Supporting Information

Heterogenization of Homogeneous Linear Chiral polymers in Metal−Organic Frameworks with Enhanced Catalytic Performance for Asymmetric Catalysis

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Keywords: *Metal-organic framework (MOF); multiple functionalized polymers; Asymmetric Catalyst; Heterogeneous; Homogeneous polymer; Cooperative effect*

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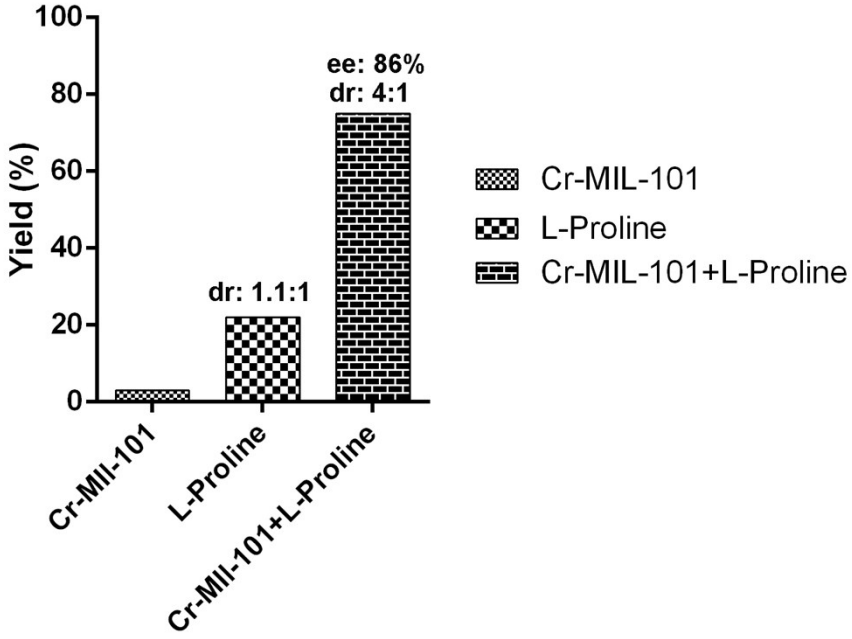


Figure S1. Catalytic performance of *L*-proline, Cr-MIL-101 and L-Proline+ Cr-MIL-101, all of the reactions were performed for 24 h and the yield was determined by ^{1}H NMR spectroscopy using dibromomethane as an internal standard. The ee values were determined by chiral HPLC. The dr values (*anti*:*syn*) were determined from ^{1}H NMR of the crude reaction mixtures.

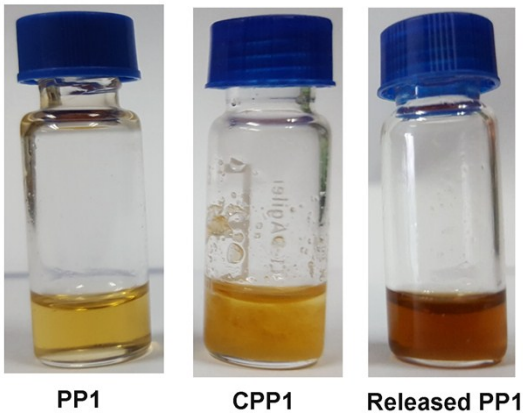


Figure S2. The comparison of solubility of linear polymers (**PP1**, 50mg/mL) prepared in solution approach, the release **PP1** from **MIL-101-PP1** and heterogeneously cross-linked *L*-proline containing resin **CPP1** in cyclohexanone (the reaction solvent in the catalytic system).

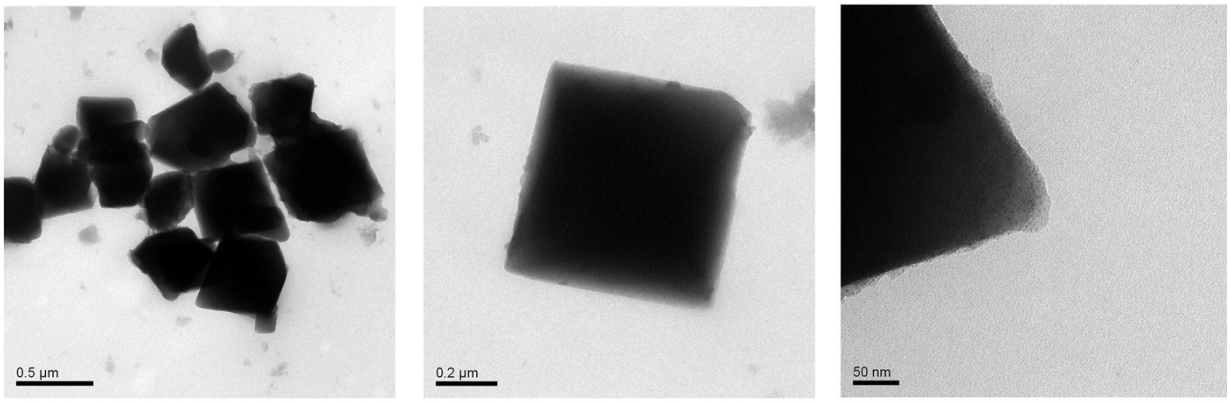


Figure S3. Transmission electron microscopy (TEM) images of MIL-101-PP1.

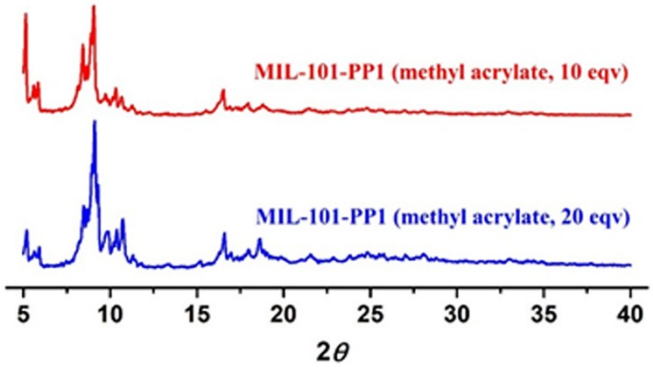


Figure S4. PXRD of **MIL-101-PP1-1** (methyl acrylate, 10 eqv) and **MIL-101-PP1-2** (methyl acrylate, 20 eqv).

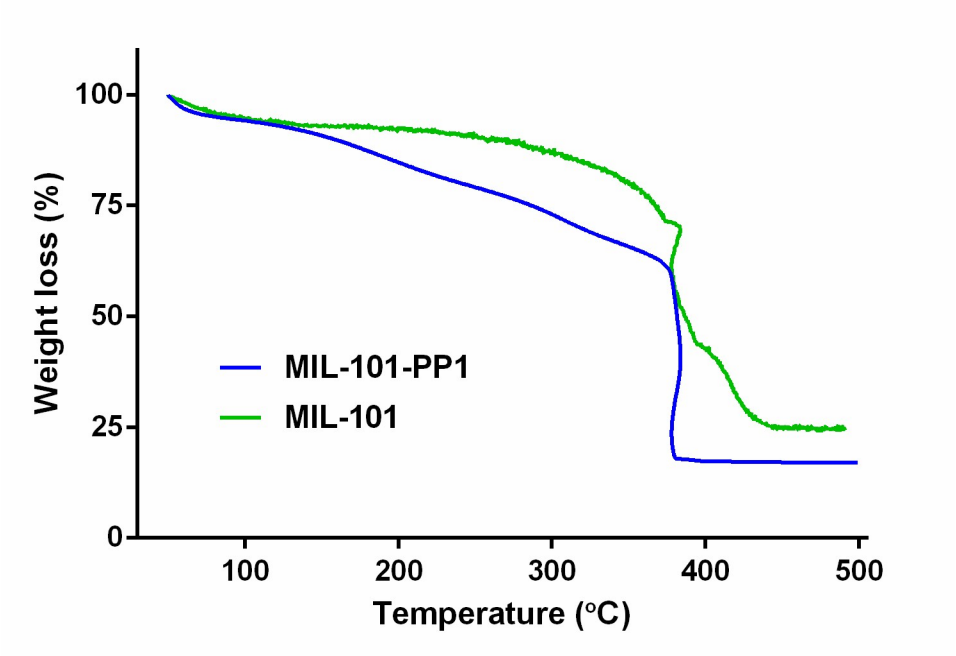
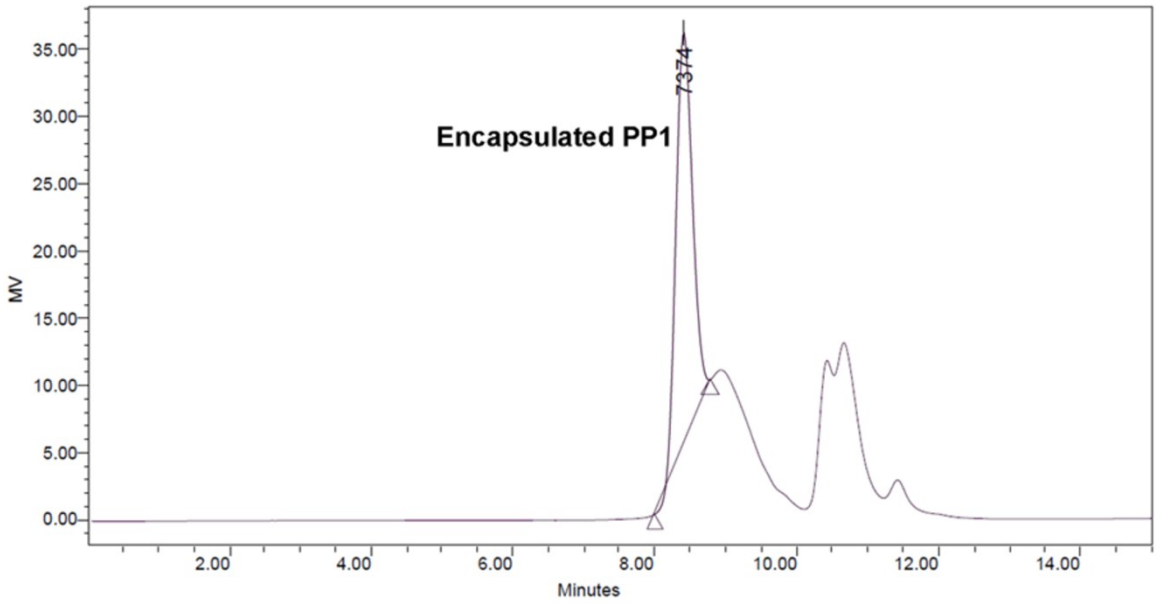


Figure S5. Thermogravimetric analyses (TGA) of Cr-MIL-101 and MIL-101-PP1.



