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Supplementary Information

Dimeric Cinchona Ammonium Salts with Benzophenone Linkers: Enantioselective Phase Transfer Catalysts for the Synthesis of α-Amino Acids

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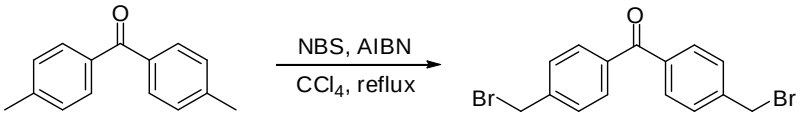
1. Materials and Instruments

Infrared (IR) spectra were recorded on a NICOLET iS10 spectrometer. Nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR) spectra were measured on a Bruker DPX 300 [300 MHz (^{1}H), 75 MHz (^{13}C)] spectrometer, Varian VNS 600 [600 MHz (^{1}H), 150 MHz (^{13}C)] spectrometer, using $CHCl_3$-*d* or 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}H-NMR and relative to the central DMSO-d_6 (δ 39.51) or $CHCl_3$-*d* (δ 77.23) resonance for ^{13}C-NMR. Coupling constants (*J*) in ^{1}H-NMR are in Hz. High performance liquid chromatography (HPLC) was performed on Shimadzu 20A instruments using 4.6 mm × 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 F_{254}, 0.25 mm) were 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

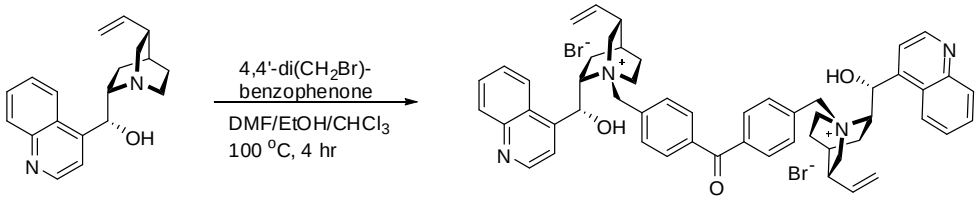
(a) 4,4'-Di(bromomethyl)benzophenone[S1]



4,4'-dimethylbenzophenone 4,4'-di(bromomethyl)benzophenone

2,2'-Azobis(isobutyronitrile) (8 mg, 0.048 mmol) was added to the solution of 4,4'-dimethylbenzophenone (1.0 gr, 4.8 mmol) and N-bromosuccinimide (NBS) (1.830 gr, 10.3 mmol) in carbon tetrachloride (10.0 mL) and the reaction mixture was refluxed for 18 hr. After cooling, the precipitate was filtered off and the filtrate was concentrated and purified with flash column chromatography (95:5, hexane/ethyl acetate) to afford the yellowish solid, yield (1.55 gr, 88%). ^{1}H NMR (300 MHz, Chloroform-*d*): δ 7.77 (d, J = 8.0, 4H), 7.55 (d, J = 8.0, 4H), 4.53 (s, 4H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 195.11, 142.22, 137.15, 130.42, 128.94, 32.14.[S1]

(b) *Bis*(4-(cinchonidium-N-methyl)phenyl)methanone

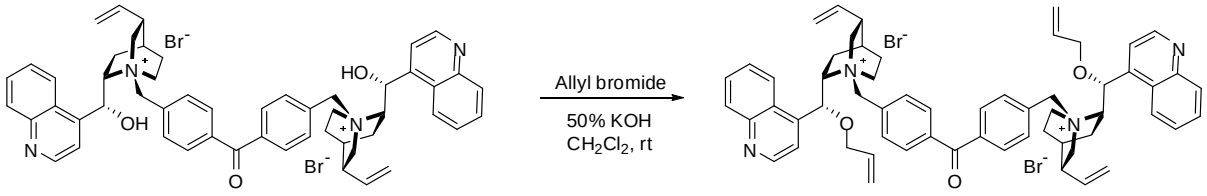


(-)-cinchonidine

bis(4-(cinchonidium-N-methyl)phenyl)methanone

A mixture of 4,4'-di(bromomethyl) benzophenone (100 mg, 0.27 mmol) and (-)-cinchonidine (145 mg, 0.49 mmol) in a mixed solvent (5 mL, DMF:EtOH:$CHCl_3$, v/v 6:5:2) was stirred for 4 hr at 100 °C under nitrogen atmosphere. After cooling the mixture was diluted with 3 mL of dichloromethane and dropped into 150 mL ethyl ether. The resulting solid was filtered and purified by flash column chromatography (10:1, CH_2Cl_2/MeOH) to afford the yellowish solid, yield (205 mg, 87%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.00 (d, *J* = 4.5, 2H), 8.32 (d, *J* = 8.6 Hz, 2H), 8.12 (d, *J* = 8.3 Hz, 2H), 7.97 (m, 8H), 7.92 – 7.72 (m, 6H), 6.79 (m, 2H), 6.58 (m, 2H), 5.77 – 5.62 (m, 2H), 5.32 – 5.09 (m, 6H), 4.97 (d, *J* = 11.1 Hz, 2H), 4.32 (m, 2H), 3.97 (m, 2H), 3.83 (m, 2H), 3.41 (m, 2H), 3.17 (m, 2H), 2.72 (m, 2H), 2.21 – 2.05 (m, 4H), 2.03 (m, 2H), 1.83 (m, 2H), 1.31 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 195.20, 150.14, 147.58, 145.18, 137.99, 137.88, 134.10, 132.65, 129.89, 129.78, 129.40, 127.31, 124.27, 123.81, 120.12, 116.42, 67.80, 64.03, 61.85, 59.39, 50.84, 36.89, 25.84, 24.28, 21.09. $[\alpha]_D^{24}$ -105 (*c* 1.00, CH_3OH). IR (KBr): 3441, 3420, 2942, 1952, 1853, 1732, 1655, 1509, 1282, 931, 778. HRMS (FAB$^+$) calcd for $C_{53}H_{56}BrN_4O_3^+$, $[M\text{-}Br]^+$: 875.3536 (86.3%), 877.3529 (100.0%), found: 875.3534, 877.3520.

(c) *Bis*(4-(O(9)-allylcinchonidium-N-methyl)phenyl)methanone dibromide (5pp)



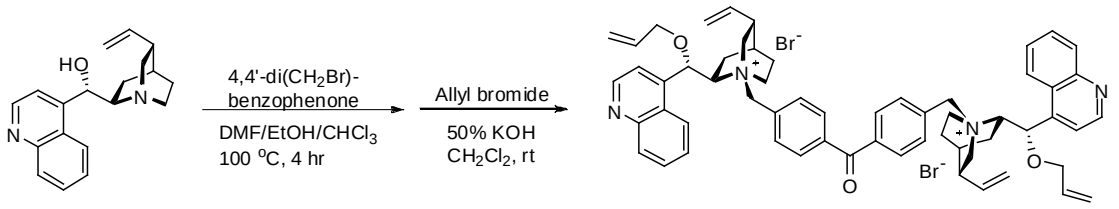
bis(4-(cinchonidium-N-methyl)phenyl)methanone

bis(4-(O(9)-allylcinchonidium-N-methyl)phenyl)methanone

A suspension of *bis*(4-(cinchonidium-N-methyl)phenyl)methanone (304 mg, 0.31 mmol) and allyl bromide (0.16 mL, 1.9 mmol)) in dichloromethane (10 mL) was mixed with 50% KOH aqueous solution (0.35 mL, 3.1mmol). The suspension was stirred at 0 °C 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, yield (293 mg, 90%). ^{1}H NMR (300 MHz, Chloroform-*d*): δ 8.95 (d, *J* = 4.5 Hz, 2H), 8.72 (d, *J* = 8.4 Hz, 2H), 8.12 (d, *J* = 8.3 Hz, 6H), 7.85 – 7.64 (m, 10H), 6.47 (d, *J* = 11.3 Hz, 2H), 6.31 (m, 2H), 6.14 (m, 2H), 5.60 (m, 2H), 5.46 – 5.27 (m, 6H), 4.95 (dd, *J* = 14.8, 10.9 Hz, 4H), 4.76 (m, 2H), 4.56 (m, 2H), 4.32 (m, 2H), 4.24 (d, *J* = 5.9 Hz, 4H), 3.58 (m, 2H), 3.44 (m, 2H), 2.73 (m, 2H), 2.32 – 2.11 (m, 8H), 1.45 (m, 2H). ^{13}C NMR(75 MHz, $CDCl_3$-*d*) : δ 195.95, 149.67, 148.64, 140.43, 138.91, 136.66, 134.45, 132.93, 131.99, 130.60, 130.33, 130.17, 128.96, 125.44, 124.53, 119.79, 118.16, 77.43, 70.50, 67.19, 62.04, 59.90, 51.95, 37.58, 26.98, 25.20, 22.66. $[\alpha]_D^{24}$ -80 (*c* 1.00, CH_2Cl_2). IR (KBr): 3385, 3072, 2948, 1962, 1858, 1733, 1657, 1460, 1283, 1069, 934, 770, 627. HRMS (FAB$^+$) calcd for $C_{59}H_{64}BrN_4O_3^+$, $[M\text{-}Br]^+$: 955.4162 (82.8%), 957.4157 (100.0%), found: 955.4160, 957.4241.

(d) *Bis*(4-(O(9)-allylcinchonium-N-methyl)phenyl)methanone dibromide (6pp)



***Bis*(4-(cinchonium-N-methyl)phenyl)methanone dibromide**:

A mixture of 4,4'-di(bromomethyl) benzophenone (101 mg, 0.27 mmol) and (+)-cinchonine (144 mg, 0.49 mmol) in a mixed solvent (5 mL, DMF:EtOH:$CHCl_3$, 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 50 mL ethyl ether. The resulting solid was filtered and purified by flash column chromatography (10:1, CH_2Cl_2/MeOH) to afford the yellowish solid, yield (223 mg, 95%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.98 (d, *J* = 4.5 Hz, 2H), 8.40 (d, *J* = 8.0 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.99 (m, 8H), 7.84 (m, 4H), 7.76 (m, 2H), 6.89 (m, 2H), 6.55 (m, 2H), 6.02 (m, 2H), 5.37 – 5.07 (m, 8H), 4.30 (m, 2H), 4.10 – 3.96 (m, 4H), 3.59 (m, 2H), 3.17 – 3.01 (m, 2H), 2.68 (m, 2H), 2.31 (m, 2H), 1.91 (m, 2H), 1.80 (m, 4H), 1.05 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 195.31, 150.21, 147.63, 145.05, 138.00, 137.08, 134.18, 132.58, 130.00, 129.76, 129.54, 127.45, 124.42, 123.97, 120.14, 117.17, 67.46, 64.85, 61.74, 56.37, 54.21, 36.80, 26.37, 23.15, 20.87. $[\alpha]_D^{24}$ +82 (*c* 1.00, CH_3OH). IR (KBr): 3390, 3188, 1660, 1611, 1509, 1280, 1118, 1009, 930. HRMS (FAB$^+$) calcd for $C_{53}H_{56}BrN_4O_3^+$, $[M\text{-}Br]^+$: 875.3536 (86.3%), 877.3529 (100.0%), found: 875.3540, 877.3581.

***Bis*(4-(O(9)-allylcinchonium-N-methyl)phenyl)methanone dibromide**:

A suspension of *bis*(4-(cinchonium-N-methyl)phenyl)methanone (70 mg, 0.0352 mmol) and allyl bromide (38 mg, 0.31 mmol)) in dichloromethane (3 mL) was mixed with 50% KOH aqueous solution (0.25 mL, 2.2 mmol). The suspension was stirred at 0 °C 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, yield (52 mg, 67%). ^{1}H NMR (300 MHz, Chloroform-*d*): δ 8.99 (d, *J* = 4.4 Hz, 2H), 8.97 – 8.86 (m, 2H), 8.14 (dd, *J* = 8.3, 4.0 Hz, 6H), 7.88 - 7.77 (m, 8H), 7.69 (m, 2H), 6.65 (m, 2H), 6.35 – 6.22 (m, 2H), 6.14 (m, 2H), 5.93 (m, 2H), 5.60 – 5.22 (m, 10H), 4.72 (m, 2H), 4.59 (m, 2H), 4.31 (m, 4H), 4.10 (m, 2H), 3.64 (t, *J* = 11.3 Hz, 2H), 2.98 (m, 2H), 2.66 (m, 2H), 2.40 (m, 2H), 2.01 (d, *J* = 3.6 Hz, 6H), 1.12 (m, 2H). ^{13}C NMR(75 MHz, $CDCl_3$-*d*) : δ 195.28, 149.62, 148.64, 139.76, 138.70, 135.41, 134.46, 132.63, 131.88, 130.62, 130.30, 130.09, 129.10, 125.41, 124.92, 119.98, 118.37, 77.44, 70.61, 66.68, 61.39, 56.51, 55.21, 37.62, 27.19, 23.58, 22.34. $[\alpha]_D^{24}$ +60 (*c* 1.00, CH_2Cl_2). IR (KBr): 3362, 2918, 1733, 1659, 1508, 1278, 1129, 1056, 930, 867, 779. HRMS (FAB^+) calcd for $C_{59}H_{64}BrN_4O_3^+$, $[M\text{-}Br]^+$: 955.4162 (82.3%), 957.4157 (100.0%), found: 955.4150, 957.4271.

(2) Product Analysis

a) α-Alkylated Products

***tert*-Butyl 2-(diphenylmethyleneamino)-3-phenylpropanoate**[S2] (from benzyl bromide): ^{1}H 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 (s, 9H).

***tert*-Butyl 2-(diphenylmethyleneamino)pent-4-enoate**[S2] (from allyl bromide): ^{1}H 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 (s, 9H).

***tert*-Butyl 2-(diphenylmethyleneamino)-4-methylpent-4-enoate**[S2] (from methallyl bromide): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.63 (dt, *J* = 6.6, 1.6 Hz, 2H), 7.42 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.32 (dd, *J* = 9.1, 3.3 Hz, 3H), 7.21-7.13 (m, 2H), 4.77-4.68 (m, 2H), 4.08 (dd, *J* = 8.2, 5.3 Hz, 1H), 2.60 (qd, *J* = 13.8, 6.7 Hz, 2H), 1.52 (s, 3H), 1.45 (s, 9H).

(E)-*tert*-Butyl 2-(diphenylmethyleneamino)-5-phenylpent-4-enoate[S3] (from cinnamyl bromide): ^{1}H 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 (s, 9H).

***tert*-Butyl 2-(diphenylmethyleneamino)pent-4-ynoate**[S4] (from propargyl bromide): ^{1}H 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 (s, 9H).

