

Supporting Information

Counter-rotatable Dual Cinchona Quinuclidinium Salts and Their Phase Transfer Catalysis in Enantioselective Alkylation of Glycine Imines

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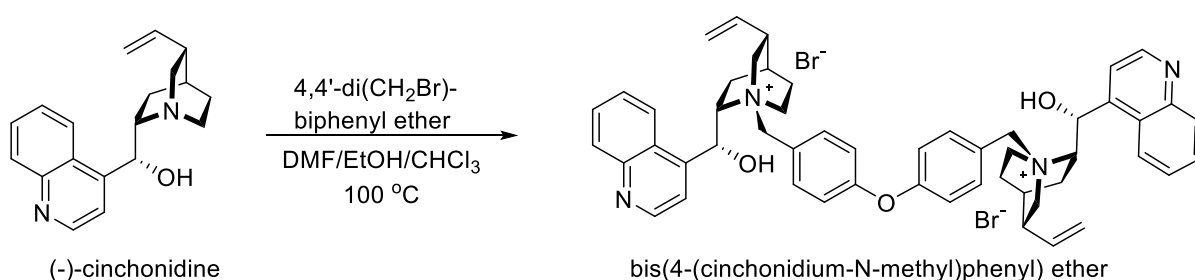
1. Materials and Instruments

Infrared (IR) spectra were recorded on a NICOLET iS10 spectrometer. Nuclear magnetic resonance ($^1\text{H-NMR}$ and $^{13}\text{C-NMR}$) spectra were measured on a Bruker DPX 300 [300 MHz (^1H), 75 MHz (^{13}C)] spectrometer and Varian VNS 600 [600 MHz (^1H), 150 MHz (^{13}C)] spectrometer at Core Research Support Center for Natural Products and Medical Materials at Yeungnam University, using CHCl_3-d or $\text{DMSO-}d_6$ as a solvent, and were reported in ppm relative to DMSO (δ 2.50) or CHCl_3 (δ 7.26) for $^1\text{H-NMR}$ and relative to the central $\text{DMSO-}d_6$ (δ 39.51) or CHCl_3-d (δ 77.23) resonance for $^{13}\text{C-NMR}$. Coupling constants (J) in $^1\text{H-NMR}$ are in Hz. High performance liquid chromatography (HPLC) was performed on Shimadzu 20A instruments using 4.6 mm \times 25 cm DAICEL Chiralcel OD. Optical rotations were measured on a JASCO P-2000 digital polarimeter. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-700 spectrometer. Melting points were measured on a Buchi B-540 melting point apparatus and were not corrected. For thin-layer chromatography (TLC) analysis, Merck precoated TLC plate (silica gel 60 F₂₅₄, 0.25 mm) was used. For flash column chromatography, Merck Kieselgel 60 (230–400 mesh) was used. All solvents and commercially available chemicals were used without additional purification.

2. Experiments

(1) Synthesis of PTC

(a) *Bis*(4-(cinchonidinium-N-methyl)phenyl)ether dibromide

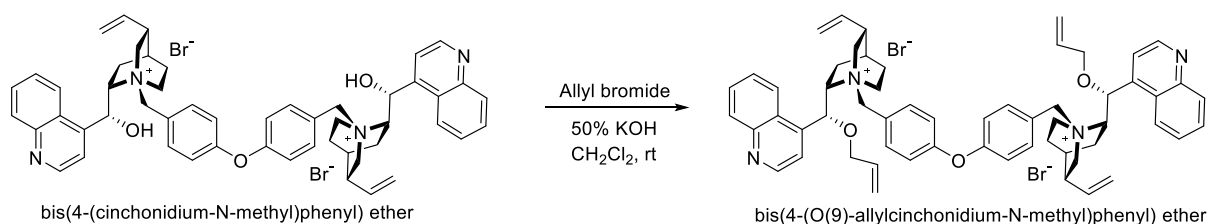


A mixture of 4,4'-oxybis(bromomethyl)benzene^[S1] (5.00 g, 0.014 mol) and (-)-cinchonidine (7.40 g, 0.025 mol) in a mixed solvent (70 mL, DMF:EtOH:CHCl₃, v/v 6:5:2) was stirred for 4 hr at 110 °C under nitrogen atmosphere. After cooling, the mixture was diluted with 20 mL of dichloromethane and

dropped into 150 mL ethyl ether. The resulting solid was filtered and purified by flash column chromatography (10:1, CH₂Cl₂/MeOH) to afford the pink solid, yield (10.88 g, 82%).

¹H NMR (300 MHz, DMSO-*d*₆): δ 8.98 (d, *J* = 4.5 Hz, 2H), 8.39-8.28 (d, 2H), 8.11 (d, *J* = 8.3, 1.4 Hz, 2H), 7.92-7.70 (m, 10H), 7.28 (d, *J* = 8.2 Hz, 4H), 6.74 (d, *J* = 4.8 Hz, 2H), 6.66-6.51 (m, 2H), 5.79-5.59 (m, 2H), 5.27 (d, *J* = 12.4 Hz, 2H), 5.19 (d, *J* = 17.2, 1.3 Hz, 2H), 5.11 (d, *J* = 12.2 Hz, 2H), 4.96 (d, *J* = 10.5, 1.4 Hz, 2H), 4.32 (m, 2H), 3.97 (t, *J* = 9.2 Hz, 2H), 3.81 (m, 2H), 3.41 (t, *J* = 11.6 Hz, 2H), 3.25 (m, 2H), 2.11 (m, 6H), 1.86 (m, 2H), 1.32 ppm (m, 2H); ¹³C NMR (75.5 MHz, DMSO-*d*₆): δ 157.49, 150.14, 147.57, 145.27, 138.05, 135.77, 129.76, 129.41, 127.34, 124.27, 123.79, 123.23, 120.12, 119.03, 116.38, 67.50, 63.98, 61.81, 59.07, 50.41, 36.84, 25.95, 24.27, 21.05 ppm; m.p. 230°C (decomp.); [α]_D²⁴ = -128.3 (*c* 1.00, CH₂Cl₂); IR (KBr), cm⁻¹: 3402(broad), 3130, 1689, 1265, 862; HRMS (FAB⁺) calcd. for C₅₂H₆₄BrN₄O₃⁺, [M-Br]⁺: 863.3536 (86.4%), 865.3529 (100.0%), found: 863.3538, 865.3566.

(b) Bis(4-(O(9)-allyl)cinchonidinium-N-methyl)phenyl)ether dibromide (7)

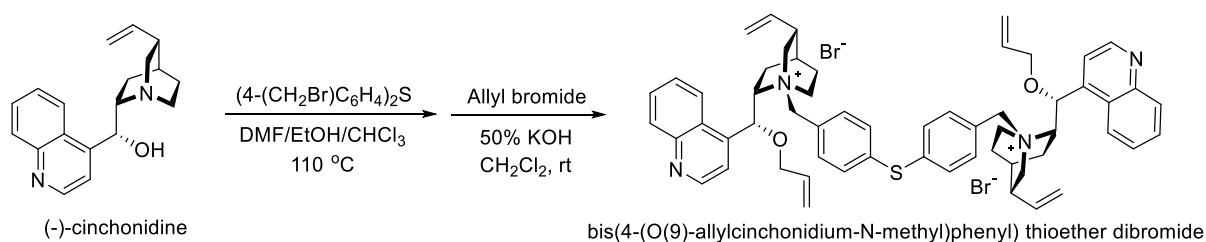


A suspension of *bis*(4-(cinchonidinium-N-methyl)phenyl)ether (2.00 g, 2.1 mmol) and allyl bromide (1.29 mL, 15.1 mmol) in dichloromethane (30 mL) was mixed with 50% KOH aqueous solution (6.4 mL, 57.00mmol). The suspension was stirred at rt for 4 hr, then diluted with water (10 mL) and extracted with dichloromethane (2 x 10 mL). The organic solution was dried over MgSO₄, concentrated, and purified by flash column chromatography (10:1, CH₂Cl₂/MeOH) to afford the yellowish solid, yield (1.81 g, 83%).

¹H NMR (300 MHz, Chloroform-*d*): δ 8.98 (d, *J* = 4.1 Hz, 2H), 8.85 (d, *J* = 8.5 Hz, 2H), 8.16 (d, *J* = 8.4, 1.4 Hz, 2H), 8.00 (d, *J* = 8.8 Hz, 4H), 7.93 (m, 2H), 7.85-7.78 (m, 4H), 7.13 (d, *J* = 8.2 Hz, 4H), 6.45 (d, *J* = 11.8 Hz, 2H), 6.32-6.21 (m, 2H), 6.18-6.04 (m, 2H), 5.48 – 5.33 (m, 4H), 4.71 (m, *J* = 12.2 Hz, 2H), 4.61 (d, *J* = 11.5 Hz, 2H), 4.29 (m, 4H), 4.06 (m, 2H), 3.49-3.36 (m, 2H), 3.24 (m, 2H), 2.15 (m, 4H), 2.07 (m, 2H), 1.79-1.68 (m, 4H), 1.59-1.35 (m, 6H), 1.33-1.23 (m, 2H), 0.83-0.65 ppm

(m, 6H); ^{13}C NMR (75 MHz, Chloroform-*d*): δ 158.28, 149.46, 148.38, 140.06, 136.32, 135.83, 132.58, 129.84, 128.56, 124.43, 122.31, 119.47, 117.75, 70.12, 66.47, 61.64, 59.21, 51.17, 37.39, 26.77, 24.93, 22.31 ppm; m.p. 227°C (decomp.); $[\alpha]_{\text{D}}^{24} = -67.4$ (*c* 1.00, CH_2Cl_2); IR (KBr), cm^{-1} : 3379 (broad), 1501, 1238, 1064, 755; HRMS (FAB⁺) calcd. for $\text{C}_{58}\text{H}_{64}\text{BrN}_4\text{O}_3^+$, $[\text{M}-\text{Br}]^+$: 943.4162 (83.3%), 945.4157 (100.0%), found: 943.4161, 945.4308.

(c) Bis(4-(cinchonidinium-N-methyl)phenyl) thioether dibromide



To a stirred suspension of (-)-cinchonine (408 mg, 1.39 mmol, 2.0 eq.) in Ethanol:DMF:CHCl₃ (5:6:2) (3 mL) was added bis(4-(bromomethyl)phenyl)sulfane^[S21] (257 mg, 0.690 mmol, 1.0 eq.), and the mixture was refluxed at 110°C for 4-5 hours, then cooled to 20°C and poured into dimethyl ether (80 mL). The solid was filtered off and isolated column from CH₂Cl₂/MeOH to obtain product **12** as a crystalline solid. (495 mg, 75%)

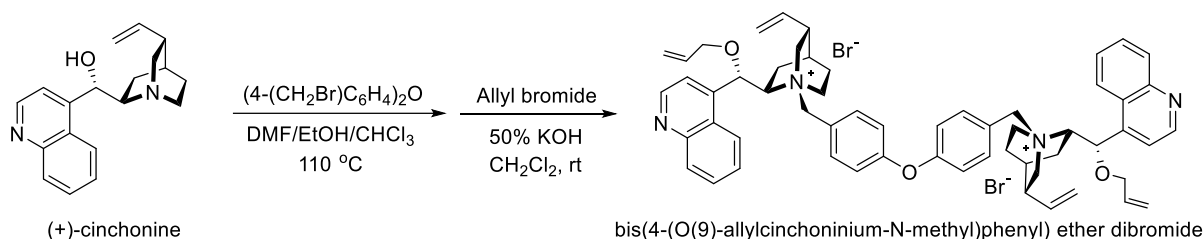
^1HMR (300 MHz, DMSO-*d*₆): δ 8.97 (d, *J* = 4.5 Hz, 2H), 8.30 (d, *J* = 7.9 Hz, 2H), 8.10 (d, *J* = 8.5 Hz, 2H), 7.91–7.69 (m, 10H), 7.56 (m, 4H), 6.76 (m, 2H), 6.54 (m, 2H), 5.75 (m, 2H), 5.66 (m, 2H), 5.29–5.01 (m, 6H), 4.94 (m, 2H), 4.26 (m, 2H), 3.91 (m, 2H), 3.78 (m, 2H), 3.36 (m, 2H), 3.26 (m, 2H), 2.68 (m, 2H), 2.03 (m, 6H), 1.82 (m, 2H), 1.27 ppm (m, 2H); ^{13}C NMR (75 MHz, DMSO-*d*₆): δ 150.06, 147.53, 145.13, 137.98, 136.33, 134.92, 130.64, 129.74, 129.70, 129.33, 127.23, 124.21, 123.72, 120.03, 116.33, 67.57, 63.94, 61.82, 59.15, 50.57, 40.33, 40.05, 39.77, 39.50, 39.22, 38.94, 38.66, 36.80, 25.84, 24.19, 20.96 ppm; m.p. 228°C (decomp.); $[\alpha]_{\text{D}}^{24} = -159.7$ (*c* 1.00, CH_2Cl_2); IR (KBr), cm^{-1} : 3383(broad), 2930, 1511, 1296, 744; HRMS (FAB⁺) calcd for $\text{C}_{52}\text{H}_{56}\text{BrN}_4\text{O}_2\text{S}^+$, $[\text{M}-\text{Br}]^+$: 943.4162 (83.3%), 945.4157 (100.0%), found: 943.4161, 945.4308.

(d) Bis(4-(O(9)-allyl)cinchonidinium-N-methyl)phenyl thioether dibromide (8)

The same as in (b);

^1H NMR (300 MHz, Chloroform-*d*): δ 8.97 (d, $J = 7.6, 4.4$ Hz, 2H), 8.85 (d, $J = 8.9$ Hz, 2H), 8.13 (d, $J = 8.3, 4.8$ Hz, 2H), 7.97 (m, 4H), 7.90 (m, 2H), 7.69 (m, 2H), 7.61 (m, 2H), 7.44 (d, $J = 8.3$ Hz, 4H), 6.60 (d, $J = 11.9$ Hz, 2H), 6.23 (m, 2H), 6.20-6.02 (m, 2H), 5.66 (m, 2H), 5.48-5.34 (m, 6H), 4.98 (d, $J = 10.6$ Hz, 2H), 4.91 (m, 2H), 4.62 (m, 4H), 4.29 (m, 4H), 4.12-3.99 (m, 2H), 3.52-3.41 (m, 2H), 3.27 (m, 2H), 2.73 (m, 2H), 2.17 (m, 4H), 2.10 (m, 2H), 1.41 ppm (m, 2H); ^{13}C NMR (75 MHz, Chloroform-*d*): δ 149.62, 148.53, 140.05, 138.29, 136.29, 135.16, 132.59, 131.51, 130.31, 130.05, 129.10, 127.87, 126.26, 125.27, 124.60, 120.13, 118.41, 77.65, 77.22, 76.80, 70.45, 66.50, 61.78, 59.76, 51.49, 37.67, 26.91, 25.25, 22.85 ppm; m.p. 224°C (decomp.); $[\alpha]_{\text{D}}^{24} = -207.2$ (c 1.00, CH_2Cl_2); IR (KBr), cm^{-1} : 3403(broad), 2927, 1593, 1455, 1076; HRMS (FAB $^+$) calcd for $\text{C}_{58}\text{H}_{64}\text{BrN}_4\text{O}_2\text{S}^+$, $[\text{M}-\text{Br}]^+$: 959.3930 (75.1%), 961.4083 (100.0%), found: 960.4186, 962.4000.

(e) Bis(4-cinchoninium-N-methyl)phenyl)ether dibromide



A mixture of 4,4'-oxybis(bromomethyl)benzene^[S1] (200 mg, 0.562 mmol) and (+)-cinchonine (314 mg, 1.067 mmol) in a mixed solvent (5 mL, DMF:EtOH:CHCl₃, v/v 6:5:2) was stirred for 4 hr at 110 °C under nitrogen atmosphere. After cooling, the mixture was diluted with 3 mL of dichloromethane and dropped into 30 mL ethyl ether. The resulting solid was filtered and purified by flash column chromatography (10:1, CH₂Cl₂/MeOH) to afford the yellowish solid, yield (426 mg, 84%).

^1H NMR (300 MHz, DMSO-*d*₆): δ 9.00 (d, $J = 4.4$ Hz, 2H), 8.36 (d, $J = 8.5$ Hz, 2H), 8.12 (d, $J = 8.4$ Hz, 2H), 7.93-7.67 (m, 10H), 7.28 (d, $J = 8.3$ Hz, 4H), 6.82 (d, $J = 3.7$ Hz, 2H), 6.53 (m, 2H), 6.13-5.93 (m, 2H), 5.27 (s, 2H), 5.22 (d, $J = 6.9$ Hz, 2H), 5.13 (d, $J = 12.3$ Hz, 2H), 4.93 (d, $J = 12.6$ Hz, 2H), 4.21 (t, $J = 10.1$ Hz, 2H), 3.93 (m, 4H), 3.49 (m, 2H), 3.00 (m, 2H), 2.67 (m, 2H), 2.30 (t, $J = 11.5$ Hz, 2H), 1.84 (m, 6H), 1.10-1.05 ppm (m, 2H); ^{13}C NMR (75 MHz, Chloroform-*d*): δ 157.53, 150.25, 147.61, 145.16, 137.22, 135.89, 129.78, 129.49, 127.43, 124.38, 124.16, 123.28, 120.16, 119.13, 117.10, 66.95, 64.61, 61.36, 55.80, 53.57, 36.70, 26.44, 22.99, 20.79 ppm; m.p. 230°C (decomp.); $[\alpha]_{\text{D}}^{24} = +121.4$ (c 1.00, CH_2Cl_2); IR (KBr), cm^{-1} : 3213 (broad), 1658, 1502, 1239, 881; HRMS (FAB $^+$) calcd

for $C_{53}H_{56}BrN_4O_3^+$, $[M-Br]^+$: 863.3536 (86.8%), 865.3528 (100.0%), found: 863.3539, 865.3561.

(f) *Bis(4-(O(9)-allyl)cinchoninium-N-methyl)phenyl)ether dibromide (9)*

A suspension of *bis(4-(cinchoninium-N-methyl)phenyl)ether* (500 mg, 0.529 mmol) and allyl bromide (0.29 mL, 3.4 mmol) in dichloromethane (6 mL) was mixed with 50% KOH aqueous solution (1.42 mL, 12.68 mmol). The suspension was stirred at room temperature for 4 hr, then diluted with water (5 mL) and extracted with dichloromethane (2 x 10 mL). The organic solution was dried over $MgSO_4$, concentrated, and purified by flash column chromatography (10:1, $CH_2Cl_2/MeOH$) to afford the yellowish solid. (462 mg, 85%).

1H NMR (300 MHz, Chloroform-*d*): δ 8.98 (d, $J = 4.1$ Hz, 2H), 8.85 (d, $J = 8.5$ Hz, 2H), 8.16 (d, $J = 8.4$, 1.4 Hz, 2H), 8.00 (d, $J = 8.8$ Hz, 4H), 7.93 (m, 2H), 7.85-7.78 (m, 4H), 7.13 (d, $J = 8.2$ Hz, 4H), 6.45 (d, $J = 11.8$ Hz, 2H), 6.32-6.21 (m, 2H), 6.18-6.04 (m, 2H), 5.48-5.33 (m, 4H), 4.71 (m, $J = 12.2$ Hz, 2H), 4.61 (d, $J = 11.5$ Hz, 2H), 4.29 (m, 4H), 4.06 (m, 2H), 3.49-3.36 (m, 2H), 3.24 (m, 2H), 2.15 (m, 4H), 2.07 (m, 2H), 1.79-1.68 (m, 4H), 1.59-1.35 (m, 6H), 1.33-1.23 (m, 2H), 0.83-0.65 ppm (m, 6H); ^{13}C NMR(75 MHz, $CDCl_3-d$): δ 162.42, 158.49, 149.58, 148.57, 139.70, 136.03, 135.43, 132.49, 130.02, 124.88, 122.41, 119.95, 119.80, 118.32, 70.51, 61.27, 56.00, 54.67, 37.63, 27.26, 23.52, 22.25 ppm; m.p. 228°C (decomp.); $[\alpha]_D^{24} = +84.8$ (c 1.00, CH_2Cl_2); IR (KBr), cm^{-1} : 3384 (broad), 1598, 1501, 1238, 756; HRMS (FAB $^+$) calcd for $C_{58}H_{64}BrN_4O_3^+$, $[M-Br]^+$: 943.4162 (83.8%), 945.4157 (100.0%), found: 943.4160, 945.4224.

(2) Catalytic Alkylation and Product Analysis

General alkylation procedure: Benzyl bromide (14.5 μ L, 0.122 mmol) was added to a solution of N-(diphenylmethylene)glycine *tert*-butyl ester (**5**, 30.0 mg, 0.102 mmol) and PTC **7** (50 μ L, 1×10^{-3} M in CH_2Cl_2 , 0.05 mol%, solvent evaporated) in toluene/chloroform (7:3, 0.75 mL). The solution was then cooled (0 $^\circ\text{C}$), purged with nitrogen (10 min), and aqueous 50% KOH (0.25 mL, 22 eq.) was added. The solution was stirred at 0 $^\circ\text{C}$ until the starting ester **5** had been consumed (4 h). The reaction mixture was washed with brine (3 x 2 mL). The organic layer was dried over MgSO_4 and concentrated. Purification by flash column chromatography on silica gel (hexanes/ethyl acetate 98:2) afforded the desired product **6** (36 mg, 93% yield) as a colorless oil. Enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralcel OD, hexane/2-propanol (100:1.0), flow rate 0.5 mL/min, 25 $^\circ\text{C}$, $\lambda = 254$ nm, retention times: R (minor) 12.2 min, S (major) 20.5 min, 99% *ee*) The absolute configuration was confirmed by comparison of the HPLC retention time with the authentic sample synthesized by the reported procedure.^{10,11,15,22-24}

The aldimine of alanine **10** was alkylated with $\text{CsOH}\cdot\text{H}_2\text{O}$ instead of KOH in a similar process for the ketimine **5**.

(a) α -Alkylated Products (**6**)

***tert*-Butyl 2-(diphenylmethyleneamino)-3-phenylpropanoate**^[S3] (from benzyl bromide): ^1H NMR (300 MHz, Chloroform-*d*): δ 7.58 (dt, $J = 8.7, 2.1$ Hz, 2H), 7.37-7.24 (m, 6H), 7.22-7.14 (m, 3H), 7.05 (dd, $J = 7.2, 2.3$ Hz, 2H), 6.59 (d, $J = 7.2$ Hz, 2H), 4.11 (dd, $J = 9.1, 4.5$ Hz, 1H), 3.24 (dd, $J = 13.3, 4.4$ Hz, 1H), 3.16 (dd, $J = 13.3, 9.1$ Hz, 1H), 1.44 ppm (s, 9H).

***tert*-Butyl 2-(diphenylmethyleneamino)pent-4-enoate**^[S3] (from allyl bromide): ^1H NMR (300 MHz, Chloroform-*d*): δ 7.68-7.59 (m, 2H), 7.46-7.39 (m, 3H), 7.37-7.28 (m, 3H), 7.17 (dt, $J = 5.7, 2.4$ Hz, 2H), 5.73 (ddt, $J = 17.2, 10.2, 7.1$ Hz, 1H), 5.13-4.96 (m, 2H), 4.00 (dd, $J = 7.4, 5.4$ Hz, 1H), 2.62 (hept, $J = 7.1$ Hz, 2H), 1.44 ppm (s, 9H).

(E)-*tert*-Butyl 2-(diphenylmethyleneamino)-5-phenylpent-4-enoate^[S4] (from cinnamyl bromide): ^1H NMR (300 MHz, Chloroform-*d*): δ 7.64 (d, $J = 7.5$ Hz, 2H), 7.43-7.38 (m, 3H), 7.33 (d, $J = 7.4$ Hz, 2H), 7.28 (d, $J = 4.0$ Hz, 5H), 7.20 (d, $J = 4.1$ Hz, 1H), 7.16-7.10 (m, 2H), 6.40 (d, $J = 16.0$ Hz, 1H), 6.08 (dt, $J = 15.6, 7.6$ Hz, 1H), 4.08 (dd, $J = 7.5, 5.3$ Hz, 1H), 2.88-2.69 (m, $J = 7.9, 7.4$ Hz, 2H), 1.44 ppm (s, 9H).

