

Organocatalytic asymmetric Michael addition in aqueous media by a hydrogen-bonding catalyst and application for inhibitors of GABA_B receptor

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General information

IR spectra were recorded on a NICOLET 380 FT-IR spectrophotometer. Optical rotations were measured with a Rudolph Automatic polarimeter (model name: A20766 APV/6w). ^1H NMR spectra were recorded on a Varian Mercury 400 (400 MHz) or Varian Germini 300 (300 MHz) with TMS as an internal reference. ^{13}C NMR spectra were recorded on a Varian Mercury 400 (100 MHz) with TMS or CDCl_3 as an internal reference. Chiral HPLC analysis was performed on a Jasco LC-1500 Series HPLC system with a UV detector. All reactions were carried out in oven-dried glassware under an argon atmosphere. Toluene (CaH_2), THF (Na, benzophenone) were dried by distillation before use. Commercial grade reagents and solvents were used without further purification. Liquid reagents were freshly distilled under an atmosphere of dry argon, and solid reagents were purified by flash chromatography on silica gel.

Reagents

The fluorescent Ca^{2+} indicator Fluo-3 AM was purchased from Invitrogen (Leiden, the Netherlands). Cell Counting Kit-8 (CCK-8) solution was obtained from Dojindo Molecular Technologies.

Cell culture

HEK293T was maintained in Dulbecco's modified Eagle's medium (DMEM; Invitrogen) supplemented with 10% fetal bovine serum (FBS) and 1% antibiotics at 37 °C in 100-mm cell culture dishes (Corning, NY, USA), under a humidified air atmosphere containing 5% CO_2 .

Cytotoxicity analysis

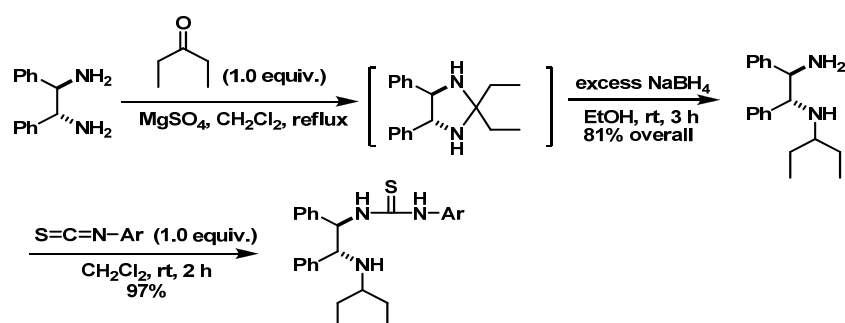
HEK293T cells (1×10^4 cells/well) were seeded in a 96-well plate. The next day, cells were treated with compounds (10-fold, 6 points) and incubated for 24 h, 48 h, and 72 h. Cells were then added to Cell Counting Kit-8 (CCK-8) solution (Dojindo Molecular Technologies, Inc) following the manufacturer's procedure. The absorbance was detected at 450 nm via a microplate reader (Spectra MAX 340, Molecular Devices). The data was analyzed through Prism software (GraphPad).

Intracellular Ca^{2+} measurements using confocal laser scanning microscopy (CLSM)

To detect intracellular Ca^{2+} level, HEK293T cells were seeded and incubated to 40–60% confluence in a 35 mm diameter confocal dish 24 h prior to the experiment. The cells were loaded with 5 mM of the fluorescent radiometric calcium indicator Fluo-3-AM (Invitrogen) for 30 min at 37 °C. The Ca^{2+} concentration was determined using CLSM (Zeiss LSM 700 Meta; Zeiss, Oberkochen, Germany). After washing with the medium, the culture plates were placed on a temperature-controlled microscope stage and observed under 200 \times microscope magnification. The excitation and emission wavelengths for signal detection were 488 and 515 nm, respectively. The intensity analysis of intracellular calcium was performed using Zen software (Carl Zeiss).

Synthesis of catalysts (1a-n); general procedure

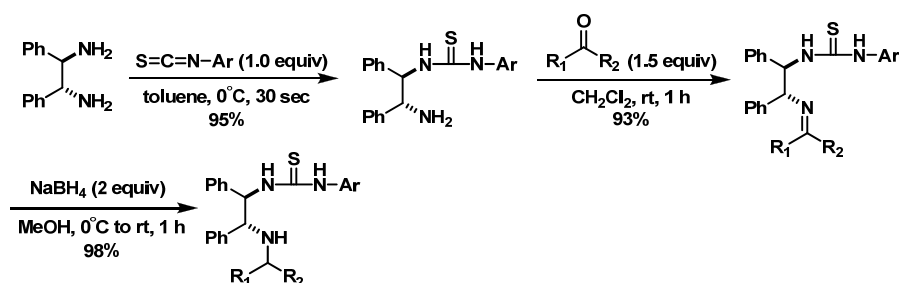
1. Synthesis of monoalkylated thiourea catalysts.



Scheme 1.

To a suspension of (*R, R*)-1,2-diphenylethylenediamine (1.0 equiv.) in toluene (0.1 M) was added a solution of 3-pentanone (1.1 equiv.), MgSO_4 and the mixture was reflux for 48h. then remove the MgSO_4 to celite filter and concentrated in vacuo. NaBH_4 (4.0 equiv.) and ethanol was added, and the mixture was stirred at room temperature for 1h. quenched with 1*N* NaOH solution, and the mixture was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried (MgSO_4), and concentrated in vacuo. The product was purified by chromatography on a silica-gel column (methanol/methylene chloride 1:20). The monoalkylated DPEN (1.0 equiv.) in CH_2Cl_2 (0.1 M) was added thiourea (1.1 equiv.) and the mixture was stirred at room temperature for 1h. purified by flash column chromatography on silica gel with ethyl acetate/hexanes (1:5) to give the pure amide product(quantitative yield) as a white foamy solid.

2. Synthesis of arylated thiourea catalysts.



Scheme 2.

To a suspension of (*R, R*)-1,2-diphenylethylenediamine (1.0 equiv.) in toluene (0.5 M) was added thiourea (1.0 equiv.) at 0°C and the mixture was stirred for 30 sec. the product was concentrated in vacuo and purified by flash column chromatography on silica gel with ethyl (methanol/methylene chloride 1:20). The thiourea substituted DPEN (1.0 equiv.) in CH_2Cl_2 (0.1 M) was added aryl ketone (1.1 equiv.) and the mixture was stirred at room temperature for 1h. NaBH_4 (2.0 equiv.) and ethanol was added at 0°C and the mixture was stirred at room temperature for 1h. The product celite filter and the mixture were extracted with ethyl acetate. The combined organic extracts were washed with brine, dried (MgSO_4), and concentrated in vacuo. The product was purified by chromatography on a silica-gel column (methanol/methylene chloride 1:20) to give the pure amide product(quantitative yield) as a brown foamy solid.

3. Synthesis of product compounds.

(1) General procedure for the asymmetric Michael reaction

The trans- β -nitrostyrene (1.0 equiv.), malononitrile (2.0 equiv.), and 10~1 mol% of catalyst were added in the water (0.4 ml), and the reaction mixture was stirred at rt. The reaction conversion was monitored by TLC. After completion, 6 N HCl was added, and the mixture was heated to 100 °C for 6 h. After cooling the reaction mixture to room temperature, added dialkyl carbonate (1.5 equiv.) and the solution was heated under magnetic stirring at 100°C for 3 h, on cooling the homogeneous reaction mixture to room temperature. The reaction mixture was poured into 10% aq NaHCO₃ under stirring. Ethyl acetate (0.2ml) was added to the reaction mixture. This solution was washed twice with water (2×1.0 mL), dried over magnesium sulfate, and concentrated to yield the desired product. The product was purified by chromatography on a silica-gel column (hexane/methylene chloride 2:1).

Table S1. Catalyst screening.

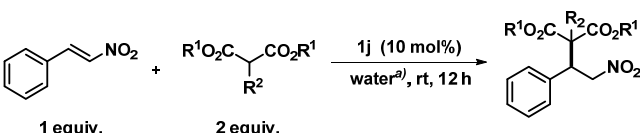
Entry	Cat.	Yield[%] ^{a)}	ee[%] ^{b)}
1	1a	-	-
2	1b	-	-
3	1c	44	53
4	1d	85	90
5	1e	67	72
6	1f	86	78
7	1g	64	74
8	1h	65	74
9	1i	51	52

^{a)} Isolated yield; ^{b)} Determined by chiral HPLC using an AD-H column.

Table S2. Catalyst effects on the Michael reaction.

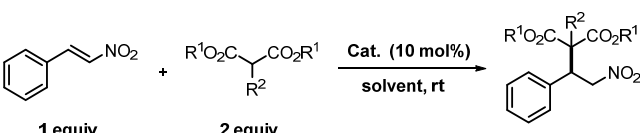
Entry	R	Solvent ^{a)}	Cat.	Time[hour] ^[3]	Yield [%] ^{b)}	ee [%] ^{c)}
1	Me	water	1d	14	97	99
2	Me	toluene	1d	96	89	80
3	Me	water	1j	10	98	99
4	Me	water	1k	19	95	94
5	Et	water	1j	12	97	99
6	Et	toluene	1j	96	81	80
7	Et	water	1l	12	81	94
8	Et	toluene	1l	96	86	93
9	Bn	water	1j	14	93	98
10	Bn	water	1k	26	91	98

a) Using 0.4 mL solvent on a 0.1 mmol scale; b) Isolated yield; c) Determined by chiral HPLC.

Table S3. Substrate effects of malonate.


Entry	R ₁	R ₂	additive [mol%]	Yield [%] ^{b)}	ee [%] ^{c)}
1 ^{d)}	Et	H	Et ₃ N [10]	97	10
2 ^{e)}	Et	H	Et ₃ N [5]	98	50
3 ^{f)}	Et	H	PhCO ₂ H [10]	99	99
4	<i>n</i> -Bu	H	-	92	99
5	<i>n</i> -Pr	H	-	95	99

a) Using 0.4 mL water on a 0.1 mmol scale; b) Isolated yield; c) Determined by chiral HPLC; d) The reaction was run for 15 min; e) The reaction was run for 1 h; f) The reaction was run for 3 h.

Table S4. Catalyst effects on the Michael reaction.


Entry	R ₁	R ₂	Solvent ^{a)}	Cat.	Time [min] ^[3]	Yield [%] ^{b)}	ee [%] ^{c)}
1	Et	H	-	1m	60	97	91
2	Et	H	-	1n	60	95	99
3	Et	H	water	1m	5	99	99
4 ^{d)}	Et	Et	water	1m	30	95	99
5	Et	H	water	1n	60	96	90
6	Bn	H	water	1m	15	94	99
7	Bn	H	water	1n	60	92	99

a) Using 0.4 mL solvent on the 0.1 mmol scale; b) Isolated yield; c) Determined by chiral HPLC; d) The reaction was run using 1 mol% of catalyst.

(2) General Procedure of the Asymmetric Michael reaction

Trans- β -nitrostyrene (27 mmol, 1.0 equiv.), the desired ester (54 mmol, 2.0 equiv.), and catalyst (10~1 mol%) was added to water (50 mL), and the reaction mixture was stirred at rt. The reaction conversion was monitored by TLC. Upon completion of the reaction, ethyl acetate (20 mL) was added to the reaction mixture, and the obtained solution was washed twice with water (2×10 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated to yield the desired product. Each product was purified via column chromatography on a silica-gel column using hexane/methylene chloride (2:1) as the eluent.

4. Synthesis of baclofen, phenibut

Under argon atmosphere, to the suspension of 2b, 2h, 3a, 3d (1.0 equiv, 99% ee) and NiCl₂·6H₂O (1.0 equiv) in MeOH (8.0 ml) was added NaBH₄ (10 equiv) at 0 °C. After the reaction mixture was stirred 7.5 h at rt, the reaction mixture was quenched with NH₄Cl and diluted with CHCl₃. The

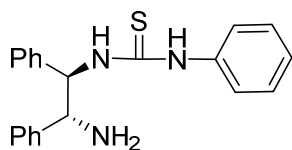
organic layer was separated and dried over MgSO_4 , filtrated and concentrated in vacuo. The residue was purified by column chromatography on silica gel ($\text{MeOH}/\text{CHCl}_3 = 1/20$ as eluent) to afford desired product 2n, 2o (94%) as a colorless powder. Product 2n, 2o (1.0 equiv) in 6N HCl (2.7 ml) was refluxed at 100 °C. After 12 h, the reaction mixture was concentrated in vacuo to afford (R)-baclofen, Phenibut (97~98%) as colorless solid.

5. Synthesis of phenyl-piracetam

The solution of 4-phenyl-2-pyrrolidinone (1.0 eq.) in 1,4-dioxane (30 ml) was added to the suspension of sodium hydride (1.1 eq.) in 1,4-dioxane (30 ml). The mixture was heated at 90°C for 30 min and then cooled to room temperature. Ethyl bromoacetate (1.1 eq.) was added, and the reaction mixture was refluxed at 120°C for 6 hours. The obtained mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with ethylacetate-hexane mixture 1:1, giving N-ethoxy carbonyl methyl-4-phenyl-2-pyrrolidinone. The solution of N-ethoxy carbonyl methyl-4-phenyl-2-pyrrolidinone (250 mg, 1.01 mM) in methanol (30 ml) saturated by a stream of gaseous ammonia for 5 hours. The reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography with ethylacetate-hexane mixture 1:1 silica gel giving N-carbamoyl methyl-4-phenyl-2-pyrrolidinone (5e, 5f) (85%).

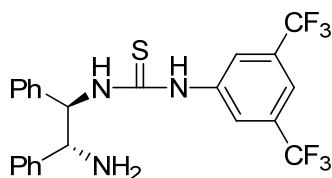
Compound Characterization Data

1-[(1*R*,2*R*)-2-Amino-1,2-diphenylethyl]-3-phenylthiourea (1a)



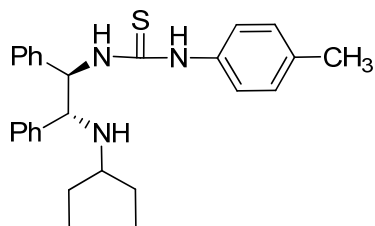
94% yield; $[\alpha]_{\text{D}}^{20} = +62.0$ ($c = 0.02$, CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3) δ 7.76 (s, 1 H), 7.54~7.19 (m, 15 H), 5.54 (s, 1 H), 4.42 (d, 1 H, $J = 5$ Hz), 1.35 (br s, 1 H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 182.09, 134.48, 133.93, 129.89, 128.70, 128.10, 127.91, 127.15, 126.94, 126.82, 126.74, 126.23, 125.59, 125.24, 122.98, 63.07, 59.09; IR (KBr) 3287.86, 3027.84, 1521.63, 1241.99, 1072.28, 939.20, 698.13 cm^{-1} ; HRMS (FAB $^+$) for $\text{C}_{21}\text{H}_{22}\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$ Calcd: 348.1534, Found: 348.1530.

1-[(1*R*,2*R*)-2-Amino-1,2-diphenylethyl]-3-[3,5-Bis(trifluoromethyl)phenyl]thiourea (1b)



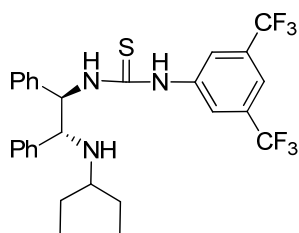
94% yield; $[\alpha]_{\text{D}}^{25} +13.5$ (c 1.00, CH_3Cl); ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 10.70 (s, 1H), 8.32 (s, 2H), 7.71 (s, 1H), 7.22~7.43 (m, 13H), 5.57 (d, $J = 3$ Hz, 1H), 4.44 (d, $J = 3$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 180.80, 143.41, 142.67, 130.94, 130.62, 128.81, 128.61, 127.75, 127.57, 127.51, 125.25, 122.54, 121.68, 116.40, 63.86, 60.06 ppm; IR (KBr) 3305, 3032, 2963, 1652, 1601, 1557, 1383, 1277, 1262, 803, 700 cm^{-1} ; HRMS (FAB $^+$) for $\text{C}_{22}\text{H}_{20}\text{N}_4\text{S}$ $[\text{M}+\text{H}]^+$ Calcd: 372.1487, Found: 372.1456

1-[(1*R*,2*R*)-2-(Pentan-3-ylamino)-1,2-diphenylethyl]-3-(*p*-tolyl)thiourea (1c)



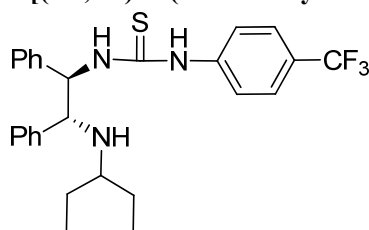
86% yield; $[\alpha]_{\text{D}}^{20} = +0.19$ ($c = 1.00$, CH_2Cl_2); ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 9.76 (s, 1 H), 7.89 (d, $J = 7.0$ Hz, 1 H), 7.32~7.18 (m, 14 H), 5.44 (s, 1 H), 4.08 (d, $J = 5.1$ Hz, 1 H), 2.29 (s, 2 H), 2.02 (s, 1 H), 1.39 (s, 1 H), 1.20~1.06 (m, 4 H), 0.68 (t, $J = 7.5$ Hz, 3 H), 0.41 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 181.04, 141.83, 141.55, 136.71, 134.88, 130.03, 128.67, 128.51, 127.49, 127.40, 124.67, 64.28, 63.77, 55.84, 26.71, 24.02, 21.20, 10.94, 8.30; IR (KBr) 3180.2, 2958.4, 1948.8, 1510.1, 1240.1, 821.6, 700.1, 565.1 cm^{-1} ; HRMS (FAB $^+$) for $\text{C}_{27}\text{H}_{34}\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$ Calcd: 432.2473, Found: 432.2460

1-[3,5-Bis(trifluoromethyl)phenyl]-3-[(1*R*,2*R*)-2-(pentan-3-ylamino)-1,2-diphenylethyl]thiourea (1d)



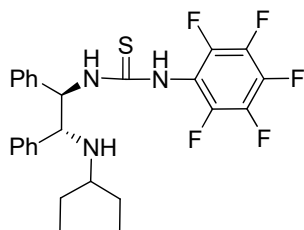
90% yield; $[\alpha]_D^{20} = +0.31$ ($c = 0.11$, CH_2Cl_2); ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 10.5 (br, 1 H), 8.30 (s, 2 H), 7.74 (s, 1 H), 7.40~7.19 (m, 10 H), 5.57 (br, 1 H), 4.18 (d, $J = 4.9$ Hz, 1 H), 2.09 (m, 1 H), 1.24~1.20 (m, 4 H), 0.75 (t, $J = 7.1$ Hz, 3 H), 0.50 (t, $J = 6.0$ Hz, 3 H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 181.10, 142.49, 140.88, 130.96, 130.64, 128.70, 128.59, 128.56, 127.60, 125.22, 122.52, 122.19, 116.70, 64.34, 63.62, 56.48, 26.64, 23.90, 10.98, 8.54; IR (KBr) 3239.9, 2964.2, 1471.5, 1278.6, 1135.9, 885.2, 700.1 cm^{-1} ; HRMS (FAB $^+$) for $\text{C}_{28}\text{H}_{30}\text{F}_6\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$ Calcd: 554.2065, Found: 554.2065

1-[(1R,2R)-2-(Pentan-3-ylamino)-1,2-diphenylethyl]-3-[4-(trifluoromethyl) phenyl]thiourea (1e)



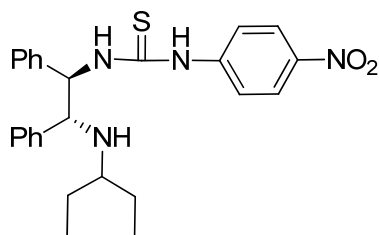
88% yield; $[\alpha]_D^{20} = +45.5$ ($c = 0.02$, CH_2Cl_2); ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 10.2 (br s, 1H), 8.41 (br s, 1H), 7.79 (d, $J = 8.0$ Hz, 2H), 7.64 (d, $J = 8.5$ Hz, 2H), 7.35~7.15 (m, 10H), 5.53 (br s, 1H), 4.13 (d, $J = 5.5$ Hz, 1H), 2.07 (m, 1H), 1.30~1.15 (m, 4H), 0.73 (t, $J = 7.1$ Hz, 3H), 0.49 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 180.91, 143.97, 141.18, 128.64, 128.52, 127.69, 127.48, 126.29, 122.41, 64.43, 63.71, 56.32, 26.68, 23.98, 10.98, 8.53; IR (KBr) 3205.3, 2962.3, 1945.9, 1741.5, 1517.8, 1324.9, 1245.9, 1066.5, 840.9, 700.1, 597.9 cm^{-1} ; HRMS (FAB $^+$) for $\text{C}_{27}\text{H}_{31}\text{F}_3\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$ Calcd: 486.2191, Found: 486.2190.

1-[(1R,2R)-2-(Pentan-3-ylamino)-1,2-diphenylethyl]-3-(perfluorophenyl)thiourea (1f)



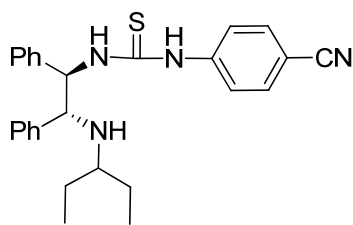
89% yield; $[\alpha]_D^{20} = +80.4$ ($c = 0.02$, CH_2Cl_2); ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 9.47 (s, 1 H), 8.61 (s, 1 H), 7.30~7.15 (m, 10 H), 5.48 (br s, 1 H), 4.13 (d, $J = 6.1$ Hz, 1 H), 2.08 (m, 1 H), 1.54 (br, 1 H), 1.30~1.14 (m, 4 H), 0.74 (t, $J = 7.4$ Hz, 3 H), 0.55 (t, $J = 6.3$ Hz, 3 H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 183.63, 145.82, 143.43, 141.90, 140.77, 139.01, 138.84, 136.56, 129.39, 128.61, 128.43, 127.68, 127.60, 115.93, 64.77, 64.53, 56.37, 26.72, 24.16, 10.86, 8.58; IR (KBr) 3299.8, 2964.2, 1525.5, 1344.2, 1145.6, 991.3, 912.2, 700.1, 605.6 cm^{-1} ; HRMS (FAB $^+$) for $\text{C}_{26}\text{H}_{27}\text{F}_5\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$ Calcd: 508.1846, Found: 508.1848.

1-(4-Nitrophenyl)-3-[(1R,2R)-2-(pentan-3-ylamino)-1,2-diphenylethyl]thiourea (1g)



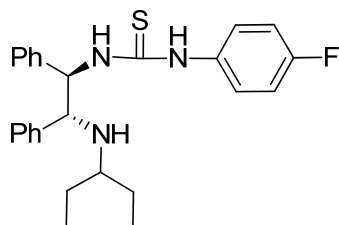
89% yield; $[\alpha]_{\text{D}}^{20} = +37.7$ ($c = 0.02$, CH_2Cl_2); ^1H NMR (300 MHz, DMSO-d_6) δ 10.5 (s, 1 H), 8.16 (m, 2 H), 7.90 (d, $J = 9.1$ Hz, 2 H), 7.37~7.15 (m, 10 H), 5.54 (br s, 1 H), 4.16 (d, $J = 5.5$ Hz, 1 H), 2.07 (m, 1 H), 1.30~1.15 (m, 4 H), 0.75 (t, $J = 7.4$ Hz, 3 H), 0.50 (t, $J = 7.4$ Hz, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 180.51, 146.95, 142.46, 141.92, 140.92, 128.68, 128.56, 127.72, 125.16, 120.92, 64.35, 63.80, 56.35, 55.59, 26.70, 23.96, 11.03, 8.61; IR (KBr) 3330.5, 2960.2, 2599.6, 2456.4, 2345.0, 1951.6, 1743.3, 1496.5, 1346.1, 1110.8, 1072.2, 852.4, 700.0, 586.3 cm^{-1} ; HRMS (FAB^+) for $\text{C}_{26}\text{H}_{31}\text{N}_4\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ Calcd: 463.2168, Found: 463.2165.

1-(4-Cyanophenyl)-3-[(1R,2R)-2-(pentan-3-ylamino)-1,2-diphenylethyl]thiourea (1h)



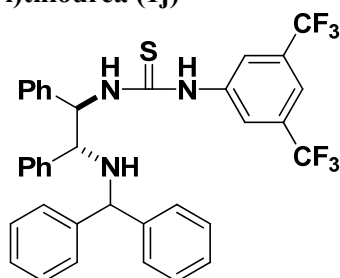
69% yield; $[\alpha]_{\text{D}}^{20} = +55.5$ ($c = 0.02$, CH_2Cl_2); ^1H NMR (300 MHz, DMSO-d_6) δ 10.3 (br s, 1 H), 8.54 (br s, 1 H), 7.84~7.72 (m, 4 H), 7.35~7.17 (m, 10 H), 5.54 (br s, 1 H), 4.14 (d, $J = 5.2$ Hz, 1 H), 2.07 (br s, 1 H), 1.56 (br s, 1 H), 1.21 (m, 4H), 0.74 (t, $J = 7.4$ Hz, 3 H), 0.49 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 180.62, 144.83, 141.92, 141.05, 133.40, 128.67, 128.33, 127.68, 127.64, 127.51, 121.76, 119.76, 105.41, 64.41, 63.72, 60.43, 56.33, 26.74, 23.98, 21.42, 14.74, 11.02, 8.56; IR (KBr) 3317.0, 2960.2, 2360.4, 2225.5, 1949.7, 1739.5, 1508.1, 1315.2, 1176.4, 1072.2, 837.0, 700.0, 545.8 cm^{-1} ; HRMS (FAB^+) for $\text{C}_{27}\text{H}_{31}\text{N}_4\text{S}$ $[\text{M}+\text{H}]^+$ Calcd: 443.2269, Found: 443.2271.

1-(4-Fluorophenyl)-3-[(1R,2R)-2-(pentan-3-ylamino)-1,2-diphenylethyl]thiourea (1i)



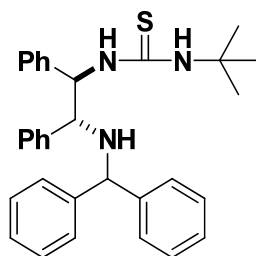
84% yield; $[\alpha]_{\text{D}}^{20} = +17.9$ ($c = 0.02$, CH_2Cl_2); ^1H NMR (300 MHz, DMSO-d_6) δ 9.83 (s, 1 H), 8.00 (d, $J = 6.7$ Hz, 1 H), 7.48~7.43 (m, 2 H), 7.31~7.16 (m, 11 H), 5.46 (br s, 1 H), 4.09 (d, $J = 5.22$ Hz, 1 H), 2.03 (br s, 1 H), 1.44 (br s, 1 H), 1.14 (m, 4 H), 0.70 (t, $J = 10.1$, 3 H), 0.44 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 181.42, 161.03, 158.62, 141.90, 141.44, 135.97, 128.65, 128.51, 127.57, 127.42, 126.49, 116.13, 115.90, 64.39, 63.76, 56.03, 26.72, 24.02, 10.98, 8.39; IR (KBr) 3193.7, 2962.3, 1889.9, 1511.9, 1218.8, 848.6, 701.9, 555.42 cm^{-1} ; HRMS (FAB^+) for $\text{C}_{26}\text{H}_{31}\text{FN}_3\text{S}$ $[\text{M}+\text{H}]^+$ Calcd: 436.6172, Found: 436.2223. pattern 436.5, 349.3, 266.4, 176.3, 106.1

1-((1R,2R)-2-(benzhydrylamino)-1,2-diphenylethyl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea (1j)



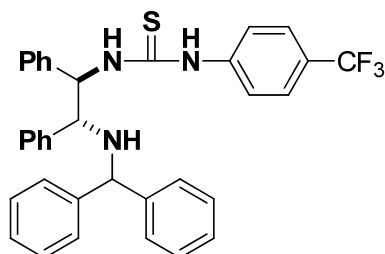
95% yield; $[\alpha]_{\text{D}}^{20} = +0.39$ ($c = 0.16$, CH_2Cl_2); ^1H NMR (400 MHz, DMSO-d_6) δ 7.82~7.09 (m, 23 H), 5.72 (s, 1 H), 3.98 (s, 1 H), 3.35 (s, 1 H), 2.47 (br, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 181.06, 156.63, 153.35, 143.36, 142.03, 141.31, 138.68, 129.48, 129.34, 126.90, 125.59, 123.65, 122.55, 122.14, 70.83, 65.14, 55.50; IR (KBr) 3239.9, 2964.2, 1471.5, 1278.6, 1135.9, 885.2, 700.1 cm^{-1} ; HRMS (EI^+) for $\text{C}_{28}\text{H}_{30}\text{F}_6\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$ Calcd: 649.1986, Found: 649.1932

1-((1R,2R)-2-(benzhydrylamino)-1,2-diphenylethyl)-3-tert-butylthiourea(1k)



93% yield; $[\alpha]_{\text{D}}^{20} = +115$ ($c = 0.17$, CH_2Cl_2); ^1H NMR (400 MHz, DMSO-d_6) δ 7.61~7.03 (m, 20H), 4.13 (q, 3H), 2.92 (s, 9H), 1.76 (br, 2H); IR(KBr) 3679.6, 2978.4, 1414.3, 1262.8, 1059.4, 886.1, 735.0 cm^{-1} ; HRMS(EI^+) for $\text{C}_{32}\text{H}_{35}\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$ Calcd: 493.2552, Found: 493.2587

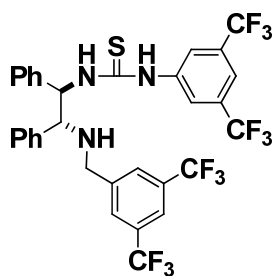
1-((1R,2R)-2-(benzhydrylamino)-1,2-diphenylethyl)-3-(4-(trifluoromethyl)phenyl)thiourea (1l)



89% yield; $[\alpha]_{\text{D}}^{20} = +124$ ($c = 0.10$, CH_2Cl_2); ^1H NMR (300 MHz, DMSO-d_6) δ 9.44 (br, 1H), 7.77~7.10 (m, 26H), 4.90 (s, 1H), 4.82 (s, 2H), 1.92 (s, 1H); IR(KBr) 3679.5, 3352.2, 2985.3, 1402.4, 1265.9, 1065.7, 726.8 cm^{-1} ; HRMS(FAB^+) for $\text{C}_{35}\text{H}_{30}\text{F}_3\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$ Calcd: 581.2113, Found: 581.2133

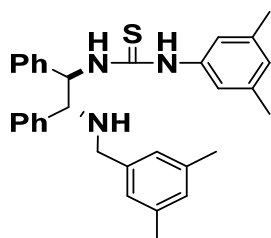
1-((1R,2R)-2-(3,5-bis(trifluoromethyl)benzylamino)-1,2-diphenylethyl)-3-(3,5-

bis(trifluoromethyl)phenyl)thiourea (1m)



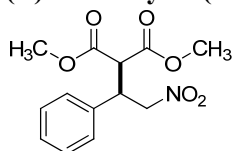
93% yield; $[\alpha]_D^{20} = +0.45$ ($c = 0.11$, CH_2Cl_2); ^1H NMR (500 MHz, DMSO-d_6) δ 7.61 (br, 3 H), 7.39~7.29 (m, 16 H), 4.54 (s, 4 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.58, 157.99, 142.12, 131.29 (q, $J_{\text{CF}} = 33.3$ Hz), 129.17, 127.28, 125.67, 122.96, 112.29, 89.59, 89.05, 84.78; ^{19}F NMR (470 MHz, MeOH-d_4) δ 64.60, 64.48, 64.38, 64.32; IR (KBr) 3032.6, 2871.3, 1663.5, 1386.6, 1275.9, 1117.5, 930.2, 700.2 cm^{-1} ; HRMS (LCMS $^+$) for $\text{C}_{32}\text{H}_{23}\text{F}_{12}\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$ Calcd: 709.1421, Found: 709.1428

1-((1R,2R)-2-(3,5-dimethylbenzylamino)-1,2-diphenylethyl)-3-(3,5-dimethylphenyl)thiourea (1n)



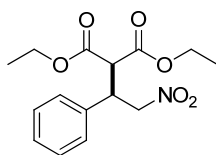
89% yield; $[\alpha]_D^{20} = +112$ (c 0.13, CH_2Cl_2); ^1H NMR (500 MHz, DMSO-d_6) δ 7.38 (t, 6H), 7.32 (d, 2H), 7.27 (d, 4H), 7.00 (s, 4H), 4.54 (s, 4H), 2.21 (s, 12H), 1.25 (br, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.08, 157.71, 156.95, 143.07, 138.05, 131.22, 129.00, 128.93, 127.09, 127.03, 123.43, 118.64, 112.63, 70.28, 68.05, 67.38, 21.63; IR(KBr) 3155.0, 2960.2, 2360.4, 1951.6, 1735.6, 1469.5, 1294.0, 1241.9, 1006.7, 837.0, 700.0, 572.8 cm^{-1} ; HRMS(LCMS $^+$) for $\text{C}_{26}\text{H}_{30}\text{F}_2\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$ Calcd: 454.2129, Found: 454.2133

(R)-Dimethyl 2-(2-nitro-1-phenylethyl)malonate (2a)^{1,2}



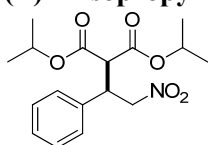
^1H NMR (300 MHz, CDCl_3) δ 7.40~7.15 (m, 5H), 5.15~5.03 (m, 1H), 4.93 (dd, $J = 4.5, 12.8$ Hz, 1H), 4.88~4.76 (m, 2H), 4.20 (td, $J = 4.5, 9.5$ Hz, 1H), 3.76 (d, $J = 9.5$ Hz, 1H), 1.24 (d, $J = 6.1$ Hz, 3H), 1.07 (d, $J = 6.4$ Hz, 3H), 1.01 (d, $J = 6.4$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.1, 166.4, 136.3, 128.9, 128.3, 128.2, 77.9, 69.9, 69.5, 55.1, 42.9, 21.5, 21.4, 21.19, 21.17 ppm; IR(KBr) 3030, 2985, 1727, 1557 cm^{-1} ; HRMS(ESI) for $\text{C}_{13}\text{H}_{16}\text{N}_1\text{O}_6$ $[\text{M}+\text{H}]^+$ Calcd: 282.09721, Found: 282.09726; HPLC [Chiralcel AD-H, hexane/2-propanol = 95/5, 1.0 mL/min, $\lambda = 254$ nm, retention times: (major) 23.3 min, (minor) 38.0 min].

(R)-Diethyl 2-(2-nitro-1-phenylethyl)malonate (2b)^{1,2}



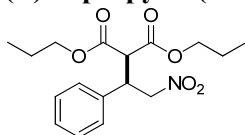
^1H NMR (300 MHz, CDCl_3) δ 7.30~7.20 (m, 5H), 4.93 (dd, J = 4.6, 13.1 Hz, 1H), 4.86 (dd, J = 9.2, 13.1 Hz, 1H), 4.24~4.17 (m, 3H), 3.98~3.97 (q, J = 7.2 Hz, 2H), 3.81~3.79 (d, J = 9.5 Hz, 1H), 1.25 (t, J = 7.2 Hz, 3H), 1.03 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.4, 166.7, 136.2, 128.8, 128.2, 127.9, 77.6, 62.0, 61.8, 54.9, 42.9, 13.9, 13.6 ppm; IR(KBr) 2989, 2938, 1731, 1557 cm^{-1} ; HRMS(ESI) for $\text{C}_{15}\text{H}_{20}\text{N}_1\text{O}_6[\text{M}+\text{H}]^+$ Calcd: 310.12851, Found: 310.12936; HPLC [Chiralcel AD-H, hexane/ethanol = 90/10, 1.0 mL/min, λ = 254 nm, retention times: (major) 11.5 min, (minor) 15.3 min].

(*R*)-Diisopropyl 2-(2-nitro-1-phenylethyl)malonate (2c)^{1,3}



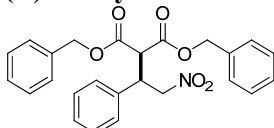
^1H NMR (300 MHz, CDCl_3) δ 7.32~7.22 (m, 5H), 5.10 (dd, J = 5.0, 13.1 Hz, 1H), 4.91~4.979 (m, 3H), 4.21~4.19 (m, 1H), 1.25 (d, J = 2.0 Hz, 6H), 1.07 (dd, J = 2.0, 2.0 Hz, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.27, 166.54, 136.47, 129.07, 128.34, 127.9, 78.15, 70.15, 69.75, 55.35, 43.14, 21.80, 21.67, 21.48 ppm; IR(KBr) 3029, 2956, 1737, 1558 cm^{-1} ; HRMS(ESI) for $\text{C}_{17}\text{H}_{24}\text{N}_1\text{O}_6[\text{M}+\text{H}]^+$ Calcd: 338.15981 Found: 338.16336; HPLC [Chiralcel AD-H, hexane/2-propanol = 95/5, 1.0 mL/min, λ = 254 nm, retention times: (major) 14.8 min, (minor) 34.4 min].

(*R*)-Dipropyl 2-(2-nitro-1-phenylethyl)malonate (2d)^{1,3}



^1H NMR (300 MHz, CDCl_3) δ 7.31~7.22 (m, 5H), 4.92~4.87 (t, J = 5.0, 9.5 Hz, 2H), 4.24 (m, 1H), 4.15~4.09 (m, 2H), 3.92~3.83 (dd, J = 6.6, 9.7 Hz, 3H), 1.68~1.61 (m, 2H), 1.49~1.42 (m, 2H), 0.93~0.88 (t, J = 7.4, 7.4 Hz, 3H), 0.82~0.77 (t, J = 7.4, 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.79, 167.17, 136.46, 129.14, 128.52, 128.17, 77.85, 67.86, 67.65, 55.17, 43.16, 21.97, 21.81, 10.48 ppm; IR(KBr) 3029, 2956, 1737, 1558 cm^{-1} ; HRMS(ESI) for $\text{C}_{17}\text{H}_{24}\text{N}_1\text{O}_6[\text{M}+\text{H}]^+$ Calcd: 338.15981 Found: 338.16336; HPLC [Chiralcel AD-H, hexane/2-propanol = 95/5, 1.0 mL/min, λ = 254 nm, retention times: (major) 18.4 min, (minor) 38.9 min].

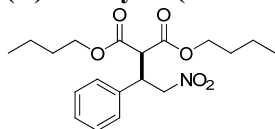
(*R*)-Benzyl 2-carbobenzyloxy-4-nitro-3-phenylbutyrate (2e)^{1,3}



^1H NMR (400 MHz, CDCl_3) δ 7.33~7.25 (m, 10H), 7.17~7.07 (m, 5H), 5.16 (d, 1H, J = 12.2 Hz), 5.18 (d, 1H, J = 12.2 Hz), 4.93 (s, 1H), 4.84~4.82 (m, 2H), 4.28~4.22 (q, 1H), 3.94 (d, 1H, 9.3 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 167.39, 166.78, 136.14, 134.85, 129.25, 128.90, 128.15, 77.63, 68.04, 67.86, 55.14, 43.16 ppm; IR(KBr) 3068, 3036, 2963, 1736, 1558, 1498, 1456, 1378, 1326, 1286, 1217, 1156,

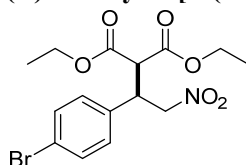
1003, 975, 908, 562 cm^{-1} ; HRMS(EI) for $\text{C}_{25}\text{H}_{23}\text{N}_1\text{O}_6[\text{M}+\text{H}]^+$ Calcd: 433.1525 Found: 433.1525; HPLC [Chiralcel AD-H, hexane/2-propanol = 70/30, 1.0 mL/min, λ = 254 nm, retention times: (major) 26.0 min, (minor) 24.1 min].

(R)-dibutyl 2-(2-nitro-1-phenylethyl)malonate (2f)^{1,3}



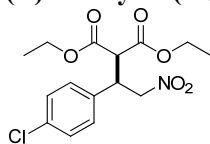
^1H NMR (400 MHz, CDCl_3) δ 7.31~7.22 (m, 5H), 4.92~4.87 (t, J = 5.0, 9.5 Hz, 2H), 4.24 (m, 1H), 4.15~4.09 (m, 2H), 3.92~3.83 (dd, s , J = 6.6, 9.7 Hz, 3H), 1.68~1.61 (m, 2H), 1.49~1.42 (m, 2H), 0.93~0.88 (t, J = 7.4, 7.4 Hz, 3H), 0.82~0.77 (t, J = 7.4, 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.79, 167.17, 136.46, 129.14, 128.52, 128.17, 77.85, 67.86, 67.65, 55.17, 43.16, 21.97, 21.81, 10.48 ppm; HRMS(EI) for $\text{C}_{17}\text{H}_{24}\text{N}_1\text{O}_6[\text{M}+\text{H}]^+$ Calcd: 338.15981 Found: 338.16336; HPLC [Chiralcel AD-H, hexane/2-propanol = 95/5, 1.0 mL/min, λ = 254 nm, retention times: (major) 18.4 min, (minor) 38.9 min].

(R)-Diethyl 2-[1-(4-bromophenyl)-2-nitroethyl]malonate (2g)³



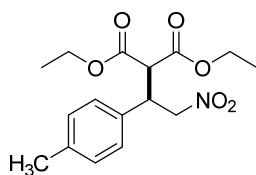
^1H NMR (300 MHz, CDCl_3) δ 7.44~7.42 (d, J = 8.5 Hz, 2H), 7.13~7.11 (d, J = 8.2 Hz, 2H), 4.88~4.81 (m, 2H), 4.22~4.16 (m, 3H), 4.04~3.97 (q, J = 7.1, 6.9 Hz, 2H), 3.78~3.75 (d, J = 9.4 Hz, 1H), 1.26~1.21 (t, J = 7.2, 7.1 Hz, 3H), 1.08~1.03 (t, J = 7.1, 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.42, 166.83, 135.52, 132.29, 130.00, 122.62, 77.55, 62.50, 62.26, 54.86, 42.60, 14.17, 13.99 ppm; IR (KBr) 2983, 2950, 1732, 1556, 1490, 1445 cm^{-1} HRMS(ESI) for $\text{C}_{15}\text{H}_{19}\text{N}_1\text{O}_6\text{Br}[\text{M}+\text{H}]^+$ Calcd: 388.03903 Found: 388.04495; HPLC [Chiralcel AD-H, hexane/ethanol = 95/5, 1.0 mL/min, λ = 254 nm, retention times: (major) 35.9 min, (minor) 44.4 min].

(R)-diethyl 2-(1-(4-chlorophenyl)-2-nitroethyl)malonate (2h)³



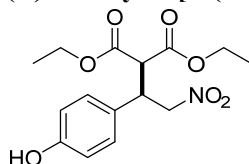
^1H NMR (300 MHz, CDCl_3) δ 7.29~7.17 (dd, J = 20.6, 8.2 Hz, 4H), 4.88~4.81 (m, 2H), 4.23~4.16 (m, 3H), 4.04~3.97 (q, J = 7.1, 7.1 Hz, 2H), 3.78~3.75 (d, J = 9.3 Hz, 1H), 1.26~1.21 (t, J = 7.1, 7.2 Hz, 3H), 1.08~1.03 (t, J = 7.2, 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.44, 166.83, 134.98, 134.46, 129.69, 129.32, 77.63, 62.49, 62.23, 54.92, 42.55, 14.15, 13.97 ppm; IR (KBr) 2984, 1733, 1557, 1478, 1445, 1371 cm^{-1} HRMS(ESI) for $\text{C}_{15}\text{H}_{19}\text{N}_1\text{O}_6\text{Cl}[\text{M}+\text{H}]^+$ Calcd: 344.08954 Found: 344.09119; HPLC [Chiralcel AD-H, hexane/ethanol = 90/10, 1.0 mL/min, λ = 254 nm, retention times: (major) 17.9 min, (minor) 24.1 min].

(R)-Diethyl 2-[2-nitro-1-(p-tolyl)ethyl]malonate (2i)³



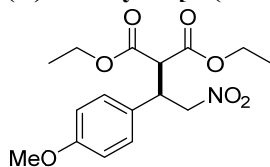
^1H NMR (300 MHz, CDCl_3) δ 7.09 (d, $J = 15.2$ Hz, 4H), 4.89~4.78 (m, 2H), 4.22~4.14 (m, 3H), 4.01~3.96 (q, $J = 7.0, 7.1$ Hz, 2H), 3.79 (d, $J = 9.3$ Hz, 1H), 2.27 (s, 3H), 1.25~1.22 (t, $J = 7.1, 7.0$ Hz, 3H), 1.06~1.02 (t, $J = 7.1, 8.6$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.74, 167.08, 138.27, 138.23, 133.30, 129.80, 128.05, 78.00, 62.32, 62.06, 55.24, 42.84, 21.28, 14.18, 13.97 ppm; IR(KBr) 3030, 2987, 1732, 1612, 1557 cm^{-1} ; HRMS(ESI) for $\text{C}_{16}\text{H}_{22}\text{N}_1\text{O}_6[\text{M}+\text{H}]^+$ Calcd: 324.14416 Found: 324.14648; HPLC [Chiralcel AD-H, hexane/ethanol = 98/2, 1.0 mL/min, $\lambda = 254$ nm, retention times: (major) 36.0 min, (minor) 42.8 min].

(R)-Diethyl 2-[1-(4-hydroxyphenyl)-2-nitroethyl]malonate (2j)³



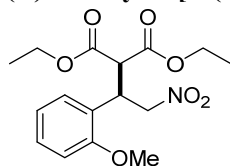
^1H NMR (300 MHz, CDCl_3) δ 7.09~7.06 (d, $J = 8.3$ Hz, 2H), 6.72~6.70 (d, $J = 8.2$ Hz, 2H), 5.63 (br, 1H), 4.91~4.74 (m, 2H), 4.25~4.12 (m, 3H), 4.05~3.98 (q, $J = 7.1, 6.8$ Hz, 2H), 3.79 (d, $J = 9.7$ Hz, 1H), 1.29~1.24 (t, $J = 7.1, 6.6$ Hz, 3H), 1.09~1.05 (t, $J = 7.1, 7.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.74, 167.28, 155.88, 129.54, 128.06, 78.17, 62.44, 62.23, 55.29, 42.53, 29.92, 14.20, 14.00 ppm; HRMS(ESI) for $\text{C}_{15}\text{H}_{20}\text{N}_1\text{O}_7[\text{M}+\text{H}]^+$ Calcd: 326.12343 Found: 326.12903; HPLC [Chiralcel AD-H, hexane/ethanol = 90/10, 1.0 mL/min, $\lambda = 254$ nm, retention times: (major) 20.4 min, (minor) 50.6 min].

(R)-Diethyl 2-[1-(4-methoxyphenyl)-2-nitroethyl]malonate (2k)³



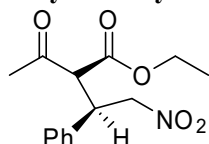
^1H NMR (300 MHz, CDCl_3) δ 7.16~7.13 (d, $J = 8.5$ Hz, 2H), 6.84~6.81 (d, $J = 8.8$ Hz, 2H), 4.87~4.80 (m, 2H), 4.24~4.16 (m, 3H), 4.04~3.97 (q, $J = 7.1, 7.1$ Hz, 2H), 3.79~3.78 (d, $J = 2.7$ Hz, 1H), 3.76 (s, 3H), 1.28~1.23 (t, $J = 7.1, 7.2$ Hz, 3H), 1.08~1.03 (t, $J = 7.1, 7.1$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 167.73, 167.08, 159.61, 129.36, 128.17, 114.48, 78.12, 62.34, 62.06, 55.42, 55.30, 42.53, 14.19, 14.01 ppm; IR(KBr) 2988, 2936, 2904, 1730, 1612, 1552 cm^{-1} ; HRMS(ESI) for $\text{C}_{16}\text{H}_{22}\text{N}_1\text{O}_7[\text{M}+\text{H}]^+$ Calcd: 340.13908 Found: 340.13901; HPLC [Chiralcel AD-H, hexane/ethanol = 90/10, 1.0 mL/min, $\lambda = 254$ nm, retention times: (major) 23.8 min, (minor) 39.5 min].

(R)-Diethyl 2-[1-(2-methoxyphenyl)-2-nitroethyl]malonate (2l)³



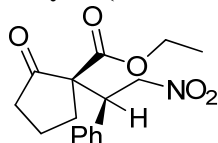
^1H NMR (300 MHz, CDCl_3) δ 7.26~7.21(m, 1H), 7.15~7.12 (m, 1H), 6.87~6.83 (m, 2H), 5.06~4.98 (dd, $J = 3.6, 1.1$ Hz, 1H), 4.89~4.83 (dd, $J = 3.6, 1.1$ Hz, 1H), 4.37~4.34 (m, 1H), 4.24~4.12 (m, 3H), 3.97~3.90 (q, $J = 7.2, 7.2$ Hz, 2H), 3.85 (s, 3H), 1.28~1.23 (t, $J = 7.1, 6.9$ Hz, 3H), 1.01~0.96 (t, $J = 7.2, 7.1$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 168.14, 167.41, 157.62, 131.09, 129.83, 123.87, 120.96, 111.27, 76.40, 62.18, 61.77, 55.62, 52.89, 40.74, 14.20, 13.94 ppm; IR (KBr) 2984, 2939, 2908, 1732, 1613, 1556 cm^{-1} HRMS(ESI) for $\text{C}_{16}\text{H}_{22}\text{N}_1\text{O}_6[\text{M}]$ Calcd: 339.13125 Found: 339.12933; HPLC [Chiralcel AD-H, hexane/2-propanol = 95/5, 1.0 mL/min, $\lambda = 254$ nm, retention times: (major) 14.9 min, (minor) 20.6 min].

Ethyl 2-acetyl-4-nitro-3-phenylbutanoate (2m)⁴



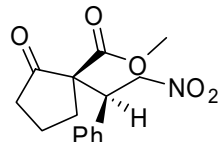
^1H NMR (300 MHz, CDCl_3) δ 7.30 (m, 3H), 7.21 (d, $J = 6.6$ Hz, 2H), 4.80 (m, 2H), 4.22 (m, 1.8H), 4.12 (d, $J = 10.1$ Hz, 0.6H), 4.03 (d, $J = 9.0$ Hz, 0.4H), 3.96 (q, $J = 15$ Hz, 1.2H), 2.30 (s, 1.6H), 2.06 (s, 1.4H), 1.28 (t, $J = 15.0$ Hz, 1.2H), 1.00 (t, $J = 12.0$ Hz, 1.8H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.3, 200.5, 167.7, 167.0, 136.6, 136.5, 129.3, 129.1, 128.4, 128.1, 78.1, 78.0, 62.4, 62.1, 61.8, 42.7, 42.5, 30.5, 30.3, 14.2, 13.8; IR (CHCl_3) ν 3031, 2987, 1741, 1718, 1556, 1375 cm^{-1} ; HRMS (FAB^+) Calcd. for $[\text{C}_{14}\text{H}_{18}\text{NO}_5]^+$: 280.1185; Found: 280.1187; HPLC [Chiralcel AD-H, hexane/2-propanol = 80/20, 0.8 mL/min, $\lambda = 210$ nm] retention times: (major diastereomer) 10.0, 11.4 min, (minor diastereomer) 8.0, 19.9 min.

