Electronic Supplementary Information

Heterogeneous Rh and Rh/Ag Bimetallic Nanoparticle Catalysts Immobilized on Chiral Polymer

*Hyemin Min, Hiroyuki Miyamura, Tomohiro Yasukawa, and Shū Kobayashi**

Department of Chemistry, School of Science, The University of Tokyo

Hongo, Bunkyo-ku, Tokyo, 113-0033

E-mail: shu_kobayashi@chem.s.u-tokyo.ac.jp

Table of Contents

1. General Remarks

・Reactions were monitored with analytical thin-layer chromatography (TLC) on silica gel 60 F_{254} glass plates purchased from Merck KGaA and were visualized under UV light (254 nm) and/or by staining with $KMnO_4$.

・NMR spectra were recorded with JEOL JMN-LA 500 or 600 spectrometers operating at 500, 600 MHz (^1H) and 125, 150 MHz (^{13}C) respectively. Chemical shifts were recorded in parts per million (ppm), from relative to internal references of the $CDCl_3$, defined at 7.24 ppm (^1H NMR) and 77.00 ppm (^{13}C NMR). The structures of the known compounds were confirmed by comparison with commercially available compounds or data shown in literature.

・Inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis was performed on Shimadzu ICPS-7510 equipment.

・STEM/EDS images were obtained using a JEOL JEM-2100F instrument operated at 200 kV. All STEM specimens were prepared by placing a drop of the solution on carbon-coated copper grids and allowed to dry in air (without staining).

・IR spectra were measured on a JASCO FT/IR-610 spectrometer.

・Direct Analysis in Real Time (DART) mass spectra were recorded on JEOL JMS-T100TD mass spectrometer.

・Optical rotations were measured with JASCO P-1010.

・Melting point was recorded on a standard melting point apparatus and is uncorrected.

・HPLC analysis was conducted on Shimadu LC-20AB, SPD-M20A and DGU-$20A_3$.

・Daicel Chiralpak AD, AD-H, AD-3, OD-H, AS-H, AS-3, OJ-H column were used for HPLC analysis.

・The absolute configuration of reported compounds was determined by comparison of results of HPLC analysis to literature and that of other products was assumed by analogy.

・XPS analysis was performed on JPS-9010MC with a Mg Kα X-ray source and the C 1s line at 284.0 eV was used as reference to correct the binding energies.

▪GC analysis was performed on a Shimadzu GC-2010 apparatus. ***Condition I:*** Column = GL Science TCWAX, 0.25 mm ID, 0.25 μm, 60.0 m; Gas pressure: 214.2 kPa; Total flow: 90.6 mL/min; Column flow: 1.86 mL/min; Velocity: 30.8 cm/sec; Purge flow: 3.0 mL/min; Split ratio: 46.0; Injector: 250 ºC; FID: 250 ºC; Column

program: starting from 50 ºC, 10 ºC/min to 220 ºC, 18 min hold. ***Condition II:*** Column = J & W SCIENTIFIC DB-1, 0.25 mm ID, 0.25 μm, 60.0 m; Gas pressure: 157.5 kPa; Total flow: 41.3 mL/min; Column flow: 0.93 mL/min; Velocity: 21.1 cm/sec; Purge flow: 3.0 mL/min; Split ratio: 40.1; Injector: 300 ºC; FID: 300 ºC; Column program: starting from 100 ºC, 10 ºC/min to 300 ºC, 30 min hold.

▪H_2 adsorption was conducted by BELLCAT II (Microtrac BEL Corp.)

- 24~27 mg of sample was used for analysis, and H_2 adsorption was conducted at 50 ^oC after pretreatment.

-Analysis was conducted by pulse method, and the result is average of at least 4 pulses.

- Pretreatment conditions

Temp (^oC)	Gas	Flow (mL/min)	Time (min)
200	Ar	50	35
200	O_2	50	15
200	Ar	50	20
200	H_2	50	20
250	Ar	50	180
50	Ar	50	10

・Preparative TLC (PTLC) was performed using Wakogel® B-5F from Wako Pure Chemical Industries.

・0.45 μm PTFE membrane filter (WhatmanTM cat. No. 6784-2504) was used for filtration of catalyst in the preparation of leaching test samples.

・Reaction was conducted using carousel 12 Plus Reaction System™ by Radleys (www.radleys.com) using one-neck tube equipped with septum after Ar substitution.

・$NaBH_4$ was purchased from Wako Pure Chemical Company and recrystallized from diglyme by heating according to the literature[1] and stored in a glove box. It is important to manipulate all operations under Ar atmosphere during recrystallization. Activity of catalyst and reproducibility are highly influenced by the purity and condition of $NaBH_4$ in the course of catalyst preparation.

・$[Rh(OAc)_2]_2$ was purchased from Strem Chemicals, inc.

・$AgSbF_6$ was purchased from Sigma-Aldrich Corporation.

・Ketjen black (Carbon black) EC 300J was purchased from Lion Corporation.

・Trimethoxysilylstyrene was purchased from Shin-Etsu Silicons.

・Substrate **3a, 3b, 3d-f**, **3k, 3m** were purchased from Tokyo Chemical Industry or Sigma-Aldrich Corporation. **3c**[2], **3g**[3], **3h**[3], **3i**[4], **3j**[4], **3l**[5,6], **3n**[7], **3o**[8], **8a-c**[9], **8d**[10] were symthesized following the literatures. Arylimine **9** were

prepared by condensation of tosylimine and corresponding aldehydes.

・Arylboronic acids **4a**-**k** were prepared from the corresponding Grignard reagent or purchased from Wako Pure Chemical Company or Tokyo Chemical Industry.

・Arylboronic acids **4a-k** were recrystallized using hexane/ethyl acetate and ratio between boronic acid and boroxine was determined by ^{1}H NMR analysis.

・Chiral diene ligand precursor (in Scheme S1) was prepared following the literature.[11]

・Toluene was purchased in dried grade from Wako Pure Chemical Company and used without further purification.

・Deionized water from a MILLIPORE MilliQ machine (Gradient A10) was used as solvent without further treatment.

・Celite (Celite® 545) was purchased from Kokusan Chemical Co., Ltd.

・For flow system,

- Pump : Shimadzu LC-10ATvp (x2)

- Column : 10Φ x 5 cm from Tokyo Rikakikai Co. Ltd.

- Column heater : from Tokyo Rikakikai Co. Ltd.

- Column heater controller : EYELA TTM204

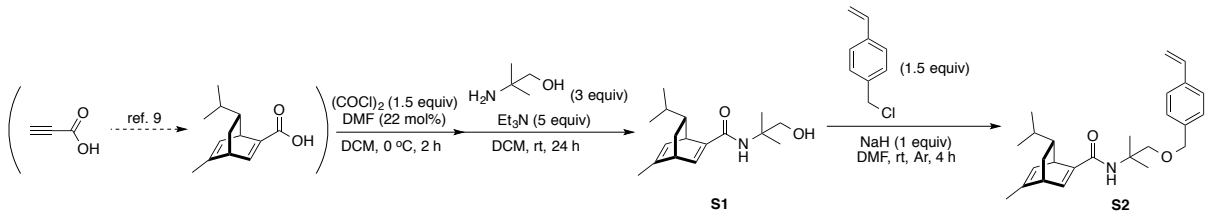
- Back pressure controller (regulator) : Swagelok KCB1G0D2D5P60000BK

- Back pressure monitor : Nagano keiki Co. Ltd. GC61-174

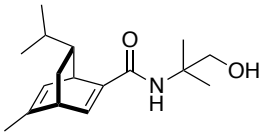
2. Monomer, Copolymer and Catalyst Preparation

2.1. Polymer-Incarcerated Carbon Black Pd (PICB-Pd) Catalyst

Ligand preparation (Scheme S1)[8,12,13]

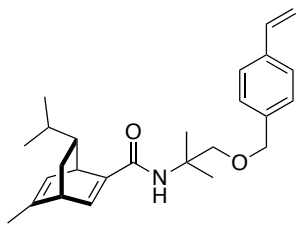


(1*R*,4*R*,7*R*)-*N*-(1-Hydroxy-2-methylpropan-2-yl)-7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxamide (**S1**)



(1*R*,4*R*,7*R*)-7-Isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylic acid (988 mg, 4.79 mmol, 1 equiv) was setted in a flask and atmosphere was changed to Ar. After addition of DCM, oxalyl chloride (0.62 mL, 7.20 mmol, 1.5 equiv and DMF (83 μL, 1.06 mmol, 0.22 equiv) were added at 0 ºC. After stirring for 3 h at 0 ºC, triethyl amine (3.4 mL, 24.0 mmol, 5 equiv) and 2-amino-2-methyl-1-propanol (1.4 ml, 14.37 mmol, 3 equiv) in DCM (5 mL) were added at 0 ºC, and the mixture was stirred for 24 h at room temperature. NH_4Cl (sat. aq., 15 ml) was added and an aqueous phase was extracted with DCM (3 x 30 ml). The combined organic layers were washed with water and brine, dried over Na_2SO_4, then solvents were removed *in vacuo*. The residue was purified by flash chromathgraphy to afford the desired product (804 mg, 60 %). $[\alpha]^{20}_D$ = +27.3 (c = 1.25, $CHCl_3$). IR (KBr): 3725, 3660, 3320, 3040, 2958, 2935, 2871, 1740, 1660, 1636, 1605, 1530, 1450, 1383, 1363, 1283, 1233, 1173, 1064, 1029, 886, 816, 740, 667 cm^{-1}. DART-MS (m/z) calcd. for $C_{17}H_{28}NO_2$ (MH^+): 278.21200, found: 278.21108. M.p : 97-98 °C. **^{1}H NMR ($CDCl_3$, 600 MHz):** δ (ppm) 6.72 (dd, *J* = 6.2, 1.4 Hz, 1H), 5.74 (d, *J* = 5.5 Hz, 1H), 5.64 (brs, 1H), 4.93 (t, *J* = 5.5 Hz, 1H), 3.91 (td, *J* = 4.0, 1.8 Hz, 1H), 3.53 (d, *J* = 4.8 Hz, 2H), 3.29-3.24 (m, 1H), 1.75 (s, 3H), 1.53-1.49 (m, 1H), 1.24 (d, *J* = 8.9 Hz, 6H), 1.16-1.11 (m, 1H), 1.04-1.00 (m, 1H), 0.93 (d, *J* = 6.2 Hz, 3H), 0.91-0.87 (m, 1H), 0.75 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR ($CDCl_3$, 150 MHz):** δ (ppm) 167.1, 145.1, 143.8, 138.4, 124.1, 71.0, 56.1, 47.7, 43.6, 40.1, 33.8, 31.7, 24.9, 24.8, 21.8, 21.3, 19.0.

(1*R*,4*R*,7*R*)-7-Isopropyl-5-methyl-*N*-(2-methyl-1-((4-vinylbenzyl)oxy)propan-2-yl)bicyclo[2.2.2]octa-2,5-diene-2-carboxamide (**S2**, Diene monomer 1)



Sodium hydride (55% in mineral oil, 87.3 mg, 2.0 mmol, 1 equiv) was setted in flask and atmosphere was changed to Ar. After addition of DMF (2 ml), (1*R*,4*R*,7*R*)-*N*-(1-hydroxy-2-methylpropan-2-yl)-7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxamide (**S1**) (557 mg, 2.0 mmol, 1 equiv) in DMF (1 ml) was added at 0 °C. After stirring for a few minutes, 1-(chloromethyl)-4-vinylbenzene (0.43 ml, 3.0 mmol, 1.5 equiv) in DMF (2 ml) was added at 0 °C, and this mixture was further stirred for 4 h at room temperature. NH_4Cl (sat. aq., 30 ml) was

added for quenching, then an aqueous layer was extracted with hexane/ethyl acetate (2:1). The combined organic layers were washed with water, dried over Na_2SO_4, and solvents were removed *in vacuo*. The residue was purified by flash chromathgraphy to afford the desired product (586.4 g, 75%). $[\alpha]^{20}_D$ = +22.8 (c = 0.75, $CHCl_3$). IR (KBr): 3668, 3430, 3348, 3086, 3039, 2959, 2868, 2726, 2608, 2423, 2399, 2296, 2136, 1907, 1815, 1738, 1644, 1611, 1451, 1402, 1365, 1230, 1204, 1097, 1021, 988, 907, 822, 770, 738, 665, 642 cm^{-1}. DART-MS (m/z) calcd. for $C_{24}H_{36}NO_2$ (MH^+): 394.27460, found: 394.27443. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ (ppm) 7.37 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 6.75-6.65 (m, 2H), 5.86 (s, 1H), 5.77 (d, *J* = 5.5 Hz, 1H), 5.73 (d, *J* = 17.9 Hz, 1H), 5.23 (d, *J* = 11.0 Hz, 1H), 4.50 (s, 2H), 3.96 (td, *J* = 4.1, 2.1 Hz, 1H), 3.42 (q, *J* = 9.4 Hz, 2H), 3.29-3.26 (m, 1H), 1.79 (s, 3H), 1.54-1.52 (m, 1H), 1.36 (d, *J* = 3.4 Hz, 6H), 1.19-1.16 (m, 1H), 1.08-1.02 (m, 1H), 0.96 (d, *J* = 6.2 Hz, 3H), 0.93-0.89 (m, 1H), 0.78 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ (ppm) 165.9, 145,9, 143.8, 137.8, 137.1, 137.0, 136.5, 127.8, 126.2, 124.2, 113.9, 76.7, 73.0, 53.6, 47.7, 43.5, 39.9, 33.9, 31.9, 24.03, 24.00, 21.8, 21.3, 19.0.

General procedure for preparation of ligand immobilized hybrid polymers (LIHBPs)

Styrene (822 mg, 7.89 mmol, 3 equiv), *p*-styryltrimethoxysilane (590 mg, 2.63 mmol, 1 equiv), diene monomer **1** (1.04 g, 2.63 mmol, 1 equiv) and dimethyl-2,2'-azobis(2-methylpropionate) (v-601®) (18.2 mg, 0.079 mmol, 0.03 equiv) were combined in a flask with chloroform (10~16 ml) and the atmosphere was changed to Ar with sonication. The mixture was stirred for 24 h at 80 °C (reflux). The resulting polymer solution was slowly poured into methanol. The solvent was removed by decantation and the residue was disolved again in chloroform. The polymer solution was slowly poured into methanol again. The same procedure was repeated three times. The precipitated polymer was washed with methanol several times and dried *in vacuo* to afford the corresponding **ligand immobilized hybrid polymers (LIHBPs)**. The molar ratio of the components was determined by ^{1}H NMR analysis.

Preparation of LIHBCB-Rh(/Ag)

$NaBH_4$ (63.8 mg, 1.68 mmol) in 5 ml of diglyme was added to a solution of LIHBP (250 mg) in diglyme (7 ml) and Ketjenblack (250 mg) dropwise at 0 °C. Then, a solution of $[Rh(OAc)_2]_2$ (22.1 mg, 0.05 mmol) or mixture of $[Rh(OAc)_2]_2$ (22.1 mg) and $AgSbF_6$ (34.4 mg for Rh/Ag (1:1), 68.8 mg for Rh/Ag (1:2)) in THF (5~10 ml) was added at 0 °C, and it was stirred for overnight at room temperature. After addition of 1 N NaOH (aq., 70 ml) and isopropyl alcohol (70 ml), the mixture was heated at 90 °C with stirring for 5 h. The resulting catalyst was filtered, washed several times with isopropyl alcohol and dried *in vacuo*. Next, the catalyst was heated (no stirring) at 100 °C for 5 h under neat conditions. $NaBH_4$ (63.8 mg) was added to catalyst and this mixture was stirred in diglyme for 2 h at room temperature. The resulting catalyst was washed with water, isopropyl alcohol and DCM several times, and dried *in vacuo* to afford the desired LIHBCB-Rh(/Ag) catalyst (Target loading for Rh : 0.2 mmol/g, actual loading of Rh : 0.17~0.22 mmol/g).

* Carbon black was used for enhancing the stability of metal nanoparticles during the preparation step. Also, high dispersion of metal nanoparticle can be achieved in the presence of carbon black due to its high specific

surface area. In our previous paper,[14] the scanning electron microscopy (SEM) image of CB, polymer-CB composite material are shown; CB has relatively uniform spheres (around 45 nm) and similar structure was observed in polymer-CB composite material with slightly larger spheres (around 55 nm), and the increase observed size of the microsphere is likely derived from the absorption of polymer on the surface of the CB. Schematic image of CB and polymer-CB composite material are shown in below[15]. Although in the absence of CB, metal nanoparticles can be stabilized by polymer, thanks to multiple weak interactions with π-electrons of benzene rings.

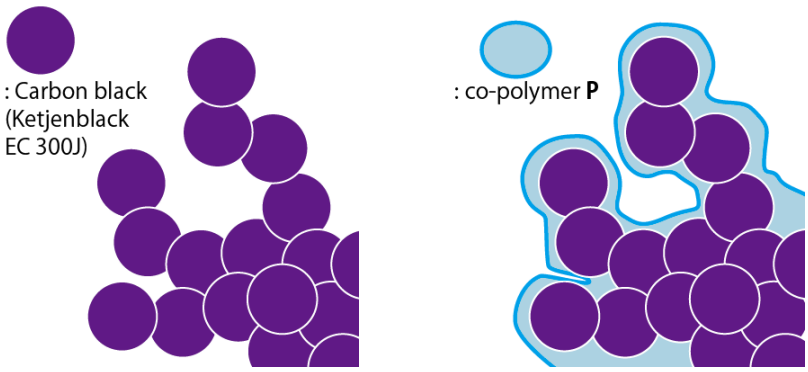
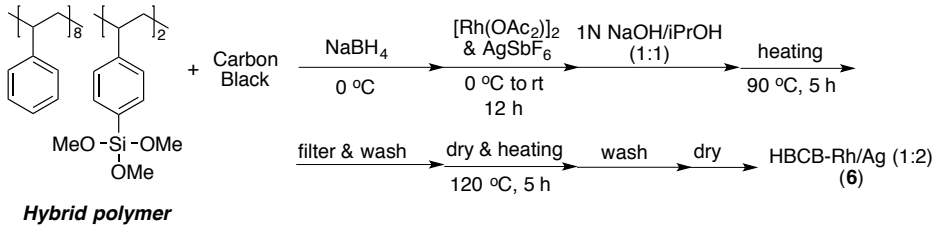


Figure S1. Schematic images of CB and polymer-CB composite material

Preparation of HBCB-Rh/Ag (1:2) (Scheme S2)



$NaBH_4$ (68.4 mg, 1.80 mmol) in 5 ml of diglyme was added to a solution of hybrid polymer (250 mg)[16] in diglyme (7 ml) and Ketjenblack (250 mg) dropwise at 0 °C. Then, a solution of $[Rh(OAc)_2]_2$ (22.1 mg) and $AgSbF_6$ (68.8 mg) mixture in THF (5~10 ml) was added at 0 °C, and it was stirred for overnight at room temperature. After addition of 1 N NaOH (aq., 70 ml) and isopropyl alcohol (70 ml), the mixture was heated at 90 °C with stirring for 5 h. The resulting catalyst was filtered, washed several times with isopropyl alcohol and dried *in vacuo*. Next, the catalyst was heated (no stirring) at 100 °C for 5 h under neat conditions. The resulting catalyst was washed with water, isopropyl alcohol and DCM several times, and dried *in vacuo* to afford the desired HBCB-Rh/Ag (1:2) catalyst (Target loading for Rh : 0.2 mmol/g, actual loading of Rh : 0.17~0.22 mmol/g).

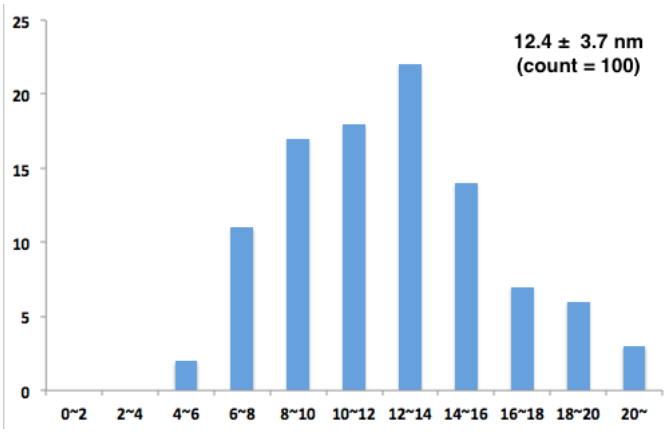


Figure S2. Size distribution of HBCB-Rh/Ag (1:2) (**6**)

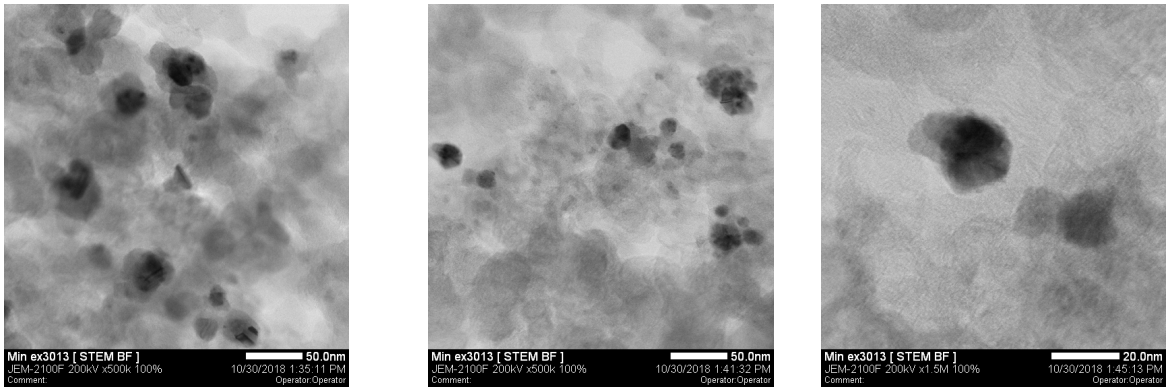
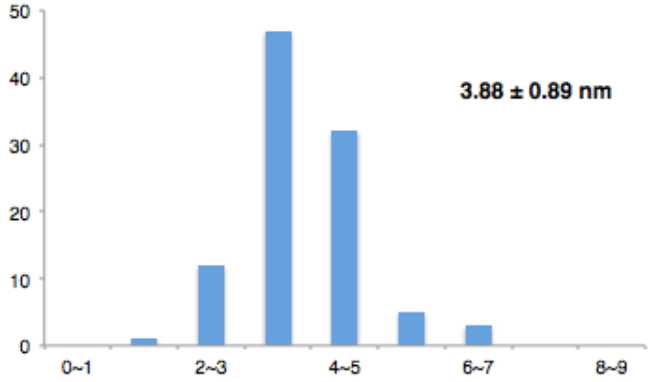


Figure S3. STEM analysis of HBCB-Rh/Ag (1:2) (**6**)

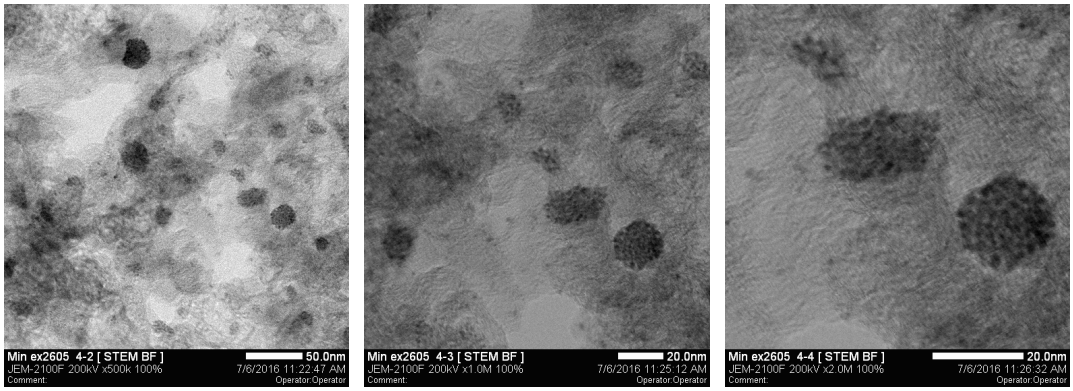
3. *Characterization of LIHBCB-Rh(/Ag) catalyst*

- Size distribution of LIHBCB-Rh/Ag (1:2) (2f) catalyst (Figure S4)

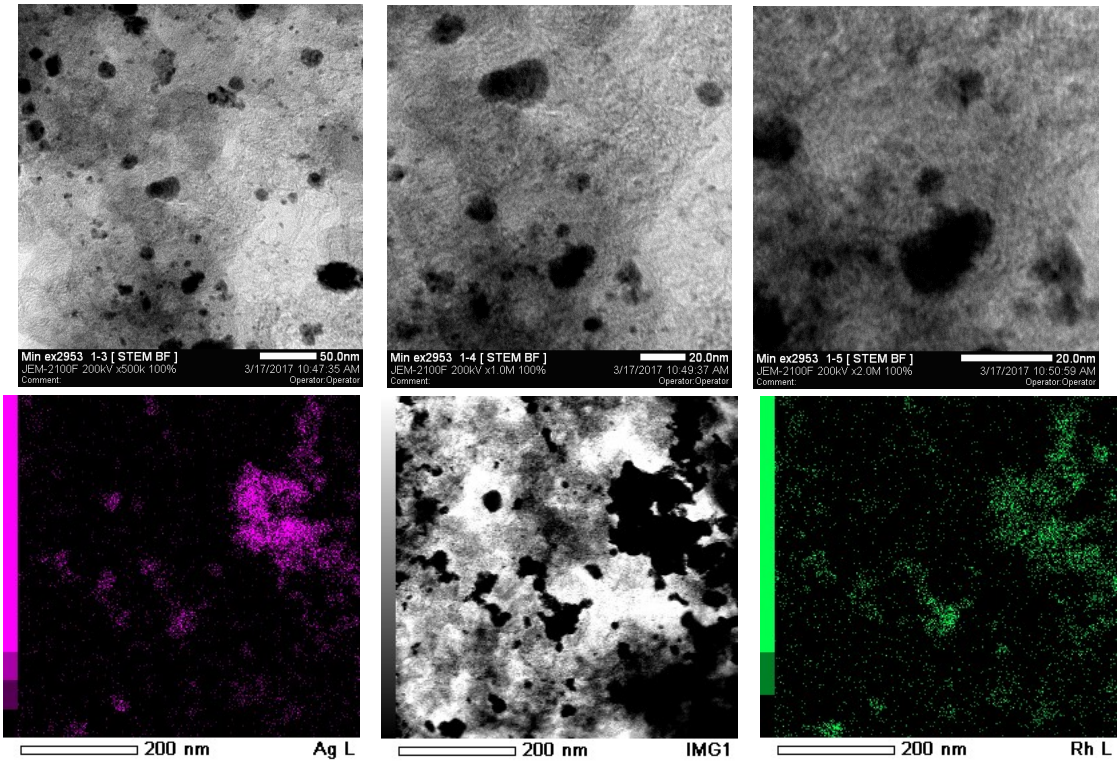


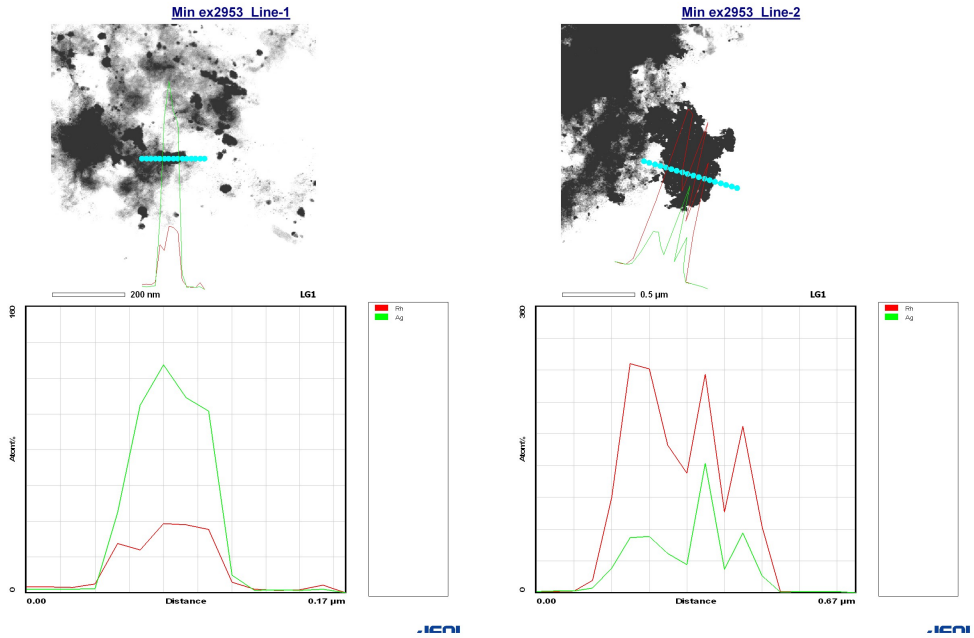
- STEM, Mapping, and Line analysis

■ LIHBCB-Rh catalyst (2b) (Figure S5)

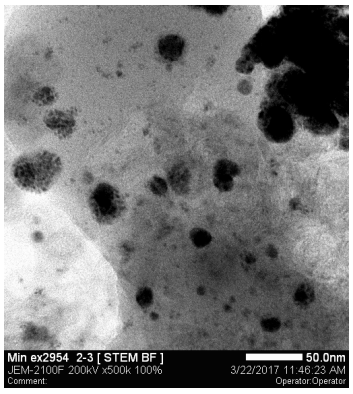


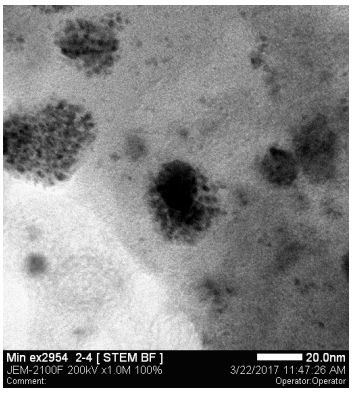
■ *LIHBCB-Rh/Ag (1:1) catalyst (2d) (Figure S6)*

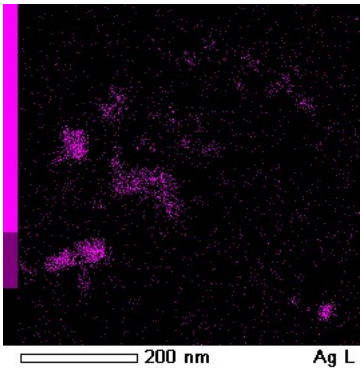


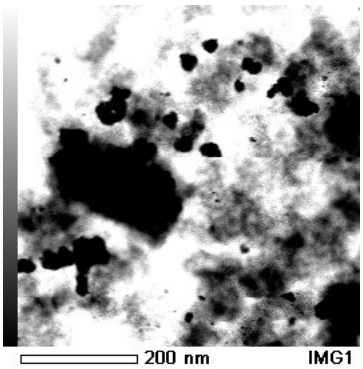


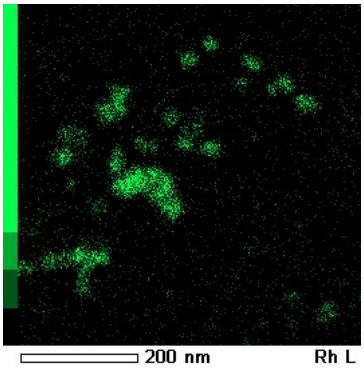
■ *LIHBCB-Rh/Ag (2:1) catalyst (2e) (Figure S7)*

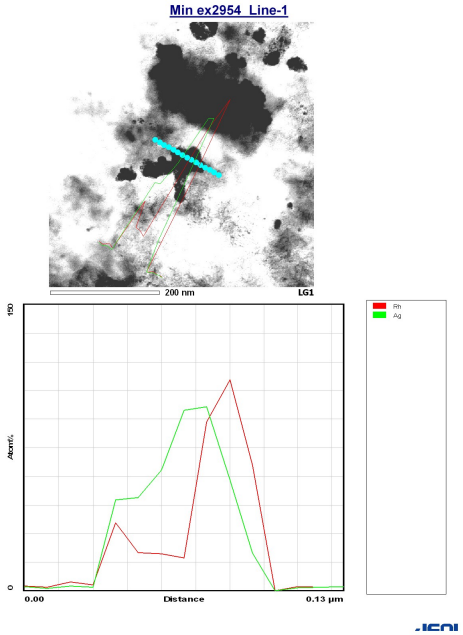


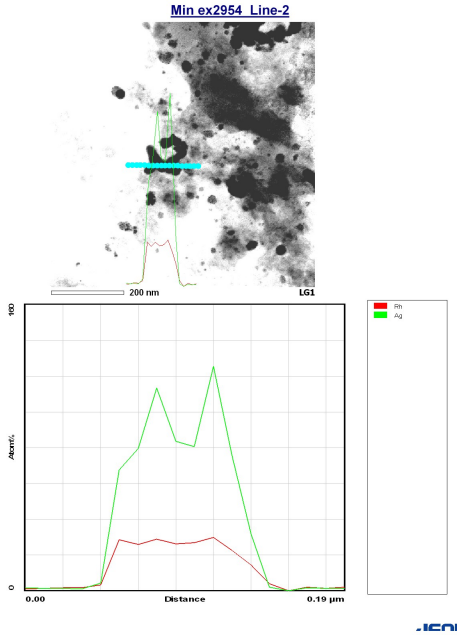




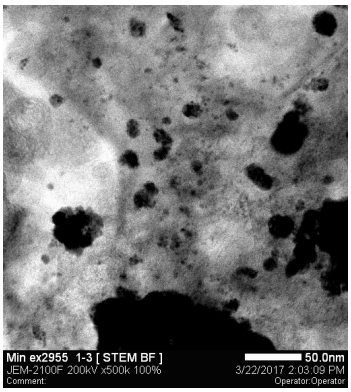


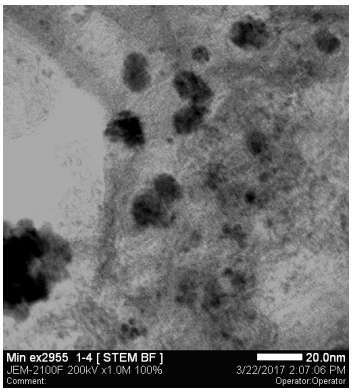


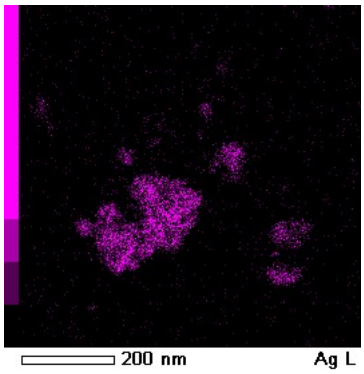


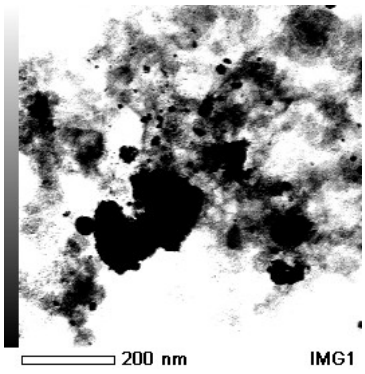


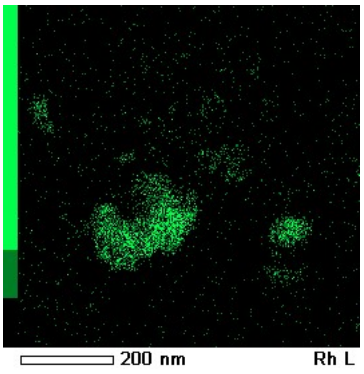
■ *LIHBCB-Rh/Ag (1:2) catalyst (2f) (Figure S8)*

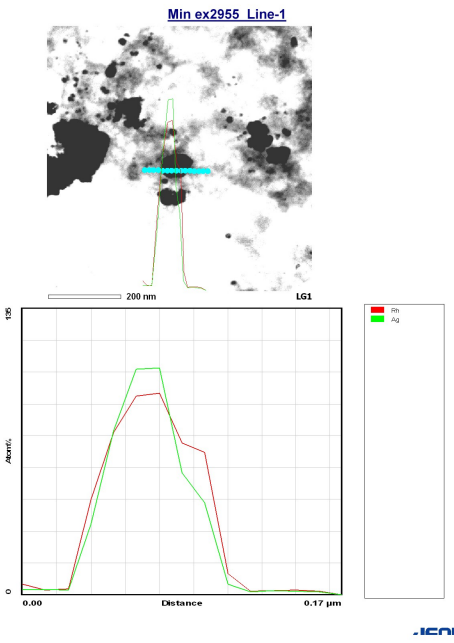


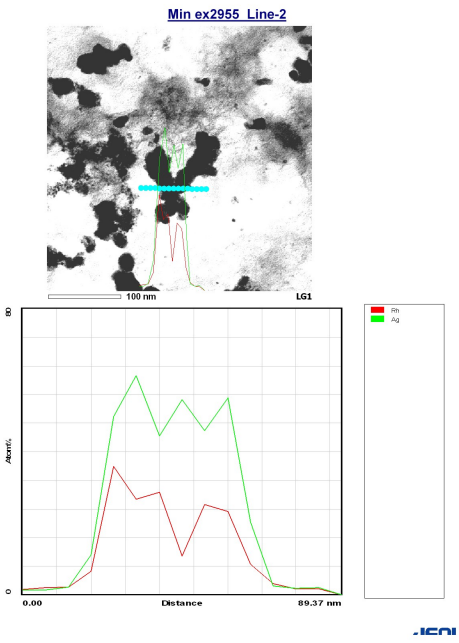




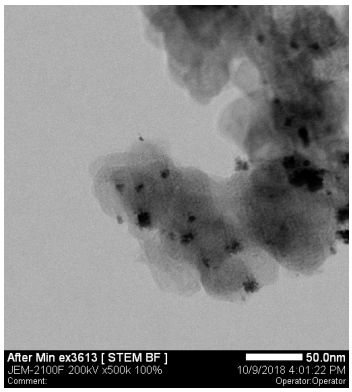


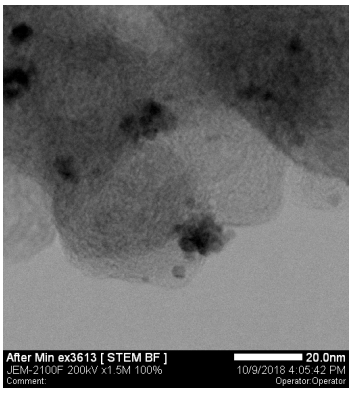


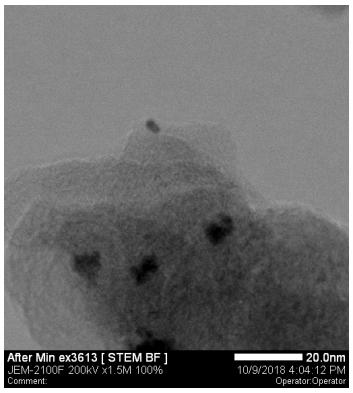




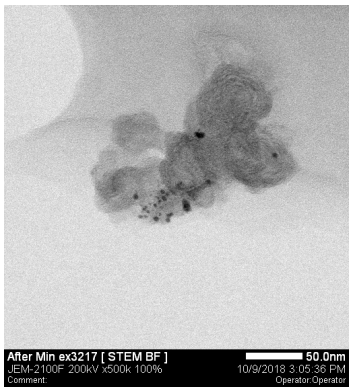
■ *After use (1) (LIHBCB-Rh (2b), Table 4 for 5aa, Figure S9)*

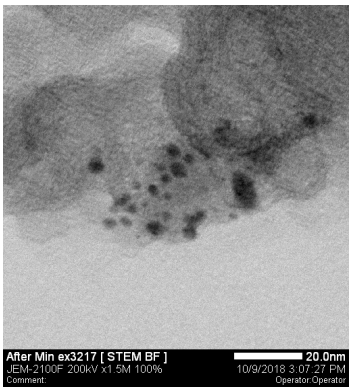


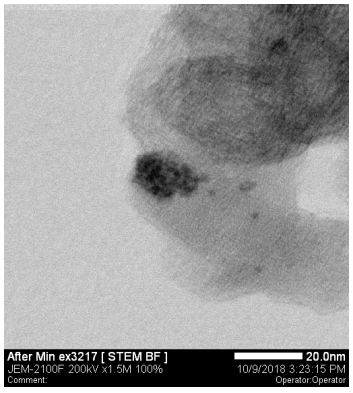




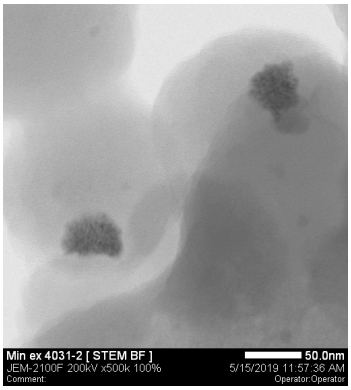
■ *After use (2) (LIHBCB-Rh/Ag (2f), Table 4 for 5ia, Figure S10)*

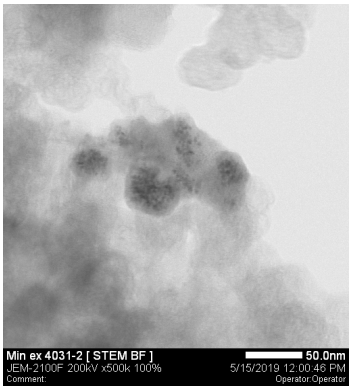






■ *Lower loading LIHBCB-Rh catalyst (Target loading : 0.02 mmol/g) (Figure S11)*





4. General Procedures

General procedure for addition of aryl boronic acids to α,ß-unsaturated carbonyl compounds (Table 1, 2 and 3)

LIHBCB-Rh(/Ag) catalyst (**2**) (0.003-0.006 mmol, 1-2 mol% as Rh), arylboronic acid (0.45-0.6 mmol, 1.5-2 equiv), substrate (0.3 mmol) (if needed, K_2CO_3 (0.3 mmol, 1 equiv)), toluene (0.7 ml), and water (1.4 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution. The reaction mixture was stirred for 24 h at 100 ^oC (reflux) (using a Carousel system). After the reaction, the catalyst was seperated by filtration and washed with EtOAc (20 mL) and water using a KIRIYAMA funnel. The organic layers were washed with brine and dried over Na_2SO_4 and the solvents were removed *in vacuo*. The residue was purified by preparative TLC.

General procedure for leaching test

LIHBCB-Rh(/Ag) catalyst (**2**) (0.003-0.006 mmol, 1-2 mol% as Rh), arylboronic acid (0.45-0.6 mmol, 1.5-2 equiv), substrate (0.3 mmol) (if needed, K_2CO_3 (0.3 mmol, 1 equiv)), toluene (0.7 ml), and water (1.4 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution. The reaction mixture was stirred for 24 h at 100 ^oC (reflux) (using a Carousel system). After the reaction, the mixture was filtered with THF (~10 ml) using an eluting tube with cotton. This filtrate was filtered again with a membrane filter. The final filtrate was massed-up to 25 ml, then it was divided to two portions; 15 ml for isolation, and 10 ml for a leaching test. In the case of the leaching test, 10 ml of filtrate was transferred to a test tube and the solvents were evaporated in an aluminum block under heating (120~150 ^oC). After removing all the solvents, 0.2 ml of H_2SO_4 was added and the mixture was heated at 200 ^oC. To this mixture, HNO_3 was added dropwise until it turned transparent. After all HNO_3 was evaporated, the solution was cooled to room temperature and was diluted and massed-up to 10 ml with deionized water to afford a leaching test sample. The leaching of metals was determied by ICP-AES analysis.

Recovery and reuse of the catalyst (Table 4)

LIHBCB-Rh(/Ag) catalyst (**2**) (for **5aa** : 0.006 mmol of **2b**, 1 mol% as Rh / for **5ia** : 0.018 mmol of **2f**, 2 mol% as Rh) , phenylboronic acid (93.6 mg, 0.9 mmol, 1.5 equiv for **5aa** / 189.9 mg, 1.8 mmol, 2 equiv for **5ia**) and 2-cyclohexenone (57.7 mg (58.2 µl), 0.6 mmol for **5aa**) or *N*-benzylcrotonamide (157.7 mg, 0.9 mmol for **5ia**), toluene (0.7 ml), and water (1.4 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution. The reaction mixture was stirred for 24 h at 100 ^oC (reflux) (using a Carousel system). After the reaction, the catalyst was separated by filtration and washed with EtOAc (20 mL) and water, then the organic layer was washed with brine. The organic layers were dried over Na_2SO_4 and the solvents were removed *in vacuo*. The residue was purified by preparative TLC. The recovered catalyst was placed in a round-bottom flask (50 ml) and was stirred in a toluene (7 ml)/water (7 ml) solution for 2 h at room temperature. The catalyst was

filtered by a KIRIYAMA funnel and washed with toluene and water. The combined catalyst was dried *in vacuo* and was used for next run. A reaction scale was adjusted based on the amount of the recovered catalyst.

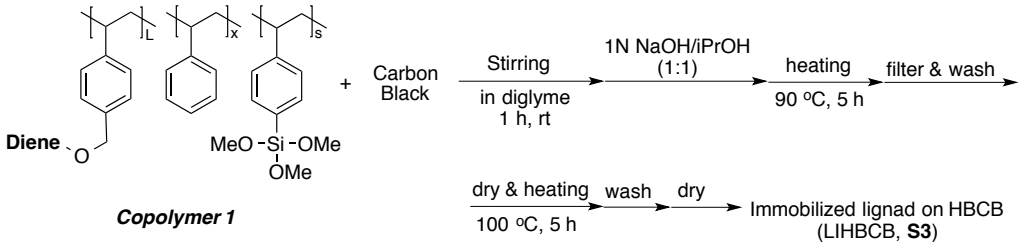
Control experiment (Table 5)

LIHBCB-Rh/Ag (1:2) catalyst (**2f**) (0.006 mmol, 2 mol% as Rh) and phenylboronic acid (**4a**) (64.7 mg, 0.6 mmol, 2 equiv) or *N*-benzylcrotonamide (**3i**) (52.6 mg, 0.3 mmol, 1 equiv) (none for entry 1, **3i** for entry 2, **4a** for entries 3 and 4), toluene (0.7 ml), and water (1.4 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution, then the reaction mixture was stirred for 96 h at 100 ^{o}C (reflux) (using a Carousel system). After heating for 96 h, phenylboronic acid (**4a**) (64.7 mg, 0.6 mmol, 2 equiv) and/or *N*-benzylcrotonamide (**3i**) (52.6 mg, 0.3 mmol, 1 equiv) (both **3i** and **4a** for entries 1 and 4, **4a** for entry 2, **3i** for entry 3) were added to reaction mixture, and it was stirred further 24 h at 100 ^{o}C. After the reaction, the catalyst was separated by filtration and washed with EtOAc (20 mL) and water, then the organic layer was washed with brine. The organic layers were dried over Na_2SO_4 and the solvents were removed *in vacuo*. The residue was purified by preparative TLC.

Hot filtration test (Figure 1)

LIHBCB-Rh/Ag (1:2) catalyst (**2f**) (0.0045 mmol, 1 mol% as Rh), phenylboronic acid (**4a**) (0.9 mmol, 2 equiv), substrate **3a** or **3e** (0.45 mmol), durene (internal standard, 30~35 mg), toluene (1 ml), and water (2 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution. After 5 h, catalyst was removed by membrane filter with keeping 100 ^{o}C, then filtrate was further heated and stirred for 19 h at 100 ^{o}C. During the reaction, aliquots were taken by gas-tight microsyringe (~30 µl) and it was diluted with EtOAc (~3 ml). After wash with small amount of water (~3 ml), GC samples were prepared after passing through Na_2SO_4 and silica short column.

Preparation of immobilized ligand on polymer/carbon black (S3) (used in Table 6 and Scheme 4) (Scheme S3)



The solution of LIHBP (250 mg) and Ketjenblack (250 mg) in diglyme (15 ml) was stirred for 1 h at room temperature. After addition of 1 N NaOH (aq., 70 ml) and isopropyl alcohol (70 ml), the mixture was heated at 90 ^{o}C with stirring for 5 h. The resulting mixture was filtered, washed several times with isopropyl alcohol and dried *in vacuo*. Next, the catalyst was heated (no stirring) at 100 °C for 5 h under neat conditions. It was washed

with water, isopropyl alcohol and DCM several times, and dried *in vacuo* to afford the desired immobilized ligand on hybrid polymer/carbon black (HBCB) (**S3**).

Reaction with the mixture of Rh NPs and chiral ligand on different support (Scheme 4)

Rh/Cellulose catalyst (0.0015 mmol, 0.5 mol% as Rh), immobilized ligand on hybrid carbon black (**S3**) (0.9 mg, 0.000375 mmol, 0.125 mol%), 3-methoxyphenylboronic acid (**4c**) (82.9 mg, 0.9 mmol, 2 equiv), ethyl-(E)-4-methylcinnamate (**3g**) (57.1 mg (55.0 μl), 0.6 mmol, 2 equiv), toluene (0.7 ml), and water (1.4 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution. The reaction mixture was stirred for 24 h at 100 ^{o}C (reflux) (using a Carousel system). After the reaction, the catalyst was seperated by filtration and washed with EtOAc (20 mL) and water using a KIRIYAMA funnel. The organic layers were washed with brine and dried over Na_2SO_4 and the solvents were removed *in vacuo*. Yield was determined by ^{1}H NMR analysis in the presence of internal standard (1,1,2,2-tetrachloroethane).

Procedure for addition of aryl boronic acids to nitroolefin and imine substrates (Table 8)

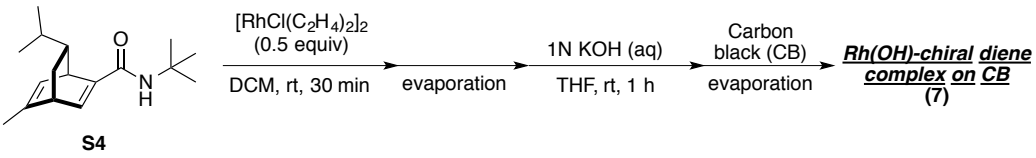
LIHBCB-Rh/Ag (1:1) catalyst (**2d**) (0.003-0.006 mmol, 1-2 mol% as Rh), arylboronic acid (0.6-0.9 mmol, 2-3 equiv), substrate (0.3 mmol), toluene (2 ml for imine, 1.75 ml for nitroolefin), and water (0.25 ml for imine, 0.35 ml for a nitroolefin) were placed in a reaction tube, which was capped with a septum after Ar substitution. The mixture was stirred for 24-48 h at 100 ^{o}C (reflux) (using a Carousel system). After the reaction, the catalyst was separated by filtration and washed with EtOAc (20 mL) and water using a KIRIYAMA funnel. The organic phase was separated and was washed with brine. The organic layers were dried over Na_2SO_4 and the solvents were removed *in vacuo*. The residue was purified by preparative TLC.

Application to a flow system (Scheme 5)

LIHBCB-Rh/Ag (1:2) catalyst (**2d**) (240 mg) and celite (600 mg) were mixed well and a column (10Φ X 5 cm) was packed with this mixture of the catalyst and celite. An aqueous solution of phenylboronic acid (0.1 M) and a toluene solution of 2-cyclohexenone (0.15 M) were flowed into the column using separate pumps (aqueous phase = 70 μl/min, toluene phase = 30 μl/min). These two different solvents were mixed in a T-shape mixer. To prevent evaporation of the solvents in the column, a back pressure controller was used (~0.2 MPa). Each fraction was collected for some hours, and the collected solutions were extracted with EtOAc. After washed with water and brine, the organic layers were dried over Na_2SO_4 and the solvents were removed *in vacuo*. A yield was determined by ^{1}H NMR analysis using an internal standard (1,1,2,2-tetrachloroethane) based on the collected amount of the solvent. The residue was purified by preparative TLC.

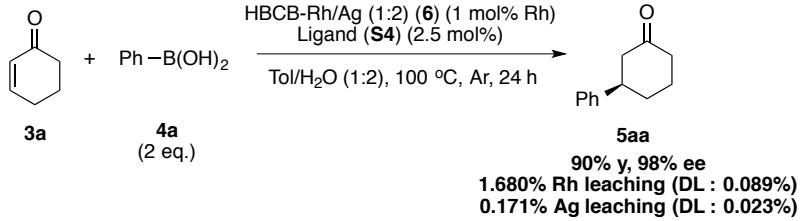
5. XPS Analysis & Possible Reaction Mechanism

Preparation of Rh(OH)-diene complex (7) (Scheme S4)



Amide substituted chiral diene (**S4**, 0.2 mmol, 52.3 mg) and $[RhCl(C_2H_4)_2]_2$ (0.1 mmol, 38.9 mg) were combined in DCM (30 ml), and mixture was stirred at room temperature for 30 min. After evaporation of DCM, 1N KOH (aqueous solution, 4 ml) and 20 ml of THF were added and it was stirred at room temparature for 1 h. Carbon black (100 mg) was added to this solution, and solvent was evaporated. After dry *in vacuo*, black solid was kept in glove box.

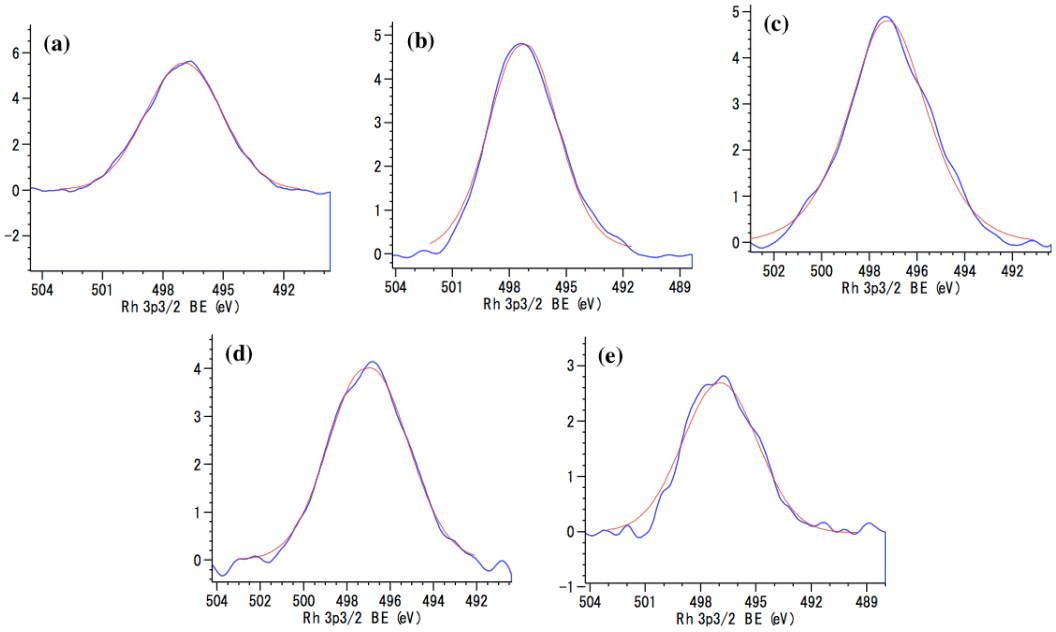
Reaction with HBCB-Rh/Ag (1:2) together with externally added chiral diene ligand (Scheme S5)



HBCB-Rh/Ag (1:2) catalyst (**6**) (0.003 mmol, 1 mol% as Rh), phenylboronic acid (65.6 mg, 0.6 mmol, 2 equiv), 2-cyclohexenone (28.9 mg (29.1 μl), 0.30 mmol, 1 equiv), chiral diene ligand (**S4**) in toluene (use stock solution), toluene (0.7 ml), and water (1.4 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution. The reaction mixture was stirred for 24 h at 100 ^{o}C (reflux) (using a Carousel system). After the reaction, the mixture was filtered with THF (~10 ml) using an eluting tube with cotton. This filtrate was filtered again with a membrane filter. The final filtrate was massed-up to 25 ml, which was divided to two portions; 15 ml for isolation, and 10 ml for a leaching test. In the case of the leaching test, 10 ml of filtrate was transferred to a test tube and the solvents were evaporated in an aluminum block under heating (120~150 ^{o}C). After removing all the solvents, 0.2 ml of H_2SO_4 was added and the mixture was heated at 200 ^{o}C. To this mixture, HNO_3 was added dropwise until it turned transparent. After all HNO_3 was evaporated, the solution was cooled to room temperature and was diluted and massed-up to 10 ml with deionized water to afford a leaching test sample. For isolation, solvent was evaporated and the residue was purified by preparative TLC.

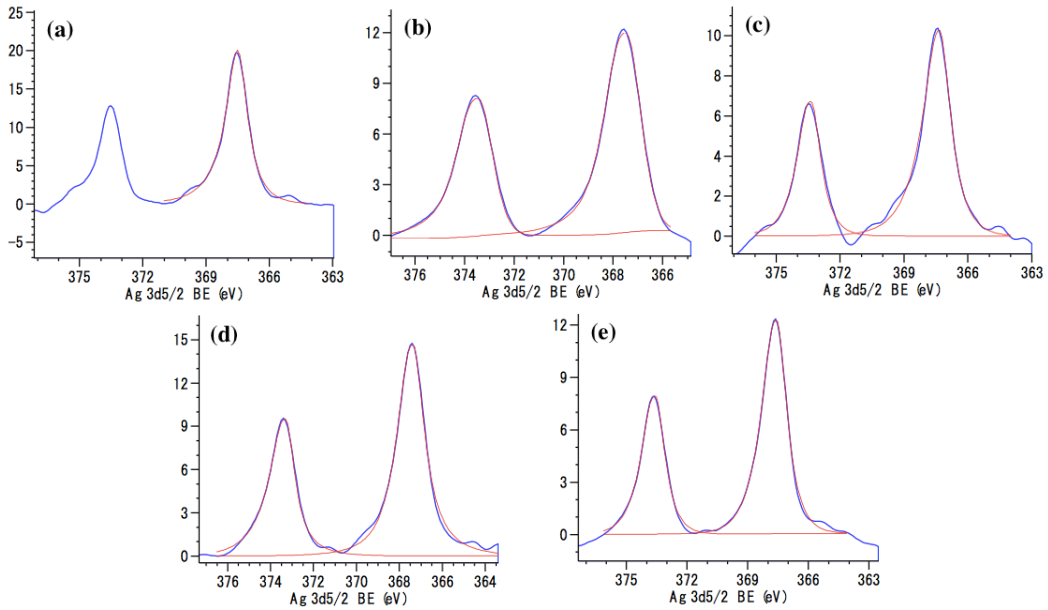
XPS Analysis Data

Figure S12. XPS analysis (1) - Rh binding energy (BE) of catalyst **2f**



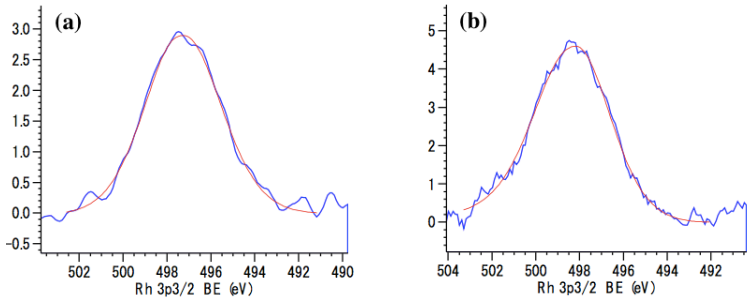
(a) fresh catalyst; (b) *in situ* sample (1 h); (c) *in situ* sample (5 h); (d) after use; (e) after 4th use

Figure S13. XPS analysis (2) - Ag binding energy (BE) of catalyst **2f**



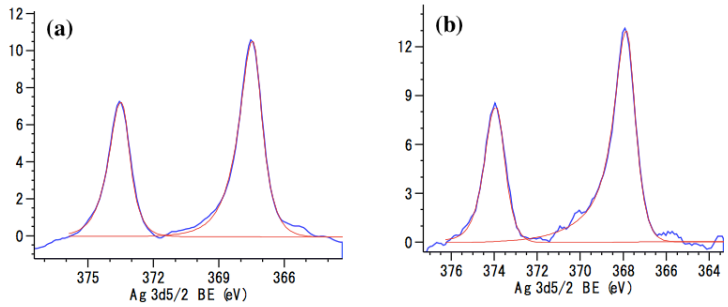
(a) fresh catalyst; (b) *in situ* sample (1 h); (c) *in situ* sample (5 h); (d) after use; (e) after 4th use

Figure S14. XPS Analysis (3) - Rh BE of HBCB-Rh/Ag (1:2) catalyst (**6**) with external added ligand (**S4**)



(a) fresh catalyst; (b) after use

Figure S15. XPS Analysis (4) - Ag BE of HBCB-Rh/Ag (1:2) catalyst (**6**) with external added ligand (**S4**)



(a) fresh catalyst; (b) after use

Figure S16. XPS Analysis (5) -Rh BE of Rh(OH)-diene complex (**7**)

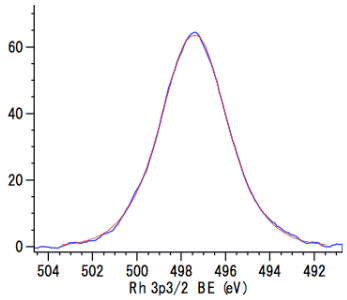


Table S1. Binding energy of Rh and Ag

LIHBCB-Rh/Ag (1:2) (**2f**)						Rh(OH)-diene (**7**)
State	(a) Fresh	(b) 1 h	(c) 5 h	(d) After	(e) After_4th	
Rh (3p 3/2, eV)	496.967	497.389	497.219	496.931	496.944	497.344
Ag (3d 5/2, eV)	373.468	373.729	373.374	373.312	373.578	-
	367.508	367.731	367.354	367.391	367.588	-

HBCB-Rh/Ag (1:2) (**6**) + chiral ligand (2.5 mol%)		
State	(a) Before	(b) After
Rh (3p 3/2, eV)	497.232	498.171
Ag (3d 5/2, eV)	373.479	373.927
	367.499	367.916

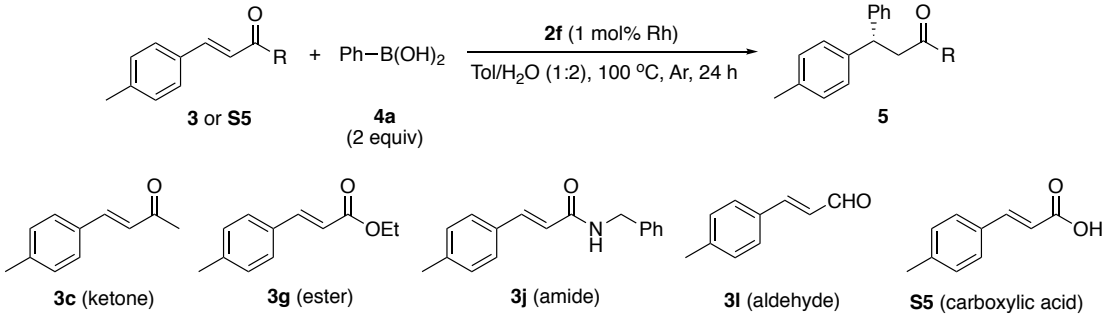
6. Reaction Profiles

Difference in reaction rate of ketone, ester, amide and aldehyde substrates

LIHBCB-Rh/Ag (1:1 or 1:2) catalyst (**2d** or **2f**) (0.003 mmol, 1 mol% as Rh), phenylboronic acid (**4a**) (64.5 mg, 0.6 mmol, 2 equiv), 4-methylcinnamyl group containing substrate (0.3 mmol, 1 equiv), dodecane (internal standard, 59~61 mg), toluene (0.7 ml), and water (1.4 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution. During the reaction, aliquots were taken by gas-tight microsyringe (10~20 μl) in corresponding time and GC samples were prepared after passing through Na_2SO_4 and silica short column with EtOAc.

Firstly, reaction was conducted under same conditins; 1 mol% of catalyst, 2 equiv of pehnylboronic acid (4a), Tol/H_2O (1:2), 100 ^oC for 24 h. Then, optimization of each reaction was conducted and all the results are shown in Table S2.

Table S2. Reactivity difference of ketone, ester, amide and aldehyde substrates

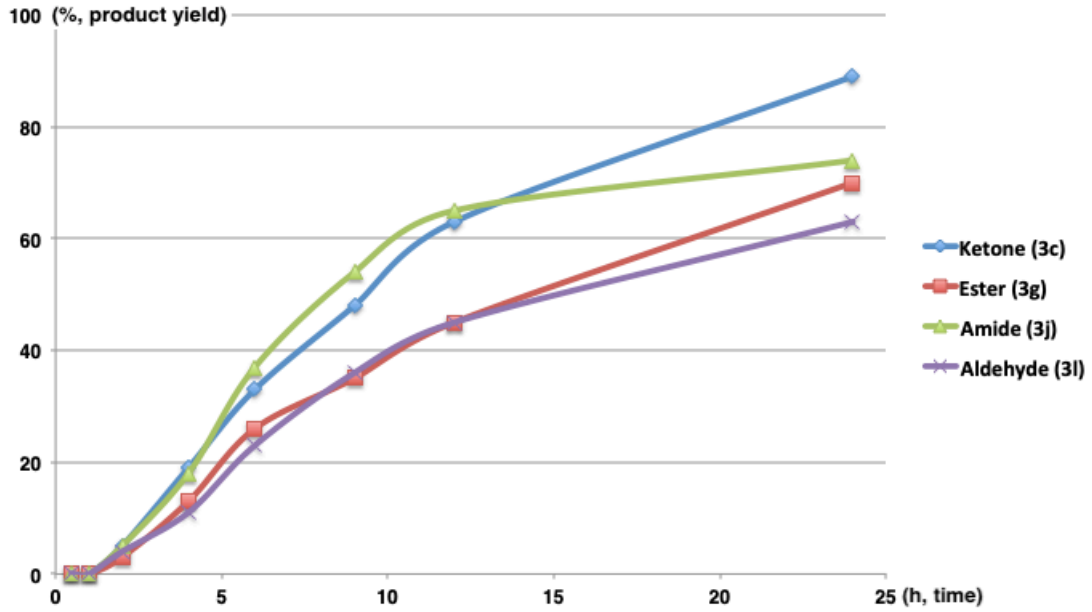


Substrate	**3c** (ketone)	**3g** (ester)	**3j** (amide)
Conditions in Scheme	93% y, 91% ee	74% y, 97% ee	69% y, 98% ee
Optimal conditions	-	Quant. y, 97% ee (1 equiv K_2CO_3)	90% y, 98% ee (2 mol% Cat.)

Substrate	**3l** (aldehyde)	**S5** (carboxylic acid)
Conditions in Scheme	55% y, 93% ee	No desired product
Optimal conditions	71% y, 93% ee (Cat. 2d (Rh/Ag (1:1))	

* Yield was determined by isolation. Ee was determined by HPLC analysis.

Figure S17. Difference in reaction rate of ketone, ester, amide and aldehyde substrates



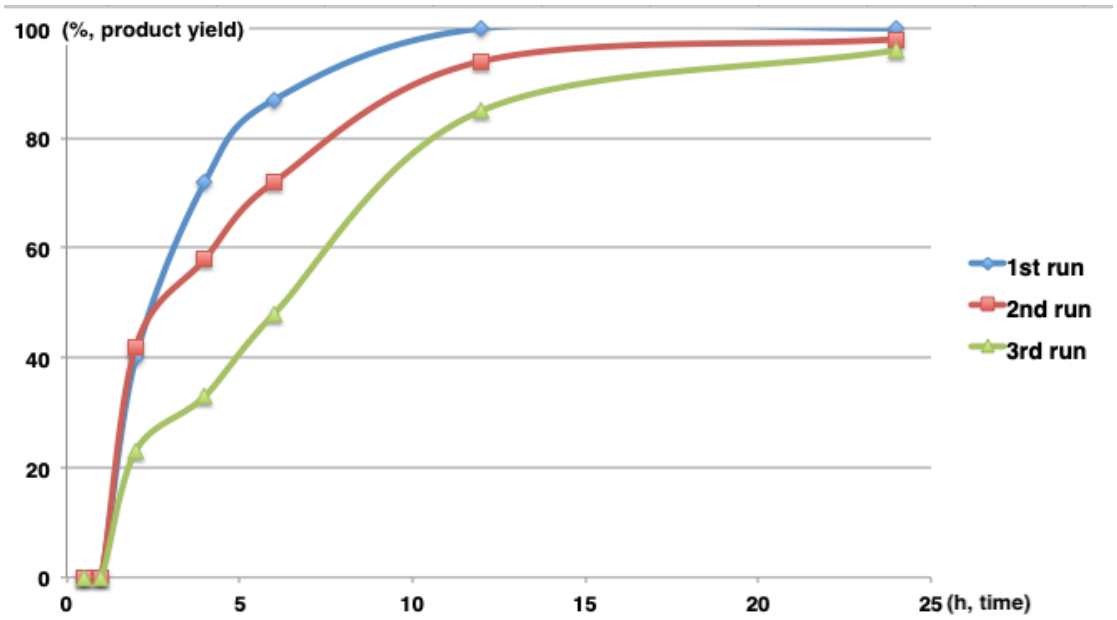
In all cases, induction period was found in initial 2 h regardless of the kinds of substrate. After the induction period, the initial rate of ketone substrate **3c** was faster than that of ester **3g**, and in both cases, reactions gradually proceeded in entire 24 h. In the case of ketone **3c** and amide **3i**, initial rate was similar but the rate of amide **3i** decreased more after 9 h. From these results, we concluded that reactivity cannot be simply discussed based on LUMO level of substrates. Lewis basic amides (both substrates and products) can easily coordinate to the catalyst, and release from the catalyst would be difficult. As a result, decrease in the reaction rate of amide in late stage would be derived from product inhibition. Moreover, in previous report[17], we showed that the rate determining step is different between ester and nitroolefin substrates suggested by reactions in deuterated water. We think that the rate determining step of amide substrates can also be protonation step, unlike ketone or ester substrates. In the case of aldehyde **3l**, it showed similar initial reaction rate with ester **3g** but the reaction rate decreased after 12 h. We think that small amount of side products derived from aldehyde substrate, such as 1,2-addition outcome, can inhibit the reaction.

Reaction profile in rcovery/reuse of catalyst

LIHBCB-Rh/Ag (1:2) catalyst (**2f**) (0.006 mmol, 2 mol% as Rh), phenylboronic acid (**4a**) (64.5 mg, 0.6 mmol, 2 equiv), *N*-benzylcrotonamide (**3i**) (52.6 mg, 0.3 mmol, 1 equiv), dodecane (internal standard, 59~61 mg), toluene (0.7 ml), and water (1.4 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution. During the reaction, aliquots were taken by gas-tight microsyringe (10~20 μl) in corresponding time and GC samples were prepared after passing through Na_2SO_4 and silica short column with EtOAc.

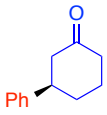
In the profile of 2nd run and 3rd run, catalyst, which was recovered and treated proper washing method as shown in above (Recovery and reuse of catalyst), was used instead of fresh catalyst.

Figure S18. Reaction profile in recovery/reuse of catalyst



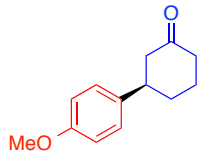
7. Reaction Products

***(R)*-3-Phenylcyclohexanone (5aa)**



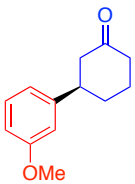
Following the above general procedure with 2-cyclohexenone (28.9 mg (29.1 µl), 0.30 mmol, 1 equiv) and phenylboronic acid (49.6 mg, 0.45 mmol, 1.5 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide **5aa** (51.1 mg, 98%) as a colorless oil. **GC Retention time (*Condition I*)**: 21.2 (internal standard (durene)), 21.5 (starting material (2-cyclohexenone)), 36.1 (product). **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.34 (t, *J* = 7.6 Hz, 2H), 7.27-7.23 (m, 3H), 3.02 (tt, *J* = 12.0, 3.9 Hz, 1H), 2.62-2.59 (m, 1H), 2.56-2.52 (m, 1H), 2.49-2.46 (m, 1H), 2.42-2.37 (m, 1H), 2.18-2.15 (m, 1H), 2.11-2.09 (m, 1H), 1.90-1.76 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 211.0, 144.3, 128.7, 126.7, 126.6, 48.9, 44.7, 41.2, 32.8, 25.5. The ee value of product was determined on Daicel Chiralpak AD column with hexane/2-propanol = 98:2, flow = 0.5 ml/min by HPLC analysis. Retention times: 18.0 min [*(S)*-enantiomer], 21.3 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[18] (No Rh leaching (UDL) with LIHBCB-Rh (**2b**), No Rh leaching (UDL), 0.0533% Ag leaching (Rh DL: 0.1496%, Ag DL: 0.0227%) with LIHBCB-Rh/Ag (1:2) (**2f**)).

