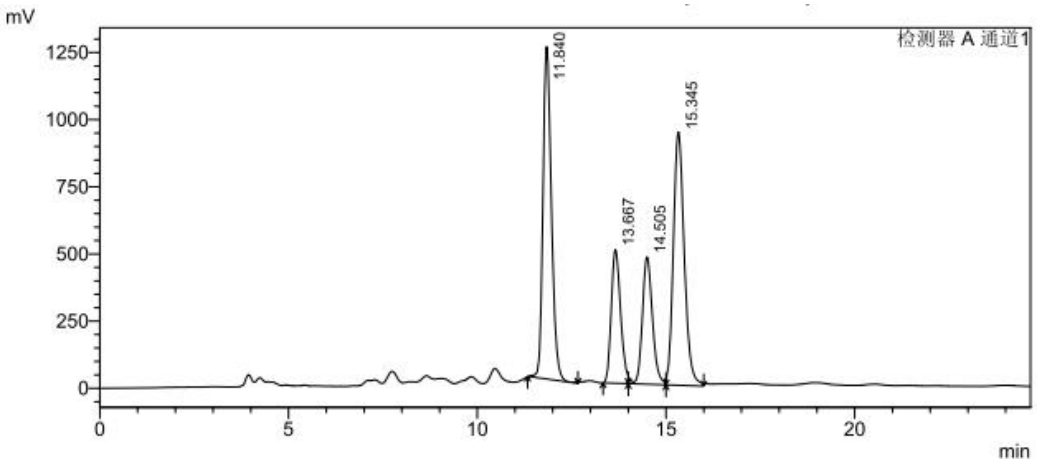
Peak	Retention Time/min	Area %
1	23.180	34.926
2	26.923	16.232
3	29.703	15.731
4	31.198	33.112

Figure 14. Enantioselective product of (*E*)-1-fluoro-4-(2-nitrovinyl)benzene and propyl aldehyde.



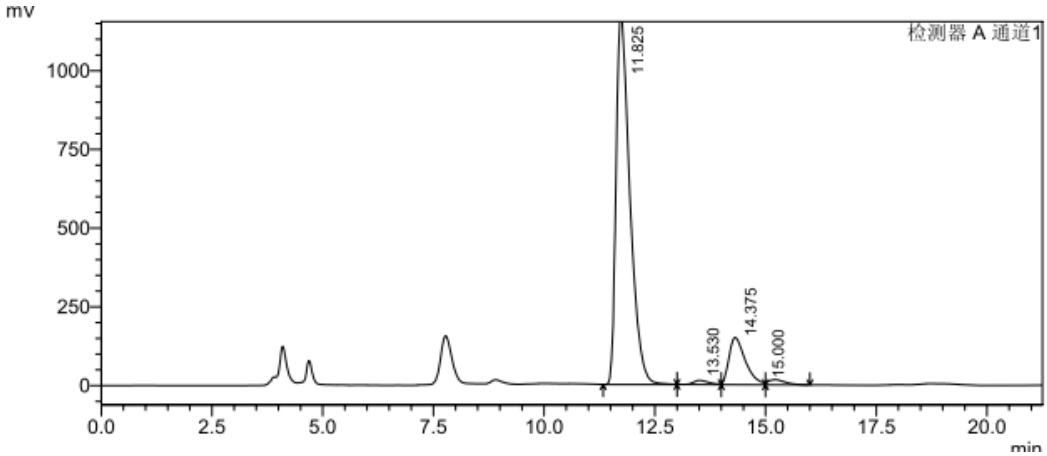
Peak	Retention Time/min	Area %
1	22.991	88.959
2	27.000	1.566
3	29.442	8.101
4	30.858	1.374

Figure 15. Racemic product of (*E*)-1-(2-nitrovinyl)-4-(trifluoromethyl)benzene and propyl aldehyde: Chiral AD-H column, Hex: *i*-PrOH 90:10, UV 210 nm, 0.8 ml/min.



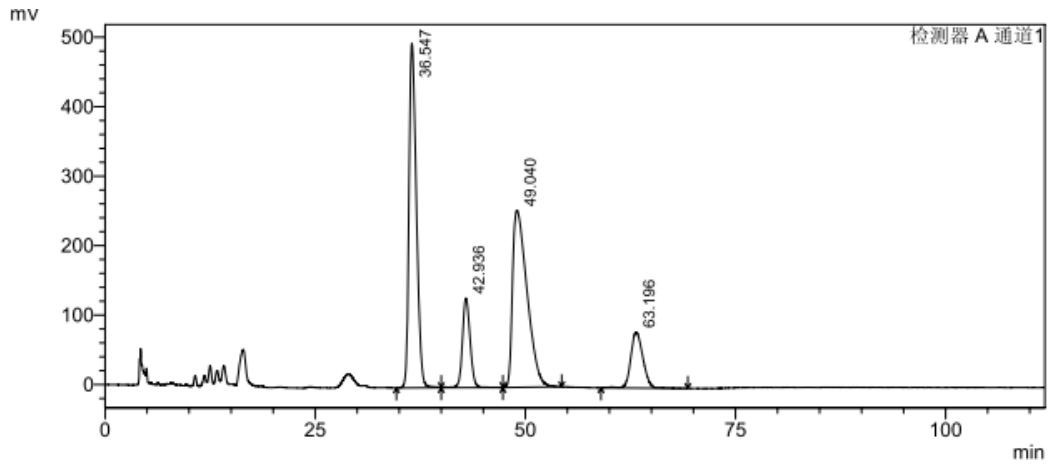
Peak	Retention Time/min	Area %
1	11.840	34.698
2	13.667	15.267
3	14.505	15.971
4	15.345	34.064

Figure 16. Enantioselective product of (*E*)-1-(2-nitrovinyl)-4-(trifluoromethyl)benzene and propyl aldehyde.



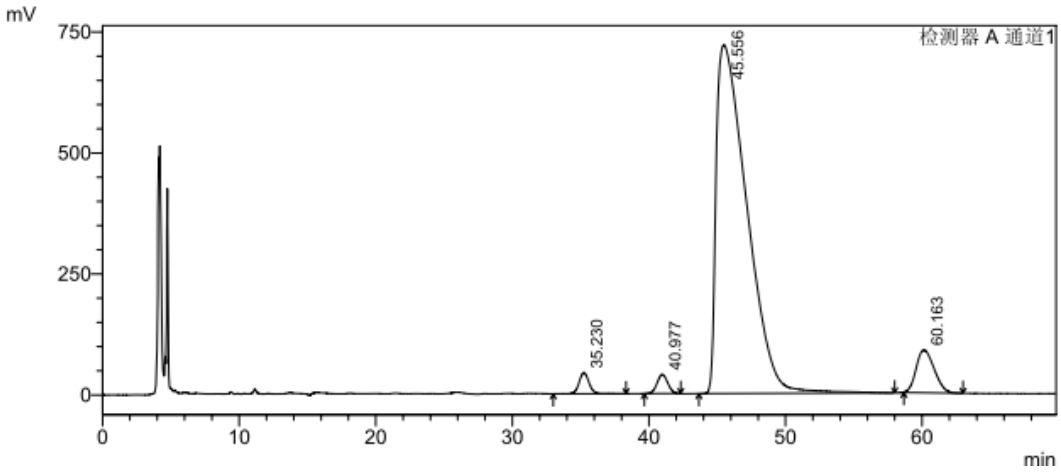
Peak	Retention Time/min	Area %
1	11.825	84.720
2	13.530	1.055
3	14.375	12.796
4	15.000	1.429

Figure 17. Racemic product of (*E*)-1-methoxy-4-(2-nitrovinyl)benzene and propyl aldehyde: Using Chiral AS-H column, Hex: *i*-PrOH 85:15, UV 210 nm, 0.8 ml/min.



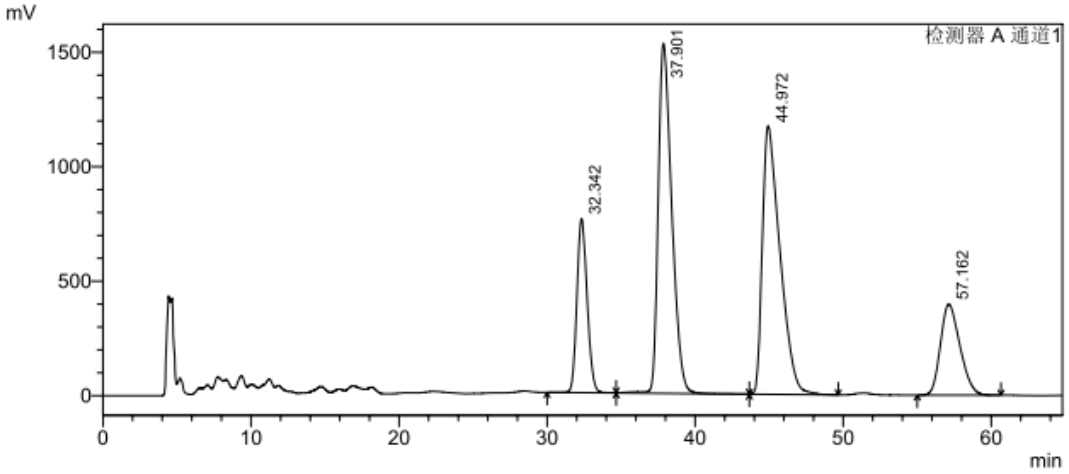
Peak	Retention Time/min	Area %
1	36.547	39.140
2	42.936	10.592
3	49.040	39.685
4	63.196	10.583

Figure 18. Enantioselective product of (*E*)-1-methoxy-4-(2-nitrovinyl)benzene and propyl aldehyde.



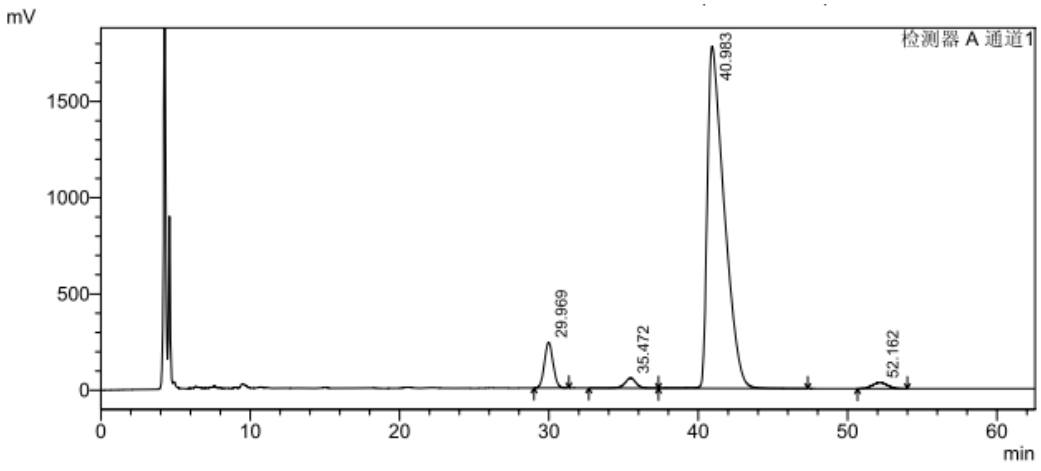
Peak	Retention Time/min	Area %
1	35.230	1.750
2	40.977	1.707
3	45.556	90.022
4	60.163	6.521

Figure 19. Racemic product of (*E*)-1-methoxy-3-(2-nitrovinyl)benzene and propyl aldehyde: Using Chiral OZ-H column, Hex: *i*-PrOH 90:10, UV 210 nm, 0.8 ml/min.



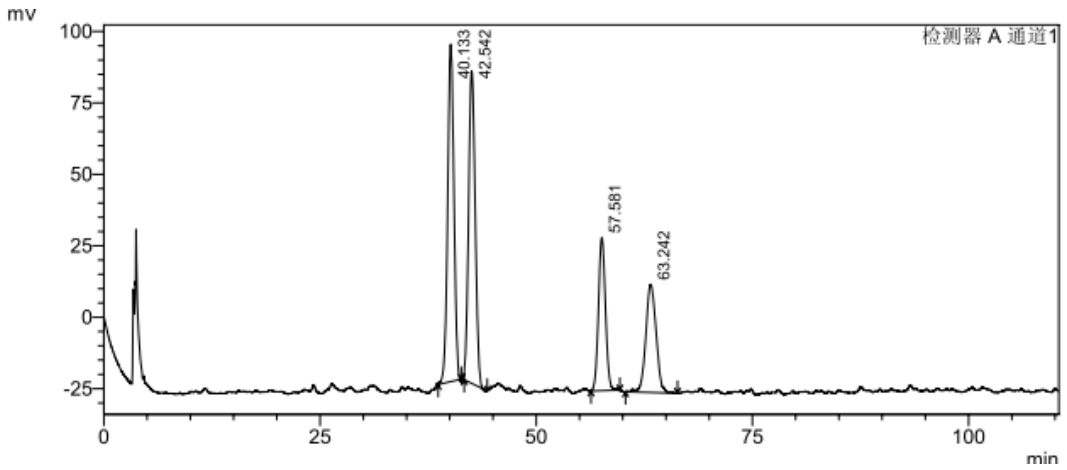
Peak	Retention Time/min	Area %
1	32.342	13.679
2	37.901	36.431
3	44.972	36.299
4	57.162	13.591

Figure 20. Enantioselective product of (*E*)-1-methoxy-3-(2-nitrovinyl)benzene and propyl aldehyde.



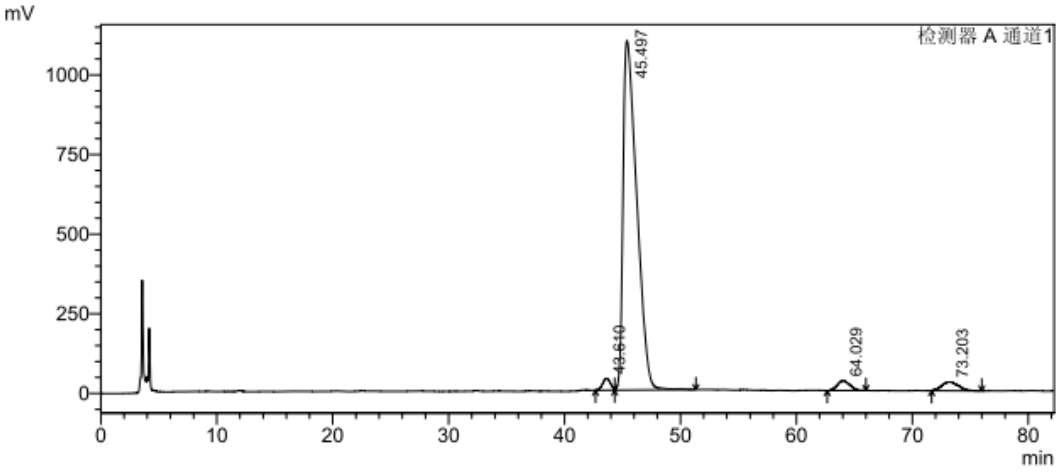
Peak	Retention Time/min	Area %
1	29.969	6.205
2	35.472	1.819
3	40.983	90.544
4	52.162	1.431

Figure 21. Racemic product of (*E*)-1-methoxy-2-(2-nitrovinyl)benzene and propyl aldehyde: Using Chiral AS-H column, Hex: *i*-PrOH 98:2, UV 210 nm, 0.95 ml/min.