Ethyl 1-(2-nitro-1-phenylethyl)-2-oxocyclopentanecarboxylate (2n)^{5,6}



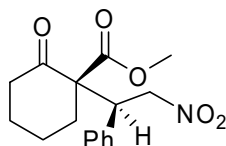
^1H NMR (300 MHz, CDCl_3) δ 7.20~7.27 (m, 5 H), 5.15~5.21 (dd, $J = 4.2$ Hz, 3.9 Hz, 1 H), 4.98~5.06 (dd, $J = 11.2$ Hz, 11.0 Hz, 1 H), 4.18~4.25 (m, 2 H), 4.06~4.11 (dd, $J = 3.8$ Hz, 3.8 Hz, 1 H), 2.30~2.45 (m, 2 H), 1.79~2.07 (m, 4 H), 1.25~1.30 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 207.3, 169.8, 135.5, 129.6, 128.6, 128.4, 77.7, 62.17, 47.9, 41.6, 37.2, 28.1, 22.5, 14.2; IR (CHCl_3) ν 3031, 2957, 1751, 1727, 1556, cm^{-1} HRMS (FAB^+) Calcd. for $[\text{C}_{16}\text{H}_{20}\text{NO}_5]^+$: 306.1341, found: 306.1341; Major diastereomer: *ee* was determined by HPLC [Chiralpak OD-H column, hexanes/2-propanol = 93/7, flow rate = 1 mL/min, $\lambda = 220$ nm] retention times: (major enantiomer) = 16.5 min, (minor enantiomer) = 22.6 min.

Methyl 1-(2-nitro-1-phenylethyl)-2-oxocyclopentanecarboxylate (2o)^{5,6}



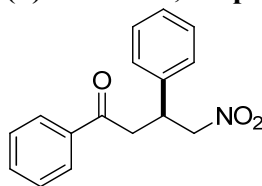
^1H NMR (300 MHz, CDCl_3) δ 7.34~7.22 (m, 5H), 5.17 (dd, $J = 3.8, 13.5$ Hz, 1H), 5.01 (dd, $J = 10.7, 13.5$ Hz, 1H), 4.08 (dd, $J = 3.9, 10.8$ Hz, 1H), 3.76 (s, 3H), 2.42~2.30 (m, 2H), 2.09~1.79 (m, 4H); ^{13}C NMR for major diastereomer (100 MHz, CDCl_3) δ 212.5, 170.0, 135.4, 129.5, 129.0, 128.5, 76.6, 62.6, 53.2, 46.3, 38.1, 31.2, 19.5; IR (CHCl_3) ν 3031, 2957, 1751, 1727, 1556, cm^{-1} ; HRMS (FAB^+) Calcd. for $[\text{C}_{15}\text{H}_{19}\text{NO}_5]^+$: 292.1185, found: 292.1180; HPLC [Chiralcel OD-H, hexanes/2-propanol = 93/7, 0.5 mL/min, $\lambda = 210$ nm] retention times: (major enantiomer) 28.8 min, (minor enantiomer) 23.3 min, (minor diastereomers) 15.7, 18.5 min.

Methyl 1-(2-nitro-1-phenylethyl)-2-oxocyclohexanecarboxylate (2p)^{5,6}



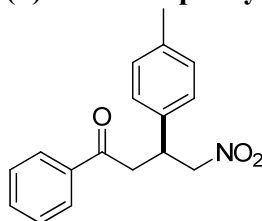
^1H NMR (300 MHz, CDCl_3) δ 7.30–7.27 (m, 3H), 7.17–7.12 (m, 2H), 5.06 (dd, J = 3.1, 13.5 Hz, 0.96H), 4.78 (dd, J = 11.2, 13.2 Hz, 1H), 4.01 (dd, J = 3, 11.3 Hz, 0.96H), 3.75 (s, 2.88H), 3.68 (s, 0.12H), 2.57–2.39 (m, 2H), 2.14–1.98 (m, 2H), 1.77–1.45 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 207.1, 170.3, 135.4, 129.5, 128.7, 128.4, 77.6, 63.2, 52.7, 47.8, 41.6, 37.1, 28.1, 22.5; IR (CHCl_3) ν 3027, 2951, 1713, 1556 cm^{-1} ; HRMS (FAB $^+$) Calcd. for $[\text{C}_{16}\text{H}_{20}\text{NO}_5]^+$: 306.1341, found: 306.1340; HPLC [Chiralcel OJ-H, hexanes/2-propanol = 80/20, 0.5 mL/min, λ = 210 nm] retention times: (major enantiomer) 56.2 min, (minor enantiomer) 51.9 min, (minor diastereomers) 70.0, 102.4 min.

(S)-4-Nitro-1,3-diphenyl-butan-1-one (3a)⁷



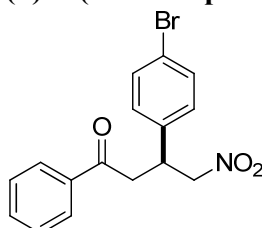
^1H NMR (500 MHz, CDCl_3) δ 7.91~7.92 (m, 2H), 7.59~7.26 (m, 8H), 4.85~4.81 (dd, J = 12.5, 6.7 Hz, 1H), 4.71~4.67 (dd, J = 12.5, 7.8 Hz, 1H), 4.26~4.20 (m, 1H), 3.51~3.46 (dd, J = 17.7, 6.4 Hz, 1H), 3.45~3.40 (dd, J = 17.7, 7.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 196.87, 139.15, 136.39, 133.60, 129.09, 128.77, 128.04, 127.90, 127.48, 79.58, 41.54, 39.30 ppm; IR (KBr) 3058, 3029, 2920, 1687, 1544, 1440, 1367, 1268, 1224, 1084, 988, 764, 703, 623, 559 cm^{-1} ; LRMS (ESI $^+$) for $\text{C}_{16}\text{H}_{15}\text{NO}_3$ $[\text{M}+\text{Na}]^+$ Calcd: 292.1, Found: 292.1; HPLC [Chiralcel AD-H, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention times: (major) 14.3 min, (minor) 19.9 min];

(S)-4-nitro-1-phenyl-3-(p-tolyl)butan-1-one (3b)



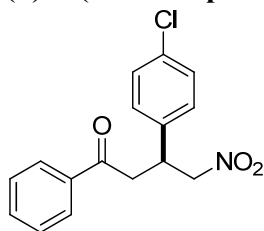
^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, J = 7.0 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 7.18~7.13 (m, 4H), 4.83~4.79 (dd, J = 12.5, 6.5 Hz, 1H), 4.68~4.64 (dd, J = 12.5, 8.0 Hz, 1H), 4.22~4.16 (m, 1H), 3.48~3.44 (dd, J = 17.5, 6.5 Hz, 1H), 3.43~3.38 (dd, J = 18.0, 7.5 Hz, 1H), 2.31 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 196.96, 137.60, 136.42, 136.05, 133.56, 129.76, 128.75, 128.05, 127.31, 79.73, 41.59, 38.96, 21.07 ppm; IR (KBr) 3058, 2922, 2862, 1685, 1551, 1516, 1446, 1377, 1270, 1225, 998, 817, 755, 691, 551 cm^{-1} ; LRMS (ESI $^+$) for $\text{C}_{17}\text{H}_{17}\text{NO}_3$ $[\text{M}+\text{Na}]^+$ Calcd: 306.1, Found: 306.2; HPLC [Chiralcel AD-H, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention times: (major) 11.9 min, (minor) 16. min];

(S)-3-(4-Bromophenyl)-4-nitro-1-phenylbutan-1-one (3c)



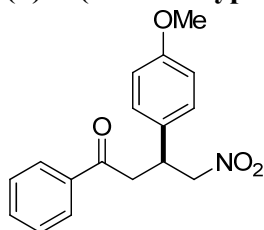
¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, *J* = 7.0 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.48~7.45 (m, 4H), 7.18~7.16 (m, 2H), 4.83~4.79 (dd, *J* = 12.5, 6.5 Hz, 1H), 4.68~4.64 (dd, *J* = 12.5, 8.5 Hz, 1H), 4.23~4.17 (m, 1H), 3.48~3.43 (dd, *J* = 17.0, 6.5 Hz, 1H), 3.43~3.38 (dd, *J* = 17.0, 7.0 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 196.47, 138.14, 136.21, 133.74, 132.22, 129.24, 128.82, 128.02, 121.85, 79.28, 41.30, 38.76 ppm; LRMS (ESI⁺) for C₁₆H₁₄BrNO₃ [M+Na]⁺ Calcd: 370.0, Found: 370.1; HPLC [Chiralcel AD-H, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention times: (major) 13.7 min];

(S)-3-(4-Chlorophenyl)-4-nitro-1-phenylbutan-1-one (3d)⁸



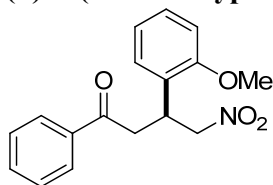
¹H NMR (500 MHz, CDCl₃) δ 7.92~7.90 (m, 2H), 7.60~7.57 (m, 1H), 7.48~7.45 (m, 2H), 7.32~7.29 (m, 2H), 7.24~7.22 (m, 2H), 4.83~4.80 (dd, *J* = 12.5, 6.5 Hz, 1H), 4.68~4.64 (dd, *J* = 12.5, 8.1 Hz, 1H), 4.25~4.19 (m, 1H), 3.48~3.43 (dd, *J* = 18.2, 6.4 Hz, 1H), 3.43~3.38 (dd, *J* = 18.2, 7.3 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 196.50, 137.59, 136.23, 133.74, 129.27, 128.90, 128.82, 128.02, 79.36, 41.36, 38.70 ppm; LRMS (ESI⁺) for C₁₆H₁₄ClNO₃ [M+Na]⁺ Calcd: 326.1, Found: 326.1; HPLC [Chiralcel AD-H, hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention times: (major) 23.4 min, (minor) 38.8 min];

(S)-3-(4-Methoxyphenyl)-4-nitro-1-phenylbutan-1-one (3e)⁸



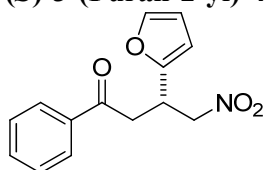
¹H NMR (500 MHz, CDCl₃) δ 7.93~7.91 (m, 2H), 7.59~7.44 (m, 3H), 7.20 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7, 2H), 4.82~4.78 (dd, *J* = 12.3, 6.7 Hz, 1H), 4.67~4.63 (dd, *J* = 12.3, 7.9 Hz, 1H), 4.21~4.15 (m, 1H), 3.78 (s, 3H), 3.47~3.43 (dd, *J* = 16.5, 6.5 Hz, 1H), 3.43~3.37 (dd, *J* = 16.5, 6.6 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 196.99, 159.10, 136.42, 133.56, 130.99, 128.75, 128.52, 128.04, 114.45, 79.85, 55.27, 41.67, 38.65 ppm; LRMS (ESI⁺) for C₁₇H₁₇NO₄ [M+Na]⁺ Calcd: 322.1, Found: 322.2; HPLC [Chiralcel AD-H, hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention times: (major) 11.9 min, (minor) 16.2 min];

(S)-3-(2-Methoxyphenyl)-4-nitro-1-phenylbutan-1-one (3f)



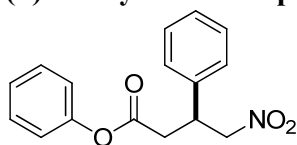
¹H NMR (500 MHz, CDCl₃) δ 7.94~7.92 (m, 2H), 7.58~7.55 (m, 1H), 7.47~7.44 (m, 2H), 7.26~7.20 (m, 2H), 6.92~6.88 (m, 2H), 4.89~4.82 (m, 2H), 4.45~4.39 (m, 1H), 3.86 (s, 3H), 3.54 (d, *J* = 7.5 Hz, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 197.64, 157.20, 136.63, 133.38, 129.52, 128.99, 128.68, 128.05, 126.70, 120.96, 110.05, 77.90, 55.38, 39.80, 35.95 ppm; IR (KBr) 3063, 2923, 2852, 1684, 1598, 1550, 1494, 1445, 1377, 1246, 1120, 1025, 754, 690 cm⁻¹; LRMS (ESI⁺) for C₁₇H₁₇NO₄ [M+Na]⁺ Calcd: 322.1, Found: 322.2; HPLC [Chiralcel AD-H, hexane/2-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention times: (major) 9.9 min, (minor) 14.1 min];

(S)-3-(Furan-2-yl)-4-nitro-1-phenylbutan-1-one (3g)



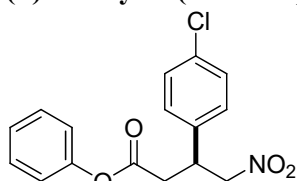
^1H NMR (500 MHz, CDCl_3) δ 7.96~7.94 (m, 2H), 7.61~7.58 (m, 1H), 7.49~7.46 (m, 2H), 7.34 (m, 1H), 6.30~6.29 (m, 1H), 6.19 (d, J = 3.3 Hz, 1H), 4.83~4.79 (dd, J = 11.6, 5.4 Hz, 1H), 4.77~4.73 (dd, J = 11.6, 6.0 Hz, 1H), 4.36~4.31 (m, 1H), 3.55~3.50 (dd, J = 17.7, 6.1 Hz, 1H), 3.46~3.41 (dd, J = 17.7, 7.3 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 196.55, 151.95, 142.32, 136.26, 133.69, 128.80, 128.07, 110.53, 107.20, 77.27, 38.99, 33.19 ppm; IR (KBr) 3121, 3062, 2918, 1685, 1596, 1553, 1505, 1448, 1377, 1213, 1183, 1012, 917, 749, 691, 599 cm^{-1} ; LRMS(ESI^+) for $\text{C}_{14}\text{H}_{13}\text{NO}_4$ [$\text{M}+\text{Na}$] $^+$ Calcd: 282.1, Found: 282.1; HPLC [Chiralcel AD-H, hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention times: (major) 12.7 min];

(S)-Phenyl 4-nitro-3-phenylbutanoate (4a)⁹



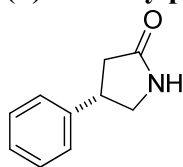
$[\alpha]_{\text{D}}^{20}$ +7.83 (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.38~7.16 (m, 8H), 6.87~6.85 (m, 2H), 4.75~4.71 (dd, J = 11.6, 6.6 Hz, 1H), 4.68~4.64 (dd, J = 11.6, 6.4 Hz, 1H), 4.10~4.04 (m, 1H), 3.04~3.0 (dd, J = 13.7, 4.6 Hz, 1H), 2.99~2.94 (dd, J = 13.7, 5.6 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 169.33, 150.33, 137.96, 129.50, 129.22, 128.29, 127.55, 126.12, 121.39, 79.38, 40.38, 37.87 ppm; LRMS (ESI^+) for $\text{C}_{16}\text{H}_{15}\text{NO}_4$ [$\text{M}+\text{Na}$] $^+$ Calcd: 308.1, Found: 308.1;

(S)-Phenyl 3-(4-chlorophenyl)-4-nitrobutanoate (4b)⁸



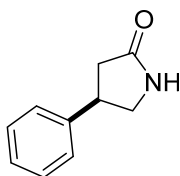
$[\alpha]_{\text{D}}^{20}$ +20.72 (c 1.0, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.35~7.22 (m, 7H), 6.92~6.90 (m, 2H), 4.79~4.75 (dd, J = 12.7, 7.3 Hz, 1H), 4.71~4.67 (dd, J = 12.7, 7.9 Hz, 1H), 4.11~4.06 (m, 1H), 3.08~3.03 (dd, J = 14.7, 5.3 Hz, 1H), 3.01~2.96 (dd, J = 14.7, 6.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 169.01, 150.17, 136.37, 134.23, 129.53, 129.43, 128.88, 126.20, 121.26, 79.08, 39.70, 37.67 ppm; LRMS (ESI^+) for $\text{C}_{16}\text{H}_{14}\text{ClNO}_4$ [$\text{M}+\text{Na}$] $^+$ Calcd: 342.1, Found: 342.1;

(S)-4-Phenylpyrrolidin-2-one (4c)^{10,12}



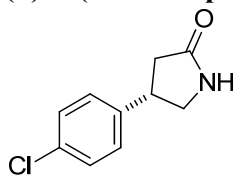
$[\alpha]_{\text{D}}^{20}$ +35.94 (c 1.0, MeOH);

(R)-4-Phenylpyrrolidin-2-one (4e)^{10,12}



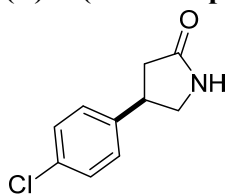
$[\alpha]_D^{20}$ -36.03 (*c* 1.0, MeOH); ^1H NMR (500 MHz, CDCl_3) δ 7.37~7.33 (m, 2H), 7.29~7.27 (m, 2H), 7.26~7.25 (m, 1H), 5.92 (br s, 1H), 3.81~3.77 (m, 1H), 3.71 (q, J = 8.0 Hz, 1H), 3.45~3.41 (dd, J = 9.4, 2.0 Hz, 1H), 2.77~2.72 (dd, J = 16.8, 8.7 Hz, 1H), 2.54~2.49 (dd, J = 17.0, 8.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 177.93, 142.14, 128.88, 127.13, 126.79, 49.60, 40.31, 38.02 ppm; LRMS (ESI^+) for $\text{C}_{10}\text{H}_{11}\text{NO}$ $[\text{M}+\text{H}]^+$ Calcd: 162.1, Found: 162.2; HPLC [Chiralcel AD-H, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention times: (minor) 15.2 min, (major) 19.4 min];

(S)-4-(4-Chlorophenyl)pyrrolidin-2-one (4d)^{11,12}



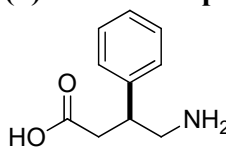
$[\alpha]_D^{22}$ -32.06 (*c* 1.0, EtOH);

(R)-4-(4-Chlorophenyl)pyrrolidin-2-one (4f)^{11,12}



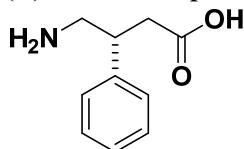
$[\alpha]_D^{22}$ +31.17 (*c* 1.0, EtOH); ^1H NMR (500 MHz, CDCl_3) δ 7.32 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 8.3 Hz, 2H), 5.72 (br s, 1H), 3.80~3.77 (m, 1H), 3.69 (q, J = 8.5 Hz, 1H), 3.40~3.36 (dd, J = 8.4, 2.5 Hz, 1H), 2.77~2.71 (dd, J = 17.8, 8.5 Hz, 1H), 2.48~2.43 (dd, J = 16.9, 8.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 177.68, 140.59, 132.93, 129.03, 128.15, 49.49, 39.66, 37.90 ppm; HRMS (ESI^+) for $\text{C}_{10}\text{H}_9\text{ClNO}$ $[\text{M}+\text{H}]^+$ Calcd: 196.0445, Found: 196.1160.; HPLC [Chiralcel AD-H, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention times: (minor) 14.7 min, (major) 18.7 min];

(S)-4-Amino-3-phenylbutanoic acid (5a)⁹



$[\alpha]_D^{25}$ +5.34 (*c* 0.5, H_2O);

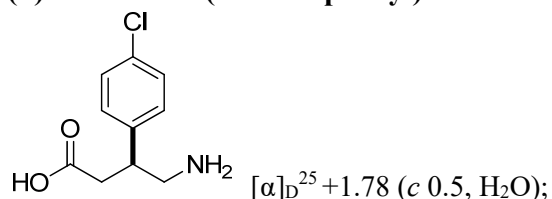
(R)-4-amino-3-phenylbutanoic acid (5c)



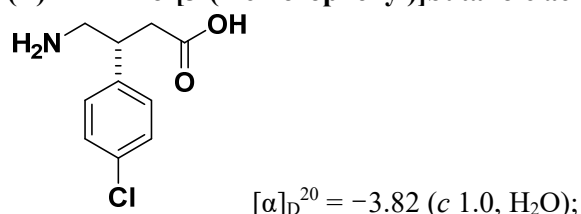
$[\alpha]_D^{25}$ = -5.51 (*c* 1.0, H_2O);

^1H NMR (500 MHz, D_2O) δ 7.47~7.44 (m, 2H), 7.41~7.36 (m, 3H), 3.47~3.36 (m, 2H), 3.27 (t, J = 11.0 Hz, 1H), 2.89~2.85 (dd, J = 16.0, 5.9 Hz, 1H), 2.81~2.76 (dd, J = 16.0, 8.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, D_2O) δ 175.62, 138.37, 129.37, 128.30, 127.87, 43.81, 40.0, 38.34 ppm; LRMS (ESI^+) for $\text{C}_{10}\text{H}_{13}\text{NO}_2$ $[\text{M}+\text{H}]^+$ Calcd: 180.1, Found: 180.2; R_f (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{MeOH}$ = 10/1) = 0.48

(S)-4-Amino-3-(4-chlorophenyl)butanoic acid (5b)⁹

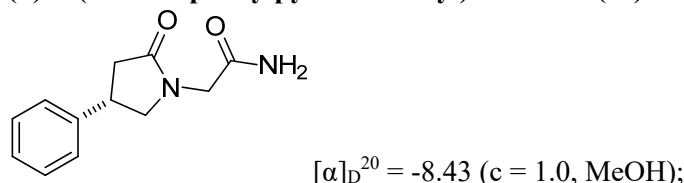


(R)-4-Amino-[3-(4-chlorophenyl)]butanoic acid (5d)

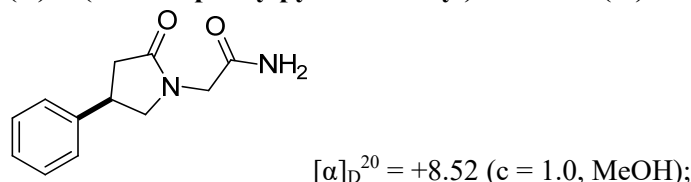


¹H NMR (500 MHz, D₂O) δ 7.40~7.37 (m, 2H), 7.29~7.26 (m, 2H), 3.39~3.30 (m, 2H), 3.22~3.16 (m, 1H), 2.81~2.76 (dd, *J* = 16.1, 5.9 Hz, 1H), 2.70~2.65 (dd, *J* = 16.1, 8.9 Hz, 1H) ppm; ¹³C NMR (125 MHz, D₂O) δ 175.46, 137.02, 133.38, 129.41, 129.25, 43.60, 39.47, 38.33 ppm; HRMS (FAB⁺) for C₁₀H₁₂ClNO₂ [M+H]⁺ Calcd: 214.0635, Found: 214.0627;

(S)-2-(2-oxo-4-phenylpyrrolidin-1-yl)acetamide(5e)



(R)-2-(2-oxo-4-phenylpyrrolidin-1-yl)acetamide(5f)



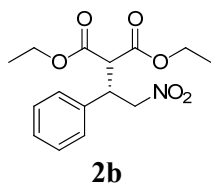
¹H NMR spectrum (CDCl₃), δ , ppm: 2.59 d.d (1H, 3-H, 3J_{HH} = 8.4, 2J_{HH} = 17.0 Hz), 2.81 d.d (1H, 3-H, 3J_{HH} = 8.4, 2J_{HH} = 17.0 Hz), 3.53 m (1H, 5-H), 3.63 m (1H, 4-H), 3.85 m (1H, 5-H), 3.97 d.d (2H, NCH₂CO, 3J_{HH} = 16.3, 2J_{HH} = 33.0 Hz); 6.24 br.s and 6.66 br.s (1H each, NH₂), 7.22~7.31 m (5H, Ph). ¹³C NMR spectrum (CDCl₃), δ C, ppm: 37.48, 38.54, 46.25, 55.55, 126.89, 127.27, 129.01, 141.97, 170.78, 175.03 pp; HRMS (ESI⁺) for C₁₀H₁₃NO₂ [M+Na]⁺ Calcd: 241.0957, Found: 241.0947;

References

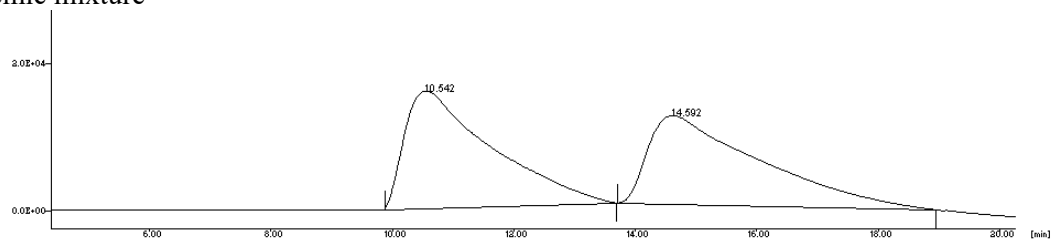
1. D. Almaşı, D. Alonso, E. Gómez-Bengoa, C. Nájera, *J. Org. Chem.* 2009, **74**, 6163;
2. Manzano, R.; Andrés, J. M.; Muruzábal, M.; Pedrosa, R. *Adv. Synth. Cat.* 2010, **352**, 3364;
3. Okino, Y. Hoashi, T. Furukawa, X. Xu, Y. Takemoto *J. Am. Chem. Soc.* 2005, **127**, 119;
4. X. Jiang, Y. Zhang, X. Liu, G. Zhang, L. Lai, L. Wu, J. Zhang, R. Wang, *J. Org. Chem.* 2009, **74**, 5562;
5. K. Murai, S. Fukushima, S. Hayashi, Y. Takahara, H. Fujioka, *Org. Lett.* 2010, **12**, 964;
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9. M. Tsakos, C. G. Kokotos, and G. Kokotos, *Adv. Synth. Catal.* **2012**, **354**, 740-746
10. J. Wang, W. Li, Y. Liu, Y. Chu, L. Lin, X. Liu, X. Feng, *Org. Lett.* **2010**, **12**, 1280-1283

11. T. Okino, Y. Hoashi, T. Furukawa, X. Xu, Y. Takemoto, *J. Am. Chem. Soc.* **2005**, *127*, 119-125.
12. Q. Lang, G. Gu, Y. Cheng, Q. Yin, X. Zhang, *ACS Catal.* **2018**, *8*, 4824–4828

Copy of HPLC Chromatograms

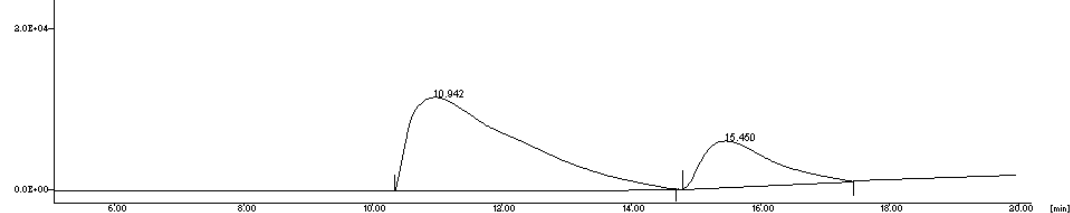


Racemic mixture



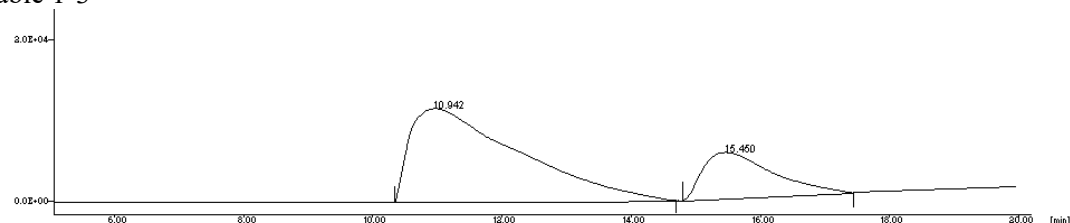
#	Name	RT	Area[uV.Sec]	Quantity
1		10.542	1553861.500	0.000
2		14.592	1514396.259	0.000
Total Area of Peak = 3068257.759 [uV.Sec]				

asymmetric



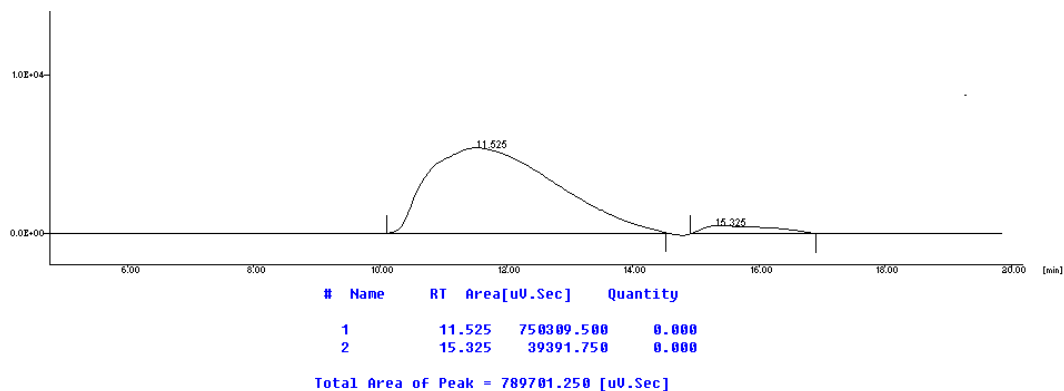
#	Name	RT	Area[uV.Sec]	Quantity
1		10.942	1398174.488	0.000
2		15.450	429596.250	0.000
Total Area of Peak = 1827770.738 [uV.Sec]				

SI Table 1-3

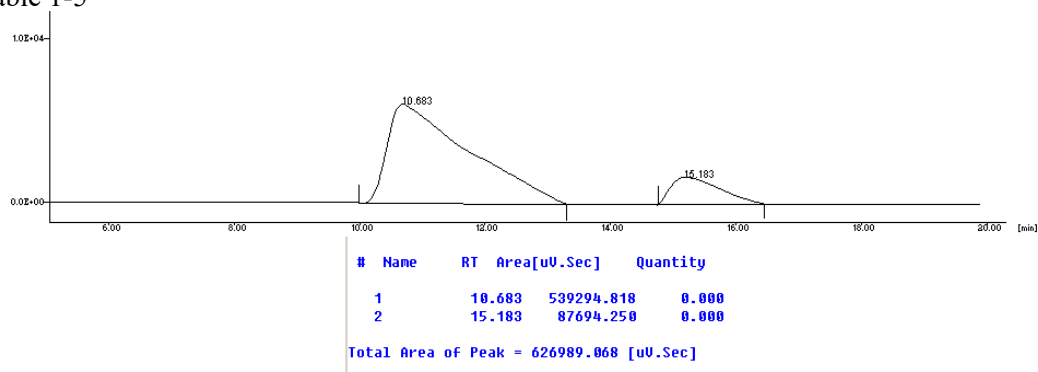


#	Name	RT	Area[uV.Sec]	Quantity
1		10.942	1398174.488	0.000
2		15.450	429596.250	0.000
Total Area of Peak = 1827770.738 [uV.Sec]				

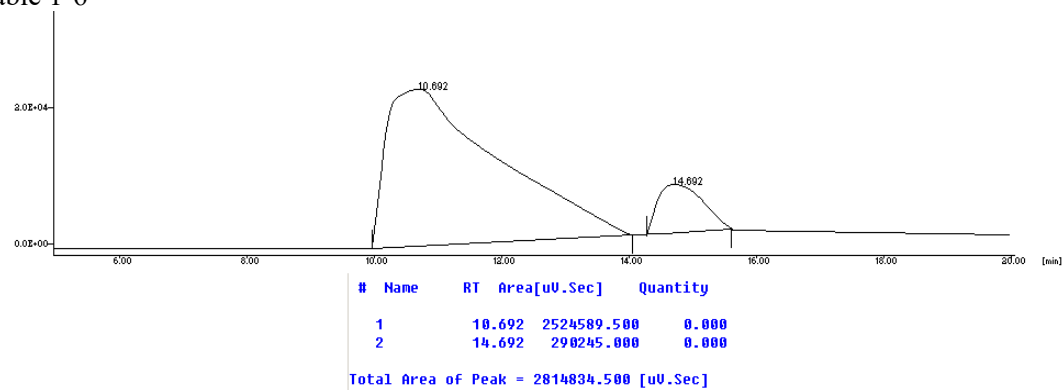
SI Table 1-4



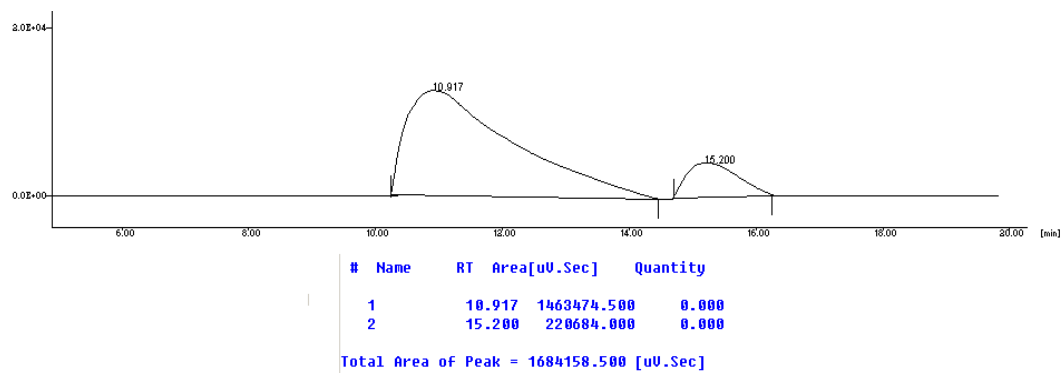
SI Table 1-5



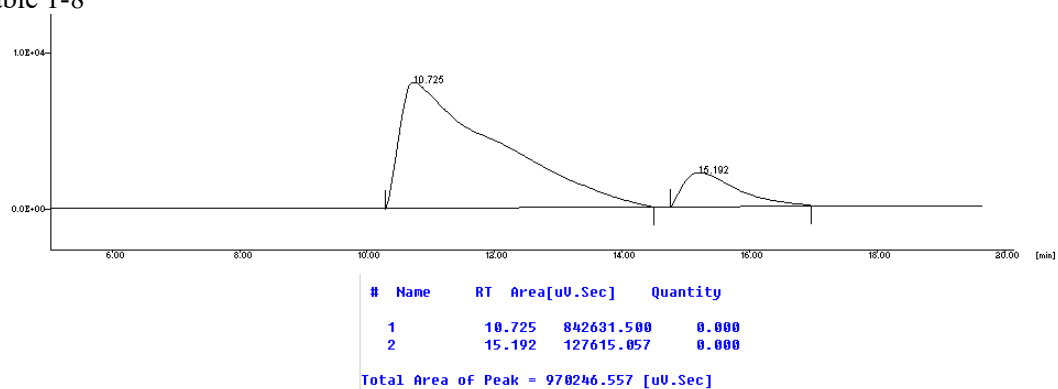
SI Table 1-6



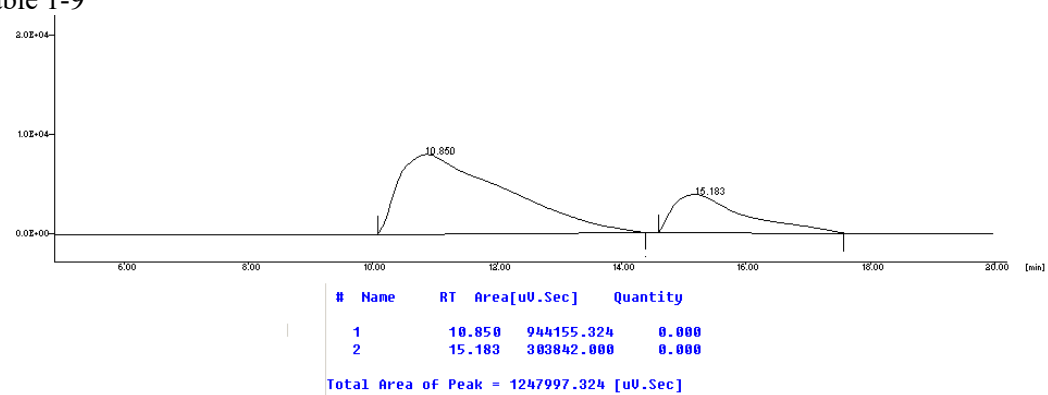
SI Table 1-7



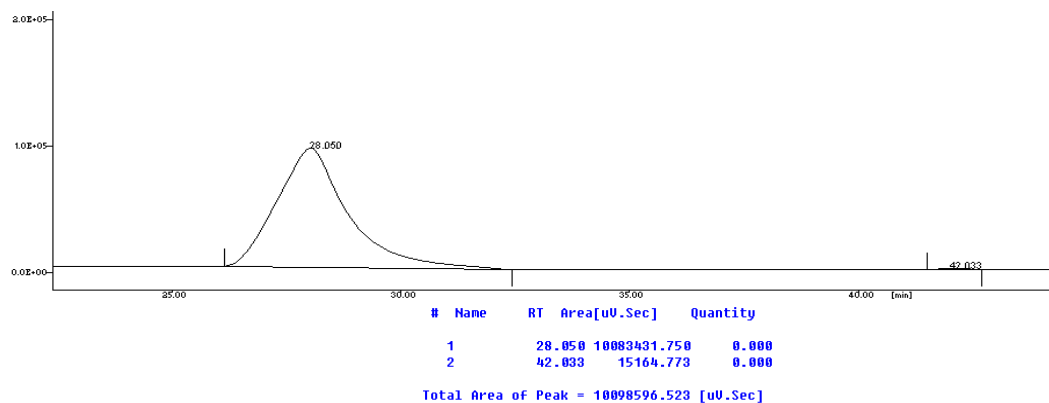
SI Table 1-8



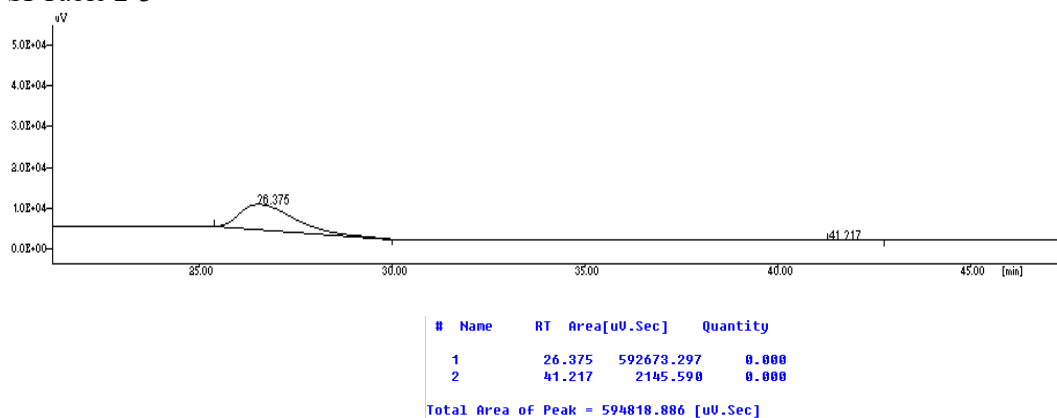
SI Table 1-9



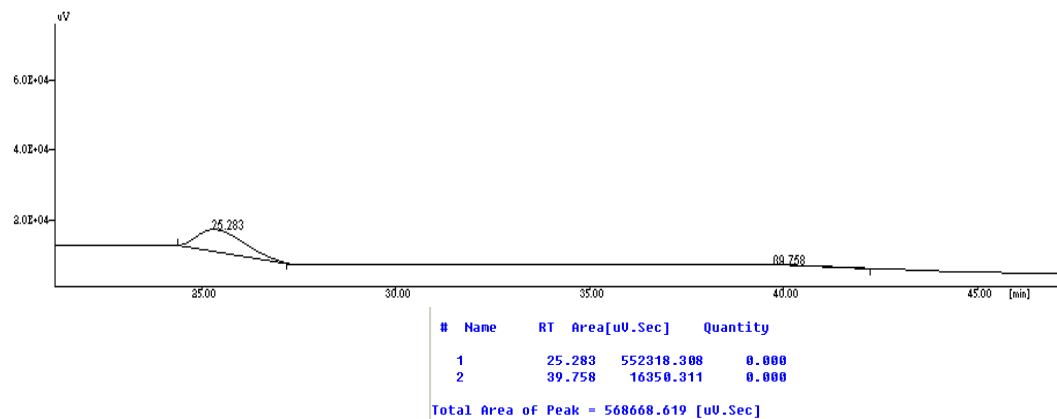
SI Table 2-1



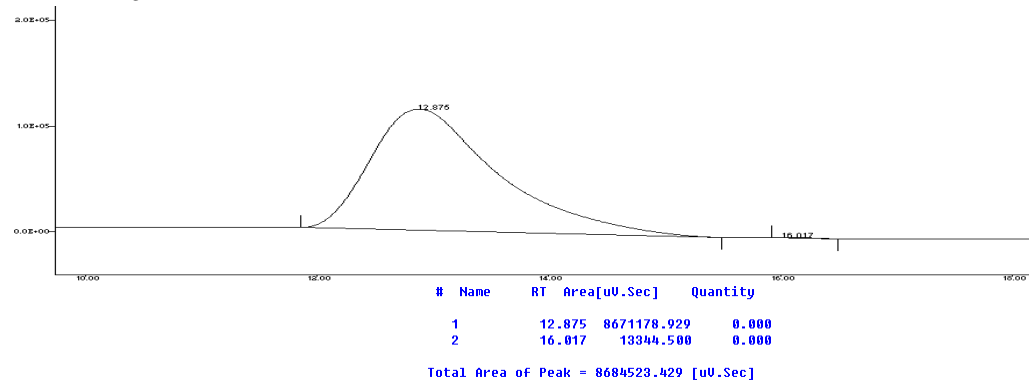
SI Table 2-3



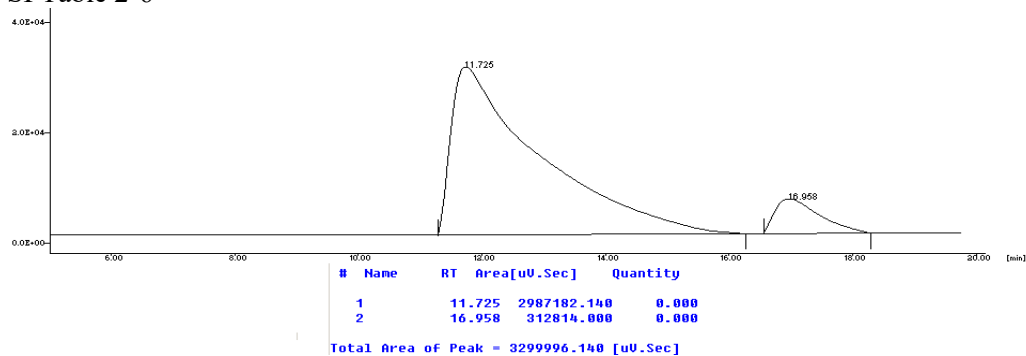
SI Table 2-4



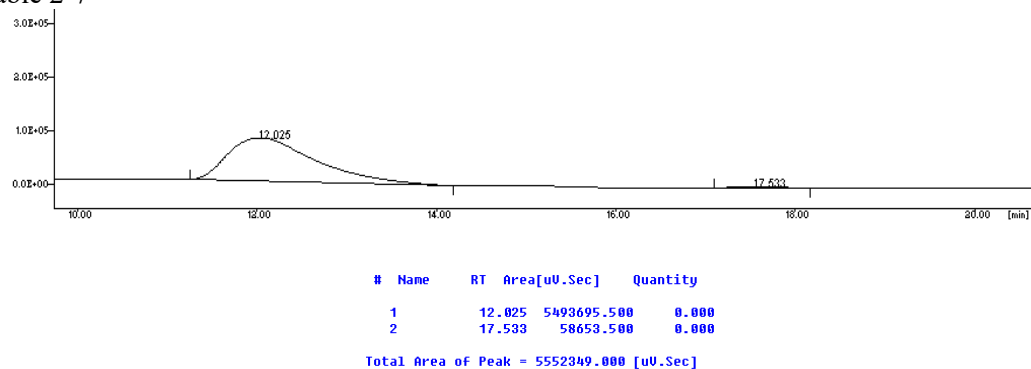
SI Table 2-5



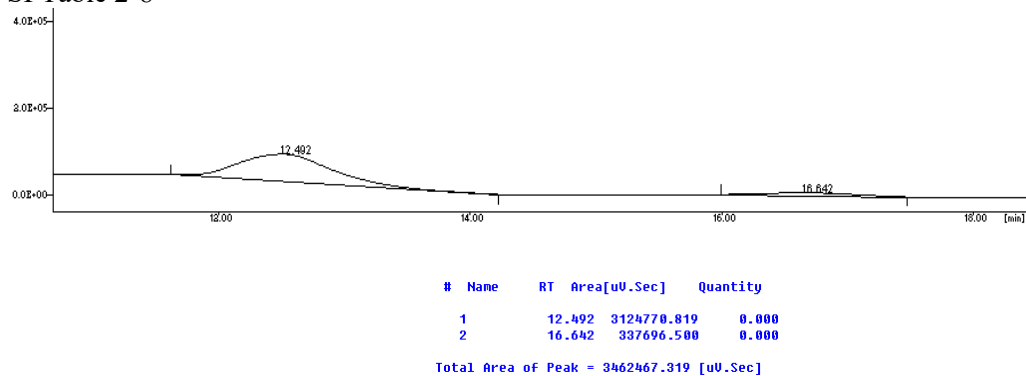
SI Table 2-6



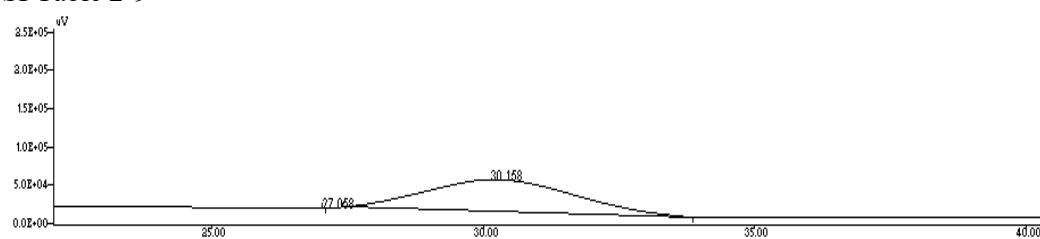
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SI Table 2-8



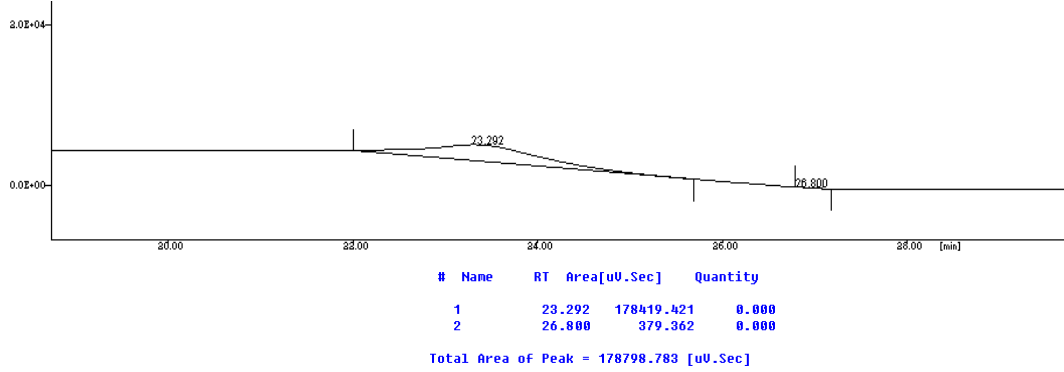
SI Table 2-9



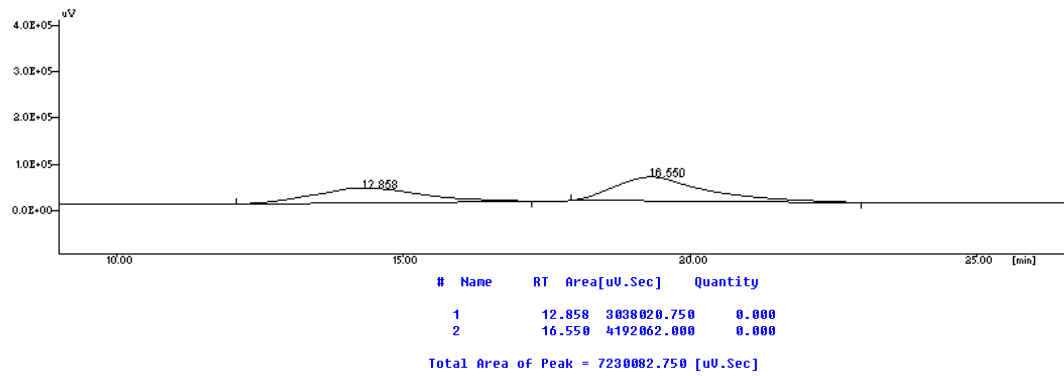
#	Name	RT	Area[uV.Sec]	Quantity
1		27.058	41.000	0.000
2		30.158	7905472.750	0.000

Total Area of Peak = 7905513.750 [uV.Sec]

