Electronic Supplementary Material (ESI) for ChemComm.


# Supporting Information

## Enantioselective Formation of Tertiary and Quaternary Allylic C-N Bonds via Allylation of Tetrazoles

Kun Xu, Wilfried Raimondi, Timm Bury and Bernhard Breit*

*Institut für Organische Chemie, Albert-Ludwigs-Universität Freiburg, Albertstrasse 21, 79104 Freiburg, Germany*

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## General

**FCC** (Flash Column Chromatography) was accomplished using MACHEREY-NAGEL silica gel 60® (230-400 mesh). **TLC** (Thin Layer Chromatography) was performed on aluminum plates pre-coated with silica gel (MERCK, $60F_{254}$), which were visualized by UV fluorescence ($\lambda_{max}$ = 254 nm) and/or by staining with 1% w/v $KMnO_4$ in 0.5 M aqueous $K_2CO_3$. **NMR** (Nuclear Magnetic Resonance) spectra were acquired on a BRUKER Avance 400 spectrometer (400 MHz and 100.6 MHz for $^1H$ and $^{13}C$ respectively) and/or on a VARIAN Mercury (300 MHz and 75.5 MHz for $^1H$ and $^{13}C$ respectively). All $^1H$ NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals at 7.26 ppm ($CHCl_3$). All $^{13}C$ NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.16 ppm) and were obtained with $^1H$-decoupling. Data for $^1H$ NMR are described as following: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sx, sextet; m, multiplet; app, apparent; br, broad signal), coupling constant (Hz), integration. Data for $^{13}C$ NMR spectra are described in terms of chemical shift (δ in ppm). **HRMS** (High resolution mass spectra) were obtained on a FINNIGAN MAT 8200 instrument (CI/$NH_3$: 110 eV; EI: 70 eV). **MS-CI** (Chemical ionization mass spectrometry) was performed on a TSQ 700 or MAT 95XL mass spectrometer from Thermo Fisher Scientific Inc. at an ionization energy of 110 eV and a source temperature of 200 °C. Ammonia or isobutene were used as reactant gases. Ammonia or isobutene were used as reactant gases. **Chiral HPLC** was performed on a MERCK HITACHI HPLC apparatus (pump: L-7100, UV detector: D-7400, oven: L-7360; columns: AD-H, AD-3, AS, OD-3, OD-H and OJ-H 15-25 cm 4.6 cm, DAICEL). The **Optical Rotation** of chiral compounds was determined on a PERKIN-ELMER PE 241 apparatus and transformed for a given temperature according to the following formula:

$$[\alpha]_D^T = \frac{\alpha \cdot 100}{c \cdot d}$$

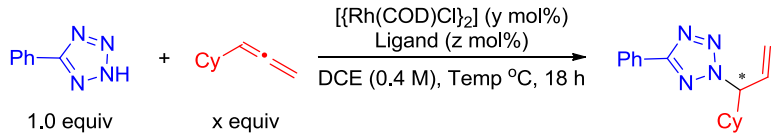
α: measured value for optical rotation; *c*: concentration in g/100 ml; *d*: length of the cuvette in dm; T: temperature in °C.

## Materials

**Solvents**: 1,2-Dichloroethane (DCE) were freshly distilled over $CaH_2$ and degassed by three Freeze-Pump-Thaw cycles prior to use. Tetrahydrofuran (THF) was purchased in HPLC grade quality and was purified by continuous destillation over potassium under argon. Solvents employed for work-up and column chromatography were purchased in technical grade quality and distilled by rotary evaporator before use. **Substrates:** Tetrazoles were purchased from Sigma-Aldrich, ABCR, Alfa Aesar and used without further purification, 5-(naphthalen-2-yl)-1*H*-tetrazole[1] was prepared according to the literature. Cyclohexylallene, propa-1,2-dien-1-ylcyclopentane, octa-1,2-diene, hexa-4,5-dien-1-ylbenzene, methyl hepta-5,6-dienoate, 2-(hexa-4,5-dien-1-yl)isoindoline-1,3-dione, (3-methylpenta-3,4-dien-1-yl)benzene, *tert*-butyldimethyl((2-methylbuta-2,3-dien-1-yl)oxy)silane, buta-2,3-dien-2-yltrimethylsilane and (2-methylbuta-2,3-dien-1-yl)benzene were synthesized according to literature procedures.[2] 5-phenyl-1*D*-tetrazole was prepared according to the literature.[3] **Ligands and catalysts**: $[Rh(COD)Cl]_2$ and ligands were purchased from Sigma-Aldrich, ABCR, Alfa Aesar and used without further purification.

