Supporting Information for

Asymmetric Organocatalysts Supported on Vinyl Addition Polynorbornenes for Work in Aqueous Media

Irina K. Sagamanova,[†] Sonia Sayalero,[†] Sheila Martínez-Arranz,[‡] Ana C. Albéniz,*[,‡] and Miquel A. Pericàs*[,†,§]

[†]*Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans, 16, 43007 Tarragona, Spain.* [‡]*IU CINQUIMA/Química Inorgánica, Universidad de Valladolid, 47071 Valladolid, Spain.* [§]*Departament de Química Orgànica, Universitat de Barcelona (UB), 08028 Barcelona, Spain*

mapericas@iciq.es, albeniz@qi.uva.es

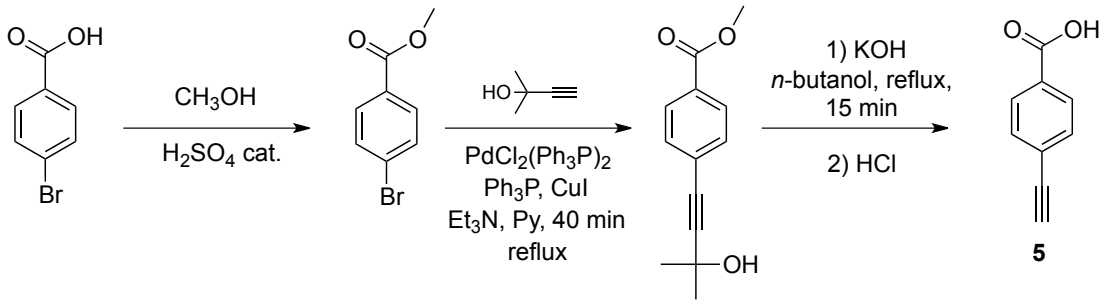
General Information

Unless otherwise stated, all commercial reagents were used as received. The aldehydes were vacuum distilled before use. Solvents were dried using a solvent purification system (SPS). Reactions requiring anhydrous conditions were performed under nitrogen using standard Schlenk line techniques. Thin layer chromatography was carried out using Merck TLC Silicagel 60 F254 aluminium sheets. Components were visualized by UV light (λ = 254 nm) or by staining with *p*-anisaldehyde solution. Flash chromatography separations were carried out using 60-mesh silicagel and dry-packed columns. NMR spectra were acquired on Bruker Avance Ultrashield spectrometers in $CDCl_3$ at room temperature, operating at 400 or 500 MHz (^1H) and 100 or 126 MHz ($^{13}C\{^1H\}$). TMS was used as internal standard for ^1H NMR and $CDCl_3$ for ^{13}C NMR. Chemical shifts are reported in ppm referred to TMS. ATR-FTIR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. FT-Raman spectra were measured on a Via Raman spectrometer with laser excitation in 785 nm, equipped with a Leica microscope and Peltiercooled CCD detectors (-70 ^0C). Elemental analyses were performed on a LECO CHNS 932 micro-analyzer at the Universidad Complutense de Madrid, Spain. The halogen content in the polymers was determined by oxygen-flask combustion of a sample and analysis of the residue by mercurimetric titration of the chloride.[S1] Scanning Electron Microscopy (SEM) was performed on a JSM-6400 scanning microscope at the Microscopy Unit of the Universitat Rovira i Virgili, Spain. High performance liquid chromatography (HPLC) was performed on an Agilent Technologies chromatograph (1200 Series), using Chiralcel OD-H, Chiralpak AD-H and Chiralpak AS-H columns and guard columns. Racemic standards of reaction products were prepared using DL-proline as catalyst according to reported procedures in order to establish HPLC conditions.

Solvent absorption measurements were performed by gravimetric analysis according to common practice.[S2] Dried samples (30-32 mg) were weighed and then immersed in an excess of the swelling solvent (0.4 mL) at room temperature. At regular time intervals, the samples were taken out, wiped of excessive solvent with filter paper, weighed, and returned to the swelling medium. The experiment was continued until a constant weight of the samples was achieved. The equilibrium swelling ratio (SR) in each solvent was determined

gravimetrically with the formula: Swelling Ratio (SR, %) = $100(W_s-W_{dry})/W_{dry}$, where W_s is the weight of swollen samples after the certain time and Wdry is the weight of dried samples.

Preparation and characterization of 4-ethynylbenzoic acid (**5**)



a) Synthesis of methyl *p*-bromobenzoate. Methyl *p*-bromobenzoate was prepared quantitatively (10.6 g, 99% yield) by refluxing *p*-bromobenzoic acid (10 g, 49.7 mmol) with an excess of methanol (60 mL, 1.54 mmol) and a catalytic amount of sulfuric acid (0.66 mL, 12.4 mmol).

b) Synthesis of 4-(4-(methoxycarbonyl))-phenyl-2-methyl-3-butyn-2-ol. To a solution of Ph_3P (67 mg, 0.011 mmol), CuI (18 mg, 0.093 mmol), methyl *p*-bromobenzoate (5.0 g, 23.25 mmol) and 2-methyl-3-butyn-2-ol (2.33 g, 27.7 mmol) in Et_3N (32 mL) and pyridine (18 mL) was added dichloro-*bis*(triphenylphosphine)palladium (20 mg, 0.0028 mmol) under N_2 and the mixture was refluxed for 40 min. After cooling to room temperature, the reaction mixture was filtered to remove the insoluble triethylamine hydrobromide formed. The salt was washed with triethylamine and ethyl ether until the ether washings were clear. The combined filtrates were reduced to dryness under reduced pressure. The obtained solid was stirred twice with H_2O (40 mL) and then with 3% HCl (40 mL) and again twice with H_2O (40 mL). 4-(4-(Methoxycarbonyl)-phenyl-2-methyl-3-butyn-2-ol was isolated as a slightly tan solid after filtration and drying under reduced pressure (4.32 g, 85% yield).

c) Synthesis of *p*-Ethynylbenzoic acid (**5**). 4-(4-(Methoxycarbonyl)-phenyl-2-methyl-3-butyn-2-ol (1 g, 4.58 mmol) was dissolved in a refluxing solution of KOH (1 g, 18.33 mmol) in *n*-butanol (30 mL). After refluxing for 15 min, the mixture was cooled with an ice-bath, acidified with 1 M HCl to pH 2 and extracted with ethyl acetate (3 × 40 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to

give *p*-ethynylbenzoic acid as yellow solid (630 mg, 94% yield). All the spectroscopic data of the product matched with those reported in the literature.[S3]

Solvent effects on the aldol reaction of cyclohexanone with *p*-nitrobenzaldehyde catalyzed by polymers **1a,b**

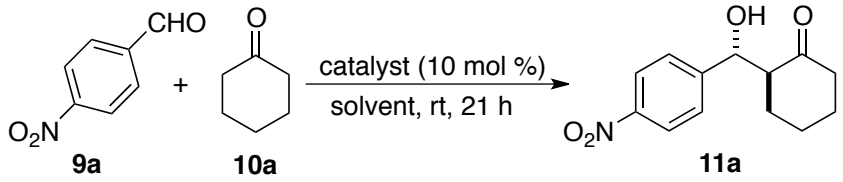


Table SI-1. Solvent effects on the aldol reaction of cyclohexanone with *p*-nitrobenzaldehyde catalyzed by polymers **1a,b**.[a]

entry	catalyst	solvent	conversion (%)[b,c]	*anti:syn*[b]	ee *anti*[d] (%)
1	**1a**	CH_2Cl_2[e]	80 (17)	82:18	90
2	**1a**	DMF[e]	50 (4)	75:25	84
3	**1a**	DMSO[e]	61 (6)	74:26	91
4	**1a**	H_2O	74 (8)	71:29	73
5	**1a**	CH_2Cl_2/H_2O (50:50)	57 (16)	80:20	73
6	**1a**	IPA/H_2O (50:50)	65 (17)	71:29	54
7	**1a**	THF/H_2O (50:50)	68 (3)	72:28	62
8	**1a**	DMF/H_2O (50:50)	88 (4)	78:22	78
9	**1a**	DMSO/H_2O (50:50)	94	81:19	85
10	**1a**	DMSO/H_2O (83:17)	100[f] (97)[g]	89:11	90
11	**1a**	DMSO/H_2O (91:9)	100[f] (95)[g]	88:12	91
12	**1a**	neat	10	77:23	76
13	**1b**	DMSO[e]	82	76:24	92
14	**1b**	H_2O	81	79:21	78
15	**1b**	DMSO/H_2O (50:50)	96	86:14	93
16	**1b**	DMSO/H_2O (83:17)	100[h] (98)[g]	91:9	91
17	**1b**	DMSO/H_2O (91:9)	100[h] (96)[g]	90:10	93
18	**1b**	neat	17	77:23	75
19	**1b**	neat[i]	72	84:16	78
20	**1b**	neat[j]	94	78:22	76

[a] Reactions were performed with polymer **1a** or **1b** (0.015 mmol), *p*-nitrobenzaldehyde **9a** (0.15 mmol) and cyclohexanone **10a** (0.75 mmol) in different solvents (54 μL). [b] Determined by ^{1}H NMR on the crude mixture. [c] In parentheses % of enone from dehydration of the product. [d] Determined by HPLC analysis of the crude mixture using a

chiral stationary phase. [e] Synthesis grade. [f] 16 h. [g] In parentheses combined yield of the isolated diastereomers. [h] 19 h. [i] 0.33 mmol (2.2 equiv) of cyclohexanone were used (44 h). [j] Reaction conducted in a ball-mill.

Reactions in the ball-mill were conducted using a Retsch Mixer Mill model "MM200". The milling instrument consists of a main disk, which can rotate at a frecuency of 30 s^{-1} and accommodates two grinding bowls. Both bowls (5 mL) and balls (9 mm diameter) are made of stainless steel. Typical experimental procedure for the solvent-free aldol reaction performed in the ball-mill: A ball-mill vessel was charged with cyclohexanone (67 mL, 0.65 mmol), *p*-nitrobenzaldehyde (89 mg, 0.59 mmol), **1b** (40 mg, 0.059 mmol) and 2 balls. Stirring was started in a grinding bowl using the ball-mill with a frecuency of 30 s^{-1}. After 6 h 40 min total reaction time (40 min each cycle and 10 min pause), the crude product was washed off the reaction vessel with dichloromethane (2 x 10 mL) and the combined organic fractions were filtered and concentrated under reduced pressure.

Temperature effects on the aldol reaction of cyclohexanone with *p*-nitrobenzaldehyde catalyzed by polymers **1a,b**

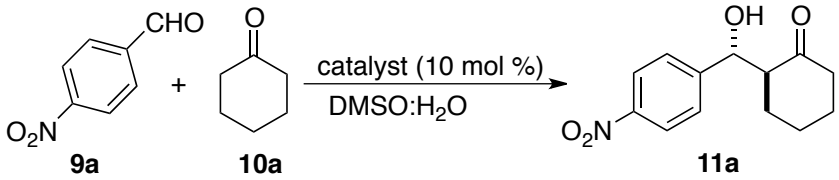


Table SI-2. Temperature effects on the aldol reaction of cyclohexanone with *p*-nitrobenzaldehyde catalyzed by polymers **1a,b**.[a]

entry	catalyst	T (ºC)	solvent	time (h)	conversion[b] (%)	yield[c] (%)	anti:syn[b]	ee anti[d] (%)
1	**1a**	35	DMSO/H_2O (83:17)	14	100	96	89:11	91
2	**1a**	35	DMSO/H_2O (91:9)	14	100	94	85:15	93
3	**1b**	35	DMSO/H_2O (83:17)	14	100	95	88:12	93
4	**1b**	35	DMSO/H_2O (91:9)	14	100	91	89:11	93
5	**1b**	60	DMSO/H_2O (83:17)	11	90	86	82:18	89

[a] Reactions were performed with polymer **1a** or **1b** (0.015 mmol), *p*-nitrobenzaldehyde (0.15 mmol) and cyclohexanone (0.75 mmol) in a mixture of DMSO:H_2O (54 μL). [b] Determined by ^1H NMR on the crude mixture. [c] Combined yield of the isolated diastereomers. [d] Determined by HPLC analysis of the crude mixture using a chiral stationary phase.

Screening of additives on the aldol reaction of cyclohexanone with *p*-nitrobenzaldehyde catalyzed by polymer **1b**

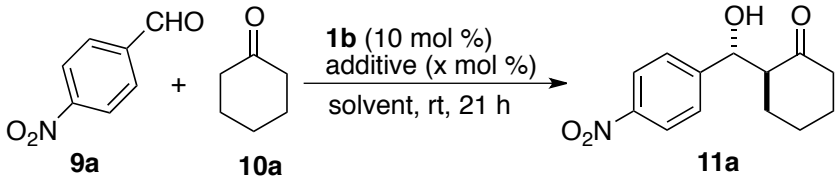


Table SI-3. Screening of additives on the aldol reaction of cyclohexanone with *p*-nitrobenzaldehyde catalyzed by **1b**.[a]

entry	solvent	additive (mol %)	conversion[b] (%)	yield[c] (%)	*anti:syn*[b]	ee *anti*[d] (%)
1	DMSO/H_2O (91:9)	none	100[e]	98	91:9	91
2	DMSO/H_2O (91:9)	4-NO_2-$C_6H_4CO_2H$ (15)	98	96	91:9	93
3	DMSO/H_2O (91:9)	CF_3CO_2H (10)	84	-	93:7	96
4	DMSO/H_2O (83:17)	none	100[e]	96	90:10	93
5	DMSO/H_2O (83:17)	DiMePEG (10)	97	90	89:11	94
6	DMSO/H_2O (83:17)	CH_3CO_2H (10)	100	97	89:11	94
7	DMSO/H_2O (83:17)	4-NO_2-$C_6H_4CO_2H$ (15)	100	97	92:8	93
8	DMSO/H_2O (83:17)	CF_3CO_2H (10)	99	90	96:4	96
9	H_2O	none	74	-	71:29	73
10	H_2O	DiMePEG (10)	71	58	90:10	89
11	H_2O	CF_3CO_2H (10)	27	-	93:7	94

[a] Reactions were performed with polymer **1b** (0.015 mmol, 10.2 mg), *p*-nitrobenzaldehyde (0.15 mmol) and cyclohexanone (0.75 mmol) in the corresponding solvent (54 μL). [b] Determined by ^{1}H NMR on the crude mixture. [c] The data in parentheses indicate the combined yield of the isolated diastereomers. [d] Determined by HPLC analysis of the crude mixture using a chiral stationary phase. [e] 19 h.

Solvent and additives effects on the aldol reaction of cyclohexanone with *p*-nitrobenzaldehyde catalyzed by polymer **2**

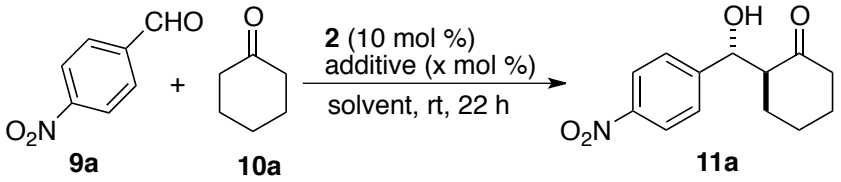


Table SI-4. Solvent and additives effects on the aldol reaction of cyclohexanone with *p*-nitrobenzaldehyde catalyzed by polymer **2**.[a]

entry	solvent	additive (mol %)	conversion[b] (%)	yield[c] (%)	*anti:syn*[b]	ee *anti*[d] (%)
1	H_2O	none	91	90	95:5	96
2	DMSO/H_2O (50:50)	none	96	95	95:5	96
3	DMF/H_2O (50:50)	none	96	94	95:5	96
4	H_2O	CF_3CO_2H (10)	90	87	92:8	95
5	H_2O	DiMePEG (10)	69	65	89:11	95

[a] Reactions were performed with polymer **2** (0.015 mmol, 10.2 mg), *p*-nitrobenzaldehyde (0.15 mmol) and cyclohexanone (0.75 mmol) in the corresponding solvent (54 μL). [b] Determined by ^{1}H NMR on the crude mixture. [c] The data in parentheses indicate the combined yield of the isolated diastereomers. [d] Determined by HPLC analysis of the crude mixture using a chiral stationary phase.

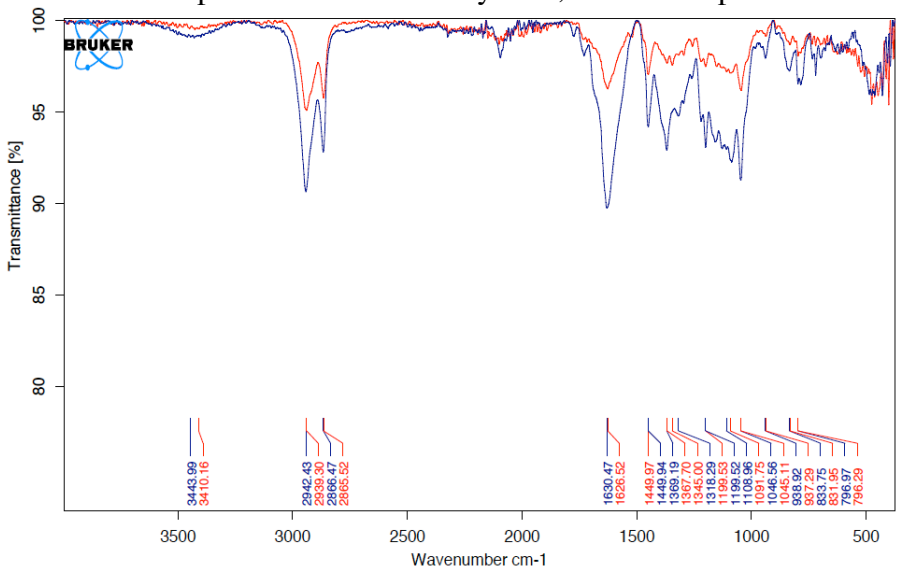
Recycling experiments with catalysts **1b** and **2**

a) Recycling experiments with catalyst **1b**. After performing the aldol reaction of *p*-nitrobenzaldehyde (**9a**, 49 mg, 0.32 mmol) with cyclohexanone (**10a**, 168 μL, 1.62 mmol) in the presence of polymer **1b** (22 mg, 0.032 mmol) swollen in 116 μL of a DMSO/H_2O (87:13) mixture containing TFA (0.015 mmol) at room temperature for 23 h, the polymer was separated by filtration and rinsed with water (2 mL) and dichloromethane (2 mL). The polymer was then dried under reduced pressure for 1 h and reused in the next run. Results have been collected in the following table:

cycle	conversion [a] (%)	yield (%)[b]	*anti:syn*[a]	ee *anti* (%)[c]
1	93	90	96:4	96
2	90	87	96:4	96
3	87	85	96:4	96
4	87	84	96:4	96
5	88	85	96:4	96
6	83	79	96:4	96
7	82	80	96:4	96

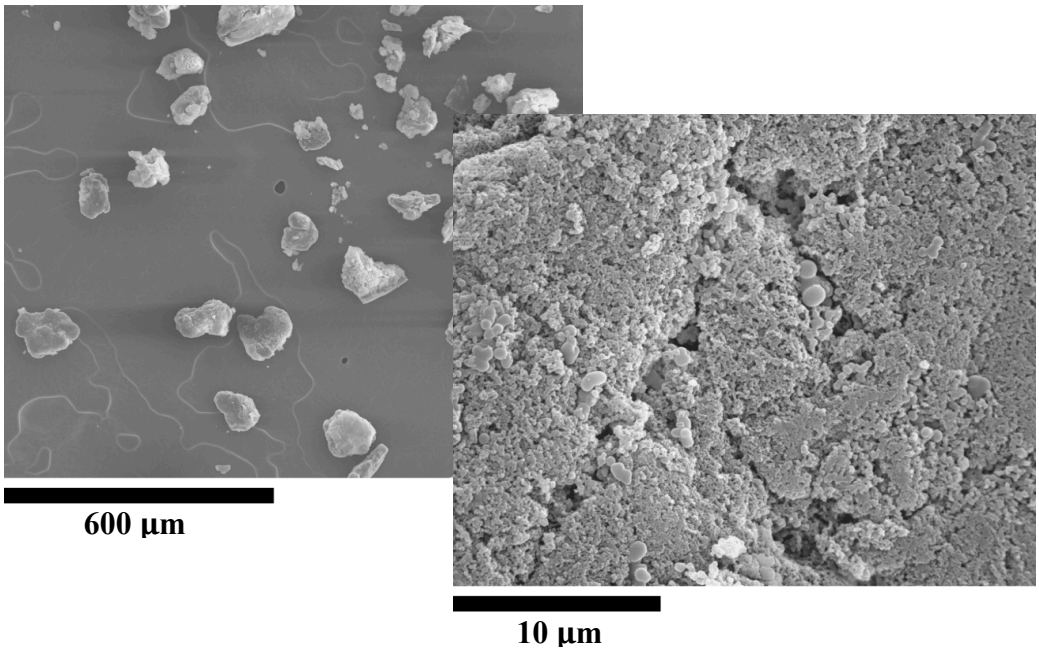
[a] Determined by ^{1}H NMR on the crude mixture. [b] Combined yield of the isolated isomers after flash chromatography. [c] Determined by HPLC analysis of the crude mixture using a chiral stationary phase.

Figure SI-1. In blue: IR spectrum of fresh catalyst **1b**; In red: IR spectrum after seven runs.

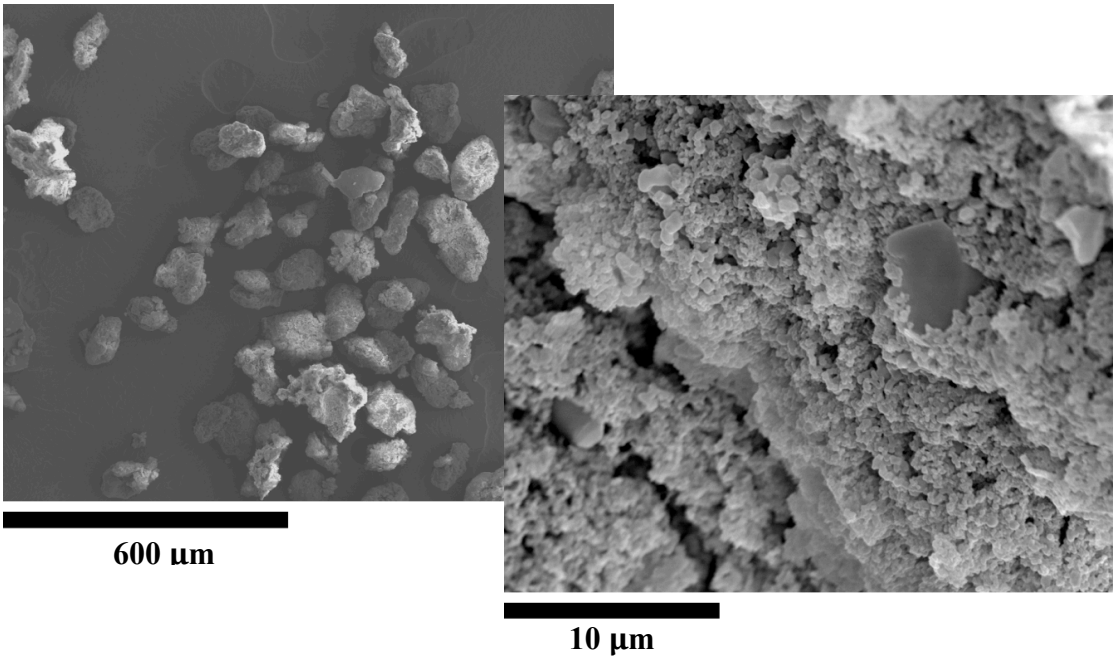


Fresh catalyst **1b**: Elemental analysis (%): N, 8.26; f = 1.47 mmol g^{-1}. Elemental analysis after seven runs (%): N, 7.53; f = 1.34 mmol g^{-1}

Figure SI-2. SEM picture of fresh catalyst **1b** (A) and after seven runs (B).



A



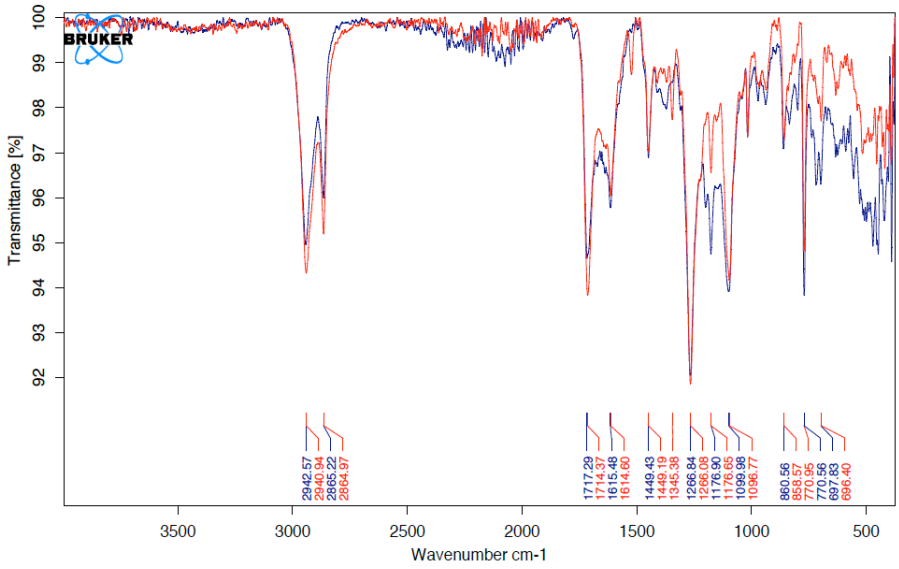
B

b) Recycling experiments with catalyst **2**. After performing the aldol reaction of *p*-nitrobenzaldehyde (**9a**, 41 mg, 0.27 mmol) with cyclohexanone (**10a**, 140 μL, 1.35 mmol) in DMF:H_2O (50:50, 98 μL) in the presence of polymer **2** (0.027 mmol, 31 mg) at room temperature for 22 h following the general procedure, the polymer was separated by filtration and rinsed with water (2 mL) and dichloromethane (2 mL). The polymer was then dried under reduced pressure for 1 h and reused in the next run. Results have been collected in the following table:

cycle	yield (%)[a]	*anti*:*syn*[b]	ee *anti* (%)[c]
1	97	96:4	97
2	98	96:4	96
3	99	96:4	96
4	98	96:4	96
5	99	95:5	95
6	99	95:5	95
7	98	96:4	94

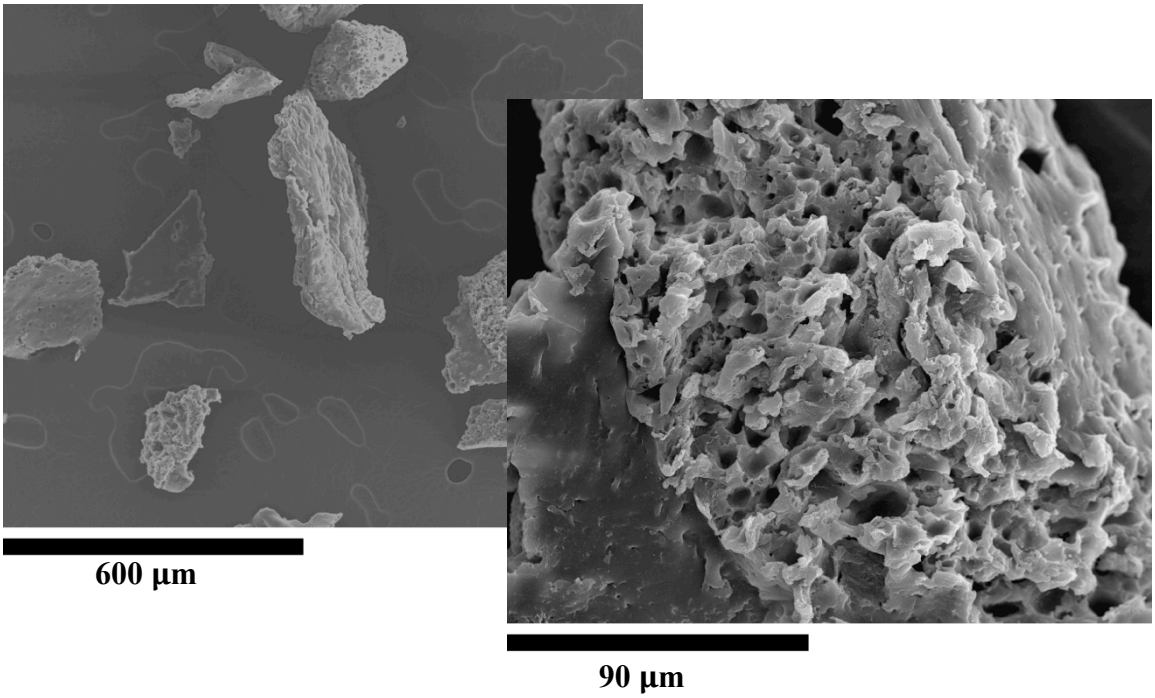
[a] Combined yield of the isolated isomers after flash chromatography. [b] Determined by ^{1}H NMR on the crude mixture. [c] Determined by HPLC analysis of the crude mixture using a chiral stationary phase.

