Supporting Information

Highly Enantioselective Copper-Catalyzed Propargylic Amination to Access N-tethered 1,6-Enynes

Si-Jia Li,[†,§] Jian Huang,[†,§] Jin-Yu He,[†] Rui-Jin Zhang, [†] Hao-Dong Qian,[†] Xue-Lin Dai,[†] Han-Han Kong, [†] and Hao Xu[*,†]*

[†] CCNU-uOttawa Joint Research Centre, Key Laboratory of Pesticides & Chemical Biology Ministry of Education, Interna-tional Joint Research Center for Intelligent Biosensing Technology and Health, College of Chemistry, Central China Normal University, 152 Luoyu Road, Wuhan, 430079, China

[§]S. L. and J. H. contributed equally.

Table of Contents **page**

1. General Information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Dry solvents (MeOH, CH_2Cl_2, THF, MeCN, toluene) were purified by distillation over the drying agents.

All reactions were monitored by thin-layer chromatography (TLC) on silica gel plates using UV light as visualizing agent. Compounds were visualized by irradiation with UV light or potassium permanganate staining. Flash column chromatography was performed using 200-300 or 300-400 mesh silica gel. Solvent mixtures are understood as volume/volume.

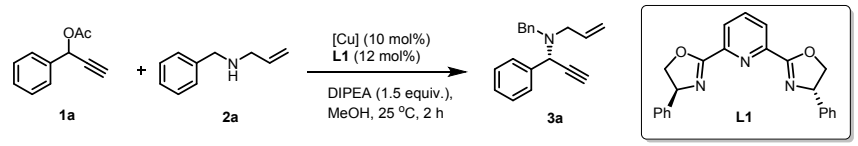
^1H NMR spectra were recorded on 400 or 600 MHz spectrophotometers, ^{13}C NMR spectra were recorded on 101 or 150 MHz with complete proton decoupling spectrophotometers using $CDCl_3$ or CD_2Cl_2 or CD_3COCD_3 as solvent. Data were reported in the following order: chemical shift (δ) values are reported in ppm with the solvent resonance as internal standard ($CDCl_3$: δ = 7.26 ppm for ^1H,TMS: δ = 0 ppm for ^1H, δ = 77.16 ppm for ^{13}C; CD_2Cl_2: δ = 5.32 ppm for ^1H, δ = 53.84 ppm for ^{13}C; CD_3COCD_3: δ = 2.05 ppm for ^1H, δ = 29.84 ppm for ^{13}C, δ = 206.26 ppm for ^{13}C); multiplicities are indicated brs (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet) m (multiplet); coupling constants (*J*) are given in Hertz (Hz).

Enantiomeric excess (ee) values were determined by chiral HPLC of the purified products. Optical rotations were measured by the polarimeter. All air- and moisture-sensitive reactions were performed under the atmosphere of N_2 in fire dried glasswares.

HRMS was recorded on Agilent technologies 6224 TOF LC/MS instrument or Bruker ultrafleXtreme MALDI-TOF/TOF mass spectrometer.

2. Optimization Studies

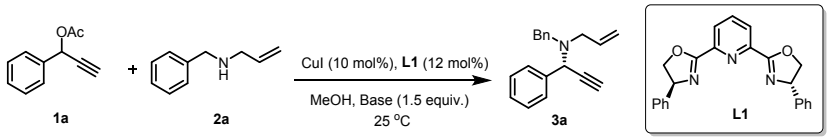
Table S1. The effect of the copper salt on the reaction.



Entry[a]	[Cu]	Yield[b]/%	ee[c]/%
1	CuI	81	50
2[d]	CuI	77	50
3	$Cu(CH_3CN)_4BF_4$	87	21
4	$Cu(CH_3CN)_4PF_6$	80	49
5	CuCl	75	47
6	CuOAc	77	39
7	$CuOTf•(C_6H_6)_{1/2}$	59	44
8	$Cu(OTf)_2$	34	40
9	$Cu(OAc)_2•H_2O$	73	47

[a] Unless otherwise noted, reactions were conducted with **1a** (0.2 mmol), **2a** (1.5 equiv.) and Copper salts (10 mol%), chiral ligand **L1** (12 mol%) in MeOH (2.0 mL). [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Repeat Entry **1**.

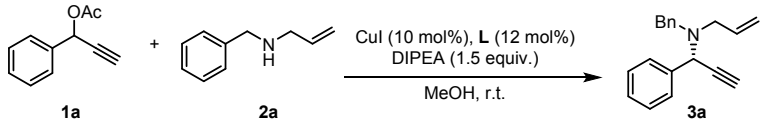
Table S2. The effect of base on the reaction.

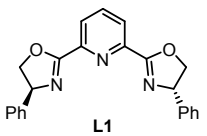


Entry[a]	Base	Time/h	Yield[b]/%	ee[c]/%
1	**DIPEA**	**2**	**81**	**50**
2[d]	DIPEA	2	77	50
3	Et_3N	3	80	50
4	Cs_2CO_3	2	35	48
5	^{t}BuOK	4	33	47
6	DBU	1	70	40
7	KOH	2	73	49
8	Py	2	80	42
9	Piperidine	4	48	51

[a] Unless otherwise noted, reactions were conducted with **1a** (0.2 mmol), **2a** (1.5 equiv.) Copper salts (10 mol%), and chiral ligand **L1** (12 mol%) in MeOH (2.0 mL). [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Repeat Entry **1**

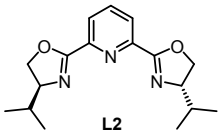
Table S3. The effect of the ligand on the reaction.





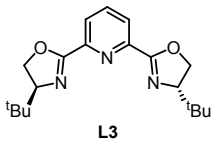
L1

2 h, 81%, 50% ee



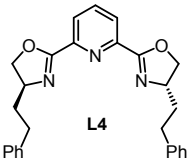
L2

2 h, 82%, 25% ee



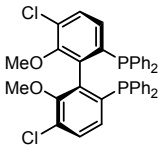
L3

2 h, 15%, 19% ee



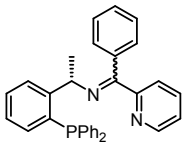
L4

2 h, 82%, 21% ee



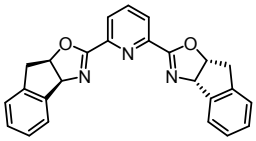
L5

2 h, trace



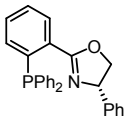
L6

2 h, 78%, 82% ee



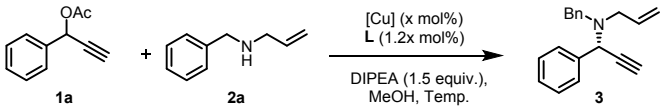
L8

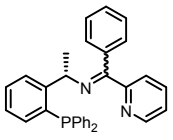
2 h, 70%, 31% ee



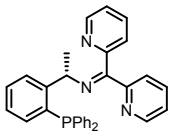
L9

2 h, trace





L6
Z/E = 50/50



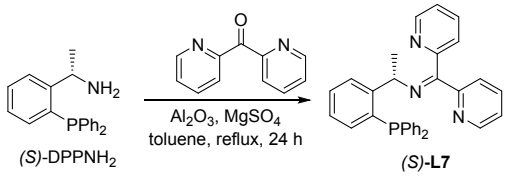
L7

Entry[a]	[Cu]	x	L	T/°C	Time/h	Yield[b]/%	ee[c]/%
1	CuI	10	**L6**	25	2	78	82
2	CuI	10	**L7**	25	2	83	86
3	$Cu(CH_3CN)_4PF_6$	10	**L7**	25	3	90	91
4	$Cu(OAc)_2•H_2O$	10	**L7**	25	2	87	93
5	$Cu(OAc)_2•H_2O$	5	**L7**	25	2	64	91
6	$Cu(OAc)_2•H_2O$	5	**L7**	0	3	84	97
7	**$Cu(OAc)_2•H_2O$**	**5**	**L7**	**-20**	**3**	**90**	**97**
8	$Cu(OAc)_2•H_2O$	2.5	**L7**	-20	24	77	96
9	$Cu(OAc)_2•H_2O$	5	**L7**	-40	4	93	97

[a] Unless otherwise noted, reactions were conducted with **1a** (0.2 mmol), **2a** (1.5 equiv.), MeOH (2.0 mL). [b] Isolated Yield. [c] Determined by HPLC analysis on a chiral stationary phase.

3. Experimental Procedures

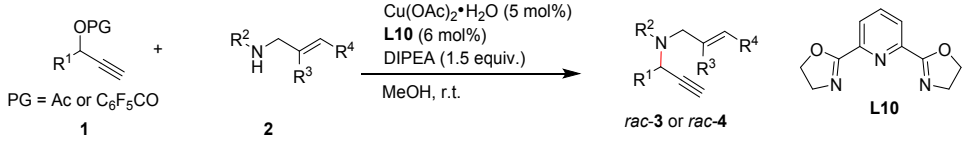
Procedure A: Synthesis of chiral *P,N,N*-ligand.



To a solution of (*S*)-DPPNH$_2$ (160 mg, 1.05 equiv.) in 3 mL anhydrous toluene was added di(2-pyridyl) ketone (92 mg, 0.5 mmol), active Al_2O_3 (250 mg), and anhydrous $MgSO_4$ (250 mg). The reaction mixture was refluxed for 13 h under nitrogen atmosphere, then cooled to room temperature. Al_2O_3 and $MgSO_4$ were removed by the filtration. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel.

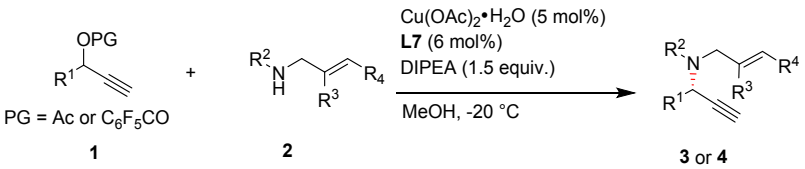
[1] F.-L. Zhu, X.-P. Hu, *Angew. Chem. Int. Ed.* **2014**, *53*, 1410–1414.

Procedure B: General procedure for the preparation of racemic products.



In a schlenk tube, Cu(OAc)$_2$•H$_2$O (5 mol%) and **L10** (6 mol%) were stirred at room temperature in anhydrous methanol (1 mL) under nitrogen atmosphere for 1 h. *N*-allyl amine **2** (0.3 mmol, 1.5 equiv.) and the solution of **1** (0.2 mmol, 1 equiv.) in anhydrous methanol (1 mL) was added to the above solution. Subsequently, ^{i}Pr$_2$NEt (1.5 equiv.) was added. 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 °C)/ethyl acetate as eluent, affording *N*-tethered 1,6-enynes *rac*-**3** or *rac*-**4**.

Procedure C: General procedure for the preparation of enantioenriched product



In a schlenk tube, Cu(OAc)$_2$•H$_2$O (5 mol%) and **L7** (6 mol%) were stirred at room temperature in anhydrous methanol (1 mL) under nitrogen atmosphere for 1 h. *N*-allyl amine **2** (0.3 mmol, 1.5 equiv.) was added, then the solution of propargyl ester **1** (0.2 mmol, 1 equiv.) in anhydrous methanol (1 mL) was added. Subsequently, ^{i}Pr$_2$NEt (1.5 equiv.) was added at -20 °C. 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 °C)/ethyl acetate as eluent, affording chiral *N*-tethered 1,6-enynes **3** or **4**.

Procedure D: Synthesis of propargyl esters according to the following literature:

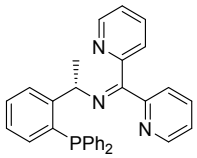
[2] a) M. J. Ardolino, M. S. Eno, J. P. Morken, *Adv. Synth. Catal*. **2013**, *355*, 3413-3419. b) A. Yoshida, G. Hattori, Y. Miyake, Y. Nishibayashi, *Org. Lett*. **2011**, *13*, 2460-2463.

Procedure E: Synthesis of allyl benzylamine according to the following literature:

[3] M.-Y. Wang, L.-N. He, S.-H. Li, *Green Chem.*, **2017**, *19*, 1240-1244.

4. Product Characterization

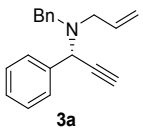
(*S*)-*N*-(1-(2-(diphenylphosphanyl)phenyl)ethyl)-1,1-di(pyridin-2-yl)methanimine



L7

L7: 13 h, 66% yield; amorphous yellow solid; According to procedure A; ^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 8.58 (d, *J* = 4.8 Hz, 1H), 8.41 (d, *J* = 4.8 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 8.06 (dd, *J* = 7.6, 3.8 Hz, 1H), 7.78 (td, *J* = 7.8, 1.8 Hz, 1H), 7.60 (td, *J* = 7.8, 1.8 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.32 – 7.25 (m, 8H), 7.15 – 7.09 (m, 3H), 7.07 – 7.03 (m, 2H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.83 (dd, *J* = 7.8, 4.2 Hz, 1H), 5.50 – 5.43 (m, 1H), 1.31 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, Methylene Chloride-d2) δ 165.47, 157.81, 155.99, 151.33, 151.17, 149.93, 148.92, 137.76, 137.68, 137.67, 137.60, 136.75, 136.25, 134.69, 134.55, 134.39, 134.30, 134.18, 133.97, 133.84, 129.93, 129.22, 128.99, 128.98, 128.94, 128.91, 128.09, 128.06, 127.34, 124.64, 124.03, 123.36, 122.60, 59.62, 59.45, 25.66. ^{31}P NMR (162 MHz, Methylene Chloride-d2) δ -18.18. HRMS: calcd. for $[M+H]^+$ $C_{31}H_{27}N_3P$ = 472.19371, found: 472.19331; $[\alpha]_D^{RT}$ = -46.37 (c = 1.0 in $CHCl_3$);

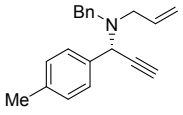
(*R*)-*N*-benzyl-*N*-(1-phenylprop-2-yn-1-yl)prop-2-en-1-amine



3a

3a: 3 h, 90% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.20 (m, 8H), 5.89 – 5.79 (m, 1H), 5.29 (d, *J* = 17.2 Hz, 1H), 5.13 (d, *J* = 10.2 Hz, 1H), 4.82 (s, 1H), 3.79 (d, *J* = 13.6 Hz, 1H), 3.40 (d, *J* = 13.6 Hz, 1H), 3.19 – 3.14 (m, 1H), 3.02 – 2.96 (m, 1H), 2.57 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.65, 138.80, 136.56, 128.92, 128.39, 128.22, 127.60, 127.09, 117.63, 79.18, 75.87, 55.75, 54.51, 53.39. HRMS: calcd. for $[M+H]^+$ $C_{19}H_{20}N$ = 262.15903, found: 262.15972; $[\alpha]_D^{RT}$ = -90.50 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ODH column, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 7.1 min; minor enantiomer: t_R = 7.9 min, 97% ee.

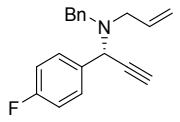
(*R*)-*N*-benzyl-*N*-(1-(*p*-tolyl)prop-2-yn-1-yl)prop-2-en-1-amine



3b

3b: 3 h, 82% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.48 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.18 – 7.14 (m, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 5.84 – 5.74 (m, 1H), 5.24 (d, *J* = 17.6 Hz, 1H), 5.08 (d, *J* = 9.8 Hz, 1H), 4.73 (s, 1H), 3.74 (d, *J* = 13.6 Hz, 1H), 3.34 (d, *J* = 13.6 Hz, 1H), 3.14 – 3. 10 (m, 1H), 2.94 (dd, *J* = 14.2, 8.4 Hz, 1H), 2.50 (d, *J* = 2.2 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.73, 137.19, 136.62, 135.77, 128.91, 128.89, 128.36, 128.13, 127.03, 117.54, 79.42, 75.65, 55.49, 54.41, 53.33, 21.23. HRMS: calcd. for $[M+H]^+$ $C_{20}H_{22}N$ = 276.17468, found: 276.17535; $[\alpha]_D^{RT}$ = -65.13 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 234 nm, major enantiomer: t_R = 12.4 min; minor enantiomer: t_R = 18.4 min, 99% ee.

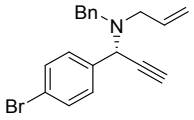
(*R*)-*N*-benzyl-*N*-(1-(4-fluorophenyl)prop-2-yn-1-yl)prop-2-en-1-amine



3c

3c: 5 h, 93% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 – 7.51 (m, 2H), 7.29 – 7.13 (m, 5H), 6.93 (t, *J* = 8.8 Hz, 2H), 5.79 – 5.69 (m, 1H), 5.20 (d, *J* = 17.0 Hz, 1H), 5.06 (d, *J* = 10.0 Hz, 1H), 4.68 (s, 1H), 3.70 (d, *J* = 13.6 Hz, 1H), 3.31 (d, *J* = 13.6 Hz, 1H), 3.09 – 3.04 (m, 1H), 2.90 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.51 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.35 (d, *J* = 245.7 Hz), 139.48, 136.39, 134.55 (d, *J* = 3.0 Hz), 129.83 (d, *J* = 8.1 Hz), 128.90, 128.44, 127.18, 117.75, 115.01(d, *J* = 21.5 Hz), 78.96, 76.11, 55.14, 54.51, 53.33. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.47. HRMS: calcd. for $[M+H]^+$ $C_{19}H_{19}FN$ = 280.14960, found: 280.14975; $[\alpha]_D^{RT}$ = -96.80 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 13.0 min; minor enantiomer: t_R = 15.0 min, 98% ee.

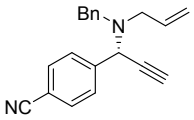
(*R*)-*N*-benzyl-*N*-(1-(4-bromophenyl)prop-2-yn-1-yl)prop-2-en-1-amine



3d

3d: 3 h, 85% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.45 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.21 (m, 4H), 7.19 – 7.14 (m, 1H), 5.79 – 5.69 (m, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.07 (d, *J* = 10.0 Hz, 1H), 4.66 (s, 1H), 3.69 (d, *J* = 13.6 Hz, 1H), 3.31 (d, *J* = 13.6 Hz, 1H), 3.08 – 3.04 (m, 1H), 2.90 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.52 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.36, 138.03, 136.29, 131.33, 129.98, 128.90, 128.47, 127.23, 121.57, 117.85, 78.61, 76.31, 55.33, 54.58, 53.40. HRMS: calcd. for $[M+H]^+$ $C_{19}H_{19}{}^{79}BrN$ = 340.06954, found: 340.06962; $[\alpha]_D^{RT}$ = -29.03 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 13.1 min; minor enantiomer: t_R = 14.8 min, 97% ee.

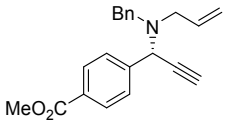
(*R*)-4-(1-(allyl(benzyl)amino)prop-2-yn-1-yl)benzonitrile



3e

3e: 5 h, 82% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.21 (m, 4H), 7.18 – 7.14 (m, 1H), 5.78 – 5.68 (m, 1H), 5.21 (d, *J* = 17.4 Hz, 1H), 5.08 (d, *J* = 10.2 Hz, 1H), 4.72 (s, 1H), 3.68 (d, *J* = 13.6 Hz, 1H), 3.34 (d, *J* = 13.6 Hz, 1H), 3.05 – 3.01 (m, 1H), 2.91 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.57 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.54, 138.94, 135.91, 132.07, 128.93, 128.88, 128.54, 127.40, 118.94, 118.19, 111.53, 77.78, 76.99, 55.64, 54.80, 53.56. HRMS: calcd. for $[M+H]^+$ $C_{20}H_{19}N_2$ = 287.15428, found: 287.15471; $[\alpha]_D^{RT}$ = -9.87 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 27.1 min; minor enantiomer: t_R = 34.6 min, 97% ee.

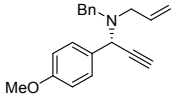
Methyl (*R*)-4-(1-(allyl(benzyl)amino)prop-2-yn-1-yl)benzoate



3f

3f: 15 h, 81% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.14 – 7.12 (m, 1H), 5.76 – 5.71 (s, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.05 (d, *J* = 10.2 Hz, 1H), 4.74 (s, 1H), 3.80 (s, 3H), 3.67 (d, *J* = 13.6 Hz, 1H), 3.32 (d, *J* = 13.6 Hz, 1H), 3.04 (d, *J* = 13.0 Hz, 1H), 2.90 (dd, *J* = 13.8, 8.6 Hz, 1H), 2.53 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.02, 144.17, 139.23, 136.18, 129.51, 128.89, 128.44, 128.22, 127.23, 117.91, 78.40, 76.48, 55.66, 54.65, 53.48, 52.16. HRMS: calcd. for $[M+H]^+$ $C_{21}H_{22}NO_2$ = 320.16451, found: 320.16547; $[\alpha]_D^{RT}$ = -9.33 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ADH column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 254 nm, minor enantiomer: t_R = 28.0 min; major enantiomer: t_R = 31.2 min, 98% ee.

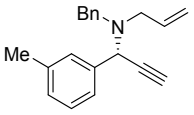
(*R*)-*N*-benzyl-*N*-(1-(4-methoxyphenyl)prop-2-yn-1-yl)prop-2-en-1-amine



3g

3g: 4 h, 74% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 (d, *J* = 7.4 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.20 (m, 1H), 6.88 – 6.85 (m, 2H), 5.88 – 5.78 (m, 1H), 5.28 (d, *J* = 18.2 Hz, 1H), 5.13 (d, *J* = 10.2 Hz, 1H), 4.76 (s, 1H), 3.80 – 3.77 (m, 4H), 3.38 (d, *J* = 13.6 Hz, 1H), 3.19 – 3.14 (m, 1H), 2.98 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.56 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.08, 139.75, 136.64, 130.84, 129.35, 128.89, 128.36, 127.04, 117.51, 113.55, 79.50, 75.65, 55.38, 55.17, 54.38, 53.26. HRMS: calcd. for $[M+H]^+$ $C_{20}H_{22}NO$ = 292.16959, found: 292.17042; $[\alpha]_D^{RT}$ = -122.73 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ODH column, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL min^{-1}, λ = 234 nm, major enantiomer: t_R = 9.4 min; minor enantiomer: t_R = 15.9 min, 90% ee.

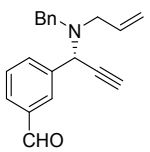
(*R*)-*N*-benzyl-*N*-(1-(*m*-tolyl)prop-2-yn-1-yl)prop-2-en-1-amine



3h

3h: 13 h, 96% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.36 (m, 2H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.16 – 7.12 (m, 2H), 6.98 (d, *J* = 7.4 Hz, 1H), 5.81 – 5.71 (m, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.06 (d, *J* = 10.2 Hz, 1H), 4.71 (s, 1H), 3.70 (d, *J* = 13.6 Hz, 1H), 3.32 (d, *J* = 13.6 Hz, 1H), 3.12 – 3.07 (m, 1H), 2.91 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.48 (d, *J* = 2.2 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.69, 138.69, 137.76, 136.60, 128.92, 128.89, 128.37, 128.33, 128.10, 127.05, 125.35, 117.59, 79.35, 75.76, 55.74, 54.48, 53.42, 21.65. HRMS: calcd. for $[M+H]^+$ $C_{20}H_{22}N$ = 276.17468, found: 276.17518; $[\alpha]_D^{RT}$ = -74.10 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.2 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 18.3 min; minor enantiomer: t_R = 20.7 min, 99% ee.

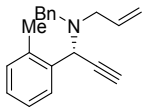
(*R*)-3-(1-(allyl(benzyl)amino)prop-2-yn-1-yl)benzaldehyde



3i

3i: 17 h, 89% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 9.95 (s, 1H), 8.09 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.28 (m, 2H), 7.23 (t, *J* = 7.4 Hz, 2H), 7.18 – 7.14 (m, 1H), 5.81 – 5.71 (m, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 5.08 (d, *J* = 10.2 Hz, 1H), 4.78 (s, 1H), 3.71 (d, *J* = 13.6 Hz, 1H), 3.35 (d, *J* = 13.6 Hz, 1H), 3.10 – 3.05 (m, 1H), 2.93 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.58 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.45, 140.28, 139.19, 136.50, 136.15, 134.38, 129.63, 129.05, 128.97, 128.91, 128.50, 127.29, 118.04, 78.28, 76.76, 55.48, 54.66, 53.53. HRMS: calcd. for $[M+H]^+$ $C_{20}H_{20}NO$ = 290.15394, found: 290.15421; $[\alpha]_D^{RT}$ = -75.87 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ADH column, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL min^{-1}, λ = 254 nm, minor enantiomer: t_R = 14.3 min; major enantiomer: t_R = 15.5 min, 97% ee.

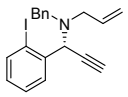
(*R*)-*N*-benzyl-*N*-(1-(*o*-tolyl)prop-2-yn-1-yl)prop-2-en-1-amine



3j

3j: 3 h, 83% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.75 – 7.73 (m, 1H), 7.24 – 7.18 (m, 5H), 7.17 – 7.11 (m, 3H), 5.88 – 5.77 (m, 1H), 5.24 (d, *J* = 17.2 Hz, 1H), 5.12 (d, *J* = 10.0 Hz, 1H), 4.94 (d, *J* = 2.2 Hz, 1H), 3.76 (d, *J* = 13.4 Hz, 1H), 3.29 (d, *J* = 13.4 Hz, 1H), 3.23 – 3.19 (m, 1H), 2.98 (dd, *J* = 13.6, 9.2 Hz, 1H), 2.59 (d, *J* = 2.2 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.49, 137.69, 136.12, 136.02, 130.81, 129.58, 129.38, 128.17, 127.88, 126.99, 125.37, 118.11, 79.41, 76.12, 54.36, 54.28, 54.23, 19.45. HRMS: calcd. for $[M+H]^+$ $C_{20}H_{22}N$ = 276.17468, found: 276.17468; $[\alpha]_D^{RT}$ = -194.67 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ADH column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 234 nm, minor enantiomer: t_R = 13.0 min; major enantiomer: t_R = 13.6 min, 95% ee.

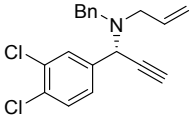
(*R*)-*N*-benzyl-*N*-(1-(2-iodophenyl)prop-2-yn-1-yl)prop-2-en-1-amine



3k

3k: 3 h, 72% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.15 (m, 6H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.11 – 6.01 (m, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 4.98 (d, *J* = 2.2 Hz, 1H), 3.66 (d, *J* = 13.6 Hz, 1H), 3.36 – 3.27 (m, 2H), 3.08 (dd, *J* = 13.6, 8.6 Hz, 1H), 2.65 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.55, 140.14, 139.41, 135.93, 131.27, 129.60, 129.25, 128.11, 127.67, 126.87, 117.88, 100.64, 79.27, 76.81, 60.70, 55.14, 53.85. HRMS: calcd. for $[M+H]^+$ $C_{19}H_{19}IN$ = 388.05567, found: 388.05653; $[\alpha]_D^{RT}$ = -96.10 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ADH column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 15.9 min; minor enantiomer: t_R = 16.8 min, 95% ee.

(*R*)-*N*-benzyl-*N*-(1-(3,4-dichlorophenyl)prop-2-yn-1-yl)prop-2-en-1-amine

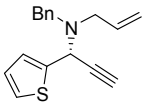


3l

3l: 5 h, 96% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.65 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.27 – 7.20 (m, 4H), 7.17 – 7.13 (m, 1H), 5.78 – 5.68 (m, 1H), 5.20 (d, *J* = 17.4 Hz, 1H), 5.07 (d, *J* = 10.2 Hz, 1H), 4.64 (s, 1H), 3.68 (d, *J* = 13.6 Hz, 1H), 3.30 (d, *J* = 13.6 Hz, 1H), 3.07 – 3.02 (m, 1H), 2.88 (dd, *J* = 14.0, 8.6 Hz, 1H), 2.53 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 139.40, 139.05, 136.04, 132.35, 131.60, 130.17, 128.90, 128.53, 127.58, 127.34, 118.10, 78.00, 76.78, 54.96, 54.66, 53.47. HRMS: calcd. for $[M+H]^+$ $C_{19}H_{18}{}^{35}Cl_2N$ = 330.08108, found: 330.08130; $[\alpha]_D^{RT}$ = -22.83 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ODH column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 14.0 min; minor enantiomer: t_R = 15.4 min, 97% ee.

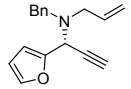
(*R*)-*N*-benzyl-*N*-(1-(thiophen-2-yl)prop-2-yn-1-yl)prop-2-en-1-amine



3m

3m: 2 h, 91% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.19 – 7.14 (m, 3H), 6.86 (dd, *J* = 5.2, 3.6 Hz, 1H), 5.84 – 5.74 (m, 1H), 5.25 (d, *J* = 17.6 Hz, 1H), 5.08 (d, *J* = 10.2 Hz, 1H), 4.86 (s, 1H), 3.82 (d, *J* = 13.8 Hz, 1H), 3.34 (d, *J* = 13.8 Hz, 1H), 3.22 – 3.17 (m, 1H), 2.92 (dd, *J* = 14.2, 8.2 Hz, 1H), 2.47 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.44, 139.35, 136.22, 128.78, 128.45, 127.19, 126.39, 126.05, 125.64, 117.70, 78.88, 74.66, 54.48, 53.41, 52.36. HRMS: calcd. for $[M+H]^+$ $C_{17}H_{18}NS$ = 268.11545, found: 268.11673; $[\alpha]_D^{RT}$ = -80.83 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ADH column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 16.3 min; minor enantiomer: t_R = 17.1 min, 96% ee.

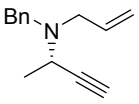
(*R*)-*N*-benzyl-*N*-(1-(furan-2-yl)prop-2-yn-1-yl)prop-2-en-1-amine



3n

3n: 6 h, 48% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.33 (s, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.21 (m, 2H), 7.18 – 7.13 (m, 1H), 6.37 (d, *J* = 3.6 Hz, 1H), 6.25 – 6.24 (m, 1H), 5.82 – 5.72 (m, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 5.07 (d, *J* = 10.2 Hz, 1H), 4.78 (s, 1H), 3.71 (d, *J* = 13.8 Hz, 1H), 3.41 (d, *J* = 13.8 Hz, 1H), 3.16 – 3.12 (m, 1H), 3.00 (dd, *J* = 14.0, 7.8 Hz, 1H), 2.39 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.88, 142.72, 139.35, 136.13, 128.90, 128.41, 127.11, 117.84, 110.24, 109.22, 78.09, 74.00, 54.58, 53.77, 50.71. HRMS: calcd. for $[M+H]^+$ $C_{17}H_{18}NO$ = 252.13829, found: 252.13921; $[\alpha]_D^{RT}$ = -42.60 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IC column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.5 mL min^{-1}, λ = 234 nm, major enantiomer: t_R = 8.2 min; minor enantiomer: t_R = 9.0 min, 94% ee.

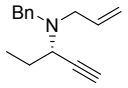
(*S*)-*N*-allyl-*N*-benzylbut-3-yn-2-amine



3o

3o: 21 h, 77% yield; slightly yellow liquid; According to procedure C, at -40 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.21 (m, 1H), 5.88 – 5.78 (m, 1H), 5.25 (d, *J* = 17.4 Hz, 1H), 5.11 (d, *J* = 10.0 Hz, 1H), 3.84 (d, *J* = 14.0 Hz, 1H), 3.65 (q, *J* = 8.0, 7.0 Hz, 1H), 3.37 (d, *J* = 14.0 Hz, 1H), 3.27 – 3.23 (m, 1H), 2.95 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.26 (d, *J* = 2.2 Hz, 1H), 1.33 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.98, 136.76, 128.82, 128.34, 126.96, 117.27, 83.03, 72.06, 54.62, 53.81, 46.98, 20.14. HRMS: calcd. for $[M+H]^+$ $C_{14}H_{18}N$ = 200.14338, found: 200.14322; $[\alpha]_D^{RT}$ = -109.67 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.2 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 21.8 min; minor enantiomer: t_R = 23.8 min, 86% ee.

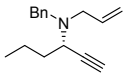
(*S*)-*N*-allyl-*N*-benzylpent-1-yn-3-amine



3p

3p: 21 h, 77% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.20 (m, 1H), 5.87 – 5.77 (m, 1H), 5.24 (d, *J* = 17.2 Hz, 1H), 5.10 (d, *J* = 10.2 Hz, 1H), 3.85 (d, *J* = 14.0 Hz, 1H), 3.38 – 3.34 (m, 2H), 3.26 – 3.22 (m, 1H), 2.93 (dd, *J* = 14.2, 8.2 Hz, 1H), 2.26 (d, *J* = 2.2 Hz, 1H), 1.70 – 1.63 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.05, 136.84, 128.81, 128.31, 126.92, 117.17, 82.31, 72.50, 54.78, 53.91, 53.83, 27.08, 11.27. HRMS: calcd. for $[M+H]^+$ $C_{15}H_{20}N$ = 214.15903, found: 214.15903; $[\alpha]_D^{RT}$ = -18.60 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.2 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 20.1 min; minor enantiomer: t_R = 21.0 min, 93% ee.

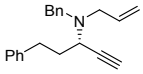
(*S*)-*N*-allyl-*N*-benzylhex-1-yn-3-amine



3q

3q: 19 h, 72% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 5.87 – 5.77 (m, 1H), 5.24 (d, *J* = 17.2 Hz, 1H), 5.10 (d, *J* = 10.2 Hz, 1H), 3.85 (d, *J* = 13.8 Hz, 1H), 3.48 (td, *J* = 7.6, 2.2 Hz, 1H), 3.35 (d, *J* = 13.8 Hz, 1H), 3.27 – 3.21 (m, 1H), 2.93 (dd, *J* = 14.2, 8.2 Hz, 1H), 2.25 (d, *J* = 2.2 Hz, 1H), 1.69 – 1.56 (m, 2H), 1.48 – 1.38 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.06, 136.86, 128.86, 128.32, 126.93, 117.16, 82.51, 72.36, 54.82, 53.93, 51.79, 36.06, 19.70, 13.84. HRMS: calcd. for $[M+H]^+$ $C_{16}H_{22}N$ = 228.17468, found: 228.17486; $[\alpha]_D^{RT}$ = -128.63 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ODH column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.5 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 7.5 min; minor enantiomer: t_R = 7.7 min, 95% ee.

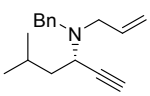
(*S*)-*N*-allyl-*N*-benzyl-5-phenylpent-1-yn-3-amine



3r

3r: 8 h, 79% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.28 (d, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.17 – 7.14 (m, 3H), 7.09 – 7.03 (m, 3H), 5.79 – 5.69 (m, 1H), 5.15 (d, *J* = 17.2 Hz, 1H), 5.02 (d, *J* = 10.2 Hz, 1H), 3.80 (d, *J* = 13.8 Hz, 1H), 3.43 (t, *J* = 7.8 Hz, 1H), 3.31 (d, *J* = 13.8 Hz, 1H), 3.20 (d, *J* = 13.8 Hz, 1H), 2.88 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.72 – 2.57 (m, 2H), 2.22 (s, 1H), 1.97 – 1.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.86, 139.83, 136.64, 128.94, 128.58, 128.44, 128.38, 127.01, 125.94, 117.32, 82.09, 72.89, 54.94, 54.10, 51.78, 35.69, 32.70. HRMS: calcd. for $[M+H]^+$ $C_{21}H_{24}N$ = 290.19033, found: 290.19051; $[\alpha]_D^{RT}$ = -147.7 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ODH column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 254 nm, minor enantiomer: t_R = 20.8 min; major enantiomer: t_R = 21.6 min, 92% ee.

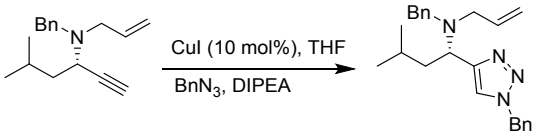
(*S*)-*N*-allyl-*N*-benzyl-5-methylhex-1-yn-3-amine



3s

3s: 16 h, 72% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.26 – 7.21 (m, 1H), 5.87 – 5.77 (m, 1H), 5.24 (d, *J* = 17.2 Hz, 1H),

5.11 (d, *J* = 10.2 Hz, 1H), 3.85 (d, *J* = 13.8 Hz, 1H), 3.56 (t, *J* = 7.8 Hz, 1H), 3.34 (d, *J* = 13.8 Hz, 1H), 3.23 (d, *J* = 14.2 Hz, 1H), 2.92 (dd, *J* = 14.2, 8.2 Hz, 1H), 2.25 (s, 1H), 1.87 – 1.81 (m, 1H), 1.63 – 1.56 (m, 1H), 1.50 – 1.43 (m, 1H), 0.84 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.99, 136.82, 128.93, 128.31, 126.95, 117.27, 82.61, 72.30, 54.77, 53.99, 50.04, 42.88, 24.78, 22.78, 22.30. HRMS: calcd. for $[M+H]^+$ $C_{17}H_{24}N$ = 242.19033, found: 242.19053; $[\alpha]_D^{RT}$ = -113.93 (c = 1.0 in $CHCl_3$); *rac*-**3s** can't be separated by chiral columns. The ee was determined by checking the ee of the click reaction product **17** .



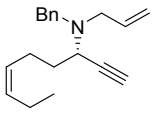
3s **17**

(*S*)-*N*-allyl-*N*-benzyl-1-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-3-methylbutan-1-amine

In a schlenk tube, **3s** (0.1 mmol, 1.0 equiv.), CuI (10 mol%), and anhydrous THF (0.5 mL) were added under nitrogen atmosphere. Diisopropylethylamine (2.0 equiv.) and a solution of benzyl azide (1.1 equiv.) in THF (0.5 mL) were added to the solution and the mixture was stirred for 16 h at room temperature. Then the mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to provide the desired product **17**.

17: 16 h, 83% yield; slightly yellow liquid; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.39 – 7.20 (m, 11H), 5.86 – 5.76 (m, 1H), 5.55 (s, 2H), 5.16 (d, *J* = 17.2 Hz, 1H), 5.08 (d, *J* = 10.2 Hz, 1H), 4.04 (t, *J* = 7.6 Hz, 1H), 3.84 (d, *J* = 14.0 Hz, 1H), 3.23 (dd, *J* = 14.2, 4.6 Hz, 1H), 3.15 (d, *J* = 14.0 Hz, 1H), 2.72 (dd, *J* = 14.2, 7.8 Hz, 1H), 1.94 – 1.84 (m, 1H), 1.83 – 1.72 (m, 1H), 1.62 – 1.55 (m, 1H), 0.85 (d, *J* = 6.6 Hz, 3H), 0.78 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.46, 140.49, 137.40, 135.13, 129.19, 128.85, 128.73, 128.22, 127.92, 126.74, 121.83, 116.91, 54.08, 53.31, 52.40, 40.83, 24.77, 23.17, 22.28. HRMS: calcd. for $[M+H]^+$ $C_{24}H_{31}N_4$ = 375.25430, found: 375.25490; $[\alpha]_D^{RT}$ = -45.23 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ADH column, hexane/^{i}PrOH = 90/10, flow rate = 0.5 mL min^{-1}, λ = 214 nm, major enantiomer: t_R = 14.1 min; minor enantiomer: t_R = 15.1 min, 88% ee.

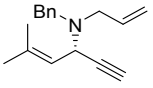
(*S*, *Z*)-*N*-allyl-*N*-benzylnon-6-en-1-yn-3-amine



3t

3t: 5 h, 91% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.35 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.20 (m, 1H), 5.86 – 5.77 (m, 1H), 5.38 – 5.31 (m, 1H), 5.28 – 5.22 (m, 2H), 5.10 (d, *J* = 10.2 Hz, 1H), 3.85 (d, *J* = 13.8 Hz, 1H), 3.49 (t, *J* = 7.6 Hz, 1H), 3.36 (d, *J* = 13.8 Hz, 1H), 3.26 – 3.22 (m, 1H), 2.94 (dd, *J* = 14.2, 8.2 Hz, 1H), 2.26 (s, 1H), 2.23 – 2.12 (m, 1H), 2.14 – 1.99 (m, 3H), 1.73 – 1.66 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.92, 136.70, 132.57, 128.84, 128.31, 128.11, 126.94, 117.26, 82.20, 72.64, 54.80, 54.08, 51.75, 34.03, 24.14, 20.67, 14.49. HRMS: calcd. for $[M+H]^+$ $C_{19}H_{26}N$ = 268.20598, found: 268.20614; $[\alpha]_D^{RT}$ = -27.87 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 234 nm, major enantiomer: t_R = 12.6 min; minor enantiomer: t_R = 13.1 min, 95% ee.

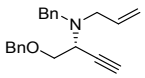
(*S*)-*N*-allyl-*N*-benzyl-5-methylhex-4-en-1-yn-3-amine



3u

3u: 4 h, 95% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.27 (d, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.16 – 7.13 (m, 1H), 5.82 – 5.72 (m, 1H), 5.24 (d, *J* = 7.8 Hz, 1H), 5.17 (d, *J* = 17.0 Hz, 1H), 5.05 (d, *J* = 10.2 Hz, 1H), 4.16 (d, *J* = 8.0 Hz, 1H), 3.73 (d, *J* = 13.6 Hz, 1H), 3.38 (d, *J* = 13.6 Hz, 1H), 3.15 (dd, *J* = 14.0, 4.8 Hz, 1H), 2.97 (dd, *J* = 14.0, 7.8 Hz, 1H), 2.23 (d, *J* = 2.2 Hz, 1H), 1.64 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.83, 137.01, 136.61, 129.03, 128.26, 126.97, 122.02, 117.54, 82.18, 72.30, 54.66, 53.74, 49.77, 25.94, 18.38. HRMS: calcd. for $[M+H]^+$ $C_{17}H_{22}N$ = 240.17468, found: 240.17553; $[\alpha]_D^{RT}$ = -44.90 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/(CH_2Cl_2/EtOH = 100/2) = 99/1, flow rate = 0.5 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 9.5 min; minor enantiomer: t_R = 10.4 min, 79% ee.

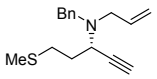
(*R*)-*N*-allyl-*N*-benzyl-1-(benzyloxy)but-3-yn-2-amine



3v

3v: 17 h, 97% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.32 – 7.20 (m, 8H), 5.88 – 5.78 (m, 1H), 5.28 – 5.23 (m, 1H), 5.12 (d, *J* = 10.0 Hz, 1H), 4.52 (s, 2H), 3.88 – 3.83 (m, 2H), 3.66 – 3.56 (m, 2H), 3.44 (d, *J* = 14.0 Hz, 1H), 3.30 – 3.25 (m, 1H), 3.02 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.32 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.62, 138.23, 136.38, 128.84, 128.46, 128.34, 127.74, 127.69, 127.05, 117.57, 80.02, 73.66, 73.16, 71.53, 55.36, 54.76, 52.47. HRMS: calcd. for $[M+H]^+$ $C_{21}H_{24}NO$ = 306.18524, found: 306.18609; $[\alpha]_D^{RT}$ = -71.53 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ODH column, hexane/^{i}PrOH = 99/1, flow rate = 0.2 mL min^{-1}, λ = 234 nm, major enantiomer: t_R = 26.4 min; minor enantiomer: t_R = 28.1 min, 92% ee.

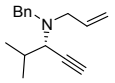
(*S*)-*N*-allyl-*N*-benzyl-5-(methylthio)pent-1-yn-3-amine



3w

3w: 18 h, 77% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.28 (m, 4H), 7.25 – 7.21 (m, 1H), 5.87 – 5.77 (m, 1H), 5.25 (d, *J* = 17.2 Hz, 1H), 5.12 (d, *J* = 10.2 Hz, 1H), 3.85 (d, *J* = 13.8 Hz, 1H), 3.67 – 3.63 (m, 1H), 3.37 (d, *J* = 13.8 Hz, 1H), 3.28 – 3.22 (m, 1H), 2.95 (dd, *J* = 14.2, 8.0 Hz, 1H), 2.64 – 2.52 (m, 2H), 2.29 (d, *J* = 2.2 Hz, 1H), 2.04 (s, 3H), 2.01 – 1.84 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.65, 136.51, 128.82, 128.37, 127.05, 117.43, 81.56, 73.08, 54.91, 54.06, 51.15, 33.35, 30.98, 15.52. HRMS: calcd. for $[M+H]^+$ $C_{16}H_{22}NS$ = 260.14675, found: 260.14630; $[\alpha]_D^{RT}$ = -73.13 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IC column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.5 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 9.8 min; minor enantiomer: t_R = 10.6 min, 93% ee.

(*S*)-*N*-allyl-*N*-benzyl-4-methylpent-1-yn-3-amine

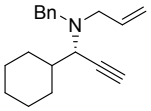


3x

3x: 16 h, 70% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.20 (m, 1H), 5.87 – 5.77 (m, 1H), 5.24 (d, *J* = 17.2 Hz, 1H), 5.10 (d, *J* = 10.2 Hz, 1H), 3.85 (d, *J* = 13.8 Hz, 1H), 3.33 (d, *J* = 13.8 Hz, 1H), 3.25 – 3.20 (m, 1H), 2.97 (dd, *J* = 10.4, 2.2 Hz, 1H), 2.89 (dd, *J* = 14.2, 8.4 Hz, 1H), 2.28 (d, *J* = 2.2 Hz, 1H), 1.90 – 1.80 (m, 1H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.98 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.01, 136.90, 128.87, 128.31, 126.91, 117.12, 81.62, 73.07, 59.36, 55.02, 53.87, 30.93, 20.82, 20.00. HRMS: calcd. for $[M+H]^+$ $C_{16}H_{22}N$ = 228.17468, found: 228.17505; $[\alpha]_D^{RT}$ = -160.30 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ADH column, hexane/^{i}PrOH =

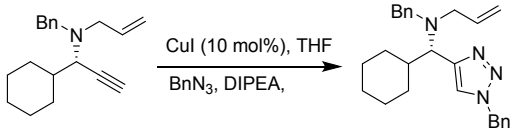
99.9/0.1, flow rate = 0.2 mL min^{-1}, λ = 234 nm, minor enantiomer: t_R = 17.0 min; major enantiomer: t_R = 17.7 min, 92% ee.

(*S*)-*N*-benzyl-*N*-(1-cyclohexylprop-2-yn-1-yl)prop-2-en-1-amine



3y

3y: 5 h, 76% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.35 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.20 (m, 1H), 5.86 – 5.76 (m, 1H), 5.24 (d, *J* = 17.0 Hz, 1H), 5.10 (d, *J* = 10.2 Hz, 1H), 3.85 (d, *J* = 14.0 Hz, 1H), 3.33 (d, *J* = 14.0 Hz, 1H), 3.22 (d, *J* = 14.2 Hz, 1H), 3.11 – 3.08 (m, 1H), 2.89 (dd, *J* = 14.2, 8.4 Hz, 1H), 2.27 (d, *J* = 2.2 Hz, 1H), 2.18 (d, *J* = 12.8 Hz, 1H), 2.01 (d, *J* = 13.4 Hz, 1H), 1.72 – 1.51 (m, 4H), 1.28 – 1.05 (m, 3H), 0.92 – 0.72 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ140.02, 136.94, 128.83, 128.30, 126.88, 117.09, 81.39, 73.20, 57.96, 54.91, 53.76, 39.86, 31.28, 30.36, 26.75, 26.24, 26.03. HRMS: calcd. for $[M+H]^+$ $C_{19}H_{26}N$ = 268.20598, found: 268.20602; $[\alpha]_D^{RT}$ = -98.23 (c = 1.0 in $CHCl_3$); *rac*-**3y** can't be separated by chiral columns. The ee was determined by checking the ee of the click reaction product **18**.



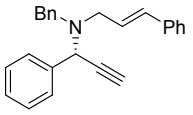
3y **18**

(*S*)-*N*-benzyl-*N*-((1-benzyl-1*H*-1,2,3-triazol-4-yl)(cyclohexyl)methyl)prop-2-en-1-amine

In a schlenk tube, **3y** (0.1 mmol, 1.0 equiv.), CuI (10 mol%), and anhydrous THF (0.5 mL) were added under nitrogen atmosphere. Diisopropylethylamine (2.0 equiv.) and a solution of benzyl azide (1.1 equiv.) in THF (0.5 mL) were added to the solution and the mixture was stirred for 17 h at room temperature. Then the mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to provide the desired product **18**.

18: 17 h, 68% yield; slightly yellow liquid; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.41 – 7.16 (m, 10H), 5.87 – 5.77 (m, 1H), 5.56 (s, 2H), 5.16 – 5.06 (m, 2H), 3.93 (d, *J* = 14.2 Hz, 1H), 3.52 (d, *J* = 10.8 Hz, 1H), 3.35 (d, *J* = 10.8 Hz, 1H), 2.94 (d, *J* = 14.2 Hz, 1H), 2.54 – 2.48 (m, 1H), 2.38 – 2.35 (m, 1H), 2.12 – 2.04 (m, 1H), 1.80 – 1.72 (m, 1H), 1.62 – 1.53 (m, 2H), 1.26 – 1.12 (m, 4H), 0.97 – 0.83 (m, 2H), 0.70 – 0.60 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.77, 140.40, 137.48, 135.21, 129.19, 128.69, 128.26, 127.79, 126.68, 122.52, 116.68, 60.07, 54.18, 53.99, 53.03, 38.44, 31.34, 30.74, 26.81, 26.22, 26.18. HRMS: calcd. for $[M+H]^+$ $C_{26}H_{33}N_4$ = 401.26997, found: 401.26980; $[\alpha]_D^{RT}$ = -35.23 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ADH column, hexane/^{i}PrOH = 90/10, flow rate = 1 mL min^{-1}, λ = 210 nm, minor enantiomer: t_R = 14.0 min; major enantiomer: t_R = 28.2 min, 97% ee.

(*R, E*)-*N*-benzyl-3-phenyl-*N*-(1-phenylprop-2-yn-1-yl)prop-2-en-1-amine

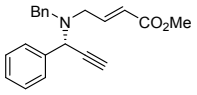


4a

4a: 19 h, 49% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.33 – 7.11 (m, 13H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.18 – 6.10 (m, 1H), 4.79 (s, 1H), 3.76 (d, *J* = 13.6 Hz, 1H), 3.38 (d, *J* = 13.6 Hz, 1H), 3.27 – 3.22 (m, 1H), 3.09 (dd, *J* = 14.0, 8.6 Hz, 1H), 2.54 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.62, 138.77, 137.26, 132.72, 128.96, 128.63, 128.42, 128.27, 128.26, 128.22, 127.65, 127.48, 127.13, 126.43, 79.23, 76.03, 55.99, 54.72, 52.91. HRMS: calcd. for $[M+H]^+$ $C_{25}H_{24}N$ =

338.19033, found: 338.19223; $[\alpha]_D^{RT}$ = -1.83 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ODH column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 254 nm, major enantiomer: t_R =18.3 min; minor enantiomer: t_R = 22.6 min, 91% ee.

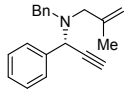
Methyl (*R, E*)-4-(benzyl(1-phenylprop-2-yn-1-yl)amino)but-2-enoate



4b

4b: 1 h, 50% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 (d, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 7.3 Hz, 2H), 7.27 – 7.21 (m, 4H), 7.19 – 7.13 (m, 2H), 6.89 – 6.80 (m, 1H), 6.02 (d, *J* = 15.8 Hz, 1H), 4.66 (s, 1H), 3.69 (d, *J* = 13.6 Hz, 1H), 3.63 (s, 3H), 3.41 (d, *J* = 13.6 Hz, 1H), 3.21 – 3.15 (m, 1H), 3.10 (dd, *J* = 16.0, 7.4 Hz, 1H), 2.52 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.83, 147.05, 138.77, 138.10, 128.91, 128.54, 128.33, 128.12, 127.85, 127.40, 122.41, 78.66, 76.36, 56.17, 55.27, 51.63, 51.29. HRMS: calcd. for $[M+H]^+$ $C_{21}H_{22}NO_2$ = 320.16451, found: 320.16432; $[\alpha]_D^{RT}$ = -0.50 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL min^{-1}, λ = 234 nm, minor enantiomer: t_R = 21.5 min; major enantiomer: t_R = 23.9 min, 96% ee.

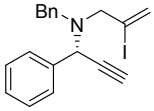
(*R*)-*N*-benzyl-2-methyl-*N*-(1-phenylprop-2-yn-1-yl)prop-2-en-1-amine



4c

4c: 2 h, 77% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.35 – 7.27 (m, 4H), 7.25 – 7.20 (m, 2H), 5.04 (s, 1H), 4.88 (s, 1H), 4.78 (s, 1H), 3.76 (d, *J* = 13.6 Hz, 1H), 3.36 (d, *J* = 13.6 Hz, 1H), 3.01 – 2.94 (m, 2H), 2.58 (d, *J* = 2.2 Hz, 1H), 1.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.30, 139.65, 138.75, 128.94, 128.41, 128.26, 128.19, 127.57, 127.09, 113.63, 78.96, 75.98, 56.96, 55.47, 54.41, 20.87. HRMS: calcd. for $[M+H]^+$ $C_{20}H_{22}N$ = 276.17468, found: 276.17570; $[\alpha]_D^{RT}$ = -104.87 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ODH column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 15.1 min; minor enantiomer: t_R = 20.4 min, 99% ee.

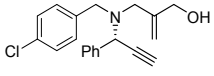
(*R*)-*N*-benzyl-2-iodo-*N*-(1-phenylprop-2-yn-1-yl)prop-2-en-1-amine



4d

4d: 3 h, 78% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.67 (d, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.27 – 7.19 (m, 4H), 7.19 – 7.11 (m, 2H), 6.36 (s, 1H), 5.82 (s, 1H), 4.71 (s, 1H), 3.69 (d, *J* = 13.6 Hz, 1H), 3.30 (d, *J* = 13.6 Hz, 1H), 3.15 (d, *J* = 14.2 Hz, 1H), 2.99 (d, *J* = 14.2 Hz, 1H), 2.50 (d, *J* = 2.2 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 138.60, 137.69, 129.22, 128.58, 128.43, 128.22, 127.85, 127.35, 110.87, 78.55, 76.35, 61.41, 55.14, 53.89. HRMS: calcd. for $[M+H]^+$ $C_{19}H_{19}IN$ = 388.05567, found: 388.05531; $[\alpha]_D^{RT}$ = -109.37 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ODH column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 13.8 min; minor enantiomer: t_R = 15.2 min, 97% ee.

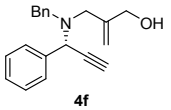
(*R*)-2-(((4-chlorobenzyl)(1-phenylprop-2-yn-1-yl)amino)methyl)prop-2-en-1-ol



4e

4e: 48 h, 81% yield; slightly yellow liquid; According to procedure C, with 10 mol% catalyst, **1a** (0.3 mmol, 1.5 equiv.), **2j** (0.2 mmol); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.31 – 7.25 (m, 5H), 5.14 (d, *J* = 8.2 Hz, 2H), 4.78 (s, 1H), 4.06 (s, 2H), 3.79 (d, *J* = 13.2 Hz, 1H), 3.35 (d, *J* = 13.2 Hz, 1H), 3.20 (d, *J* = 13.2 Hz, 1H), 3.09 (d, *J* = 13.2 Hz, 1H), 2.82 (s, 1H), 2.63 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.84, 137.71, 137.15, 133.30, 130.54, 128.85, 128.54, 128.40, 128.13, 115.03, 77.97, 76.84, 66.09, 55.57, 54.40, 54.04. HRMS: calcd. for $[M+H]^+$ $C_{20}H_{21}ClNO$ = 326.13062, found: 326.13152; $[\alpha]_D^{RT}$ = -53.87 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/^{i}PrOH = 90/10, flow rate = 0.5 mL min^{-1}, λ = 234 nm, major enantiomer: t_R = 11.3 min; minor enantiomer: t_R = 12.1 min, 95% ee.

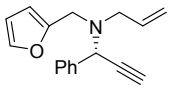
(*R*)-2-((benzyl(1-phenylprop-2-yn-1-yl)amino)methyl)prop-2-en-1-ol



4f

4f: 8 h, 97% yield; slightly yellow liquid; According to procedure C, with 10 mol% catalyst, **1a** (0.3 mmol, 1.5 equiv.), **2i** (0.2 mmol); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.34 – 7.18 (m, 8H), 5.11 – 5.10 (m, 2H), 4.80 (s, 1H), 4.03 (s, 2H), 3.83 (d, *J* = 13.2 Hz, 1H), 3.35 (d, *J* = 13.2 Hz, 1H), 3.23 – 3.18 (m, 2H), 3.07 (d, *J* = 13.2 Hz, 1H), 2.61 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.88, 138.49, 137.80, 129.09, 128.58, 128.36, 128.30, 127.89, 127.44, 114.57, 78.04, 76.69, 65.84, 55.37, 54.58, 54.28. HRMS: calcd. for $[M+H]^+$ $C_{20}H_{22}NO$ = 292.16959, found: 292.16986; $[\alpha]_D^{RT}$ = -113.87 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/^{i}PrOH = 90/10, flow rate = 0.5 mL min^{-1}, λ = 224 nm, major enantiomer: t_R = 10.3 min; minor enantiomer: t_R = 12.4 min, 95% ee.

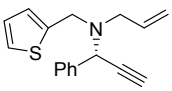
(*R*)-*N*-(furan-2-ylmethyl)-*N*-(1-phenylprop-2-yn-1-yl)prop-2-en-1-amine



4g

4g: 3 h, 65% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.56 (d, *J* = 7.4 Hz, 2H), 7.27 – 7.23 (m, 3H), 7.19 – 7.15 (m, 1H), 6.21 (t, *J* = 2.6 Hz, 1H), 6.15 (d, *J* = 3.2 Hz, 1H), 5.79 – 5.69 (m, 1H), 5.21 (d, *J* = 17.0 Hz, 1H), 5.05 (d, *J* = 10.2 Hz, 1H), 4.77 (s, 1H), 3.63 (d, *J* = 14.4 Hz, 1H), 3.46 (d, *J* = 14.4 Hz, 1H), 3.15 – 3.10 (m, 1H), 2.94 (dd, *J* = 14.2, 8.2 Hz, 1H), 2.46 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.05, 142.07, 138.50, 136.15, 128.25, 128.21, 127.66, 117.72, 110.24, 108.46, 79.18, 75.87, 56.21, 53.54, 47.44. HRMS: calcd. for $[M+H]^+$ $C_{17}H_{18}NO$ = 252.13829, found: 252.13839; $[\alpha]_D^{RT}$ = -74.43 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ADH column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 234 nm, major enantiomer: t_R = 12.8 min; minor enantiomer: t_R = 13.4 min, 96% ee.

(*R*)-*N*-(1-phenylprop-2-yn-1-yl)-*N*-(thiophen-2-ylmethyl)prop-2-en-1-amine

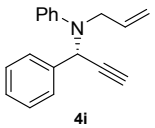


4h

4h: 6 h, 92% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.62 (d, *J* = 7.2 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.20 – 7.16 (m, 1H), 7.13 (d, *J* = 5.0 Hz, 1H), 6.87 (d, *J* = 3.4 Hz, 1H), 6.84 – 6.82 (m, 1H), 5.81 – 5.71 (m, 1H), 5.23 (d, *J* = 17.2 Hz, 1H), 5.06 (d, *J* = 10.2 Hz, 1H), 4.81 (s, 1H), 3.78 (d, *J* = 14.2 Hz, 1H), 3.68 (d, *J* = 14.2 Hz, 1H), 3.18 – 3.11 (m, 1H), 2.93 (dd, *J* = 14.2, 8.4 Hz, 1H), 2.49 (d, *J* = 2.2 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 144.02, 138.52, 136.27, 128.26, 128.16, 127.69, 126.54, 125.60, 124.98, 117.67, 79.06, 75.91, 55.71, 53.15, 49.55. HRMS: calcd. for $[M+H]^+$ $C_{17}H_{18}NS$ = 268.11545, found: 268.11627;

$[\alpha]_D^{RT}$ = -102.90 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 13.6 min; minor enantiomer: t_R = 14.4 min, 95% ee.

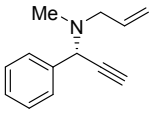
(*R*)-*N*-allyl-*N*-(1-phenylprop-2-yn-1-yl)aniline



4i

4i: 2 h, 82% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.30 – 7.20 (m, 3H), 7.18 – 7.13 (m, 2H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 5.75 – 5.65 (m, 2H), 5.12 – 5.08 (m, 1H), 5.00 – 4.97 (m 1H), 3.85 – 3.72 (m, 2H), 2.44 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.58, 138.00, 135.70, 129.02, 128.54, 127.94, 127.79, 119.08, 116.53, 116.26, 80.95, 74.81, 55.98, 51.40. HRMS: calcd. for $[M+H]^+$ $C_{18}H_{18}N$ = 248,14338, found: 248.14360; $[\alpha]_D^{RT}$ = +6.07 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ADH column, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL min^{-1}, λ = 234 nm, major enantiomer: t_R = 10.3 min; minor enantiomer: t_R = 12.0 min, 94% ee.

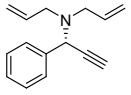
(*R*)-*N*-methyl-*N*-(1-phenylprop-2-yn-1-yl)prop-2-en-1-amine



4j

4j: 14 h, 67% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.24 (m, 1H), 5.93 – 5.83 (m, 1H), 5.27 (d, *J* = 17.0 Hz, 1H), 5.16 (d, *J* = 10.2 Hz, 1H), 4.78 (s, 1H), 3.16 – 3.05 (m, 2H), 2.54 (d, *J* = 2.2 Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.38, 136.14, 128.38, 128.26, 127.69, 117.87, 78.93, 76.01, 59.06, 57.78, 37.63. HRMS: calcd. for $[M+H]^+$ $C_{13}H_{16}N$ = 186.12773, found: 186.12785; $[\alpha]_D^{RT}$ = -1.47 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IA column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 254 nm, major enantiomer: t_R =12.6 min; minor enantiomer: t_R = 13.7 min, 95% ee.

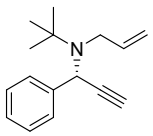
(*R*)-*N*-allyl-*N*-(1-phenylprop-2-yn-1-yl)prop-2-en-1-amine



4k

4k: 2 h, 74% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.22 – 7.15 (m, 1H), 5.78 – 5.68 (m, 2H), 5.21 – 5.16 (m, 2H), 5.04 (d, *J* = 10.2 Hz, 2H), 4.82 (d, *J* = 2.2 Hz, 1H), 3.16 – 3.11 (m, 2H), 2.87 (dd, *J* = 14.2, 8.2 Hz, 2H), 2.44 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.83, 136.50, 128.24, 128.21, 127.57, 117.51, 79.46, 75.54, 55.95, 53.44. HRMS: calcd. for $[M+H]^+$ $C_{15}H_{18}N$ = 212.14338, found: 212.14411; $[\alpha]_D^{RT}$ = -10.0 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ADH column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.2 mL min^{-1}, λ = 234 nm, major enantiomer: t_R =17.0 min; minor enantiomer: t_R = 17.8 min, 98% ee.

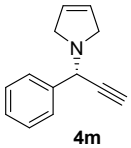
(*R*)-*N*-(*tert*-butyl)-*N*-(1-phenylprop-2-yn-1-yl)prop-2-en-1-amine



4l

4l: 4 h, 60% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 5.48 – 5.38 (m, 1H), 4.99 (s, 1H), 4.73 (dd, *J* = 17.4, 1.8 Hz, 1H), 4.57 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.30 – 3.19 (m, 2H), 2.45 (d, *J* = 2.2 Hz, 1H), 1.19 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.23, 141.19, 128.29, 127.87, 127.05, 113.19, 83.93, 75.39, 56.56, 53.01, 48.81, 28.70. HRMS: calcd. for $[M+H]^+$ $C_{16}H_{22}N$ = 228.17468, found: 228.17532; $[\alpha]_D^{RT}$ = -0.23 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ODH column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 234 nm, major enantiomer: t_R =11.7 min; minor enantiomer: t_R = 13.2 min, 97% ee.

(*R*)-1-(1-phenylprop-2-yn-1-yl)-2,5-dihydro-1*H*-pyrrole

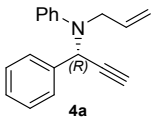


4m

4m: 14 h, 71% yield; slightly yellow liquid; According to procedure C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.52 (d, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.19 (m, 1H), 5.69 (s, 2H), 4.77 (d, *J* = 1.6 Hz, 1H), 3.57 – 3.51 (m, 2H), 3.48 – 3.42 (m, 2H), 2.48 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.92, 128.47, 128.14, 127.81, 127.50, 80.91, 75.95, 58.21, 56.37. HRMS: calcd. for $[M+H]^+$ $C_{13}H_{14}N$ = 184.11208, found: 184.11261; $[\alpha]_D^{RT}$ = -36.77 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/^{i}PrOH = 99/1, flow rate = 0.5 mL min^{-1}, λ = 214 nm, minor enantiomer: t_R = 8.8 min; major enantiomer: t_R = 9.8 min, 84% ee.

5. Absolute configuration determination

The absolute configuration of 4a was assigned by comparison with the literature (G. Hattori, K. Sakata, H. Matsuzawa, Y. Tanabe, Y. Miyake, Y. Nishibayashi, *J. Am. Chem. Soc.* **2010**, *132*, 10592-10608). All other compounds was assigned by analogy.

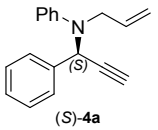


4a

94% ee

+6.07 (c = 1.0 in $CHCl_3$)

This work



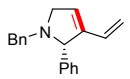
(*S*)-**4a**

-87% ee

-3.7 (c = 1.62, $CHCl_3$)

Nishimayashi's work

6. Derivatization of the enantiomerically enriched *N*-tethered 1,6-enynes

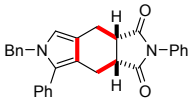


7

(*S*)-1-benzyl-2-phenyl-3-vinyl-2,5-dihydro-1*H*-pyrrole

A typical procedure for the ring closing enyne metathesis is as follows: **3a** (0.2 mmol, 1 equiv.) was dissolved in freshly distilled and degassed dichloromethane (2 mL) under nitrogen atmosphere. This solution was degassed again using nitrogen. After stirring for 10 minutes at room temperature, Grubbs catalyst 1st Generation (0.02 mmol, 0.1 equiv.) dissolved in dichloromethane (2 mL) was added by syringe. After refluxing for 26 hours, the reaction was complete as indicated by TLC. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to give the corresponding pyrrolidine derivative **7**.

7: 27 h, 71% yield; slightly yellow liquid; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.31 (m, 4H), 7.27 – 7.19 (m, 6H), 6.27 (dd, *J* = 17.8, 11.2 Hz, 1H), 5.95 (s, 1H), 4.87 (d, *J* = 11.2 Hz, 1H), 4.80 (d, *J* = 17.8 Hz, 1H), 4.72 (d, *J* = 4.8 Hz, 1H), 3.81 (d, *J* = 13.4 Hz, 1H), 3.74 (d, *J* = 15.8 Hz, 1H), 3.55 (d, *J* = 13.4 Hz, 1H), 3.42 (d, *J* = 15.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.61, 142.17, 139.75, 130.86, 128.87, 128.67, 128.30, 128.24, 127.50, 127.43, 126.85, 116.00, 73.43, 58.31, 56.78. HRMS: calcd. for $[M+H]^+$ $C_{19}H_{20}N$ = 262.15903, found: 262.15989; $[\alpha]_D^{RT}$ = +2.50 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ODH column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 15.9 min; minor enantiomer: t_R = 20.7 min, 99% ee.

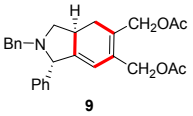


8

(3a*R*, 8a*S*)-6-benzyl-2,5-diphenyl-4,6,8,8a-tetrahydropyrrolo[3,4-*f*]isoindole-1,3(2*H*, 3a*H*)-dione

In a dried schleck tube, the precursor enyne **3a** was diluted with degassed toluene (3 mL) and to this solution was added $[IrCl(cod)]_2$ (0.02 mmol, 0.1 equiv.), AcOH (7 µL, 0.12 mmol) and *N*-phenylmaleimide (0.3 mmol, 1.5 equiv.). The solution was refluxed for 16 h under nitrogen atmosphere. After evaporation of the solvent, the residue was purified by flash column chromatography on silica gel eluted with hexane/AcOEt to give **8**.

8: 16 h, 54% yield; amorphous brown solid; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.32 (m, 5H), 7.28 – 7.22 (m, 3H), 7.18 – 7.12 (m, 2H), 7.02 (d, *J* = 7.2 Hz, 2H), 6.81 (d, *J* = 7.2 Hz, 1H), 6.54 (s, 1H), 5.07 (d, *J* = 16.0 Hz, 1H), 4.94 (d, *J* = 16.0 Hz, 1H), 3.44 – 3.42 (m, 4H), 3.33 – 3.29 (m, 2H), 2.87 – 2.82 (m, 1H), 2.76 – 2.72 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.73, 179.65, 139.01, 132.23, 131.63, 130.35, 129.91, 129.22, 128.66, 128.63, 128.60, 127.34, 127.26, 126.53, 126.38, 117.51, 117.29, 115.82, 50.57, 41.20, 40.99, 22.84, 21.90. HRMS: calcd. for $[M+H]^+$ $C_{29}H_{25}N_2O_2$ = 433.19105, found: 433.19252; $[\alpha]_D^{RT}$ = -15.7 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ADH column, hexane/^{i}PrOH = 80/20, flow rate = 1.0 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 16.5 min; minor enantiomer: t_R = 22.5 min, 84% ee.



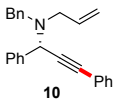
9

((*1S,3aS*)-2-benzyl-1-phenyl-2,3,3a,4-tetrahydro-1*H*-isoindole-5,6-diyl)bis(methylene) diacetate

A solution of **3a** (0.2 mmol, 1 equiv.), but-2-yne-1,4-diyl diacetate (0.6 mmol) and [RuCl(cod)(Cp*)] (0.02 mmol) in THF (1 mL). The mixture was stirred at 60 °C until completion of the reaction (monitoring by TLC). Then

cooled the mixture to room temperature, concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1).

9: 13 h, 50% yield; slightly yellow liquid; ^{1}H NMR (400 MHz, Acetone-d6) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.28 (m, 5H), 7.25 – 7.21 (m, 1H), 5.52 (s, 1H), 4.83 (d, *J* = 12.6 Hz, 1H), 4.70 (d, *J* = 12.4 Hz, 1H), 4.58 (d, *J* = 12.6 Hz, 1H), 4.52 (d, *J* = 12.4 Hz, 1H) 4.20 (s, 1H), 3.86 (d, *J* = 13.2 Hz, 1H), 3.33 – 3.25 (m, 2H), 2.92 – 2.83 (m, 1H), 2.43 (dd, *J* = 16.2, 7.8 Hz, 1H), 2.10 (d, *J* = 9.8 Hz, 1H), 2.09 – 2.03 (m, 1H), 1.99 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, Acetone) δ 170.92, 170.76, 150.43, 143.61, 139.87, 131.34, 131.01, 129.45, 129.27, 128.99, 128.95, 128.21, 127.70, 117.95, 71.93, 63.52, 62.42, 59.15, 58.01, 38.73, 30.62, 20.77, 20.67. HRMS: calcd. for $[M+H]^+$ $C_{27}H_{30}NO_4$ = 432.21693, found: 432.21718; $[\alpha]_D^{RT}$ = +8.87 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK IBN-5 column, hexane/^{i}PrOH = 90/10, flow rate = 0.3 mL min^{-1}, λ = 254 nm, major enantiomer: t_R = 26.8 min; minor enantiomer: t_R = 28.8 min, 97% ee; The relative configuration of the compound **9** was determined by 2D NMR spectroscopy.

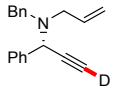


10

(*S*)-*N*-benzyl-*N*-(1,3-diphenylprop-2-yn-1-yl)prop-2-en-1-amine

A dried schlenk tube charged with $Pd(PPh_3)_2Cl_2$ (5 mol%) and CuI (7.5 mol%) was filled with nitrogen for three times. The solution of iodobenzene (1.1 equiv.) and **3a** (0.2 mmol, 1 equiv.) in anhydrous acetonitrile (2 mL) was added and heated to 50 °C. At last, triethylamine (3.0 equiv.) was added to the mixture and the resulting mixture was stirred for 5 hours at 50 °C. After the reaction was finished, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to provide the desired product **10**.

10: 5 h, 85% yield; slightly yellow liquid; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.62 – 7.54 (m, 1H), 7.44 – 7.19 (m, 12H), 5.93 – 5.83 (m, 1H), 5.31 (d, *J* = 17.0 Hz, 1H), 5.15 (d, *J* = 10.2 Hz, 1H), 5.02 (s, 1H), 3.86 (d, *J* = 13.6 Hz, 1H), 3.56 – 3.45 (m, 1H), 3.24 (d, *J* = 12.8 Hz, 1H), 3.09 (dd, *J* = 14.2, 8.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.80, 139.43, 136.70, 132.04, 128.97, 128.50, 128.39, 128.37, 128.32, 128.23, 127.55, 127.07, 123.41, 117.57, 88.37, 85.17, 56.45, 54.76, 53.62. HRMS: calcd. for $[M+H]^+$ $C_{25}H_{24}N$ = 338.19033, found: 388.19211; $[\alpha]_D^{RT}$ = -182.33 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ADH column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 254 nm, minor enantiomer: t_R = 16.2 min; major enantiomer: t_R = 19.8 min, 96% ee.



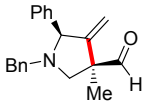
11

(*R*)-*N*-benzyl-*N*-(1-phenylprop-2-yn-1-yl-3-*d*)prop-2-en-1-amine

A flame dried 10 mL round bottomed flask was charged with **3a** (0.2 mmol, 1 equiv.) and potassium carbonate (0.4 mmol, 2 equiv.) in anhydrous MeCN (2 mL). This was allowed to stir at room temperature for 30 minutes. To this D_2O (500 μL, ~50 equiv.) was added and left to stir for 1 hour. After the reaction was finished according to TLC, the solvent was removed under reduced pressure and the obtained residue was then purified by column chromatography on silica gel with petroleum ether/ethyl acetate 100/1 as eluent, affording the product **11**.