## Optimization

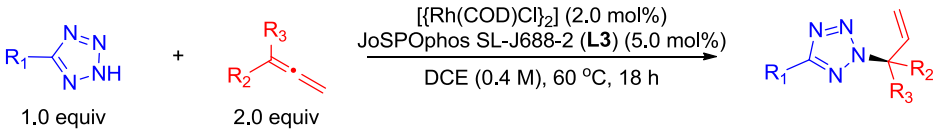
Optimization of Rhodium Catalyzed Coupling of 5-Phenyl-1*H*-tetrazole with Cyclohexylallene




| Entry | Ligand | x | y | z | Temp | yield[a] | *ee*[b] |
|---|---|---|---|---|---|---|---|
| 1 | DPEphos | 1.2 | 1.0 | 3.0 | 80 | 98 | - |
| 2 | (*R*)-Segphos | 1.2 | 1.0 | 3.0 | 80 | 89 | 33 |
| 3 | (*S*)-(-)-MeO-BIPHEP | 1.2 | 1.0 | 3.0 | 80 | 84 | 48 |
| 4 | (*R*)-DIFLUORPHOS | 1.2 | 1.0 | 3.0 | 80 | 99 | 10 |
| 5 | (*S*)-SYNPHOS | 1.2 | 1.0 | 3.0 | 80 | 91 | 43 |
| 6 | (*R*)-$C_3$-TunePhos | 1.2 | 1.0 | 3.0 | 80 | 93 | 51 |
| 7 | Josiphos SL-J001-1 | 1.2 | 1.0 | 3.0 | 80 | Quant. | 0 |
| 8 | Josiphos SL-J002-1 | 1.2 | 1.0 | 3.0 | 80 | 49 | 41 |
| 9 | Josiphos SL-J004-1 | 1.2 | 1.0 | 3.0 | 80 | 83 | 14 |
| 10 | **L5** | 1.2 | 1.0 | 3.0 | 60 | n.r[c] | - |
| 11 | - | 1.2 | 1.0 | 3.0 | 60 | n.r[d] | - |

[a] Isolated yield; [b] Determined by chiral HPLC; [c] Reaction in the absence of $[Rh(COD)Cl]_2$; [d] Reaction in the absence of Ligand.

## General Procedure for Rhodium Catalyzed Coupling of Tetrazoles with Allenes

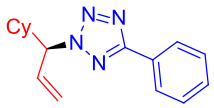



The reaction was performed in a 2.0 ml Schlenk tube under argon. $[Rh(COD)Cl]_2$ (2.0 mg, 0.004 mmol, 2.0 mol%), JoSPOphos SL-J688-2 (4.8 mg, 0.01 mmol, 5.0 mol%), tetrazole (0.2 mmol, 1.0 equiv) were dissolved in DCE (1.0 mL), then allene (0.4 mmol, 2.0 equiv.) was added and the tube was sealed. The reaction mixture was stirred at corresponding temperature for 18 hours. After cooling to room temperature, the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography on silica gel and dried *in vacuo*.

## Syntheses and Characterization of $N^2$-allylated Tetrazoles

**1** Enantioselective Formation of Tertiary Allylic C-N Bonds (**1a-l**)

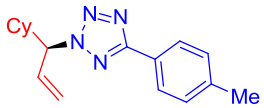
**1.1** (*S*)-2-(1-cyclohexylallyl)-5-phenyl-2*H*-tetrazole **(1a)**