	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		6930	7345	7374	7752	8146	1.059879	1.055478	1.109129

Figure S6. The molecular weight of encapsulated PP1 determined by gel permeation chromatography (GPC)

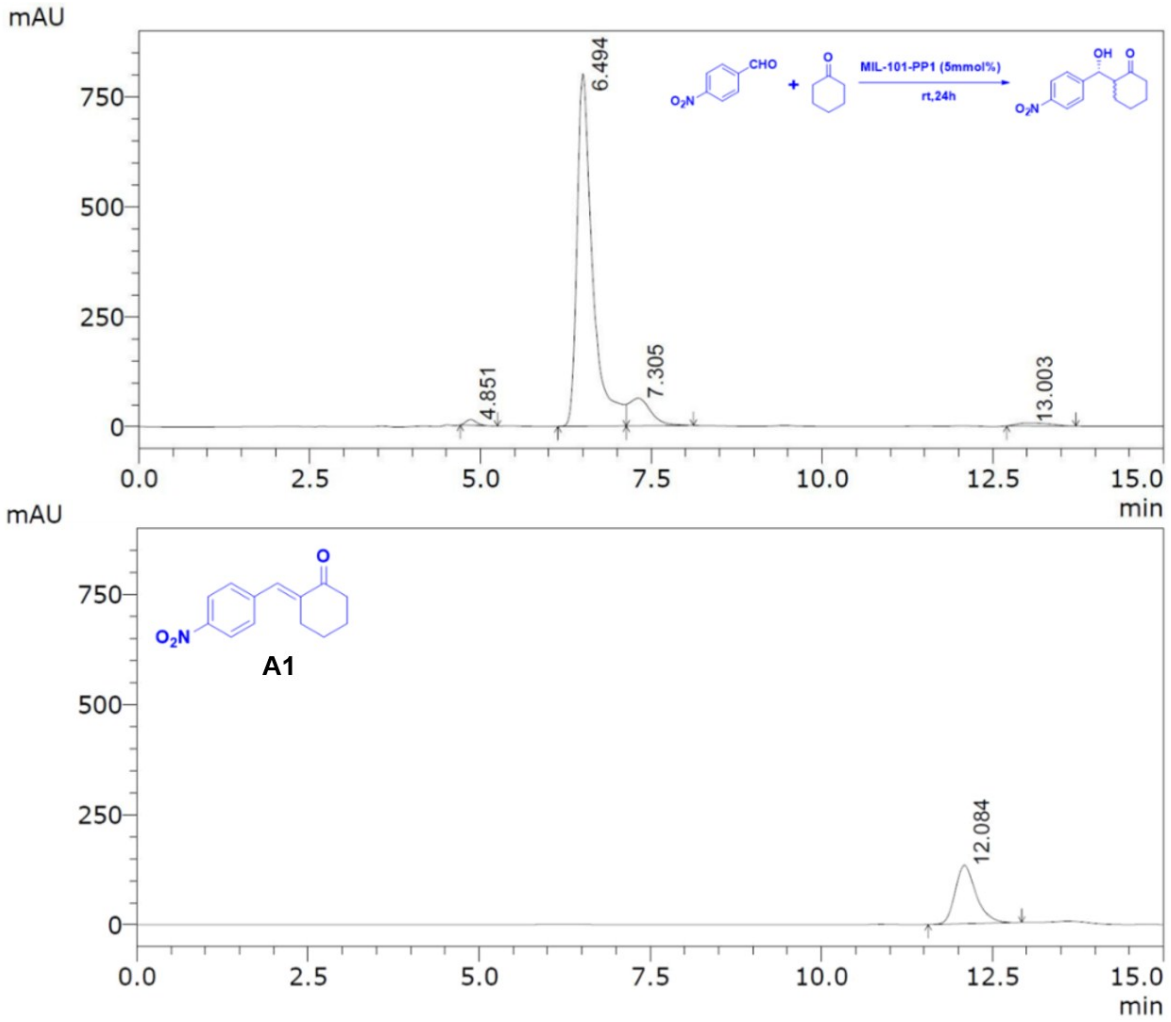


Figure S7. The analysis of crotonization byproduct. The crotonization byproduct **A1** was synthesized according to the literature (Molecules **2014**, *19*, 1976-1989). HPLC analysis method (Column: InertSustain^{R} C18; Column temperature: 40 ^{o}C; Mobile phase: methanol: water=70:30; Flow rate: 1ml/min; Detection wavelength: 254nm).

Table S1. The loading amount of *L*-proline moiety in the composites when we change the Molar ratio of the L-proline-containing vinyl derivative S1 to methyl acrylate in *in situ* polymerization.

Sample	Molar ratio of the L-proline-containing vinyl derivative **S1** to methyl acrylate	Amount of active site[a] (mmol/g)
MIL-101-PP1	1:5	0.28
MIL-101-PP1-1 (methyl acrylate, 10 eqv)	1:10	0.05
MIL-101-PP1-2 (methyl acrylate, 20 eqv)	1:20	< 0.01

[a] Active site is defined as *L*-proline groups on the polymer and the amount is determined based on the loadings of polymer in the composites.

Table S2. Textural structure and active site amount of the catalytic composites.

Sample	BET surface area (m^3/g)	Pore volume (mL/g)	Amount of active site (mmol/g)
Cr-MIL-101	2980.2	1.81	0
MIL-101-PP1	531.2	0.33	0.28[a]
MIL-101-PP1-1 (methyl acrylate, 10 eqv)	1336.4	0.94	0.05[a]
MIL-101-PP1-2 (methyl acrylate, 10 eqv)	2024.3	1.21	< 0.01[a]
Recovered MIL-101-PP1	978.0	0.61	0.23[a]

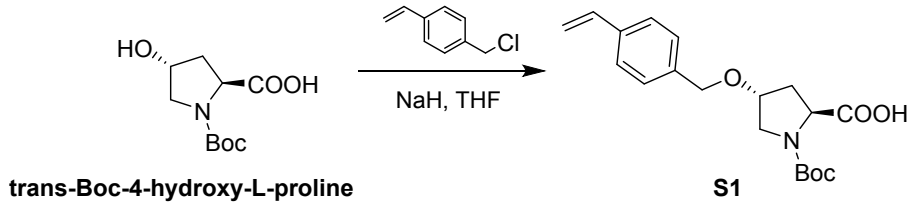
[a] Active site is defined as *L*-proline groups on the polymer and the amount is determined based on the loadings of polymer in the composites (eq. 1)**.**

Experimental section:

1) The synthesis of Cr-MIL-101

Cr-MIL-101 was synthesized via hydrothermal reaction according to the literature[S1]. A solution of $Cr(NO_3)_3.9H_2O$ (2.4 g, 6.6 mmol, fluorhydric acid (6.6 mmol) and 1,4-benzene dicarboxylic acid (984 mg, 6.6 mol) in water (29 mL) was placed in a Teflon-lined Parr stainless steel vessel. The vessel was sealed and placed in oven at 120 °C for 8 hours. After natural cooling, the mixture is filtered firstly using a large pore fritted glass filter (n°2), the water and the MIL-101 powder can pass through the filter while the free acid stays inside the glass filter. Then, the MIL-101 powder is separated from the solution using a small pores fritted glass filter (n°5), washed with hot ethanol, and dried *in vacuum* at 100 °C for 2 hours.

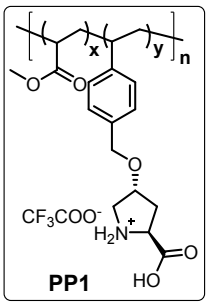
2) The synthesis of *L-proline-containing vinyl derivative S1*



trans-Boc-4-hydroxy-L-proline **S1**

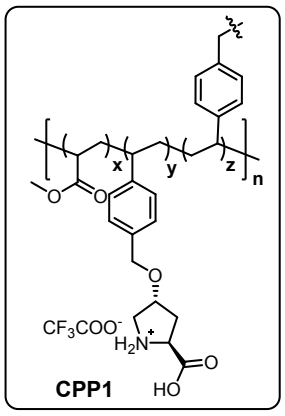
A solution of *trans*-Boc-4-hydroxy-*L*-proline (2.0 g, 8.65 mmol) in anhydrous THF (30 mL) was added dropwise under nitrogen at 0 °C to a suspension of NaH (60% mineral oil, 751 mg, 18.77 mmol) in anhydrous THF (20 mL), and stirred at r.t. for 1 h. Then, the mixture was added 4-chloromethylstyrene (90%, 3.66 g, 21.6 mmol), and stirred at r.t. for 1 h and then at 50 °C for overnight. After cooling to r.t., water (100 mL) was added. The aqueous phase was extracted with petroleum ether in order to remove the unreacted 4-chloromethylstyrene. The aqueous phase was acidified to pH 2–3 by adding a solution of $KHSO_4$, and was then extracted with ethyl acetate. The organic phase was dried ($MgSO_4$) and concentrated in *vacuum*. The crude product was purified by column chromatography on silica gel to give desired compound **S1** as a pale yellow and viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$): (two rotamers): δ =10.96 (brs, 1H), 7.39 (d, *J* = 8.2Hz, 2H), 7.28 (d, *J* = 8.2Hz, 2H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.74 (dd, *J* = 17.6, 2.4 Hz, 1H), 5.24 (dd, *J* = 10.9, 2.4 Hz, 1H), 4.56 – 4.34 (m, 3H), 4.20 – 4.15 (m, 1H), 3.76–3.60 (m, 2H), 2.50 – 2.05 (m, 2H), 1.41 and 1.46 (s, 9 H). ^{13}C NMR(125 MHz, $CDCl_3$):(two rotamers): δ 179.27, 177.66, 176.45, 155.92, 153.97, 137.32, 137.25, 136.47, 127.96, 126.45, 126.44, 114.19, 81.50, 80.90, 76.44, 76.01, 71.08, 70.92, 58.00, 57.94, 52.06, 51.43, 36.72, 34.87, 28.44, 28.30, 20.97. ESI-MS: m/z $[M+H]^+$348.

3) The synthesis of linear polymer PP1 in solution approach



A solution of compound **S1** (300 mg, 0.86 mmol), methyl acrylate (4.3 mmol, as co-polymerization vinyl monomers) and 2,2-azobisisobutyronitrile (AIBN**,** 42.3 mg, 0.26 mmol**,** as radical initiator) in toluene (5 mL) was to 80 ^{o}C for 24 hours under nitrogen atmosphere. Then, the reaction mixture was concentrated in *vacuum* to remove toluene. The residue was added isopropanol to form precipitation. The desired polymer was obtained by further deprotection of N-Boc group in CH_2Cl_2 (4 mL) and CF_3CO_2H (1 mL) for 4 hours at room temperature. ^{1}H NMR (400 MHz, DMSO-*d6*): 7.5–6.5 (m, 4H), 4.6– 4.2 (m, 4H), 3.9 –3.1 (m, 20H), 2.4 –1.1 (m, 20H). IR (KBr pellet): 3685, 296, 2904, 1747, 1706, 1461, 1284, 1213, 1203, 1060, 1004, 841 cm^{-1}. The weight average (Mw) molecular weights determined by Gel permeation chromatography (GPC): 4834.

4) The synthesis of cross-linked polymer CPP1



A solution of compound **S1** (300 mg, 0.86 mmol), methyl acrylate (4.3 mmol, as co-polymerization vinyl monomers), 1,4-diethenylbenzene (67 mg, 0.51 mmol, as cross-linking agent) and 2,2-azobisisobutyronitrile (AIBN**,** 42.3 mg, 0.26 mmol**,** as radical initiator) in toluene (5 mL) was heated to 80 ^{o}C for 24 h under nitrogen atmosphere. The suspension was cooled to room temperature, and methanol was added and the supernatant was decanted off. The process was repeated once more, the polymer beads were then filtered, washed with methanol, and dried at room temperature. The desired beads was obtained by further deprotection reaction of N-Boc group in CH_2Cl_2 (4 mL) and CF_3CO_2H (1 mL) for 4 hours at room temperature. The beads were then filtered and washed with CH_2Cl_2 and MeOH successively, and then was dried in a desiccator over P_2O_5 for 36 hours to give pale yellow solid. CHN-Analysis (%): N 2.18, C 55.32, H 6.33 (catalyst loading: 1.55 mmol/g). IR (KBr): 3755, 2987, 2794, 1695, 1637, 1367, 1209, 1176, 1051, 966 cm^{-1}.

5) The procedure for Post-synthetic modification of PP1~MIL-101 with pyridine

Dehydrated **PP1~MIL-101** (0.5 g) and **pyridine** (0.825 g) were mixed with anhydrous toluene (150 mL) in a 250mL round-bottom flask. The mixture was then refluxed for 24 h. After cooling down to room temperature, the mixture was collected via filtration. After thoroughly washing with dichloromethane, the **pyridine-grafted PP1~MIL-101** was then dispersed in ethanol under

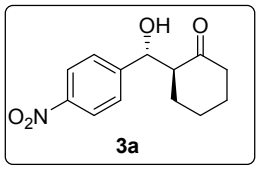
ultrasonication for 1 h and collected via filtration. The washing process was repeated at least 3 times to remove the unreacted pyridine from the pyridine-grafted PP1~MIL-101. The product was then dried in vacuum under 80℃ for 12 h.

6) Filtration experiment:

A suspension of *p*-nitrobenzaldehyde (0.1 mmol), cyclohexanone (0.1 mL) and **MIL-101-PP1** (0.005 mmol, 17.8 mg) was stirred at room temperature for 4 hours, then **MIL-101-PP1** was removed and the mixture was stired for another 20 hours. The reaction was quenched by adding ethyl acetate. Upon filtration, the catalyst was washed with ethyl acetate (10 mL). The organic layers were collected and washed with water (3 mL×3). The crude product was obtained after concentration in vacuum. Reaction yield was obtained by ^{1}H-NMR spectroscopy using dibromomethane (12.1 mg) as an internal standard.

