Organocatalyzed Asymmetric Michael Addition by Efficient Bifunctional Carbohydrate-Thiourea Hybrid with Mechanistic DFT Analysis

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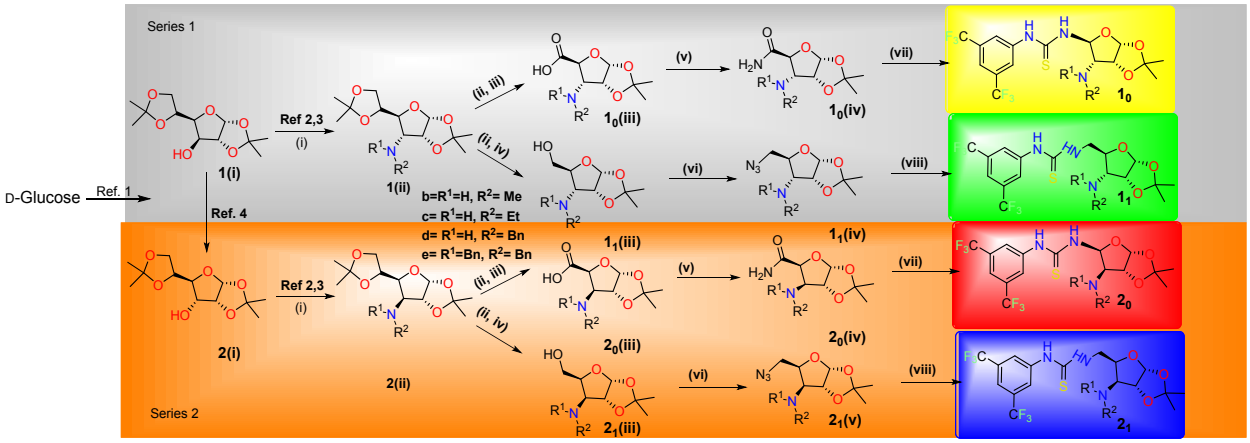
Supporting Information

Contents

General

^{1}H NMR, ^{13}C NMR and ^{19}F spectra were recorded at ambient temperature using 400 MHz spectrometer. The data are reported as follows: chemical shift in ppm (from internal tetramethylsilane on the δ scale in case of ^{1}H and $CDCl_3$ triplet in case of ^{13}C), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra were obtained by peak matching. Melting points are reported uncorrected and measured on BUCHI M-565 melting point apparatus. Infrared spectra were obtained using a diamond attenuated total reflectance (ATR) accessory on Shimadzu IR-affinity 1S. HPLC data were recorded on Shimadzu SIL 20HT (UFCL) with UV detected and Lachrom (Merck) with daad detector. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV-254 fluorescent indicator. Liquid chromatography was performed using indicated solvent system on 60-120/100-200 mesh silica gel (SiO_2). All reactions were carried out under an atmosphere of nitrogen in glassware, which had been oven-dried as per standard procedure. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Solvents were dried prior to use.

General methods for the synthesis of catalysts



Scheme S1: complete schematic representation for the synthesis of catalysts with the appropriate condition number

The synthesis of catalyst started with the protection of D-Glucose in the form of acetonide using published literature, the 1,2:5,6-Di-O-isopropylidene-α–D-glucofuranose (**1(i)**) was formed in 55 % yield after crystallization with hexane[1].In the next step we triflated the Glucose diacetonide **1(i)** with triflic anhydride in DCM at 0°C for 5h stirring according to published literature[2], TLC (50 % EtOAc/Hexane, R_f 0.6), showed formation of product and after workup yellow crystalline C-3 triflate was formed in 95% yield in both series 1 and 2. The formation of products further confirmed by the ^{1}H and ^{13}C NMR which was in agreement with the published literature[2]. To synthesis the C-3 azido sugar, authors treat the C-3 triflate with NaN_3 (2 equivalent) in DMF at 50°C according to published patent and after work up, we got C-3 azide in 68 % yield (for series 2 we got 66% yield). The C-3 Azide was reduced was LAH (1.2 equivalent) in dry THFfrom 0°C to rt for 5h and after workup we got C-3 amine in 76% yield (75% for series 2)[3].

For the synthesis of series 2 catalysts we flip the stereocentre of C3-alcohol by using the methodology published by Lee at al.,[4]the procedure includes (a) oxidizing the C-3 alcohol by using PCC and acetic anhydride in anhydrous DCM under nitrogen atmosphere. After refluxing for 2h, the solvent of cooled reaction mixture was evaporated under reduced pressure and extracted with EtOAc, and concentration of organic layer yielded the C-3 ketone in 89 % yield, (b) the crude ketone was used as such for the reduction with $NaBH_4$ by stirring the reaction mixture in in MeOH: H_2O (1:1) for 3h and after work up and recrystallization in hexane, the inverted**2(i)** alcohol was obtained in 80% yield.

Reaction condition (i): The light yellow colored anime was alkylated with suitable alkylated agent (Scheme 1), for methylation methyl iodide, for ethylation ethyl iodide and for benzylation benzylbromide were used. The alkylation achieved by using RX (1.25 equivalent) in dry DMF (5 ml for 1 mmol of C-3 amine) using NaH (1.3 equivalent, after hexane washing) under nitrogen atmosphere. In mono-alkylation cases reactions were completed in 12h. After evaporating solvent under reduced pressure water was added and reaction mixture was extracted with EtOAc (3X). After drying over anh. Na_2SO_4, EtOAc evaporated under reduced pressure and mono-alkylated products was isolated after column chromatography (EtOAC: Hexane 20%) in good to excellent yield. The double alkylated products were synthesized by adding the alkylated agent (1.5 equivalent with respect to initial) and NaH (1.2 equivalnt) both again after 12 h and TBAI (tetrabutyl ammonium iodide, 1.5 equivalent with respect to initial) was also added to facilitate the double alkylation, the yields of double alkylated products were not good and bi-Bn derivatives were formed in 24% and 44% for series 1 and 2 respectively. The alkylation of product further confirmed by the ^1H NMR and Mass spectrometry.

Reaction condition (ii): The alkylated amine**1**(**ii**) or **2**(**ii**) (1 mmol) so formed by condition (i) was dissolved in 60% AcOH (5 ml for 1mmol of **1**(**ii**) or **2**(**ii**)). The reaction was stirred at 50^oC for 4h and after that reaction was evaporated to dryness and evaporated with toluene. The crude di-ols were used as such for oxidative elimination. To a mixture of diol (1 mmol) in MeOH: H_2O (1:1) (10 ml for 1 mmol of diol) $NaIO_4$(1.5 equivalent) was added in small portions. The white suspension so formed was stirred for additional 60 min, filtered through a pad of celite. The white residue was extracted with THF (5X), and the combined organic extracts were dried, filtered and evaporated to give a crude aldehyde which was used in the next step without further purification[5].

Reaction condition (iii): To the crude aldehyde (1 mmol) was added in aqueous solution of $AgNO_3$ (0.6 M, 4.5 ml).To the resulting emulsion was added aq. KOH solution (0.9 M, 6 ml). A dark black precipitate was formed, which was stirred for 1 h and then filtered through a celite pad. The filtrate was acidified with AcOH to pH= 6. The acidified mixture was then extracted with DCM (3X). The combined organic layer washed with brine, dried and evaporated under reduced pressure to give crude β-amioacid as light yellow color solid (in case of Bn derivatives white colored acid was formed[6] . The acidic methods for the oxidation of aldehyde were avoided due to the presence of amino functionalities in the substrate.

Reaction condition (iv): The crude aldehyde so formed after completing reaction condition (ii) was added into cooled mixture of MeOH and Water (1:1, 4 ml per 1 mmol of aldehyde). The reaction mixture was stirred for 3h, after completing the reaction (EtOAc:Hexane; 50%, R_f, 0.32~0.4), it was quenched with saturated NH_4Cl (10 ml). MeOH was evaporated under reduced pressure and residue was extracted with EtOAc (4X) and organic layer was dried over anhydrous Na_2SO_4. The crude alcohol was subjected to Colum chromatography (15 % EtOAc:Hexane) yielded C-4 alcohol in excellent yield.

Reaction condition (v): The β-amioacid (1 mmol) so formed after oxidation of aldehyde dissolved in dry DCM (10 ml) and cooled to 0^oC, in which the cooled solution of oxalyl chloride (1.1 mmol) was added. After stirring for 1 hr the reaction mixture was refluxed for 4 h[6]. After 4 h the solvent evaporated to half and then methanol was added (10 ml) and again cooled to 0^oC. The resulting cooled reaction mixture carefully added in small portions in to precooled saturated methanolic ammonia solution (50 ml) and then lest for overnight. After 12-15 h reaction completed which was evidenced by the TLC (MeOH: $CHCl_3$ 20%, R*f* = 0.2~0.3), after that reaction aloow to attain the room temperature in fuming methanol removed very carefully. The crude amide was purified by the column chromatography using 5 % MeOH:$CHCl_3$.

Reaction condition (vi): The C-4 alcohol obtained by completing the reaction condition (iv) dissolved in dry DCM (4 ml per 1 mmol of alcohol), triethyl amine (1.2 mmol) and cooled to 0^oC and MsCl is added in small portion keeping temperature low. After stirring for 2 h at 0 ^oC reaction allowed to stir at room temperature for addition 10h. After completing the reaction water was added (25 ml) and reaction mixture was extracted with EtOAc (3X). The combined organic layer was washed with brine and evaporated under vacuum to yield C-4 meslylated product which was used in the next step without further purification. The mesylated compound(1mmol) and NaN_3 (1.2 equivalent) were added in anhydrous DMF and heated at 80^oC for 12h. The reaction mixture was allow to attain the room temperature and then solvent was removed under vaccum. To the resulting crude solid sticky mass (in most of the cases) water was added (15 ml) and extracted with EtOAc (caution: avoid halogenated solvent) (3X). The combined organic layer dried over anhydrous Na_2SO_4 and evaporated under vacuum to yield the desired C-4 azide in excellent yield[7] . (In case of C-3 methylated amine, some de methylated product formed which isolated and charactarized).

Reaction condition (vii): The 1_0 (iv) amide was dissolved in the mixture of Acetonitrile and water (1:1, 5 ml per 1 mol of 1_0 (iv)) and then [bis(trifluoroacetoxy)iodo]benzene (1.5 equivalent) was added. The reaction mixture allowed to stir for 4 h and then 5 ml saturated aq. solution of $NaHCO_3$ was added. The solvent removed under vacuum and crude reaction mixture was extracted with DCM (3X). The combined organic layer dried and evaporated under reduced pressure to yield dark yellow colored sticky amine which was diluted in anhydrous THF[8] . The reaction mixture cooled to 0^oC and then isothiocyanates were added under nitrogen atmosphere. The reaction took 12 to 14 h to complete. The water was added in the reaction mixture and then extracted with EtOAc (3X) after solvent evaporation the desired bi-functional organocatalysts was formed which purify by the column chromatography (EtOAc:DCM; 5:95).

Reaction condition (viii): The 1_1 or 2_1 (v) azide was dissolved in anhydrous THF. The reaction mixture cooled to 0°C and then triphenyl phosphine (1.2 equivalent) was added under nitrogen atmosphere and reaction allow to stir for 5 h. After 5h isothiocyanates were added and after 12 h reaction competed (checked by TLC). The water was added in the reaction mixture and then extracted with EtOAc (3X). The combined organic layer dried under vacuum and crude dissolved in Et_2O (25 ml) and cooled to -10°C to separate out the triphenyl phosphine oxide. The PPh_3O was filtered and the desired bi-functional organocatalysts was purified by the column chromatography (EtOAc:DCM; 5:95).

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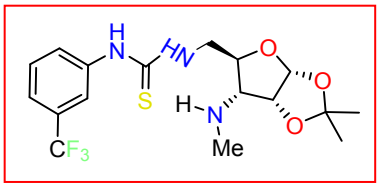
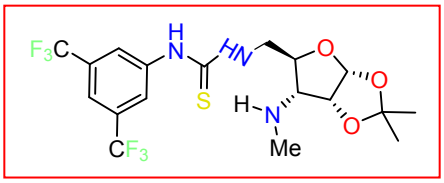
Analytical data of the synthesized catalyst/ligands

1-(((3aR,5R,6R,6aR)-2,2-dimethyl-6-(methylamino)tetrahydrofuro[2,3-d][1,3]dioxol-5-yl)methyl)-3-(3-(trifluoromethyl)phenyl)thiourea ($1a_1$)



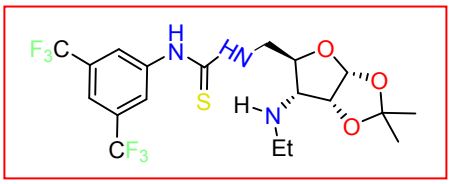
Light yellow solid, Yield 62%, m.p. 89-92°C; $[\alpha]_D^{20}$ -23.4 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-d) δ 10.12 (bs, 1H), 8.21 – 8.08 (m, 2H), 7.81 – 7.73 (m, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.12 (bs, 1H), 5.80 (d, *J* = 7.0 Hz, 1H), 4.73 (q, *J* = 6.9 Hz, 1H), 4.38 – 4.26 (m, 2H), 3.82 (dd, *J* = 12.3, 6.8 Hz, 1H), 2.86 (t, *J* = 7.0 Hz, 1H), 2.71 (s, 3H), 1.95 (bs, 1H), 1.52 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 181.23, 141.97, 129.46 (quat, J_{CF}, 32.09), 128.76, 125.8, 125.63, 122.96, 121.47-121.35 (m), 118.58-118.46 (m), 112.39, 105.57, 84.37, 81.27, 68.53, 45.26, 35.53, 26.6, 26.19; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.93; HRMS (ESI) *m/z* cal'd for $C_{17}H_{22}F_3N_3O_3S$ $[M+H]^+$:406.1407, found 406.1412.

1-(3,5-bis(trifluoromethyl)phenyl)-3-(((3aR,5R,6R,6aR)-2,2-dimethyl-6-(methylamino)tetrahydrofuro[2,3-d][1,3]dioxol-5-yl)methyl)thiourea ($1b_1$)



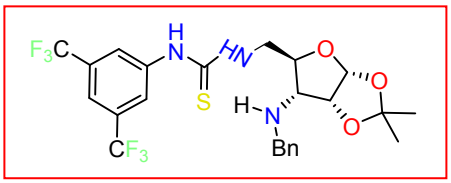
Light yellow solid, Yield 69%, m.p. 102-105°C; $[\alpha]_D^{20}$ -4.2 (c 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-d) δ 10.20 (bs, 1H), 8.22 (s, 2H), 7.97 (s, 1H), 7.19 (bs, 1H), 5.72 (d, *J* = 6.7 Hz, 1H), 4.77 – 4.64 (m, 2H), 4.32 (t, *J* = 6.9 Hz, 1H), 3.89 – 3.76 (m, 1H), 3.30 – 3.19 (m, 1H), 2.76 (s, 3H), 1.96 (bs, 1H), 1.49 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 180.35, 144.12, 130.84 (quat, J_{CF}, 31.91), 128.7, 126.01, 123.33, 120.66, 119.88-119.76 (m), 117.75-117.59 (m), 112.51, 105.69, 84.49, 81.39, 68.65, 45.38, 36.62, 26.72, 26.31; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.98; HRMS (ESI) m/z cal'd for $C_{18}H_{21}F_6N_3O_3S$ $[M+Na]^+$: 496.1100, found 496.1114.

1-(3,5-bis(trifluoromethyl)phenyl)-3-(((3aR,5R,6R,6aR)-6-(ethylamino)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)methyl)thiourea ($1c_1$)



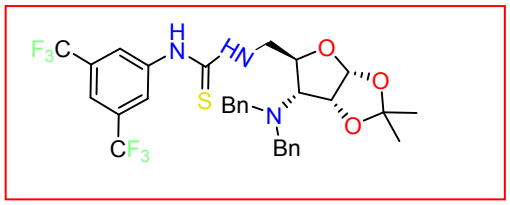
yellow solid, Yield 72%, m.p. 114-116°C; $[\alpha]_D^{20}$ -42.9 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-d) δ 10.12 (bs, 1H), 8.03 (d, *J* = 1.9 Hz, 2H), 7.86 (s, 1H), 7.52 (bs, 1H), 5.82 (d, *J* = 6.8 Hz, 1H), 4.80 (q, *J* = 6.9 Hz, 1H), 4.58 (dd, *J* = 12.3, 6.8 Hz, 1H), 4.25 (t, *J* = 6.8 Hz, 1H), 4.02 (dd, *J* = 12.3, 7.0 Hz, 1H), 3.91 – 3.78 (m, 1H), 3.38 (t, *J* = 6.9 Hz, 1H), 2.73 – 2.61 (m, 1H), 2.54 (bs, 1H), 1.49 (s, 3H), 1.38 (s, 3H), 1.07 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 181.63, 144.2, 130.92 (quat, J_{CF}, 31.54), 128.78, 126.09, 123.41, 120.73, 119.95-119.83 (m), 117.83-117.67 (m), 112.59, 105.77, 85.04, 82.35, 64.15, 45.45, 42.83, 31.14, 26.89, 26.5, 13.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.30; HRMS (ESI) m/z cal'd for $C_{19}H_{23}F_6N_3O_3S$ $[M+H]^+$: 488.1437, found 488.1432.

1-(((3aR,5R,6R,6aR)-6-(benzylamino)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)methyl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea ($1d_1$)



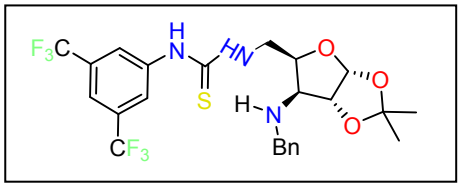
White, Yield 62%, m.p. 83-86°C; $[\alpha]_D^{20}$-34.2 (c 0.96, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-d) δ 10.03 (bs, 1H), 8.62 (s, 2H), 8.10 (s, 1H), 7.97 (s, 1H), 7.38 – 7.21 (m, 5H), 5.71 (d, *J* = 7.0 Hz, 1H), 4.61 (dd, *J* = 12.0, 7.0 Hz, 1H), 4.54 (q, *J* = 6.7 Hz, 1H), 4.32 (t, *J* = 6.9 Hz, 1H), 4.17 (d, *J* = 12.4 Hz, 1H), 3.79 (d, *J* = 12.3 Hz, 1H), 3.54 (dd, *J* = 12.0, 6.7 Hz, 1H), 2.96 (t, *J* = 6.9 Hz, 1H), 2.51 (s, 1H), 1.51 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 181.45, 144.12, 140.63, 130.85(quat, J_{CF}, 32.53), 128.7, 128.56, 128, 127.39, 126.01, 123.33, 120.66, 119.88-119.77 (m), 117.74-117.59 (m), 112.51, 105.69, 84.97, 82.27, 63.81, 52.83, 45.38, 26.52, 26.22; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.10; HRMS (ESI) m/z cal'd for $C_{24}H_{25}F_6N_3O_3S$ $[M+H]^+$: 550.1594, found 550.1596.

1-(3,5-bis(trifluoromethyl)phenyl)-3-(((3aR,5R,6R,6aR)-6-(dibenzylamino)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)methyl)thiourea ($1e_1$)



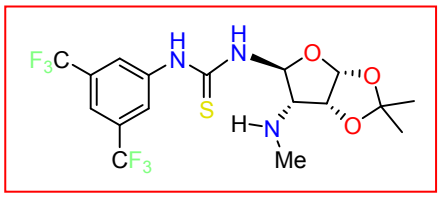
Dirty brown solid, Yield 66%, m.p. 121-123°C; $[\alpha]_D^{20}$ -2.3 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-d) δ 10.23 (s, 1H), 8.32 (s, 2H), 8.01 (s, 1H), 7.66 (s, 1H), 7.45 – 7.18 (m, 10H), 5.70 (d, *J* = 6.8 Hz, 1H), 4.93 (dd, *J* = 12.3, 6.7 Hz, 1H), 4.78 (q, *J* = 6.9 Hz, 1H), 4.54 – 4.39 (m, 2H), 4.07 – 3.91 (m, 2H), 3.71 – 3.58 (m, 2H), 2.96 (t, *J* = 6.9 Hz, 1H), 1.53 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 180.91, 144.18, 138.24, 130.91 (quat, J_{CF}, 32.77),128.88, 128.62, 127.76, 126.07, 123.4, 120.72, 119.95-119.83 (m), 117.81-117.65 (m), 112.58, 105.62, 84.78, 80.34, 67.66, 57.72, 57.49, 45.91, 26.48, 26.18; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.96; HRMS (ESI) m/z cal'd for $C_{31}H_{31}F_6N_3O_3S$ $[M+H]^+$: 640.2063, found 640.2067.

1-(((3aR,5R,6S,6aR)-6-(benzylamino)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)methyl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea ($2d_1$)



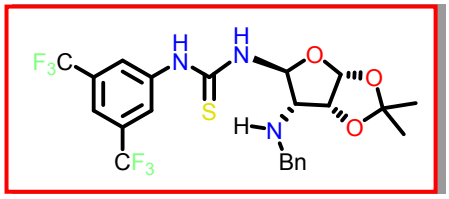
Light yellow solid, Yield 63%, m.p. 102-105°C; $[\alpha]_D^{20}$+16.6 (c 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-d) δ 10.14 (s, 1H), 8.28 (s, 2H), 7.97 (s, 1H), 7.72 (s, 1H), 7.38 – 7.29 (m, 4H), 7.28 – 7.18 (m, 1H), 5.66 (d, *J* = 7.2 Hz, 1H), 4.71 – 4.58 (m, 2H), 4.17 (d, *J* = 12.4 Hz, 1H), 4.08 (dd, *J* = 7.3, 6.4 Hz, 1H), 3.90 – 3.72 (m, 2H), 3.33 – 3.23 (m, 1H), 2.17 (s, 1H), 1.52 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 182.54, 144.22, 140.71, 131.91 (quat, J_{CF}, 31.49), 128.82, 128.65, 128.45, 128.33, 127.48, 125.76, 123.08, 120.41, 119.98-119.85, (m),117.83-117.71 (m), 112.6, 105.78, 85.05, 82.36, 63.9, 51.91, 45.46, 26.4, 26; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.22; HRMS (ESI) m/z cal'd for $C_{24}H_{25}F_6N_3O_3S$ $[M+H]^+$: 550.1594, found 550.1596.

1-(3,5-bis(trifluoromethyl)phenyl)-3-((3aR,5S,6S,6aR)-2,2-dimethyl-6-(methylamino)tetrahydrofuro[2,3-d][1,3]dioxol-5-yl)thiourea ($1b_0$)



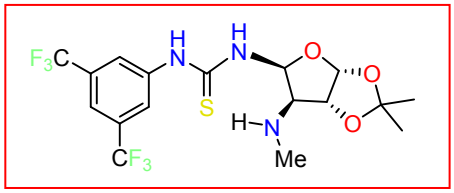
White solid, Yield 42%, m.p. 86-89°C; $[\alpha]_D^{20}$+15.9 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-d) δ 10.10 (s, 1H), 8.28 (s, 2H), 8.13 (m, 1H), 7.80 (s, 1H), 6.35 (d, *J* = 6.7 Hz, 1H), 5.75 (d, *J* = 7.9 Hz, 1H), 4.33 (t, *J* = 7.7 Hz, 1H), 3.37 (t, *J* = 7.1 Hz, 1H), 2.93 (s, 1H), 2.83(s, 3H) 2.51 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 180.65, 143.84, 131.53 (quat, J_{CF}, 32.07), 129.37, 126.69, 124, 121.33, 119.6-119.47 (m), 118.42-118.26 (m), 112.22, 105.51, 87.05, 82.34, 64.89, 35.36, 25.62, 25.03; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.49; HRMS (ESI) m/z cal'd for $C_{17}H_{19}F_6N_3O_3S[M+Na]^+$: 482.0944, found 482.0951.

1-((3aR,5S,6S,6aR)-6-(benzylamino)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea ($1d_0$)



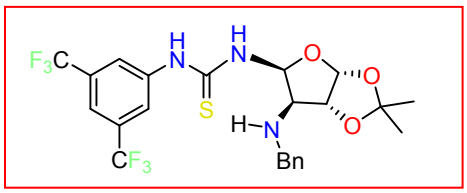
Light yellow solid, Yield 44%, m.p. 103-106°C; $[\alpha]_D^{20}$ -72.9 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-d) δ 10.21 (s, 1H), 8.43 (s, 2H), 8.12 (s, 1H), 7.89 (s, 1H), 7.39 – 7.24 (m, 5H), 5.92 (d, *J* = 6.8 Hz, 1H), 5.80 (d, *J* = 7.5 Hz, 1H), 4.37 (t, *J* = 7.0 Hz, 1H), 4.18 (dt, *J* = 12.5, 1.0 Hz, 1H), 3.77 (dt, *J* = 12.4, 1.0 Hz, 1H), 3.48 (t, *J* = 7.3 Hz, 1H), 2.69 (s, 1H), 1.49 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 182.24, 144.11, 140.61, 131.81 (quat, J_{CF}, 31.87), 129.65, 129.52, 129.03, 127.38, 126.97, 124.28, 121.61, 119.87-119.75 (m), 117.74-117.57 (m), 112.5, 105.78, 87.75, 83.47, 62.21, 52.82, 27.41, 27.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.17 ;HRMS (ESI) m/z cal'd for $C_{23}H_{23}F_6N_3O_3S[M+H]^+$: 536.1437, found 536.1442.

1-((3aR,5S,6R,6aR)-6-(benzylamino)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea ($2b_0$)



white solid, Yield 39%, m.p. 81-84°C; $[\alpha]_D^{20}$ +38.4 (c 1.0, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-d) δ 10.22 (s, 1H), 8.39 (s, 2H), 8.14 (s, 1H), 7.73 (s, 1H), 6.45 (d, *J* = 7.7 Hz, 1H), 5.87 (d, *J* = 7.2 Hz, 1H), 4.31 (t, *J* = 6.8 Hz, 1H), 3.67 (dd, *J* = 7.7, 6.7 Hz, 1H), 2.75 (s, 3H), 1.99 (s, 1H), 1.49 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 181.31, 143.88, 129.6 (quat, J_{CF}, 31.48),129.74, 129.44,129.13, 126.84, 124.16, 121.47, 119.35-119.23 (m), 117.5-117.35 (m), 112.27, 106.59, 87.1, 82.39, 64.93, 35.4, 26.57, 26.07; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.33; HRMS (ESI) m/z cal'd for $C_{17}H_{19}F_6N_3O_3S$ $[M+H]^+$: 460.1124, found 460.1128.

1-((3aR,5S,6R,6aR)-6-(benzylamino)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea ($2d_0$)



White solid, Yield 42%, m.p. 94-96°C; $[\alpha]_D^{20}$ -44.9 (c 0.96, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-d) δ 10.23 (s, 1H), 8.49 (s, 2H), 8.16 (s, 1H), 7.73 (s, 1H), 7.38 – 7.24 (m, 5H), 6.36 (d, *J* = 7.2 Hz, 1H), 5.95 (d, *J* = 7.3 Hz, 1H), 4.34 (t, *J* = 7.0 Hz, 1H), 4.04 – 3.95 (m, 1H), 3.87 (d, *J* = 12.1 Hz, 1H), 3.39 (t, *J* = 6.9 Hz, 1H), 2.24 (s, 1H), 1.47 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 180.35, 143.83, 140.33, 130.24 (quat, J_{CF}, 32.19),128.4, 128.04, 127.1, 125.72, 123.04, 120.36, 119.59-119.47 (m), 117.45-117.32 (m), 112.22, 106.54, 87.46, 83.19, 60.89, 53.53, 23.42, 23.02; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.22; HRMS (ESI) m/z cal'd for $C_{23}H_{23}F_6N_3O_3S[M+H]^+$: 536.1437, found 536.1442.

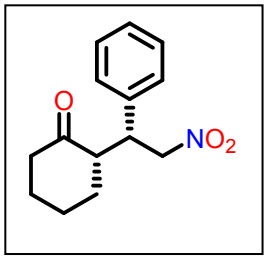
Note : The nitroolefines used in the current study were prepared by the method described by David E. Worrall in *Org. Synth.* 1929, *9*, 66.

General reaction condition for the Michael addition of ketones to Nitroolefines by using $1d_0$ as bifunctional organocatalyst

To the precooled (-10°C) cyclohexanone (2.6 ml, 25 mmol) the catalyst $1d_0$ (5.35 mg, 10 mol%) was added under nitrogen atmosphere. The reaction allow to stir for about 1h and then trans-nitrostyrene (1 mmol) and degassed triethyl amine (0.028 ml, 20 mol%)were added by maintaining the nitrogen atmosphere. The reaction was evaporated under reduced pressure after completion. To the reaction crude water was added and then extracted with EtOAc (10 ml X3) and combined organic layer dried over Na_2SO_4 and evaporated by rotatory evaporator. The Michael products was purified by column chromatography using15-20% EtOAc and hexane as eluent.

All the analytical data crosschecked with the reported literature and found similar. The absolute configurations wereassigned on the basis of optical rotation reported.

(S)-2-((R)-2-nitro-1-phenylethyl)cyclohexan-1-one (5a)

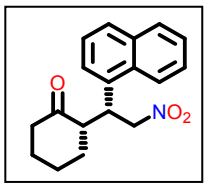


White solid, Yield 98%, m.p. 122-125 °C; $[\alpha]_D^{20}$ -17.2 (c 1.2, $CHCl_3$);*syn/anti* = 99/1, 94% *ee*; ^1H NMR (400 MHz, Chloroform-d) δ

7.53 – 7.45 (m, 2H), 7.33 – 7.23 (m, 2H), 7.23 – 7.13 (m, 1H), 4.95 (dd, *J* = 12.5, 5.0 Hz, 1H), 4.65 (dd, *J* = 12.5, 9.5 Hz, 1H), 3.76 – 3.65 (m, 1H), 2.71 (dt, *J* = 12.0, 8.2 Hz, 1H), 2.68 - 3.75 (m, 2H), 2.03 – 1.81 (m, 3H), 1.78 – 1.56 (m, 2H), 1.27 – 1.12 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-d) δ 211.68, 141.09, 130, 128.28, 128.04, 77.4, 53.15, 43.2, 38.91, 28.71, 25.48, 23.48. ES-MS (M+H$^+$) 248.12 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane/ACN) = 3:96:1, flow rate = 0.6mL/min, 254nm, t_r (minor) = 34.26 min, t_r (major) = 34.96 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9, 10].

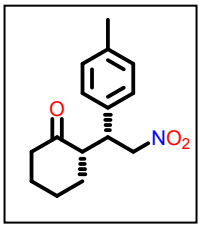
(S)-2-((R)-1-(naphthalen-1-yl)-2-nitroethyl)cyclohexan-1-one (5b)



Light brown solid, Yield 92%, m.p. 116-118 °C; $[\alpha]_D^{20}$ -95.2 (c 0.94, $CHCl_3$); *syn/anti* = 95/5, 93% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.03 – 7.90 (m, 2H), 7.81 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.59 (td, *J* = 7.4, 1.5 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.31-7.27 (m, 1H), 5.07 (dd, *J* = 12.4, 4.6 Hz, 1H), 4.91 (dd, *J* = 12.3, 8.9 Hz, 1H), 4.77 (bs, 1H), 2.85 (bs, 1H), 2.57-2.40 (m, 1H), 2.0-1.84 (m, 3H), 1.760-1.62 (m, 2H), 1.33 – 1.18 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-d) δ 211.75, 137.28, 134.46, 133.22, 129.49, 127.61, 127.57, 127.32, 127.23, 126.72, 78.14, 52.96, 42.1, 38.99, 28.79, 25.59, 25.55, 23.55. ES-MS (M+H$^+$) 298.14 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 96:2, flow rate = 0.5 mL/min, 254nm, t_r (minor) = 37.94 min, t_r (major) = 39.49 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9, 10].

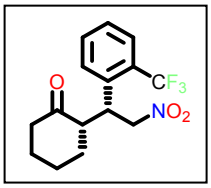
(S)-2-((R)-2-nitro-1-(p-tolyl)ethyl)cyclohexan-1-one (5c)



White solid, Yield 89%, m.p. 122-125 °C; $[\alpha]_D^{20}$ -26.4 (c 0.73, $CHCl_3$); *syn/anti* = 96/4, 87% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.16 – 7.08 (m, 2H), 7.08 – 7.00 (m, 2H), 4.91 (dd, *J* = 12.5, 4.8 Hz, 1H), 4.62 (dd, *J* = 12.4, 9.6 Hz, 1H), 3.75-3.57 (m, 1H), 2.72-2.62 (m, 1H), 2.52 – 2.28 (m, 3H), 2.31 (s, 2H), 2.13 – 1.99 (m, 1H), 1.72 – 1.48 (m, 4H), 1.32 – 1.14 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-d) δ 211.72, 137.64, 136.75, 130.55, 128.9, 77.44, 53.2, 43.24, 38.96, 28.76, 25.52, 23.52, 21.02. ES-MS (M+H$^+$) 262.14 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane/ACN) = 3:94:3, flow rate = 0.5 mL/min, 254nm, t_r (minor) = 17.34 min, t_r (major) = 18.06 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9, 10].

(S)-2-((R)-2-nitro-1-(2-(trifluoromethyl)phenyl)ethyl)cyclohexan-1-one (5d)

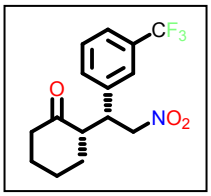


Brown waxy, Yield 94% ; $[\alpha]_D^{20}$ -14.2 (c 1, $CHCl_3$); *syn/anti* = 98/2, 90% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.71 (dd, *J* = 7.0, 2.5 Hz, 1H), 7.56 – 7.48 (m, 1H), 7.44 – 7.31 (m, 2H), 5.03 (dd, *J* = 11.9, 7.5 Hz, 1H), 4.74 (dd, *J* = 12.0, 3.5 Hz, 1H), 4.10 (s, 1H), 3.04 – 2.94 (m, 1H), 2.47 – 2.29 (m, 2H),

2.21 – 2.05 (m, 1H), 1.85 – 1.49 (m, 4H), 1.40 – 1.25 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-d) δ 211.71,140.23 (q, *J* = 3.73 Hz), 132.91,132.79-132.82 (m), 131.54, 131.23, 131.22, 130.01, 127.33, 126.64(d, *J* = 2.42 Hz), 126.31, 126.27, 126.24 (q, *J* = 3.77 Hz), 124.65, 121.98, 121.97, 76.18, 52.71, 38.95, 38.92, 28.75, 25.51, 23.51. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.53; ES-MS ($M+H^+$) 316.12 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 5:95, flow rate = 0.6mL/min, 254nm, t_r (minor) = 14.42 min, t_r (major) = 16.34 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature.

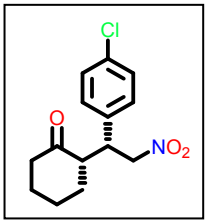
(S)-2-((R)-2-nitro-1-(3-(trifluoromethyl)phenyl)ethyl)cyclohexan-1-one (5e)



Canary yellow oily, Yield 92%,;$[\alpha]_D^{20}$ -15.4 (c 0.82, $CHCl_3$); *syn/anti* = 94/6, 91% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 (d, *J* = 5.0 Hz, 2H), 7.52 – 7.39 (m, 2H), 4.98 (dd, *J* = 13.0, 4.7 Hz, 1H), 4.67 (dd, *J* = 13.0, 11.0 Hz, 1H), 3.92 – 3.80 (m, 1H), 2.79 – 2.69 (m, 1H), 2.47 – 2.26 (m, 2H), 2.10 – 1.96 (m, 1H), 1.79 – 1.52 (m, 5H); ^{13}C NMR (100 MHz, Chloroform-d) δ 211.81, 141.17, 141.15 (*J* = 2.49 Hz),134.53,134.2, 133.88, 133.56, 131.58, 129.87-129.92 (m), 128.4, 127.72-127.85 (m), 125.72,123.04, 122.08, 122.07, 122.05, 122.01, 120.36, 77.53, 53.29, 43.08, 39.05, 28.84, 25.61, 23.61. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.63; ES-MS ($M+H^+$) 316.12 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane/ACN) = 4:95:1, flow rate = 0.5 mL/min, 254nm, t_r (minor) = 76.42 min, t_r (major) = 80.43 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9, 10].

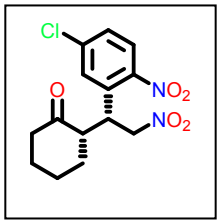
(S)-2-((R)-1-(4-chlorophenyl)-2-nitroethyl)cyclohexan-1-one (5f)



Yellow solid, Yield 96%, m.p. 93-96°C; $[\alpha]_D^{20}$ -23.4 (c 1.1, $CHCl_3$); *syn/anti* = 95/5, 94% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 5.07 (dd, *J* = 12.6, 4.7 Hz, 1H), 4.69 (dd, *J* = 12.7, 9.4 Hz, 1H), 3.90 – 3.81 (m, 1H), 2.73 – 2.67 (m, 1H), 2.48 – 2.30 (m, 2H), 2.17 – 2.05 (m, 1H), 1.88 – 1.57 (m, 4H), 1.24 – 1.08 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-d) δ 211.82, 140.05, 134.15, 131.25, 128.63, 77.54, 53.3, 43.34, 39.06, 28.86, 25.62, 23.62. ES-MS ($M+H^+$) 283.1 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 5:95, flow rate = 0.5 mL/min, 254nm, t_r (minor) = 23.5 min, t_r (major) = 54.69 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9, 10].

(S)-2-((R)-1-(5-chloro-2-nitrophenyl)-2-nitroethyl)cyclohexan-1-one (5g)

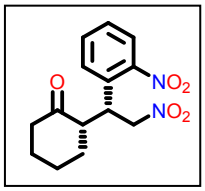


Oily brown colored, Yield 95%, $[\alpha]_D^{20}$ -122.8 (c 1.34, $CHCl_3$); *syn/anti* = 96/4, 93% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.83 (d, *J* = 8.2 Hz, 1H), 7.42 (s, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 4.91 (dd, *J* = 12.4, 8.9 Hz, 1H), 4.42 (dd, *J*

= 12.4, 5.2 Hz, 1H), 2.97 – 2.87 (m, 1H), 2.50 – 2.32 (m, 2H), 2.23 – 2.07 (m, 2H), 1.99 – 1.79 (m, 2H), 1.72 – 1.58 (m, 2H), 1.59 – 1.44 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-d) δ 211.53, 153.69, 147.86, 138.05, 130.84, 130.23, 130.2, 125.69, 52.53, 40.3, 38.76, 28.56, 25.33, 23.33. ES-MS (M+H$^+$) 328.1 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane/ACN) = 4:95:1, flow rate = 0.5 mL/min, 254nm, t_r (minor) = 22.54 min, t_r (major) = 39.58 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9, 10].

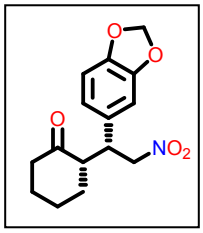
(S)-2-((R)-2-nitro-1-(2-nitrophenyl)ethyl)cyclohexan-1-one (5h)



White solid, Yield 94%, m.p. 103-105^{o}C; $[\alpha]_D^{20}$ -142.6 (c 1.1, $CHCl_3$); *syn/anti* = 93/7, 91% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.84 (d, *J* = 8.3 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.50 – 7.40 (m, 2H), 4.97 – 4.87 (m, 2H), 4.48 – 4.38 (m, 1H), 2.90 – 2.80 (m, 1H), 2.51 – 2.32 (m, 2H), 2.23 – 2.05 (m, 2H), 1.85 – 1.58 (m, 3H), 1.58 – 1.43 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-d) δ 211.93, 153.27, 145.85, 133.89, 133.03, 129.99, 124.58, 76.4, 52.94, 41.07, 39.17, 28.97, 25.73, 23.73. ES-MS (M+H$^+$) 293.12 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 4:96, flow rate = 05mL/min, 254nm, t_r (minor) = 56.24 min, t_r (major) = 62.28 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[11].

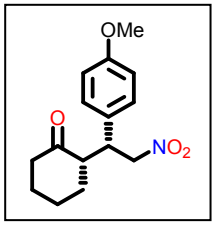
(S)-2-((R)-1-(benzo[d][1,3]dioxol-5-yl)-2-nitroethyl)cyclohexan-1-one (5i)



Light brown solid, Yield 91%, m.p. 144+145^{o}C; $[\alpha]_D^{20}$ -28.2 (c 0.92, $CHCl_3$); *syn/anti* = 94/6, 93% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 6.75 (d, *J* = 7.6 Hz, 1H), 6.65 (s, 1H), 6.61 (d, *J* = 7.7 Hz, 1H), 5.95 (s, 2H), 4.92 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.57 (dd, *J* = 12.3, 9.7 Hz, 1H), 3.73 – 3.63 (m, 1H), 2.68 – 2.57 (m, 1H), 2.51 – 2.31 (m, 2H), 2.17 – 2.03 (m, 1H), 1.82 – 1.56 (m, 4H), 1.24 – 1.09 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-d) δ 211.52, 147.88, 146.92, 136.5, 126.49, 109.9, 109.86, 101.68, 77.24, 52.99, 42.78, 38.75, 28.55, 25.32, 23.32. ES-MS (M+H$^+$) 292.1 *m/z*.HPLC: Chirapak IA in series with Chirapak OD (i-PrOH/Hexane/ACN) = 4:94:2, flow rate = 0.6mL/min, 254nm, t_r (minor) = 49.58 min, t_r (major) = 50.23 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9, 10].

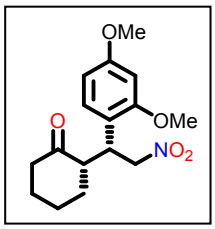
(S)-2-((R)-1-(4-methoxyphenyl)-2-nitroethyl)cyclohexan-1-one (5j)



White solid, Yield 86%, m.p. 115-117^{o}C; $[\alpha]_D^{20}$ -21.3 (c 0.5, $CHCl_3$); *syn/anti* = 93/7, 93% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.07 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.91 (dd, *J* = 12.3, 4.4 Hz, 1H), 4.59 (dd, *J* = 12.3, 9.8 Hz, 1H), 3.78 (s, 3H), 3.72 – 3.62 (m, 1H), 2.69 – 2.59 (m, 1H), 2.56 – 2.44 (m, 1H), 2.49 – 2.38 (m, 1H), 2.13 – 1.99 (m, 1H), 1.81 – 1.53 (m, 4H), 1.30 – 1.15 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-d) δ 211.97, 159.58, 133.42, 131.57, 131.54, 114.43, 77.69, 56.23, 53.45, 43.49, 39.21, 29, 25.77, 23.77. ES-MS (M+H$^+$) 278.11 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 10:90, flow rate = 0.5mL/min, 254nm, t_r (minor) = 6.11 min, t_r (major) = 7.93 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9, 10].

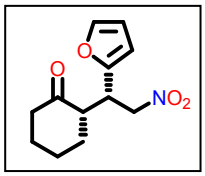
(S)-2-((R)-1-(2,4-dimethoxyphenyl)-2-nitroethyl)cyclohexan-1-one (5k)



Yellow oily, Yield 88%, $[\alpha]_D^{20}$ -33.3 (c 1.5, $CHCl_3$); *syn/anti* = 92/8, 88% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 6.70 (d, *J* = 8.0 Hz, 1H), 6.55 – 6.45 (m, 2H), 4.83 – 4.69 (m, 2H), 3.94 – 3.84 (m, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 2.92 (td, *J* = 11.6, 5.1 Hz, 1H), 2.43 – 2.25 (m, 2H), 2.13 – 1.99 (m, 1H), 1.72 – 1.45 (m, 4H), 1.24 – 1.11 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-d) δ 211.89, 160.47, 159.8, 131.81, 123.24, 107.35, 100.78, 76.36, 56.9, 56.15, 52.89, 39.13, 35.73, 28.93, 25.69, 23.69. ES-MS (M+H$^+$) 308.17 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane/ACN) = 3:95:2, flow rate = 0.5mL/min, 254nm, t_r (minor) = 24.6 min, t_r (major) = 45.78 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9, 10].

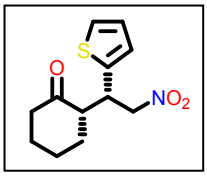
(S)-2-((S)-1-(furan-2-yl)-2-nitroethyl)cyclohexan-1-one (5l)



Light brown oily, Yield 90%, m.p. 122-125 °C; $[\alpha]_D^{20}$ -12.4 (c 1.2, $CHCl_3$); *syn/anti* = 94/6, 91% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.35 (s, 1H), 6.29 (d, *J* = 3.3 Hz, 1H), 6.18 (d, *J* = 3.3 Hz, 1H), 4.81 (dd, *J* = 12.6, 5.0 Hz, 1H), 4.67 (dd, *J* = 12.6, 9.5 Hz, 1H), 4.05 – 3.95 (m, 1H), 2.80 – 2.61 (m, 2H), 2.52 – 2.40 (m, 1H), 2.42 – 2.30 (m, 1H), 2.15 – 2.01 (m, 1H), 1.71 – 1.48 (m, 3H), 1.24 – 1.08 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-d) δ 210.86, 153.34, 142.72, 111.92, 110.92, 70.27, 51.36, 38.97, 35.79, 28.3, 25.57, 25.53, 23.53. ES-MS (M+H$^+$) 238.12 *m/z*. HPLC: Chirapak IA in series with Chirapak OD (i-PrOH/Hexane/ACN) = 4:95:1, flow rate = 0.5mL/min, 254nm, t_r (major) = 20.68 min, t_r (minor) = 31.14 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9, 10].

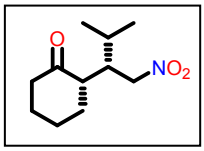
(S)-2-((S)-2-nitro-1-(thiophen-2-yl)ethyl)cyclohexan-1-one (5m)



Crystalline solid, Yield 85%, m.p. 82-83°C; $[\alpha]_D^{20}$ -21.4 (c 0.62, $CHCl_3$); *syn/anti* = 98/2, 92% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.21 (d, *J* = 7.4 Hz, 1H), 6.99 – 6.90 (m, 1H), 6.85 (d, *J* = 5.6 Hz, 1H), 4.91 (dd, *J* = 12.4, 4.7 Hz, 1H), 4.63 (dd, *J* = 12.4, 10.2 Hz, 1H), 4.09 – 3.99 (m, 1H), 2.84 – 2.68 (m, 1H), 2.65 (q, *J* = 7.0 Hz, 1H), 2.51 – 2.39 (m, 1H), 2.43 – 2.29 (m, 1H), 2.11 – 1.96 (m, 1H), 1.81 – 1.59 (m, 3H), 1.42 – 1.26 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-d) δ 210.98, 143.12, 130.11, 127.67, 125.33, 73.71, 52.83, 40.07, 39.1, 28.43, 25.66, 23.66. ES-MS (M+H$^+$) 254.1 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane/ACN) = 3:95:2, flow rate = 0.5mL/min, 254nm, t_r (minor) = 6.40 min, t_r (major) = 9.82 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9, 10].

(S)-2-((S)-3-methyl-1-nitrobutan-2-yl)cyclohexan-1-one (5n)

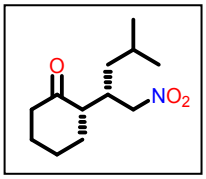


Colorless liquid, Yield 62%, $[\alpha]_D^{20}$ -17.8 (c 0.82, $CHCl_3$); *syn/anti* = 96/4, 92% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 4.64 (dd, *J* = 13.5, 6.2 Hz, 1H), 4.34 (dd, *J* = 13.4, 5.3 Hz, 1H), 2.69 – 2.57 (m, 1H), 2.44 – 2.23 (m, 3H), 2.20 –

2.03 (m, 2H), 2.01 – 1.89 (m, 1H), 1.94 – 1.82 (m, 1H), 1.80 – 1.56 (m, 3H), 0.95 (d, J = 6.7 Hz, 3H), 0.91 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 210.92, 74.97, 52.75, 43.73, 39.15, 29.89, 27.6, 25.71, 23.71, 20.54. ES-MS (M+H$^+$) 214.15 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 5:95, flow rate = 0.6mL/min, 254nm, t_r (minor) = 59.94 min, t_r (major) = 66.13 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9, 10].

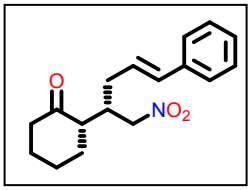
(S)-2-((S)-4-methyl-1-nitropentan-2-yl)cyclohexan-1-one (5o)



Colorless oily, Yield 58%, m.p. 122-125 °C; $[\alpha]_D^{20}$ -17.2 (c 1.2, $CHCl_3$); *syn/anti* = 80/10, 90% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 4.66 (dd, J = 13.4, 6.8 Hz, 1H), 4.23 (dd, J = 13.3, 11.1 Hz, 1H), 2.48 – 2.34 (m, 1H), 2.36 – 2.18 (m, 2H), 2.04 – 1.83 (m, 3H), 1.87 – 1.56 (m, 5H), 1.51 – 1.36 (m, 1H), 1.06 (d, J = 6.8 Hz,3H), 1.01 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 210.76, 78.44, 52.11, 39.52, 39.44, 38.97, 27.28, 26.28, 25.53, 23.53, 23.06. ES-MS (M+H$^+$) 228.18 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 8:92, flow rate = 0.5mL/min, 254nm, t_r (minor) = 12.75 min, t_r (major) = 19.12 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9, 10].

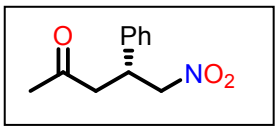
(S)-2-((S,E)-1-nitro-5-phenylpent-4-en-2-yl)cyclohexan-1-one (5p)



Yellow solid, Yield 72%, m.p. 78-80°C; $[\alpha]_D^{20}$ -32.6 (c 0.86, $CHCl_3$); *syn/anti* = 95/5, 89% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.24 – 7.14 (m, 5H), 6.50 (d, J = 15.7 Hz, 1H), 6.02 (dt, J = 15.7, 6.2 Hz, 1H), 4.74 (dd, J = 12.4, 4.7 Hz, 1H), 4.57 (dd, J = 12.4, 9.3 Hz, 1H), 3.41 – 3.31 (m, 1H), 2.53 – 2.35 (m, 2H), 2.26 – 2.13 (m, 2H), 2.06 – 1.90 (m, 2H), 1.95 – 1.80 (m, 2H), 1.75 – 1.57 (m, 2H), 1.52 – 1.38 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-d) δ 210.88, 137.27, 129.03, 128.98, 128.24, 128.22, 127.69, 126.87, 126.83, 125.61, 125.57, 79.22, 52.59, 39.26, 39.09, 35.49, 27.4, 25.65, 23.65. ES-MS (M+H$^+$) 288.2 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane/ACN) = 4:95:1, flow rate = 0.6mL/min, 254nm, t_r (minor) = 22.64 min, t_r (major) = 39.85 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[10].

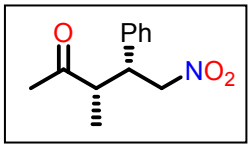
(R)-5-nitro-4-phenylpentan-2-one (6a)



White solid, Yield 70%, m.p. 84-86 °C; $[\alpha]_D^{20}$ -4.6 (c 0.95, $CHCl_3$); 30 % *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.32 – 7.23 (m, 2H), 7.26 – 7.10 (m, 3H), 4.69 (dd, J = 12.3, 6.9 Hz, 1H), 4.59 (dd, J = 12.3, 7.9 Hz, 1H), 4.02 – 3.88 (m, 1H), 2.91 (d, J = 7.0 Hz, 2H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 204.94, 142.18, 128.58, 128.45, 127.72, 127.22, 79.02, 46.11, 39, 29.57. ES-MS (M+H$^+$) 209.01 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 8:92, flow rate = 0.6mL/min, 254nm, t_r (major) = 20.51 min, t_r (minor) = 50.63 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9].

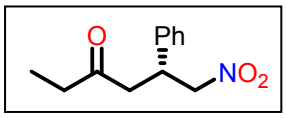
(3S,4R)-3-methyl-5-nitro-4-phenylpentan-2-one (7a)



White solid, Yield 36%, m.p. 81-82 °C; $[\alpha]_D^{20}$ -22.6 (c 0.23, $CHCl_3$); *syn/anti* = 62/38, 64% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) syn δ 7.40 – 7.24 (m, 3H), 7.23 – 7.10 (m, 2H), 4.73 – 4.58 (m, 2H), 3.84 – 3.74 (m, 1H), 3.00 – 2.88 (m, 1H), 2.24 (d, *J* = 7.3 Hz, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 206.03, 141.24, 130.27, 128.61, 128.37, 78.1, 49.22, 45.68, 29.75, 12.00. ES-MS ($M+H^+$) 222.14 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 10:90, flow rate = 0.5mL/min, 254nm, t_r (minor) = 23.5 min, t_r (major) = 55.88 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9], [11].

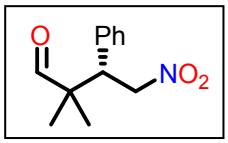
(R)-6-nitro-5-phenylhexan-3-one (7b)



White solid, Yield 42%, m.p. 86-87 °C; $[\alpha]_D^{20}$ -32.6 (c 0.86, $CHCl_3$); 75% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.25 (m, 3H), 7.29 – 7.14 (m, 2H), 4.73 (dd, *J* = 13.1, 5.9 Hz, 1H), 4.56 (dd, *J* = 13.1, 9.4 Hz, 1H), 4.05 – 3.93 (m, 1H), 2.88 (d, *J* = 7.1 Hz, 2H), 2.49 – 2.31 (m, 2H), 1.02 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 207.94, 142.18, 128.58, 128.49, 128.45, 127.73, 79.02, 44.83, 36.39, 34.71, 9.1. ES-MS ($M+H^+$) 222.14 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 5:95, flow rate = 0.5mL/min, 254nm, t_r (minor) = 56.19 min, t_r (major) = 64.11 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9], [12].

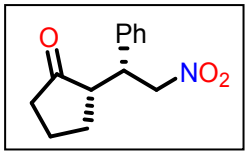
(S)-2,2-dimethyl-4-nitro-3-phenylbutanal (8a)



White solid, Yield 82%, m.p. 79-82 °C; $[\alpha]_D^{20}$ -4.9 (c 1, $CHCl_3$); 79% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 9.53 (s, 1H), 7.41 – 7.27 (m, 3H), 7.29 – 7.13 (m, 2H), 4.87 (dd, *J* = 12.9, 4.2 Hz, 1H), 4.69 (dd, *J* = 12.9, 11.4 Hz, 1H), 3.79 (ddd, *J* = 11.4, 4.2, Hz, 1H), 1.15 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 206.64, 141.21, 128.7, 128.13, 127.64, 78.75, 52.84, 45.09, 17.75. ES-MS ($M+H^+$) 222.12 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 8:92, flow rate = 1.0 mL/min, 254nm, t_r (minor) = 24.61 min, t_r (major) = 34.68 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9, 13].

(S)-2-((R)-2-nitro-1-phenylethyl)cyclopentan-1-one (9a)



Brown oily, Yield 83%, $[\alpha]_D^{20}$ -26.5 (c 1.4, $CHCl_3$); *syn/anti* = 83/17, 58% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) syn δ 7.37 – 7.09 (m, 5H), 5.33 (dd, *J* = 12.6, 6.7 Hz, 1H), 4.71 (dd, *J* = 12.6, 10.6 Hz, 1H), 3.83 – 3.71 (m, 1H), 2.47 – 2.39 (m, 1H), 2.43 – 2.32 (m, 1H), 2.20 – 2.06 (m, 1H), 2.03 – 1.84 (m, 2H), 1.83 – 1.67 (m, 1H), 1.57 – 1.43 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-d) δ 219.03,141.14,130.05, 128.33, 128.09, 77.44, 54.09, 43.93, 36.85, 31.57, 22.4. ES-MS ($M+H^+$)

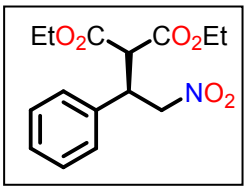
234.13 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 10:90, flow rate = 1.0 mL/min, 254nm, t_r (minor) = 16.82 min, t_r (major) = 19.58 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[9, 10].

General reaction condition for the Michael addition of Michael donors (10) to Nitroolefines by using $1d_0$ as bifunctional organocatalysts

To the precooled (-10°C) **10** (3.05 ml, 20mmol) the catalyst $1d_0$ (5.35 mg, 10 mol%) was added under nitrogen atmosphere. The reaction allows to stir for about 1h and then trans-nitrostyrene (1 mmol) was added by maintaining the nitrogen atmosphere. The reaction was evaporated under reduced pressure after completion. To the reaction crude water was added and then extracted with EtOAc (10 ml X3) and combined organic layer dried over Na_2SO_4 and evaporated by rotatory evaporator. The products were purified by column chromatography using 20% EtOAc and hexane as eluent.

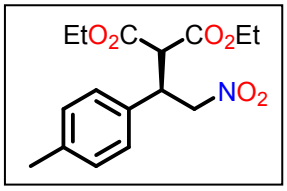
diethyl (R)-2-(2-nitro-1-phenylethyl)malonate (11a)



Colorless oily, Yield 95%, $[\alpha]_D^{20}$ -3.7 (c 1.1, $CHCl_3$); 94% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.40 – 7.32 (m, 2H), 7.36 – 7.24 (m, 2H), 7.23 – 7.13 (m, 1H), 4.94 (dd, *J* = 13.2, 5.9 Hz, 1H), 4.85 (dd, *J* = 13.2, 9.0 Hz, 1H), 4.29 – 4.11 (m, 3H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.82 (d, *J* = 9.2 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 169.14, 136.81, 129.3, 128.04, 127.58, 77.51, 61.64, 50.89, 47.29, 13.79, 13.39. ES-MS ($M+H^+$) 310.14 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 4:96, flow rate = 1.0mL/min, 254nm, t_r (major) = 36.65 min, t_r (minor) = 38.90 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[14, 15].

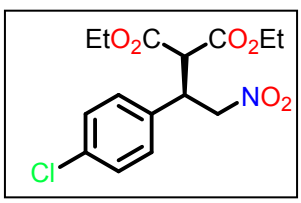
diethyl (R)-2-(2-nitro-1-(p-tolyl)ethyl)malonate (11b)



Colorless oily, Yield 92%, $[\alpha]_D^{20}$ -2.8 (c 1.2, $CHCl_3$); 92% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.14 – 7.09 (m, 2H), 7.18 – 7.05 (m, 2H), 4.93 (dd, *J* = 12.9, 5.3 Hz, 1H), 4.82 (dd, *J* = 12.8, 8.9 Hz, 1H), 4.29 – 4.11 (m, 3H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.81 (d, *J* = 9.2 Hz, 1H), 2.32 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 169.15, 138.53, 135.19, 130.32, 129.31, 77.53, 61.66, 54.91, 42.31, 21.03, 14.58. ES-MS ($M+H^+$) 324.14 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 5:95, flow rate = 1.0 mL/min, 254nm, t_r (major) = 36.51 min, t_r (minor) = 77.28 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[14, 15].

diethyl (R)-2-(2-nitro-1-(p-tolyl)ethyl)malonate (11c)

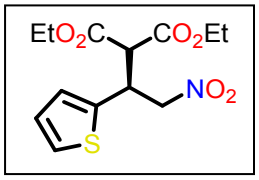


Colorless oily, Yield 85%, $[\alpha]_D^{20}$ -5.7 (c 1.0, $CHCl_3$); 89% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.35 – 7.24 (m, 2H), 7.24 – 7.15 (m, 2H), 4.92 (dd, *J* = 13.0, 4.8 Hz, 1H), 4.81 (dd, *J* = 13.0, 9.8 Hz, 1H), 4.32 – 4.13 (m, 3H), 4.04 (q, *J* = 7.2 Hz, 2H), 3.78 (d, *J* = 7.0 Hz, 1H), 1.25 (t,

J = 7.1 Hz, 3H), 1.09 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 167.13, 166.13, 139.7, 133.43, 132.67, 132.65, 128.24, 77.52, 61.65, 55.11, 42.31, 13.6. ES-MS (M+H$^+$) 345.1*m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) =10:90, flow rate = 1.0 mL/min, 254nm, t_r (major) = 6.10 min, t_r (minor) = 7.92 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[14, 15].

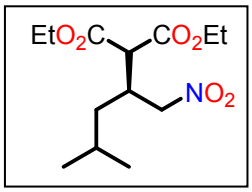
diethyl (S)-2-(2-nitro-1-(thiophen-2-yl)ethyl)malonate (11d)



Yellow oily, Yield 60%, $[\alpha]_D^{20}$ +8.6 (c 0.92, $CHCl_3$); 92% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.29 – 7.18 (m, 1H), 7.00 – 6.88 (m, 2H), 4.96 (dd, J = 13.4, 6.2 Hz, 1H), 4.88 (dd, J = 13.5, 7.8 Hz, 1H), 4.55 (td, J = 7.9, 6.2 Hz, 1H), 4.30 – 4.15 (m, 2H), 4.11 (q, J = 7.0 Hz, 2H), 3.86 (d, J = 8.1 Hz, 1H), 1.26 (t, J = 7.0 Hz, 3H), 1.15 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 166.83, 166.24, 137.82, 128.37, 127.54, 125.21, 77.22, 61.66, 61.61, 56.02, 38.91, 13.8, 13.61. ES-MS (M+H$^+$) 316.1 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 10:90, flow rate = 1.0 mL/min, 254nm, t_r (major) = 7.83 min, t_r (minor) = 9.93 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[14, 15].

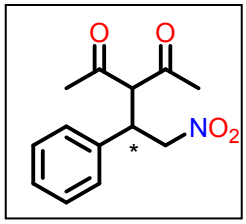
diethyl (S)-2-(2-nitro-1-(thiophen-2-yl)ethyl)malonate (11e)



Colorless oily, Yield 84%, $[\alpha]_D^{20}$ -7.2 (c 1.0, $CHCl_3$); 85% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 4.71 (dd, J = 12.3, 5.0 Hz, 1H), 4.56 (dd, J = 12.3, 6.6 Hz, 1H), 4.34 – 4.09 (m, 4H), 3.62 (d, J = 5.6 Hz, 1H), 2.92 (ddt, J = 12.1, 6.8, 5.2 Hz, 1H), 1.61 (ddd, J = 11.9, 6.6, 5.0 Hz, 1H), 1.44 – 1.22 (m, 8H), 0.98 – 0.87 (m, 6H); ^{13}C NMR (100 MHz, Chloroform-d) δ 167.93, 167.83, 76.41, 61.65, 52.51, 38.7, 34.61, 26.27, 23.05, 13.8. ES-MS (M+H$^+$) 290.21 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 10:90, flow rate = 1.0 mL/min, 254nm, t_r (major) = 10.44 min, t_r (minor) = 16.24 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature[14, 15].

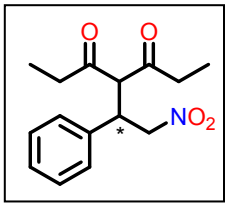
(S)-3-(2-nitro-1-phenylethyl)pentane-2,4-dione (11f)



White solid, Yield 96%, mp: 120-122 °C; $[\alpha]_D^{20}$ + 195.3 (c 1.0, $CHCl_3$); 82% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.25 (m, 3H), 7.21-7.09 (m, 2H), 4.67 – 4.50 (m, 2H), 4.38-4.29 (m, 1H), 4.24 (d, J = 2.41 Hz, 1H), 2.25 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 201.75, 201.04, 136.13, 129.32, 128.05, 127.6, 77.82, 69.81, 42.61, 30.49, 29.51. ES-MS (M+H$^+$) 250.32 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 5:95, flow rate = 1.0 mL/min, 254nm, t_r (major) = 17.23 min, t_r (minor) = 18.58 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature.[16]

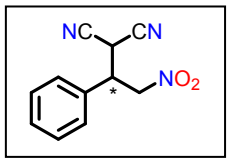
(S)-4-(2-nitro-1-phenylethyl)heptane-3,5-dione (11g)



White solid, Yield 95%, mp: 96-98 °C; $[\alpha]_D^{20}$ + 149.25 (c 0.9, $CHCl_3$); 96% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.39-7.21 (m, 3H), 7.20 – 7.09 (m, 2H), 4.74 – 4.58 (m, 2H),4.41 – 4.27 (m, 2H), 2.30 (m, 1H), 2.12 (m, 1H), 1.06 (t, *J* = 7.02 Hz, 3H), 0.76 (t, *J* = 7.20 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 204.45, 203.85, 136.13, 129.13, 128.33, 127.83, 77.82, 69.12, 42.81, 36.71. 36.31, 7.3, 7.21. ES-MS ($M+H^+$) 278.12 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane/ACN) = 9:90:1, flow rate = 1.0 mL/min, 254nm, t_r (minor) = 8.64 min, t_r (major) = 11.63 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature.[16]

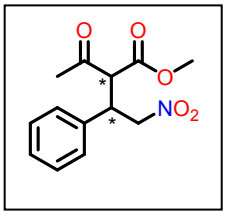
(R)-2-(2-nitro-1-phenylethyl)malononitrile (11h)



White solid, Yield 88%, mp: 62-65 °C; $[\alpha]_D^{20}$ + 4.82 (c 0.76, $CHCl_3$); 92% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.55-7.37(m, 3H), 7.37-7.21 (m, 2H),5.14-4.90 (m, 2H), 4.45 (d, J= 5.8 Hz, 1H), 4.14-3.99 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-d) δ 131.73, 130.33, 129.33, 127.6, 110.53, 110.33, 75.12, 43.41, 27.31. ES-MS ($M+H^+$) 216.22 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 15:85, flow rate = 1.0 mL/min, 254nm, t_r (major) = 9.86 min, t_r (minor) = 12.96 min.

^{1}H NMR, ^{13}C NMR and optical rotation were consistent with those reported in the literature.[15a]

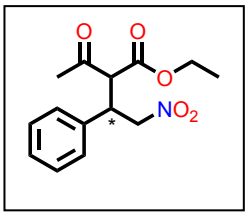
methyl 2-acetyl-4-nitro-3-phenylbutanoate (11i)



White solid, Yield 92%, mp: 102-104 °C; $[\alpha]_D^{20}$ + 72.32 (c 1.1, $CHCl_3$); 96:4 *dr*; 94% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.13 (m, 5H), 4.89 – 4.77 (m, 1H), 4.77-4.60 (m, 2H), 4.12 (d, *J* = 9.55 Hz, 1H), 3.75 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 200.15, 167.42, 136.22, 129.23, 127.93, 127.47, 77.51, 61.4, 52.5, 42.3, 30.19. ES-MS ($M+H^+$) 266.12 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane/ACN) = 8:90:2, flow rate = 0.5 mL/min, 254nm, t_r (minor) = 28.27 min, t_r (major) = 30.74 min.

^{1}H NMR, and ^{13}C NMR consistent with those reported in the literature.[16]

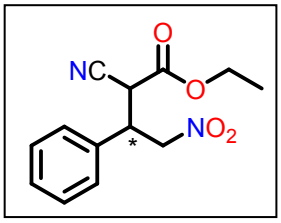
ethyl 2-acetyl-4-nitro-3-phenylbutanoate (11j)



White solid, Yield 95%, mp: 77-79 °C; $[\alpha]_D^{20}$ + 49.23 (c 0.91, $CHCl_3$); 92:8 *dr*; 96% *ee*; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36-7.24 (m, 3H), 7.23-7.14 (m, 2H), 4.86-4.71 (m, 2H), 4.29-4.20 (m, 1H), 4.15-4.05 (m, 2H), 3.95 (bs, 1H), 2.31 (s, 3H), 1.27 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 200.16, 166.82, 136.22, 129.24, 127.93, 127.47, 77.51, 62.2, 61.4, 42.3, 30.1, 13.59. ES-MS ($M+H^+$) 216.22 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane/Hexane) = 8:90:2, flow rate = 0.5 mL/min, 254nm, t_r (major) = 8.83 min, t_r (minor) = 10.09 min.

^{1}H NMR and ^{13}C NMR consistent with those reported in the literature.[16]

ethyl 2-cyano-4-nitro-3-phenylbutanoate (11k)



Light yellow oily liquid, Yield 78%, $[\alpha]_D^{20}$ + 32.6 (c 1.23, $CHCl_3$); *dr* <5%; 72% *ee*; (*dr* ≈ 1.1:1 from ^{1}H NMR integrals of the CH_3 signals) ^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.20 (m, 8H),d 7.19 – 7.09 (m, 2H),5.09-4.79 (m, 4H), 4.31 (q, *J* = 5.92 Hz, 2H), 4.21 (q, *J* = 5.86, 6.40 Hz, 4H), 3.92 (d, *J* = 4.32 Hz, 2H), 1.23 (t, *J* = 5.89 Hz, 3H), 1.13 (t, *J* = 5.91 Hz, 3H)^{13}C NMR (100 MHz, Chloroform-d) δ 166.34, 163.73, 139.82, 130.32, 129.42, 129.32, 128.22, 128.05, 127.72, 127.59, 127.23, 114.62, 114.32, 76.52, 76.11, 63.61, 63.31, 42.91, 42.71, 41.31, 41.11, 13.8, 13.3. ES-MS ($M+H^+$) 263.32 *m/z*. HPLC: Chirapak IA (i-PrOH/Hexane) = 10:90, flow rate = 1.0 mL/min, 254nm, First diastereomer: major t_r = 12.07 min, minor t_r = 16.01 min; 72% ee; Second diastereomer: major t_r = 10.98 min, major t_r =14.60.