The reaction was performed with 5-phenyl-1*H*-tetrazole (29.2 mg, 0.2 mmol) and cyclohexylallene (58 µL, 48.9 mg, 0.4 mmol) at 60 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:30, $R_f$ = 0.35) to afford the product as a yellowish oil (43.0 mg, 80%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.19 - 8.14 (m, 2 H), 7.51 - 7.45 (m, 3 H), 6.23 (ddd, *J* = 8.8, 10.4, 17.1 Hz, 1 H), 5.39 - 5.32 (m, 2 H), 5.06 (t, *J* = 9.0 Hz, 1 H), 2.19 - 2.07 (m, 1 H), 1.93 - 1.85 (m, 1 H), 1.83 - 1.75 (m, 1 H), 1.74 - 1.62 (m, 2 H), 1.35 - 1.12 (m, 4 H), 1.09 - 0.95 (m, 2 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 164.9, 133.7, 130.2, 128.9, 127.8, 126.9, 120.5, 72.9, 41.9, 29.5, 29.4, 26.1, 25.8, 25.6; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{16}H_{21}N_4$, 269.17662; found, 269.17660. **HPLC (**CHIRALCEL® L-C2, *n*-heptane / $^i$PrOH = 100:1, 0.5 mL/min) $t_R$ = 7.95 min (minor), $t_R$ = 9.61 min (major), 87% *ee* (***S***); $[\alpha]_D^{25}$ = + 81.9 (c = 0.675, $CH_2Cl_2$).

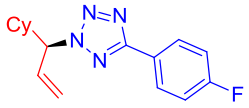
**1.2** (*S*)-2-(1-cyclohexylallyl)-5-(p-tolyl)-2*H*-tetrazole **(1b)**



The reaction was performed with 5-(p-tolyl)-1*H*-tetrazole (32.0 mg, 0.2 mmol) and cyclohexylallene (58 µL, 48.9 mg, 0.4 mmol) at 60 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:30, $R_f$ = 0.29) to afford the product as a yellowish solid (46.3 mg, 82%).

**m.p.**: 48 – 49 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.07 - 8.02 (m, 2 H), 7.32 - 7.27 (m, 2 H), 6.23 (ddd, *J* = 8.9, 10.3, 17.0 Hz, 1 H), 5.38 - 5.31 (m, 2 H), 5.04 (t, *J* = 9.0 Hz, 1 H), 2.41 (s, 3 H), 2.19 - 2.07 (m, 1 H), 1.93 - 1.84 (m, 1 H), 1.83 - 1.75 (m, 1 H), 1.73 - 1.62 (m, 2 H), 1.35 - 1.12 (m, 4 H), 1.08 - 0.94 (m, 2 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 165.0, 140.4, 133.8, 129.6, 126.9, 125.0, 120.4, 72.8, 41.9, 29.5, 29.4, 26.1, 25.8, 25.6, 21.6; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{17}H_{23}N_4$, 283.19227; found, 283.19170. **HPLC (**CHIRALCEL® AD-3, *n*-heptane /$^i$PrOH = 100:1, 1 mL/min) $t_R$ = 21. 51 min (minor), $t_R$ = 23.26 min (major), 91% *ee* (***S***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = + 81.0 (c = 0.815, $CH_2Cl_2$).

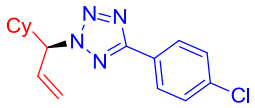
**1.3** (*S*)-2-(1-cyclohexylallyl)-5-(4-fluorophenyl)-2*H*-tetrazole **(1c)**




The reaction was performed with 5-(4-fluorophenyl)-1*H*-tetrazole (32.8 mg, 0.2 mmol) and cyclohexylallene (58 µL, 48.9 mg, 0.4 mmol) at 60 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:30, $R_f$ = 0.31) to afford the product as a yellowish oil (43.0 mg, 75%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.19 - 8.12 (m, 2 H), 7.21 - 7.13 (m, 2 H), 6.22 (ddd, *J* = 8.9, 10.3, 17.1 Hz, 1 H), 5.39 - 5.32 (m, 2 H), 5.05 (t, *J* = 9.0 Hz, 1 H), 2.18 - 2.07 (m, 1 H), 1.93 - 1.85 (m, 1 H), 1.83 - 1.75 (m, 1 H), 1.74 - 1.62 (m, 2 H), 1.35 - 1.09 (m, 4 H), 1.09 - 0.94 (m, 2 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 164.2, 164.0 (d, *J* = 250.3 Hz), 133.6, 129.0 (d, *J* = 8.5 Hz), 124.0, 124.0, 120.6, 116.0 (d, *J* = 22.9 Hz), 73.0, 41.9, 29.5, 29.4, 26.1, 25.8, 25.6; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{16}H_{20}N_4F$, 287.16720; found, 287.16680. **HPLC (**CHIRALCEL® L-C4, *n*-heptane / $^i$PrOH = 600:1, 1 mL/min) $t_R$ = 14.92 min (major), $t_R$ = 23.15 min (minor), 87% *ee* (***S***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = + 74.3 (c = 0.580, $CH_2Cl_2$).