11: 40 h, 65% yield; colorless liquid; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.65 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.20 (m, 8H), 5.88 – 5.79 (m, 1H), 5.29 (d, *J* = 17.2 Hz, 1H), 5.13 (d, *J* = 10.0 Hz, 1H), 4.81 (s, 1H), 3.79 (d, *J* = 13.6 Hz, 1H), 3.40 (d, *J* = 13.6 Hz, 1H), 3.23 – 3.10 (m, 1H), 2.99 (dd, *J* = 14.0, 8.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.64, 138.79, 136.55, 128.91, 128.39, 128.21, 127.59, 127.09, 117.64, 78.68 (t, *J* = 7.7 Hz), 75.89 (t, *J*

= 14.2 Hz), 55.70, 54.49, 53.38. HRMS: calcd. for $[M+H]^+$ $C_{19}H_{19}DN$ = 263.16530, found: 263.16619; $[\alpha]_D^{RT}$ = -61.07 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ODH column, hexane/^{i}PrOH = 99.9/0.1, flow rate = 0.3 mL min^{-1}, λ = 224 nm, major enantiomer: t_R = 11.7 min; minor enantiomer: t_R = 12.8 min, 97% ee.



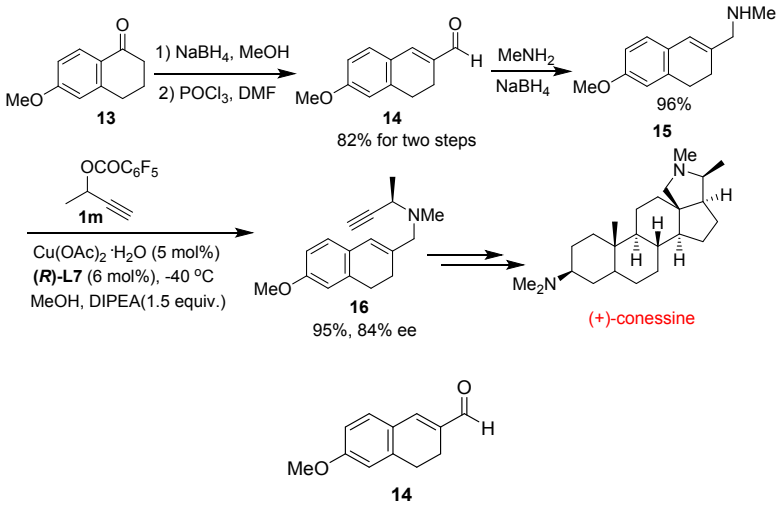
12

(*3R, 5S*)-1-benzyl-3-methyl-4-methylene-5-phenylpyrrolidine-3-carbaldehyde

A solution of $[Rh(cod)Cl]_2$ (0.02 mmol) ,*rac*-BINAP (0.024 mmol) and $NaBAr^F$ (0.042 mmol) in DCM (0.6 mL) was stirred under N_2 atmosphere at room temperature for 0.5 h. Then the reaction mixture was degassed, and the reaction vessel was flushed with H_2 atmosphere at room temperature for 2 h. To the mixture was added a solution of **4f** (0.2 mmol, 1 equiv.) in degassed DCM (1.0 mL) and the reaction mixture was stirred at 40 °C until the reaction was finished determined by TLC. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to give product **12**.

12: 4 h, 60% yield; slightly yellow liquid; ^{1}H NMR (400 MHz, Chloroform-d) δ 9.56 (s, 1H), 7.41 – 7.24 (m, 10H), 5.00 (d, *J* = 2.6 Hz, 1H), 4.70 (d, *J* = 2.2 Hz, 1H), 4.01 – 4.00 (m, 1H), 3.90 (d, *J* = 13.4 Hz, 1H), 3.42 (d, *J* = 9.8 Hz, 1H), 3.12 (d, *J* = 13.4 Hz, 1H), 2.28 (d, *J* = 9.8 Hz, 1H), 1.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.24, 154.75, 141.25, 138.33, 128.78, 128.73, 128.64, 128.42, 127.91, 127.19, 111.47, 72.83, 59.52, 57.02, 55.94, 18.58. HRMS: calcd. for $[M+H]^+$ $C_{20}H_{22}NO$ = 292.16959, found: 292.16934; $[\alpha]_D^{RT}$ = -23.77 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ADH column, hexane/^{i}PrOH = 99/1, flow rate = 0.3 mL min^{-1}, λ = 224 nm, minor enantiomer: t_R = 18.8 min; major enantiomer: t_R = 23.8 min, 92% ee; The relative configuration of the compound **12** was determined by 2D NMR spectroscopy.

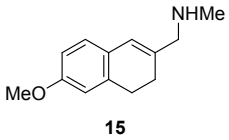
7. Formal total synthesis of (+)-Conessine



6-methoxy-3,4-dihydronaphthalene-2-carbaldehyde

To a solution of 6-methoxy-3,4-dihydronaphthalene-2-carbaldehyde **13** (5.29 g, 30 mmol) in MeOH (90 mL) was added $NaBH_4$ (2.27 g, 60 mmol) at 0 °C within 30 min. The cooling bath was removed and stirring continued for 2 hours. The reaction was completed as indicated by TLC analysis. Water (50 mL) was added to the mixture and extraction with Et_2O (3 x 50 mL). The combined organic phase was washed with water (30 mL) and brine (30 mL) then dried over anhydrous sodium sulfate, filtered, concentrated under reduced pressure. The residue was dissolved in anhydrous DMF (20 mL) under nitrogen atmosphere. Afterward, $POCl_3$ (7.0 mL) was added dropwise over 1 hour at 0 °C. Then the mixture was heated in 100 °C for 4 hours. Saturated aqueous NaOAc solution (30 mL) was added at 0 °C. After stirring for 10 min, the solution was neutralized with 2 M NaOH and extracted with Et_2O (3 x 50 mL). The combined organic phases were washed with saturated $NaHCO_3$ (30 mL) then dried over anhydrous sodium sulfate, filtered, concentrated under reduced pressure. Recrystallization with Ethyl acetate/Hexane provided the target compound **14** (4.62 g).

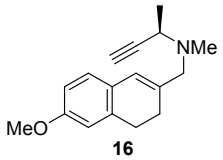
14: 4 h, 82% yield for two steps; white solid; ^{1}H NMR (400 MHz, Chloroform-d) δ 9.61 (s, 1H), 7.27 – 7.22 (m, 2H), 6.79 – 6.76 (m, 2H), 3.84 (s, 3H), 2.85 (t, J = 8.2 Hz, 2H), 2.55 (t, J = 8.2 Hz, 2H).



1-(6-methoxy-3,4-dihydronaphthalen-2-yl)-*N*-methylmethanamine

To a solution of **14** (1.88 g, 10 mmol) in anhydrous MeOH (20 mL) was added CH_3NH_2 (30-33% in MeOH, 1.58 mL, 12 mmol) at 0 °C. The cooling bath was removed and stirring continued at room temperature. The reaction was finished in 3 hours determined by GC-MS. $NaBH_4$ (0.453 g, 12 mmol) was added to the above mixture at 0 °C within 20 min and stirred for additional 2 hours at room temperature. Water (50 mL) was added to the mixture and the organic solvent was removed under reduced pressure. Subsequently, extraction with dichloromethane (3 x 50 mL). The combined organic phase was washed with brine (30 mL) then dried over anhydrous sodium sulfate, filtered, concentrated under reduced pressure, providing the target compound **15** (2.03 g).

15: 2 h, 96% yield; slightly yellow liquid; ^{1}H NMR (400 MHz, Chloroform-d) δ 6.95 (d, *J* = 9.0 Hz, 1H), 6.69 – 6.66 (m, 2H), 6.32 (s, 1H), 3.79 (s, 3H), 3.31 (s, 2H), 2.81 (t, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 2.27 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.49, 137.03, 136.73, 127.69, 126.78, 122.86, 113.68, 111.20, 57.45, 55.40, 36.12, 28.70, 25.73; HRMS: calcd. for $[M+Na]^+$ $C_{13}H_{17}NONa$ = 226.12024, found: 262.12050.



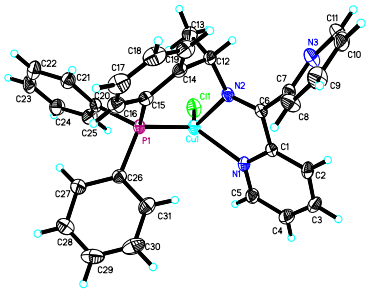
16

(*R*)-*N*-((6-methoxy-3,4-dihydronaphthalen-2-yl)methyl)-*N*-methylbut-3-yn-2-amine

16: 95% yield; slightly yellow liquid; According to procedure C, with (*R*)-**L7**, -40 °C, **1m** (0.4 mmol), **15** (0.6 mmol), MeOH (2 mL); ^{1}H NMR (400 MHz, Chloroform-d) δ 6.96 (d, *J* = 8.0 Hz, 1H), 6.70 – 6.68 (m, 2H), 6.36 (s, 1H), 3.80 (s, 3H), 3.64 (qd, *J* = 7.0, 2.4 Hz, 1H), 3.18 (d, *J* = 13.0 Hz, 1H), 3.05 (d, *J* = 13.0 Hz, 1H), 2.83 – 2.78 (m, 2H), 2.35 – 2.26 (m, 3H), 2.24 (s, 3H), 1.35 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.54, 136.96, 136.28, 127.68, 126.80, 124.73, 113.68, 111.14, 82.35, 72.56, 60.73, 55.37, 49.94, 37.51, 28.78, 25.57, 19.98. HRMS: calcd. for $[M+H]^+$ $C_{17}H_{22}NO$ = 256.16959, found: 256.16897; $[\alpha]_D^{RT}$ = +140.53 (c = 1.0 in $CHCl_3$); HPLC conditions: CHIRALPAK ADH column, hexane/^{i}PrOH = 95/5, flow rate = 0.3 mL min^{-1}, λ = 254 nm, minor enantiomer: t_R = 13.8 min; major enantiomer: t_R = 14.7 min, 84% ee.

8. X-ray Crystallographic Data

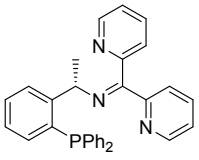
Crystal data and structure refinement for complexes of CuCl and **L7**.



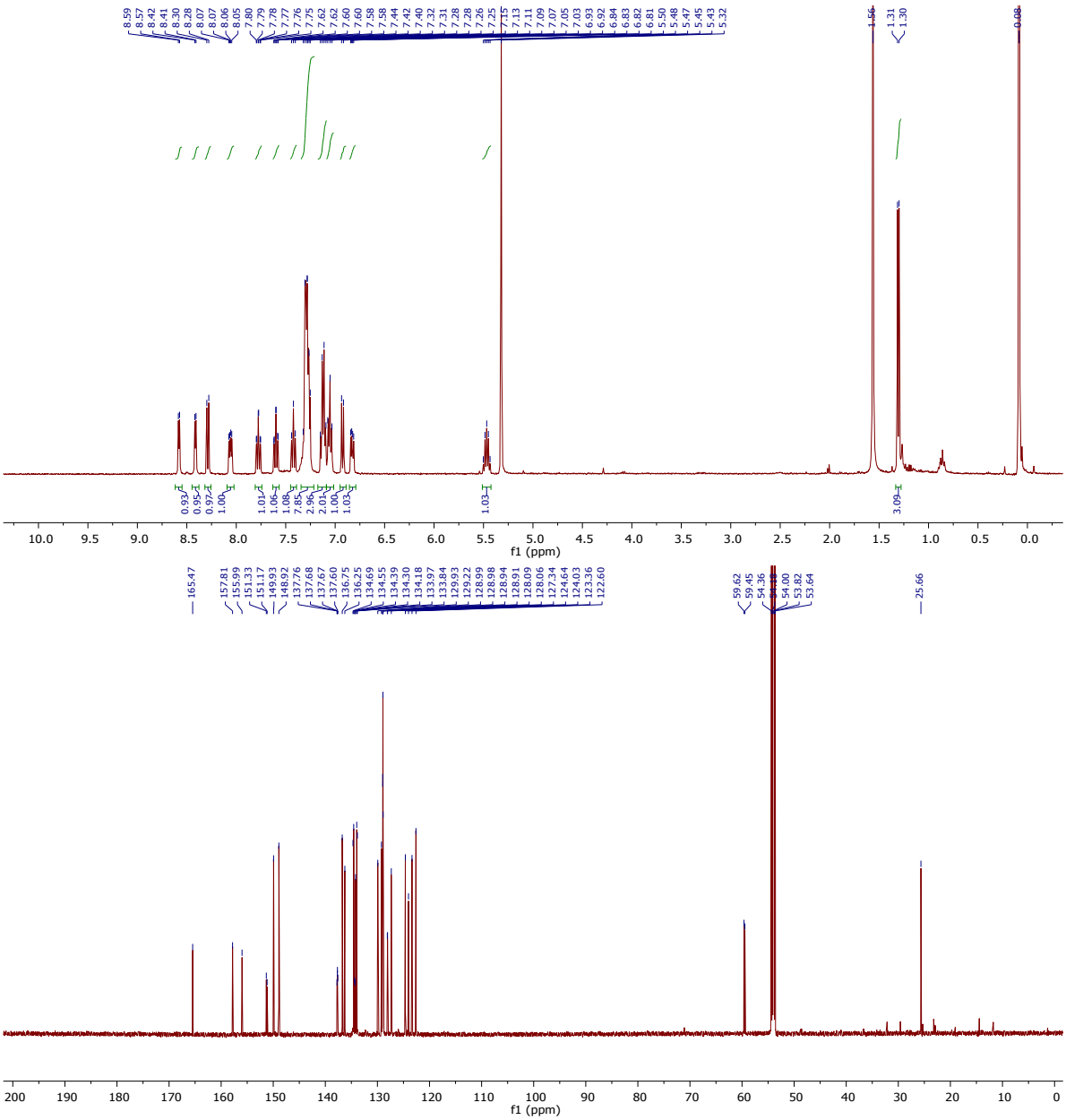
Compound	**CuCl + L7**
Empirical formula	$C_{31}H_{26}ClCuN_3P$
Formula weight/g·mol^{-1}	570.51
Temperature/K	296(2)
Crystal system	Triclinic
Space group	P1
a/Å	8.8768(17)
b/Å	8.8907(18)
c/Å	9.3073(18)
α/°	87.751(3)
β/°	68.299(2)
γ/°	82.837(3)
Volume/Å^3	677.1(2)
Z	1
ρ_{calc} g/cm^3	1.399
μ/mm^{-1}	0.989
F(000)	294.0
Crystal size/mm^3	0.12 x 0.1 x 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.618 to 54.874
Index ranges	-11<=h<=11 -11<=k<=11 -11<=l<=12
Reflections collected	5695
Independent reflections	4709 [R_{int} = 0.0219, R_{sigma} = 0.0676]
Data/restraints/parameters	4709/3/324
Goodness-of-fit on F^2	0.999
Final R indexes [I>=2σ (I)]	R_1 = 0.0360, wR_2 = 0.0894

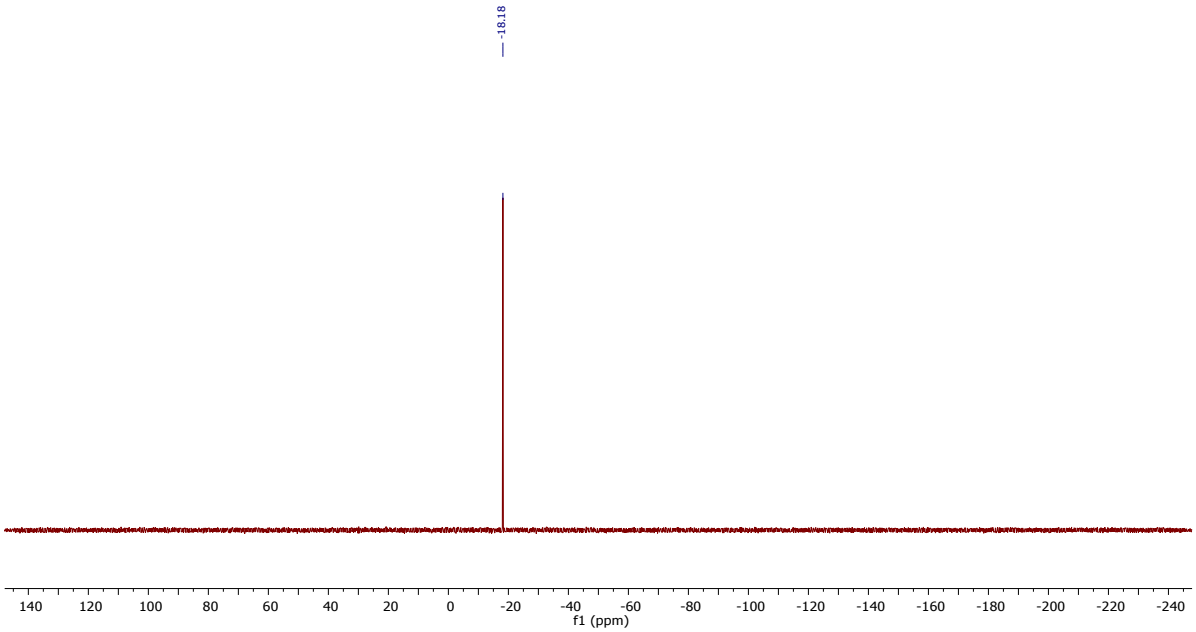
Final R indexes [all data]	R_1 = 0.0443, wR_2 = 0.0930
Largest diff. peak/hole / e Å^{-3}	0.63/-0.42
Flack parameter	0.041(17)

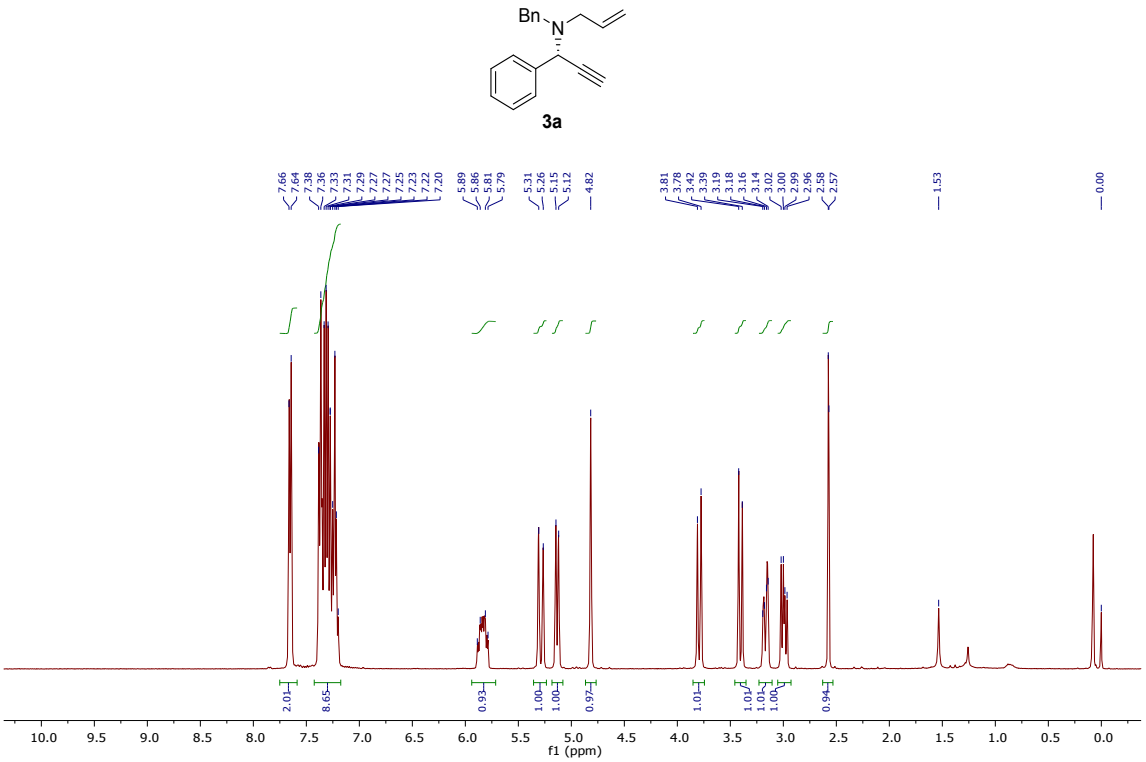
9. NMR Spectra and HPLC Data

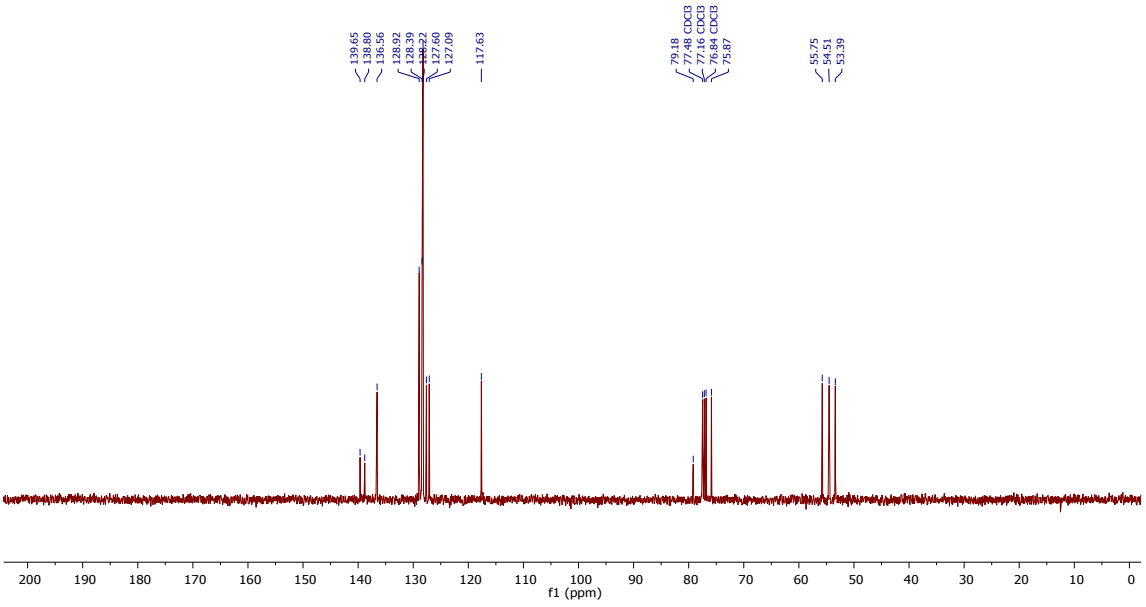


L7

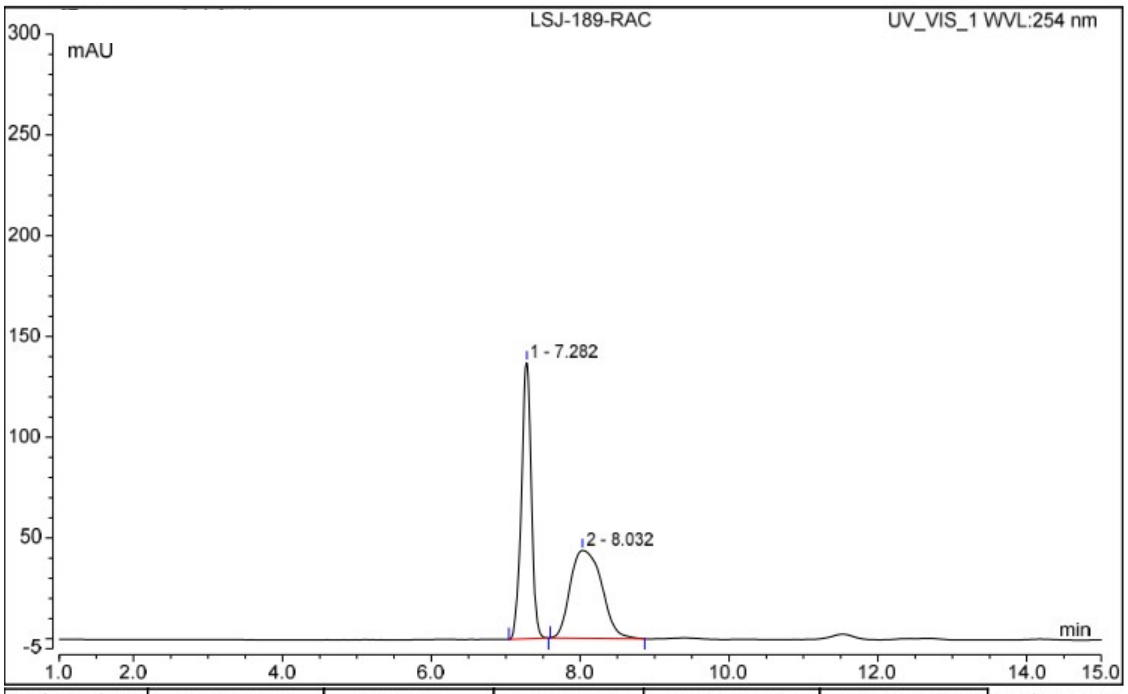



-18.18
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)


Bn
N
3a
7.66
7.64
7.38
7.36
7.33
7.31
7.29
7.27
7.27
7.25
7.23
7.22
7.20
5.89
5.86
5.81
5.79
5.31
5.26
5.15
5.12
4.82
3.81
3.78
3.42
3.39
3.19
3.18
3.16
3.14
3.02
3.00
2.99
2.96
2.58
2.57
1.53
0.00
2.01
8.65
0.93
1.00
1.00
0.97
1.01
1.01
1.01
1.00
0.94
f1 (ppm)

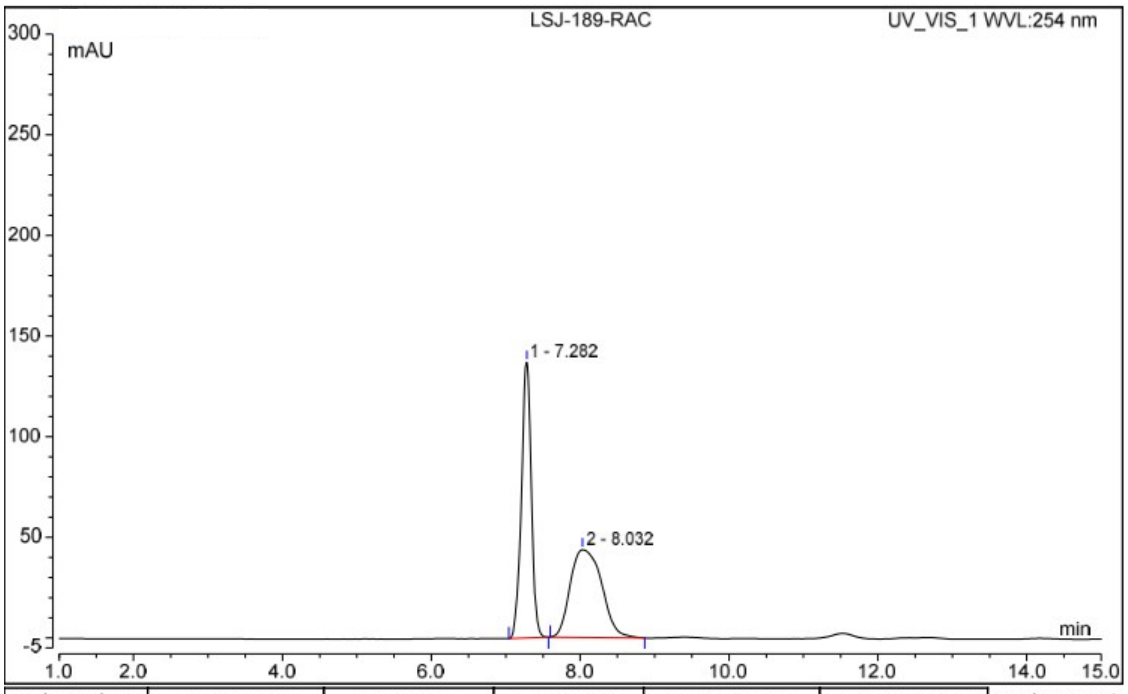

139.65
138.80
136.56
128.92
128.39
128.22
127.66
127.09
117.63
79.18
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.87
55.75
54.51
53.39
f1 (ppm)

HPLC trace of *rac*-3a

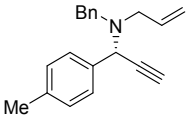


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	7.282	21.021	137.032	49.63	75.89	n.a.
2	8.032	21.338	43.536	50.37	24.11	n.a.

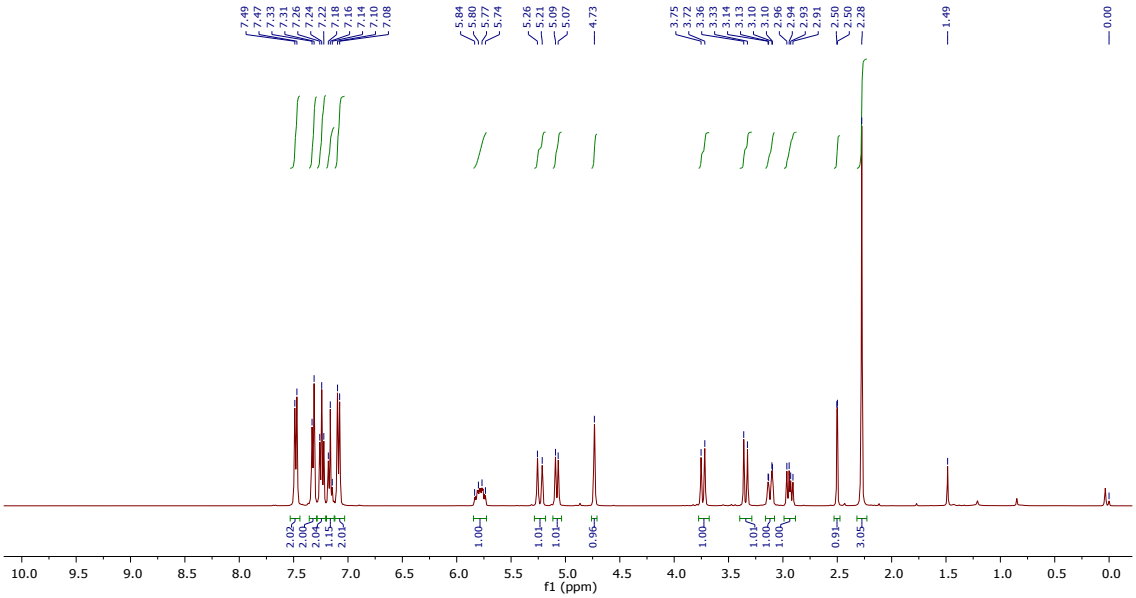
HPLC trace of 3a

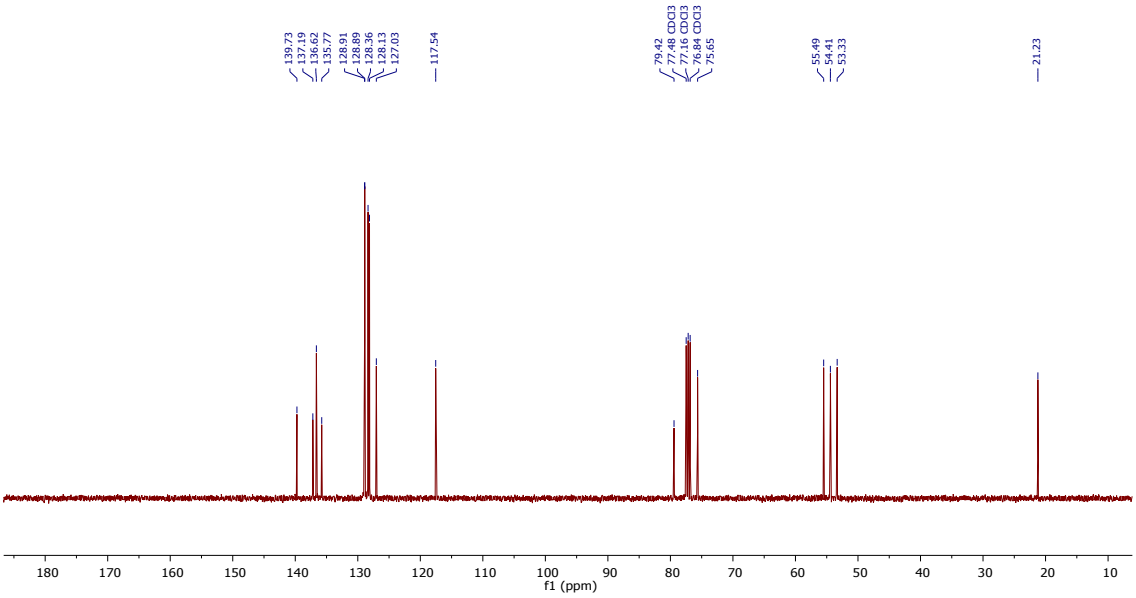


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	7.282	21.021	137.032	49.63	75.89	n.a.
2	8.032	21.338	43.536	50.37	24.11	n.a.

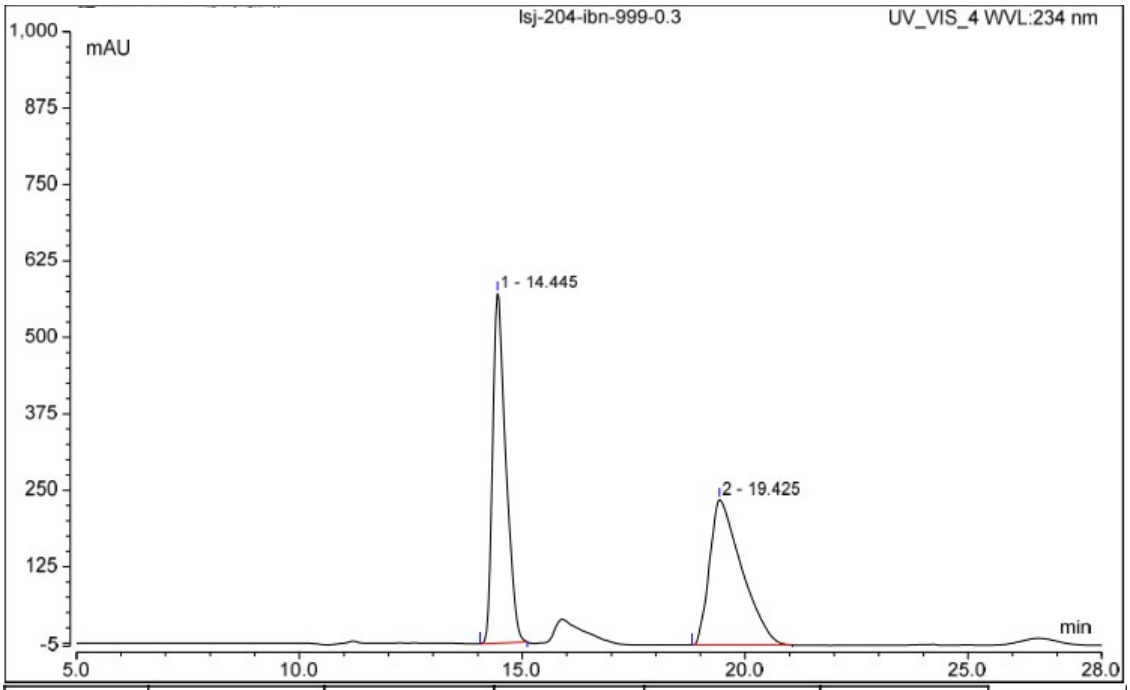

Bn
N
Me

3b


7.49
7.47
7.33
7.31
7.26
7.24
7.22
7.18
7.16
7.14
7.10
7.08
5.84
5.80
5.77
5.74
5.26
5.21
5.09
5.07
4.73
3.75
3.72
3.36
3.33
3.14
3.13
3.10
3.10
2.96
2.94
2.93
2.91
2.50
2.50
2.28
1.49
0.00
2.02
2.00
2.04
1.15
2.01
1.00
1.01
1.01
0.96
1.00
1.01
1.00
1.00
0.91
3.05
f1 (ppm)

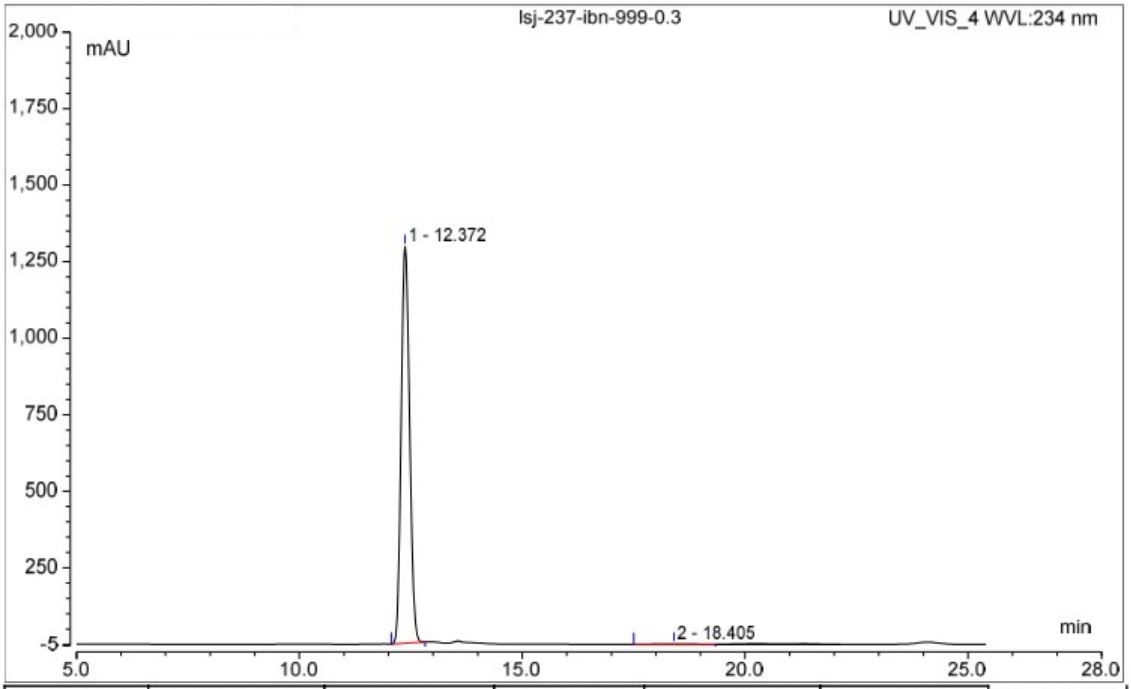

139.73
137.19
136.62
135.77
128.91
128.89
128.36
128.13
127.03
117.54
79.42
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.65
55.49
54.41
53.33
21.23
f1 (ppm)

HPLC trace of *rac*-3b

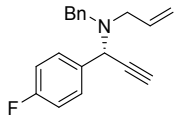


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	14.445	196.975	571.987	49.89	70.65	n.a.
2	19.425	197.877	237.641	50.11	29.35	n.a.

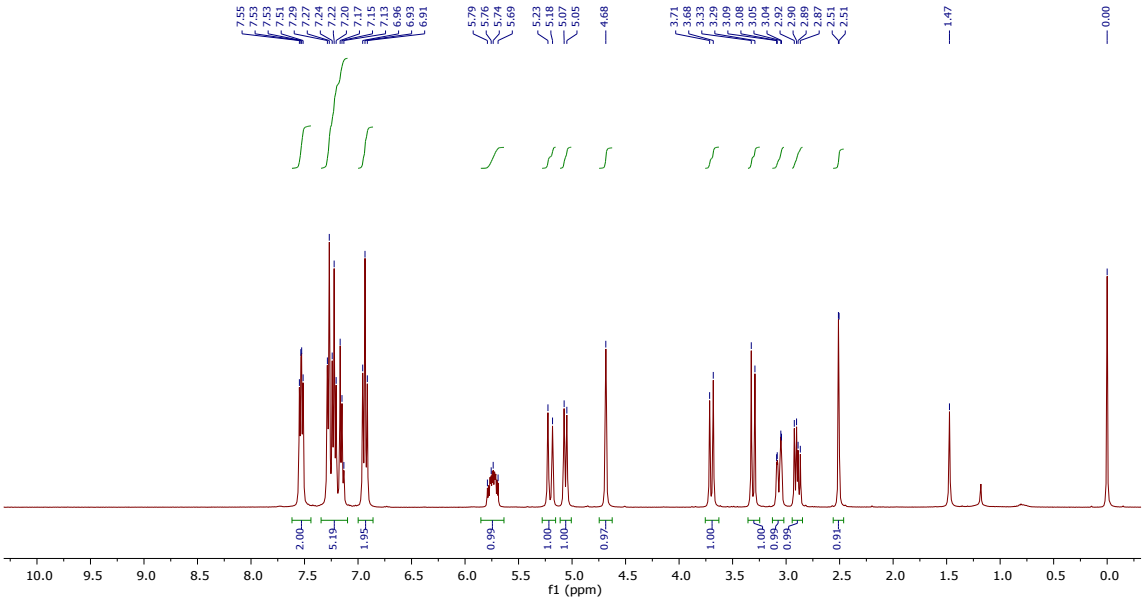
HPLC trace of 3b

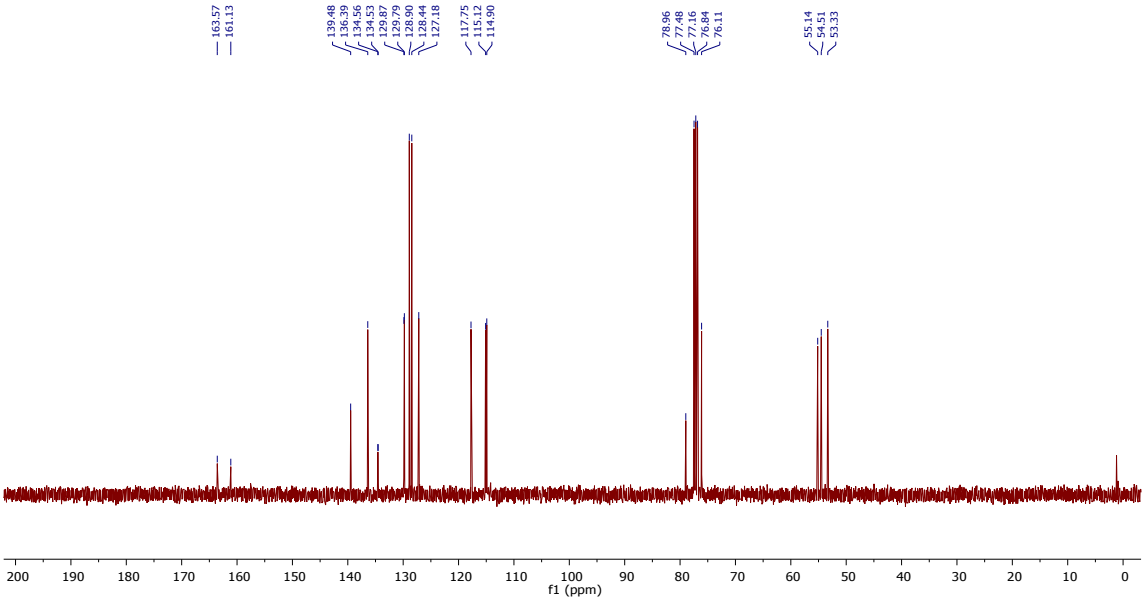


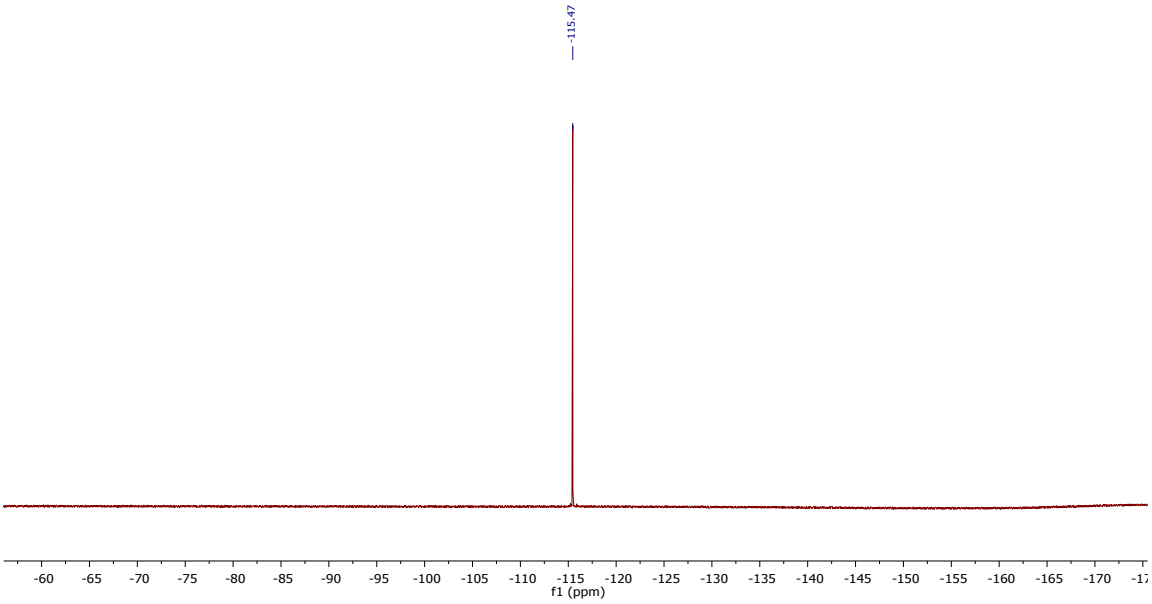
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	12.372	280.290	1296.395	99.72	99.93	n.a.
2	18.405	0.781	0.914	0.28	0.07	n.a.


Bn
N
F

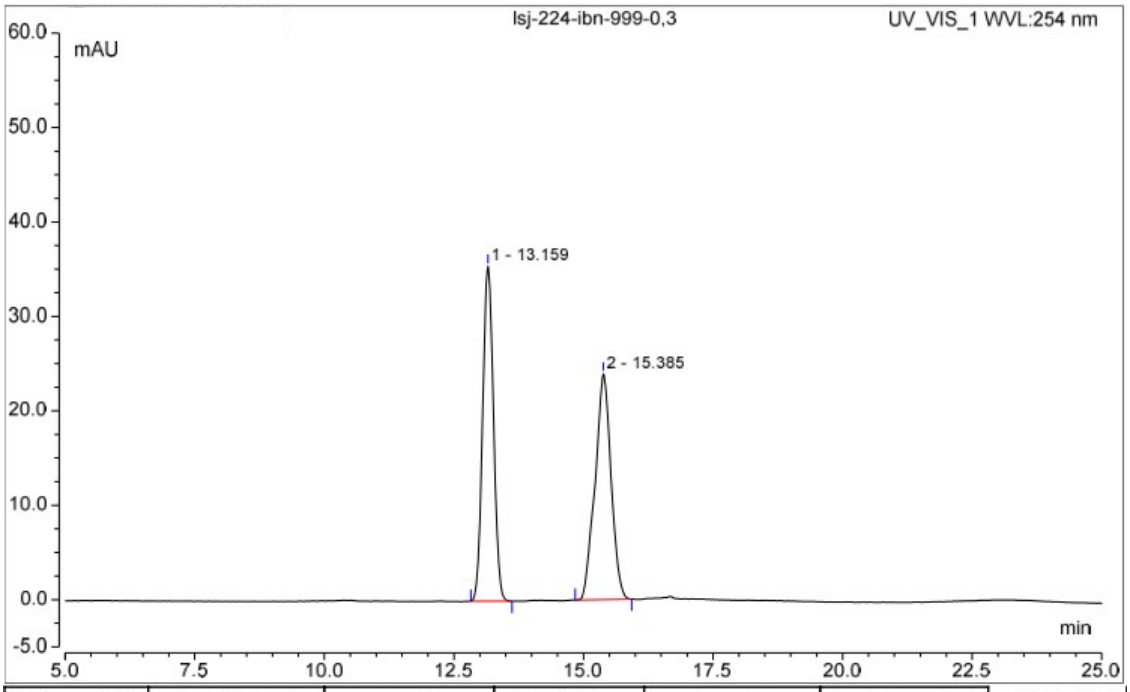
3c


7.55
7.53
7.53
7.51
7.29
7.27
7.24
7.22
7.20
7.17
7.15
7.13
6.96
6.93
6.91
5.79
5.76
5.74
5.69
5.23
5.18
5.07
5.05
4.68
3.71
3.68
3.33
3.29
3.09
3.08
3.05
3.04
2.92
2.90
2.89
2.87
2.51
2.51
1.47
0.00
2.00
5.19
1.95
0.99
1.00
1.00
0.97
1.00
1.00
0.99
0.99
0.91
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)


163.57
161.13
139.48
136.39
134.56
134.53
129.87
129.79
128.90
128.44
127.18
117.75
115.72
114.90
78.96
77.48
77.16
76.84
76.11
55.14
54.51
53.33
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

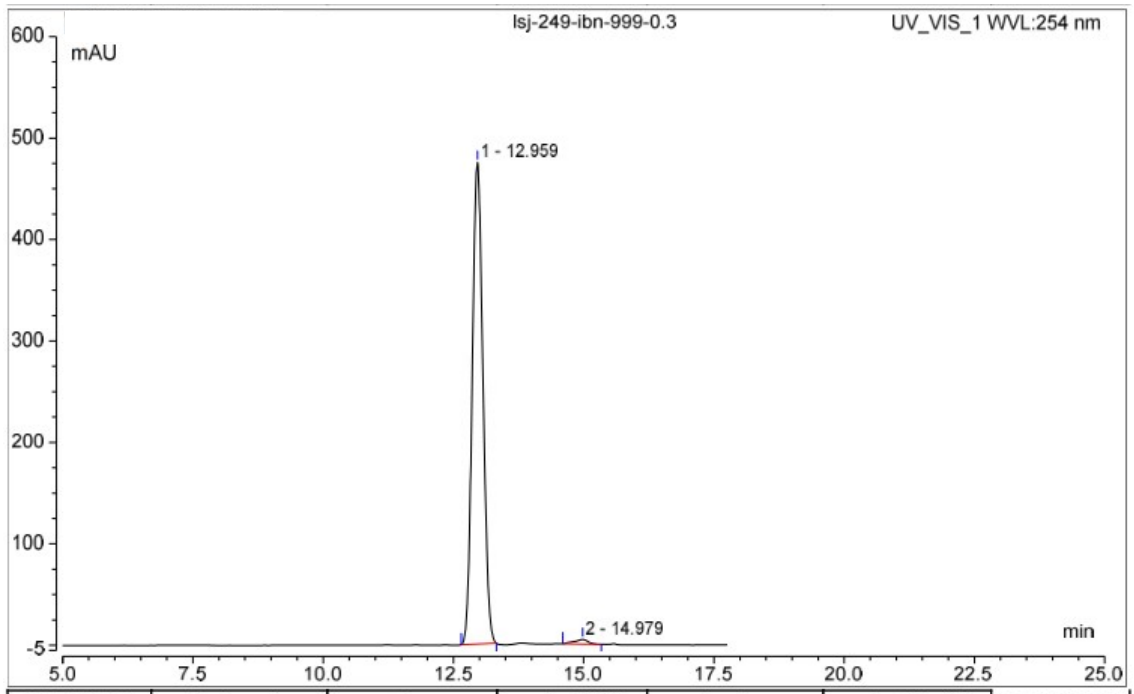

-115.47
-60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170
f1 (ppm)

HPLC trace of *rac*-3c

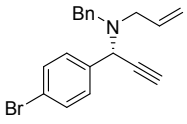


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	13.159	8.548	35.487	50.03	59.75	n.a.
2	15.385	8.537	23.906	49.97	40.25	n.a.

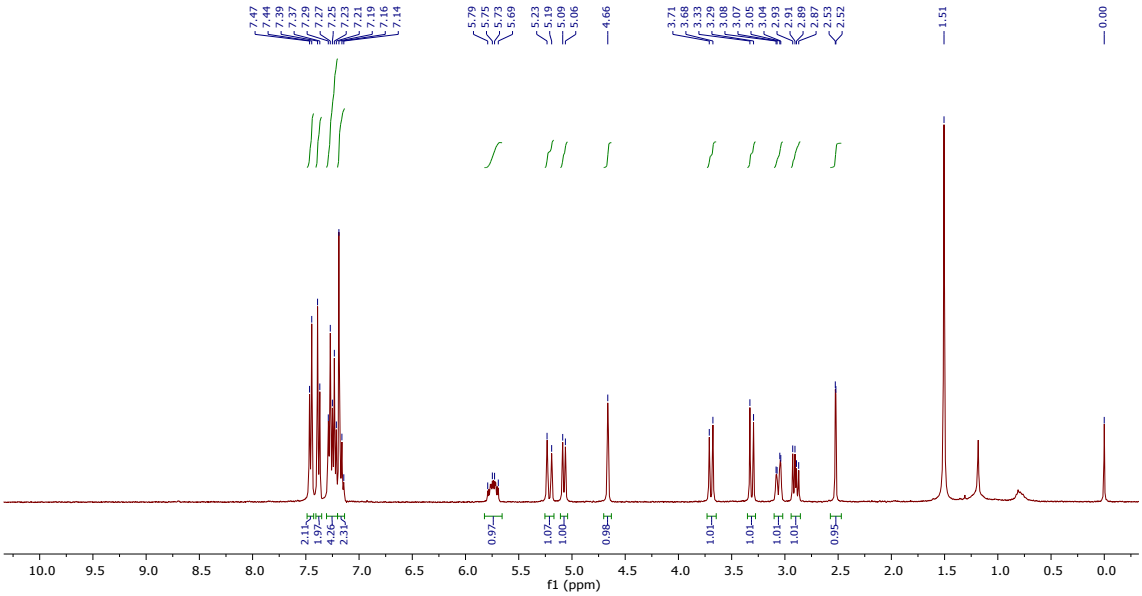
HPLC trace of 3c

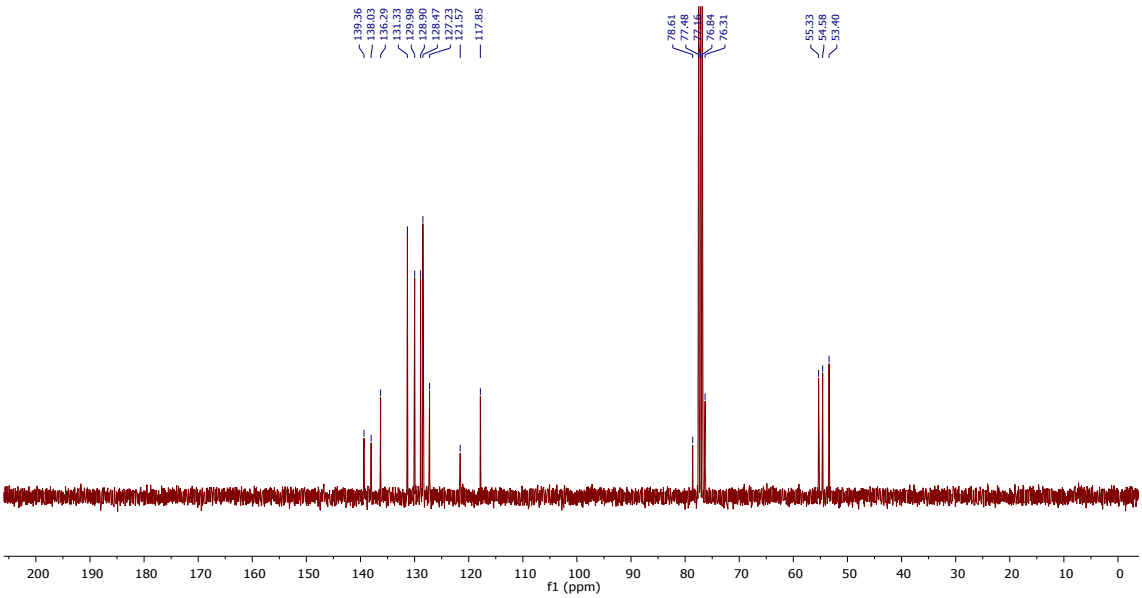


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	12.959	112.398	474.772	98.80	99.04	n.a.
2	14.979	1.370	4.596	1.20	0.96	n.a.

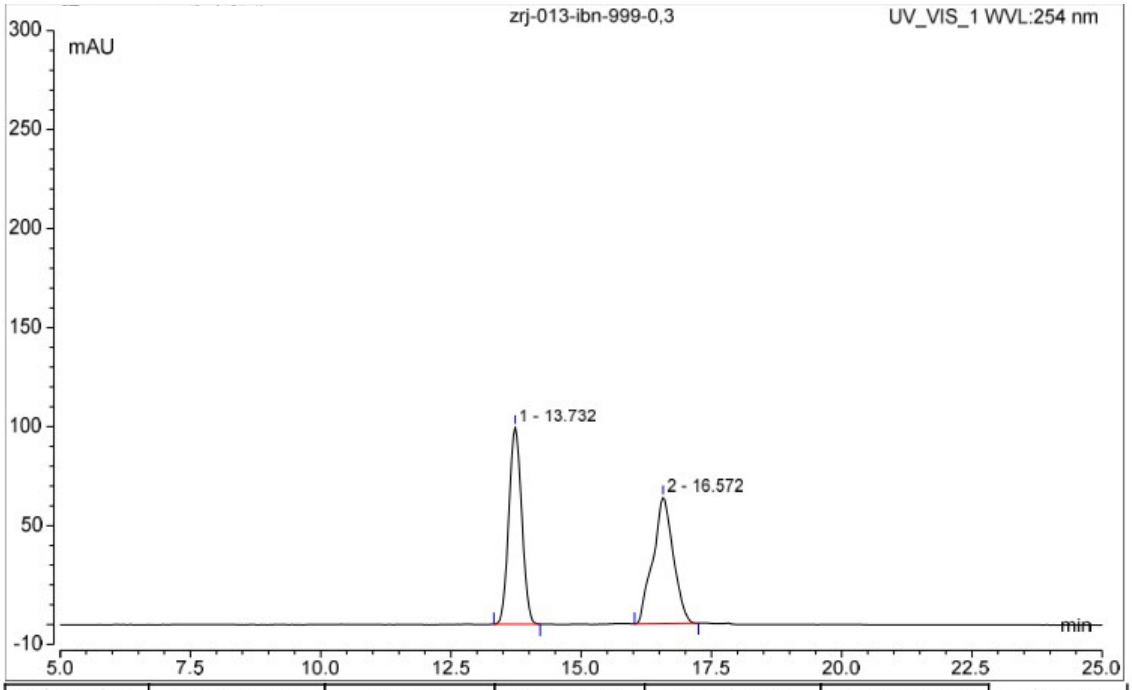

Bn
N
Br

3d


7.47
7.44
7.39
7.37
7.29
7.27
7.25
7.23
7.21
7.19
7.16
7.14
5.79
5.75
5.73
5.69
5.23
5.19
5.09
5.06
4.66
3.71
3.68
3.33
3.29
3.08
3.07
3.05
3.04
2.93
2.91
2.89
2.87
2.53
2.52
1.51
0.00
2.11
1.97
4.26
2.31
0.97
1.07
1.00
0.98
1.01
1.01
1.01
1.01
0.95
f1 (ppm)

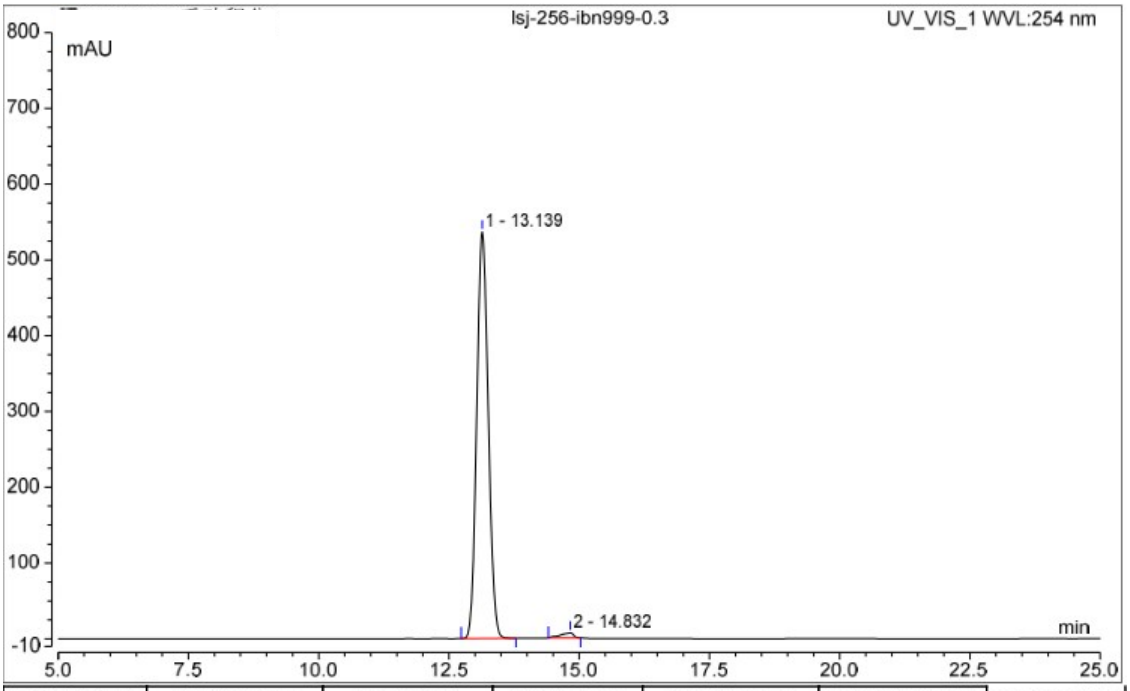

139.36
138.03
136.29
131.33
129.98
128.90
128.47
127.23
121.57
117.85
78.61
77.48
77.16
76.84
76.31
55.33
54.58
53.40
f1 (ppm)

HPLC trace of *rac*-3d

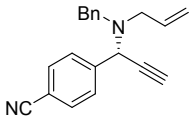


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	13.732	28.552	99.613	49.72	60.95	n.a.
2	16.572	28.874	63.813	50.28	39.05	n.a.

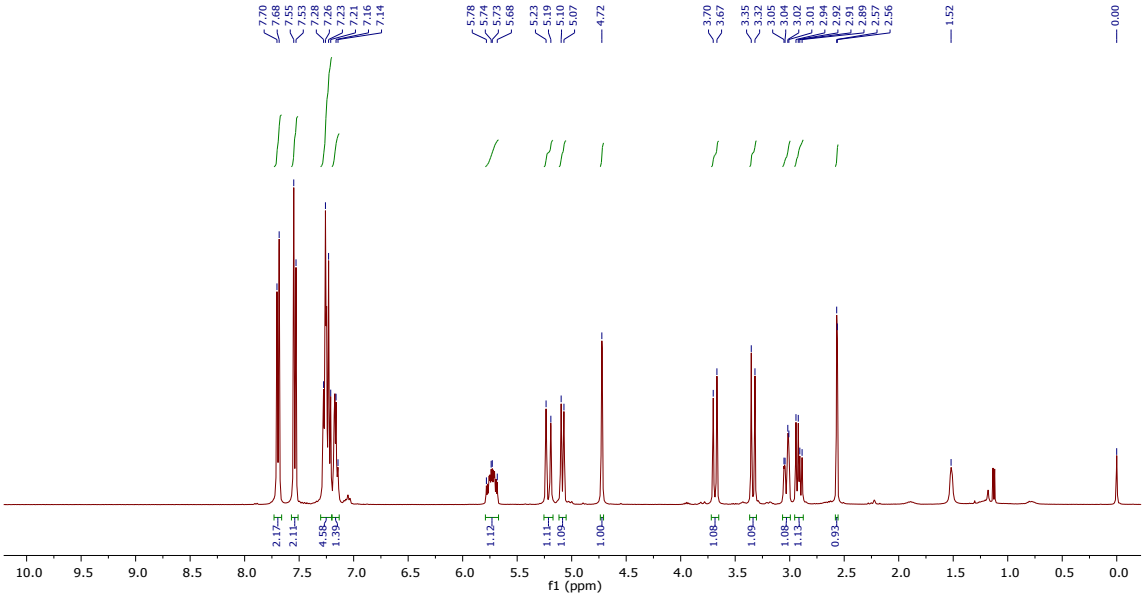
HPLC trace of 3d

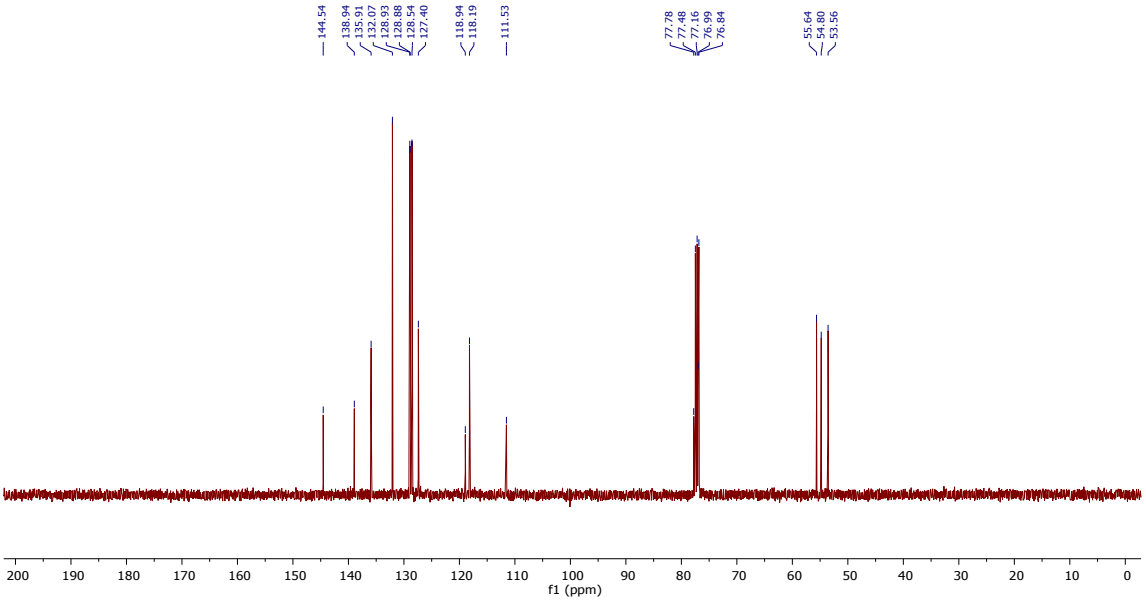


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	13.139	136.902	536.871	98.58	98.74	n.a.
2	14.832	1.975	6.851	1.42	1.26	n.a.

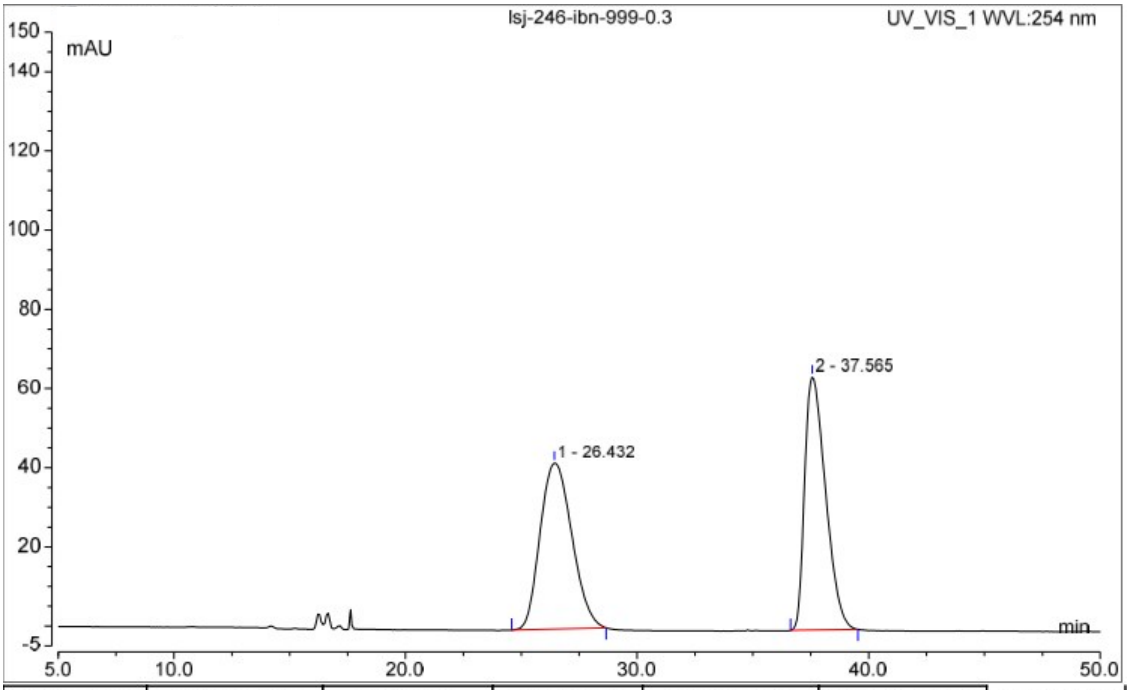

Bn
N
NC

3e


7.70
7.68
7.55
7.53
7.28
7.26
7.23
7.21
7.16
7.14
5.78
5.74
5.73
5.68
5.23
5.19
5.10
5.07
4.72
3.70
3.67
3.35
3.32
3.05
3.04
3.02
3.01
2.94
2.92
2.91
2.89
2.57
2.56
1.52
0.00
2.17
2.11
4.58
1.39
1.12
1.11
1.09
1.00
1.08
1.09
1.08
1.13
0.93
f1 (ppm)

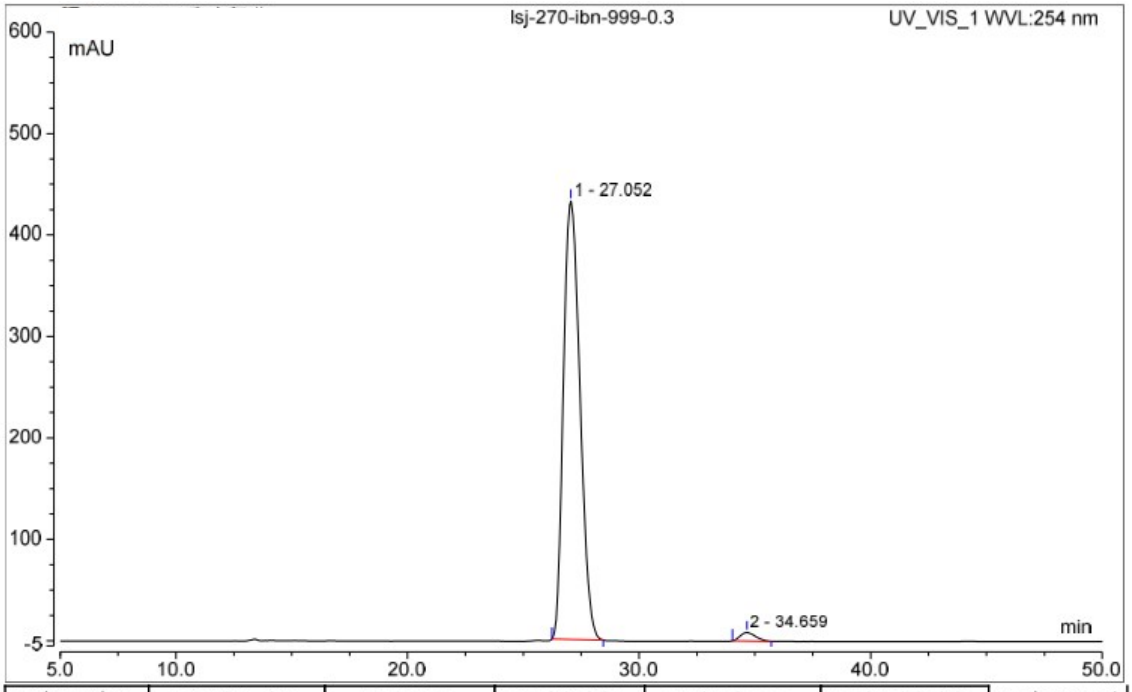

144.54
138.94
135.91
132.07
128.93
128.88
128.54
127.40
118.94
118.19
111.53
77.78
77.48
77.16
76.99
76.84
55.64
54.80
53.56
f1 (ppm)

HPLC trace of *rac*-3e

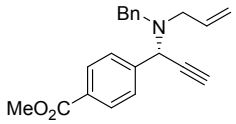


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	26.432	66.735	41.940	49.86	39.60	n.a.
2	37.565	67.117	63.966	50.14	60.40	n.a.

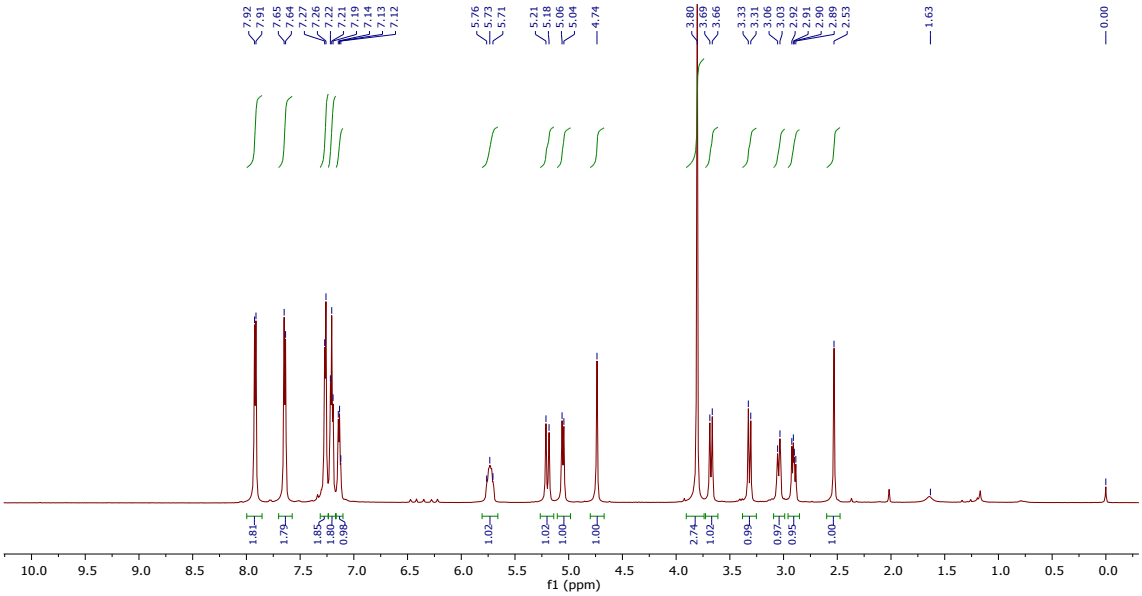
HPLC trace of 3e

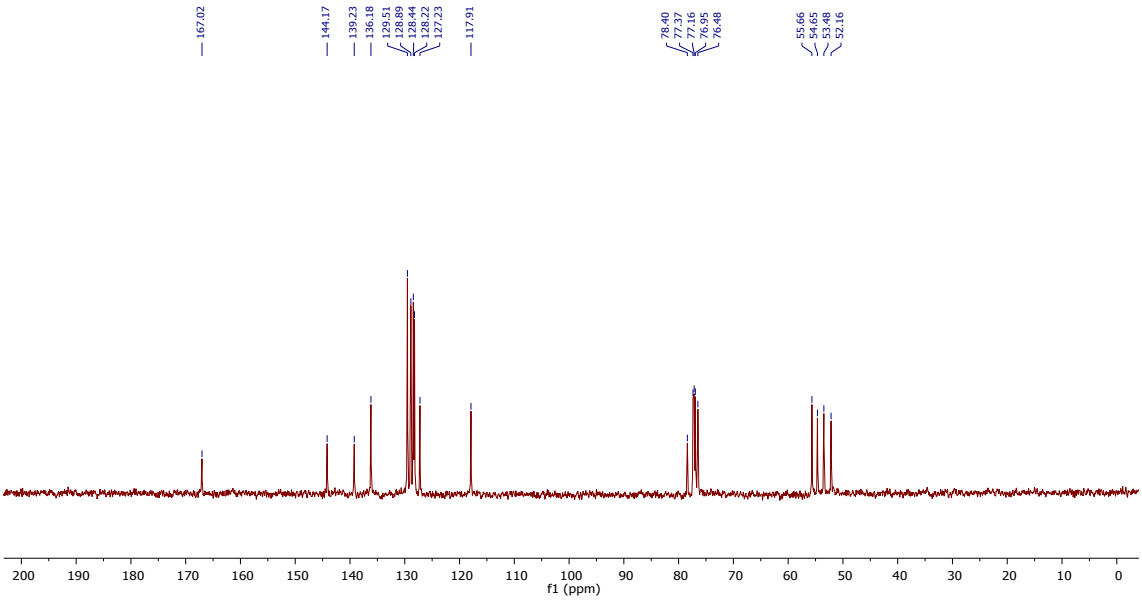


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	27.052	357.722	432.161	98.27	98.14	n.a.
2	34.659	6.283	8.206	1.73	1.86	n.a.