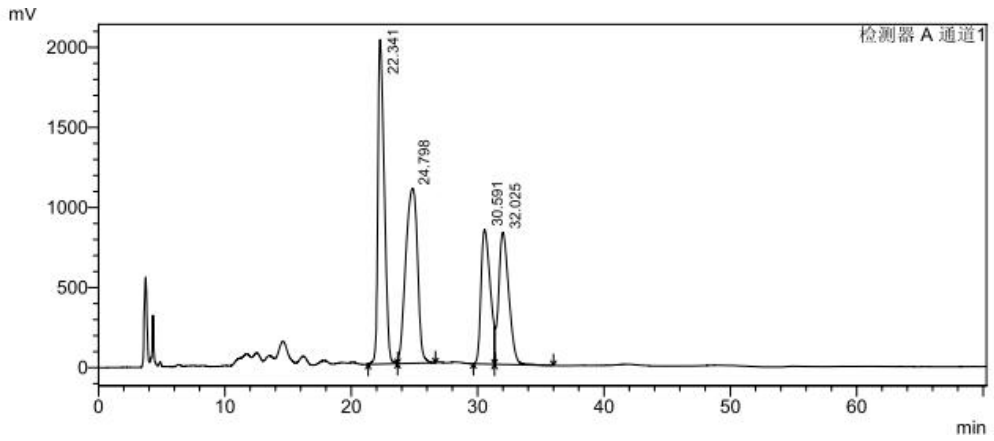
Peak	Retention Time/min	Area %
1	40.133	33.120
2	42.542	32.406
3	57.581	16.894
4	63.242	17.579

Figure 22. Enantioselective product of (*E*)-1-methoxy-2-(2-nitrovinyl)benzene and propyl aldehyde.



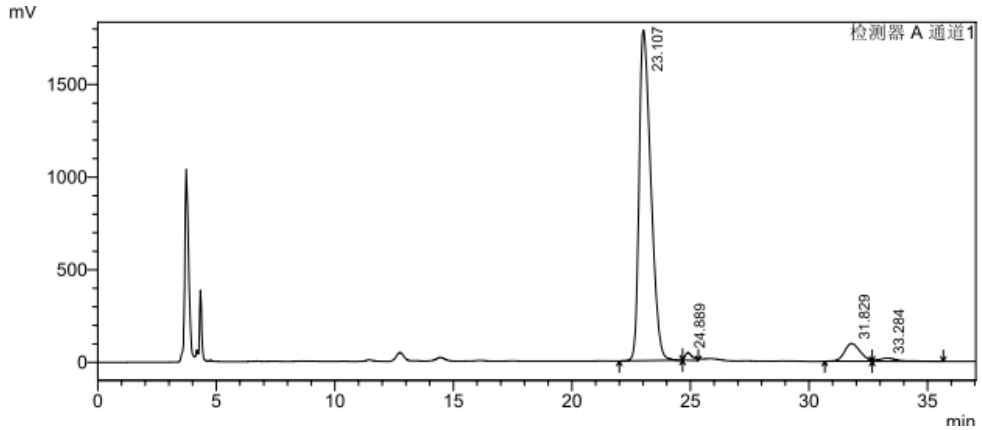
Peak	Retention Time/min	Area %
1	43.610	1.794
2	45.497	92.960
3	64.029	2.361
4	73.203	2.885

Figure 23. Racemic product of (*E*)-1-methyl-2-(2-nitrovinyl)benzene and propyl aldehyde: Using Chiral AS-H column, Hex: *i*-PrOH 95:5, UV 210 nm, 0.9 ml/min.



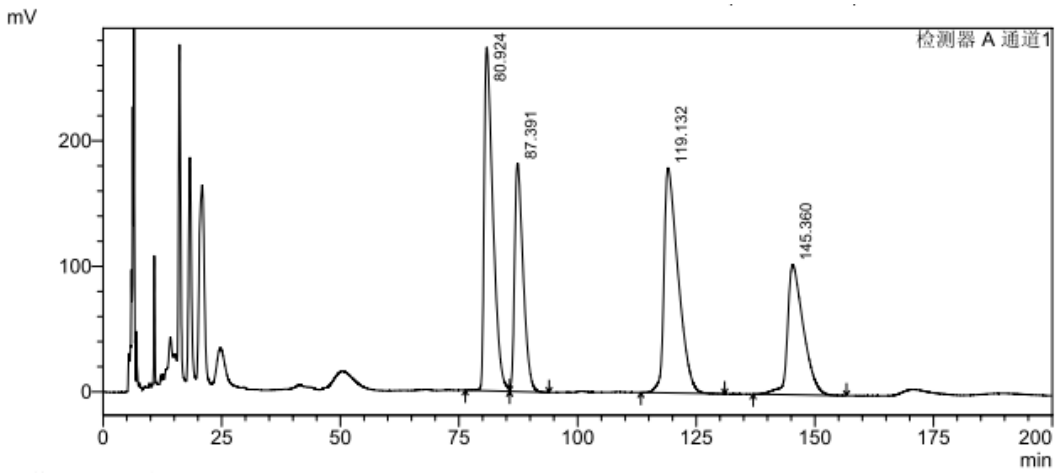
Peak	Retention Time/min	Area %
1	22.341	30.772
2	24.798	30.748
3	30.591	19.206
4	32.025	19.273

Figure 24. Enantioselective product of (*E*)-1-methyl-2-(2-nitrovinyl)benzene and propyl aldehyde.



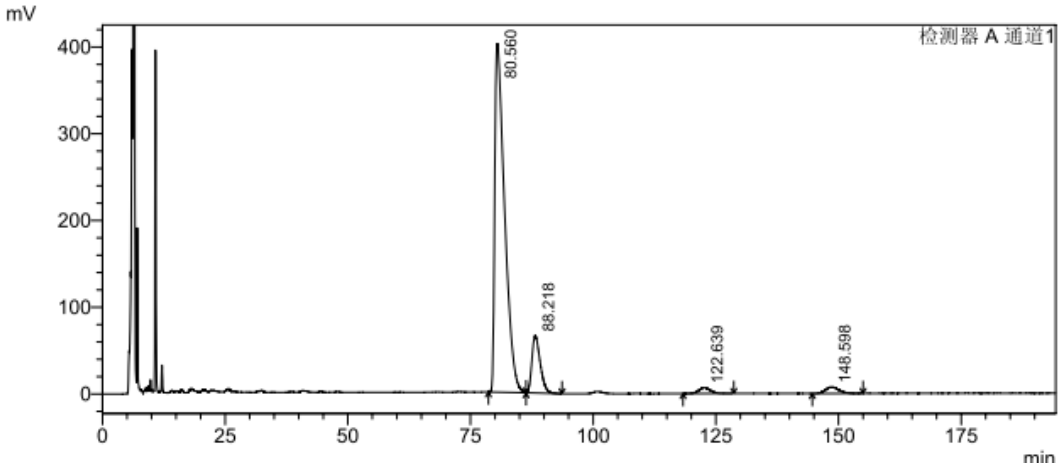
Peak	Retention Time/min	Area %
1	23.107	90.976
2	24.889	1.305
3	31.829	6.445
4	33.284	1.274

Figure 25. Racemic product of (*E*)-1,2-dimethoxy-4-(2-nitrovinyl)benzene and propyl aldehyde: Using Chiral OJ-H column, Hex: *i*-PrOH 75:25, UV 210 nm, 0.6 ml/min.



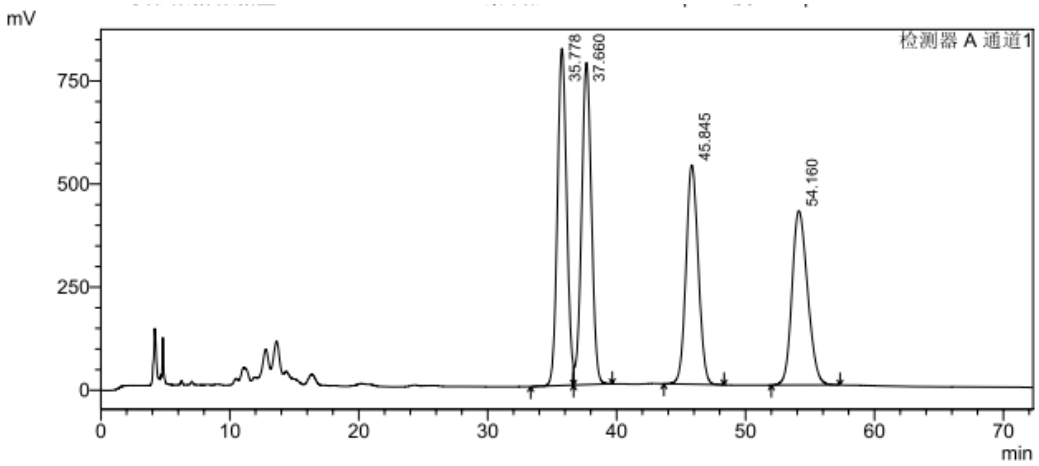
Peak	Retention Time/min	Area %
1	80.924	29.504
2	87.391	19.145
3	119.132	30.122
4	145.360	20.229

Figure 26. Enantioselective product of (*E*)-1,2-dimethoxy-4-(2-nitrovinyl)benzene and propyl aldehyde.



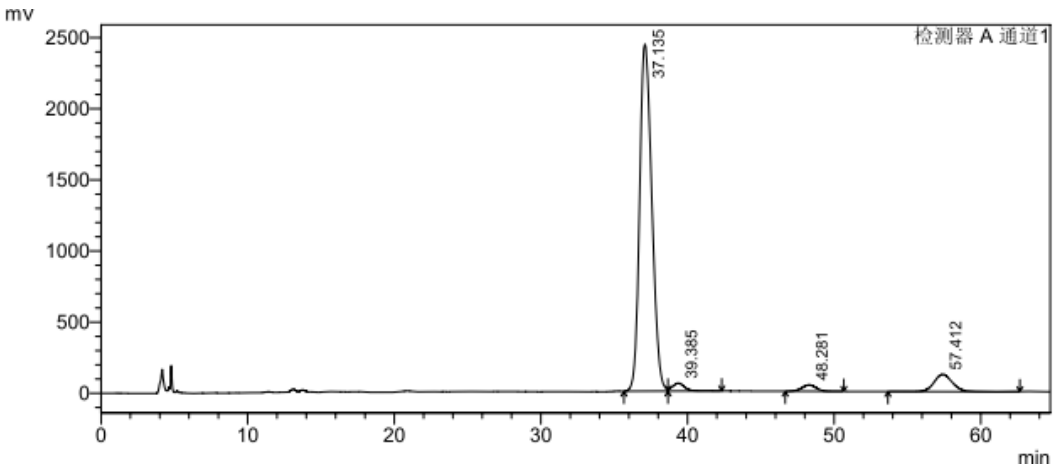
Peak	Retention Time/min	Area %
1	80.560	84.390
2	88.218	11.784
3	122.639	1.660
4	148.598	2.165

Figure 27. Racemic product of (*E*)-1-(2-nitrovinyl)naphthalene and propyl aldehyde: Using Chiral AS-H column, Hex: *i*-PrOH 90:10, UV 210 nm, 0.8 ml/min.



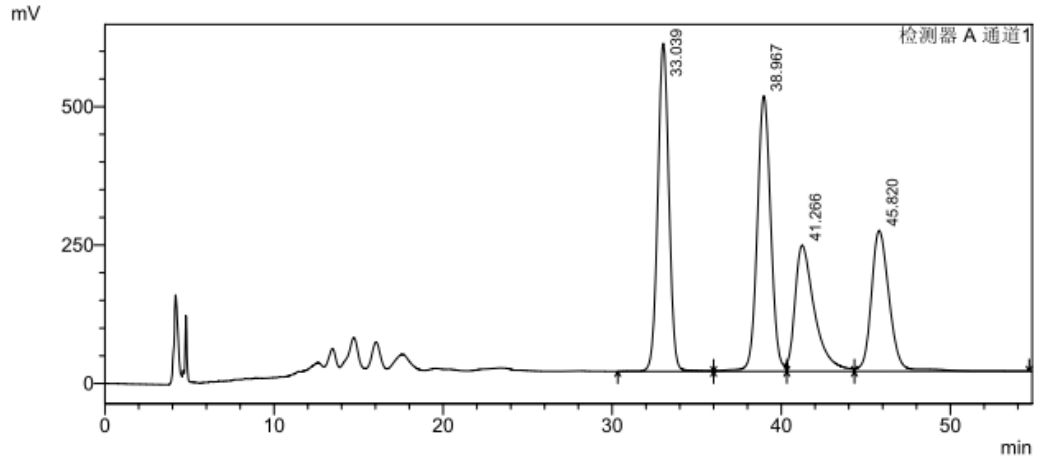
Peak	Retention Time/min	Area %
1	35.778	26.719
2	37.660	27.091
3	45.845	22.975
4	54.160	23.214

Figure 28. Enantioselective product of (*E*)-1-(2-nitrovinyl)naphthalene and propyl aldehyde.



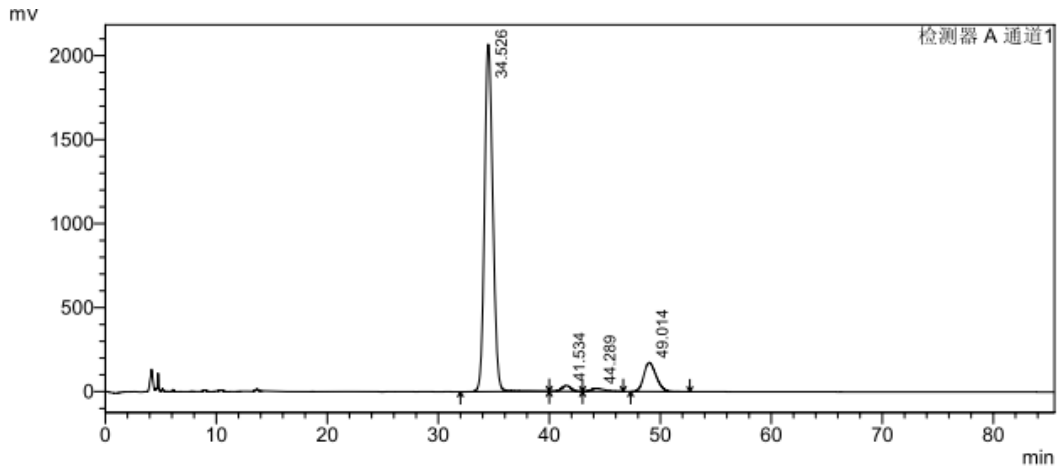
Peak	Retention Time/min	Area %
1	37.135	89.367
2	39.385	2.085
3	48.281	1.910
4	57.412	6.638

Figure 29. Racemic product of (*E*)-2-(2-nitrovinyl)naphthalene and propyl aldehyde: Using Chiral AS-H column, Hex: *i*-PrOH 90:10, UV 210 nm, 0.8 ml/min.