7) The characterization of the products in asymmetric Aldol reaction

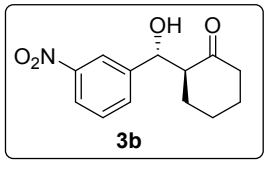
(S)-2-((R)-Hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one **3a**



3a

Yield: 91%, diastereoselectivity (dr value): 12:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 4.90 (dd, *J* = 8.4, 3.2 Hz, 1H), 4.08 (d, *J* = 3.2 Hz, 1H), 2.63-2.56 (m, 1H), 2.52-2.47 (m, 1H), 2.41-2.32 (m, 1H), 2.14-2.08 (m, 1H), 1.85-1.81 (m, 1H), 1.72-1.65 (m, 1H), 1.60-1.54 (m, 2H), 1.42-1.36 (m, 1H); ^{13}CNMR (100 MHz, $CDCl_3$): δ 214.7, 148.3, 147.5, 127.8, 123.5, 74.0, 57.1, 42.6, 30.7, 27.6, 24.6. The ee value was 92 % [Daicel Chiralpak AD-H, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 270 nm, t_R(minor) = 26.5 min, t_R(major) = 35.5 min].

(S)-2-((R)-hydroxy(3-nitrophenyl)methyl)cyclohexan-1-one **3b**

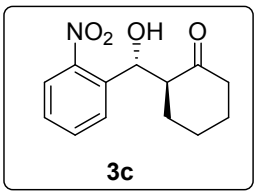


3b

Yield: 86%, diastereoselectivity (dr value): 11:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14-8.13 (m, 1H), 8.09-8.06 (m, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 4.83 (d, *J* = 8.4 Hz, 1H), 4.08 (br, 1H), 2.59-2.52 (m, 1H), 2.44-2.40 (m, 1H), 2.34-2.26 (m, 1H), 2.06-2.02 (m, 1H), 1.77-1.74 (m, 1H), 1.61-1.48 (m, 3H), 1.36-1.29 (m, 1H); ^{13}CNMR (100 MHz, $CDCl_3$): δ 214.9, 148.2, 143.2, 133.2, 129.3, 122.8, 122.0, 74.0, 57.1, 42.6, 30.7, 27.6, 24.6. The ee value was 92% [Daicel Chiralpak AD-H,

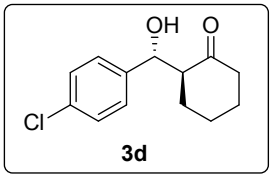
isopropanol/hexane = 10/90, 1.0 mL/min, λ = 214 nm,t_R(major) = 22.5 min,t_R(minor) = 29.5 min].

(S)-2-((R)-hydroxy(2-nitrophenyl)methyl)cyclohexan-1-one **3c**



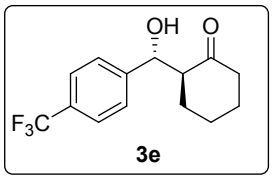
Yield: 87%, diastereoselectivity (dr value): 13:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.84 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.64 (td, *J* = 7.6, 0.8 Hz, 1H), 7.43 (td, *J* = 8.4, 1.6 Hz, 1H), 5.54 (d, *J* = 7.2Hz, 1H), 4.12 (br, 1H), 2.79-2.73 (m, 1H), 2.47-2.43 (m, 1H), 2.38-2.30 (m, 1H), 2.12-2.07 (m, 1H), 1.87-1.84 (m, 1H), 1.78-1.56 (m, 4H); ^{13}CNMR (100 MHz, $CDCl_3$): δ 214.9, 148.7, 136.6, 133.1, 129.0, 128.4, 124.0, 69.7, 57.3, 42.8, 31.1, 27.7, 24.9. The ee of **1c** was 93 % [Daicel Chiralpak AS-H, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 214 nm, t_R(minor) = 18.1 min, t_R(major) = 21.4 min].

(S)-2-((R)-(4-Chlorophenyl)(hydroxy)methyl)cyclohexan-1-one **3d**



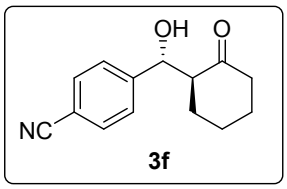
Yield: 63%, diastereoselectivity (dr value): 8:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 4.76 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.00 (d, *J* = 2.8 Hz, 1H), 2.59-2.52 (m, 1H), 2.49-2.46 (m, 1H), 2.39-2.31 (m, 1H), 2.10-2.06 (m, 1H), 1.81-1.78 (m, 1H), 1.67-1.52 (m, 3H), 1.33-1.26 (m, 1H); ^{13}CNMR (100 MHz, $CDCl_3$): δ 215.3, 139.4, 133.5, 128.5, 128.4, 74.1, 57.3, 42.6, 30.7, 27.7, 24.7. The ee value was 87 % [Daicel ChiralpakAS-H, isopropanol/hexane = 10/90, 0.5 mL/min, λ = 220 nm, t_R(minor) = 36.1 min, t_R(major) = 42.4 min].

(S)-2-((R)-hydroxy(4-(trifluoromethyl)phenyl)methyl)cyclohexan-1-one **3e**



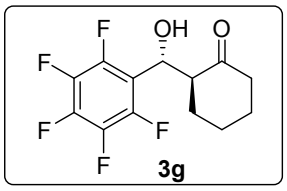
Yield: 70%, diastereoselectivity (dr value): > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), (dd, *J* = 8.8, 2.8 Hz, 1H), 4.08 (d, *J* = 2.8 Hz, 1H), 2.61-2.56 (m, 1H), 2.50-2.46 (m, 1H), 2.40-2.31 (m, 1H), 2.11-2.07 (m, 1H), 1.82-1.76 (m, 1H), 1.67-1.53 (m, 3H), 1.37-1.27 (m, 1H); ^{13}CNMR (100 MHz, $CDCl_3$): δ 215.0, 145.0, 130.1 (q, J_{CF}= 32.2 Hz), 127.3, 125.3 (q, J_{CF}= 3.8 Hz), 124.1 (q, J_{CF}= 270.4 Hz), 74.2, 57.2, 42.6, 30.7, 27.7, 24.6; ^{19}F NMR (376 MHz,$CDCl_3$): δ -62.5 (s, 3F). The ee value of **1d** was 93 % [Daicel ChiralpakIA, isopropanol/hexane = 10/90, 0.5 mL/min, λ = 210 nm, t_R(minor) = 24.8 min, t_R(major) = 35.5 min].

4-((R)-Hydroxy((S)-2-oxocyclohexyl)methyl)benzonitrile **3f**



Yield: 99%, diastereoselectivity (dr value): 8:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 4.84 (dd, *J* = 8.4, 3.2 Hz, 1H), 4.07 (d, *J* = 2.8 Hz, 1H), 2.59-2.54 (m, 1H), 2.50-2.46 (m, 1H), 2.40-2.32 (m, 1H), 2.13-2.08 (m, 1H), 1.84-1.80 (m, 1H), 1.72-1.50 (m, 3H), 1.40-1.30 (m, 1H); ^{13}CNMR (100 MHz, $CDCl_3$): δ 214.8, 146.3, 132.2, 127.7, 118.7, 111.6, 74.2, 57.1, 42.6, 30.7, 27.6, 24.6. The ee value was 91 % [Daicel ChiralpakAD-H, isopropanol/hexane = 20/80, 0.5 mL/min, λ = 230 nm, t_R(minor) = 28.1 min, t_R(major) = 36.2 min].

(S)-2-((R)-Hydroxy(perfluorophenyl)methyl)cyclohexan-1-one **3g**

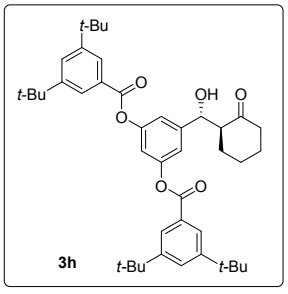


Yield: 89%, diastereoselectivity (d.r. value): > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.32 (dd, *J* = 9.6, 3.2Hz, 1H), 3.96 (d, *J* = 3.2 Hz, 1H), 3.04-2.97 (m, 1H), 2.54-2.50 (m, 1H), 2.44-2.36 (m, 1H), 2.16-2.12 (m, 1H), 1.88-1.85 (m, 1H), 1.70-1.58 (m, 3H), 1.34-1.30 (m, 1H); ^{13}CNMR (100 MHz, $CDCl_3$): δ 214.1, 146.5-113.7 (multiplet, C_6F_5), 65.9, 54.1, 42.3, 30.1, 27.4, 24.4; ^{19}F NMR (376 MHz,$CDCl_3$): δ -141.2--141.3 (m, 1F), -141.3--141.4 (m, 1F), -154.3 (t, *J* = 21.0 Hz, 1F), -161.6--161.8 (m, 2F). The ee value was 96 % [Daicel ChiralpakIA, isopropanol/hexane = 10/90, 0.5 mL/min, λ = 210 nm, t_R(major) = 17.5 min, t_R(minor) = 21.0 min].

8) Reaction procedure for Aldol reaction for buky aldehyde catalyzed by *L*-proline in homogenous system

A solution of 5-formyl-1,3-phenylene bis(3,5-di-tert-butylbenzoate) **1h** (57 mg, 0.1 mmol) and cyclohexanone (0.1 mL) and *L*-proline (2.3 mg, 0.02 mmol), and was stirred at room temperature for indicated time (Table 1). The reaction was quenched by adding ethyl acetate, upon filtration, the catalyst was washed with CH_2Cl_2. The organic layers were collected and concentrated in *vacuum*. The crude product was purified by chromatography (petroleum ether/ethyl acetate) to afford desired product.

5-((R)-Hydroxy((S)-2-oxocyclohexyl)methyl)-1,3-phenylene bis(3,5-di-tert-butylbenzoate) **3h**



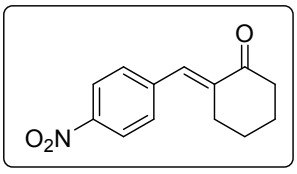
Yield: 81%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 2.0Hz, 4H), 7.71 (t, *J* = 2.0Hz, 2H), 7.16-7.13 (m, 3H), 4.86 (dd, *J* = 8.4, 2.0Hz, 1H), 4.04 (d, *J* = 2.8Hz, 1H), 2.67-2.61 (m, 1H), 2.50-2.47 (m, 1H), 2.40-2.32 (m, 1H), 2.13-2.09 (m, 1H), 1.88-1.81 (m, 2H), 1.68-1.59 (m, 1H),1.38 (s, 36H);

^{13}CNMR (100 MHz, $CDCl_3$): δ 215.2, 165.5, 151.5, 151.4, 143.6, 128.6, 128.0, 124.4, 117.8, 115.3, 74.2, 57.4, 42.7, 35.0, 31.3, 30.8, 27.8, 24.7. ESI-MS: m/z $[M+H]^+$ 669.

9) Reaction procedure for crotonization byproduct A1

A solution of Cyclohexanone (98 mg, 1 mmol) and pyrrolidine (85.2 mg, 1.2 mmol) in 10 mL CH_2Cl_2 was stirred about 5 min at room temperature. Then, *p*-nitrobenzaldehyde (151 mg, 1 mmol) was added and the mixture was stirred for 4 h at 40 °C. After completion of the reaction (TLC), the solvent was removed under vacuum. The crude product was subjected to column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to afford the product.

2-(4-nitrobenzylidene)cyclohexan-1-one **A1**

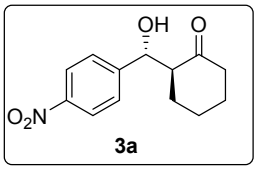


Yield: 52%, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.46 (s, 1H), 2.82 (m, 2H), 2.58 (t, *J* = 6.5 Hz, 2H), 1.97 (m, 2H), 1.81 (m, 2H).

References:

[S1] Ferey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surble S.; Margiolaki, I. *Science,* 2005, **309**, 2040.