***tert*-Butyl 2-(diphenylmethyleneamino)-3-(naphthalene-1-yl)propanoate**^[S5] (from 1-bromomethyl naphthalene): ^1H NMR (300 MHz, Chloroform-*d*): δ 7.86-7.61 (m, 4H), 7.39 (d, $J = 7.0$ Hz, 1H), 7.37-7.20 (m, 8H), 6.96 (t, $J = 7.7$ Hz, 2H), 6.26 (s, 2H), 4.31 (dd, $J = 9.6, 4.1$ Hz, 1H), 3.80 (dd, $J = 13.8, 4.1$ Hz, 1H), 3.50 (dd, $J = 13.8, 9.5$ Hz, 1H), 1.46 ppm (s, 9H).

***tert*-Butyl 2-(diphenylmethyleneamino)pent-4-ynoate**^[S4] (from propargyl bromide): ^1H NMR (300 MHz, Chloroform-*d*): δ 7.69-7.63 (m, 2H), 7.48-7.43 (m, 3H), 7.38-7.32 (m, 3H), 7.26 (m, 2H), 4.17

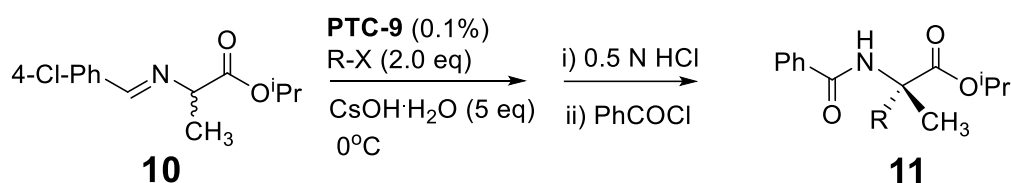
(dd, $J = 8.0, 5.5$ Hz, 1H), 2.78 (dq, $J = 6.0, 2.9$ Hz, 2H), 1.95 (t, $J = 2.7$ Hz, 1H), 1.45 ppm (s, 9H).

tert-Butyl 3-(carbo-tert-butoxy)-2-aminopropanoate^[S6] (from tert-butyl bromoacetate): ¹H NMR (300 MHz, Chloroform-*d*): δ 3.63 (t, $J = 6.0$ Hz, 1H), 2.68 (dd, $J = 16.3, 4.7$ Hz, 1H), 2.56 (dd, $J = 16.3, 7.1$ Hz, 1H), 1.73 (s, 2H), 1.47 ppm (d, $J = 1.4$ Hz, 18H).

tert-Butyl 2-(diphenylmethyleamino)propanoate^[S3] (from methyl iodide): ¹H NMR (300 MHz, Chloroform-*d*): δ 7.67-7.60 (m, 2H), 7.45 (m, 3H), 7.39-7.29 (m, 3H), 7.19 (m, 2H), 4.04 (q, $J = 6.7$ Hz, 1H), 1.45 (s, 9H), 1.40 ppm (d, $J = 6.7$ Hz, 3H).

tert-Butyl 2-(diphenylmethyleamino)butanoate^[S4] (from ethyl iodide): ¹H NMR (300 MHz, Chloroform-*d*): δ 7.69-7.63 (m, 2H), 7.43 (dd, $J = 5.2, 1.9$ Hz, 3H), 7.37-7.30 (m, 3H), 7.17 (dt, $J = 5.1, 2.6$ Hz, 2H), 3.85 (dd, $J = 7.6, 5.3$ Hz, 1H), 2.01-1.79 (m, 2H), 1.44 (s, 9H), 0.87 ppm (t, $J = 7.4$ Hz, 3H).

(b) α,α -Dialkylated Products (11)



Isopropyl 2-(4-Cl-benzylideneamino)propanoate^[S7] (**10**): ¹H NMR (600 MHz, CDCl₃): δ 8.27 (s, 1H), 7.72 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.5$ Hz, 2H), 5.07 (p, $J = 6.3$ Hz, 1H), 4.13-4.08 (m, 1H), 1.51 (d, $J = 6.8$ Hz, 3H), 1.25 ppm (dd, $J = 10.4, 6.3$ Hz, 6H); ¹³C NMR (150 MHz, CDCl₃): δ 171.88, 161.32, 136.95, 134.35, 129.66, 128.83, 68.44, 67.87, 21.75, 21.73, 19.32 ppm.

Isopropyl 2-benzamido-2-methyl-3-phenylpropanoate (**11**, from benzyl bromide): ¹H NMR (300 MHz, CDCl₃): δ 7.68 (d, $J = 7.1$ Hz, 2H), 7.51-7.44 (m, 1H), 7.43-7.36 (m, 2H), 7.20 (dd, $J = 5.1, 2.0$ Hz, 3H), 7.08 (dd, $J = 6.7, 3.0$ Hz, 2H), 6.86 (s, 1H), 4.33-4.19 (m, 2H), 3.74 (d, $J = 13.6$ Hz, 1H), 3.29 (d, $J = 13.5$ Hz, 1H), 1.80 (s, 3H), 1.33 ppm (t, $J = 7.2$ Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 174.22, 167.00, 136.70, 135.34, 131.60, 130.08, 128.73, 128.39, 127.08, 127.02, 62.13, 61.72, 41.27, 23.67, 14.32 ppm; HRMS (ESI): [M+H]⁺ calcd. for C₂₀H₂₄NO₃⁺, 326.1751; found, 326.1745.

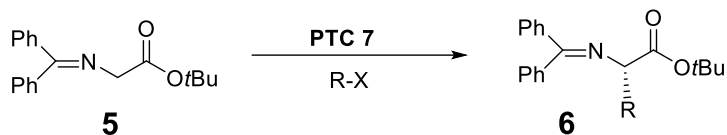
Isopropyl 2-benzamido-2-methylpent-4-enoate (**11**, from allyl bromide): ¹H NMR (600 MHz, CDCl₃): δ 7.80-7.74 (m, 2H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.06 (s, 1H), 5.68 (ddt, $J = 17.4, 10.2, 7.4$ Hz, 1H), 5.16-5.05 (m, 3H), 3.23-3.17 (m, 1H), 2.64 (dd, $J = 13.9, 7.5$ Hz, 1H), 1.73 (s, 3H), 1.29 ppm (t, $J = 6.1$ Hz, 6H); ¹³C NMR (150 MHz, CDCl₃): δ 173.73, 166.37, 135.05, 132.51, 131.42, 128.55, 126.84, 119.27, 69.61, 60.24, 40.37, 22.97, 21.74, 21.71 ppm; HRMS (ESI): [M+H]⁺ calcd. for C₁₆H₂₂NO₃⁺, 276.1594; found, 276.1587.

Isopropyl 2-benzamido-2-methylbutanoate (11, from ethyl iodide): ^1H NMR (300 MHz, CDCl_3): δ 7.84-7.80 (m, 2H), 7.53-7.42 (m, 3H), 7.17 (s, 1H), 5.14 (p, $J = 6.3$ Hz, 1H), 2.63-2.50 (m, 1H), 1.99-1.86 (m, 1H), 1.74 (s, 3H), 1.31 (dd, $J = 6.3, 1.2$ Hz, 6H), 0.84 ppm (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 174.42, 166.17, 135.14, 131.38, 128.55, 126.85, 69.50, 61.39, 29.01, 22.97, 21.69, 8.58 ppm; HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{15}\text{H}_{22}\text{NO}_3^+$, 264.1594 (100.0%): found, 264.1592.

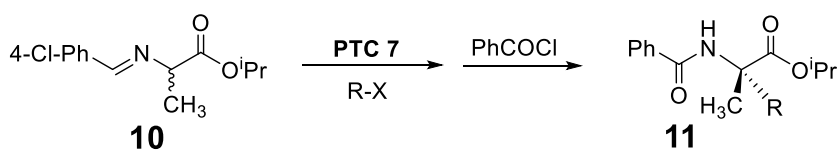
Isopropyl 2-benzamido-2-methylpent-4-ynoate (11, from propargyl bromide): ^1H NMR (600 MHz, CDCl_3) δ 7.83-7.77 (m, 2H), 7.53-7.49 (m, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.09 (s, 1H), 5.13 (p, $J = 6.3$ Hz, 1H), 3.32 (dd, $J = 16.9, 2.6$ Hz, 1H), 2.96 (dd, $J = 16.8, 2.7$ Hz, 1H), 1.97 (t, $J = 2.6$ Hz, 1H), 1.72 (s, 3H), 1.29 ppm (dd, $J = 10.3, 6.3$ Hz, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 172.62, 166.75, 134.66, 131.59, 128.58, 126.99, 70.95, 69.91, 59.26, 26.25, 22.77, 21.65, 21.61 ppm; HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{16}\text{H}_{20}\text{NO}_3^+$, 274.1438: found, 274.1435.

(c) Chiral HPLC Conditions

Chiral column: DAICEL Chiralcel OD (4.6 x 250 mm), temperature: 23 °C, detection: $\lambda = 254$ nm. The retention time was established by analysis of the racemate of which the enantiomers were fully resolved. Eluents were adjusted on each alkylated product.



alkylated imine (6) R-X	eluent : (hexane : 2-propanol)	flow rate (mL/min)	retention times (min)	
			minor (<i>R</i>)	major (<i>S</i>)
PhCH ₂ -Br	100 : 1.0	0.5	12.7	19.7
	100 : 1.0	0.5	9.1	8.5
	100 : 1.0	0.5	18.1	14.4
	100 : 1.0	0.5	19.6	21.2
	100 : 1.0	0.5	11.6	11.0
	100 : 4.0	0.5	12.0	15.0
CH ₃ I	100 : 1.0	0.5	9.5	8.9
CH ₃ CH ₂ I	100 : 1.0	0.8	9.5	8.8



alkylated imine (11) R-X	eluent : (hexane : 2-propanol)	flow rate (mL/min)	retention times (min)	
			minor (<i>R</i>)	major (<i>S</i>)
benzyl Br	100 : 2.0	0.5	9.7	11.4
allyl Br	100 : 2.0	0.5	21.8	26.8
Ethyl iodide	100 : 2.0	0.5	17.4	21.1
Propargyl Br	100 : 2.0	0.5	22.6	27.6

(3) References

- S1. Beever, W. H.; Stille, J. K. *Macromolecules* **1979**, *12*, 1033–8.
- S2. S. Yao, H.-Y. Ahn, X. Wang, J. Fu, E. W. Van Stryland, D. J. Hagan, K. D. Belfield, *J. Org. Chem.*, **2010**, *75*, 3965-3974
- S3. S.-s. Jew, B.-S. Jeong, M.-S. Yoo, H. Huh, H.-g. Park, *Chem. Commun.*, **2001**, 1244.
- S4. S. Shirakawa, Y. Tanaka, K. Maruoka, *Org. Lett.*, **2004**, *6*, 1429.
- S5. Sanjeev Kumar and Uma Ramachandran, *Tetrahedron*, **2005**, *61*, 7022.
- S6. T. Ooi, M. Takeuchi, M. Kameda, K. Maruoka, *J. Am. Chem. Soc.* **2000**, *122*, 5228.
- S7. Y.N Belokon, K.A Kochetkov, T.D. Churkina, N.S. Ikonnikov, A.A. Chesnokov, O.V. Larionov, I.Singh, V.S. Parmar, Š. Vyskočil, H.B. Kagan *J. Org. Chem.*, **2010**, *75*, 3965-3974

(4) Quantum Calculation Data

Energy is in Hartree. All calculations were performed with GAUSSIAN 09. (Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, Revision C.01; Gaussian, Inc.: Wallingford, CT, 2010)

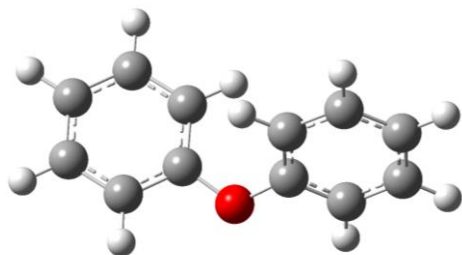
(a) Torsional energy of diphenyl ether/thioether and benzophenone

Torsion of diphenyl ether and diphenyl thioether was calculated at M062X/6-31G(d,p). Torsional angle was between C_{ipso}-(O/S)-C_{ipso}-C_{ortho}, and fixed at 0 ~ 90° with a 10° interval.

Around the angle of 40°, there was a minimum which was energy-minimized at no frozen angle; the free torsional angle was 39.5° for diphenyl ether; 43.3° for diphenyl thioether; benzophenone has 30.3° of the free torsional angle. The butterfly forms were calculated with two fixed 90° torsional angles between phenyl rings each other.

Torsion angle (C-X-C-C)	Diphenyl ether	Diphenyl thioether	Benzophenone
	E	E	E
0.0	-538.293606	-861.257618	-576.394732
10.0	-538.293734	-861.257695	-576.396057
20.0	-538.293978	-861.257870	-576.396945
30.0	-538.294173	-861.258057	-576.397259 (30.3°)
40.0	-538.294230 (39.5°)	-861.258173 (43.3°)	-576.396949
50.0	-538.294164	-861.258152	-576.396014
60.0	-538.294001	-861.258052	-576.394571
70.0	-538.293817	-861.257876	-576.392935
80.0	-538.293664	-861.257697	-576.391557
90.0	-538.293606	-861.257617	-576.390971
90.0 (butterfly)	-538.287583	-861.255239	-576.376611

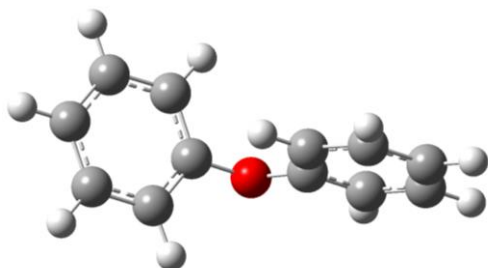
Diphenyl ether (unfrozen; torsional angle = 39.5°)



$$E(\text{RM062X}) = -538.294230021$$

C	-3.68189200	0.70694900	-0.15211100
C	-2.60092800	1.25150900	-0.84132600
C	-1.35055200	0.64316000	-0.79576500
C	-1.18853700	-0.51817200	-0.04145800
C	-2.26028900	-1.07322500	0.65153500
C	-3.50648400	-0.45853900	0.58976400
O	0.00000000	-1.20933400	-0.00037800
C	1.18858700	-0.51835400	0.04158900
C	1.35055900	0.64284300	0.79608100
C	2.60082900	1.25149300	0.84134800
C	3.68174800	0.70720700	0.15187400
C	3.50652700	-0.45846800	-0.58975700
C	2.26045900	-1.07338900	-0.65128700
H	-4.65364500	1.18666400	-0.19456000
H	-2.72994500	2.15530600	-1.42814300
H	-0.50625300	1.05767800	-1.33620100
H	-2.09674800	-1.97967900	1.22364500
H	-4.34250900	-0.89174900	1.12923600
H	0.50631900	1.05716300	1.33676200
H	2.72974000	2.15535600	1.42808300
H	4.65337100	1.18721500	0.19404400
H	4.34257400	-0.89157700	-1.12927500
H	2.09693900	-1.97978700	-1.22348900

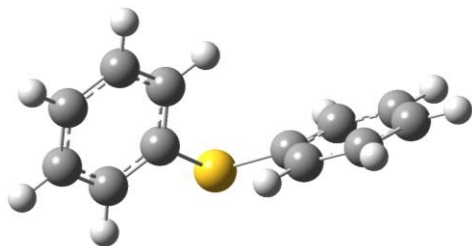
Diphenyl ether (skewed; torsional angle = 90.0°)



$$E(\text{RM062X}) = -538.293605728$$

C	-3.66243100	0.59302800	0.00207900
C	-3.02269000	0.32558800	-1.20632900
C	-1.76819200	-0.27734600	-1.21759400
C	-1.16590500	-0.61128600	-0.00930500
C	-1.79105900	-0.34790500	1.20457600
C	-3.04561000	0.25535300	1.20464000
O	0.05537700	-1.25524900	-0.01575800
C	1.19473300	-0.48778000	-0.00433500
C	1.18956000	0.90508000	0.02914700
C	2.40672900	1.58481900	0.03916500
C	3.61260800	0.89390600	0.01646900
C	3.59985800	-0.50048800	-0.01675200
C	2.39794400	-1.19408200	-0.02743700
H	-4.64081100	1.06155700	0.00642600
H	-3.50166000	0.58533100	-2.14473100
H	-1.24816600	-0.49800600	-2.14374300
H	-1.28849500	-0.62266800	2.12584500
H	-3.54212600	0.46067200	2.14739000
H	0.25274300	1.44968900	0.04733400
H	2.40272800	2.66994000	0.06528800
H	4.55344200	1.43309600	0.02453300
H	4.53365500	-1.05335200	-0.03492100
H	2.36240500	-2.27759700	-0.05330600

Diphenyl thioether (unfrozen; torsional angle = 43.3°)

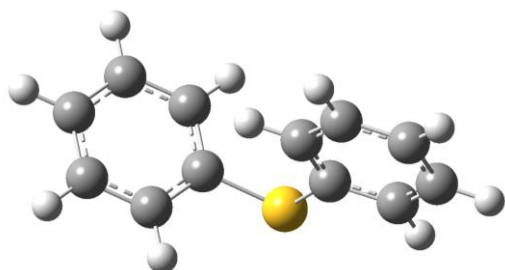


E(RM062X) = -861.258173356

C	3.64202300	-1.10775800	-0.20624000
C	2.49932700	-1.42344900	-0.93979000
C	1.37733000	-0.60523700	-0.88167400
C	1.38561000	0.52793600	-0.06368600
C	2.52436700	0.83999200	0.67976900
C	3.65267000	0.02738100	0.59778000
S	0.00234400	1.65105800	0.00258300
C	-1.38493500	0.53276900	0.06614200
C	-1.39153600	-0.58420700	0.90639700
C	-2.51484000	-1.40068500	0.96141200
C	-3.64433500	-1.09877500	0.20180200

C	-3.64056100	0.02029700	-0.62432200
C	-2.51026200	0.83072700	-0.70280700
H	4.51776500	-1.74582300	-0.26077000
H	2.48508800	-2.30587800	-1.57154900
H	0.49075000	-0.84333300	-1.46113600
H	2.52040400	1.71304400	1.32470900
H	4.53571300	0.27749100	1.17693800
H	-0.51488100	-0.81080500	1.50529500
H	-2.51237700	-2.27059400	1.61043100
H	-4.52144200	-1.73520200	0.25380400
H	-4.51339200	0.25916400	-1.22335200
H	-2.49428400	1.69104900	-1.36439100

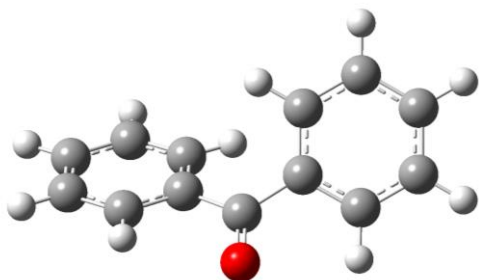
Diphenyl thioether (skewed; torsional angle = 90.0°)



$E(\text{RM062X}) = -861.257617357$

C	3.67542200	0.94334100	0.00116500
C	3.09450700	0.56101300	1.20800300
C	1.94479400	-0.22373200	1.21118000
C	1.37497300	-0.62802100	0.00226700
C	1.95863800	-0.24575600	-1.20710600
C	3.10753800	0.54034500	-1.20501800
S	-0.08261700	-1.65432700	0.00301600
C	-1.39937000	-0.44948300	-0.00044300
C	-1.19741000	0.93037900	-0.01007500
C	-2.29570500	1.78781400	-0.01228600
C	-3.59212600	1.28465500	-0.00515400
C	-3.78895000	-0.09469600	0.00432600
C	-2.70184500	-0.95942600	0.00681500
H	4.57232800	1.55426300	0.00075800
H	3.53653800	0.87314700	2.14856000
H	1.48170300	-0.52717900	2.14441600
H	1.50613500	-0.56590400	-2.13992900
H	3.55971100	0.83632200	-2.14598100
H	-0.19200600	1.33712900	-0.01597000
H	-2.12901200	2.86046300	-0.01985600
H	-4.44171800	1.95902400	-0.00689300
H	-4.79482000	-0.50248000	0.00995700
H	-2.85978900	-2.03415200	0.01465100

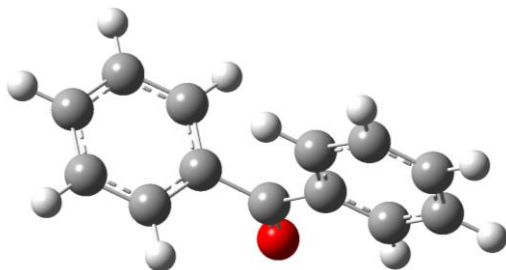
Benzophenone (unfrozen; torsional angle = 30.3°)



E(RM062X) = -576.397259190

C	3.79187600	-0.90376100	-0.12257200
C	2.67911800	-1.53186400	-0.67499300
C	1.43267100	-0.91415600	-0.62298600
C	1.29907100	0.34288600	-0.02668500
C	2.42563700	0.98010000	0.50198700
C	3.66454000	0.35405400	0.46602000
C	0.00003000	1.09183800	0.00029600
C	-1.29908600	0.34304500	0.02724900
C	-1.43298800	-0.91388500	0.62371900
C	-2.67945500	-1.53159300	0.67516900
C	-3.79189400	-0.90363100	0.12191900
C	-3.66427200	0.35407400	-0.46681800
C	-2.42535500	0.98013300	-0.50220500
O	0.00009400	2.30859500	0.00009600
H	4.76120200	-1.39092700	-0.15644100
H	2.78135600	-2.50218600	-1.14964200
H	0.56804300	-1.39778900	-1.06635800
H	2.30418500	1.96816900	0.93351200
H	4.53378000	0.84630800	0.88966900
H	-0.56856900	-1.39741100	1.06762500
H	-2.78196000	-2.50182500	1.14994200
H	-4.76122100	-1.39083100	0.15530000
H	-4.53327300	0.84619200	-0.89111400
H	-2.30365400	1.96810700	-0.93387800

Benzophenone (skewed; torsional angle = 90.0°)



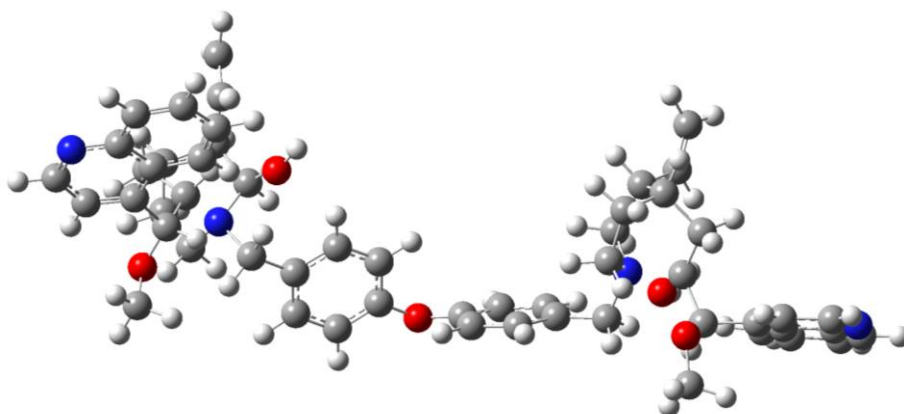
$$E(RM062X) = -576.390970763$$

C	-3.75922000	-0.79681400	-0.00531200
C	-3.12990000	-0.50826800	1.20303200
C	-1.88484100	0.11410700	1.21020400
C	-1.26948800	0.45376500	0.00548600
C	-1.89884500	0.16302700	-1.20472900
C	-3.14288900	-0.46134400	-1.20827400
C	0.06077900	1.16534300	0.01083400
C	1.30382600	0.33303300	0.00320500
C	1.25690900	-1.06279400	-0.01000300
C	2.43999500	-1.79659600	-0.01766600
C	3.66666900	-1.13866000	-0.01204500
C	3.71624000	0.25608900	0.00113500
C	2.53873900	0.98999300	0.00872200
O	0.11015600	2.37759100	0.01724000
H	-4.72966500	-1.28229900	-0.00950500
H	-3.60901700	-0.76716200	2.14166300
H	-1.39063100	0.34174200	2.15018700
H	-1.41576500	0.42960200	-2.14021400
H	-3.63201900	-0.68390400	-2.15104500
H	0.29739100	-1.57057700	-0.01460500
H	2.40408300	-2.88091500	-0.02810100
H	4.58801500	-1.71255000	-0.01804800
H	4.67449700	0.76511900	0.00544500
H	2.54401700	2.07494600	0.01877300

(b) TS of 4,4'-bis(O(9)-allyl-cinchonidinium-N-methyl)diphenyl ether, Enolate 5 and benzylbromide

The geometry of a simple model of PTC 7 (*Bis*(4-(O(9)-methylcinchonidinium-N-methyl)phenyl)ether dihydroxide) was energy-minimized at B3LYP/6-31G(d). The TS of PTC 7 and PTC 4, the (*Z*)-enolate 5, and benzyl bromide were energy-minimized at B3LYP/6-31G(d) and LANL2DZ (for bromine). Each TS has only one imaginary frequency. Their energies were not corrected. The secondary counter anion was a hydroxide.

