# Supporting Information

## Asymmetric Copper–Catalyzed Propargylic Amination with Amine Hydrochloride Salts

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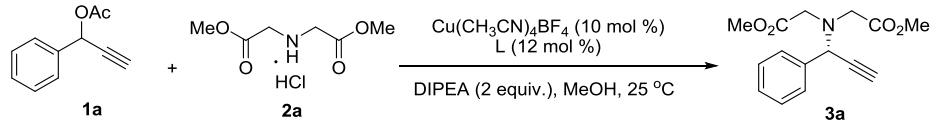
# Contents

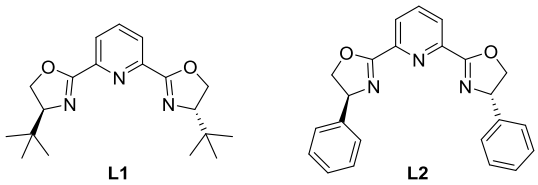
# 1. General Information

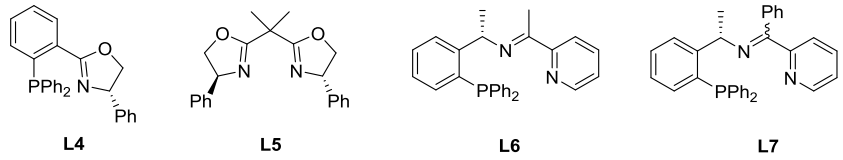
All reactions were carried out under a nitrogen atmosphere. Solvents were purified by standard procedure before use. Commercial reagents were used without further purification. Flash column chromatography was performed using 300-400 mesh silica gel. Thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 with F254 indicator. Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded on a Bruker 400 MHz or Varian 600 MHz spectrometer. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard ($CDCl_3$: δ = 7.26 ppm for $^1$H, TMS: δ = 0 ppm for $^1$H, δ = 77.16 ppm for $^{13}$C). $^{13}$C NMR spectra were recorded on 100 MHz or 150 MHz with complete proton decoupling spectrophotometers. Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (*J*) are given in Hertz (Hz). Enantiomeric ratios were determined by chiral HPLC with chiral AD-H, OD-H, OJ-H, IA, IBN-5, IC columns with hexane and $^i$PrOH as solvents.

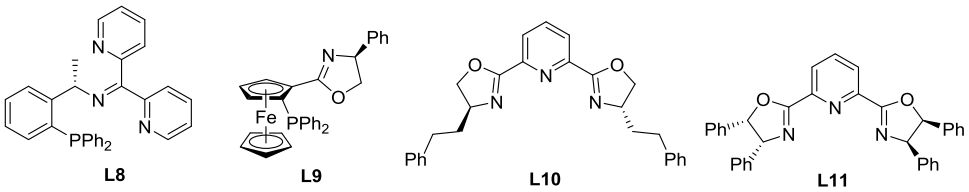
## 2. Optimization Studies

**Table S1.** The Effect of the Ligands on the Reaction.



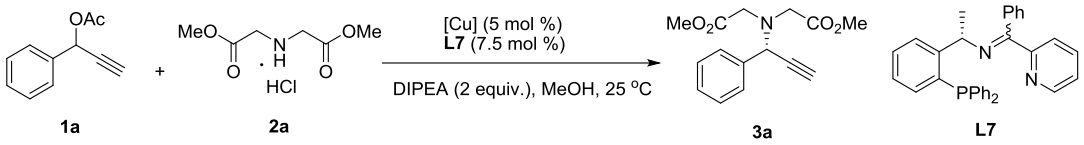




| Entry[a] | L | t / h | yield /%[b] | ee /%[c] |
|---|---|---|---|---|
| 1 | **L1** | 14 | 54 | 5 |
| 2 | **L2** | 3 | 91 | 23 |
| 3 | **L3** | 4 | 77 | 73 |
| 4 | **L4** | 48 | 9 | 3 |
| 5 | **L5** | 6 | 32 | 10 |
| 6 | **L6** | 8 | 50 | 75 |
| 7 | **L7** | 7 | 74 | 80 |
| 8 | **L8** | 7 | 72 | 63 |
| 9 | **L9** | 8 | 24 | 0 |
| 10 | **L10** | 10 | 73 | 15 |
| 11 | **L11** | 10 | 81 | 12 |
| 12[d] | **L7** | 3 | 75 | 87 |

| | | | | |
|---|---|---|---|---|
| 13[e] | **L7** | 3 | 71 | 80 |
| 14[e] | **L6** | 4 | 44 | 75 |
| 15[e] | **L8** | 3 | 71 | 63 |

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), $Cu(CH_3CN)_4BF_4$ (10 mol %), **L** (12 mol %), MeOH (2 mL), DIPEA (2 equiv.), 25 ℃. [b] Yield of the isolated product after column chromatography. [c] The ee value was determined by HPLC analysis on a chiral stationary phase. [d] 15 mol % of ligand was used. [e] $Cu(CH_3CN)_4BF_4$ (5 mol %), **L** (7.5 mol %), MeOH (2 mL), DIPEA (2 equiv.), 25 ℃.

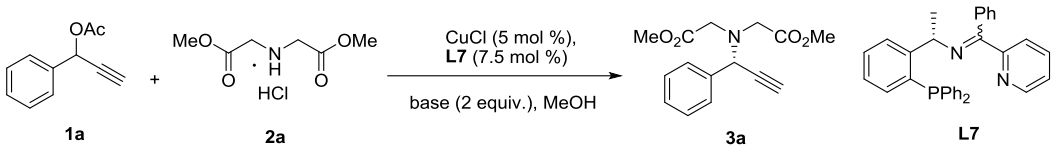
**Table S2.** The Effect of the Copper Salts on the Reaction.




| Entry[a] | [Cu] | t / h | yield /%[b] | ee /%[c] |
|---|---|---|---|---|
| 1 | $Cu(CH_3CN)_4BF_4$ | 3 | 71 | 80 |
| 2 | $Cu(CH_3CN)_4PF_6$ | 5 | 58 | 85 |
| 3 | $Cu(OTf)_2$ | 4 | 58 | 78 |
| 4 | CuCl | 4 | 76 | 84 |
| 5 | CuI | 7 | 64 | 82 |
| 6 | CuOAc | 5 | 58 | 68 |
| 7 | $Cu(OAc)_2 \cdot H_2O$ | 5 | 64 | 83 |
| 8 | $Cu(ClO_4)_2 \cdot 6H_2O$ | 7 | 75 | 79 |

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), [Cu] (5 mol %), **L7** (7.5 mol %), MeOH (2 mL), DIPEA (2 equiv.), 25 ℃. [b] Yield of the isolated product after column chromatography. [c] The ee value was determined by HPLC analysis on a chiral stationary phase.

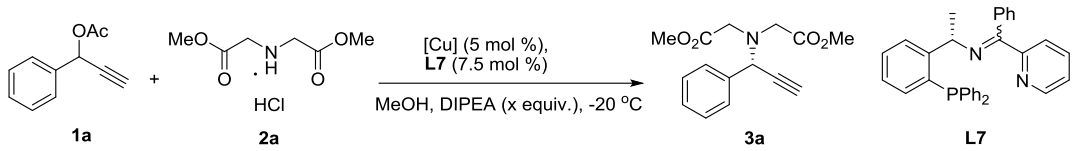
**Table S3.** The Effect of the Base and Temperature on the Reaction.




| Entry[a] | base | T/°C | t / h | yield /%[b] | ee /%[c] |
|---|---|---|---|---|---|
| 1 | $Et_3N$ | 25 | 4 | 49 | 83 |
| 2 | $^t$BuOK | 25 | 4 | 12 | 22 |
| 3 | $Cs_2CO_3$ | 25 | 4 | 48 | 73 |
| 4 | DIPEA | 0 | 12 | 58 | 91 |
| 5 | DIPEA | -20 | 24 | 71 | 95 |
| 6 | DIPEA | -40 | 76 | 62 | 97 |

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), CuCl (5 mol %), **L7** (7.5 mol %), MeOH (2 mL), DIPEA (2 equiv.) [b] Yield of the isolated product after column chromatography. [c] The ee value was determined by HPLC analysis on a chiral stationary phase.

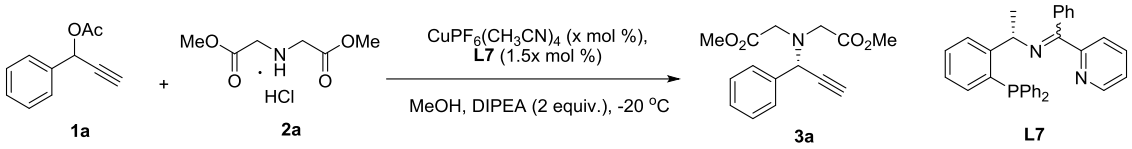
**Table S4.** The Effect of the Ratio of **1a** and **2a** on the Reaction.




| Entry[a] | [Cu] | **1a**:**2a** | base (x equiv.) | t / h | yield /%[b] | ee /%[c] |
|---|---|---|---|---|---|---|
| 1 | CuCl | 1.5:1 | 2 | 24 | 85 | 96 |
| 2 | CuCl | 1:1 | 2 | 24 | 71 | 95 |
| 3 | CuCl | 1:1.5 | 3 | 24 | 75 | 95 |
| 4 | $Cu(CH_3CN)_4PF_6$ | 1.5:1 | 2 | 24 | 97 | 95 |

[a] Reaction conditions: 0.2 mmol scale, [Cu] (5 mol %), **L7** (7.5 mol %), MeOH (2.0 mL). -20 ℃. [b] Yield of the isolated product after column chromatography. [c] The ee value was determined by HPLC analysis on a chiral stationary phase.

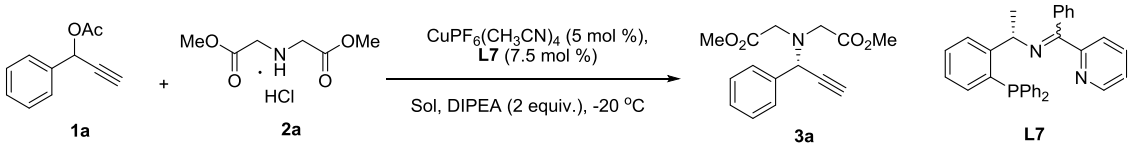
**Table S5.** The Effect of the Catalyst Loading on the Reaction.




| Entry[a] | x | t / h | yield /%[b] | ee /%[c] |
|---|---|---|---|---|
| 1 | 5 | 24 | 97 | 95 |
| 2[d] | 2.5 | 70 | 82 | 96 |

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), MeOH (2.0 mL), -20 ℃. [b] Yield of the isolated product after column chromatography. [c] The ee value was determined by HPLC analysis on a chiral stationary phase. [d] **1a** (0.6 mmol), **2a** (0.4 mmol), MeOH (4.0 mL).

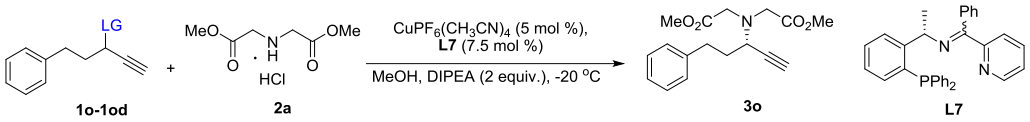
**Table S6.** The Effect of Solvents on the Reaction.

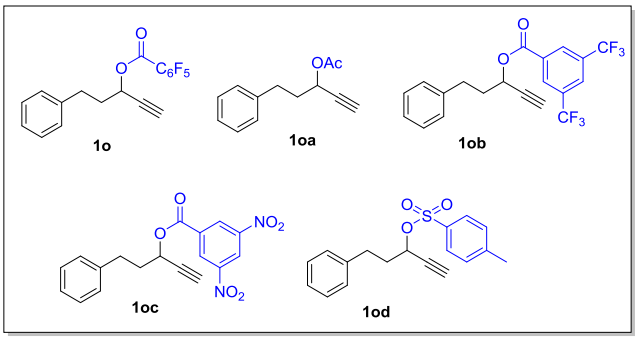



| Entry[a] | Sol. | t / h | yield /%[b] | ee /%[c] |
|---|---|---|---|---|
| 1 | MeOH | 24 | 97 | 95 |
| 2 | EtOH | 48 | 21 | 90 |
| 3 | THF | 48 | NR | - |
| 4 | Toluene | 48 | NR | - |
| 5 | DCM | 48 | NR | - |
| 6 | $CH_3CN$ | 48 | NR | - |
| 7 | $Et_2O$ | 48 | NR | - |
| 8 | $^{i}$PrOH | 48 | NR | - |
| 9 | DCE | 48 | NR | - |

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), Solvents (2.0 mL), -20 ℃. [b] Yield of the isolated product after column chromatography. [c] The ee value was determined by HPLC analysis on a chiral stationary phase.

**Table S7.** The Effect of Leaving Groups of Aliphatic Propargylic Esters on the Reaction.

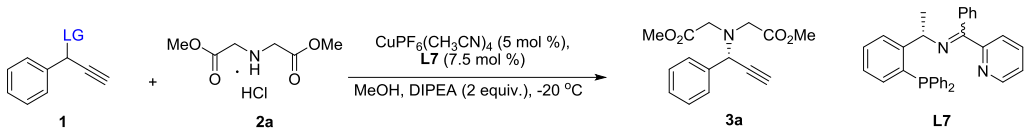



| Entry[a] | **1** | t / h | yield /%[b] | ee /%[c] |
|---|---|---|---|---|
| 1 | **1o** | 48 | 89 | 88 |
| 2 | **1oa** | 48 | trace | - |
| 3 | **1ob** | 48 | 41 | 88 |
| 4 | **1oc** | 48 | 11 | 87 |
| 5 | **1od** | 48 | 47 | 2 |

[a] Reaction conditions: **1o-1od** (0.3 mmol), **2a** (0.2 mmol), MeOH(2.0 mL), -20 ℃. [b] Yield of the isolated product after column chromatography. [c] The ee value was determined by HPLC analysis on a chiral stationary phase.

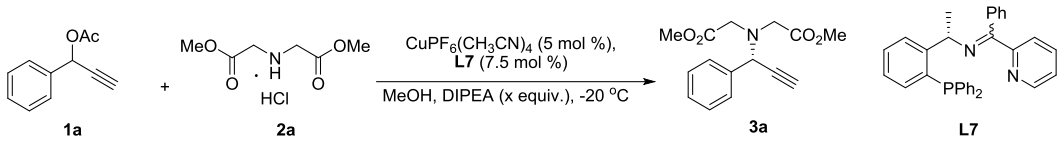
**Table S8.** The Effect of Leaving Groups of Aryl Propargylic Esters on the Reaction.




| Entry[a] | LG | t / h | yield /%[b] | ee /%[c] |
|---|---|---|---|---|
| 1 | OAc | 24 | 97 | 95 |
| 2 | OBoc | 48 | 98 | 89 |
| 3 | OBz | 48 | 60 | 95 |
| 4 | OPiv | 48 | 44 | 97 |

[a] Reaction conditions: **1** (0.3 mmol), **2a** (0.2 mmol), MeOH(2.0 mL), -20 ℃. [b] Yield of the isolated product after column chromatography. [c] The ee value was determined by HPLC analysis on a chiral stationary phase.

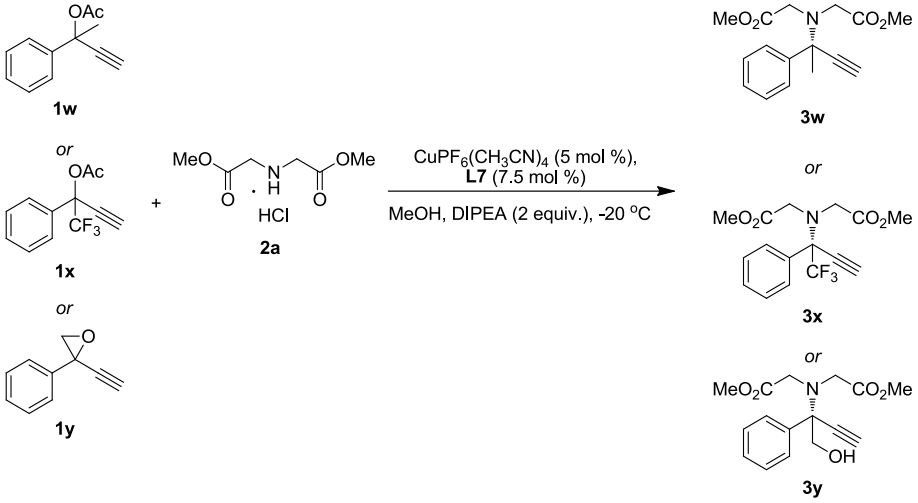
**Table S9.** The Effect of Equivalence of Base on the Reaction.




| Entry[a] | X | t / h | yield /%[b] | ee /%[c] |
|---|---|---|---|---|
| 1 | 0.5 | 48 | NR | - |
| 2 | 1 | 48 | trace | - |
| 3 | 1.2 | 48 | 27 | 97 |
| 4 | 1.5 | 48 | 46 | 96 |
| 5 | 2 | 48 | 96 | 95 |
| 6 | 4 | 48 | 97 | 93 |

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), MeOH(2.0 mL), -20 ℃. [b] Yield of the isolated product after column chromatography. [c] The ee value was determined by HPLC analysis on a chiral stationary phase.

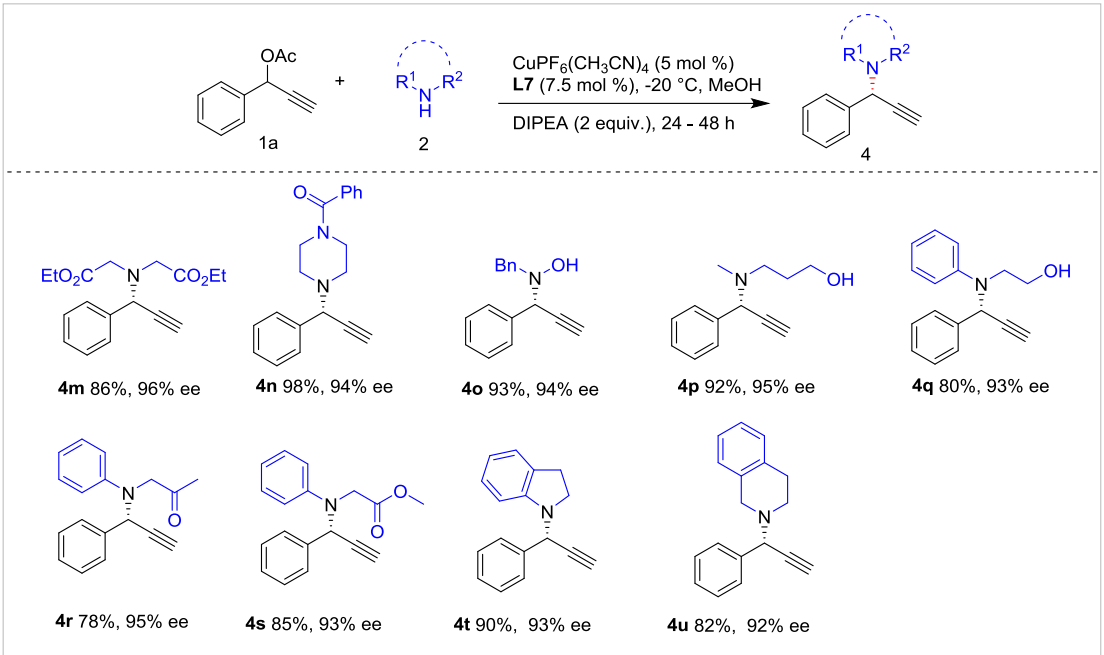
**Table S10.** The Efforts to Constructed Chiral Quaternary Center.




| Entry[a] | **1** | t / h | yield /%[b] | ee /%[c] |
|---|---|---|---|---|
| 1 | **1w** | 48 | 71 | 3 |
| 2 | **1x** | 48 | NR | - |
| 3 | **1y** | 48 | NR | - |

[a] Reaction conditions: **1** (0.3 mmol), **2a** (0.2 mmol), MeOH (2.0 mL), -20 ℃. [b] Yield of the isolated product after column chromatography. [c] The ee value was determined by HPLC analysis on a chiral stationary phase.

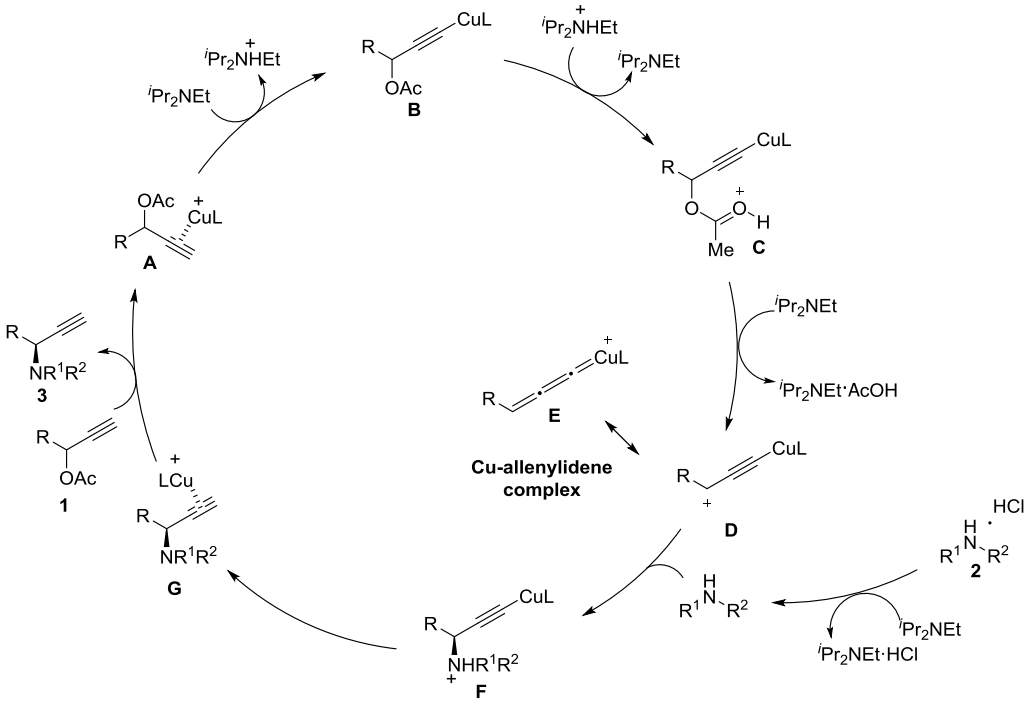
**Table S11.** Scope of free Amines. [a]




[a] Reaction conditions: **1a** (0.3 mmol), **2** (0.2 mmol), MeOH (0.1 M), DIPEA (2 equiv.), $CuPF_6(CH_3CN)_4$ (5 mol %), **L7** (7.5 mol %), -20 ℃.

## 3. Proposed mechanism and model for enantioinduction

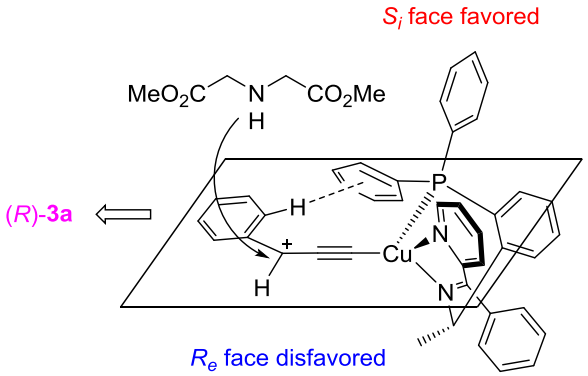
According to previous mechanistic studies on related propargylic substitution reactions and our experimental observations, a plausible mechanism is proposed as shown in Scheme S1. In the first step, the copper complex forms π-complex **A** with substrate **1**. Deprotonation with DIPEA gives the copper acetylide **B**. This intermediate loses the acetate group forms Cu–allenylidene complex **D**, where the intermediate **E** bearing a cationic γ-carbon exists as a resonance structure of **D**. Subsequently, amines are released from the AHS in the presence of DIPEA, the amine attacks the copper–allenylidene complex **D**, followed by a hydrogen atom shift, giving rise to a Cu-π-alkyne complex **G**. After the ligand exchange, the product is released, completing the catalytic cycle.




**Scheme S1** Proposed mechanism

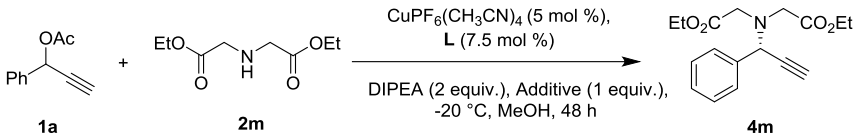
Based on the observed absolute stereochemistry of the major enantiomer, we proposed a preliminary model for the enantioinduction (Firgure S1). An edge-to-face aromatic interaction makes a phenyl group of the substrate close to a phenyl group of the ligand in the copper complex. Therefore, nucleophiles favorably attack *γ*-carbon

atoms from $S_i$ surface to form (*R*)-products, while $R_e$ surface is hindered by steric hindrance of ligands.




**Firgure S1.** Proposed model for enantioinduction

# 4. Control experiments

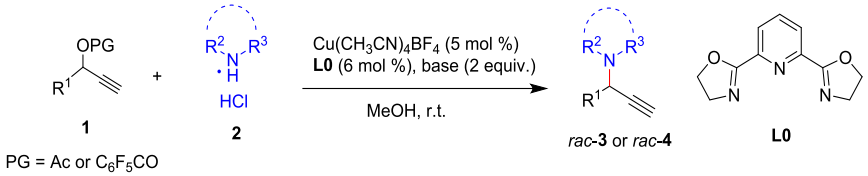



| Entry[a] | L | Additive | yield/%[b] | ee/%[c] |
|---|---|---|---|---|
| 1 | **L7** | none | 86 | 96 |
| 2 | **L7** | $Me_3N$•HCl | 78 | 96 |
| 3 | **L7** | NaCl | 79 | 95 |
| 4 | **L3** | none | 46 | 71 |
| 5[d] | **L3** | $Me_3N$•HCl | 23 | 36 |
| 6 | **L3** | NaCl | 20 | 60 |
| 7[e] | **L7** | none | 81 | 93 |

[a] Reaction conditions: **1a** (0.3 mmol), **2m** (0.2 mmol), $Cu(CH_3CN)_4PF_6$ (5 mol %), **L** (7.5 mol %), and additive (1 equiv.), MeOH (2 mL), DIPEA (2 equiv.), - 20 ℃. [b] Yield of the isolated product after column chromatography. [c] The ee value was determined by HPLC analysis on a chiral stationary phase. [d] t = 72 h. [e] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), $Cu(CH_3CN)_4PF_6$ (5 mol %), **L7** (5 mol %), MeOH (2 mL), DIPEA (2 equiv.), - 20 ℃.

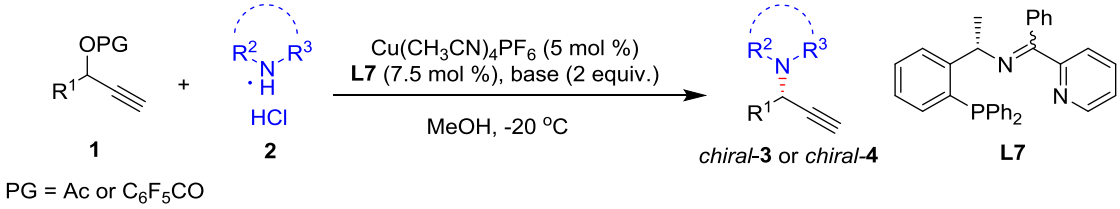
## 5. Experimental Procedures

### Procedure A: General procedure for the preparation of racemic products.




A solution of $Cu(CH_3CN)_4BF_4$ (5 mol %) and **L0** (6 mol %) in 1 mL of anhydrous methanol was placed in an over-dried schlenk flask then stirred at room temperature for 1 h under nitrogen atmosphere. Then a solution of propargylic ester **1** (0.2 mmol, 1 equiv.) and amine hydrochloride salts **2** (0.2 mmol, 1 equiv.) in 1 mL of anhydrous methanol was added, then $^{i}Pr_2NEt$ (2 equiv.) was added at room temperature. After the reaction was finished according to TLC, the solvent was removed under reduced pressure and the obtained residue was purified by silica gel chromatography using petroleum ether (40 - 60 ℃)/ethyl acetate as eluent, affording the substitution products *rac*-**3** or *rac*-**4**.

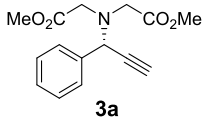
### Procedure B: General procedure for the preparation of enantioenriched products.




In a schlenk tube, $Cu(CH_3CN)_4PF_6$ (5 mol %) and **L7** (7.5 mol %) were stirred at room temperature in anhydrous methanol (1 mL) under nitrogen atmosphere for 1 h. The solution of propargylic ester **1** (0.3 mmol, 1.5 equiv.) and amine hydrochloride salts **2** (0.2 mmol, 1 equiv.) in anhydrous methanol (1 mL) was added. $^{i}Pr_2NEt$ (2 equiv.) was added at -20 ℃. After the reaction was finished according to TLC, the solvent was removed under reduced pressure and the obtained residue was then purified by silica gel chromatography using petroleum ether (40 - 60 ℃)/ethyl acetate as eluent, affording the chiral substitution products **3** or **4.**

## 6. Product Characterization

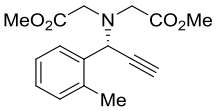
**(*R*)-dimethyl 2,2'-((1-phenylprop-2-yn-1-yl)azanediyl)diacetate**




**3a**

**3a**: 97% yield; white solid; According to procedure B; $^{1}$H NMR (600 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.37 – 7.30 (m, 3H), 5.07 (s, 1H), 3.68 (s, 6H), 3.52 (d, *J* = 17.2 Hz, 2H), 3.47 (d, *J* = 17.2 Hz, 2H), 2.57 (s, 1H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 171.35, 137.37, 128.49, 128.23, 79.29, 76.32, 57.90, 52.22, 51.77; HRMS: calcd. for $[M+H]^+$ $C_{15}H_{18}NO_4$ = 276.12303, found: 276.12302; $[\alpha]_D^{RT}$ = -21.10 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IA column, hexane/$^{i}$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 224 nm, major enantiomer: $t_R$ = 9.7 min, minor enantiomer: $t_R$ = 11.5 min; 95% ee.

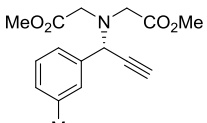
**(*R*)-dimethyl 2,2'-((1-(*o*-tolyl)prop-2-yn-1-yl)azanediyl)diacetate**




**3b**

**3b**: 96% yield; white solid; According to procedure B; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.58 – 7.56 (m, 1H), 7.16 – 7.08 (m, 3H), 5.15 (d, *J* = 2.4 Hz, 1H), 3.57 (s, 6H), 3.45 (s, 4H), 2.47 (d, *J* = 2.4 Hz, 1H), 2.45 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 171.35, 138.37, 135.05, 131.05, 129.19, 128.44, 125.77, 79.85, 76.17, 56.23, 52.46, 51.63, 19.33; HRMS: calcd. for $[M+Na]^+$ $C_{16}H_{19}NO_4Na$ = 312.12063, found: 312.12175; $[\alpha]_D^{RT}$ = -26.30 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK AD-H column, hexane/$^{i}$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, major enantiomer: $t_R$ = 15.1 min, minor enantiomer: $t_R$ = 19.0 min; 94% ee.

**(*R*)-dimethyl 2,2'-((1-(*m*-tolyl)prop-2-yn-1-yl)azanediyl)diacetate**

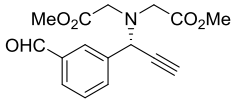



**3c**

**3c**: 94% yield; white solid; According to procedure B; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.38 (m, 2H), 7.19 – 7.14 (m, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 4.96 (s, 1H), 3.61

(s, 6H), 3.47 – 3.38 (m, 4H), 2.48 (d, *J* = 2.4 Hz, 1H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.38, 138.16, 137.27, 129.15, 129.02, 128.35, 125.64, 79.51, 76.20, 57.88, 52.21, 51.75, 21.53; HRMS: calcd. for $[M+Na]^+$ $C_{16}H_{19}NO_4Na$ = 312.12063, found: 312.12214; $[\alpha]_D^{RT}$ = -15.17 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IA column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, major enantiomer: $t_R$ = 10.9 min, minor enantiomer: $t_R$ = 12.4 min; 94% ee.

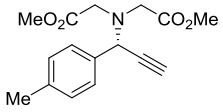
**(*R*)-dimethyl 2,2'-((1-(3-formylphenyl)prop-2-yn-1-yl)azanediyl)diacetate**




**3d**

**3d**: 86% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 8.13 (s, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 5.07 (s, 1H), 3.62 (s, 6H), 3.45 (d, *J* = 17.4 Hz, 2H), 3.37 (d, *J* = 17.4 Hz, 2H), 2.57 (d, *J* = 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.30, 171.16, 138.89, 136.65, 134.74, 130.08, 129.30, 129.25, 78.36, 77.18, 57.48, 52.28, 51.87; HRMS: calcd. for $[M+Na]^+$ $C_{16}H_{17}NO_5Na$ = 326.09989, found: 326.10061; $[\alpha]_D^{RT}$ = -0.50 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK AD-H column, hexane/$^i$PrOH = 90/10, flow rate = 1 mL min$^{-1}$, λ = 224 nm, major enantiomer: $t_R$ = 12.2 min, minor enantiomer: $t_R$ = 13.9 min; 97% ee.

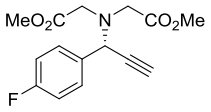
**(*R*)-dimethyl 2,2'-((1-(p-tolyl)prop-2-yn-1-yl)azanediyl)diacetate**




**3e**

**3e**: 90% yield; white solid; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 4.95 (d, *J* = 1.9 Hz, 1H), 3.60 (s, 6H), 3.44 (d, *J* = 17.2 Hz, 2H), 3.39 (d, *J* = 17.2 Hz, 2H), 2.47 (d, *J* = 2.4 Hz, 1H), 2.27 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.42, 137.97, 134.38, 129.17, 128.43, 79.55, 76.10, 57.65, 52.18, 51.77, 21.24; HRMS: calcd. for $[M+Na]^+$ $C_{16}H_{19}NO_4Na$ = 312.12063, found: 312.12184; $[\alpha]_D^{RT}$ = -15.20 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IA column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, major enantiomer: $t_R$ =12.2 min, minor enantiomer: $t_R$ = 17.7 min; 93% ee.

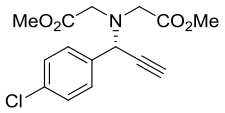
**(*R*)-dimethyl 2,2'-((1-(4-fluorophenyl)prop-2-yn-1-yl)azanediyl)diacetate**




**3f**

**3f**: 89% yield; white solid; According to procedure B; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 8.6, 5.6 Hz, 2H), 6.97 (t, *J* = 8.6 Hz, 2H), 4.95 (s, 1H), 3.61 (s, 6H), 3.42 (d, *J* = 17.2 Hz, 2H), 3.36 (d, *J* = 17.2 Hz, 2H), 2.51 (d, *J* = 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.30, 162.68 (d, *J* = 246.6 Hz), 133.22 (d, *J* = 3.1 Hz), 130.25 (d, *J* = 8.1 Hz), 115.31 (d, *J* = 21.5 Hz), 79.03, 76.53, 57.23, 52.18, 51.81; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -114.28; HRMS: calcd. for $[M+Na]^+$ $C_{15}H_{16}FNO_4Na$ = 316.09556, found: 316.09820; $[\alpha]_D^{RT}$ = -19.67 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IA column, hexane/$^{i}$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, major enantiomer: $t_R$ = 11.6 min, minor enantiomer: $t_R$ = 14.9 min; 95% ee.

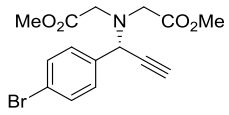
**(*R*)-dimethyl 2,2'-((1-(4-chlorophenyl)prop-2-yn-1-yl)azanediyl)diacetate**




**3g**

**3g**: 88% yield; white solid; According to procedure B; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.96 (d, *J* = 2.4 Hz, 1H), 3.61 (s, 6H), 3.41 (d, *J* = 17.2 Hz, 2H), 3.35 (d, *J* = 17.2 Hz, 2H), 2.51 (d, *J* = 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 171.22, 136.08, 134.07, 129.89, 128.62, 78.75, 76.69, 57.29, 52.19, 51.82; HRMS: calcd. for $[M+Na]^+$ $C_{15}H_{16}ClNO_4Na$ = 332.06601, found: 332.06742; $[\alpha]_D^{RT}$ = -10.13 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IA column, hexane/$^{i}$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 234 nm, major enantiomer: $t_R$ = 12.7 min, minor enantiomer: $t_R$ = 17.1 min; 95% ee.

**(*R*)-dimethyl 2,2'-((1-(4-bromophenyl)prop-2-yn-1-yl)azanediyl)diacetate**

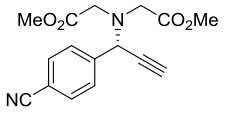



**3h**

**3h**: 87% yield; white solid; According to procedure B; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 4.94 (d, *J* = 2.4 Hz, 1H), 3.62 (s,

6H), 3.42 (d, *J* = 17.2 Hz, 2H), 3.35 (d, *J* = 17.2 Hz, 2H), 2.51 (d, *J* = 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.24, 136.63, 131.61, 130.25, 122.32, 78.68, 76.74, 57.36, 52.21, 51.86; HRMS: calcd. for $[M+Na]^+$ $C_{15}H_{16}{}^{79}BrNO_4Na$ = 376.01549, found: 376.01601; $[\alpha]_D^{RT}$ = -6.4 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IA column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, major enantiomer: $t_R$ = 13.3 min, minor enantiomer: $t_R$ = 17.8 min; 95% ee.

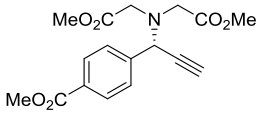
**(*R*)-dimethyl 2,2'-((1-(4-cyanophenyl)prop-2-yn-1-yl)azanediyl)diacetate**




**3i**

**3i**: 80% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 5.04 (d, *J* = 2.4 Hz, 1H), 3.62 (s, 6H), 3.42 (d, *J* = 17.2 Hz, 2H), 3.33 (d, *J* = 17.2 Hz, 2H), 2.57 (d, *J* = 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 171.01, 143.01, 132.31, 129.20, 118.77, 112.15, 77.86, 77.39, 57.53, 52.30, 51.90; HRMS: calcd. for $[M+Na]^+$ $C_{16}H_{16}N_2O_4Na$ = 323.10023, found: 323.09897; $[\alpha]_D^{RT}$ = -1.17 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IA column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, major enantiomer: $t_R$ = 13.9 min, minor enantiomer: $t_R$ = 17.9 min; 93% ee.

**(*R*)-dimethyl 2,2'-((1-(4-(methoxycarbonyl)phenyl)prop-2-yn-1-yl)azanediyl) diacetate**

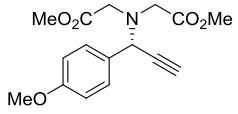



**3j**

**3j**: 88% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 5.04 (s, 1H), 3.84 (s, 3H), 3.61 (s, 6H), 3.43 (d, *J* = 17.2 Hz, 2H), 3.35 (d, *J* = 17.2 Hz, 2H), 2.55 (d, *J* = 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.16, 166.91, 142.57, 130.06, 129.76, 128.50, 78.50, 76.92, 57.63, 52.25, 52.23, 51.83; HRMS: calcd. for $[M+Na]^+$ $C_{17}H_{19}NO_6Na$ = 356.11046, found: 356.11028; $[\alpha]_D^{RT}$ = -0.27 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IA column, hexane/$^i$PrOH = 95/5, flow rate = 1 mL min$^{-1}$, λ = 214 nm,

major enantiomer: $t_R$ = 14.4 min, minor enantiomer: $t_R$ = 19.6 min; 95% ee.

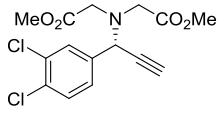
**(*R*)-dimethyl 2,2'-((1-(4-methoxyphenyl)prop-2-yn-1-yl)azanediyl)diacetate**




**3k**

**3k**: 94% yield; white solid; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.56 (m, 2H), 6.90 – 6.86 (m, 2H), 5.00 (d, *J* = 2.4 Hz, 1H), 3.80 (s, 3H), 3.68 (s, 6H), 3.53 – 3.43 (m, 4H), 2.55 (d, *J* = 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.42, 159.56, 129.73, 129.47, 113.80, 79.65, 76.03, 57.35, 55.35, 52.14, 51.73; $[\alpha]_D^{RT}$ = -8.57 (c = 1.0 in $CHCl_3$); HRMS: calcd. for $[M+K]^+$ $C_{16}H_{19}NO_5K$ = 344.08948, found: 344.08834; HPLC conditions: CHIRALPAK OD-H column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 224 nm, minor enantiomer: $t_R$ = 14.0 min, major enantiomer: $t_R$ = 23.1 min; 90% ee.

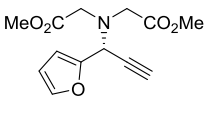
**(*R*)-dimethyl 2,2'-((1-(3,4-dichlorophenyl)prop-2-yn-1-yl)azanediyl)diacetate**




**3l**

**3l**: 89% yield; white solid; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 2.0 Hz, 1H), 7.51 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 4.95 (d, *J* = 2.4 Hz, 1H), 3.62 (s, 6H), 3.41 (d, *J* = 17.2 Hz, 2H), 3.34 (d, *J* = 17.2 Hz, 2H), 2.55 (d, *J* = 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.08, 137.94, 132.56, 132.31, 130.46, 130.38, 127.92, 78.09, 77.19, 56.92, 52.21, 51.90; HRMS: calcd. for $[M+H]^+$ $C_{15}H_{16}{}^{35}Cl_2NO_4$ = 344.04509, found: 344.04591; $[\alpha]_D^{RT}$ = -2.43 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IA column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 234 nm, major enantiomer: $t_R$ = 12.8 min, minor enantiomer: $t_R$ = 15.5 min; 96% ee.

**(*R*)-dimethyl 2,2'-((1-(furan-2-yl)prop-2-yn-1-yl)azanediyl)diacetate**

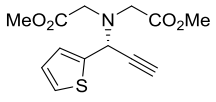



**3m**

**3m**: 91% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ

7.35 (s, 1H), 6.39 (d, *J* = 3.2 Hz, 1H), 6.26 (dd, *J* = 3.2, 2.0 Hz, 1H), 5.03 (d, *J* = 2.4 Hz, 1H), 3.61 (s, 6H), 3.50 (s, 4H), 2.43 (d, *J* = 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.00, 150.06, 143.32, 110.24, 110.07, 77.64, 74.87, 52.40, 52.24, 51.87; HRMS: calcd. for $[M+Na]^+$ $C_{13}H_{15}NO_5Na$ = 288.08424, found: 288.08426; $[\alpha]_D^{RT}$ = -11.6 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/$^i$PrOH = 90/10, flow rate = 1 mL min$^{-1}$, λ = 234 nm, minor enantiomer: $t_R$ = 10.6 min, major enantiomer: $t_R$ = 13.4 min; 90% ee.

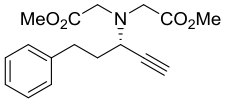
**(*R*)-dimethyl 2,2'-((1-(thiophen-2-yl)prop-2-yn-1-yl)azanediyl)diacetate**




**3n**

**3n**: 98% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 5.2 Hz, 1H), 7.14 (d, *J* = 3.4 Hz, 1H), 6.87 (dd, *J* = 5.2, 3.4 Hz, 1H), 5.16 (s, 1H), 3.63 (s, 6H), 3.46 (s, 4H), 2.48 (d, *J* = 2.3 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.12, 142.01, 127.00, 126.59, 126.43, 78.86, 75.36, 53.97, 52.07, 51.85; HRMS: calcd. for $[M+H]^+$ $C_{13}H_{16}NO_4S$ = 282.07946, found: 282.08280; $[\alpha]_D^{RT}$ = -30.60 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IA column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, major enantiomer: $t_R$ = 17.4 min, minor enantiomer: $t_R$ = 19.9 min; 91% ee.

**(*S*)-dimethyl 2,2'-((5-phenylpent-1-yn-3-yl)azanediyl)diacetate**

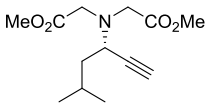



**3o**

**3o**: 89% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.22 – 7.18 (m, 2H), 7.14 – 7.09 (m, 3H), 3.62 (s, 6H), 3.55 – 3.51 (m, 1H), 3.48 (d, *J* = 17.0 Hz, 2H), 3.36 (d, *J* = 17.0 Hz, 2H), 2.80 – 2.66 (m, 2H), 2.28 (d, *J* = 2.2 Hz, 1H), 2.03 – 1.94 (m, 1H), 1.87 – 1.78 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.41, 141.27, 128.58, 128.44, 126.03, 81.05, 74.05, 54.70, 53.32, 51.84, 35.70, 32.34; $[\alpha]_D^{RT}$ = -15.23 (c = 1.0 in $CHCl_3$); HRMS: calcd. for $[M+H]^+$ $C_{17}H_{22}NO_4$ = 304.15433, found: 304.15534; HPLC conditions: CHIRALPAK AD-H column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, major enantiomer: $t_R$ =

25.5 min, minor enantiomer: $t_R$ = 30.8 min; 88% ee.

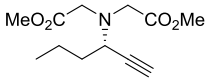
**(*S*)-dimethyl 2,2'-((5-methylhex-1-yn-3-yl)azanediyl)diacetate**



**3p**

**3p**: 78% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 3.72 – 3.68 (m, 7H), 3.54 (d, *J* = 17.0 Hz, 2H), 3.41 (d, *J* = 17.0 Hz, 2H), 2.29 (d, *J* = 2.2 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.61 – 1.47 (m, 2H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.47, 81.38, 73.52, 53.42, 53.27, 51.83, 42.86, 25.01, 22.96, 22.05; HRMS: calcd. for $[M+H]^+$ $C_{13}H_{22}NO_4$ = 256.15433, found: 256.15564; $[\alpha]_D^{RT}$ = -46.53 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, minor enantiomer: $t_R$ = 9.8 min, major enantiomer: $t_R$ = 11.3 min; 85% ee.

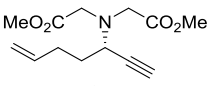
**(*S*)-dimethyl 2,2'-(hex-1-yn-3-ylazanediyl)diacetate**



**3q**

**3q**: 77% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 3.72 (s, 6H), 3.65 – 3.61 (m,1H), 3.54 (d, *J* = 17.0 Hz, 2H), 3.43 (d, *J* = 17.0 Hz, 2H), 2.28 (d, *J* = 2.2 Hz, 1H), 1.75 – 1.67 (m, 1H), 1.62 – 1.42 (m, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 171.60, 81.43, 73.59, 55.01, 53.32, 51.95, 36.11, 19.66, 13.84; HRMS: calcd. for $[M+H]^+$ $C_{12}H_{20}NO_4$ = 242.13870, found: 242.13990; $[\alpha]_D^{RT}$ = -41.87 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK OD-H column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 234 nm, minor enantiomer: $t_R$ = 14.0 min, major enantiomer: $t_R$ = 19.9 min; 92% ee.

**(*S*)-dimethyl 2,2'-(hept-6-en-1-yn-3-ylazanediyl)diacetate**

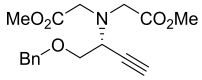


**3r**

**3r**: 91% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 5.87 – 5.76 (m, 1H), 5.06 (d, *J* = 17.2 Hz, 1H), 4.99 (d, *J* = 10.2 Hz, 1H), 3.72 (s, 6H), 3.66 – 3.62 (m, 1H), 3.55 (d, *J* = 17.2 Hz, 2H), 3.43 (d, *J* = 17.2 Hz, 2H), 2.32 (d, *J* =

2.2 Hz, 1H), 2.29 – 2.15 (m, 2H), 1.87 – 1.79 (m, 1H), 1.73 – 1.64 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.51, 137.56, 115.44, 81.10, 73.86, 54.63, 53.31, 51.87, 33.16, 30.32; HRMS: calcd. for $[M+K]^+$ $C_{13}H_{19}NO_4K$ = 292.09457, found: 292.09485; $[\alpha]_D^{RT}$ = -38.10 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK OD-H column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, minor enantiomer: $t_R$ = 14.3 min, major enantiomer: $t_R$ = 18.0 min; 92% ee.

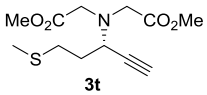
**(*R*)-dimethyl 2,2'-((1-(benzyloxy)but-3-yn-2-yl)azanediyl)diacetate**




**3s**

**3s**: 97% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.25 (m, 5H), 4.56 (s, 2H), 3.98 (td, *J* = 5.8, 2.4 Hz, 1H), 3.73 – 3.64 (m, 10H), 3.55 (d, *J* = 17.4 Hz, 2H), 2.37 (d, *J* = 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.51, 137.89, 128.38, 127.67, 127.66, 79.45, 74.48, 73.21, 71.83, 54.74, 53.80, 51.74; HRMS: calcd. for $[M+Na]^+$ $C_{17}H_{21}NO_5Na$ = 342.13119, found: 342.13099; $[\alpha]_D^{RT}$ = -19.43 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK AD-H column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, major enantiomer: $t_R$ = 56.8 min, minor enantiomer: $t_R$ = 62.5 min; 91% ee.

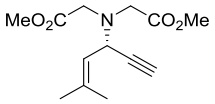
**(*S*)-dimethyl 2,2'-((5-(methylthio)pent-1-yn-3-yl)azanediyl)diacetate**




**3t**

**3t**: 84% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 3.84 (td, *J* = 7.4, 2.2 Hz, 1H), 3.72 (s, 6H), 3.55 (d, *J* = 17.2 Hz, 2H), 3.44 (d, *J* = 17.2 Hz, 2H), 2.76 – 2.60 (m, 2H), 2.34 (d, *J* = 2.2 Hz, 1H), 2.10 (s, 3H), 2.05 – 1.96 (m, 1H), 1.90 – 1.81 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.41, 80.78, 74.12, 53.95, 53.35, 51.87, 33.48, 30.60, 15.46; HRMS: calcd. for $[M+H]^+$ $C_{12}H_{20}NO_4S$ = 274.11076, found: 274.11093; $[\alpha]_D^{RT}$ = -34.07 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, minor enantiomer: $t_R$ = 23.4 min, major enantiomer: $t_R$ = 29.5 min; 87% ee.

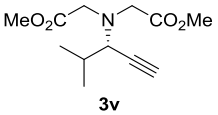
**(*S*)-dimethyl 2,2'-((5-methylhex-4-en-1-yn-3-yl)azanediyl)diacetate**



3u

**3u**: 93% yield; yellow oil; According to procedure B; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 5.22 (d, *J* = 8.8 Hz, 1H), 4.61 (dd, *J* = 8.8, 2.2 Hz, 1H), 3.71 (s, 6H), 3.63 (s, 4H), 2.35 (d, *J* = 2.2 Hz, 1H), 1.75 (s, 3H), 1.73 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.61, 138.48, 121.54, 81.77, 73.31, 52.17, 51.73, 51.59, 25.90, 18.34; HRMS: calcd. for $[M+Na]^+$ $C_{13}H_{19}NO_4Na$ = 276.12063, found: 276.12180; $[\alpha]_D^{RT}$ = 40.5 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IC column, hexane/$^{i}$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, minor enantiomer: $t_R$ = 43.1 min, major enantiomer: $t_R$ = 44.6 min; 81% ee.

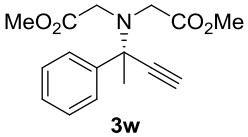
**(*S*)-dimethyl 2,2'-((4-methylpent-1-yn-3-yl)azanediyl)diacetate**



3v

**3v**: 95% yield; yellow oil; According to procedure B; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 3.71 (s, 6H), 3.51 (d, *J* = 17.2 Hz, 2H), 3.44 (d, *J* = 17.2 Hz, 2H),3.26 (dd, *J* = 9.0, 2.2 Hz,1H), 2.31 (d, *J* = 2.2 Hz, 1H), 1.83 – 1.74 (m, 1H), 1.05 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 171.61, 80.74, 74.05, 61.68, 53.24, 51.69, 31.44, 19.64, 19.59; HRMS: calcd. for $[M+Na]^+$ $C_{12}H_{19}NO_4Na$ = 264.12063, found: 264.12251; $[\alpha]_D^{RT}$ = -69.60 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/$^{i}$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, minor enantiomer: $t_R$ = 11.3 min, major enantiomer: $t_R$ = 14.2 min, 97% ee.

**(*R*)-dimethyl 2,2'-((2-phenylbut-3-yn-2-yl)azanediyl)diacetate**

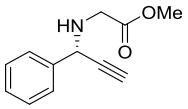


3w

**3w**: 71% yield; yellow oil; According to procedure B; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 7.4 Hz, 1H), 3 .68 (s, 6H), 3.61 (d, J = 17.2 Hz, 2H), 3.36 (d, J = 17.2 Hz, 2H), 2.63 (s, 1H), 1.64 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 172.06, 144.12, 128.53, 127.81, 126.55, 83.09, 75.04, 63.44, 52.86, 51.74, 31.20; HRMS: calcd. for $[M+H]^+$ $C_{16}H_{20}NO_4$ = 290.1387,

found:290.1382.

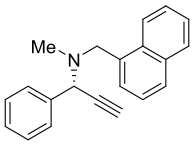
**(*R*)-methyl-(1-phenylprop-2-yn-1-yl)glycinate**




**4a**

**4a**: 86% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.54 (m, 2H), 7.39 – 7.29 (m, 3H), 4.72 (d, *J* = 2.2 Hz, 1H), 3.73 (s, 3H), 3.62 – 3.46 (m, 2H), 2.51 (d, *J* = 2.2 Hz, 1H); $[\alpha]_D^{RT}$ = -24.97 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK AD-H column, hexane/$^i$PrOH = 90/10, flow rate = 1 mL min$^{-1}$, λ = 224 nm, major enantiomer: $t_R$ = 7.6 min, minor enantiomer: $t_R$ = 8.7 min; 86% ee.