***(R)*-3-(4-Methoxyphenyl)cyclohexanone (5ab)**



Following the above general procedure with 2-cyclohexenone (28.9 mg (29.1 µl), 0.30 mmol, 1 equiv) and 4-methoxyphenylboronic acid (61.4 mg, 0.45 mmol, 1.5 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide **5ab** (57.7 mg, 94%) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.07 (d, *J* = 8.2 Hz, 2H)), 6.80 (d, *J* = 8.2 Hz, 2H), 3.73 (s, 3H), 2.90 (tt, *J* = 11.7, 4.1 Hz, 1H), 2.52-2.49 (m, 1H), 2.44-2.37 (m, 2H), 2.33-2.27 (m, 1H), 2.10-2.05 (m, 1H), 2.00-1.98 (m, 1H), 1.78-1.65 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 211.2, 158.2, 136.5, 127.4, 114.0, 55.2, 49.2, 43.9, 41.1, 33.0, 25.5. The ee value of product was determined on Daicel Chiralpak AD-H column with hexane/2-propanol = 98:2, flow = 0.5 ml/min by HPLC analysis. Retention times: 25.8 min [*(S)*-enantiomer], 27.4 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[12]

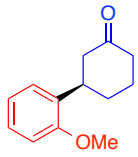
***(R)*-3-(3-Methoxyphenyl)cyclohexanone (5ac)**



Following the above general procedure with 2-cyclohexenone (28.9 mg (29.1 µl), 0.3 mmol, 1 equiv) and 3-methoxyphenylboronic acid (61.4 mg, 0.45 mmol, 1.5 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide **5ac** (58.7 mg, 96%) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.25-7.23 (m, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.78-6.75 (m, 2H), 3.80 (s, 3H), 2.97 (tt, *J* = 12.0, 3.9 Hz, 1H), 2.60-2.56 (m, 1H), 2.53-2.48 (m, 1H), 2.47-2.43 (m, 1H), 2.40-2.34 (m, 1H), 2.17-2.12 (m, 1H), 2.09-2.05 (m, 1H), 1.87-1.74 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 210.9, 159.8, 146.0, 129.6, 118.9, 112.7, 111.6, 55.2, 48.9, 44.7, 41.1, 32.6, 25.5. The ee value of product was determined on Daicel Chiralpak AD-H column with hexane/2-

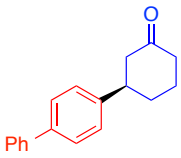
propanol = 98:2, flow = 0.5 ml/min by HPLC analysis. Retention times: 27.9 min [*(S)*-enantiomer], 30.0 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[19]

***(R)*-3-(2-Methoxyphenyl)cyclohexanone (5ad)**



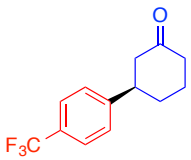
Following the above general procedure with 2-cyclohexenone (28.9 mg (29.1 µl), 0.30 mmol, 1 equiv) and 2-methoxyphenylboronic acid (68.4 mg, 0.45 mmol, 1.5 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide **5ad** (58.4 mg, 95%) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.21-7.16 (m, 2H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.2, 1H), 3.80 (s, 3H), 3.40 (tt, *J* = 11.7, 3.7 Hz, 1H), 2.58-2.54 (m, 1H), 2.51-2.42 (m, 2H), 2.38-2.33 (m, 1H), 2.13-2.09 (m, 1H), 2.02-1.98 (m, 1H), 1.88-1.75 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 211.7, 156.6, 132.4, 127.5, 126.5, 120.6, 110.5, 55.2, 47.5, 41.3, 37.9, 30.9, 25.5. The ee value of product was determined on Daicel Chiralpak AD-H column with hexane/2-propanol = 98:2, flow = 0.5 ml/min by HPLC analysis. Retention times: 20.2 min [*(S)*-enantiomer], 22.2 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[20]

***(R)*-3-([1,1'-biphenyl]-4]yl)cyclohexanone (5ae)**



Following the above general procedure with 2-cyclohexenone (28.9 mg (29.1 µl), 0.3 mmol, 1 equiv) and 4-biphenylboronic acid (88.7 mg, 0.45 mmol, 1.5 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 9:1 and 7:3) to provide **5ae** (66.8 mg, 89%) as a white solid (Mp. 165-166 °C). **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.51-7.48 (m, 4H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 2H), 2.98 (tt, *J* = 12.0, 3.9 Hz, 1H), 2.57-2.54 (m, 1H), 2.50-2.46 (m, 1H), 2.41-2.38 (m, 1H), 2.34-2.29 (m, 1H), 2.10-2.08 (m, 1H), 2.04-2.03 (m, 1H), 1.84-1.70 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 210.9, 143.4, 140.7, 139.6, 128.7, 127.4, 127.2, 127.0, 48.9, 44.4, 41.2, 32.8, 25.5. The ee value of product was determined on Daicel Chiralpak AD-3 column with hexane/2-propanol = 98:2, flow = 1.0 ml/min by HPLC analysis. Retention times: 17.7 min [*(R)*-enantiomer], 25.3 min [*(S)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[20]

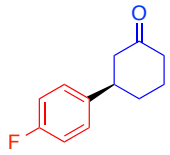
***(R)*-3-(4-trifluoromethylphenyl)cyclohexanone (5af)**



Following the above general procedure with 2-cyclohexenone (28.9 mg (29.1 µl), 0.3 mmol, 1 equiv) and 4-trifluoromethylphenylboronic acid (108.8 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide **5af** (64.4 mg, 89%) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.56 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 3.05 (tt, *J* = 11.7, 3.8 Hz, 1H), 2.58-2.56 (m, 1H), 2.51-2.45 (m, 2H), 2.38-2.36 (m, 1H), 2.15-2.14 (m, 1H), 2.08-2.06 (m, 1H), 1.88-1.74 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 210.1, 148.2, 129.0 (q, *J* = 32.3 Hz), 127.0, 125.6 (q, *J* = 3.9 Hz), 124.1 (d, *J* = 271.7 Hz), 48.5, 44.4, 41.0, 32.5, 25.3. The ee value of product was determined on Daicel Chiralpak OD-H, AS-H connected column with hexane/2-propanol = 90:10, flow = 0.5 ml/min by HPLC analysis. Retention times: 29.8

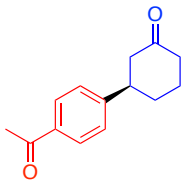
min [*(R)*-enantiomer], 32.7 min [*(S)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[21]

***(R)*-3-(4-Fluorophenyl)cyclohexanone (5ag)**



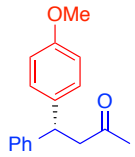
Following the above general procedure with 2-cyclohexenone (28.9 mg (29.1 µl), 0.3 mmol, 1 equiv) and 4-fluorophenylboronic acid (72.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide **5ag** (52.8 mg, 92%) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.16-7.15 (m, 2H), 7.00-6.97 (m, 2H), 2.97 (tt, *J* = 12.0, 3.8 Hz, 1H), 2.56-2.54 (m, 1H), 2.46-2.44 (m, 2H), 2.38-2.32 (m, 1H), 2.13-2.11 (m, 1H), 2.05-2.03 (m, 1H), 1.83-1.73 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 210.6, 161.5 (d, *J* = 244.2 Hz), 140.0, 127.9 (d, *J* = 7.2 Hz), 115.4 (d, *J* = 21.7 Hz), 49.0, 44.0, 41.1, 32.9, 25.4. The ee value of product was determined on Daicel Chiralpak AD-H column with hexane/2-propanol = 97:3, flow = 1.0 ml/min by HPLC analysis. Retention times: 8.2 min [*(S)*-enantiomer], 10.1 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[22]

***(R)*-3-(4-acetylphenyl)cyclohexanone (5ah)**



Following the above general procedure with 2-cyclohexenone (28.9 mg (29.1 µl), 0.3 mmol, 1 equiv) and 4-acetylphenylboronic acid (97.1 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 7:3) to provide **5ah** (58.8 mg, 91%) as a white solid (Mp. 67-68 °C). **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.90 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 3.05 (tt, *J* = 11.7, 4.0 Hz, 1H), 2.57-2.56 (m, 4H), 2.52-2.49 (m, 1H), 2.46-2.43 (m, 1H), 2.38-2.35 (m, 1H), 2.15-2.13 (m, 1H), 2.08-2.05 (m, 1H), 1.88-1.75 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 210.2, 197.6, 149.6, 135.8, 128.8, 126.8, 48.4, 44.6, 41.1, 32.4, 26.5, 25.4. The ee value of product was determined on Daicel Chiralpak AD-3 column with hexane/2-propanol = 90:10, flow = 0.6 ml/min by HPLC analysis. Retention times: 26.2 min [*(R)*-enantiomer], 28.2 min [*(S)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[23]

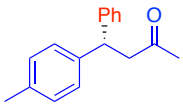
***(R)*-4-(4-Methoxyphenyl)-4-phenylbutan-2-one (5bb)**



Following the above general procedure with benzalacetone (44.1 mg, 0.30 mmol, 1 equiv) and 4-methoxyphenylboronic acid (88.1 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 15:1) to provide **5bb** (66.9 mg, 88%) as a yellowish white solid (Mp. 45-47 °C). **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.27-7.25 (m, 2H), 7.20-7.19 (m, 2H), 7.17-7.12 (m, 3H), 6.80 (d, *J* = 8.2 Hz, 2H), 4.53 (t, *J* = 7.6 Hz, 1H) 3.74 (s, 3H), 3.14 (d, *J* = 7.6 Hz, 2H), 2.06 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 207.0, 158.0, 144.2, 135.9, 128.6, 128.5, 127.5, 126.3, 113.9, 55.2, 49.8, 45.2, 30.6. The ee value of product was determined on Daicel Chiralpak AD-3, OD-H connected column with hexane/2-propanol = 98:2, flow = 1.0 ml/min by HPLC analysis. Retention times:

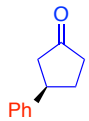
40.2 min [*(S)*-enantiomer], 43.3 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[24]

***(S)*-4-(4-Methylphenyl)-4-phenylbutan-2-one (5ca)**



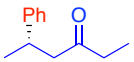
Following the above general procedure with (E)-4-(4-methylphenyl)-3-buten-2-one (48.1 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (66.9 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 15:1) to provide **5ca** (66.2 mg, 93%) as a colorless oil. **GC Retention time (*Condition II*)**: 12.9 (internal standard (dodecane)), 17.1 (starting material), 24.8 (product). **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.30-7.27 (m, 2H), 7.24-7.23 (m, 2H), 7.20-7.17 (m, 1H), 7.14-7.09 (m, 4H), 4.57 (t, *J* = 7.6 Hz, 1H), 3.18 (d, *J* = 7.6 Hz, 2H), 2.31 (s, 3H), 2.09 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 207.0, 144.0, 140.8, 135.9, 129.2, 128.5, 127.6, 127.5, 126.3, 49.7, 45.7, 30.6, 20.9. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 90:10, flow = 0.5 ml/min by HPLC analysis. Retention times: 12.8 min [*(S)*-enantiomer], 14.5 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[25]

***(R)*-3-Phenylcyclopentanone (5da)**



Following the above general procedure with 2-cyclopentenone (24.7 mg (25.3 µl), 0.3 mmol, 1 equiv) and phenylboronic acid (65.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide **5da** (45.3 mg, 94%) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.35 (t, *J* = 7.6 Hz, 2H), 7.28-7.26 (m, 3H), 3.46-3.40 (m, 1H), 2.67 (dd, *J* = 17.9, 7.6 Hz, 1H), 2.49-2.43 (m, 2H), 2.35-2.30 (m, 2H), 2.01-1.98 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 218.4, 143.0, 128.7, 126.7, 45.8, 42.2, 38.9, 31.2. The ee value of product was determined on Daicel Chiralpak AS-H column with hexane/2-propanol = 99:1, flow = 0.5 ml/min by HPLC analysis. Retention times: 41.6 min [*(R)*-enantiomer], 47.5 min [*(S)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[26]

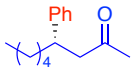
***(S)*-5-Phenylhexan-3-one (5ea)**



Following the above general procedure with (E)-4-hexen-3-one (29.5 mg (34.7 µl), 0.3 mmol, 1 equiv) and phenylboronic acid (49.4 mg, 0.45 mmol, 1.5 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide **5ea** (47.4 mg, 90%) as a colorless oil. **GC Retention time (*Condition I*)**: 15.8 (starting material (hexenone)), 21.2 (internal standard (durene)), 28.2 (product). **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.27 (t, *J* = 7.9 Hz, 2H), 7.20-7.16 (m, 3H), 3.32-3.29 (m, 1H), 2.71 (dd, *J* = 15.8, 6.9 Hz, 1H), 2.62 (dd, *J* = 15.8, 7.6 Hz, 1H), 2.35-2.25 (m, 2H), 1.24 (d, *J* = 6.9 Hz, 3H), 0.97 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 210.5, 146.3, 128.5, 126.7, 126.2, 50.8, 36.6, 35.5, 21.9, 7.6. The ee value of product was determined on Daicel Chiralpak AD-H, AD-3 connected column with hexane/2-propanol = 99.5:0.5, flow = 0.5 ml/min by HPLC analysis. Retention times: 28.2 min

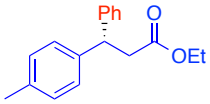
[*(S)*-enantiomer], 32.2 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[27] (0.3687% Rh leaching, 0.1167% Ag leaching (Rh DL: 0.1496%, Ag DL: 0.0227%))

_(S)_-4-Phenylnonan-2-one (5fa)



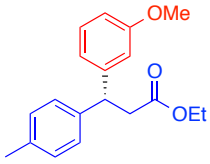
Following the above general procedure with (E)-3-nonen-2-one (42.1 mg (49.7 µl), 0.3 mmol, 1 equiv) and phenylboronic acid (65.5 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 15:1) to provide **5fa** (57.3 mg, 87%) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.26 (t, *J* = 7.6 Hz, 2H), 7.18-7.14 (m, 3H), 3.11-3.07 (m, 1H), 2.73-2.66 (m, 2H), 1.99 (s, 3H), 1.61-1.52 (m, 2H), 1.22-1.08 (m, 6H), 0.80 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 208.0, 144.6, 128.4, 127.4, 126.3, 50.9, 41.3, 36.4, 31.7, 30.6, 27.0, 22.5, 14.0. The ee value of product was determined on Daicel Chiralpak OJ-H column with hexane/2-propanol = 99:1, flow = 0.25 ml/min by HPLC analysis. Retention times: 26.5 min [*(S)*-enantiomer], 29.2 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[20]

Ethyl _(S)_-3-phenyl-3-(_p_-tolyl)propanoate (5ga)



Following the above general procedure with ethyl-*(E)*-4-methylcinnamate (57.1 mg (55.0 µl), 0.3 mmol, 1 equiv), phenylboronic acid (66.9 mg, 0.6 mmol, 2 equiv) and K_2CO_3 (41.5 mg, 0.3 mmol, 1 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 19:1) to provide **5ga** (85.8 mg, quant.) as a colorless oil. **GC Retention time (*Condition II*)**: 12.9 (internal standard (dodecane)), 18.8 (starting material), 25.9 (product). **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.19-7.16 (m, 4H), 7.08-7.03 (m, 5H), 4.43 (t, *J* = 7.9 Hz, 1H), 3.95 (q, *J* = 7.1 Hz, 2H), 2.95 (d, *J* = 8.2 Hz, 2H), 2.21 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 171.9, 143.7, 140.5, 136.0, 129.2, 128.5, 127.6, 127.5, 126.4, 60.4, 46.6, 40.9, 21.0, 14.0. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 99:1, flow = 1.0 ml/min by HPLC analysis. Retention times: 7.6. min [*(R)*-enantiomer], 11.6 min [*(S)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[11]

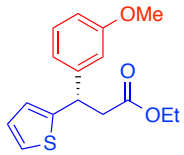
Ethyl _(R)_-3-(3-methoxyphenyl)-3-(_p_-tolyl)propanoate (5gc)



Following the above general procedure with ethyl-*(E)*-4-methylcinnamate (57.1 mg (55.0 µl), 0.3 mmol, 1 equiv), 3-methoxyphenylboronic acid (82.1 mg, 0.6 mmol, 2 equiv) and K_2CO_3 (41.8 mg, 0.3 mmol, 1 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide **5gc** (81.1 mg, 91%) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.17 (t, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.78-6.76 (m, 1H), 6.71-6.70 (m, 1H), 4.47 (t, *J* = 8.2 Hz, 1H), 4.02 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 3.00 (d, *J* = 7.6 Hz, 2H), 2.28 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 171.8, 159.6, 145.4, 140.3, 136.0, 129.4, 129.2, 127.5, 120.0, 113.7, 111.4, 60.4, 55.1, 46.6, 40.8, 21.0, 14.1. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 99:1, flow = 0.5 ml/min by HPLC analysis. Retention times: 34.5 min [*(S)*-enantiomer],

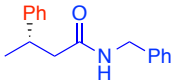
50.6 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[11]

Ethyl *(S)*-3-(3-methoxyphenyl)-3-(thiophen-2-yl)propanoate (5hc)



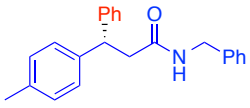
Following the above general procedure with ethyl (E)-3-(thiophen-2-yl)acrylate (54.7 mg (48.1 µl), 0.3 mmol, 1 equiv), 3-methoxyphenylboronic acid (82.2 mg, 0.6 mmol, 2 equiv) and K_2CO_3 (41.6 mg, 0.3 mmol, 1 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide **5hc** (63.7 mg, 73%) as a yellowish oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.20 (t, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 4.8 Hz, 1H), 6.87-6.83 (m, 4H), 6.75 (d, *J* = 8.2 Hz, 1H), 4.72 (t, *J* = 7.6 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 3.08 (dd, *J* = 15.1, 8.2 Hz, 1H), 3.00 (dd, *J* = 15.1, 8.2 Hz, 1H), 1.13 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 171.2, 159.7, 147.3, 144.7, 129.6, 126.6, 124.1, 124.0, 119.8, 113.5, 112.2, 60.6, 55.2, 42.8, 42.2, 14.1. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 99:1, flow = 1.0 ml/min by HPLC analysis. Retention times: 17.2 min [*(R)*-enantiomer], 18.5 min [*(S)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[11]

***(S)*-*N*-Benzyl-3-phenylbutanamide (5ia)**



Following the above general procedure with N-benzyl crotonamide (52.7 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (65.8 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (DCM / acetone, 49:1) to provide **5ia** (67.8 mg, 89%) as a white solid (Mp. 70-71 ^{o}C). **GC Retention time (*Condition II*)**: 12.9 (internal standard (dodecane)), 20.1 (starting material), 28.5 (product). **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.22-7.12 (m, 8H), 6.94-6.93 (m, 2H), 5.63 (brs, 1H), 4.28 (dd, *J* = 14.8, 5.8 Hz, 1H), 4.19 (dd, *J* = 14.4, 5.5 Hz, 1H), 3.25-3.24 (m, 1H), 2.37 (d, *J* = 7.6 Hz, 2H), 1.24 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 171.5, 145.7, 138.1, 128.6, 128.5, 127.5, 127.3, 126.8, 126.4, 45.8, 43.3, 37.0, 21.8. The ee value of product was determined on Daicel Chiralpak AD-3 column with hexane/2-propanol = 80:20, flow = 0.5 ml/min by HPLC analysis. Retention times: 10.8 min [*(S)*-enantiomer], 12.2 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[28]

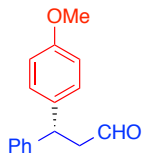
***(S)*-*N*-Benzyl-3-phenyl-3-(*p*-tolyl)propanamide (5ja)**



Following the above general procedure with (E)-N-benzyl-4'-methylcinnamamide (75.4 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (64.5 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (DCM / acetone, 49:1) to provide **5ja** (88.6 mg, 90%) as a white solid (Mp. 115-117 ^{o}C). **GC Retention time (*Condition II*)**: 12.9 (internal standard (dodecane)), 33.2 (starting material), 41.1 (product). **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.28-7.18 (m, 8H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.87 (q, *J* = 3.0 Hz, 2H), 5.55 (brs, 1H), 4.56 (t, *J* = 7.9 Hz, 1H), 4.29 (q, *J* = 3.0 Hz, 2H), 2.91 (d, *J* = 8.2 Hz, 2H), 2.30 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 171.0, 143.8, 140.5, 137.9, 136.0, 129.3, 128.6, 128.4, 127.7, 127.6, 127.4, 127.2, 126.4, 47.1,

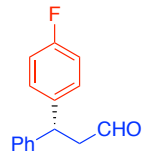
43.5, 43.3, 21.0. The ee value of product was determined on Daicel Chiralpak AD-H column with hexane/2-propanol = 80:20, flow = 0.5 ml/min by HPLC analysis. Retention times: 18.6 min [*(R)*-enantiomer], 20.1 min [*(S)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[28]

(*R*)-3-(4-Methoxyphenyl)-3-phenylpropanal (5kb)



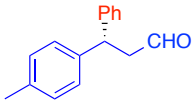
Following the above general procedure with trans-cinnamaldehyde (39.7 mg (37.9 µl), 0.3 mmol, 1 equiv) and 4-methoxyphenylboronic acid (81.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 5:1) to provide **5kb** (46.4 mg, 64%) as a yellowish oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 9.71 (t, *J* = 1.7 Hz. 1H), 7.29-7.13 (m, 7H), 6.85-6.81 (m, 2H), 4.56 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 3H), 3.12 (dd, *J* = 7.9, 1.7 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 201.2, 158.2, 143.6, 135.3, 128.7, 127.6, 126.6, 114.1, 55.2, 49.5, 44.2. The ee value of corresponding alcohol (obtained by reduction with $NaBH_4$ in DCM/MeOH) was determined on Daicel Chiralpak AD-H column with hexane/2-propanol = 92:8, flow = 1.0 ml/min by HPLC analysis. Retention times: 14.1 min [*(R)*-enantiomer], 15.9 min [*(S)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[29]

(*R*)-3-(4-Fluotophenyl)-3-phenylpropanal (5kg)



Following the above general procedure with trans-cinnamaldehyde (39.7 mg, 0.3 mmol, 1 equiv) and 4-fluorophenylboronic acid (74.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide **5kg** (48.1 mg, 70%) as a yellowish oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 9.72 (t, *J* = 1.7 Hz, 1H), 7.33-7.15 (m, 7H), 6.98-6.95 (m, 2H), 4.61 (t, *J* = 7.6 Hz, 1H), 3.14 (dd, *J* = 7.6, 2.1 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 200.6, 161.5 (d, *J* = 245.6 Hz), 143.0, 139.0, 129.2 (d, *J* = 7.2 Hz), 128.8 127.6, 126.8, 115.5 (d, *J* = 21.7 Hz), 49.5, 44.1. The ee value of corresponding alcohol (obtained by reduction with $NaBH_4$ in DCM/MeOH) was determined on Daicel Chiralpak OJ-H column with hexane/2-propanol = 90:10, flow = 1.0 ml/min by HPLC analysis. Retention times: 14.6 min [*(S)*-enantiomer], 18.9 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[29]

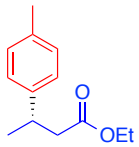
(*S*)-3-Phenyl-3-(*p*-tolyl)propanal (5la)



Following the above general procedure with (E)-4-methylcinnamaldehyde (43.9 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (66.9 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide **5la** (47.8 mg, 71%) as a yellowish oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 9.71 (t, *J* = 1.7 Hz, 1H), 7.28-7.16 (m, 5H), 7.11-7.08 (m, 4H), 4.57 (t, *J* = 7.9 Hz, 1H), 3.12 (dd, *J* = 7.9, 1.7 Hz, 2H), 2.28 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 201.2, 143.4, 140.2, 136.3, 129.4, 128.7, 127.62, 127.55, 126.6, 49.4, 44.6, 20.9. The ee value of corresponding alcohol (obtained by reduction with $NaBH_4$ in DCM/MeOH) was determined on Daicel Chiralpak AS-3 column with hexane/2-propanol = 98:2, flow = 1.0 ml/min by HPLC analysis. Retention times:

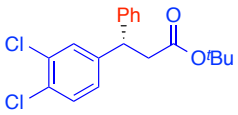
31.5 min [*(R)*-enantiomer], 34.5 min [*(S)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[30]

Ethyl *(S)*-3-(*p*-tolyl)butanoate (5mi)



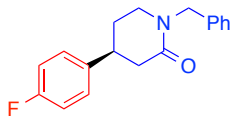
Following the above general procedure with ethyl crotonate (34.3 mg, 0.3 mmol, 1 equiv) and 4-methylphenylboronic acid (81.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 9:1) to provide **5mi** (53.8 mg, 87%) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.09 (s, 4H), 4.06 (q, *J* = 7.3 Hz, 2H), 3.26-3.20 (m, 1H), 2.57 (dd, *J* = 15.1, 6.9 Hz, 1H), 2.50 (dd, *J* = 15.1, 8.2 Hz, 1H), 2.30 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 172.5, 142.7, 135.8, 129.1, 126.6, 60.2, 43.1, 36.1, 21.9, 21.0, 14.2. The ee value of product was determined on Daicel Chiralpak AD-3 column with hexane/2-propanol = 99:1, flow = 1.0 ml/min by HPLC analysis. Retention times: 5.1 min [*(S)*-enantiomer], 5.4 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[31]

***tert*-Butyl *(S)*-3-(3,4-dichlorophenyl)-3-phenylpropanoate (5na)**



Following the above general procedure with *tert*-butyl *(E)*-3-(3,4-dichlorophenyl)acrylate (82.0 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (99.1 mg, 0.9 mmol, 3 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide **5na** (89.5 mg, 85%) as a yellowish stick oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.28-7.12 (m, 7H), 7.00 (dd, *J* = 8.2, 2.1 Hz, 1H), 4.37 (t, *J* = 7.9 Hz, 1H), 2.85 (d, *J* = 8.2 Hz, 2H), 1.23 (s, 9H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 170.5, 143.9, 142.4, 132.4, 130.43, 130.36, 129.7, 128.7, 127.6, 127.2, 126.9, 81.0, 46.5, 41.7, 27.9. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 99:1, flow = 0.2 ml/min by HPLC analysis. Retention times: 35.2 min [*(R)*-enantiomer], 39.9 min [*(S)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[32]

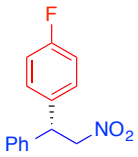
***(R)*-1-Benzyl-4-(4-fluorophenyl)piperidin-2-one (5og)**



Following the above general procedure with *N*-benzyl-Δ^3-piperidein-2-one (56.2 mg, 0.3 mmol, 1 equiv) and 4-fluorophenylboronic acid (116.3 mg, 0.9 mmol, 3 equiv). The crude reaction mixture was purified by preparative TLC (DCM / acetone, 49:1) to provide **5og** (64.9 mg, 76%) as a white solid (Mp. 110-112 ^{o}C). **^{1}H NMR (500 MHz, $CDCl_3$):** δ (ppm) 7.27 (t, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 4H), 7.09-7.07 (m, 2H), 6.94 (t, *J* = 8.6 Hz, 2H), 4.67 (d, *J* = 14.4 Hz, 1H), 4.48 (d, *J* = 14.4 Hz, 1H), 3.26-3.17 (m, 2H), 3.09-2.99 (m, 1H), 2.78-2.70 (m, 1H), 2.48 (dd, *J* = 17.9, 11.0 Hz, 2H), 2.04-1.96 (m, 1H), 1.87-1.80 (m, 1H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ (ppm) 169.0, 161.6 (d, *J* = 245.6 Hz), 139.0, 137.0, 128.6, 128.1, 127.9 (d, *J* = 8.7 Hz), 127.4, 115.5 (d, *J* = 20.2 Hz), 50.0, 46.2, 39.6, 37.9, 30.2. The ee value of product was determined on Daicel Chiralpak AD-H column with hexane/2-propanol = 90:10,

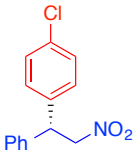
flow = 0.5 ml/min by HPLC analysis. Retention times: 25.0 min [*(S)*-enantiomer], 26.5 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[33]

_(R)_-1-Fluoro-4-(2-nitro-1-phenylethyl)benzene (10ag)



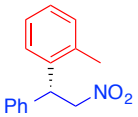
Following the above general procedure with nitrostyrene (44.8 mg, 0.3 mmol, 1 equiv) and 4-fluorophenylboronic acid (74.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (toluene / hexane, 2:1) to provide **10ag** (61.9 mg, 84%) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.32 (t, *J* = 7.6 Hz, 2H), 7.26-7.24 (m, 1H), 7.20-7.18 (m, 4H), 7.02-6.98 (m, 2H), 4.95-4.93 (m, 2H), 4.91-4.86 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 162.0 (d, *J* = 247.1 Hz), 138.9, 134.9 (d, *J* = 2.9 Hz), 129.3 (d, *J* = 8.7 Hz), 129.1, 127.7, 127.5, 115.9 (d, *J* = 20.2 Hz), 79.2, 48.2. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 60:40, flow = 1.0 ml/min by HPLC analysis. Retention times: 11.0 min [*(S)*-enantiomer], 18.8 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[34]

_(R)_-1-Chloro-4-(2-nitro-1-phenylethyl)benzene (10aj)



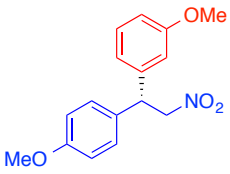
Following the above general procedure with nitrostyrene (44.8 mg, 0.3 mmol, 1 equiv) and 4-chlorophenylboronic acid (86.9 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (toluene / hexane, 2:1) to provide **10aj** (80.4 mg, quant.) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.27-7.17 (m, 5H), 7.13-7.09 (m, 4H), 4.88 (d, *J* = 8.2 Hz, 2H), 4.81 (t, *J* = 8.2 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 138.7, 137.7, 133.5, 129.2, 129.1, 129.0, 127.8, 127.5, 79.0, 48.3. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 60:40, flow = 1.0 ml/min by HPLC analysis. Retention times: 14.9 min [*(S)*-enantiomer], 22.7 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[34]

_(R)_-1-Methyl-2-(2-nitro-1-phenylethyl)benzene (10ak)



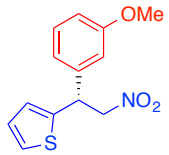
Following the above general procedure with 1-methoxy-4-(2-nitroethenyl)benzene (53.8 mg, 0.3 mmol, 1 equiv) and 3-methoxyphenylboronic acid (81.8 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 20:1) to provide **5mc** (75.6 mg, 88%) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.31 (t, *J* = 7.9 Hz, 2H), 7.26-7.18 (m, 7H), 5.12 (t, *J* = 7.9 Hz, 1H), 4.98-4.93 (m, 2H), 2.32 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 138.7, 137.1, 136.5, 131.3, 128.9, 128.0, 127.5, 126.4, 125.8, 79.2, 45.0, 19.6. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 60:40, flow = 1.0 ml/min by HPLC analysis. Retention times: 18.6 min [*(S)*-enantiomer], 29.0 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[35]

***(S)*-1-Methoxy-3-(1-(4-methoxyphenyl)-2-nitroethyl)benzene (10bc)**



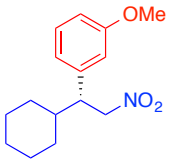
Following the above general procedure with 1-methoxy-4-(2-nitroethenyl)benzene (53.8 mg, 0.3 mmol, 1 equiv) and 3-methoxyphenylboronic acid (82.9 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 20:1) to provide **10bc** (80.5 mg, 93%) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.24-7.21 (m, 1H), 7.14 (d, *J* = 8.9 Hz, 2H), 6.84-6.73 (m, 5H), 4.94-4.88 (m, 2H), 4.80 (t, *J* = 8.2 Hz, 1H), 3.76 (s, 6H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 159.9, 158.9, 141.1, 131.0, 130.0, 128.7, 119.7, 114.3, 113.9, 112.4, 79.4, 55.23, 55.18, 48.2. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 50:50, flow = 1.0 ml/min by HPLC analysis. Retention times: 19.8 min [*(S)*-enantiomer], 37.3 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[34]

***(R)*-2-(1-(3-Methoxyphenyl)-2-nitroethyl)thiophene (10cc)**



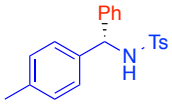
Following the above general procedure with 2-(2-thienyl)nitrostyrene (46.6 mg, 0.3 mmol, 1 equiv) and 3-methoxyphenylboronic acid (124.4 mg, 0.9 mmol, 3 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 20:1) to provide **10cc** (77.5 mg, 98%) as a yellowish oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.27-7.24 (m, 1H), 7.21 (d, *J* = 5.5 Hz, 1H), 6.93 (t, *J* = 4.5 Hz, 1H), 6.90 (d, *J* = 2.7 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.82-6.81 (m, 2H), 5.09 (t, *J* = 7.9 Hz, 1H), 4.96-4.90 (m, 2H), 3.77 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 160.0, 142.2, 140.2, 130.1, 127.0, 125.2, 125.1, 119.6, 113.7, 113.1, 79.8, 55.2, 44.6. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 60:40, flow = 1.0 ml/min by HPLC analysis. Retention times: 13.3 min [*(R)*-enantiomer], 36.3 min [*(S)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[17]

***(R)*-1-(1-Cyclohexyl-2-nitroethyl)-3-methoxybenzene (10dc)**



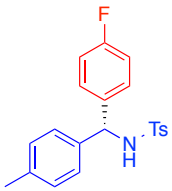
Following the above general procedure with 1-methoxy-4-(2-nitroethenyl)benzene (53.8 mg, 0.3 mmol, 1 equiv) and 3-methoxyphenylboronic acid (81.8 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 20:1) to provide **10dc** (75.6 mg, 88%) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.21 (t, *J* = 7.9 Hz, 1H), 6.76 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.71 (d, *J* = 6.2 Hz, 1H), 6.65 (s, 1H), 4.76-4.72 (m, 1H), 4.60-4.55 (m, 1H), 3.77 (s, 3H), 3.23-3.19 (m, 1H), 1.76 (t, *J* = 15.5 Hz, 2H), 1.65-1.53 (m, 3H), 1.46 (d, *J* = 12.4 Hz, 1H), 1.23-1.19 (m, 1H), 1.13-0.98 (m, 3H), 0.89-0.82 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 159.6, 140.4, 129.5, 120.4, 114.5, 112.1, 78.8, 55.2, 50.2, 40.9, 30.9, 30.6, 26.13, 26.07. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 60:40, flow = 1.0 ml/min by HPLC analysis. Retention times: 5.7 min [*(R)*-enantiomer], 9.6 min [*(S)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[17]

***(S)*-4-Methyl-*N*-(phenyl(*p*-tolyl)methyl)benzenesulfonamide (11aa)**



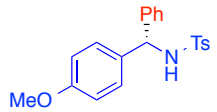
Following the above general procedure with *N*-(4-methylbenzylidene)-4-methylbenzenesulfonamide (82.4 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (63.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 3:1) to provide **11aa** (40.7 mg, 50%) as a white solid (Mp. 120-122 ^{o}C). **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.49 (d, *J* = 6.9 Hz, 2H), 7.13-7.12 (m, 3H), 7.07-7.03 (m, 4H), 6.95-6.89 (m, 4H), 5.45 (d, *J* = 6.9 Hz, 1H), 4.98 (d, *J* = 6.2 Hz, 1H), 2.31 (s, 3H), 2.21 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 143.1, 140.7, 137.6, 137.3, 137.2, 129.3, 129.2, 128.4, 127.4, 127.3, 127.23, 127.16, 61.1, 21.4, 21.0. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 95:5, flow = 1.0 ml/min by HPLC analysis. Retention times: 15.9 min [*(S)*-enantiomer], 24.2 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[36] (No Rh leaching (UDL), No Ag leaching (UDL) (Rh DL: 04910%, Ag DL: 0.1380%))

***(R)*-*N*-((4-Fluorophenyl)(p-tolyl)methyl)-4-methylbenzenesulfonamide (11ag)**



Following the above general procedure with *N*-(4-methylbenzylidene)-4-methylbenzenesulfonamide (82.4 mg, 0.3 mmol, 1 equiv) and 4-fluorophenylboronic acid (74.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 3:1) to provide **11ag** (59.1 mg, 53%) as a white solid (Mp. 117-118 ^{o}C). **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.53 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.08-7.06 (m, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 2H), 6.86 (t, *J* = 8.9 Hz, 2H), 5.48 (d, *J* = 6.9 Hz, 1H), 5.22 (d, *J* = 6.9 Hz, 1H), 2.37 (s, 3H), 2.26 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 162.0 (d, *J* = 245.6 Hz), 143.3, 137.5, 137.4, 137.2, 136.5 (d, *J* = 2.9 Hz), 129.33, 129.29, 129.0 (d, *J* = 8.7 Hz), 127.15, 127.13, 115.2 (d, *J* = 21.7 Hz), 60.4, 21.4, 21.0. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 95:5, flow = 1.0 ml/min by HPLC analysis. Retention times: 20.6 min [*(R)*-enantiomer], 27.5 min [*(S)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[37]

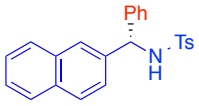
***(S)*-*N*-((4-Methoxyphenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (11ba)**



Following the above general procedure with *N*-(4-methoxybenzylidene)-4-methylbenzenesulfonamide (82.4 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (63.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 3:1) to provide **11ba** (40.7 mg, 50%) as a white solid (Mp. 131-133 ^{o}C). **^{1}H NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.47 (d, *J* = 8.2 Hz, 2H), 7.13-7.09 (m, 3H), 7.06-7.01 (m, 4H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 8.2 Hz, 2H), 5.44 (d, *J* = 6.9 Hz, 1H), 5.23 (d, *J* = 6.9 Hz, 1H), 3.66 (s, 3H), 2.29 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$):** δ (ppm) 158.9, 143.0, 140.7, 137.4, 132.7, 129.3, 128.6, 128.4, 127.4, 127.2, 127.1, 113.8, 60.8, 55.2, 21.4. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 95:5, flow = 1.0 ml/min by HPLC analysis. Retention times: 26.2 min [*(S)*-enantiomer],

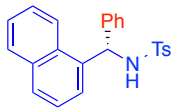
41.8 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[38]

_(S)_-4-Methyl-_N_-(naphthalen-2-yl(phenyl)methyl)benzenesulfonamide (11ca)



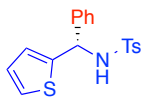
Following the above general procedure with *N*-(4-methylbenzylidene)-4-methylbenzenesulfonamide (82.4 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (63.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 3:1) to provide **11ca** (40.7 mg, 50%) as a white solid (Mp. 130-131 ^{o}C). **^{1}H NMR (600 MHz, CDCl$_3$):** δ (ppm) 7.75-7.72 (m, 1H), 7.57 (d, *J* = 8.9 Hz, 1H), 7.63-7.60 (m, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.42 (s, 1H), 7.42 (q, *J* = 3.4 Hz, 2H), 7.22-7.18 (m, 3H), 7.18-7.12 (m, 3H), 6.93 (d, *J* = 8.2 Hz, 2H), 5.65 (d, *J* = 7.6 Hz, 1H), 5.36 (d, *J* = 7.6 Hz, 1H), 2.17 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$):** δ (ppm) 143.2, 140.4, 137.5, 137.3, 133.0, 132.6, 129.3, 128.6, 128.5, 127.9, 127.7, 127.5, 127.4, 127.2, 126.3, 126.2, 126.1, 125.1, 61.4, 21.3. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 95:5, flow = 1.0 ml/min by HPLC analysis. Retention times: 33.9 min [*(R)*-enantiomer], 39.4 min [*(S)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[37]

_(S)_-4-Methyl-_N_-(naphthalen-1-yl(phenyl)methyl)benzenesulfonamide (11da)



Following the above general procedure with *N*-(4-methylbenzylidene)-4-methylbenzenesulfonamide (82.4 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (63.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 3:1) to provide **11da** (40.7 mg, 50%) as a white solid (Mp. 145-147 ^{o}C). **^{1}H NMR (600 MHz, CDCl$_3$):** δ (ppm) 7.79 (t, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.19-7.11 (m, 5H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.29 (d, *J* = 7.6 Hz, 1H), 5.16 (d, *J* = 6.9 Hz, 1H), 2.33 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$):** δ (ppm) 143.1, 140.2, 137.2, 135.4, 133.9, 130.4, 129.2, 128.8, 128.6, 127.6, 127.5, 127.1, 126.5, 126.1, 125.7, 125.0, 123.4, 58.5, 21.4. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 90:10, flow = 1.0 ml/min by HPLC analysis. Retention times: 19.3 min [*(R)*-enantiomer], 24.4 min [*(S)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[38]

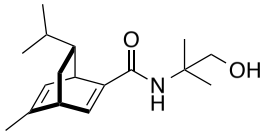
_(S)_-4-Methyl-_N_-(phenyl(thiophen-2-yl)methyl)benzenesulfonamide (11ea)



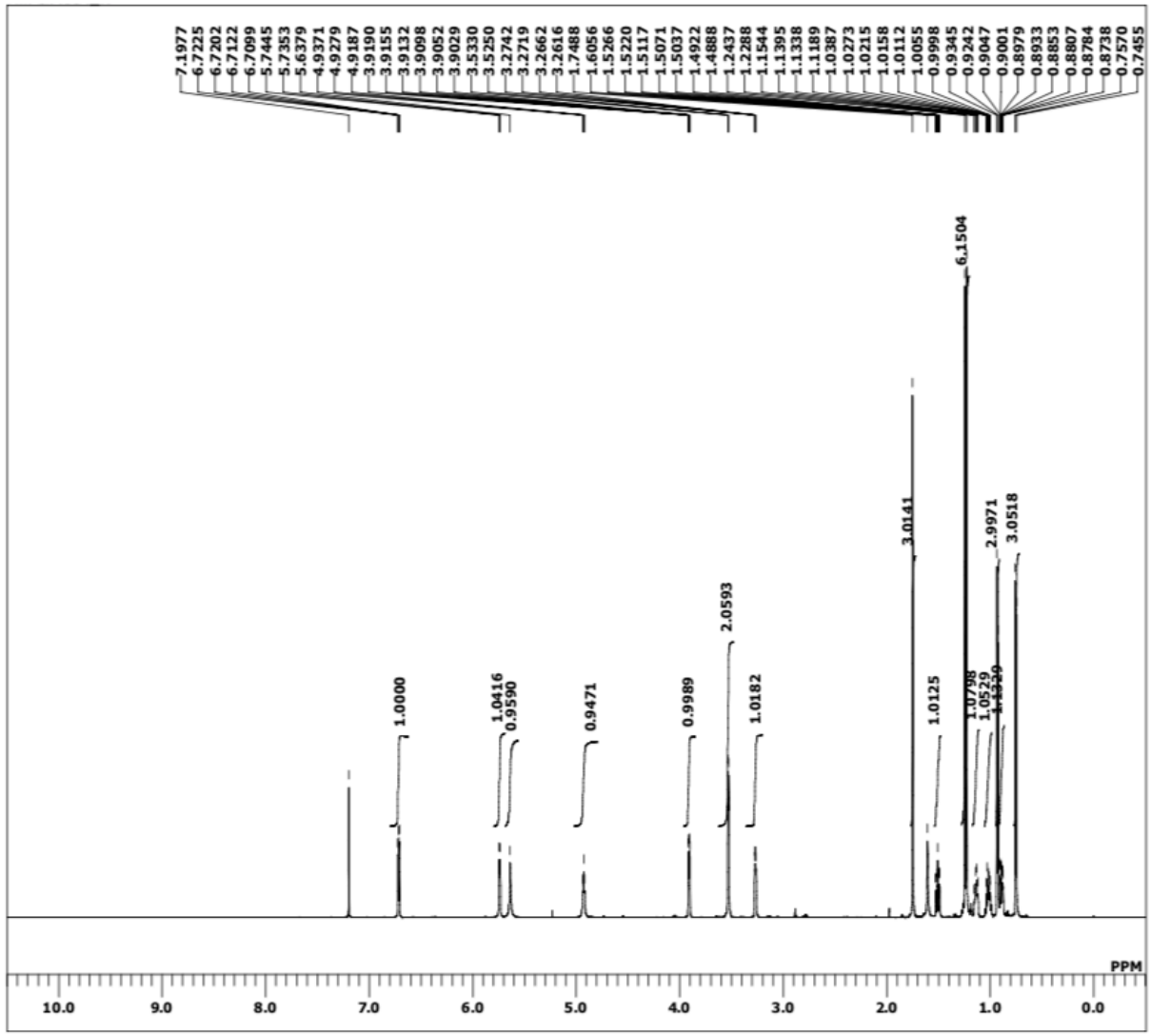
Following the above general procedure with *N*-(4-methylbenzylidene)-4-methylbenzenesulfonamide (82.4 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (63.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 3:1) to provide **11ea** (40.7 mg, 50%) as a white solid (Mp. 141-143 ^{o}C). **^{1}H NMR (600 MHz, CDCl$_3$):** δ (ppm) 7.56 (d, *J* = 8.2 Hz, 2H), 7.21 (t, *J* = 3.1 Hz, 3H), 7.18-7.12 (m, 5H), 6.83-6.80 (m, 1H), 6.67-6.64 (m, 1H), 5.77 (d, *J* = 6.9 Hz, 1H), 5.11 (d, *J* = 7.6 Hz, 1H), 2.36 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$):** δ (ppm) 144.8, 143.2, 140.1, 137.2, 129.3, 128.5, 127.9, 127.1, 126.7, 126.1, 125.7, 57.4, 21.5. The ee value of

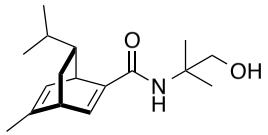
product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 95:5, flow = 1.0 ml/min by HPLC analysis. Retention times: 20.0 min [*(S)*-enantiomer], 28.4 min [*(R)*-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.[36]

8. NMR & HPLC Charts

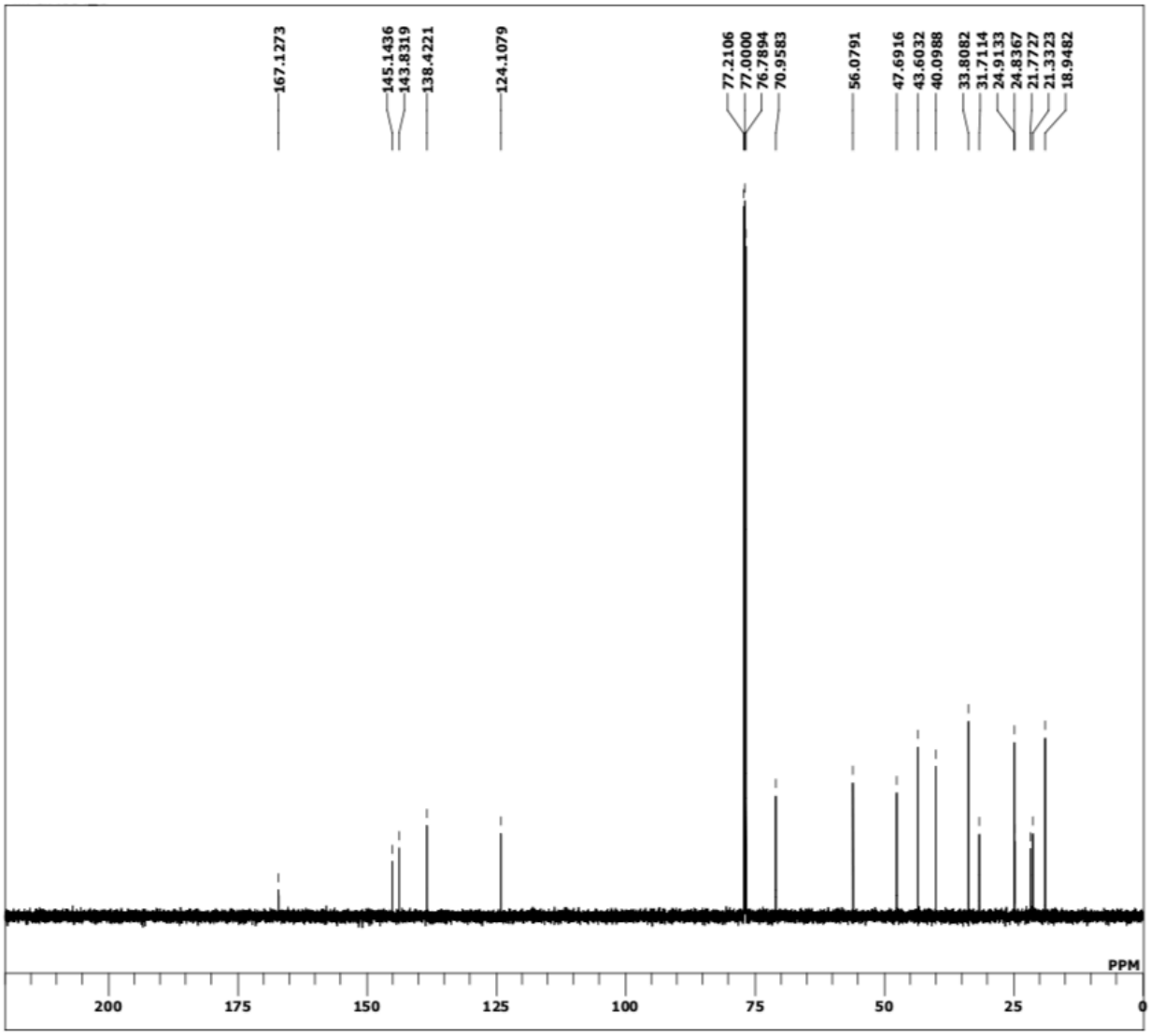


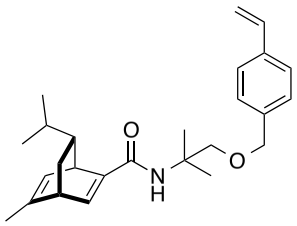
S1



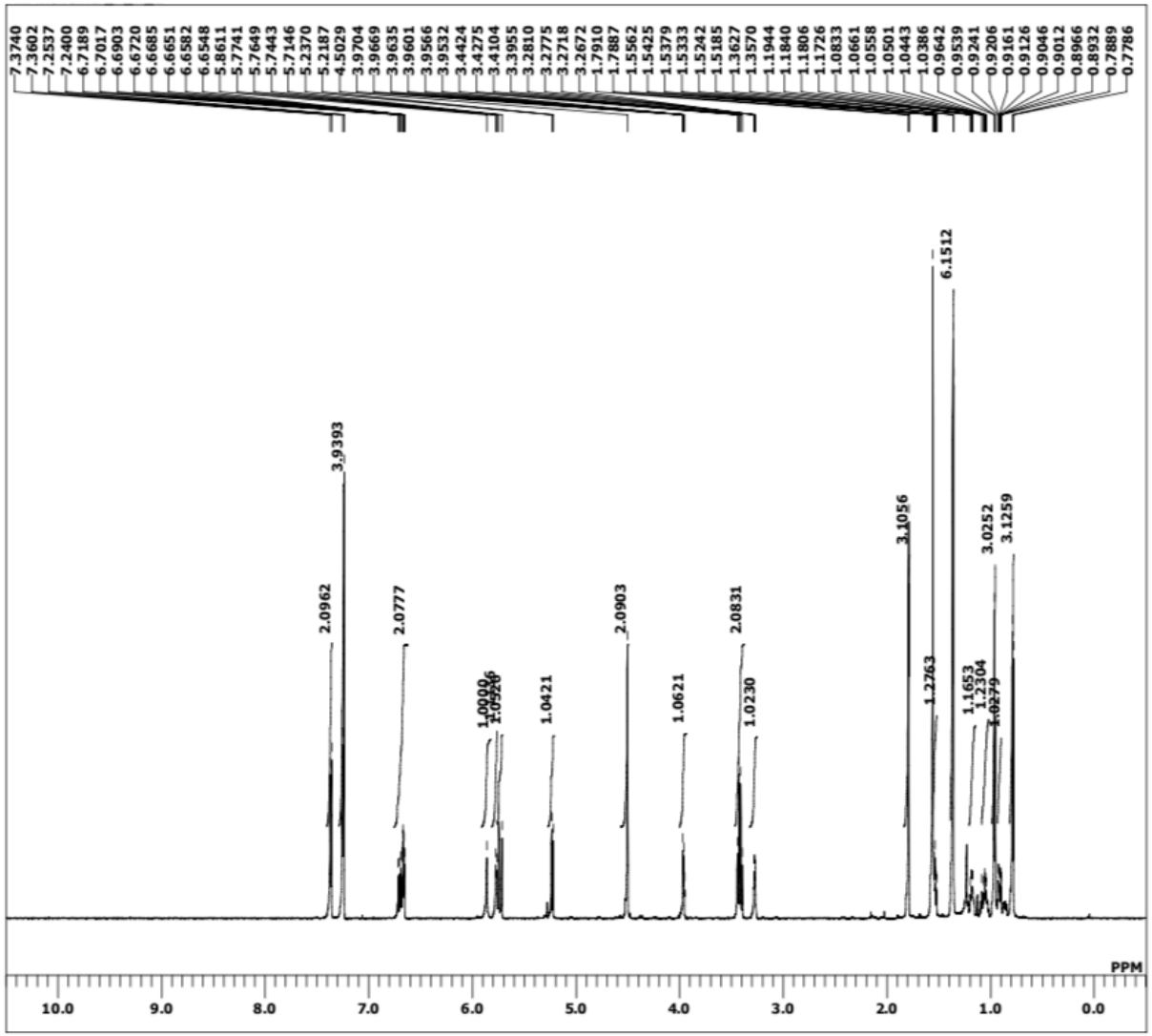

O
N
H
OH

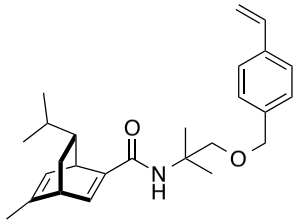
S1


167.1273
145.1436
143.8319
138.4221
124.1079
77.2106
77.0000
76.7894
70.9583
56.0791
47.6916
43.6032
40.0988
33.8082
31.7114
24.9133
24.8367
21.7727
21.3323
18.9482
PPM
200
175
150
125
100
75
50
25
0

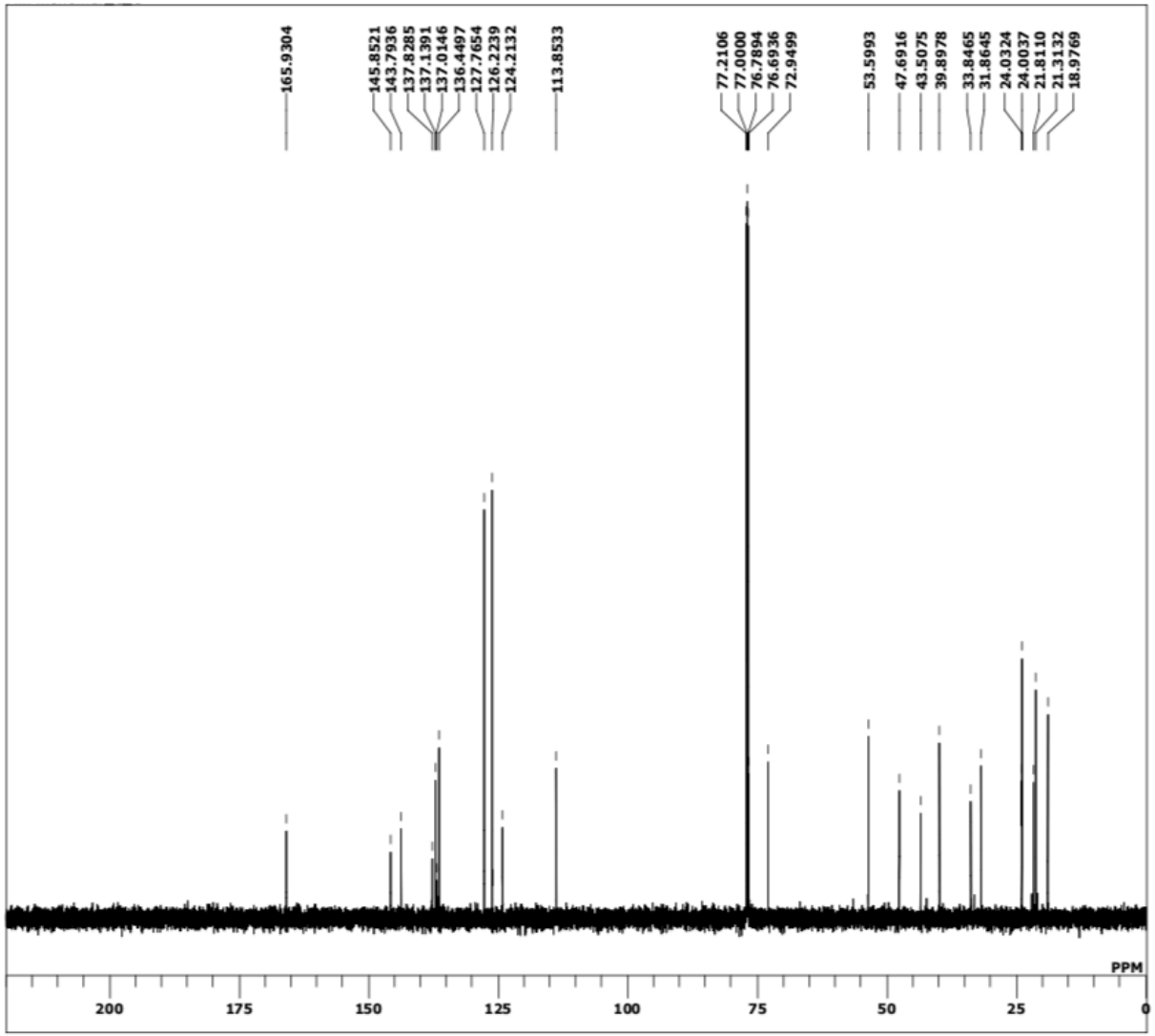

O
N
H
O

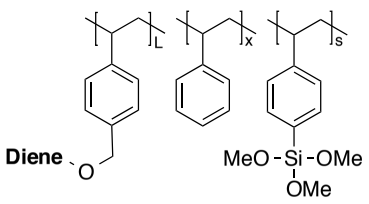
S2


7.3740
7.3602
7.2537
7.2400
6.7189
6.7017
6.6903
6.6720
6.6685
6.6651
6.6582
6.6548
5.8611
5.7741
5.7649
5.7443
5.7146
5.2370
5.2187
4.5029
3.9704
3.9669
3.9635
3.9601
3.9566
3.9532
3.4424
3.4275
3.4104
3.3955
3.2810
3.2775
3.2718
3.2672
1.7910
1.7887
1.5562
1.5425
1.5379
1.5333
1.5242
1.5185
1.3627
1.3570
1.1944
1.1840
1.1806
1.1726
1.0833
1.0661
1.0558
1.0501
1.0443
1.0386
0.9642
0.9539
0.9241
0.9206
0.9161
0.9126
0.9046
0.9012
0.8966
0.8932
0.7889
0.7786
2.0962
3.9393
2.0777
1.0421
2.0903
1.0621
2.0831
1.0230
3.1056
6.1512
1.2763
1.1653
1.2304
3.0252
3.1259
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

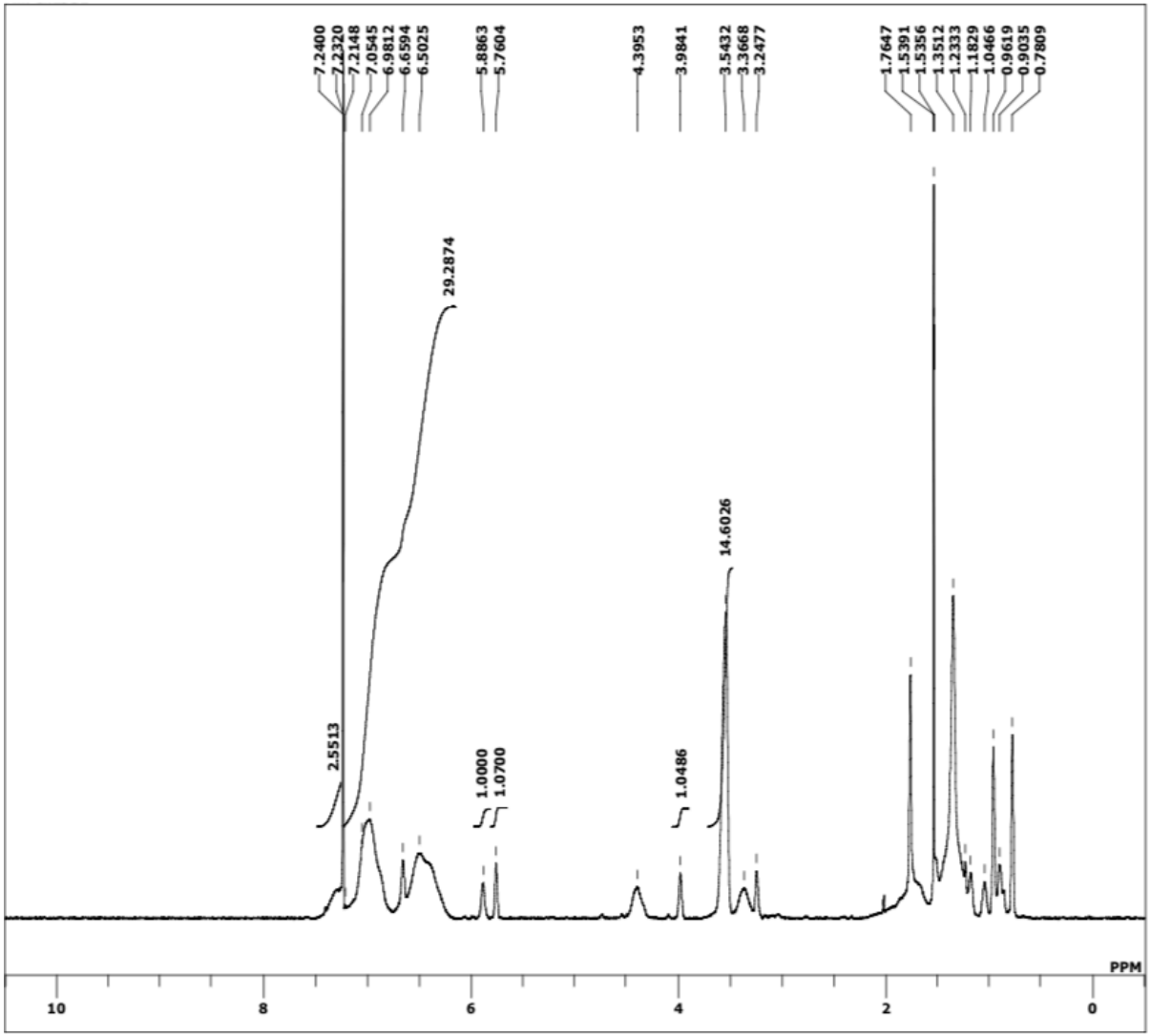

O
N
H
O

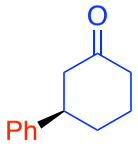
S2


165.9304
145.8521
143.7936
137.8285
137.1391
137.0146
136.4497
127.7654
126.2239
124.2132
113.8533
77.2106
77.0000
76.7894
76.6936
72.9499
53.5993
47.6916
43.5075
39.8978
33.8465
31.8645
24.0324
24.0037
21.8110
21.3132
18.9769
PPM
200
175
150
125
100
75
50
25
0

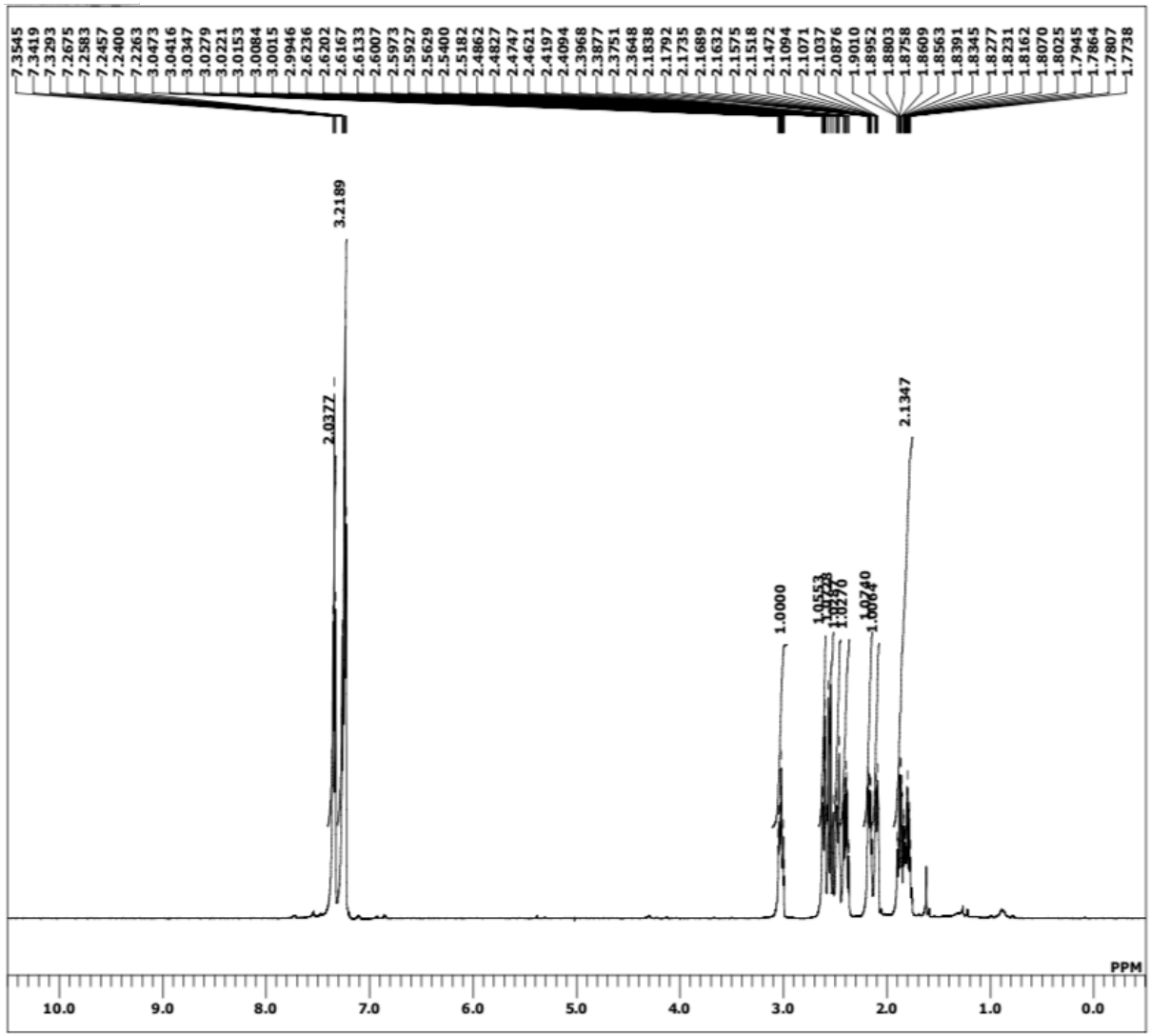


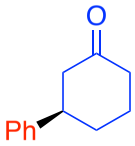
Copolymer 1
(L : x : s ≈ 1 : 3 : 1)



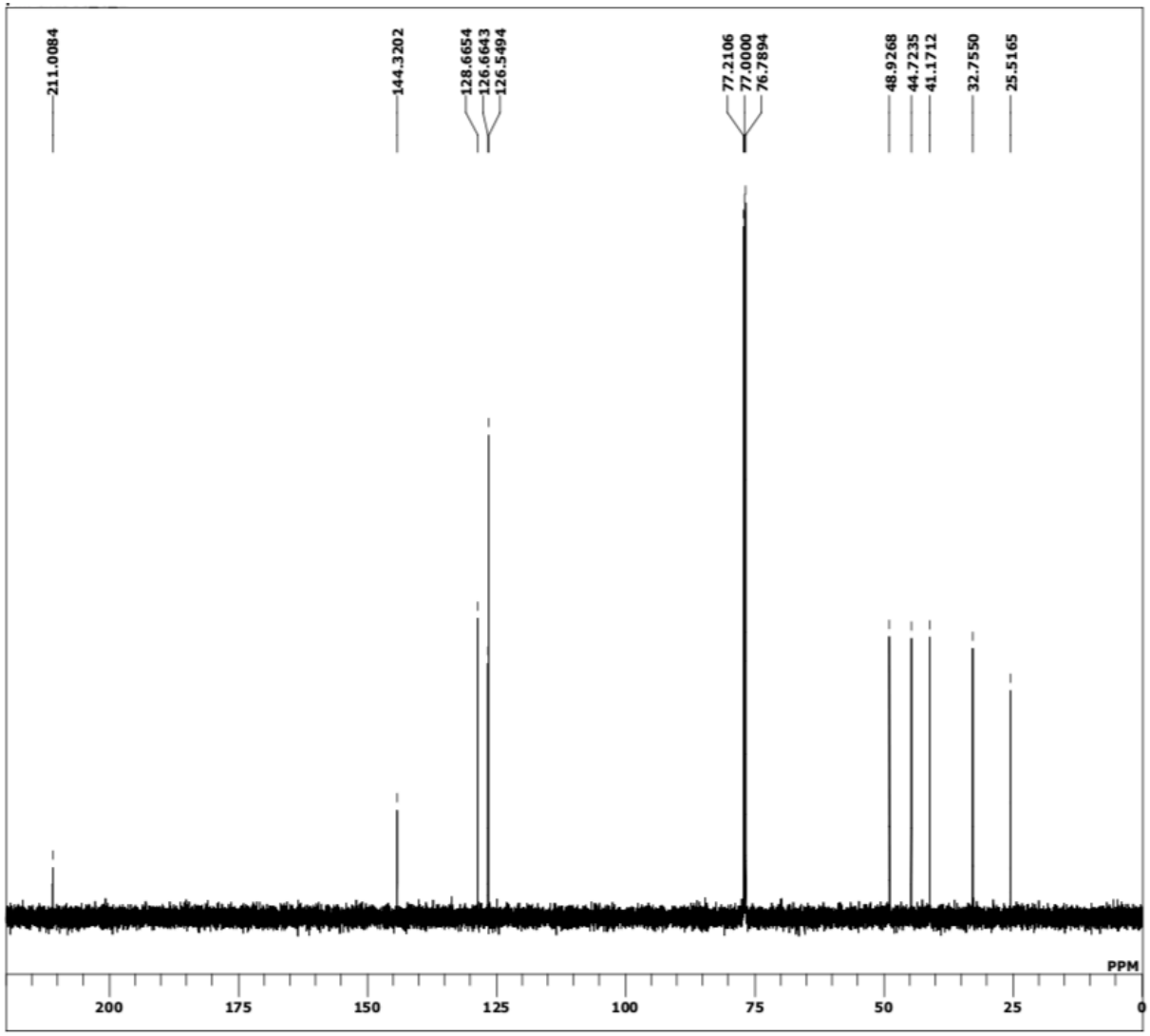

O
Ph

5aa

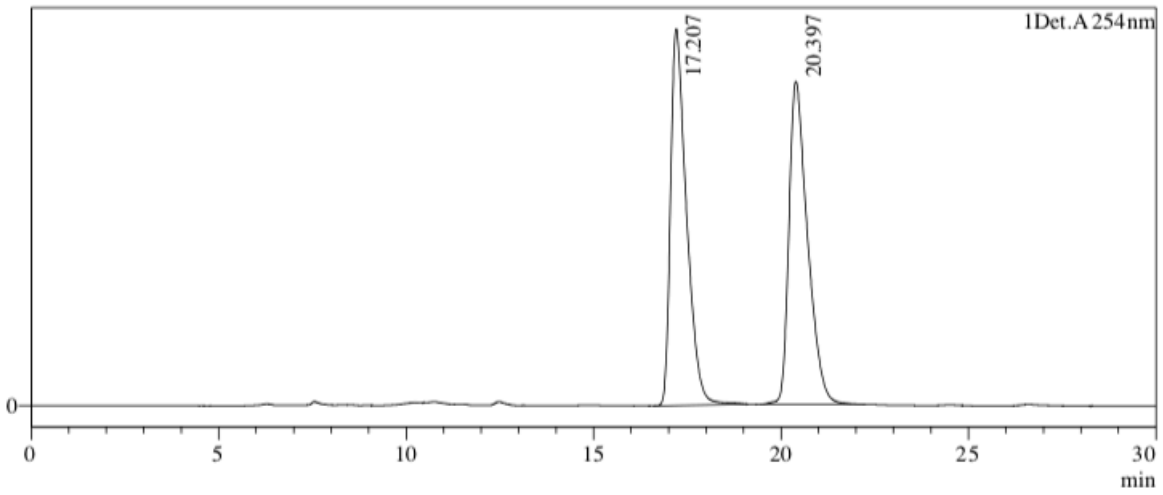

7.3545
7.3419
7.3293
7.2675
7.2583
7.2457
7.2400
7.2263
3.0473
3.0416
3.0347
3.0279
3.0221
3.0153
3.0084
3.0015
2.9946
2.6236
2.6202
2.6167
2.6133
2.6007
2.5973
2.5927
2.5629
2.5400
2.5182
2.4862
2.4827
2.4747
2.4621
2.4197
2.4094
2.3968
2.3877
2.3751
2.3648
2.1838
2.1792
2.1735
2.1689
2.1632
2.1575
2.1518
2.1472
2.1094
2.1071
2.1037
2.0876
1.9010
1.8952
1.8803
1.8758
1.8609
1.8563
1.8391
1.8345
1.8277
1.8231
1.8162
1.8070
1.8025
1.7945
1.7864
1.7807
1.7738
3.2189
2.0372
1.0000
2.1347
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


O
Ph

5aa

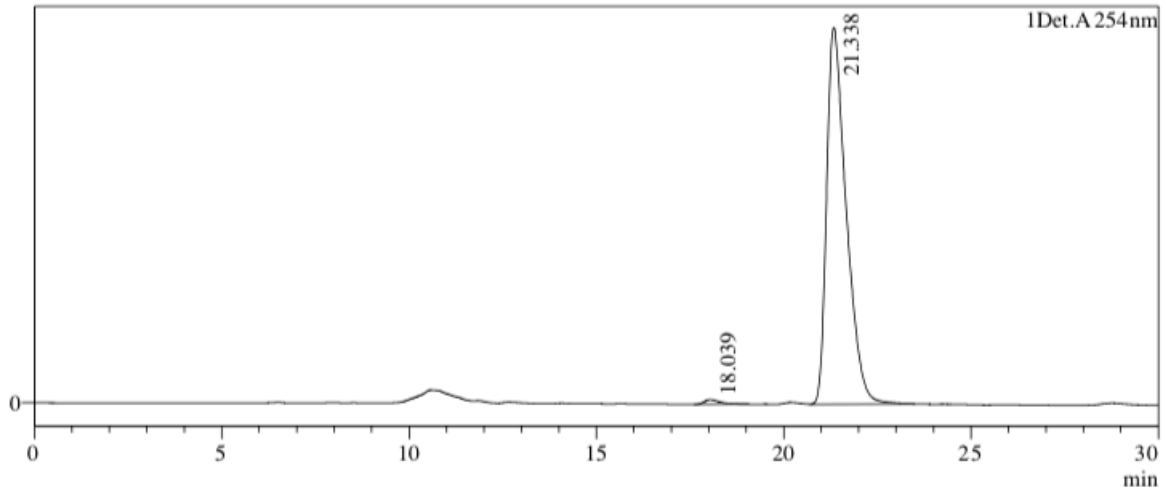

211.0084
144.3202
128.6654
126.6643
126.5494
77.2106
77.0000
76.7894
48.9268
44.7235
41.1712
32.7550
25.5165
PPM
200
175
150
125
100
75
50
25
0

5aa, condition : AD, 0.5 ml/min, Hex/IPA = 98:2, 254 nm



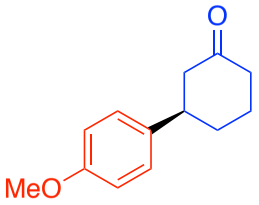
Det.A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	17.207	816831	27599	49.924
2	20.397	819326	23681	50.076