Spectrum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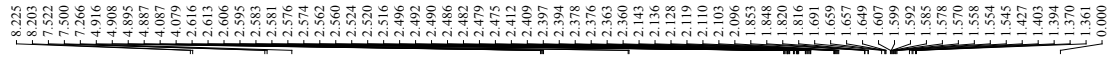
O
O_2N
3a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2.613
2.606
2.595
2.583
2.581
2.576
2.574
2.562
2.560
2.524
2.520
2.516
2.496
2.492
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2.482
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2.397
2.394
2.378
2.376
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2.360
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2.136
2.128
2.119
2.110
2.103
2.096
1.853
1.848
1.820
1.816
1.691
1.659
1.657
1.649
1.607
1.599
1.592
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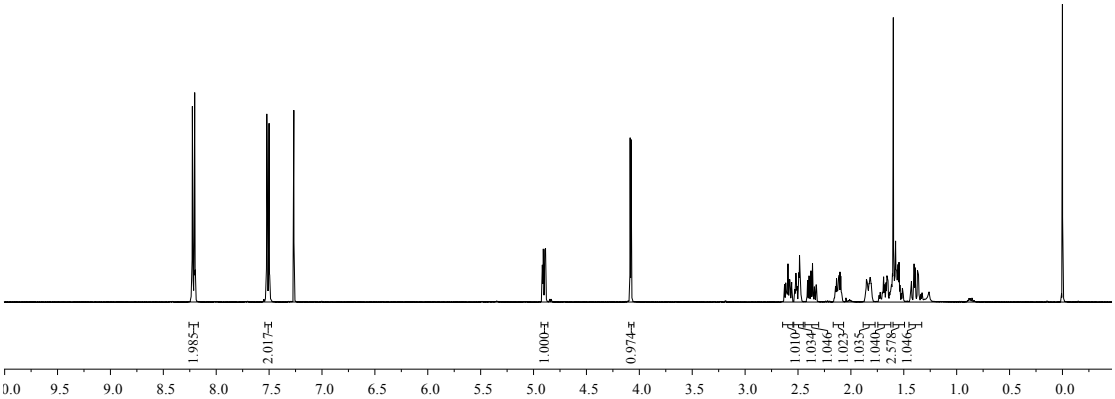
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1.046
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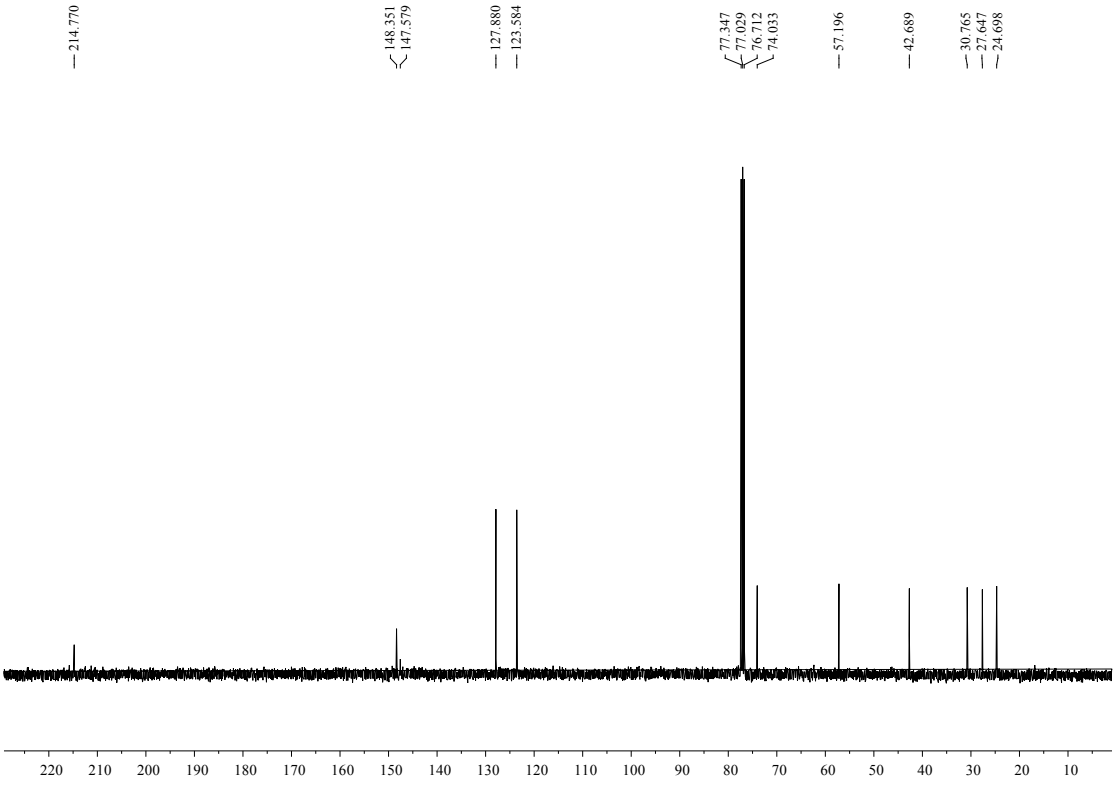
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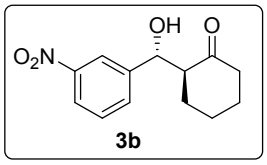
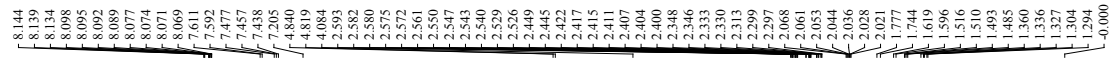

OH
O
O_2N

3b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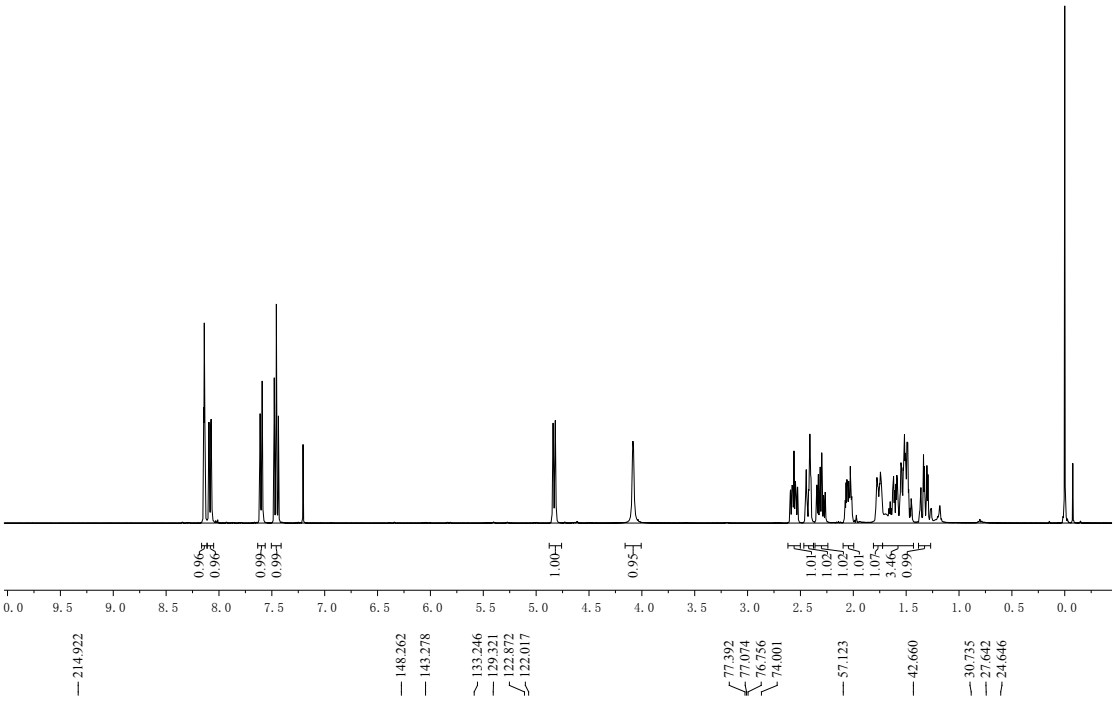
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0.99
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

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148.262
143.278
133.246
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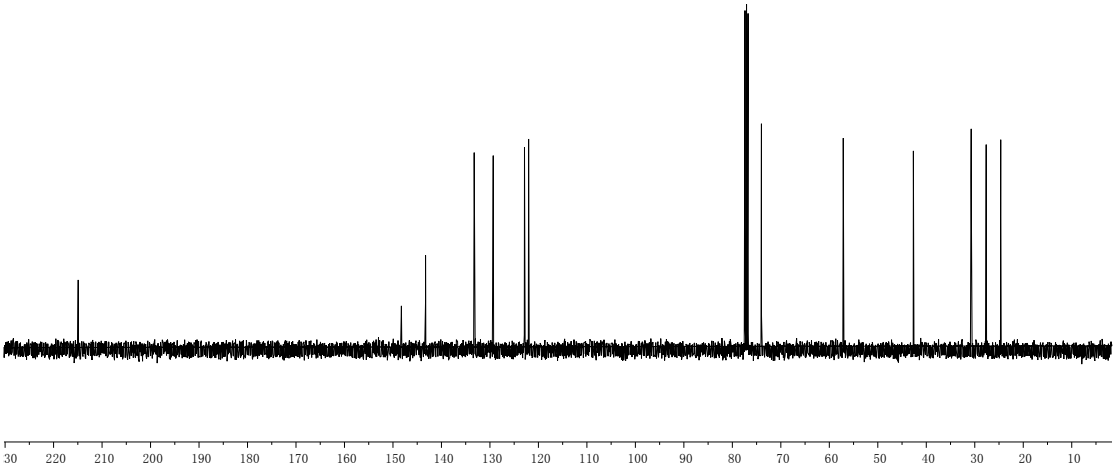
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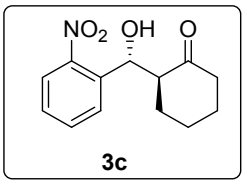
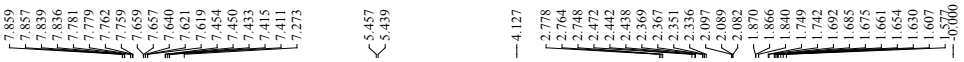

NO2 OH O

3c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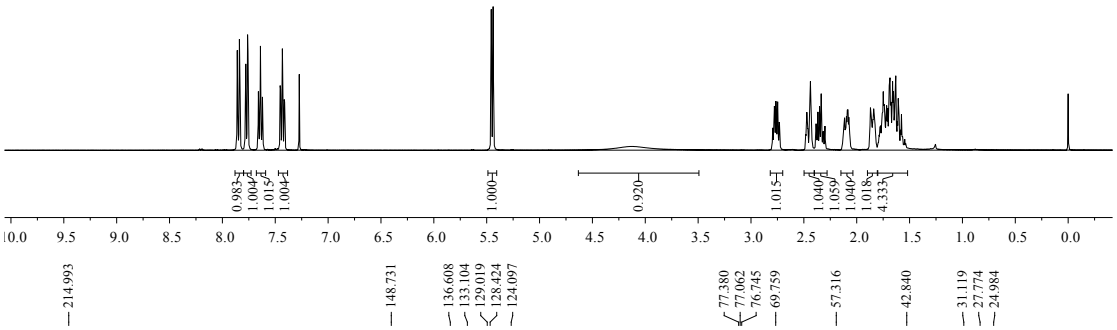
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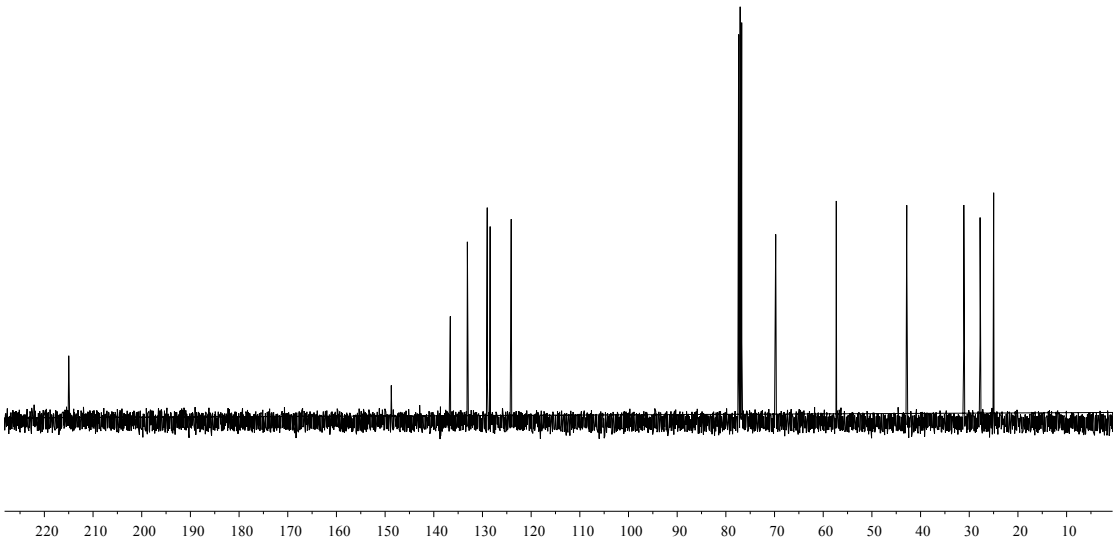
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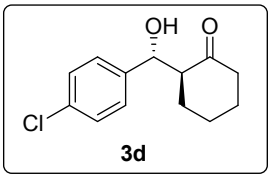
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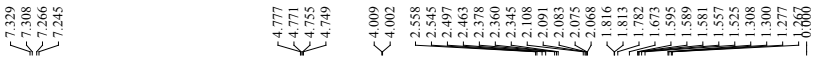
O
Cl