^{1}H NMR and ^{13}C NMR were consistent with those reported in the literature.[17]

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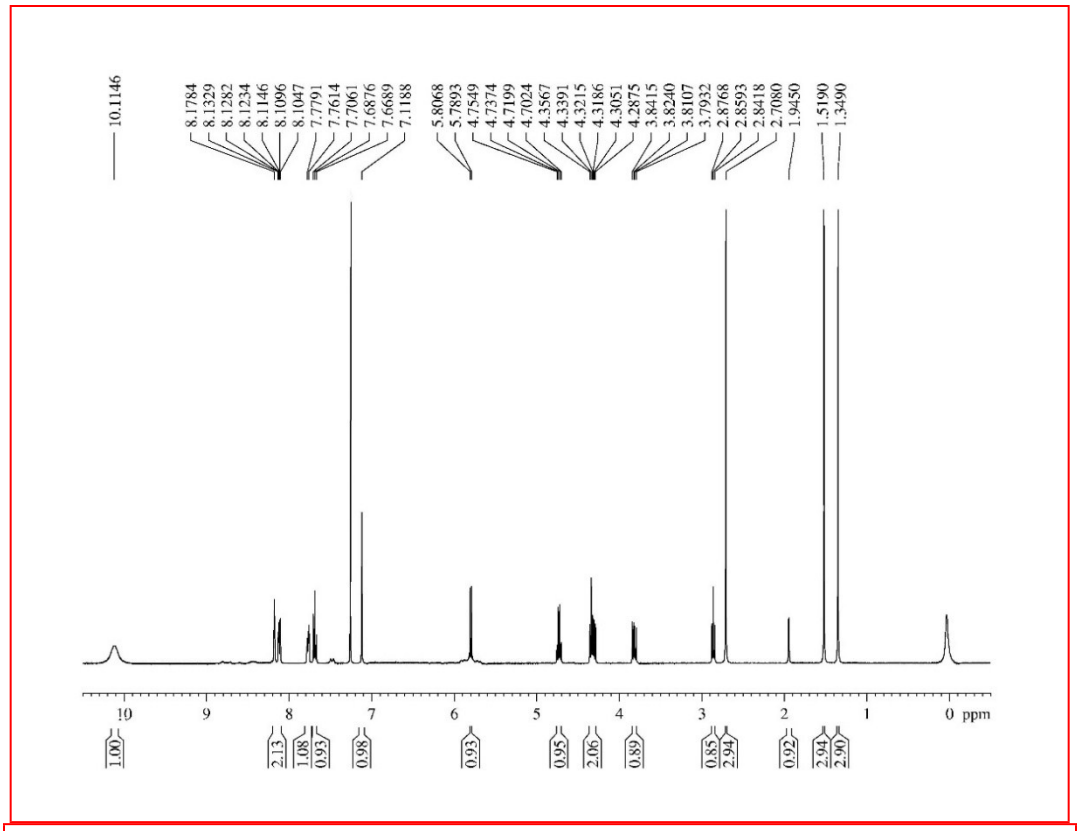
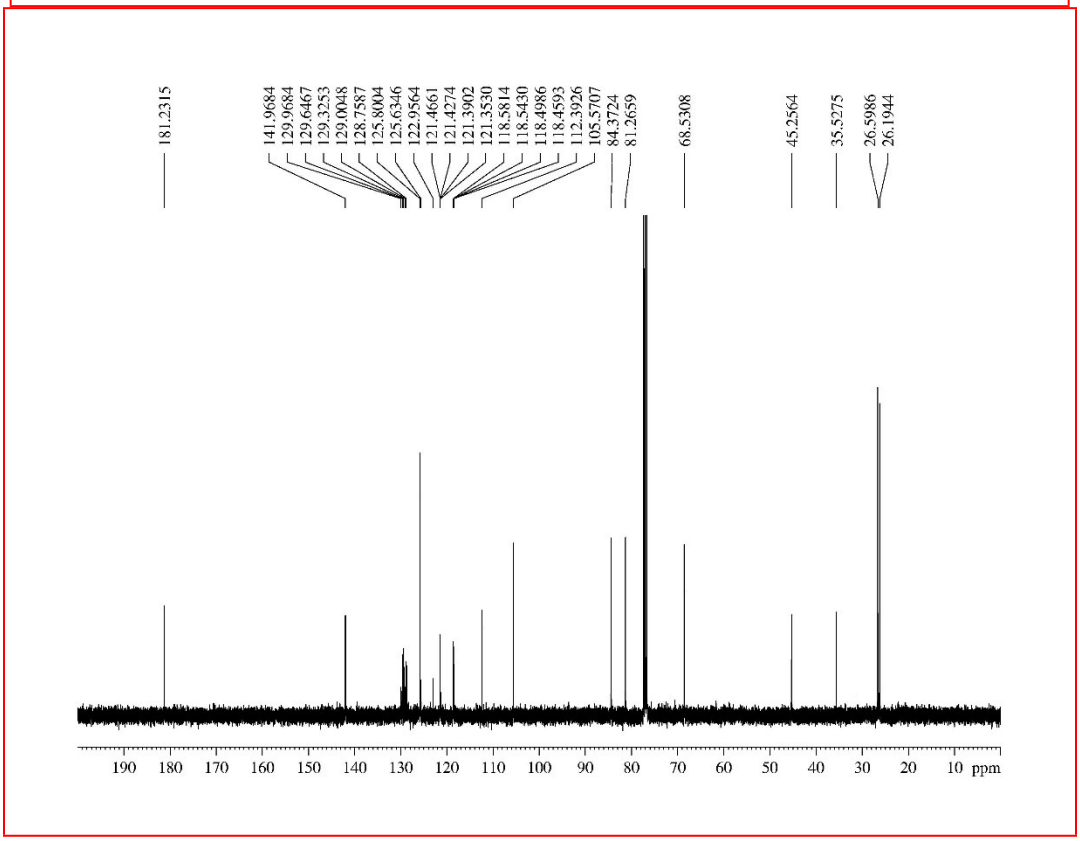
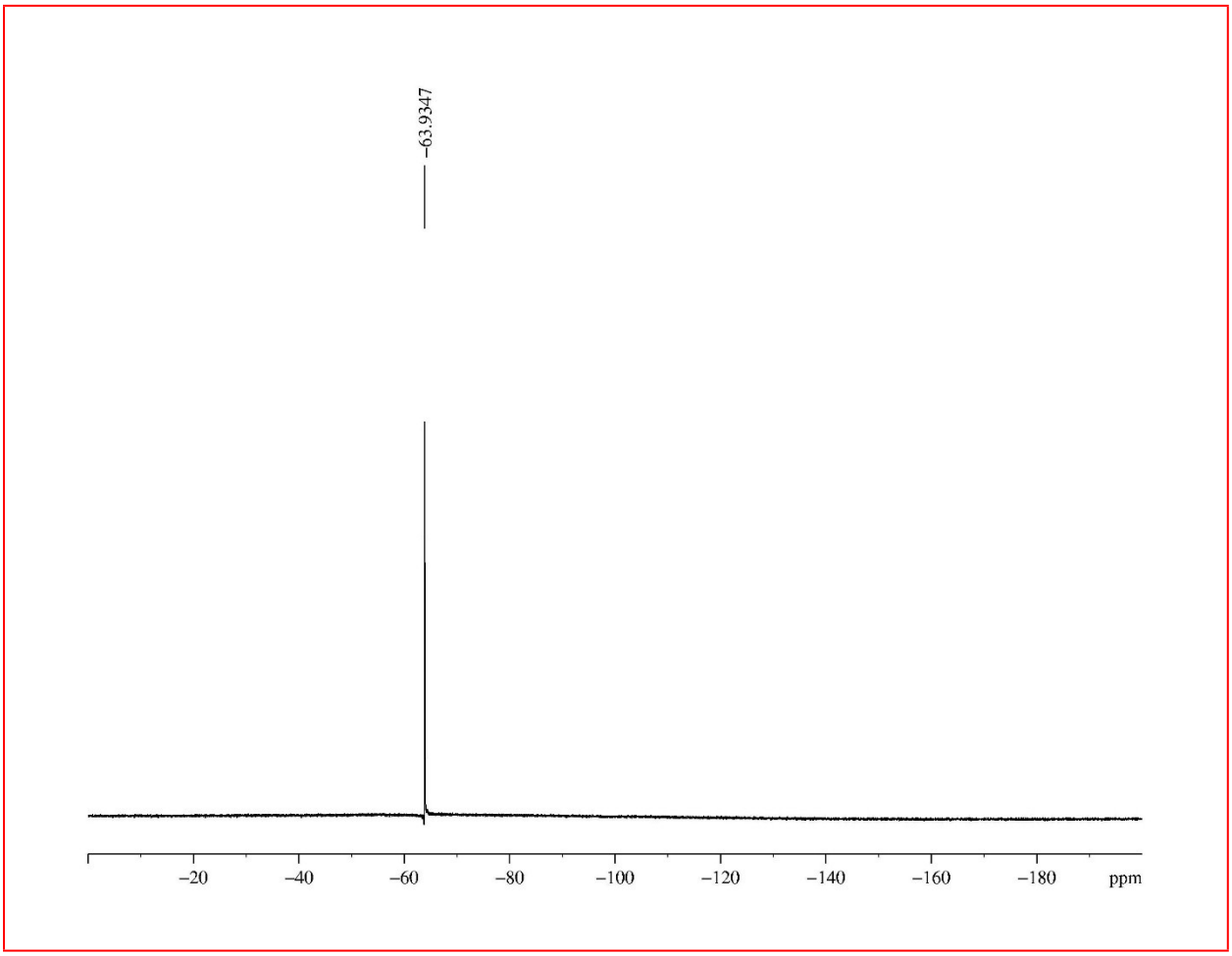
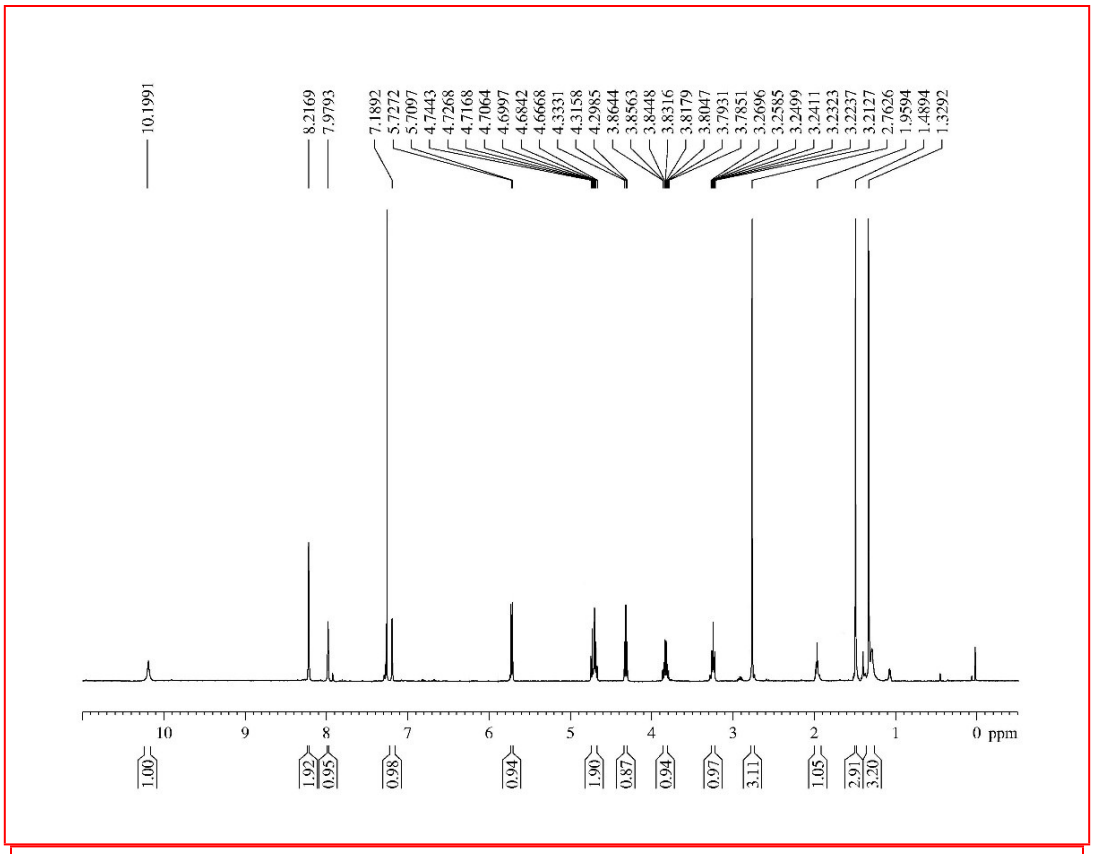


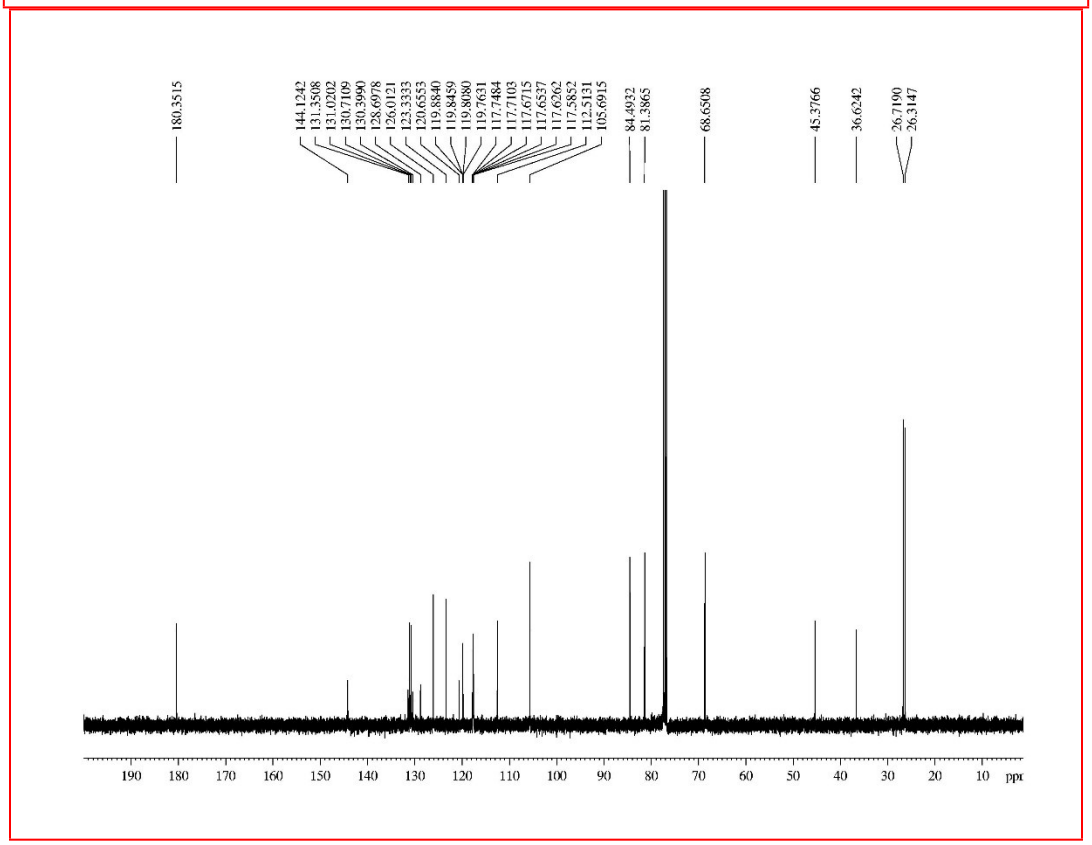


^{1}H and ^{13}C NMR spectra of 1a$_1$



^{19}F NMR spectra of 1a$_1$





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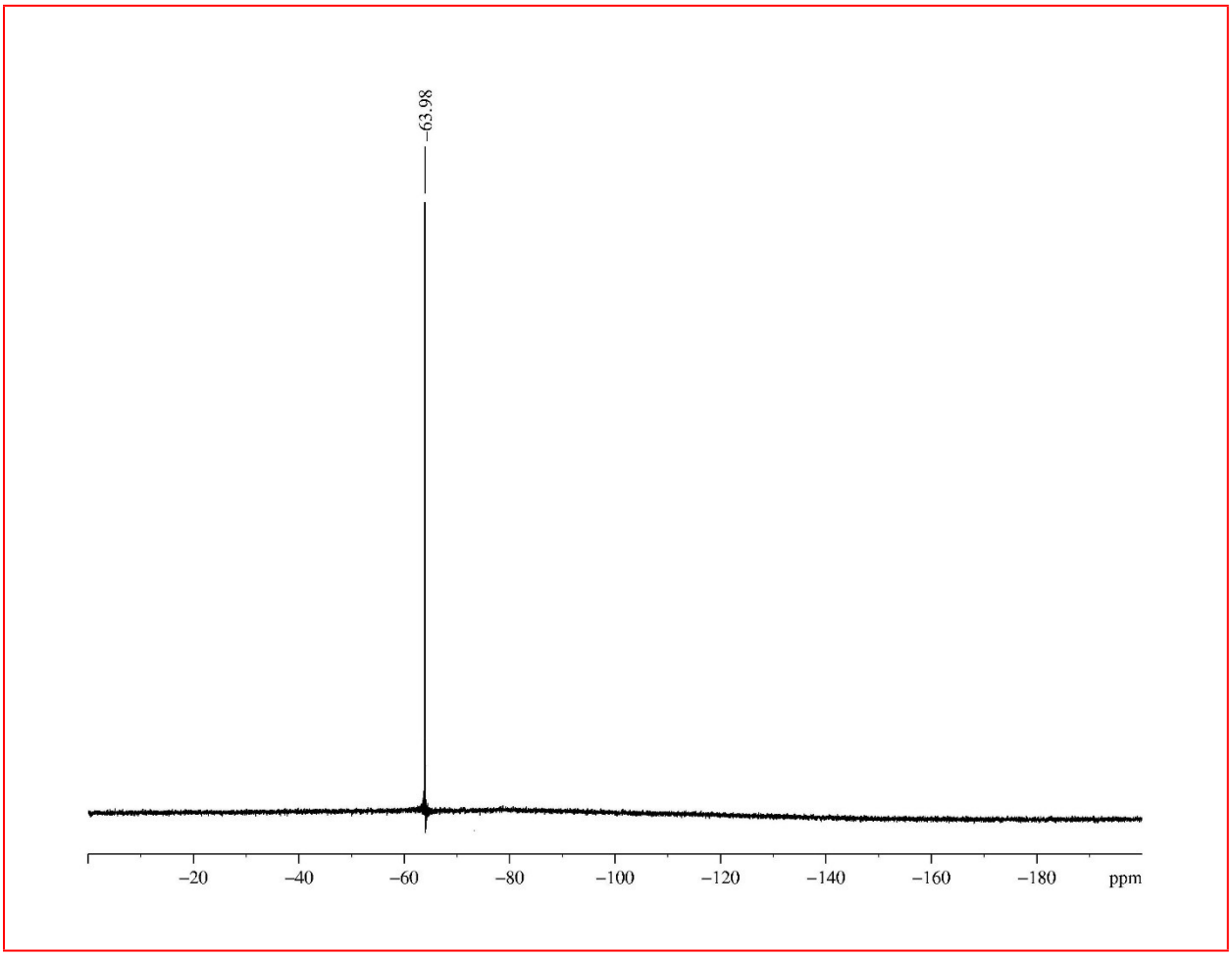

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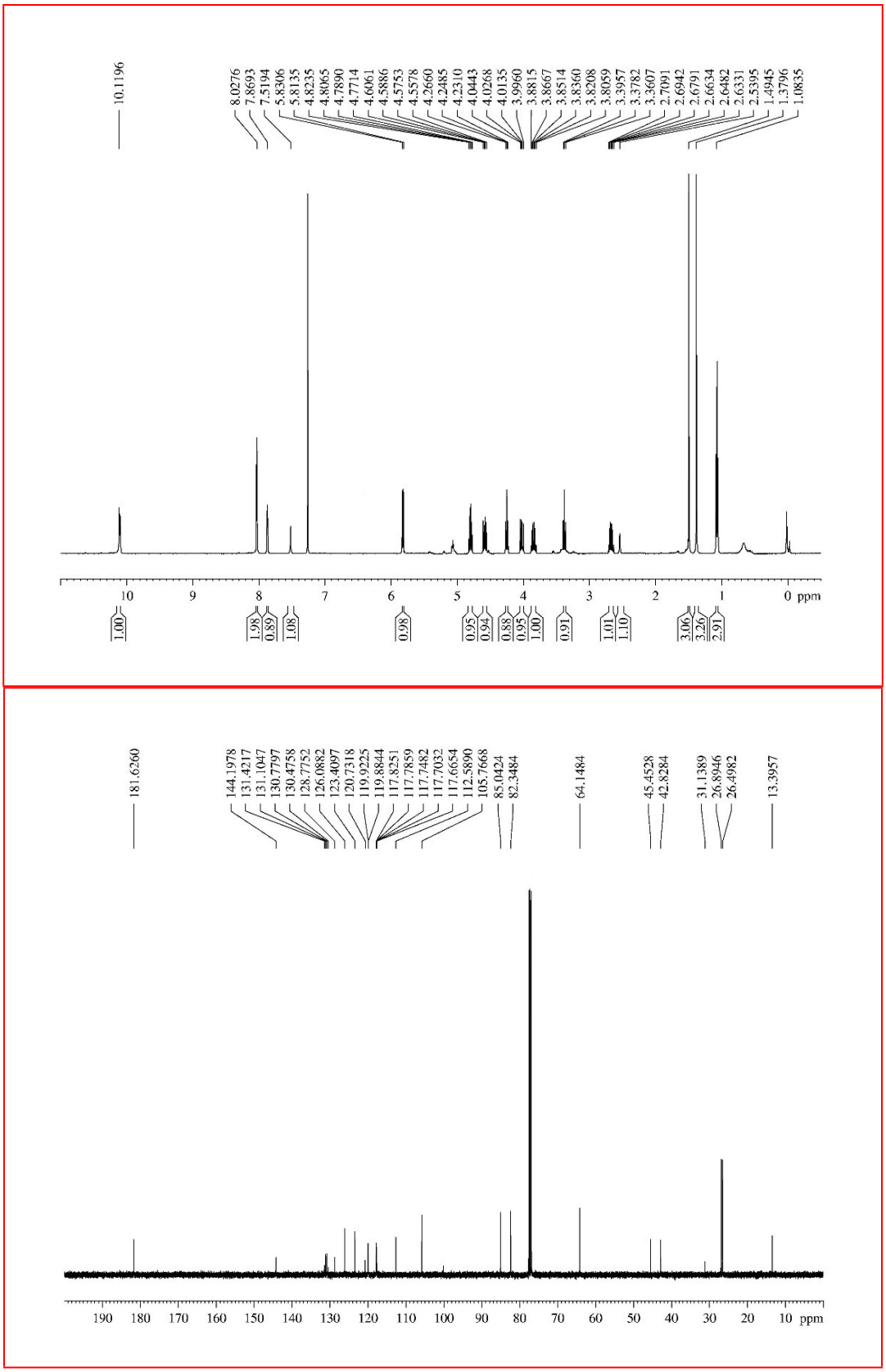

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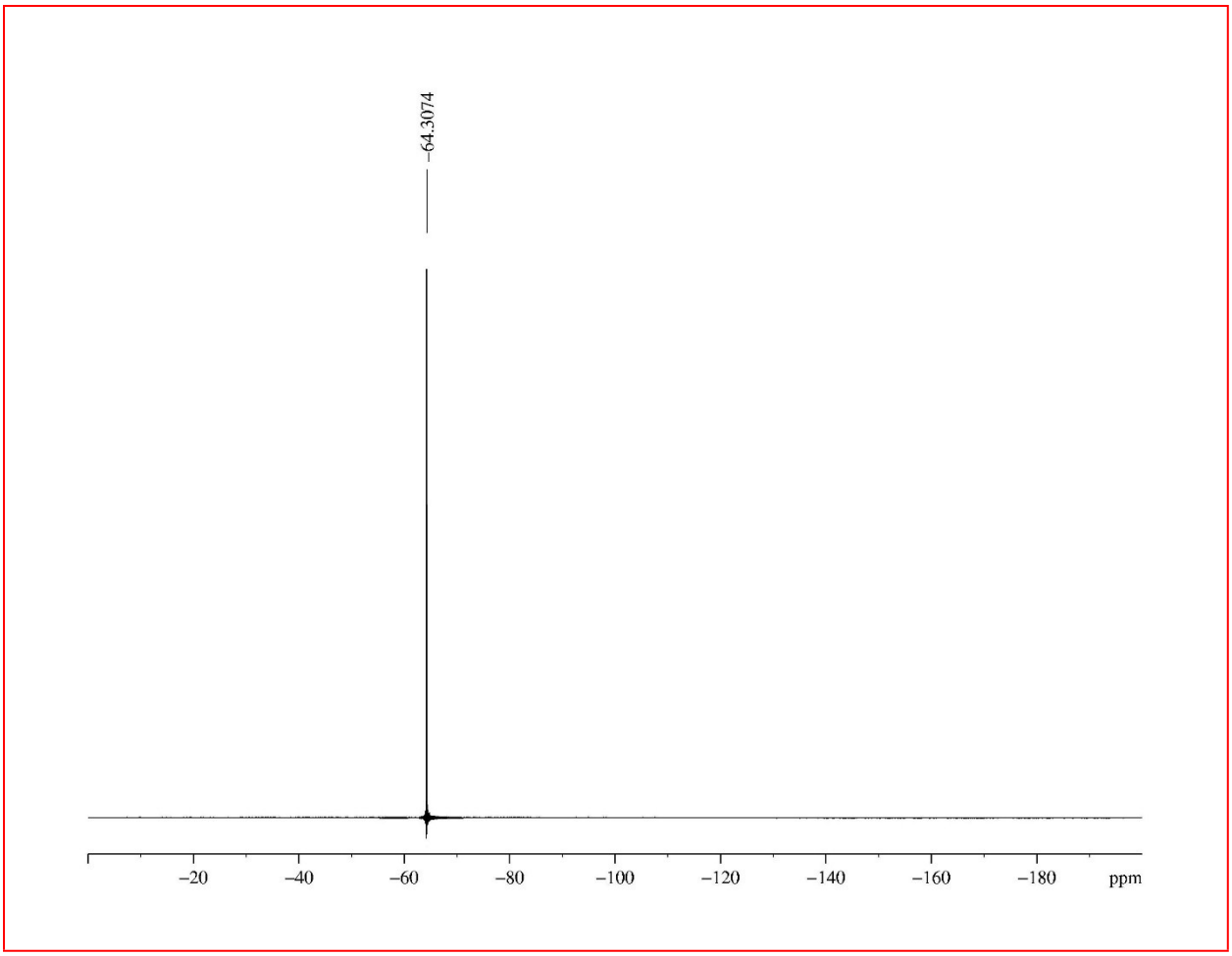

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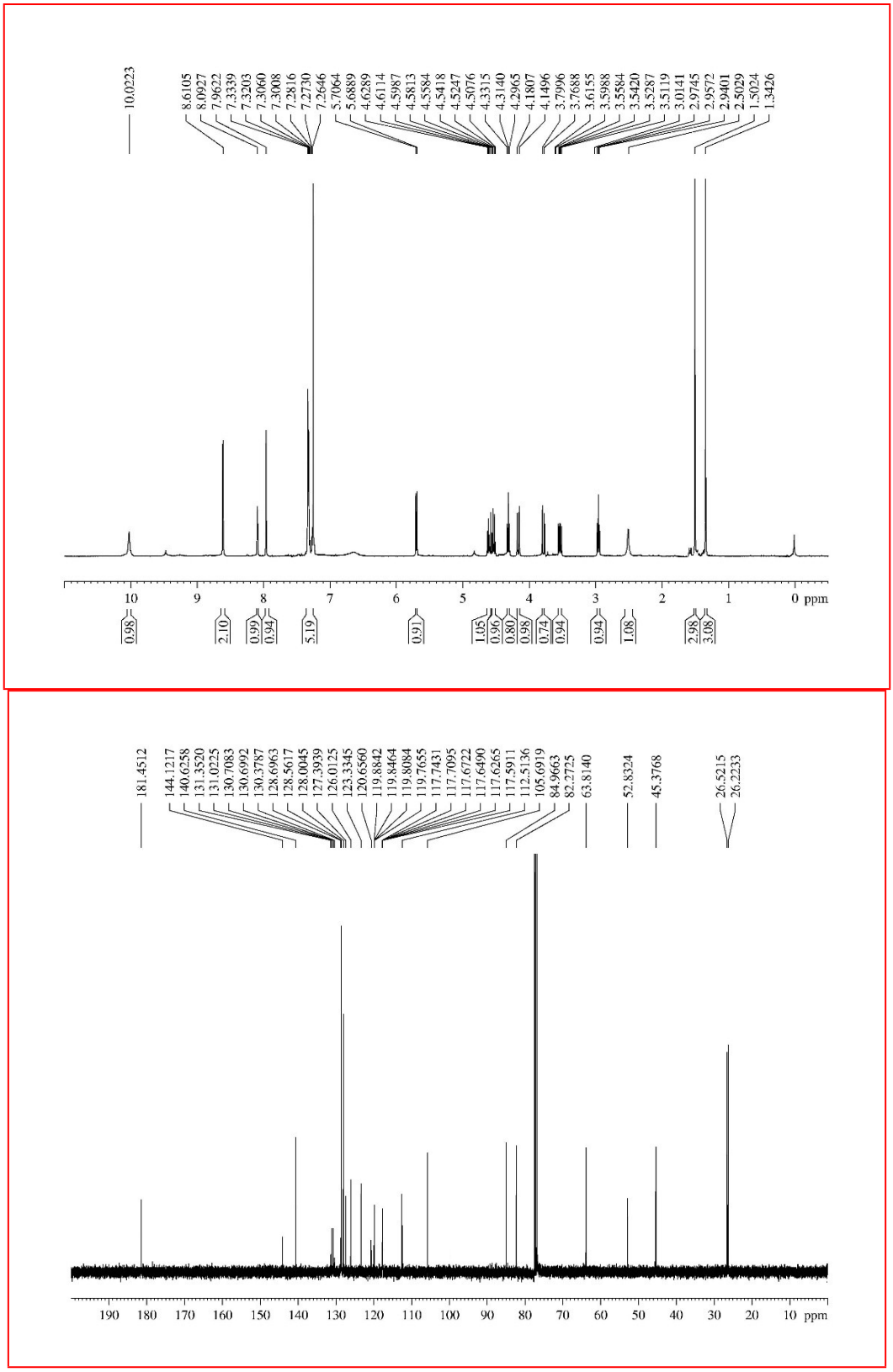

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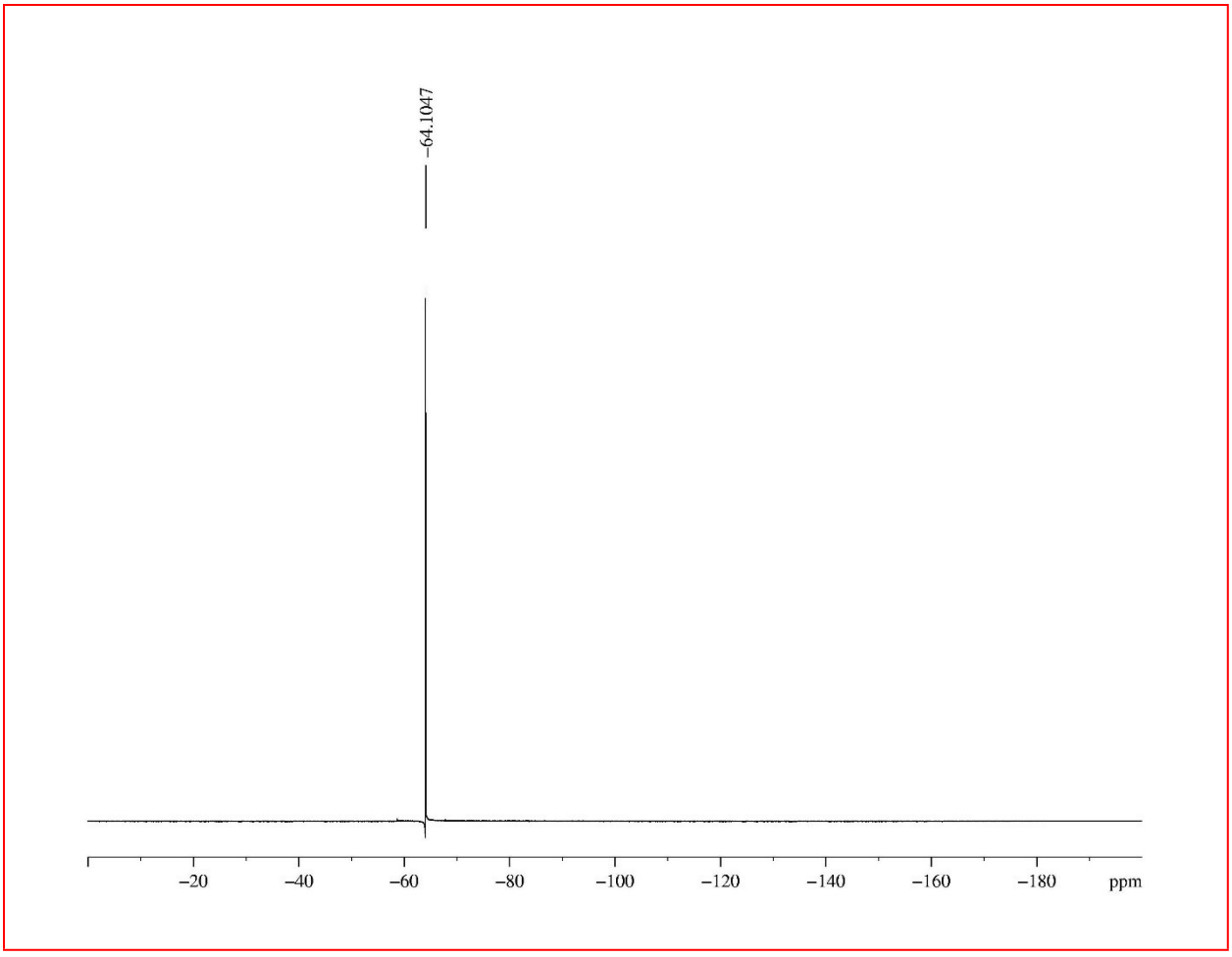

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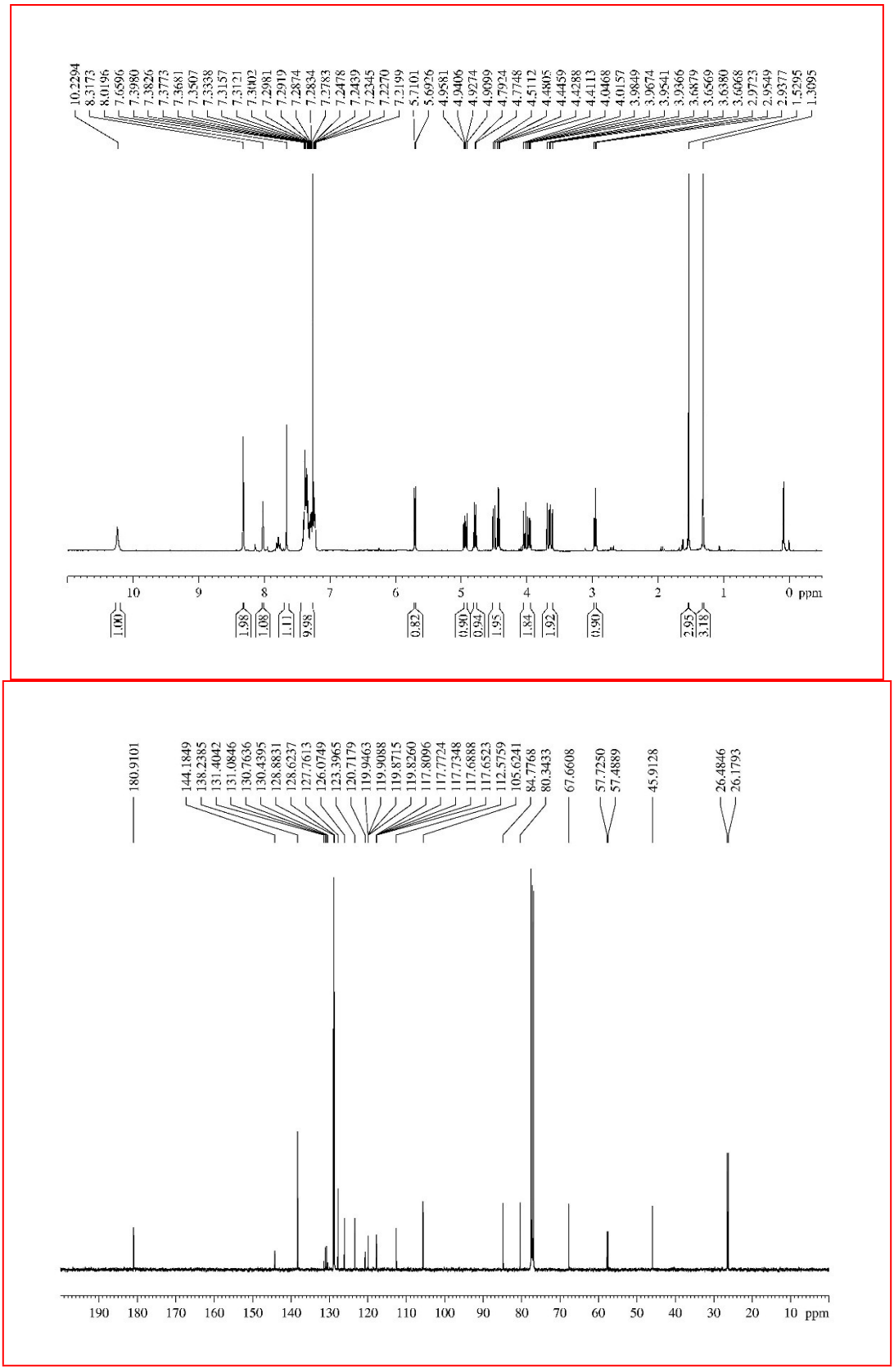

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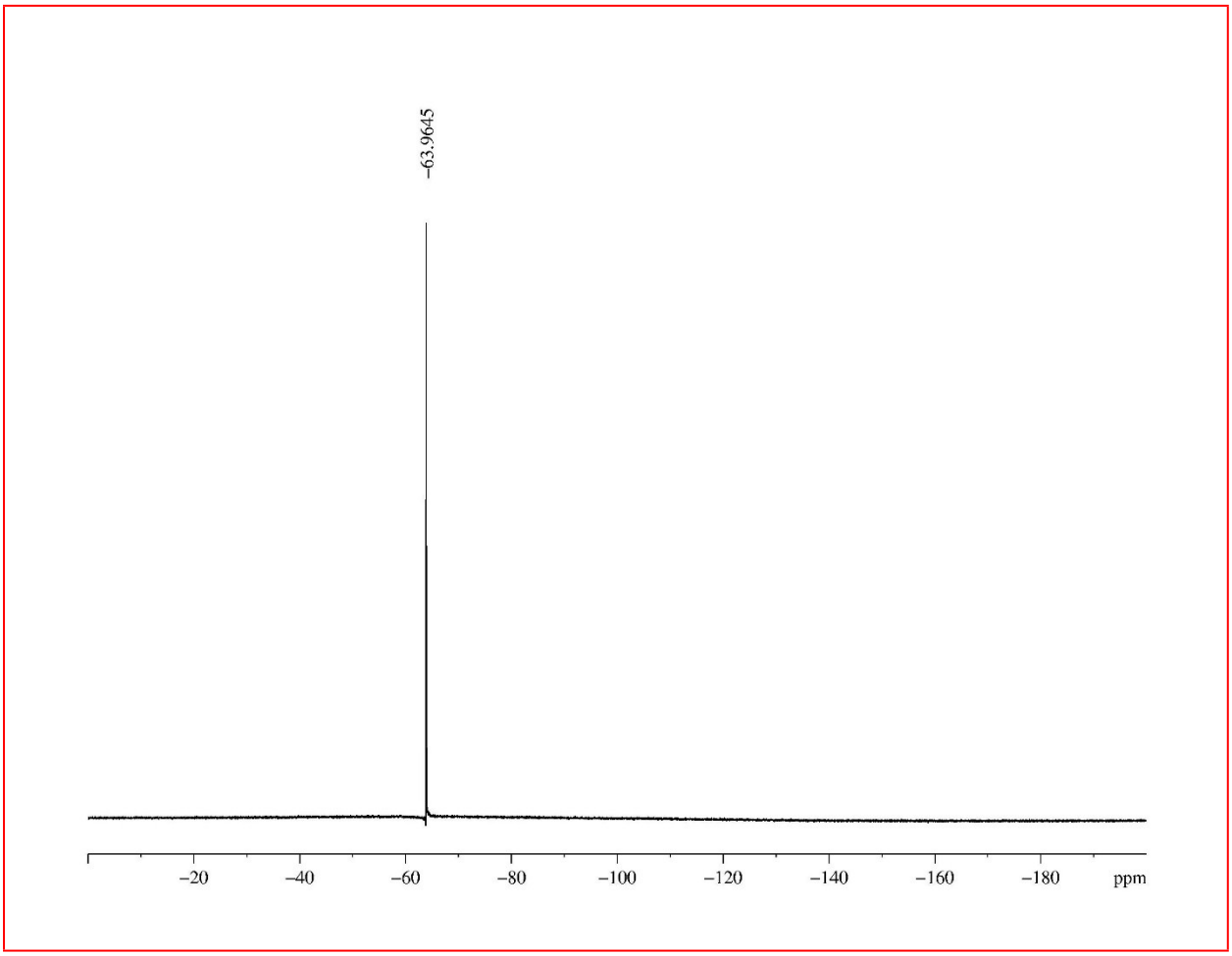

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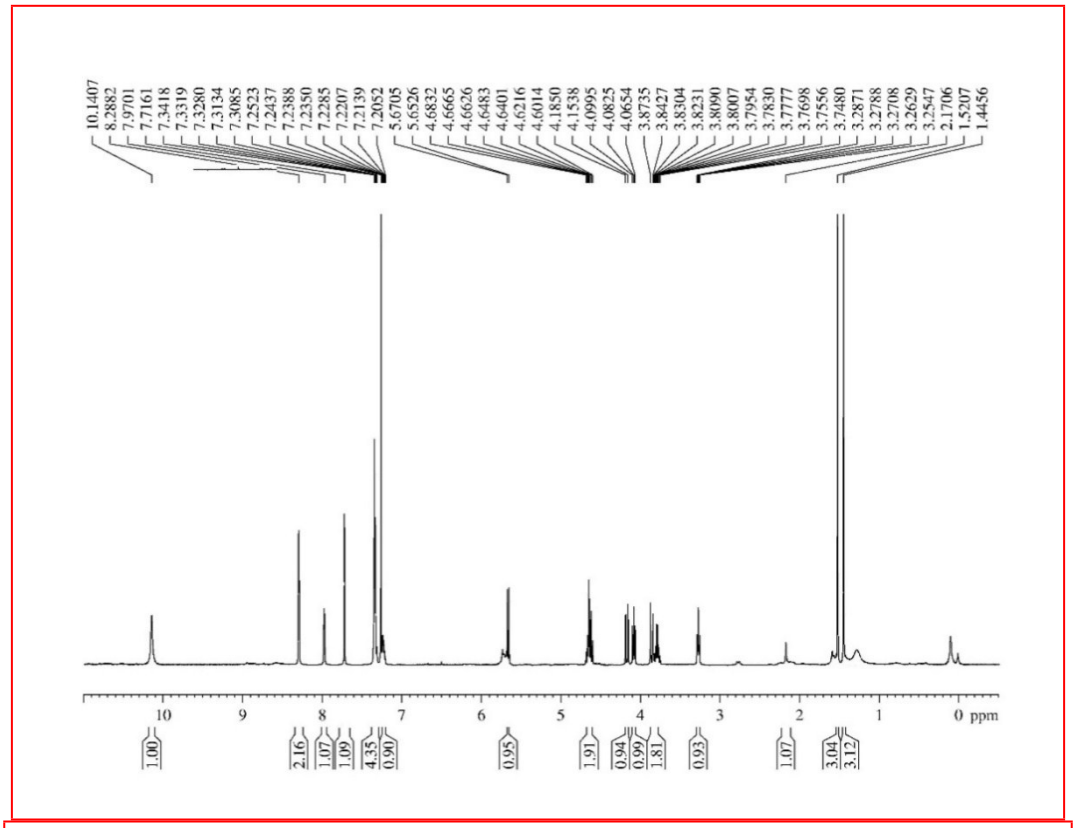
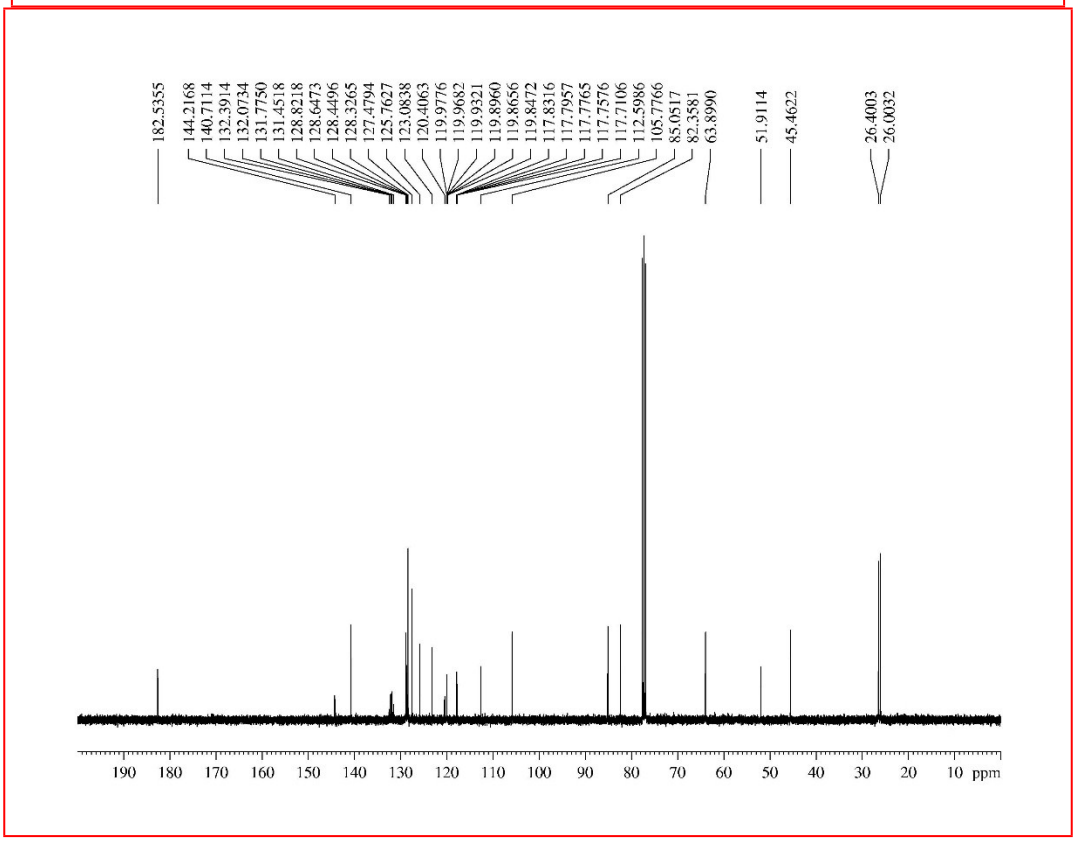
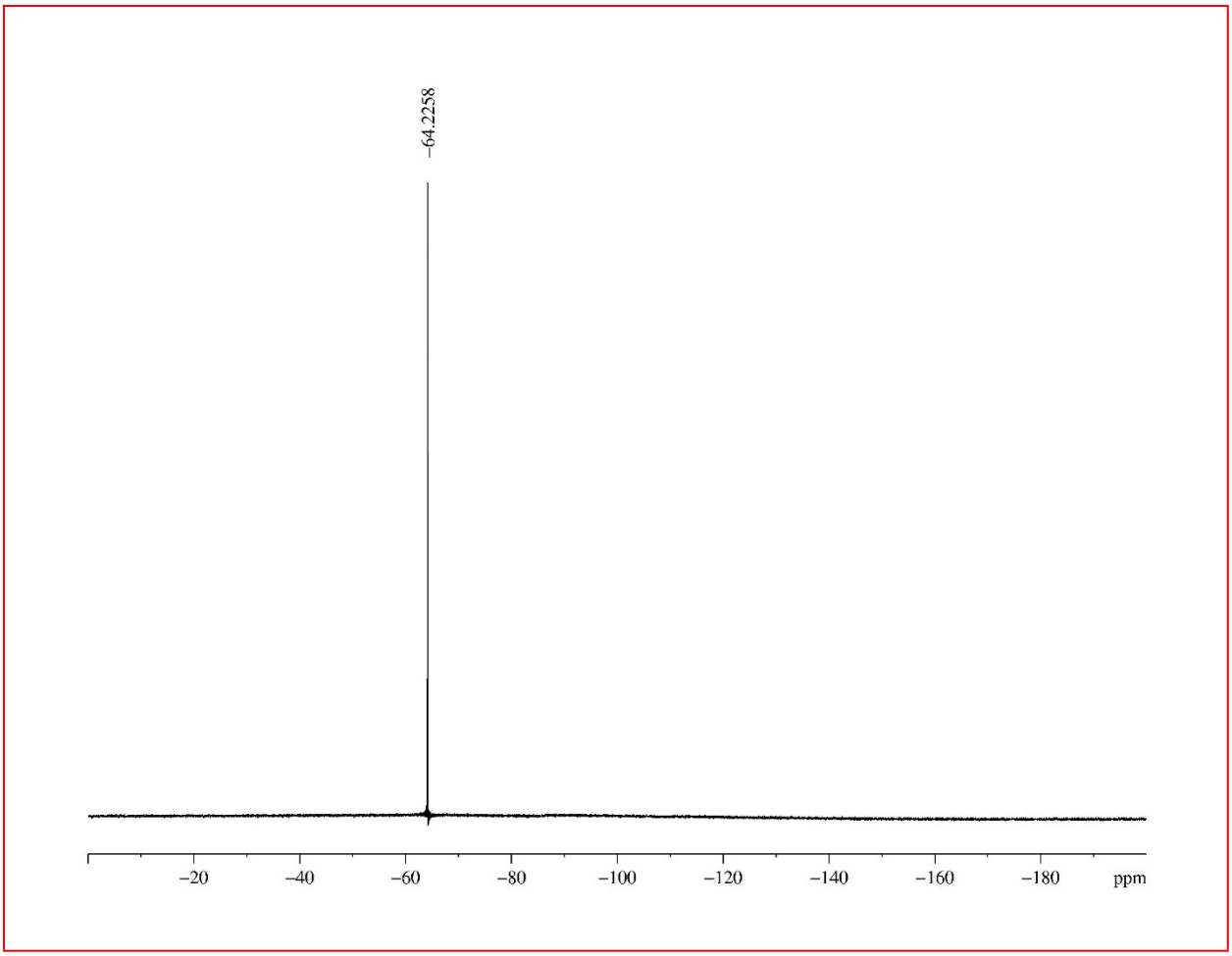




^{1}H and ^{13}C NMR spectra of 2d$_1$



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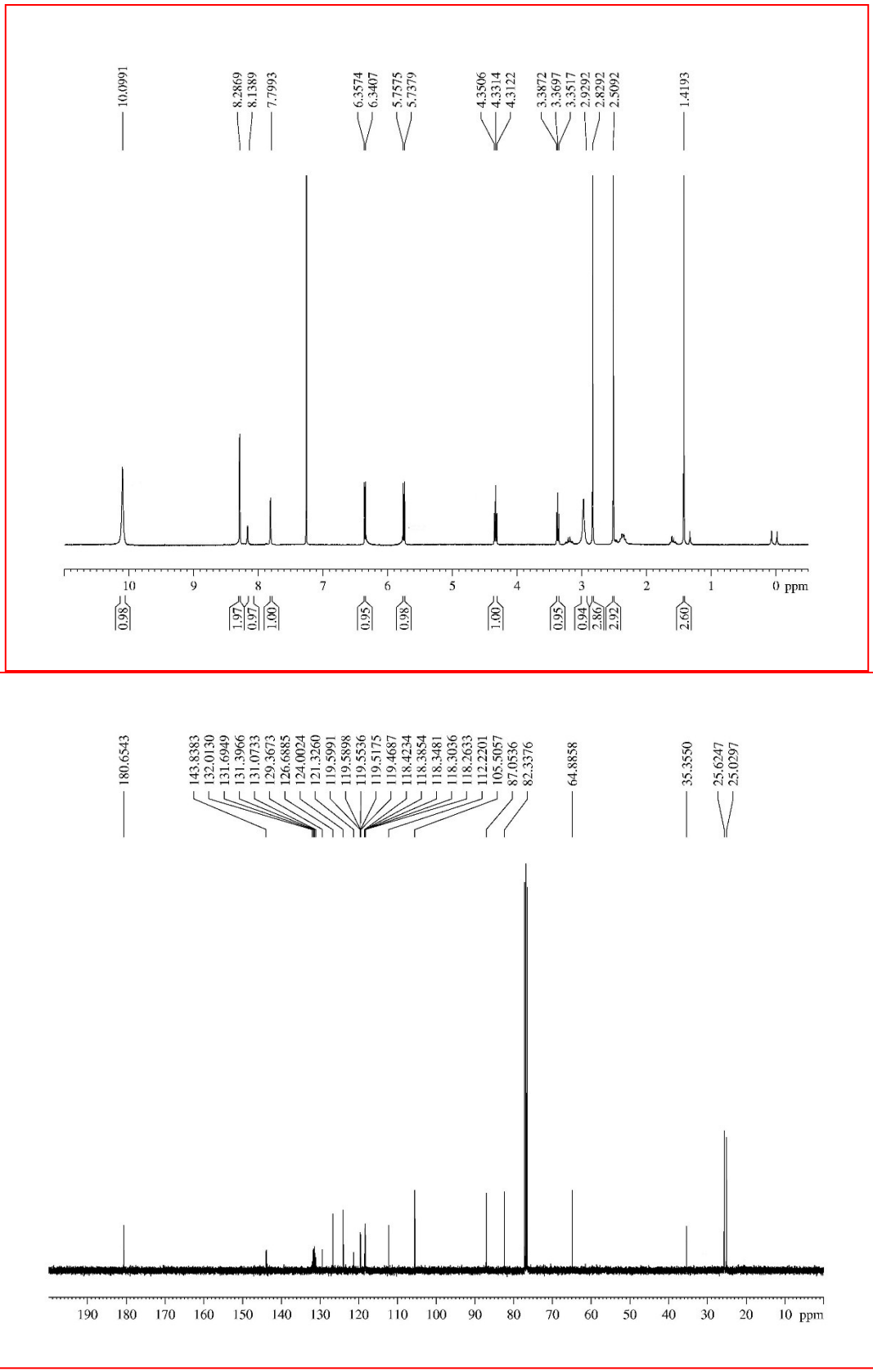
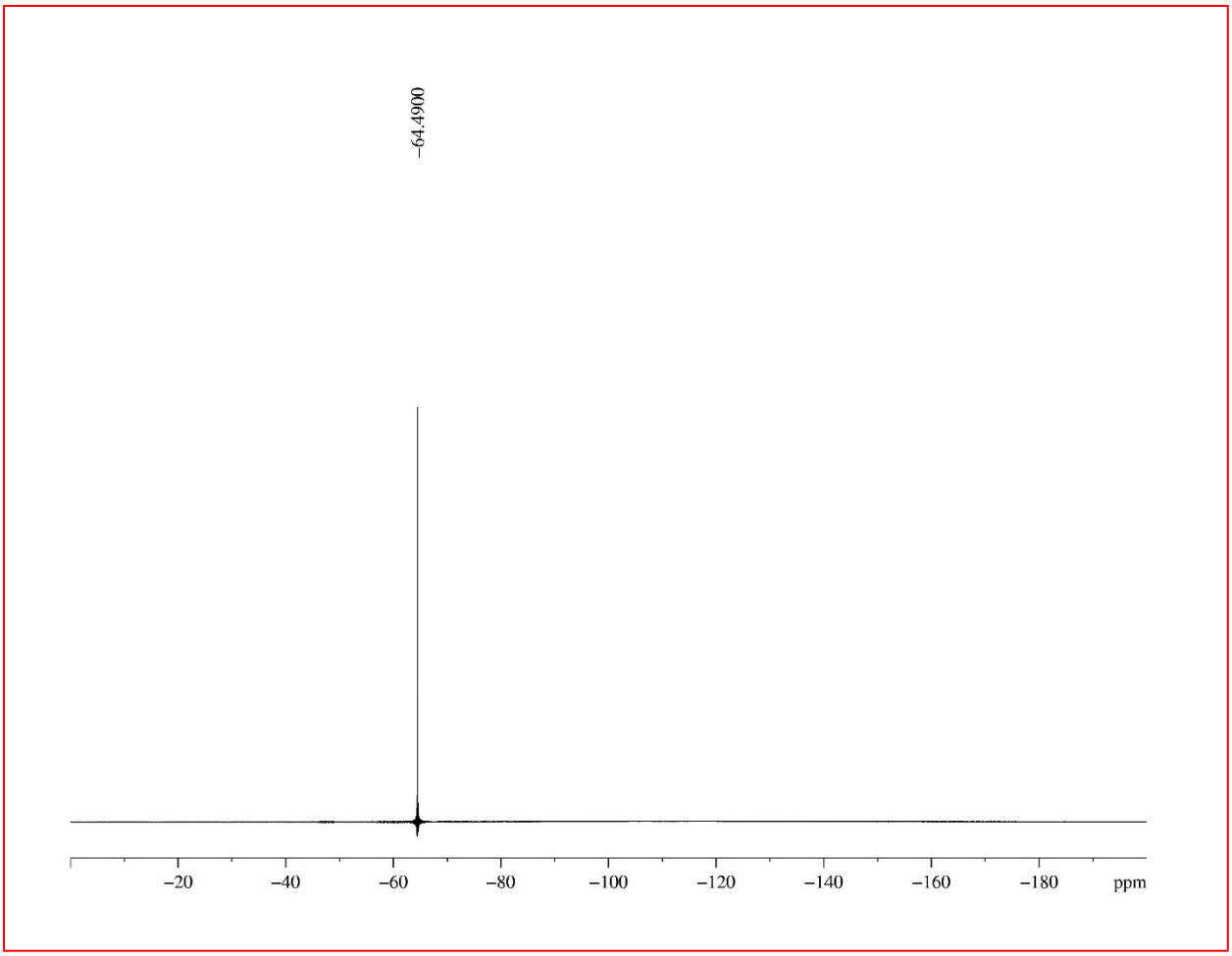


^{1}H and ^{13}C NMR spectra of 1b$_0$



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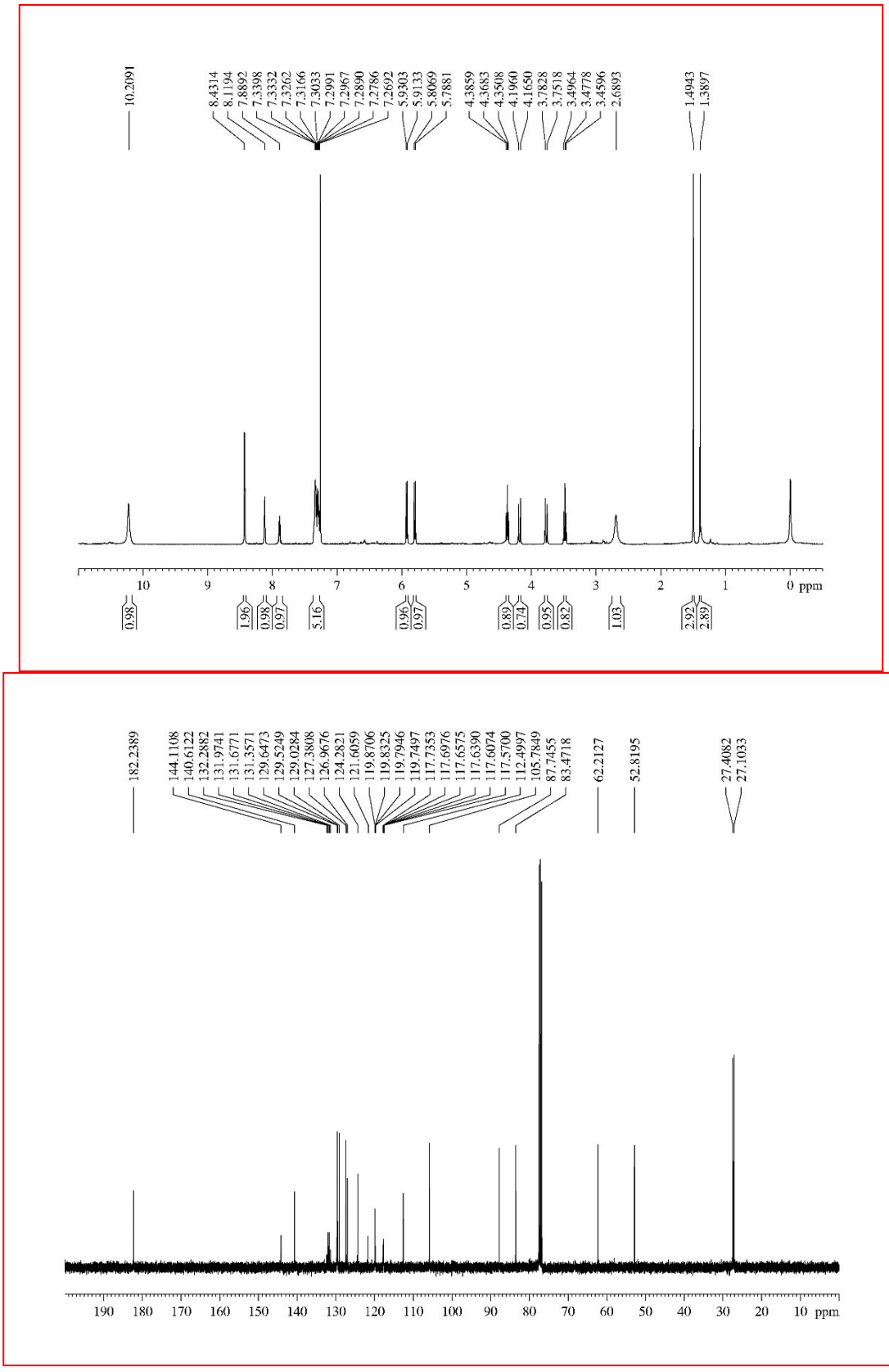

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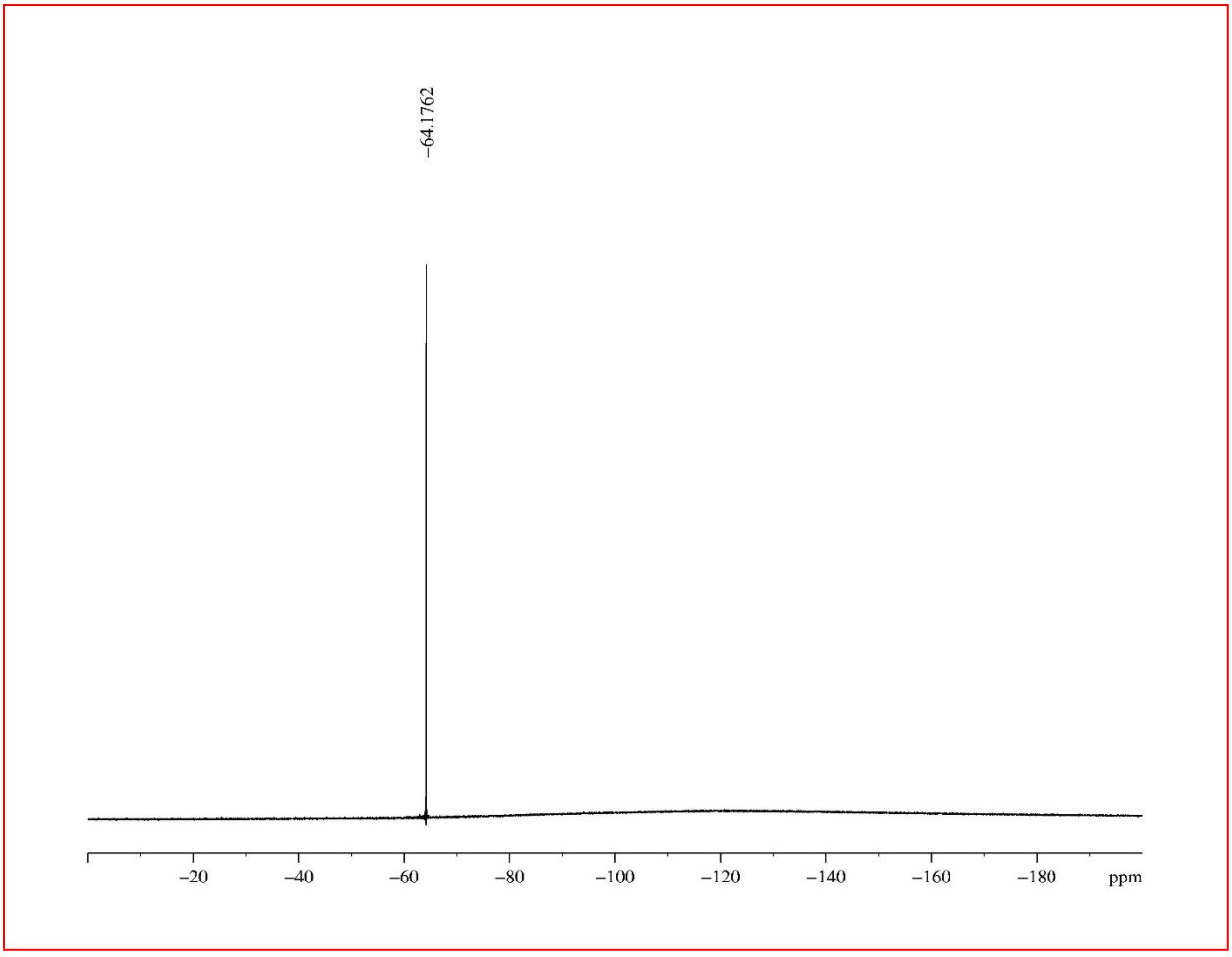

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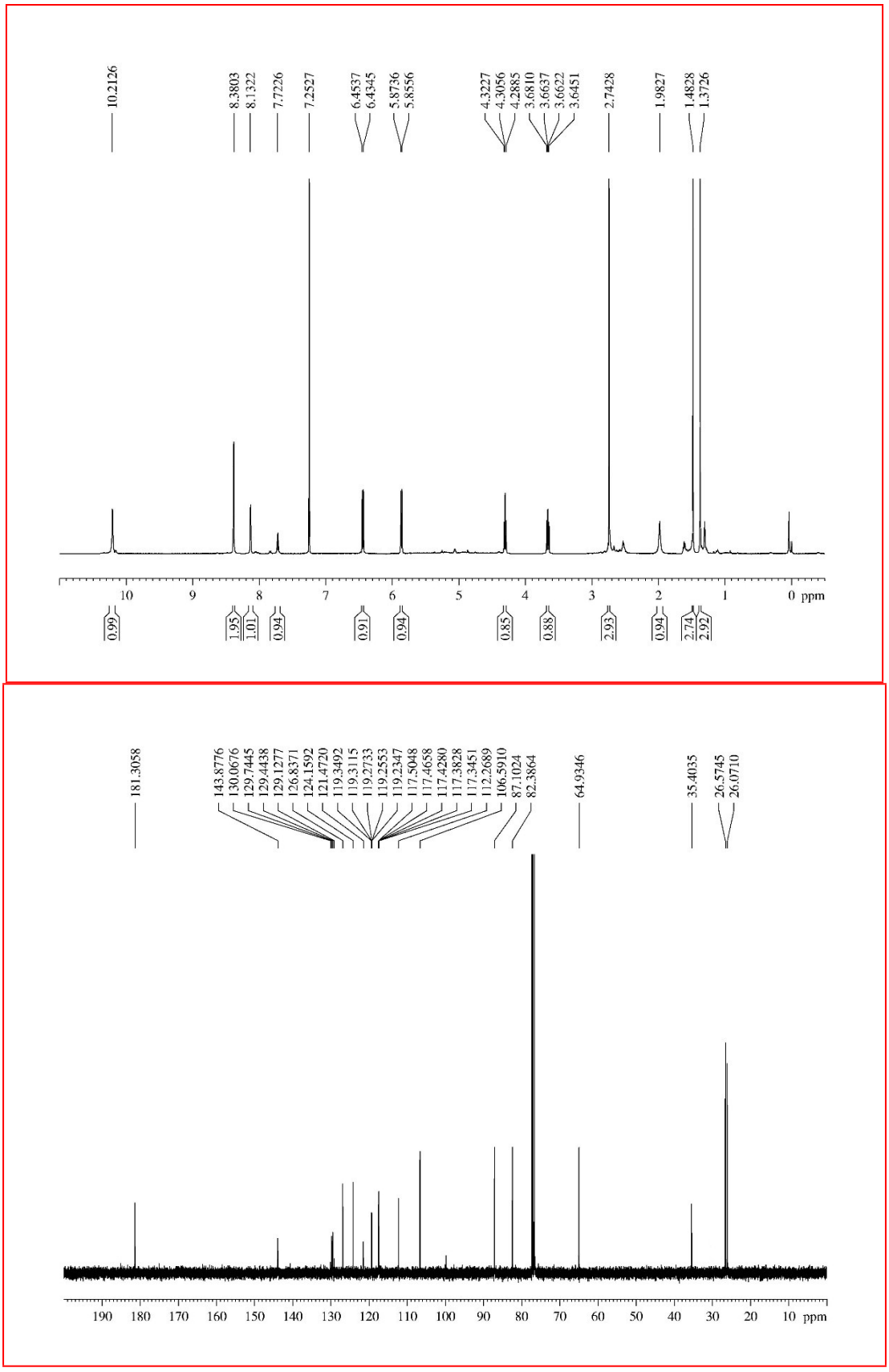
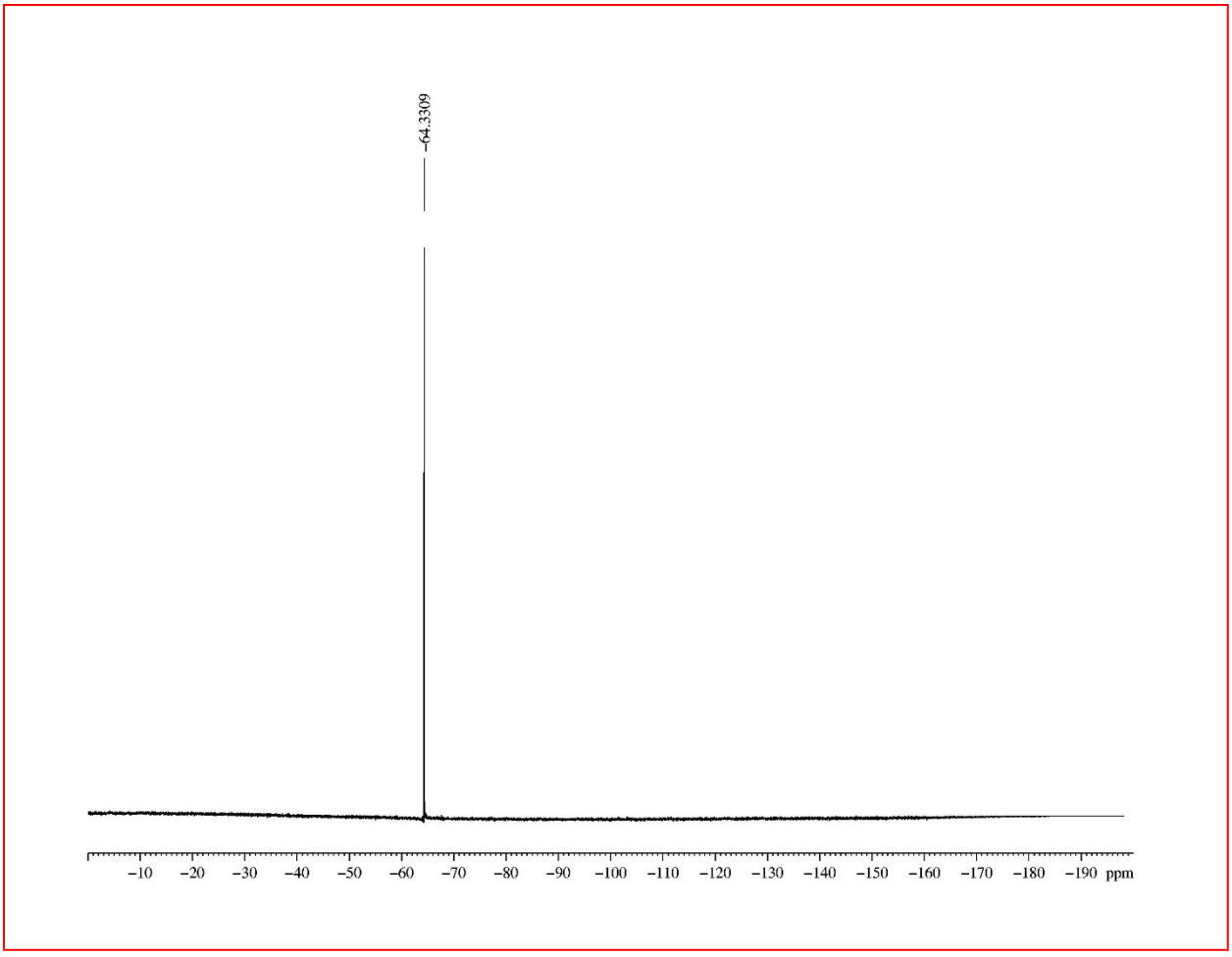
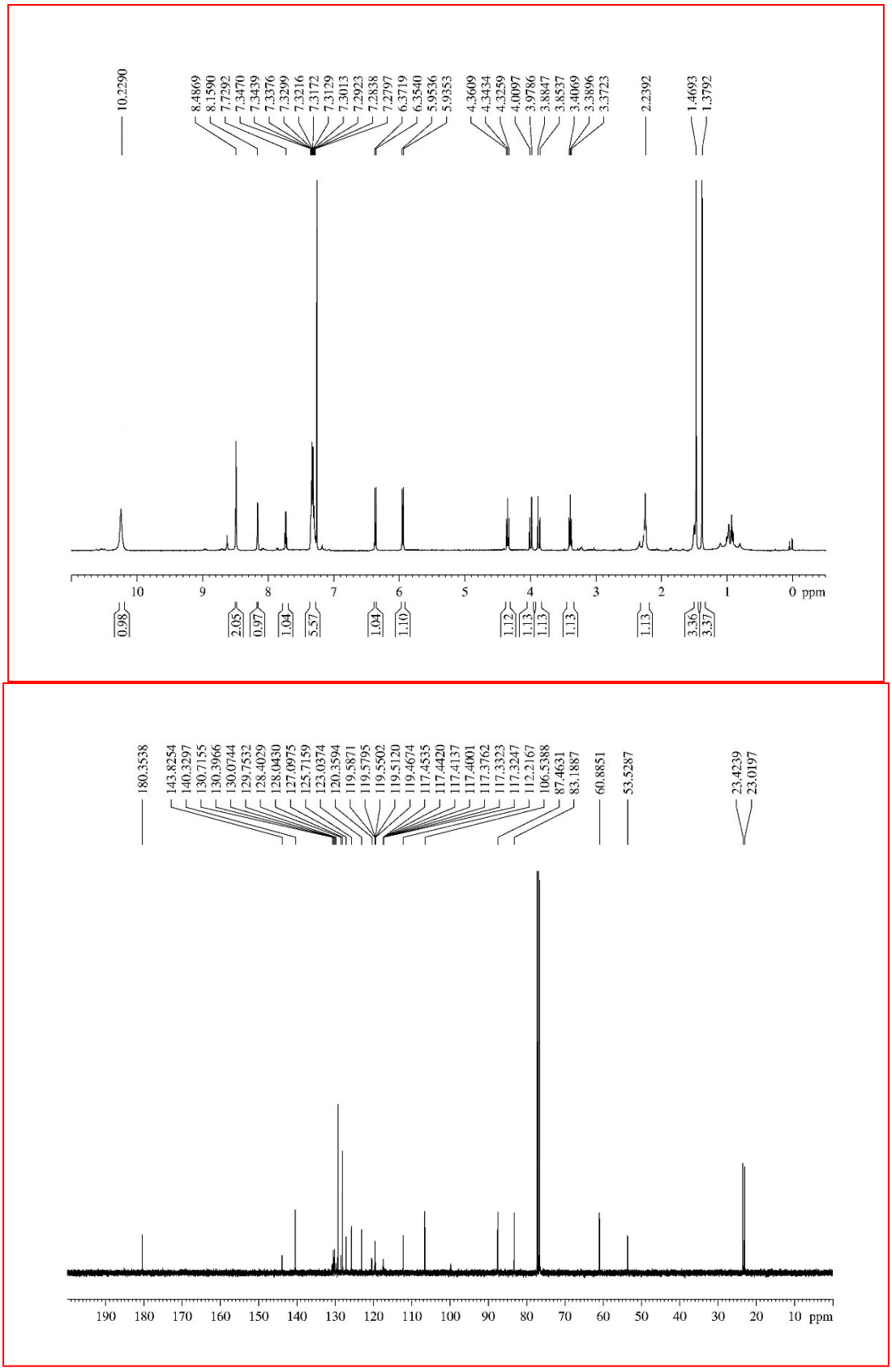