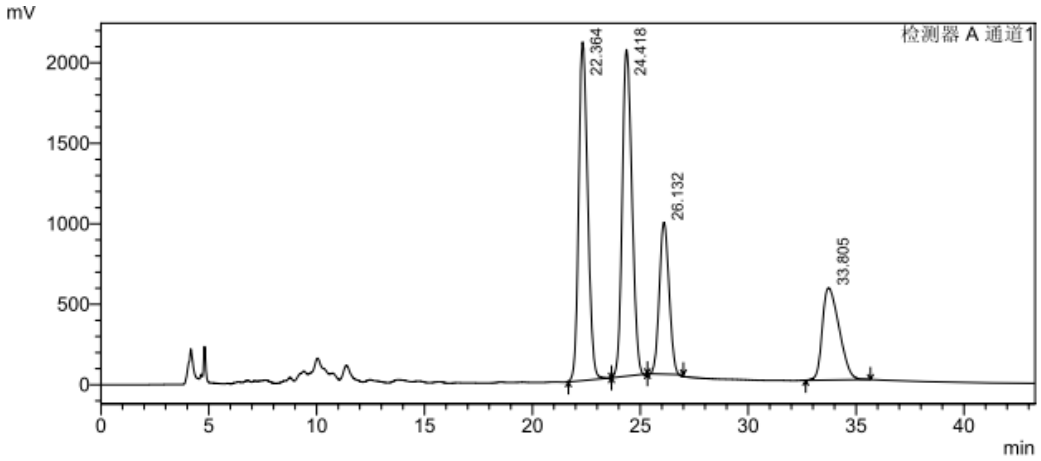
Peak	Retention Time/min	Area %
1	33.039	29.512
2	38.967	30.101
3	41.266	19.884
4	45.820	20.502

Figure 30. Enantioselective product of (*E*)-2-(2-nitrovinyl)naphthalene and propyl aldehyde.



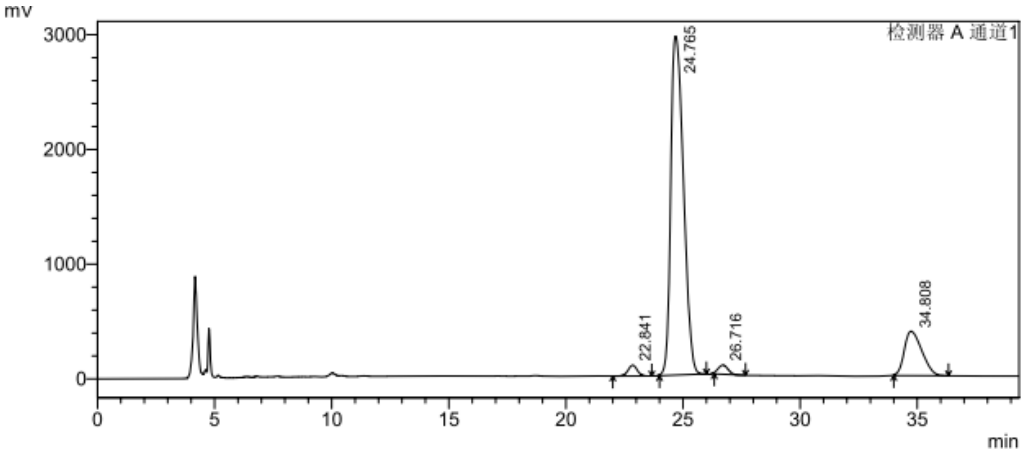
Peak	Retention Time/min	Area %
1	34.526	86.507
2	41.534	1.557
3	44.289	1.178
4	49.014	10.758

Figure 31. Racemic product of (*E*)-2-(2-nitrovinyl)furan and propyl aldehyde: Using Chiral AS-H column, Hex: *i*-PrOH 90:10, UV 210 nm, 0.8 ml/min.



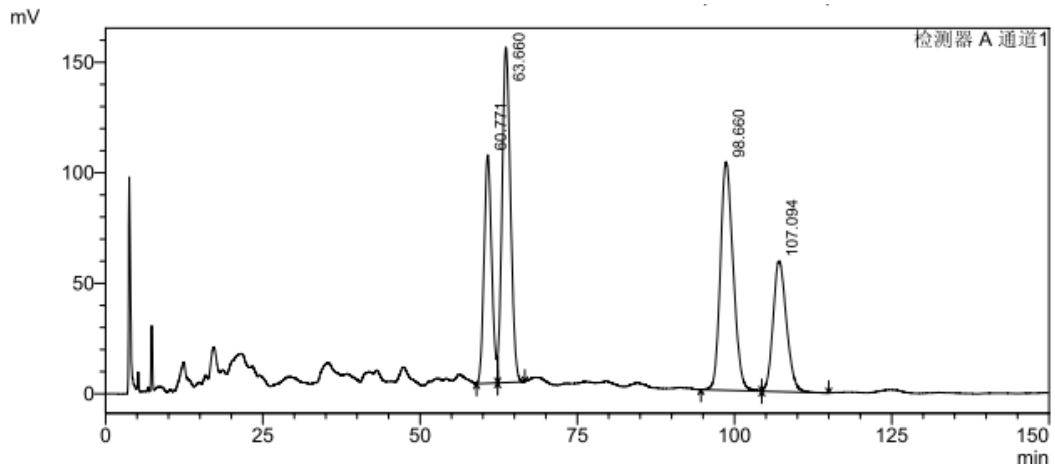
Peak	Retention Time/min	Area %
1	22.364	33.136
2	24.418	34.265
3	26.132	15.875
4	33.805	16.725

Figure 32. Enantioselective product of (*E*)-2-(2-nitrovinyl)furan and propyl aldehyde.



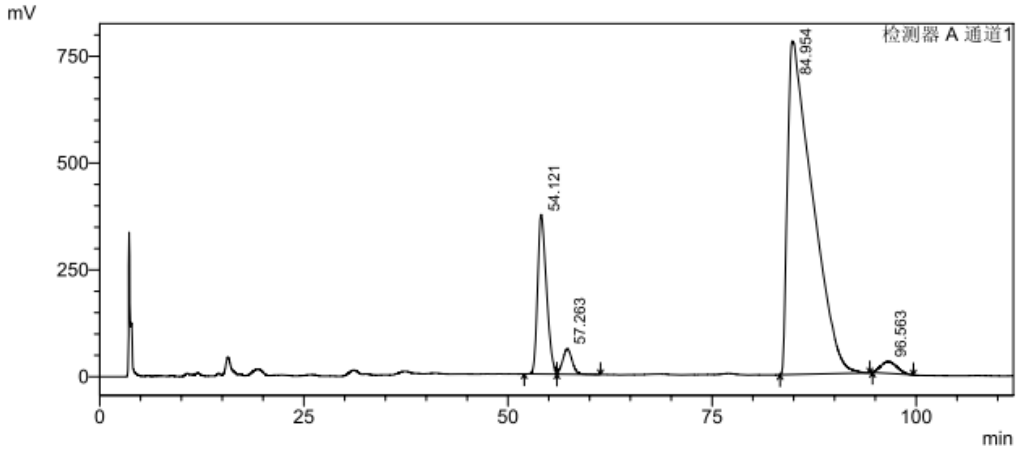
Peak	Retention Time/min	Area %
1	22.841	1.871
2	24.765	81.711
3	26.716	1.668
4	34.808	14.749

Figure 33. Racemic product of (*E*)-2-(2-nitrovinyl)thiophene and propyl aldehyde: Using Chiral OZ-H column, Hex: *i*-PrOH 98:2, UV 230 nm, 0.95 ml/min.



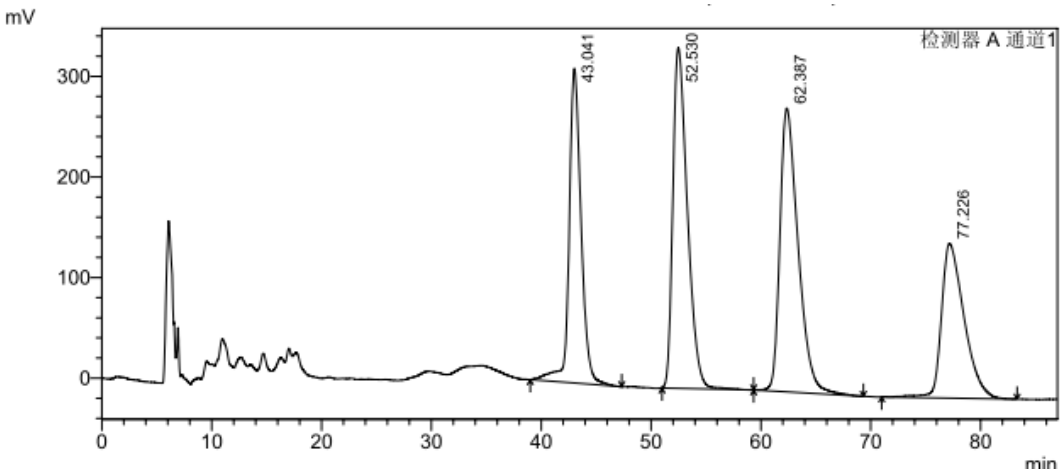
Peak	Retention Time/min	Area %
1	60.771	18.906
2	63.660	30.464
3	98.660	31.633
4	107.094	18.996

Figure 34. Enantioselective product of (*E*)-2-(2-nitrovinyl)thiophene and propyl aldehyde.



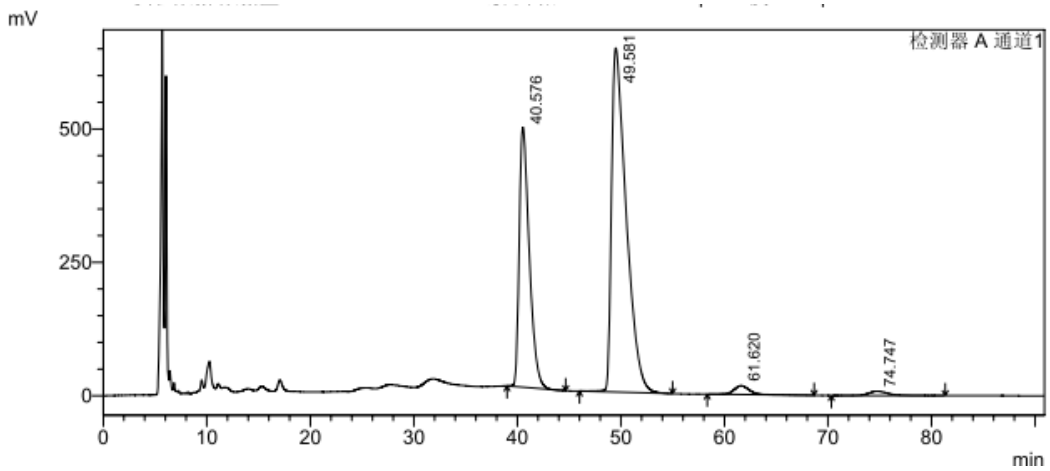
Peak	Retention Time/min	Area %
1	54.121	13.915
2	57.263	2.398
3	84.954	81.800
4	96.563	1.887

Figure 35. Racemic product of (*E*)-3-(2-nitrovinyl)pyridine and propyl aldehyde: Using Chiral OZ-H column, Hex: *i*-PrOH 75:25, UV 210 nm, 0.6 ml/min.



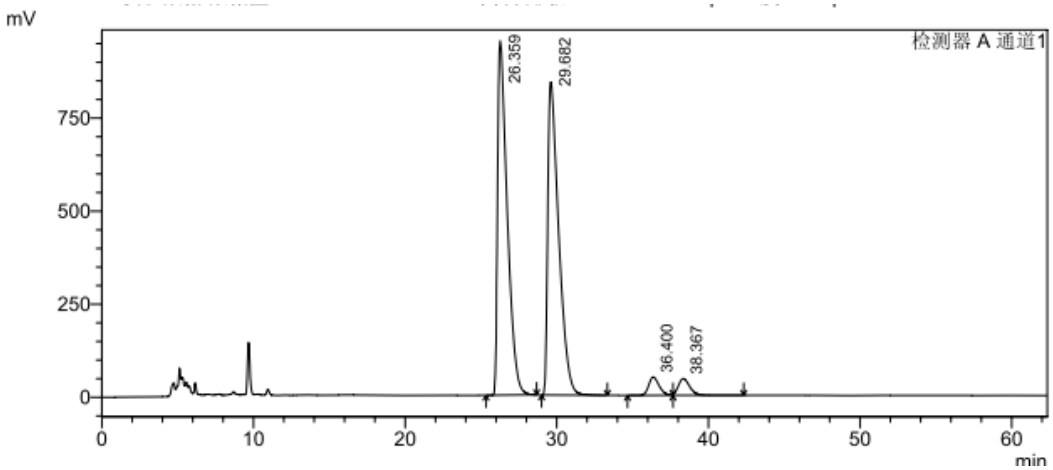
Peak	Retention Time/min	Area %
1	43.041	20.673
2	52.530	29.443
3	62.387	29.684
4	77.226	20.200

Figure 36. Enantioselective product of (*E*)-3-(2-nitrovinyl)pyridine and propyl aldehyde.