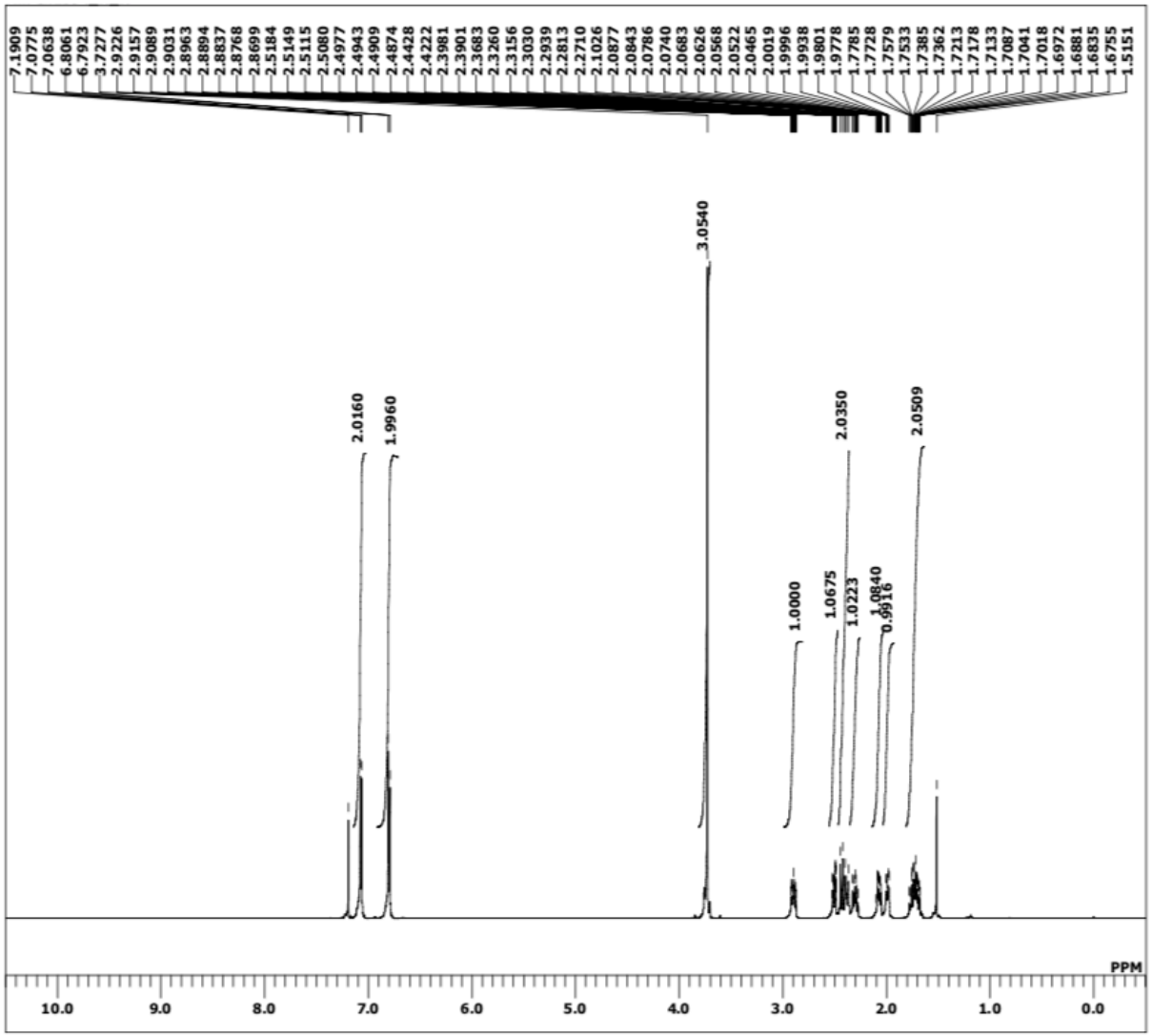


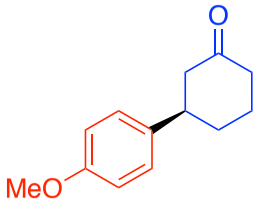
Det.A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	18.039	15312	506	1.020
2	21.338	1485433	40888	98.980

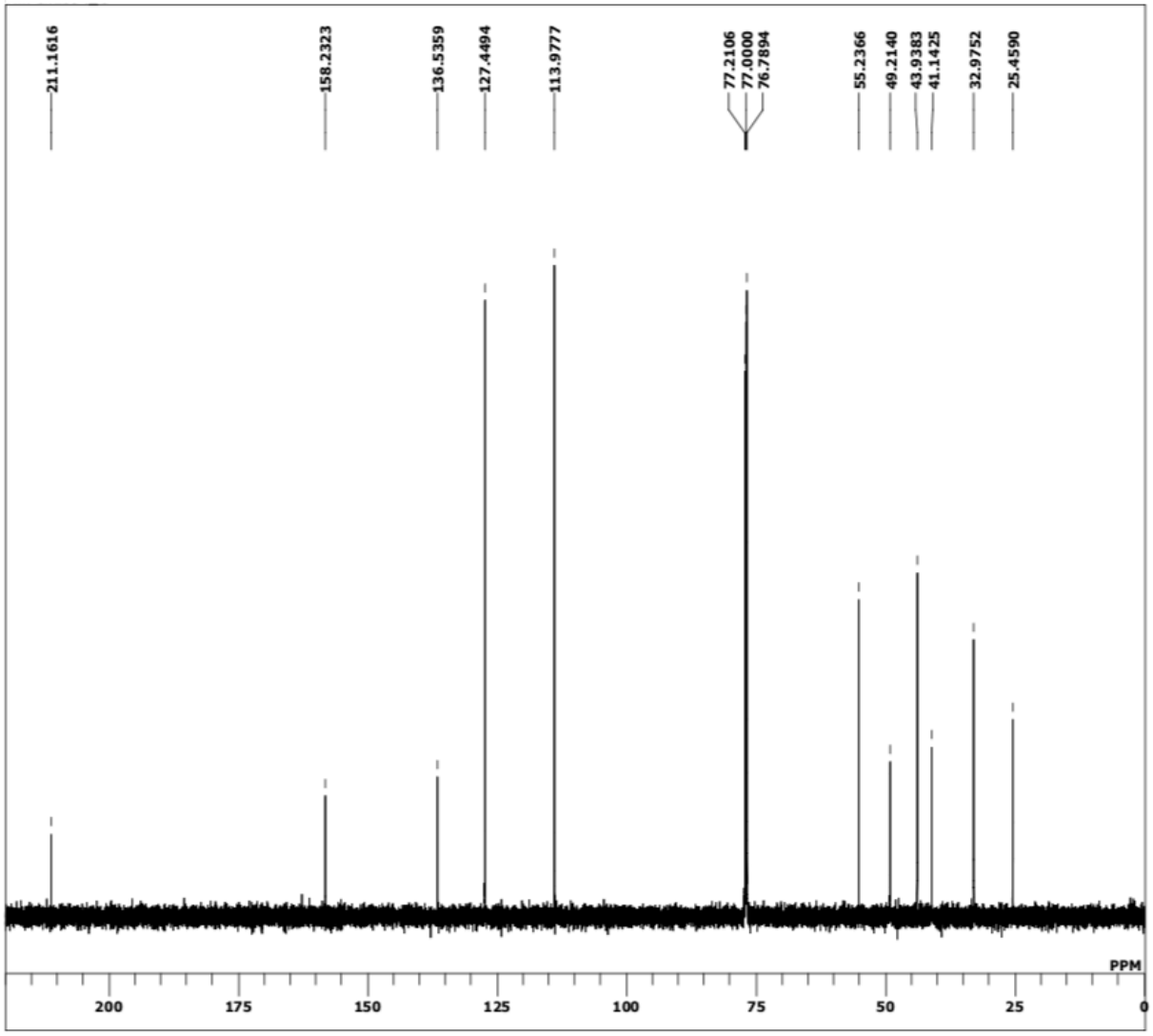

O
MeO

5ab

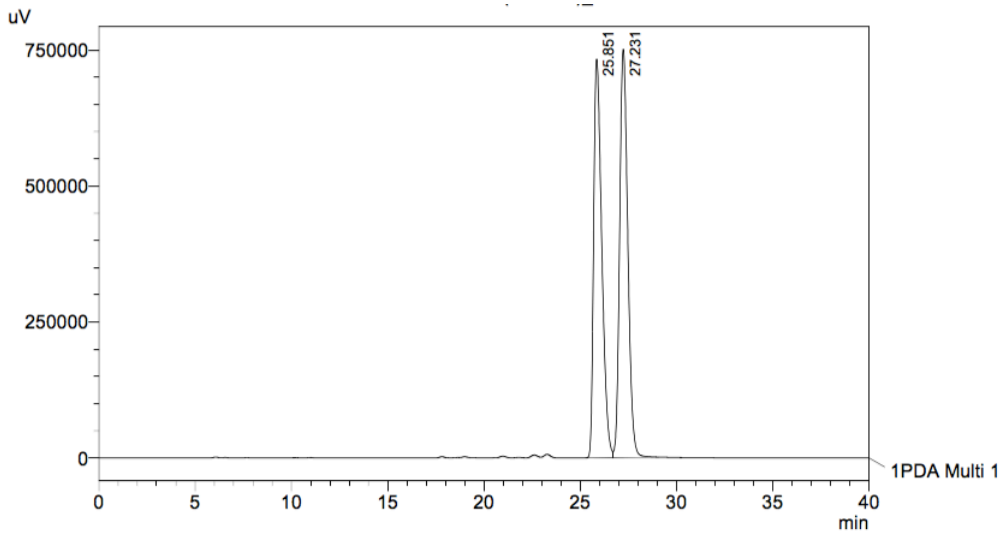

7.1909
7.0775
7.0638
6.8061
6.7923
3.7277
2.9226
2.9157
2.9089
2.9031
2.8963
2.8894
2.8837
2.8768
2.8699
2.5184
2.5149
2.5115
2.5080
2.4977
2.4943
2.4909
2.4874
2.4428
2.4222
2.3981
2.3901
2.3683
2.3260
2.3156
2.3030
2.2939
2.2813
2.2710
2.1026
2.0877
2.0843
2.0786
2.0740
2.0683
2.0626
2.0568
2.0522
2.0465
2.0019
1.9996
1.9938
1.9801
1.9778
1.7785
1.7728
1.7579
1.7533
1.7385
1.7362
1.7213
1.7178
1.7133
1.7087
1.7041
1.7018
1.6972
1.6881
1.6835
1.6755
1.5151
3.0540
2.0160
1.9960
2.0350
2.0509
1.0000
1.0675
1.0223
1.0840
0.9916
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


O
MeO

5ab


211.1616
158.2323
136.5359
127.4494
113.9777
77.2106
77.0000
76.7894
55.2366
49.2140
43.9383
41.1425
32.9752
25.4590
PPM
200
175
150
125
100
75
50
25
0

5ab, condition : AD-H, 0.5 ml/min, Hex/IPA = 98:2, 220 nm

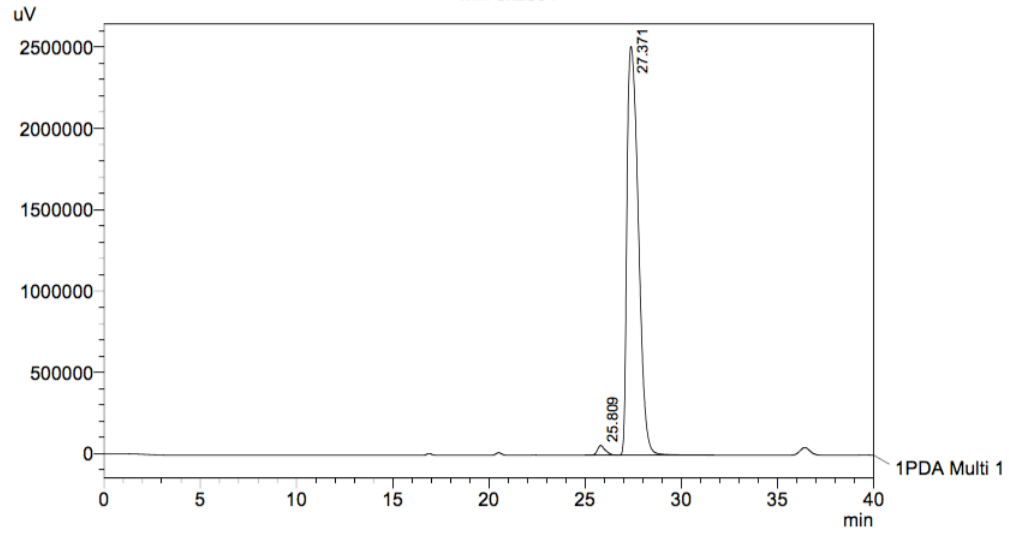


1 PDA Multi 1 / 220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.851	21497959	732929	49.287	49.399
2	27.231	22119982	750760	50.713	50.601
Total		43617942	1483689	100.000	100.000

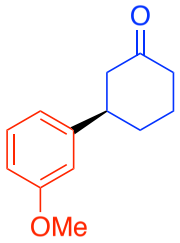


1 PDA Multi 1 / 220nm 4nm

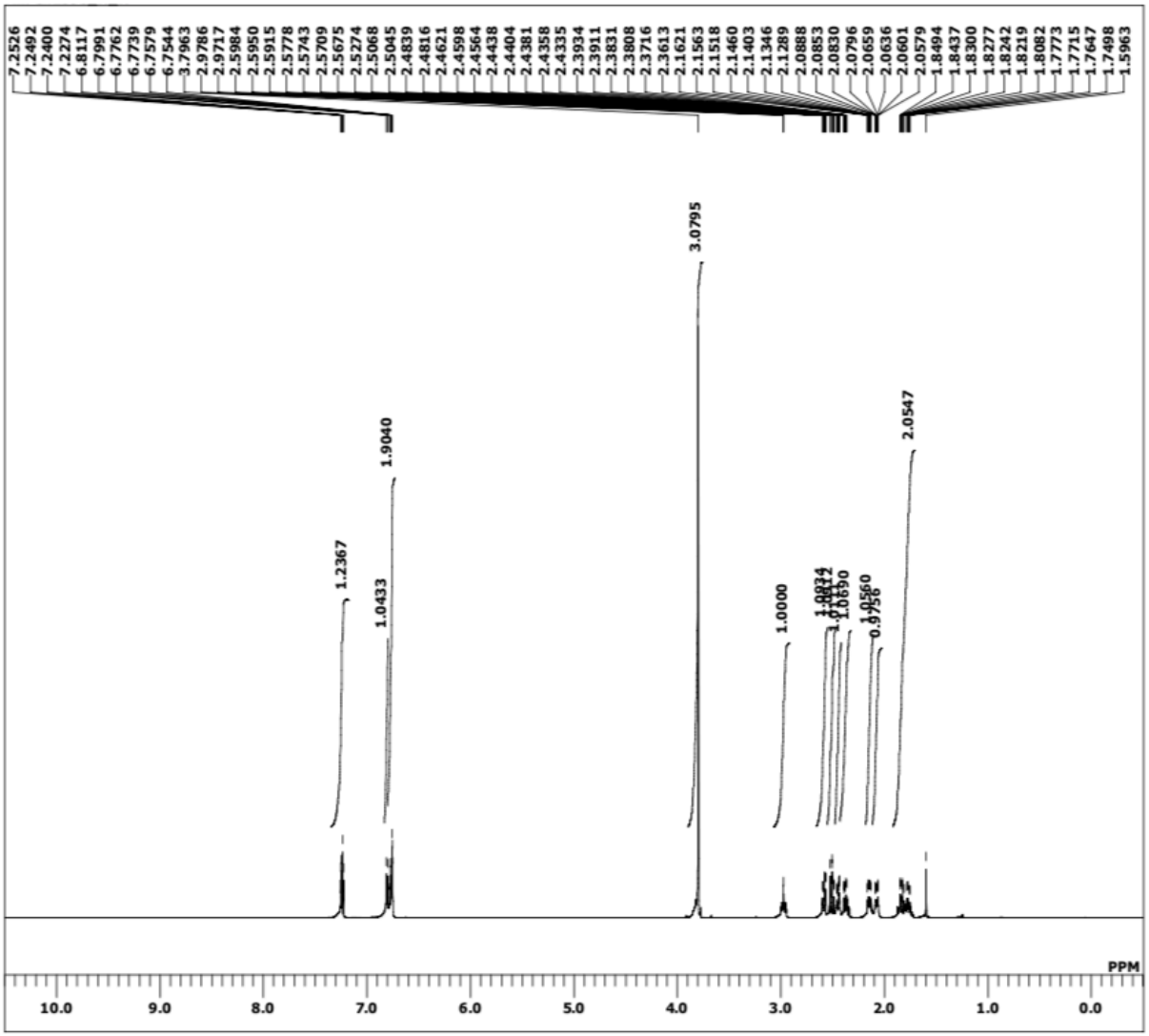
PeakTable

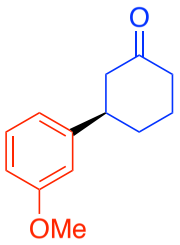
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.809	1746779	60252	1.655	2.344
2	27.371	103780374	2509914	98.345	97.656
Total		105527153	2570166	100.000	100.000

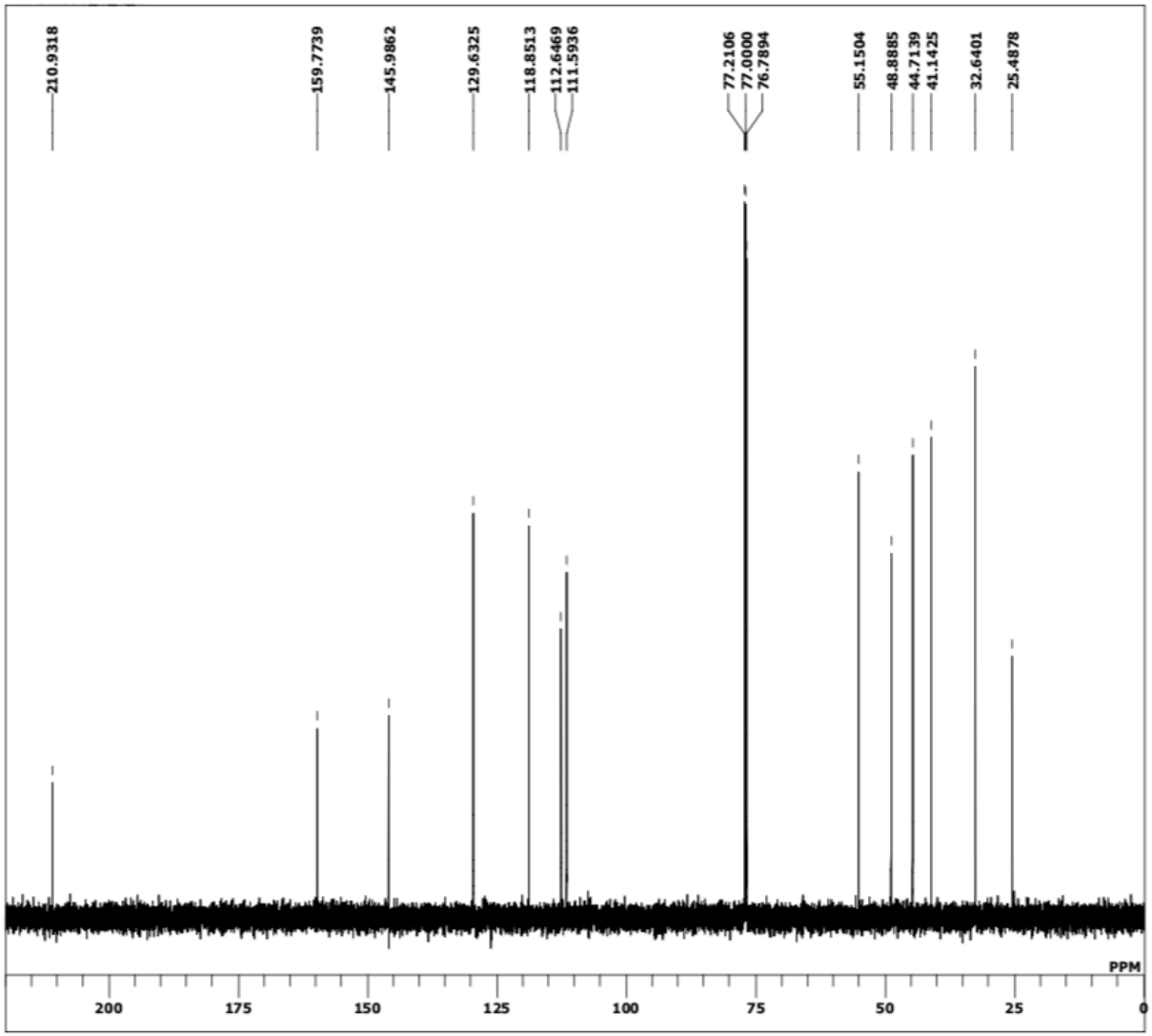

O
OMe

5ac

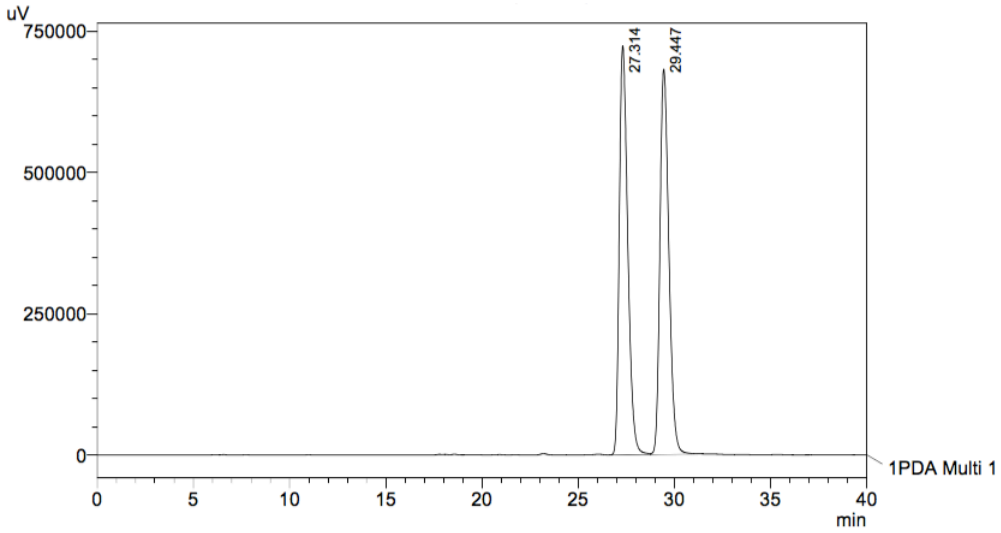

7.2526
7.2492
7.2400
7.2274
6.8117
6.7991
6.7762
6.7739
6.7579
6.7544
3.7963
2.9786
2.9717
2.5984
2.5950
2.5915
2.5778
2.5743
2.5709
2.5675
2.5274
2.5068
2.5045
2.4839
2.4816
2.4621
2.4598
2.4564
2.4438
2.4404
2.4381
2.4358
2.4335
2.3934
2.3911
2.3831
2.3808
2.3716
2.3613
2.1621
2.1563
2.1518
2.1460
2.1403
2.1346
2.1289
2.0888
2.0853
2.0830
2.0796
2.0659
2.0636
2.0601
2.0579
1.8494
1.8437
1.8300
1.8277
1.8242
1.8219
1.8082
1.7773
1.7715
1.7647
1.7498
1.5963
1.2367
1.0433
1.9040
3.0795
1.0000
1.0690
1.0560
2.0547
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


O
OMe

5ac


210.9318
159.7739
145.9862
129.6325
118.8513
112.6469
111.5936
77.2106
77.0000
76.7894
55.1504
48.8885
44.7139
41.1425
32.6401
25.4878
PPM
200
175
150
125
100
75
50
25
0

5ac, condition : AD-H, 0.5 ml/min, Hex/IPA = 98:2, 220 nm

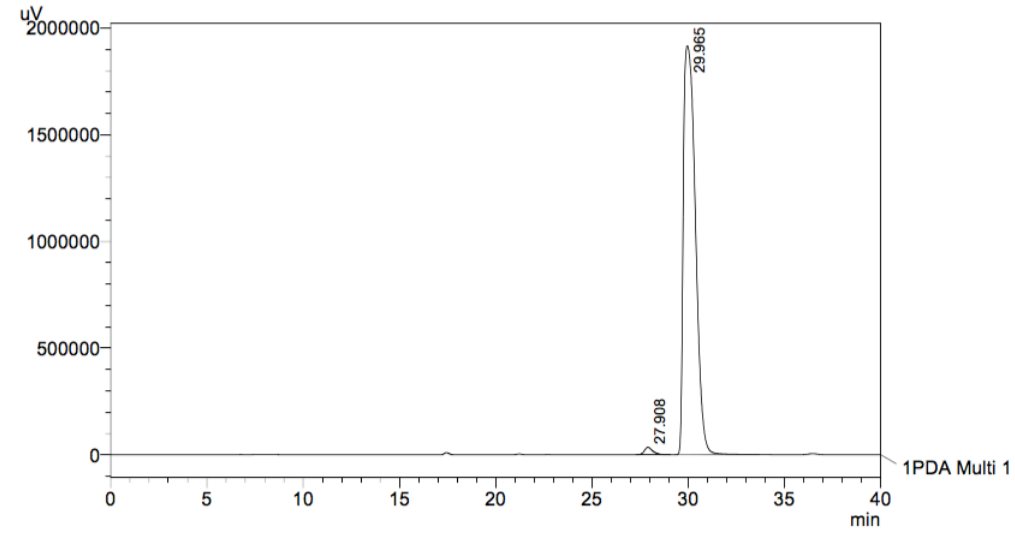


1 PDA Multi 1 / 220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.314	22127731	723496	50.079	51.490
2	29.447	22057501	681615	49.921	48.510
Total		44185232	1405111	100.000	100.000

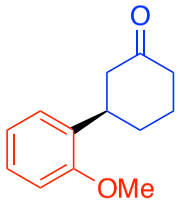


1 PDA Multi 1 / 220nm 4nm

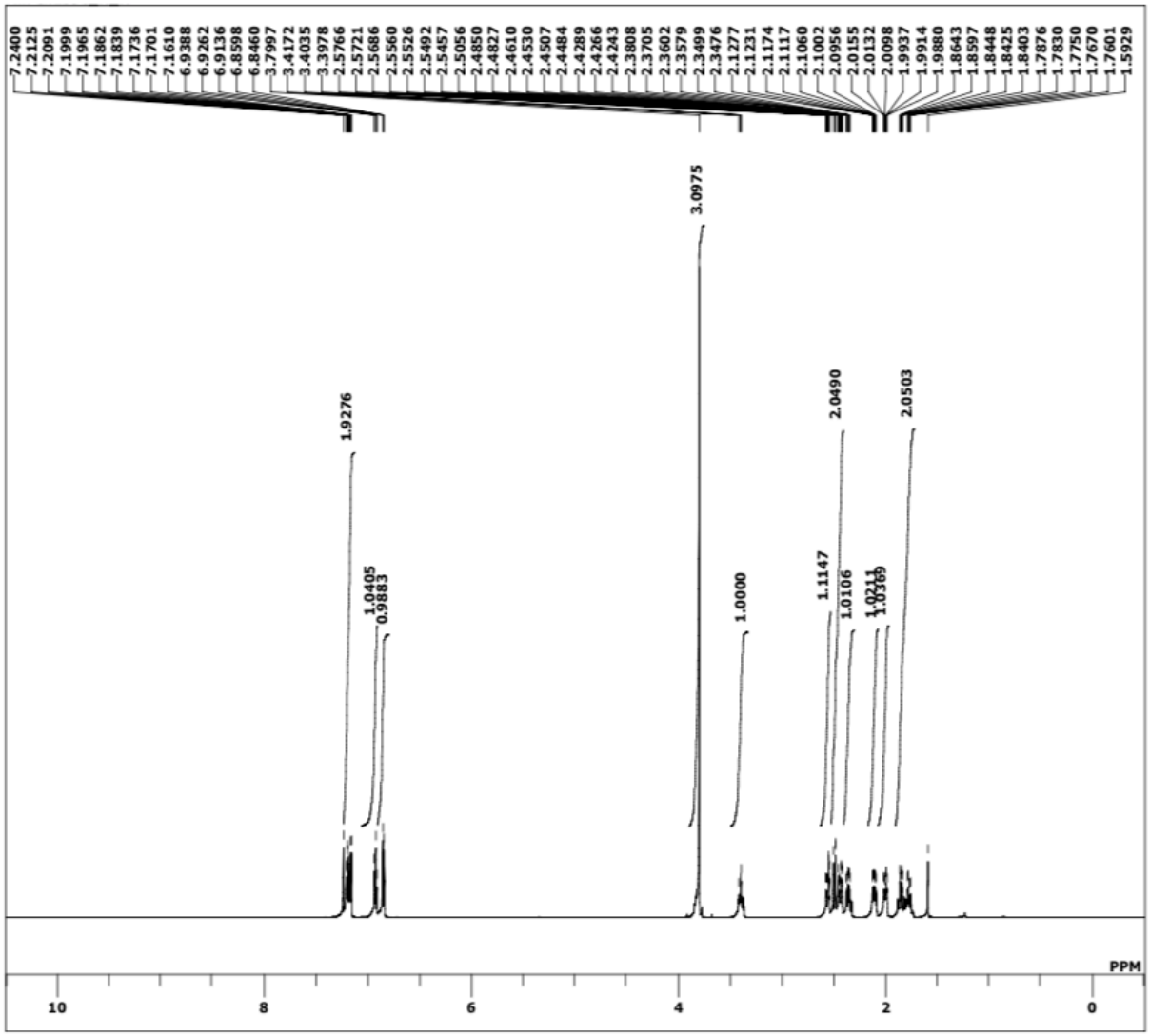
PeakTable

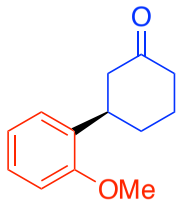
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.908	1091903	34942	1.292	1.791
2	29.965	83412903	1915660	98.708	98.209
Total		84504806	1950602	100.000	100.000

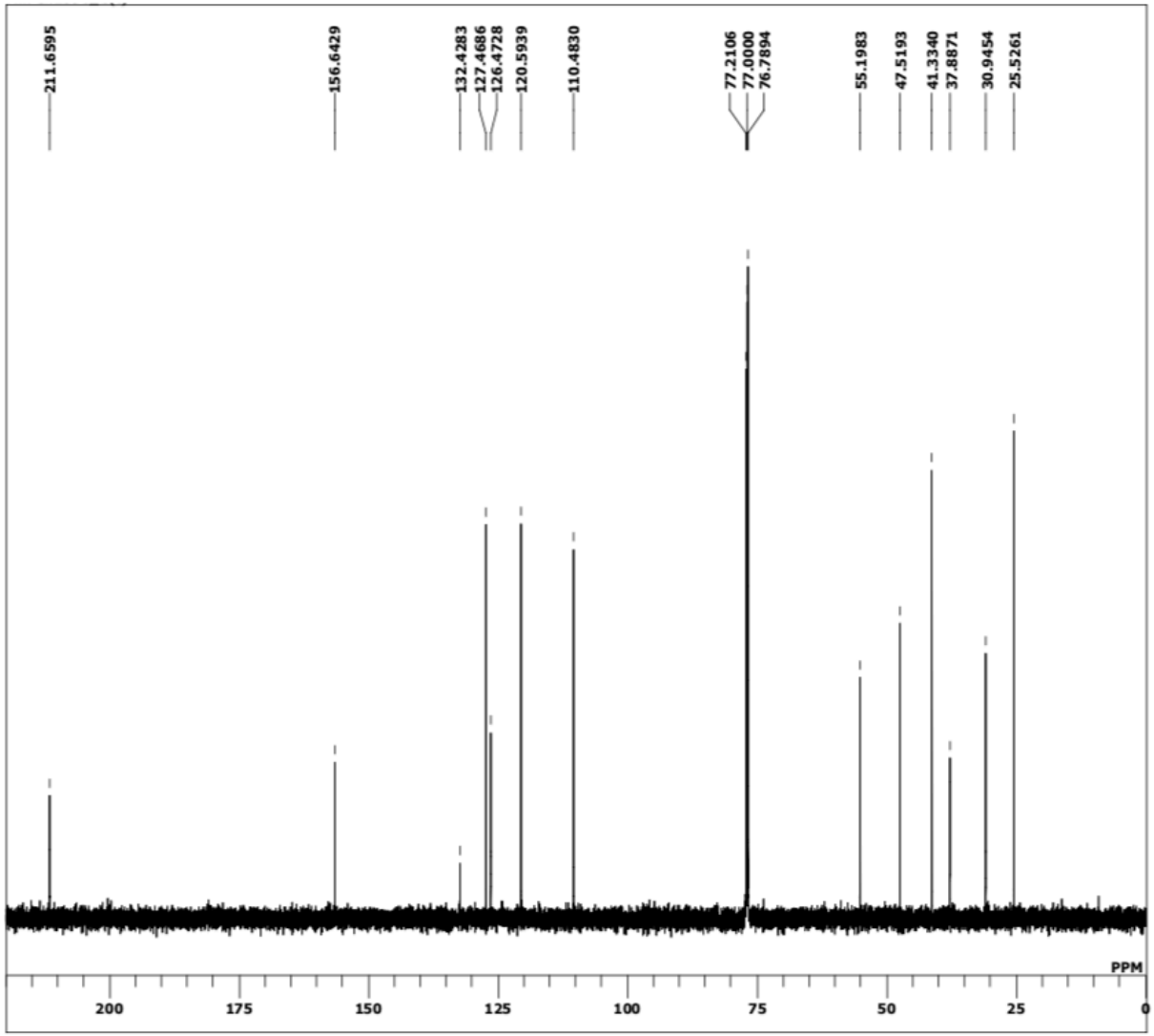

O
OMe

5ad

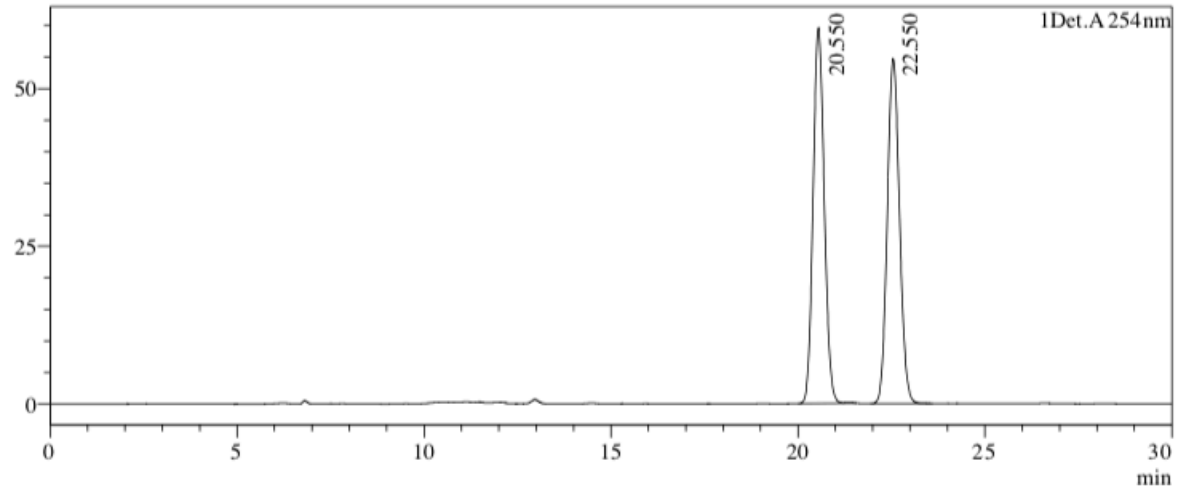

7.2400
7.2125
7.2091
7.1999
7.1965
7.1862
7.1839
7.1736
7.1701
7.1610
6.9388
6.9262
6.9136
6.8598
6.8460
3.7997
3.4172
3.4035
3.3978
2.5766
2.5721
2.5686
2.5560
2.5526
2.5492
2.5457
2.5056
2.4850
2.4827
2.4610
2.4530
2.4507
2.4484
2.4289
2.4266
2.4243
2.3808
2.3705
2.3602
2.3579
2.3499
2.3476
2.1277
2.1231
2.1174
2.1117
2.1060
2.1002
2.0956
2.0155
2.0132
2.0098
1.9937
1.9914
1.9880
1.8643
1.8597
1.8448
1.8425
1.8403
1.7876
1.7830
1.7750
1.7670
1.7601
1.5929
3.0975
1.9276
1.0405
0.9883
1.0000
1.1147
2.0490
1.0106
1.0211
1.0369
2.0503
PPM
10
8
6
4
2
0


O
OMe

5ad

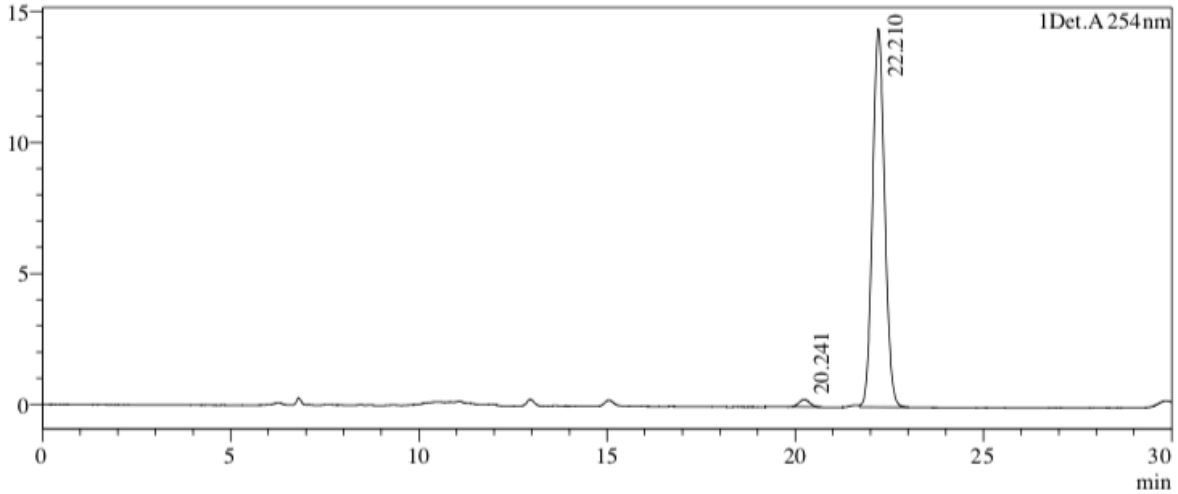

211.6595
156.6429
132.4283
127.4686
126.4728
120.5939
110.4830
77.2106
77.0000
76.7894
55.1983
47.5193
41.3340
37.8871
30.9454
25.5261
PPM
200
175
150
125
100
75
50
25
0

5ad, condition : AD-H, 0.5 ml/min, Hex/IPA = 98:2, 254 nm



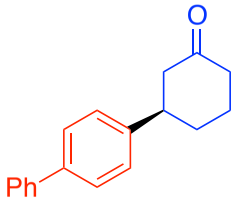
Det.A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	20.550	1238370	59517	49.985
2	22.550	1239127	54637	50.015

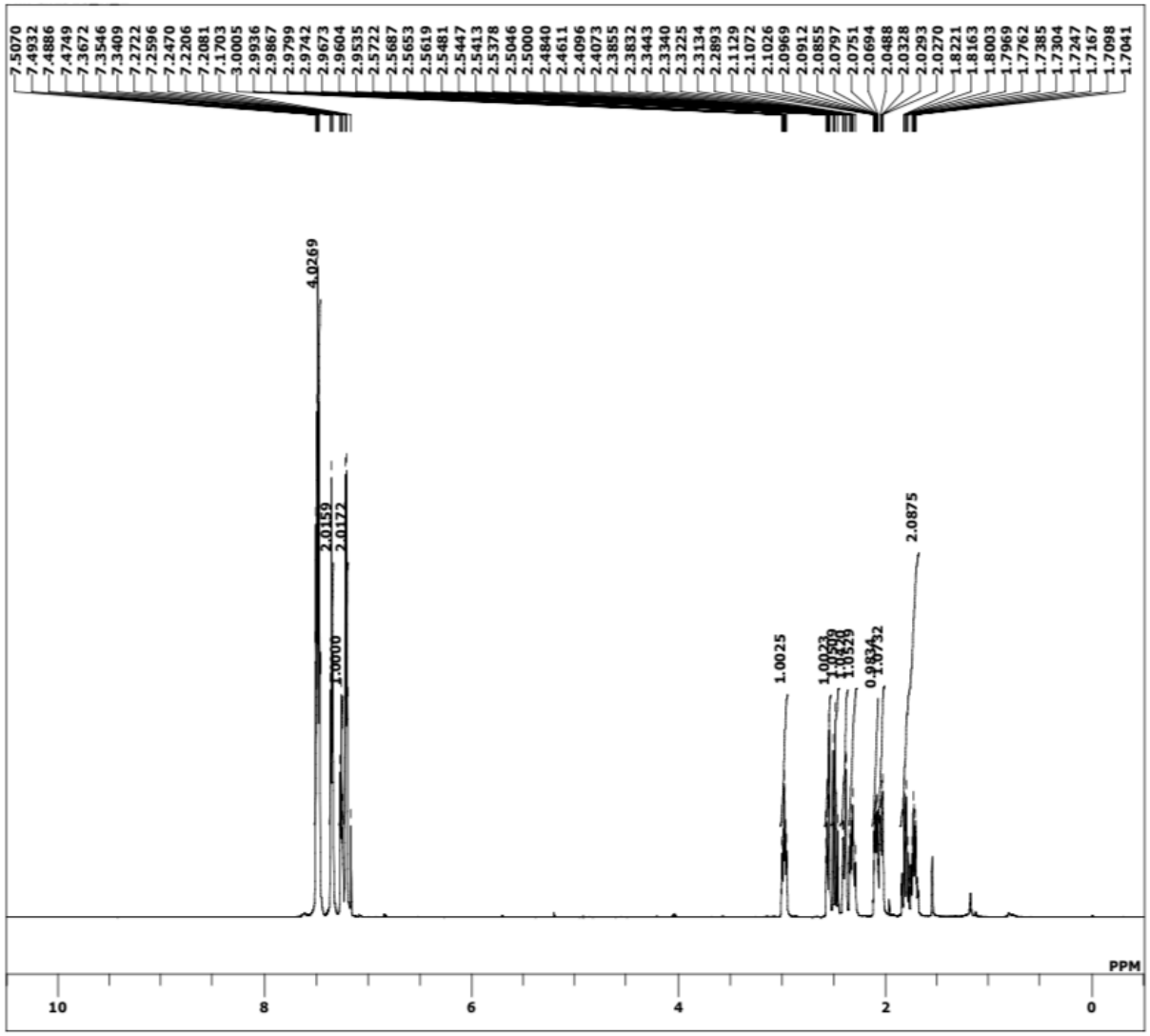


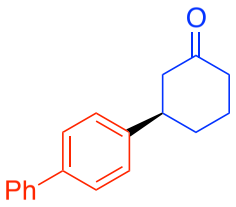
Det.A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	20.241	5531	280	1.681
2	22.210	323572	14439	98.319

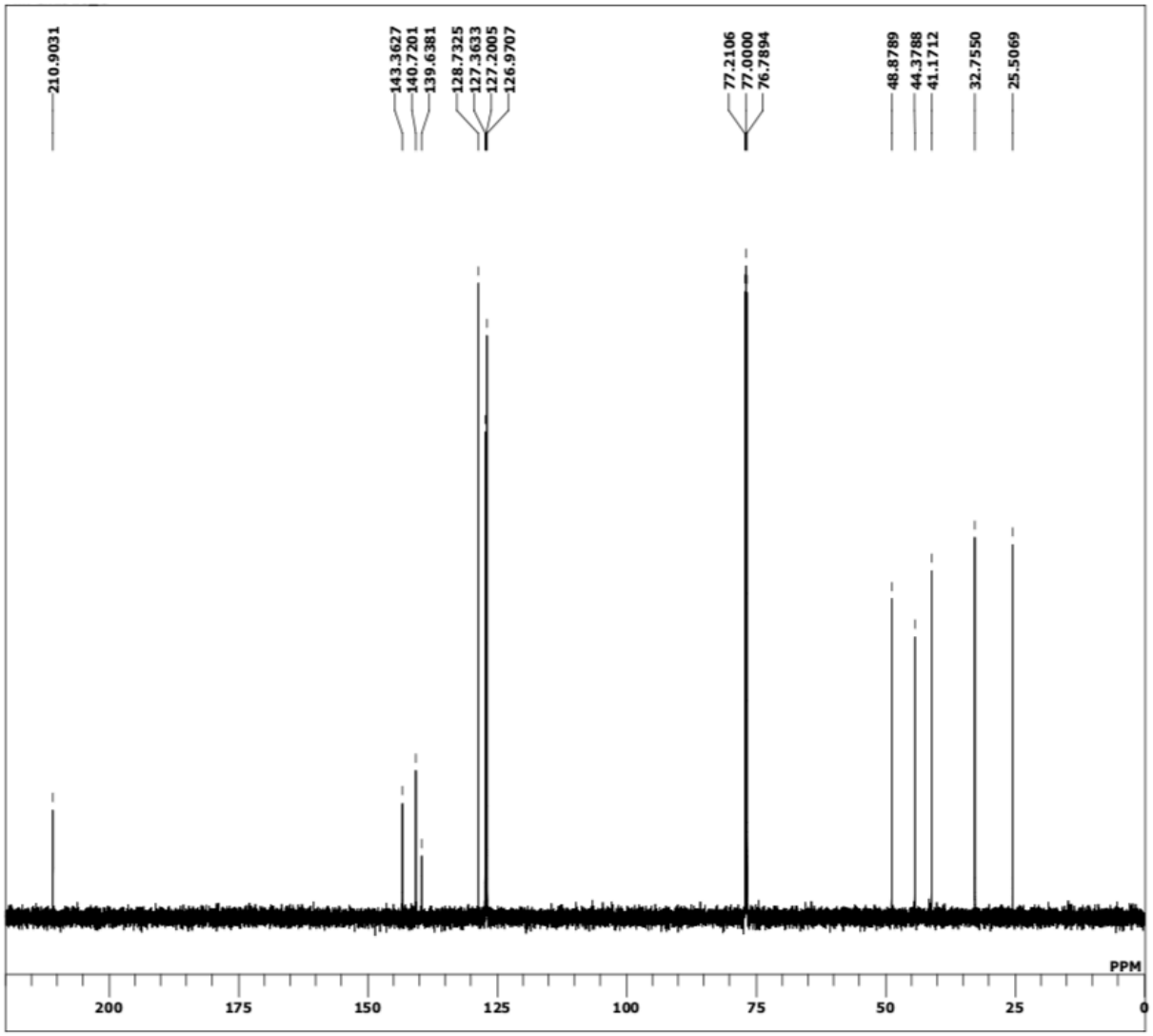

O
Ph

5ae

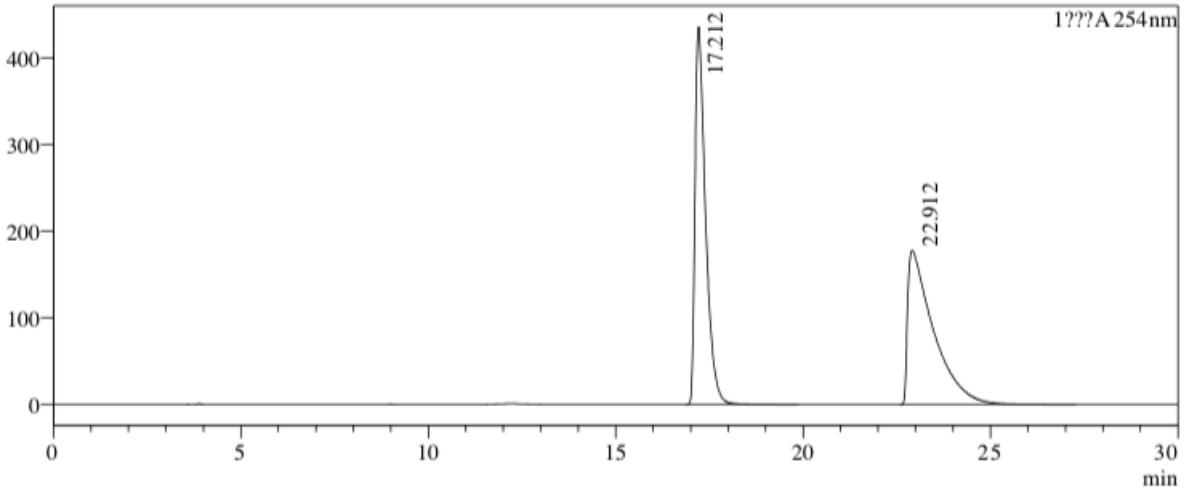

7.5070
7.4932
7.4886
7.4749
7.3672
7.3546
7.3409
7.2722
7.2596
7.2470
7.2206
7.2081
7.1703
3.0005
2.9936
2.9867
2.9799
2.9742
2.9673
2.9604
2.9535
2.5722
2.5687
2.5653
2.5619
2.5481
2.5447
2.5413
2.5378
2.5046
2.5000
2.4840
2.4611
2.4096
2.4073
2.3855
2.3832
2.3443
2.3340
2.3225
2.3134
2.2893
2.1129
2.1072
2.1026
2.0969
2.0912
2.0855
2.0797
2.0751
2.0694
2.0488
2.0328
2.0293
2.0270
1.8221
1.8163
1.8003
1.7969
1.7762
1.7385
1.7304
1.7247
1.7167
1.7098
1.7041
4.0269
2.0159
2.0172
1.0000
1.0025
2.0875
PPM
10
8
6
4
2
0


O
Ph

5ae

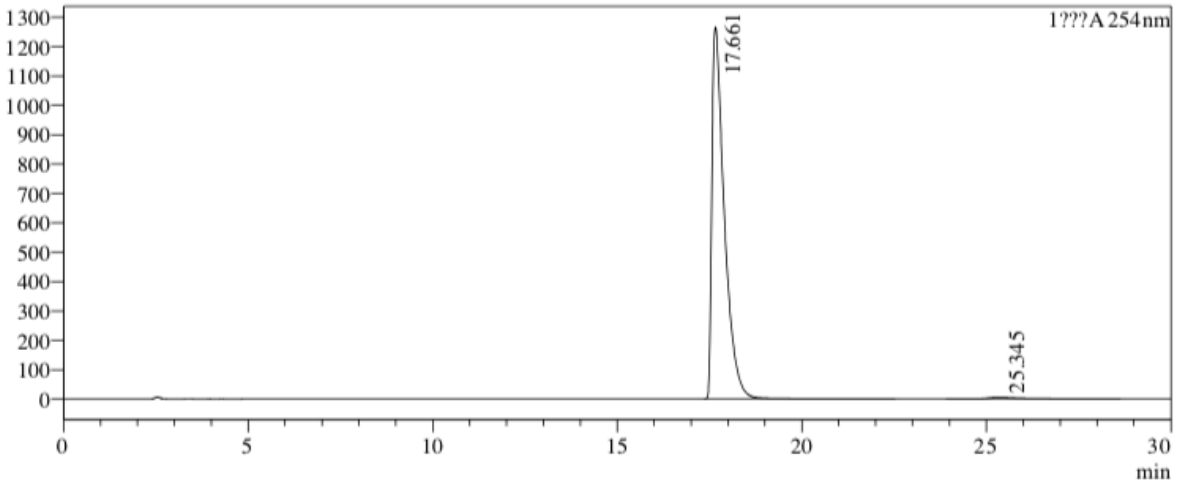

210.9031
143.3627
140.7201
139.6381
128.7325
127.3633
127.2005
126.9707
77.2106
77.0000
76.7894
48.8789
44.3788
41.1712
32.7550
25.5069
PPM
200
175
150
125
100
75
50
25
0

5ae, condition : AD-3, 1.0 ml/min, Hex/IPA = 98:2, 254 nm



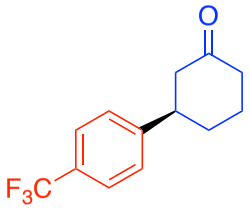
???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	17.212	8562223	435742	50.026
2	22.912	8553330	177747	49.974

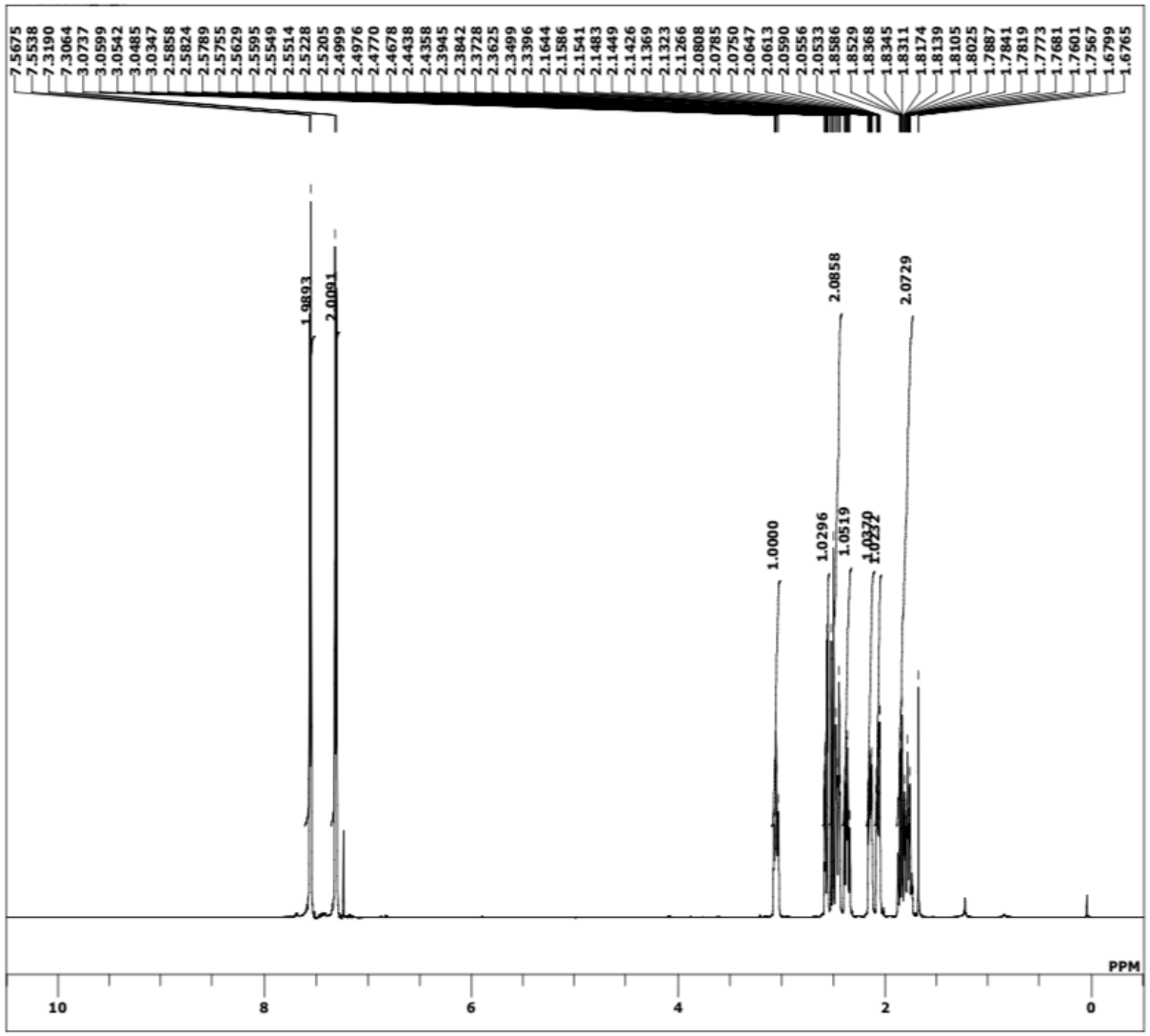


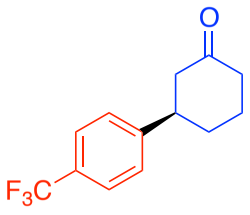
???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	17.661	29718765	1265086	98.819
2	25.345	355149	5158	1.181

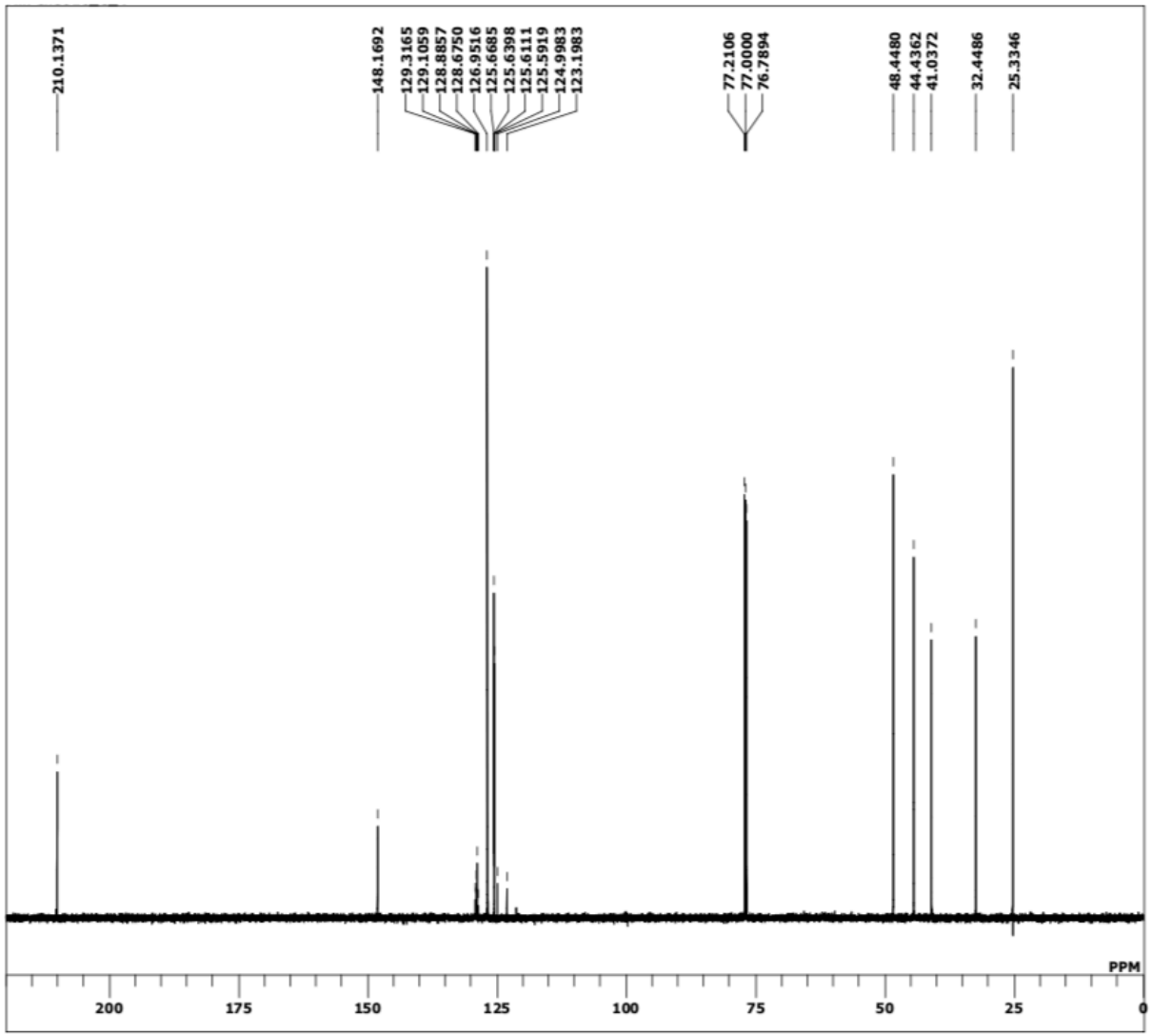

O
F3C

5af

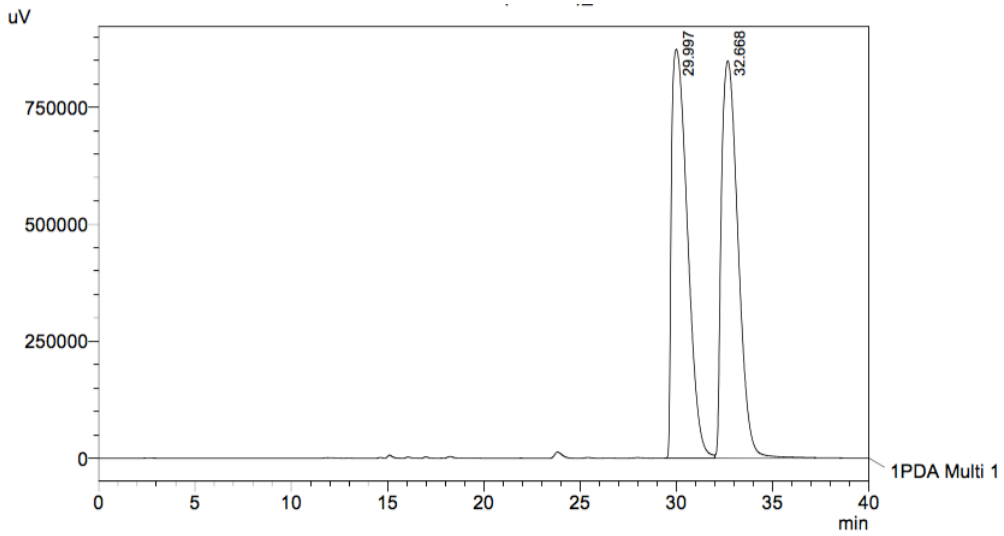

7.5675
7.5538
7.3190
7.3064
3.0737
3.0599
3.0542
3.0485
3.0347
2.5858
2.5824
2.5789
2.5755
2.5629
2.5595
2.5549
2.5514
2.5228
2.5205
2.4999
2.4976
2.4770
2.4678
2.4438
2.4358
2.3945
2.3842
2.3728
2.3625
2.3499
2.3396
2.1644
2.1586
2.1541
2.1483
2.1449
2.1426
2.1369
2.1323
2.1266
2.0808
2.0785
2.0750
2.0647
2.0613
2.0590
2.0556
2.0533
1.8586
1.8529
1.8368
1.8345
1.8311
1.8174
1.8139
1.8105
1.8025
1.7887
1.7841
1.7819
1.7773
1.7681
1.7601
1.7567
1.6799
1.6765
1.9893
2.0091
2.0858
2.0729
1.0000
1.0296
1.0519
PPM
10
8
6
4
2
0


O
F3C

5af


210.1371
148.1692
129.3165
129.1059
128.8857
128.6750
126.9516
125.6685
125.6398
125.6111
125.5919
124.9983
123.1983
77.2106
77.0000
76.7894
48.4480
44.4362
41.0372
32.4486
25.3346
PPM
200
175
150
125
100
75
50
25
0

5af, condition : OD-H_AS-H (connected column), 0.5 ml/min, Hex/IPA = 90:10, 220 nm

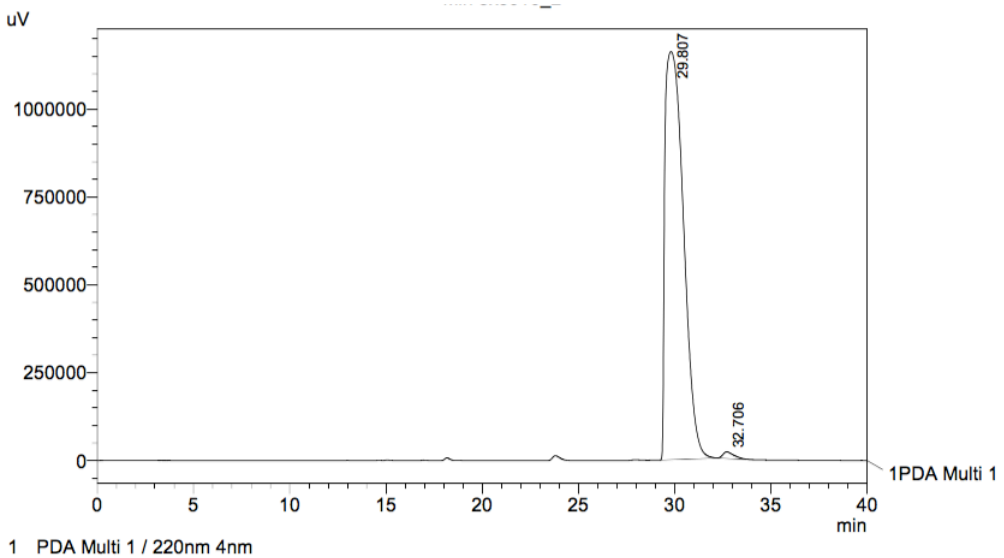


1 PDA Multi 1 / 220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.997	50197227	873420	49.696	50.718
2	32.668	50810920	848695	50.304	49.282
Total		101008148	1722115	100.000	100.000

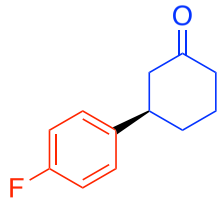


1 PDA Multi 1 / 220nm 4nm

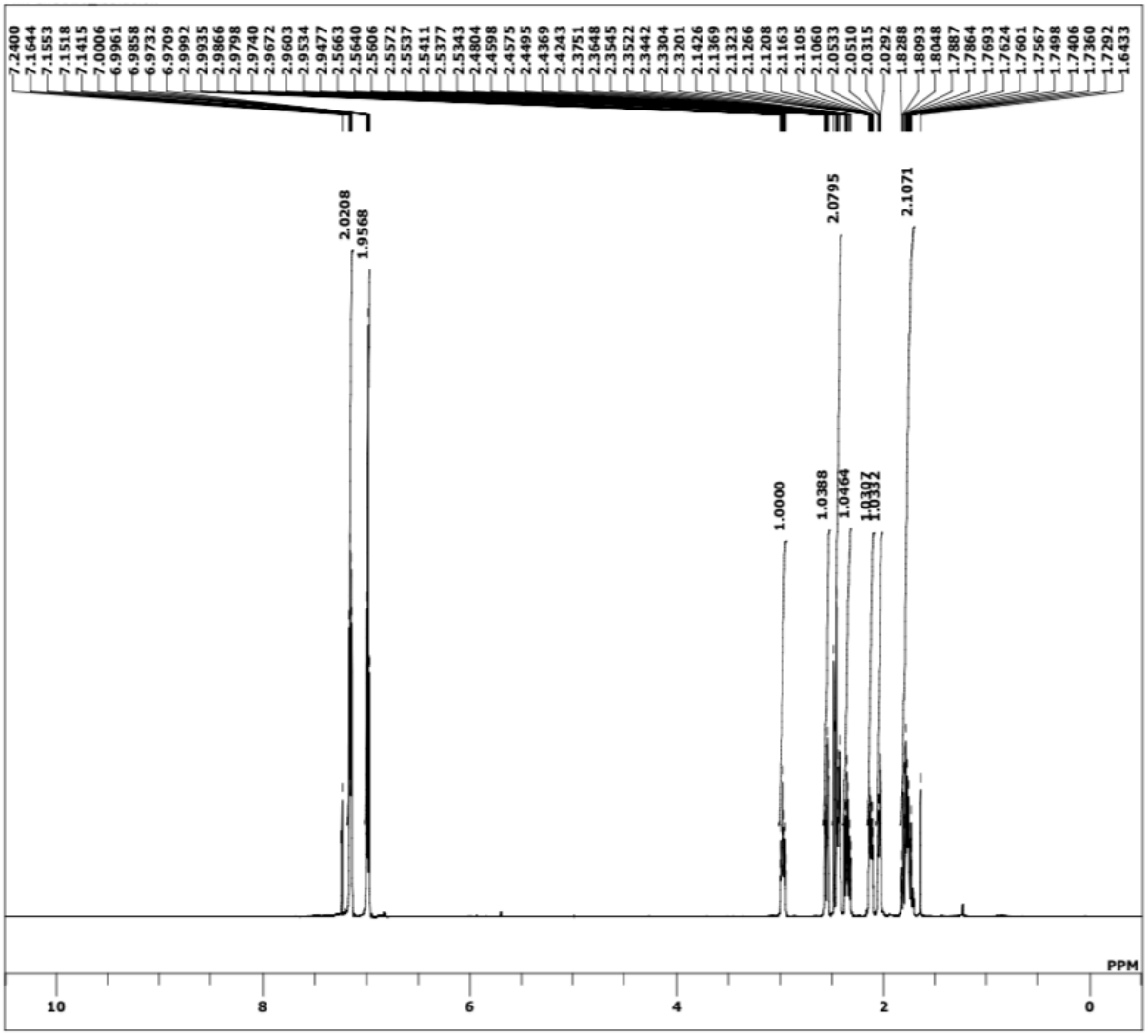
PeakTable

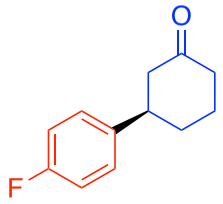
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.807	77387259	1161403	99.037	98.402
2	32.706	752574	18855	0.963	1.598
Total		78139833	1180258	100.000	100.000

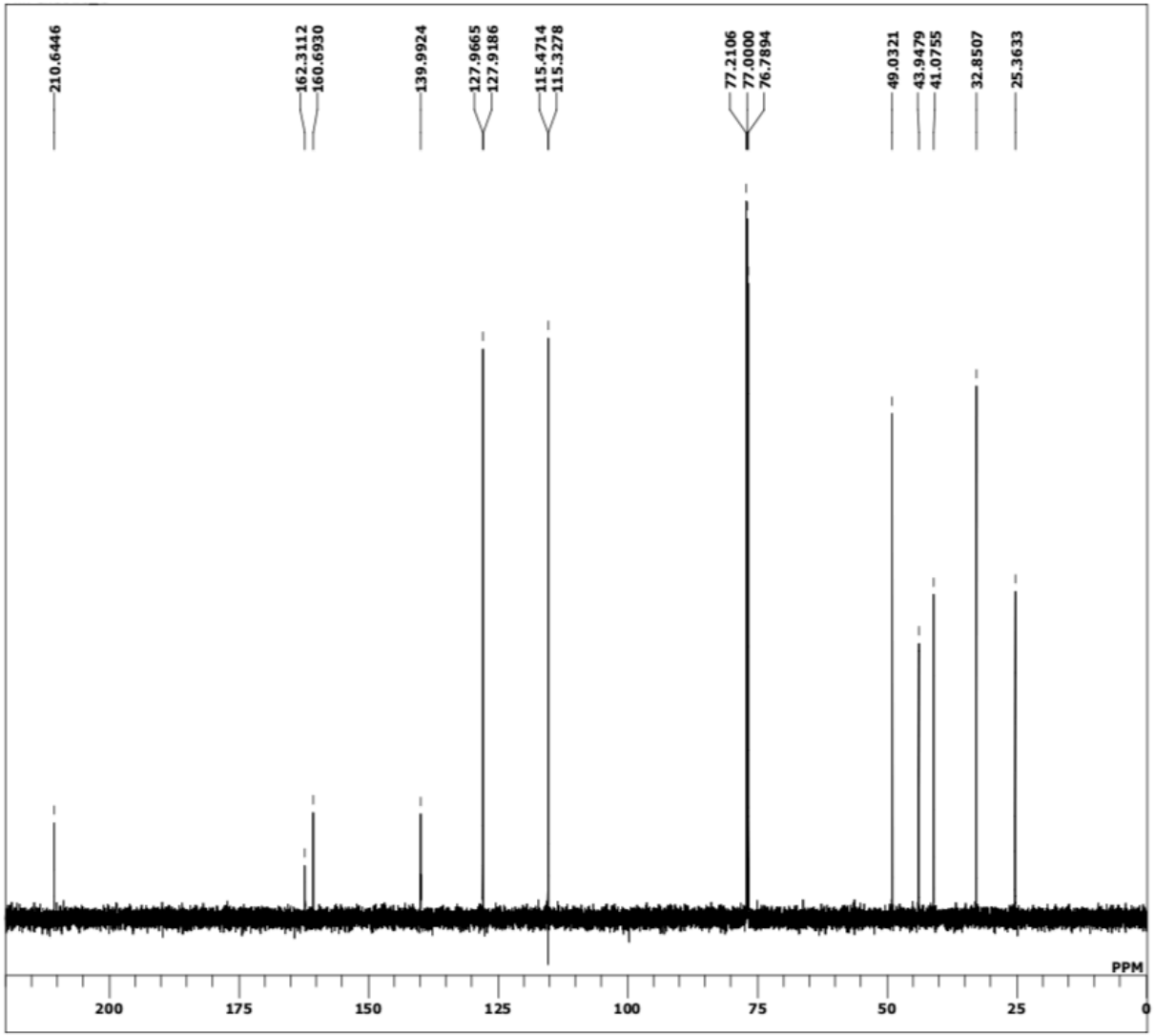

O
F

5ag

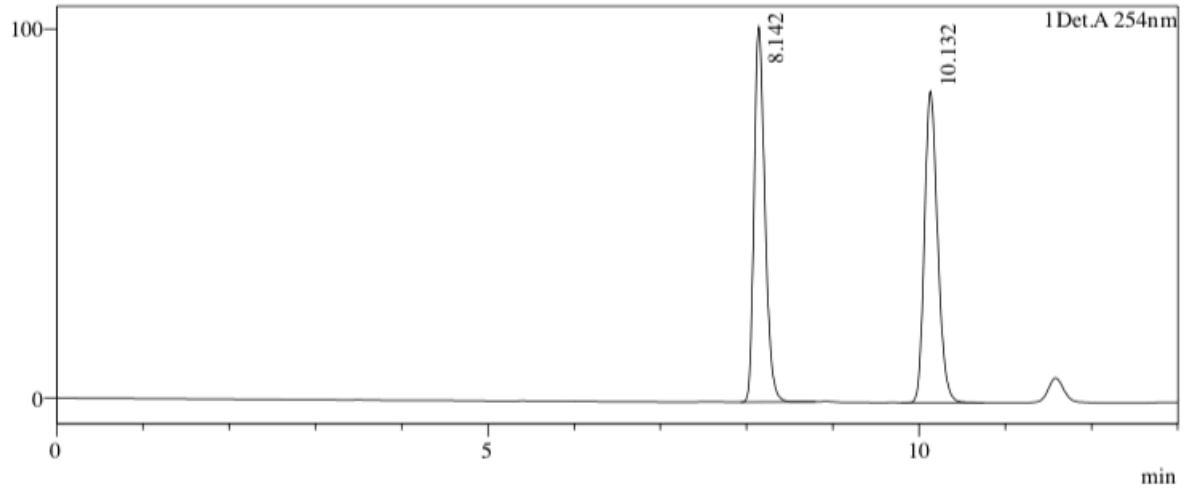

7.2400
7.1644
7.1553
7.1518
7.1415
7.0006
6.9961
6.9858
6.9732
6.9709
2.9992
2.9935
2.9866
2.9798
2.9740
2.9672
2.9603
2.9534
2.9477
2.5663
2.5640
2.5606
2.5572
2.5537
2.5411
2.5377
2.5343
2.4804
2.4598
2.4575
2.4495
2.4369
2.4243
2.3751
2.3648
2.3545
2.3522
2.3442
2.3304
2.3201
2.1426
2.1369
2.1323
2.1266
2.1208
2.1163
2.1105
2.1060
2.0533
2.0510
2.0315
2.0292
1.8288
1.8093
1.8048
1.7887
1.7864
1.7693
1.7624
1.7601
1.7567
1.7498
1.7406
1.7360
1.7292
1.6433
2.0208
1.9568
2.0795
2.1071
1.0000
1.0388
1.0464
1.0392
PPM
10
8
6
4
2
0