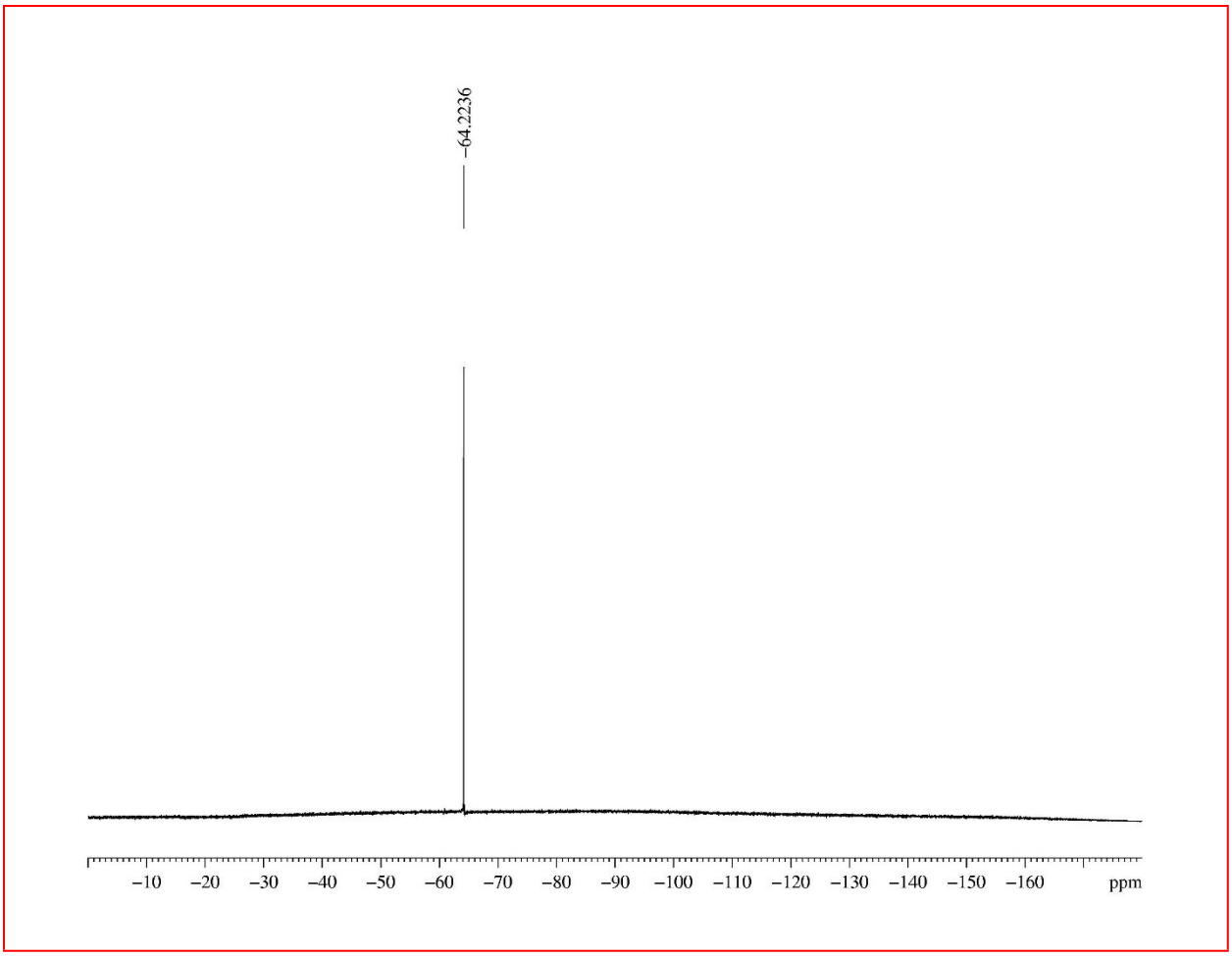
^{1}H and ^{13}C NMR spectra of 2b$_0$



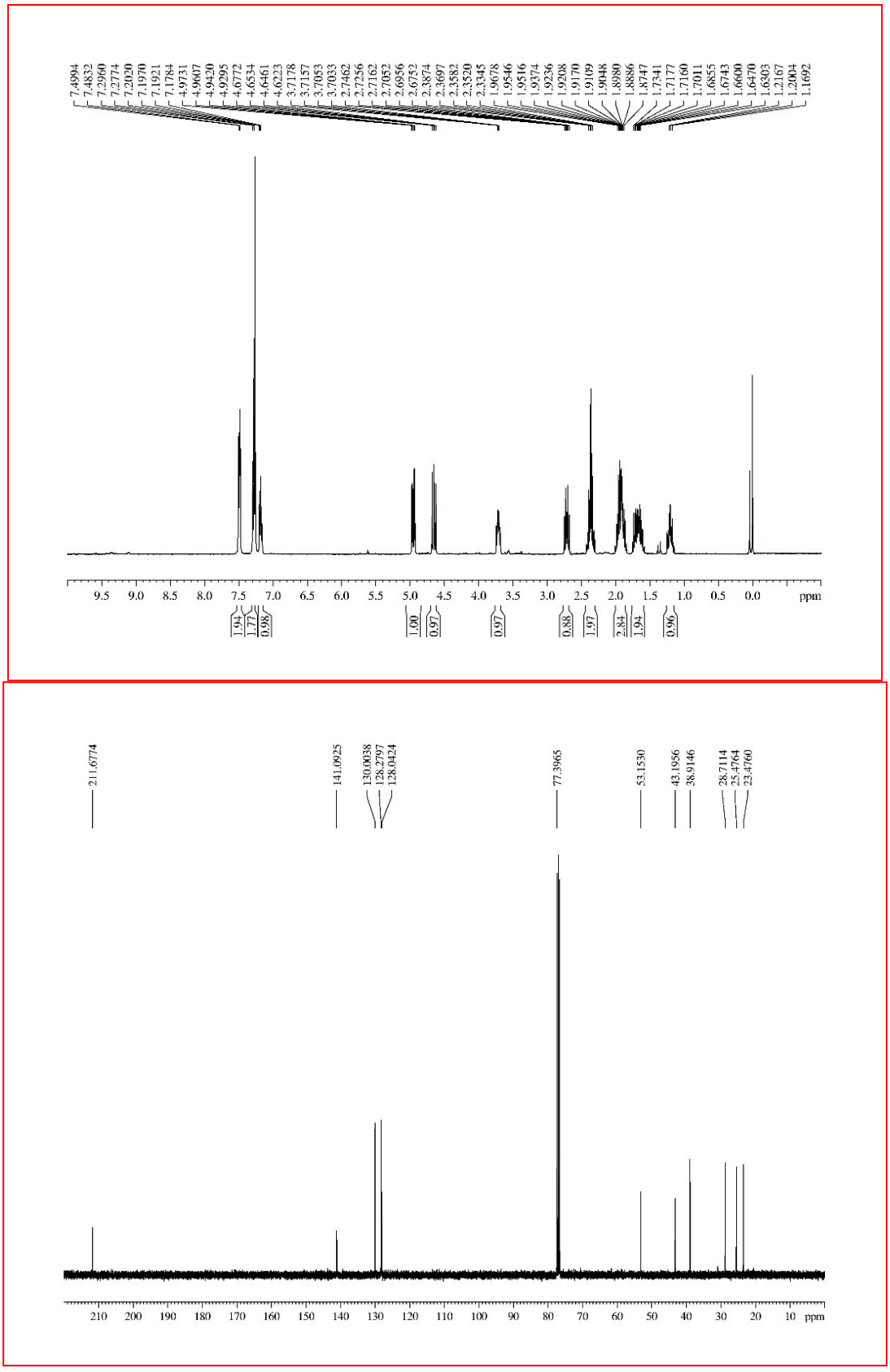
^{19}F NMR spectra of 2b$_0$



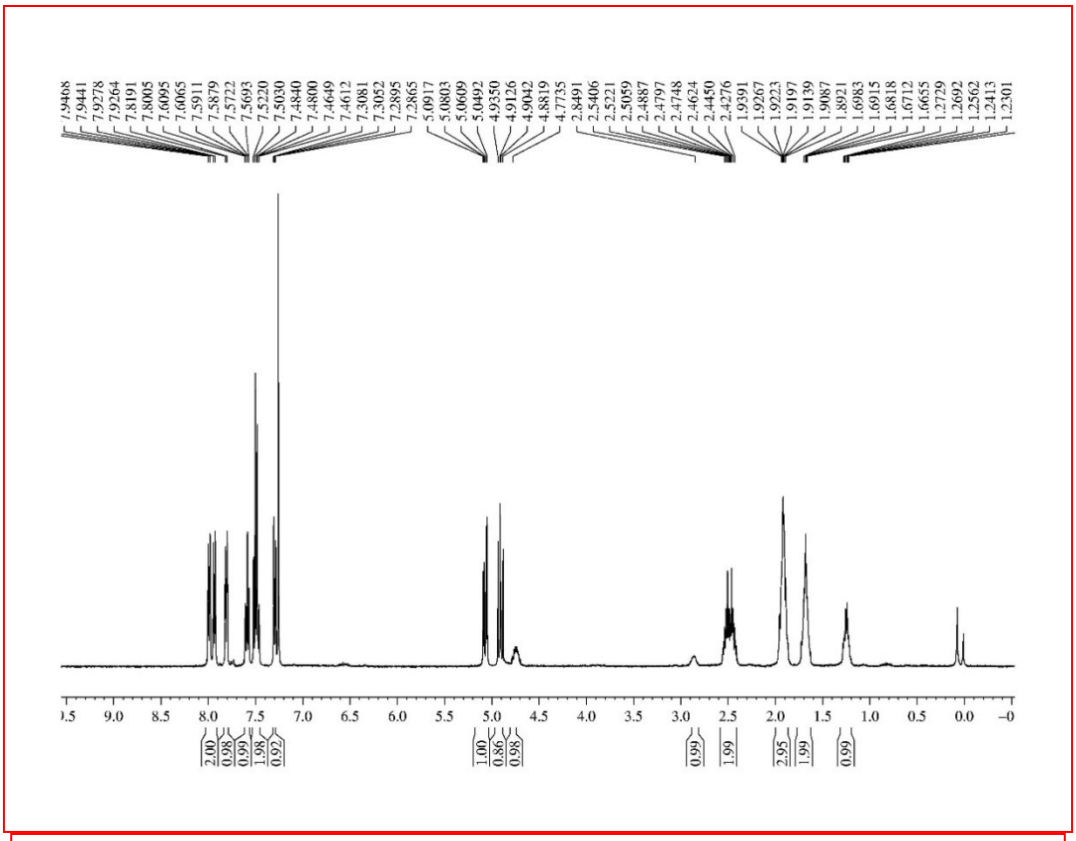
^{1}H and ^{13}C NMR spectra of 2d$_0$

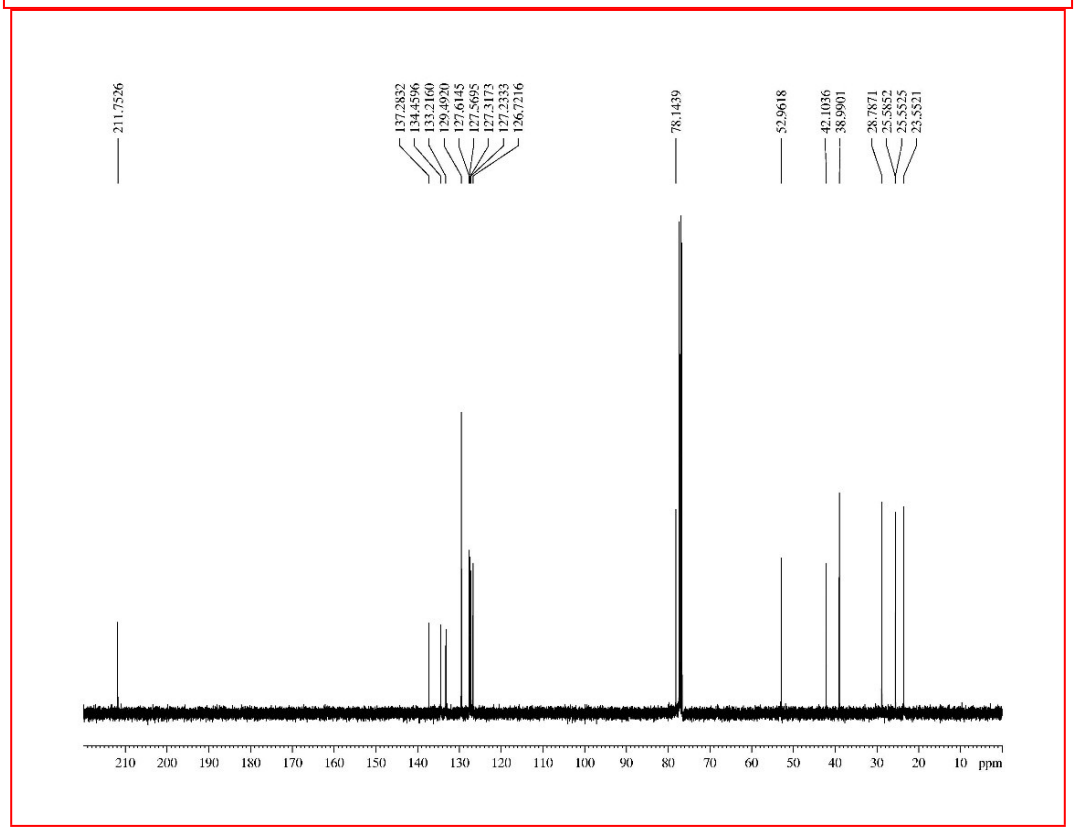


^{19}F NMR spectra of 2d$_0$

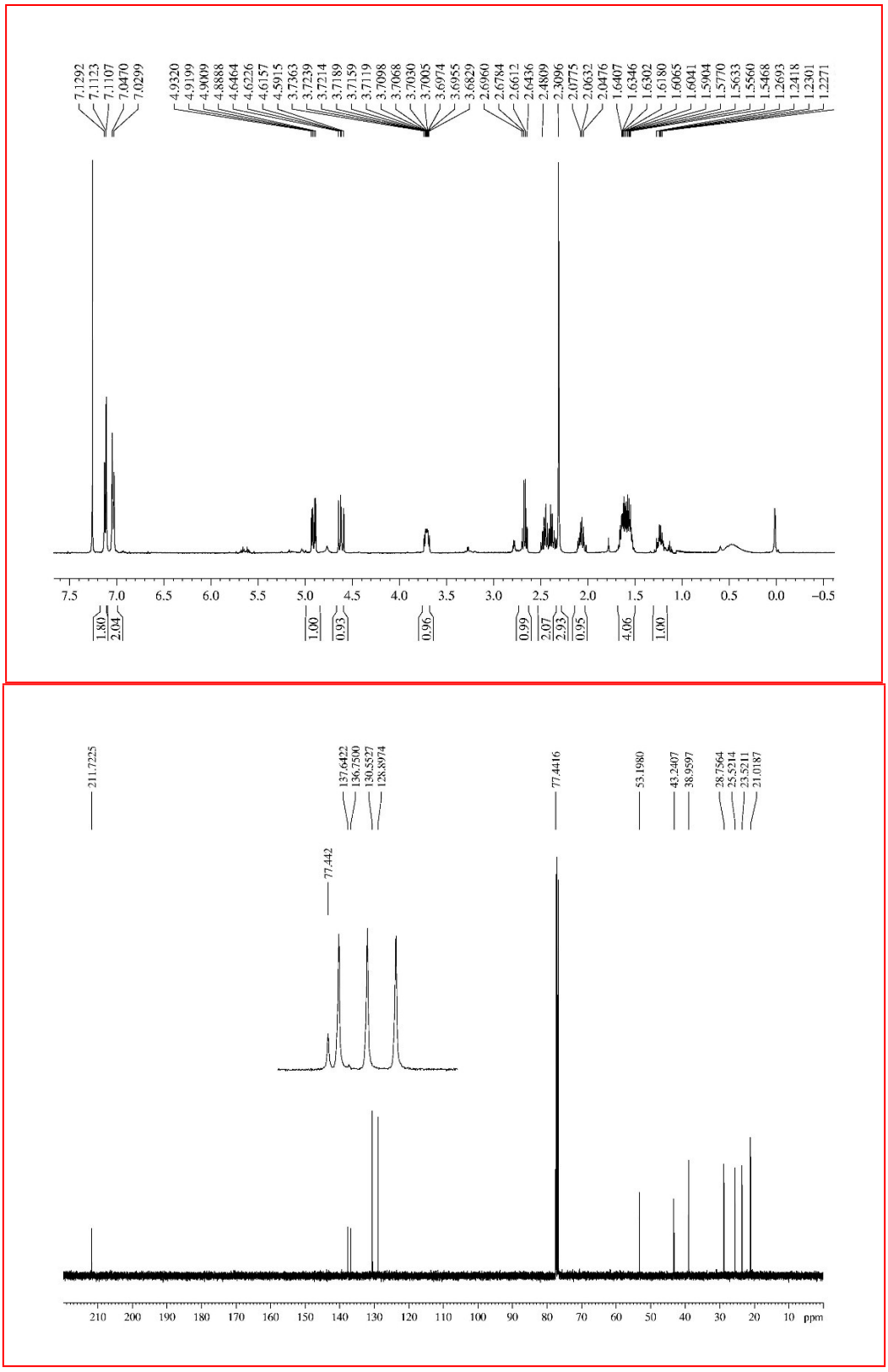


^{1}H and ^{13}C NMR spectra of 5a

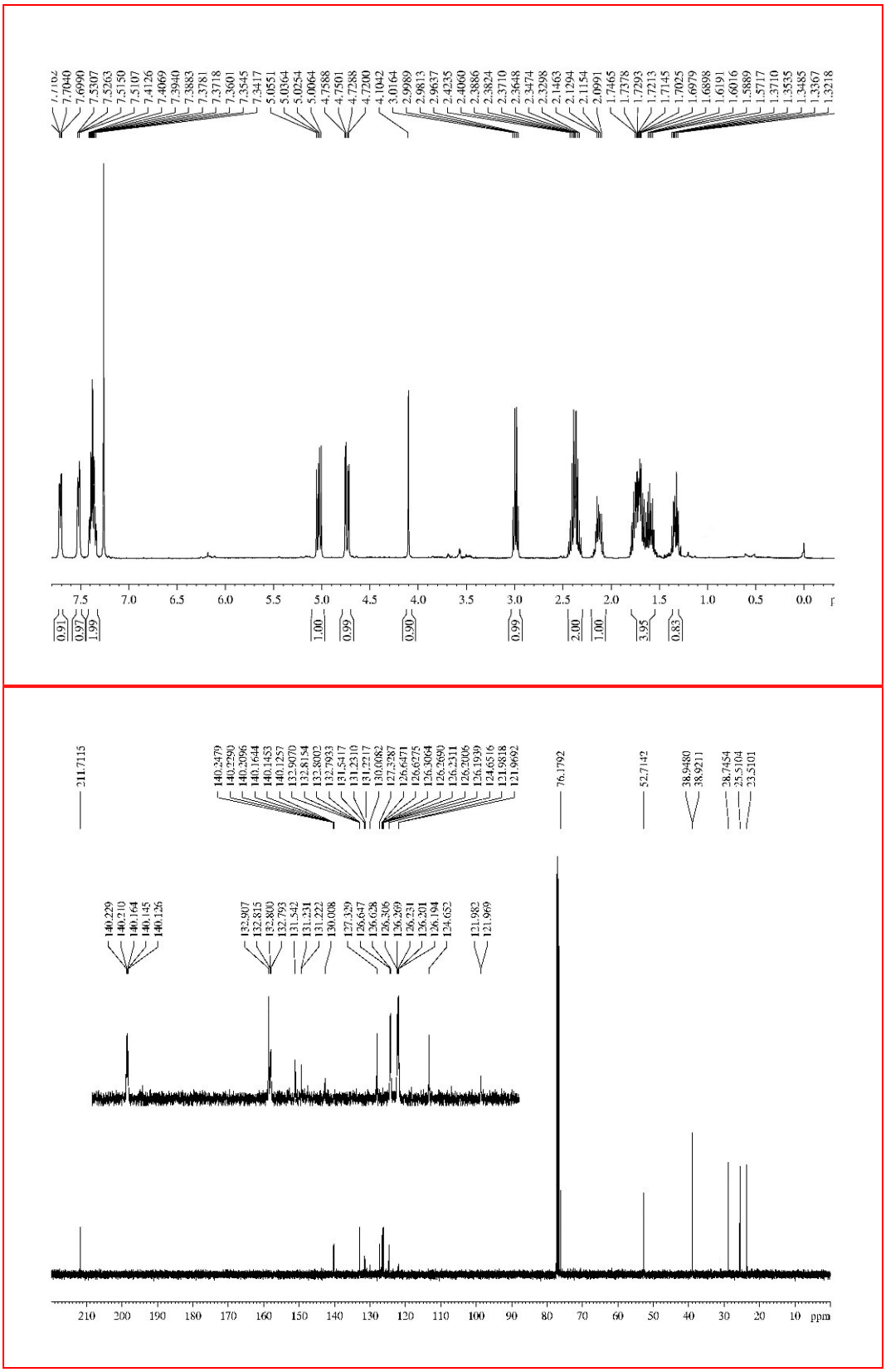




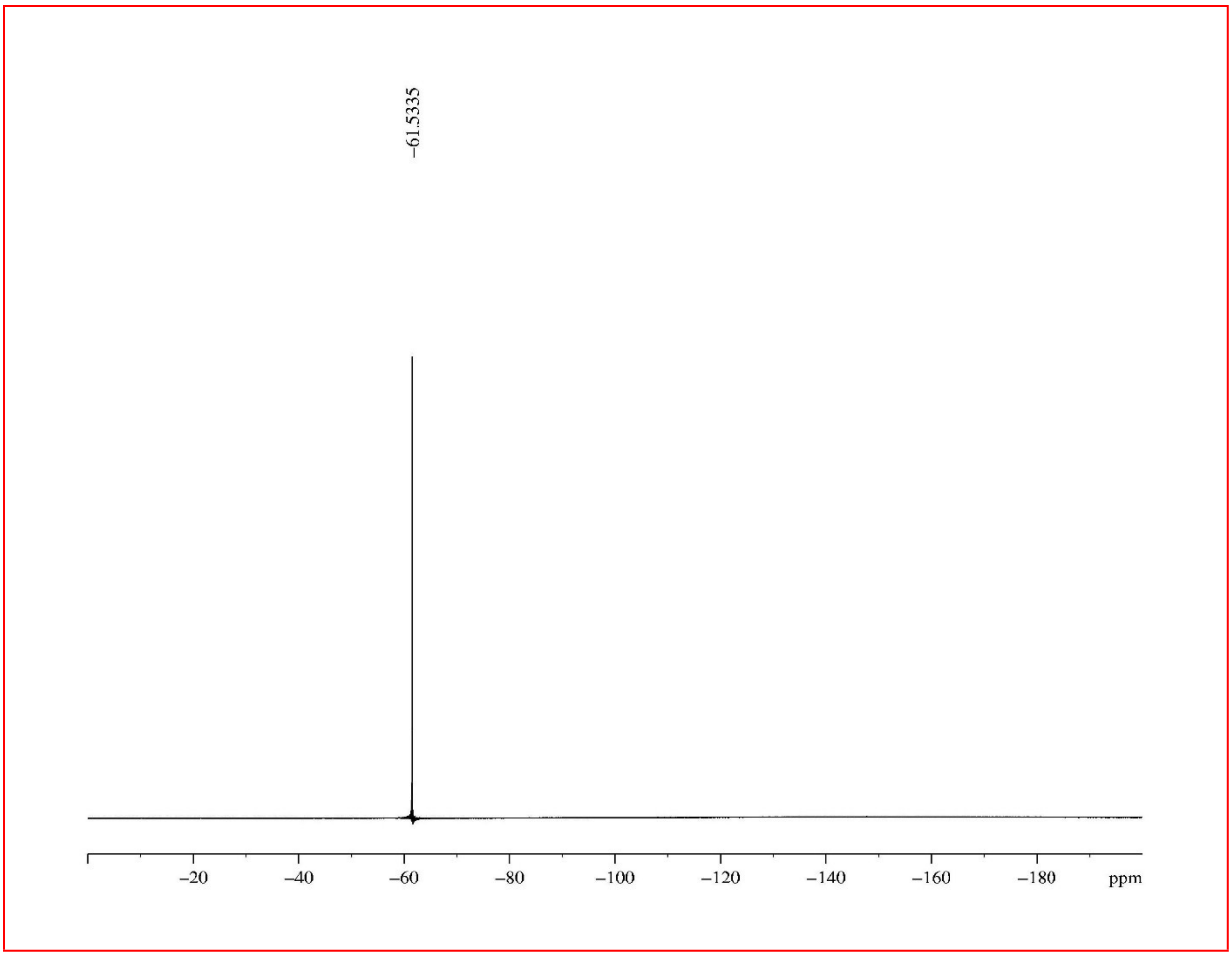
^{1}H and ^{13}C NMR spectra of 5b



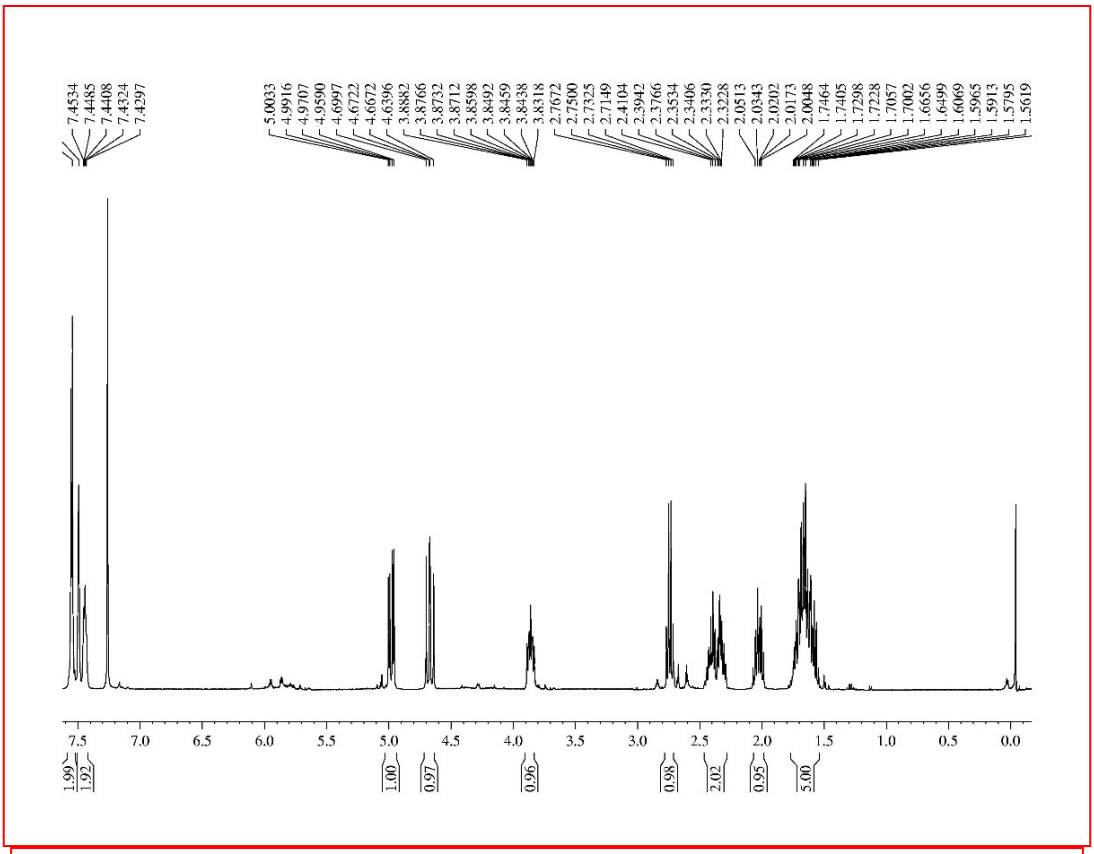
^{1}H and ^{13}C NMR spectra of 5c

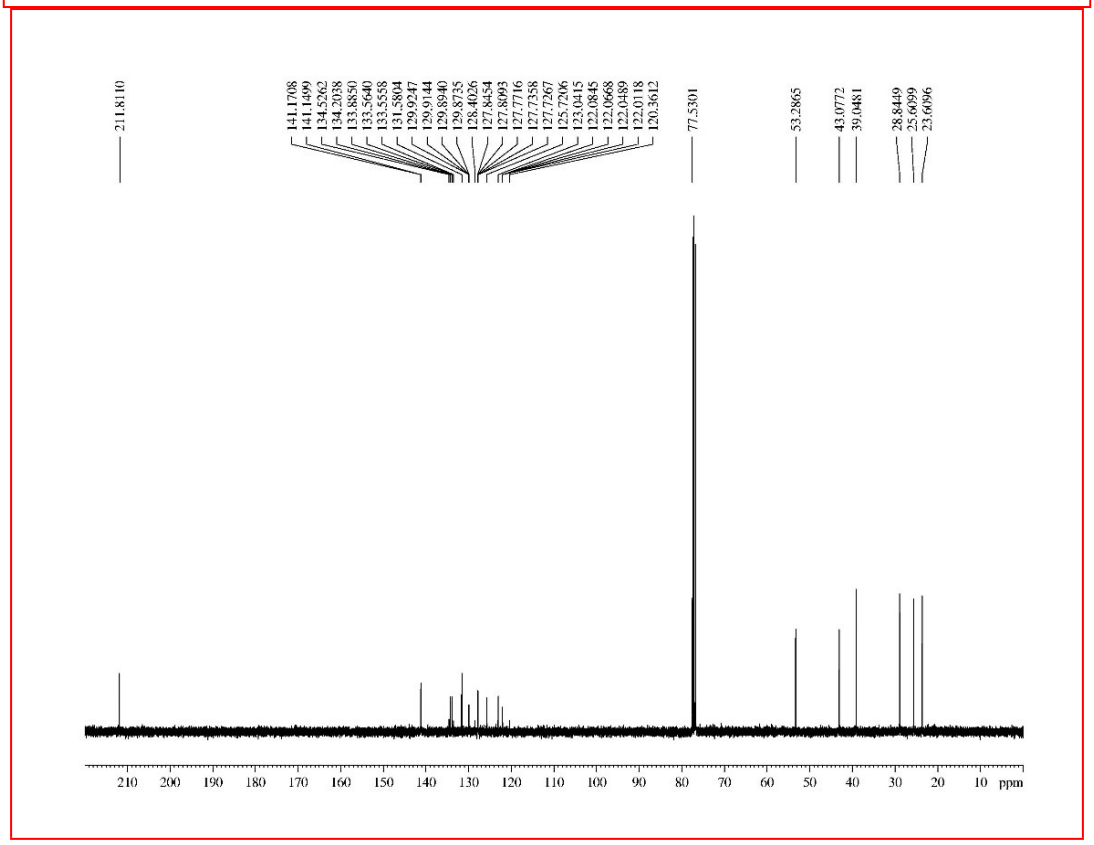


^{1}H and ^{13}C NMR spectra of 5d

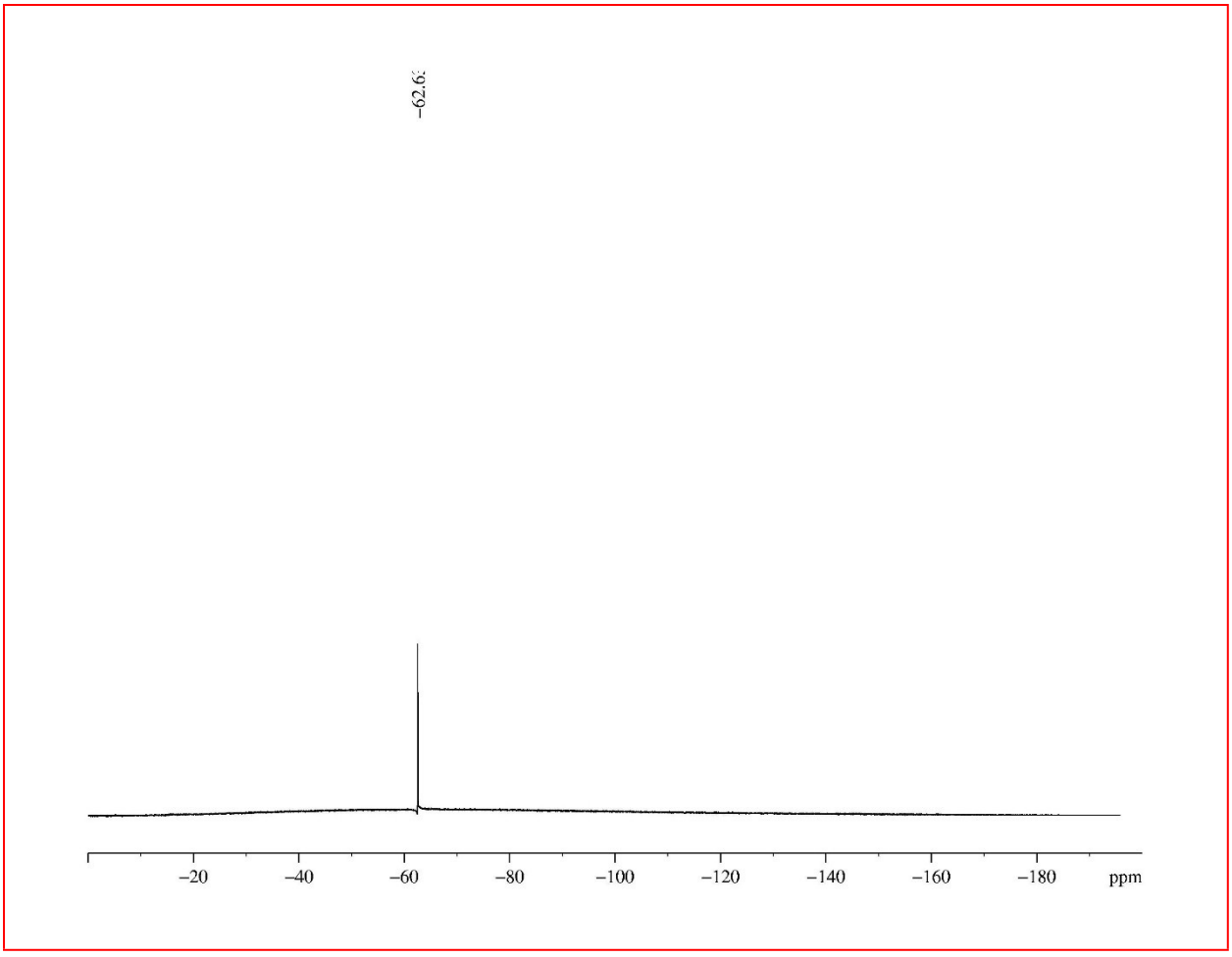


^{19}F NMR spectra of 5d

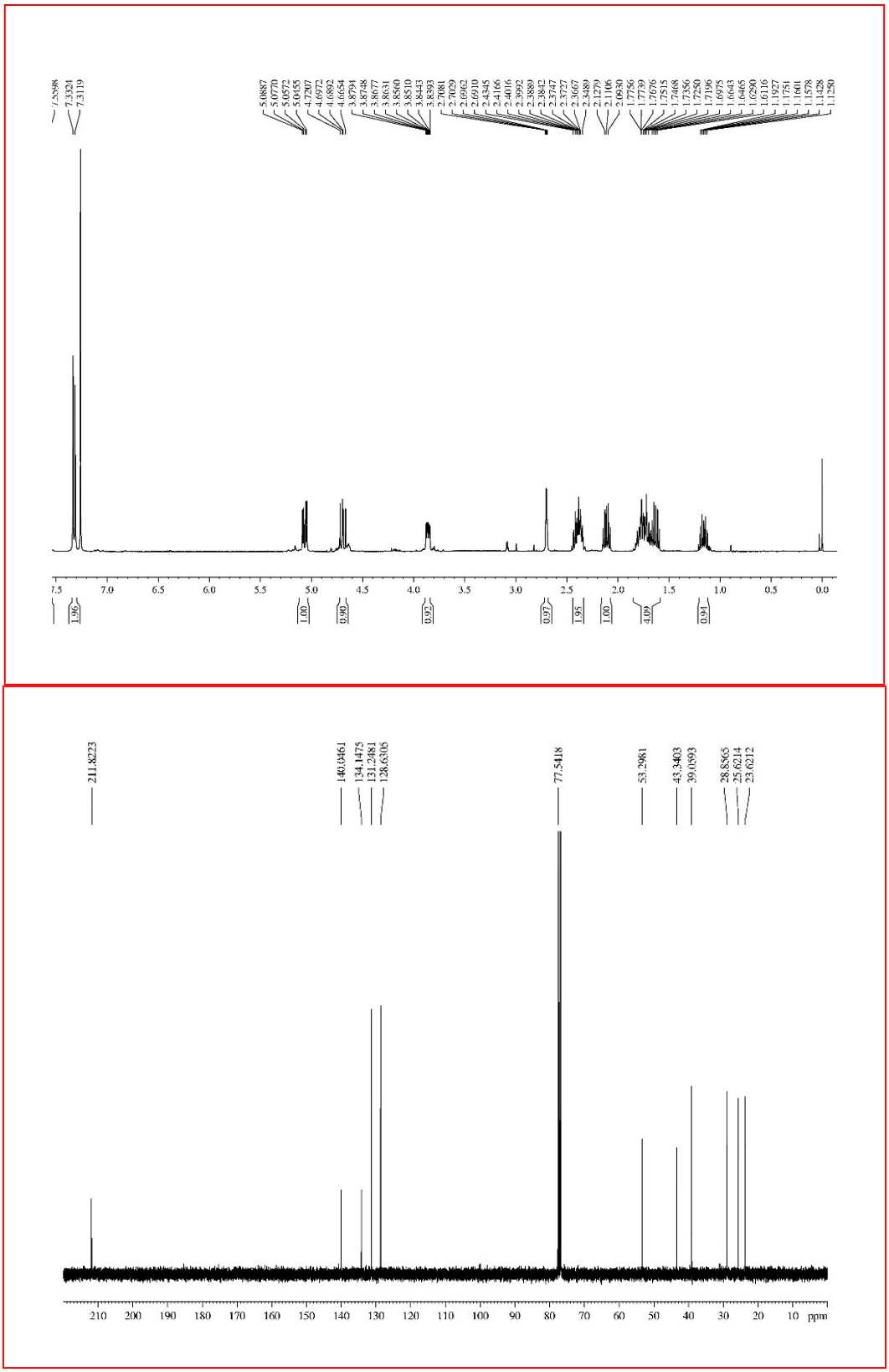




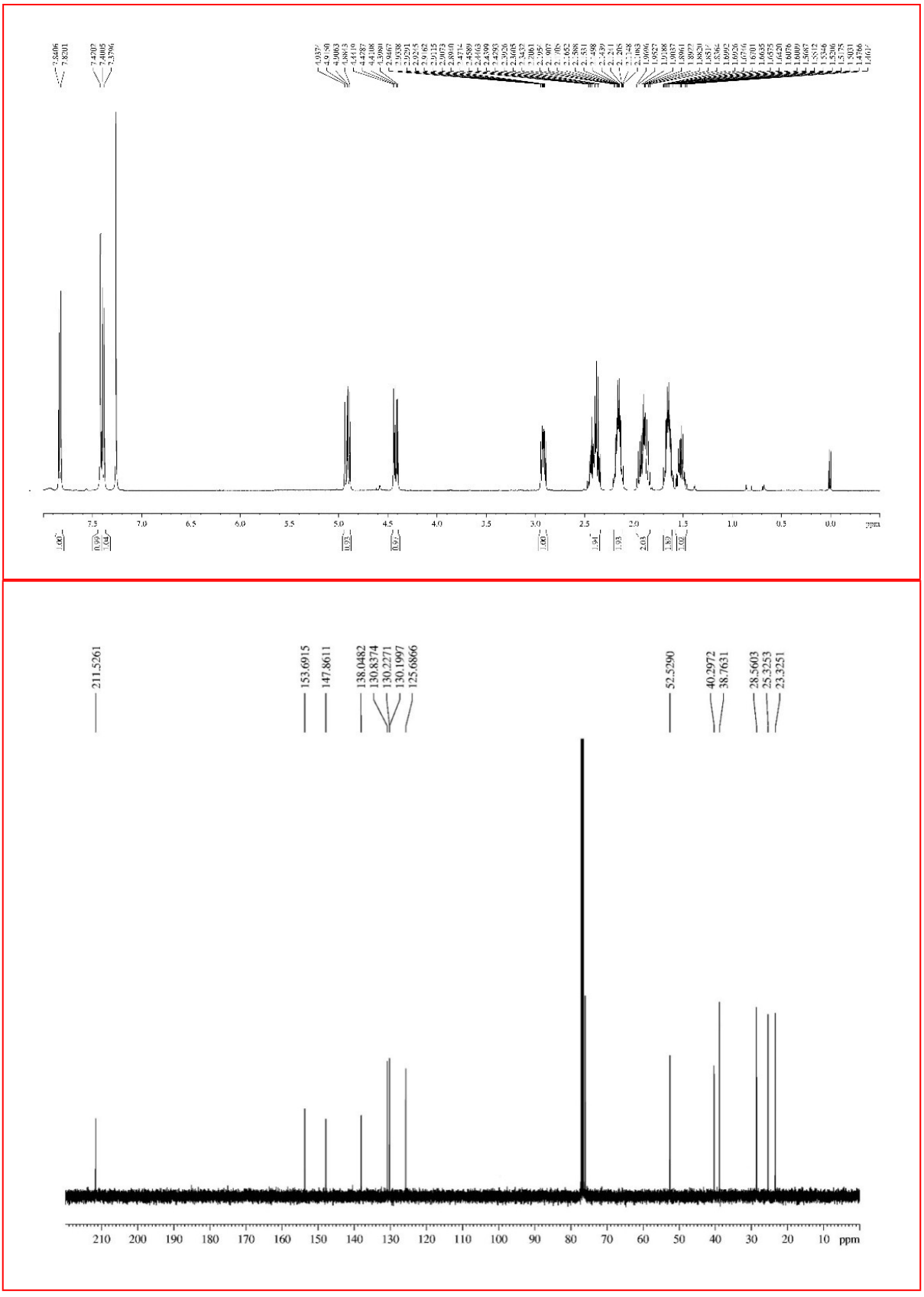
^{1}H and ^{13}C NMR spectra of 5e



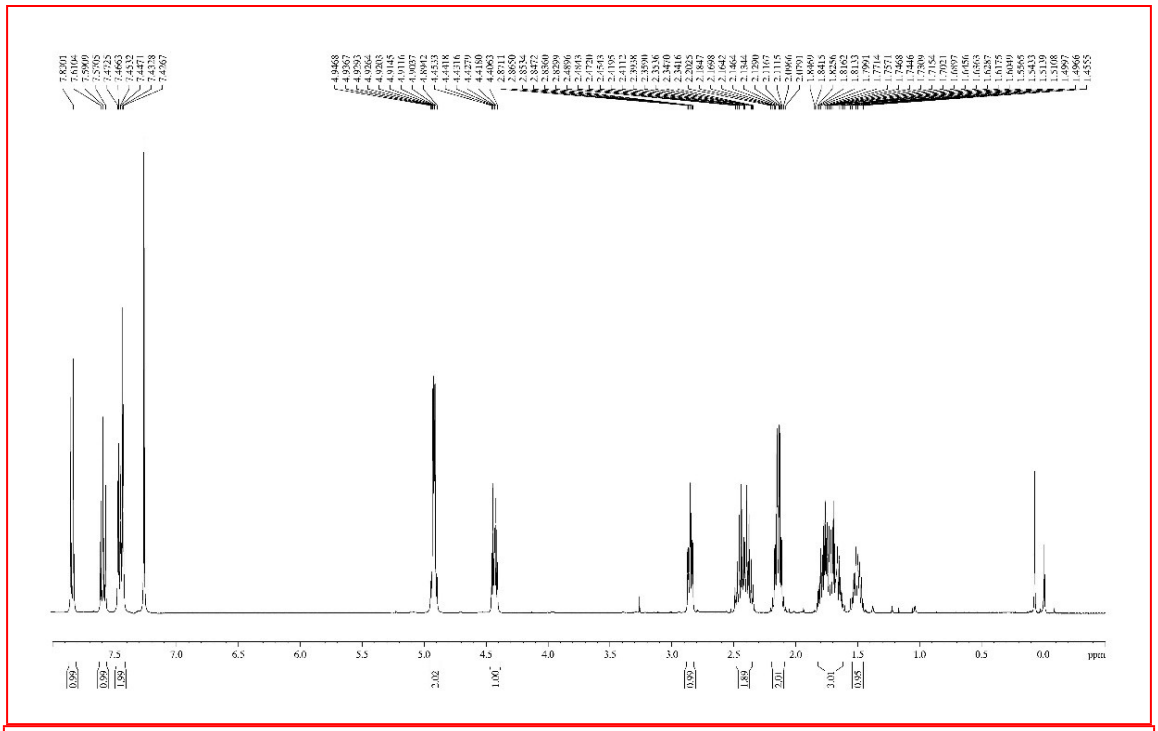
^{19}F NMR spectra of 5e

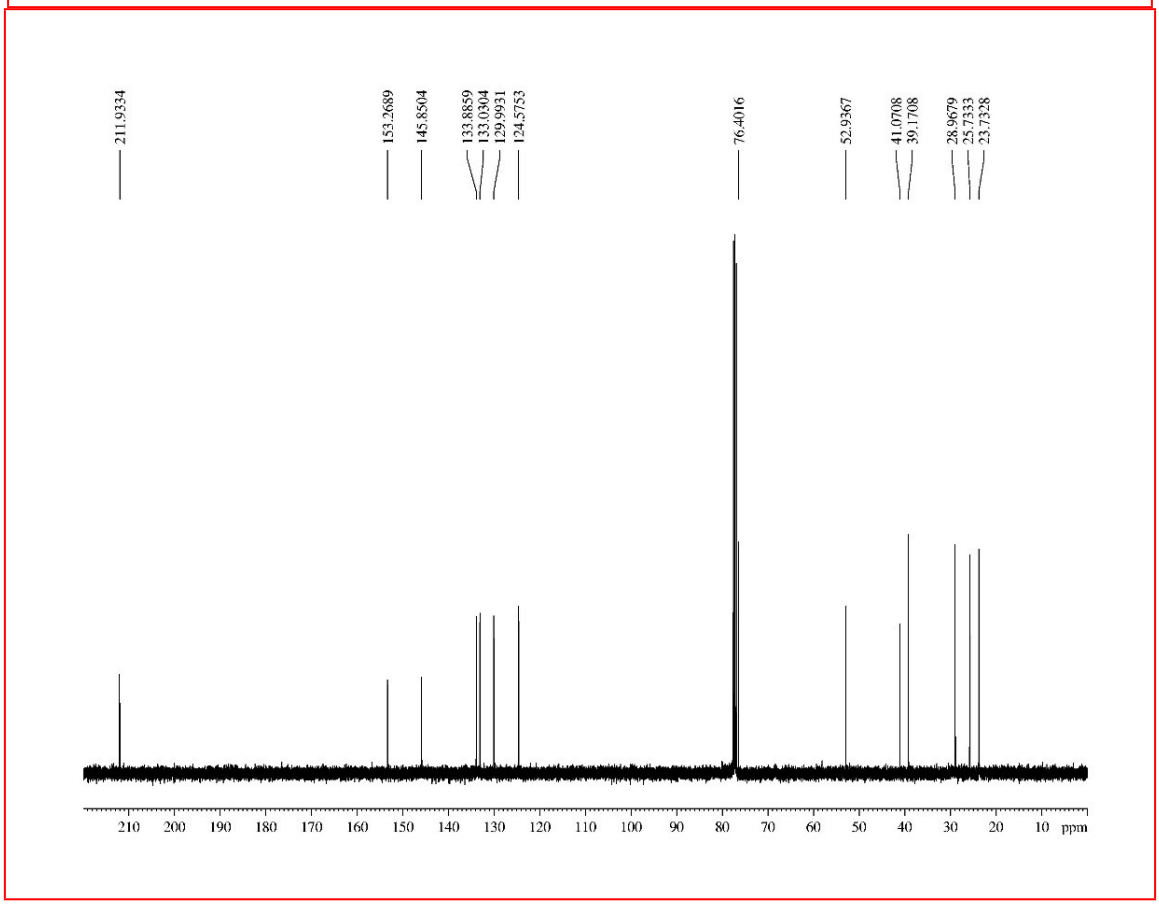


^{1}H and ^{13}C NMR spectra of 5f

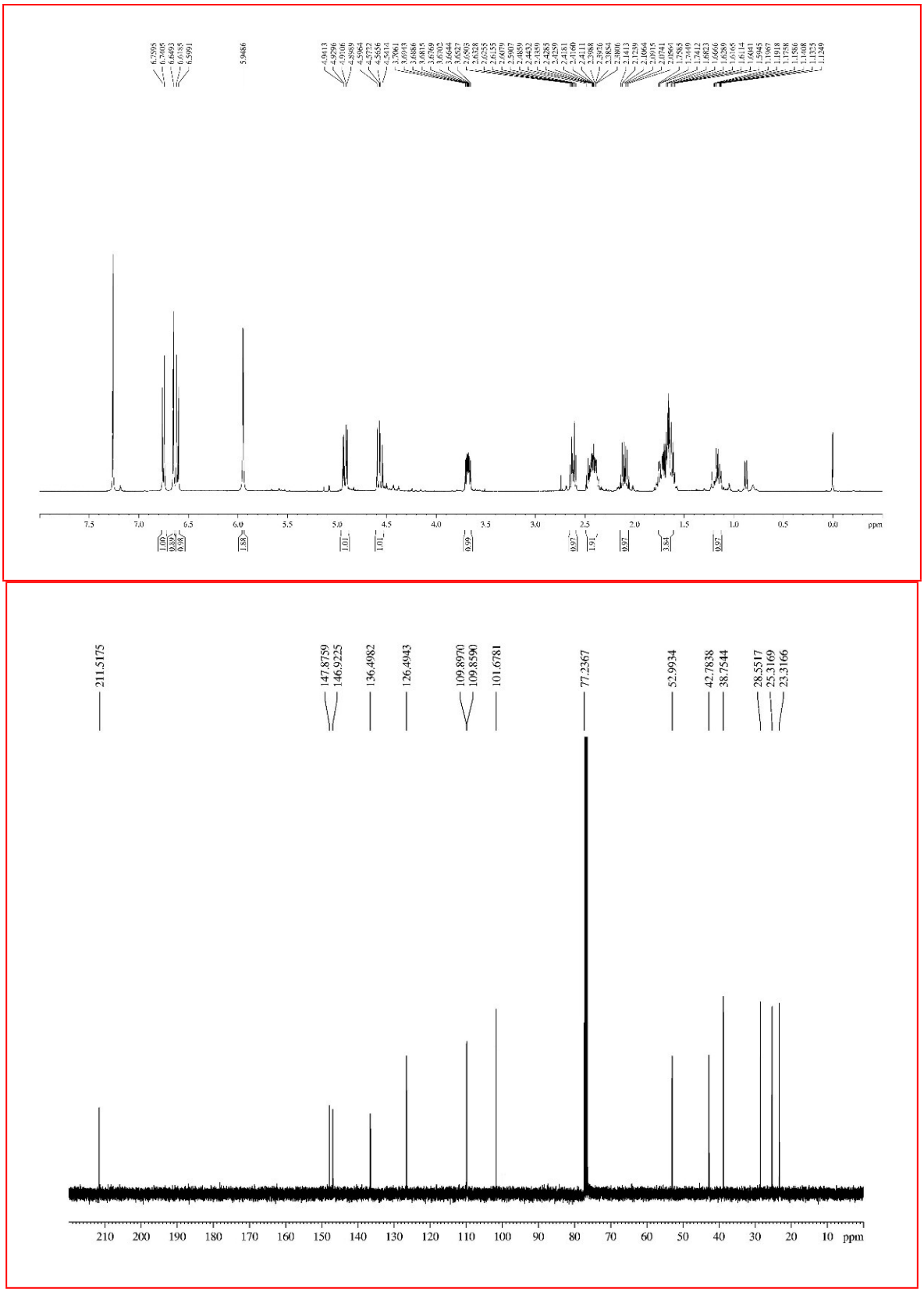


^{1}H and ^{13}C NMR spectra of 5g

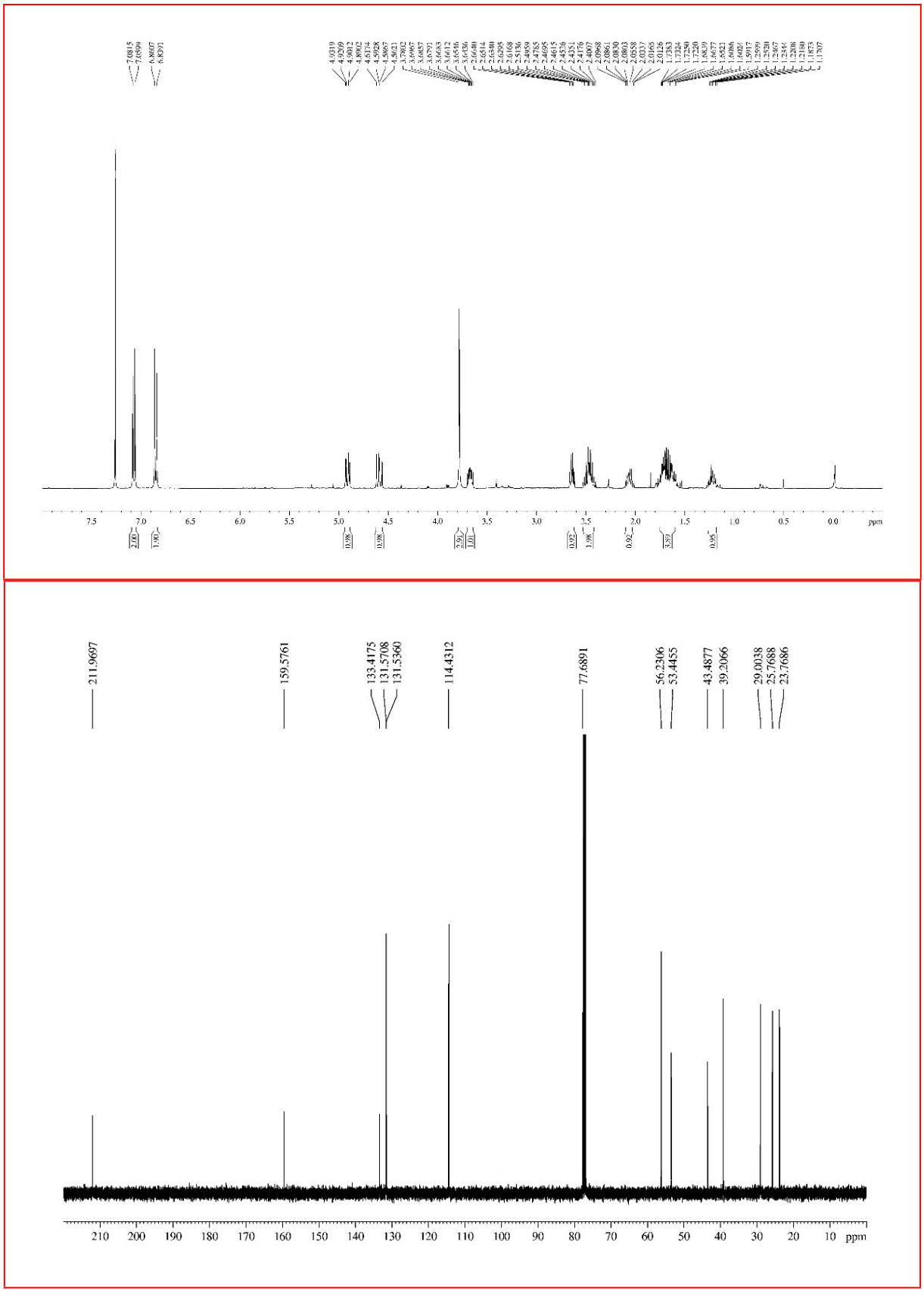




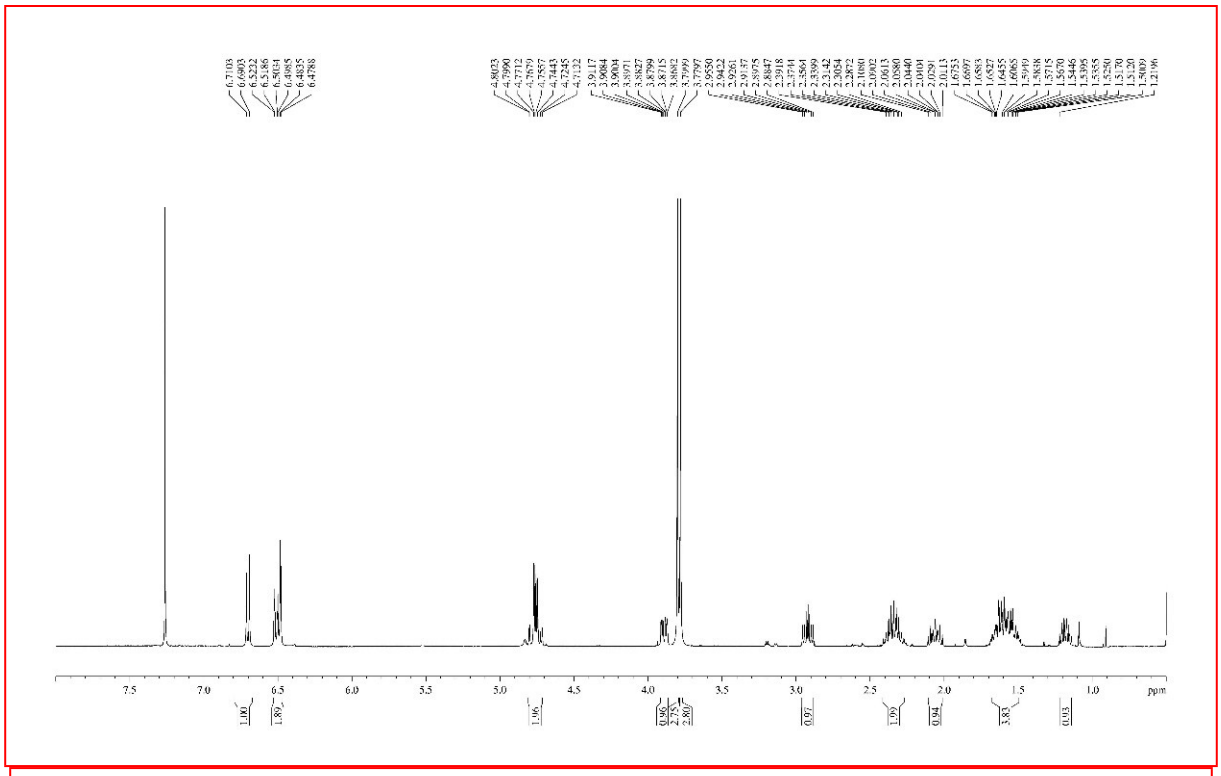
^{1}H and ^{13}C NMR spectra of 5h

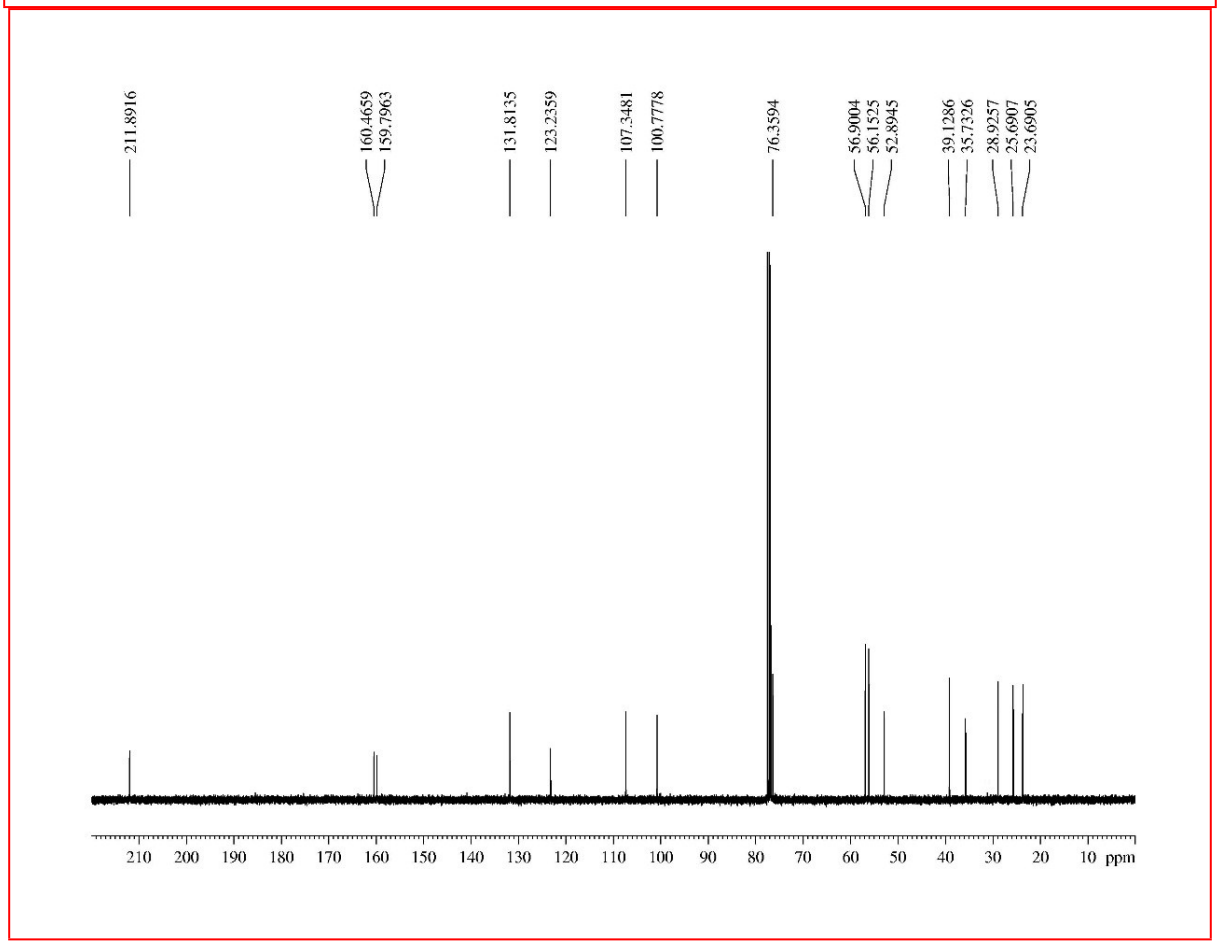


^{1}H and ^{13}C NMR spectra of 5i

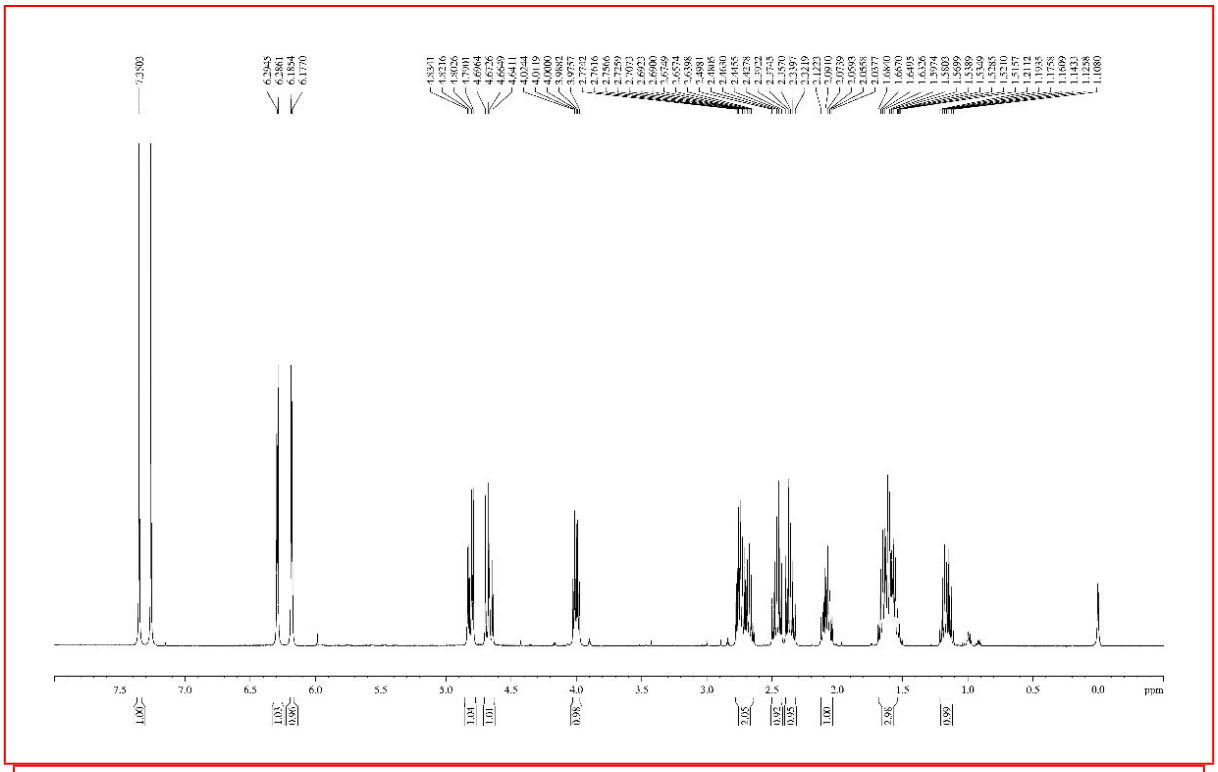


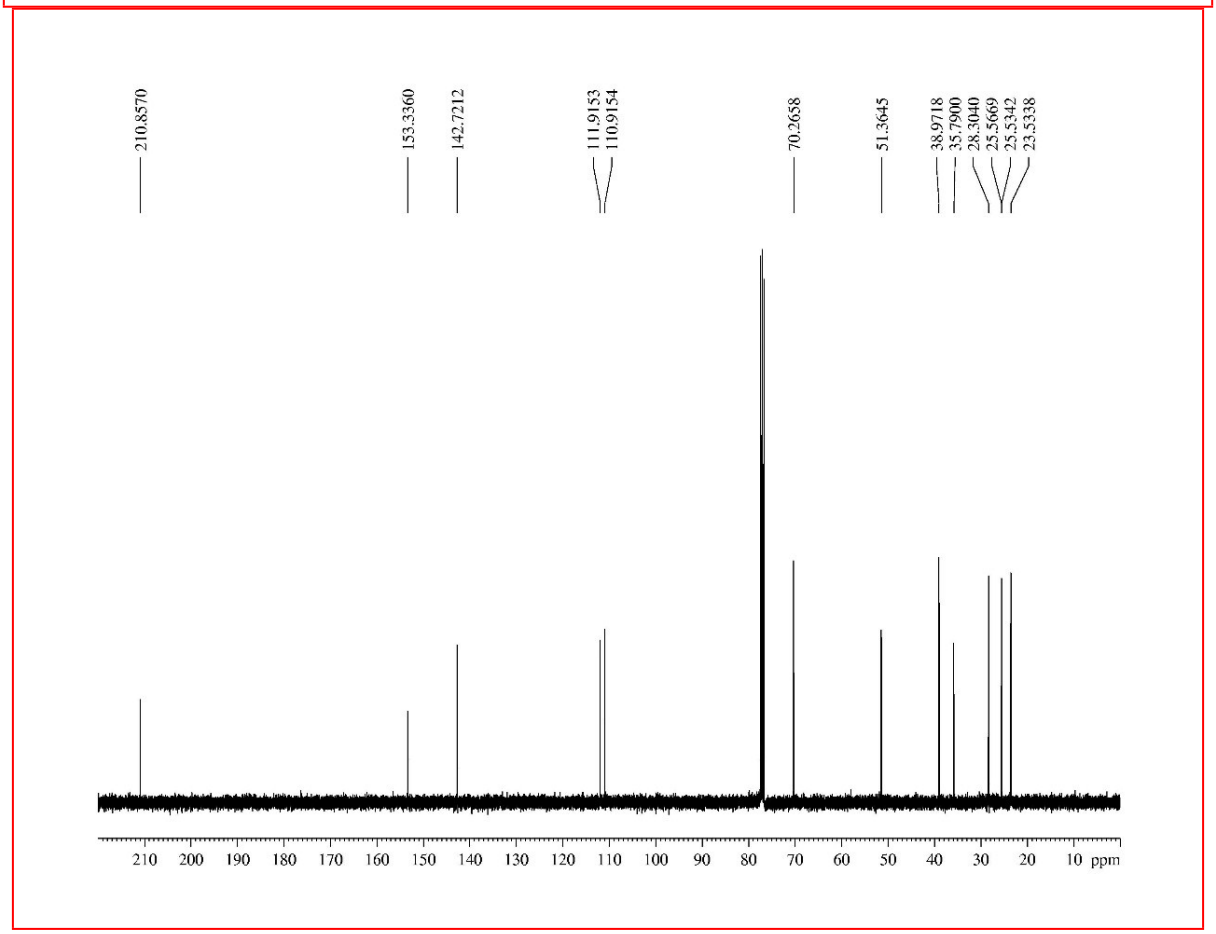
^{1}H and ^{13}C NMR spectra of 5j



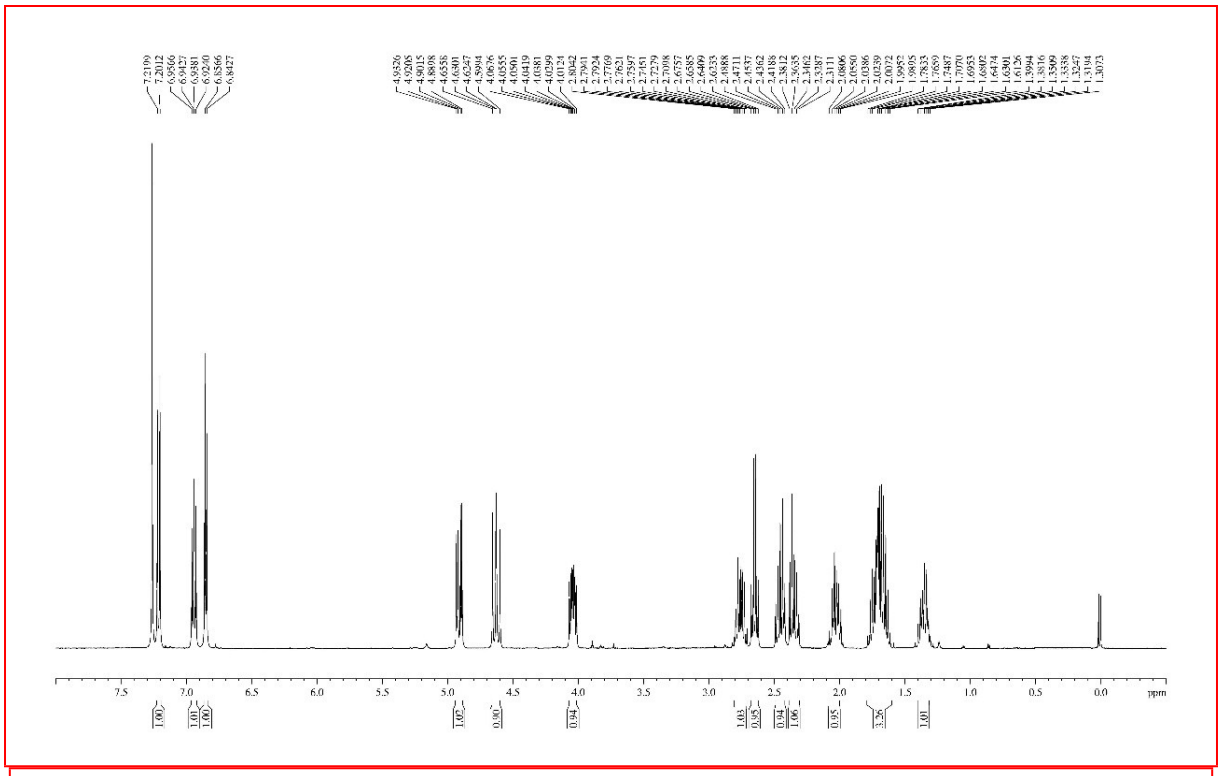


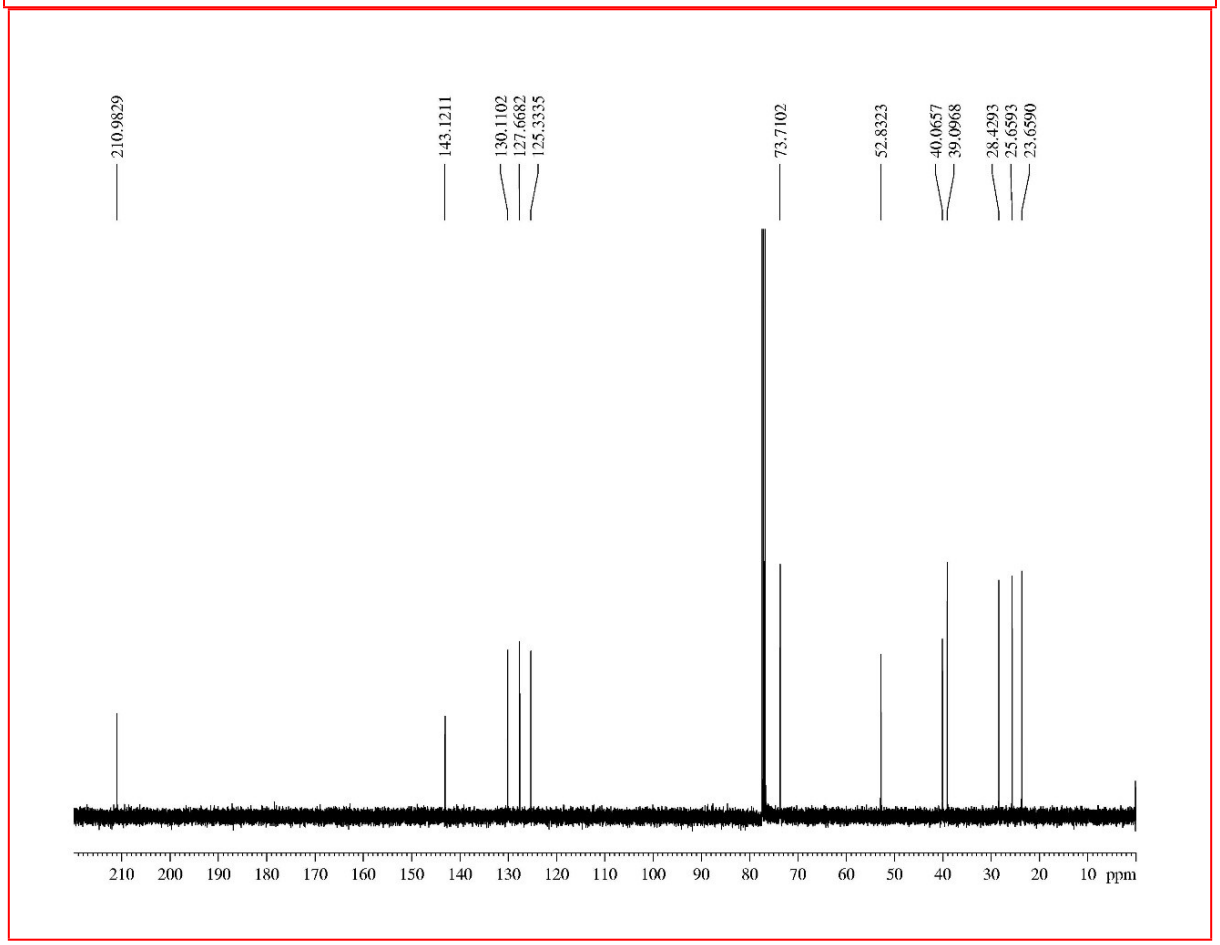
^{1}H and ^{13}C NMR spectra of 5k



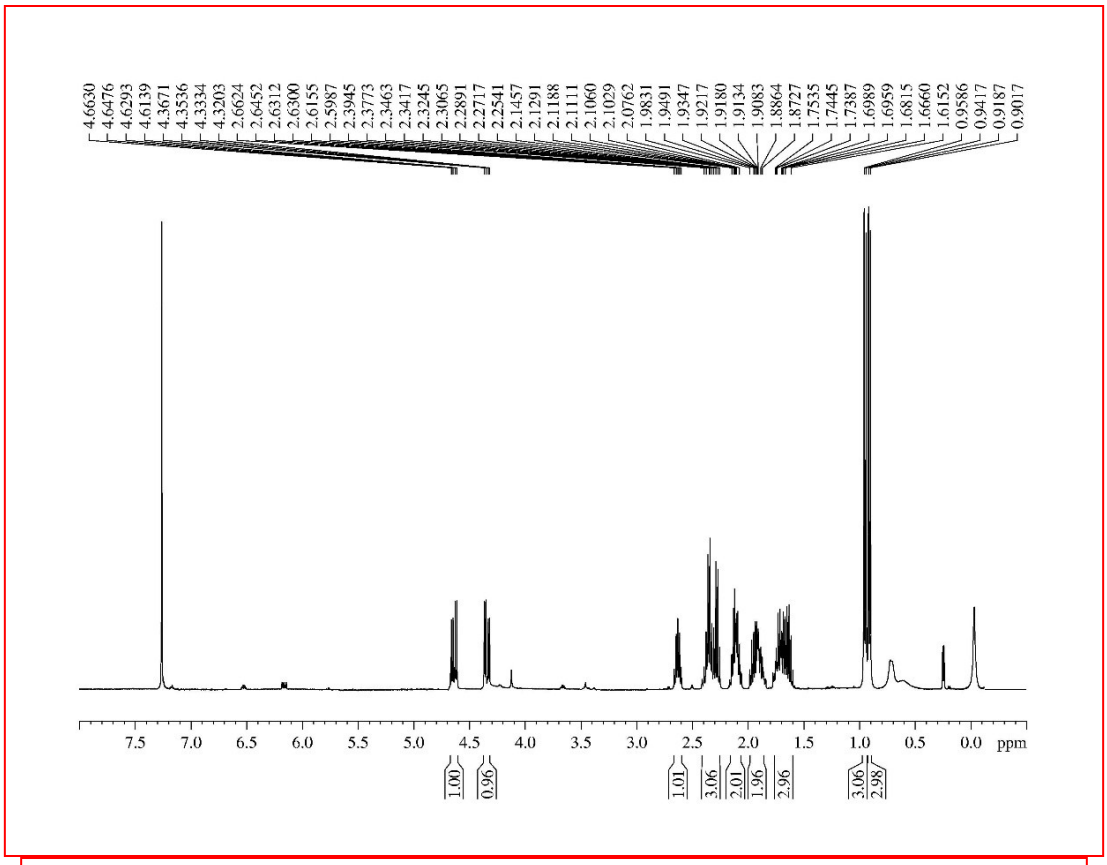


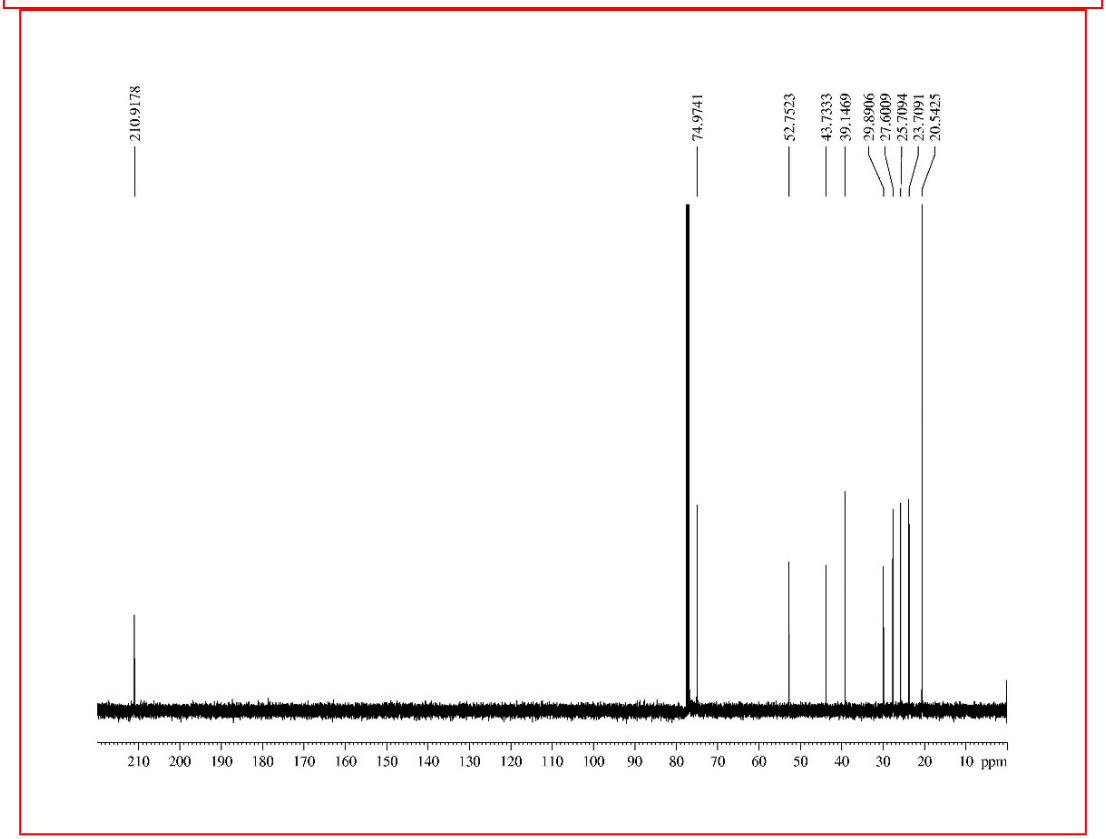