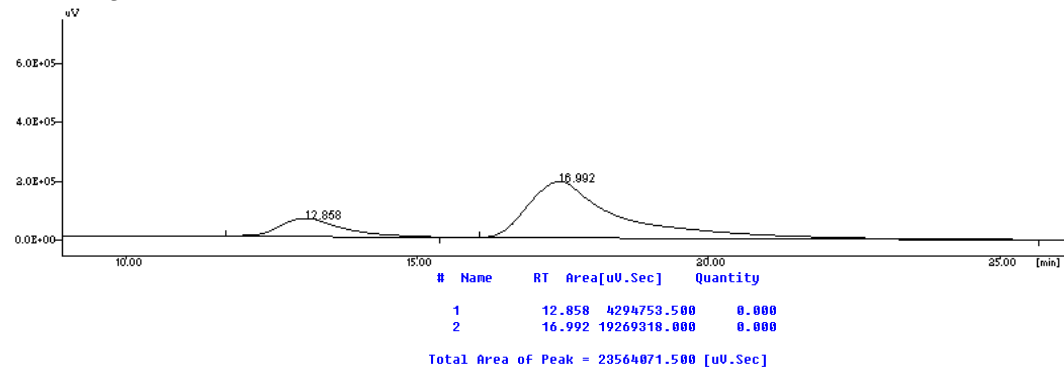
SI Table 2-10



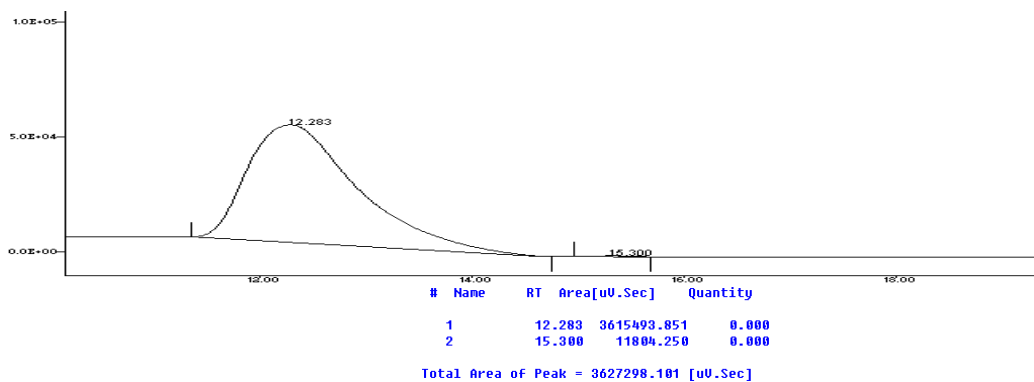
SI Table 3-1



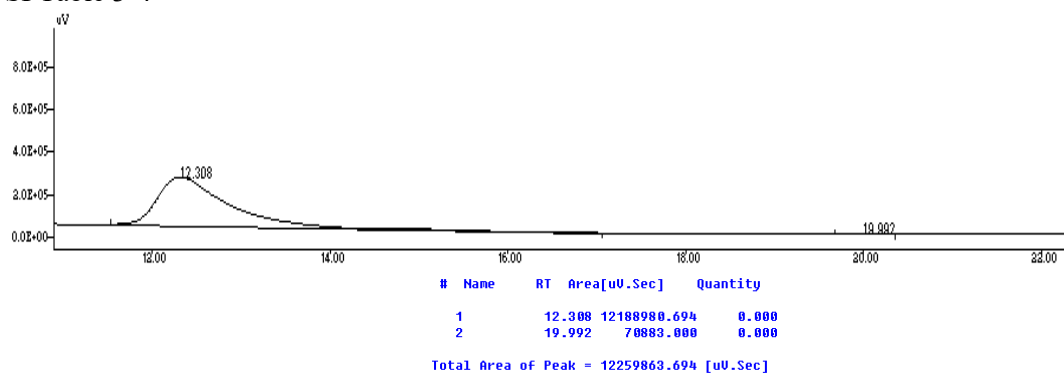
SI Table 3-2



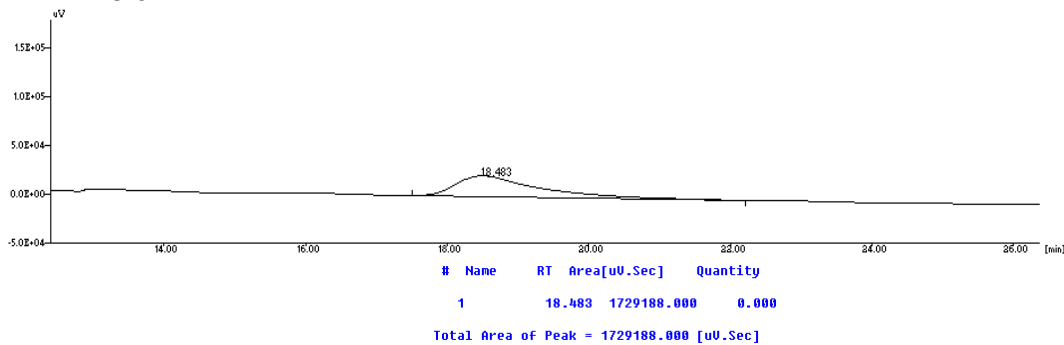
SI Table 3-3



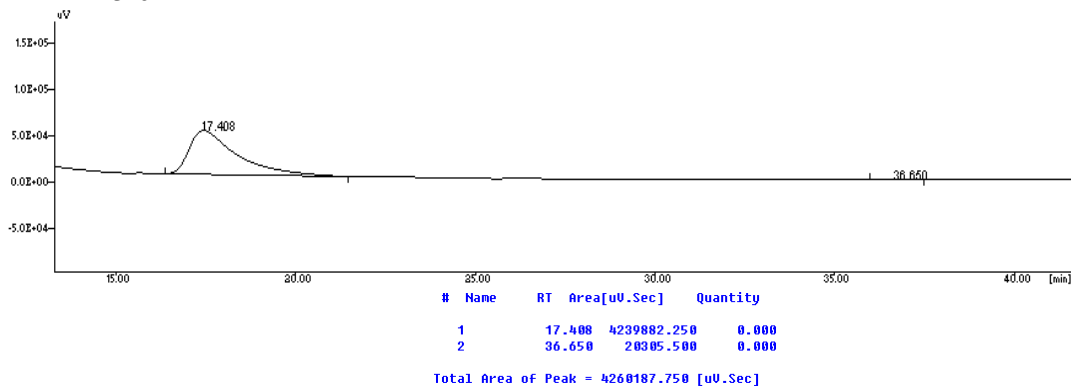
SI Table 3-4



SI Table 3-5

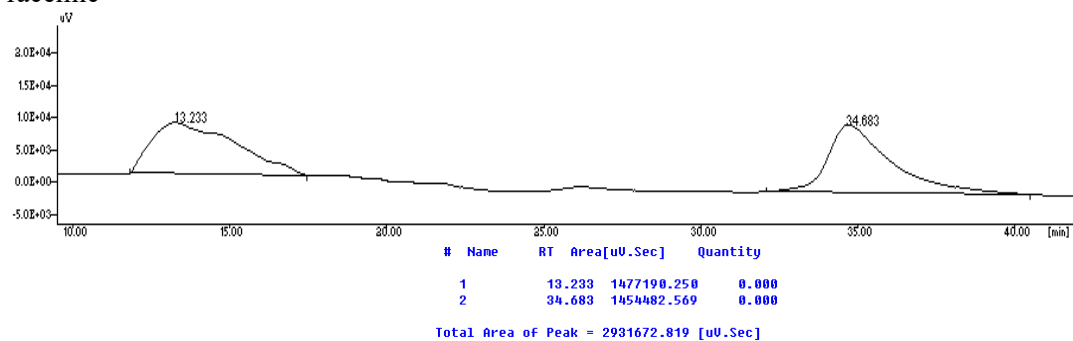


SI Table 3-6

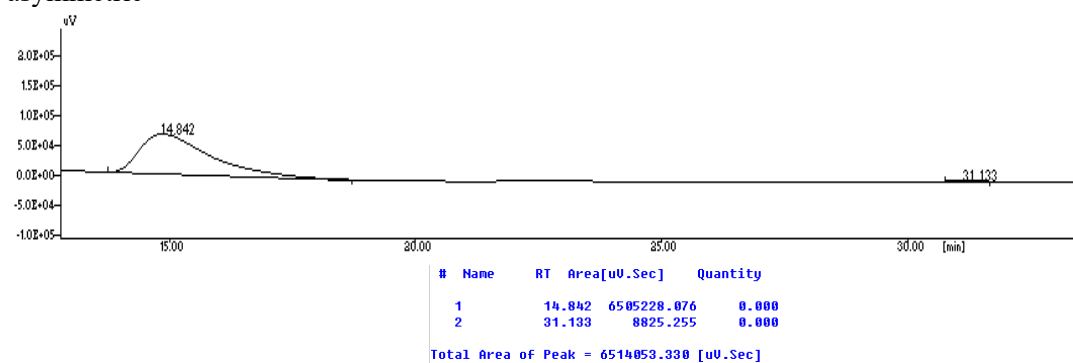


SI Table 3-7

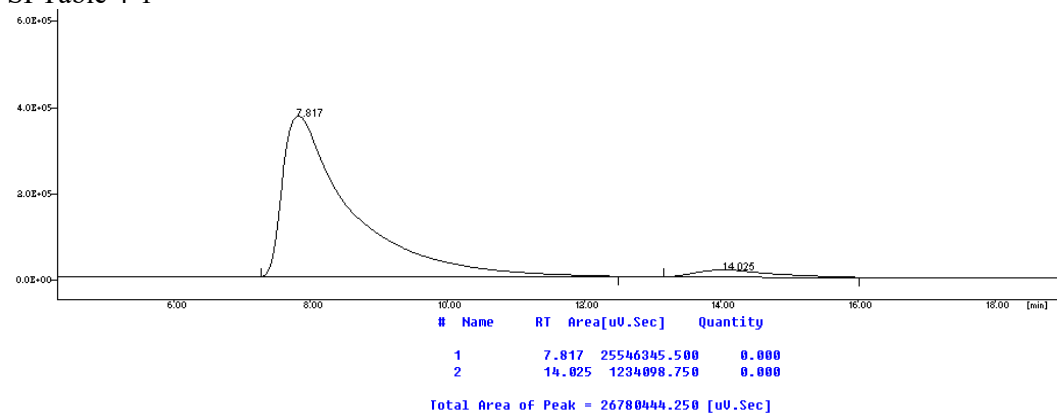
racemic



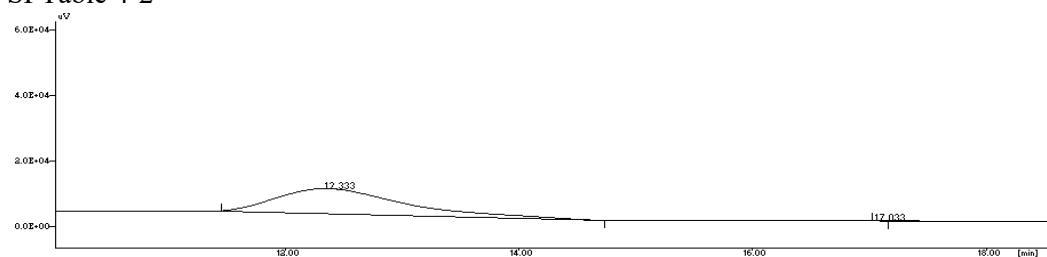
asymmetric



SI Table 4-1



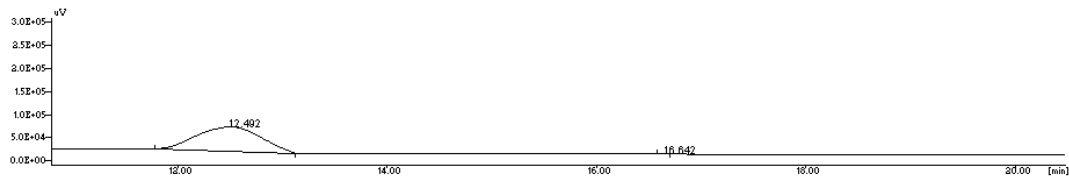
SI Table 4-2



#	Name	RT	Area[uV.Sec]	Quantity
1		12.333	580025.591	0.000
2		17.033	83.625	0.000

Total Area of Peak = 580109.216 [uV.Sec]

SI Table 4-3



#	Name	RT	Area[uV.Sec]	Quantity
1		12.492	2247941.750	0.000
2		16.642	390.750	0.000

Total Area of Peak = 2248332.500 [uV.Sec]

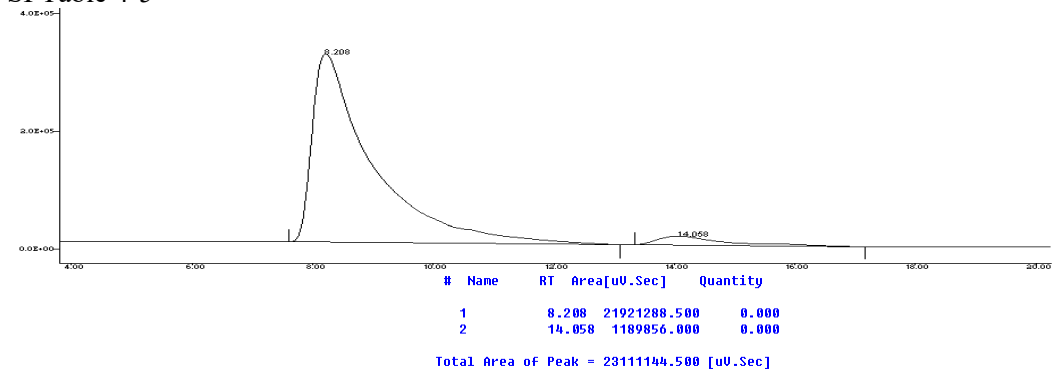
SI Table 4-4



#	Name	RT	Area[uV.Sec]	Quantity
1		12.492	2247941.750	0.000
2		16.642	390.750	0.000

Total Area of Peak = 2248332.500 [uV.Sec]

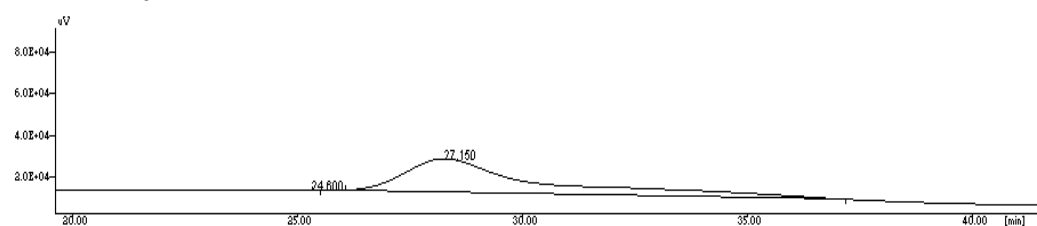
SI Table 4-5



#	Name	RT	Area[uV.Sec]	Quantity
1		8.208	21921288.500	0.000
2		14.058	1189856.000	0.000

Total Area of Peak = 23111144.500 [uV.Sec]

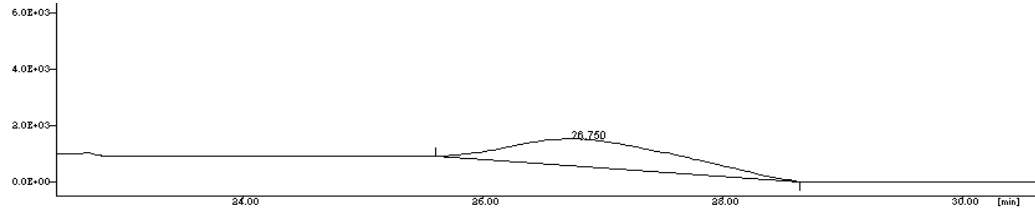
SI Table 4-6



#	Name	RT	Area[uV.Sec]	Quantity
1		24.600	31.500	0.000
2		27.150	2867886.500	0.000

Total Area of Peak = 2867918.000 [uV.Sec]

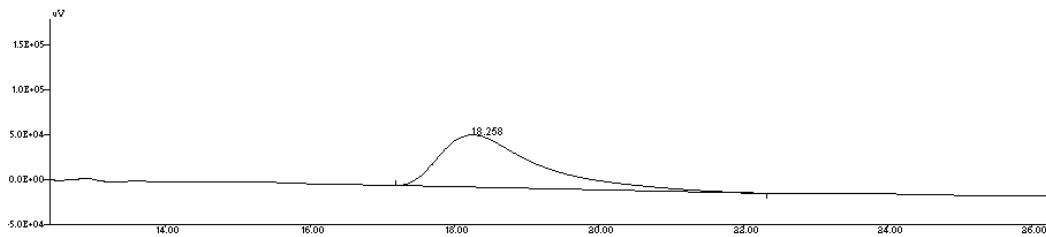
SI Table 4-7



#	Name	RT	Area[uV.Sec]	Quantity
1		26.750	94661.455	0.000

Total Area of Peak = 94661.455 [uV.Sec]

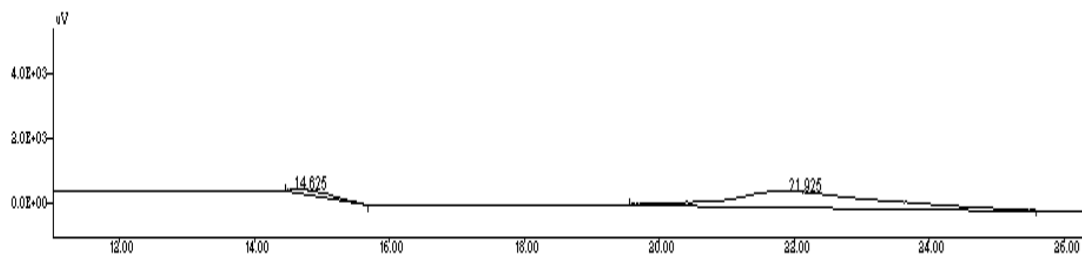
SI Table 4-8



#	Name	RT	Area[uV.Sec]	Quantity
1		18.258	5471407.250	0.000

Total Area of Peak = 5471407.250 [uV.Sec]

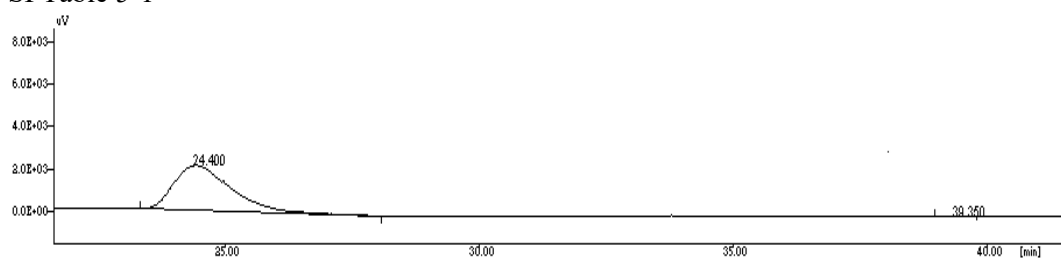
SI Table 4-9



#	Name	RT	Area[uV.Sec]	Quantity
1		14.625	5413.750	0.000
2		21.925	71422.801	0.000

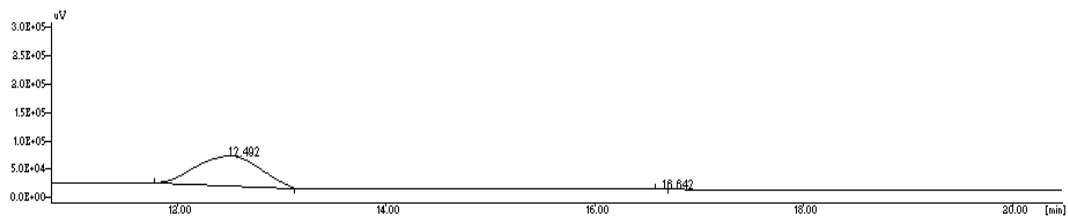
Total Area of Peak = 76836.551 [uV.Sec]

SI Table 5-1



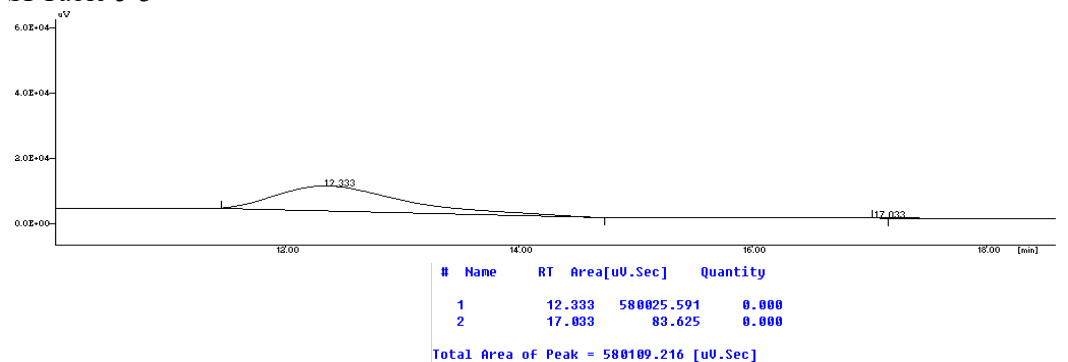
#	Name	RT	Area[uV.Sec]	Quantity
1		24.400	164065.859	0.000
2		39.350	753.500	0.000
Total Area of Peak = 164819.359 [uV.Sec]				

SI Table 5-2



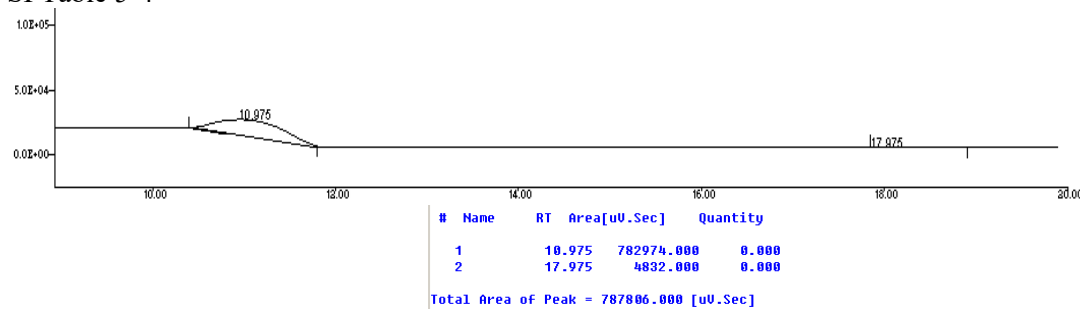
#	Name	RT	Area[uV.Sec]	Quantity
1		12.492	2247941.750	0.000
2		16.642	390.750	0.000
Total Area of Peak = 2248332.500 [uV.Sec]				

SI Table 5-3



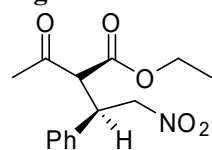
#	Name	RT	Area[uV.Sec]	Quantity
1		12.333	580025.591	0.000
2		17.033	83.625	0.000
Total Area of Peak = 580109.216 [uV.Sec]				

SI Table 5-4



#	Name	RT	Area[uV.Sec]	Quantity
1		10.975	782974.000	0.000
2		17.975	4832.000	0.000
Total Area of Peak = 787806.000 [uV.Sec]				

Fig. 2b-2m



Racemic

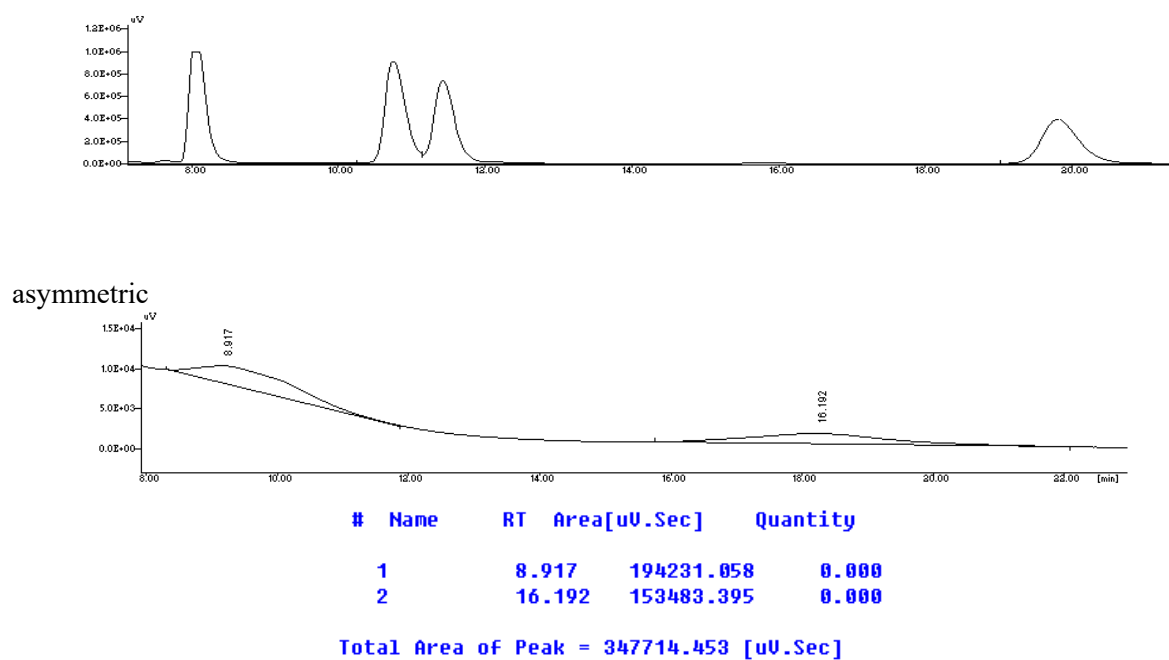
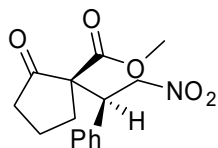
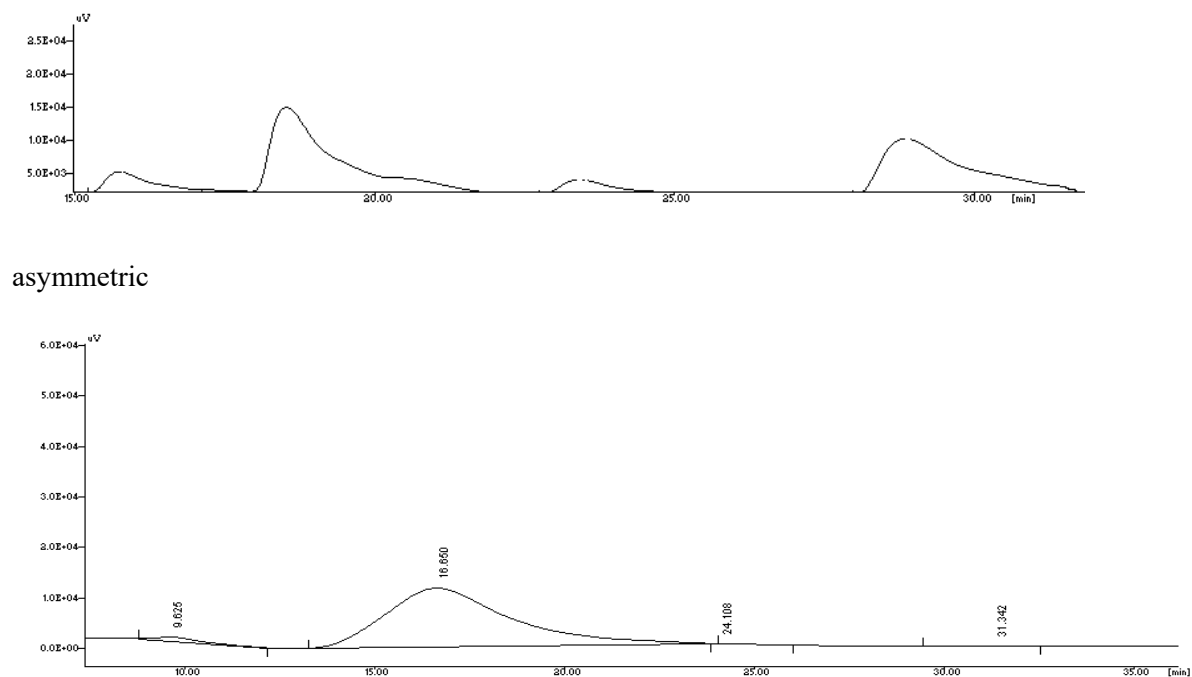


Fig. 2b-2o



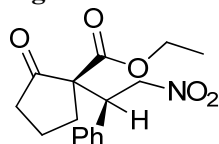
Racemic



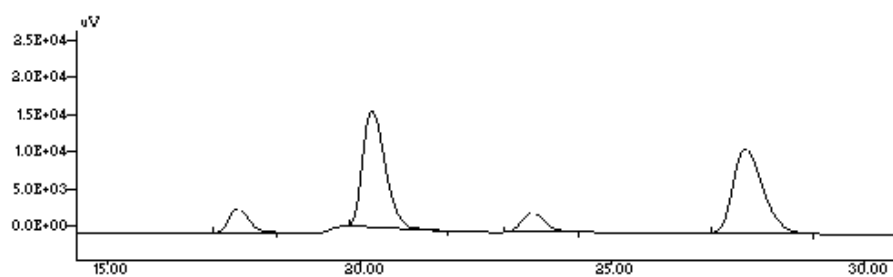
#	Name	RT	Area[uV.Sec]	Quantity
1		9.625	56432.025	0.000
2		16.650	2633157.636	0.000
3		24.108	1256.584	0.000
4		31.342	3908.821	0.000

Total Area of Peak = 2694755.065 [uV.Sec]

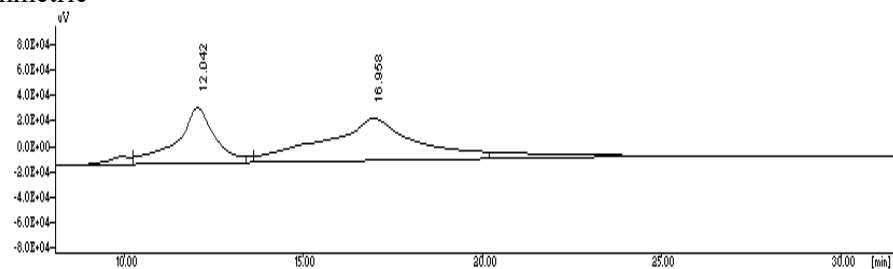
Fig. 2b-2n



Racemic



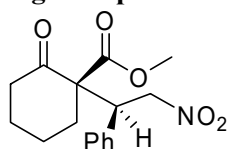
asymmetric



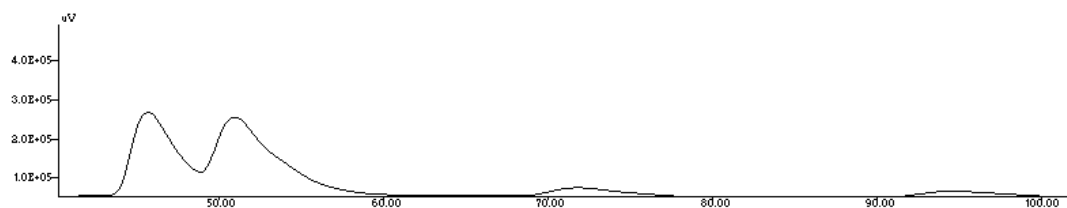
#	Name	RT	Area[uV.Sec]	Quantity
1		12.042	3208268.903	0.000
2		16.958	5774614.138	0.000

Total Area of Peak = 8982883.041 [uV.Sec]

Fig. 2b-2p



Racemic



asymmetric

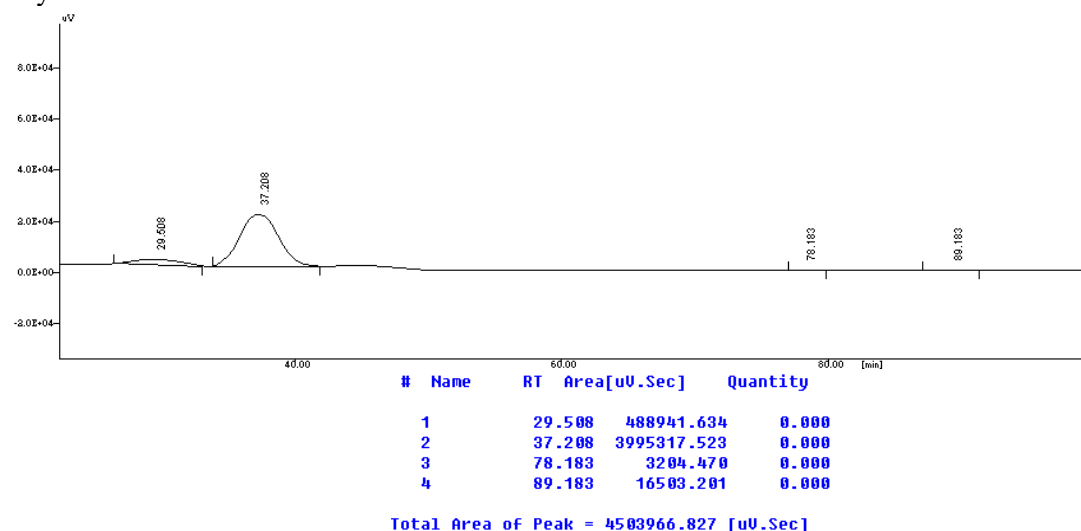
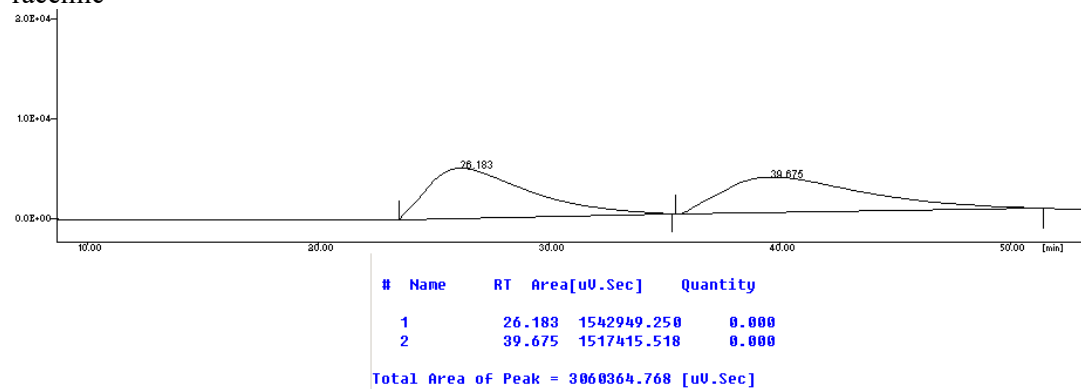


Fig. 2c-2a

racemic



asymmetric

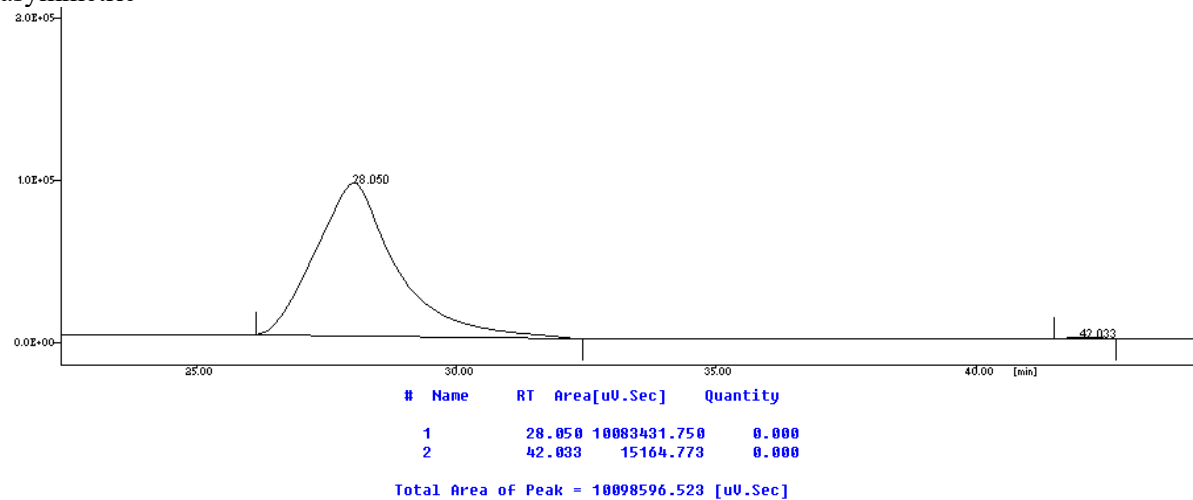
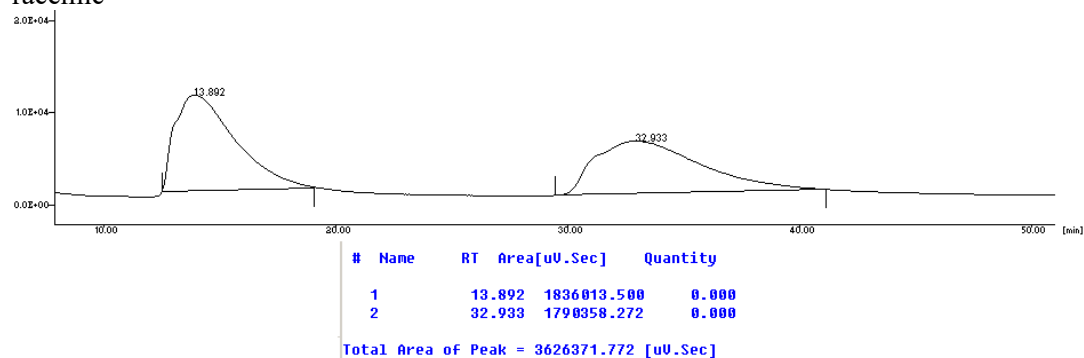


Fig. 2c-2c

racemic



asymmetric

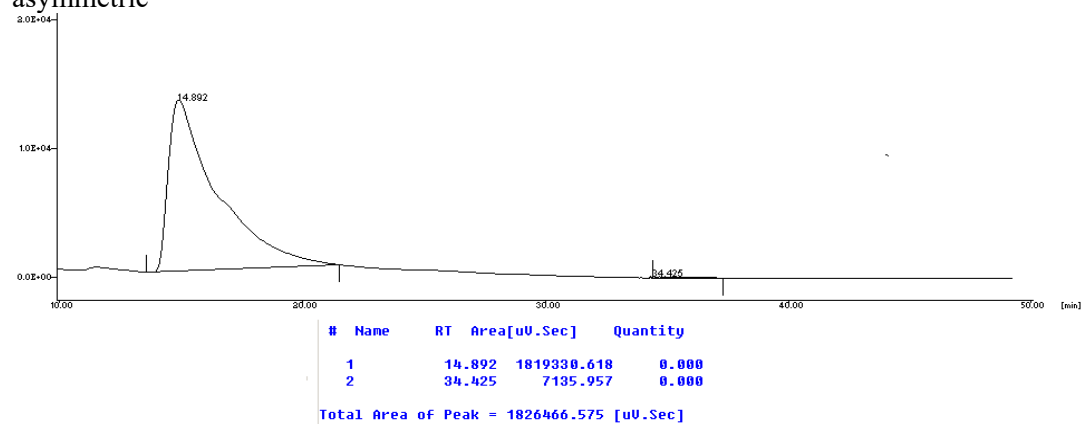
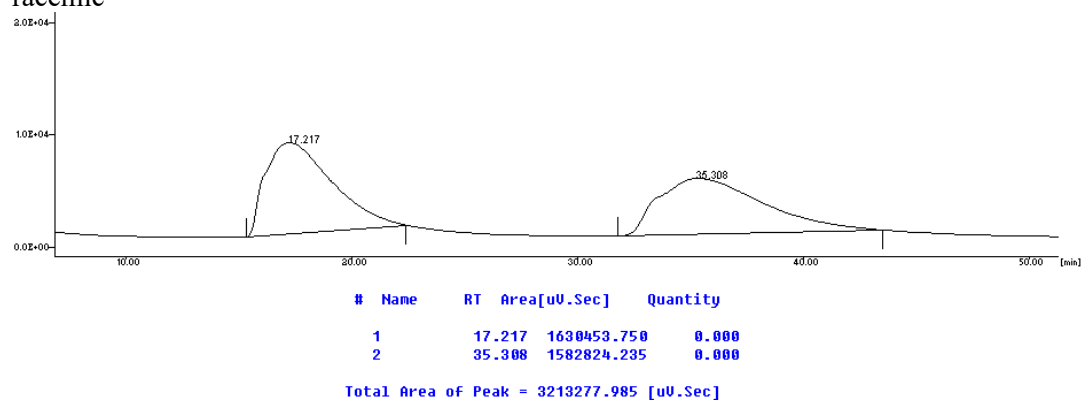


Fig. 2c-2d

racemic



asymmetric

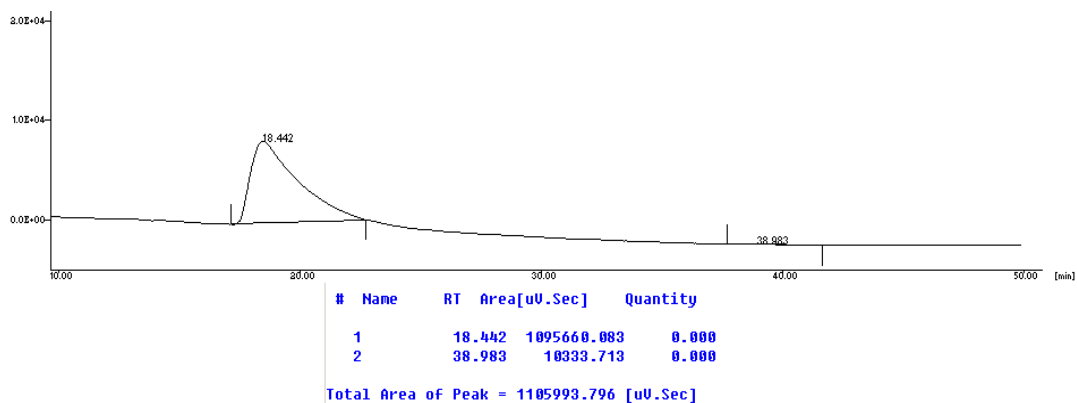
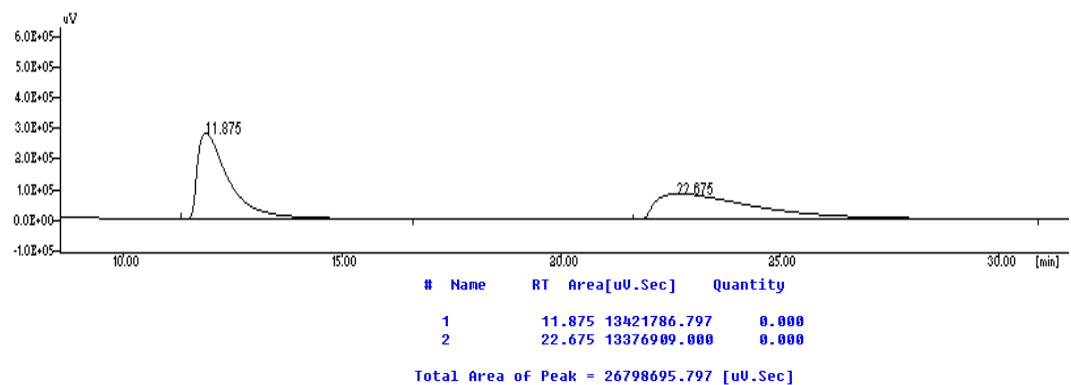


Fig. 2c-2f

racemic



asymmetric

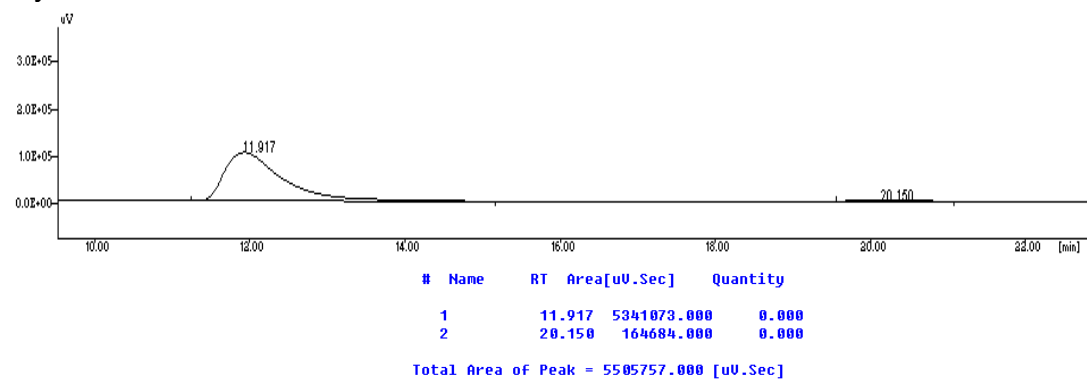
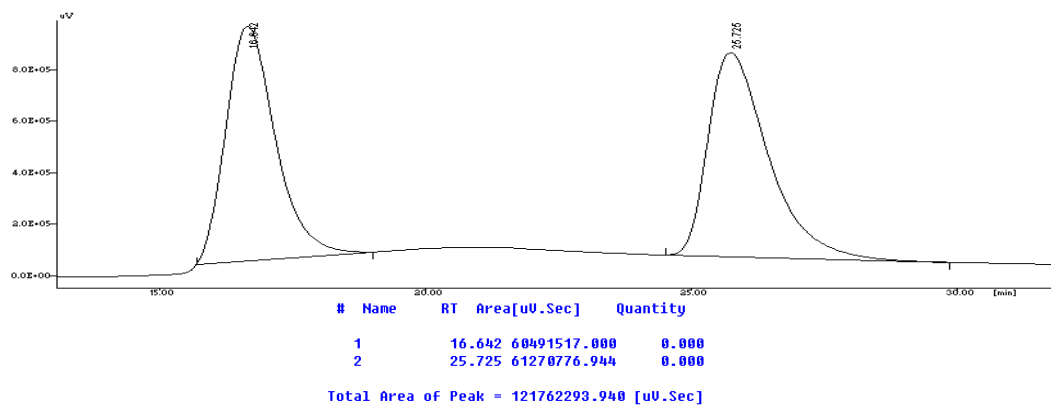


Fig. 2c-2g

racemic



asymmetric

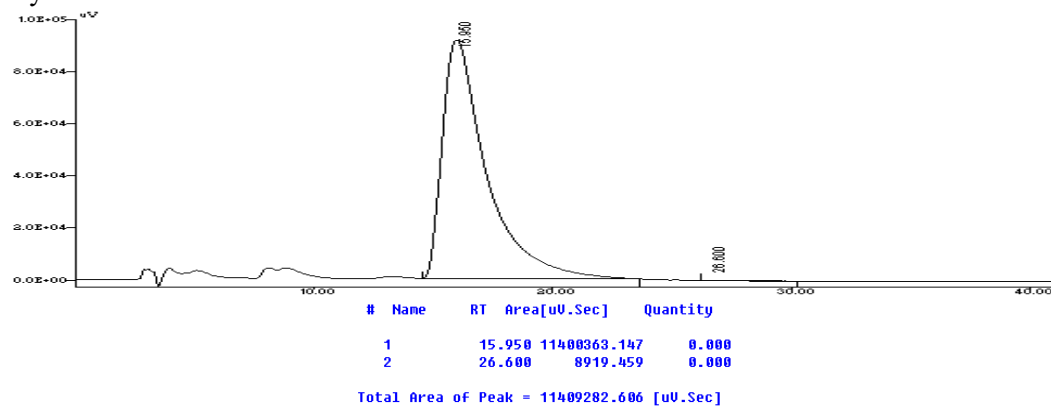
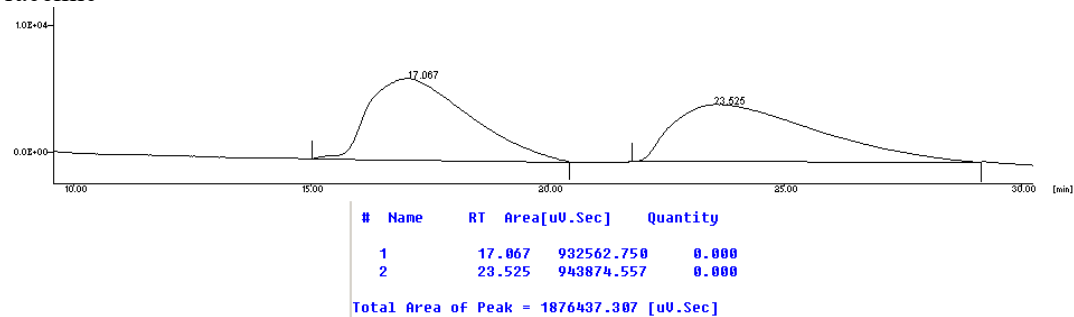
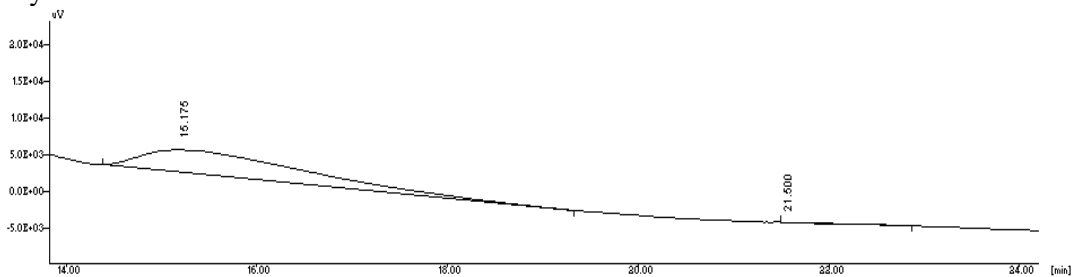


Fig. 2c-2h

racemic



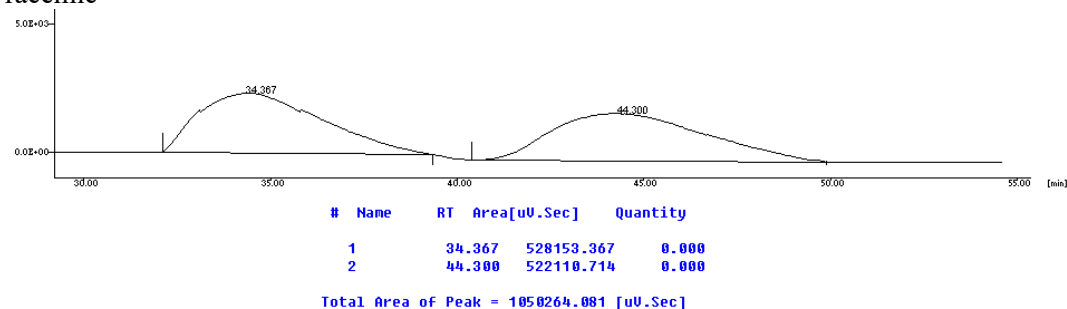
asymmetric



#	Name	RT	Area[uV.Sec]	Quantity
1		15.175	376171.659	0.000
2		21.500	1239.500	0.000
Total Area of Peak = 377411.159 [uV.Sec]				

Fig. 2c-2i

racemic



asymmetric

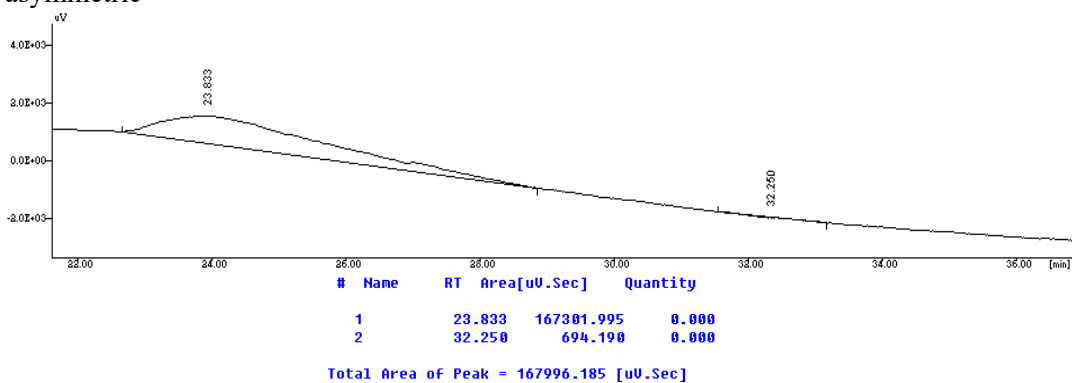
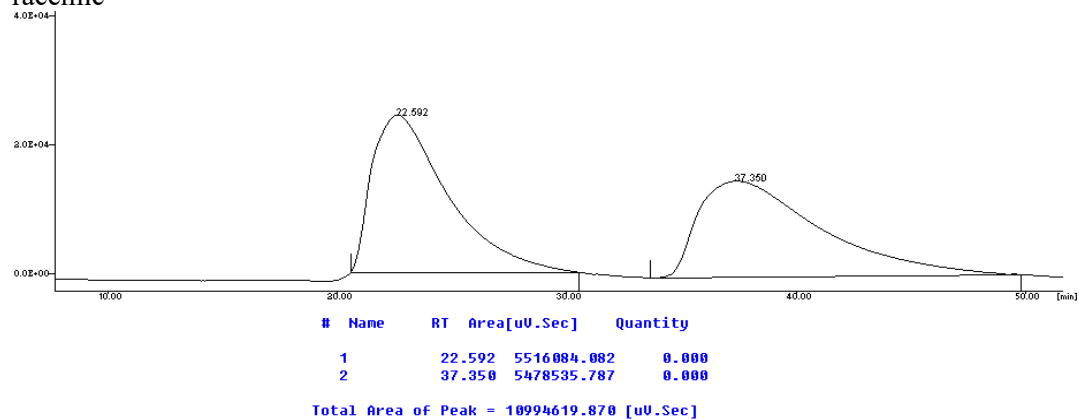