Figure SI-3. In blue: IR spectrum of fresh catalyst **2**; In red: IR spectrum after seven runs.

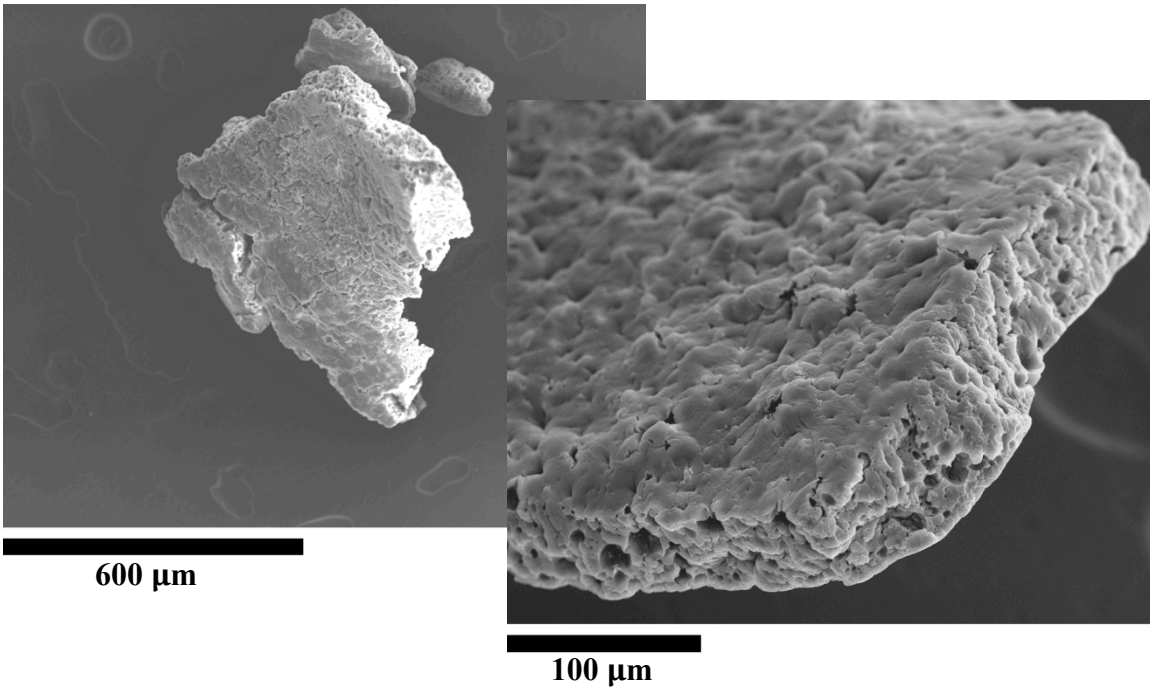


Fresh catalyst **2**: Elemental analysis (%): N, 4.89; $f = 0.87$ mmol g^{-1}. Elemental analysis after seven runs (%): N, 4.91; $f = 0.876$ mmol g^{-1}

Figure SI-4. SEM picture of fresh catalyst **2** (A) and after seven runs (B).



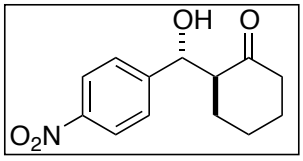
A



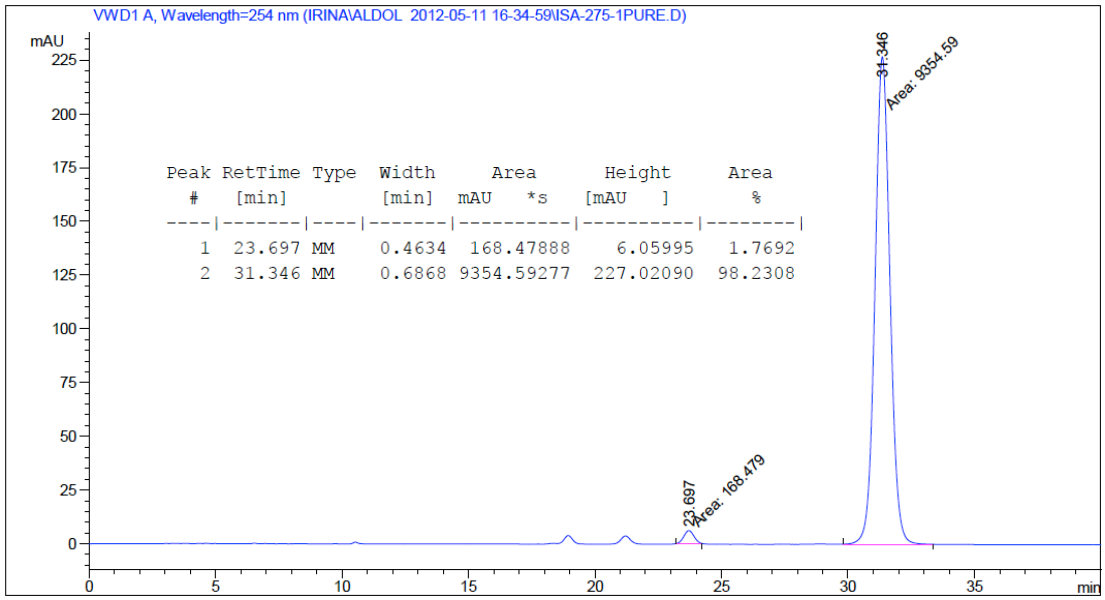
B

[1]HNMR and [13]CNMR spectra and chromathographic data of aldol products **11**

(2*S*,1'*R*)-2-(Hydroxy-4-nitrophenylmethyl)cyclohexan-1-one **11a**:

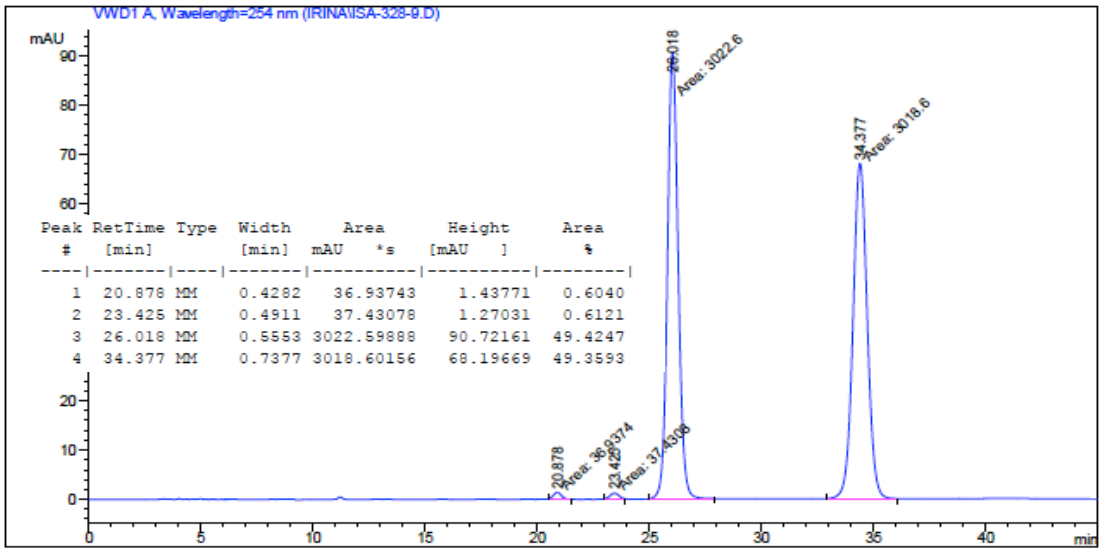


Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 Hexane:2-propanol), 1.0 mL/min, λ = 254 nm; major enantiomer t_r = 31.4 min, minor enantiomer t_r = 24.7 min. All the spectroscopic data matched with literature.[S4, S5]



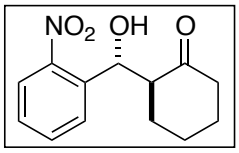
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.697	MM	0.4634	168.47888	6.05995	1.7692
2	31.346	MM	0.6868	9354.59277	227.02090	98.2308

Racemic mixture:

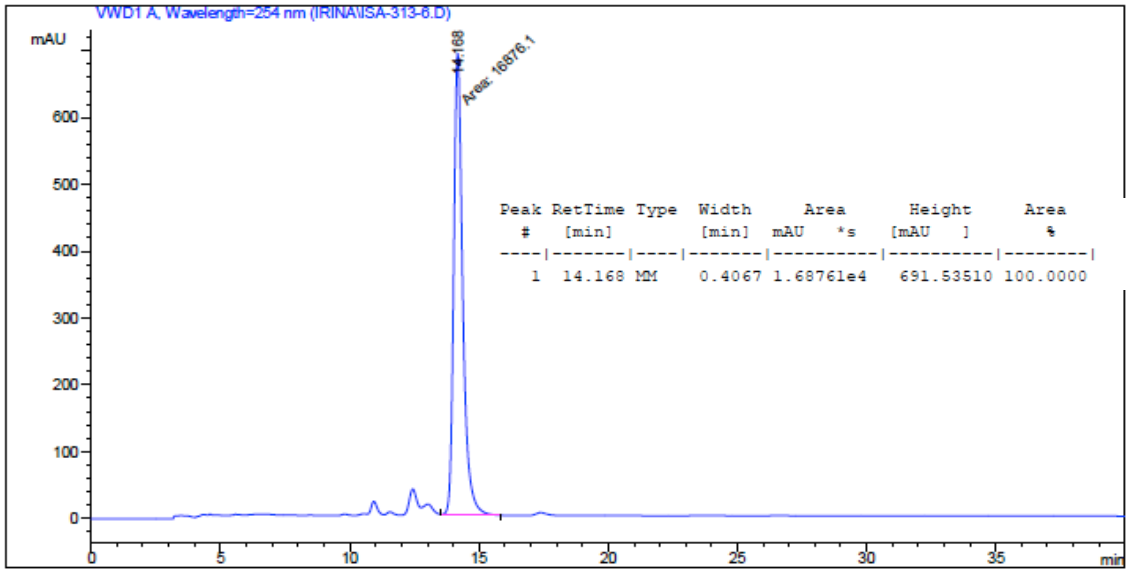


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.878	MM	0.4282	36.93743	1.43771	0.6040
2	23.425	MM	0.4911	37.43078	1.27031	0.6121
3	26.018	MM	0.5553	3022.59888	90.72161	49.4247
4	34.377	MM	0.7377	3018.60156	68.19669	49.3593

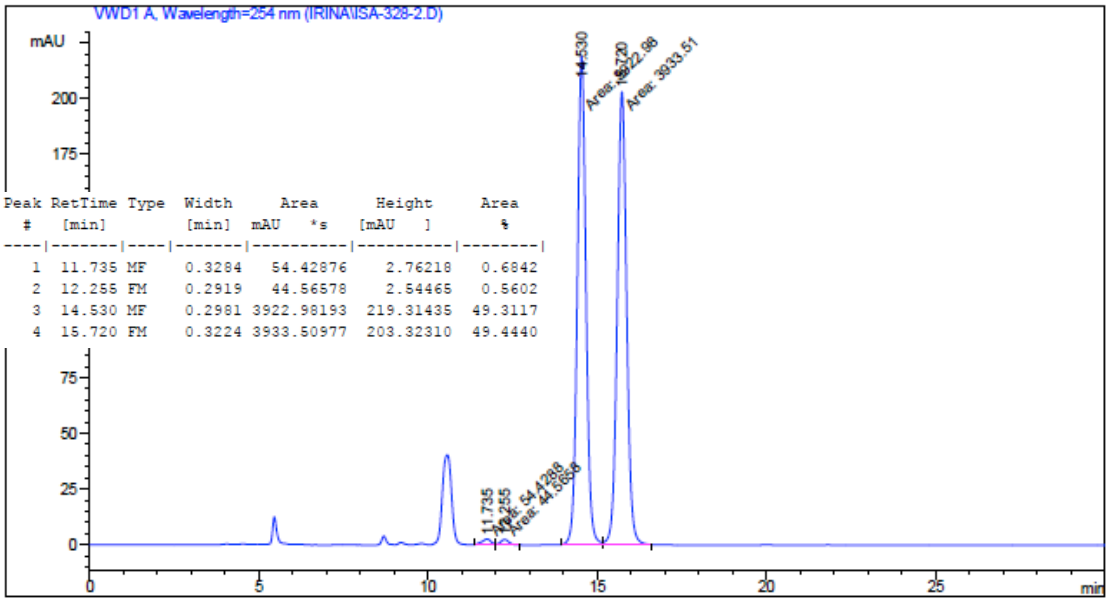
(2*S*,1'*R*)-2-(Hydroxy-2-nitrophenylmethyl)cyclohexan-1-one **11b**:



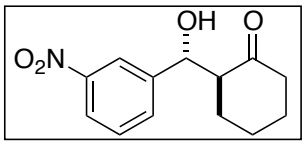
Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 hexane:2-propanol), 1.0 mL/min, λ = 254 nm; major enantiomer t_r= 14.2 min. All the spectroscopic data matched with literature.[S4, S6]



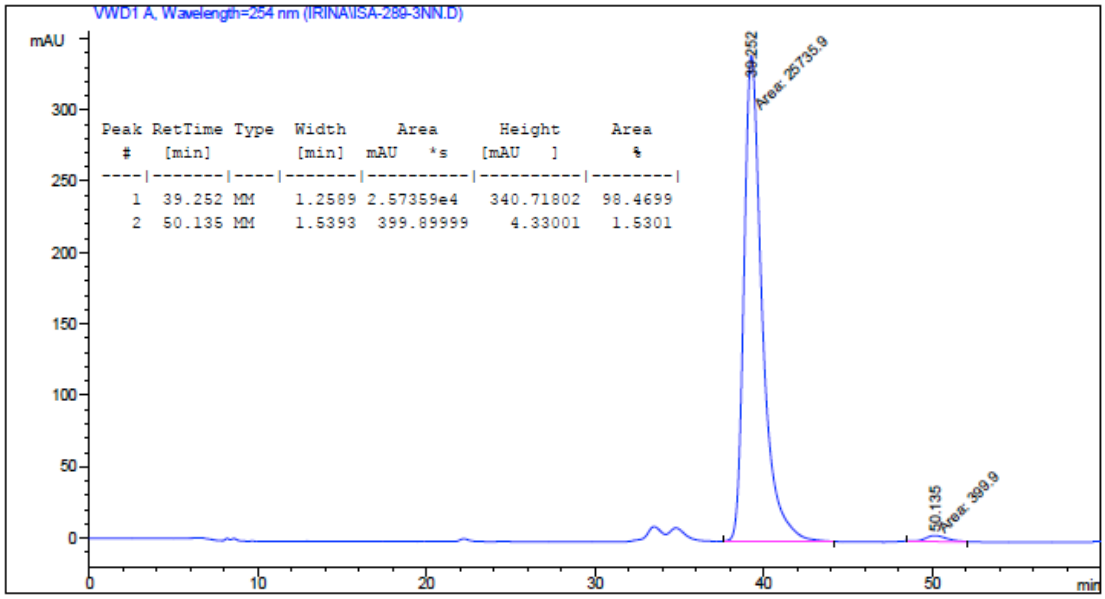
Racemic mixture:



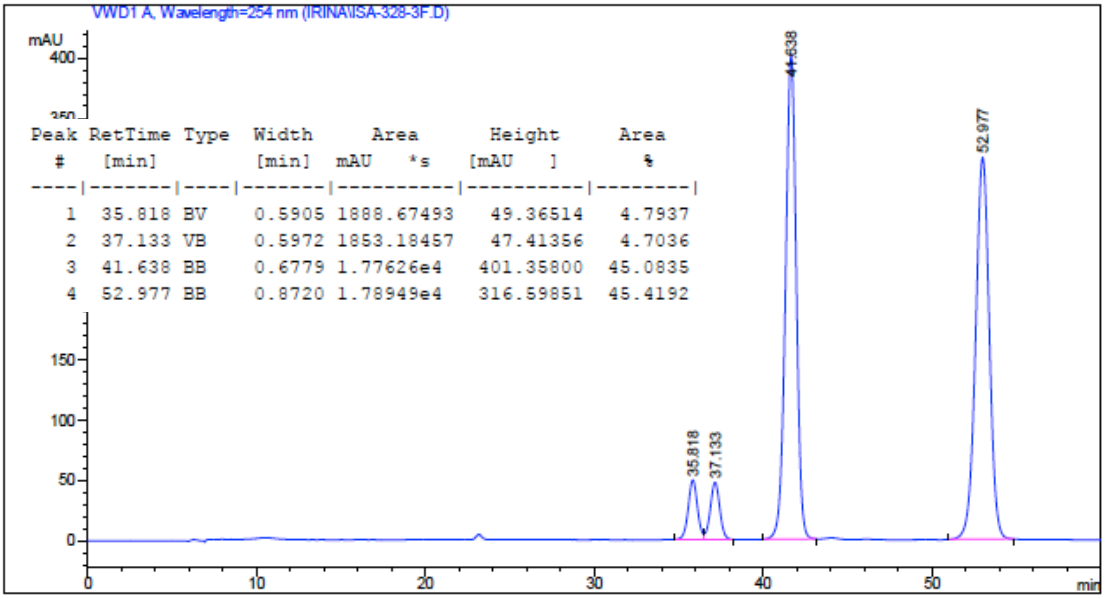
(2*S*,1'*R*)-2-(Hydroxy-3-nitrophenylmethyl)cyclohexan-1-one **11c**:



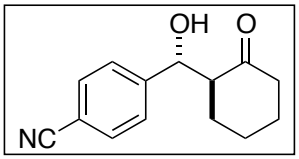
Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (95:5 hexane:2-propanol), 0.8 mL/min, λ = 254 nm; major enantiomer t_r= 39.2 min, minor enantiomer t_r= 50.1 min. All the spectroscopic data matched with literature.[S4, S6]



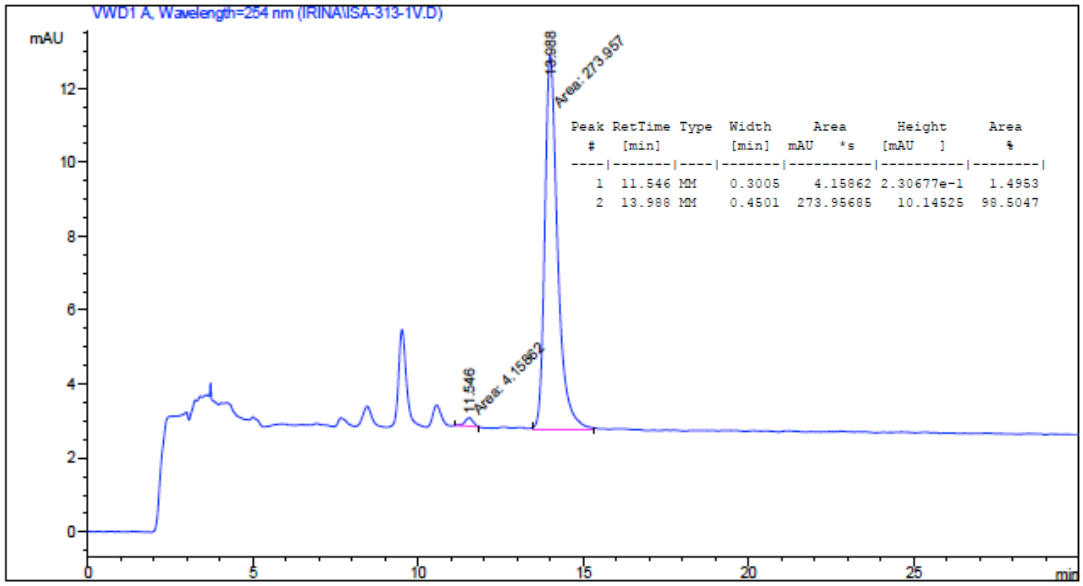
Racemic mixture:



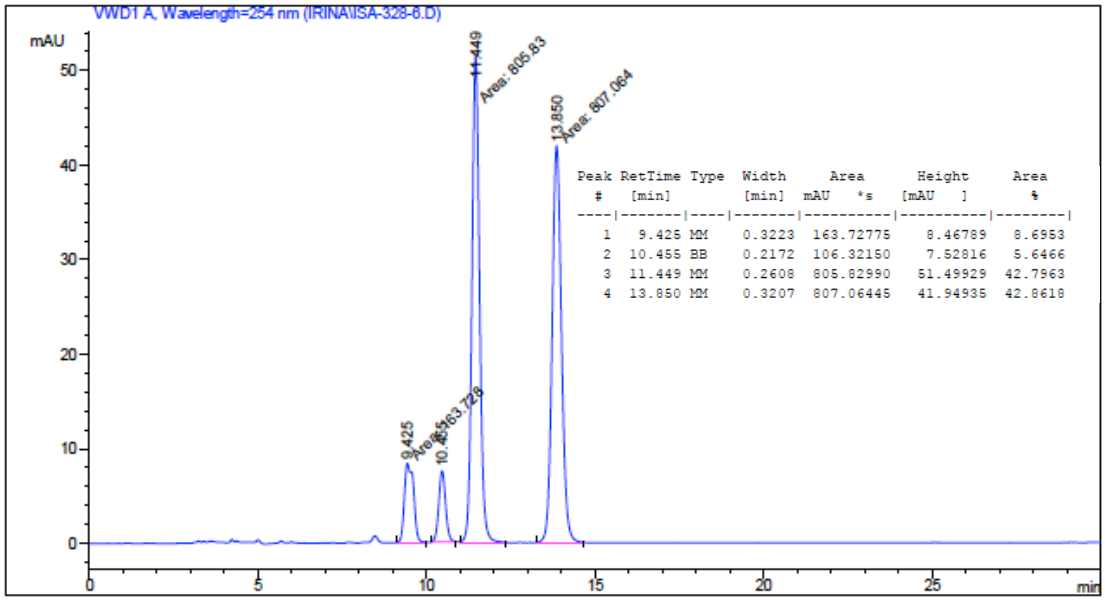
(2*S*,1'*R*)-2-(Hydroxy-4-cyanophenylmethyl)cyclohexan-1-one **11d**:



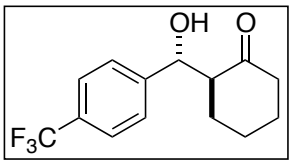
Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (80:20 Hexane:2-propanol), 1.0 mL/min, λ = 254 nm; major enantiomer t_r = 14.0 min, minor enantiomer t_r = 11.5 min. All the spectroscopic data matched with literature.[S4, S5]



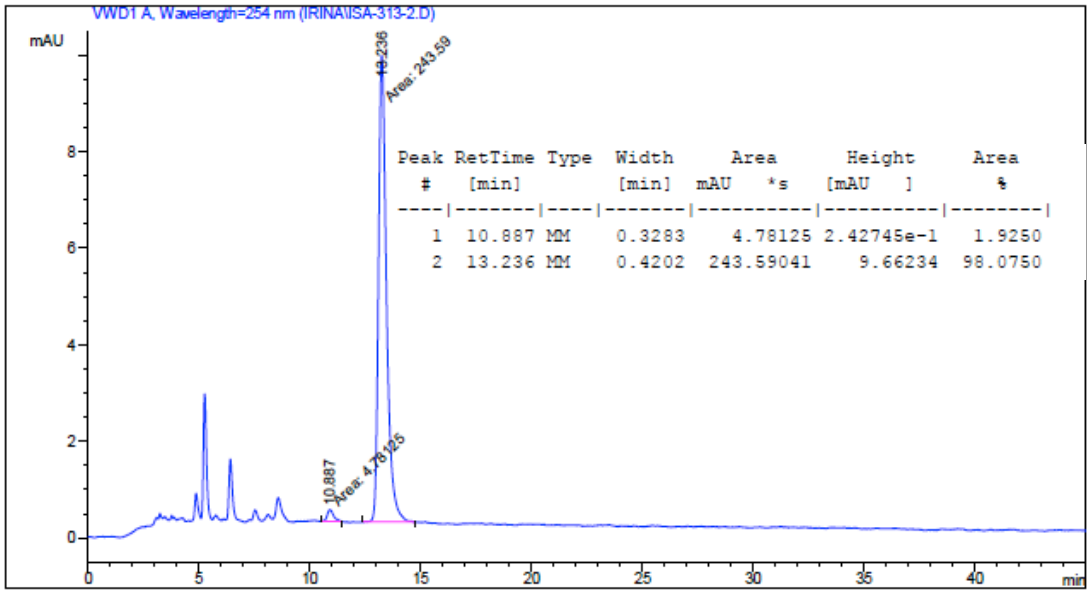
Racemic mixture:



(2*S*,1'*R*)-2-(Hydroxy-4-trifluoromethylphenylmethyl)cyclohexan-1-one **11e**:

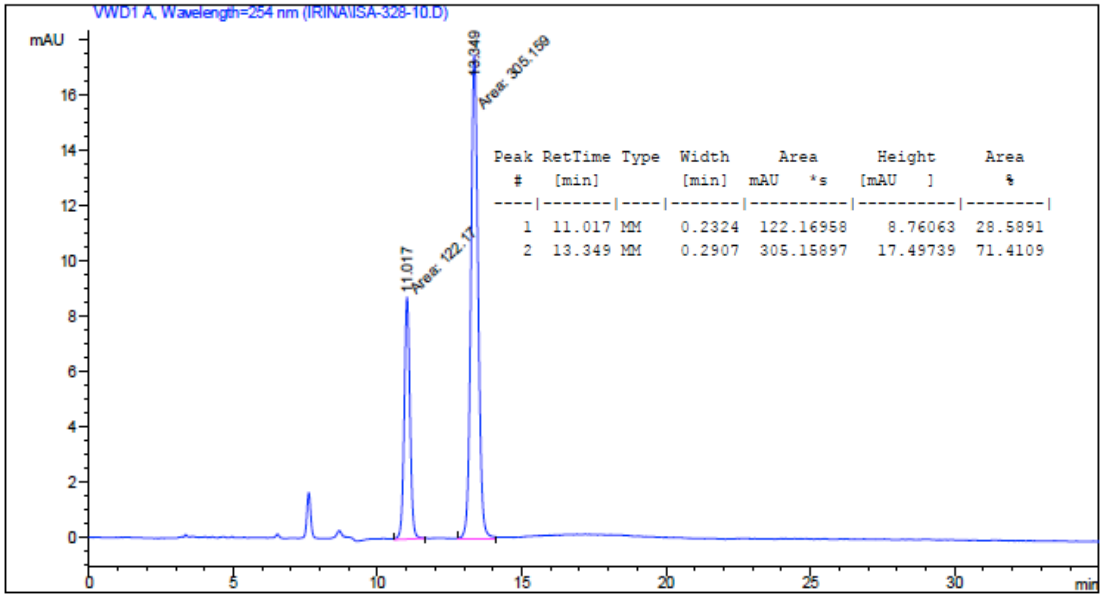


Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 Hexane:2-propanol), 1.0 mL/min, λ = 254 nm; major enantiomer t_r = 13.2 min, minor enantiomer t_r = 10.9 min. All the spectroscopic data matched with literature.[S5]