^{1}H and ^{13}C NMR spectra of 5l



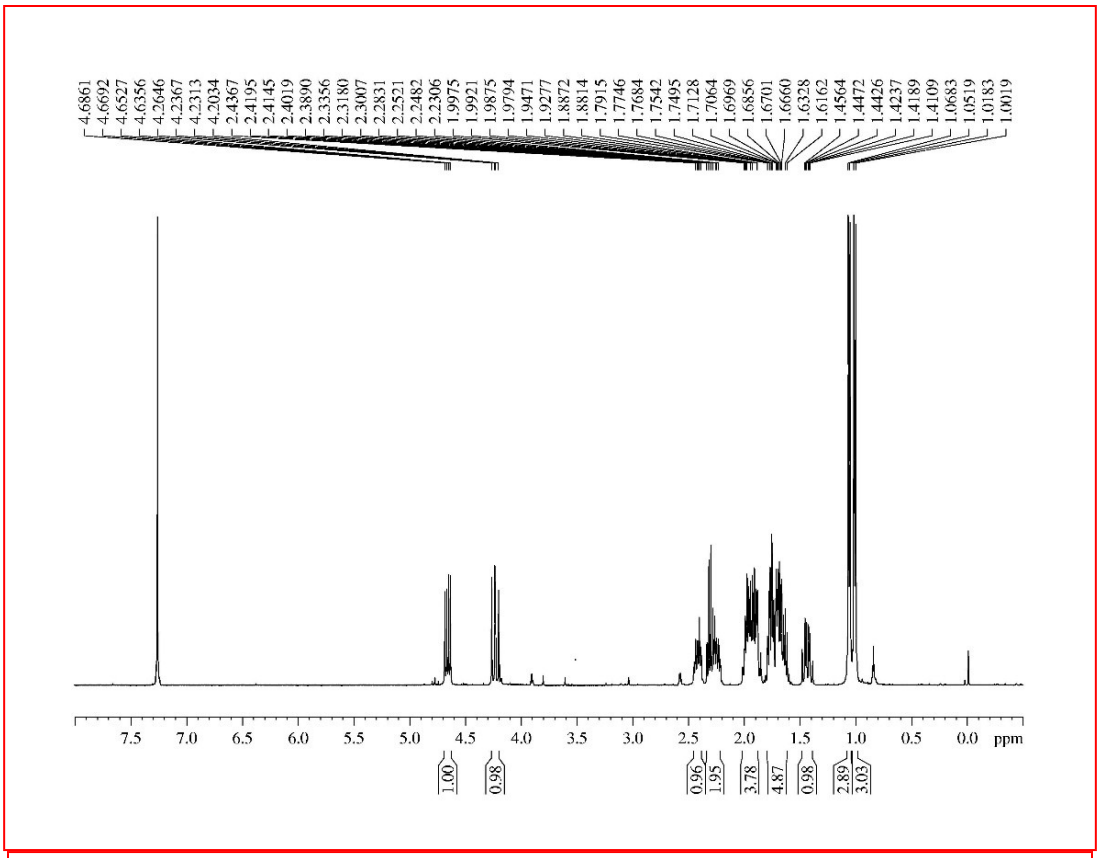


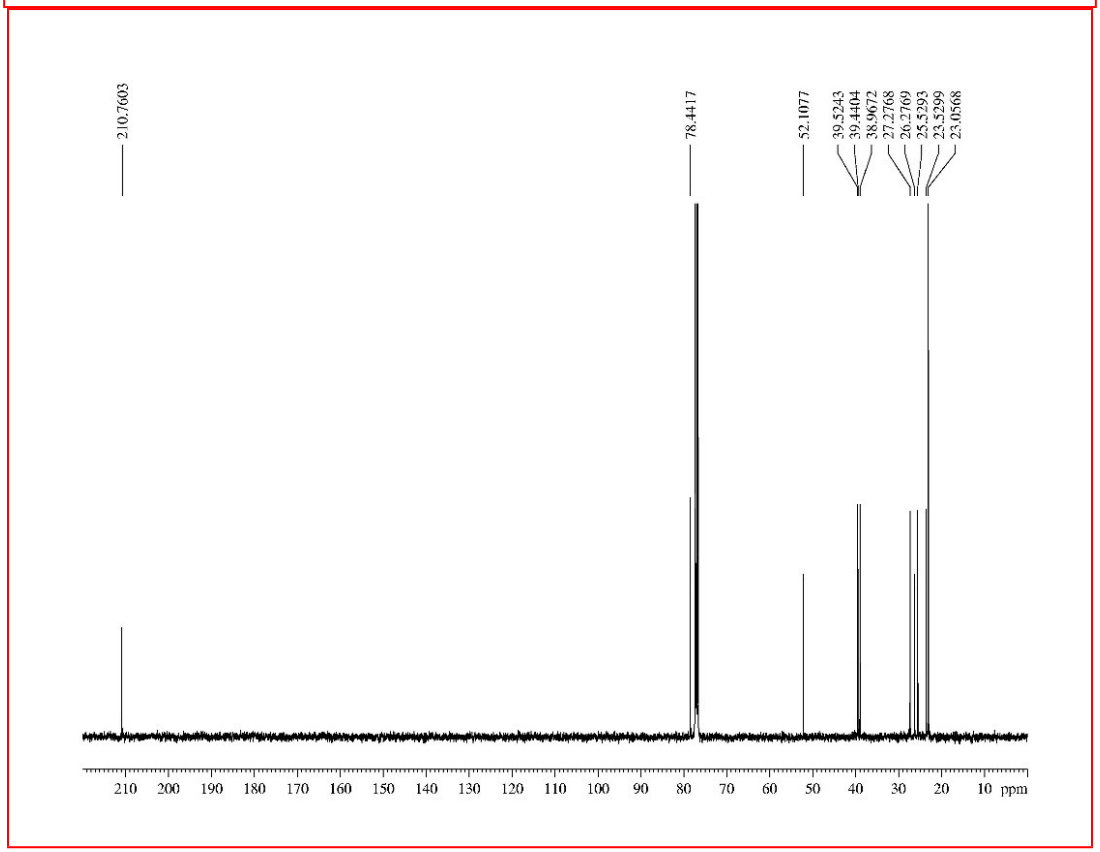
^{1}H and ^{13}C NMR spectra of 5m



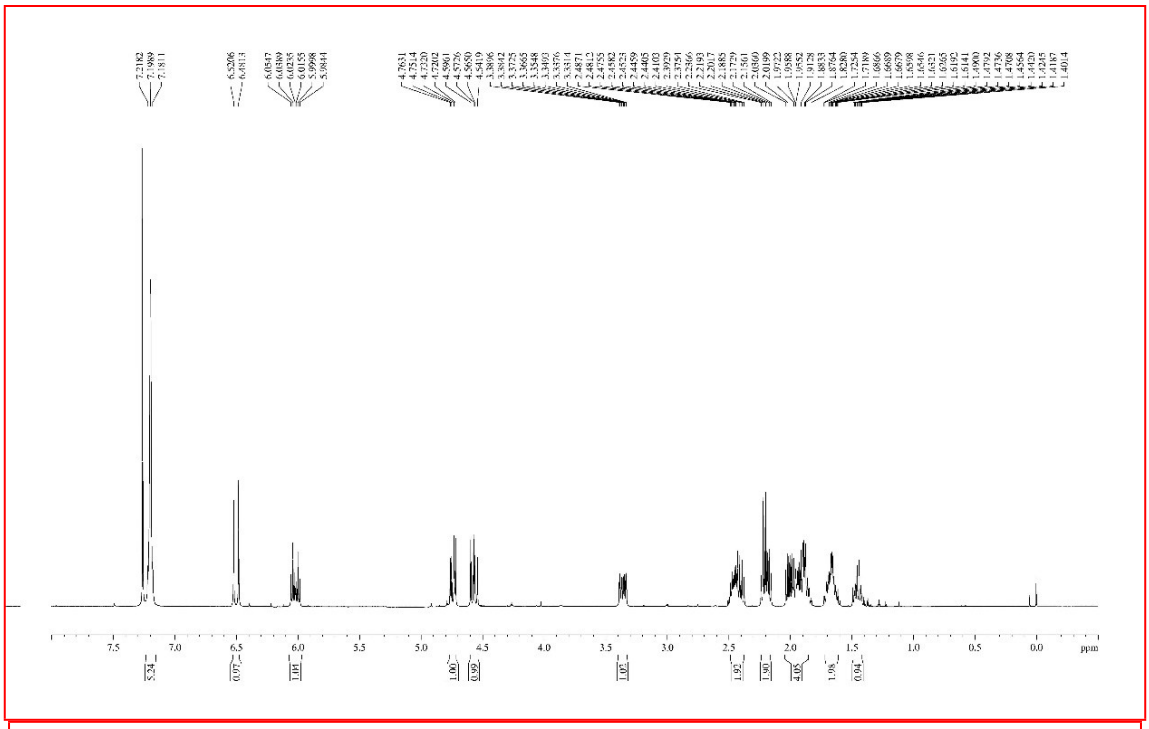


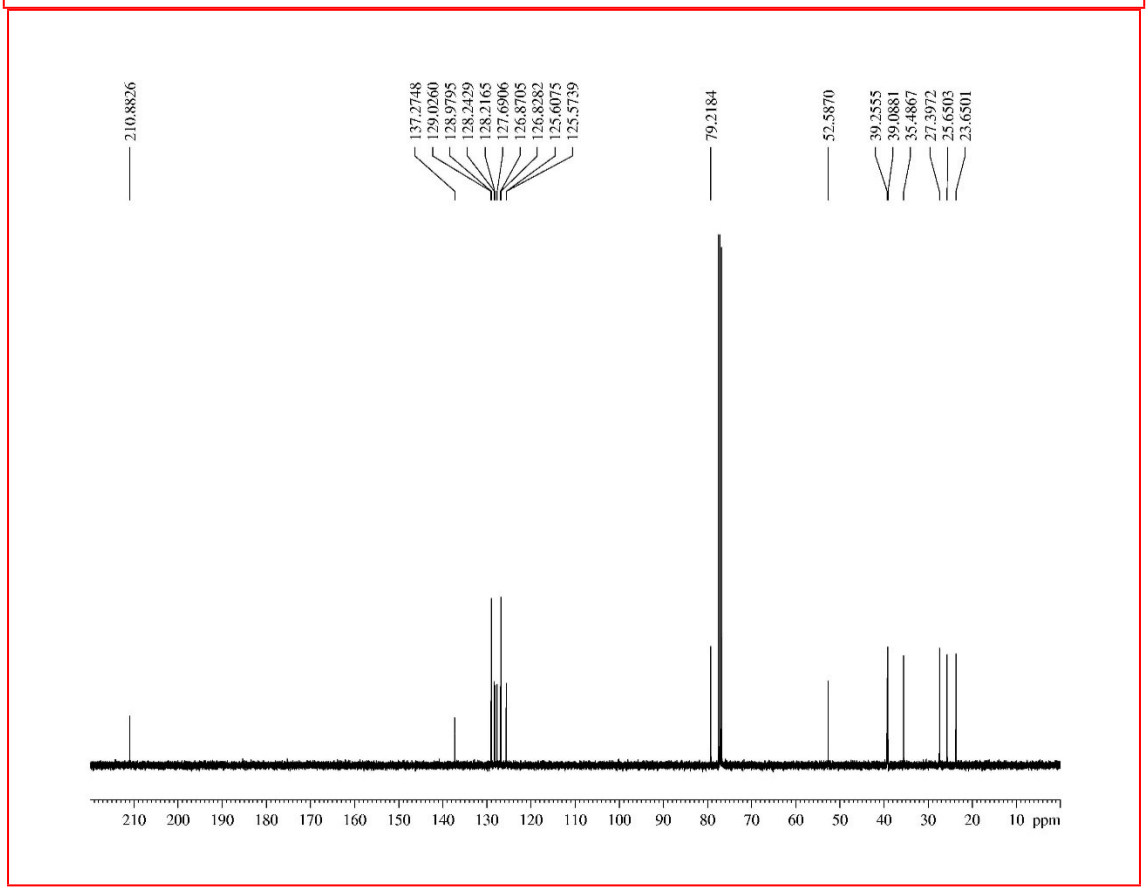
^{1}H and ^{13}C NMR spectra of 5n



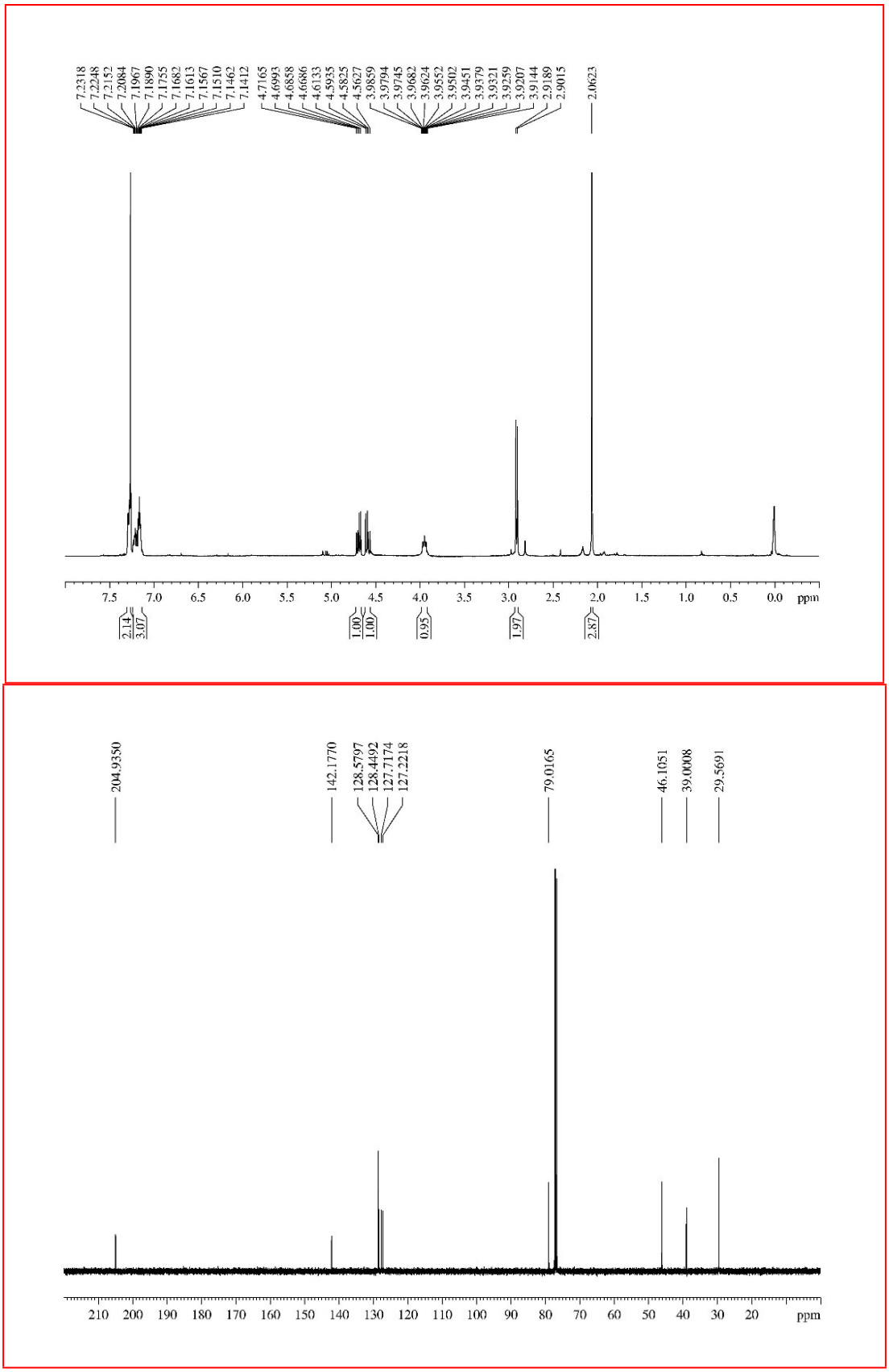


^{1}H and ^{13}C NMR spectra of 5n

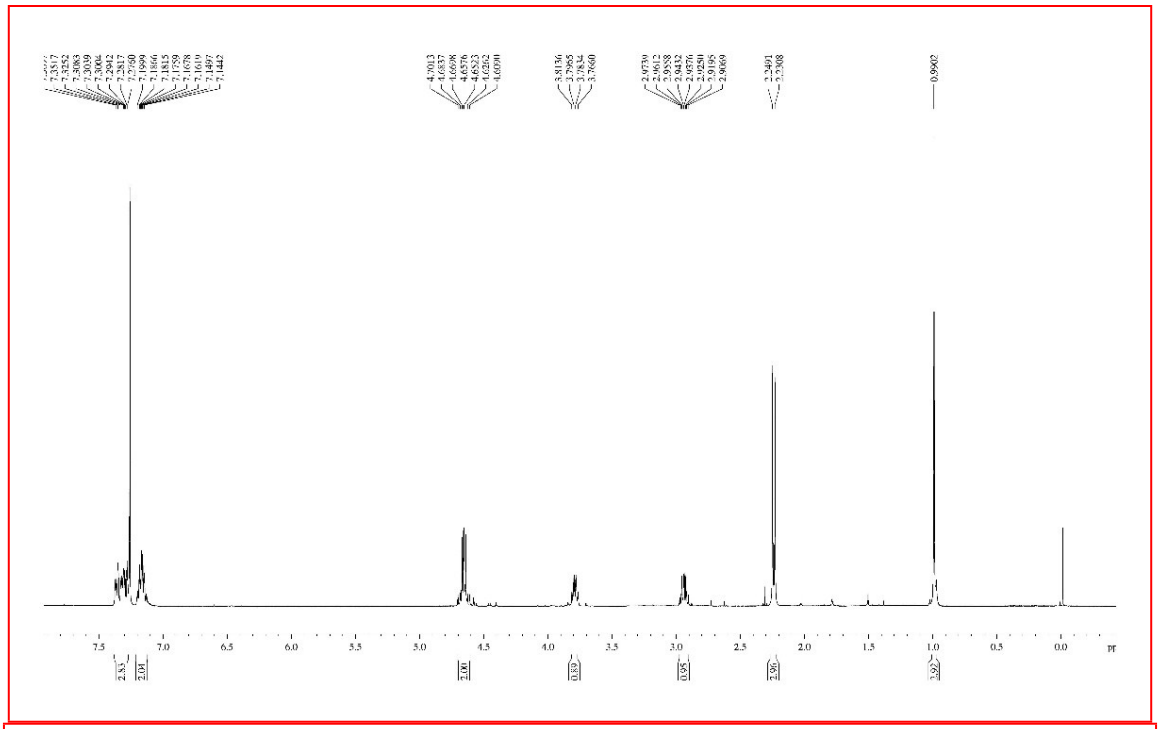


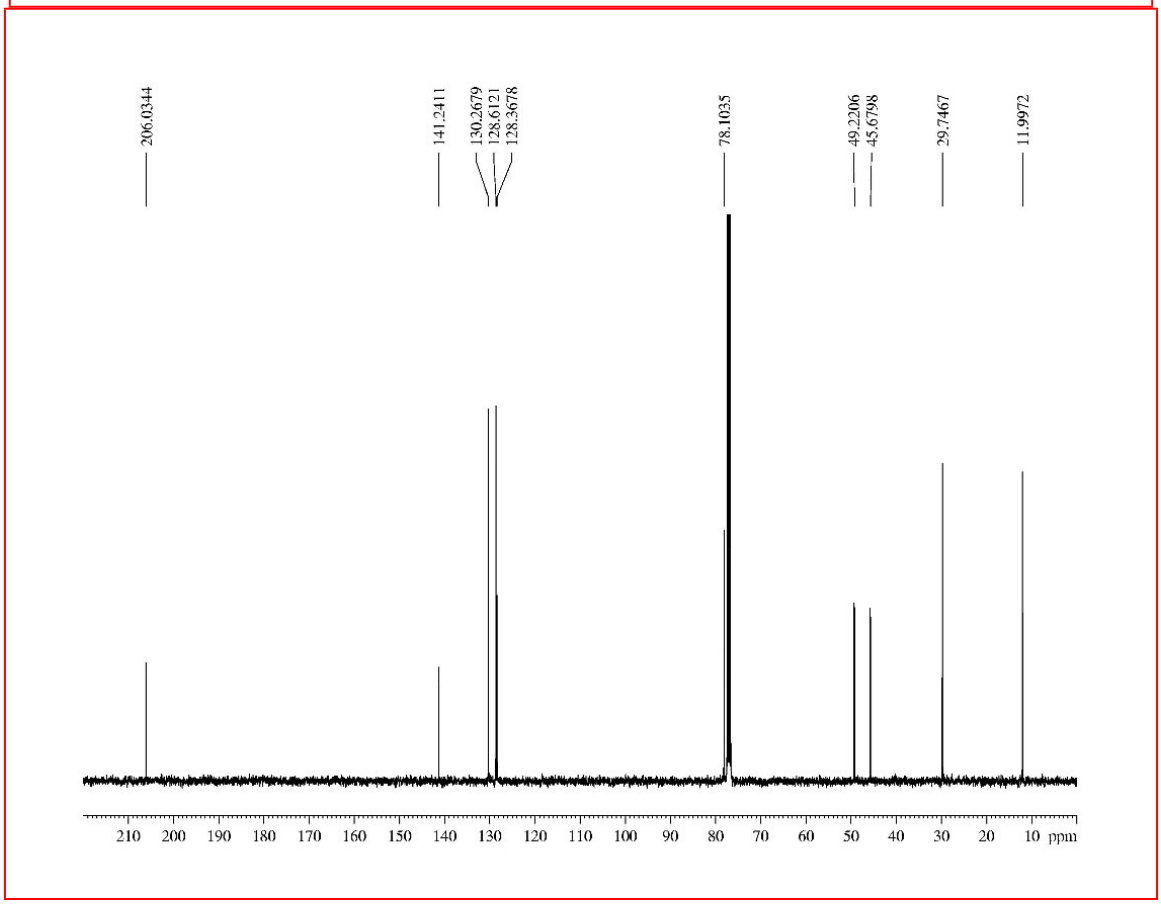


^{1}H and ^{13}C NMR spectra of 5p

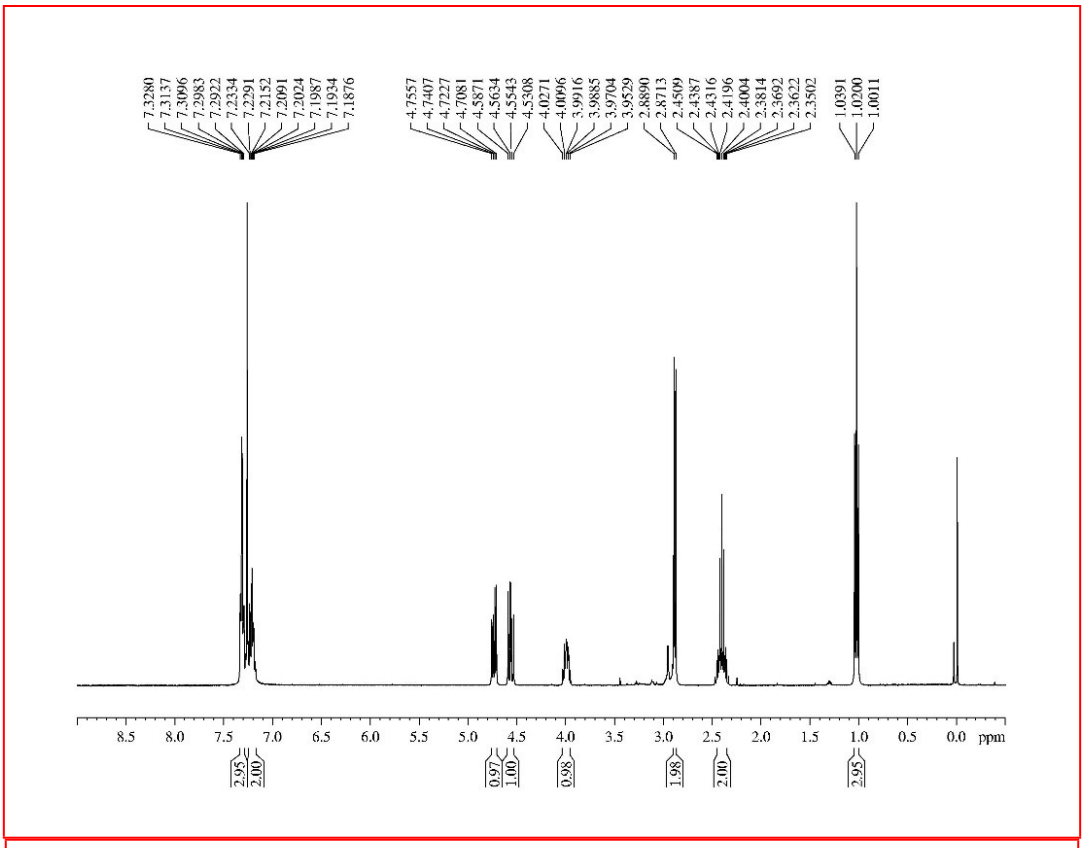


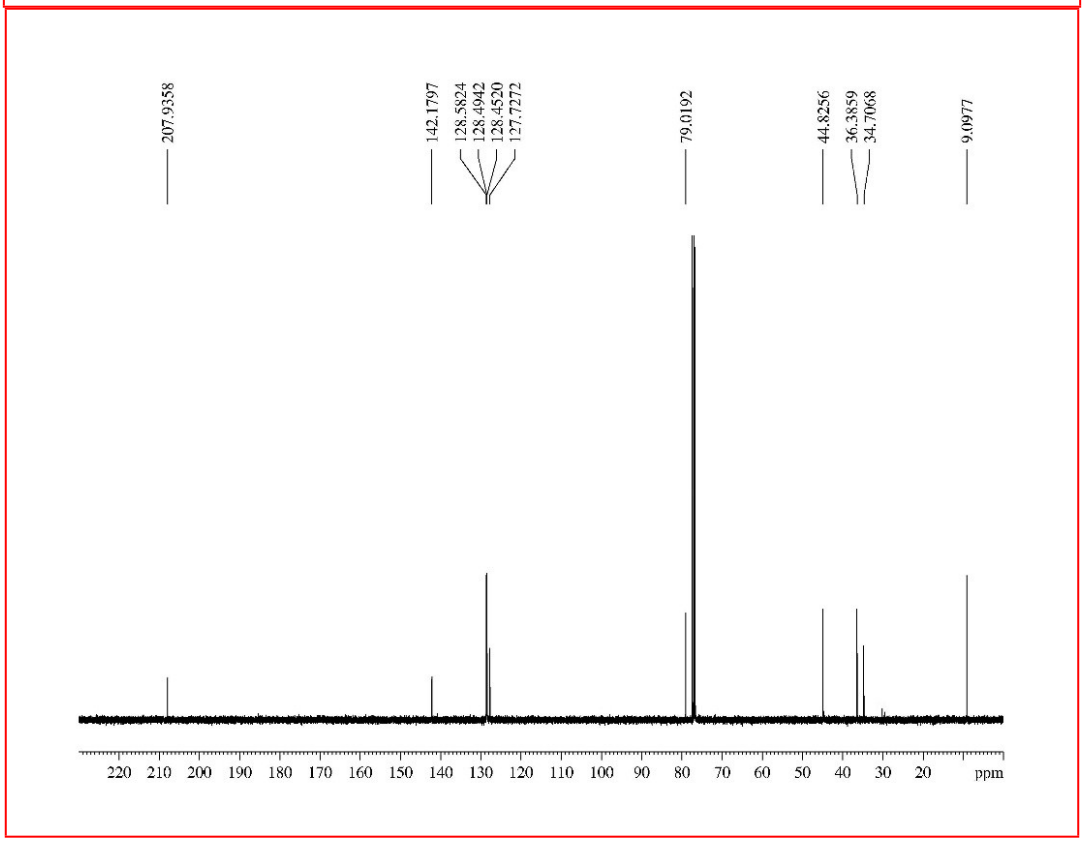
^{1}H and ^{13}C NMR spectra of 6a



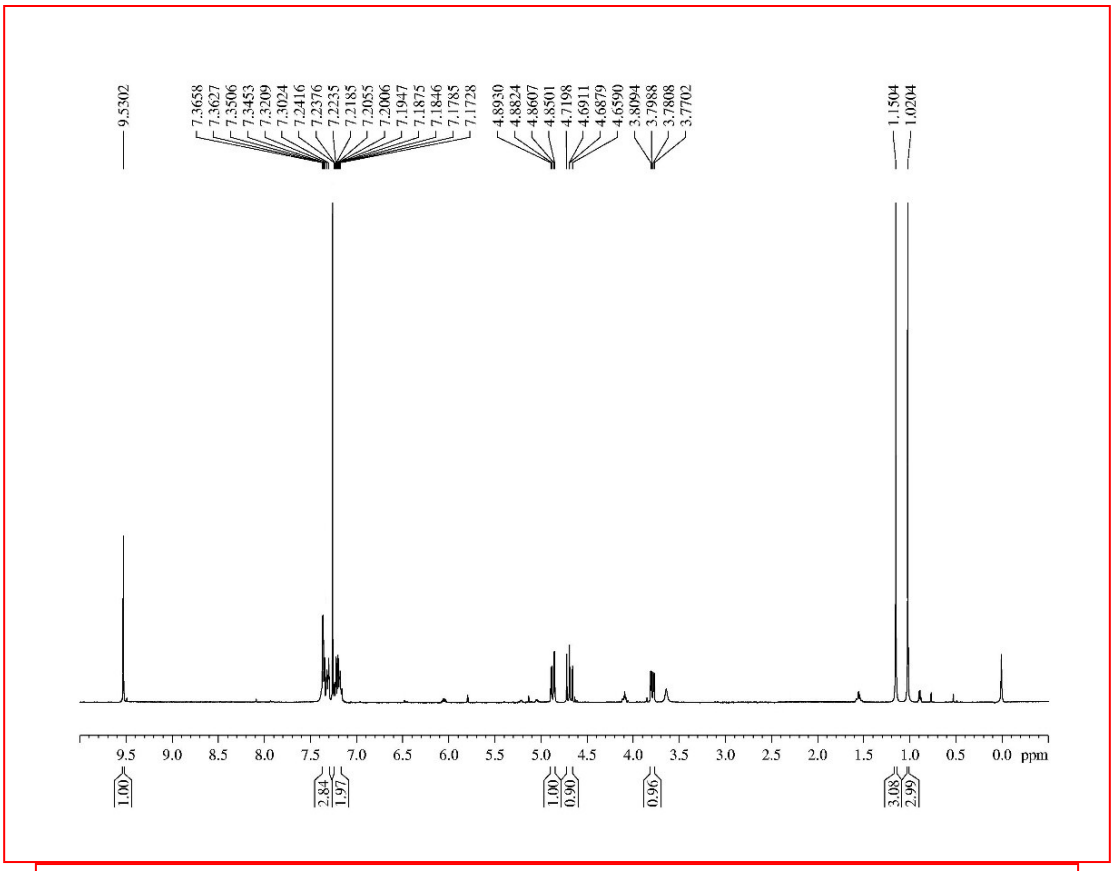


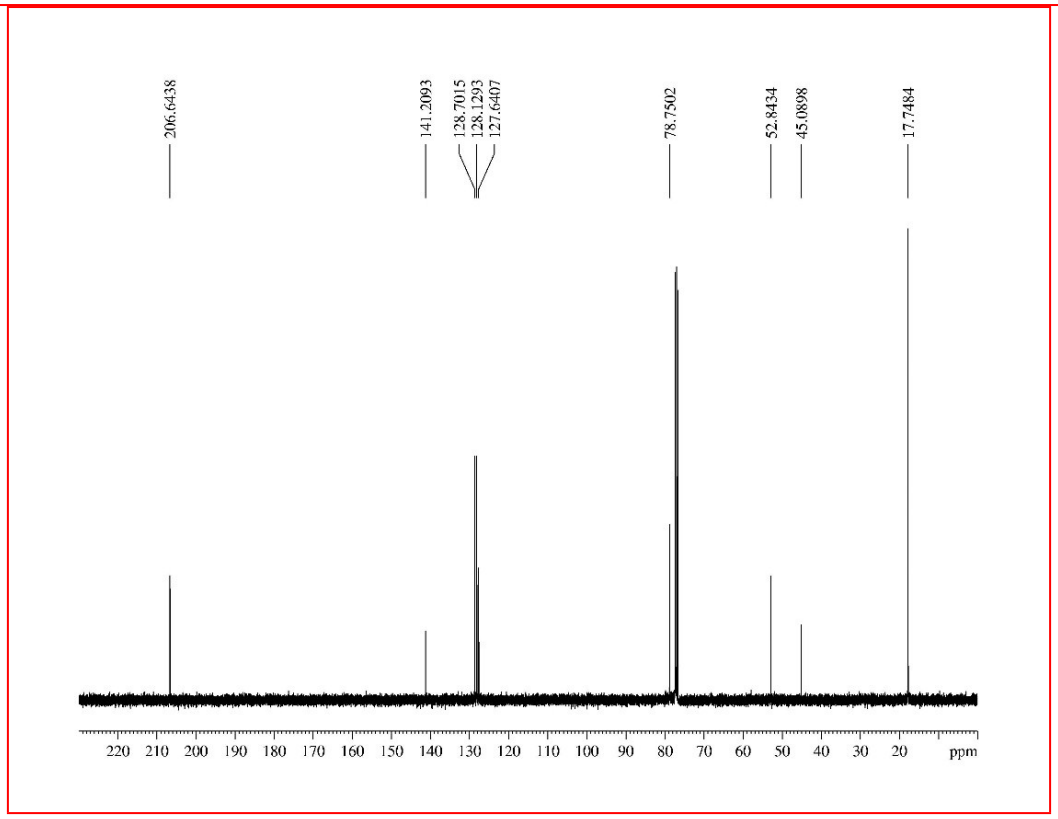
^{1}H and ^{13}C NMR spectra of 7a



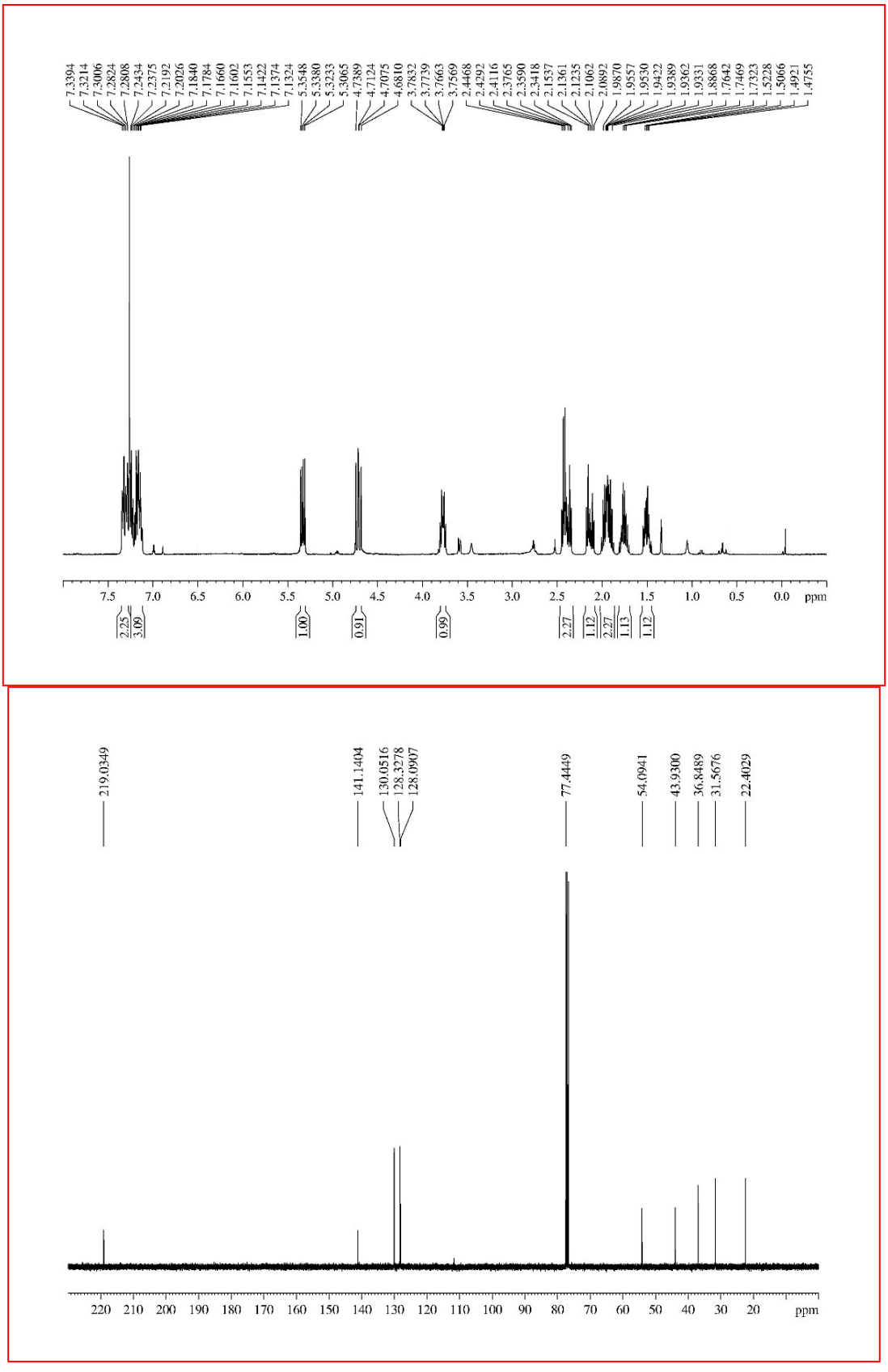


^{1}H and ^{13}C NMR spectra of 7b

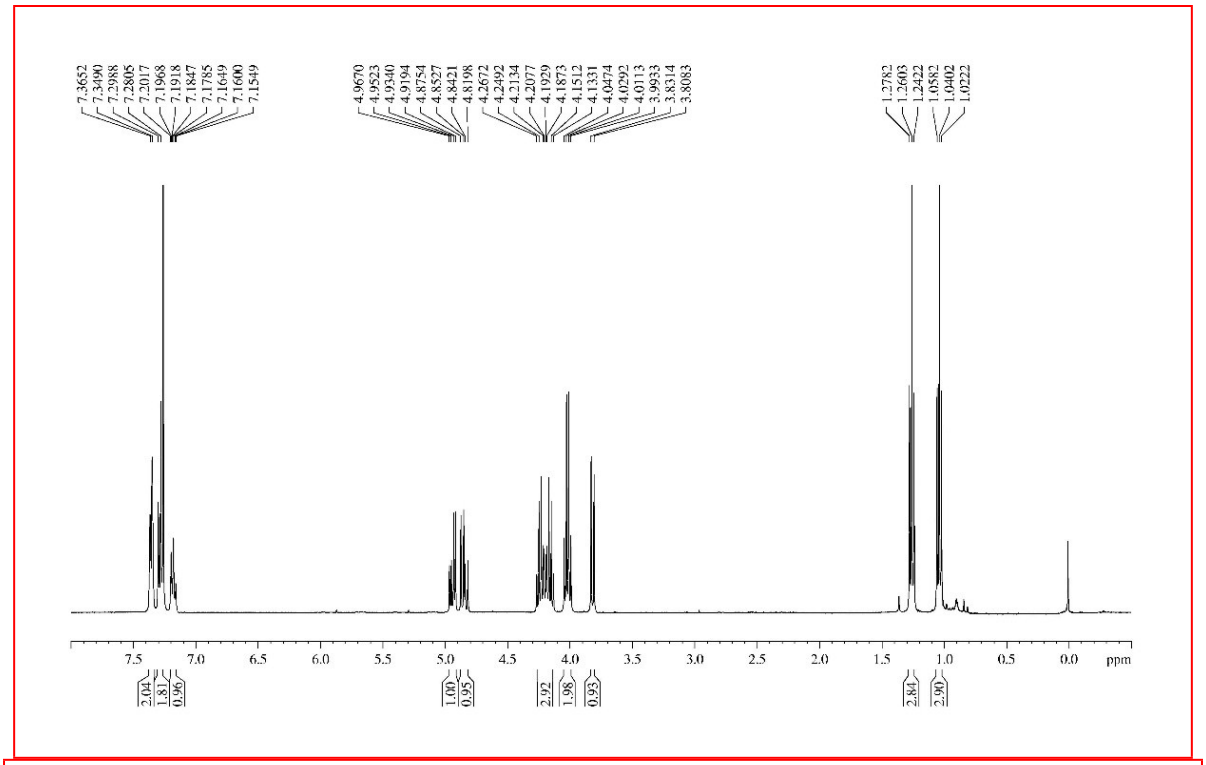


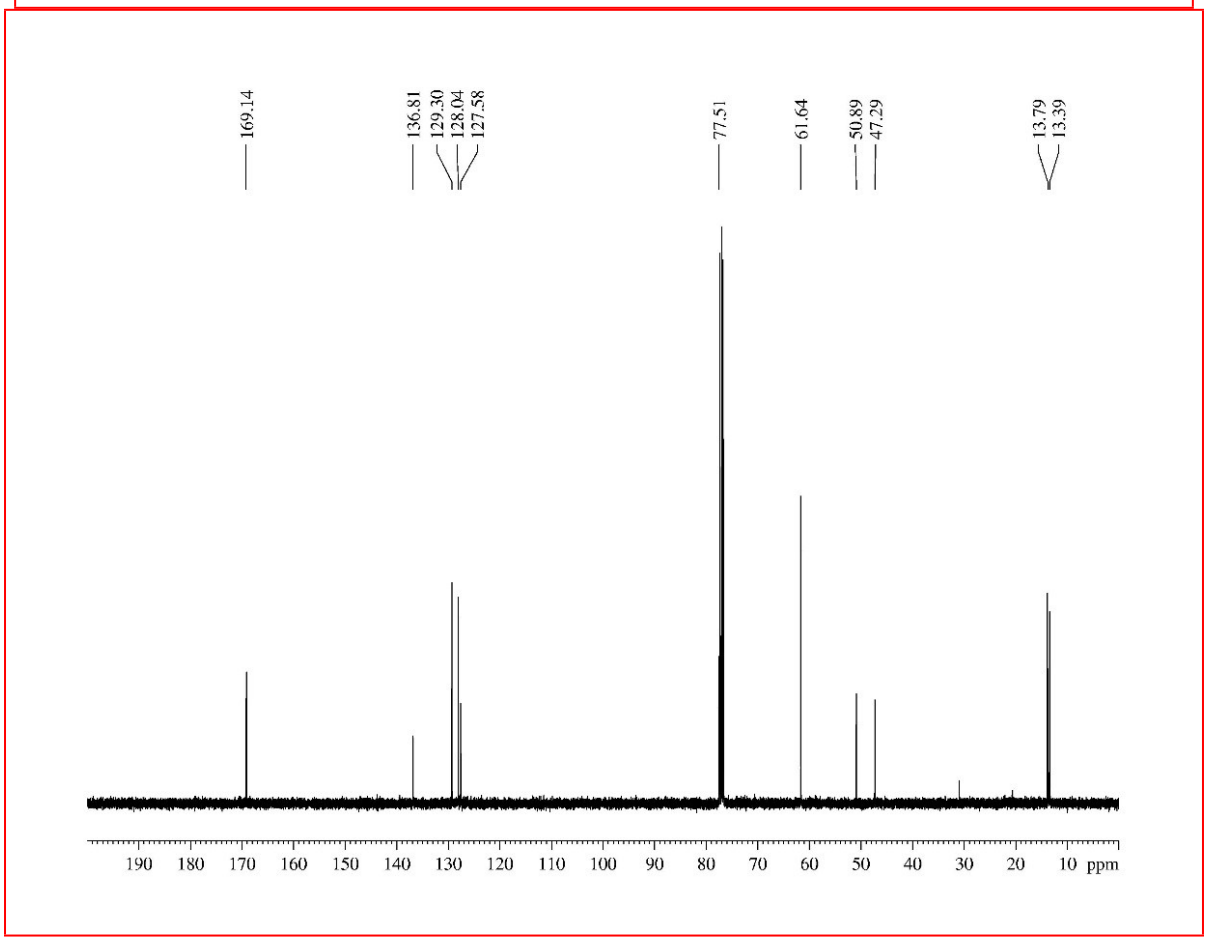


^{1}H and ^{13}C NMR spectra of 8a

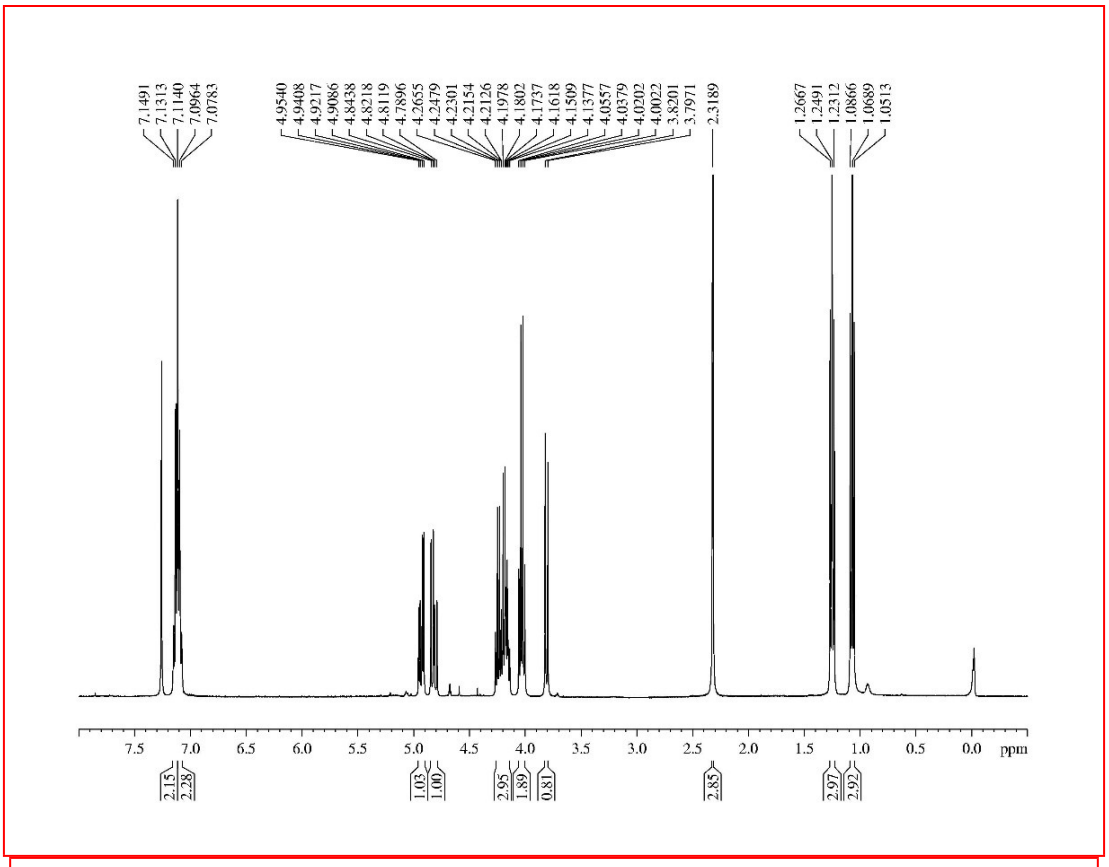


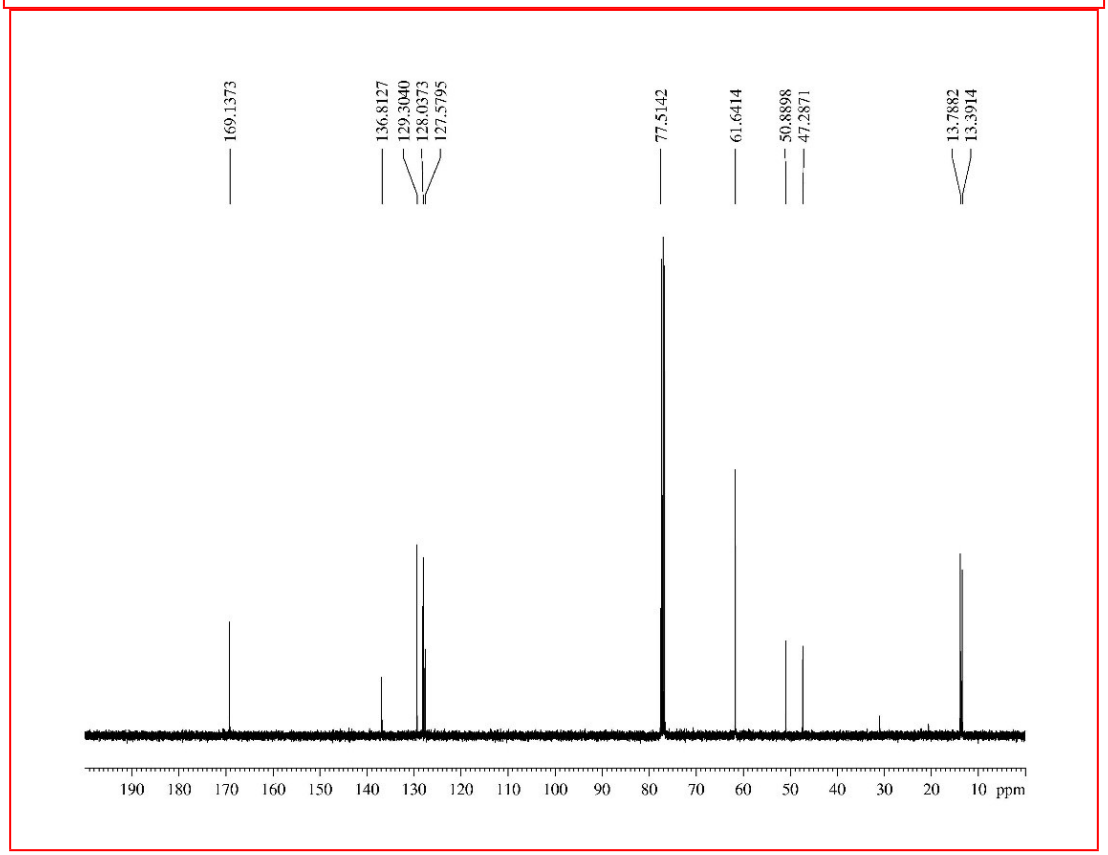
^{1}H and ^{13}C NMR spectra of 9a



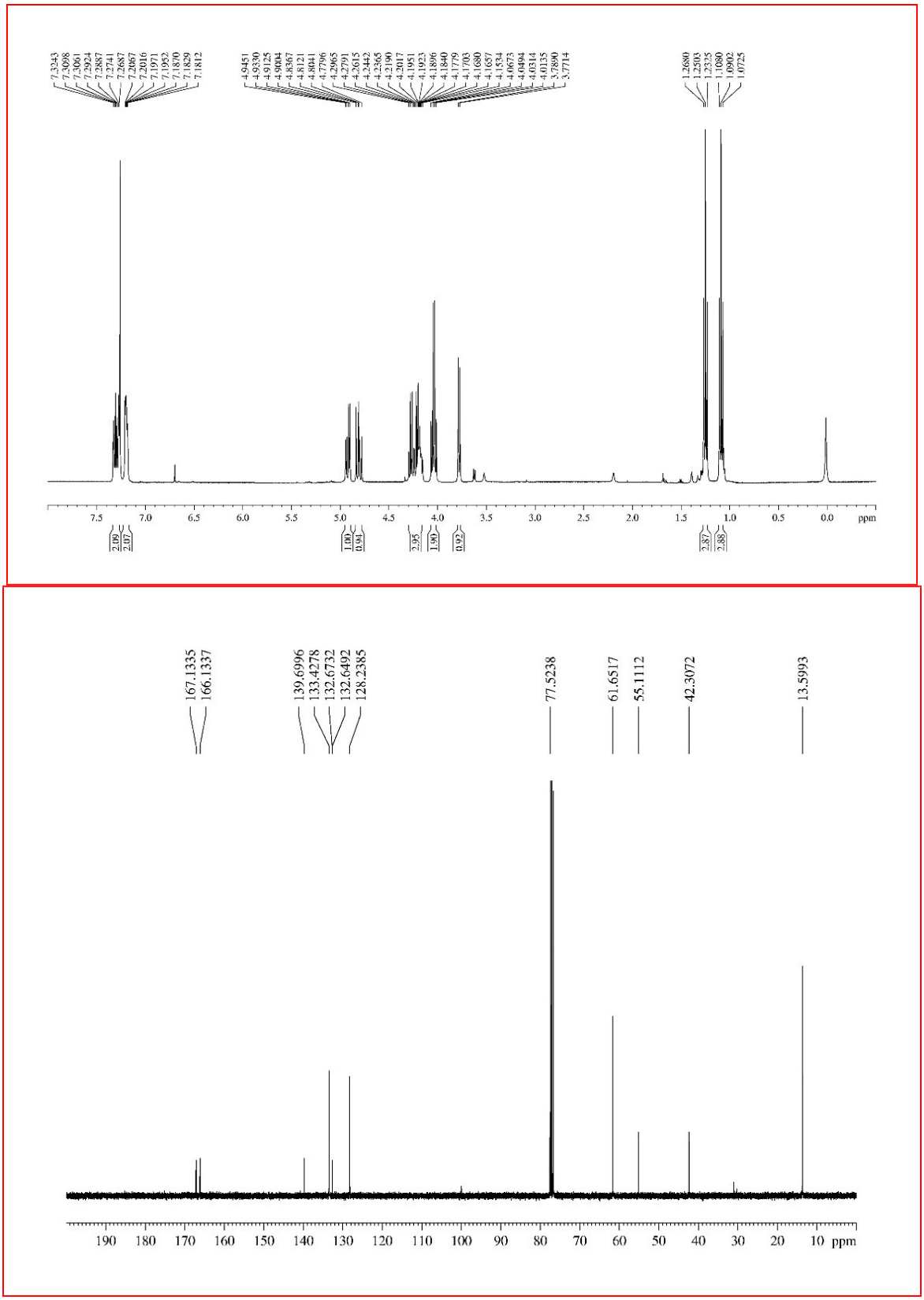


^{1}H and ^{13}C NMR spectra of 11a

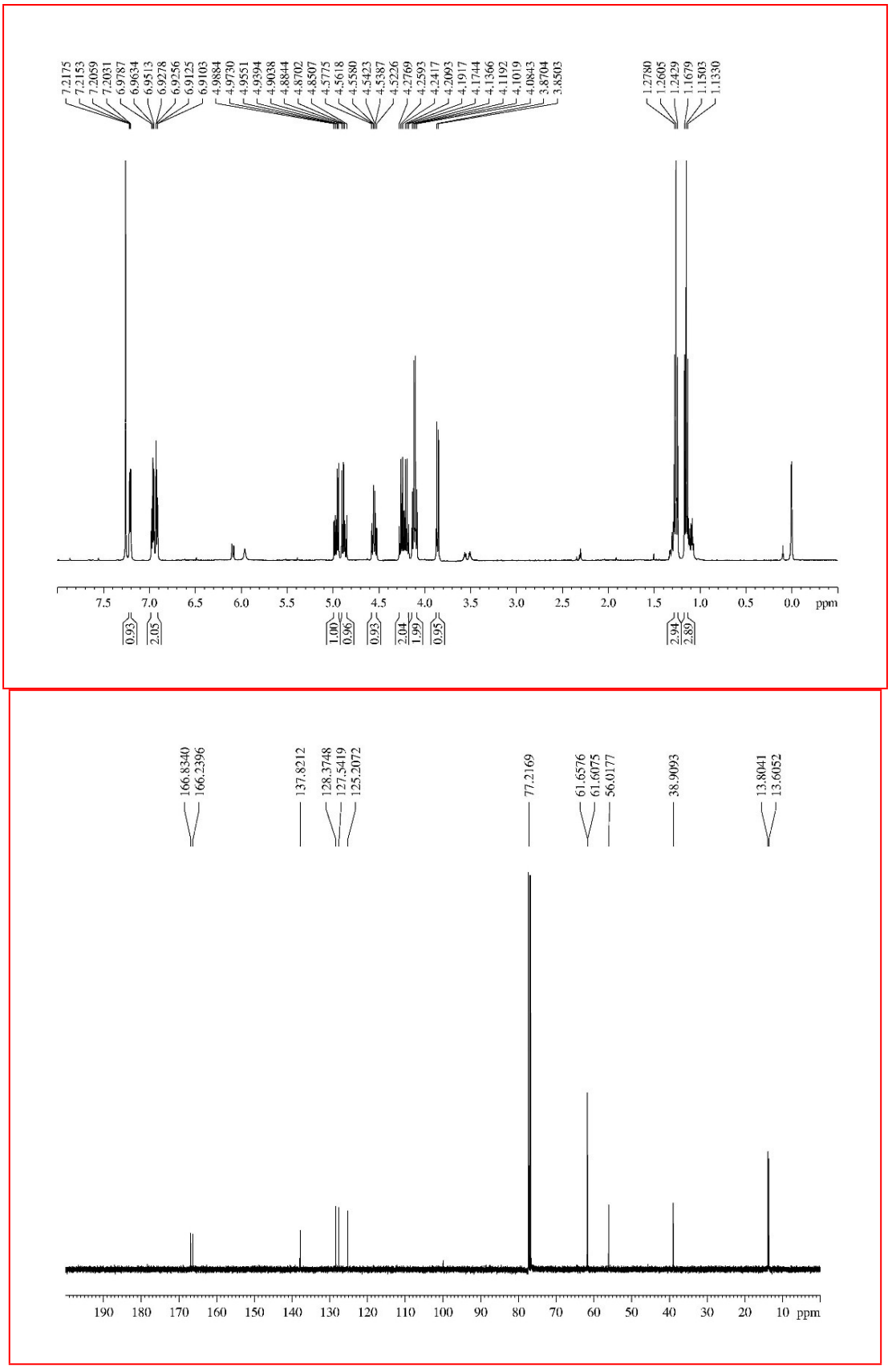




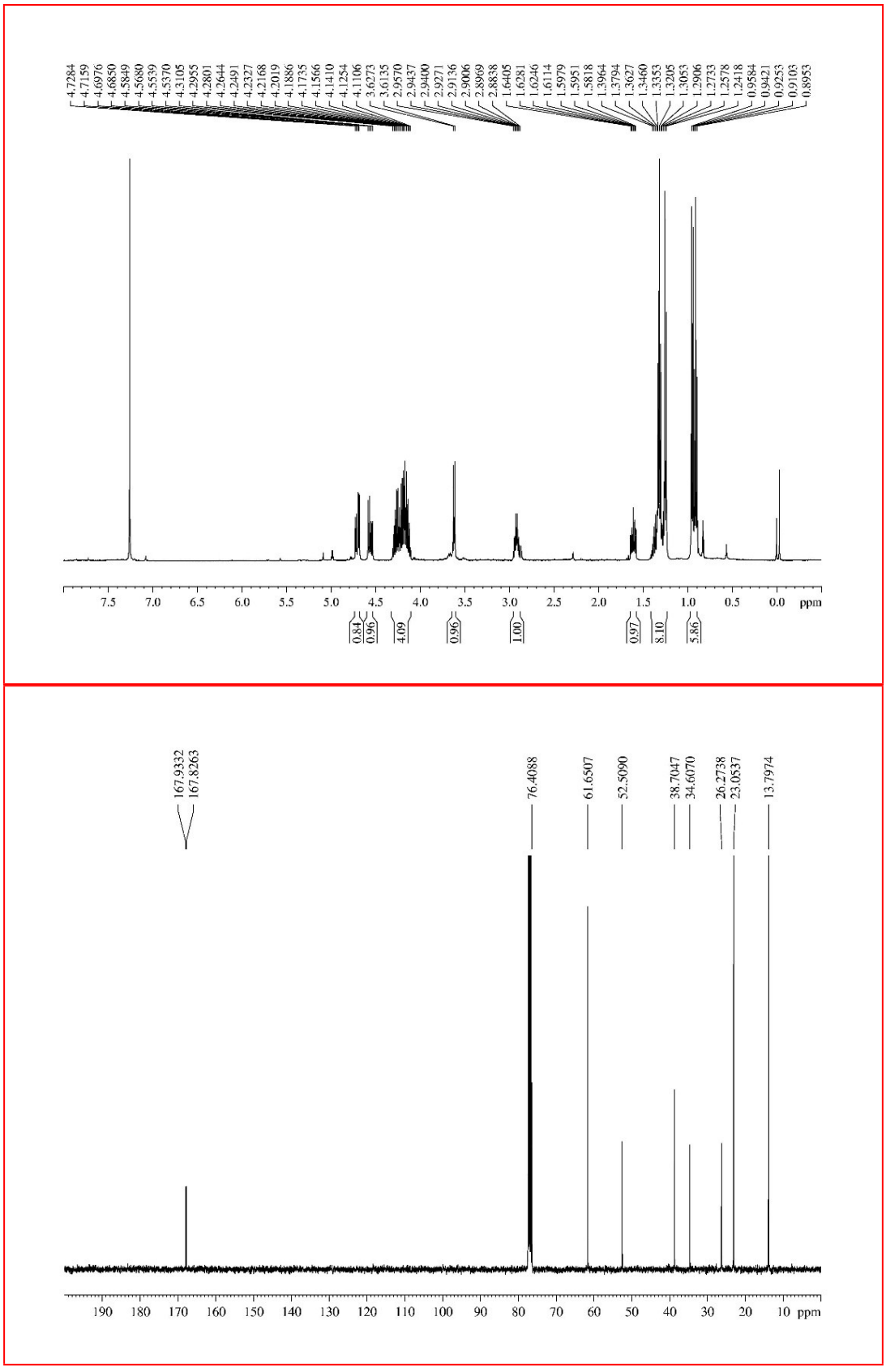
^{1}H and ^{13}C NMR spectra of 11b



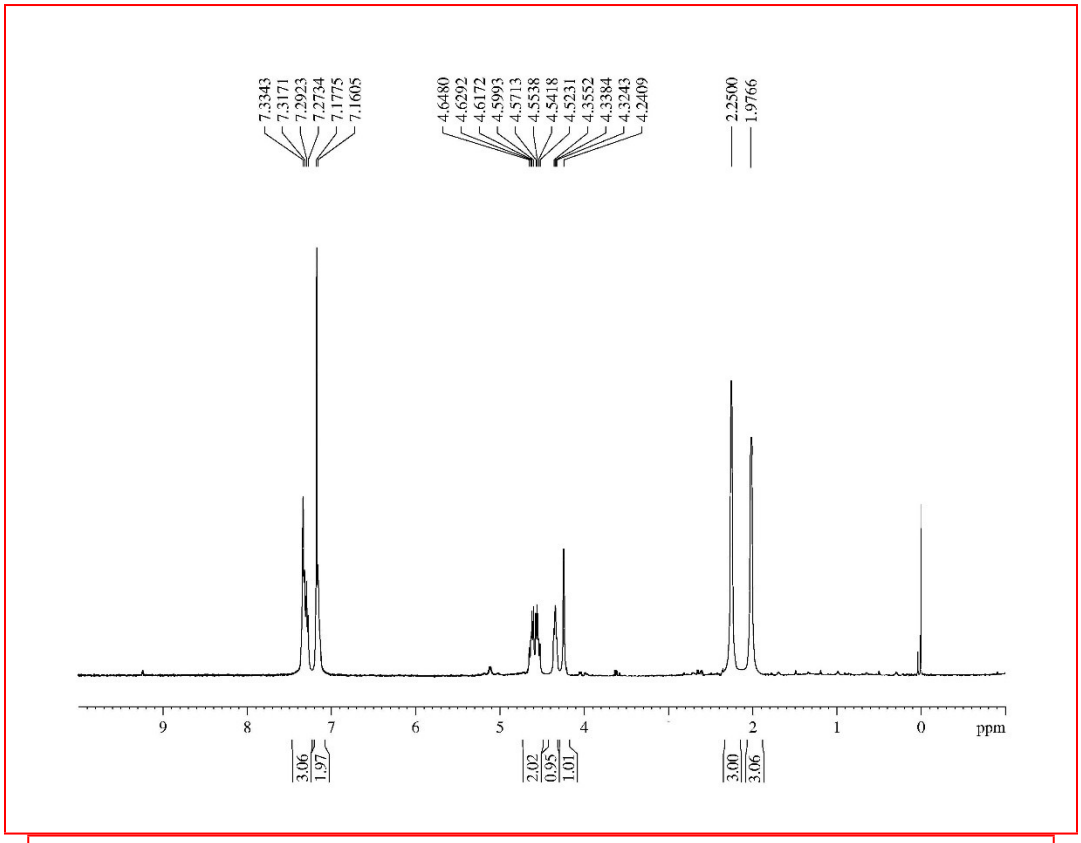
^{1}H and ^{13}C NMR spectra of 11c

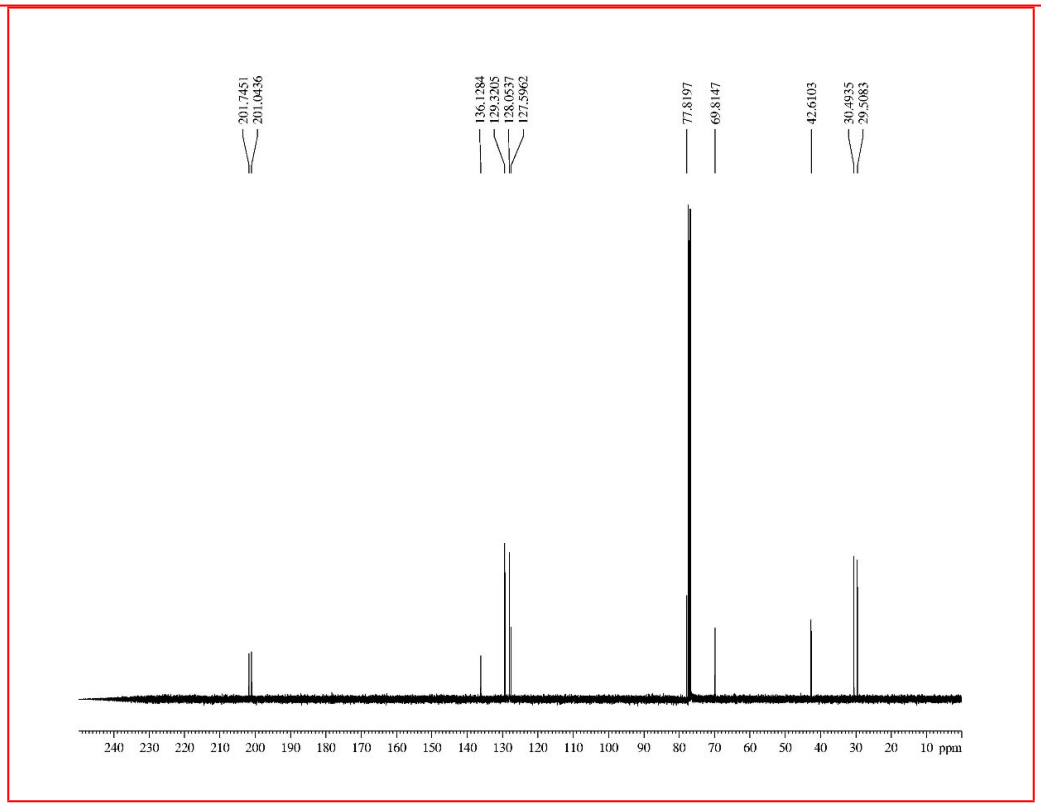


^{1}H and ^{13}C NMR spectra of 11d

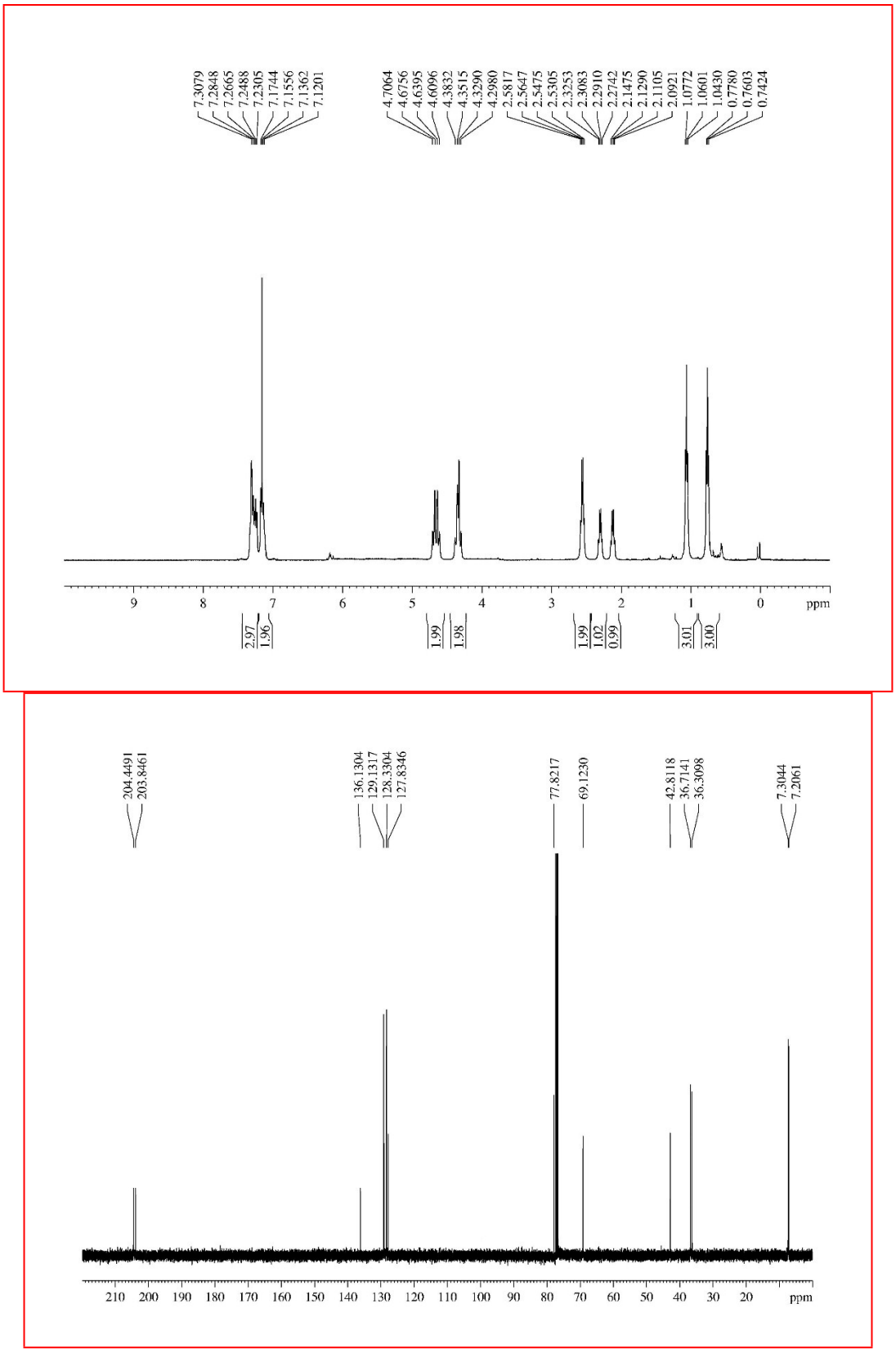


^{1}H and ^{13}C NMR spectra of 11e

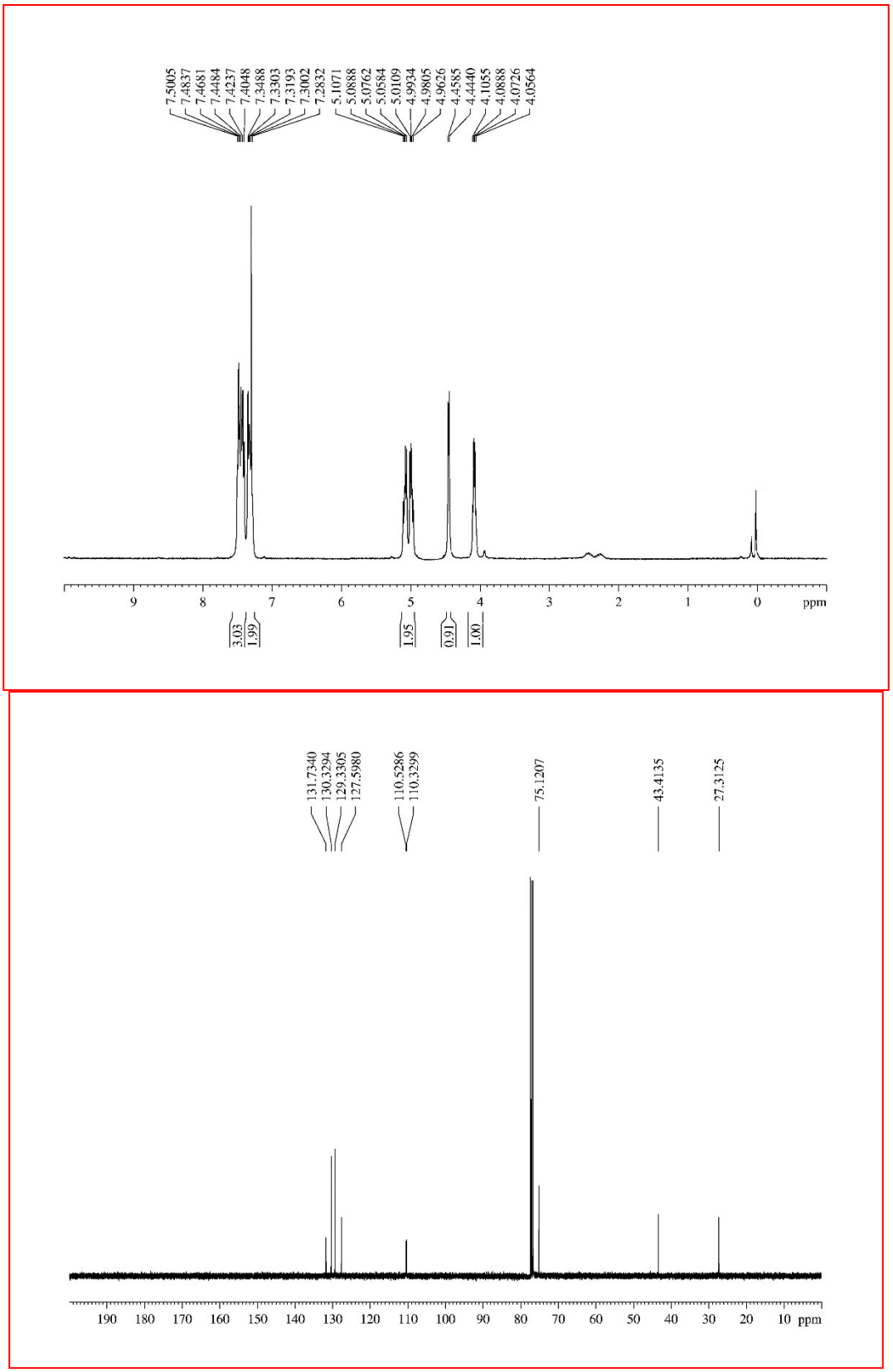




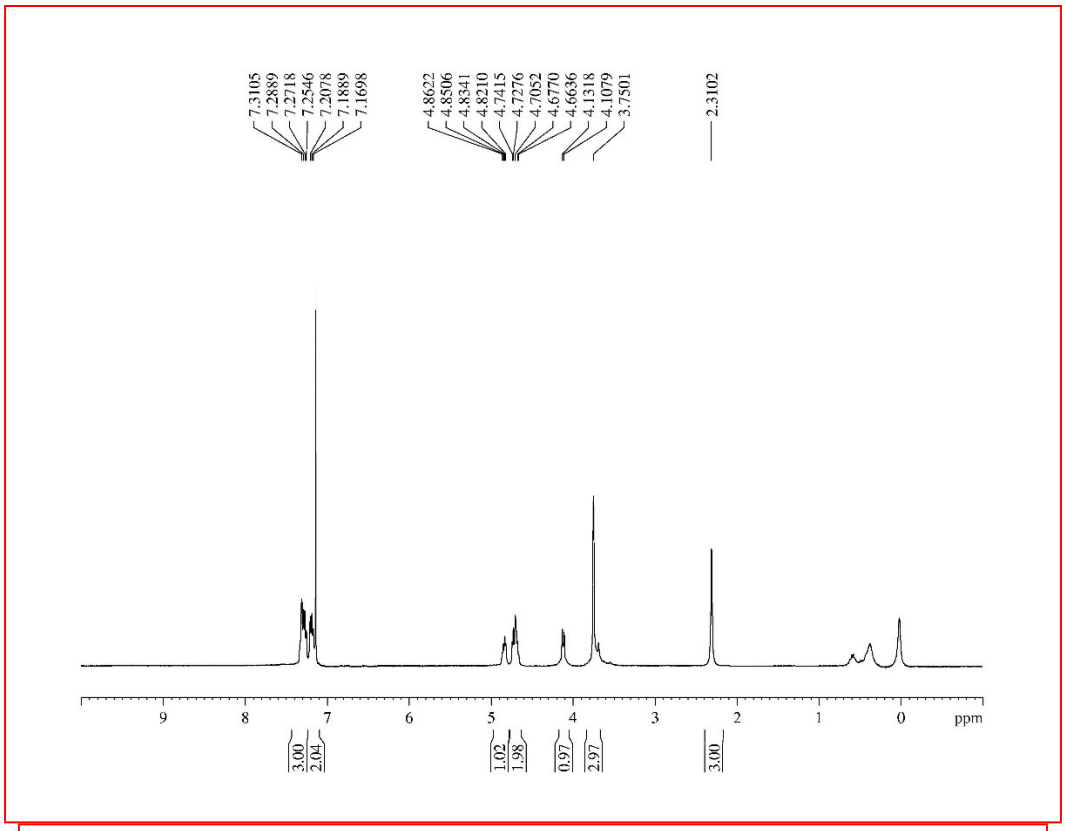