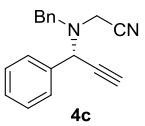
**(*R*)-*N*-methyl-*N*-(naphthalen-2-ylmethyl)-1-phenylprop-2-yn-1-amine**




**4b**

**4b:** 93% yield; yellow solid; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 7.8 Hz 1H), 7.77 – 7.74 (m, 1H), 7.69 (d, *J* = 8.2 Hz 1H ), 7.45 – 7.38 (m, 5H), 7.32 (t, *J* = 7.6 Hz 1H ), 7.23 – 7.14 (m, 3H), 4.64 (s, 1H), 4.08 (d, *J* = 12.8 Hz, 1H), 3.90 (d, *J* = 12.8 Hz, 1H), 2.57 (d, *J* = 2.2 Hz, 1H), 2.11 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 138.53, 134.51, 134.08, 132.75, 128.53, 128.43, 128.31, 128.18, 127.89, 127.64, 125.85, 125.77, 125.29, 125.09, 78.71, 76.55, 58.81, 57.57, 37.66; HRMS: calcd. for $[M+H]^+$ $C_{21}H_{20}N$ = 286.15903, found: 286.15898; $[\alpha]_D^{RT}$ = -287.80 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK AD-H column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 234 nm, major enantiomer: $t_R$ = 4.2 min, minor enantiomer: $t_R$ = 5.2 min; 90% ee.

**(*R*)-2-(benzyl(1-phenylprop-2-yn-1-yl)amino)acetonitrile**

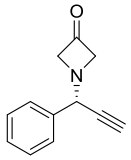



**4c**

**4c**: 98% yield; yellow solid; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.4 Hz, 2H), 7.40 – 7.26 (m, 8H), 4.78 (s, 1H), 3.96 (d, *J* = 13.2 Hz, 1H),

3.70 (d, *J* = 13.2 Hz, 1H), 3.47 – 3.32 (m, 2H), 2.69 (d, *J* = 2.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 137.00, 136.93, 129.14, 128.79, 128.77, 128.60, 128.32, 128.02, 116.12, 78.18, 77.74, 57.46, 55.46, 38.53; HRMS: calcd. for $[M+H]^+$ $C_{18}H_{17}N_2$ = 261.13862, found: 261.13866; $[\alpha]_D^{RT}$ = -34.50 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, major enantiomer: $t_R$ = 10.0 min, minor enantiomer: $t_R$ = 11.4 min; 92% ee.

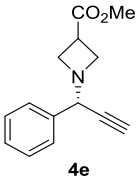
**(*R*)-1-(1-phenylprop-2-yn-1-yl)azetidin-3-one**



**4d**

**4d**: 75% yield; yellow solid; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.40 – 7.31 (m, 3H), 4.91 (d, *J* = 2.2 Hz, 1H), 4.27 – 4.10 (m, 4H), 2.59 (d, *J* = 2.2 Hz, 1H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 200.77, 137.66, 128.76, 128.40, 127.85, 78.29, 76.05, 71.39, 59.63; HRMS: calcd. for $[M+H]^+$ $C_{12}H_{12}NO$ = 186.09134, found: 186.09073; $[\alpha]_D^{RT}$ = -83.70 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, minor enantiomer: $t_R$ = 9.5 min, major enantiomer: $t_R$ = 10.3 min; 96% ee.

**(*R*)-methyl-1-(1-phenylprop-2-yn-1-yl)azetidine-3-carboxylate**

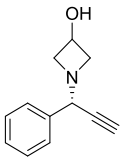


**4e**

**4e**: 80% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.0 Hz, 2H), 7.35 – 7.28 (m, 3H), 4.42 (d, *J* = 2.2 Hz, 1H), 3.70 (s, 3H), 3.54 (t, *J* = 7.4 Hz, 1H), 3.49 – 3.45 (m, 3H), 3.32 – 3.34 (m, 1H), 2.55 (d, *J* = 2.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 173.53, 137.38, 128.61, 128.14, 127.97, 80.09, 75.34, 60.56, 53.61, 53.02, 52.05, 33.46; HRMS: calcd. for $[M+Na]^+$ $C_{14}H_{15}NO_2Na$ = 252.09950, found: 252.09985; $[\alpha]_D^{RT}$ = -11.90 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 254

nm, minor enantiomer: $t_R$ = 10.8 min, major enantiomer: $t_R$ = 14.3 min; 99% ee.

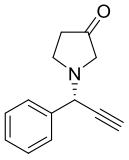
**(*R*)-1-(1-phenylprop-2-yn-1-yl)azetidin-3-ol**




**4f**

**4f**: 63% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.4 Hz, 2H), 7.35 – 7.26 (m, 3H), 4.45 (s, 1H), 4.40 – 4.35 (m, 1H), 3.55 (t, *J* = 7.2 Hz, 1H), 3.47 (t, *J* = 7.2 Hz, 1H), 3.17 – 3.12 (m, 2H), 3.01 – 2.90 (m, 1H), 2.56 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 137.51, 128.60, 128.16, 127.94, 80.16, 75.48, 62.37, 60.95, 60.41, 59.94; HRMS: calcd. for $[M+Na]^+$ $C_{12}H_{13}NONa$ = 210.08894, found: 210.08910; $[\alpha]_D^{RT}$ = -46.53 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/$^i$PrOH = 90/10, flow rate = 1 mL min$^{-1}$, λ = 224 nm, minor enantiomer: $t_R$ = 7.4 min, major enantiomer: $t_R$ = 8.3 min; 80% ee.

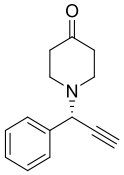
**(*R*)-1-(1-phenylprop-2-yn-1-yl)pyrrolidin-3-one**




**4g**

**4g**: 49% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.0 Hz, 2H), 7.39 – 7.30 (m, 3H), 4.85 (d, *J* = 2.2 Hz, 1H), 3.11 – 2.96 (m, 4H), 2.60 (d, *J* = 2.2 Hz, 1H), 2.49 – 2.35 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 213.82, 137.18, 128.58, 128.24, 128.10, 78.51, 76.88, 58.24, 57.47, 47.61, 37.98; HRMS: calcd. for $[M+H]^+$ $C_{13}H_{14}NO$ = 200.10699, found: 200.10624; $[\alpha]_D^{RT}$ = -1.50 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, major enantiomer: $t_R$ = 10.6 min, minor enantiomer: $t_R$ = 13.0 min; 92% ee.

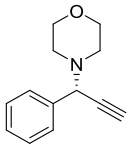
**(*R*)-1-(1-phenylprop-2-yn-1-yl)piperidin-4-one**




**4h**

**4h:** 96% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 4.81 (d, *J* = 2.2 Hz, 1H), 2.83 (t, *J* = 6.1 Hz, 4H), 2.58 (d, *J* = 2.2 Hz, 1H), 2.53 – 2.37 (m, 4H); $[\alpha]_D^{RT}$ = -27.90 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/$^i$PrOH = 99/1, flowrate = 1 mL min$^{-1}$, λ = 214 nm, major enantiomer: $t_R$ = 11.6 min, minor enantiomer: $t_R$ = 12.9 min; 91% ee.

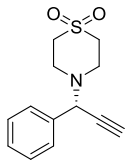
**(*R*)-4-(1-phenylprop-2-yn-1-yl)morpholine**



**4i**

**4i**: 96% yield; yellow oil; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 4.58 (d, *J* = 2.2 Hz, 1H), 3.71 (m, 4H), 2.57 – 2.53 (m, 5H); $[\alpha]_D^{RT}$ = -53.40 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IA column, hexane/$^i$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, major enantiomer: $t_R$ = 6.0 min, minor enantiomer: $t_R$ = 10.1min; 96% ee.

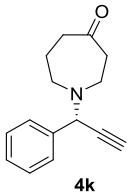
**(*R*)-4-(1-phenylprop-2-yn-1-yl)thiomorpholine 1,1-dioxide**



**4j**

**4j**: 78% yield; yellow solid; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.40 – 7.31 (m, 3H), 4.78 (s, 1H), 3.11 – 3.01 (m, 8H), 2.65 (d, *J* = 2.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 136.72, 128.64, 128.46, 128.13, 77.80, 77.34, 60.73, 52.09, 47.65; HRMS: calcd. for $[M+Na]^+$ $C_{13}H_{15}NO_2SNa$ = 272.07157, found: 272.07228; $[\alpha]_D^{RT}$ = -260.90 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK AD-H column, hexane/$^i$PrOH = 90/10, flow rate = 1 mL min$^{-1}$, λ = 214 nm, minor enantiomer: $t_R$ = 22.6 min, major enantiomer: $t_R$ = 24.3 min; 96% ee.

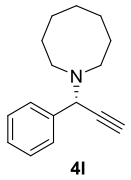
**(*R*)-1-(1-phenylprop-2-yn-1-yl)azepan-4-one**



4k

**4k**: 96% yield; yellow oil; According to procedure B; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.30 – 7.26 (m, 1H), 4.76 (s, 1H), 2.85 – 2.69 (m, 4H), 2.59 – 2.45 (m, 5H), 1.91 – 1.77 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 213.42, 138.07, 128.35, 128.08, 127.87, 79.32, 75.84, 62.37, 55.27, 47.70, 44.57, 42.85, 24.97; HRMS: calcd. for $[M+H]^+$ $C_{15}H_{18}NO$ = 228.13829, found: 228.13819; $[\alpha]_D^{RT}$ = -10.30 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK AD-H column, hexane/$^{i}$PrOH = 99/1, flow rate = 1 mL min$^{-1}$, λ = 214 nm, major enantiomer: $t_R$ = 15.8 min, minor enantiomer: $t_R$ = 17.5 min; 92% ee.

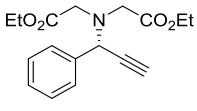
**(*R*)-1-(1-phenylprop-2-yn-1-yl)azocane**



4l

**4l**: 99% yield; yellow oil; According to procedure B; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.0 Hz, 2H), 7.38 – 7.24 (m, 3H), 4.70 (d, *J* = 2.2 Hz, 1H), 2.65 – 2.54 (m, 4H), 2.48 (d, *J* = 2.2 Hz, 1H), 1.69 – 1.62 (m, 2H), 1.59 – 1.49 (m, 6H), 1.44 – 1.35 (m, 2H); $[\alpha]_D^{RT}$ = -42.20 (c = 1.0 in CHCl3); HPLC conditions: CHIRALPAK OJ-H column, hexane/$^{i}$PrOH = 97/3, flow rate = 1 mL min$^{-1}$, λ = 250 nm, minor enantiomer: $t_R$ = 3.9 min, major enantiomer: $t_R$ = 4.7 min; 94% ee.

**(*R*)-diethyl 2,2'-((1-phenylprop-2-yn-1-yl)azanediyl)-diacetate**

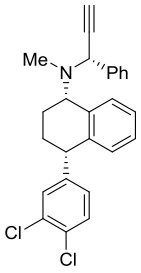



4m

**4m**: 86% yield; yellow oil; According to procedure B; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.0 Hz, 2H), 7.30 – 7.19 (m, 3H), 5.00 (d, *J* = 2.4 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 4H), 3.43 (d, *J* = 17.2 Hz, 2H), 3.38 (d, *J* = 17.2 Hz, 2H), 2.48 (d, *J* = 2.4 Hz, 1H), 1.17 (t, *J* = 7.2 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 170.97, 137.60, 128.55, 128.46, 128.18, 79.52, 76.21, 60.70, 57.92, 52.47, 14.28; HRMS: calcd. for $[M+Na]^+$

$C_{17}H_{21}NO_4Na$ = 326.13628, found: 326.13763; $[\alpha]_D^{RT}$ = -21.03 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IA column, hexane/$^i$PrOH = 99/1, flow rate = 0.7 mL $min^{-1}$, λ = 214 nm, major enantiomer: $t_R$ = 13.9 min, minor enantiomer: $t_R$ = 17.1 min; 96% ee.

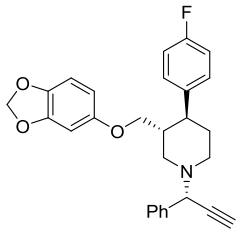
**(1*S*,4*S*)-4-(3,4-dichlorophenyl)-*N*-methyl-*N*-((*R*)-1-phenylprop-2-yn-1-yl)-1,2,3,4-tetrahydronaphthalen-1-amine**



**6**

**6:** 96% yield; dr > 20:1; white solid; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.41 – 7.31 (m, 4H), 7.26 – 7.19 (m, 3H), 6.97 – 6.93 (m,2H), 4.92 (s, 1H), 4.16 – 4.15 (m, 1H), 4.02 – 4.00 (m, 1H), 2.65 (s, 1H), 2.21 – 2.06 (m, 6H), 2.00 – 1.91 (m, 1H); $^{13}$C NMR (100 MHz, Acetone-d6): δ 149.66, 140.71, 139.55, 139.45, 132.36, 131.42, 131.29, 131.05, 130.07, 130.03, 129.66, 128.99, 128.63, 128.26, 128.18, 127.21, 82.02, 78.13, 62.54, 58.87, 44.61, 29.75, 31.54, 21.54; HRMS: calcd. for $[M+H]^+$ $C_{26}H_{24}Cl_2N$ = 420.12803, found: 420.12858; $[\alpha]_D^{RT}$ = +5.74 (c = 1.0 in $CHCl_3$).

**(3*R*,4*S*)-3-((benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)-1-((*R*)-1-phenylprop-2-yn-1-yl)piperidine**

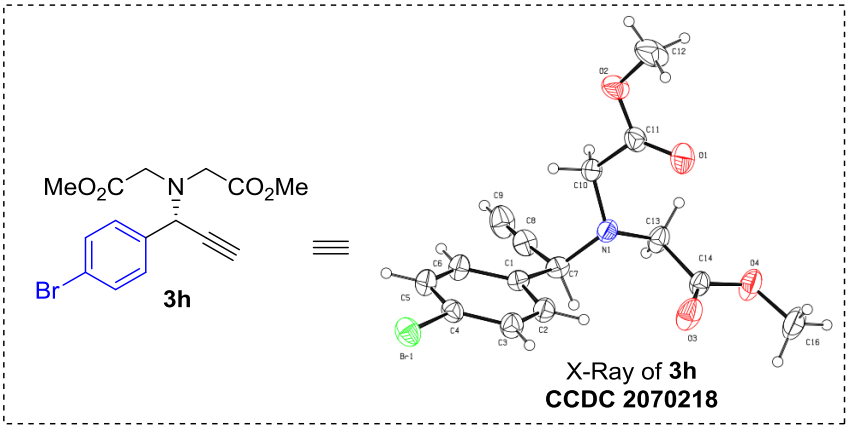


**10**

**10:** 97% yield; dr > 20:1; white solid; According to procedure B; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.2 Hz, 2H), 7.46 – 7.35 (m, 3H), 7.24 – 7.21 (m, 2H), 7.03 (t, *J* = 8.6 Hz, 2H), 6.70 (d, *J* = 8.6 Hz, 1H), 6.44 (d, *J* = 2.4 Hz, 1H), 6.21 (dd, *J* = 8.6, 2.4 Hz, 1H), 5.93 (s, 2H), 4.84 (s, 1H), 3.66 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.58 – 3.54 (m,

1H), 3.39 (d, *J* = 9.2 Hz, 1H), 2.72 – 2.61 (m, 3H), 2.54 – 2.30 (m, 3H), 1.81 – 1.76 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 162.76, 160.34, 154.45, 148.21, 141.59, 139.84 (d, *J* = 3.2 Hz), 137.84, 128.86 (d, *J* = 7.5 Hz), 128.41, 128.25, 127.77, 115.57, 115.36, 107.92, 105.56, 101.14, 98.04, 79.45, 76.13, 69.78, 61.32, 56.66, 46.96, 44.34, 42.52, 34.38; HRMS: calcd. for $[M+H]^+$ $C_{28}H_{27}FNO_3$ = 444.1969, found: 444.1975; $[\alpha]_D^{RT}$ = -243.40 (c = 1.0 in $CHCl_3$).

## 7. Crystal Data and Structure Refinement for 3h



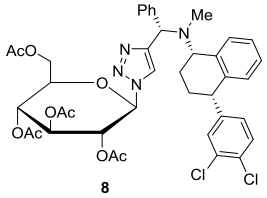

Crystal data and structure refinement for **3h**

| | | |
|---|---|---|
| Identification code | **3h** | |
| Empirical formula | C15 H16 Br N O4 | |
| Formula weight | 354.20 | |
| Temperature | 273.15 K | |
| Wavelength | 1.34139 Å | |
| Crystal system | Monoclinic | |
| Space group | P 1 21 1 | |
| Unit cell dimensions | a = 6.6884(10) Å | a= 90 °. |
| b = 13.820(2) Å | b= 92.210(2) °. | |
| c = 8.5300(13) Å | g = 90 °. | |
| Volume | 787.9(2) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.493 $Mg/m^3$ | |
| Absorption coefficient | 2.434 $mm^{-1}$ | |
| F(000) | 360 | |
| Crystal size | 0.2 x 0.1 x 0.1 $mm^3$ | |
| Theta range for data collection | 7.463 to 72.333 °. | |
| Index ranges | -9<=h<=9, -19<=k<=19, -12<=l<=12 | |
| Reflections collected | 11510 | |
| Independent reflections | 3566 [R(int) = 0.0621] | |
| Completeness to theta = 53.594 ° | 65.5 % | |

| | |
|---|---|
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.0000 and 0.4284 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3566 / 1 / 192 |
| Goodness-of-fit on $F^2$ | 1.202 |
| Final R indices [I>2sigma(I)] | R1 = 0.0638, wR2 = 0.1662 |
| R indices (all data) | R1 = 0.0639, wR2 = 0.1663 |
| Absolute structure parameter | 0.008(18) |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.840 and -0.888 e.$Å^{-3}$ |

## 8. Transformations of Products

**(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(4-((*R*)-(((1*S*,4*S*)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)(methyl)amino)(phenyl)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate**

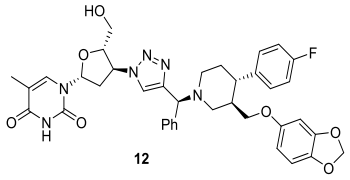



**8**

The product **6** (0.10 mmol, 1 equiv.) obtained from propargylation step was dissolved in DCM and $H_2O$ (v/v = 1:1, 3 mL), $Cu(OAc)_2$ (0.2 equiv.), sodium ascorbate (0.4 equiv.), 2,3,4,6-Tetra-*O*-acetyl-D-glucopyranosyl azide (1.5 equiv.) were added successively. The mixture was stirred at room temperature for 24 h. The product was then extracted with DCM (10 mL x 2). The combined organic layer was dried over $Na_2SO_4$. Solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel to afford pure compound.

**8:** 82% yield; dr > 20:1; white solid; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.9 Hz, 1H), 7.74 (s, 1H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.35 – 7.20 (m, 5H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 2.2 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.79 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.84 (d, *J* = 9.4 Hz, 1H), 5.47 (t, *J* = 9.4 Hz, 1H), 5.39 (t, *J* = 9.4 Hz, 1H), 5.25 (t, *J* = 9.6 Hz, 1H), 5.15 (s, 1H), 4.31 (dd, *J* = 12.6, 5.1 Hz, 1H), 4.14 (dd, *J* = 12.6, 2.1 Hz, 1H), 4.05 (t, *J* = 4.2 Hz, 1H), 4.01 – 3.95 (m, 2H), 2.09 – 1.91 (m, 15H), 1.66 – 1.56 (m, 2H), 1.28 – 1.26 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 170.64, 170.00, 169.49, 168.96, 151.36, 147.58, 141.51, 139.73, 138.15, 132.23, 130.83, 130.37, 130.07, 129.95, 128.83, 128.30, 128.05, 127.64, 127.23, 126.84, 120.24, 85.77, , 75.34, 72.78, 70.18, 67.91, 64.34, 61.70, 58.19, 43.50, 34.19, 30.07, 20.86, 20.68, 20.64, 20.06, 14.99; HRMS: calcd. for $[M+H]^+$ $C_{40}H_{43}Cl_2N_4O_9$ = 793.2402, found: 793.2398; $[\alpha]_D^{RT}$ = +11.93 (c = 1.0 in $CHCl_3$).

**1-((2*R*,4*S*,5*S*)-4-(4-((*S*)-((3*R*,4*S*)-3-((benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidin-1-yl)(phenyl)methyl)-1*H*-1,2,3-triazol-1-yl)-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione**

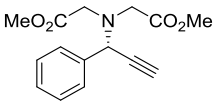



12

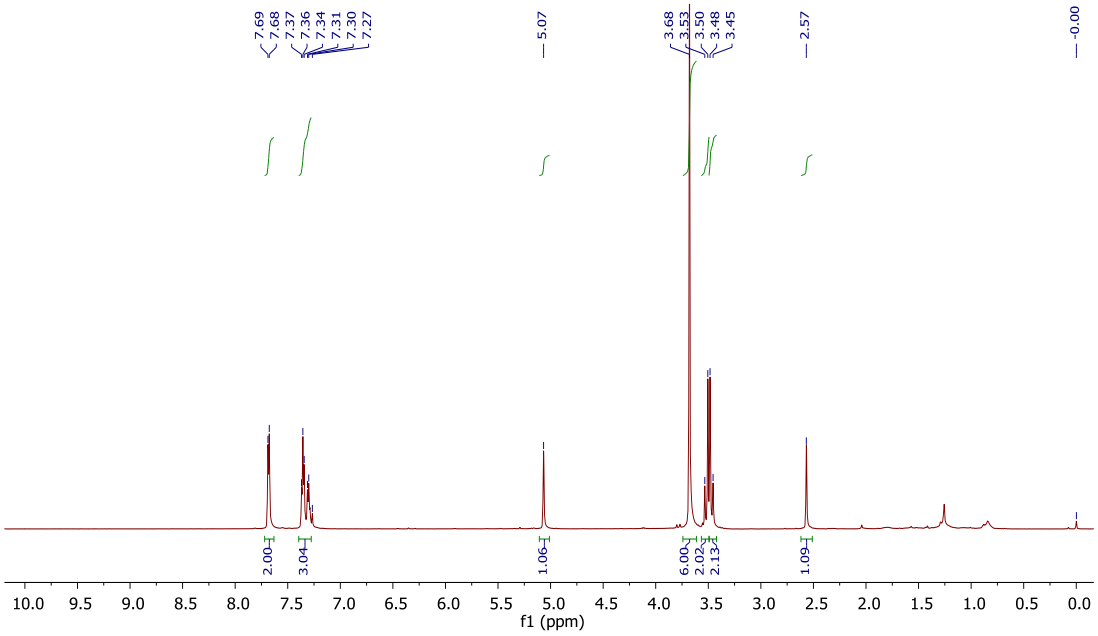
The product **10** (0.10 mmol, 1.0 equiv.) and copper(I) thiophene-2-carboxylate (CuTc) (0.2 equiv) in anhydrous toluene (1 mL) was cooled in an ice-water bath. Subsequently, 3′-Azido-3′-deoxythymidine (1.1 equiv.) was added slowly, and the reaction mixture allowed to warm to roomtemperature and stirred for 48 h. The reaction was quenched by addition of $H_2O$, the mixture was then extracted with EtOAc (10 mL x 3). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated under vacuum. The residue was purified by silica gel columnchromatography (petroleum ether (40 - 60 ℃)/ethyl acetate = 1:1) to afford the desired triazole **12** as a white solid.

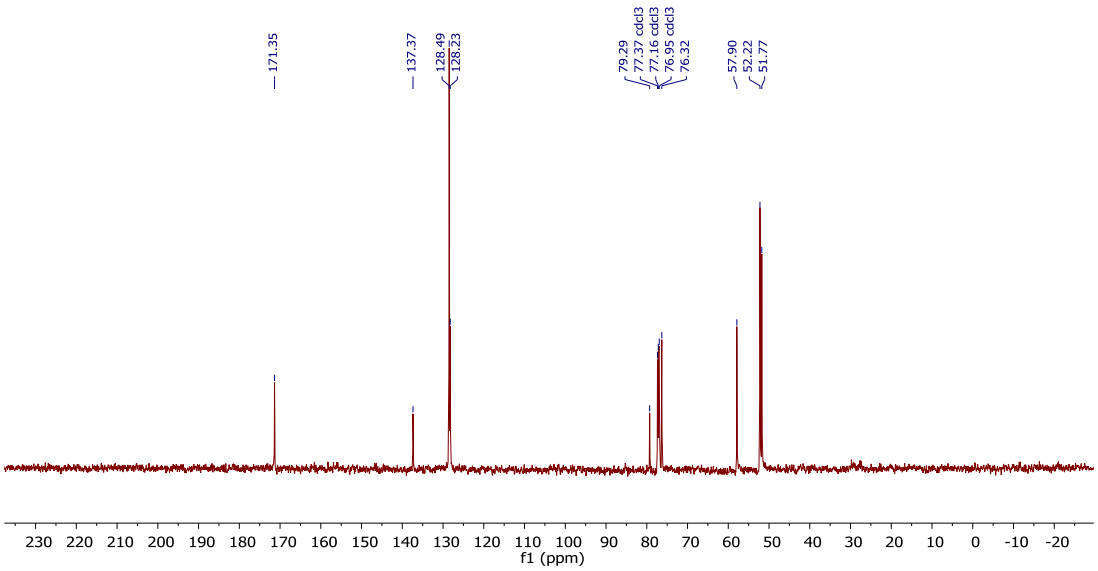
**12:** 76% yield; dr > 20:1; white solid; $^1$H NMR (400 MHz, DMSO-d6): δ 11.36 (s, 1H), 8.26 (s, 1H), 7.83 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.24 (m, 3H), 7.08 (t, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 8.6 Hz, 1H), 6.44 (t, *J* = 6.4 Hz, 1H), 6.30 (d, *J* = 2.4 Hz, 1H), 6.04 (dd, *J* = 8.6, 2.4 Hz, 1H), 5.90 (s, 2H), 5.39 – 5.34 (m, 1H), 4.86 (s, 1H), 4.25 – 4.21 (m, 1H), 3.72 – 3.61 (m, 2H), 3.39 – 3.37 (m, 2H), 3.14 (d, *J* = 10.0 Hz, 1H), 2.86 (d, *J* = 10.8 Hz, 1H), 2.79 – 2.61 (m, 2H), 2.47 – 2.40 (m, 1H), 2.20 – 2.11 (m, 1H), 2.05 – 1.9 (m, 2H), 1.81 (s, 3H), 1.75 – 1.66 (m, 2H), 1.22 (s, 1H); $^{13}$C NMR (100 MHz, DMSO): δ 163.79, 161.99, 159.58, 153.84, 150.50, 147.81, 147.27, 141.13, 140.56, 140.27, 136.30, 129.15 (d, *J* = 6.5 Hz), 128.31 (d, *J* = 4.8 Hz), 127.15, 123.02, 115.13 (d, *J* = 20.5 Hz), 109.67, 107.93, 105.66, 100.96, 97.75, 84.49, 83.91, 69.43, 66.18, 60.81, 59.23, 55.17, 50.65, 43.41, 41.65, 37.17, 34.08, 12.30; HRMS: calcd. for $[M+H]^+$ $C_{38}H_{40}FN_6O_7$ = 711.2937, found: 711.2922; $[\alpha]_D^{RT}$ = +24.97 (c = 1.0 in $CHCl_3$).

# 9. NMR Spectra and HPLC Data



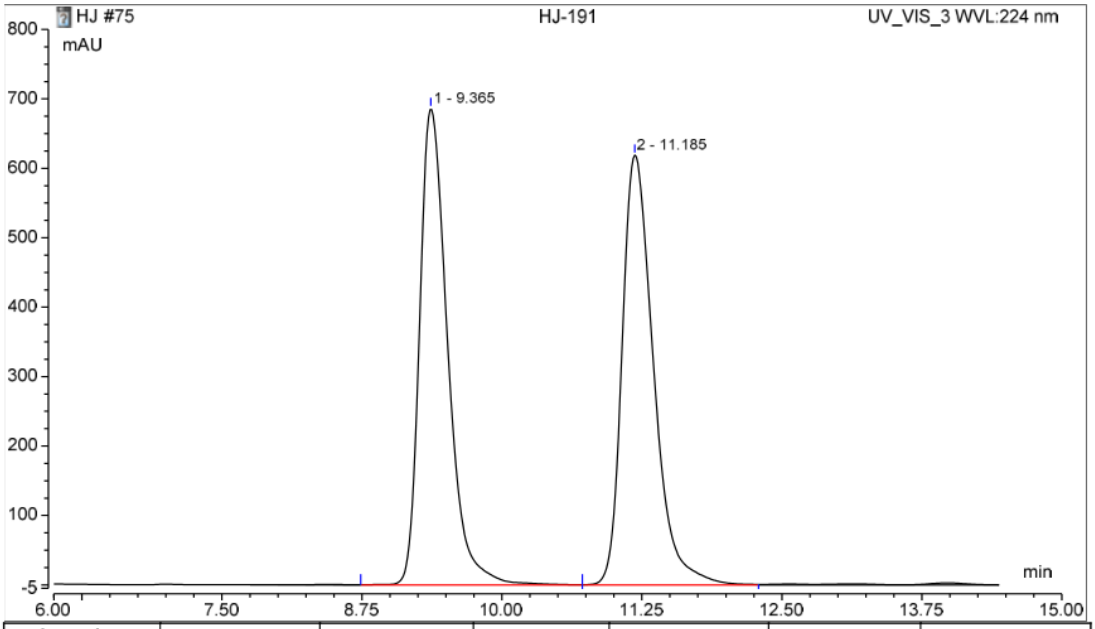

**3a**



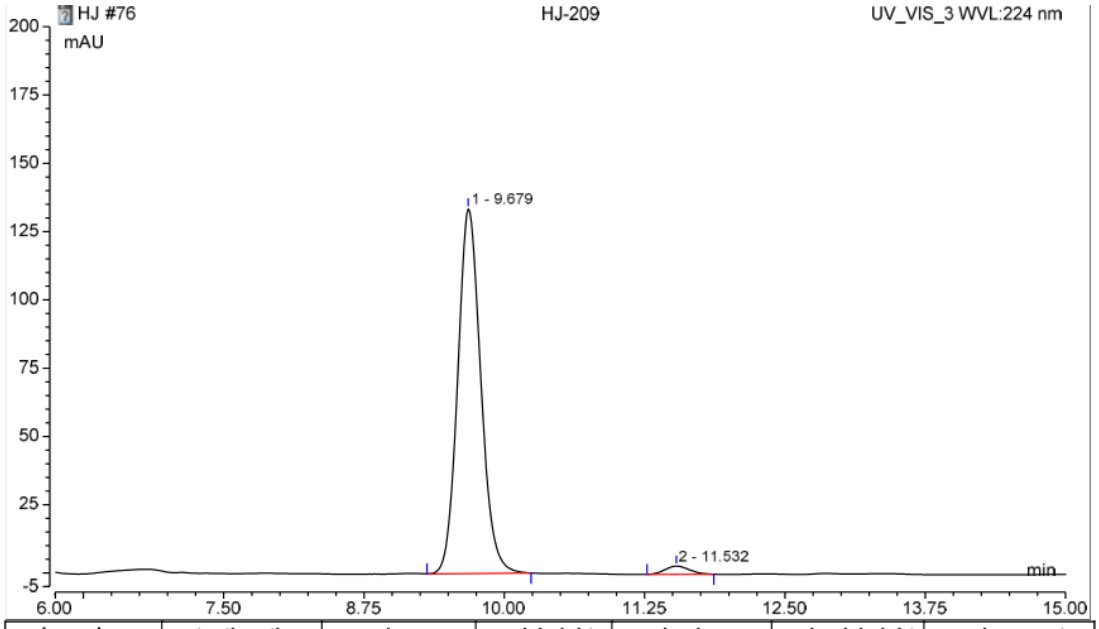
**Compound (-)-3a:** IA, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 224 nm

## HPLC trace of *rac*-3a

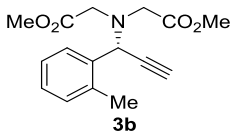



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 9.365 | 198.557 | 686.030 | 49.76 | 52.57 | n.a. |
| 2 | 11.185 | 200.453 | 619.032 | 50.24 | 47.43 | n.a. |

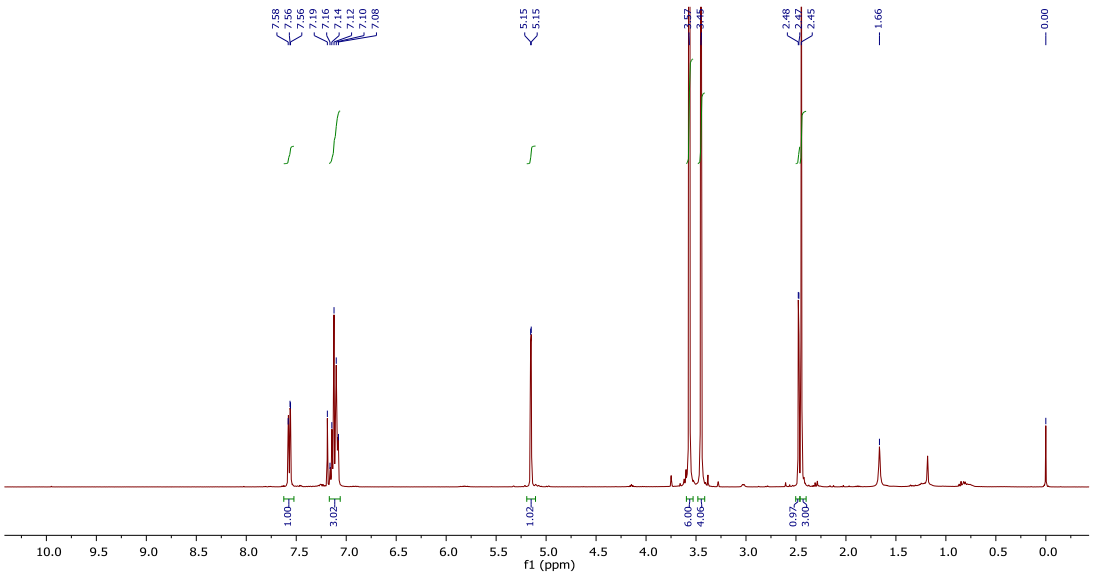
## HPLC trace of 3a

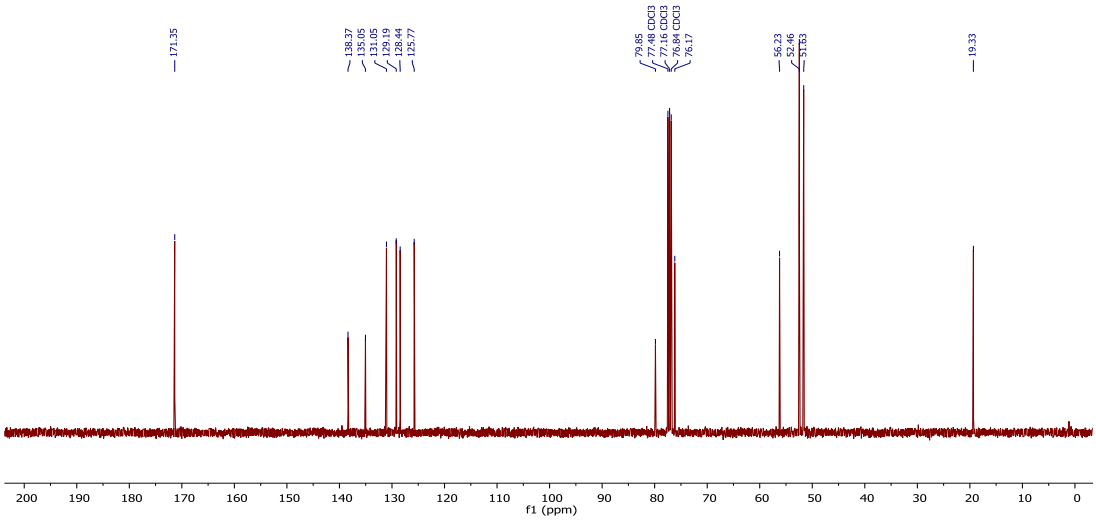



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 9.679 | 31.824 | 133.483 | 97.68 | 97.80 | n.a. |
| 2 | 11.532 | 0.755 | 3.008 | 2.32 | 2.20 | n.a. |


MeO2C
N
CO2Me
Me

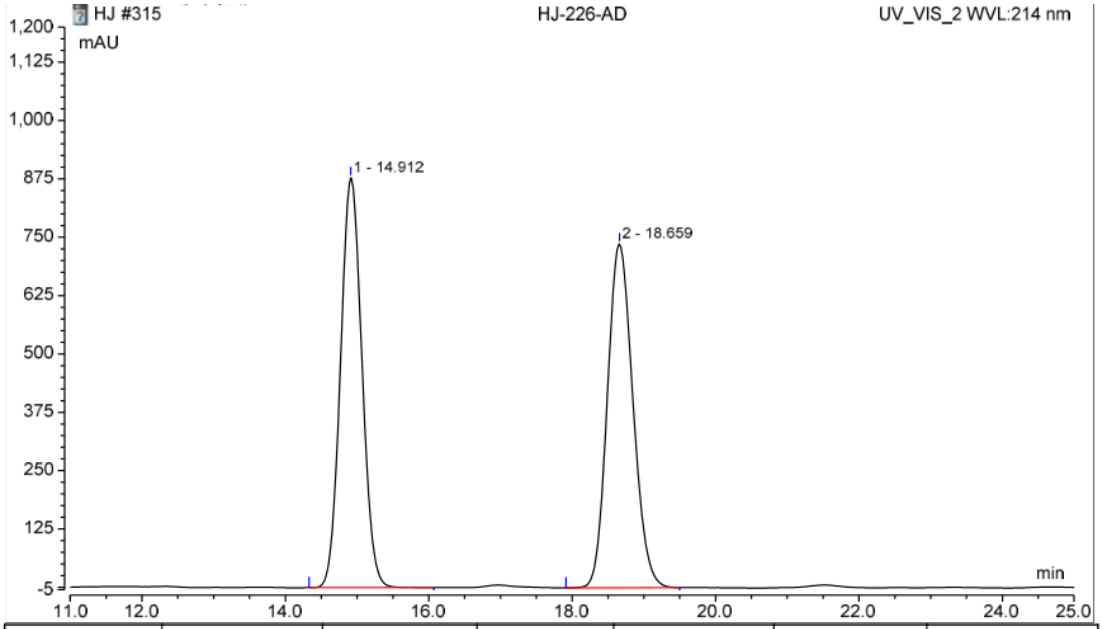
**3b**


7.58
7.56
7.56
7.19
7.16
7.14
7.12
7.10
7.08
5.15
5.15
3.52
3.48
2.48
2.42
2.45
1.66
0.00
1.00
3.02
1.02
6.00
4.06
0.97
3.00
f1 (ppm)


171.35
138.37
135.05
131.05
129.19
128.44
125.77
79.85
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.17
56.23
52.46
51.83
19.33
f1 (ppm)

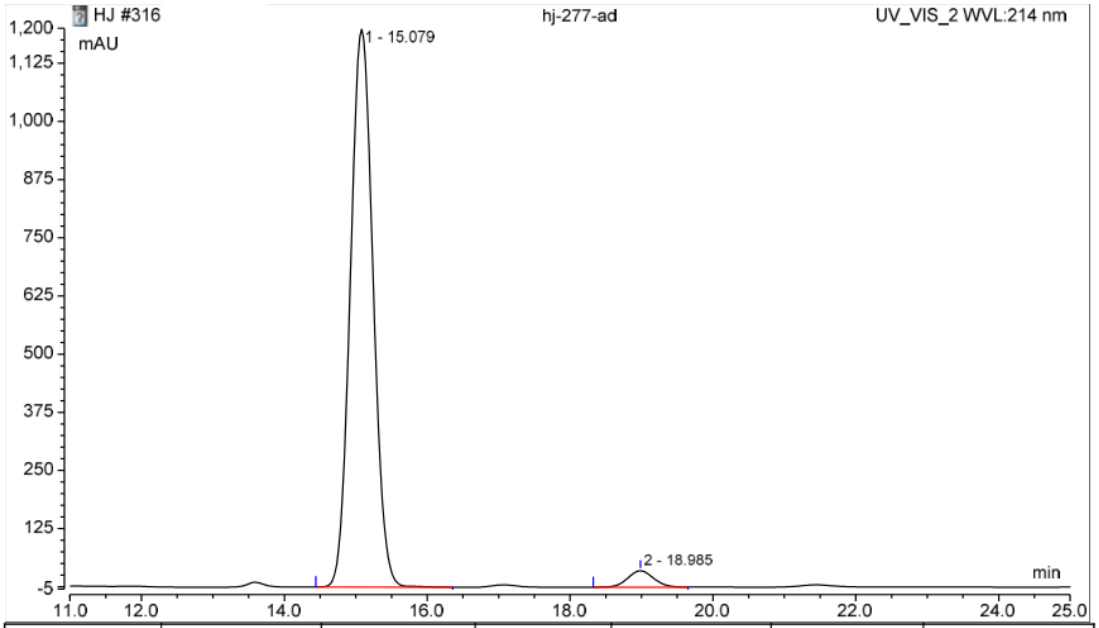
**Compound (-)-3b:** AD-H, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-3b

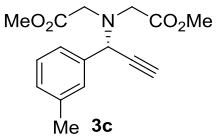



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 14.912 | 303.556 | 877.849 | 49.98 | 54.37 | n.a. |
| 2 | 18.659 | 303.792 | 736.725 | 50.02 | 45.63 | n.a. |

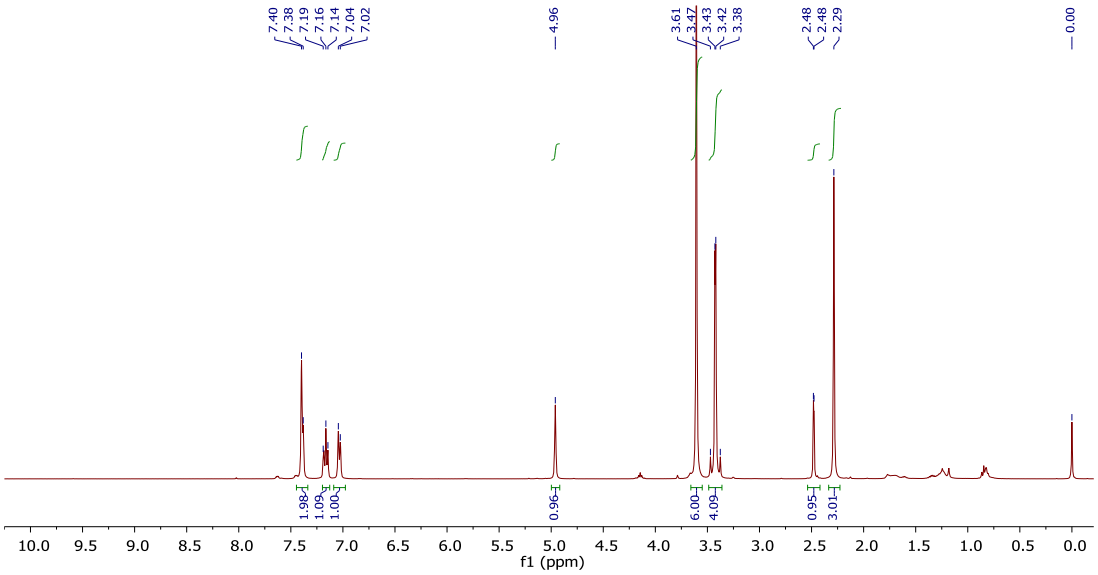
## HPLC trace of 3b

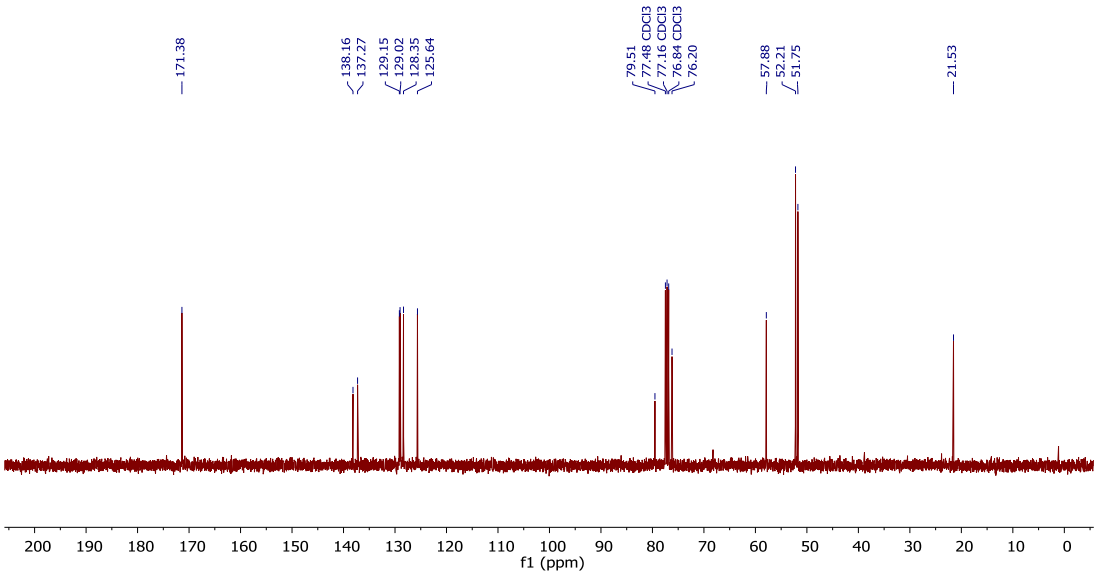



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 15.079 | 440.037 | 1198.071 | 96.75 | 97.14 | n.a. |
| 2 | 18.985 | 14.802 | 35.280 | 3.25 | 2.86 | n.a. |


MeO2C
N
CO2Me
Me

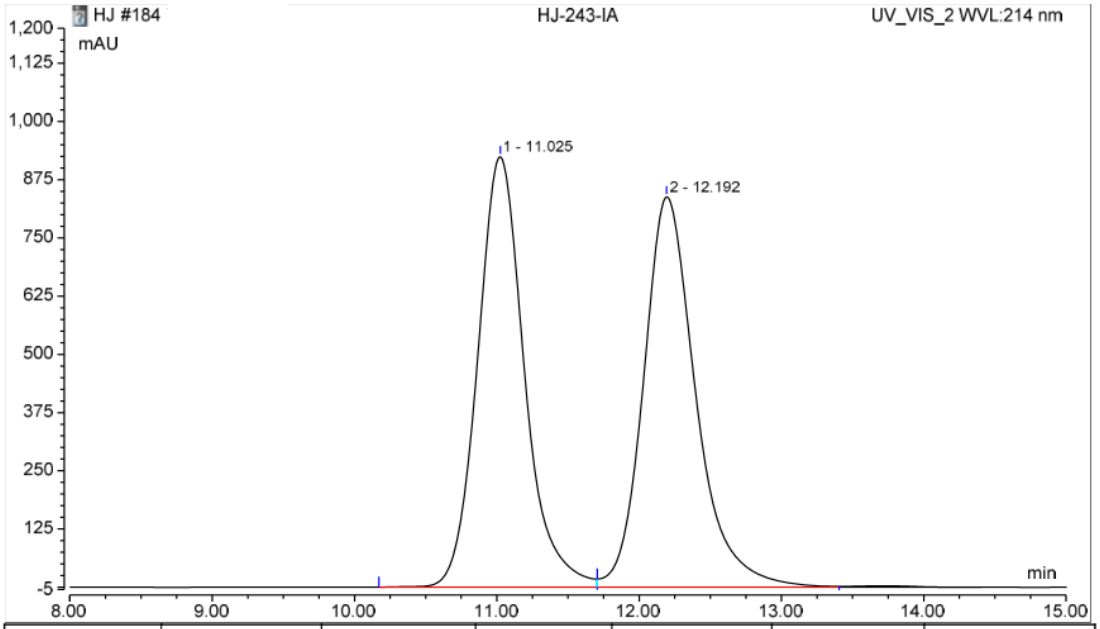
**3c**


7.40
7.38
7.19
7.16
7.14
7.04
7.02
4.96
3.61
3.47
3.43
3.42
3.38
2.48
2.48
2.29
0.00
1.98
1.09
1.00
0.96
6.00
4.09
0.95
3.01
f1 (ppm)


171.38
138.16
137.27
129.15
129.02
128.35
125.64
79.51
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.20
57.88
52.21
51.75
21.53
f1 (ppm)

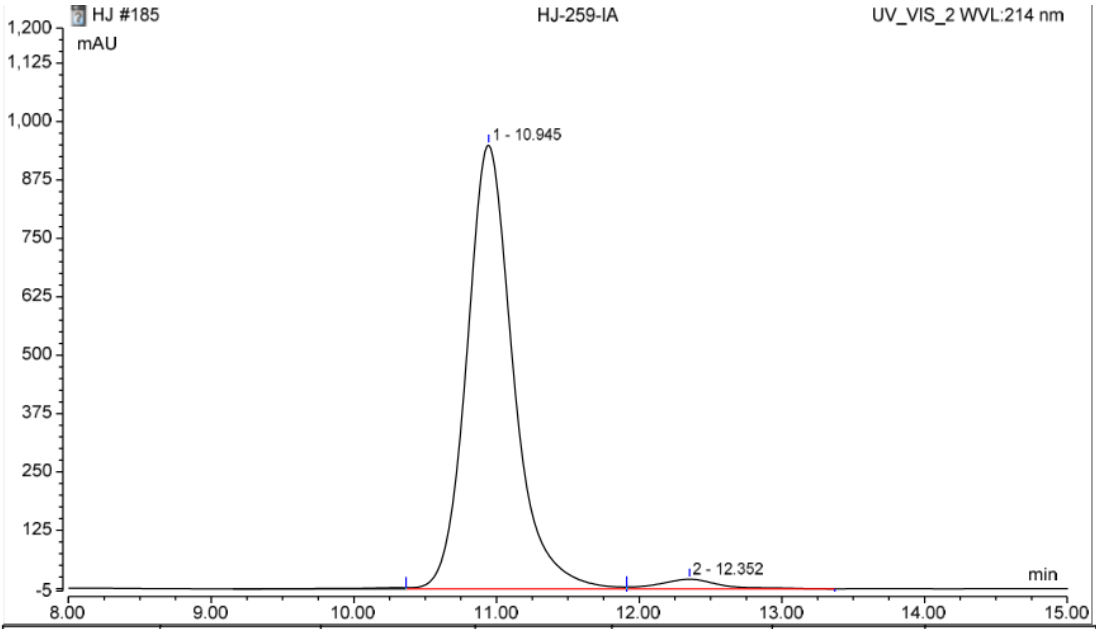
**Compound (-)-3c:** IA, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-3c

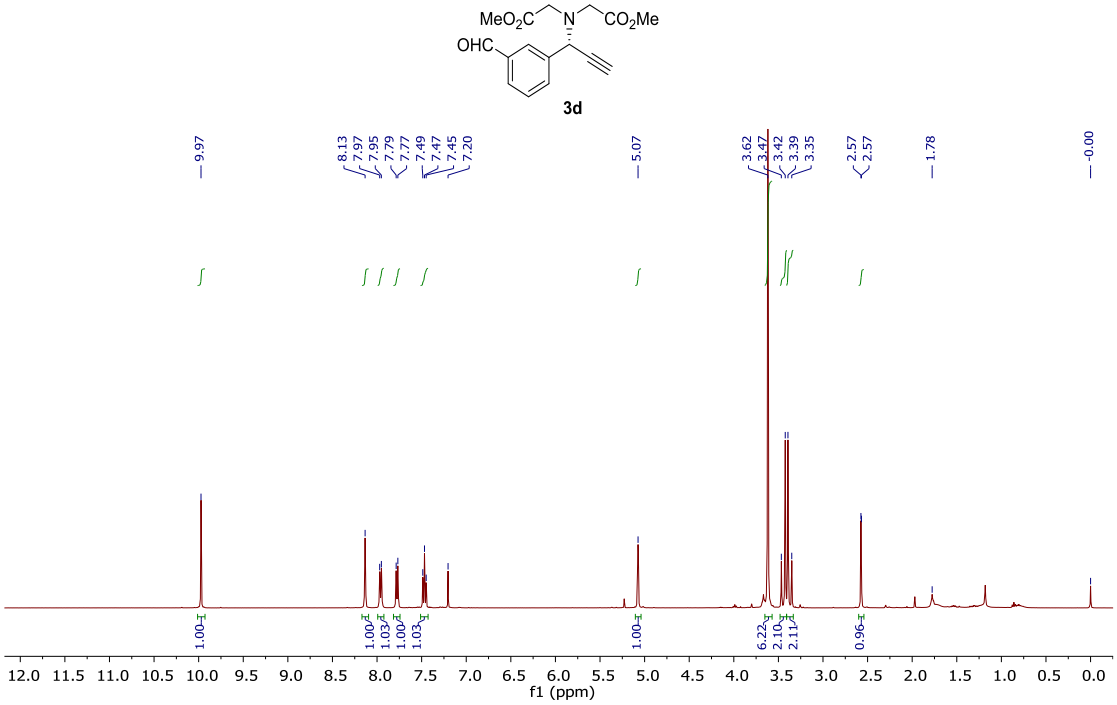


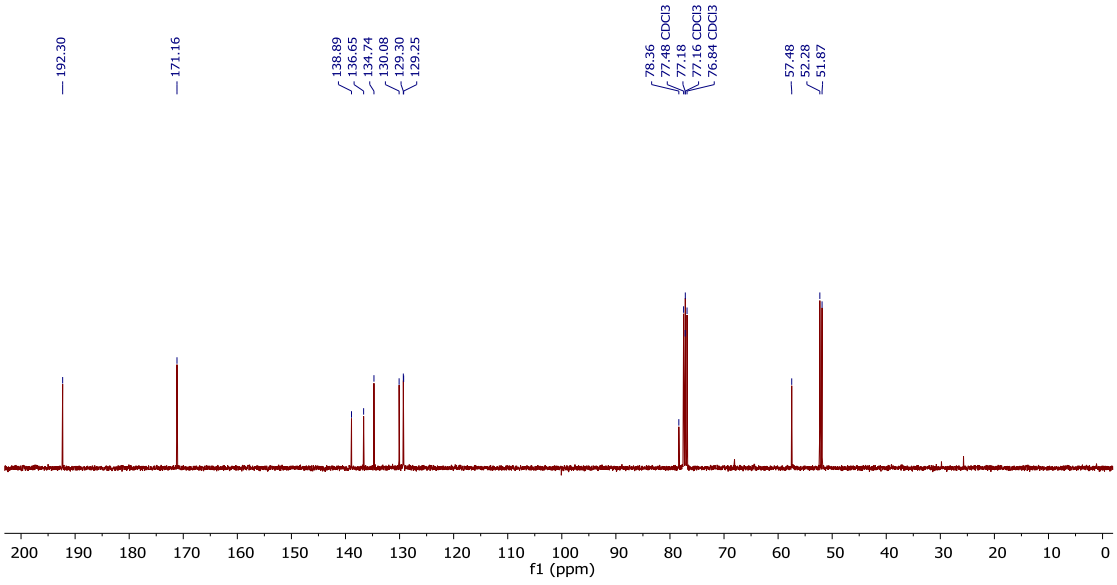

| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 11.025 | 350.390 | 924.284 | 49.61 | 52.44 | n.a. |
| 2 | 12.192 | 355.934 | 838.129 | 50.39 | 47.56 | n.a. |