O
F

5ag

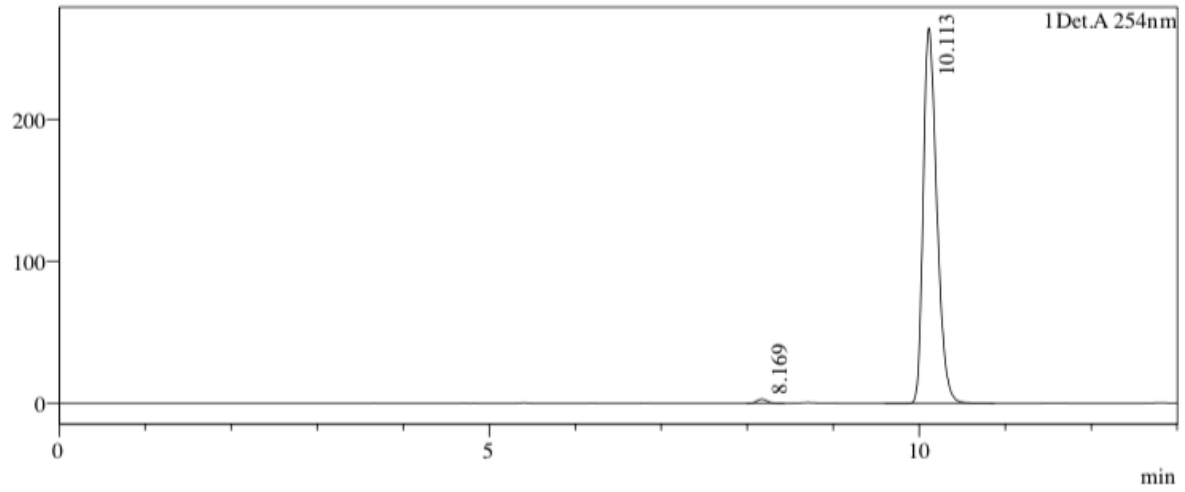

210.6446
162.3112
160.6930
139.9924
127.9665
127.9186
115.4714
115.3278
77.2106
77.0000
76.7894
49.0321
43.9479
41.0755
32.8507
25.3633
PPM
200
175
150
125
100
75
50
25
0

5ag, condition : AD-H, 1.0 ml/min, Hex/IPA = 97:3, 254 nm



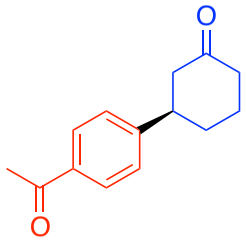
Det.A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.142	886960	101477	49.719
2	10.132	896992	84304	50.281

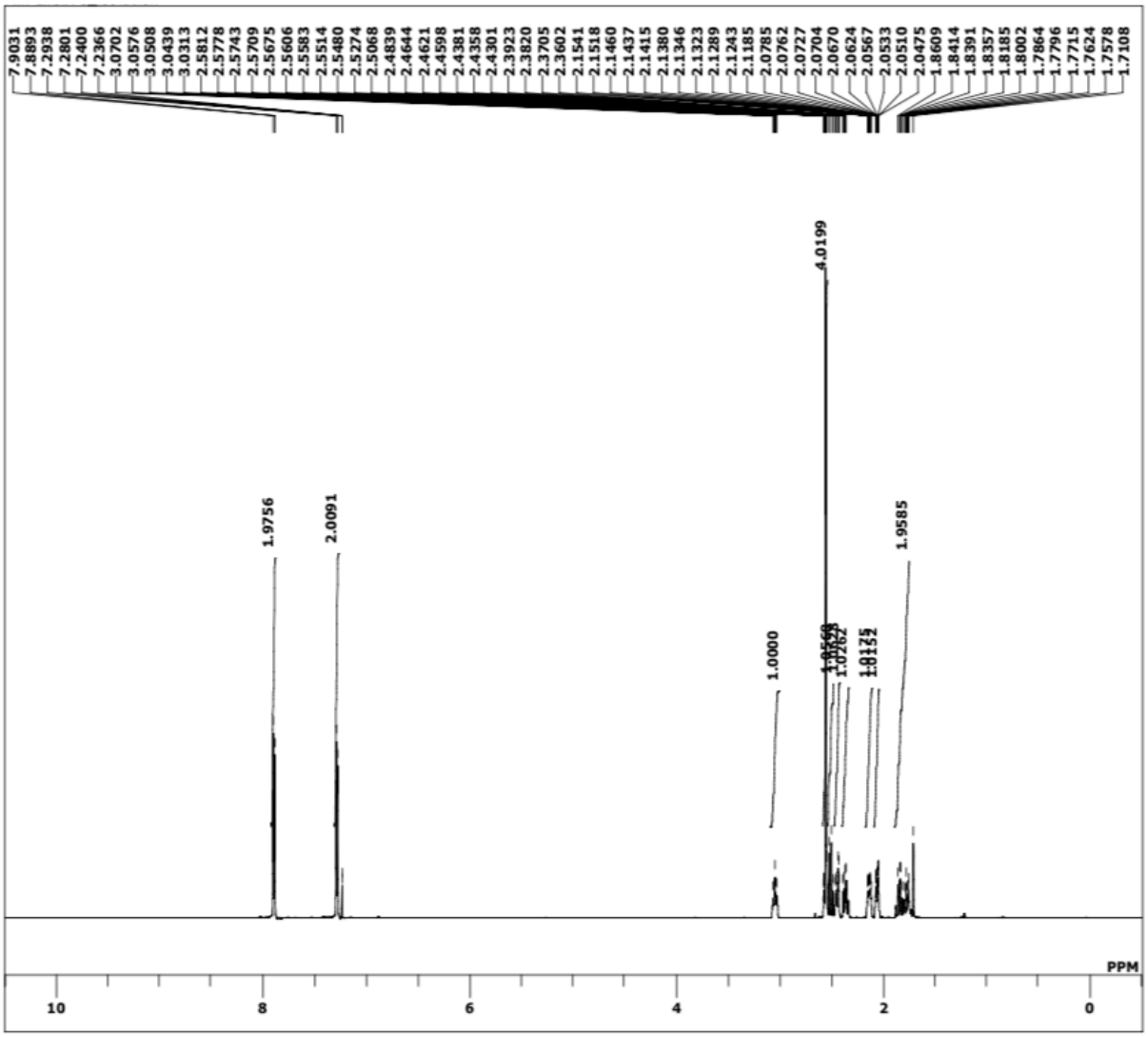


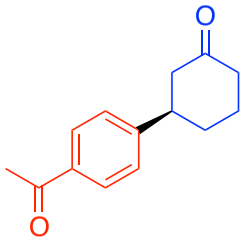
Det.A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.169	25191	2945	0.857
2	10.113	2913620	264114	99.143

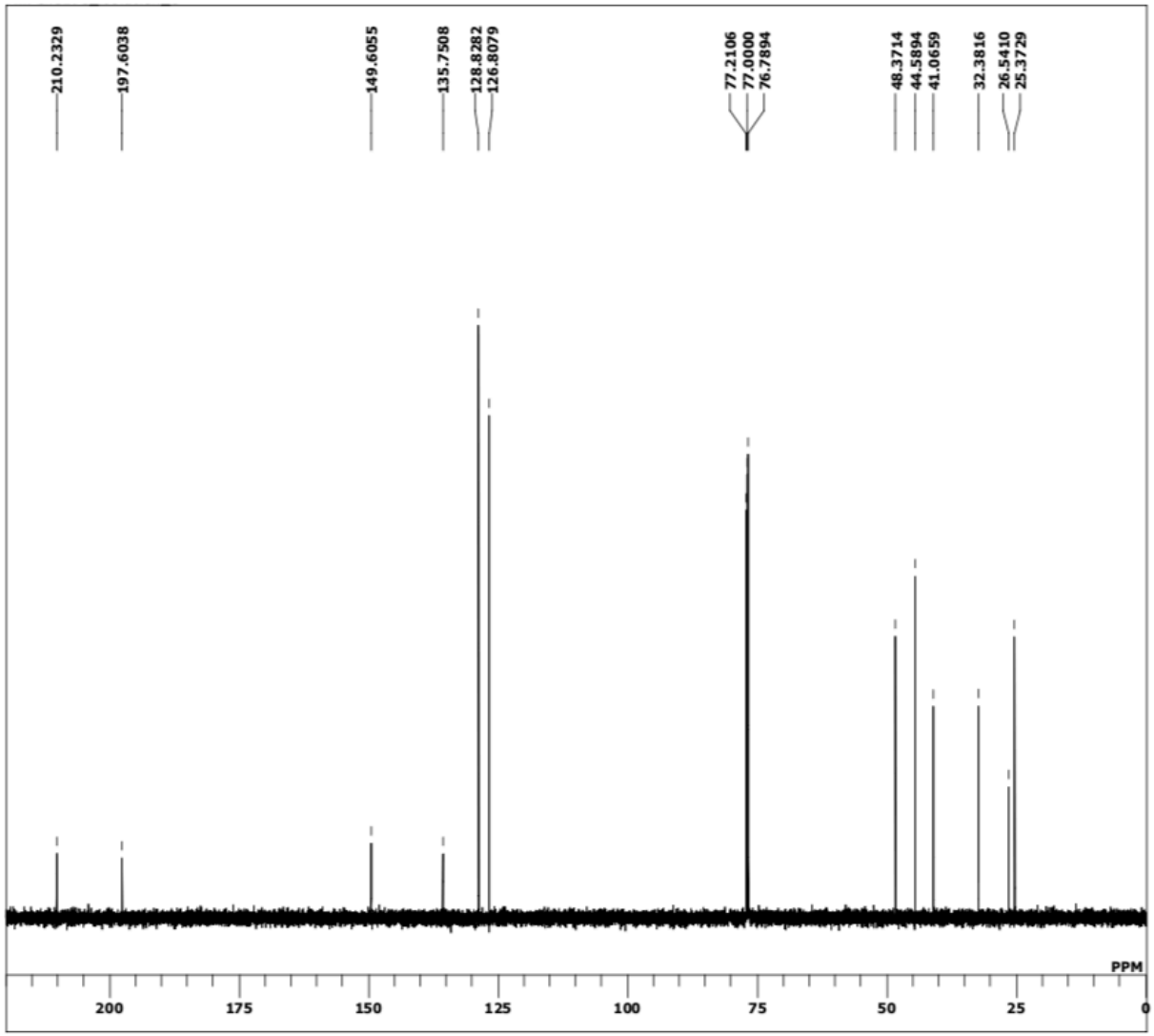


5ah

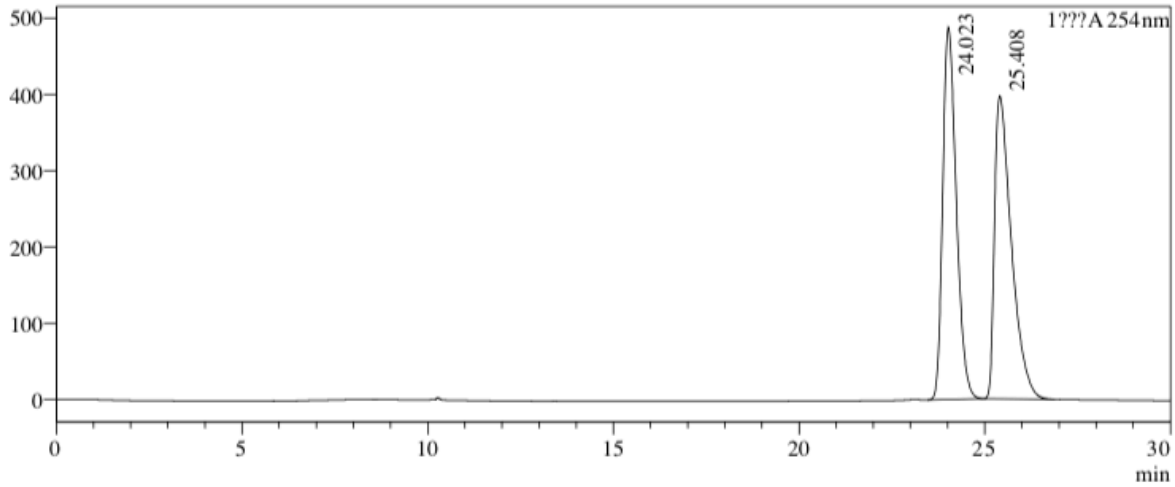

7.9031
7.8893
7.2938
7.2801
7.2400
7.2366
3.0702
3.0576
3.0508
3.0439
3.0313
2.5812
2.5778
2.5743
2.5709
2.5675
2.5606
2.5583
2.5514
2.5480
2.5274
2.5068
2.4839
2.4644
2.4621
2.4598
2.4381
2.4358
2.4301
2.3923
2.3820
2.3705
2.3602
2.1541
2.1518
2.1460
2.1437
2.1415
2.1380
2.1346
2.1323
2.1289
2.1243
2.1185
2.0785
2.0762
2.0727
2.0704
2.0670
2.0624
2.0567
2.0533
2.0510
2.0475
1.8609
1.8414
1.8391
1.8357
1.8185
1.8002
1.7864
1.7796
1.7715
1.7624
1.7578
1.7108
4.0199
1.9756
2.0091
1.9585
1.0000
1.0262
PPM
10
8
6
4
2
0



5ah

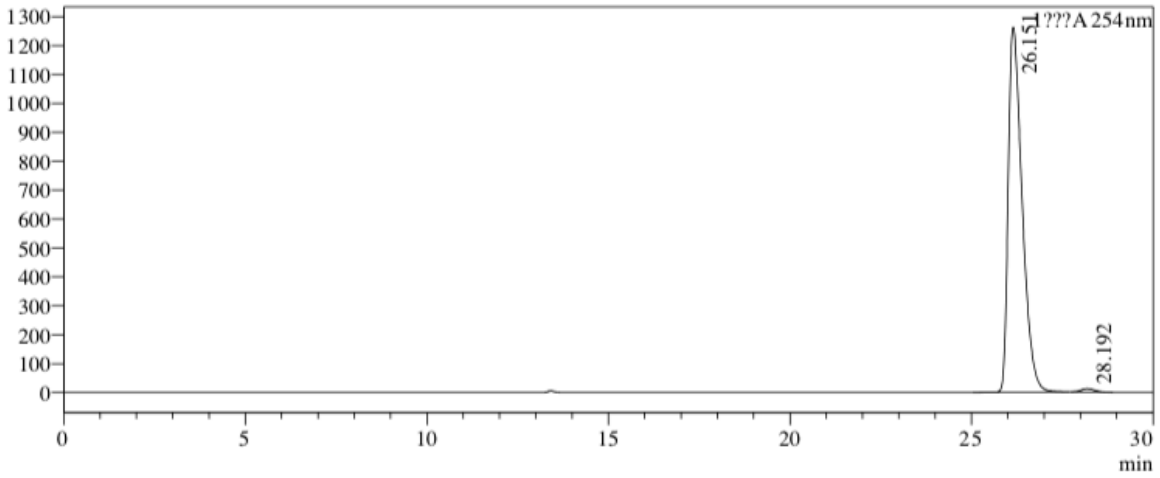

210.2329
197.6038
149.6055
135.7508
128.8282
126.8079
77.2106
77.0000
76.7894
48.3714
44.5894
41.0659
32.3816
26.5410
25.3729
PPM
200
175
150
125
100
75
50
25
0

5ah, condition : AD-3, 0.6 ml/min, Hex/IPA = 90:10, 254 nm



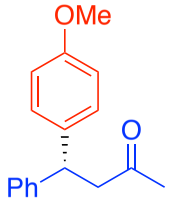
???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	24.023	12397070	487679	49.630
2	25.408	12581811	397315	50.370

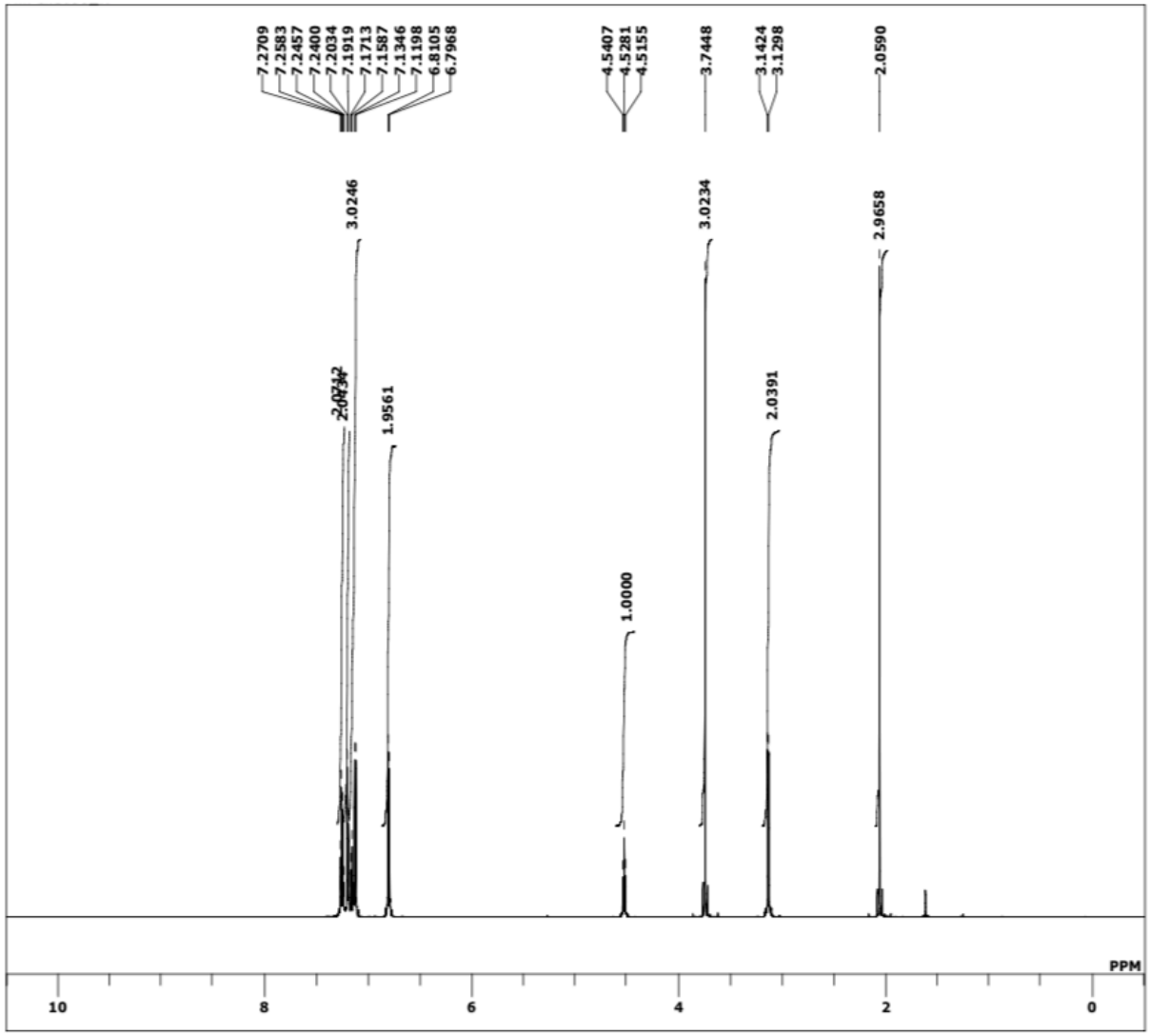


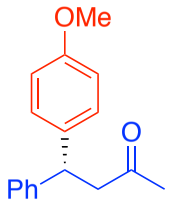
???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	26.151	33620942	1262054	99.159
2	28.192	285176	11276	0.841

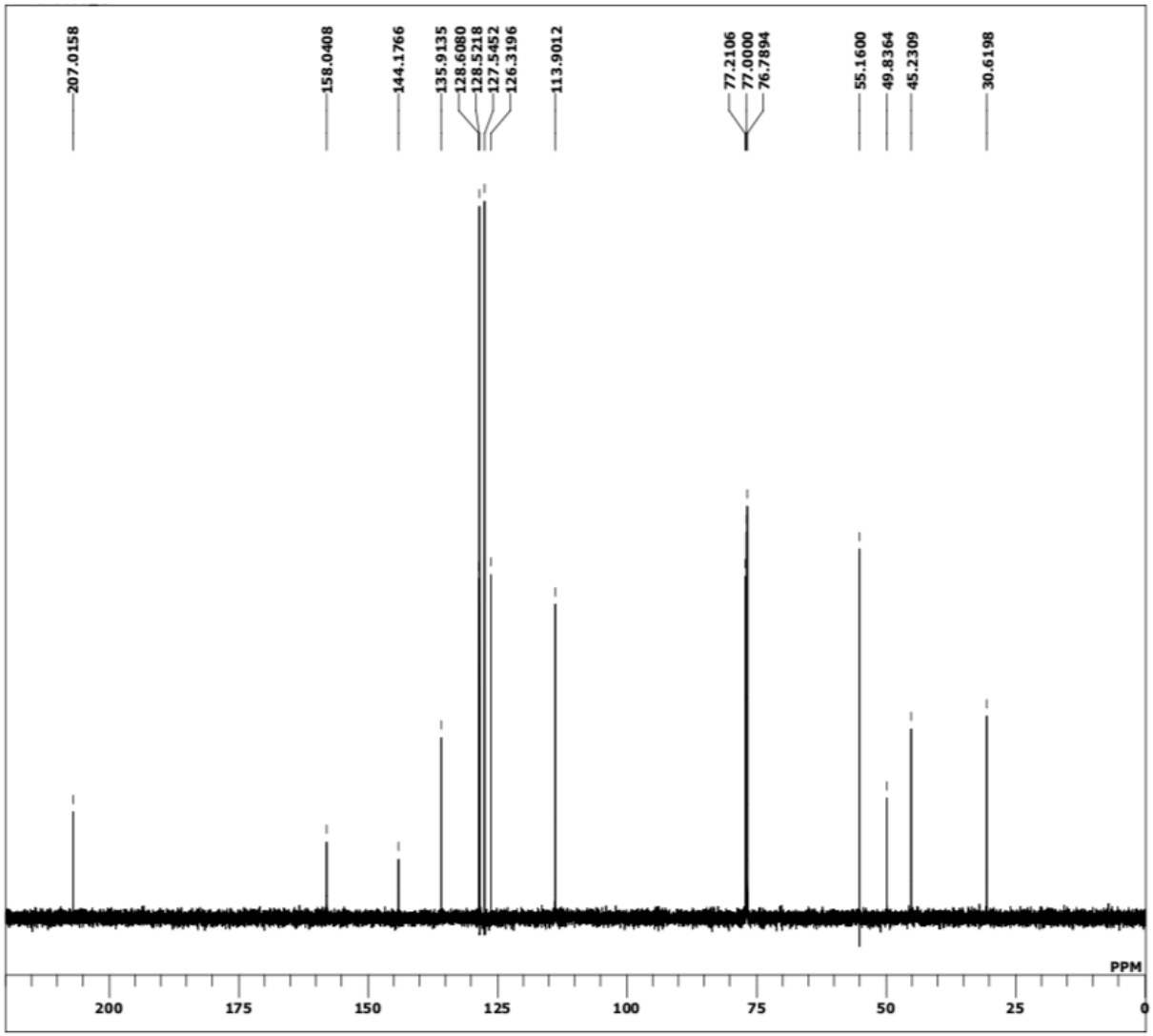

OMe
O
Ph

5bb

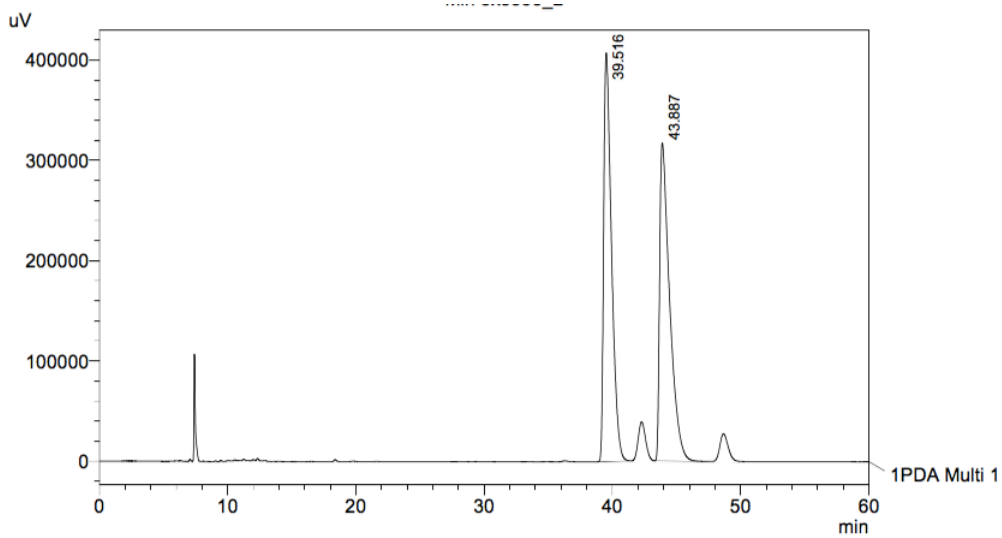

7.2709
7.2583
7.2457
7.2400
7.2034
7.1919
7.1713
7.1587
7.1346
7.1198
6.8105
6.7968
4.5407
4.5281
4.5155
3.7448
3.1424
3.1298
2.0590
3.0246
3.0234
2.9658
2.0391
1.9561
1.0000
PPM
10
8
6
4
2
0


OMe
O
Ph

5bb


207.0158
158.0408
144.1766
135.9135
128.6080
128.5218
127.5452
126.3196
113.9012
77.2106
77.0000
76.7894
55.1600
49.8364
45.2309
30.6198
PPM
200
175
150
125
100
75
50
25
0

5bb, condition : AD-3_OD-H (connected column), 1.0 ml/min, Hex/IPA = 98:2, 220 nm

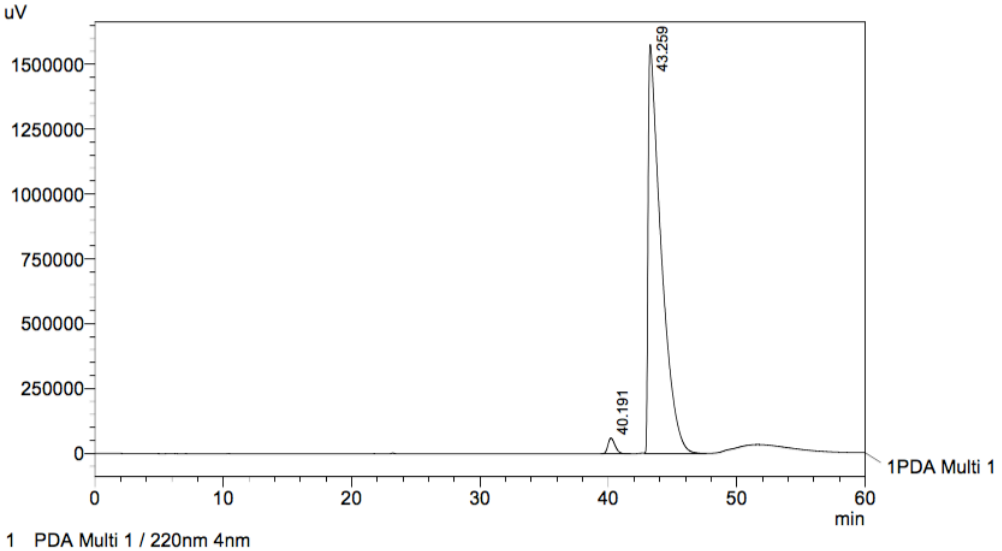


1 PDA Multi 1 / 220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	39.516	17242048	407703	49.989	56.253
2	43.887	17249762	317069	50.011	43.747
Total		34491810	724772	100.000	100.000

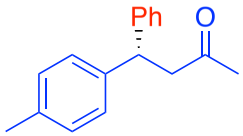


1 PDA Multi 1 / 220nm 4nm

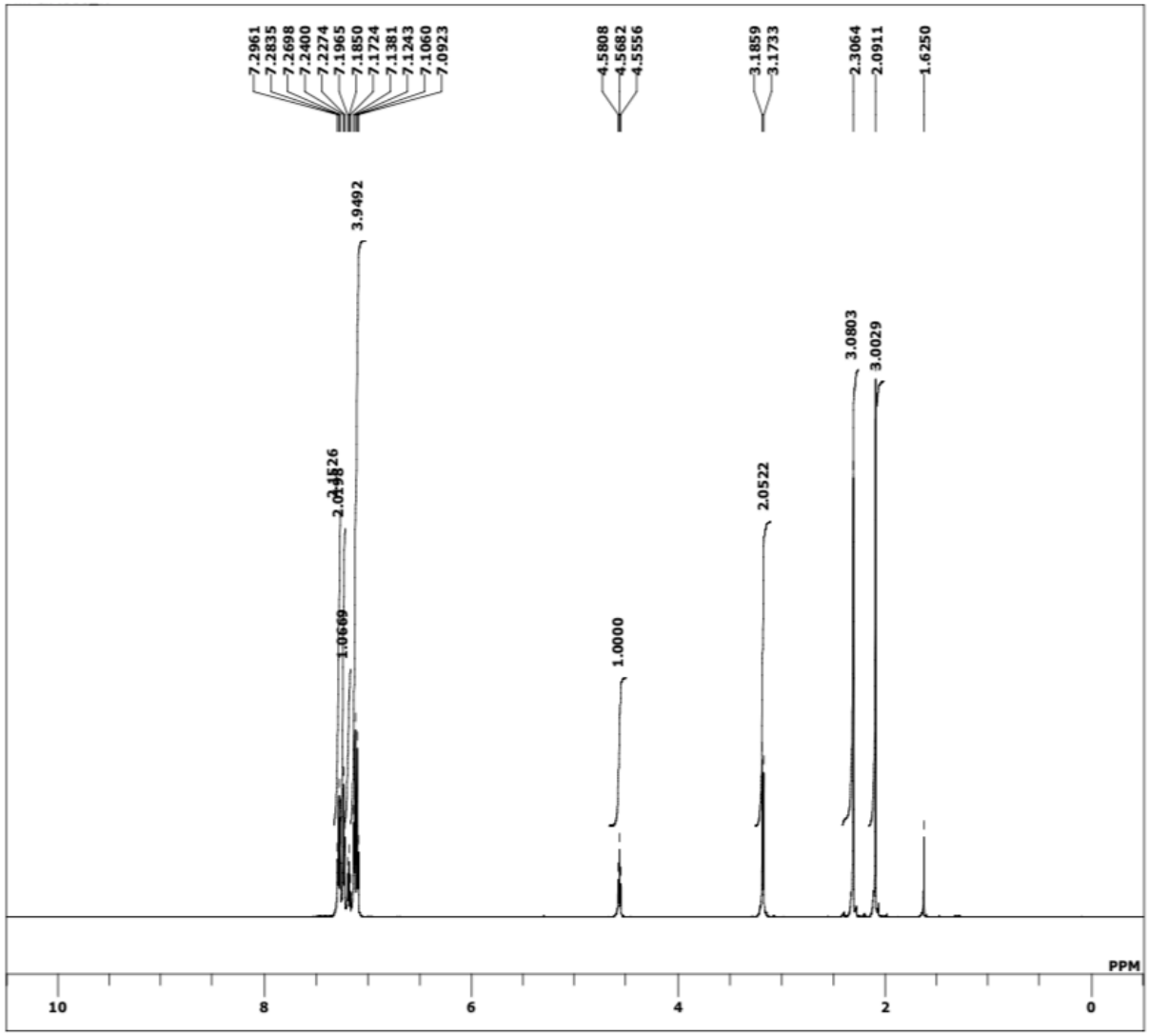
PeakTable

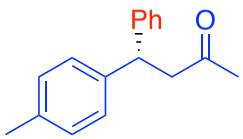
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.191	2374923	60823	2.099	3.717
2	43.259	110791390	1575342	97.901	96.283
Total		113166314	1636164	100.000	100.000

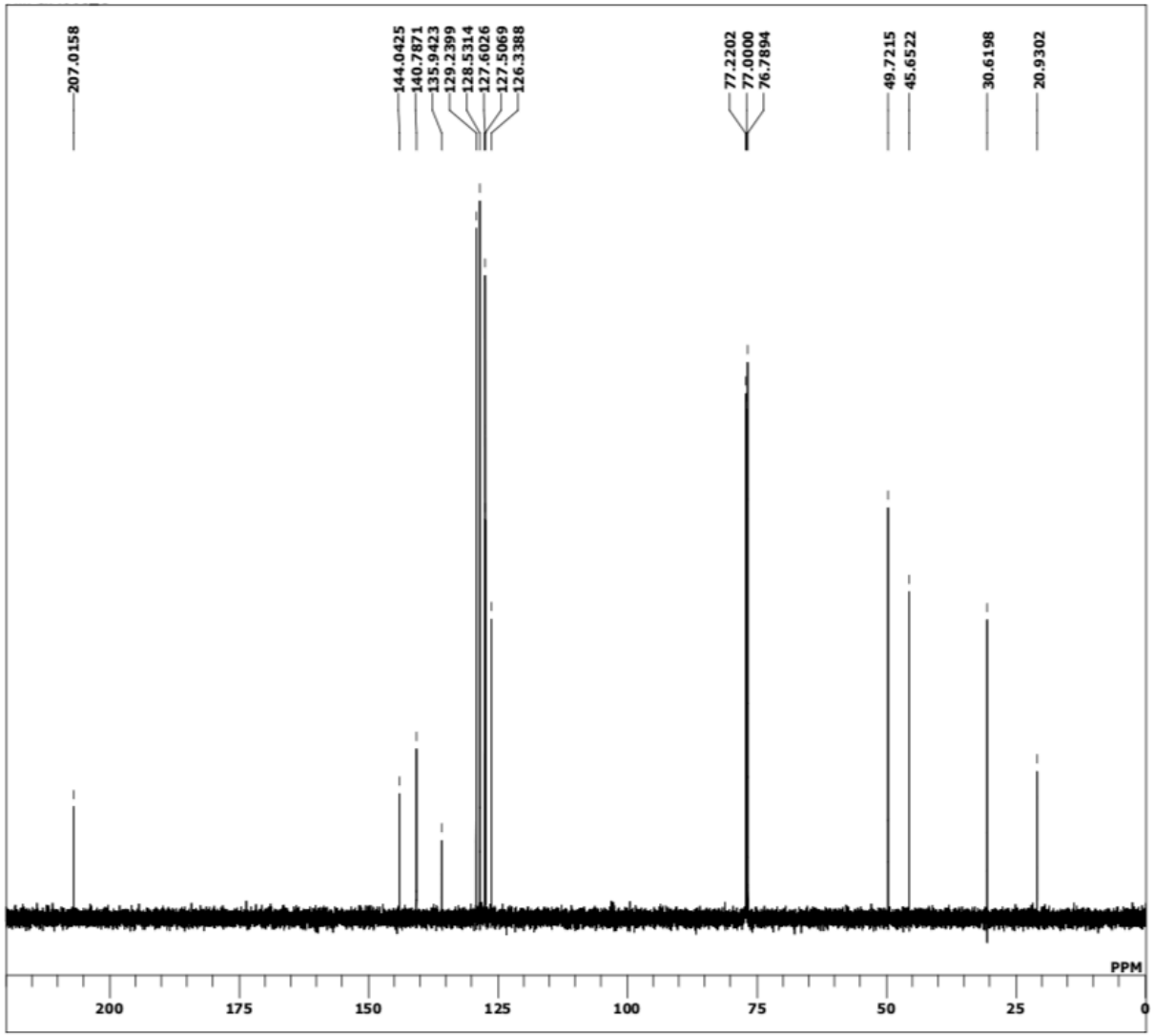

Ph
O

5ca

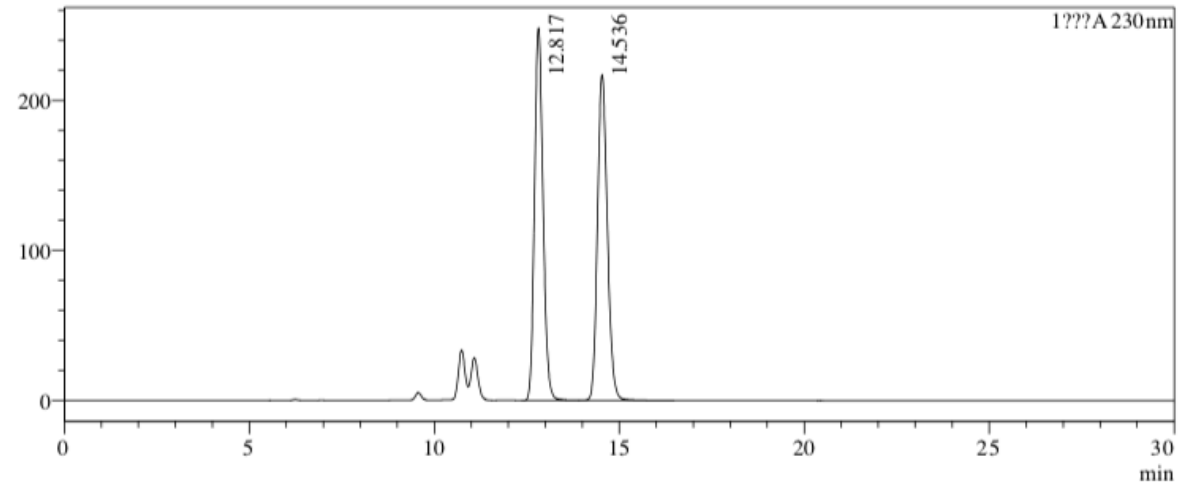

7.2961
7.2835
7.2698
7.2400
7.2274
7.1965
7.1850
7.1724
7.1381
7.1243
7.1060
7.0923
4.5808
4.5682
4.5556
3.1859
3.1733
2.3064
2.0911
1.6250
3.9492
3.0803
3.0029
2.0522
1.0000
1.0669
PPM
10
8
6
4
2
0


Ph
O

5ca

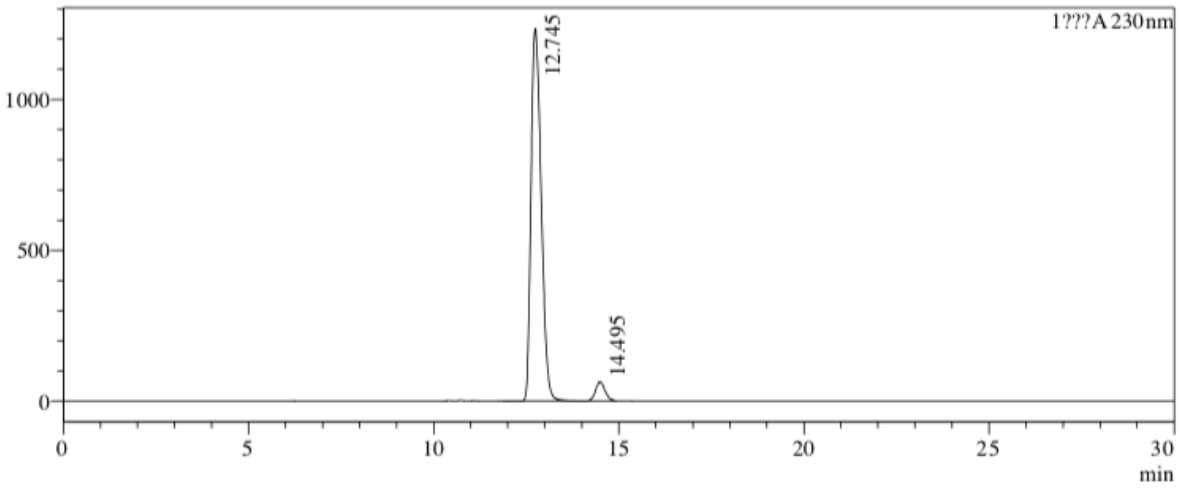

207.0158
144.0425
140.7871
135.9423
129.2399
128.5314
127.6026
127.5069
126.3388
77.2202
77.0000
76.7894
49.7215
45.6522
30.6198
20.9302
PPM
200
175
150
125
100
75
50
25
0

5ca, condition : OD-H, 0.5 ml/min, Hex/IPA = 90:10, 230 nm



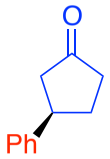
???A 230nm

Peak#	Ret. Time	Area	Height	Area%
1	12.817	4013223	248060	49.778
2	14.536	4049031	216989	50.222

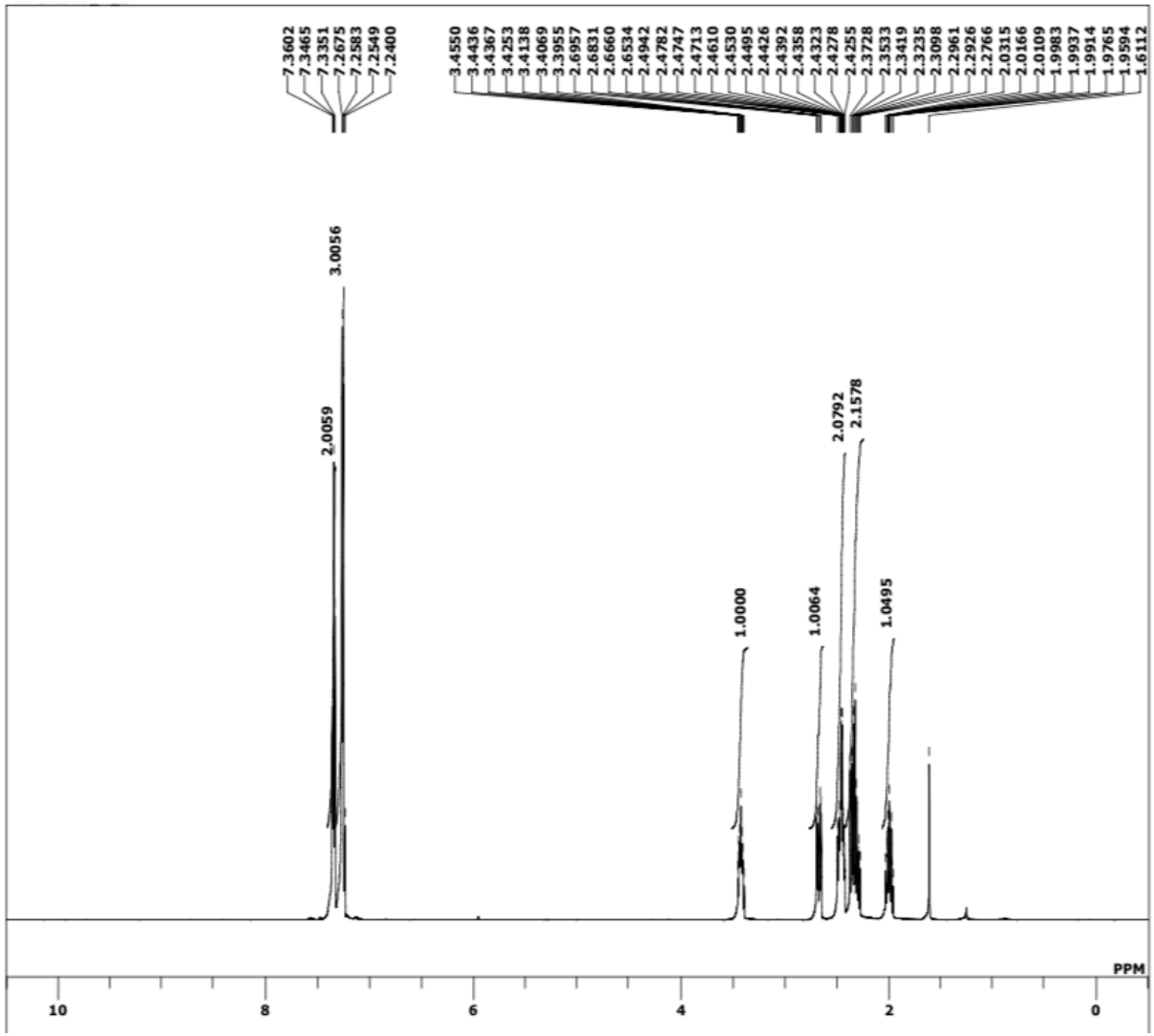


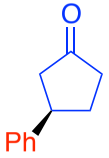
???A 230nm

Peak#	Ret. Time	Area	Height	Area%
1	12.745	23543846	1233384	95.466
2	14.495	1118171	62863	4.534

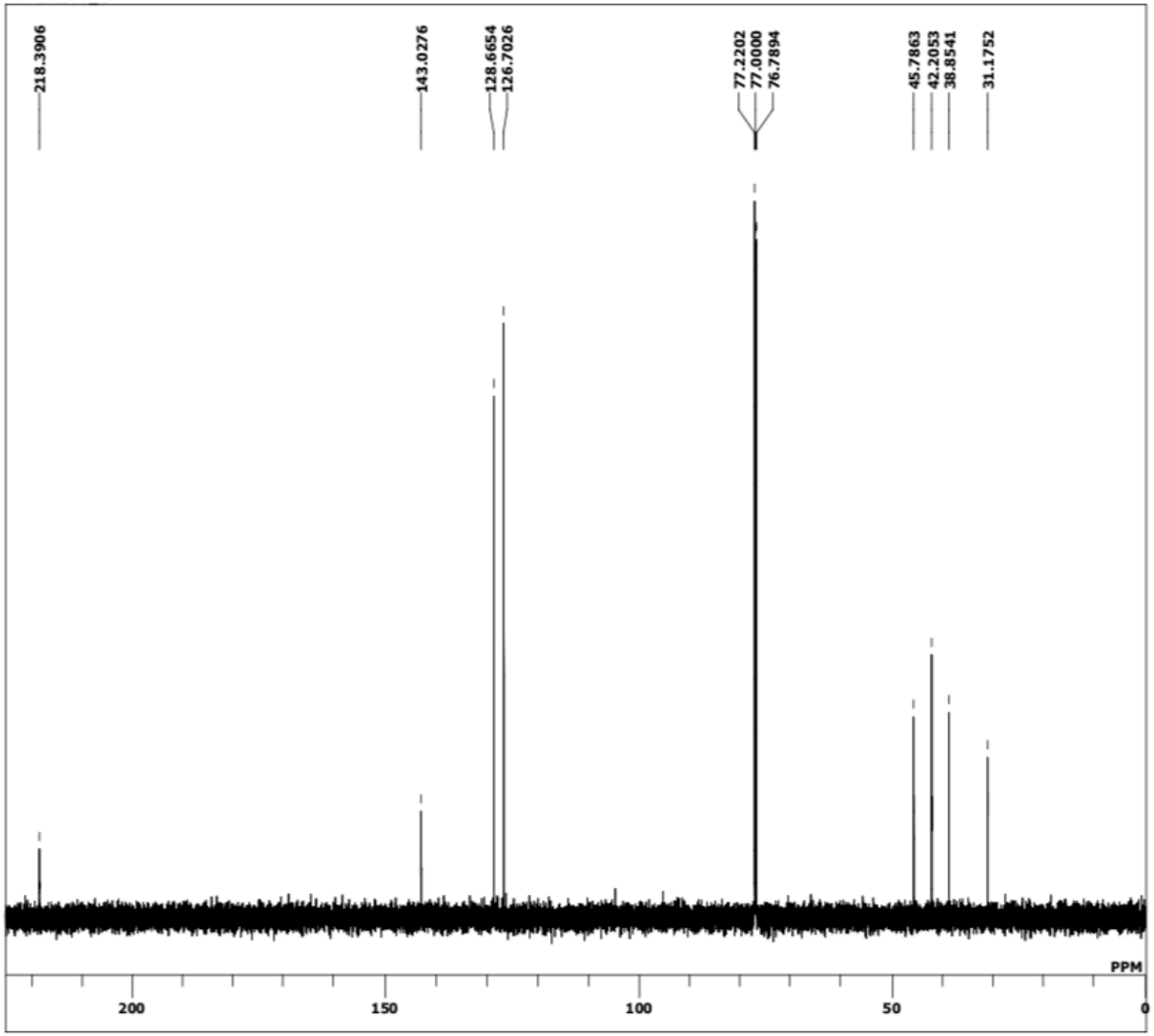

O
Ph

5da

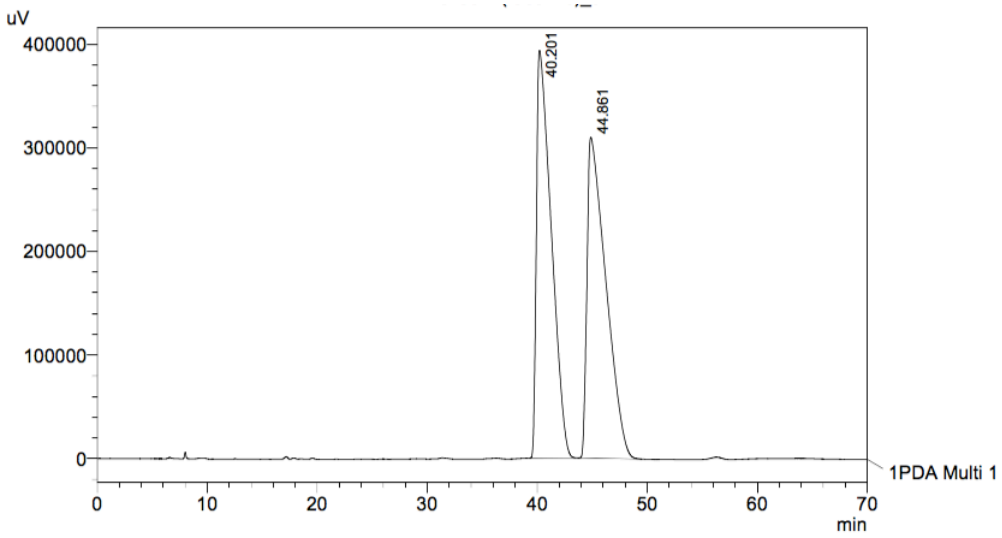

7.3602
7.3465
7.3351
7.2675
7.2583
7.2549
7.2400
3.4550
3.4436
3.4367
3.4253
3.4138
3.4069
3.3955
2.6957
2.6831
2.6660
2.6534
2.4942
2.4782
2.4747
2.4713
2.4610
2.4530
2.4495
2.4426
2.4392
2.4358
2.4323
2.4278
2.4255
2.3728
2.3533
2.3419
2.3235
2.3098
2.2961
2.2926
2.2766
2.0315
2.0166
2.0109
1.9983
1.9937
1.9914
1.9765
1.9594
1.6112
3.0056
2.0059
2.0792
2.1578
1.0000
1.0064
1.0495
PPM
10
8
6
4
2
0


O
Ph

5da


218.3906
143.0276
128.6654
126.7026
77.2202
77.0000
76.7894
45.7863
42.2053
38.8541
31.1752
PPM
200
150
100
50
0

5da, condition : AS-H, 0.5 ml/min, Hex/IPA = 99:1, 220 nm

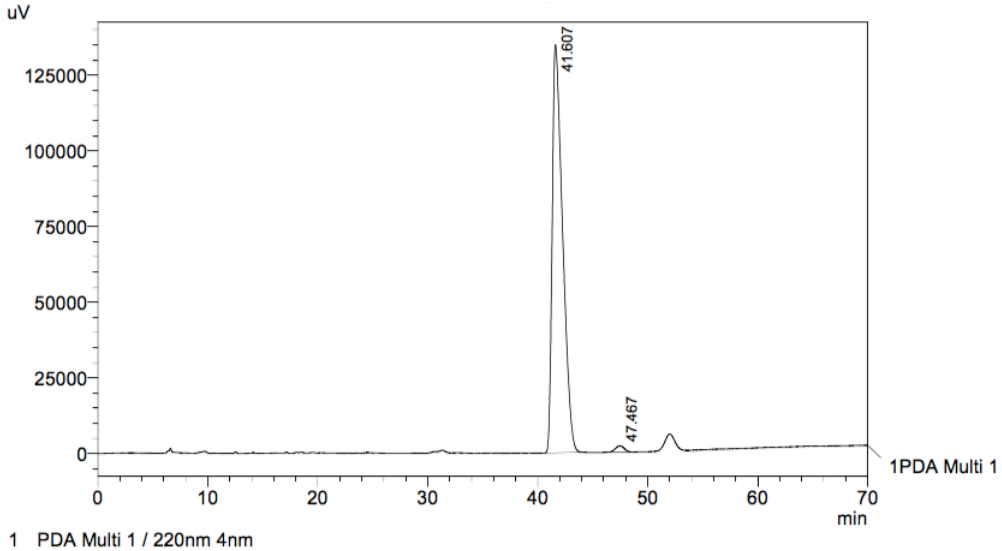


1 PDA Multi 1 / 220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.201	36813230	393492	49.918	55.965
2	44.861	36934669	309614	50.082	44.035
Total		73747899	703106	100.000	100.000

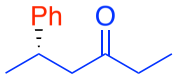


1 PDA Multi 1 / 220nm 4nm

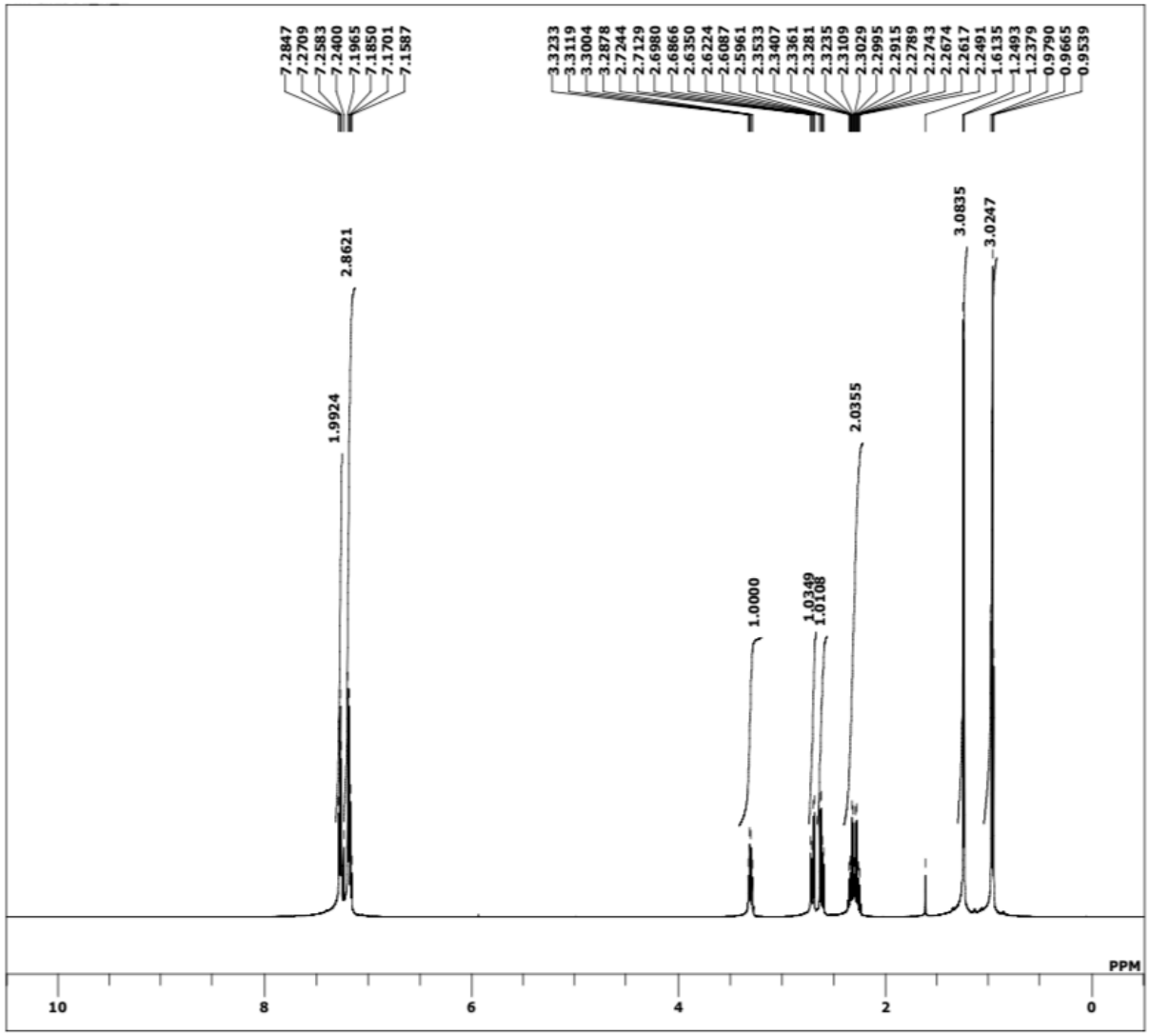
PeakTable

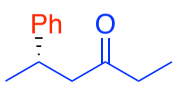
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	41.607	8838124	134857	98.696	98.472
2	47.467	116805	2093	1.304	1.528
Total		8954928	136949	100.000	100.000

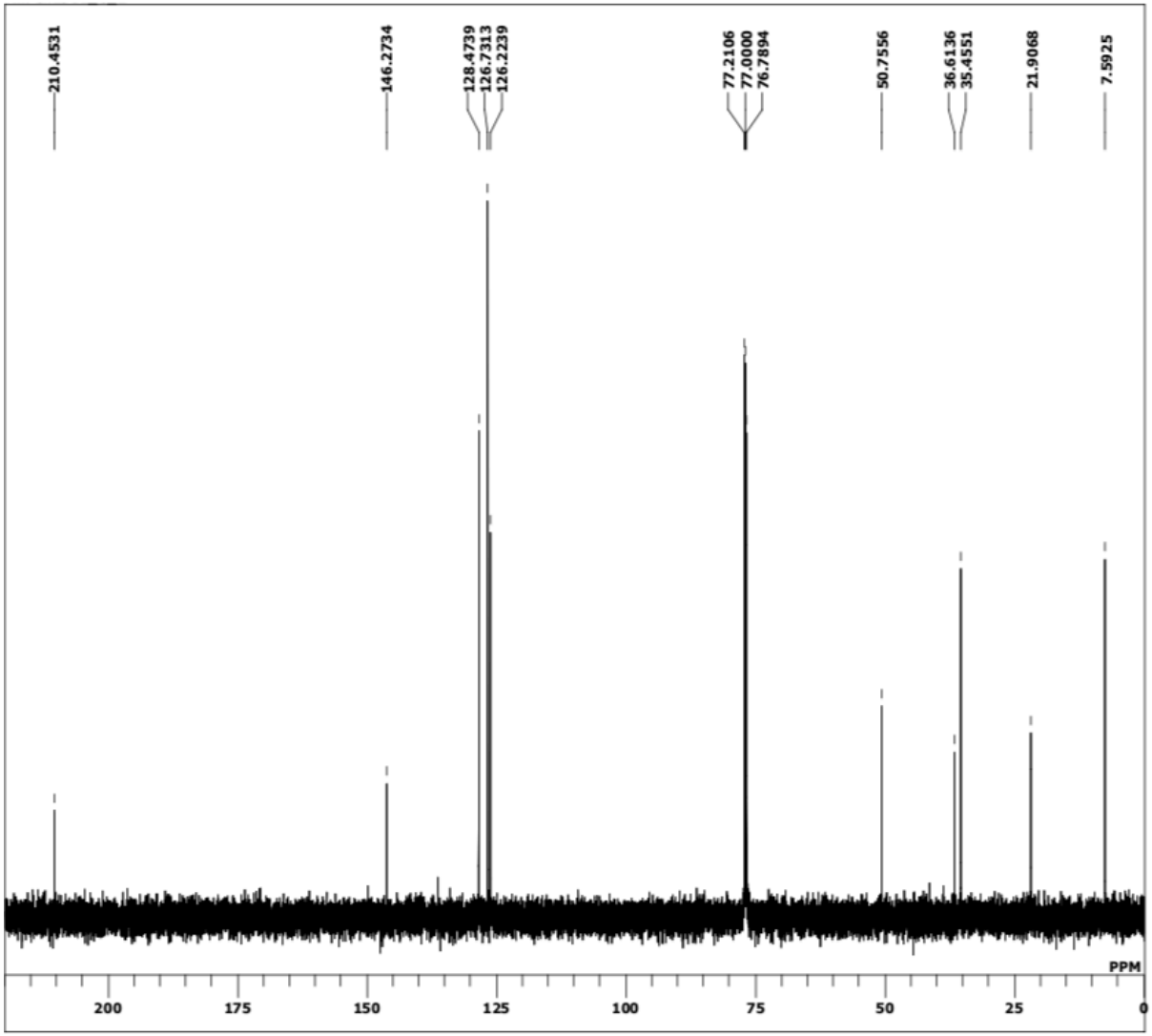

Ph
O

5ea

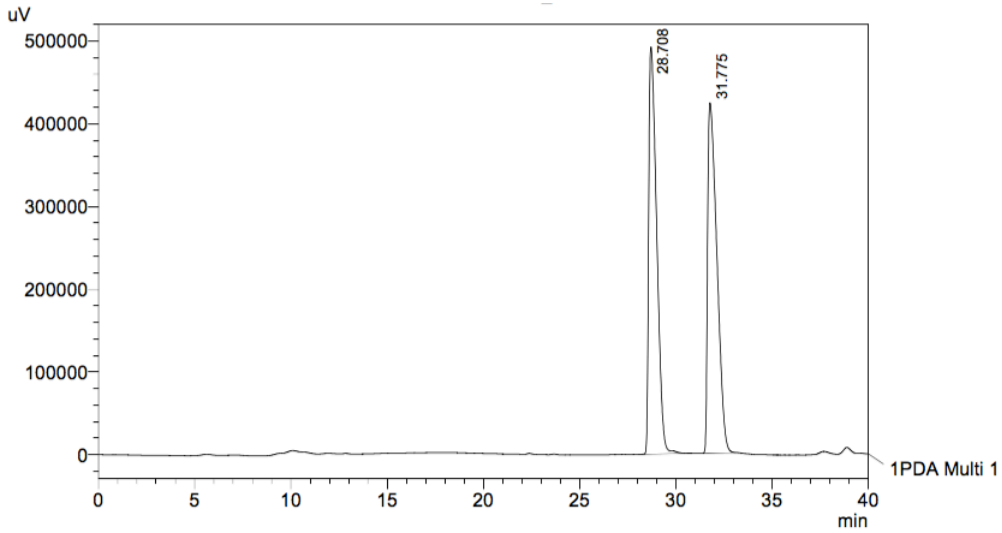

7.2847
7.2709
7.2583
7.2400
7.1965
7.1850
7.1701
7.1587
3.3233
3.3119
3.3004
3.2878
3.2744
3.2129
3.2980
3.2866
3.2350
3.2224
3.2087
3.1961
3.1533
3.1407
3.1361
3.1281
3.1235
3.1109
3.1029
3.0995
3.0915
3.0789
3.0743
3.0674
3.0617
3.0491
3.0135
3.0493
3.0379
3.0790
3.0665
3.0539
2.8621
1.9924
3.0835
3.0247
2.0355
1.0000
1.0349
1.0108
PPM
10
8
6
4
2
0


Ph
O

5ea


210.4531
146.2734
128.4739
126.7313
126.2239
77.2106
77.0000
76.7894
50.7556
36.6136
35.4551
21.9068
7.5925
PPM
200
175
150
125
100
75
50
25
0

5ea, condition : AD-H_AD-3 (connected column), 0.5 ml/min, Hex/IPA = 99.5:0.5, 220 nm

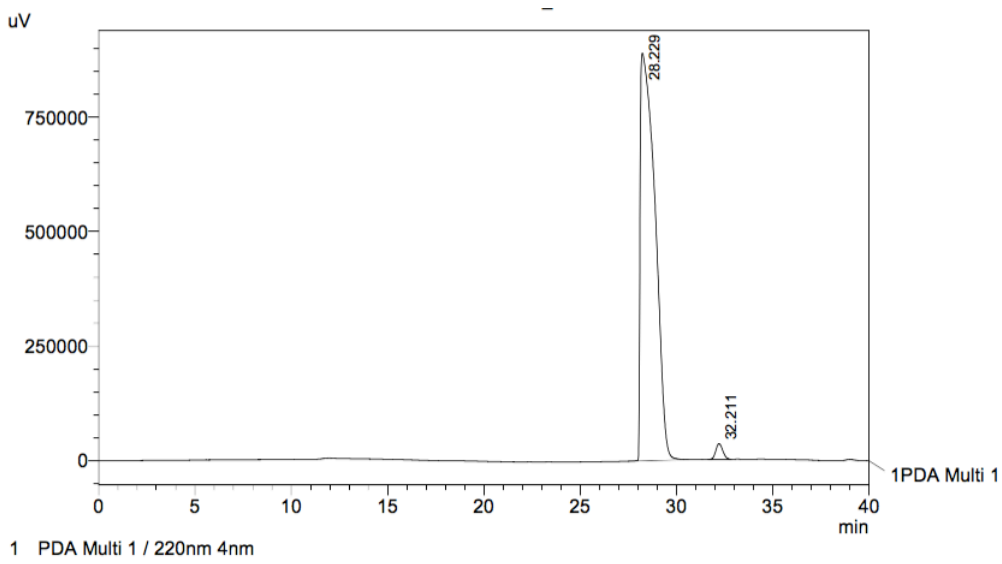


1 PDA Multi 1 / 220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.708	14200732	492260	49.992	53.745
2	31.775	14205429	423659	50.008	46.255
Total		28406162	915919	100.000	100.000

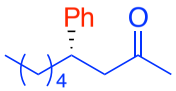


1 PDA Multi 1 / 220nm 4nm

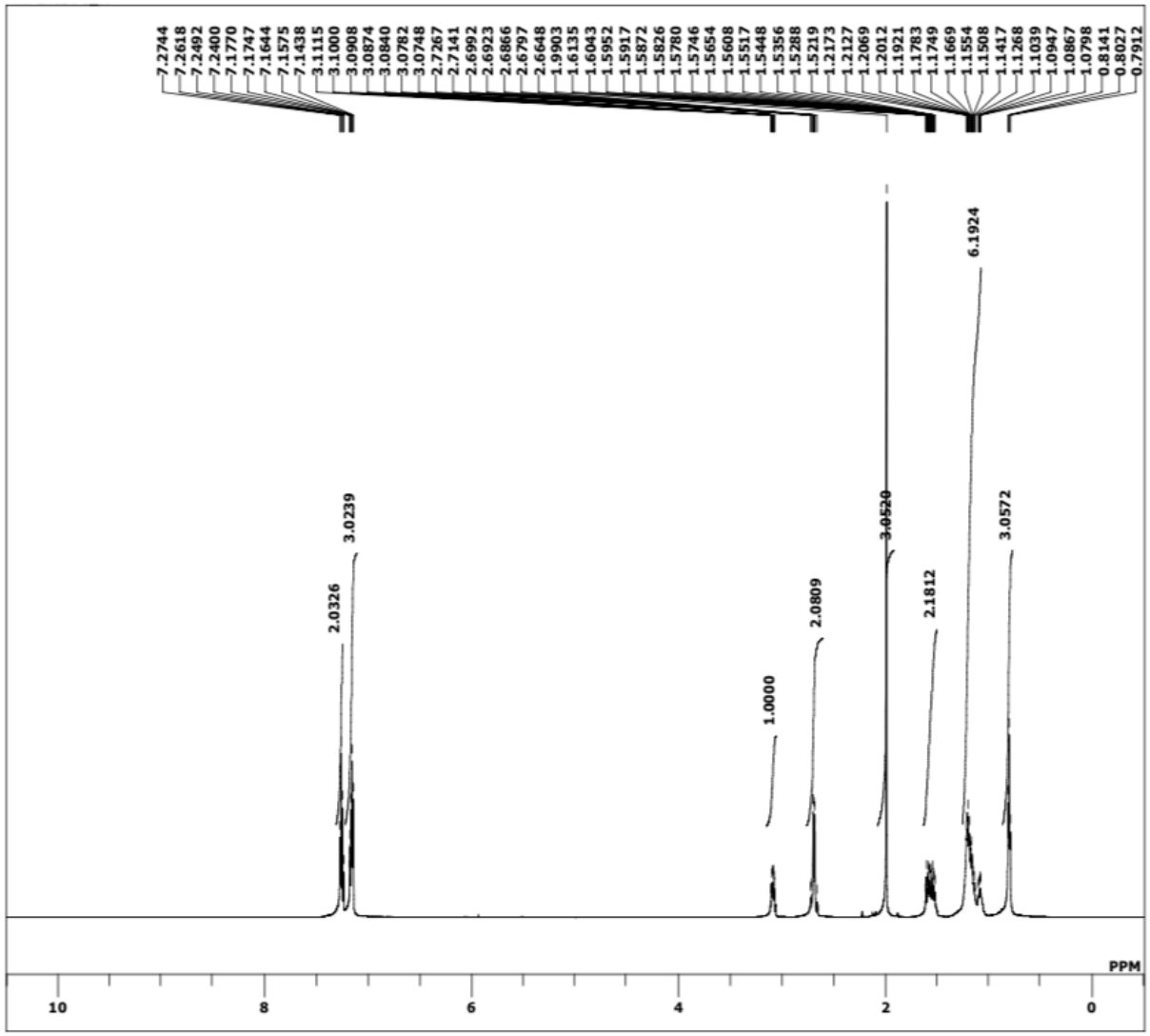
PeakTable

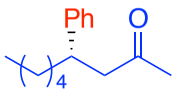
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.229	47254796	890084	98.192	96.281
2	32.211	870304	34381	1.808	3.719
Total		48125101	924465	100.000	100.000

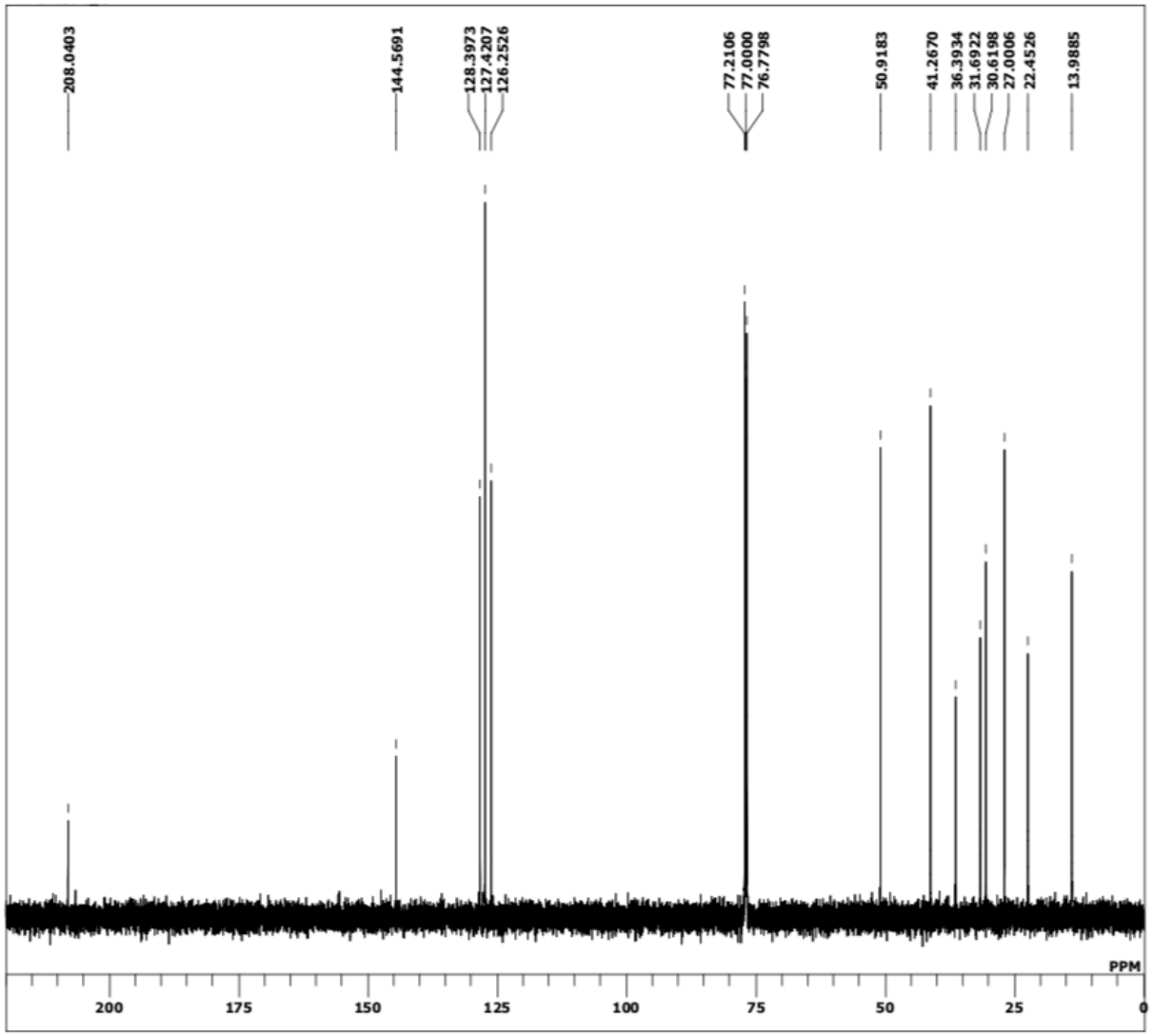

Ph
O
4

5fa

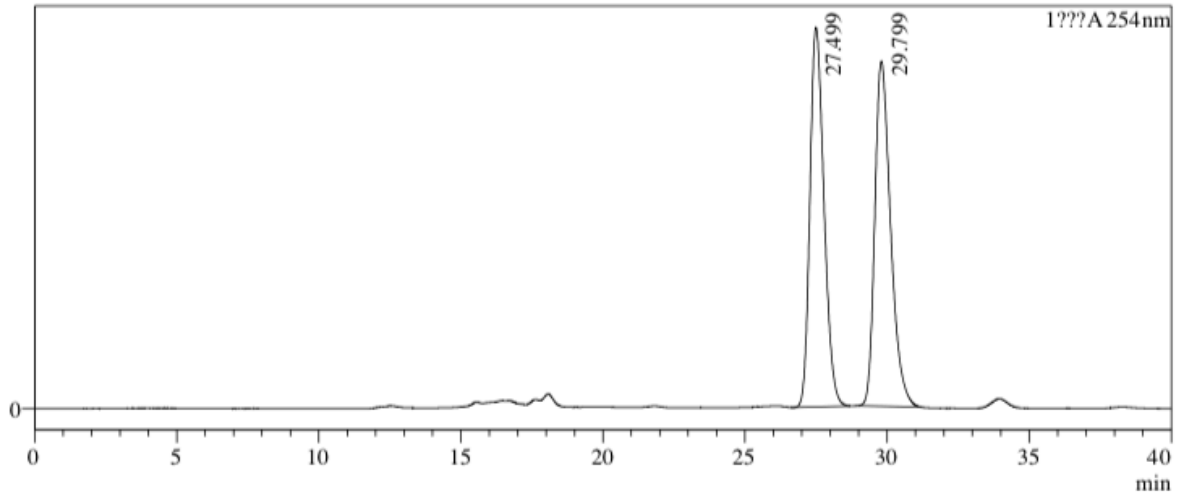

7.2744
7.2618
7.2492
7.2400
7.1770
7.1747
7.1644
7.1575
7.1438
3.1115
3.1000
3.0908
3.0874
3.0840
3.0782
3.0748
2.7267
2.7141
2.6992
2.6923
2.6866
2.6797
2.6648
1.9903
1.6135
1.6043
1.5952
1.5917
1.5872
1.5826
1.5780
1.5746
1.5654
1.5608
1.5517
1.5448
1.5356
1.5288
1.5219
1.2173
1.2127
1.2069
1.2012
1.1921
1.1783
1.1749
1.1669
1.1554
1.1508
1.1417
1.1268
1.1039
1.0947
1.0867
1.0798
0.8141
0.8027
0.7912
2.0326
3.0239
1.0000
2.0809
3.0520
2.1812
6.1924
3.0572
PPM
10
8
6
4
2
0