^{1}H and ^{13}C NMR spectra of 11f

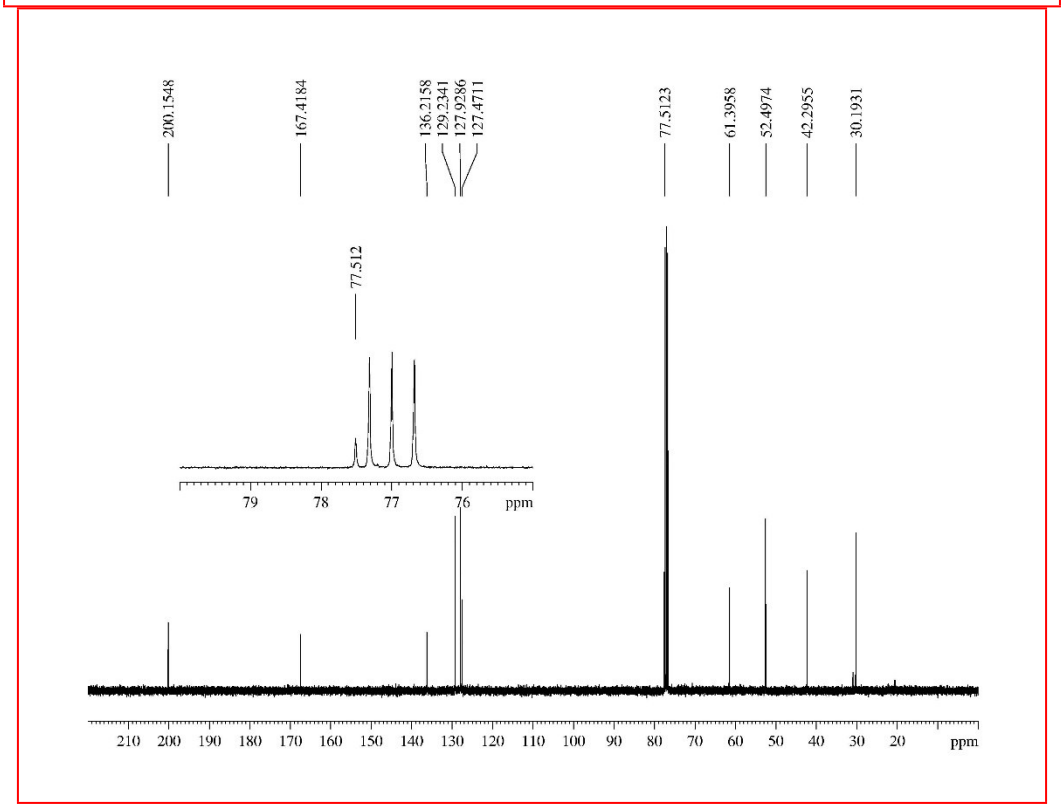


^{1}H and ^{13}C NMR spectra of 11g

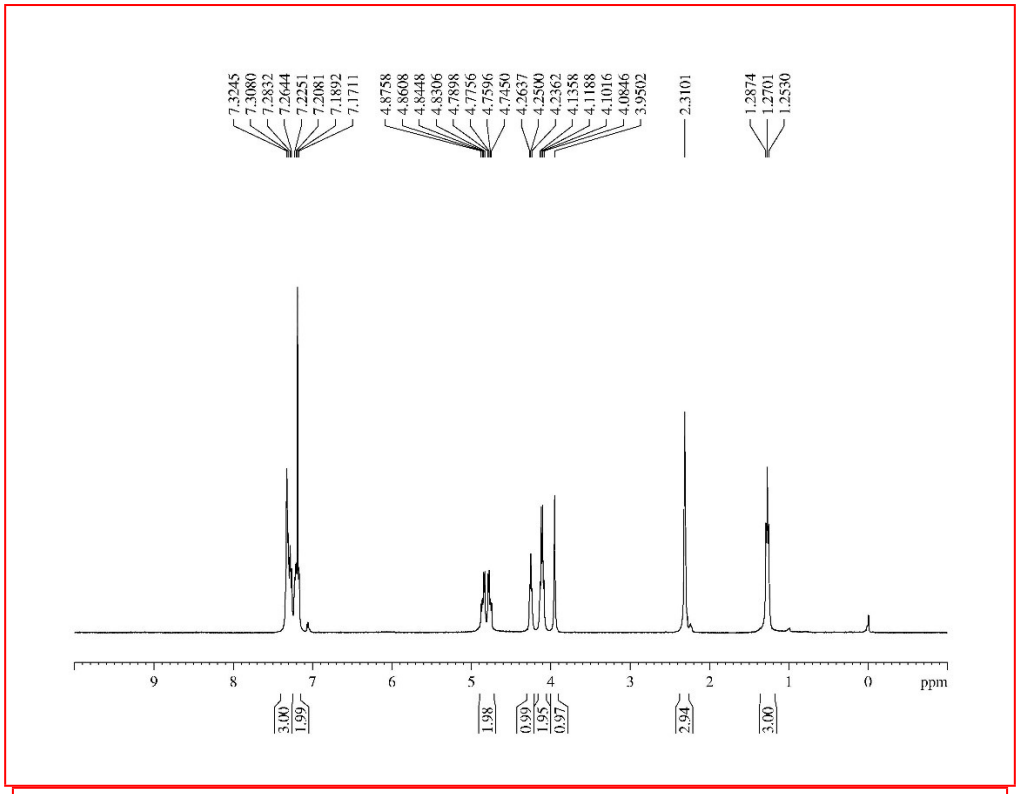


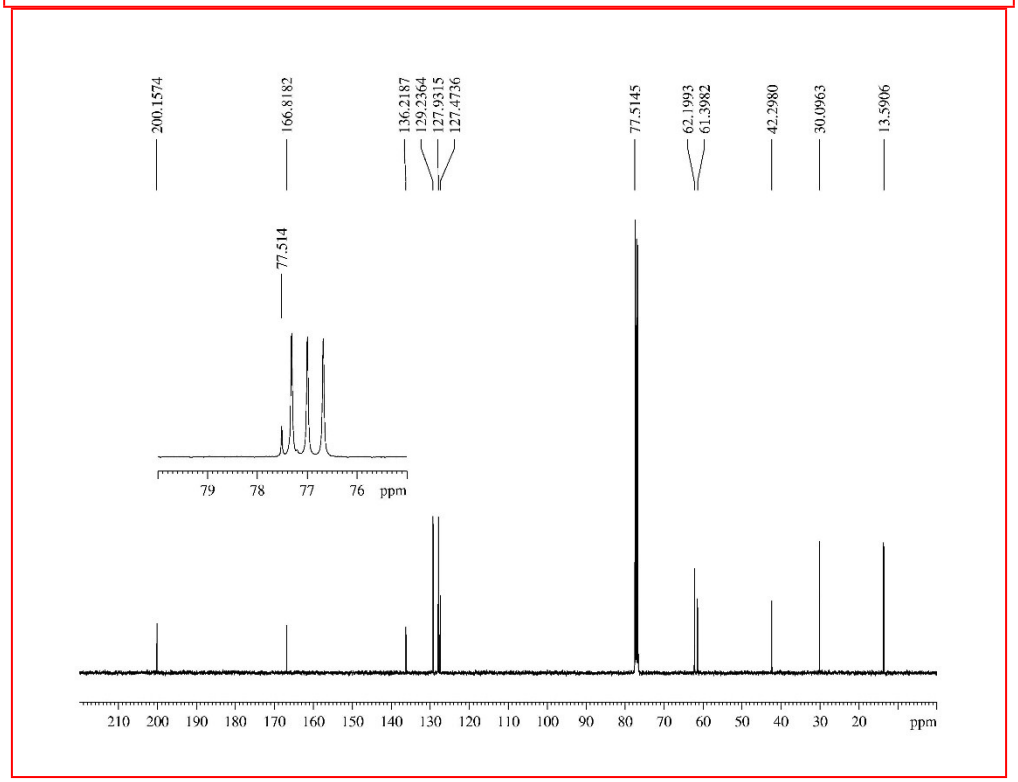
^{1}H and ^{13}C NMR spectra of 11h



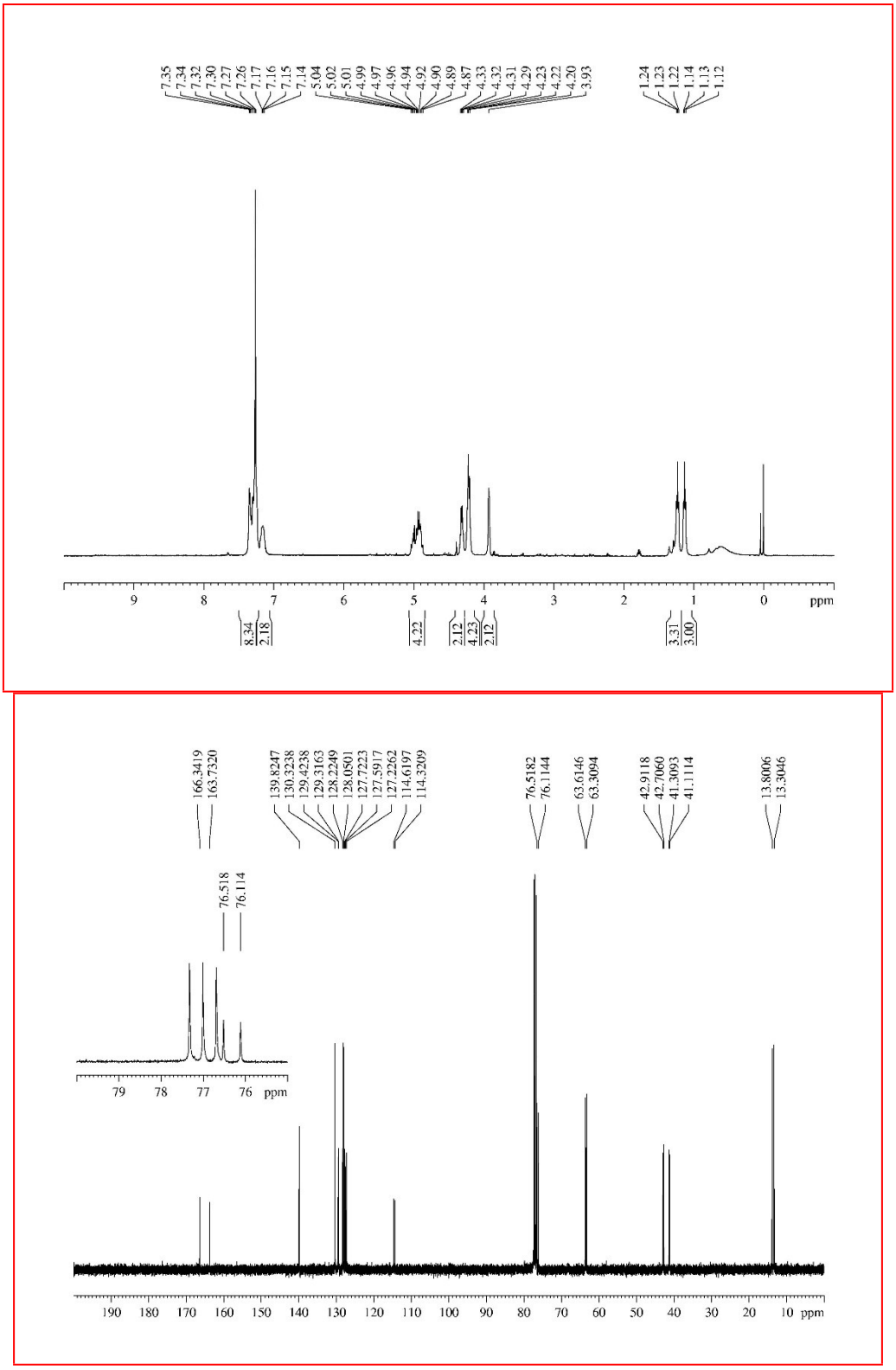


^{1}H and ^{13}C NMR spectra of 11i

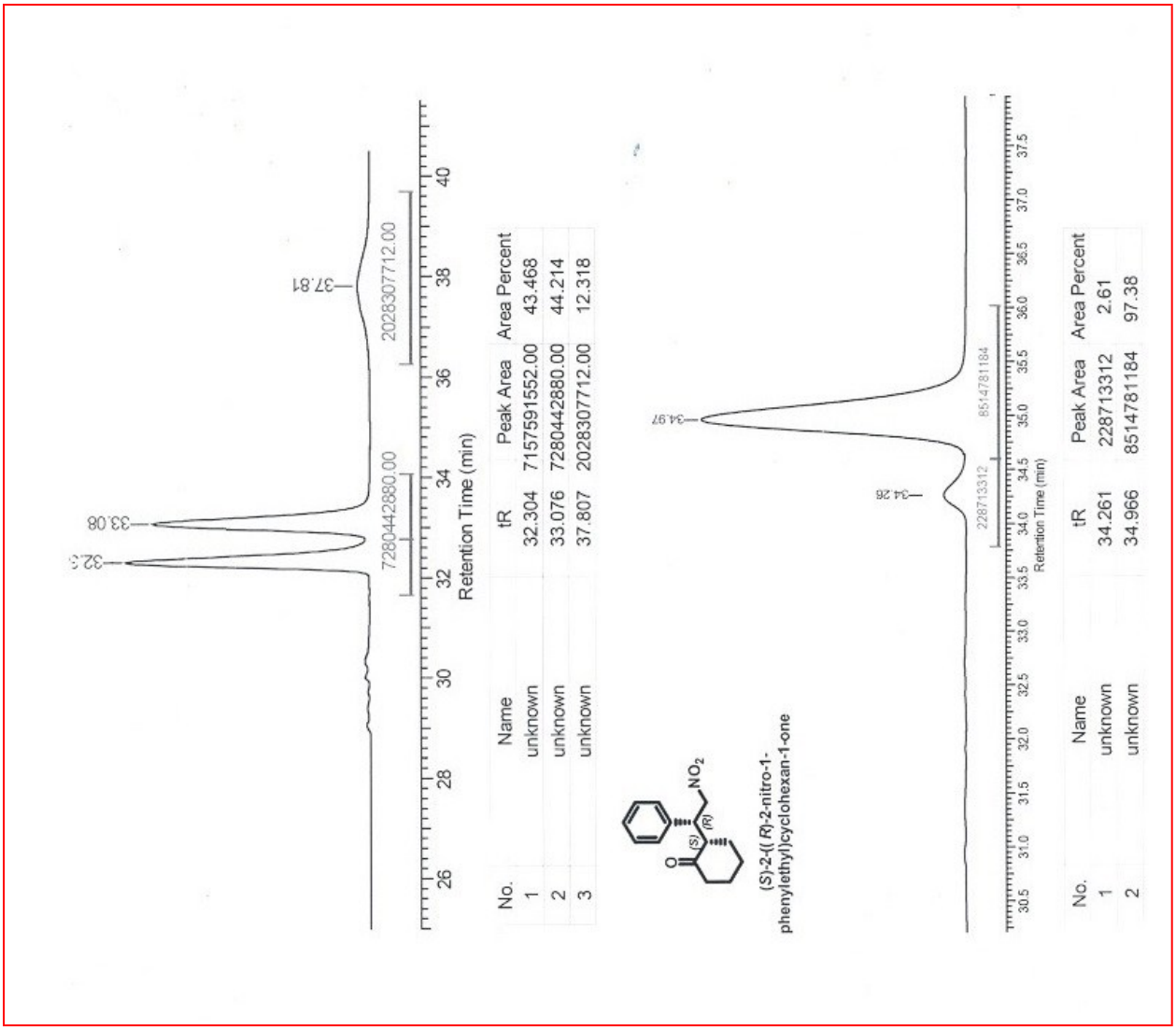




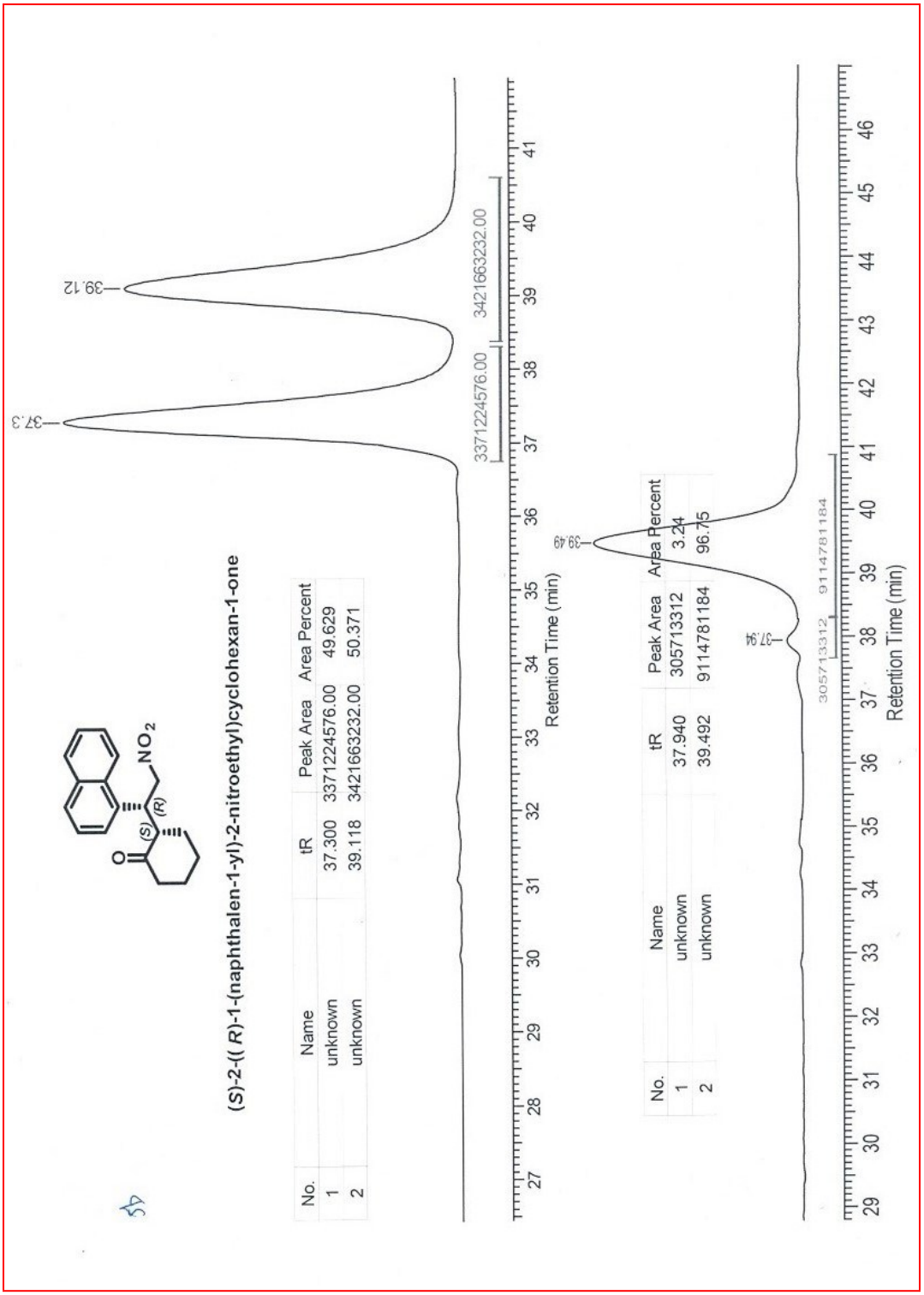
^{1}H and ^{13}C NMR spectra of 11j



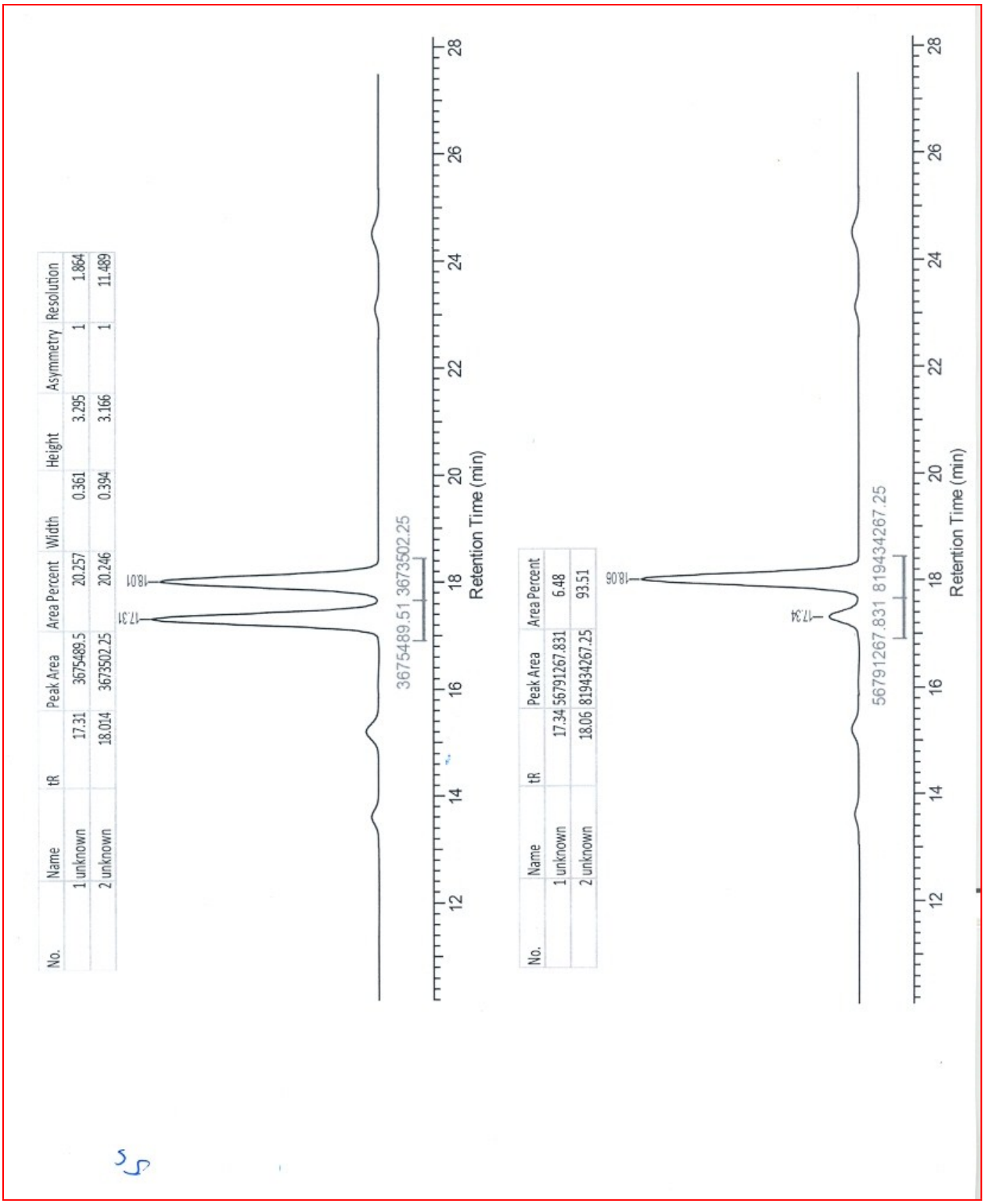
^{1}H and ^{13}C NMR spectra of 11k



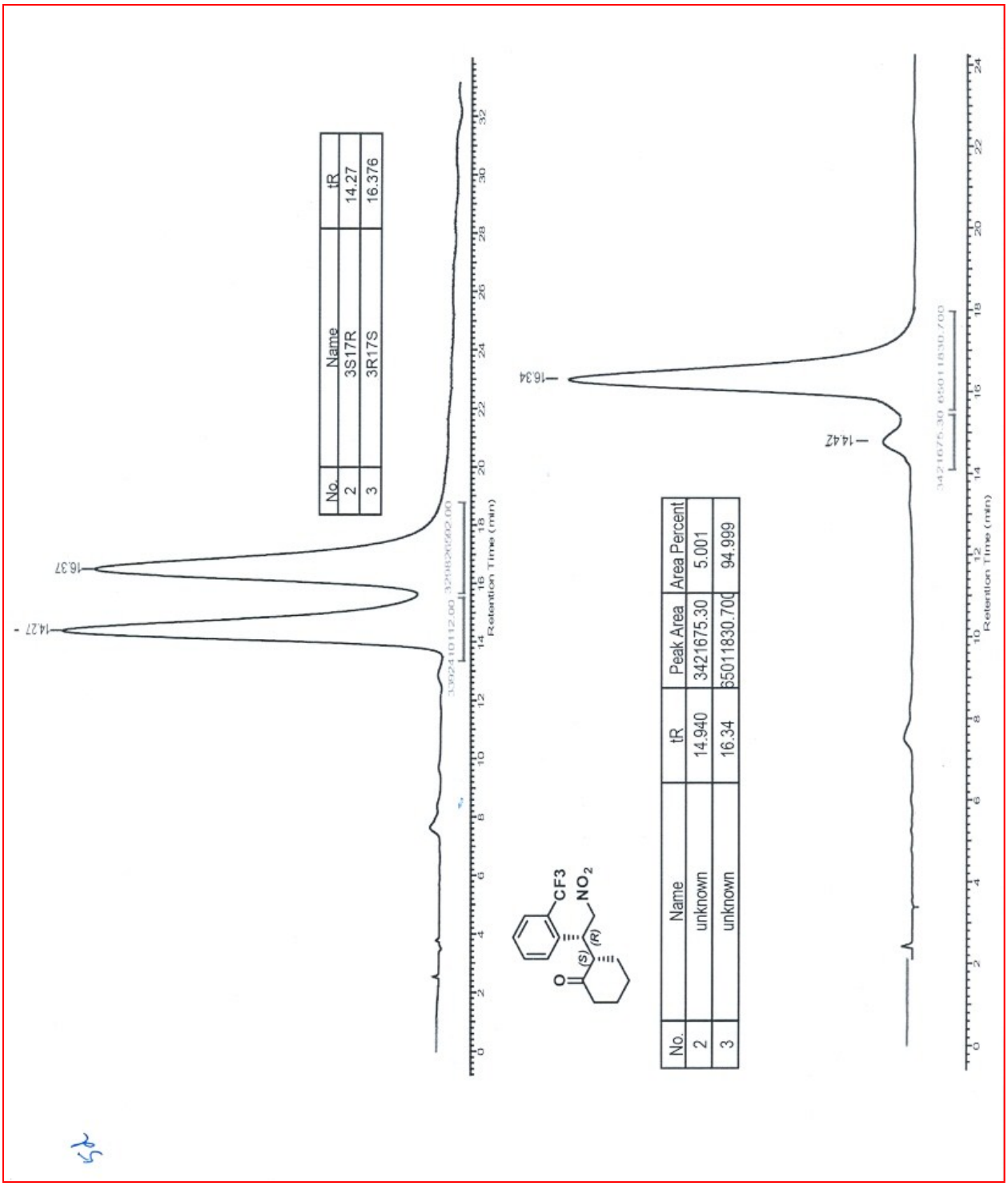
HPL Chromatograph of 5a



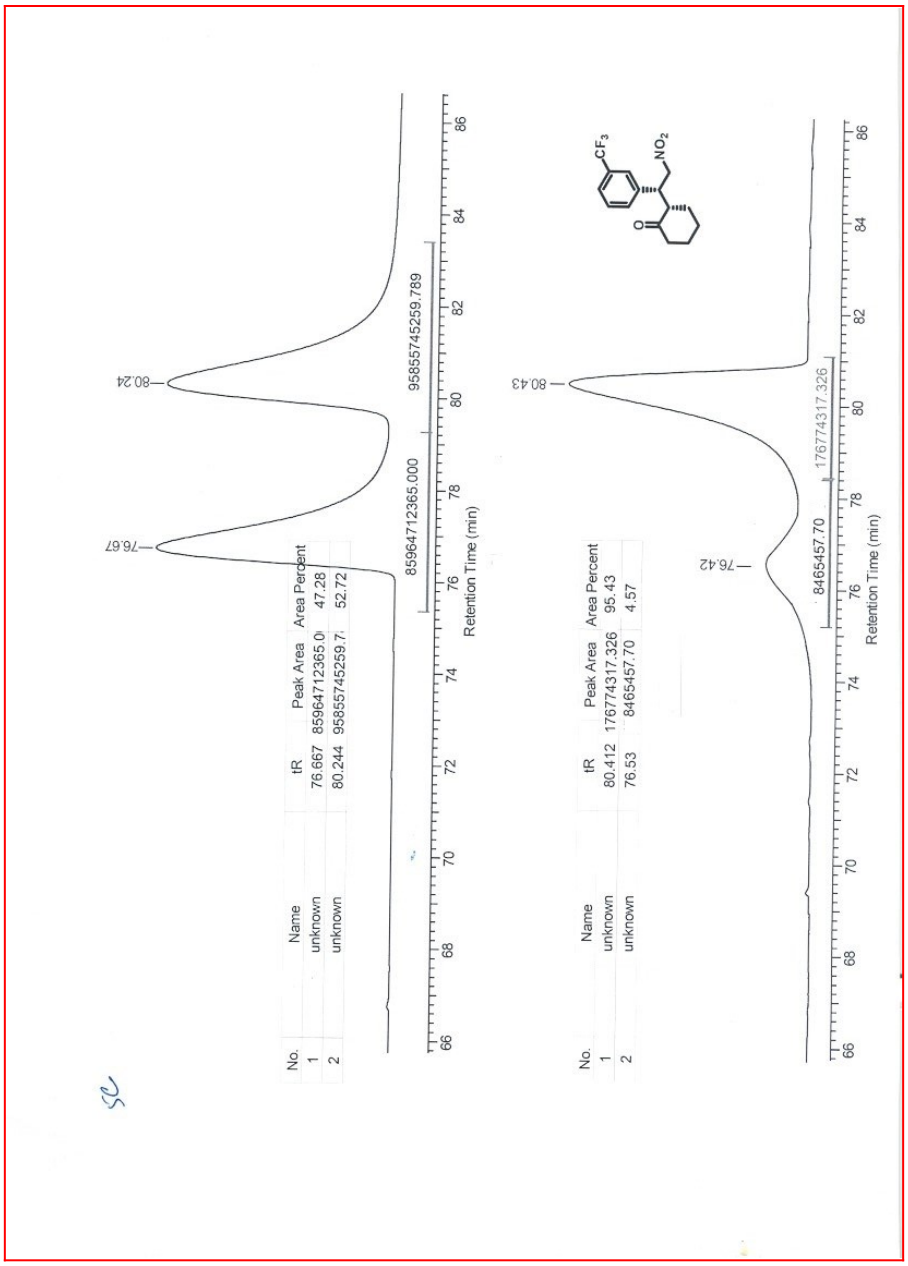
HPL Chromatograph of 5b



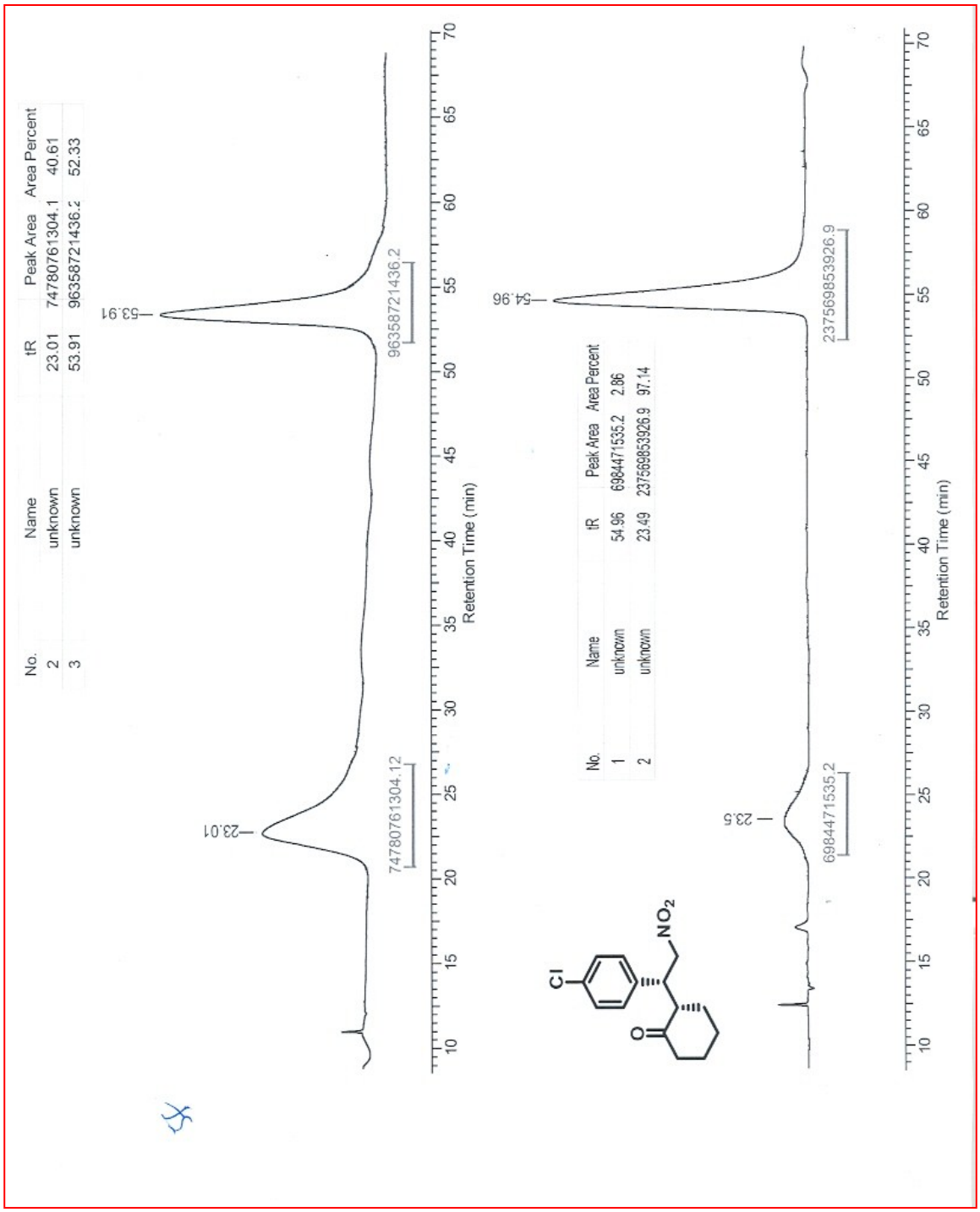
HPL Chromatograph of 5c



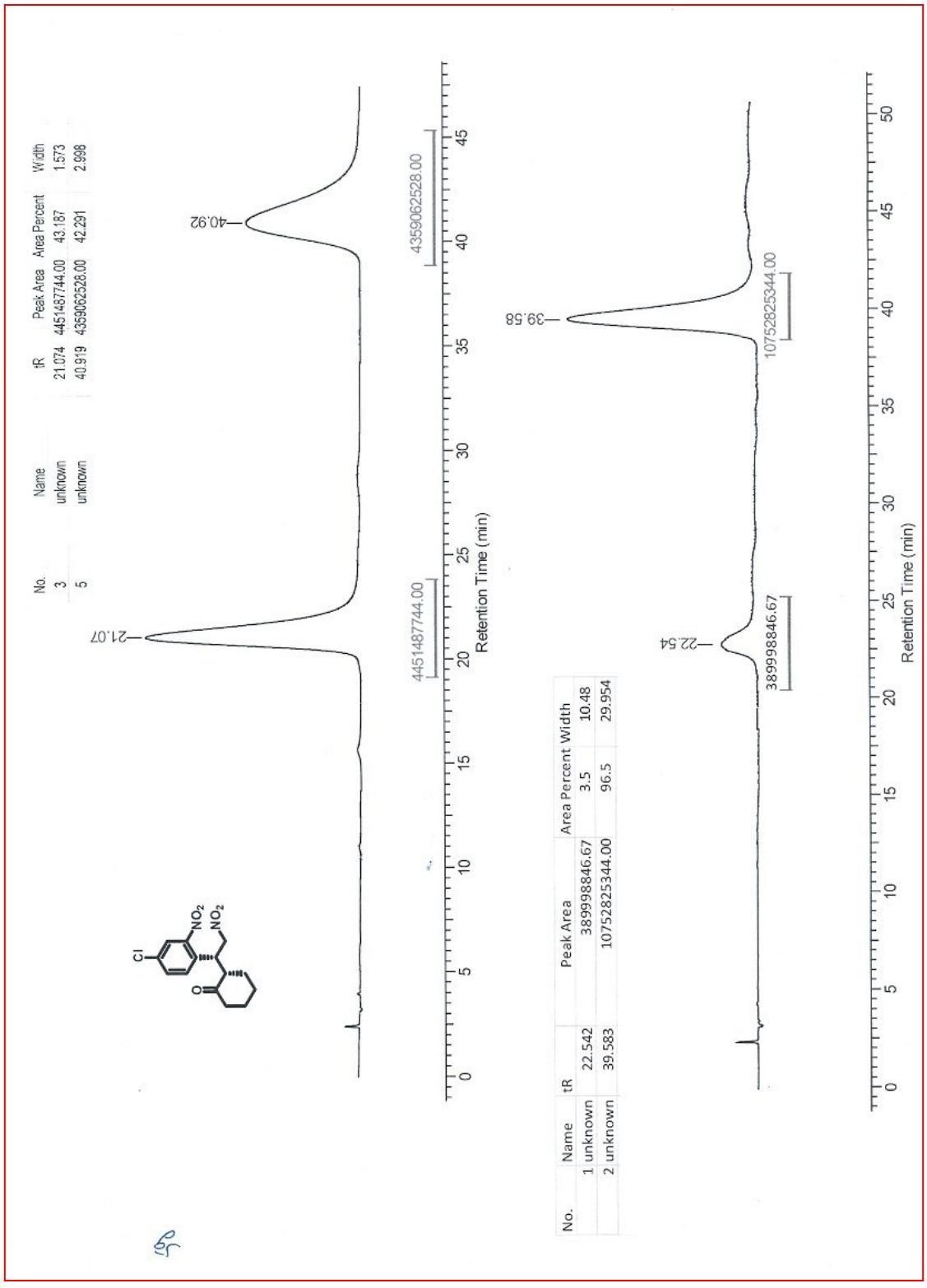
HPL Chromatograph of 5d



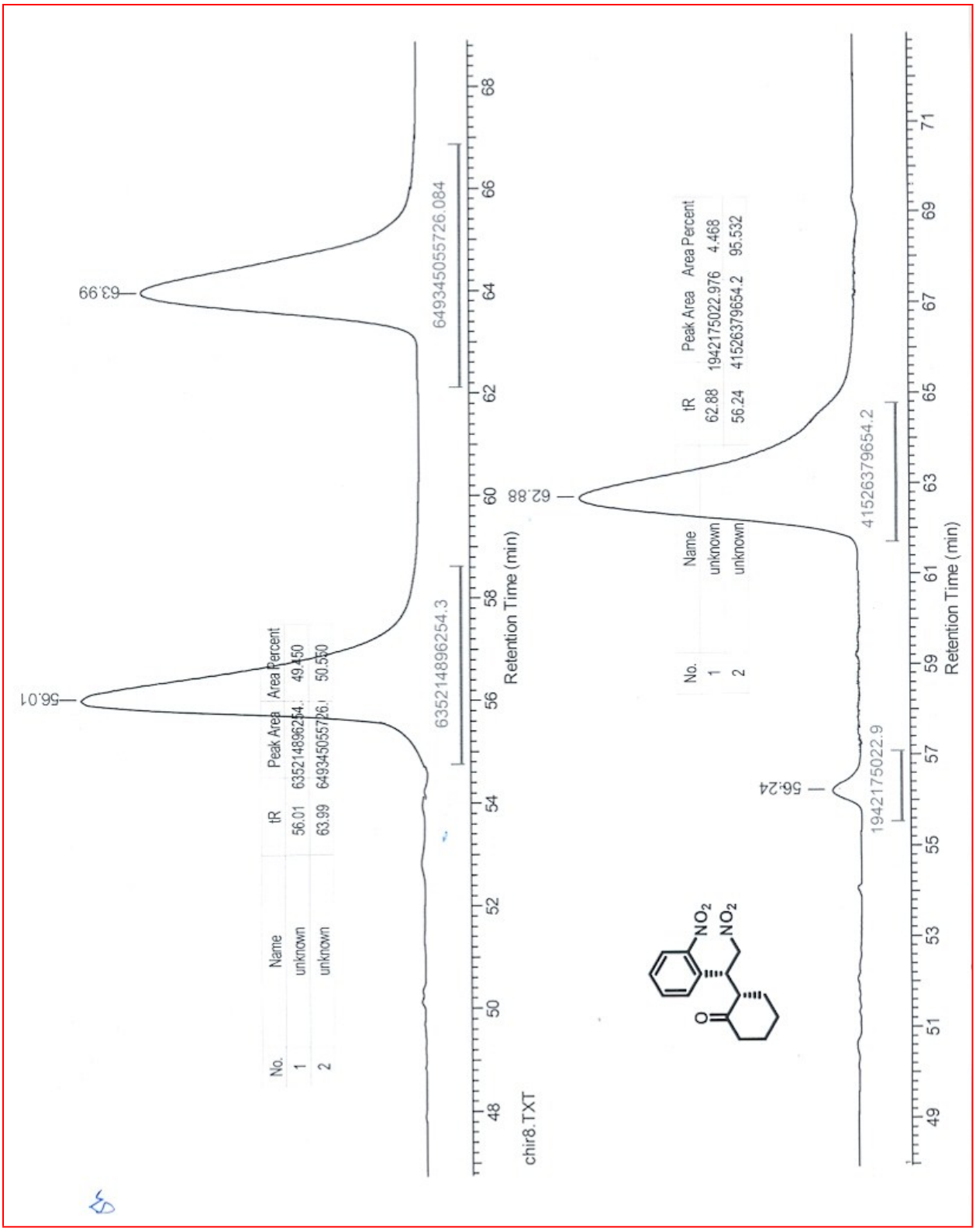
HPL Chromatograph of 5e



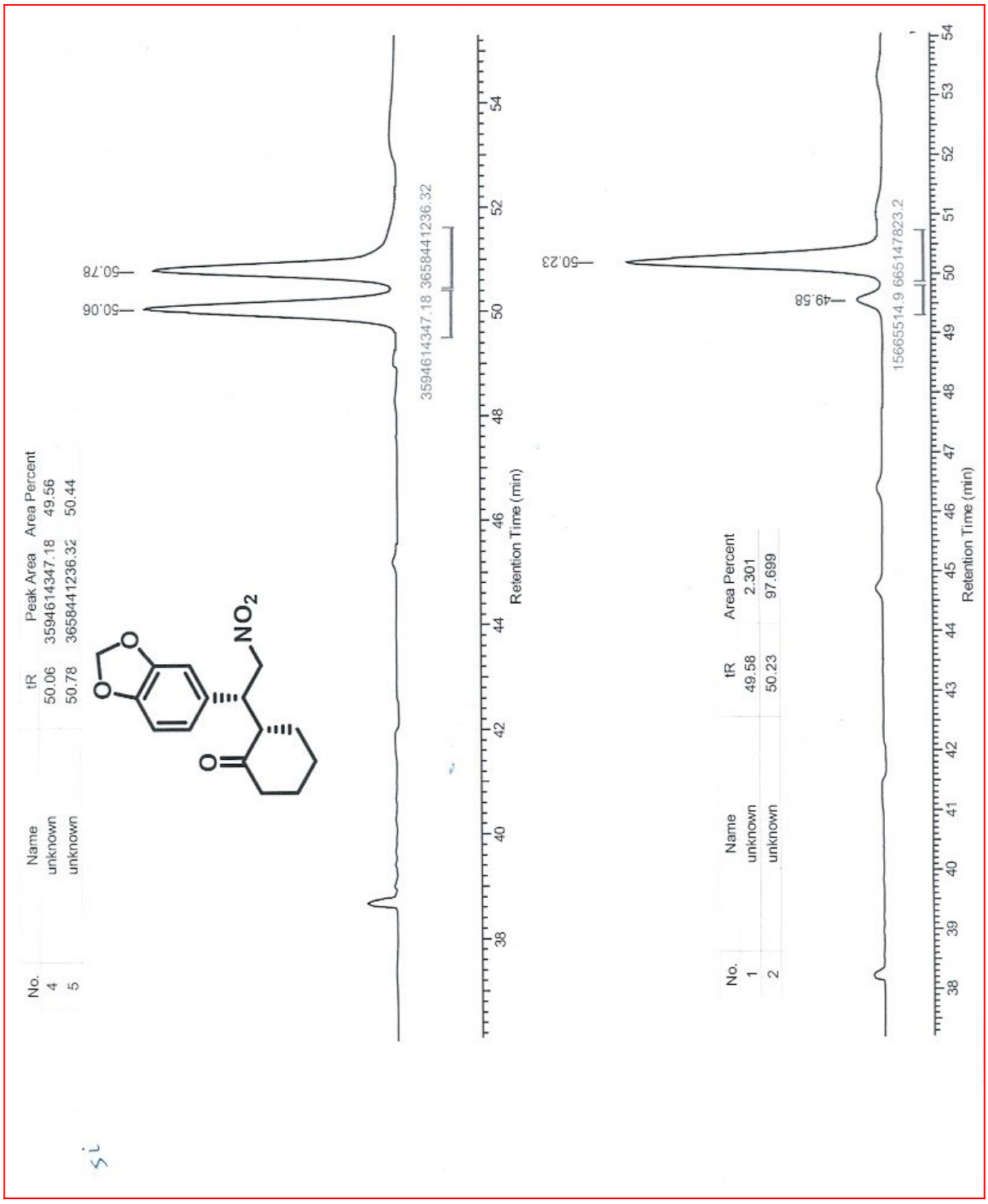
HPL Chromatograph of 5f



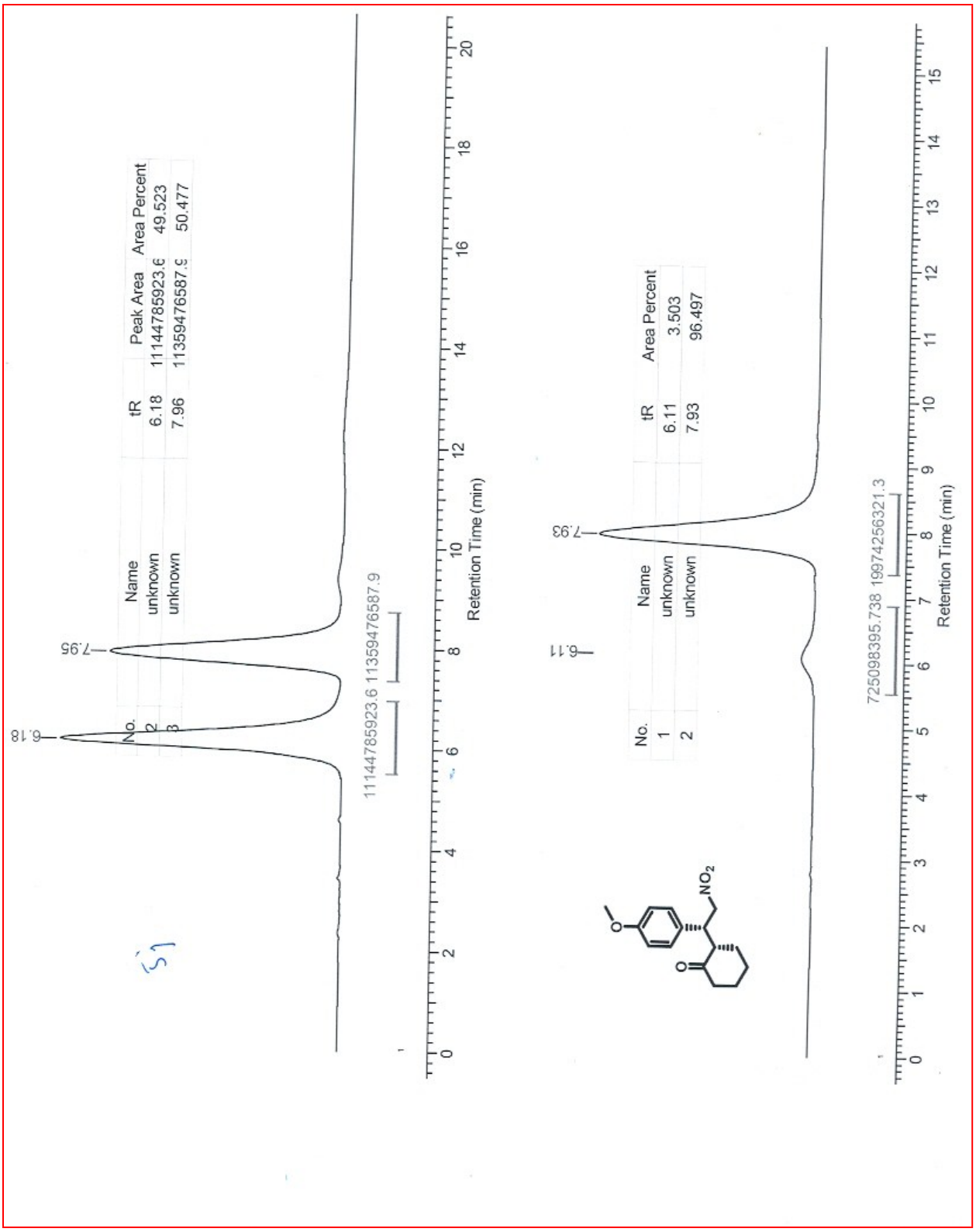
HPL Chromatograph of 5g



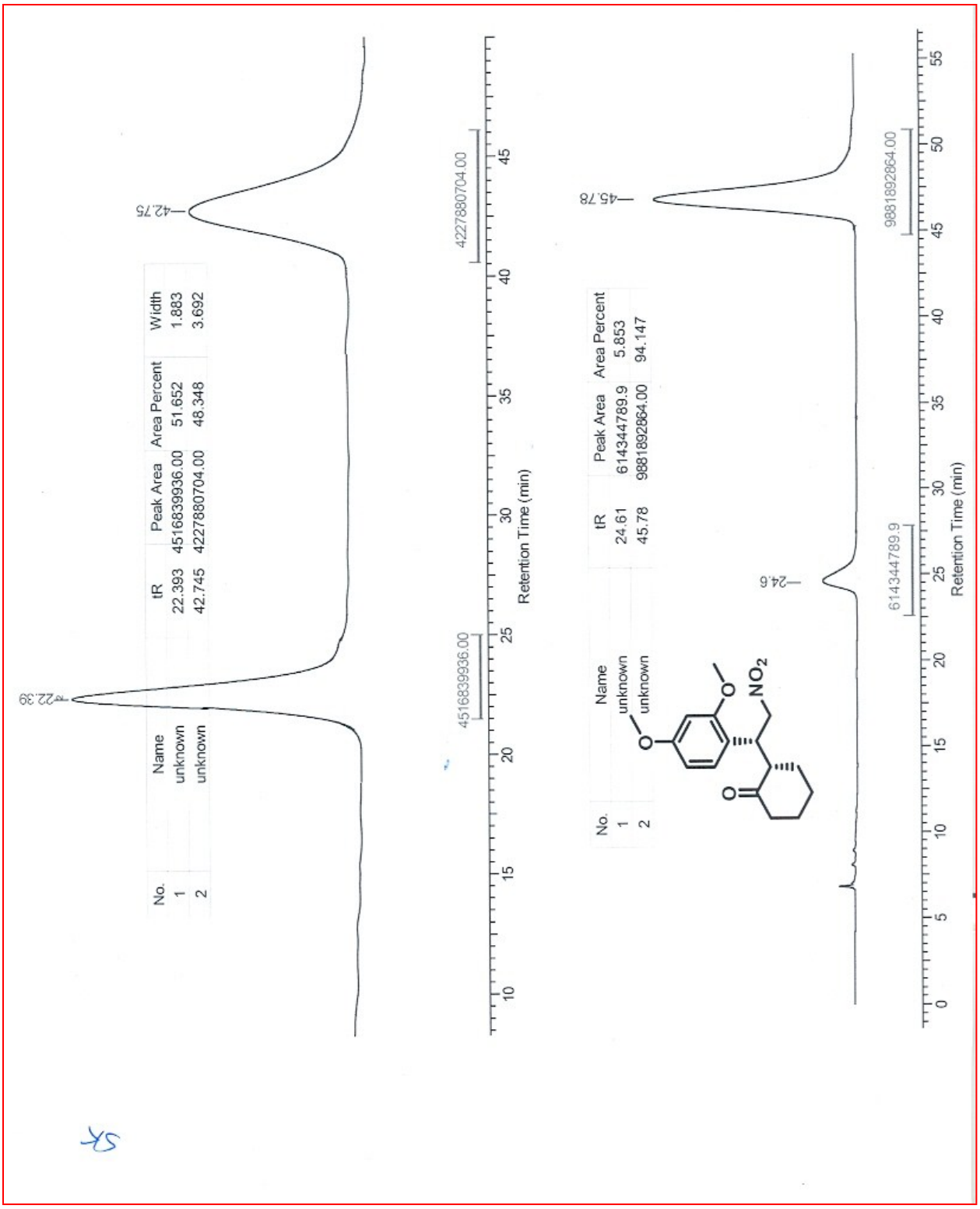
HPL Chromatograph of 5h



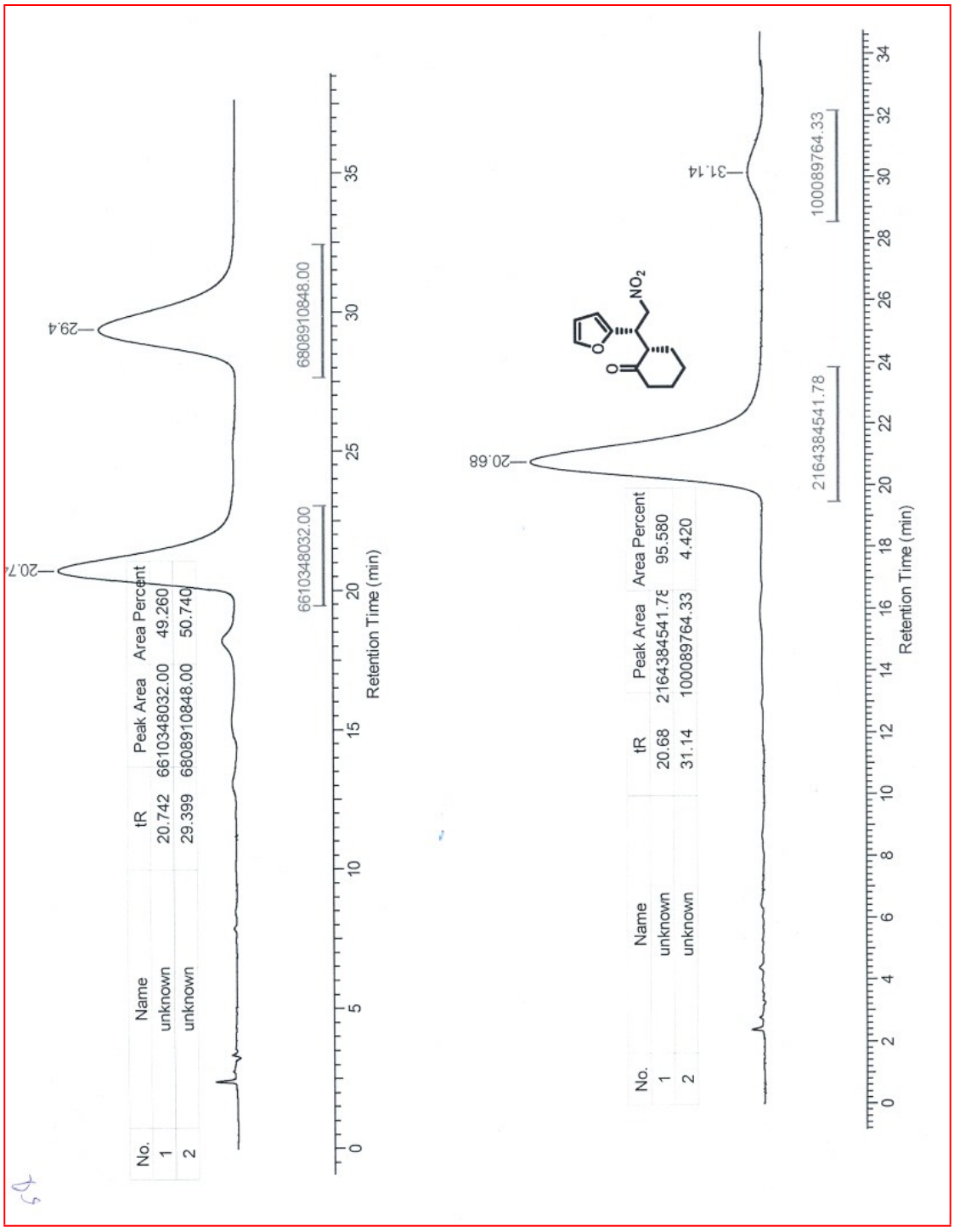
HPL Chromatograph of 5i



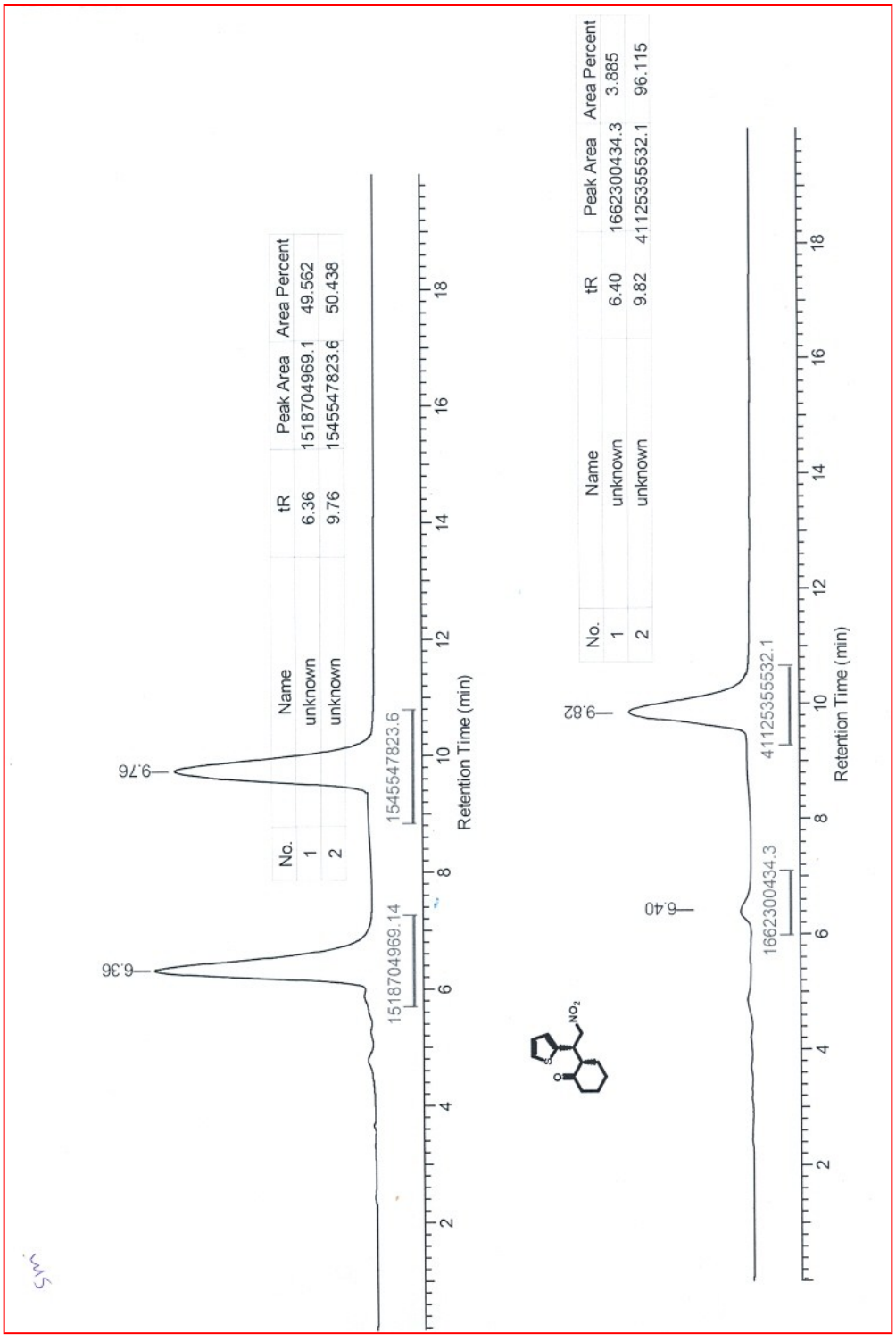
HPL Chromatograph of 5j



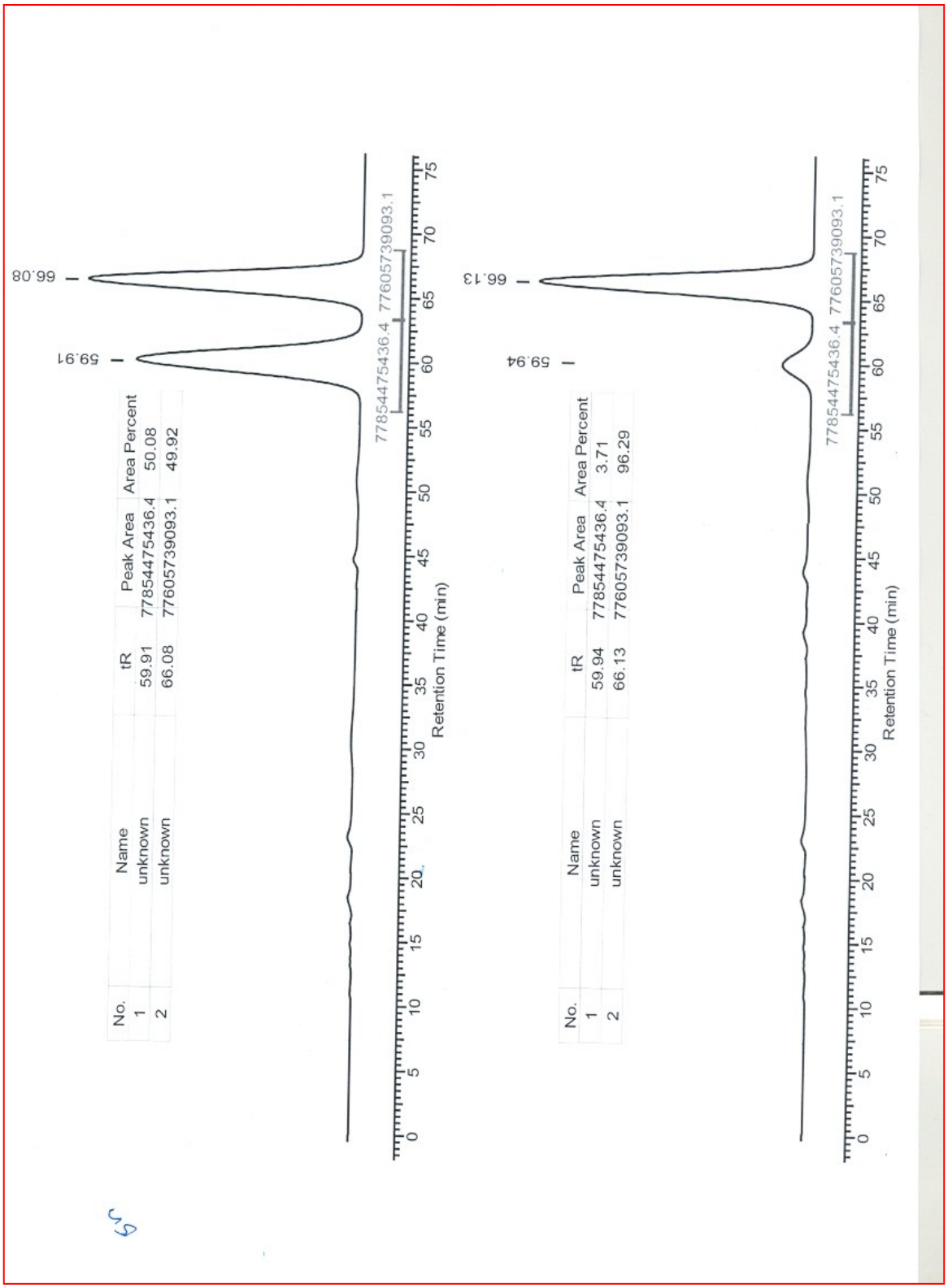
HPL Chromatograph of 5k



HPL Chromatograph of 5l



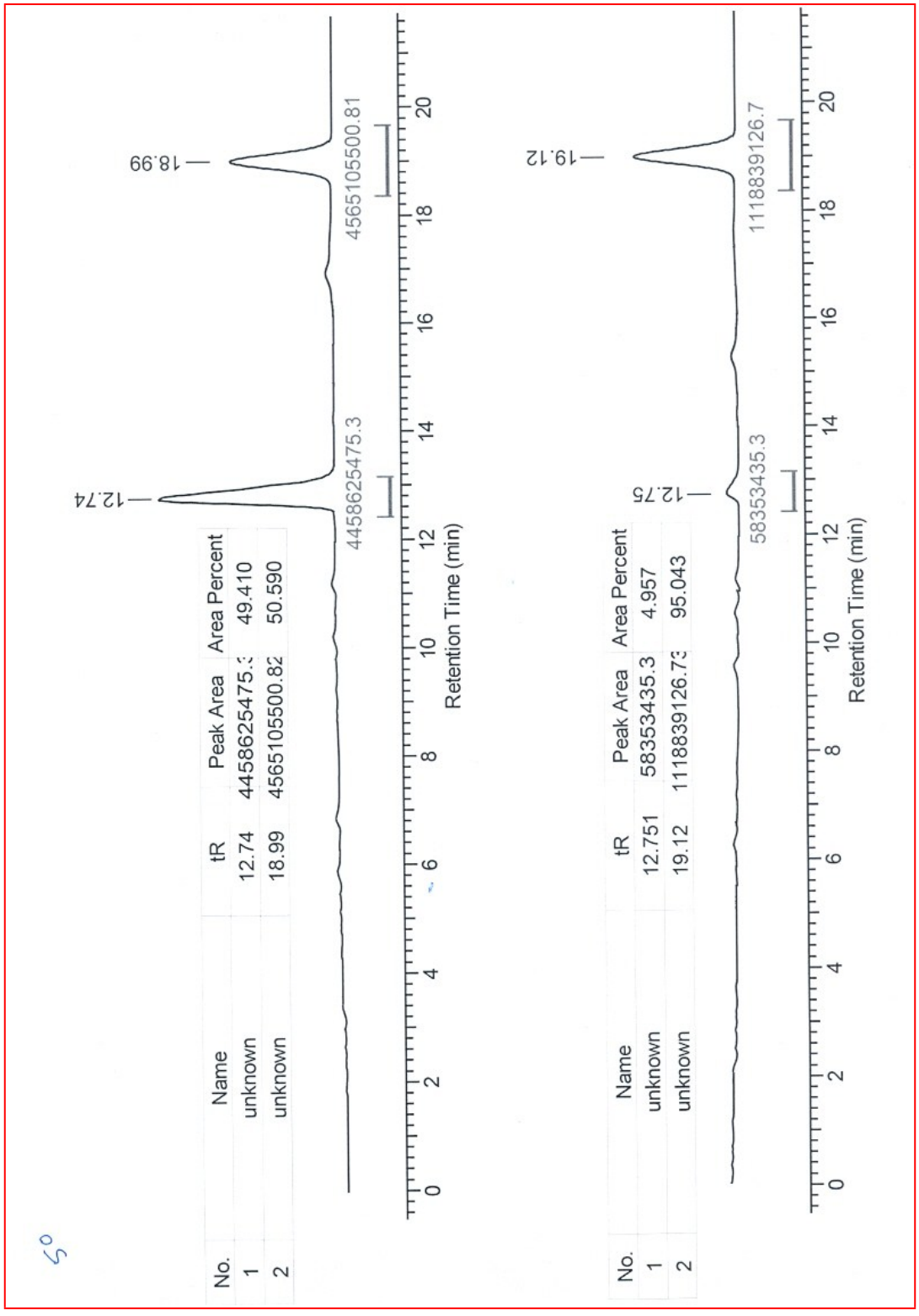
HPL Chromatograph of 5m



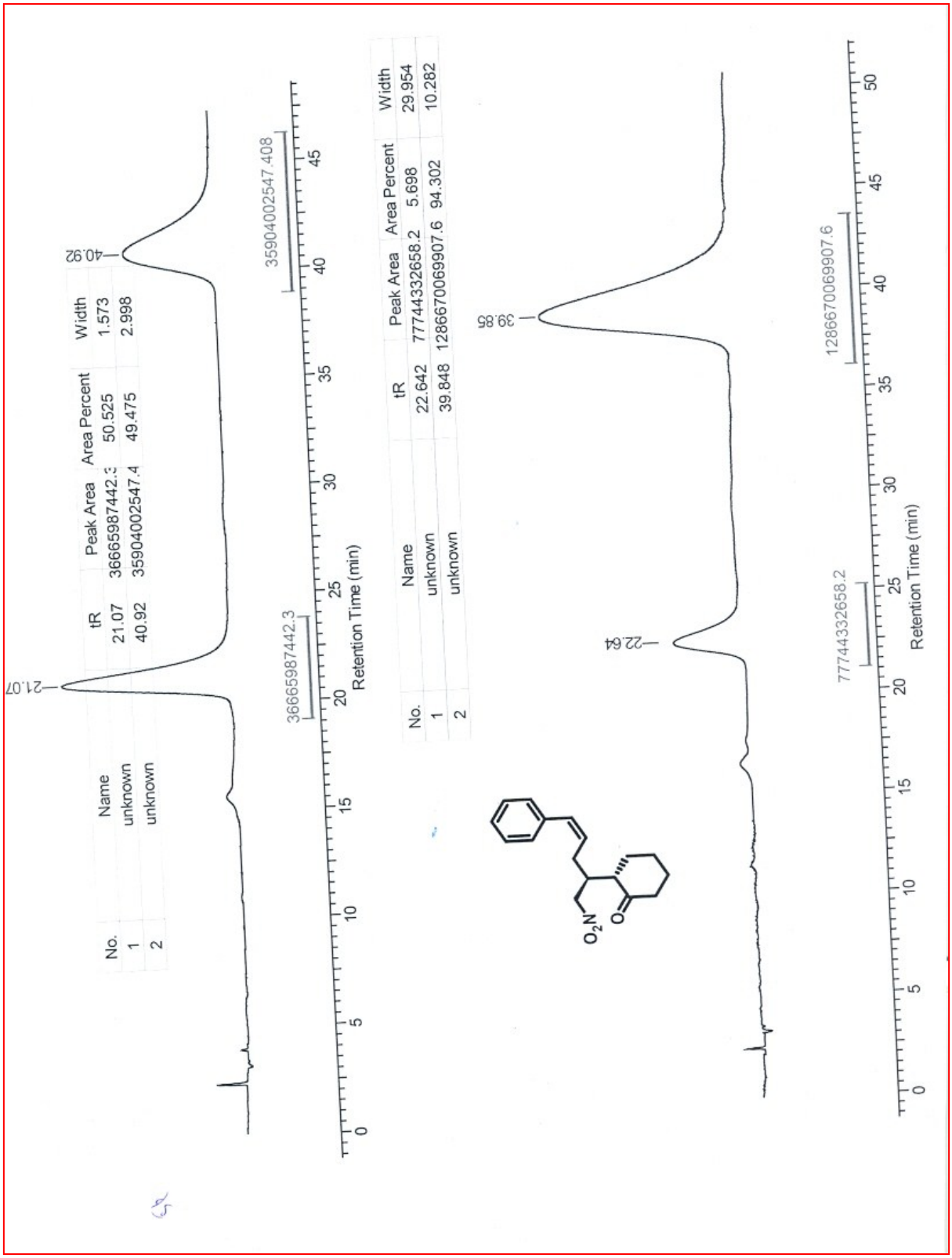
No.	Name	tR	Peak Area	Area Percent
1	unknown	59.91	77854475436.4	50.08
2	unknown	66.08	77605739093.1	49.92

No.	Name	tR	Peak Area	Area Percent
1	unknown	59.94	77854475436.4	3.71
2	unknown	66.13	77605739093.1	96.29