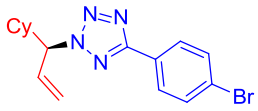
**1.4** (*S*)-5-(4-chlorophenyl)-2-(1-cyclohexylallyl)-2*H*-tetrazole **(1d)**




The reaction was performed with 5-(4-chlorophenyl)-1*H*-tetrazole (36.1 mg, 0.2 mmol) and cyclohexylallene (58 µL, 48.9 mg, 0.4 mmol) at 60 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:30, $R_f$ = 0.34) to afford the product as a yellowish oil (51.5 mg, 85%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.12 - 8.07 (m, 2 H), 7.48 - 7.43 (m, 2 H), 6.21 (ddd, *J* = 8.8, 10.3, 17.0 Hz, 1 H), 5.39 - 5.31 (m, 2 H), 5.05 (t, *J* = 9.0 Hz, 1 H), 2.18 - 2.06 (m, 1 H), 1.92 - 1.84 (m, 1 H), 1.83 - 1.74 (m, 1 H), 1.73 - 1.60 (m, 2 H), 1.33 - 1.12 (m, 4 H), 1.08 - 0.94 (m, 2 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 164.1, 136.3, 133.6, 129.2, 128.2, 126.3, 120.7, 73.0, 41.9, 29.5, 29.4, 26.1, 25.7, 25.6; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{16}H_{20}N_4{}^{35}Cl$, 303.13765; found, 303.13710. **HPLC (**CHIRALCEL® L-C4, *n*-heptane / $^i$PrOH = 600:1, 1 mL/min) $t_R$ = 14.77 min (major), $t_R$ = 21.39 min (minor), 87% *ee* (***S***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = + 78.2 (c = 0.680, $CH_2Cl_2$).

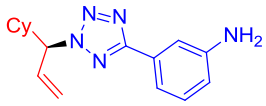
**1.5** (*S*)-5-(4-bromophenyl)-2-(1-cyclohexylallyl)-2*H*-tetrazole **(1e)**



The reaction was performed with 5-(4-bromophenyl)-1*H*-tetrazole (45.0 mg, 0.2 mmol) and cyclohexylallene (58 µL, 48.9 mg, 0.4 mmol) at 60 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:30, $R_f$ = 0.34) to afford the product as a yellowish solid (55.5 mg, 80%).

**m.p.**: 52 – 53 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.05 - 8.01 (m, 2 H), 7.64 - 7.59 (m, 2 H), 6.21 (ddd, *J* = 8.9, 10.3, 17.1 Hz, 1 H), 5.38 - 5.31 (m, 2 H), 5.04 (t, *J* = 9.0 Hz, 1 H), 2.17 - 2.06 (m, 1 H), 1.92 - 1.84 (m, 1 H), 1.82 - 1.74 (m, 1 H), 1.74 - 1.61 (m, 2 H), 1.34 - 1.12 (m, 4 H), 1.10 - 0.93 (m, 2 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 164.1, 133.6, 132.2, 128.5, 126.7, 124.6, 120.7, 73.0, 41.9, 29.5, 29.4, 26.1, 25.7, 25.6; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{16}H_{20}N_4{}^{79}Br$, 347.08713; found, 347.08650. **HPLC (**CHIRALCEL® L-C4, *n*-heptane / $^i$PrOH = 1000:1, 1 mL/min) $t_R$ = 31.88 min (major), $t_R$ = 47.36 min (minor), 89% *ee* (***S***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = + 72.2 (c = 0.615, $CH_2Cl_2$).