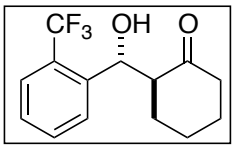
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.887	MM	0.3283	4.78125	2.42745e-1	1.9250
2	13.236	MM	0.4202	243.59041	9.66234	98.0750

Racemic mixture:

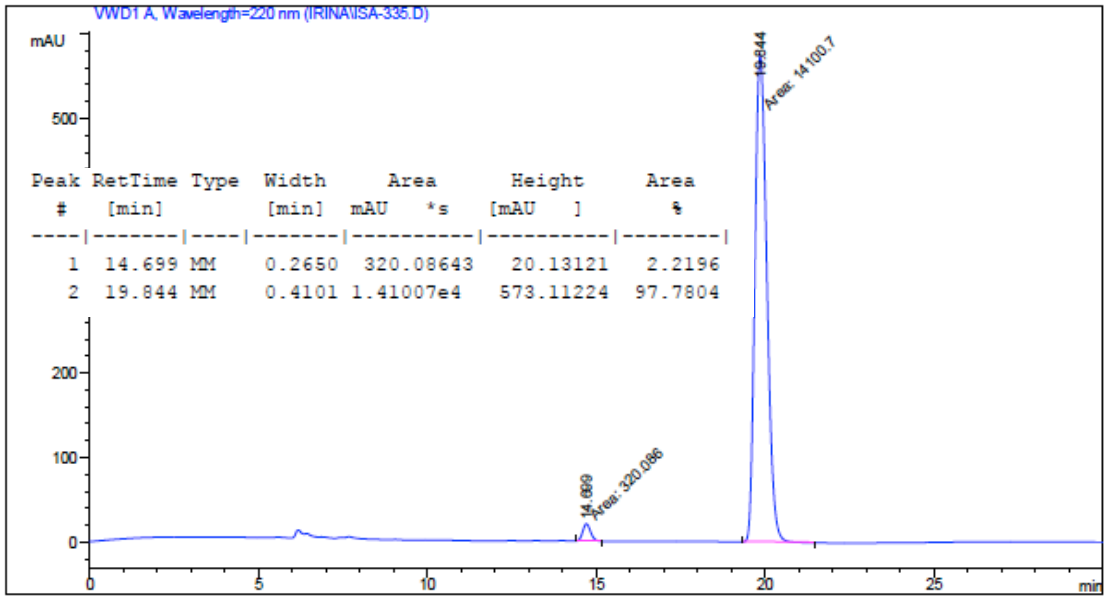


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.017	MM	0.2324	122.16958	8.76063	28.5891
2	13.349	MM	0.2907	305.15897	17.49739	71.4109

(2*S*,1'*R*)-2-(Hydroxy-2-trifluoromethylphenylmethyl)cyclohexan-1-one **11f**:

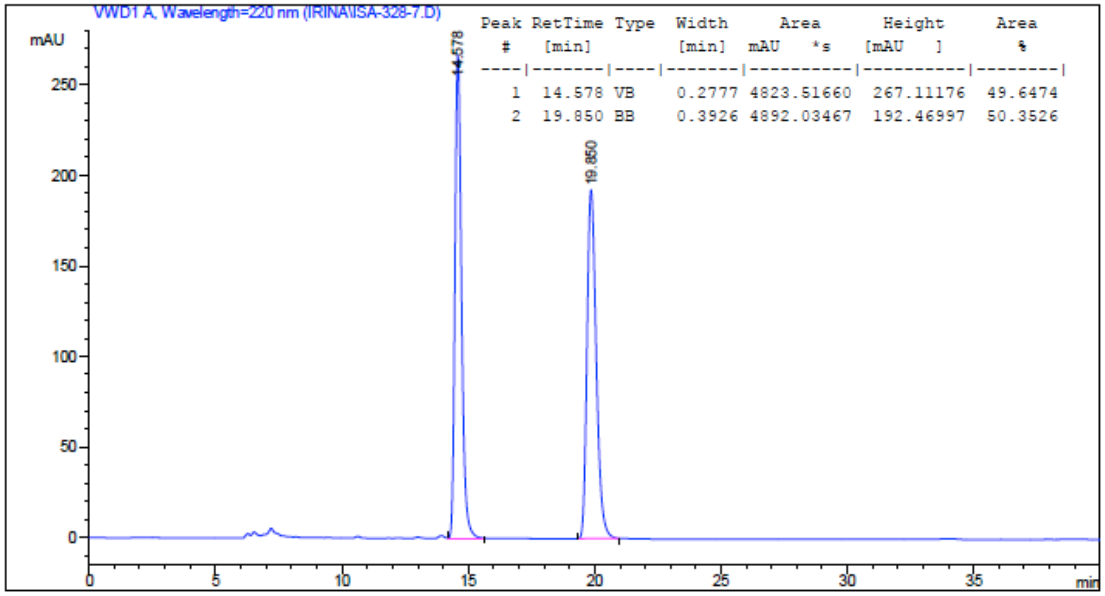


Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (90:10 Hexane:2-propanol), 0.5 mL/min, λ = 220 nm; major enantiomer t_r = 19.8 min, minor enantiomer t_r = 14.7 min. All the spectroscopic data matched with literature.[S6]



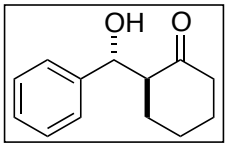
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.699	MM	0.2650	320.08643	20.13121	2.2196
2	19.844	MM	0.4101	1.41007e4	573.11224	97.7804

Racemic mixture:

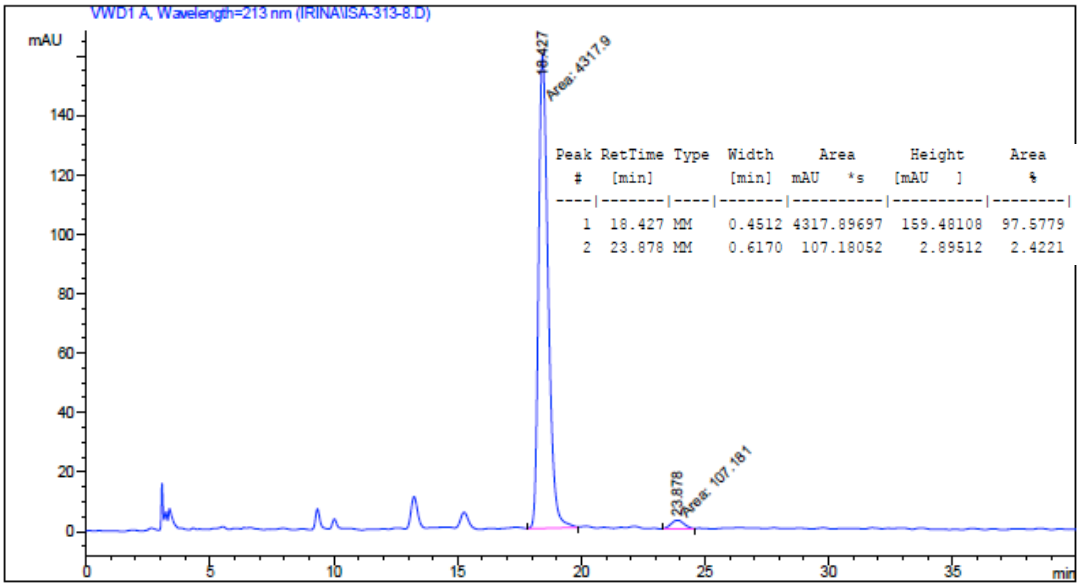


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.578	VB	0.2777	4823.51660	267.11176	49.6474
2	19.850	BB	0.3926	4892.03467	192.46997	50.3526

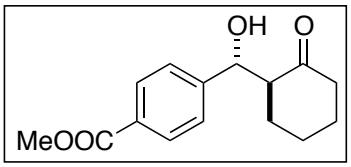
(2*S*,1'*R*)-2-(Hydroxyphenylmethyl)cyclohexan-1-one **11g**:



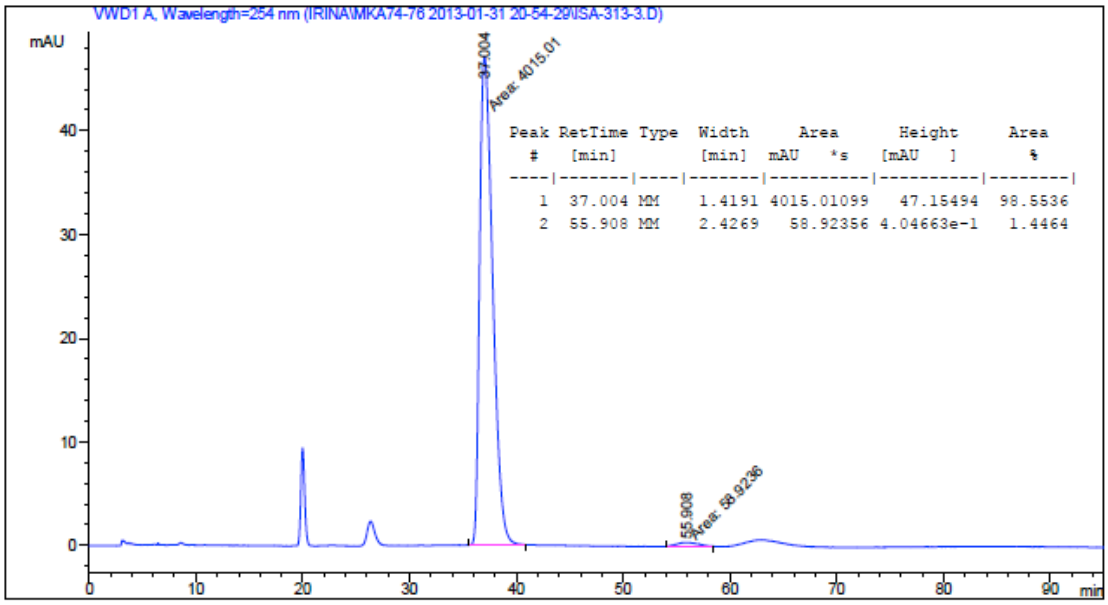
Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (99:1 Hexane:2-propanol), 1.0 mL/min, λ = 213 nm; major enantiomer t_r = 18.4 min, minor enantiomer t_r = 23.9 min. All the spectroscopic data matched with literature.[S5,S7]



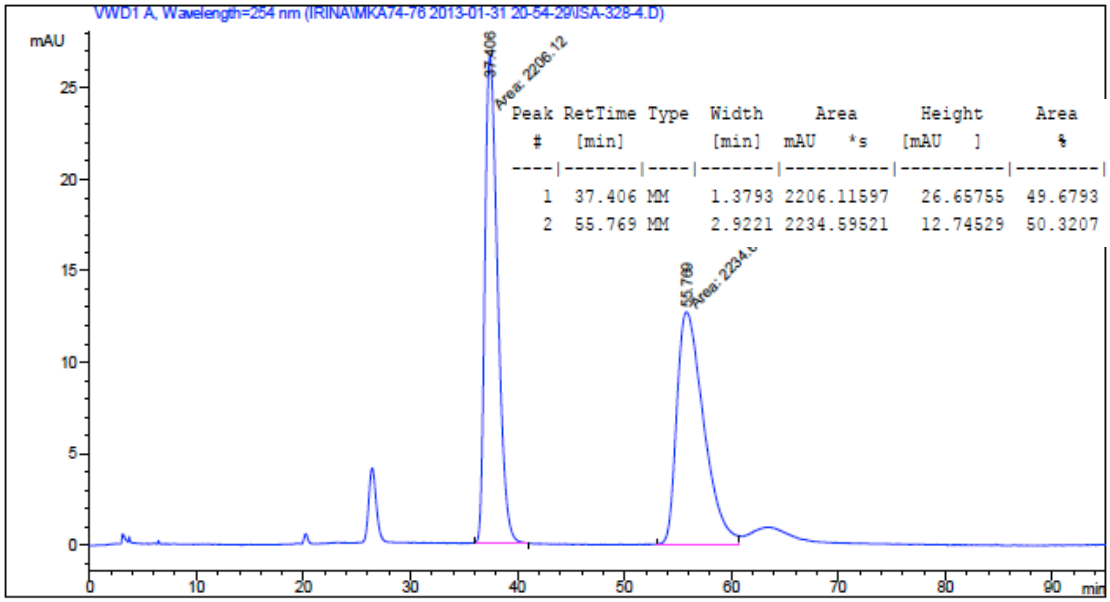
Methyl 4-((*R*)-hydroxy((*S*)-2-oxocyclohexyl)methyl)benzoate **11h**:



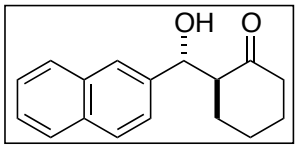
Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (90:10 Hexane:2-propanol), 1.0 mL/min; λ = 254 nm; major enantiomer t_r = 37.0 min, minor enantiomer t_r = 55.9 min. All the spectroscopic data matched with literature.[S4, S5]



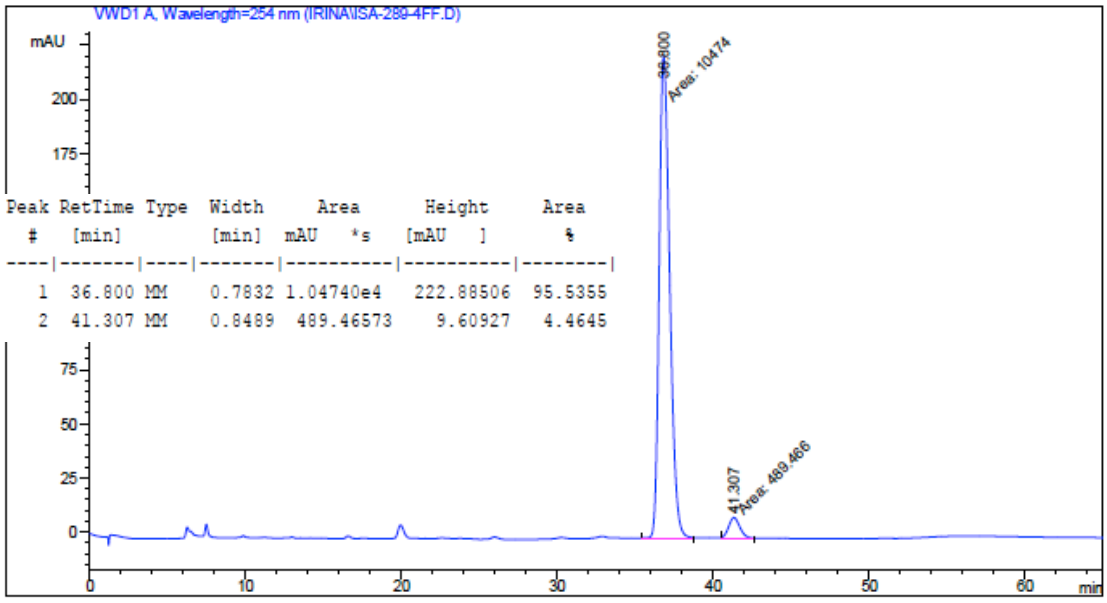
Racemic mixture:



(2*S*,1'*R*)-2-(Hydroxynaphtalen-2-ylmethyl)cyclohexan-1-one **11i**:

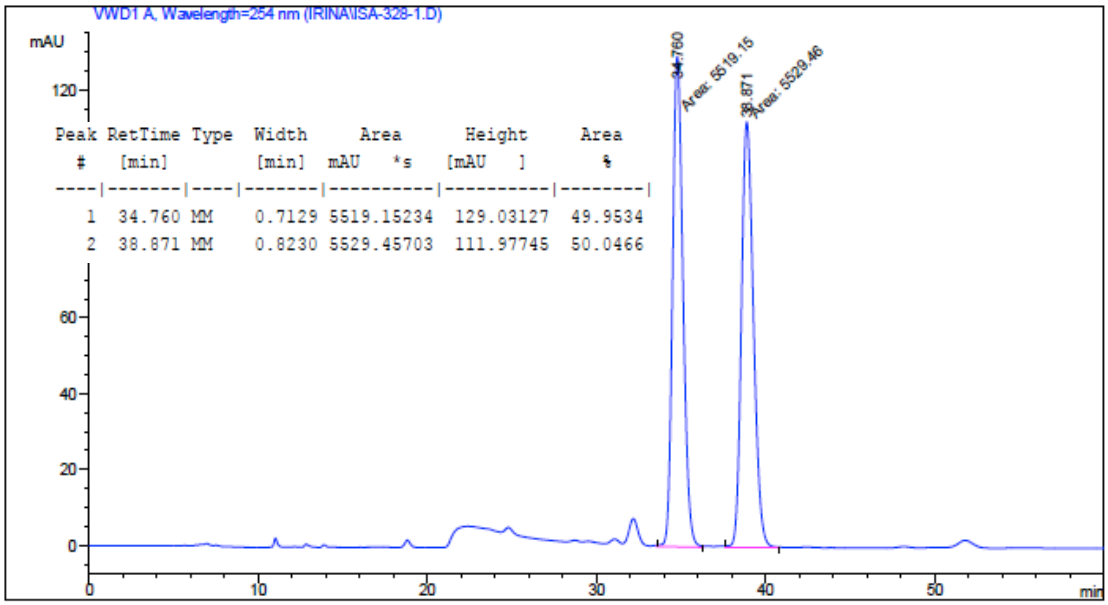


Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (90:10 Hexane:2-propanol), 0.5 mL/min, λ = 254 nm; major enantiomer t_r = 36.8 min, minor enantiomer t_r = 41.3 min. All the spectroscopic data matched with literature.[S7]



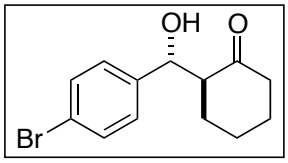
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	36.800	MM	0.7832	1.04740e4	222.88506	95.5355
2	41.307	MM	0.8489	489.46573	9.60927	4.4645

Racemic mixture:

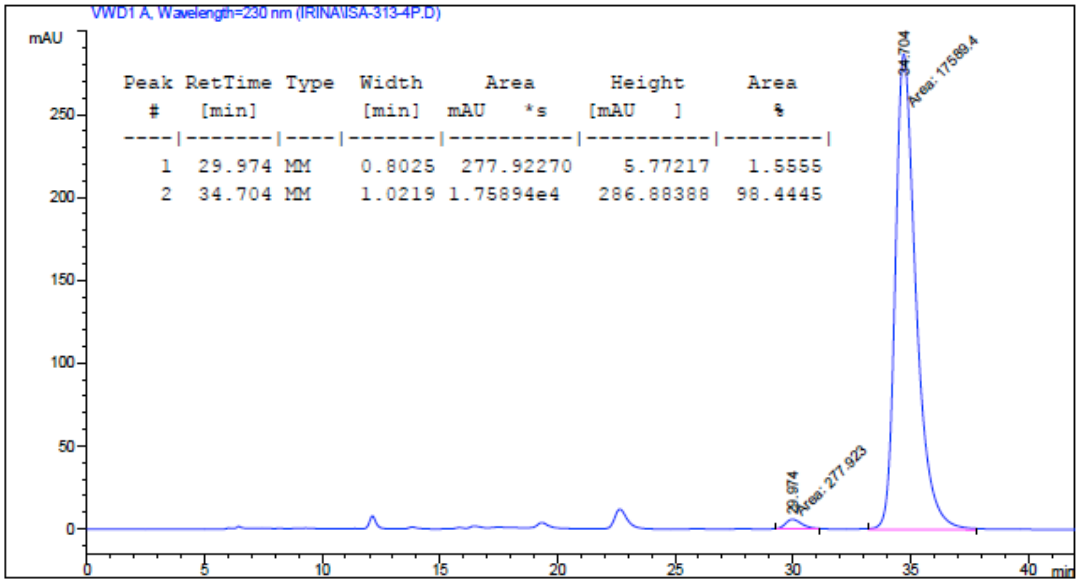


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.760	MM	0.7129	5519.15234	129.03127	49.9534
2	38.871	MM	0.8230	5529.45703	111.97745	50.0466

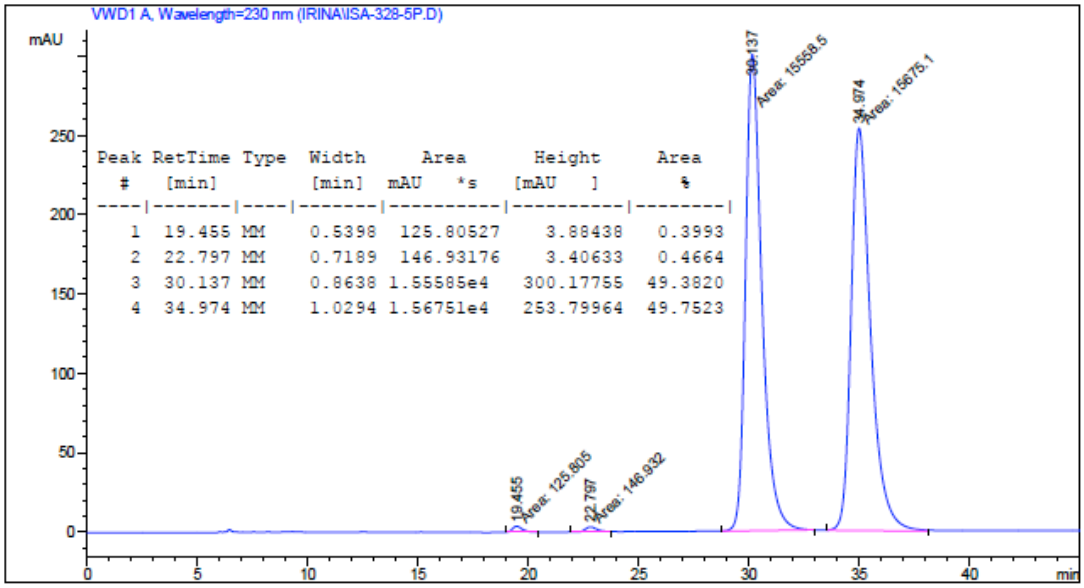
(2*S*,1'*R*)-2-(Hydroxy-4-bromophenylmethyl)cyclohexan-1-one **11j**:



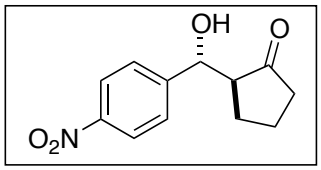
Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 Hexane:2-propanol), 1.0 mL/min; λ = 230 nm; major enantiomer t_r = 34.7 min, minor enantiomer t_r = 29.9 min. All the spectroscopic data matched with literature.[S8]



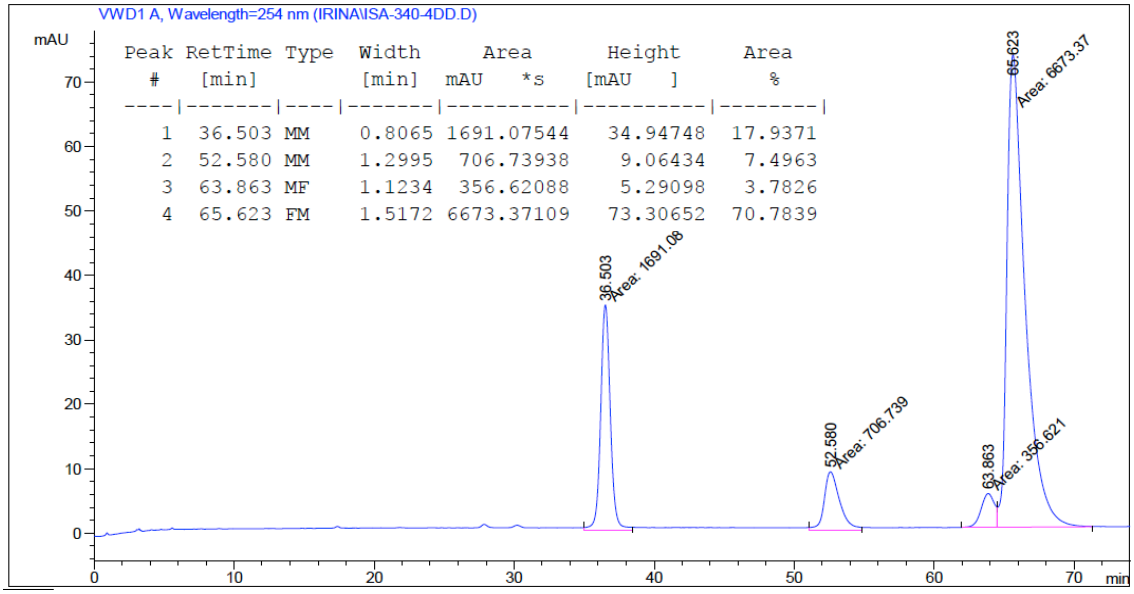
Racemic mixture:



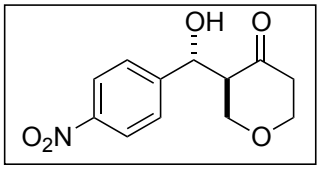
(2*S*,1'*R*)-2-(Hydroxy-4-nitrophenylmethyl)cyclopentan-1-one **11k**:



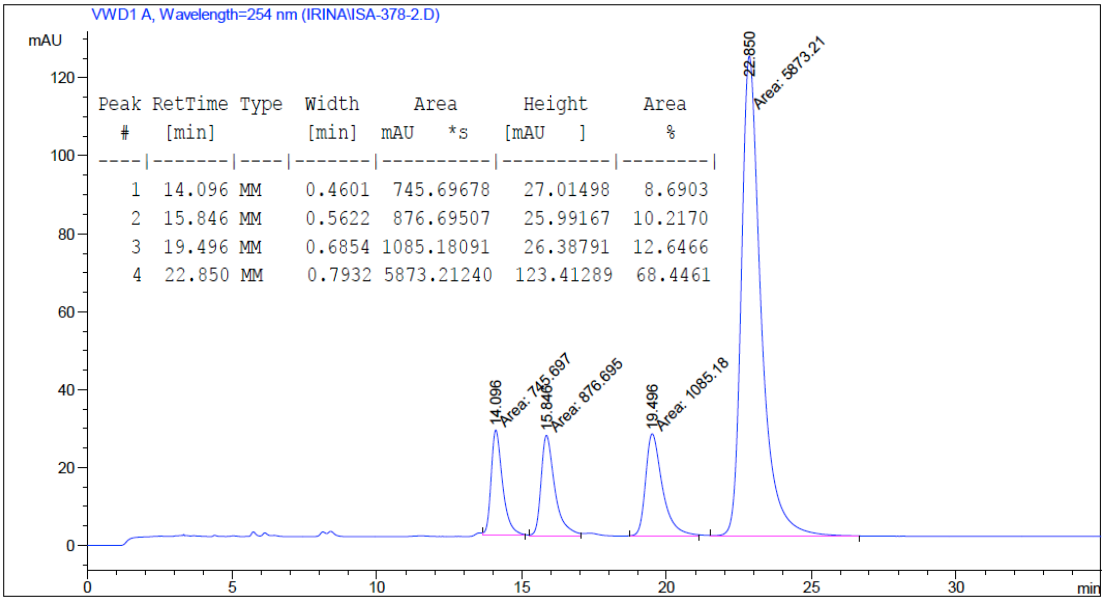
Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (97:3 Hexane:2-propanol), 1.0 mL/min; λ = 254 nm; major enantiomer t_r = 65.6 min, minor enantiomer t_r = 63.9 min. All the spectroscopic data matched with literature.[S4, S8]