Fig. 2c-2k

racemic



asymmetric

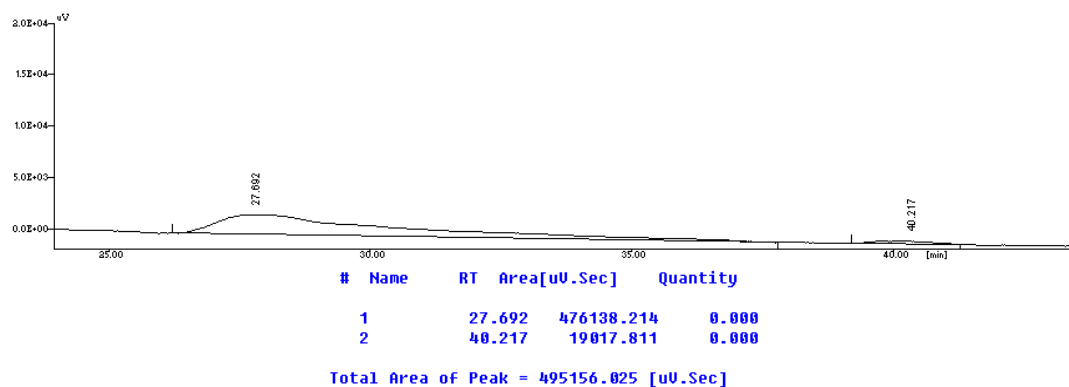
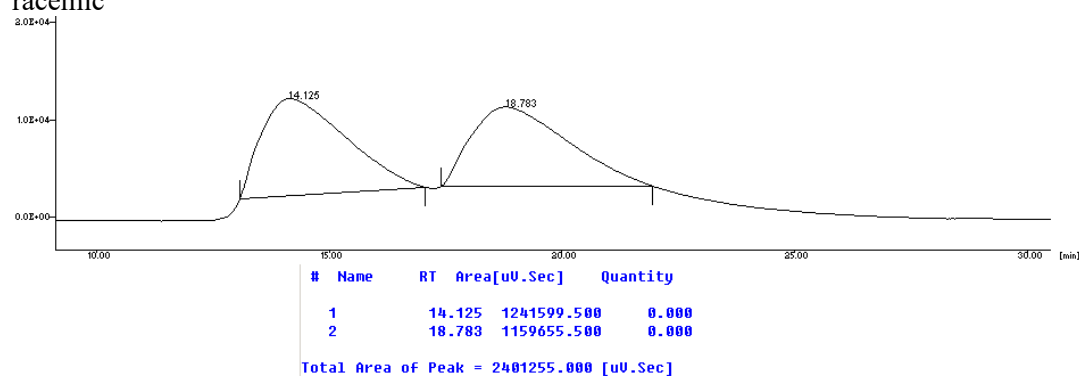


Fig. 2c-2i

racemic



asymmetric

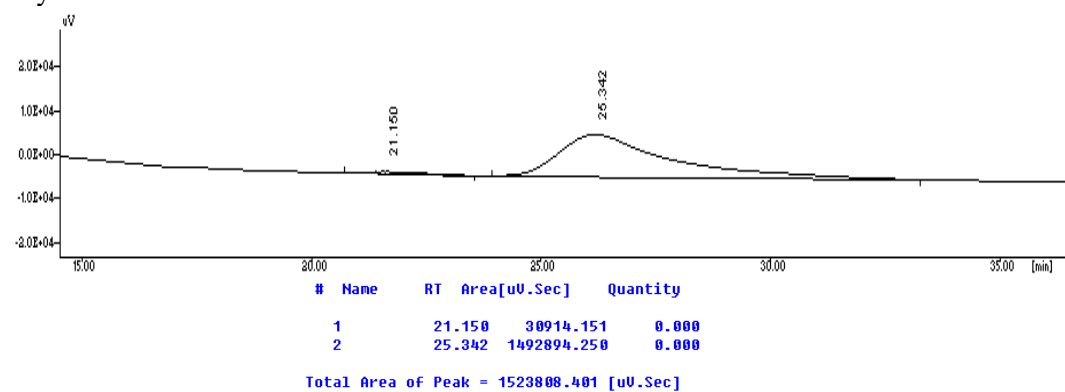
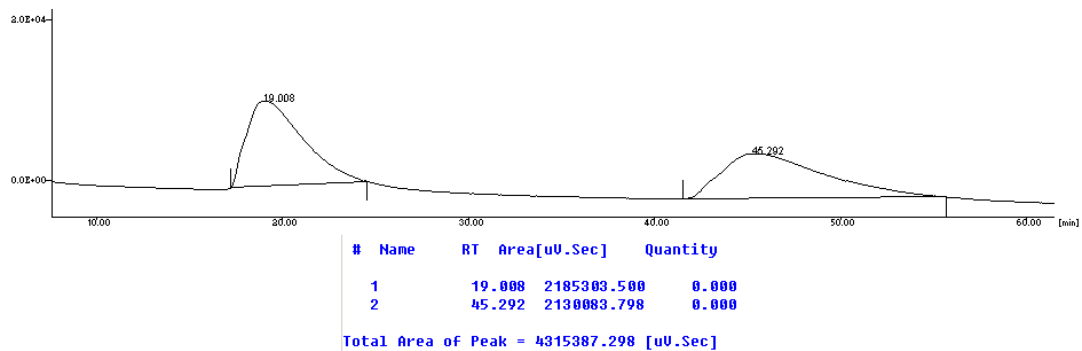
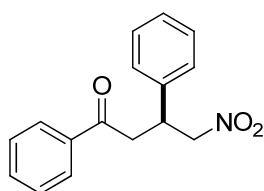
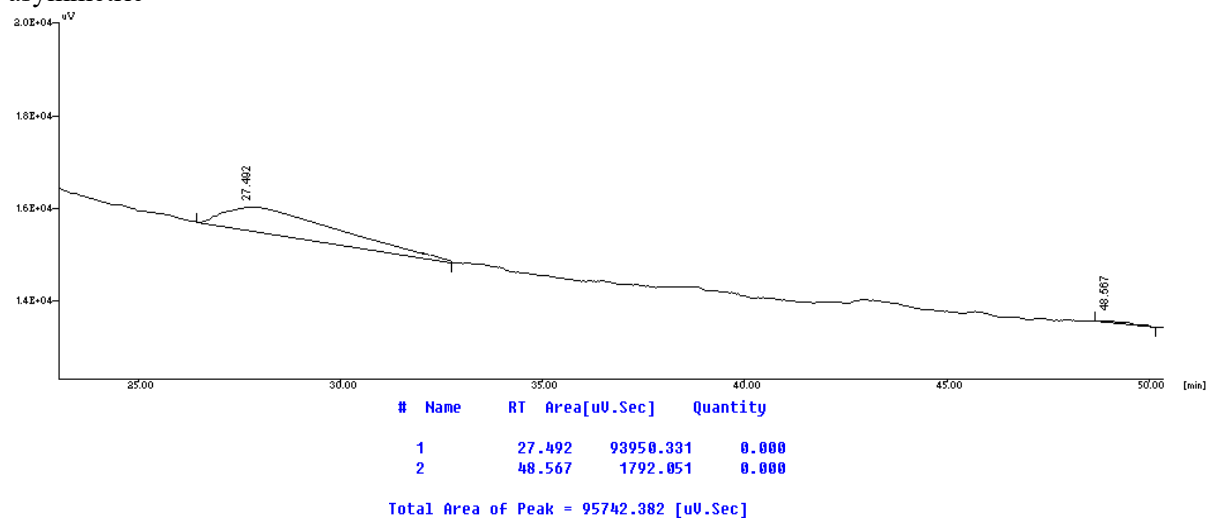


Fig. 2c-2j

racemic

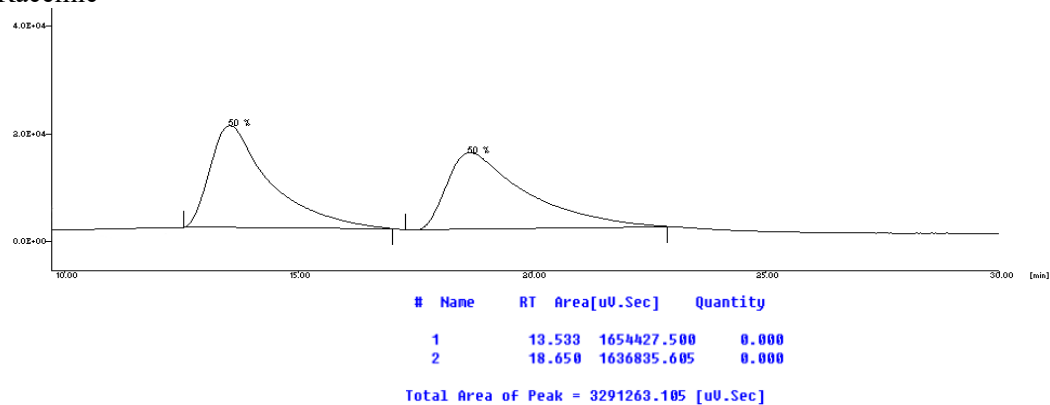


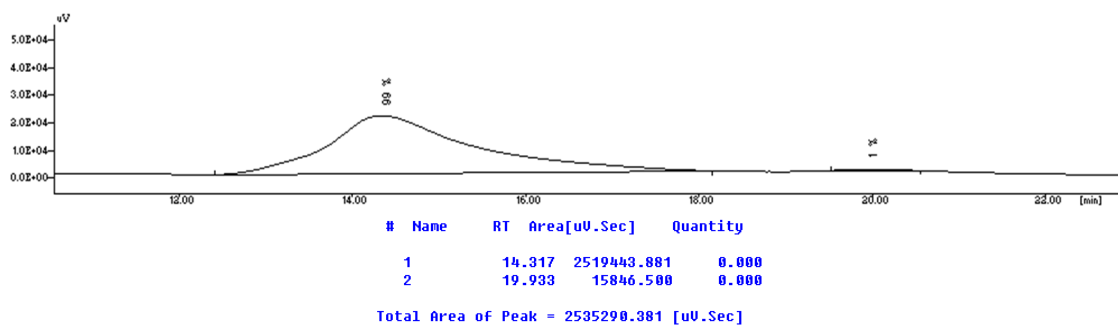
asymmetric



3a

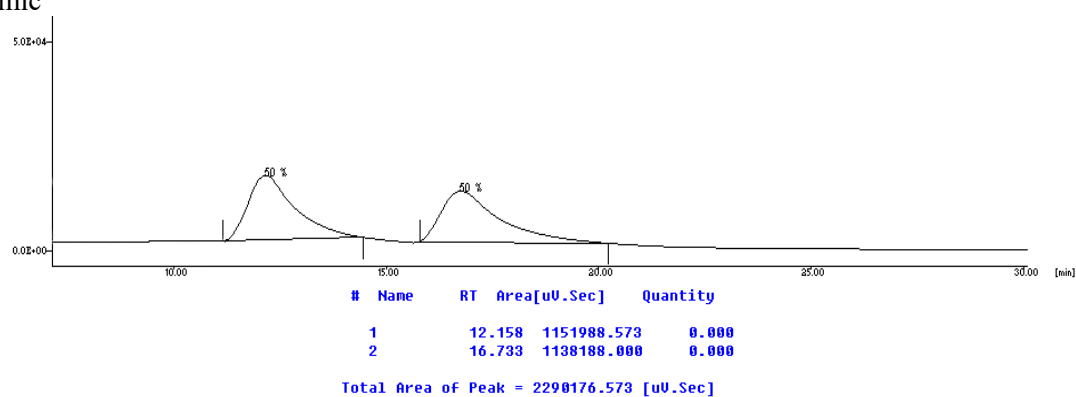
Racemic



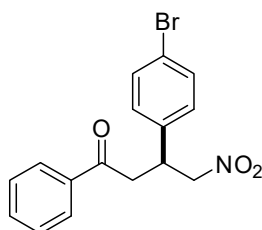
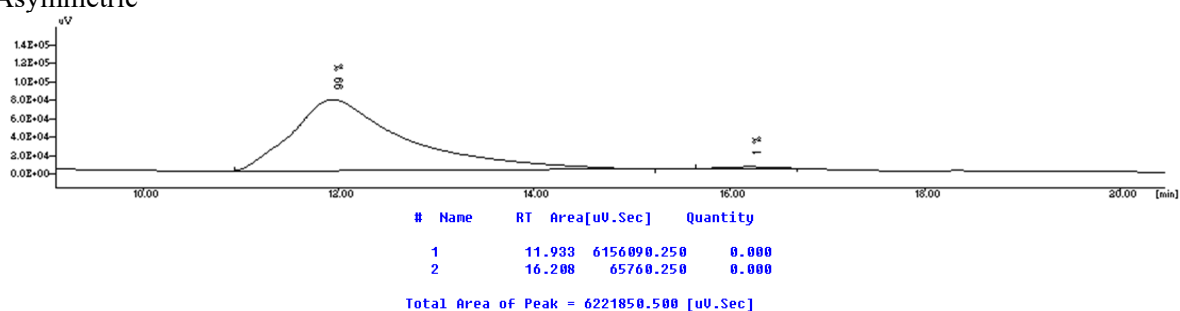


3b

Racemic

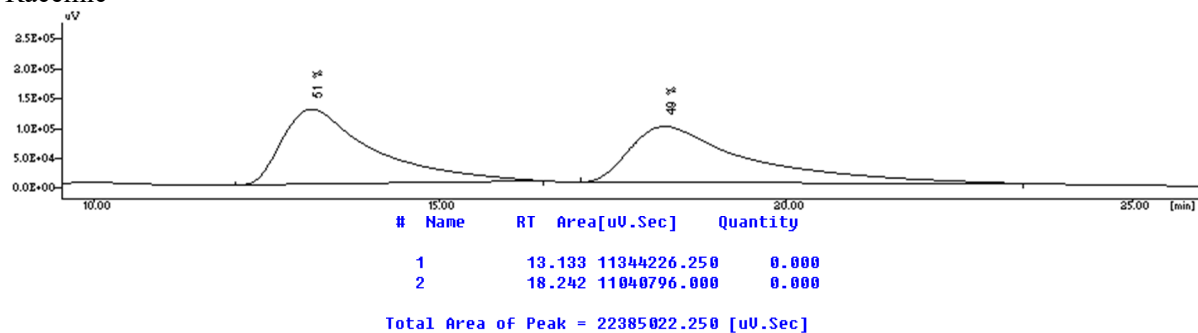


Asymmetric



3c

Racemic



Asymmetric

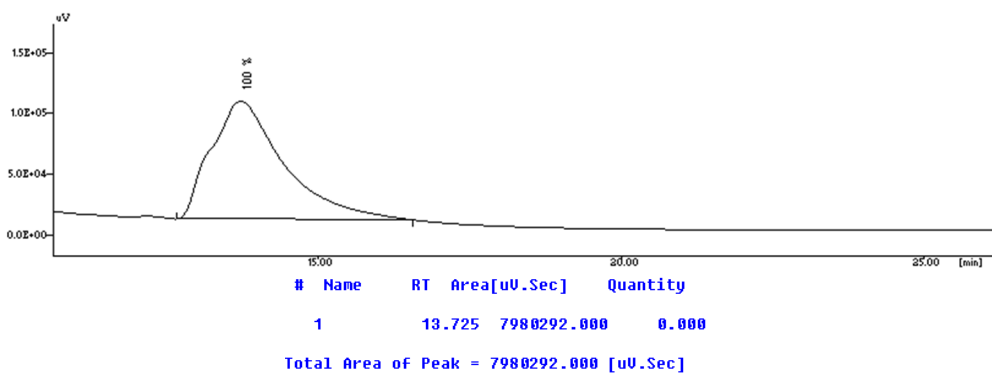
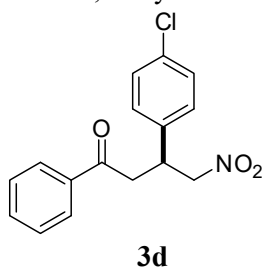
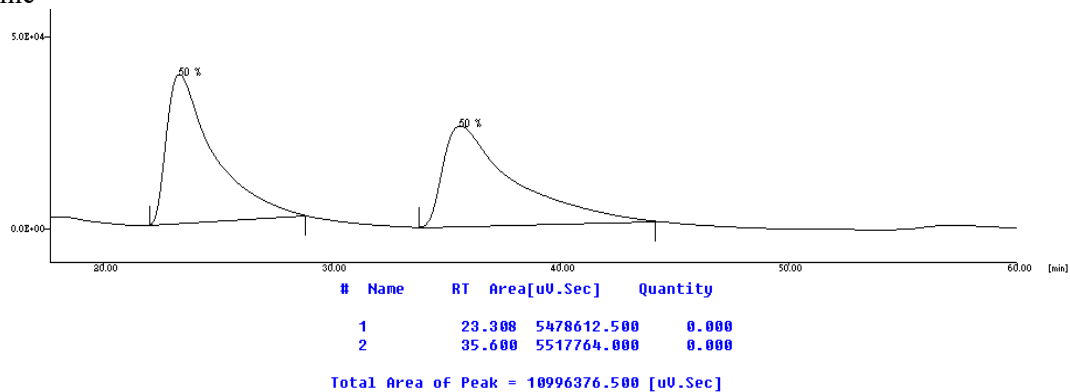


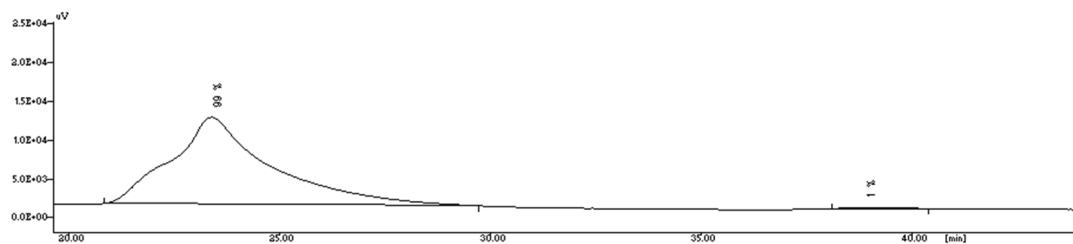
Table 7, entry 3



Racemic

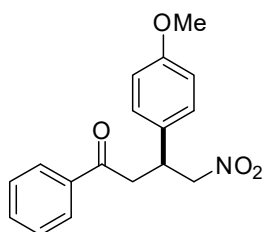


Asymmetric



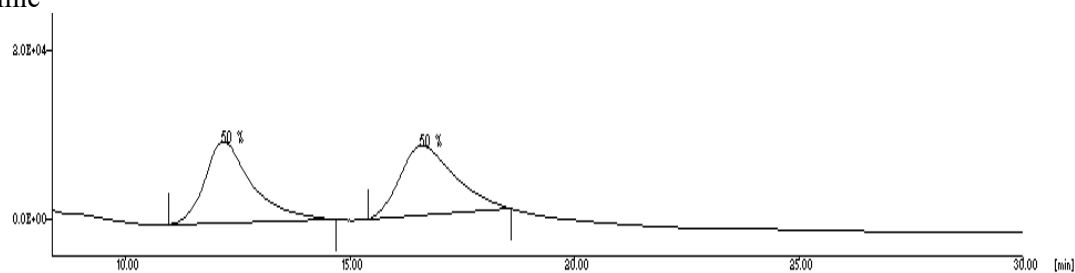
#	Name	RT	Area[uV.Sec]	Quantity
1		23.400	1818559.000	0.000
2		38.883	9253.723	0.000

Total Area of Peak = 1827812.723 [uV.Sec]



3e

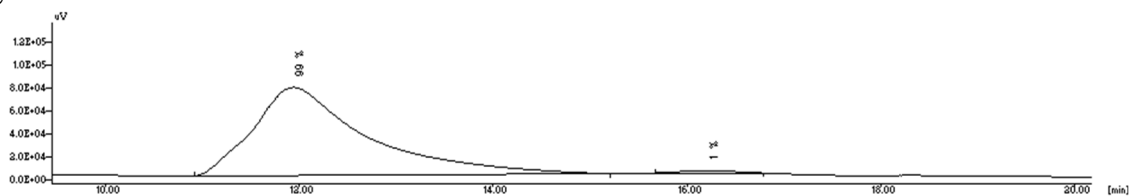
Racemic



#	Name	RT	Area[uV.Sec]	Quantity
1		12.150	688459.962	0.000
2		16.550	702212.750	0.000

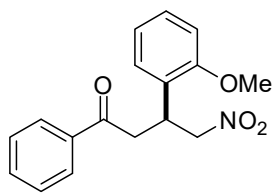
Total Area of Peak = 1390672.712 [uV.Sec]

Asymmetric



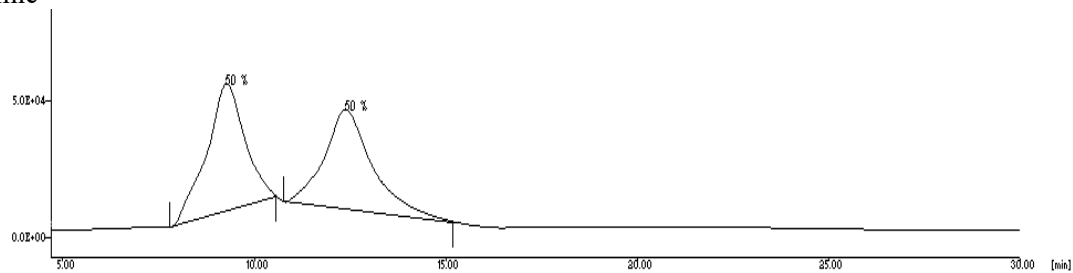
#	Name	RT	Area[uV.Sec]	Quantity
1		11.933	6194063.500	0.000
2		16.208	77154.750	0.000

Total Area of Peak = 6271218.250 [uV.Sec]



3f

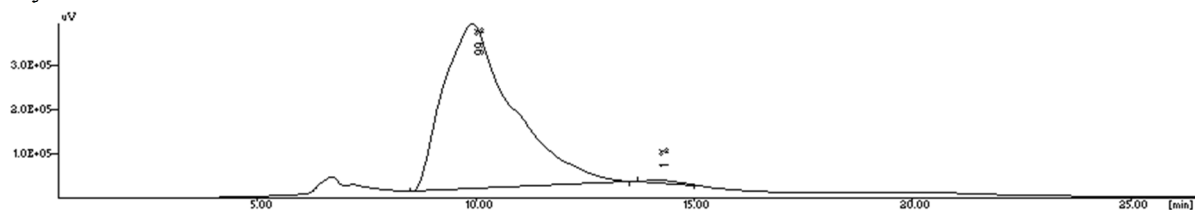
Racemic



#	Name	RT	Area[uV.Sec]	Quantity
1		9.258	3130431.565	0.000
2		12.367	3107225.040	0.000

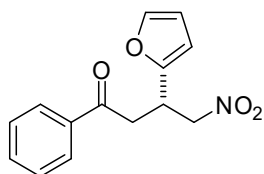
Total Area of Peak = 6237656.605 [uV.Sec]

Asymmetric



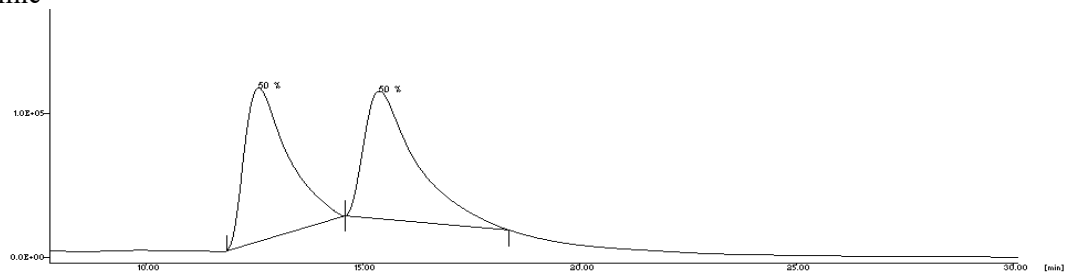
#	Name	RT	Area[uV.Sec]	Quantity
1		9.908	40342558.053	0.000
2		14.133	261316.500	0.000

Total Area of Peak = 40603874.553 [uV.Sec]



3g

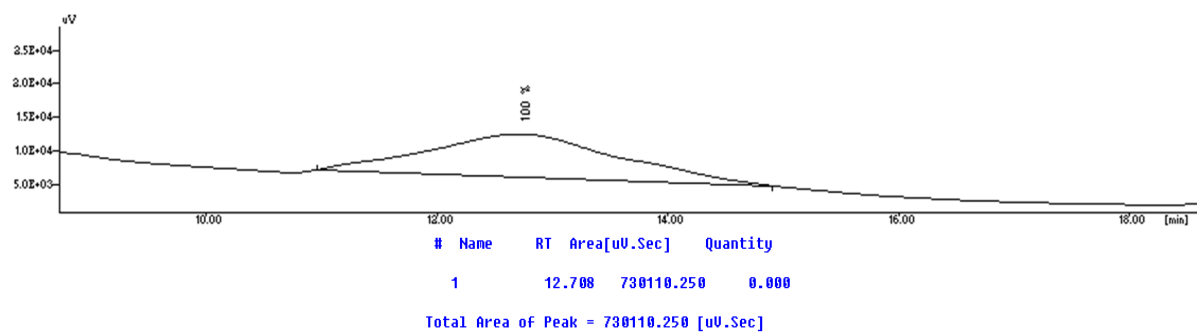
Racemic



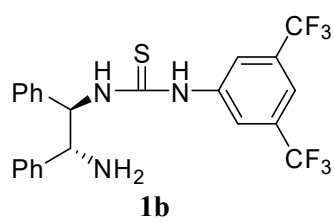
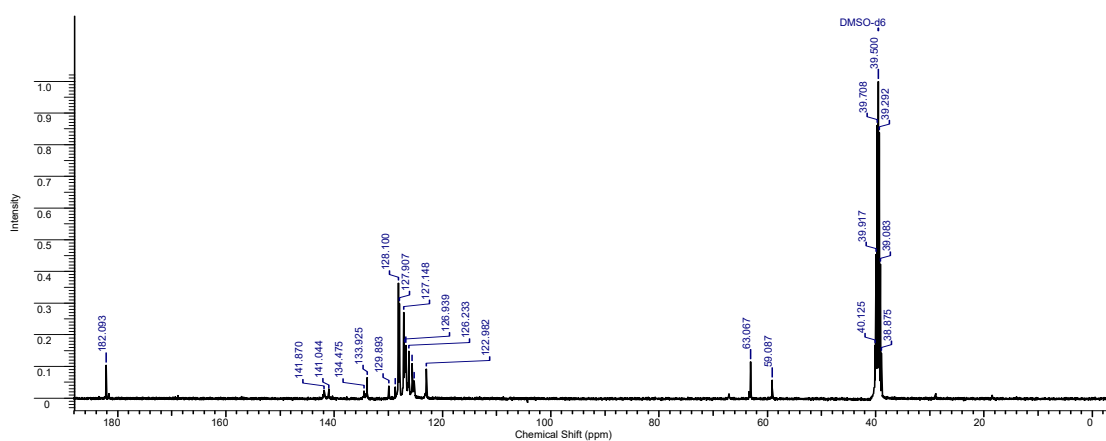
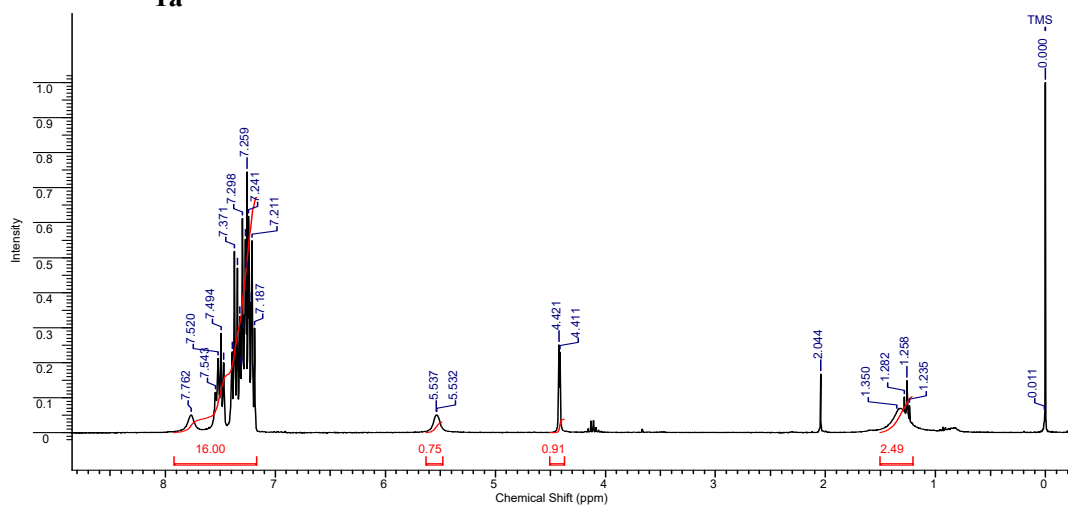
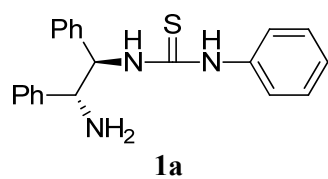
#	Name	RT	Area[uV.Sec]	Quantity
1		12.600	7304910.284	0.000
2		15.383	7270880.500	0.000

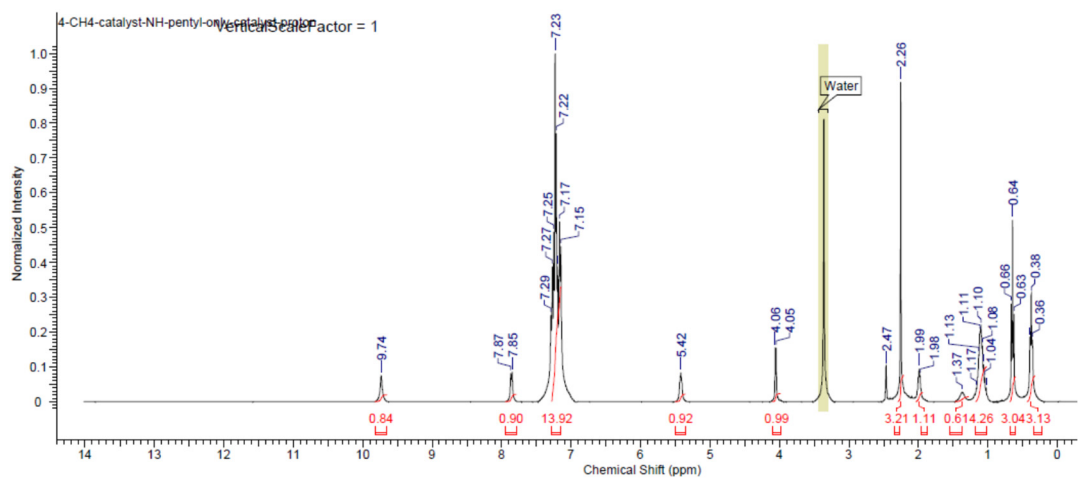
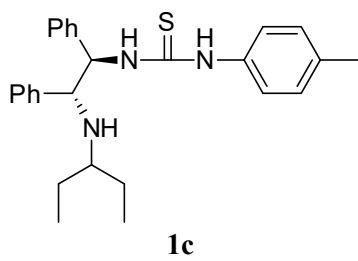
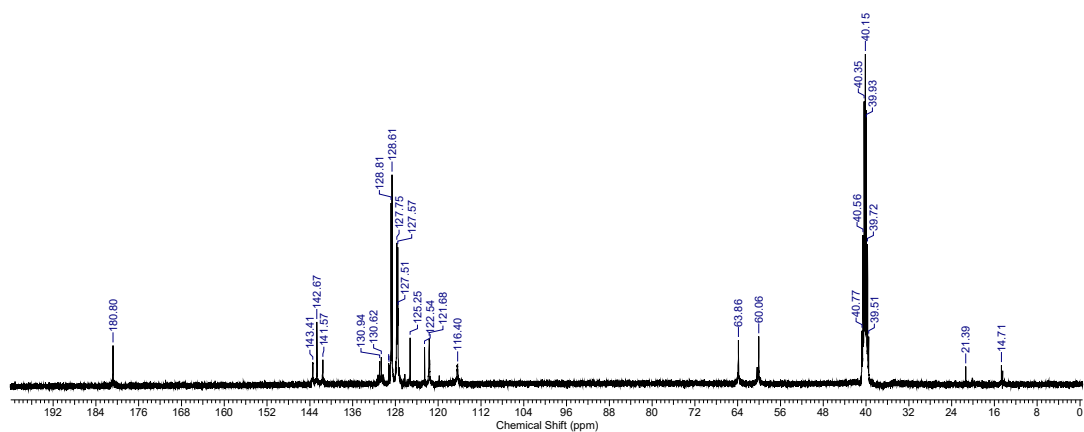
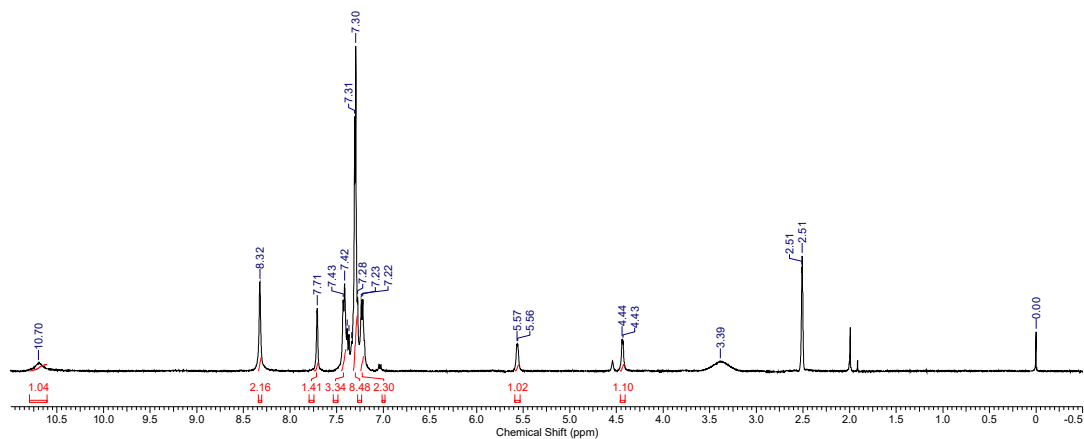
Total Area of Peak = 14575790.784 [uV.Sec]

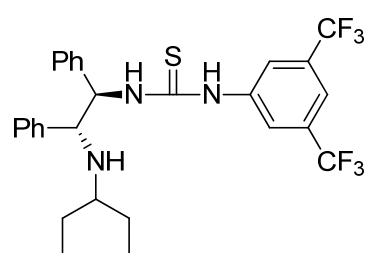
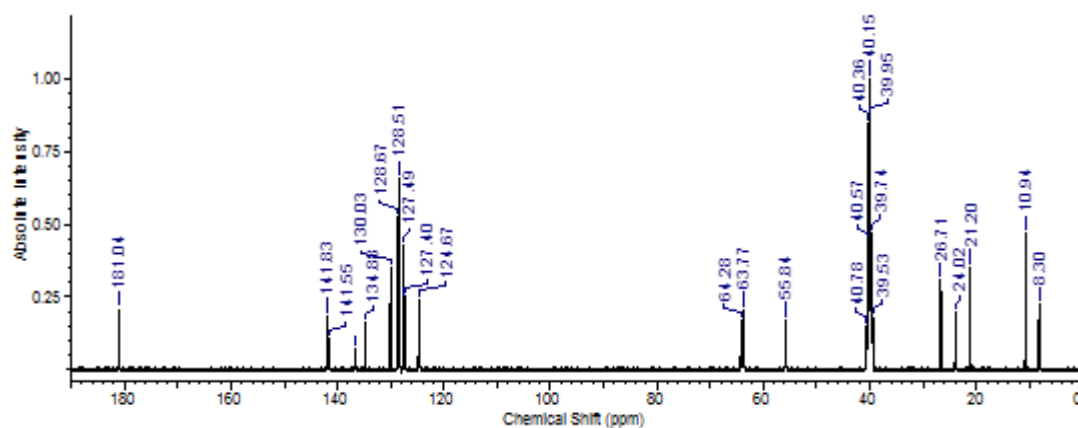
Asymmetric



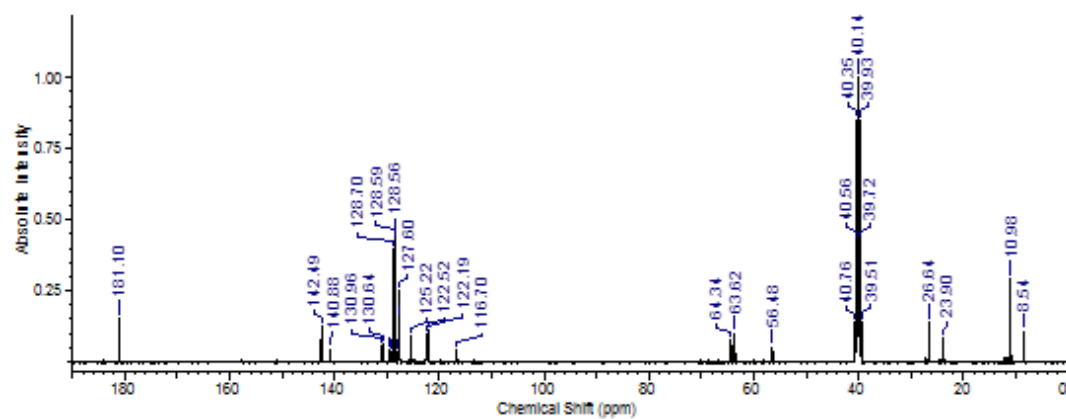
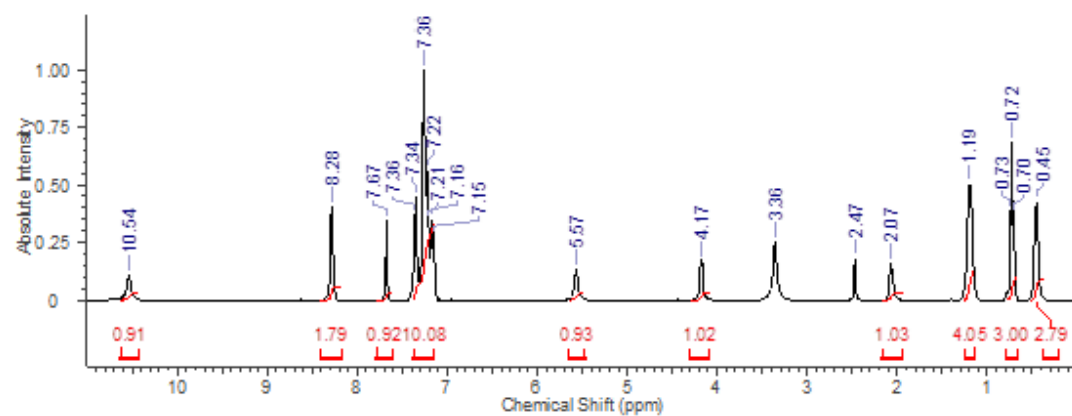
Copy of NMR Spectra

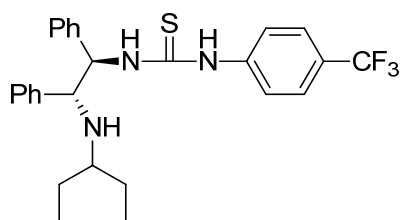




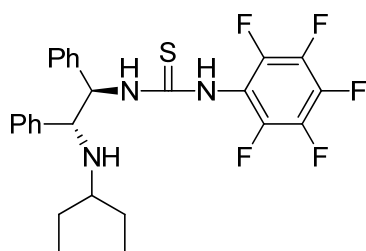
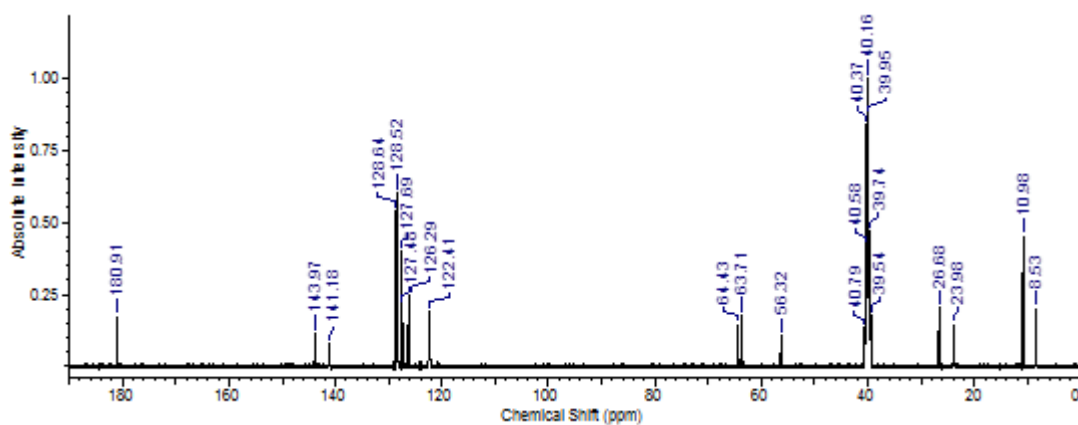
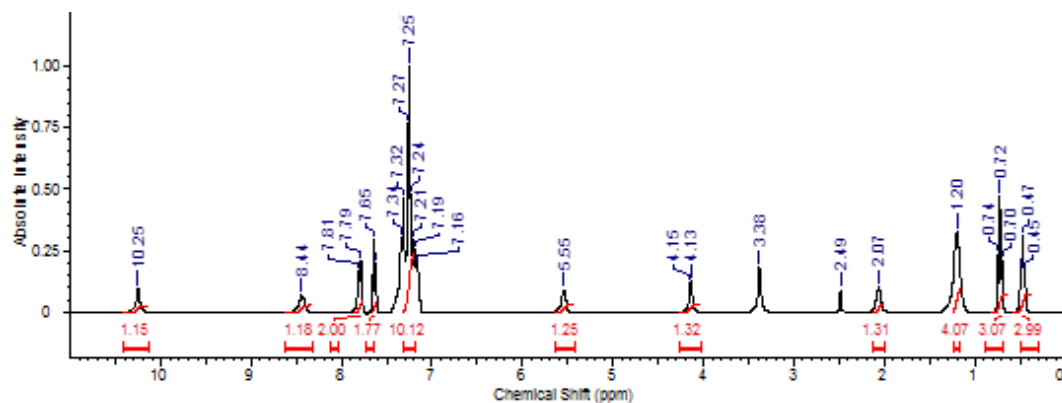


1d

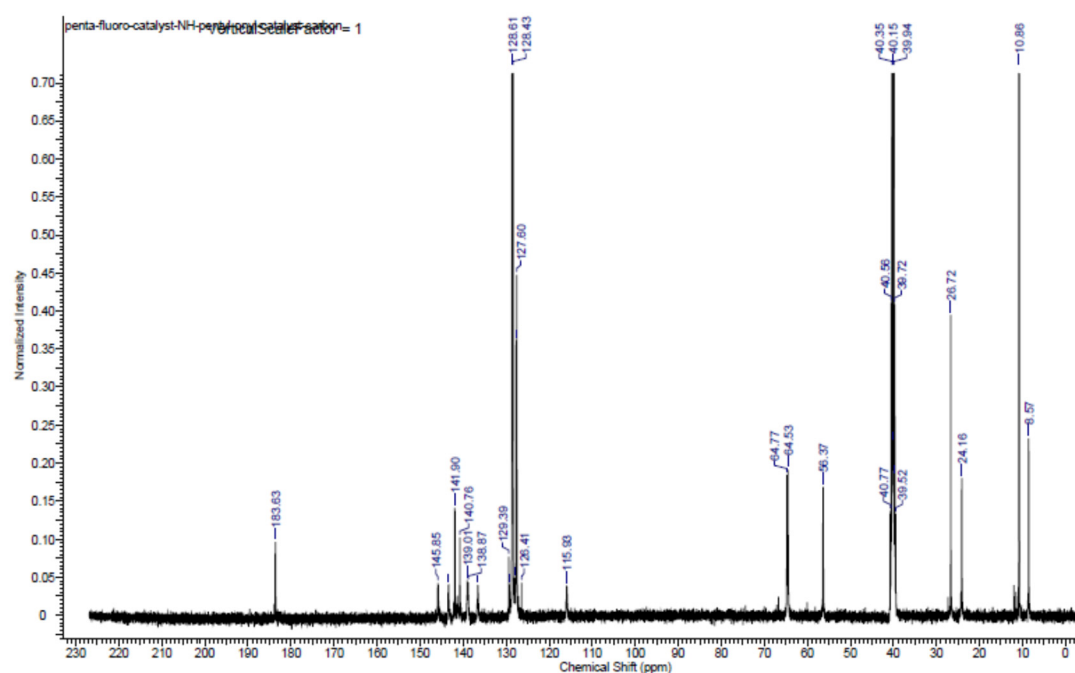
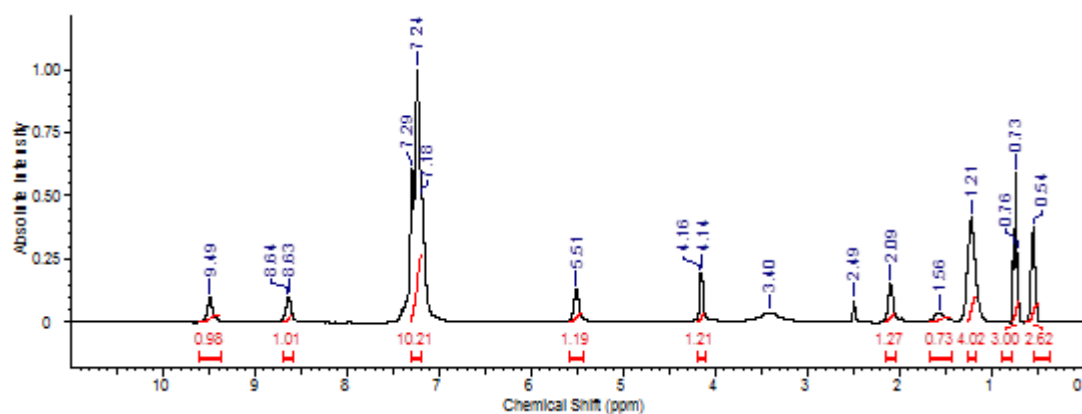




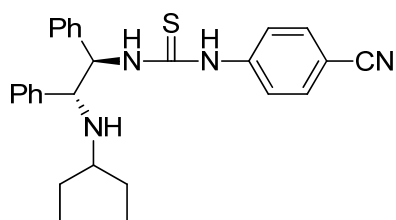
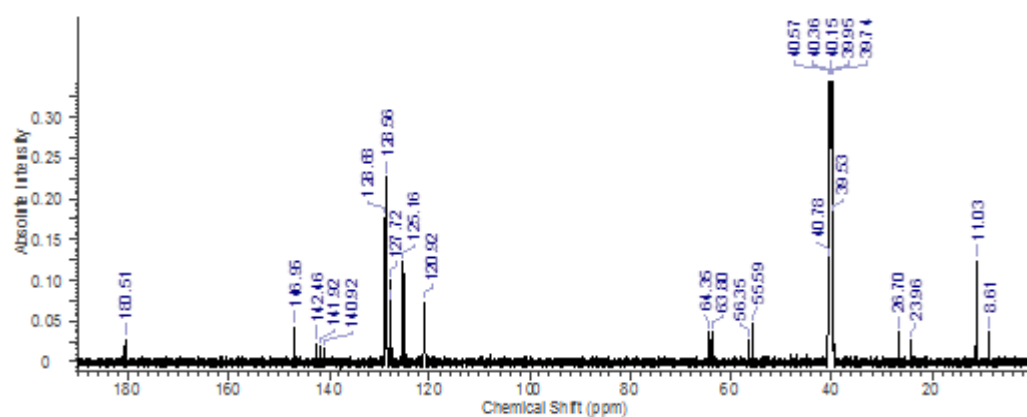
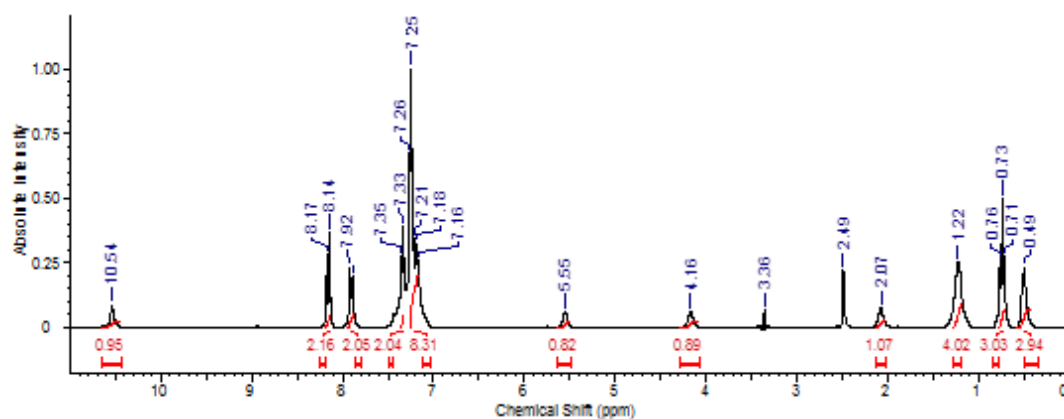
1e



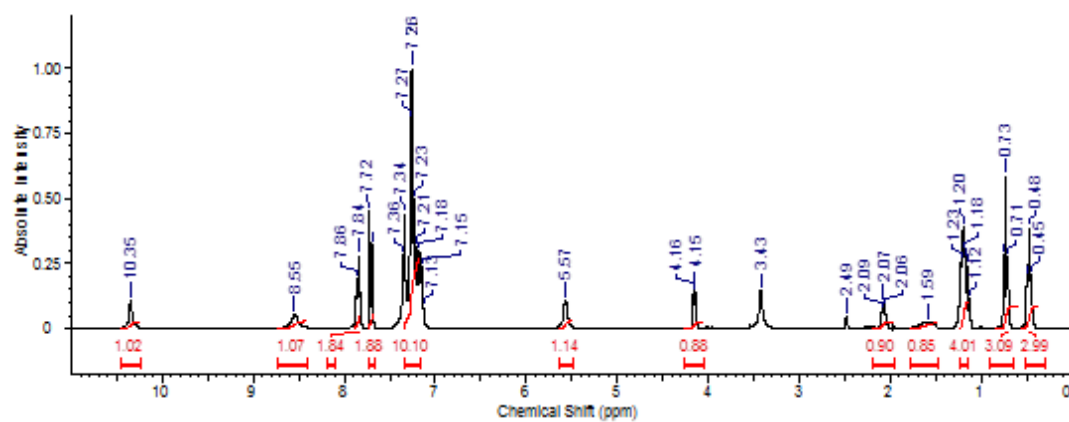
1f

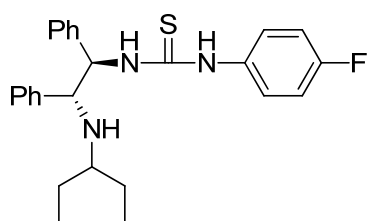
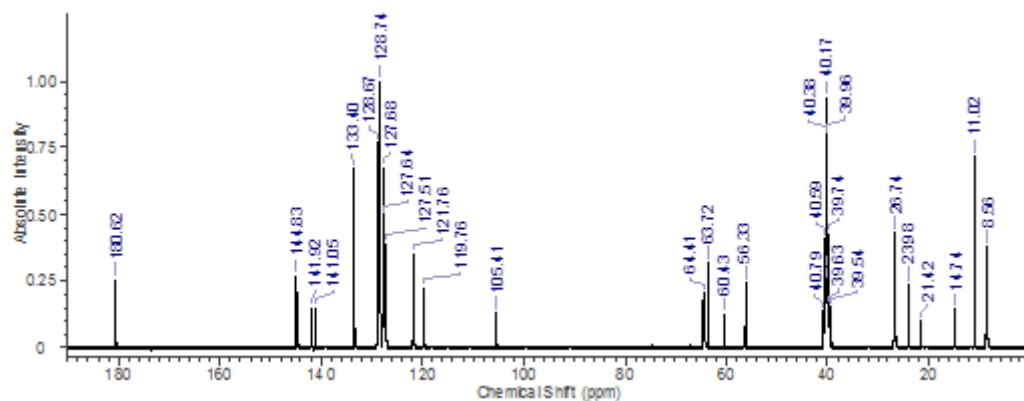