Ph
O
4

5fa

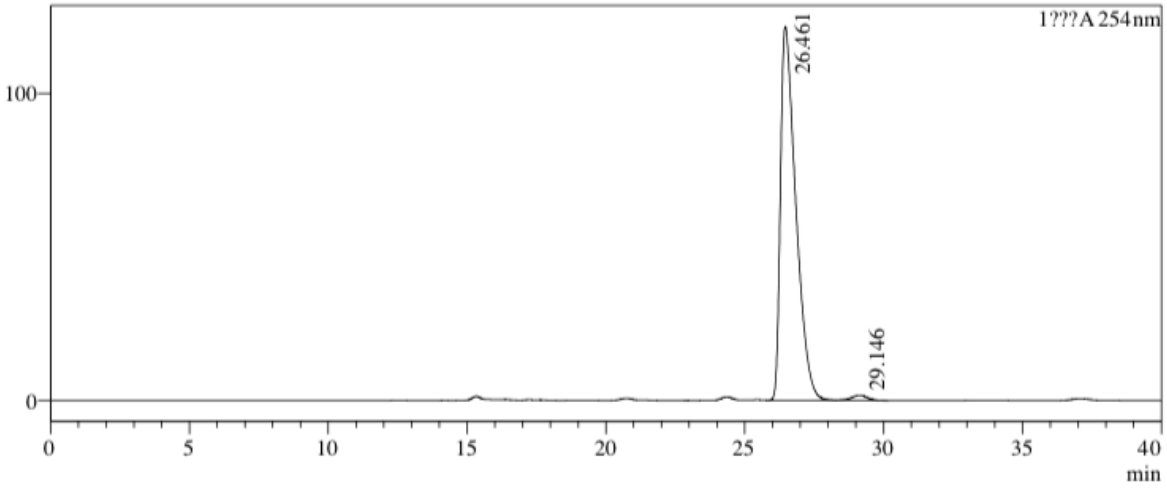

208.0403
144.5691
128.3973
127.4207
126.2526
77.2106
77.0000
76.7798
50.9183
41.2670
36.3934
31.6922
30.6198
27.0006
22.4526
13.9885
PPM
200
175
150
125
100
75
50
25
0

5fa, condition : OJ-H, 0.25 ml/min, Hex/IPA = 99:1, 254 nm



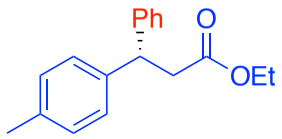
???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	27.499	719940	20908	49.470
2	29.799	735377	19004	50.530

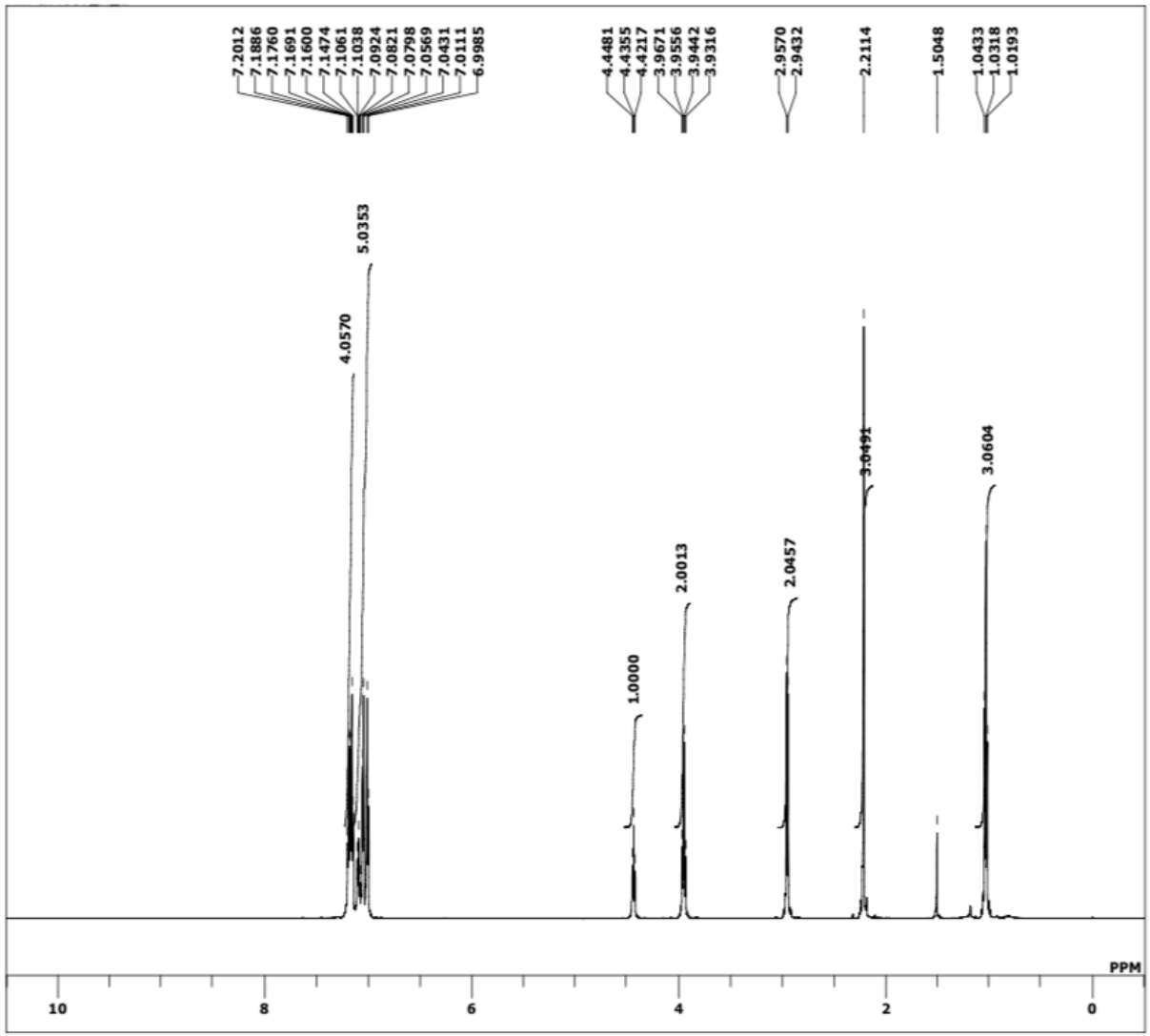


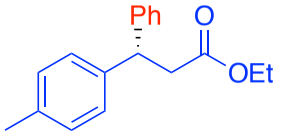
???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	26.461	4681759	121601	98.516
2	29.146	70530	1706	1.484

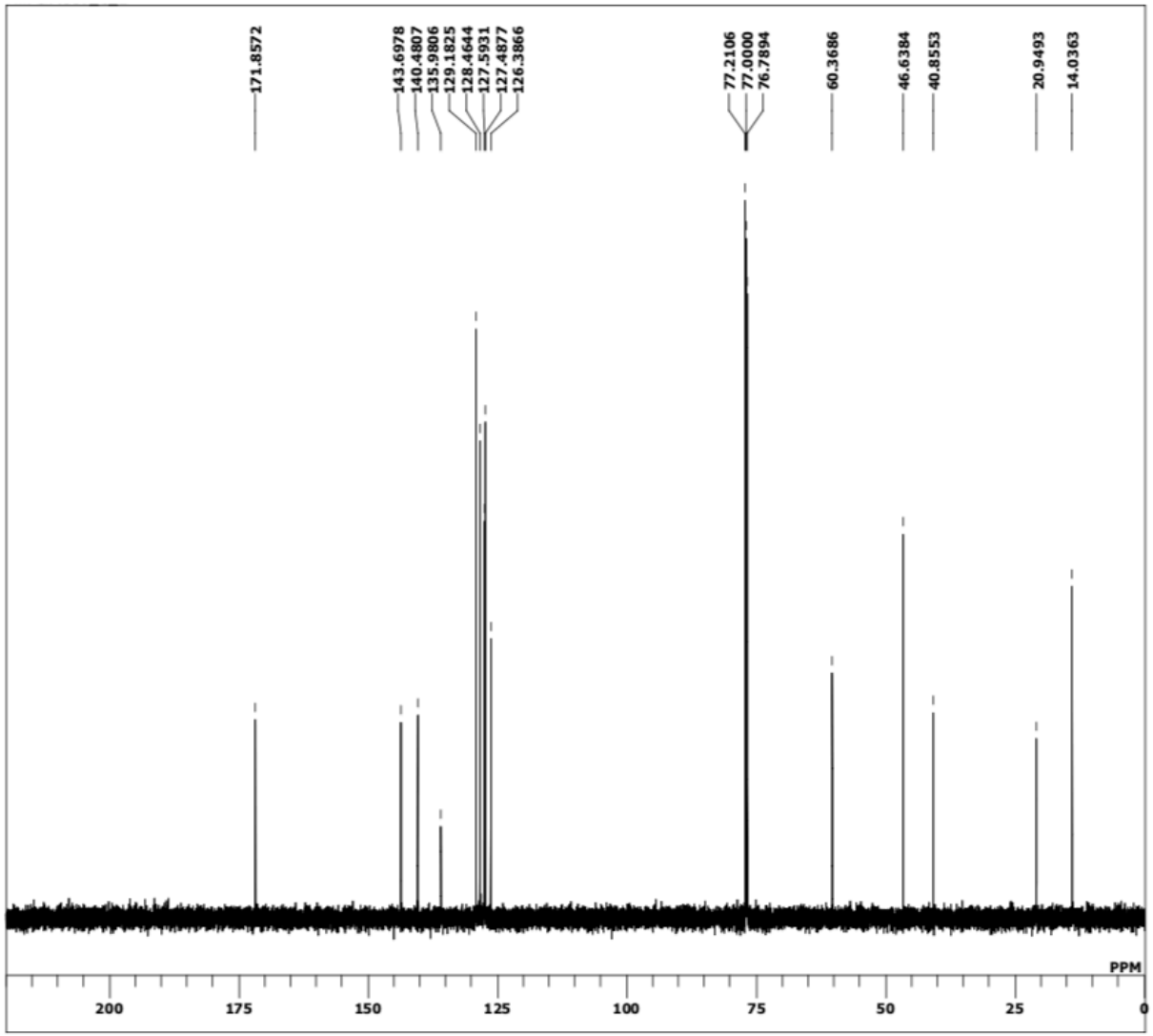

Ph
O
OEt

5ga

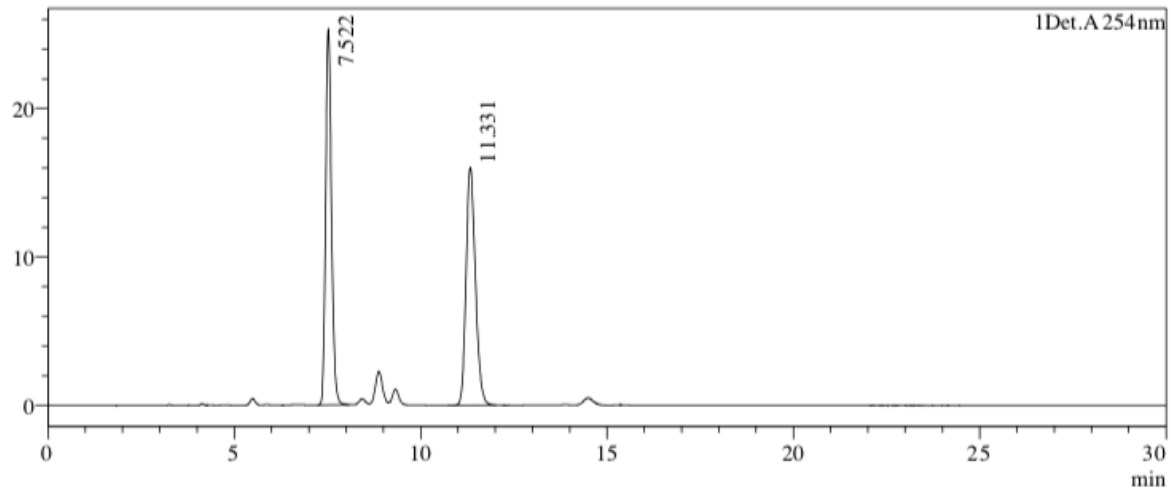

7.2012
7.1886
7.1760
7.1691
7.1600
7.1474
7.1061
7.1038
7.0924
7.0821
7.0798
7.0569
7.0431
7.0111
6.9985
4.4481
4.4355
4.4217
3.9671
3.9556
3.9442
3.9316
2.9570
2.9432
2.2114
1.5048
1.0433
1.0318
1.0193
5.0353
4.0570
1.0000
2.0013
2.0457
3.0491
3.0604
PPM
10
8
6
4
2
0


Ph
O
OEt

5ga

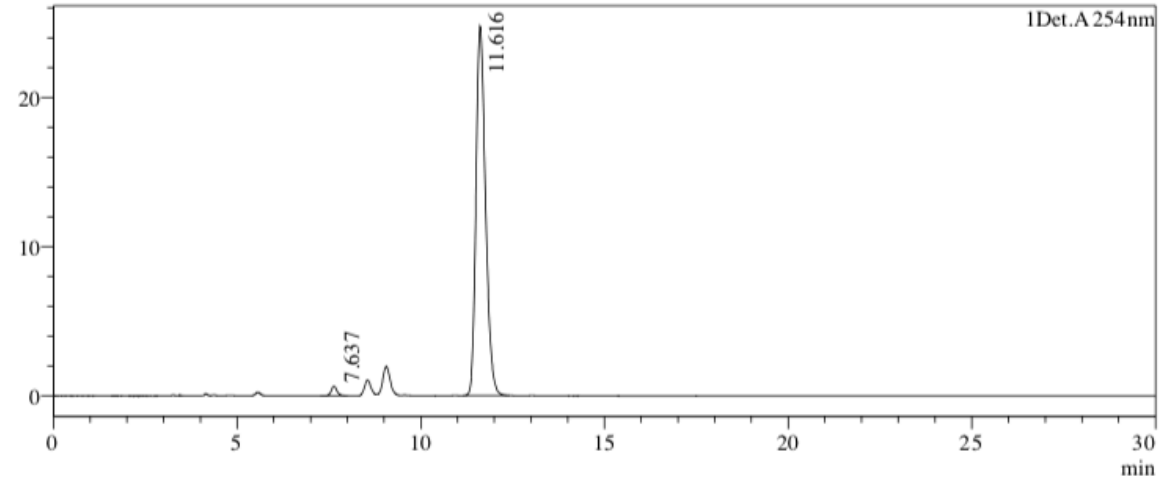

171.8572
143.6978
140.4807
135.9806
129.1825
128.4644
127.5931
127.4877
126.3866
77.2106
77.0000
76.7894
60.3686
46.6384
40.8553
20.9493
14.0363
PPM
200
175
150
125
100
75
50
25
0

5ga, condition : OD-H, 1.0 ml/min, Hex/IPA = 99:1, 254 nm



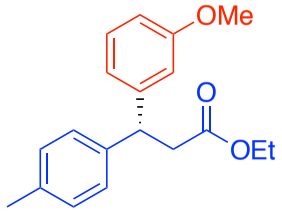
Det.A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.522	276217	25291	49.779
2	11.331	278673	16010	50.221

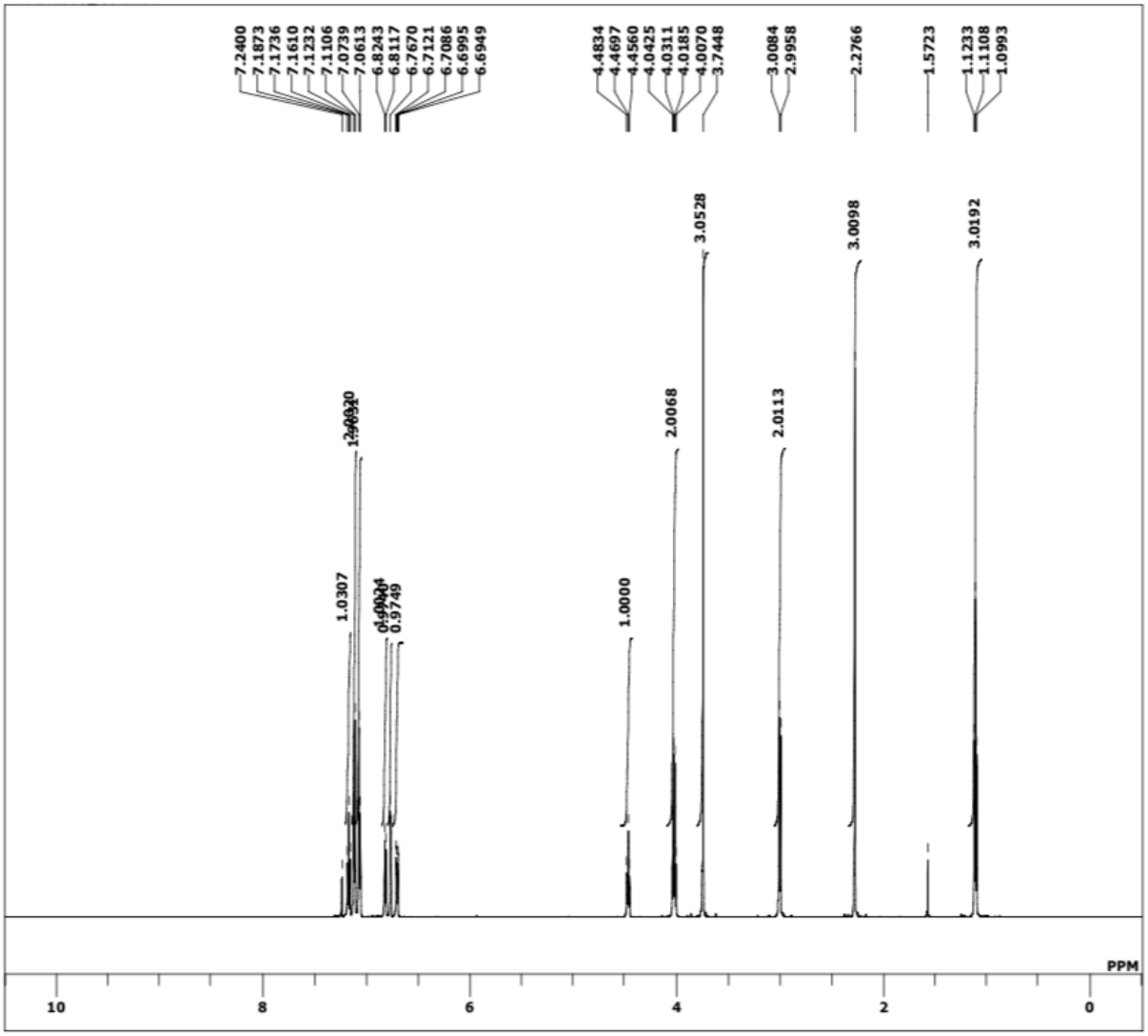


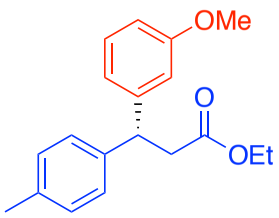
Det.A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.637	6842	625	1.504
2	11.616	447990	24731	98.496

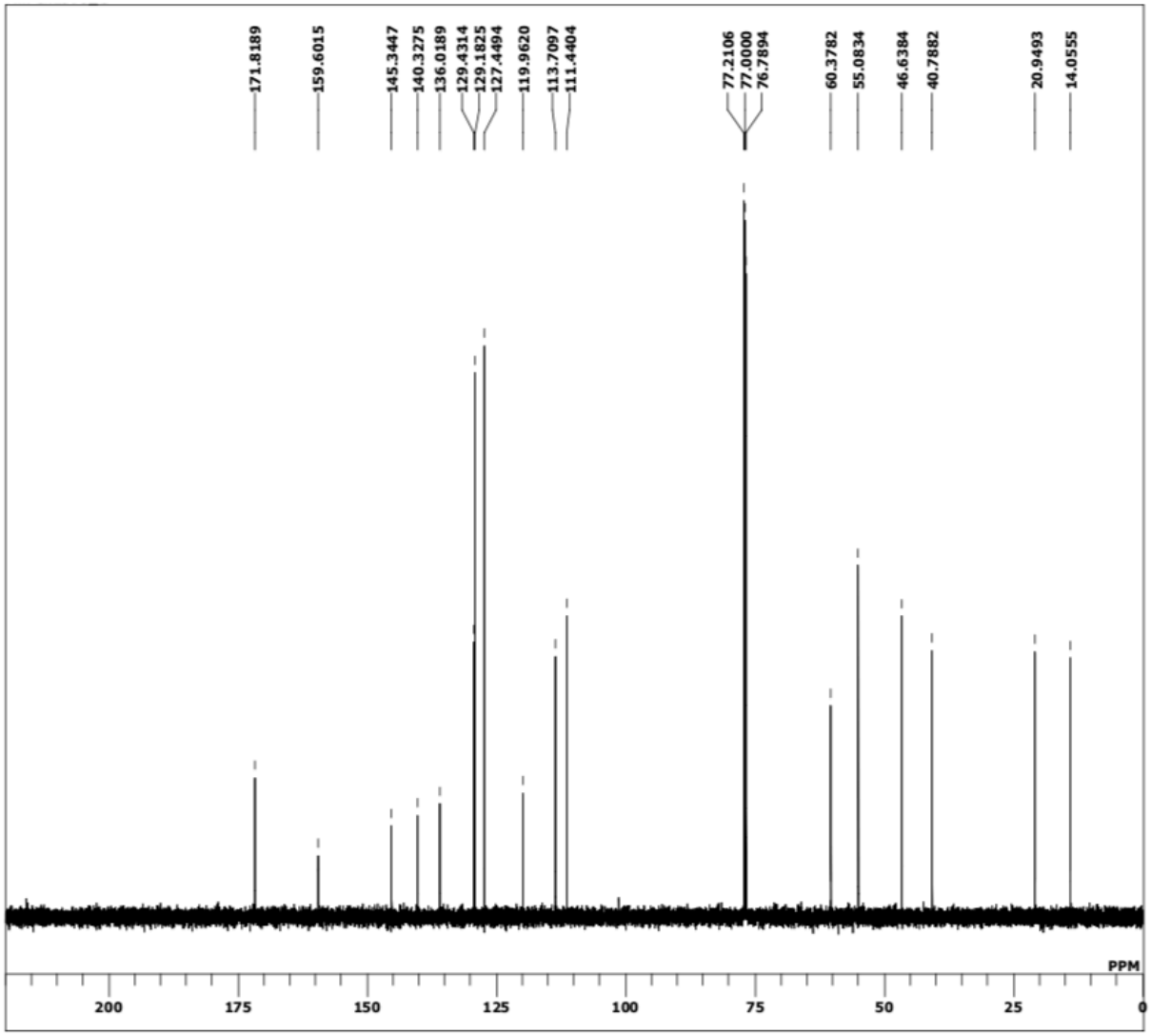

OMe
O
OEt

5gc

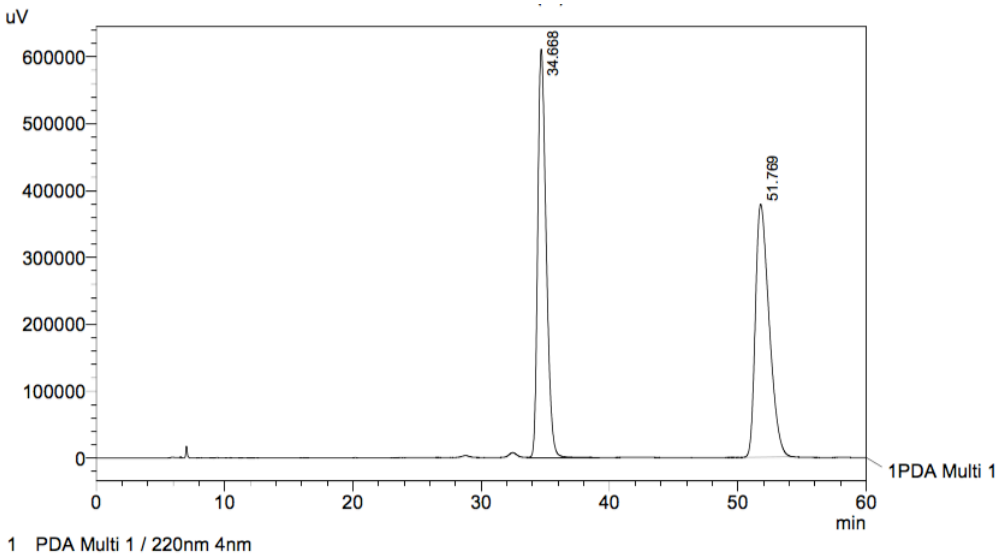

7.2400
7.1873
7.1736
7.1610
7.1232
7.1106
7.0739
7.0613
6.8243
6.8117
6.7670
6.7121
6.7086
6.6995
6.6949
4.4834
4.4697
4.4560
4.0425
4.0311
4.0185
4.0070
3.7448
3.0084
2.9958
2.2766
1.5723
1.1233
1.1108
1.0993
3.0528
3.0098
3.0192
2.0068
2.0113
1.0307
0.9749
1.0000
PPM
10
8
6
4
2
0


OMe
O
OEt

5gc


171.8189
159.6015
145.3447
140.3275
136.0189
129.4314
129.1825
127.4494
119.9620
113.7097
111.4404
77.2106
77.0000
76.7894
60.3782
55.0834
46.6384
40.7882
20.9493
14.0555
PPM
200
175
150
125
100
75
50
25
0

5gc, condition : OD-H, 0.5 ml/min, Hex/IPA = 99:1, 220 nm

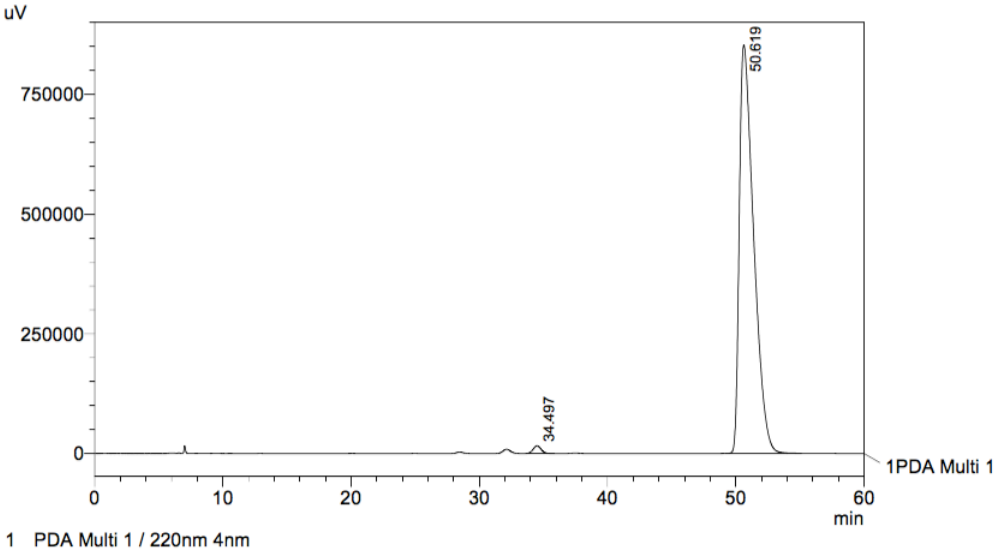


1 PDA Multi 1 / 220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.668	27896217	610224	49.734	61.733
2	51.769	28194059	378267	50.266	38.267
Total		56090276	988491	100.000	100.000

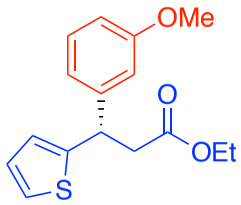


1 PDA Multi 1 / 220nm 4nm

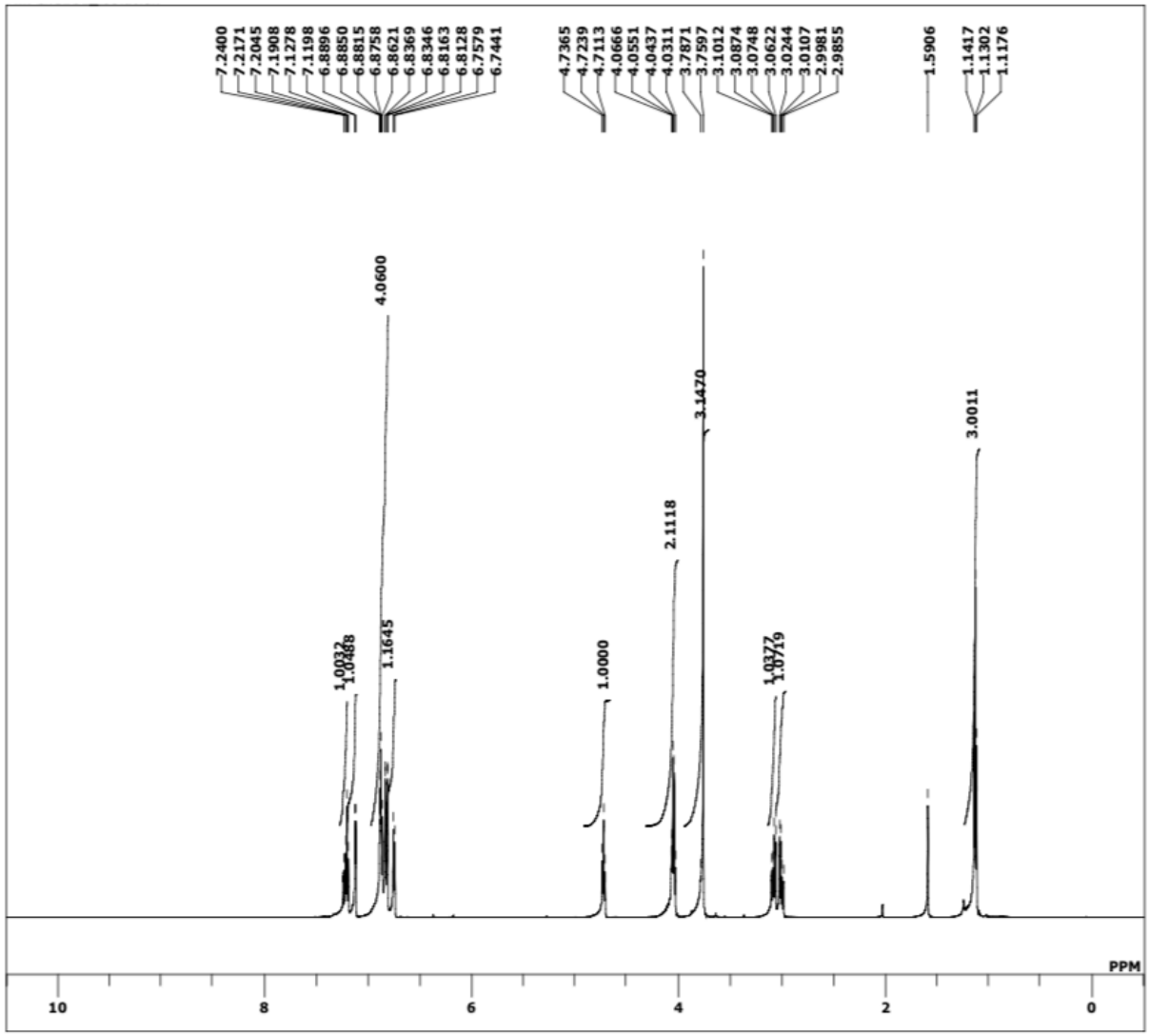
PeakTable

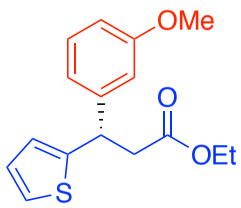
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.497	719026	16390	1.073	1.886
2	50.619	66271654	852563	98.927	98.114
Total		66990679	868953	100.000	100.000

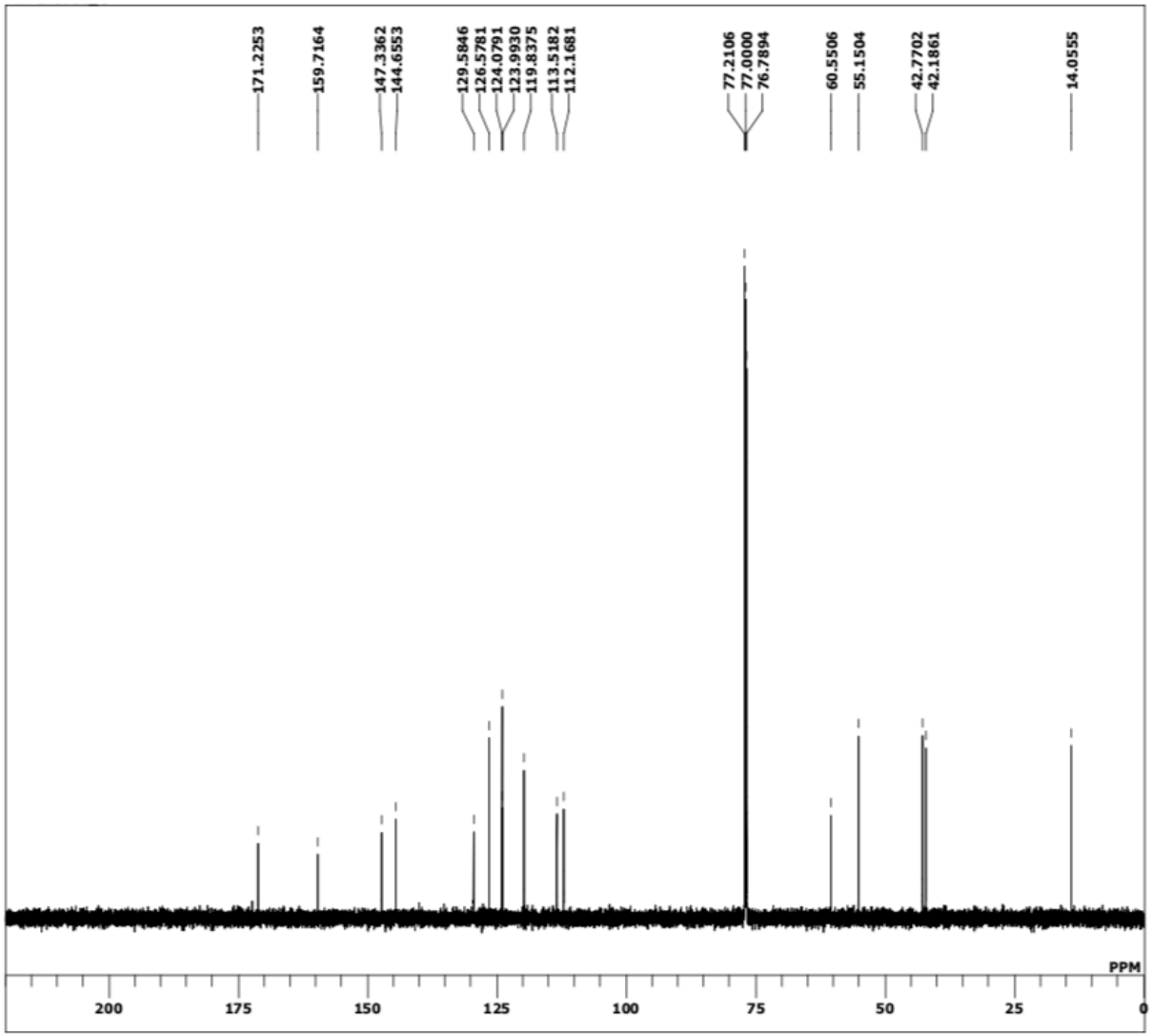

OMe
O
OEt
S

5hc

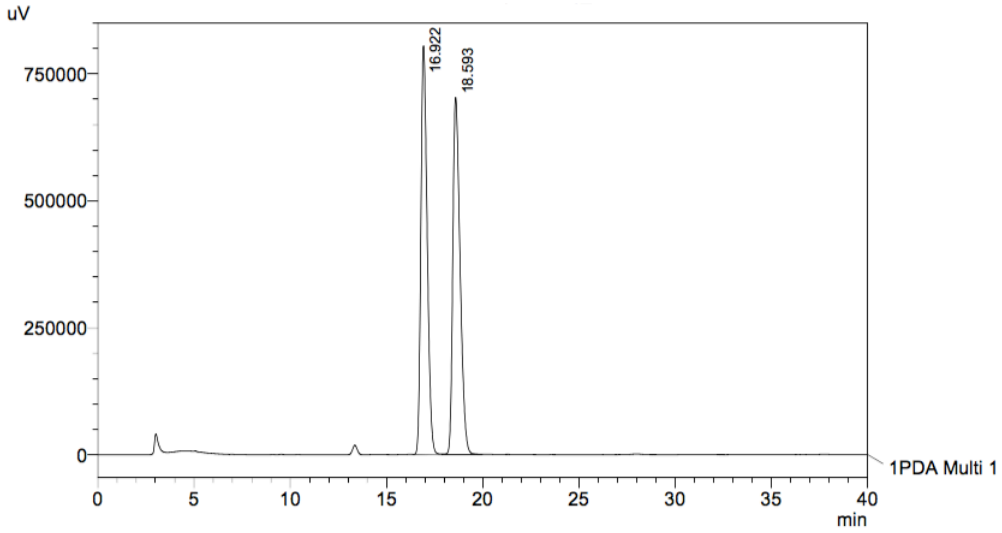

7.2400
7.2171
7.2045
7.1908
7.1278
7.1198
6.8896
6.8850
6.8815
6.8758
6.8621
6.8369
6.8346
6.8163
6.8128
6.7579
6.7441
4.7365
4.7239
4.7113
4.0666
4.0551
4.0437
4.0311
3.7871
3.7597
3.1012
3.0874
3.0748
3.0622
3.0244
3.0107
2.9981
2.9855
1.5906
1.1417
1.1302
1.1176
4.0600
3.1470
3.0011
2.1118
1.1645
1.0488
1.0000
1.0377
1.0179
PPM
10
8
6
4
2
0


OMe
O
OEt
S

5hc


171.2253
159.7164
147.3362
144.6553
129.5846
126.5781
124.0791
123.9930
119.8375
113.5182
112.1681
77.2106
77.0000
76.7894
60.5506
55.1504
42.7702
42.1861
14.0555
PPM
200
175
150
125
100
75
50
25
0

5hc, condition : OD-H, 1.0 ml/min, Hex/IPA = 99:1, 220 nm

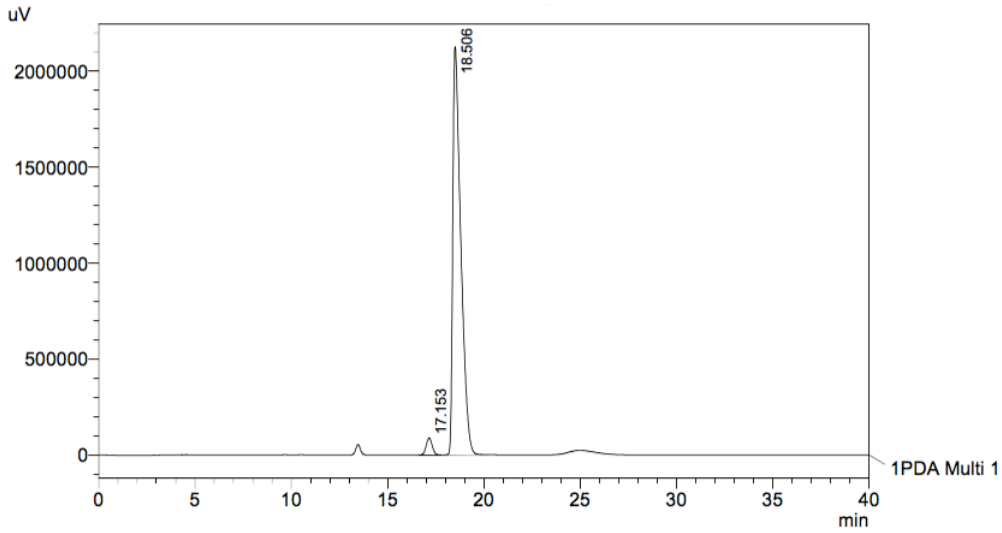


1 PDA Multi 1 / 220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.922	18335675	804583	49.841	53.375
2	18.593	18452552	702833	50.159	46.625
Total		36788227	1507416	100.000	100.000

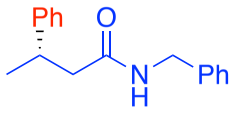


1 PDA Multi 1 / 220nm 4nm

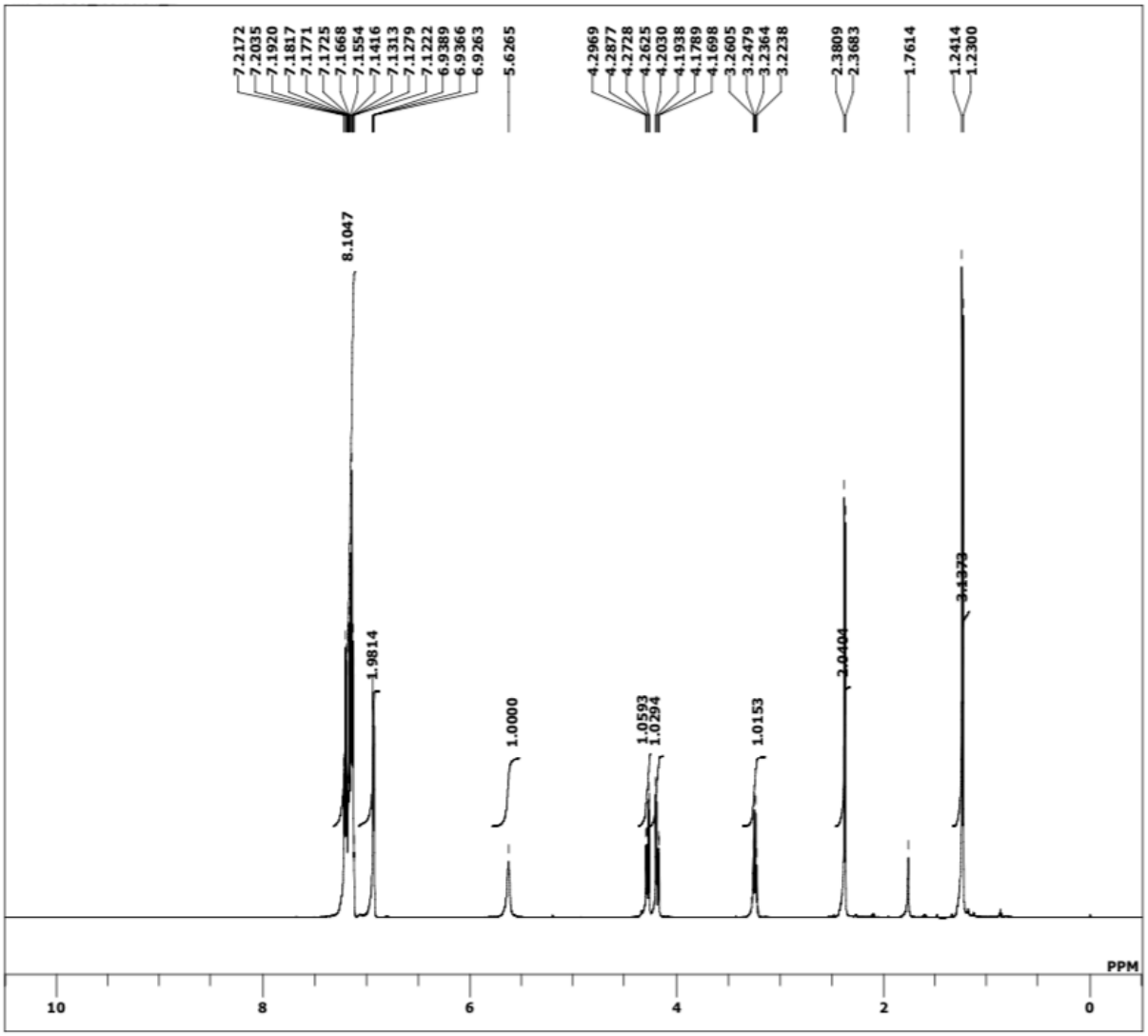
PeakTable

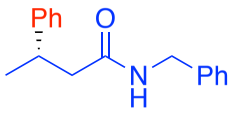
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.153	1927036	88964	3.026	4.013
2	18.506	61765505	2128137	96.974	95.987
Total		63692541	2217101	100.000	100.000

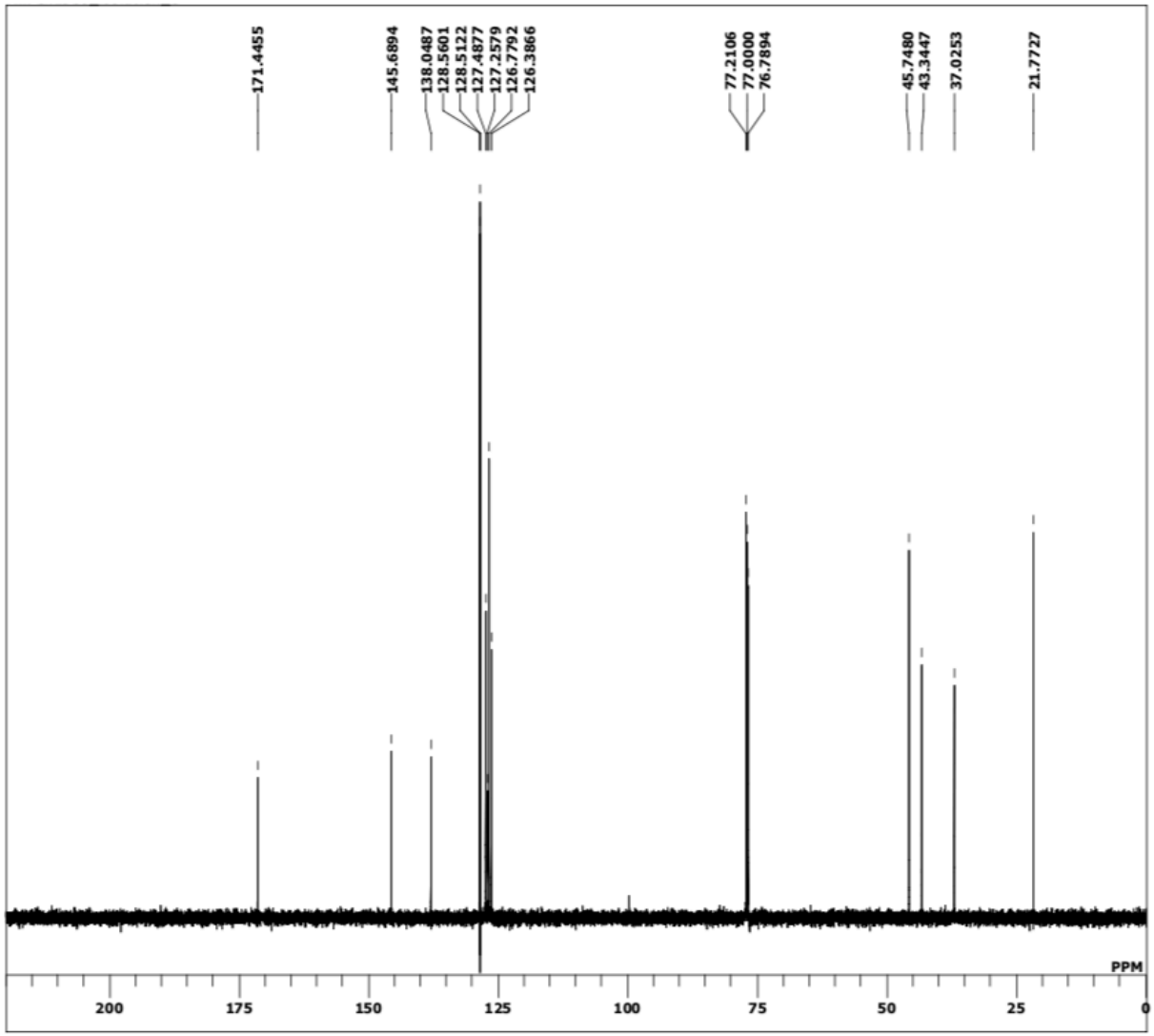

Ph
O
N
H
Ph

5ia

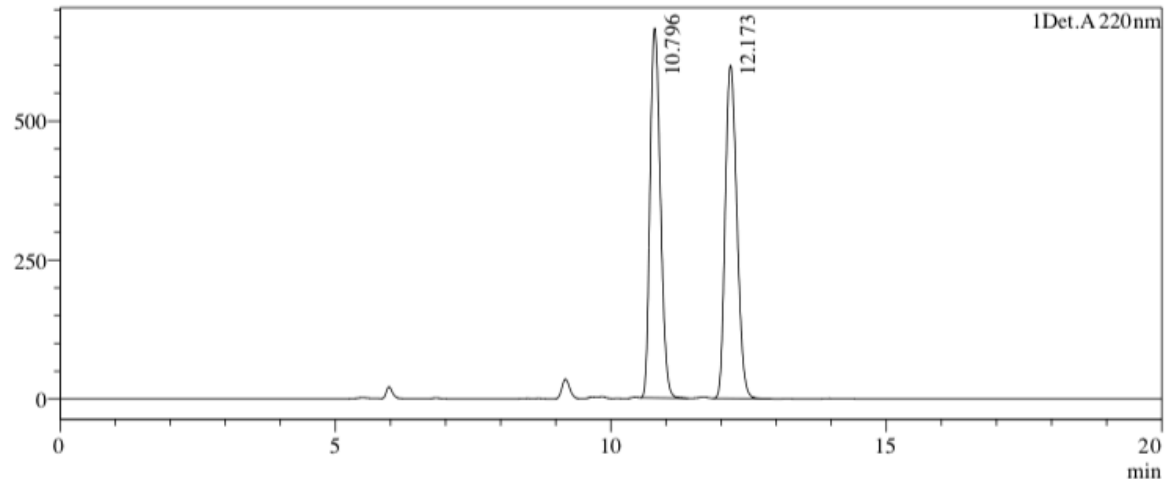

7.2172
7.2035
7.1920
7.1817
7.1771
7.1725
7.1668
7.1554
7.1416
7.1313
7.1279
7.1222
6.9389
6.9366
6.9263
5.6265
4.2969
4.2877
4.2728
4.2625
4.2030
4.1938
4.1789
4.1698
3.2605
3.2479
3.2364
3.2238
2.3809
2.3683
1.7614
1.2414
1.2300
8.1047
1.9814
1.0000
1.0593
1.0294
1.0153
3.0404
3.1373
PPM
10
8
6
4
2
0


Ph
O
N
H
Ph

5ia

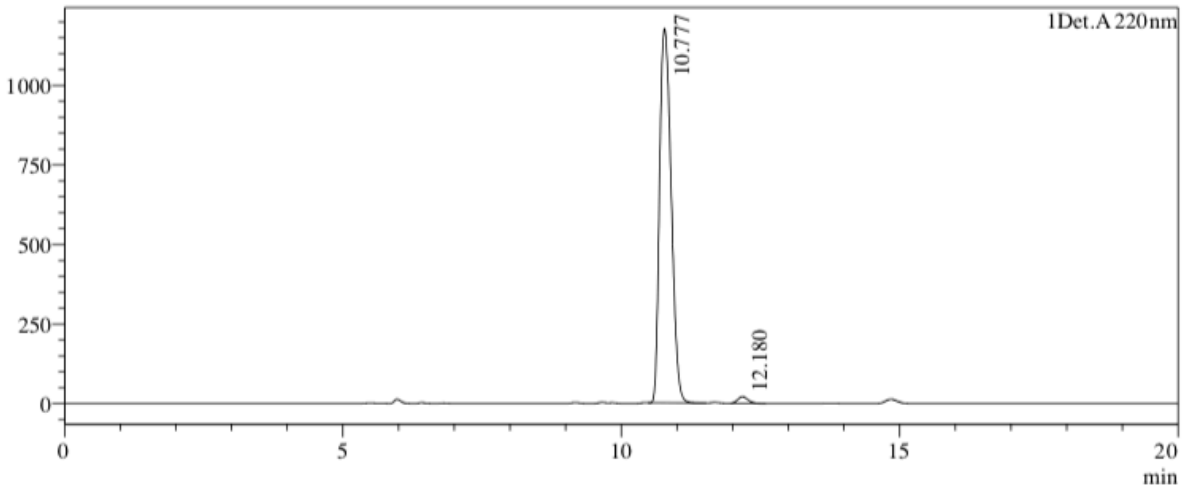

171.4455
145.6894
138.0487
128.5601
128.5122
127.4877
127.2579
126.7792
126.3866
77.2106
77.0000
76.7894
45.7480
43.3447
37.0253
21.7727
PPM
200
175
150
125
100
75
50
25
0

5ia, condition : AD-3, 0.5 ml/min, Hex/IPA = 80:20, 220 nm



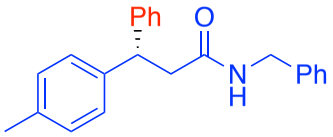
Det.A 220nm

Peak#	Ret. Time	Area	Height	Area%
1	10.796	8716558	664283	49.705
2	12.173	8820015	598687	50.295

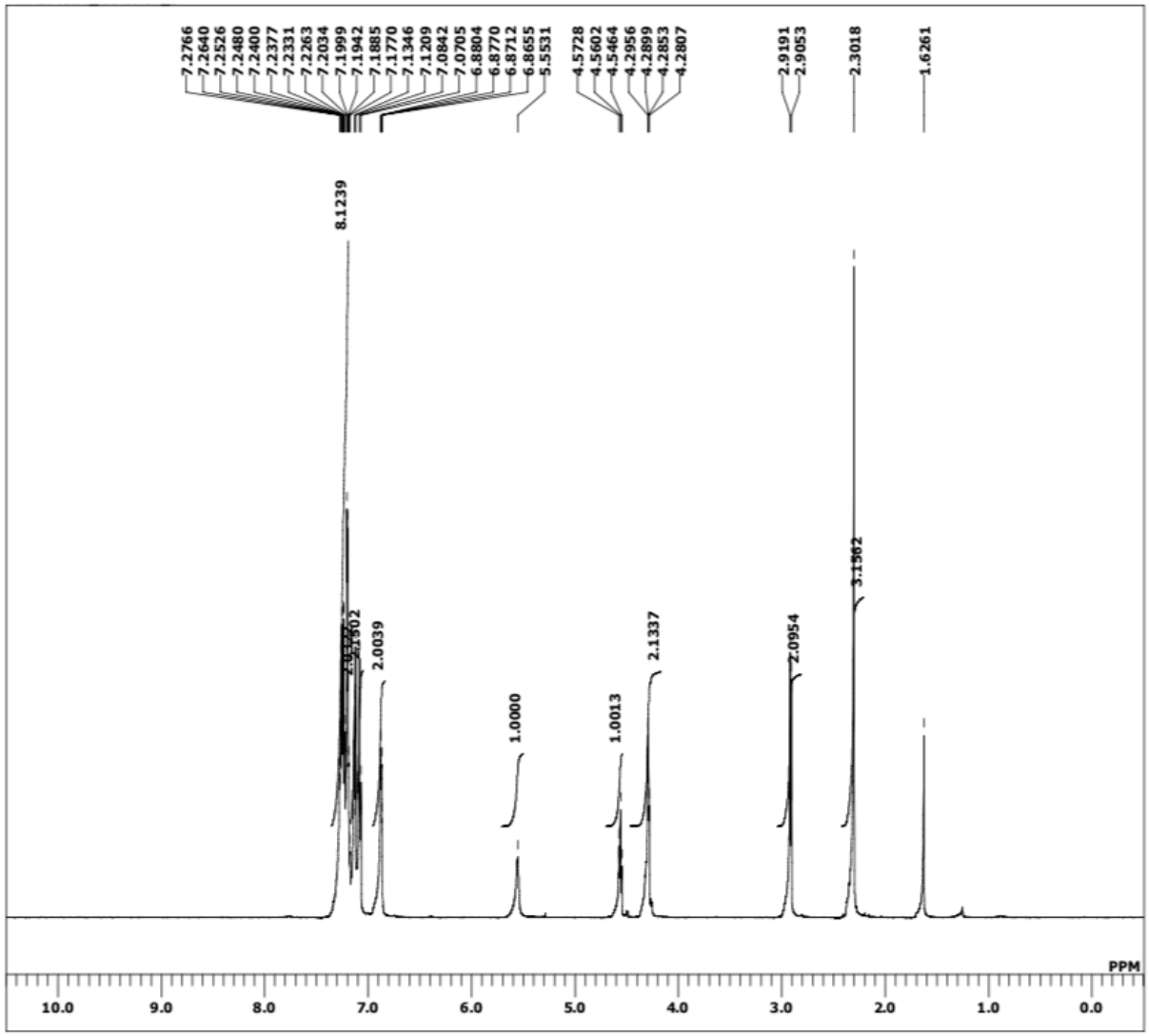


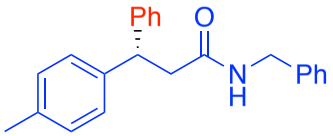
Det.A 220nm

Peak#	Ret. Time	Area	Height	Area%
1	10.777	17070695	1176045	98.397
2	12.180	278099	21281	1.603

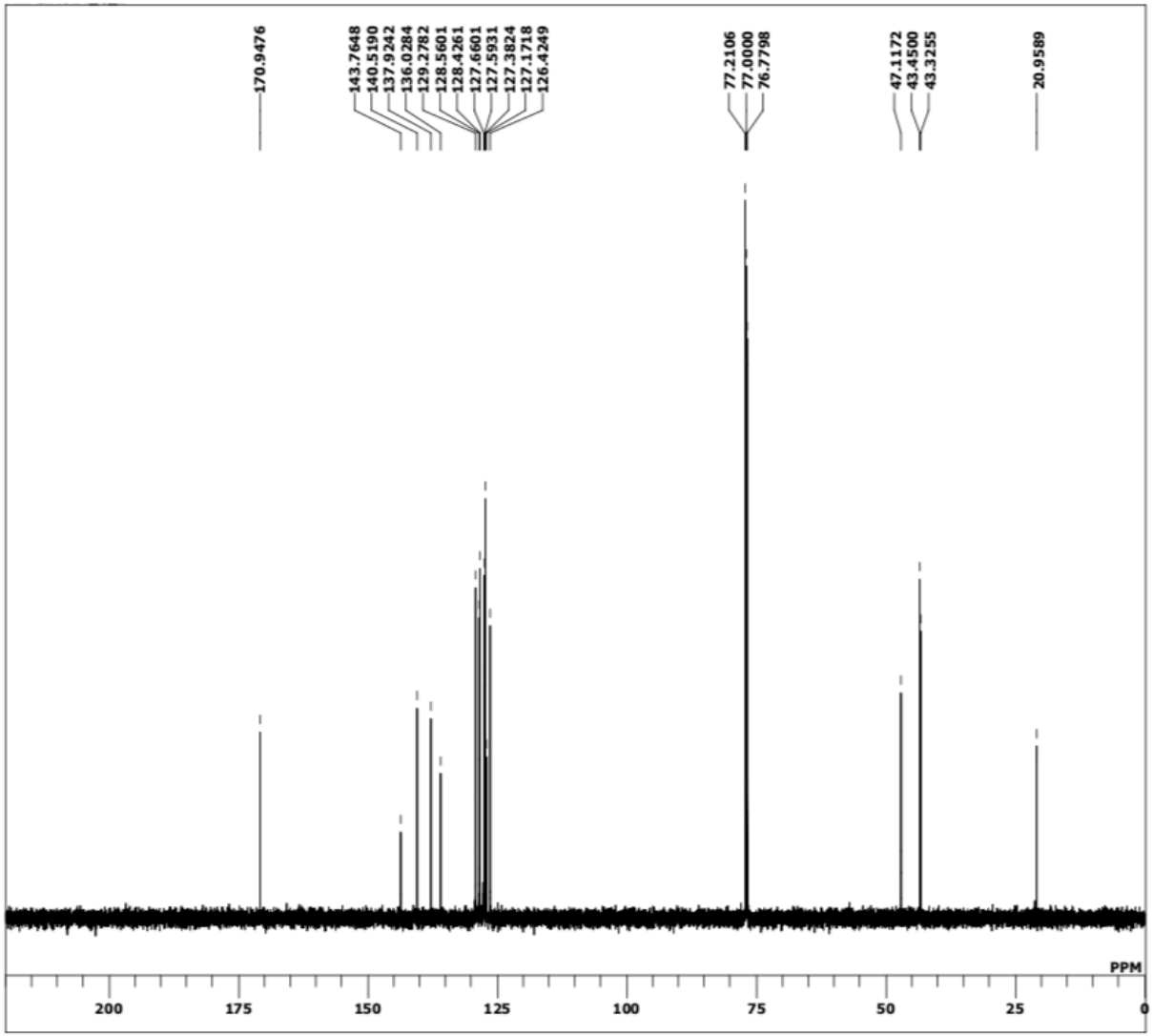

Ph
O
N
H
Ph

5ja

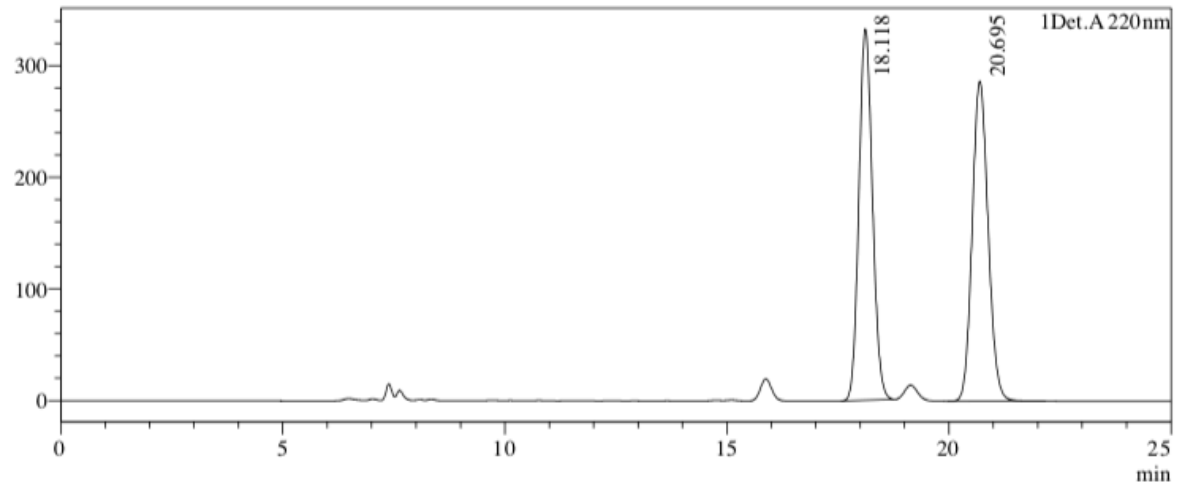

7.2766
7.2640
7.2526
7.2480
7.2400
7.2377
7.2331
7.2263
7.2034
7.1999
7.1942
7.1885
7.1770
7.1346
7.1209
7.0842
7.0705
6.8804
6.8770
6.8712
6.8655
5.5531
4.5728
4.5602
4.5464
4.2956
4.2899
4.2853
4.2807
2.9191
2.9053
2.3018
1.6261
8.1239
2.0039
1.0000
1.0013
2.1337
2.0954
3.1562
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


Ph
O
N
H
Ph

5ja

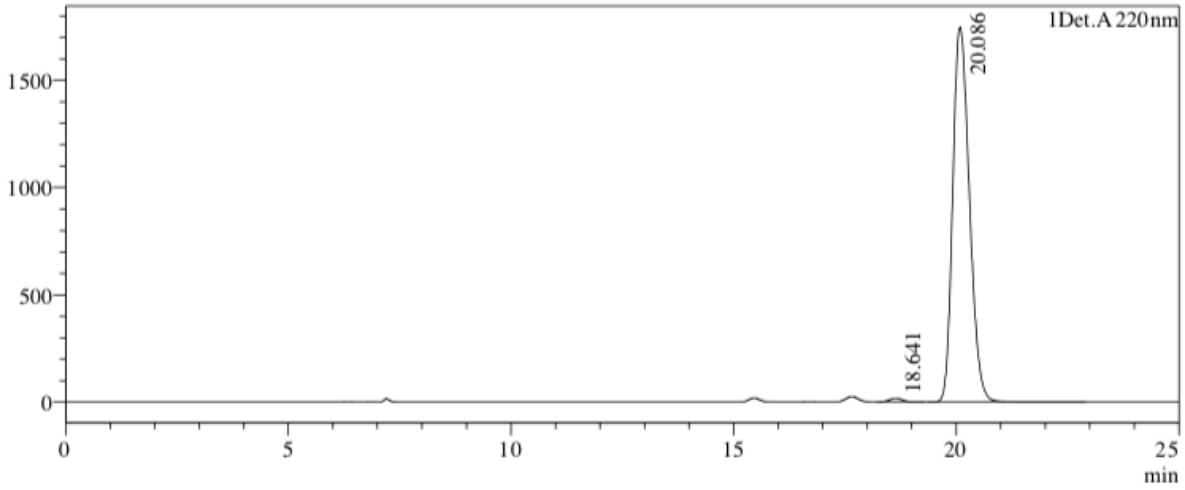

170.9476
143.7648
140.5190
137.9242
136.0284
129.2782
128.5601
128.4261
127.6601
127.5931
127.3824
127.1718
126.4249
77.2106
77.0000
76.7798
47.1172
43.4500
43.3255
20.9589
PPM
200
175
150
125
100
75
50
25
0

5ja, condition : AD-H, 0.5 ml/min, Hex/IPA = 80:20, 220 nm



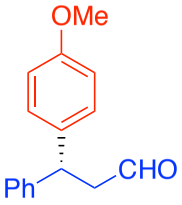
Det.A 220nm

Peak#	Ret. Time	Area	Height	Area%
1	18.118	7057143	332756	49.662
2	20.695	7153191	286737	50.338

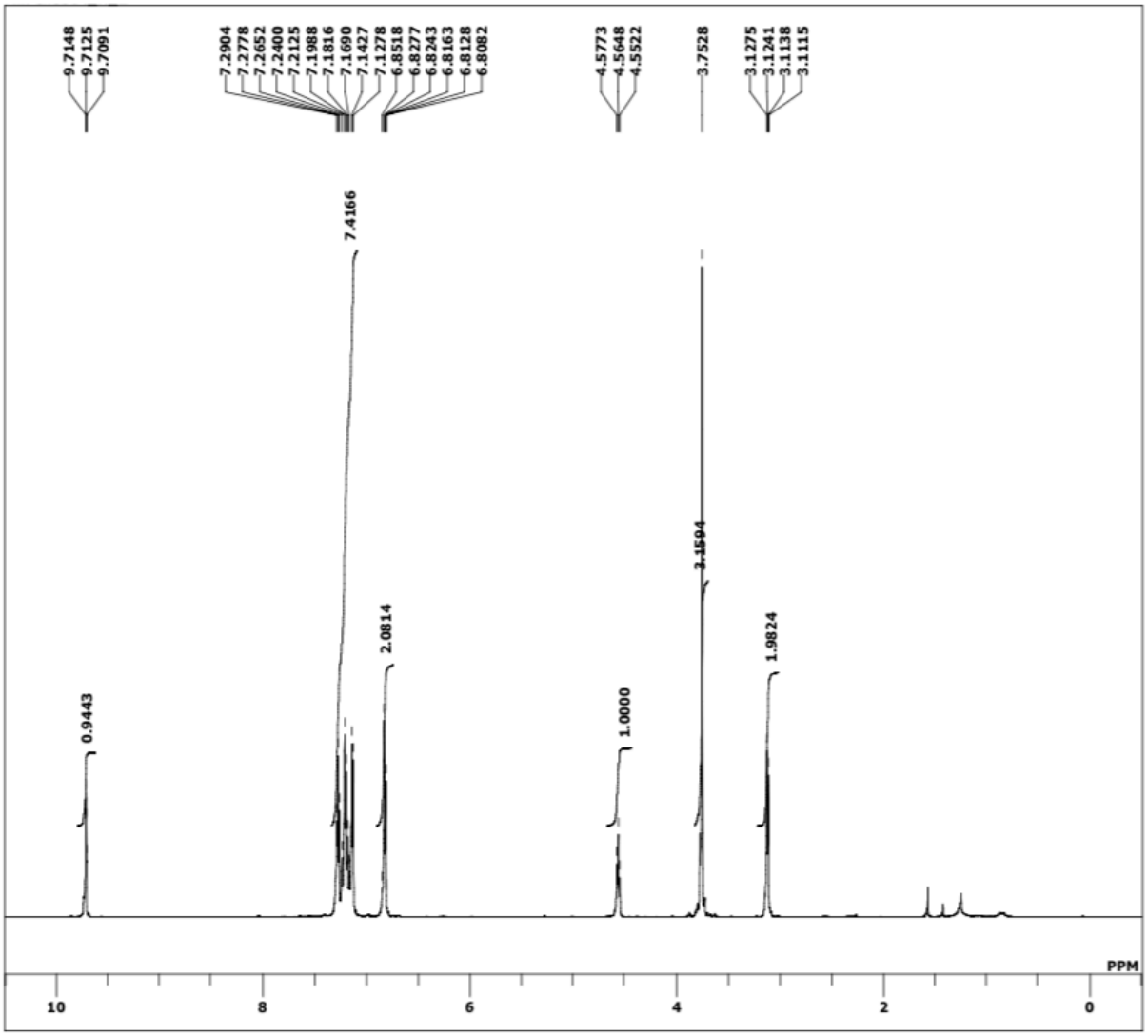


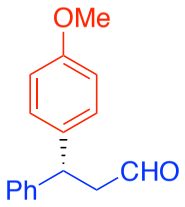
Det.A 220nm

Peak#	Ret. Time	Area	Height	Area%
1	18.641	368813	17844	0.803
2	20.086	45572226	1748730	99.197

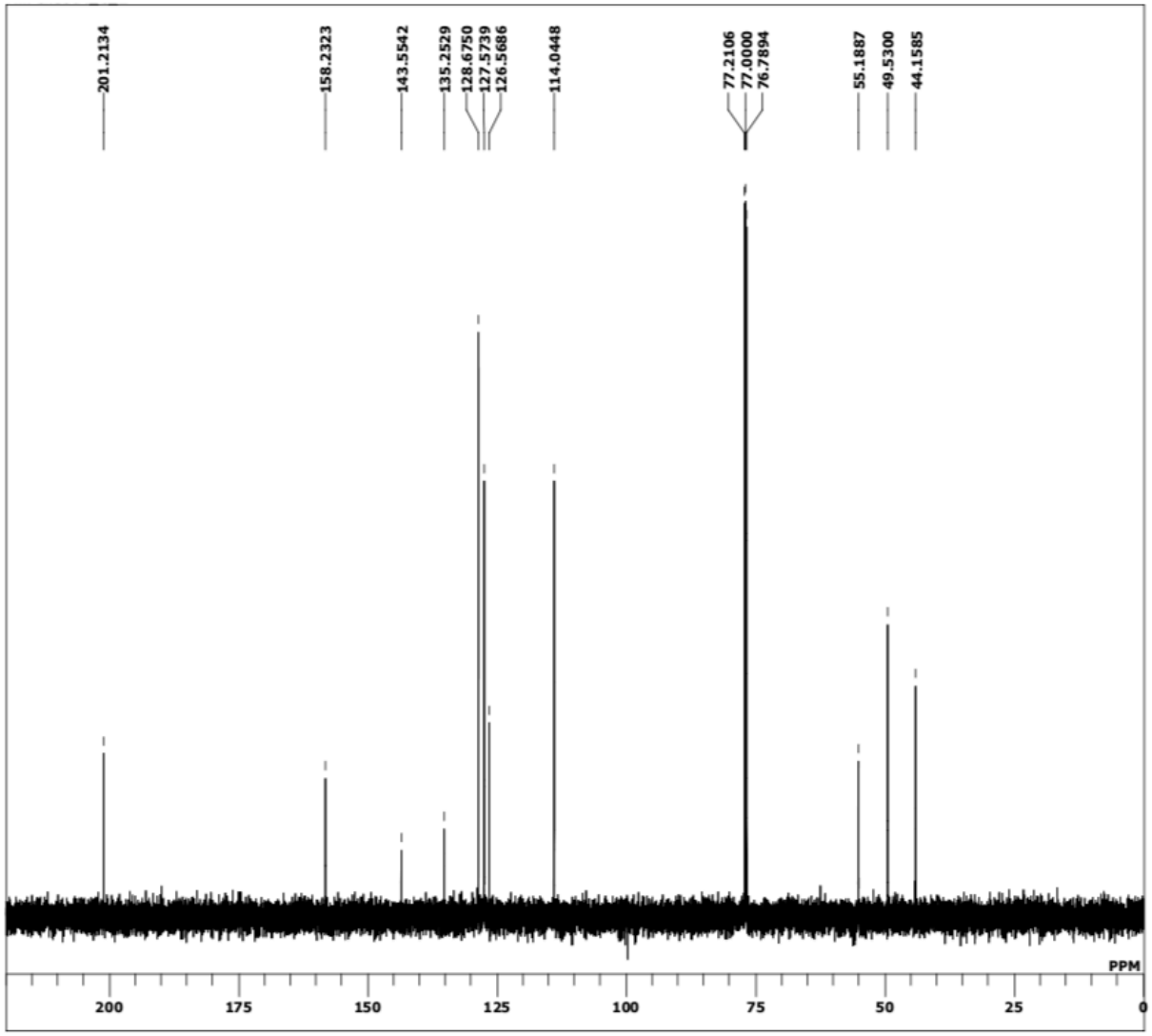

OMe
Ph
CHO

5kb

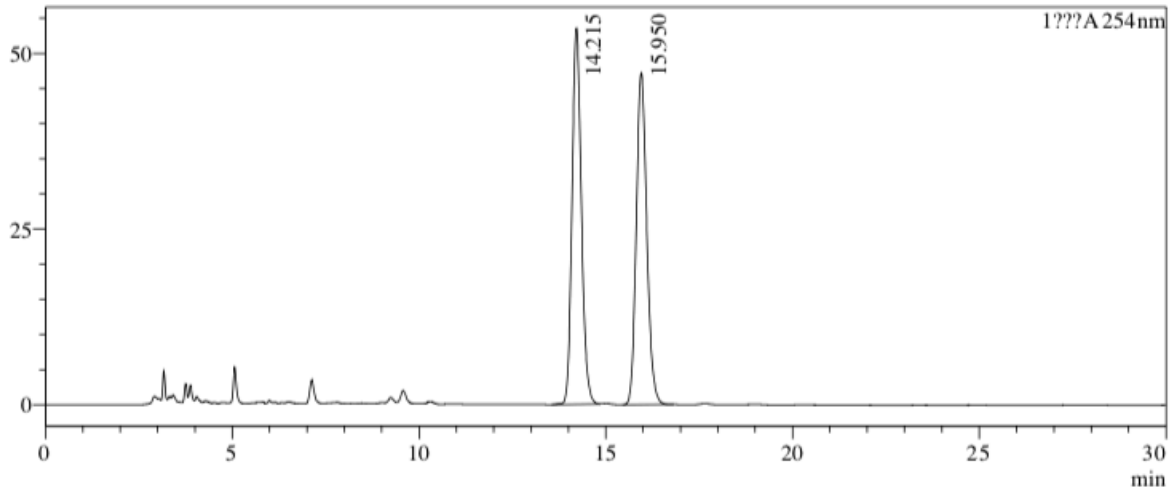

9.7148
9.7125
9.7091
7.2904
7.2778
7.2652
7.2400
7.2125
7.1988
7.1816
7.1690
7.1427
7.1278
6.8518
6.8277
6.8243
6.8163
6.8128
6.8082
4.5773
4.5648
4.5522
3.7528
3.1275
3.1241
3.1138
3.1115
7.4166
2.0814
3.1594
1.9824
0.9443
1.0000
PPM
10
8
6
4
2
0