***Bis*(4-(O(9)-methylcinchonidinium-N-methyl)phenyl)ether dihydroxide (unfrozen; torsional angle = 57.9°)**



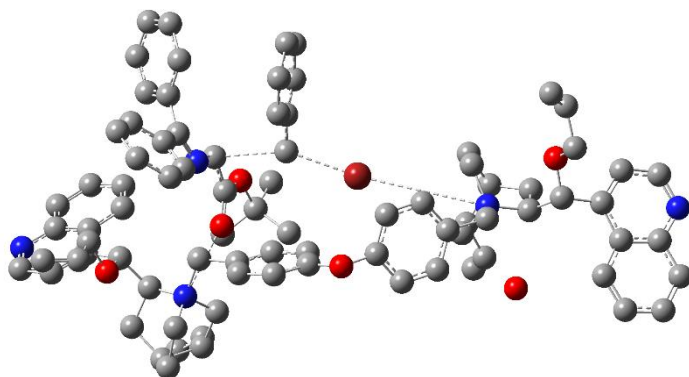
E(RB3LYP) = -2689.96678808

C	5.15090000	-1.04056700	-0.98352900
C	6.66067300	-2.91300600	-0.22720300
C	5.48258700	-1.54667200	1.46247700
C	7.32450400	-0.49900600	0.20742400
C	3.77977800	-1.66335300	-0.92691600
C	7.50494500	-3.45007500	0.95029600
N	6.15347600	-1.52267200	0.08578700
C	6.52346900	-1.82772700	2.57785600
C	8.43262400	-1.14507200	1.06135800
C	7.84005900	-2.28668300	1.89932700
C	2.77236500	-0.99135900	-0.21338800
C	3.44491600	-2.83217500	-1.62457400
C	1.47299200	-1.48946200	-0.17232500
C	1.16284700	-2.66457800	-0.86658700
O	-0.08137400	-3.25890800	-0.81548200
C	-1.23726200	-2.50359400	-0.84170700
C	-1.36939100	-1.34921300	-1.61874500
C	-2.59688100	-0.68732000	-1.64816800
C	-3.69389000	-1.15779600	-0.91375500

C	-3.54720400	-2.33807400	-0.16436600
C	7.80868900	0.08708600	-1.13341800
C	8.95768500	1.07634300	-0.90882200
C	8.73273500	2.42427500	-0.47855100
C	9.88559100	3.27964700	-0.38599500
N	11.15850800	2.85833400	-0.65255800
C	11.31595600	1.60408900	-1.01580100
C	10.25465200	0.68123200	-1.16476600
C	7.45331600	2.95764700	-0.14656500
C	7.33927700	4.28090200	0.22692400
C	8.46901600	5.12929600	0.29300800
C	9.71889000	4.63543500	-0.00141700
O	8.19169300	-0.97529200	-2.01027300
C	6.69640000	-0.63507500	3.49544700
C	6.94301400	-0.73096900	4.80247600
C	-5.05399200	-0.51187900	-0.97255100
N	-5.31489000	0.60335100	0.06160600
C	-4.57929200	1.87356900	-0.30404300
C	-4.84837300	0.15165600	1.44844800
C	-6.85001200	0.84868500	0.19376800
C	-4.69392100	2.90413300	0.84188900
C	-5.29036500	1.16600200	2.53552500
C	-7.05552500	2.14241200	1.00479900
C	-5.79056200	2.44742000	1.81921600
C	-7.62647200	0.79508500	-1.13671200
C	-9.11925200	1.05281600	-0.90346900
C	-9.64982600	2.29121500	-1.20120700
C	-11.03623500	2.52146300	-1.04316000
N	-11.89387100	1.61266000	-0.63272800
C	-11.39865000	0.37634800	-0.32399400
C	-10.00467100	0.03475200	-0.42158100
C	-12.32781000	-0.60377300	0.11169000
C	-11.90251200	-1.86759600	0.45039000
C	-10.52839900	-2.19486400	0.37887200
C	-9.59030500	-1.27556100	-0.04347400
O	-7.06691200	1.73583000	-2.05672000
C	-6.30694000	0.56293300	3.48318000
C	-6.38754300	0.86605000	4.77933200
C	-7.39301700	1.47347800	-3.41662300
C	8.22935600	-0.60276800	-3.38298700
C	2.14559200	-3.33628200	-1.59648400
C	-2.32617300	-3.00352300	-0.12177800
O	5.06889300	1.18312400	0.74253100
O	-6.68988200	-1.93404900	0.82805300
H	-7.04025300	-2.73169700	1.25479700
H	4.69113600	1.97916900	1.14851400
H	5.05154900	0.03492900	-0.77024500
H	5.64142700	-1.24322100	-1.93750100
H	7.23825900	-2.82754700	-1.14613200
H	5.77805500	-3.52863700	-0.41074600
H	4.72248900	-2.32711500	1.41081000
H	5.02783700	-0.54296000	1.54629700
H	6.81656900	0.33333700	0.72113400

H	6.96177100	-4.23490400	1.48935800
H	8.42400900	-3.90181500	0.56137400
H	6.16445500	-2.67172400	3.18097000
H	9.23925800	-1.53563100	0.43054200
H	8.87006200	-0.37471000	1.70267000
H	8.55498200	-2.60987900	2.66280600
H	3.05115300	-0.07060600	0.30090600
H	4.19686700	-3.34574700	-2.22006300
H	0.70174900	-0.97218200	0.38908800
H	-0.53033400	-0.98458000	-2.20167300
H	-2.70200800	0.19337300	-2.27846800
H	-4.42264500	-2.70594600	0.37159600
H	6.97701700	0.63880200	-1.58641200
H	12.33721300	1.28139500	-1.21982700
H	10.46142200	-0.32887400	-1.50175600
H	6.55639700	2.32601900	-0.10942200
H	6.35936200	4.67376800	0.48674500
H	8.34829100	6.16896900	0.58704700
H	10.61129000	5.25121200	0.05159000
H	6.58097700	0.34515800	3.03255700
H	7.02611200	-1.69391400	5.30492000
H	7.06777800	0.15046200	5.42551700
H	-5.22904900	-0.04056500	-1.94149700
H	-5.80996600	-1.27172100	-0.71917400
H	-5.02833000	2.23097600	-1.22926000
H	-3.54315700	1.58621600	-0.49272600
H	-3.76245700	0.07050100	1.38619700
H	-5.32309200	-0.83883900	1.57144900
H	-7.15639100	-0.05540100	0.74438400
H	-3.73699100	3.00746400	1.36652000
H	-4.94062500	3.88593100	0.42330100
H	-4.40698000	1.45241500	3.12085500
H	-7.27951400	2.98964500	0.34658000
H	-7.92025500	2.00692200	1.66052500
H	-5.99263300	3.22836900	2.55934300
H	-7.52242700	-0.21343600	-1.55302500
H	-9.01087400	3.08285600	-1.57757200
H	-11.44513200	3.50392600	-1.28056700
H	-13.37153800	-0.31056900	0.16702300
H	-12.61959800	-2.61380700	0.78346700
H	-10.19896000	-3.18821000	0.67342100
H	-8.53023400	-1.55879500	-0.00963700
H	-6.98053300	-0.17837100	3.05259300
H	-5.70563400	1.57307900	5.25030900
H	-7.13682400	0.41577200	5.42471400
H	-6.88570200	2.23530600	-4.01375300
H	-8.47328100	1.53478400	-3.59548600
H	-7.03924300	0.47817100	-3.72380000
H	8.97272700	0.18102100	-3.57208700
H	7.24565400	-0.24746200	-3.72400700
H	8.50180900	-1.49990200	-3.94441200
H	1.87521900	-4.23786900	-2.13676300
H	-2.20027900	-3.91633500	0.45222300

TS of PTC 7, Enolate 5 and benzylbromide



E(RB3LYP) = -3994.29291875, imaginary frequency = -217.6784

C	-3.66913900	-1.44041700	1.55638300
C	-4.49682600	-3.71639500	2.24774600
C	-3.15597000	-3.48890400	0.18772400
C	-5.45491700	-2.62833000	0.17339100
C	-2.32997600	-1.47102800	2.24495300
C	-4.79760100	-5.15168500	1.76736200
N	-4.19779300	-2.80945200	1.06515600
C	-3.72228500	-4.79437200	-0.44663200
C	-6.09915900	-4.01835400	-0.01272400
O	-3.01629700	-0.78107900	-1.52074600
C	-2.91103000	0.33562900	-2.06450300
C	-5.05955500	-5.12090400	0.25281400
C	-1.15307300	-1.23992500	1.51496900
C	-2.22007000	-1.62217800	3.63919900
C	0.09441500	-1.17985100	2.13316200
C	0.17922800	-1.35767000	3.52015700
O	1.34864500	-1.32787300	4.22810300
C	2.53791800	-1.01713000	3.56452200
C	2.90141900	0.31756600	3.40256000
C	4.10756200	0.61770400	2.76955500
C	4.93931000	-0.40389000	2.29336700
C	4.57070600	-1.74388500	2.50262300
C	-6.44411200	-1.52589600	0.63644600
C	-7.65066000	-1.49865000	-0.31012300
C	-7.59373300	-0.88381400	-1.60079900
C	-8.77482300	-0.94995500	-2.41638700
N	-9.93018400	-1.55421200	-2.00955100
C	-9.94183400	-2.09229500	-0.80898700
C	-8.83470300	-2.09433200	0.07296000
C	-6.44947200	-0.21749800	-2.11849200
C	-6.47000700	0.33977100	-3.38002600

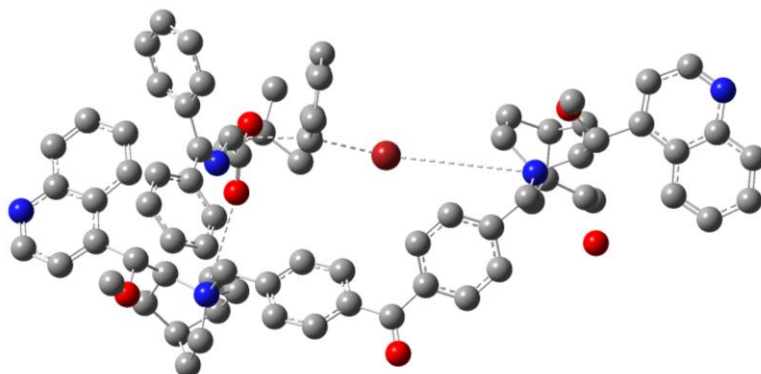
C	-7.63264700	0.26496000	-4.18405100
C	-8.76124000	-0.36405800	-3.70983300
O	-6.83282200	-1.78591900	1.97864900
C	-3.76401400	-4.72118000	-1.95975300
C	-4.67037800	-5.27875000	-2.76454400
C	-3.23061300	1.61166600	-1.48429600
N	-3.78963300	1.65286500	-0.24328500
C	-4.39770600	2.70365700	0.24975600
C	-4.73967800	3.93402400	-0.53674200
C	-4.81489900	2.65342200	1.67143100
O	-2.44126900	0.49722700	-3.34040500
C	-1.96685900	-0.61071000	-4.17059900
C	-3.13186500	-1.54939500	-4.51019700
C	-0.80375400	-1.35328300	-3.49984800
C	-1.47594000	0.10594600	-5.43411600
C	-5.53077500	3.84766400	-1.69564400
C	-5.87555300	4.99264800	-2.41401100
C	-5.43328400	6.24810700	-1.99027100
C	-4.64963500	6.34869000	-0.83893600
C	-4.31175600	5.20394300	-0.11648300
C	-5.91696400	3.39130100	2.14835000
C	-6.31028500	3.31607300	3.48483700
C	-5.60899600	2.51237000	4.38724600
C	-4.50410200	1.78335500	3.93336700
C	-4.11390400	1.85294000	2.59755600
C	-0.72521100	1.86985600	-0.98121000
Br	1.71927700	1.00520900	-0.85023100
C	-0.68401900	3.21926100	-0.47042500
C	-0.88340800	3.47440300	0.90185400
C	-0.82429000	4.77412600	1.39787500
C	-0.57185900	5.84336400	0.53328200
C	-0.37893400	5.60609900	-0.83311400
C	-0.43256700	4.30964600	-1.32971700
C	6.26462200	-0.13293900	1.62520600
N	6.21545700	0.07651300	0.10088900
C	5.68444300	1.45427500	-0.24497200
C	5.29733400	-0.96530200	-0.54755900
C	7.62930900	-0.18201900	-0.50159700
C	5.51405700	1.59416300	-1.77431200
C	5.37729800	-0.88331500	-2.09475600
C	7.62056800	0.28863800	-1.96889700
C	6.17396600	0.39305900	-2.47069900
C	8.79802800	0.37201100	0.33896600
C	10.14376000	0.07574600	-0.33242400
C	10.79835300	1.08021200	-1.01616900
C	12.06708300	0.83368500	-1.59033200
N	12.70404500	-0.31450300	-1.51031900
C	12.08033000	-1.33245800	-0.84369600
C	10.77944500	-1.20559800	-0.24245500
C	12.77315000	-2.56801400	-0.75197200
C	12.20484500	-3.64134100	-0.10474300
C	10.91492000	-3.52277900	0.46382000
C	10.20583200	-2.34027100	0.40271700

O	8.61239500	1.77390700	0.54825400
C	5.95176700	-2.14896100	-2.69215800
C	5.51762000	-2.70588500	-3.82414400
O	7.18477100	-2.67903800	0.85748000
C	9.33228600	2.29655900	1.66877000
C	-7.41053900	-0.64652200	2.65217400
C	-0.98367500	-1.57677900	4.27304900
C	3.36785100	-2.05221900	3.13533400
C	9.06169600	3.76844400	1.76062500
C	8.60516600	4.38014400	2.85339600
C	-7.70528300	-1.03951800	4.06719400
C	-8.91161100	-0.95657200	4.62803000
H	-3.62822700	-0.80627500	0.66708600
H	-4.44247800	-1.07647300	2.23191900
H	-5.34246000	-3.26327000	2.76128600
H	-3.61767200	-3.67500700	2.89073600
H	-2.30325100	-3.68747200	0.83732800
H	-2.86358700	-2.75118100	-0.56110000
H	-5.03508200	-2.27987500	-0.77289400
H	-3.96183900	-5.82199900	1.99803800
H	-5.67518600	-5.53328100	2.29943700
H	-3.01505100	-5.59700300	-0.19005500
H	-6.94118400	-4.14232900	0.67609800
H	-6.49877400	-4.07566800	-1.02660300
H	-1.21352600	-1.08727800	0.44116300
H	-3.11583500	-1.75453700	4.24253100
H	0.97557100	-0.96538900	1.53818200
H	2.24467400	1.10243900	3.76363900
H	4.39740200	1.65846500	2.64942200
H	5.25827600	-2.51245300	2.14259800
H	-0.89573300	-1.68900600	5.34899700
H	3.06629400	-3.08209100	3.30213200
H	-5.93601100	-0.55437300	0.58899900
H	-10.87344900	-2.56435300	-0.49725200
H	-8.92198300	-2.55763600	1.04985000
H	-5.54456500	-0.13653200	-1.52740200
H	-5.58044800	0.83896400	-3.75333000
H	-7.63099200	0.70988300	-5.17532800
H	-9.67137600	-0.43450000	-4.29697100
H	-2.92763000	-4.18790900	-2.41184700
H	-5.52505200	-5.83990700	-2.39551600
H	-4.58173800	-5.19806200	-3.84397500
H	-5.43770500	-6.09178000	-0.08158000
H	-3.24842000	2.46645800	-2.15690600
H	-3.94595600	-0.99442200	-4.98923200
H	-3.52292800	-2.03000500	-3.61195300
H	-2.79348100	-2.32417000	-5.20857400
H	-1.13992800	-1.90429400	-2.62039600
H	-0.01900600	-0.65630300	-3.18678500
H	-0.36403700	-2.06158500	-4.21223100
H	-0.65434000	0.78876800	-5.19496100
H	-2.28626500	0.68703400	-5.88680500
H	-1.11724100	-0.62280500	-6.16905600

H	-5.88979900	2.87639800	-2.02343800
H	-6.49571800	4.90451700	-3.30261600
H	-5.70023700	7.14020900	-2.55091100
H	-4.29871700	7.32073300	-0.50149200
H	-3.69839400	5.28811900	0.77511700
H	-6.47343500	4.02096000	1.46115100
H	-7.16978100	3.89000800	3.82254500
H	-5.90960800	2.46523400	5.43048600
H	-3.92869600	1.17483000	4.62765700
H	-3.24214300	1.30813900	2.25257600
H	-0.66223800	1.68032300	-2.03946600
H	-0.96873800	1.05226400	-0.32614900
H	-1.06443100	2.64091000	1.57382100
H	-0.97211900	4.95451800	2.45935100
H	-0.52168600	6.85734800	0.92140400
H	-0.18219600	6.43597200	-1.50637500
H	-0.26920100	4.12164900	-2.38743700
H	6.73164800	0.77162600	2.01988900
H	6.89158100	-1.02732200	1.74785000
H	6.39517400	2.16912300	0.16591800
H	4.72287200	1.54900600	0.26274400
H	4.28986500	-0.73925700	-0.19730800
H	5.66703700	-1.92293100	-0.14794900
H	7.69607700	-1.27791500	-0.40171700
H	6.15797200	0.52692900	-3.55749000
H	4.44947300	1.64827600	-2.02344400
H	5.98471800	2.52571100	-2.10904800
H	4.35901100	-0.74926300	-2.47888700
H	8.10958100	1.26409900	-2.07134100
H	8.19730400	-0.42454500	-2.56570300
H	8.79217400	-0.13591600	1.30987600
H	10.35119400	2.06503200	-1.09725400
H	12.57419000	1.63443000	-2.12964500
H	13.75449700	-2.62366100	-1.21287700
H	12.74117500	-4.58487300	-0.03802900
H	10.46318800	-4.38385700	0.95049300
H	9.17850900	-2.32707700	0.79459100
H	6.75491500	-2.62546900	-2.12937900
H	4.69436100	-2.27849500	-4.39492100
H	5.96530800	-3.61220900	-4.22368600
H	7.36001800	-3.63289100	0.89493500
H	9.28136000	4.34304900	0.86124000
H	10.40890700	2.11242300	1.53393300
H	9.02008300	1.78464200	2.59233700
H	-8.32570600	-0.32840300	2.13837100
H	-6.69247400	0.18600100	2.62078500
H	-6.85340700	-1.38663300	4.65165000
H	8.45313500	5.45551900	2.88567800
H	8.37408000	3.82941800	3.76309800
H	-9.07793400	-1.21877700	5.66921700
H	-9.77845000	-0.60872800	4.07004500

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TS of PTC 4 (O(9)-CH₃), Enolate 5 and benzylbromide



E(RB3LYP) = -3877.62590434, imaginary frequency = -227.9924

C	3.93235100	-1.77989700	-1.27329100
C	5.05826000	-4.01072300	-1.54597600
C	3.93573800	-3.47096200	0.59249800
C	6.03096500	-2.30347700	0.06014000
C	2.54658100	-2.17221400	-1.72950400
C	5.70155900	-5.20693300	-0.81315200
N	4.73753900	-2.88978900	-0.56884000
C	4.77301800	-4.51054900	1.39542900
C	6.91993400	-3.48916100	0.49980400
O	3.52031400	-0.45548400	1.60319700
C	3.26922100	0.73421700	1.88028800
C	6.08215500	-4.77251000	0.60994400
C	1.44202400	-1.92894300	-0.90004200
C	2.32035300	-2.69545100	-3.01537300
C	0.14427900	-2.19538700	-1.33874100
C	-0.07252600	-2.73398800	-2.61588400
C	-1.44138000	-3.12271200	-3.11736500
C	-2.63796800	-2.35993300	-2.65740700
C	-2.57587000	-0.99425700	-2.34433300
C	-3.71875400	-0.31621600	-1.92662700
C	-4.93105100	-0.99826000	-1.77239600
C	-5.00529700	-2.36000600	-2.12169700
C	6.76615600	-1.24180100	-0.80093200
C	8.04077400	-0.79409300	-0.07489500
C	8.01025100	0.12295200	1.02324300
C	9.26212400	0.43979900	1.65343100
N	10.45720000	-0.07777200	1.24196400
C	10.43977600	-0.90277200	0.21754200
C	9.26474500	-1.29410700	-0.46830900
C	6.82689800	0.73123400	1.52437400
C	6.87926000	1.59183800	2.60120500
C	8.11321700	1.89357300	3.22564300
C	9.27951400	1.33189400	2.75805100
O	7.05009100	-1.79799300	-2.07673900

C	5.00089600	-4.08863600	2.82592000
C	4.66744700	-4.82821100	3.88419600
C	3.27930300	1.85010100	0.97213000
N	3.68704900	1.65103900	-0.31312800
C	4.04295900	2.61738500	-1.12284000
C	4.24460600	4.04415700	-0.70611300
C	4.30705800	2.26771100	-2.53932900
O	2.92274600	1.14557800	3.13695700
C	2.73310300	0.22991300	4.26493200
C	4.06896600	-0.42339300	4.64069600
C	1.64796000	-0.81122100	3.96261500
C	2.26744200	1.17145800	5.38170900
C	5.16434900	4.37232000	0.30503300
C	5.37697100	5.70029900	0.67552500
C	4.67109400	6.72748900	0.04478100
C	3.75682100	6.41567500	-0.96353400
C	3.55061600	5.08797000	-1.33932200
C	5.20079700	3.01361200	-3.33345800
C	5.45253400	2.66079600	-4.65967400
C	4.81129700	1.56125500	-5.23580400
C	3.91138400	0.81661500	-4.46504200
C	3.66403100	1.16458000	-3.13878100
C	0.75157100	1.62344100	0.82079700
Br	-1.52427000	0.43058700	1.29958200
C	0.41430000	2.76235900	-0.00005500
C	0.41817900	2.66192400	-1.40642800
C	0.06827900	3.75296900	-2.19800700
C	-0.28451100	4.96687900	-1.60094900
C	-0.28378000	5.08459300	-0.20567000
C	0.06031800	3.99586200	0.58607300
C	-6.19037000	-0.31697500	-1.29297900
N	-6.35113400	-0.23058900	0.23431900
C	-5.45651500	0.84133600	0.82851800
C	-5.98462200	-1.57395900	0.87265600
C	-7.85133000	0.00591200	0.58700000
C	-5.50512400	0.77653200	2.37108000
C	-6.33923400	-1.58096200	2.38272900
C	-7.93896600	0.35898200	2.08412500
C	-6.67239800	-0.12572100	2.80371800
C	-8.58491600	0.98912700	-0.34779100
C	-10.04549400	1.16314500	0.08469100
C	-10.41738400	2.29804700	0.77651400
C	-11.77221900	2.49733300	1.12991900
N	-12.74496300	1.66438700	0.82894700
C	-12.40879800	0.52733700	0.14803400
C	-11.06133500	0.20628400	-0.24084800
C	-13.46124400	-0.36606700	-0.18249000
C	-13.19847800	-1.53571100	-0.85834200
C	-11.86967900	-1.86250000	-1.21730500
C	-10.81549500	-1.02258300	-0.92068100
O	-7.89371800	2.23929600	-0.37091000
C	-7.44181200	-2.57131000	2.69368200
C	-7.50855500	-3.28472200	3.81900300