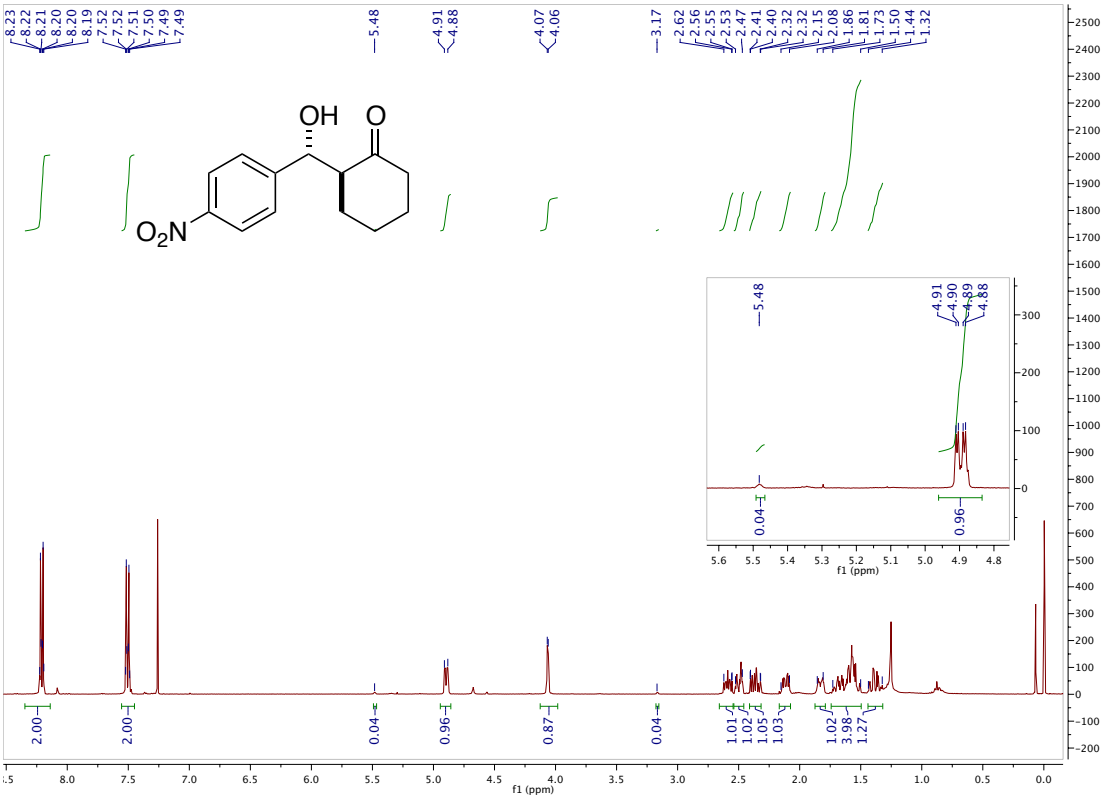
(2*S*,1'*R*)-2-(Hydroxy-4-nitrophenylmethyl)tetrahydropyran-4-one **11l**:

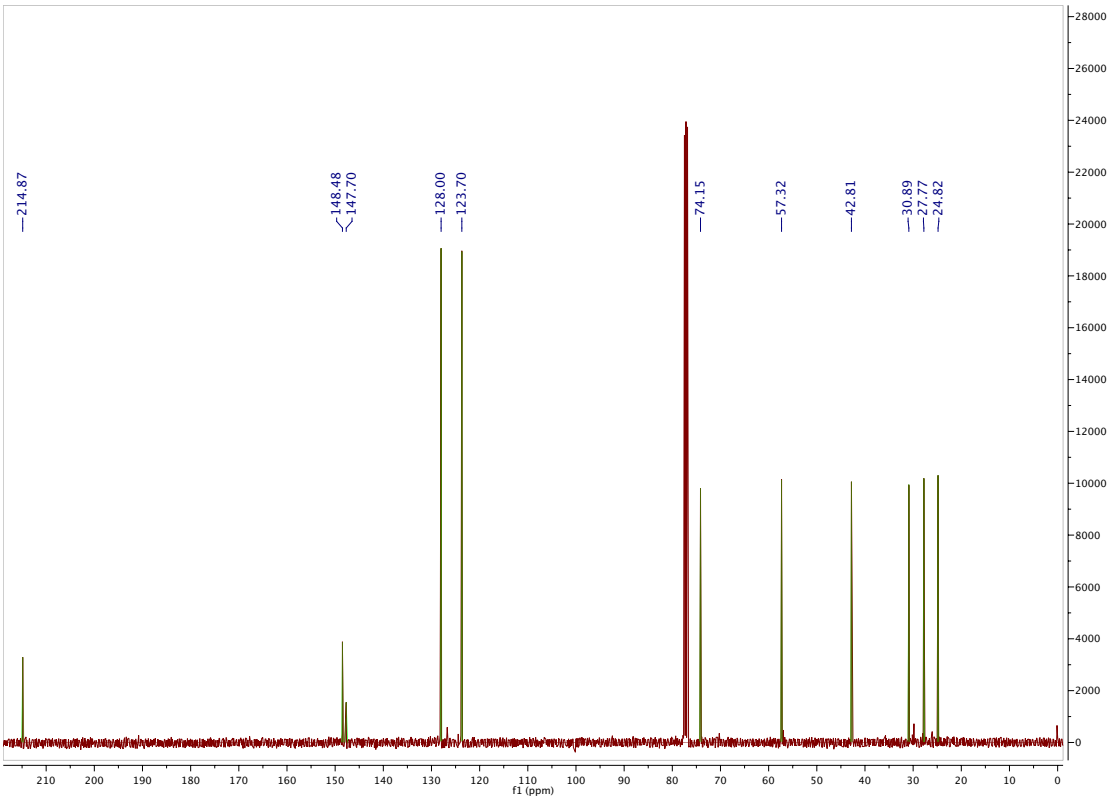


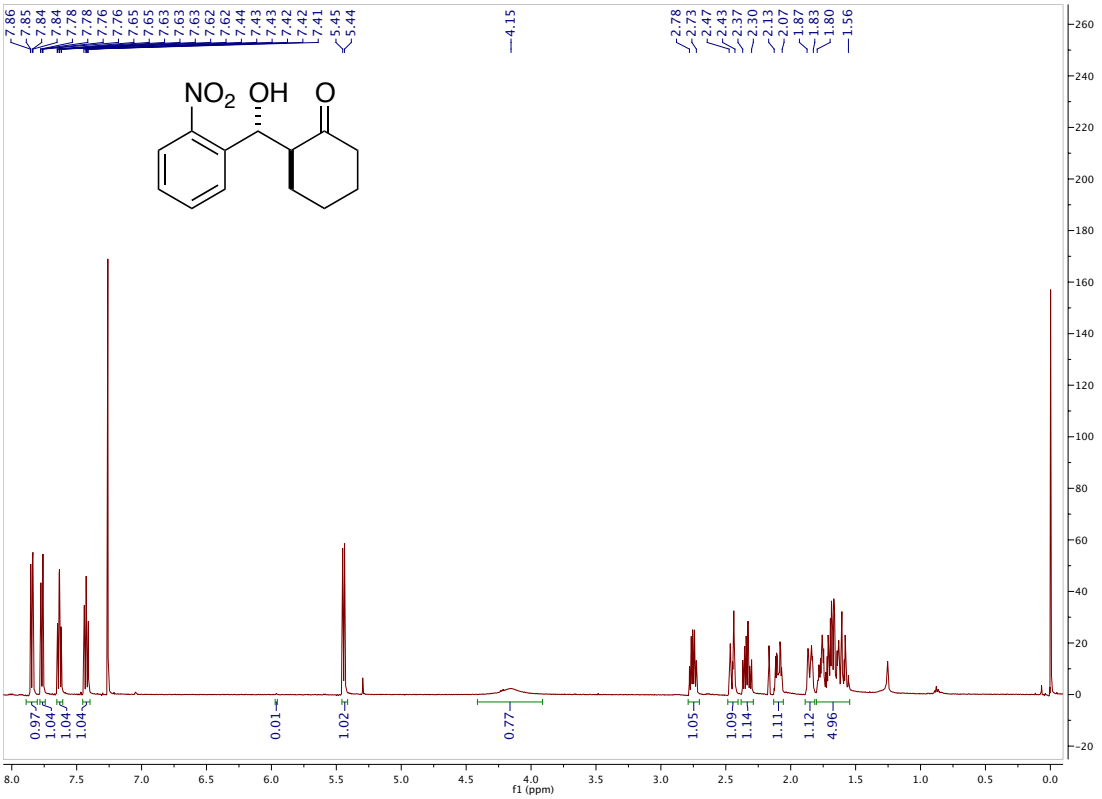
Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (80:20 Hexane:2-propanol), 1.0 mL/min; λ = 254 nm; major enantiomer t_r = 22.9 min, minor enantiomer t_r = 19.5 min. All the spectroscopic data matched with literature.[S9]

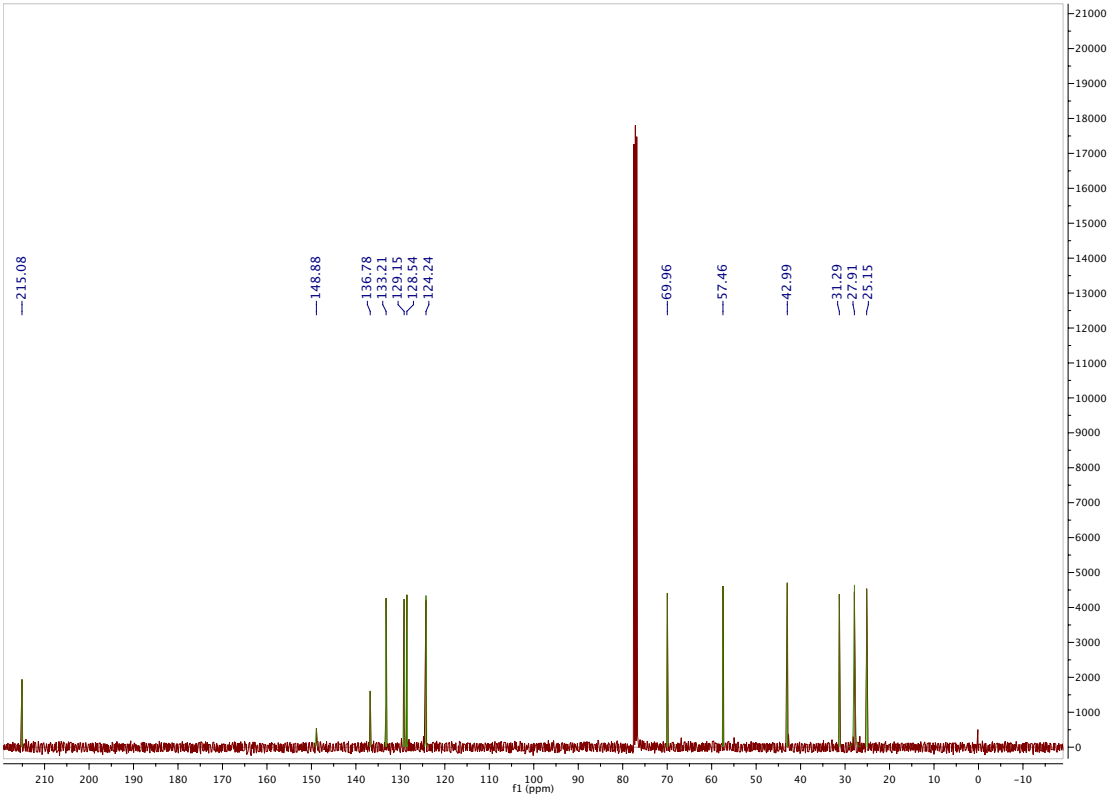


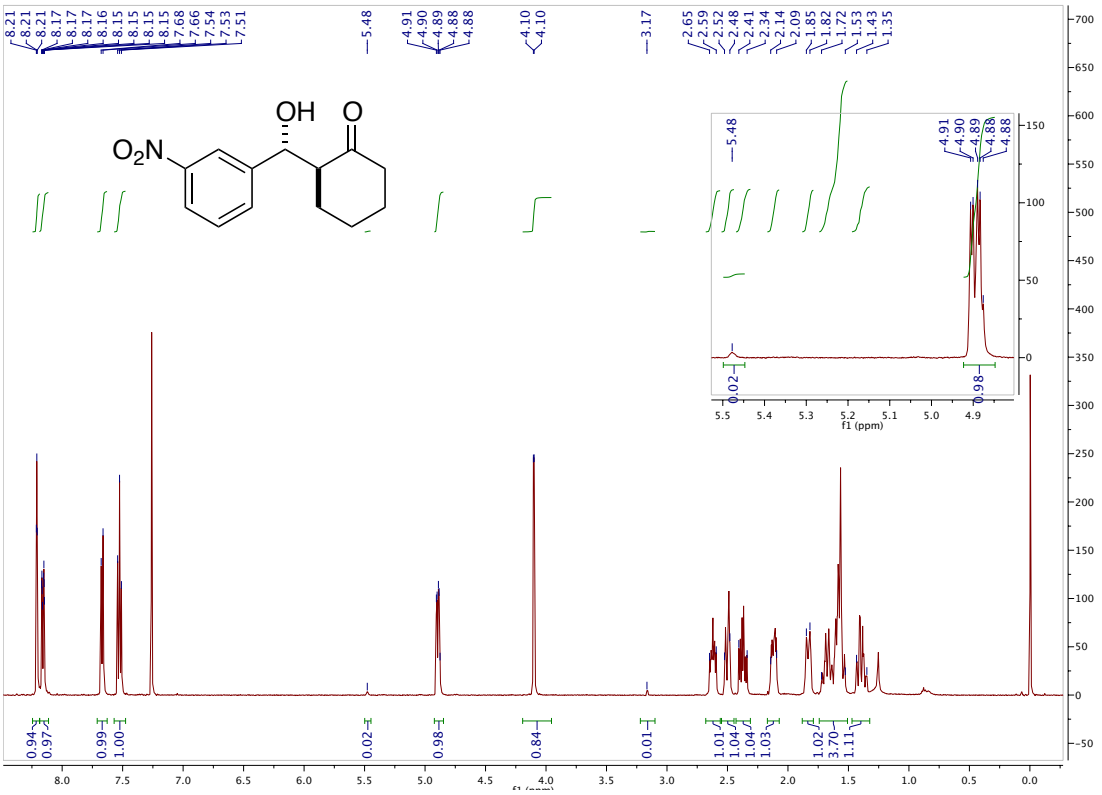
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.096	MM	0.4601	745.69678	27.01498	8.6903
2	15.846	MM	0.5622	876.69507	25.99167	10.2170
3	19.496	MM	0.6854	1085.18091	26.38791	12.6466
4	22.850	MM	0.7932	5873.21240	123.41289	68.4461

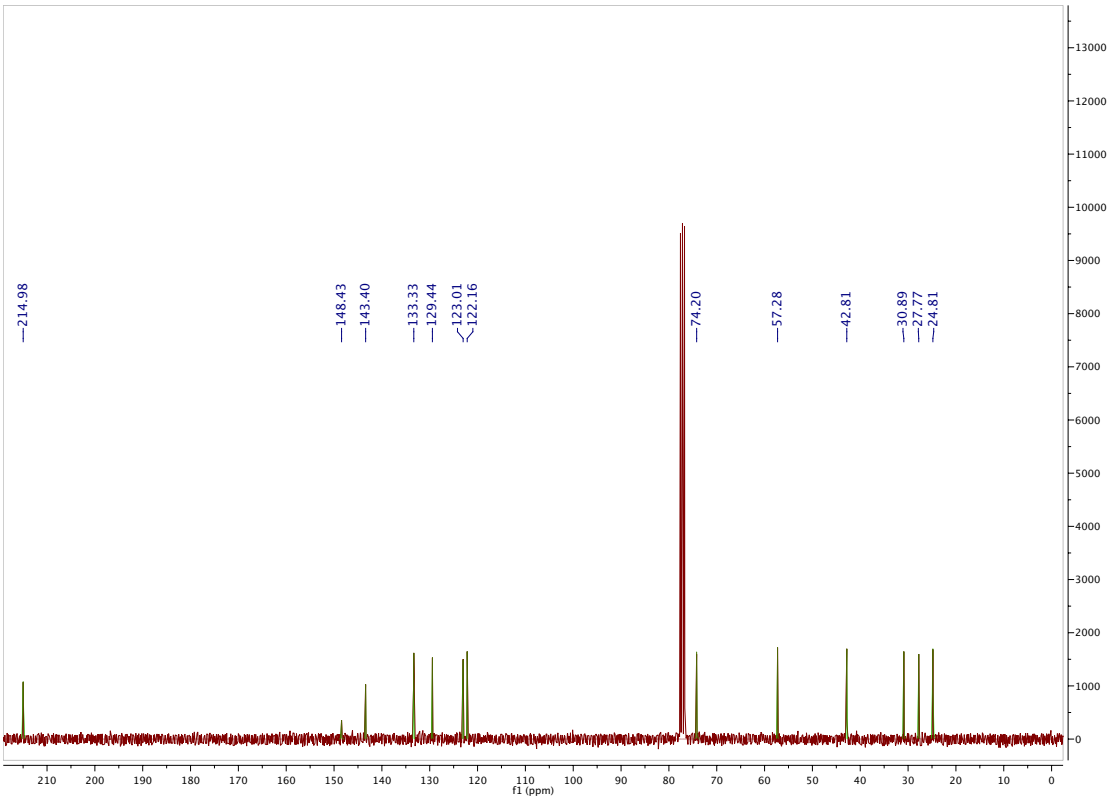

OH
O
O_2N
8.23 8.22 8.21 8.20 8.20 8.19 7.52 7.52 7.51 7.50 7.49 7.49
5.48
4.91 4.88
4.07 4.06
3.17
2.62 2.56 2.55 2.53 2.47 2.41 2.40 2.32 2.32 2.15 2.08 1.86 1.81 1.73 1.50 1.44 1.32
2.00 2.00 0.04 0.96 0.87 0.04 1.01 1.02 1.05 1.03 1.02 3.98 1.27
f1 (ppm)

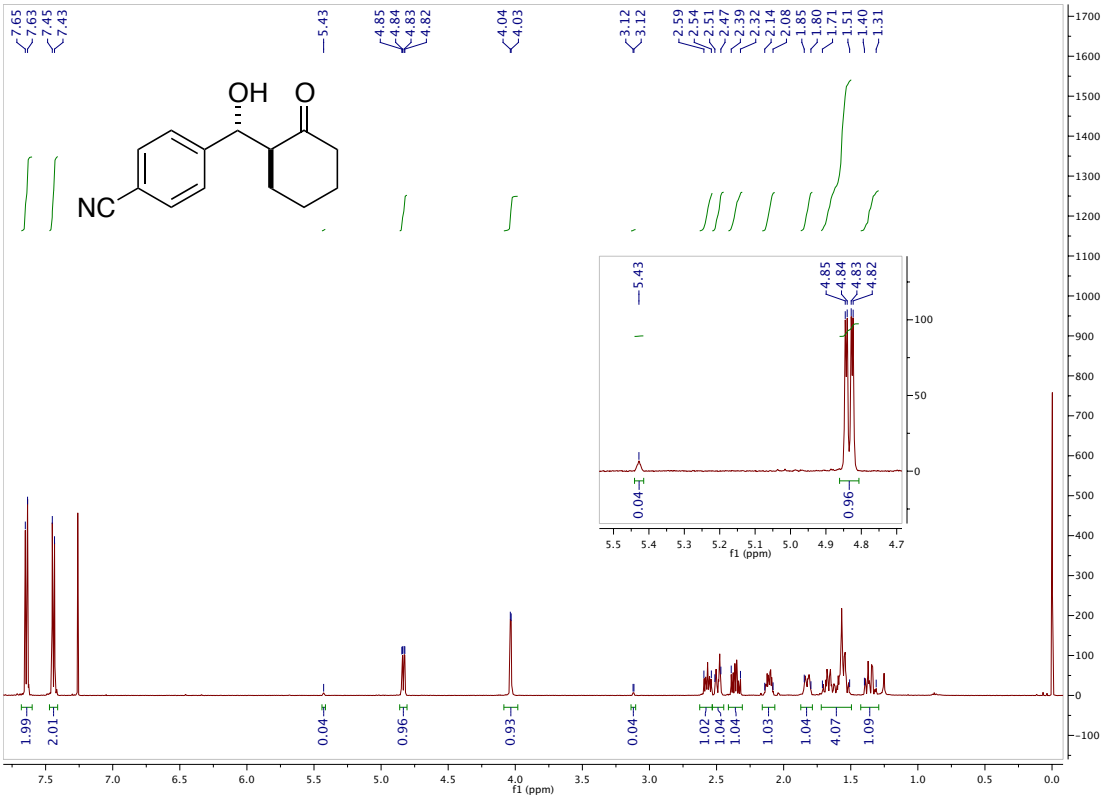

214.87
148.48 147.70
128.00 123.70
74.15
57.32
42.81
30.89 27.77 24.82
f1 (ppm)

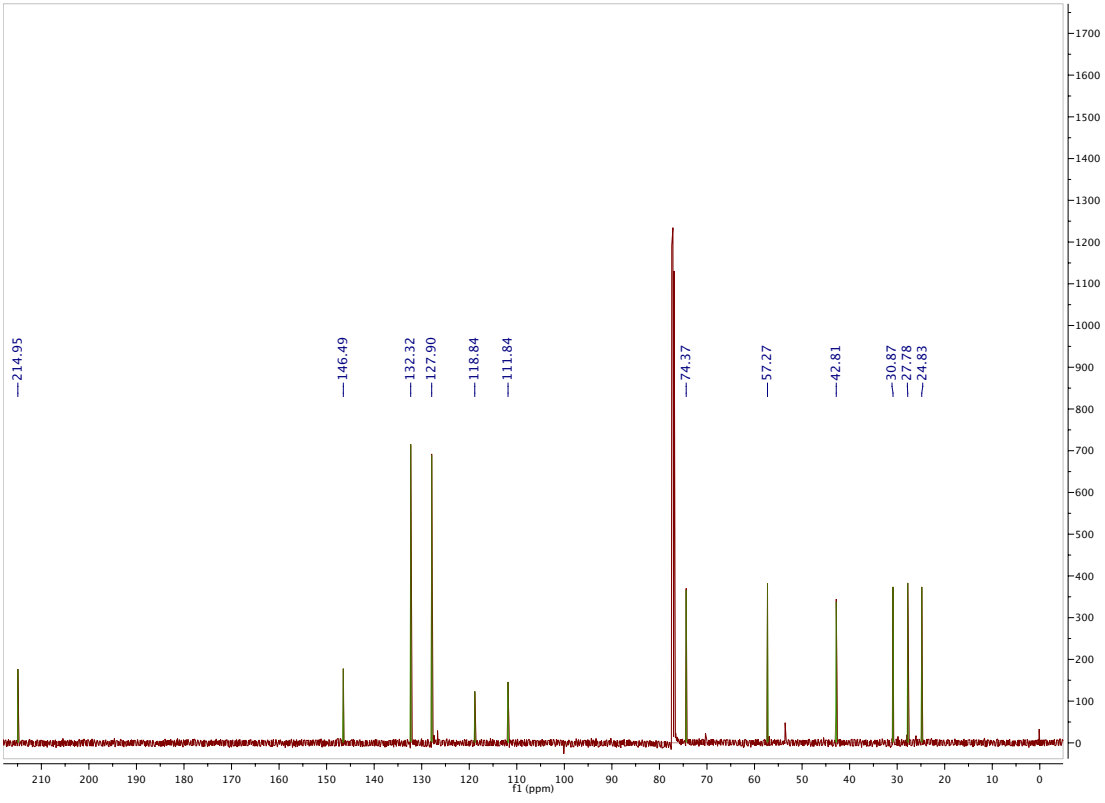

7.86
7.85
7.84
7.84
7.78
7.78
7.76
7.76
7.65
7.65
7.63
7.63
7.63
7.62
7.62
7.44
7.43
7.43
7.42
7.42
7.41
5.45
5.44
4.15
2.78
2.73
2.47
2.43
2.37
2.30
2.13
2.07
1.87
1.83
1.80
1.56
NO2 OH O
0.97
1.04
1.04
1.04
0.01
1.02
0.77
1.05
1.09
1.14
1.11
1.12
4.96
f1 (ppm)

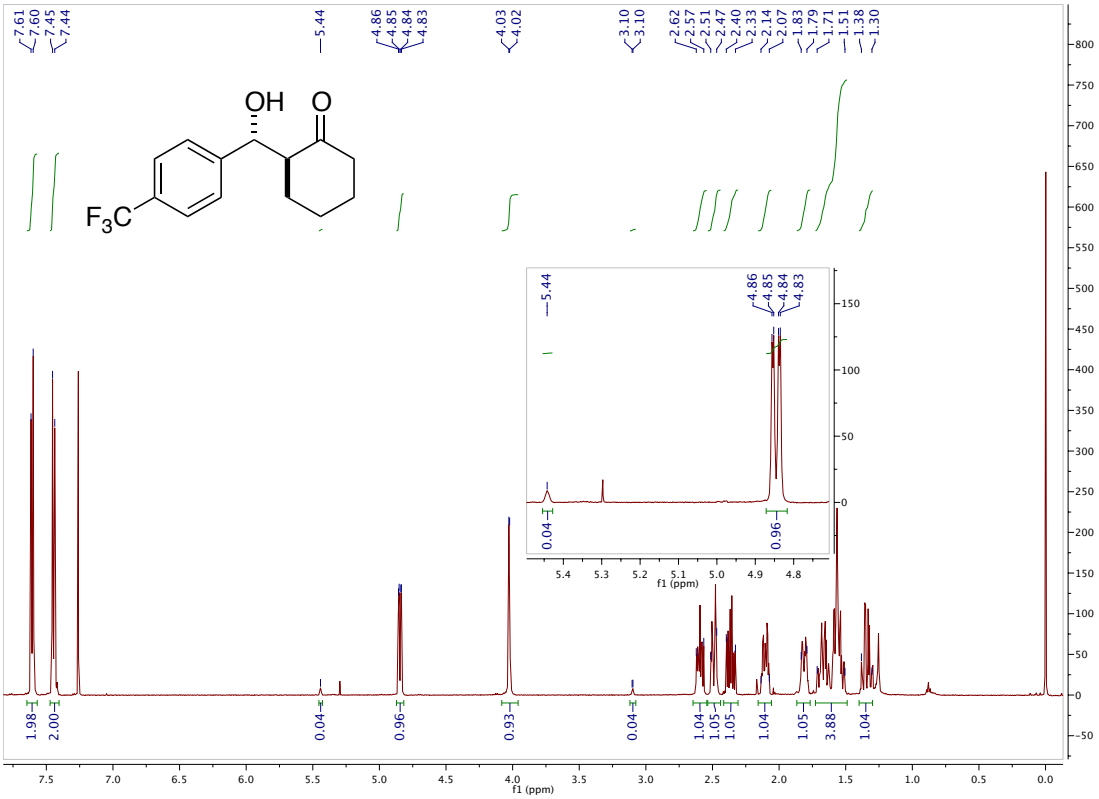

215.08
148.88
136.78
133.21
129.15
128.54
124.24
69.96
57.46
42.99
31.29
27.91
25.15
f1 (ppm)