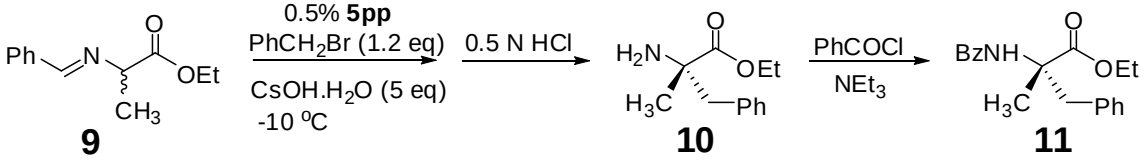
***tert*-Butyl 2-(diphenylmethyleneamino)-3-(naphthalene-1-yl)propanoate**[S5] (from 1-bromomethyl naphthalene): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.86-7.61 (m, 4H), 7.39 (d, *J* = 7.0 Hz, 1H), 7.37-7.20 (m, 8H), 6.96 (t, *J* = 7.7 Hz, 2H), 6.26 (s, 2H), 4.31 (dd, *J* = 9.6, 4.1 Hz, 1H), 3.80 (dd,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

***tert*-Butyl 2-(diphenylmethyleneamino)butanoate**[S2] (from ethyl iodide): ^{1}H 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 (t, *J* = 7.4 Hz, 3H).

***tert*-Butyl 2-(diphenylmethyleneamino)propanoate**[S2] (from methyl iodide): ^{1}H 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 (d, *J* = 6.7 Hz, 3H).

***tert*-Butyl 2-benzamido-3-(carbo-*tert*-butoxy)-propionate**[S6] (from tert-butyl bromoacetate): ^{1}H NMR (300 MHz, Chloroform-*d*) δ

b) α,α-Dialkylated Product



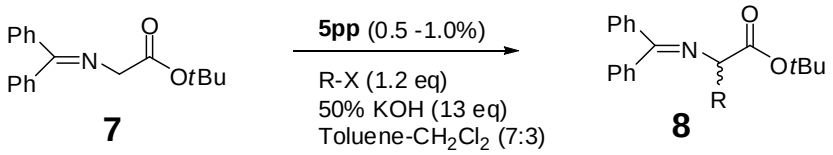
Ethyl 2-(benzylideneamino)propanoate[S7] **(9):** ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.32 (s, 1H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 6.9 Hz, 3H), 7.24 (s, 2H), 7.18 (d, *J* = 7.3 Hz, 2H), 4.24 – 4.12 (m, 3H), 2.36 (s, 2H), 1.53 (d, *J* = 6.9 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 172.76, 163.10, 135.90, 131.26, 128.76, 128.67, 68.24, 61.26, 19.63, 14.37.

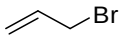
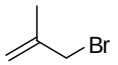
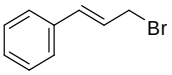
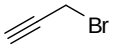
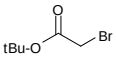
Ethyl 2-amino-2-methyl-3-phenylpropionate[S8] **(10):** ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 6.5 Hz, 3H), 7.16 (dd, *J* = 7.7, 1.9 Hz, 2H), 4.23-4.06 (m, 2H), 3.14 (d, *J* = 13.2 Hz, 1H), 2.80 (d, *J* = 13.1 Hz, 1H), 1.39 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.27, 136.78, 130.19, 128.49, 127.10, 61.29, 58.85, 46.97, 26.90, 14.41.

Ethyl 2-benzamido-2-methyl-3-phenylpropionate (11): ^{1}H NMR (300 MHz, Chloroform-*d*) 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 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) 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.

c) Chiral HPLC Conditions

Chiral column: DAICEL Chiralcel OD (4.6 x 250 mm), temperature: 23 °C, detection: λ= 254 nm. Retention time was established by analysis of the racemate of which the enantioisomers were fully resolved.[S9] Eluents were adjusted on each alkylated products.



alkylated imine (**8**) R-X	eluent : (hexane : 2-propanol)	flow rate (mL/min)	retention times (min) minor (*R*)	major (*S*)
$PhCH_2$-Br	100 : 1.0	0.5	12.5	18.1
	100 : 1.0	0.5	9.1	8.5
	100 : 1.0	0.5	19.6	13.5
	100 : 1.0	0.5	18.1	14.4
	100 : 1.0	0.5	11.6	11.0
	100 : 1.0	0.5	19.6	21.2
CH_3CH_2I	100 : 1.0	0.8	9.5	8.8
CH_3I	100 : 1.0	0.5	9.5	8.9
	100 : 6.5	0.5	12.0[a]	15.0[a]
11	100 : 2.0	0.5	20.1	24.3

[a] N-benzoylated derivative.

(3) References

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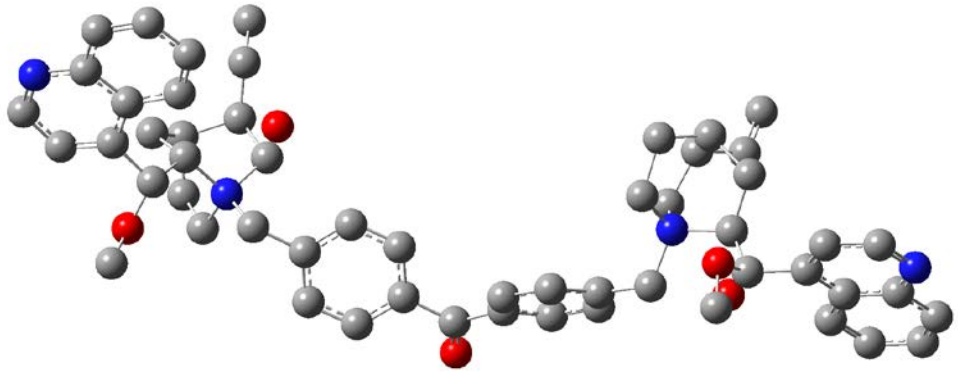
(4) Quantum Calculation Data

Geometry of the simplified model of **5PP** was optimized at B3LYP/6-31G(d). Frequency calculation has been carried out to determine minima. 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)

***Bis*(4-(O(9)-methylcinchonidium-N-methyl)phenyl)methanone dihydroxide**



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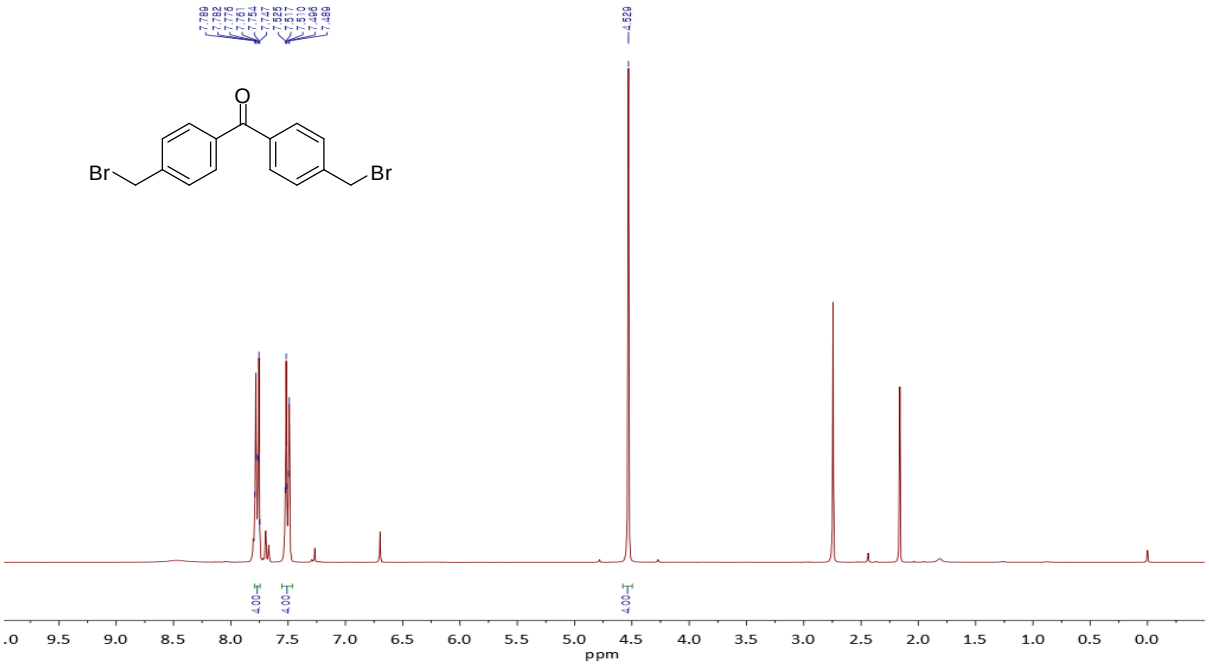
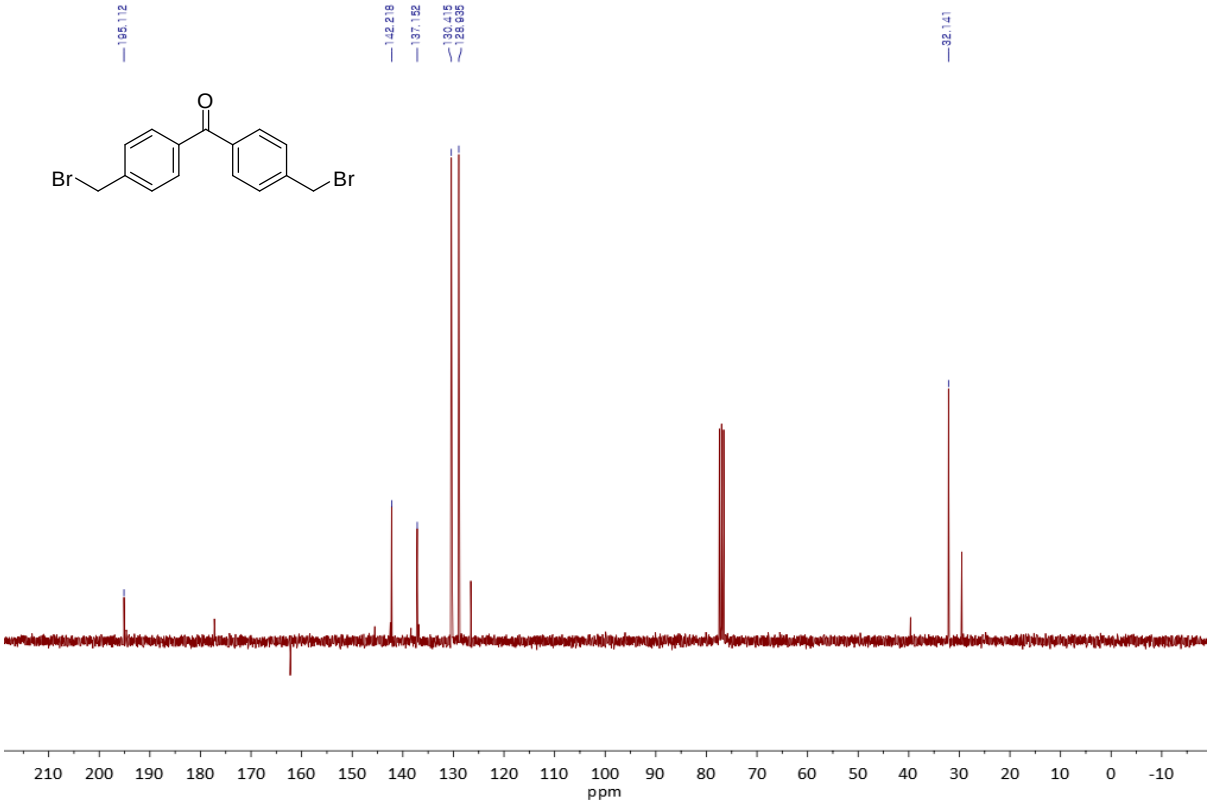
3. Spectroscopic data