OMe
Ph
CHO

5kb

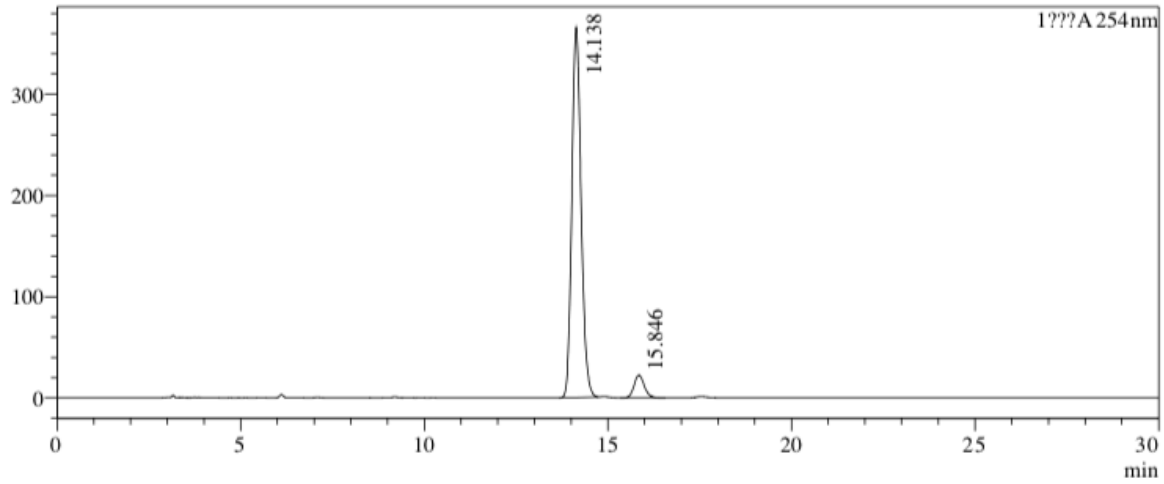

201.2134
158.2323
143.5542
135.2529
128.6750
127.5739
126.5686
114.0448
77.2106
77.0000
76.7894
55.1887
49.5300
44.1585
PPM
200
175
150
125
100
75
50
25
0

Corresponding alcohol of **5kb**, condition : AD-H, 1.0 ml/min, Hex/IPA = 92:8, 254 nm



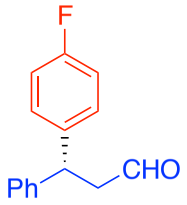
???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.215	928919	53504	50.164
2	15.950	922842	47215	49.836

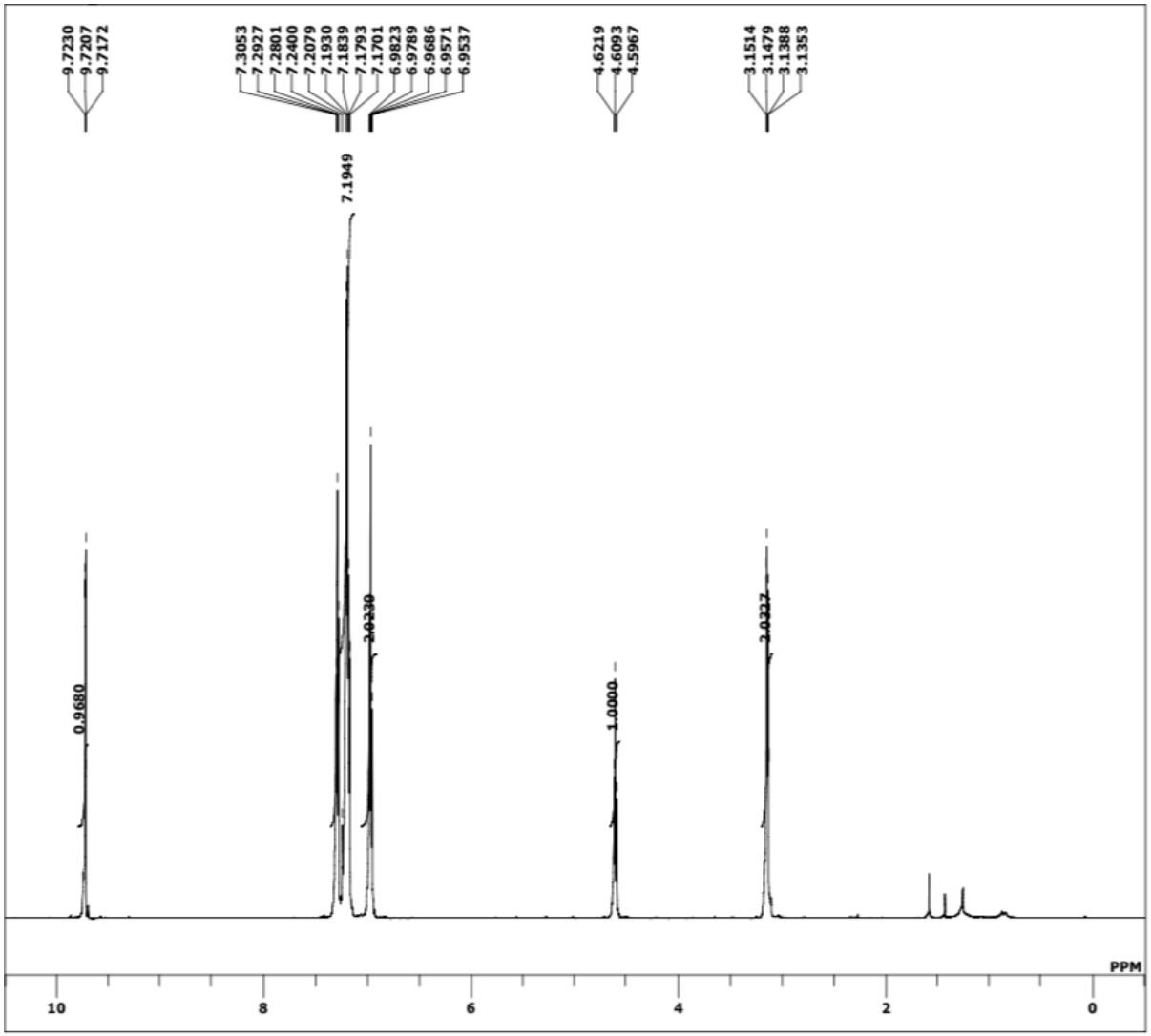


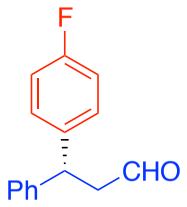
???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.138	6415440	365365	93.651
2	15.846	434922	22550	6.349

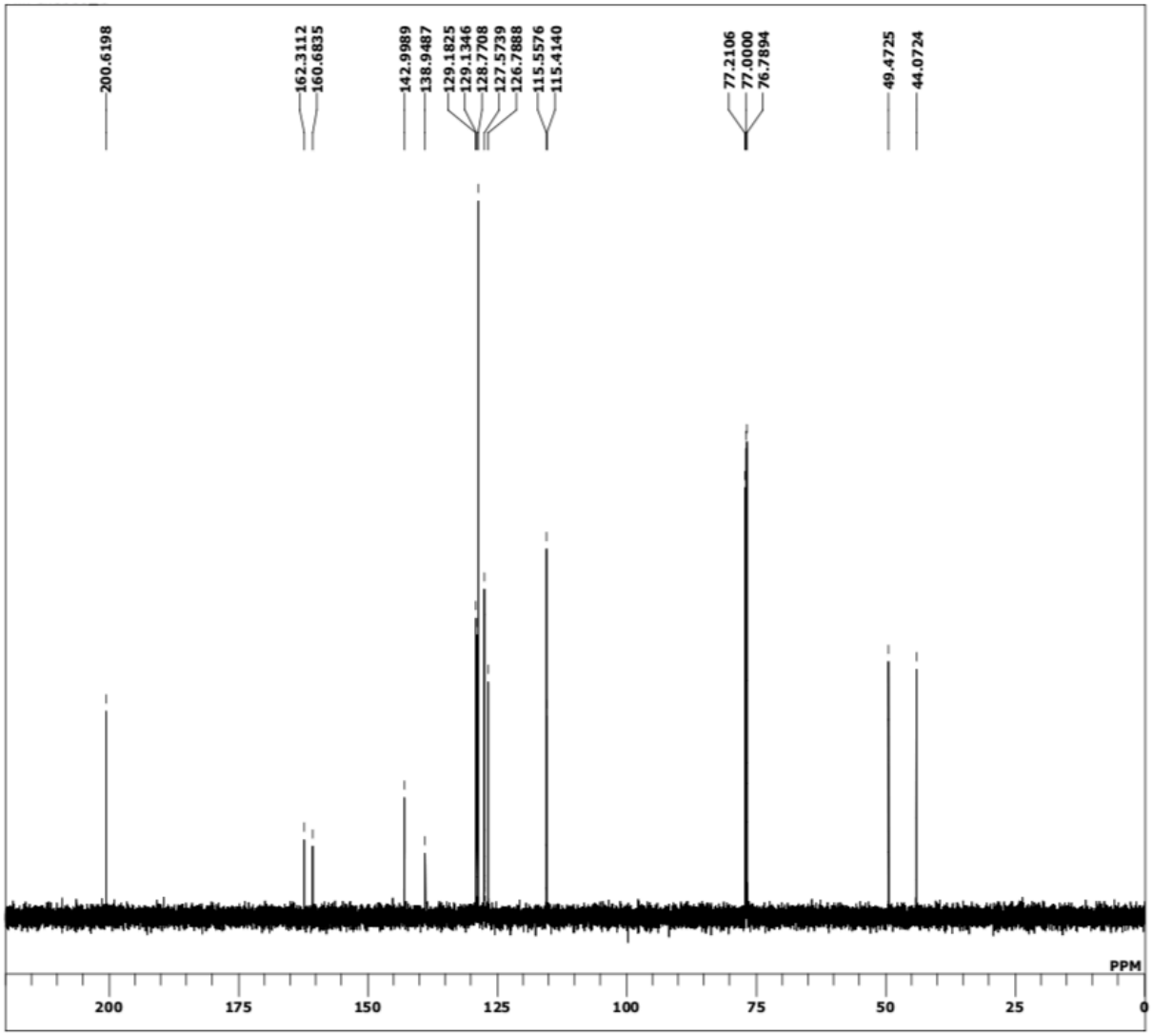

F
Ph
CHO

5kg

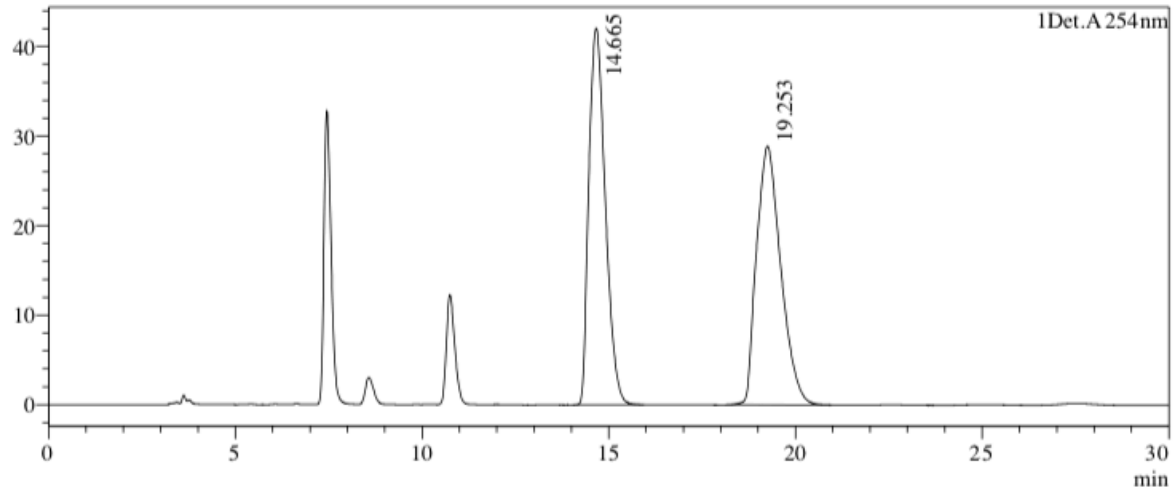

9.7230
9.7207
9.7172
7.3053
7.2927
7.2801
7.2400
7.2079
7.1930
7.1839
7.1793
7.1701
6.9823
6.9789
6.9686
6.9571
6.9537
4.6219
4.6093
4.5967
3.1514
3.1479
3.1388
3.1353
7.1949
0.9680
2.0330
1.0000
2.0327
PPM
10
8
6
4
2
0


F
Ph
CHO

5kg

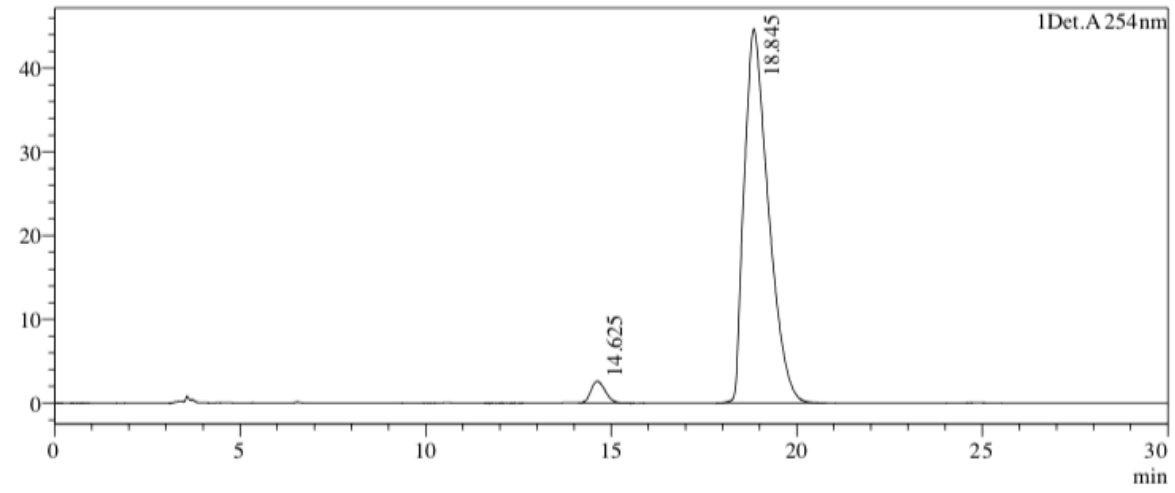

200.6198
162.3112
160.6835
142.9989
138.9487
129.1825
129.1346
128.7708
127.5739
126.7888
115.5576
115.4140
77.2106
77.0000
76.7894
49.4725
44.0724
PPM
200
175
150
125
100
75
50
25
0

Corresponding alcohol of **5kg**, condition : OJ-H, 1.0 ml/min, Hex/IPA = 90:10, 254 nm



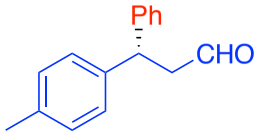
Det.A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.665	1289518	42065	49.689
2	19.253	1305634	28886	50.311

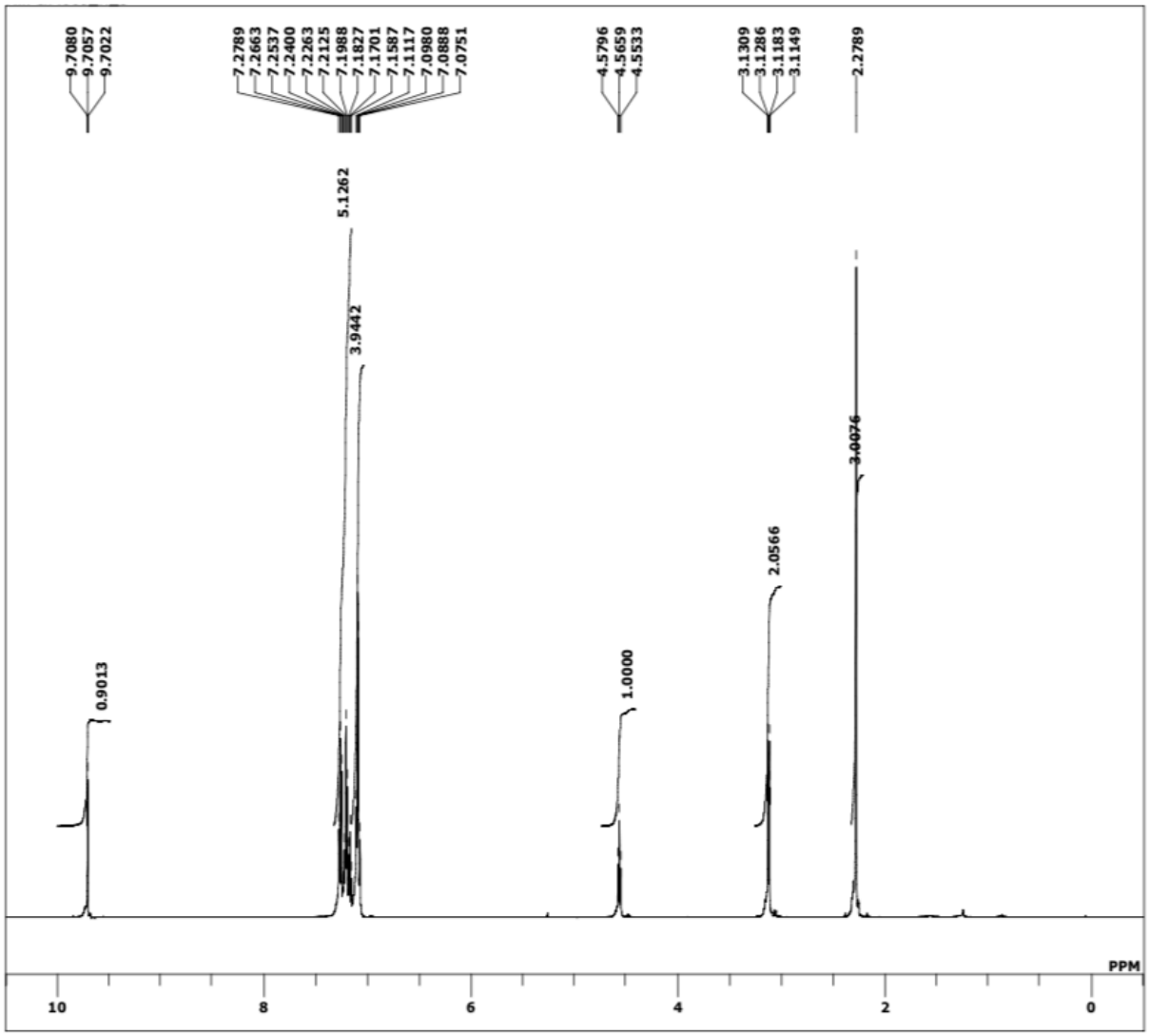


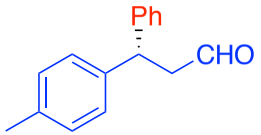
Det.A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.625	69487	2601	3.322
2	18.845	2022099	44690	96.678

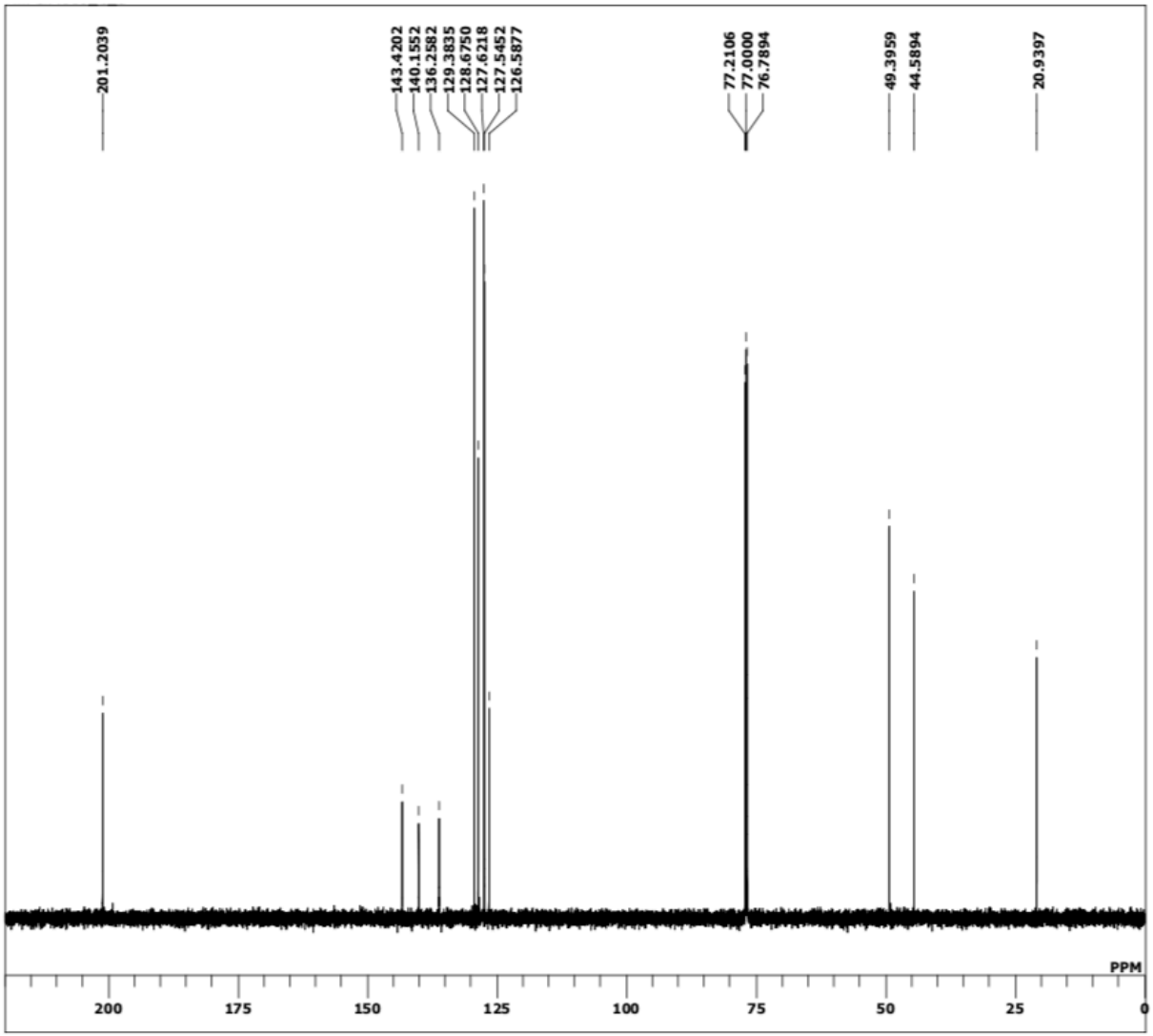

Ph
CHO

5la

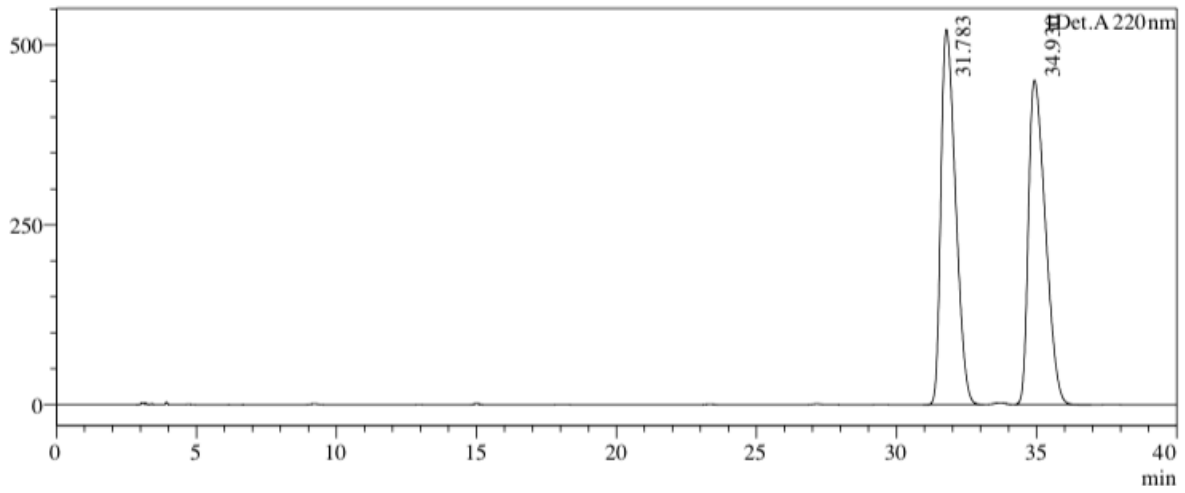

9.7080
9.7057
9.7022
7.2789
7.2663
7.2537
7.2400
7.2263
7.2125
7.1988
7.1827
7.1701
7.1587
7.1117
7.0980
7.0888
7.0751
4.5796
4.5659
4.5533
3.1309
3.1286
3.1183
3.1149
2.2789
5.1262
3.9442
3.0076
2.0566
1.0000
0.9013
PPM
10
8
6
4
2
0


Ph
CHO

5la

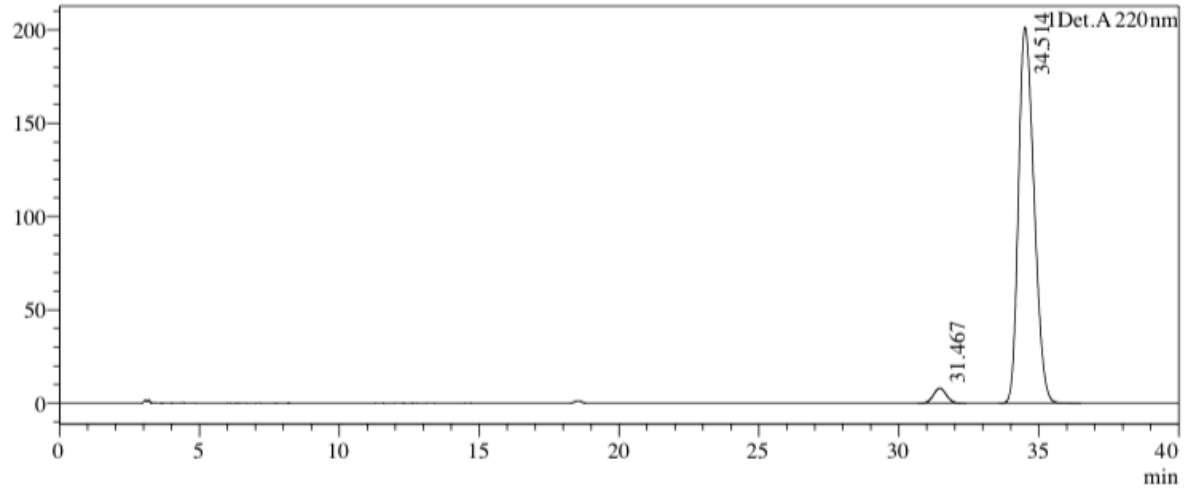

201.2039
143.4202
140.1552
136.2582
129.3835
128.6750
127.6218
127.5452
126.5877
77.2106
77.0000
76.7894
49.3959
44.5894
20.9397
PPM
200
175
150
125
100
75
50
25
0

Corresponding alcohol of **5la**, condition : AS-3, 1.0 ml/min, Hex/IPA = 98:2, 220 nm



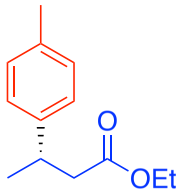
Det.A 220nm

Peak#	Ret. Time	Area	Height	Area%
1	31.783	18965371	522031	49.936
2	34.930	19014301	451583	50.064

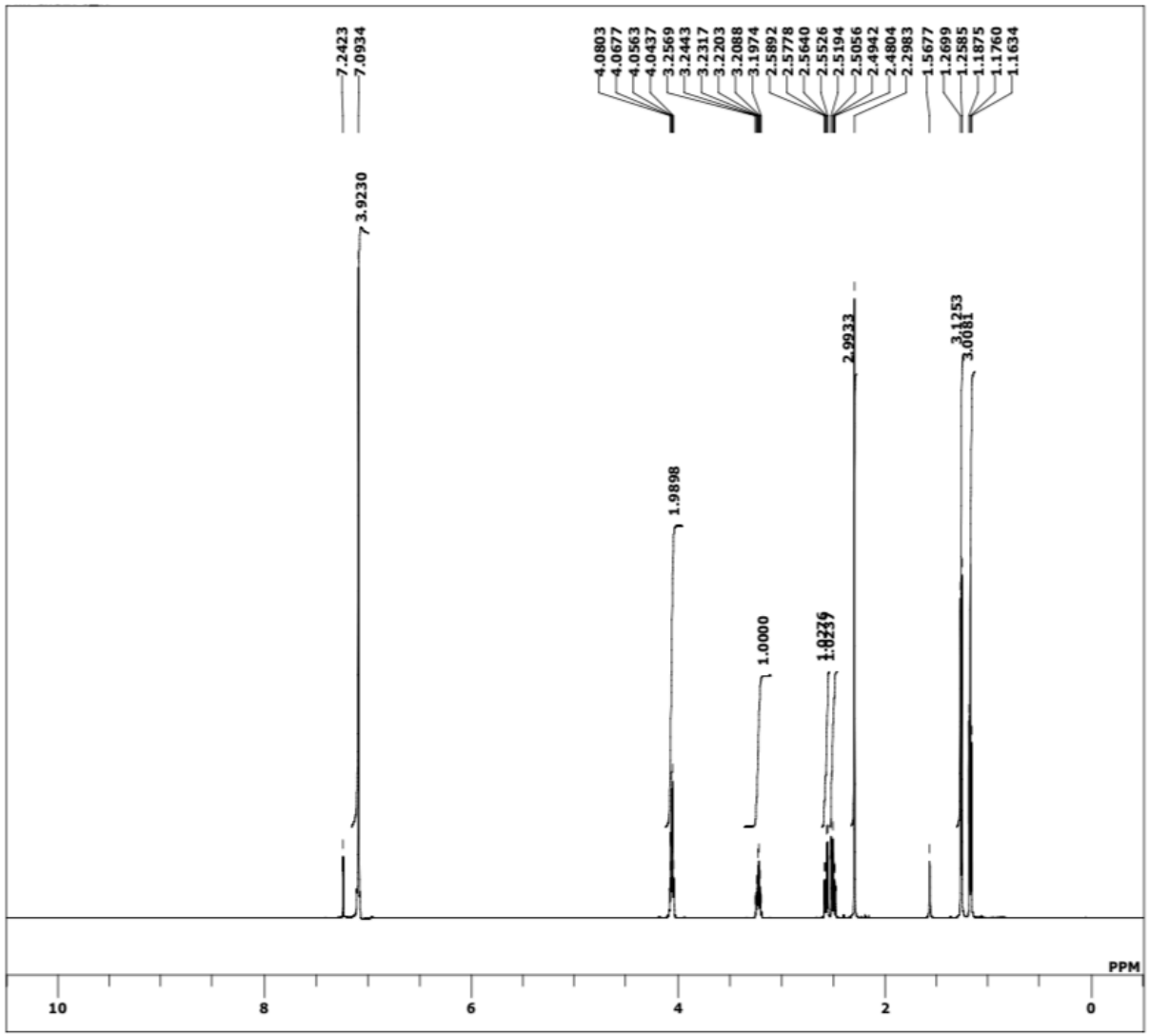


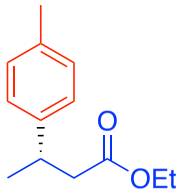
Det.A 220nm

Peak#	Ret. Time	Area	Height	Area%
1	31.467	262585	8105	3.254
2	34.514	7806116	201511	96.746

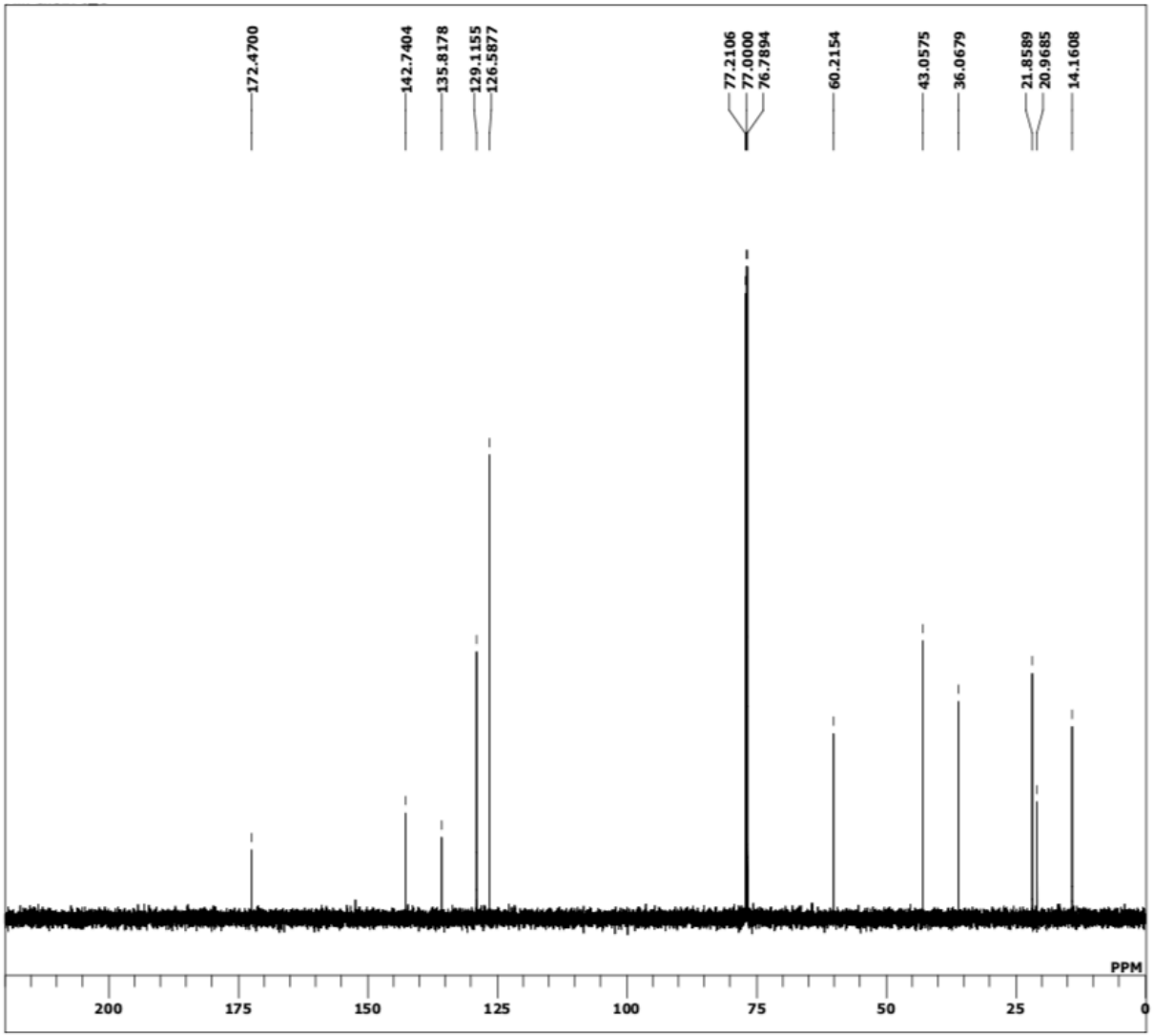

O
OEt

5mi

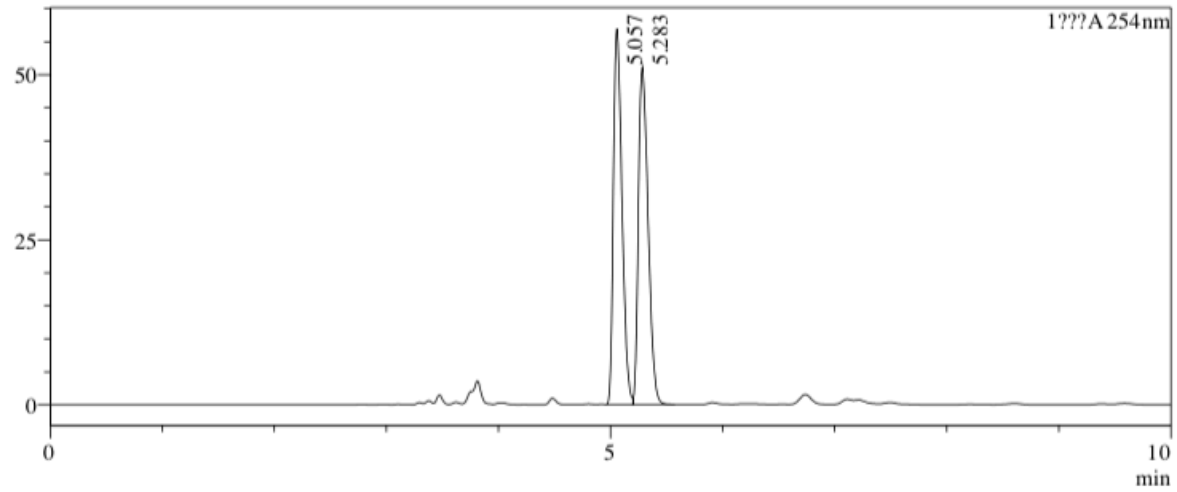

7.2423
7.0934
4.0803
4.0677
4.0563
4.0437
3.2569
3.2443
3.2317
3.2203
3.2088
3.1974
2.5892
2.5778
2.5640
2.5526
2.5194
2.5056
2.4942
2.4804
2.2983
1.5677
1.2699
1.2585
1.1875
1.1760
1.1634
3.9230
1.9898
1.0000
1.0236
1.0239
2.9933
3.1253
3.0081
PPM
10
8
6
4
2
0


O
OEt

5mi

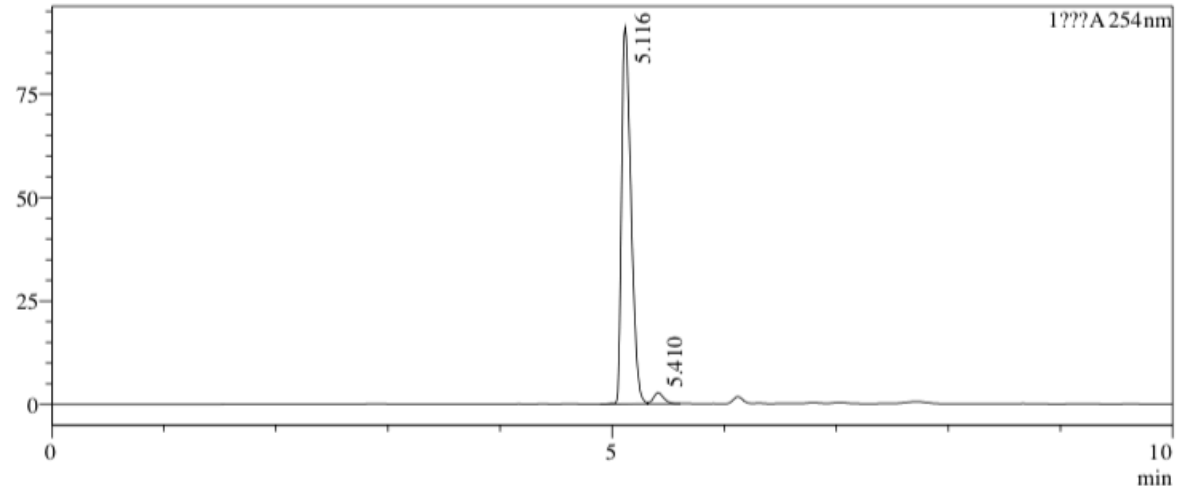

172.4700
142.7404
135.8178
129.1155
126.5877
77.2106
77.0000
76.7894
60.2154
43.0575
36.0679
21.8589
20.9685
14.1608
PPM
200
175
150
125
100
75
50
25
0

5mi, condition : AD-3, 1.0 ml/min, Hex/IPA = 99:1, 254 nm



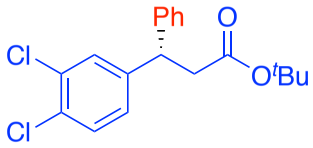
???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.057	304326	56919	49.803
2	5.283	306734	51038	50.197

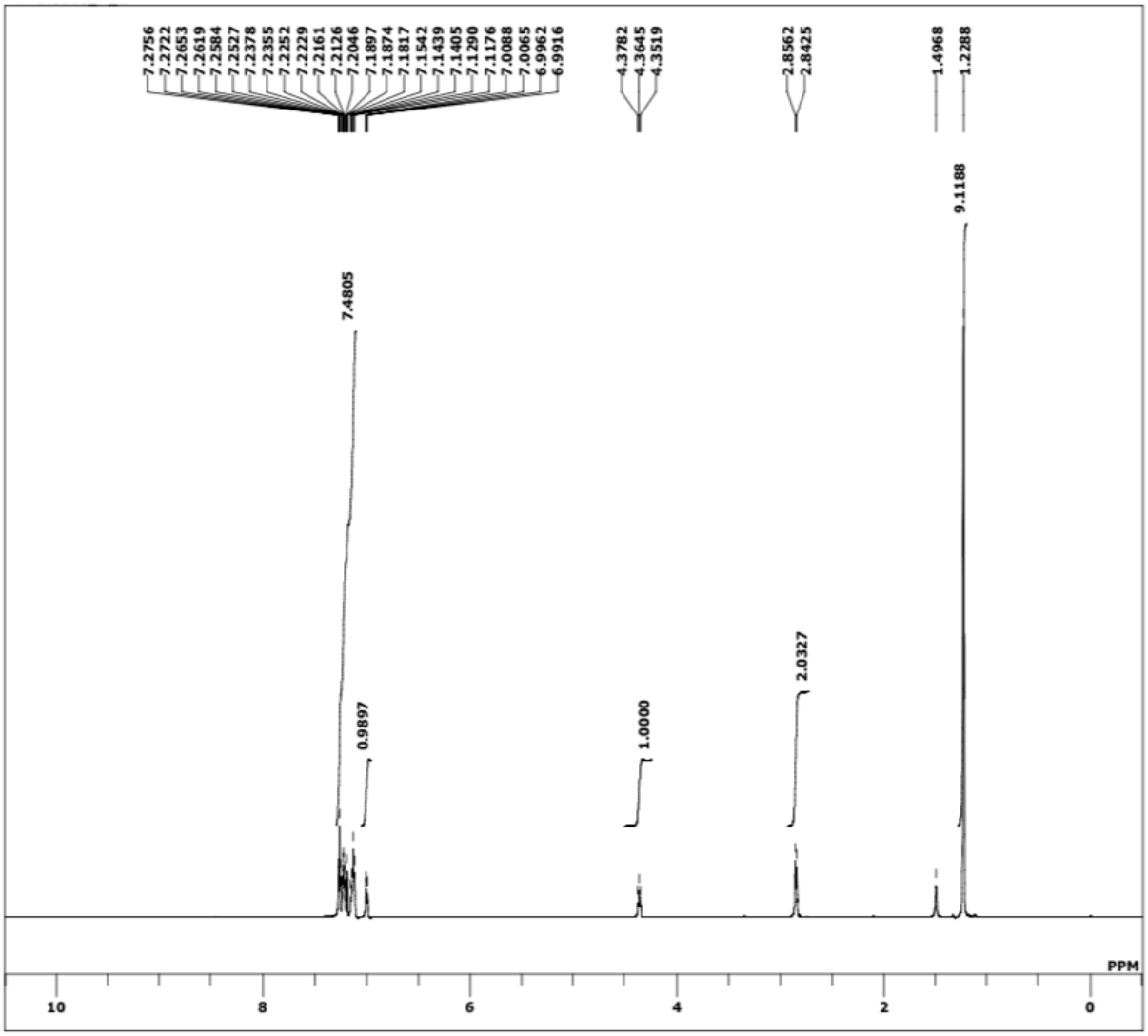


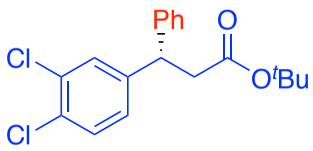
???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.116	532128	90950	96.795
2	5.410	17617	2690	3.205

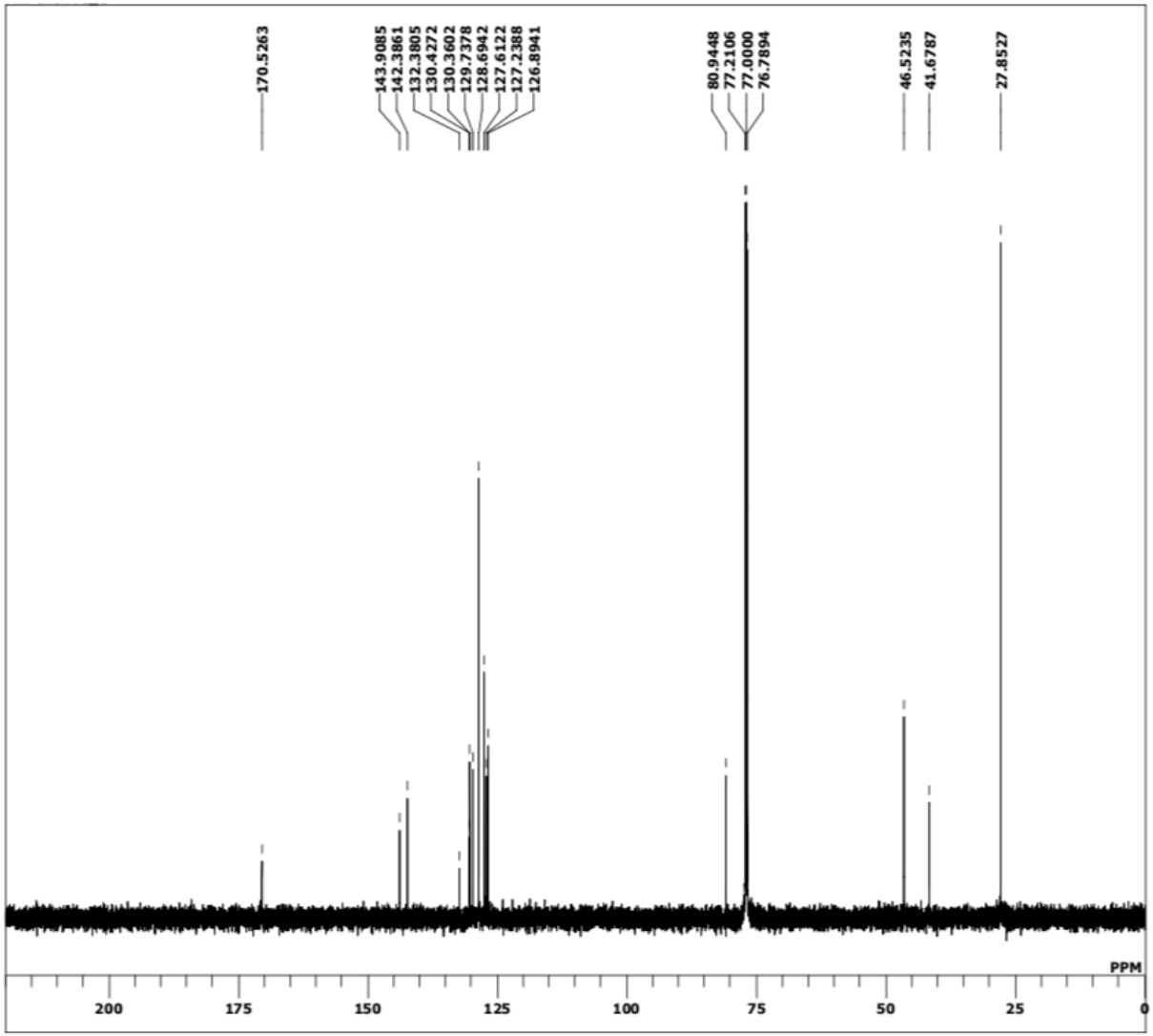

Ph
O
Cl
O^{t}Bu
Cl

5na

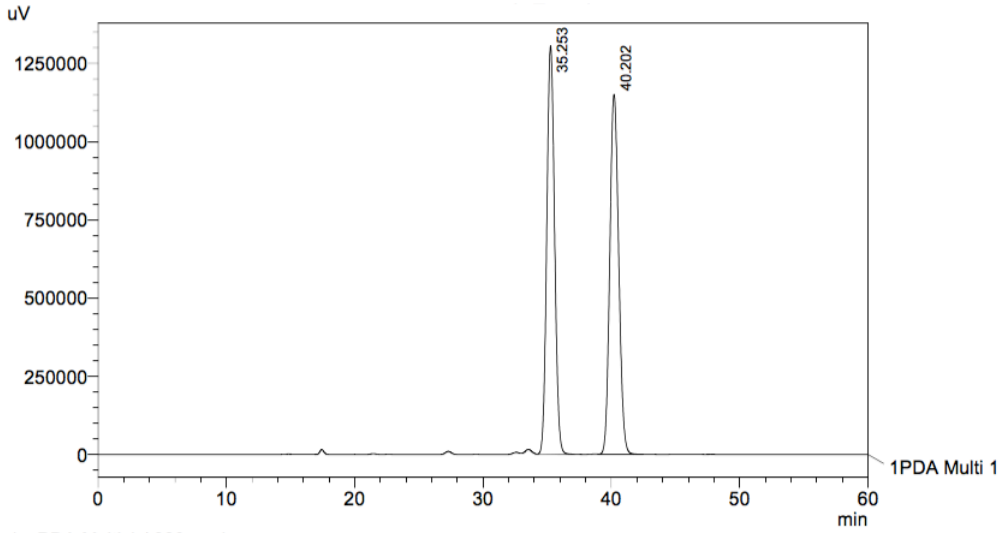

7.2756
7.2722
7.2653
7.2619
7.2584
7.2527
7.2378
7.2355
7.2252
7.2229
7.2161
7.2126
7.2046
7.1897
7.1874
7.1817
7.1542
7.1439
7.1405
7.1290
7.1176
7.0088
7.0065
6.9962
6.9916
4.3782
4.3645
4.3519
2.8562
2.8425
1.4968
1.2288
9.1188
7.4805
0.9897
1.0000
2.0327
PPM
10
8
6
4
2
0


Ph
O
Cl
Cl
O^{t}Bu

5na


170.5263
143.9085
142.3861
132.3805
130.4272
130.3602
129.7378
128.6942
127.6122
127.2388
126.8941
80.9448
77.2106
77.0000
76.7894
46.5235
41.6787
27.8527
PPM
200
175
150
125
100
75
50
25
0

5na, condition : OD-H, 0.2 ml/min, Hex/IPA = 99:1, 220 nm

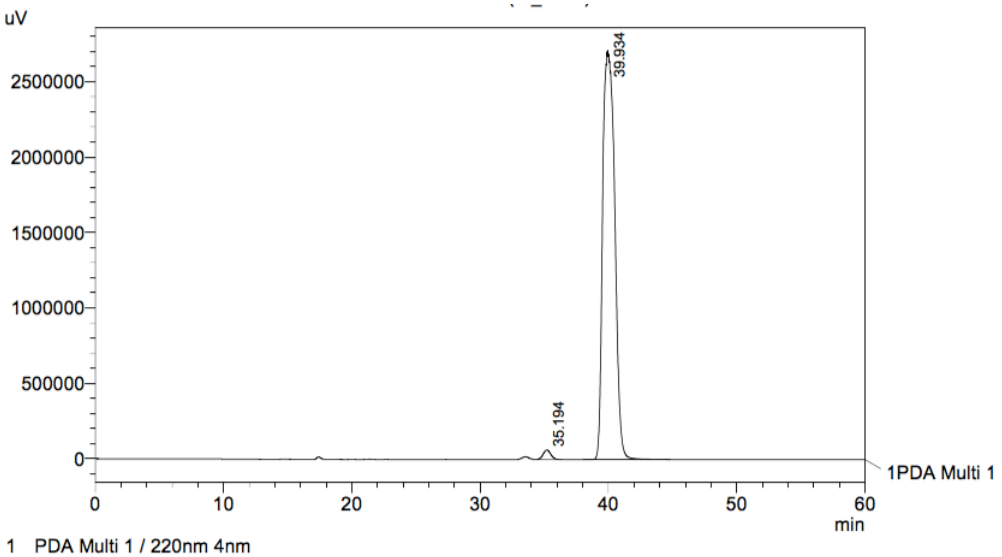


1 PDA Multi 1 / 220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.253	54982983	1304743	49.833	53.154
2	40.202	55351598	1149913	50.167	46.846
Total		110334581	2454657	100.000	100.000

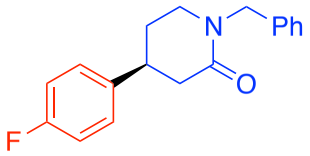


1 PDA Multi 1 / 220nm 4nm

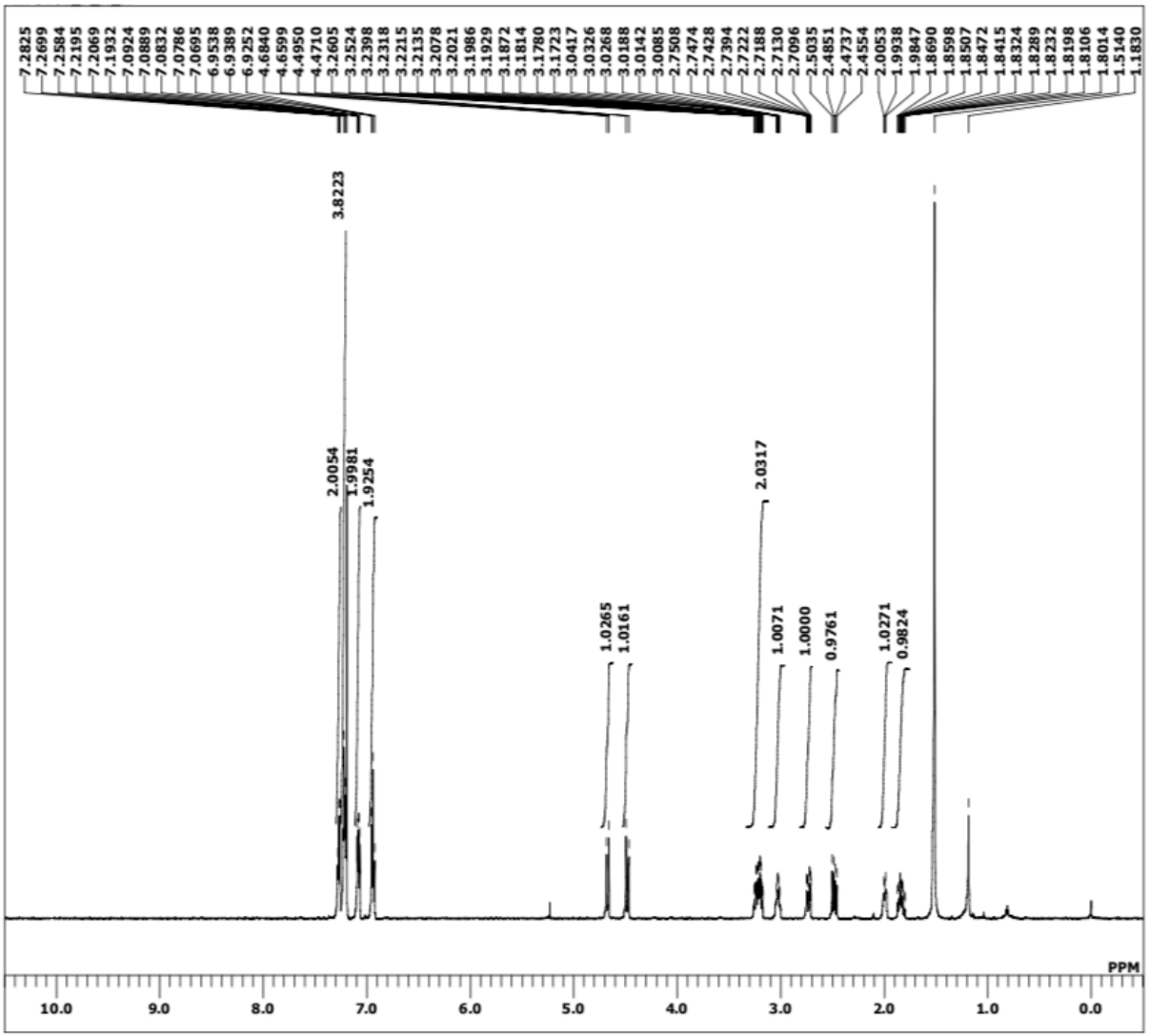
PeakTable

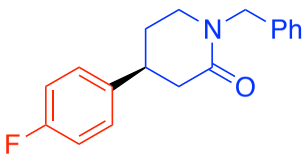
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.194	2653479	63524	1.475	2.288
2	39.934	177250523	2713050	98.525	97.712
Total		179904002	2776574	100.000	100.000

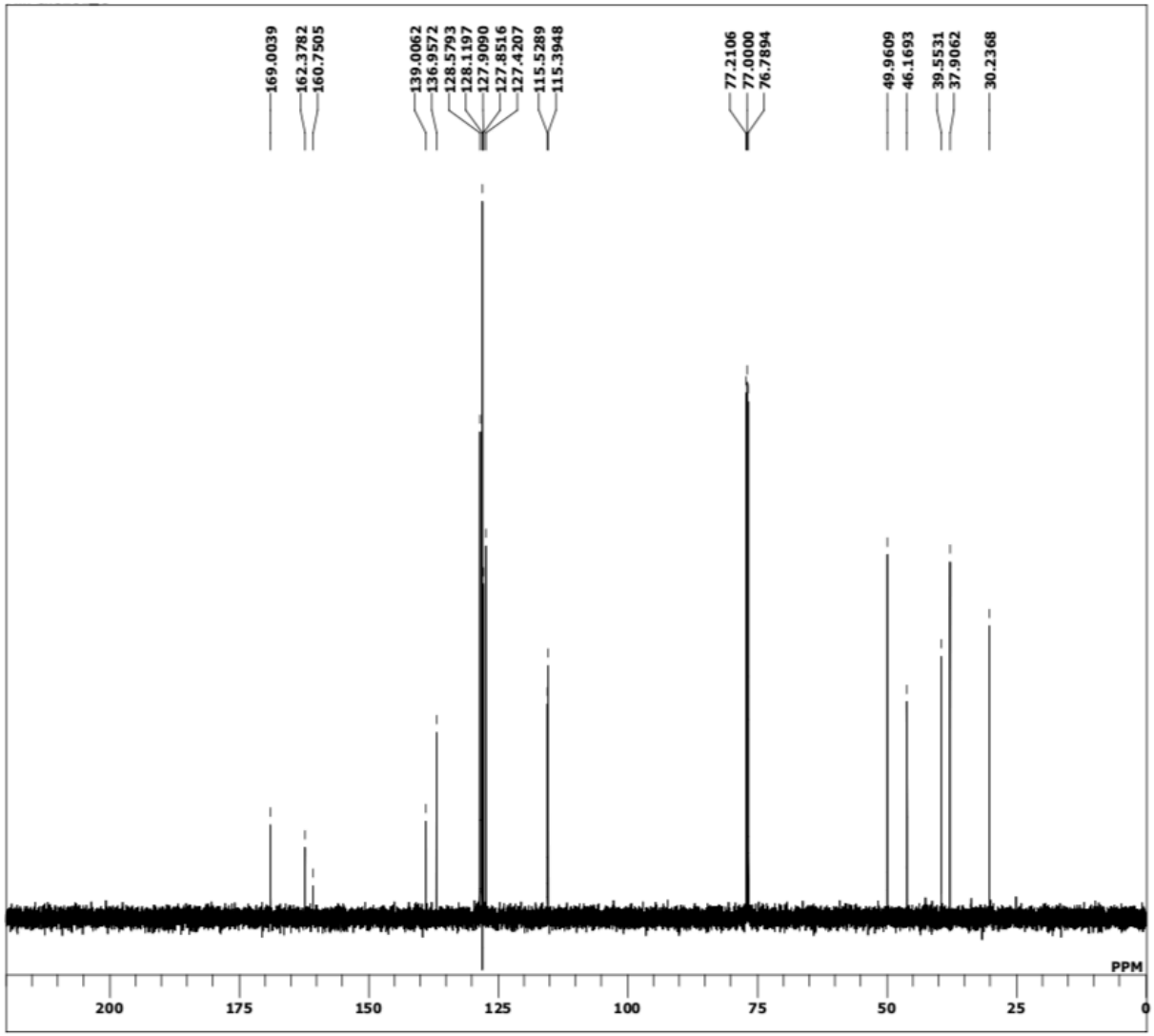

N
Ph
O
F

5og

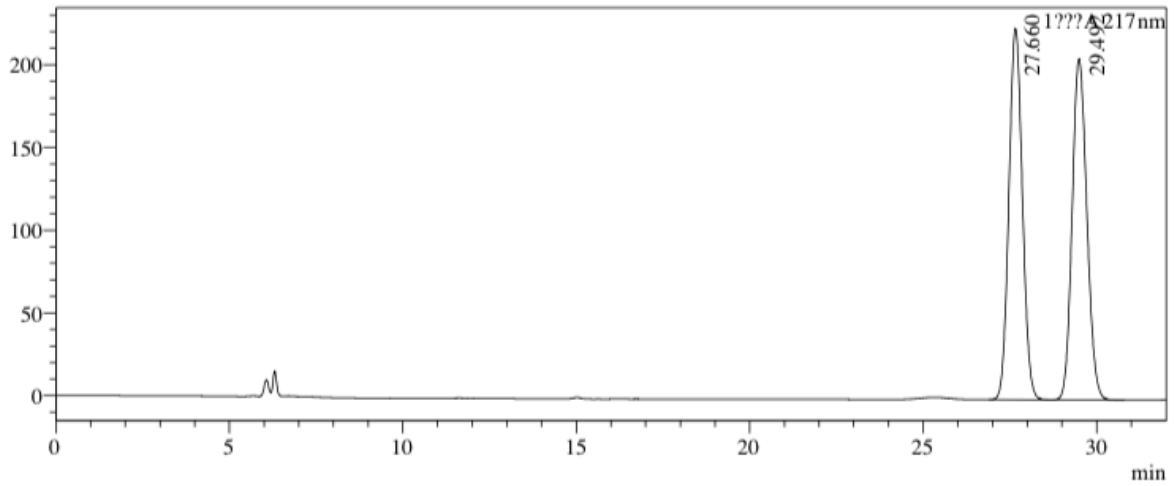

7.2825 7.2699 7.2584 7.2195 7.2069 7.1932 7.0924 7.0889 7.0832 7.0786 7.0695 6.9538 6.9389 6.9252 4.6840 4.6599 4.4950 4.4710 3.2605 3.2524 3.2398 3.2318 3.2215 3.2135 3.2078 3.2021 3.1986 3.1929 3.1872 3.1814 3.1780 3.1723 3.0417 3.0326 3.0268 3.0188 3.0142 3.0085 2.7508 2.7474 2.7428 2.7394 2.7222 2.7188 2.7130 2.7096 2.5035 2.4851 2.4737 2.4554 2.0053 1.9938 1.9847 1.8690 1.8598 1.8507 1.8472 1.8415 1.8324 1.8289 1.8232 1.8198 1.8106 1.8014 1.5140 1.1830
3.8223
2.0054
1.9981
1.9254
1.0265
1.0161
2.0317
1.0071
1.0000
0.9761
1.0271
0.9824
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


N
Ph
O
F

5og

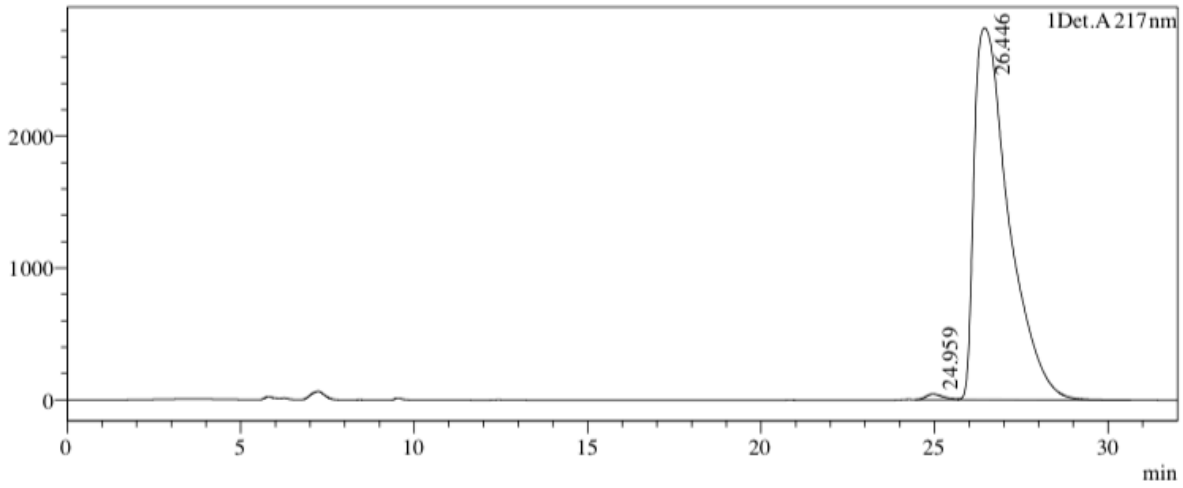

169.0039
162.3782
160.7505
139.0062
136.9572
128.5793
128.1197
127.9090
127.8516
127.4207
115.5289
115.3948
77.2106
77.0000
76.7894
49.9609
46.1693
39.5531
37.9062
30.2368
PPM
200
175
150
125
100
75
50
25
0

5og, condition : AD-H, 0.5 ml/min, Hex/IPA = 90:10, 217 nm



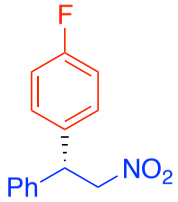
???A 217nm

Peak#	Ret. Time	Area	Height	Area%
1	27.660	6066860	224399	49.933
2	29.492	6083052	206259	50.067

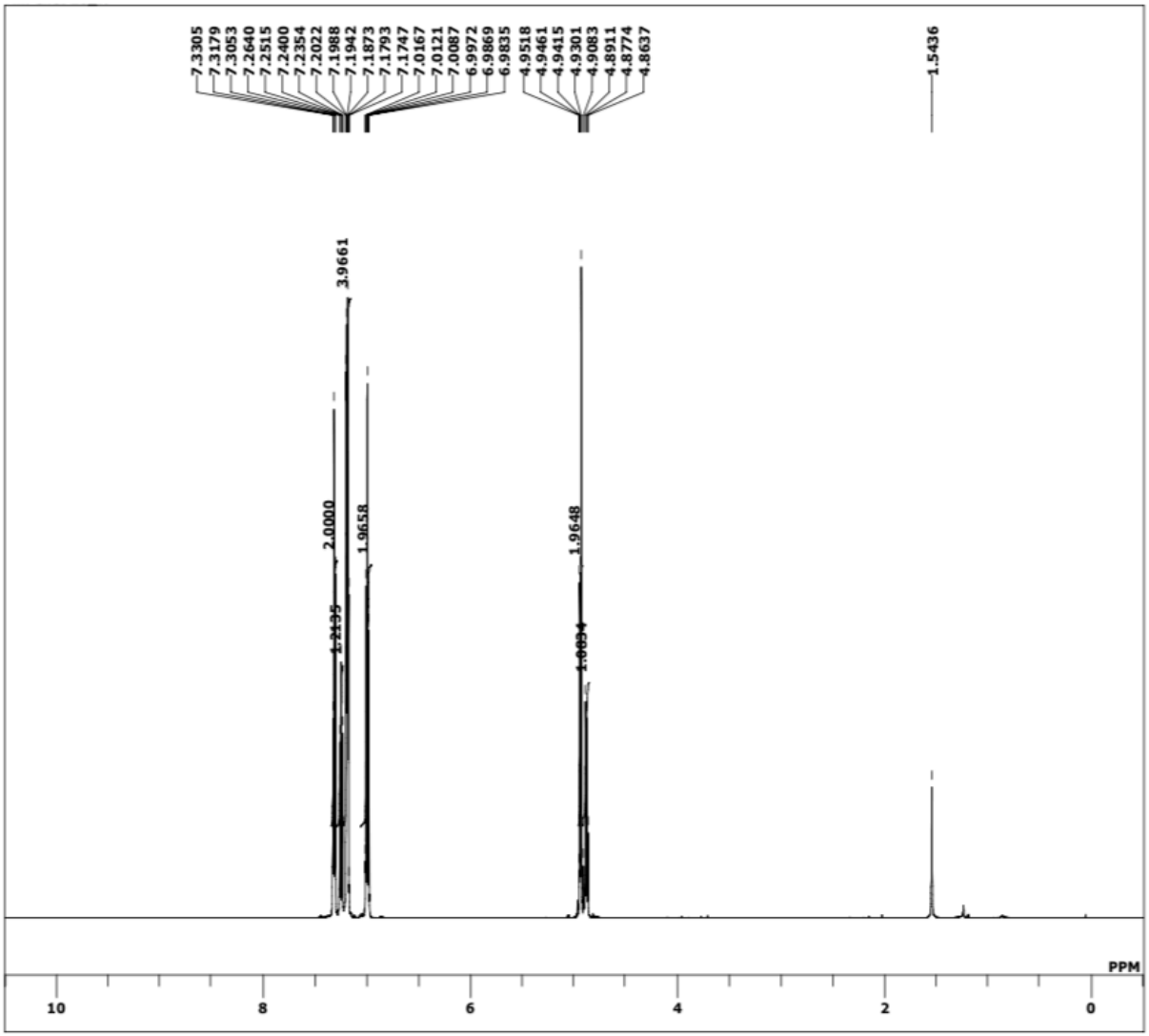


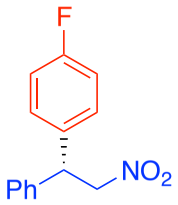
Det.A 217nm

Peak#	Ret. Time	Area	Height	Area%
1	24.959	1423033	42016	0.721
2	26.446	195835080	2820710	99.279

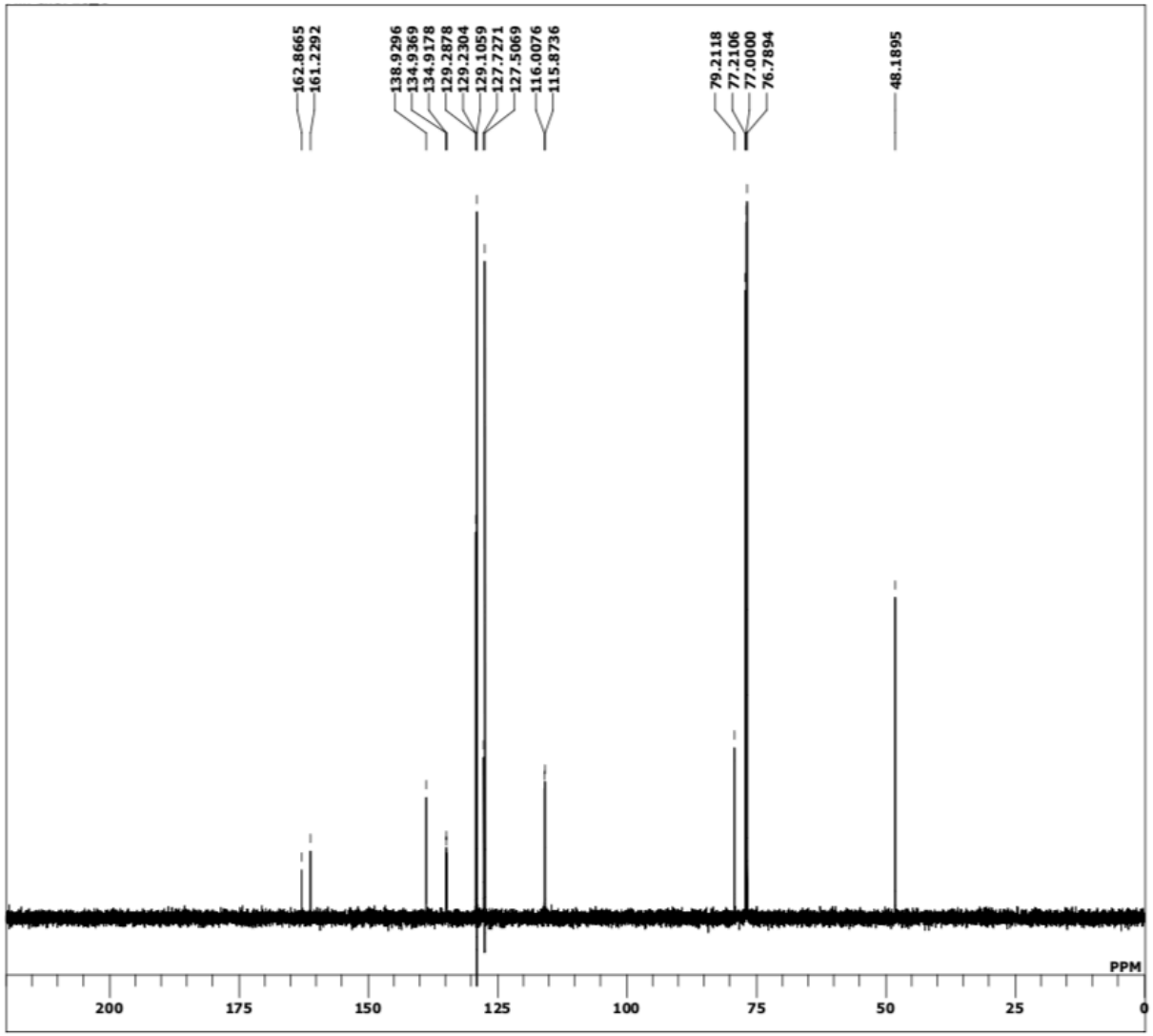

F
Ph
NO2

10ag

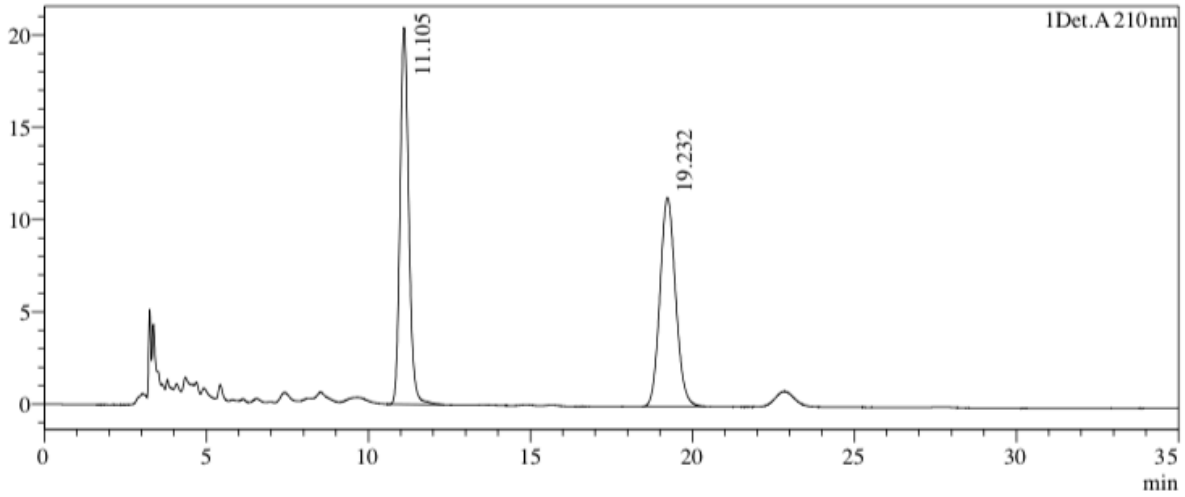

7.3305
7.3179
7.3053
7.2640
7.2515
7.2400
7.2354
7.2022
7.1988
7.1942
7.1873
7.1793
7.1747
7.0167
7.0121
7.0087
6.9972
6.9869
6.9835
4.9518
4.9461
4.9415
4.9301
4.9083
4.8911
4.8774
4.8637
1.5436
3.9661
2.0000
1.9658
1.9648
PPM
10
8
6
4
2
0