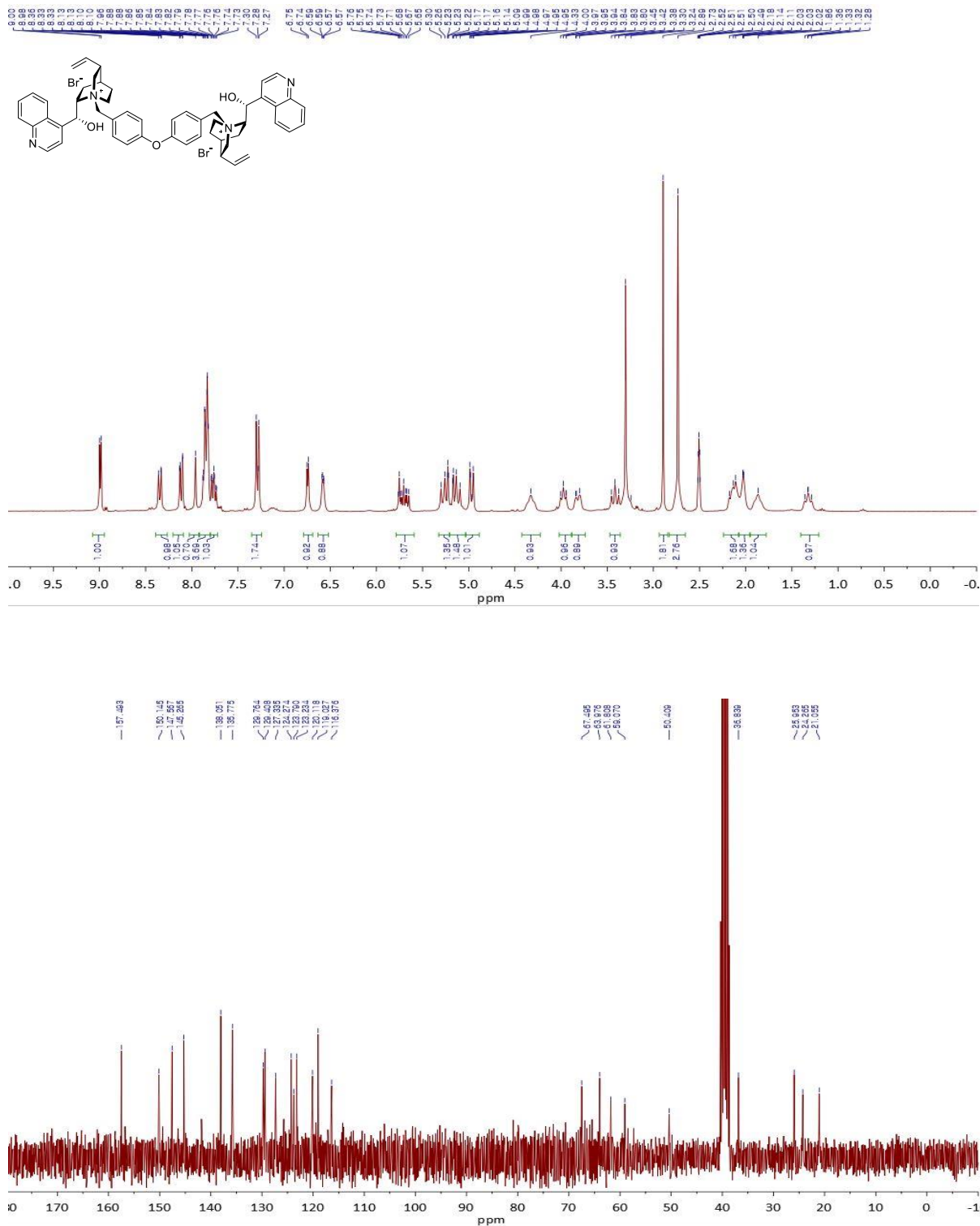
O	-8.06475600	-2.39563800	-0.95838100
C	-8.19670700	3.04326700	-1.50263300
C	7.32944200	-0.81958400	-3.08413400
C	1.03065000	-2.99593100	-3.44235700
O	-1.54487000	-4.07621800	-3.88144400
C	-3.87367800	-3.02672300	-2.57607900
H	3.87539000	-0.95266200	-0.56071100
H	4.54451900	-1.49006700	-2.12660900
H	5.72074300	-3.57272200	-2.28961100
H	4.11259300	-4.27952900	-2.01640800
H	3.05032300	-3.92716500	0.14907500
H	3.62342500	-2.62084400	1.20085700
H	5.65044100	-1.76608300	0.93131300
H	5.01112900	-6.05705500	-0.78102000
H	6.59085000	-5.53280500	-1.36266800
H	4.21004000	-5.45150900	1.41385000
H	7.72577000	-3.64564600	-0.22416200
H	7.39433300	-3.23699300	1.45170400
H	1.59805400	-1.51019800	0.08980000
H	3.15838300	-2.85332100	-3.69087900
H	-0.68742800	-1.97237400	-0.67749300
H	-1.64025500	-0.45232100	-2.42902400
H	-3.64974700	0.74367400	-1.70035500
H	-5.97020600	-2.85506900	-2.00318300
H	0.85428400	-3.42523300	-4.42347600
H	-3.91908600	-4.07486100	-2.85542400
H	6.10754700	-0.37262700	-0.92404400
H	11.40239600	-1.30131800	-0.10215500
H	9.33160900	-1.98242500	-1.30377500
H	5.86604600	0.53000100	1.06482100
H	5.95955500	2.03855400	2.96786800
H	8.13568300	2.57404400	4.07235400
H	10.24340300	1.54644400	3.20843800
H	5.46557200	-3.11589200	2.98614300
H	4.18785500	-5.79939100	3.77773900
H	4.85618800	-4.48889000	4.89855000
H	6.65738100	-5.55787300	1.10954300
H	3.22324800	2.84234500	1.41429600
H	4.83007700	0.33958200	4.83743300
H	4.42203600	-1.07043500	3.83627400
H	3.94626400	-1.02477700	5.54901300
H	1.98173800	-1.52519100	3.20852400
H	0.73043500	-0.33257100	3.60402300
H	1.40724400	-1.36131700	4.88010700
H	1.32136600	1.65114200	5.11118700
H	3.01195300	1.95409700	5.56196400
H	2.11786500	0.61216100	6.31150500
H	5.72686000	3.57996700	0.79027500
H	6.09944600	5.93334500	1.45375000
H	4.83518800	7.76212200	0.33452200
H	3.20115800	7.20749500	-1.45954500
H	2.83524400	4.85166000	-2.12073800
H	5.70709500	3.87157200	-2.90241400

H	6.15214400	3.25104600	-5.24645500
H	4.99674200	1.29766900	-6.27373500
H	3.38195900	-0.02525200	-4.90580300
H	2.94556100	0.60497600	-2.55015800
H	0.83218200	1.71871000	1.89033300
H	1.04191000	0.69477000	0.36310000
H	0.68277000	1.71528500	-1.86826700
H	0.06836600	3.65736400	-3.28057700
H	-0.56178900	5.81719800	-2.21846100
H	-0.55769600	6.02724900	0.26022000
H	0.04555100	4.08061800	1.66926200
H	-6.24101400	0.71572000	-1.64383400
H	-7.04932300	-0.92486800	-1.61309600
H	-5.82049800	1.79016700	0.43863300
H	-4.44448100	0.65643300	0.46510200
H	-4.91288400	-1.69642300	0.71351500
H	-6.57139000	-2.30653700	0.29364200
H	-8.27693500	-0.98355300	0.35418000
H	-6.81116900	-0.08125500	3.88902100
H	-4.55217200	0.39991100	2.75778600
H	-5.64018400	1.78737100	2.77154700
H	-5.44434000	-1.87714100	2.94425200
H	-8.04687100	1.44009500	2.22827300
H	-8.83455400	-0.11287000	2.49917400
H	-8.58512100	0.56487600	-1.35851700
H	-9.67669900	3.04836000	1.03124100
H	-12.05462800	3.39693300	1.67780100
H	-14.46509000	-0.08706900	0.12250800
H	-14.00938200	-2.21555900	-1.10844500
H	-11.66858000	-2.80129100	-1.72772000
H	-9.79613000	-1.36074200	-1.15534600
H	-8.19845500	-2.70450300	1.91995400
H	-6.75032100	-3.20504000	4.59708000
H	-8.32237900	-3.98016600	4.00666000
H	-8.52493400	-3.22458600	-1.16490600
H	-9.25589000	3.32845900	-1.52940300
H	-7.94807200	2.52075400	-2.43859000
H	-7.58354400	3.94439000	-1.42146100
H	6.48026600	-0.13882200	-3.22003200
H	7.50346700	-1.37383900	-4.00891700
H	8.22456900	-0.23735200	-2.83703500

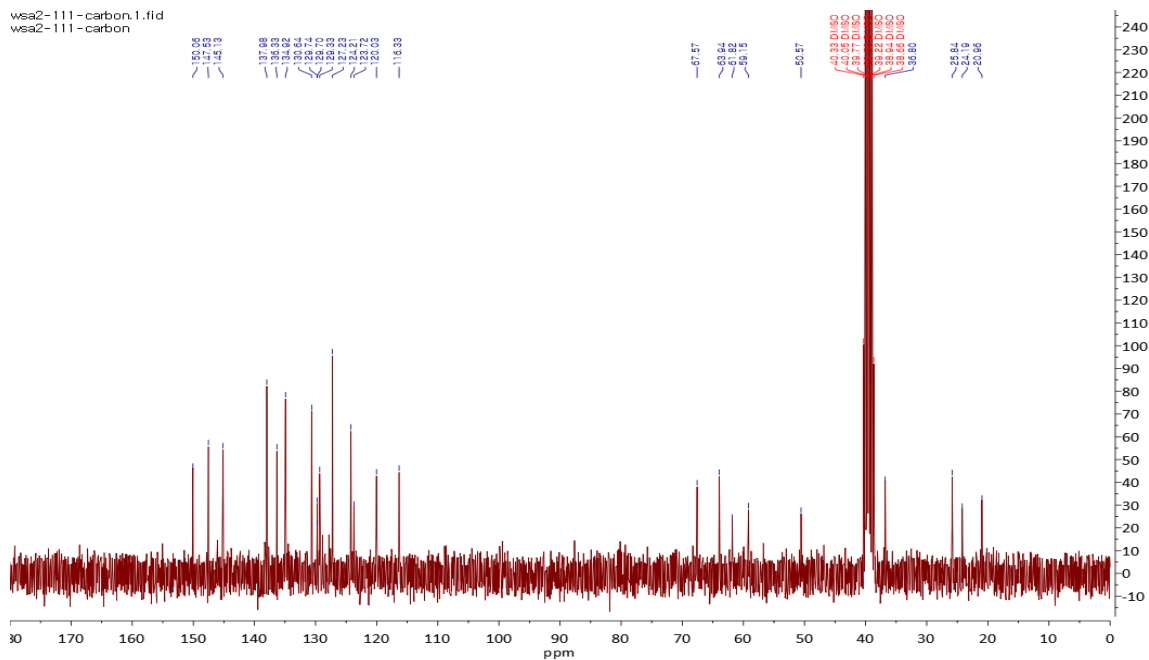
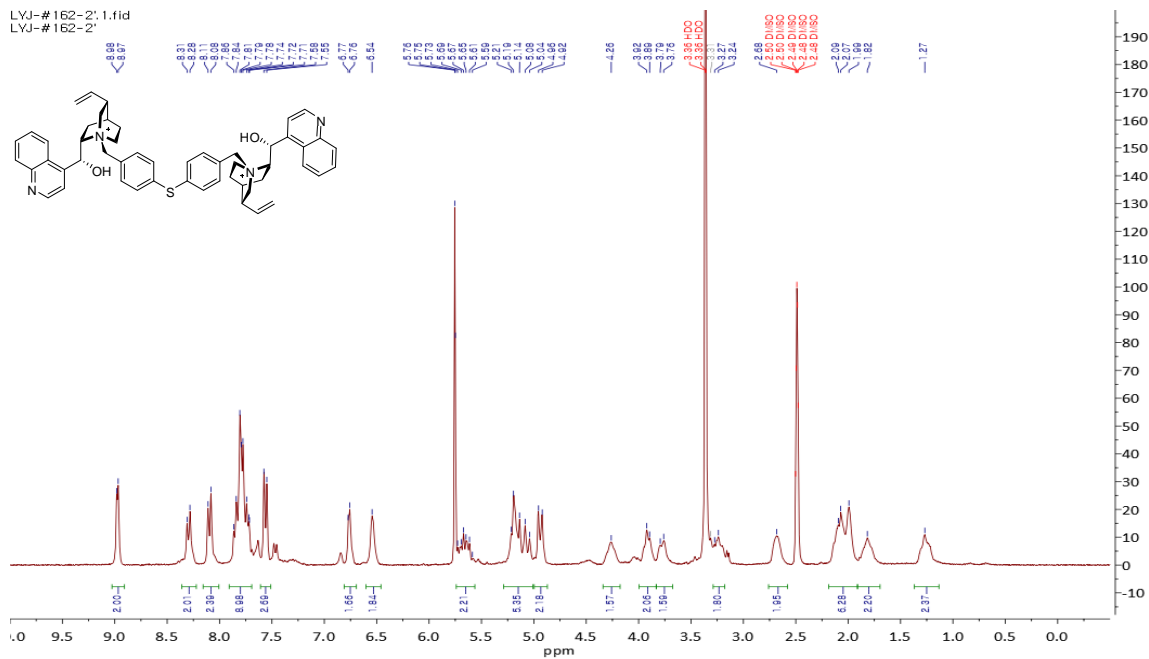
3. Spectroscopic data

(1) Catalysts

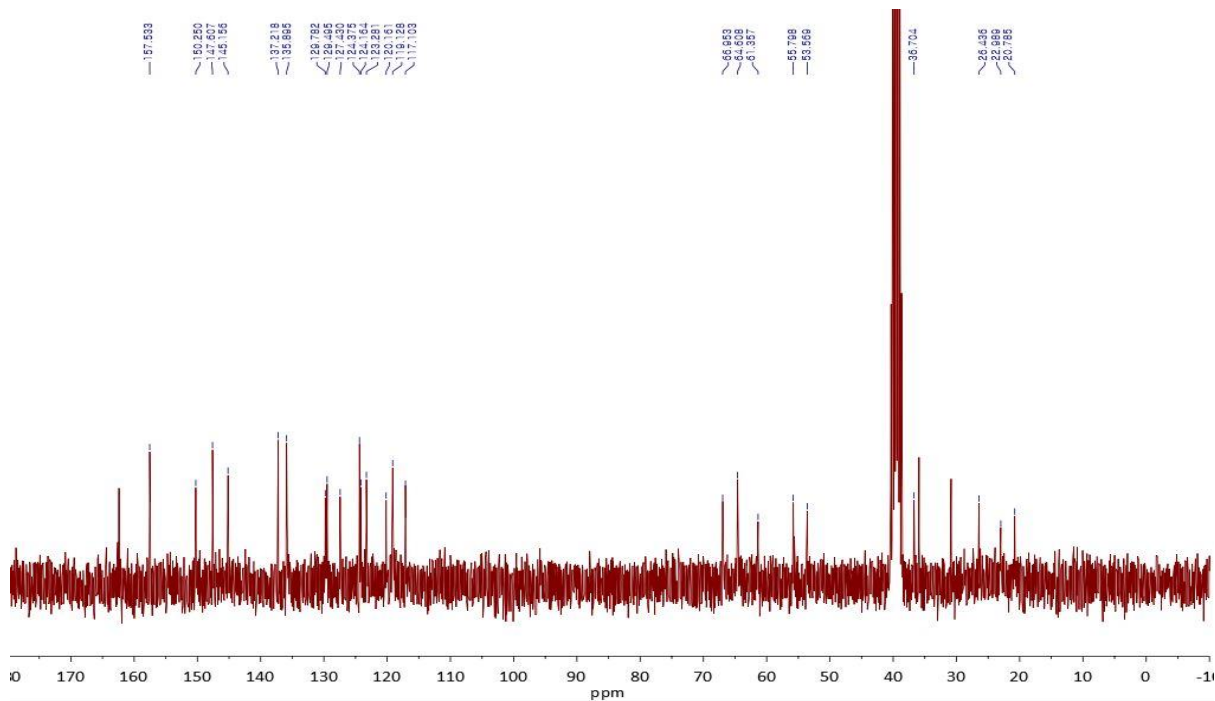
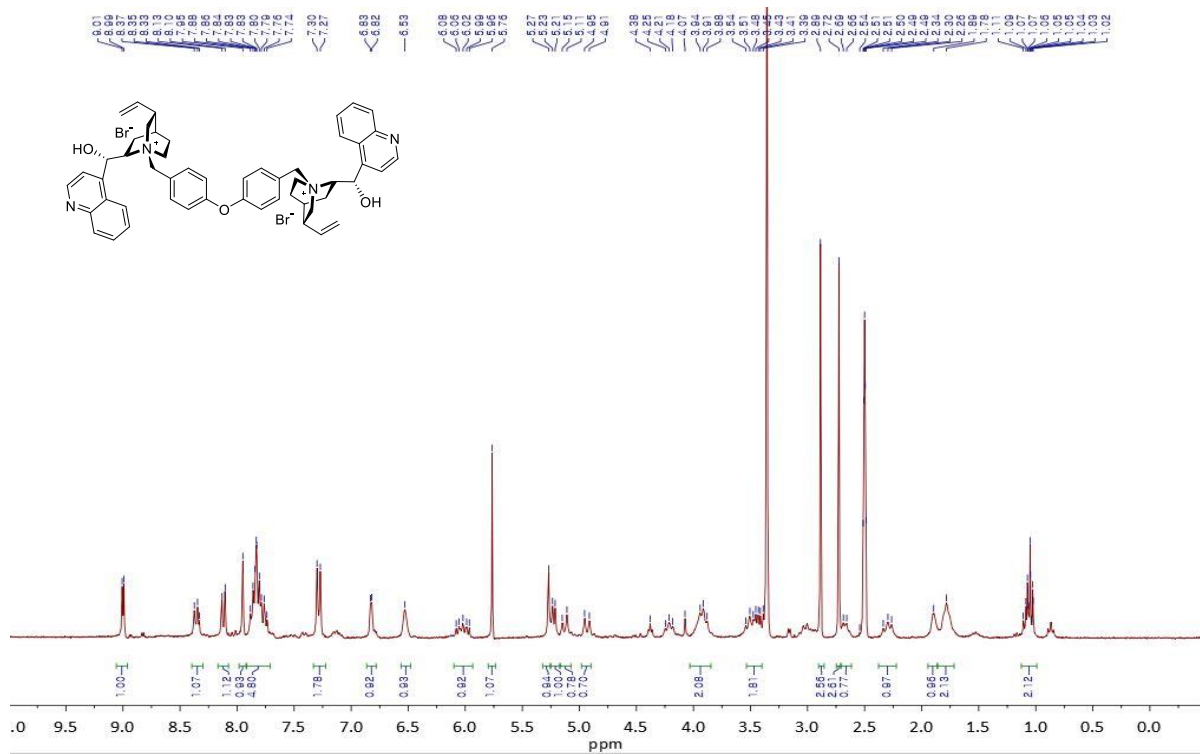
(a) *Bis*(4-(cinchonidinium-N-methyl)phenyl)ether dibromide



(c) *Bis*(4-(cinchonidium-N-methyl)phenyl) thioether dibromide

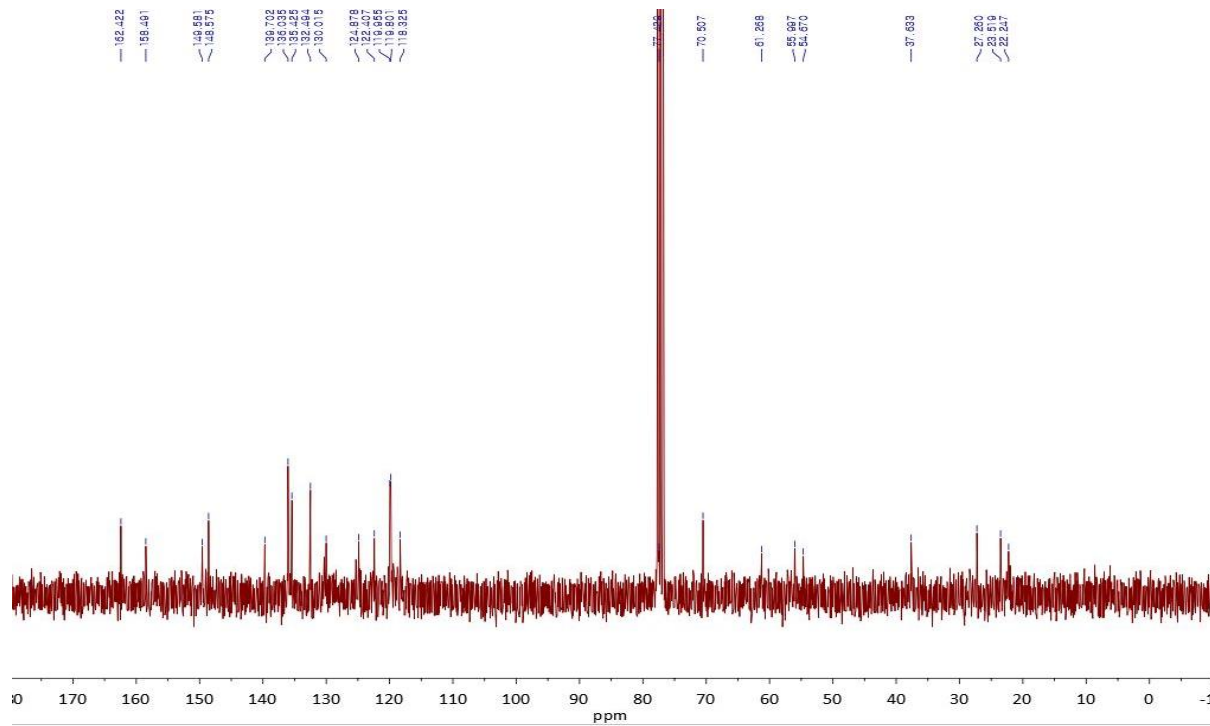
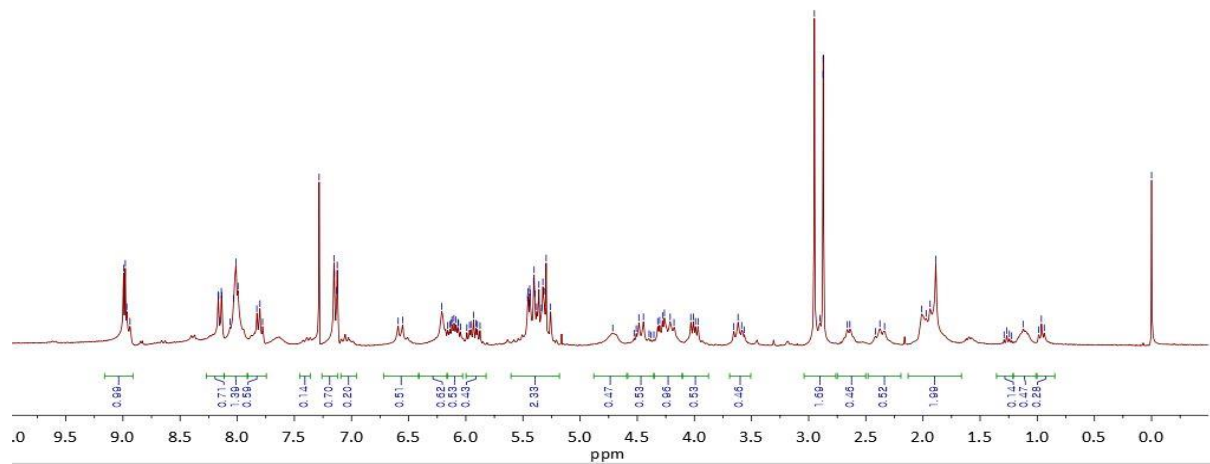
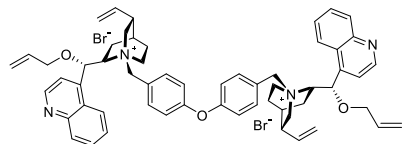