## HPLC trace of 3c



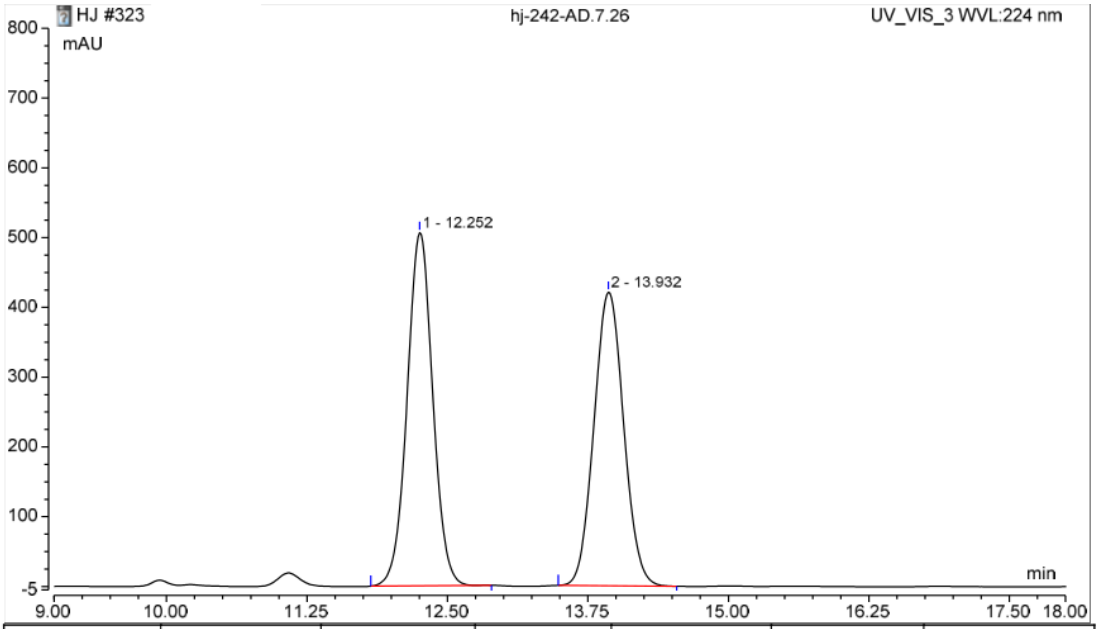

| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 10.945 | 357.686 | 949.886 | 97.26 | 97.88 | n.a. |
| 2 | 12.352 | 10.063 | 20.557 | 2.74 | 2.12 | n.a. |


MeO2C
N
CO2Me
OHC
3d
9.97
8.13
7.97
7.95
7.79
7.77
7.49
7.47
7.45
7.20
5.07
3.62
3.47
3.42
3.39
3.35
2.57
2.57
1.78
-0.00
1.00
1.00
1.03
1.00
1.03
1.00
6.22
2.10
2.11
0.96
f1 (ppm)


192.30
171.16
138.89
136.65
134.74
130.08
129.30
129.25
78.36
77.48 CDCl3
77.18
77.16 CDCl3
76.84 CDCl3
57.48
52.28
51.87
f1 (ppm)

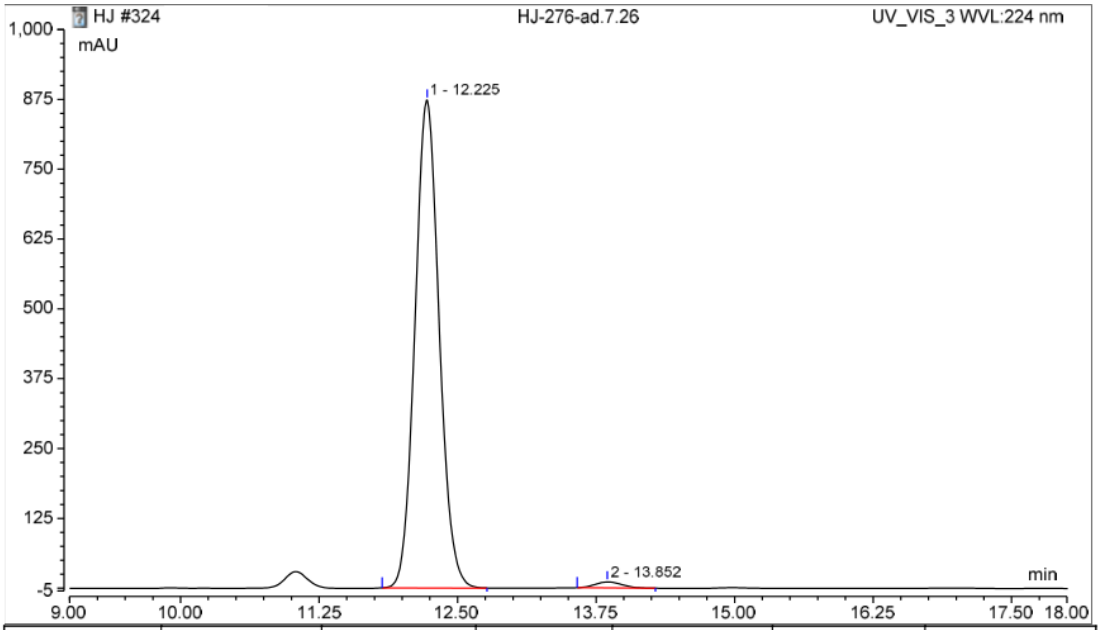
**Compound (-)-3d:** AD-H, hexane/$^{i}$PrOH = 90/10, v = 1.0 mL/min, λ = 224 nm

## HPLC trace of *rac*-3d

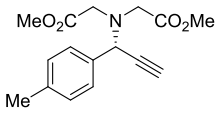



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 12.252 | 133.761 | 506.399 | 50.94 | 54.61 | n.a. |
| 2 | 13.932 | 128.815 | 420.848 | 49.06 | 45.39 | n.a. |

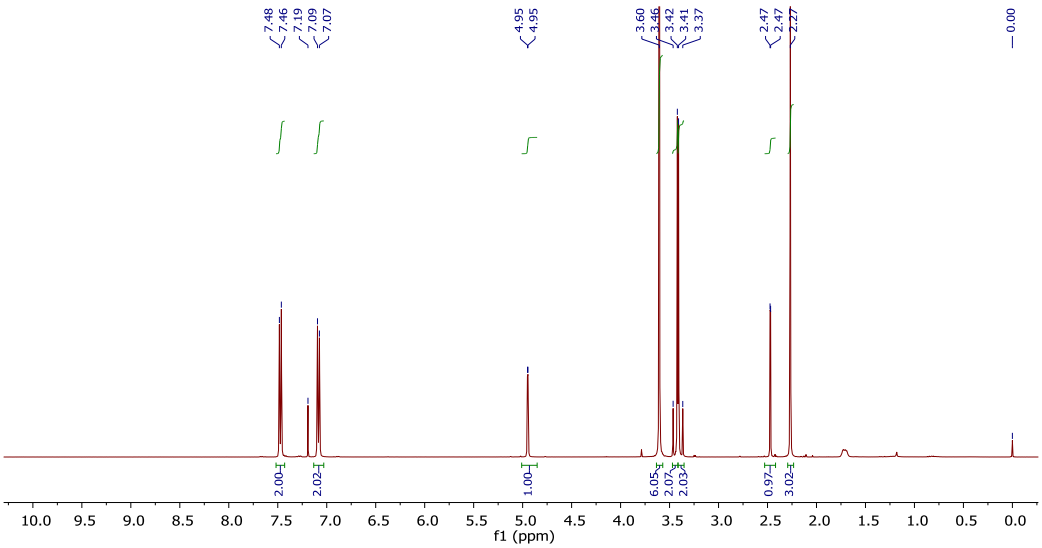
## HPLC trace of 3d

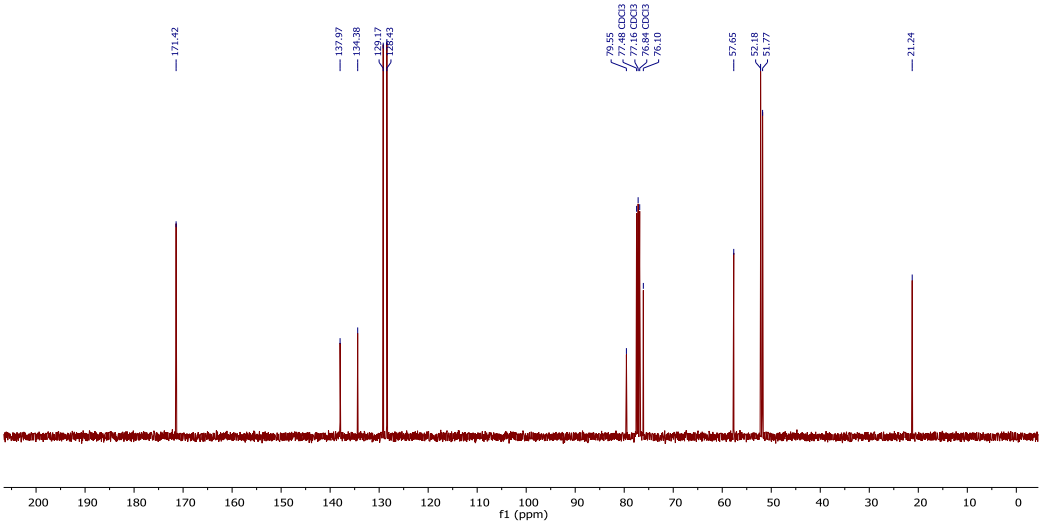



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 12.225 | 220.240 | 873.142 | 98.66 | 98.79 | n.a. |
| 2 | 13.852 | 2.992 | 10.709 | 1.34 | 1.21 | n.a. |


MeO2C
N
CO2Me
Me

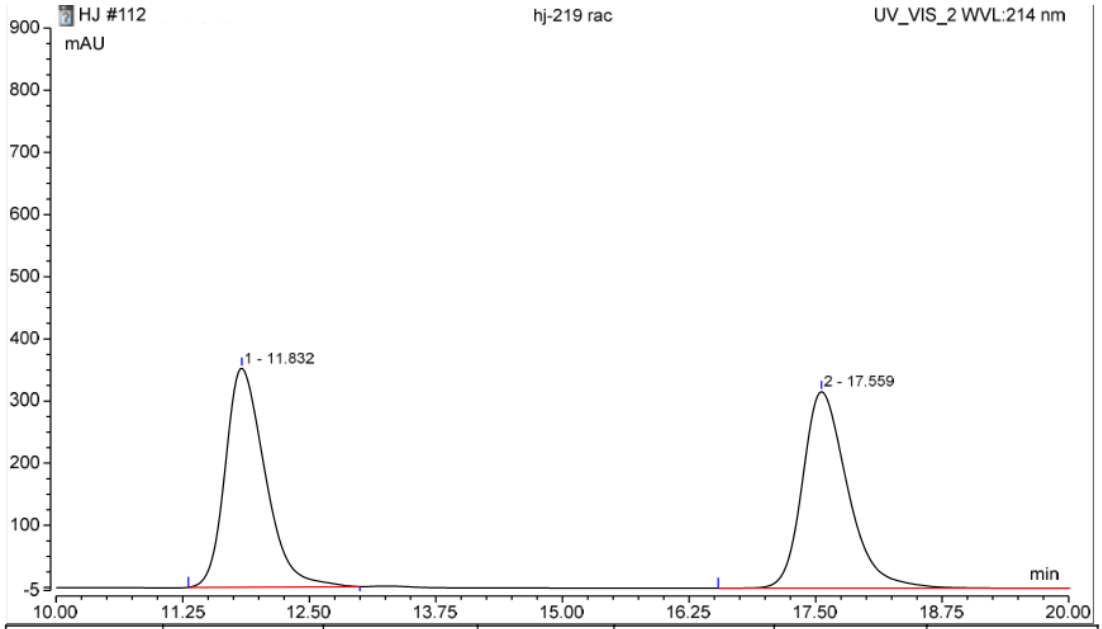
**3e**


7.48
7.46
7.19
7.09
7.07
4.95
4.95
3.60
3.46
3.42
3.41
3.37
2.47
2.47
2.27
0.00
2.00
2.02
1.00
6.05
2.07
2.03
0.97
3.02
f1 (ppm)


171.42
137.97
134.38
129.17
128.43
79.55
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.10
57.65
52.18
51.77
21.24
f1 (ppm)

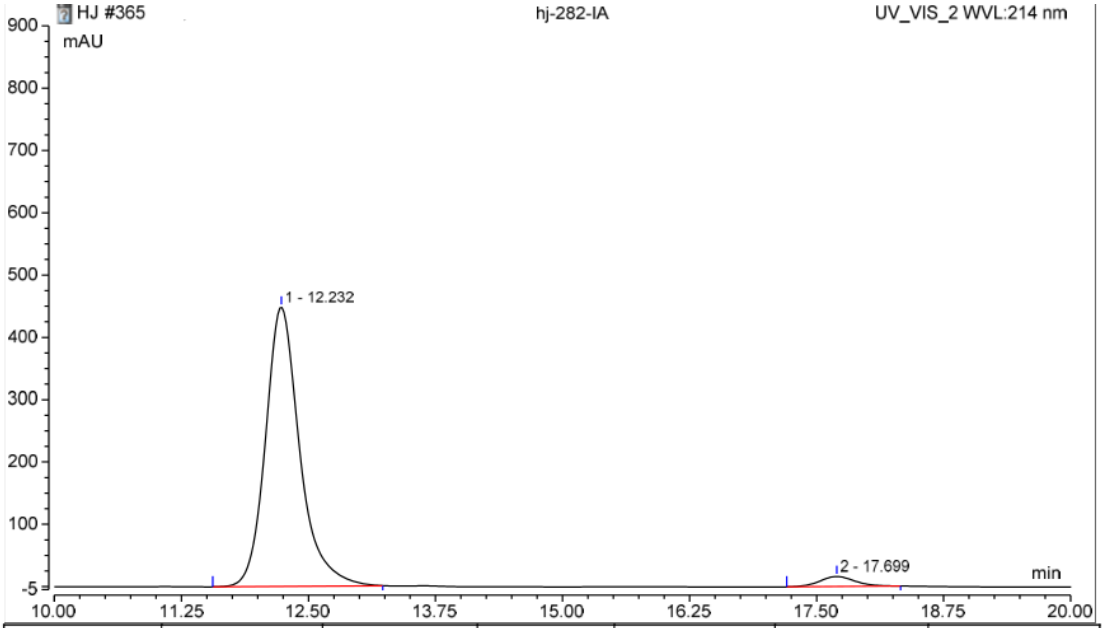
**Compound (-)-3e:** IA, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-3e

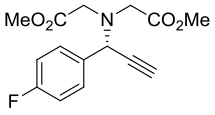



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 11.832 | 160.527 | 352.262 | 49.50 | 52.69 | n.a. |
| 2 | 17.559 | 163.762 | 316.238 | 50.50 | 47.31 | n.a. |

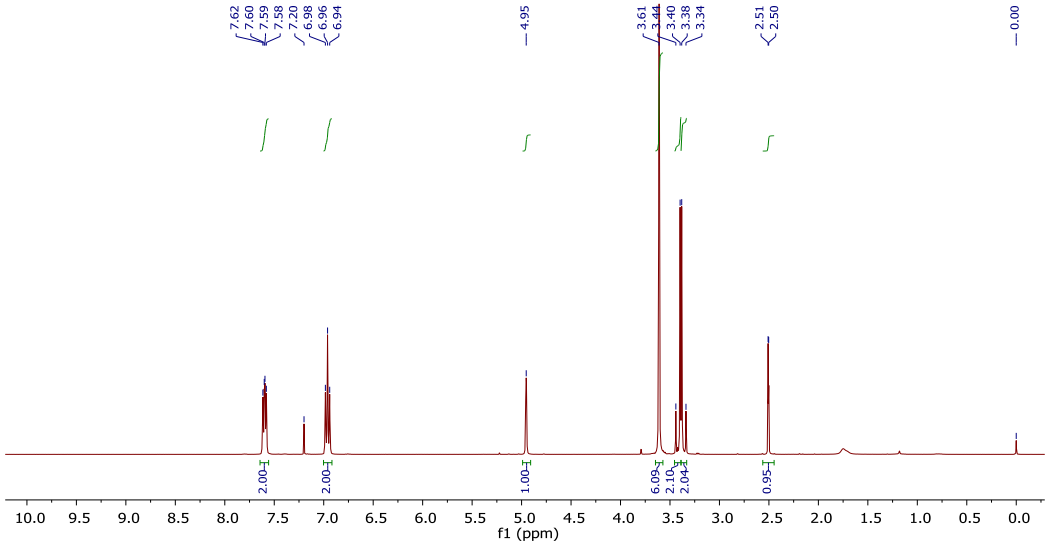
## HPLC trace of 3e

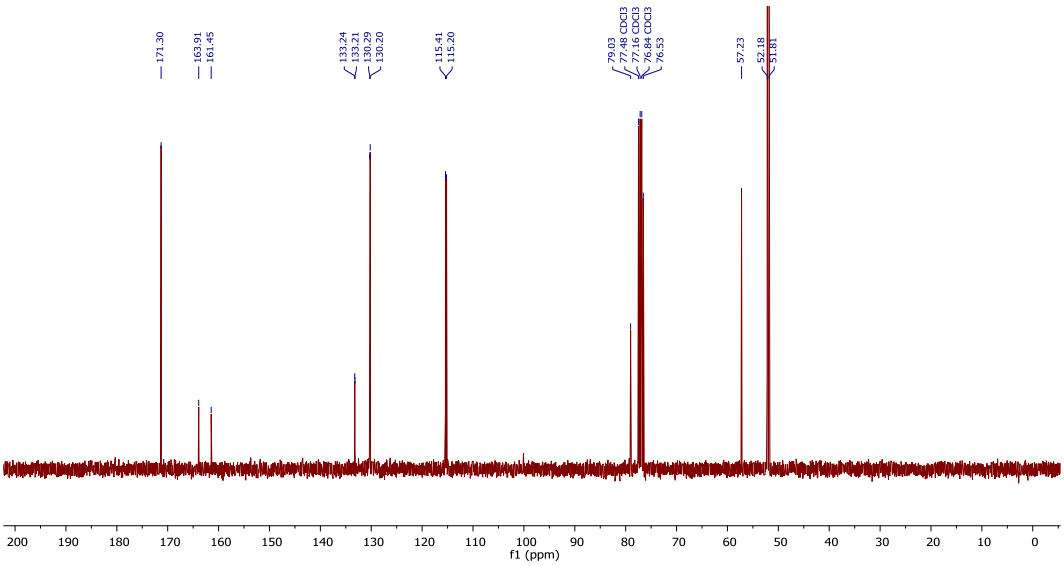


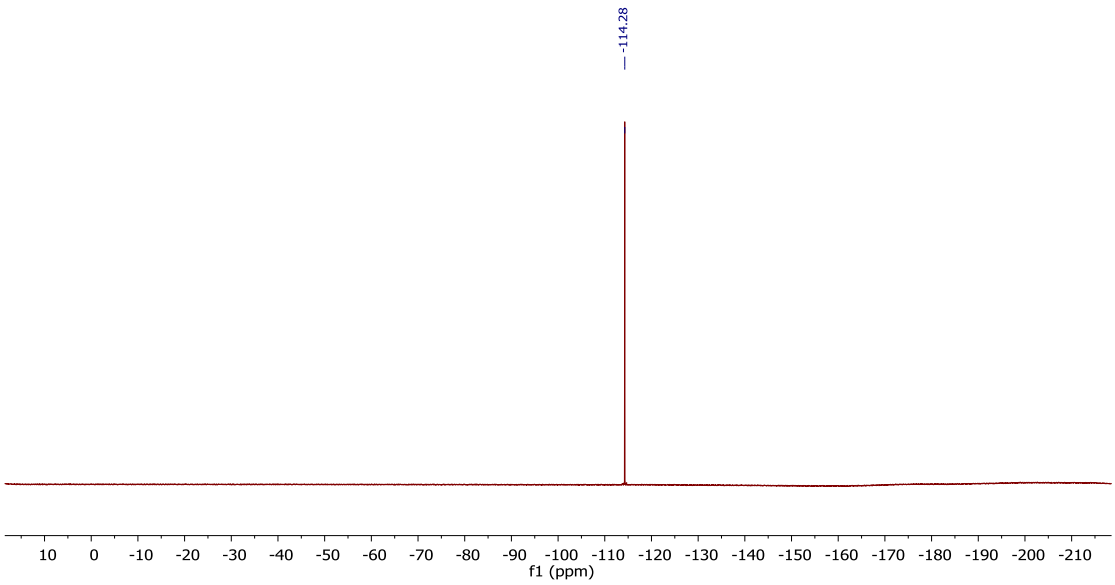

| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 12.232 | 174.808 | 448.439 | 96.41 | 96.53 | n.a. |
| 2 | 17.699 | 6.504 | 16.102 | 3.59 | 3.47 | n.a. |


MeO2C
N
CO2Me
F

**3f**

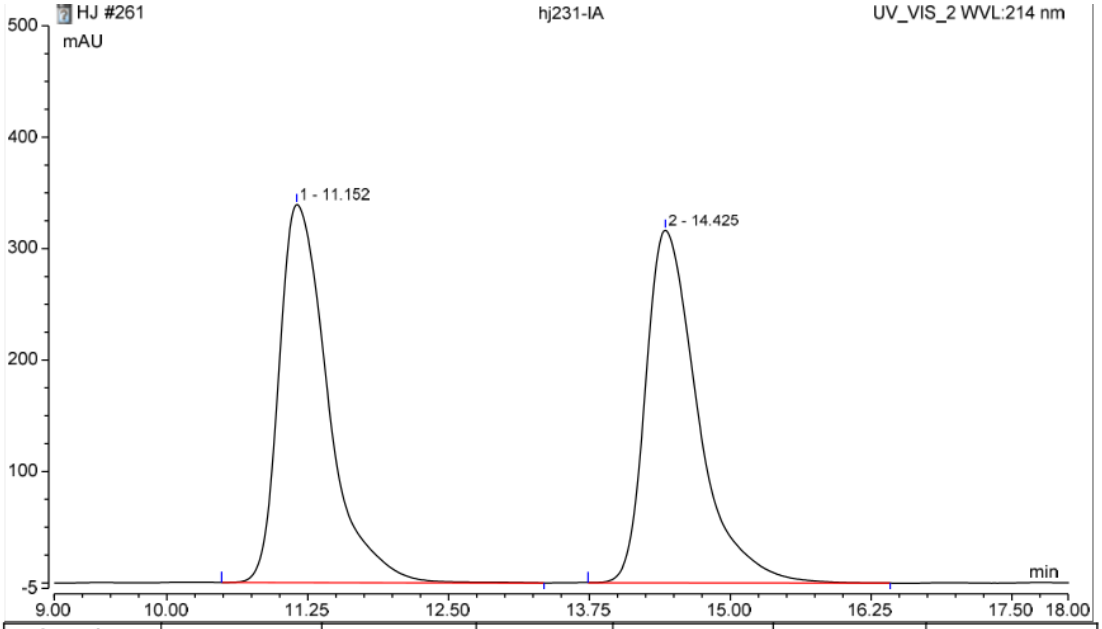

7.62
7.60
7.59
7.58
7.20
6.98
6.96
6.94
4.95
3.61
3.44
3.40
3.38
3.34
2.51
2.50
0.00
2.00
2.00
1.00
6.09
2.10
2.04
0.95
f1 (ppm)


171.30
163.91
161.45
133.24
133.21
130.29
130.20
115.41
115.20
79.03
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.53
57.23
52.18
51.81
f1 (ppm)


-114.28
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

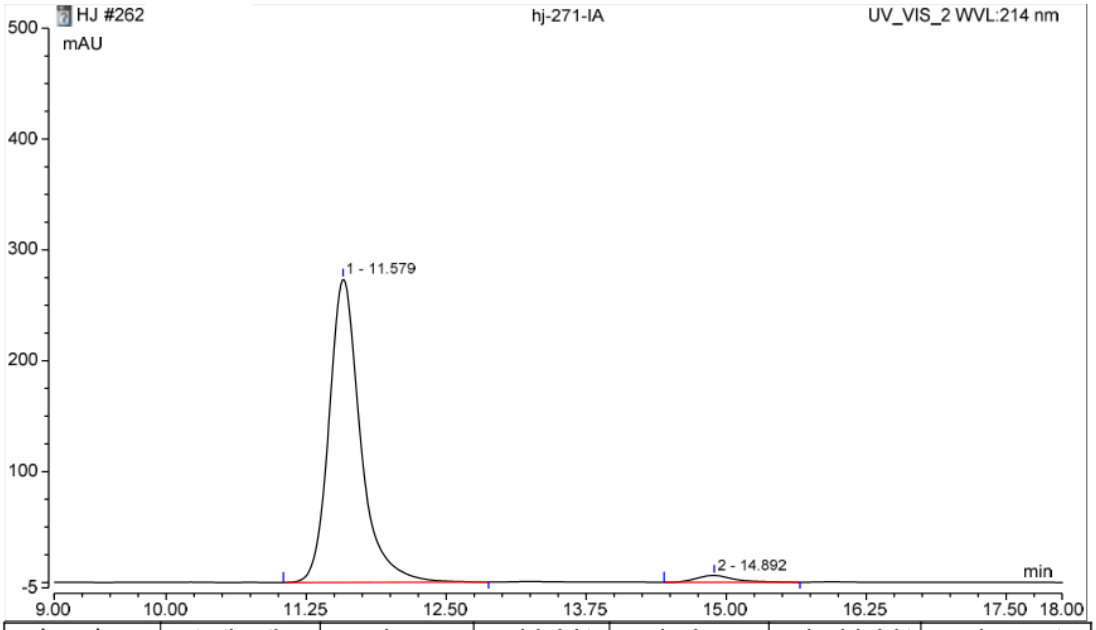
**Compound (-)-3f:** IA, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-3f

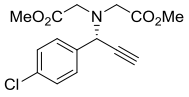



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 11.152 | 171.000 | 339.193 | 50.19 | 51.74 | n.a. |
| 2 | 14.425 | 169.734 | 316.331 | 49.81 | 48.26 | n.a. |

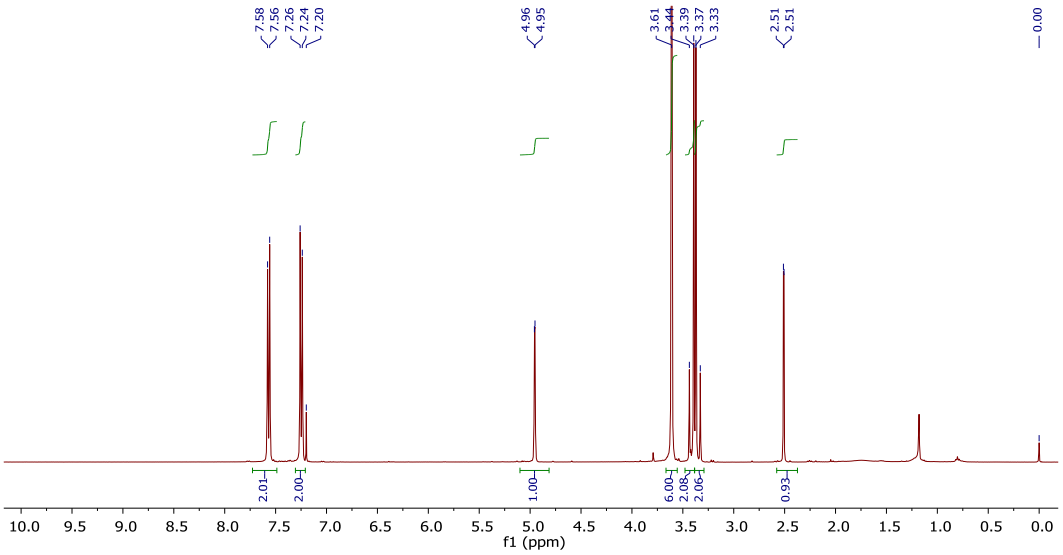
## HPLC trace of 3f

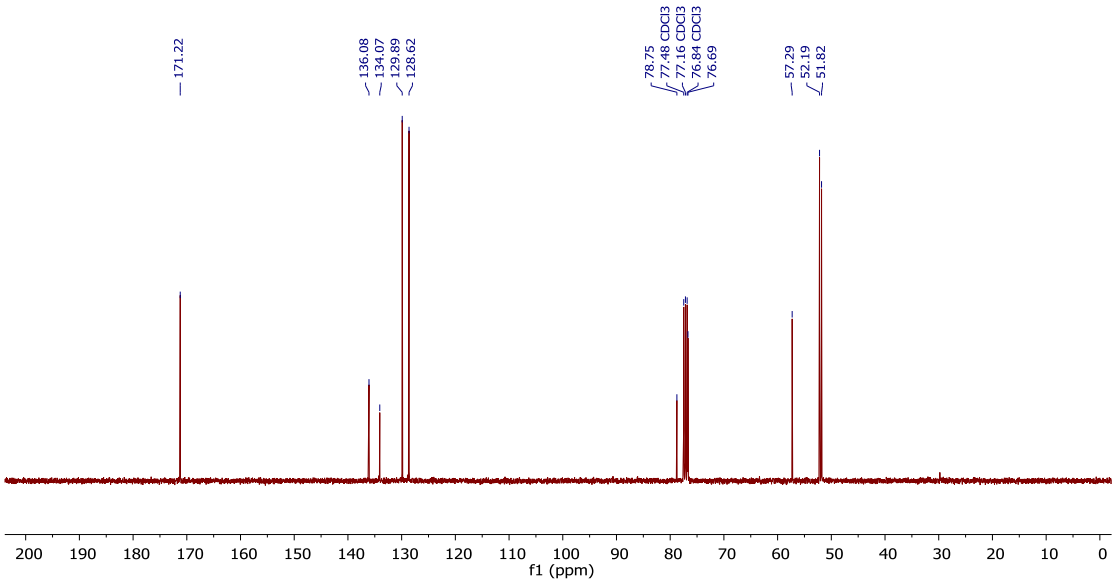



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 11.579 | 89.304 | 273.544 | 97.34 | 97.78 | n.a. |
| 2 | 14.892 | 2.438 | 6.202 | 2.66 | 2.22 | n.a. |


MeO2C
N
CO2Me
Cl

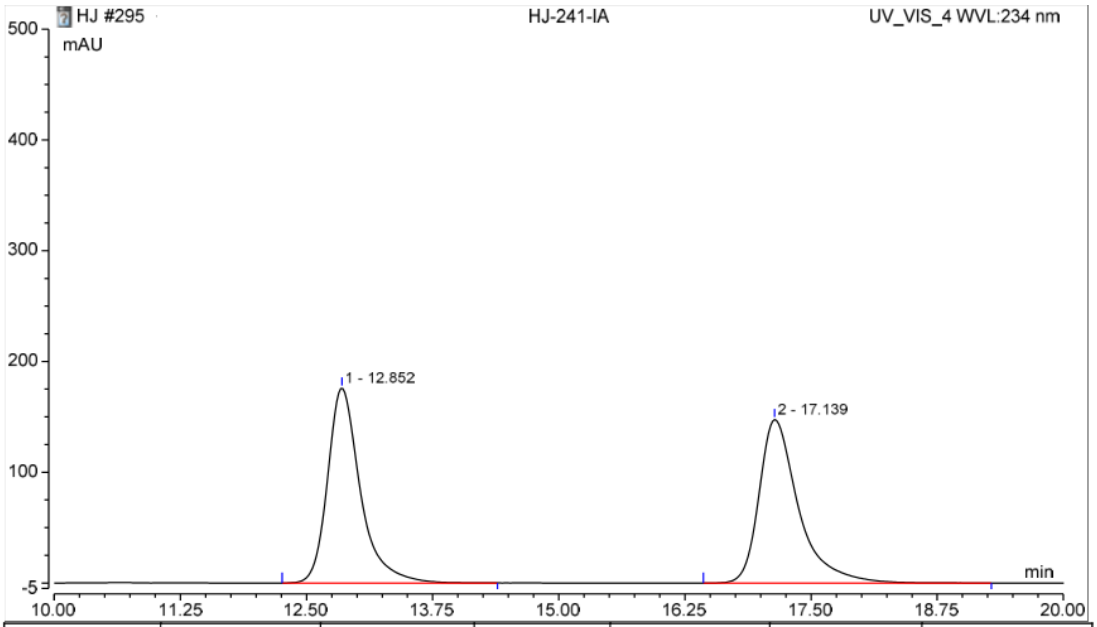
**3g**


7.58
7.56
7.26
7.24
7.20
4.96
4.95
3.61
3.44
3.39
3.37
3.33
2.51
2.51
0.00
2.01
2.00
1.00
6.00
2.08
2.06
0.93
f1 (ppm)


171.22
136.08
134.07
129.89
128.62
78.75
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.69
57.29
52.19
51.82
f1 (ppm)

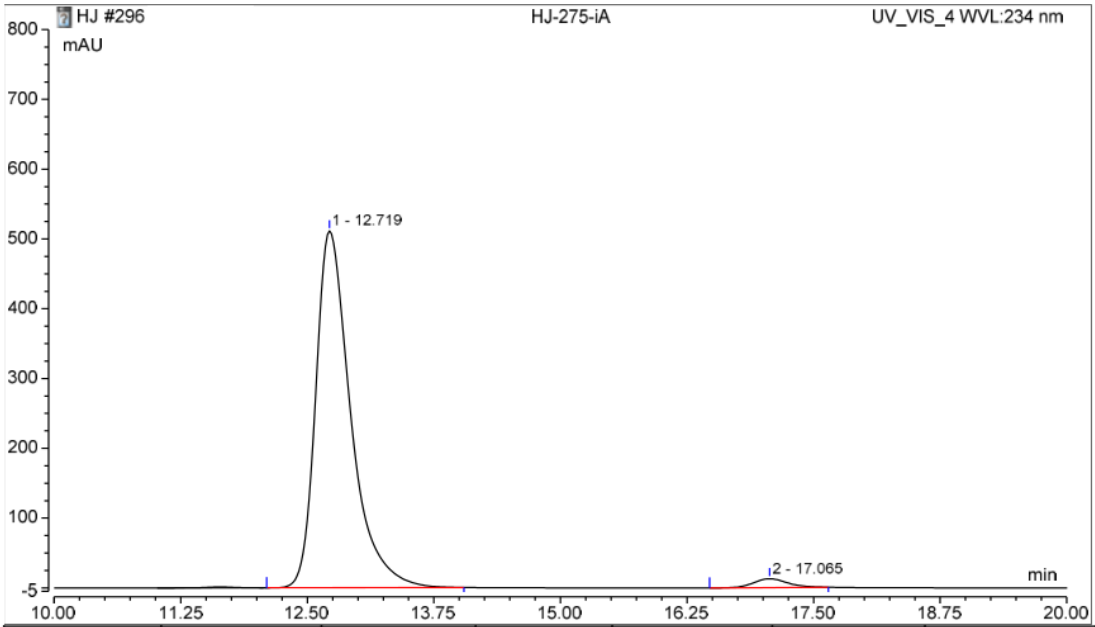
**Compound (-)-3g:** IA, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 234 nm

## HPLC trace of *rac*-3g

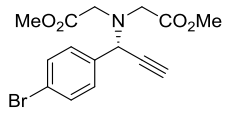



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 12.852 | 66.393 | 176.026 | 49.75 | 54.40 | n.a. |
| 2 | 17.139 | 67.048 | 147.577 | 50.25 | 45.60 | n.a. |

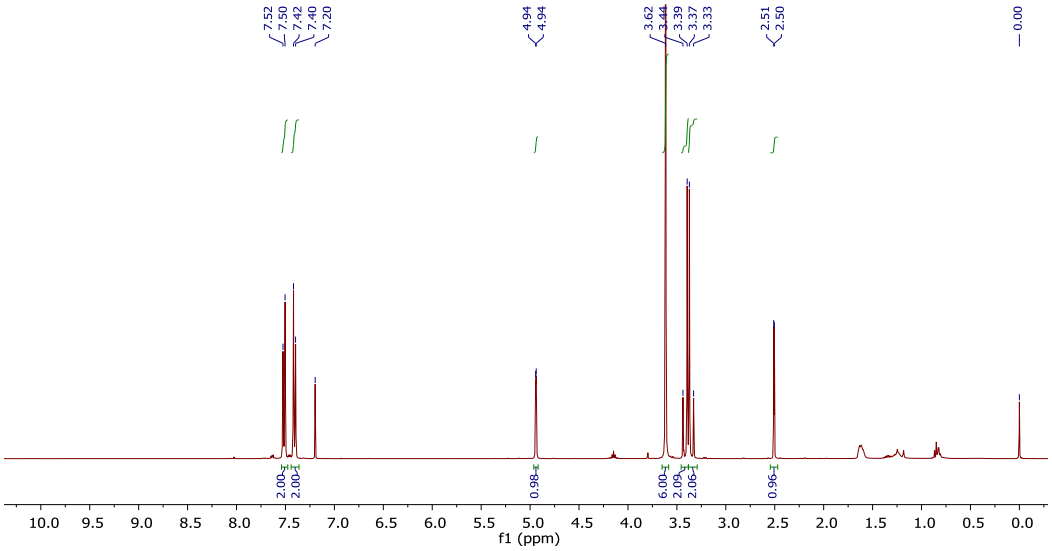
## HPLC trace of 3g

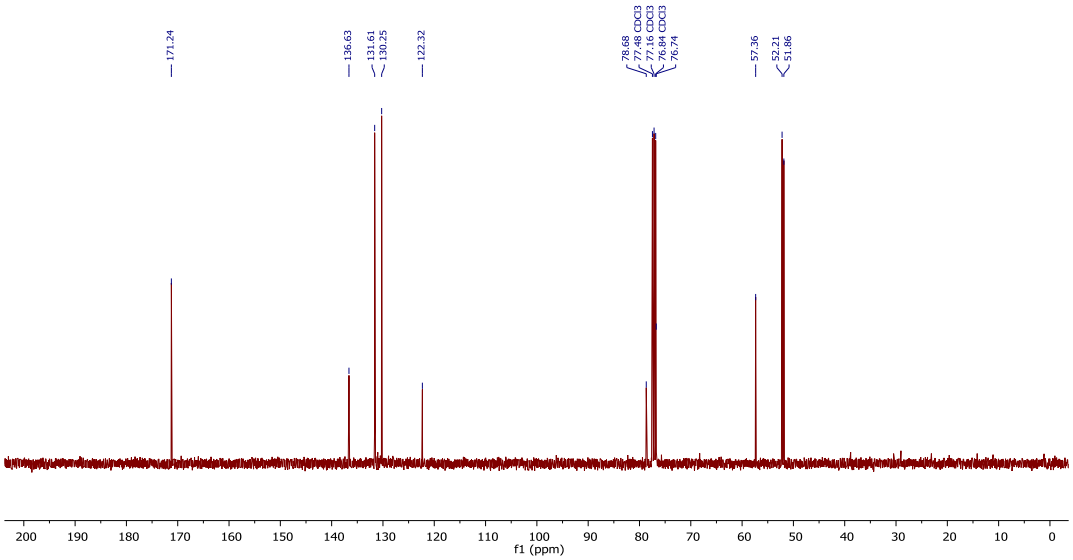



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 12.719 | 204.234 | 511.411 | 97.64 | 97.58 | n.a. |
| 2 | 17.065 | 4.945 | 12.671 | 2.36 | 2.42 | n.a. |


MeO2C
N
CO2Me
Br

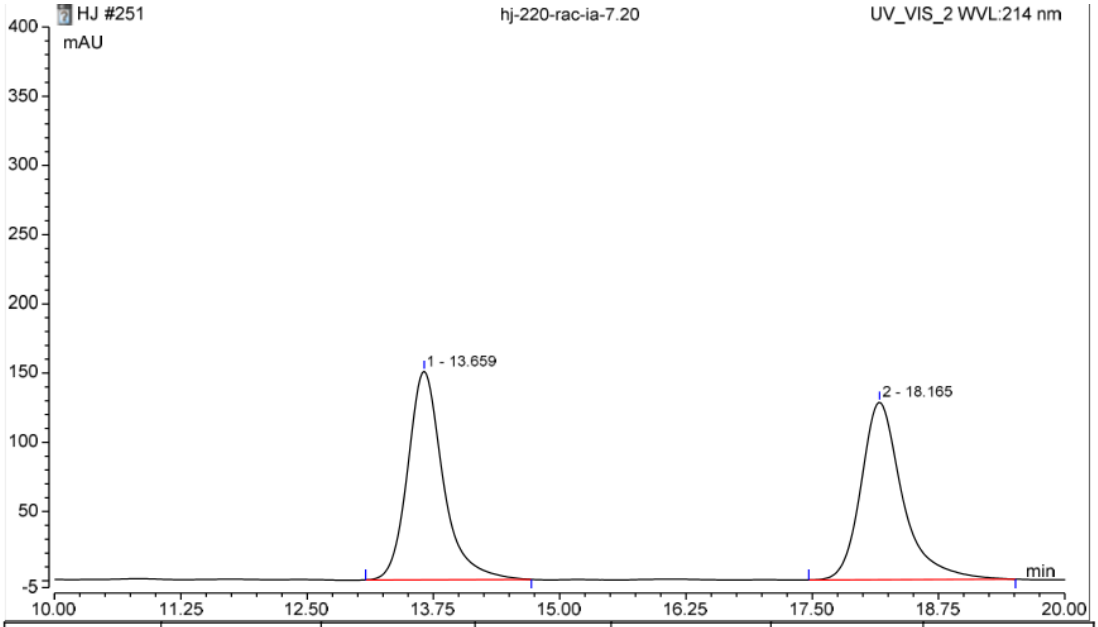
**3h**


7.52
7.50
7.42
7.40
7.20
4.94
4.94
3.62
3.44
3.39
3.37
3.33
2.51
2.50
0.00
2.00
2.00
0.98
6.00
2.09
2.06
0.96
f1 (ppm)


171.24
136.63
131.61
130.25
122.32
78.68
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.74
57.36
52.21
51.86
f1 (ppm)

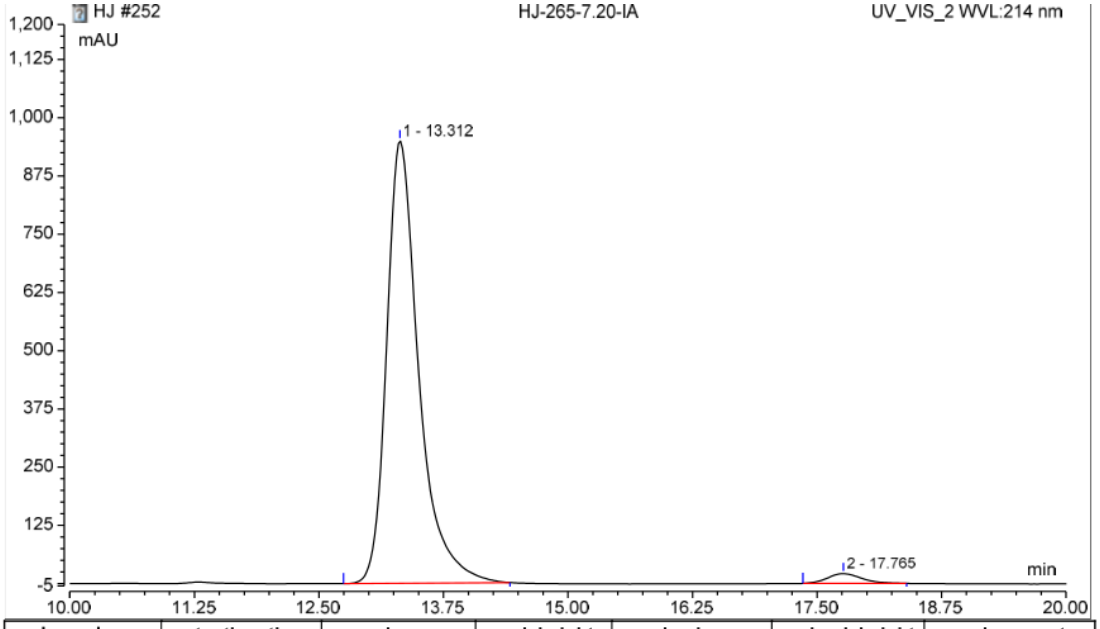
**Compound (-)-3h:** IA, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of rac-3h

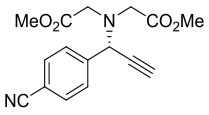



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 13.659 | 61.206 | 150.563 | 50.07 | 54.01 | n.a. |
| 2 | 18.165 | 61.022 | 128.183 | 49.93 | 45.99 | n.a. |

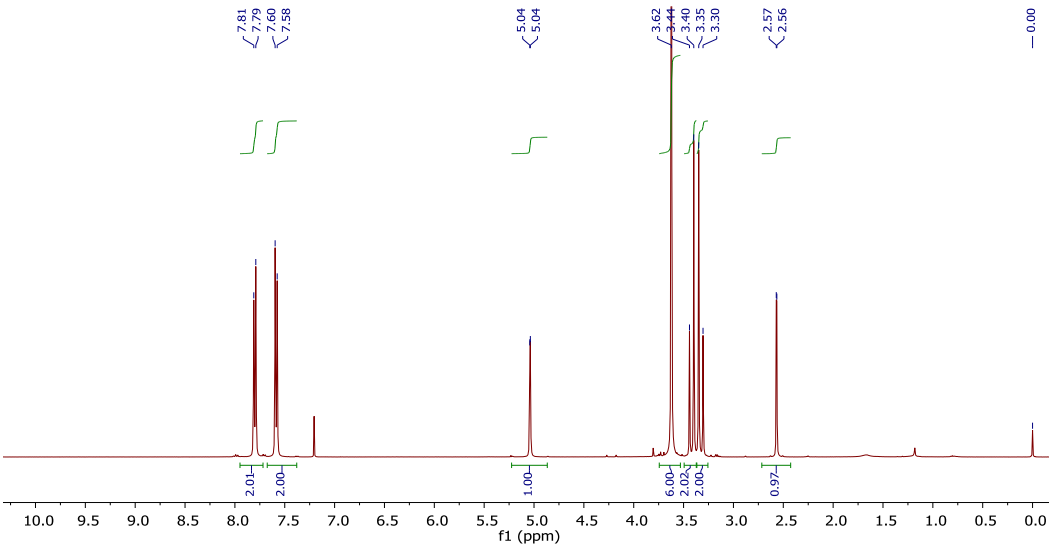
## HPLC trace of 3h

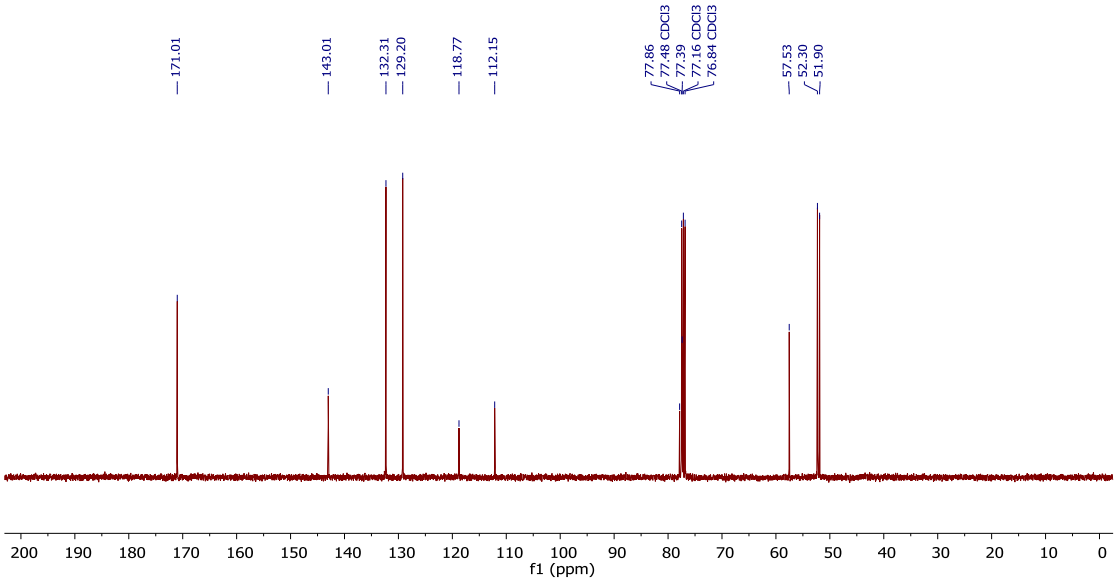



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 13.312 | 354.715 | 949.644 | 97.71 | 97.83 | n.a. |
| 2 | 17.765 | 8.302 | 21.079 | 2.29 | 2.17 | n.a. |


MeO2C
N
CO2Me
NC

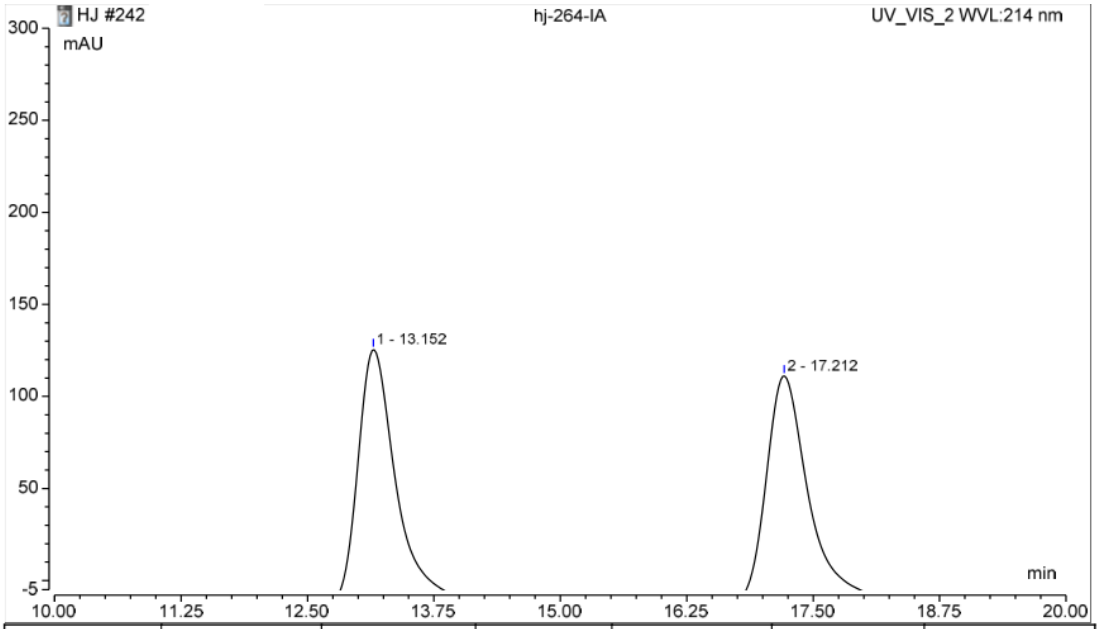
**3i**


7.81
7.79
7.60
7.58
5.04
5.04
3.62
3.44
3.40
3.35
3.30
2.57
2.56
0.00
2.01
2.00
1.00
6.00
2.02
2.00
0.97
f1 (ppm)


171.01
143.01
132.31
129.20
118.77
112.15
77.86
77.48 CDCl3
77.39
77.16 CDCl3
76.84 CDCl3
57.53
52.30
51.90
f1 (ppm)