3d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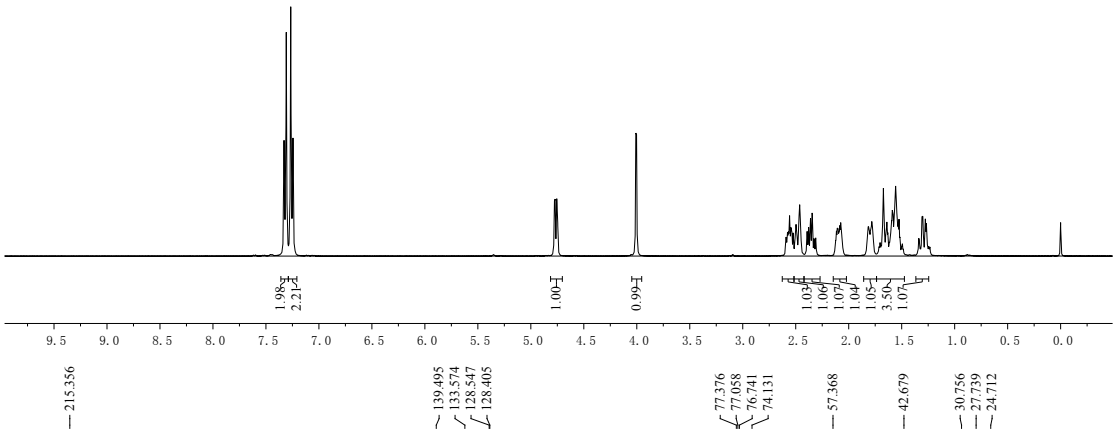
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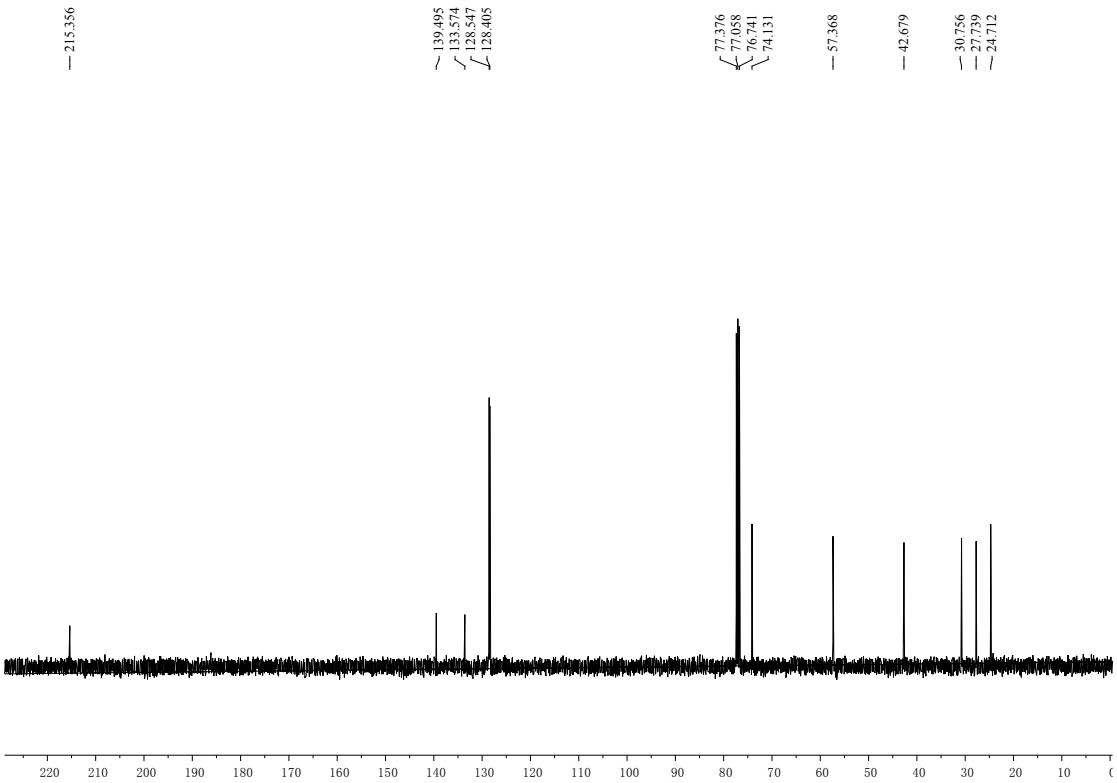
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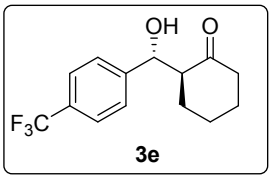
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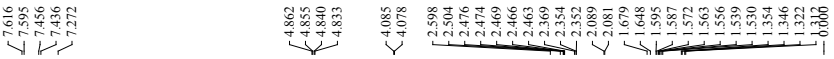
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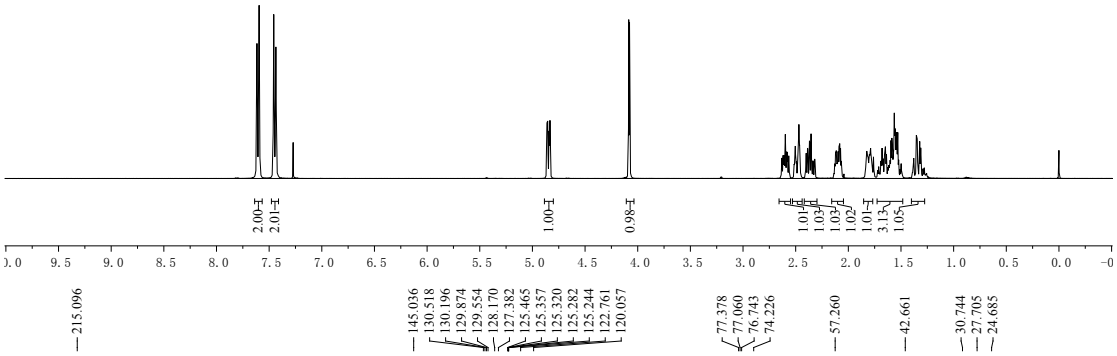
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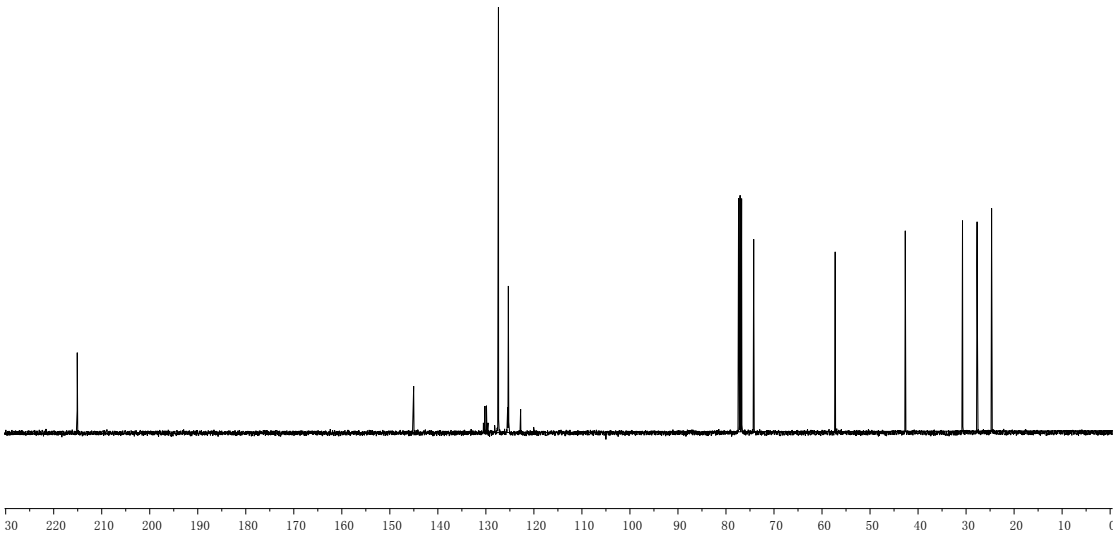

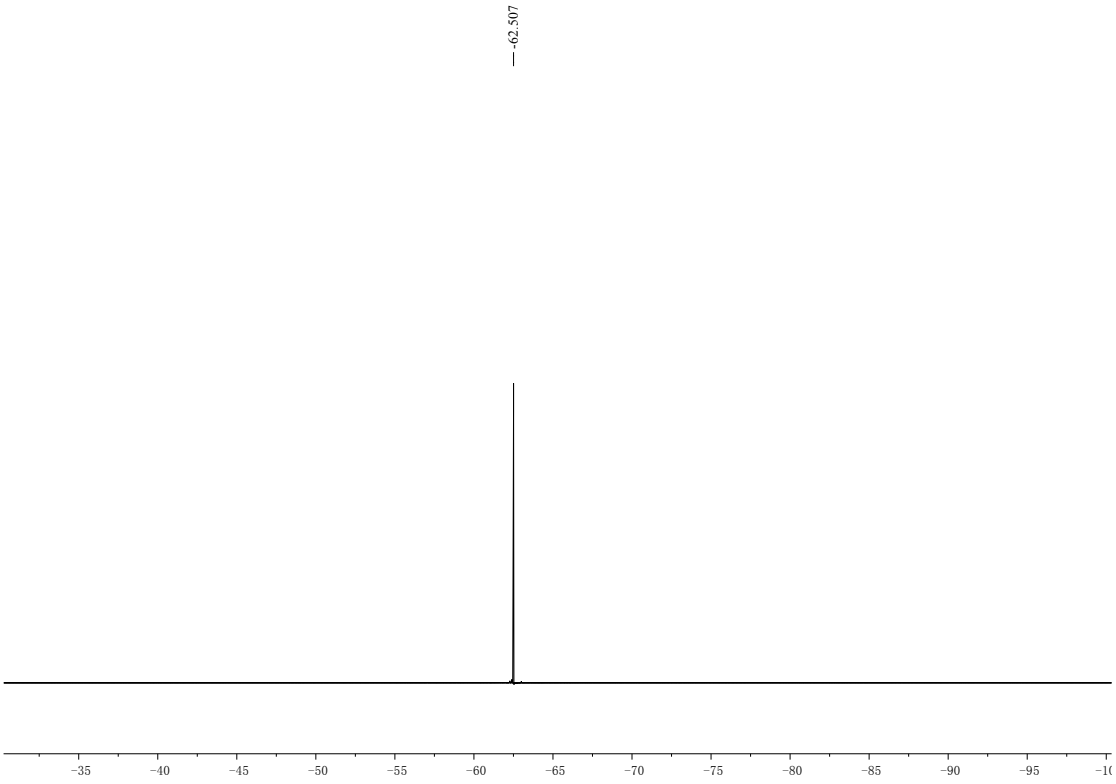
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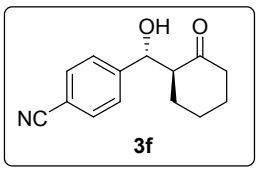
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O
NC