(e) *Bis*(4-(cinchoninium-N-methyl) biphenyl ether) dibromide



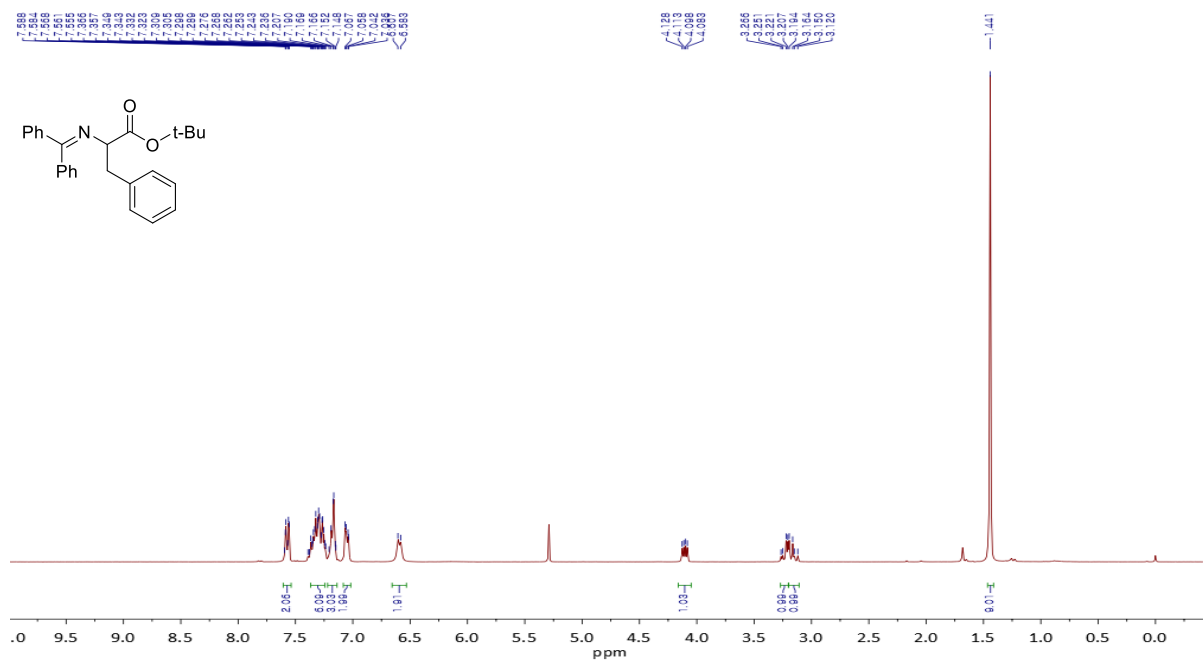
(f) 4,4'-bis(O(9)-allylcinchoninium-N-methyl)biphenyl ether dibromide (9)

0.00 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.10 0.11 0.12 0.13 0.14 0.15 0.16 0.17 0.18 0.19 0.20 0.21 0.22 0.23 0.24 0.25 0.26 0.27 0.28 0.29 0.30 0.31 0.32 0.33 0.34 0.35 0.36 0.37 0.38 0.39 0.40 0.41 0.42 0.43 0.44 0.45 0.46 0.47 0.48 0.49 0.50 0.51 0.52 0.53 0.54 0.55 0.56 0.57 0.58 0.59 0.60 0.61 0.62 0.63 0.64 0.65 0.66 0.67 0.68 0.69 0.70 0.71 0.72 0.73 0.74 0.75 0.76 0.77 0.78 0.79 0.80 0.81 0.82 0.83 0.84 0.85 0.86 0.87 0.88 0.89 0.90 0.91 0.92 0.93 0.94 0.95 0.96 0.97 0.98 0.99 1.00

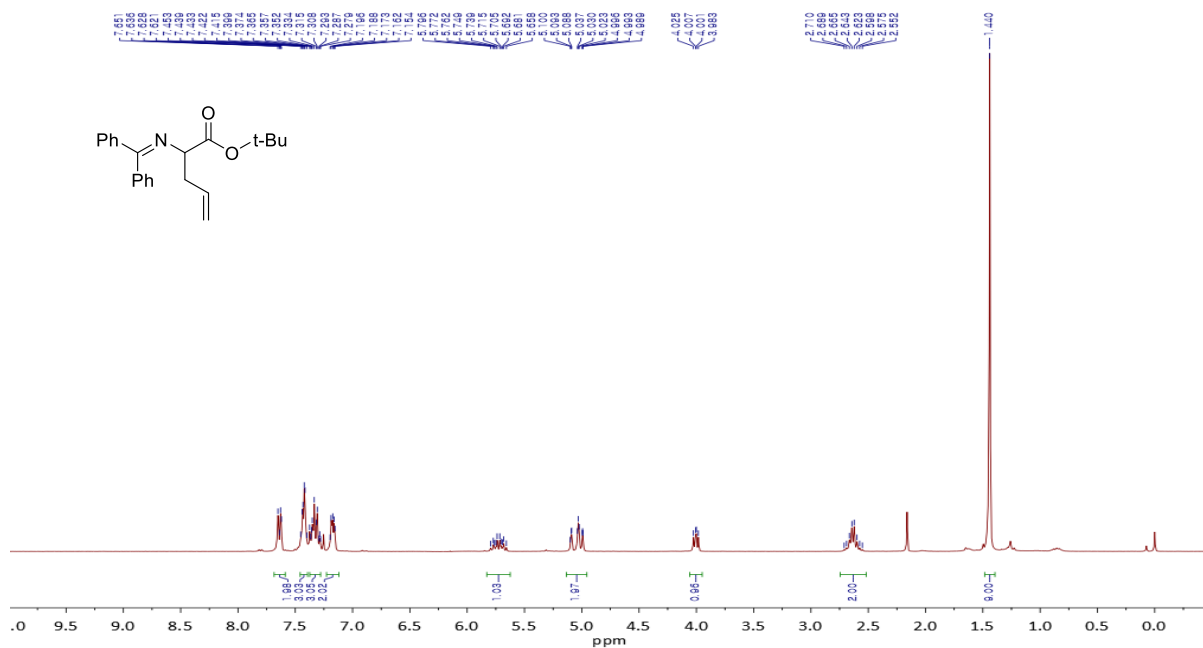


(2) Alkylated Products (6)

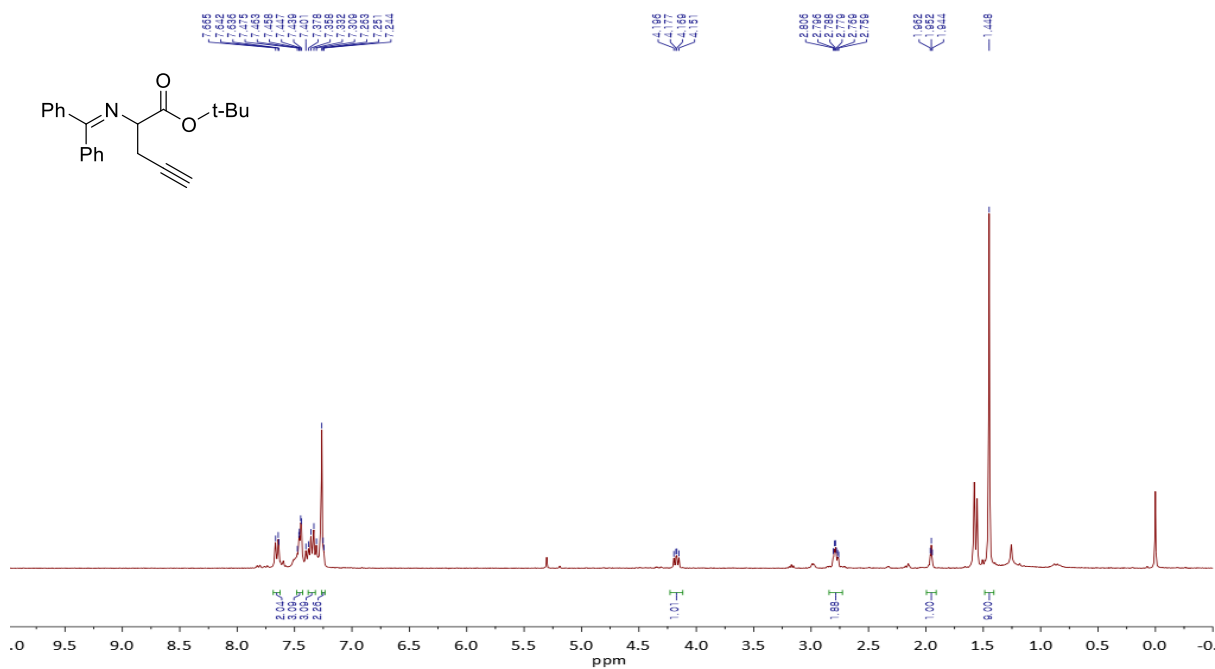
(a) *tert*-Butyl 2-(diphenylmethyleneamino)-3-phenylpropanoate



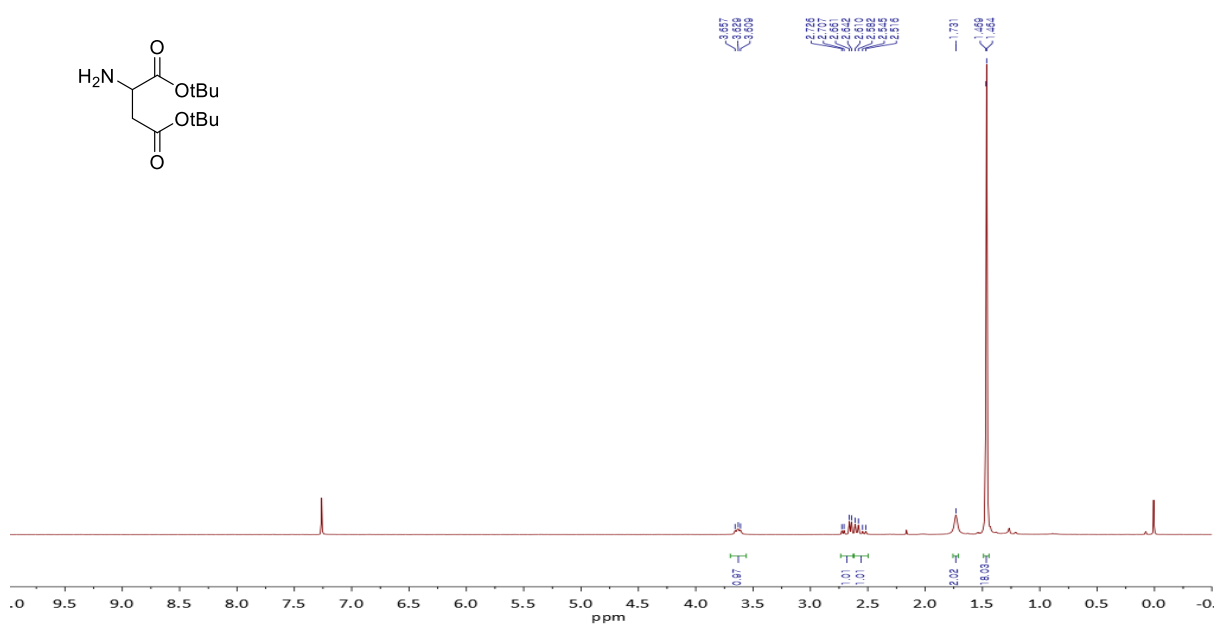
(b) *tert*-Butyl 2-(diphenylmethyleneamino)pent-4-enoate

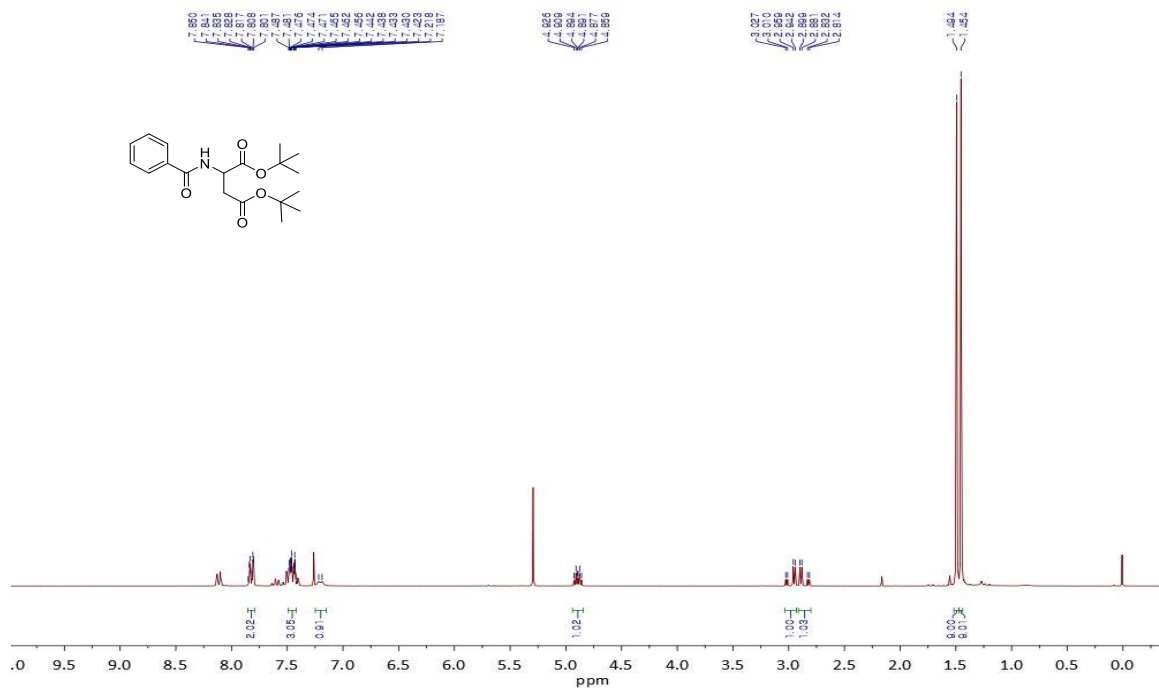


(e) *tert*-Butyl 2-(diphenylmethyleneamino)pent-4-ynoate

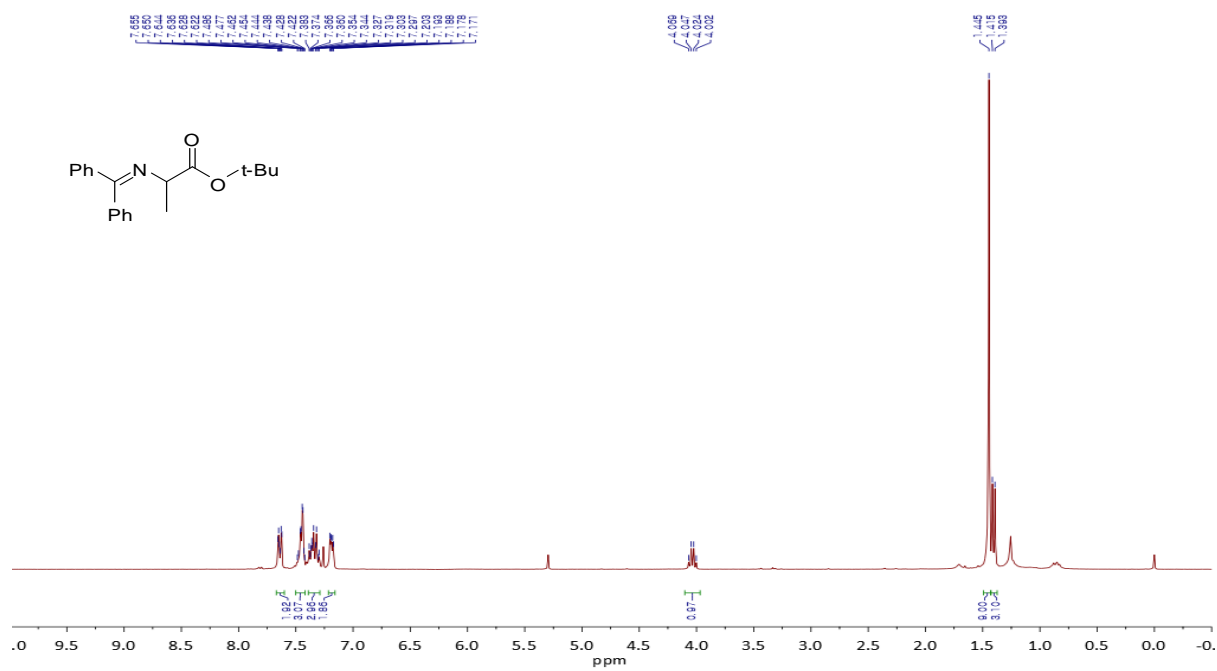


(f) Di-*tert*-butyl aspartate and *tert*-Butyl 2-benzamido-3-(carbo-*t*-butoxy)-propanoate



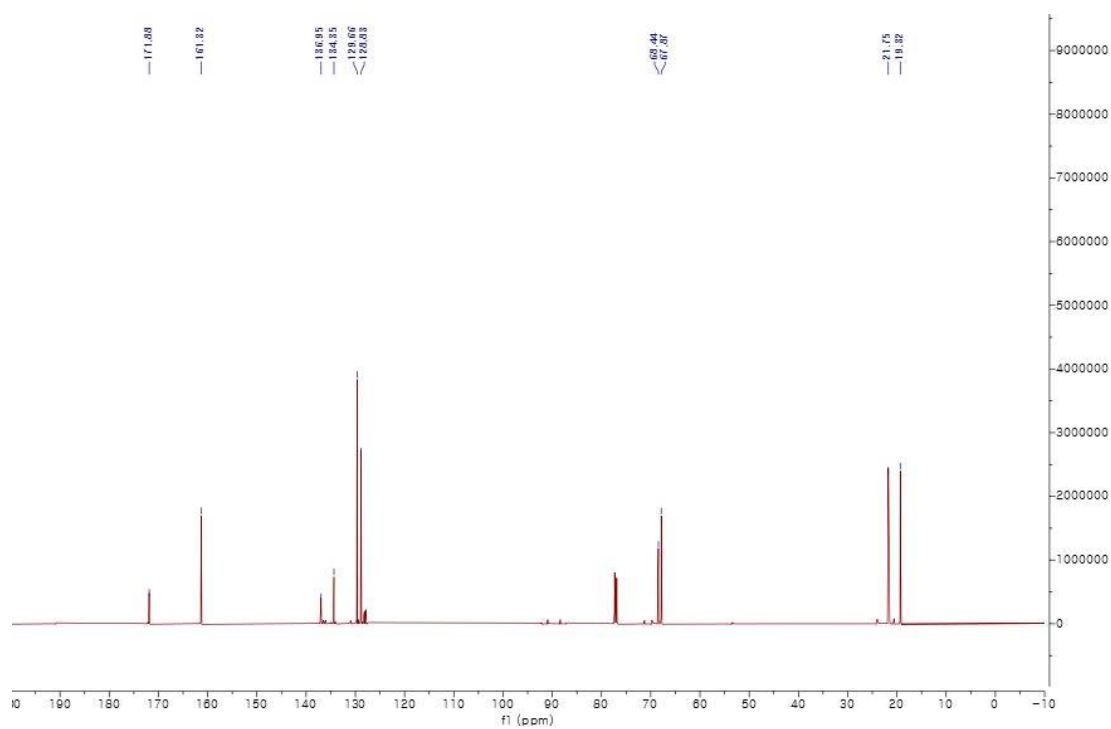
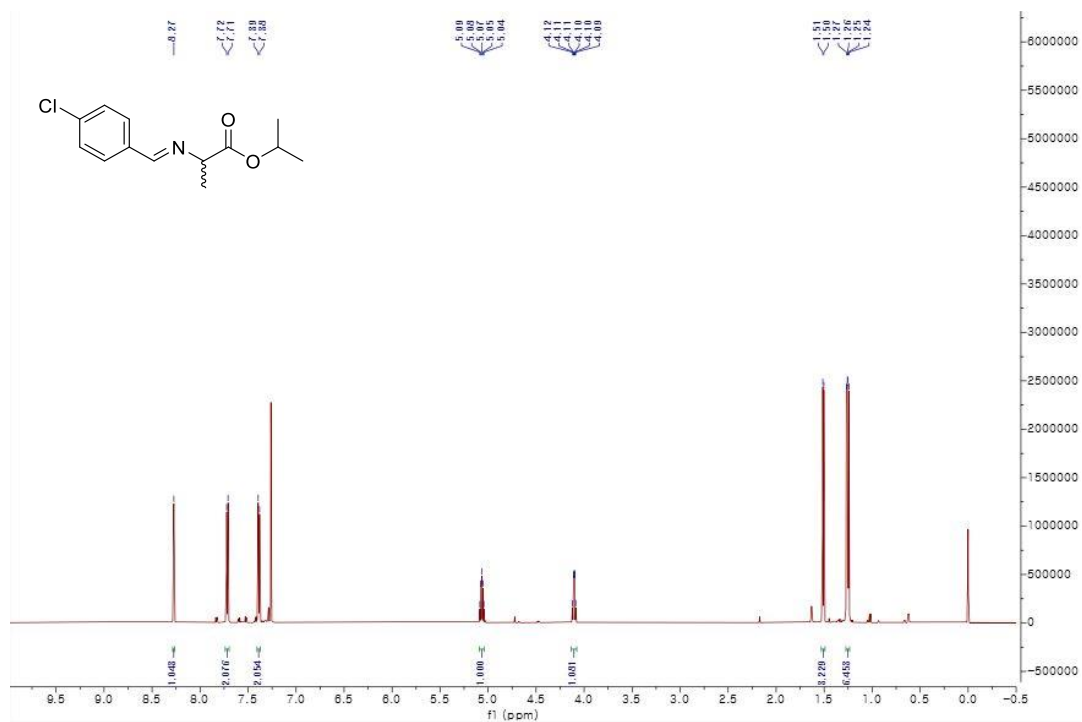