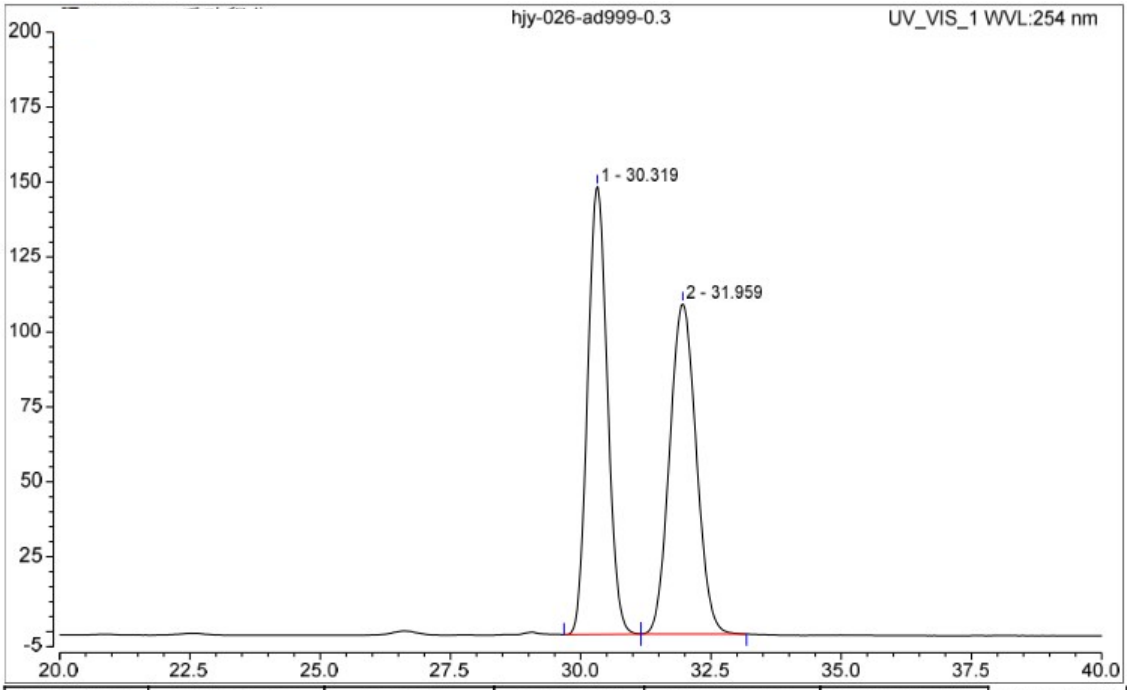

Bn
N
MeO2C

3f


7.92
7.91
7.65
7.64
7.27
7.26
7.22
7.21
7.19
7.14
7.13
7.12
5.76
5.73
5.71
5.21
5.18
5.06
5.04
4.74
3.80
3.69
3.66
3.33
3.31
3.06
3.03
2.92
2.91
2.90
2.89
2.53
1.63
0.00
1.81
1.79
1.85
1.80
0.98
1.02
1.02
1.00
1.00
2.74
1.02
0.99
0.97
0.95
1.00
f1 (ppm)

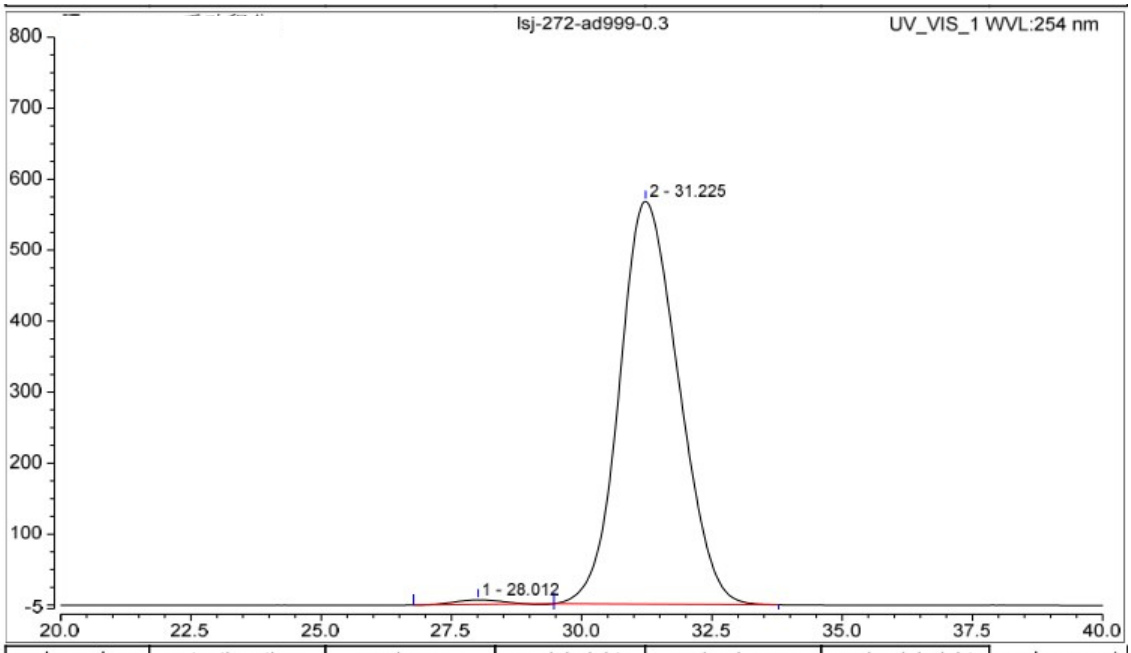

167.02
144.17
139.23
136.18
129.51
128.89
128.44
128.22
127.23
117.91
78.40
77.37
77.16
76.95
76.48
55.66
54.65
53.48
52.16
f1 (ppm)

HPLC trace of *rac*-3f

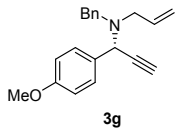


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	30.319	65.431	149.389	50.11	57.54	n.a.
2	31.959	65.142	110.243	49.89	42.46	n.a.

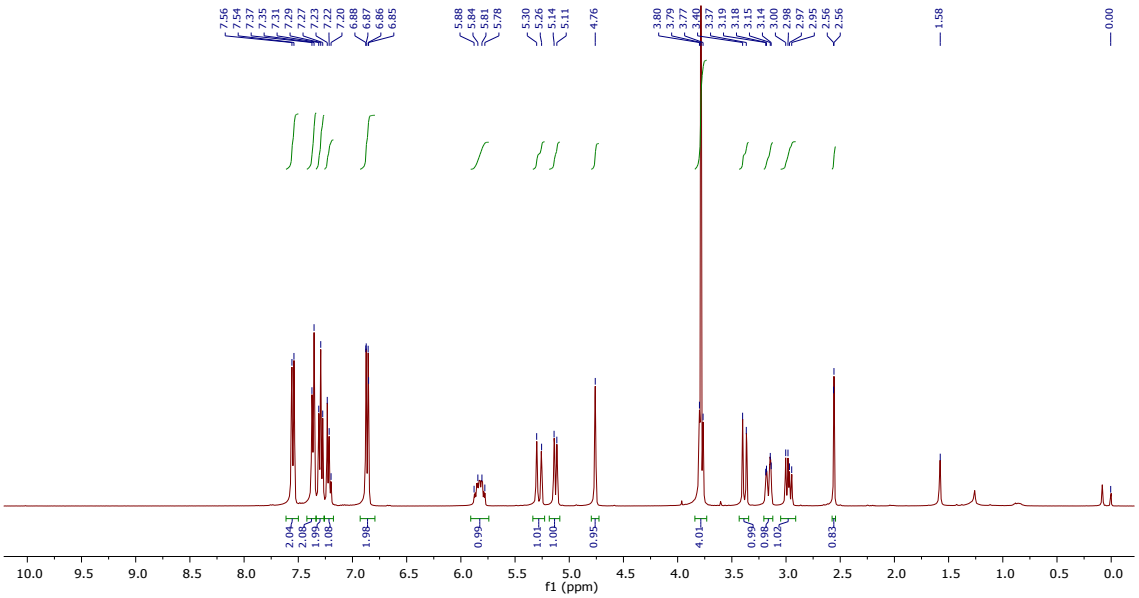
HPLC trace of 3f

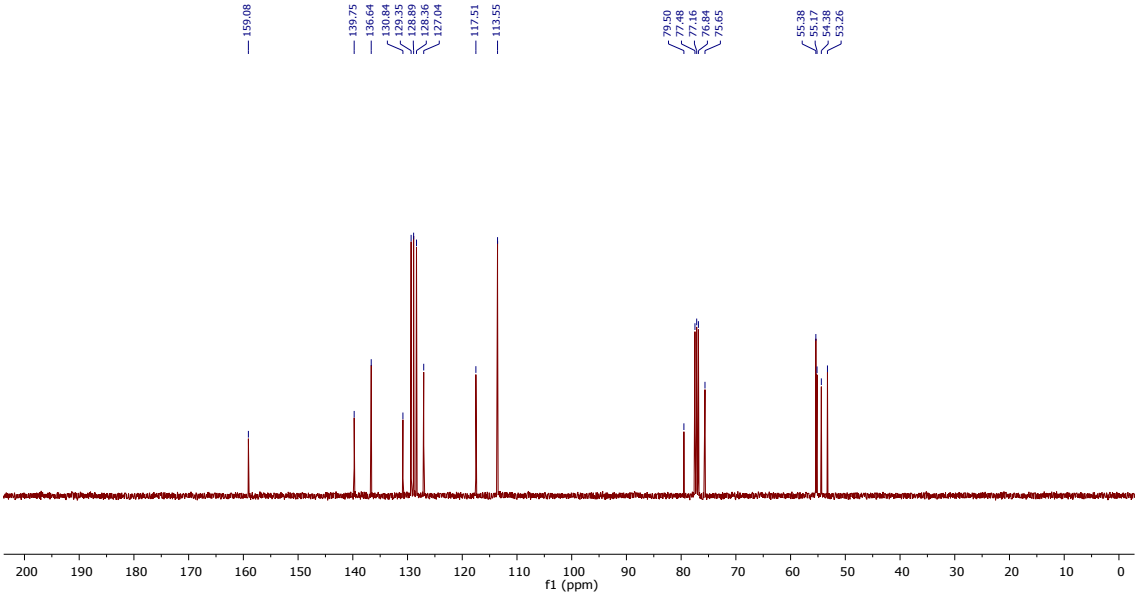


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	28.012	6.521	6.421	0.87	1.12	n.a.
2	31.225	745.538	567.463	99.13	98.88	n.a.

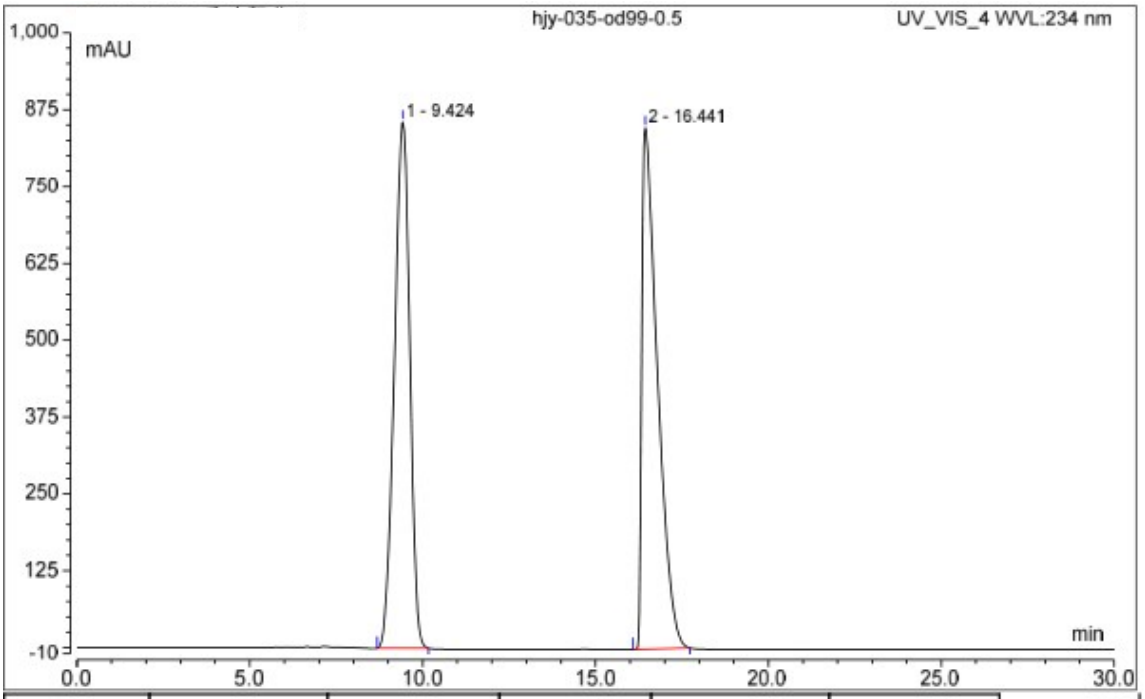

Bn
N
MeO

3g


7.56
7.54
7.37
7.35
7.31
7.29
7.27
7.23
7.22
7.20
6.88
6.87
6.86
6.85
5.88
5.84
5.81
5.78
5.30
5.26
5.14
5.11
4.76
3.80
3.79
3.77
3.40
3.37
3.19
3.18
3.15
3.14
3.00
2.98
2.97
2.95
2.56
2.56
1.58
0.00
2.04
2.08
1.99
1.08
1.98
0.99
1.01
1.00
0.95
4.01
0.99
0.98
1.02
0.83
f1 (ppm)

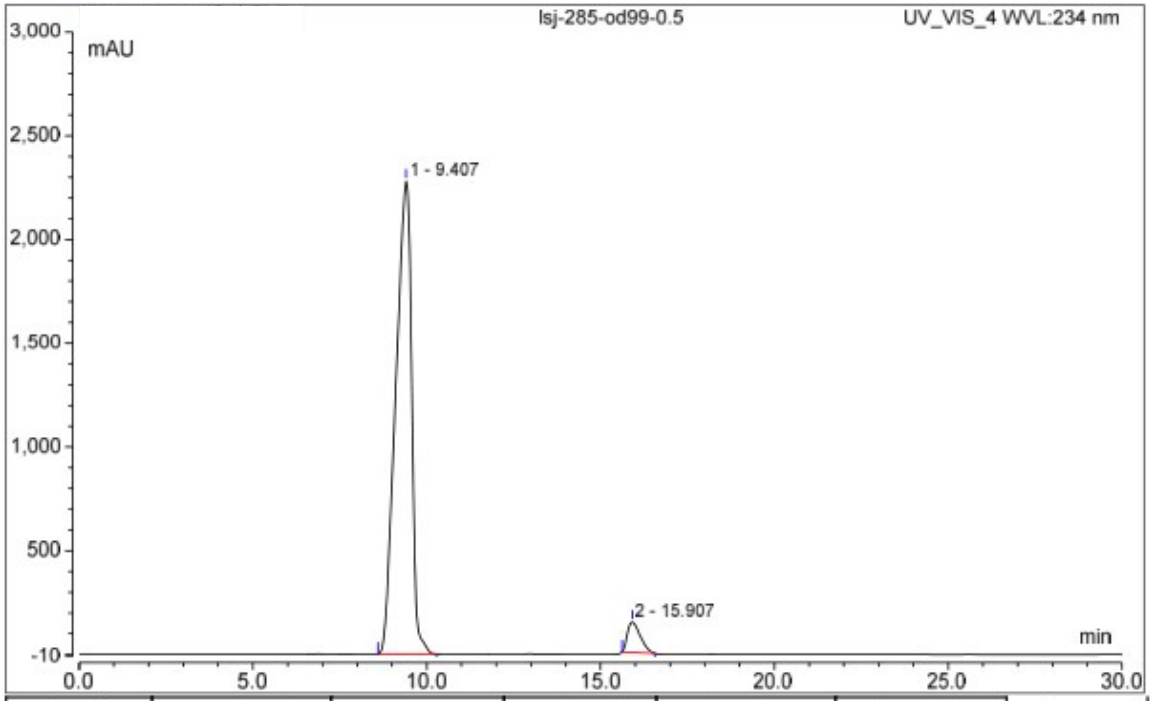

159.08
139.75
136.64
130.84
129.35
128.89
128.36
127.04
117.51
113.55
79.50
77.48
77.16
76.84
75.65
55.38
55.17
54.38
53.26
f1 (ppm)

HPLC trace of *rac*-3g

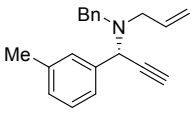


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	9.424	442.595	856.357	49.88	50.24	n.a.
2	16.441	444.684	848.043	50.12	49.76	n.a.

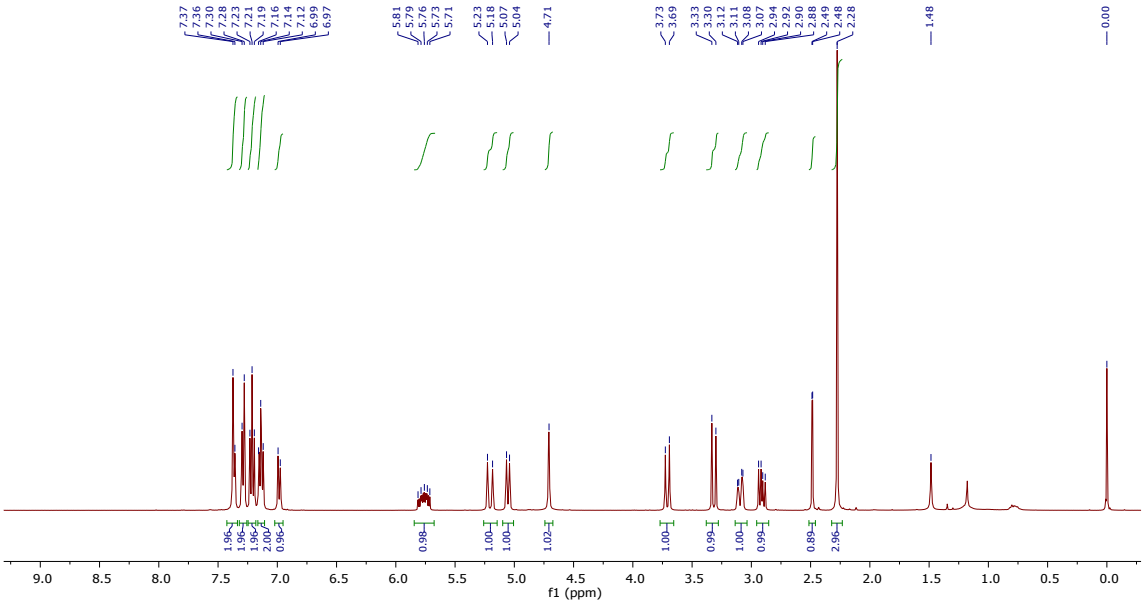
HPLC trace of 3g

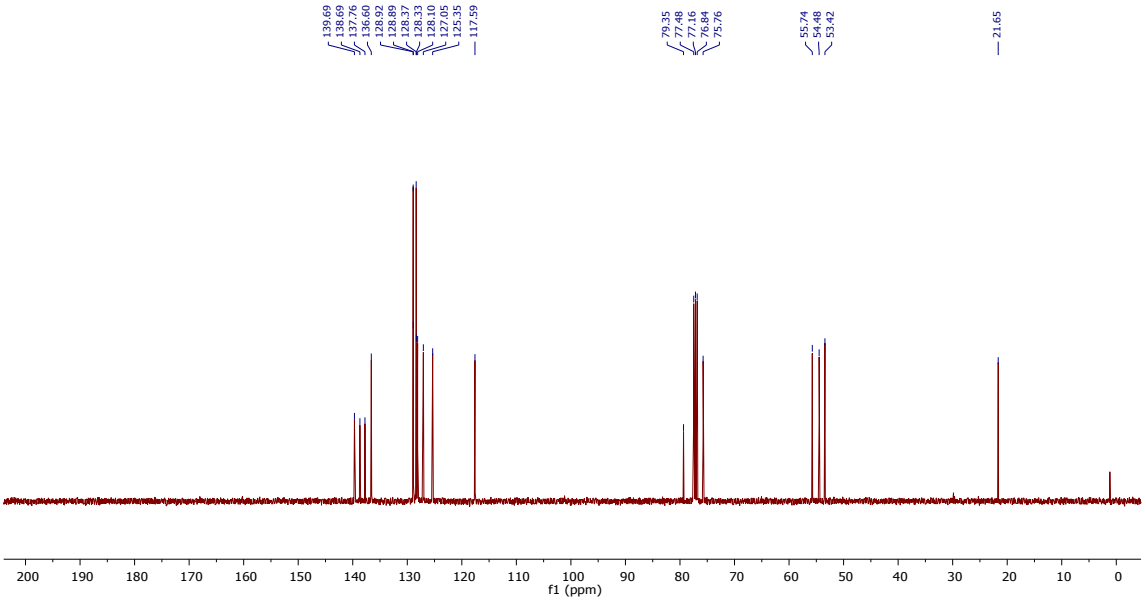


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	9.407	1205.070	2280.058	95.09	93.97	n.a.
2	15.907	62.284	146.409	4.91	6.03	n.a.

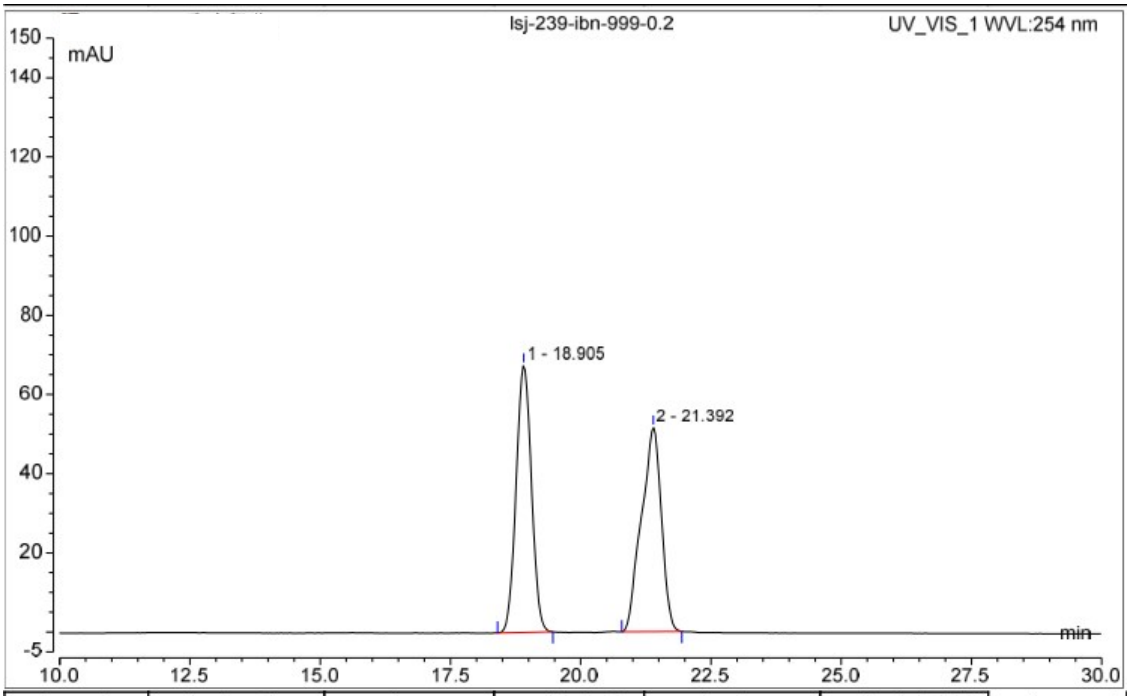

Bn
N
Me

3h


7.37
7.36
7.30
7.28
7.23
7.21
7.19
7.16
7.14
7.12
6.99
6.97
5.81
5.79
5.76
5.73
5.71
5.23
5.18
5.07
5.04
4.71
3.73
3.69
3.33
3.30
3.12
3.11
3.08
3.07
2.94
2.92
2.90
2.88
2.49
2.48
2.28
1.48
0.00
1.96
1.96
1.96
2.00
0.96
0.98
1.01
1.00
1.02
1.00
0.99
1.00
0.99
0.89
2.96
f1 (ppm)

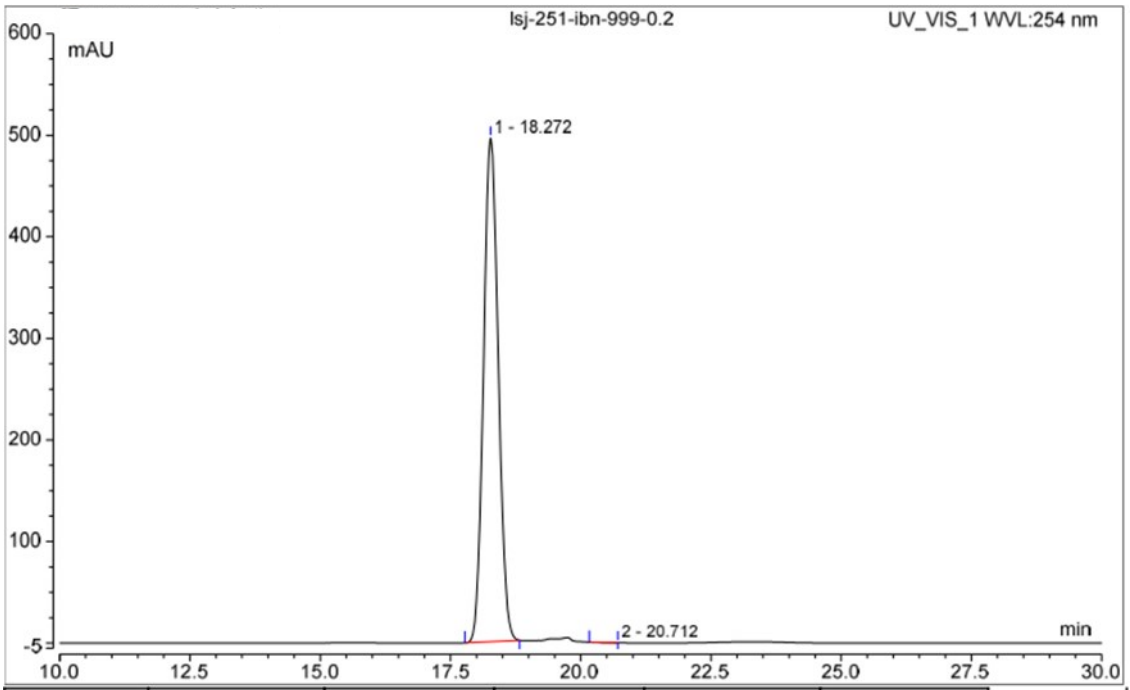

139.69
138.69
137.76
136.60
128.92
128.89
128.37
128.33
128.10
127.05
125.35
117.59
79.35
77.48
77.16
76.84
75.76
55.74
54.48
53.42
21.65
f1 (ppm)

HPLC trace of *rac*-3h

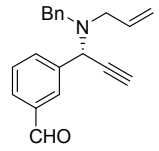


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	18.905	23.017	67.496	50.07	56.68	n.a.
2	21.392	22.951	51.586	49.93	43.32	n.a.

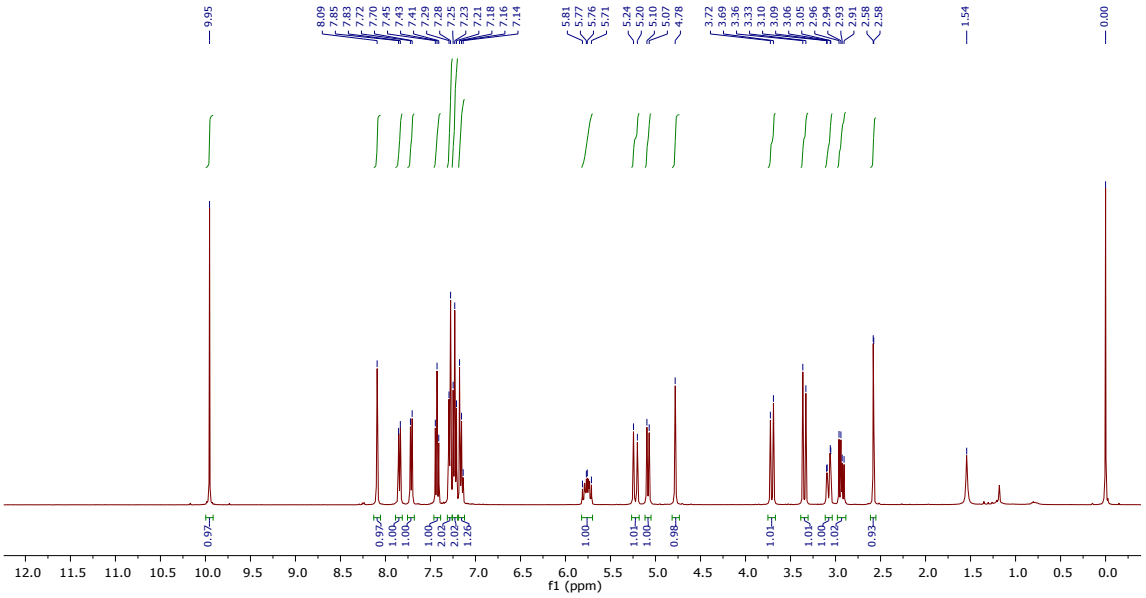
HPLC trace of 3h

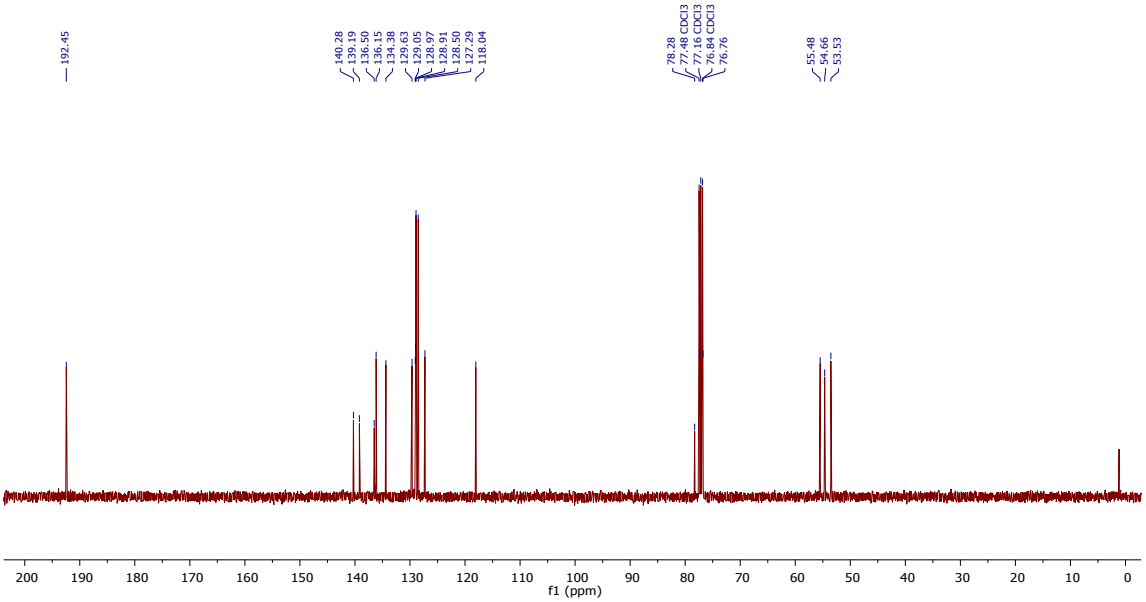


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	18.272	162.149	495.885	99.97	100.00	n.a.
2	20.712	0.056	0.000	0.03	0.00	n.a.

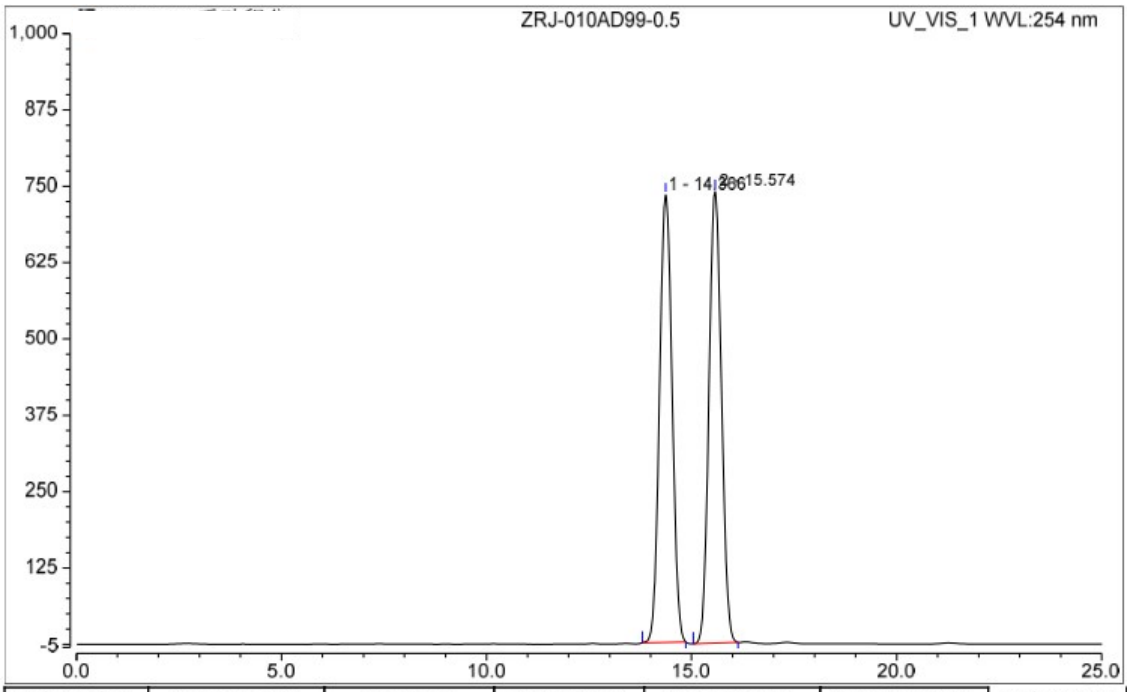

Bn
N
CHO

3i


9.95
8.09
7.85
7.83
7.72
7.70
7.45
7.43
7.41
7.29
7.28
7.25
7.23
7.21
7.18
7.16
7.14
5.81
5.77
5.76
5.71
5.24
5.20
5.10
5.07
4.78
3.72
3.69
3.36
3.33
3.10
3.09
3.06
3.05
2.96
2.94
2.93
2.91
2.58
2.58
1.54
0.00
0.97
0.97
1.00
1.00
1.00
2.02
2.02
1.26
1.00
1.01
1.00
0.98
1.01
1.01
1.00
1.02
0.93
f1 (ppm)

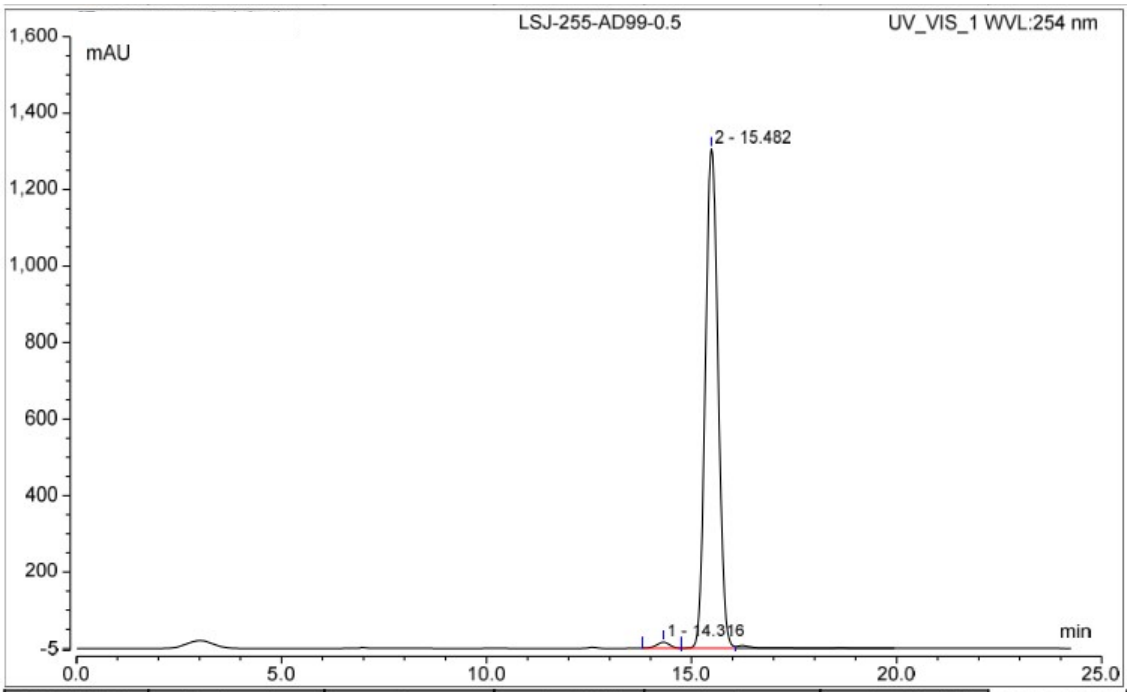

192.45
140.28
139.19
136.50
136.15
134.38
129.63
129.05
128.97
128.91
128.50
127.29
118.04
78.28
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.76
55.48
54.66
53.53
f1 (ppm)

HPLC trace of *rac*-3i

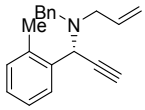


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	14.366	259.191	732.991	49.91	49.78	n.a.
2	15.574	260.163	739.507	50.09	50.22	n.a.

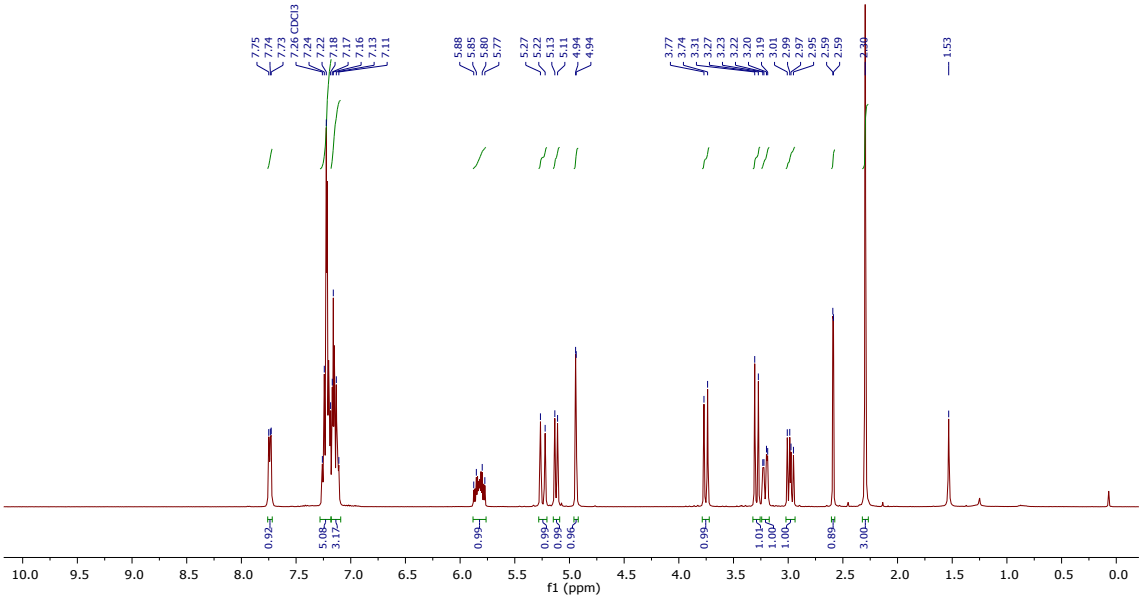
HPLC trace of 3i

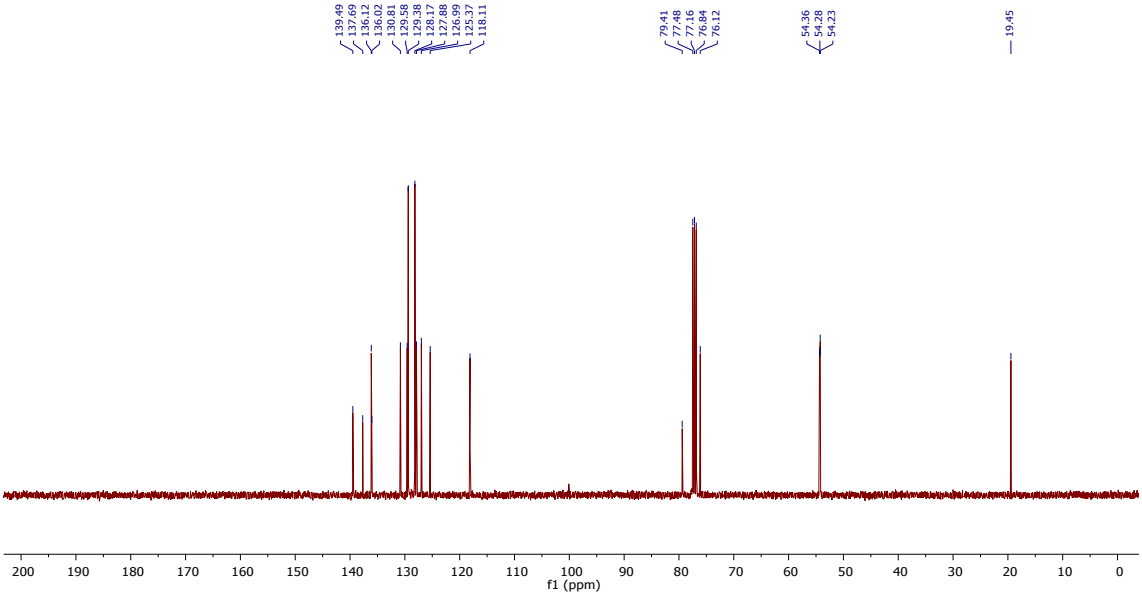


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	14.316	5.776	16.000	1.22	1.21	n.a.
2	15.482	469.318	1305.967	98.78	98.79	n.a.

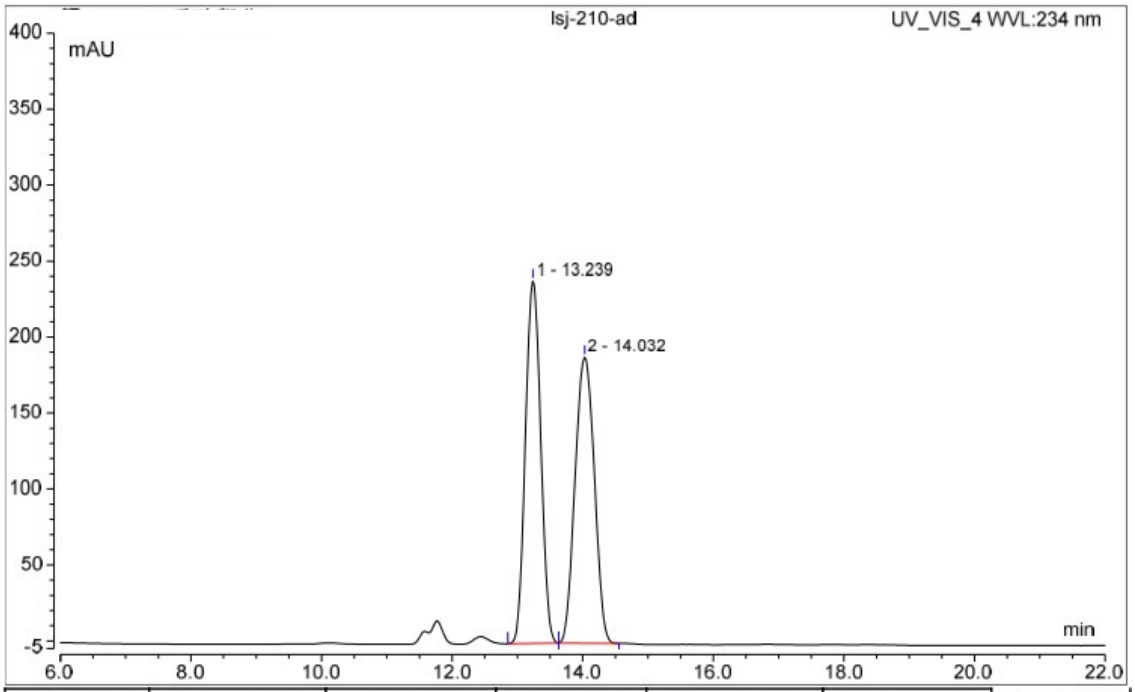

Bn
Me
N

3j


7.75
7.74
7.73
7.26 CDCl3
7.24
7.22
7.18
7.17
7.16
7.13
7.11
5.88
5.85
5.80
5.77
5.27
5.22
5.13
5.11
4.94
4.94
3.77
3.74
3.31
3.27
3.23
3.22
3.20
3.19
3.01
2.99
2.97
2.95
2.59
2.59
2.30
1.53
0.92
5.08
3.17
0.99
0.99
0.99
0.96
0.99
1.01
1.00
1.00
0.89
3.00
f1 (ppm)

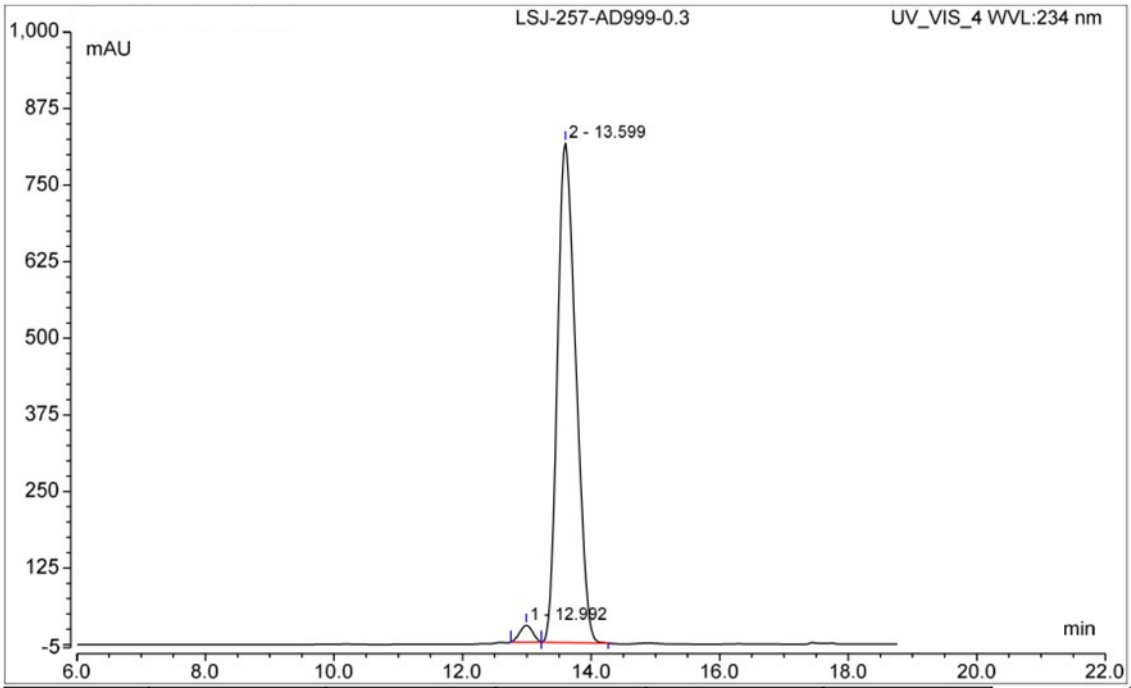

139.49
137.69
136.12
136.02
130.81
129.58
129.38
128.17
127.88
126.99
125.37
118.11
79.41
77.48
77.16
76.84
76.12
54.36
54.28
54.23
19.45
f1 (ppm)

HPLC trace of *rac*-3j

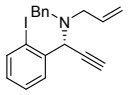


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	13.239	64.521	238.556	50.09	55.87	n.a.
2	14.032	64.284	188.445	49.91	44.13	n.a.

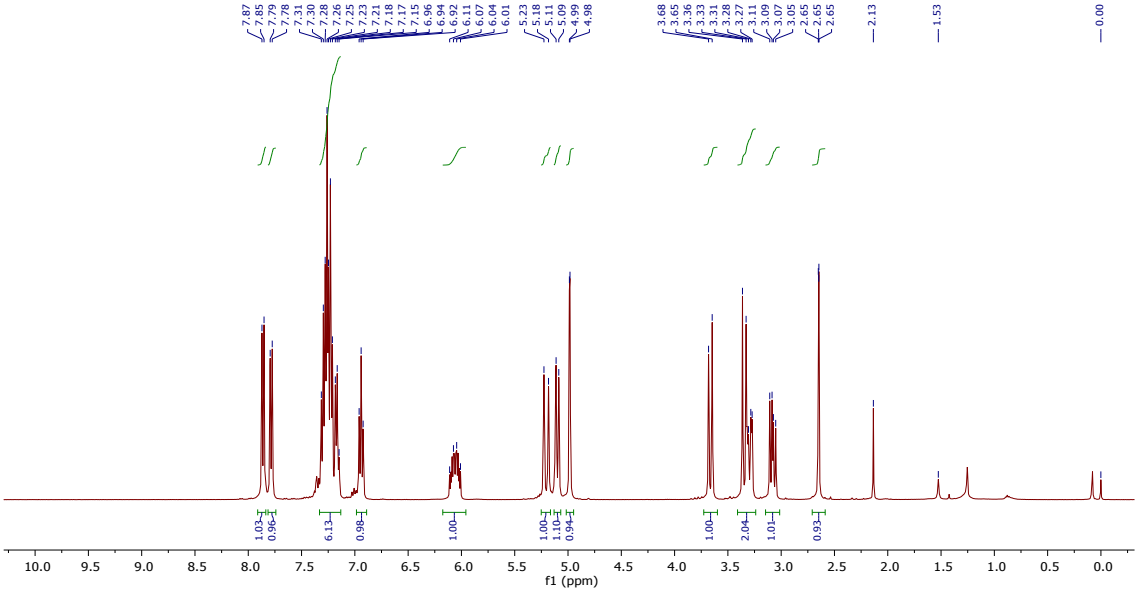
HPLC trace of 3j

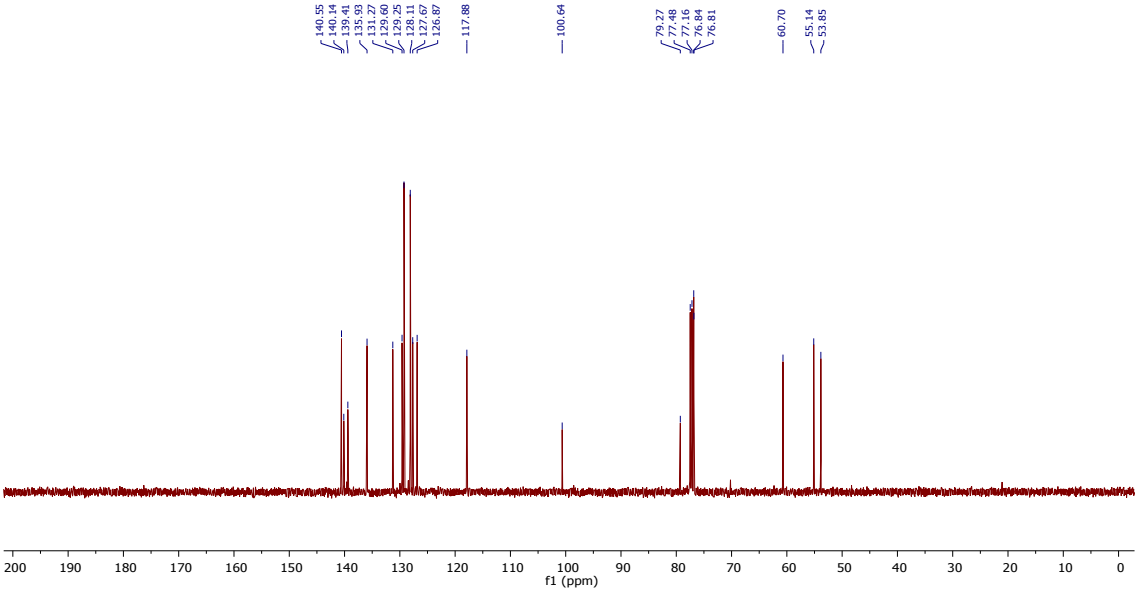


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	12.992	6.419	27.334	2.31	3.24	n.a.
2	13.599	271.029	815.481	97.69	96.76	n.a.

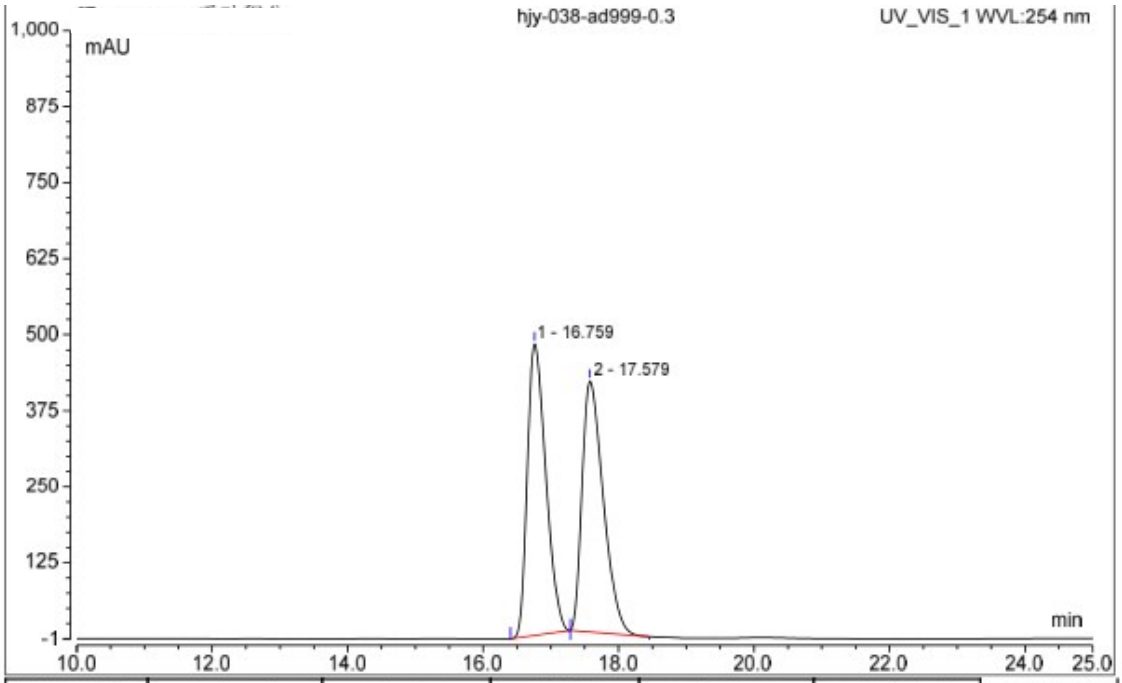

Bn
N
I

3k


7.87
7.85
7.79
7.78
7.31
7.30
7.28
7.26
7.25
7.23
7.21
7.18
7.17
7.15
6.96
6.94
6.92
6.11
6.07
6.04
6.01
5.23
5.18
5.11
5.09
4.99
4.98
3.68
3.65
3.36
3.33
3.31
3.28
3.27
3.11
3.09
3.07
3.05
2.65
2.65
2.65
2.13
1.53
0.00
1.03
0.96
6.13
0.98
1.00
1.00
1.10
0.94
1.00
2.04
1.01
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)

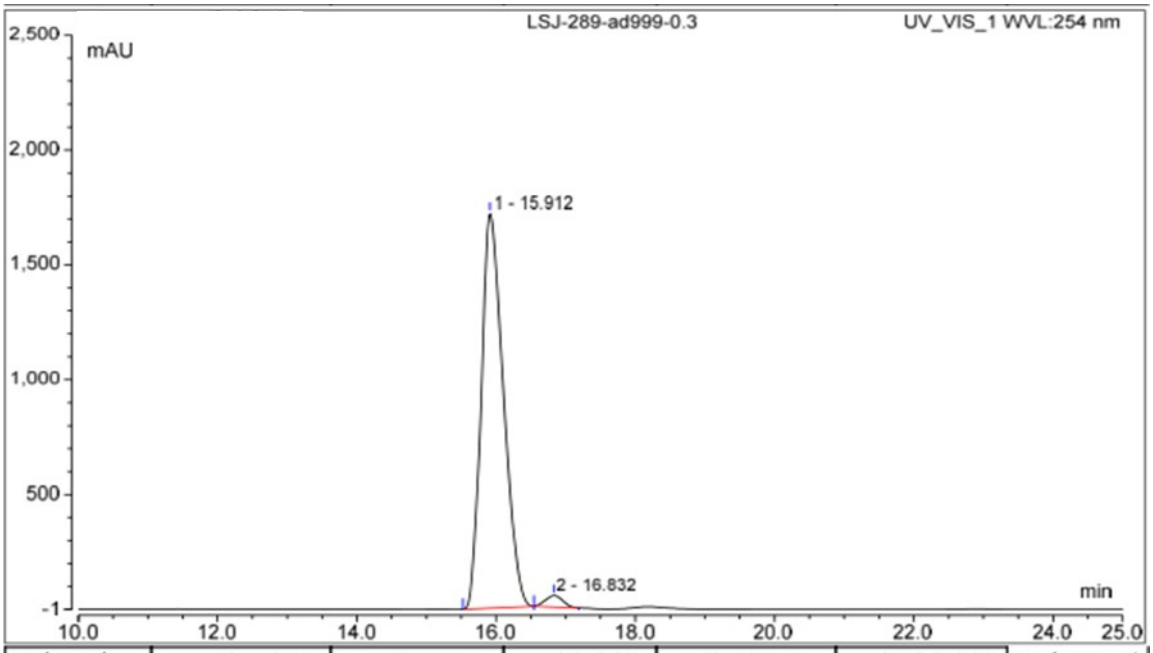

140.55
140.14
139.41
135.93
131.27
129.60
129.25
128.11
127.67
126.87
117.88
100.64
79.27
77.48
77.16
76.84
76.81
60.70
55.14
53.85
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

HPLC trace of *rac*-3k

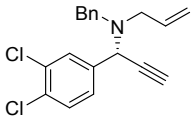


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	16.759	151.242	479.927	50.25	53.73	n.a.
2	17.579	149.756	413.285	49.75	46.27	n.a.

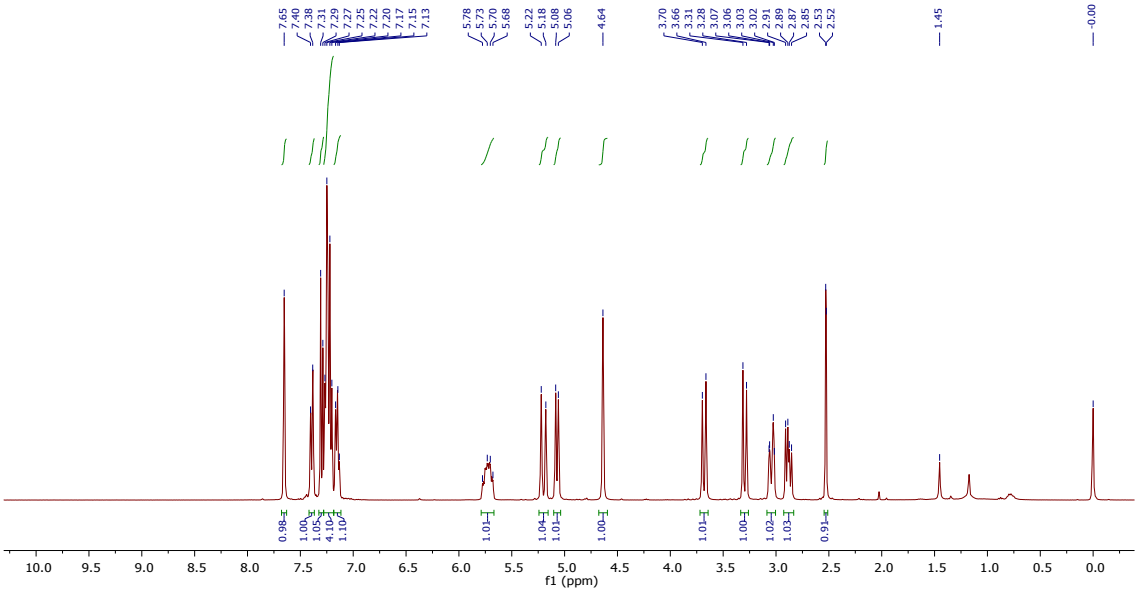
HPLC trace of 3k

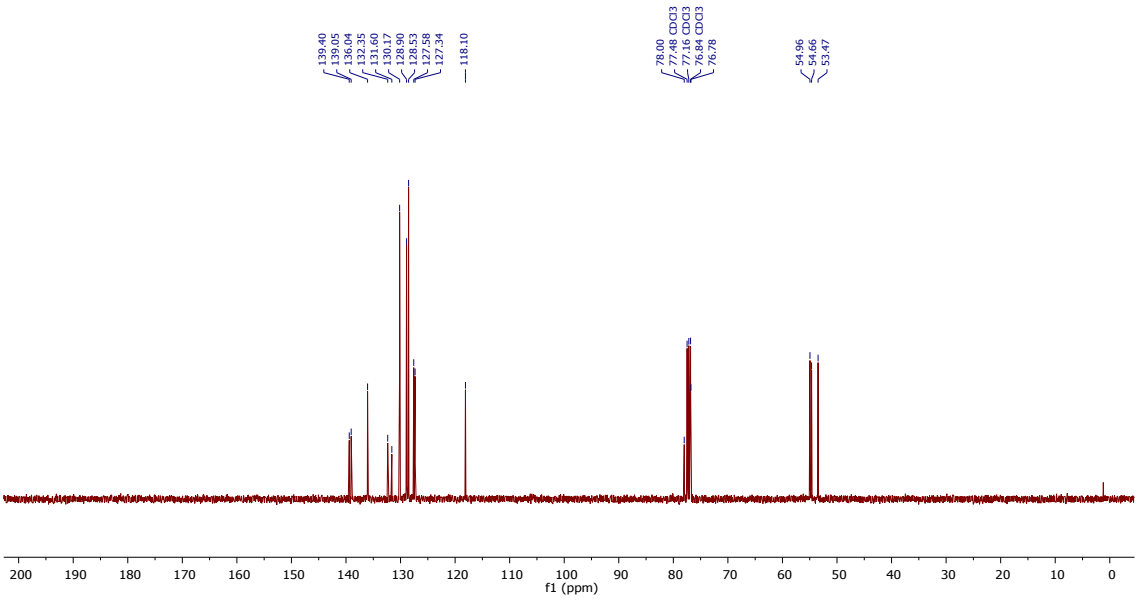


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	15.912	629.821	1719.550	97.76	97.18	n.a.
2	16.832	14.416	49.852	2.24	2.82	n.a.

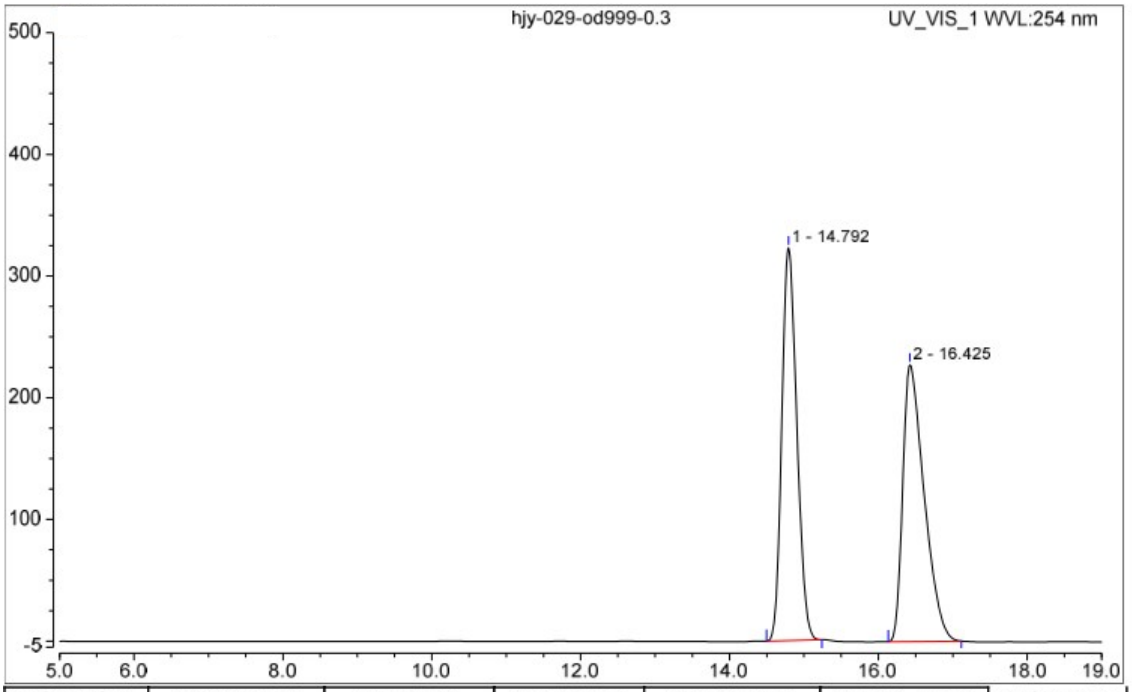

Bn
N
Cl
Cl

3l


7.65
7.40
7.38
7.31
7.29
7.27
7.25
7.22
7.20
7.17
7.15
7.13
5.78
5.73
5.70
5.68
5.22
5.18
5.08
5.06
4.64
3.70
3.66
3.31
3.28
3.07
3.06
3.03
3.02
2.91
2.89
2.87
2.85
2.53
2.52
1.45
-0.00
0.98
1.00
1.05
4.10
1.10
1.01
1.04
1.01
1.00
1.01
1.00
1.02
1.03
0.91
f1 (ppm)

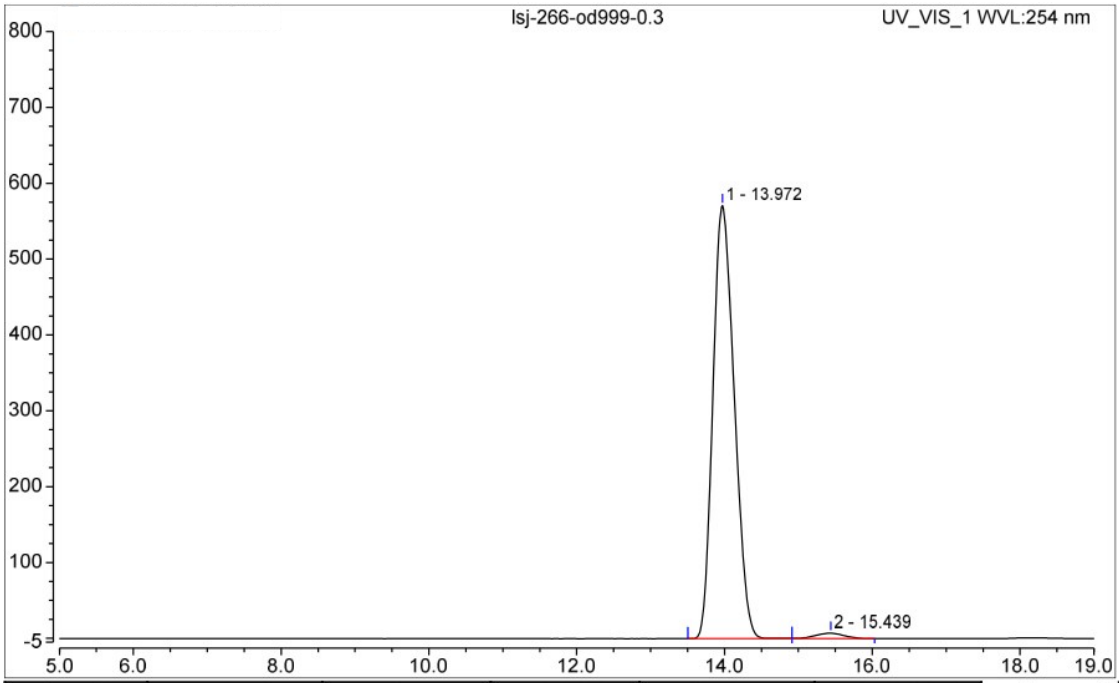

139.40
139.05
136.04
132.35
131.60
130.17
128.90
128.53
127.58
127.34
118.10
78.00
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.78
54.96
54.66
53.47
f1 (ppm)

HPLC trace of *rac*-3l

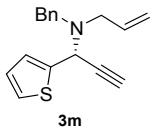


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	14.792	75.016	322.778	49.78	58.67	n.a.
2	16.425	75.685	227.404	50.22	41.33	n.a.

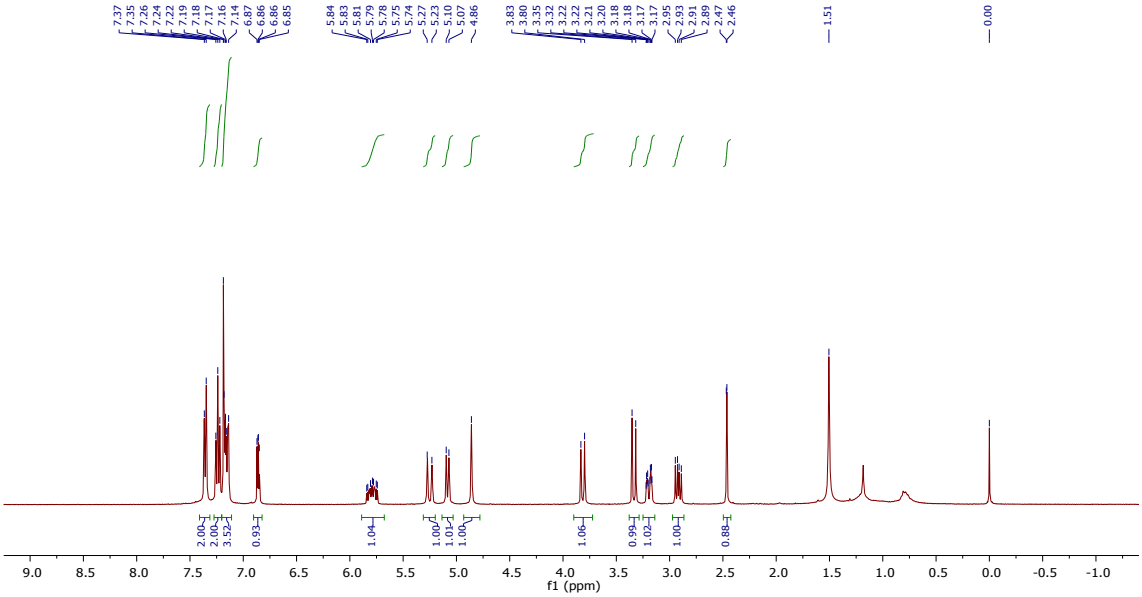
HPLC trace of 3l

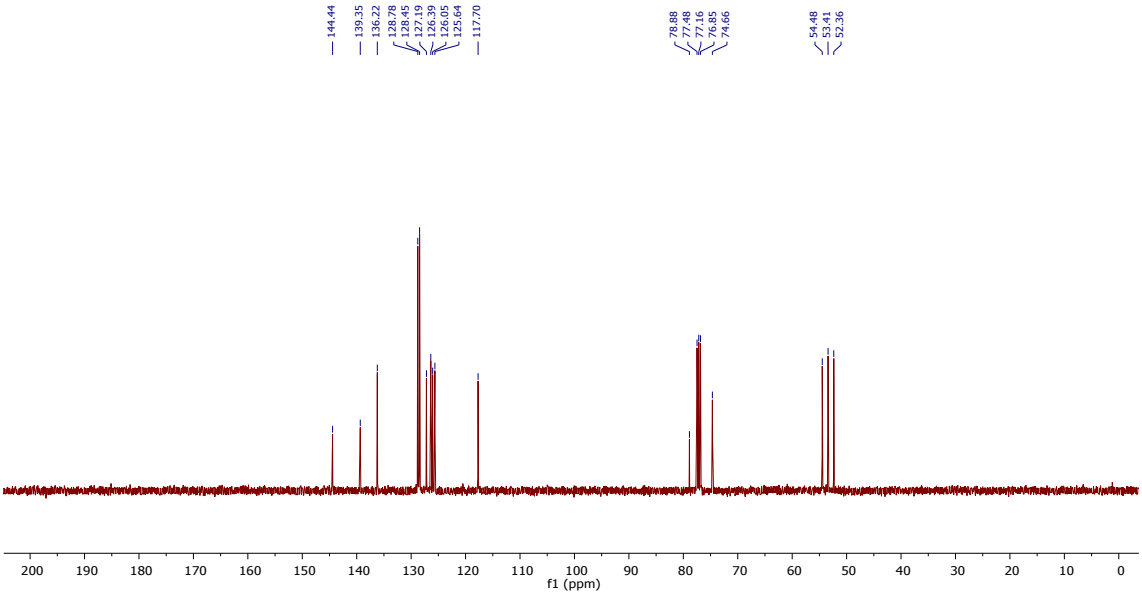


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	13.972	191.123	570.936	98.30	98.75	n.a.
2	15.439	3.303	7.256	1.70	1.25	n.a.