(1) 4,4’-Di(bromomethyl)benzophenone





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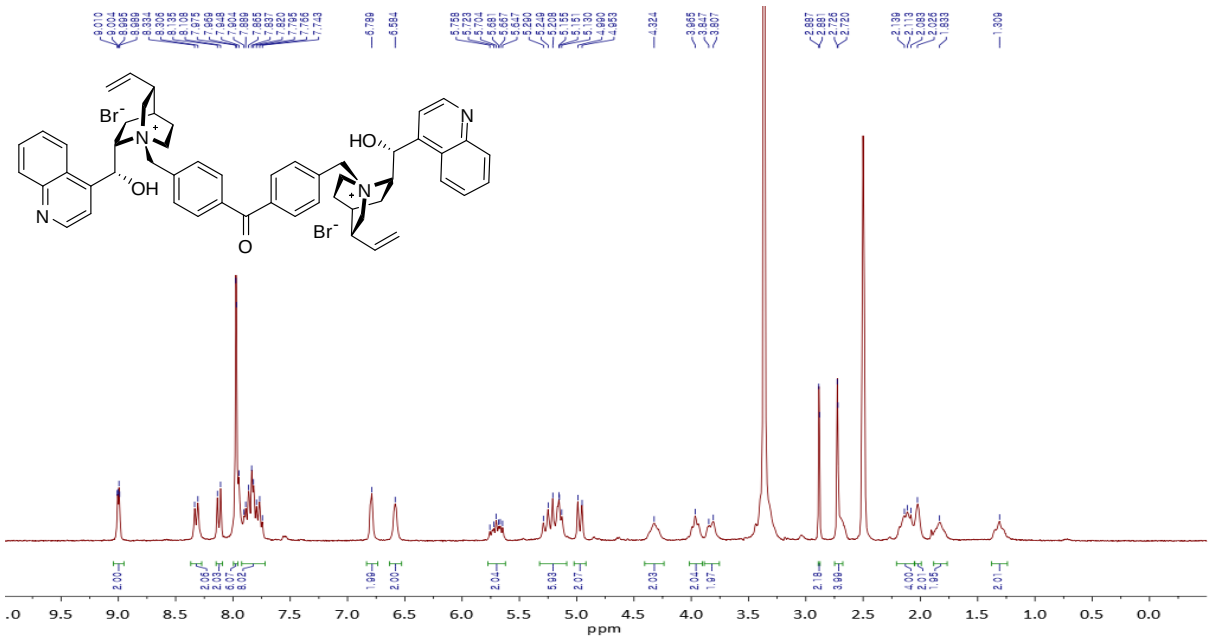
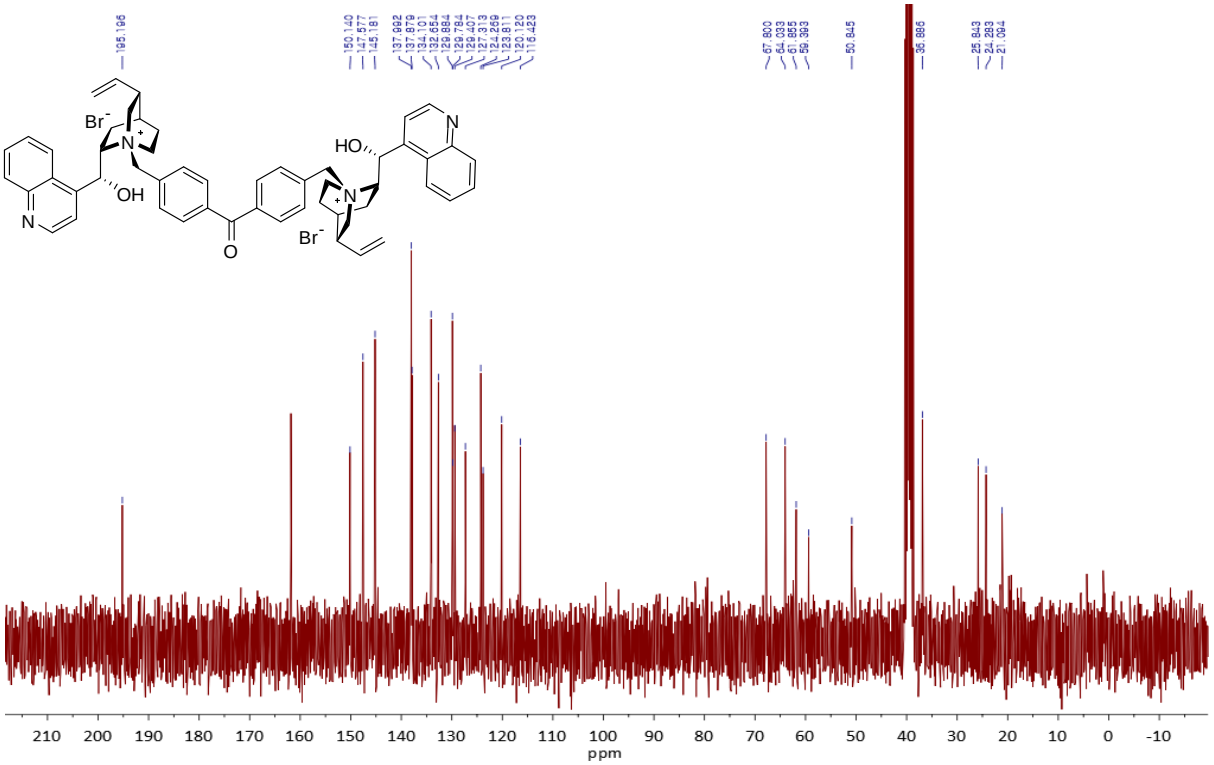
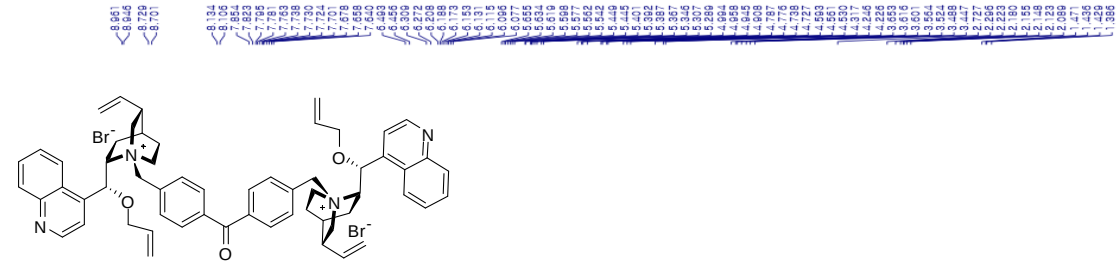
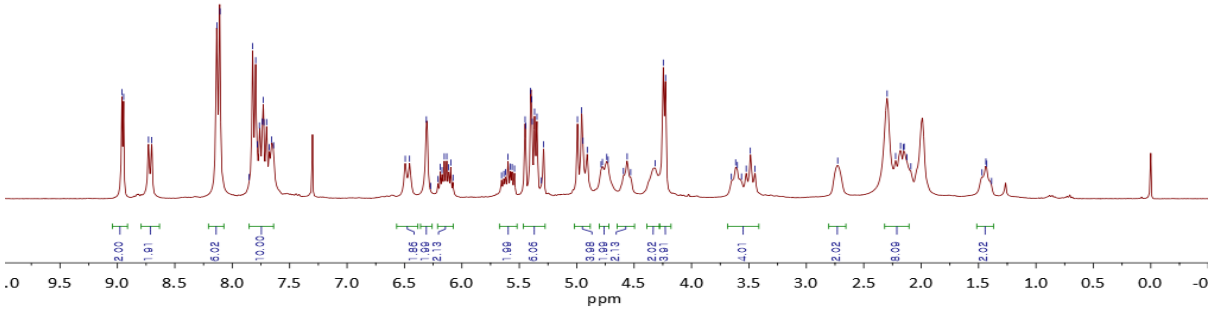
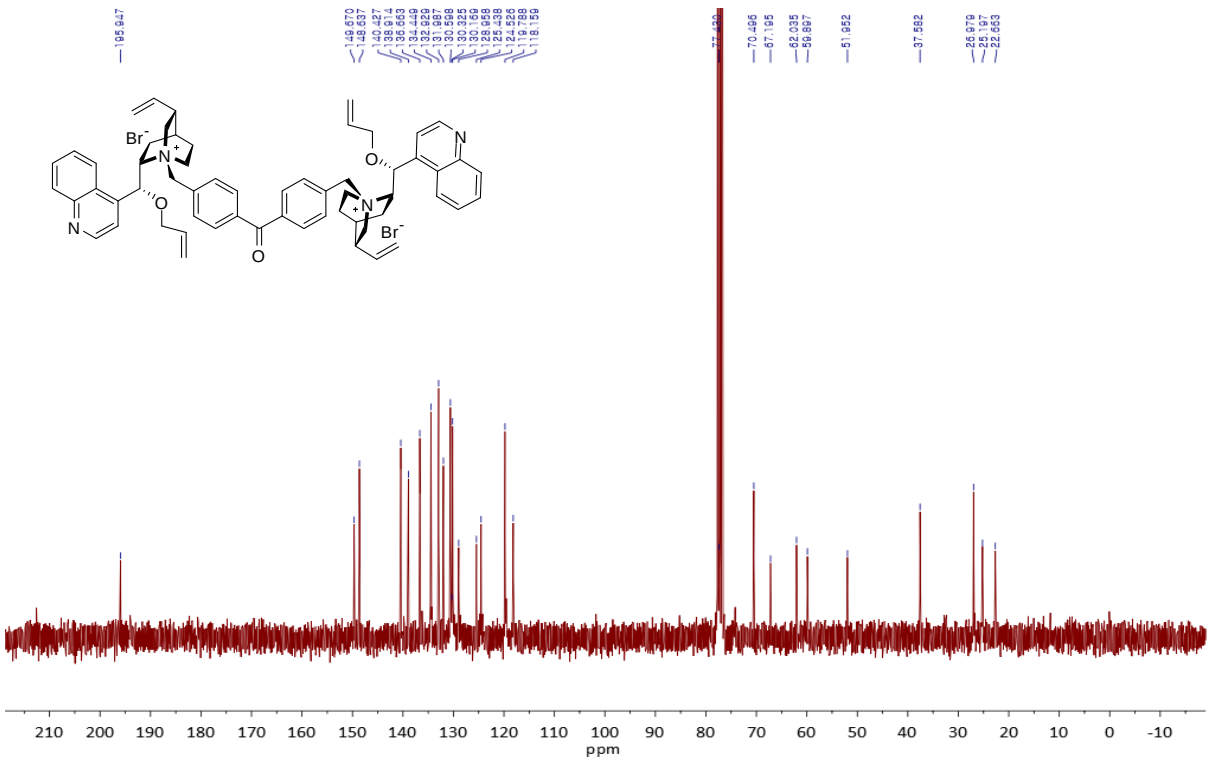




(3) *Bis*(4-(O(9)-allylcinchonidium-N-methyl)phenyl)methanone dibromide (5pp)







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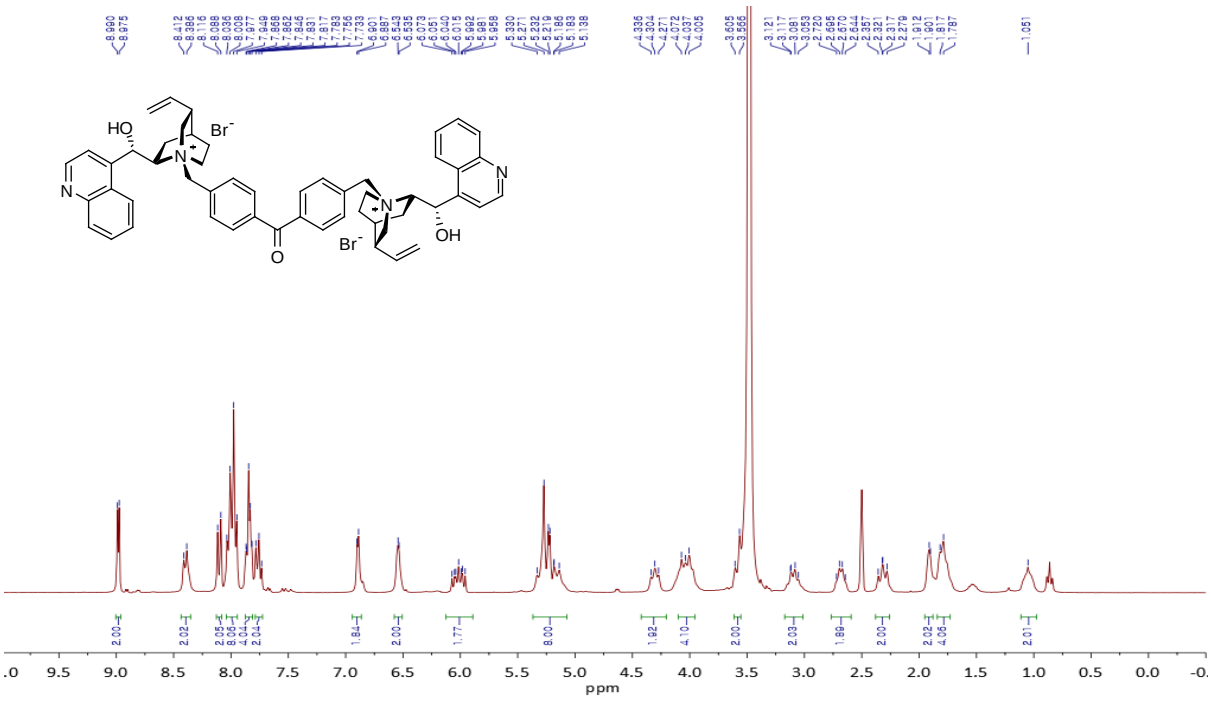