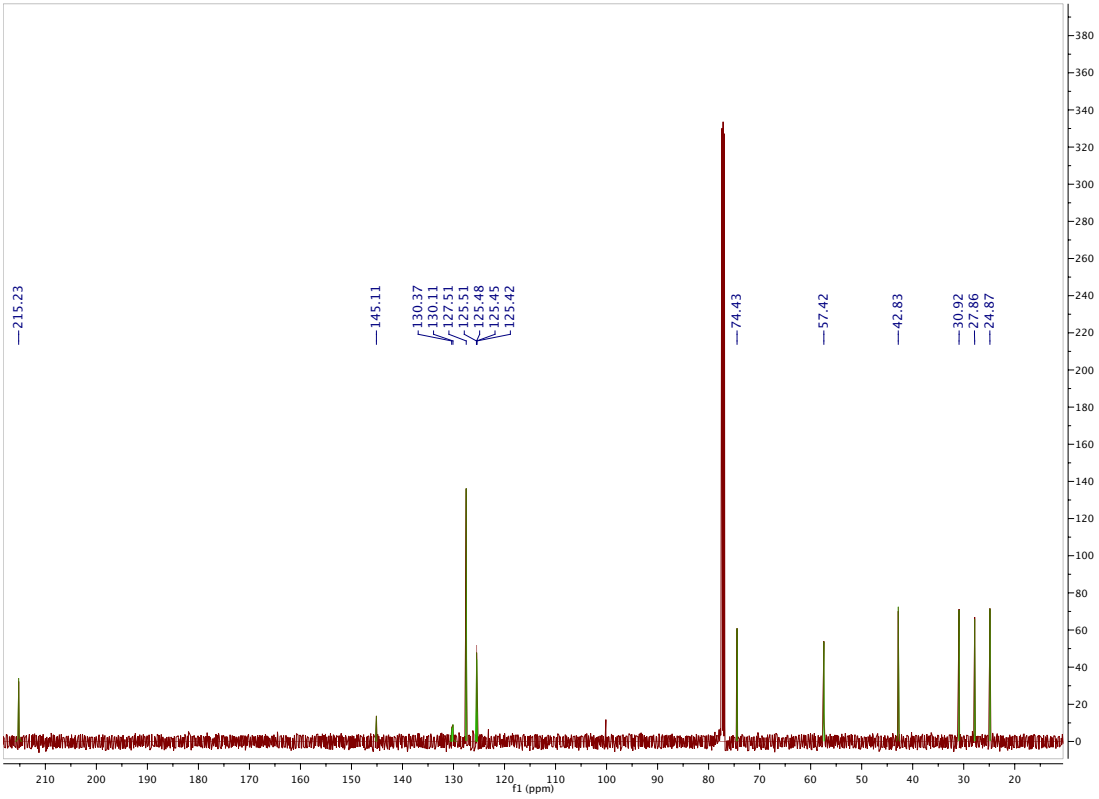

OH
O
O_2N
f1 (ppm)

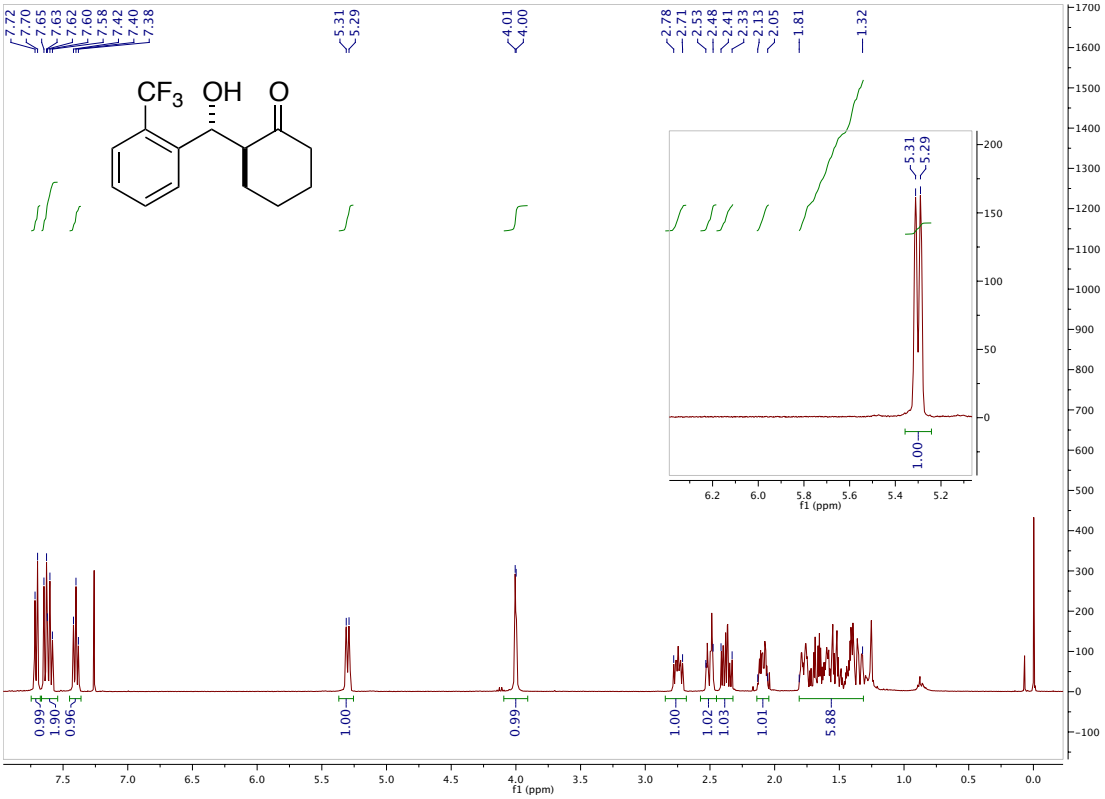

214.98
148.43
143.40
133.33
129.44
123.01
122.16
74.20
57.28
42.81
30.89
27.77
24.81
f1 (ppm)

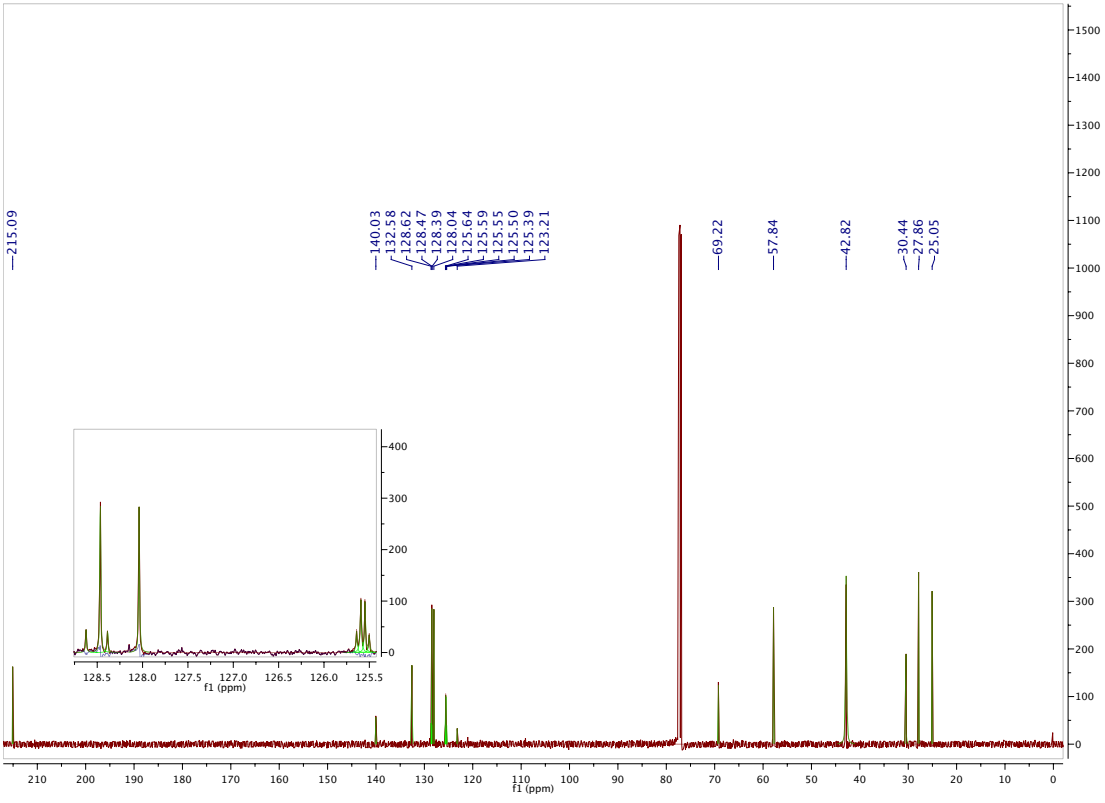

OH
O
NC
7.65
7.63
7.45
7.43
5.43
4.85
4.84
4.83
4.82
4.04
4.03
3.12
3.12
2.59
2.54
2.51
2.47
2.39
2.32
2.14
2.08
1.85
1.80
1.71
1.51
1.40
1.31
1.99
2.01
0.04
0.96
0.93
0.04
1.02
1.04
1.04
1.03
1.04
4.07
1.09
f1 (ppm)

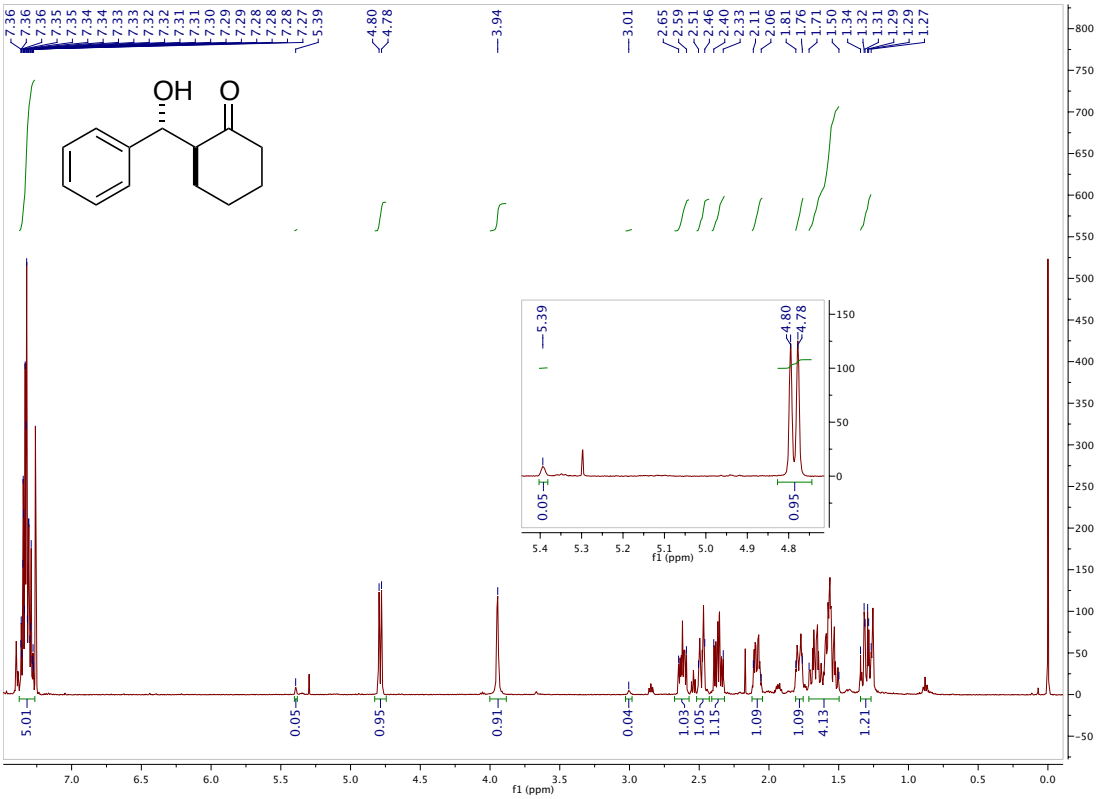

214.95
146.49
132.32
127.90
118.84
111.84
74.37
57.27
42.81
30.87
27.78
24.83
f1 (ppm)

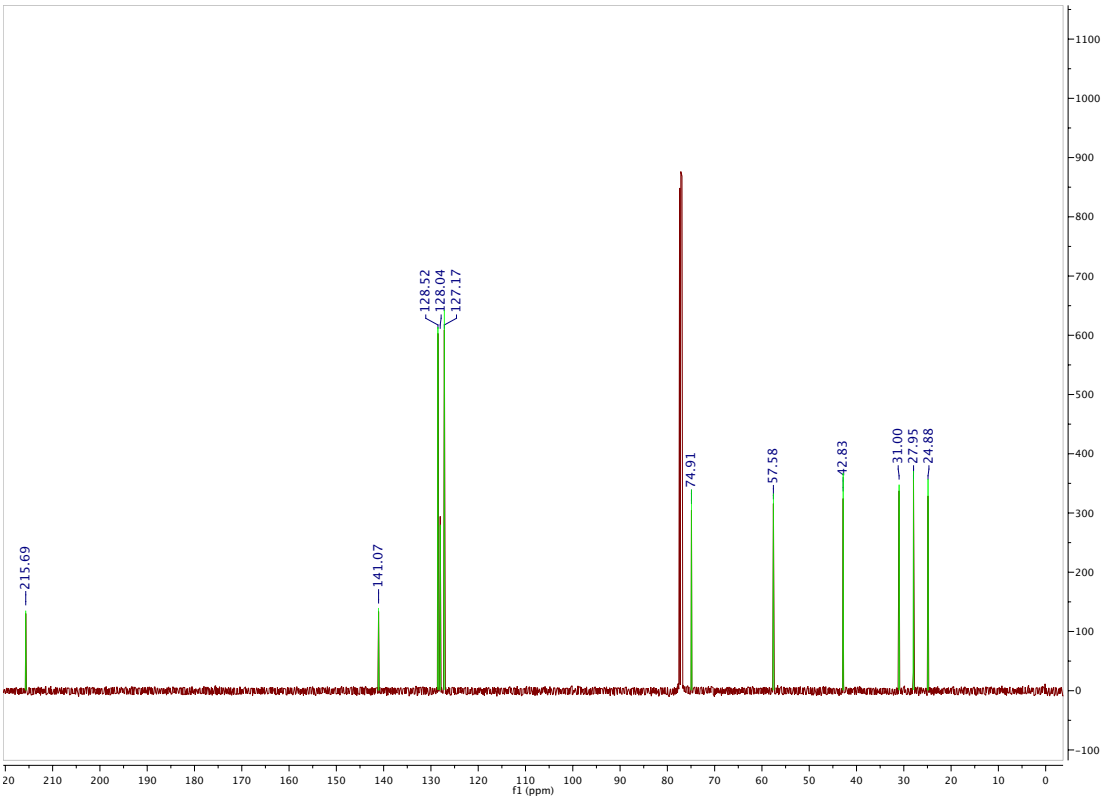

OH
O
F3C
7.61
7.60
7.45
7.44
5.44
4.86
4.85
4.84
4.83
4.03
4.02
3.10
3.10
2.62
2.57
2.51
2.47
2.40
2.33
2.14
2.07
1.83
1.79
1.71
1.51
1.38
1.30
1.98
2.00
0.04
0.96
0.93
0.04
1.04
1.05
1.05
1.04
1.05
3.88
1.04
f1 (ppm)

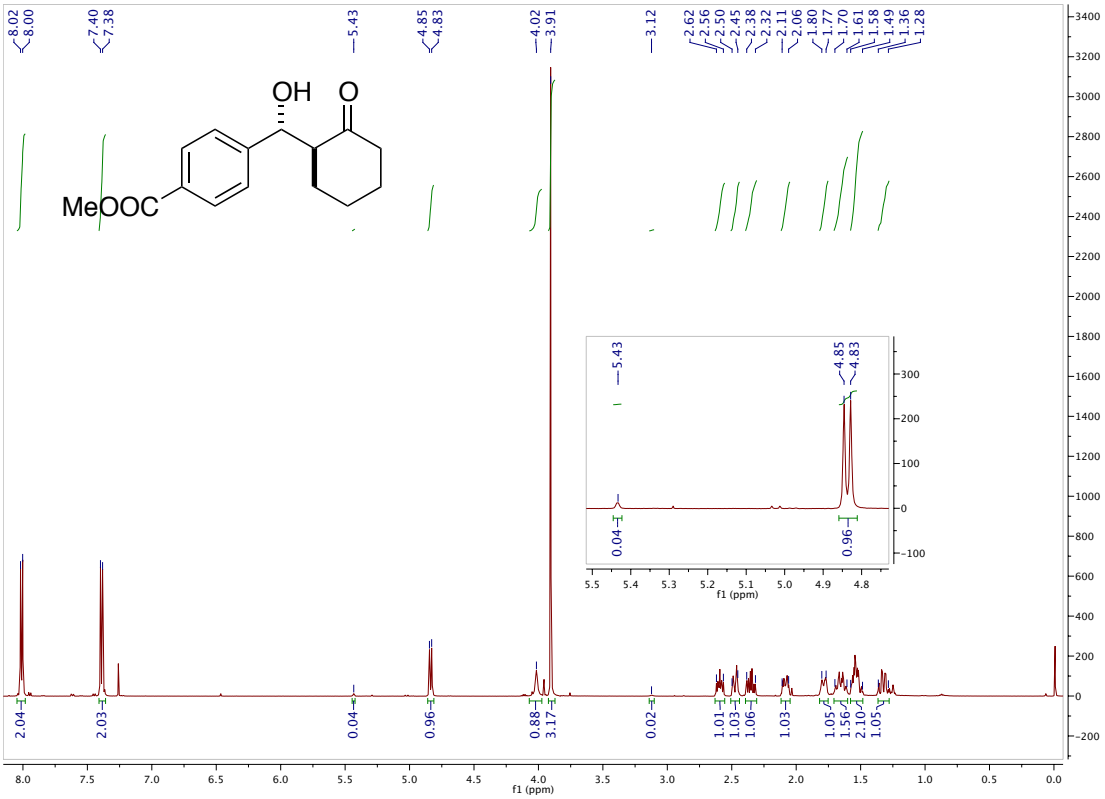

215.23
145.11
130.37
130.11
127.51
125.51
125.48
125.45
125.42
74.43
57.42
42.83
30.92
27.86
24.87
f1 (ppm)

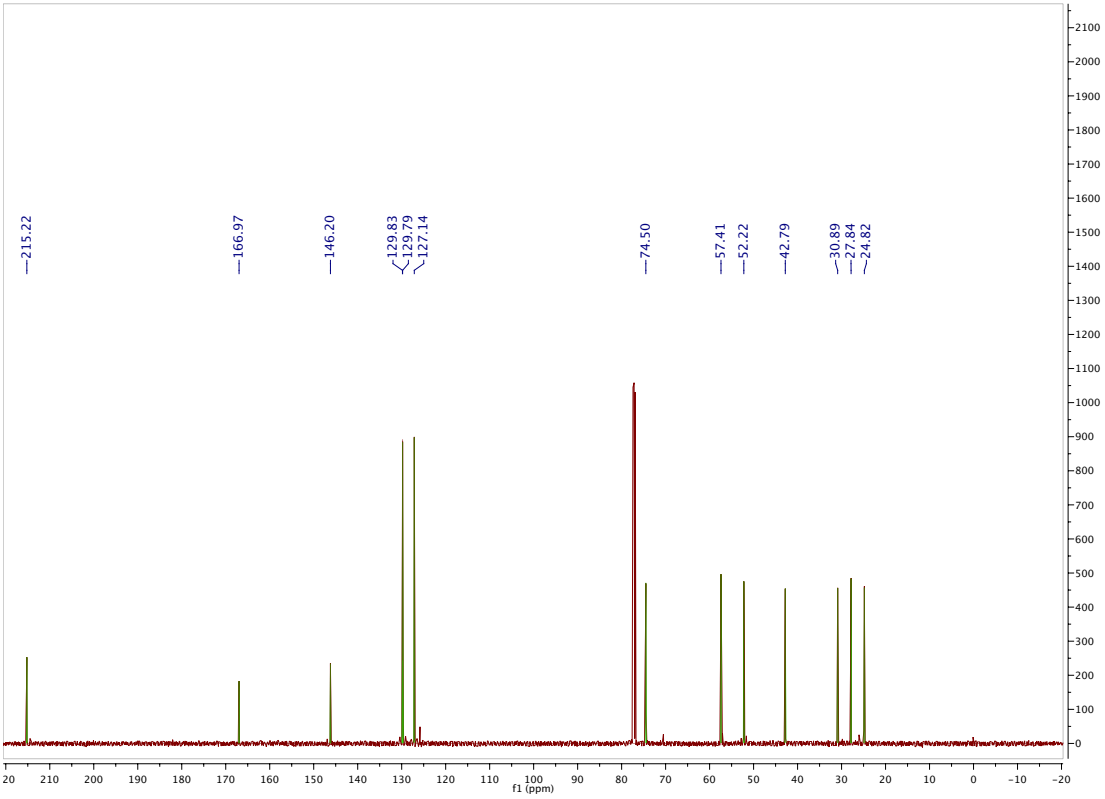

7.72
7.70
7.65
7.63
7.62
7.60
7.58
7.42
7.40
7.38
5.31
5.29
4.01
4.00
2.78
2.71
2.53
2.48
2.41
2.33
2.13
2.05
1.81
1.32
CF3 OH O
0.99
1.90
0.96
1.00
0.99
1.00
1.02
1.03
1.01
5.88
f1 (ppm)

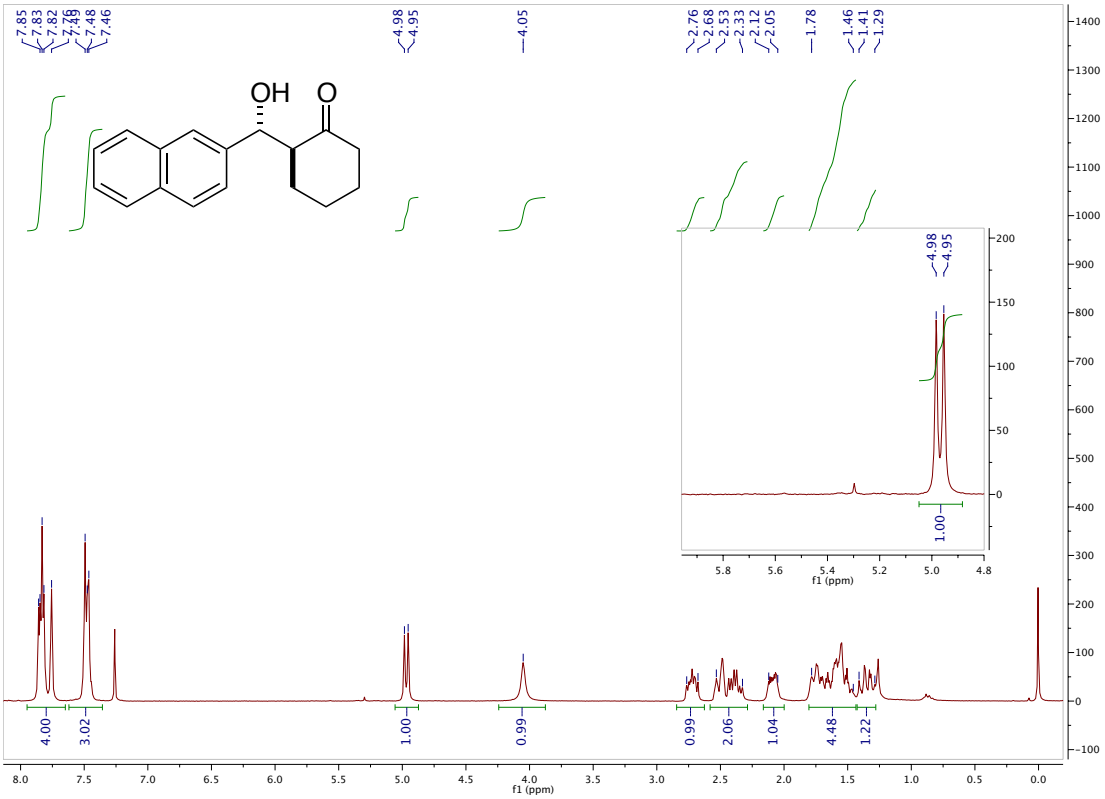

215.09
140.03
132.58
128.62
128.47
128.39
128.04
125.64
125.59
125.55
125.50
125.39
123.21
69.22
57.84
42.82
30.44
27.86
25.05
f1 (ppm)

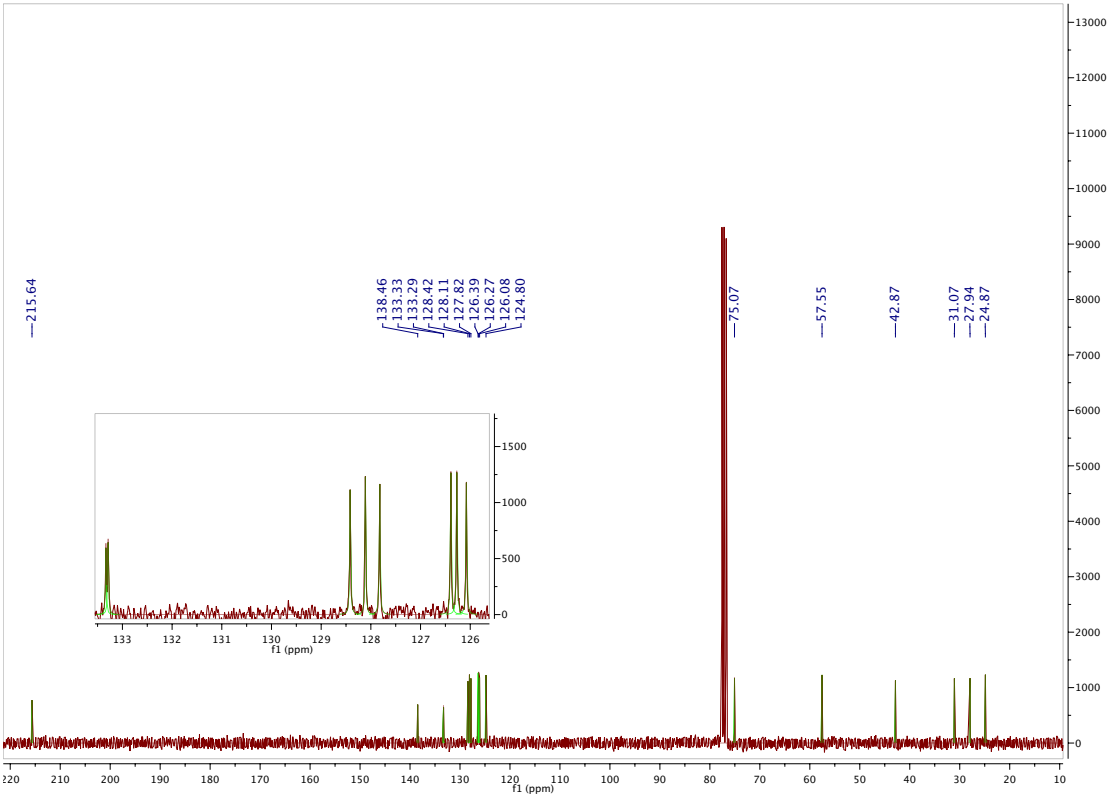

OH
O
7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.28 7.28 7.28 7.27 5.39
4.80 4.78
3.94
3.01
2.65 2.59 2.51 2.46 2.40 2.33 2.11 2.06 1.81 1.76 1.71 1.50 1.34 1.32 1.31 1.29 1.29 1.27
5.01 0.05 0.95 0.91 0.04 1.03 1.05 1.15 1.09 1.09 4.13 1.21
f1 (ppm)