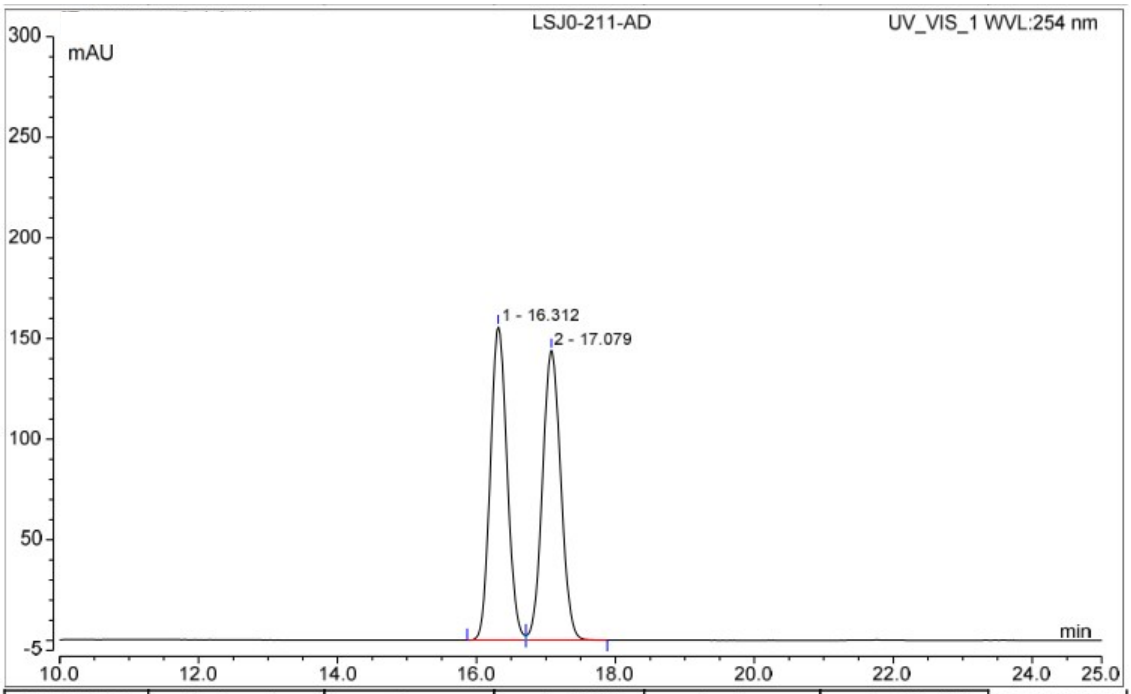

Bn
N
S

3m


7.37
7.35
7.26
7.24
7.22
7.19
7.18
7.17
7.16
7.14
6.87
6.86
6.86
6.85
5.84
5.83
5.81
5.79
5.78
5.75
5.74
5.27
5.23
5.10
5.07
4.86
3.83
3.80
3.35
3.32
3.22
3.21
3.20
3.18
3.18
3.17
3.17
2.95
2.93
2.91
2.89
2.47
2.46
1.51
0.00
2.00
2.00
3.52
0.93
1.04
1.00
1.01
1.00
1.06
0.99
1.02
1.00
0.88
f1 (ppm)

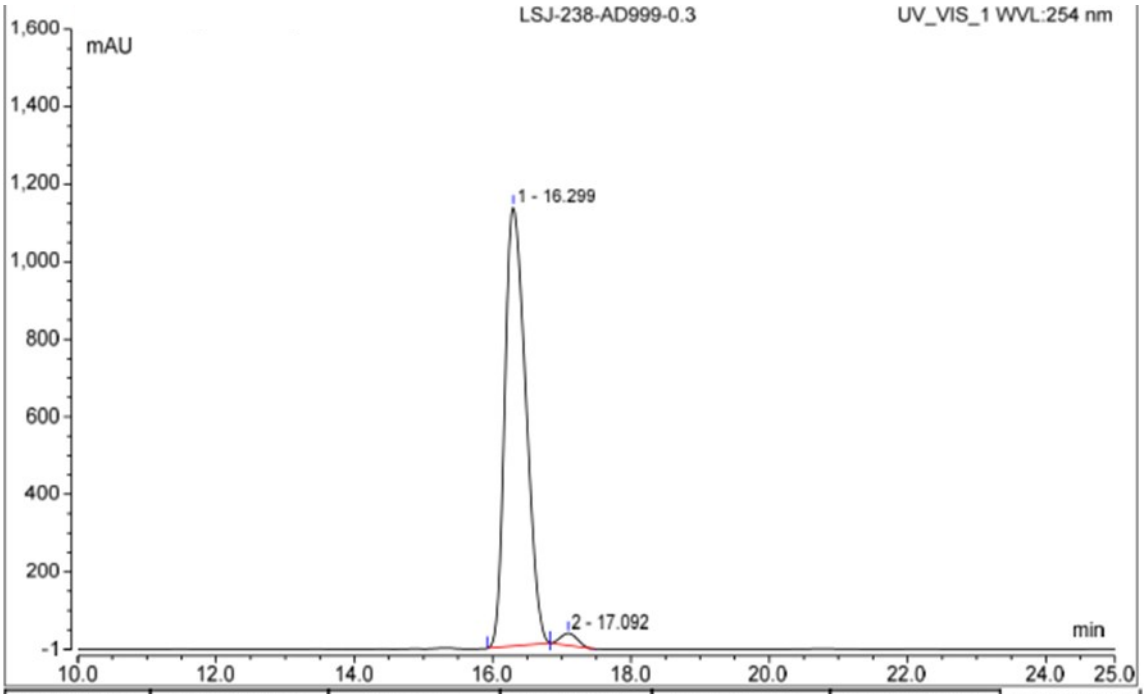

144.44
139.35
136.22
128.78
128.45
127.19
126.39
126.05
125.64
117.70
78.88
77.48
77.16
76.85
74.66
54.48
53.41
52.36
f1 (ppm)

HPLC trace of *rac*-3m

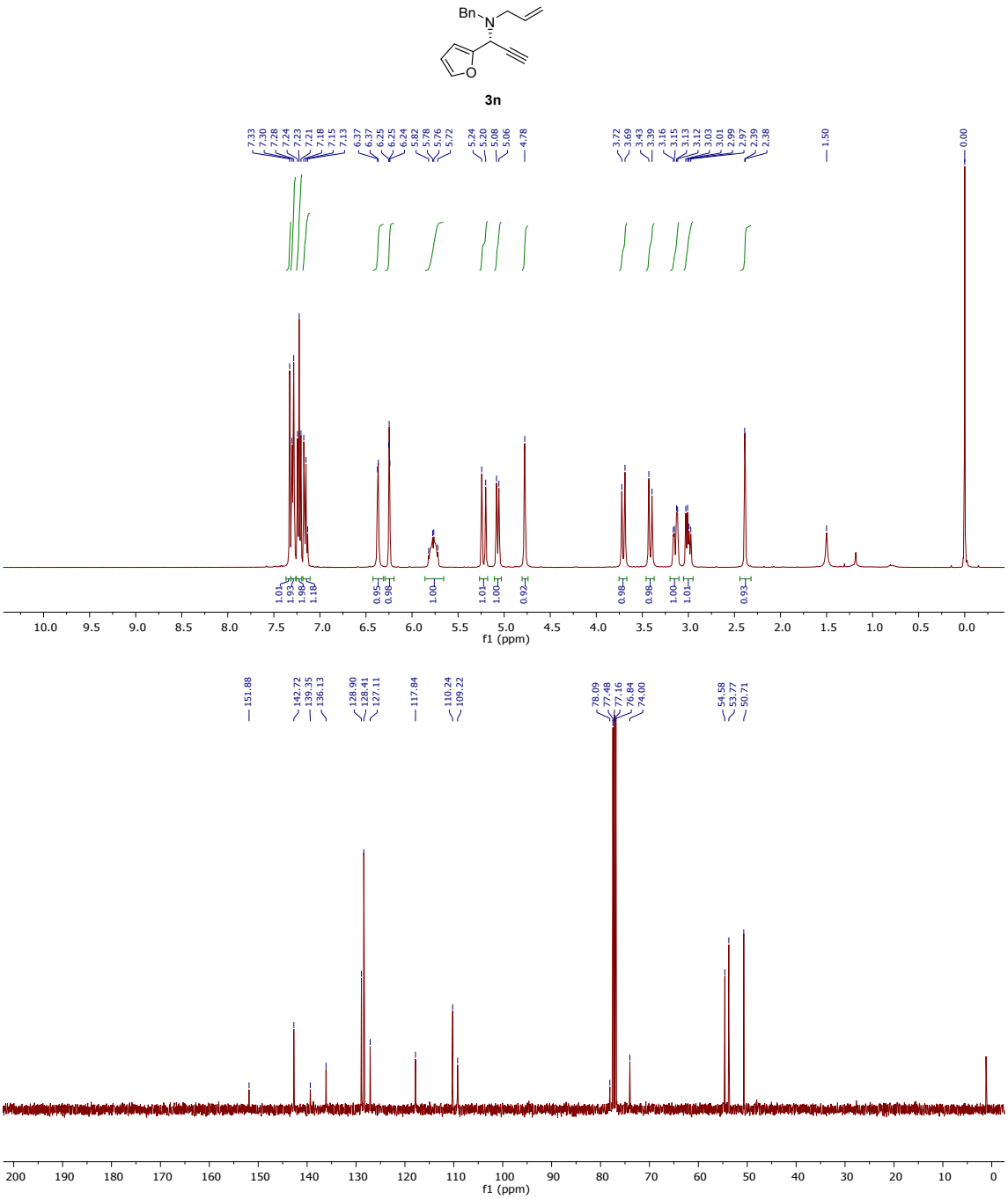


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	16.312	43.688	155.794	49.88	51.96	n.a.
2	17.079	43.905	144.013	50.12	48.04	n.a.

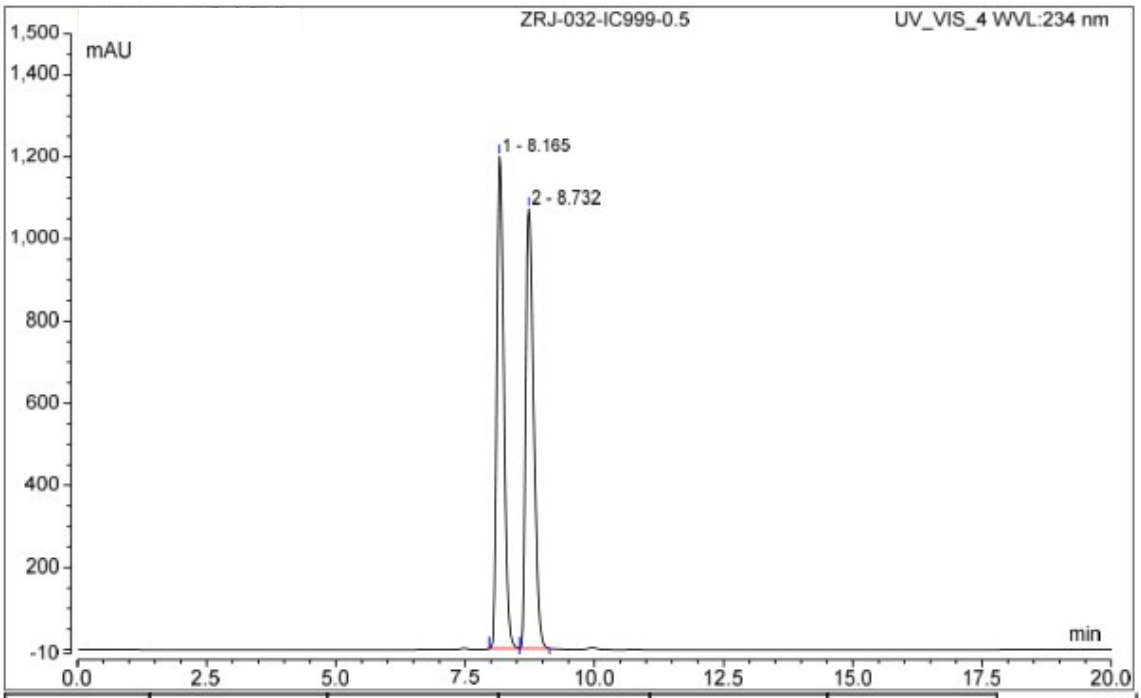
HPLC trace of 3m



peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	16.299	395.576	1132.972	97.84	97.35	n.a.
2	17.092	8.725	30.819	2.16	2.65	n.a.

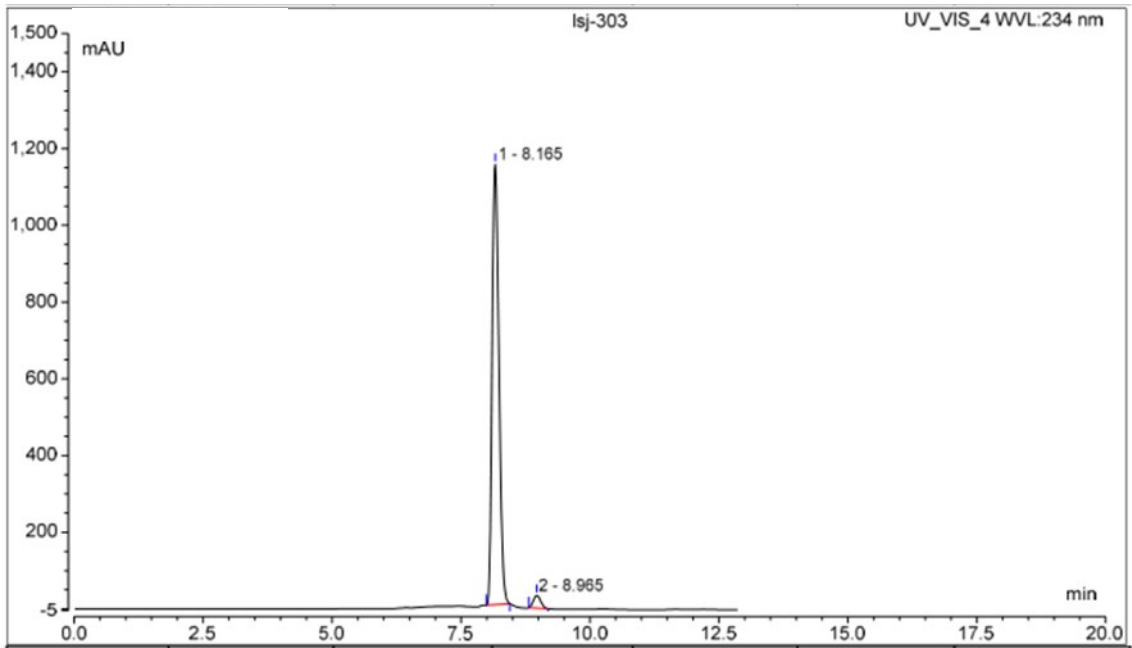

Bn
N
O
3n
7.33
7.30
7.28
7.24
7.23
7.21
7.18
7.15
7.13
6.37
6.37
6.25
6.25
6.24
5.82
5.78
5.76
5.72
5.24
5.20
5.08
5.06
4.78
3.72
3.69
3.43
3.39
3.16
3.15
3.13
3.12
3.03
3.01
2.99
2.97
2.39
2.38
1.50
0.00
1.01
1.93
1.98
1.18
0.95
0.98
1.00
1.01
1.00
0.92
0.98
0.98
1.00
1.01
0.93
f1 (ppm)
151.88
142.72
139.35
136.13
128.90
128.41
127.11
117.84
110.24
109.22
78.09
77.48
77.16
76.84
74.00
54.58
53.77
50.71
f1 (ppm)

HPLC trace of *rac*-3n

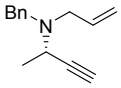


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	8.165	189.155	1198.452	49.68	52.82	n.a.
2	8.732	191.611	1070.473	50.32	47.18	n.a.

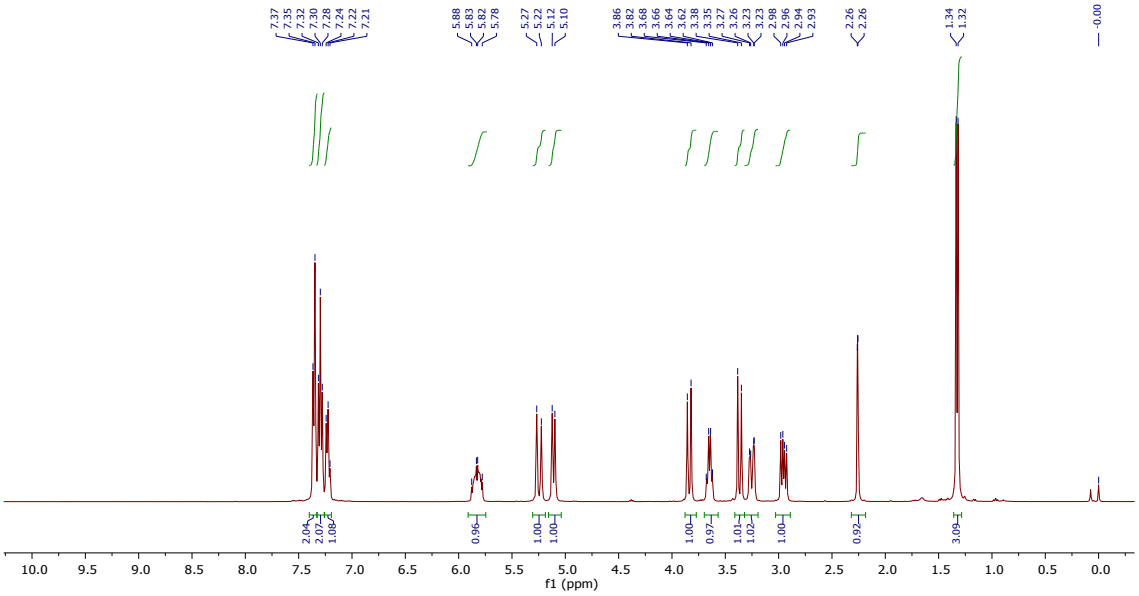
HPLC trace of 3n

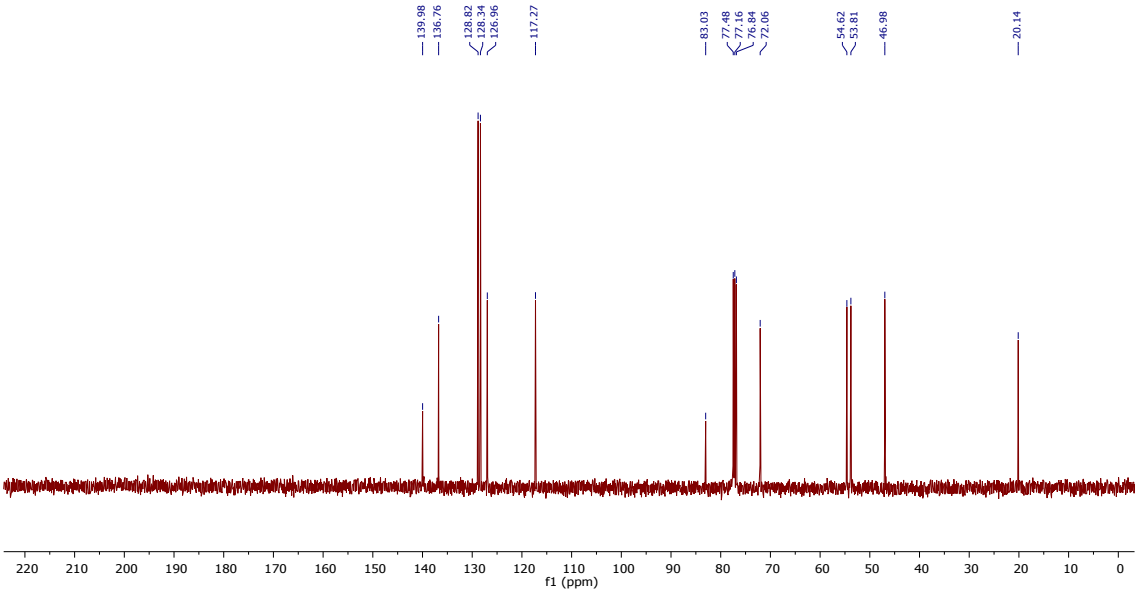


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	8.165	175.583	1147.766	96.99	97.20	n.a.
2	8.965	5.445	33.108	3.01	2.80	n.a.

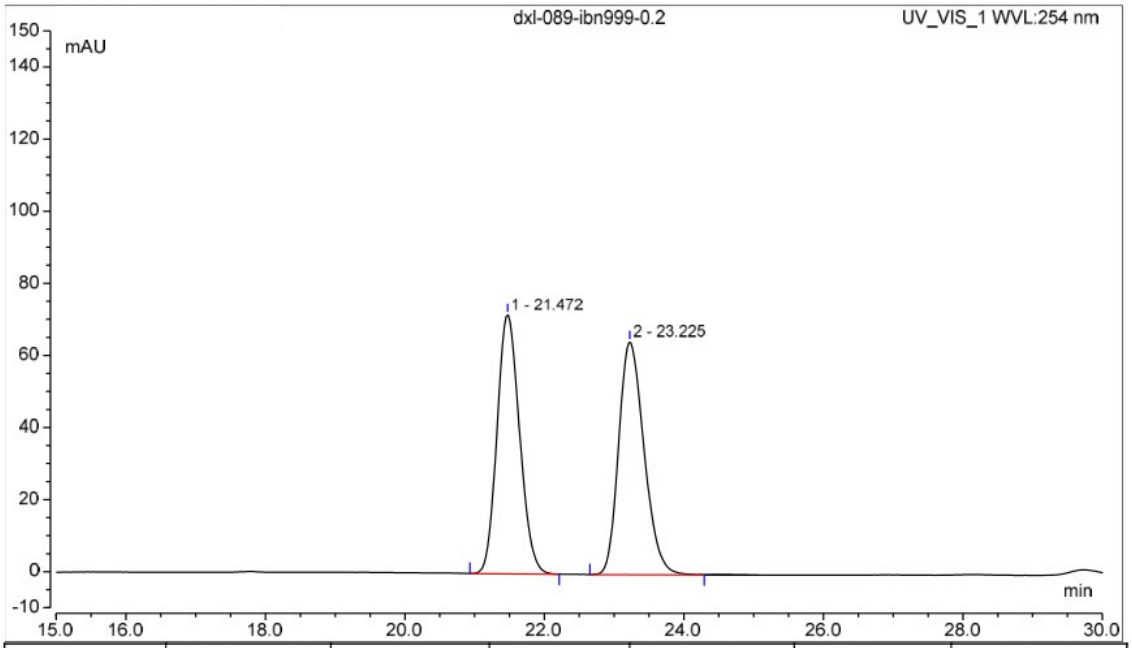

Bn
N

3o


7.37
7.35
7.32
7.30
7.28
7.24
7.22
7.21
5.88
5.83
5.82
5.78
5.27
5.22
5.12
5.10
3.86
3.82
3.68
3.66
3.64
3.62
3.38
3.35
3.27
3.26
3.23
3.23
2.98
2.96
2.94
2.93
2.26
2.26
1.34
1.32
-0.00
2.04
2.07
1.08
0.96
1.00
1.00
1.00
0.97
1.01
1.02
1.00
0.92
3.09
f1 (ppm)

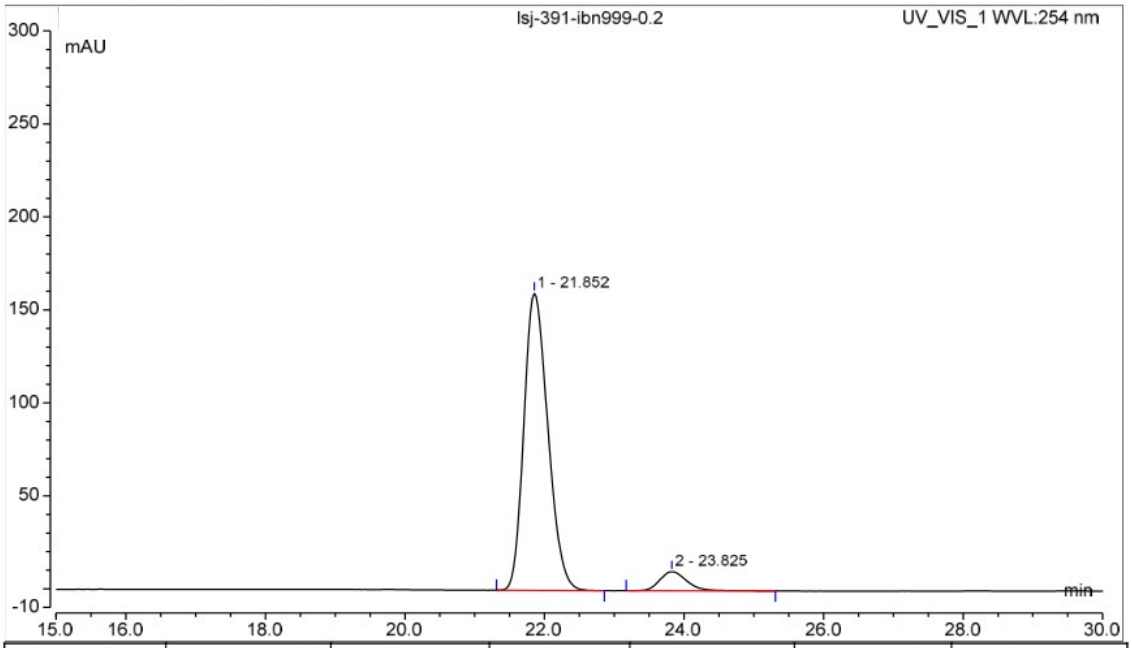

139.98
136.76
128.82
128.34
126.96
117.27
83.03
77.48
77.16
76.84
72.06
54.62
53.81
46.98
20.14
f1 (ppm)

HPLC trace of *rac*-3o

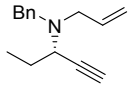


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	21.472	26.922	71.874	49.71	52.66	n.a.
2	23.225	27.234	64.605	50.29	47.34	n.a.

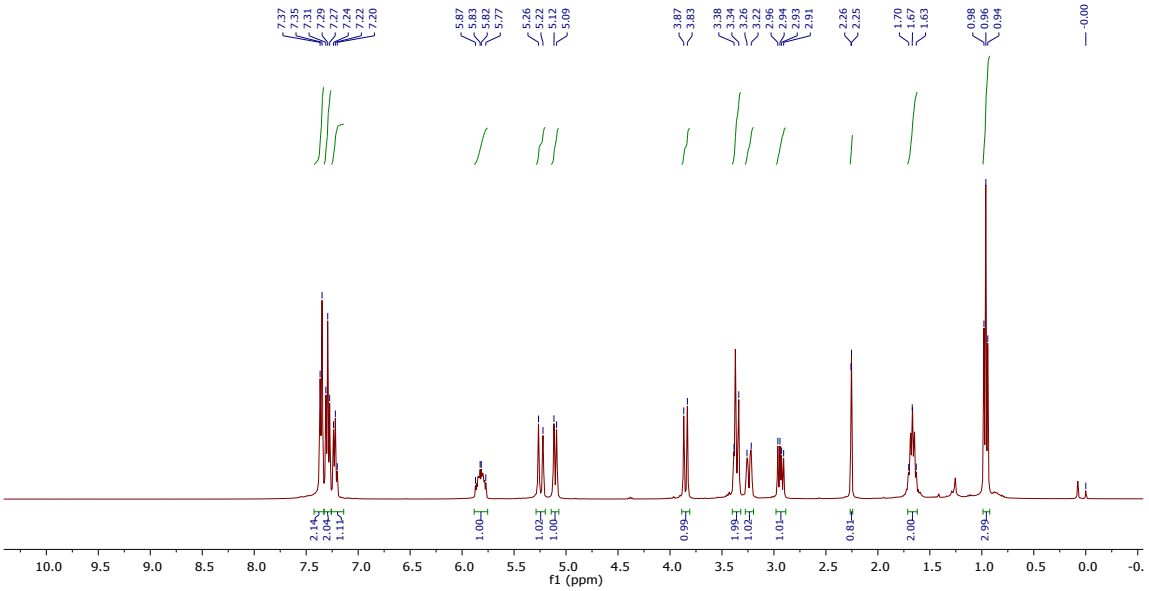
HPLC trace of 3o

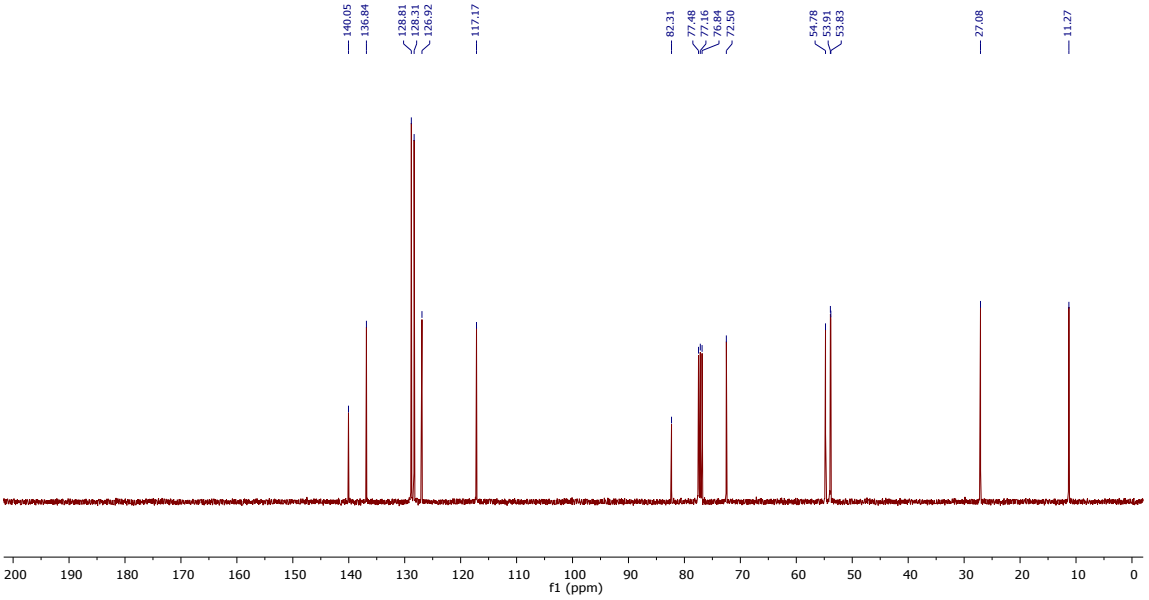


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	21.852	63.721	159.788	93.11	93.91	n.a.
2	23.825	4.716	10.360	6.89	6.09	n.a.

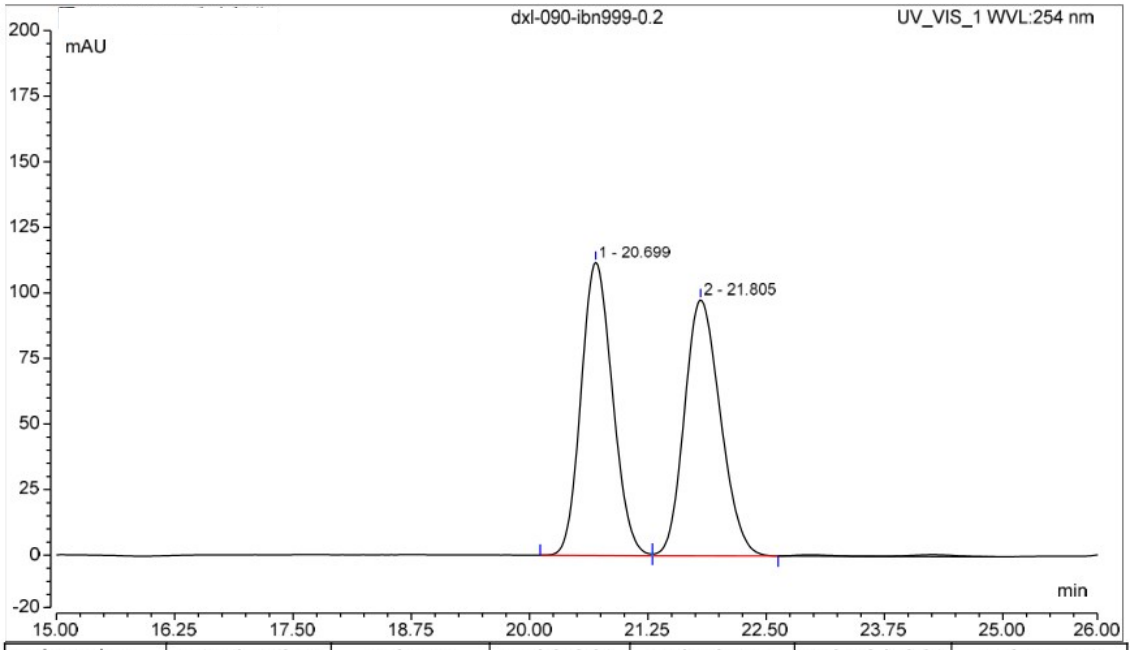

Bn
N

3p


7.37
7.35
7.31
7.29
7.27
7.24
7.22
7.20
5.87
5.83
5.82
5.77
5.26
5.22
5.12
5.09
3.87
3.83
3.38
3.34
3.26
3.22
2.96
2.94
2.93
2.91
2.26
2.25
1.70
1.67
1.63
0.98
0.96
0.94
-0.00
2.14
2.04
1.12
1.00
1.02
1.00
0.99
1.99
1.02
1.01
0.81
2.00
2.99
f1 (ppm)

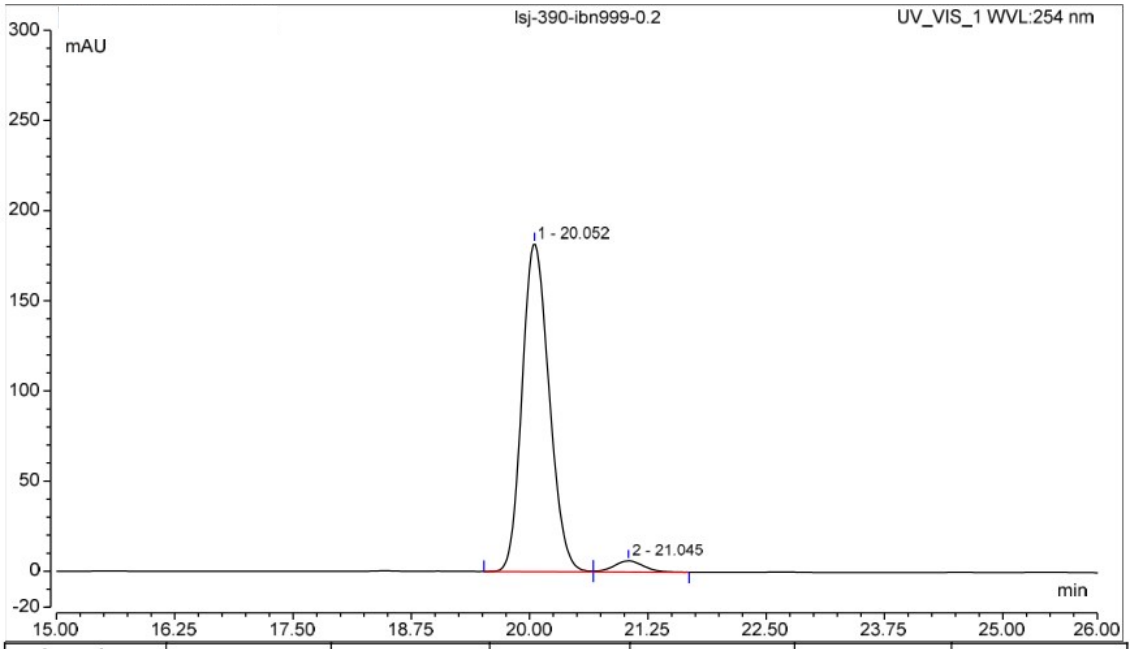

140.05
136.84
128.81
128.31
126.92
117.17
82.31
77.48
77.16
76.84
72.50
54.78
53.91
53.83
27.08
11.27
f1 (ppm)

HPLC trace of *rac*-3p

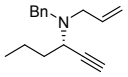


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	20.699	42.980	111.758	49.99	53.40	n.a.
2	21.805	42.994	97.542	50.01	46.60	n.a.

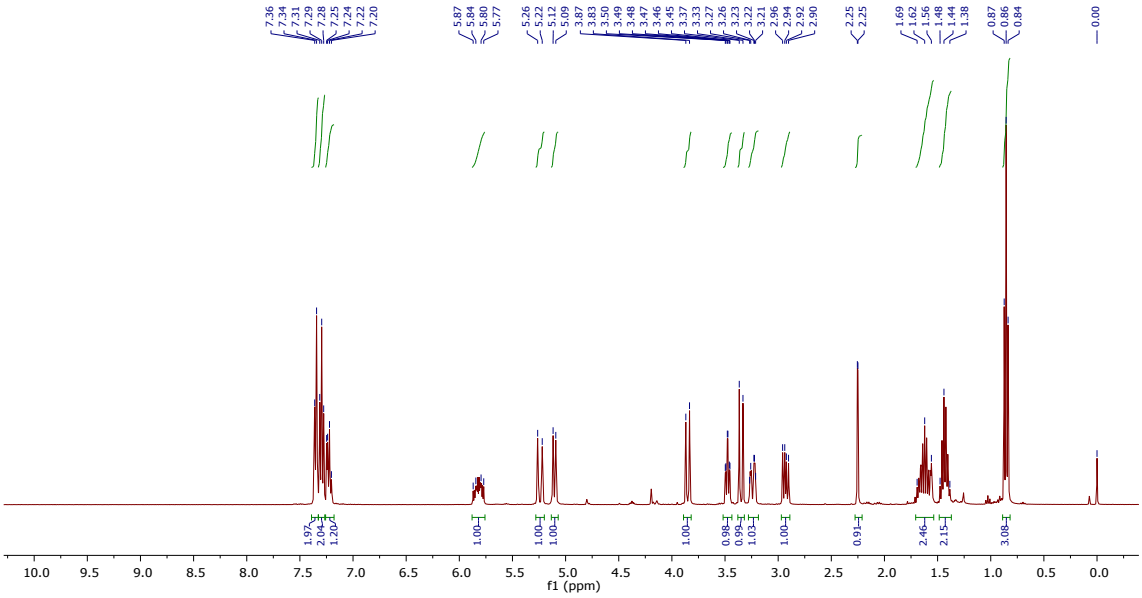
HPLC trace of 3p

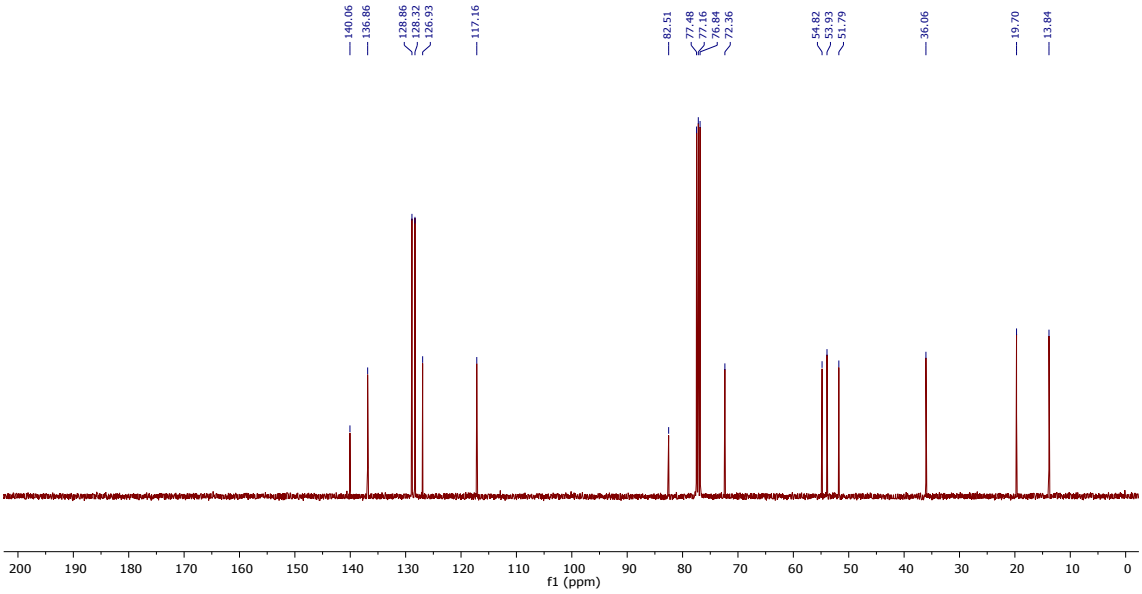


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	20.052	60.161	181.890	96.41	96.72	n.a.
2	21.045	2.241	6.174	3.59	3.28	n.a.

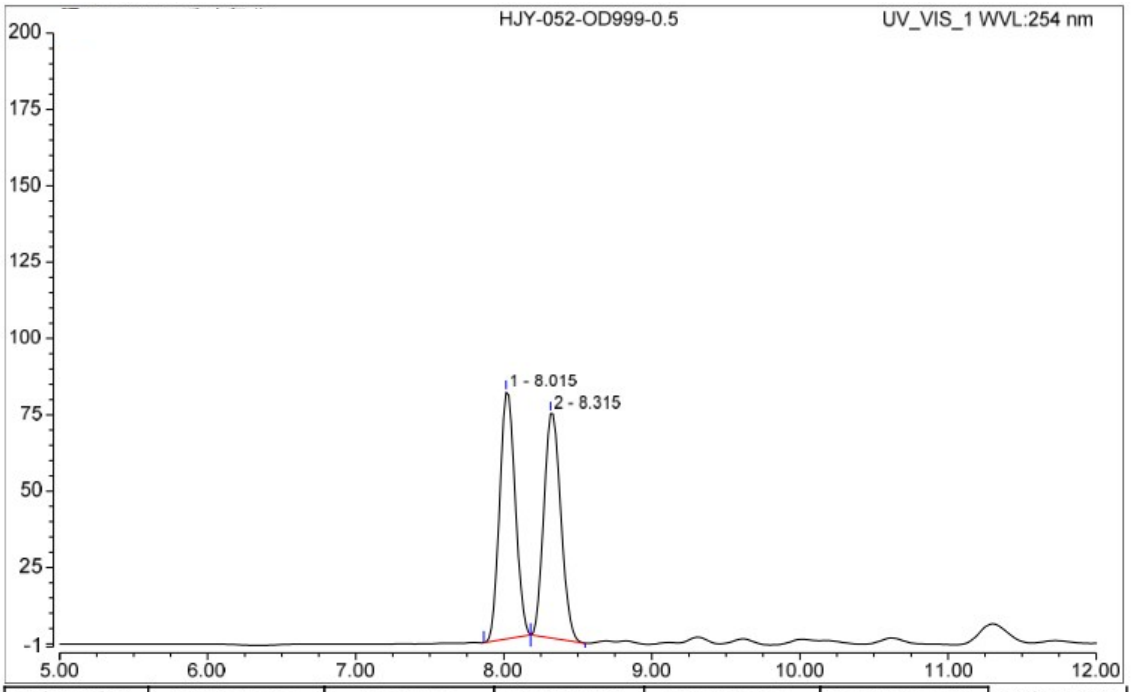

Bn
N

3q


7.36
7.34
7.31
7.29
7.28
7.25
7.24
7.22
7.20
5.87
5.84
5.80
5.77
5.26
5.22
5.12
5.09
3.87
3.83
3.50
3.49
3.48
3.47
3.46
3.45
3.37
3.33
3.27
3.26
3.23
3.22
3.21
2.96
2.94
2.92
2.90
2.25
2.25
1.69
1.62
1.55
1.48
1.44
1.38
0.87
0.86
0.84
0.00
1.97
2.04
1.20
1.00
1.00
1.00
1.00
0.98
0.99
1.03
1.00
0.91
2.46
2.15
3.08
f1 (ppm)

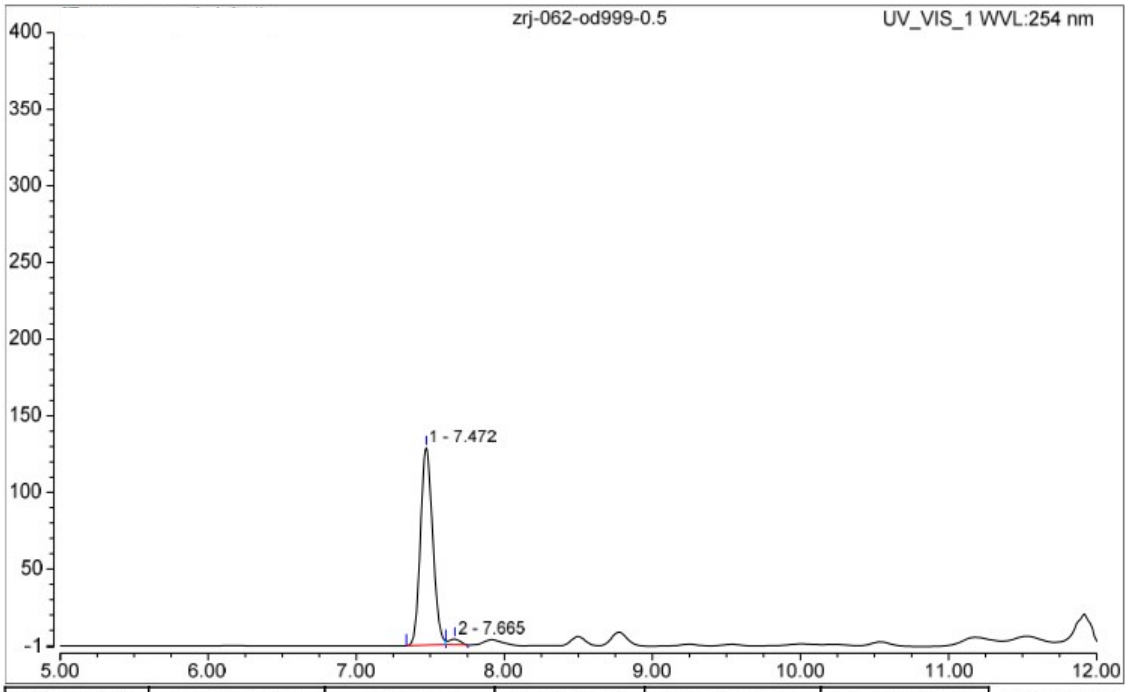

140.06
136.86
128.86
128.32
126.93
117.16
82.51
77.48
77.16
76.84
72.36
54.82
53.93
51.79
36.06
19.70
13.84
f1 (ppm)

HPLC trace of *rac*-3q

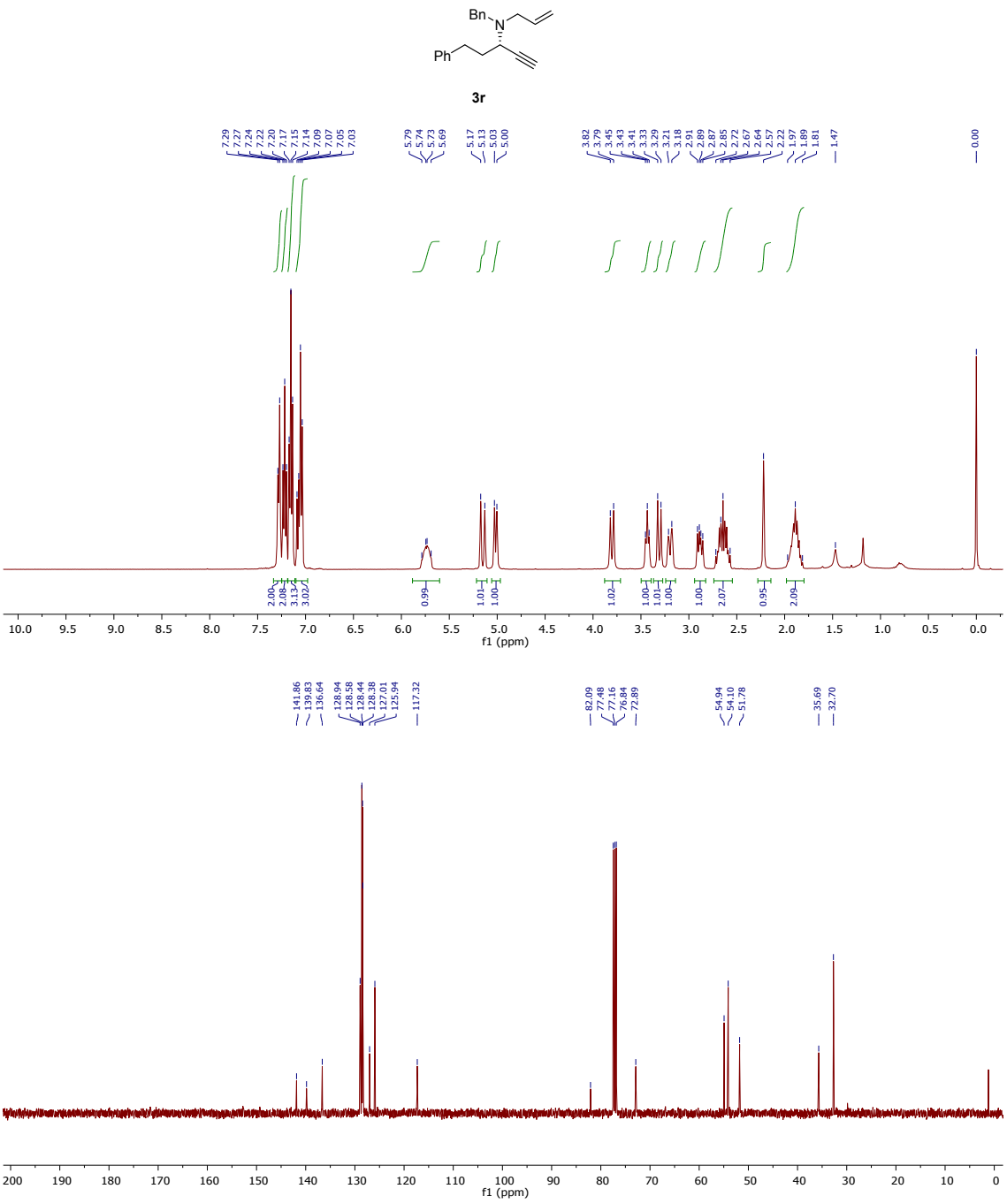


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	8.015	9.853	80.872	50.13	52.38	n.a.
2	8.315	9.804	73.527	49.87	47.62	n.a.

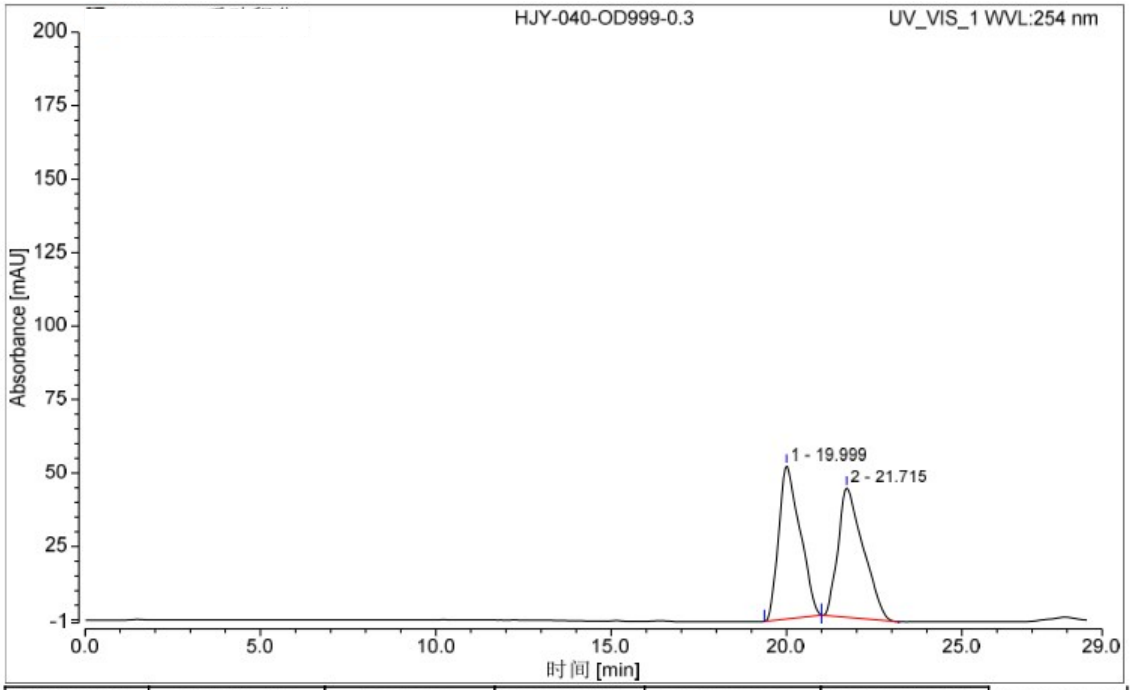
HPLC trace of 3q



peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	7.472	12.375	128.842	97.50	97.28	n.a.
2	7.665	0.317	3.607	2.50	2.72	n.a.

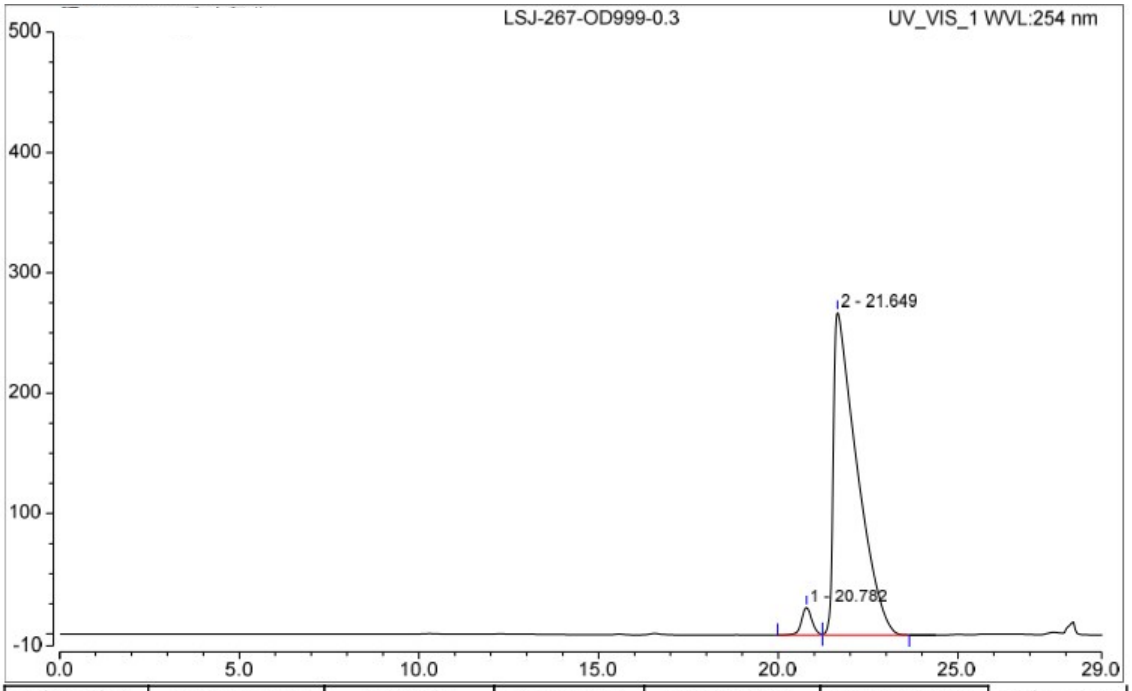

Bn
N
Ph
3r
7.29
7.27
7.24
7.22
7.20
7.17
7.15
7.14
7.09
7.07
7.05
7.03
5.79
5.74
5.73
5.69
5.17
5.13
5.03
5.00
3.82
3.79
3.45
3.43
3.41
3.33
3.29
3.21
3.18
2.91
2.89
2.87
2.85
2.72
2.67
2.64
2.57
2.22
1.97
1.89
1.81
1.47
0.00
2.00
2.08
3.13
3.02
0.99
1.01
1.00
1.02
1.00
1.01
1.05
1.00
2.07
0.95
2.09
f1 (ppm)
141.86
139.83
136.64
128.94
128.58
128.44
128.38
127.01
125.94
117.32
82.09
77.48
77.16
76.84
72.89
54.94
54.10
51.78
35.69
32.70
f1 (ppm)

HPLC trace of *rac*-3r

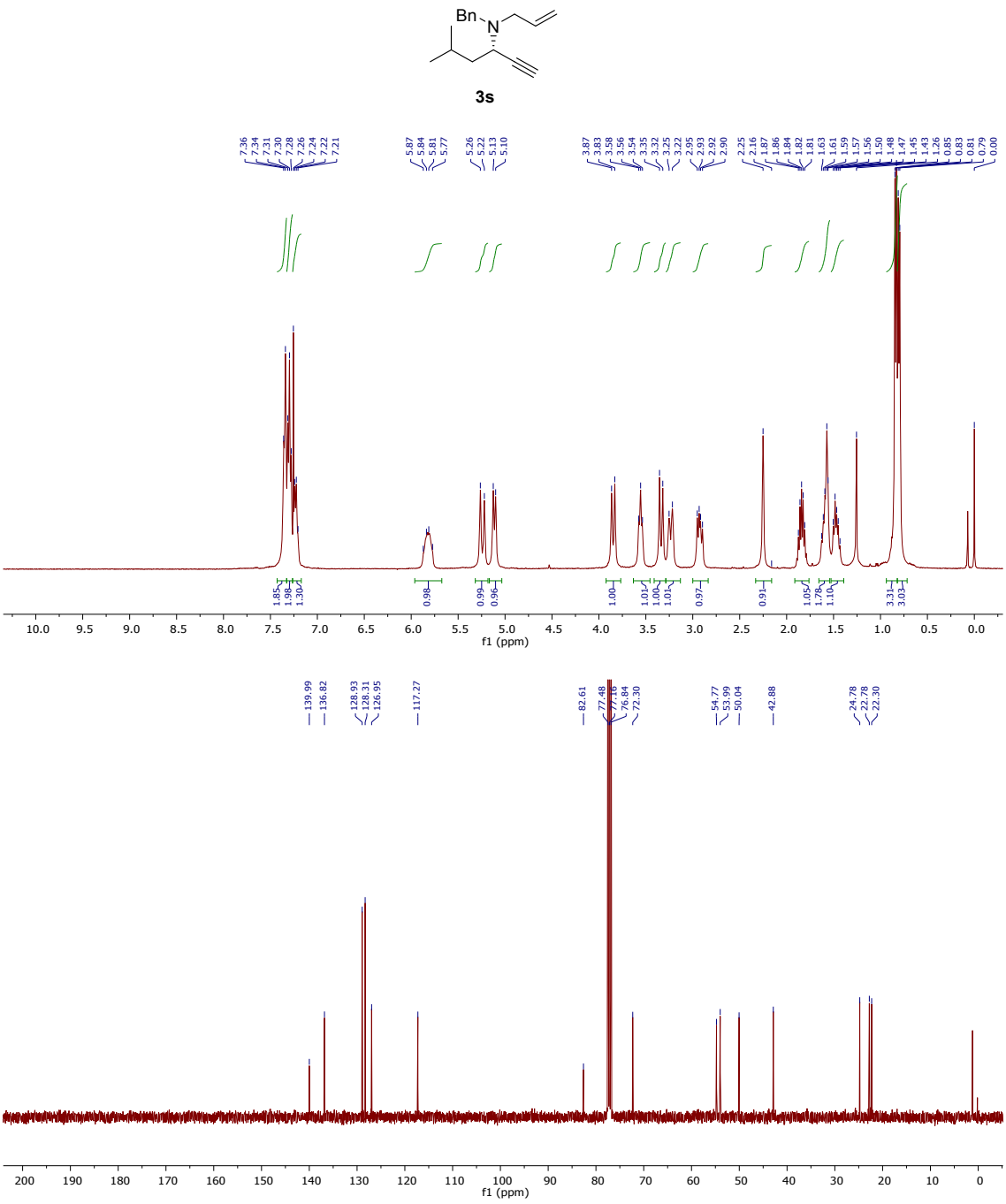


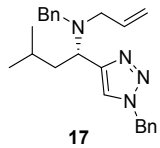
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	19.999	36.775	52.127	50.09	54.23	n.a.
2	21.715	36.644	44.001	49.91	45.77	n.a.

HPLC trace of 3r

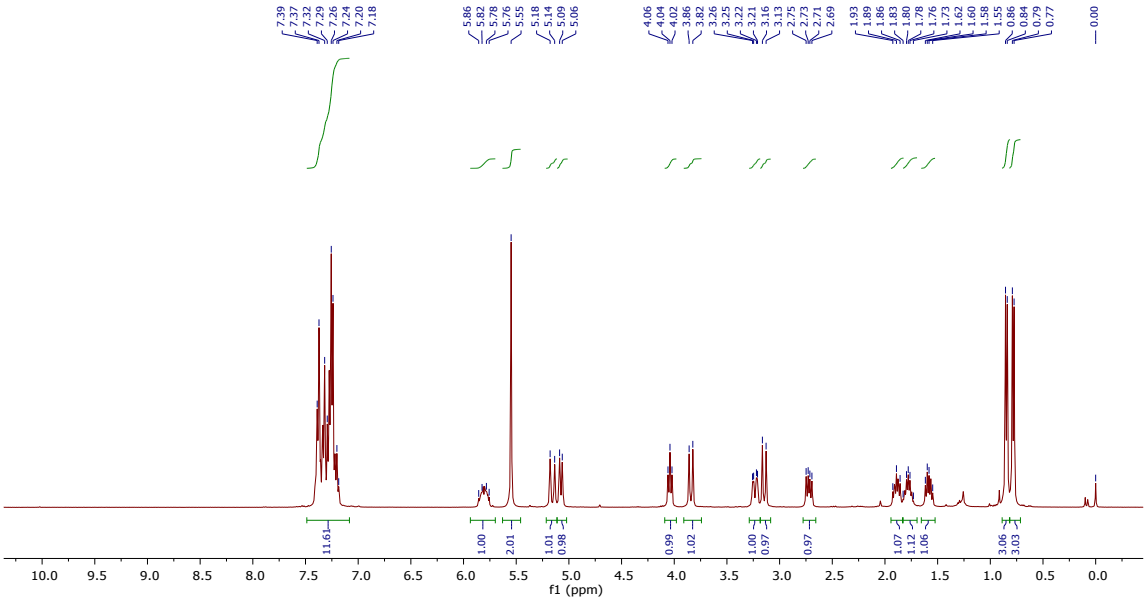


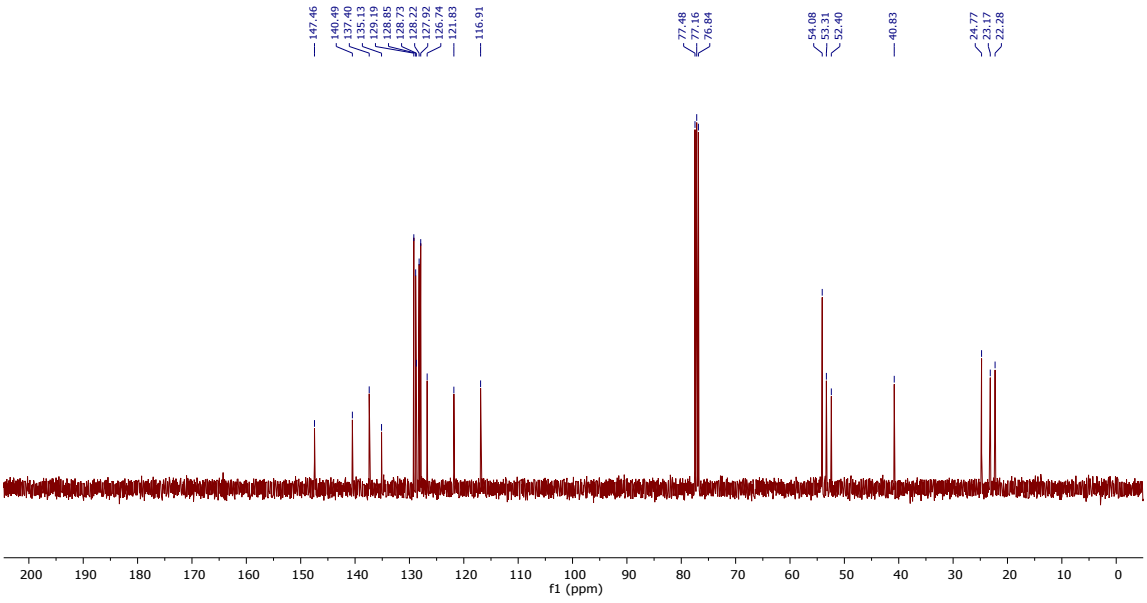
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	20.782	7.929	23.038	3.75	7.90	n.a.
2	21.649	203.405	268.486	96.25	92.10	n.a.


Bn
N
3s
7.36
7.34
7.31
7.30
7.28
7.26
7.24
7.22
7.21
5.87
5.84
5.81
5.77
5.26
5.22
5.13
5.10
3.87
3.83
3.58
3.56
3.54
3.35
3.32
3.25
3.22
2.95
2.93
2.92
2.90
2.25
2.16
1.87
1.86
1.84
1.82
1.81
1.63
1.61
1.59
1.57
1.56
1.55
1.48
1.47
1.45
1.43
1.26
0.85
0.83
0.81
0.79
0.00
1.85
1.98
1.30
0.98
0.99
0.96
1.00
1.01
1.00
1.01
0.97
0.91
1.05
1.78
1.10
3.31
3.03
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)
139.99
136.82
128.93
128.31
126.95
117.27
82.61
77.48
77.16
76.84
72.30
54.77
53.99
50.04
42.88
24.78
22.78
22.30
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

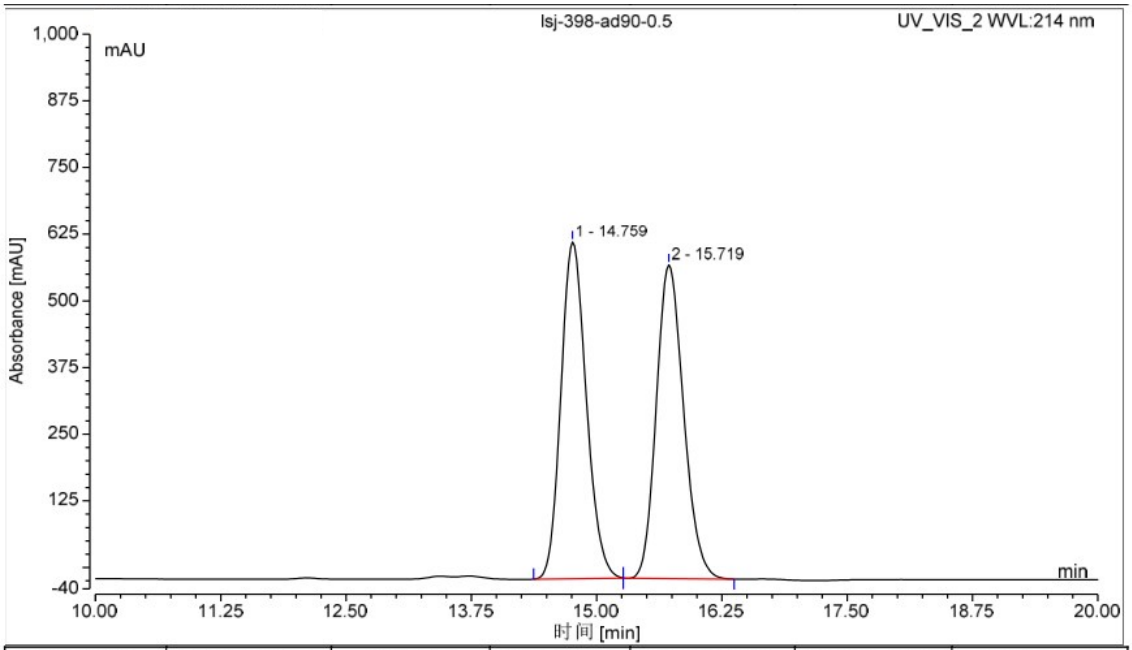

Bn
N
N
N
N
Bn

17


7.39
7.37
7.32
7.29
7.26
7.24
7.20
7.18
5.86
5.82
5.78
5.76
5.55
5.18
5.14
5.09
5.06
4.06
4.04
4.02
3.86
3.82
3.26
3.25
3.22
3.21
3.16
3.13
2.75
2.73
2.71
2.69
1.93
1.89
1.86
1.83
1.80
1.78
1.76
1.73
1.62
1.60
1.58
1.55
0.86
0.84
0.79
0.77
0.00
11.61
1.00
2.01
1.01
0.98
0.99
1.02
1.00
0.97
0.97
1.07
1.12
1.06
3.06
3.03
f1 (ppm)

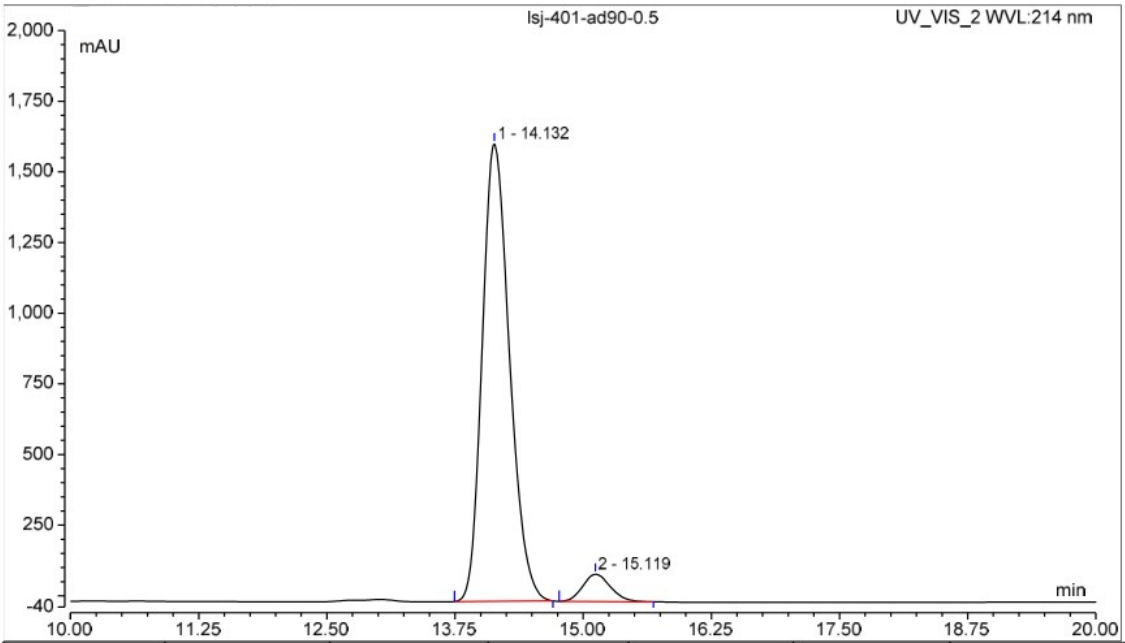

147.46
140.49
137.40
135.13
129.19
128.85
128.73
128.22
127.92
126.74
121.83
116.91
77.48
77.16
76.84
54.08
53.31
52.40
40.83
24.77
23.17
22.28
f1 (ppm)

HPLC trace of *rac*-17

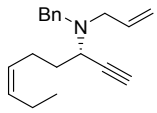


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	14.759	185.080	631.641	49.99	51.78	n.a.
2	15.719	185.169	588.239	50.01	48.22	n.a.