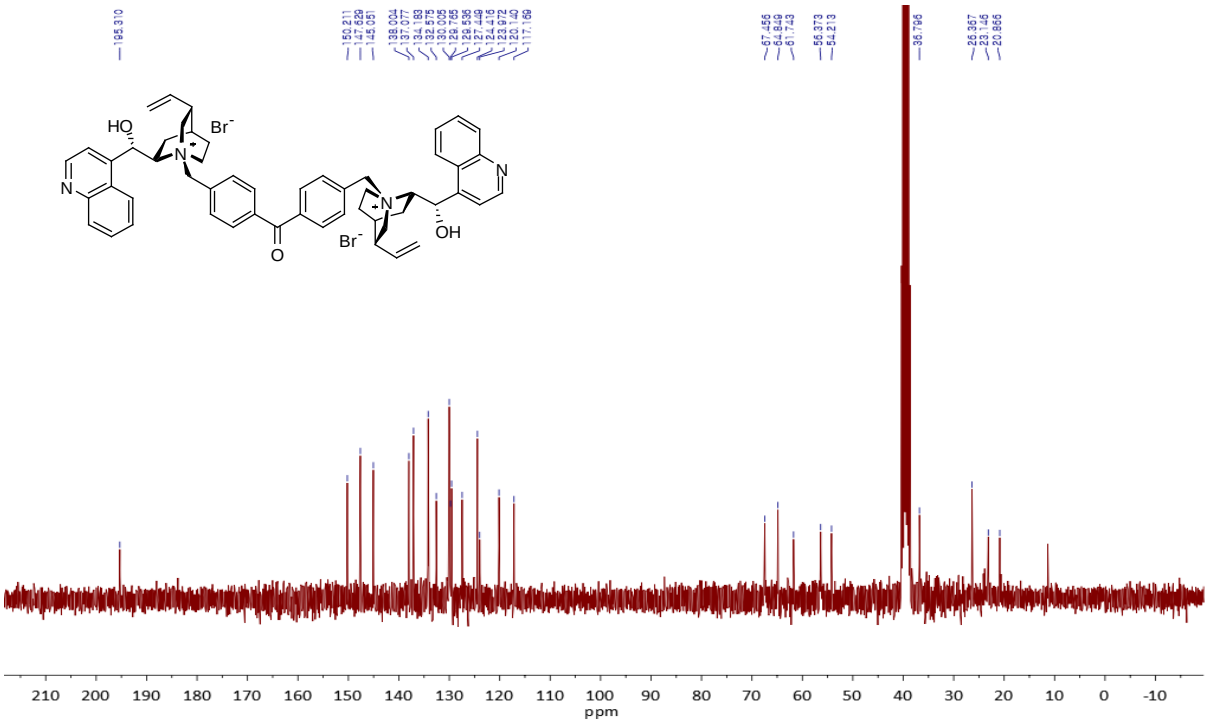

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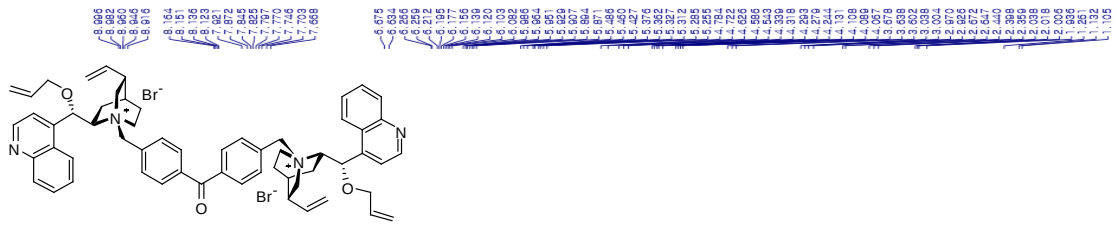
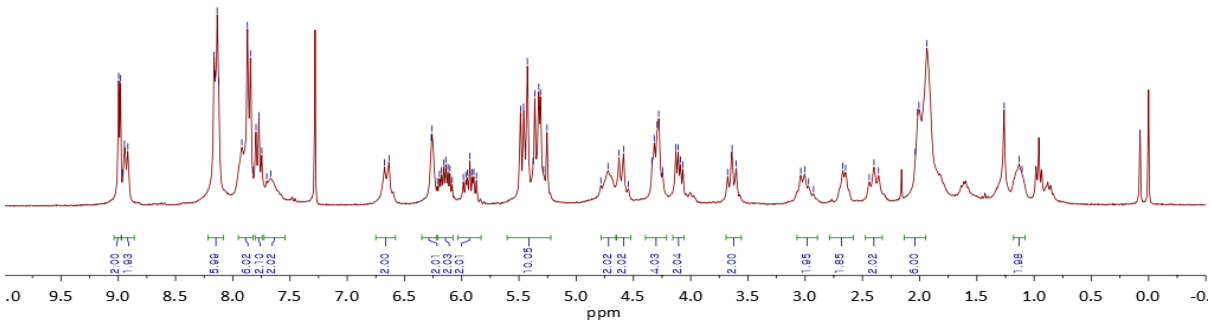
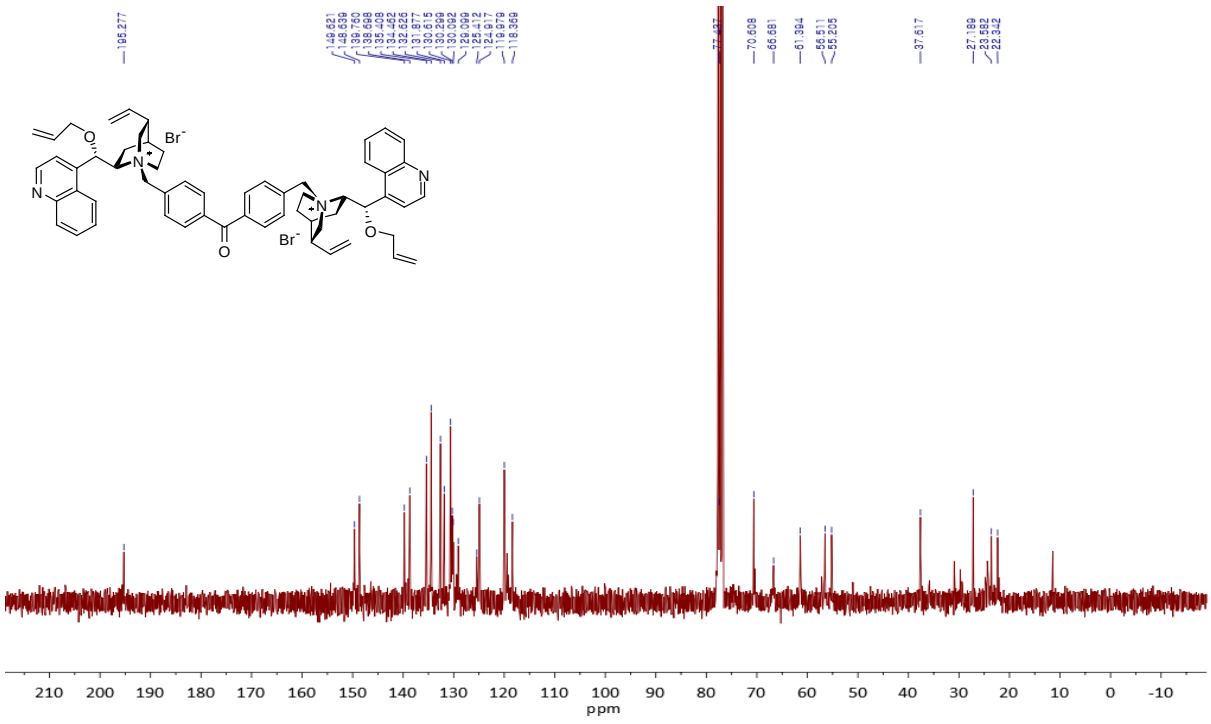
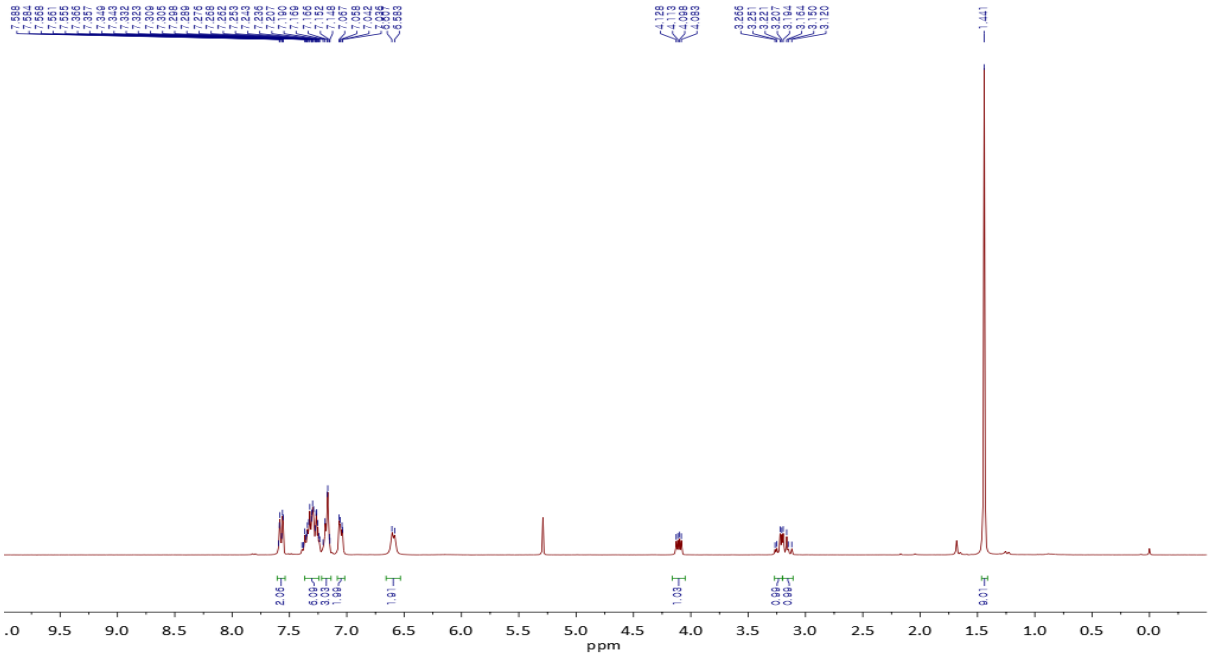






(6) *tert*-Butyl 2-(diphenylmethyleneamino)-3-phenylpropanoate



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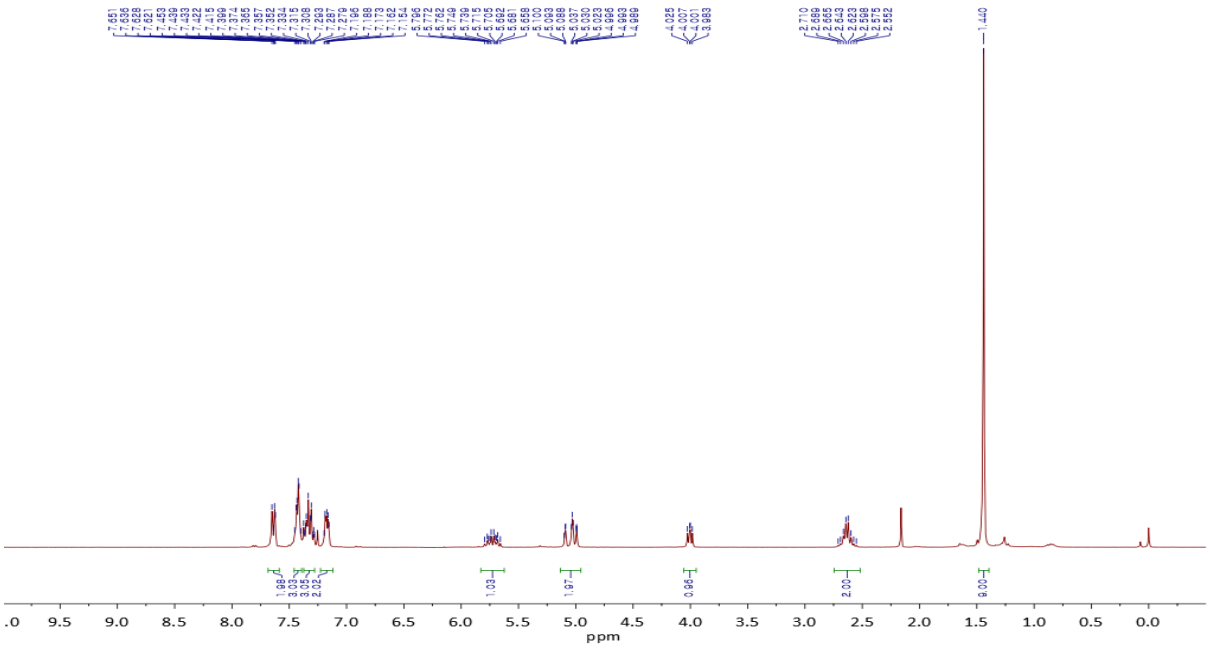

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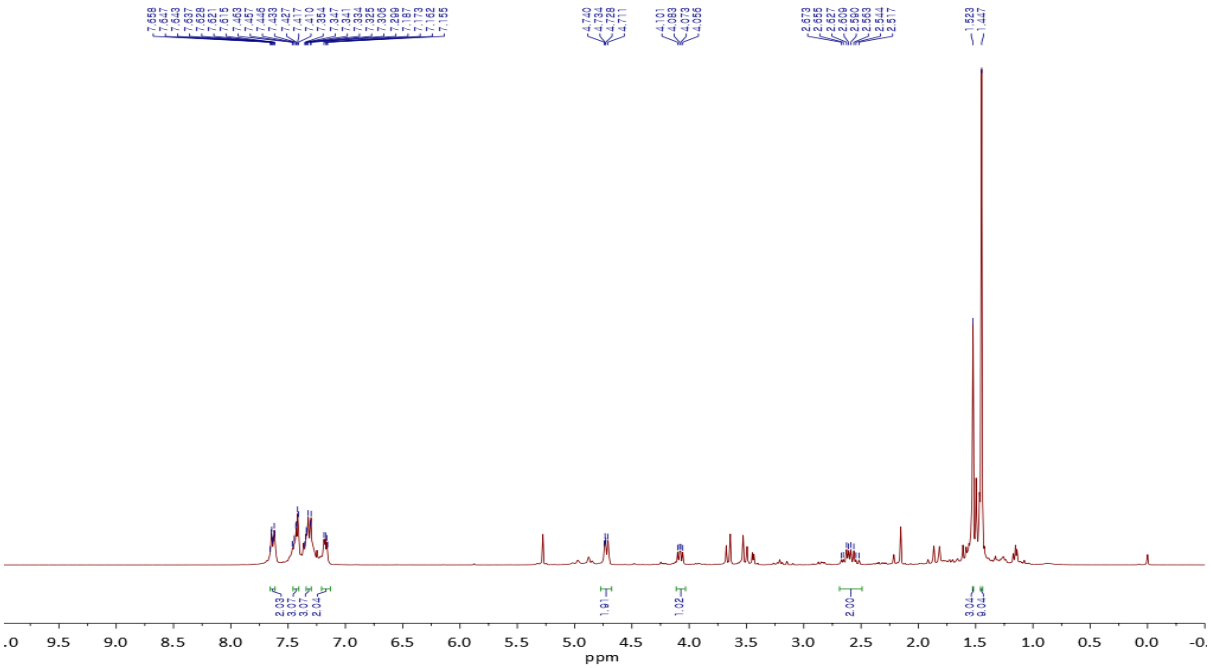
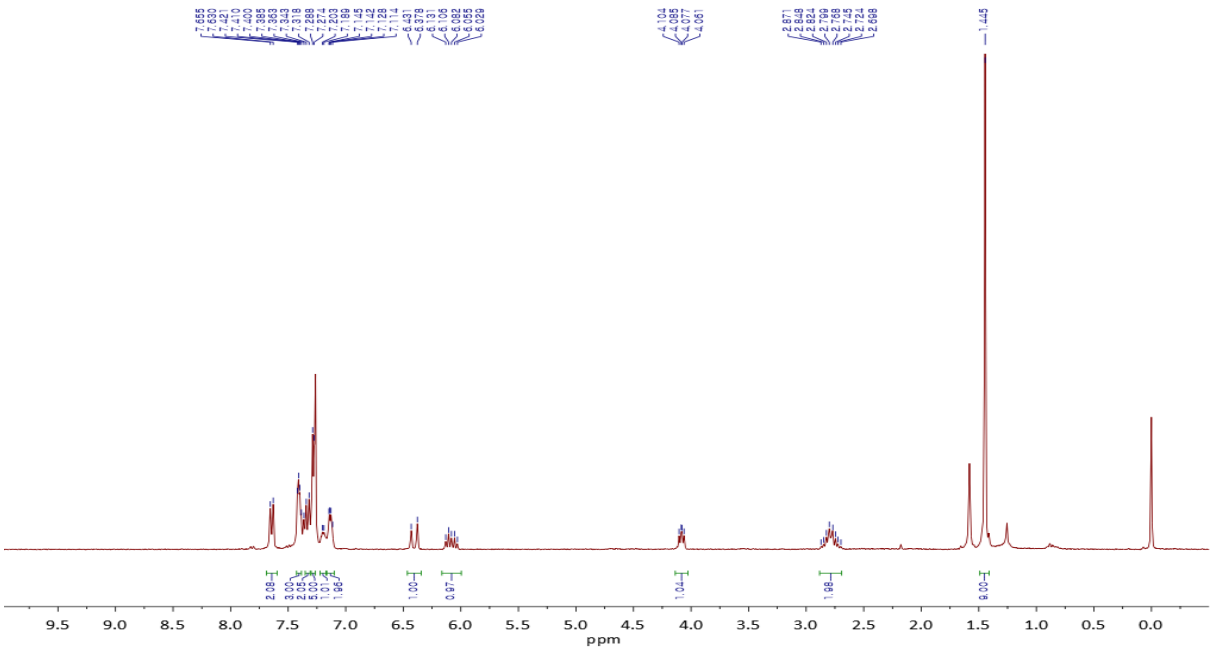