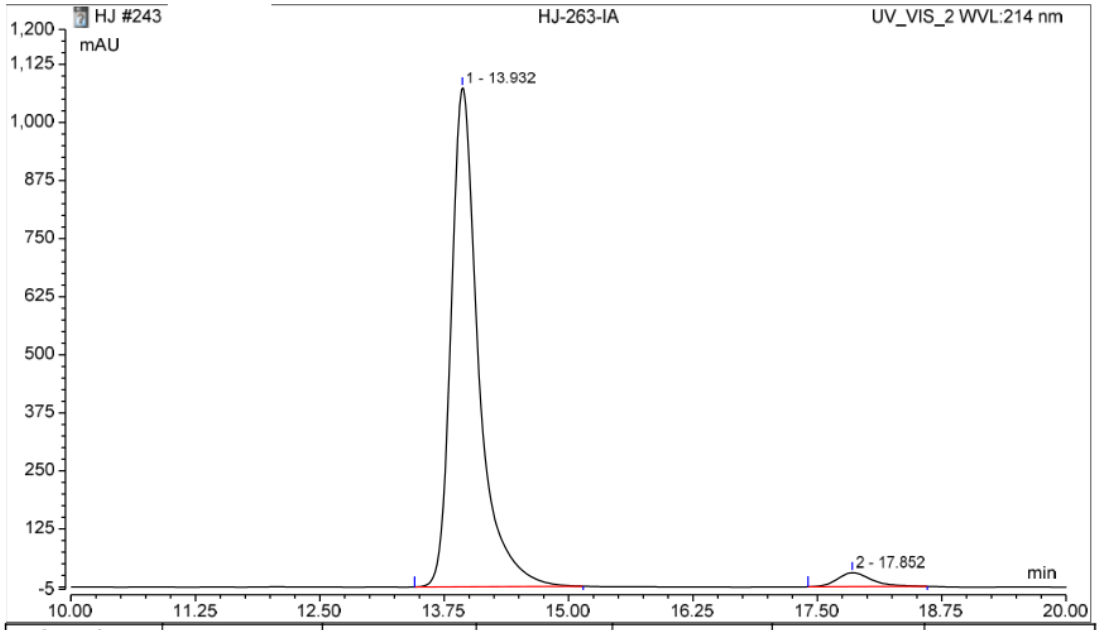
**Compound (-)-3i:** IA, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-3i

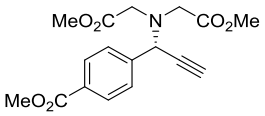



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 13.152 | 63.935 | 139.964 | 50.26 | 52.90 | n.a. |
| 2 | 17.212 | 63.282 | 124.633 | 49.74 | 47.10 | n.a. |

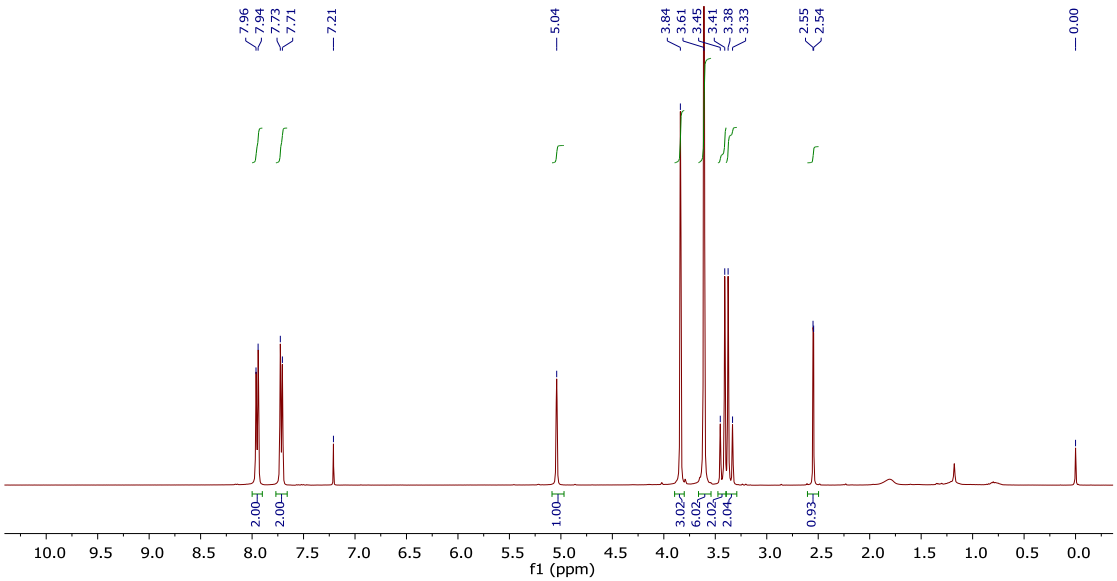
## HPLC trace of 3i

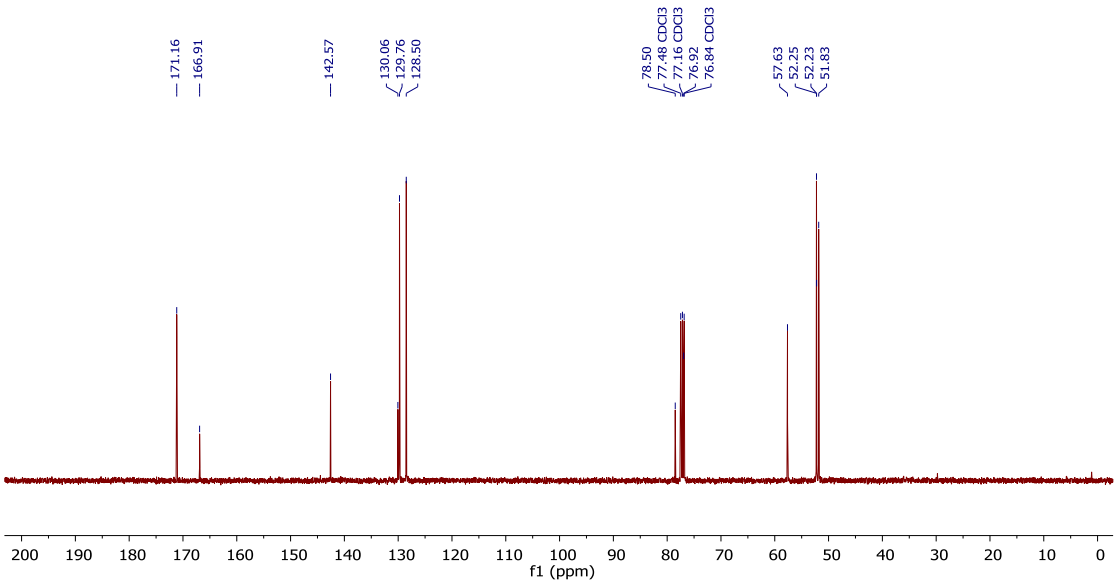



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 13.932 | 342.479 | 1073.760 | 96.60 | 97.28 | n.a. |
| 2 | 17.852 | 12.041 | 30.006 | 3.40 | 2.72 | n.a. |


MeO2C
N
CO2Me
MeO2C

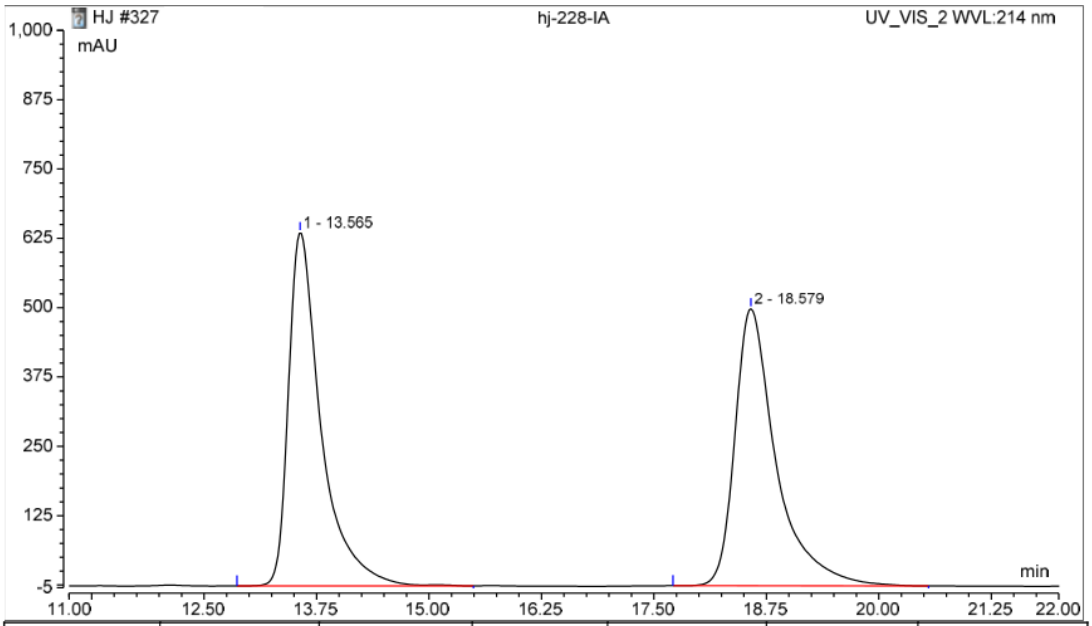
**3j**


7.96
7.94
7.73
7.71
7.21
5.04
3.84
3.61
3.45
3.41
3.38
3.33
2.55
2.54
0.00
2.00
2.00
1.00
3.02
6.02
2.02
2.04
0.93
f1 (ppm)


171.16
166.91
142.57
130.06
129.76
128.50
78.50 CDCl3
77.48 CDCl3
77.16 CDCl3
76.92
76.84 CDCl3
57.63
52.25
52.23
51.83
f1 (ppm)

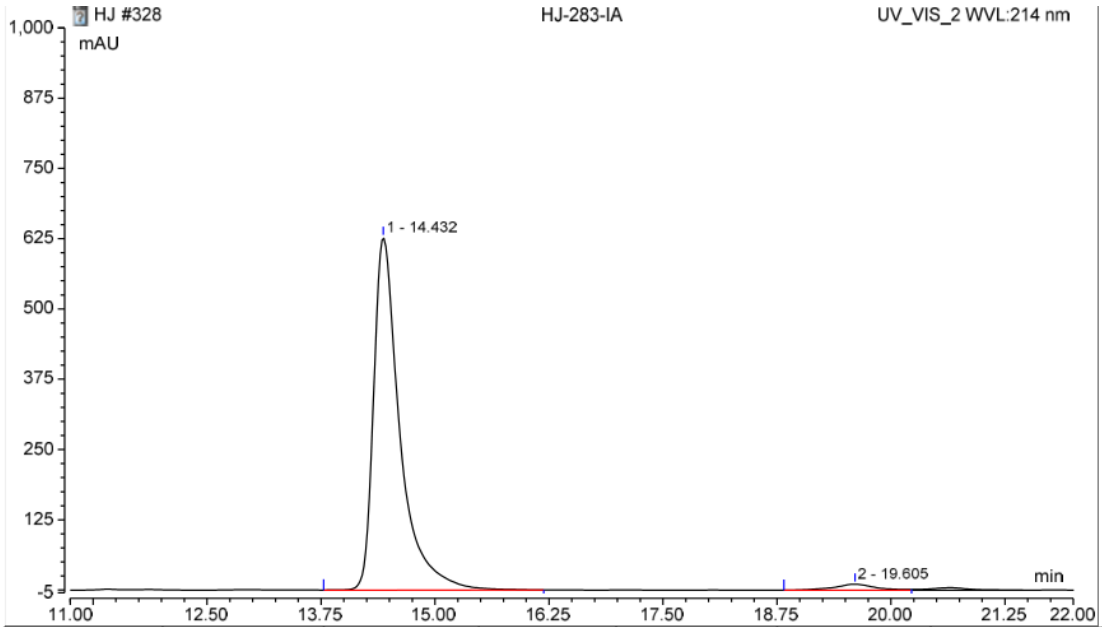
**Compound (-)-3j:** IA, hexane/$^{i}$PrOH = 95/5, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-3j

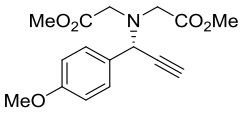



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 13.565 | 266.802 | 637.084 | 50.16 | 56.06 | n.a. |
| 2 | 18.579 | 265.110 | 499.379 | 49.84 | 43.94 | n.a. |

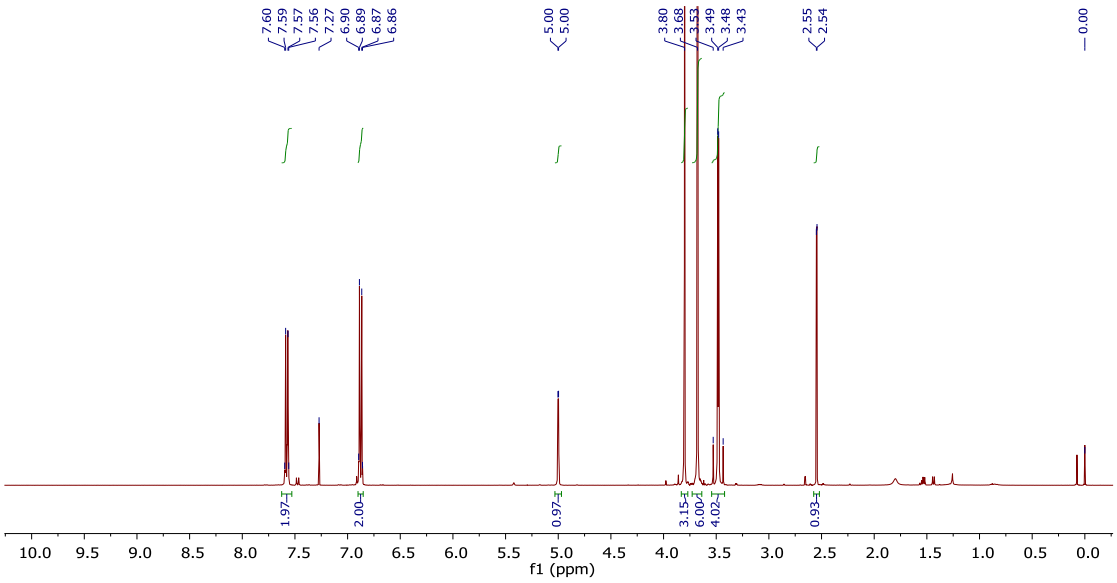
## HPLC trace of 3j

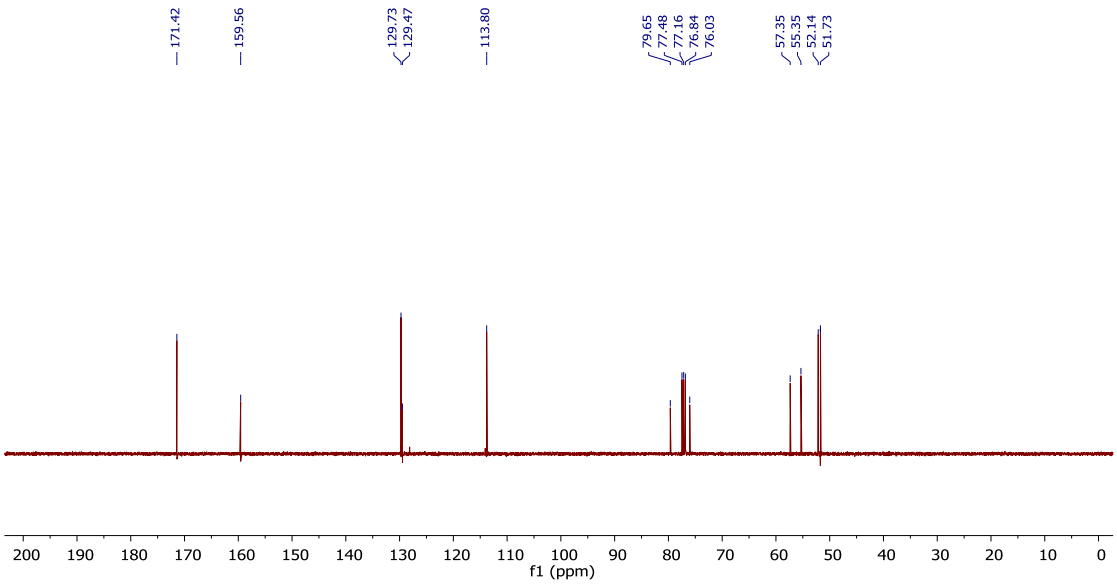



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 14.432 | 209.716 | 626.991 | 97.37 | 98.31 | n.a. |
| 2 | 19.605 | 5.671 | 10.750 | 2.63 | 1.69 | n.a. |


MeO2C
N
CO2Me
MeO

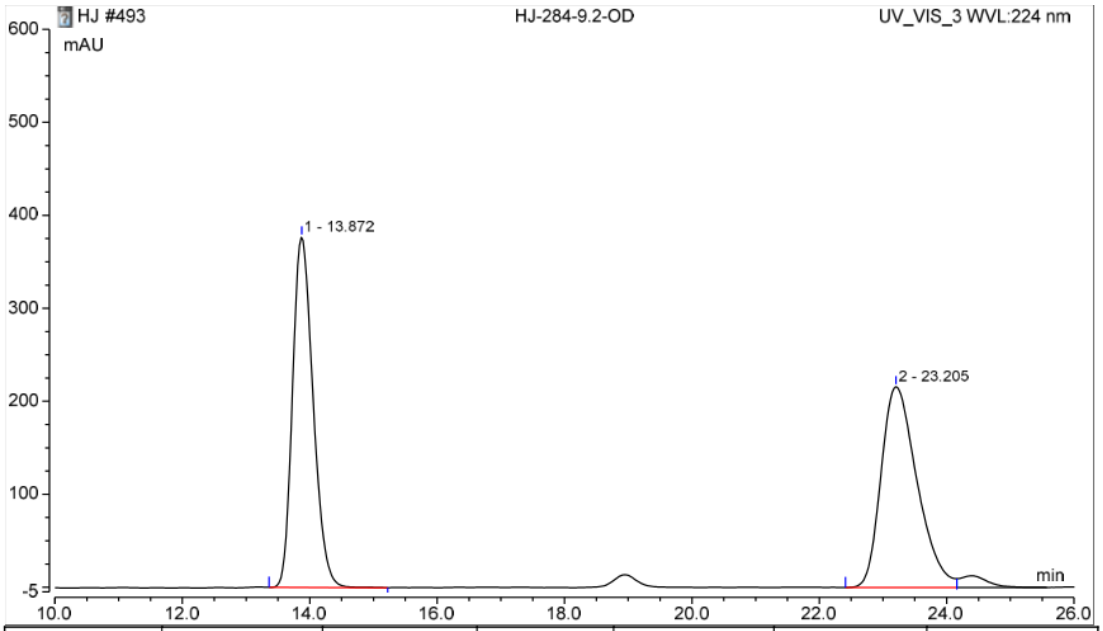
**3k**


7.60
7.59
7.57
7.56
7.27
6.90
6.89
6.87
6.86
5.00
5.00
3.80
3.68
3.53
3.49
3.48
3.43
2.55
2.54
0.00
1.97
2.00
0.97
3.15
6.00
4.02
0.93
10.0 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
f1 (ppm)


171.42
159.56
129.73
129.47
113.80
79.65
77.48
77.16
76.84
76.03
57.35
55.35
52.14
51.73
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

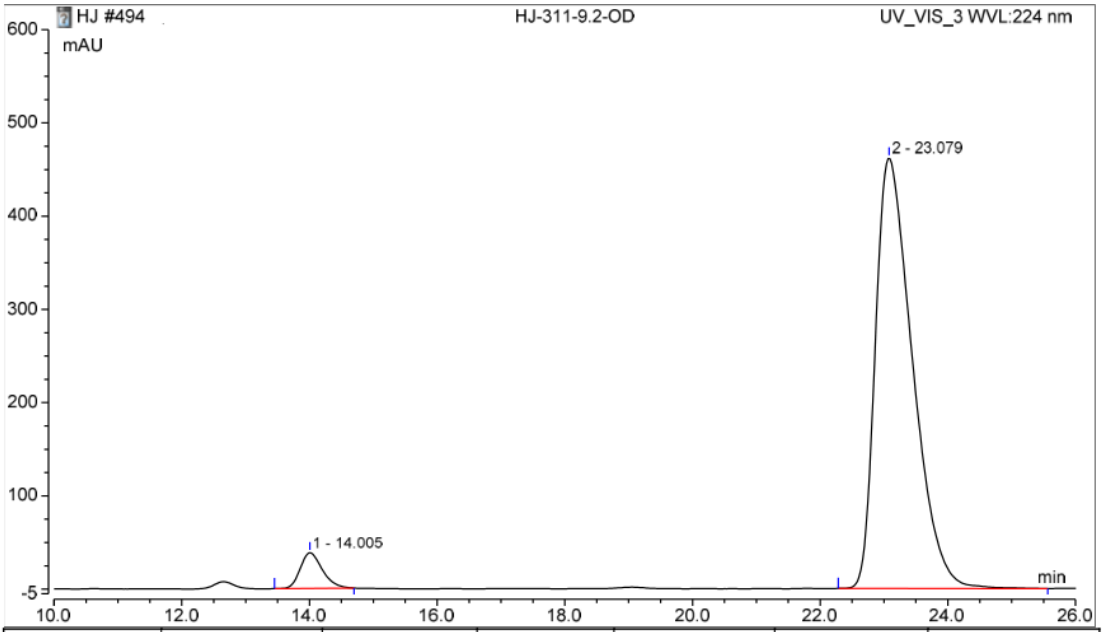
**Compound (-)-3k:** OD-H, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 224 nm

## HPLC trace of *rac*-3k

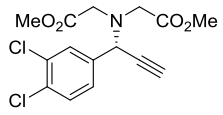



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 13.872 | 140.903 | 376.772 | 49.93 | 63.59 | n.a. |
| 2 | 23.205 | 141.299 | 215.772 | 50.07 | 36.41 | n.a. |

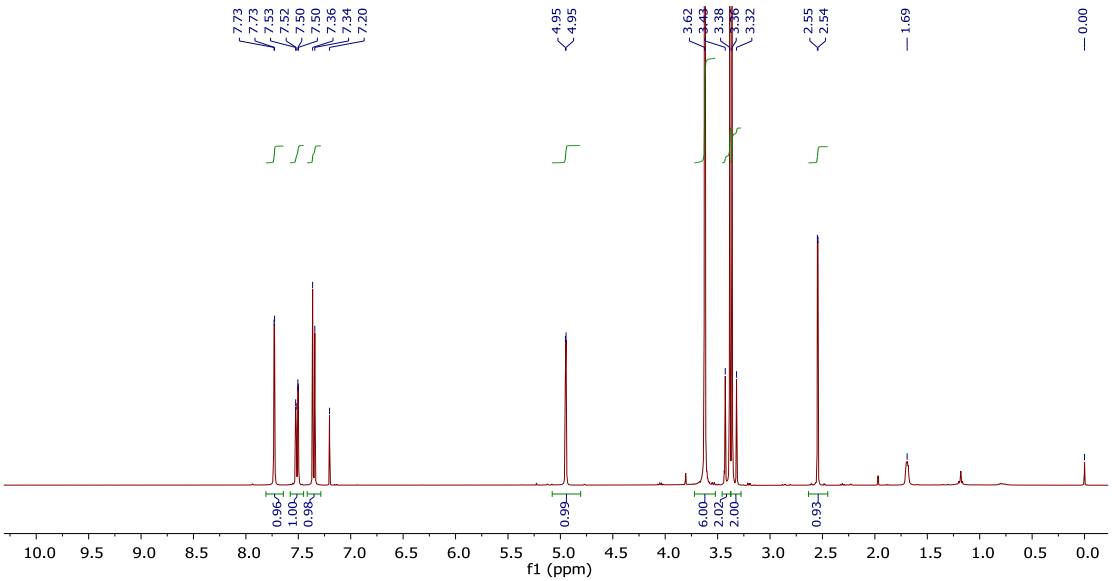
## HPLC trace of 3k

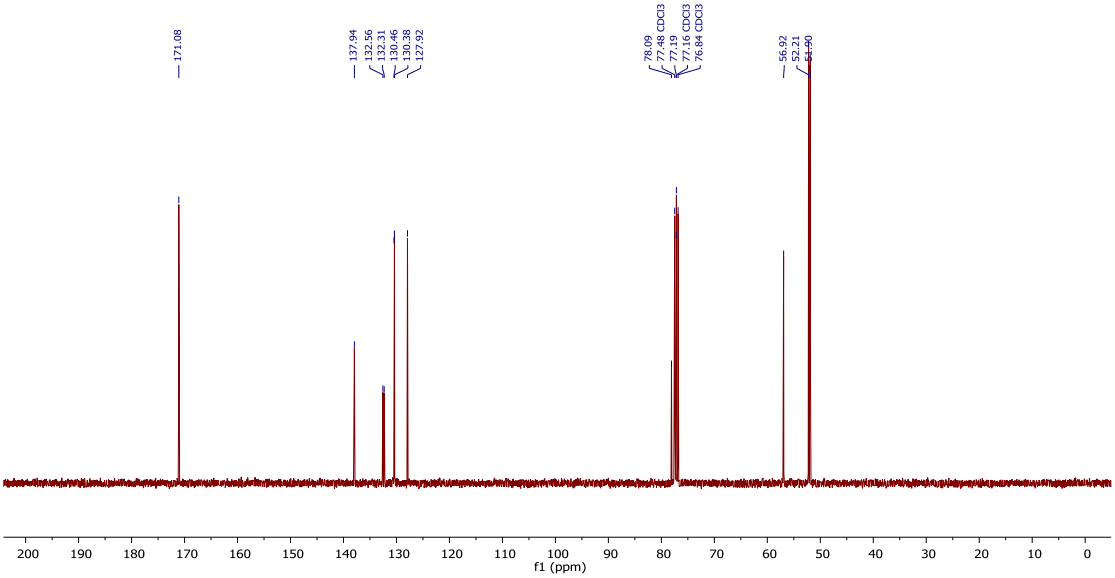



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 14.005 | 15.353 | 38.282 | 4.73 | 7.66 | n.a. |
| 2 | 23.079 | 309.466 | 461.678 | 95.27 | 92.34 | n.a. |


MeO2C
N
CO2Me
Cl
Cl

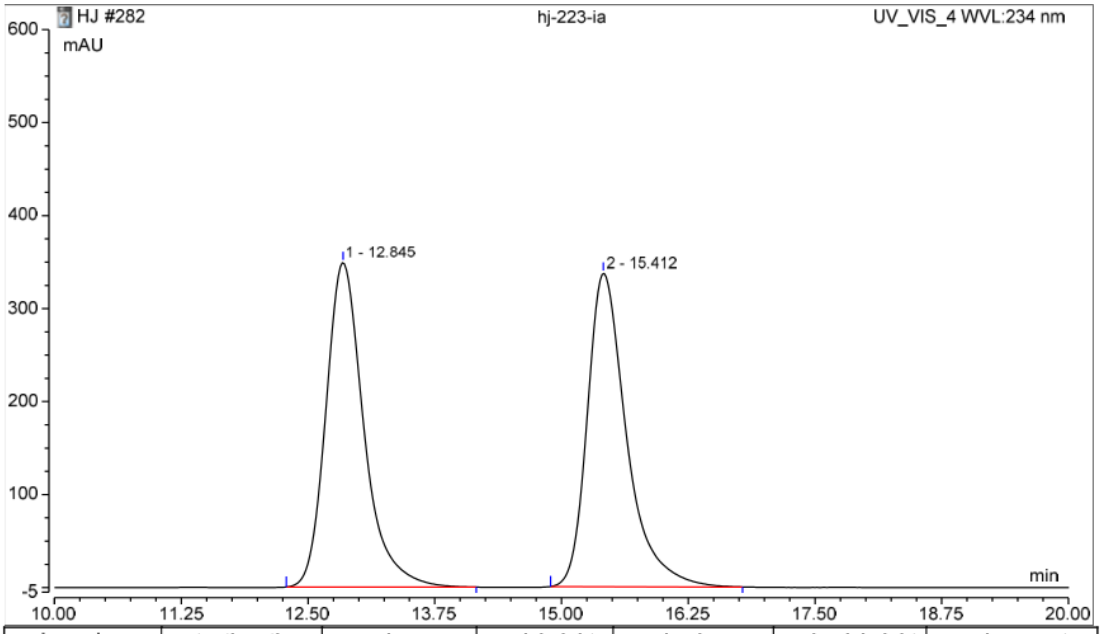
**3l**


7.73
7.73
7.53
7.52
7.50
7.50
7.36
7.34
7.20
4.95
4.95
3.62
3.43
3.38
3.36
3.32
2.55
2.54
1.69
0.00
0.96
1.00
0.98
0.99
6.00
2.02
2.00
0.93
f1 (ppm)


171.08
137.94
132.56
132.31
130.46
130.38
127.92
78.09
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.92
52.21
51.90
f1 (ppm)

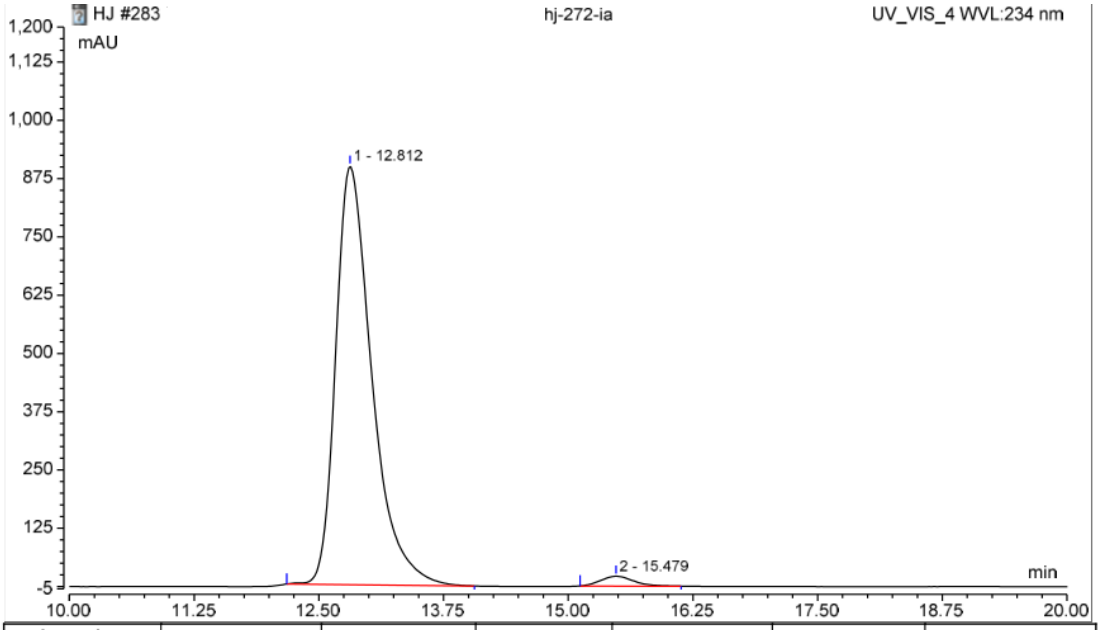
**Compound (-)-3l:** IA, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 234 nm

## HPLC trace of *rac*-3l

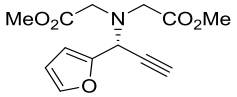



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 12.845 | 151.336 | 349.001 | 50.07 | 50.87 | n.a. |
| 2 | 15.412 | 150.935 | 337.021 | 49.93 | 49.13 | n.a. |

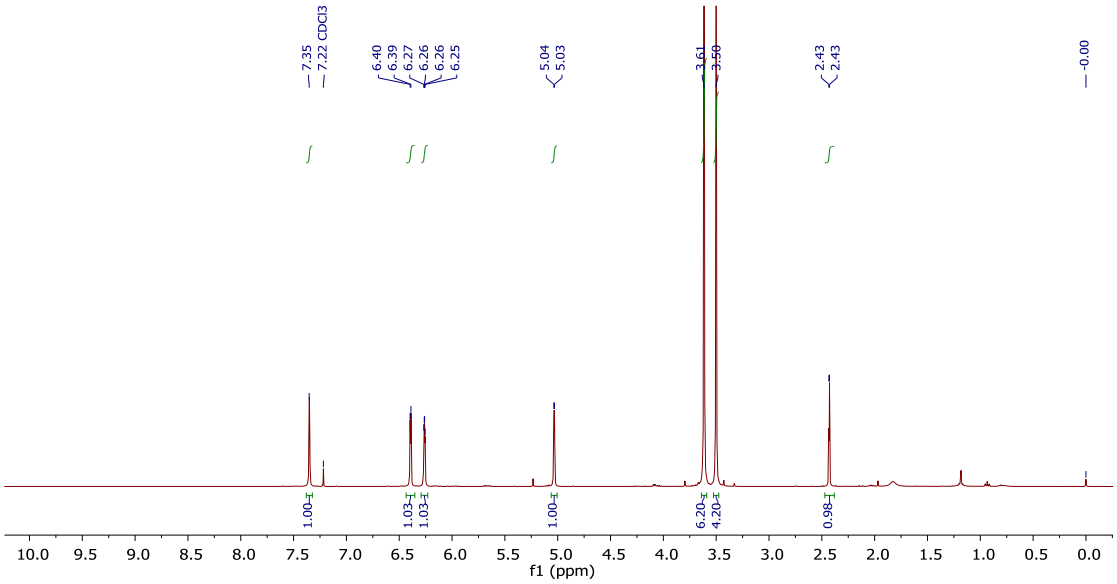
## HPLC trace of 3l

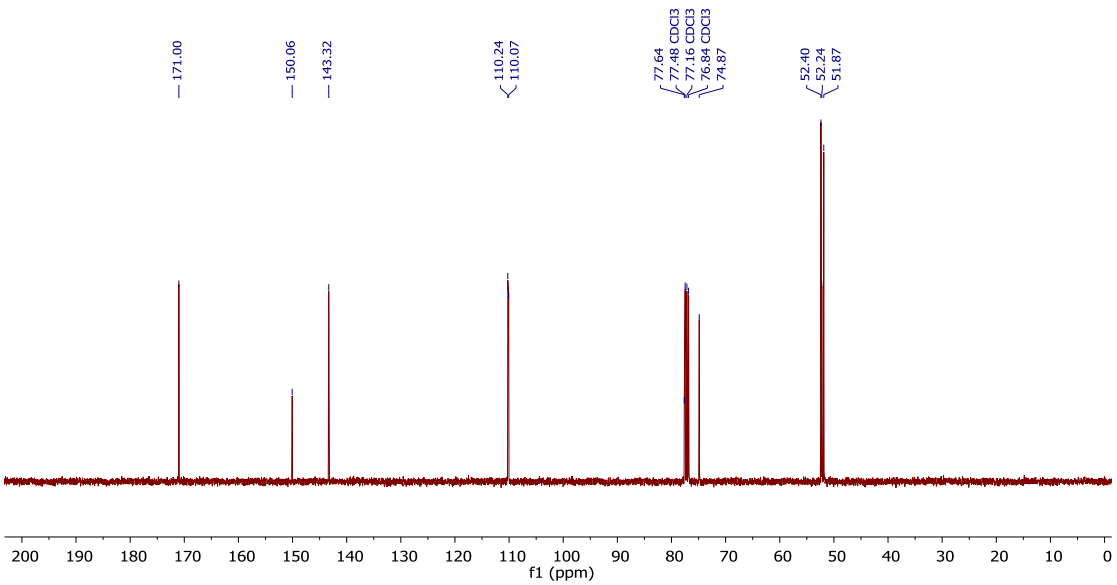



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 12.812 | 377.179 | 897.440 | 97.94 | 97.72 | n.a. |
| 2 | 15.479 | 7.937 | 20.967 | 2.06 | 2.28 | n.a. |


MeO2C
N
CO2Me
O

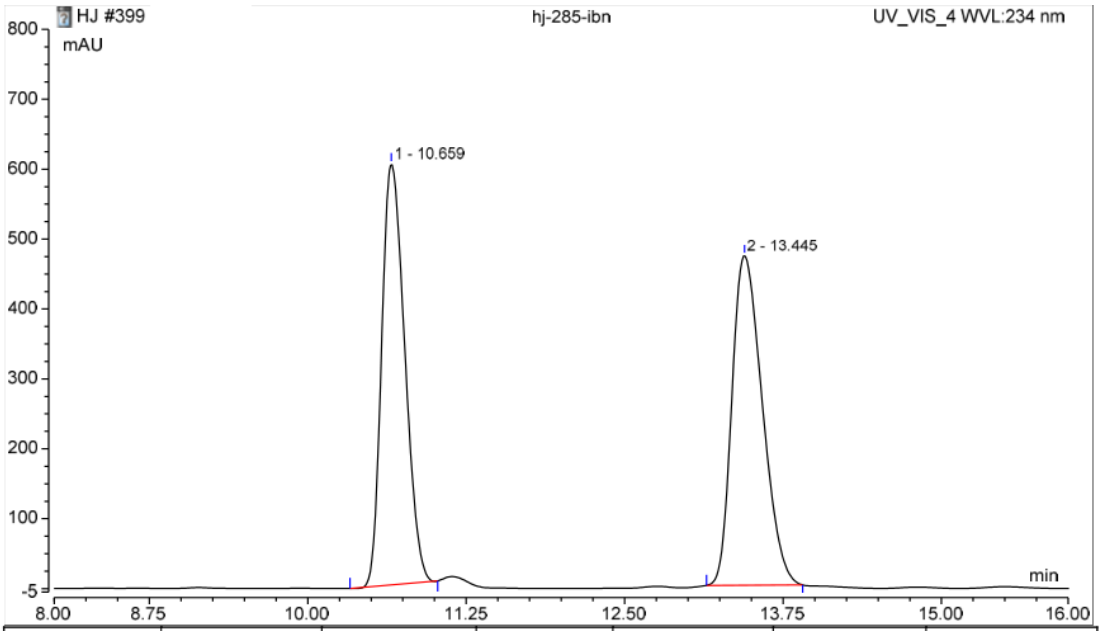
**3m**


7.35
7.22 CDCl3
6.40
6.39
6.27
6.26
6.26
6.25
5.04
5.03
3.61
3.50
2.43
2.43
-0.00
1.00
1.03
1.03
1.00
6.20
4.20
0.98
10.0 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
f1 (ppm)


171.00
150.06
143.32
110.24
110.07
77.64
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.87
52.40
52.24
51.87
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

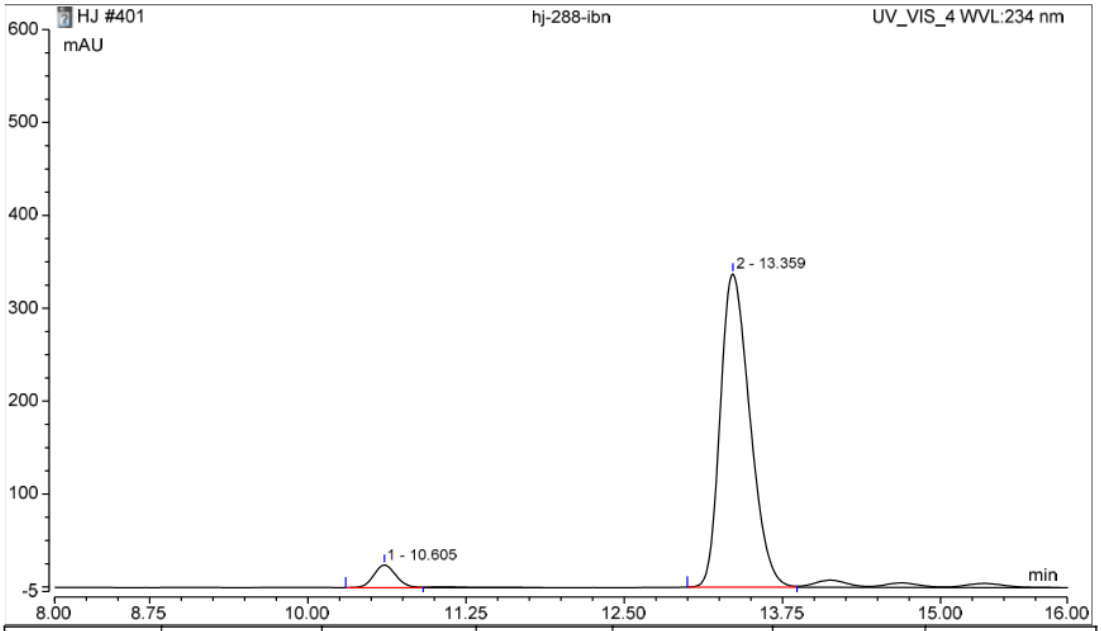
**Compound (-)-3m:** IBN-5, hexane/$^{i}$PrOH = 90/10, v = 1.0 mL/min, λ = 234 nm

## HPLC trace of *rac*-3m

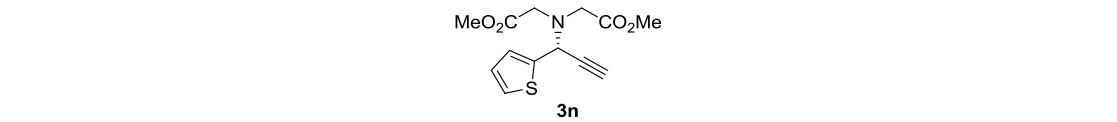



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 10.659 | 126.816 | 602.487 | 49.19 | 56.09 | n.a. |
| 2 | 13.445 | 131.009 | 471.567 | 50.81 | 43.91 | n.a. |

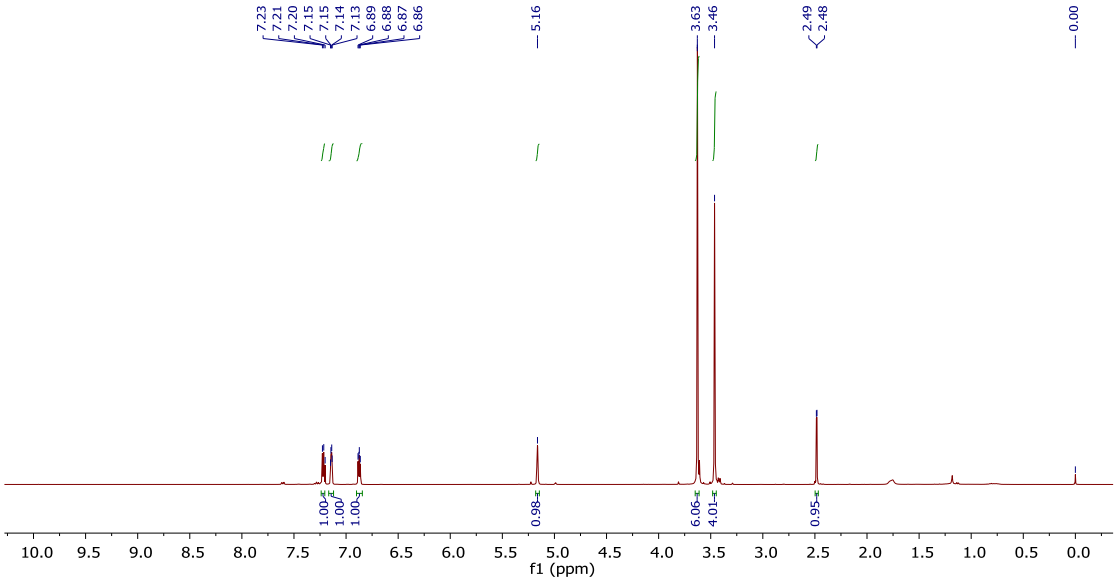
## HPLC trace of 3m

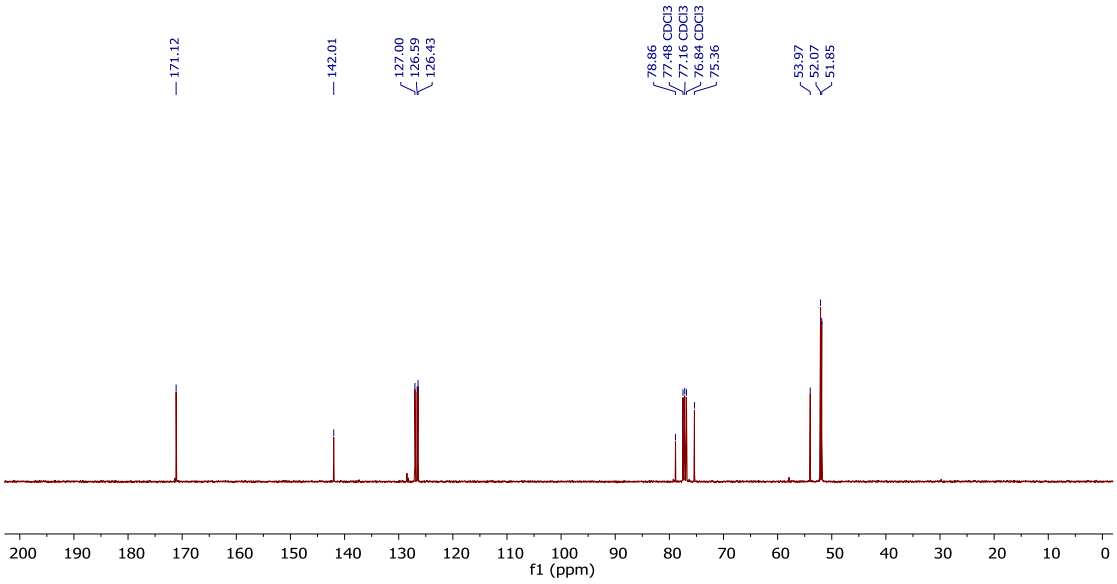



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 10.605 | 4.948 | 24.274 | 5.13 | 6.71 | n.a. |
| 2 | 13.359 | 91.424 | 337.250 | 94.87 | 93.29 | n.a. |


MeO2C
N
CO2Me
S

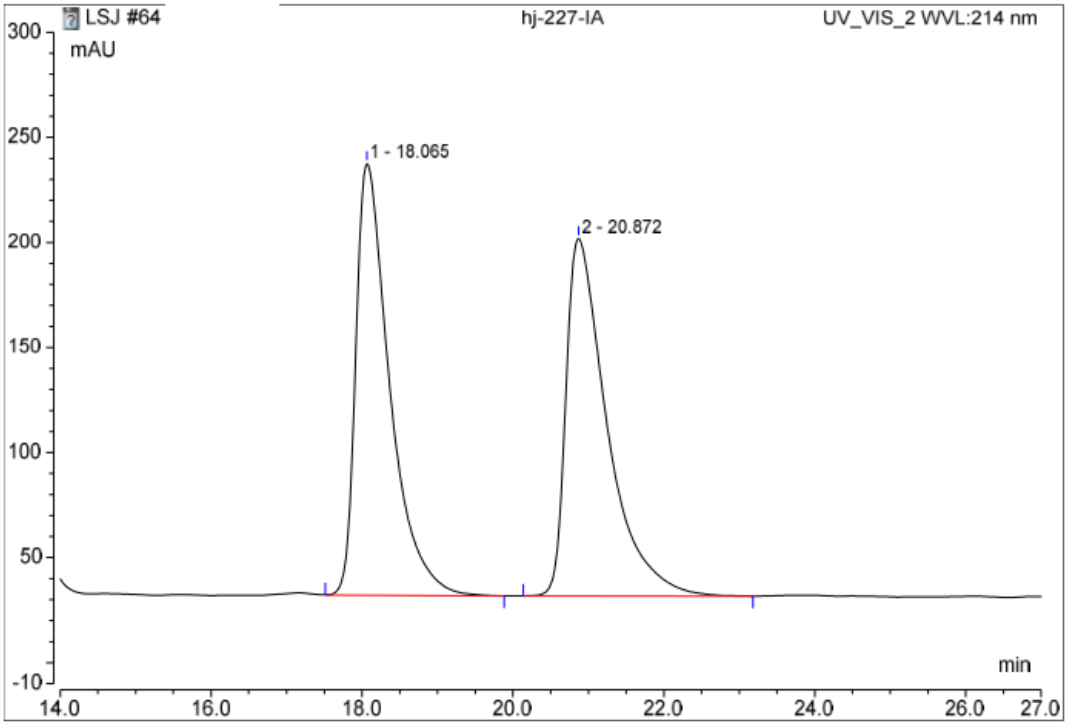
**3n**


7.23
7.21
7.20
7.15
7.15
7.14
7.13
6.89
6.88
6.87
6.86
5.16
3.63
3.46
2.49
2.48
0.00
1.00
1.00
1.00
0.98
6.06
4.01
0.95
f1 (ppm)


171.12
142.01
127.00
126.59
126.43
78.86
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.36
53.97
52.07
51.85
f1 (ppm)

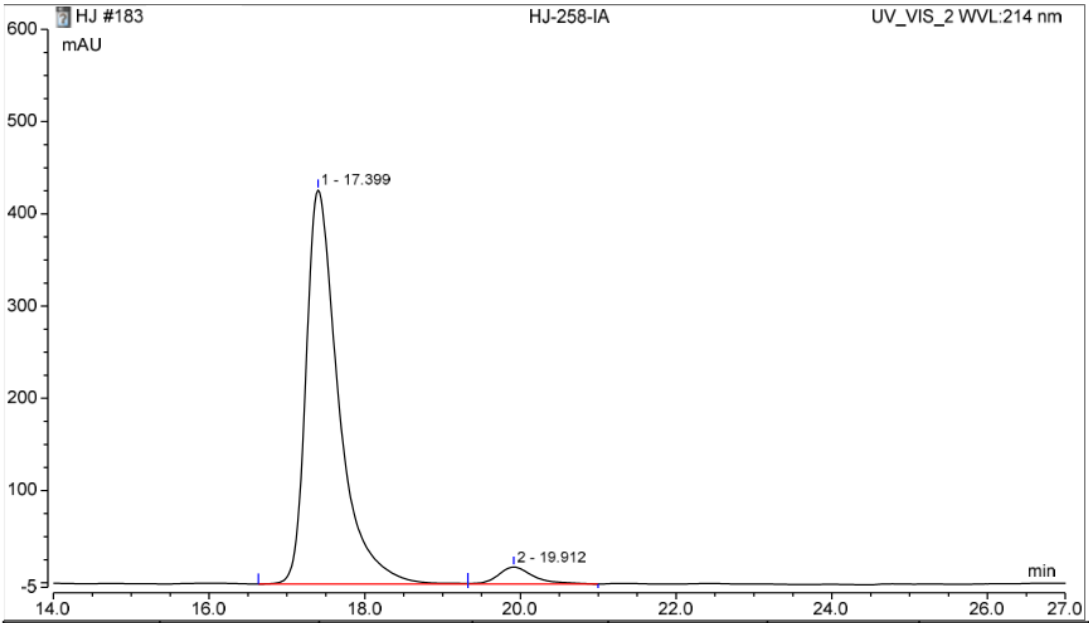
**Compound (-)-3n:** IA, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-3n

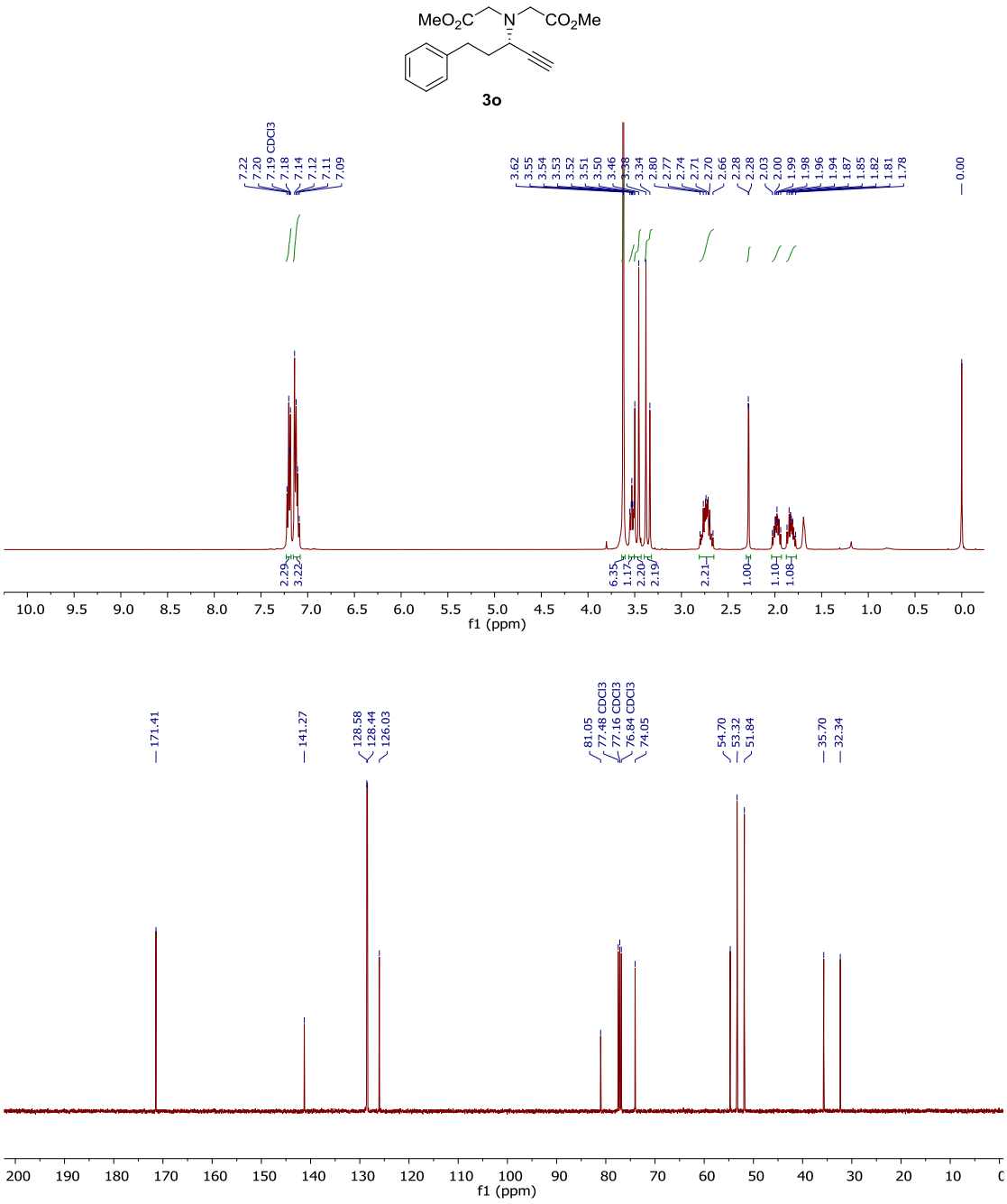



| peak.number | peak.name<br>min | peak.area<br>mAU*min | peak.height<br>mAU | peak.rel_area<br>% | peak.rel_height<br>% |
|---|---|---|---|---|---|
| 1 | 18.065 | 106.666 | 205.645 | 49.87 | 54.72 |
| 2 | 20.872 | 107.206 | 170.195 | 50.13 | 45.28 |