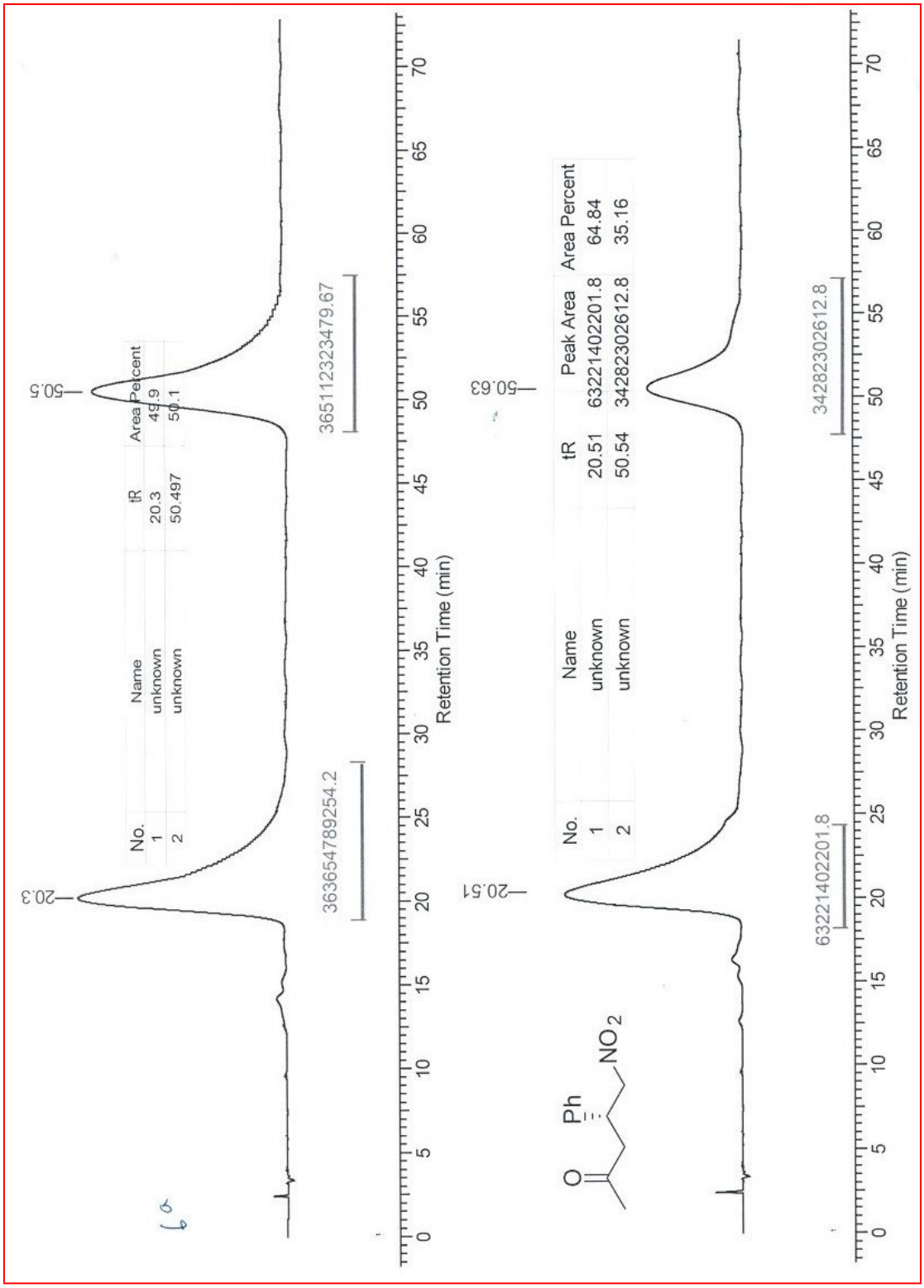
HPL Chromatograph of 5n



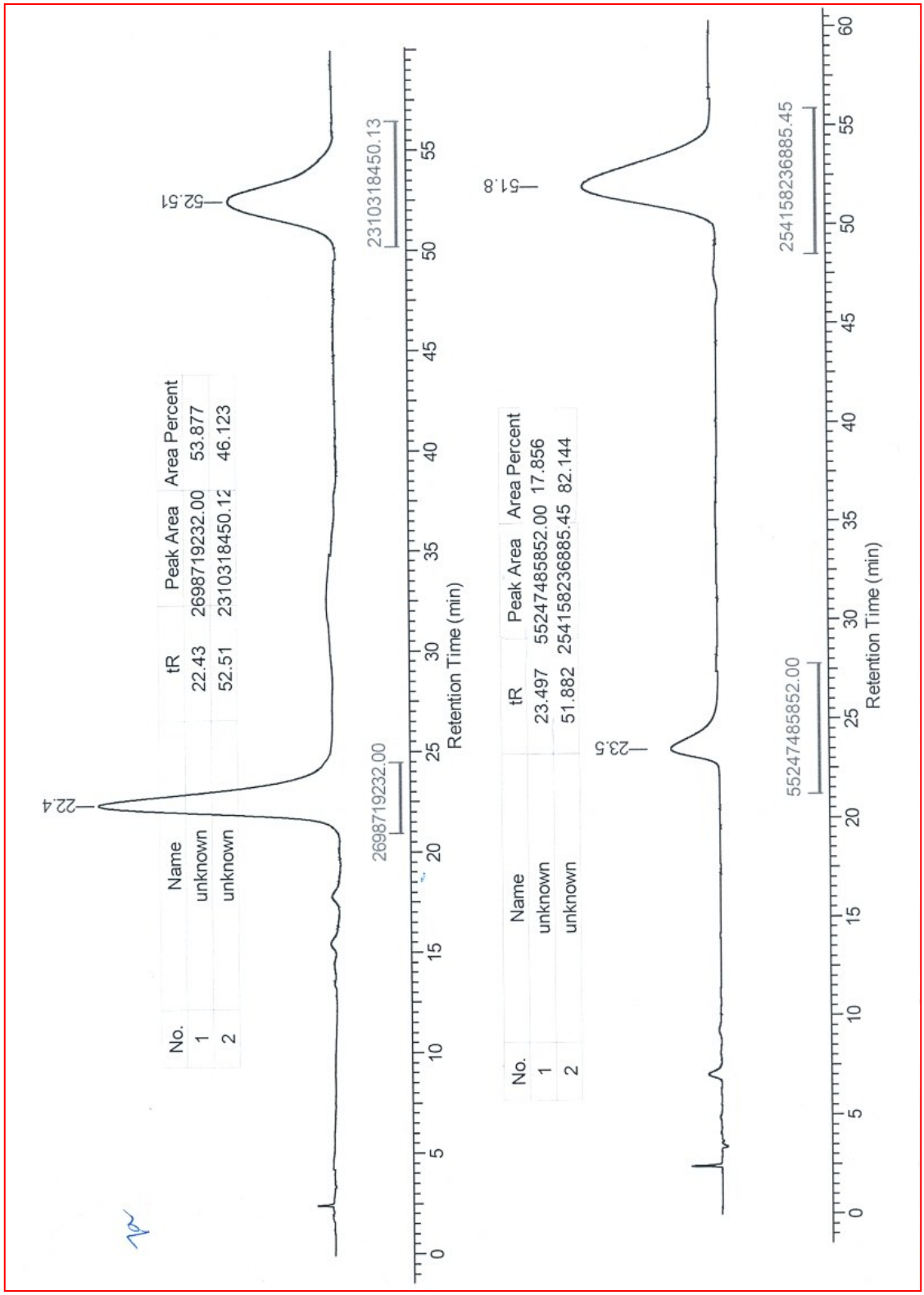
HPL Chromatograph of 5o



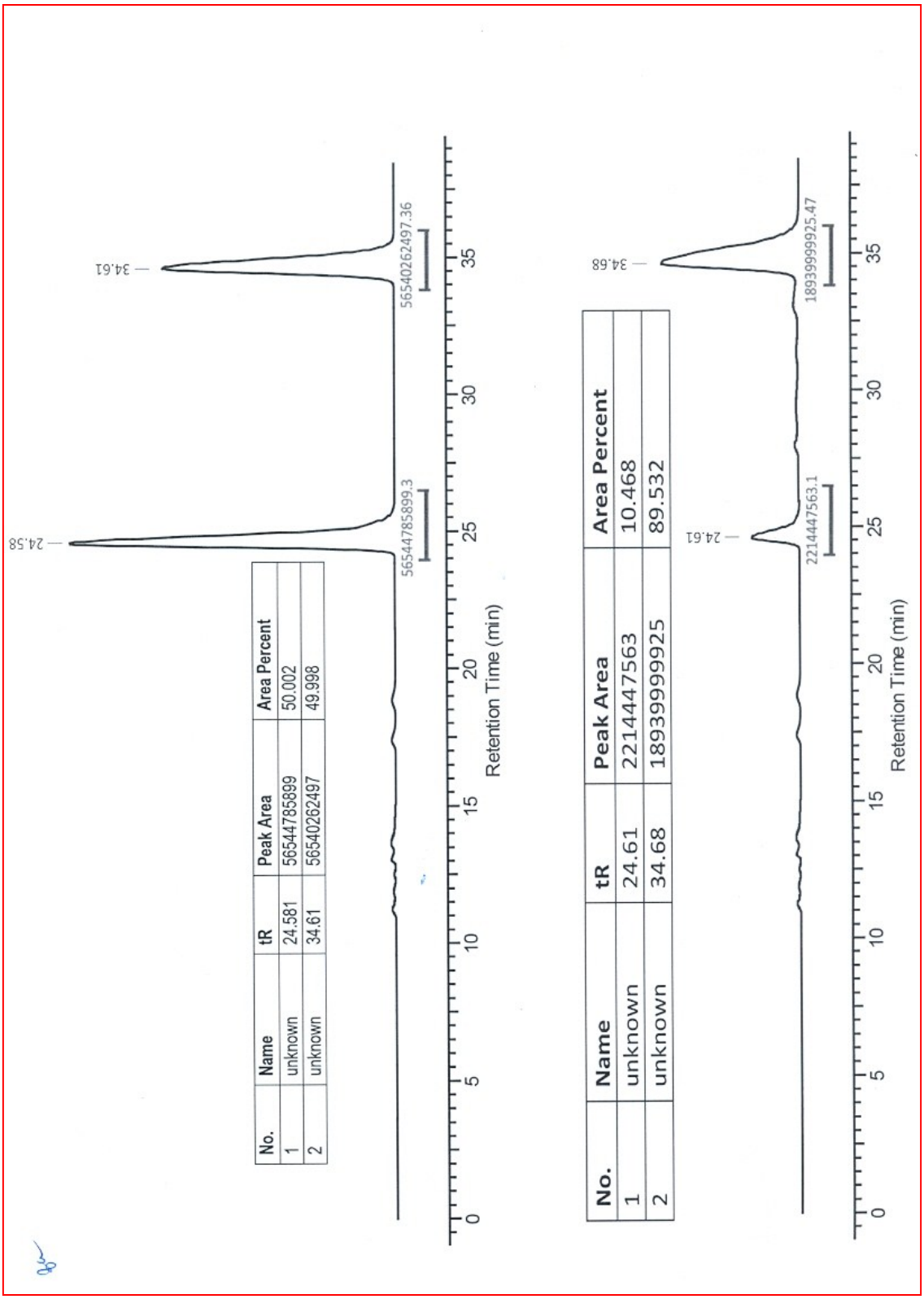
HPL Chromatograph of 5p



HPL Chromatograph of 6a



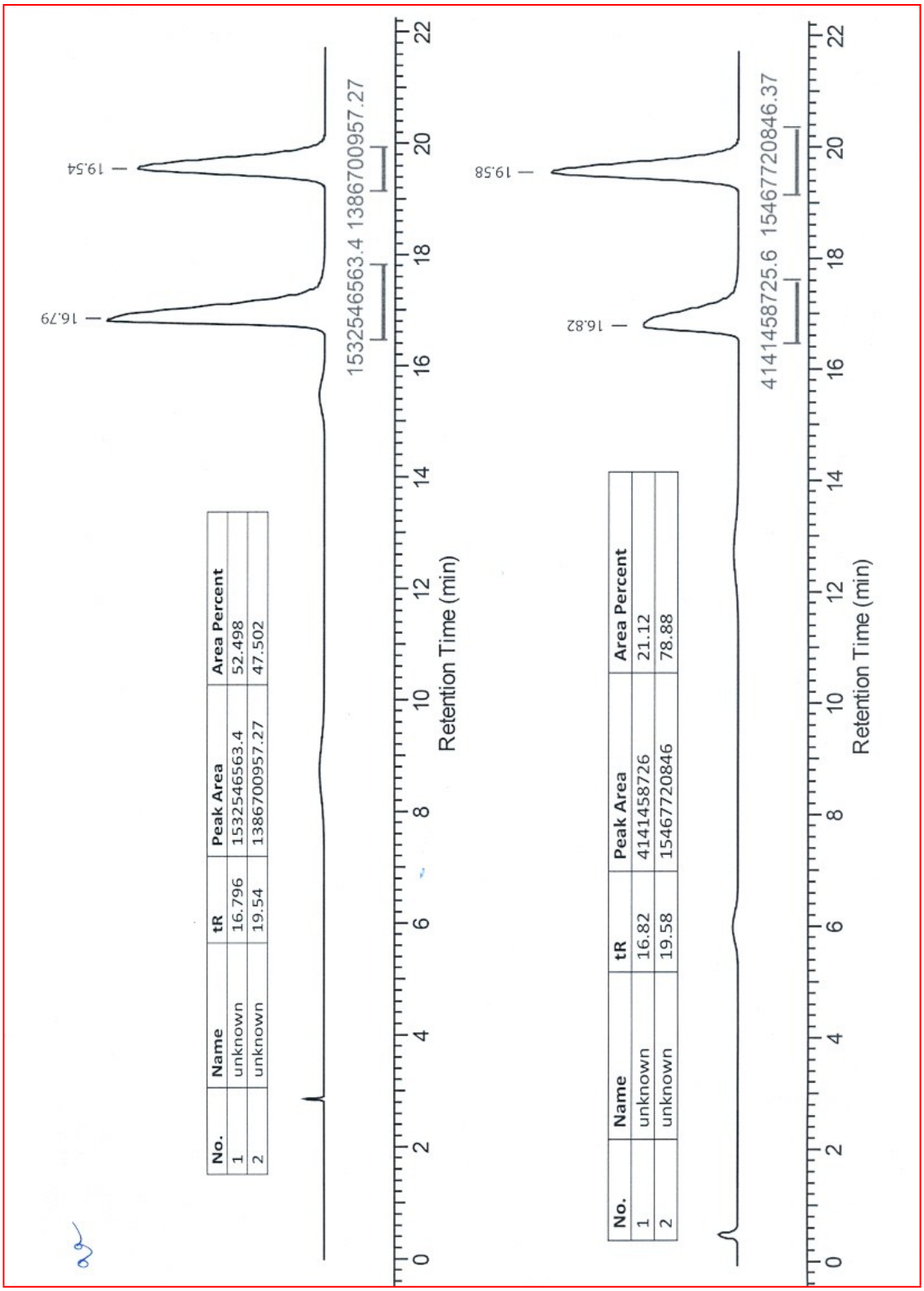
HPL Chromatograph of 7b



No.	Name	tR	Peak Area	Area Percent
1	unknown	24.581	56544785899	50.002
2	unknown	34.61	56540262497	49.998

No.	Name	tR	Peak Area	Area Percent
1	unknown	24.61	2214447563	10.468
2	unknown	34.68	18939999925	89.532

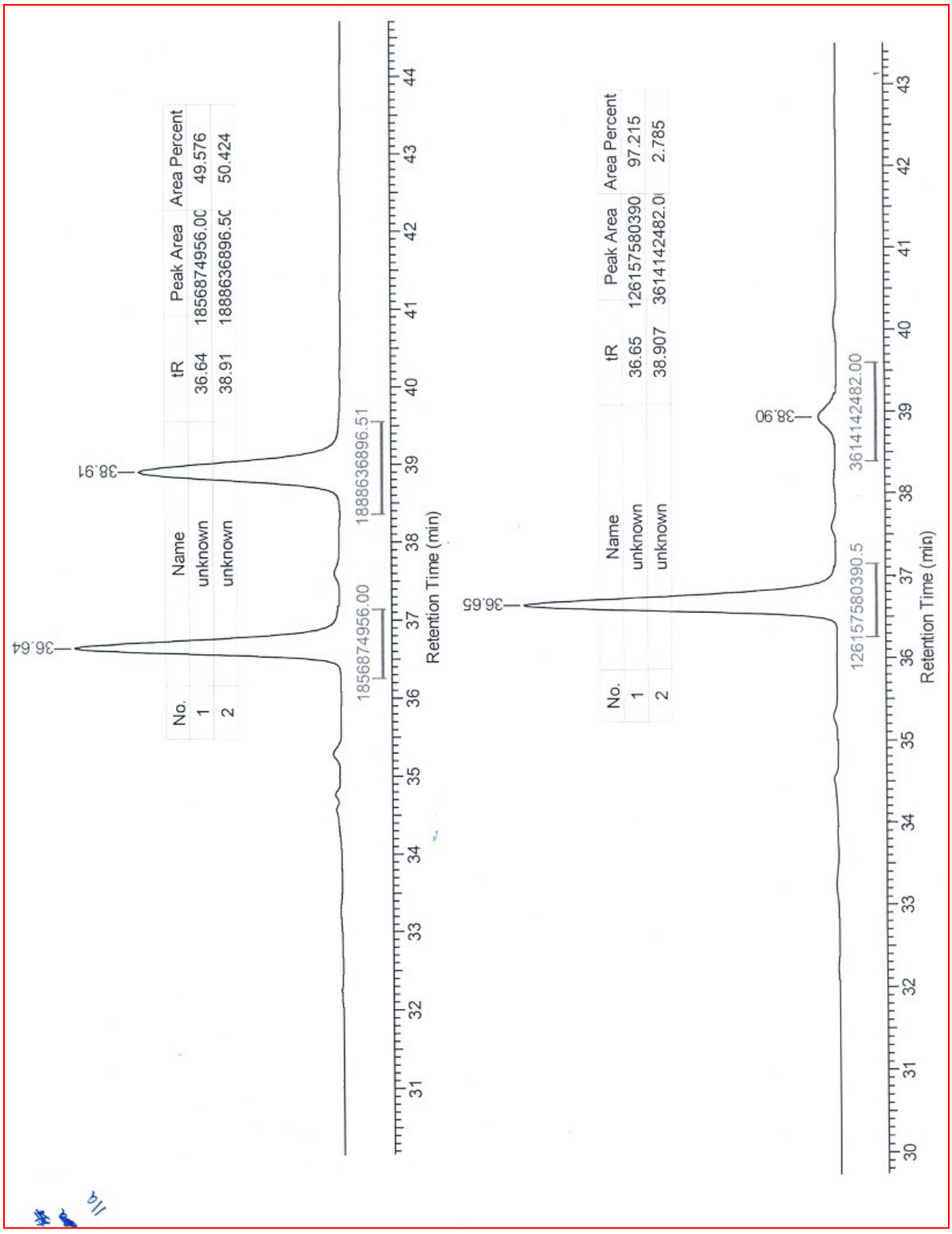
HPL Chromatograph of 8a



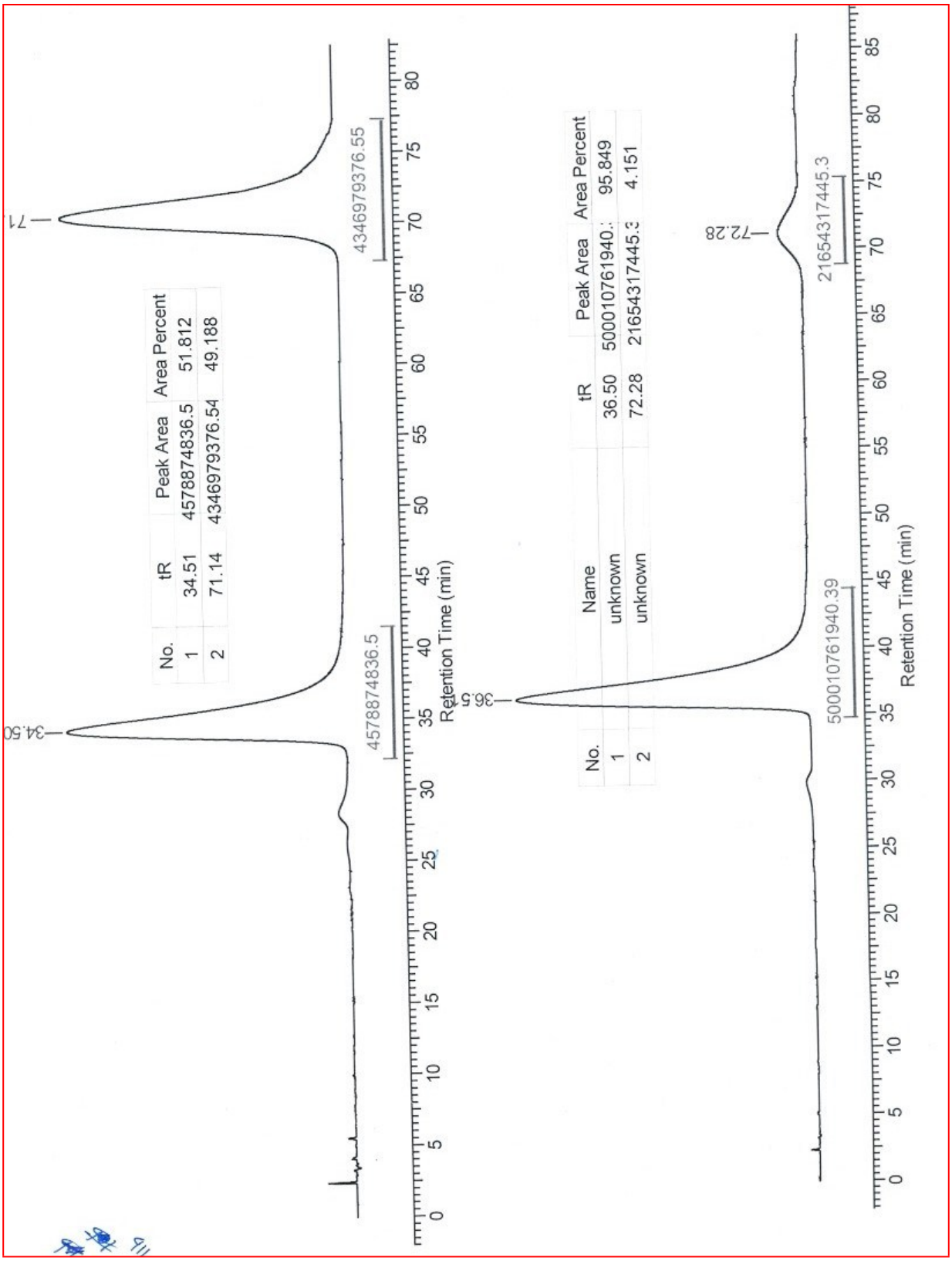
No.	Name	tR	Peak Area	Area Percent
1	unknown	16.796	1532546563.4	52.498
2	unknown	19.54	1386700957.27	47.502

No.	Name	tR	Peak Area	Area Percent
1	unknown	16.82	4141458726	21.12
2	unknown	19.58	15467720846	78.88

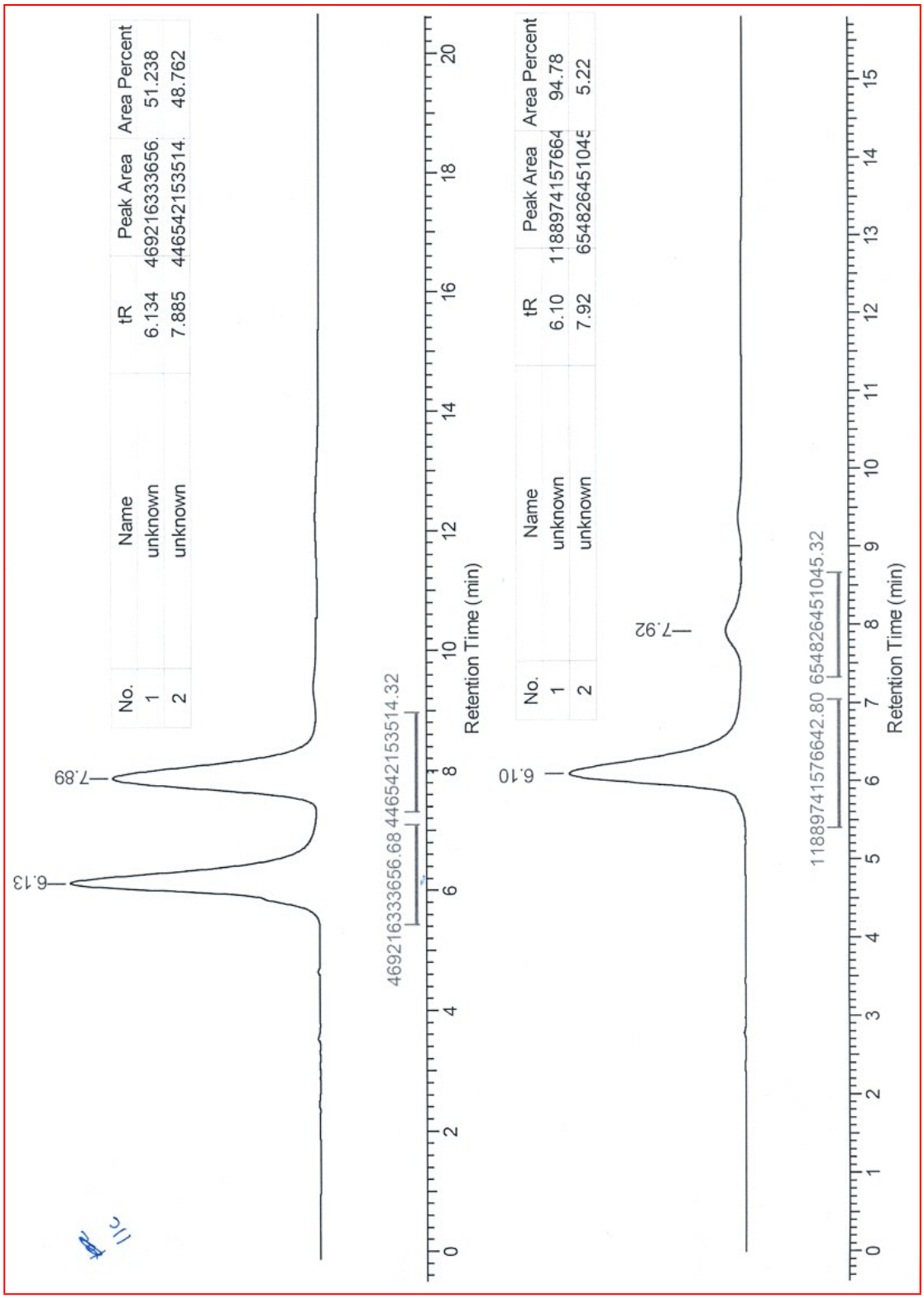
HPL Chromatograph of 9a



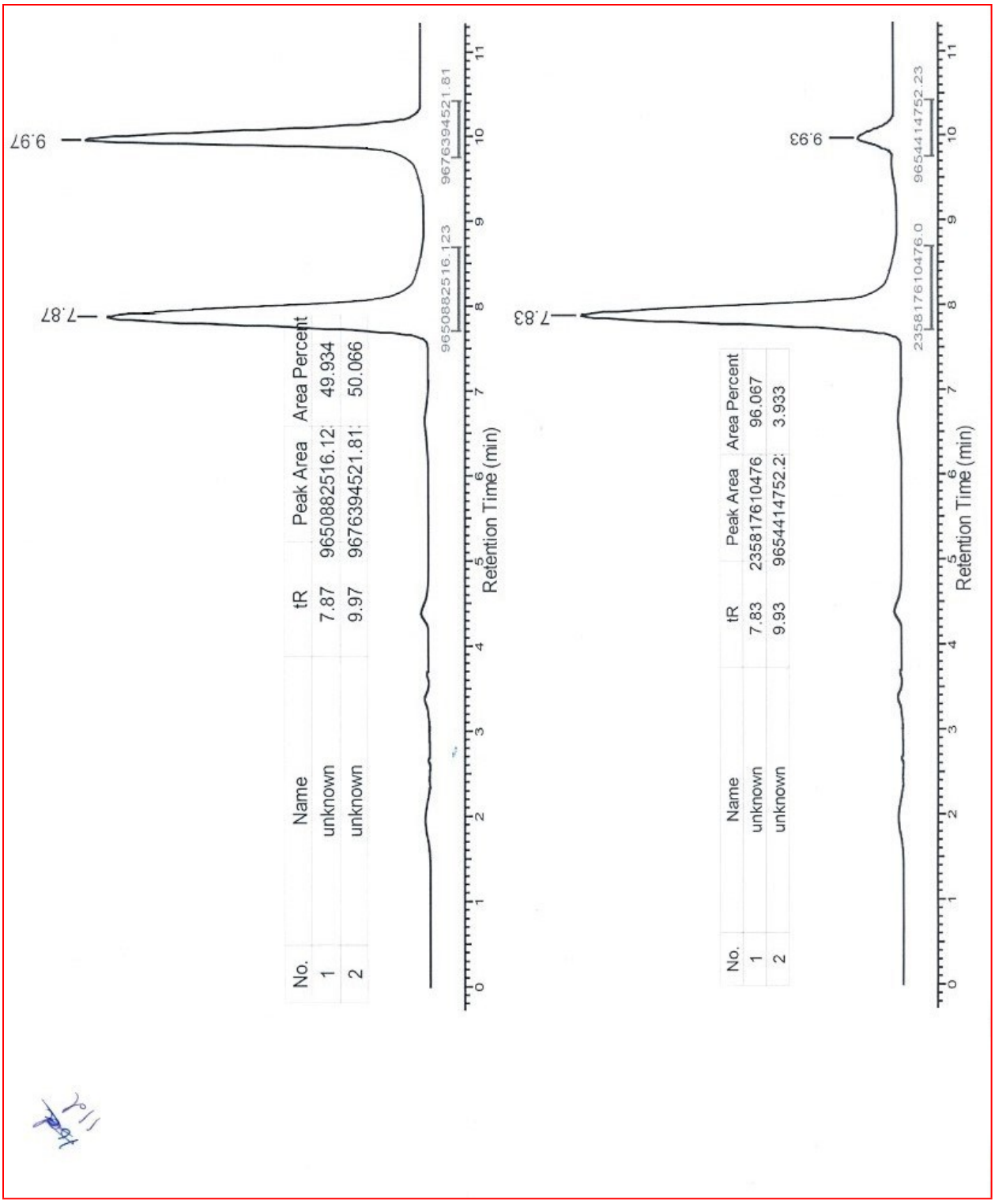
HPL Chromatograph of 11a



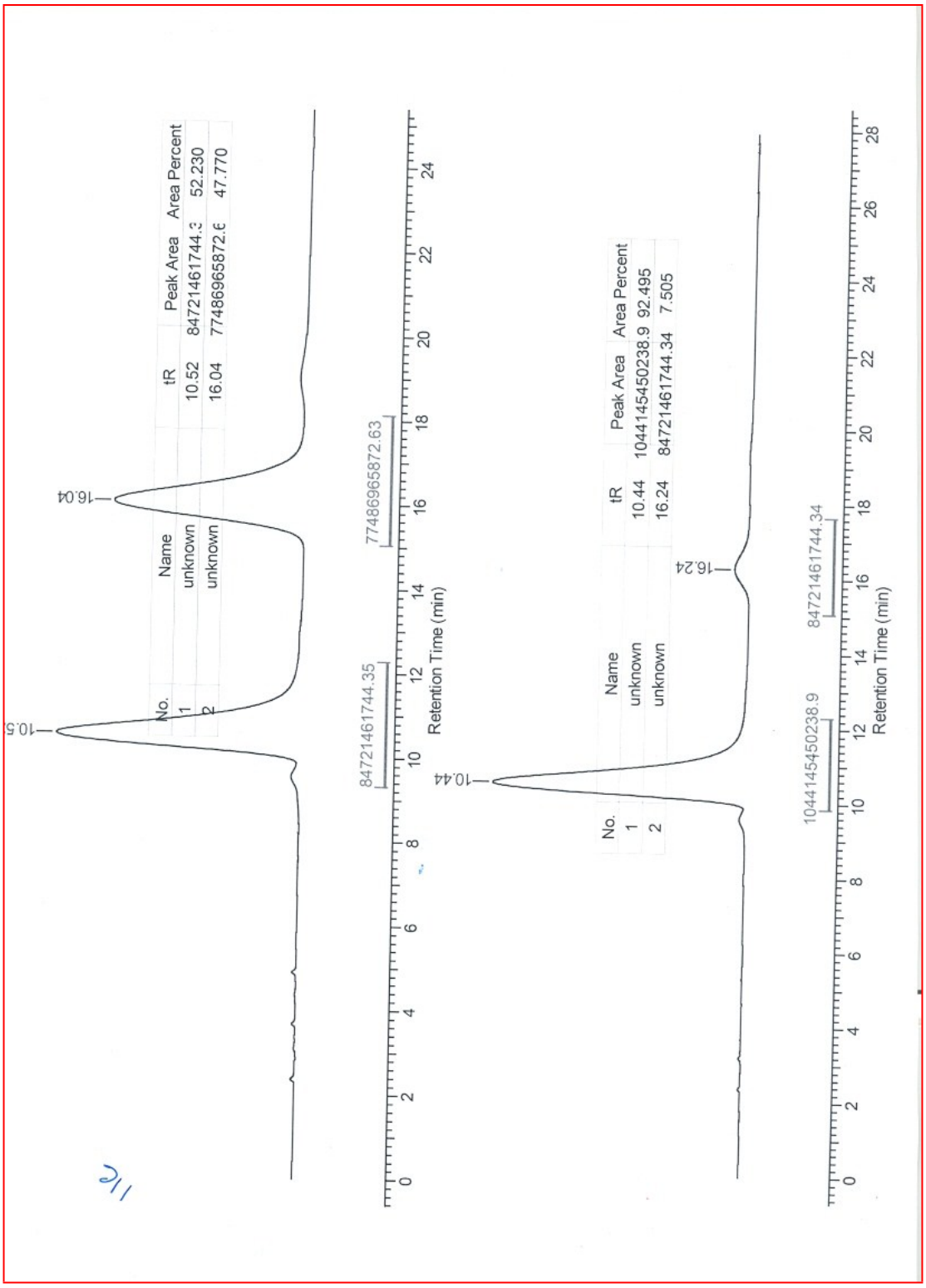
HPL Chromatograph of 11b



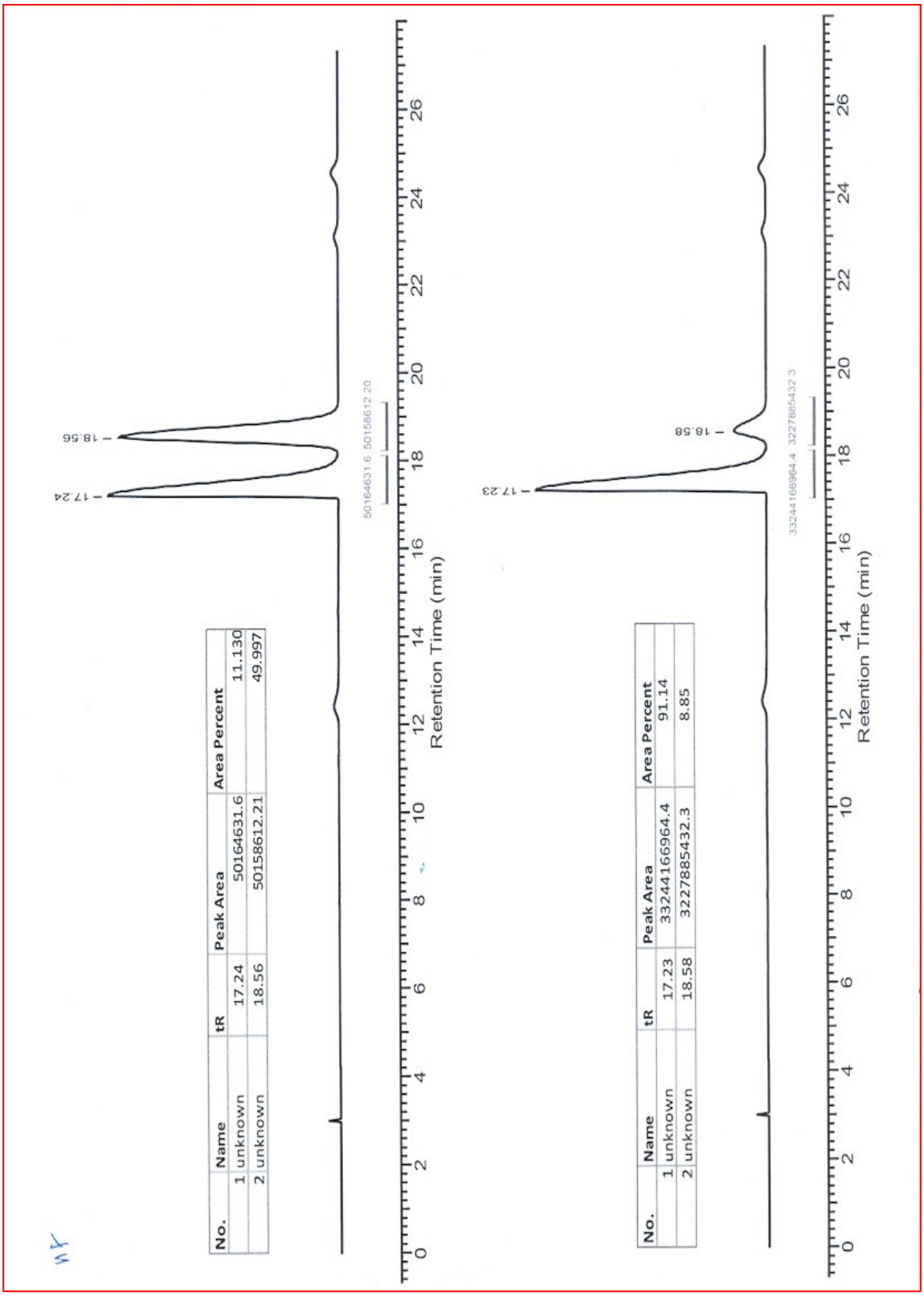
HPL Chromatograph of 11c



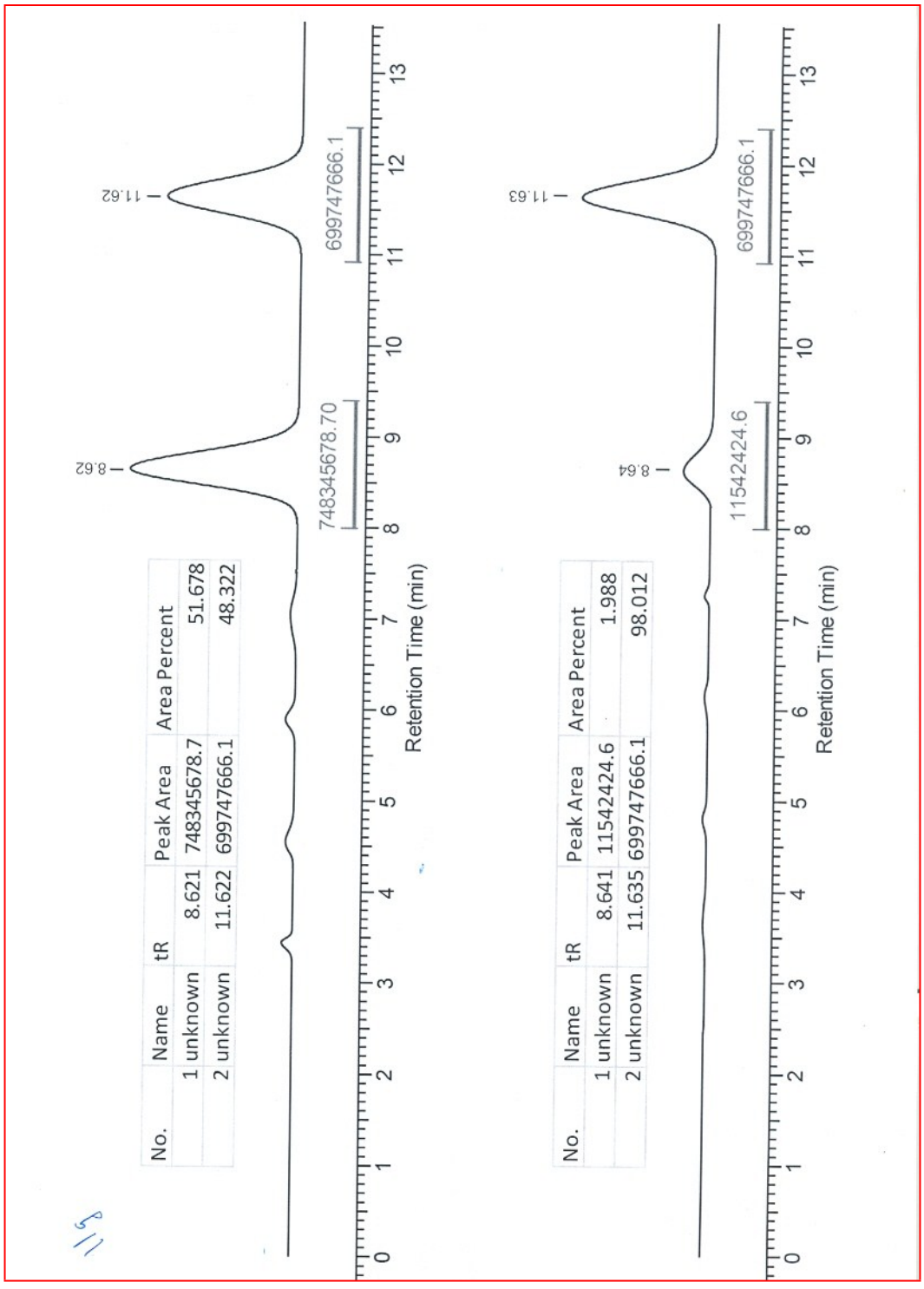
HPL Chromatograph of 11d



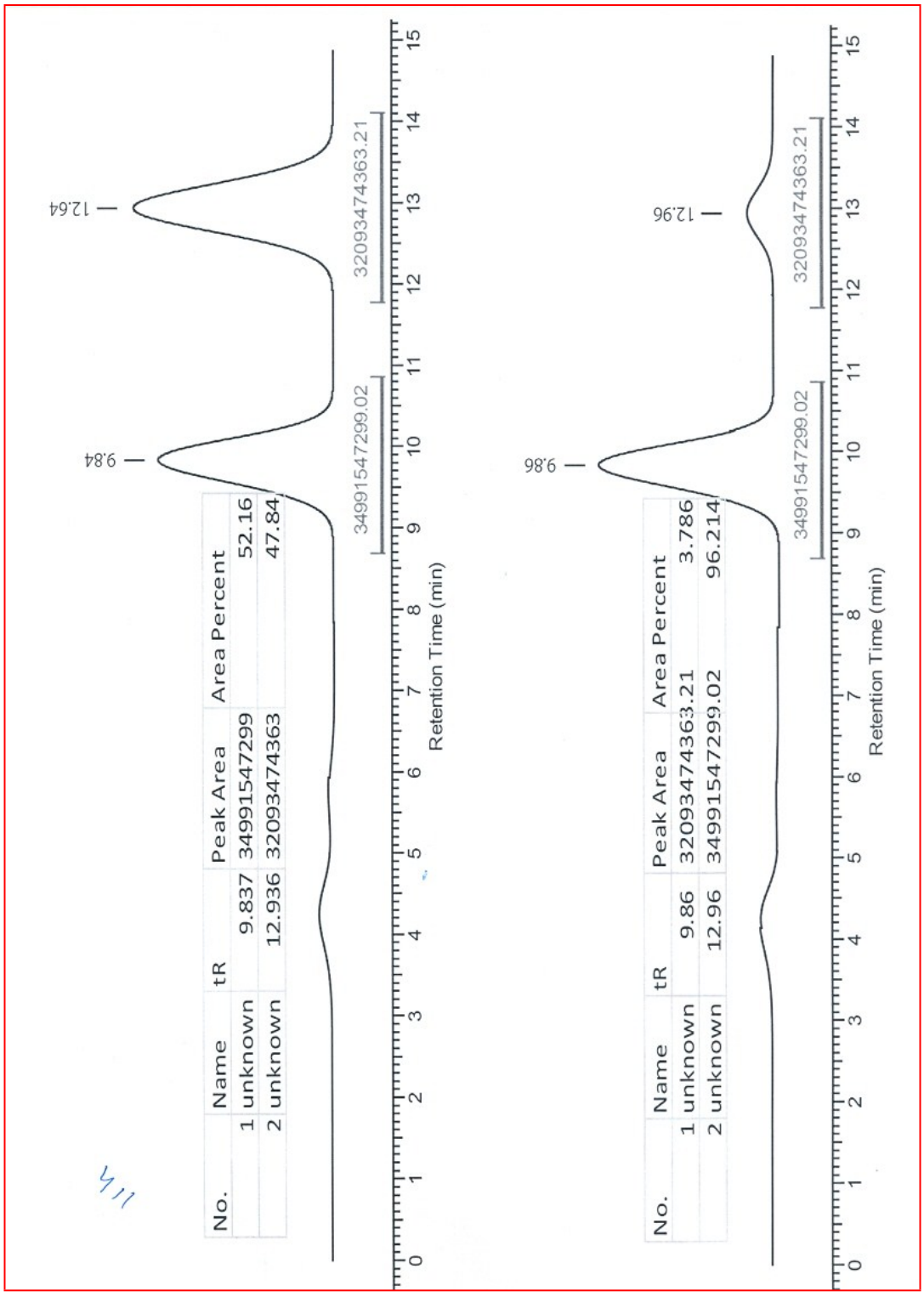
HPL Chromatograph of 11e



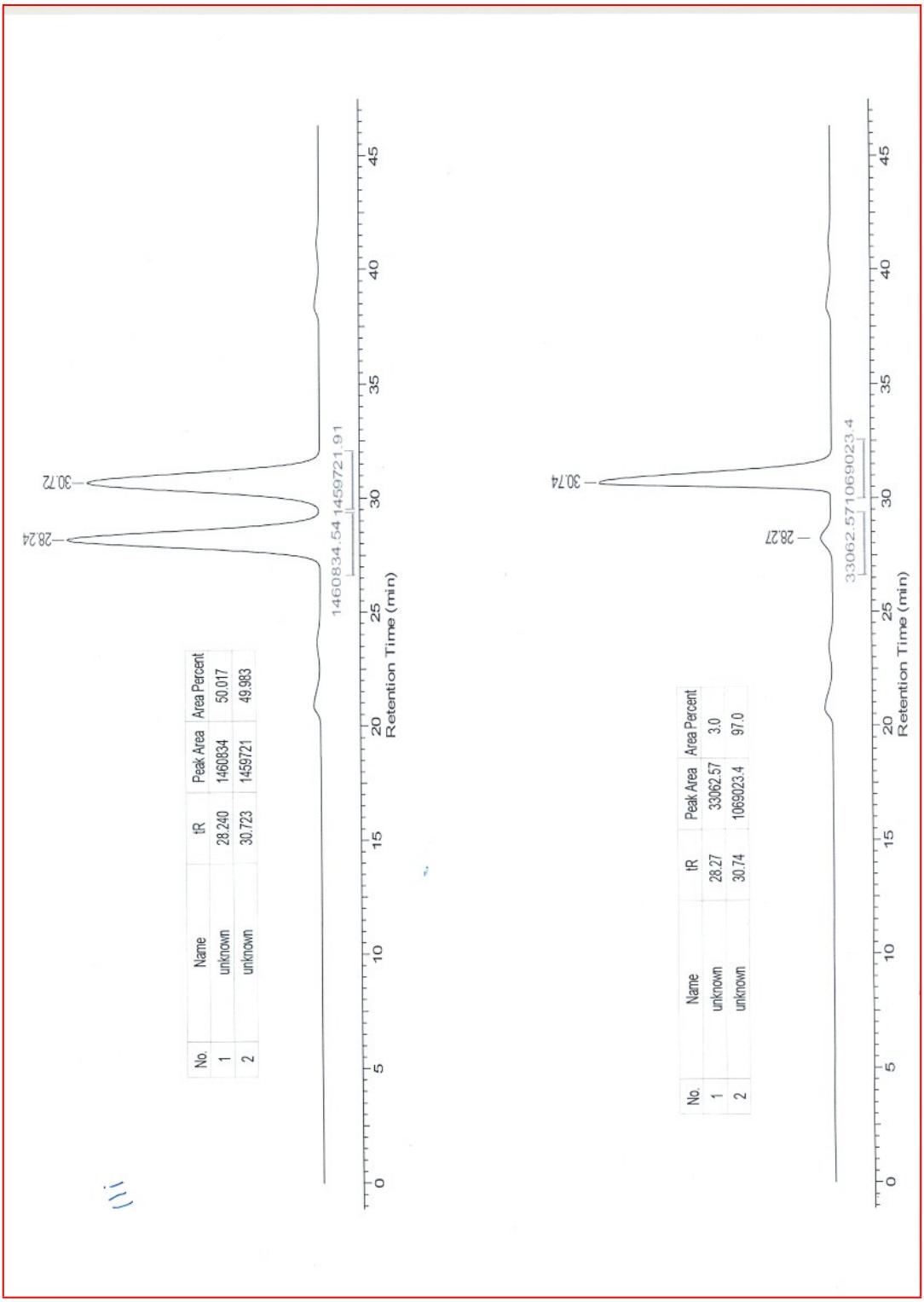
HPL Chromatograph of 11f



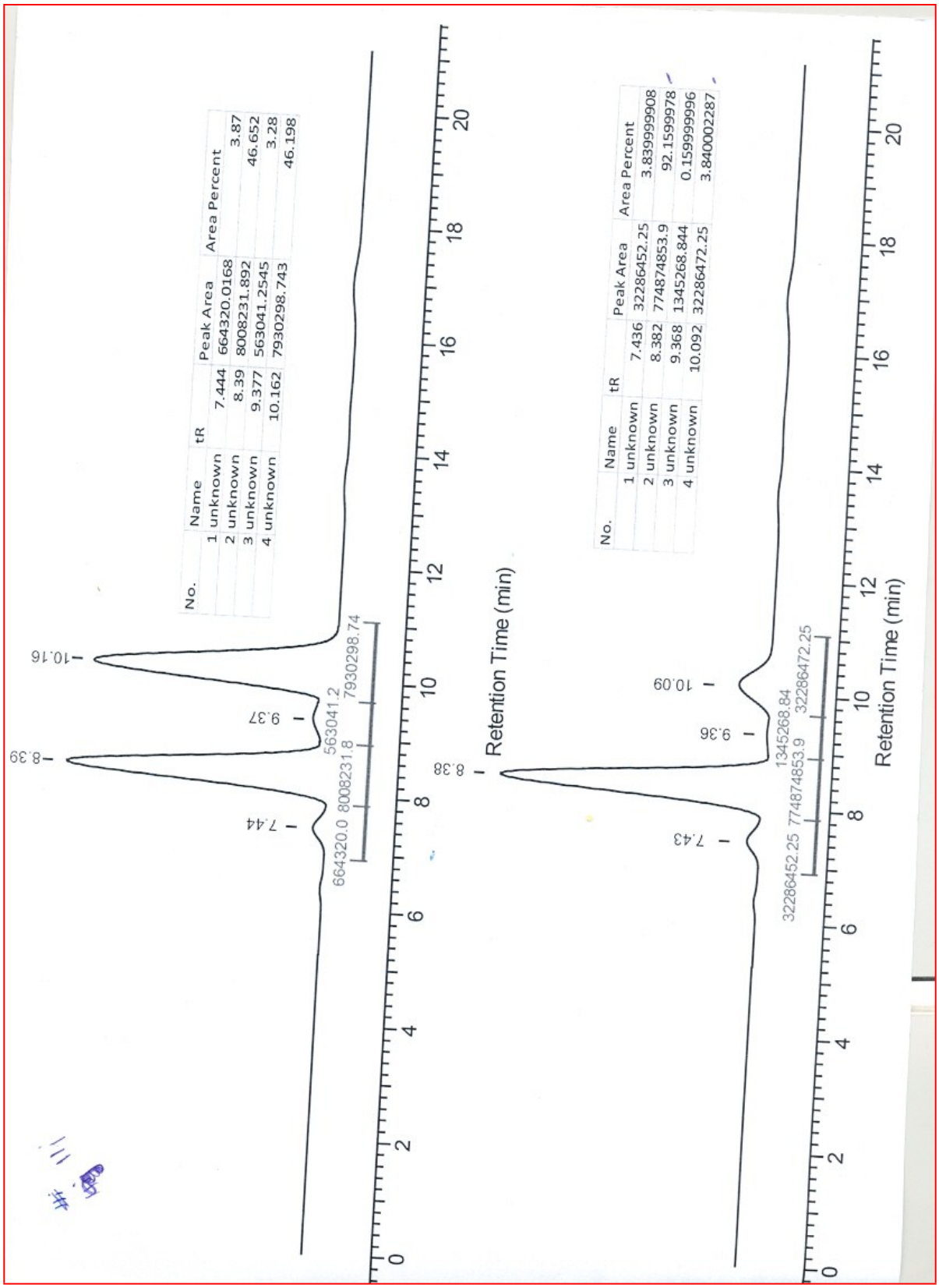
HPL Chromatograph of 11g



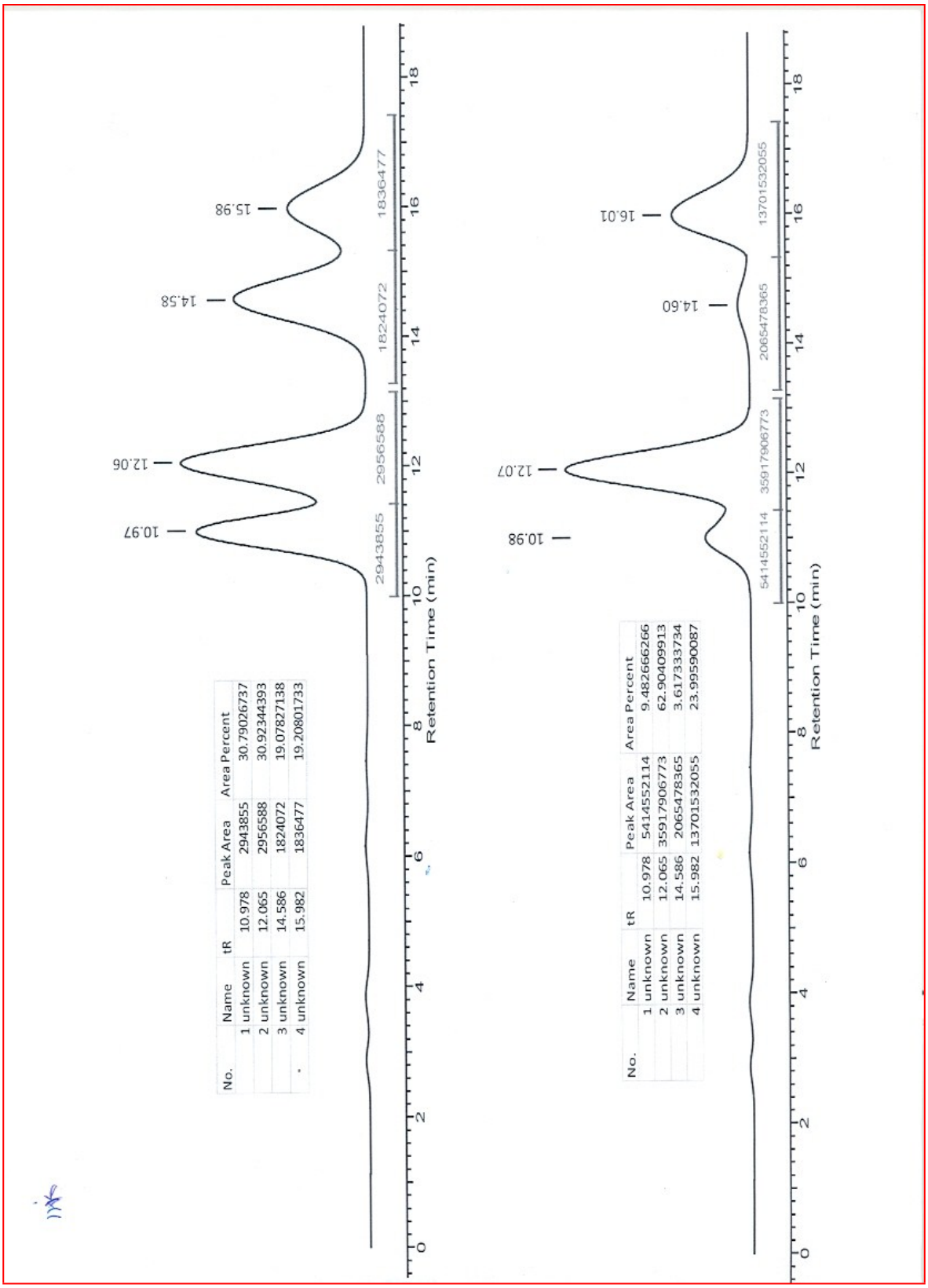
HPL Chromatograph of 11h



HPL Chromatograph of 11i



HPL Chromatograph of 11j



HPL Chromatograph of 11k

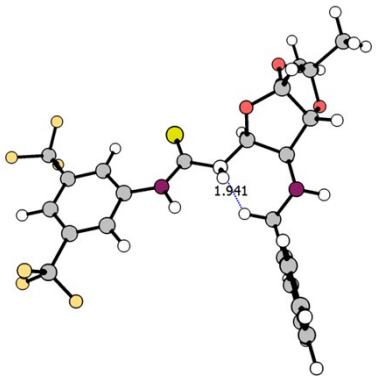


Figure 1. optimized structure of catalyst

Zero-point correction	0.36273
Thermal correction to Energy	0.391794
Thermal correction to Enthalpy	0.392738
Thermal correction to Gibbs Free Energy	0.294849
Sum of electronic and zero-point Energies	-2046.538498
Sum of electronic and thermal Energies	-2046.509434
Sum of electronic and thermal Enthalpies	-2046.50849
Sum of electronic and thermal Free Energies	-2046.606379

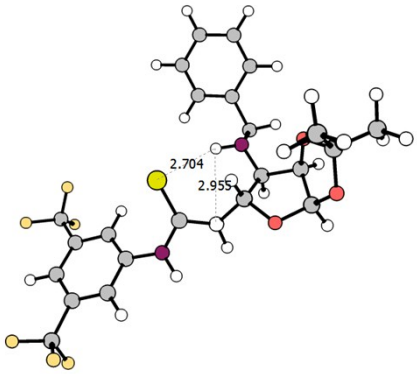


Figure 2. optimized structure of the catalyst in inverted form

Zero-point correction	0.362737255
Thermal correction to Energy	0.391801836
Thermal correction to Enthalpy	0.392745855
Thermal correction to Gibbs Free Energy	0.294854897
Sum of electronic and zero-point Energies	-2046.579429
Sum of electronic and thermal Energies	-2046.550364
Sum of electronic and thermal Enthalpies	-2046.54942
Sum of electronic and thermal Free Energies	-2046.647311

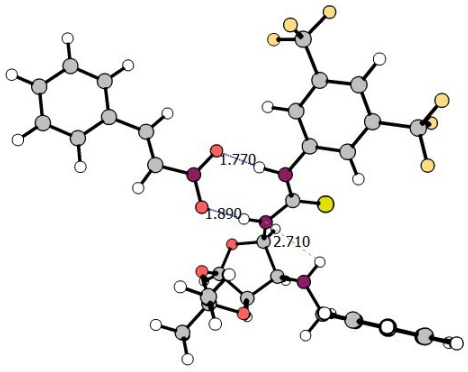


Figure 3. Adduct formed due to Nitrostyrene (NS) and thiourea

Zero-point correction	0.675183
Thermal correction to Energy	0.71691
Thermal correction to Enthalpy	0.717855
Thermal correction to Gibbs Free Energy	0.582611
Sum of electronic and zero-point Energies	-2741.862913
Sum of electronic and thermal Energies	-2741.821186
Sum of electronic and thermal Enthalpies	-2741.820241
Sum of electronic and thermal Free Energies	-2741.955485

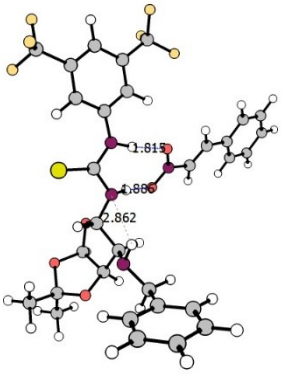
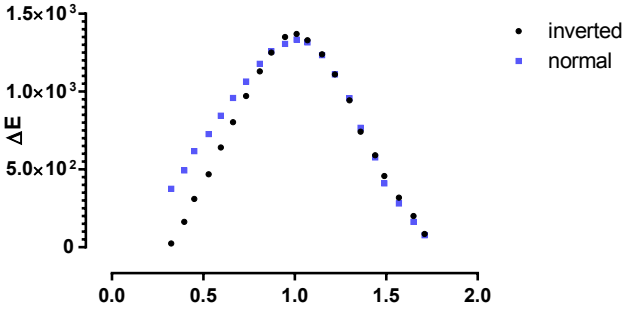


Figure 4. Adduct formed due to Nitrostyrene (NS) and thiourea (inverted)

Zero-point correction	0.675076
Thermal correction to Energy	0.716621
Thermal correction to Enthalpy	0.717565
Thermal correction to Gibbs Free Energy	0.583911
Sum of electronic and zero-point Energies	-2741.857609
Sum of electronic and thermal Energies	-2741.816064
Sum of electronic and thermal Enthalpies	-2741.81512
Sum of electronic and thermal Free Energies	-2741.948774



IRC 1. Figure 3 and 4

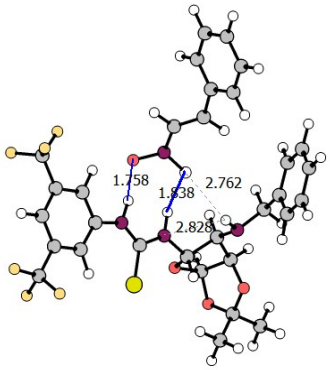


Figure 5. Adduct formed due to the orientation of the phenyl NS away from the aryl half of the catalyst

Zero-point correction	0.675196504
Thermal correction to Energy	0.716924338
Thermal correction to Enthalpy	0.717869357
Thermal correction to Gibbs Free Energy	0.582622652
Sum of electronic and zero-point Energies	-2741.91775
Sum of electronic and thermal Energies	-2741.876022
Sum of electronic and thermal Enthalpies	-2741.875077
Sum of electronic and thermal Free Energies	-2742.010324

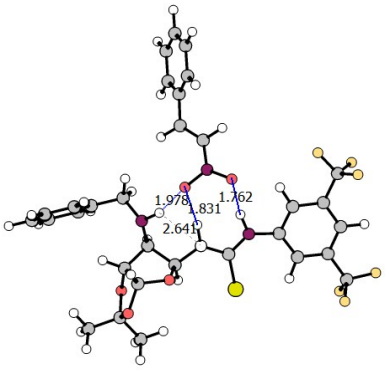


Figure 6. Adduct formed due to the orientation of the phenyl NS away from the aryl half of the catalyst (inverted)

Zero-point correction	0.675184
Thermal correction to Energy	0.716911
Thermal correction to Enthalpy	0.717856
Thermal correction to Gibbs Free Energy	0.582612
Sum of electronic and zero-point Energies	-2741.87
Sum of electronic and thermal Energies	-2741.83
Sum of electronic and thermal Enthalpies	-2741.83
Sum of electronic and thermal Free Energies	-2741.96

Figure 7-13 for the formation of SR product; figure **14-20** for the formation of SS product; **Figure 21-27** for the formation of RS product; **Figure 28-34** for the formation of RR product.

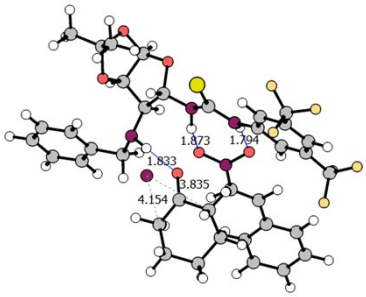


Figure 7

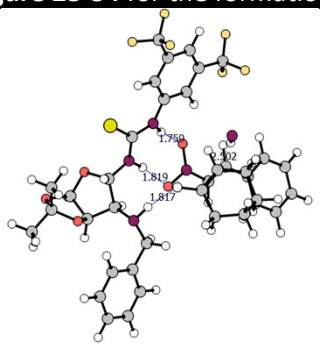


Figure 8

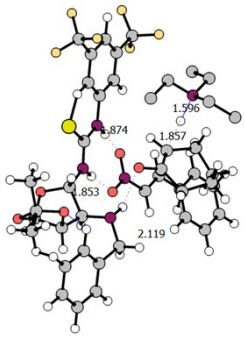


Figure 9

Zero-point correction	0.838426538
Thermal correction to Energy	0.887466406
Thermal correction to Enthalpy	0.888410365
Thermal correction to Gibbs Free Energy	0.734520057
Sum of electronic and zero-point Energies	-3045.099512
Sum of electronic and thermal Energies	-3045.050472
Sum of electronic and thermal Enthalpies	-3045.049528
Sum of electronic and thermal Free Energies	-3045.203419

Zero-point correction	0.838453902
Thermal correction to Energy	0.88749537
Thermal correction to Enthalpy	0.88843936
Thermal correction to Gibbs Free Energy	0.73454403
Sum of electronic and zero-point Energies	-3045.198896
Sum of electronic and thermal Energies	-3045.149854
Sum of electronic and thermal Enthalpies	-3045.14891
Sum of electronic and thermal Free Energies	-3045.302806

Zero-point correction	0.838485798
Thermal correction to Energy	0.887529131
Thermal correction to Enthalpy	0.888473157
Thermal correction to Gibbs Free Energy	0.734571972
Sum of electronic and zero-point Energies	-3045.314737
Sum of electronic and thermal Energies	-3045.265694
Sum of electronic and thermal Enthalpies	-3045.26475
Sum of electronic and thermal Free Energies	-3045.418651

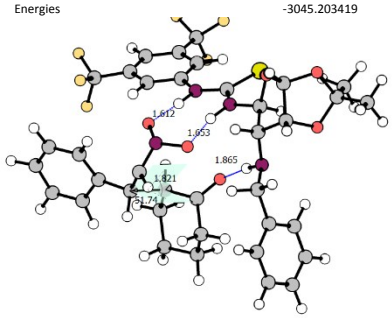


Figure 10

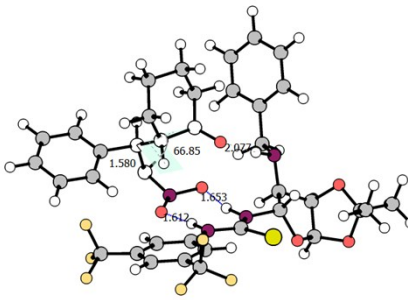


Figure 11

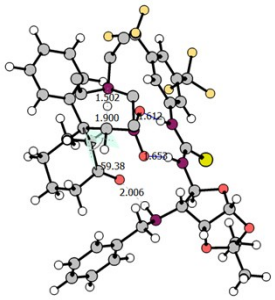


Figure 12

Zero-point correction	0.838414508
Thermal correction to Energy	0.887453672
Thermal correction to Enthalpy	0.888397617
Thermal correction to Gibbs Free Energy	0.734509518
Sum of electronic and zero-point Energies	-3045.055818
Sum of electronic and thermal Energies	-3045.006779
Sum of electronic and thermal Enthalpies	-3045.005835
Sum of electronic and thermal Free Energies	-3045.159723

Zero-point correction	0.838463
Thermal correction to Energy	0.887505
Thermal correction to Enthalpy	0.888449
Thermal correction to Gibbs Free Energy	0.734552
Sum of electronic and zero-point Energies	-3045.231938
Sum of electronic and thermal Energies	-3045.182896
Sum of electronic and thermal Enthalpies	-3045.181952
Sum of electronic and thermal Free Energies	-3045.335849

Zero-point correction	0.838440213
Thermal correction to Energy	0.887480881
Thermal correction to Enthalpy	0.888424855
Thermal correction to Gibbs Free Energy	0.734532037
Sum of electronic and zero-point Energies	-3045.149179
Sum of electronic and thermal Energies	-3045.100138
Sum of electronic and thermal Enthalpies	-3045.099194
Sum of electronic and thermal Free Energies	-3045.253087

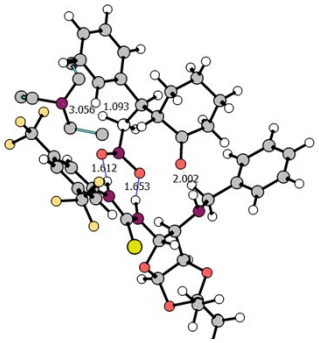


Figure 13

Zero-point correction	0.838478795
Thermal correction to Energy	0.887521719
Thermal correction to Enthalpy	0.888465737
Thermal correction to Gibbs Free Energy	0.734565837
Sum of electronic and zero-point Energies	-3045.289304
Sum of electronic and thermal Energies	-3045.240261
Sum of electronic and thermal Enthalpies	-3045.239317
Sum of electronic and thermal Free Energies	-3045.393217

Figure 14

Zero-point correction	0.838423175
Thermal correction to Energy	0.887462846
Thermal correction to Enthalpy	0.888406801
Thermal correction to Gibbs Free Energy	0.734517111
Sum of electronic and zero-point Energies	-3045.087298
Sum of electronic and thermal Energies	-3045.038258
Sum of electronic and thermal Enthalpies	-3045.037314
Sum of electronic and thermal Free Energies	-3045.191204

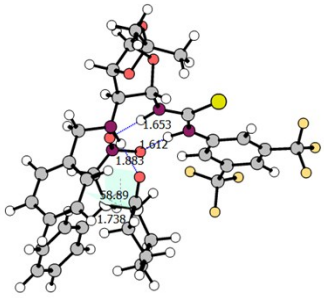


Figure 17

Zero-point correction	0.838450696
Thermal correction to Energy	0.887491977
Thermal correction to Enthalpy	0.888435963
Thermal correction to Gibbs Free Energy	0.734541221
Sum of electronic and zero-point Energies	-3045.187252
Sum of electronic and thermal Energies	-3045.13821
Sum of electronic and thermal Enthalpies	-3045.137266
Sum of electronic and thermal Free Energies	-3045.291161

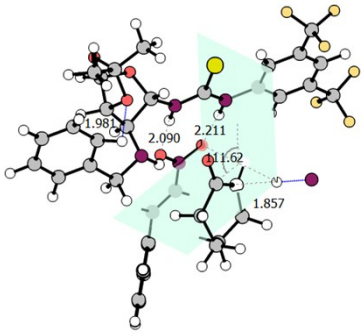


Figure 15

Zero-point correction	0.83845522
Thermal correction to Energy	0.887496765
Thermal correction to Enthalpy	0.888440757
Thermal correction to Gibbs Free Energy	0.734545184
Sum of electronic and zero-point Energies	-3045.203683
Sum of electronic and thermal Energies	-3045.154641
Sum of electronic and thermal Enthalpies	-3045.153697
Sum of electronic and thermal Free Energies	-3045.307593

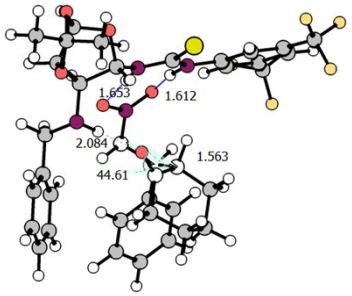


Figure 18

Zero-point correction	0.838466071
Thermal correction to Energy	0.887508251
Thermal correction to Enthalpy	0.888452254
Thermal correction to Gibbs Free Energy	0.73455469
Sum of electronic and zero-point Energies	-3045.243091
Sum of electronic and thermal Energies	-3045.194049
Sum of electronic and thermal Enthalpies	-3045.193105
Sum of electronic and thermal Free Energies	-3045.347003

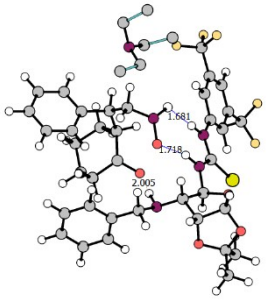


Figure 20

Zero-point correction	0.838476261
Thermal correction to Energy	0.887519036
Thermal correction to Enthalpy	0.888463051
Thermal correction to Gibbs Free Energy	0.734563617
Sum of electronic and zero-point Energies	-3045.2801
Sum of electronic and thermal Energies	-3045.231057
Sum of electronic and thermal Enthalpies	-3045.230113
Sum of electronic and thermal Free Energies	-3045.384012

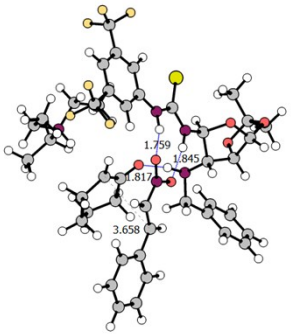


Figure 16

Zero-point correction	0.838478339
Thermal correction to Energy	0.887521236
Thermal correction to Enthalpy	0.888465254
Thermal correction to Gibbs Free Energy	0.734565438
Sum of electronic and zero-point Energies	-3045.287648
Sum of electronic and thermal Energies	-3045.238606
Sum of electronic and thermal Enthalpies	-3045.237662
Sum of electronic and thermal Free Energies	-3045.391561

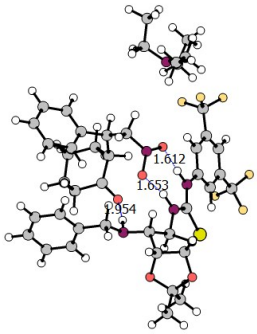


Figure 19

Zero-point correction	0.838441939
Thermal correction to Energy	0.887482707
Thermal correction to Enthalpy	0.888426683
Thermal correction to Gibbs Free Energy	0.734533549
Sum of electronic and zero-point Energies	-3045.155446
Sum of electronic and thermal Energies	-3045.106405
Sum of electronic and thermal Enthalpies	-3045.105461
Sum of electronic and thermal Free Energies	-3045.259354

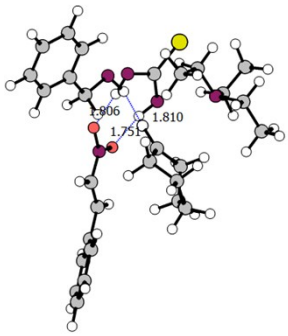


Figure 21

Zero-point correction	0.838426531
Thermal correction to Energy	0.887466397
Thermal correction to Enthalpy	0.888410356
Thermal correction to Gibbs Free Energy	0.73452005
Sum of electronic and zero-point Energies	-3045.099484
Sum of electronic and thermal Energies	-3045.050444
Sum of electronic and thermal Enthalpies	-3045.0495
Sum of electronic and thermal Free Energies	-3045.20339

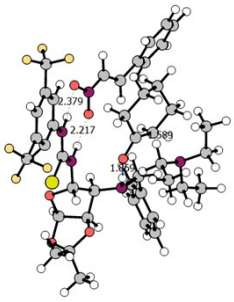


Figure 22

Weaker H-bond formation in the TS1 between NS and TU

Zero-point correction	0.838453464
Thermal correction to Energy	0.887494906
Thermal correction to Enthalpy	0.888438895
Thermal correction to Gibbs Free Energy	0.734543646
Sum of electronic and zero-point Energies	-3045.197303
Sum of electronic and thermal Energies	-3045.148262
Sum of electronic and thermal Enthalpies	-3045.147318
Sum of electronic and thermal Free Energies	-3045.301213