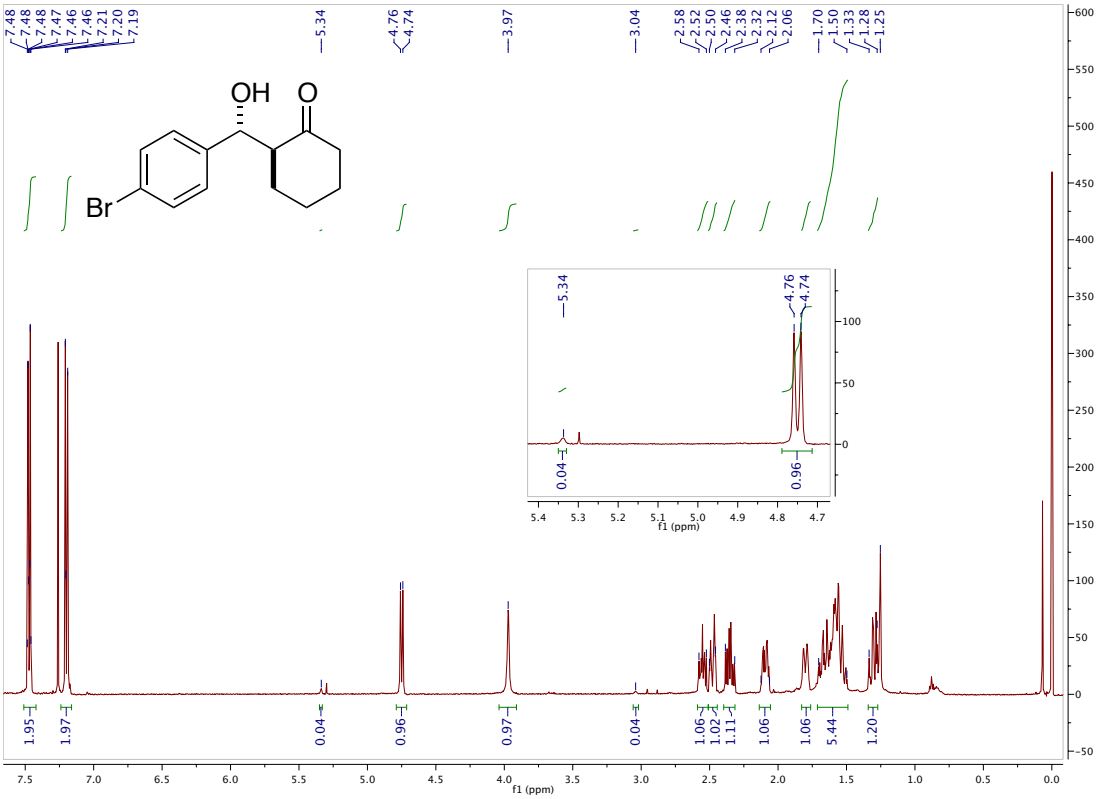

215.69
141.07
128.52
128.04
127.17
74.91
57.58
42.83
31.00
27.95
24.88
f1 (ppm)

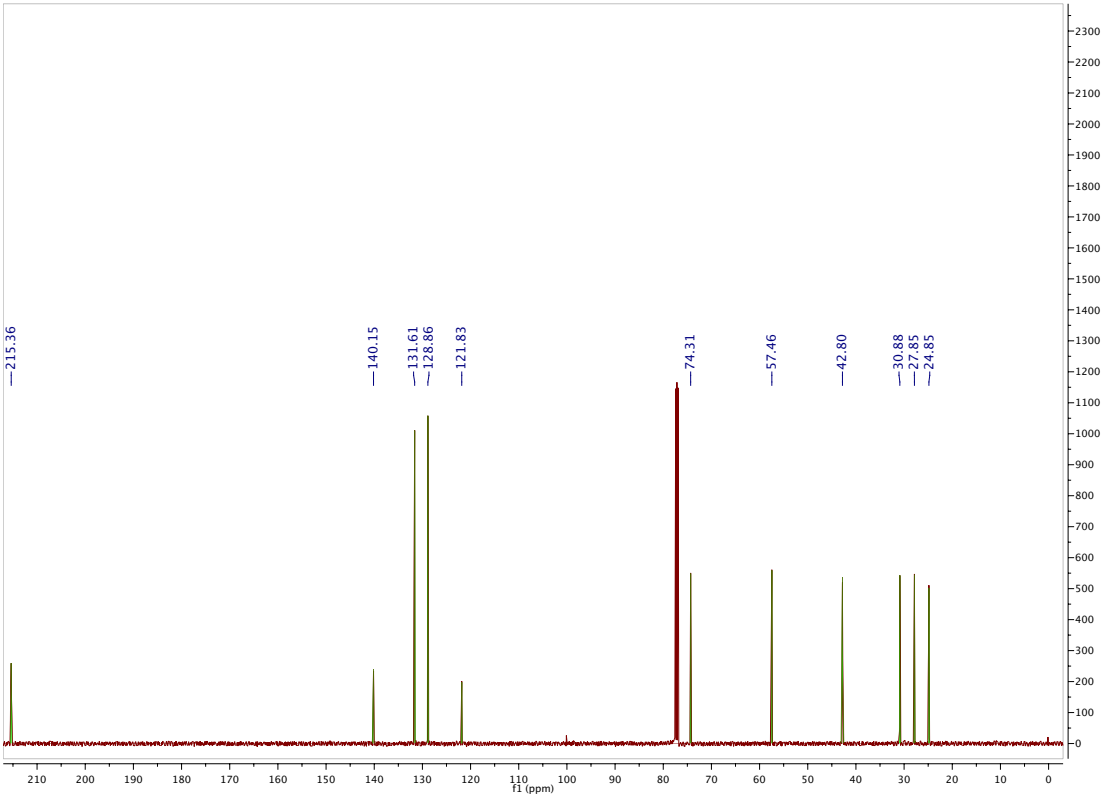

OH
O
MeOOC
f1 (ppm)

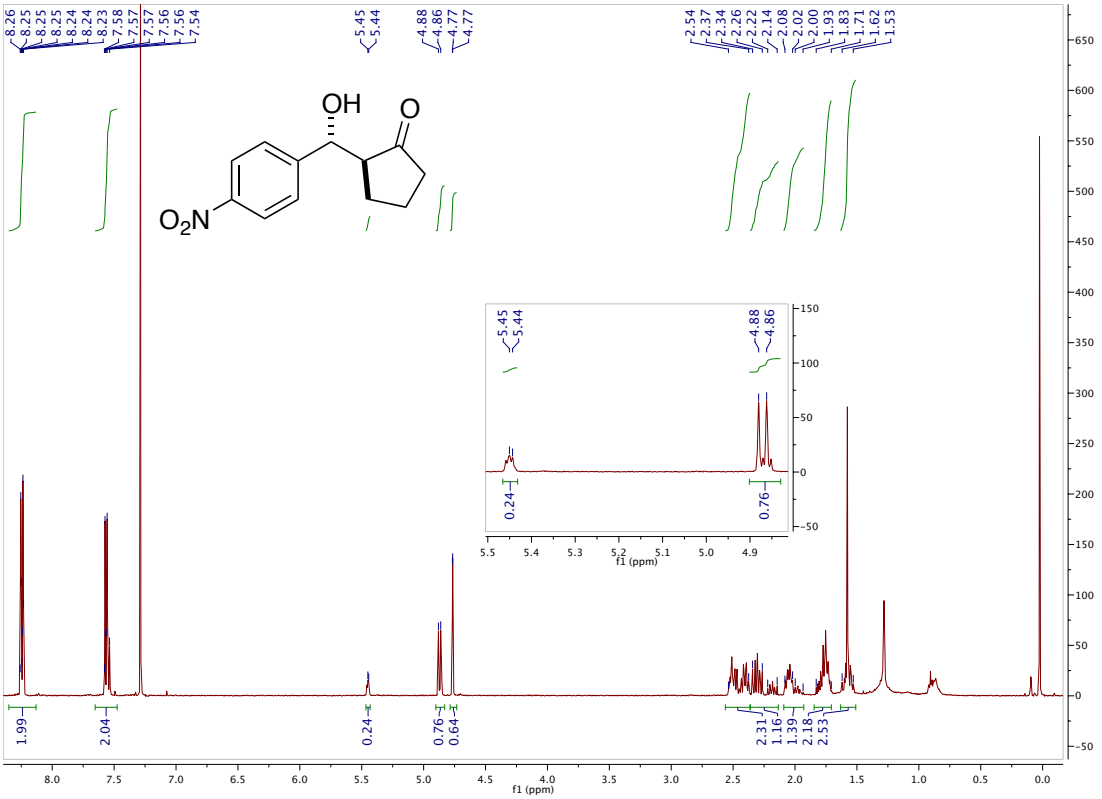

f1 (ppm)

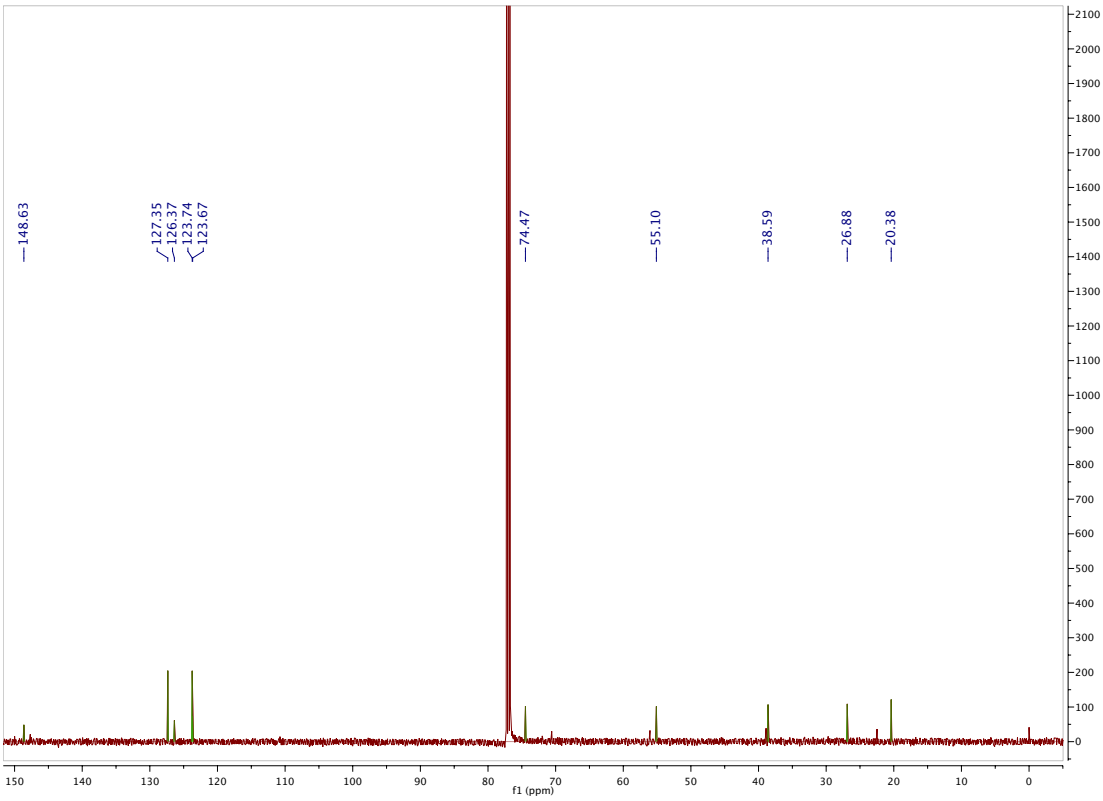

OH
O
7.85
7.83
7.82
7.48
7.46
4.98
4.95
4.05
2.76
2.68
2.53
2.33
2.12
2.05
1.78
1.46
1.41
1.29
4.00
3.02
1.00
0.99
0.99
2.06
1.04
4.48
1.22
1.00
f1 (ppm)

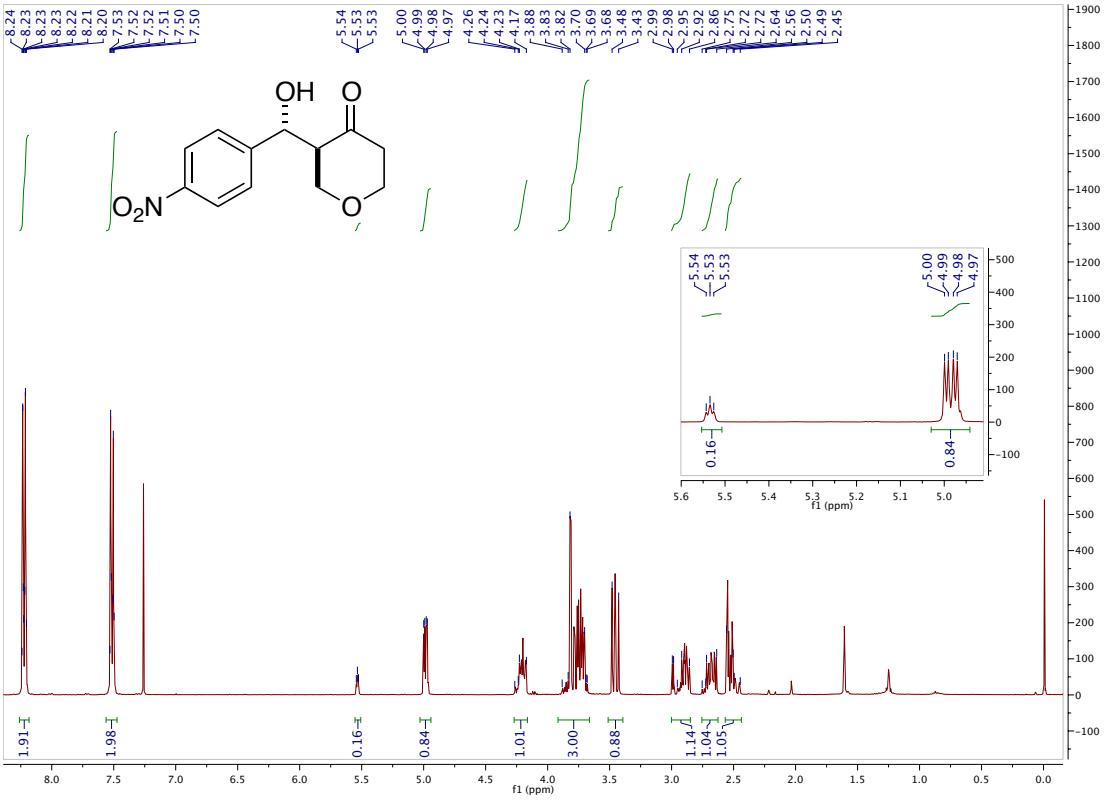

215.64
138.46
133.33
133.29
128.42
128.11
127.82
126.39
126.27
126.08
124.80
75.07
57.55
42.87
31.07
27.94
24.87
f1 (ppm)

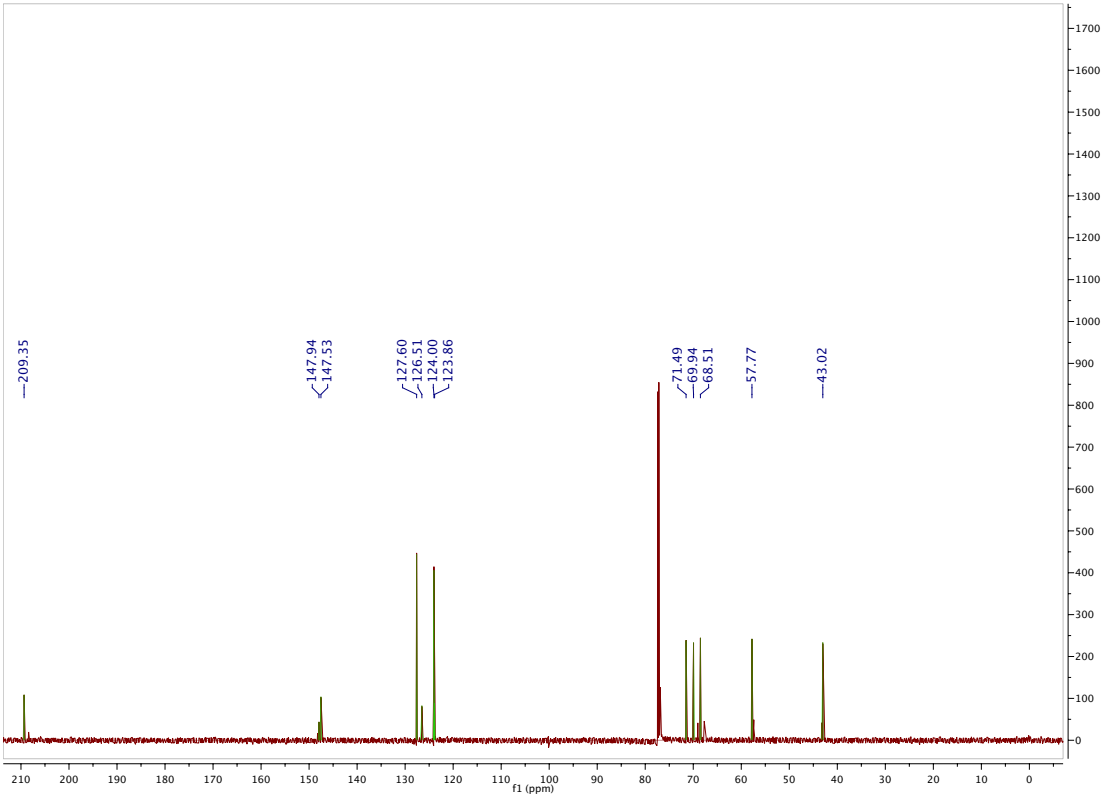

OH
O
Br
f1 (ppm)


215.36
140.15
131.61
128.86
121.83
74.31
57.46
42.80
30.88
27.85
24.85
f1 (ppm)


8.26
8.25
8.25
8.25
8.24
8.24
8.23
7.58
7.57
7.57
7.56
7.56
7.54
5.45
5.44
4.88
4.86
4.77
4.77
2.54
2.37
2.34
2.26
2.22
2.14
2.08
2.02
2.00
1.93
1.83
1.71
1.62
1.53
OH
O
O2N
1.99
2.04
0.24
0.76
0.64
2.31
1.16
1.39
2.18
2.53
f1 (ppm)

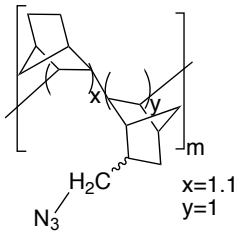
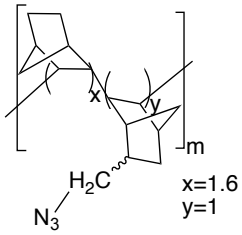
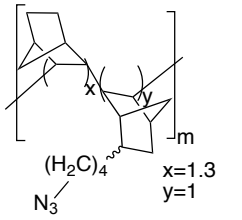
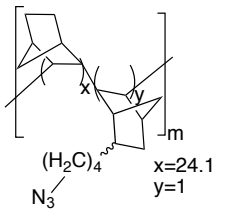
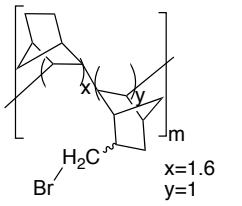

148.63
127.35
126.37
123.74
123.67
74.47
55.10
38.59
26.88
20.38
f1 (ppm)


OH
O
O2N
O
f1 (ppm)


209.35
147.94
147.53
127.60
126.51
124.00
123.86
71.49
69.94
68.51
57.77
43.02
f1 (ppm)

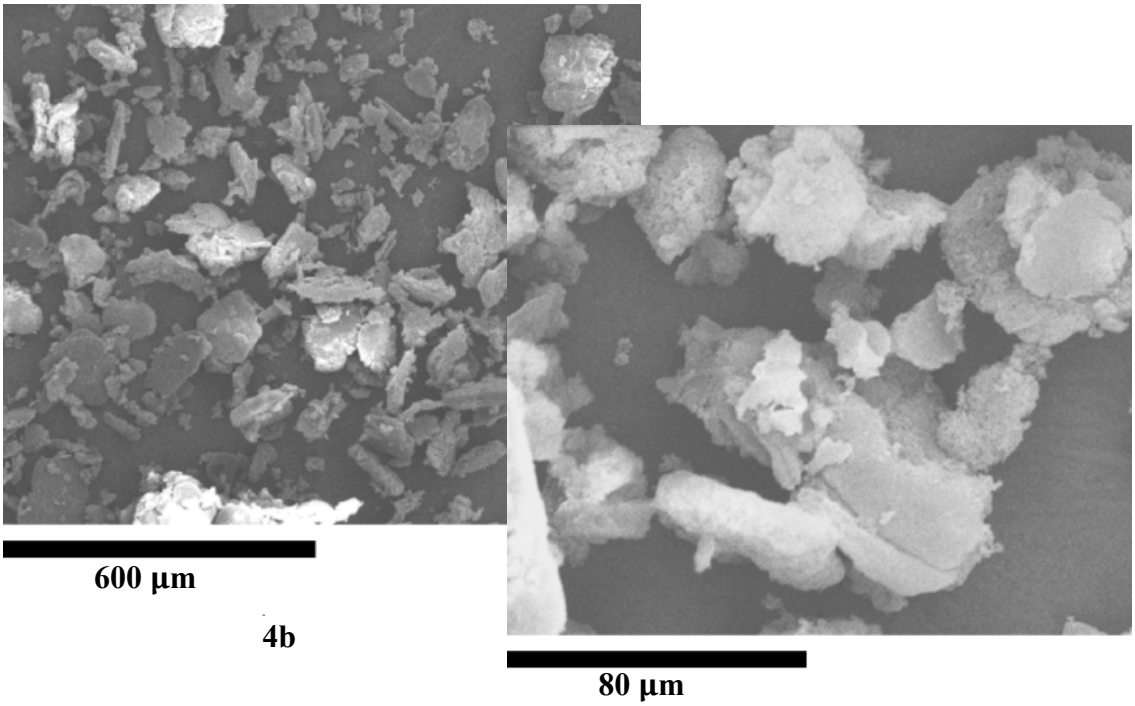
Characterization of azido-copolymers **4a-d** and bromo-copolymer **3b**

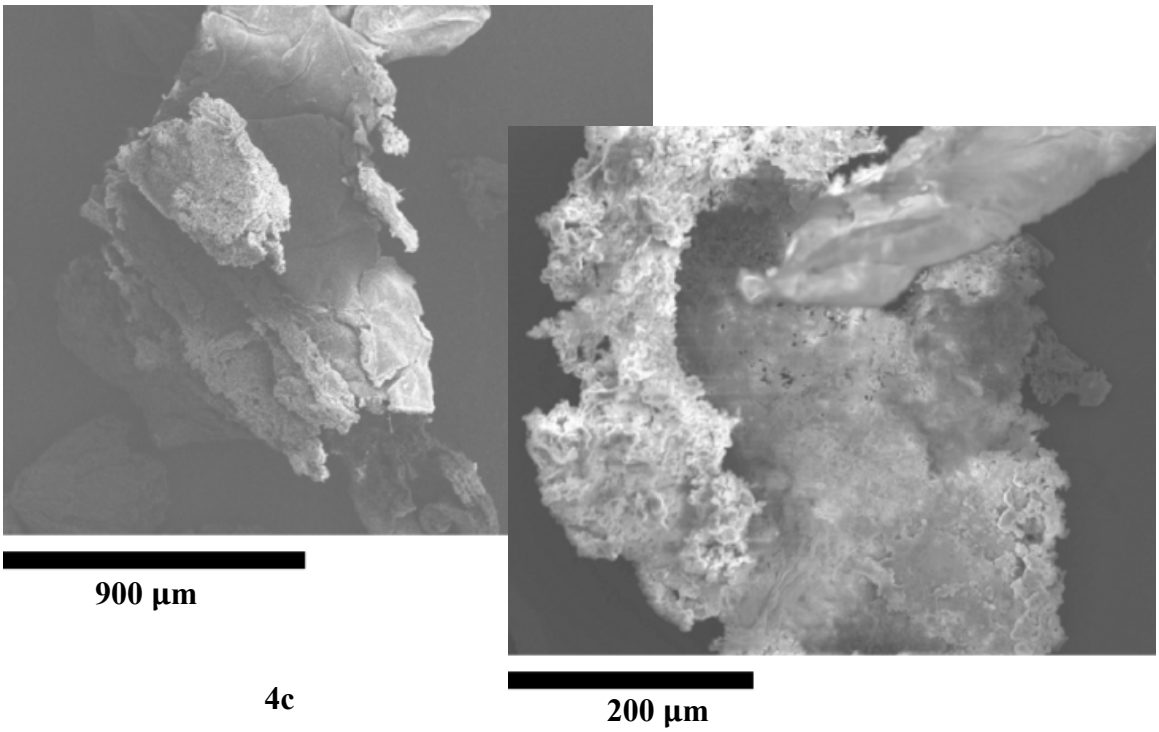
Table SI-5. Azido-copolymers **4a-d** and bromo-copolymer **3b**

			elemental analysis			
copolymer	structure	mmolBr/gCop [a]	%N	%C	%H	*f* (mmol/g) [b]
4a		0.27	12.96	74.55	8.44	3.08
4b		0.13	9.94	76.60	8.68	2.37
4c		0	12.43	76.61	9.26	2.96
4d		0.015	2.01	86.69	10.16	0.48
3b		2.98		nd		2.98[a]

[a] Determined by quantitative analysis of bromine in the copolymer. [b] Calculated from the results of elemental analysis with the formula $f = (0.714/n)\%N$, where n is the number of nitrogen atoms in the functional unit and %N is the percent of nitrogen provided by the elemental analysis.