(g) *tert*-Butyl 2-(diphenylmethyleneamino)propanoate

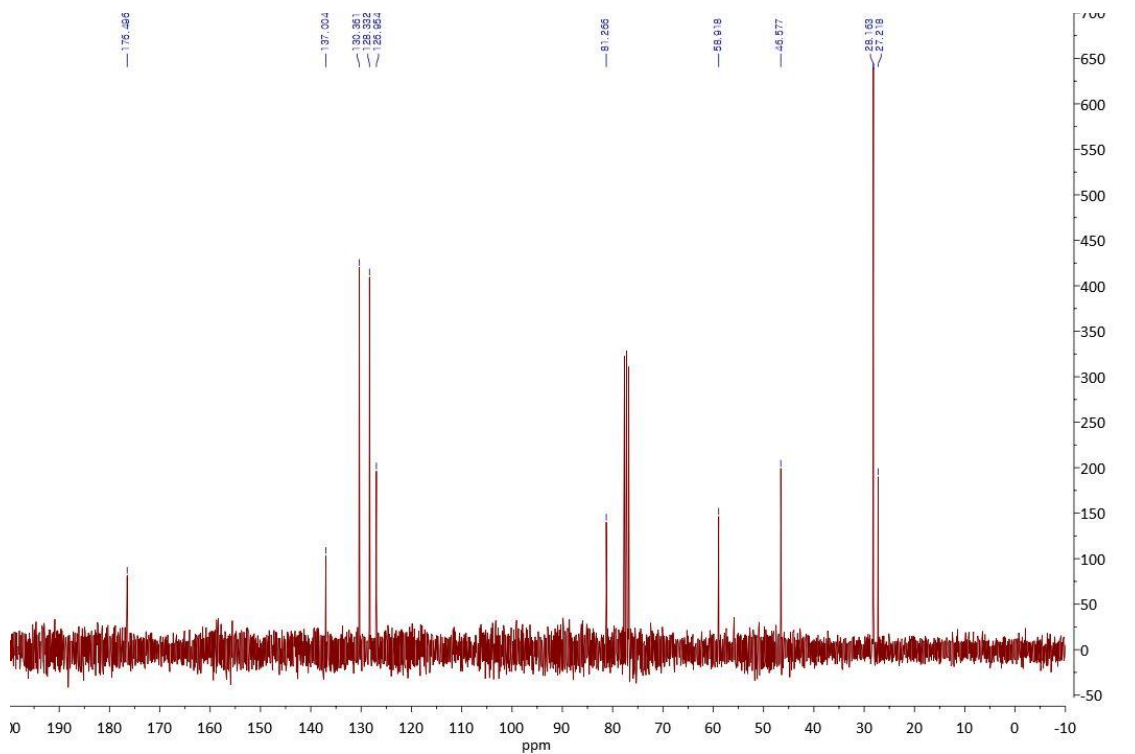
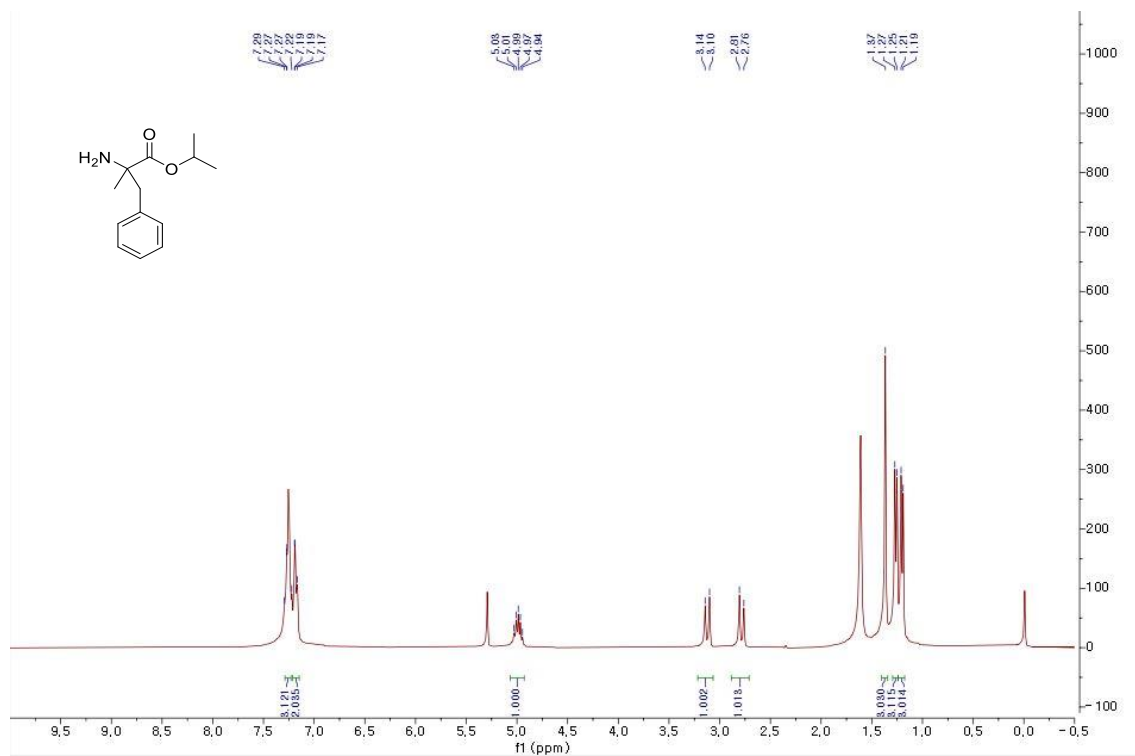


(3) α,α -Dialkylated Products (11)

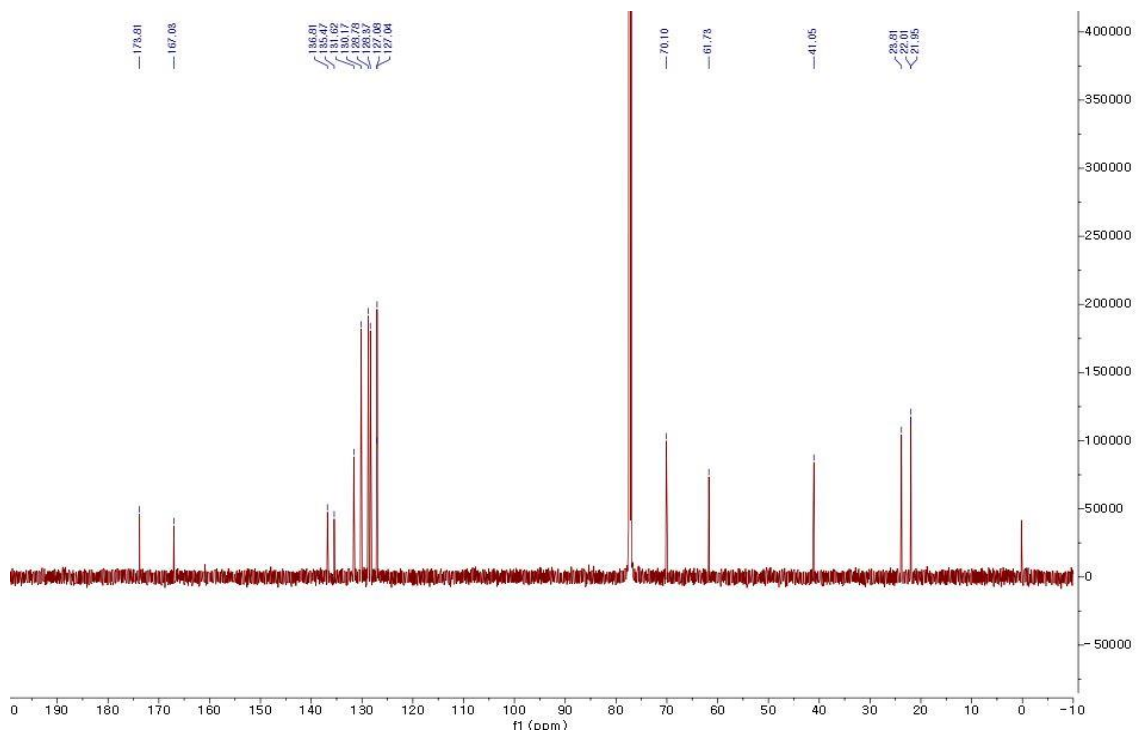
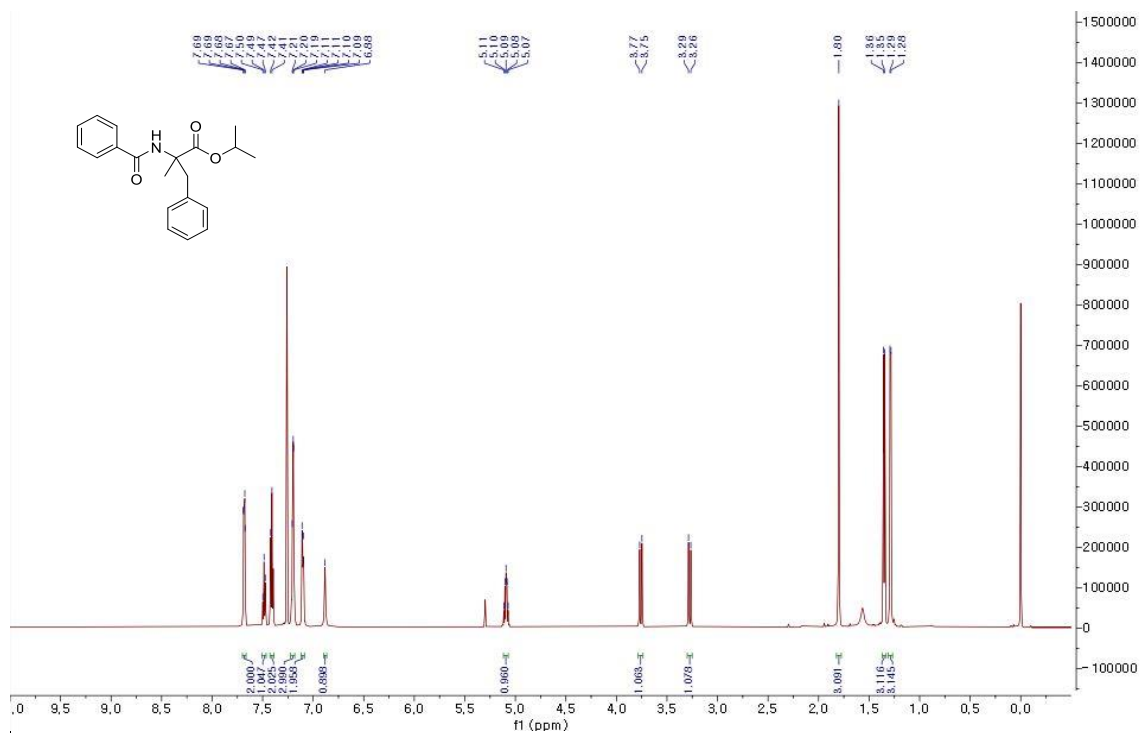
(a) (E)-rac-Isopropyl-2-(4-chlorobenzylideneamino)propanoate



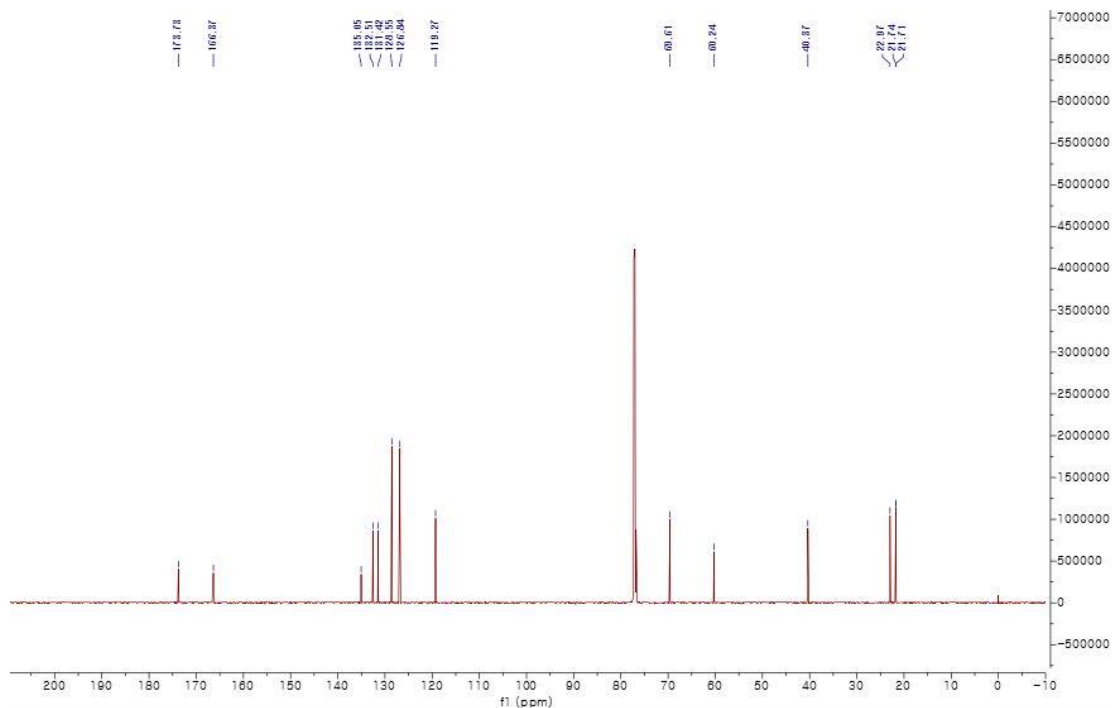
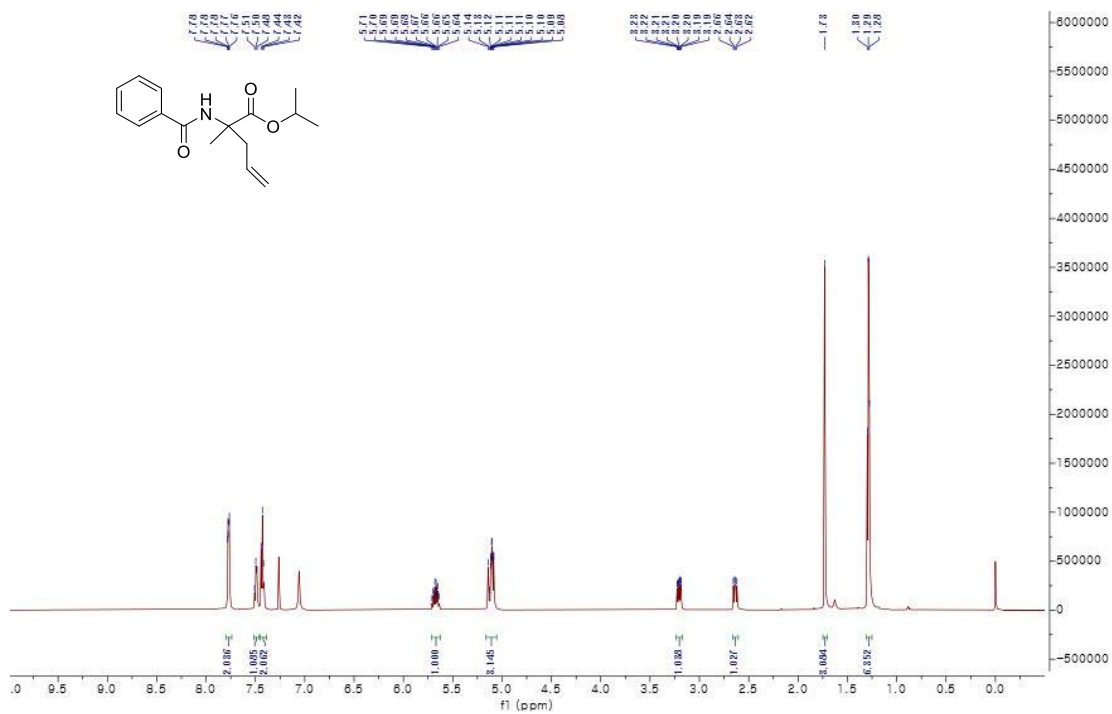
(b) Isopropyl 2-amino-2-methyl-3-phenylpropionate



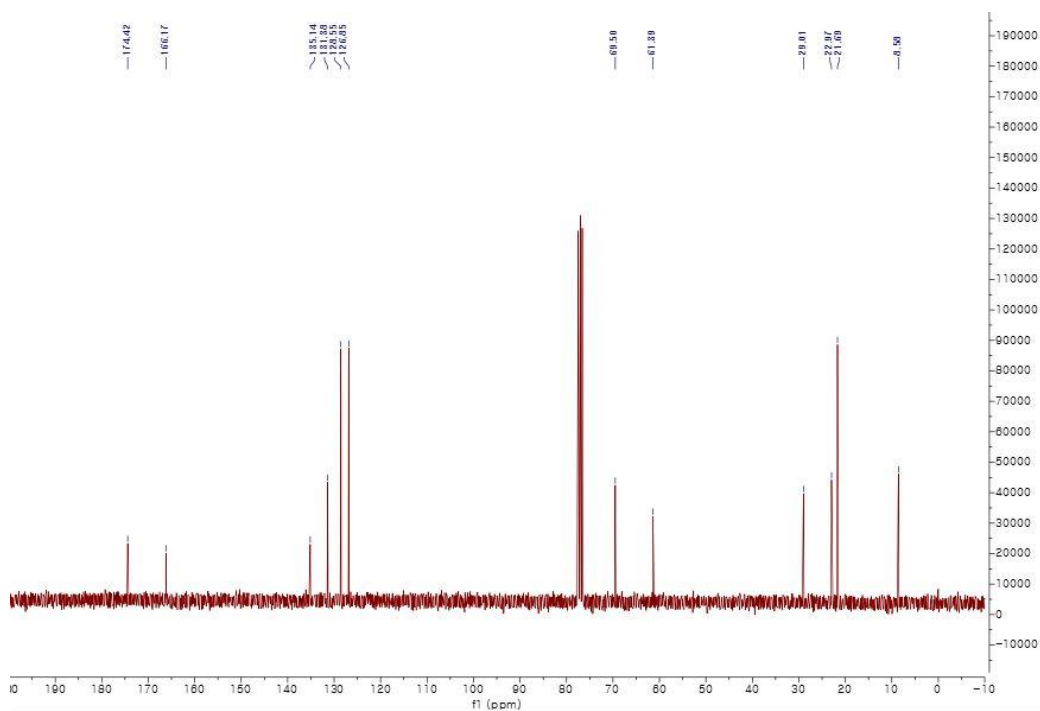
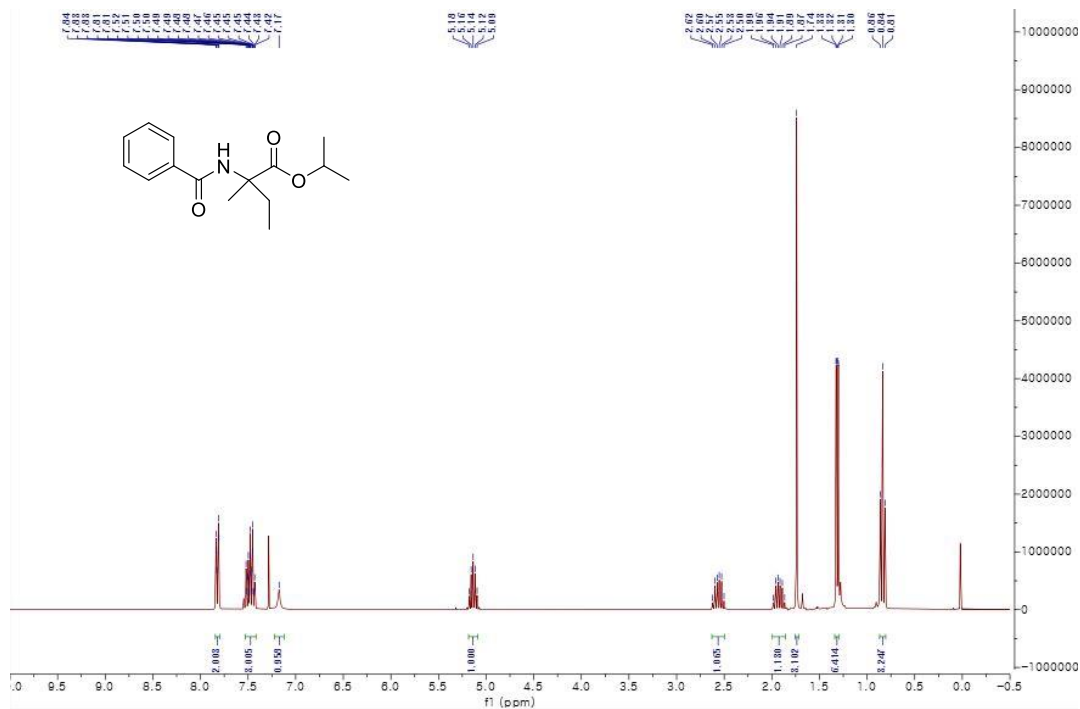
(c) Isopropyl 2-benzamido-2-methyl-3-phenylpropionate



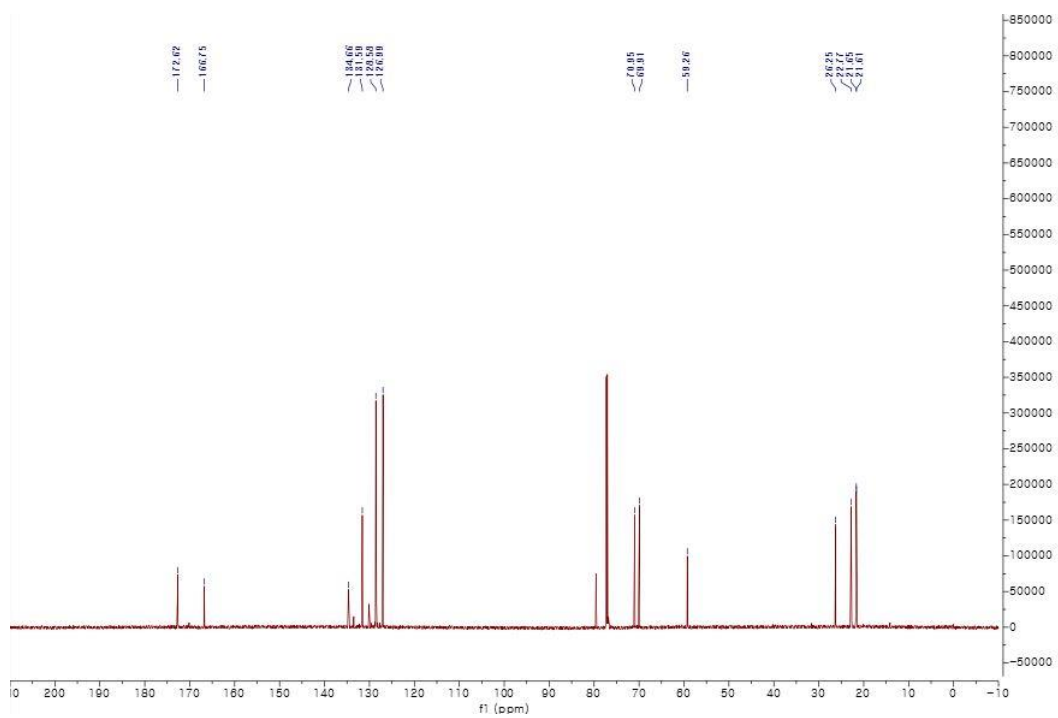
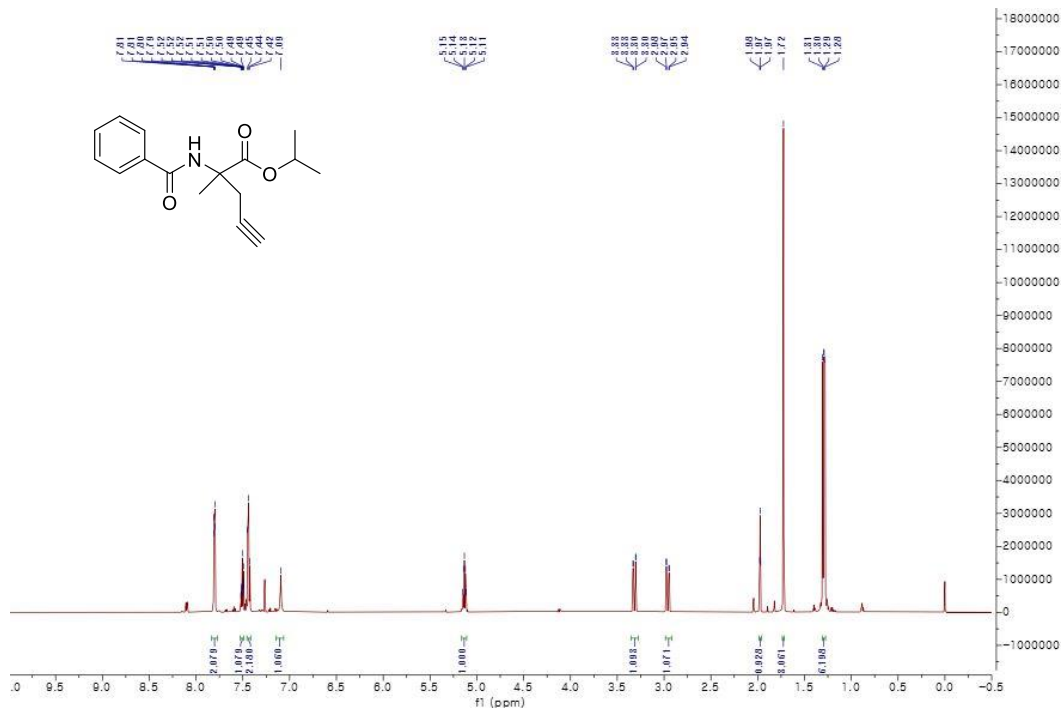
(d) Isopropyl 2-benzamido-2-methylpent-4-enoate