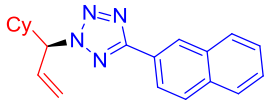
**1.6** (*S*)-3-(2-(1-cyclohexylallyl)-2*H*-tetrazol-5-yl)aniline **(1f)**



The reaction was performed with 3-(1*H*-tetrazol-5-yl)aniline (32.2 mg, 0.2 mmol) and cyclohexylallene (58 µL, 48.9 mg, 0.4 mmol) at 60 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:3, $R_f$ = 0.32) to afford the product as a yellowish oil (39.1 mg, 69%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.57 - 7.52 (m, 1 H), 7.49 (dd, *J* = 1.3, 2.5 Hz, 1 H), 7.30 - 7.22 (m, 1 H), 6.77 (ddd, *J* = 1.0, 2.5, 8.0 Hz, 1 H), 6.22 (ddd, *J* = 8.8, 10.3, 17.0 Hz, 1 H), 5.37 - 5.30 (m, 2 H), 5.04 (t, *J* = 9.0 Hz, 1 H), 3.77 (br. s., 2 H), 2.17 - 2.05 (m, 1 H), 1.92 - 1.83 (m, 1 H), 1.82 - 1.59 (m, 4 H), 1.34 - 0.92 (m, 6 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 165.0, 146.9, 133.7, 129.9, 128.6, 120.4, 117.2, 116.9, 113.2, 72.8, 41.9, 29.5, 29.4, 26.1, 25.7, 25.6; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{16}H_{22}N_4$, 284.18752; found, 284.18770. **HPLC (**CHIRALCEL® OD-H, *n*-heptane / $^i$PrOH = 80:20, 1 mL/min) $t_R$ = 12.43 min (minor), $t_R$ = 14.54 min (major), 80% *ee* (***S***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = + 63.9 (c = 0.735, $CH_2Cl_2$).

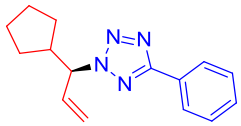
**1.7** (*S*)-2-(1-cyclohexylallyl)-5-(naphthalen-2-yl)-2*H*-tetrazole **(1g)**



The reaction was performed with 5-(naphthalen-2-yl)-1*H*-tetrazole (39.2 mg, 0.2 mmol) and cyclohexylallene (58 µL, 48.9 mg, 0.4 mmol) at 60 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:30, $R_f$ = 0.25) to afford the product as a white solid (45.9 mg, 72%).

**m.p.**: 57 – 59 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (dd, *J* = 0.8, 1.5 Hz, 1 H), 8.25 (dd, *J* = 1.6, 8.6 Hz, 1 H), 7.99 - 7.93 (m, 2 H), 7.90 - 7.84 (m, 1 H), 7.56 - 7.50 (m, 2 H), 6.27 (ddd, *J* = 8.8, 10.5, 16.8 Hz, 1 H), 5.40 - 5.35 (m, 2 H), 5.14 - 5.07 (m, 1 H), 2.24 - 2.11 (m, 1 H), 1.96 - 1.88 (m, 1 H), 1.85 - 1.76 (m, 1 H), 1.74 - 1.61 (m, 2 H), 1.37 - 0.98 (m, 6 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 165.1, 134.3, 133.7, 133.4, 128.8, 128.7, 128.0, 127.1, 126.7, 125.1, 124.1, 120.6, 73.0, 42.0, 29.6, 29.5, 26.2, 25.8, 25.6; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{20}H_{23}N_4$, 319.19227; found, 31.19220. **HPLC (**CHIRALCEL® OD-3, *n*-heptane / $^i$PrOH = 300:1, 0.5 mL/min) $t_R$ = 23.91 min (major), $t_R$ = 26.79 min (minor), 86% *ee* (***S***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = + 83.3 (c = 0.545, $CH_2Cl_2$).

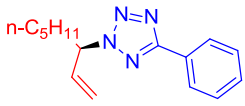
**1.8** (*S*)-2-(1-cyclopentylallyl)-5-phenyl-2*H*-tetrazole **(1h)**