(9) (E)-*tert*-Butyl 2-(diphenylmethyleneamino)-5-phenylpent-4-enoate



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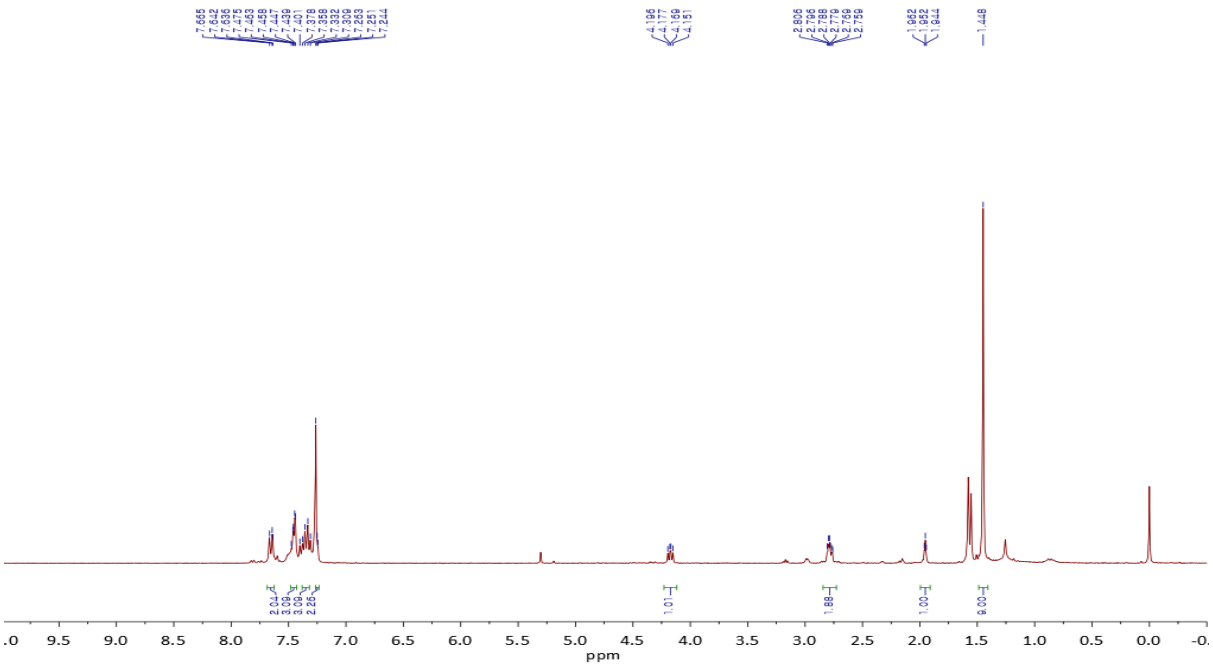
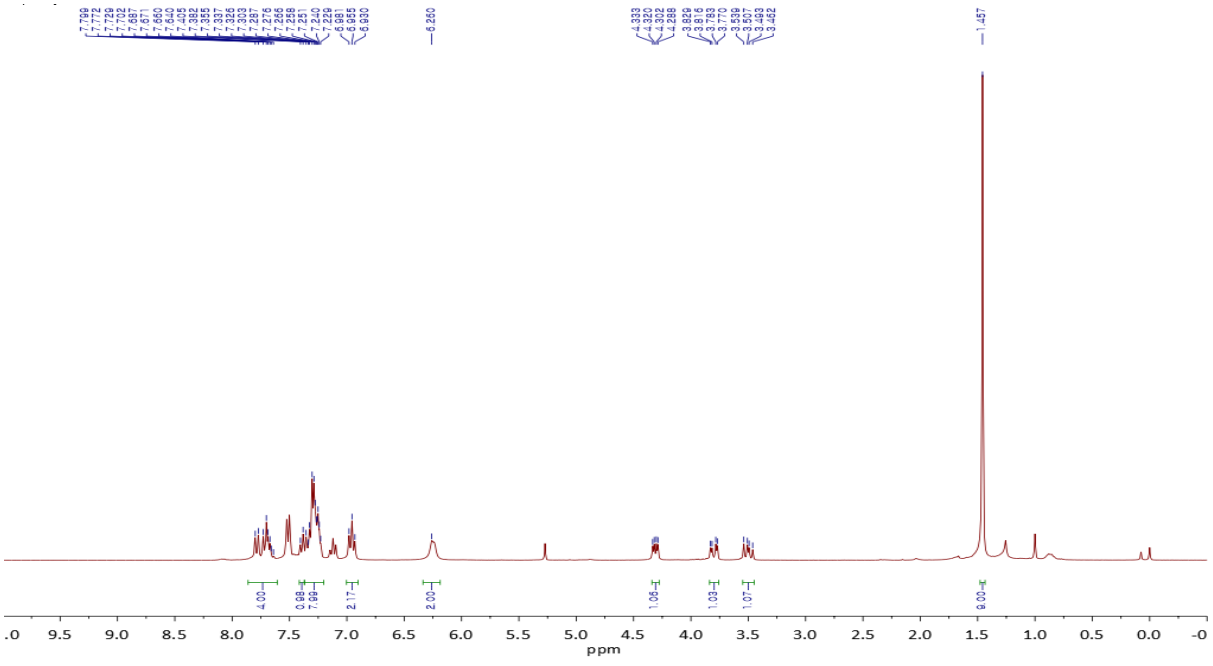
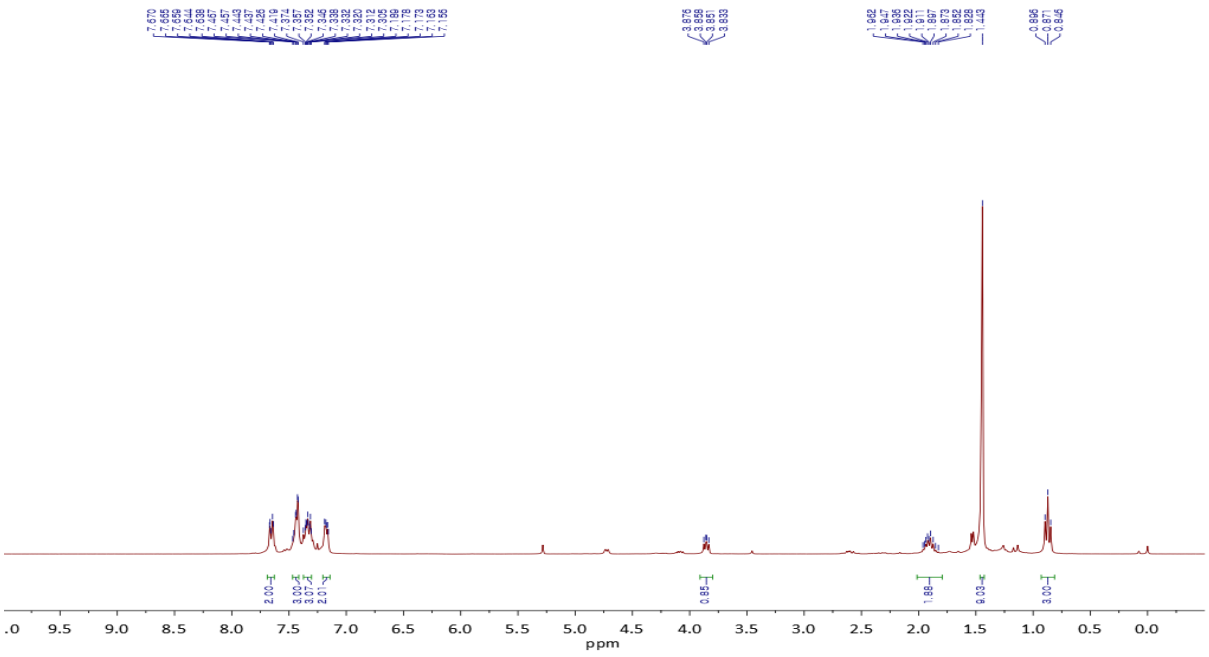


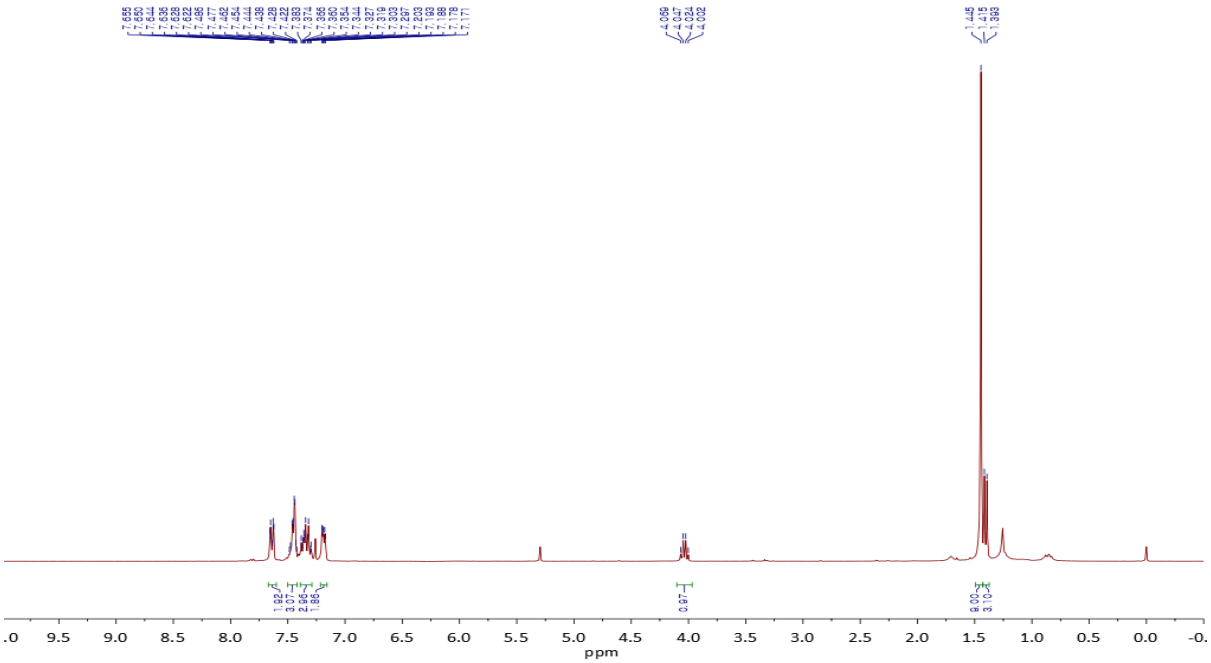
(11) *tert*-Butyl 2-(diphenylmethyleneamino)-3-(naphthalene-1-yl)propanoate



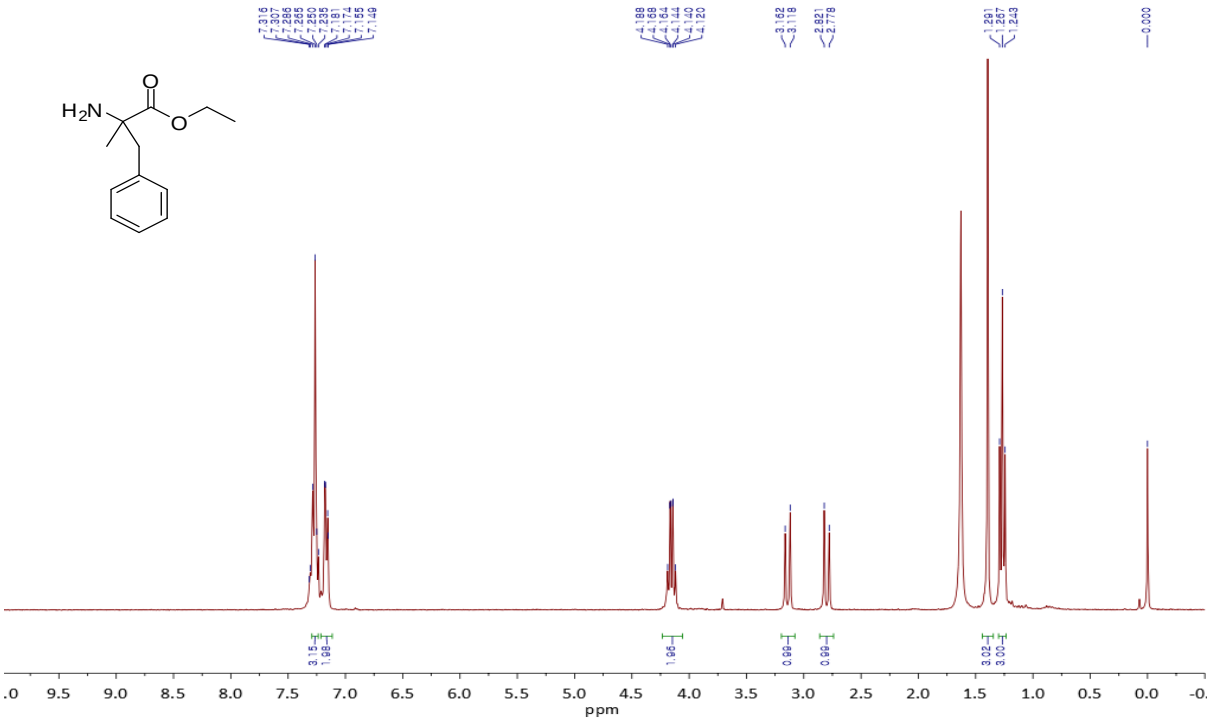
(12) *tert*-Butyl 2-(diphenylmethyleneamino)butanoate