## HPLC trace of 3n

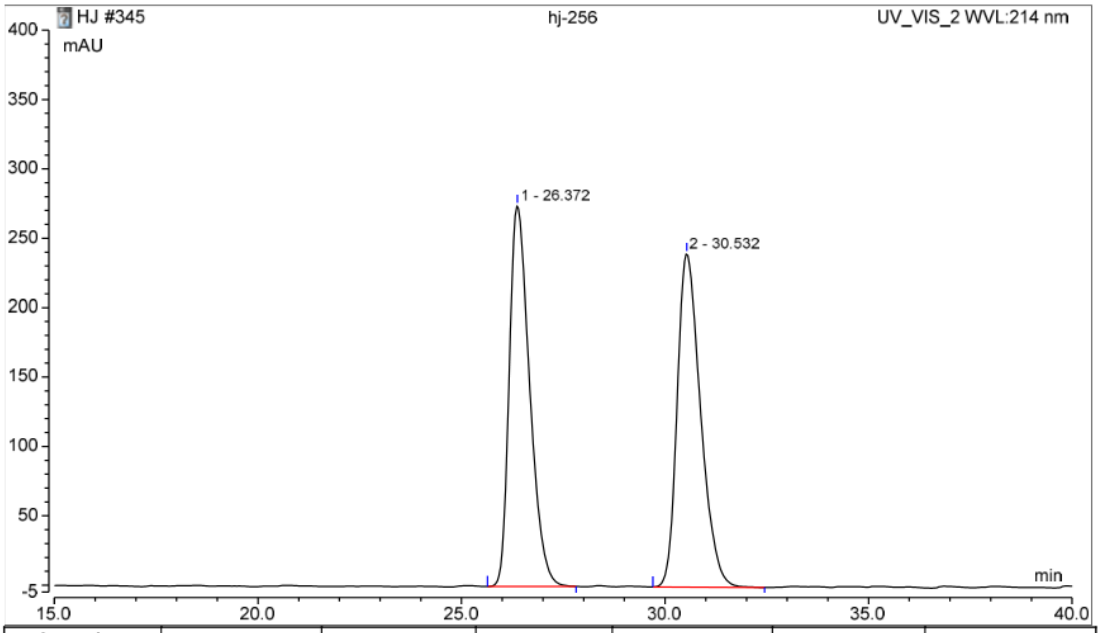



| peak.number | retention_time<br>min | peak.area<br>mAU*min | peak.height<br>mAU | peak.rel_area<br>% | peak.rel_height<br>% | peak.amount<br>n.a. |
|---|---|---|---|---|---|---|
| 1 | 17.399 | 206.766 | 427.079 | 95.53 | 95.87 | n.a. |
| 2 | 19.912 | 9.666 | 18.385 | 4.47 | 4.13 | n.a. |


MeO2C
N
CO2Me
3o
7.22
7.20
7.19 CDCl3
7.18
7.14
7.12
7.11
7.09
3.62
3.55
3.54
3.53
3.52
3.51
3.50
3.46
3.38
3.34
2.80
2.77
2.74
2.71
2.70
2.66
2.28
2.28
2.03
2.00
1.99
1.98
1.96
1.94
1.87
1.85
1.82
1.81
1.78
0.00
2.29
3.22
6.35
1.17
2.20
2.19
2.21
1.00
1.10
1.08
f1 (ppm)
171.41
141.27
128.58
128.44
126.03
81.05
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.05
54.70
53.32
51.84
35.70
32.34
f1 (ppm)

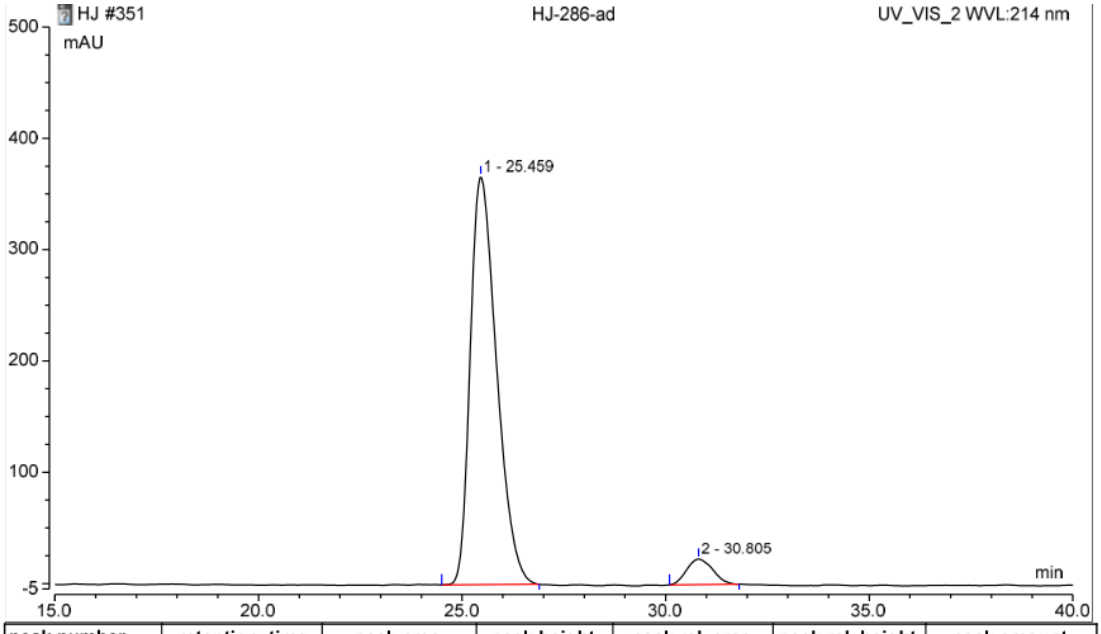
**Compound (-)-3o:** AD-H, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-3o

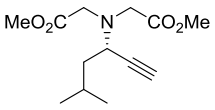



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 26.372 | 158.978 | 274.660 | 49.82 | 53.34 | n.a. |
| 2 | 30.532 | 160.159 | 240.308 | 50.18 | 46.66 | n.a. |

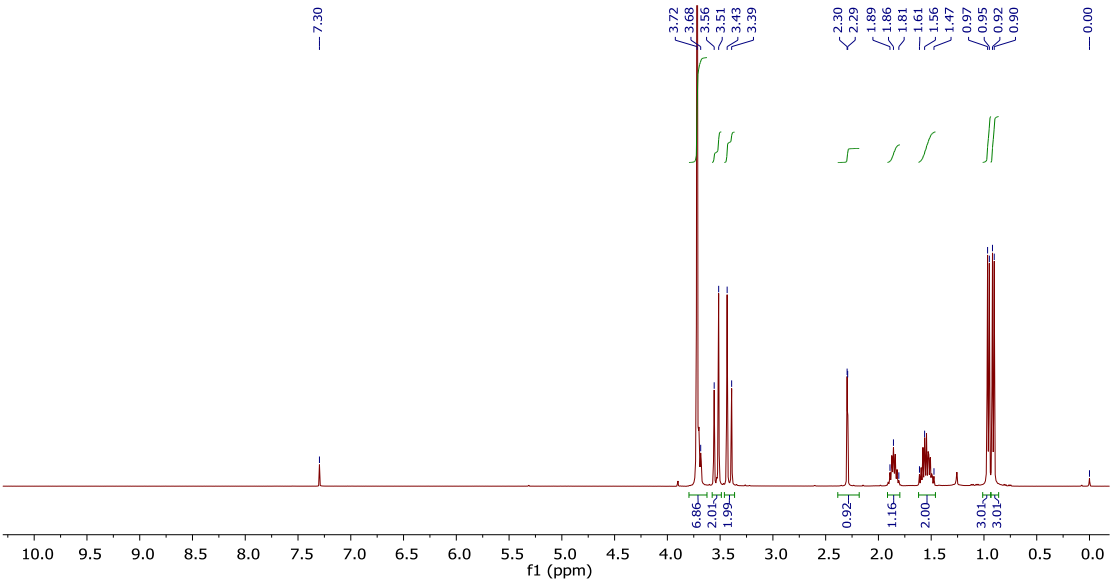
## HPLC trace of 3o

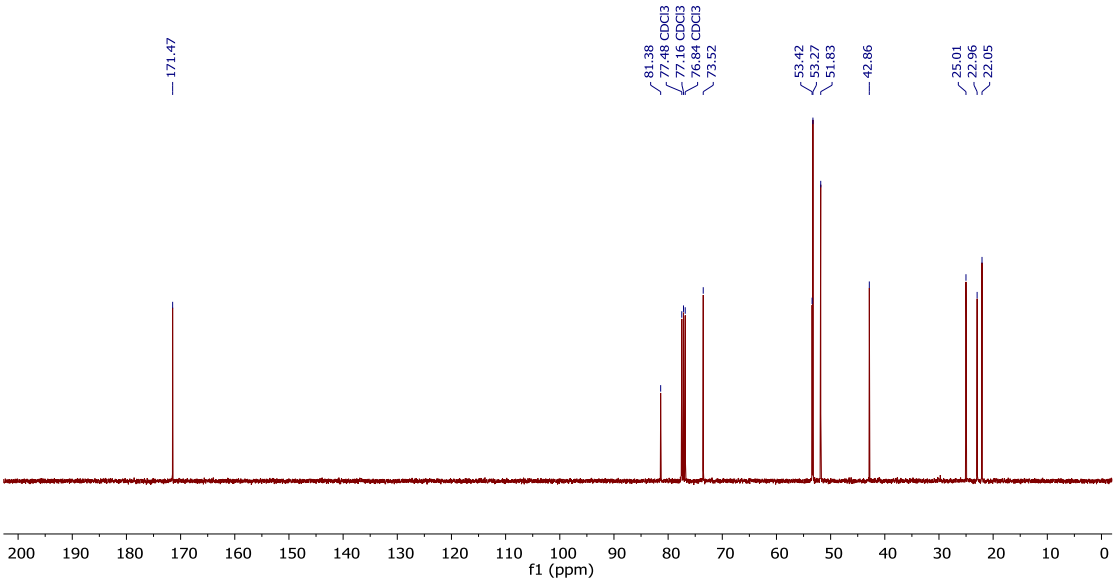



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 25.459 | 274.418 | 366.578 | 94.22 | 94.14 | n.a. |
| 2 | 30.805 | 16.839 | 22.817 | 5.78 | 5.86 | n.a. |


MeO2C
N
CO2Me

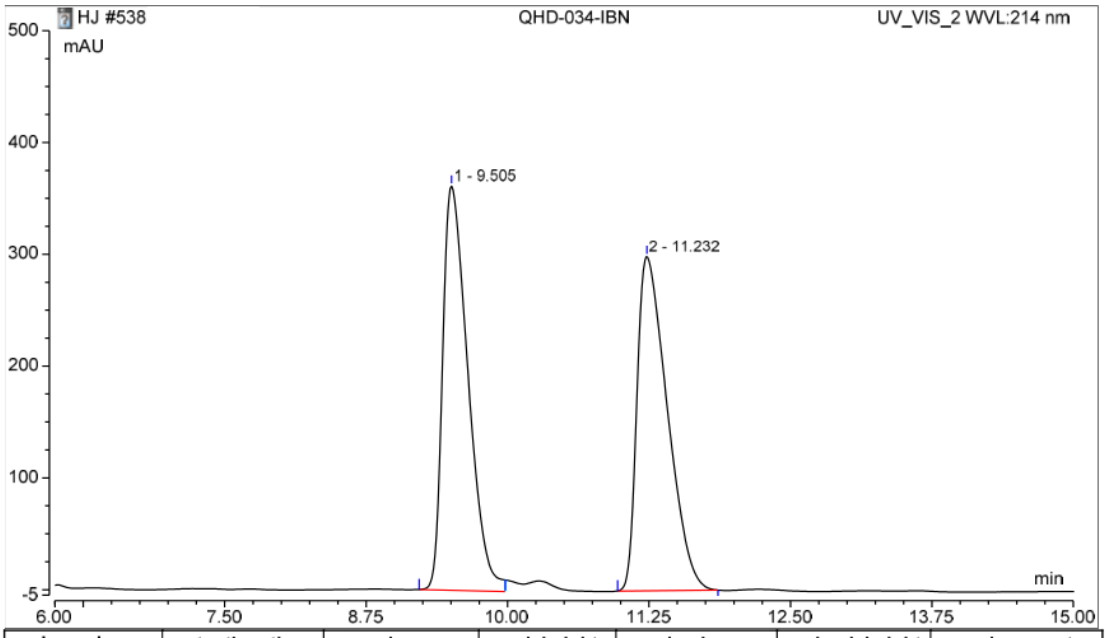
**3p**


7.30
3.72
3.68
3.56
3.51
3.43
3.39
2.30
2.29
1.89
1.86
1.81
1.61
1.56
1.47
0.97
0.95
0.92
0.90
0.00
6.86
2.01
1.99
0.92
1.16
2.00
3.01
3.01
f1 (ppm)


171.47
81.38
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
73.52
53.42
53.27
51.83
42.86
25.01
22.96
22.05
f1 (ppm)

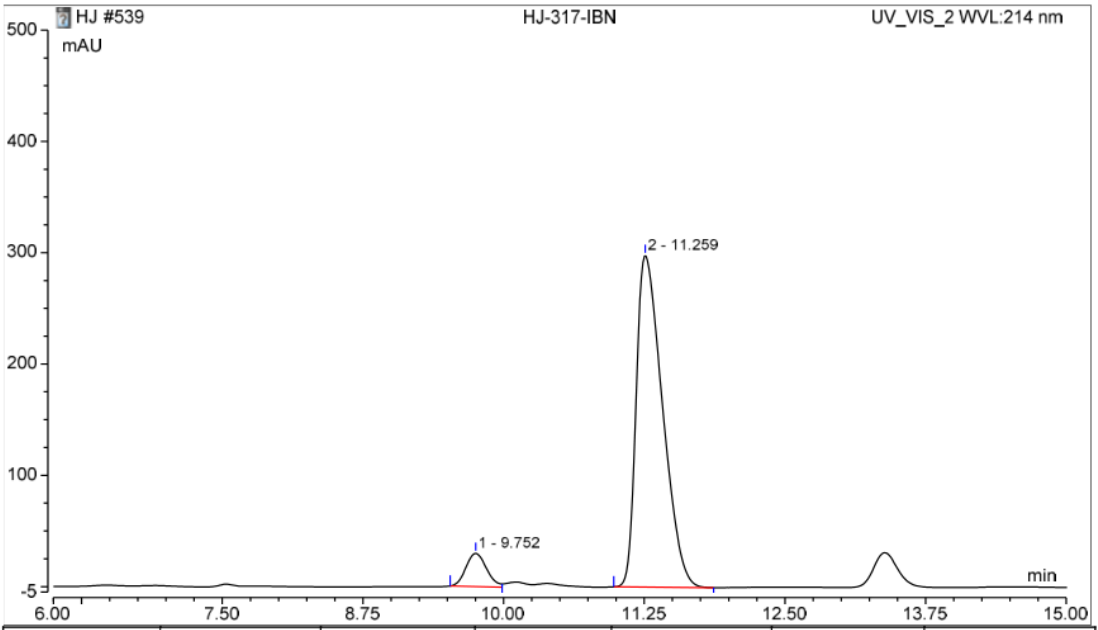
**Compound (-)-3p:** IBN-5, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-3p

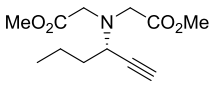



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 9.505 | 93.899 | 361.586 | 50.37 | 54.73 | n.a. |
| 2 | 11.232 | 92.521 | 299.038 | 49.63 | 45.27 | n.a. |

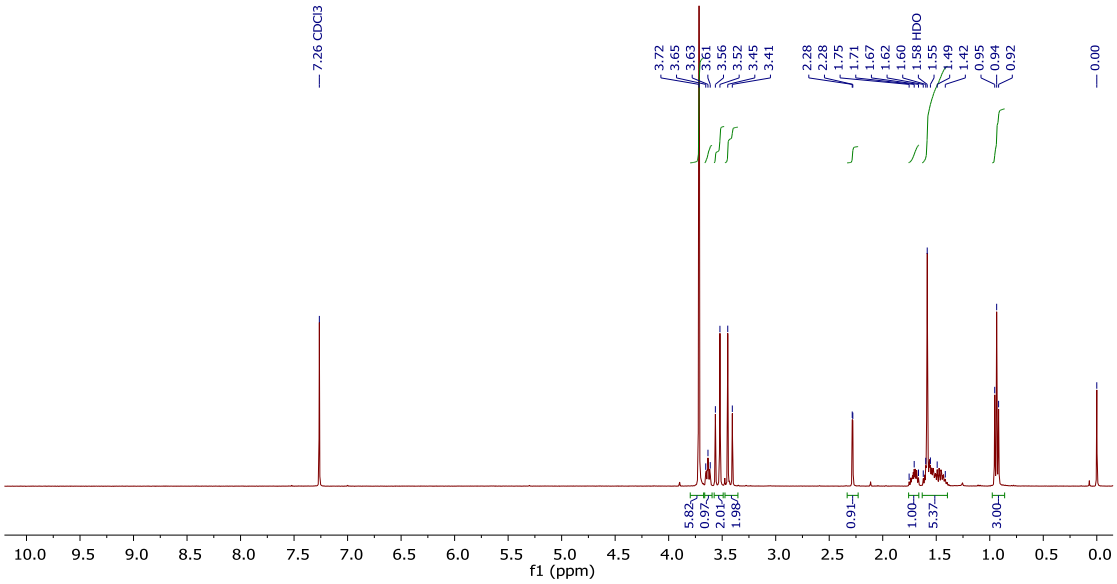
## HPLC trace of 3p

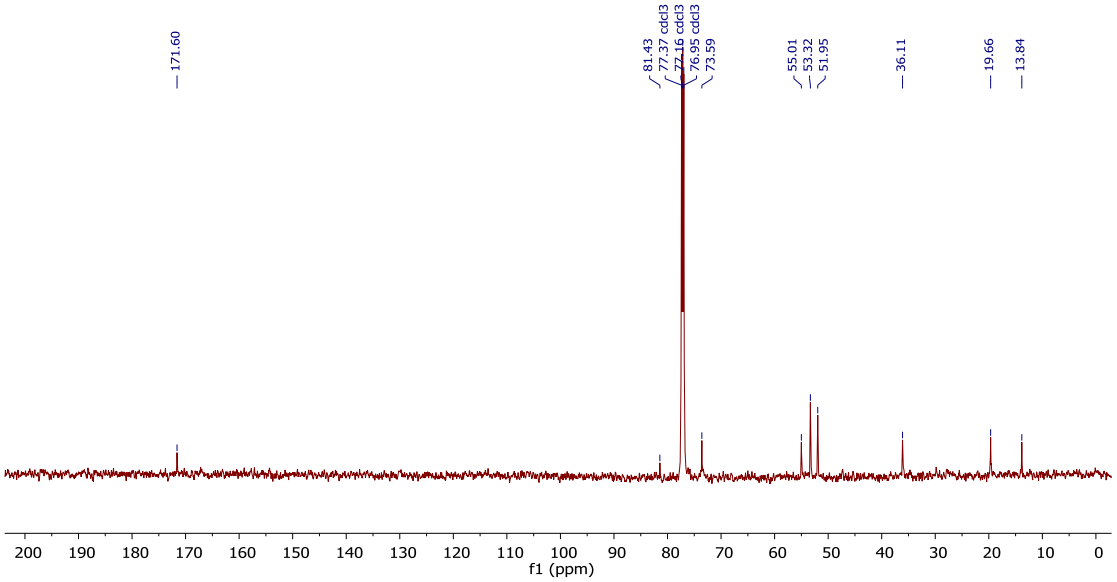



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 9.752 | 6.342 | 29.832 | 7.29 | 9.10 | n.a. |
| 2 | 11.259 | 80.630 | 298.083 | 92.71 | 90.90 | n.a. |


MeO2C
N
CO2Me

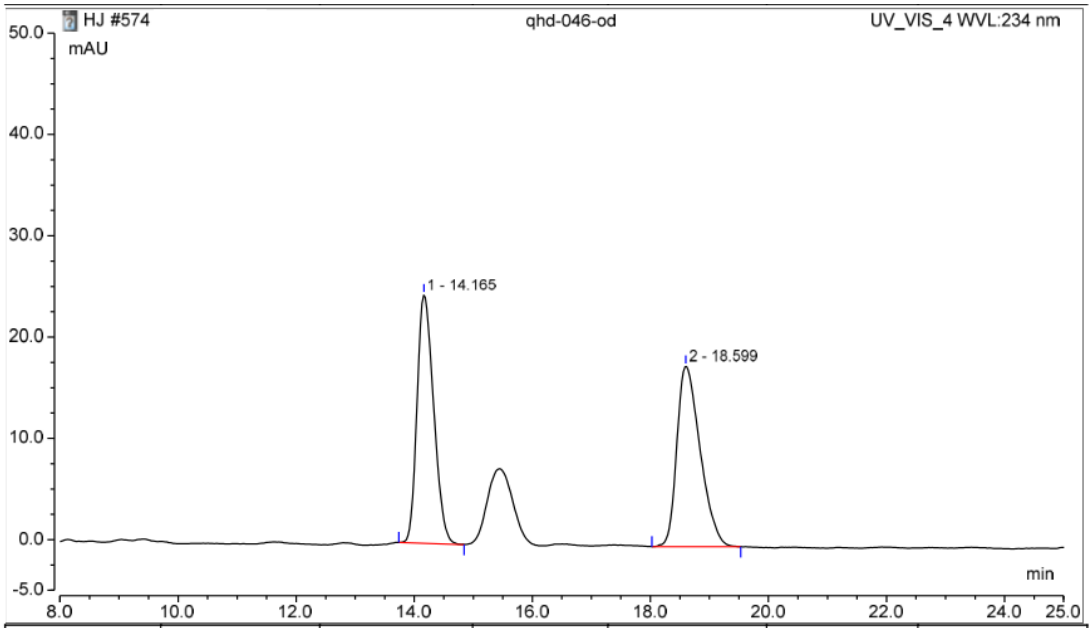
**3q**


7.26 CDCl3
3.72
3.65
3.63
3.61
3.56
3.52
3.45
3.41
2.28
2.28
1.75
1.71
1.67
1.62
1.60
1.58 HDO
1.55
1.49
1.42
0.95
0.94
0.92
0.00
5.82
0.97
2.01
1.98
0.91
1.00
5.37
3.00
f1 (ppm)


171.60
81.43
77.37 cdcl3
77.16 cdcl3
76.95 cdcl3
73.59
55.01
53.32
51.95
36.11
19.66
13.84
f1 (ppm)

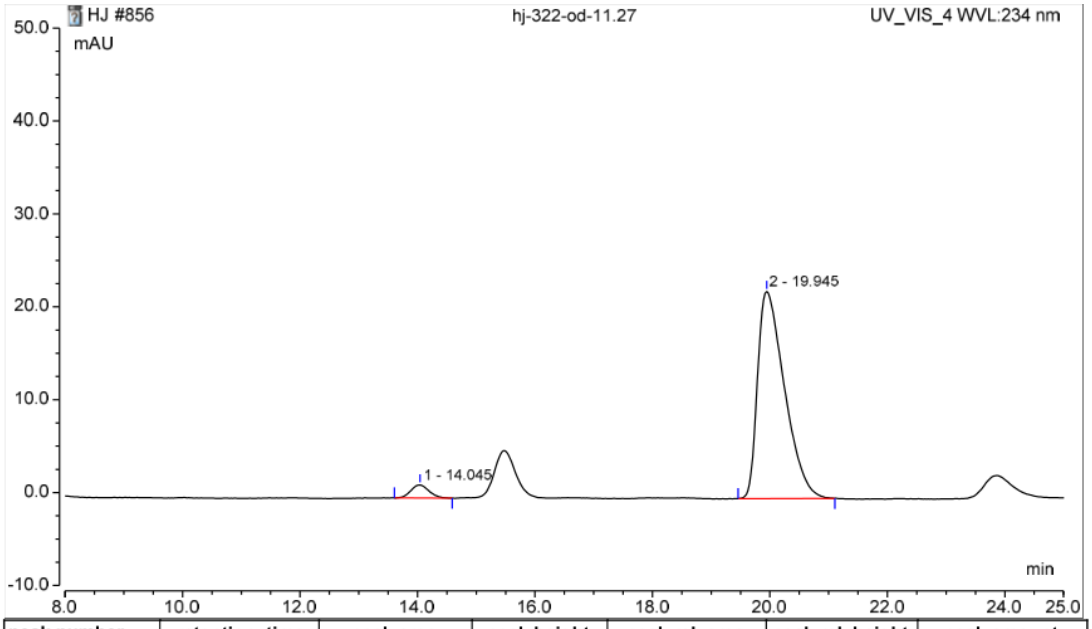
**Compound (-)-3q:** OD-H, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 234 nm

## HPLC trace of *rac*-3q

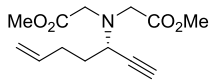



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 14.165 | 8.005 | 24.542 | 49.54 | 57.90 | n.a. |
| 2 | 18.599 | 8.153 | 17.842 | 50.46 | 42.10 | n.a. |

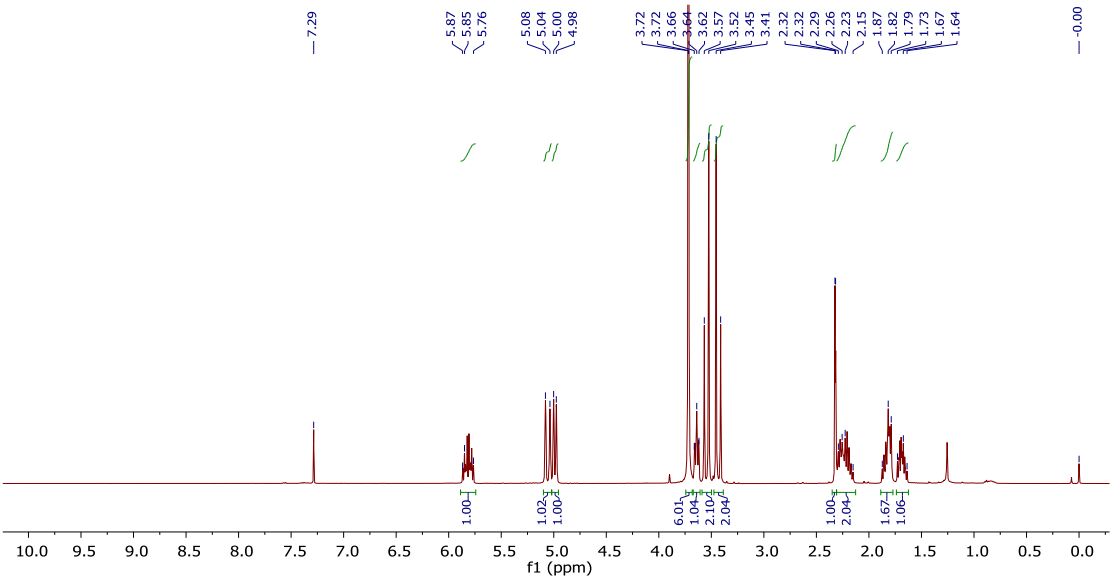
## HPLC trace of 3q

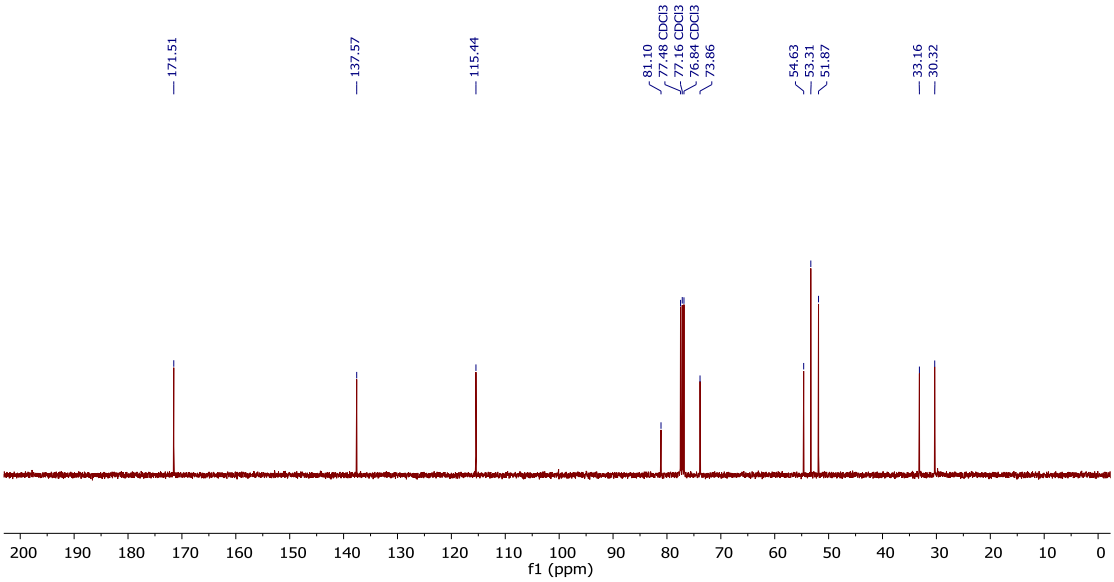



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 14.045 | 0.499 | 1.403 | 4.04 | 5.92 | n.a. |
| 2 | 19.945 | 11.851 | 22.287 | 95.96 | 94.08 | n.a. |


MeO2C
N
CO2Me

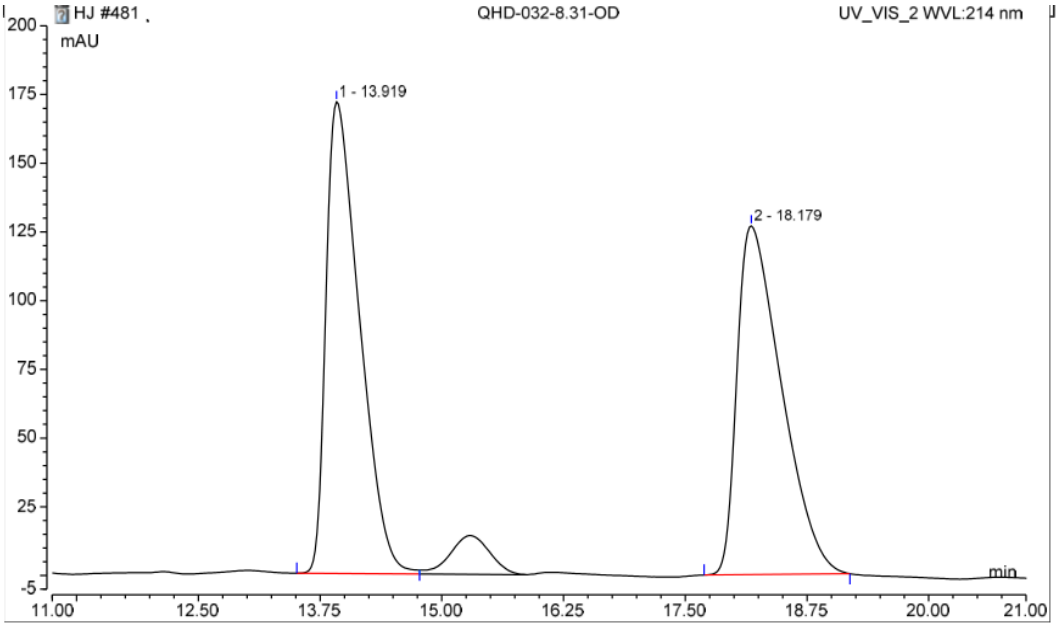
**3r**


7.29
5.87
5.85
5.76
5.08
5.04
5.00
4.98
3.72
3.72
3.66
3.64
3.62
3.57
3.52
3.45
3.41
2.32
2.32
2.29
2.26
2.23
2.15
1.87
1.82
1.79
1.73
1.67
1.64
0.00
1.00
1.02
1.00
6.01
1.04
2.10
2.04
1.00
2.04
1.67
1.06
f1 (ppm)


171.51
137.57
115.44
81.10
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
73.86
54.63
53.31
51.87
33.16
30.32
f1 (ppm)

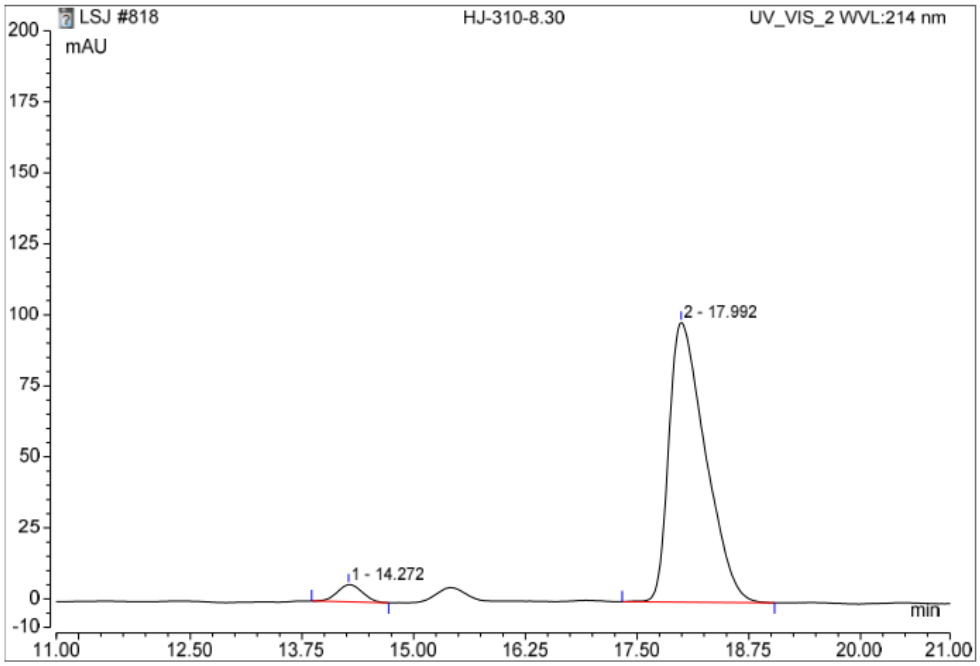
**Compound (-)-3r:** OD-H, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-3r

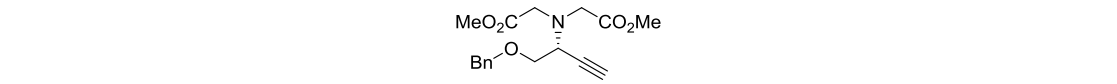



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 13.919 | 68.435 | 171.670 | 50.55 | 57.51 | n.a. |
| 2 | 18.179 | 66.939 | 126.844 | 49.45 | 42.49 | n.a. |

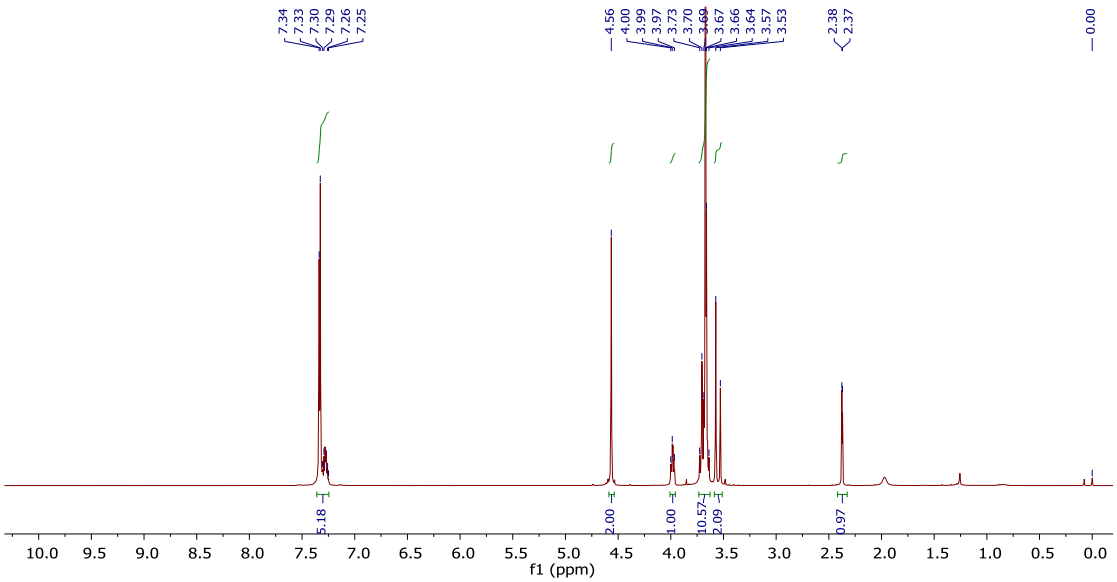
## HPLC trace of 3r

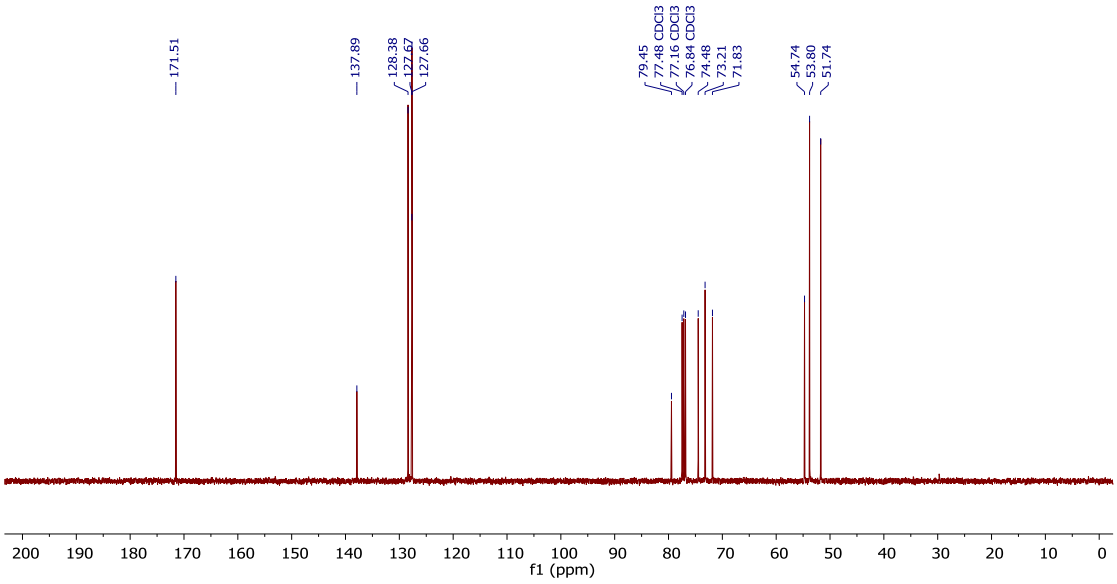



| peak.number | peak.name min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % |
|---|---|---|---|---|---|
| 1 | 14.272 | 1.965 | 6.029 | 4.05 | 5.77 |
| 2 | 17.992 | 46.502 | 98.479 | 95.95 | 94.23 |


MeO2C
N
CO2Me
Bn
O

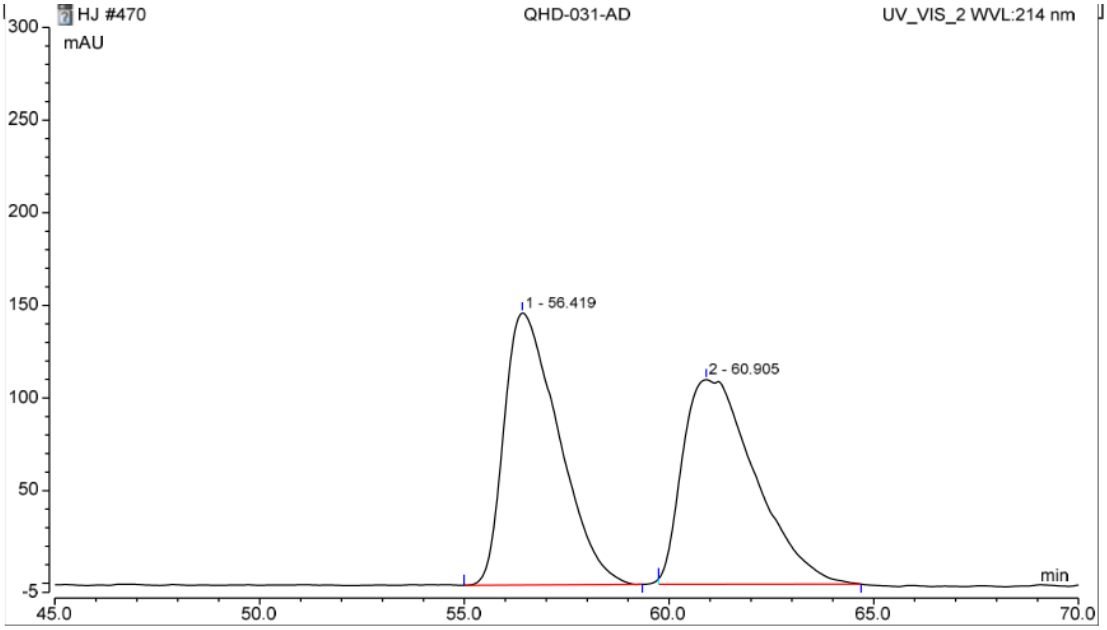
**3s**


7.34
7.33
7.30
7.29
7.26
7.25
4.56
4.00
3.99
3.97
3.73
3.70
3.69
3.67
3.66
3.64
3.57
3.53
2.38
2.37
0.00
5.18
2.00
1.00
10.57
2.09
0.97
f1 (ppm)


171.51
137.89
128.38
127.67
127.66
79.45
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.48
73.21
71.83
54.74
53.80
51.74
f1 (ppm)

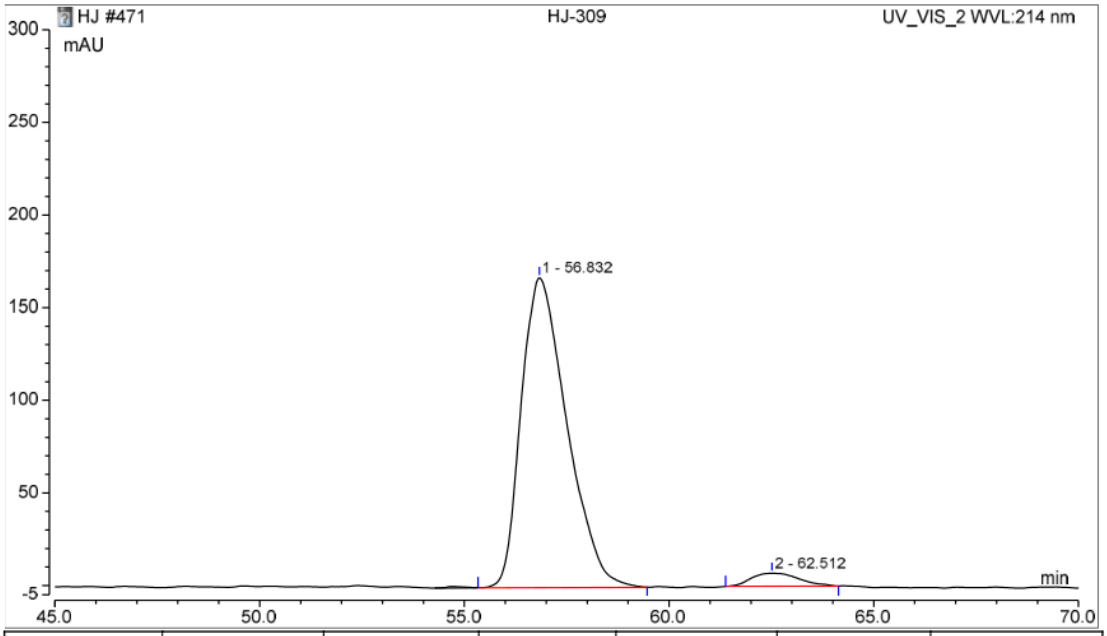
**Compound (-)-3s:** AD-H, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-3s

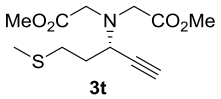



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 56.419 | 226.961 | 146.827 | 49.97 | 57.07 | n.a. |
| 2 | 60.905 | 227.279 | 110.458 | 50.03 | 42.93 | n.a. |

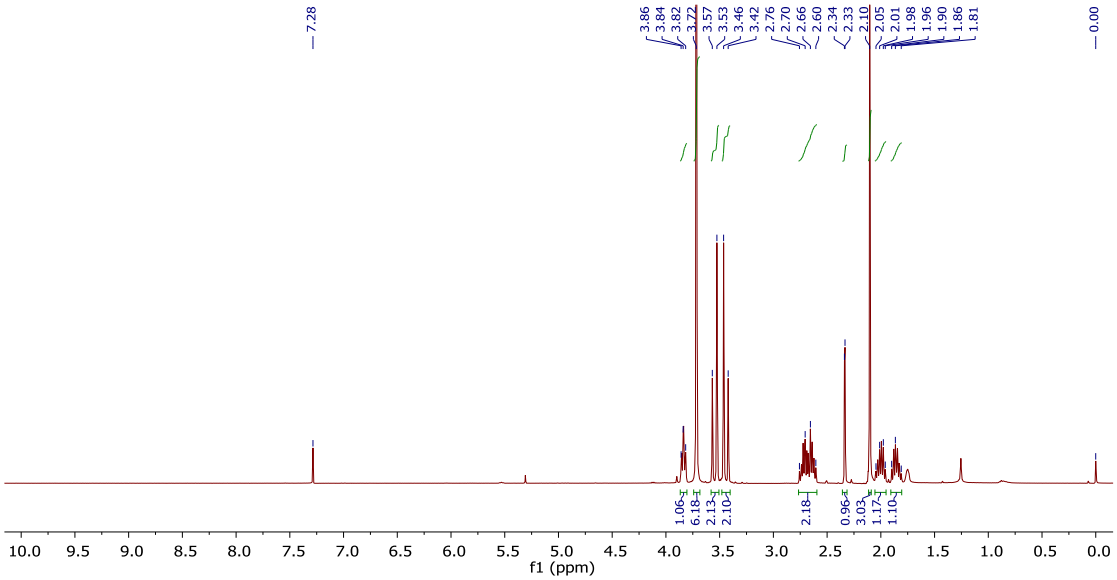
## HPLC trace of 3s

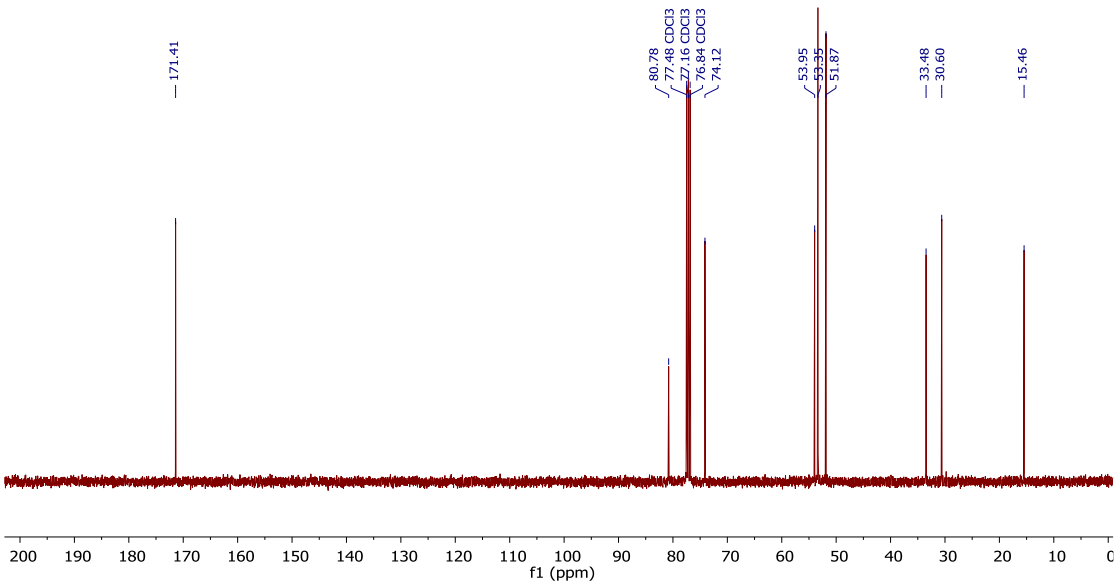



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 56.832 | 215.805 | 167.292 | 95.73 | 95.97 | n.a. |
| 2 | 62.512 | 9.621 | 7.021 | 4.27 | 4.03 | n.a. |


MeO2C
N
CO2Me
S

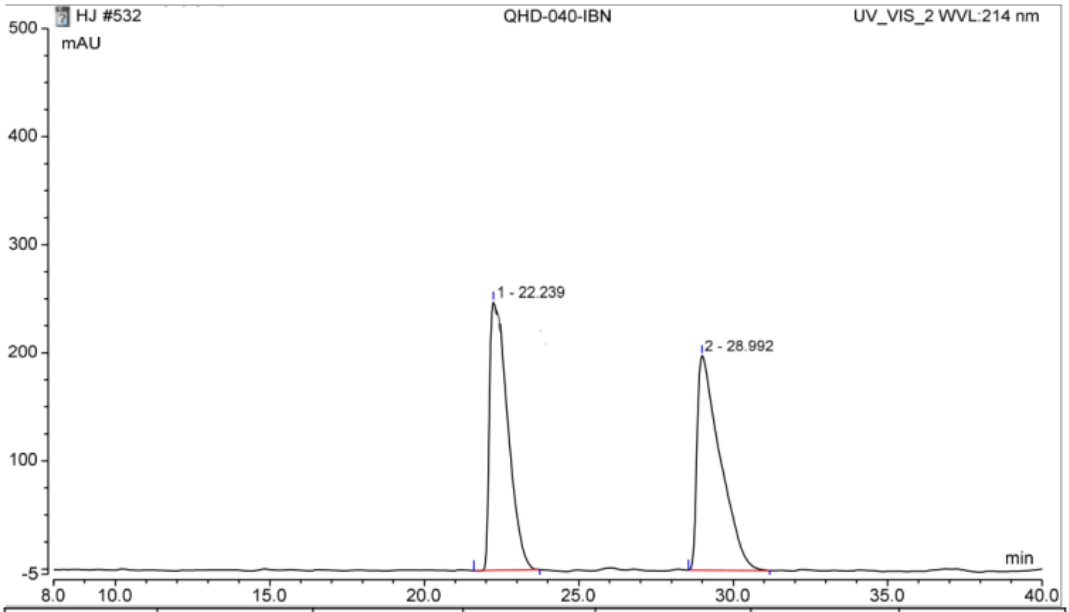
**3t**


7.28
3.86
3.84
3.82
3.72
3.57
3.53
3.46
3.42
2.76
2.70
2.66
2.60
2.34
2.33
2.10
2.05
2.01
1.98
1.96
1.90
1.86
1.81
0.00
1.06
6.18
2.13
2.10
2.18
0.96
3.03
1.17
1.10
f1 (ppm)


171.41
80.78
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.12
53.95
53.35
51.87
33.48
30.60
15.46
f1 (ppm)

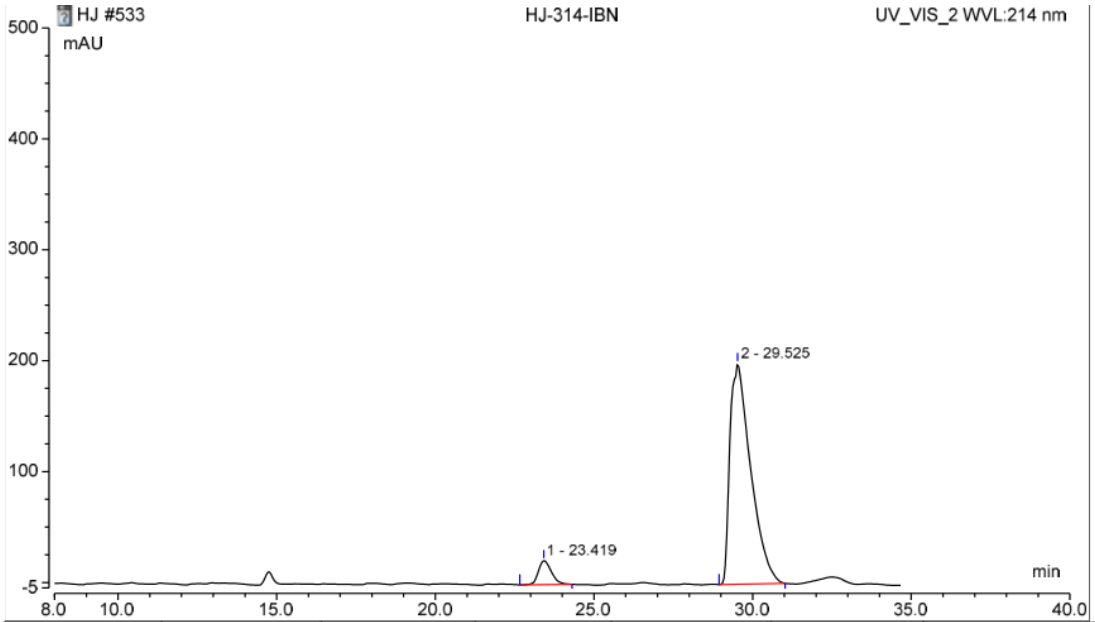
**Compound (-)-3t:** IBN-5, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-3t