1g

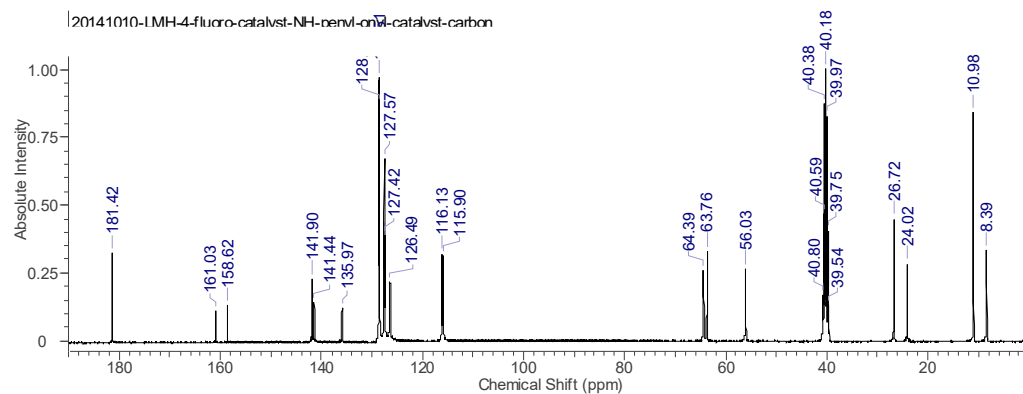
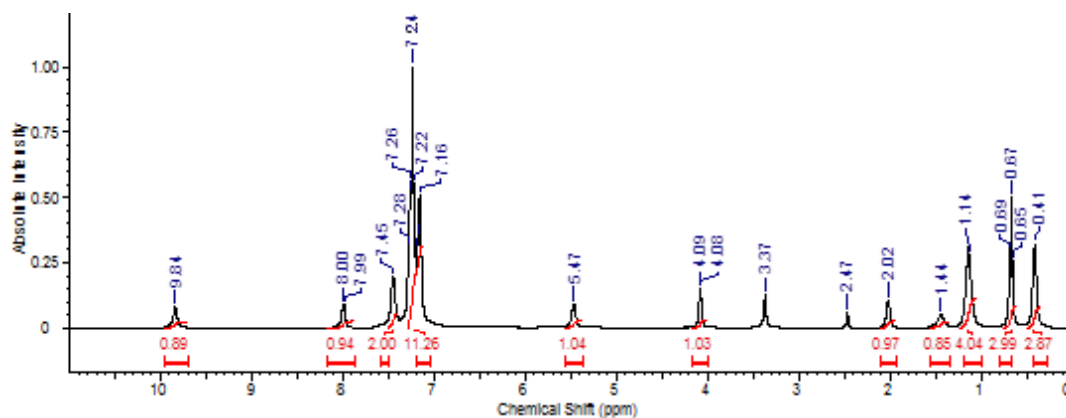


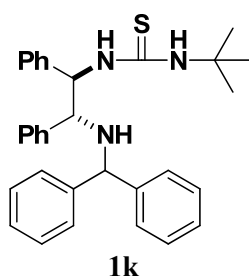
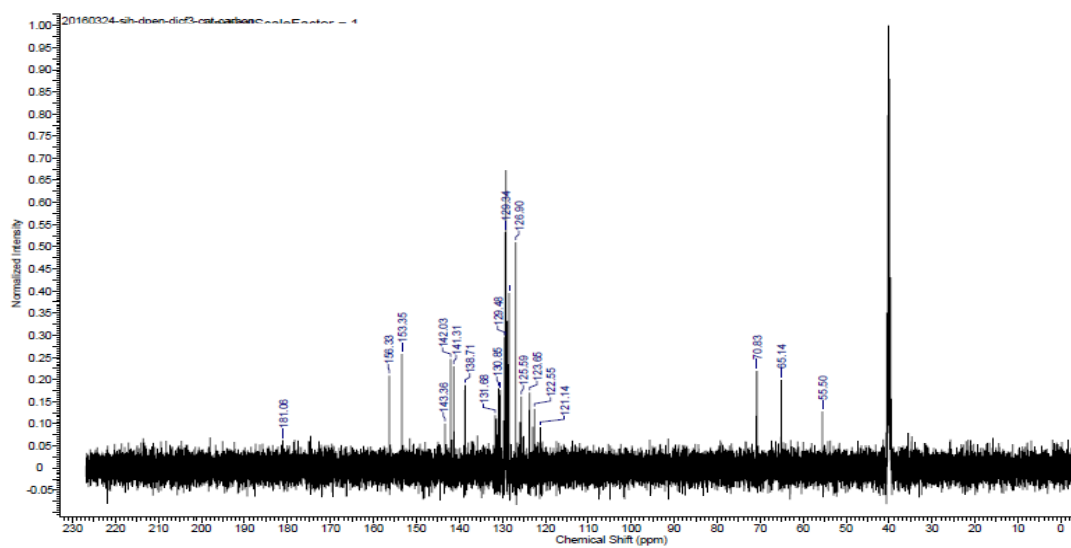
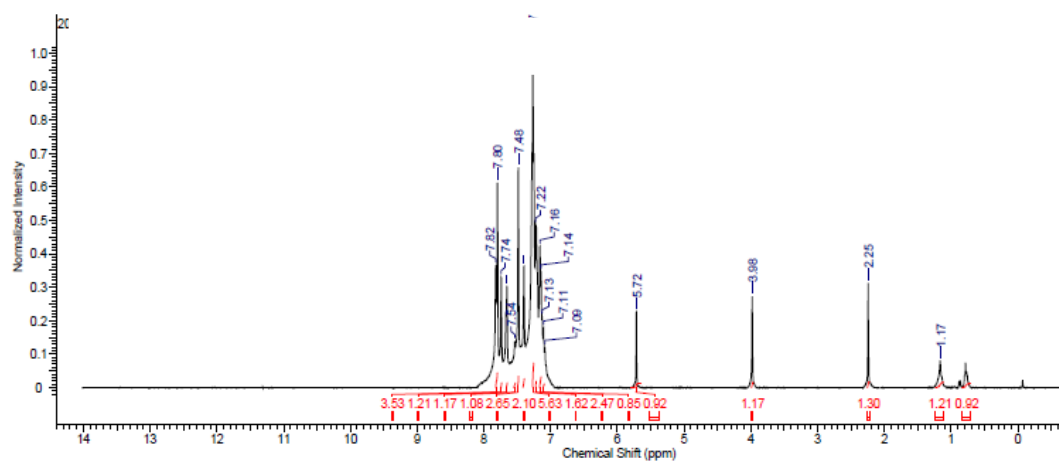
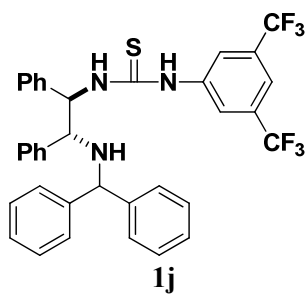
1h

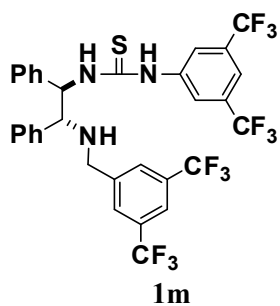
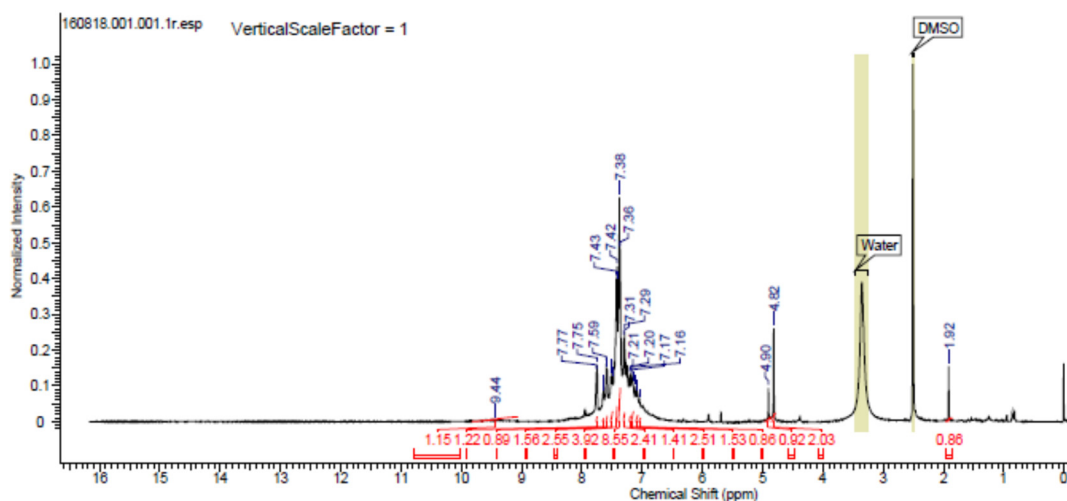
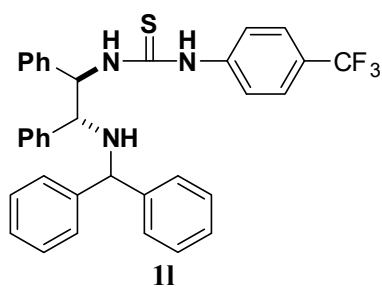
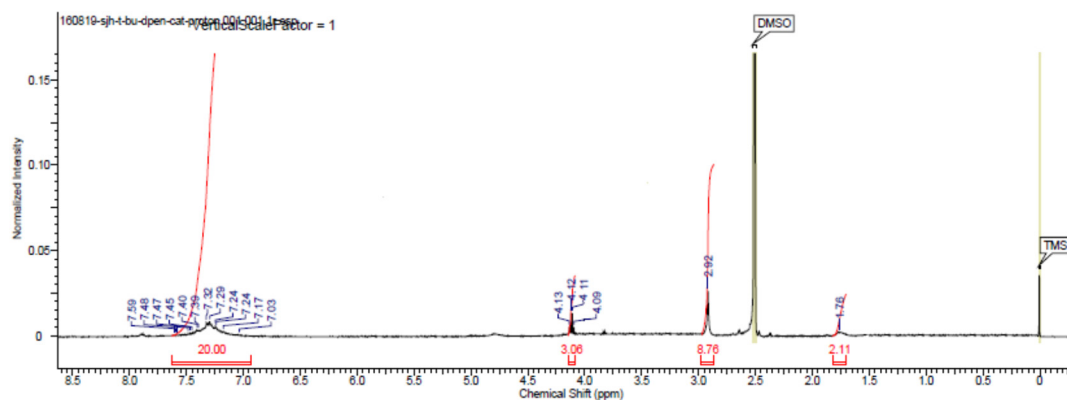


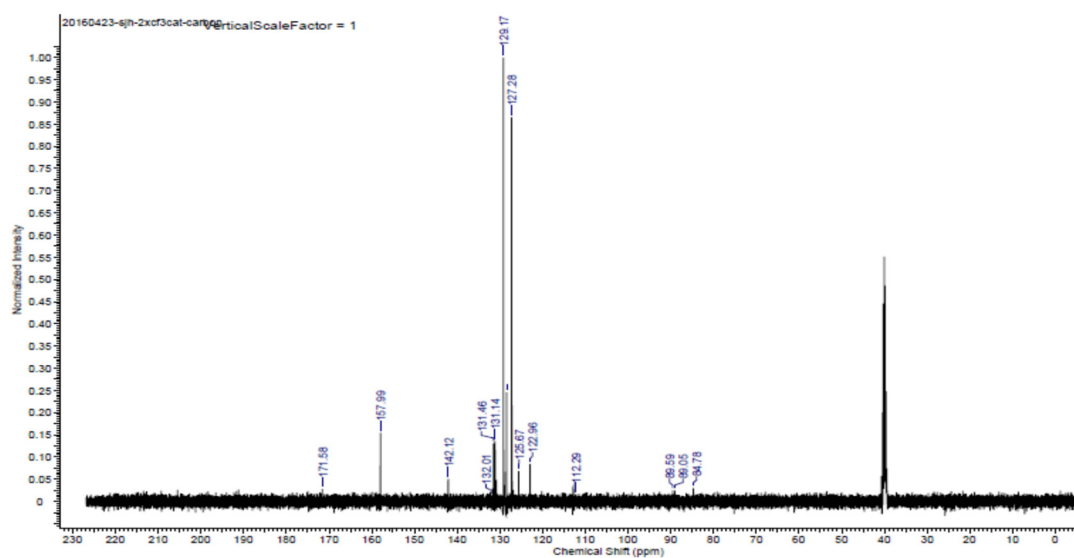
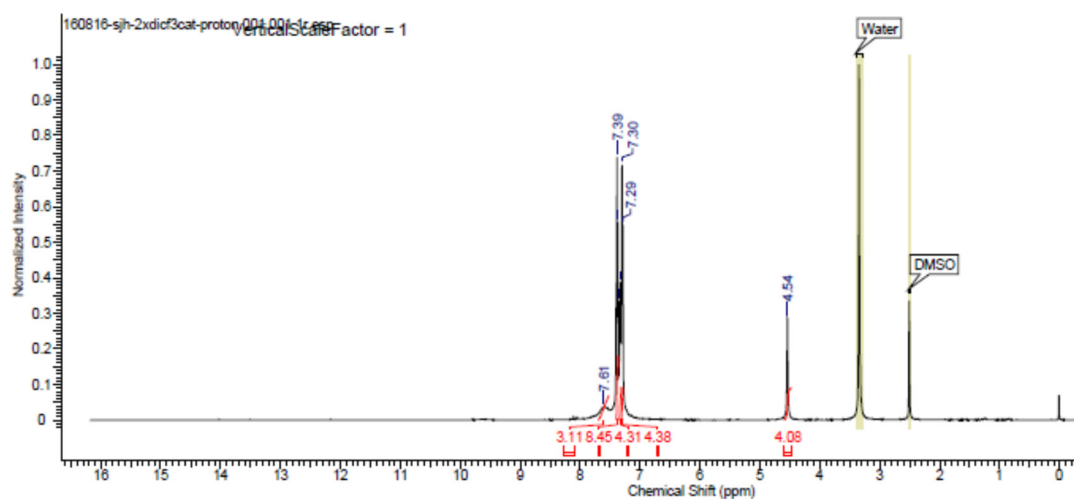


1i

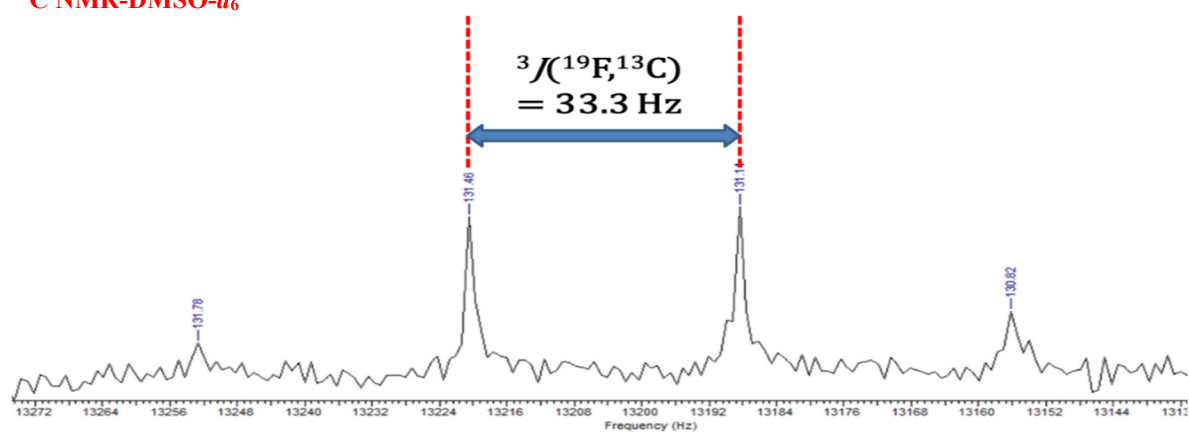




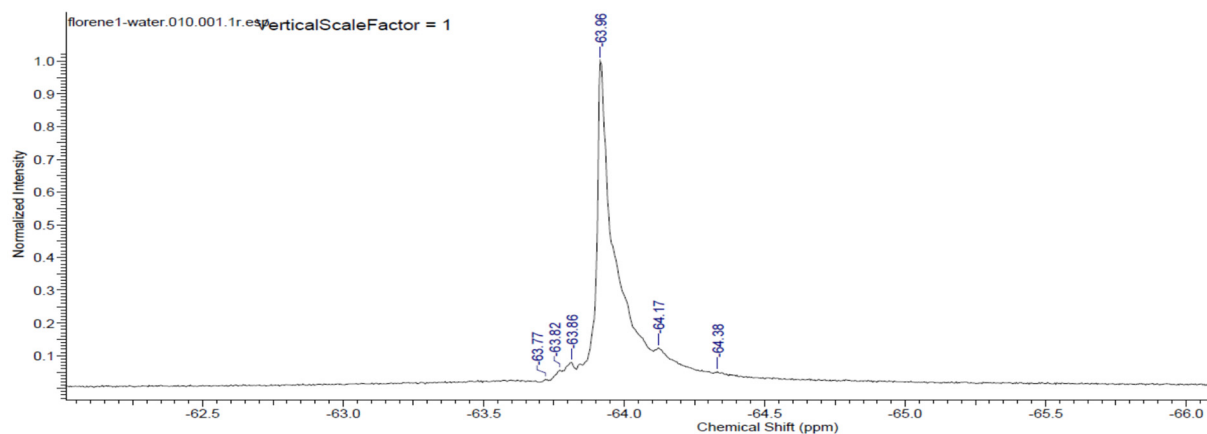




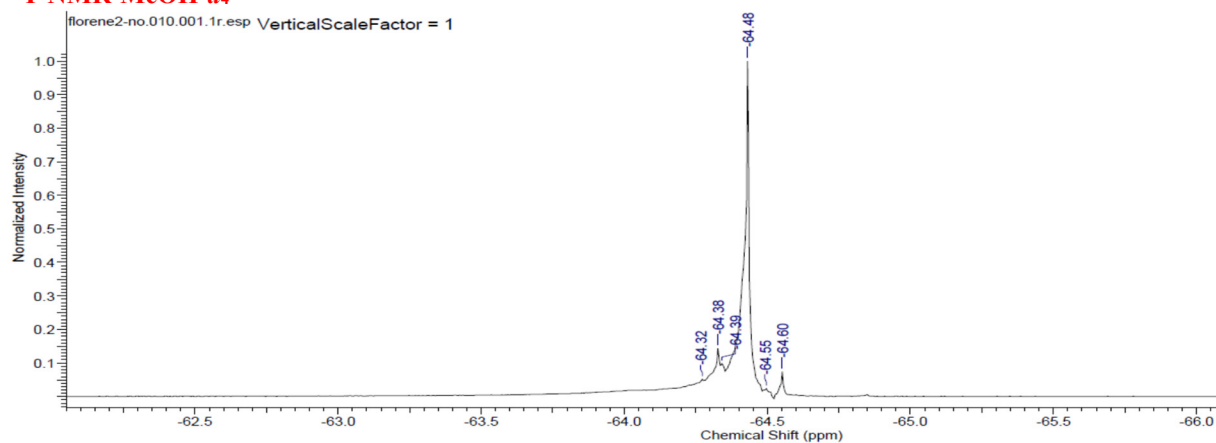
^{13}C NMR-DMSO- d_6



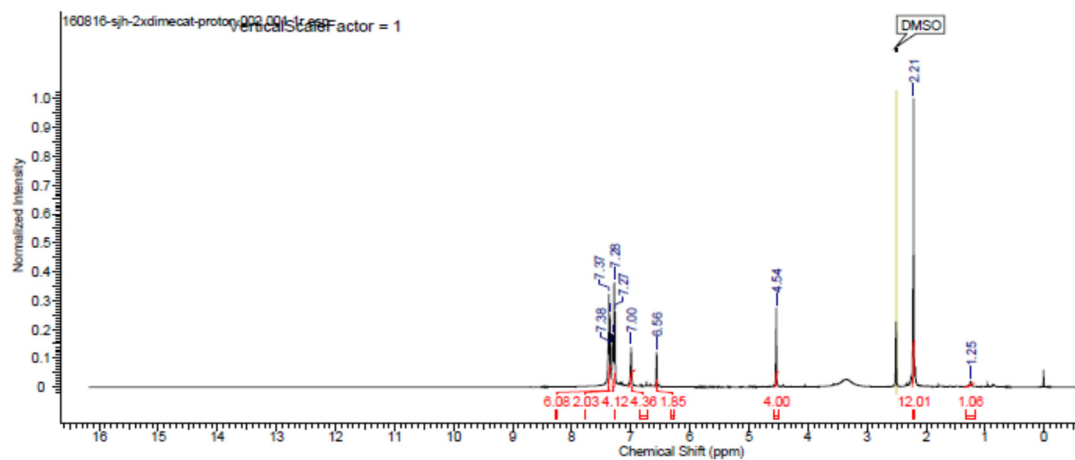
^{19}F NMR-MeOH+ D_2O

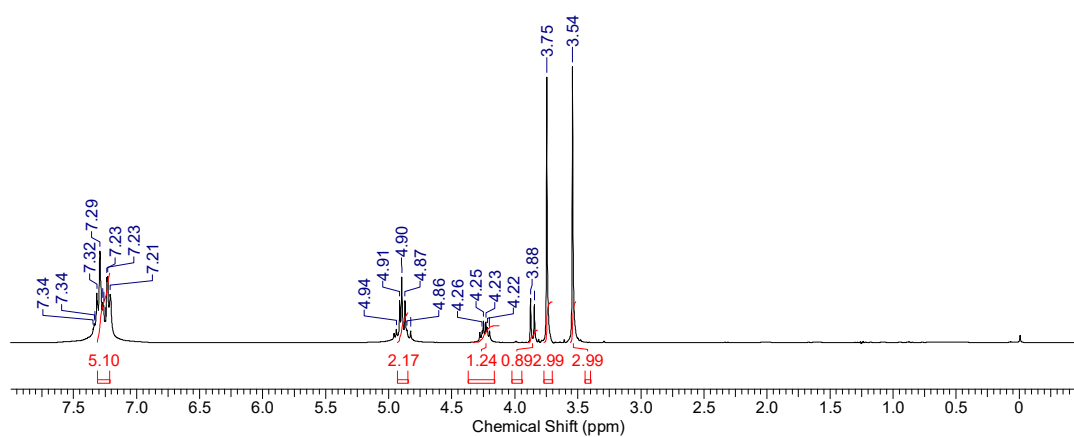
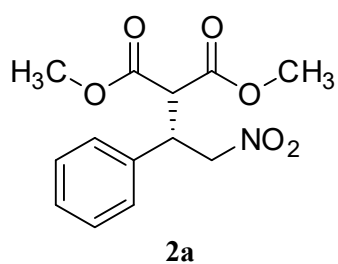
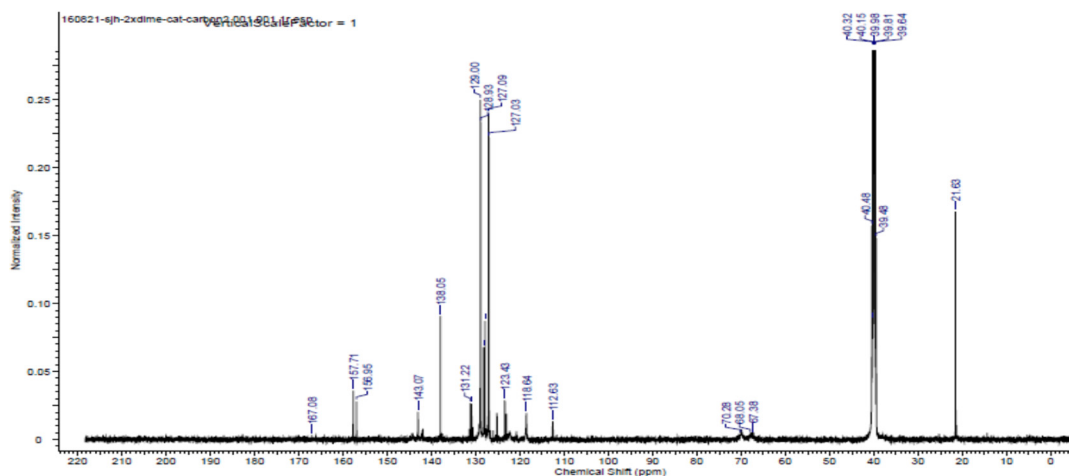


¹⁹F NMR-MeOH-*d*₄

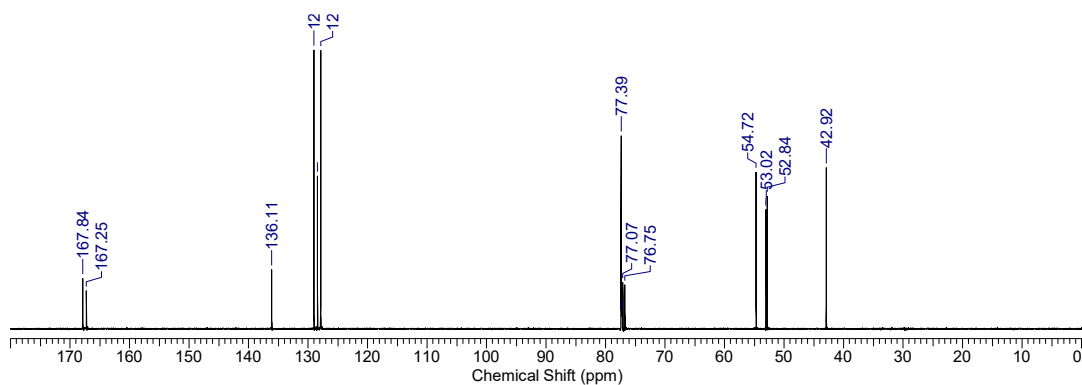


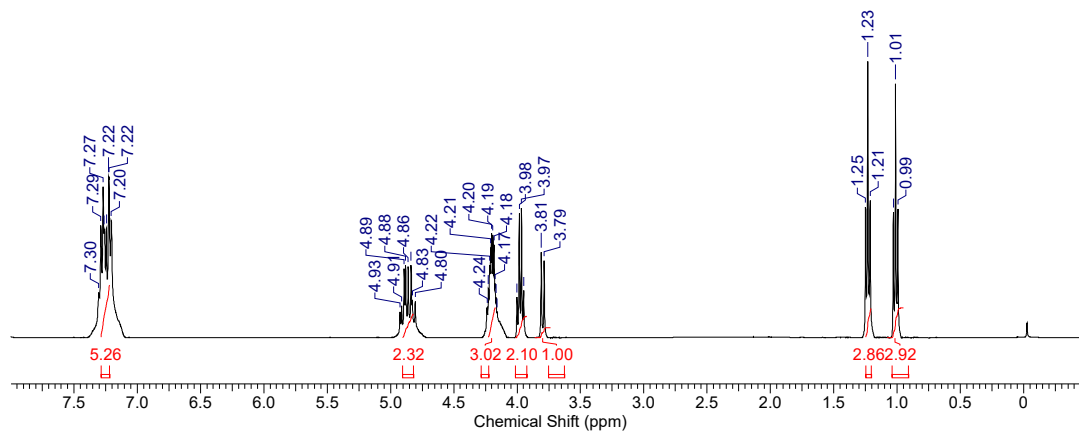
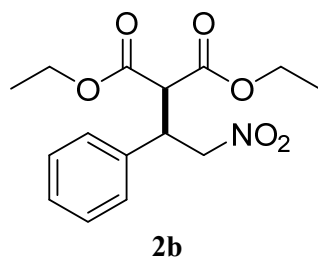
1n



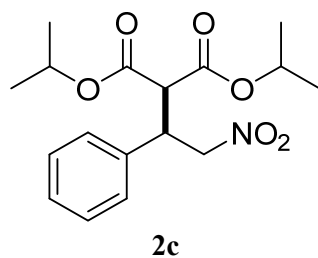
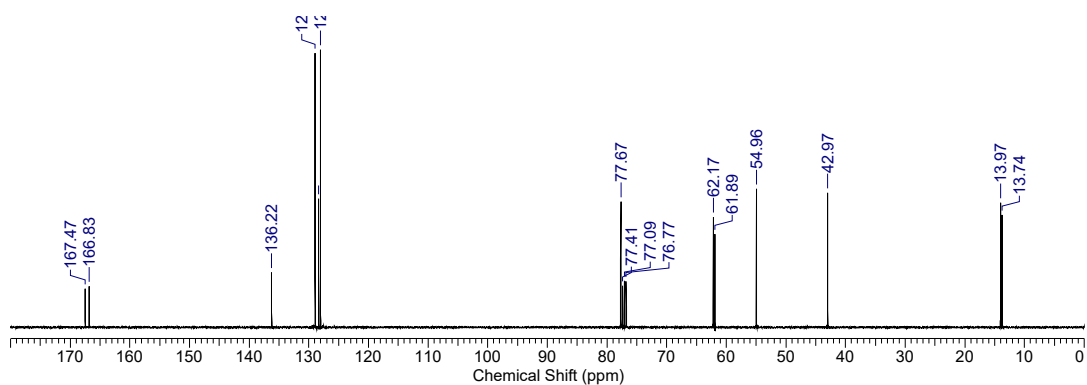


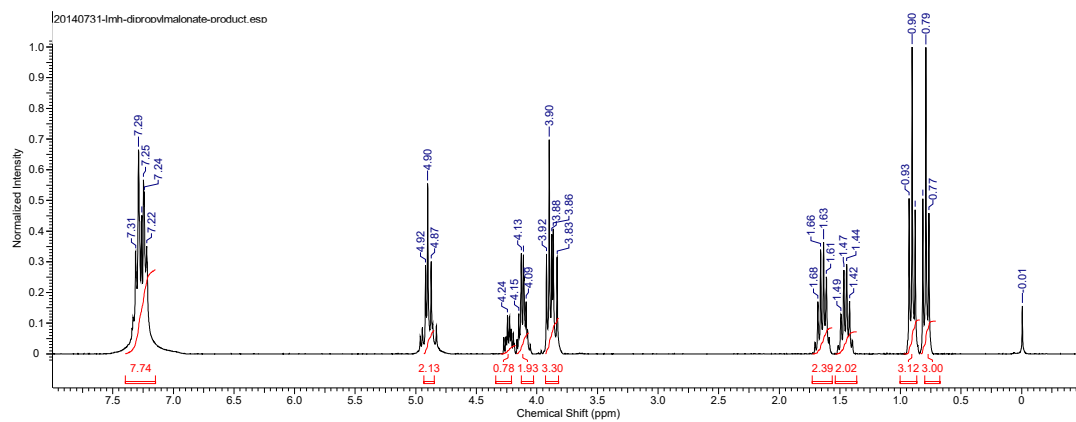
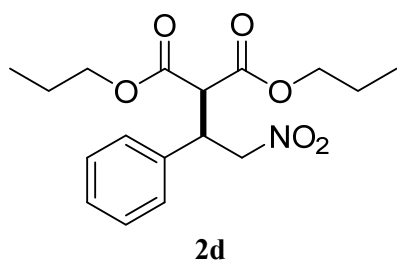
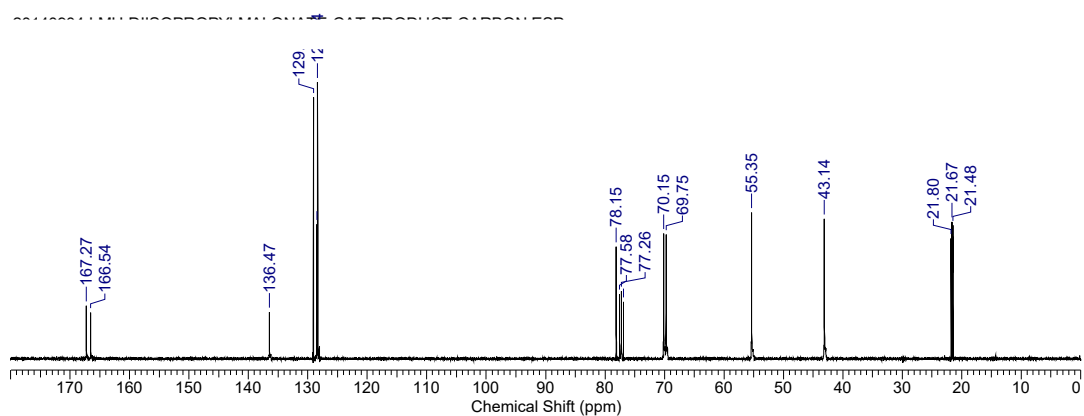
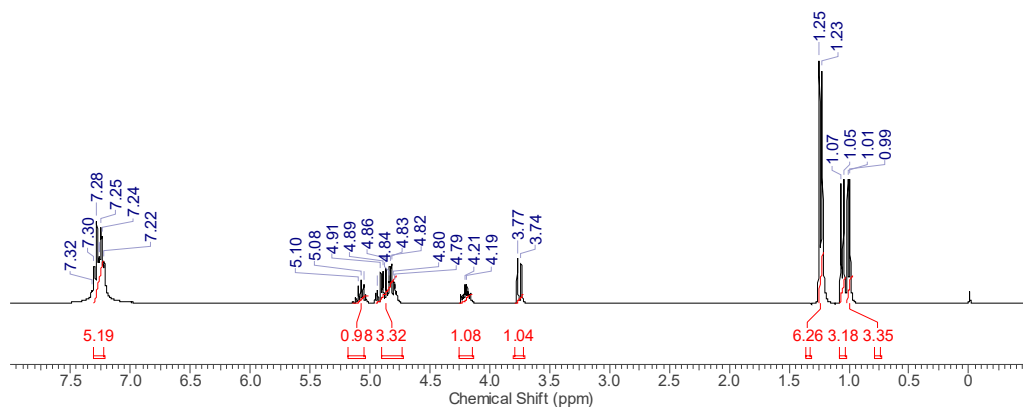
20140004 1 MU DIMETHYL MALONATE X 6 PRODUCT CARBON-13

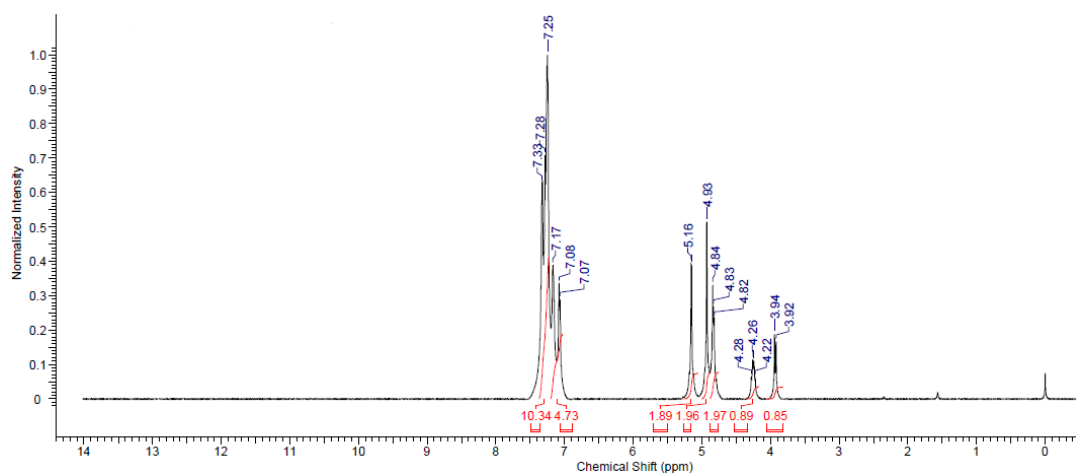
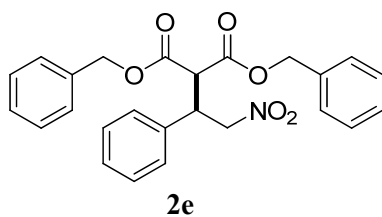
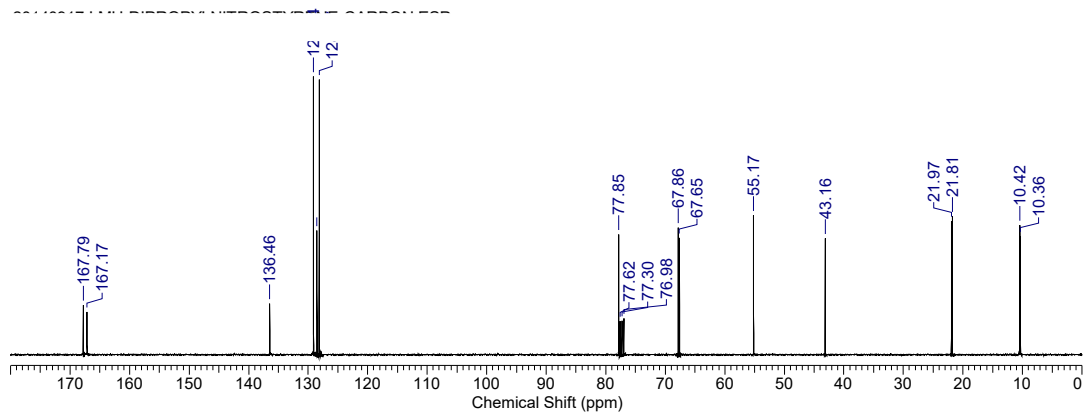


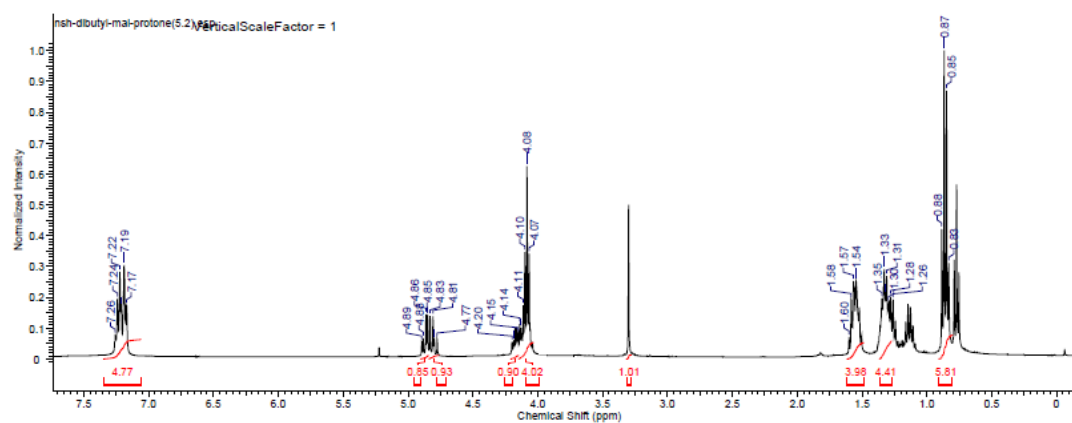
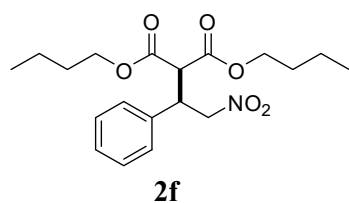
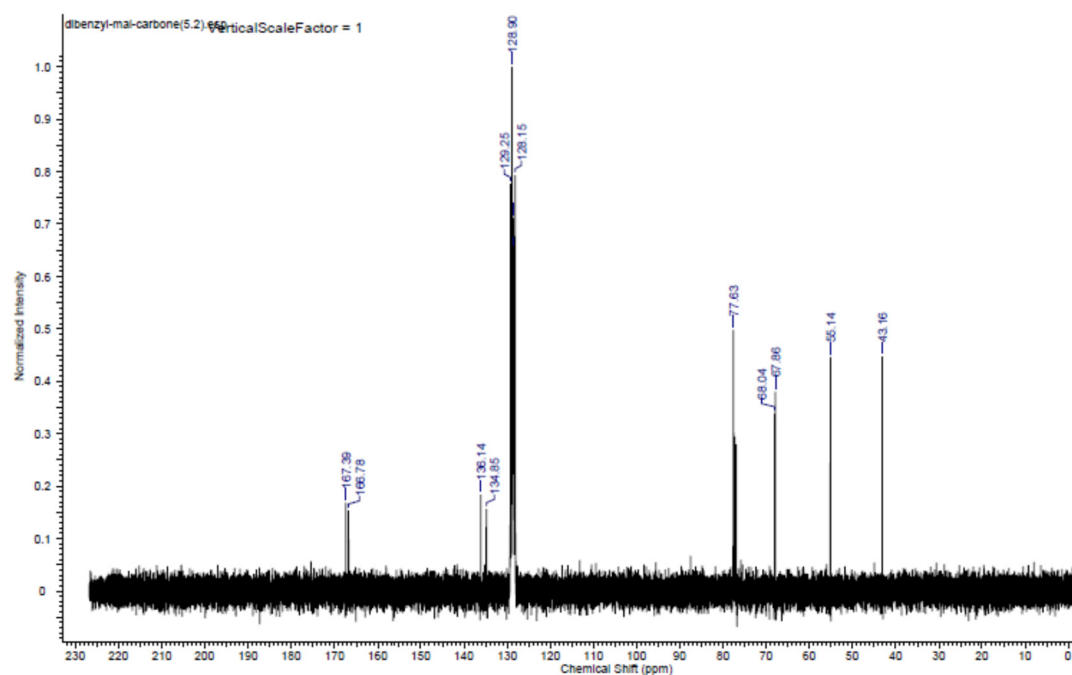


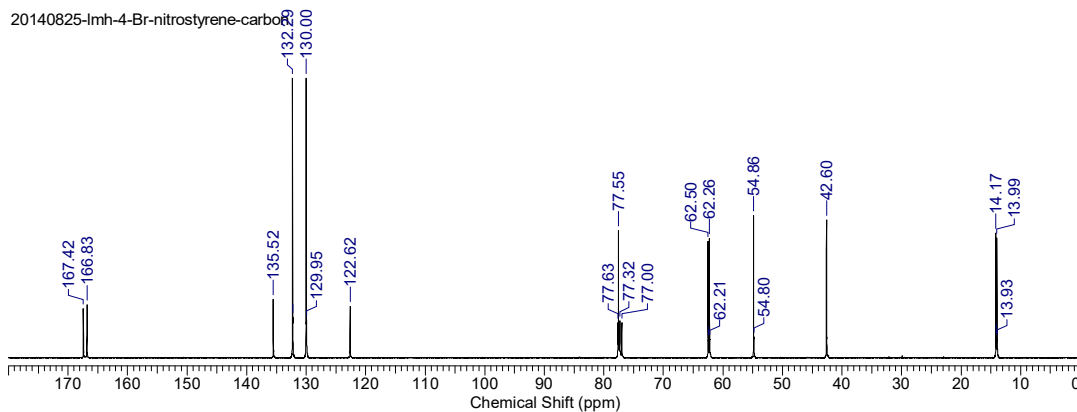
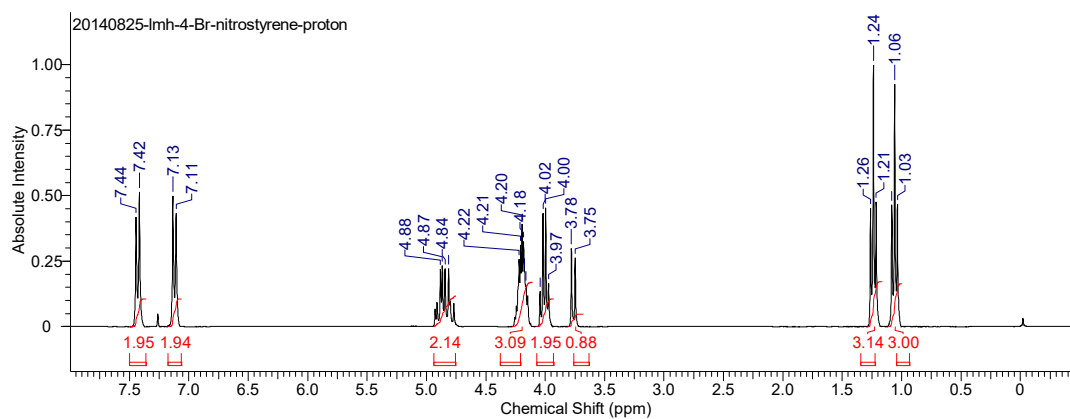
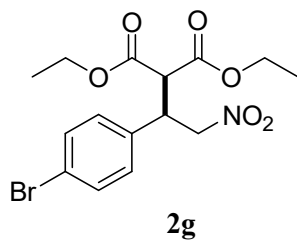
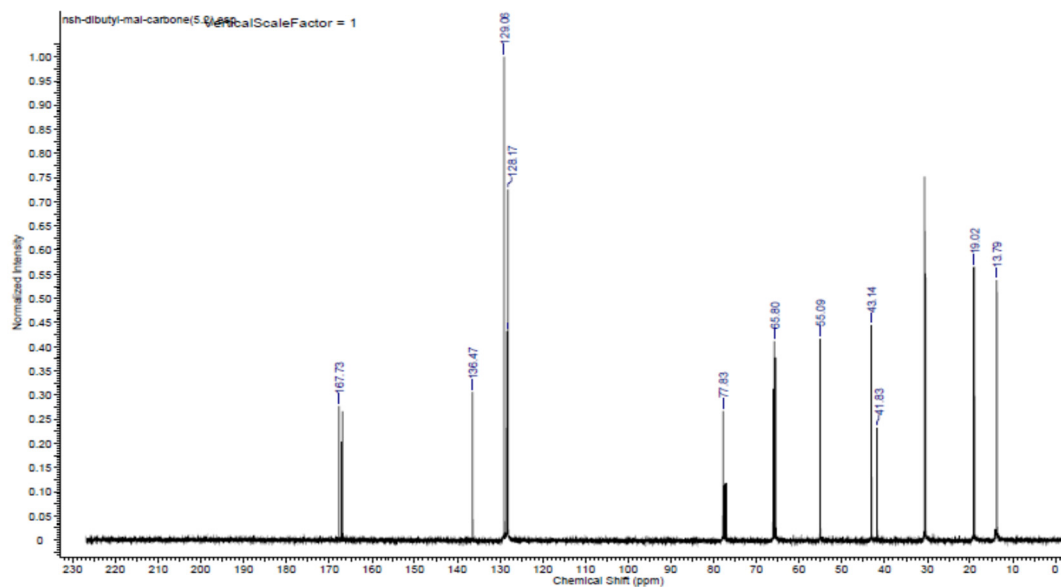
20414047 13C NMR DIETYL NITROSTYRENE CARBON-13

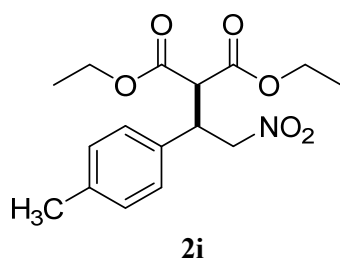
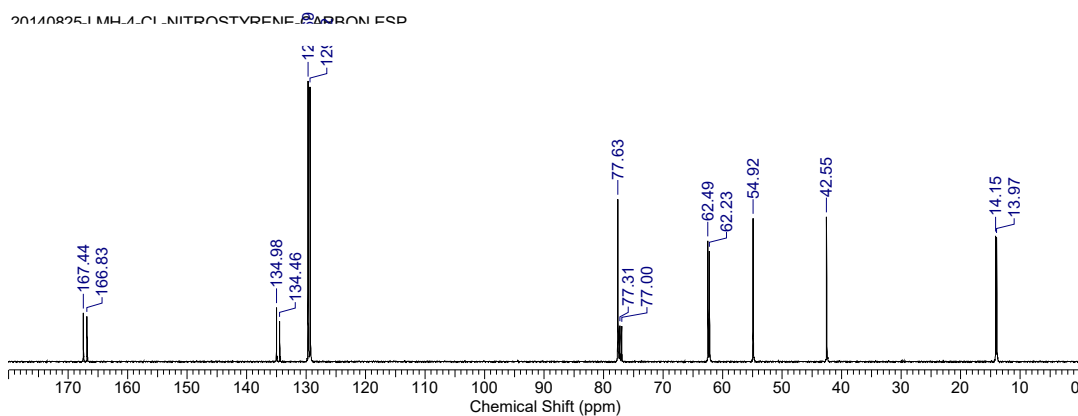
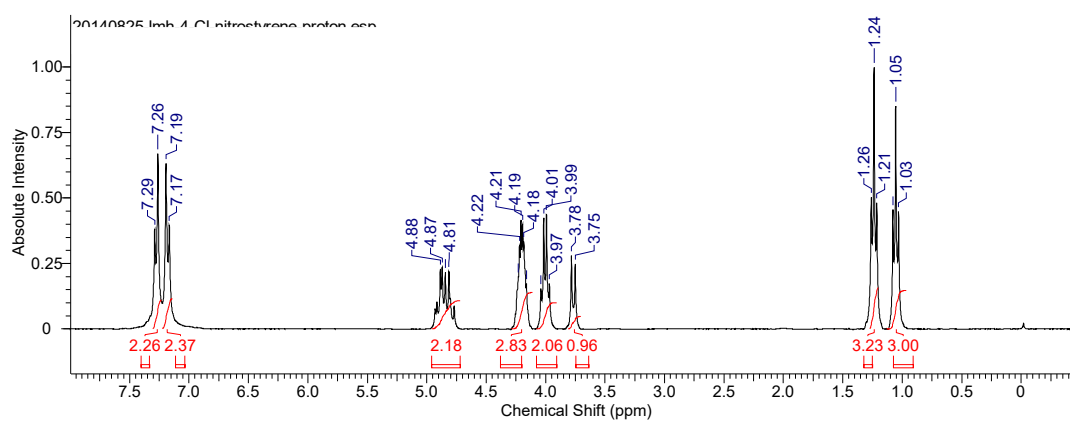
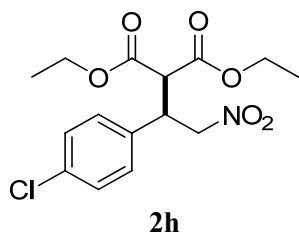