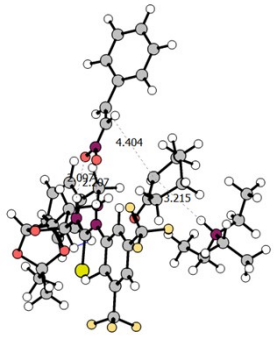


Figure 23

Zero-point correction	0.838475724
Thermal correction to Energy	0.887518468
Thermal correction to Enthalpy	0.888462482
Thermal correction to Gibbs Free Energy	0.734563147
Sum of electronic and zero-point Energies	-3045.278149
Sum of electronic and thermal Energies	-3045.229107
Sum of electronic and thermal Enthalpies	-3045.228163
Sum of electronic and thermal Free Energies	-3045.382062

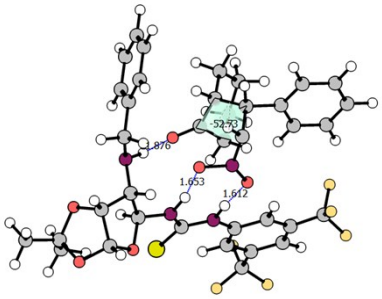


Figure 24

Zero-point correction	0.83844276
Thermal correction to Energy	0.887483576
Thermal correction to Enthalpy	0.888427553
Thermal correction to Gibbs Free Energy	0.734534268
Sum of electronic and zero-point Energies	-3045.158427
Sum of electronic and thermal Energies	-3045.109386
Sum of electronic and thermal Enthalpies	-3045.108442
Sum of electronic and thermal Free Energies	-3045.262335

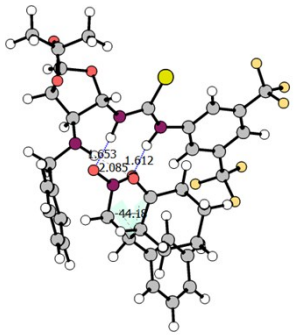


Figure 25

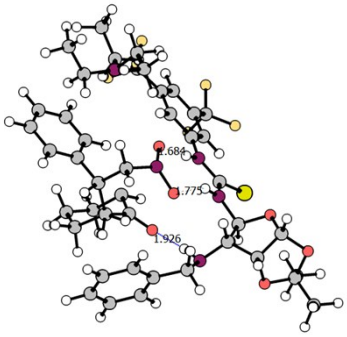


Figure 26

Zero-point correction	0.838462122
Thermal correction to Energy	0.887504071
Thermal correction to Enthalpy	0.88844807
Thermal correction to Gibbs Free Energy	0.734551231
Sum of electronic and zero-point Energies	-3045.228751
Sum of electronic and thermal Energies	-3045.179709
Sum of electronic and thermal Enthalpies	-3045.178765
Sum of electronic and thermal Free Energies	-3045.332662

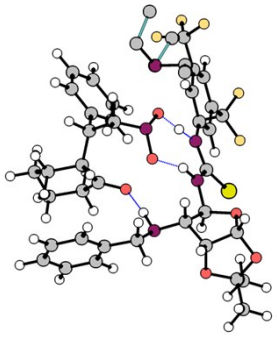


Figure 27

Zero-point correction	0.838443821
Thermal correction to Energy	0.887484699
Thermal correction to Enthalpy	0.888428677
Thermal correction to Gibbs Free Energy	0.734535198
Sum of electronic and zero-point Energies	-3045.162281
Sum of electronic and thermal Energies	-3045.11324
Sum of electronic and thermal Enthalpies	-3045.112296
Sum of electronic and thermal Free Energies	-3045.266189

Zero-point correction	0.838478444
Thermal correction to Energy	0.887521347
Thermal correction to Enthalpy	0.888465364
Thermal correction to Gibbs Free Energy	0.73456553
Sum of electronic and zero-point Energies	-3045.288028
Sum of electronic and thermal Energies	-3045.238985
Sum of electronic and thermal Enthalpies	-3045.238041
Sum of electronic and thermal Free Energies	-3045.391941

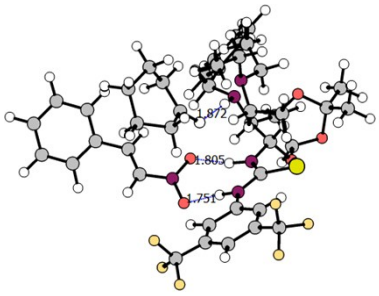


Figure 28

Zero-point correction	0.838422528
Thermal correction to Energy	0.887462161
Thermal correction to Enthalpy	0.888406115
Thermal correction to Gibbs Free Energy	0.734516544
Sum of electronic and zero-point Energies	-3045.084948
Sum of electronic and thermal Energies	-3045.035908
Sum of electronic and thermal Enthalpies	-3045.034964
Sum of electronic and thermal Free Energies	-3045.188853

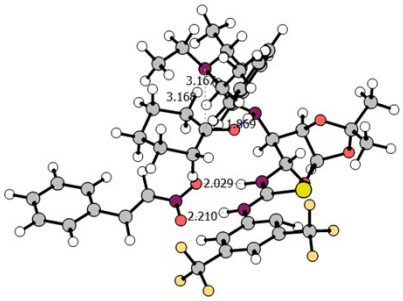


Figure 29

Zero-point correction	0.83845476
Thermal correction to Energy	0.887496278
Thermal correction to Enthalpy	0.888440268
Thermal correction to Gibbs Free Energy	0.734544781
Sum of electronic and zero-point Energies	-3045.20201
Sum of electronic and thermal Energies	-3045.152968
Sum of electronic and thermal Enthalpies	-3045.152024
Sum of electronic and thermal Free Energies	-3045.30592

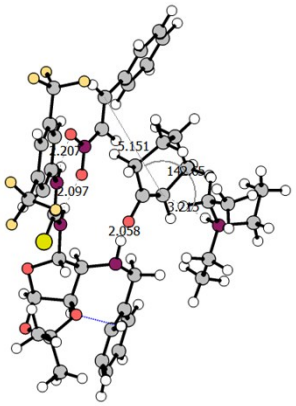


Figure 30

Zero-point correction	0.83847439
Thermal correction to Energy	0.887517056
Thermal correction to Enthalpy	0.888461069
Thermal correction to Gibbs Free Energy	0.734561979
Sum of electronic and zero-point Energies	-3045.273307
Sum of electronic and thermal Energies	-3045.224264
Sum of electronic and thermal Enthalpies	-3045.22332
Sum of electronic and thermal Free Energies	-3045.377219

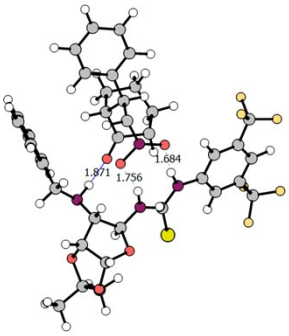


Figure 31

Zero-point correction	0.838447635
Thermal correction to Energy	0.887488736
Thermal correction to Enthalpy	0.888432719
Thermal correction to Gibbs Free Energy	0.734538539
Sum of electronic and zero-point Energies	-3045.176134
Sum of electronic and thermal Energies	-3045.127092
Sum of electronic and thermal Enthalpies	-3045.126148
Sum of electronic and thermal Free Energies	-3045.280043

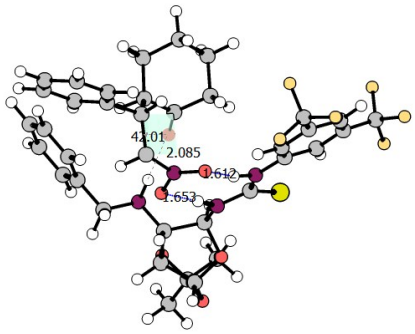


Figure 32

Zero-point correction	0.838464532
Thermal correction to Energy	0.887506621
Thermal correction to Enthalpy	0.888450623
Thermal correction to Gibbs Free Energy	0.734553342
Sum of electronic and zero-point Energies	-3045.237501
Sum of electronic and thermal Energies	-3045.188459
Sum of electronic and thermal Enthalpies	-3045.187515
Sum of electronic and thermal Free Energies	-3045.341412

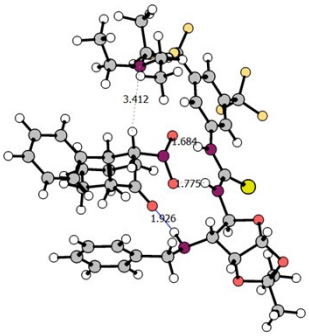


Figure 33

Zero-point correction	0.838439306
Thermal correction to Energy	0.887479921
Thermal correction to Enthalpy	0.888423894
Thermal correction to Gibbs Free Energy	0.734531243
Sum of electronic and zero-point Energies	-3045.145885
Sum of electronic and thermal Energies	-3045.096844
Sum of electronic and thermal Enthalpies	-3045.0959
Sum of electronic and thermal Free Energies	-3045.249793

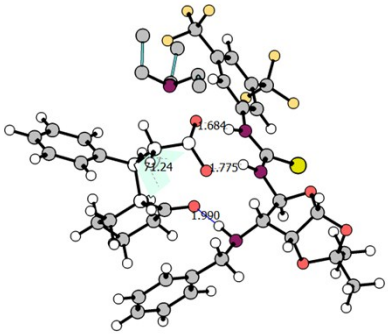
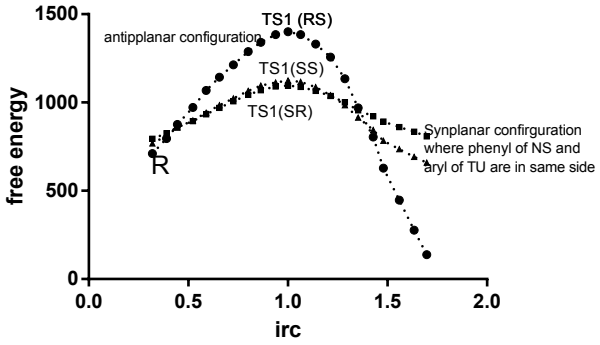
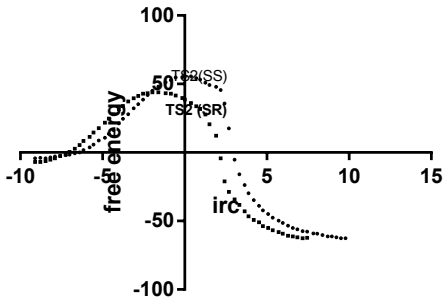


Figure 34

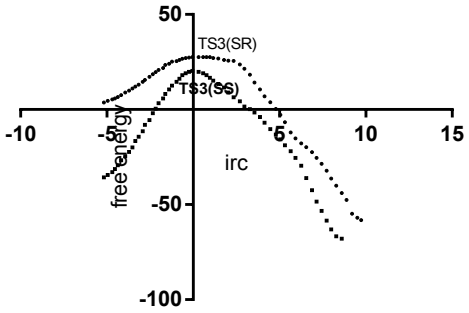
Zero-point correction	0.838476651
Thermal correction to Energy	0.88751945
Thermal correction to Enthalpy	0.888463465
Thermal correction to Gibbs Free Energy	0.734563959
Sum of electronic and zero-point Energies	-3045.281518
Sum of electronic and thermal Energies	-3045.232475
Sum of electronic and thermal Enthalpies	-3045.231531
Sum of electronic and thermal Free Energies	-3045.385431



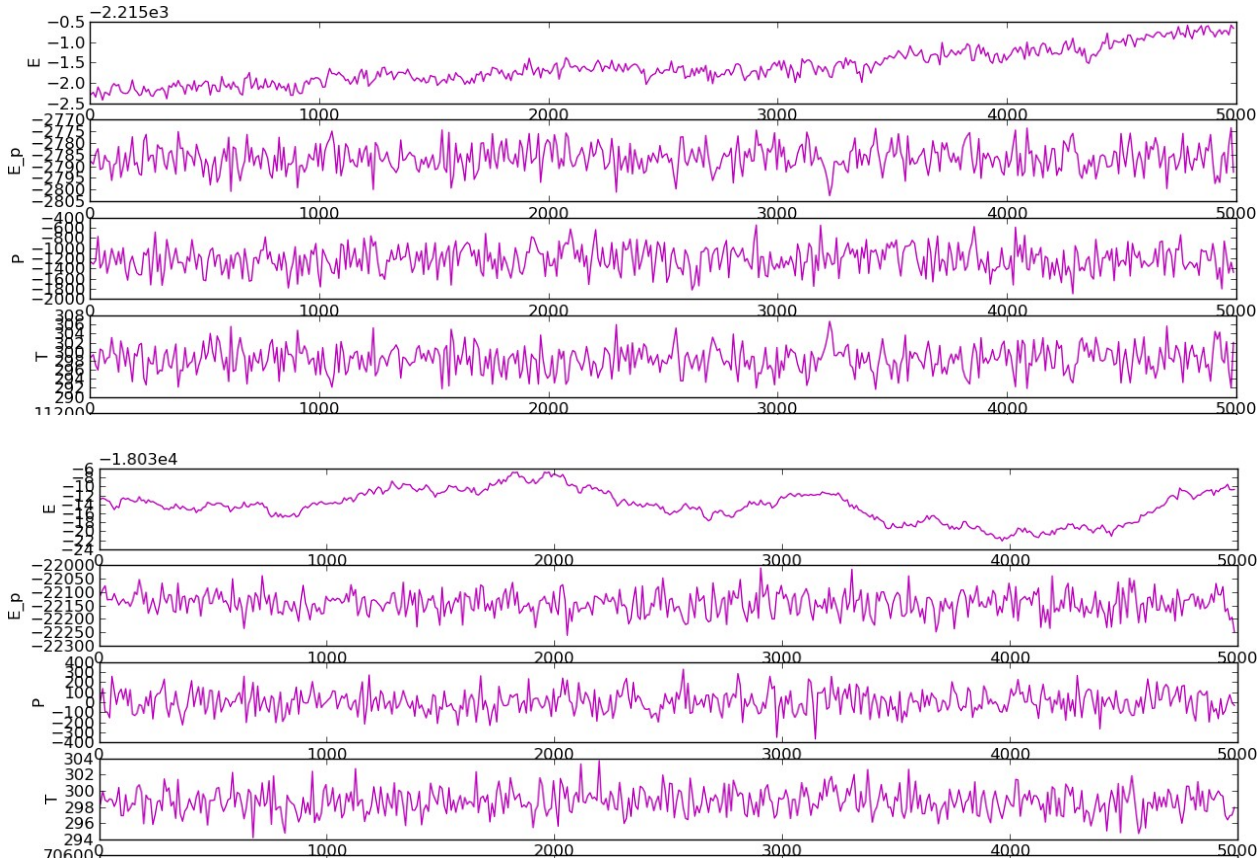
IRC 2



IRC 3

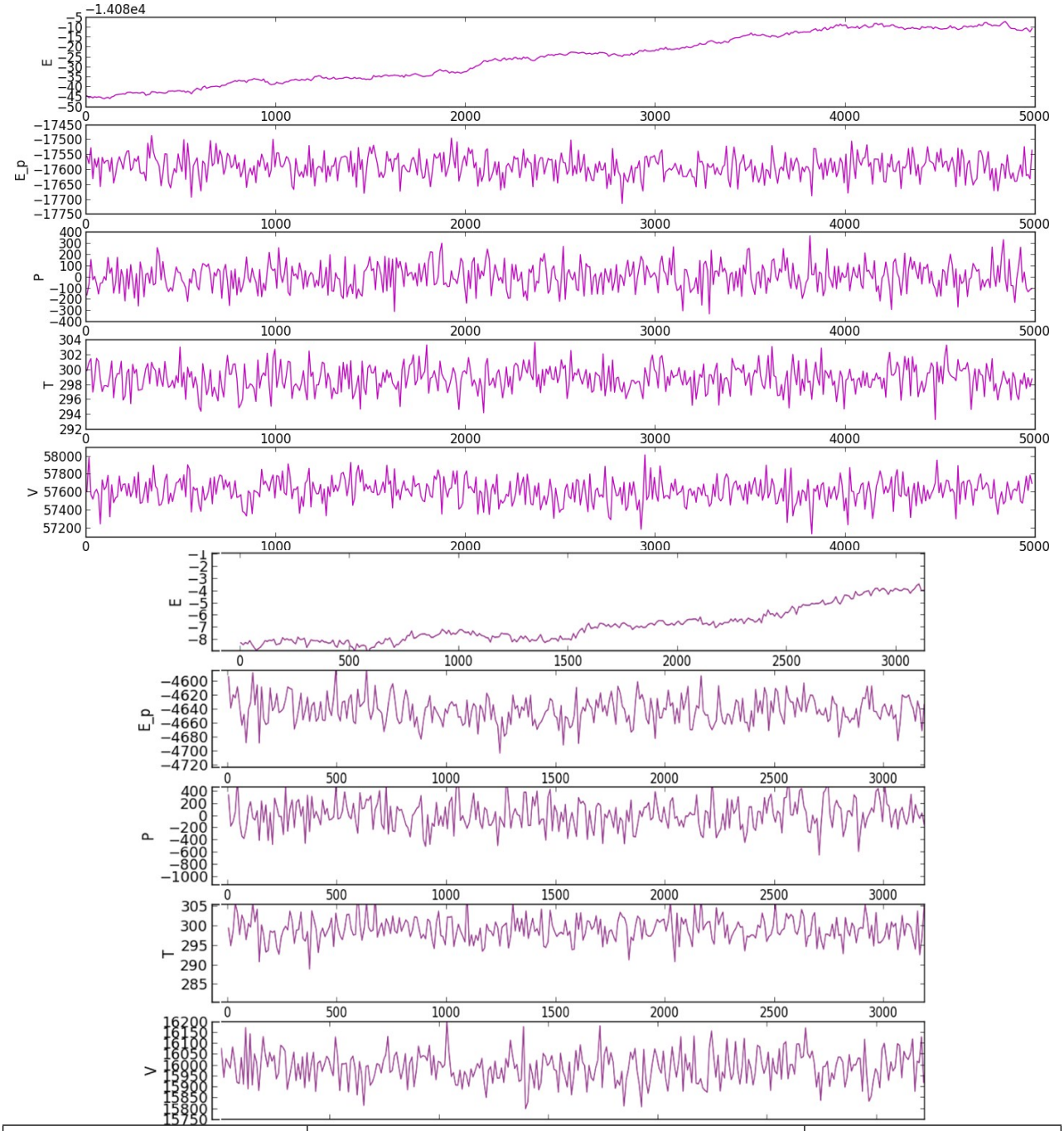


IRC 4



	Structure 3 (**Figure 2 in manuscript**) (above)	TS2 (below)
Total energy (kcal/mol)	-2216.614	-3663.197
Potential energy (kcal/mol)	-2786.500	-4642.240
Temperature (K)	263.331	263.331
Pressure (bar)	1218.862	1239.45

Figure 35: Molecular dynamics resulted curves for **Stage 3 (above) and TS3 (below)** in cyclohexanone (120 molecules) (3ns and 5ns). (The solvent system with cyclohexanone was prepared using protocol at https://www.schrodinger.com/kb/1006)



	Structure 5 (Figure 2 in manuscript) (above)	**TS3 (below)**
Total energy (kcal/mol)	3921.927	4105.499
Potential energy (kcal/mol)	4868.468	7591.719
Temperature (K)		
Pressure (bar)	12.096	12.9

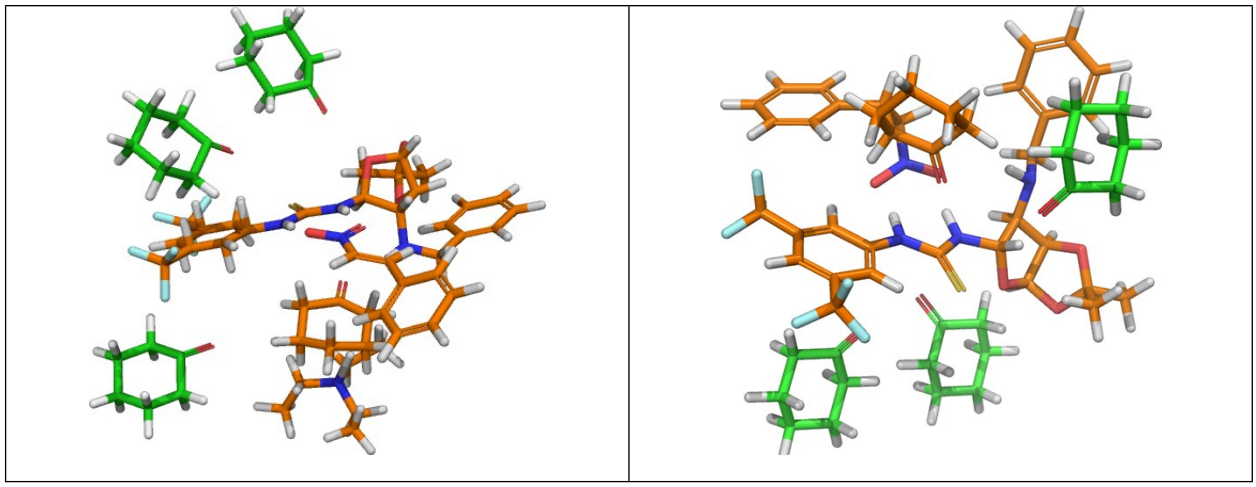


Figure 36: The optimized structure of the TS2 and TS3 with the three more cyclohexanone moieties from the catalyst (two molecules at NH of thiourea (at distance of 5.4 and 5.52A) and one molecule at 5.9 A from CF_3 Aryl part of the catalyst) using Qsite (B3LYP-6-31g(d)/RHF-6-31g) in Schrodinger 2016-01.

Table (Figure 36): Qsite results for the stage V and VI of the reaction after the consideration of MD simulation.

	Stage 5	**TS2**	**Stage 6**	**TS3**
QM/MM Energy	-1137.426612	-1137.558168	-1137.518965	-1137.450012
Zero Point Energy (kJ/mol)	155.7094811	155.7841665	155.76668452	155.711311
Entropy (J/mol/K, 263K)	192.6882142	192.7687974	192.75894632	192.645142
Enthalpy (kJ/mol, 263K)	11.15089467	11.20252456	11.478996532	11.15289676
Free Energy (kJ/mol, 263K)	-46.30060769	-46.25814072	-46.26314789	-46.3220789
Total Internal Energy at 263K (au)	-1137.162629	-1137.294143	-1137.282389	-1137.328322
Total Enthalpy at 263K (au)	-1137.160272	-1137.291786	-1137.280032	-1137.325965
Total Free Energy at 263K (au)	-1137.252195	-1137.383723	-1137.371969	-1137.417902

Table 1. The calculated relative free energies for the various step of the reaction mechanism with reference to E(TEAH$^+$+TU+R2$^-$+NS) = -3162.711kcal/mol.

	$\Delta E_{(SR)}$ = (E-E(TEAH$^+$+TU+R_{2^-}+NS))	**$\Delta E_{(SS)}$ = (E-E(TEAH$^+$+TU+R_{2^-}+NS))**	**$\Delta E_{(RS)}$ = (E-E(TEAH$^+$+TU+$_{R2^-}$+NS))**	**$\Delta E_{(RR)}$ = (E-E(TEAH$^+$+TU+R_{2^-}+NS))**
0	-60.365	-35.5214	-59.201	-36.244
TS1	-33.265	-25.6	-33.247	-24.125
2	-95.631	-98.635	-94.6315	-97.585
3	-168.325	-151.326	-145.365	-142.326
TS2	-105.314	-88.324	-70.2354	-81.347
5	-116.366	-123.365	-114.366	-119.857
TS3	-78.553	-68.365	-72.654	-62.365

7	-152.365	-146.589	-151.564	-147.479

Tables: x,y,x coordinate of the optimized molecules used in the construction of the energy profile diagram shown in the manuscript.

Table A1: The xyz coordinates of the substrates resulting the formation of SS product.

Structure TS1				Structure 2				Structure 3				Structure TS2			
O	2.78	-2.408	-2.343	O	2.798	-1.458	-2.192	O	2.774	-2.313	-2.049	O	2.866	-2.905	-1.821
C	2.389	-1.747	-1.053	C	2.269	-0.899	-0.954	C	2.383	-1.652	-0.759	C	2.566	-1.847	-0.793
C	3.295	-0.5	-1.012	C	3.218	0.291	-0.689	C	3.289	-0.405	-0.718	C	3.498	-0.693	-1.204
C	4.577	-1.037	-1.612	C	4.451	-0.51	-0.787	C	4.599	-1.009	-1.228	C	4.761	-1.465	-1.586
C	4.038	-1.878	-2.738	C	4.26	-1.275	-2.076	C	4.148	-1.964	-2.351	C	4.219	-2.723	-2.298
O	5.297	-1.969	-0.788	O	4.334	-1.527	0.192	O	5.112	-1.945	-0.21	O	5.38	-2.012	-0.368
C	5.615	-3.07	-1.649	C	4.987	-2.667	-0.401	C	5.464	-3.222	-0.868	C	5.622	-3.462	-0.562
O	5.026	-2.883	-2.938	O	5.104	-2.405	-1.83	O	5.071	-3.074	-2.275	O	5.137	-3.774	-1.911
N	3.334	0.128	0.307	N	3.024	0.942	0.612	N	3.328	0.223	0.601	N	3.685	0.266	-0.126
C	7.129	-3.112	-1.826	C	6.404	-2.884	0.169	C	6.977	-3.404	-0.835	C	7.125	-3.716	-0.549
C	5.112	-4.366	-1.023	C	4.131	-3.913	-0.103	C	4.676	-4.348	-0.211	C	4.839	-4.246	0.484
C	3.782	1.533	0.294	C	4.038	1.987	0.797	C	3.776	1.628	0.588	C	4.47	1.415	-0.537
C	5.295	1.704	0.414	C	5.439	1.382	0.6	C	5.289	1.799	0.708	C	4.906	2.262	0.704
C	5.882	2.956	0.185	C	6.491	2.201	0.169	C	5.876	3.051	0.479	C	5.255	3.617	0.519
C	7.258	3.138	0.338	C	7.768	1.659	-0.023	C	7.252	3.233	0.632	C	5.724	4.358	1.598
C	8.066	2.062	0.716	C	7.993	0.296	0.216	C	8.06	2.157	1.01	C	5.884	3.761	2.844
C	7.487	0.81	0.935	C	6.941	-0.524	0.645	C	7.481	0.905	1.229	C	5.593	2.412	3.021
C	6.108	0.629	0.791	C	5.664	0.021	0.844	C	6.102	0.724	1.085	C	5.122	1.649	1.958
N	1.003	-1.401	-1.064	N	0.86	-0.481	-1.068	N	0.997	-1.306	-0.77	N	1.198	-1.447	-0.844
C	0.009	-2.27	-0.74	C	-0.144	-1.309	-0.741	C	0.003	-2.175	-0.446	C	0.194	-2.15	-0.256
S	0.334	-3.922	-0.292	S	0.192	-2.965	-0.181	S	0.328	-3.827	0.002	S	0.49	-3.626	0.631
N	-1.228	-1.677	-0.835	N	-1.406	-0.867	-0.839	N	-1.234	-1.582	-0.541	N	-1.024	-1.552	-0.464
C	-2.512	-2.148	-0.568	C	-2.552	-1.718	-0.466	C	-2.518	-2.053	-0.274	C	-2.311	-1.913	-0.08
C	-3.564	-1.23	-0.788	C	-3.853	-1.197	-0.564	C	-3.57	-1.135	-0.494	C	-3.352	-1.098	-0.586
C	-4.883	-1.595	-0.571	C	-4.93	-1.953	-0.225	C	-4.889	-1.5	-0.277	C	-4.676	-1.349	-0.269
C	-5.22	-2.872	-0.132	C	-4.757	-3.268	0.223	C	-5.226	-2.777	0.162	C	-5.035	-2.42	0.547
C	-4.186	-3.771	0.093	C	-3.472	-3.811	0.33	C	-4.192	-3.676	0.387	C	-4.016	-3.222	1.044
C	-2.851	-3.436	-0.117	C	-2.358	-3.031	-0.014	C	-2.857	-3.341	0.177	C	-2.674	-2.991	0.749
C	-4.512	-5.12	0.628	C	-3.293	-5.256	0.825	C	-4.518	-5.025	0.922	C	-4.365	-4.329	1.973
F	-5.77	-5.521	0.221	F	-4.376	-5.985	0.483	F	-5.776	-5.426	0.515	F	-5.643	-4.796	1.727
F	-4.527	-5.16	2.007	F	-3.155	-5.258	2.167	F	-4.533	-5.065	2.301	F	-4.351	-3.942	3.298
F	-3.602	-6.066	0.22	F	-2.192	-5.792	0.258	F	-3.608	-5.971	0.514	F	-3.492	-5.384	1.867
C	-5.956	-0.585	-0.76	C	-6.35	-1.365	-0.33	C	-5.962	-0.49	-0.466	C	-5.732	-0.427	-0.761
F	-5.627	0.328	-1.737	F	-6.384	-0.444	-1.316	F	-5.633	0.423	-1.443	F	-5.36	0.204	-1.936
F	-6.216	0.147	0.381	F	-6.685	-0.783	0.841	F	-6.222	0.242	0.675	F	-6.024	0.592	0.125
F	-7.148	-1.186	-1.111	F	-7.229	-2.353	-0.607	F	-7.154	-1.091	-0.817	F	-6.919	-1.091	-0.984
H	2.673	-2.423	-0.238	H	2.352	-1.613	-0.162	H	2.629	-2.321	0.071	H	2.887	-2.229	0.181
H	2.887	0.221	-1.734	H	3.153	1.051	-1.442	H	2.927	0.303	-1.474	H	3.127	-0.207	-2.116
H	5.276	-0.266	-1.95	H	5.378	0.017	-0.711	H	5.396	-0.321	-1.517	H	5.525	-0.925	-2.149
H	3.894	-1.312	-3.664	H	4.556	-0.785	-2.981	H	4.177	-1.512	-3.346	H	4.19	-2.627	-3.387
H	7.488	-2.178	-2.273	H	7.001	-2.016	-0.017	H	7.476	-2.555	-1.314	H	7.624	-3.113	-1.316
H	7.64	-3.226	-0.864	H	6.343	-3.056	1.224	H	7.342	-3.459	0.196	H	7.56	-3.441	0.417
H	7.43	-3.927	-2.493	H	6.854	-3.732	-0.302	H	7.278	-4.309	-1.373	H	7.35	-4.766	-0.76
H	5.344	-5.228	-1.658	H	4.584	-4.773	-0.548	H	4.973	-5.318	-0.624	H	5.105	-5.308	0.444
H	5.548	-4.522	-0.031	H	4.063	-4.054	0.956	H	4.834	-4.36	0.872	H	5.04	-3.869	1.492
H	4.026	-4.347	-0.896	H	3.148	-3.777	-0.505	H	3.603	-4.256	-0.39	H	3.763	-4.2	0.316
H	3.4	2.067	-0.584	H	3.892	2.766	0.08	H	3.4	2.16	-0.294	H	5.395	1.119	-1.044
H	3.35	2.028	1.172	H	3.951	2.391	1.786	H	3.348	2.119	1.47	H	3.89	2.047	-1.219
H	5.25	3.789	-0.107	H	6.319	3.241	-0.013	H	5.263	3.9	0.188	H	5.171	4.067	-0.465
H	7.697	4.114	0.16	H	8.572	2.286	-0.35	H	7.696	4.209	0.458	H	6	5.4	1.459
H	9.137	2.194	0.835	H	8.969	-0.117	0.069	H	9.131	2.291	1.131	H	6.277	4.341	3.676
H	8.101	-0.036	1.232	H	7.113	-1.566	0.822	H	8.101	0.065	1.534	H	5.763	1.94	3.984
H	5.67	-0.341	1.014	H	4.862	-0.602	1.179	H	5.683	-0.246	1.337	H	4.93	0.586	2.078
H	0.877	-0.532	-0.525	H	0.646	0.44	-1.393	H	0.79	-0.336	-0.937	H	1.023	-0.481	-1.244
H	-1.179	-0.781	-1.308	H	-1.574	0.061	-1.17	H	-1.209	-0.664	-0.966	H	-1.006	-0.639	-1.016
H	-3.361	-0.226	-1.132	H	-3.997	-0.195	-0.909	H	-3.37	-0.139	-0.864	H	-3.165	-0.257	-1.231
H	-6.255	-3.15	0.049	H	-5.61	-3.858	0.484	H	-6.266	-3.06	0.333	H	-6.075	-2.6	0.805
H	-2.109	-4.192	0.085	H	-1.37	-3.435	0.067	H	-2.118	-4.107	0.365	H	-1.98	-3.662	1.214
H	2.345	0.142	0.64	H	2.114	1.354	0.661	H	2.37	0.214	0.976	H	2.773	0.543	0.264
O	0.676	0.582	1.127	O	0.477	0.524	1.72	O	0.67	0.677	1.421	O	1.215	1.173	1.072
C	0.104	1.098	2.129	C	-0.12	1.576	2.061	C	0.016	1.683	1.883	C	0.766	2.321	0.966
C	-1.311	0.812	2.419	C	-1.436	1.799	1.623	C	-1.314	1.914	1.529	C	-0.689	2.595	0.597
C	0.792	2.13	2.923	C	0.608	2.613	2.939	C	0.725	2.713	2.773	C	1.544	3.551	1.421
C	-2.049	2.121	2.695	C	-2.297	2.919	2.237	C	-2.15	3.068	1.98	C	-1.353	3.108	1.915
H	-1.39	0.166	3.298	C	-0.398	3.443	3.758	C	-0.265	3.548	3.61	H	-1.193	1.637	0.423
C	0.006	2.494	4.179	H	1.289	2.117	3.6	H	1.42	2.189	3.438	C	-0.981	3.472	-0.772
H	1.793	1.799	3.218	H	1.149	3.276	2.295	H	1.307	3.371	2.119	C	0.866	4.07	2.726
H	0.919	3.033	2.31	C	-1.417	4.056	2.788	C	-1.329	4.174	2.684	H	2.588	3.307	1.626
C	-1.435	2.9	3.864	H	-2.857	2.501	3.048	H	-2.876	2.687	2.709	H	1.512	4.315	0.636
H	-3.108	1.924	2.897	H	-2.967	3.31	1.501	H	-2.756	3.492	1.181	C	-0.635	4.35	2.492

H	-2.015	2.75	1.796	H	-0.914	2.832	4.47	H	-0.74	2.916	4.359	H	-1.293	2.31	2.669
H	-0.006	1.632	4.856	H	0.135	4.212	4.273	H	0.279	4.338	4.138	H	-2.417	3.302	1.783
H	0.509	3.304	4.719	H	-0.895	4.555	2	H	-0.831	4.793	1.93	C	-0.268	2.899	-1.882
H	-1.477	3.971	3.633	H	-2.046	4.758	3.297	H	-1.999	4.823	3.257	H	0.977	3.322	3.521
H	-2.045	2.758	4.764	N	-0.966	2.838	-1.954	N	-0.566	1.852	-0.987	H	1.367	4.985	3.059
N	-0.56	1.757	-1.281	O	-1.92	2.06	-2.062	O	-1.519	1.007	-1.42	H	-0.744	5.194	1.802
O	-1.513	0.912	-1.714	O	0.149	2.41	-1.882	O	0.695	1.478	-0.85	H	-1.105	4.638	3.439
O	0.701	1.383	-1.144	H	-1.852	1.172	0.862	C	-0.843	3.229	-0.897	H	0.689	3.418	-2.084
C	-0.837	3.134	-1.191	N	-3.244	0.101	4.026	H	-1.9053	3.4123	-0.9049	N	-0.166	1.544	-2.039
H	0.026	3.673	-0.832	C	-3.249	-1.273	3.509	C	0.1357	4.1441	-0.729	O	-1.292	0.791	-1.702
C	-2.031	3.647	-1.558	C	-1.809	-1.815	3.489	H	1.1758	3.8168	-0.6931	O	1.092	1.105	-1.703
H	-2.819	3.002	-1.946	H	-3.649	-1.278	2.517	C	-0.0539	5.5756	-0.537	C	-0.4186	4.887	-0.5415
H	-1.803	0.291	1.589	H	-3.853	-1.892	4.141	C	1.0795	6.3939	-0.3366	C	0.602	5.3736	-1.3588
N	0.869	-1.713	3.826	H	-1.809	-2.816	3.111	C	-1.3216	6.2008	-0.5283	C	-0.9297	5.6821	0.4842
C	0.797	-1.886	5.286	H	-1.204	-1.196	2.86	C	0.9552	7.7664	-0.1409	C	1.1119	6.6549	-1.1499
H	1.553	-1.253	5.762	H	-1.412	-1.809	4.483	H	2.0796	5.9621	-0.322	H	1.0052	4.7462	-2.1669
H	1.024	-2.918	5.578	C	-2.695	0.107	5.387	C	-1.4425	7.5727	-0.3337	C	-0.4204	6.9642	0.6927
C	-0.54	-1.469	5.892	C	-2.691	1.546	5.932	H	-2.2379	5.635	-0.6631	H	-1.7342	5.2988	1.1284
H	-0.47	-1.482	6.985	H	-1.693	-0.271	5.369	C	-0.307	8.3678	-0.1387	C	0.6003	7.4506	-0.124
H	-1.347	-2.152	5.612	H	-3.299	-0.512	6.017	H	1.842	8.3772	0.0184	H	1.9168	7.0383	-1.7936
H	-0.818	-0.456	5.591	H	-2.292	1.549	6.925	H	-2.4255	8.0383	-0.3235	H	-0.8238	7.591	1.5013
C	-0.174	-2.45	3.086	H	-2.086	2.165	5.303	H	-0.4055	9.4386	0.0205	H	1.0025	8.4608	0.0405
H	-1.163	-2.086	3.383	H	-3.692	1.923	5.948	H	-1.831	1.069	1.056	H	-2.0303	3.5124	-0.9777
H	-0.102	-2.178	2.033	C	-4.617	0.62	4.049	N	-2.868	0.018	4.037				
C	-0.175	-3.969	3.232	C	-5.194	0.608	2.621	C	-2.694	-1.437	3.568				
H	-0.336	-4.271	4.271	H	-4.614	1.623	4.425	C	-1.265	-1.755	3.18				
H	0.762	-4.418	2.891	H	-5.221	0.004	4.683	H	-3.339	-1.569	2.699				
H	-0.993	-4.401	2.647	H	-6.195	0.985	2.638	H	-3.039	-2.088	4.379				
C	2.208	-2.044	3.3	H	-4.592	1.225	1.987	H	-1.208	-2.783	2.812				
H	2.18	-2.043	2.204	H	-5.195	-0.394	2.246	H	-0.922	-1.093	2.385				
H	2.517	-3.051	3.607	H	-2.394	0.877	2.92	H	-0.573	-1.683	4.023				
C	3.284	-1.044	3.71	C	-0.008	5.251	-1.772	C	-1.912	0.292	5.203				
H	3.497	-1.084	4.782	H	0.987	4.863	-1.704	C	-2.282	1.503	6.043				
H	3.004	-0.023	3.449	C	-1.2	4.287	-1.913	H	-0.925	0.442	4.756				
H	4.219	-1.274	3.187	H	-2.09	4.587	-1.976	H	-1.896	-0.601	5.838				
C	-2.344	5.079	-1.497	C	-0.242	6.773	-1.727	H	-1.444	1.77	6.696				
C	-3.045	7.797	-1.426	C	0.841	7.642	-1.599	H	-2.528	2.375	5.433				
C	-1.868	5.912	-0.474	C	-1.538	7.282	-1.815	H	-3.134	1.286	6.696				
C	-3.194	5.622	-2.469	C	0.629	9.02	-1.559	C	-4.323	0.277	4.424				
C	-3.537	6.975	-2.438	H	1.863	7.241	-1.529	C	-5.235	0.194	3.223				
C	-2.214	7.265	-0.443	C	-1.75	8.66	-1.776	H	-4.389	1.297	4.807				
H	-1.233	5.522	0.317	H	-2.392	6.597	-1.917	H	-4.6	-0.434	5.209				
H	-3.591	4.997	-3.267	C	-0.667	9.529	-1.647	H	-6.231	0.567	3.483				
H	-4.19	7.385	-3.204	H	1.483	9.705	-1.457	H	-4.844	0.81	2.408				
H	-1.839	7.903	0.353	H	-2.772	9.061	-1.846	H	-5.359	-0.833	2.872				
H	-3.314	8.849	-1.402	H	-0.834	10.616	-1.615	H	-2.636	0.645	3.232				

Structure 5				**Structure TS3**				**Structure 7**							
O	2.923	-3.178	-1.427	O	2.4181	-2.5998	-1.2026	O	2.7800	-3.4260	-0.8200				
C	2.621	-2.005	-0.596	C	2.1091	-1.4888	-0.2986	C	2.4710	-2.3150	0.0840				
C	3.581	-0.897	-1.123	C	3.0801	-0.3528	-0.7376	C	3.4460	-1.1770	-0.3480				
C	4.796	-1.722	-1.472	C	4.3041	-1.1618	-1.0966	C	4.6760	-1.9860	-0.7150				
C	4.178	-2.972	-2.039	C	3.7031	-2.3798	-1.7486	C	4.0770	-3.2050	-1.3720				
O	5.551	-2.155	-0.323	O	5.0181	-1.6538	0.0504	O	5.3800	-2.4800	0.4330				
C	5.641	-3.569	-0.458	C	5.1271	-3.0578	-0.1576	C	5.4890	-3.8840	0.2250				
O	5.112	-4.001	-1.713	O	4.6191	-3.4278	-1.4416	O	4.9810	-4.2540	-1.0590				
N	3.903	0.231	-0.214	N	3.2998	0.6999	0.2719	N	3.7170	-0.1170	0.6350				
C	7.117	-3.87	-0.472	C	6.6061	-3.3408	-0.1616	C	6.9680	-4.1670	0.2210				
C	4.989	-4.297	0.714	C	4.4571	-3.8508	0.9594	C	4.8190	-4.6770	1.3420				
C	4.386	1.37	-0.972	C	3.9808	1.8582	-0.2875	C	4.4220	1.0090	0.0500				
C	4.817	2.527	-0.008	C	4.3632	2.8953	0.7491	C	4.9000	1.9910	1.1690				
C	4.548	3.858	-0.373	C	4.5545	4.2288	0.3559	C	5.0440	3.3610	0.8670				
C	4.944	4.888	0.474	C	4.9429	5.1990	1.2828	C	5.5160	4.2310	1.8430				
C	5.592	4.602	1.673	C	5.1605	4.8456	2.6126	C	5.8670	3.7520	3.1020				
C	5.847	3.282	2.039	C	5.0016	3.5213	3.0130	C	5.7640	2.3960	3.3920				
C	5.463	2.236	1.208	C	4.6147	2.5519	2.0856	C	5.2960	1.5040	2.4340				
N	1.19	-1.601	-0.767	N	0.6791	-1.0718	-0.4566	N	1.0410	-1.8980	-0.0740				
C	0.186	-2.304	-0.179	C	-0.3249	-1.7748	0.1314	C	0.0370	-2.6010	0.5140				
S	0.482	-3.78	0.708	S	-0.0289	-3.2508	1.0184	S	0.3330	-4.0770	1.4010				
N	-1.032	-1.706	-0.387	N	-1.5429	-1.1768	-0.0766	N	-1.1810	-2.0030	0.3060				
C	-2.319	-2.067	-0.003	C	-2.8299	-1.5378	0.3074	C	-2.4680	-2.3640	0.6900				
C	-3.36	-1.252	-0.509	C	-3.8709	-0.7228	-0.1986	C	-3.5140	-1.7240	0.0160				
C	-4.684	-1.503	-0.192	C	-5.1949	-0.9738	0.1184	C	-4.8590	-1.9480	0.3340				
C	-5.043	-2.574	0.624	C	-5.5539	-2.0448	0.9344	C	-5.1920	-2.8710	1.3170				
C	-4.024	-3.376	1.121	C	-4.5349	-2.8468	1.4314	C	-4.1460	-3.5460	1.9780				
C	-2.682	-3.145	0.826	C	-3.1929	-2.6158	1.1364	C	-2.7880	-3.2850	1.6700				
C	-4.373	-4.483	2.05	C	-4.8839	-3.9538	2.3604	C	-4.5090	-4.5560	3.0860				
F	-5.651	-4.95	1.804	F	-6.1619	-4.4208	2.1144	F	-5.6480	-5.2180	2.7790				
F	-4.359	-4.096	3.375	F	-4.8699	-3.5668	3.6854	F	-4.7150	-3.9150	4.2580				
F	-3.5	-5.538	1.944	F	-4.0109	-5.0088	2.2544	F	-3.5380	-5.4750	3.2760				
C	-5.74	-0.581	-0.684	C	-6.2509	-0.0518	-0.3736	C	-5.9570	-1.1740	-0.4100				
F	-5.368	0.05	-1.859	F	-5.8789	0.5792	-1.5486	F	-6.0540	-1.5860	-1.6920				
F	-6.032	0.438	0.202	F	-6.5429	0.9672	0.5124	F	-5.6750	0.1520	-0.4270				
F	-6.927	-1.245	-0.907	F	-7.4379	-0.7158	-0.5966	F	-7.1660	-1.3260	0.1720				
H	2.885	-2.229	0.444	H	2.3181	-1.7723	0.7379	H	2.6590	-2.6230	1.1170				
H	3.163	-0.51	-2.063	H	2.6738	0.0893	-1.6563	H	3.0580	-0.7330	-1.2750				
H	5.492	-1.238	-2.164	H	5.0206	-0.6413	-1.7395	H	5.3940	-1.4670	-1.3570				
H	4.035	-2.929	-3.123	H	3.6044	-2.2791	-2.8338	H	3.9740	-3.1050	-2.4570				
H	7.612	-3.354	-1.304	H	7.1096	-2.7766	-0.9564	H	7.4720	-3.6020	-0.5740				
H	7.609	-3.535	0.447	H	7.0789	-3.0496	0.7831	H	7.4410	-3.8760	1.1660				
H	7.31	-4.94	-0.607	H	6.8137	-4.4004	-0.3483	H	7.1760	-5.2260	0.0340				
H	5.163	-5.377	0.65	H	4.6370	-4.9250	0.8408	H	5.0010	-5.7510	1.2250				
H	5.373	-3.929	1.671	H	4.8179	-3.5327	1.9432	H	5.1790	-4.3570	2.3260				
H	3.907	-4.164	0.731	H	3.3738	-3.7210	0.9584	H	3.7350	-4.5490	1.3400				

H	5.275	1.107	-1.559	H 4.9103 1.5553 -0.7838	H 5.3230 0.6920 -0.4880		
H	3.621	1.741	-1.663	H 3.3357 2.3291 -1.0393	H 3.7720 1.5440 -0.6510		
H	4.014	4.056	-1.298	H 4.4011 4.5148 -0.6816	H 4.7910 3.7220 -0.1240		
H	4.721	5.914	0.201	H 5.0796 6.2287 0.9664	H 5.6260 5.2870 1.6170		
H	5.879	5.41	2.338	H 5.4602 5.5978 3.3360	H 6.2430 4.4380 3.8580		
H	6.324	3.053	2.986	H 5.1761 3.2337 4.0460	H 6.0560 2.0220 4.3700		
H	5.624	1.196	1.483	H 4.4975 1.5181 2.4106	H 5.2260 0.4410 2.6490		
H	1.015	-0.635	-1.167	H 0.5041 -0.1058 -0.8566	H 0.8660 -0.9320 -0.4740		
H	-1.014	-0.793	-0.939	H -1.5249 -0.2638 -0.6286	H -1.1630 -1.0900 -0.2460		
H	-3.14	-0.426	-1.171	H -3.6350 0.1017 -0.8539	H -3.3200 -1.0320 -0.7960		
H	-6.082	-2.757	0.88	H -6.5943 -2.2296 1.1929	H -6.2290 -3.0730 1.5780		
H	-1.945	-3.787	1.277	H -2.4520 -3.2595 1.5849	H -2.0110 -3.8030 2.2250		
H	2.968	0.461	0.2	H 2.3640 0.9728 0.6192	H 2.8210 0.1820 1.0610		
O	1.207	1.019	1.149	O 0.6961 1.5482 1.4594	O 1.0580 0.7220 1.8420		
C	0.758	2.167	1.043	C 0.2519 2.6906 1.6022	C 0.7020 2.0010 1.7570		
C	-0.697	2.441	0.674	C -1.0743 3.1633 0.9639	C -0.6830 2.4000 1.3470		
C	1.536	3.397	1.498	C 0.9854 3.6592 2.5046	C 1.6490 3.0570 2.1400		
C	-1.361	2.954	1.992	C -1.9303 3.8160 2.0851	C -1.2430 3.2150 2.5500		
H	-1.209	1.493	0.486	H -1.6210 2.2357 0.7611	H -1.3190 1.5090 1.2810		
C	-0.831	3.373	-0.595	C -1.1071 4.0075 -0.3794	C -0.8110 3.2020 -0.0040		
C	0.858	3.916	2.803	C 0.0572 4.1843 3.5837	C 1.0690 3.9120 3.2650		
H	2.574	3.133	1.722	H 1.8187 3.1302 2.9781	H 2.6000 2.6400 2.4830		
H	1.545	4.168	0.723	H 1.4122 4.4718 1.9185	H 1.8690 3.6830 1.2680		
C	-0.643	4.196	2.569	C -1.1918 4.8084 2.9802	C -0.3450 4.3900 2.9430		
H	-1.337	2.155	2.745	H -2.3057 3.0095 2.7315	H -1.3330 2.5450 3.4160		
H	-2.415	3.194	1.82	H -2.8227 4.2937 1.6642	H -2.2550 3.5800 2.3490		
C	-0.367	2.846	-1.985	C -0.8524 3.3669 -1.7840	C -0.4660 2.5600 -1.3810		
H	0.967	3.167	3.597	H -0.2345 3.3633 4.2507	H 1.0410 3.3210 4.1900		
H	1.359	4.83	3.137	H 0.5832 4.9242 4.1974	H 1.7220 4.7710 3.4550		
H	-0.757	5.042	1.882	H -0.9215 5.7102 2.4260	H -0.3130 5.1310 2.1370		
H	-1.113	4.482	3.516	H -1.8603 5.1308 3.7872	H -0.7660 4.8960 3.8190		
H	0.652	3.242	-2.119	H 0.0406 3.7379 -2.2944	N -0.3230 1.0930 -1.2690		
N	-0.174	1.39	-1.962	N -0.6849 1.9192 -1.6516	O -1.4490 0.3400 -0.9320		
O	-1.3	0.637	-1.625	O -1.8109 1.1662 -1.3146	O 0.9350 0.6540 -0.9330		
O	1.084	0.951	-1.626	O 0.5731 1.4802 -1.3156	N -1.6720 3.6980 -5.0130		
H	-1.8627	3.6423	-0.6848	N -0.1814 1.7517 -4.8255	C -0.4720 3.1160 -5.4580		
C	-0.0366	4.6599	-0.3043	C 1.1640 1.1694 -4.7289	C 0.6190 3.1910 -4.3800		
C	-0.6648	5.7436	0.3099	H 1.4464 0.6503 -5.6518	C -1.5460 4.9980 -4.4940		
C	1.3109	4.742	-0.6551	H 1.1771 0.4128 -3.9341	C -1.4500 6.0900 -5.5780		
C	0.0542	6.9094	0.5728	C 2.2345 2.1966 -4.3710	C -2.7370 3.5340 -5.9090		
H	-1.7274	5.6789	0.5856	H 1.9871 2.7232 -3.4444	C -2.3880 4.0560 -7.3150		
C	2.0305	5.9078	-0.3914	H 2.3726 2.9413 -5.1599	H -1.2260 2.7480 -2.1430		
H	1.8062	3.8879	-1.1391	H 3.1955 1.6936 -4.2197	H 0.4990 2.9330 -1.7390		
C	1.4024	6.9915	0.2223	C -0.3713 2.7682 -5.8638	C 0.1090 4.4320 0.1068		
H	-0.441	7.7639	1.0564	H 0.0629 3.7052 -5.4925	C 1.3563 4.4287 -0.5183		
H	3.0931	5.9721	-0.6676	H -1.4412 2.9870 -5.9739	C -0.3046 5.5494 0.8320		
H	1.9692	7.9107	0.4297	C 0.2221 2.5045 -7.2461	C 2.1900 5.5423 -0.4177		
				H 1.3142 2.4511 -7.2185	H 1.6824 3.5473 -1.0893		
				H -0.0424 3.3266 -7.9201	C 0.5288 6.6638 0.9319		
				H -0.1513 1.5822 -7.6945	H -1.2877 5.5522 1.3246		
				C -1.2331 0.7200 -4.7791	C 1.7760 6.6603 0.3074		
				H -1.0706 0.0865 -3.8980	H 3.1734 5.5395 -0.9098		
				H -2.1969 1.2120 -4.5958	H 0.2022 7.5448 1.5035		
				C -1.3768 -0.1896 -5.9920	H 2.4334 7.5383 0.3866		
				H -0.4290 -0.6619 -6.2656	H -1.8187 3.5567 -0.0650		
				H -1.7674 0.3544 -6.8561			
				H -2.0907 -0.9900 -5.7687			
				H -1.7074 3.5237 -2.4510			
				H -2.1766 4.2631 -0.4636			
				C -0.3947 5.3539 -0.3304			
				C -1.1350 6.5408 -0.2041			
				C 0.9973 5.4449 -0.4662			
				C -0.4970 7.7821 -0.1930			
				H -2.2184 6.5095 -0.1056			
				C 1.6332 6.6878 -0.4574			
				H 1.6030 4.5455 -0.5732			
				C 0.8873 7.8553 -0.3184			
				H -1.0823 8.6915 -0.0855			
				H 2.7137 6.7430 -0.5554			
				H 1.3855 8.8207 -0.3075			

Table A2: The xyz coordinates of the substrates resulting the formation of RR product.

Structure TS1	Structure 2	Structure 3	Structure TS2
O 2.7930 -2.3850 -2.4180	O 2.6200 -0.8340 -1.7710	O 2.5600 -0.6410 -1.8090	O 3.1340 -3.1240 -1.7040
C 2.4020 -1.7240 -1.1280	C 2.0910 -0.2750 -0.5330	C 2.0310 -0.0820 -0.5710	C 2.8340 -2.0660 -0.6760
C 3.3080 -0.4770 -1.0870	C 3.0400 0.9150 -0.2680	C 2.9800 1.1080 -0.3060	C 3.7660 -0.9120 -1.0870
C 4.5900 -1.0140 -1.6870	C 4.2730 0.1140 -0.3660	C 4.2130 0.3070 -0.4040	C 5.0290 -1.6840 -1.4690
C 4.0510 -1.8550 -2.8130	C 4.0820 -0.6510 -1.6550	C 4.0220 -0.4580 -1.6930	C 4.4870 -2.9420 -2.1810
O 5.3100 -1.9460 -0.8630	O 4.1560 -0.9030 0.6130	O 4.0960 -0.7100 0.5750	O 5.6480 -2.2310 -0.2510
C 5.6280 -3.0470 -1.7240	C 4.8090 -2.0430 0.0200	C 4.7490 -1.8500 -0.0180	C 5.8900 -3.6810 -0.4450
O 5.0390 -2.8600 -3.0130	O 4.9260 -1.7810 -1.4090	O 4.8660 -1.5880 -1.4470	O 5.4050 -3.9930 -1.7940
N 3.3470 0.1510 0.2320	N 2.9220 1.6350 1.0100	N 2.7860 1.7590 0.9950	N 3.9640 0.1590 -0.0990
C 7.1420 -3.0890 -1.9010	C 6.2260 -2.2600 0.5900	C 6.1660 -2.0670 0.5520	C 7.3930 -3.9350 -0.4320
C 5.1250 -4.3430 -1.0980	C 3.9530 -3.2890 0.3180	C 3.8930 -3.0960 0.2800	C 5.1070 -4.4650 0.6010
C 3.7950 1.5560 0.2190	C 3.2200 3.0580 0.9280	C 3.8000 2.8040 1.1800	C 4.6580 1.3160 -0.6410
C 5.3080 1.7270 0.3390	C 4.6440 3.3570 0.5240	C 5.2010 2.1990 0.9830	C 4.5440 2.5720 0.1990
C 5.8950 2.9790 0.1100	C 4.9310 3.9840 -0.6970	C 6.2530 3.0180 0.5520	C 4.7180 3.8260 -0.4130
C 7.2710 3.1610 0.2630	C 6.2520 4.2400 -1.0670	C 7.5300 2.4760 0.3600	C 4.6240 5.0050 0.3310
C 8.0790 2.0850 0.6410	C 7.2980 3.8750 -0.2210	C 7.7550 1.1130 0.5990	C 4.3650 4.9470 1.6980
C 7.5000 0.8330 0.8600	C 7.0260 3.2550 0.9960	C 6.7030 0.2930 1.0280	C 4.2150 3.7120 2.3230
C 6.1210 0.6520 0.7160	C 5.7060 2.9990 1.3680	C 5.4260 0.8380 1.2270	C 4.3160 2.5330 1.5820
N 1.0160 -1.3780 -1.1390	N 0.6820 0.1430 -0.6470	N 0.6220 0.3360 -0.6850	N 1.4660 -1.6660 -0.7270

C 0.0220 -2.2470 -0.8150	C -0.3220 -0.6850 -0.3200	C -0.3820 -0.4920 -0.3580	C 0.4620 -2.3690 -0.1390
S 0.3470 -3.8990 -0.3670	S 0.0140 -2.3410 0.2400	S -0.0460 -2.1480 0.2020	S 0.7580 -3.8450 0.7480
N -1.2150 -1.6540 -0.9100	N -1.5840 -0.2430 -0.4180	N -1.6440 -0.0500 -0.4560	N -0.7560 -1.7710 -0.3470
C -2.4990 -2.1250 -0.6430	C -2.7300 -1.0940 -0.0450	C -2.7900 -0.9010 -0.0830	C -2.0430 -2.1320 0.0370
C -3.5510 -1.2070 -0.8630	C -4.0310 -0.5730 -0.1430	C -4.0910 -0.3800 -0.1810	C -3.0840 -1.3170 -0.4690
C -4.8700 -1.5720 -0.6460	C -5.1080 -1.3290 0.1960	C -5.1680 -1.1360 0.1580	C -4.4080 -1.5680 -0.1520
C -5.2070 -2.8490 -0.2070	C -4.9350 -2.6440 0.6440	C -4.9950 -2.4510 0.6060	C -4.7670 -2.6390 0.6640
C -4.1730 -3.7480 0.0180	C -3.6500 -3.1870 0.7510	C -3.7100 -2.9940 0.7130	C -3.7480 -3.4410 1.1610
C -2.8380 -3.4130 -0.1920	C -2.5360 -2.4070 0.4070	C -2.5960 -2.2140 0.3690	C -2.4060 -3.2100 0.8660
C -4.4990 -5.0970 0.5530	C -3.4710 -4.6320 1.2460	C -3.5310 -4.4390 1.2080	C -4.0970 -4.5480 2.0900
F -5.7570 -5.4980 0.1460	F -4.5540 -5.3610 0.9040	F -4.6140 -5.1680 0.8660	F -5.3750 -5.0150 1.8440
F -4.5140 -5.1370 1.9320	F -3.3330 -4.6340 2.5880	F -3.3930 -4.4410 2.5500	F -4.0830 -4.1610 3.4150
F -3.5890 -6.0430 0.1450	F -2.3700 -5.1680 0.6790	F -2.4300 -4.9750 0.6410	F -3.2240 -5.6030 1.9840
C -5.9430 -0.5620 -0.8350	C -6.5280 -0.7410 0.0910	C -6.5880 -0.5480 0.0530	C -5.4640 -0.6460 -0.6440
F -5.6140 0.3510 -1.8120	F -6.5620 0.1800 -0.8950	F -6.6220 0.3730 -0.9330	F -5.0920 -0.0150 -1.8190
F -6.2030 0.1700 0.3060	F -6.8630 -0.1590 1.2620	F -6.9230 0.0340 1.2240	F -5.7560 0.3730 0.2420
F -7.1350 -1.1630 -1.1860	F -7.4070 -1.7290 -0.1860	F -7.4670 -1.5360 -0.2240	F -6.6510 -1.3100 -0.8670
H 2.6670 -2.4030 -0.3110	H 2.1440 -1.0040 0.2720	H 2.0830 -0.8110 0.2330	H 3.1140 -2.4330 0.3140
H 2.8960 0.2420 -1.8090	H 2.9450 1.6180 -1.1070	H 2.8910 1.8420 -1.1200	H 3.3650 -0.4840 -2.0150
H 5.2900 -0.2450 -2.0300	H 5.2350 0.6260 -0.2870	H 5.1440 0.7780 -0.7610	H 5.7910 -1.1390 -2.0320
H 3.9070 -1.2890 -3.7390	H 4.4190 -0.1130 -2.5460	H 4.3490 0.0650 -2.5990	H 4.4580 -2.8460 -3.2700
H 7.5010 -2.1550 -2.3490	H 6.8460 -1.3750 0.4070	H 6.9670 -1.6050 -0.0300	H 7.8920 -3.3320 -1.2000
H 7.6530 -3.2020 -0.9390	H 6.1940 -2.4170 1.6730	H 6.1830 -2.0640 1.6450	H 7.8280 -3.6590 0.5330
H 7.4440 -3.9030 -2.5680	H 6.7200 -3.1110 0.1090	H 6.4170 -3.1200 0.3350	H 7.6180 -4.9850 -0.6430
H 5.3560 -5.2050 -1.7330	H 4.4480 -4.1970 -0.0420	H 4.2870 -3.9660 -0.2560	H 5.3600 -5.5290 0.5490
H 5.5610 -4.4990 -0.1060	H 3.7480 -3.3860 1.3880	H 3.8690 -3.3280 1.3460	H 5.3210 -4.0980 1.6090
H 4.0390 -4.3240 -0.9700	H 2.9970 -3.2310 -0.2080	H 2.8690 -2.9610 -0.0690	H 4.0300 -4.4030 0.4430
H 3.4240 0.2860 -0.6660	H 2.5150 3.5540 0.2510	H 3.6340 3.6210 0.4670	H 5.7230 1.0860 -0.7590
H 3.3640 2.0530 1.0940	H 3.0630 3.5110 1.9130	H 3.7320 3.2060 2.1960	H 4.2530 1.5530 -1.6330
H 5.2790 3.8270 -0.1770	H 4.1280 4.2740 -1.3710	H 6.0960 4.0790 0.3690	H 4.9330 3.8890 -1.4760
H 7.7150 4.1380 0.0900	H 6.4680 4.7240 -2.0160	H 8.3540 3.1150 0.0510	H 4.7570 5.9680 -0.1540
H 9.1500 2.2190 0.7620	H 8.3270 4.0730 -0.5110	H 8.7690 0.7220 0.5550	H 4.2830 5.8600 2.2810
H 8.1210 -0.0070 1.1610	H 7.8400 2.9650 1.6560	H 7.0730 -0.4750 1.7070	H 4.0090 3.6550 3.3890
H 5.7010 -0.3220 0.9500	H 5.5010 2.4990 2.3140	H 4.8210 0.4070 2.0430	H 4.1880 1.5770 2.0910
H 0.7980 -0.3980 -1.2360	H 0.4630 1.0720 -0.9430	H 0.4030 1.2340 -1.0720	H 1.2910 -0.7000 -1.1270
H -1.1940 -0.7100 -1.2740	H -1.7610 0.6780 -0.7760	H -1.8290 0.8580 -0.8500	H -0.7380 -0.8580 -0.8990
H -3.3460 -0.2020 -1.2060	H -4.1610 0.4470 -0.4960	H -4.2250 0.6370 -0.5420	H -2.8580 -0.4660 -1.0880
H -6.2440 -3.1260 -0.0220	H -5.8020 -3.2490 0.9140	H -5.8640 -3.0570 0.8710	H -5.8070 -2.8190 0.9280
H -2.0970 -4.1700 0.0150	H -1.9220 -3.1120 -0.1580	H -1.9900 -2.9150 -0.2130	H -1.6660 -3.8470 1.3250
H 2.3840 0.1560 0.6050	H 2.0050 1.4530 1.4410	H 1.8400 2.1220 1.0720	H 3.0500 0.4020 0.3170
O 0.6890 0.6050 1.0520	O 0.2990 1.1480 2.1410	O 0.2390 1.3410 2.1030	O 1.4830 0.9540 1.1890
C 0.1560 1.1690 2.0120	C -0.4740 2.1240 2.3710	C -0.5330 2.3430 2.1830	C 0.4920 1.6760 1.0900
C -1.2950 0.9220 2.3730	C -1.9420 1.9470 2.1190	C -2.0100 2.1670 2.0260	C -0.9230 1.1600 1.2930
C 0.8920 2.2190 2.8200	C 0.1030 3.3990 2.3650	C 0.0430 3.5920 2.3270	C 0.4700 3.1430 0.6700
C -1.9310 2.2180 2.8520	C -2.7940 3.0580 2.7190	C -2.7960 3.2370 2.7710	C -1.4260 1.8540 2.5670
H -1.3470 0.1640 3.1550	C -0.7990 4.5310 2.9220	C -0.8200 4.7500 2.8350	H -0.7780 0.0990 1.5940
C 0.2480 2.4030 4.1850	C -2.2180 4.4300 2.3880	C -2.2740 4.6230 2.4120	C -0.3140 3.5190 -0.6560
H 1.9320 1.9100 2.9450	H -2.8500 2.9350 3.8040	H -2.7110 3.0800 3.8540	C -0.0130 3.9080 1.9130
H 0.8710 3.1580 2.2560	H -3.8190 2.9810 2.3390	H -3.8580 3.1580 2.5150	H 1.5190 3.4070 0.4880
C -1.2310 2.7820 4.0900	H -0.7970 4.4840 4.0150	H -0.7440 4.7810 3.9280	C -1.3290 3.3820 2.5040
H -2.9940 2.0650 3.0650	H -0.3570 5.4930 2.6390	H -0.4030 5.6880 2.4530	H -0.8490 1.4950 3.4300
H -1.8770 2.9630 2.0490	H -2.2180 4.5770 1.3030	H -2.3610 4.7800 1.3310	H -2.4680 1.5650 2.7500
H 0.3400 1.4680 4.7500	H -2.8410 5.2150 2.8290	H -2.8750 5.3940 2.9060	C 0.1070 2.6670 -1.9500
H 0.7870 3.1650 4.7590	N -1.1440 3.4620 -1.5330	N -1.2040 3.6550 -1.5710	H 0.7570 3.8200 2.6910
H -1.3350 3.8740 4.0850	O -2.0980 2.6840 -1.6410	O -2.1580 2.8770 -1.6790	H -0.1050 4.9790 1.6940
H -1.7410 2.4320 4.9960	O -0.0974 3.0088 -1.1713	O -0.0890 3.2270 -1.4990	H -2.1730 3.7780 1.9340
N -0.5470 1.7800 -1.3560	H -2.0930 1.9430 1.0360	H -2.2460 2.2240 0.9600	H -1.4550 3.7900 3.5150
O -1.5000 0.9350 -1.7890	N -0.2370 2.1060 5.5300	N -0.3770 1.9960 6.2340	H 1.0730 3.0710 -2.2840
O 0.7140 1.4060 -1.2190	C -0.6300 2.9370 6.6880	C -0.1960 3.1290 7.2090	N 0.1020 1.3250 -1.9220
C -0.8740 3.1360 -1.0170	C -2.1120 3.2940 6.7540	C -1.0570 4.3290 6.8550	O -1.0240 0.5720 -1.5850
H -1.8934 3.3745 -1.2742	H -0.1000 3.8940 6.6350	H 0.8550 3.4310 7.1580	O 1.3600 0.8860 -1.5860
C 0.0609 3.9156 -0.4627	H -0.3310 2.4650 7.6320	H -0.3950 2.7620 8.2210	C -0.1832 4.9793 -1.0292
H 1.0575 3.5423 -0.2343	H -2.2920 3.9600 7.6050	H -0.7770 5.1840 7.4780	C -1.3409 5.7781 -1.1009
H -1.8210 0.5510 1.4870	H -2.4310 3.8250 5.8530	H -0.9280 4.6200 5.8090	C 1.0493 5.6071 -1.2236
N 0.8820 -1.6900 3.7510	H -2.7490 2.4160 6.8890	H -2.1170 4.1340 7.0360	C -1.2658 7.1477 -1.3690
C 0.8100 -1.8630 5.2110	C -0.9910 0.8310 5.4540	C -1.7870 1.4500 6.1670	H -2.3257 5.3384 -0.9580
H 1.5660 -1.2290 5.6860	C -0.9800 -0.0760 6.6840	C -2.2700 0.9730 7.4870	C 1.1276 6.9762 -1.4973
H 1.0380 -2.8950 5.5030	H -0.6190 0.2450 4.6040	H -1.7830 0.6280 5.4490	H 1.9767 5.0375 -1.2211
C -0.5270 -1.4460 5.8170	H -2.0330 1.0530 5.1990	H -2.4240 2.2510 5.8050	C -0.0283 7.7474 -1.5665
H -0.4550 -1.4500 6.9100	H -1.5750 -0.9740 6.4810	H -3.2120 0.4430 7.3570	H -2.1726 7.7403 -1.4346
H -1.3320 -2.1350 5.5440	H 0.0290 -0.4080 6.9410	H -1.5740 0.2730 7.9600	H 2.0989 7.4269 -1.6806
H -0.8120 -0.4370 5.5080	H -1.4190 0.4110 7.5590	H -2.4580 1.7930 8.1850	H 0.0416 8.8074 -1.7927
C -0.1610 -2.4270 3.0110	C 1.2180 1.8140 5.5610	C 0.6530 0.9020 6.3860	H -1.4088 3.3737 -0.6578
H -1.1500 -2.0640 3.3100	C 2.1270 3.0410 5.6170	C 1.9540 1.3040 5.7110	
H -0.0910 -2.1480 1.9580	H 1.4820 1.2550 4.6550	H 0.2640 -0.0000 5.9000	
C -0.1620 -3.9460 3.1570	H 1.4750 1.1750 6.4140	H 0.7890 0.7040 7.4540	
H -0.3220 -4.2480 4.1960	H 3.1600 2.7480 5.4010	H 2.6720 0.4810 5.7670	
H 0.7750 -4.3940 2.8150	H 1.8350 3.8030 4.8900	H 1.7930 1.5400 4.6540	
H -0.9810 -4.3780 2.5720	H 2.1200 3.4980 6.6120	H 2.4110 2.1740 6.1900	
C 2.2210 -2.0210 3.2250	C -2.3783 5.3140 -2.1341	C -2.6535 5.4504 -1.6486	
H 2.1900 -2.0130 2.1290	C -1.3740 4.7080 -1.4790	C -1.4340 4.9010 -1.5170	
H 2.5300 -3.0290 3.5280	H -0.7071 5.3187 -0.8491	H -0.5850 5.5743 -1.3141	
C 3.2970 -1.0210 3.6350	C -2.5890 6.7644 -2.0969	C -2.8856 6.8974 -1.5926	
H 3.5180 -1.0710 4.7050	C -1.5186 7.6660 -2.0280	C -1.9643 7.8159 -2.1104	
H 3.0060 0.0020 3.3870	C -3.8926 7.2695 -2.1818	C -4.0817 7.3758 -1.0423	
H 4.2280 -1.2400 3.1010	C -1.7481 9.0434 -2.0239	C -2.2252 9.1878 -2.0612	
C -0.1810 5.3187 -0.0948	H -0.4916 7.3102 -1.9982	H -1.0375 7.4795 -2.5701	
C -0.5216 8.0070 0.6454	C -4.1222 8.6480 -2.1763	C -4.3418 8.7479 -0.9919	
C -1.0332 6.1574 -0.8264	H -4.7462 6.5978 -2.2465	H -4.8210 6.6912 -0.6332	
C 0.5131 5.8528 0.9999	C -3.0501 9.5334 -2.0953	C -3.4122 9.6528 -1.5004	
C 0.3395 7.1881 1.3712	H -0.9112 9.7342 -1.9716	H -1.5035 9.8940 -2.4633	
C -1.2041 7.4938 -0.4543	H -5.1389 9.0294 -2.2385	H -5.2686 9.1106 -0.5538	
H -1.5672 5.7993 -1.7024	H -3.2291 10.6061 -2.0939	H -3.6150 10.7201 -1.4603	
H 1.1937 5.2342 1.5826	H -2.2720 0.9760 2.5050	H -2.3090 1.1750 2.3810	
H 0.8780 7.5888 2.2264	H -3.0740 4.7370 -2.7330	H -3.5271 4.8247 -1.7941	
H -1.8682 8.1378 -1.0277	H 0.3470 3.6350 1.3260	H 1.0860 3.6000 2.6410	

H -0.6547 9.0468 0.9331	H 1.0430 3.3520 2.9150	H -0.2750 2.3830 5.2890 H -0.2070 2.6420 4.6530	
Structure 5	**Structure TS3**	**Structure 7**	
O 3.3080 -3.3030 -1.6550 C 3.0060 -2.1300 -0.8240 C 3.9660 -1.0220 -1.3510 C 5.1610 -1.8290 -1.8120 C 4.5010 -3.0550 -2.3800 O 6.0090 -2.3160 -0.7600 C 6.1950 -3.7070 -1.0400 O 5.4690 -4.0860 -2.2120 N 4.2880 0.1060 -0.4420 C 7.6770 -3.9420 -1.3140 C 5.7380 -4.5340 0.1570 C 4.7950 1.2520 -1.1890 C 5.0850 2.4240 -0.2800 C 4.2030 3.5120 -0.2270 C 4.4620 4.5950 0.6130 C 5.6040 4.6000 1.4140 C 6.4810 3.5160 1.3810 C 6.2210 2.4320 0.5410 N 1.5750 -1.7260 -0.9950 C 0.5710 -2.4290 -0.4070 S 0.8670 -3.9050 0.4800 N -0.6470 -1.8310 -0.6150 C -1.9340 -2.1920 -0.2310 C -2.9750 -1.3770 -0.7370 C -4.2990 -1.6280 -0.4200 C -4.6580 -2.6990 0.3960 C -3.6390 -3.5010 0.8930 C -2.2970 -3.2700 0.5980 C -3.9880 -4.6080 1.8220 F -5.2660 -5.0750 1.5760 F -3.9740 -4.2210 3.1470 F -3.1150 -5.6630 1.7160 C -5.3550 -0.7060 -0.9120 F -4.9830 -0.0750 -2.0870 F -5.6470 0.3130 -0.0260 F -6.5420 -1.3700 -1.1350 H 3.2320 -2.3560 0.2240 H 3.4870 -0.6190 -2.2540 H 5.7960 -1.3140 -2.5400 H 4.2450 -2.9530 -3.4400 H 8.0060 -3.3460 -2.1740 H 8.2930 -3.6430 -0.4600 H 7.8770 -4.9920 -1.5540 H 5.8600 -5.6060 -0.0330 H 6.2940 -4.2630 1.0600 H 4.6790 -4.3660 0.3740 H 5.7270 0.9920 -1.7060 H 4.0870 1.5650 -1.9660 H 3.2920 3.4990 -0.8270 H 3.7560 5.4200 0.6510 H 5.7940 5.4370 2.0780 H 7.3570 3.5030 2.0210 H 6.8860 1.5710 0.5380 H 1.4000 -0.7600 -1.3950 H -0.6290 -0.9180 -1.1670 H -2.7390 -0.5550 -1.3990 H -5.6980 -2.8810 0.6540 H -1.5560 -3.9140 1.0440 H 3.3810 0.3910 -0.0250 O 1.5920 0.8940 0.9210 C 0.5160 1.4550 1.1330 C -0.6720 0.7240 1.7000 C 0.3610 2.9350 0.8720 C -1.0830 1.3880 3.0040 H -0.4000 -0.3210 1.8780 C -0.3490 3.3430 -0.4460 C -0.1380 3.5900 2.1760 H 1.3950 3.2930 0.7540 C -1.3340 2.8840 2.8230 H -0.2920 1.2470 3.7510 H -1.9850 0.9070 3.3980 C 0.0230 2.6170 -1.7520 H 0.6870 3.5610 2.9030 H -0.3550 4.6520 2.0250 H -2.2400 3.0310 2.2290 H -1.5320 3.3380 3.8010 H 1.0050 3.0350 -2.0280 N 0.2080 1.1790 -1.7330 O -0.9150 0.5120 -1.8530 O 1.4690 0.8260 -1.8540 C -0.2583 4.8469 -0.6768 C 0.8966 5.5855 -0.4179 C -1.3846 5.5485 -1.1510 C 0.9385 6.9660 -0.6373 H 1.7698 5.0869 -0.0168 C -1.3464 6.9260 -1.3815 H -2.3095 5.0086 -1.3357 C -0.1788 7.6368 -1.1264 H 1.8472 7.5120 -0.4083 H -2.2311 7.4359 -1.7465	O 2.6710 -2.5180 -1.1540 C 2.3620 -1.4070 -0.2500 C 3.3330 -0.2710 -0.6890 C 4.5570 -1.0800 -1.0480 C 3.9560 -2.2980 -1.7000 O 5.2710 -1.5720 0.0990 C 5.3800 -2.9760 -0.1090 O 4.8720 -3.3460 -1.3930 N 3.5010 0.8360 0.2660 C 6.8590 -3.2590 -0.1130 C 4.7100 -3.7690 1.0080 C 4.1460 1.9890 -0.3530 C 3.8360 3.2920 0.3590 C 3.6050 4.4600 -0.3870 C 3.3760 5.6810 0.2510 C 3.3790 5.7510 1.6430 C 3.6150 4.6020 2.3960 C 3.8490 3.3820 1.7580 N 0.9320 -0.9900 -0.4080 C -0.0720 -1.6930 0.1800 S 0.2240 -3.1690 1.0670 N -1.2900 -1.0950 -0.0280 C -2.5770 -1.4560 0.3560 C -3.6180 -0.6410 -0.1500 C -4.9420 -0.8920 0.1670 C -5.3010 -1.9630 0.9830 C -4.2820 -2.7650 1.4800 C -2.9400 -2.5340 1.1850 C -4.6310 -3.8720 2.4090 F -5.9090 -4.3390 2.1630 F -4.6170 -3.4850 3.7340 F -3.7580 -4.9270 2.3030 C -5.9980 0.0300 -0.3250 F -5.6260 0.6610 -1.5000 F -6.2900 1.0490 0.5610 F -7.1850 -0.6340 -0.5480 H 2.5720 -1.6880 0.7870 H 2.9080 0.1280 -1.6210 H 5.2720 -0.5540 -1.6890 H 3.8570 -2.1970 -2.7860 H 7.3620 -2.6950 -0.9080 H 7.3320 -2.9670 0.8310 H 7.0660 -4.3180 -0.3000 H 4.8890 -4.8430 0.8890 H 5.0710 -3.4510 1.9910 H 3.6270 -3.6380 1.0070 H 5.2330 1.8480 -0.3630 H 3.8180 2.0950 -1.3940 H 3.6350 4.4290 -1.4760 H 3.2290 6.5850 -0.3390 H 3.2280 6.7050 2.1440 H 3.6430 4.6550 3.4830 H 4.0600 2.4960 2.3590 H 0.5970 0.7970 -0.7090 H -1.1940 0.0950 -0.7970 H -3.4010 0.1960 -0.7950 H -6.3420 -2.1450 1.2450 H -2.2080 -3.1810 1.6450 H 2.5840 1.0660 0.6600 O 0.9490 1.6300 1.5080 C -0.0400 2.3510 1.5280 C -1.3570 1.9220 2.1500 C 0.0390 3.7810 0.9850 C -1.5420 2.7650 3.4140 H -1.1750 0.8920 2.5150 C -0.8690 4.2240 -0.2770 C -0.2930 4.6800 2.2820 H 0.8490 3.3600 0.4050 H 0.9680 4.3240 1.0400 C -1.5160 4.2540 3.0990 H -0.7580 2.5260 4.1430 H -2.4990 2.5100 3.8840 C -0.6270 3.4360 -1.5960 H 0.5720 4.6510 2.9630 H -0.4100 5.7300 1.9810 H -2.4360 4.5370 2.5850 H -1.5260 4.8190 4.0400 H 0.2800 3.8630 -2.0500 N -0.4320 2.0010 -1.6030 O -1.5580 1.2480 -1.2660 O 0.8260 1.5620 -1.2670 N -3.8070 3.8220 -4.7520 C -3.7150 3.2690 -6.1110 H -4.6130 3.4900 -6.6990 H -3.6430 2.1760 -6.0520 C -2.4770 3.7450 -6.8650 H -1.5650 3.5150 -6.3040 H -2.4980 4.8220 -7.0580 H -2.4120 3.2370 -7.8330 C -3.9290 5.2790 -4.6550	O 2.8560 -3.1670 -1.0860 C 2.5470 -2.0560 -0.1820 C 3.5220 -0.9180 -0.6140 C 4.7520 -1.7270 -0.9810 C 4.1530 -2.9460 -1.6380 O 5.4560 -2.2210 0.1670 C 5.5650 -3.6250 -0.0410 O 5.0570 -3.9950 -1.3250 N 3.7000 0.1630 0.3700 C 7.0440 -3.9080 -0.0450 C 4.8950 -4.4180 1.0760 C 4.6430 1.1860 -0.0720 C 4.7110 2.3550 0.8880 C 4.8470 3.6620 0.3960 C 4.9650 4.7430 1.2720 C 4.9520 4.5310 2.6490 C 4.8250 3.2380 3.1520 C 4.7140 2.1570 2.2770 N 1.1170 -1.6390 -0.3400 C 0.1130 -2.3420 0.2480 S 0.4090 -3.8180 1.1350 N -1.1050 -1.7440 0.0400 C -2.3920 -2.1050 0.4240 C -3.4380 -1.4650 -0.2500 C -4.7830 -1.6890 0.0680 C -5.1160 -2.6120 1.0510 C -4.0700 -3.2870 1.7120 C -2.7120 -3.0260 1.4040 C -4.4330 -4.2970 2.8200 F -5.5720 -4.9590 2.5130 F -4.6390 -3.6560 3.9920 F -3.4620 -5.2160 3.0100 C -5.8810 -0.9150 -0.6760 F -5.9780 -1.3270 -1.9580 F -5.5990 0.4110 -0.6930 F -7.0900 -1.0670 -0.0940 H 2.7540 -2.3410 0.8550 H 3.1310 -0.4820 -1.5430 H 5.4680 -1.2030 -1.6210 H 4.0500 -2.8460 -2.7230 H 7.5480 -3.3440 -0.8400 H 7.5170 -3.6170 0.9000 H 7.2520 -4.9680 -0.2320 H 5.0750 -5.4920 0.9580 H 5.2560 -4.1000 2.0600 H 3.8120 -4.2890 1.0750 H 5.6540 0.7720 -0.1580 H 4.3410 1.5540 -1.0610 H 4.8730 3.8450 -0.6750 H 5.0740 5.7510 0.8800 H 5.0460 5.3720 3.3320 H 4.8200 3.0670 4.2250 H 4.6340 1.1490 2.6840 H 0.8990 -0.7540 -0.7840 H -1.0370 -0.5860 -0.7740 H -3.2280 -0.7800 -1.0640 H -6.1550 -2.8140 1.3110 H -1.9680 -3.5390 2.0000 H 2.7890 0.6020 0.5380 O 1.1340 0.9810 1.5760 C 0.7940 2.1020 2.0390 C 0.4430 2.2020 3.5510 C 0.6700 3.3100 1.0650 C 0.7480 3.5790 4.1050 H 1.0130 1.4460 4.1020 C -0.6240 3.3250 0.2010 C 0.8920 4.6230 1.8370 H 1.5200 3.2360 0.3730 C 0.2060 4.6730 3.1960 H 1.8320 3.6970 4.2090 H 0.3180 3.6760 5.1080 C -0.4480 2.7580 -1.2390 H 1.9700 4.7390 2.0030 H 0.5940 5.4890 1.2350 H -0.8800 4.5810 3.0880 H 0.3990 5.6480 3.6580 N -0.2470 1.3520 -1.5350 O -1.3730 0.5990 -1.1980 O 1.0110 0.9130 -1.1990 N -0.6840 2.9260 -6.1930 C -0.4450 1.9160 -7.1380 C 0.5860 2.3920 -8.1760 C -1.2660 4.0790 -6.7480 C -2.5650 3.7620 -7.5120 C -1.3810 2.4510 -5.0670 C -2.7170 1.7920 -5.4590 H -1.3300 3.0720 -1.8180 H 0.3800 3.3090 -1.7070 C -1.3347 4.6692 0.1452 C -0.8187 5.7862 -0.5237	

H -0.1402 8.7077 -1.2902 H -1.4427 3.2151 -0.3392 H -1.4860 0.7400 0.9720	H -2.9310 5.7070 -4.8140 H -4.1860 5.5600 -3.6260 C -4.8890 5.9850 -5.6110 H -4.5770 5.8820 -6.6540 H -4.9060 7.0570 -5.3860 H -5.9130 5.6180 -5.5260 C -4.7600 3.0700 -3.9160 H -4.4970 2.0050 -3.9520 H -4.6030 3.3560 -2.8690 C -6.2420 3.2160 -4.2370 H -6.4570 3.0090 -5.2900 H -6.6090 4.2150 -3.9870 H -6.8190 2.5040 -3.6370 H -1.4170 3.6750 -2.3210 H -1.9453 4.0463 -0.0991 C -0.8087 5.7227 -0.5359 C -1.9707 6.5006 -0.3706 C 0.3763 6.3763 -0.8847 C -1.9472 7.8837 -0.5624 H -2.9133 6.0396 -0.0845 C 0.3944 7.7590 -1.0889 H 1.2956 5.8218 -1.0555 C -0.7625 8.5127 -0.9234 H -2.8545 8.4676 -0.4333 H 1.3164 8.2406 -1.3998 H -0.7377 9.5859 -1.0882	C -2.5635 4.8197 0.8134 C -1.5151 6.9974 -0.5550 H 0.1291 5.7395 -1.0523 C -3.2535 6.0347 0.7969 H -3.0101 3.9858 1.3528 C -2.7309 7.1231 0.1082 H -1.1101 7.8416 -1.1082 H -4.2051 6.1273 1.3145 H -3.2727 8.0640 0.0827 H -1.3563 2.6598 0.6858 H -0.6170 1.9700 3.6850	

Table A3: The xyz coordinates of the substrates resulting the formation of RS product.