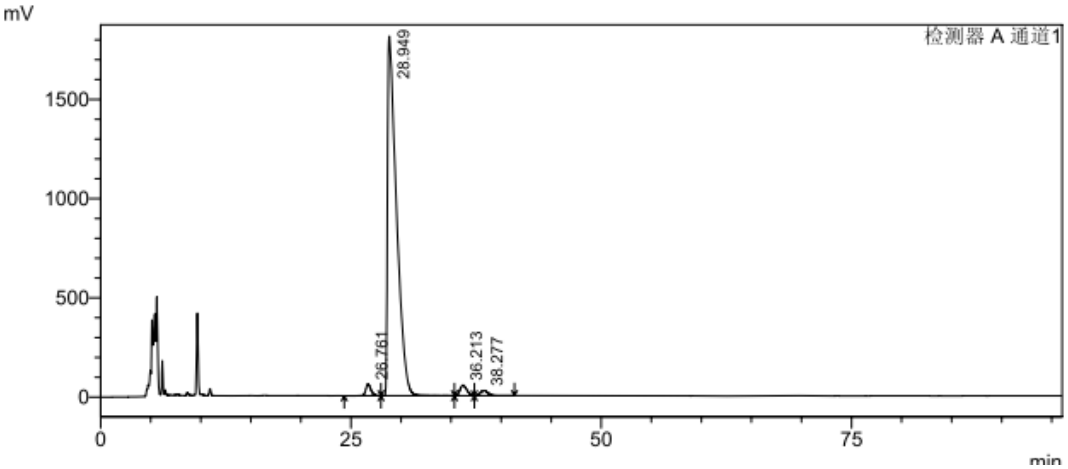
Peak	Retention Time/min	Area %
1	40.576	33.128
2	49.581	64.003
3	61.620	1.773
4	74.747	1.096

Figure 37. Racemic product of (*E*)-1-chloro-4-(2-nitrovinyl)benzene and isovaleraldehyde: Using Chiral OJ-H column, Hex: *i*-PrOH 85:15, UV 210 nm.



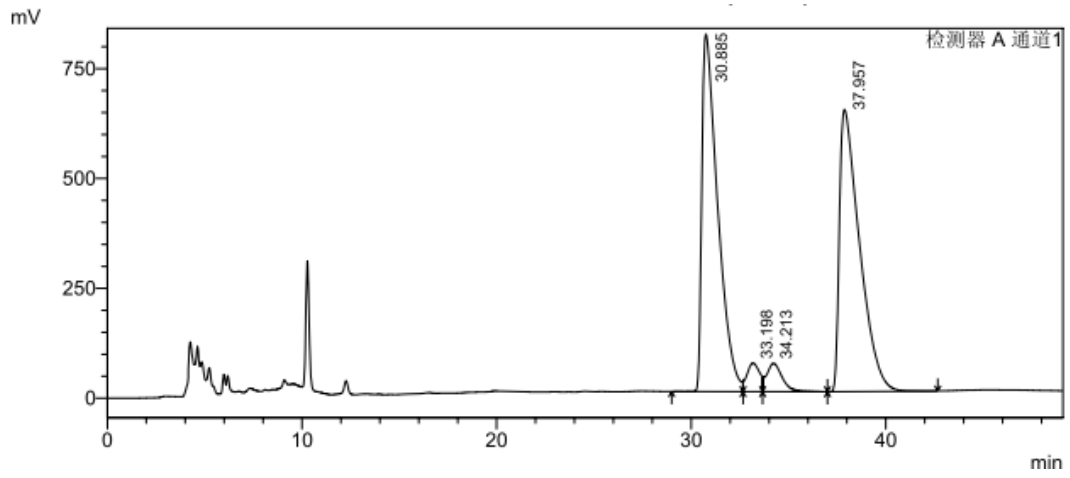
Peak	Retention Time/min	Area %
1	26.359	47.305
2	29.682	47.396
3	36.400	2.661
4	38.367	2.638

Figure 38. Enantioselective product of (*E*)-1-chloro-4-(2-nitrovinyl)benzene and isovaleraldehyde.



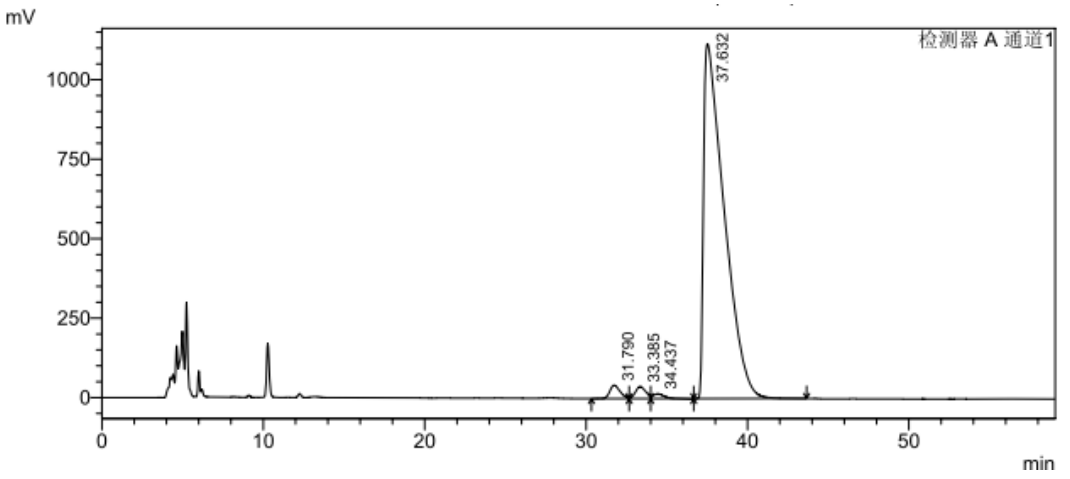
Peak	Retention Time/min	Area %
1	26.761	1.680
2	28.949	94.868
3	36.213	2.155
4	38.277	1.164

Figure 39. Racemic product of (*E*)-1-methoxy-2-(2-nitrovinyl)benzene and isovaleraldehyde: Using Chiral OJ-H column, Hex: *i*-PrOH 96:4, UV 210 nm, 0.8 ml/min.



Peak	Retention Time/min	Area %
1	30.885	46.624
2	33.198	2.918
3	34.213	3.681
4	37.957	46.777

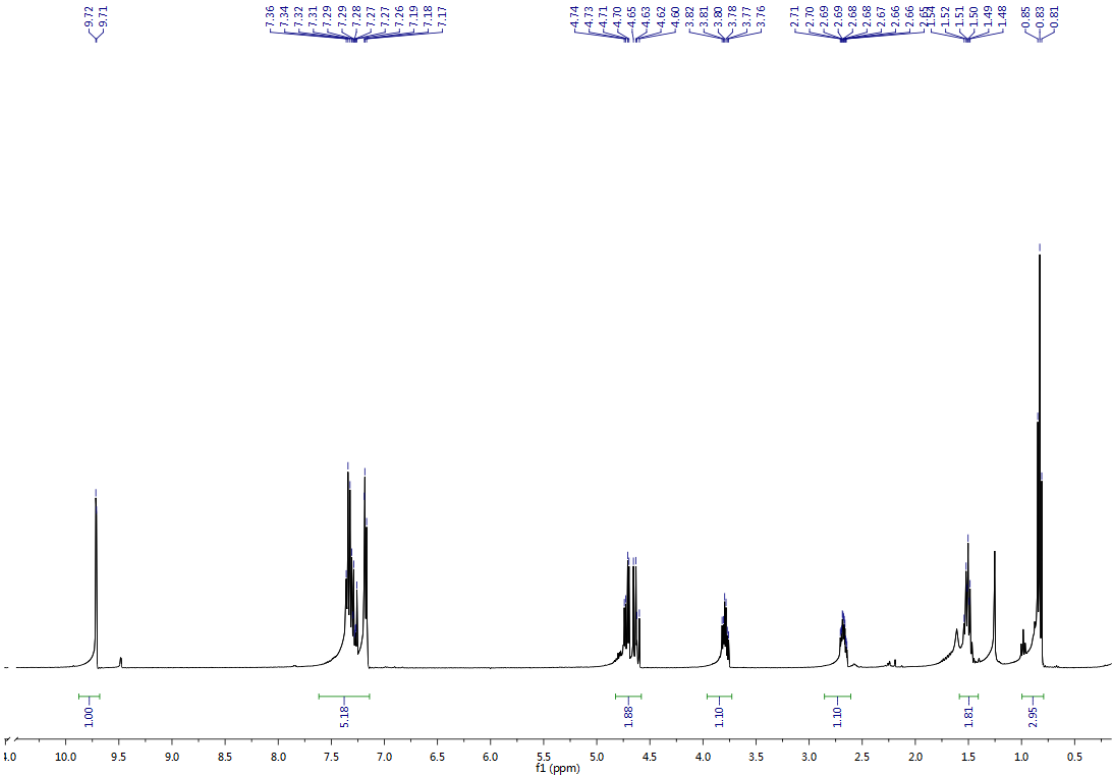
Figure 40. Enantioselective product of (*E*)-1-methoxy-2-(2-nitrovinyl)benzene and isovaleraldehyde.



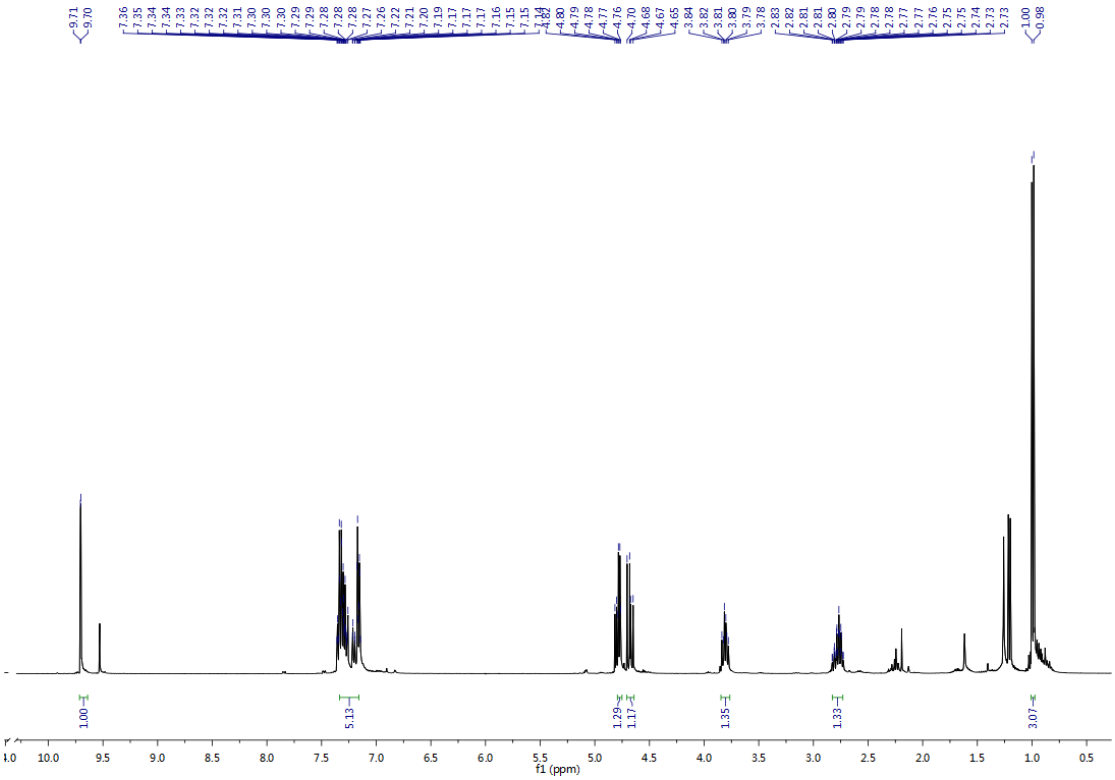
Peak	Retention Time/min	Area %
1	31.790	1.799
2	33.385	1.623
3	34.437	0.712
4	37.632	95.865