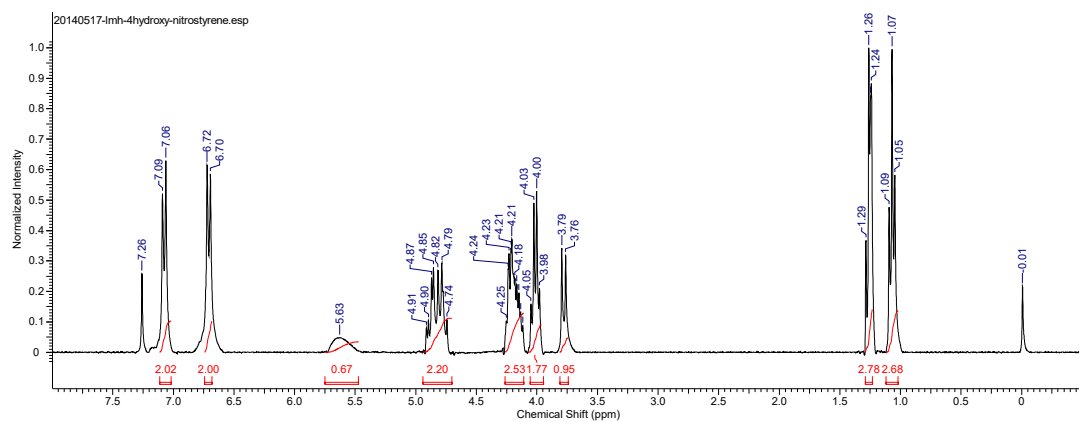
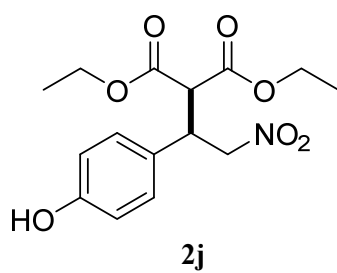
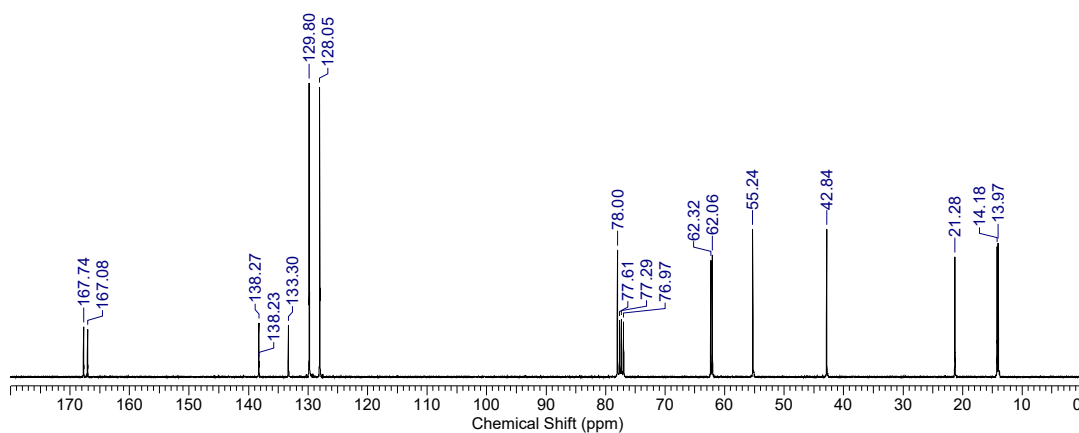
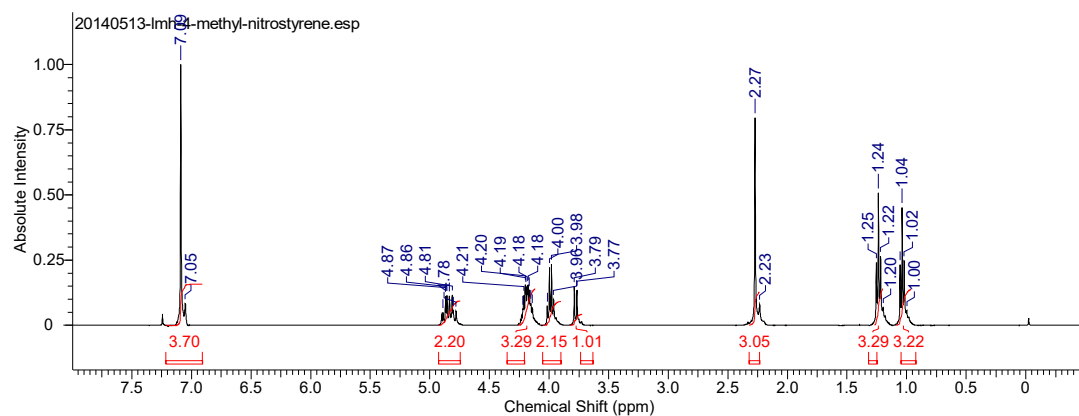




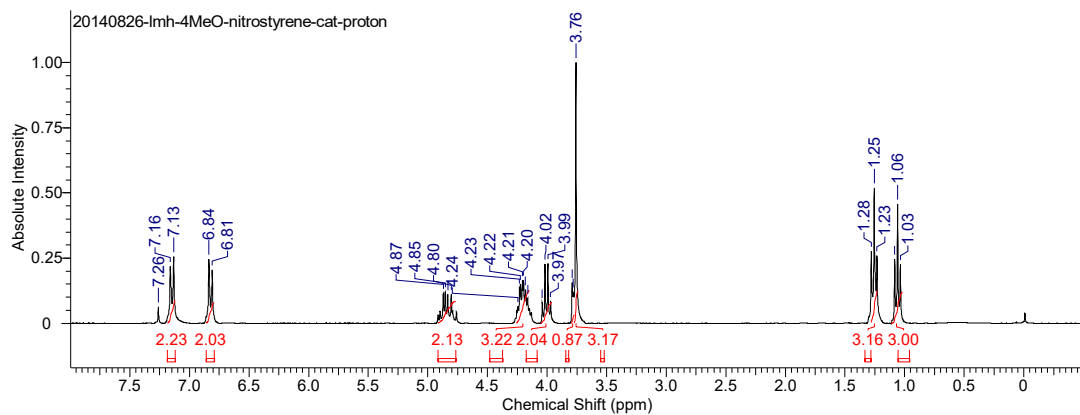
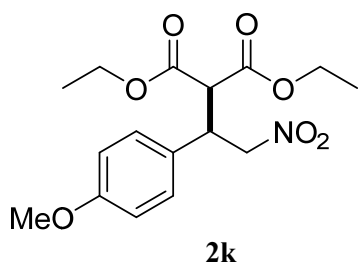
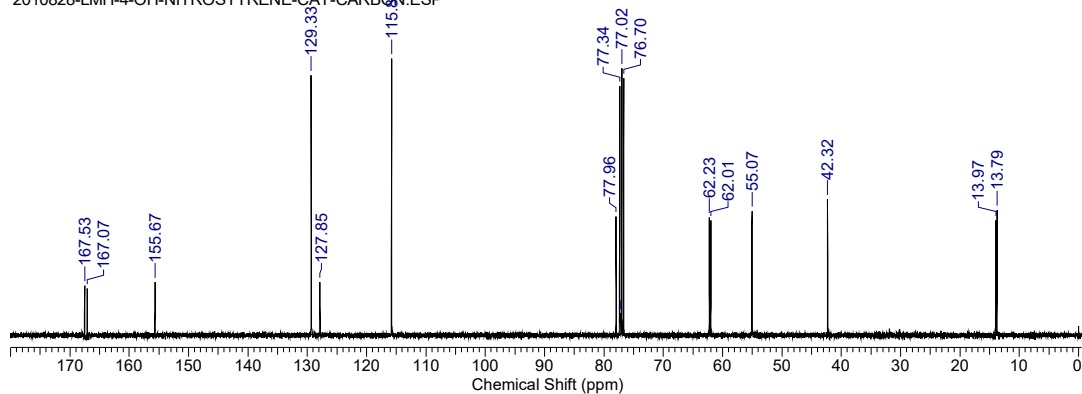




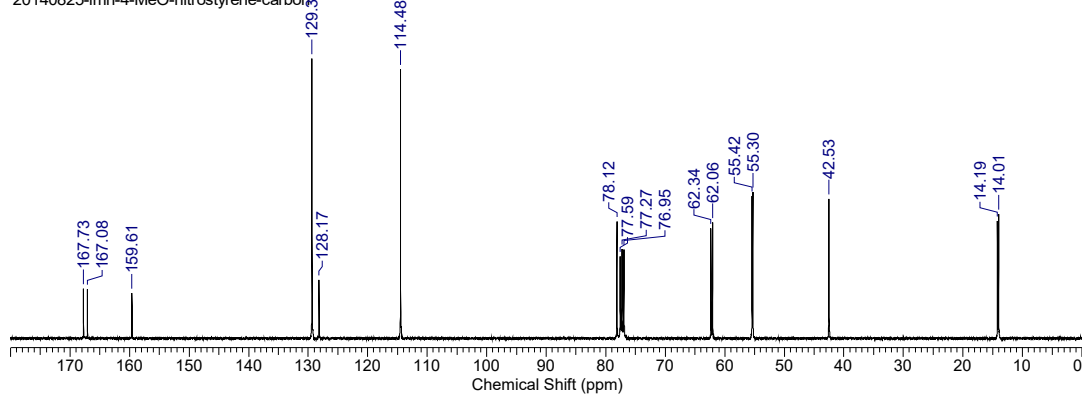


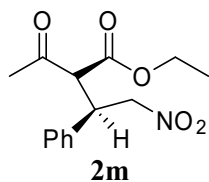
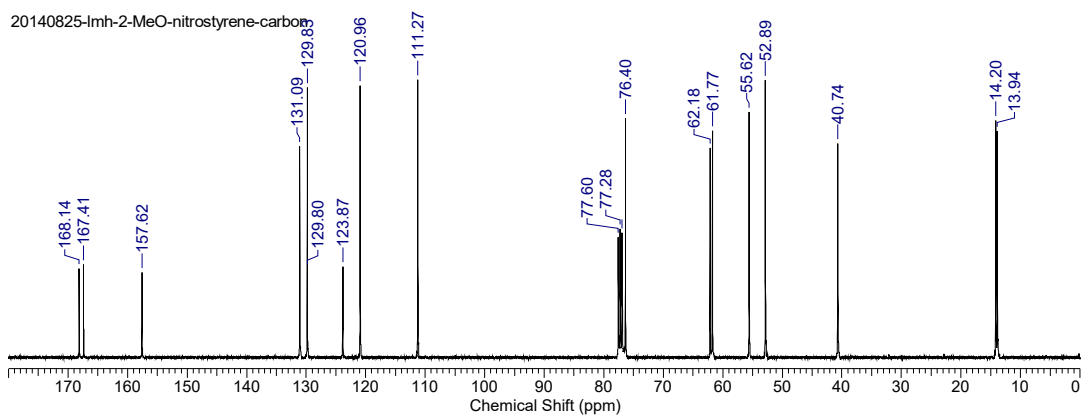
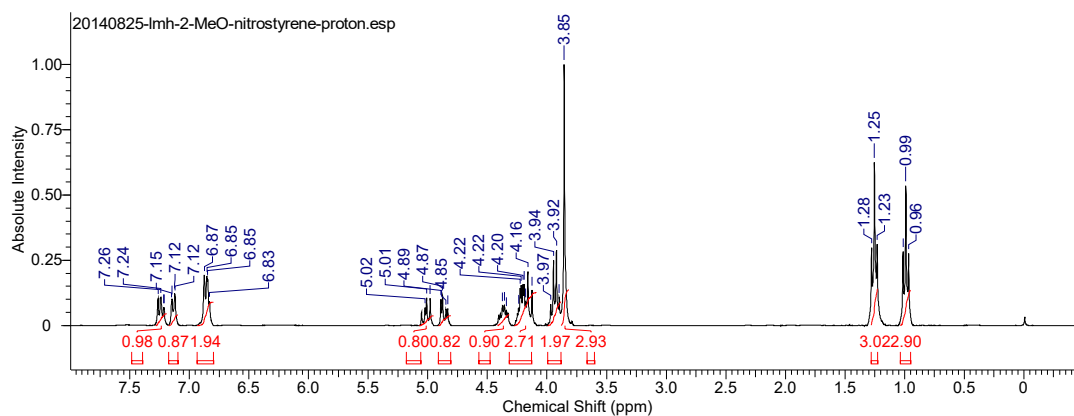
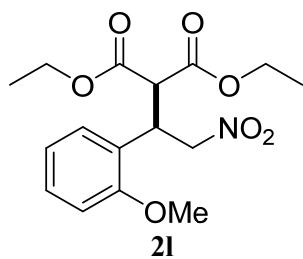


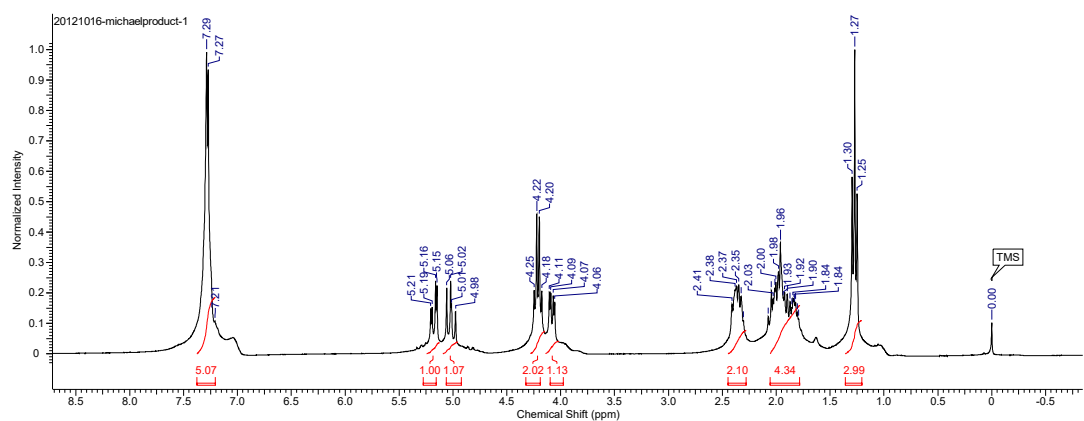
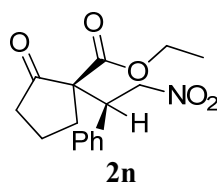
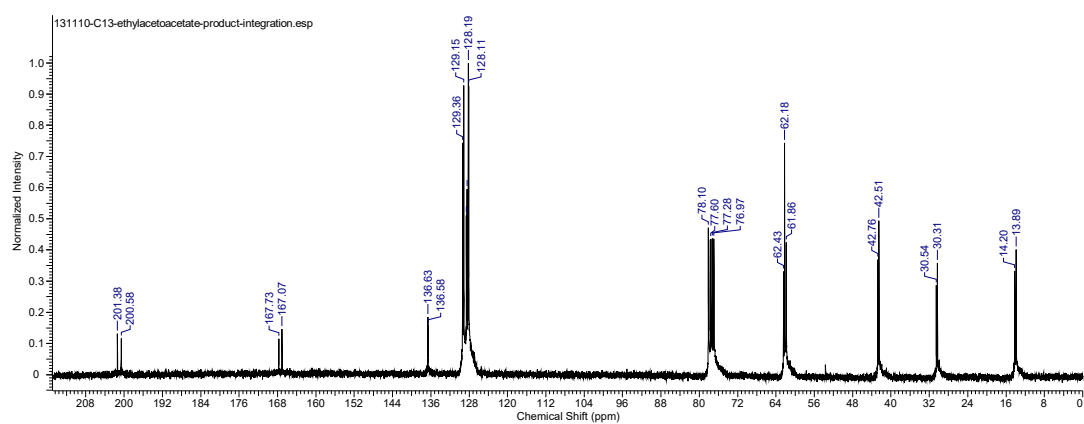
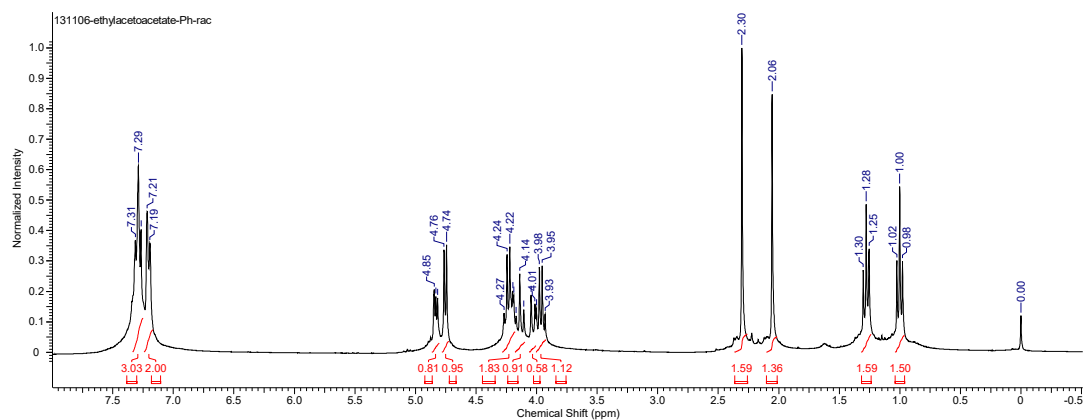
2010828-LMH-4-OH-NITROSTYRENE-CAT-CARBON.ESP

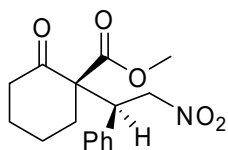
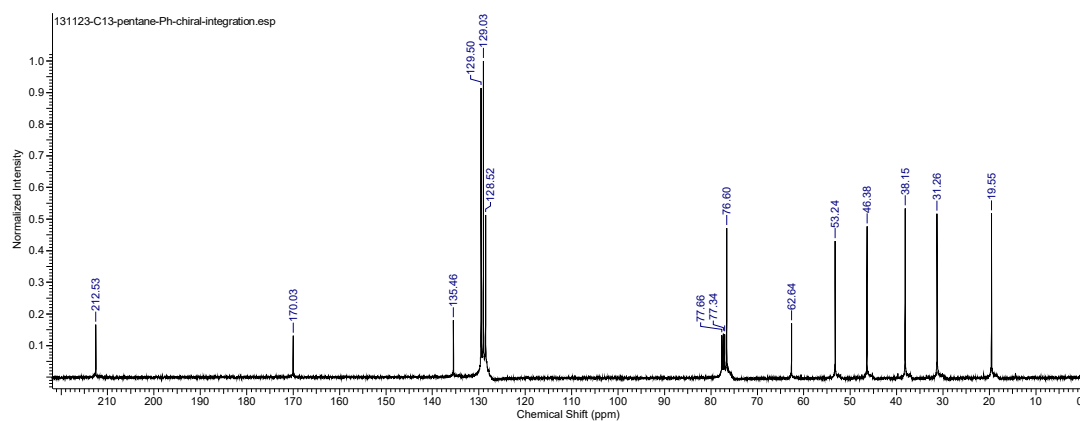
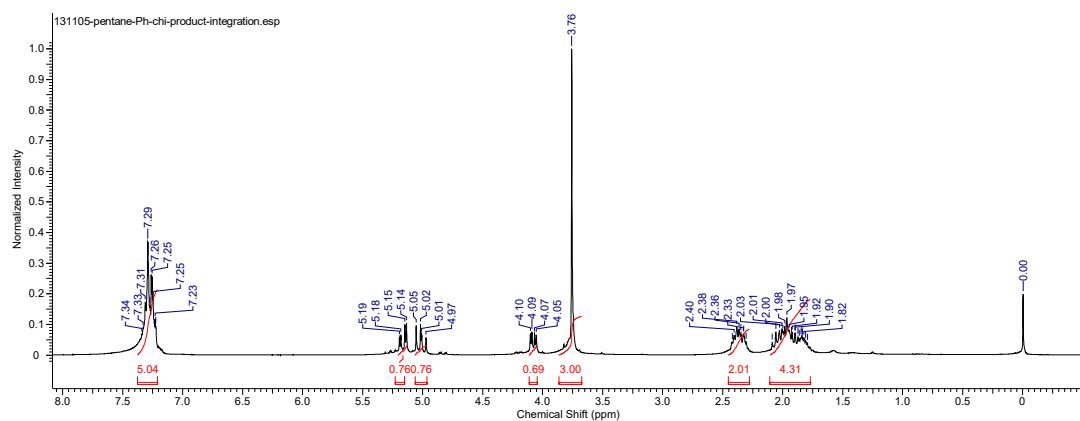
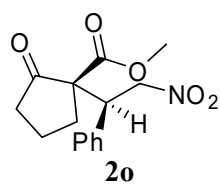
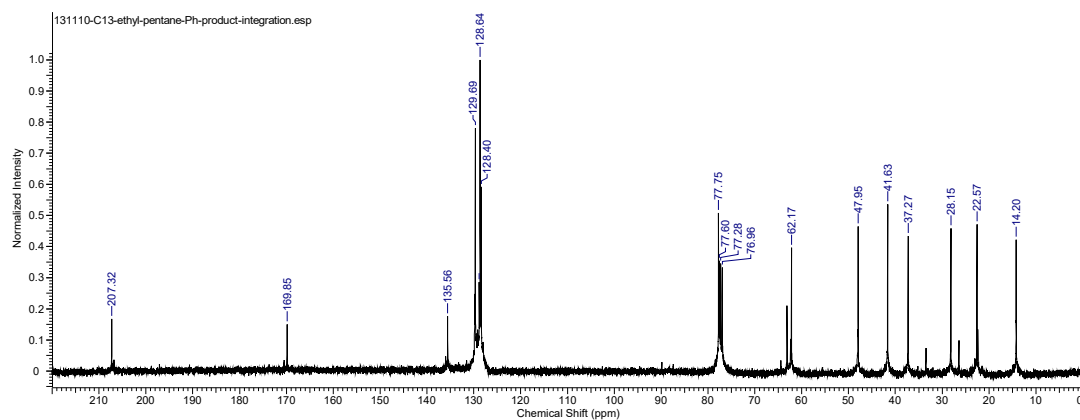


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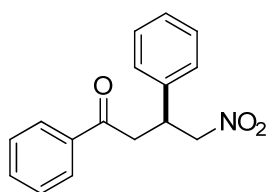
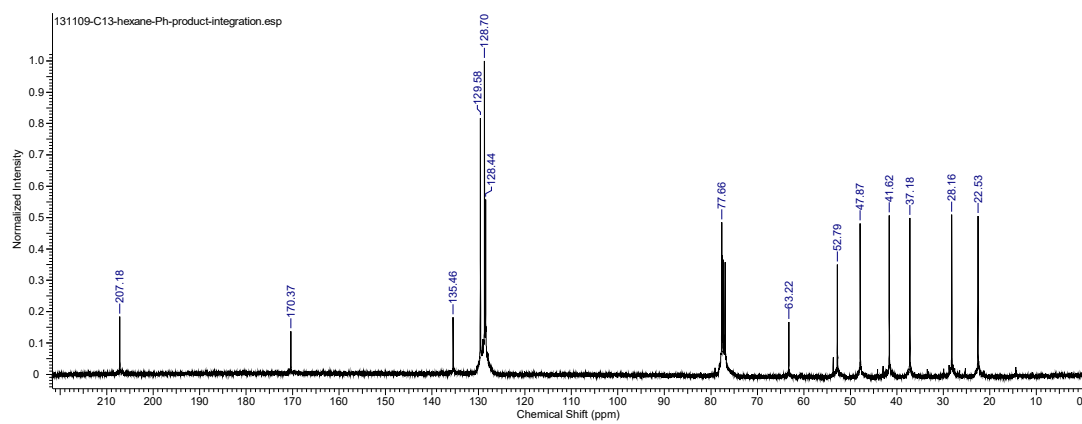
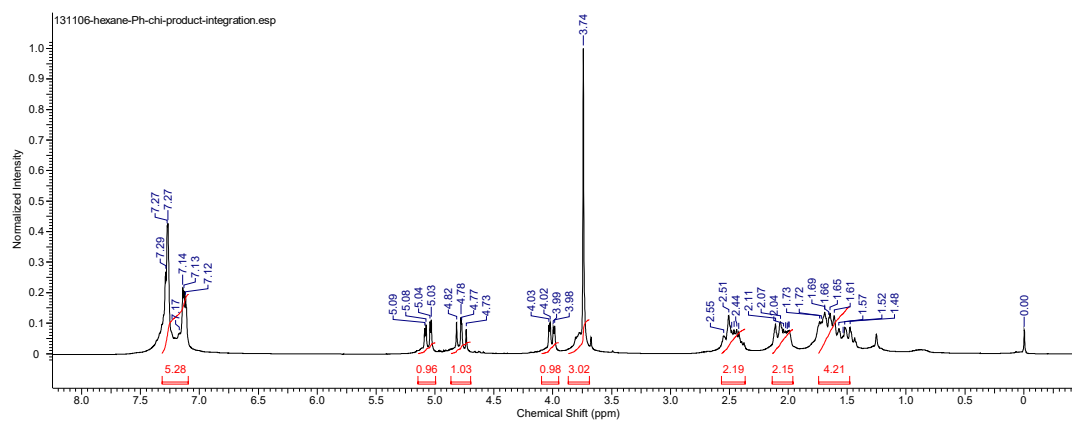




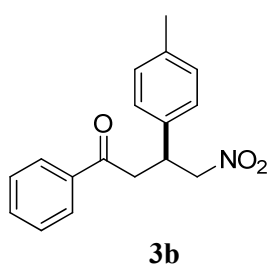
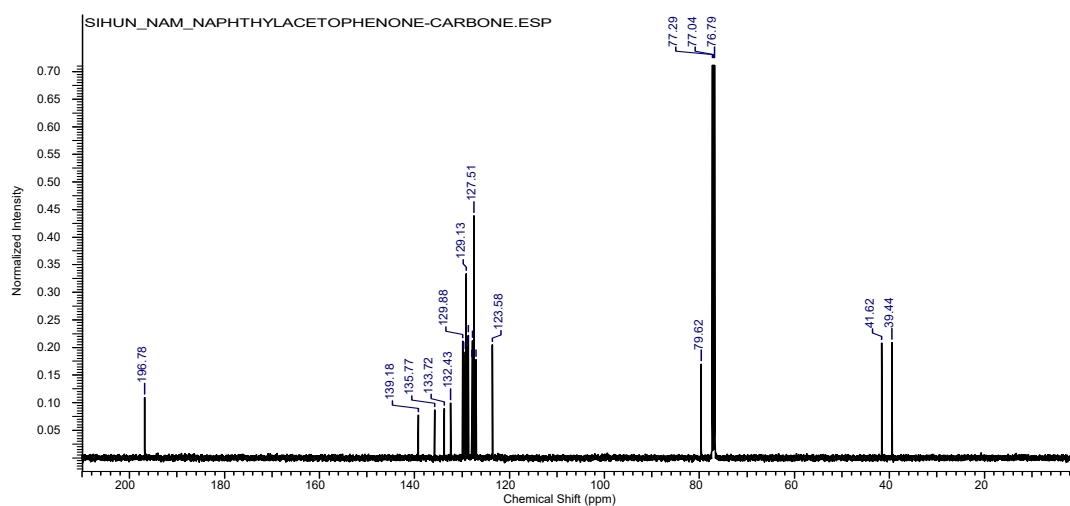
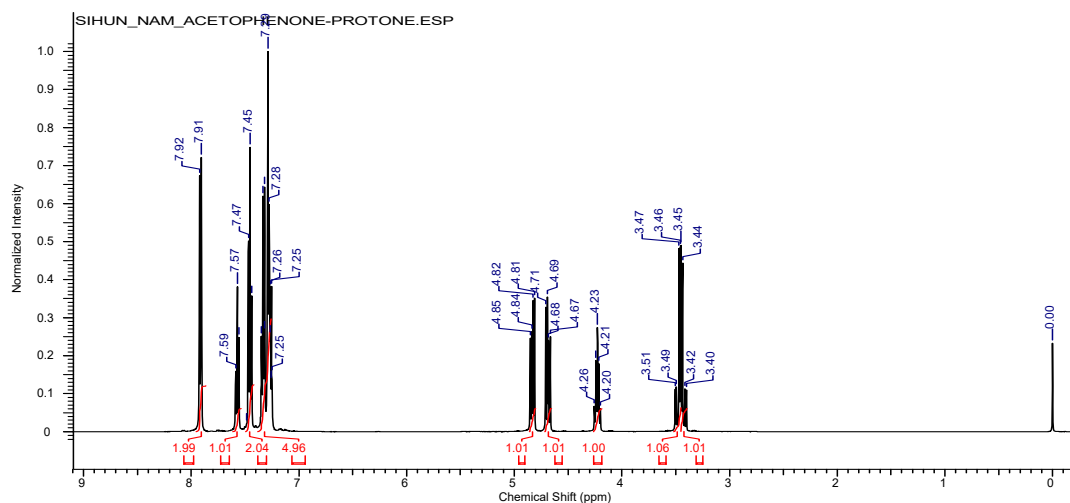


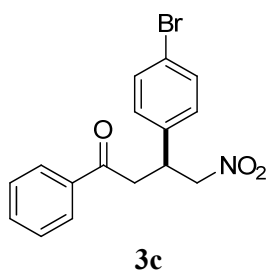
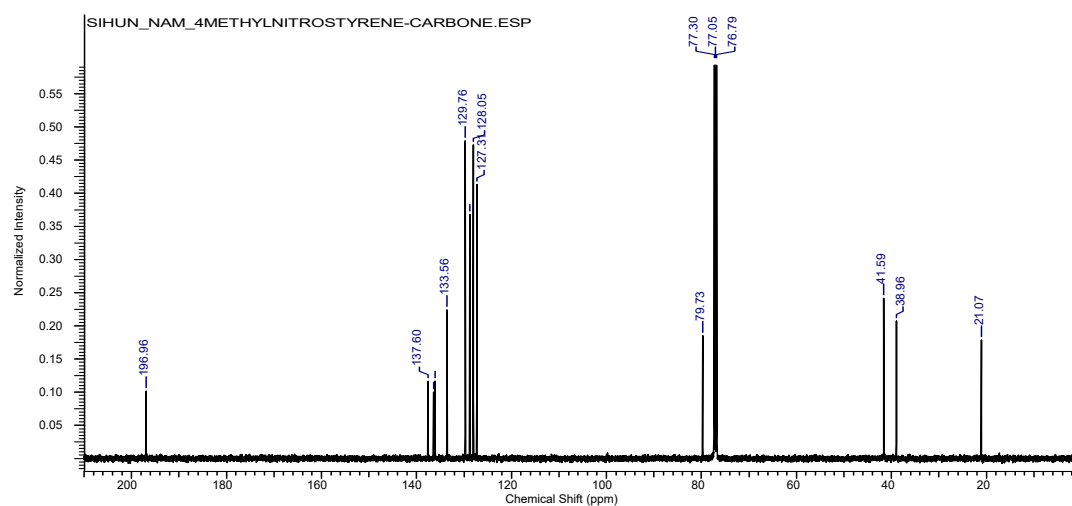
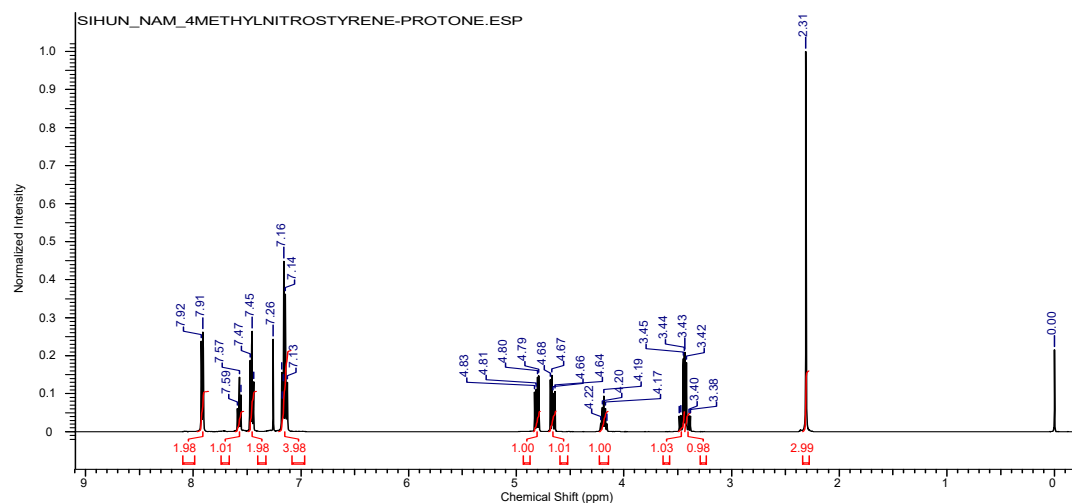


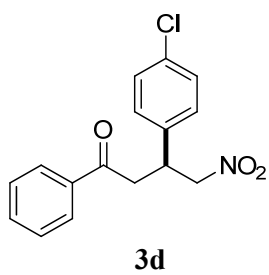
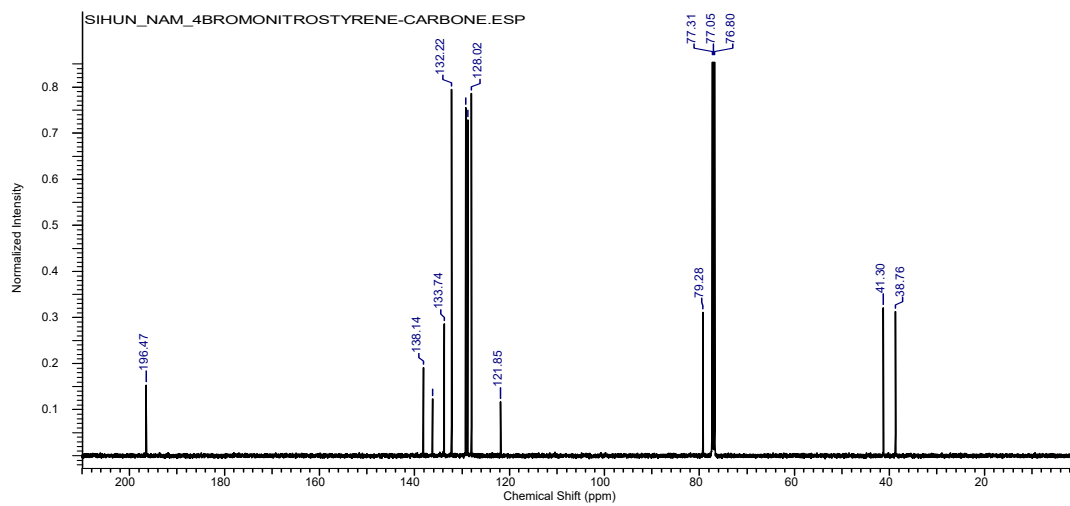
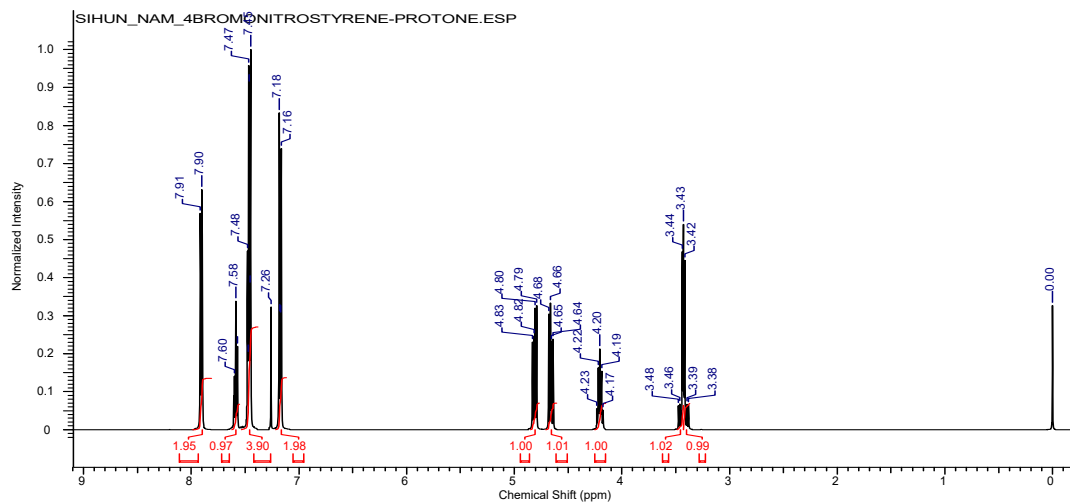
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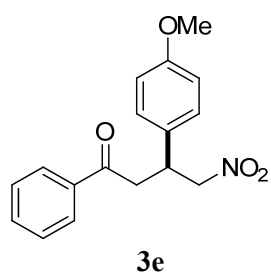
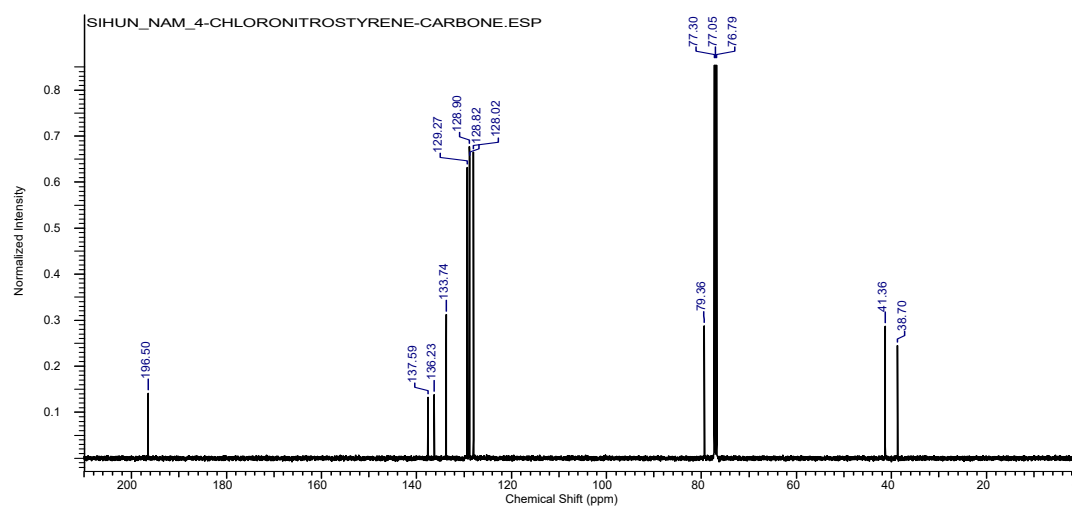
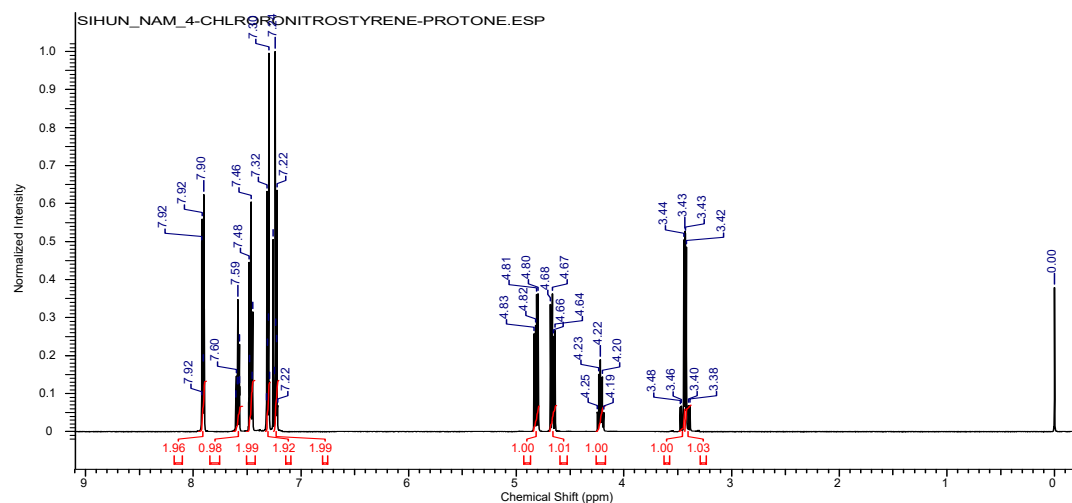


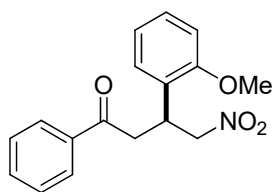
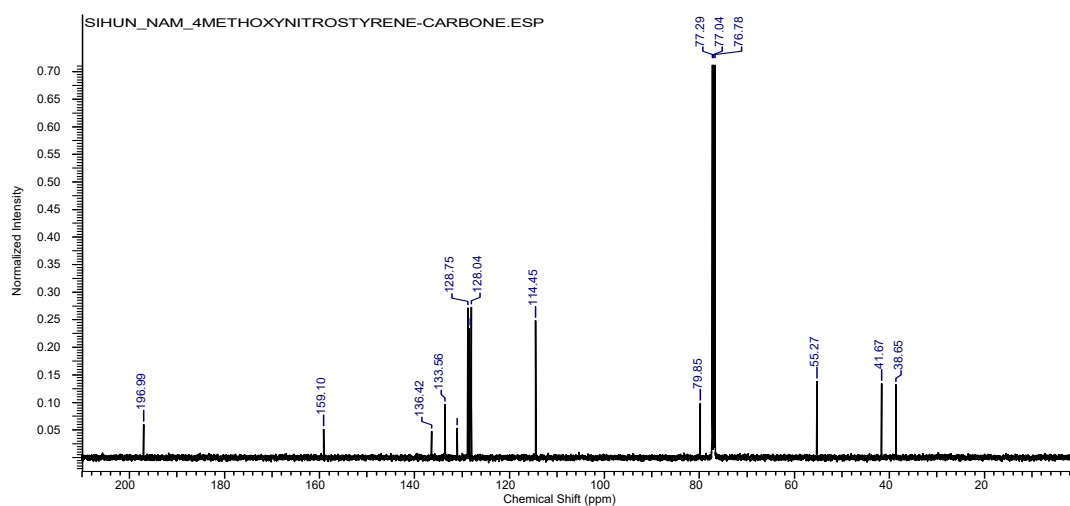
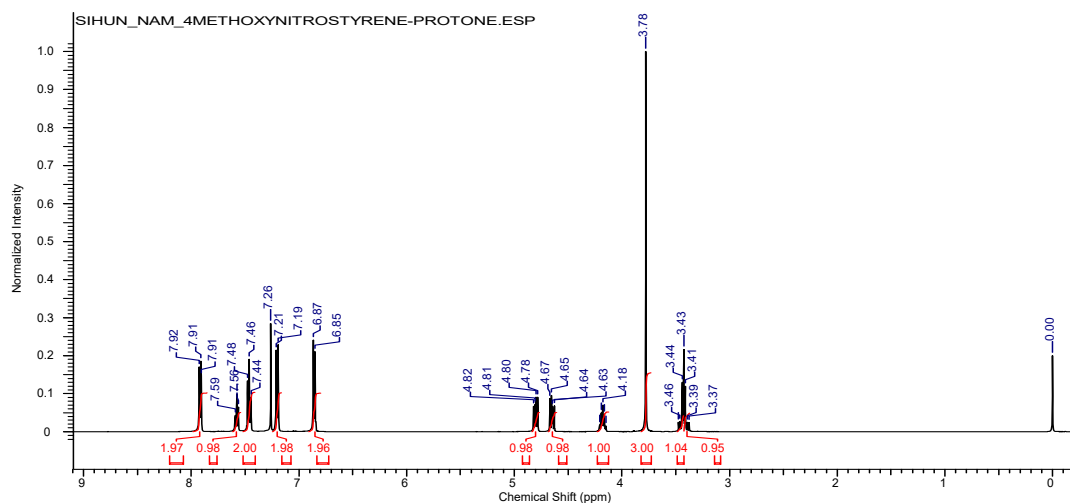
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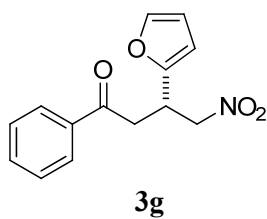
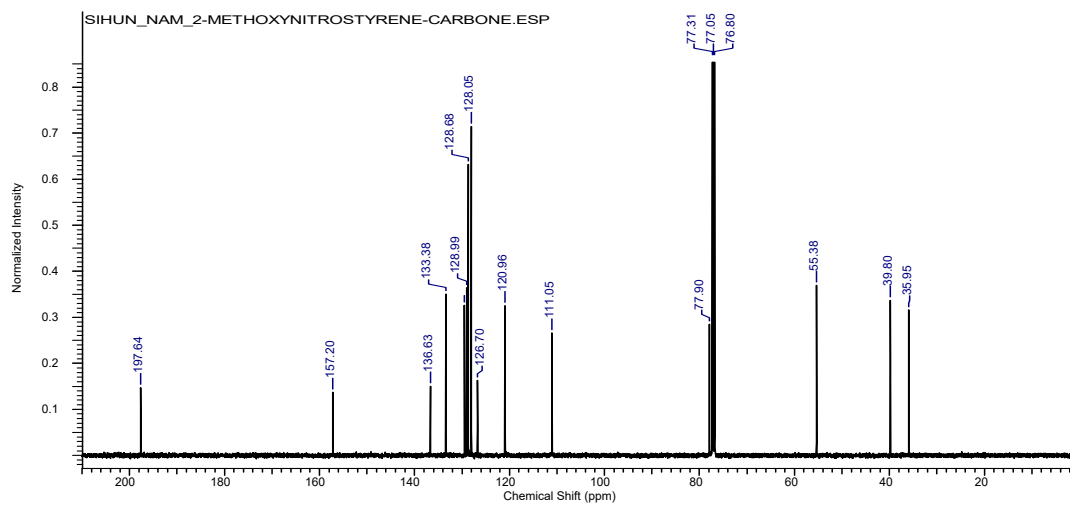
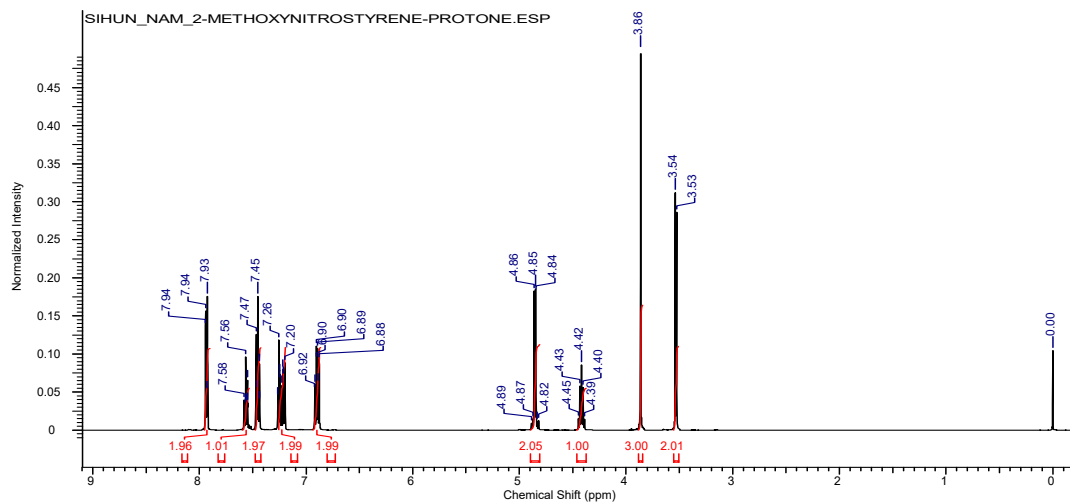


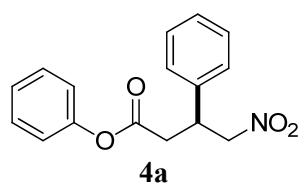
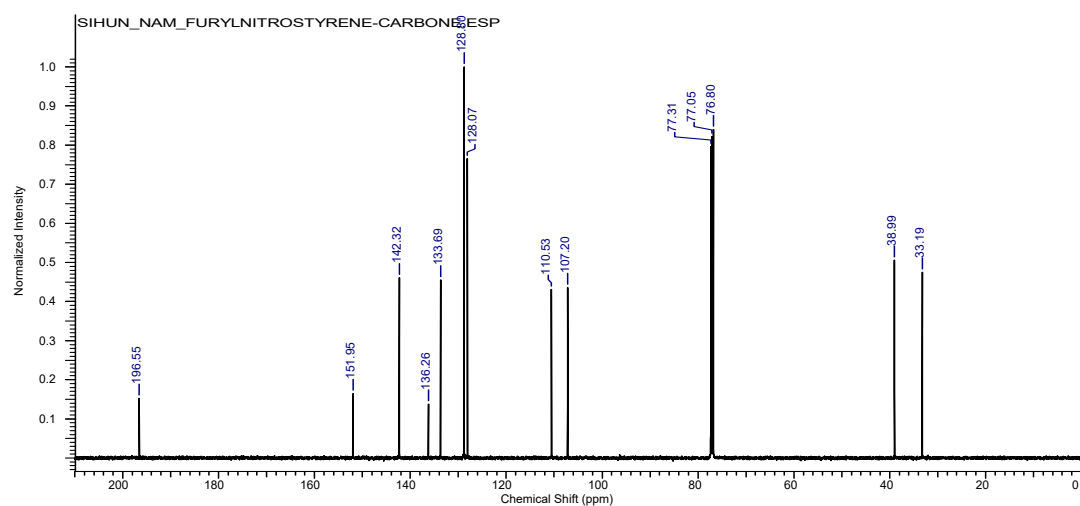
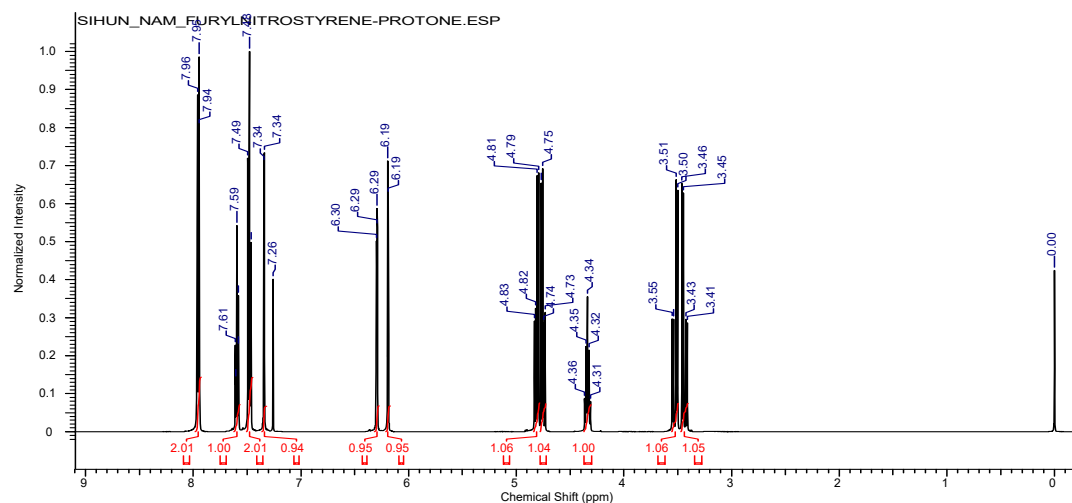