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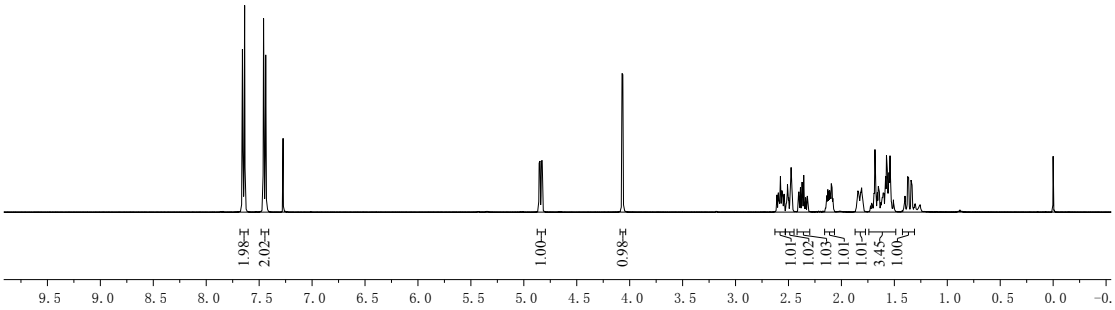
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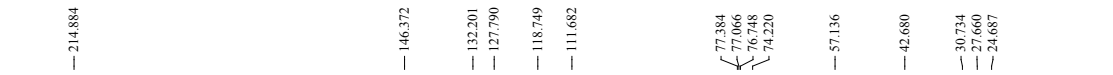
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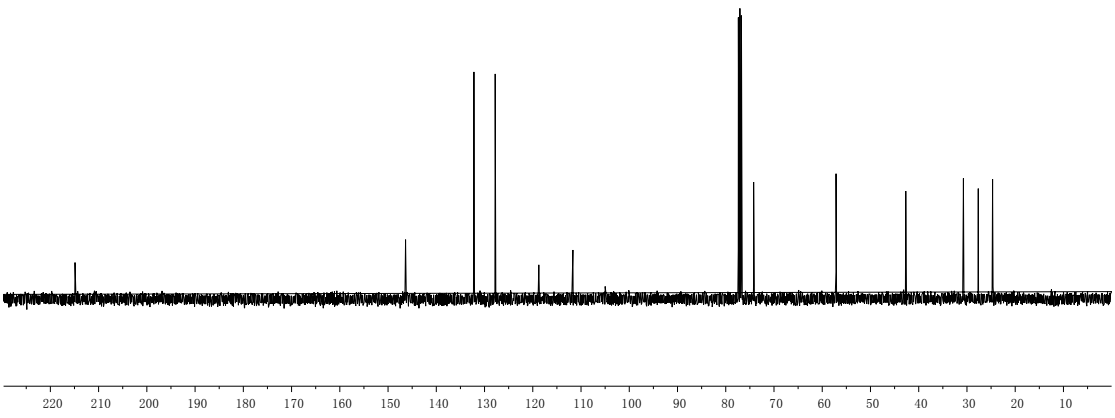
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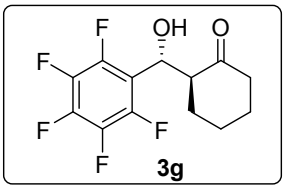
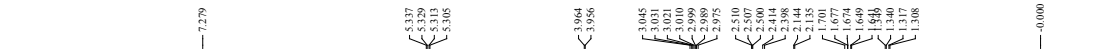

F
OH
O
F
F
F
F
3g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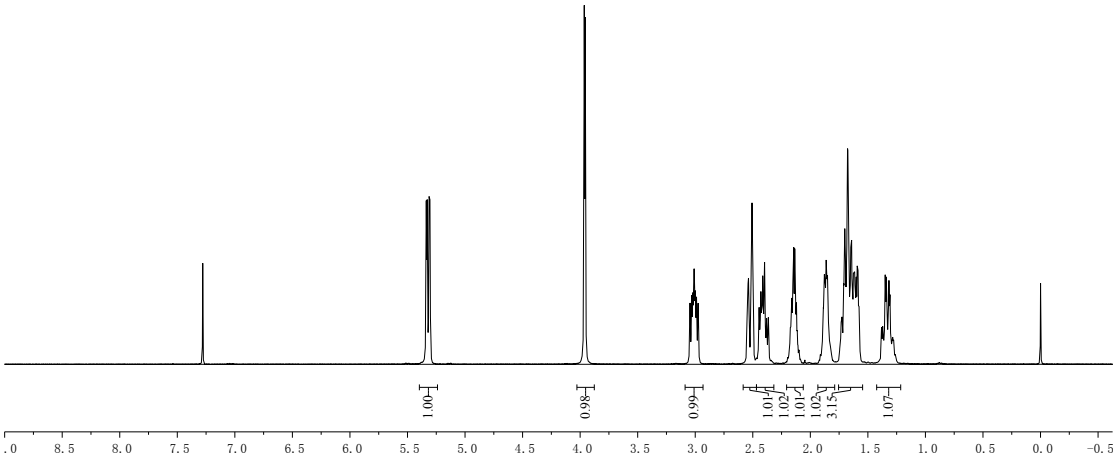
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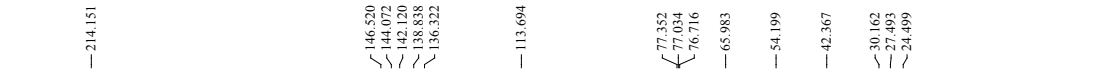
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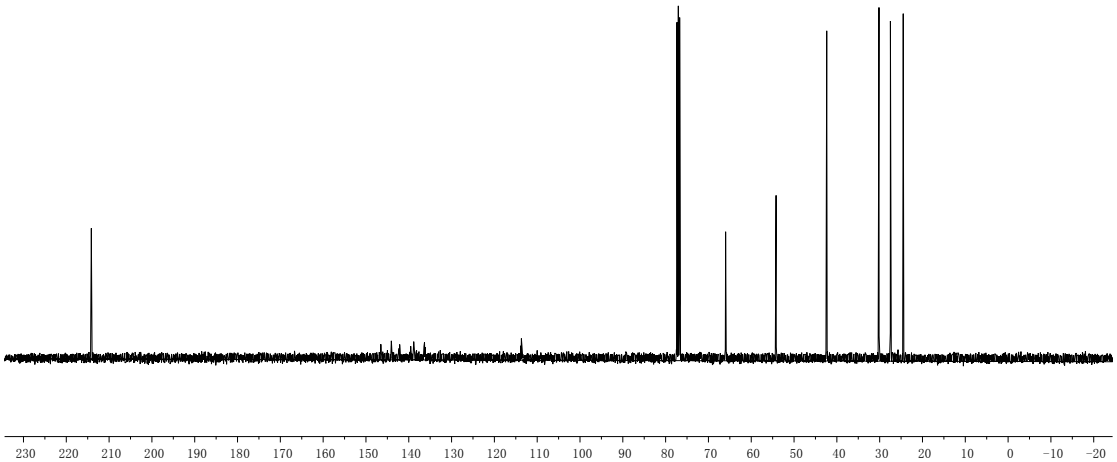
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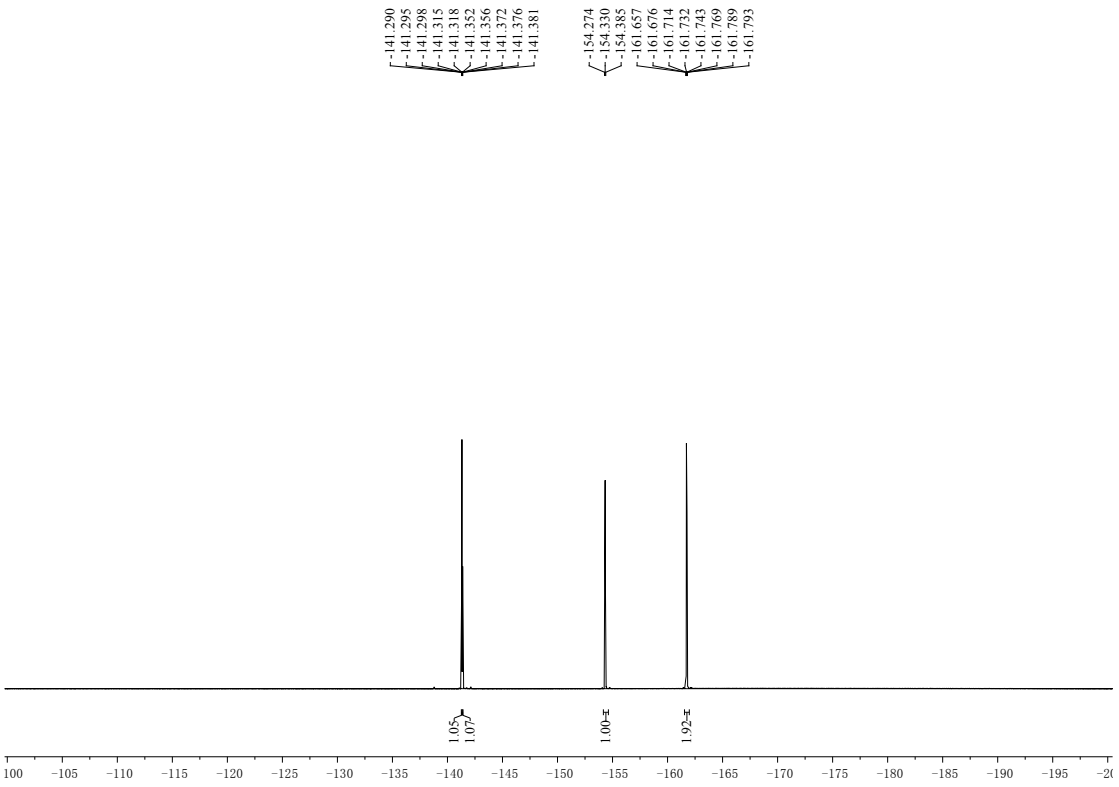
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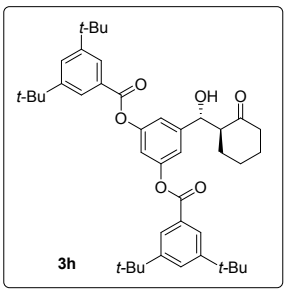
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OH
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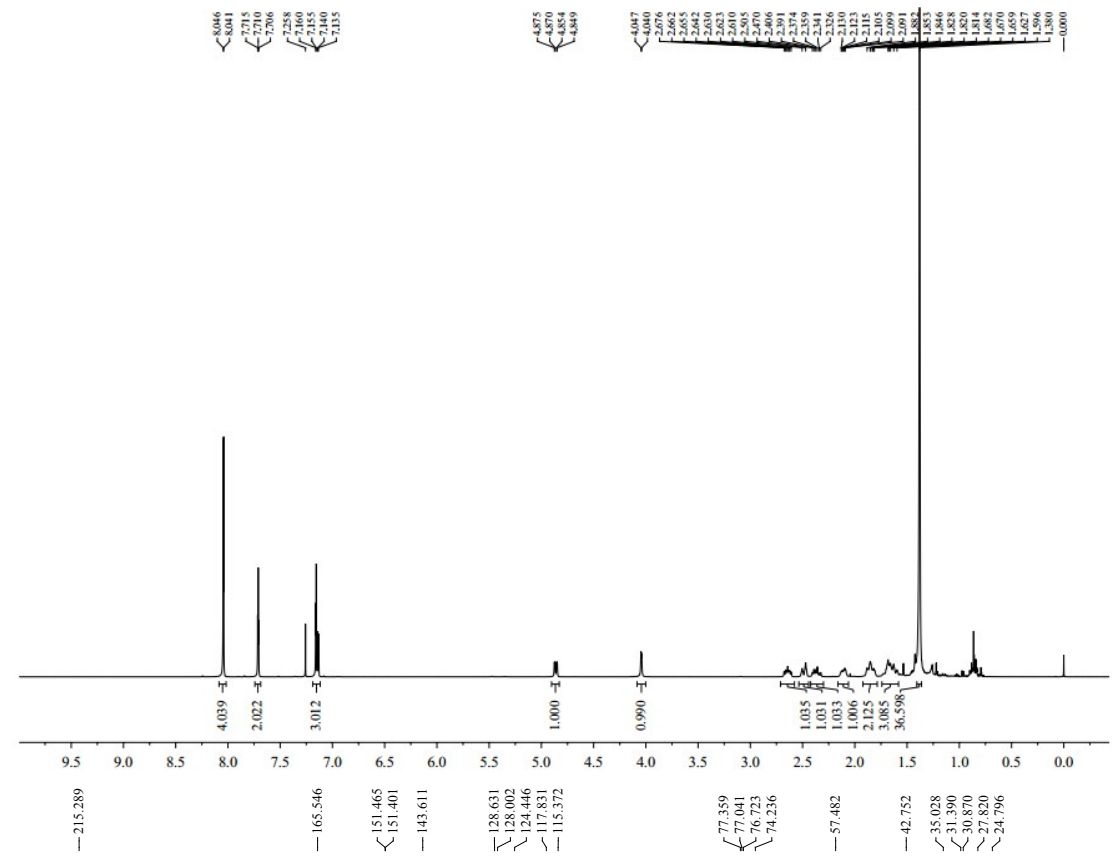
O
O
t-Bu
t-Bu