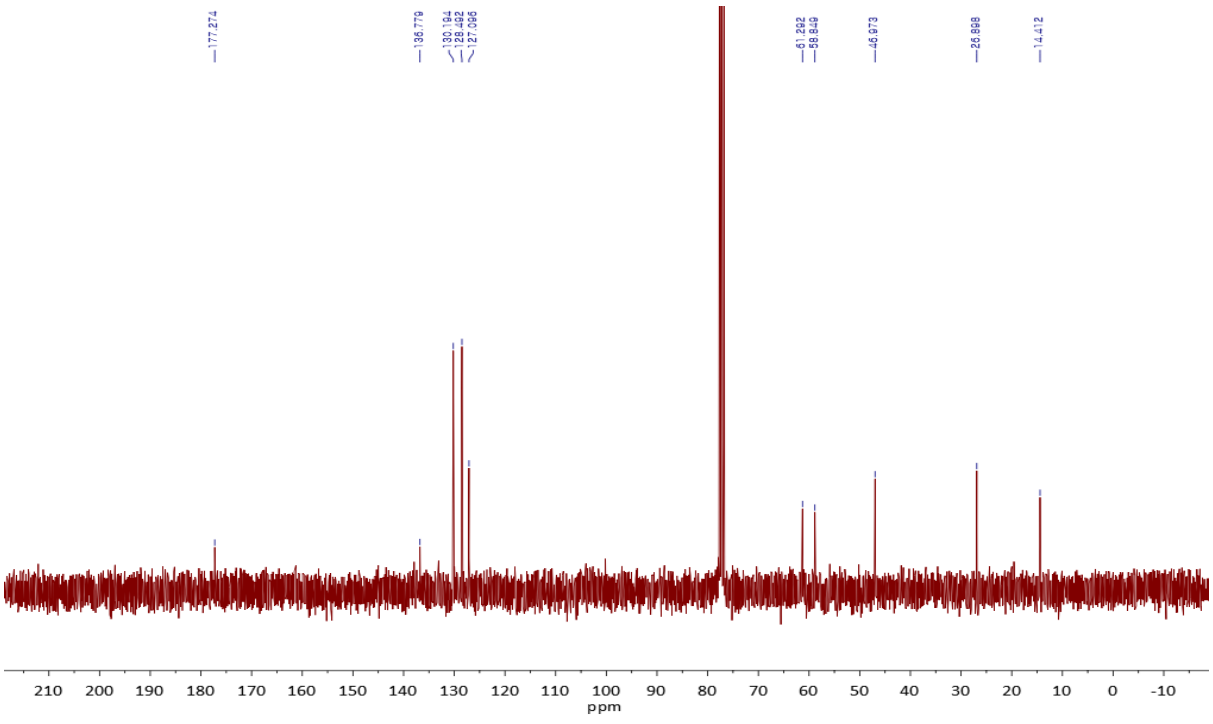


(13) *tert*-Butyl 2-(diphenylmethyleneamino)propanoate

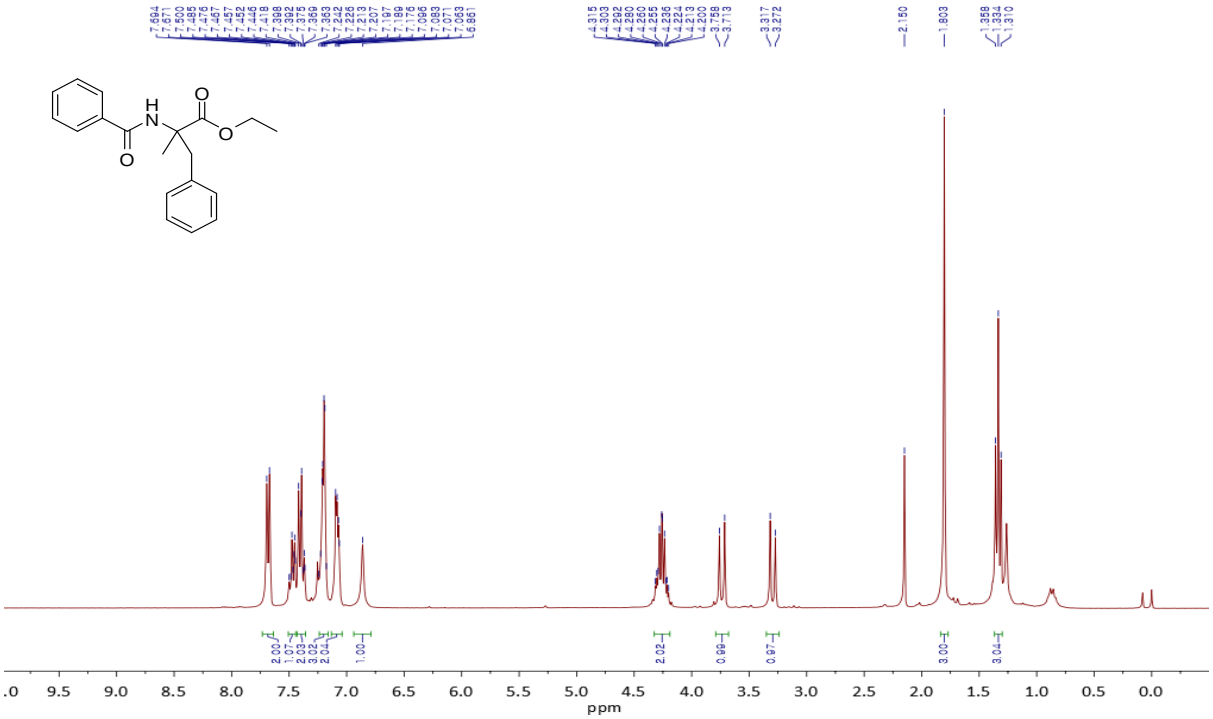


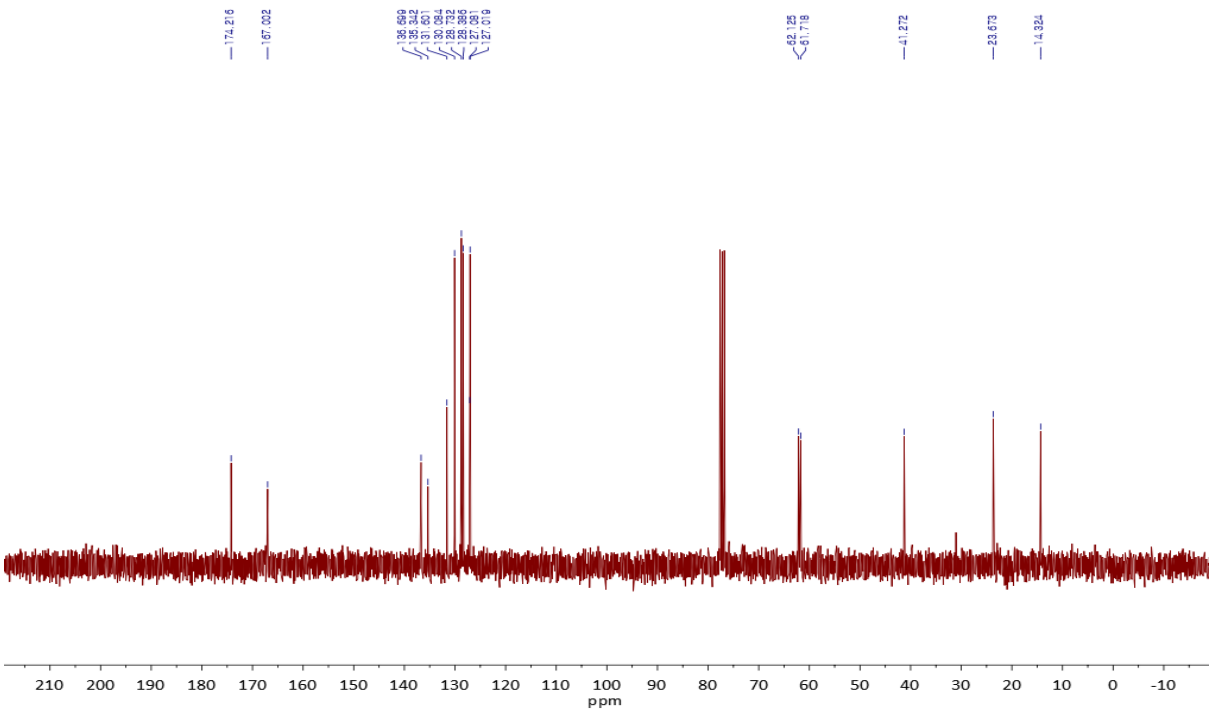
(14) Ethyl 2-amino-2-methyl-3-phenylpropionate (10)





(15) Ethyl 2-benzamido-2-methyl-3-phenylpropionate (11)



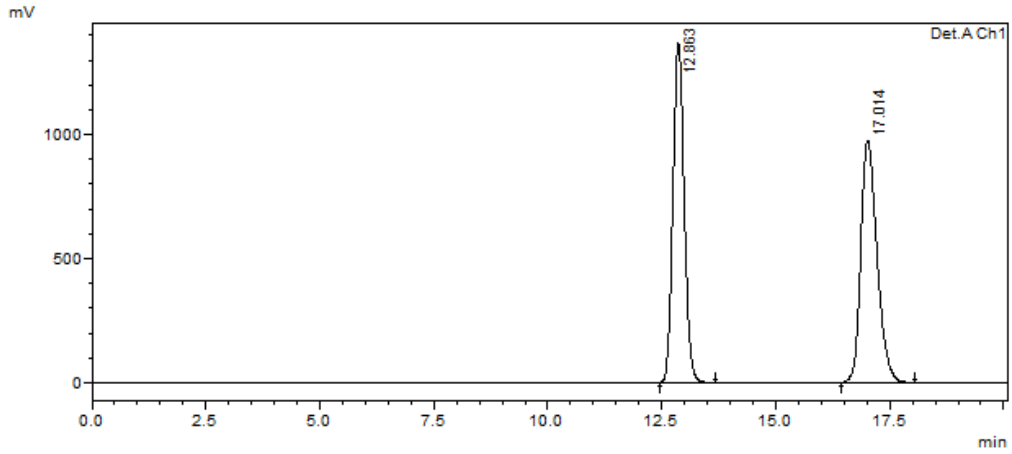


4. HPLC data

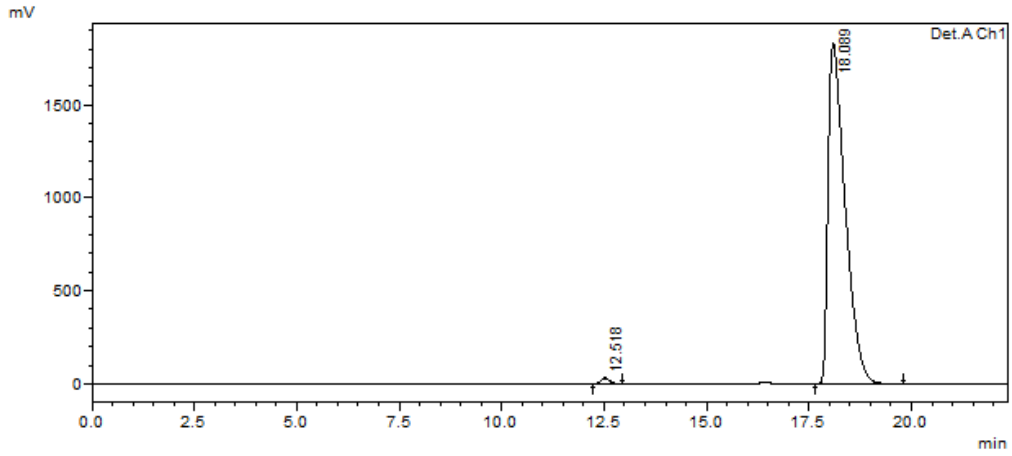
(1) Product **8**. (Table 2)

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

racemate



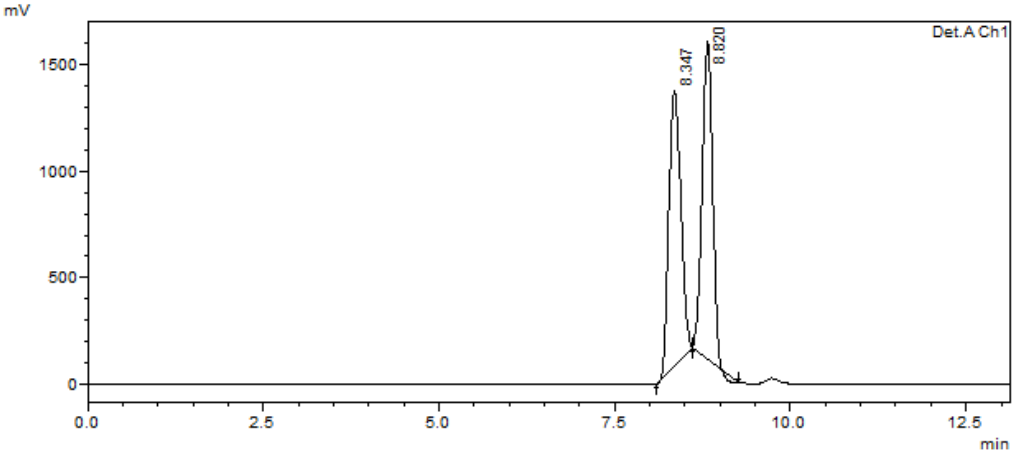
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT12.863	12.863	0.00000	Detector A - Ch	1	23450825	1369173		12.467	13.667	49.2892
2	RT17.014	17.014	0.00000	Detector A - Ch	2	24127187	975856		16.433	18.058	50.7108



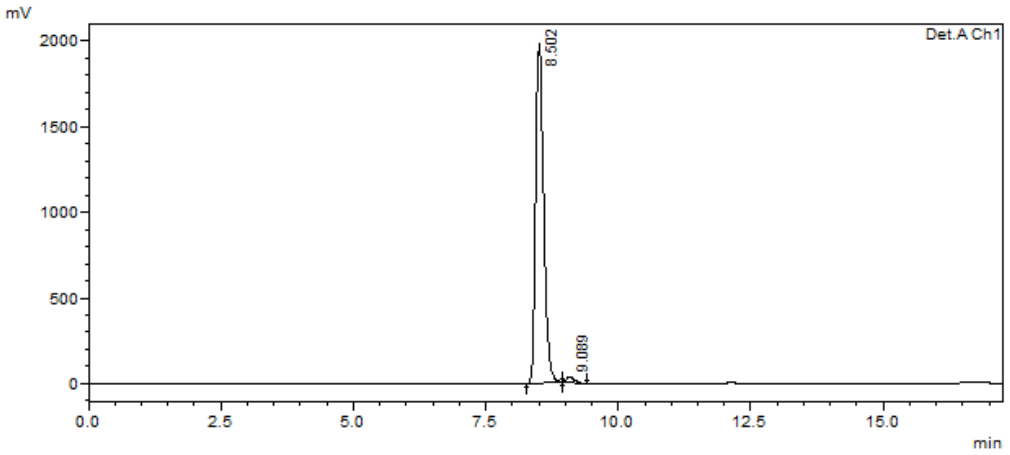
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT12.518	12.518	0.00000	Detector A - Ch	1	449952	30301		12.233	12.958	0.8413
2	RT18.089	18.089	0.00000	Detector A - Ch	2	53033745	1830752		17.667	19.800	99.1587