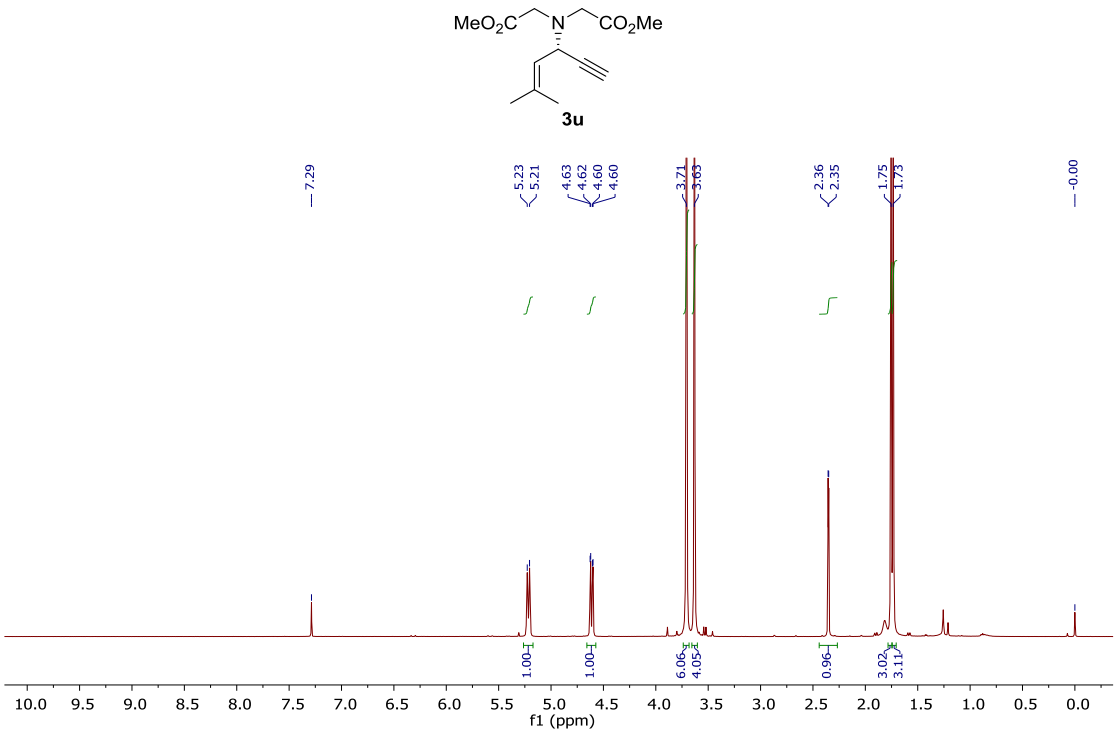


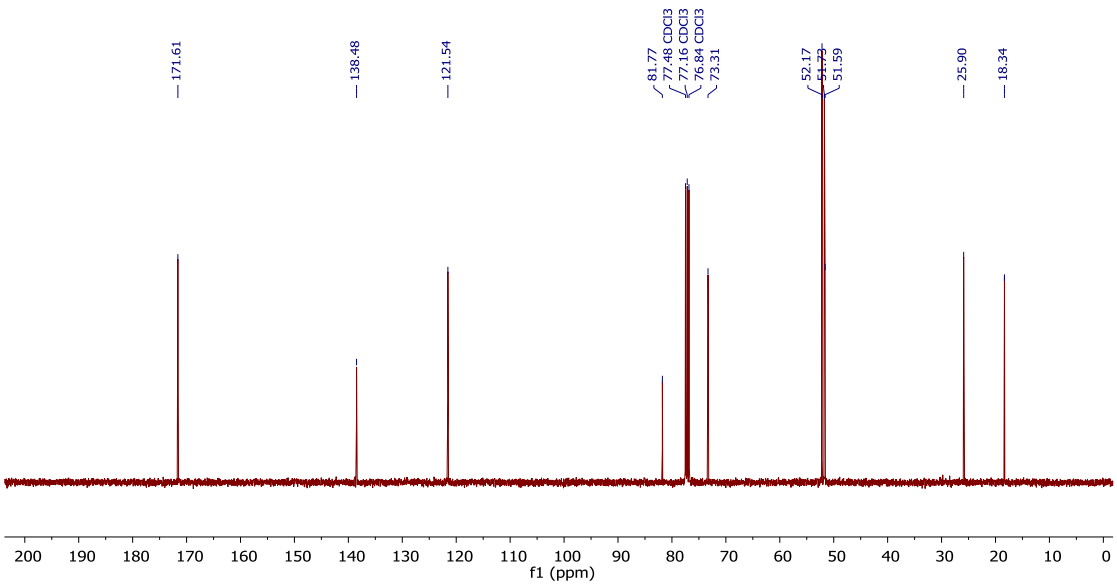

| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 22.239 | 170.197 | 248.215 | 49.84 | 55.55 | n.a. |
| 2 | 28.992 | 171.322 | 198.593 | 50.16 | 44.45 | n.a. |

## HPLC trace of 3t



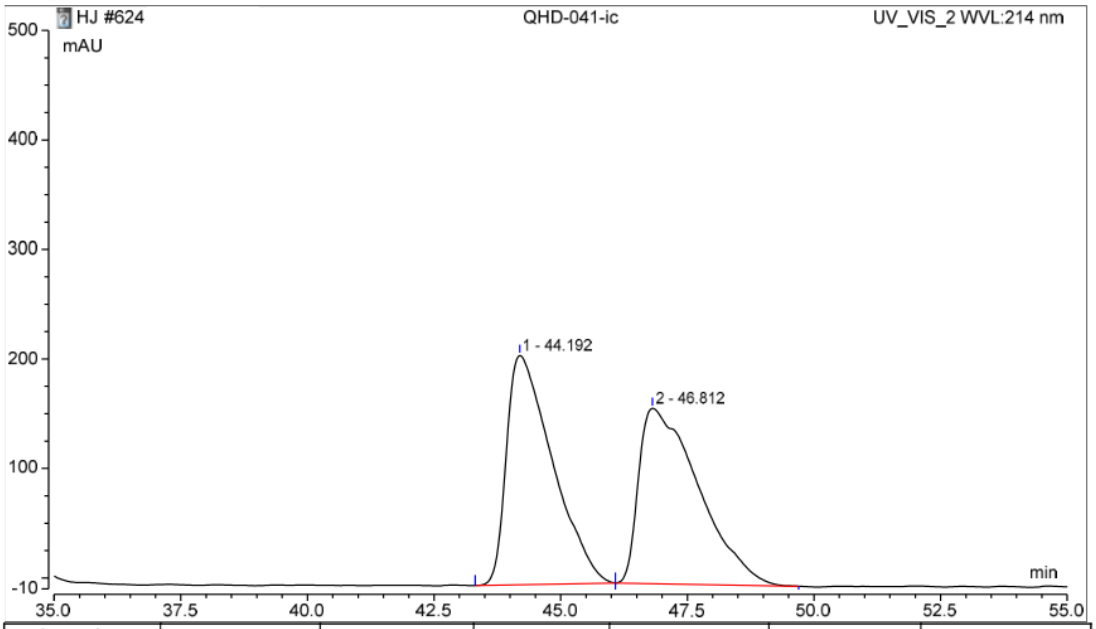

| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 23.419 | 10.220 | 21.606 | 6.35 | 9.80 | n.a. |
| 2 | 29.525 | 150.657 | 198.917 | 93.65 | 90.20 | n.a. |


MeO2C
N
CO2Me
3u
7.29
5.23
5.21
4.63
4.62
4.60
4.60
3.71
3.63
2.36
2.35
1.75
1.73
-0.00
1.00
1.00
6.06
4.05
0.96
3.02
3.11
10.0 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
f1 (ppm)


171.61
138.48
121.54
81.77
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
73.31
52.17
51.73
51.59
25.90
18.34
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

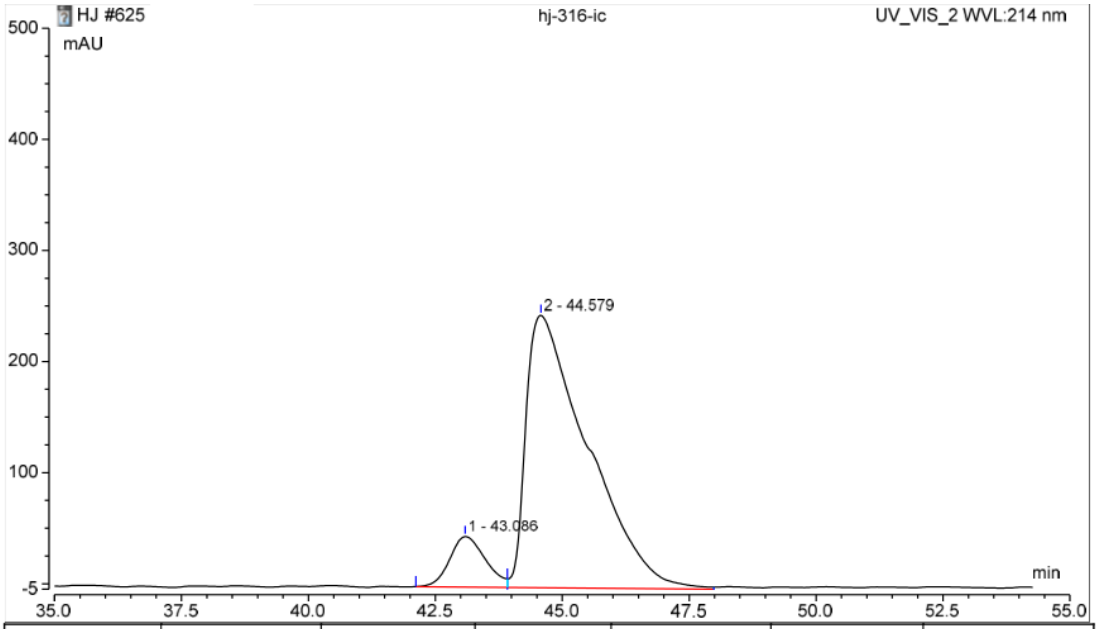
**Compound (+)-3u:** IC, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-3u

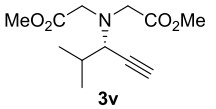



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 44.192 | 219.504 | 209.408 | 50.02 | 56.66 | n.a. |
| 2 | 46.812 | 219.323 | 160.150 | 49.98 | 43.34 | n.a. |

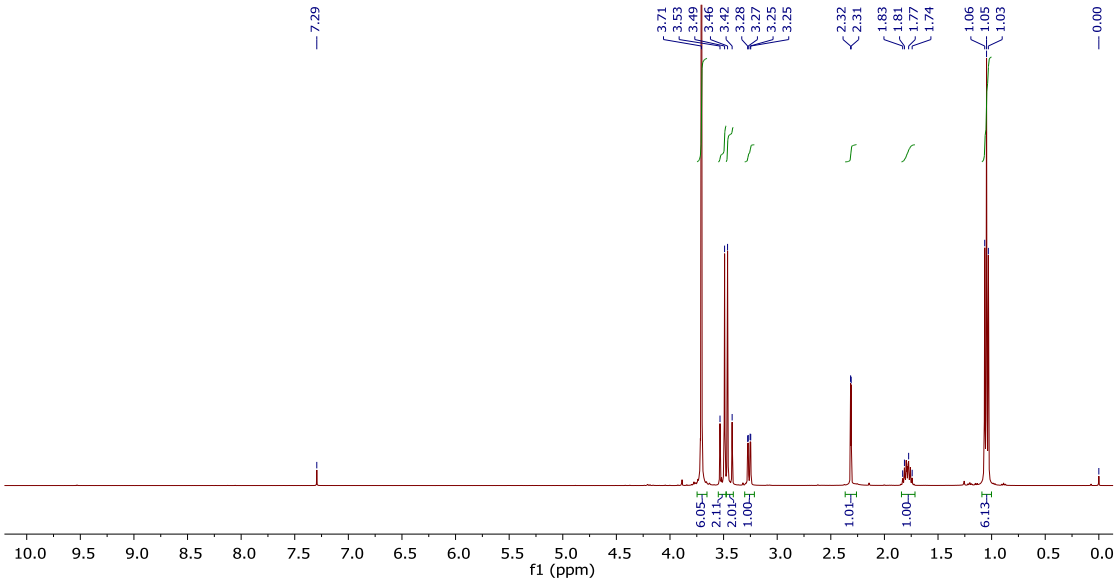
## HPLC trace of 3u

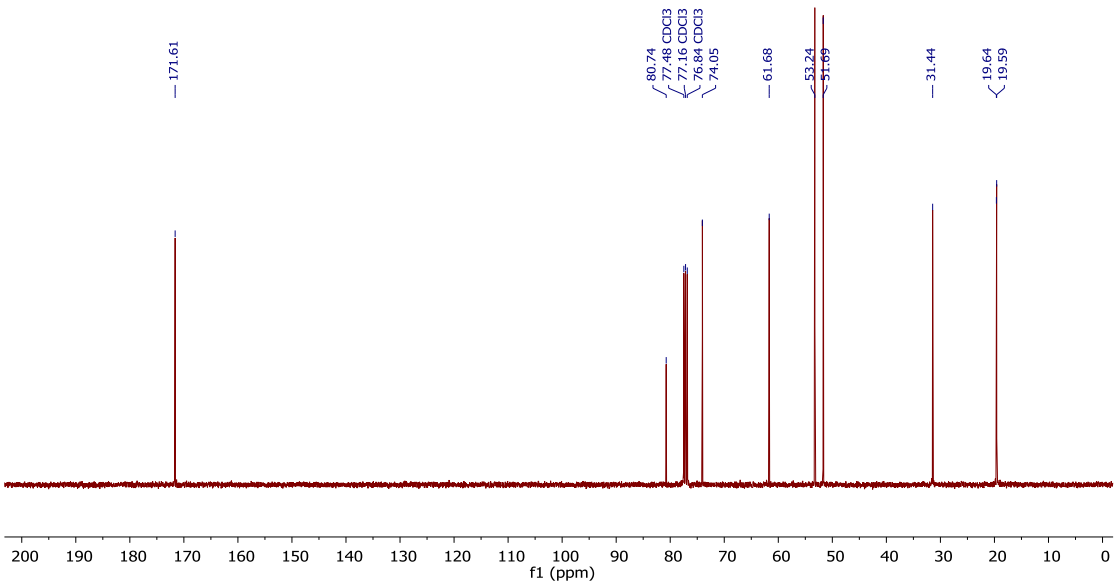



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 43.086 | 36.912 | 45.468 | 9.68 | 15.65 | n.a. |
| 2 | 44.579 | 344.607 | 245.130 | 90.32 | 84.35 | n.a. |


MeO2C
N
CO2Me

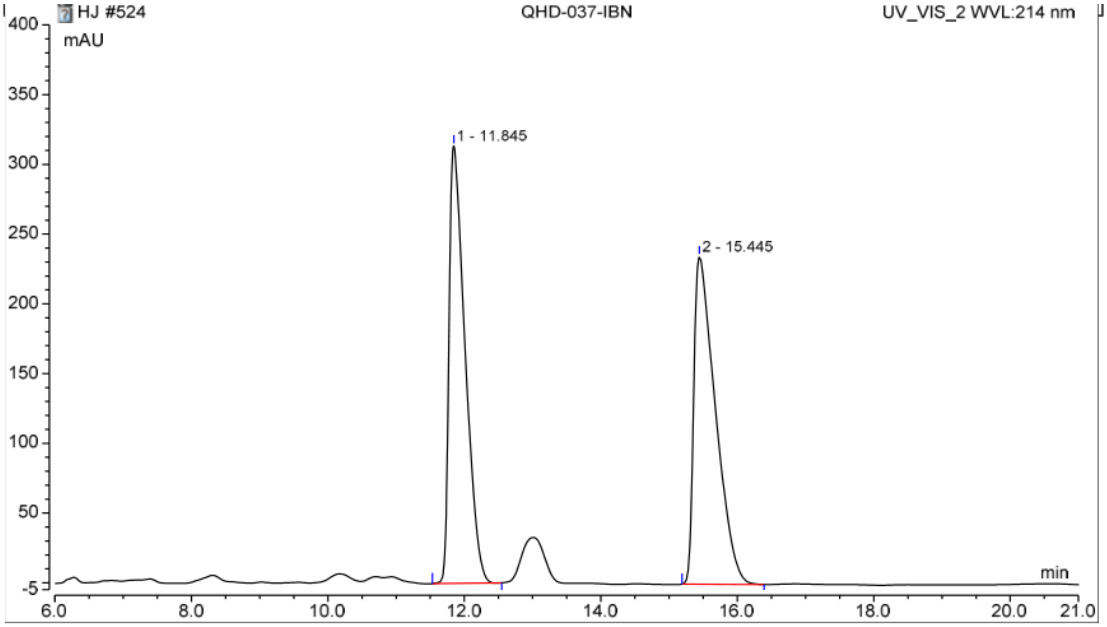
**3v**


7.29
3.71
3.53
3.49
3.46
3.42
3.28
3.27
3.25
3.25
2.32
2.31
1.83
1.81
1.77
1.74
1.06
1.05
1.03
0.00
6.05
2.11
2.01
1.00
1.01
1.00
6.13
f1 (ppm)


171.61
80.74
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.05
61.68
53.24
51.69
31.44
19.64
19.59
f1 (ppm)

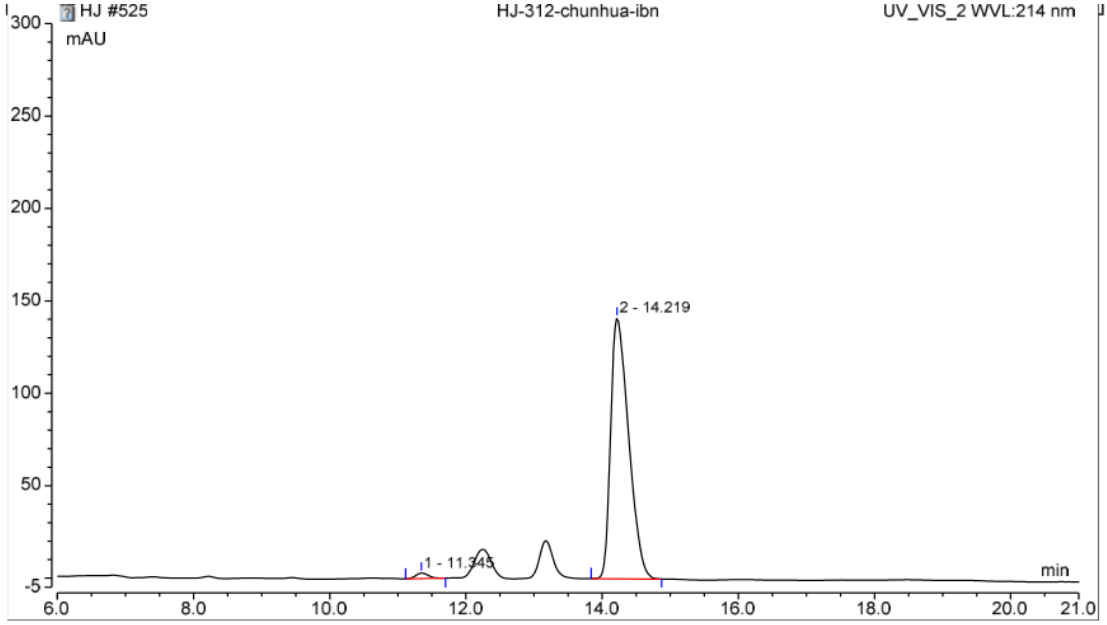
**Compound (-)-3v:** IBN-5, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-3v

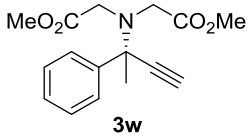



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 11.845 | 85.077 | 313.580 | 49.73 | 57.18 | n.a. |
| 2 | 15.445 | 85.996 | 234.832 | 50.27 | 42.82 | n.a. |

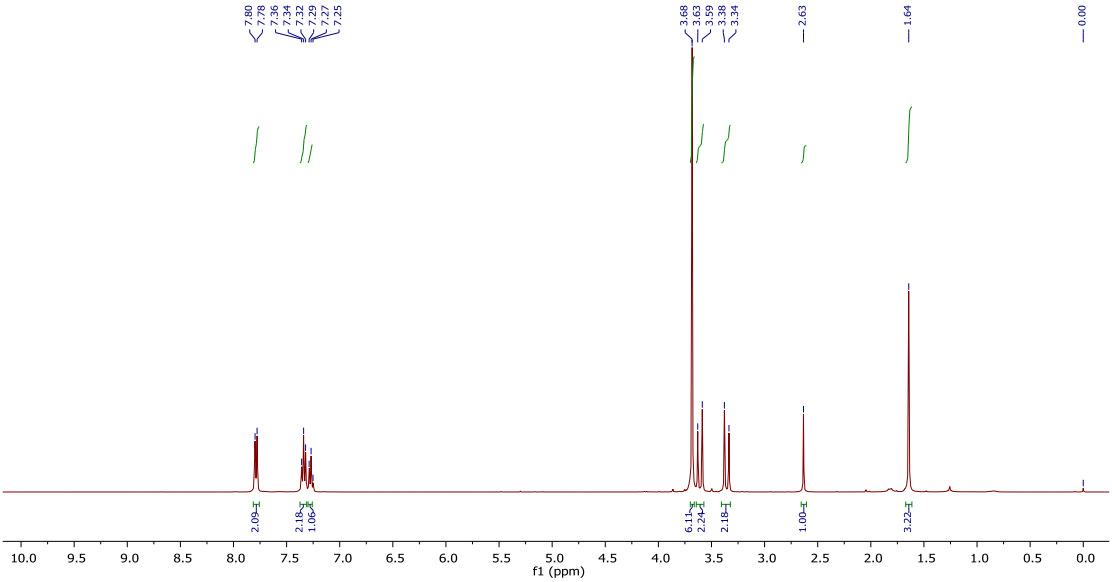
## HPLC trace of 3v

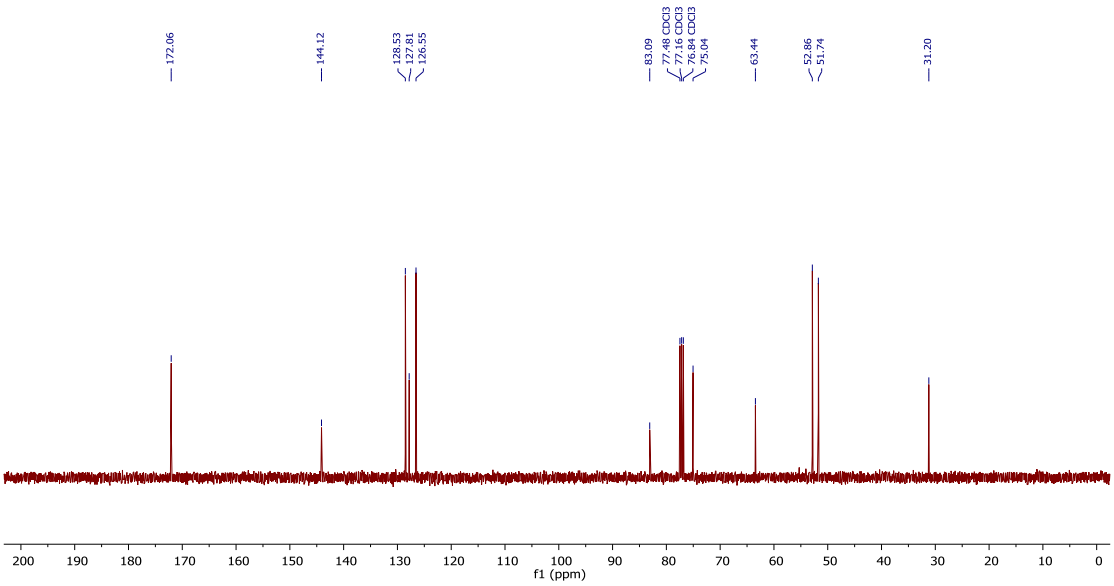


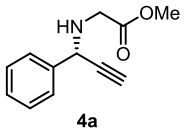

| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 11.345 | 0.637 | 2.983 | 1.46 | 2.07 | n.a. |
| 2 | 14.219 | 43.111 | 141.059 | 98.54 | 97.93 | n.a. |



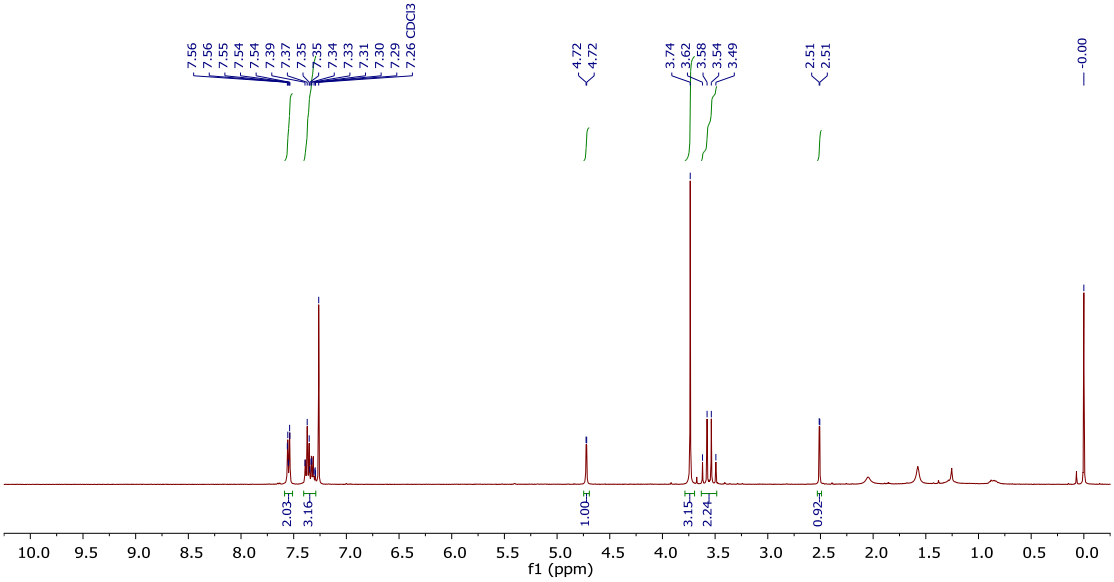
**3w**


7.80
7.78
7.36
7.34
7.32
7.29
7.27
7.25
3.68
3.63
3.59
3.38
3.34
2.63
1.64
0.00
2.09
2.18
1.06
6.11
2.24
2.18
1.00
3.22
f1 (ppm)


172.06
144.12
128.53
127.81
126.55
83.09
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.04
63.44
52.86
51.74
31.20
f1 (ppm)

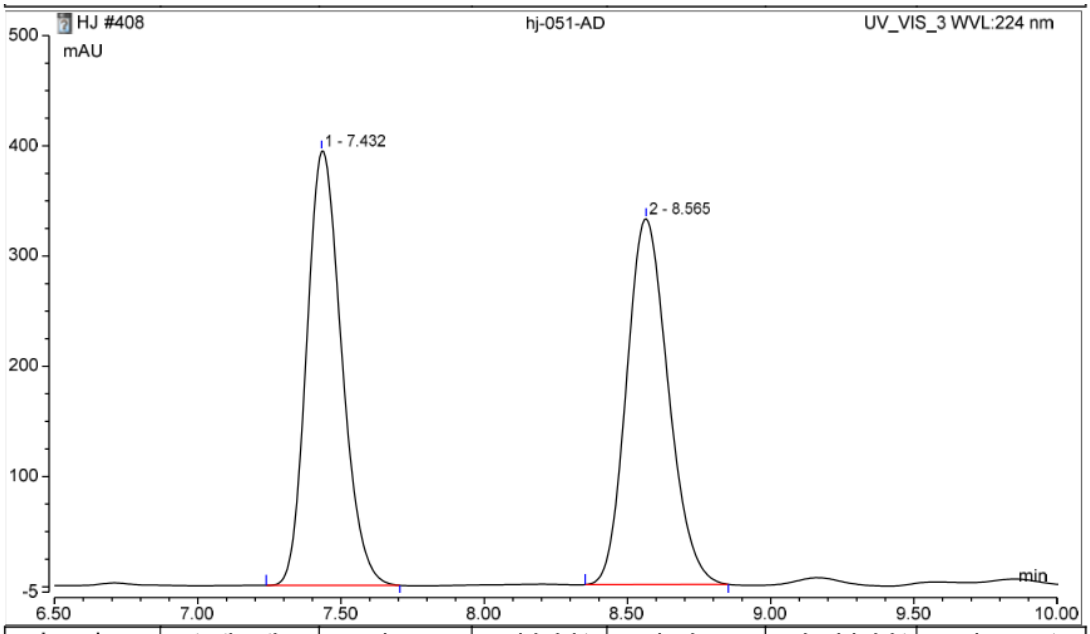

HN
OMe
O

**4a**


7.56
7.56
7.55
7.54
7.54
7.39
7.37
7.35
7.35
7.34
7.33
7.31
7.30
7.29
7.26 CDCl3
4.72
4.72
3.74
3.62
3.58
3.54
3.49
2.51
2.51
-0.00
2.03
3.16
1.00
3.15
2.24
0.92
10.0 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
f1 (ppm)

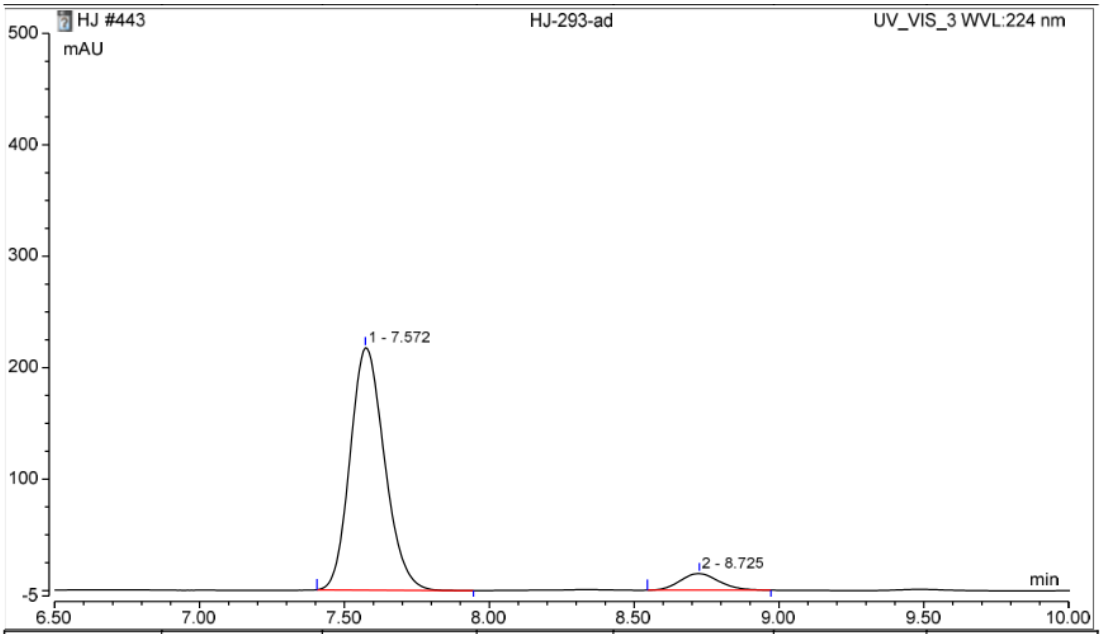
**Compound (-)-4a:** AD-H, hexane/$^{i}$PrOH = 90/10, v = 1.0 mL/min, λ = 224 nm

## HPLC trace of *rac*-4a

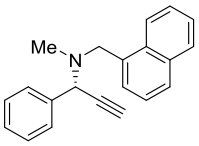



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 7.432 | 55.660 | 394.027 | 49.88 | 54.29 | n.a. |
| 2 | 8.565 | 55.935 | 331.821 | 50.12 | 45.71 | n.a. |

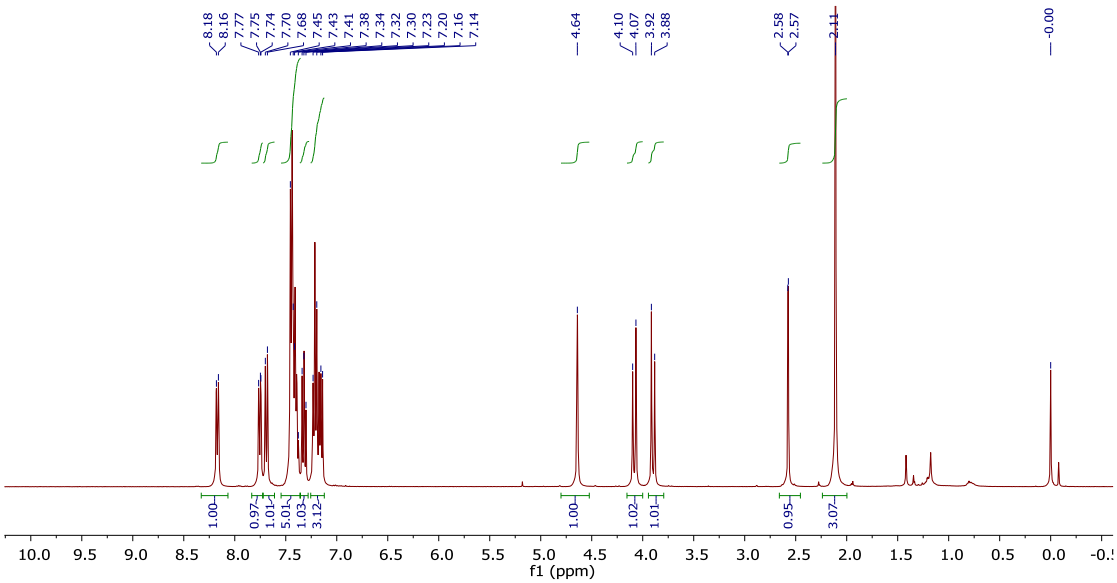
## HPLC trace of 4a

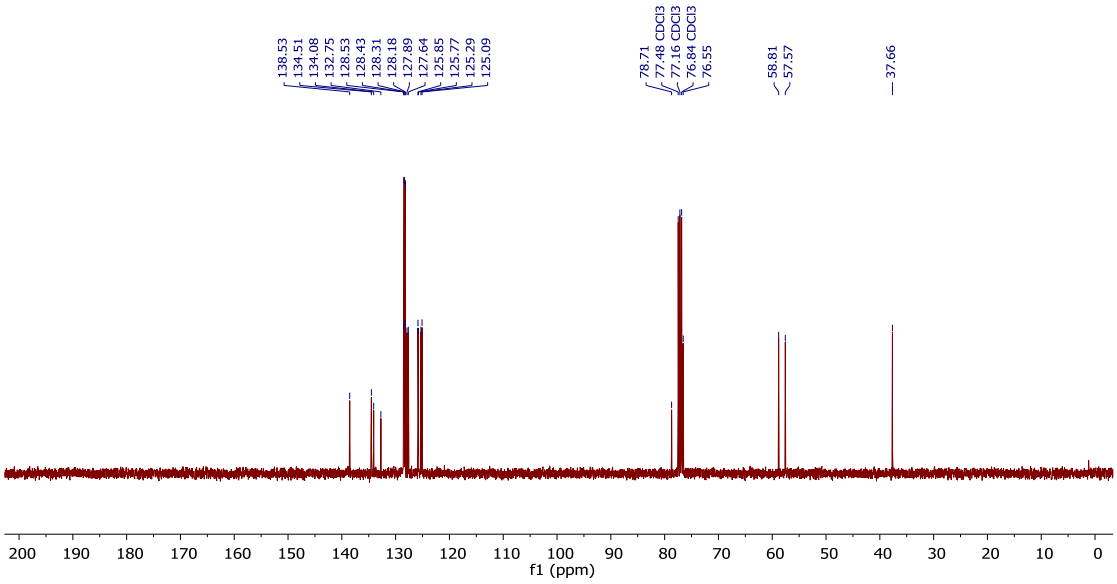



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 7.572 | 29.926 | 217.361 | 92.77 | 93.56 | n.a. |
| 2 | 8.725 | 2.334 | 14.960 | 7.23 | 6.44 | n.a. |


Me
N

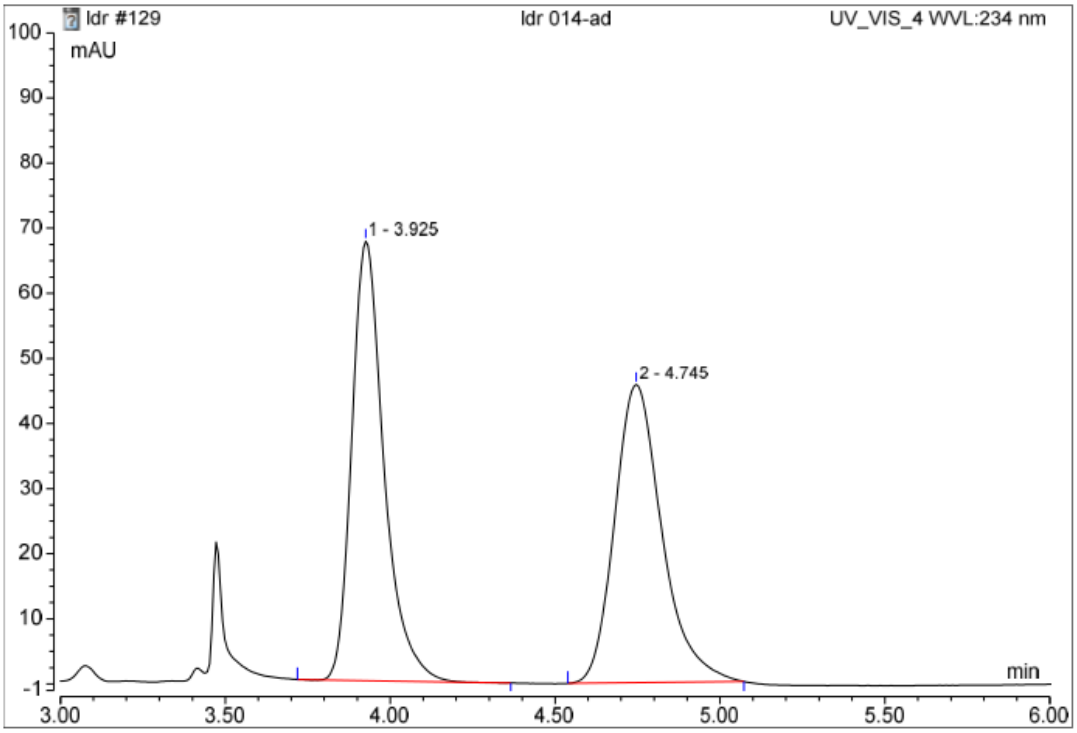
**4b**


8.18
8.16
7.77
7.75
7.74
7.70
7.68
7.45
7.43
7.41
7.38
7.34
7.32
7.30
7.23
7.20
7.16
7.14
4.64
4.10
4.07
3.92
3.88
2.58
2.57
2.11
-0.00
1.00
0.97
1.01
5.01
1.03
3.12
1.00
1.02
1.01
0.95
3.07
f1 (ppm)


138.53
134.51
134.08
132.75
128.53
128.43
128.31
128.18
127.89
127.64
125.85
125.77
125.29
125.09
78.71
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.55
58.81
57.57
37.66
f1 (ppm)

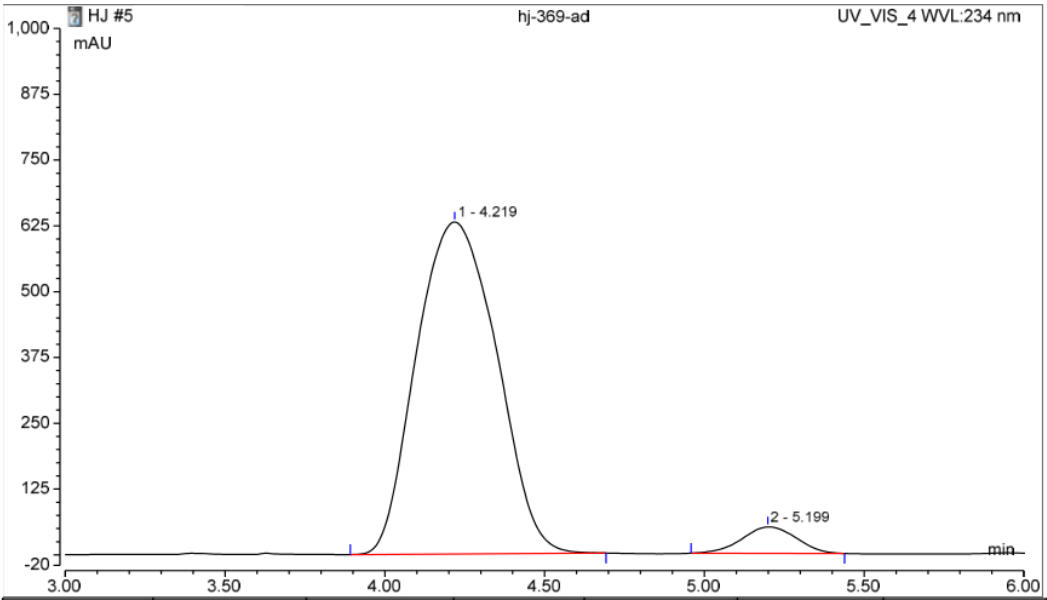
**Compound (-)-4b:** AD-H, hexane/$^{i}$PrOH = 90/10, v = 1.0 mL/min, λ = 234 nm

## HPLC trace of *rac*-4b

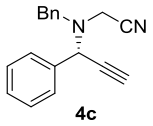



| peak.number | peak.name<br>min | peak.area<br>mAU*min | peak.height<br>mAU | peak.rel_area<br>% | peak.rel_height<br>% |
|---|---|---|---|---|---|
| 1 | 3.925 | 7.650 | 67.523 | 50.12 | 59.58 |
| 2 | 4.745 | 7.613 | 45.809 | 49.88 | 40.42 |

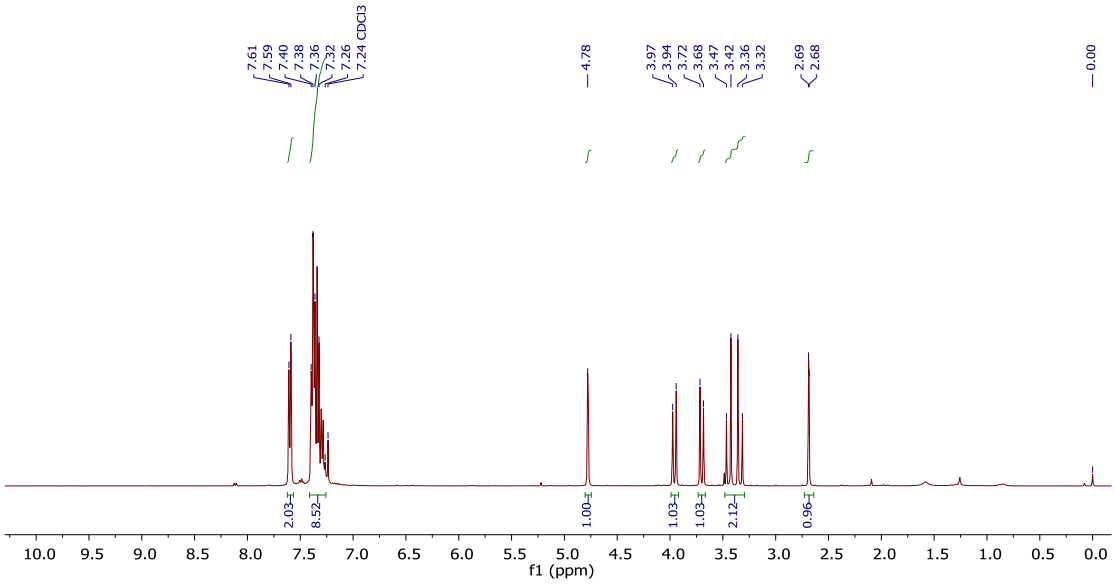
## HPLC trace of 4b

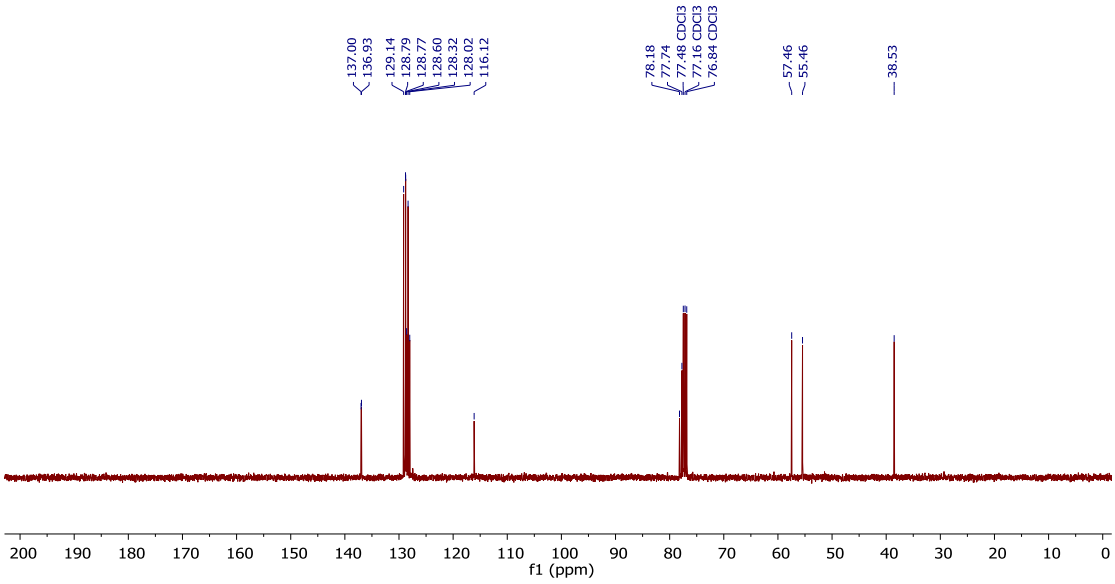



| peak.number | retention_time<br>min | peak.area<br>mAU*min | peak.height<br>mAU | peak.rel_area<br>% | peak.rel_height<br>% | peak.amount<br>n.a. |
|---|---|---|---|---|---|---|
| 1 | 4.219 | 183.700 | 630.580 | 94.89 | 92.63 | n.a. |
| 2 | 5.199 | 9.889 | 50.137 | 5.11 | 7.37 | n.a. |


Bn
N
CN

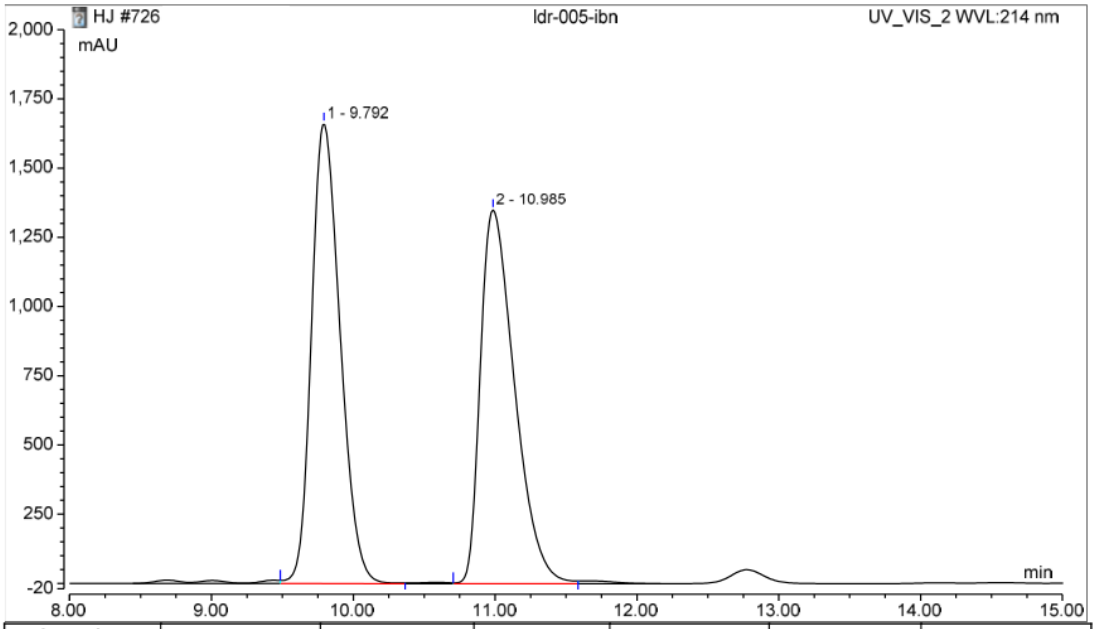
**4c**


7.61
7.59
7.40
7.38
7.36
7.32
7.26
7.24 CDCl3
4.78
3.97
3.94
3.72
3.68
3.47
3.42
3.36
3.32
2.69
2.68
0.00
2.03
8.52
1.00
1.03
1.03
2.12
0.96
f1 (ppm)


137.00
136.93
129.14
128.79
128.77
128.60
128.32
128.02
116.12
78.18
77.74
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
57.46
55.46
38.53
f1 (ppm)

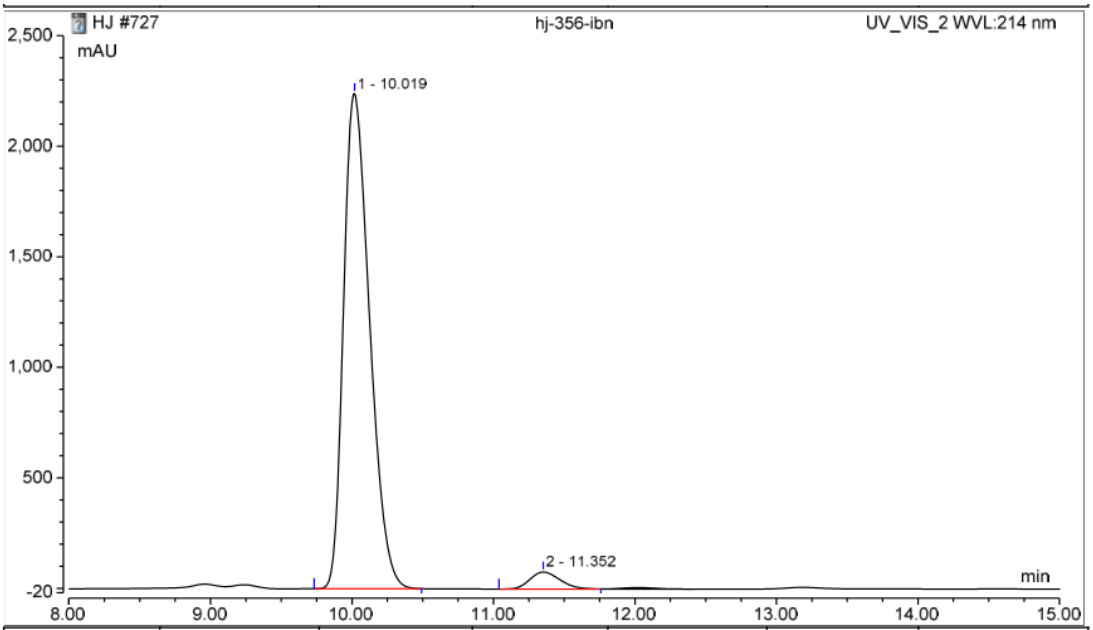
**Compound (-)-4c:** IBN-5, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-4c

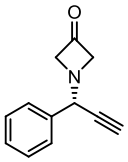



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 9.792 | 389.322 | 1662.747 | 50.81 | 55.18 | n.a. |
| 2 | 10.985 | 376.868 | 1350.415 | 49.19 | 44.82 | n.a. |

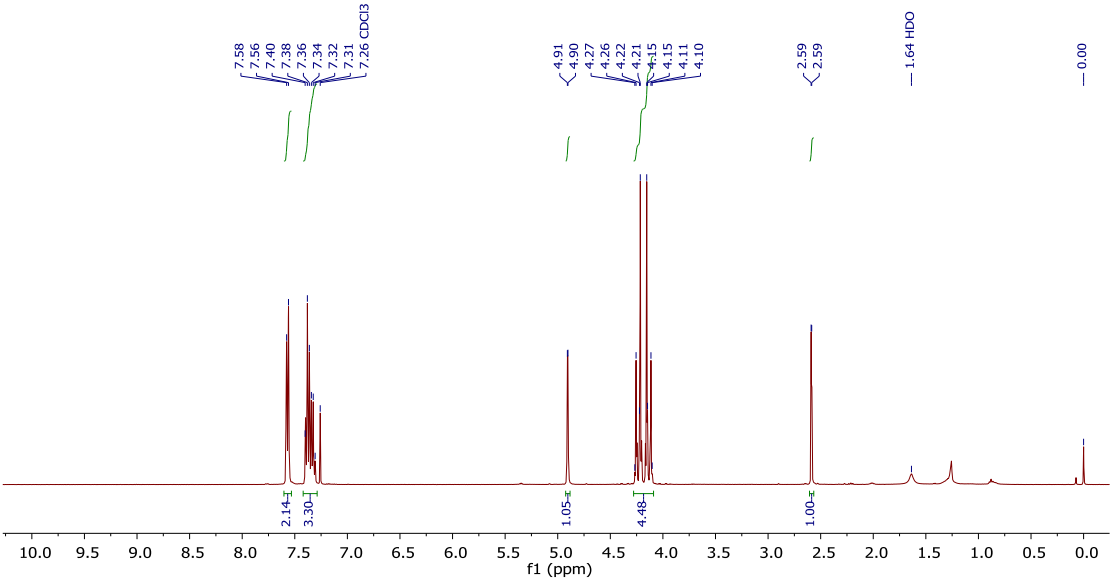
## HPLC trace of 4c

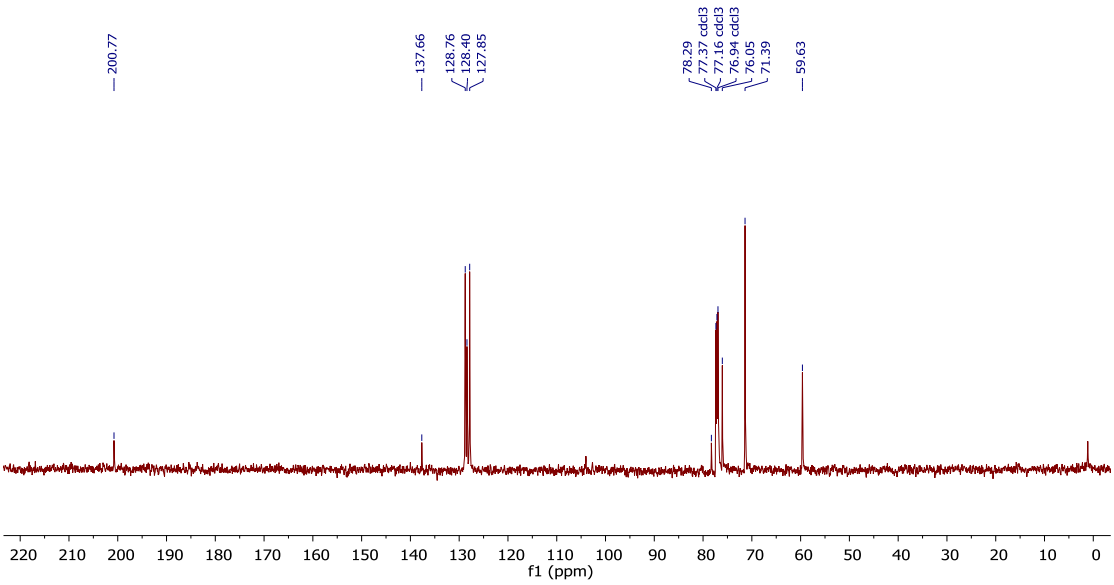



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 10.019 | 477.479 | 2239.081 | 96.16 | 96.68 | n.a. |
| 2 | 11.352 | 19.080 | 77.009 | 3.84 | 3.32 | n.a. |