3h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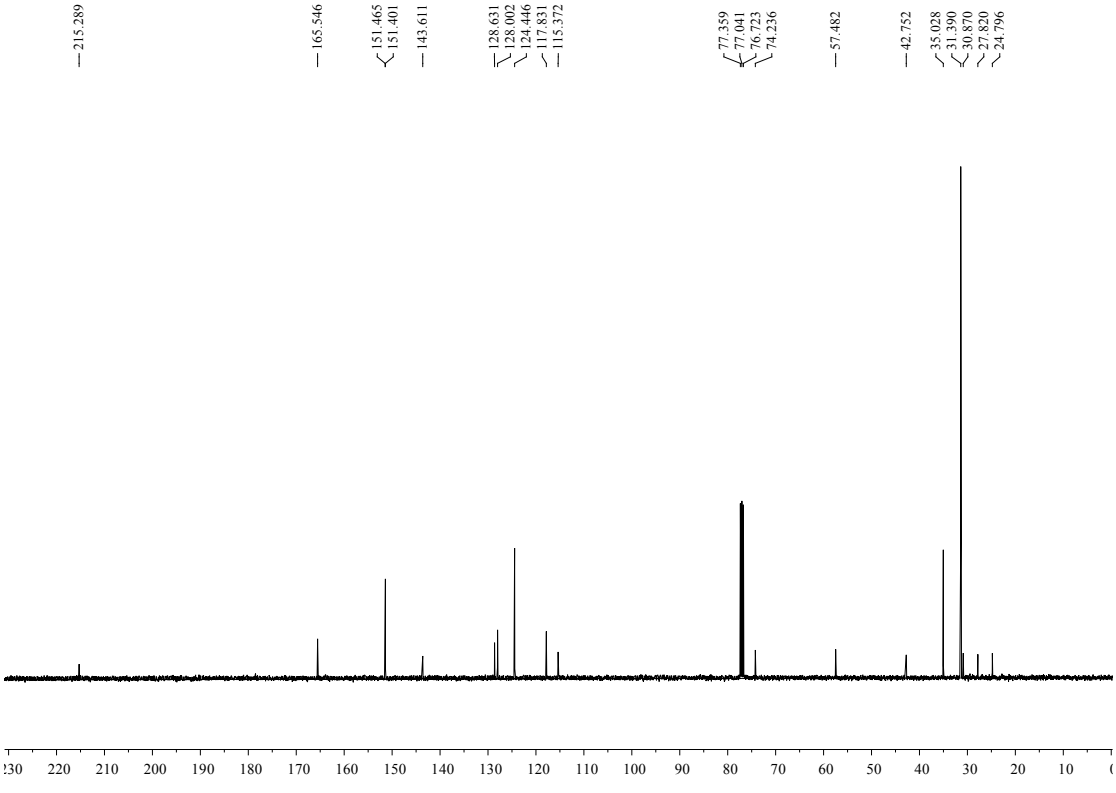
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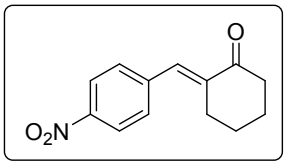
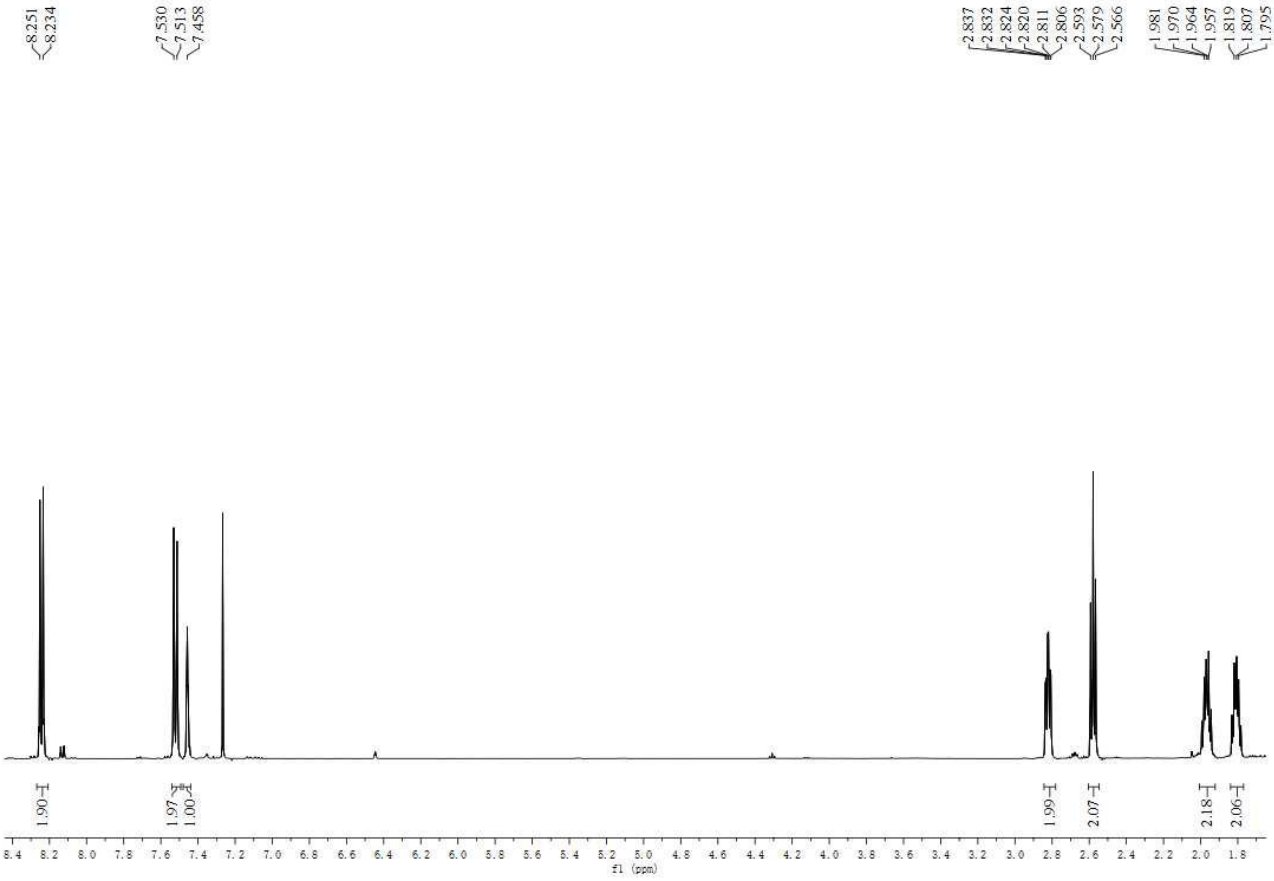

O
O2N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1.819
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1.00
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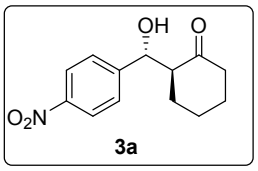
2.07
2.18
2.06
f1 (ppm)

HPLC spectra



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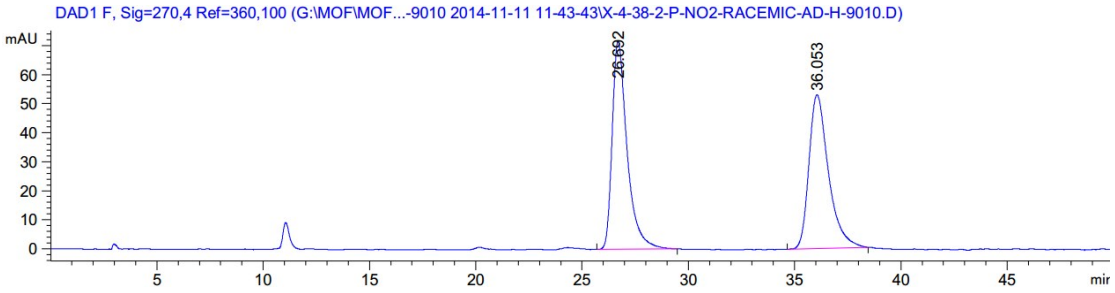
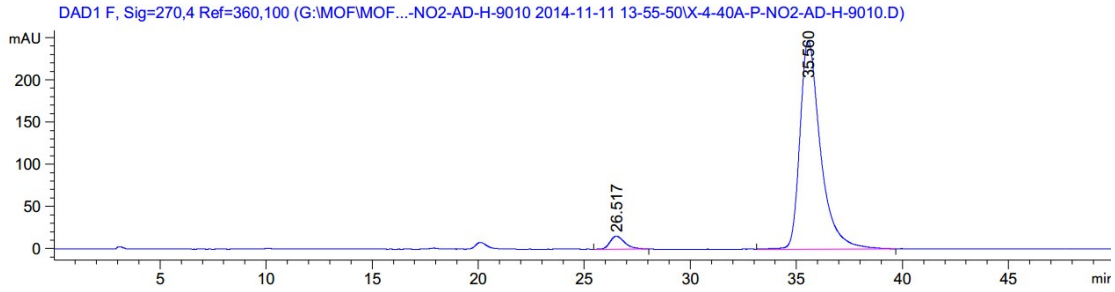
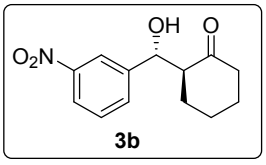


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.692	BB	0.7355	3510.08740	71.90866	50.9042
2	36.053	BB	0.9589	3385.38501	53.02438	49.0958



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.517	BB	0.7186	742.75928	15.40171	4.2678
2	35.560	BB	1.0052	1.66609e4	246.90947	95.7322



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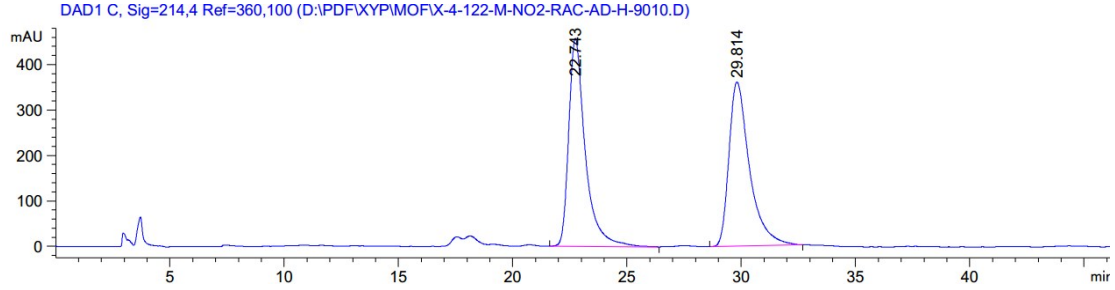
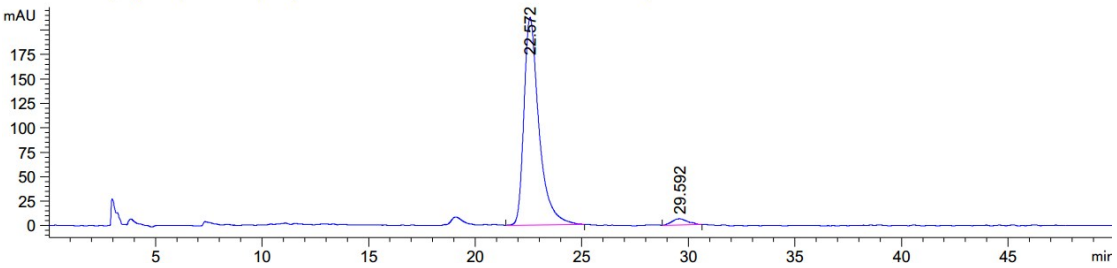
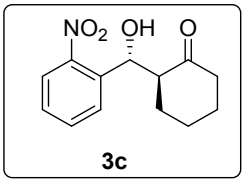


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.743	BB	0.7522	2.30630e4	457.41266	50.4307
2	29.814	BB	0.9320	2.26691e4	361.30002	49.5693

DAD1 C, Sig=214,4 Ref=360,100 (D:\PDF\XYP\MOF\X-4-40B-M-NO2-AD-H-9010.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.572	BB	0.7326	1.04312e4	212.51794	96.9494
2	29.592	BB	0.7383	328.22607	6.29467	3.0506



3c

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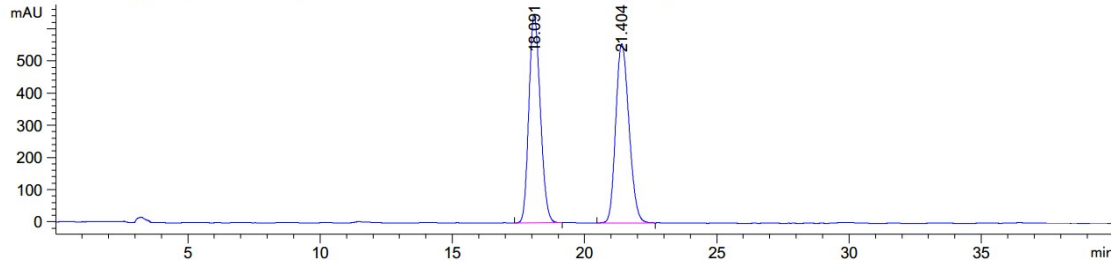