Figure SI-5. SEM pictures of azido-copolymers **4b-c** and bromo-copolymer **3b**





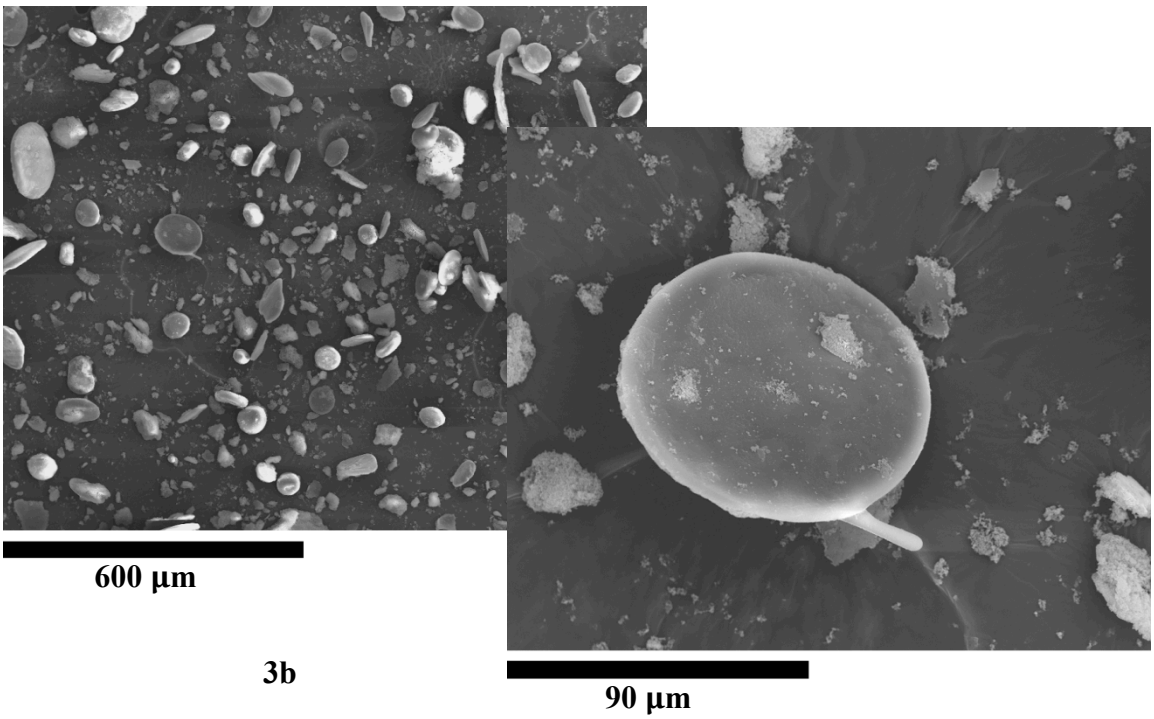
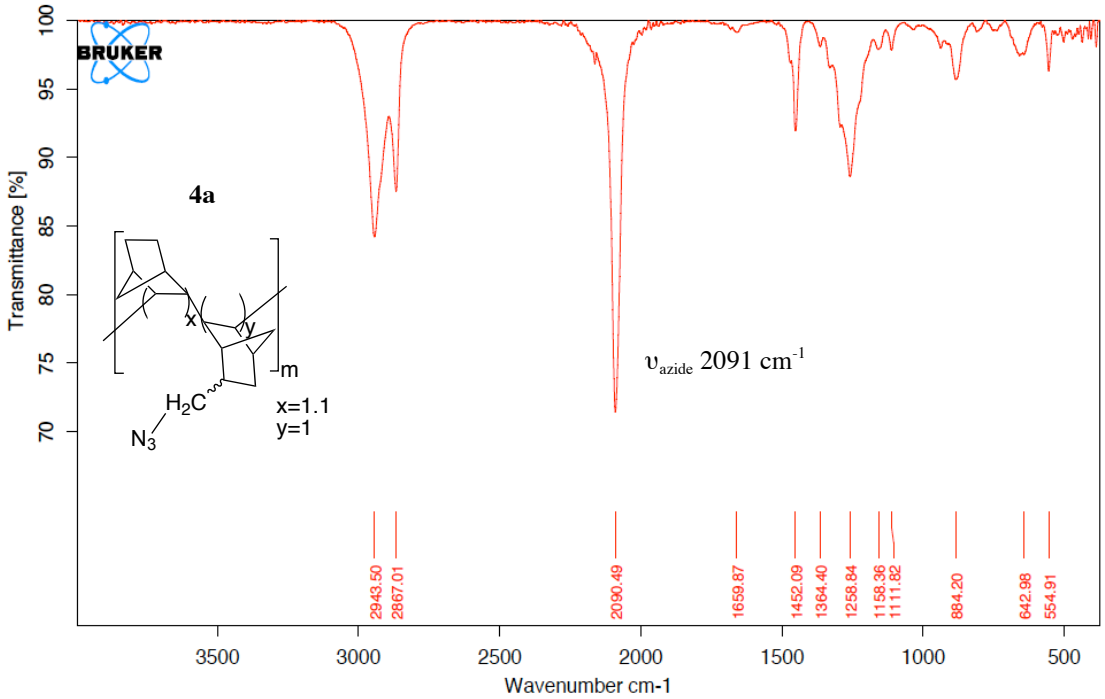
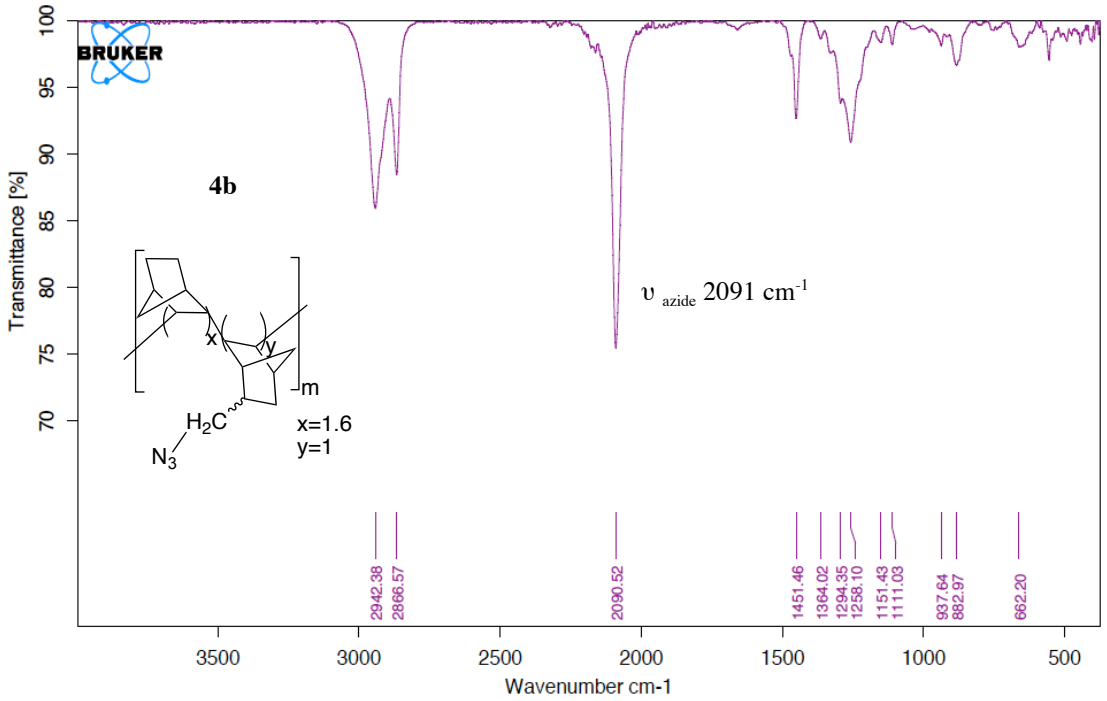
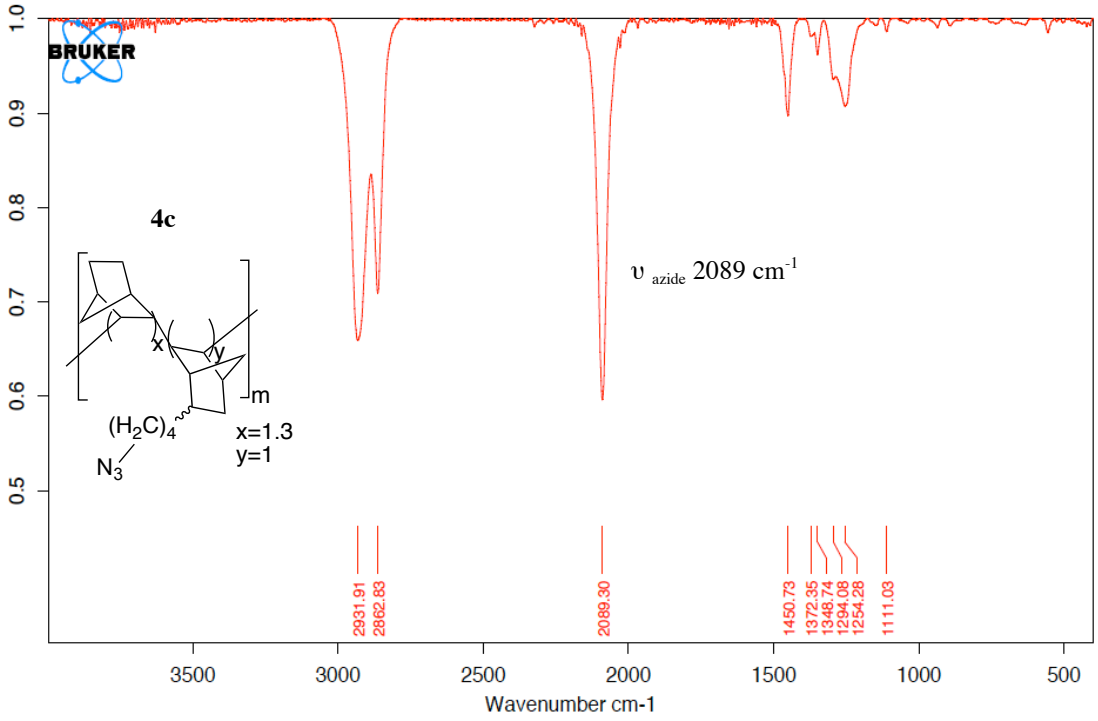
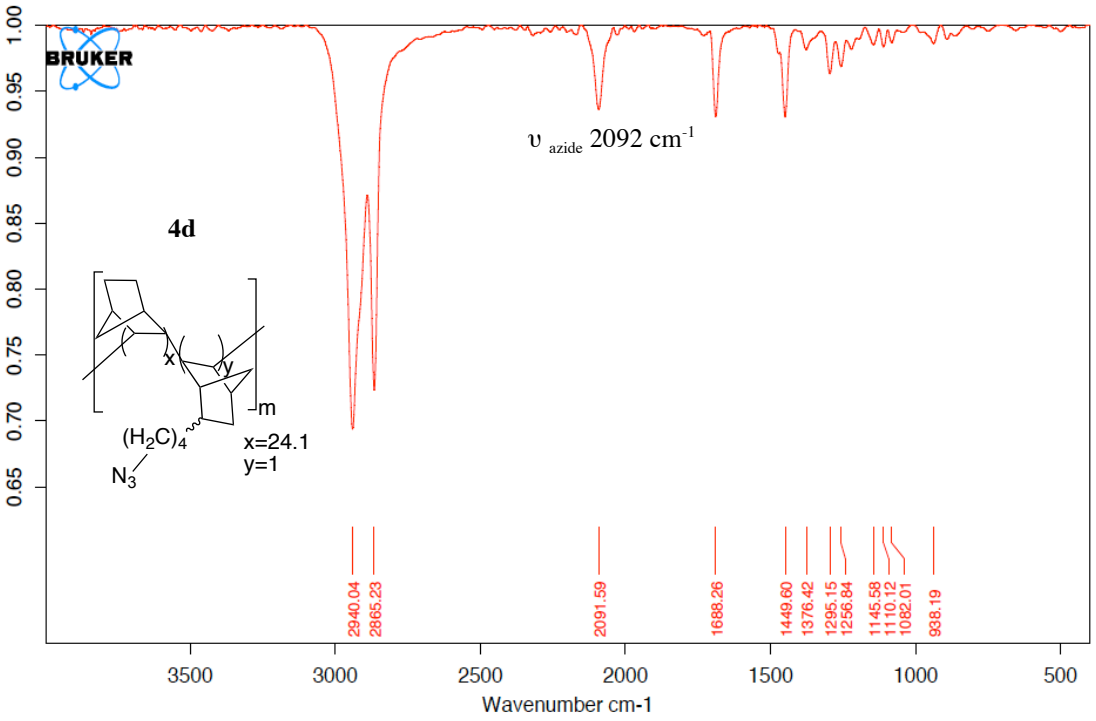


Figure SI-6. IR spectra of Azido-copolymers **4a-d** and bromo-copolymer **3b**.




BRUKER
4b
x
y
m
H2C
N3
x=1.6
y=1
υ azide 2091 cm-1
Transmittance [%]
100
95
90
85
80
75
70
2942.38
2866.57
2090.52
1451.46
1364.02
1294.35
1258.10
1151.43
1111.03
937.64
882.97
662.20
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1


BRUKER
4c
x
y
m
(H2C)4
N3
x=1.3
y=1
υ azide 2089 cm-1
1.0
0.9
0.8
0.7
0.6
0.5
2931.91
2862.83
2089.30
1450.73
1372.35
1348.74
1294.08
1254.28
1111.03
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1


BRUKER
υ azide 2092 cm-1
4d
x
y
m
(H2C)4
N3
x=24.1
y=1
2940.04
2865.23
2091.59
1688.26
1449.60
1376.42
1295.15
1256.84
1145.58
1110.12
1082.01
938.19
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

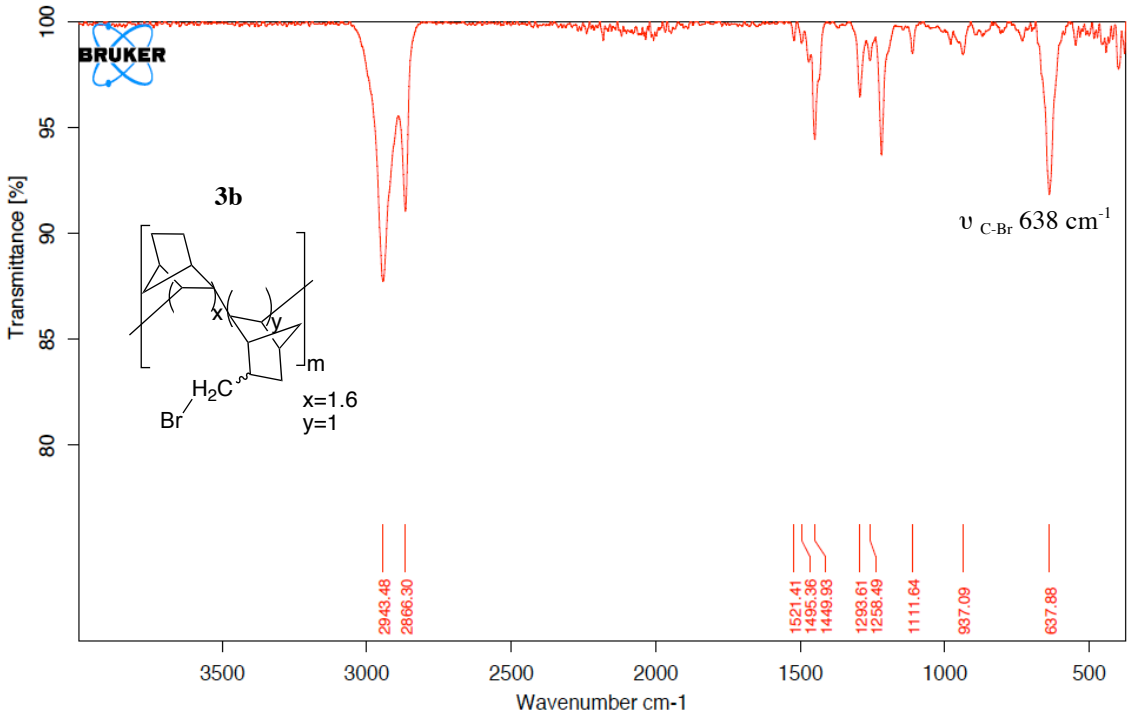
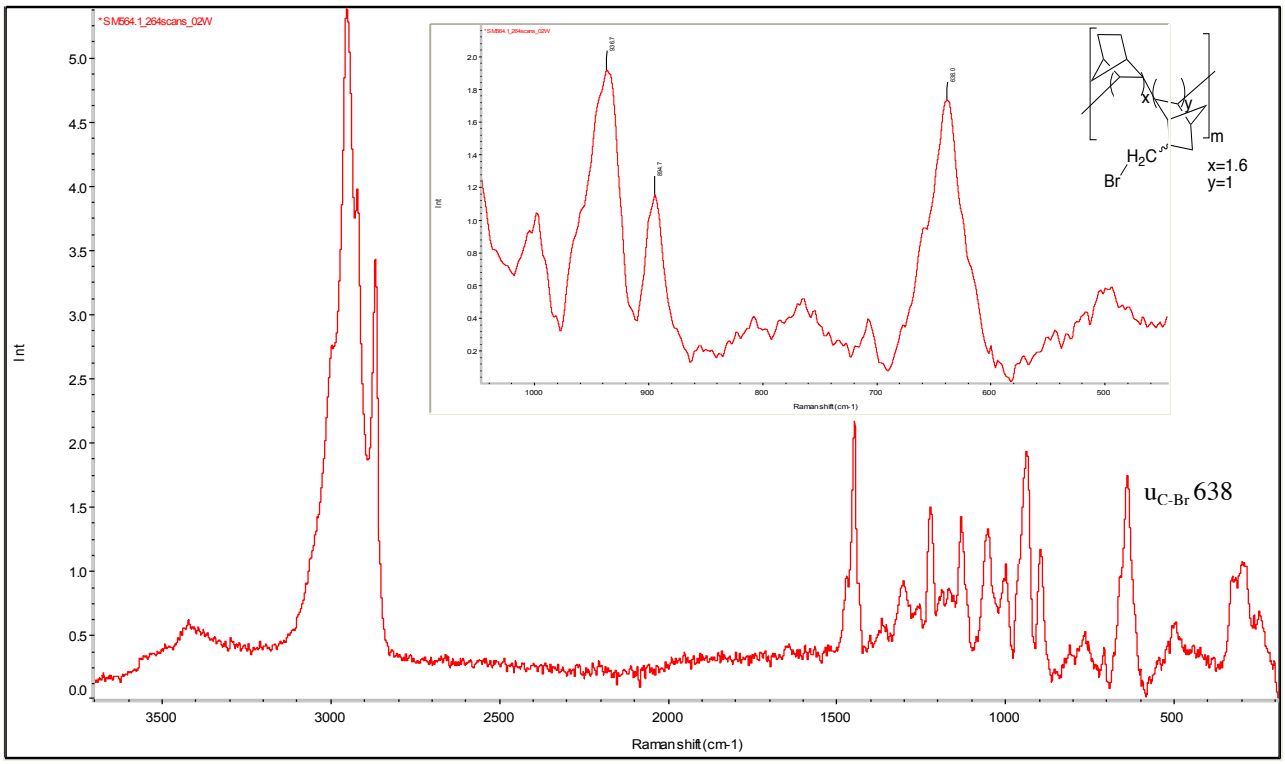
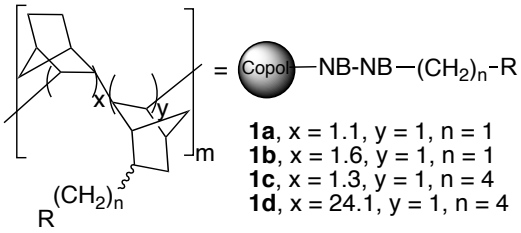

BRUKER
Transmittance [%]
3b
υ C-Br 638 cm-1
x
y
m
H2C
Br
x=1.6
y=1
2943.48
2866.30
1521.41
1495.36
1449.83
1293.61
1258.49
1111.64
937.09
637.88
100
95
90
85
80
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

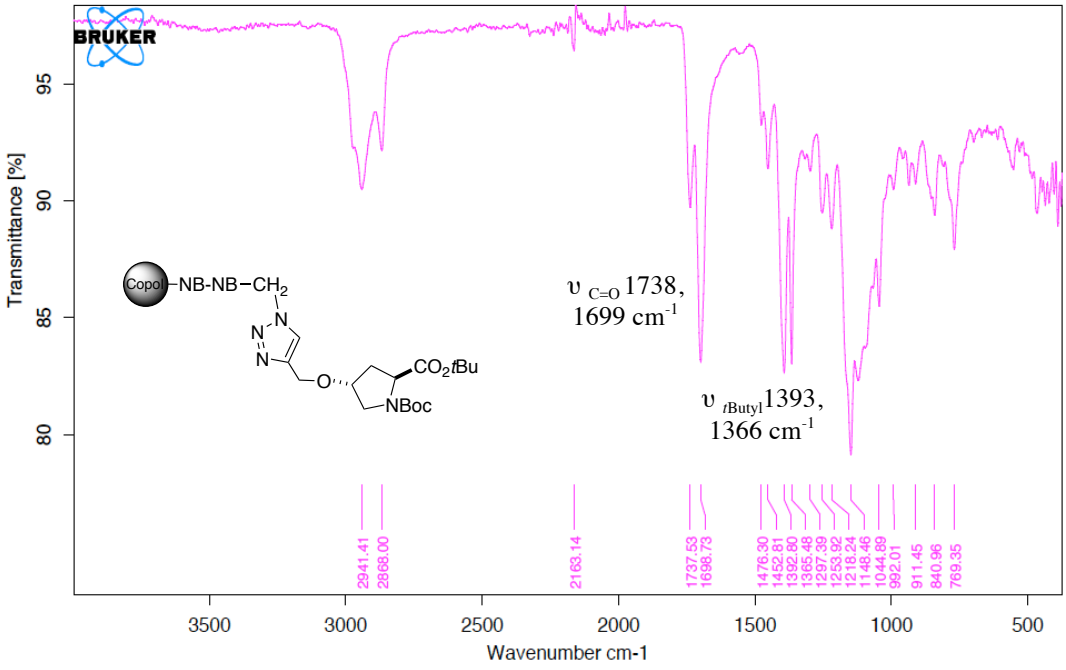
Figure SI-7. Raman spectrum of bromo-copolymer **3b**.

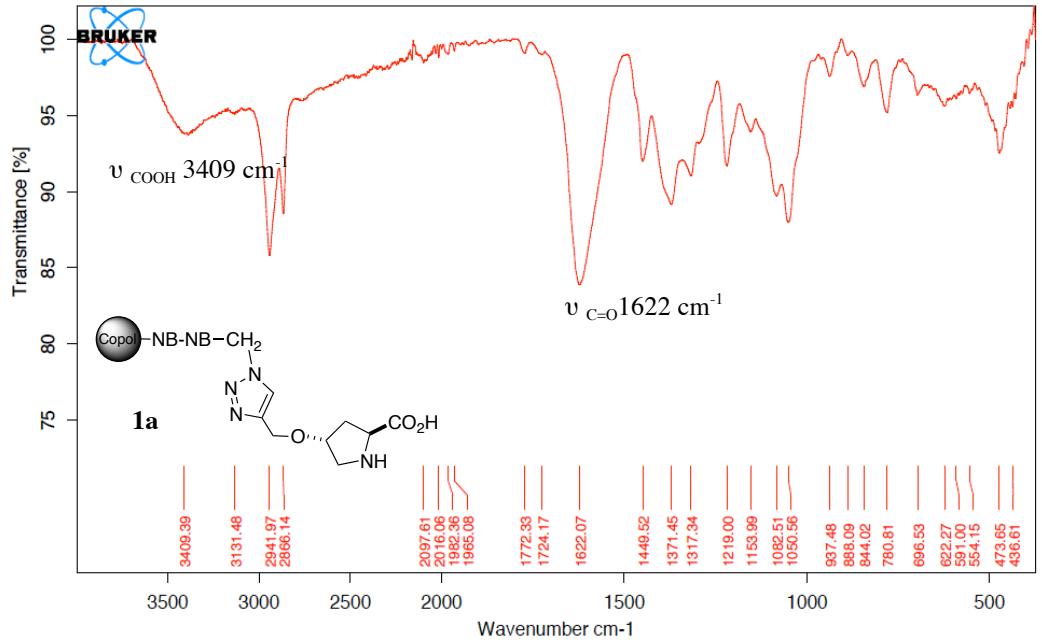


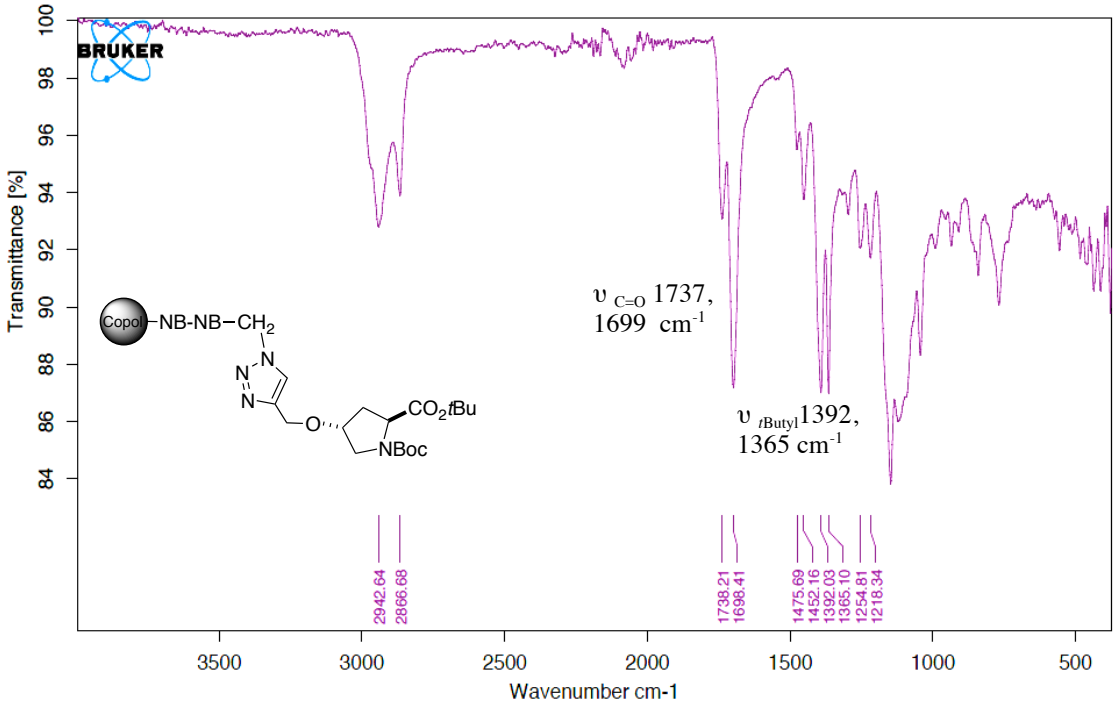
IR spectra of catalysts **1a-d**

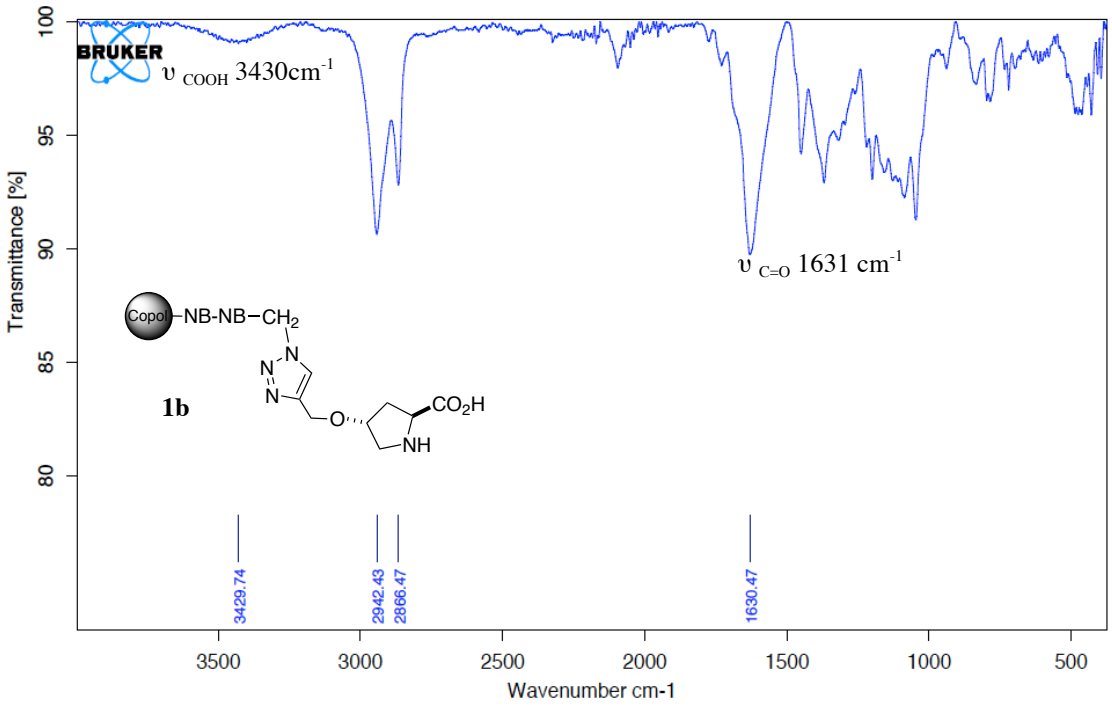


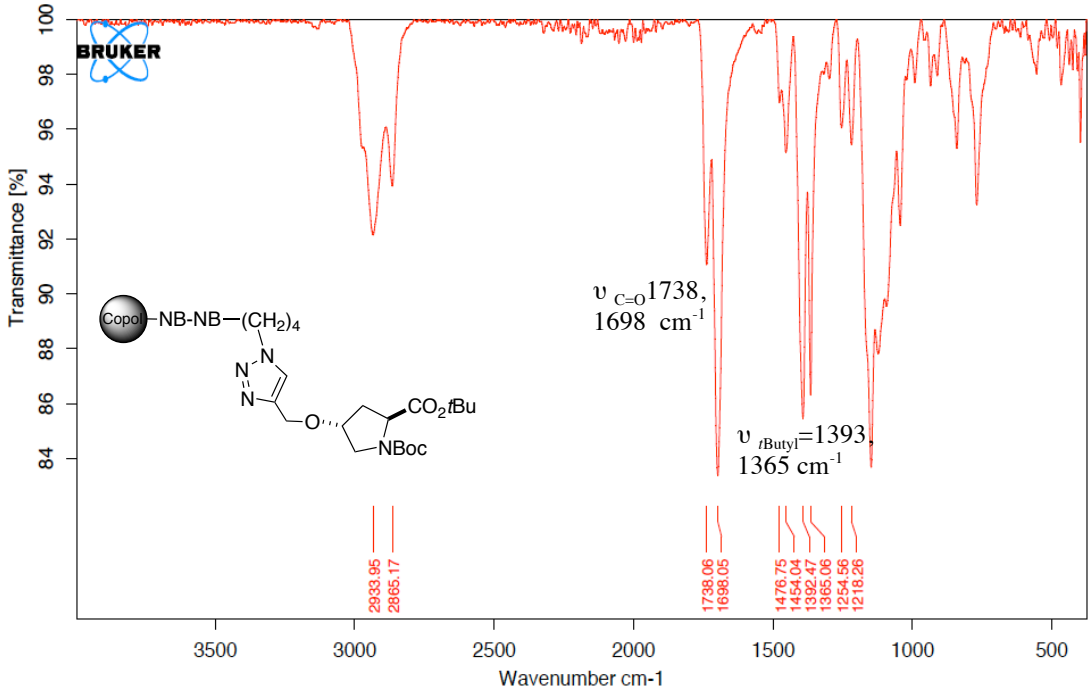
1a, x = 1.1, y = 1, n = 1
1b, x = 1.6, y = 1, n = 1
1c, x = 1.3, y = 1, n = 4
1d, x = 24.1, y = 1, n = 4