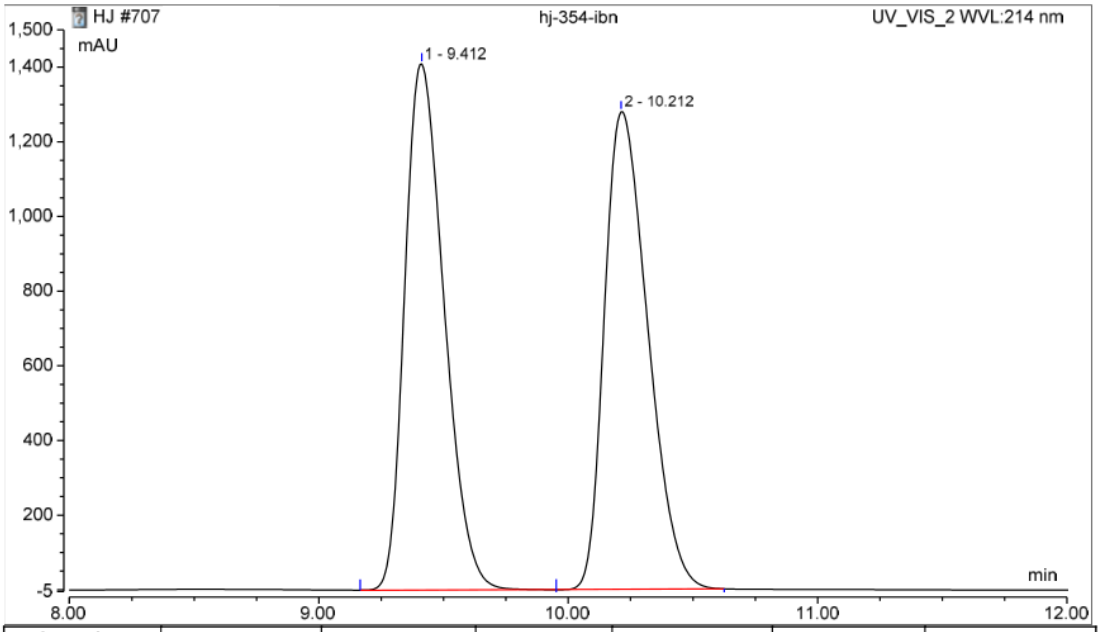
**4d**


7.58
7.56
7.40
7.38
7.36
7.34
7.32
7.31
7.26 CDCl3
4.91
4.90
4.27
4.26
4.22
4.21
4.15
4.11
4.10
2.59
2.59
1.64 HDO
0.00
2.14
3.30
1.05
4.48
1.00
f1 (ppm)


200.77
137.66
128.76
128.40
127.85
78.29
77.37 cdcl3
77.16 cdcl3
76.94 cdcl3
76.05
71.39
59.63
f1 (ppm)

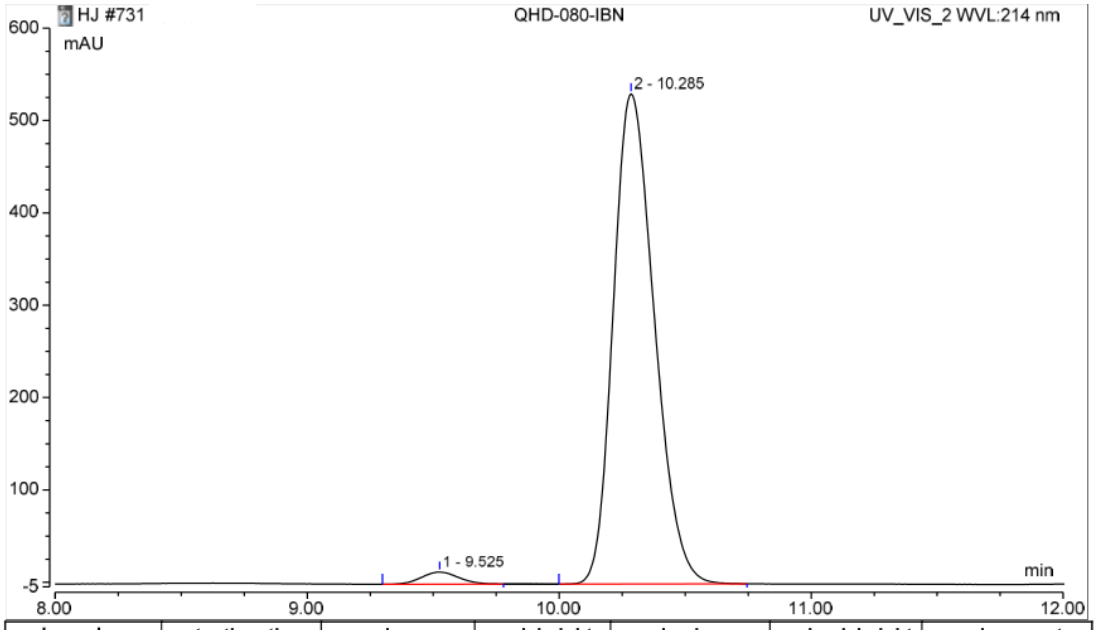
**Compound (-)-4d:** IBN-5, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-4d

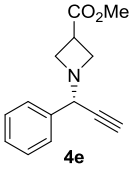



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 9.412 | 257.333 | 1409.067 | 49.95 | 52.42 | n.a. |
| 2 | 10.212 | 257.836 | 1279.204 | 50.05 | 47.58 | n.a. |

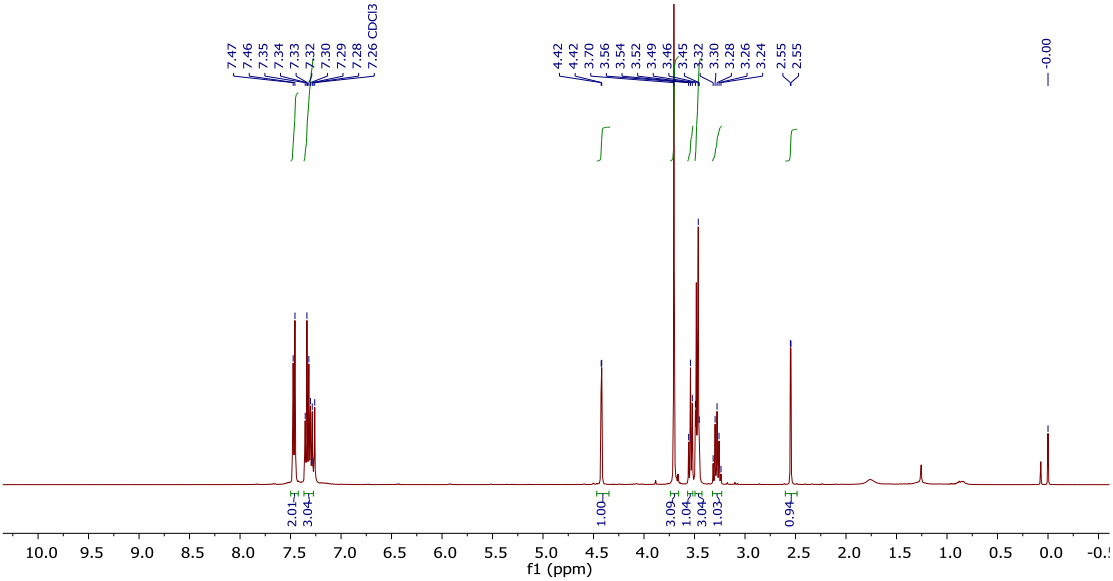
## HPLC trace of 4d

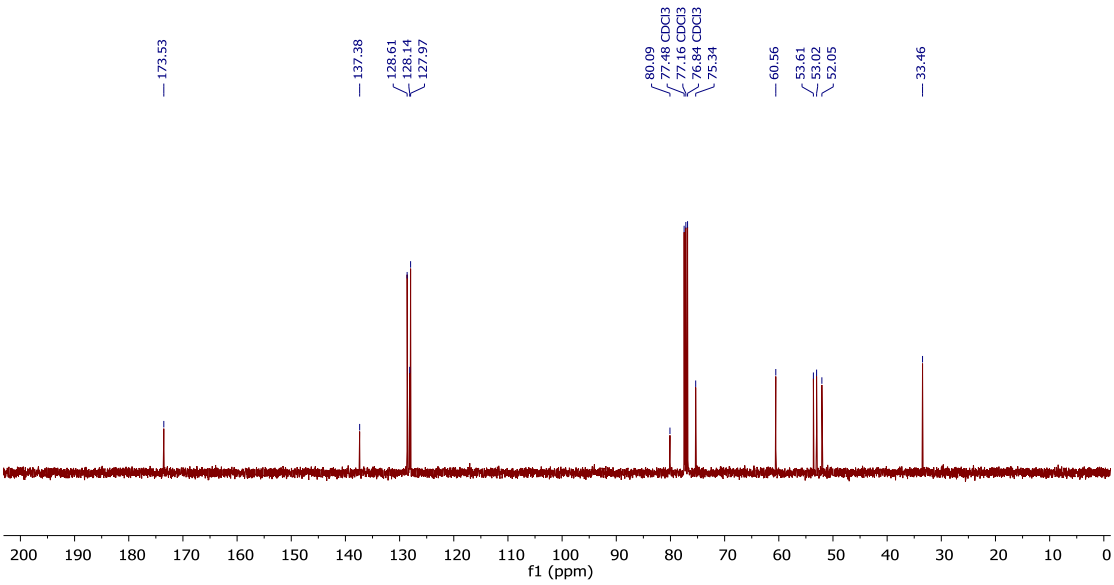



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 9.525 | 2.275 | 13.141 | 2.23 | 2.42 | n.a. |
| 2 | 10.285 | 99.941 | 530.684 | 97.77 | 97.58 | n.a. |


CO2Me
N

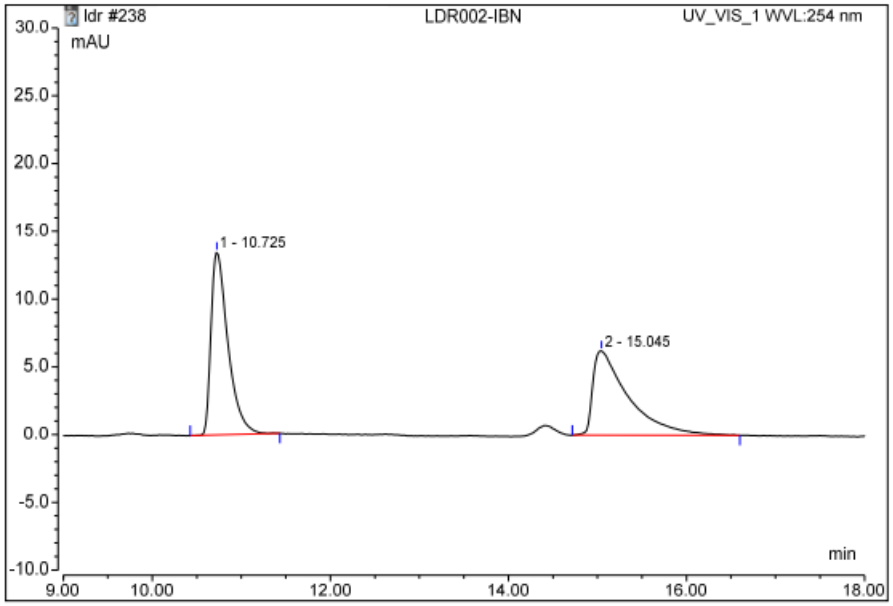
**4e**


7.47
7.46
7.35
7.34
7.33
7.32
7.30
7.29
7.28
7.26 CDCl3
4.42
4.42
3.70
3.56
3.54
3.52
3.49
3.46
3.45
3.32
3.30
3.28
3.26
3.24
2.55
2.55
-0.00
2.01
3.04
1.00
3.09
1.04
3.04
1.03
0.94
f1 (ppm)


173.53
137.38
128.61
128.14
127.97
80.09
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.34
60.56
53.61
53.02
52.05
33.46
f1 (ppm)

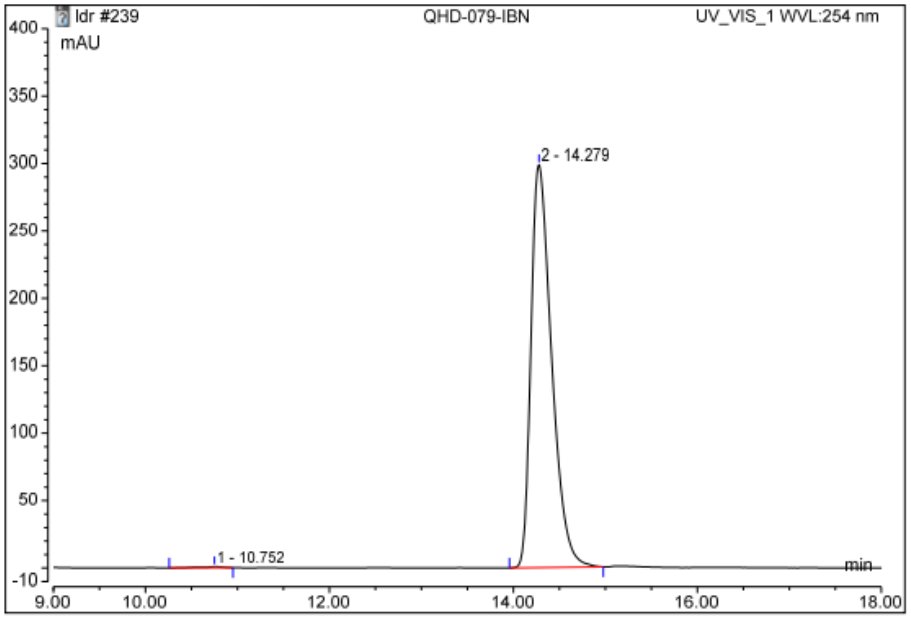
**Compound (-)-4e:** IBN-5, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 254 nm

## HPLC trace of *rac*-4e

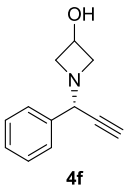



| peak.number | peak.name<br>min | peak.area<br>mAU*min | peak.height<br>mAU | peak.rel_area<br>% | peak.rel_height<br>% |
|---|---|---|---|---|---|
| 1 | 10.725 | 2.969 | 13.477 | 50.82 | 68.38 |
| 2 | 15.045 | 2.873 | 6.233 | 49.18 | 31.62 |

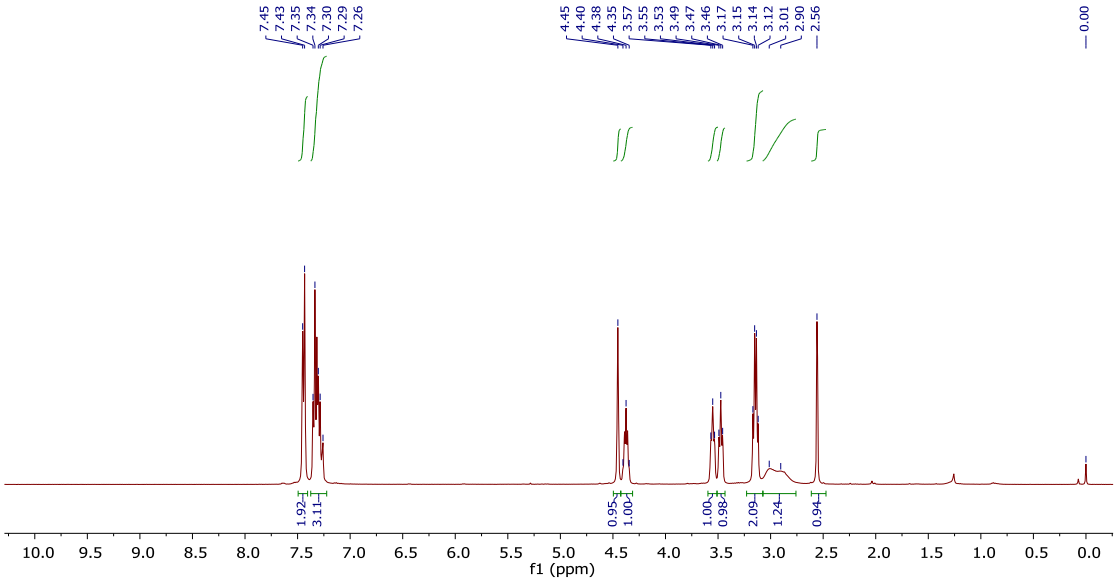
## HPLC trace of 4e

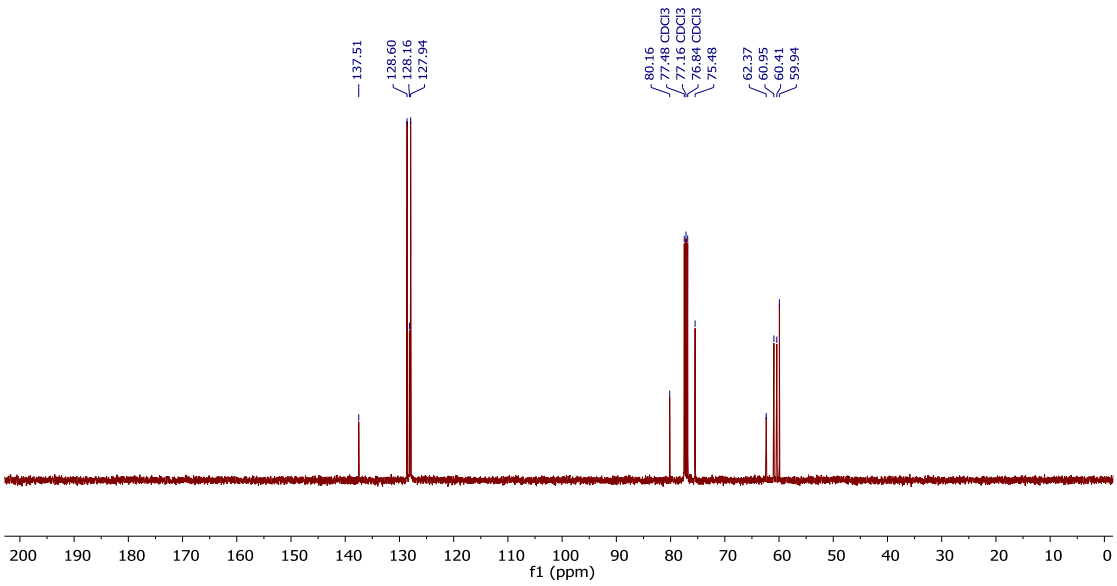



| peak.number | peak.name<br>min | peak.area<br>mAU*min | peak.height<br>mAU | peak.rel_area<br>% | peak.rel_height<br>% |
|---|---|---|---|---|---|
| 1 | 10.752 | 0.226 | 0.767 | 0.29 | 0.26 |
| 2 | 14.279 | 77.670 | 298.799 | 99.71 | 99.74 |


OH
N

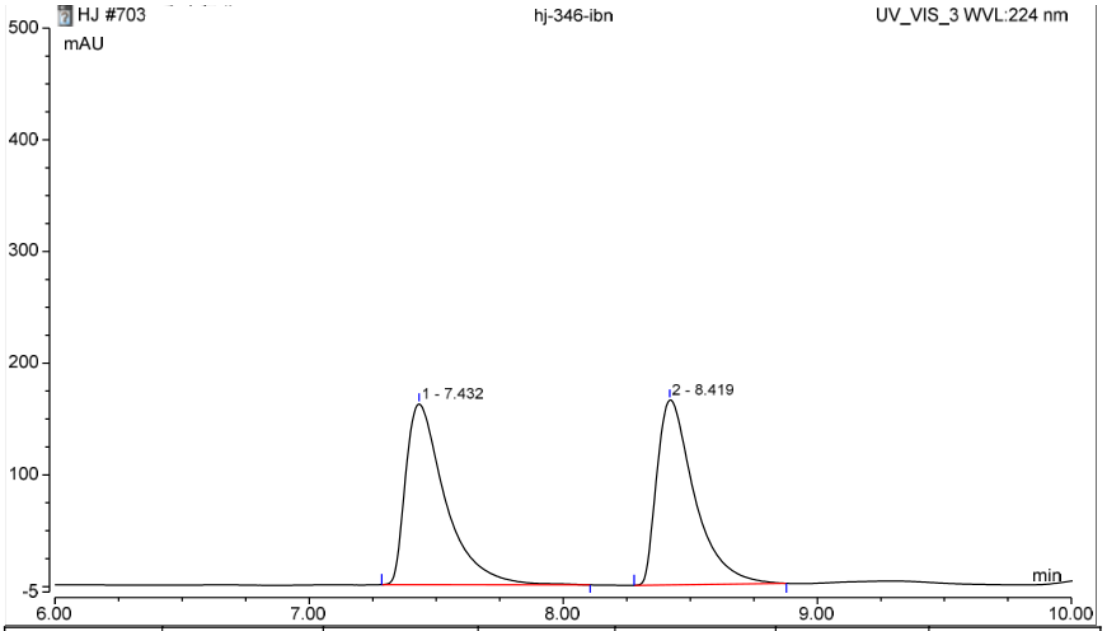
**4f**


7.45
7.43
7.35
7.34
7.30
7.29
7.26
4.45
4.40
4.38
4.35
3.57
3.55
3.53
3.49
3.47
3.46
3.17
3.15
3.14
3.12
3.01
2.90
2.56
0.00
1.92
3.11
0.95
1.00
1.00
0.98
2.09
1.24
0.94
f1 (ppm)


137.51
128.60
128.16
127.94
80.16
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.48
62.37
60.95
60.41
59.94
f1 (ppm)

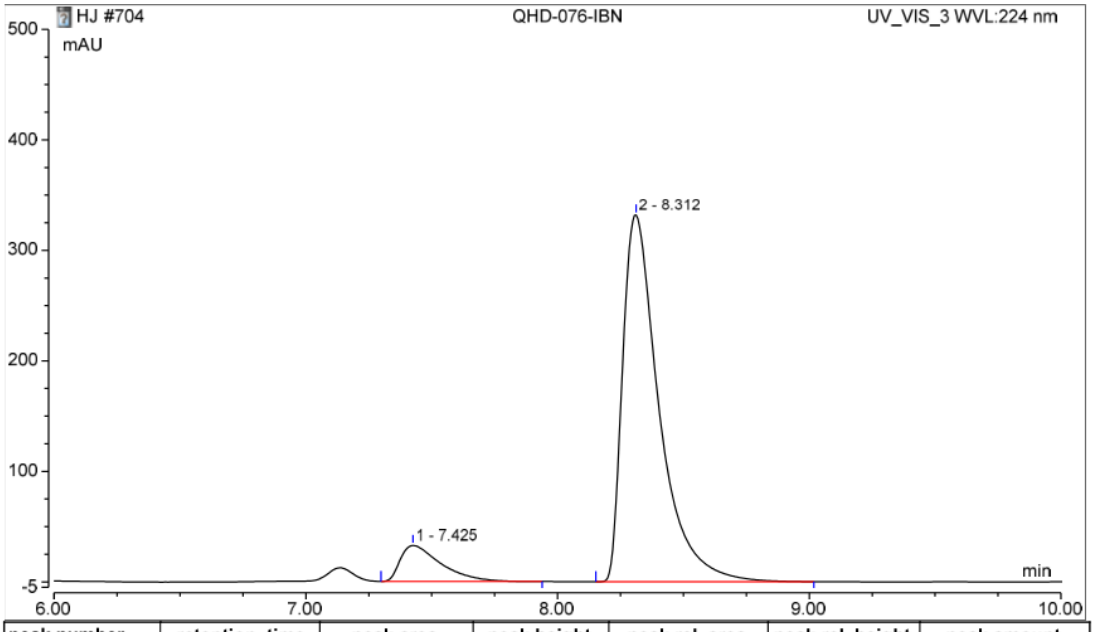
**Compound (-)-4f:** IBN-5, hexane/$^{i}$PrOH = 90/10, v = 1.0 mL/min, λ = 224 nm

## HPLC trace of *rac*-4f

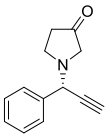



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 7.432 | 29.253 | 161.782 | 50.80 | 49.43 | n.a. |
| 2 | 8.419 | 28.332 | 165.492 | 49.20 | 50.57 | n.a. |

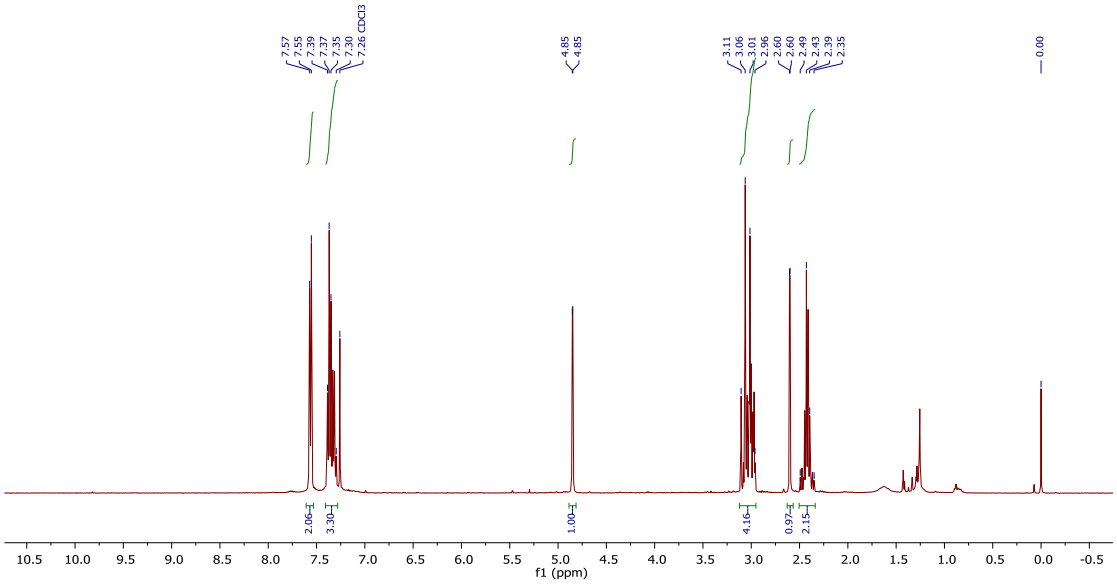
## HPLC trace of 4f

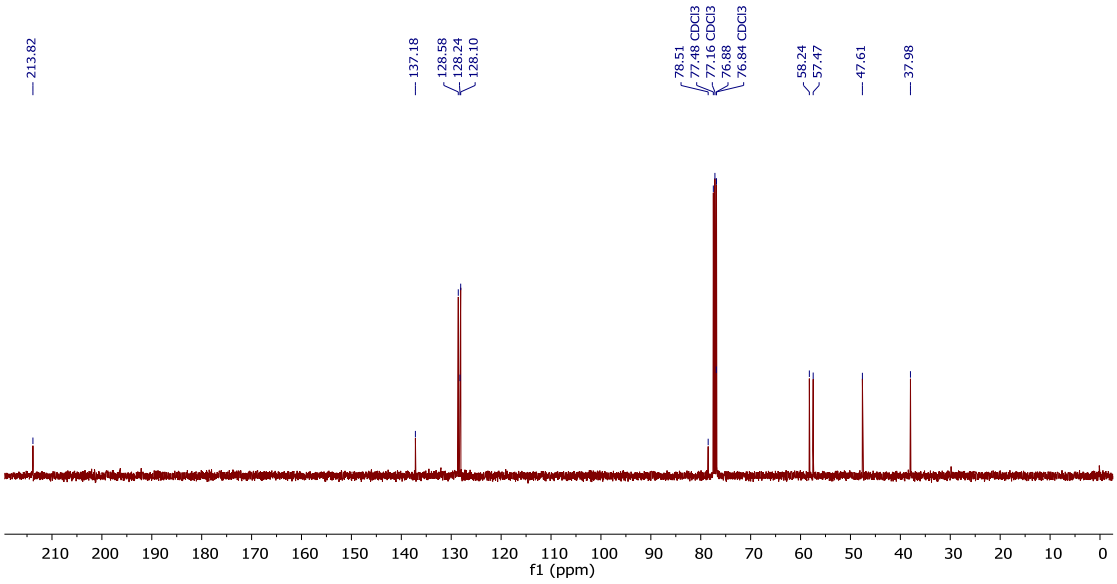



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 7.425 | 6.085 | 32.599 | 9.86 | 8.94 | n.a. |
| 2 | 8.312 | 55.645 | 331.923 | 90.14 | 91.06 | n.a. |



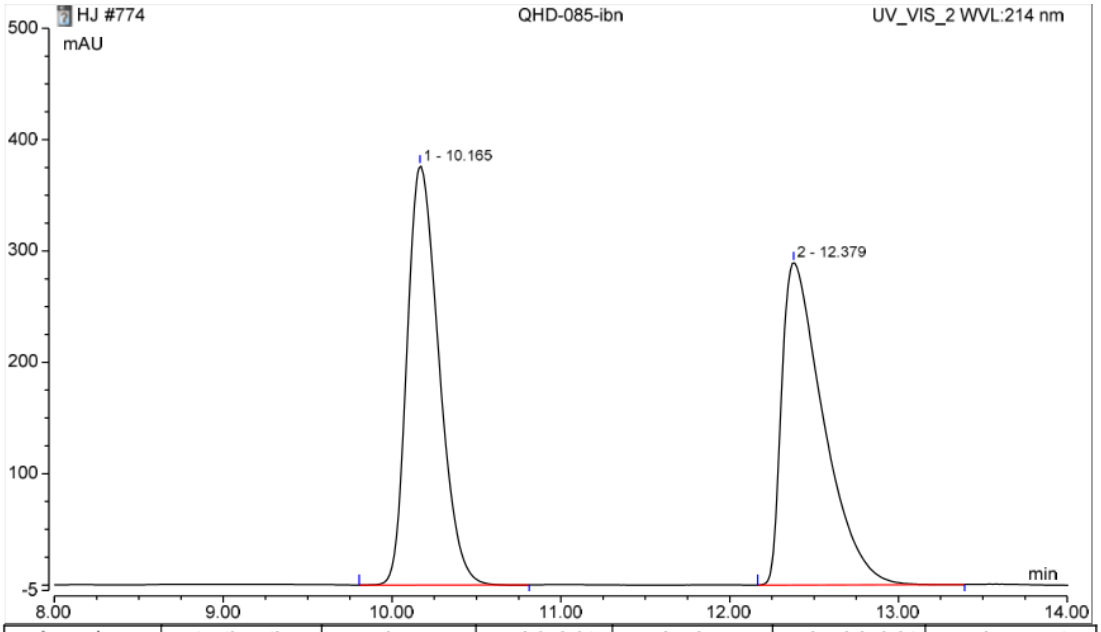
**4g**


7.57
7.55
7.39
7.37
7.35
7.30
7.26 CDCl3
4.85
4.85
3.11
3.06
3.01
2.96
2.60
2.60
2.49
2.43
2.39
2.35
0.00
2.06
3.30
1.00
4.16
0.97
2.15
f1 (ppm)


213.82
137.18
128.58
128.24
128.10
78.51
77.48 CDCl3
77.16 CDCl3
76.88
76.84 CDCl3
58.24
57.47
47.61
37.98
f1 (ppm)

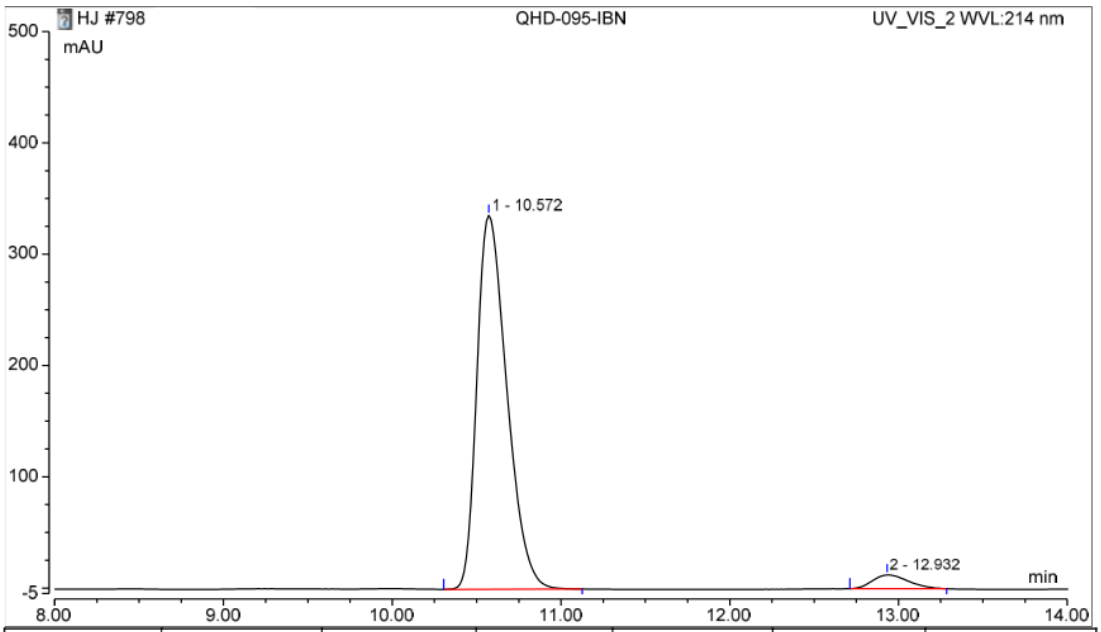
**Compound (-)-4g:** IBN-5, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-4g

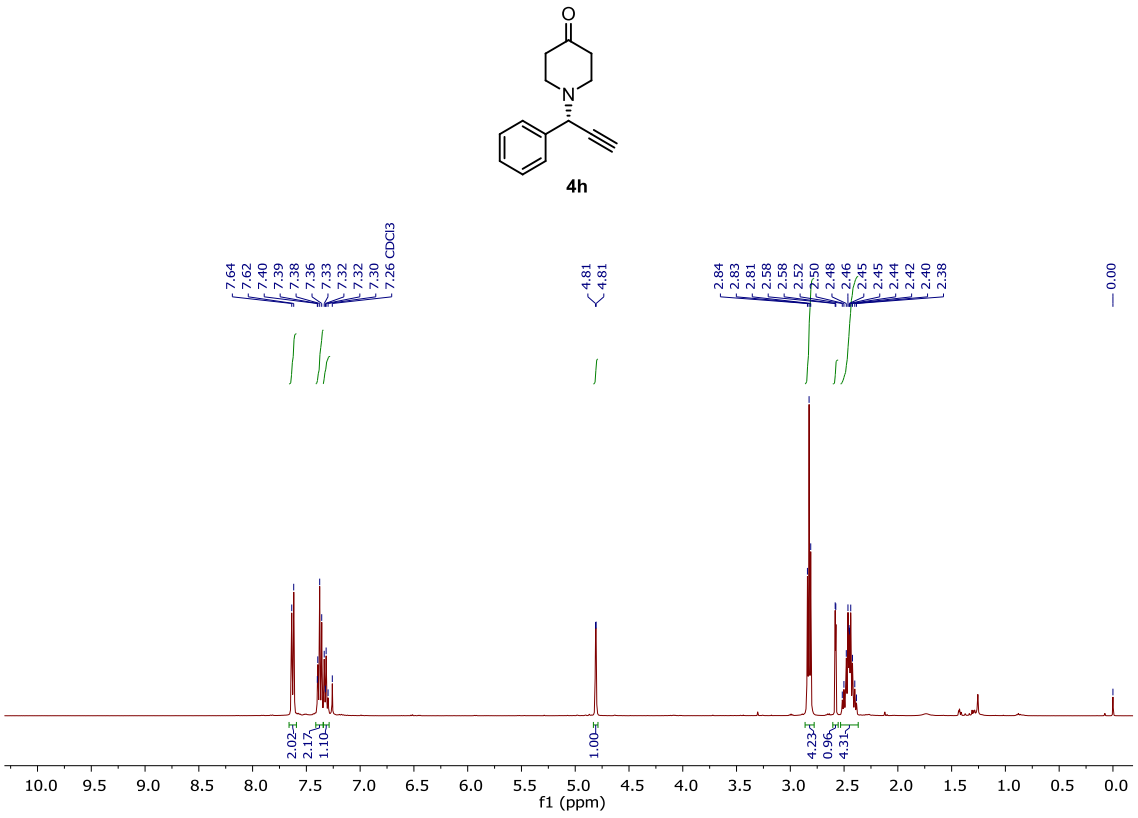



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 10.165 | 82.057 | 376.569 | 49.79 | 56.53 | n.a. |
| 2 | 12.379 | 82.764 | 289.602 | 50.21 | 43.47 | n.a. |

## HPLC trace of 4g

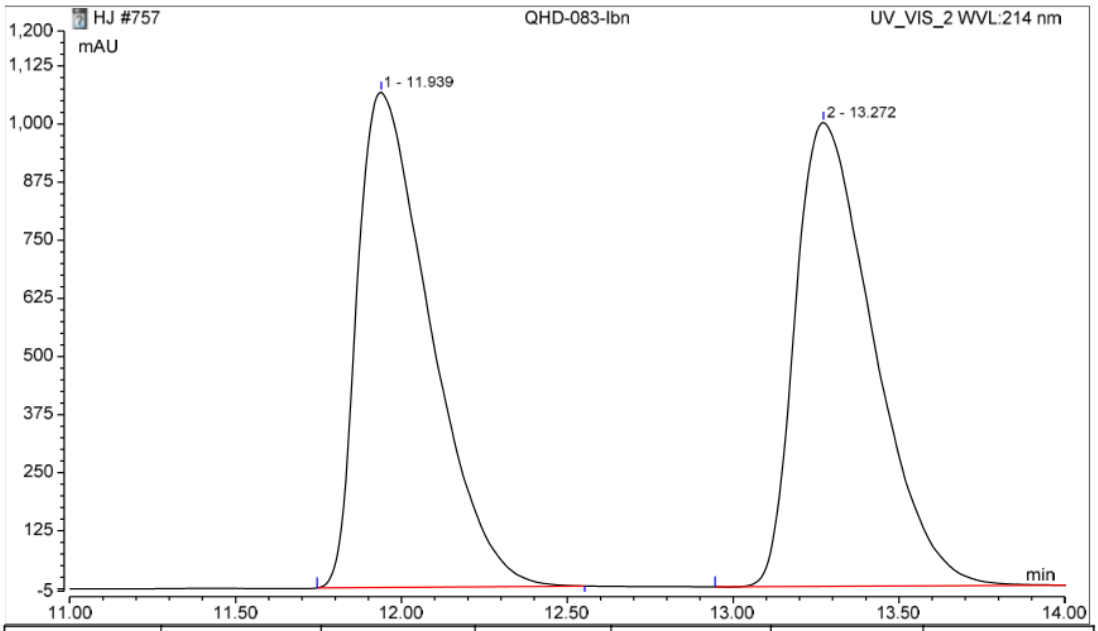



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 10.572 | 68.945 | 336.078 | 95.78 | 96.44 | n.a. |
| 2 | 12.932 | 3.039 | 12.404 | 4.22 | 3.56 | n.a. |


4h
7.64
7.62
7.40
7.39
7.38
7.36
7.33
7.32
7.32
7.30
7.26 CDCl3
4.81
4.81
2.84
2.83
2.81
2.58
2.58
2.52
2.50
2.48
2.46
2.45
2.45
2.44
2.42
2.40
2.38
0.00
2.02
2.17
1.10
1.00
4.23
0.96
4.31
10.0 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
f1 (ppm)

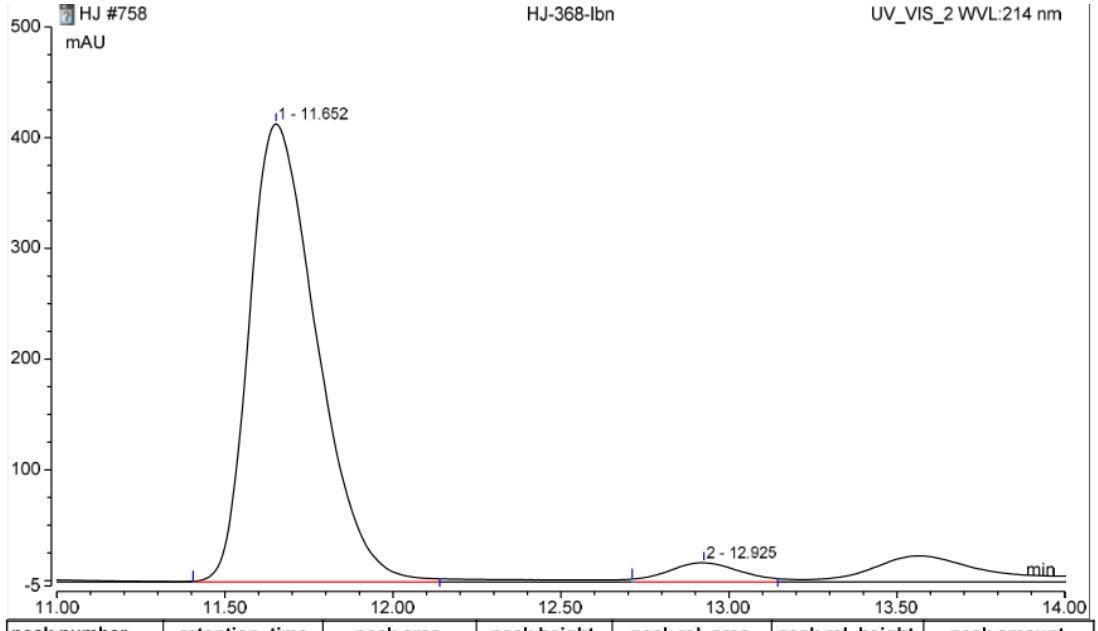
**Compound (-)-4h:** IBN-5, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-4h

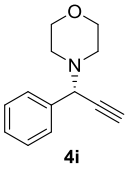



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 11.939 | 270.837 | 1065.106 | 49.86 | 51.63 | n.a. |
| 2 | 13.272 | 272.367 | 997.851 | 50.14 | 48.37 | n.a. |

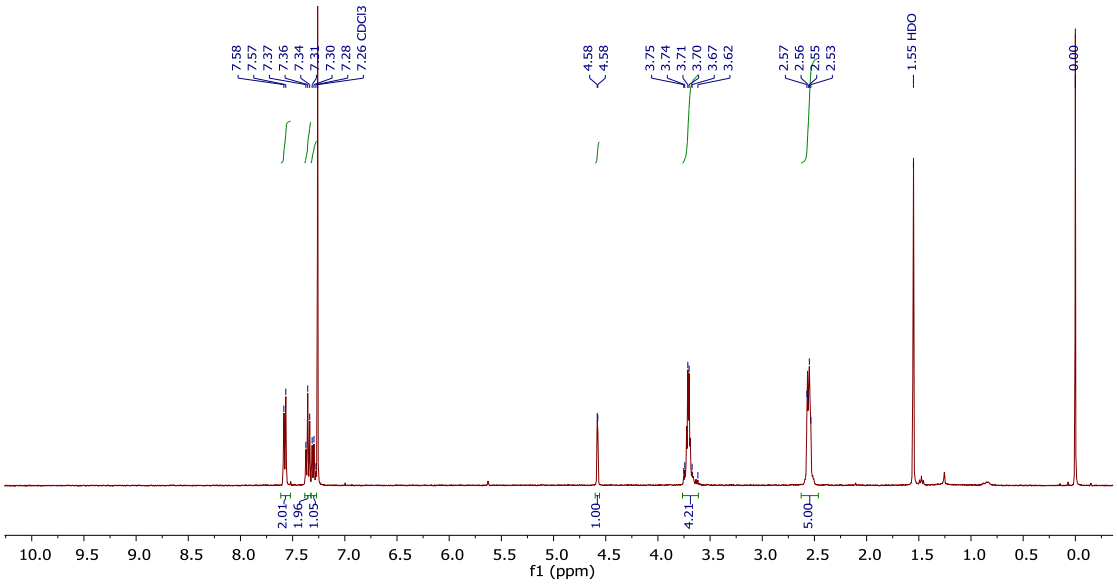
## HPLC trace of 4h




| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 11.652 | 96.211 | 413.847 | 95.68 | 95.97 | n.a. |
| 2 | 12.925 | 4.342 | 17.378 | 4.32 | 4.03 | n.a. |

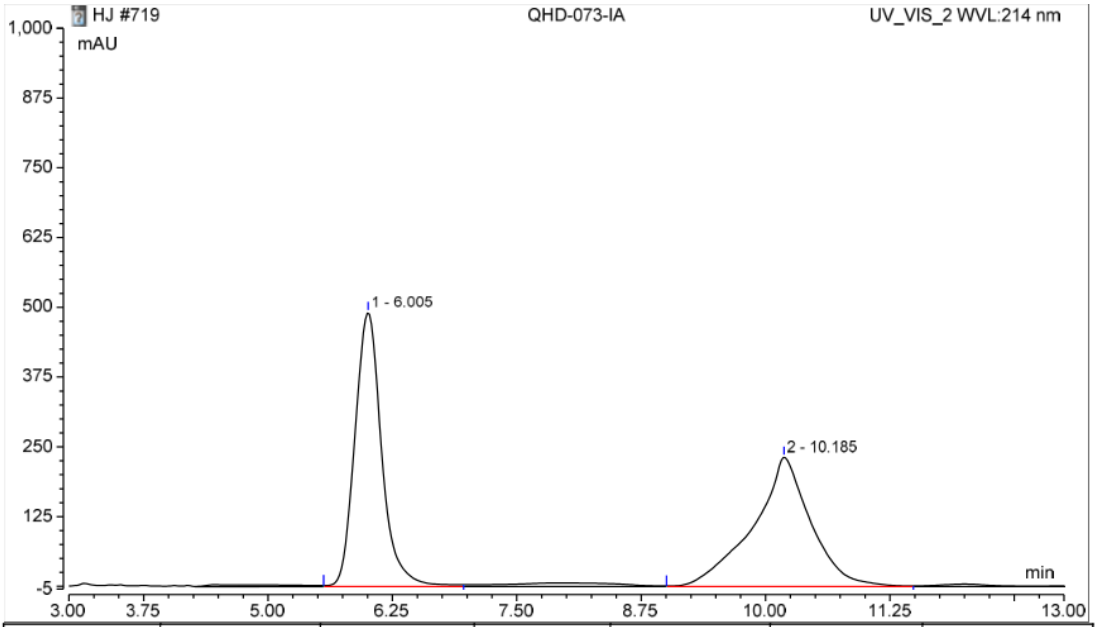


**4i**


7.58
7.57
7.37
7.36
7.34
7.31
7.30
7.28
7.26 CDCl3
4.58
4.58
3.75
3.74
3.71
3.70
3.67
3.62
2.57
2.56
2.55
2.53
1.55 HDO
0.00
2.01
1.96
1.05
1.00
4.21
5.00
10.0 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
f1 (ppm)

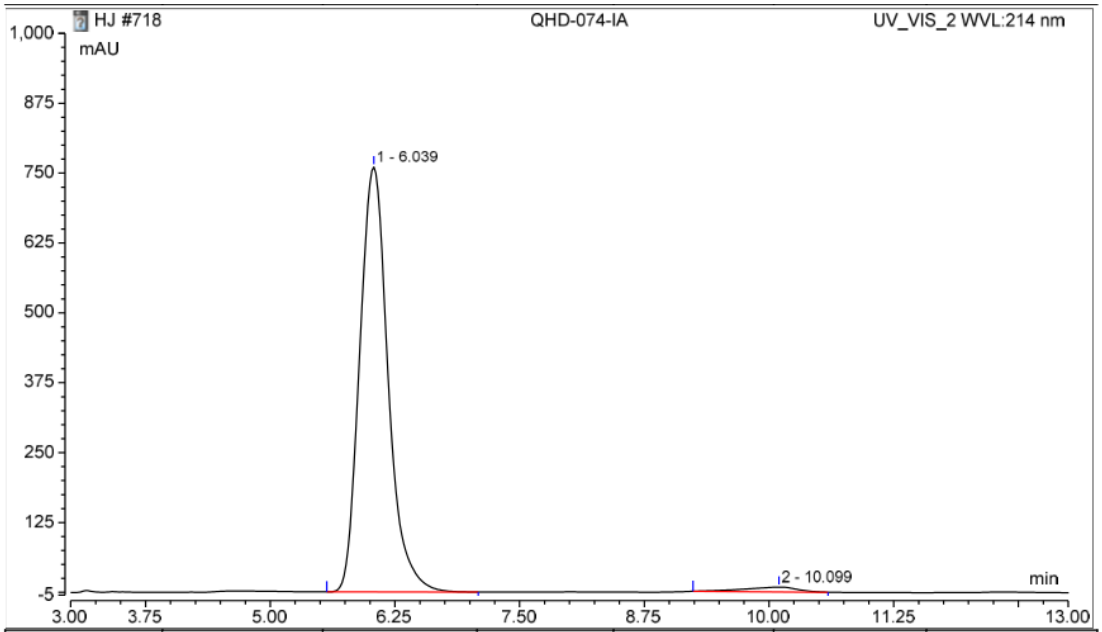
**Compound (-)-4i:** IA, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-4i

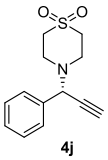



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 6.005 | 153.259 | 491.173 | 49.70 | 67.97 | n.a. |
| 2 | 10.185 | 155.097 | 231.430 | 50.30 | 32.03 | n.a. |

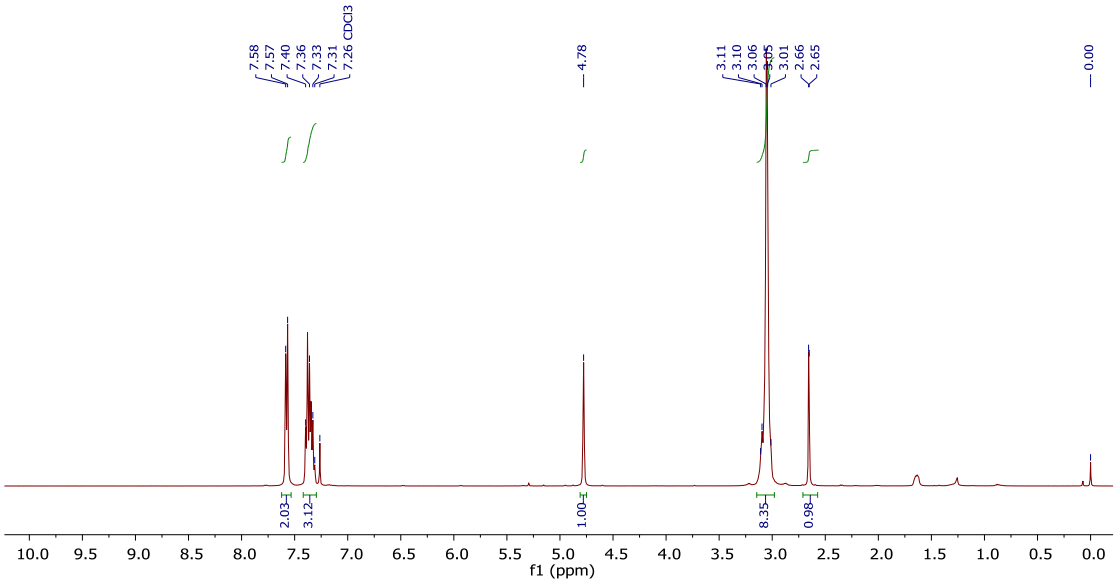
## HPLC trace of 4i

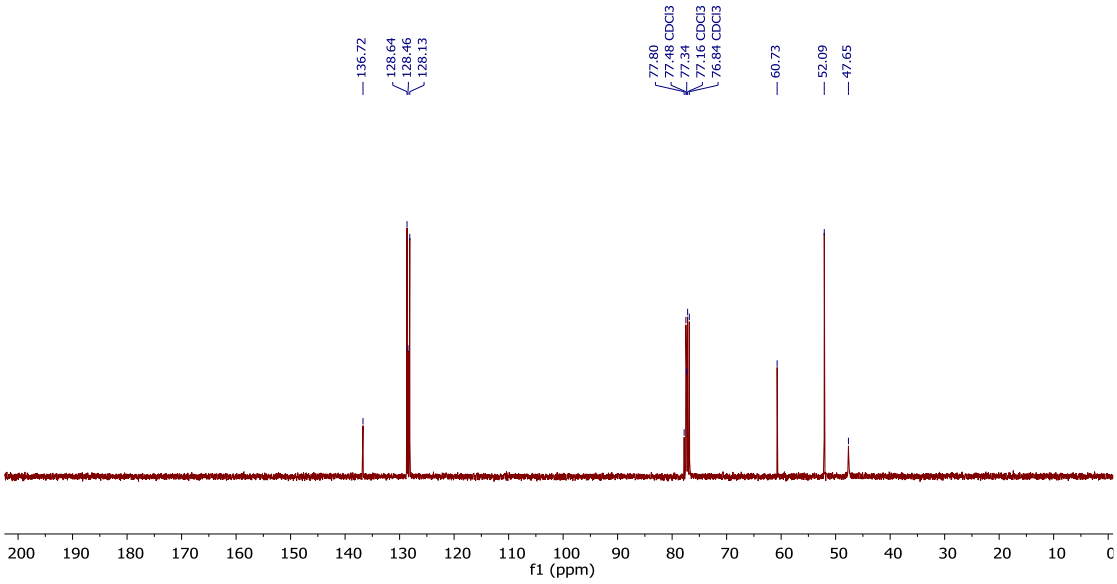



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 6.039 | 250.602 | 760.422 | 97.95 | 98.88 | n.a. |
| 2 | 10.099 | 5.248 | 8.607 | 2.05 | 1.12 | n.a. |