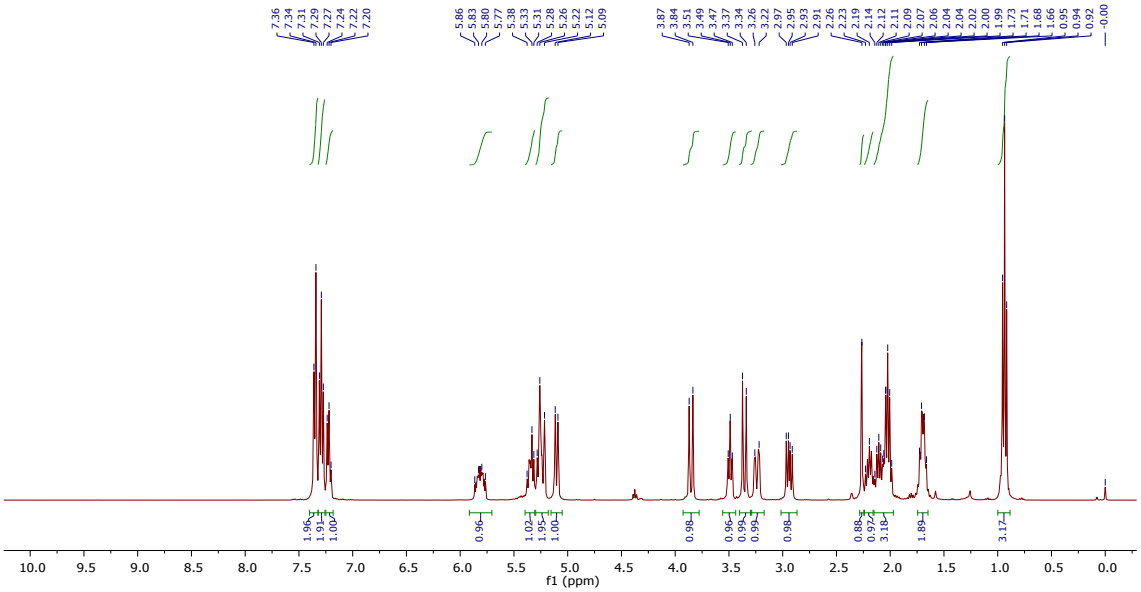
HPLC trace of 17

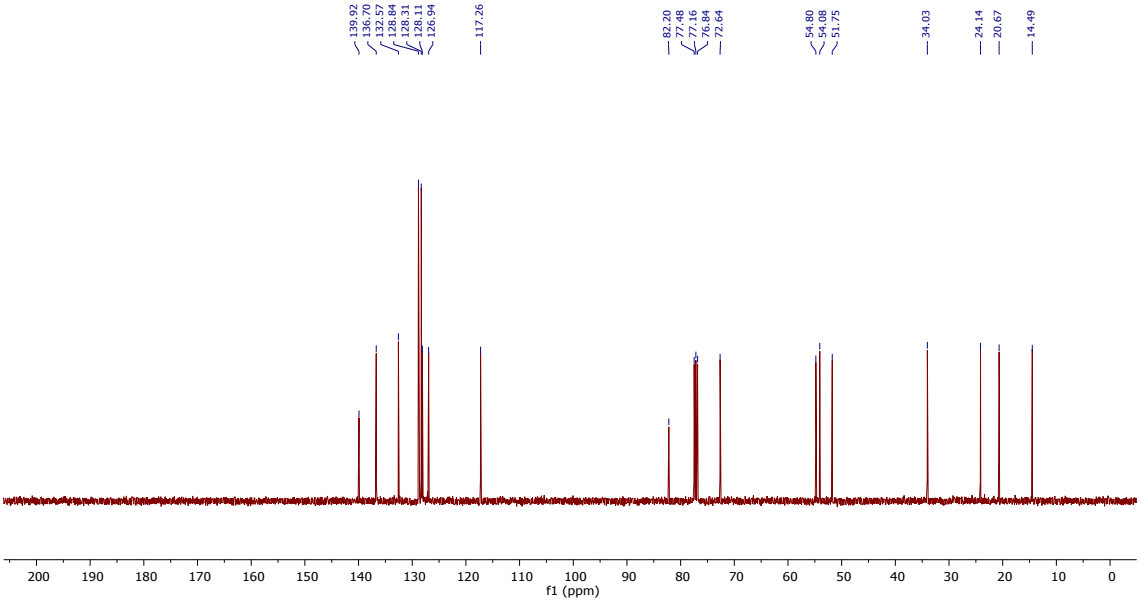


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	14.132	499.203	1618.258	94.28	94.37	n.a.
2	15.119	30.290	96.536	5.72	5.63	n.a.

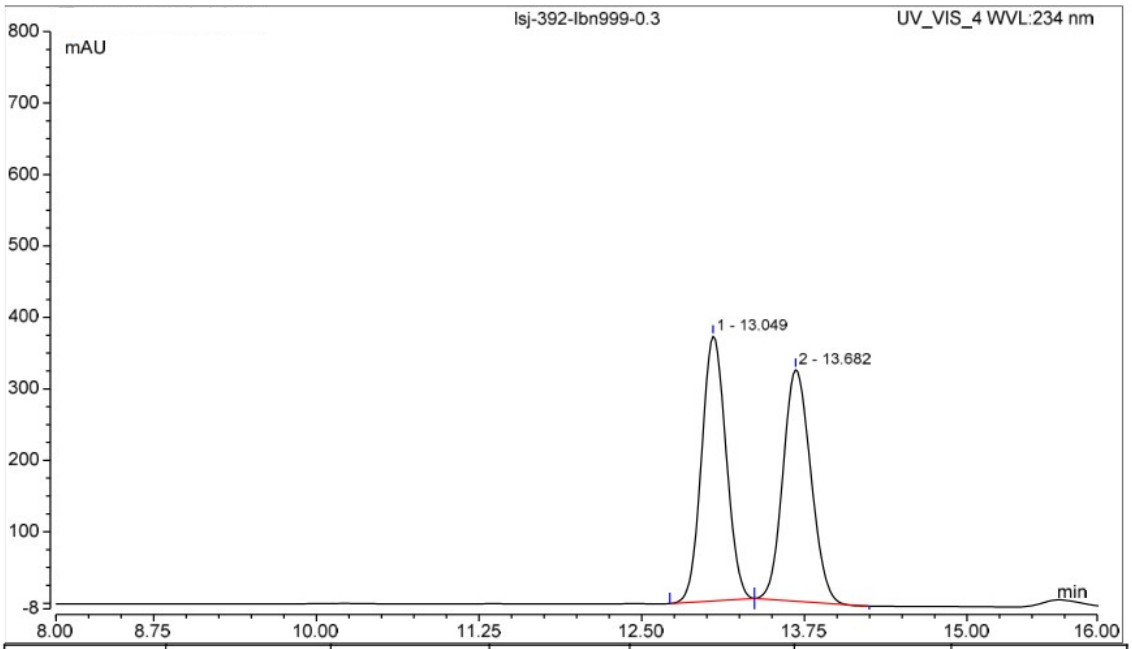

Bn
N

3t


7.36 7.34 7.31 7.29 7.27 7.24 7.22 7.20
5.86 5.83 5.80 5.77 5.38 5.33 5.31 5.28 5.26 5.22 5.12 5.09
3.87 3.84 3.51 3.49 3.47 3.37 3.34 3.26 3.22 2.97 2.95 2.93 2.91 2.26 2.23 2.19 2.14 2.12 2.11 2.09 2.07 2.06 2.04 2.04 2.02 2.00 1.99 1.73 1.71 1.68 1.66 0.95 0.94 0.92 -0.00
1.96 1.91 1.00 0.96 1.02 1.95 1.00 0.98 0.96 0.95 0.95 0.98 0.88 0.97 3.18 1.89 3.17
f1 (ppm)

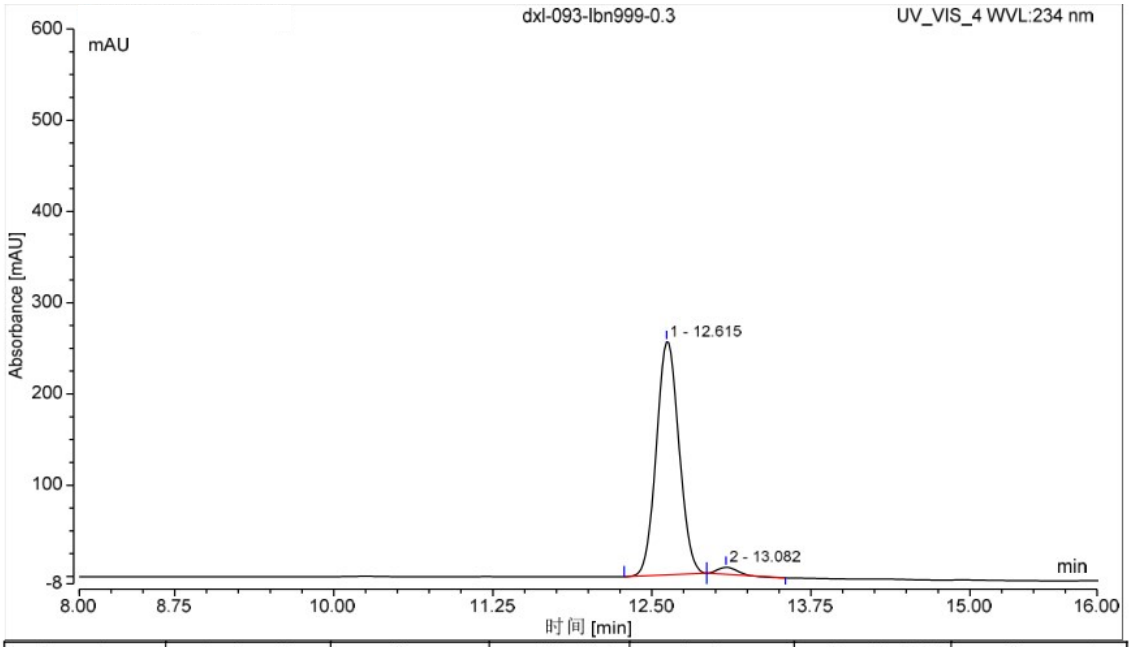

139.92 136.70 135.57 128.84 128.31 128.11 126.94 117.26 82.20 77.48 77.16 76.84 72.64 54.80 54.08 51.75 34.03 24.14 20.67 14.49
f1 (ppm)

HPLC trace of *rac*-3t

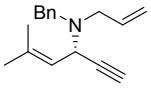


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	13.049	80.837	370.648	50.21	53.35	n.a.
2	13.682	80.168	324.087	49.79	46.65	n.a.

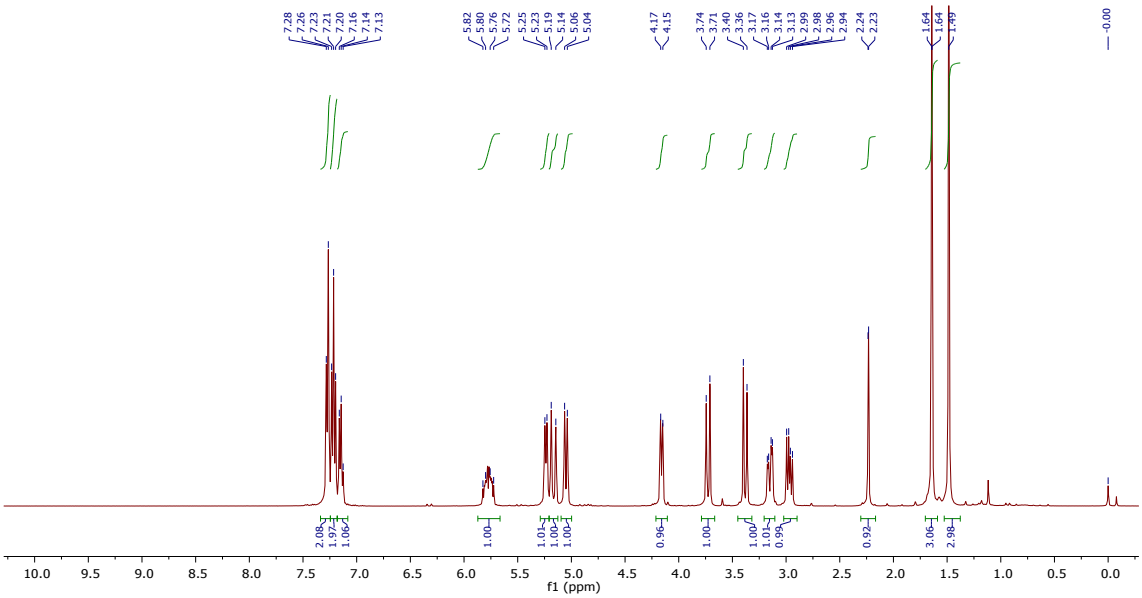
HPLC trace of 3t

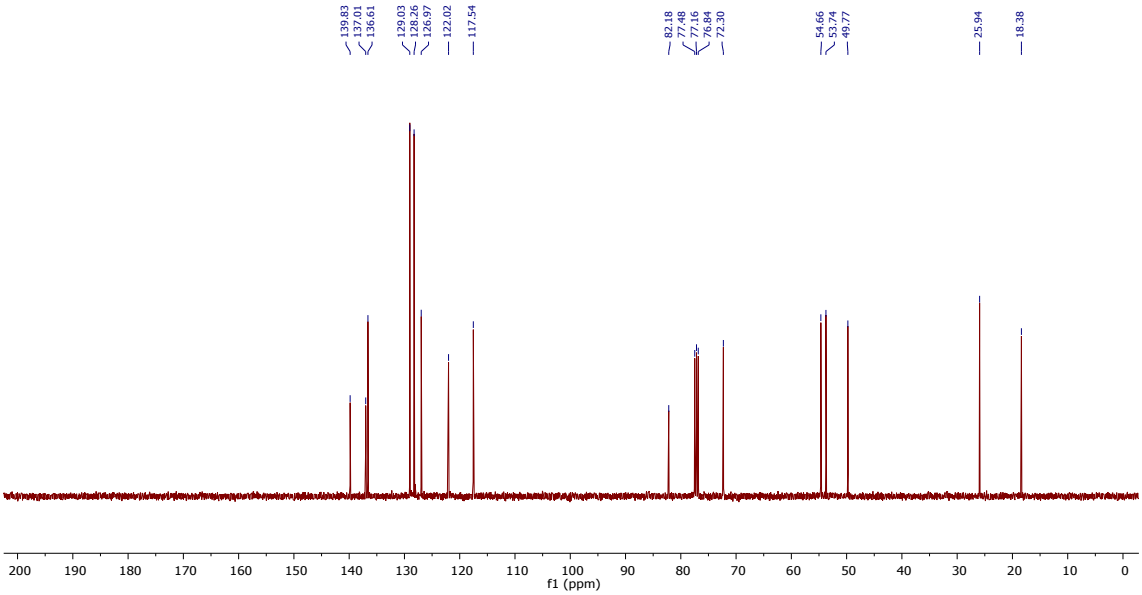


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	12.615	52.770	255.512	97.58	97.12	n.a.
2	13.082	1.306	7.584	2.42	2.88	n.a.

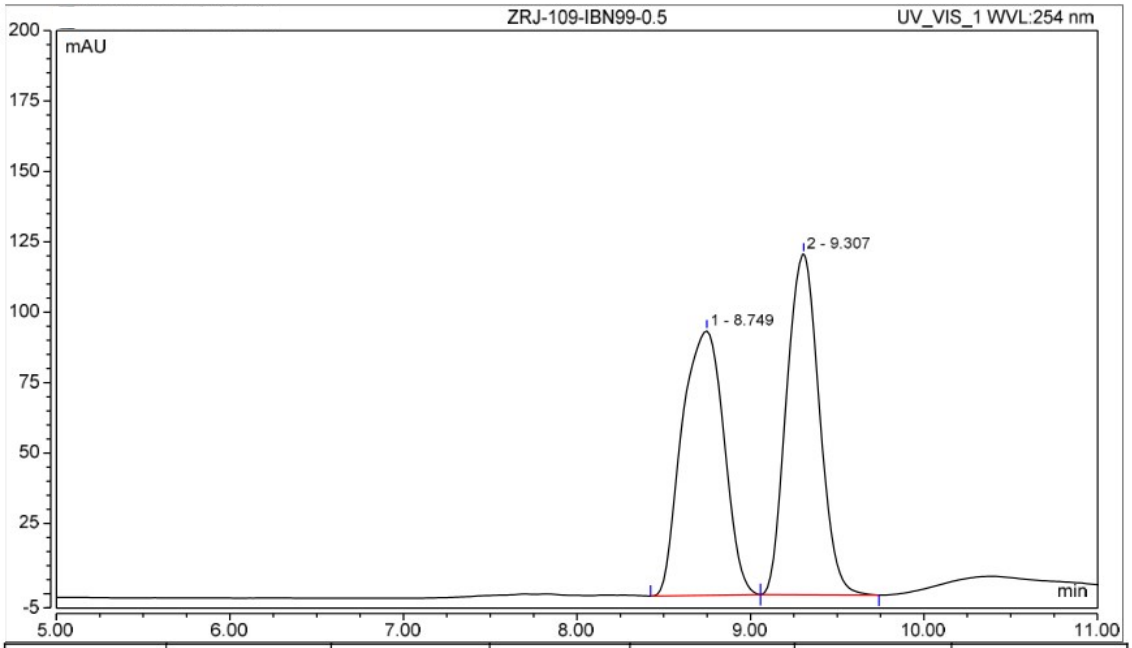

Bn
N

3u


7.28
7.26
7.23
7.21
7.20
7.16
7.14
7.13
5.82
5.80
5.76
5.72
5.25
5.23
5.19
5.14
5.06
5.04
4.17
4.15
3.74
3.71
3.40
3.36
3.17
3.16
3.14
3.13
2.99
2.98
2.96
2.94
2.24
2.23
1.64
1.64
1.49
-0.00
2.08
1.97
1.06
1.00
1.01
1.00
1.00
0.96
1.00
1.00
1.01
0.99
0.92
3.06
2.98
f1 (ppm)

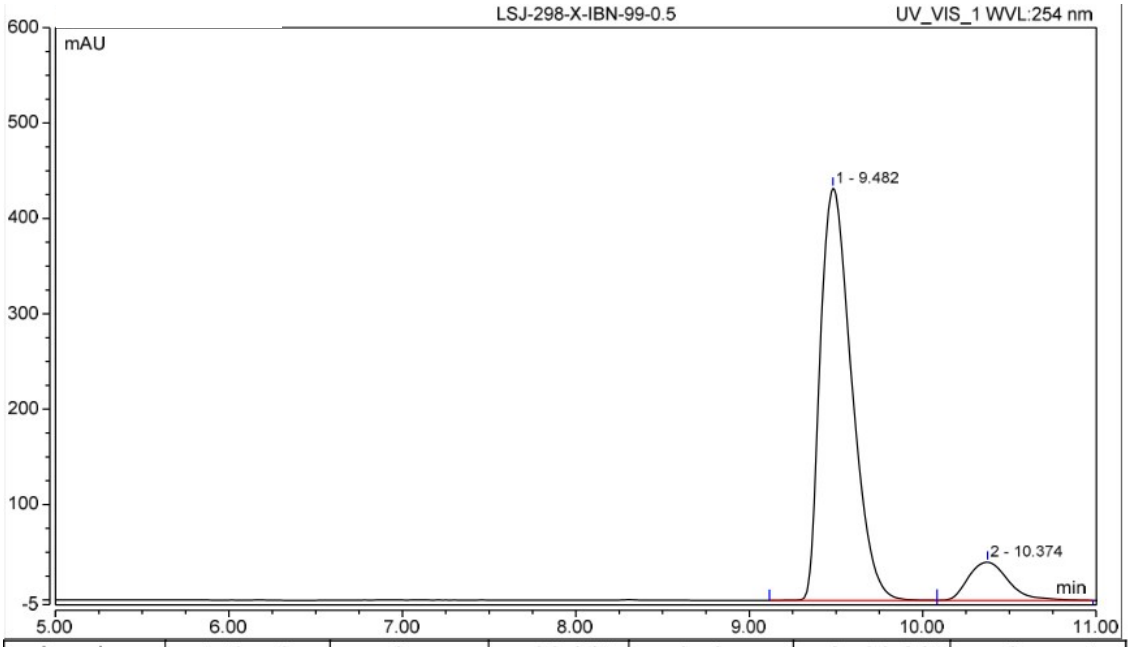

139.83
137.01
136.61
129.03
128.26
126.97
122.02
117.54
82.18
77.48
77.16
76.84
72.30
54.66
53.74
49.77
25.94
18.38
f1 (ppm)

HPLC trace of *rac*-3u

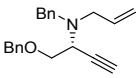


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	8.749	26.306	93.874	49.90	43.69	n.a.
2	9.307	26.411	120.970	50.10	56.31	n.a.

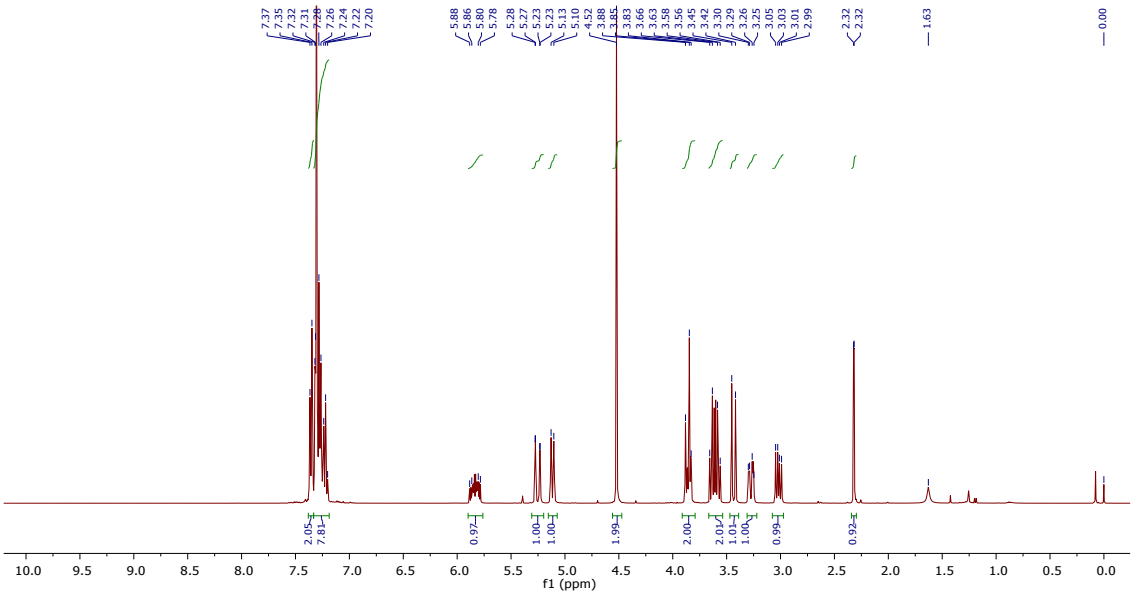
HPLC trace of 3u

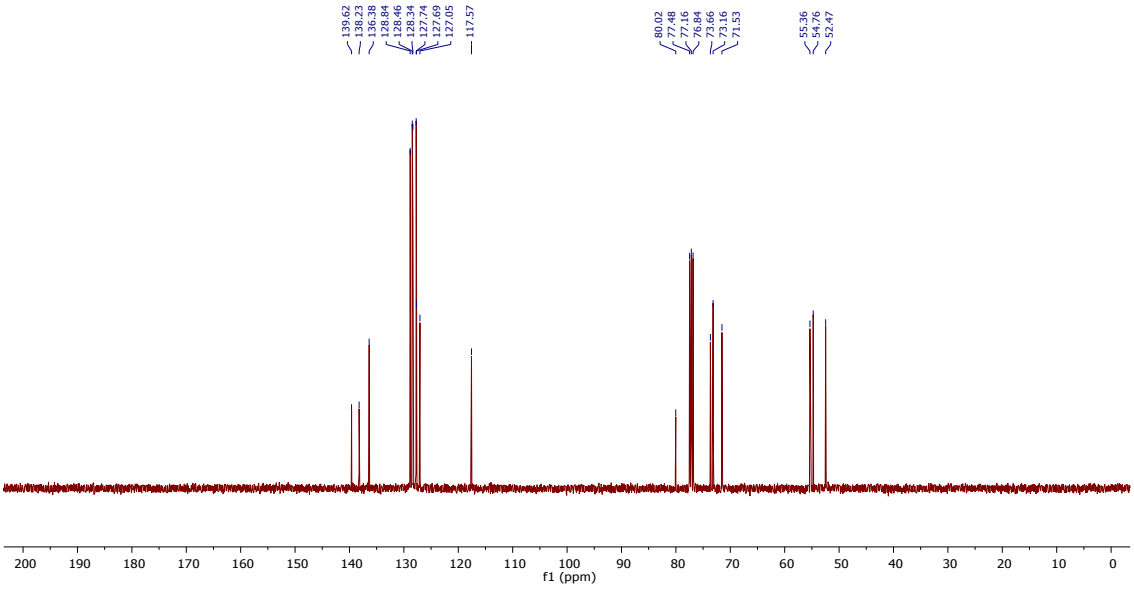


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	9.482	90.609	431.973	89.40	91.53	n.a.
2	10.374	10.748	39.998	10.60	8.47	n.a.

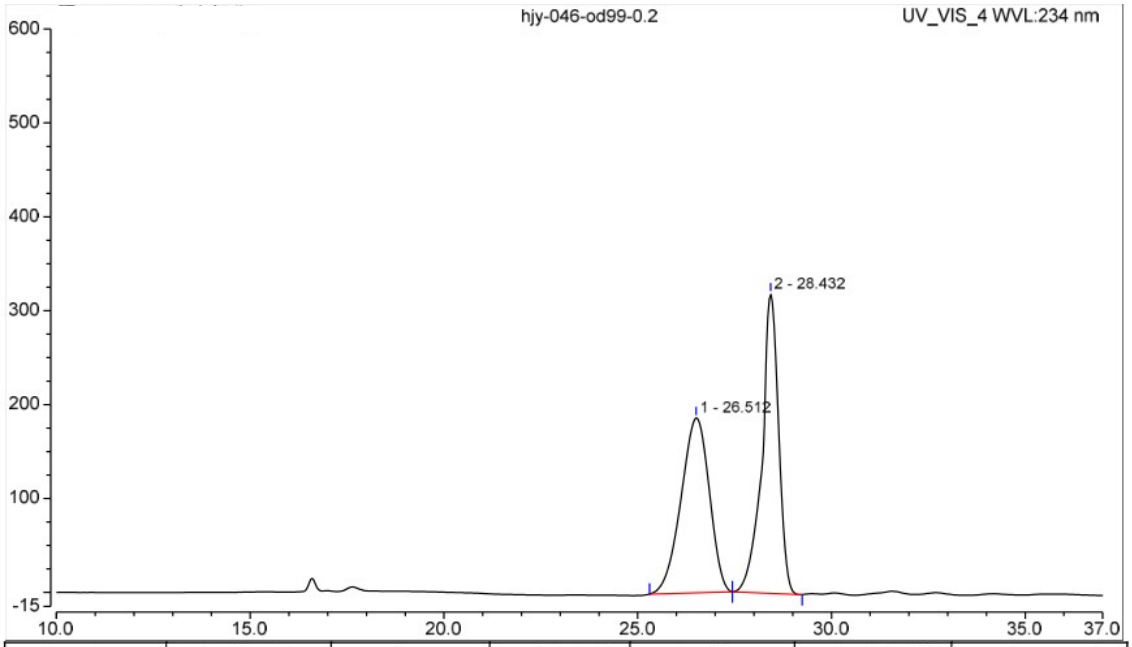

Bn
N
BnO

3v


7.37
7.35
7.32
7.31
7.28
7.26
7.24
7.22
7.20
5.88
5.86
5.80
5.78
5.28
5.27
5.23
5.23
5.13
5.10
4.52
3.88
3.85
3.83
3.66
3.63
3.58
3.56
3.45
3.42
3.30
3.29
3.26
3.25
3.05
3.03
3.01
2.99
2.32
2.32
1.63
0.00
2.05
7.81
0.97
1.00
1.00
1.99
2.00
2.01
1.01
1.00
0.99
0.92
f1 (ppm)

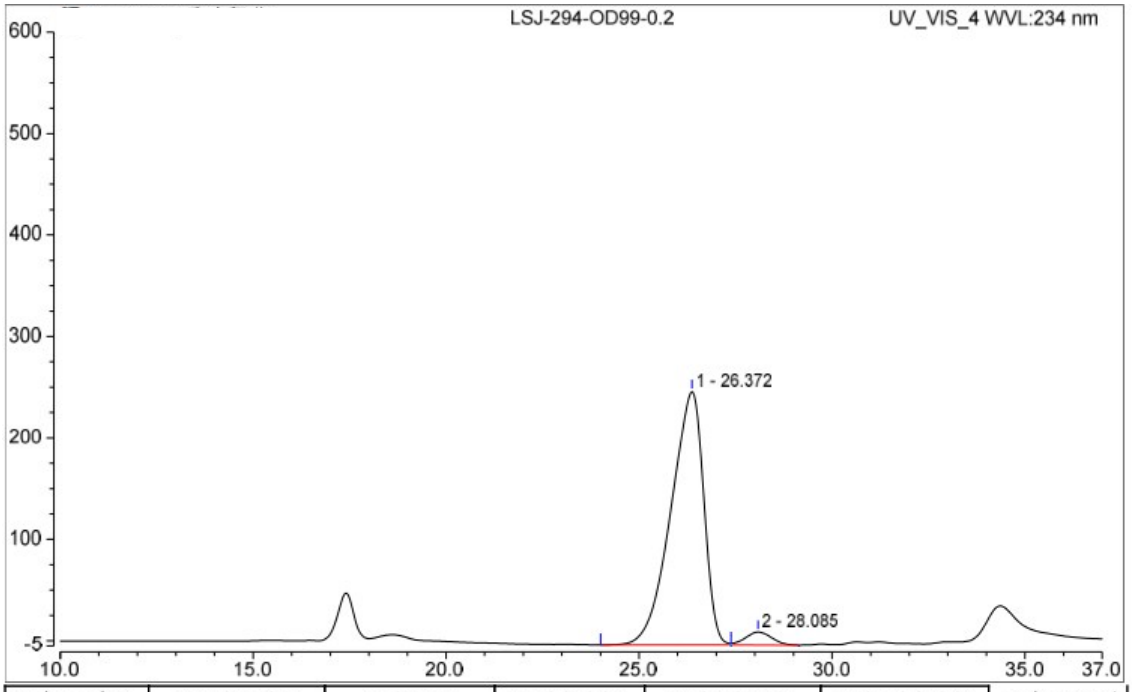

139.62
138.23
136.38
128.84
128.46
128.34
127.74
127.69
127.05
117.57
80.02
77.48
77.16
76.84
73.66
73.16
71.53
55.36
54.76
52.47
f1 (ppm)

HPLC trace of *rac*-3v

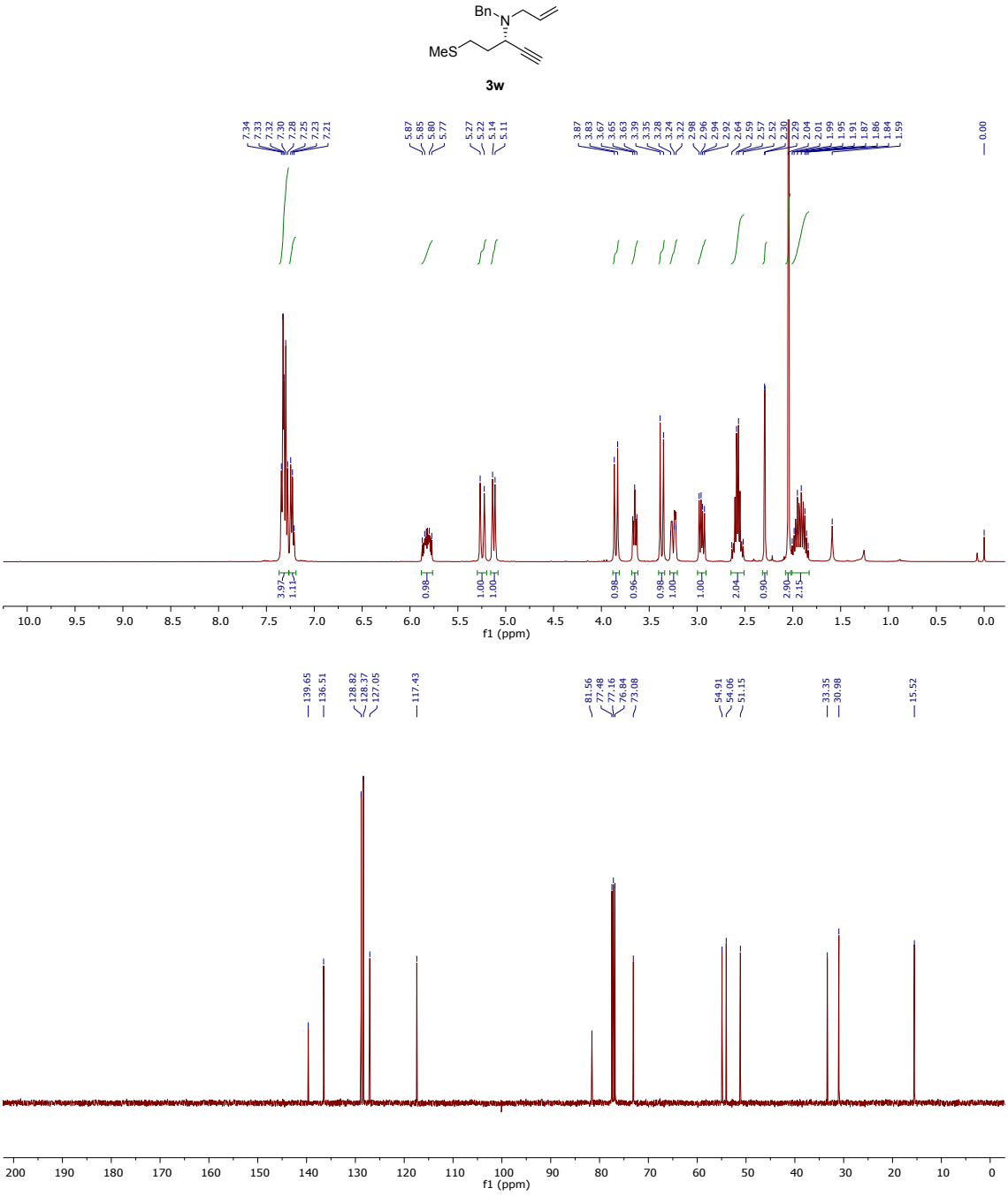


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	26.512	157.661	186.408	49.86	36.90	n.a.
2	28.432	158.531	318.797	50.14	63.10	n.a.

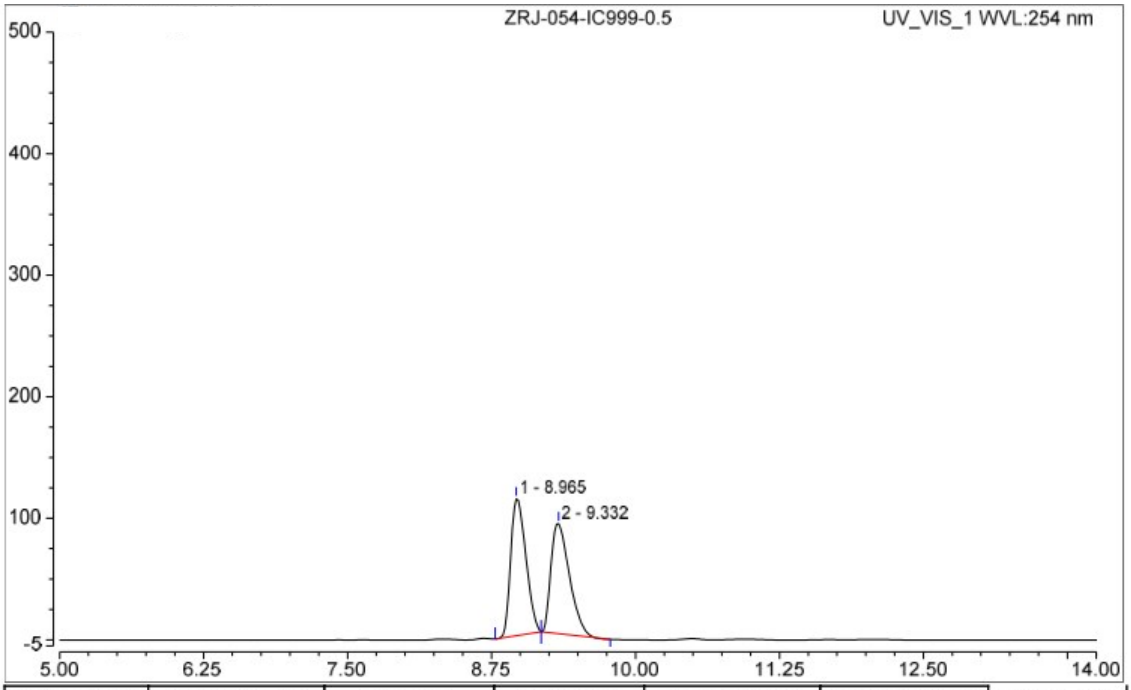
HPLC trace of 3v



peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	26.372	246.726	250.051	96.06	95.11	n.a.
2	28.085	10.111	12.849	3.94	4.89	n.a.

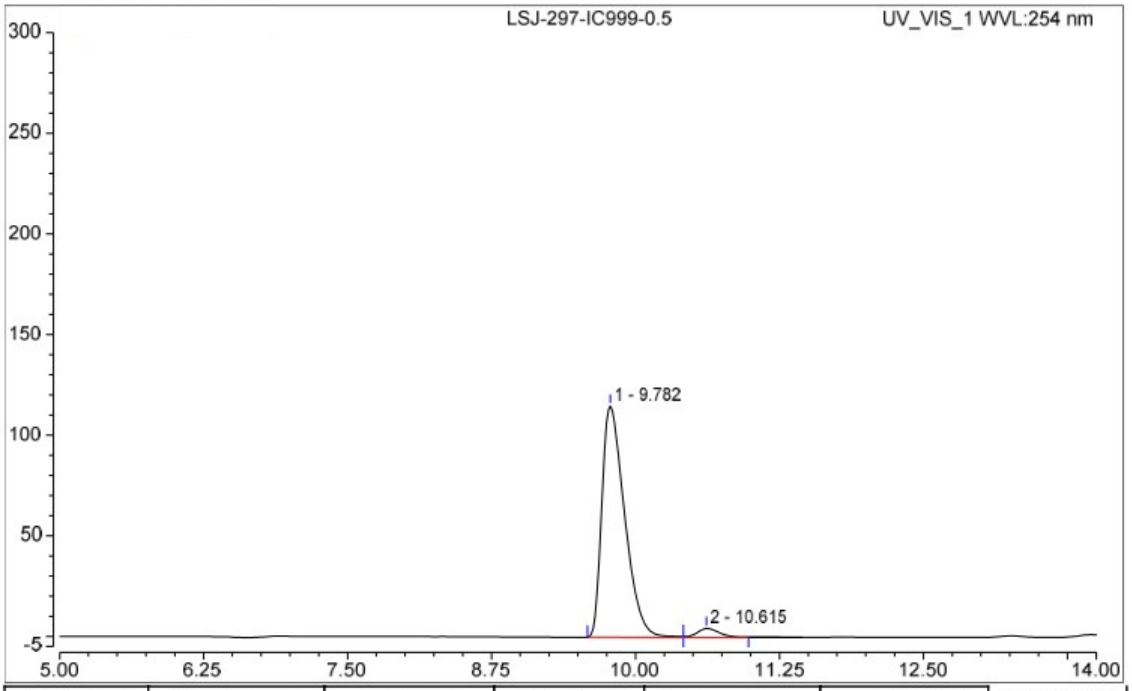

Bn
N
MeS
3w
7.34 7.33 7.32 7.30 7.28 7.25 7.23 7.21
5.87 5.85 5.80 5.77
5.27 5.22 5.14 5.11
3.87 3.83 3.67 3.65 3.63 3.39 3.35 3.28 3.24 3.22 2.98 2.96 2.94 2.92 2.64 2.59 2.57 2.52 2.30 2.29 2.04 2.01 1.99 1.95 1.91 1.87 1.86 1.84 1.59
0.00
3.97 1.11 0.98 1.00 1.00 0.98 0.96 0.98 1.00 1.00 2.04 0.90 2.90 2.15
f1 (ppm)
139.65 136.51 128.82 128.37 127.05 117.43 81.56 77.48 77.16 76.84 73.08 54.91 54.06 51.15 33.35 30.98 15.52
f1 (ppm)

HPLC trace of *rac*-3w

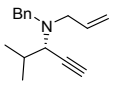


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	8.965	17.233	112.842	50.56	55.48	n.a.
2	9.332	16.853	90.537	49.44	44.52	n.a.

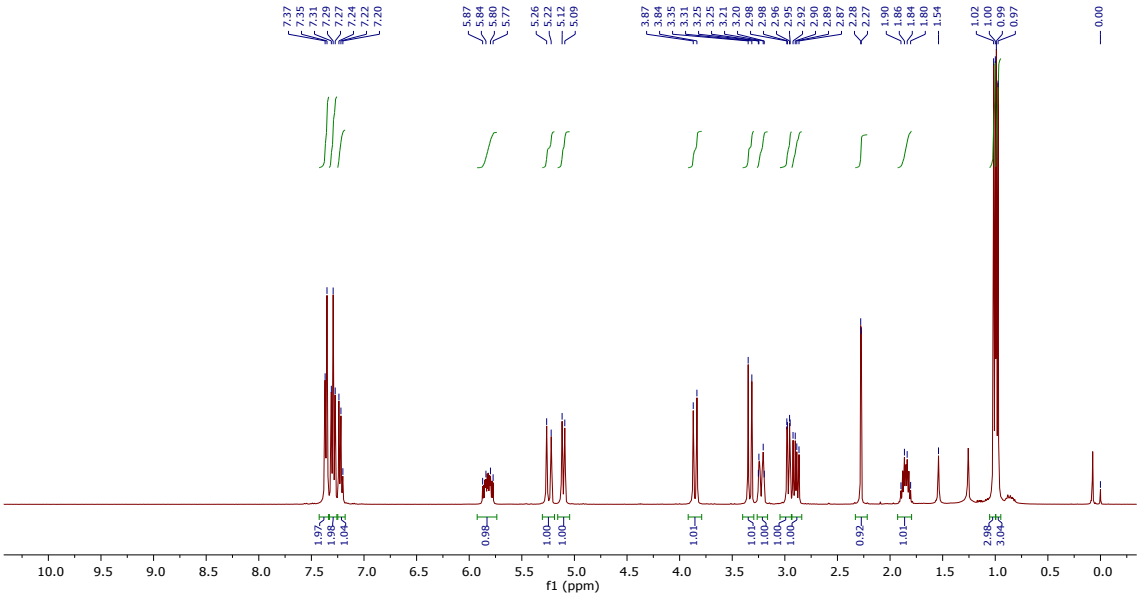
HPLC trace of 3w

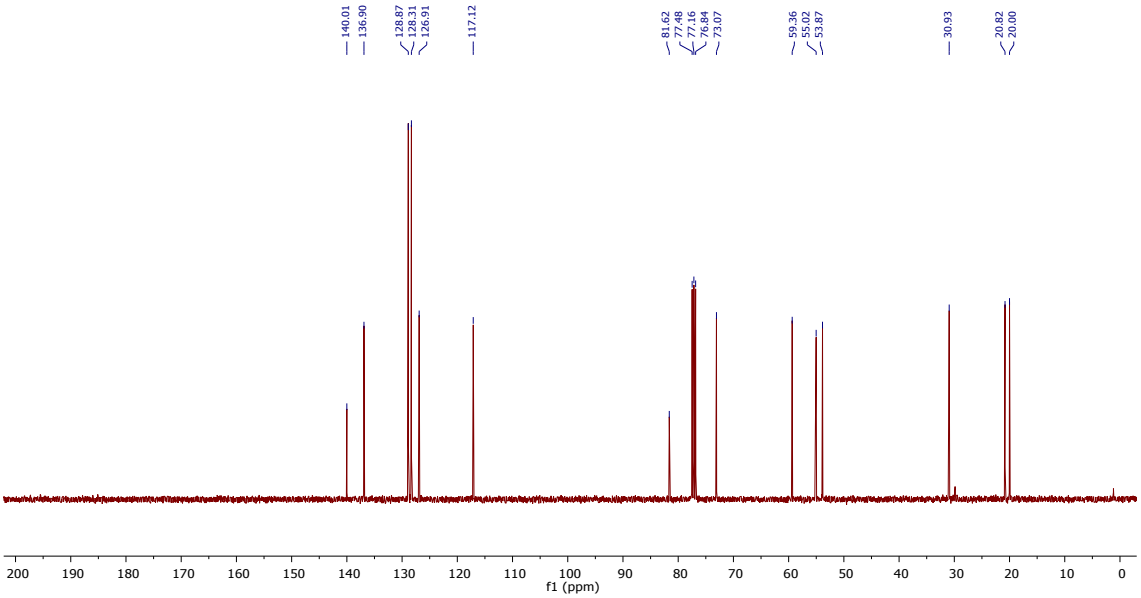


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	9.782	26.268	114.821	96.44	96.34	n.a.
2	10.615	0.968	4.368	3.56	3.66	n.a.

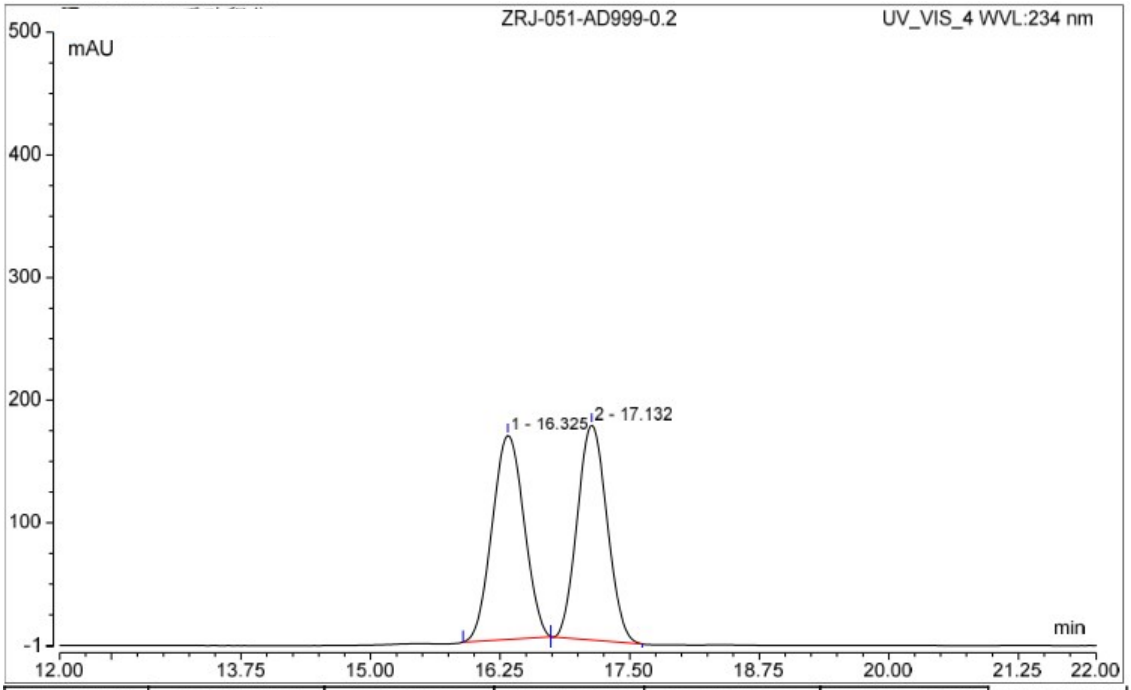

Bn
N

3x


7.37
7.35
7.31
7.29
7.27
7.24
7.22
7.20
5.87
5.84
5.80
5.77
5.26
5.22
5.12
5.09
3.87
3.84
3.35
3.31
3.25
3.25
3.21
3.20
2.98
2.98
2.96
2.95
2.92
2.90
2.89
2.87
2.28
2.27
1.90
1.86
1.84
1.80
1.54
1.02
1.00
0.99
0.97
0.00
1.97
1.98
1.04
0.98
1.00
1.00
1.01
1.01
1.00
1.00
0.92
1.01
2.98
3.04
f1 (ppm)

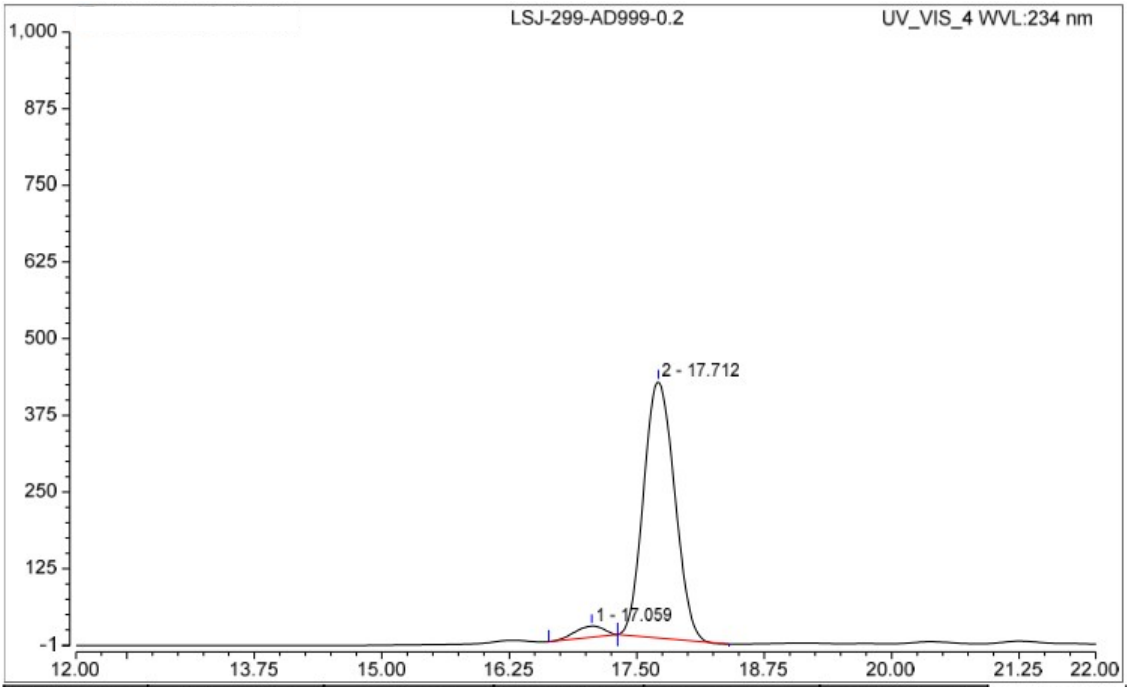

140.01
136.90
128.87
128.31
126.91
117.12
81.62
77.48
77.16
76.84
73.07
59.36
55.02
53.87
30.93
20.82
20.00
f1 (ppm)

HPLC trace of *rac*-3x

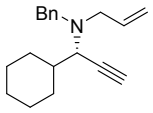


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	16.325	59.391	166.389	50.44	48.69	n.a.
2	17.132	58.349	175.324	49.56	51.31	n.a.

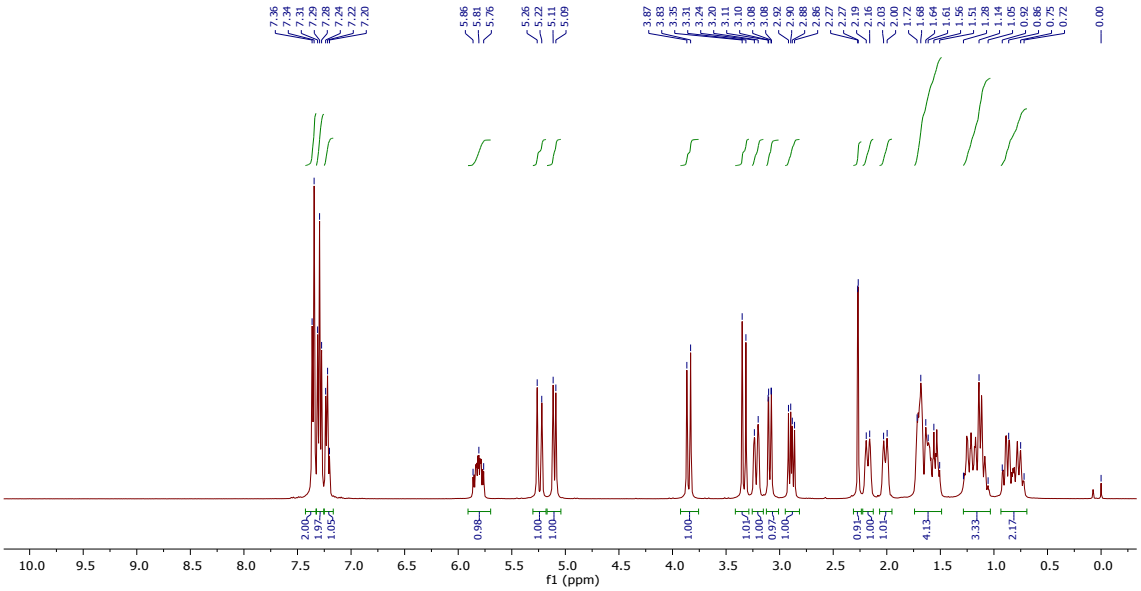
HPLC trace of 3x

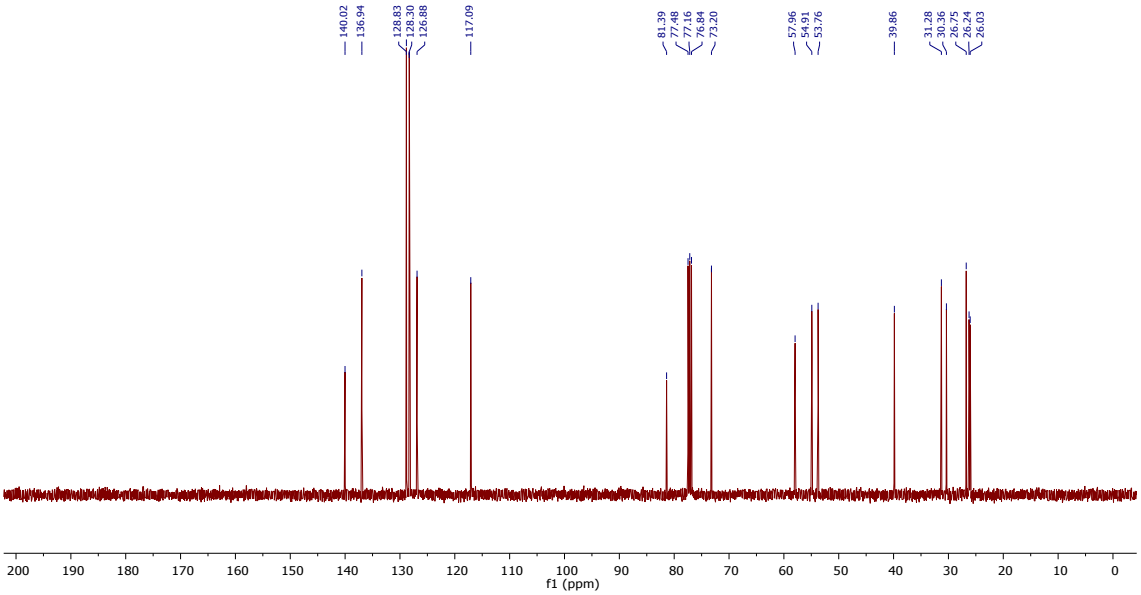


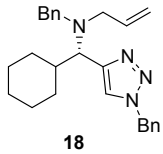
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	17.059	5.967	17.964	3.89	4.12	n.a.
2	17.712	147.272	417.868	96.11	95.88	n.a.


Bn
N

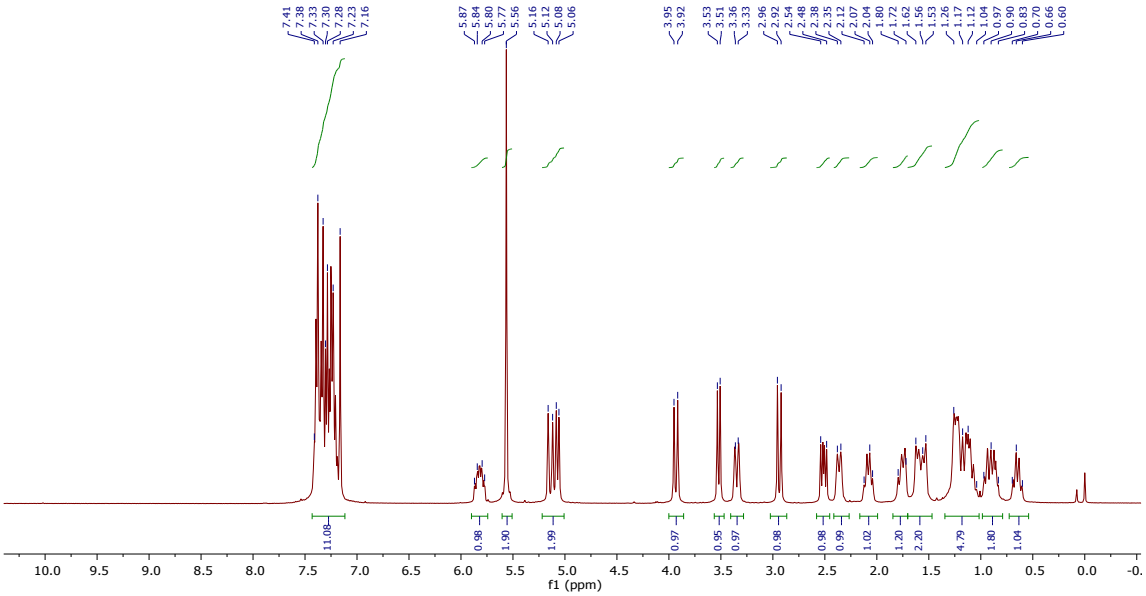
3y

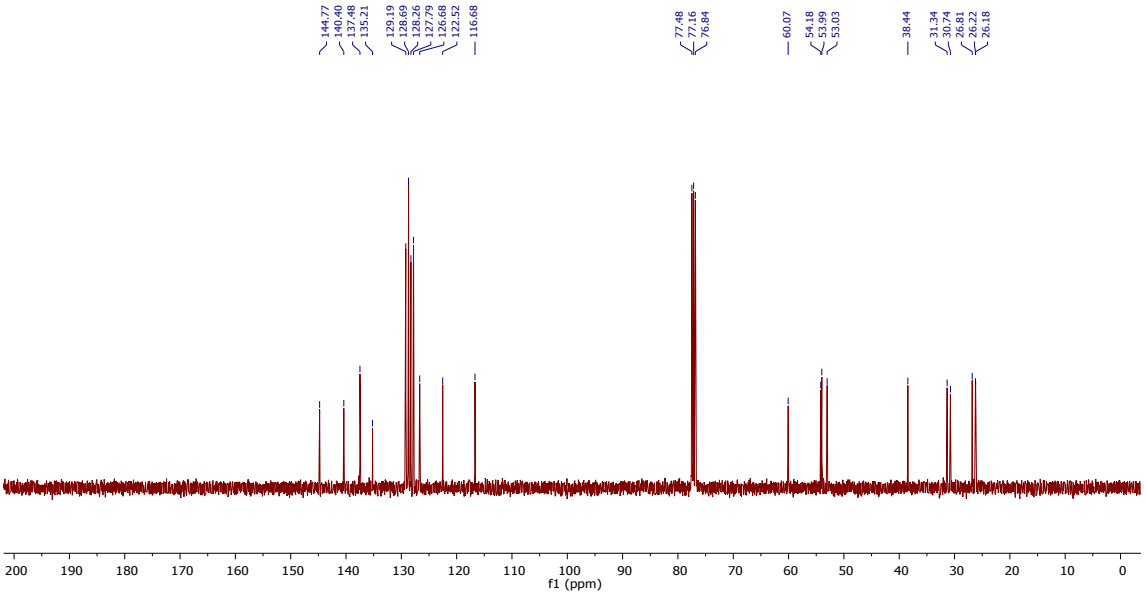

7.36
7.34
7.31
7.29
7.28
7.24
7.22
7.20
5.86
5.81
5.76
5.26
5.22
5.11
5.09
3.87
3.83
3.35
3.31
3.24
3.20
3.11
3.10
3.08
3.08
2.92
2.90
2.88
2.86
2.27
2.19
2.16
2.03
2.00
1.72
1.68
1.64
1.61
1.56
1.51
1.28
1.14
1.05
0.92
0.86
0.75
0.72
0.00
2.00
1.97
1.05
0.98
1.00
1.00
1.00
1.02
1.00
0.97
1.00
0.91
1.00
1.01
4.13
3.33
2.17
f1 (ppm)


140.02
136.94
128.83
128.30
126.88
117.09
81.39
77.48
77.16
76.84
73.20
57.96
54.91
53.76
39.86
31.28
30.36
26.75
26.24
26.03
f1 (ppm)

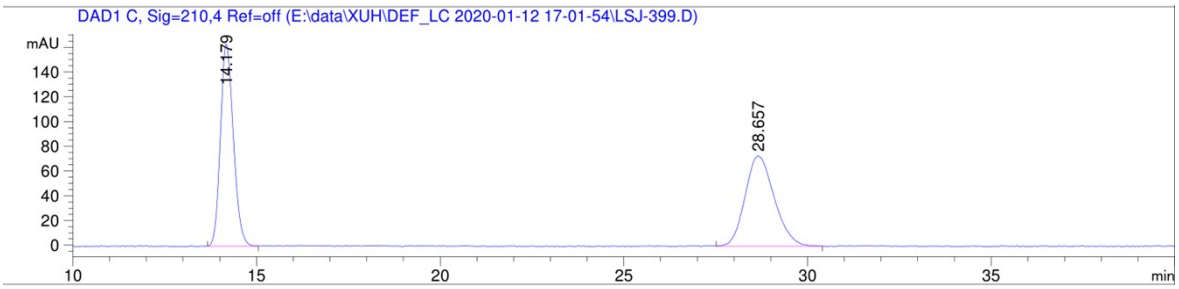

Bn
N
N
N
N
Bn

18


7.41
7.38
7.33
7.30
7.28
7.23
7.16
5.87
5.84
5.80
5.77
5.56
5.16
5.12
5.08
5.06
3.95
3.92
3.53
3.51
3.36
3.33
2.96
2.92
2.54
2.48
2.38
2.35
2.12
2.07
2.04
1.80
1.72
1.62
1.56
1.53
1.26
1.17
1.12
1.04
0.97
0.90
0.83
0.70
0.66
0.60
11.08
0.98
1.90
1.99
0.97
0.95
0.97
0.98
0.98
0.99
1.02
1.20
2.20
4.79
1.80
1.04
f1 (ppm)

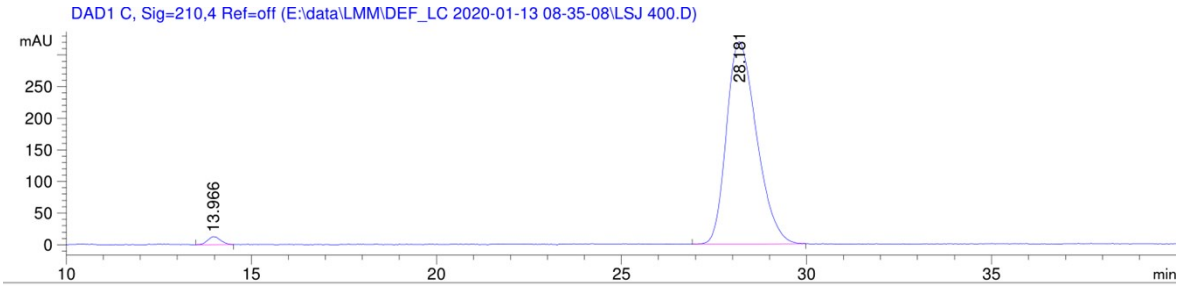

144.77
140.40
137.48
135.21
129.19
128.69
128.26
127.79
126.68
122.52
116.68
77.48
77.16
76.84
60.07
54.18
53.99
53.03
38.44
31.34
30.74
26.81
26.22
26.18
f1 (ppm)

HPLC trace of *rac*-18

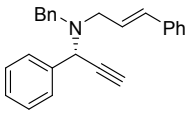


Retention time [min]		Width [min]	Area [mAU*s]	Hight [mAU]	Hight %
14.179	BB	0.3804	4006.81714	163.21062	49.8895
28.657	VV R	0.6754	4024.56909	72.97977	50.1105

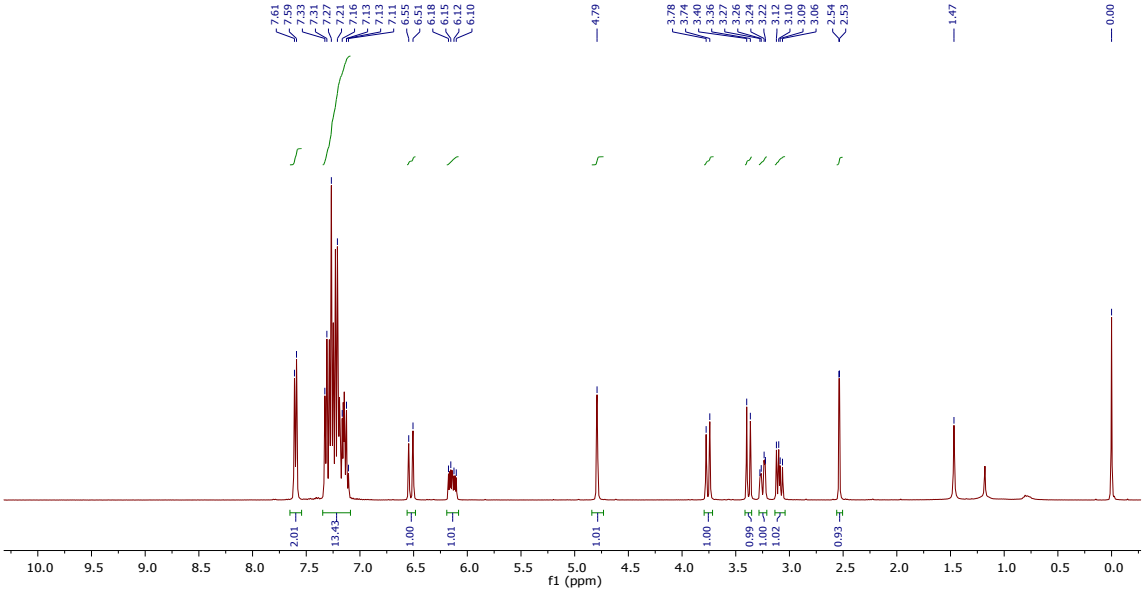
HPLC trace of 18

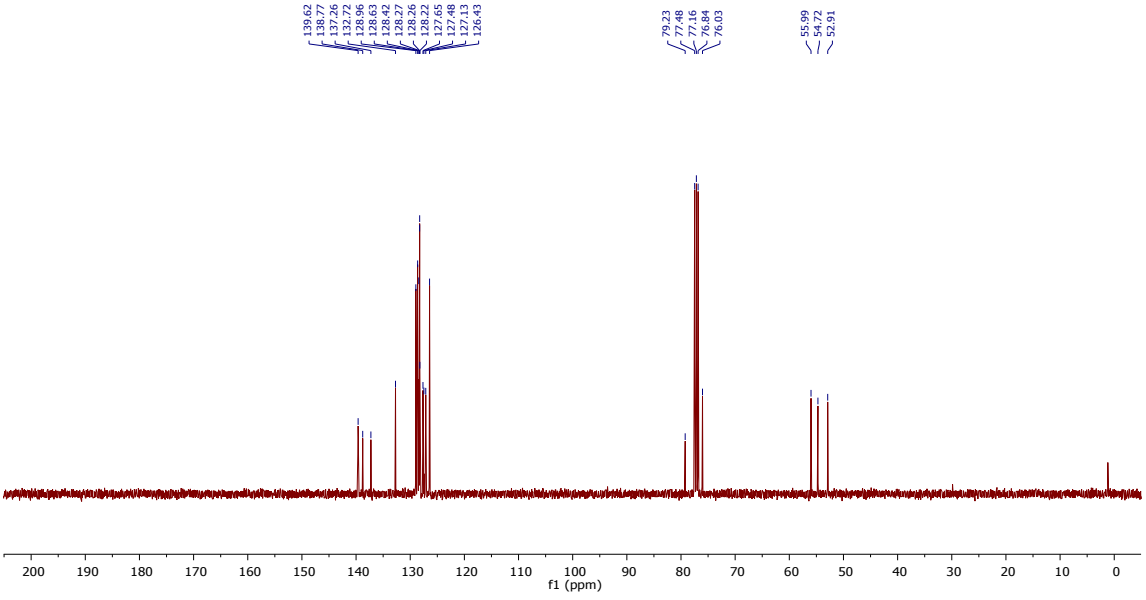


Retention time [min]		Width [min]	Area [mAU*s]	Hight [mAU]	Hight %
13.966	VB R	0.2967	304.91458	12.58221	1.6620
28.181	VV R	0.7769	1.80410e4	319.44904	98.3380

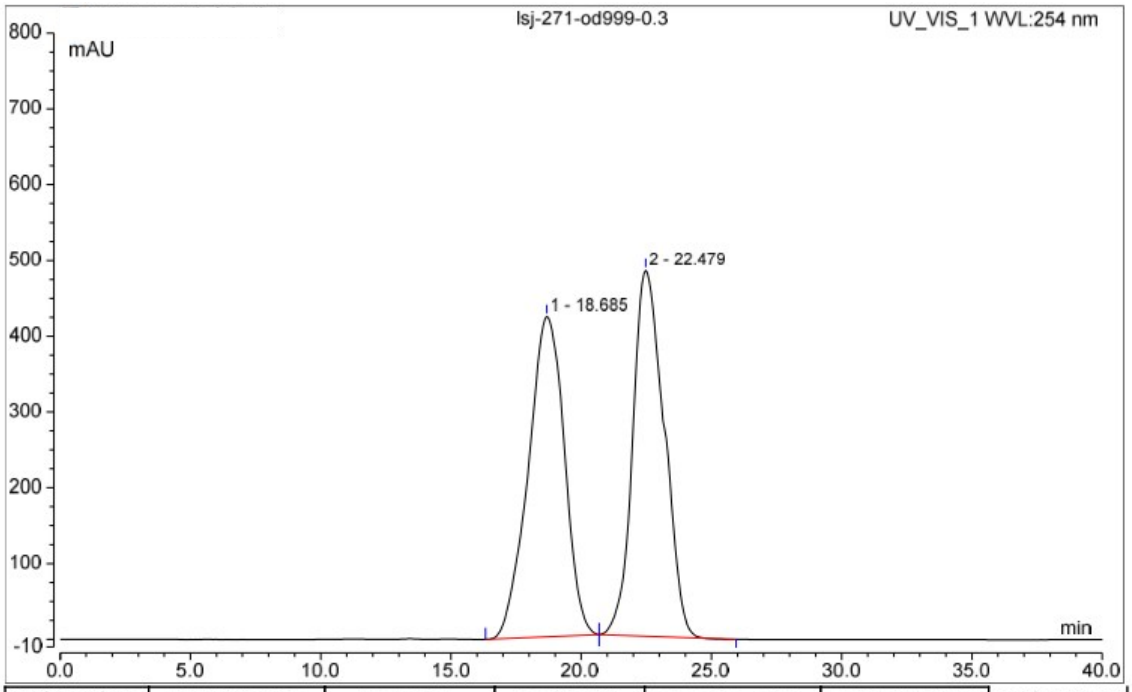

Bn
N
Ph

4a


7.61
7.59
7.33
7.31
7.27
7.21
7.16
7.13
7.13
7.11
6.55
6.51
6.18
6.15
6.12
6.10
4.79
3.78
3.74
3.40
3.36
3.27
3.26
3.24
3.22
3.12
3.10
3.09
3.06
2.54
2.53
1.47
0.00
2.01
13.43
1.00
1.01
1.01
1.00
0.99
1.00
1.02
0.93
f1 (ppm)

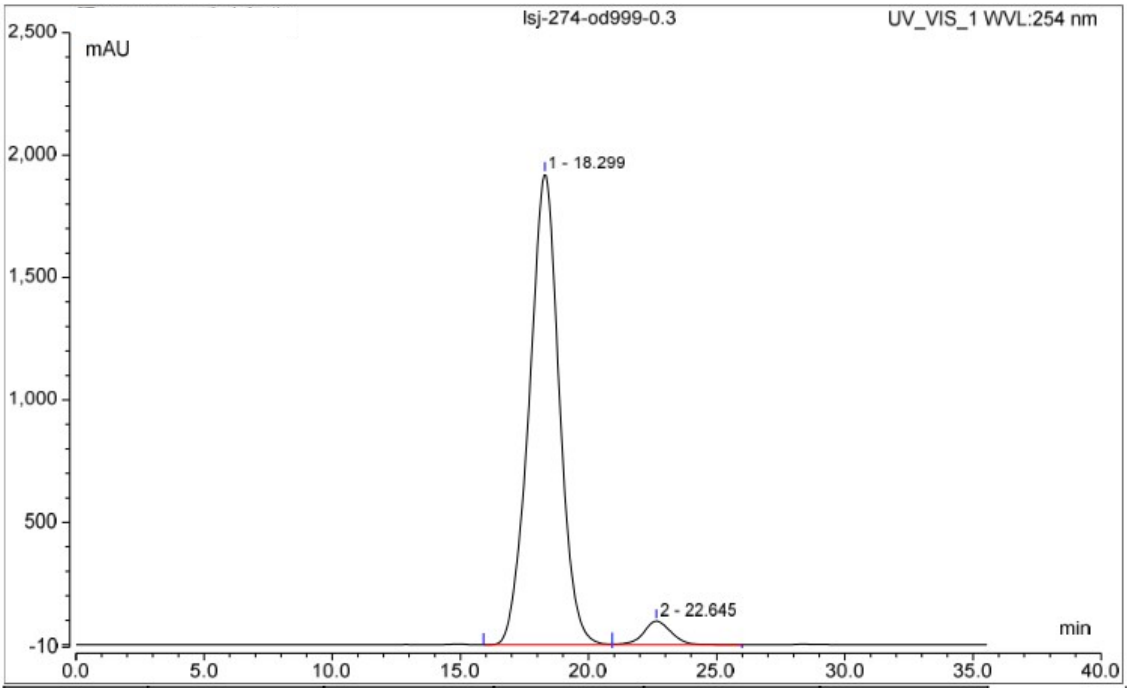

139.62
138.77
137.26
132.72
128.96
128.63
128.42
128.27
128.26
128.22
127.65
127.48
127.13
126.43
79.23
77.48
77.16
76.84
76.03
55.99
54.72
52.91
f1 (ppm)

HPLC trace of *rac*-4a

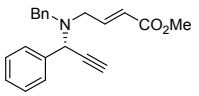


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	18.685	678.816	422.936	50.11	46.69	n.a.
2	22.479	675.793	482.999	49.89	53.31	n.a.