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

racemate



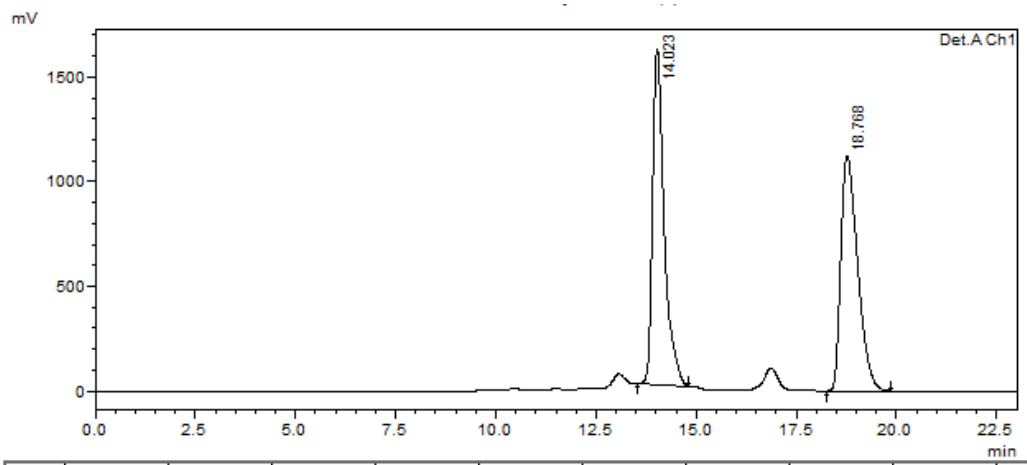
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT8.347	8.347	0.00000	Detector A - Ch	1	15402908	1291688		8.092	8.600	50.3486
2	RT8.820	8.820	0.00000	Detector A - Ch	2	15189641	1492721		8.600	9.267	49.6514



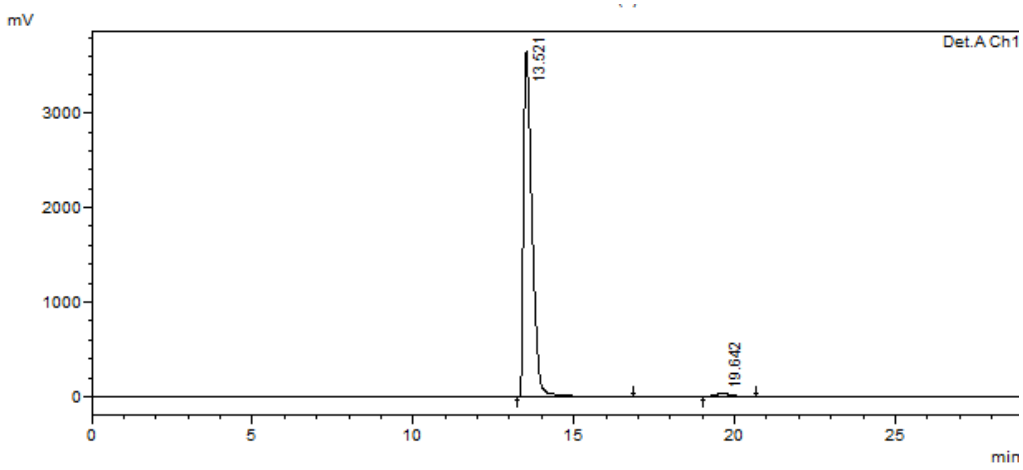
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT8.502	8.502	0.00000	Detector A - Ch	1	20849175	1981803		8.267	8.933	98.4991
2	RT9.089	9.089	0.00000	Detector A - Ch	2	317697	32213		8.942	9.392	1.5009

(c) *tert*-Butyl 2-(diphenylmethyleneamino)-4-methylpent-4-enoate
(Entry 3, from methallyl-Br)

racemate



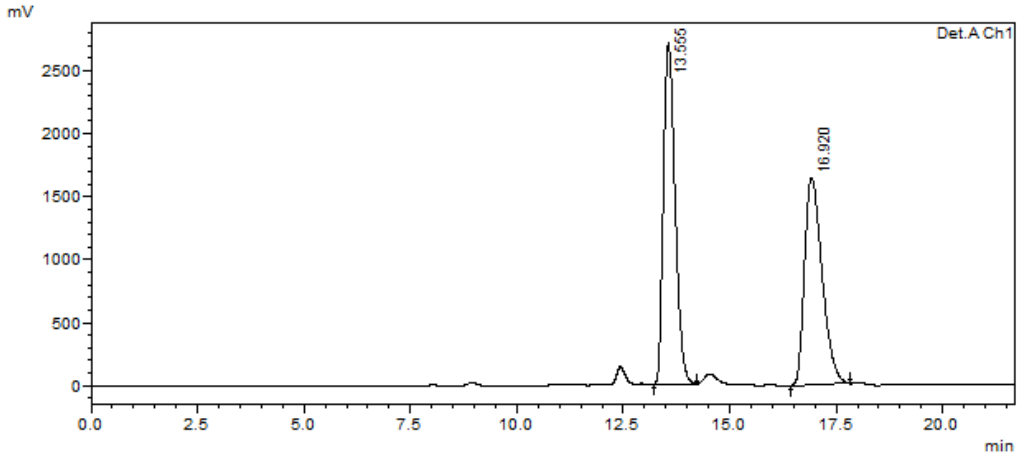
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT14.023	14.023	0.00000	Detector A - Ch	1	32746484	1602417		13.525	14.800	49.9332
2	RT18.768	18.768	0.00000	Detector A - Ch	2	32834121	1123859		18.275	19.858	50.0668



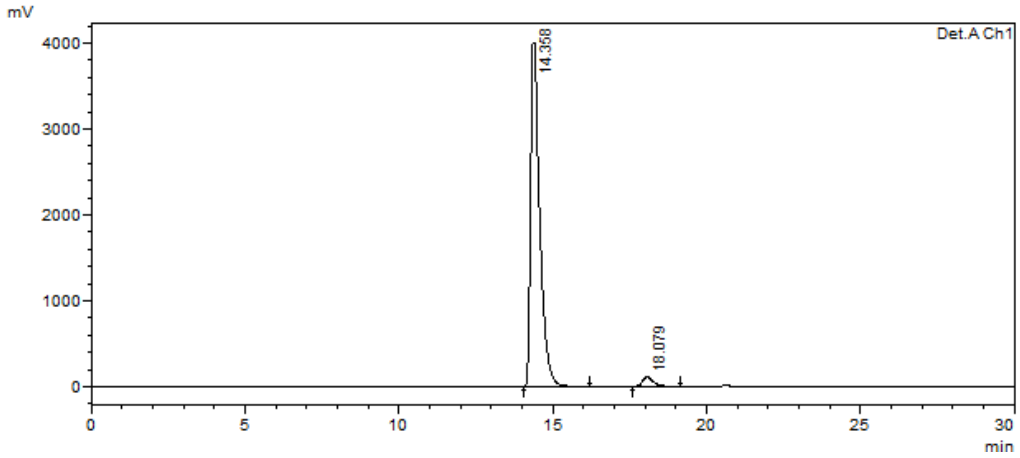
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT13.521	13.521	0.00000	Detector A - Ch	1	66955434	3652152		13.217	16.867	98.5449
2	RT19.642	19.642	0.00000	Detector A - Ch	2	988683	30349		19.025	20.658	1.4551

(d) (E)-*tert*-Butyl 2-(diphenylmethyleneamino)-5-phenylpent-4-enoate
(Entry 4, from cinnamyl-Br)

racemate



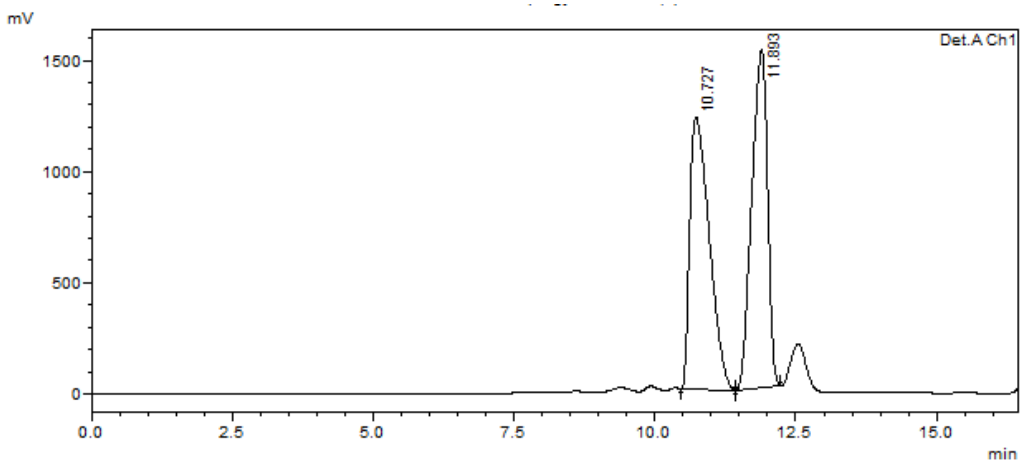
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT13.555	13.555	0.00000	Detector A - Ch	1	51699316	2709526		13.208	14.217	52.3031
2	RT16.920	16.920	0.00000	Detector A - Ch	2	47146217	1644352		16.433	17.817	47.6969



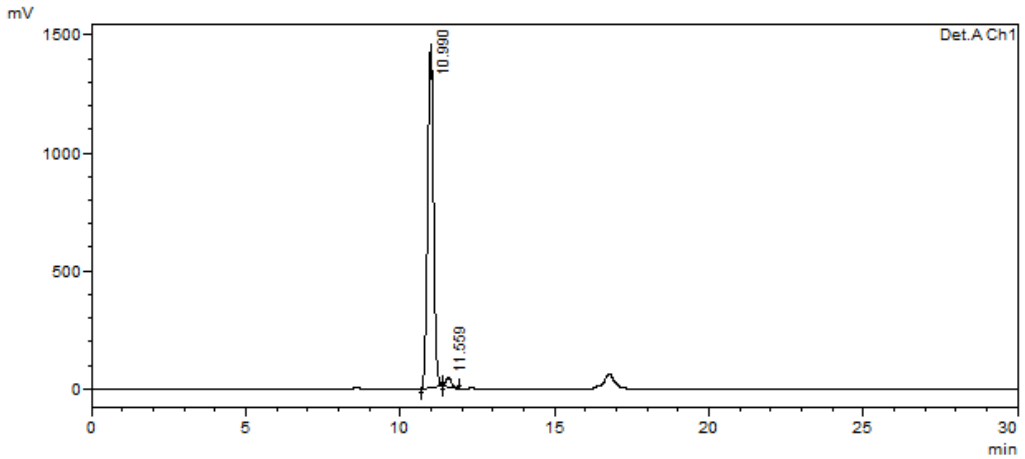
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT14.358	14.358	0.00000	Detector A - Ch	1	83113377	3999421		14.050	16.200	96.7909
2	RT18.079	18.079	0.00000	Detector A - Ch	2	2755619	106101		17.608	19.167	3.2091

(e) *tert*-Butyl 2-(diphenylmethyleneamino)pent-4-ynoate
(Entry 5, from propargyl-Br)

racemate



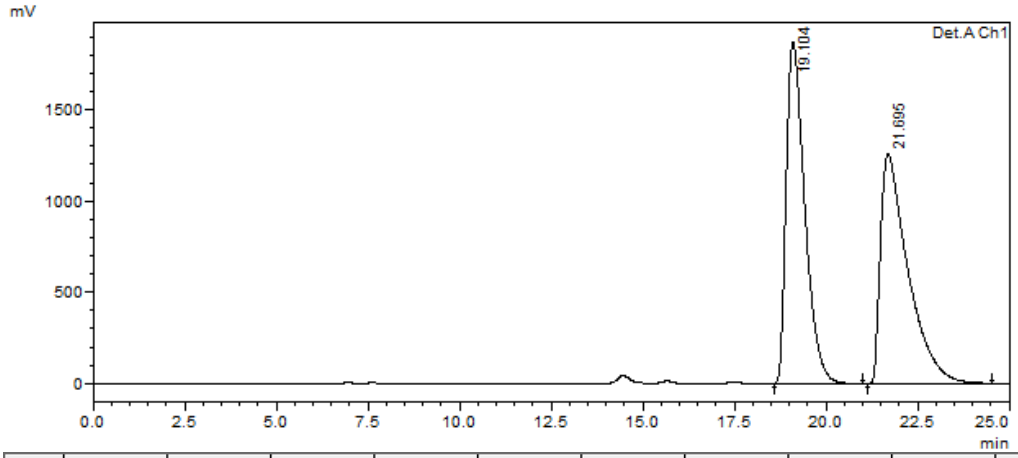
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT10.727	10.727	0.00000	Detector A - Ch	1	29540048	1224114		10.458	11.425	50.1211
2	RT11.893	11.893	0.00000	Detector A - Ch	2	29397356	1519534		11.442	12.233	49.8789



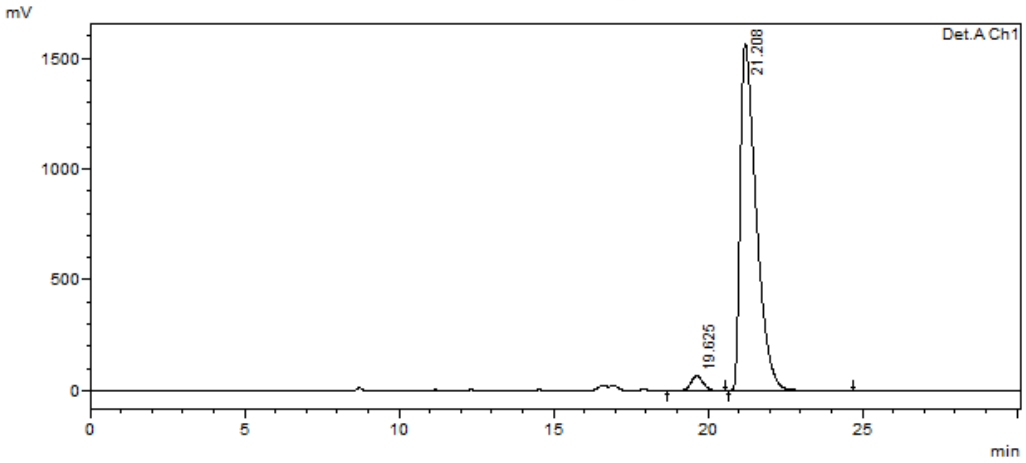
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT10.990	10.990	0.00000	Detector A - Ch	1	19193478	1455804		10.667	11.367	97.4681
2	RT11.559	11.559	0.00000	Detector A - Ch	2	498581	41816		11.383	11.925	2.5319