5. NMR Spectrum

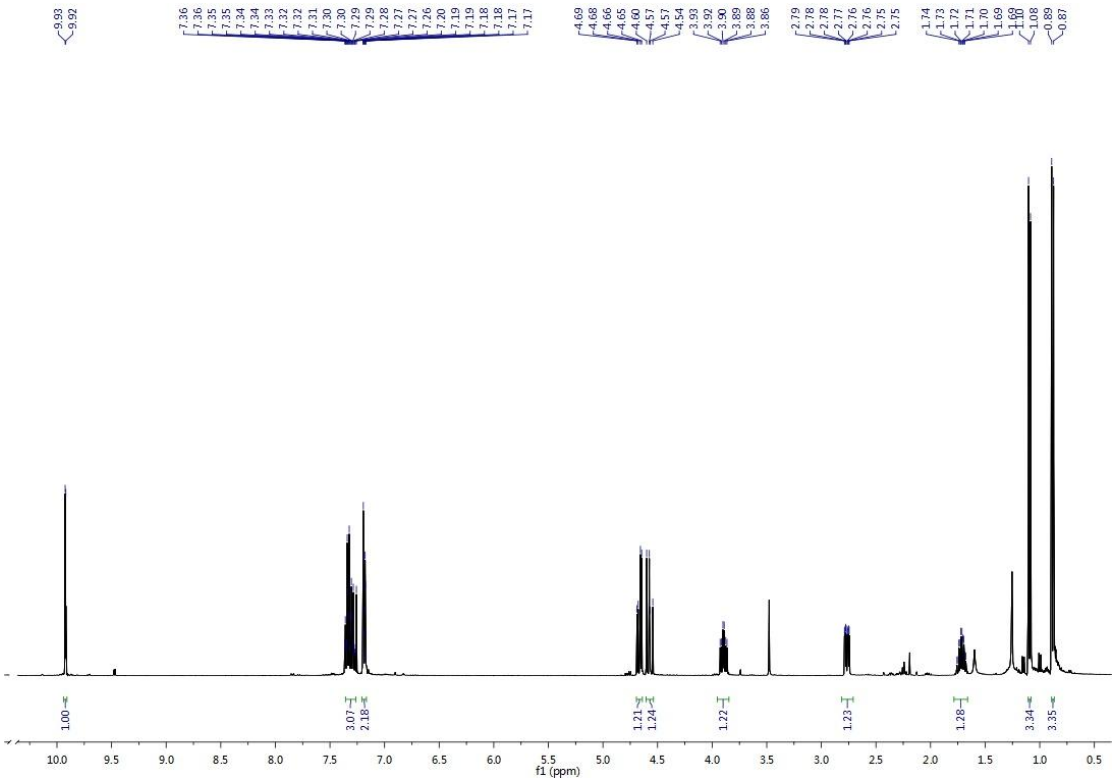
^{1}H NMR (400 MHz, $CDCl_3$) **6aa**



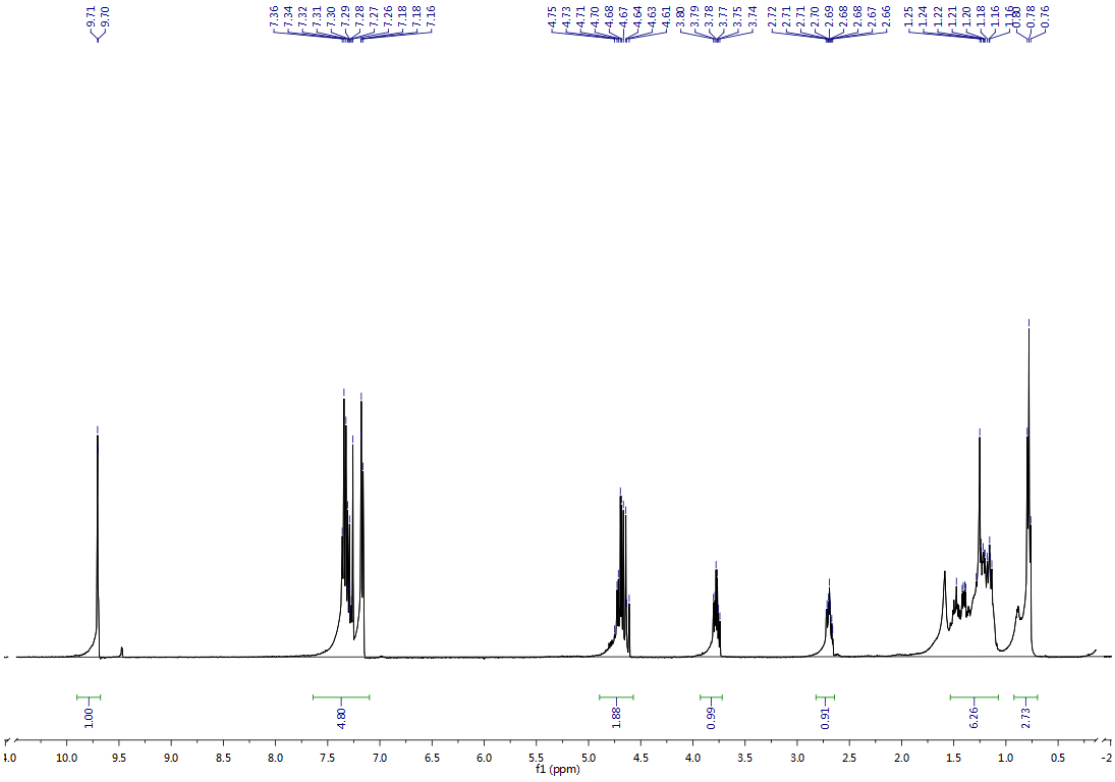
^{1}H NMR (400 MHz, $CDCl_3$) **6ba**



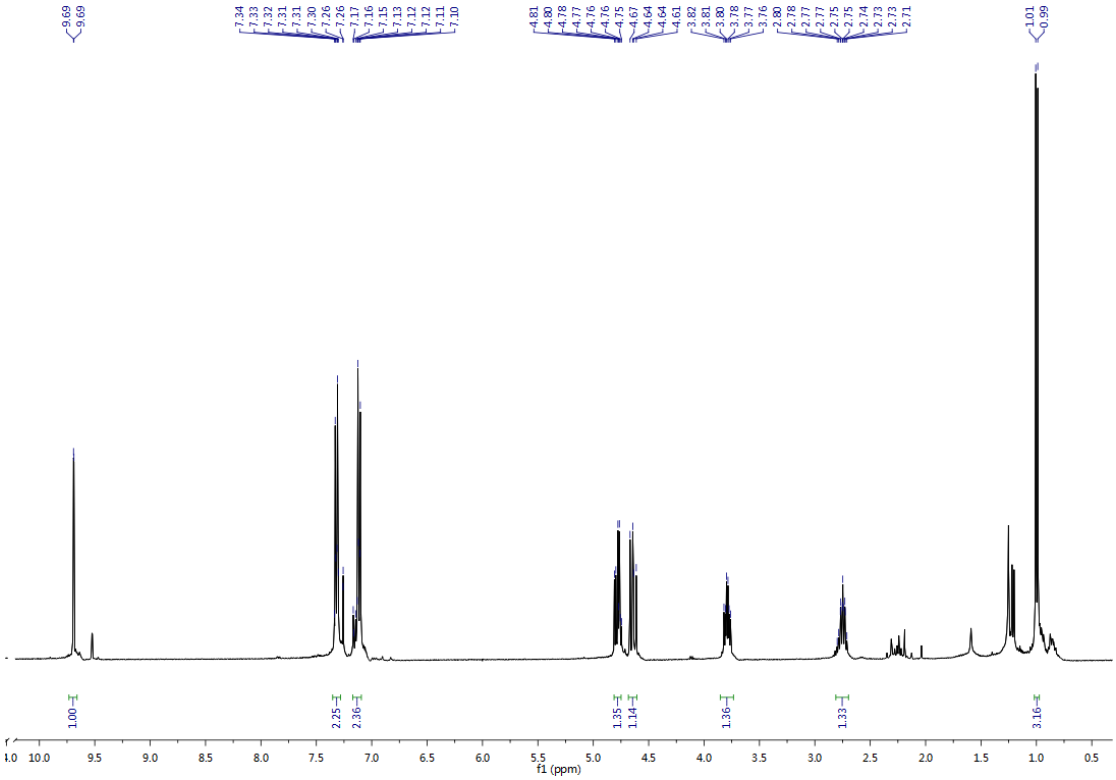
^{1}H NMR (400 MHz, $CDCl_3$) **6ca**



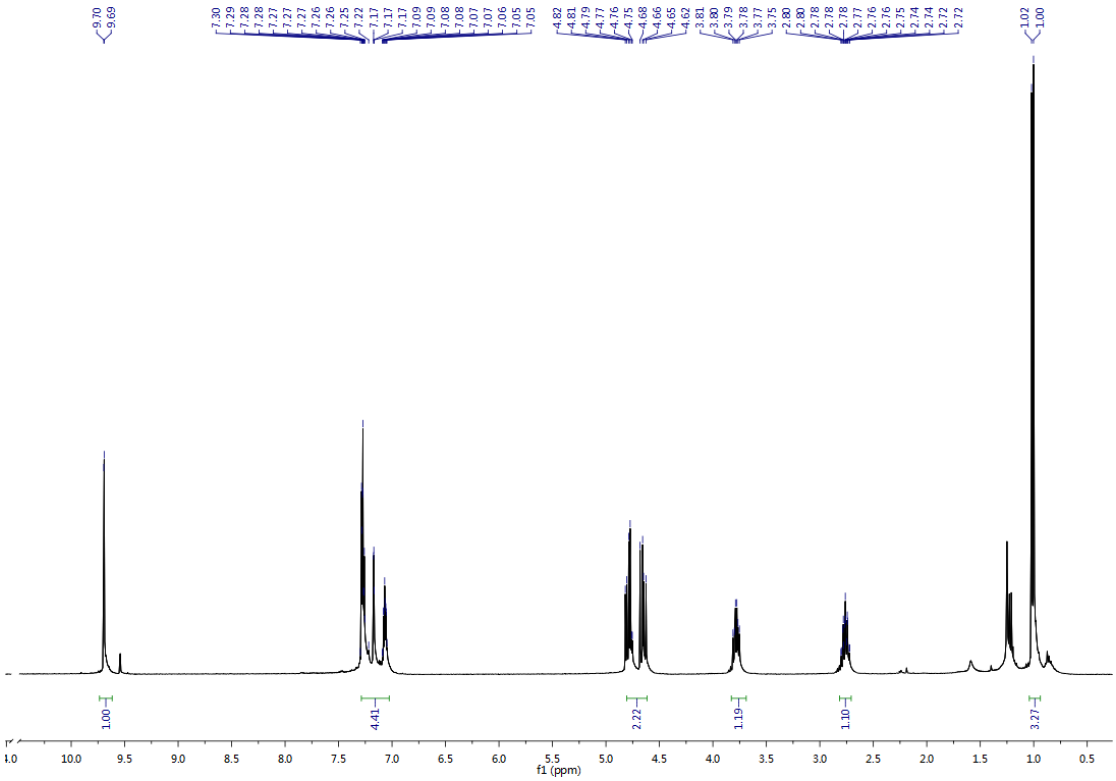
^{1}H NMR (400 MHz, $CDCl_3$) **6ea**



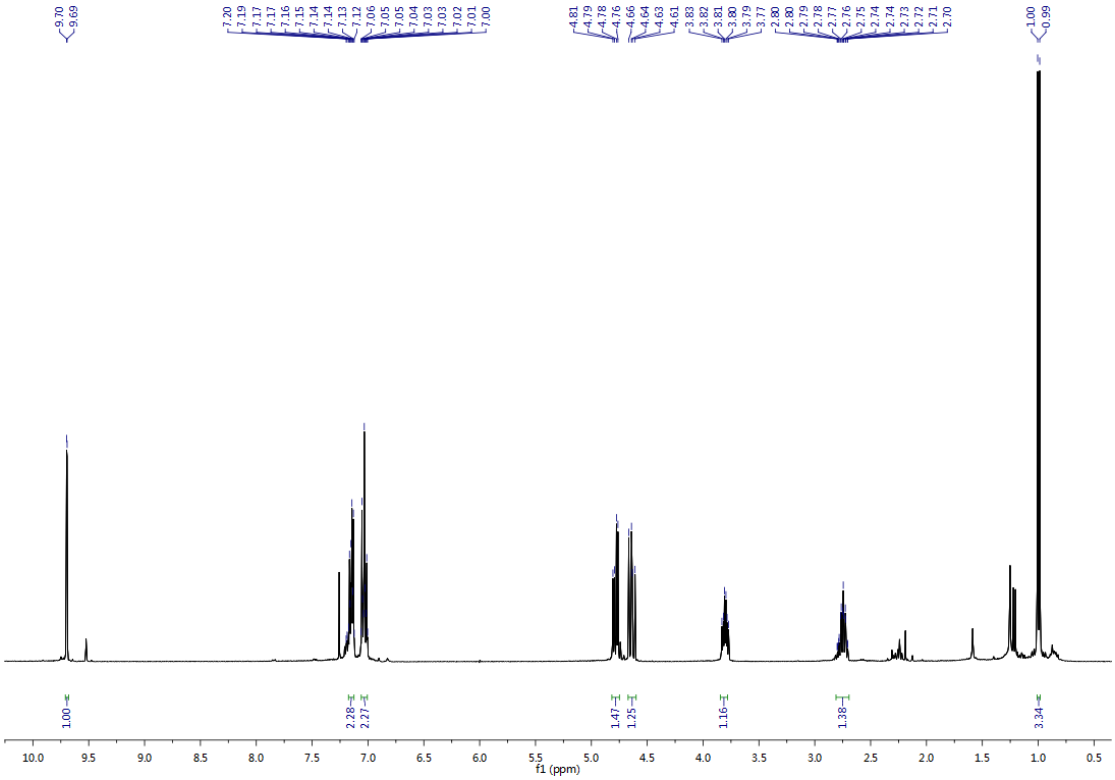
^{1}H NMR (400 MHz, $CDCl_3$) **6bb**



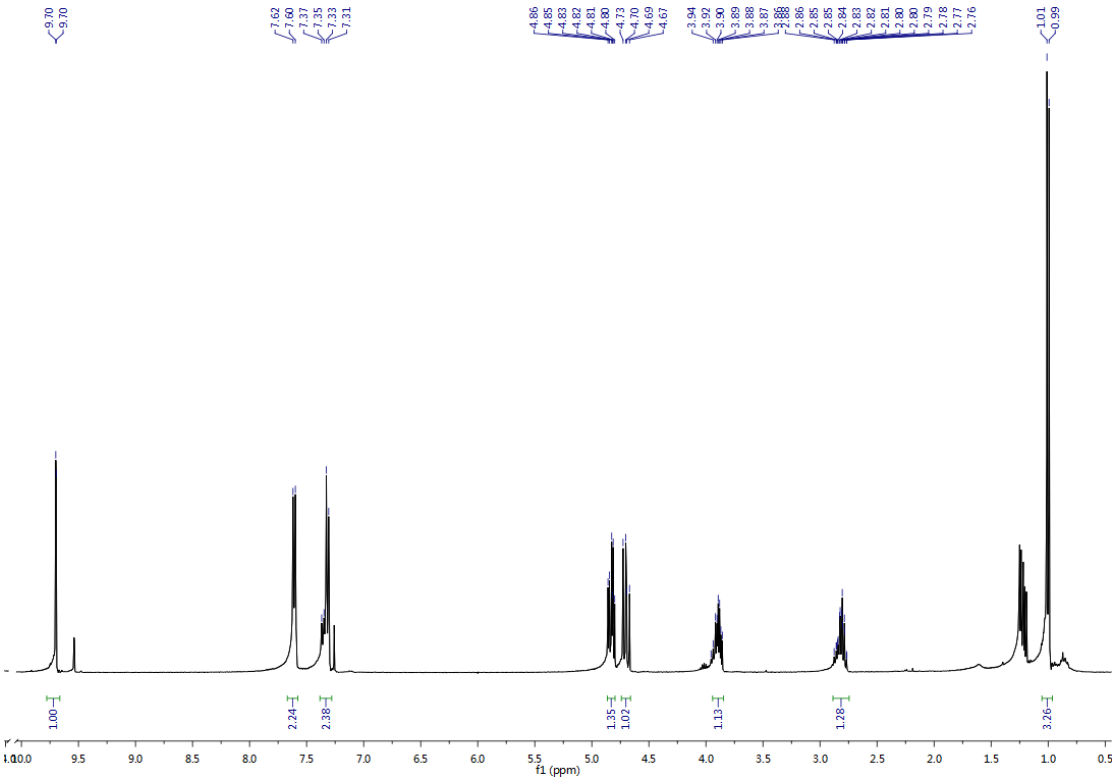