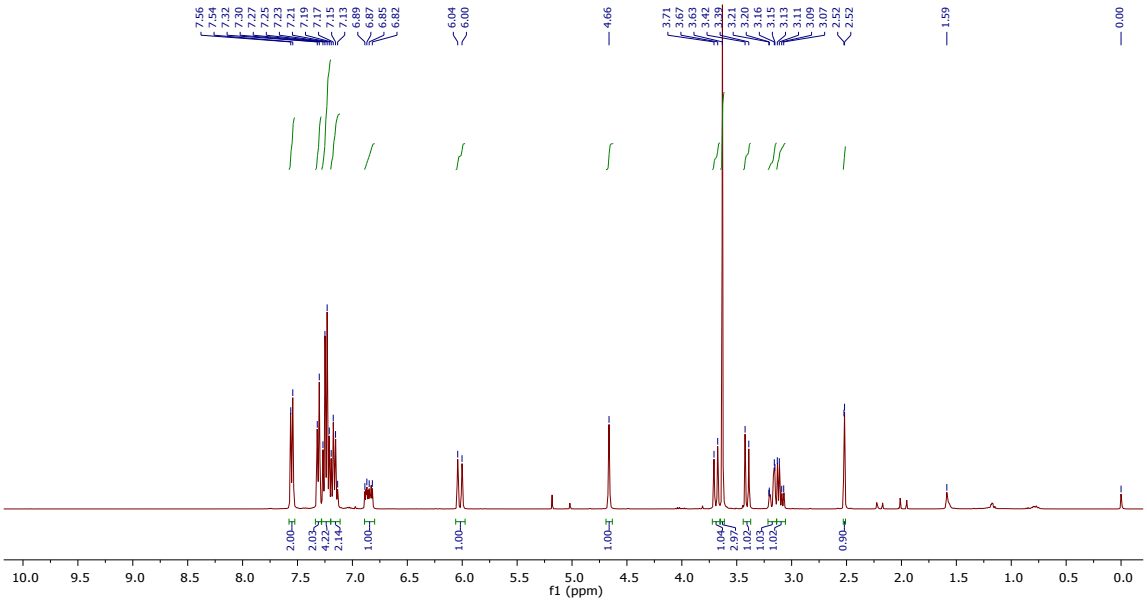
HPLC trace of 4a

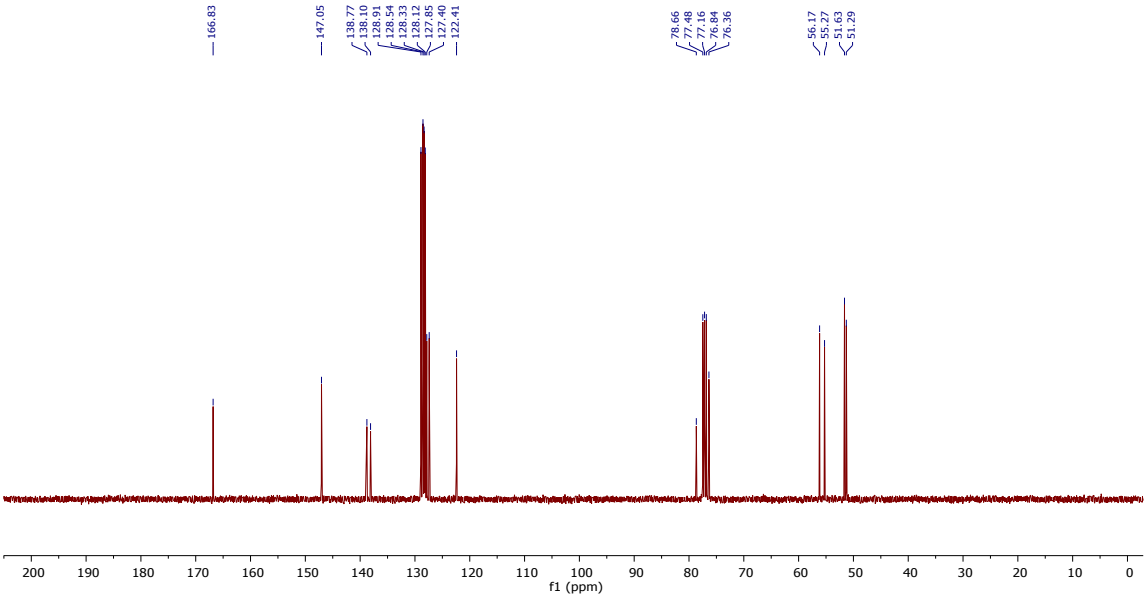


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	18.299	2607.155	1923.289	95.51	95.20	n.a.
2	22.645	122.527	96.874	4.49	4.80	n.a.

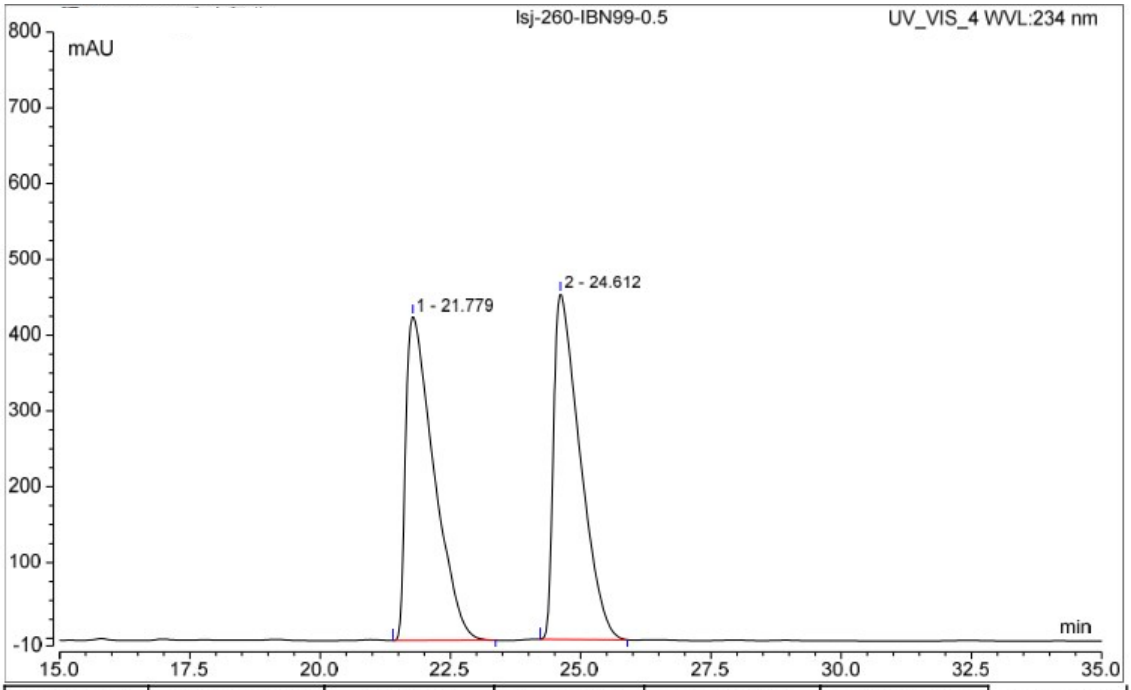

Bn
N
CO2Me

4b


7.56
7.54
7.32
7.30
7.27
7.25
7.23
7.21
7.19
7.17
7.15
7.13
6.89
6.87
6.85
6.82
6.04
6.00
4.66
3.71
3.67
3.63
3.42
3.39
3.21
3.20
3.16
3.15
3.13
3.11
3.09
3.07
2.52
2.52
1.59
0.00
2.00
2.03
4.22
2.14
1.00
1.00
1.00
1.04
2.97
1.02
1.03
1.02
0.90
f1 (ppm)

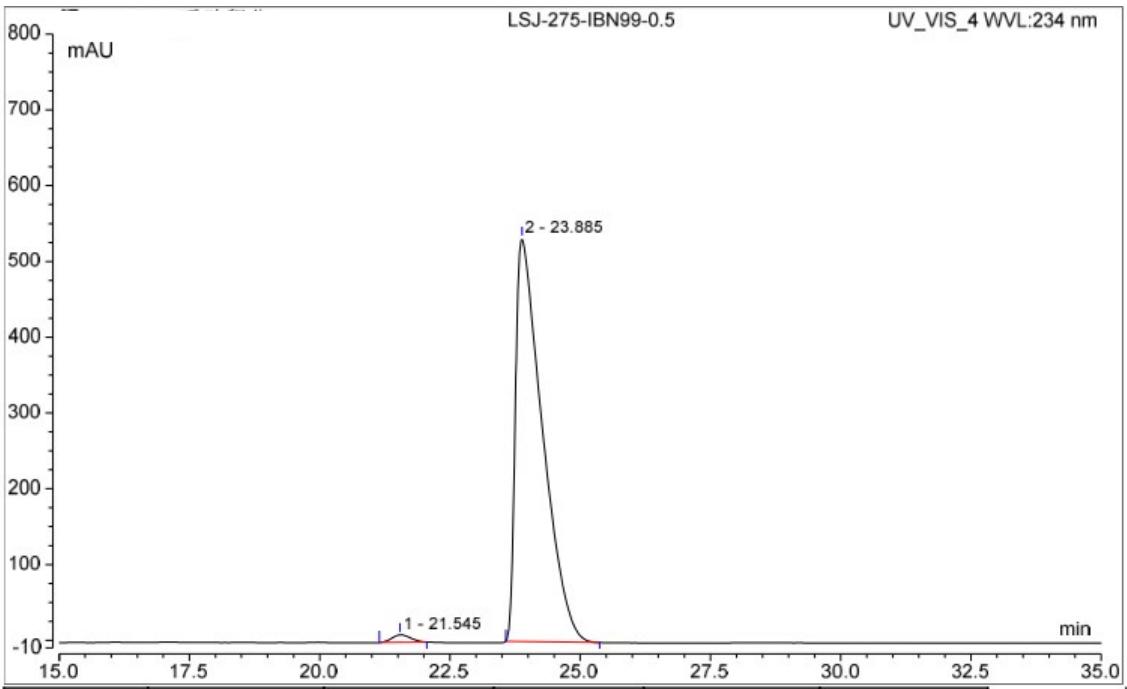

166.83
147.05
138.77
138.10
128.91
128.54
128.33
128.12
127.85
127.40
122.41
78.66
77.48
77.16
76.84
76.36
56.17
55.27
51.63
51.29
f1 (ppm)

HPLC trace of *rac*-4b

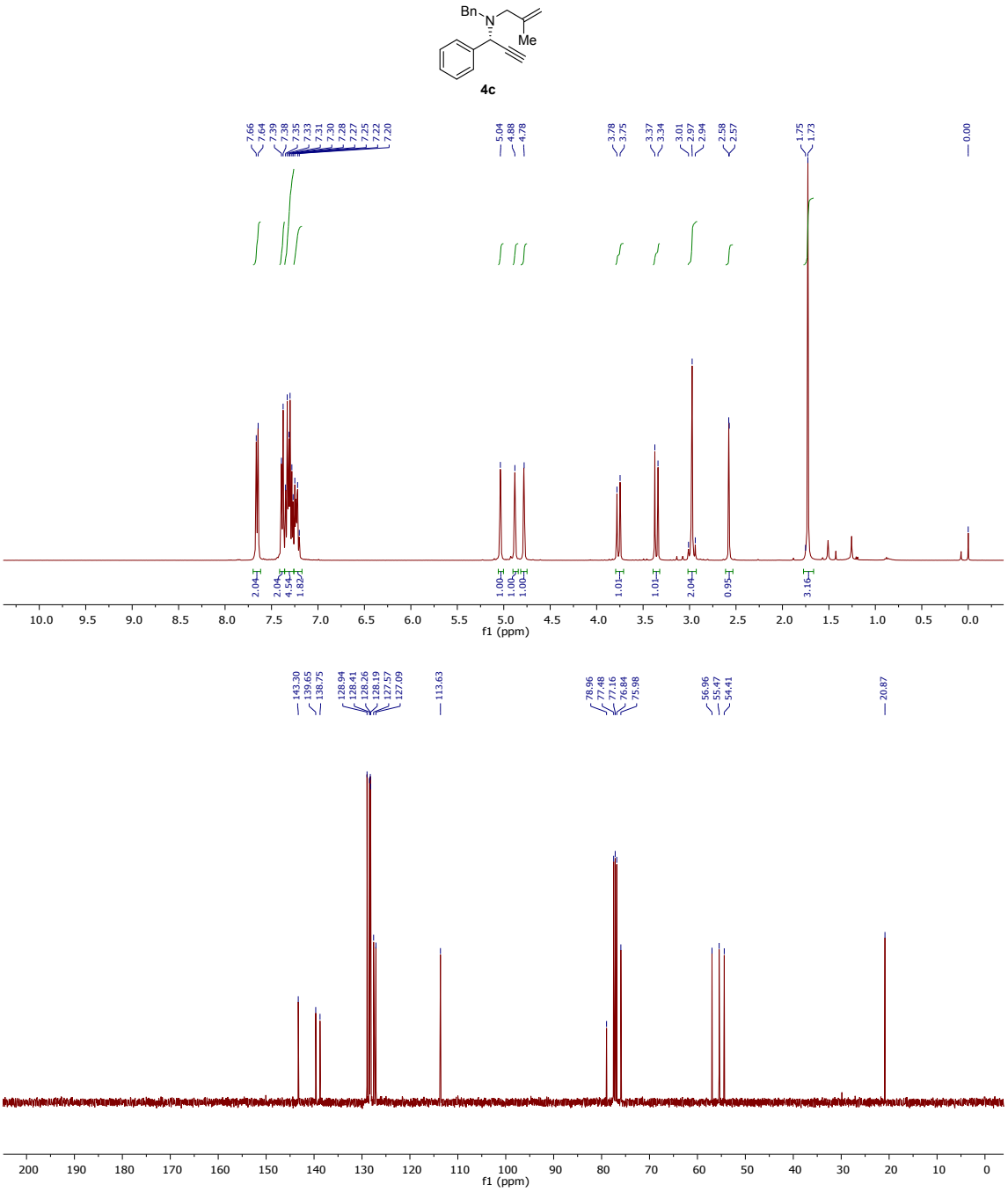


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	21.779	267.768	427.920	50.05	48.39	n.a.
2	24.612	267.267	456.306	49.95	51.61	n.a.

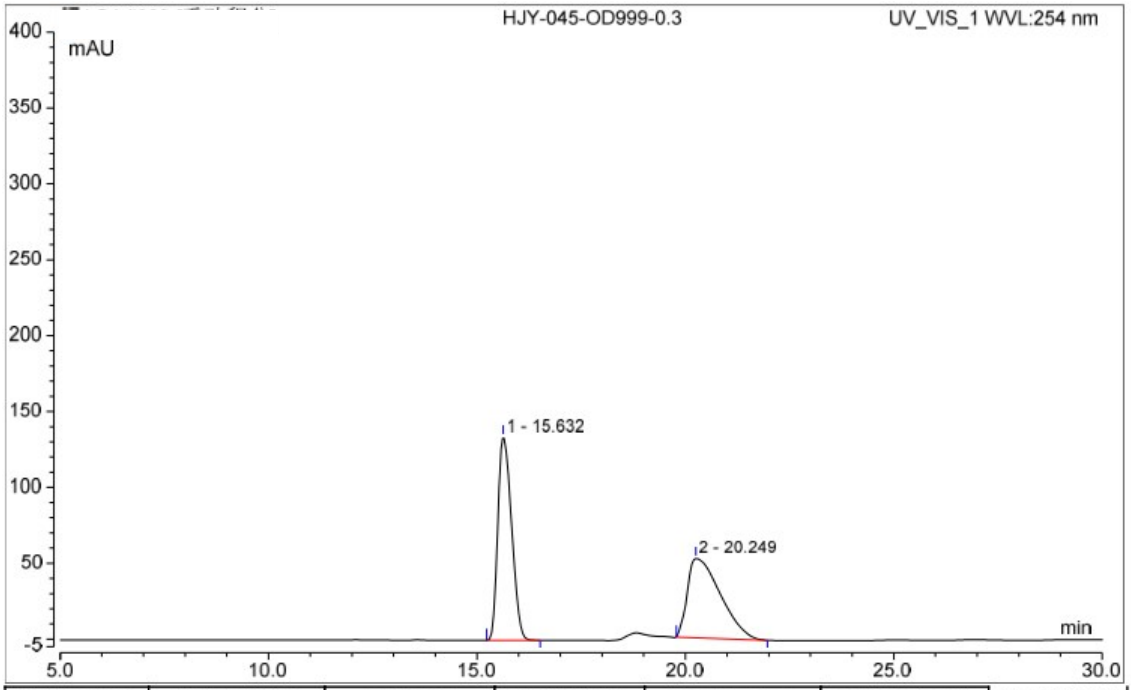
HPLC trace of 4b



peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	21.545	4.093	9.937	1.27	1.83	n.a.
2	23.885	317.064	531.949	98.73	98.17	n.a.

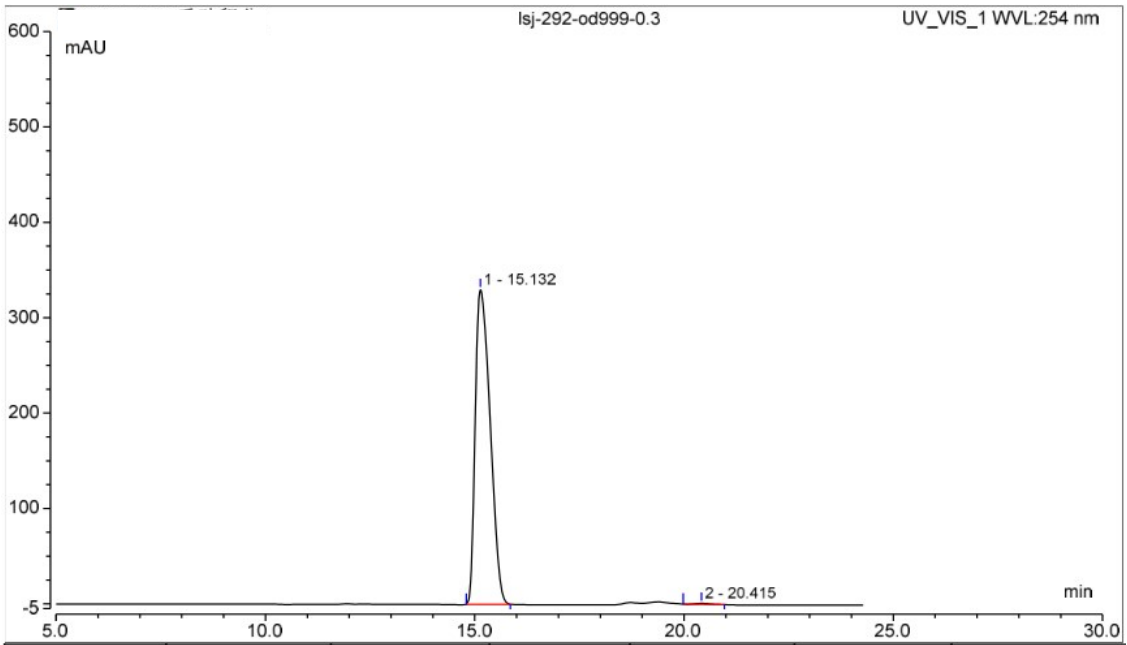

Bn
N
Me
4c
7.66
7.64
7.39
7.38
7.35
7.33
7.31
7.30
7.28
7.27
7.25
7.22
7.20
5.04
4.88
4.78
3.78
3.75
3.37
3.34
3.01
2.97
2.94
2.58
2.57
1.75
1.73
0.00
2.04
2.04
4.54
1.82
1.00
1.00
1.00
1.01
1.01
2.04
0.95
3.16
f1 (ppm)
143.30
139.65
138.75
128.94
128.41
128.26
128.19
127.57
127.09
113.63
78.96
77.48
77.16
76.84
75.98
56.96
55.47
54.41
20.87
f1 (ppm)

HPLC trace of *rac*-4c

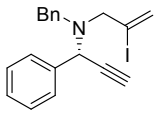


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	15.632	51.385	134.028	51.70	71.99	n.a.
2	20.249	48.011	52.139	48.30	28.01	n.a.

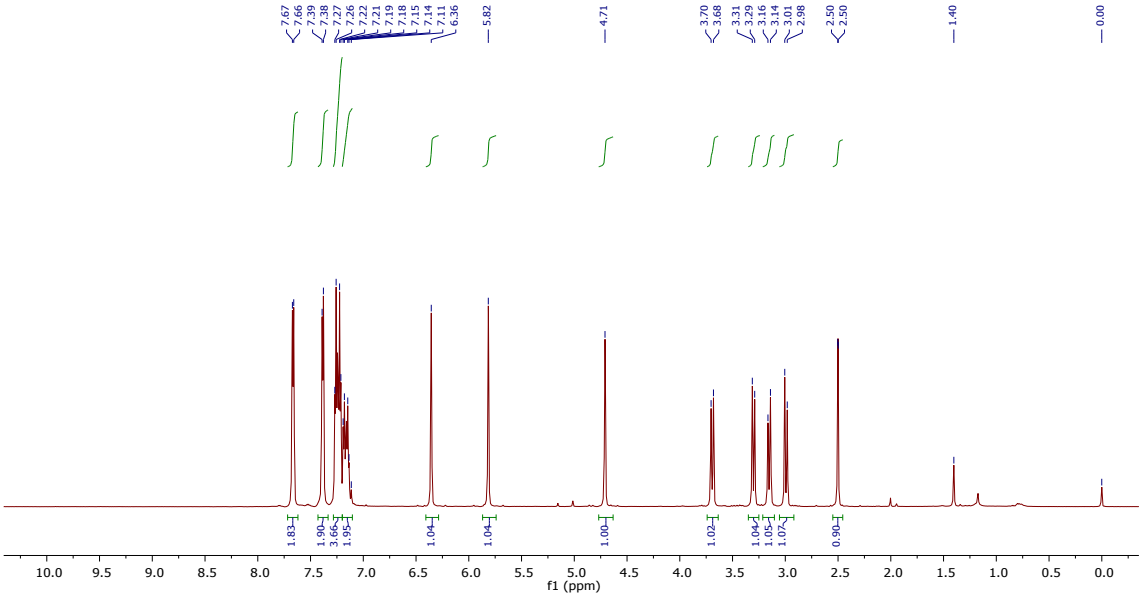
HPLC trace of 4c

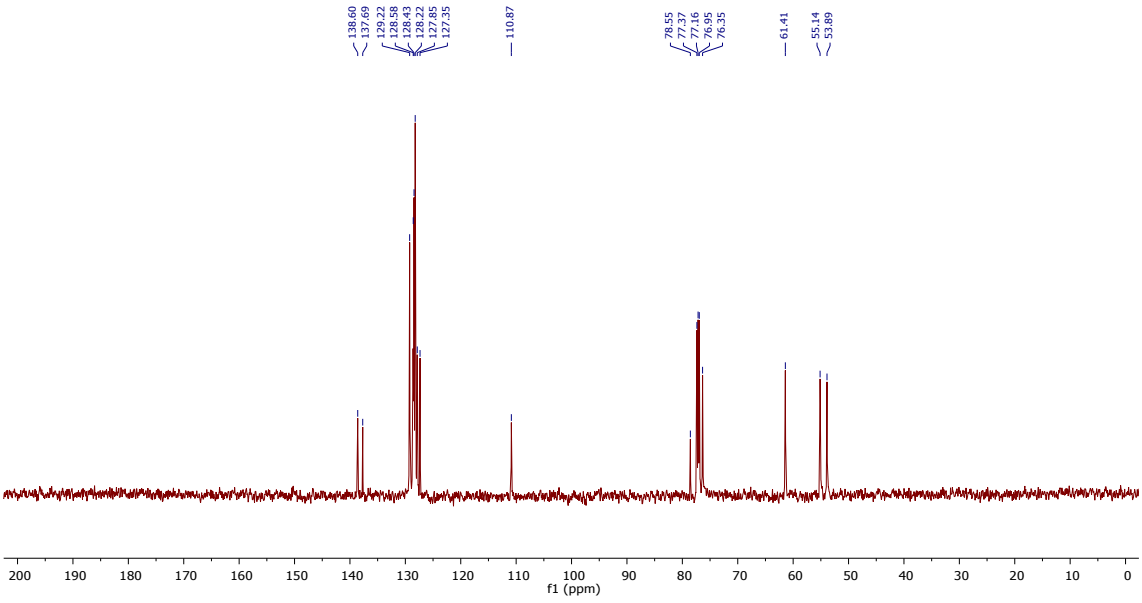


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	15.132	136.147	329.796	99.71	99.70	n.a.
2	20.415	0.403	0.995	0.29	0.30	n.a.

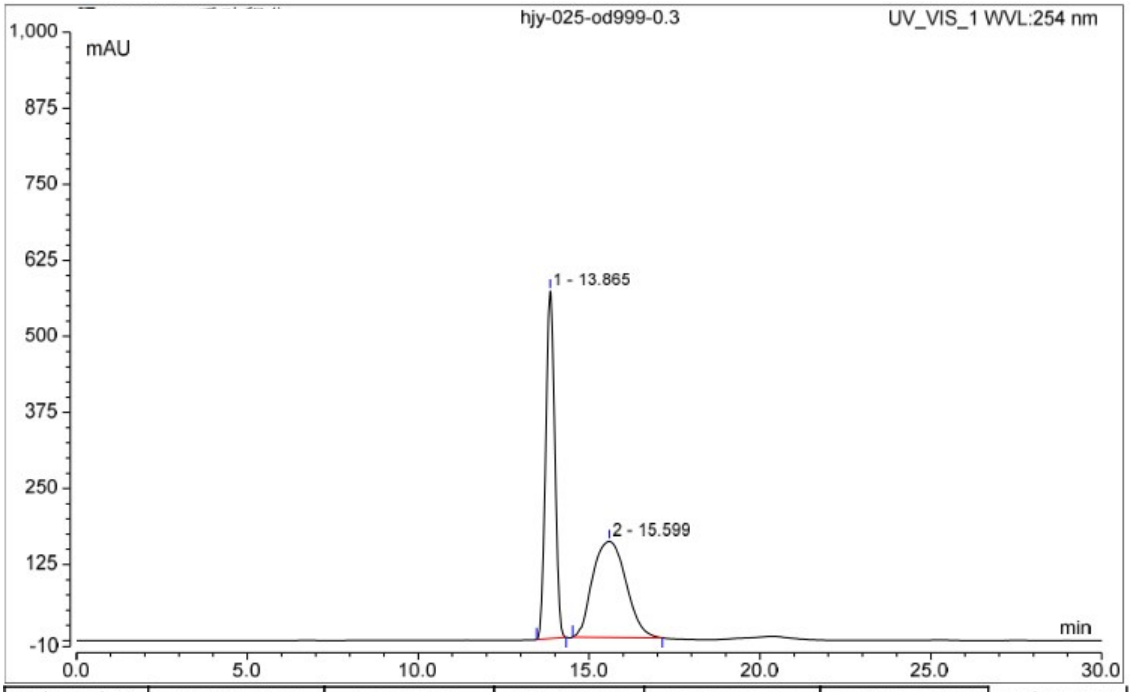

Bn
N
I

4d


7.67
7.66
7.39
7.38
7.27
7.26
7.22
7.21
7.19
7.18
7.15
7.14
7.11
6.36
5.82
4.71
3.70
3.68
3.31
3.29
3.16
3.14
3.01
2.98
2.50
2.50
1.40
0.00
1.83
1.90
3.66
1.95
1.04
1.04
1.00
1.02
1.04
1.05
1.07
0.90
f1 (ppm)

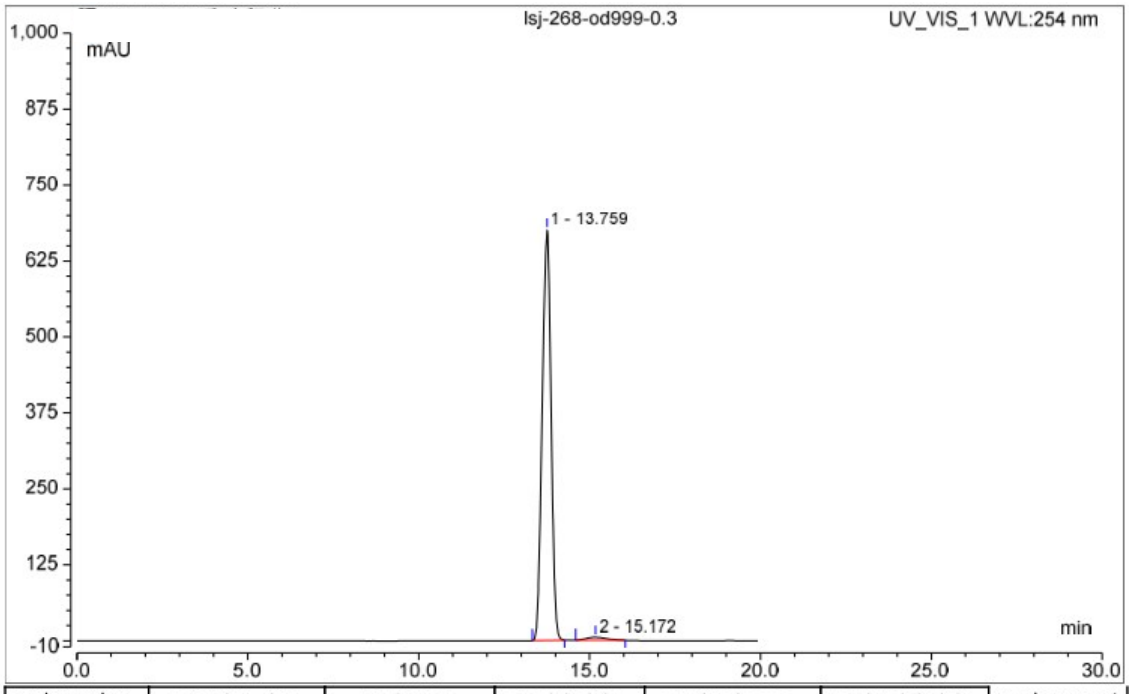

138.60
137.69
129.22
128.98
128.43
128.22
127.85
127.35
110.87
78.55
77.37
77.16
76.95
76.35
61.41
55.14
53.89
f1 (ppm)

HPLC trace of *rac*-4d

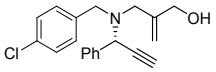


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	13.865	177.136	571.415	49.78	78.37	n.a.
2	15.599	178.696	157.701	50.22	21.63	n.a.

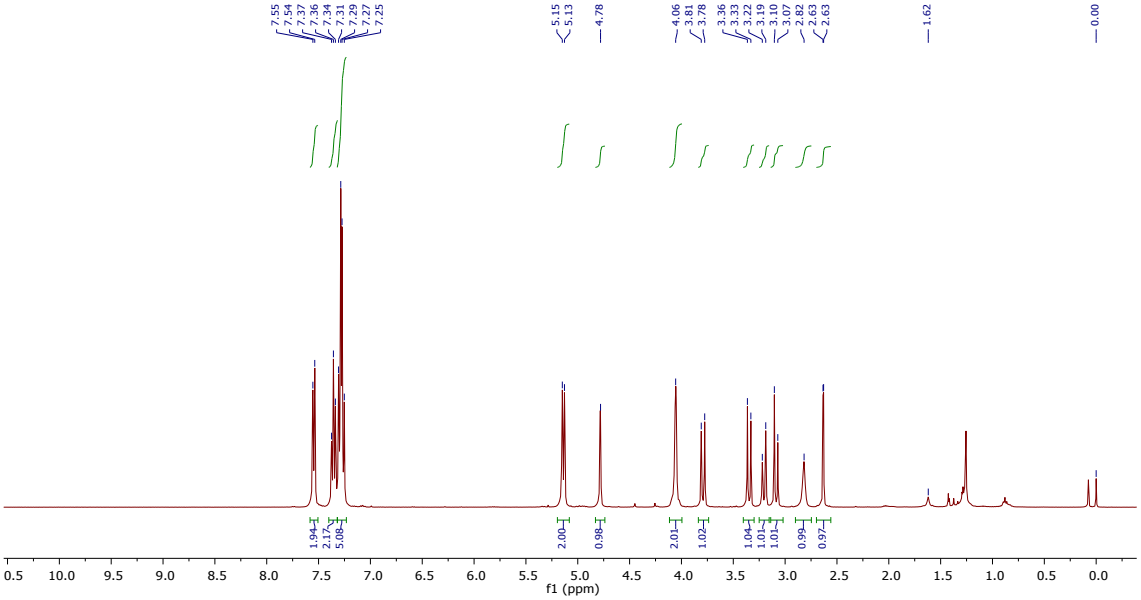
HPLC trace of 4d

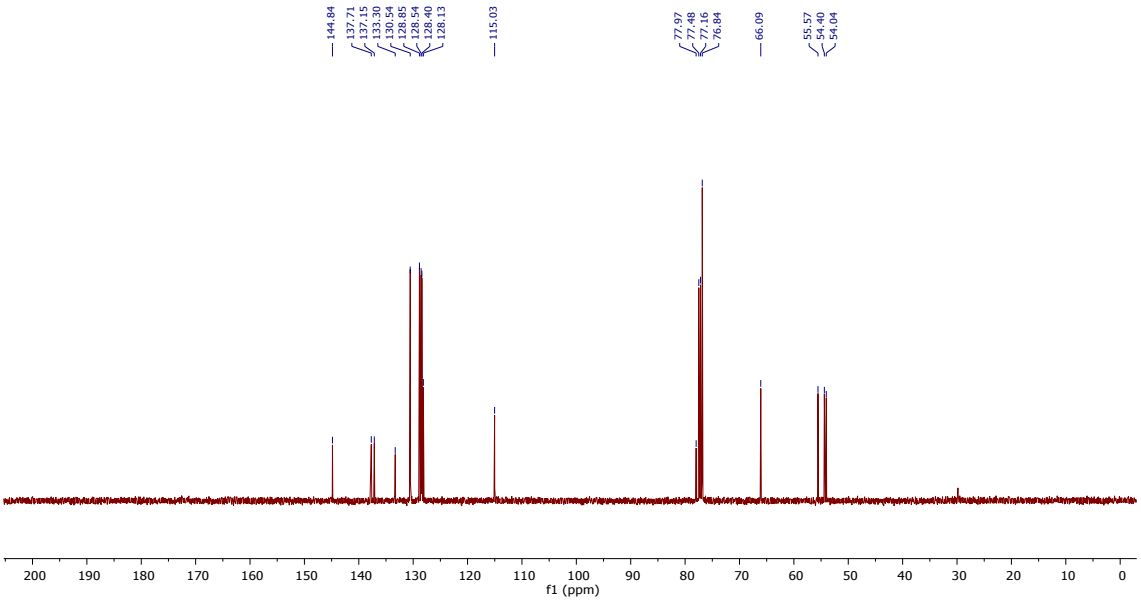


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	13.759	204.328	675.640	98.36	99.28	n.a.
2	15.172	3.407	4.933	1.64	0.72	n.a.

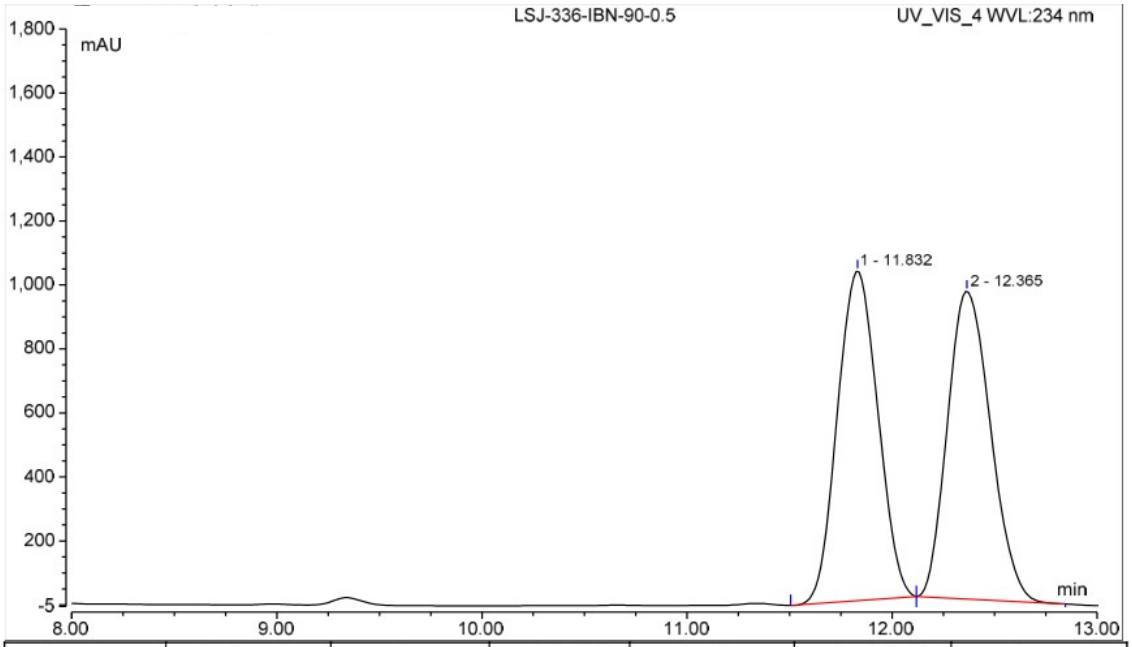

N
OH
Cl
Ph

4e


7.55
7.54
7.37
7.36
7.34
7.31
7.29
7.27
7.25
5.15
5.13
4.78
4.06
3.81
3.78
3.36
3.33
3.22
3.19
3.10
3.07
2.82
2.63
2.63
1.62
0.00
1.94
2.17
5.08
2.00
0.98
2.01
1.02
1.04
1.01
1.01
0.99
0.97
f1 (ppm)

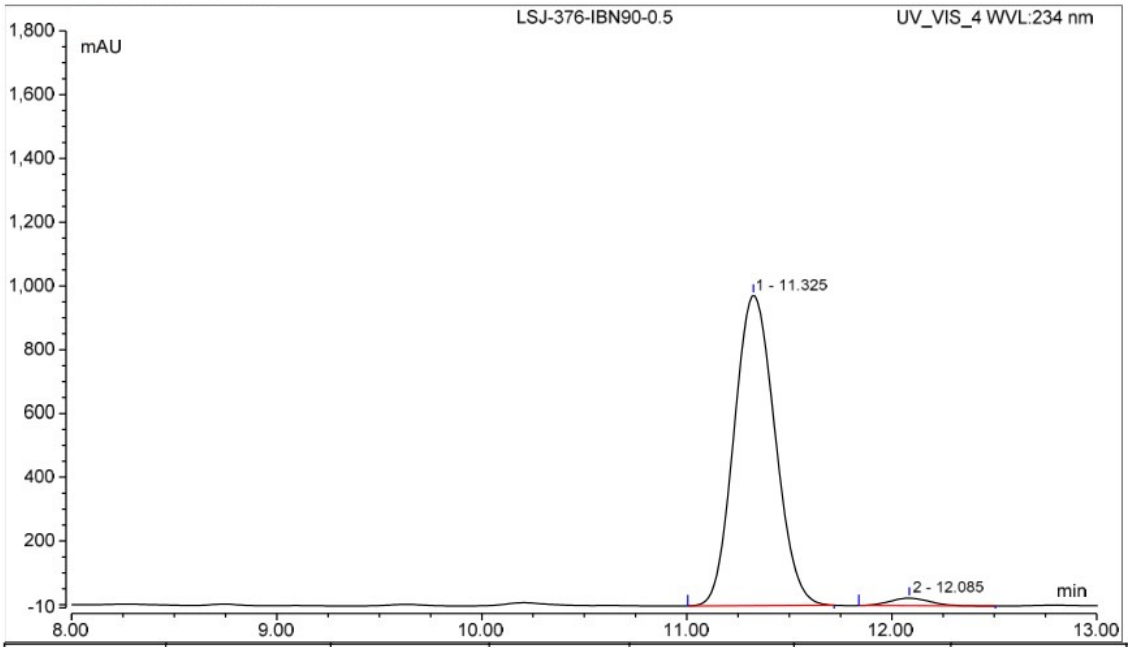

144.84
137.71
137.15
133.30
130.54
128.85
128.54
128.40
128.13
115.03
77.97
77.48
77.16
76.84
66.09
55.57
54.40
54.04
f1 (ppm)

HPLC trace of *rac*-4e

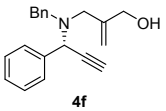


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	11.832	234.852	1030.740	50.07	51.73	n.a.
2	12.365	234.172	961.925	49.93	48.27	n.a.

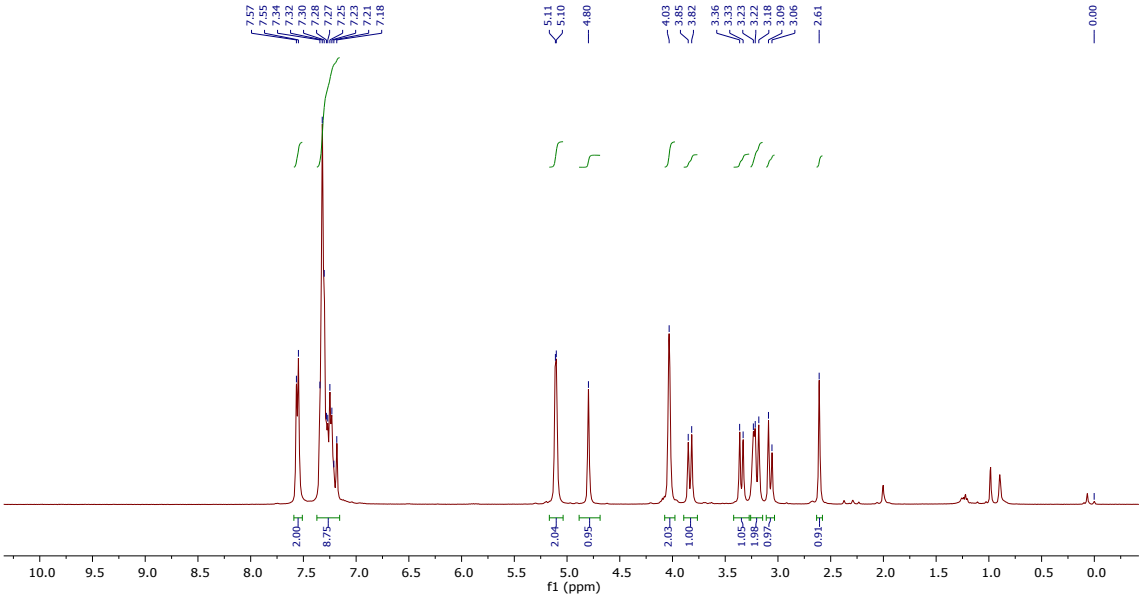
HPLC trace of 4e

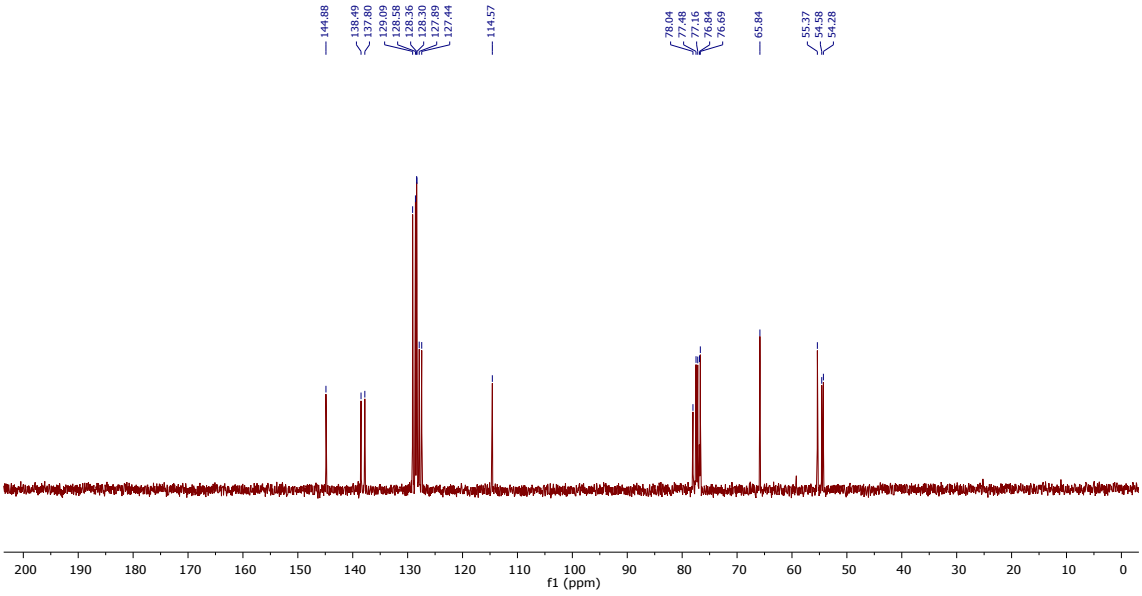


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	11.325	224.713	973.691	97.64	97.61	n.a.
2	12.085	5.424	23.839	2.36	2.39	n.a.

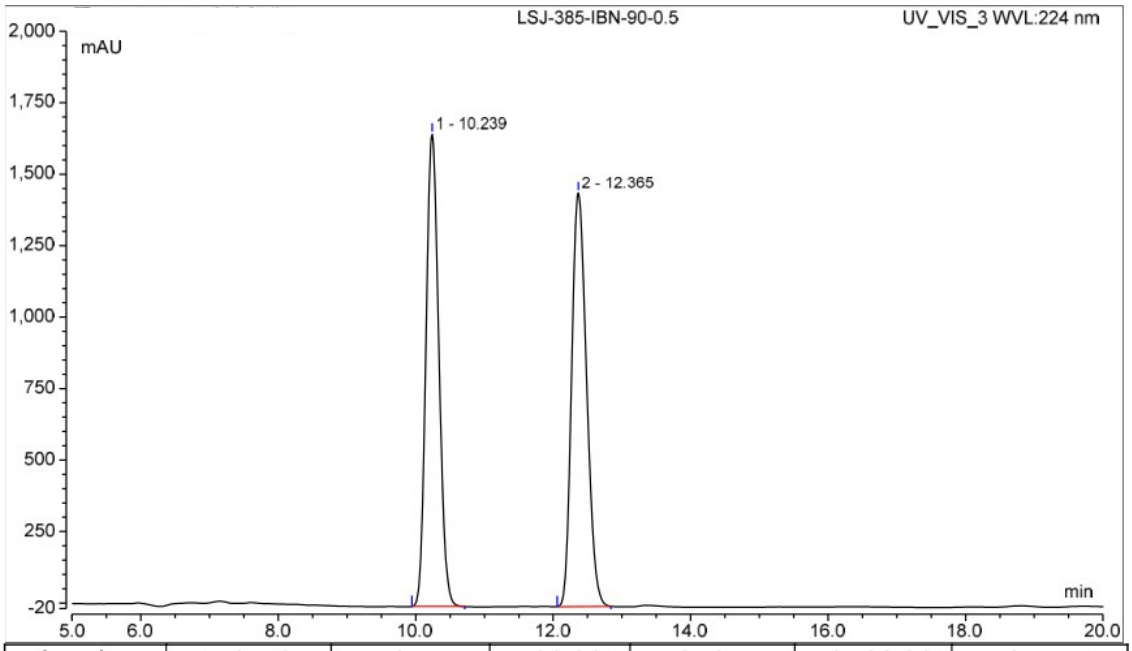

Bn
N
OH

4f


7.57
7.55
7.34
7.32
7.30
7.28
7.27
7.25
7.23
7.21
7.18
5.11
5.10
4.80
4.03
3.85
3.82
3.36
3.33
3.23
3.22
3.18
3.09
3.06
2.61
0.00
2.00
8.75
2.04
0.95
2.03
1.00
1.05
1.98
0.97
0.91
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)

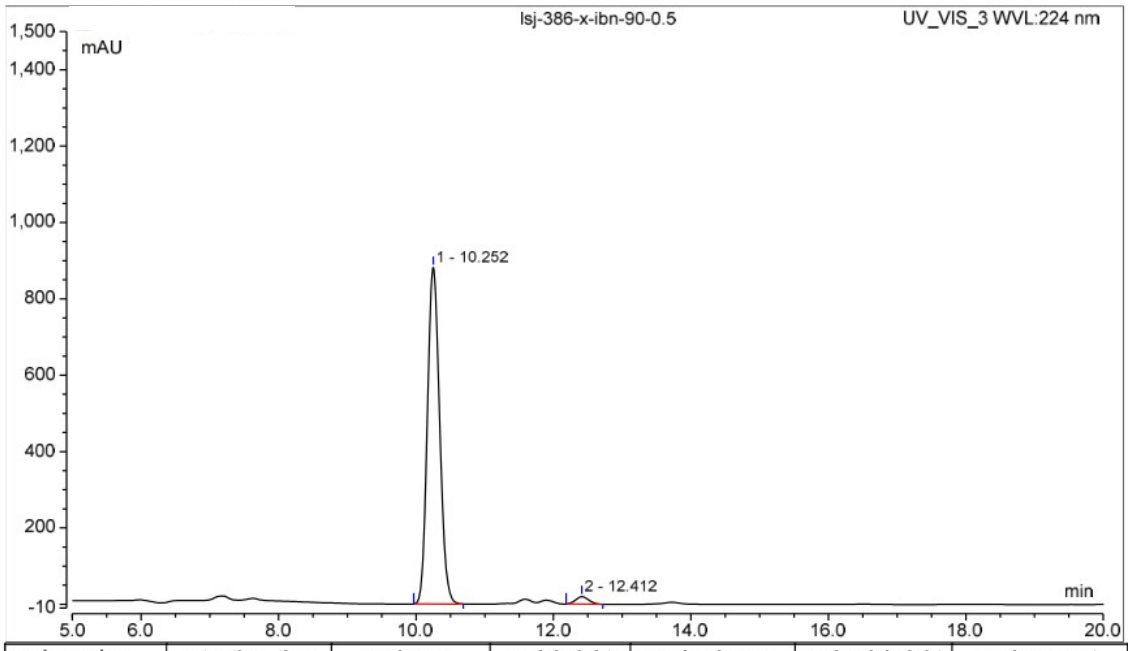

144.88
138.49
137.80
129.09
128.58
128.36
128.30
127.80
127.44
114.57
78.04
77.48
77.16
76.84
76.69
65.84
55.37
54.58
54.28
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

HPLC trace of *rac*-4f

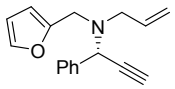


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	10.239	357.785	1652.253	49.48	53.31	n.a.
2	12.365	365.305	1447.147	50.52	46.69	n.a.

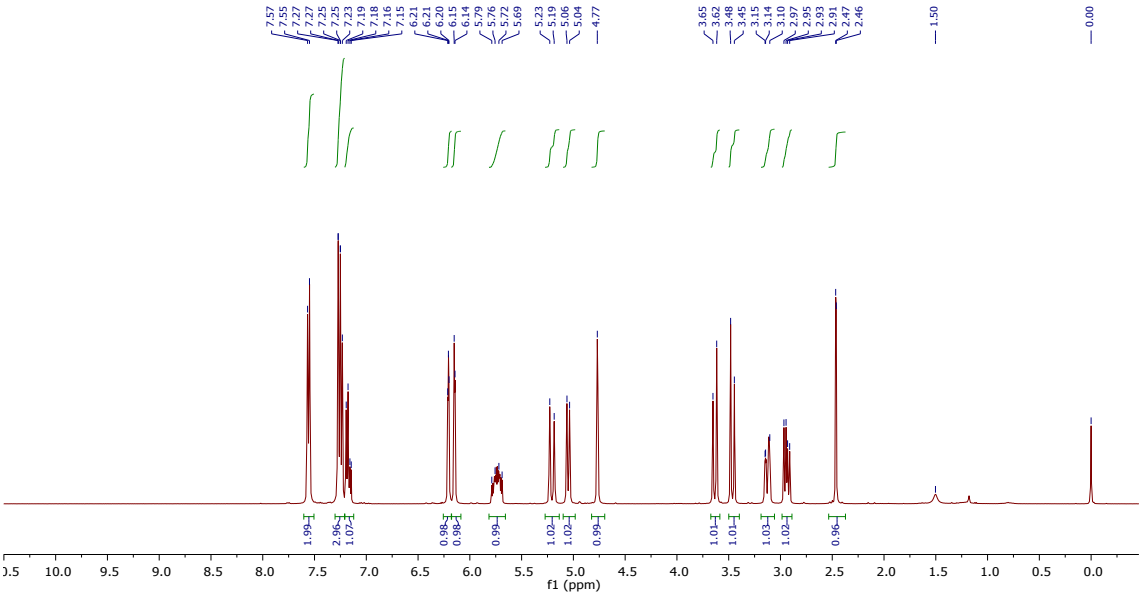
HPLC trace of 4f

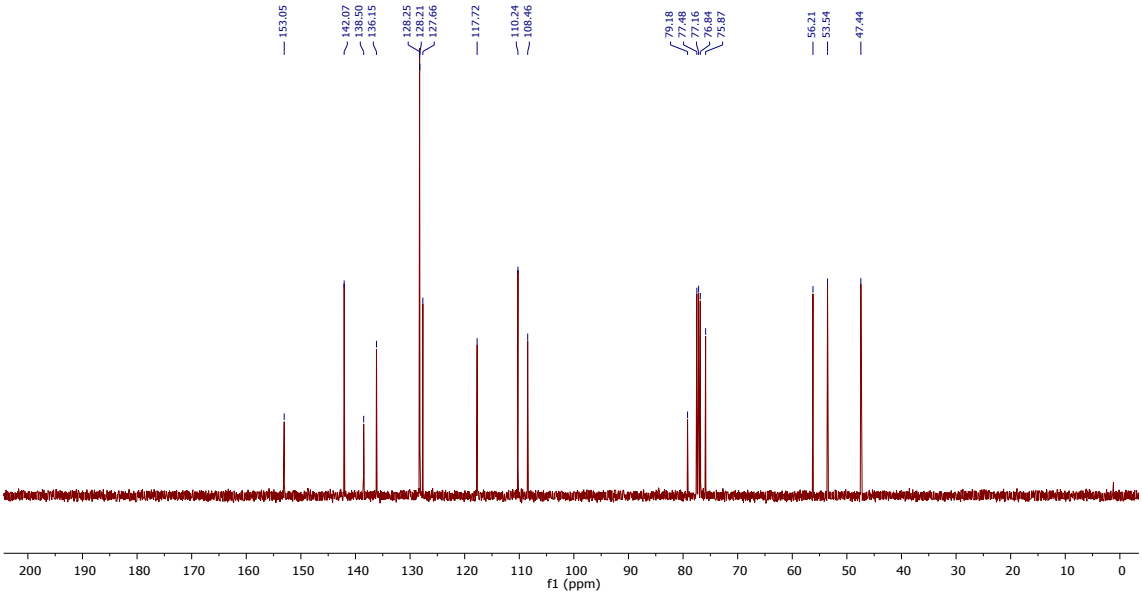


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	10.252	181.825	881.264	97.69	97.84	n.a.
2	12.412	4.297	19.496	2.31	2.16	n.a.

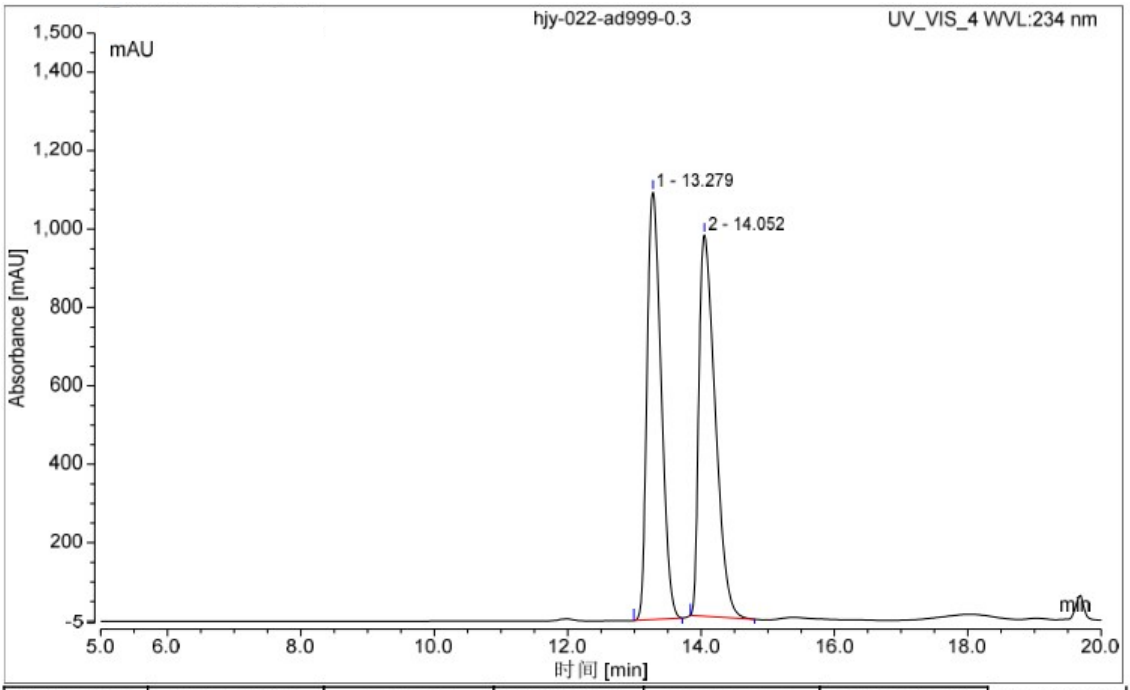

N
O
Ph

4g


7.57
7.55
7.27
7.27
7.25
7.25
7.23
7.19
7.18
7.16
7.15
6.21
6.21
6.20
6.15
6.14
5.79
5.76
5.72
5.69
5.23
5.19
5.06
5.04
4.77
3.65
3.62
3.48
3.45
3.15
3.14
3.10
2.97
2.95
2.93
2.91
2.47
2.46
1.50
0.00
1.99
2.96
1.07
0.98
0.98
0.99
1.02
1.02
0.99
1.01
1.01
1.03
1.02
0.96
f1 (ppm)

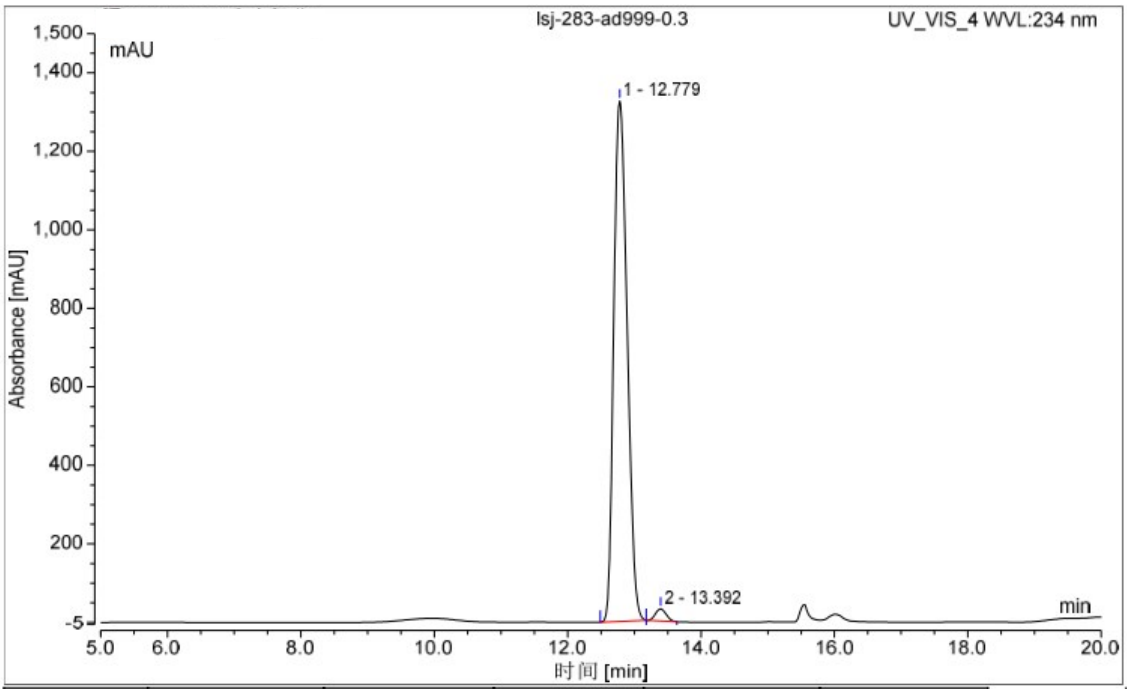

153.05
142.07
138.50
136.15
128.25
128.21
127.66
117.72
110.24
108.46
79.18
77.48
77.16
76.84
75.87
56.21
53.54
47.44
f1 (ppm)

HPLC trace of *rac*-4g

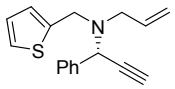


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	13.279	266.739	1090.734	49.24	52.85	n.a.
2	14.052	274.964	973.176	50.76	47.15	n.a.

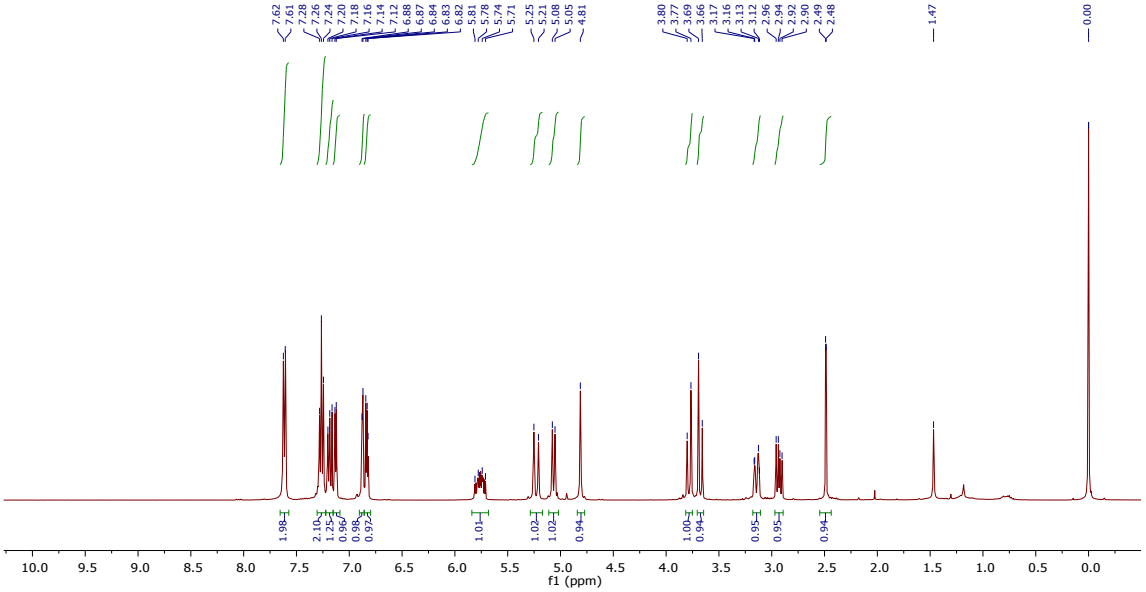
HPLC trace of 4g

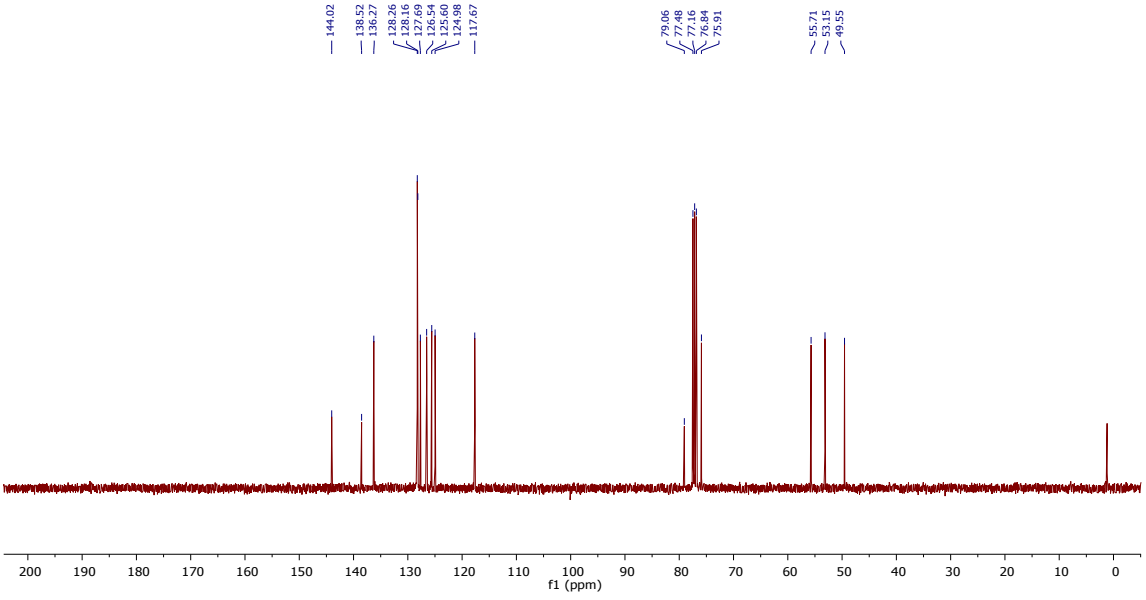


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	12.779	305.579	1326.495	98.15	97.72	n.a.
2	13.392	5.767	30.971	1.85	2.28	n.a.

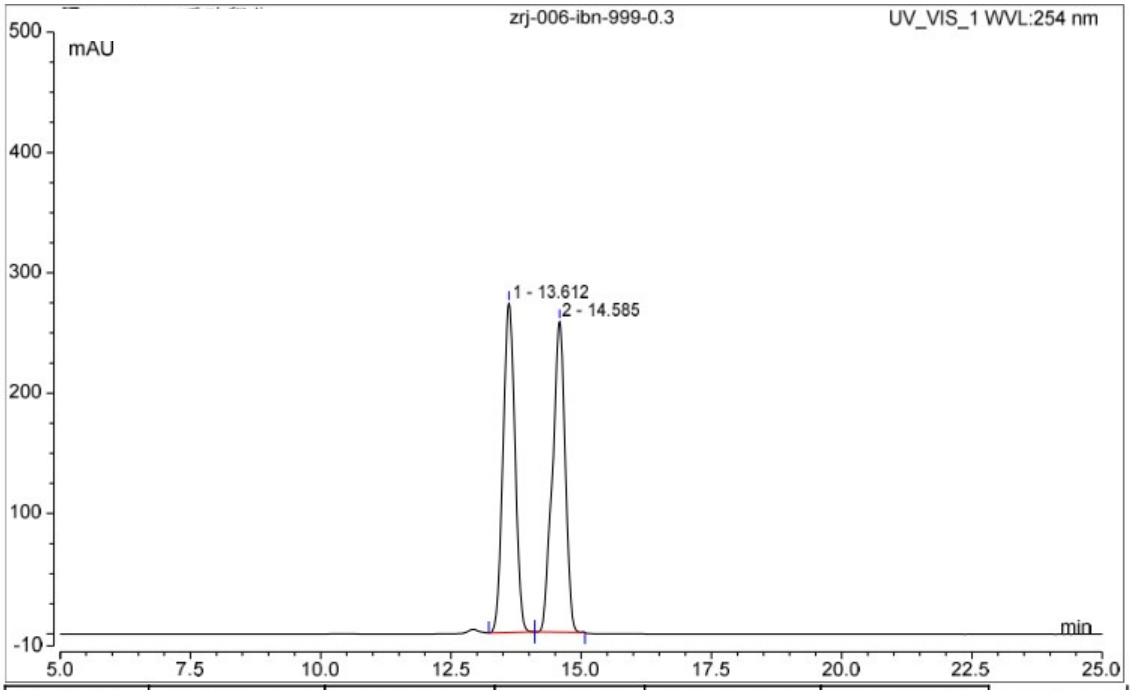

N
S
Ph

4h


7.62
7.61
7.28
7.26
7.24
7.20
7.18
7.16
7.14
7.12
6.88
6.87
6.84
6.83
6.82
5.81
5.78
5.74
5.71
5.25
5.21
5.08
5.05
4.81
3.80
3.77
3.69
3.66
3.17
3.16
3.13
3.12
2.96
2.94
2.92
2.90
2.49
2.48
1.47
0.00
1.98
2.10
1.25
0.96
0.98
0.97
1.01
1.02
1.02
0.94
1.00
0.94
0.95
0.95
0.94
f1 (ppm)

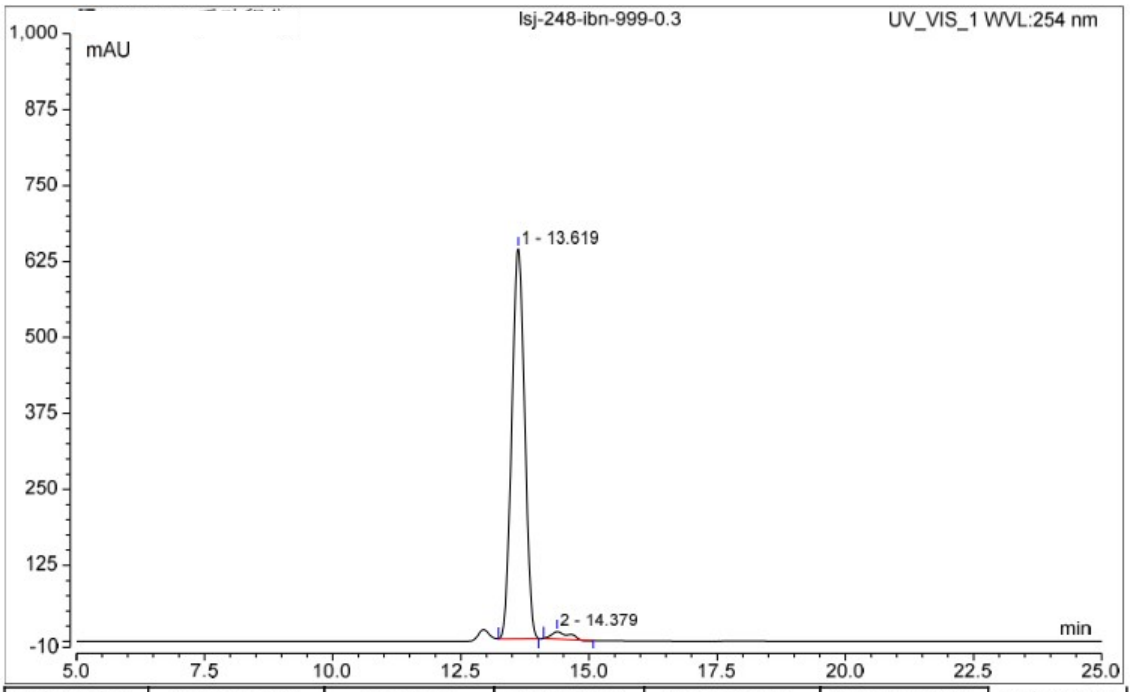

144.02
138.52
136.27
128.26
128.16
127.69
126.54
125.60
124.98
117.67
79.06
77.48
77.16
76.84
75.91
55.71
53.15
49.55
f1 (ppm)

HPLC trace of *rac*-4h

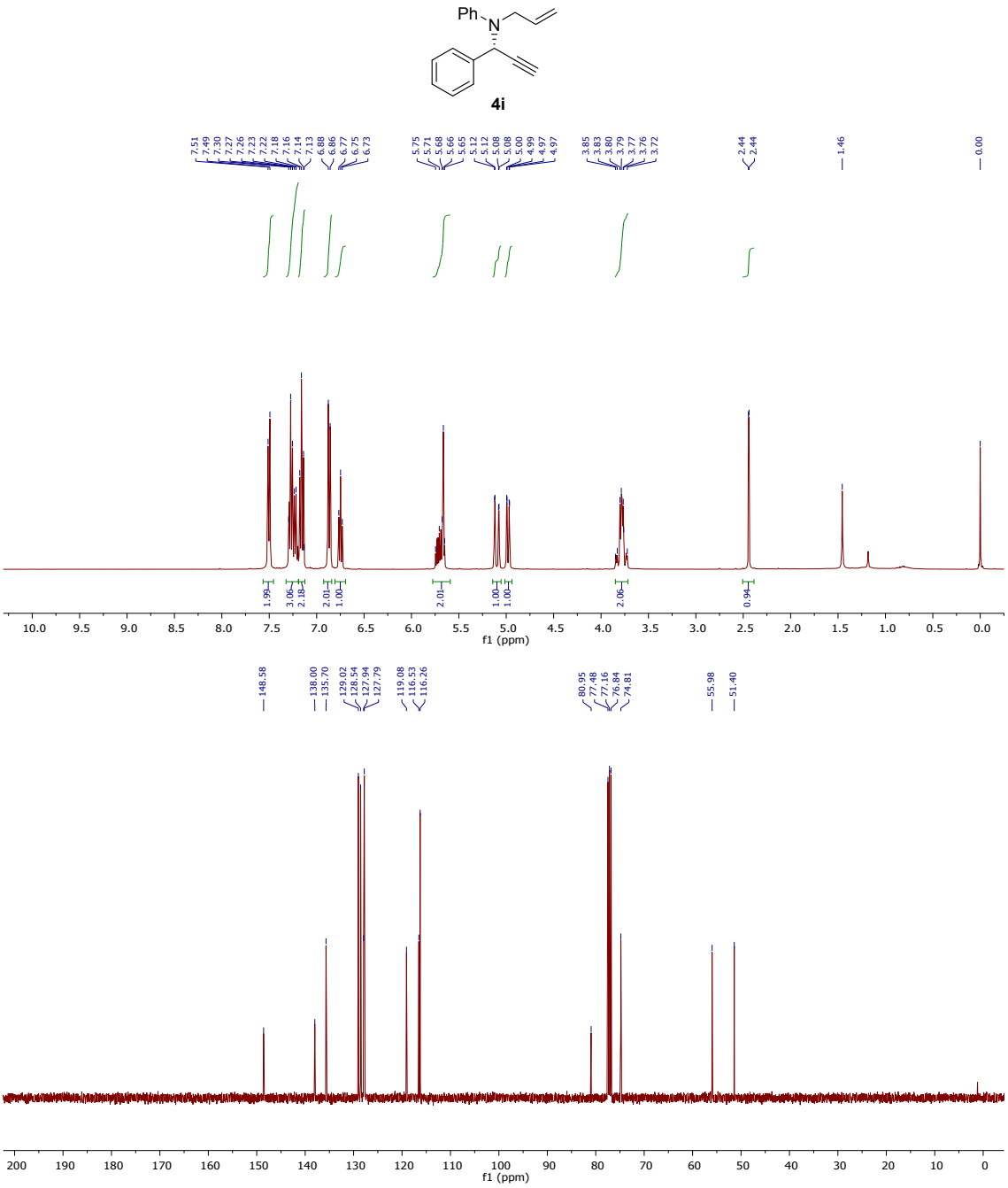


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	13.612	72.695	273.774	50.03	51.45	n.a.
2	14.585	72.620	258.362	49.97	48.55	n.a.