F
Ph
NO2

10ag

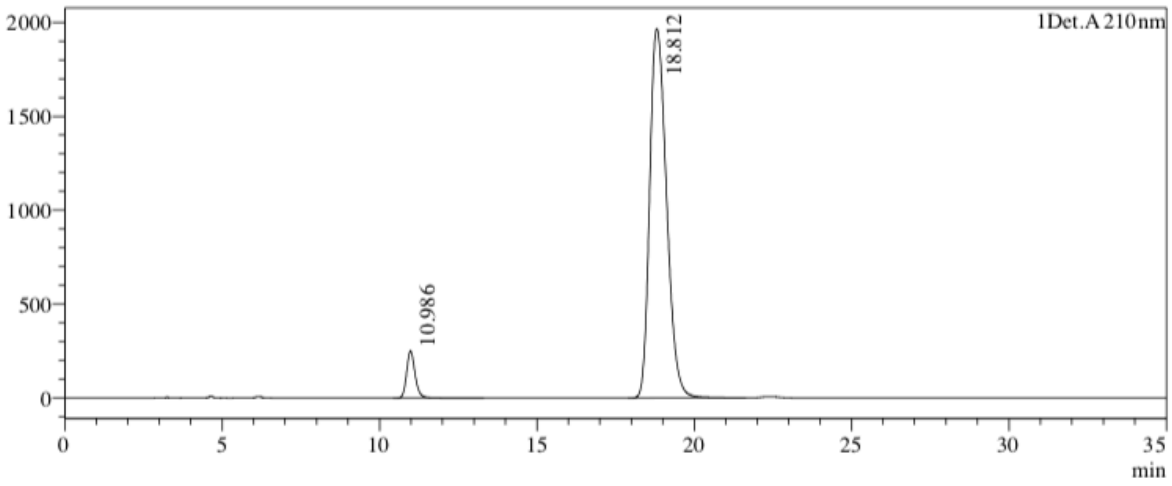

162.8665
161.2292
138.9296
134.9369
134.9178
129.2878
129.2304
129.1059
127.7271
127.5069
116.0076
115.8736
79.2118
77.2106
77.0000
76.7894
48.1895
PPM
200
175
150
125
100
75
50
25
0

10ag, condition : OD-H, 1.0 ml/min, Hex/IPA = 60:40, 210 nm



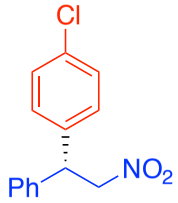
Det.A 210nm

Peak#	Ret. Time	Area	Height	Area%
1	11.105	381004	20413	50.055
2	19.232	380165	11322	49.945

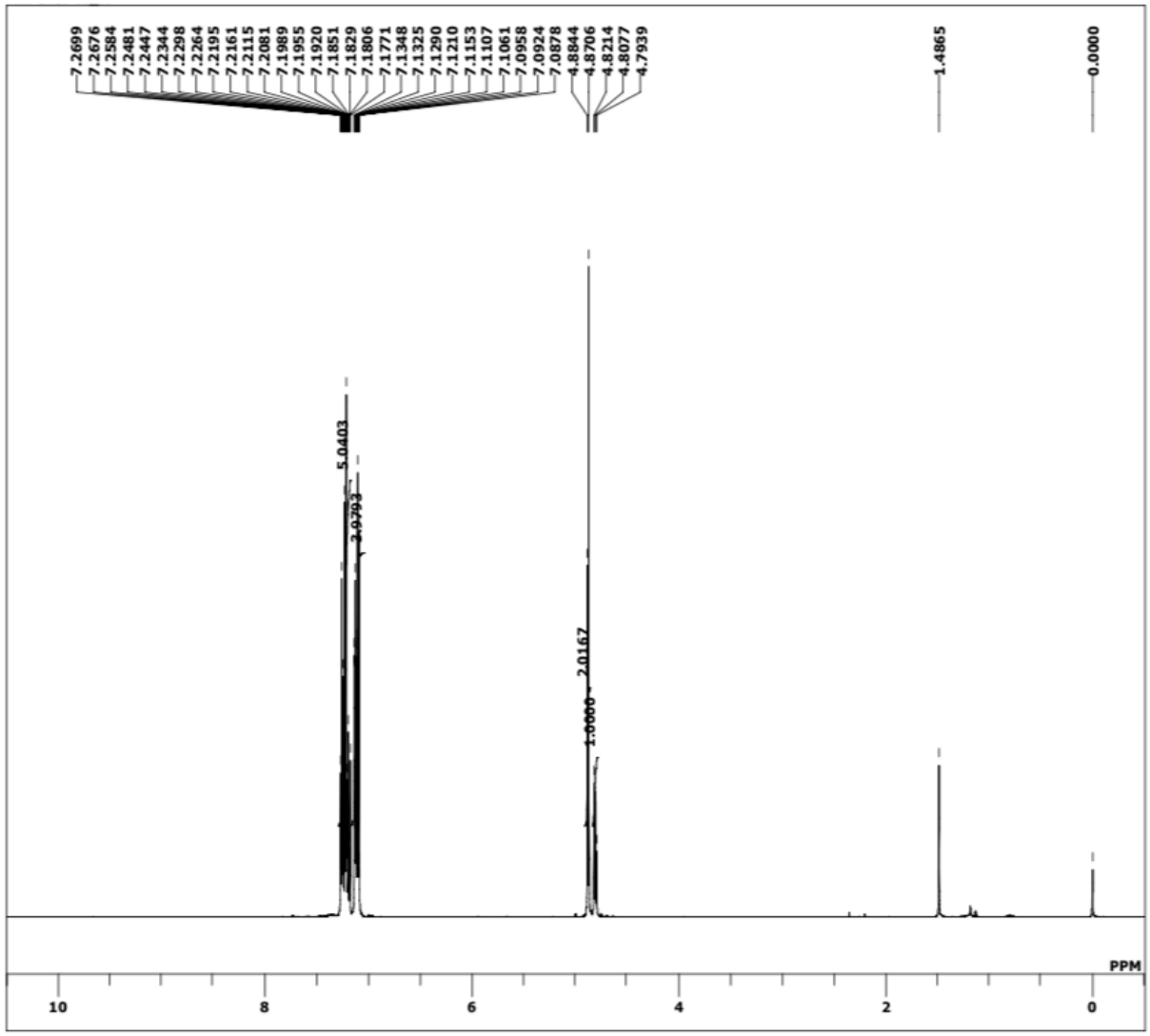


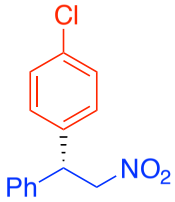
Det.A 210nm

Peak#	Ret. Time	Area	Height	Area%
1	10.986	4716571	250462	6.040
2	18.812	73372925	1966701	93.960

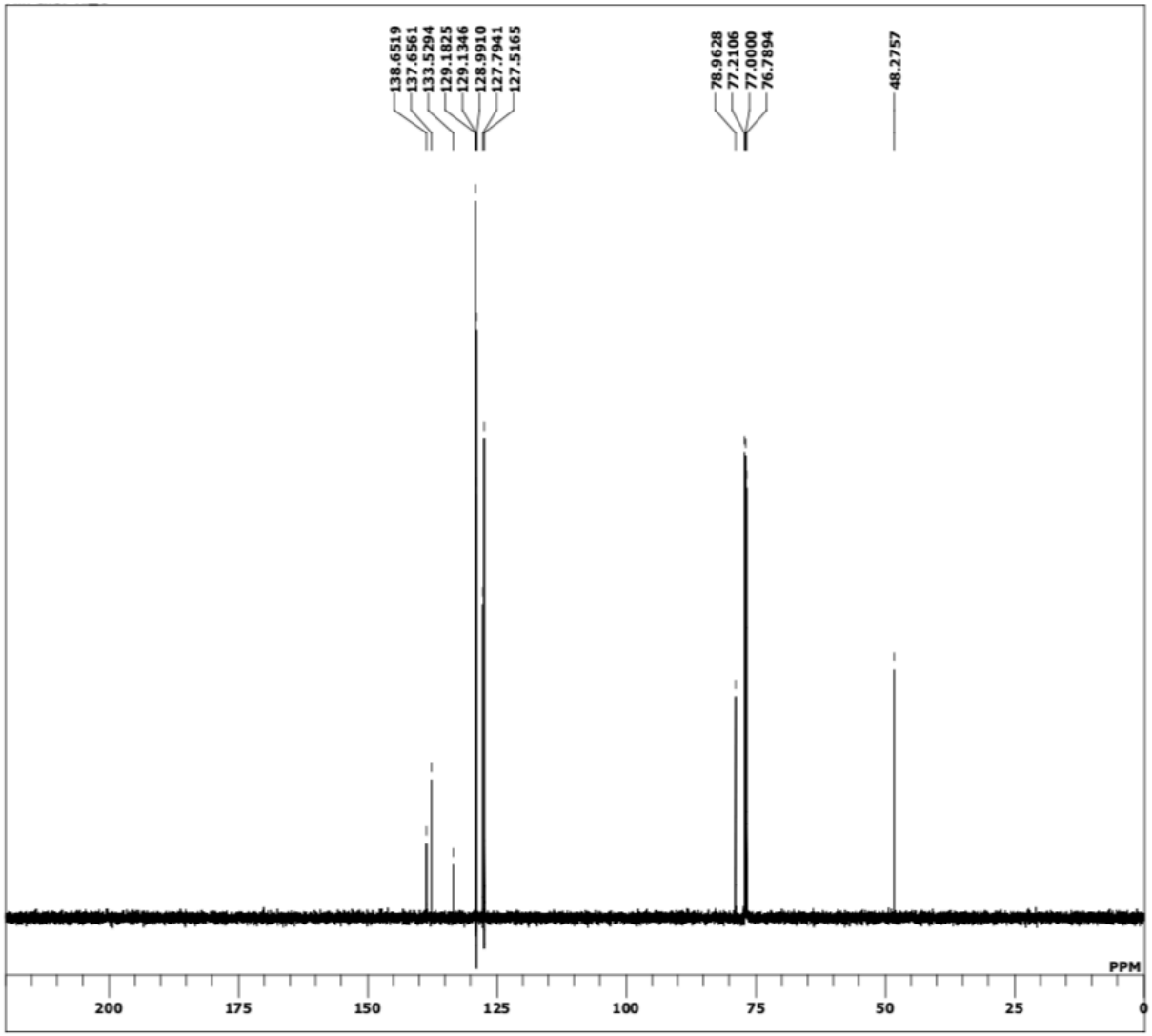

Cl
Ph
NO2

10aj

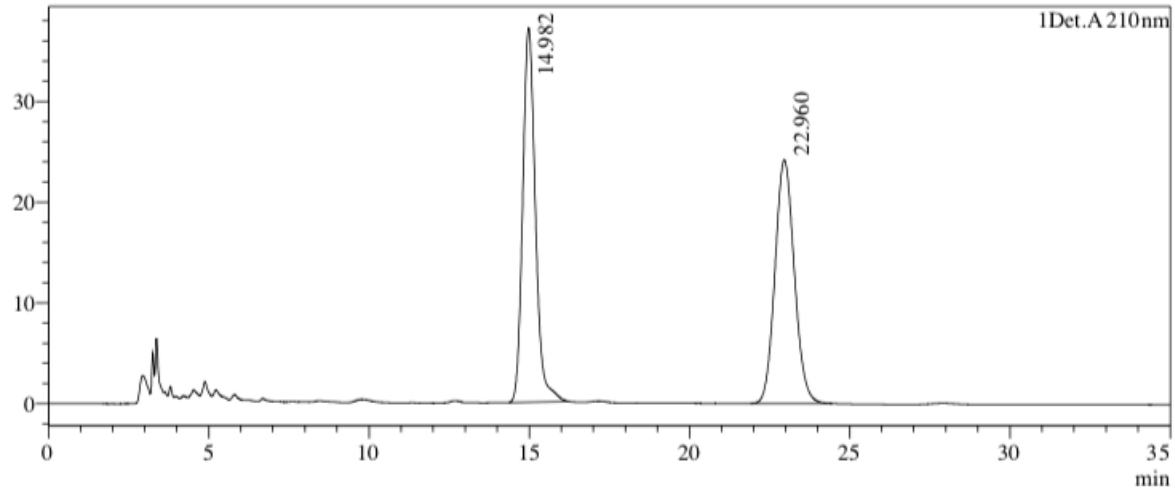

7.2699
7.2676
7.2584
7.2481
7.2447
7.2344
7.2298
7.2264
7.2195
7.2161
7.2115
7.2081
7.1989
7.1955
7.1920
7.1851
7.1829
7.1806
7.1771
7.1348
7.1325
7.1290
7.1210
7.1153
7.1107
7.1061
7.0958
7.0924
7.0878
4.8844
4.8706
4.8214
4.8077
4.7939
1.4865
0.0000
5.0403
3.0793
2.0167
1.0000
PPM
10
8
6
4
2
0


Cl
Ph
NO2

10aj

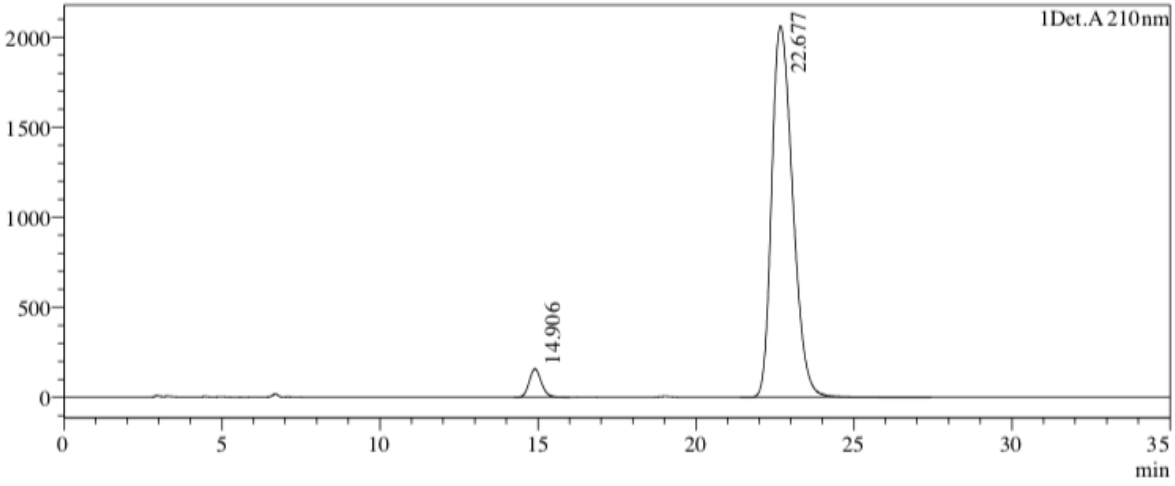

138.6519
137.6561
133.5294
129.1825
129.1346
128.9910
127.7941
127.5165
78.9628
77.2106
77.0000
76.7894
48.2757
PPM
200
175
150
125
100
75
50
25
0

10aj, condition : OD-H, 1.0 ml/min, Hex/IPA = 60:40, 210 nm



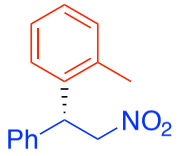
Det.A 210nm

Peak#	Ret. Time	Area	Height	Area%
1	14.982	1024220	37184	50.180
2	22.960	1016881	24190	49.820

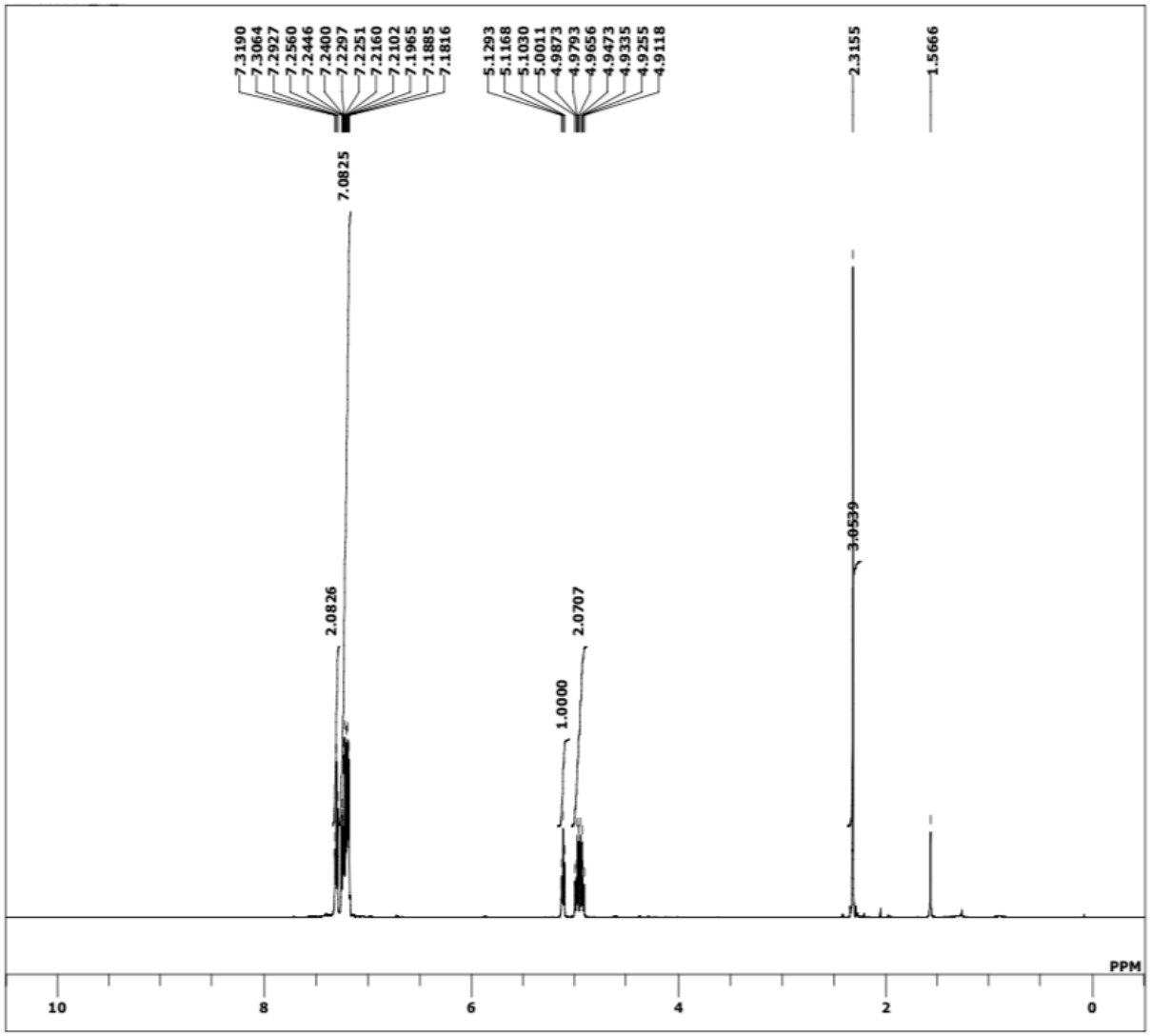


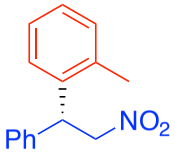
Det.A 210nm

Peak#	Ret. Time	Area	Height	Area%
1	14.906	4233693	157482	4.245
2	22.677	95501968	2063197	95.755

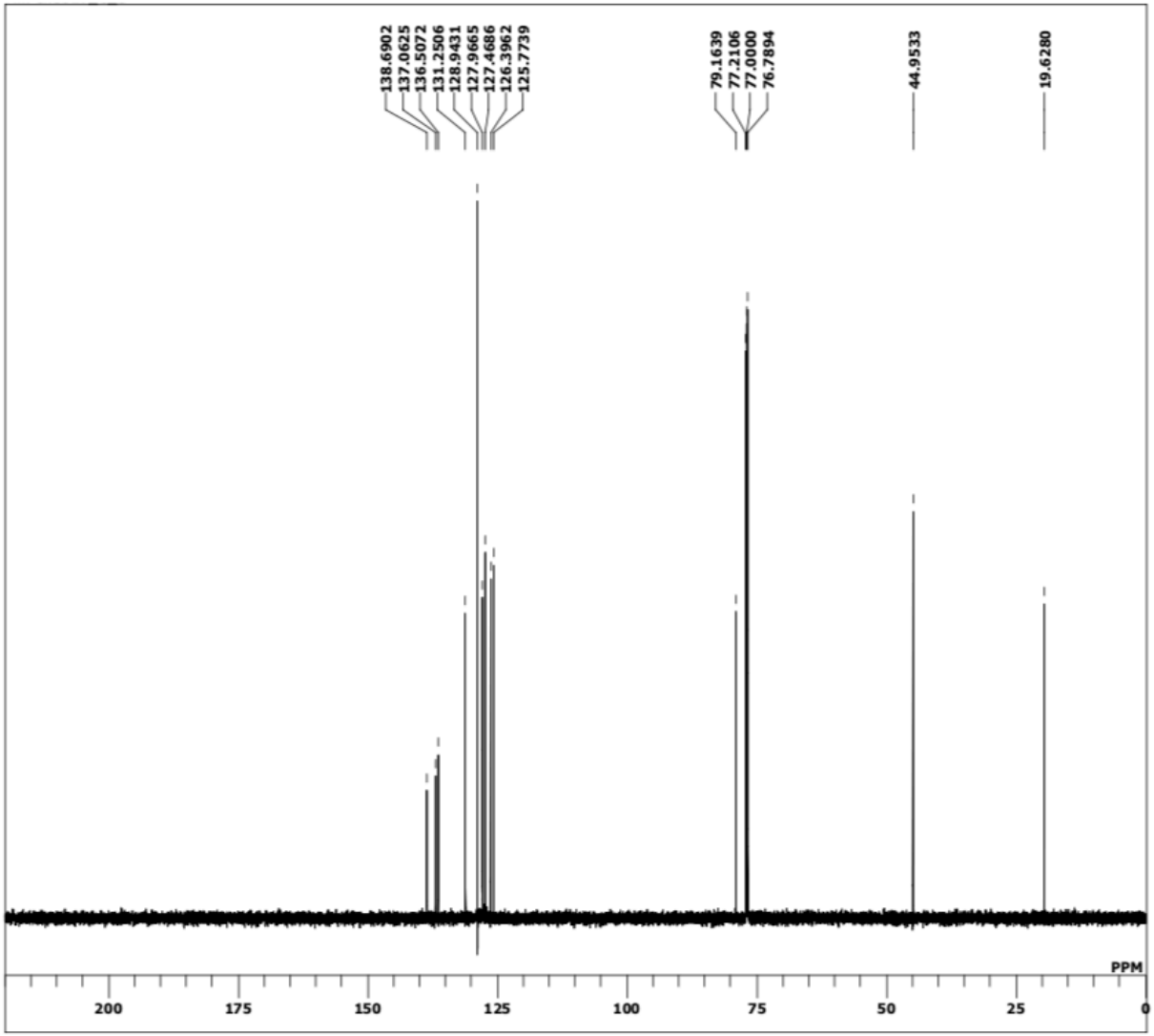

Ph
NO2

10ak

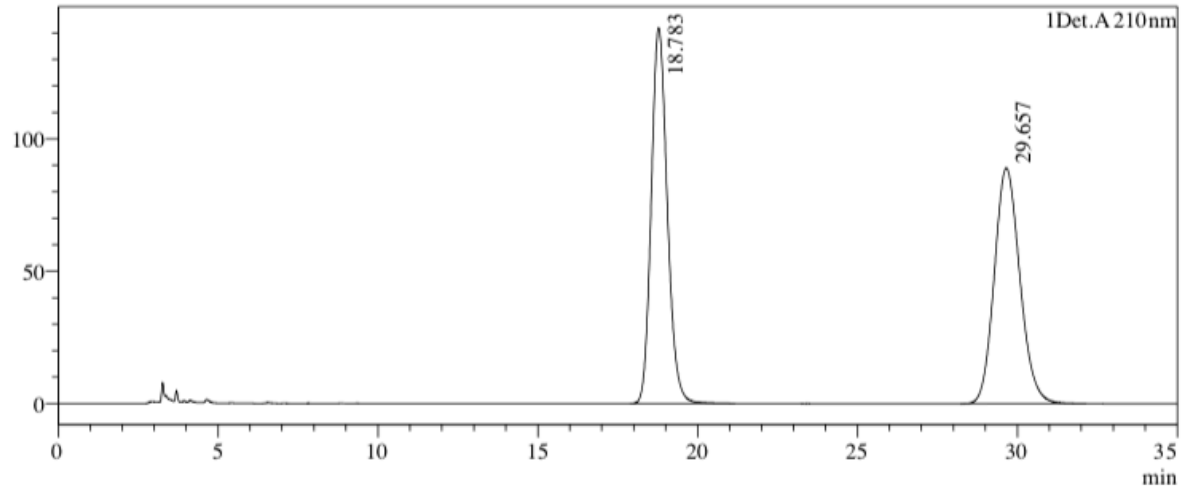

7.3190
7.3064
7.2927
7.2560
7.2446
7.2400
7.2297
7.2251
7.2160
7.2102
7.1965
7.1885
7.1816
5.1293
5.1168
5.1030
5.0011
4.9873
4.9793
4.9656
4.9473
4.9335
4.9255
4.9118
2.3155
1.5666
7.0825
3.0539
2.0826
2.0707
1.0000
PPM
10
8
6
4
2
0


Ph
NO2

10ak

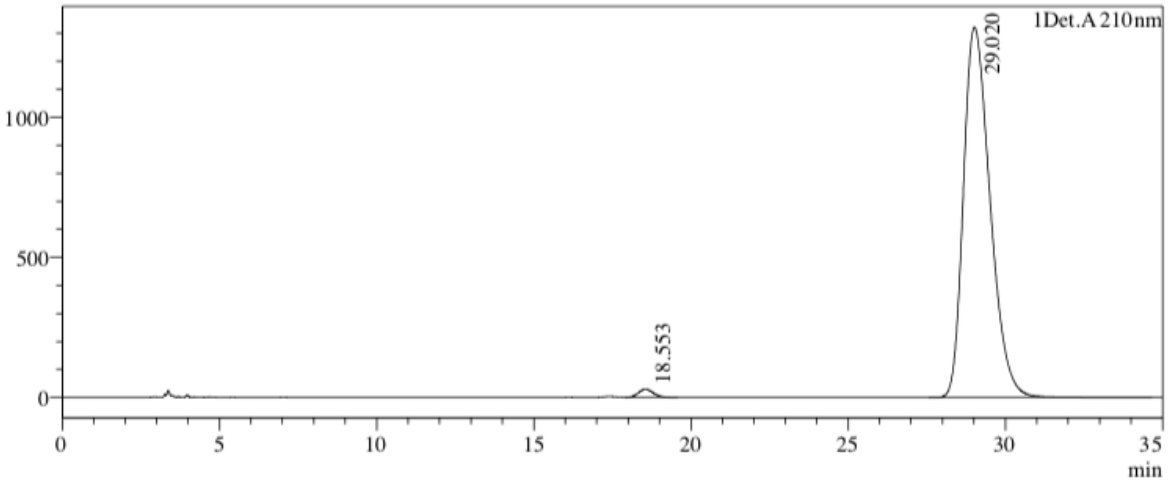

138.6902
137.0625
136.5072
131.2506
128.9431
127.9665
127.4686
126.3962
125.7739
79.1639
77.2106
77.0000
76.7894
44.9533
19.6280
PPM
200
175
150
125
100
75
50
25
0

10ak, condition : OD-H, 1.0 ml/min, Hex/IPA = 60:40, 210 nm



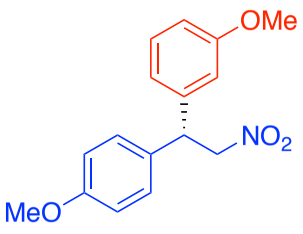
Det.A 210nm

Peak#	Ret. Time	Area	Height	Area%
1	18.783	4953550	141964	49.974
2	29.657	4958709	89048	50.026

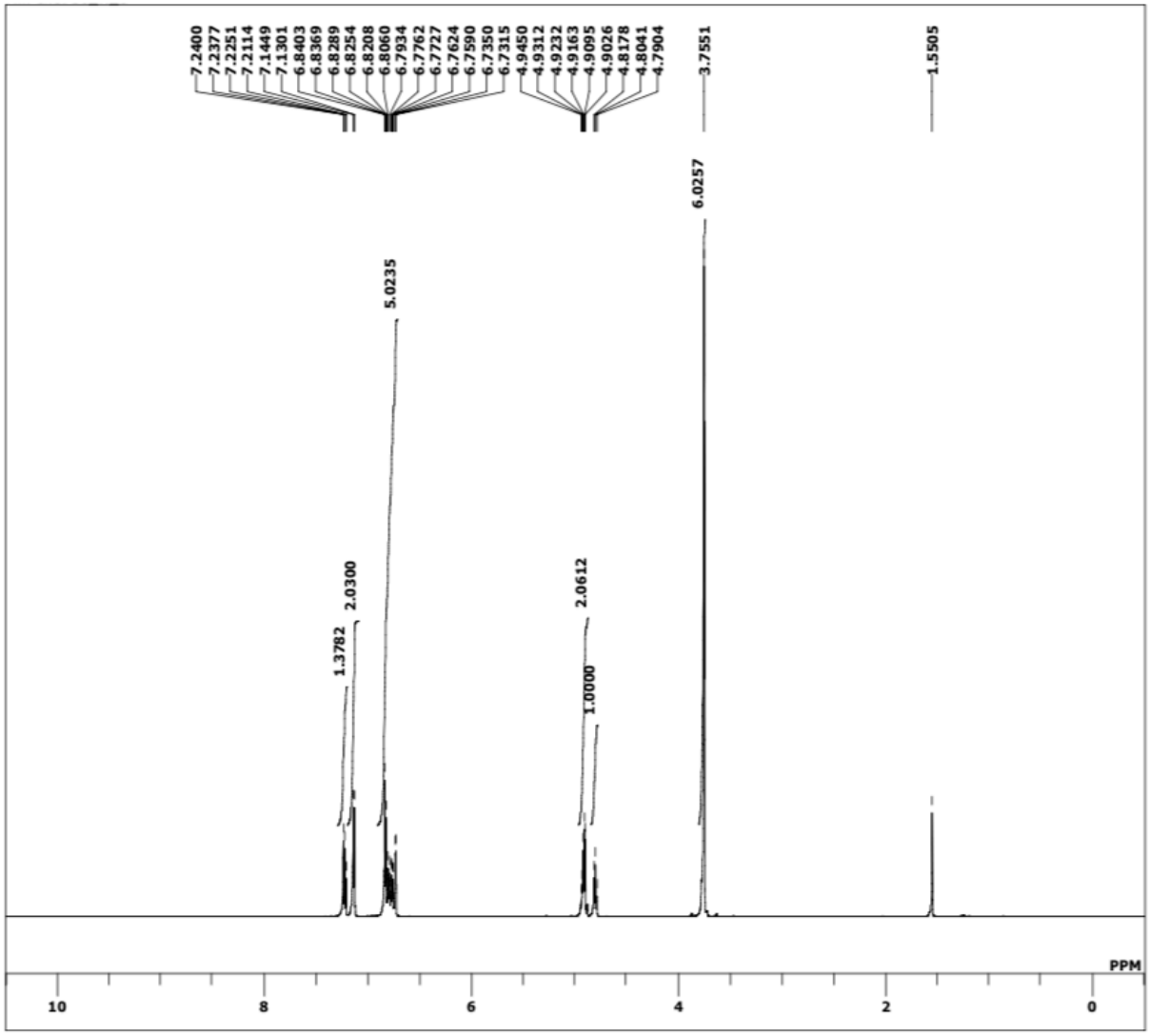


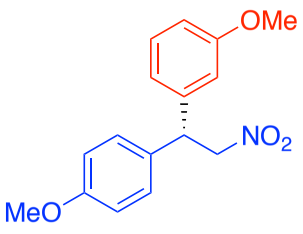
Det.A 210nm

Peak#	Ret. Time	Area	Height	Area%
1	18.553	977954	29362	1.241
2	29.020	77824551	1321852	98.759

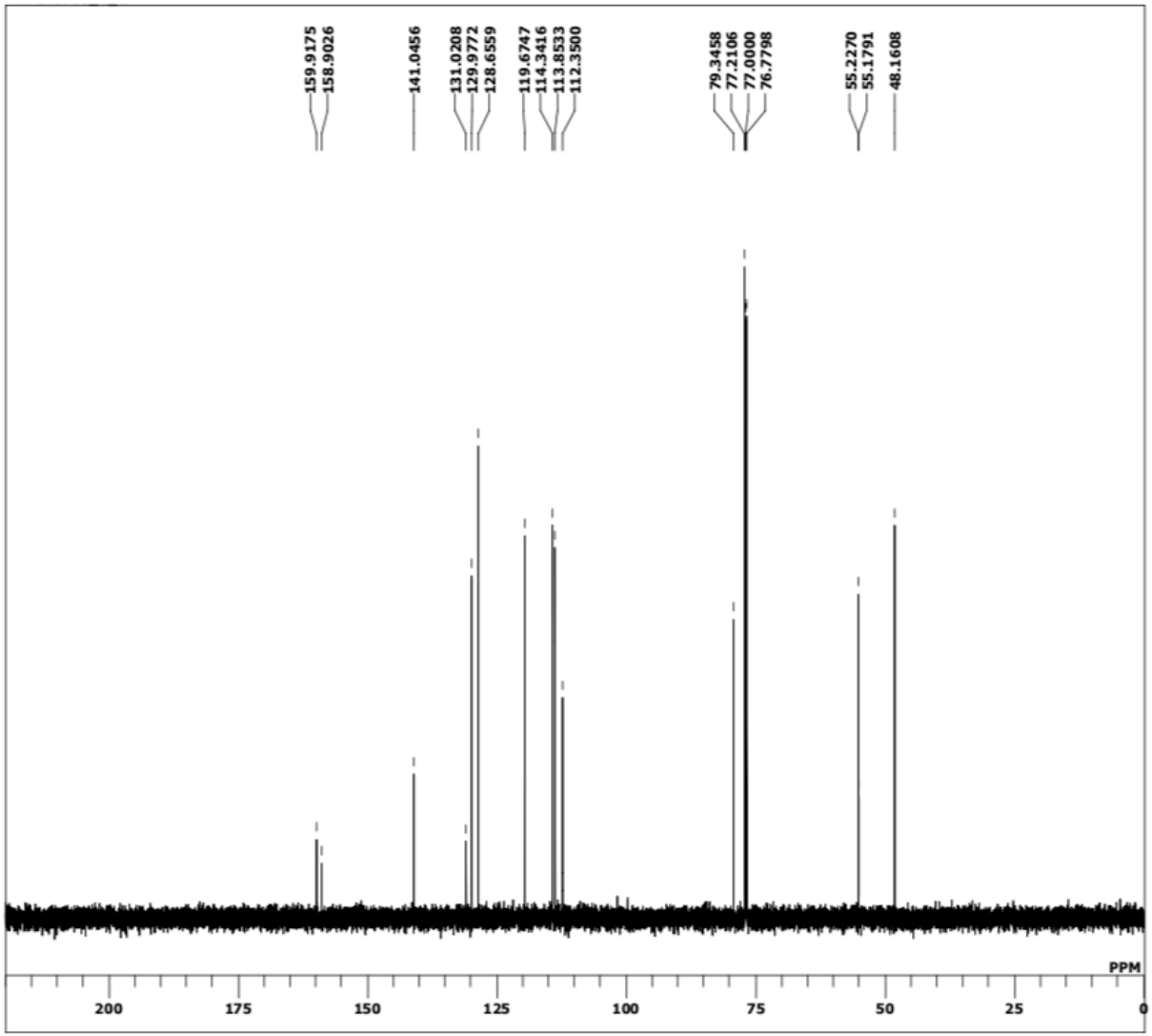

OMe
NO2
MeO

10bc

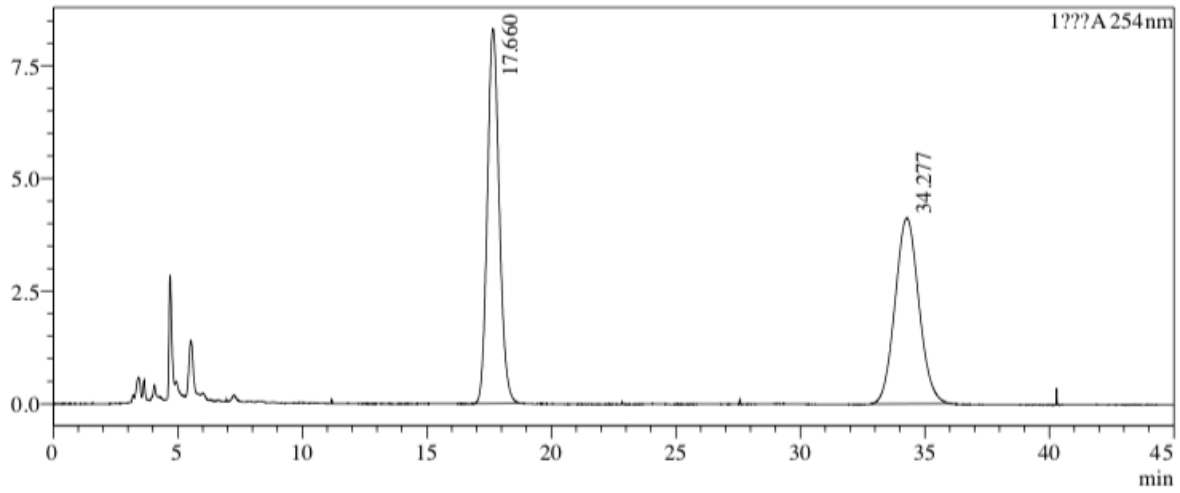

7.2400
7.2377
7.2251
7.2114
7.1449
7.1301
6.8403
6.8369
6.8289
6.8254
6.8208
6.8060
6.7934
6.7762
6.7727
6.7624
6.7590
6.7350
6.7315
4.9450
4.9312
4.9232
4.9163
4.9095
4.9026
4.8178
4.8041
4.7904
3.7551
1.5505
6.0257
5.0235
2.0300
1.3782
2.0612
1.0000
PPM
10
8
6
4
2
0


OMe
NO2
MeO

10bc

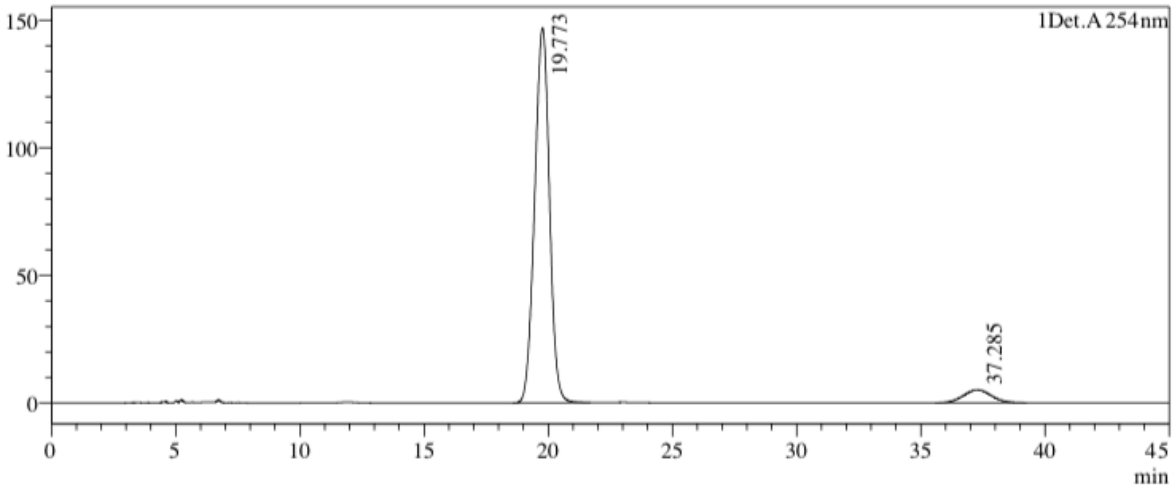

159.9175
158.9026
141.0456
131.0208
129.9772
128.6559
119.6747
114.3416
113.8533
112.3500
79.3458
77.2106
77.0000
76.7798
55.2270
55.1791
48.1608
PPM
200
175
150
125
100
75
50
25
0

10bc, condition : OD-H, 1.0 ml/min, Hex/IPA = 50:50, 254 nm



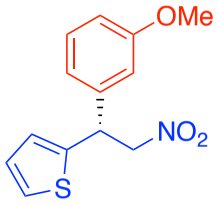
???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	17.660	276091	8321	50.172
2	34.277	274193	4123	49.828

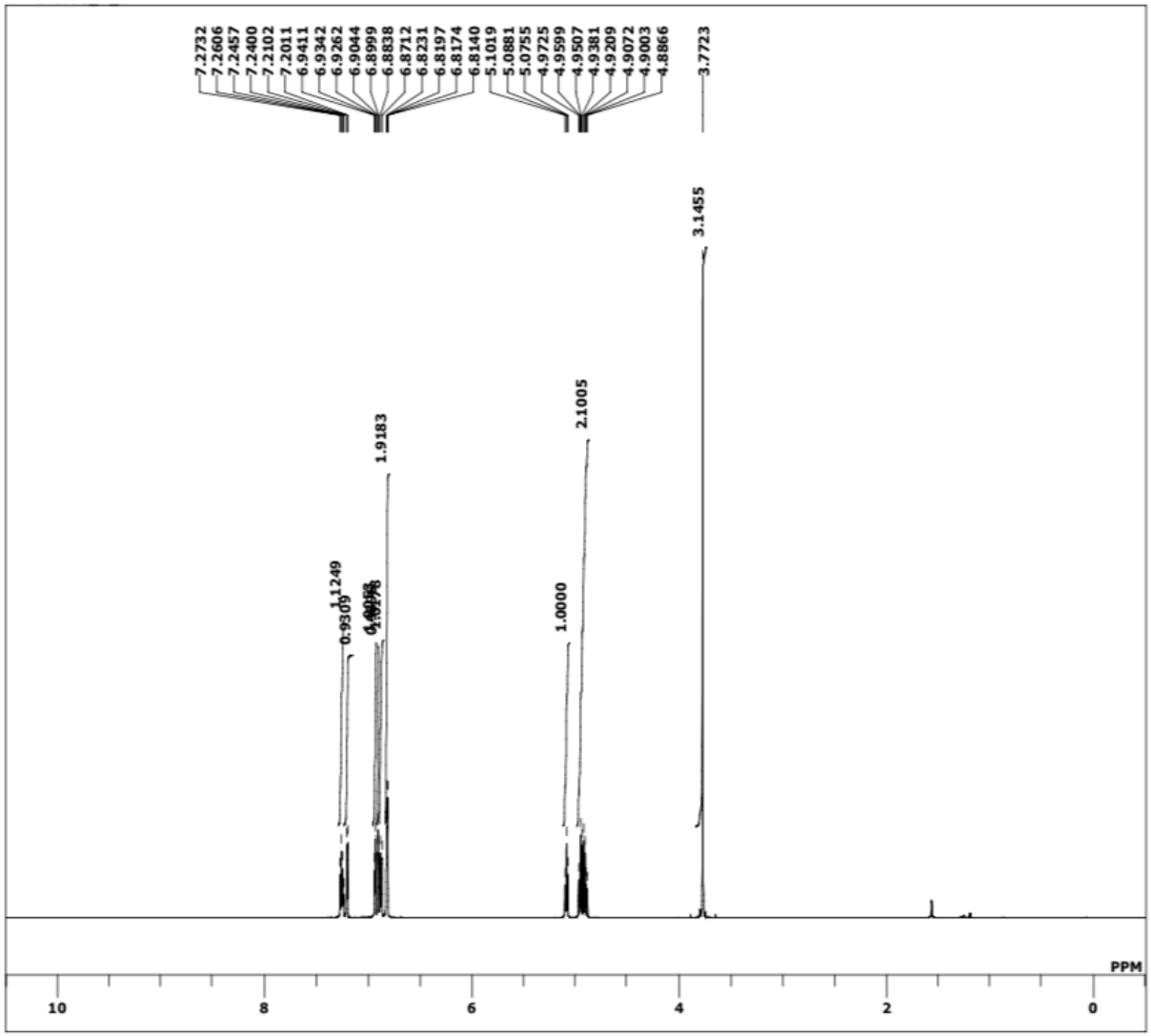


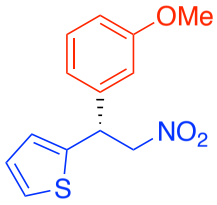
Det.A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	19.773	6090752	146819	93.915
2	37.285	394644	5047	6.085

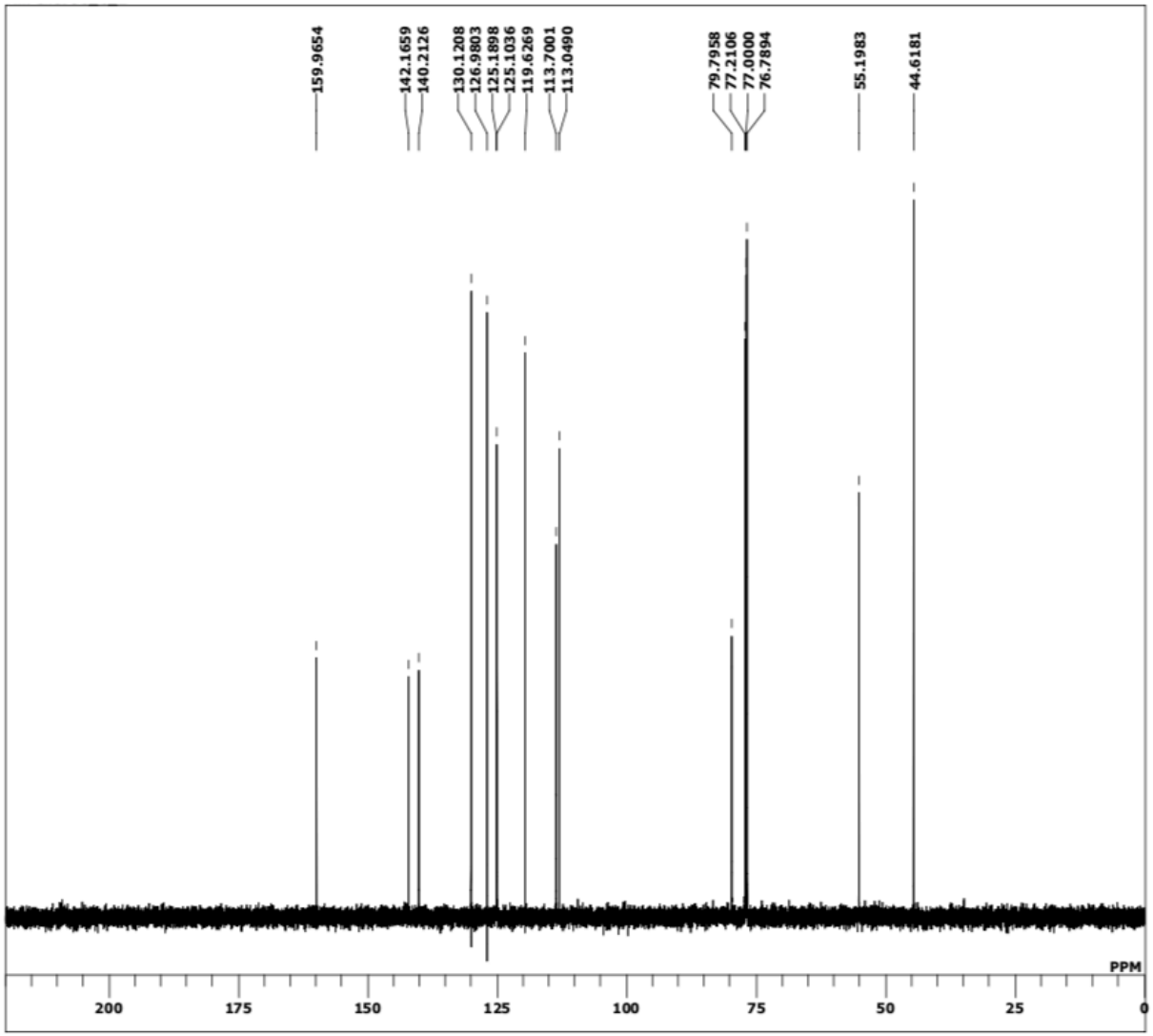

OMe
NO2
S

10cc

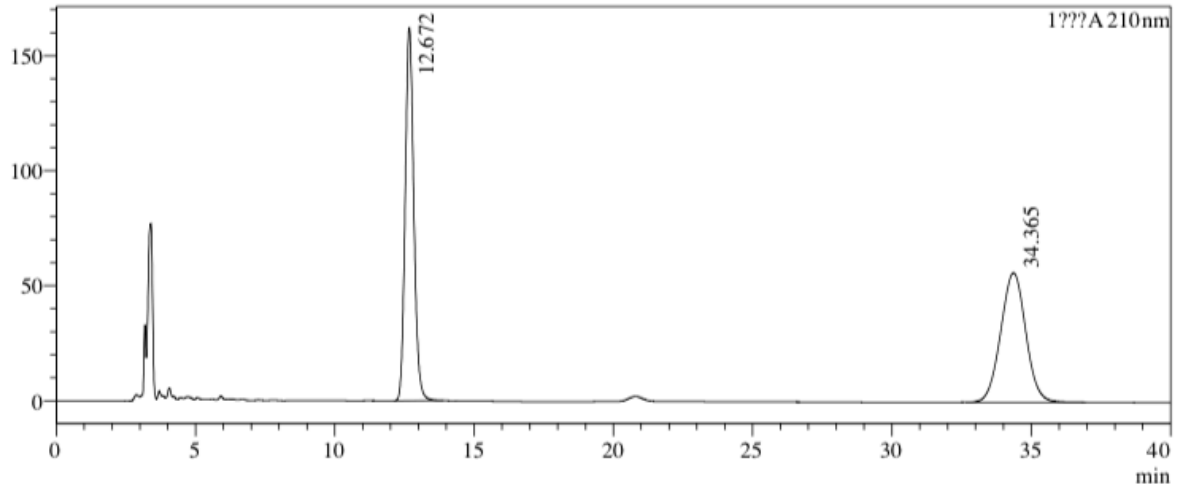

7.2732
7.2606
7.2457
7.2400
7.2102
7.2011
6.9411
6.9342
6.9262
6.9044
6.8999
6.8838
6.8712
6.8231
6.8197
6.8174
6.8140
5.1019
5.0881
5.0755
4.9725
4.9599
4.9507
4.9381
4.9209
4.9072
4.9003
4.8866
3.7723
3.1455
2.1005
1.9183
1.1249
0.9309
1.0000
PPM
10
8
6
4
2
0


OMe
NO2
S

10cc

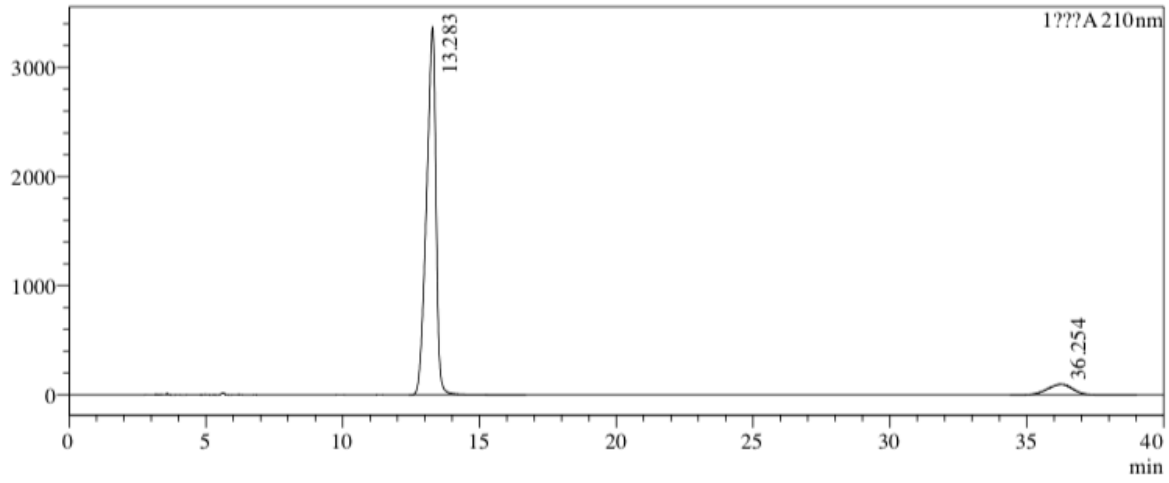

159.9654
142.1659
140.2126
130.1208
126.9803
125.1898
125.1036
119.6269
113.7001
113.0490
79.7958
77.2106
77.0000
76.7894
55.1983
44.6181
PPM
200
175
150
125
100
75
50
25
0

10cc, condition : OD-H, 1.0 ml/min, Hex/IPA = 60:40, 210 nm



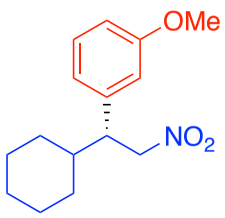
???A 210nm

Peak#	Ret. Time	Area	Height	Area%
1	12.672	3491267	162235	49.810
2	34.365	3517955	56294	50.190

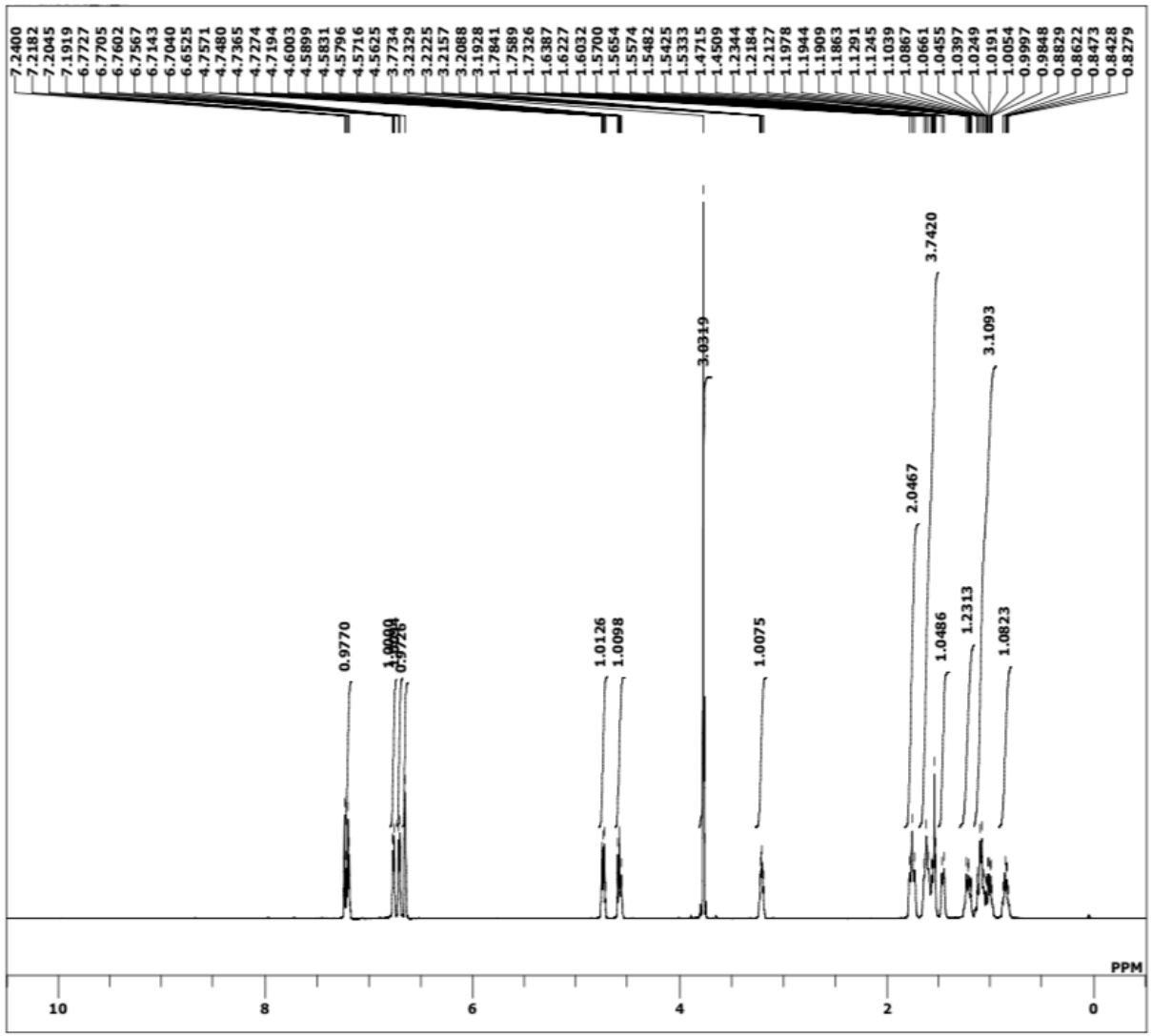


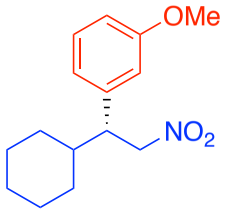
???A 210nm

Peak#	Ret. Time	Area	Height	Area%
1	13.283	81121184	3367499	92.569
2	36.254	6511643	98634	7.431

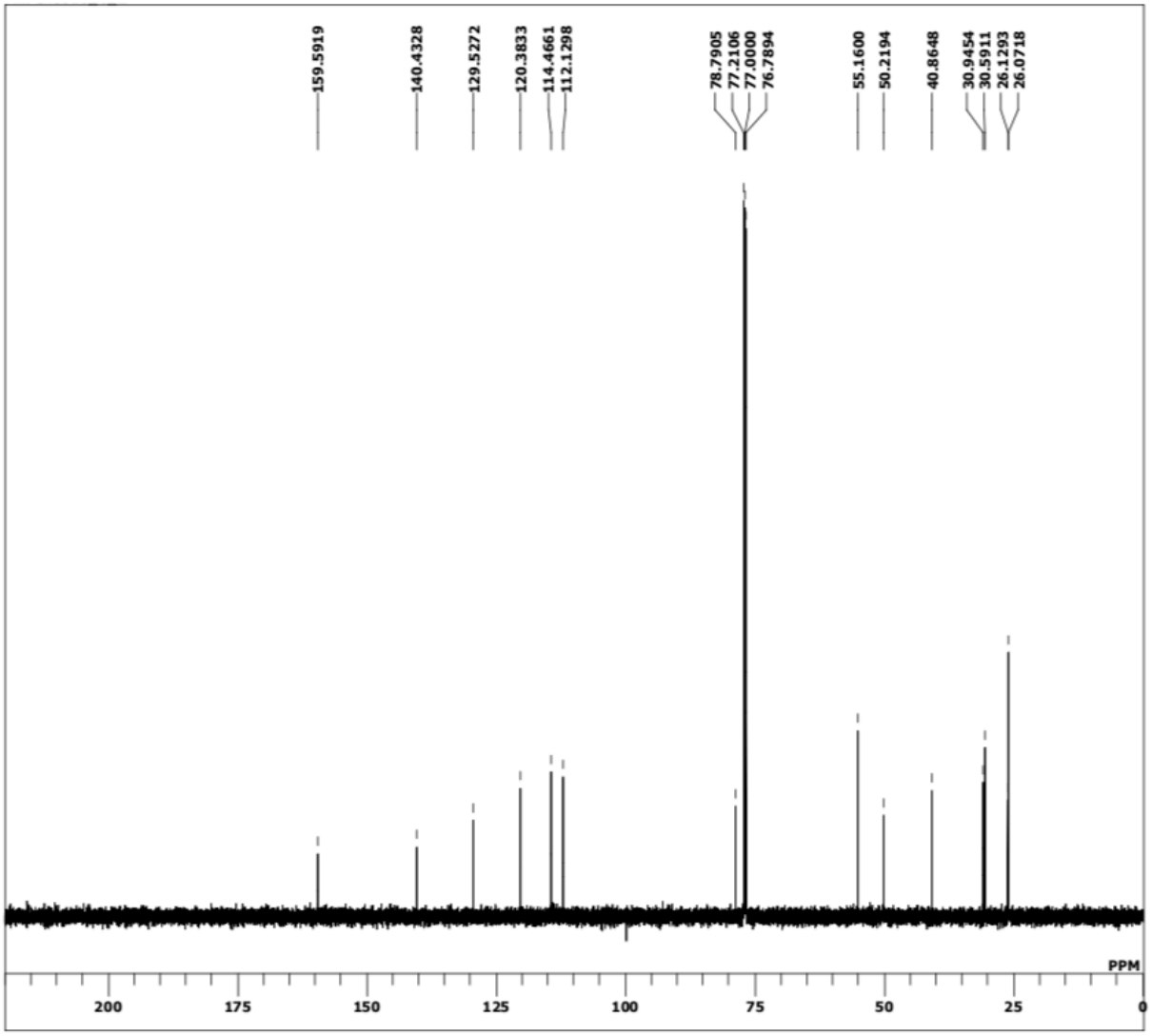

OMe
NO2

10dc

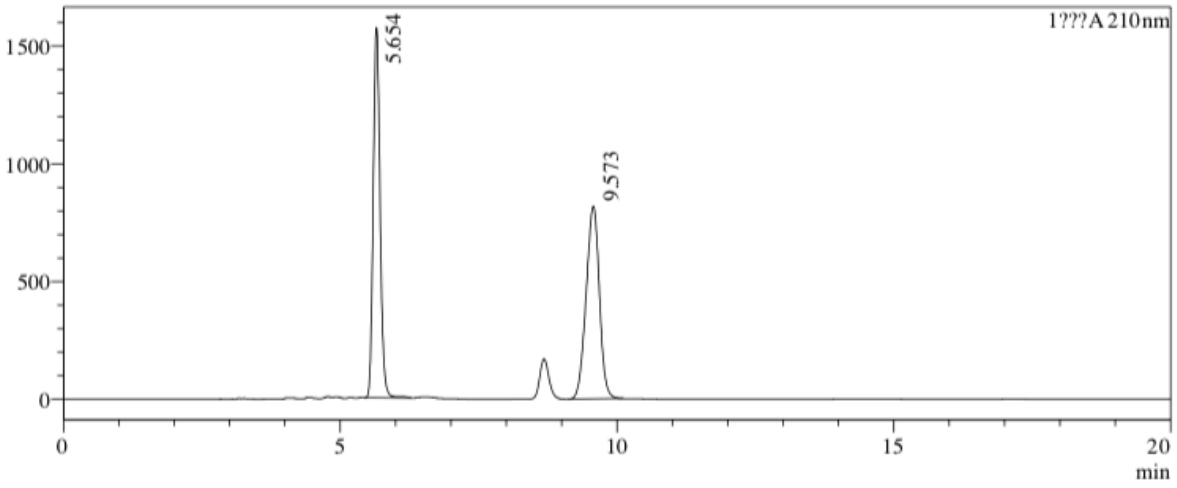

7.2400
7.2182
7.2045
7.1919
6.7727
6.7705
6.7602
6.7567
6.7143
6.7040
6.6525
4.7571
4.7480
4.7365
4.7274
4.7194
4.6003
4.5899
4.5831
4.5796
4.5716
4.5625
3.7734
3.2329
3.2225
3.2157
3.2088
3.1928
1.7841
1.7589
1.7326
1.6387
1.6227
1.6032
1.5700
1.5654
1.5574
1.5482
1.5425
1.5333
1.4715
1.4509
1.2344
1.2184
1.2127
1.1978
1.1944
1.1909
1.1863
1.1291
1.1245
1.1039
1.0867
1.0661
1.0455
1.0397
1.0249
1.0191
1.0054
0.9997
0.9848
0.8829
0.8622
0.8473
0.8428
0.8279
0.9770
1.0126
1.0098
3.0319
1.0075
2.0467
3.7420
1.0486
1.2313
3.1093
1.0823
PPM
10
8
6
4
2
0


OMe
NO2

10dc

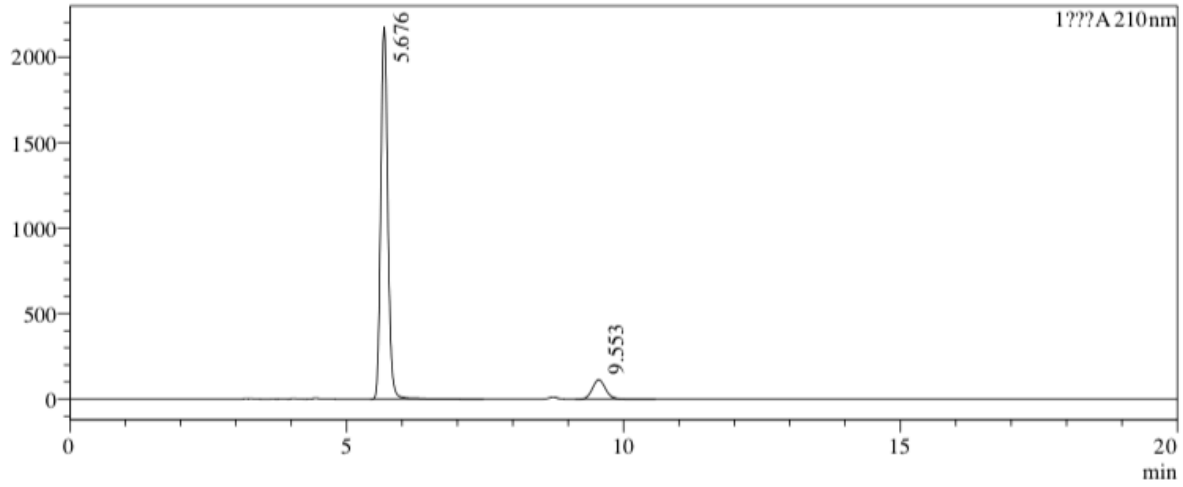

159.5919
140.4328
129.5272
120.3833
114.4661
112.1298
78.7905
77.2106
77.0000
76.7894
55.1600
50.2194
40.8648
30.9454
30.5911
26.1293
26.0718
PPM
200
175
150
125
100
75
50
25
0

10dc, condition : OD-H, 1.0 ml/min, Hex/IPA = 60:40, 210 nm



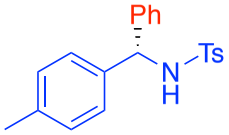
???A 210nm

Peak#	Ret. Time	Area	Height	Area%
1	5.654	13493426	1570824	49.774
2	9.573	13615920	817895	50.226

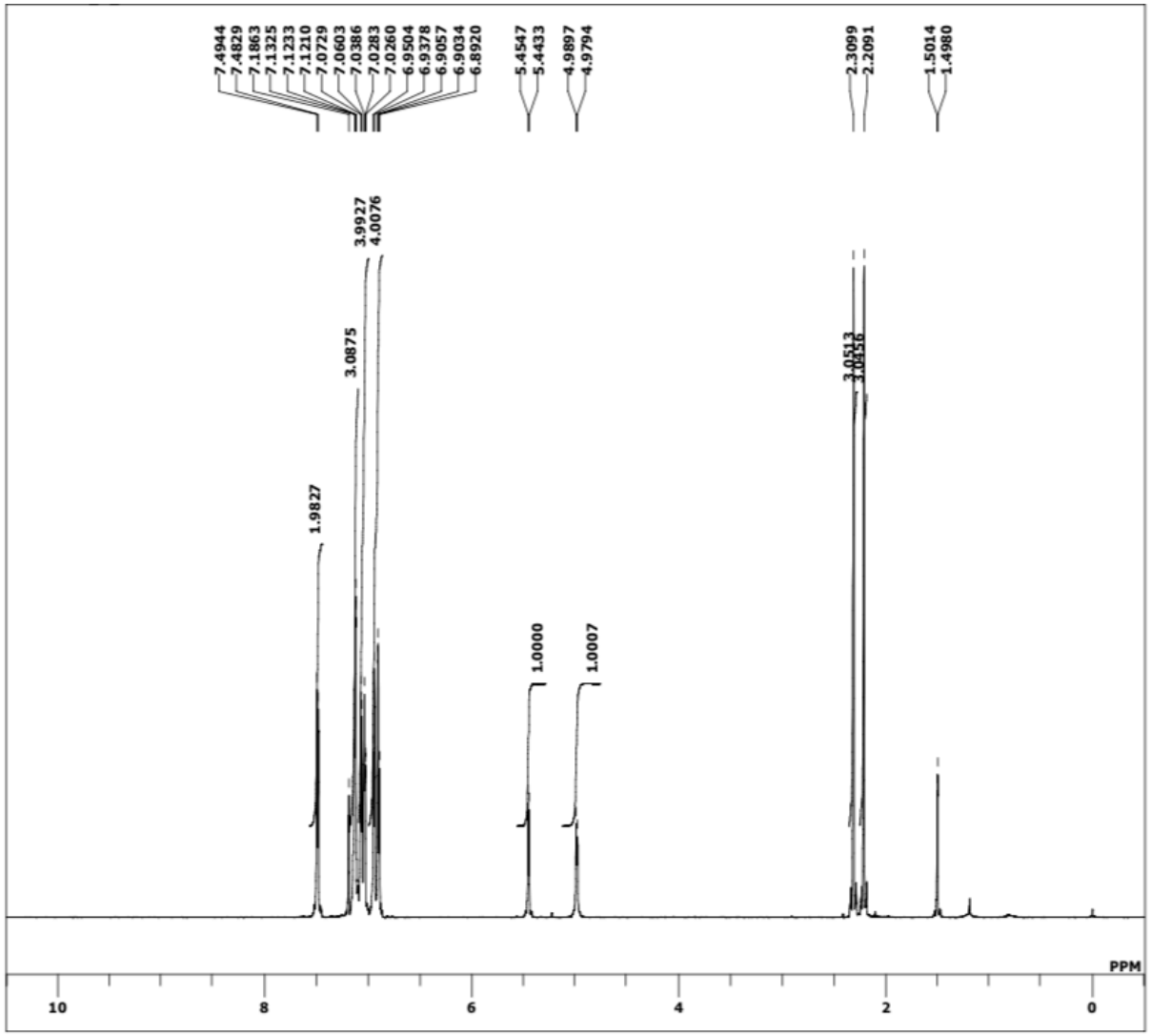


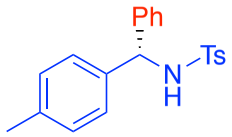
???A 210nm

Peak#	Ret. Time	Area	Height	Area%
1	5.676	19356830	2176812	91.139
2	9.553	1881911	113765	8.861