^{1}H NMR (400 MHz, $CDCl_3$) **6bc**



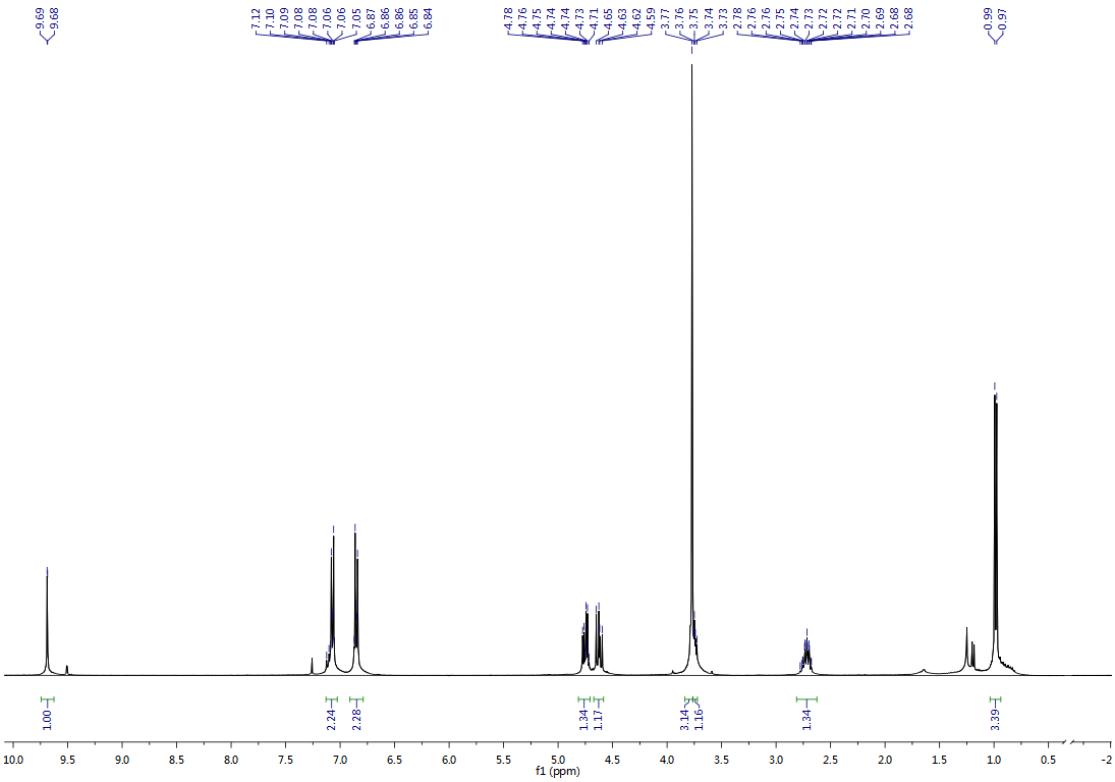
^{1}H NMR (400 MHz, $CDCl_3$) **6bd**



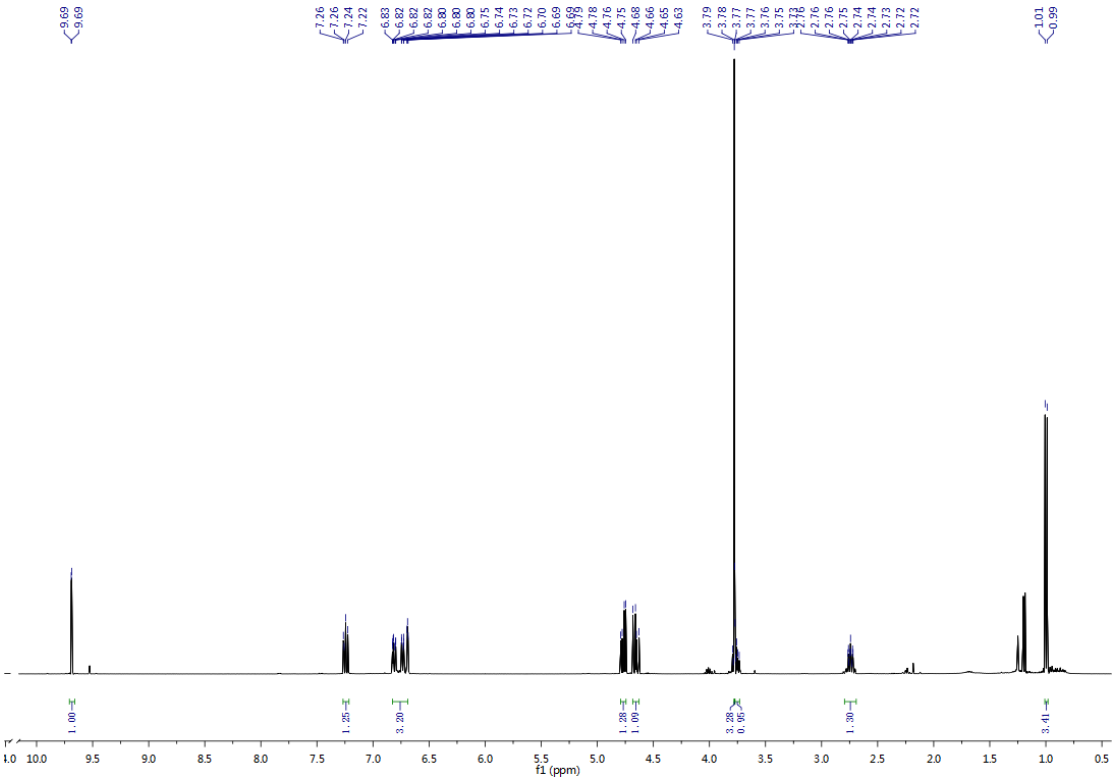
^{1}H NMR (400 MHz, $CDCl_3$) **6be**



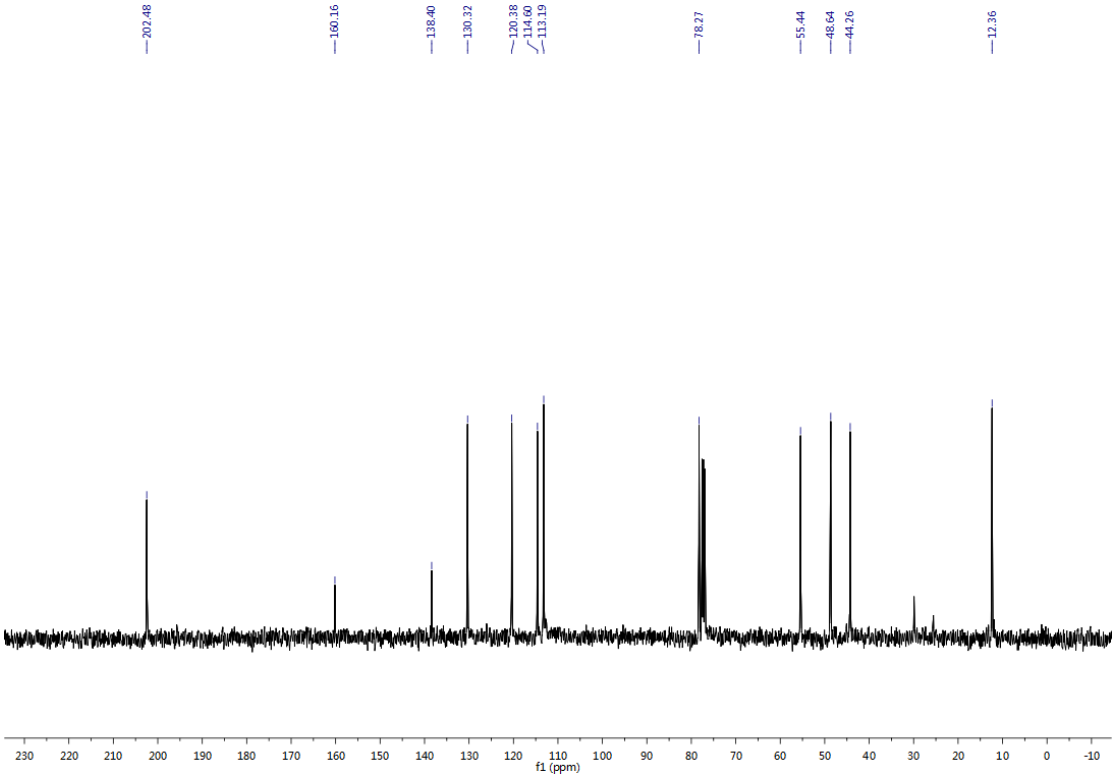
^{1}H NMR (400 MHz, $CDCl_3$) **6bf**



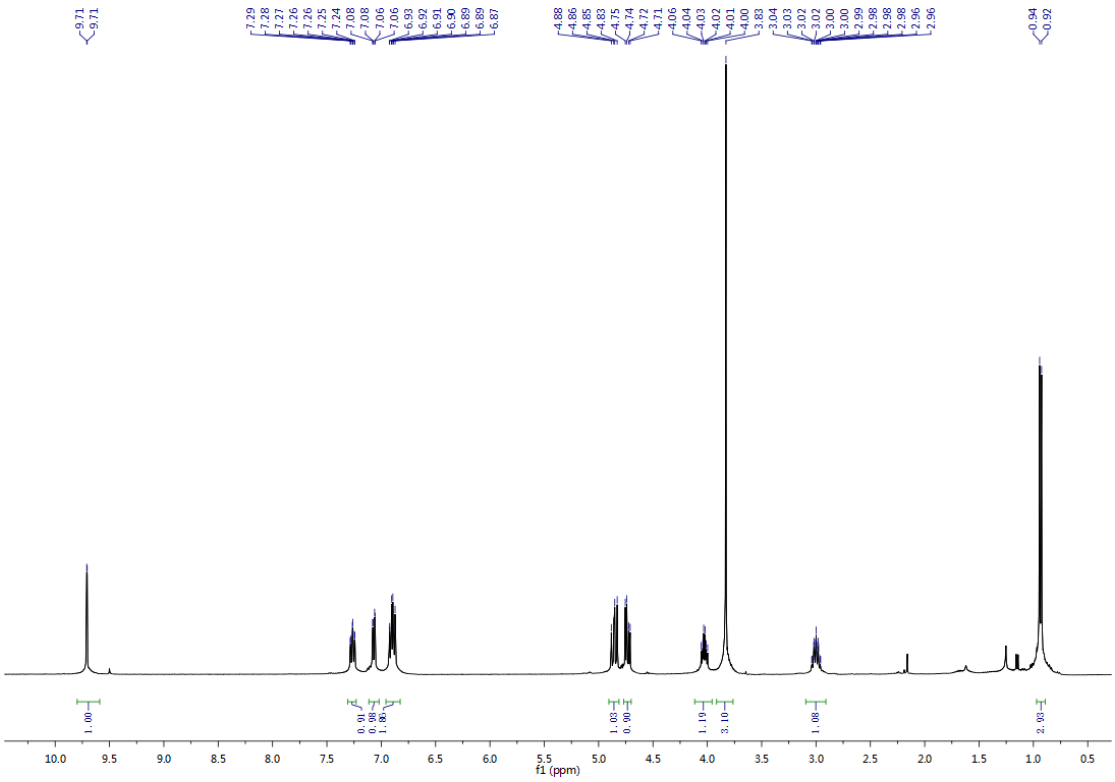
^{1}H NMR (400 MHz, $CDCl_3$) **6bg**



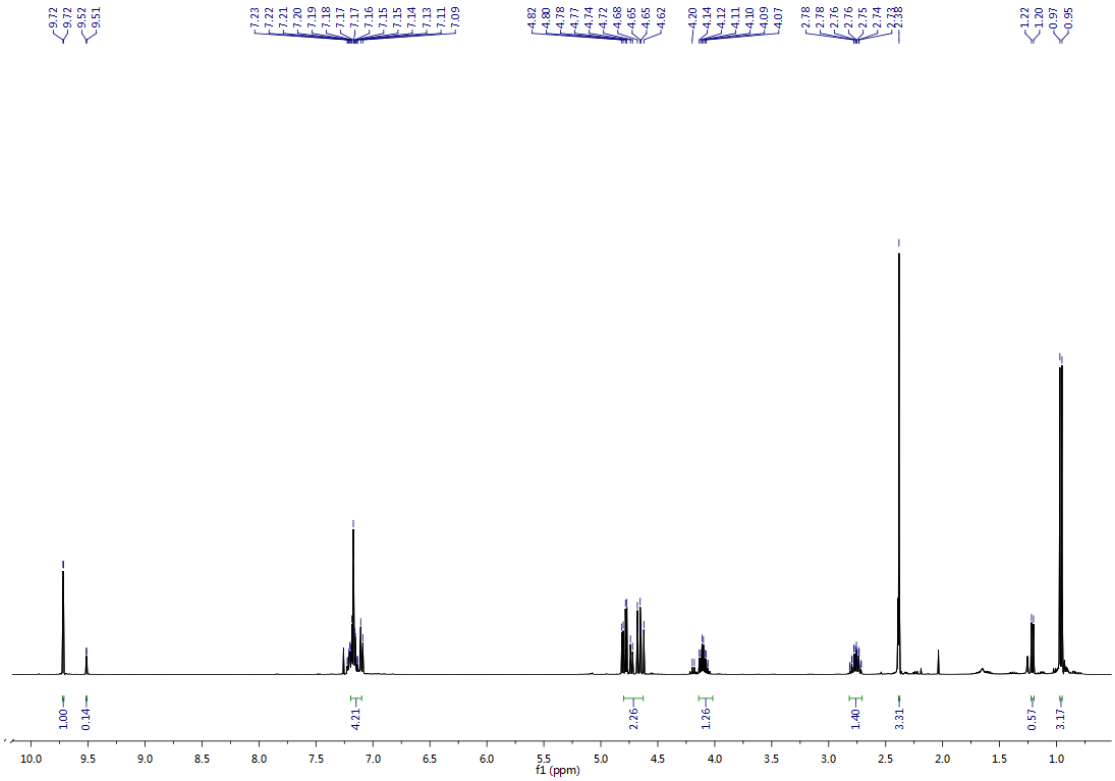
^{13}C NMR (100 MHz, $CDCl_3$) **6bg**



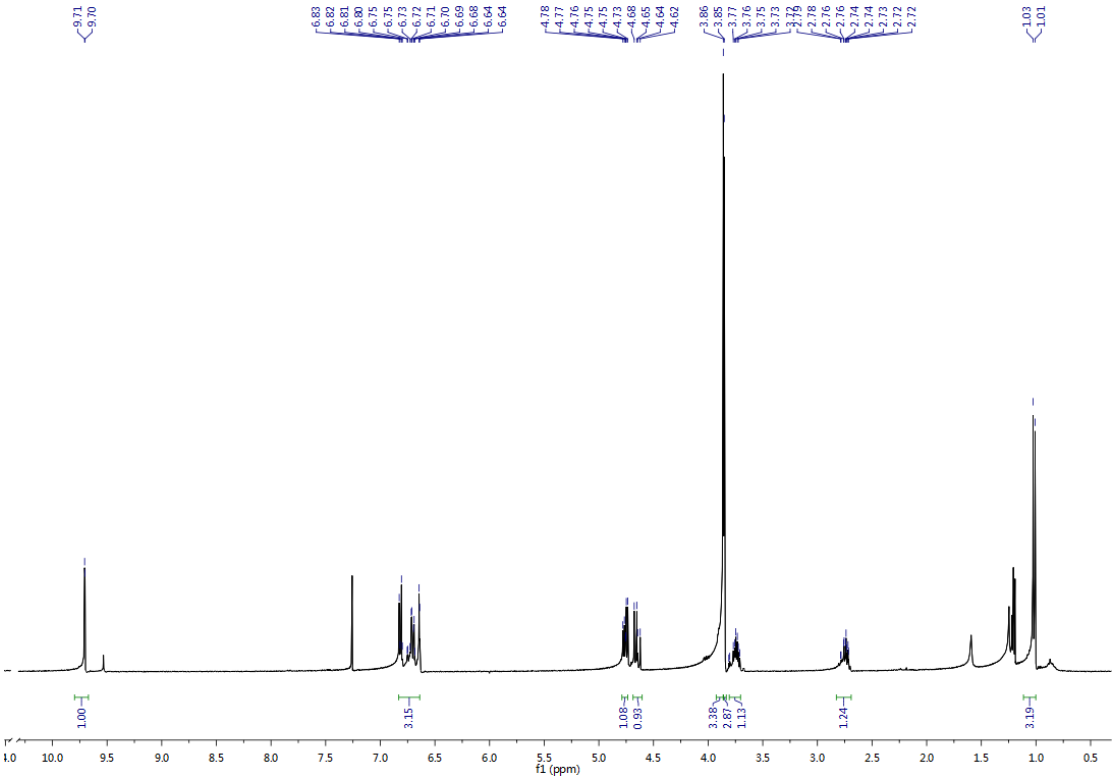