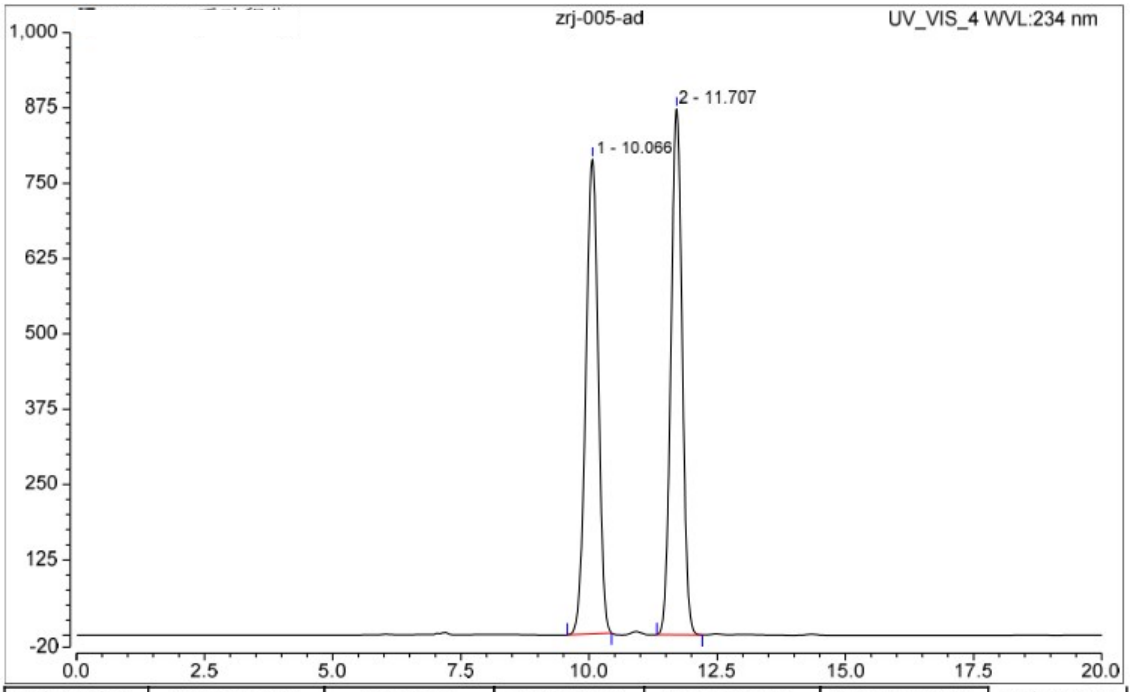
HPLC trace of 4h



peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	13.619	187.277	641.678	97.56	98.15	n.a.
2	14.379	4.686	12.113	2.44	1.85	n.a.

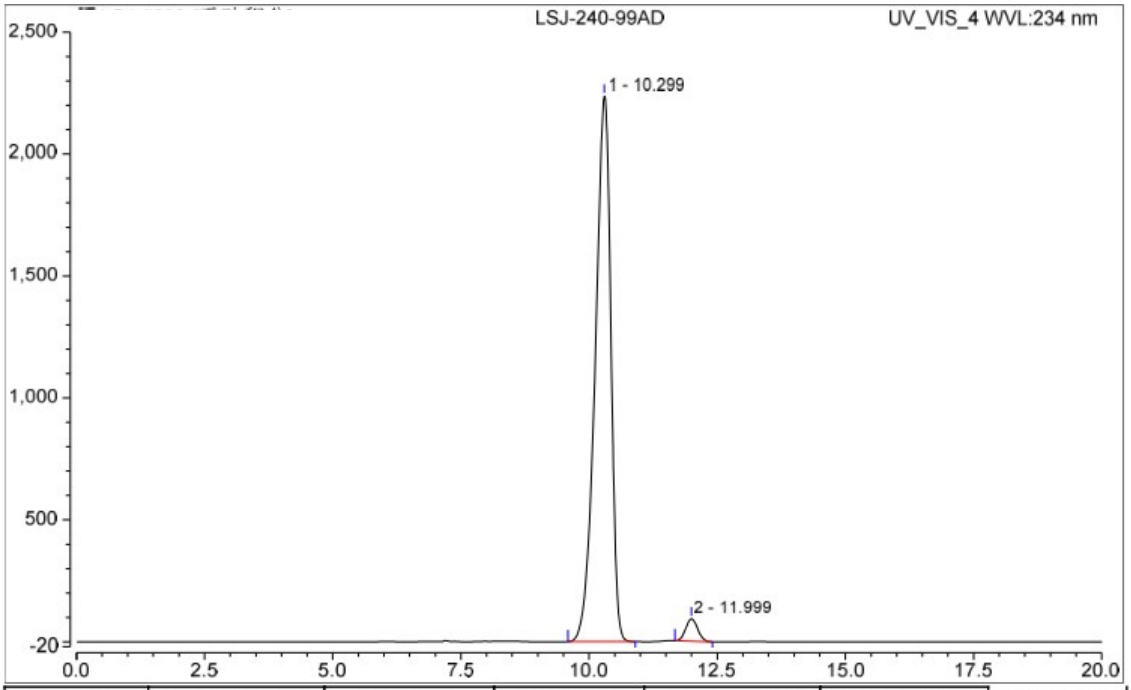

Ph
N
4i
7.51
7.49
7.30
7.27
7.26
7.23
7.22
7.18
7.16
7.14
7.13
6.88
6.86
6.77
6.75
6.73
5.75
5.71
5.68
5.66
5.65
5.12
5.12
5.08
5.08
5.00
4.99
4.97
4.97
3.85
3.83
3.80
3.79
3.77
3.76
3.72
2.44
2.44
1.46
0.00
1.99
3.06
2.18
2.01
1.00
2.01
1.00
1.00
2.06
0.94
f1 (ppm)
148.58
138.00
135.70
129.02
128.54
127.94
127.79
119.08
116.53
116.26
80.95
77.48
77.16
76.84
74.81
55.98
51.40
f1 (ppm)

HPLC trace of *rac*-4i

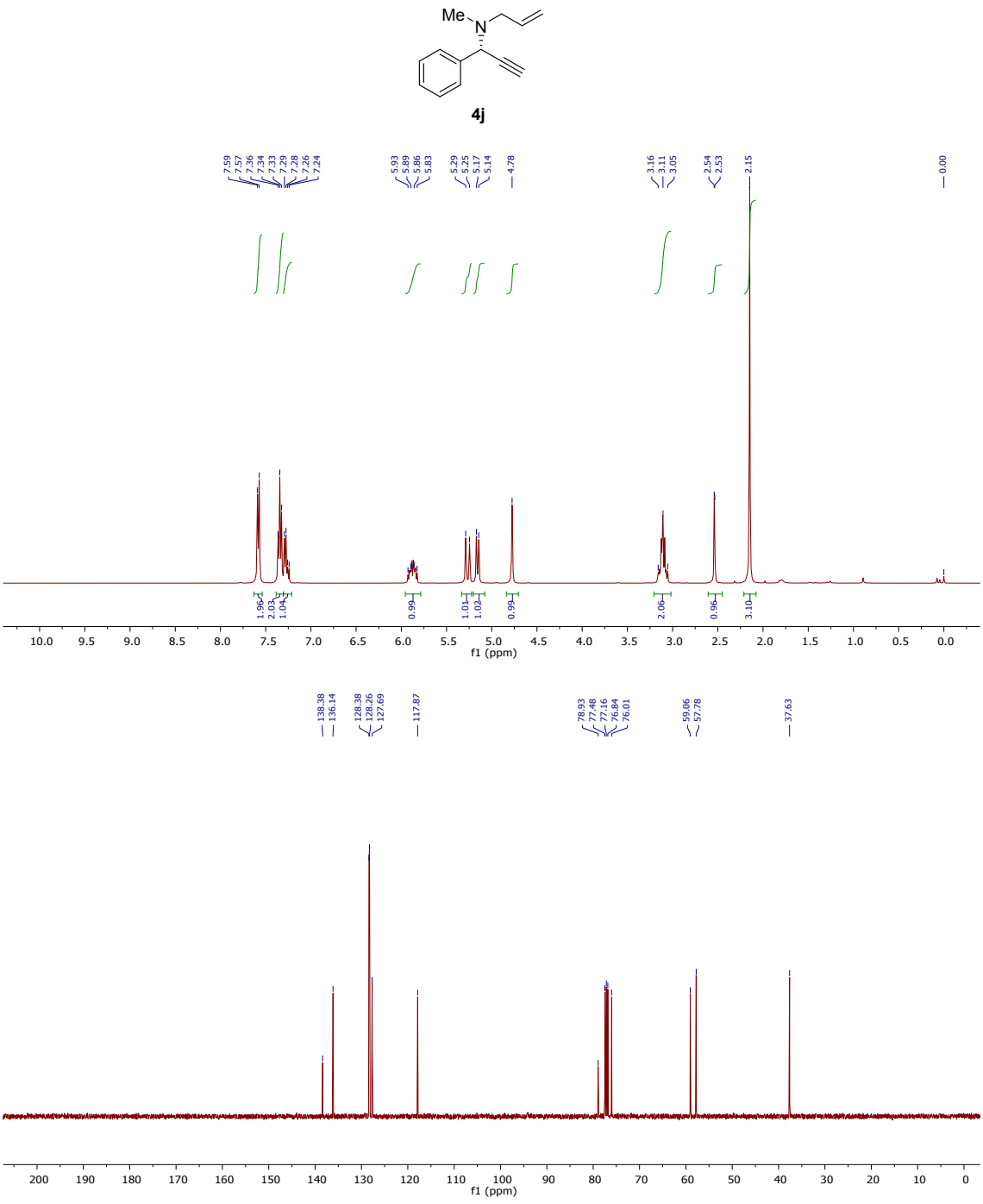


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	10.066	220.933	788.166	49.88	47.44	n.a.
2	11.707	222.013	873.109	50.12	52.56	n.a.

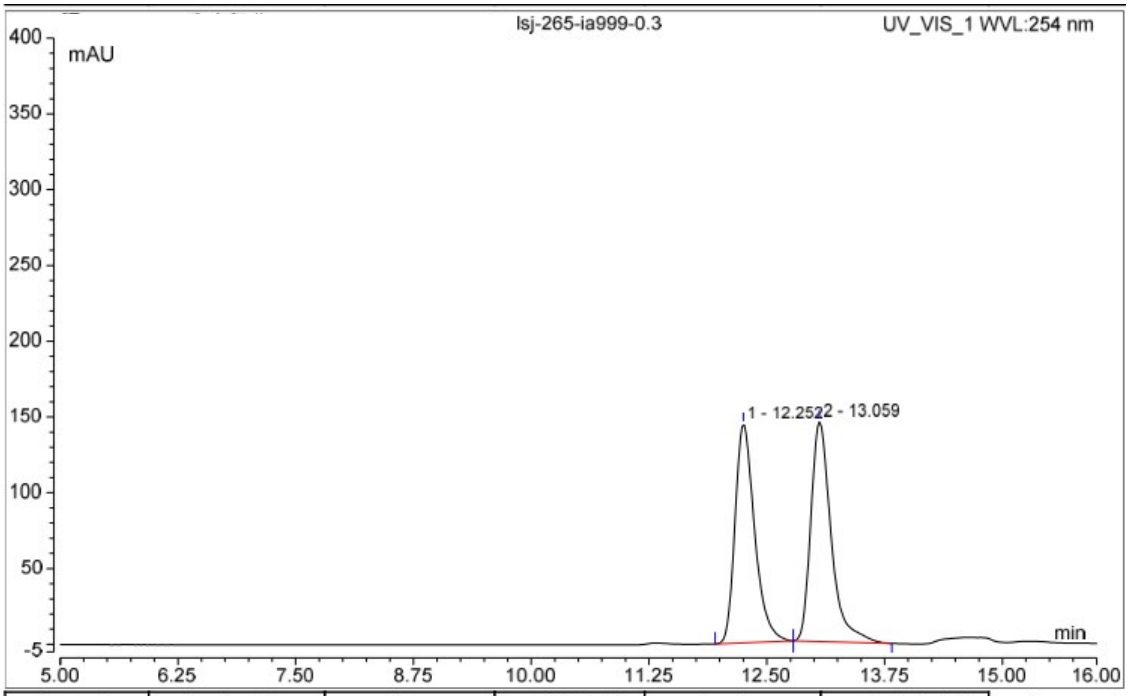
HPLC trace of 4i



peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	10.299	787.972	2237.957	96.97	96.05	n.a.
2	11.999	24.655	91.934	3.03	3.95	n.a.

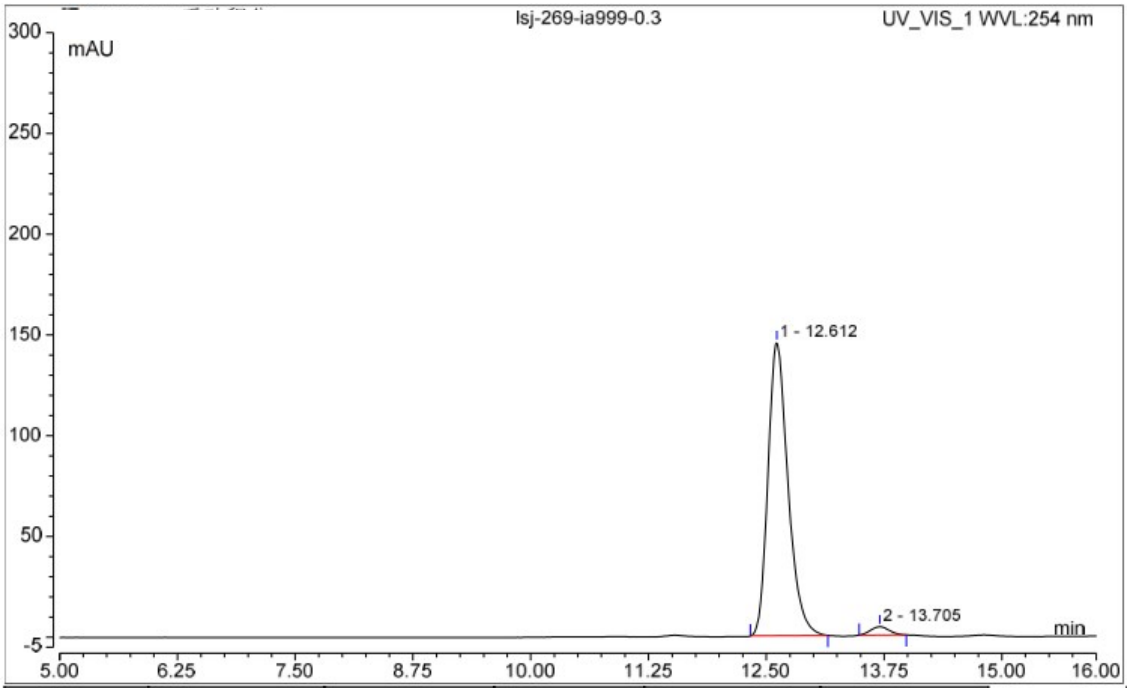

Me
N
4j
7.59
7.57
7.36
7.34
7.33
7.29
7.28
7.26
7.24
5.93
5.89
5.86
5.83
5.29
5.25
5.17
5.14
4.78
3.16
3.11
3.05
2.54
2.53
2.15
0.00
1.96
2.03
1.04
0.99
1.01
1.02
0.99
2.06
0.96
3.10
f1 (ppm)
138.38
136.14
128.38
128.26
127.69
117.87
78.93
77.48
77.16
76.84
76.01
59.06
57.78
37.63
f1 (ppm)

HPLC trace of *rac*-4j

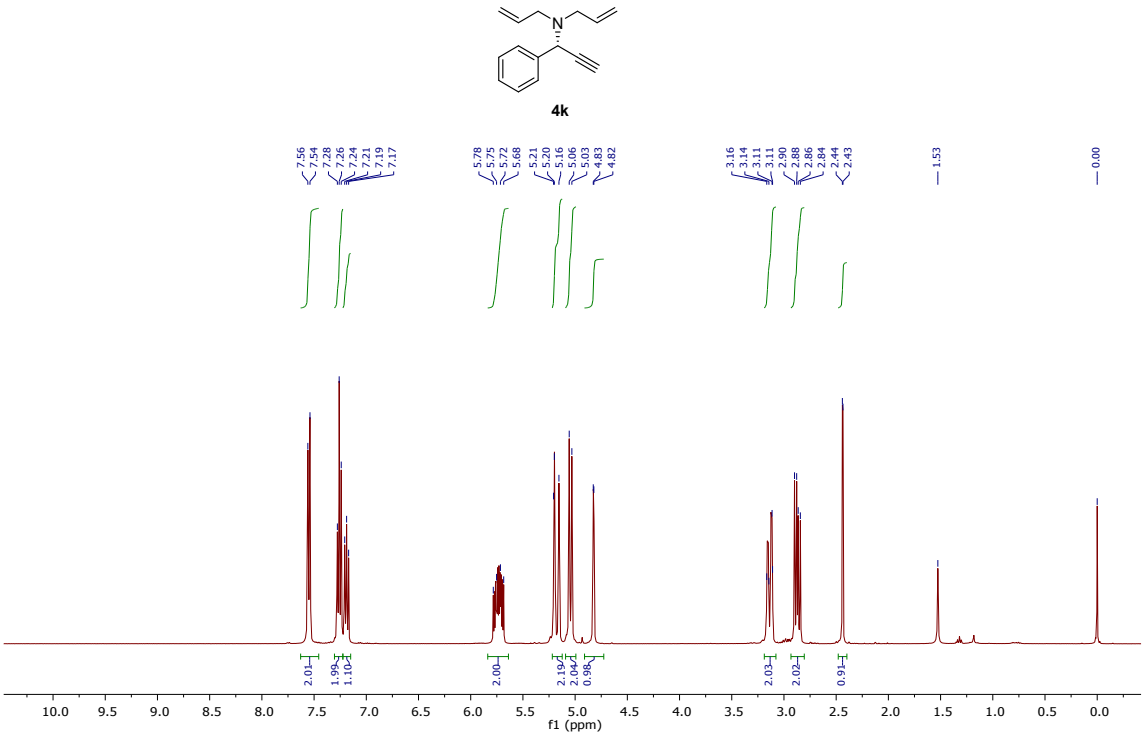


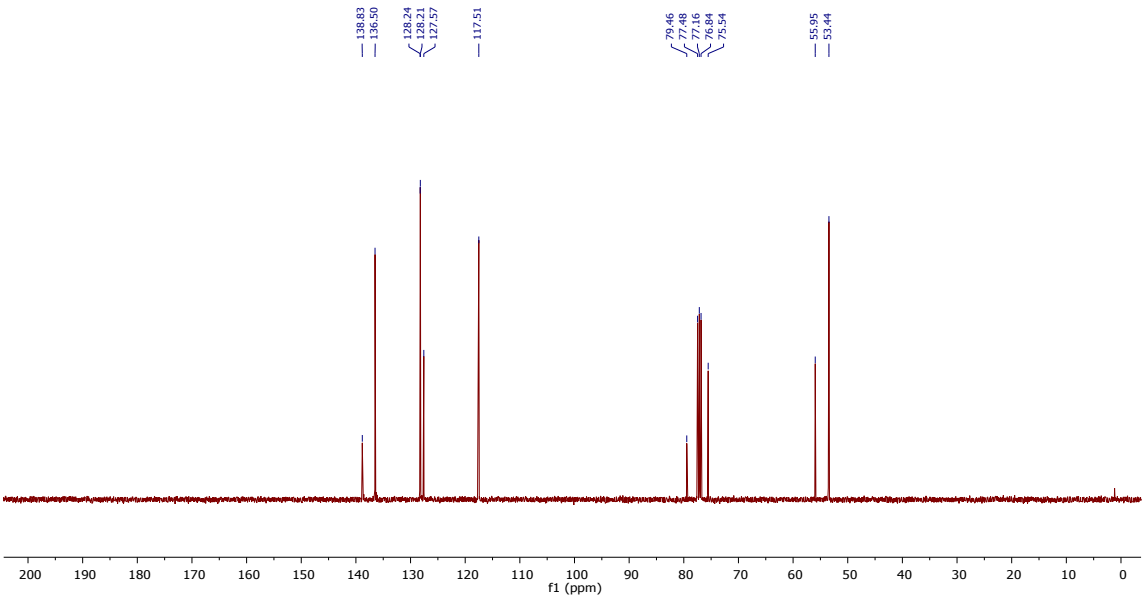
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	12.252	34.780	144.308	48.94	49.88	n.a.
2	13.059	36.281	145.007	51.06	50.12	n.a.

HPLC trace of 4j

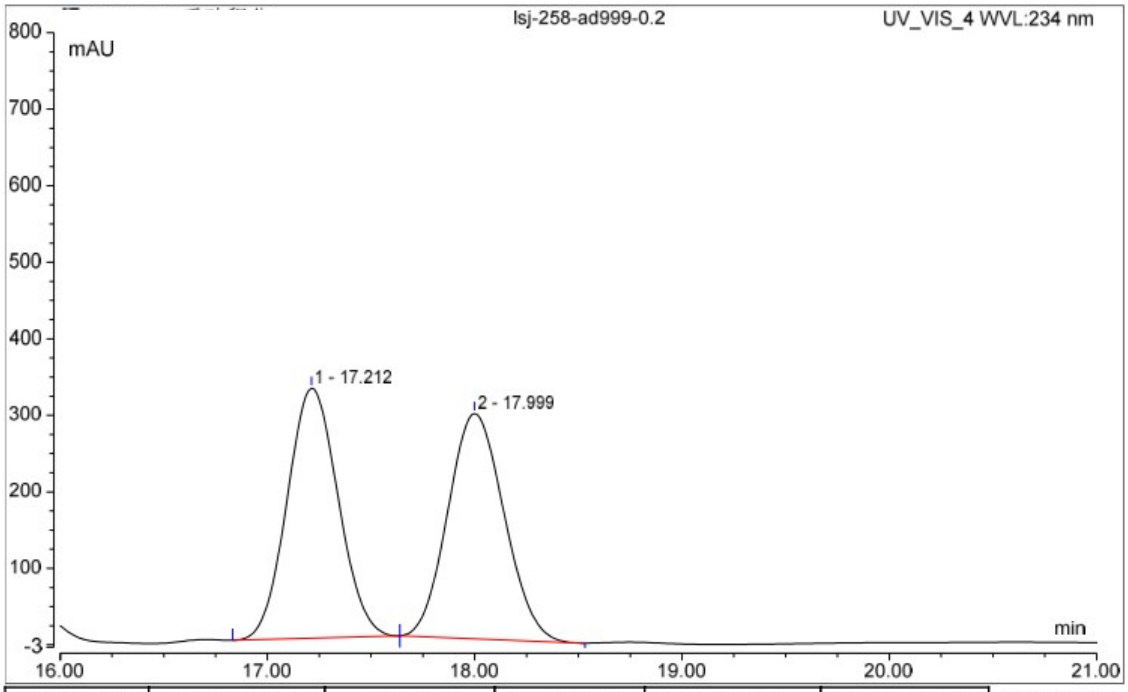


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	12.612	35.814	145.487	97.44	97.22	n.a.
2	13.705	0.942	4.155	2.56	2.78	n.a.


4k
7.56
7.54
7.28
7.26
7.24
7.21
7.19
7.17
5.78
5.75
5.72
5.68
5.21
5.20
5.16
5.06
5.03
4.83
4.82
3.16
3.14
3.11
3.11
2.90
2.88
2.86
2.84
2.44
2.43
1.53
0.00
2.01
1.99
1.10
2.00
2.19
2.04
0.98
2.03
2.02
0.91
f1 (ppm)

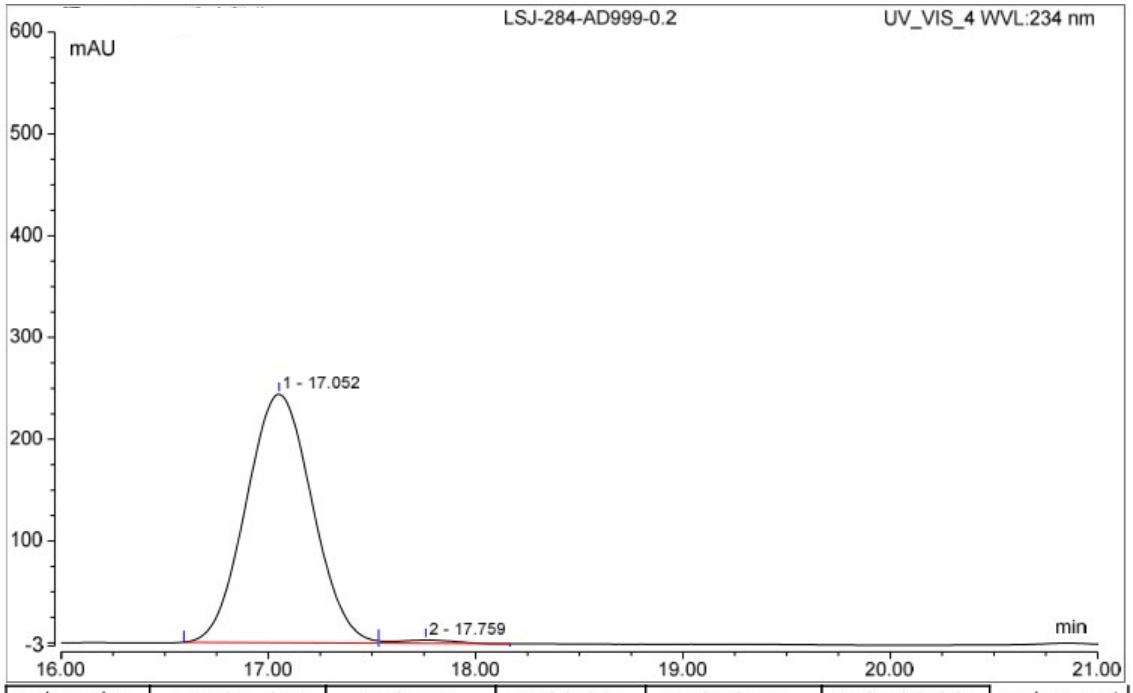

138.83
136.50
128.24
128.21
127.57
117.51
79.46
77.48
77.16
76.84
75.54
55.95
53.44
f1 (ppm)

HPLC trace of *rac*-4k

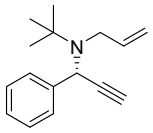


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	17.212	93.103	326.849	50.15	52.61	n.a.
2	17.999	92.551	294.450	49.85	47.39	n.a.

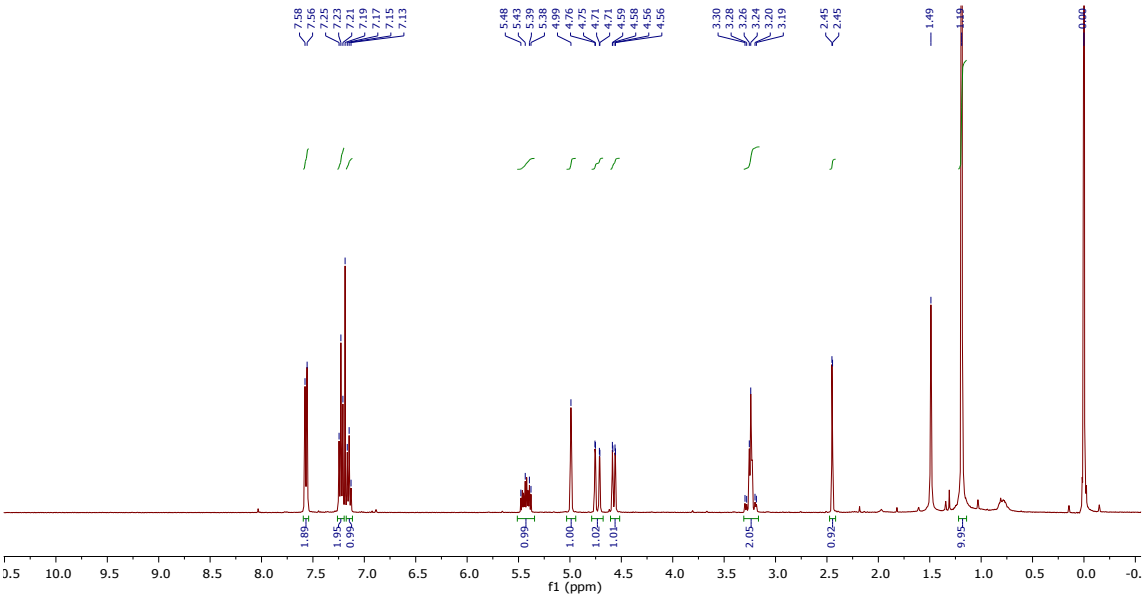
HPLC trace of 4k

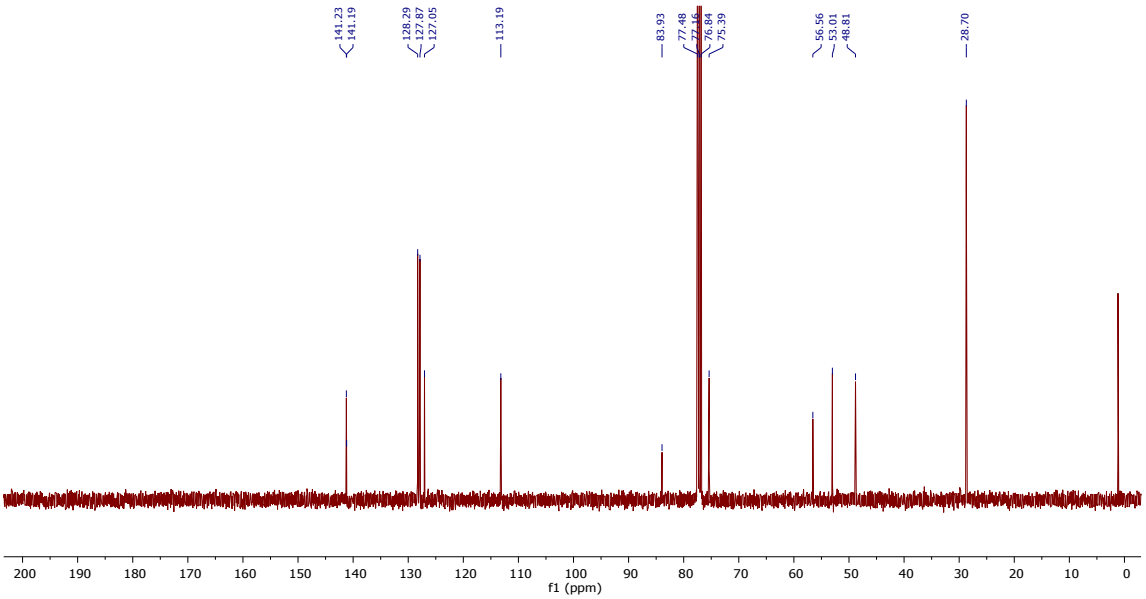


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	17.052	90.075	244.063	98.86	98.74	n.a.
2	17.759	1.038	3.127	1.14	1.26	n.a.

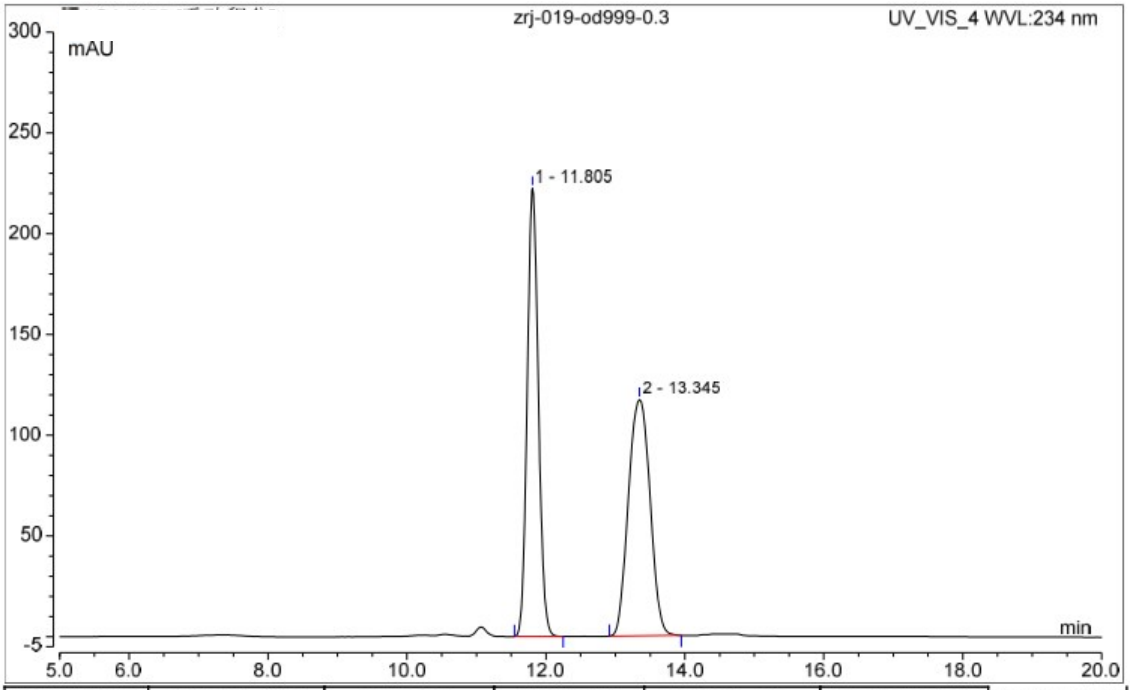


4l


7.58
7.56
7.25
7.23
7.21
7.19
7.17
7.15
7.13
5.48
5.43
5.39
5.38
4.99
4.76
4.75
4.71
4.71
4.59
4.58
4.56
4.56
3.30
3.28
3.26
3.24
3.20
3.19
2.45
2.45
1.49
1.10
0.00
1.89
1.95
0.99
0.99
1.00
1.02
1.01
2.05
0.92
9.95
f1 (ppm)

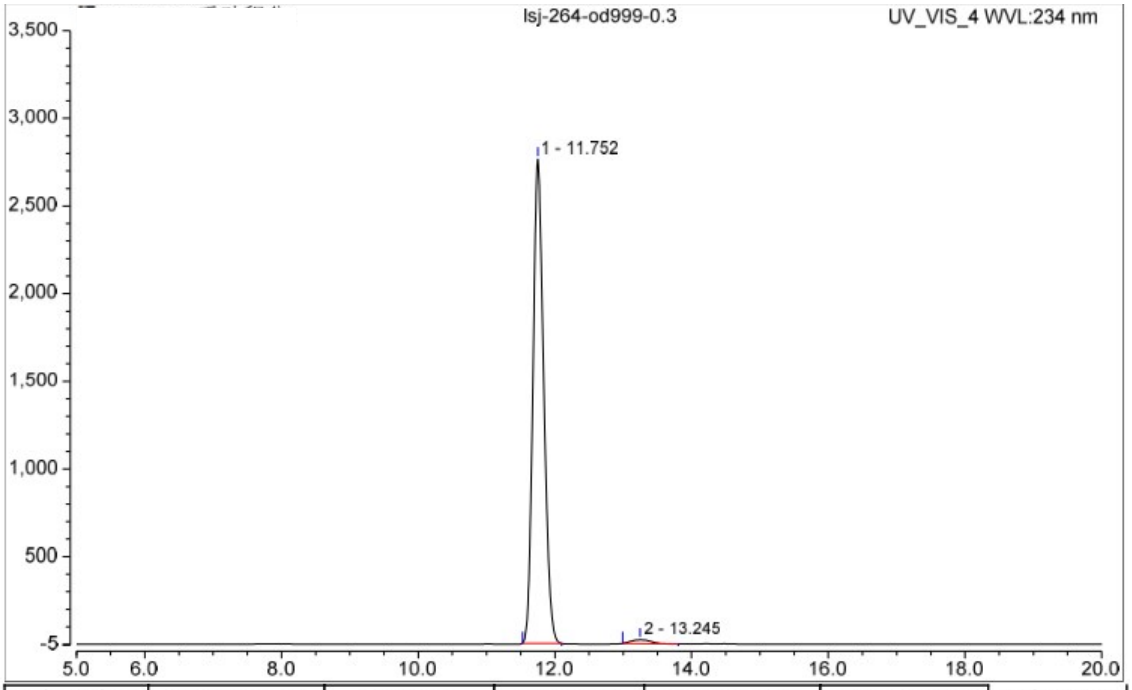

141.23
141.19
128.29
127.87
127.05
113.19
83.93
77.48
77.16
76.84
75.39
56.56
53.01
48.81
28.70
f1 (ppm)

HPLC trace of *rac*-4l

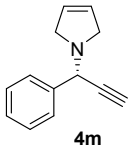


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	11.805	41.379	222.590	49.39	65.48	n.a.
2	13.345	42.400	117.365	50.61	34.52	n.a.

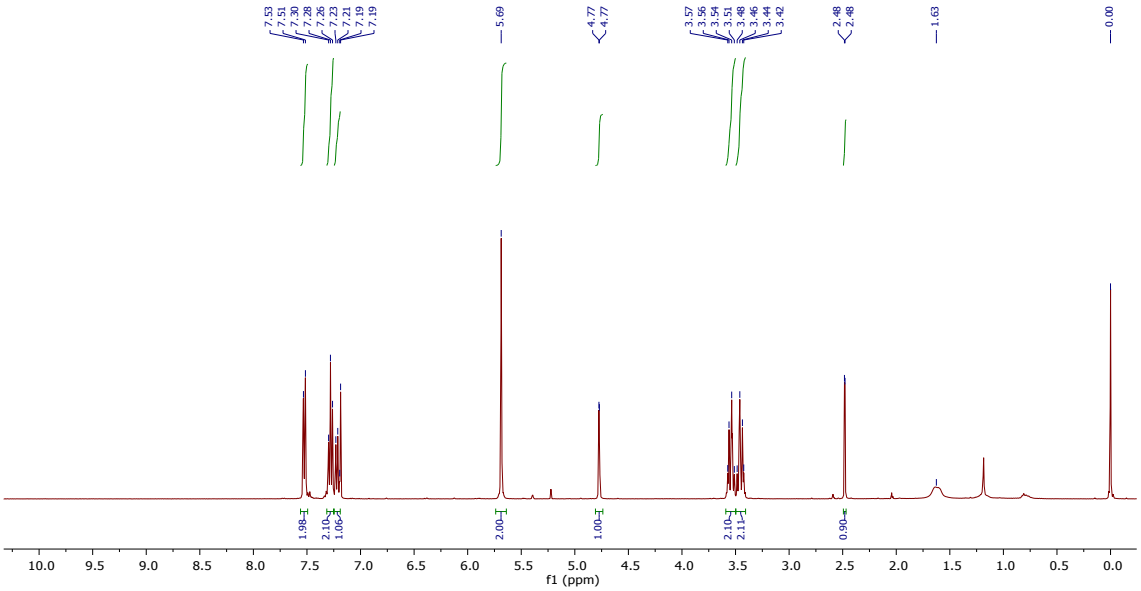
HPLC trace of 4l

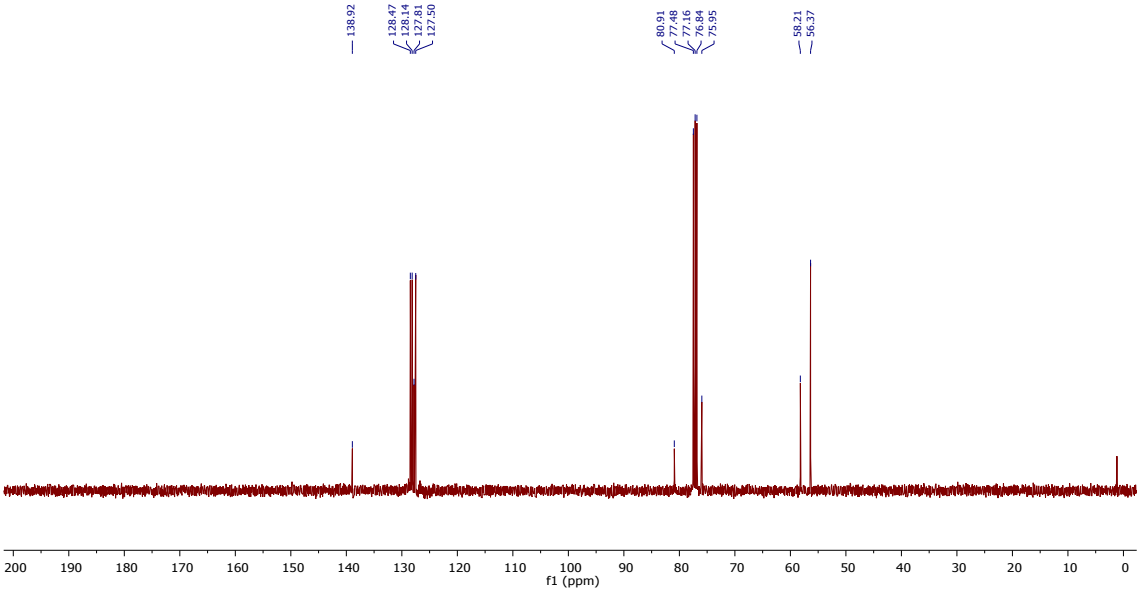


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	11.752	504.202	2762.690	98.64	99.24	n.a.
2	13.245	6.964	21.152	1.36	0.76	n.a.

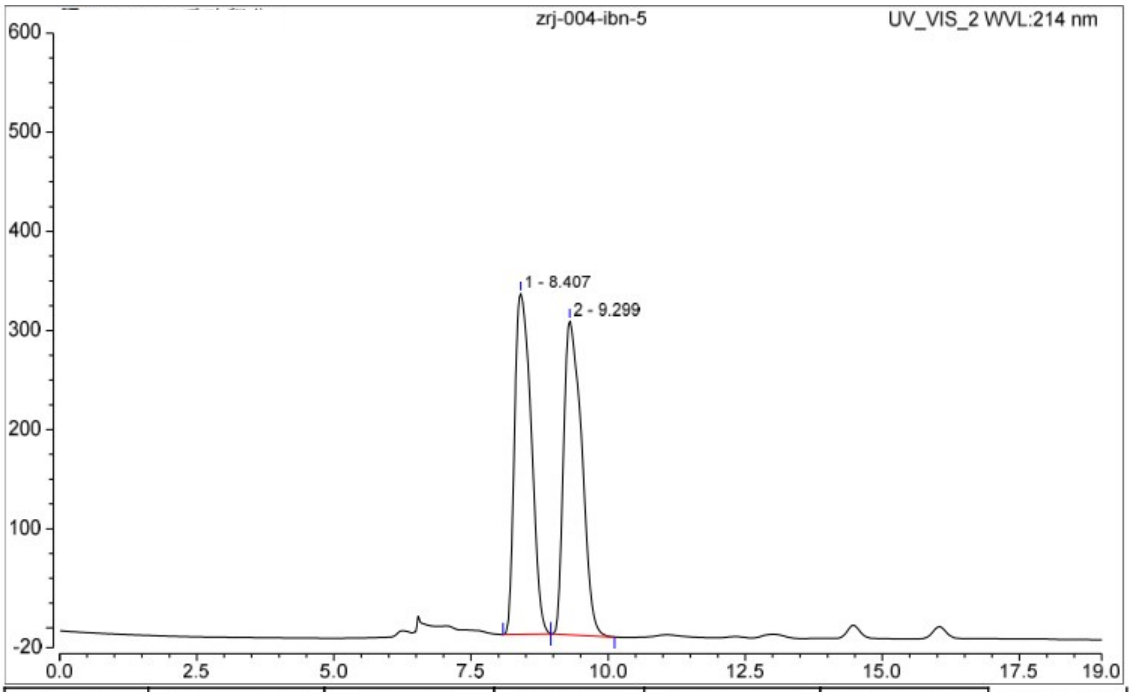


4m


7.53
7.51
7.30
7.28
7.26
7.23
7.21
7.19
7.19
5.69
4.77
4.77
3.57
3.56
3.54
3.51
3.48
3.46
3.44
3.42
2.48
2.48
1.63
0.00
1.98
2.10
1.06
2.00
1.00
2.10
2.11
0.90
f1 (ppm)

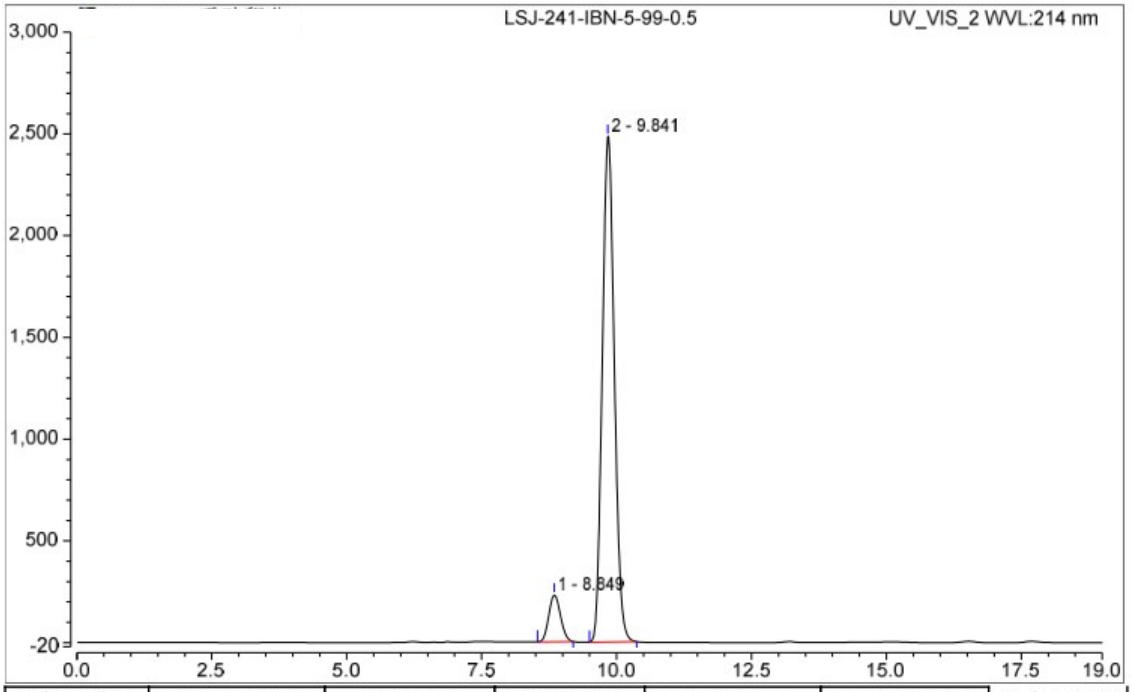

138.92
128.47
128.14
127.81
127.50
80.91
77.48
77.16
76.84
75.95
58.21
56.37
f1 (ppm)

HPLC trace of *rac*-4m

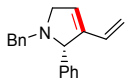


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	8.407	120.901	344.050	49.95	52.06	n.a.
2	9.299	121.136	316.879	50.05	47.94	n.a.

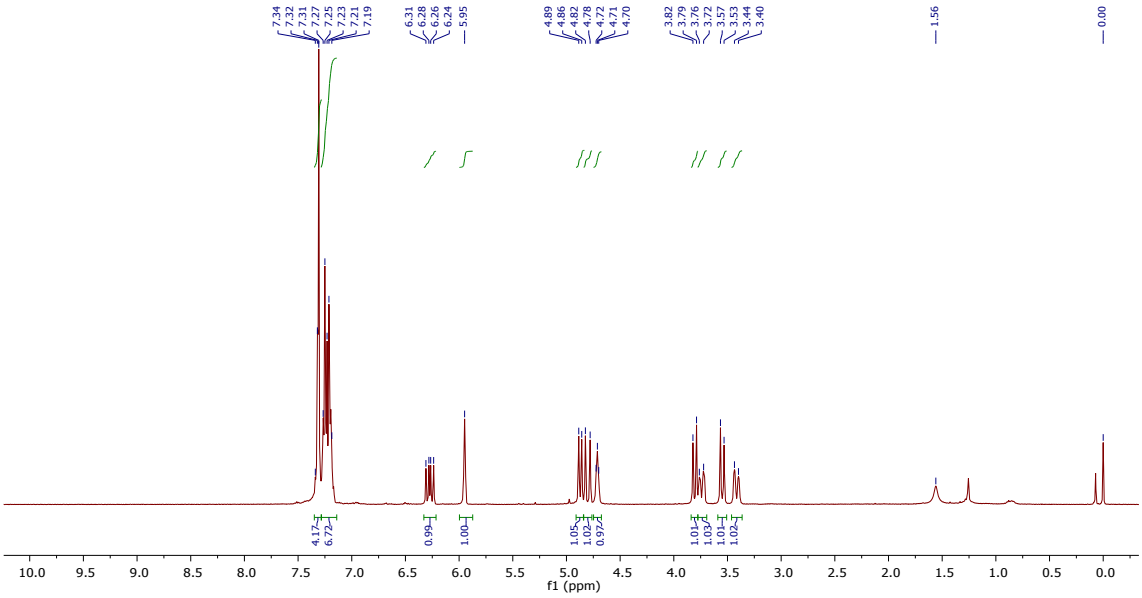
HPLC trace of 4m

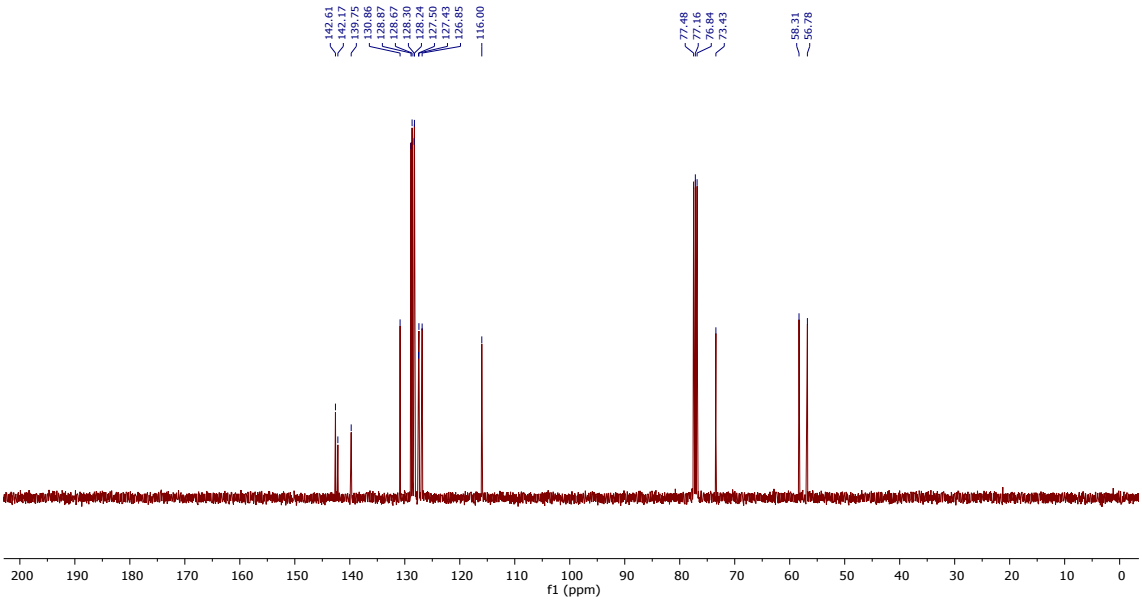


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	8.849	57.571	230.308	8.16	8.48	n.a.
2	9.841	648.322	2484.525	91.84	91.52	n.a.

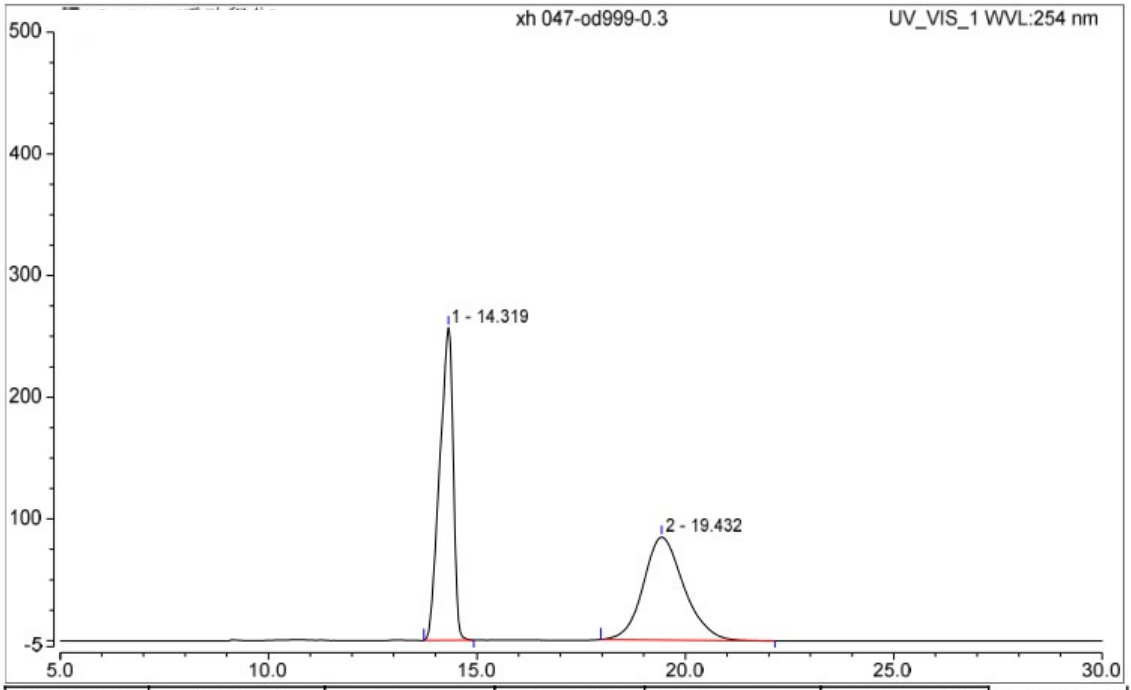

Bn
N
Ph

7


7.34
7.32
7.31
7.27
7.25
7.23
7.21
7.19
6.31
6.28
6.26
6.24
5.95
4.89
4.86
4.82
4.78
4.72
4.71
4.70
3.82
3.79
3.76
3.72
3.57
3.53
3.44
3.40
1.56
0.00
4.17
6.72
0.99
1.00
1.05
1.02
0.97
1.01
1.03
1.01
1.02
f1 (ppm)

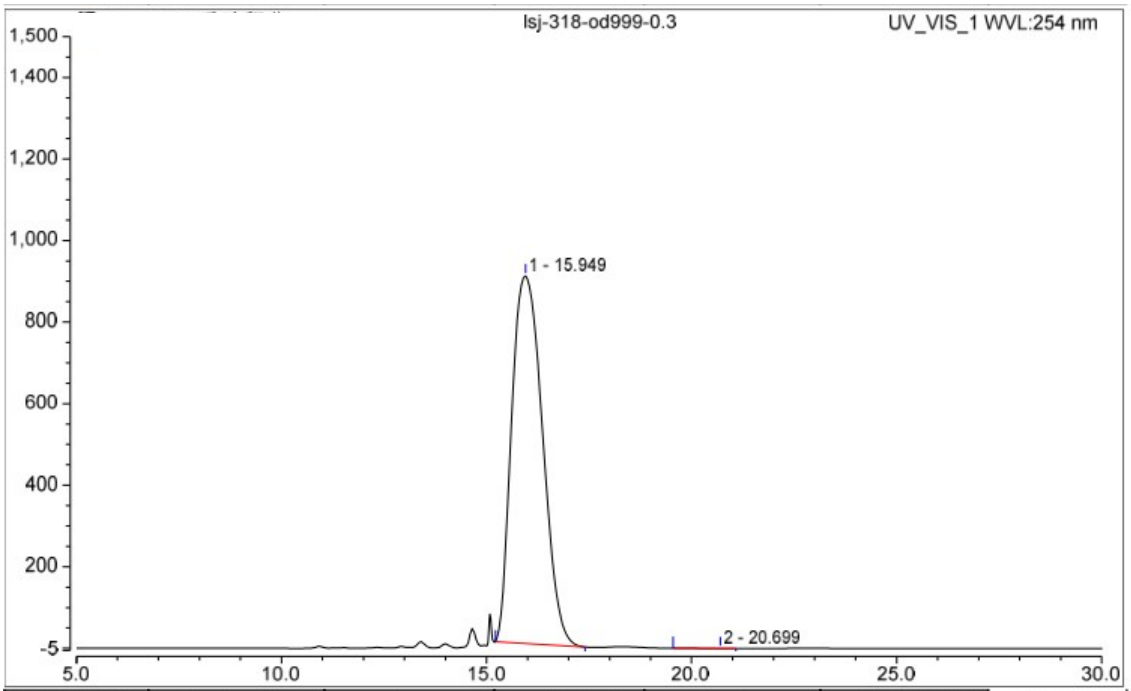

142.61
142.17
139.75
130.86
128.87
128.57
128.30
128.24
127.50
127.43
126.85
116.00
77.48
77.16
76.84
73.43
58.31
56.78
f1 (ppm)

HPLC trace of *rac*-7

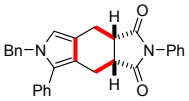


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	14.319	96.483	257.034	50.30	75.26	n.a.
2	19.432	95.345	84.492	49.70	24.74	n.a.

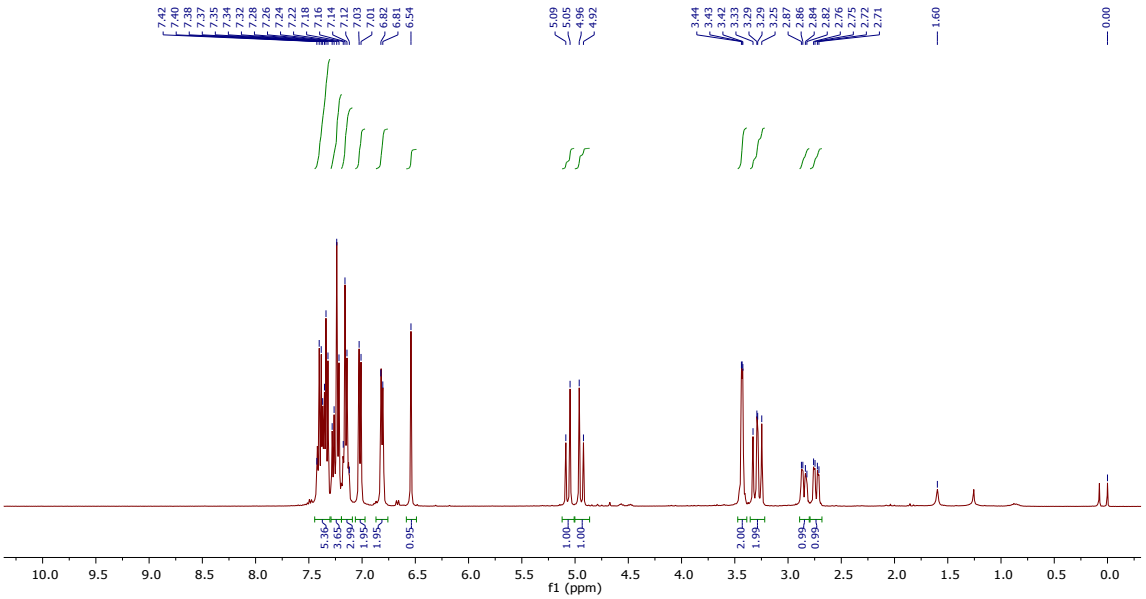
HPLC trace of 7

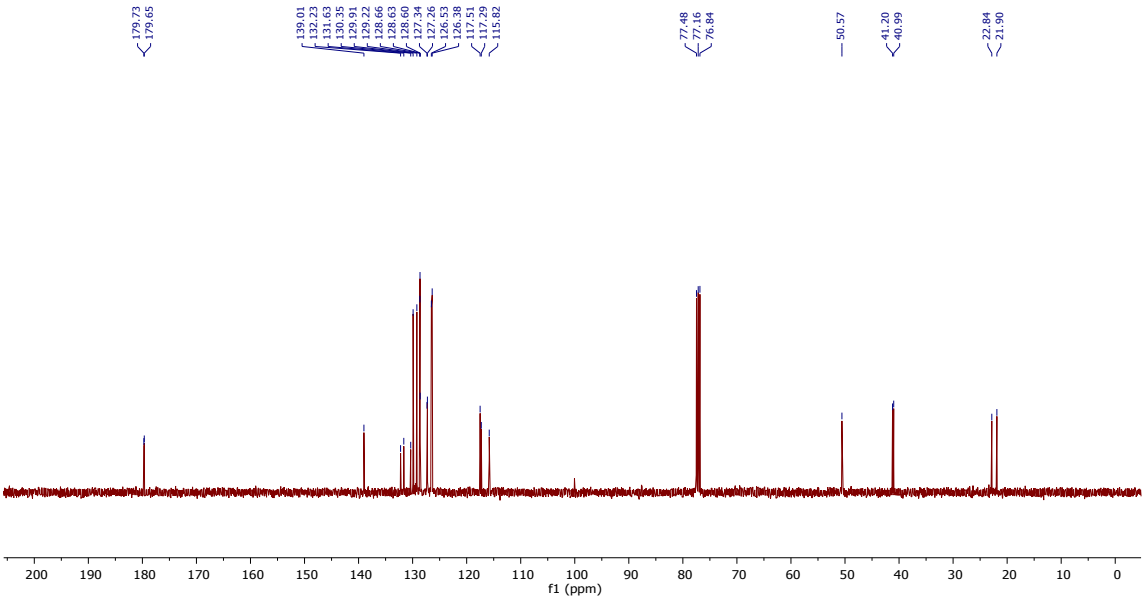


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	15.949	785.616	901.446	99.99	99.99	n.a.
2	20.699	0.117	0.087	0.01	0.01	n.a.

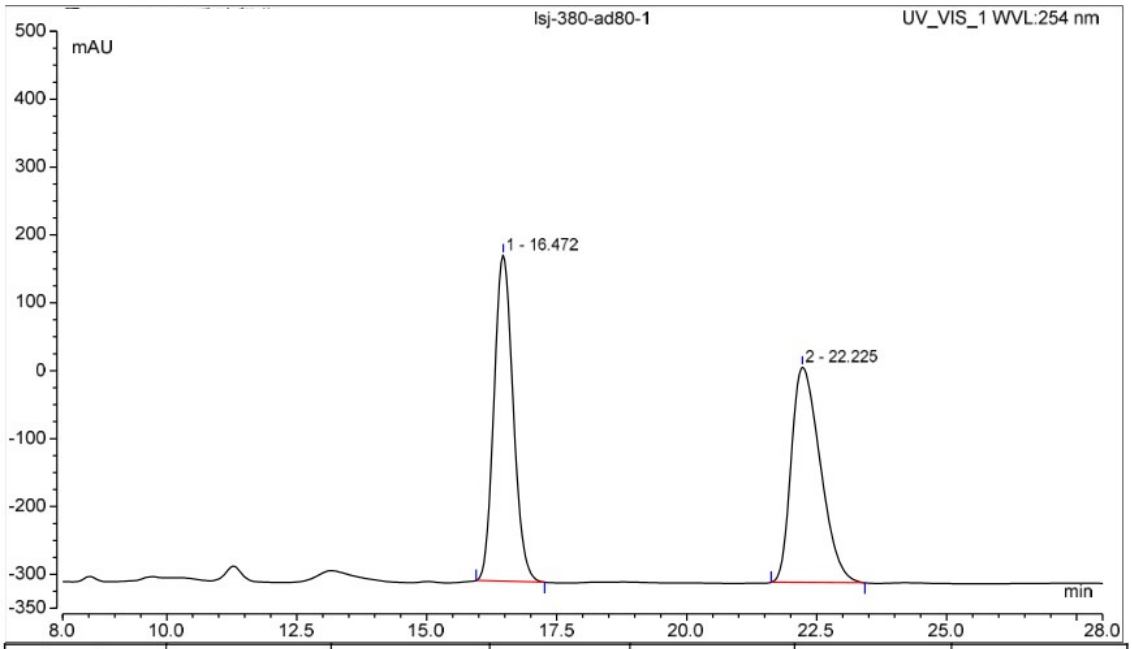

H
O
Bn−N
N−Ph
Ph
H
O

8


7.42
7.40
7.38
7.37
7.35
7.34
7.32
7.28
7.26
7.24
7.22
7.18
7.16
7.14
7.12
7.03
7.01
6.82
6.81
6.54
5.09
5.05
4.96
4.92
3.44
3.43
3.42
3.33
3.29
3.29
3.25
2.87
2.86
2.84
2.82
2.76
2.75
2.72
2.71
1.60
0.00
5.36
3.65
2.99
1.95
1.95
0.95
1.00
1.00
2.00
1.99
0.99
0.99
f1 (ppm)

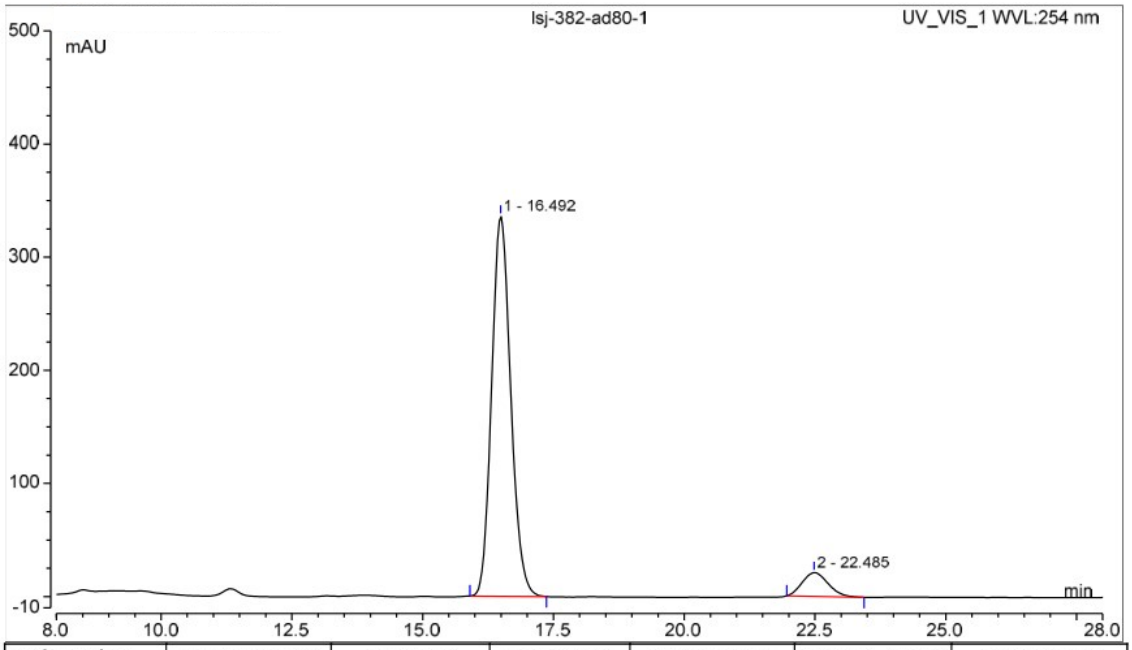

179.73
179.65
139.01
132.23
131.63
130.35
129.91
129.22
128.66
128.63
128.60
127.34
127.26
126.53
126.38
117.51
117.29
115.82
77.48
77.16
76.84
50.57
41.20
40.99
22.84
21.90
f1 (ppm)

HPLC trace of *rac*-8

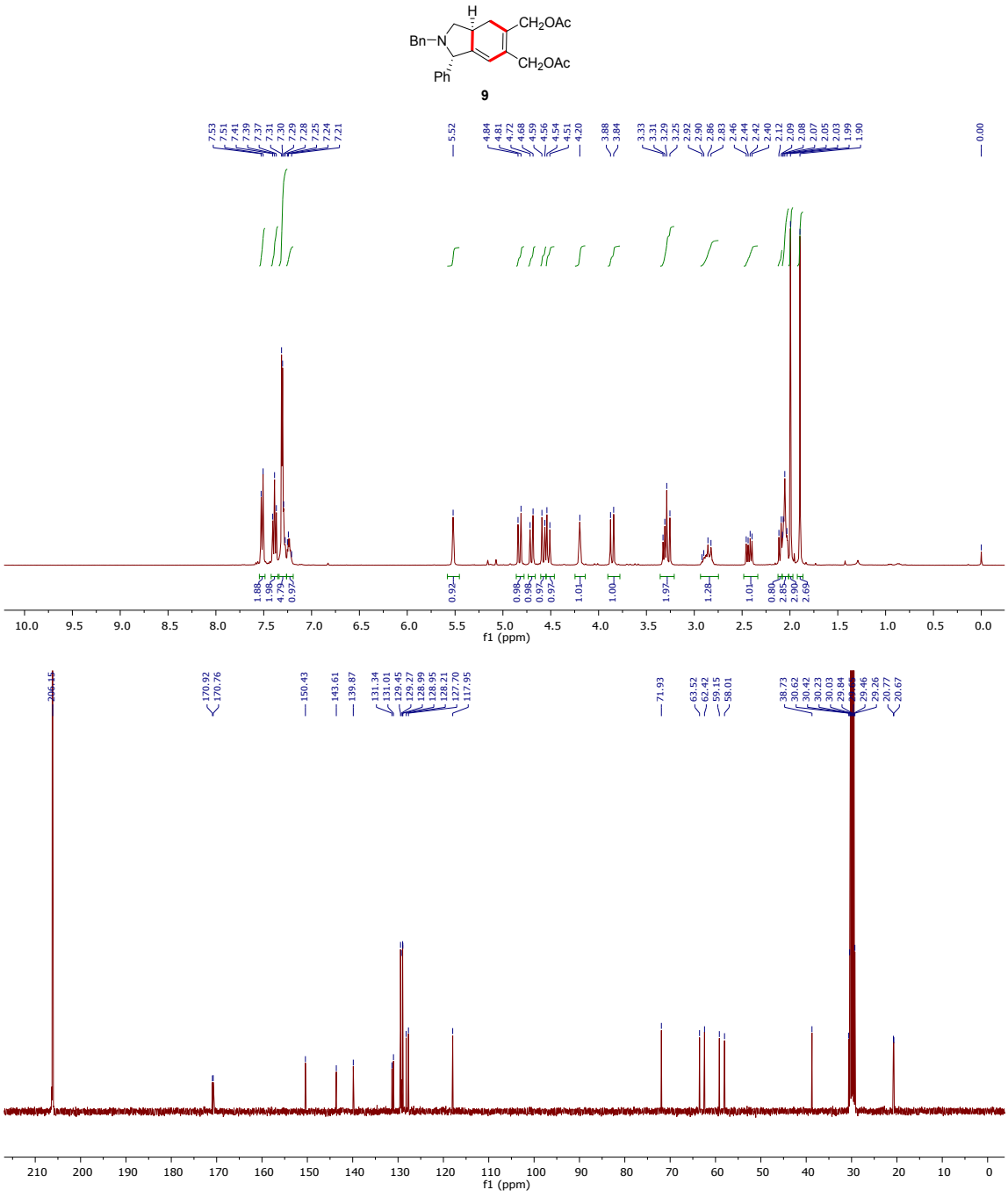


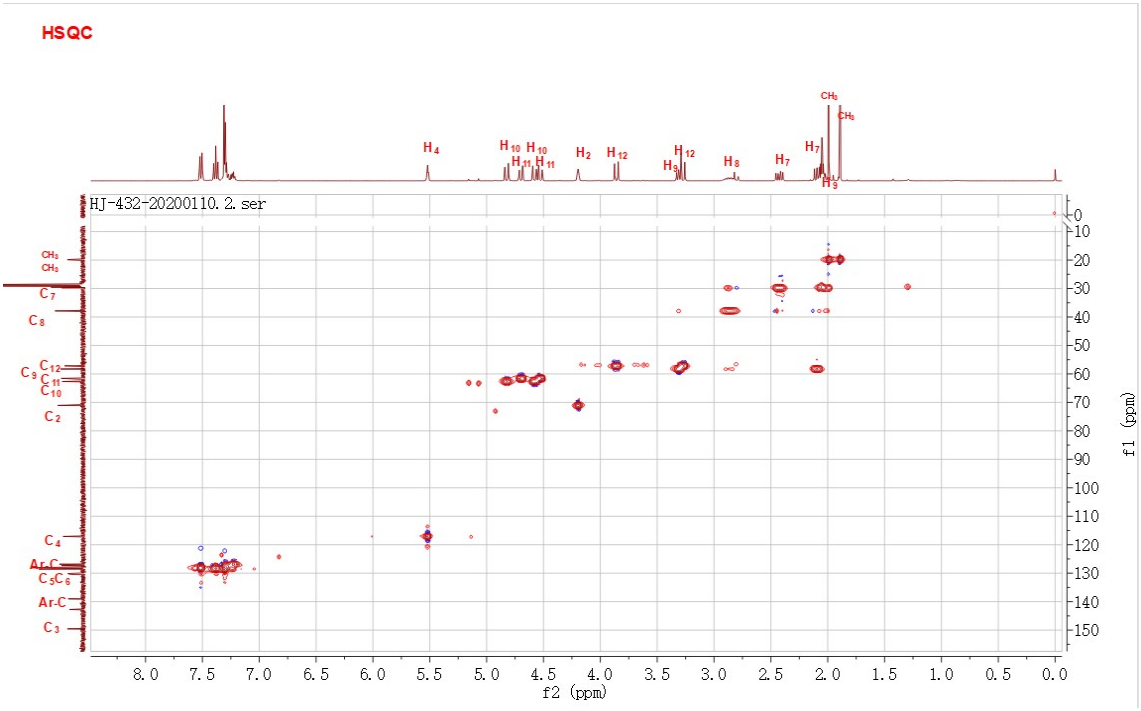
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	16.472	205.284	480.475	50.00	60.23	n.a.
2	22.225	205.314	317.279	50.00	39.77	n.a.