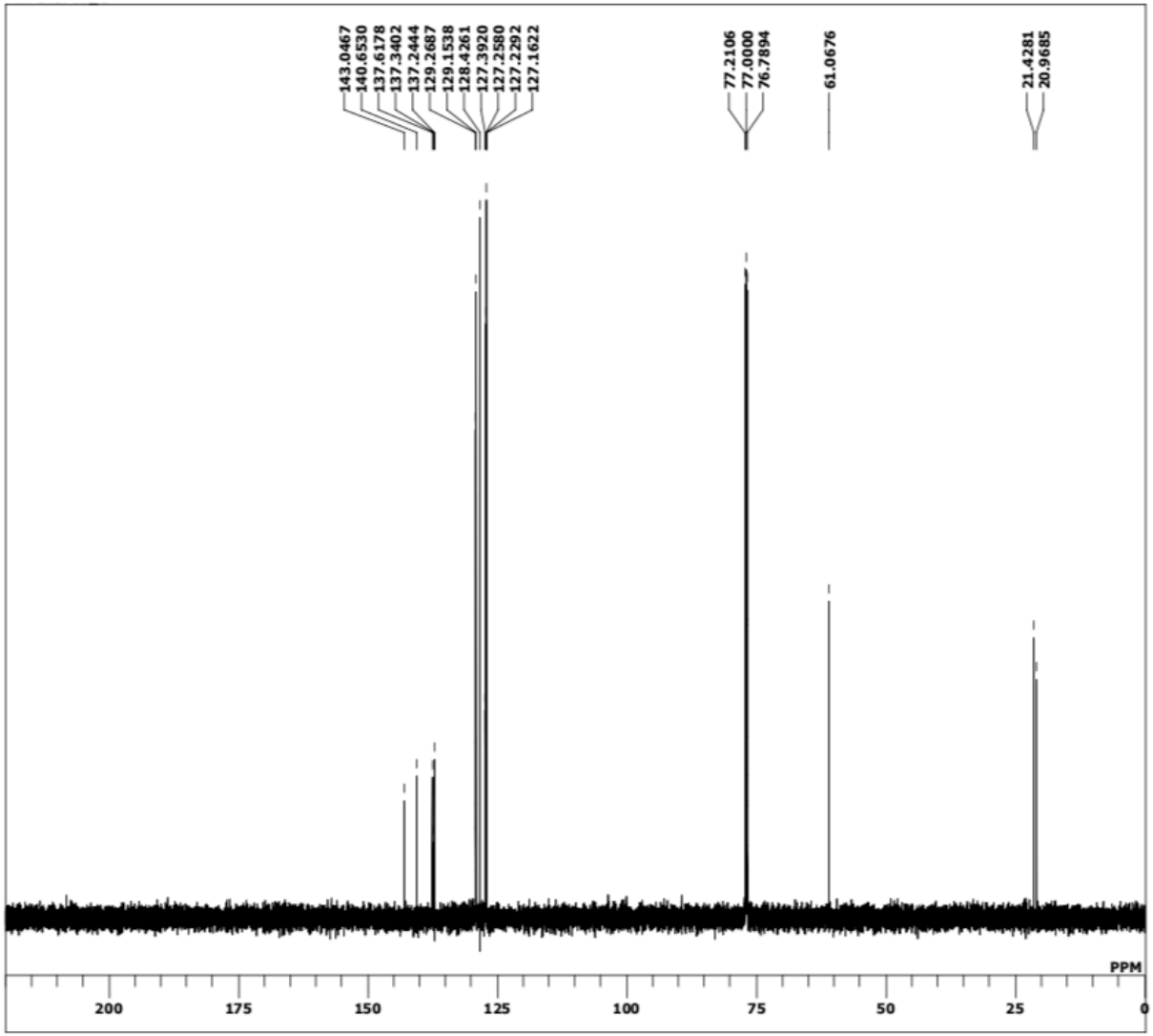

Ph
N
H
Ts

11aa

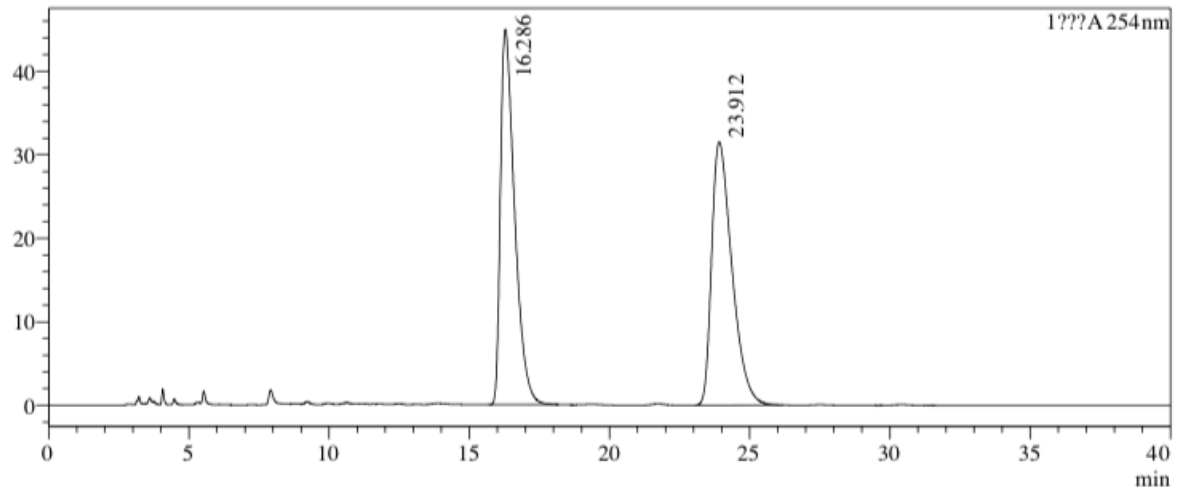

7.4944
7.4829
7.1863
7.1325
7.1233
7.1210
7.0729
7.0603
7.0386
7.0283
7.0260
6.9504
6.9378
6.9057
6.9034
6.8920
5.4547
5.4433
4.9897
4.9794
2.3099
2.2091
1.5014
1.4980
3.9927
4.0076
3.0875
3.0513
3.0456
1.9827
1.0000
1.0007
PPM
10
8
6
4
2
0


Ph
N
H
Ts

11aa

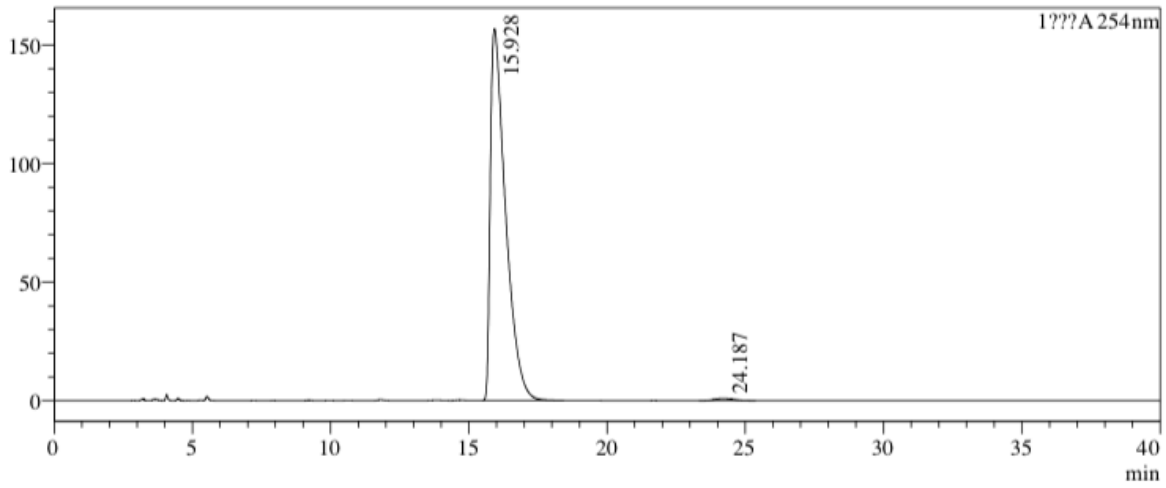

143.0467
140.6530
137.6178
137.3402
137.2444
129.2687
129.1538
128.4261
127.3920
127.2580
127.2292
127.1622
77.2106
77.0000
76.7894
61.0676
21.4281
20.9685
PPM
200
175
150
125
100
75
50
25
0

11aa, condition : OD-H, 1.0 ml/min, Hex/IPA = 95:5, 254 nm



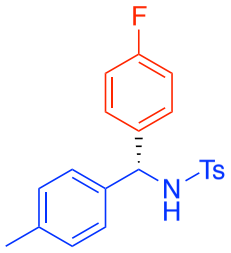
???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	16.286	1579911	44945	49.905
2	23.912	1585895	31519	50.095

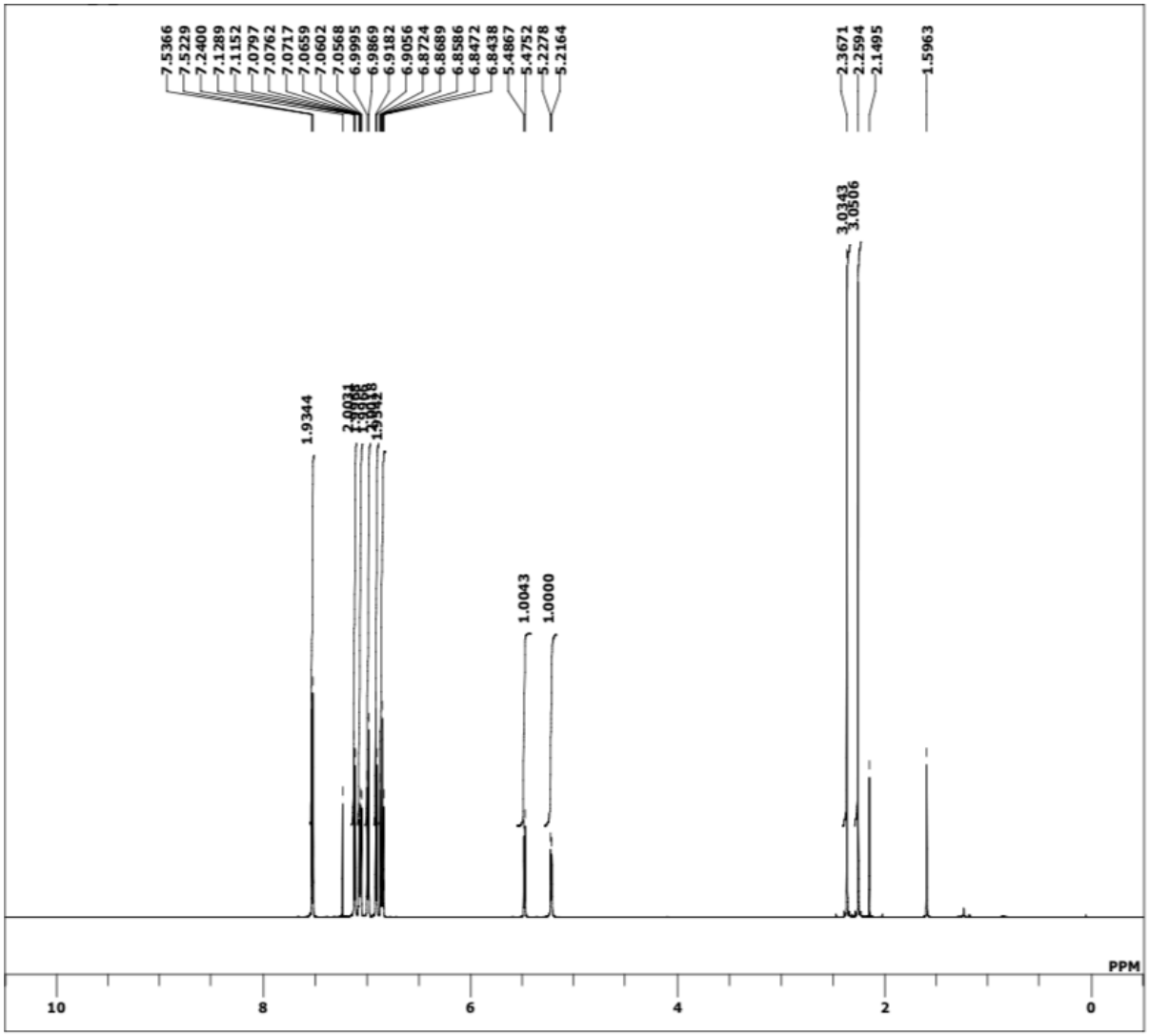


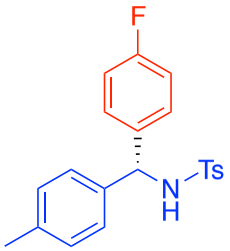
???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	15.928	6007234	156834	99.196
2	24.187	48677	1016	0.804

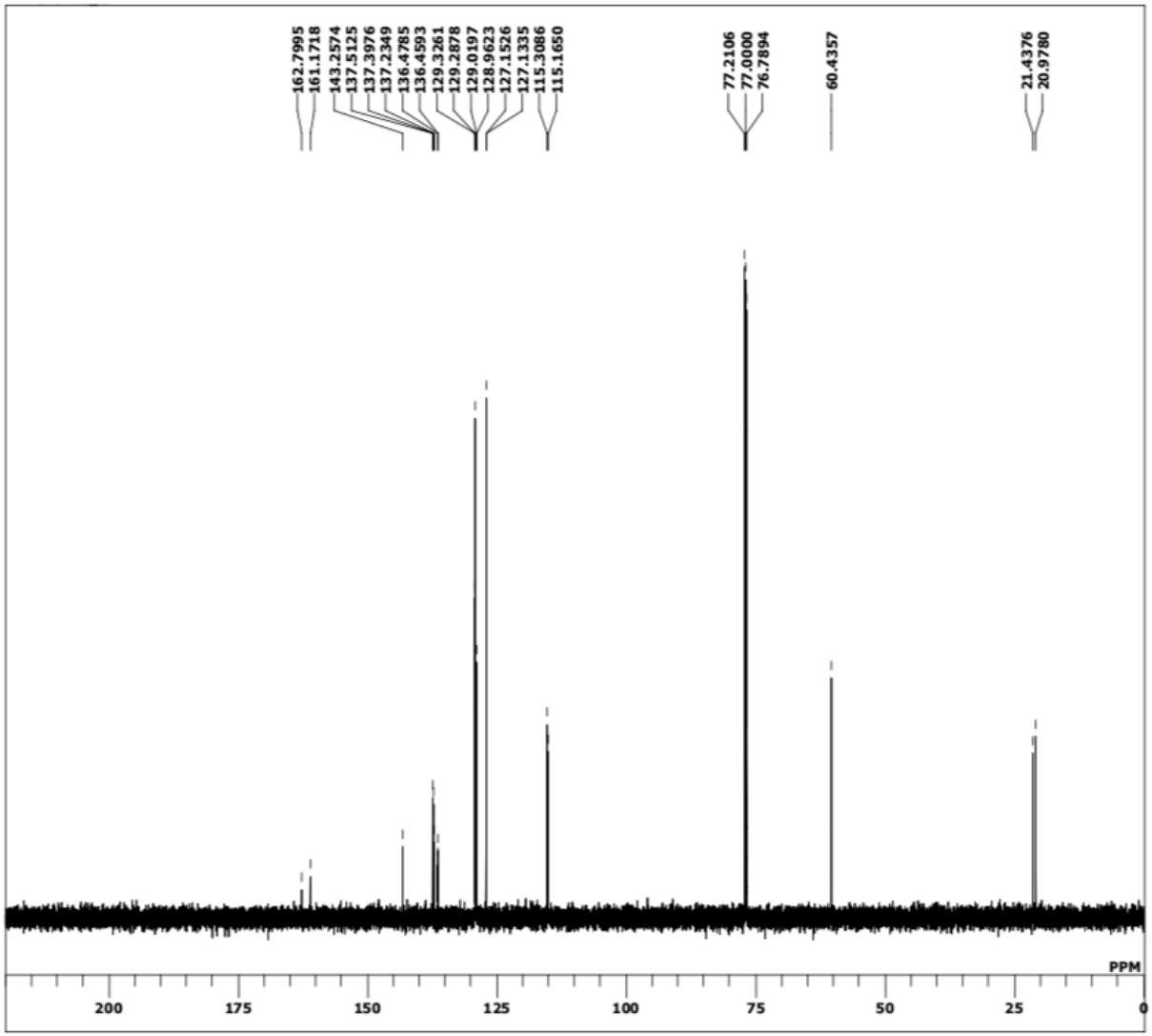

F
N
H
Ts

11ag

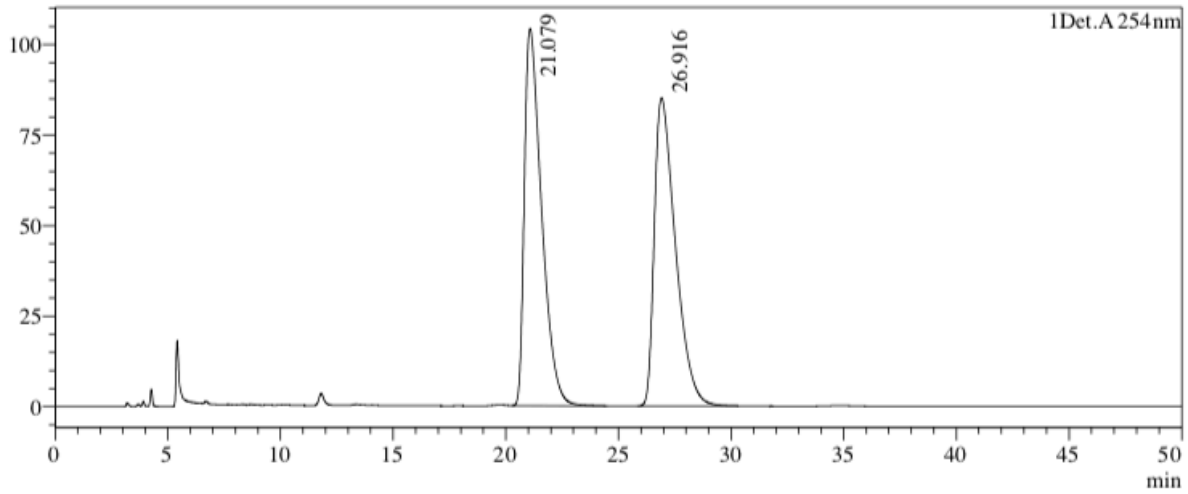

7.5366
7.5229
7.2400
7.1289
7.1152
7.0797
7.0762
7.0717
7.0659
7.0602
7.0568
6.9995
6.9869
6.9182
6.9056
6.8724
6.8689
6.8586
6.8472
6.8438
5.4867
5.4752
5.2278
5.2164
2.3671
2.2594
2.1495
1.5963
3.0343
3.0506
1.9344
1.9942
1.0043
1.0000
PPM
10
8
6
4
2
0


F
N
H
Ts

11ag

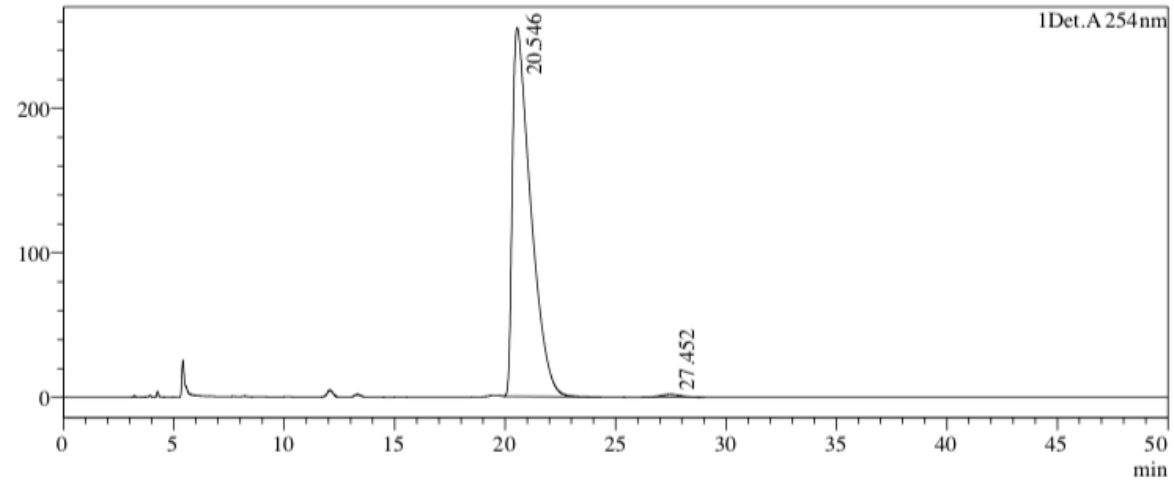

162.7995
161.1718
143.2574
137.5125
137.3976
137.2349
136.4785
136.4593
129.3261
129.2878
129.0197
128.9623
127.1526
127.1335
115.3086
115.1650
77.2106
77.0000
76.7894
60.4357
21.4376
20.9780
PPM
200
175
150
125
100
75
50
25
0

11ag, condition : OD-H, 1.0 ml/min, Hex/IPA = 95:5, 254 nm



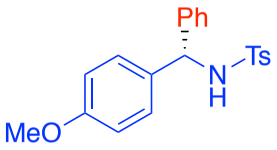
Det.A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	21.079	5529907	104154	49.921
2	26.916	5547462	85052	50.079

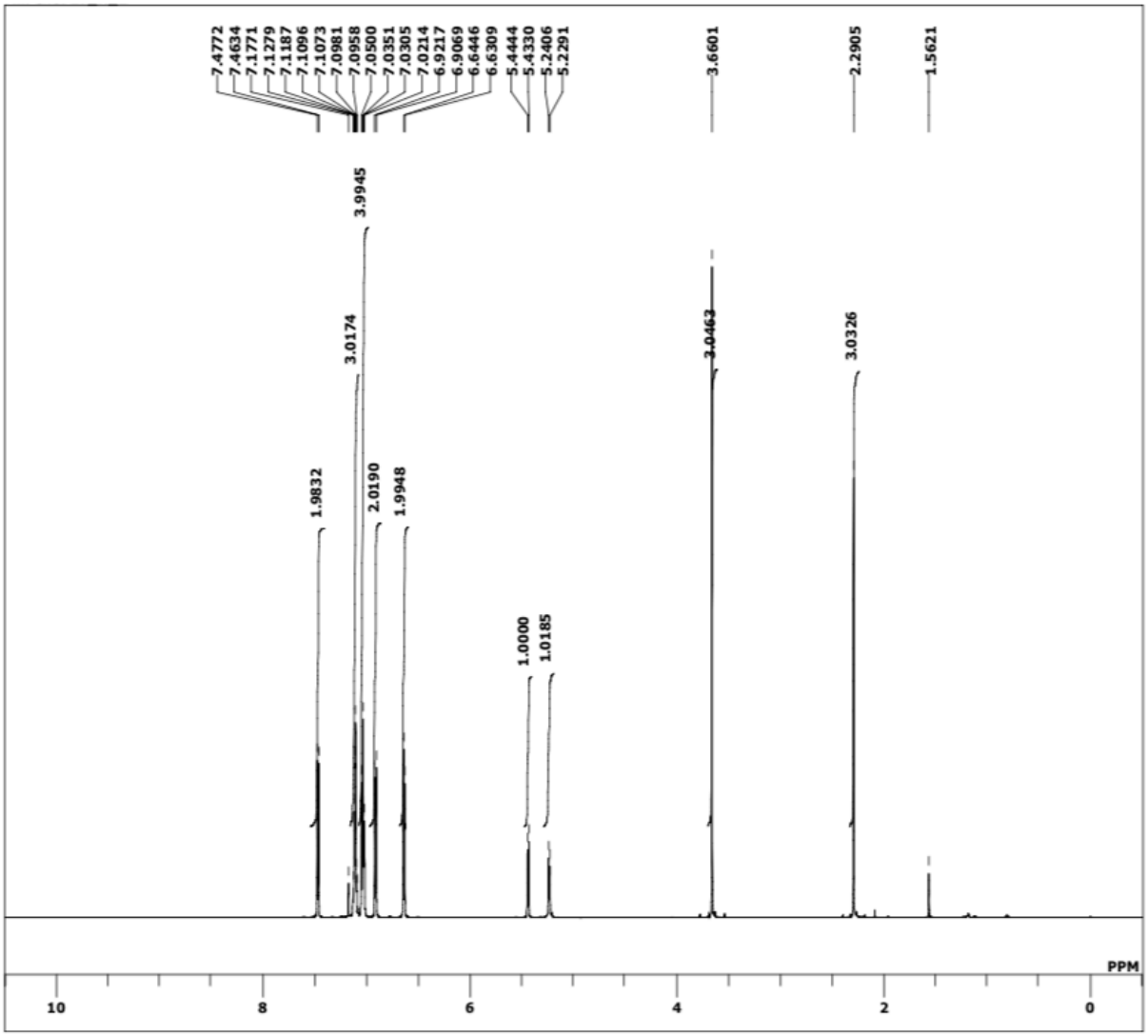


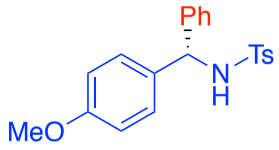
Det.A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	20.546	14700259	255067	99.227
2	27.452	114550	1883	0.773

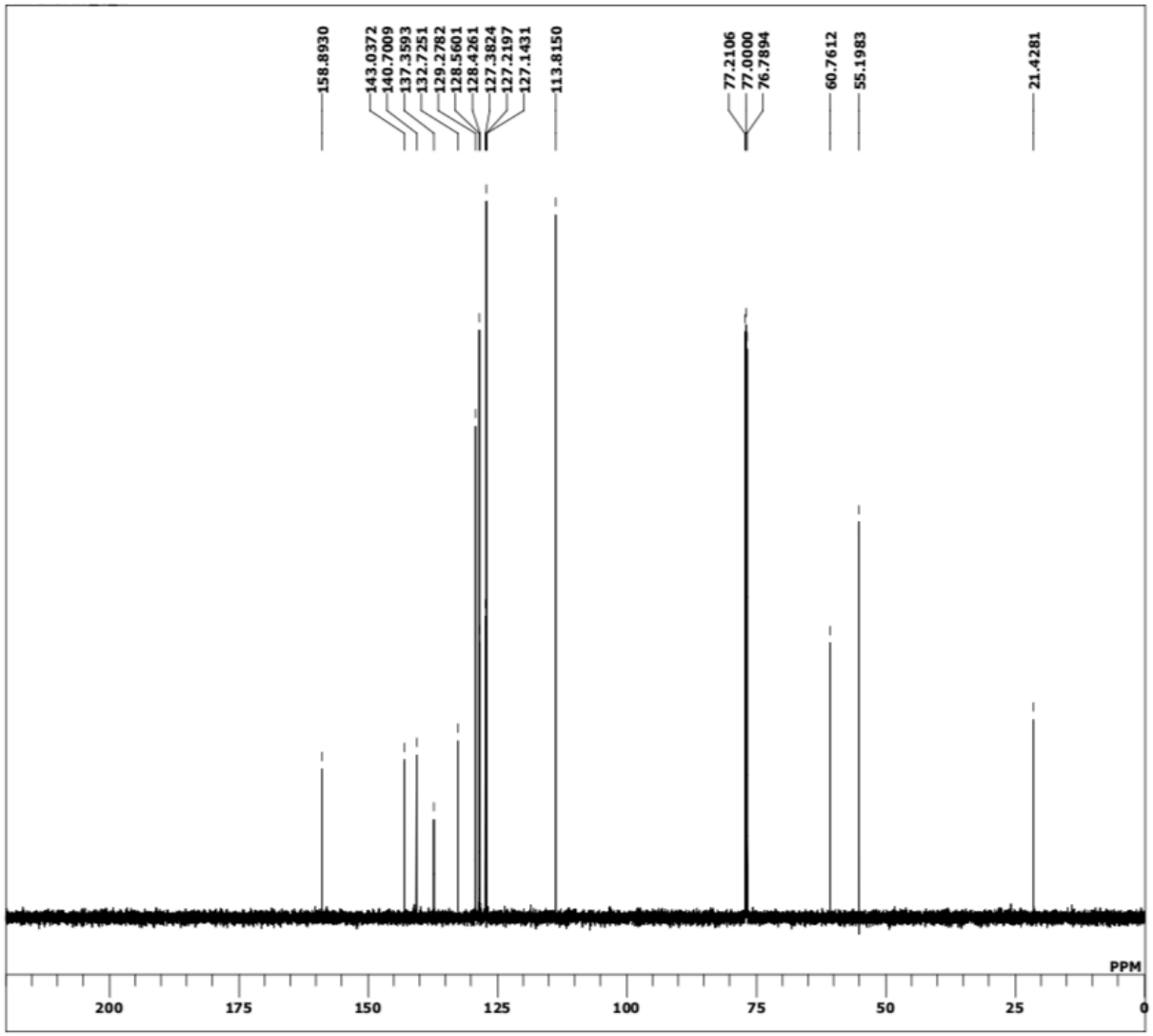

Ph
Ts
N
H
MeO

11ba

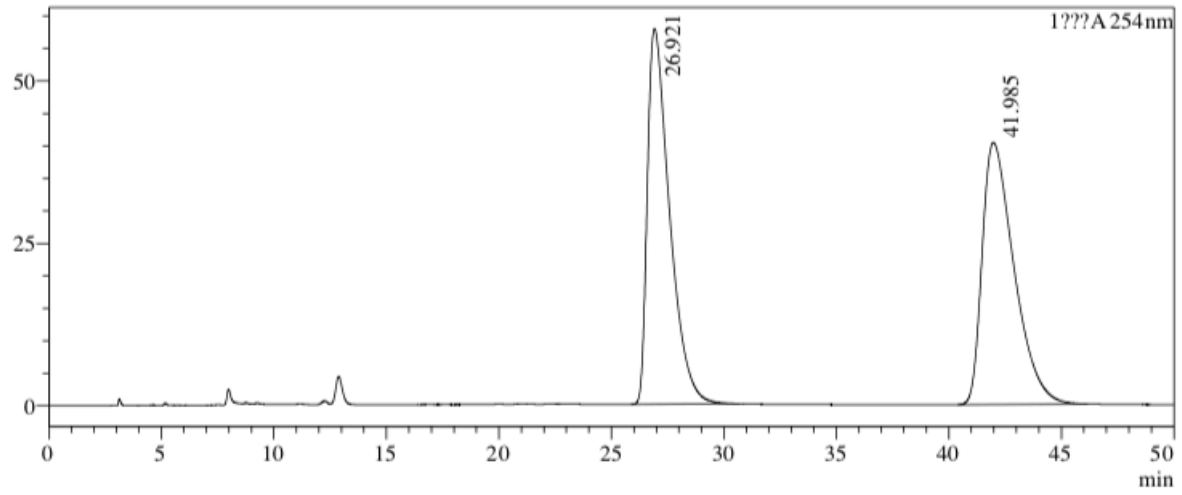

7.4772
7.4634
7.1771
7.1279
7.1187
7.1096
7.1073
7.0981
7.0958
7.0500
7.0351
7.0305
7.0214
6.9217
6.9069
6.6446
6.6309
5.4444
5.4330
5.2406
5.2291
3.6601
2.2905
1.5621
3.9945
3.0174
3.0463
3.0326
1.9832
2.0190
1.9948
1.0000
1.0185
PPM
10
8
6
4
2
0


Ph
Ts
N
H
MeO

11ba

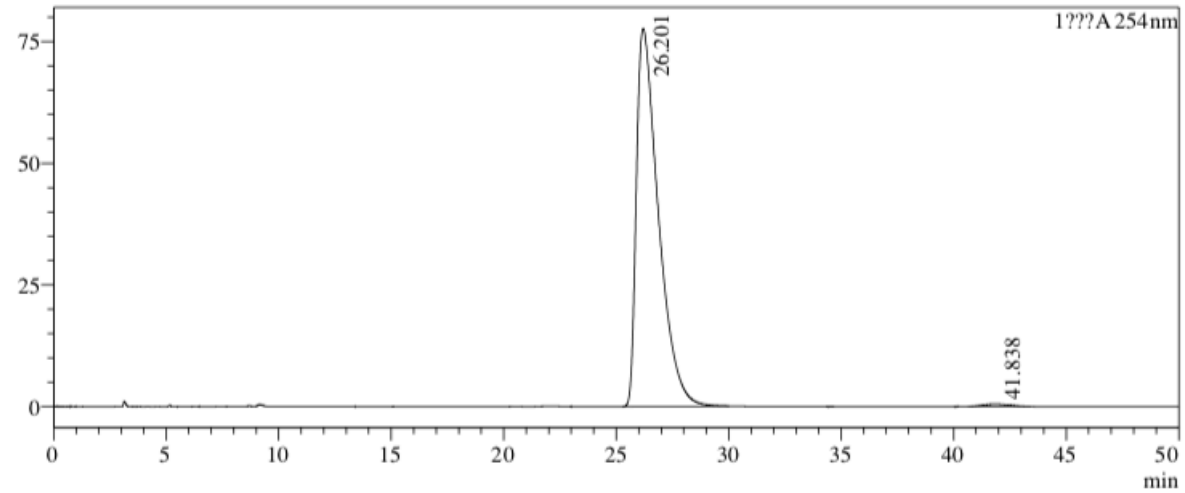

158.8930
143.0372
140.7009
137.3593
132.7251
129.2782
128.5601
128.4261
127.3824
127.2197
127.1431
113.8150
77.2106
77.0000
76.7894
60.7612
55.1983
21.4281
PPM
200
175
150
125
100
75
50
25
0

11ba, condition : OD-H, 1.0 ml/min, Hex/IPA = 95:5, 254 nm



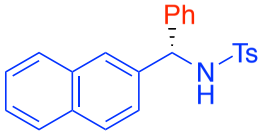
???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	26.921	3964277	57798	49.931
2	41.985	3975310	40306	50.069

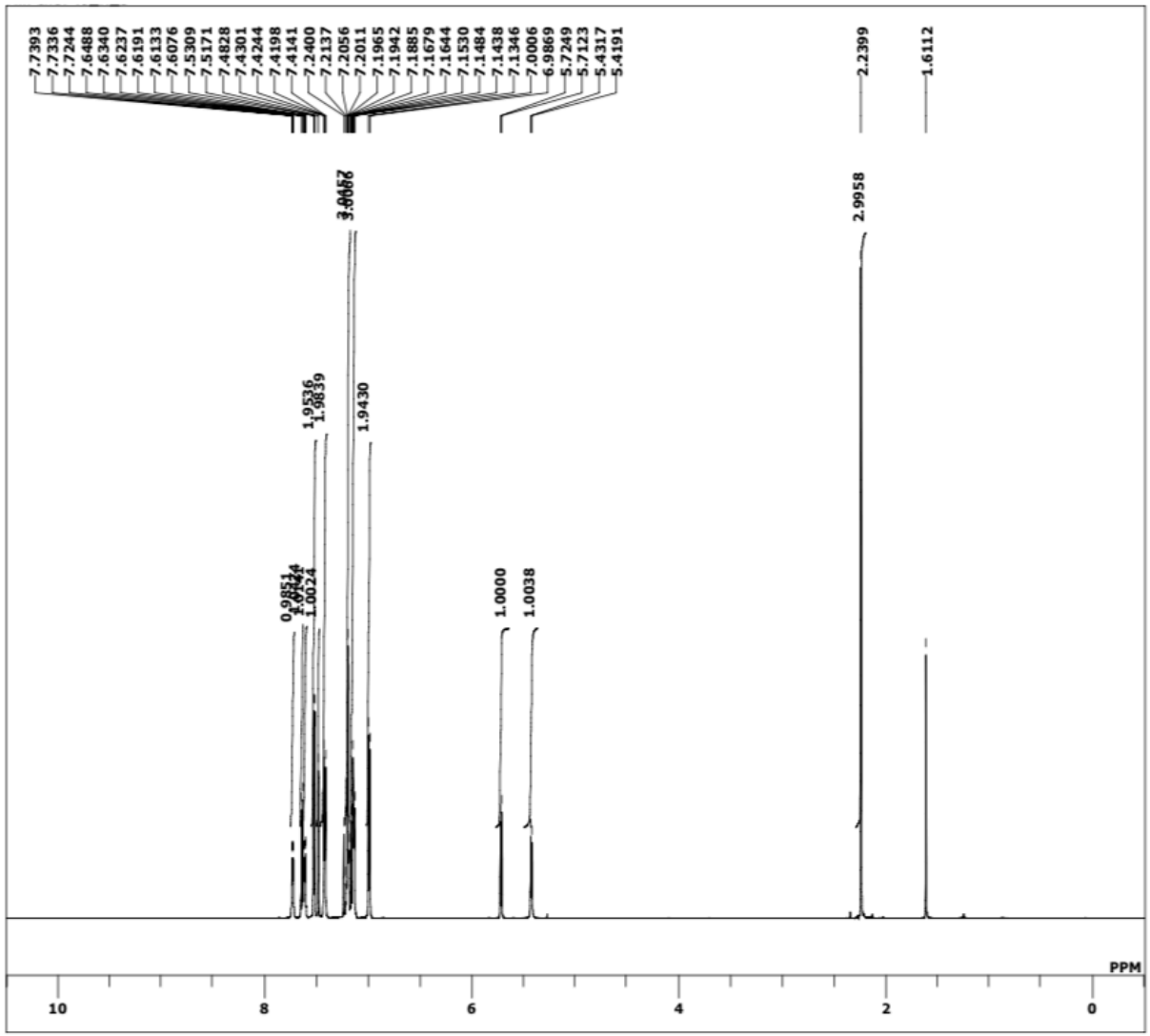


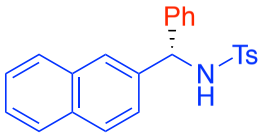
???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	26.201	5274539	77653	99.231
2	41.838	40864	500	0.769

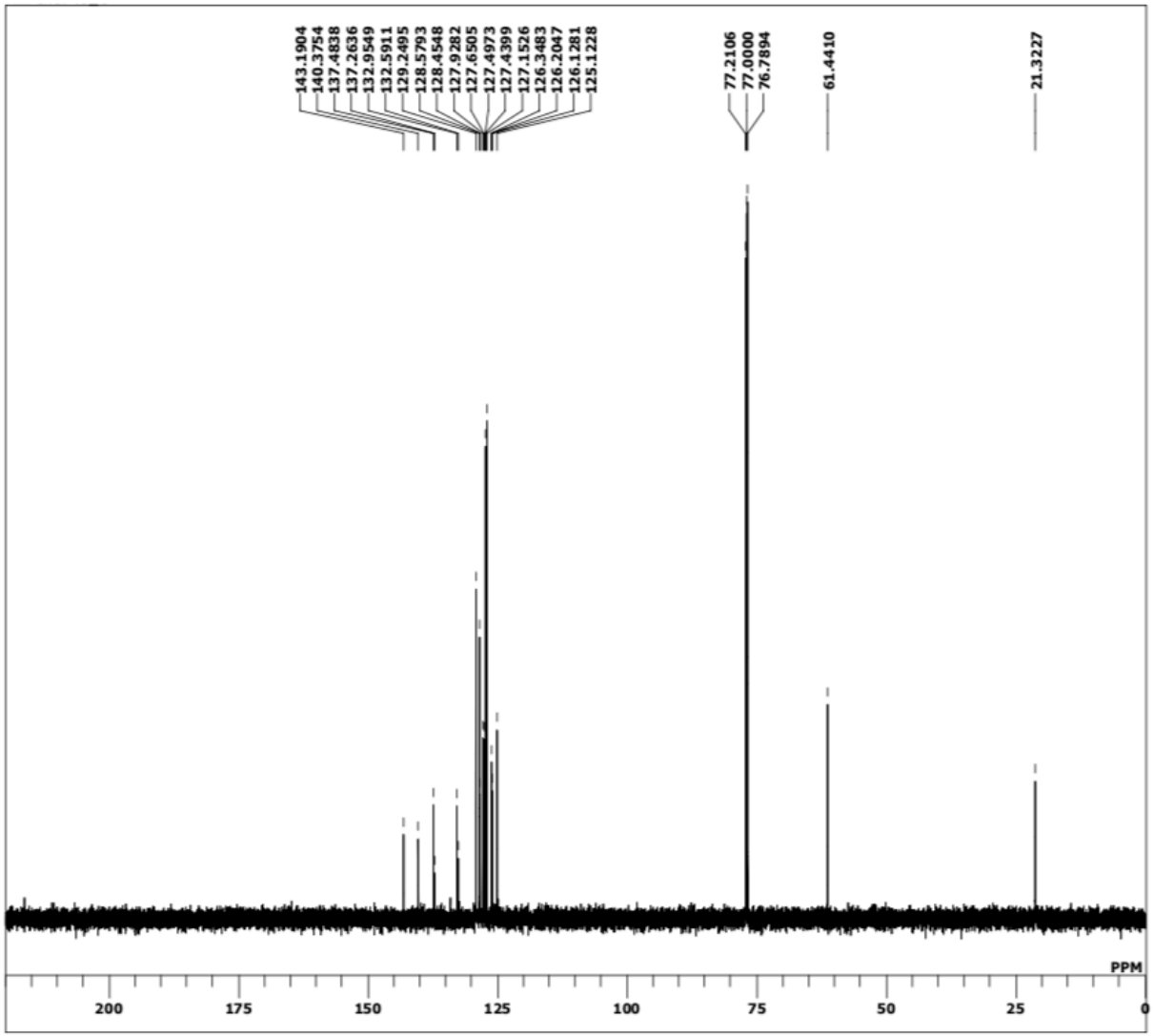

Ph
N
H
Ts

11ca

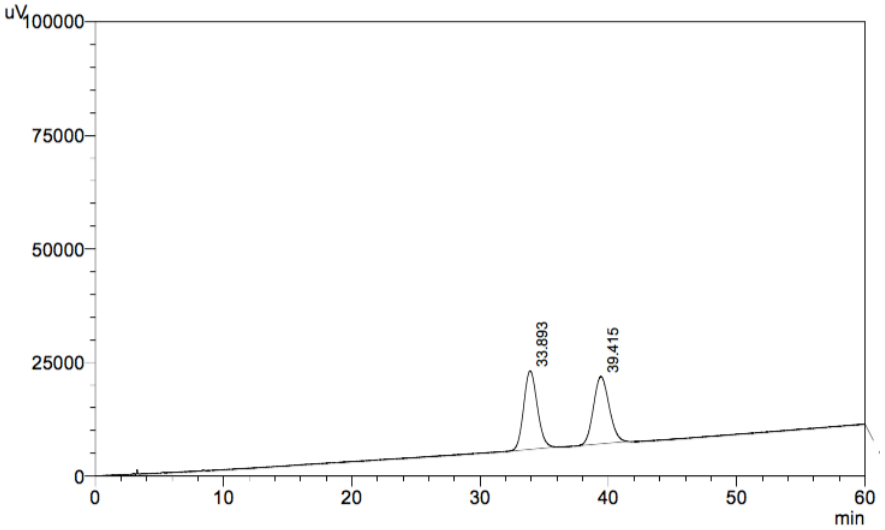

7.7393
7.7336
7.7244
7.6488
7.6340
7.6237
7.6191
7.6133
7.6076
7.5309
7.5171
7.4828
7.4301
7.4244
7.4198
7.4141
7.2400
7.2137
7.2056
7.2011
7.1965
7.1942
7.1885
7.1679
7.1644
7.1530
7.1484
7.1438
7.1346
7.0006
6.9869
5.7249
5.7123
5.4317
5.4191
2.2399
1.6112
2.9958
1.9536
1.9839
1.9430
1.0000
1.0038
PPM
10
8
6
4
2
0


Ph
N
H
Ts

11ca


143.1904
140.3754
137.4838
137.2636
132.9549
132.5911
129.2495
128.5793
128.4548
127.9282
127.6505
127.4973
127.4399
127.1526
126.3483
126.2047
126.1281
125.1228
77.2106
77.0000
76.7894
61.4410
21.3227
PPM
200
175
150
125
100
75
50
25
0

11ca, condition : OD-H, 1.0 ml/min, Hex/IPA = 95:5, 220 nm

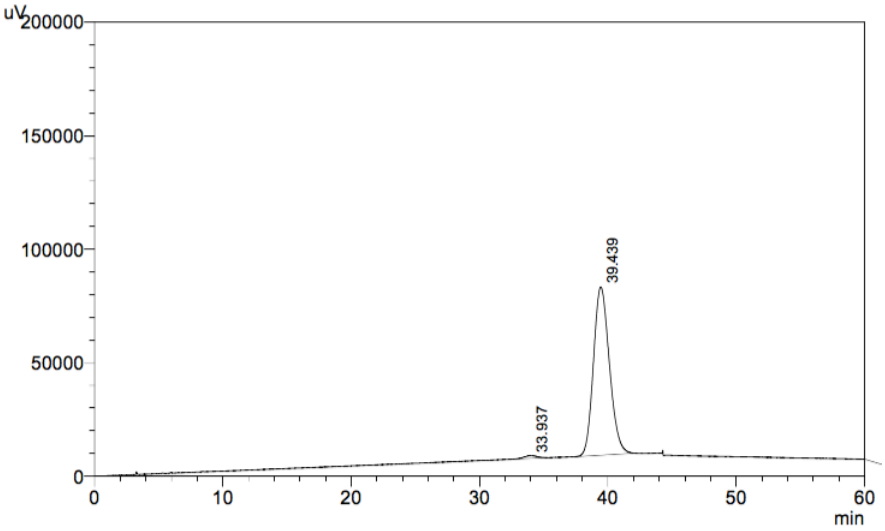


1 PDA Multi 1 / 220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.893	1276422	17289	50.323	53.819
2	39.415	1260049	14836	49.677	46.181
Total		2536471	32125	100.000	100.000

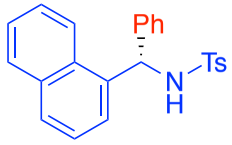


1 PDA Multi 1 / 220nm 4nm

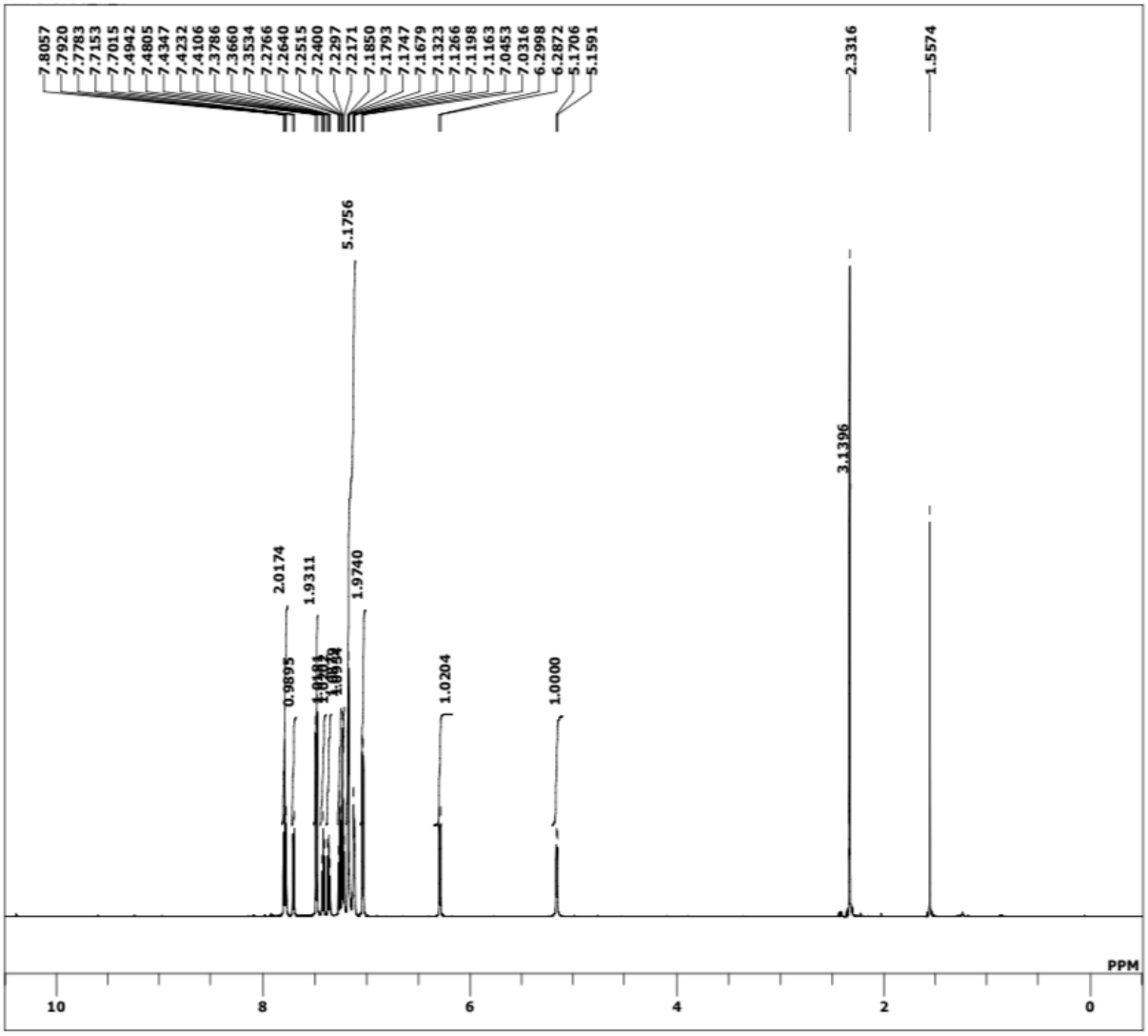
PeakTable

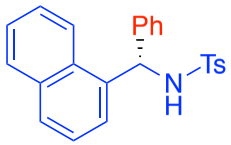
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.937	89188	1286	1.373	1.706
2	39.439	6407565	74099	98.627	98.294
Total		6496753	75385	100.000	100.000

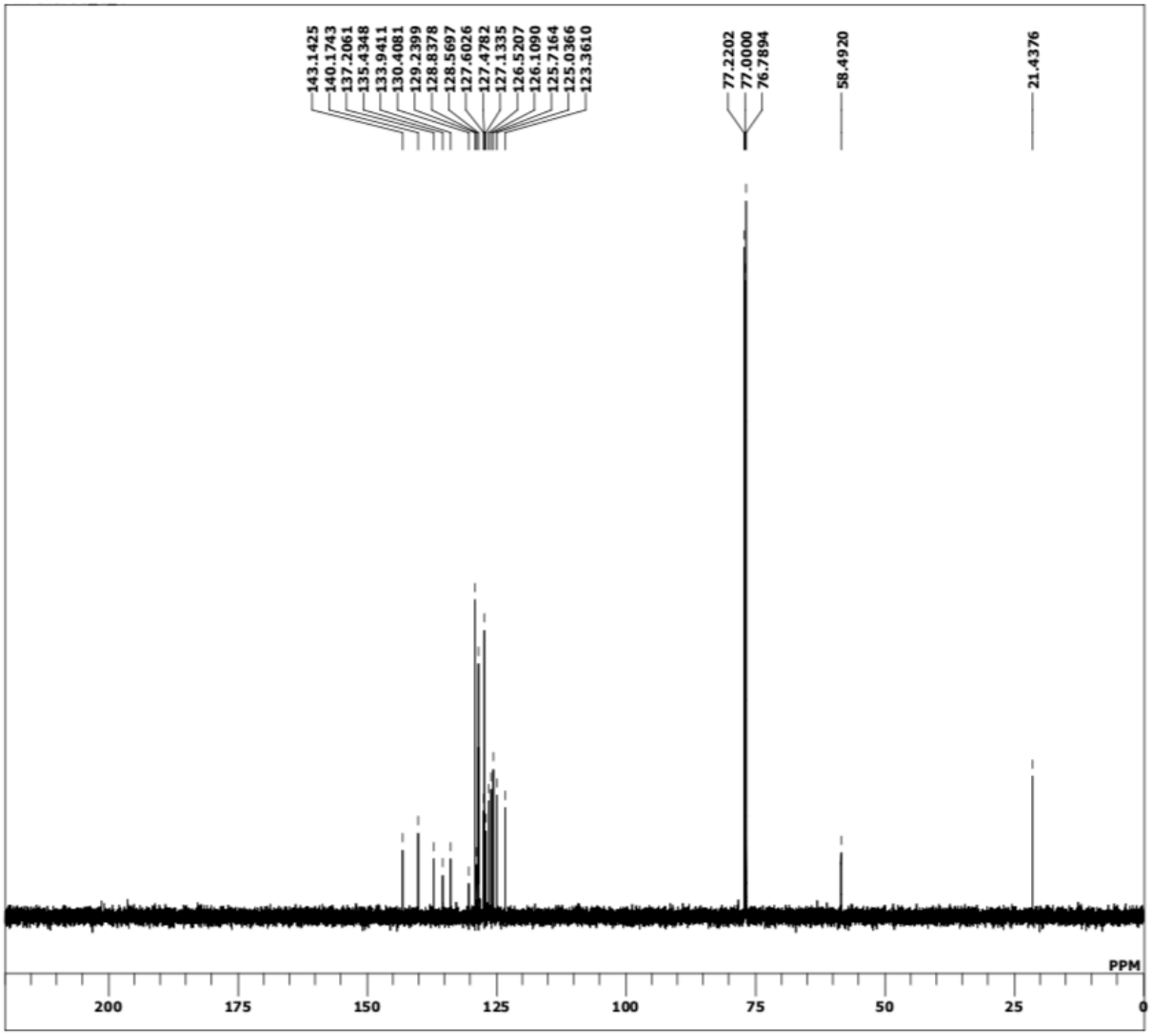

Ph
N
H
Ts

11da

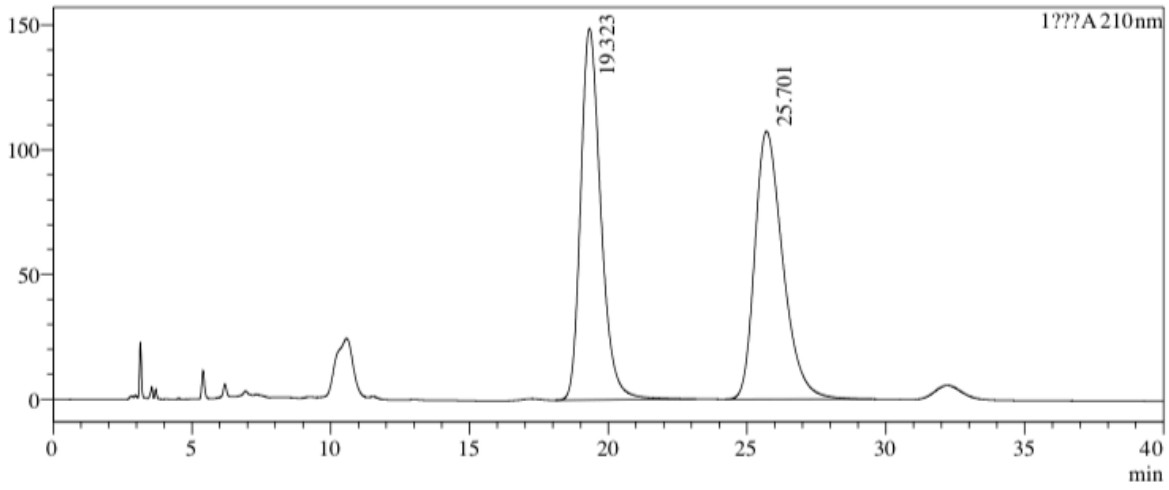

7.8057
7.7920
7.7783
7.7153
7.7015
7.4942
7.4805
7.4347
7.4232
7.4106
7.3786
7.3660
7.3534
7.2766
7.2640
7.2515
7.2400
7.2297
7.2171
7.1850
7.1793
7.1747
7.1679
7.1323
7.1266
7.1198
7.1163
7.0453
7.0316
6.2998
6.2872
5.1706
5.1591
2.3316
1.5574
5.1756
3.1396
2.0174
1.9311
1.9740
0.9895
1.0204
1.0000
PPM
10
8
6
4
2
0


Ph
N
H
Ts

11da

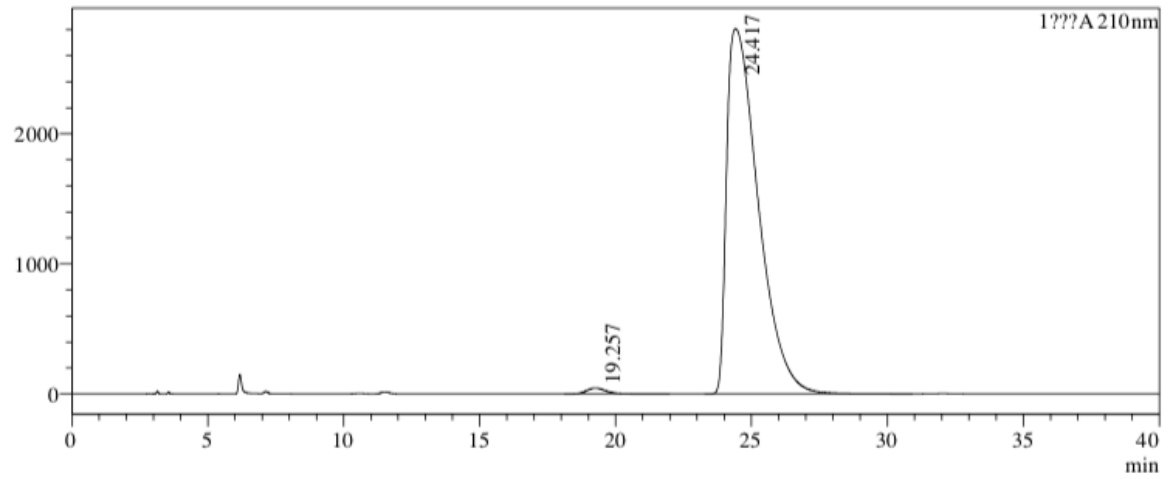

143.1425
140.1743
137.2061
135.4348
133.9411
130.4081
129.2399
128.8378
128.5697
127.6026
127.4782
127.1335
126.5207
126.1090
125.7164
125.0366
123.3610
77.2202
77.0000
76.7894
58.4920
21.4376
PPM
200
175
150
125
100
75
50
25
0

11da, condition : OD-H, 1.0 ml/min, Hex/IPA = 90:10, 210 nm



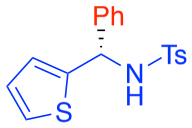
???A 210nm

Peak#	Ret. Time	Area	Height	Area%
1	19.323	7513210	148882	49.912
2	25.701	7539670	107358	50.088

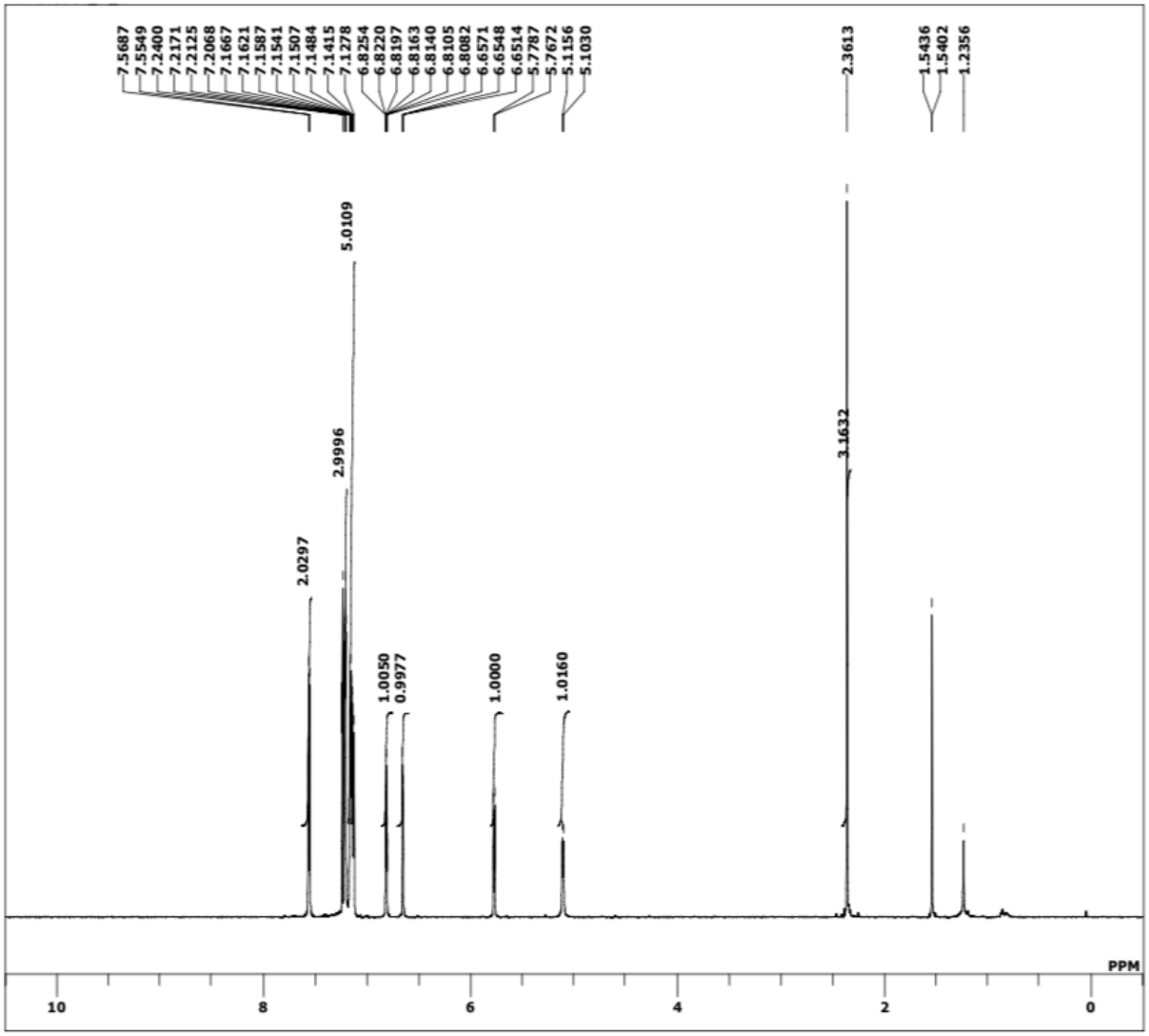


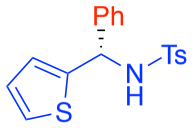
???A 210nm

Peak#	Ret. Time	Area	Height	Area%
1	19.257	2334496	46076	1.016
2	24.417	227498991	2808571	98.984

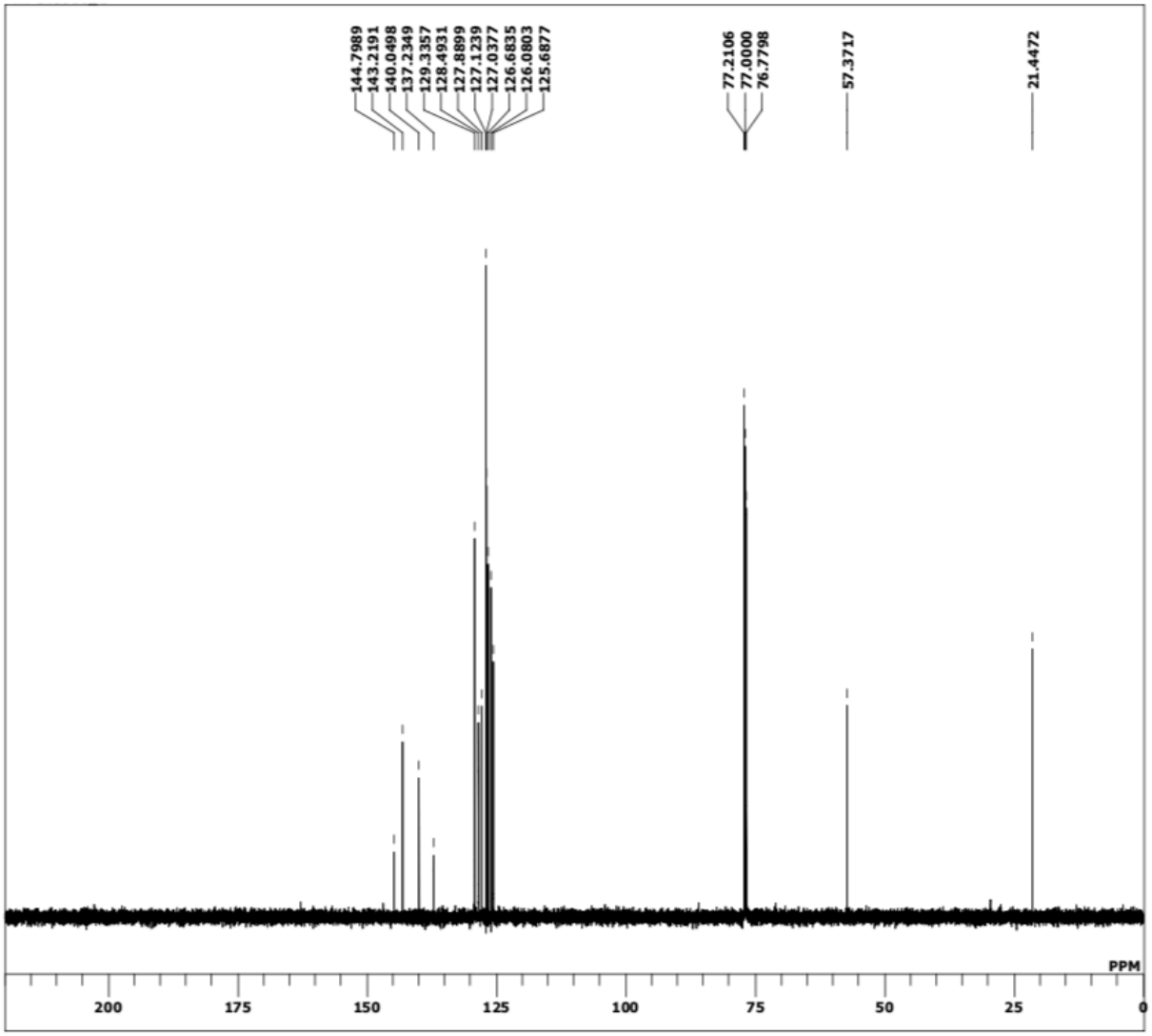

Ph
Ts
N
H
S

11ea

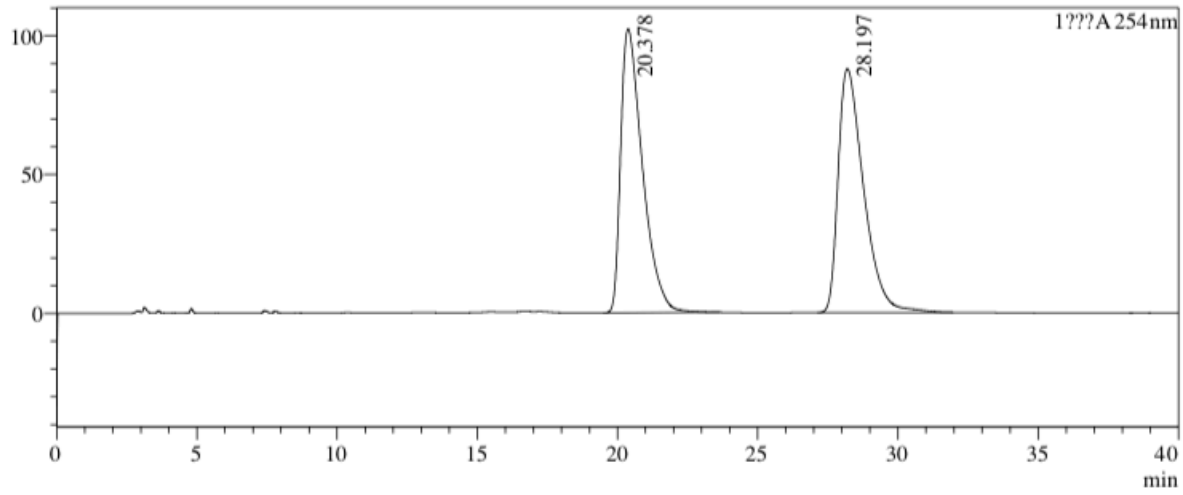

7.5687
7.5549
7.2400
7.2171
7.2125
7.2068
7.1667
7.1621
7.1587
7.1541
7.1507
7.1484
7.1415
7.1278
6.8254
6.8220
6.8197
6.8163
6.8140
6.8105
6.8082
6.6571
6.6548
6.6514
5.7787
5.7672
5.1156
5.1030
2.3613
1.5436
1.5402
1.2356
5.0109
2.9996
2.0297
3.1632
1.0050
0.9977
1.0000
1.0160
PPM
10
8
6
4
2
0


Ph
Ts
N
H
S

11ea

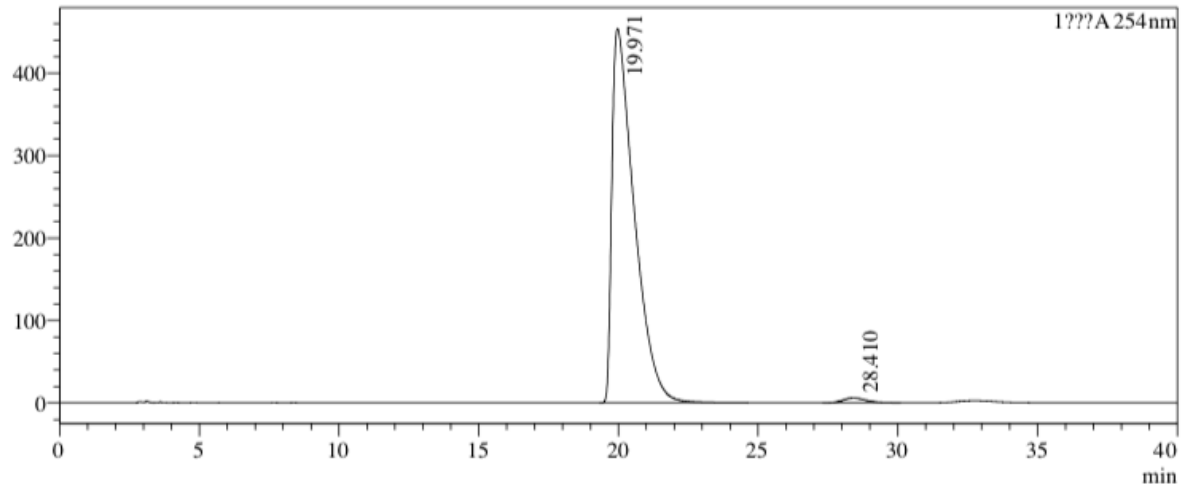

144.7989
143.2191
140.0498
137.2349
129.3357
128.4931
127.8899
127.1239
127.0377
126.6835
126.0803
125.6877
77.2106
77.0000
76.7798
57.3717
21.4472
PPM
200
175
150
125
100
75
50
25
0

11ea, condition : OD-H, 1.0 ml/min, Hex/IPA = 95:5, 254 nm



???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	20.378	5521297	102222	49.904
2	28.197	5542584	87815	50.096



???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	19.971	25216974	454005	98.685
2	28.410	336007	5935	1.315

9. Supplementary Information References

(1) H. C. Brown, E. J. Mead, B. C. S. Rao. *J. Am. Chem. Soc.* 1955, **77**, 6209.

(2) J. Hu, S. Chen, Y. Sun, J. Yang, T. Rao. *Org. Lett.* 2012, **14**, 5030.

(3) B. List, A. Doehring, M. T. H. Fonseca, K. Wobser, H. van Thienen, R. R. Torres, P. L. Galilea. A*dv. Synth. Catal.* 2005, **347**, 1558.

(4) R. Shintani, T. Kimura, T. Hayashi. *Chem. Commun.* 2005, **41**, 3213.

(5) J. Park, J. Yun, J. Kim, D. Jang, C. Park, K. Lee. *Synth. Commun.* 2014, ***44***, 1924.

(6) G. Hattori, H. Matsuzawa, Y. Miyake, Y. Nishibayashi. *Angew. Chem. Int. Ed.* 2008, **47**, 3781.

(7) Y. M. Wu, J. F. Zhao, J. B. Chen, C. X. Pan, L. Li, H. B. Zhang. *Org. Lett.* 2009, **11**, 597.

(8) B. Li, M. B. Smith. *Synth. Commun*. 1995, **25**, 1265.

(9) R. K. Bowman, J. S. Johnson. *J. Org. Chem.* 2004, **69**, 8537.

(10) S. S. Chandrasekhar, A. Shrinidhi. *Synth. Commun.* 2014, **44**, 3008.

(11) T. Yasukawa, A. Suzuki, H. Miyamura, K. Nishino, S. Kobayashi. *J. Am. Chem. Soc.* 2015, **137**, 6616.

(12) K, Okamoto, T. Hayashi, V. H. Rawal. *Org. Lett.* 2008, **10**, 4387.

(13) K. Okamoto, T. Hayashi, V. H. Rawal. *Chem. Commun.* 2009, **45**, 4815.

(14) W. J. Yoo, H. Miyamura, S. Kobayashi. *J. Am. Chem. Soc.* 2011, **133**, 3095.

(15) H. Miyamura, A. Sonoyama, D. Hayrapetyan, S. Kobayashi. *Angew. Chem. Int. Ed.* 2015, **54**, 10559.

(16) H. Miyamura, K. Maehata, S. Kobayashi. *Chem. Commun.* 2010, **46**, 8052.

(17) H. Miyamura, K. Nishino, T. Yasukawa, S. Kobayashi. *Chem. Sci.* 2017, **8**, 8362.

(18) F. Gini, C. Hessen, A. Minnaard. J. *Org. Lett.* 2005, **7**, 5309.

(19) W. Y. Qi, T. S. Zhu, M. H. Xu. *Org. Lett.* 2011, **13**, 3410.

(20) X. Q. Feng, B. B. Wei, J. Yang, H. F. Du. *Org. Biomol. Chem.* 2011, **9**, 5927.

(21) T. Hayashi, K. Ueyama, N. Tokunaga, K. Yoshida. *J. Am. Chem. Soc.* 2003, **125**, 11508.

(22) G. H. Chen, J. Y. Gui, L. C. Li, J. Liao. *Angew. Chem. Int. Ed.* 2011, **50**, 7681.

(23) Q. A. Li, Z. Dong, Z. X. Yu. *Org. Lett.* 2011, **13**, 1122.

(24) Q. Chen, L. Li, G. L. Zhou, X. L. Ma, L. Zhang, F. Guo, Y. Luo, W. J. Xia. *Chem. -Asian J.* 2016, **11**, 1518.

(25) Y. X. Liao, C. H. Xing, M. Israel, Q. S. Hu. *Org. Lett.* 2011, **13**, 2058.

(26) Y. Takaya, M. Ogasawara, T. Hayashi, M. Sakai, N. Miyaura. *J. Am. Chem. Soc.* 1998, **120**, 5579.

(27) Y. F. Luo, A. J. Carnell. *Angew. Chem. Int. Ed.* 2010, **49**, 2750.

(28) T. Yasukawa, Y. Saito, H. Miyamura, S. Kobayashi. *Angew. Chem. Int. Ed.* 2016, **55**, 8058.

(29) J. F. Paquin, C. Defieber, C. R. Stephenson, E. M. Carreira. *J. Am. Chem. Soc.* 2005, **127**, 10850.

(30) I. Ibrahem, G. Ma, S. Afewerki, A. Cordova. *Angew. Chem. Int. Ed.* 2013, **52**, 878.

(31) J. Q. Li, X. Quan, P. G. Andersson. *Chem. -Eur J.* 2012, **18**, 10609.

(32) W. T. Wei, J. Y. Yeh, T. S. Kuo, H. L. Wu. *Chem. -Eur J.* 2011, **17**, 11405.

(33) T. Senda, M. Ogasawara, T. Hayashi. *J. Org. Chem.* 2001, **66**, 6852.

(34) K. Kiyokawa, T. Nagata, J. Hayakawa, S. Minakata. *Chem. -Eur J.* 2015, **21**, 1280.

(35) L. Lin, W. Yin, X. Fu, J. Zhang, X. Ma, R. Wang. *Org. Biomol. Chem.* 2012, **10**, 83.

(36) Z. Wang, C. Feng, M. Xu, G. Lin. *J. Am. Chem. Soc.* 2007, **129**, 5336.

(37) C. C. Chen, B. Gopula, J. F. Syu, J. H. Pan, T. S. Kuo, P. Y. Wu, J. P. Henschke, H. L. Wu. *J. Org. Chem.* 2014, **79**, 8077.

(38) H. -F. Duan, Y. -X. Jia, L. -X. Wang, Q. -L. Zhou. *Org. Lett.* 2006, **8**, 2567.