^{1}H NMR (400 MHz, $CDCl_3$) **6bh**



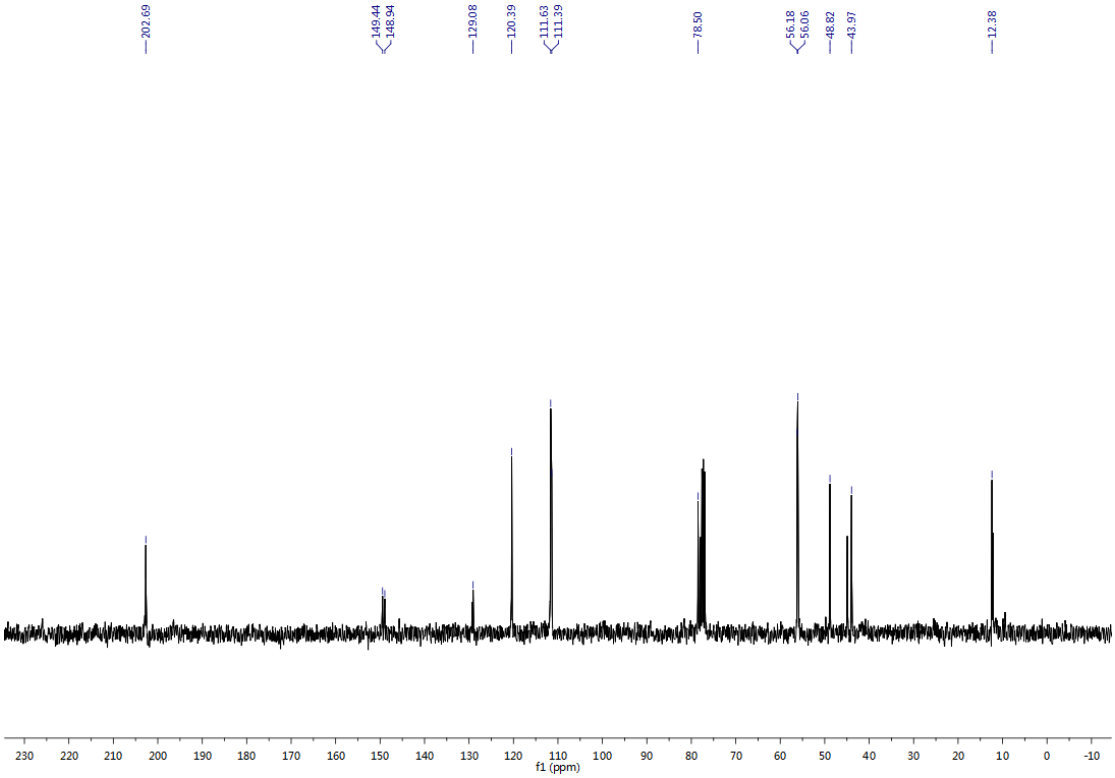
^{1}H NMR (400 MHz, $CDCl_3$) **6bi**



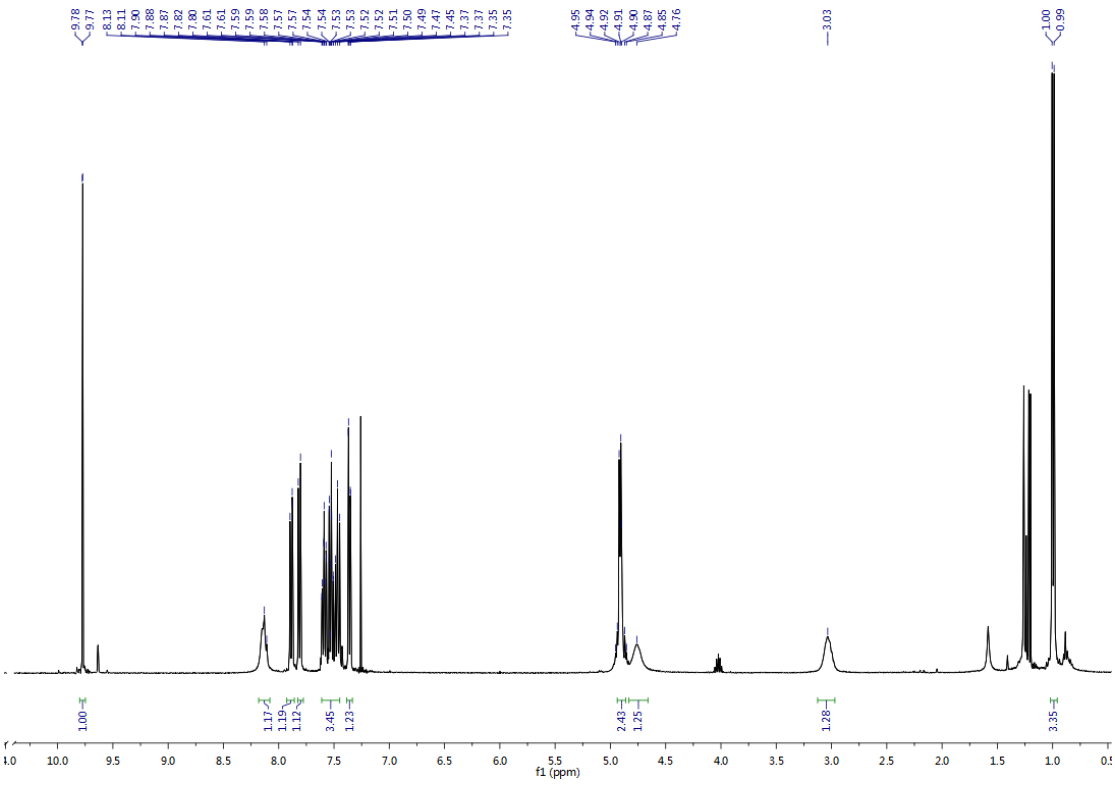
^{1}H NMR (400 MHz, $CDCl_3$) **6bj**



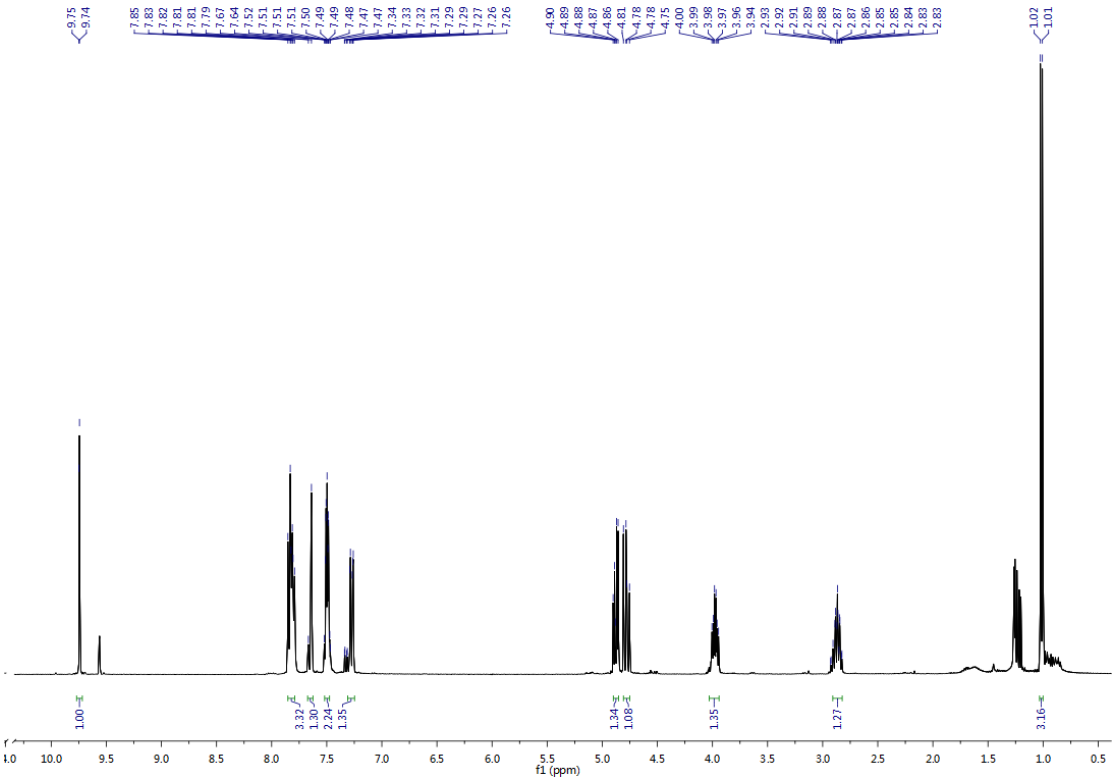
^{13}C NMR (100 MHz, CDCl3) **6bj**



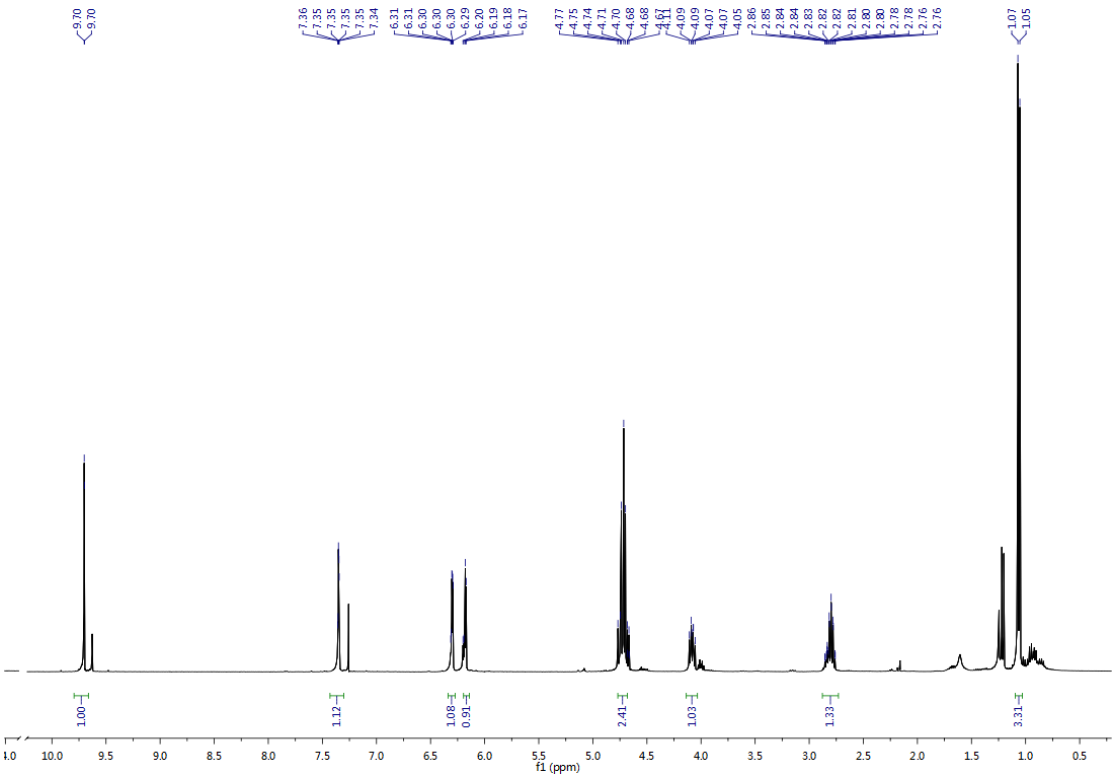
^{1}H NMR (400 MHz, $CDCl_3$) **6bk**



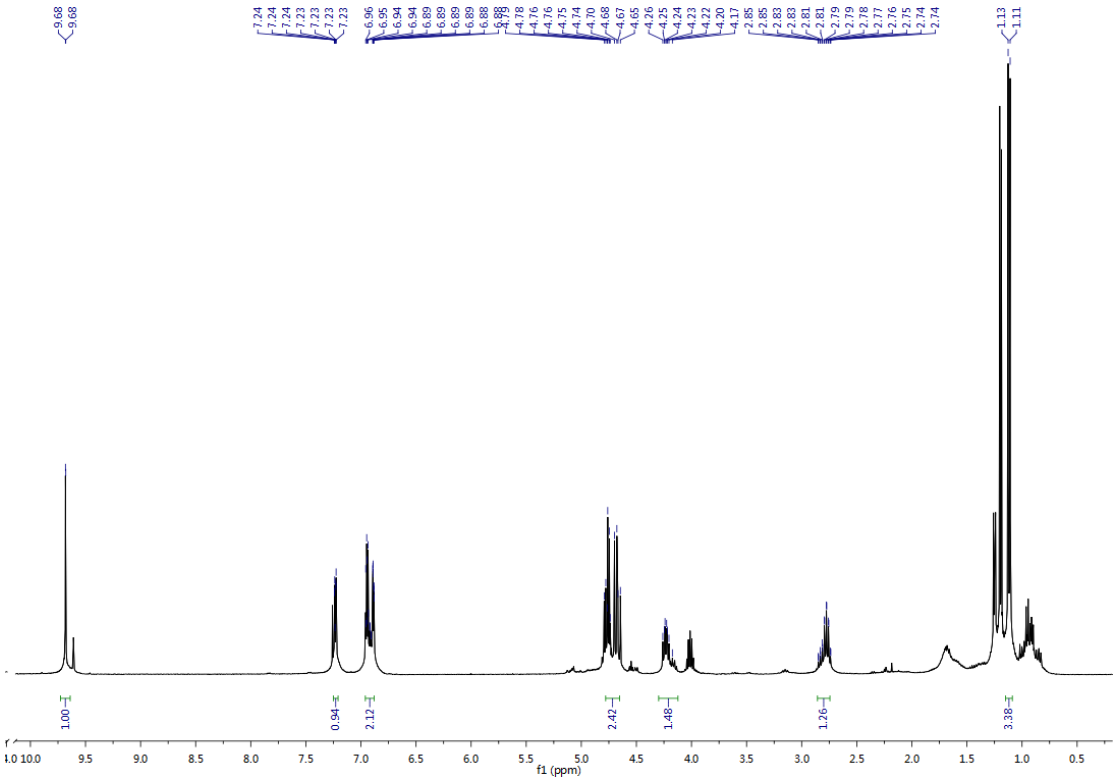
^{1}H NMR (400 MHz, $CDCl_3$) **6bl**



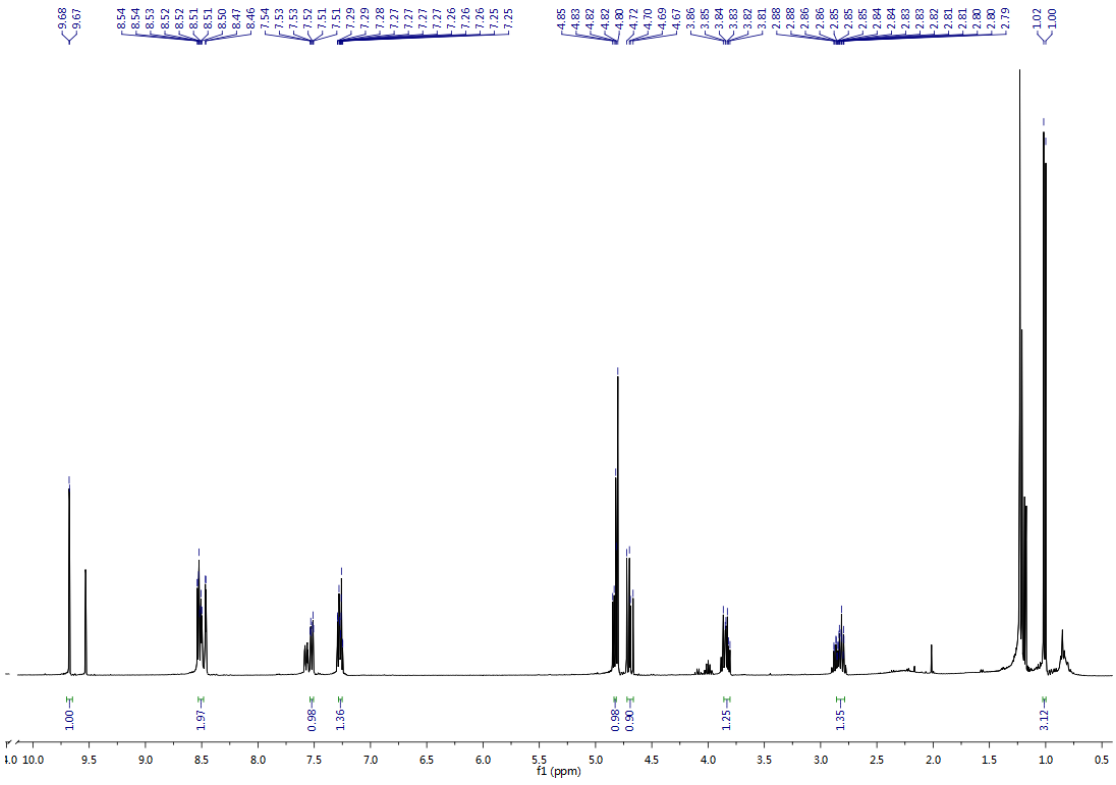