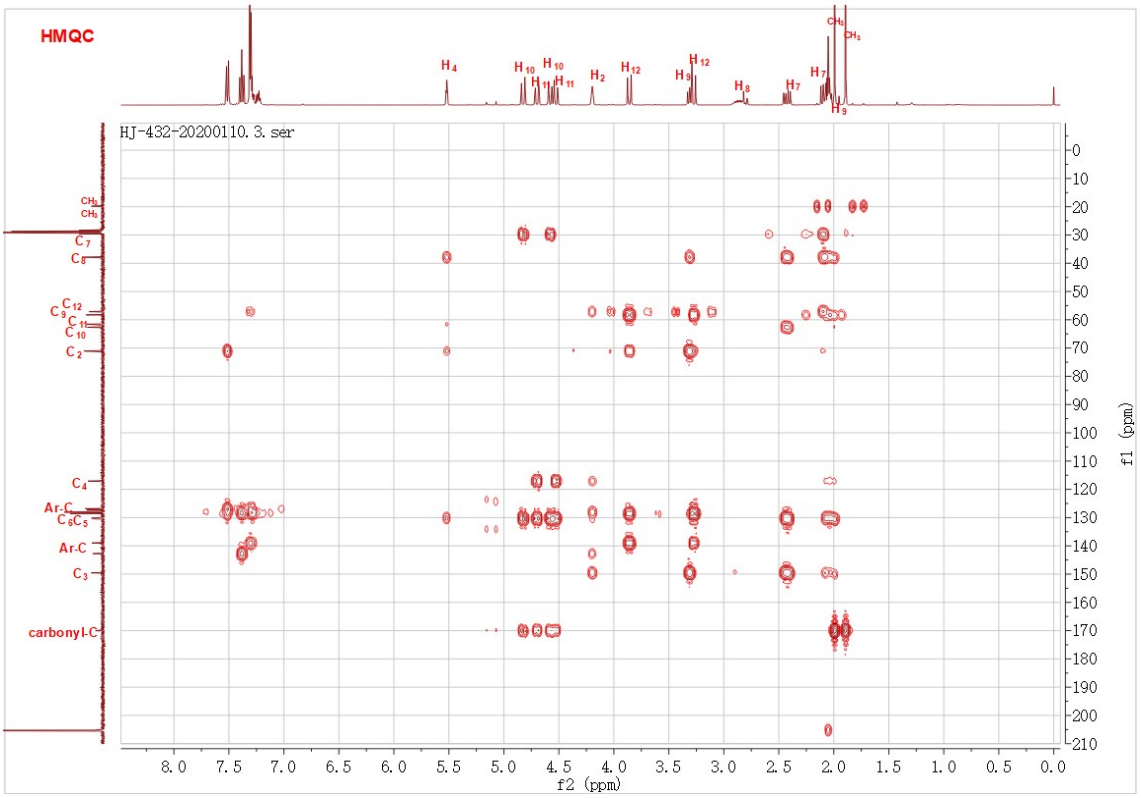
HPLC trace of 8

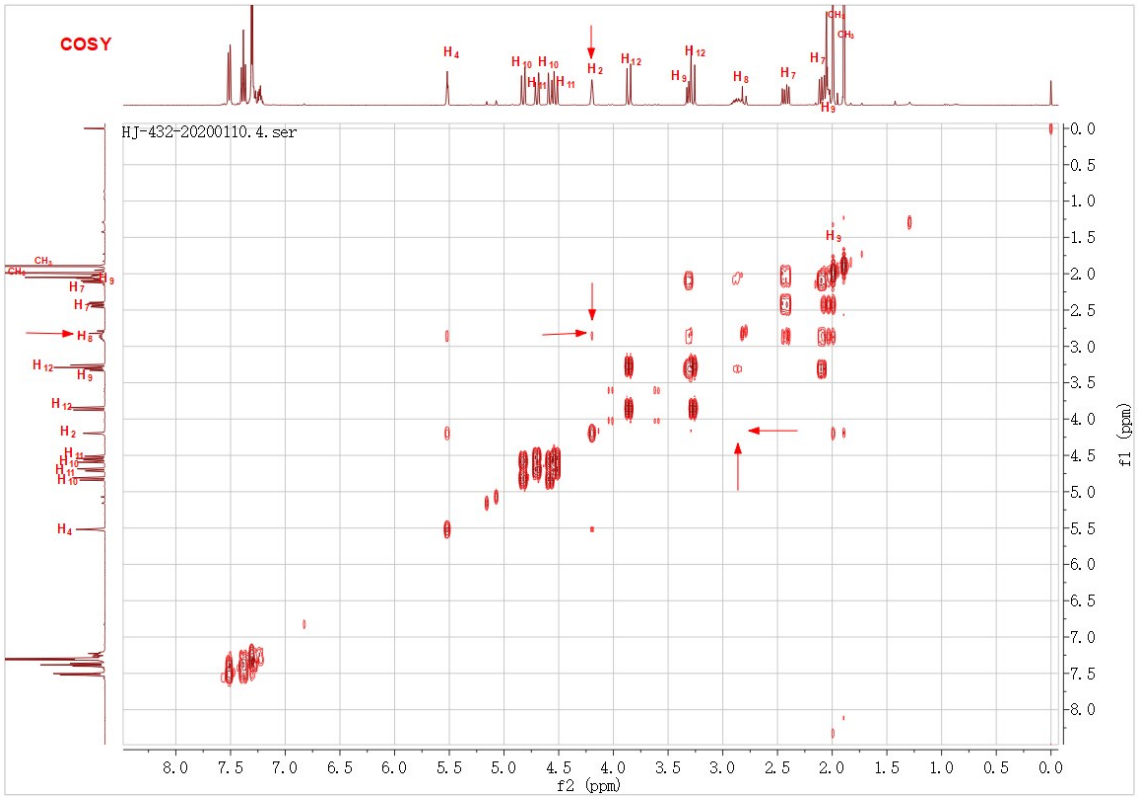


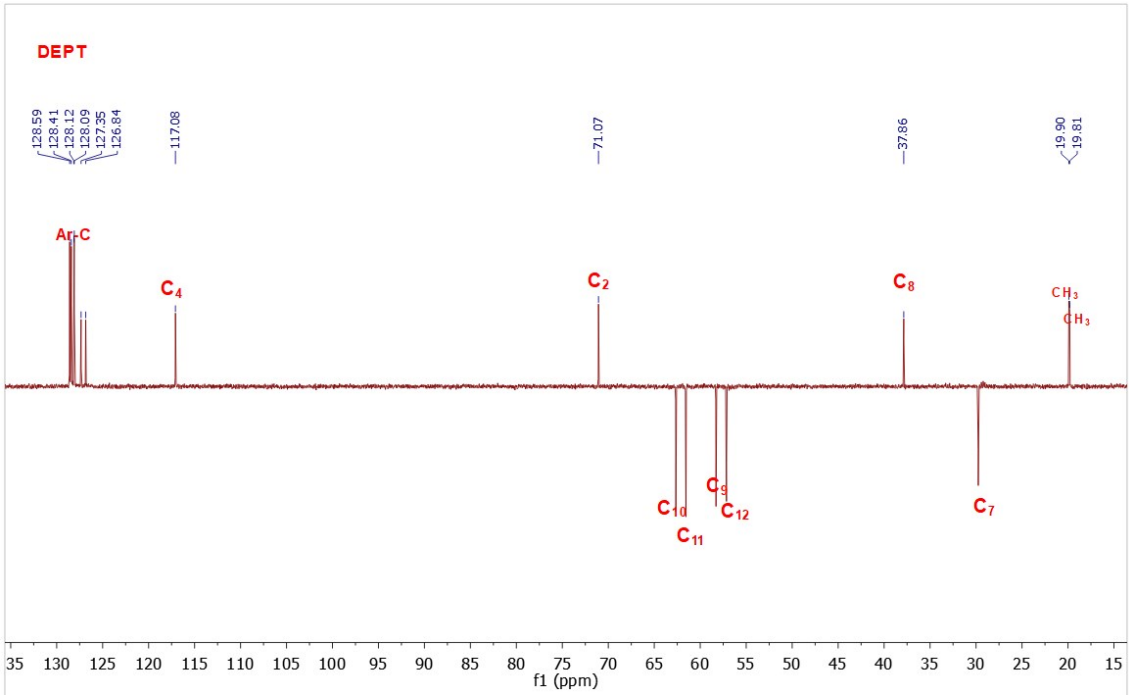
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	16.492	142.247	335.864	92.21	94.13	n.a.
2	22.485	12.013	20.963	7.79	5.87	n.a.


H
CH2OAc
Bn–N
CH2OAc
Ph
9
7.53
7.51
7.41
7.39
7.37
7.31
7.30
7.29
7.28
7.25
7.24
7.21
5.52
4.84
4.81
4.72
4.68
4.59
4.56
4.54
4.51
4.20
3.88
3.84
3.33
3.31
3.29
3.25
2.92
2.90
2.86
2.83
2.46
2.44
2.42
2.40
2.12
2.09
2.08
2.07
2.05
2.03
1.99
1.90
0.00
1.88
1.98
4.79
0.97
0.92
0.98
0.98
0.97
0.97
1.01
1.00
1.97
1.28
1.01
0.80
2.85
2.90
2.69
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)
206.15
170.92
170.76
150.43
143.61
139.87
131.34
131.01
129.45
129.27
128.99
128.95
128.21
127.70
117.95
71.93
63.52
62.42
59.15
58.01
38.73
30.62
30.42
30.23
30.03
29.84
29.46
29.26
20.77
20.67
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

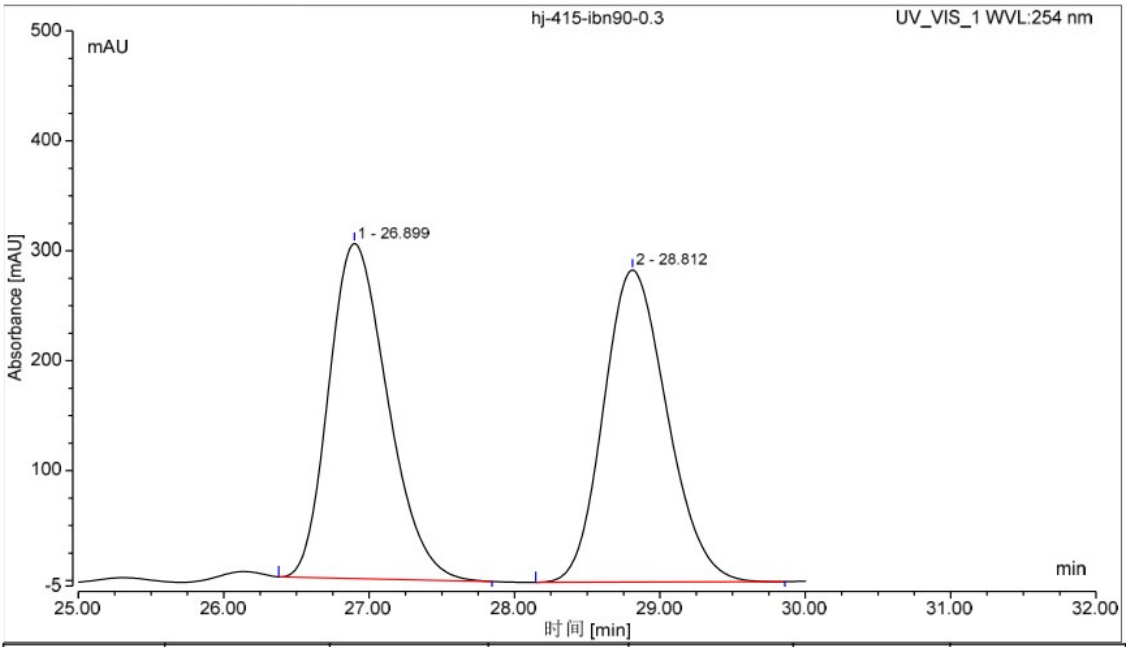

HSQC
HJ-432-20200110.2.ser
f2 (ppm)
f1 (ppm)


HMQC
HJ-432-20200110.3.ser
f2 (ppm)
f1 (ppm)


COSY
HJ-432-20200110.4.ser
f2 (ppm)
f1 (ppm)

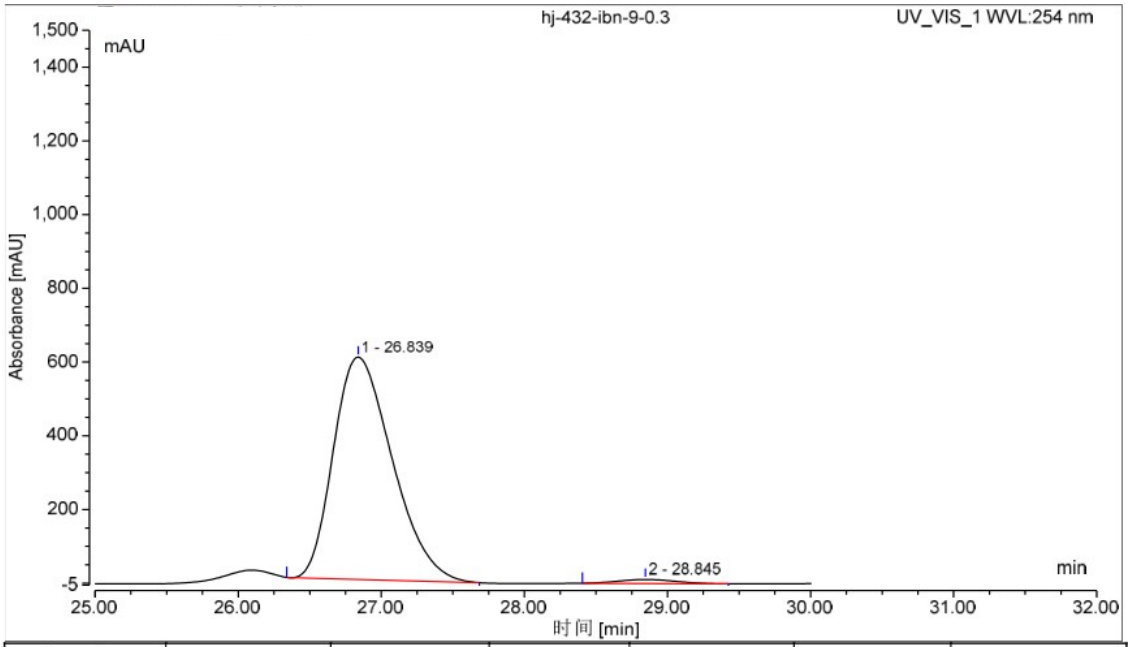

DEPT
128.59
128.41
128.12
128.09
127.35
126.84
117.08
71.07
37.86
19.90
19.81
Ar-C
C4
C2
C8
CH3
CH3
C10
C11
C9
C12
C7
f1 (ppm)

HPLC trace of *rac*-9

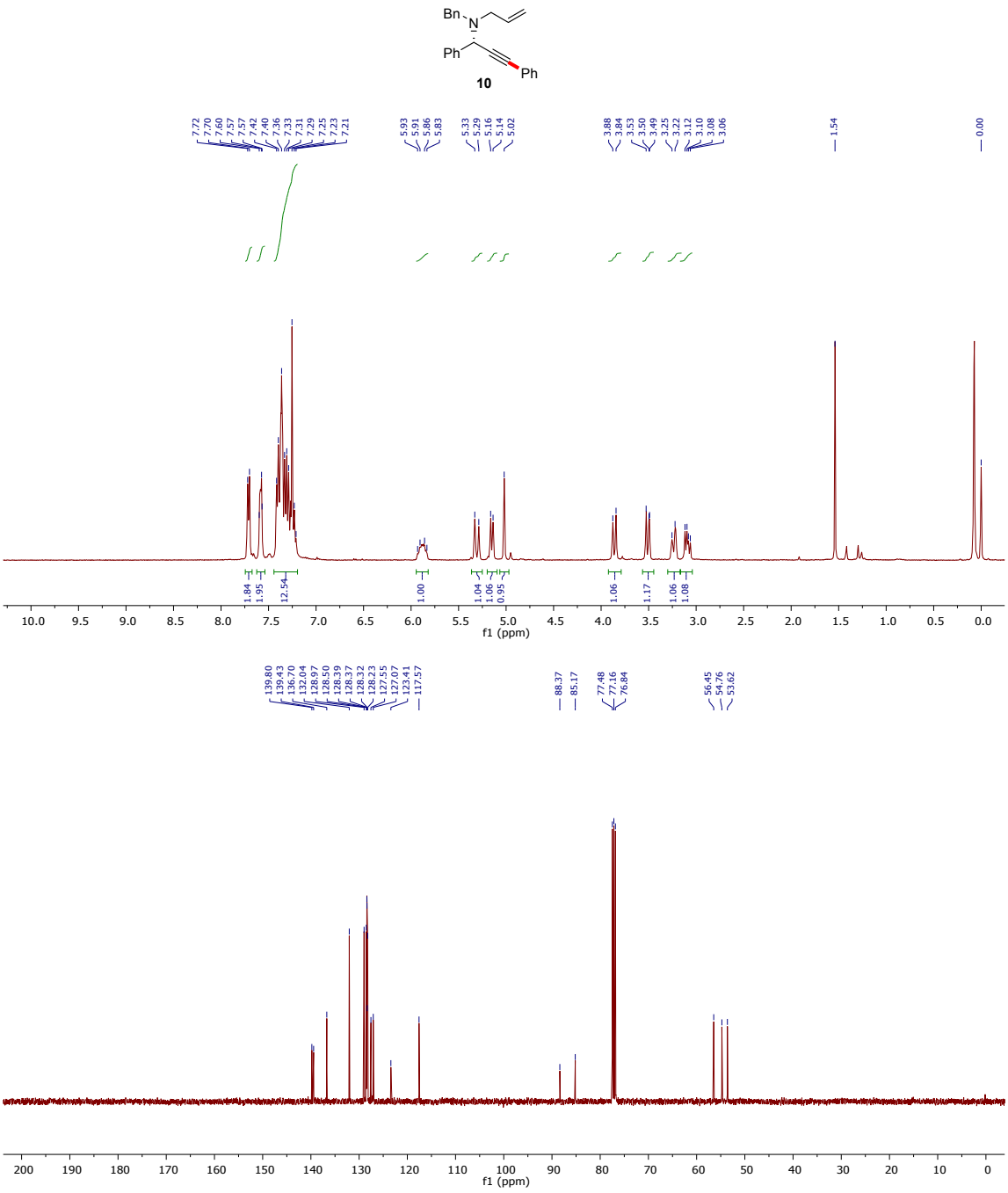


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	26.899	142.915	304.798	49.87	51.77	n.a.
2	28.812	143.680	283.929	50.13	48.23	n.a.

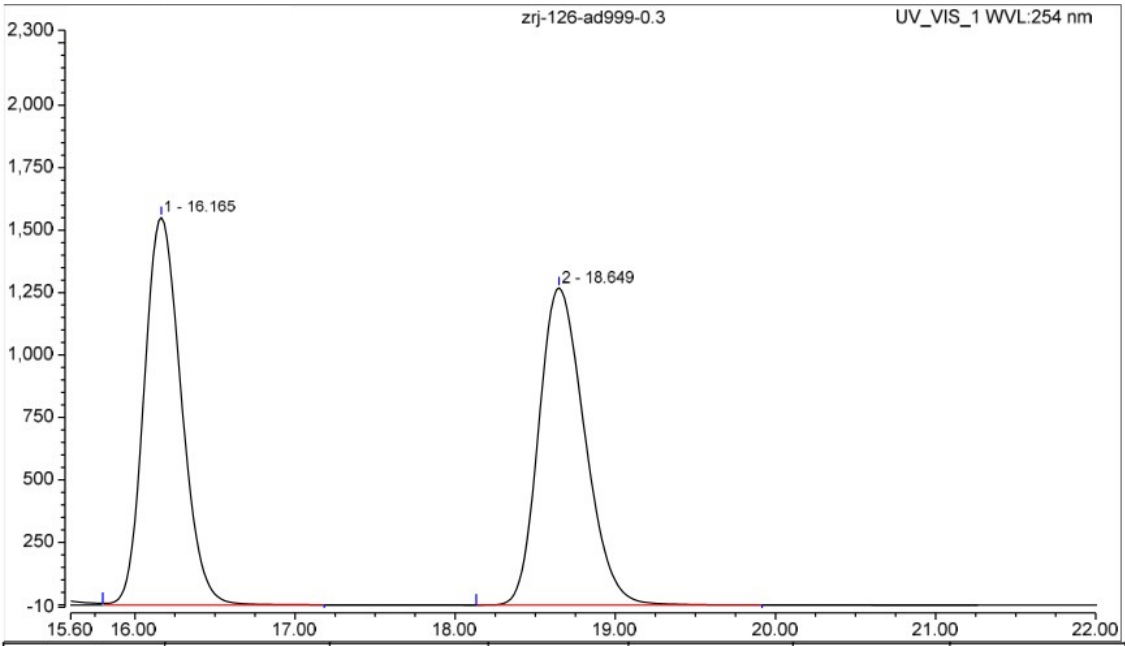
HPLC trace of 9



peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	26.839	287.817	602.981	98.31	98.24	n.a.
2	28.845	4.958	10.801	1.69	1.76	n.a.

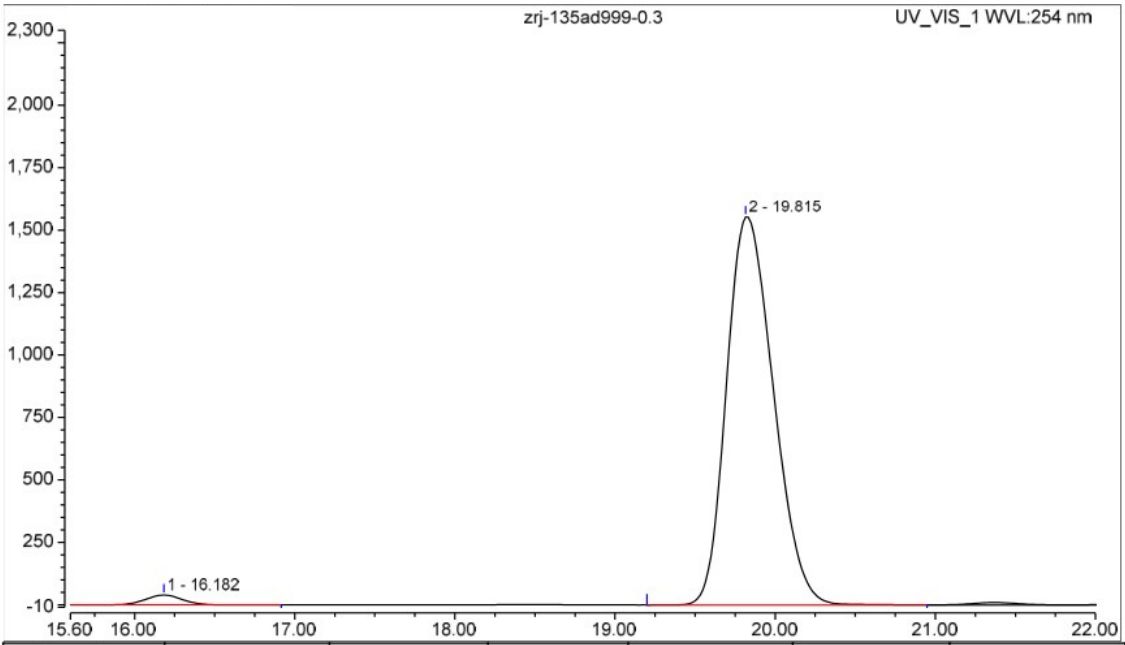

Bn
N
Ph
Ph
10
7.72
7.70
7.60
7.57
7.57
7.42
7.40
7.36
7.33
7.31
7.29
7.25
7.23
7.21
5.93
5.91
5.86
5.83
5.33
5.29
5.16
5.14
5.02
3.88
3.84
3.53
3.50
3.49
3.25
3.22
3.12
3.10
3.08
3.06
1.54
0.00
1.84
1.95
12.54
1.00
1.04
1.06
0.95
1.06
1.17
1.06
1.08
f1 (ppm)
139.80
139.43
136.70
132.04
128.97
128.50
128.39
128.37
128.32
128.23
127.55
127.07
123.41
117.57
88.37
85.17
77.48
77.16
76.84
56.45
54.76
53.62
f1 (ppm)

HPLC trace of *rac*-10

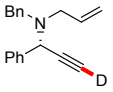


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	16.165	415.227	1551.563	49.63	54.99	n.a.
2	18.649	421.403	1269.751	50.37	45.01	n.a.

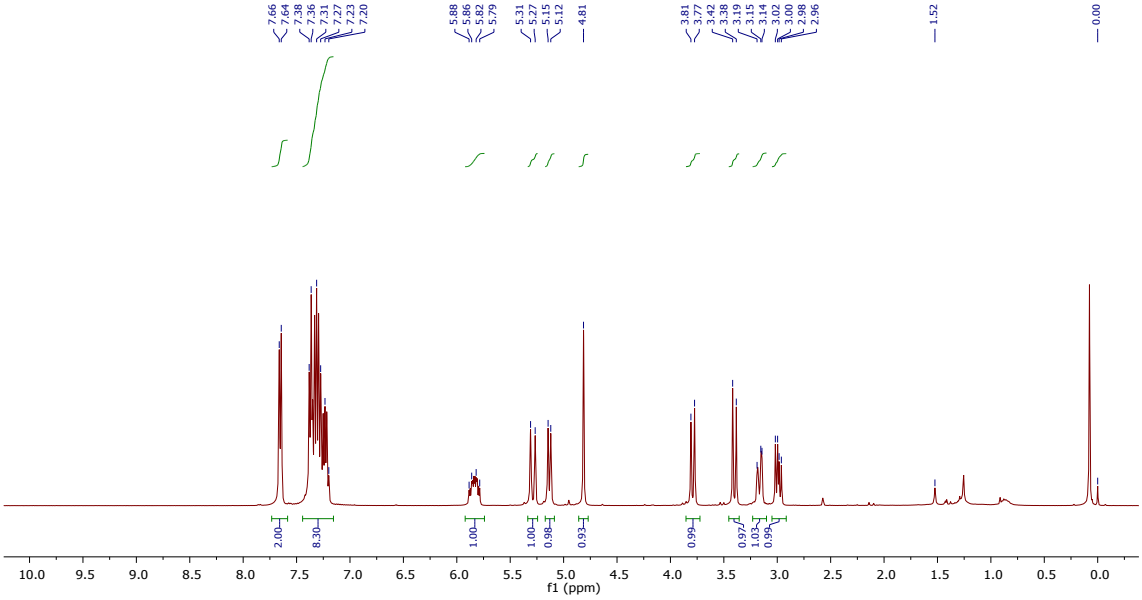
HPLC trace of 10

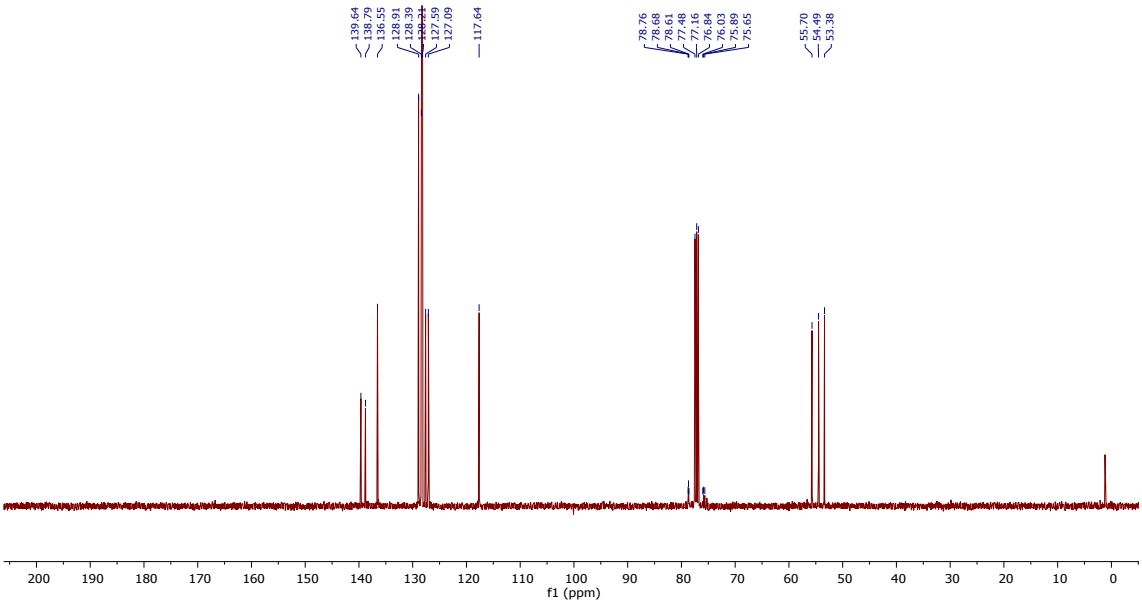


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	16.182	10.745	39.897	2.00	2.50	n.a.
2	19.815	526.706	1553.377	98.00	97.50	n.a.

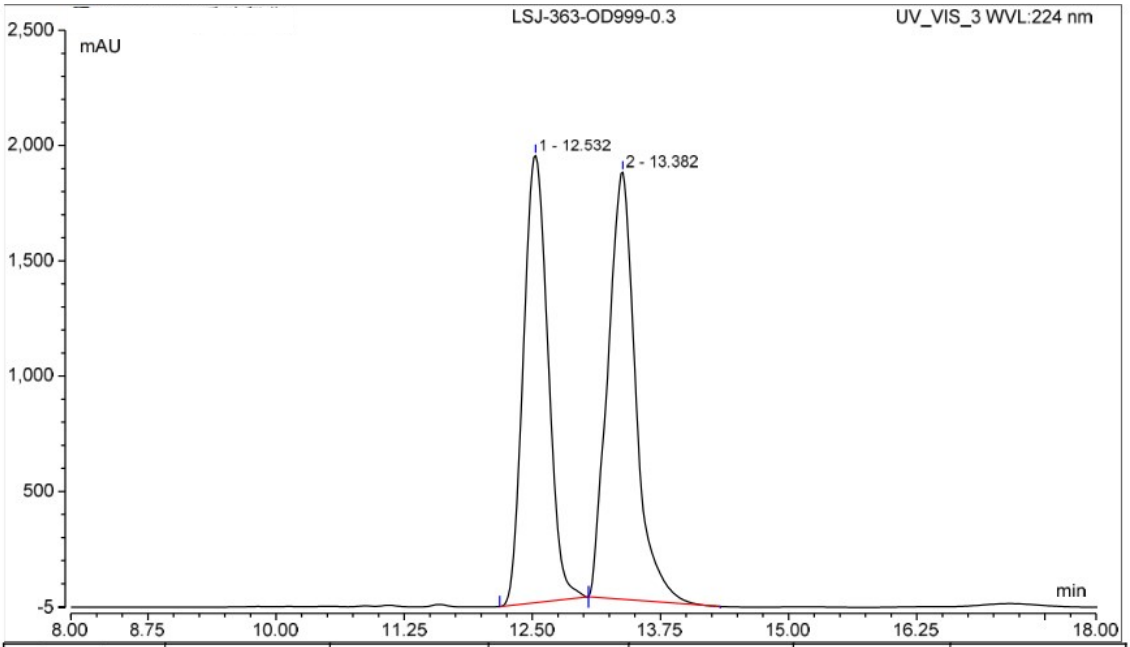

Bn
N
Ph
D

11


7.66
7.64
7.38
7.36
7.31
7.27
7.23
7.20
5.88
5.86
5.82
5.79
5.31
5.27
5.15
5.12
4.81
3.81
3.77
3.42
3.38
3.19
3.15
3.14
3.02
3.00
2.98
2.96
1.52
0.00
2.00
8.30
1.00
1.00
0.98
0.93
0.99
0.97
1.03
0.99
f1 (ppm)

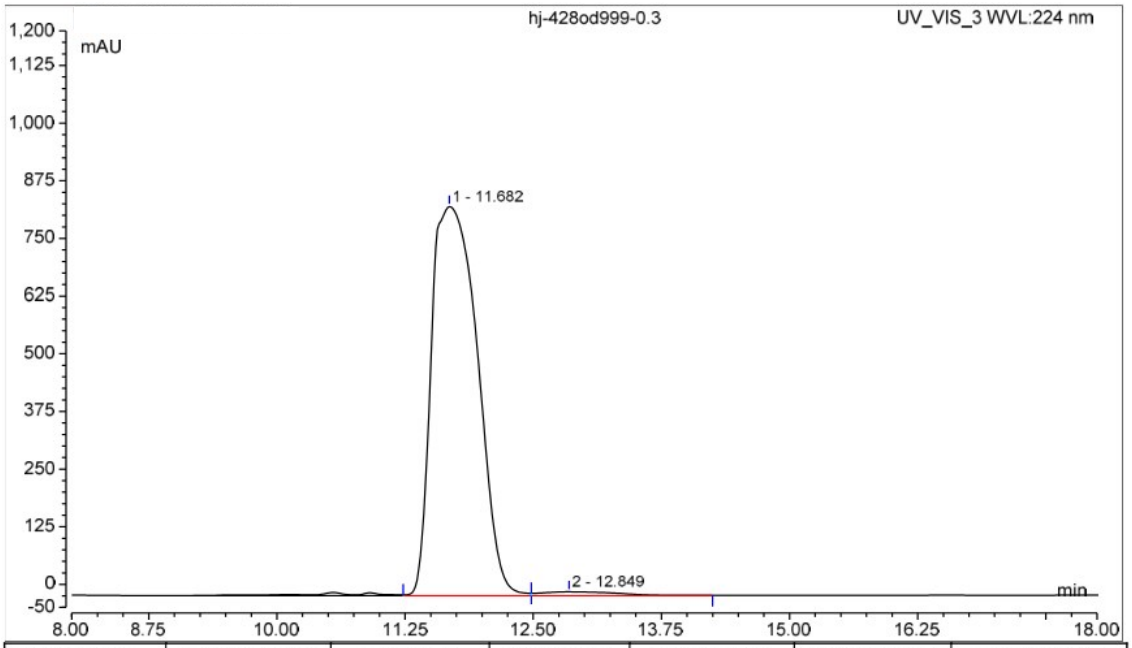

139.64
138.79
136.55
128.91
128.39
128.34
127.59
127.09
117.64
78.76
78.68
78.61
77.48
77.16
76.84
76.03
75.89
75.65
55.70
54.49
53.38
f1 (ppm)

HPLC trace of *rac*-11

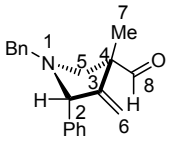


peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	12.532	538.125	1939.623	48.07	51.14	n.a.
2	13.382	581.274	1853.077	51.93	48.86	n.a.

HPLC trace of 11

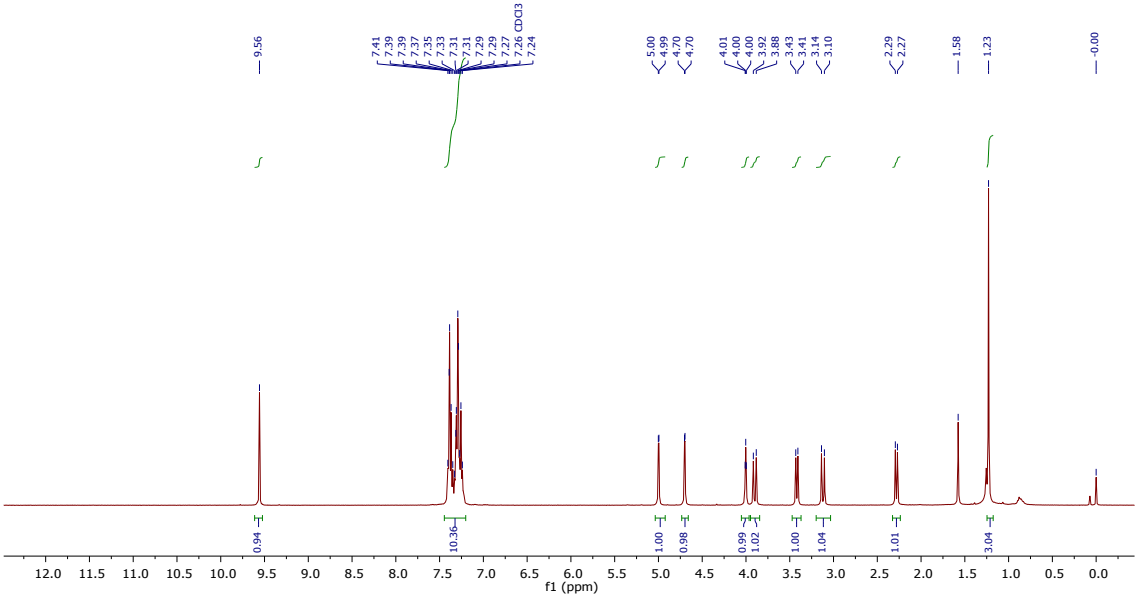


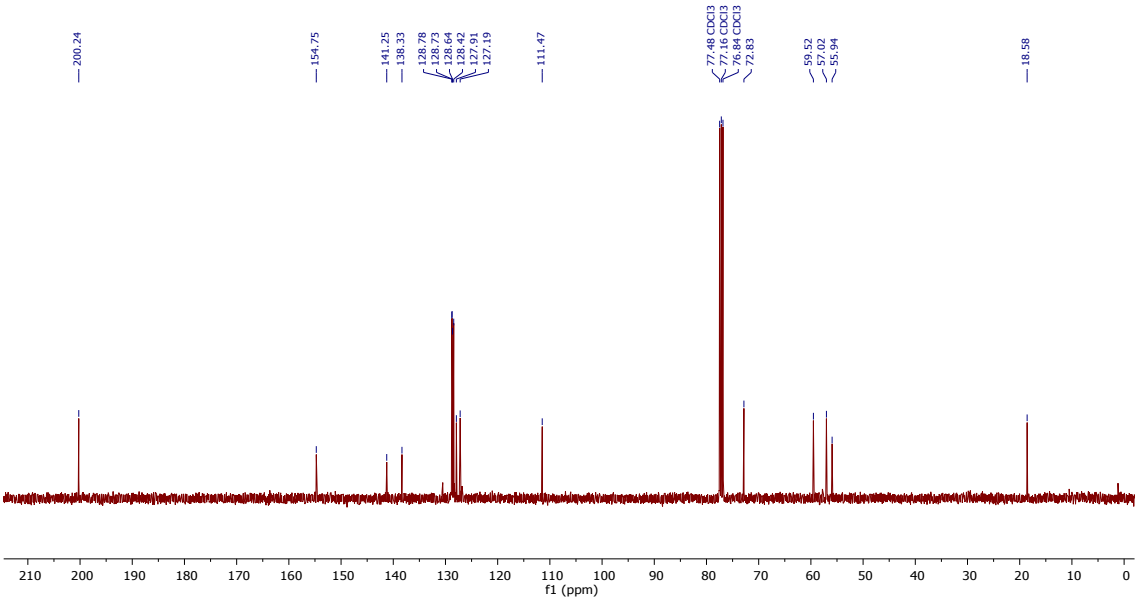
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	11.682	436.612	843.192	98.51	99.07	n.a.
2	12.849	6.623	7.954	1.49	0.93	n.a.

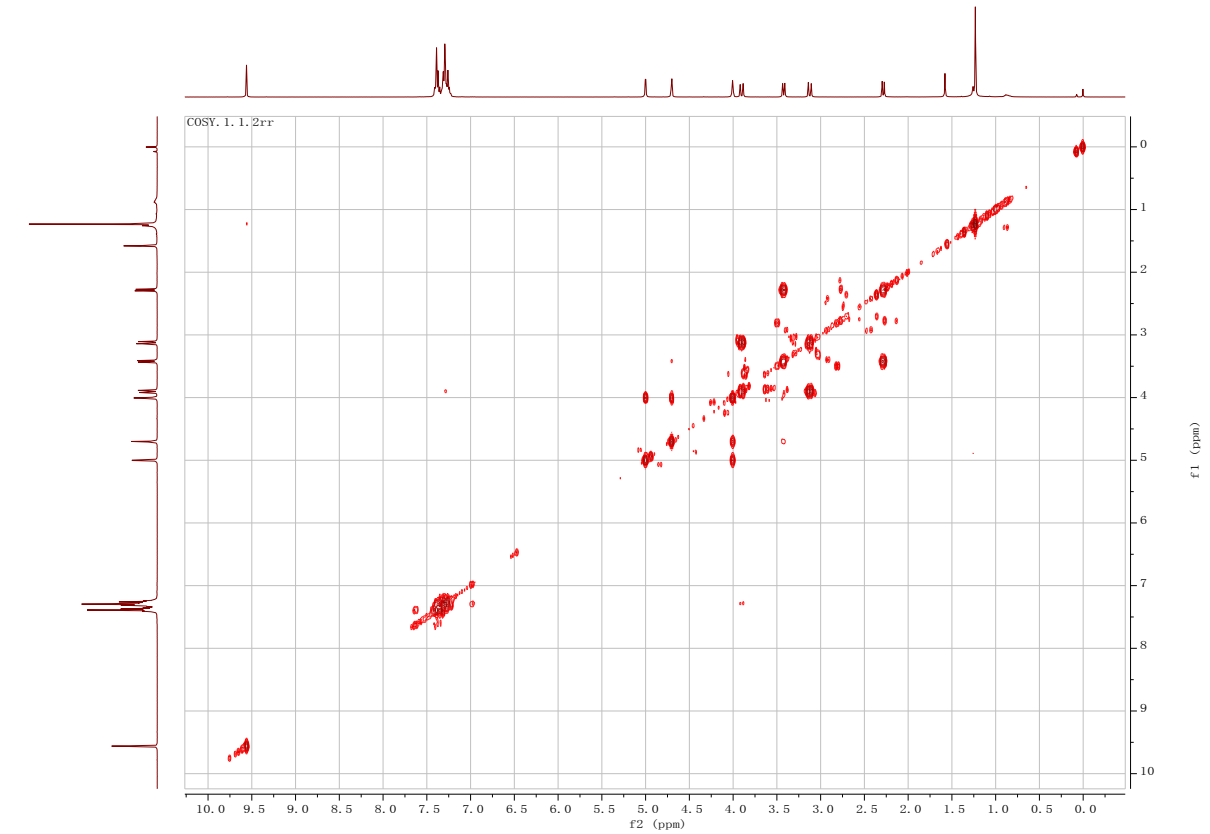


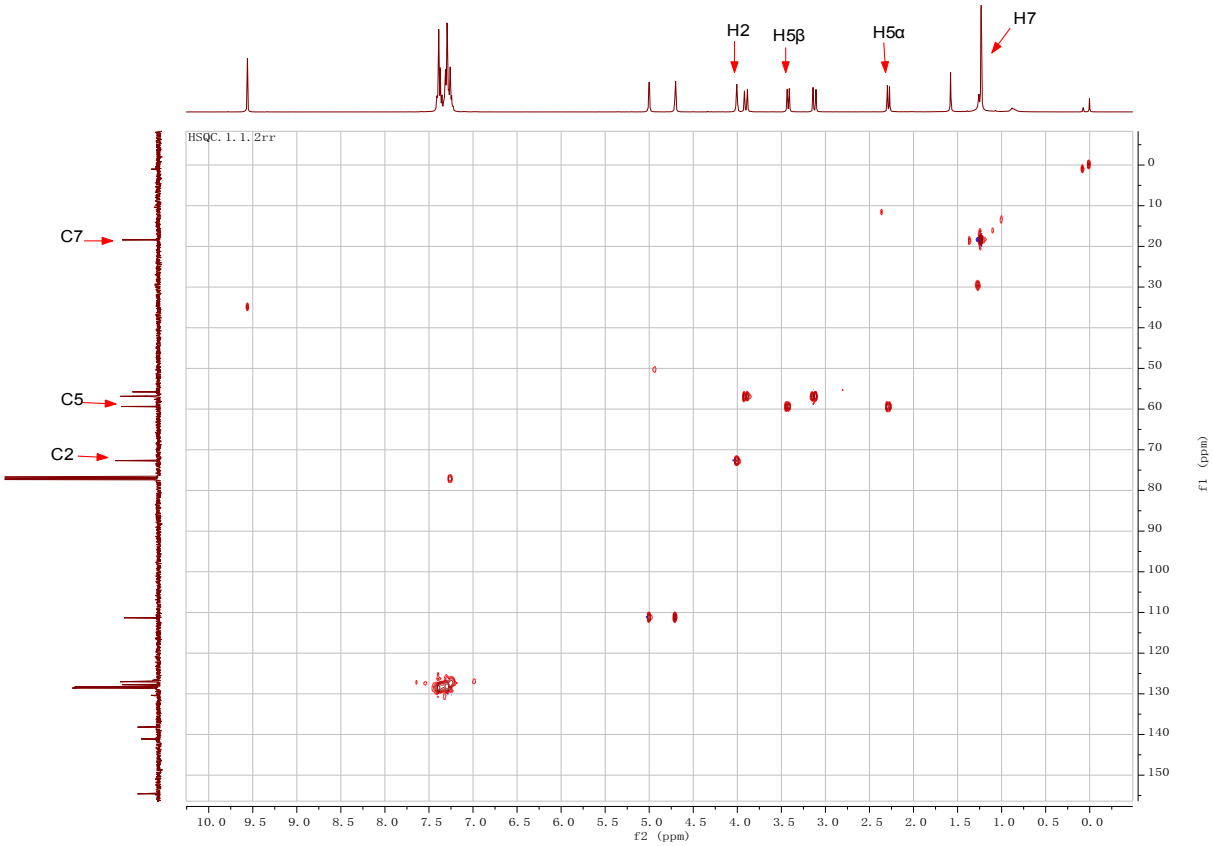
12

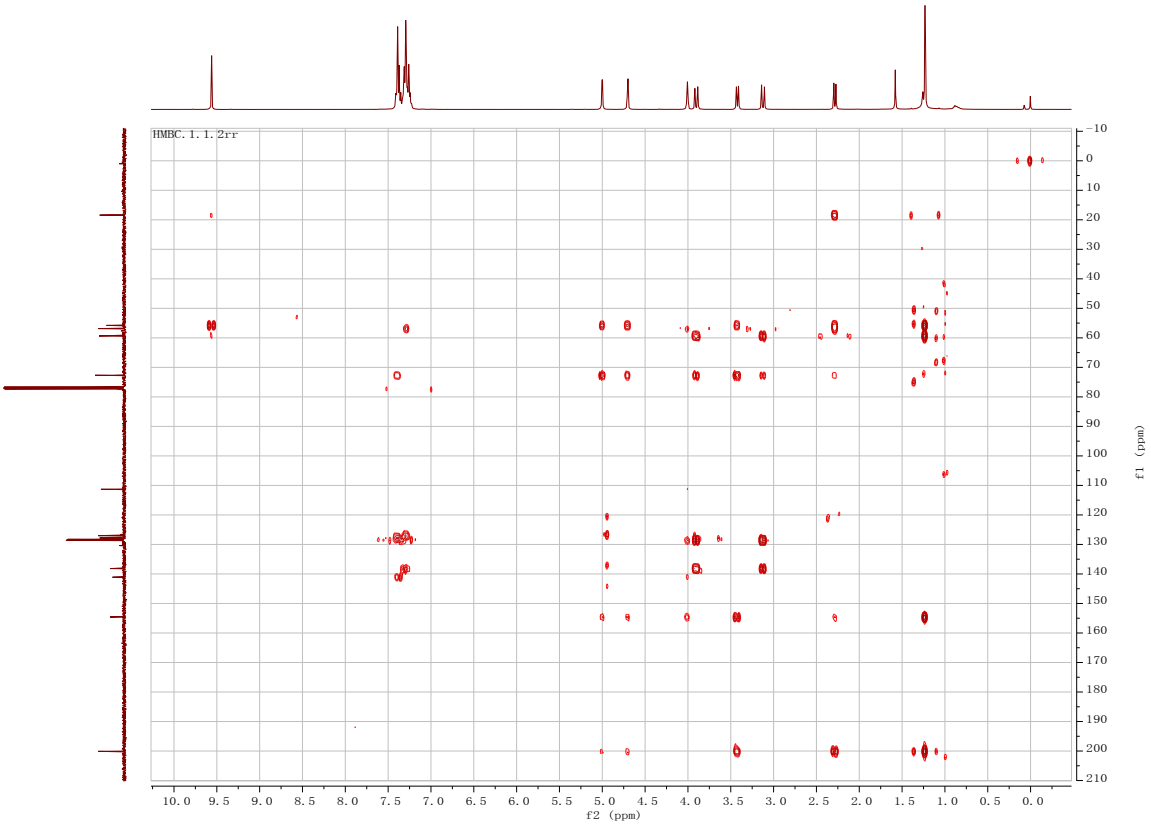
^{1}H-NMR, $CDCl_3$
400 MHz, 298K

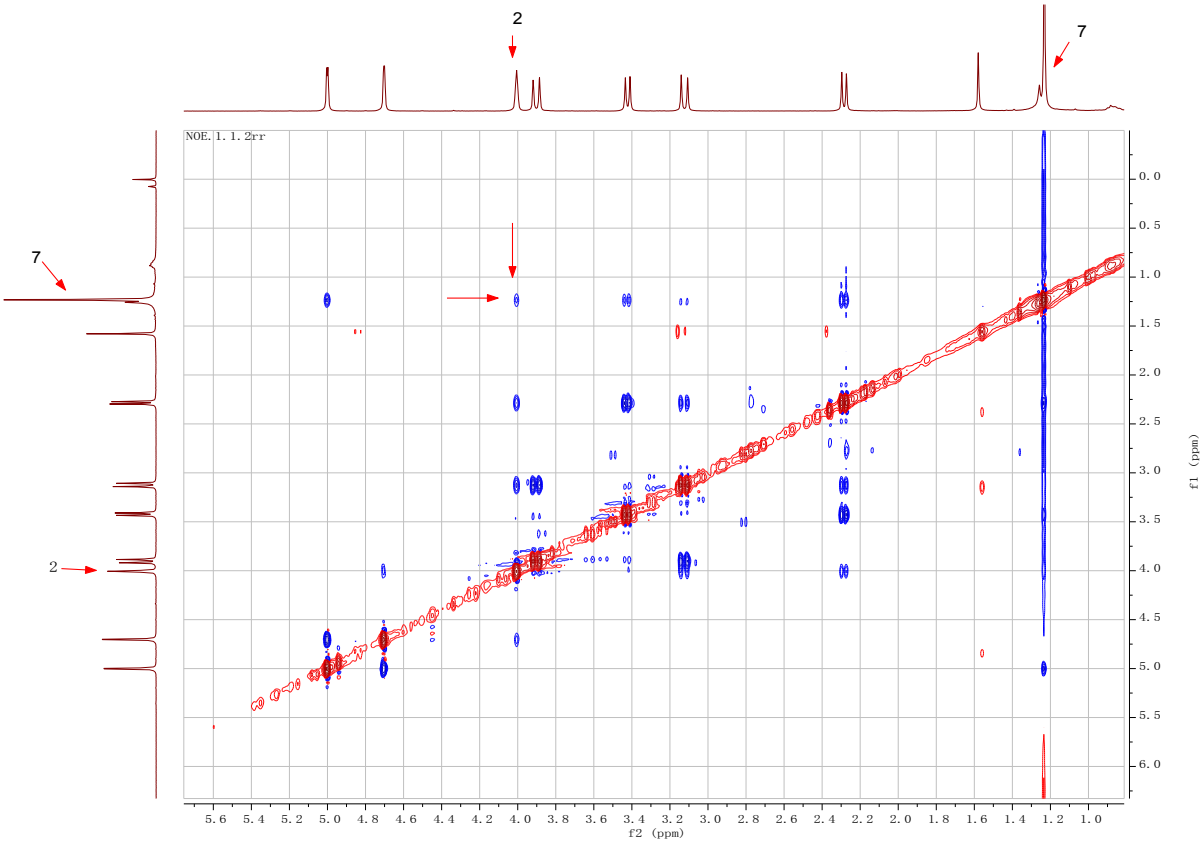




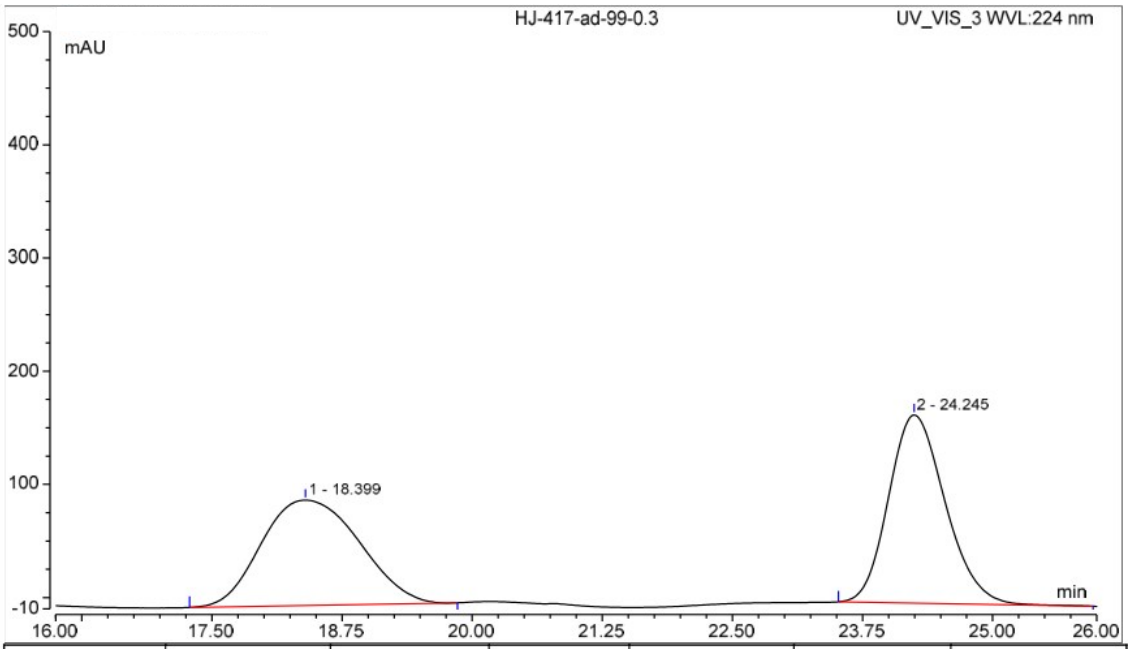

COSY.1.1.2rr
f2 (ppm)
f1 (ppm)


H2
H5β
H5α
H7
HSQC.1.1.2rr
C7
C5
C2
f2 (ppm)
f1 (ppm)


HMBC. 1. 1. 2rr
f2 (ppm)
f1 (ppm)

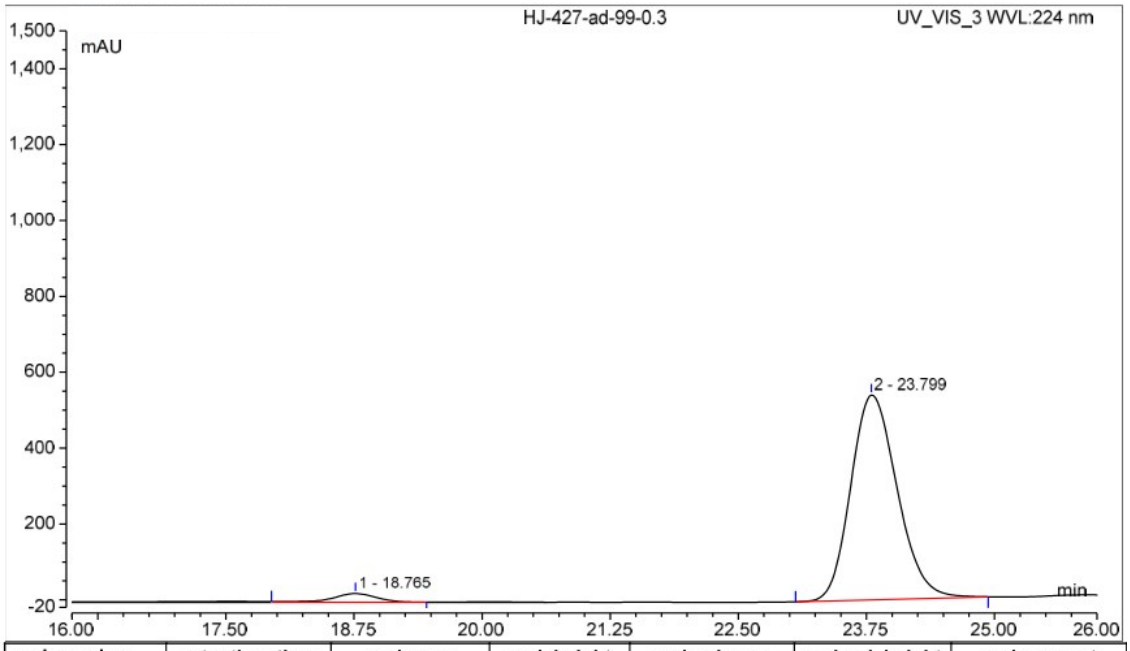

2
7
NOE. 1. 1. 2rr
7
2
f2 (ppm)
f1 (ppm)

HPLC trace of *rac*-12

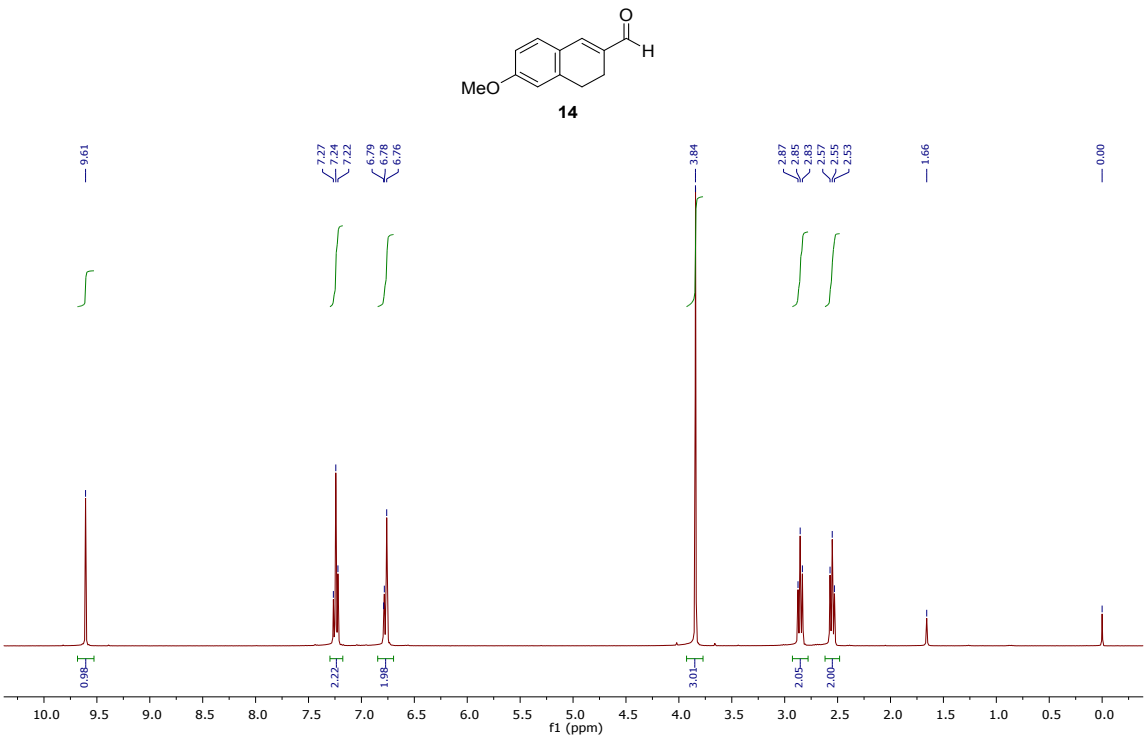


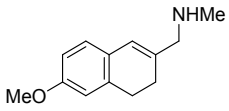
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	18.399	101.246	93.010	49.16	35.88	n.a.
2	24.245	104.723	166.234	50.84	64.12	n.a.

HPLC trace of 12

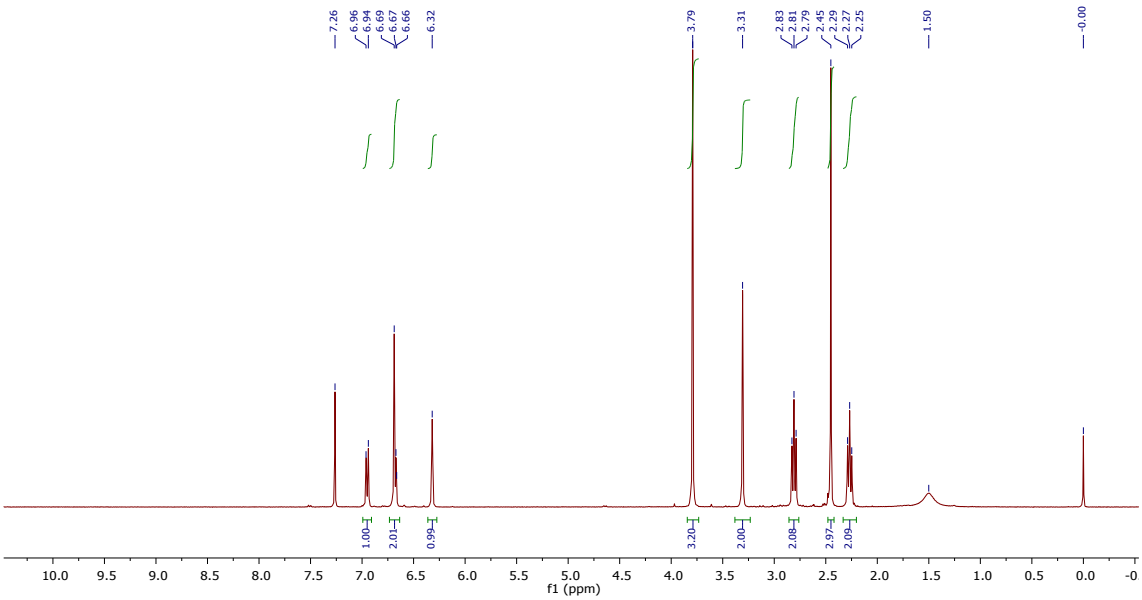


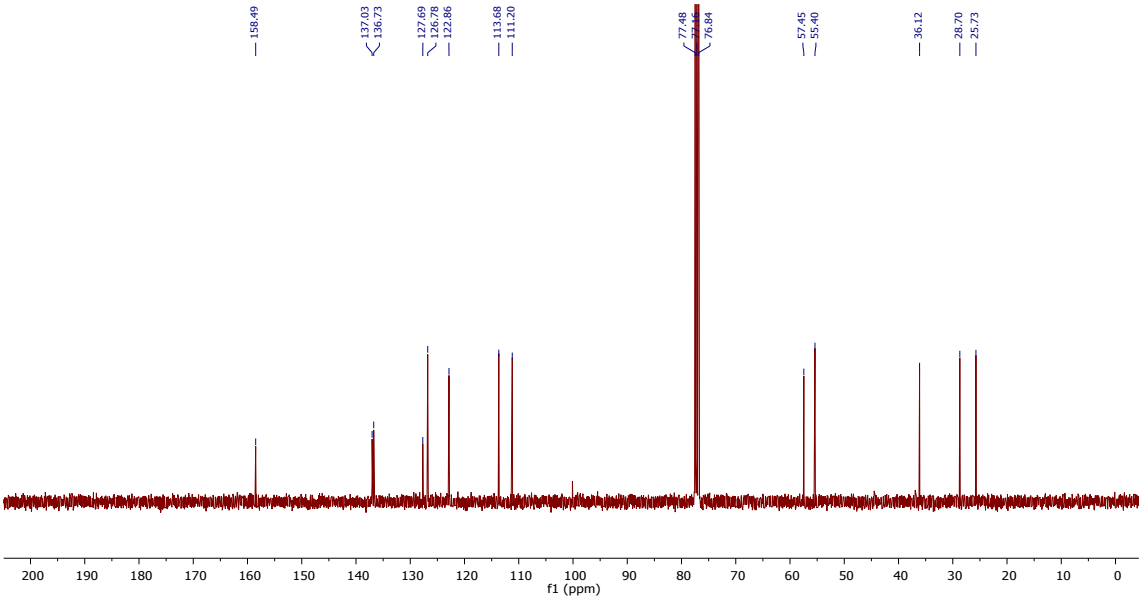
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	18.765	11.831	23.054	4.02	4.09	n.a.
2	23.799	282.704	540.114	95.98	95.91	n.a.

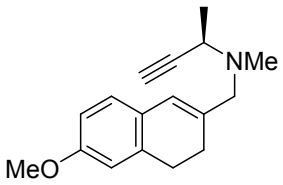

O
H
MeO
14
9.61
7.27
7.24
7.22
6.79
6.78
6.76
3.84
2.87
2.85
2.83
2.57
2.55
2.53
1.66
0.00
0.98
2.22
1.98
3.01
2.05
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


NHMe
MeO

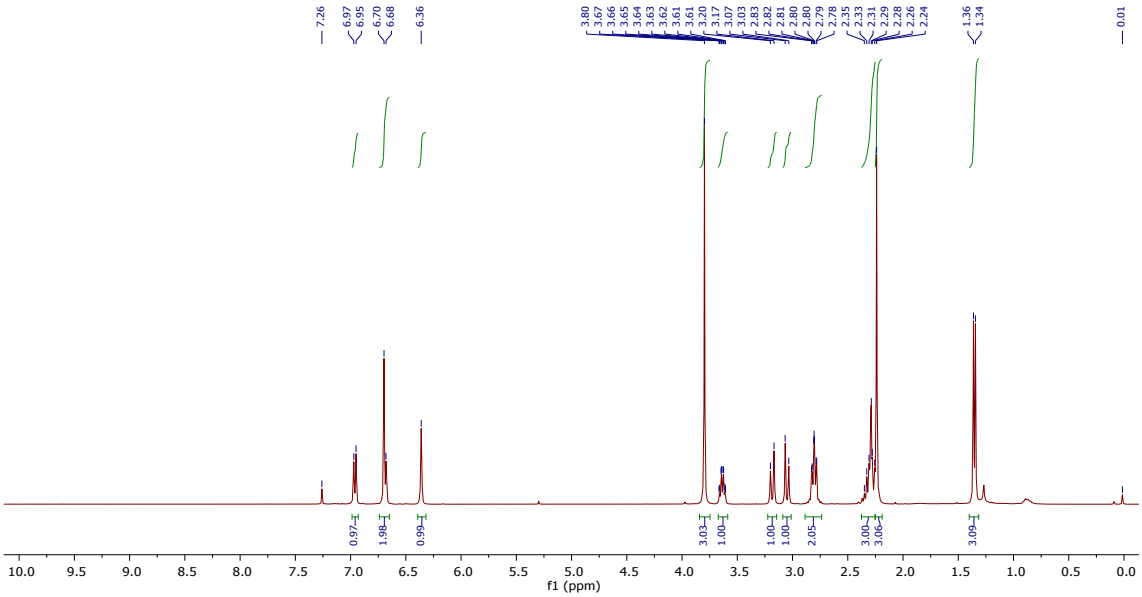
15

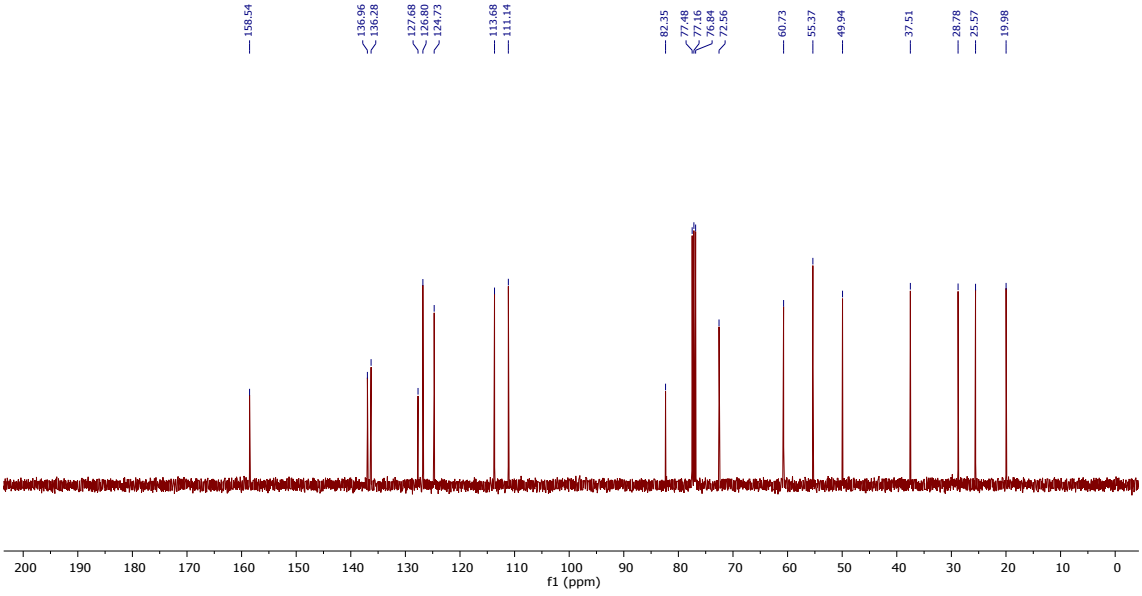

7.26
6.96
6.94
6.69
6.67
6.66
6.32
3.79
3.31
2.83
2.81
2.79
2.45
2.29
2.27
2.25
1.50
0.00
1.00
2.01
0.99
3.20
2.00
2.08
2.97
2.09
f1 (ppm)


158.49
137.03
136.73
127.69
126.78
122.86
113.68
111.20
77.48
77.16
76.84
57.45
55.40
36.12
28.70
25.73
f1 (ppm)

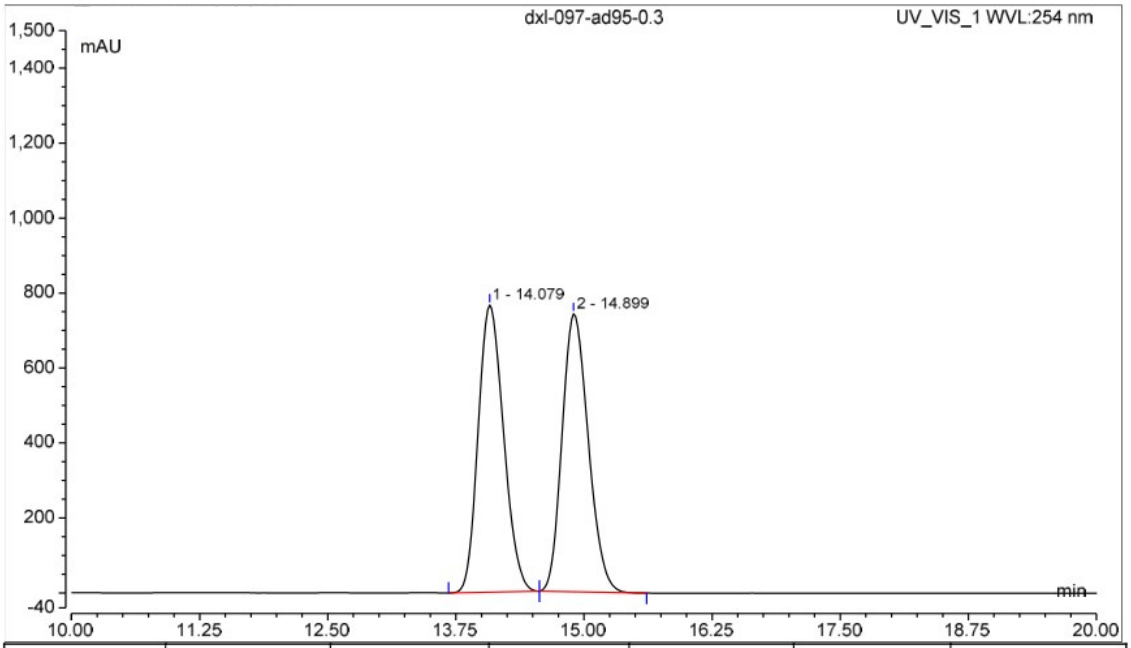

NMe
MeO

16


7.26
6.97
6.95
6.70
6.68
6.36
3.80
3.67
3.66
3.65
3.64
3.63
3.62
3.61
3.61
3.20
3.17
3.07
3.03
2.83
2.82
2.81
2.80
2.80
2.79
2.78
2.35
2.33
2.31
2.29
2.28
2.26
2.24
1.36
1.34
0.01
0.97
1.98
0.99
3.03
1.00
1.00
1.00
2.05
3.00
3.06
3.09
f1 (ppm)

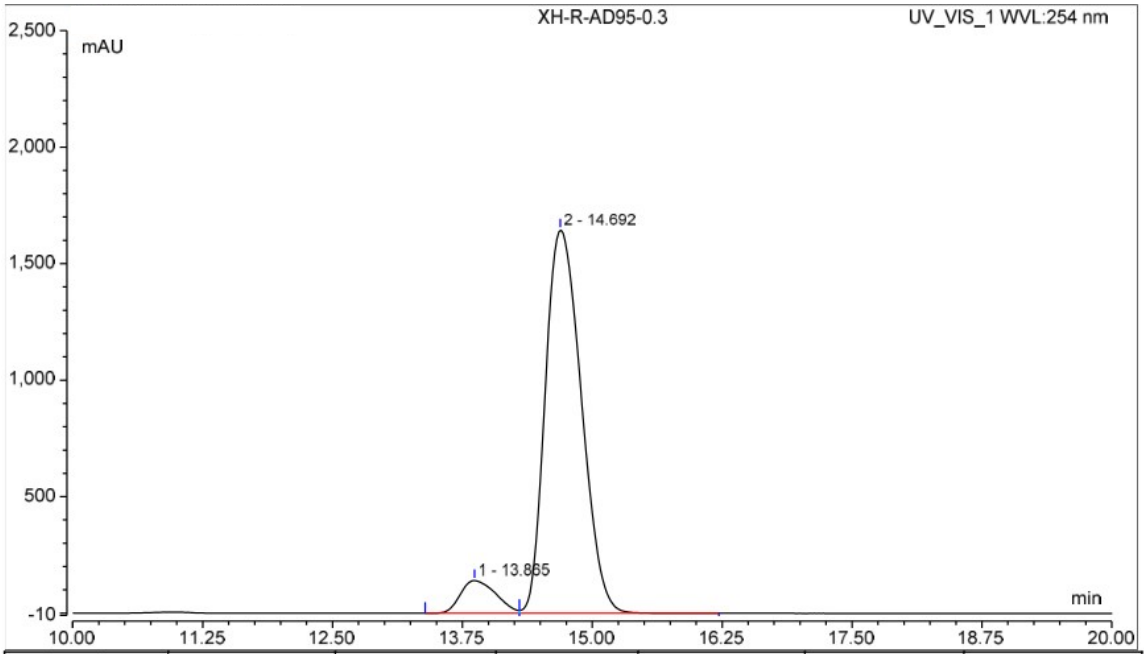

158.54
136.96
136.28
127.68
126.80
124.73
113.68
111.14
82.35
77.48
77.16
76.84
72.56
60.73
55.37
49.94
37.51
28.78
25.57
19.98
f1 (ppm)

HPLC trace of *rac*-16



peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	14.079	220.020	765.995	50.02	50.81	n.a.
2	14.899	219.812	741.589	49.98	49.19	n.a.

HPLC trace of 16



peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	13.865	55.324	140.119	7.73	7.85	n.a.
2	14.692	660.283	1645.097	92.27	92.15	n.a.