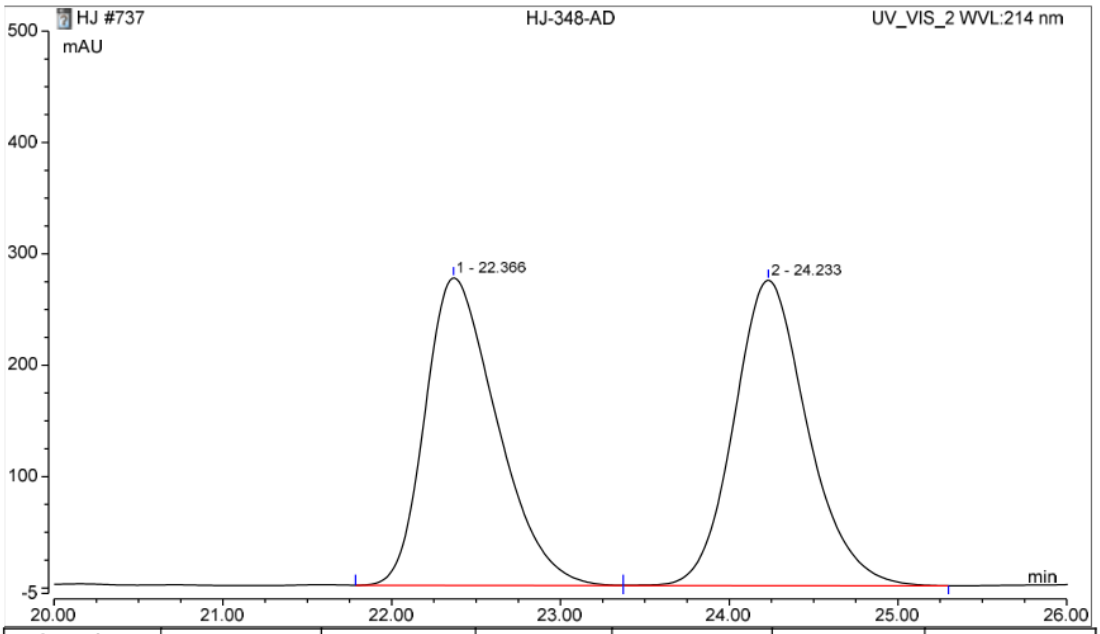
**4j**


7.58
7.57
7.40
7.36
7.33
7.31
7.26 CDCl3
4.78
3.11
3.10
3.06
3.05
3.01
2.66
2.65
0.00
2.03
3.12
1.00
8.35
0.98
f1 (ppm)


136.72
128.64
128.46
128.13
77.80 CDCl3
77.48 CDCl3
77.34
77.16 CDCl3
76.84 CDCl3
60.73
52.09
47.65
f1 (ppm)

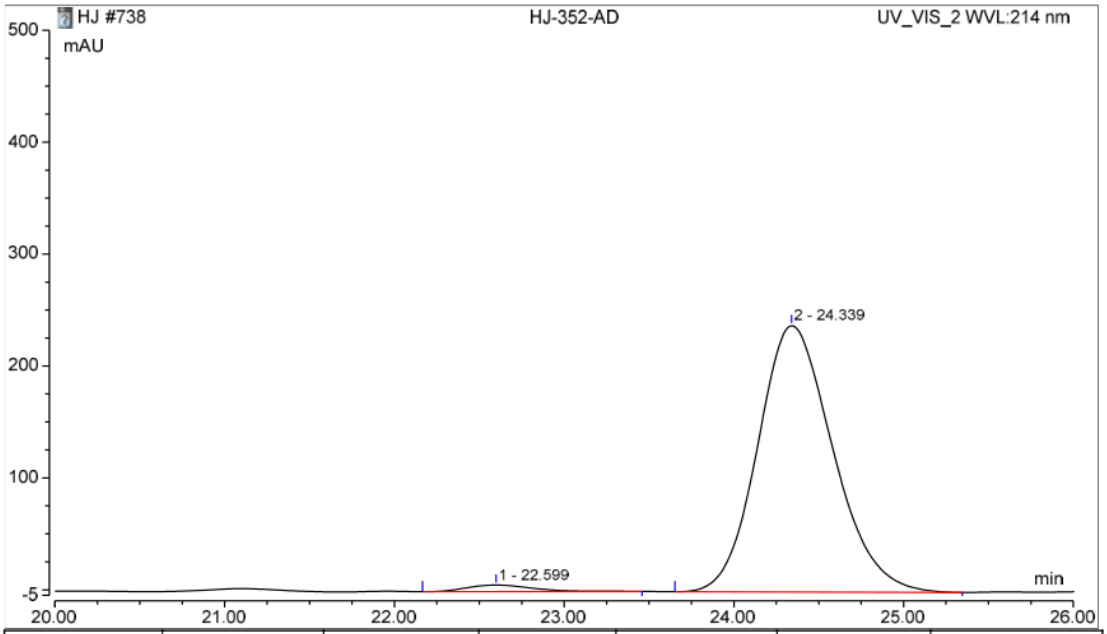
**Compound (-)-4j:** AD-H, hexane/$^{i}$PrOH = 90/10, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-4j

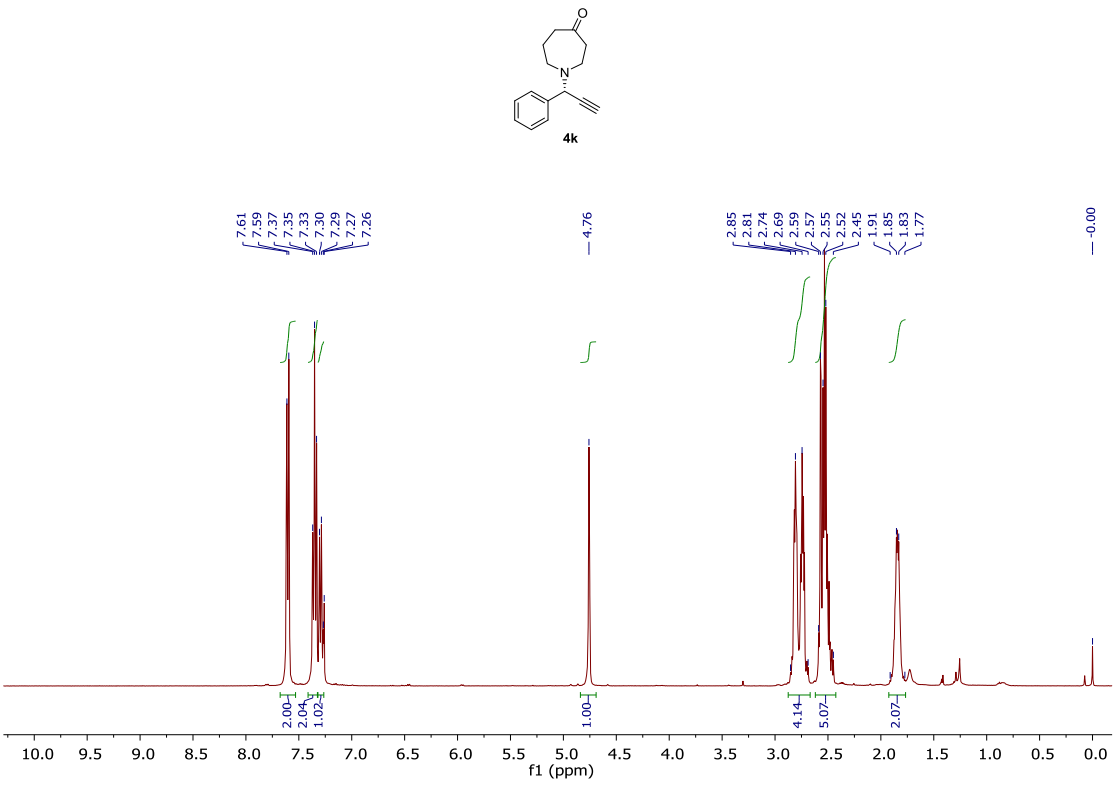


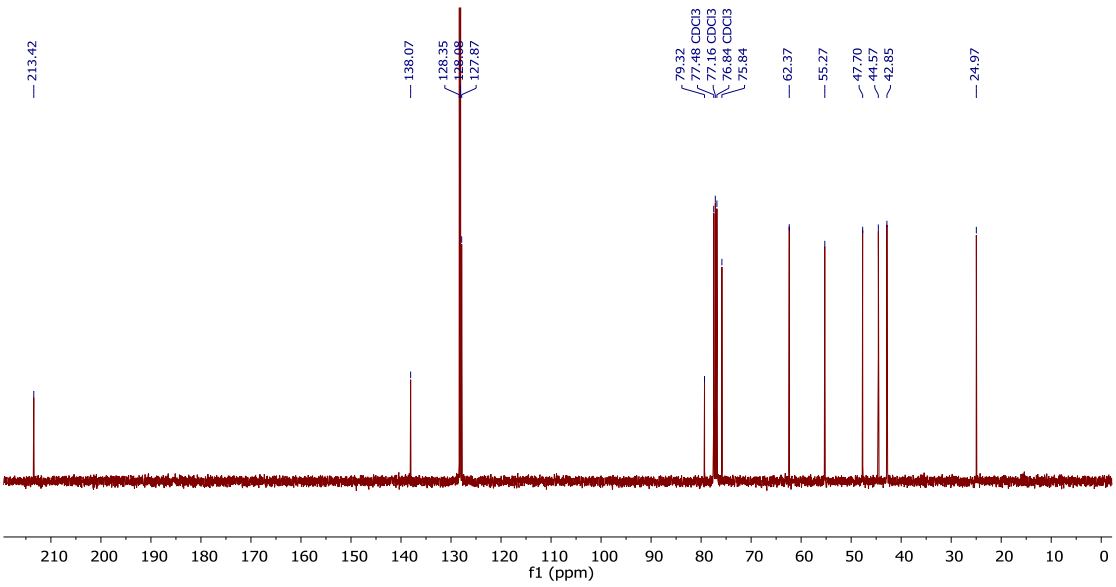

| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 22.366 | 136.162 | 276.100 | 49.57 | 50.18 | n.a. |
| 2 | 24.233 | 138.535 | 274.172 | 50.43 | 49.82 | n.a. |

## HPLC trace of 4j



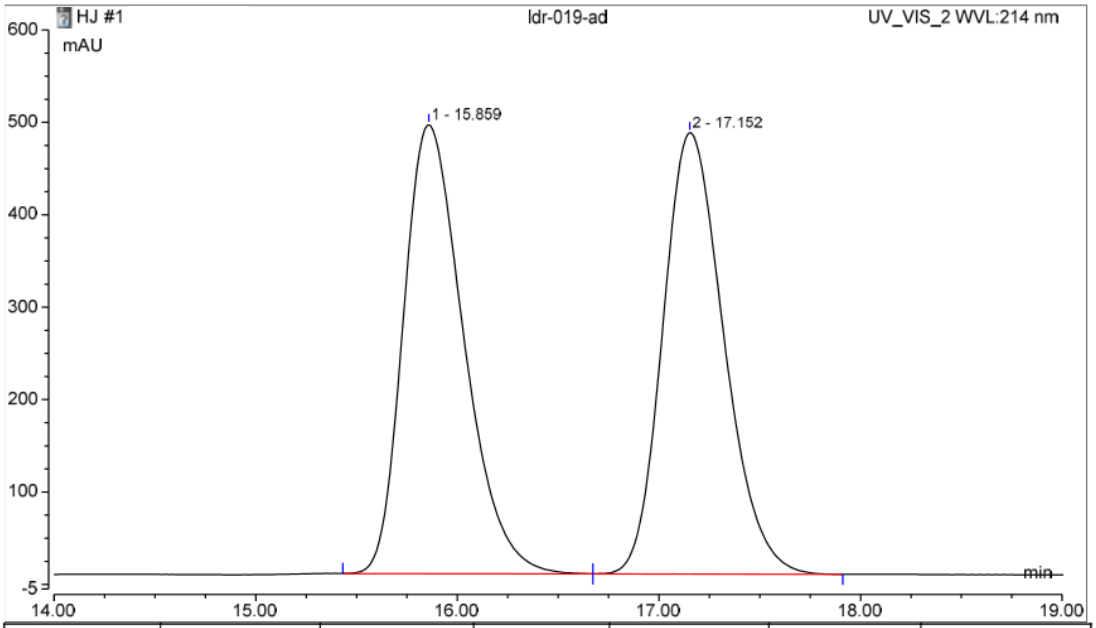

| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 22.599 | 2.673 | 5.861 | 2.14 | 2.40 | n.a. |
| 2 | 24.339 | 122.086 | 238.096 | 97.86 | 97.60 | n.a. |


4k
7.61
7.59
7.37
7.35
7.33
7.30
7.29
7.27
7.26
4.76
2.85
2.81
2.74
2.69
2.59
2.57
2.55
2.52
2.45
1.91
1.85
1.83
1.77
-0.00
2.00
2.04
1.02
1.00
4.14
5.07
2.07
f1 (ppm)


213.42
138.07
128.35
128.08
127.87
79.32
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.84
62.37
55.27
47.70
44.57
42.85
24.97
f1 (ppm)

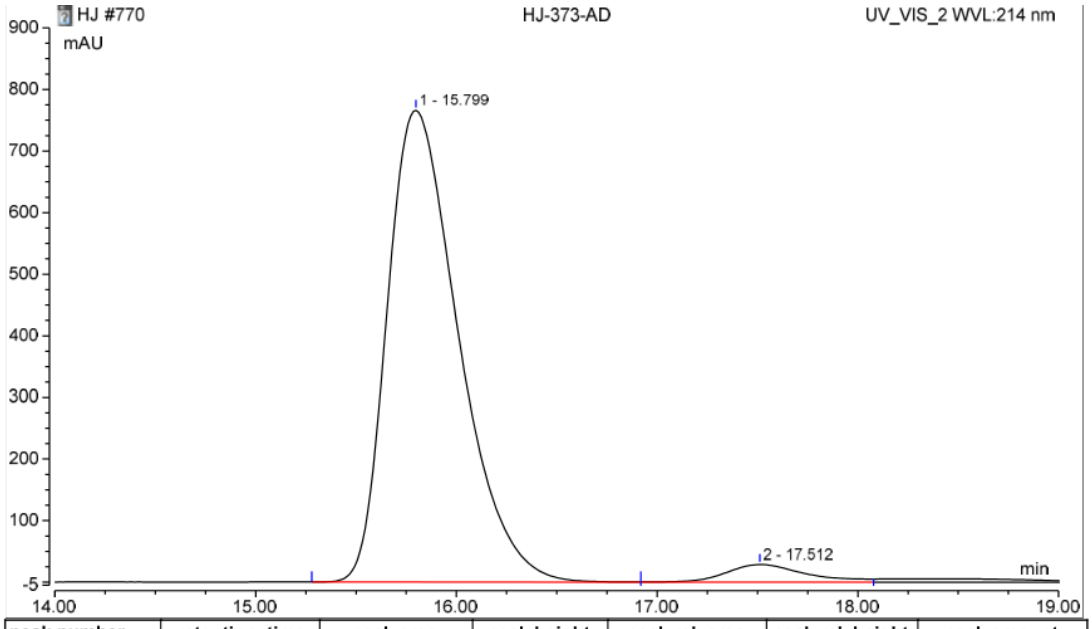
**Compound (-)-4k:** AD-H, hexane/$^{i}$PrOH = 99/1, v = 1.0 mL/min, λ = 214 nm

## HPLC trace of *rac*-4k

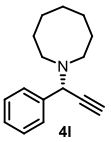



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 15.859 | 167.906 | 485.962 | 50.05 | 50.43 | n.a. |
| 2 | 17.152 | 167.575 | 477.666 | 49.95 | 49.57 | n.a. |

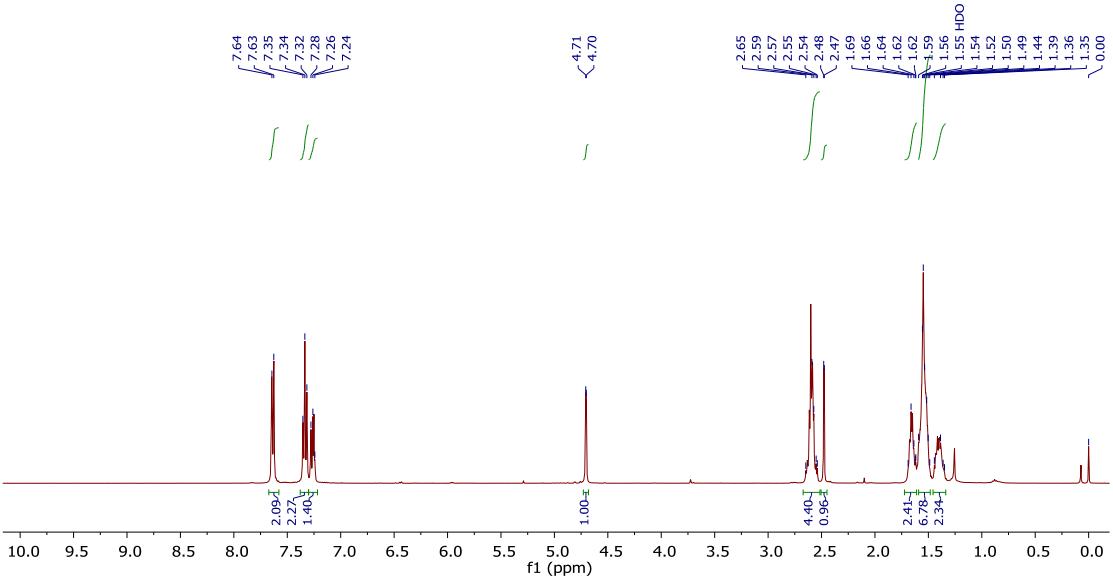
## HPLC trace of 4k




| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 15.799 | 314.395 | 765.755 | 95.98 | 96.40 | n.a. |
| 2 | 17.512 | 13.173 | 28.634 | 4.02 | 3.60 | n.a. |

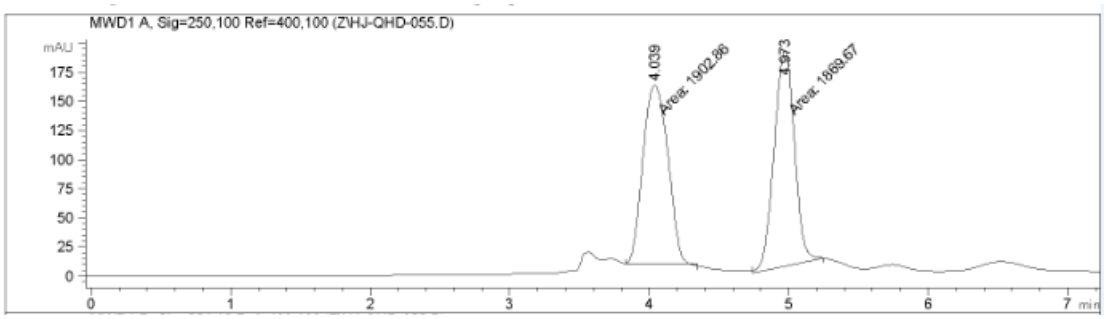


**4l**


7.64
7.63
7.35
7.34
7.32
7.28
7.26
7.24
4.71
4.70
2.65
2.59
2.57
2.55
2.54
2.48
2.47
1.69
1.66
1.64
1.62
1.62
1.59
1.56
1.55
HDO
1.54
1.52
1.50
1.49
1.44
1.39
1.36
1.35
0.00
2.09
2.27
1.40
1.00
4.40
0.96
2.41
6.78
2.34
10.0 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
f1 (ppm)

**Compound (-)-4l:** OJ-H, hexane/$^{i}$PrOH = 97/3, v = 1.0 mL/min, λ = 250 nm

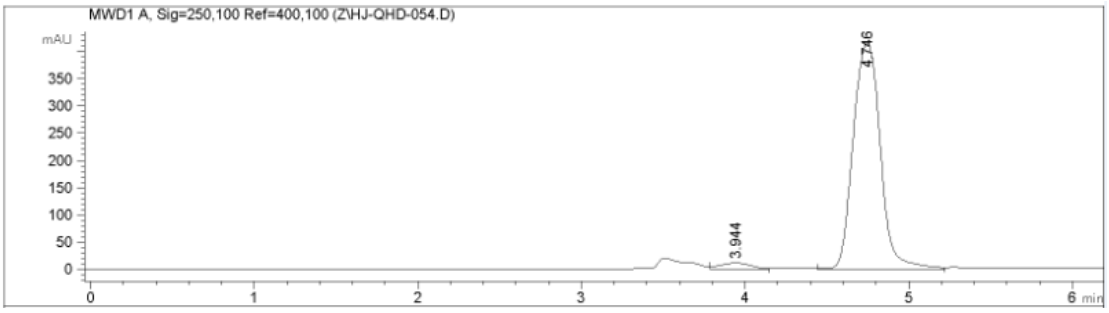
## HPLC trace of *rac*-4l




Signal 1: MWD1 A, Sig=250,100 Ref=400,100

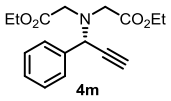
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 4.039 | MM | 0.2068 | 1902.86267 | 153.32487 | 50.4400 |
| 2 | 4.973 | MM | 0.1682 | 1869.66748 | 185.23827 | 49.5600 |
| Totals : | | | | 3772.53015 | 338.56314 | |

## HPLC trace of 4l

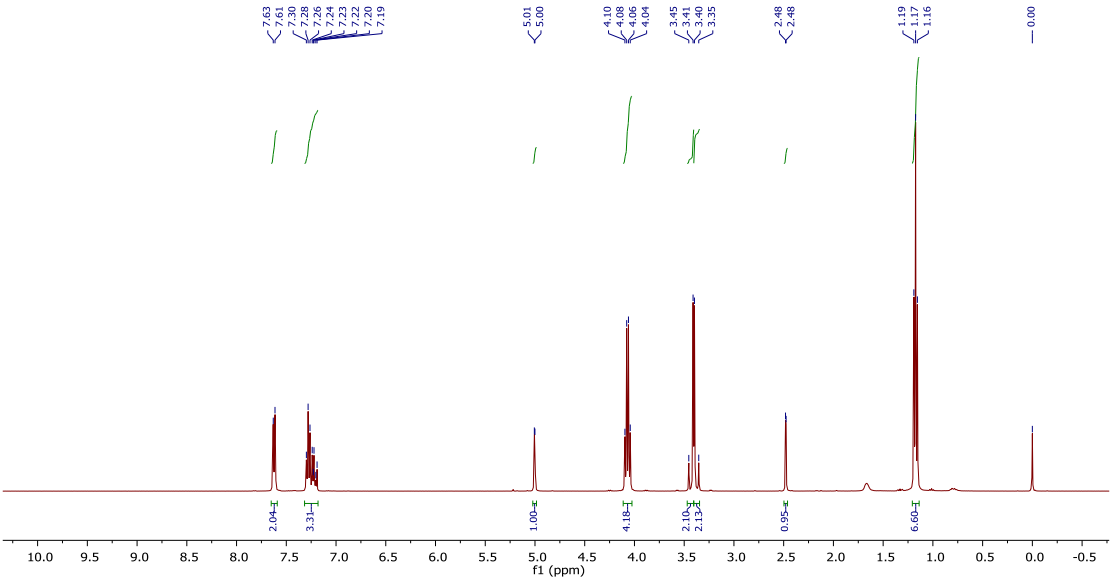


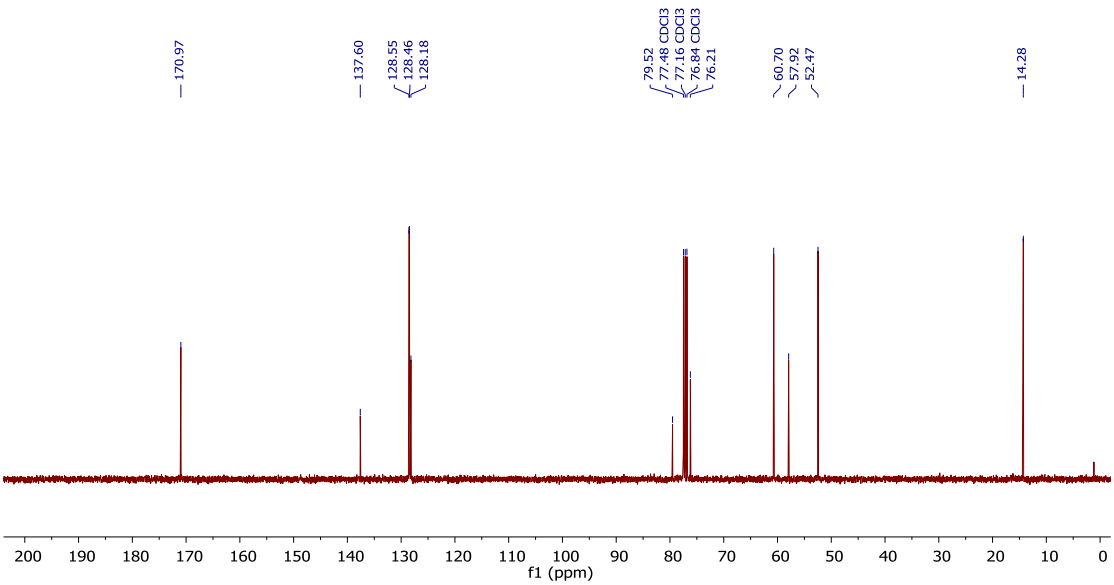

Signal 1: MWD1 A, Sig=250,100 Ref=400,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 3.944 | VV | 0.2101 | 149.45151 | 11.31824 | 3.0231 |
| 2 | 4.746 | VV | 0.1861 | 4794.21875 | 416.98465 | 96.9769 |
| Totals : | | | | 4943.67026 | 428.30289 | |


EtO2C
N
CO2Et

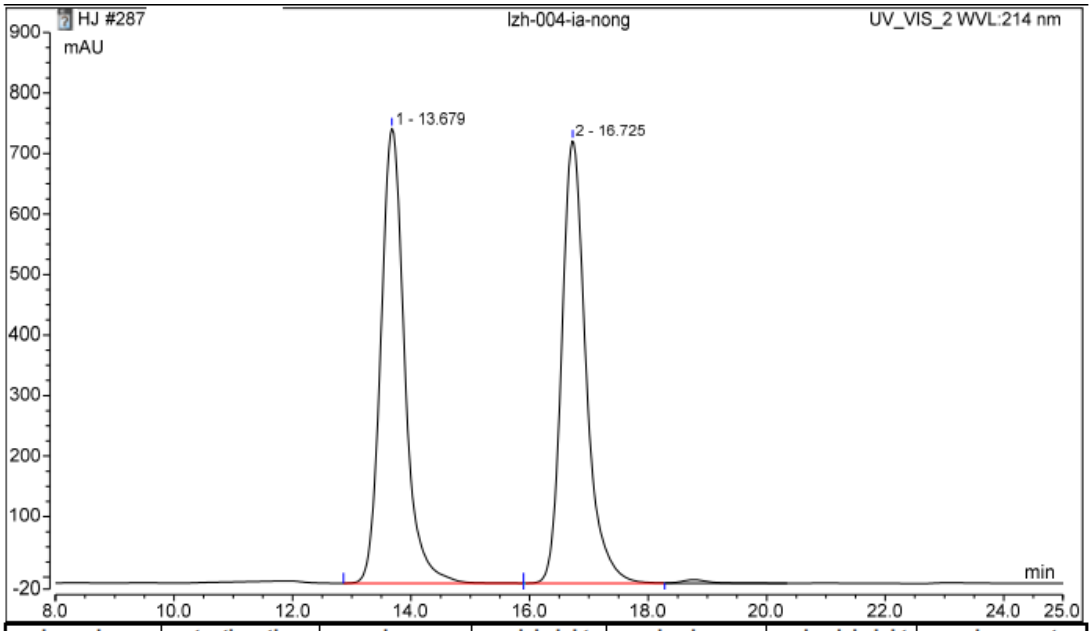
**4m**


7.63
7.61
7.30
7.28
7.26
7.24
7.23
7.22
7.20
7.19
5.01
5.00
4.10
4.08
4.06
4.04
3.45
3.41
3.40
3.35
2.48
2.48
1.19
1.17
1.16
0.00
2.04
3.31
1.00
4.18
2.10
2.13
0.95
6.60
f1 (ppm)


170.97
137.60
128.55
128.46
128.18
79.52
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.21
60.70
57.92
52.47
14.28
f1 (ppm)

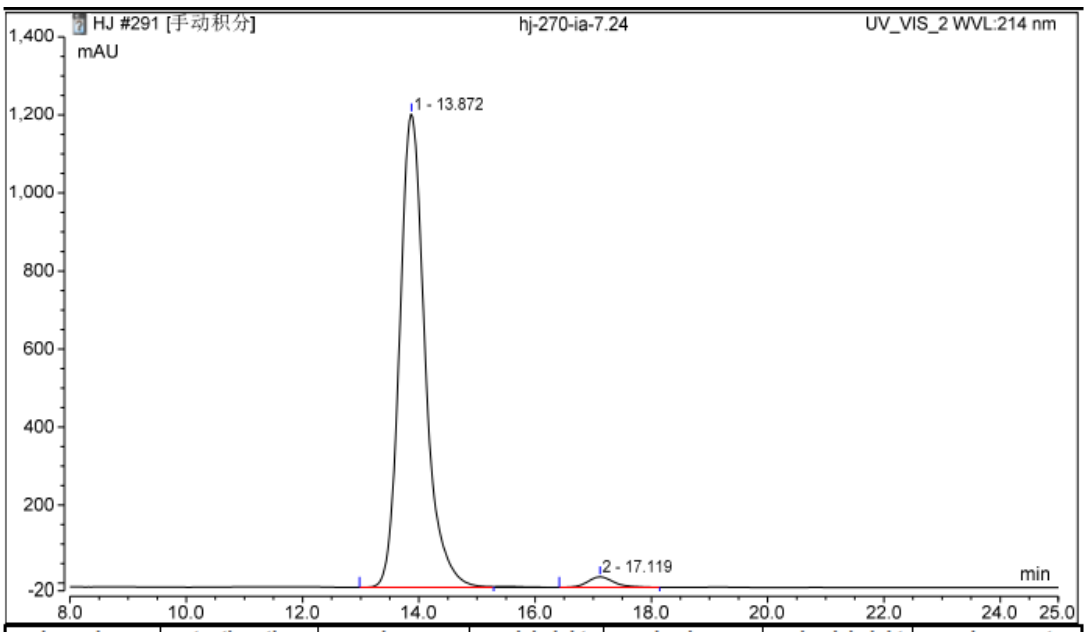
**Compound (-)-4m:** IA, hexane/$^{i}$PrOH = 99/1, v = 0.7 mL/min, λ = 214 nm

## HPLC trace of *rac*-4m

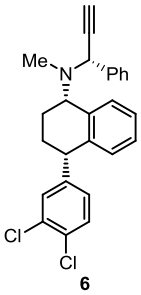



| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 13.679 | 348.543 | 751.647 | 50.15 | 50.67 | n.a. |
| 2 | 16.725 | 346.409 | 731.725 | 49.85 | 49.33 | n.a. |

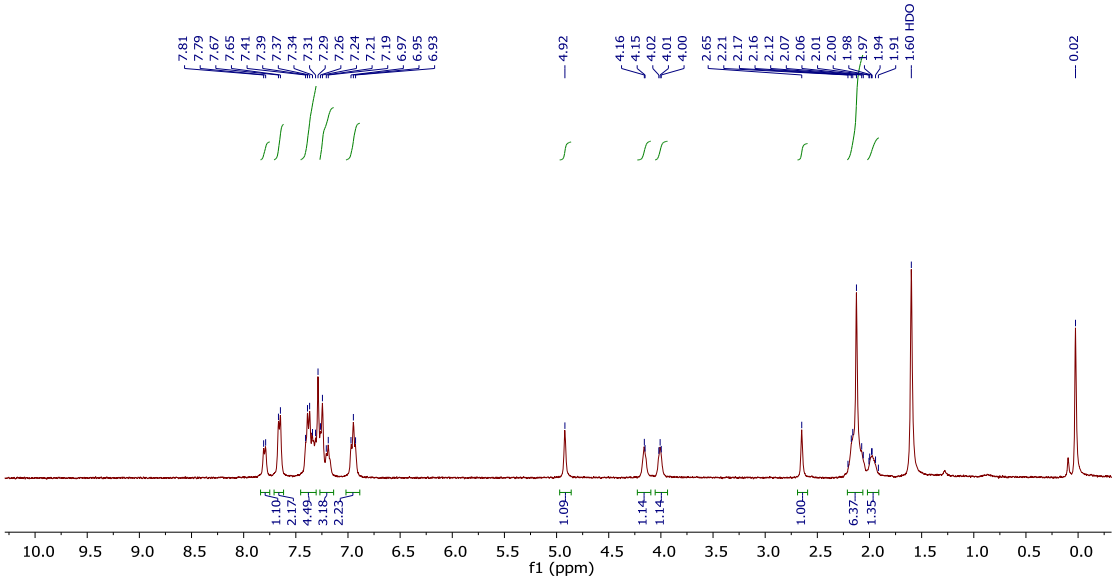
## HPLC trace of *rac*-4m

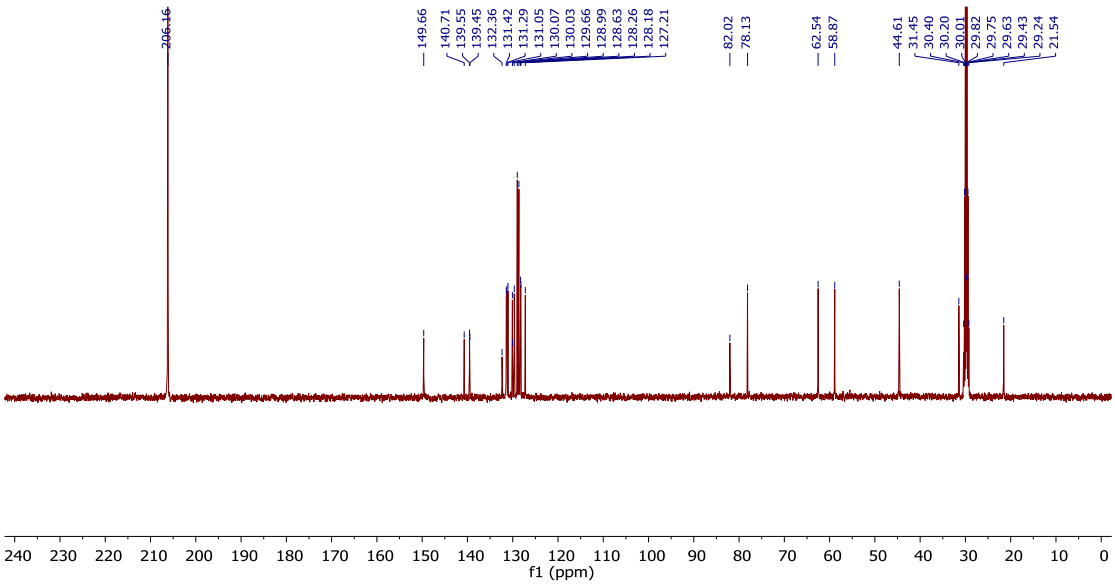


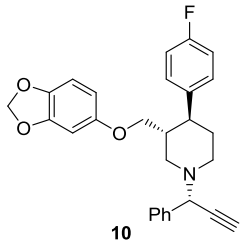

| peak.number | retention_time min | peak.area mAU*min | peak.height mAU | peak.rel_area % | peak.rel_height % | peak.amount n.a. |
|---|---|---|---|---|---|---|
| 1 | 13.872 | 611.757 | 1213.007 | 97.76 | 97.85 | n.a. |
| 2 | 17.119 | 13.989 | 26.702 | 2.24 | 2.15 | n.a. |


Me
N
Ph
Cl
Cl

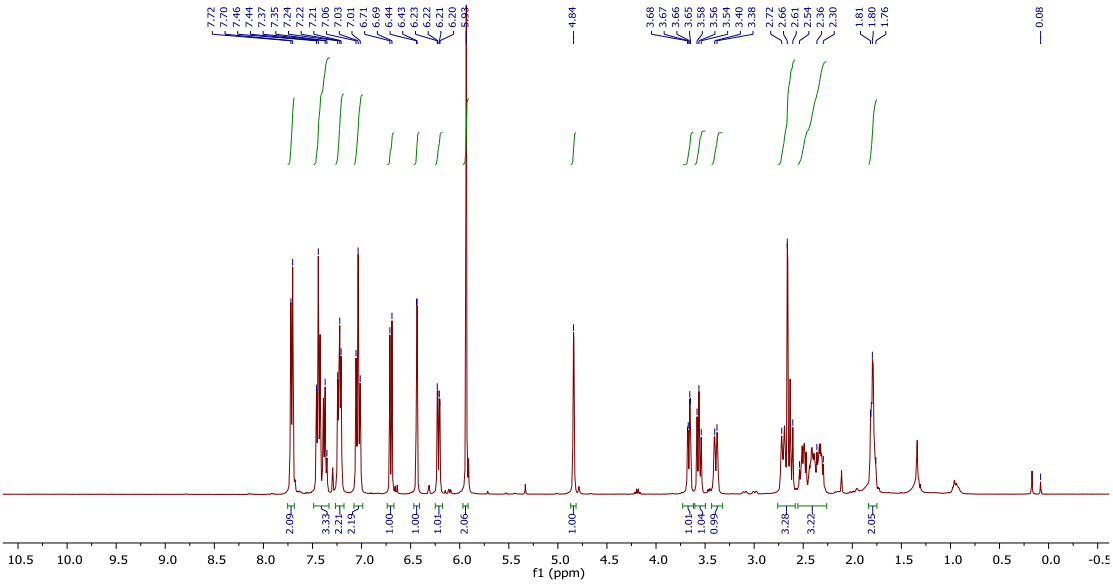
**6**

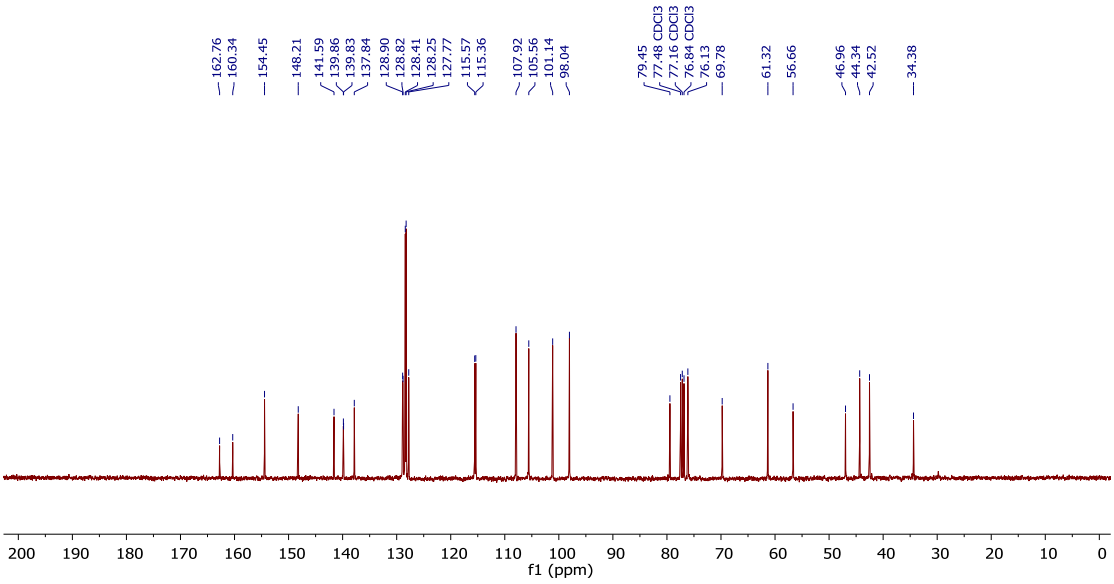

7.81
7.79
7.67
7.65
7.41
7.39
7.37
7.34
7.31
7.29
7.26
7.24
7.21
7.19
6.97
6.95
6.93
4.92
4.16
4.15
4.02
4.01
4.00
2.65
2.21
2.17
2.16
2.12
2.07
2.06
2.01
2.00
1.98
1.97
1.94
1.91
1.60 HDO
0.02
1.10
2.17
4.49
3.18
2.23
1.09
1.14
1.14
1.00
6.37
1.35
f1 (ppm)

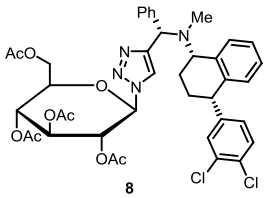

206.16
149.66
140.71
139.55
139.45
132.36
131.42
131.29
131.05
130.07
130.03
129.66
128.99
128.63
128.26
128.18
127.21
82.02
78.13
62.54
58.87
44.61
31.45
30.40
30.20
30.01
29.82
29.75
29.63
29.43
29.24
21.54
f1 (ppm)


F
O
O
O
N
Ph

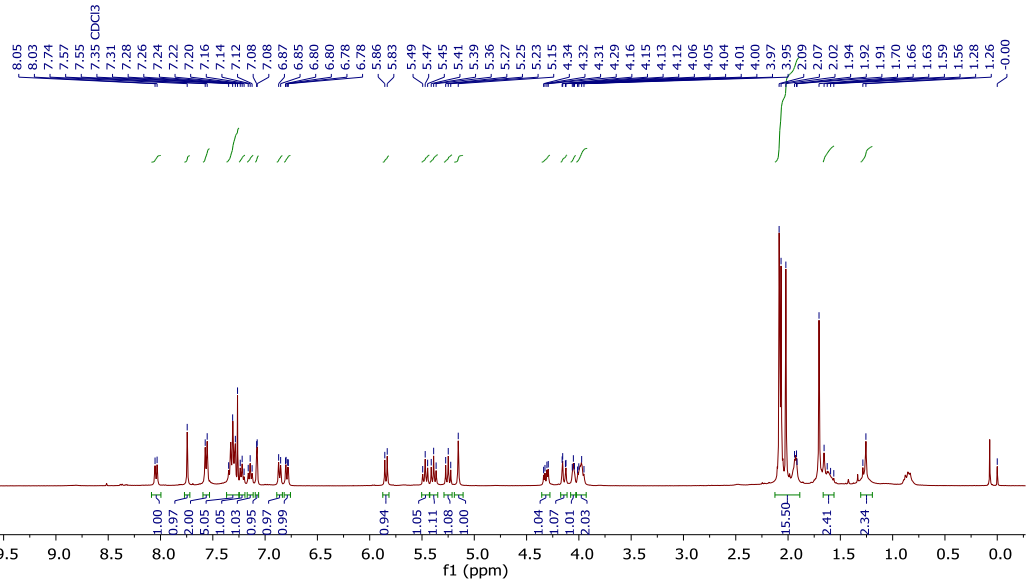
**10**

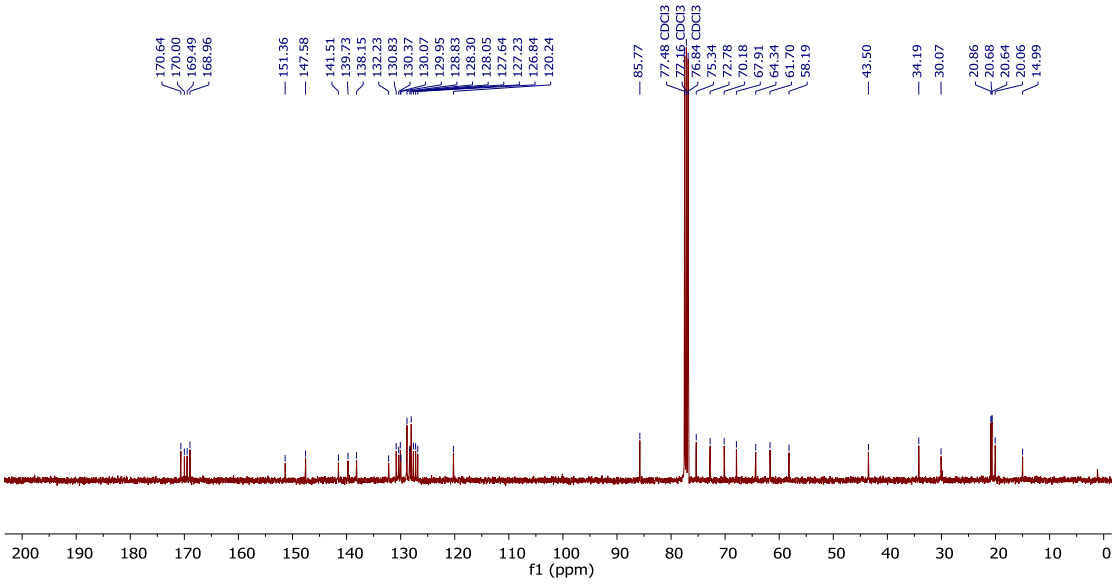

7.72
7.70
7.46
7.44
7.37
7.35
7.24
7.22
7.21
7.06
7.03
7.01
6.71
6.69
6.44
6.43
6.23
6.22
6.21
6.20
5.93
4.84
3.68
3.67
3.66
3.65
3.58
3.56
3.54
3.40
3.38
2.72
2.66
2.61
2.54
2.36
2.30
1.81
1.80
1.76
0.08
2.09
3.33
2.21
2.19
1.00
1.00
1.01
2.06
1.00
1.01
1.04
0.99
3.28
3.22
2.05
f1 (ppm)

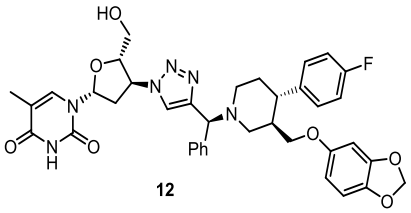

162.76
160.34
154.45
148.21
141.59
139.86
139.83
137.84
128.90
128.82
128.41
128.25
127.77
115.57
115.36
107.92
105.56
101.14
98.04
79.45
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.13
69.78
61.32
56.66
46.96
44.34
42.52
34.38
f1 (ppm)


Ph
Me
N
AcO
N
N
O
N
OAc
OAc
OAc
Cl
Cl

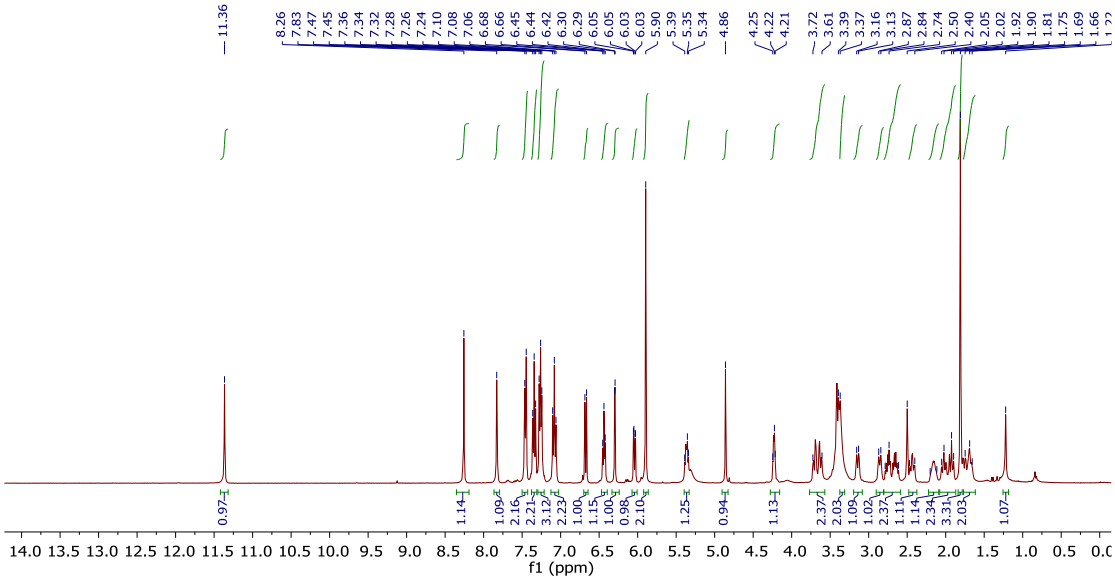
**8**

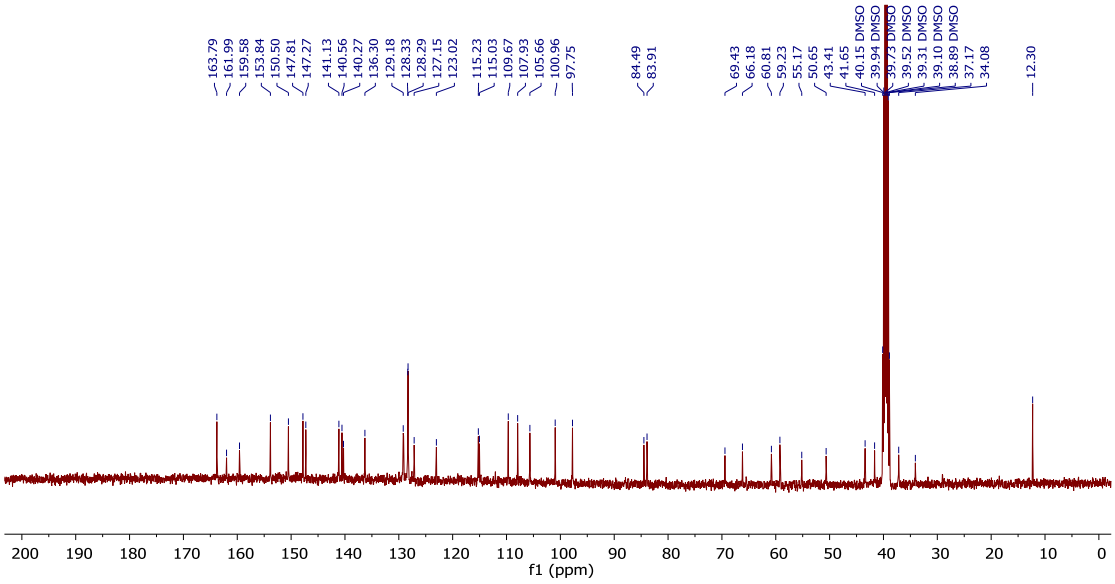

8.05
8.03
7.74
7.57
7.55
7.35 CDCl3
7.31
7.28
7.26
7.24
7.22
7.20
7.16
7.14
7.12
7.08
7.08
6.87
6.85
6.80
6.80
6.78
6.78
5.86
5.83
5.49
5.47
5.45
5.41
5.39
5.36
5.27
5.25
5.23
5.15
4.34
4.32
4.31
4.29
4.16
4.15
4.13
4.12
4.06
4.05
4.04
4.01
4.00
3.97
3.95
2.09
2.07
2.02
1.94
1.92
1.91
1.70
1.66
1.63
1.59
1.56
1.28
1.26
-0.00
1.00
0.97
2.00
5.05
1.05
1.03
0.95
0.97
0.99
0.94
1.05
1.11
1.08
1.00
1.04
1.07
1.01
2.03
15.50
2.41
2.34
10.0
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
f1 (ppm)


170.64
170.00
169.49
168.96
151.36
147.58
141.51
139.73
138.15
132.23
130.83
130.37
130.07
129.95
128.83
128.30
128.05
127.64
127.23
126.84
120.24
85.77
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.34
72.78
70.18
67.91
64.34
61.70
58.19
43.50
34.19
30.07
20.86
20.68
20.64
20.06
14.99
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HO
O
N
N
N
N
F
Ph
O
O
O
N
H
O
O

**12**


11.36
8.26
7.83
7.47
7.45
7.36
7.34
7.32
7.28
7.26
7.24
7.10
7.08
7.06
6.68
6.66
6.45
6.44
6.42
6.30
6.29
6.05
6.05
6.03
6.03
5.90
5.39
5.35
5.34
4.86
4.25
4.22
4.21
3.72
3.61
3.39
3.37
3.16
3.13
2.87
2.84
2.74
2.50
2.40
2.05
2.02
1.92
1.90
1.81
1.75
1.69
1.66
0.97
1.14
1.09
2.16
2.21
3.12
2.23
1.00
1.15
1.00
0.98
2.10
1.25
0.94
1.13
2.37
2.03
1.09
1.02
2.37
1.11
1.14
2.34
3.31
2.03
1.07
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 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
f1 (ppm)


163.79
161.99
159.58
153.84
150.50
147.81
147.27
141.13
140.56
140.27
136.30
129.18
128.33
128.29
127.15
123.02
115.23
115.03
109.67
107.93
105.66
100.96
97.75
84.49
83.91
69.43
66.18
60.81
59.23
55.17
50.65
43.41
41.65
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
37.17
34.08
12.30
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)