The reaction was performed with 5-phenyl-1*H*-tetrazole (29.2 mg, 0.2 mmol) and propa-1,2-dien-1-ylcyclopentane (43.3 mg, 0.4 mmol) at 60 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:30, $R_f$ = 0.36) to afford the product as a colorless oil (47.3 mg, 93%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.19 - 8.15 (m, 2 H), 7.51 - 7.41 (m, 3 H), 6.21 (ddd, *J* = 8.2, 10.1, 17.3 Hz, 1 H), 5.33 - 5.28 (m, 2 H), 5.14 - 5.08 (m, 1 H), 2.80 - 2.65 (m, 1 H), 1.93 - 1.80 (m, 1 H), 1.73 - 1.45 (m, 5 H), 1.44 - 1.31 (m, 1 H), 1.28 - 1.17 (m, 1 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 164.9, 134.5, 130.2, 128.9, 127.8, 126.9, 119.6, 72.1, 44.2, 29.9, 29.7, 25.4, 25.1; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{15}H_{19}N_4$, 255.16097; found, 255.16100. **HPLC (**CHIRALCEL® AD-3, *n*-heptane / $^i$PrOH = 98:2, 1 mL/min) $t_R$ = 8.60 min (minor), $t_R$ = 9.37 min (major), 90% *ee* (***S***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = + 78.5 (c = 0.480, $CH_2Cl_2$).

**1.9** (*R*)-2-(oct-1-en-3-yl)-5-phenyl-2*H*-tetrazole **(1i)**

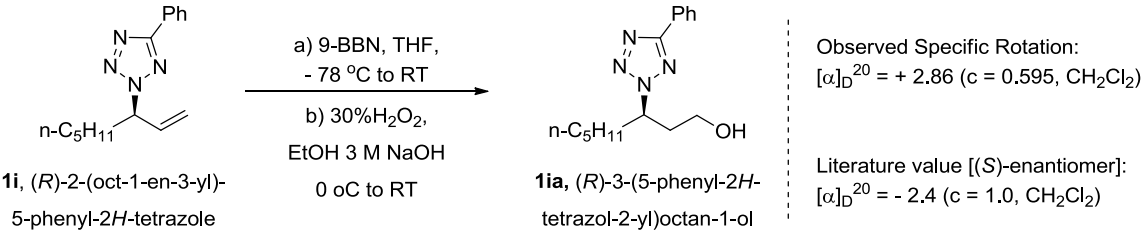


The reaction was performed with 5-phenyl-1*H*-tetrazole (29.2 mg, 0.2 mmol) and octa-1,2-diene (44.1 mg, 0.4 mmol) at 60 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:15, $R_f$ = 0.40) to afford the product as a yellowish oil (39.0 mg, 76%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ = $^1$H NMR (400MHz ,CHLOROFORM-d) d = 8.19 - 8.13 (m, 2 H), 7.51 - 7.42 (m, 3 H), 6.16 (ddd, *J* = 7.6, 10.5, 17.1 Hz, 1 H), 5.38 - 5.27 (m, 3 H), 2.29 - 2.17 (m, 1 H), 2.10 - 1.97 (m, 1 H), 1.40 - 1.14 (m, 6 H), 0.88 - 0.83 (m, 3 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = $^{13}$C NMR (101MHz ,CHLOROFORM-d) d = 165.0, 135.1, 130.3, 128.9, 127.8, 126.9, 119.0, 67.3, 34.6, 31.2, 25.4, 22.4, 14.0; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{15}H_{21}N_4$, 257.17662; found, 257.17670. **HPLC (**CHIRALCEL® AD-3, *n*-heptane / $^i$PrOH = 200:1, 1 mL/min) $t_R$ = 7.59 min (major), $t_R$ = 8.13 min (minor), 84% *ee* (***R***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = - 57.7 (c = 0.565, $CH_2Cl_2$).

**Determination of absolute configuration**: Absolute configuration was determined by comparing the specific rotation the derivatized[4] product with literature.[5] Hydroboration of **1i** followed by oxidation with $H_2O_2$ under

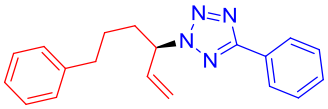
basic condition gave the corresponding anline derivatives **1ia**. (*R*)-3-(5-phenyl-2*H*-tetrazol-2-yl)octan-1-ol (**1ia**): $[\alpha]_D^{20}$ = + 2.86 (c = 0.595, $CH_2Cl_2$). Literature value of (*S*)-3-(5-phenyl-2*H*-tetrazol-2-yl)octan-1-ol: 85% *ee*, $[\alpha]_D^{20}$ = - 2.4 (c = 1.0, $CH_2Cl_2$). The absolute configurations for other allylation products were assignied by analogy.