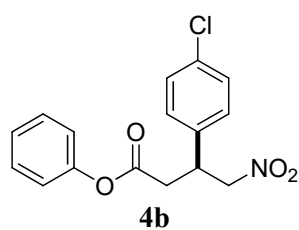
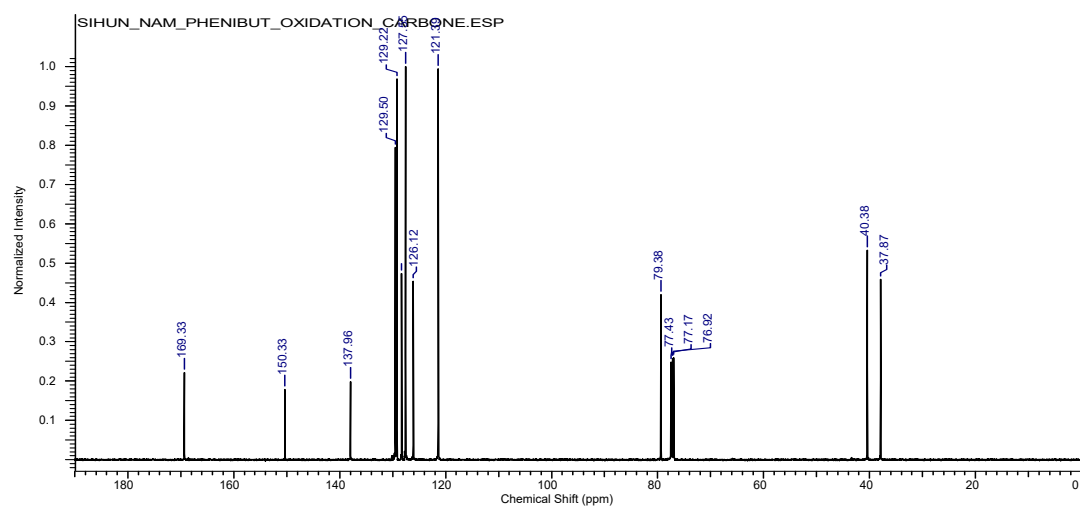
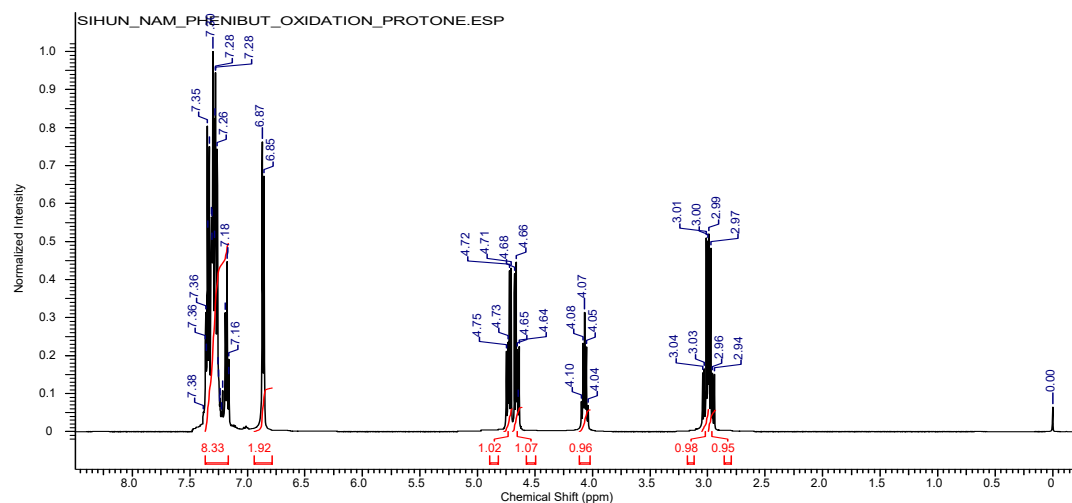


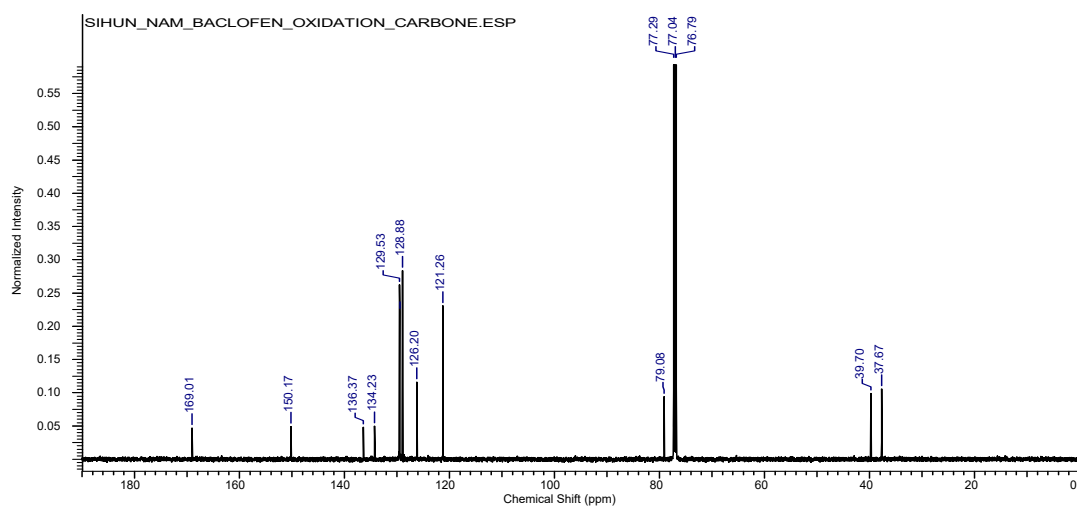
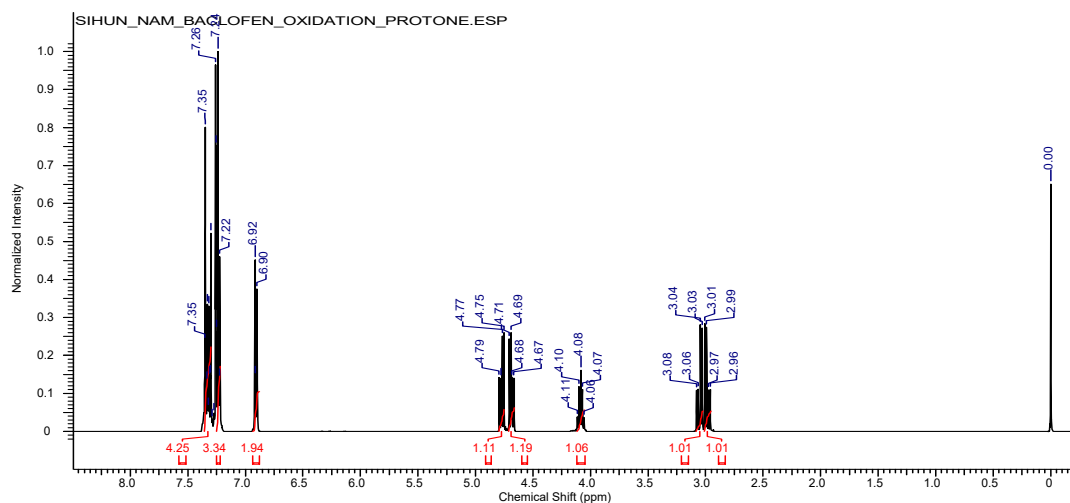


3f

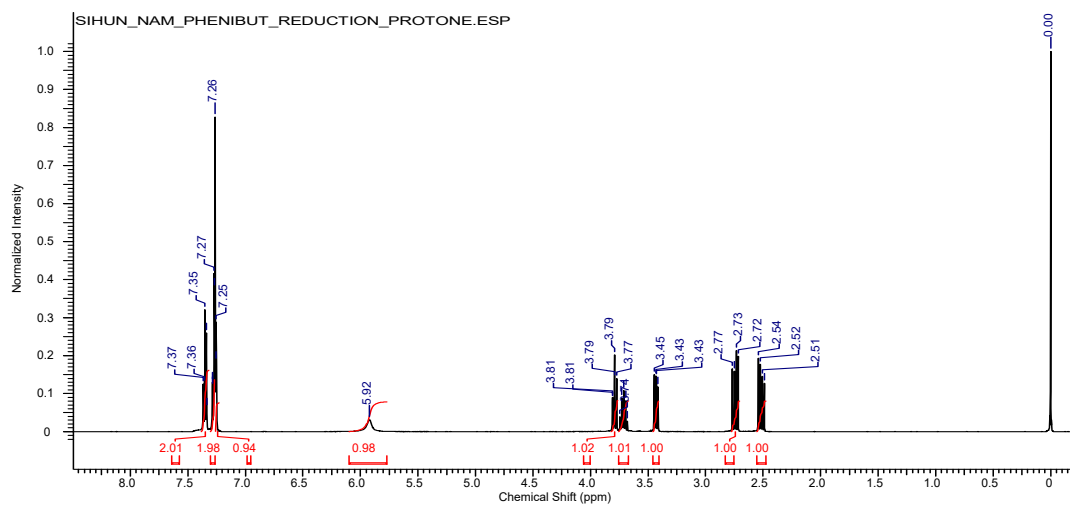


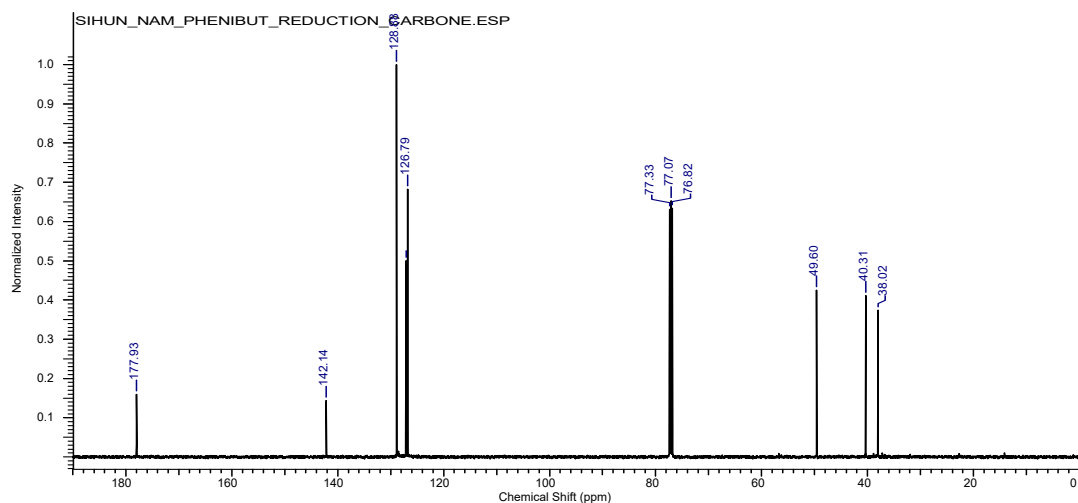




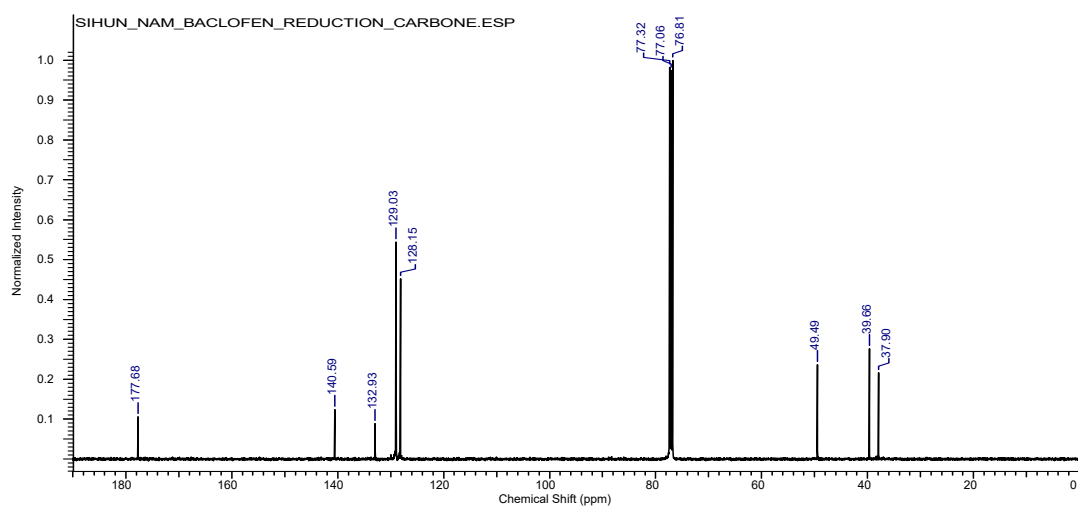
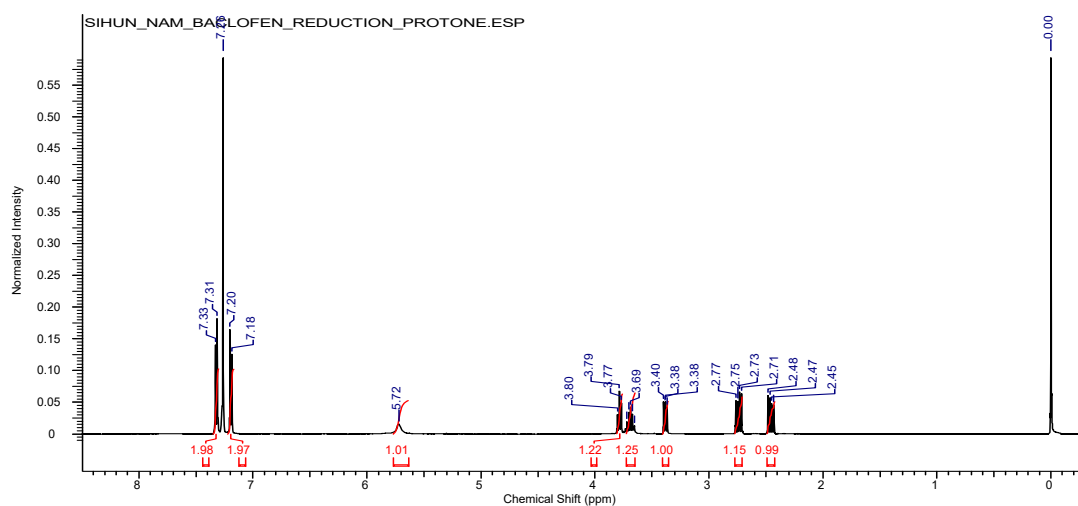


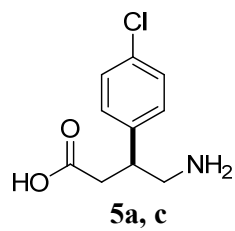
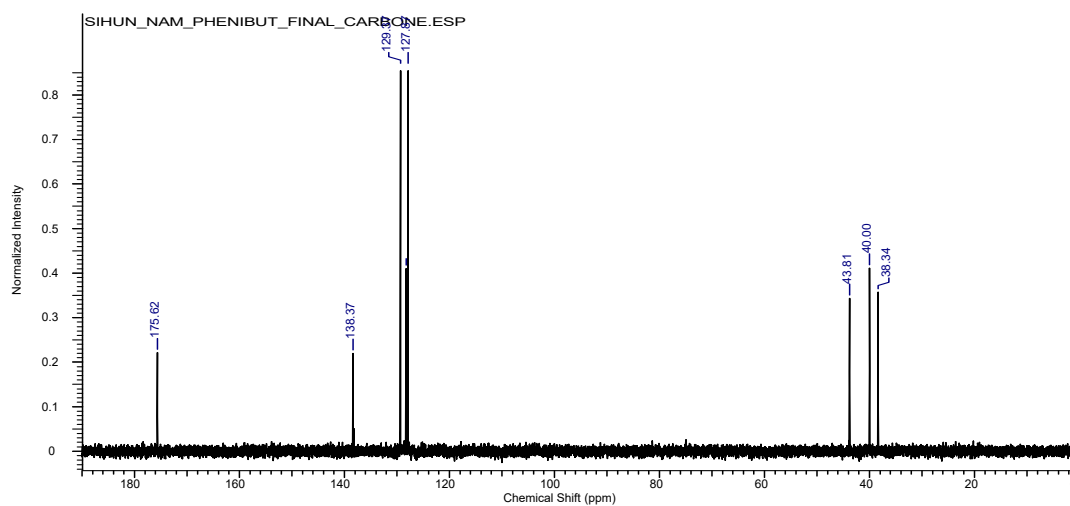
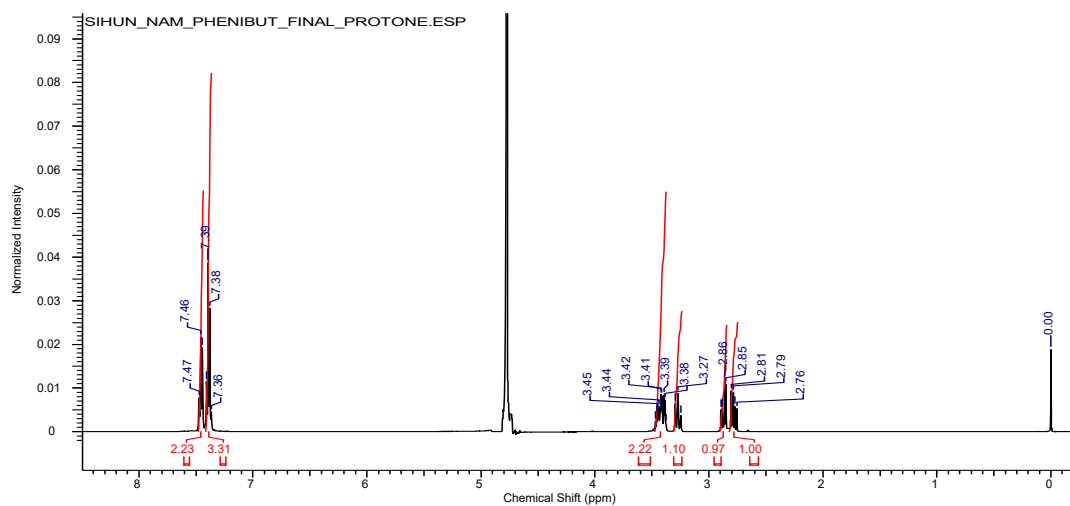
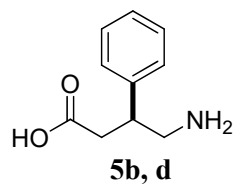
(*R* or *S*)-4-Phenylpyrrolidin-2-one(4c, 4e)

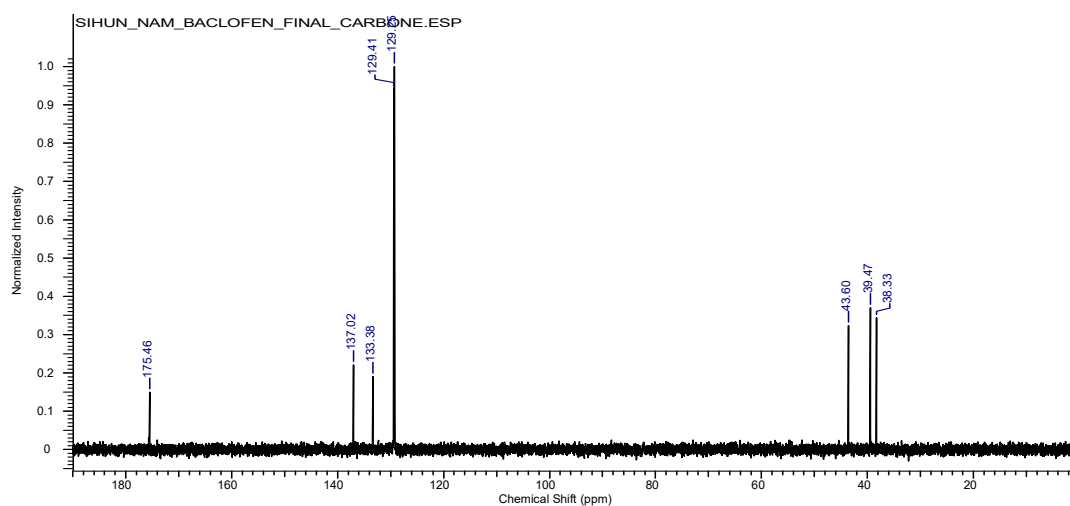
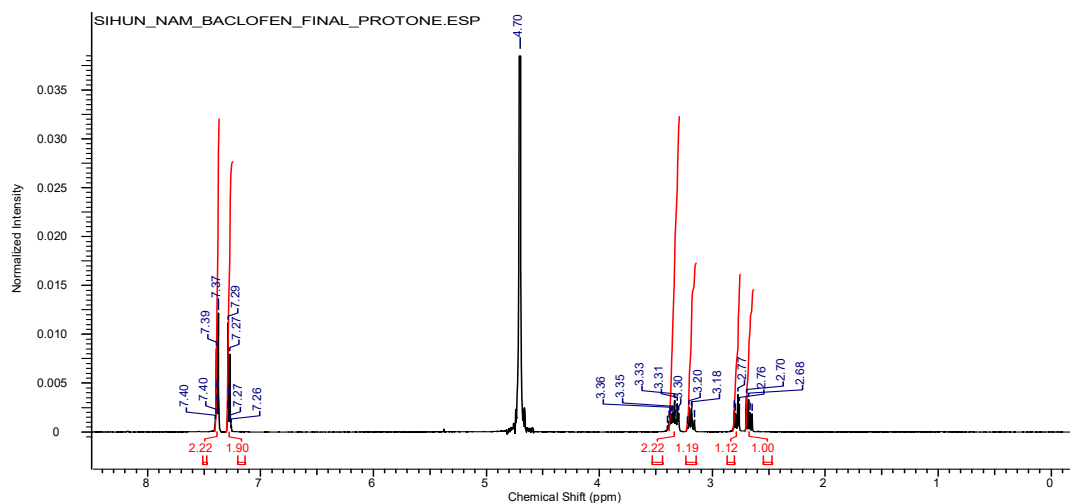




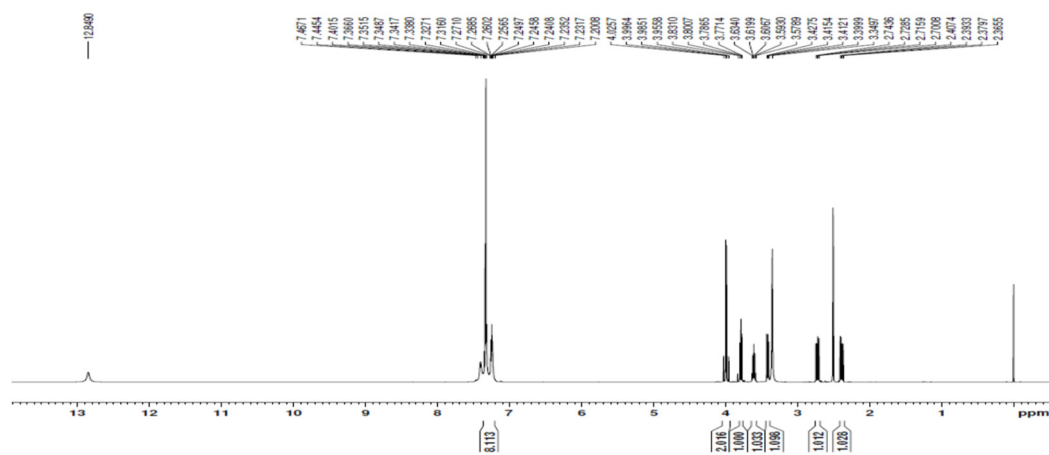
(*R* or *S*)-4-(4-Chlorophenyl)pyrrolidin-2-one (4d, 4f)

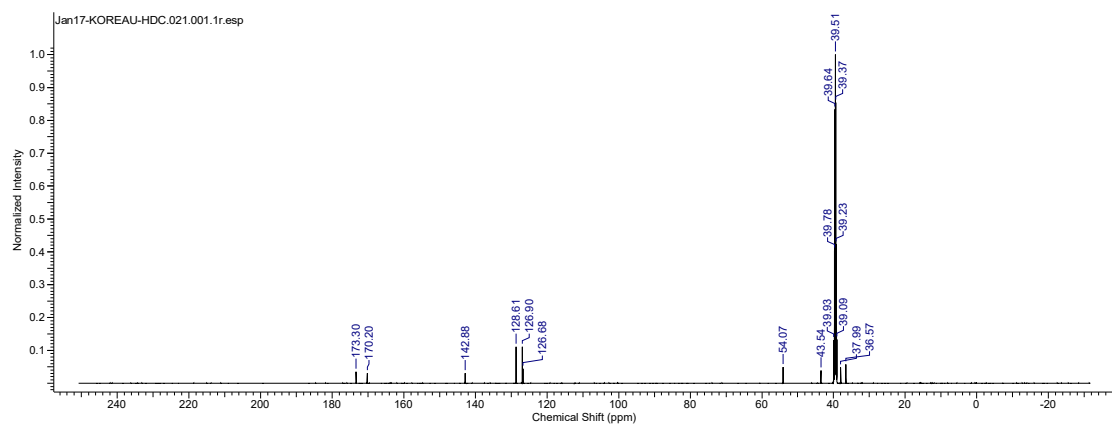






(R or S)-Phenylpiracetam(5e, f)



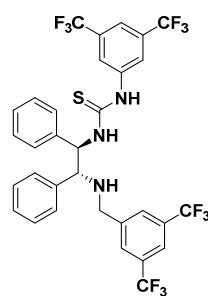
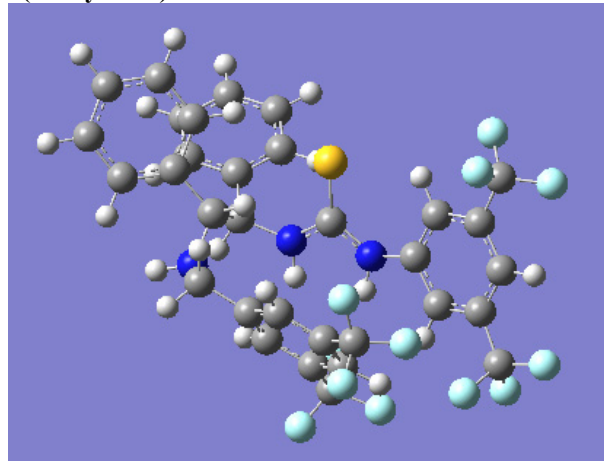


Computational Results of DFT Calculations for all Calculated Structures

Results of DFT Calculations and Discussion

Density functional theory(DFT) calculations were performed with the Gaussian 16 and Gauss-View 6.0 programs. DFT computations were performed to show the mechanism of the substrates and catalysis. B3LYP/6-31G(d,p)-calculated transition state of the DPEN-thiourea-catalyzed enantioselective Michael reaction. Transition state structures for the C–C bond formation, through which the main product (*R* or *S*) is possibly formed, are also shown.. The geometries of the reactants, intermediates (IM), transition states (TS). The temperature-dependent enthalpy corrections and the entropy effects are computed at 298 K and 1 atm of pressure

1(catalyst 1m)



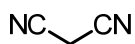
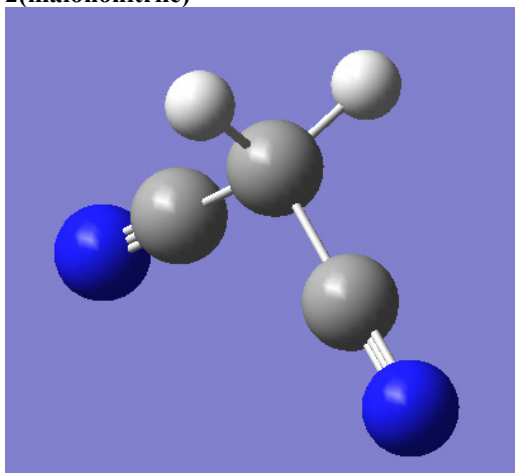
Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-5.51804	-1.90252	0.49784
C	-4.52694	-0.92761	0.66864
C	-4.72903	0.08481	1.61809
C	-5.89609	0.12257	2.38076
C	-6.87971	-0.85451	2.20577
C	-6.6883	-1.86385	1.26062
H	-5.39522	-2.68453	-0.24285
H	-3.96768	0.84793	1.74045
H	-6.03764	0.91179	3.11038
H	-7.78627	-0.82846	2.79964
H	-7.44901	-2.62322	1.11629
C	-4.32266	1.02503	-1.55162
C	-5.63206	0.65918	-1.89917
C	-6.62955	1.62295	-2.04226
C	-6.32742	2.97378	-1.85342
C	-5.0249	3.34589	-1.51794
C	-4.02677	2.3795	-1.36876
H	-5.87329	-0.38872	-2.04232
H	-7.6382	1.32112	-2.30121
H	-7.09934	3.72647	-1.96654
H	-4.78068	4.39137	-1.36739
H	-3.02715	2.66858	-1.07783

C	-3.22233	-0.93177	-0.12824
C	-3.27477	-0.08203	-1.45688
N	-1.89886	0.33479	-1.849
N	-2.7184	-2.27859	-0.5043
H	-3.53542	-0.80788	-2.23381
H	-2.46276	-0.46413	0.49821
H	-3.43699	-2.82396	-0.99002
H	-1.63245	-0.03773	-2.76664
C	-0.91949	0.88302	-1.08778
C	1.78154	2.39795	-0.55994
C	3.05303	2.74768	-0.11892
C	4.14004	1.89514	-0.27046
C	3.93035	0.66968	-0.88928
C	2.67232	0.29943	-1.35087
C	1.5748	1.15408	-1.17254
H	0.96144	3.08398	-0.42703
H	5.12522	2.18809	0.0624
H	2.54211	-0.66772	-1.816
N	0.32914	0.71344	-1.65499
H	0.38863	-0.02632	-2.36656
F	6.26389	0.29406	-0.99869
F	4.91066	-1.15723	-2.03392
F	5.06082	-1.14307	0.17064
F	3.06293	3.96191	1.93574
F	4.52324	4.52428	0.37843
F	2.35056	4.99144	0.11615
C	5.03667	-0.31718	-0.9548
C	3.24357	4.0518	0.5759
C	-2.12866	-3.03927	0.63078
C	-0.64483	-2.71686	0.74633
C	0.27034	-3.31558	-0.12524
C	-0.17298	-1.77249	1.66211
C	1.62242	-2.98153	-0.06803
H	-0.06837	-4.05184	-0.8438
C	1.17942	-1.43634	1.69866
H	-0.85654	-1.26414	2.32943
C	2.09148	-2.0358	0.84123
H	3.13114	-1.74099	0.84237
H	-2.63455	-2.83032	1.58464
H	-2.2473	-4.10765	0.41937
C	1.66446	-0.42279	2.67955
C	2.56765	-3.56672	-1.04699
F	2.13909	-1.00714	3.8359
F	2.70574	0.3032	2.14994
F	0.65709	0.43162	3.04702
F	2.61928	-2.83347	-2.24594
F	2.16424	-4.83422	-1.44998
F	3.84779	-3.63205	-0.58698
S	-1.15826	1.67832	0.44457

2(malononitrile)

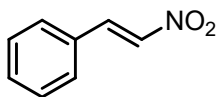
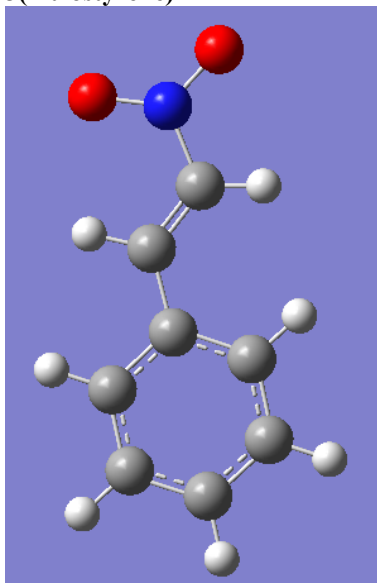


Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	0.	1.21914	0.06229
C	0.	0.	0.729
C	0.	-1.21914	0.06229
N	0.	2.25282	-0.49548
N	0.	-2.25282	-0.49548
H	0.86082	0.	1.36453
H	-0.86082	0.	1.36453

3(nitrostyrene)



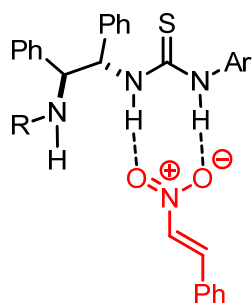
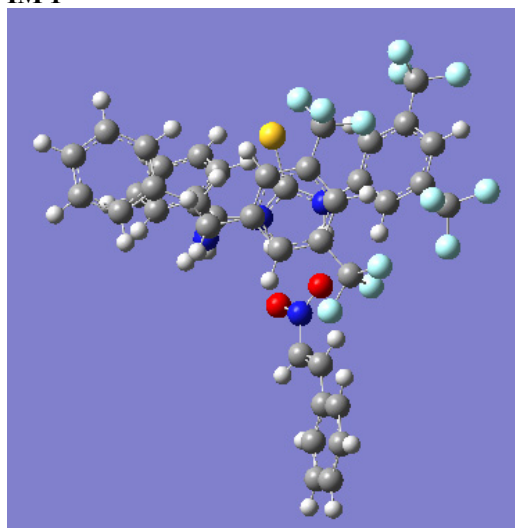
Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

O	1.76001	-1.37716	-1.98564
O	3.19823	-1.11784	-0.47478
N	2.64614	-1.84859	-1.29
C	3.02612	-3.24943	-1.44281
C	3.98661	-3.84953	-0.71215
H	4.55649	-3.30056	0.05538
C	4.32701	-5.25174	-0.89146
C	5.35038	-5.81206	-0.11593
C	3.65025	-6.05169	-1.82031
C	5.687	-7.15035	-0.27298

H	5.8857	-5.19524	0.6162
C	3.9914	-7.38882	-1.97192
H	2.84485	-5.60325	-2.42362
C	5.00976	-7.93918	-1.19895
H	6.48748	-7.58613	0.33496
H	3.45723	-8.00967	-2.69941
H	5.27819	-8.99461	-1.31863
H	2.46517	-3.83548	-2.2003

IM 1



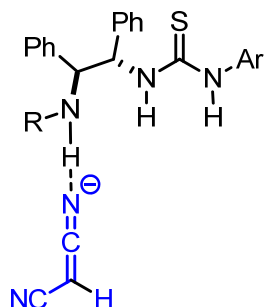
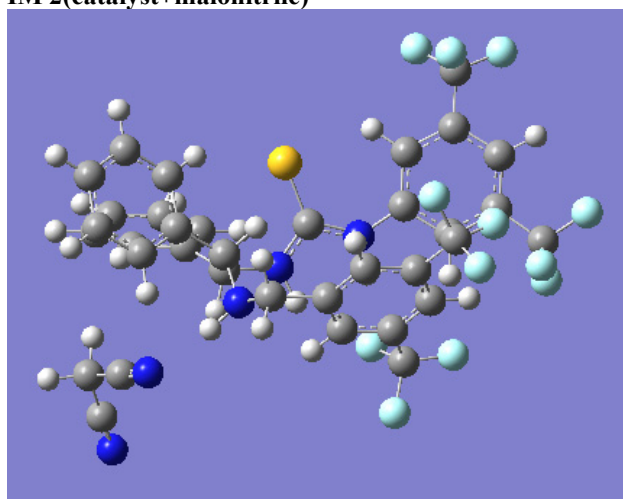
Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	4.09992	-3.08706	2.1835
C	2.80501	-3.28171	1.68628
C	2.18559	-4.52544	1.87792
C	2.84543	-5.55279	2.55191
C	4.13667	-5.35055	3.0465
C	4.76197	-4.11689	2.85727
H	4.60853	-2.14179	2.0318
H	1.18814	-4.68079	1.48051
H	2.35334	-6.50859	2.69171
H	4.65009	-6.14696	3.57313
H	5.76554	-3.95384	3.23466
C	2.63919	-3.515	-1.26366
C	4.00387	-3.84116	-1.24332
C	4.47002	-5.00479	-1.85406
C	3.57638	-5.85537	-2.5095
C	2.21923	-5.53196	-2.54279
C	1.75138	-4.36892	-1.92564
H	4.70151	-3.18669	-0.7317
H	5.52647	-5.24614	-1.81962
H	3.9351	-6.75952	-2.98806
H	1.51739	-6.18642	-3.04721
H	0.6958	-4.13826	-1.92614
C	2.03037	-2.18478	0.95572
C	2.2105	-2.20197	-0.61188
N	1.04656	-1.53935	-1.26516
N	2.32824	-0.79893	1.40293
H	3.02484	-1.49489	-0.79981
H	0.97099	-2.36443	1.13883
H	3.33412	-0.60602	1.37631
H	1.3292	-0.71681	-1.80863

C	-0.27868	-1.71208	-1.03478
C	-3.34589	-1.48013	-1.67325
C	-4.70752	-1.20638	-1.60597
C	-5.18427	0.06377	-1.30463
C	-4.25893	1.07392	-1.07661
C	-2.89197	0.83125	-1.14947
C	-2.41748	-0.45838	-1.42965
H	-3.01136	-2.47645	-1.91053
H	-6.24531	0.26466	-1.27248
H	-2.19945	1.63781	-0.95308
N	-1.02299	-0.63594	-1.47917
H	-0.49105	0.2313	-1.62767
F	-5.98129	2.69602	-1.10339
F	-3.86161	3.40751	-1.00361
F	-4.81757	2.48566	0.76251
F	-6.00156	-2.97017	-0.65172
F	-6.86022	-1.83413	-2.33877
F	-5.17001	-3.26112	-2.6771
C	-4.72676	2.40904	-0.6286
C	-5.67898	-2.31611	-1.81707
C	1.74004	-0.45367	2.72567
C	0.33702	0.10555	2.53112
C	0.16388	1.4288	2.11315
C	-0.79623	-0.69677	2.68976
C	-1.11366	1.93221	1.87347
H	1.02509	2.07277	1.9838
C	-2.06718	-0.18528	2.4321
H	-0.69901	-1.73484	2.97949
C	-2.24274	1.13033	2.02622
H	-3.22514	1.51052	1.78509
H	1.71067	-1.31404	3.41001
H	2.37093	0.3148	3.18573
C	-3.26509	-1.05751	2.60219
C	-1.27707	3.31154	1.35865
F	-3.84131	-0.90868	3.84706
F	-4.2331	-0.735	1.67984
F	-2.93568	-2.38176	2.46919
F	-1.1818	3.3749	-0.04303
F	-0.25512	4.14427	1.79897
F	-2.47661	3.8689	1.68282
S	-0.99409	-3.08962	-0.2422
C	2.47141	3.00452	-1.542
C	1.90445	4.0025	-0.82864
O	2.35031	0.82755	-2.38649
O	0.47391	1.78253	-1.50111
N	1.72677	1.83195	-1.81872
C	2.54101	5.23864	-0.43201
C	1.81579	6.09876	0.42448
C	3.83763	5.61733	-0.85293
C	2.36162	7.31166	0.83016
H	0.85054	5.77518	0.79209
C	4.37195	6.83184	-0.4427
H	4.4329	4.9654	-1.48225
C	3.63537	7.68407	0.39133
H	1.80082	7.96304	1.48898
H	5.3642	7.1186	-0.76862
H	4.05971	8.63101	0.70355
H	3.48147	2.98117	-1.91021
H	0.8751	3.85369	-0.51937

IM 2(catalyst+malonitrile)



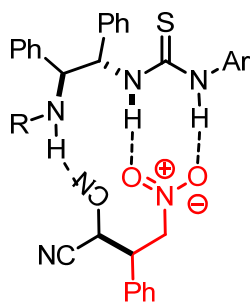
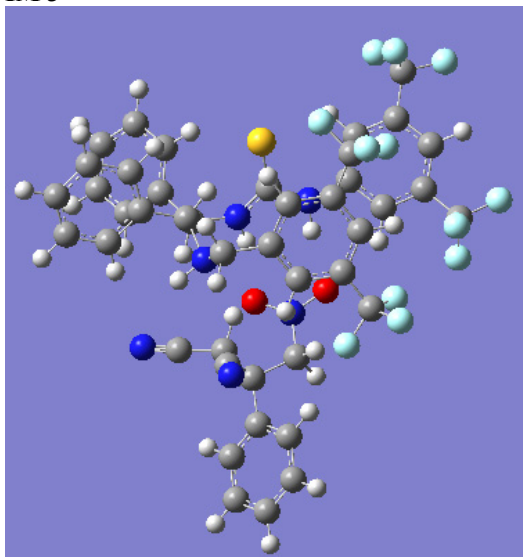
Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	4.09992	-3.08706	2.1835
C	2.80501	-3.28171	1.68628
C	2.18559	-4.52544	1.87792
C	2.84543	-5.55279	2.55191
C	4.13667	-5.35055	3.0465
C	4.76197	-4.11689	2.85727
H	4.60853	-2.14179	2.0318
H	1.18814	-4.68079	1.48051
H	2.35334	-6.50859	2.69171
H	4.65009	-6.14696	3.57313
H	5.76554	-3.95384	3.23466
C	2.63919	-3.515	-1.26366
C	4.00387	-3.84116	-1.24332
C	4.47002	-5.00479	-1.85406
C	3.57638	-5.85537	-2.5095
C	2.21923	-5.53196	-2.54279
C	1.75138	-4.36892	-1.92564
H	4.70151	-3.18669	-0.7317
H	5.52647	-5.24614	-1.81962
H	3.9351	-6.75952	-2.98806
H	1.51739	-6.18642	-3.04721
H	0.6958	-4.13826	-1.92614
C	2.03037	-2.18478	0.95572
C	2.2105	-2.20197	-0.61188
N	1.04656	-1.53935	-1.26516
N	2.32824	-0.79893	1.40293
H	3.02484	-1.49489	-0.79981
H	0.97099	-2.36443	1.13883
H	3.33412	-0.60602	1.37631
H	1.3292	-0.71681	-1.80863
C	-0.27868	-1.71208	-1.03478
C	-3.34589	-1.48013	-1.67325
C	-4.70752	-1.20638	-1.60597
C	-5.18427	0.06377	-1.30463
C	-4.25893	1.07392	-1.07661
C	-2.89197	0.83125	-1.14947
C	-2.41748	-0.45838	-1.42965
H	-3.01136	-2.47645	-1.91053
H	-6.24531	0.26466	-1.27248
H	-2.19945	1.63781	-0.95308

N	-1.02299	-0.63594	-1.47917
H	-0.49105	0.2313	-1.62767
F	-5.98129	2.69602	-1.10339
F	-3.86161	3.40751	-1.00361
F	-4.81757	2.48566	0.76251
F	-6.00156	-2.97017	-0.65172
F	-6.86022	-1.83413	-2.33877
F	-5.17001	-3.26112	-2.6771
C	-4.72676	2.40904	-0.6286
C	-5.67898	-2.31611	-1.81707
C	1.74004	-0.45367	2.72567
C	0.33702	0.10555	2.53112
C	0.16388	1.4288	2.11315
C	-0.79623	-0.69677	2.68976
C	-1.11366	1.93221	1.87347
H	1.02509	2.07277	1.9838
C	-2.06718	-0.18528	2.4321
H	-0.69901	-1.73484	2.97949
C	-2.24274	1.13033	2.02622
H	-3.22514	1.51052	1.78509
H	1.71067	-1.31404	3.41001
H	2.37093	0.3148	3.18573
C	-3.26509	-1.05751	2.60219
C	-1.27707	3.31154	1.35865
F	-3.84131	-0.90868	3.84706
F	-4.2331	-0.735	1.67984
F	-2.93568	-2.38176	2.46919
F	-1.1818	3.3749	-0.04303
F	-0.25512	4.14427	1.79897
F	-2.47661	3.8689	1.68282
S	-0.99409	-3.08962	-0.2422
C	5.47842	0.10207	-0.71714
C	5.43973	0.64252	-2.07628
H	4.39077	0.58399	-2.41957
N	5.44927	-0.3372	0.35871
C	5.83212	2.05145	-2.12411
N	6.07357	3.1884	-2.1672
H	6.07142	0.04355	-2.7436

IM 3



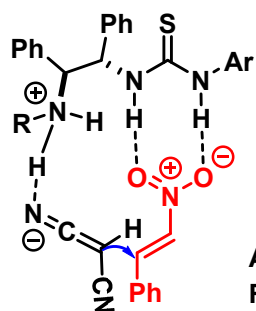
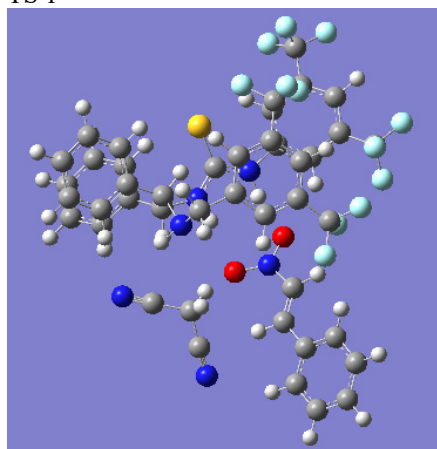
Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-4.16349	3.4134	1.2075
C	-2.76927	3.46648	1.37128
C	-2.21816	4.5019	2.13559
C	-3.03851	5.46198	2.73347
C	-4.42264	5.39741	2.57122
C	-4.98246	4.37207	1.80335
H	-4.62028	2.63489	0.60239
H	-1.14121	4.56135	2.24977
H	-2.59606	6.257	3.32258
H	-5.06137	6.14054	3.0342
H	-6.05635	4.32249	1.66461
C	-2.0202	3.76168	-1.46065
C	-3.2318	4.02349	-2.11592
C	-3.44989	5.24513	-2.75485
C	-2.45155	6.22042	-2.75157
C	-1.23903	5.96398	-2.10674
C	-1.02177	4.74454	-1.46392
H	-4.01164	3.26808	-2.12272
H	-4.39382	5.43169	-3.25408
H	-2.61559	7.16993	-3.24814
H	-0.45742	6.71521	-2.10303
H	-0.08013	4.54101	-0.97167
C	-1.86323	2.39768	0.77674
C	-1.84707	2.40248	-0.78618
N	-0.69066	1.62057	-1.32341
N	-2.27659	1.0155	1.25036
H	-2.71168	1.80329	-1.09065
H	-0.84032	2.57251	1.10807
H	-3.29936	1.03764	1.36219
H	-0.99332	0.92251	-2.00629
C	0.62359	1.63163	-0.99724
C	3.72661	1.14567	-1.42795
C	5.02987	0.69632	-1.24495
C	5.31627	-0.64863	-1.04165
C	4.26226	-1.5517	-1.02291
C	2.94954	-1.12882	-1.20353
C	2.66847	0.22932	-1.3953
H	3.537	2.19333	-1.59582
H	6.33577	-0.98511	-0.92269
H	2.14757	-1.85194	-1.1556
N	1.31495	0.59031	-1.58768
H	0.76131	-0.14833	-2.0342
F	5.81337	-3.33436	-0.98126
F	3.66676	-3.81604	-1.37721
F	4.32753	-3.2514	0.65375
F	6.38833	2.18785	0.02871
F	7.31456	1.10908	-1.66092
F	5.85459	2.76348	-2.0357
C	4.51785	-2.9786	-0.70222
C	6.14174	1.68803	-1.22778
C	-1.69142	0.66201	2.59798
C	-0.39469	-0.10855	2.42662
C	-0.44482	-1.432	1.9765
C	0.85285	0.47455	2.64732
C	0.72588	-2.13374	1.70953
H	-1.39989	-1.91908	1.84529
C	2.02119	-0.24709	2.39889
H	0.93351	1.50205	2.97391

C	1.97495	-1.54537	1.91128
H	2.8838	-2.06831	1.64696
H	-1.53173	1.55492	3.21616
H	-2.42069	0.02249	3.10645
C	3.34651	0.38741	2.65653
C	0.65686	-3.51429	1.16746
F	3.83876	0.06238	3.9033
F	4.2787	-0.0439	1.7412
F	3.26199	1.75537	2.60462
F	1.38773	-3.64259	-0.00049
F	-0.6695	-3.85424	0.84133
F	1.10597	-4.48265	2.0167
S	1.41845	2.76191	0.06786
C	-2.13396	-2.86002	-1.68041
C	-3.58578	-2.48332	-1.38178
O	-2.01759	-0.60023	-2.52846
O	-0.09945	-1.80463	-2.32316
N	-1.36737	-1.66599	-2.2213
C	-4.39014	-3.73039	-1.04348
C	-3.8852	-4.71492	-0.1786
C	-5.66426	-3.89564	-1.60132
C	-4.64919	-5.84547	0.11444
H	-2.90856	-4.60312	0.2794
C	-6.42694	-5.02525	-1.3021
H	-6.06006	-3.13794	-2.26937
C	-5.91896	-6.00326	-0.44497
H	-4.25318	-6.59918	0.78425
H	-7.41186	-5.14105	-1.73832
H	-6.50873	-6.88191	-0.21278
H	-2.07587	-3.62169	-2.46311
C	-3.88305	-1.92401	1.08955
C	-3.6735	-1.3735	-0.24926
N	-3.98944	-2.32002	2.17859
H	-1.55421	-3.17913	-0.81621
C	-4.71928	-0.39338	-0.55618
N	-5.4953	0.43897	-0.80142
H	-2.74928	-0.76774	-0.17475
H	-3.99834	-2.02808	-2.28482

TS 1



Ar = 3,5-(CF₃)₂-Ph
R = 3,5-(CF₃)₂-Ph-CH₂

Symbolic Z-matrix:

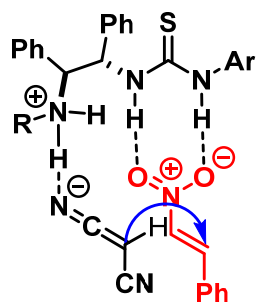
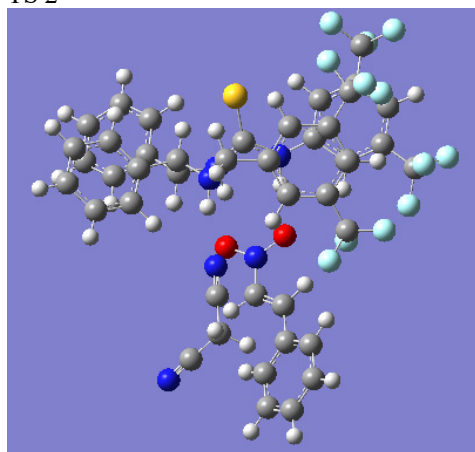
Charge = 0 Multiplicity = 1