(f) *tert*-Butyl 2-(diphenylmethyleneamino)-3-(naphthalene-1-yl)propanoate
(Entry 6. from 1-(bromomethyl)-naphthalene)

racemate



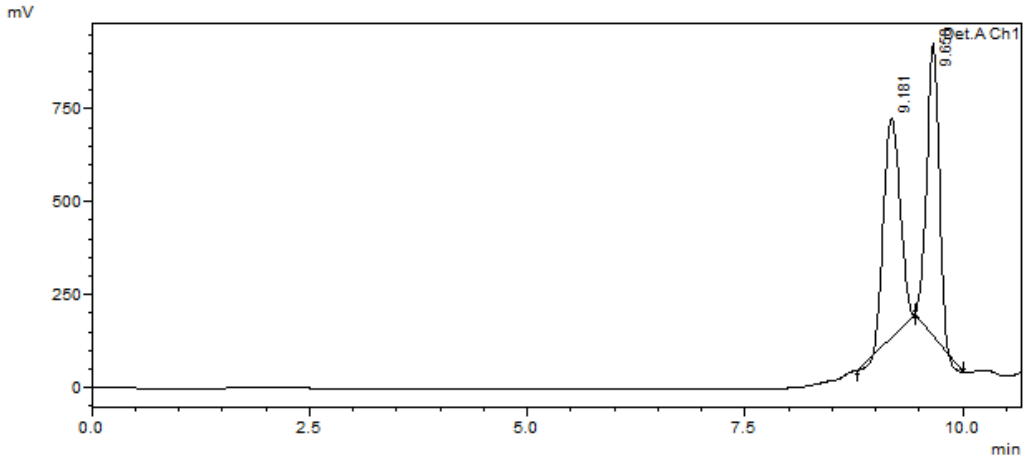
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT19.104	19.104	0.00000	Detector A - Ch	1	65940121	1870162		18.575	21.008	50.1104
2	RT21.695	21.695	0.00000	Detector A - Ch	2	65649455	1258563		21.158	24.542	49.8896



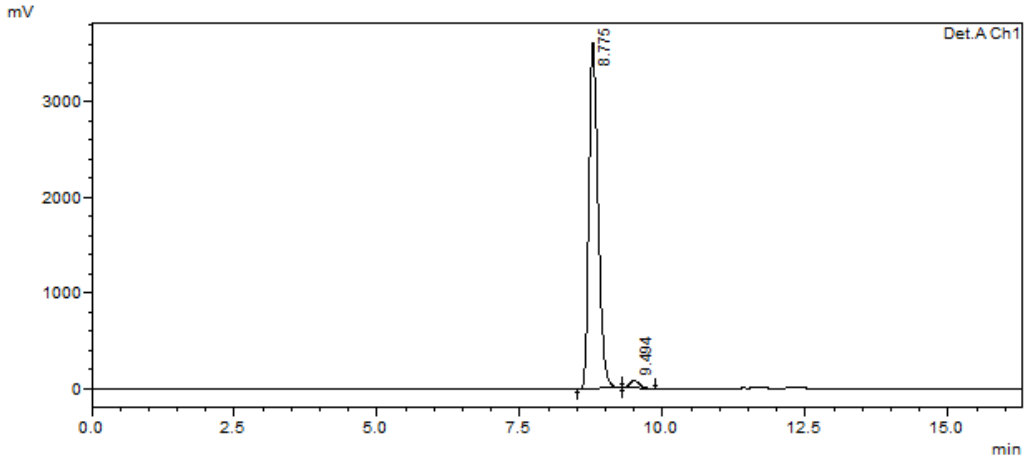
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT19.625	19.625	0.00000	Detector A - Ch	1	1815254	67889		18.700	20.583	3.1230
2	RT21.208	21.208	0.00000	Detector A - Ch	2	56310383	1564588		20.650	24.717	96.8770

(g) *tert*-Butyl 2-(diphenylmethyleneamino)butanoate
(Entry 7, from ethyl iodide)

racemate



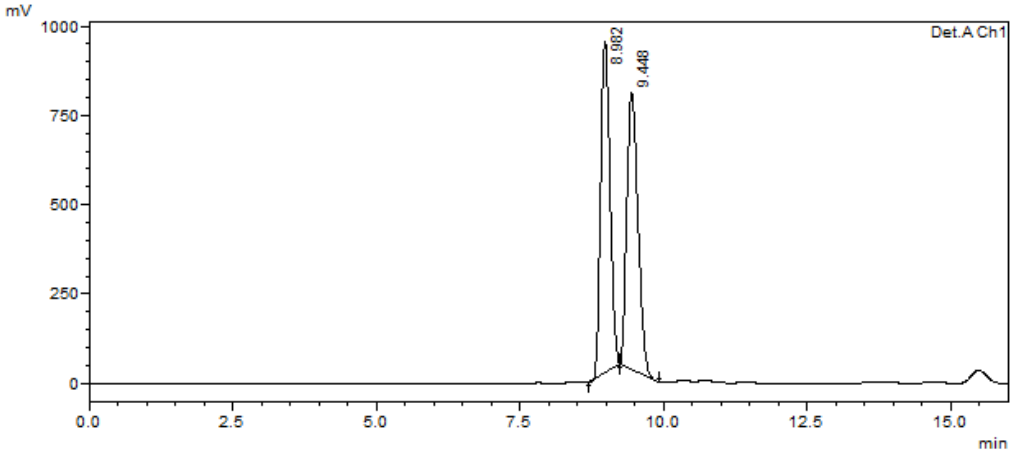
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT9.181	9.181	0.00000	Detector A - Ch	1	7668694	587264		8.783	9.450	49.8806
2	RT9.658	9.658	0.00000	Detector A - Ch	2	7705407	787652		9.450	10.000	50.1194



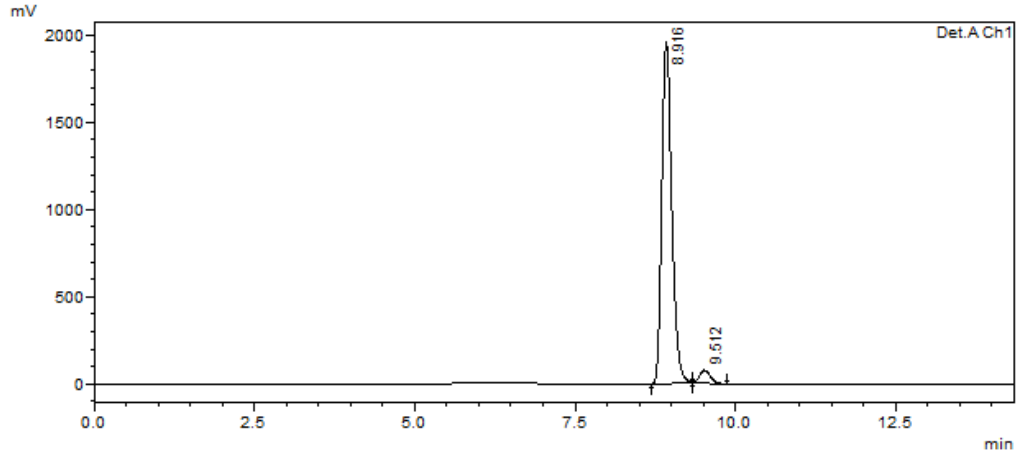
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT8.775	8.775	0.00000	Detector A - Ch	1	40618727	3609178		8.508	9.283	97.8158
2	RT9.494	9.494	0.00000	Detector A - Ch	2	906987	75676		9.292	9.858	2.1842

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

recemate



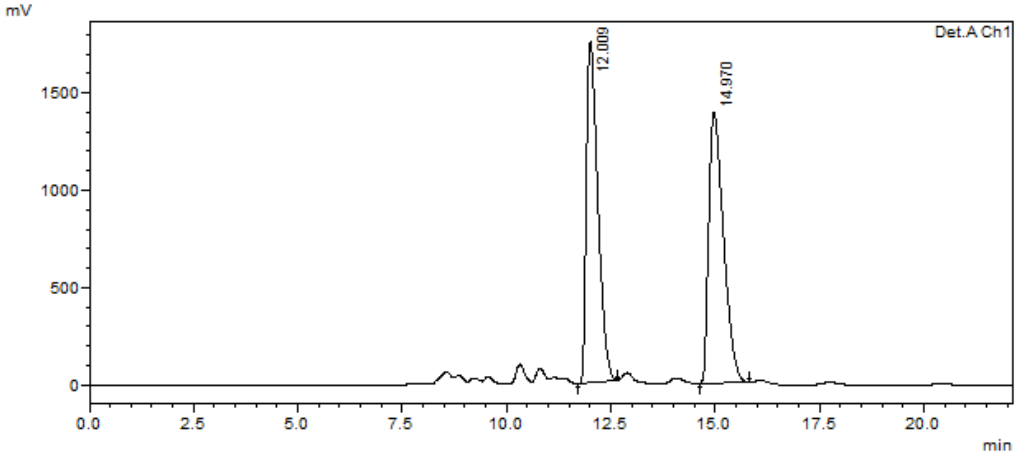
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT8.982	8.982	0.00000	Detector A - Ch	1	10561590	928656		8.708	9.250	50.1657
2	RT9.448	9.448	0.00000	Detector A - Ch	2	10491828	773786		9.250	9.917	49.8343



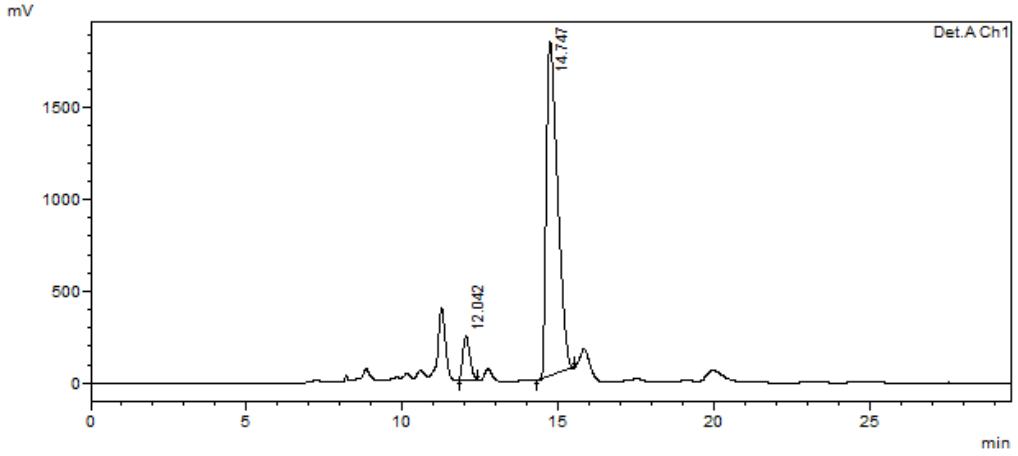
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT8.916	8.916	0.00000	Detector A - Ch	1	21459844	1956529		8.700	9.333	96.4904
2	RT9.512	9.512	0.00000	Detector A - Ch	2	780541	72084		9.333	9.875	3.5096

(i) *tert*-Butyl 2-benzamido-3-(carbo-*tert*-butoxy)-propionate
(di-*tert*-Butyl 2-benzamidosuccinate)
(Entry 9, from *tert*-butyl bromoacetate, then benzolyation)

recemate



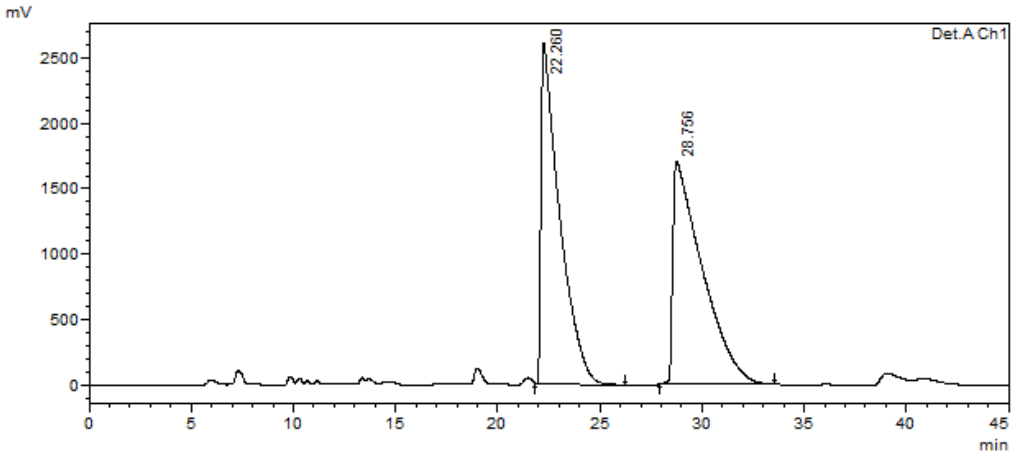
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT12.009	12.009	0.00000	Detector A - Ch	1	33431363	1752846		11.725	12.675	49.3252
2	RT14.970	14.970	0.00000	Detector A - Ch	2	34346103	1387242		14.617	15.825	50.6748



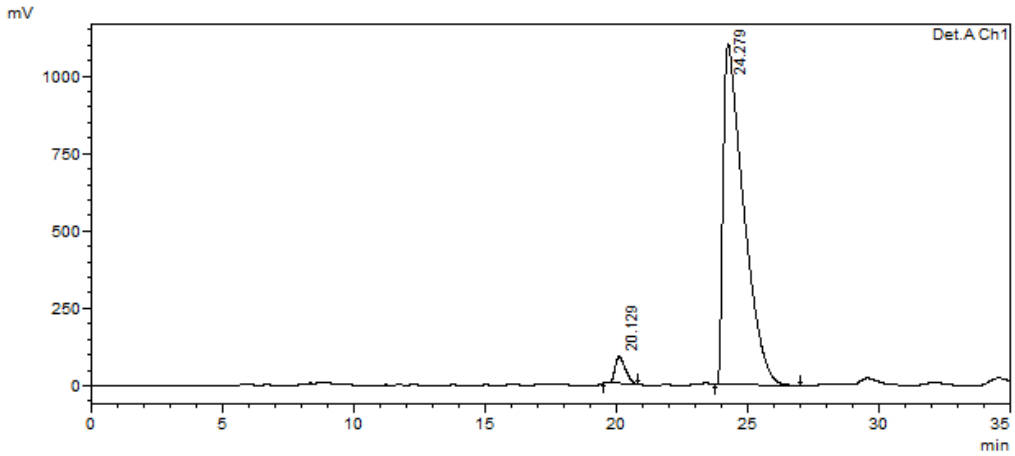
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT12.042	12.042	0.00000	Detector A - Ch	1	3696161	236303		11.817	12.417	7.4671
2	RT14.747	14.747	0.00000	Detector A - Ch	2	45803056	1820970		14.292	15.533	92.5329

(2) Product **11**. (Table 2)
Ethyl 2-benzamido-2-methyl-3-phenylpropanoate

racemate



ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT22.260	22.260	0.00000	Detector A - Ch	1	163495760	2596426		21.850	26.258	48.9064
2	RT28.756	28.756	0.00000	Detector A - Ch	2	170807729	1699920		27.892	33.583	51.0936



ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT20.129	20.129	0.00000	Detector A - Ch	1	2387302	85334		19.558	20.867	3.8498
2	RT24.279	24.279	0.00000	Detector A - Ch	2	59624291	1100884		23.808	27.033	96.1502