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.091	BB	0.4714	1.93743e4	646.92914	49.9432
2	21.404	BB	0.5448	1.94184e4	556.91858	50.0568

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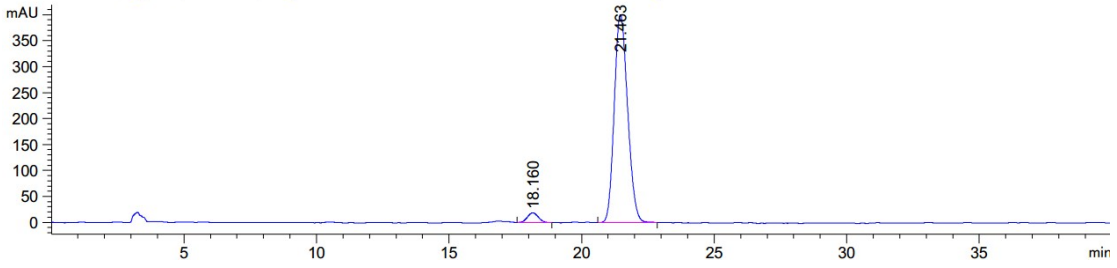
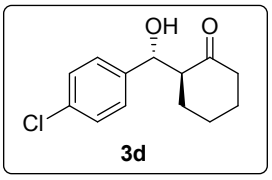


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.160	BB	0.4564	534.50317	18.64526	3.6660
2	21.463	BB	0.5476	1.40456e4	400.10629	96.3340



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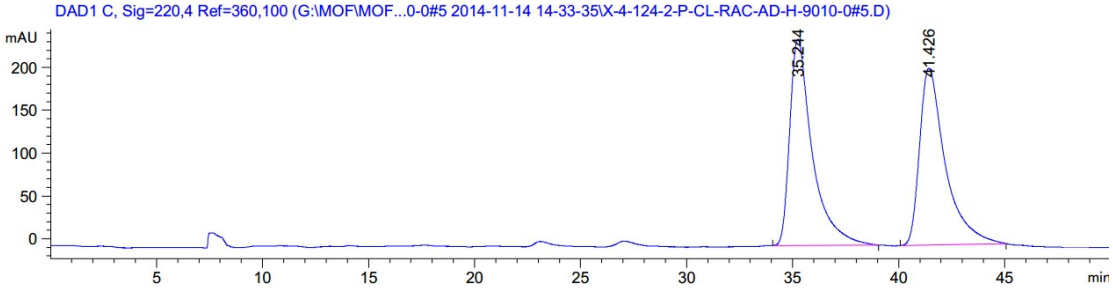
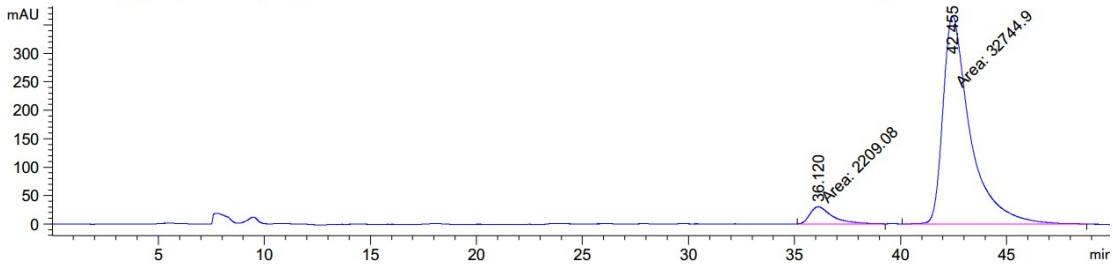
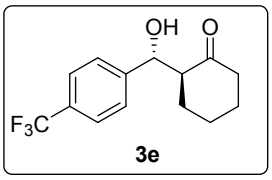


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.244	BB	1.0057	1.77906e4	240.32182	50.5851
2	41.426	BBA	1.1428	1.73790e4	206.31407	49.4149



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.120	MM	1.2260	2209.07715	30.03199	6.3200
2	42.455	MM	1.4936	3.27449e4	365.38028	93.6800



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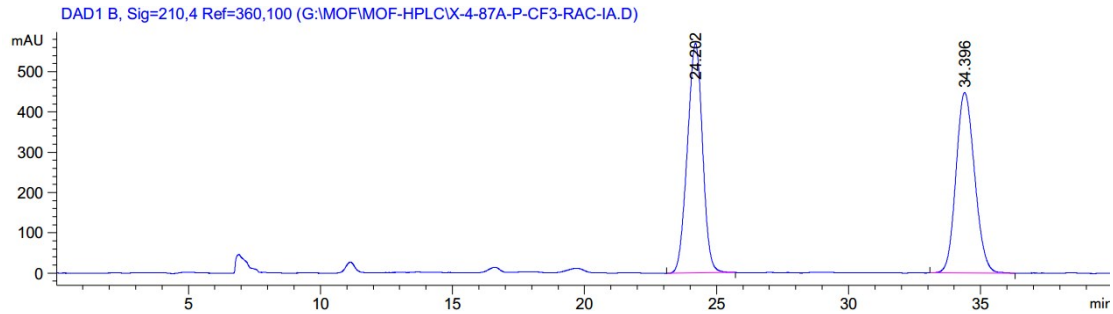
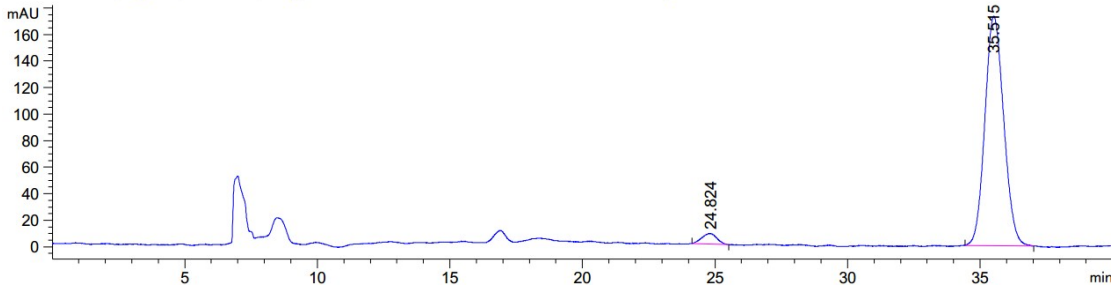
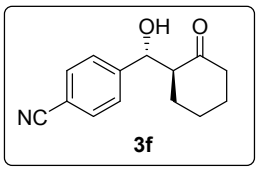


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.202	BB	0.5888	2.28066e4	570.01898	50.8714
2	34.396	BB	0.7317	2.20253e4	447.93890	49.1286

DAD1 B, Sig=210,4 Ref=360,100 (G:\MOF\MOF-HPLC\X-4-63A-P-CF3-IA-9010-0#5.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.824	BB	0.4722	316.27182	8.01716	3.5714
2	35.515	BV	0.7126	8539.35156	172.78127	96.4286



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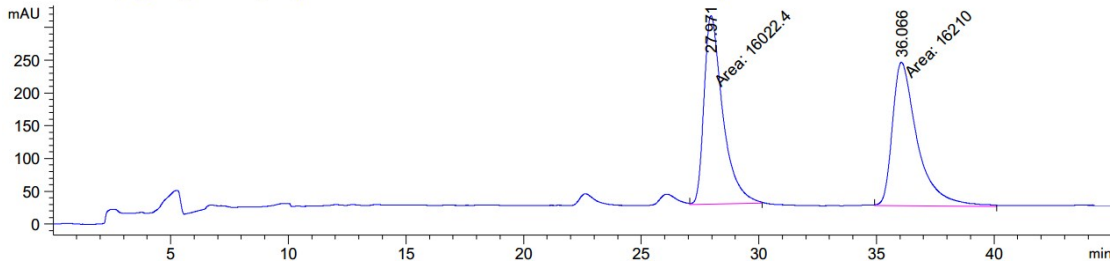
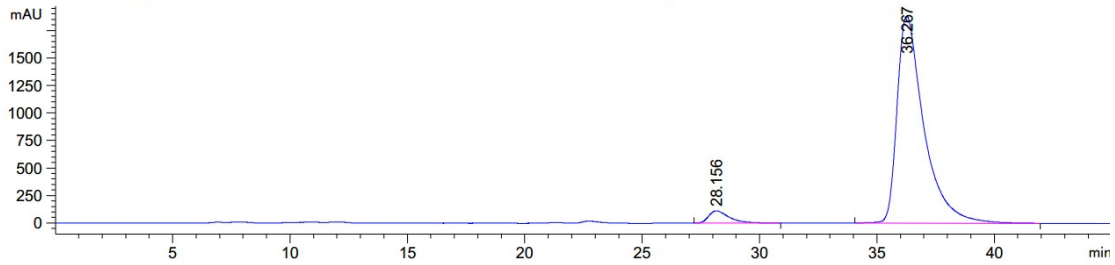
DAD1 D, Sig=230,4 Ref=360,100 (G:\MOF\MOF-HPLC\X-4-87B-P-CN-RAC-AD-H-8020-0#5.D)

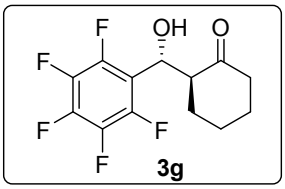


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.971	MM	0.9275	1.60224e4	287.92316	49.7090
2	36.066	MM	1.2332	1.62100e4	219.08382	50.2910

DAD1 D, Sig=230,4 Ref=360,100 (G:\MOF\MOF-HPLC\X-4-54-P-CN-AD-H-8020-0#5.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.156	BB	0.8321	6838.21240	111.72600	4.3775
2	36.267	BB	1.0847	1.49374e5	1880.57764	95.6225



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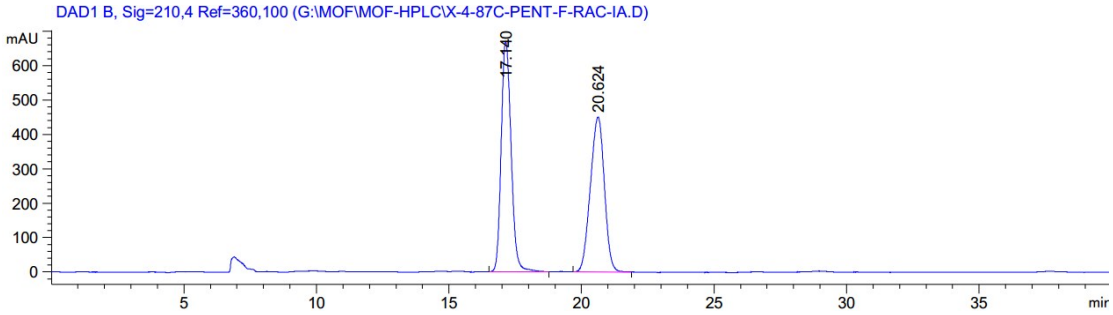
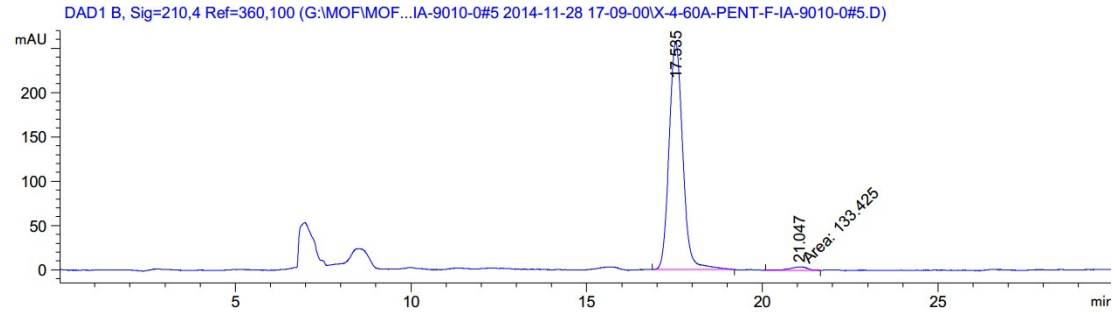


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.140	BB	0.4028	1.73714e4	669.20447	51.2589
2	20.624	BV	0.5635	1.65181e4	450.80334	48.7411



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.535	BB	0.4130	6939.87891	257.01123	98.1137
2	21.047	MM	0.5796	133.42545	3.83676	1.8863