C	-2.30021	4.78175	1.79351
C	-1.08941	4.11784	1.54788

C	0.10158	4.6923	2.01469
C	0.08386	5.89388	2.72513
C	-1.12752	6.54035	2.97683
C	-2.31782	5.98376	2.50285
H	-3.23527	4.38959	1.40776
H	1.04241	4.20221	1.78907
H	1.01425	6.3241	3.07796
H	-1.14444	7.47319	3.52865
H	-3.26078	6.48944	2.67763
C	-1.01943	4.2032	-1.44196
C	-2.19273	4.93555	-1.68382
C	-2.14456	6.17314	-2.32629
C	-0.92047	6.69374	-2.74894
C	0.24983	5.96886	-2.51739
C	0.20409	4.73381	-1.86775
H	-3.15067	4.54237	-1.36019
H	-3.06179	6.72434	-2.49998
H	-0.87947	7.6526	-3.25312
H	1.2063	6.36489	-2.83956
H	1.11489	4.18811	-1.67061
C	-1.02192	2.77972	0.81953
C	-1.16993	2.84787	-0.75023
N	-0.37972	1.73228	-1.36181
N	-2.04845	1.7753	1.29944
H	-2.20236	2.53914	-0.92783
H	-0.03921	2.35756	1.01734
H	-2.92661	2.27806	1.48057
H	-0.96842	1.06237	-1.86338
C	0.92244	1.40025	-1.17328
C	3.71151	0.11153	-1.78257
C	4.89562	-0.58613	-1.57527
C	4.89214	-1.8898	-1.09332
C	3.66985	-2.49299	-0.83433
C	2.4667	-1.8244	-1.05653
C	2.48061	-0.50355	-1.51022
H	3.74416	1.11985	-2.16076
H	5.81714	-2.42625	-0.94149
H	1.52932	-2.31036	-0.82503
N	1.24456	0.16189	-1.68231
H	0.47053	-0.44161	-1.99814
F	4.8141	-4.5109	-0.37207
F	2.59905	-4.6006	-0.63316
F	3.46675	-3.72306	1.20213
F	6.69068	0.7667	-0.74999
F	7.15621	-0.83097	-2.19808
F	6.07097	1.01454	-2.85282
C	3.64116	-3.82798	-0.19493
C	6.1971	0.0921	-1.84032
C	-1.65438	1.12925	2.59667
C	-0.6034	0.04965	2.40284
C	-0.95232	-1.22183	1.92961
C	0.74153	0.31832	2.66585
C	0.02488	-2.2032	1.74075
H	-1.98838	-1.45625	1.7215
C	1.70774	-0.65924	2.45256
H	1.05061	1.29887	3.00432
C	1.36599	-1.92425	2.00107
H	2.12959	-2.65708	1.80457
H	-1.2747	1.86665	3.31994

H	-2.55956	0.67931	3.02138
C	3.14268	-0.36218	2.72326
C	-0.36204	-3.54132	1.21351
F	3.52682	-0.75701	3.98746
F	3.94231	-1.04344	1.83541
F	3.39359	0.98212	2.62695
F	-0.14567	-3.65786	-0.17455
F	-1.72634	-3.75342	1.37652
F	0.30061	-4.59866	1.74686
S	2.10375	2.35988	-0.31204
C	-2.70419	-2.59627	-1.38173
C	-4.0519	-2.61213	-1.4325
O	-2.53431	-0.33869	-2.11953
O	-0.72831	-1.73829	-2.18703
N	-1.97241	-1.50207	-1.91649
C	-4.89956	-3.66072	-0.89826
C	-4.41393	-4.65248	-0.01548
C	-6.26032	-3.68292	-1.27692
C	-5.26018	-5.65821	0.4328
H	-3.4016	-4.59335	0.35964
C	-7.09806	-4.6989	-0.8265
H	-6.65659	-2.88124	-1.88712
C	-6.59818	-5.69388	0.01766
H	-4.88578	-6.41174	1.11498
H	-8.13923	-4.70959	-1.12407
H	-7.25108	-6.48403	0.36916
C	-4.7519	0.70497	-0.17543
H	-2.05234	-3.35638	-0.99161
C	-4.86533	2.15917	-0.0846
N	-4.9326	3.31744	-0.00591
H	-3.84842	0.43827	-0.74975
H	-4.54476	-1.79187	-1.9437
C	-5.91279	0.11711	-0.84536
N	-6.79831	-0.38379	-1.40887
H	-4.64114	0.27761	0.82813

TS 2



Ar = 3,5-(CF₃)₂-Ph
R = 3,5-(CF₃)₂-Ph-CH₂

Symbolic Z-matrix:

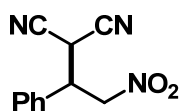
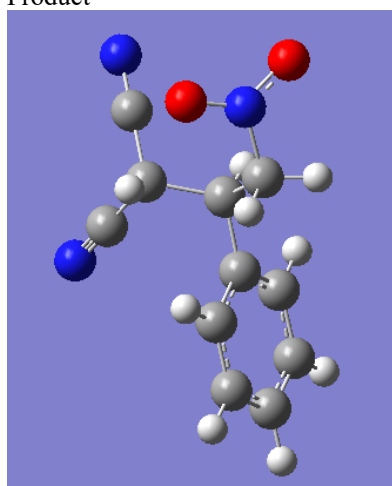
Charge = 0 Multiplicity = 1

C	-4.10702	2.80325	1.60073
C	-2.94523	3.54973	1.36493
C	-2.95906	4.92187	1.65167
C	-4.10602	5.5348	2.15728
C	-5.26178	4.78309	2.38245

C	-5.25832	3.41523	2.10203
H	-4.11148	1.7357	1.41124
H	-2.0689	5.51156	1.46457
H	-4.09776	6.59693	2.374
H	-6.15349	5.25731	2.7762
H	-6.15008	2.82387	2.27947
C	-1.83035	4.37738	-1.33501
C	-3.10523	4.80723	-1.72663
C	-3.29721	6.08579	-2.25248
C	-2.21082	6.95065	-2.39818
C	-0.93604	6.52716	-2.014
C	-0.74344	5.24867	-1.48695
H	-3.95318	4.141	-1.60948
H	-4.29053	6.40329	-2.5488
H	-2.35551	7.94316	-2.80969
H	-0.08665	7.19154	-2.12649
H	0.24148	4.91979	-1.1798
C	-1.67558	2.89669	0.80722
C	-1.66195	2.97336	-0.7629
N	-0.50503	2.23837	-1.34463
N	-1.48306	1.49125	1.186
H	-2.52497	2.38411	-1.09909
H	-0.802	3.44753	1.15996
H	-2.25705	0.86788	0.95649
H	-0.81763	1.57565	-2.06107
C	0.74714	2.07071	-0.85298
C	3.76813	1.21534	-1.1089
C	5.02683	0.6272	-1.04601
C	5.19432	-0.75182	-1.04775
C	4.05875	-1.54793	-1.13568
C	2.78938	-0.98853	-1.21577
C	2.62402	0.40832	-1.19354
H	3.67471	2.28803	-1.05674
H	6.17939	-1.18974	-0.97848
H	1.92694	-1.63999	-1.24909
N	1.31201	0.89313	-1.3031
H	0.63712	0.18887	-1.62813
F	5.37395	-3.44813	-1.62942
F	3.14678	-3.66506	-1.67037
F	4.2267	-3.50155	0.25047
F	7.28409	0.89209	-0.40593
F	6.66687	1.7826	-2.3302
F	5.97842	2.70886	-0.44776
C	4.19841	-3.02502	-1.06049
C	6.23231	1.5025	-1.05183
C	-0.86111	1.19824	2.4908
C	0.19358	0.10315	2.33929
C	-0.1533	-1.13494	1.79165
C	1.53073	0.33506	2.67561
C	0.82588	-2.10329	1.56941
H	-1.18219	-1.34023	1.52288
C	2.49396	-0.649	2.46429
H	1.84022	1.30036	3.05309
C	2.15872	-1.87008	1.8952
H	2.92577	-2.58366	1.63397
H	-0.36709	2.10763	2.8416
H	-1.59397	0.90165	3.25774
C	3.91014	-0.39728	2.85408
C	0.46855	-3.35632	0.87009

F	4.19942	-0.89954	4.10574
F	4.77654	-1.01094	1.97725
F	4.18686	0.94585	2.88871
F	0.47252	-3.22279	-0.5273
F	-0.83857	-3.74356	1.16417
F	1.30633	-4.3925	1.15607
S	1.57442	3.18323	0.20388
C	-2.81603	-1.80002	-2.27469
C	-2.57335	-2.95962	-1.64222
O	-2.1133	0.34109	-2.82656
O	-0.5889	-1.12426	-1.94505
N	-1.77799	-0.81717	-2.35668
C	-3.54133	-4.02215	-1.41018
C	-3.23456	-4.99275	-0.43209
C	-4.77361	-4.10166	-2.09122
C	-4.14544	-6.00625	-0.13733
H	-2.29943	-4.91289	0.10721
C	-5.67544	-5.11936	-1.79678
H	-5.01574	-3.37817	-2.86057
C	-5.3653	-6.07311	-0.81908
H	-3.90124	-6.74766	0.61414
H	-6.61848	-5.1735	-2.32634
H	-6.0688	-6.86652	-0.59659
H	-3.74619	-1.45817	-2.69808
H	-1.57702	-3.09587	-1.23432
C	-4.49394	-1.72797	1.23387
C	-5.49432	-2.78527	1.39645
C	-6.71748	-2.50747	0.64187
H	-5.06212	-3.73389	1.04578
H	-5.73575	-2.89345	2.46256
N	-3.69159	-0.89861	1.10024
N	-7.6895	-2.29838	0.03995

Product



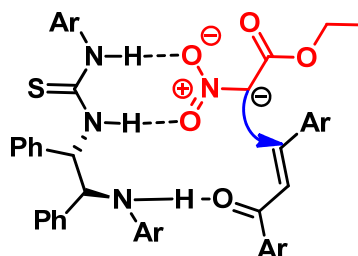
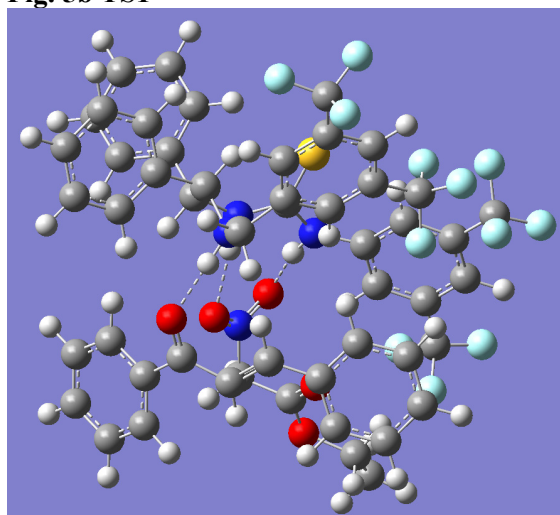
Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	0.92876	-1.48238	0.15965
C	0.29832	-0.17991	-0.38953
O	3.10281	-2.08394	-0.63948
O	2.92331	-0.69186	1.1698
N	2.4433	-1.42595	0.2258
C	-1.2106	-0.31004	-0.21308

C	-1.78629	-0.35541	1.06516
C	-2.03718	-0.41021	-1.33773
C	-3.16586	-0.49491	1.21261
H	-1.16282	-0.27017	1.94964
C	-3.41824	-0.55446	-1.19003
H	-1.60095	-0.36901	-2.32994
C	-3.98455	-0.59709	0.08469
H	-3.60147	-0.51987	2.20427
H	-4.04829	-0.62779	-2.06832
H	-5.05635	-0.70456	0.20037
H	0.68809	-2.32664	-0.4827
C	-0.07481	2.21608	0.28713
C	0.88608	1.10883	0.32478
N	-0.82029	3.10821	0.26287
H	0.60867	-1.65735	1.18606
C	2.12387	1.53892	-0.33815
N	3.08424	1.89423	-0.88934
H	1.1305	0.86159	1.36502
H	0.52589	-0.09174	-1.45539

Fig. 5b TS1



Symbolic Z-matrix:

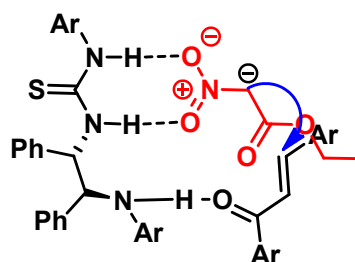
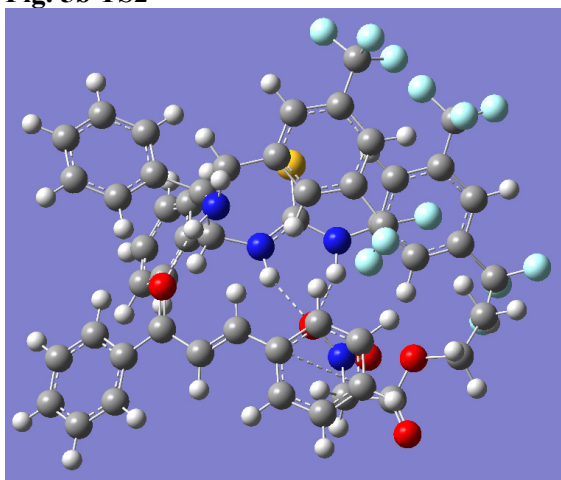
Charge = 0 Multiplicity = 1

C	3.00232	-4.34079	0.15317
C	1.75299	-3.95649	0.64098
C	1.10573	-4.76558	1.57965
C	1.68876	-5.95439	2.00135
C	2.92753	-6.33974	1.49932
C	3.5846	-5.52932	0.58024
H	3.52903	-3.70456	-0.56991
H	0.13269	-4.4521	1.99418
H	1.17067	-6.58734	2.72936
H	3.38489	-7.27805	1.82933
H	4.56375	-5.82555	0.19003
C	0.89016	-3.65128	-2.15062
C	1.78927	-3.90837	-3.19171
C	1.63043	-5.02856	-3.99701
C	0.57369	-5.90522	-3.77158
C	-0.32288	-5.65405	-2.74013
C	-0.16853	-4.53178	-1.93206
H	2.63255	-3.22844	-3.37358
H	2.33936	-5.2225	-4.80823

H	0.44993	-6.78904	-4.40565
H	-1.15891	-6.33806	-2.55943
H	-0.89673	-4.3154	-1.12873
C	1.09328	-2.66495	0.22675
C	1.11414	-2.42167	-1.30609
N	0.20093	-1.31624	-1.74592
N	1.75106	-1.48787	0.88012
H	2.13586	-2.02007	-1.5861
H	0.01336	-2.68133	0.56531
H	0.72484	-0.49793	-2.02613
C	-1.15646	-1.16698	-1.4819
C	-4.02789	-0.29027	-1.35245
C	-5.32495	0.20282	-1.31598
C	-5.66434	1.40033	-1.94317
C	-4.67305	2.10457	-2.61991
C	-3.36245	1.63557	-2.67498
C	-3.03936	0.43241	-2.03526
H	-3.66603	-1.27566	-0.84633
H	-6.69314	1.7815	-1.90387
H	-2.60837	2.22291	-3.2184
N	-1.68193	-0.03641	-2.12849
H	-1.05037	0.64764	-2.52465
F	-4.74905	3.38528	-4.6636
F	-4.23203	4.46218	-2.89268
F	-6.25492	3.86155	-3.22458
F	-6.27201	-0.46556	0.79994
F	-7.66142	-0.25611	-0.80857
F	-6.33836	-1.92784	-0.7634
C	-4.98144	3.42174	-3.32977
C	-6.37744	-0.59465	-0.54309
C	1.64244	-1.43943	2.36035
C	0.27161	-1.03917	2.81667
C	-0.04959	0.30905	2.9661
C	-0.67453	-2.02041	3.12468
C	-1.31277	0.67241	3.43123
H	0.6992	1.08303	2.72181
C	-1.92515	-1.6435	3.60418
H	-0.42156	-3.08664	2.96933
C	-2.25725	-0.29793	3.75404
H	-3.25355	-0.01655	4.12077
H	1.92577	-2.40686	2.8314
H	2.39023	-0.68412	2.70029
C	-2.96702	-2.69165	3.99954
C	-1.67	2.15204	3.56741
F	-3.18077	-2.74644	5.33635
F	-4.1931	-2.47879	3.47221
F	-2.66597	-3.96475	3.65889
F	-2.193	2.69118	2.44221
F	-0.62181	2.95716	3.8663
F	-2.57867	2.43015	4.52975
S	-2.10447	-2.24213	-0.57836
O	1.76512	1.08268	-2.2978
O	0.05523	2.11478	-2.97103
N	1.20304	2.1265	-2.56805
C	1.9423	3.44831	-2.42216
H	3.04397	3.29113	-2.47701
H	1.69095	4.12605	-3.26983
C	1.60898	4.14145	-1.10982
C	1.95117	6.1344	0.16859

H	0.86398	6.30208	0.28582
H	2.30955	5.57242	1.05736
C	2.70601	7.43428	-0.01982
H	2.35773	7.99457	-0.89762
H	2.56279	8.07473	0.86014
H	3.7856	7.2734	-0.13989
O	2.18777	5.36304	-1.02014
O	0.91811	3.68839	-0.22107
O	4.6086	-1.30803	0.6367
C	4.97535	-0.31029	0.03251
C	4.91795	1.04265	0.62849
C	5.45869	-0.40758	-1.3748
H	5.5298	1.81586	0.14602
C	4.13492	1.31673	1.68056
C	4.70385	-1.13103	-2.3002
C	6.65603	0.18936	-1.76853
H	3.51417	0.52563	2.14653
C	3.99419	2.64813	2.26168
C	5.14082	-1.2471	-3.6145
H	3.76189	-1.61324	-1.98478
C	7.09133	0.06491	-3.08349
H	7.26026	0.74409	-1.04135
C	2.75809	3.00962	2.80961
C	5.05273	3.55937	2.28836
C	6.3345	-0.6498	-4.00681
H	4.54462	-1.81878	-4.33507
H	8.03583	0.52646	-3.39059
C	2.58008	4.27513	3.35406
H	1.91843	2.2939	2.80176
C	4.87246	4.81964	2.84717
H	6.02918	3.27739	1.8774
H	6.68182	-0.74741	-5.04088
C	3.6368	5.18128	3.37366
H	1.6051	4.55119	3.77333
H	5.70758	5.52755	2.87493
H	3.49725	6.17489	3.81266
H	2.73852	-1.48886	0.65461

Fig. 5b TS2



Symbolic Z-matrix:

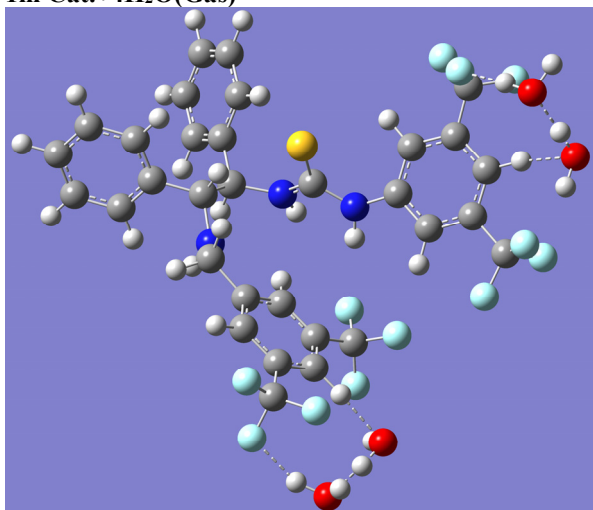
Charge = 0 Multiplicity = 1

C	-5.38196	1.32819	0.07226
C	-4.37161	2.16783	-0.42468

C	-4.72764	3.4304	-0.91478
C	-6.06377	3.84369	-0.92738
C	-7.06348	2.9953	-0.4455
C	-6.71691	1.73708	0.05493
H	-5.12319	0.35961	0.48549
H	-3.9539	4.09	-1.29508
H	-6.32162	4.82463	-1.3108
H	-8.10127	3.31218	-0.45422
H	-7.48781	1.07624	0.43841
C	-3.31797	0.77014	-2.80053
C	-4.07497	-0.28875	-3.3238
C	-4.68546	-0.19065	-4.57542
C	-4.54953	0.97942	-5.32481
C	-3.80027	2.04036	-4.81267
C	-3.18812	1.93891	-3.56246
H	-4.18472	-1.20144	-2.74575
H	-5.26573	-1.02125	-4.96178
H	-5.02238	1.06389	-6.29671
H	-3.68638	2.9515	-5.38905
H	-2.58212	2.75121	-3.18966
C	-2.90247	1.73043	-0.3895
C	-2.66709	0.57976	-1.42785
N	-1.25643	0.09785	-1.58913
N	-2.50124	1.21333	0.94155
H	-3.1586	-0.28132	-0.9561
H	-2.2673	2.58531	-0.63087
H	-1.1278	-0.86048	-1.26576
C	-0.11489	0.74937	-1.92127
C	3.01225	1.33871	-2.01381
C	4.40098	1.39442	-2.15067
C	5.16336	0.26053	-2.41132
C	4.5014	-0.96084	-2.50756
C	3.12574	-1.0526	-2.33081
C	2.35061	0.09954	-2.07845
H	2.44567	2.24518	-1.86624
H	6.23648	0.32479	-2.53551
H	2.64601	-2.02553	-2.36331
N	0.97613	-0.11269	-1.8664
H	0.73505	-1.07479	-1.61676
F	5.28219	-2.39703	-4.25957
F	4.71409	-3.32331	-2.34634
F	6.58579	-2.08794	-2.50022
F	5.35865	2.96273	-0.60859
F	6.31071	2.72395	-2.59106
F	4.32609	3.74868	-2.39926
C	5.27273	-2.1729	-2.90057
C	5.08971	2.70307	-1.95272
C	-2.4469	2.21434	2.02925
C	-1.08071	2.88277	2.14295
C	0.05607	2.07789	2.23198
C	-0.92276	4.27257	2.14993
C	1.32109	2.65403	2.39042
H	-0.06545	1.00104	2.12699
C	0.35689	4.83873	2.24406
H	-1.78636	4.92508	2.05247
C	1.49395	4.04114	2.36842
H	2.49022	4.47551	2.37045
H	-3.23305	2.98476	1.96163
H	-2.61985	1.63863	2.95281

C	0.5069	6.32537	2.27945
C	2.46242	1.75568	2.68783
F	0.48053	6.82882	3.57091
F	1.71207	6.71528	1.72746
F	-0.52442	6.93842	1.60111
F	2.43082	0.62191	1.89393
F	2.37068	1.26894	3.99988
F	3.68698	2.36339	2.56408
S	-0.00991	2.4012	-2.44306
O	-0.27318	-2.55237	-0.61696
O	1.21194	-3.69505	-1.92581
N	0.39328	-3.60514	-0.95807
C	0.15134	-4.8295	-0.11828
H	-0.23901	-5.61646	-0.76683
O	-3.81371	-1.2483	1.43888
C	-3.55796	-2.4759	1.51953
C	-2.4082	-2.98518	2.27991
C	-4.41014	-3.45457	0.77776
H	-2.25065	-4.04584	2.23008
C	-1.58699	-2.15944	2.96114
C	-5.22917	-2.9465	-0.24676
C	-4.44742	-4.82812	1.06286
H	-1.87423	-1.10321	2.95883
C	-0.35926	-2.46625	3.70858
C	-6.04785	-3.79437	-0.98531
H	-5.19538	-1.88233	-0.44572
C	-5.27885	-5.67581	0.33045
H	-3.85756	-5.23944	1.87275
C	0.57537	-1.43767	3.97722
C	-0.07692	-3.76532	4.18386
C	-6.07394	-5.16333	-0.69763
H	-6.66994	-3.3933	-1.77645
H	-5.31261	-6.73282	0.56623
C	1.76342	-1.70487	4.65559
H	0.39985	-0.41569	3.66548
C	1.09986	-4.02483	4.88357
H	-0.80116	-4.561	4.03723
H	-6.71533	-5.8257	-1.26692
C	2.02679	-2.99763	5.11535
H	2.46922	-0.89452	4.79653
H	1.29349	-5.02417	5.25772
H	2.93926	-3.20372	5.66494
H	-3.0615	0.40009	1.21175
C	1.44691	-5.34712	0.5215
C	3.68873	-4.78935	1.27069
H	3.92068	-5.81436	0.94186
H	3.5144	-4.77314	2.34924
C	4.72168	-3.76262	0.80812
H	4.35135	-2.75528	1.02739
H	5.68245	-3.92574	1.32266
H	4.87432	-3.85245	-0.27087
O	2.3819	-4.37487	0.62726
O	1.56942	-6.51208	0.88345
H	-0.58574	-4.52475	0.60267

1m Cat.+4H₂O(Gas)



Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-6.15847	0.1223	0.61868
C	-5.12785	1.04631	0.82019
C	-5.4408	2.28539	1.3989
C	-6.75243	2.59439	1.75618
C	-7.77634	1.66811	1.54011
C	-7.47529	0.43034	0.97128
H	-5.94044	-0.85487	0.20343
H	-4.65126	3.01019	1.55897
H	-6.97562	3.55616	2.2033
H	-8.79618	1.90682	1.81863
H	-8.26097	-0.29897	0.80901
C	-3.8534	2.75274	-1.2793
C	-5.09418	2.79901	-1.9316
C	-5.6722	4.01799	-2.28504
C	-5.01056	5.21345	-1.99765
C	-3.77282	5.17659	-1.35317
C	-3.19509	3.95589	-0.9967
H	-5.61778	1.87501	-2.15246
H	-6.63343	4.0332	-2.78554
H	-5.45441	6.1627	-2.27458
H	-3.25197	6.09947	-1.12486
H	-2.24911	3.93434	-0.47583
C	-3.67493	0.741	0.44533
C	-3.27124	1.37896	-0.94265
N	-1.7918	1.29263	-1.16975
N	-3.33747	-0.68198	0.34062
H	-3.67843	0.68606	-1.68814
H	-3.02497	1.1781	1.20299
H	-3.9643	-1.23332	-0.24436
H	-1.55274	0.96464	-2.10521
C	-0.73317	1.59805	-0.37085
C	2.14433	2.76265	-0.09098
C	3.48335	3.04387	0.16167
C	4.49728	2.11649	-0.0599
C	4.11889	0.86195	-0.52748
C	2.78753	0.54134	-0.77068
C	1.78328	1.49573	-0.56243
H	1.39658	3.51743	0.08563
H	5.55921	2.34872	0.13517

H	2.53943	-0.45619	-1.10542
N	0.45651	1.14163	-0.91038
H	0.39208	0.3702	-1.57759
F	6.0566	-0.25754	0.27581
F	5.93672	0.14008	-1.89121
F	4.62743	-1.40485	-0.98959
F	2.88543	5.31518	0.51056
F	3.95817	4.28535	2.15084
F	5.05517	4.81522	0.31588
C	5.17292	-0.15985	-0.79194
C	3.8359	4.36044	0.74463
C	-2.79576	-1.41525	1.48984
C	-1.7407	-2.41041	1.00665
C	-1.02022	-2.08802	-0.14129
C	-1.47483	-3.6169	1.64711
C	-0.03716	-2.93638	-0.62339
H	-1.28467	-1.17234	-0.64699
C	-0.50055	-4.48127	1.13319
H	-2.02333	-3.90638	2.5359
C	0.241	-4.15894	-0.00005
H	0.97644	-4.85581	-0.43299
H	-2.31107	-0.68179	2.14508
H	-3.55695	-1.94169	2.087
C	-0.37638	-5.83145	1.73815
C	0.71916	-2.52641	-1.83429
F	-1.22569	-6.77891	1.11524
F	0.87605	-6.36392	1.61924
F	-0.76002	-5.82958	3.05186
F	0.21464	-1.33796	-2.36381
F	0.6678	-3.46136	-2.85152
F	2.0552	-2.30822	-1.58662
S	-0.81969	2.42234	1.15682
O	6.54359	3.58607	2.92584
H	7.03901	4.44687	2.92264
H	5.59206	3.81656	2.73501
O	7.2952	2.34508	0.70015
H	7.2414	1.36055	0.82378
H	7.08904	2.76041	1.61146
O	1.88017	-6.42247	-1.85523
H	1.06777	-7.021	-1.69566
H	1.64155	-5.84255	-2.62504
O	-0.12461	-7.98455	-1.12751
H	0.35263	-8.74241	-0.69923
H	-0.69325	-7.5866	-0.40767

1m Cat.+4H₂O(THF)

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-6.22502	0.4714	0.19652
C	-5.32205	-0.25496	-0.59332
C	-5.81708	-0.99026	-1.67814
C	-7.18368	-1.00336	-1.96963
C	-8.07551	-0.27829	-1.17521
C	-7.59182	0.45905	-0.08993
H	-5.87009	1.05142	1.04239
H	-5.12728	-1.55634	-2.29464
H	-7.54955	-1.57541	-2.8146
H	-9.13584	-0.28523	-1.39934
H	-8.27746	1.02437	0.53089

C	-4.17552	-2.43928	1.05951
C	-5.2152	-2.61213	1.98465
C	-5.88293	-3.83459	2.09123
C	-5.51313	-4.90556	1.27417
C	-4.4729	-4.74381	0.35397
C	-3.80819	-3.52033	0.2449
H	-5.50668	-1.78516	2.62323
H	-6.68499	-3.94944	2.81124
H	-6.02738	-5.85625	1.35524
H	-4.17788	-5.57161	-0.28101
H	-2.9984	-3.3963	-0.46208
C	-3.82035	-0.23693	-0.3048
C	-3.48966	-1.0773	0.97554
N	-2.01616	-1.16272	1.24598
N	-3.26265	1.11106	-0.09344
H	-3.86354	-0.4842	1.81688
H	-3.29367	-0.6854	-1.14638
H	-3.82951	1.692	0.52733
H	-1.78867	-1.03027	2.2325
C	-0.96701	-1.39524	0.43119
C	1.6725	-2.95612	0.1702
C	2.94454	-3.42791	-0.13542
C	4.08644	-2.65511	0.053
C	3.911	-1.36249	0.53571
C	2.65016	-0.85035	0.82809
C	1.51397	-1.65223	0.65552
H	0.81564	-3.59631	0.03262
H	5.0943	-3.03116	-0.1717
H	2.55798	0.169	1.17239
N	0.25329	-1.14204	1.03867
H	0.27551	-0.43639	1.77754
F	5.92151	-0.50241	-0.3963
F	5.91689	-0.96027	1.76026
F	4.78187	0.79171	1.01099
F	2.01948	-5.58764	-0.48863
F	3.18385	-4.69079	-2.14637
F	4.24378	-5.40388	-0.34913
C	5.11578	-0.51001	0.73732
C	3.08525	-4.77223	-0.7445
C	-2.72181	1.86357	-1.23693
C	-1.51969	2.6982	-0.78863
C	-0.82796	2.31278	0.36149
C	-1.07649	3.81481	-1.49871
C	0.304	3.007	0.76943
H	-1.22102	1.47573	0.91735
C	0.05145	4.5135	-1.05857
H	-1.59631	4.1478	-2.38903
C	0.76733	4.11858	0.06735
H	1.6493	4.66323	0.43309
H	-2.37082	1.13155	-1.97397
H	-3.45649	2.51215	-1.73691
C	0.454	5.75922	-1.75331
C	1.04238	2.56874	1.98082
F	-0.05976	6.89888	-1.10531
F	1.82083	5.94001	-1.74598
F	0.00046	5.8219	-3.04006
F	0.45357	1.45805	2.57284
F	1.12272	3.54781	2.9507
F	2.35295	2.21629	1.70089

S	-1.05084	-1.91315	-1.23856
O	5.92705	-4.8684	-2.6137
H	6.00029	-5.72547	-2.11482
H	4.94684	-4.70559	-2.68307
O	6.86372	-3.24424	-0.75321
H	6.81683	-2.29538	-1.04399
H	6.56467	-3.8101	-1.55575
O	2.87309	5.5153	1.56452
H	2.57087	6.44093	1.23669
H	2.29786	5.29184	2.34371
O	2.1	7.76671	0.43047
H	2.69715	7.75412	-0.36457
H	1.18937	7.61594	0.05633

1m Cat.+4H₂O(EtOH)

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1			
C	6.21609	0.80515	-0.11373
C	5.42501	-0.01035	0.71019
C	6.04709	-0.73953	1.73
C	7.42665	-0.6538	1.92839
C	8.20402	0.16456	1.10707
C	7.59463	0.89407	0.08319
H	5.75935	1.37222	-0.91984
H	5.44811	-1.38181	2.36569
H	7.89257	-1.22569	2.72244
H	9.27458	0.23239	1.26071
H	8.19237	1.52835	-0.56146
C	4.29944	-2.10969	-1.07352
C	5.32576	-2.16236	-2.02664
C	6.01815	-3.34977	-2.26867
C	5.68728	-4.50599	-1.56038
C	4.6626	-4.46395	-0.61178
C	3.97226	-3.27604	-0.36704
H	5.59239	-1.26614	-2.57693
H	6.81085	-3.37087	-3.0076
H	6.22119	-5.43068	-1.74658
H	4.39781	-5.35855	-0.0597
H	3.17279	-3.24632	0.36168
C	3.91276	-0.08008	0.52137
C	3.57745	-0.78486	-0.83989
N	2.10694	-0.88542	-1.11762
N	3.30099	1.27222	0.51592
H	3.9282	-0.08636	-1.6071
H	3.47244	-0.66825	1.32536
H	3.97578	2.00321	0.28884
H	1.87947	-0.72014	-2.09867
C	1.06593	-1.27795	-0.33612
C	-1.55183	-2.90659	-0.03883
C	-2.82512	-3.4054	0.21854
C	-3.98126	-2.69851	-0.09832
C	-3.82019	-1.43855	-0.66704
C	-2.56203	-0.9005	-0.91767
C	-1.41027	-1.63926	-0.61353
H	-0.68449	-3.49415	0.21383
H	-4.99385	-3.09878	0.08308
H	-2.48672	0.09417	-1.33375
N	-0.15348	-1.09241	-0.96502
H	-0.18853	-0.37959	-1.69588

F	-5.92929	-0.604	0.04354
F	-5.72628	-1.18095	-2.07719
F	-4.71482	0.6488	-1.33933
F	-1.82628	-5.47613	0.81846
F	-3.16392	-4.51996	2.30331
F	-4.03685	-5.4347	0.49649
C	-5.03502	-0.64719	-1.02026
C	-2.94677	-4.70223	0.92508
C	2.38185	1.67234	1.59836
C	1.23455	2.50732	1.0292
C	0.7828	2.20559	-0.25735
C	0.59292	3.51643	1.74456
C	-0.32085	2.85616	-0.78986
H	1.32888	1.45814	-0.81022
C	-0.48875	4.19552	1.17112
H	0.91804	3.78274	2.74322
C	-0.97647	3.86981	-0.08983
H	-1.82017	4.39244	-0.57257
H	1.94617	0.75452	2.01123
H	2.87192	2.21771	2.41951
C	-1.08502	5.3444	1.89094
C	-0.82662	2.46742	-2.1311
F	-0.5649	6.57014	1.4266
F	-2.44545	5.44781	1.68461
F	-0.83838	5.31807	3.23392
F	-0.10209	1.3859	-2.65021
F	-0.74765	3.47713	-3.06591
F	-2.14725	2.07236	-2.10796
S	1.19192	-1.88709	1.28764
O	-5.92694	-4.8147	2.53941
H	-5.82728	-5.58621	1.91897
H	-4.98671	-4.54533	2.72801
O	-6.75404	-3.34208	0.50769
H	-6.8564	-2.36888	0.67592
H	-6.56681	-3.7916	1.40451
O	-2.82678	5.22598	-1.83724
H	-2.69115	6.16046	-1.4435
H	-2.18119	5.12226	-2.58535
O	-2.51362	7.40348	-0.38919
H	-3.2131	7.13523	0.26493
H	-1.66107	7.29957	0.11497

1m Cat.+4H₂O(MeOH)

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	6.20482	0.75372	-0.18493
C	5.39034	-0.01764	0.65855
C	5.9852	-0.70148	1.72559
C	7.36123	-0.61558	1.95043
C	8.16235	0.15746	1.1077
C	7.57992	0.8418	0.03719
H	5.77139	1.28719	-1.02601
H	5.36802	-1.30763	2.37935
H	7.80527	-1.15147	2.78135
H	9.22994	0.22563	1.28098
H	8.19595	1.44106	-0.62353
C	4.28094	-2.18417	-1.05694
C	5.31126	-2.28032	-2.00272
C	6.00679	-3.47718	-2.18508

C	5.67523	-4.59945	-1.4236
C	4.64588	-4.51426	-0.48221
C	3.95286	-3.31666	-0.29744
H	5.57697	-1.41164	-2.59582
H	6.8024	-3.53185	-2.91922
H	6.21181	-5.53084	-1.56308
H	4.38051	-5.38208	0.11094
H	3.15023	-3.25334	0.42571
C	3.88054	-0.08709	0.44321
C	3.55761	-0.84984	-0.88792
N	2.08802	-0.96467	-1.1663
N	3.26138	1.25683	0.36736
H	3.9114	-0.18933	-1.6865
H	3.42257	-0.63402	1.26594
H	3.90479	1.96572	0.012
H	1.86345	-0.83388	-2.15364
C	1.04474	-1.30474	-0.37092
C	-1.54618	-2.96244	-0.09916
C	-2.80936	-3.48005	0.16574
C	-3.97688	-2.77717	-0.11747
C	-3.83778	-1.5029	-0.65846
C	-2.58828	-0.94511	-0.91376
C	-1.4252	-1.67864	-0.64315
H	-0.66907	-3.5502	0.11825
H	-4.97394	-3.19921	0.08613
H	-2.52789	0.06028	-1.30485
N	-0.17663	-1.11861	-0.99867
H	-0.216	-0.41069	-1.73424
F	-5.97732	-0.74775	0.05678
F	-5.73084	-1.22544	-2.08244
F	-4.77311	0.59205	-1.25142
F	-1.80048	-5.5753	0.6455
F	-3.07504	-4.6806	2.21796
F	-4.02154	-5.50357	0.40584
C	-5.06383	-0.72318	-0.99131
C	-2.9175	-4.80578	0.82037
C	2.44674	1.75381	1.49211
C	1.27499	2.57881	0.95893
C	0.74471	2.23901	-0.28754
C	0.69246	3.62458	1.67335
C	-0.37423	2.8948	-0.78182
H	1.24828	1.46437	-0.84381
C	-0.41052	4.3006	1.13979
H	1.08238	3.92148	2.63966
C	-0.97366	3.94118	-0.08012
H	-1.83677	4.46253	-0.52374
H	2.02915	0.87765	2.00215
H	3.01301	2.3408	2.23082
C	-0.94553	5.48627	1.84851
C	-0.95303	2.47971	-2.0846
F	-0.40817	6.6815	1.32637
F	-2.30794	5.62256	1.69149
F	-0.64437	5.4927	3.1805
F	-0.25529	1.40108	-2.63222
F	-0.94097	3.48137	-3.03356
F	-2.27025	2.07828	-1.97856
S	1.15484	-1.86162	1.27668
O	-5.74091	-4.32925	2.97805
H	-6.1004	-5.23615	3.16268

H	-4.76794	-4.4475	2.7957
O	-6.71237	-3.50604	0.65496
H	-6.82	-2.51881	0.69587
H	-6.41363	-3.79266	1.59289
O	-2.92657	5.2954	-1.75727
H	-2.70448	6.22663	-1.39188
H	-2.30089	5.1249	-2.51039
O	-2.38602	7.52147	-0.44865
H	-3.08207	7.39687	0.25052
H	-1.52633	7.38438	0.03524

1m Cat.+4H₂O(Water)

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-6.18768	0.80776	0.18772
C	-5.31506	0.03574	-0.59271
C	-5.83959	-0.69395	-1.66722
C	-7.20603	-0.65637	-1.95828
C	-8.06779	0.11373	-1.17311
C	-7.55426	0.84558	-0.09765
H	-5.80962	1.38416	1.02613
H	-5.17465	-1.29581	-2.2773
H	-7.59482	-1.22403	-2.79595
H	-9.12767	0.14621	-1.39706
H	-8.21643	1.44571	0.51589
C	-4.30557	-2.22108	1.02569
C	-5.39974	-2.32611	1.8968
C	-6.14084	-3.50764	1.97628
C	-5.79053	-4.60626	1.18752
C	-4.69653	-4.51247	0.3219
C	-3.9587	-3.32929	0.23946
H	-5.67562	-1.47855	2.51473
H	-6.98365	-3.57011	2.655
H	-6.36104	-5.5258	1.24891
H	-4.41605	-5.36191	-0.29069
H	-3.11029	-3.25572	-0.42822
C	-3.81597	-0.01427	-0.2917
C	-3.54018	-0.90022	0.97132
N	-2.07548	-1.07204	1.24675
N	-3.19849	1.29771	-0.03481
H	-3.88624	-0.30293	1.82122
H	-3.29673	-0.46307	-1.13803
H	-3.71815	1.87066	0.63305
H	-1.84584	-0.96608	2.23607
C	-1.03525	-1.33889	0.43253
C	1.49812	-3.05951	0.20667
C	2.73696	-3.61482	-0.09257
C	3.92692	-2.9117	0.08097
C	3.83374	-1.60539	0.55047
C	2.60717	-1.012	0.83749
C	1.42211	-1.74045	0.67076
H	0.60299	-3.64864	0.0845
H	4.9037	-3.35663	-0.1579
H	2.58023	0.01348	1.17437
N	0.19481	-1.14842	1.04396
H	0.25653	-0.44015	1.77821
F	5.92637	-0.89868	-0.33843
F	5.82743	-1.31296	1.82414
F	4.83501	0.49535	1.00971

F	1.68265	-5.72619	-0.3564
F	2.87476	-4.96972	-2.0589
F	3.91351	-5.66448	-0.24035
C	5.08672	-0.83079	0.77044
C	2.79565	-4.98801	-0.65185
C	-2.6668	2.08057	-1.16146
C	-1.39585	2.81962	-0.73358
C	-0.71572	2.38453	0.40522
C	-0.882	3.89879	-1.45454
C	0.47041	2.99483	0.79407
H	-1.1591	1.57613	0.96593
C	0.30303	4.51032	-1.03645
H	-1.38994	4.26807	-2.33738
C	1.00457	4.06613	0.08045
H	1.9304	4.54329	0.43055
H	-2.39896	1.37485	-1.95675
H	-3.38466	2.79778	-1.58634
C	0.79164	5.71555	-1.74755
C	1.19027	2.50944	1.99862
F	0.38543	6.89755	-1.10067
F	2.16901	5.78314	-1.76634
F	0.32135	5.80576	-3.02671
F	0.53657	1.44003	2.59747
F	1.34417	3.48213	2.96614
F	2.47387	2.07473	1.70619
S	-1.13502	-1.83371	-1.2448
O	5.45275	-4.51551	-3.05627
H	5.81223	-5.40171	-3.32288
H	4.50545	-4.66501	-2.7876
O	6.62893	-3.6877	-0.84835
H	6.71151	-2.69878	-0.90828
H	6.22527	-3.97957	-1.74861
O	3.2332	5.29909	1.54725
H	3.00391	6.24178	1.20846
H	2.64401	5.13119	2.32993
O	2.63928	7.58869	0.38568
H	3.21362	7.50492	-0.42174
H	1.7102	7.51811	0.03391

1m Cat.+4H₂O(Toluene)

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	6.18318	0.75909	-0.07401
C	5.31363	-0.07193	0.64617
C	5.8422	-0.87588	1.66375
C	7.20735	-0.85188	1.95696
C	8.06514	-0.02115	1.23277
C	7.54883	0.7848	0.21463
H	5.8025	1.39413	-0.86812
H	5.18093	-1.52766	2.22381
H	7.59925	-1.47975	2.74882
H	9.12473	-0.00015	1.45933
H	8.20802	1.43265	-0.35199
C	4.27352	-2.24633	-1.08455
C	5.368	-2.32312	-1.95696
C	6.08759	-3.51102	-2.09989
C	5.71474	-4.64389	-1.37397
C	4.62174	-4.57738	-0.50579
C	3.90513	-3.38831	-0.35931

H	5.66513	-1.44641	-2.52265
H	6.93295	-3.55098	-2.77715
H	6.26895	-5.56885	-1.48426
H	4.32482	-5.45305	0.06026
H	3.05879	-3.33629	0.31299
C	3.81469	-0.10385	0.34728
C	3.52593	-0.92029	-0.96068
N	2.05849	-1.06143	-1.23558
N	3.20507	1.22689	0.17098
H	3.87679	-0.28308	-1.78051
H	3.29616	-0.59966	1.16714
H	3.76734	1.85816	-0.4024
H	1.82399	-0.93838	-2.22103
C	1.01935	-1.36784	-0.42243
C	-1.56137	-3.03094	-0.16572
C	-2.81717	-3.55192	0.12564
C	-3.98905	-2.82983	-0.08336
C	-3.86065	-1.5358	-0.5778
C	-2.61707	-0.97567	-0.85735
C	-1.45112	-1.72628	-0.66019
H	-0.68104	-3.63278	-0.00666
H	-4.98089	-3.25022	0.146
H	-2.56364	0.04419	-1.20877
N	-0.2086	-1.16397	-1.03472
H	-0.26032	-0.4385	-1.75191
F	-5.95306	-0.77358	0.2616
F	-5.81933	-1.20628	-1.89678
F	-4.80032	0.58267	-1.07497
F	-1.80091	-5.66734	0.48285
F	-3.02477	-4.84129	2.13059
F	-4.02727	-5.58275	0.31232
C	-5.0922	-0.735	-0.83058
C	-2.91055	-4.90486	0.72492
C	2.58105	1.90857	1.31651
C	1.36769	2.71097	0.84072
C	0.72338	2.31235	-0.33203
C	0.86845	3.80807	1.54212
C	-0.41531	2.97465	-0.77211
H	1.15905	1.48988	-0.87765
C	-0.26411	4.47788	1.06885
H	1.34785	4.14994	2.45167
C	-0.93212	4.07095	-0.08204
H	-1.81852	4.5915	-0.4785
H	2.22561	1.13235	2.00438
H	3.26434	2.56488	1.87676
C	-0.71893	5.70738	1.75928
C	-1.10137	2.51622	-2.00733
F	-0.22667	6.86547	1.12382
F	-2.08967	5.85152	1.72794
F	-0.29093	5.78036	3.05416
F	-0.44719	1.42618	-2.5817
F	-1.17406	3.49182	-2.98062
F	-2.4024	2.11318	-1.77934
S	1.13232	-1.91976	1.22591
O	-5.63108	-4.40854	3.03953
H	-6.00822	-5.29946	3.26221
H	-4.67523	-4.56151	2.80119
O	-6.70467	-3.5382	0.7815
H	-6.78841	-2.55007	0.84868

H	-6.36507	-3.84922	1.69764
O	-3.01592	5.38856	-1.63671
H	-2.77097	6.33296	-1.32287
H	-2.44749	5.19043	-2.42736
O	-2.38431	7.65996	-0.45582
H	-2.99954	7.54165	0.31652
H	-1.47617	7.54869	-0.0626

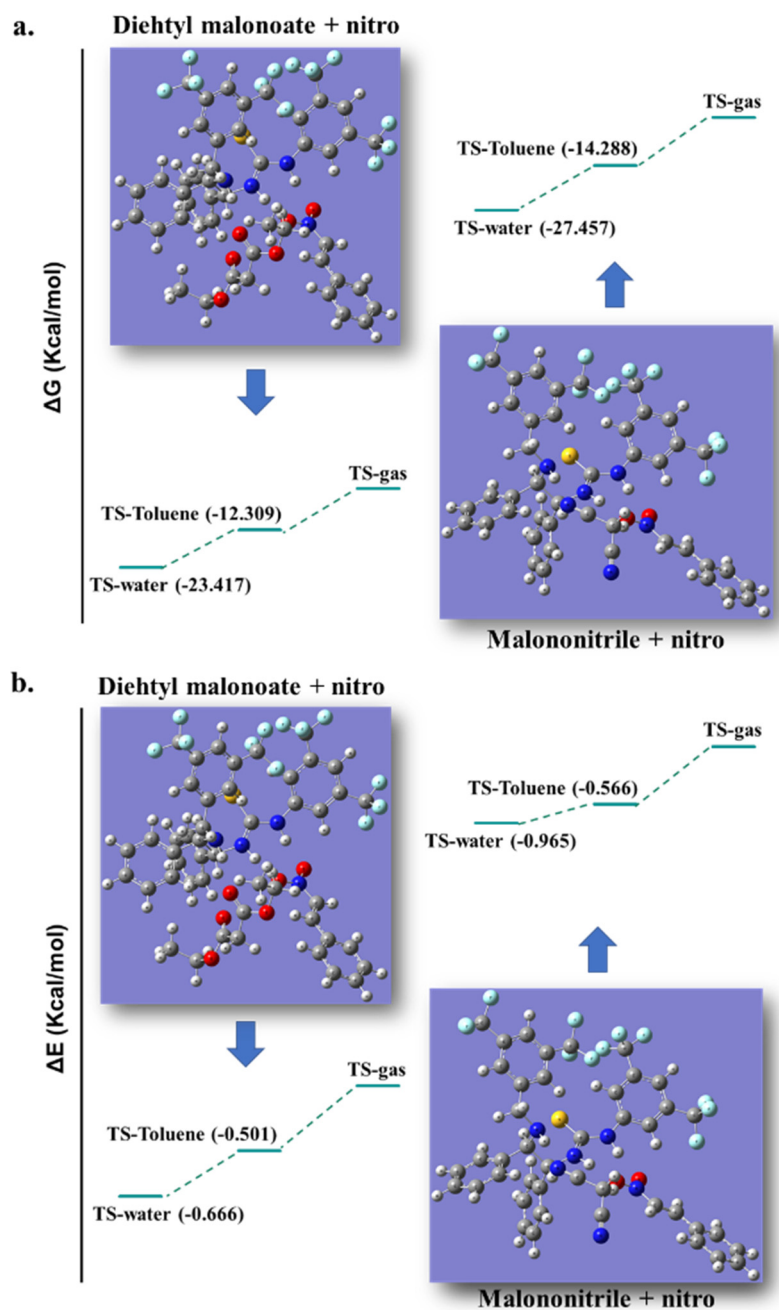


Fig. 1. DFT calculated solvent effects energy diagram for the Michael reaction using β -nitrostyrenes. (*R,R*)-1,2-diphenyleth-ylenediamine (DPEN)-thiourea catalyzed enantioselecti-ve Michael reaction calculated at the B3LYP/6-31G(d,p) level. a. expected relative free energy of Transition states in water and toluene solvents. b. expected thermal energy of Transition states in water and toluene solvents.

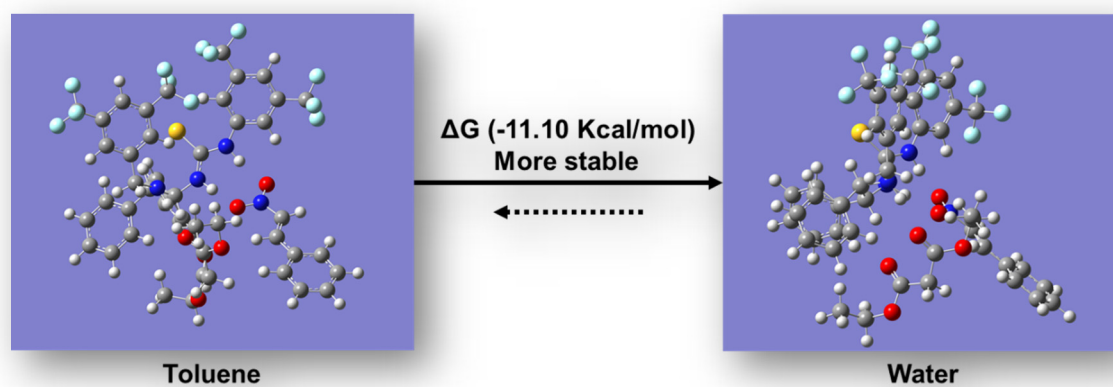


Fig. 2. Solvent effects on the Michael reaction of diethylmalonate to nitrostyrene.

Copy of X-ray Diffraction(1m Catalyst)

X-ray diffraction patterns were recorded at room temperature by a Siemens X-ray diffractometer using CuK α radiation ($\lambda = 1.54\text{\AA}$).

- (1) Equipment : Bruker, D8 ADVANCE
- (2) Step size ; 0.02°
- (3) Range : $5 \sim 90^\circ$
- (4) Target : Cu
- (5) X-Ray Generator : 40 Kv
- (6) Appearance : Solid
- (7) Chemical Formula: $\text{C}_{32}\text{H}_{23}\text{F}_{12}\text{N}_3\text{S}$