(e) Isopropyl 2-benzamido-2-methylbutanoate



(f) Isopropyl 2-benzamido-2-methylpent-4-ynoate

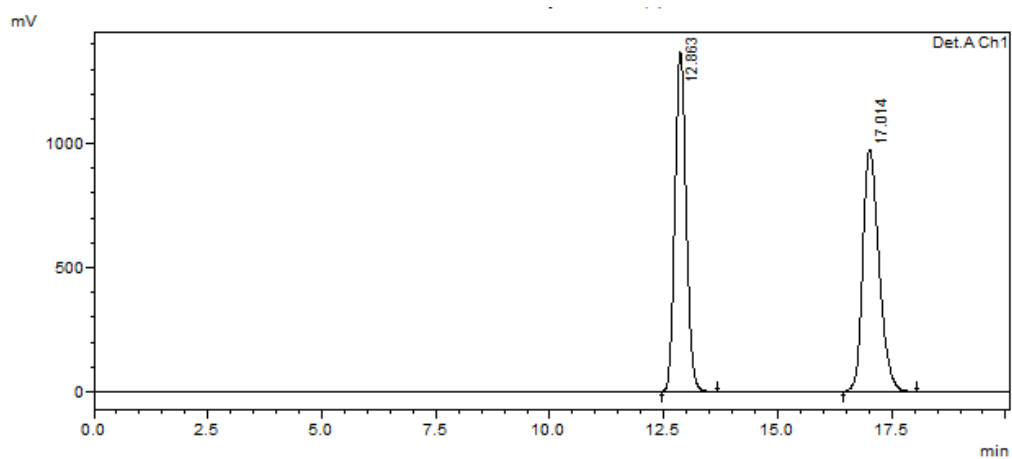


4. Chiral HPLC data

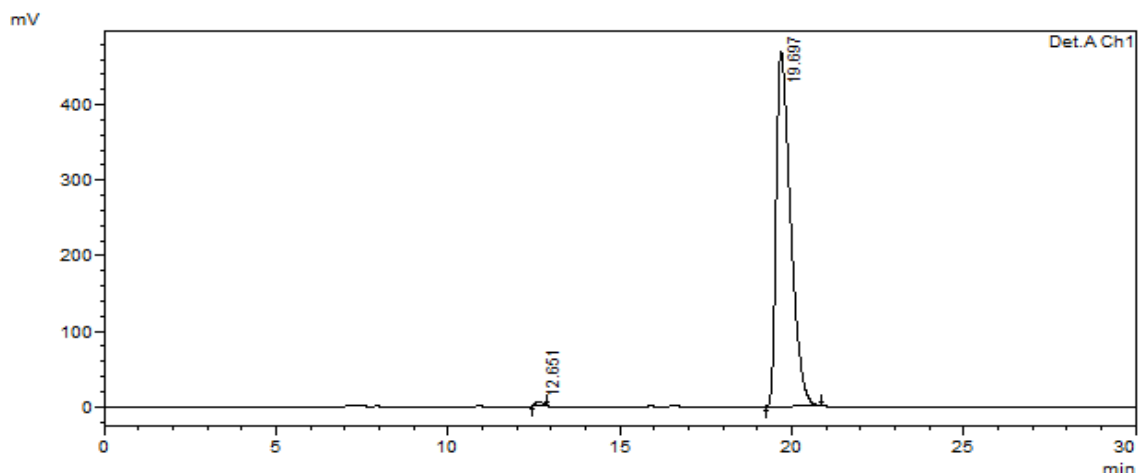
(1) Product 6. (Table 1)

(a) *tert*-Butyl 2-(diphenylmethyleneamino)-3-phenylpropanoate
(Entry 1, from benzyl-Br)

racemate



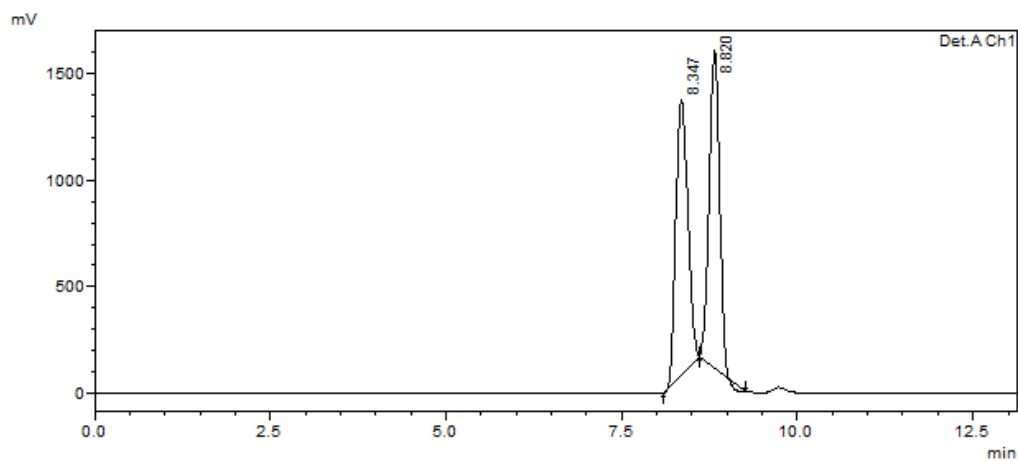
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT12.863	12.863	0.00000	Detector A - Ch	1	23450825	1369173		12.467	13.667	49.2892
2	RT17.014	17.014	0.00000	Detector A - Ch	2	24127187	975856		16.433	18.058	50.7108



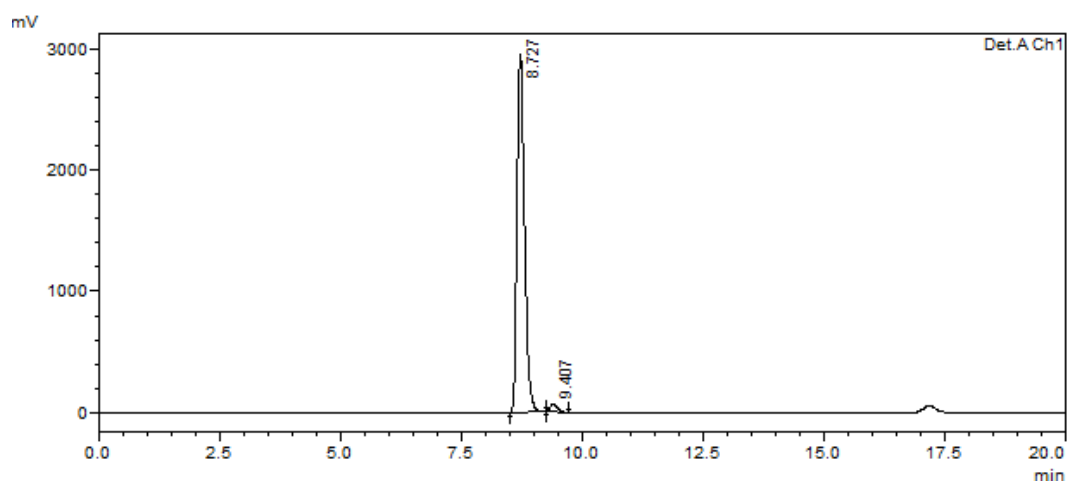
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT12.645	12.645	0.00000	Detector A - Ch	1	240696	19542		12.500	12.892	0.6086
2	RT19.482	19.482	0.00000	Detector A - Ch	2	39307122	1185522		19.133	20.800	99.3914

(b) *tert*-Butyl 2-(diphenylmethyleneamino)pent-4-enoate
(Entry 3, from allyl-Br)

racemate



ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT8.347	8.347	0.00000	Detector A - Ch	1	15402908	1291688		8.092	8.600	50.3486
2	RT8.820	8.820	0.00000	Detector A - Ch	2	15189641	1492721		8.600	9.267	49.6514

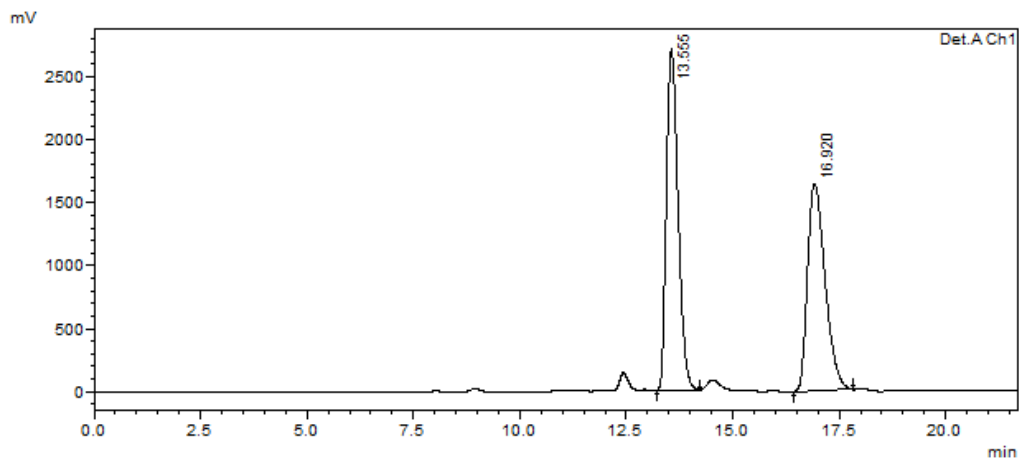


ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT8.727	8.727	0.00000	Detector A - Ch	1	31693148	2948098		8.508	9.250	97.9801
2	RT9.407	9.407	0.00000	Detector A - Ch	2	653372	61839		9.250	9.733	2.0199

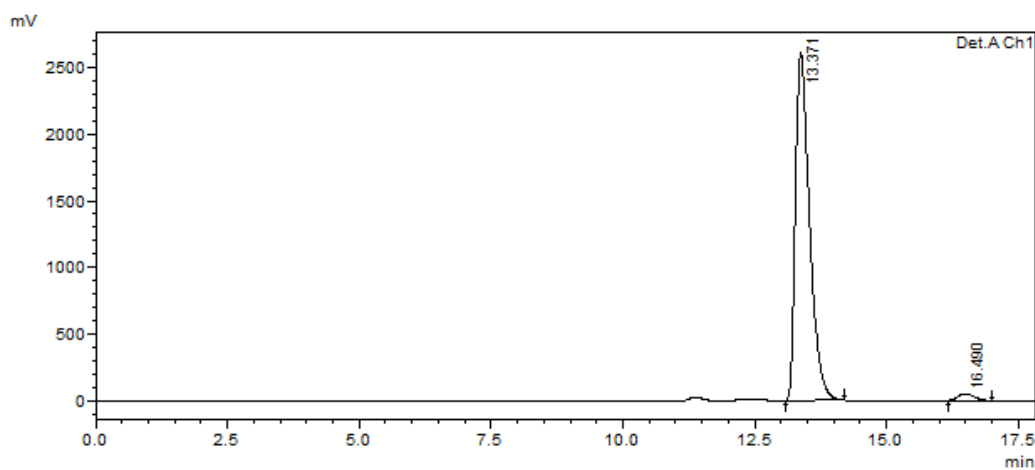
(c) (E)-*tert*-Butyl 2-(diphenylmethyleneamino)-5-phenylpent-4-enoate

(Entry 4, from cinnamyl-Br)

racemate



ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT13.555	13.555	0.00000	Detector A - Ch	1	51699316	2709526		13.208	14.217	52.3031
2	RT16.920	16.920	0.00000	Detector A - Ch	2	47146217	1644352		16.433	17.817	47.6969

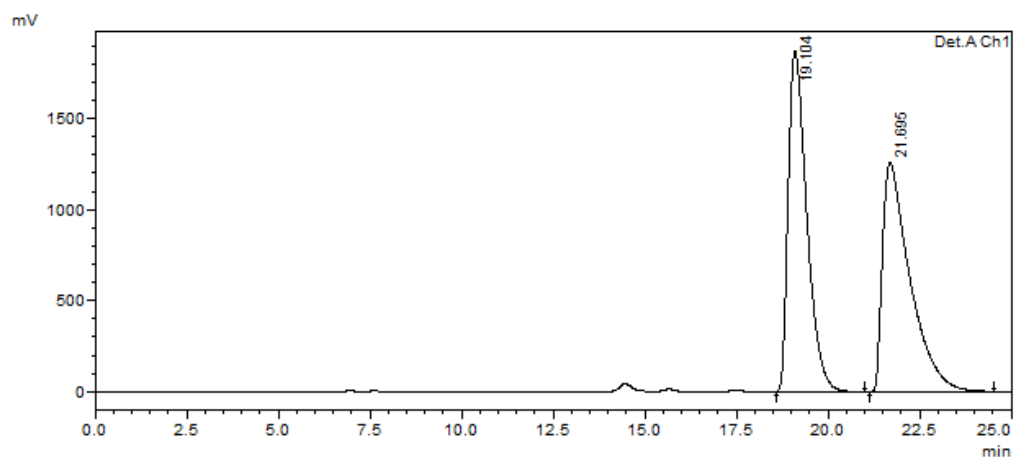


ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT13.371	13.371	0.00000	Detector A - Ch	1	48754902	2614461		13.083	14.200	98.1710
2	RT16.490	16.490	0.00000	Detector A - Ch	2	908333	47507		16.233	16.867	1.8290

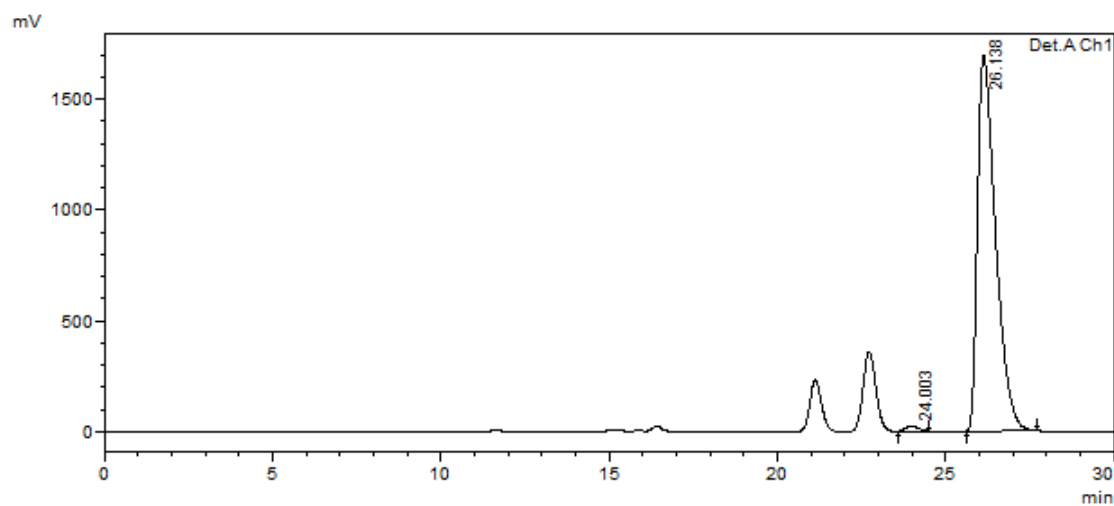
(d) *tert*-Butyl 2-(diphenylmethyleneamino)-3-(naphthalene-1-yl)propanoate

(Entry 5, from 1-(bromomethyl)-naphthalene)

racemate



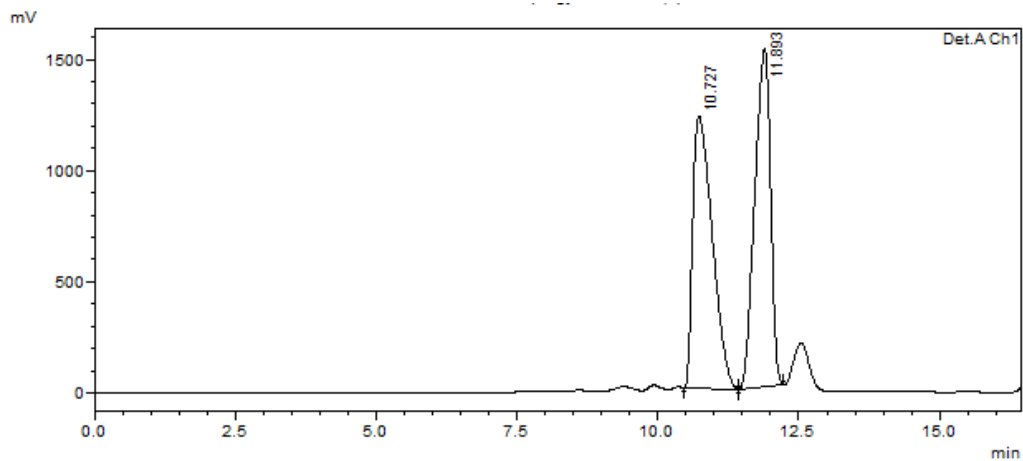
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT19.104	19.104	0.00000	Detector A - Ch	1	65940121	1870162		18.575	21.008	50.1104
2	RT21.695	21.695	0.00000	Detector A - Ch	2	65649455	1258563		21.158	24.542	49.8896



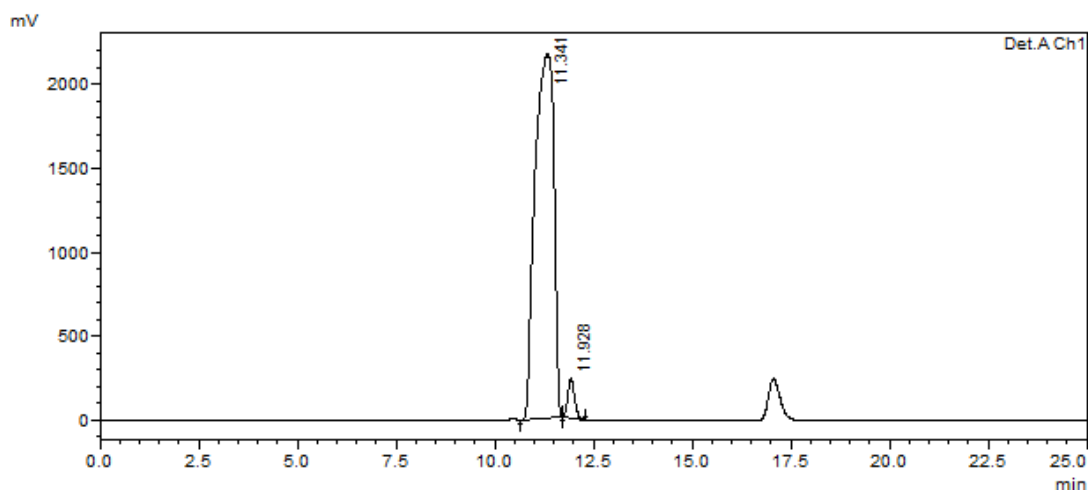
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT24.003	24.003	0.00000	Detector A - Ch	1	584531	22109		23.608	24.508	0.9135
2	RT26.138	26.138	0.00000	Detector A - Ch	2	63406467	1693606		25.617	27.725	99.0865

(e) *tert*-Butyl 2-(diphenylmethyleneamino)pent-4-ynoate
(Entry 6, from propargyl-Br)

racemate



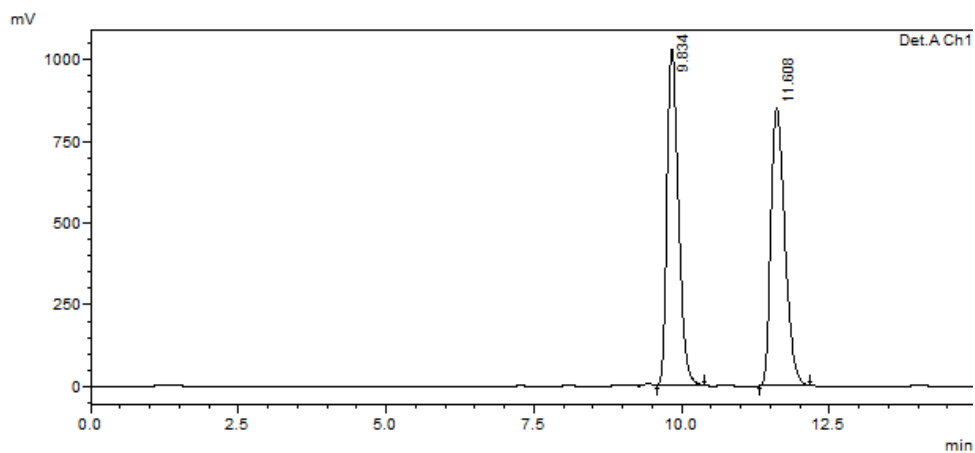
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT10.727	10.727	0.00000	Detector A - Ch	1	29540048	1224114		10.458	11.425	50.1211
2	RT11.893	11.893	0.00000	Detector A - Ch	2	29397356	1519534		11.442	12.233	49.8789



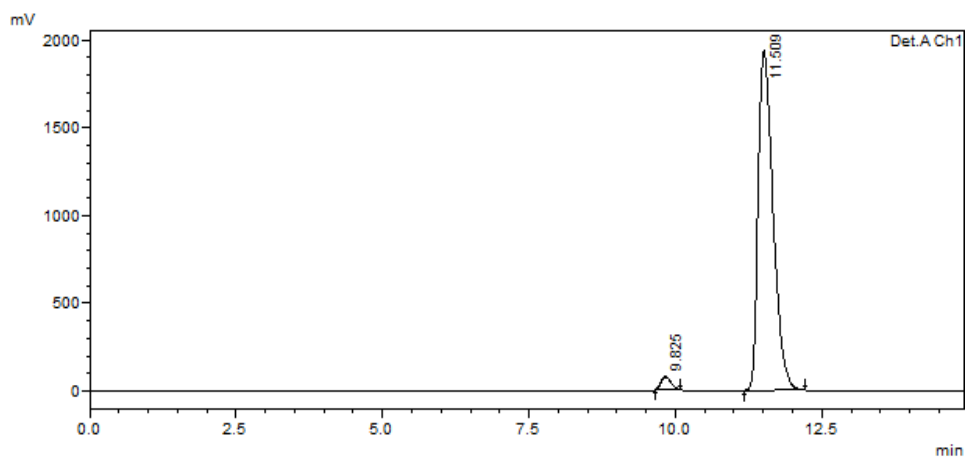
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT11.341	11.341	0.00000	Detector A - Ch	1	71964731	2162902		10.667	11.717	96.3289
2	RT11.928	11.928	0.00000	Detector A - Ch	2	2742551	231885		11.733	12.292	3.6711