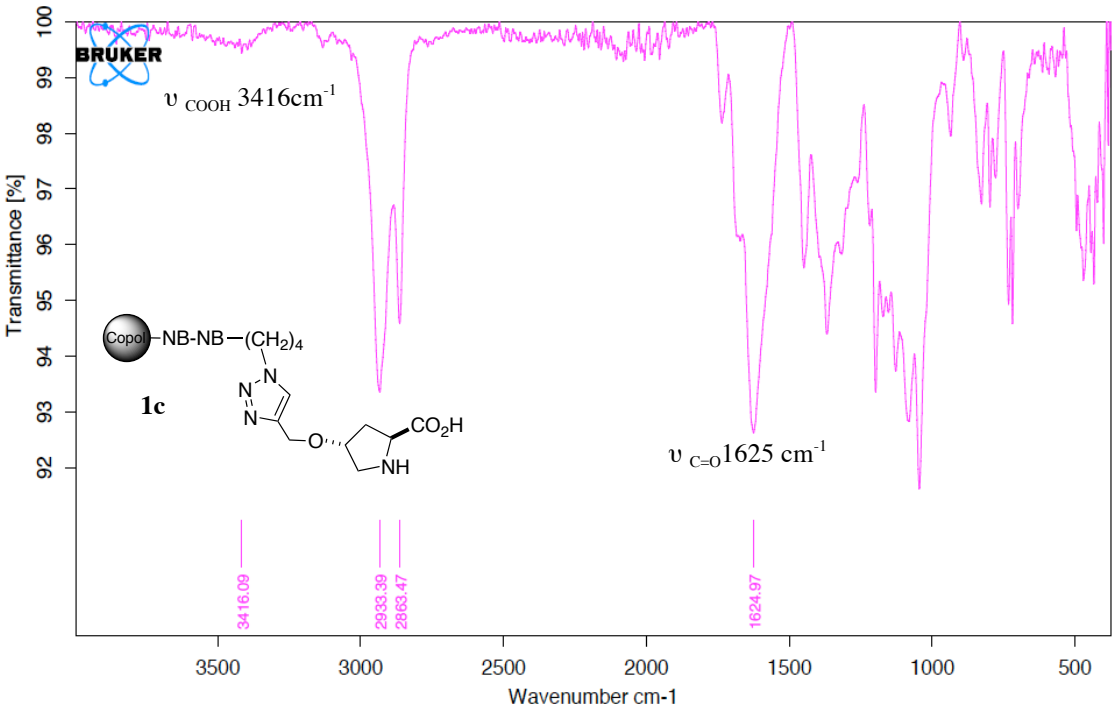


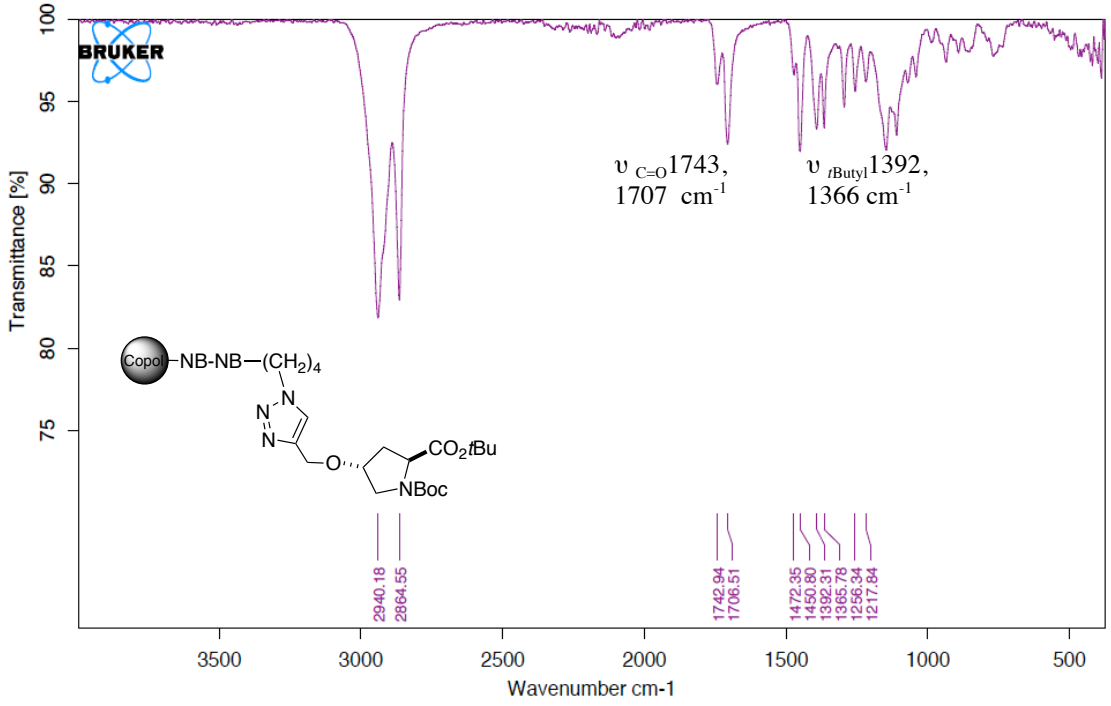


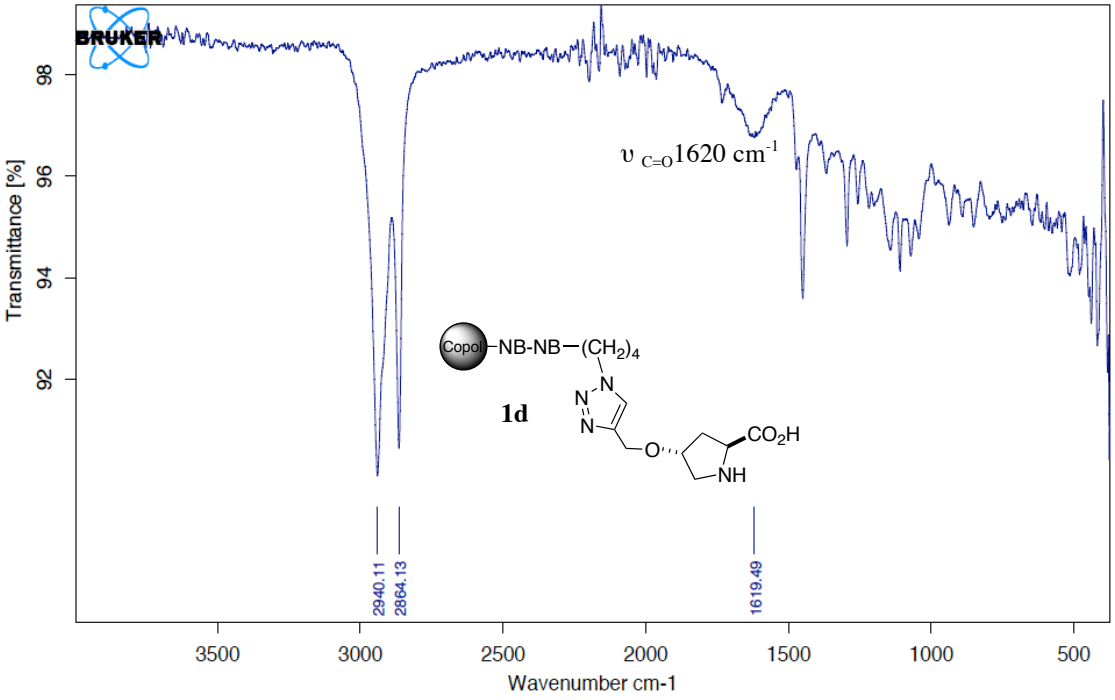

BRUKER
Transmittance [%]
100
98
96
94
92
90
88
86
84
Copol–NB-NB–CH2
N
N
N
O
CO2tBu
NBoc
υ C=O 1737,
1699 cm-1
υ tButyl 1392,
1365 cm-1
2942.64
2866.68
1738.21
1698.41
1475.69
1452.16
1392.03
1365.10
1254.81
1218.34
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1


BRUKER
Transmittance [%]
100
95
90
85
80
υ COOH 3430cm-1
υ C=O 1631 cm-1
Copol–NB-NB–CH2
N
N
N
O
CO2H
NH
1b
3429.74
2942.43
2866.47
1630.47
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1


BRUKER
Transmittance [%]
100
98
96
94
92
90
88
86
84
Copol–NB-NB–(CH2)4
CO2tBu
NBoc
υ C=O1738, 1698 cm-1
υ tButyl=1393, 1365 cm-1
2933.95
2865.17
1738.06
1698.05
1476.75
1454.04
1392.47
1365.06
1254.56
1218.26
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1


BRUKER
Transmittance [%]
100
99
98
97
96
95
94
93
92
υ COOH 3416cm-1
Copol–NB-NB–(CH2)4
1c
CO2H
NH
υ C=O1625 cm-1
3416.09
2933.99
2863.47
1624.97
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1


BRUKER
Transmittance [%]
100
95
90
85
80
75
υ C=O1743, 1707 cm-1
υ tButyl1392, 1366 cm-1
Copol-NB-NB-(CH2)4
CO2tBu
NBoc
2940.18
2864.55
1742.94
1706.51
1472.35
1450.80
1392.31
1365.78
1256.34
1217.84
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1


BRUKER
Transmittance [%]
98
96
94
92
υ C=O1620 cm-1
Copol-NB-NB-(CH2)4
1d
CO2H
NH
2940.11
2864.13
1619.49
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

Characterization of polymers **6b** and **2**

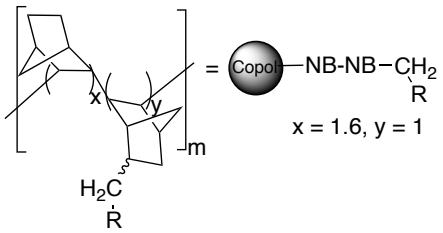


Figure SI-8. ^{13}C NMR spectrum of polymer **6b**.

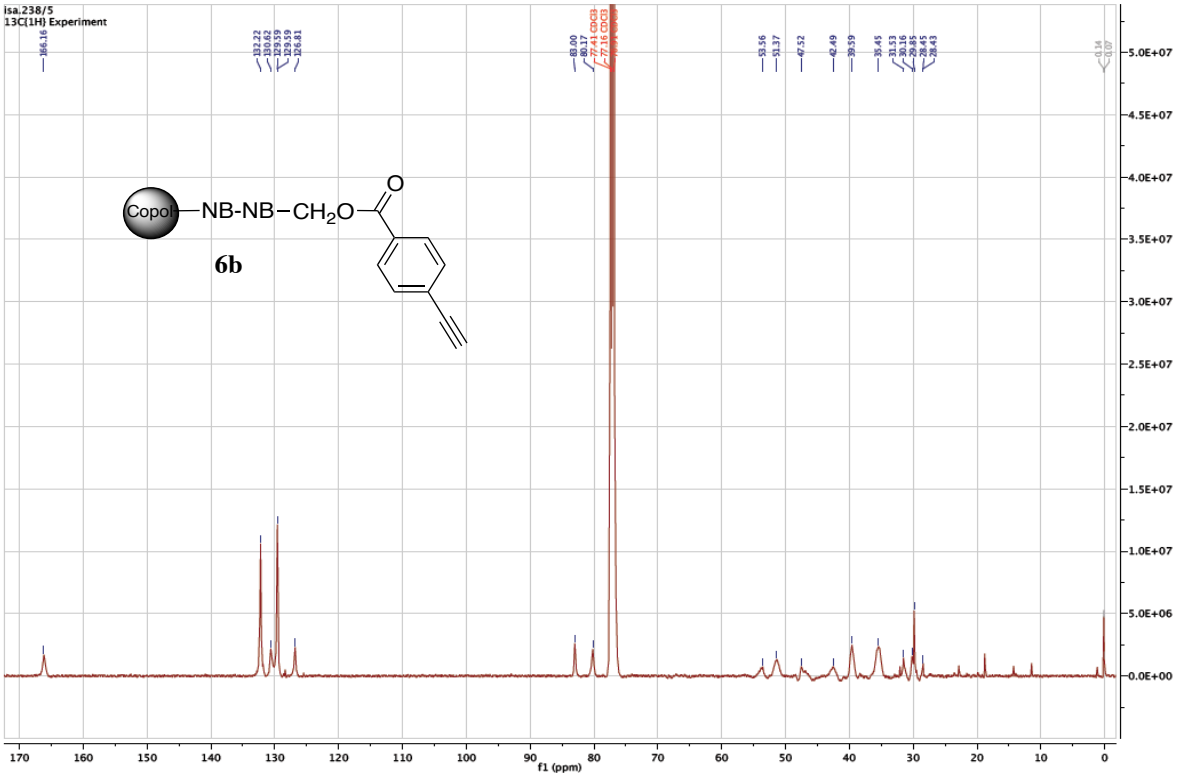


Figure SI-9. SEM pictures of polymer **6b**.

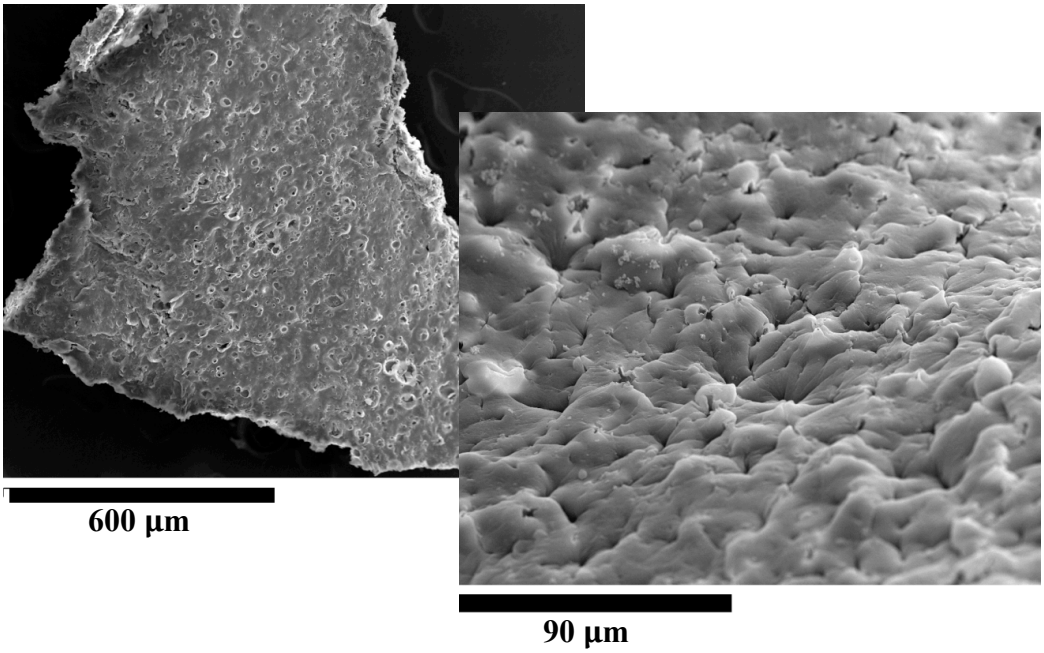


Figure SI-10. IR spectrum of polymer **6b**.

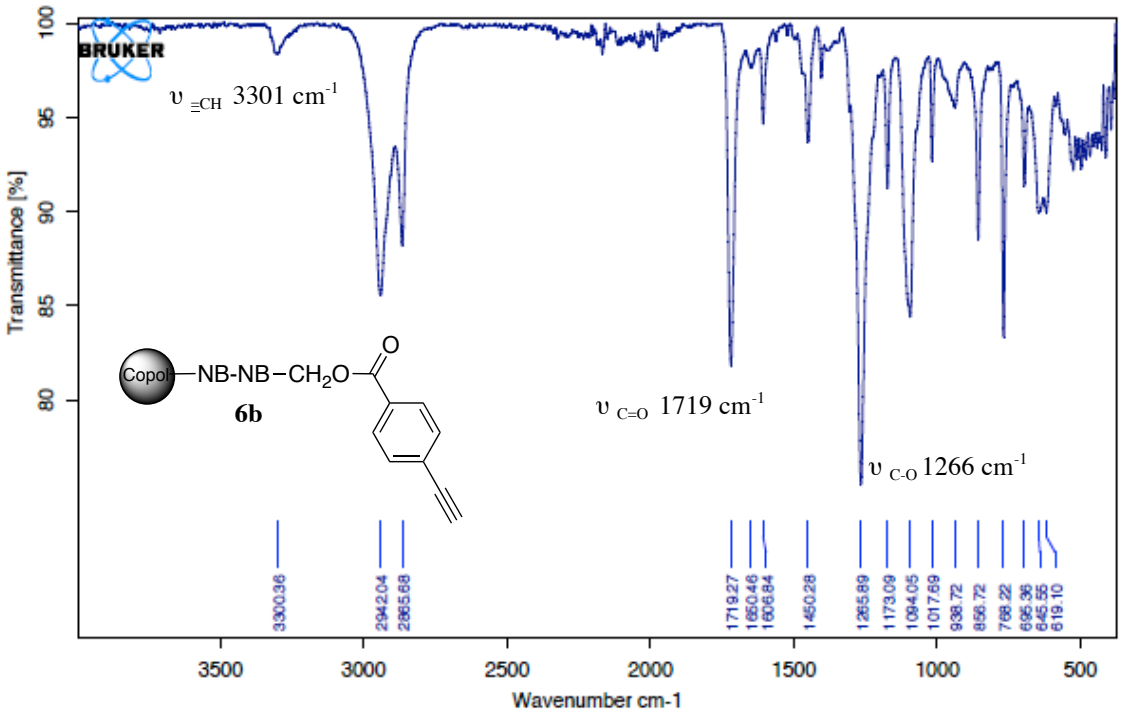


Figure SI-11. Raman spectrum of polymer **6b**.

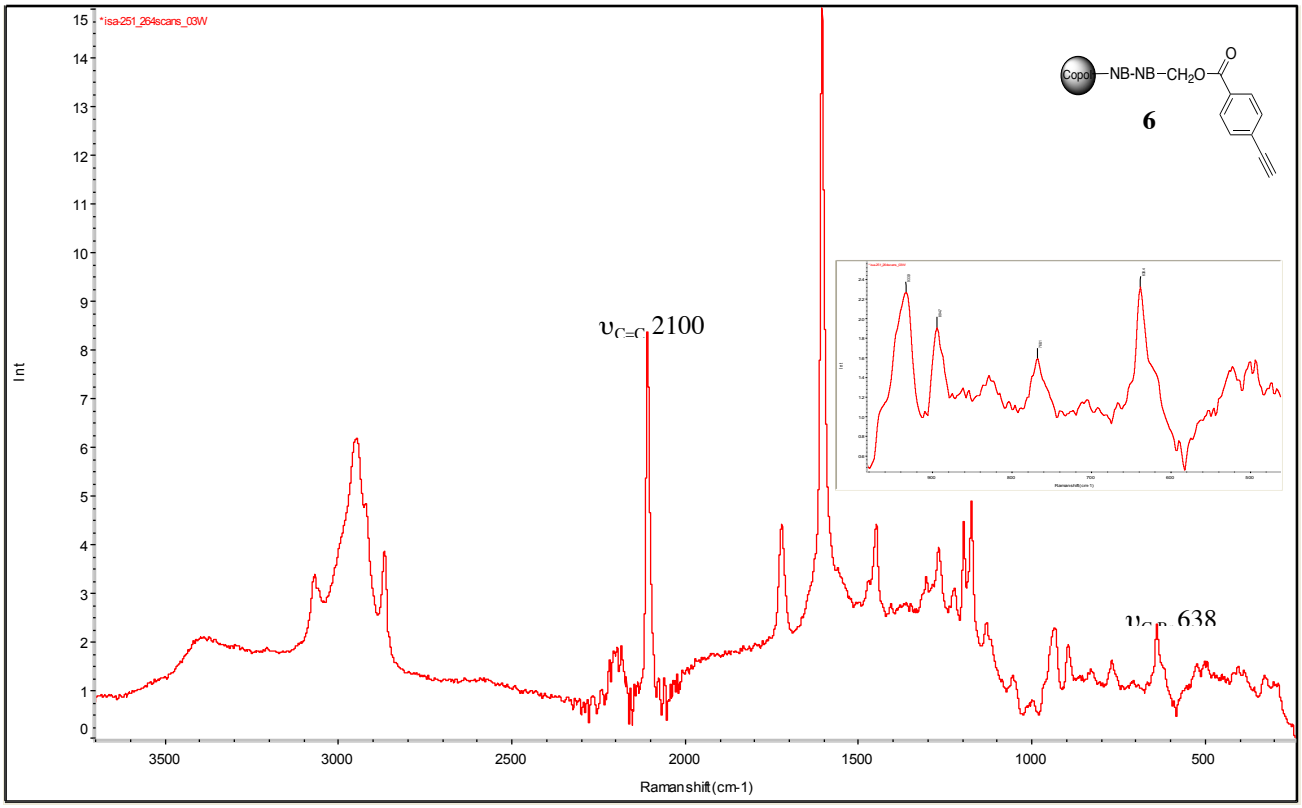
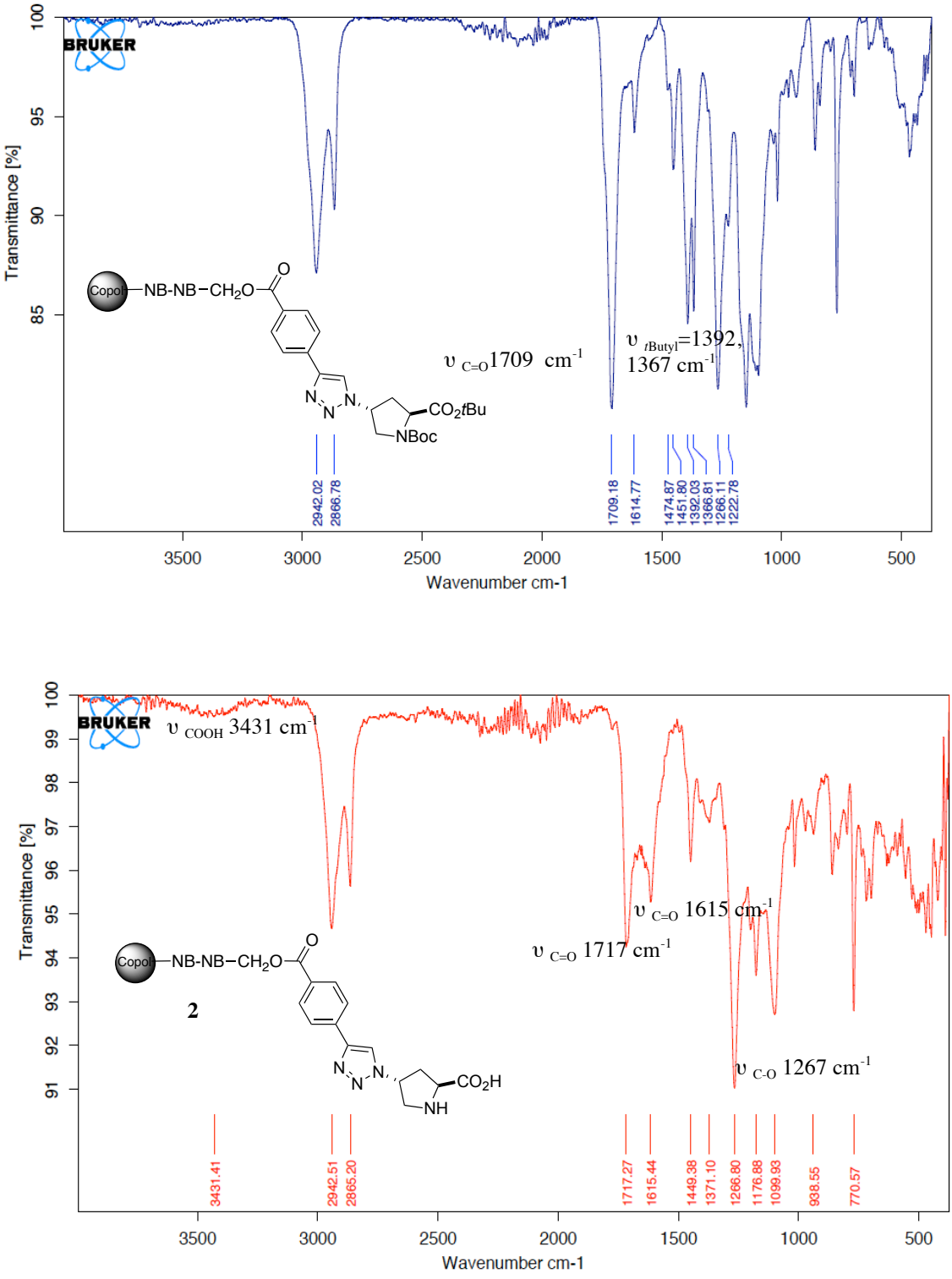


Figure SI-12. IR spectrum of catalyst **2**.



References

[S1] D. C. White, *Mikrochim. Acta* 1961, 449.

[S2] R. P. Washington and O. Steinbock, *J. Am. Chem. Soc*. 2001, **123**, 7933.

[S3] A. Melissaris, H. L. Morton, *J. Org. Chem*. 1992, **57**, 6998.

[S4] N. Mase, Y. Nakai, N. Ohara, H. Yoda, K. Takabe, F. Tanaka, C. F. Barbas III, *J. Am. Chem. Soc*. 2006, **128**, 734.

[S5] C. Ayats, A. H. Henseler, M. A. Pericàs, *ChemSusChem* 2012, **5**, 320.

[S6] J. G. Hernández, E. Juaristi, *Tetrahedron* 2011, **67**, 6953.

[S7] Y. Hayashi, T. Sumiya, J. Takahashi, H. Gotoh, T. Urushima, M. Shoji, *Angew. Chem. Int. Ed*. 2006, **45**, 958.

[S8] Z. Jiang, H. Yang., X. Han, J. Luo, M. W. Wong, Y. Lu, *Org. Biomol. Chem*. 2010, **8**, 1368.

[S9] H. Yang, S. Mahapatra, P. H. -Y. Cheong, G. R. Garter, *J. Org. Chem*. 2010, **75**, 7279.