Structure TS1	**Structure 2**	**Structure 3**	**Structure TS2**
O 2.7800 -2.4080 -2.3430 C 2.3890 -1.7470 -1.0530 C 3.2950 -0.5000 -1.0120 C 4.5770 -1.0370 -1.6120 C 4.0380 -1.8780 -2.7380 O 5.2970 -1.9690 -0.7880 C 5.6150 -3.0700 -1.6490 O 5.0260 -2.8830 -2.9380 N 3.3340 0.1280 0.3070 C 7.1290 -3.1120 -1.8260 C 5.1120 -4.3660 -1.0230 C 3.7820 1.5330 0.2940 C 5.2950 1.7040 0.4140 C 5.8820 2.9560 0.1850 C 7.2580 3.1380 0.3380 C 8.0660 2.0620 0.7160 C 7.4870 0.8100 0.9350 C 6.1080 0.6290 0.7910 N 1.0030 -1.4010 -1.0640 C 0.0090 -2.2700 -0.7400 S 0.3340 -3.9220 -0.2920 N -1.2280 -1.6770 -0.8350 C -2.5120 -2.1480 -0.5680 C -3.5640 -1.2300 -0.7880 C -4.8830 -1.5950 -0.5710 C -5.2200 -2.8720 -0.1320 C -4.1860 -3.7710 0.0930 C -2.8510 -3.4360 -0.1170 C -4.5120 -5.1200 0.6280 F -5.7700 -5.5210 0.2210 F -4.5270 -5.1600 2.0070 F -3.6020 -6.0660 0.2200 C -5.9560 -0.5850 -0.7600 F -5.6270 0.3280 -1.7370 F -6.2160 0.1470 0.3810 F -7.1480 -1.1860 -1.1110 H 2.6730 -2.4230 -0.2380 H 2.8870 0.2210 -1.7340 H 5.2760 -0.2660 -1.9500 H 3.8940 -1.3120 -3.6640 H 7.4880 -2.1780 -2.2730 H 7.6400 -3.2260 -0.8640 H 7.4300 -3.9270 -2.4930 H 5.3440 -5.2280 -1.6580 H 5.5480 -4.5220 -0.0310 H 4.0260 -4.3470 -0.8960 H 3.4000 2.0670 -0.5840 H 3.3500 2.0280 1.1720 H 5.2500 3.7890 -0.1070 H 7.6970 4.1140 0.1600 H 9.1370 2.1940 0.8350 H 8.1010 -0.0360 1.2320 H 5.6700 -0.3410 1.0140 H 0.8770 -0.5320 -0.5250 H -1.1790 -0.7810 -1.3080 H -3.3610 -0.2260 -1.1320 H -6.2550 -3.1500 0.0490 H -2.1090 -4.1920 0.0850 H 2.3450 0.1420 0.6400 O 0.6760 0.5820 1.1270 C 0.1040 1.0980 2.1290 C -1.3110 0.8120 2.4190 C 0.7920 2.1300 2.9230 C -2.0490 2.1210 2.6950	O 2.5600 -0.6410 -1.8090 C 2.0310 -0.0820 -0.5710 C 2.9800 1.1080 -0.3060 C 4.2130 0.3070 -0.4040 C 4.0220 -0.4580 -1.6930 O 4.0960 -0.7100 0.5750 C 4.7490 -1.8500 -0.0180 O 4.8660 -1.5880 -1.4470 N 2.7860 1.7590 0.9950 C 6.1660 -2.0670 0.5520 C 3.8930 -3.0960 0.2800 C 3.8000 2.8040 1.1800 C 5.2010 2.1990 0.9830 C 6.2530 3.0180 0.5520 C 7.5300 2.4760 0.3600 C 7.7550 1.1130 0.5990 C 6.7030 0.2930 1.0280 C 5.4260 0.8380 1.2270 N 0.6220 0.3360 -0.6850 C -0.3820 -0.4920 -0.3580 S -0.0460 -2.1480 0.2020 N -1.6440 -0.0500 -0.4560 C -2.7900 -0.9010 -0.0830 C -4.0910 -0.3800 -0.1810 C -5.1680 -1.1360 0.1580 C -4.9950 -2.4510 0.6060 C -3.7100 -2.9940 0.7130 C -2.5960 -2.2140 0.3690 C -3.5310 -4.4390 1.2080 F -4.6140 -5.1680 0.8660 F -3.3930 -4.4410 2.5500 F -2.4300 -4.9750 0.6410 C -6.5880 -0.5480 0.0530 F -6.6220 0.3730 -0.9330 F -6.9230 0.0340 1.2240 F -7.4670 -1.5360 -0.2240 H 2.0830 -0.8110 0.2330 H 2.8910 1.8420 -1.1200 H 5.1440 0.7780 -0.7610 H 4.3490 0.0650 -2.5990 H 6.9670 -1.6050 -0.0300 H 6.1830 -2.0640 1.6450 H 6.4170 -3.1200 0.3350 H 4.2870 -3.9660 -0.2560 H 3.8690 -3.3280 1.3460 H 2.8690 -2.9610 -0.0690 H 3.6340 3.6210 0.4670 H 3.7320 3.2060 2.1960 H 6.0960 4.0790 0.3690 H 8.3540 3.1150 0.0510 H 8.7690 0.7220 0.5550 H 7.0730 -0.4750 1.7070 H 4.8210 0.4070 2.0430 H 0.4030 1.2340 -1.0720 H -1.8290 0.8580 -0.8500 H -4.2250 0.6370 -0.5420 H -5.8640 -3.0570 0.8710 H -1.9900 -2.9150 -0.2130 H 1.8400 2.1220 1.0720 O 0.2390 1.3410 2.1030 C -0.5330 2.3430 2.1830 C -2.0100 2.1670 2.0260 C 0.0430 3.5920 2.3270 C -2.7960 3.2370 2.7710	O 2.5600 -0.6410 -1.8090 C 2.0310 -0.0820 -0.5710 C 2.9800 1.1080 -0.3060 C 4.2130 0.3070 -0.4040 C 4.0220 -0.4580 -1.6930 O 4.0960 -0.7100 0.5750 C 4.7490 -1.8500 -0.0180 O 4.8660 -1.5880 -1.4470 N 2.7860 1.7590 0.9950 C 6.1660 -2.0670 0.5520 C 3.8930 -3.0960 0.2800 C 3.8000 2.8040 1.1800 C 5.2010 2.1990 0.9830 C 6.2530 3.0180 0.5520 C 7.5300 2.4760 0.3600 C 7.7550 1.1130 0.5990 C 6.7030 0.2930 1.0280 C 5.4260 0.8380 1.2270 N 0.6220 0.3360 -0.6850 C -0.3820 -0.4920 -0.3580 S -0.0460 -2.1480 0.2020 N -1.6440 -0.0500 -0.4560 C -2.7900 -0.9010 -0.0830 C -4.0910 -0.3800 -0.1810 C -5.1680 -1.1360 0.1580 C -4.9950 -2.4510 0.6060 C -3.7100 -2.9940 0.7130 C -2.5960 -2.2140 0.3690 C -3.5310 -4.4390 1.2080 F -4.6140 -5.1680 0.8660 F -3.3930 -4.4410 2.5500 F -2.4300 -4.9750 0.6410 C -6.5880 -0.5480 0.0530 F -6.6220 0.3730 -0.9330 F -6.9230 0.0340 1.2240 F -7.4670 -1.5360 -0.2240 H 2.0830 -0.8110 0.2330 H 2.8910 1.8420 -1.1200 H 5.1440 0.7780 -0.7610 H 4.3490 0.0650 -2.5990 H 6.9670 -1.6050 -0.0300 H 6.1830 -2.0640 1.6450 H 6.4170 -3.1200 0.3350 H 4.2870 -3.9660 -0.2560 H 3.8690 -3.3280 1.3460 H 2.8690 -2.9610 -0.0690 H 3.6340 3.6210 0.4670 H 3.7320 3.2060 2.1960 H 6.0960 4.0790 0.3690 H 8.3540 3.1150 0.0510 H 8.7690 0.7220 0.5550 H 7.0730 -0.4750 1.7070 H 4.8210 0.4070 2.0430 H 0.4030 1.2340 -1.0720 H -1.8290 0.8580 -0.8500 H -4.2250 0.6370 -0.5420 H -5.8640 -3.0570 0.8710 H -1.9900 -2.9150 -0.2130 H 1.8400 2.1220 1.0720 O 0.2390 1.3410 2.1030 C -0.5330 2.3430 2.1830 C -2.0100 2.1670 2.0260 C 0.0430 3.5920 2.3270 C -2.7960 3.2370 2.7710	O 3.1270 -2.9660 -1.7850 C 2.8270 -1.9080 -0.7570 C 3.7590 -0.7540 -1.1680 C 5.0220 -1.5260 -1.5500 C 4.4800 -2.7840 -2.2620 O 5.6410 -2.0730 -0.3320 C 5.8830 -3.5230 -0.5260 O 5.3980 -3.8350 -1.8750 N 3.9590 0.3240 -0.1860 C 7.3860 -3.7770 -0.5130 C 5.1000 -4.3070 0.5200 C 4.6840 1.4570 -0.7400 C 4.7280 2.6660 0.1700 C 4.8090 3.9530 -0.3870 C 4.9130 5.0810 0.4310 C 4.9480 4.9360 1.8160 C 4.8930 3.6650 2.3820 C 4.7910 2.5370 1.5640 N 1.4590 -1.5080 -0.8080 C 0.4550 -2.2110 -0.2200 S 0.7510 -3.6870 0.6670 N -0.7630 -1.6130 -0.4280 C -2.0500 -1.9740 -0.0440 C -3.0910 -1.1590 -0.5500 C -4.4150 -1.4100 -0.2330 C -4.7740 -2.4810 0.5830 C -3.7550 -3.2830 1.0800 C -2.4130 -3.0520 0.7850 C -4.1040 -4.3900 2.0090 F -5.3820 -4.8570 1.7630 F -4.0900 -4.0030 3.3340 F -3.2310 -5.4450 1.9030 C -5.4710 -0.4880 -0.7250 F -5.0990 0.1430 -1.9000 F -5.7630 0.5310 0.1610 F -6.6580 -1.1520 -0.9480 H 3.1070 -2.2750 0.2340 H 3.3590 -0.3280 -2.0970 H 5.7840 -0.9850 -2.1150 H 4.4510 -2.6890 -3.3510 H 7.8850 -3.1750 -1.2800 H 7.8210 -3.5020 0.4530 H 7.6110 -4.8280 -0.7230 H 5.3530 -5.3720 0.4680 H 5.3140 -3.9410 1.5290 H 4.0230 -4.2450 0.3620 H 5.7200 1.1740 -0.9590 H 4.2130 1.7630 -1.6830 H 4.8210 4.0830 -1.4660 H 4.9930 6.0700 -0.0120 H 5.0440 5.8090 2.4560 H 4.9420 3.5420 3.4610 H 4.7670 1.5470 2.0220 H 1.2840 -0.5420 -1.2080 H -0.7450 -0.7000 -0.9800 H -2.8730 -0.3410 -1.2140 H -5.8150 -2.6690 0.8420 H -1.6760 -3.7020 1.2340 H 3.0510 0.5870 0.2190 O 1.4760 1.1120 1.1080 C 0.7800 2.0840 1.4400 C -0.5890 2.4360 0.7640 C 1.2680 3.0010 2.5430 C -1.6110 2.9610 1.7930

H -1.3900 0.1660 3.2980	C -0.8200 4.7500 2.8350	C -0.8200 4.7500 2.8350	H -1.0010 1.4630 0.4760
C 0.0060 2.4940 4.1790	C -2.2740 4.6230 2.4120	C -2.2740 4.6230 2.4120	C -0.7000 3.3780 -0.6920
H 1.7930 1.7990 3.2180	H -2.7110 3.0800 3.8540	H -2.7110 3.0800 3.8540	C 0.1620 3.3460 3.5220
H 0.9190 3.0330 2.3100	H -3.8580 3.1580 2.5150	H -3.8580 3.1580 2.5150	H 2.0720 2.4910 3.0840
C -1.4350 2.9000 3.8640	H -0.7440 4.7810 3.9280	H -0.7440 4.7810 3.9280	C -1.0420 3.9430 2.8090
H -3.1080 1.9240 2.8970	H -0.4030 5.6880 2.4530	H -0.4030 5.6880 2.4530	H -2.0040 2.0990 2.3500
H -2.0150 2.7500 1.7960	H -2.3610 4.7800 1.3310	H -2.3610 4.7800 1.3310	H -2.4700 3.4120 1.2850
H -0.0060 1.6320 4.8560	H -2.8750 5.3940 2.9060	H -2.8750 5.3940 2.9060	C -0.0070 2.8380 -1.8460
H 0.5090 3.3040 4.7190	N -1.2040 3.6550 -1.5710	N -1.2040 3.6550 -1.5710	H -0.1460 2.4440 4.0650
H -1.4770 3.9710 3.6330	O -2.1580 2.8770 -1.6790	O -2.1580 2.8770 -1.6790	H 0.5390 4.0560 4.2670
H -2.0450 2.7580 4.7640	O -0.0890 3.2270 -1.4990	O -0.0890 3.2270 -1.4990	H -0.7630 4.8850 2.3300
N -0.5600 1.7570 -1.2810	H -2.2460 2.2240 0.9600	H -2.2460 2.2240 0.9600	H -1.8160 4.1860 3.5470
O -1.5130 0.9120 -1.7140	N -0.2970 2.2991 5.4927	N -0.3765 1.9965 6.2341	H 0.8740 3.3880 -2.1710
O 0.7010 1.3830 -1.1440	C -0.1168 3.4320 6.4679	C -0.1963 3.1294 7.2093	N 0.0950 1.4830 -2.0030
C -0.8370 3.1340 -1.1910	C -0.9779 4.6314 6.1136	C -1.0574 4.3288 6.8550	O -1.0310 0.7300 -1.6660
H 0.0719 3.7106 -1.2659	H 0.9343 3.7336 6.4169	H 0.8548 3.4310 7.1583	O 1.3530 1.0440 -1.6670
C -2.0978 3.6015 -1.0673	H -0.3154 3.0644 7.4792	H -0.3949 2.7618 8.2206	C -2.2013 3.2236 -0.9981
H -2.9457 2.9174 -1.0416	H -0.6979 5.4865 6.7368	H -0.7774 5.1839 7.4782	C -2.7453 3.8157 -2.1383
H -1.8030 0.2910 1.5890	H -0.8488 4.9222 5.0675	H -0.9283 4.6196 5.8089	C -3.0174 2.4916 -0.1356
N 0.8690 -1.7130 3.8260	H -2.0375 4.4367 6.2947	H -2.1170 4.1341 7.0361	C -4.1051 3.6765 -2.4154
C 0.7970 -1.8860 5.2860	C -1.7070 1.7530 5.4251	C -1.7865 1.4504 6.1665	H -2.1018 4.3934 -2.8176
H 1.5530 -1.2530 5.7620	C -2.1904 1.2752 6.7461	C -2.2699 0.9726 7.4875	C -4.3774 2.3514 -0.4133
H 1.0240 -2.9180 5.5780	H -1.7031 0.9303 4.7075	H -1.7826 0.6277 5.4489	H -2.5888 2.0246 0.7629
C -0.5400 -1.4690 5.8920	H -2.3443 2.5536 5.0635	H -2.4238 2.2510 5.8049	C -4.9214 2.9438 -1.5529
H -0.4700 -1.4820 6.9850	H -3.1325 0.7457 6.6152	H -3.2120 0.4431 7.3566	H -4.5340 4.1437 -3.3138
H -1.3470 -2.1520 5.6120	H -1.4949 0.5757 7.2188	H -1.5744 0.2731 7.9602	H -5.0205 1.7738 0.2667
H -0.8180 -0.4560 5.5910	H -2.3782 2.0954 7.4439	H -2.4577 1.7928 8.1853	H -5.9935 2.8341 -1.7716
C -0.1740 -2.4500 3.0860	C 0.7329 1.2043 5.6442	C 0.6534 0.9017 6.3856	H -0.4424 4.4020 -0.5190
H -1.1630 -2.0860 3.3830	C 2.0331 1.6067 4.9700	C 1.9536 1.3041 5.7114	
H -0.1020 -2.1780 2.0330	H 0.3439 0.3024 5.1583	H 0.2644 -0.0002 5.8997	
C -0.1750 -3.9690 3.2320	H 0.8688 1.0061 6.7121	H 0.7893 0.7035 7.4535	
H -0.3360 -4.2710 4.2710	H 2.7518 0.7832 5.0254	H 2.6723 0.4806 5.7668	
H 0.7620 -4.4180 2.8910	H 1.8729 1.8422 3.9123	H 1.7934 1.5396 4.6537	
H -0.9930 -4.4010 2.6470	H 2.4907 2.4761 5.4487	H 2.4112 2.1735 6.1901	
C 2.2080 -2.0440 3.3000	C -0.4790 5.8420 -1.4230	C -0.4790 5.8420 -1.4230	
H 2.1800 -2.0430 2.2040	C -1.4340 4.9010 -1.5170	C -1.4340 4.9010 -1.5170	
H 2.5170 -3.0510 3.6070	H -2.4820 5.2360 -1.5870	H -2.4820 5.2360 -1.5870	
C 3.2840 -1.0440 3.7100	C -0.7780 7.2760 -1.3510	C -0.7780 7.2760 -1.3510	
H 3.4970 -1.0840 4.7820	C -1.9030 7.7650 -0.6760	C -1.9030 7.7650 -0.6760	
H 3.0040 -0.0230 3.4490	C 0.1080 8.1880 -1.9390	C 0.1080 8.1880 -1.9390	
H 4.2190 -1.2740 3.1870	C -2.1480 9.1390 -0.6070	C -2.1480 9.1390 -0.6070	
C -2.4220 5.0304 -0.9929	H -2.5980 7.0880 -0.1840	H -2.5980 7.0880 -0.1840	
C -3.1531 7.7375 -0.8478	C -0.1380 9.5620 -1.8710	C -0.1380 9.5620 -1.8710	
C -1.6041 5.9555 -0.3280	H 0.9930 7.8440 -2.4690	H 0.9930 7.8440 -2.4690	
C -3.6212 5.4768 -1.5627	C -1.2670 10.0360 -1.2060	C -1.2670 10.0360 -1.2060	
C -3.9815 6.8241 -1.4969	H -3.0250 9.5100 -0.0830	H -3.0250 9.5100 -0.0830	
C -1.9672 7.3028 -0.2609	H 0.5500 10.2620 -2.3390	H 0.5500 10.2620 -2.3390	
H -0.6822 5.6434 0.1553	H -1.4580 11.1050 -1.1540	H -1.4580 11.1050 -1.1540	
H -4.2837 4.7796 -2.0726	H -2.3090 1.1750 2.3810	H -2.3090 1.1750 2.3810	
H -4.9104 7.1582 -1.9516	H 0.5690 5.5640 -1.4070	H 0.5690 5.5640 -1.4070	
H -1.3261 8.0126 0.2553	H 1.0960 3.7803 2.3009	H 1.0860 3.6000 2.6410	
H -3.4354 8.7850 -0.7958	H -0.1070 3.0216 3.7240	H -0.2749 2.3827 5.2886	
Structure 5	**Structure TS3**	**Structure 7**	
O 3.3310 -3.0400 -1.6260	O 2.4180 -2.6000 -1.2030	O 3.0220 -3.4010 -0.8190	
C 3.0290 -1.8670 -0.7950	C 2.1090 -1.4890 -0.2990	C 2.7130 -2.2900 0.0850	
C 3.9890 -0.7590 -1.3220	C 3.0800 -0.3530 -0.7380	C 3.6880 -1.1520 -0.3470	
C 5.1840 -1.5660 -1.7830	C 4.3040 -1.1620 -1.0970	C 4.9180 -1.9610 -0.7140	
C 4.5240 -2.7920 -2.3510	C 3.7030 -2.3800 -1.7490	C 4.3190 -3.1800 -1.3710	
O 6.0320 -2.0530 -0.7310	O 5.0180 -1.6540 0.0500	O 5.6220 -2.4550 0.4340	
C 6.2180 -3.4440 -1.0110	C 5.1270 -3.0580 -0.1580	C 5.7310 -3.8590 0.2260	
O 5.4920 -3.8230 -2.1830	O 4.6190 -3.4280 -1.4420	O 5.2230 -4.2290 -1.0580	
N 4.3110 0.3690 -0.4130	N 3.3000 0.7000 0.2720	N 3.9160 -0.0580 0.6130	
C 7.7000 -3.6790 -1.2850	C 6.6060 -3.3410 -0.1620	C 7.2100 -4.1420 0.2220	
C 5.7610 -4.2710 0.1860	C 4.4570 -3.8510 0.9590	C 5.0610 -4.6520 1.3430	
C 4.8110 1.5240 -1.1470	C 3.9810 1.8580 -0.2870	C 4.7880 0.9830 0.0720	
C 5.0890 2.6850 -0.2190	C 4.3630 2.8950 0.7490	C 5.0020 2.1180 1.0460	
C 4.2050 3.7710 -0.1590	C 4.5540 4.2290 0.3560	C 4.8730 3.4500 0.6270	
C 4.4510 4.8400 0.7040	C 4.9430 5.1990 1.2830	C 5.1150 4.5000 1.5150	
C 5.5790 4.8300 1.5220	C 5.1610 4.8460 2.6130	C 5.4990 4.2310 2.8280	
C 6.4580 3.7480 1.4830	C 5.0020 3.5210 3.0130	C 5.6470 2.9120 3.2520	
C 6.2120 2.6790 0.6200	C 4.6150 2.5520 2.0860	C 5.4060 1.8620 2.3650	
N 1.5980 -1.4630 -0.9660	N 0.6790 -1.0720 -0.4570	N 1.2830 -1.8730 -0.0730	
C 0.5940 -2.1660 -0.3780	C -0.3250 -1.7750 0.1310	C 0.2790 -2.5760 0.5150	
S 0.8900 -3.6420 0.5090	S -0.0290 -3.2510 1.0180	S 0.5750 -4.0520 1.4020	
N -0.6240 -1.5680 -0.5860	N -1.5430 -1.1770 -0.0770	N -0.9390 -1.9780 0.3070	
C -1.9110 -1.9290 -0.2020	C -2.8300 -1.5380 0.3070	C -2.2260 -2.3390 0.6910	
C -2.9520 -1.1140 -0.7080	C -3.8710 -0.7230 -0.1990	C -3.2720 -1.6990 0.0170	
C -4.2760 -1.3650 -0.3910	C -5.1950 -0.9740 0.1180	C -4.6170 -1.9230 0.3350	
C -4.6350 -2.4360 0.4250	C -5.5540 -2.0450 0.9340	C -4.9500 -2.8460 1.3180	
C -3.6160 -3.2380 0.9220	C -4.5350 -2.8470 1.4310	C -3.9040 -3.5210 1.9790	
C -2.2740 -3.0070 0.6270	C -3.1930 -2.6160 1.1360	C -2.5460 -3.2600 1.6710	
C -3.9650 -4.3450 1.8510	C -4.8840 -3.9540 2.3600	C -4.2670 -4.5310 3.0870	
F -5.2430 -4.8120 1.6050	F -6.1620 -4.4210 2.1140	F -5.4060 -5.1930 2.7800	
F -3.9510 -3.9580 3.1760	F -4.8700 -3.5670 3.6850	F -4.4730 -3.8900 4.2590	
F -3.0920 -5.4000 1.7450	F -4.0110 -5.0090 2.2540	F -3.2960 -5.4500 3.2770	
C -5.3320 -0.4430 -0.8830	C -6.2510 -0.0520 -0.3740	C -5.7150 -1.1490 -0.4090	
F -4.9600 0.1880 -2.0580	F -5.8790 0.5790 -1.5490	F -5.8120 -1.5610 -1.6910	
F -5.6240 0.5760 0.0030	F -6.5430 0.9670 0.5120	F -5.4330 0.1770 -0.4260	
F -6.5190 -1.1070 -1.1060	F -7.4380 -0.7160 -0.5970	F -6.9240 -1.3010 0.1730	
H 3.2550 -2.0930 0.2530	H 2.3180 -1.7720 0.7380	H 2.9210 -2.5740 1.1220	
H 3.5100 -0.3550 -2.2240	H 2.6740 0.0890 -1.6560	H 3.2910 -0.7220 -1.2770	
H 5.8190 -1.0500 -2.5110	H 5.0210 -0.6410 -1.7390	H 5.6350 -1.4420 -1.3570	
H 4.2680 -2.6900 -3.4100	H 3.6040 -2.2790 -2.8340	H 4.2160 -3.0800 -2.4560	

H 8.0300 -3.0830 -2.1440	H 7.1100 -2.7770 -0.9560	H 7.7130 -3.5780 -0.5730	
H 8.3170 -3.3810 -0.4300	H 7.0790 -3.0500 0.7830	H 7.6830 -3.8510 1.1670	
H 7.9000 -4.7290 -1.5250	H 6.8140 -4.4000 -0.3480	H 7.4170 -5.2020 0.0360	
H 5.8830 -5.3430 -0.0040	H 4.6370 -4.9250 0.8410	H 5.2410 -5.7270 1.2250	
H 6.3180 -4.0000 1.0900	H 4.8180 -3.5330 1.9430	H 5.4220 -4.3340 2.3270	
H 4.7020 -4.1040 0.4030	H 3.3740 -3.7210 0.9580	H 3.9780 -4.5230 1.3420	
H 5.7460 1.2750 -1.6640	H 4.9100 1.5550 -0.7840	H 5.7760 0.5800 -0.1750	
H 4.1030 1.8410 -1.9220	H 3.3360 2.3290 -1.0390	H 4.3500 1.3770 -0.8540	
H 3.3050 3.7680 -0.7740	H 4.4010 4.5150 -0.6820	H 4.5940 3.6810 -0.3980	
H 3.7450 5.6640 0.7460	H 5.0800 6.2290 0.9660	H 5.0140 5.5300 1.1840	
H 5.7600 5.6550 2.2040	H 5.4600 5.5980 3.3360	H 5.6900 5.0460 3.5200	
H 7.3240 3.7230 2.1370	H 5.1760 3.2340 4.0460	H 5.9530 2.6970 4.2730	
H 6.8780 1.8190 0.6120	H 4.4980 1.5180 2.4110	H 5.5310 0.8340 2.7050	
H 1.4230 -0.4970 -1.3660	H 0.5040 -0.1060 -0.8570	H 1.1090 -0.9840 -0.5050	
H -0.6060 -0.6550 -1.1380	H -1.5250 -0.2640 -0.6290	H -0.9150 -1.1580 -0.2810	
H -2.7150 -0.2800 -1.3540	H -3.6350 0.1020 -0.8540	H -3.0630 -1.0040 -0.7900	
H -5.6750 -2.6190 0.6840	H -6.5940 -2.2300 1.1930	H -5.9880 -3.0480 1.5790	
H -1.5320 -3.6490 1.0750	H -2.4520 -3.2590 1.5850	H -1.8000 -3.7690 2.2660	
H 3.4000 0.6450 0.0040	H 2.3640 0.9730 0.6190	H 3.0230 0.3480 0.8990	
O 1.6150 1.1570 0.9500	O 0.6960 1.5480 1.4590	O 1.3000 0.7470 1.8430	
C 0.8750 2.0150 1.4360	C 0.2520 2.6910 1.6020	C 0.9440 2.0260 1.7580	
C -0.5970 2.1230 1.0540	C -1.0740 3.1630 0.9640	C -0.5330 2.3690 1.3160	
C 1.4200 3.0160 2.4250	C 0.9850 3.6590 2.5050	C 1.6780 2.9840 2.7520	
C -1.4640 2.3550 2.3050	C -1.9300 3.8160 2.0850	C -1.3130 2.9620 2.5080	
H -0.8630 1.1040 0.7380	H -1.6210 2.2360 0.7610	H -1.0199 1.4769 0.9814	
C -0.8970 3.0420 -0.1740	C -1.1070 4.0070 -0.3790	C -0.7110 3.1740 -0.0270	
C 0.5370 3.0750 3.6590	C 0.0570 4.1840 3.5840	C 0.7550 3.3700 3.8900	
H 2.4320 2.7090 2.7140	H 1.8190 3.1300 2.9780	H 2.5580 2.4740 3.1540	
H 1.5000 3.9930 1.9470	H 1.4120 4.4720 1.9180	C -0.5440 3.9630 3.3640	
C -0.9100 3.3810 3.2930	C -1.1920 4.8080 2.9800	H -1.5960 2.1270 3.1650	
H -1.5380 1.3980 2.8420	H -2.3060 3.0100 2.7320	H -2.2570 3.4050 2.1700	
H -2.4910 2.6120 2.0250	H -2.8230 4.2940 1.6640	C -0.2380 2.5800 -1.3850	
C 0.0570 2.8420 -1.3740	C -0.8520 3.3670 -1.7840	H 0.5320 2.4840 4.4960	
H 0.5800 2.1150 4.1890	H -0.2350 3.3630 4.2510	H 1.2570 4.0920 4.5430	
H 0.9140 3.8400 4.3470	H 0.5830 4.9240 4.1970	H -0.3350 4.8800 2.8060	
H -0.9790 4.3930 2.8860	H -0.9210 5.7100 2.4260	H -1.1710 4.2560 4.2150	
H -1.5230 3.3720 4.2020	H -1.8600 5.1310 3.7870	N -0.0810 1.1180 -1.2680	
H 1.0590 3.1970 -1.1020	H 0.0410 3.7380 -2.2940	O -1.2070 0.3650 -0.9310	
N 0.2310 1.4420 -1.7040	N -0.6850 1.9190 -1.6520	O 1.1770 0.6790 -0.9320	
O -0.8920 0.7750 -1.8240	O -1.8110 1.1660 -1.3150	N -1.4300 3.7230 -5.0120	
O 1.4920 1.0890 -1.8250	O 0.5730 1.4800 -1.3160	C -0.2300 3.1410 -5.4570	
C -2.2792 2.5906 -0.6813	N -4.0600 3.7400 -4.8010	C 0.7690 4.2360 -5.8680	
C -2.7801 3.0942 -1.8821	C -3.9680 3.1870 -6.1600	C -2.1120 4.4190 -6.0230	
C -3.0303 1.6782 0.0596	H -4.8650 3.4100 -6.7480	C -2.3990 3.5280 -7.2450	
C -4.0321 2.6860 -2.3415	H -3.9000 2.0930 -6.1040	C -2.2480 2.8010 -4.3360	
H -2.1880 3.8141 -2.4656	C -2.7300 3.6630 -6.9140	C -2.5510 1.5580 -5.1920	
C -4.2823 1.2690 -0.4003	H -1.8140 3.4420 -6.3570	H -0.9770 2.7550 -2.1680	
H -2.6356 1.2810 1.0060	H -2.7560 4.7380 -7.1150	H 0.7270 2.9600 -1.7340	
C -4.7833 1.7728 -1.6006	H -2.6620 3.1490 -7.8790	C -2.0832 3.8155 -0.1715	
H -4.4272 3.0833 -3.2877	C -4.1820 5.1970 -4.7040	C -3.2617 3.0589 -0.0965	
H -4.8741 0.5493 0.1839	H -3.1840 5.6240 -4.8650	C -2.1911 5.2040 -0.3516	
H -5.7704 1.4510 -1.9630	H -4.4380 5.4770 -3.6750	C -4.5113 3.6709 -0.2091	
H -0.9229 4.0702 0.1209	C -5.1420 5.9030 -5.6600	H -3.2272 1.9806 0.0390	
	H -4.8300 5.8000 -6.7030	C -3.4413 5.8138 -0.4641	
	H -5.1580 6.9750 -5.4340	H -1.3016 5.8277 -0.4193	
	H -6.1660 5.5370 -5.5740	C -4.6014 5.0473 -0.3928	
	C -5.0130 2.9880 -3.9650	H -5.4179 3.0711 -0.1616	
	H -4.7600 1.9220 -4.0090	H -3.5099 6.8886 -0.6134	
	H -4.8540 3.2700 -2.9160	H -5.5740 5.5229 -0.4866	
	C -6.4950 3.1340 -4.2860	H 0.0002 4.0125 0.0565	
	H -6.7080 2.9280 -5.3390	H -0.5086 3.0812 0.5178	
	H -6.8620 4.1330 -4.0360		
	H -7.0720 2.4210 -3.6870		
	H -1.7070 3.5240 -2.4510		
	H -0.2483 4.6971 -0.3152		
	C -2.3237 4.9199 -0.4788		
	C -2.1575 6.3023 -0.6625		
	C -3.6235 4.4161 -0.3335		
	C -3.2626 7.1525 -0.7204		
	H -1.1629 6.7298 -0.7693		
	C -4.7276 5.2690 -0.3896		
	H -3.7907 3.3502 -0.1824		
	C -4.5474 6.6353 -0.5854		
	H -3.1186 8.2185 -0.8718		
	H -5.7303 4.8632 -0.2837		
	H -5.4088 7.2965 -0.6320		

Table A4: The xyz coordinates of the substrates resulting the formation of SR product.

Structure TS1	**Structure 2**	**Structure 3**	**Structure TS2**
O 2.7870 -2.4150 -2.3660	O 2.7900 -2.3840 -2.0180	O 2.7980 -1.4580 -2.1920	O 2.8660 -2.9050 -1.8210
C 2.3960 -1.7540 -1.0760	C 2.3990 -1.7230 -0.7280	C 2.2690 -0.8990 -0.9540	C 2.5660 -1.8470 -0.7930
C 3.3020 -0.5070 -1.0350	C 3.3050 -0.4760 -0.6870	C 3.2180 0.2910 -0.6890	C 3.4980 -0.6930 -1.2040
C 4.6120 -1.1110 -1.5450	C 4.6150 -1.0800 -1.1970	C 4.4510 -0.5100 -0.7870	C 4.7610 -1.4650 -1.5860
C 4.1610 -2.0660 -2.6680	C 4.1640 -2.0350 -2.3200	C 4.2600 -1.2750 -2.0760	C 4.2190 -2.7230 -2.2980
O 5.1250 -2.0470 -0.5270	O 5.1280 -2.0160 -0.1790	O 4.3340 -1.5270 0.1920	O 5.3800 -2.0120 -0.3680
C 5.4770 -3.3240 -1.1850	C 5.4800 -3.2930 -0.8370	C 4.9870 -2.6670 -0.4010	C 5.6220 -3.4620 -0.5620
O 5.0840 -3.1760 -2.5920	O 5.0870 -3.1450 -2.2440	O 5.1040 -2.4050 -1.8300	O 5.1370 -3.7740 -1.9110
N 3.3410 0.1210 0.2840	N 3.3440 0.1520 0.6320	N 3.0240 0.9420 0.6120	N 3.6850 0.2660 -0.1260
C 6.9900 -3.5060 -1.1520	C 6.9930 -3.4750 -0.8040	C 6.4040 -2.8840 0.1690	C 7.1250 -3.7160 -0.5490
C 4.6890 -4.4500 -0.5280	C 4.6920 -4.4190 -0.1800	C 4.1310 -3.9130 -0.1030	C 4.8390 -4.2460 0.4840
C 3.7890 1.5260 0.2710	C 3.7920 1.5570 0.6190	C 4.0380 1.9870 0.7970	C 4.4700 1.4150 -0.5370
C 5.3020 1.6970 0.3910	C 5.3050 1.7280 0.7390	C 5.4390 1.3820 0.6000	C 4.9060 2.2620 0.7040
C 5.8890 2.9490 0.1620	C 5.8920 2.9800 0.5100	C 6.4910 2.2010 0.1690	C 5.2550 3.6170 0.5190

C 7.2650 3.1310 0.3150	C 7.2680 3.1620 0.6630	C 7.7680 1.6590 -0.0230	C 5.7240 4.3580 1.5980
C 8.0730 2.0550 0.6930	C 8.0760 2.0860 1.0410	C 7.9930 0.2960 0.2160	C 5.8840 3.7610 2.8440
C 7.4940 0.8030 0.9120	C 7.4970 0.8340 1.2600	C 6.9410 -0.5240 0.6450	C 5.5930 2.4120 3.0210
C 6.1150 0.6220 0.7680	C 6.1180 0.6530 1.1160	C 5.6640 0.0210 0.8440	C 5.1220 1.6490 1.9580
N 1.0100 -1.4080 -1.0870	N 1.0130 -1.3770 -0.7390	N 0.8600 -0.4810 -1.0680	N 1.1980 -1.4470 -0.8440
C 0.0160 -2.2770 -0.7630	C 0.0190 -2.2460 -0.4150	C -0.1440 -1.3090 -0.7410	C 0.1940 -2.1500 -0.2560
S 0.3410 -3.9290 -0.3150	S 0.3440 -3.8980 0.0330	S 0.1920 -2.9650 -0.1810	S 0.4900 -3.6260 0.6310
N -1.2210 -1.6840 -0.8580	N -1.2180 -1.6530 -0.5100	N -1.4060 -0.8670 -0.8390	N -1.0240 -1.5520 -0.4640
C -2.5050 -2.1550 -0.5910	C -2.5020 -2.1240 -0.2430	C -2.5520 -1.7180 -0.4660	C -2.3110 -1.9130 -0.0800
C -3.5570 -1.2370 -0.8110	C -3.5540 -1.2060 -0.4630	C -3.8530 -1.1970 -0.5640	C -3.3520 -1.0980 -0.5860
C -4.8760 -1.6020 -0.5940	C -4.8730 -1.5710 -0.2460	C -4.9300 -1.9530 -0.2250	C -4.6760 -1.3490 -0.2690
C -5.2130 -2.8790 -0.1550	C -5.2100 -2.8480 0.1930	C -4.7570 -3.2680 0.2230	C -5.0350 -2.4200 0.5470
C -4.1790 -3.7780 0.0700	C -4.1760 -3.7470 0.4180	C -3.4720 -3.8110 0.3300	C -4.0160 -3.2220 1.0440
C -2.8440 -3.4430 -0.1400	C -2.8410 -3.4120 0.2080	C -2.3580 -3.0310 -0.0140	C -2.6740 -2.9910 0.7490
C -4.5050 -5.1270 0.6050	C -4.5020 -5.0960 0.9530	C -3.2930 -5.2560 0.8250	C -4.3650 -4.3290 1.9730
F -5.7630 -5.5280 0.1980	F -5.7600 -5.4970 0.5460	F -4.3760 -5.9850 0.4830	F -5.6430 -4.7960 1.7270
F -4.5200 -5.1670 1.9840	F -4.5170 -5.1360 2.3320	F -3.1550 -5.2580 2.1670	F -4.3510 -3.9420 3.2980
F -3.5950 -6.0730 0.1970	F -3.5920 -6.0420 0.5450	F -2.1920 -5.7920 0.2580	F -3.4920 -5.3840 1.8670
C -5.9490 -0.5920 -0.7830	C -5.9460 -0.5610 -0.4350	C -6.3500 -1.3650 -0.3300	C -5.7320 -0.4270 -0.7610
F -5.6200 0.3210 -1.7600	F -5.6170 0.3520 -1.4120	F -6.3840 -0.4440 -1.3160	F -5.3600 0.2040 -1.9360
F -6.2090 0.1400 0.3580	F -6.2060 0.1710 0.7060	F -6.6850 -0.7830 0.8410	F -6.0240 0.5920 0.1250
F -7.1410 -1.1930 -1.1340	F -7.1380 -1.1620 -0.7860	F -7.2290 -2.3530 -0.6070	F -6.9190 -1.0910 -0.9840
H 2.6220 -2.4410 -0.2550	H 2.6330 -2.3890 0.0980	H 2.3520 -1.6130 -0.1620	H 2.8870 -2.2290 0.1810
H 2.9520 0.2040 -1.7960	H 2.9440 0.2120 -1.4760	H 3.1530 1.0510 -1.4420	H 3.1270 -0.2070 -2.1160
H 5.4090 -0.4200 -1.8290	H 5.3770 -0.3560 -1.4900	H 5.3780 0.0170 -0.7110	H 5.5250 -0.9250 -2.1490
H 4.1910 -1.6140 -3.6630	H 4.2270 -1.6520 -3.3380	H 4.5560 -0.7850 -2.9810	H 4.1900 -2.6270 -3.3870
H 7.4900 -2.6570 -1.6310	H 7.4660 -2.6100 -1.2760	H 7.0010 -2.0160 -0.0170	H 7.6240 -3.1130 -1.3160
H 7.3560 -3.5600 -0.1210	H 7.3330 -3.5530 0.2330	H 6.3430 -3.0560 1.2240	H 7.5600 -3.4410 0.4170
H 7.2920 -4.4110 -1.6890	H 7.2700 -4.3810 -1.3500	H 6.8540 -3.7320 -0.3020	H 7.3500 -4.7660 -0.7600
H 4.9760 -5.4180 -0.9520	H 4.9970 -5.3790 -0.6090	H 4.5840 -4.7730 -0.5480	H 5.1050 -5.3080 0.4440
H 4.8610 -4.4700 0.5530	H 4.8800 -4.4230 0.8970	H 4.0630 -4.0540 0.9560	H 5.0400 -3.8690 1.4920
H 3.6140 -4.3500 -0.6910	H 3.6250 -4.2740 -0.3670	H 3.1480 -3.7770 -0.5050	H 3.7630 -4.2000 0.3160
H 3.4050 2.0590 -0.6060	H 3.4290 2.1020 -0.2730	H 3.8920 2.7660 0.0800	H 5.3950 1.1190 -1.0440
H 3.3530 2.0180 1.1480	H 3.3250 2.0370 1.4890	H 3.9510 2.3910 1.7860	H 3.8900 2.0470 -1.2190
H 5.2610 3.7880 -0.1240	H 5.2670 3.8160 0.2080	H 6.3190 3.2410 -0.0130	H 5.1710 4.0670 -0.4650
H 7.7040 4.1090 0.1420	H 7.7090 4.1370 0.4830	H 8.5720 2.2860 -0.3500	H 6.0000 5.4000 1.4590
H 9.1440 2.1910 0.8170	H 9.1470 2.2220 1.1550	H 8.9690 -0.1170 0.0690	H 6.2770 4.3410 3.6760
H 8.1110 -0.0370 1.2190	H 8.1200 -0.0090 1.5400	H 7.1130 -1.5660 0.8220	H 5.7630 1.9400 3.9840
H 5.6810 -0.3410 1.0170	H 5.6580 -0.3190 1.2390	H 4.8620 -0.6020 1.1790	H 4.9300 0.5860 2.0780
H 0.8780 -0.4480 -0.7770	H 0.7990 -0.3660 -0.8260	H 0.6460 0.4400 -1.3930	H 1.0230 -0.4810 -1.2440
H -1.2140 -0.8380 -1.4270	H -1.2170 -0.6650 -0.8590	H -1.5740 0.0610 -1.1700	H -1.0060 -0.6390 -1.0160
H -3.3710 -0.2250 -1.1460	H -3.3200 -0.2100 -0.8190	H -3.9970 -0.1950 -0.9090	H -3.1650 -0.2570 -1.2310
H -6.2500 -3.1550 0.0290	H -6.2420 -3.1390 0.3220	H -5.6100 -3.8580 0.4840	H -6.0750 -2.6000 0.8050
H -2.0680 -4.1780 0.0500	H -2.0630 -4.1430 0.3650	H -1.3700 -3.4350 0.0670	H -1.9800 -3.6620 1.2140
H 2.4070 0.1010 0.6980	H 2.4060 0.1280 1.0700	H 2.1140 1.3540 0.6610	H 2.7730 0.5430 0.2640
O 0.6830 0.5750 1.1040	O 0.6860 0.6060 1.4520	O 0.4770 0.5240 1.7200	O 1.2150 1.1730 1.0720
C 0.1110 1.0910 2.1060	C 0.0320 1.6120 1.9140	C -0.1200 1.5760 2.0610	C 0.7660 2.3210 0.9660
C -1.4310 0.9280 2.2620	C -1.2980 1.8430 1.5600	C -1.4360 1.7990 1.6230	C -0.6890 2.5950 0.5970
C 0.7820 2.3110 2.8040	C 0.7410 2.6420 2.8040	C 0.6080 2.6130 2.9390	C 1.5440 3.5510 1.4210
C -2.0510 2.3100 2.3840	C -2.1340 2.9970 2.0110	C -2.2970 2.9190 2.2370	C -1.3530 3.1080 1.9150
H -1.6350 0.3270 3.1540	C -0.2490 3.4770 3.6410	C -0.3980 3.4430 3.7580	H -1.1930 1.6370 0.4230
C -0.0740 2.7300 3.9870	H 1.4450 2.0980 3.4450	H 1.2890 2.1170 3.6000	C -0.9810 3.4720 -0.7720
H 1.7810 2.0240 3.1410	H 1.3370 3.3090 2.1630	H 1.1490 3.2760 2.2950	C 0.8660 4.0700 2.7260
H 0.8790 3.1260 2.0780	C -1.3130 4.1030 2.7150	C -1.4170 4.0560 2.7880	H 2.5880 3.3070 1.6260
C -1.5050 3.0950 3.5800	H -2.9310 2.6420 2.6840	H -2.8570 2.5010 3.0480	H 1.5120 4.3150 0.6360
H -3.1420 2.2370 2.4550	H -2.6450 3.4260 1.1290	H -2.9670 3.3100 1.5010	C -0.6350 4.3500 2.4920
H -1.8300 2.8730 1.4690	H -0.7440 2.8270 4.3740	H -0.9140 2.8320 4.4700	H -1.2930 2.3100 2.6690
H -0.1150 1.8950 4.6980	H 0.2890 4.2580 4.1940	H 0.1350 4.2120 4.2730	H -2.4170 3.3020 1.7830
H 0.3880 3.5720 4.5150	H -0.8080 4.7170 1.9580	H -0.8950 4.5550 2.0000	H -0.5760 4.4910 -0.6060
H -1.5570 4.1660 3.3460	H -1.9830 4.7620 3.2800	H -2.0460 4.7580 3.2970	C -0.2680 2.8990 -1.8820
H -2.1600 2.9440 4.4470	N -0.5500 1.7810 -0.9560	N -0.9660 2.8380 -1.9540	C -2.4770 3.6030 -1.0960
N -0.5530 1.7500 -1.3040	O -1.5030 0.9360 -1.3890	O -1.9200 2.0600 -2.0620	H 0.9770 3.3220 3.5210
O -1.5060 0.9050 -1.7370	O 0.7110 1.4070 -0.8190	O 0.1490 2.4100 -1.8820	H 1.3670 4.9850 3.0590
O 0.7080 1.3760 -1.1670	C -0.8270 3.1580 -0.8660	C -1.2000 4.2870 -1.9130	H -0.7440 5.1940 1.8020
C -0.8300 3.1270 -1.2140	H 0.0310 3.7210 -0.5350	H -0.3730 4.9560 -1.8150	H -1.1050 4.6380 3.4390
H 0.0160 3.7500 -0.9230	C -2.0210 3.6710 -1.2330	C -2.4620 4.7770 -1.9990	H 0.6890 3.4180 -2.0840
C -2.0240 3.6400 -1.5810	H -2.7680 2.9590 -1.5640	H -3.2920 4.1080 -2.0920	N -0.1660 1.5440 -2.0390
H -2.8170 2.9410 -1.9050	C -2.3740 5.0840 -1.2610	C -2.6990 6.2970 -1.9630	C -3.0110 3.2290 -2.3600
C -2.3770 5.0530 -1.6090	C -3.6600 5.4580 -1.7090	C -4.0010 6.8090 -2.0510	C -3.2690 4.4800 -0.3040
C -3.6630 5.4270 -2.0570	C -1.4910 6.1170 -0.8720	C -1.6110 7.1670 -1.8390	O -1.2920 0.7910 -1.7020
C -1.4940 6.0860 -1.2200	C -4.0470 6.7940 -1.7630	C -4.2150 8.1930 -2.0100	O 1.0920 1.1050 -1.7030
C -4.0500 6.7630 -2.1110	H -4.3530 4.6810 -2.0140	H -4.8310 6.1430 -2.1510	C -4.3430 3.4860 -2.6690
H -4.3610 4.6530 -2.3640	C -1.8810 7.4510 -0.9260	C -1.8220 8.5500 -1.7970	H -2.3760 2.8010 -3.1300
C -1.8840 7.4200 -1.2740	H -0.4950 5.8690 -0.5250	H -0.6170 6.7750 -1.7780	C -4.5990 4.7160 -0.6270
H -0.4980 5.8390 -0.8700	C -3.1610 7.8020 -1.3710	C -3.1250 9.0650 -1.8800	H -2.8310 5.0140 0.5360
C -3.1640 7.7710 -1.7190	H -5.0420 7.0510 -2.1100	H -5.2100 8.5860 -2.0790	C -5.1460 4.1970 -1.7910
H -5.0450 7.0220 -2.4590	H -1.1850 8.2250 -0.6200	H -0.9880 9.2150 -1.7010	H -4.7300 3.2290 -3.6550
H -1.1880 8.1960 -0.9660	H -3.4610 8.8430 -1.4110	H -3.2870 10.1230 -1.8450	H -5.1880 5.3960 -0.0110
H -3.4640 8.8140 -1.7590	H -1.7600 1.1310 0.9080	H -1.8520 1.1720 0.8620	H -6.1640 4.4670 -2.0740
H -1.8370 0.4030 1.3930	N -2.8390 0.0700 4.0980	N -3.2440 0.1010 4.0260	
N 0.8760 -1.7200 3.8030	C -2.7630 -1.3740 3.8330	C -3.2490 -1.2730 3.5090	
C 0.8040 -1.8930 5.2630	C -2.1970 -1.6330 2.4670	C -1.8090 -1.8150 3.4890	
H 1.5610 -1.2600 5.7390	H -3.7920 -1.8000 3.9210	H -3.6490 -1.2780 2.5170	
H 1.0310 -2.9250 5.5550	H -2.1230 -1.8400 4.6210	H -3.8530 -1.8920 4.1410	
C -0.5330 -1.4760 5.8690	H -2.1390 -2.7300 2.2660	H -1.8090 -2.8160 3.1110	
H -0.4630 -1.4840 6.9620	H -2.8370 -1.1670 1.6790	H -1.2040 -1.1960 2.8600	
H -1.3400 -2.1590 5.5900	H -1.1680 -1.2070 2.3790	H -1.4120 -1.8090 4.4830	
H -0.8090 -0.4620 5.5600	C -1.8780 0.4260 5.1510	C -2.6950 0.1070 5.3870	
C -0.1670 -2.4570 3.0630	C -2.0960 1.8370 5.6140	C -2.6910 1.5460 5.9320	
H -1.1550 -2.0770 3.3440	H -0.8470 0.3000 4.7400	H -1.6930 -0.2710 5.3690	
H -0.0780 -2.2080 2.0000	H -2.0060 -0.2920 5.9980	H -3.2990 -0.5120 6.0170	
C -0.1680 -3.9760 3.2090	H -1.3650 2.1080 6.4140	H -2.2920 1.5490 6.9250	
H -0.3310 -4.2850 4.2450	H -1.9670 2.5540 4.7670	H -2.0860 2.1650 5.3030	
H 0.7670 -4.4190 2.8550	H -3.1270 1.9630 6.0250	H -3.6920 1.9230 5.9480	
H -0.9800 -4.4020 2.6090	C -4.1990 0.4160 4.5370	C -4.6170 0.6200 4.0490	
C 2.2150 -2.0510 3.2770	C -4.9600 1.0850 3.4310	C -5.1940 0.6080 2.6210	

H 2.1830 -2.0460 2.1810	H -4.1170 1.0910 5.4240	H -4.6140 1.6230 4.4250	
H 2.5240 -3.0580 3.5810	H -4.7110 -0.5230 4.8590	H -5.2210 0.0040 4.6830	
C 3.2910 -1.0510 3.6870	H -5.9930 1.3480 3.7650	H -6.1950 0.9850 2.6380	
H 3.5140 -1.1030 4.7570	H -4.4470 2.0240 3.1090	H -4.5920 1.2250 1.9870	
H 2.9930 -0.0270 3.4430	H -5.0410 0.4100 2.5440	H -5.1950 -0.3940 2.2460	
H 4.2210 -1.2660 3.1500	H -2.6200 0.5740 3.2630	H -2.3940 0.8770 2.9200	
Structure 5	**Structure TS3**	**Structure 7**	
O 2.9230 -3.1780 -1.4270	O 2.7070 -3.1200 -1.5310	O 2.7800 -3.4260 -0.8200	
C 2.6210 -2.0050 -0.5960	C 2.3980 -2.0090 -0.6270	C 2.4710 -2.3150 0.0840	
C 3.5810 -0.8970 -1.1230	C 3.3690 -0.8730 -1.0660	C 3.4460 -1.1770 -0.3480	
C 4.7960 -1.7220 -1.4720	C 4.5930 -1.6820 -1.4250	C 4.6760 -1.9860 -0.7150	
C 4.1780 -2.9720 -2.0390	C 3.9920 -2.9000 -2.0770	C 4.0770 -3.2050 -1.3720	
O 5.5510 -2.1550 -0.3230	O 5.3070 -2.1740 -0.2780	O 5.3800 -2.4800 0.4330	
C 5.6410 -3.5690 -0.4580	C 5.4160 -3.5780 -0.4860	C 5.4890 -3.8840 0.2250	
O 5.1120 -4.0010 -1.7130	O 4.9080 -3.9480 -1.7700	O 4.9810 -4.2540 -1.0590	
N 3.9030 0.2310 -0.2140	N 3.6530 0.1840 -0.0720	N 3.7170 -0.1170 0.6350	
C 7.1170 -3.8700 -0.4720	C 6.8950 -3.8610 -0.4900	C 6.9680 -4.1670 0.2210	
C 4.9890 -4.2970 0.7140	C 4.7460 -4.3710 0.6310	C 4.8190 -4.6770 1.3420	
C 4.3860 1.3700 -0.9720	C 4.2090 1.3710 -0.6820	C 4.4220 1.0090 0.0500	
C 4.8170 2.5270 -0.0080	C 4.7000 2.3820 0.4160	C 4.9000 1.9910 1.1690	
C 4.5480 3.8580 -0.3730	C 4.9130 3.7270 0.0580	C 5.0440 3.3610 0.8670	
C 4.9440 4.8880 0.4740	C 5.3650 4.6270 1.0160	C 5.5160 4.2310 1.8430	
C 5.5920 4.6020 1.6730	C 5.6120 4.2020 2.3180	C 5.8670 3.7520 3.1020	
C 5.8470 3.2820 2.0390	C 5.4170 2.8700 2.6730	C 5.7640 2.3960 3.3920	
C 5.4630 2.2360 1.2080	C 4.9680 1.9500 1.7320	C 5.2960 1.5040 2.4340	
N 1.1900 -1.6010 -0.7670	N 0.9680 -1.5920 -0.7850	N 1.0410 -1.8980 -0.0740	
C 0.1860 -2.3040 -0.1790	C -0.0360 -2.2950 -0.1970	C 0.0370 -2.6010 0.5140	
S 0.4820 -3.7800 0.7080	S 0.2600 -3.7710 0.6900	S 0.3330 -4.0770 1.4010	
N -1.0320 -1.7060 -0.3870	N -1.2540 -1.6970 -0.4050	N -1.1810 -2.0030 0.3060	
C -2.3190 -2.0670 -0.0030	C -2.5410 -2.0580 -0.0210	C -2.4680 -2.3640 0.6900	
C -3.3600 -1.2520 -0.5090	C -3.5820 -1.2430 -0.5270	C -3.5140 -1.7240 0.0160	
C -4.6840 -1.5030 -0.1920	C -4.9060 -1.4940 -0.2100	C -4.8590 -1.9480 0.3340	
C -5.0430 -2.5740 0.6240	C -5.2650 -2.5650 0.6060	C -5.1920 -2.8710 1.3170	
C -4.0240 -3.3760 1.1210	C -4.2460 -3.3670 1.1030	C -4.1460 -3.5460 1.9780	
C -2.6820 -3.1450 0.8260	C -2.9040 -3.1360 0.8080	C -2.7880 -3.2850 1.6700	
C -4.3730 -4.4830 2.0500	C -4.5950 -4.4740 2.0320	C -4.5090 -4.5560 3.0860	
F -5.6510 -4.9500 1.8040	F -5.8730 -4.9410 1.7860	F -5.6480 -5.2180 2.7790	
F -4.3590 -4.0960 3.3750	F -4.5810 -4.0870 3.3570	F -4.7150 -3.9150 4.2580	
F -3.5000 -5.5380 1.9440	F -3.7220 -5.5290 1.9260	F -3.5380 -5.4750 3.2760	
C -5.7400 -0.5810 -0.6840	C -5.9620 -0.5720 -0.7020	C -5.9570 -1.1740 -0.4100	
F -5.3680 0.0500 -1.8590	F -5.5900 0.0590 -1.8770	F -6.0540 -1.5860 -1.6920	
F -6.0320 0.4380 0.2020	F -6.2540 0.4470 0.1840	F -5.6750 0.1520 -0.4270	
F -6.9270 -1.2450 -0.9070	F -7.1490 -1.2360 -0.9250	F -7.1660 -1.3260 0.1720	
H 2.8850 -2.2290 0.4440	H 2.6550 -2.3010 0.3980	H 2.6590 -2.6230 1.1170	
H 3.1630 -0.5100 -2.0630	H 2.9800 -0.4230 -1.9900	H 3.0580 -0.7330 -1.2750	
H 5.4920 -1.2380 -2.1640	H 5.3110 -1.1620 -2.0680	H 5.3940 -1.4670 -1.3570	
H 4.0350 -2.9290 -3.1230	H 3.8940 -2.8000 -3.1620	H 3.9740 -3.1050 -2.4570	
H 7.6120 -3.3540 -1.3040	H 7.3990 -3.2960 -1.2840	H 7.4720 -3.6020 -0.5740	
H 7.6090 -3.5350 0.4470	H 7.3670 -3.5700 0.4550	H 7.4410 -3.8760 1.1660	
H 7.3100 -4.9400 -0.6070	H 7.1030 -4.9200 -0.6770	H 7.1760 -5.2260 0.0340	
H 5.1630 -5.3770 0.6500	H 4.9370 -5.4440 0.5190	H 5.0010 -5.7510 1.2250	
H 5.3730 -3.9290 1.6710	H 5.0990 -4.0450 1.6150	H 5.1790 -4.3570 2.3260	
H 3.9070 -4.1640 0.7310	H 3.6620 -4.2540 0.6230	H 3.7350 -4.5490 1.3400	
H 5.2750 1.1070 -1.5590	H 5.0860 1.1320 -1.2960	H 5.3230 0.6920 -0.4880	
H 3.6210 1.7410 -1.6630	H 3.4690 1.8700 -1.3170	H 3.7720 1.5440 -0.6510	
H 4.0140 4.0560 -1.2980	H 4.7180 4.0380 -0.9620	H 4.7910 3.7220 -0.1240	
H 4.7210 5.9140 0.2010	H 5.5240 5.6650 0.7430	H 5.6260 5.2870 1.6170	
H 5.8790 5.4100 2.3380	H 5.9600 4.9090 3.0650	H 6.2430 4.4380 3.8580	
H 6.3240 3.0530 2.9860	H 5.6040 2.5330 3.6880	H 6.0560 2.0220 4.3700	
H 5.6240 1.1960 1.4830	H 4.8020 0.9070 2.0000	H 5.2260 0.4410 2.6490	
H 1.0150 -0.6350 -1.1670	H 0.7930 -0.6260 -1.1850	H 0.8660 -0.9320 -0.4740	
H -1.0140 -0.7930 -0.9390	H -1.2360 -0.7840 -0.9570	H -1.1630 -1.0900 -0.2460	
H -3.1400 -0.4260 -1.1710	H -3.3650 -0.4320 -1.2050	H -3.3200 -1.0320 -0.7960	
H -6.0820 -2.7570 0.8800	H -6.3030 -2.7510 0.8630	H -6.2290 -3.0730 1.5780	
H -1.9450 -3.7870 1.2770	H -2.1690 -3.7820 1.2580	H -2.0110 -3.8030 2.2250	
H 2.9680 0.4610 0.2000	H 2.7130 0.3840 0.3420	H 2.8210 0.1820 1.0610	
O 1.2070 1.0190 1.1490	O 0.9850 1.0280 1.1310	O 1.0580 0.7220 1.8420	
C 0.7580 2.1670 1.0430	C 0.5360 2.1760 1.0250	C 0.7020 2.0010 1.7570	
C -0.6970 2.4410 0.6740	C -0.9190 2.4500 0.6560	C -0.6830 2.4000 1.3470	
C 1.5360 3.3970 1.4980	C 1.3140 3.4060 1.4800	C 1.6490 3.0570 2.1400	
C -1.3610 2.9540 1.9920	C -1.5830 2.9630 1.9740	C -1.2430 3.2150 2.5500	
H -1.2090 1.4930 0.4860	H -1.4260 1.4980 0.4760	H -1.3190 1.5090 1.2810	
C -0.8310 3.3730 -0.5950	C -1.1390 3.3920 -0.6040	C -0.8110 3.2020 -0.0040	
C 0.8580 3.9160 2.8030	C 0.6360 3.9250 2.7850	C 1.0690 3.9120 3.2650	
H 2.5740 3.1330 1.7220	H 2.3560 3.1540 1.6930	H 2.6000 2.6400 2.4830	
H 1.5450 4.1680 0.7230	H 1.3070 4.1740 0.7010	H 1.8690 3.6830 1.2680	
C -0.6430 4.1960 2.5690	C -0.8650 4.2050 2.5510	C -0.3450 4.3900 2.9430	
H -1.3370 2.1550 2.7450	H -1.5470 2.1640 2.7270	H -1.3330 2.5450 3.4160	
H -2.4150 3.1940 1.8200	H -2.6410 3.1940 1.8230	H -2.2550 3.5800 2.3490	
H -0.2360 4.2730 -0.4000	H -0.6040 4.3280 -0.3910	H -0.1550 4.0790 0.0750	
C -0.3670 2.8460 -1.9850	C -0.5210 2.9010 -1.9870	C -0.4660 2.5600 -1.3810	
C -2.3080 3.8890 -0.8010	C -2.6750 3.8460 -0.6740	C -2.2920 3.8020 -0.1580	
H 0.9670 3.1670 3.5970	H 0.7470 3.1770 3.5790	H 1.0410 3.3210 4.1900	
H 1.3590 4.8300 3.1370	H 1.1380 4.8400 3.1190	H 1.7220 4.7710 3.4550	
H -0.7570 5.0420 1.8820	H -0.9780 5.0550 1.8690	H -0.3130 5.1310 2.1370	
H -1.1130 4.4820 3.5160	H -1.3330 4.4890 3.5000	H -0.7660 4.8960 3.8190	
H 0.6520 3.2420 -2.1190	H 0.5310 3.2100 -1.8810	N -0.3230 1.0930 -1.2690	
N -0.1740 1.3900 -1.9620	N -0.3960 1.3990 -1.9800	C -3.4290 2.9580 -0.1530	
C -3.3830 2.9830 -0.8670	C -3.7180 2.8930 -0.7270	C -2.4550 5.1930 -0.3580	
C -2.5360 5.2610 -1.0060	C -3.0010 5.2170 -0.5420	O -1.4490 0.3400 -0.9320	
O -1.3000 0.6370 -1.6250	O -1.5220 0.6460 -1.6430	O 0.9350 0.6540 -0.9330	
O 1.0840 0.9510 -1.6260	O 0.8620 0.9600 -1.6440	C -4.6900 3.5110 -0.3360	
C -4.6720 3.4630 -1.0660	C -5.0390 3.3260 -0.7350	H -3.3310 1.8870 -0.0020	

H -3.1890 1.9220 -0.7640 C -3.8340 5.7200 -1.2040 H -1.6870 5.9330 -1.0200 C -4.9000 4.8250 -1.2260 H -5.4900 2.7500 -1.1090 H -4.0050 6.7790 -1.3600 H -5.9100 5.1830 -1.3910	H -3.4940 1.8310 -0.7590 C -4.3300 5.6180 -0.5480 H -2.2100 5.9540 -0.4370 C -5.3460 4.6780 -0.6540 H -5.8360 2.5890 -0.7970 H -4.5750 6.6730 -0.4610 H -6.3860 4.9930 -0.6550 N -0.9520 3.4400 -3.4090 C -0.0490 2.8000 -4.5300 H -0.3550 3.1710 -5.5140 H -0.2180 1.7170 -4.5630 C 1.4560 3.0440 -4.4330 H 1.8890 2.6350 -3.5180 H 1.6990 4.1080 -4.4890 H 1.9590 2.5540 -5.2740 C -0.7290 4.9920 -3.3780 H 0.3070 5.2060 -3.0870 H -1.3410 5.4340 -2.5890 C -1.0270 5.7740 -4.6500 H -0.4670 5.3990 -5.5100 H -0.7420 6.8230 -4.5100 H -2.0940 5.7640 -4.8830 C -2.4560 3.1200 -3.7000 H -2.7370 2.1850 -3.2090 H -3.0830 3.9050 -3.2640 C -2.8930 2.9580 -5.1550 H -2.4550 2.0610 -5.6030 H -2.6330 3.8190 -5.7730 H -3.9810 2.8380 -5.1990 H -0.8200 3.2750 -2.9730	C -3.7300 5.7140 -0.5380 H -1.5920 5.8520 -0.3720 C -4.8410 4.8790 -0.5280 H -5.5650 2.8630 -0.3280 H -3.8590 6.7830 -0.6900 H -5.8350 5.2970 -0.6690 N -1.6720 3.6980 -5.0130 C -0.4720 3.1160 -5.4580 C 0.6190 3.1910 -4.3800 C -1.5460 4.9980 -4.4940 C -1.4500 6.0900 -5.5780 C -2.7370 3.5340 -5.9090 C -2.3880 4.0560 -7.3150 H -1.2260 2.7480 -2.1430 H 0.4990 2.9330 -1.7390	