^{1}H NMR (400 MHz, $CDCl_3$) **6bm**



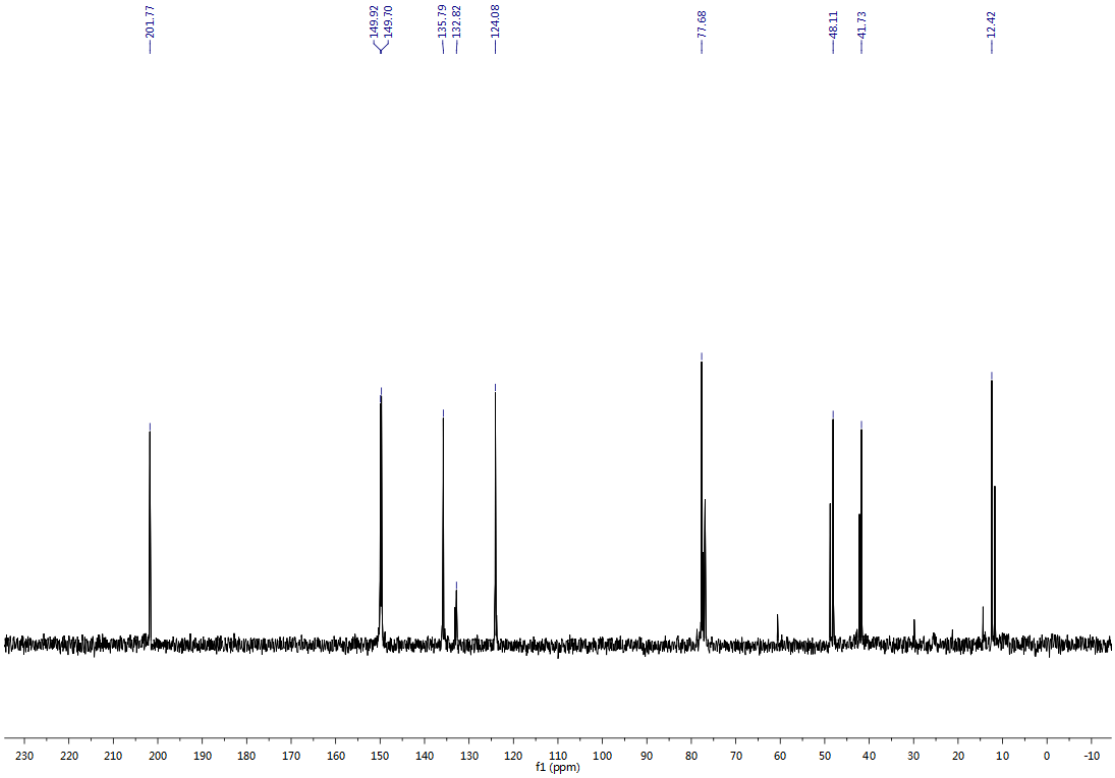
^{1}H NMR (400 MHz, $CDCl_3$) **6bn**



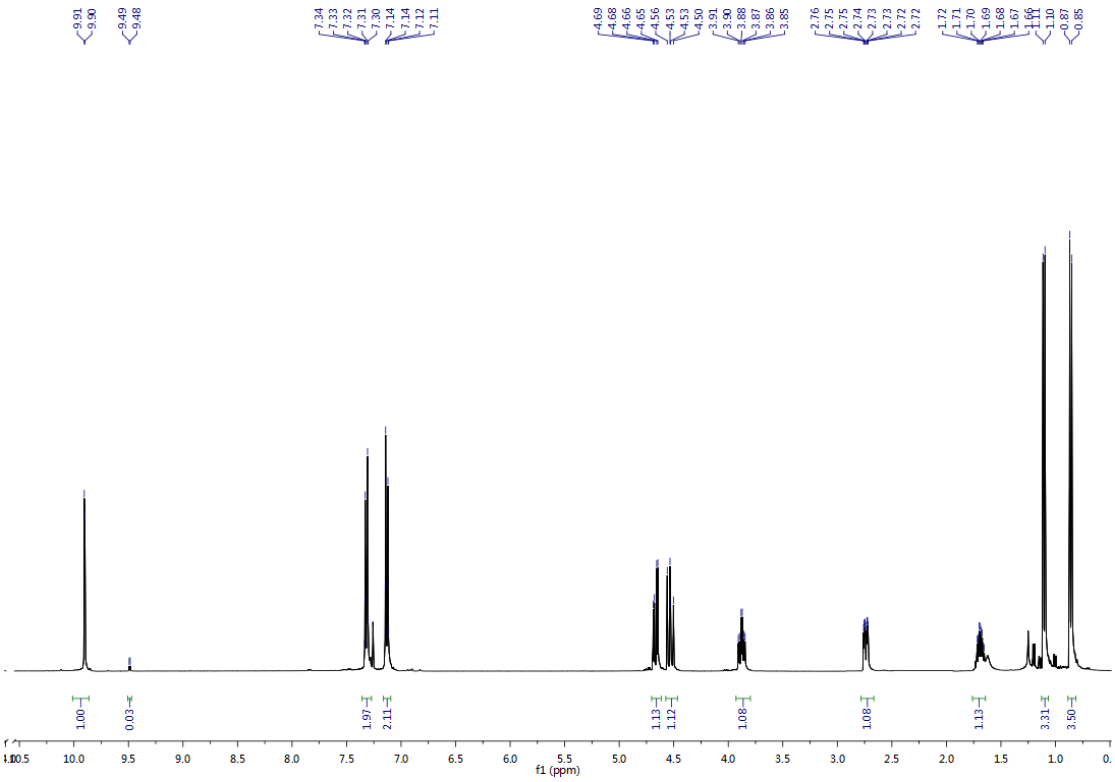
^{1}H NMR (400 MHz, $CDCl_3$) **6bo**



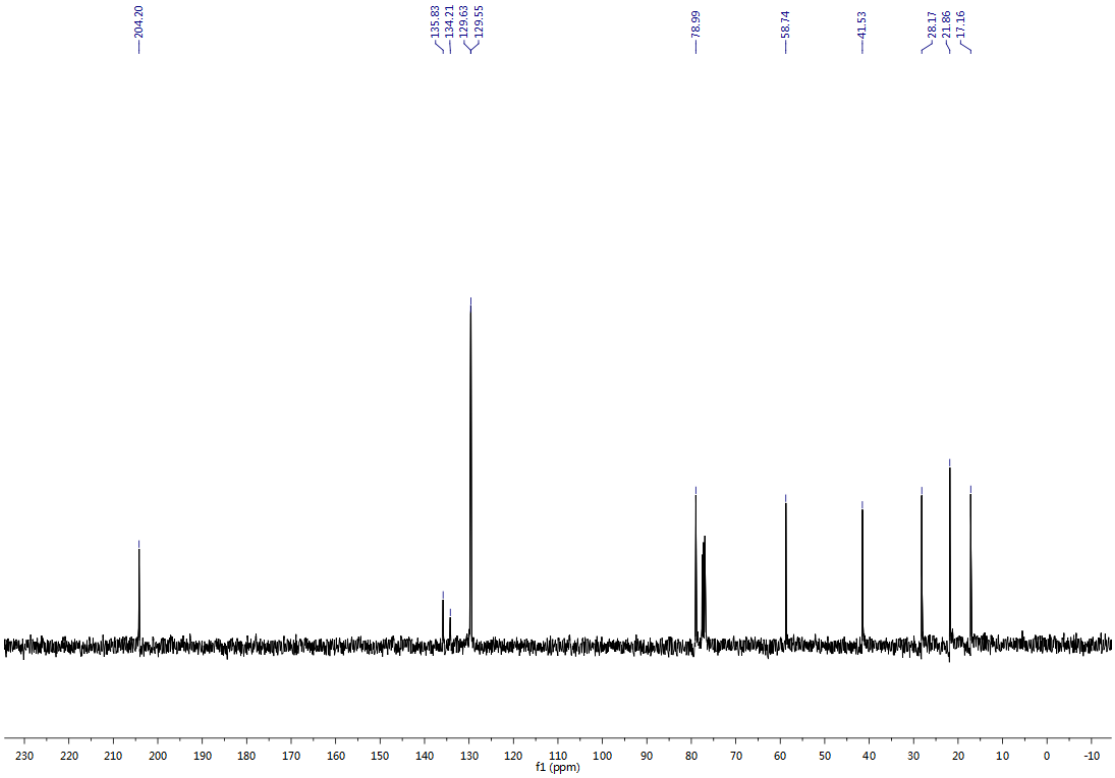
^{13}C NMR (100 MHz, $CDCl_3$) **6bo**



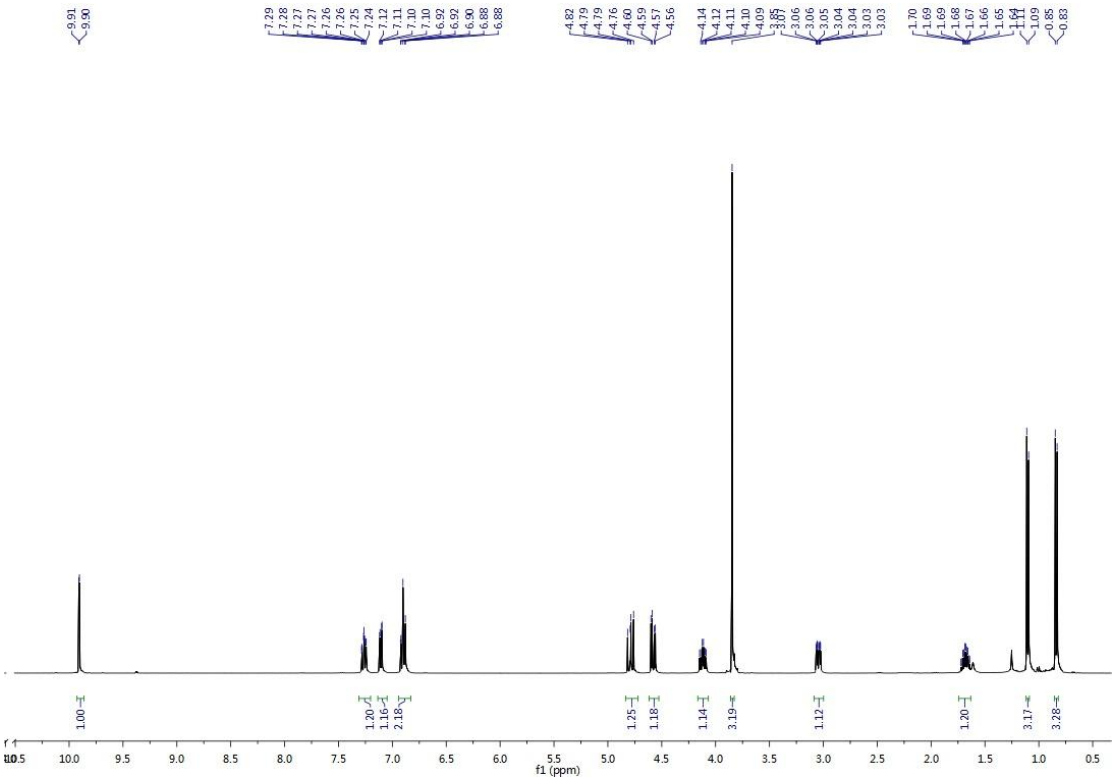
^{1}H NMR (400 MHz, $CDCl_3$) **6cb**



^{13}C NMR (100 MHz, $CDCl_3$) **6cb**



^{1}H NMR (400 MHz, $CDCl_3$) **6cc**



^{13}C NMR (100 MHz, $CDCl_3$) **6cc**