(f) *tert*-Butyl 2-benzamido-3-(carbo-*tert*-butoxy)-propanoate
 (Entry 7, from *tert*-butylbromoacetate)

racemate

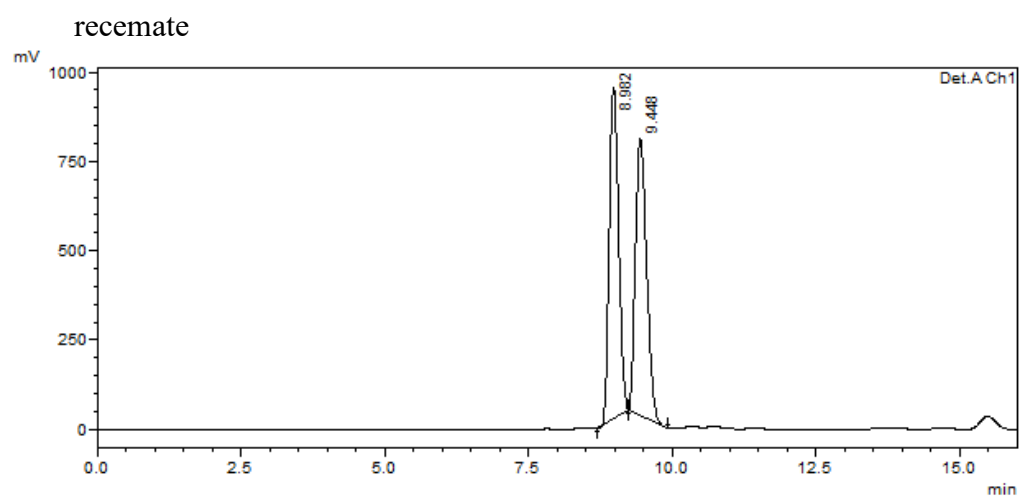


ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT9.834	9.834	0.00000	Detector A - Ch	1	13890362	1025941		9.583	10.392	49.8037
2	RT11.608	11.608	0.00000	Detector A - Ch	2	13999837	850692		11.317	12.167	50.1963

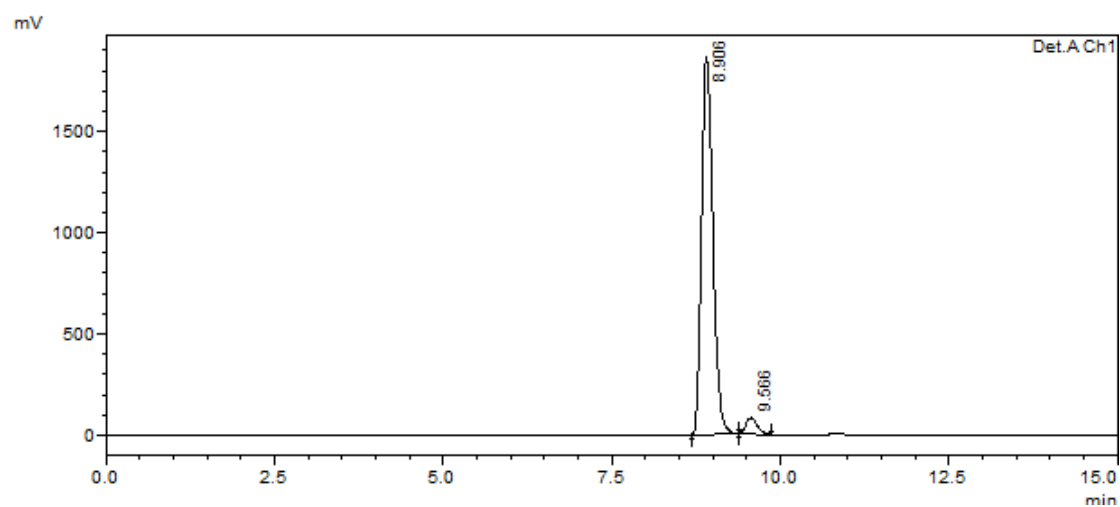


ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT9.825	9.825	0.00000	Detector A - Ch	1	875430	74120		9.667	10.092	2.4876
2	RT11.509	11.509	0.00000	Detector A - Ch	2	34316062	1937372		11.183	12.208	97.5124

(g) *tert*-Butyl 2-(diphenylmethyleneamino)propanoate
 (Entry 8, from methyl iodide)



ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT8.982	8.982	0.00000	Detector A - Ch	1	10561590	928656		8.708	9.250	50.1657
2	RT9.448	9.448	0.00000	Detector A - Ch	2	10491828	773786		9.250	9.917	49.8343

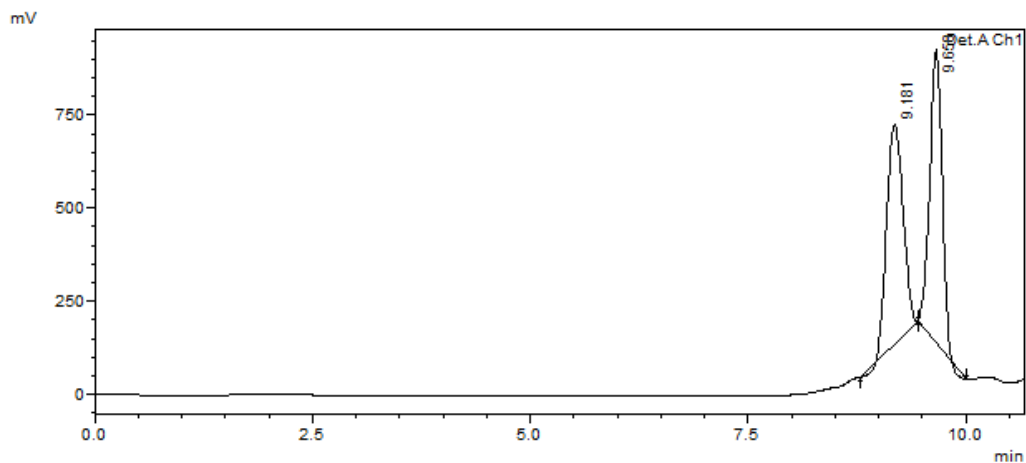


ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT8.906	8.906	0.00000	Detector A - Ch	1	21714031	1863768		8.692	9.375	95.9398
2	RT9.566	9.566	0.00000	Detector A - Ch	2	918951	78522		9.375	9.858	4.0602

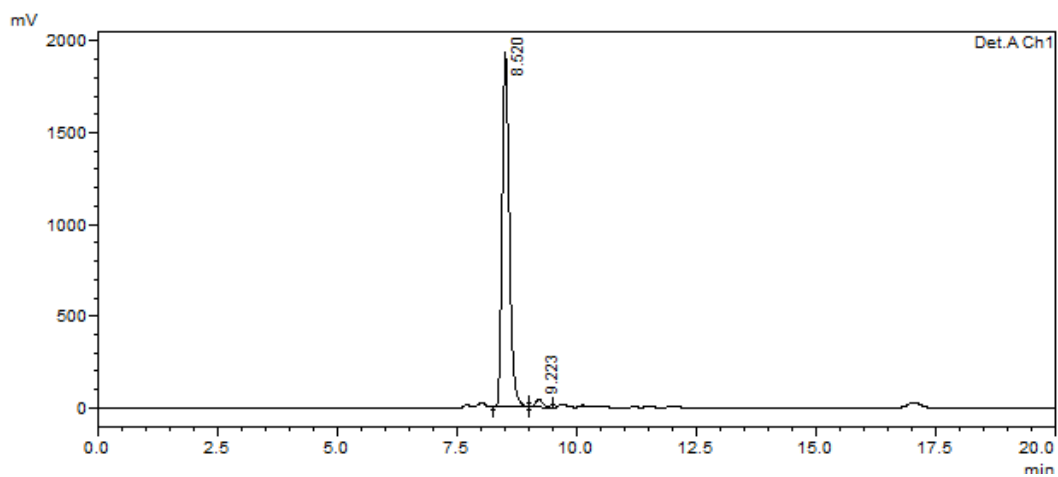
(h) *tert*-Butyl 2-(diphenylmethyleneamino)butanoate

(Entry 9, from ethyl iodide)

racemate



ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT9.181	9.181	0.00000	Detector A - Ch	1	7668694	587264		8.783	9.450	49.8806
2	RT9.658	9.658	0.00000	Detector A - Ch	2	7705407	787652		9.450	10.000	50.1194



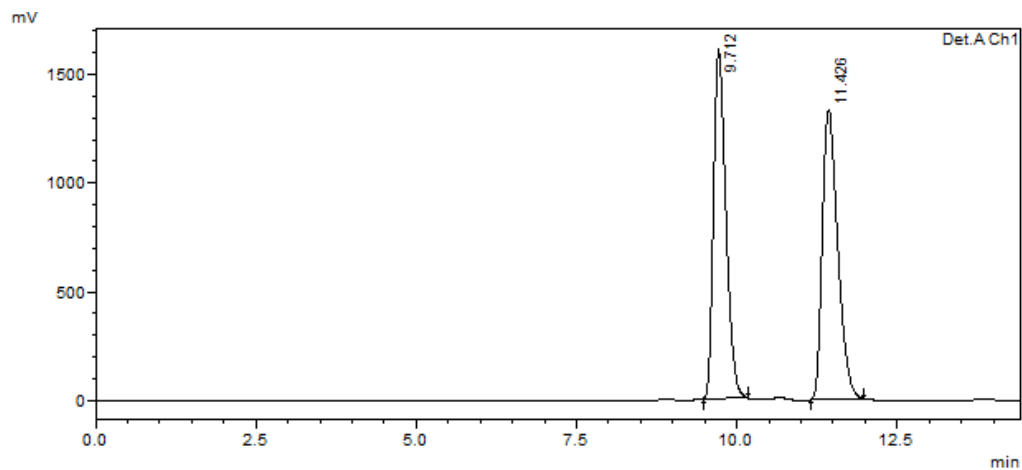
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT8.520	8.520	0.00000	Detector A - Ch	1	20180103	1932824		8.283	9.017	97.9424
2	RT9.223	9.223	0.00000	Detector A - Ch	2	423957	40343		9.017	9.500	2.0576

(2) Product **11**.

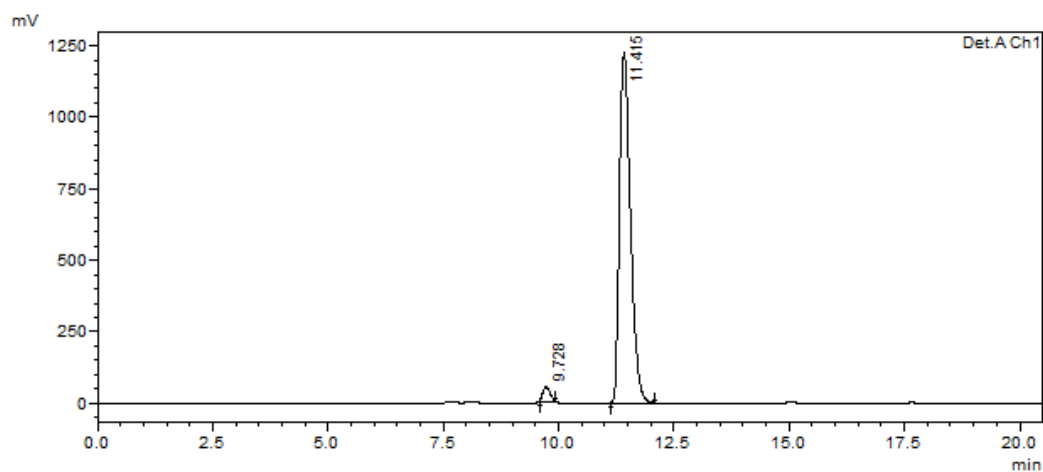
(a) Isopropyl 2-benzamido-2-methyl-3-phenylpropanoate

(Table 2, entry a)

racemate



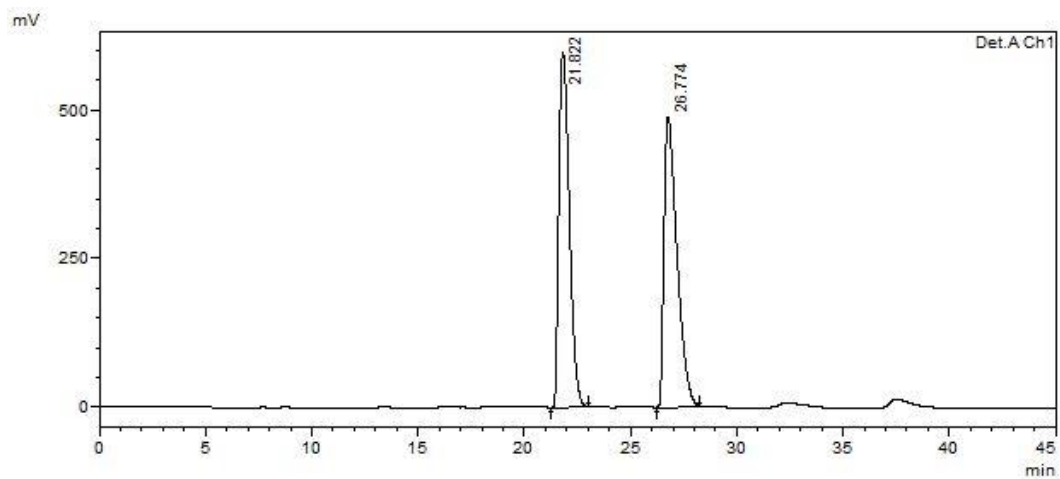
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT9.712	9.712	0.00000	Detector A - Ch	1	21755905	1605584		9.475	10.175	49.3433
2	RT11.426	11.426	0.00000	Detector A - Ch	2	22335003	1332849		11.150	11.983	50.6567



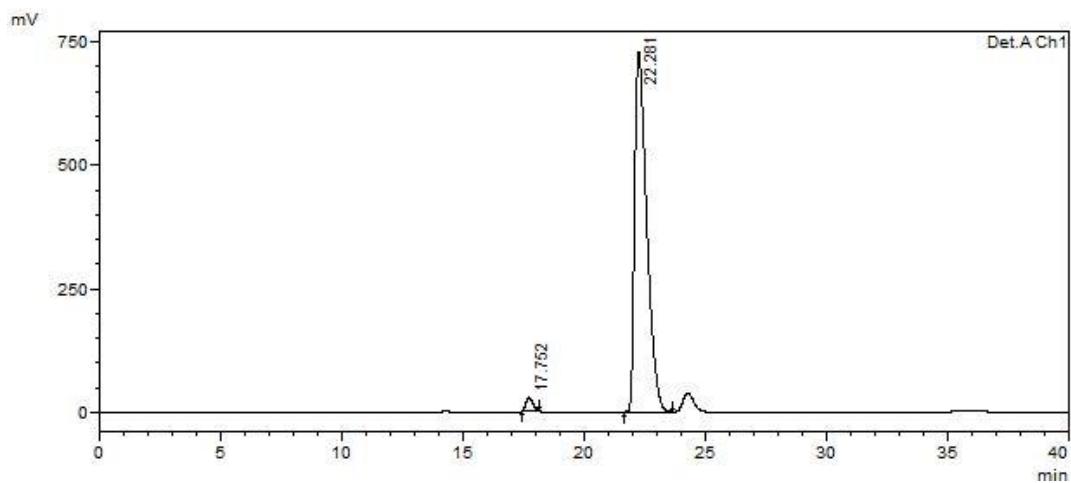
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT9.728	9.728	0.00000	Detector A - Ch	1	547744	50165		9.583	9.933	2.6223
2	RT11.415	11.415	0.00000	Detector A - Ch	2	20340023	1225278		11.133	12.075	97.3777

(b) Isopropyl 2-benzamido-2-methylpent-4-enoate
 (Table 2, entry b)

racemate



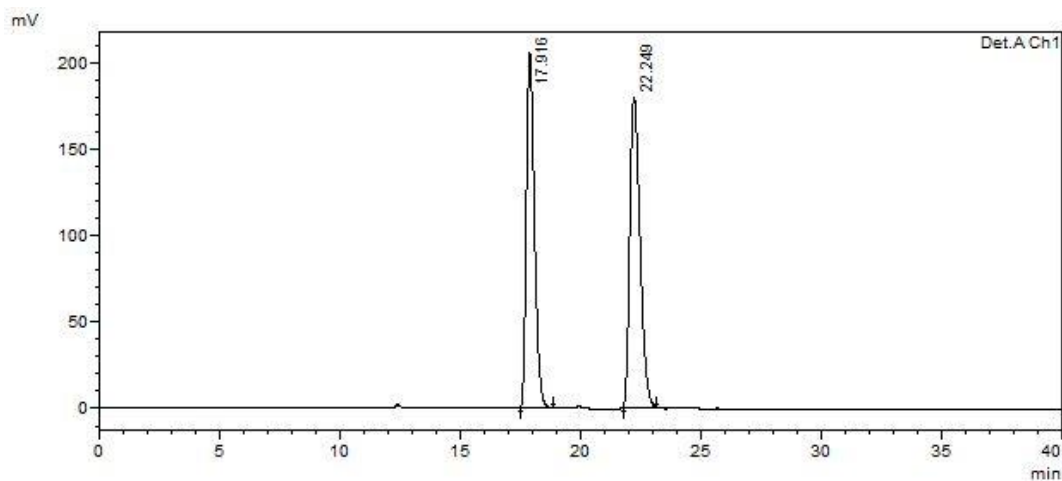
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT21.822	21.822	0.00000	Detector A - Ch	1	20619670	596514		21.258	23.058	49.9651
2	RT26.774	26.774	0.00000	Detector A - Ch	2	20648491	487350		26.200	28.225	50.0349



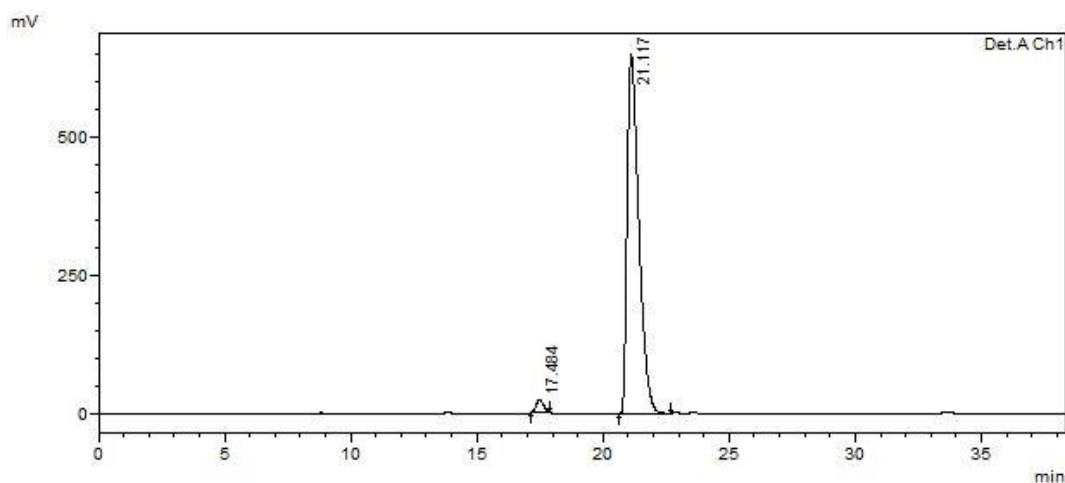
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT17.752	17.752	0.00000	Detector A - Ch	1	582367	28091		17.458	18.208	2.2461
2	RT22.281	22.281	0.00000	Detector A - Ch	2	25345825	728946		21.700	23.692	97.7539

(c) Isopropyl 2-benzamido-2-methylbutanoate
 (Table 2, entry c)

racemate



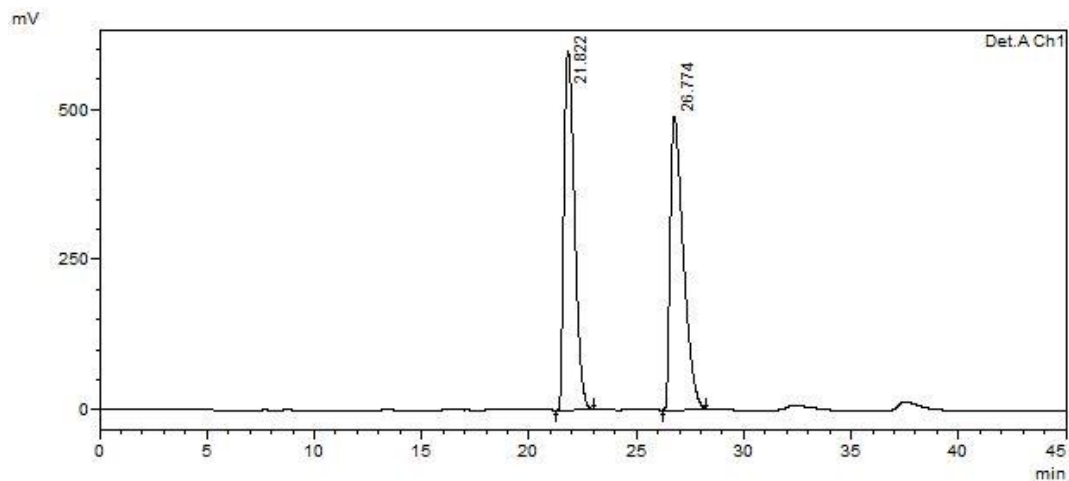
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT17.916	17.916	0.00000	Detector A - Ch	1	4764732	204945		17.542	18.875	47.4090
2	RT22.249	22.249	0.00000	Detector A - Ch	2	5285527	179037		21.792	23.167	52.5910



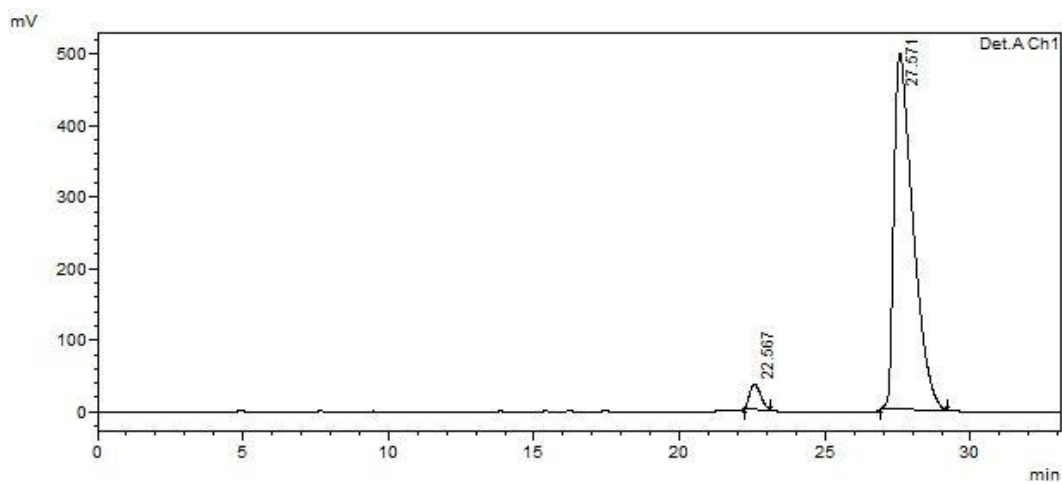
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT17.484	17.484	0.00000	Detector A - Ch	1	473424	23101		17.167	17.900	2.2273
2	RT21.117	21.117	0.00000	Detector A - Ch	2	20781774	649521		20.625	22.650	97.7727

(d) Isopropyl 2-benzamido-2-methylpent-4-ynoate
 (Table 2, entry d)

racemate



ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT21.822	21.822	0.00000	Detector A - Ch	1	20619670	596514		21.258	23.058	49.9651
2	RT26.774	26.774	0.00000	Detector A - Ch	2	20648491	487350		26.200	28.225	50.0349



ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT22.567	22.567	0.00000	Detector A - Ch	1	927608	35160		22.208	23.125	3.9141
2	RT27.571	27.571	0.00000	Detector A - Ch	2	22771277	497750		26.917	29.217	96.0859