**1i**, (*R*)-2-(oct-1-en-3-yl)-5-phenyl-2*H*-tetrazole

**1ia**, (*R*)-3-(5-phenyl-2*H*-tetrazol-2-yl)octan-1-ol

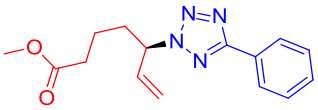
**1.10** (*R*)-5-phenyl-2-(6-phenylhex-1-en-3-yl)-2*H*-tetrazole **(1j)**



The reaction was performed with 5-phenyl-1*H*-tetrazole (29.2 mg, 0.2 mmol) and hexa-4,5-dien-1-ylbenzene (63.3 mg, 0.4 mmol) at 60 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:15, $R_f$ = 0.32) to afford the product as a yellowish oil (45.7 mg, 75%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.18 - 8.14 (m, 2 H), 7.52 - 7.46 (m, 3 H), 7.30 - 7.24 (m, 2 H), 7.21 - 7.12 (m, 3 H), 6.15 (ddd, *J* = 7.6, 10.4, 17.1 Hz, 1 H), 5.41 - 5.34 (m, 1 H), 5.34 - 5.27 (m, 2 H), 2.66 (t, *J* = 7.5 Hz, 2 H), 2.35 - 2.23 (m, 1 H), 2.14 - 2.04 (m, 1 H), 1.78 - 1.48 (m, 2 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 165.1, 141.4, 134.9, 130.3, 128.9, 128.5, 128.4, 127.7, 127.0, 126.1, 119.3, 67.1, 35.2, 34.0, 27.5; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{19}H_{21}N_4$, 305.17662; found, 305.17660. **HPLC (**CHIRALCEL® L-C2, *n*-heptane / $^i$PrOH = 200:1, 0.5 mL/min) $t_R$ = 27.57 min (major), $t_R$ = 51.47 min (minor), 90% *ee* (***R***); $[\alpha]_D^{25}$ = + 37.4 (c = 0.700, $CH_2Cl_2$).

**1.11** (*R*)-methyl 5-(5-phenyl-2*H*-tetrazol-2-yl)hept-6-enoate **(1k)**

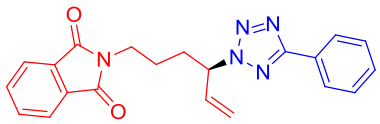


The reaction was performed with 5-phenyl-1*H*-tetrazole (29.2 mg, 0.2 mmol) and methyl hepta-5,6-dienoate (56.1 mg, 0.4 mmol) at 60 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:15, $R_f$ = 0.28) to afford the product as a colorless oil (39.5 mg, 69%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ = $^1$H NMR (400MHz ,CHLOROFORM-d) d = 8.17 - 8.12 (m, 2 H), 7.49 - 7.40 (m, 3 H), 6.14 (ddd, *J* = 7.5, 10.5, 17.0 Hz, 1 H), 5.40 - 5.29 (m, 3 H), 3.64 (s, 3 H), 2.34 (t, *J* = 7.3 Hz, 2 H), 2.32 - 2.21 (m, 1 H), 2.16 - 2.05 (m, 1 H), 1.78 - 1.63 (m, 1 H), 1.59 - 1.46 (m, 1 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = $^{13}$C NMR (101MHz ,CHLOROFORM-d) d = 173.2, 165.1, 134.6, 130.3, 128.9, 127.6, 126.9, 119.4, 66.8, 51.6, 33.8, 33.2, 21.2; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{15}H_{19}O_2N_4$, 287.15080; found, 287.15080.

**HPLC (**CHIRALCEL® AD-3, *n*-heptane / $^{i}$PrOH = 200:1, 1 mL/min) $t_R$ = 55.98 min (minor), $t_R$ = 60.81 min (major), 84% *ee* (***S***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = - 51.3 (c = 0.435, $CH_2Cl_2$).

**1.12** (*R*)-2-(4-(5-phenyl-2*H*-tetrazol-2-yl)hex-5-en-1-yl)isoindoline-1,3-dione **(1l)**

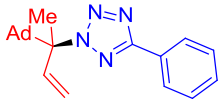


The reaction was performed with 5-phenyl-1*H*-tetrazole (29.2 mg, 0.2 mmol) and 2-(hexa-4,5-dien-1-yl)isoindoline-1,3-dione (90.9 mg, 0.4 mmol) at 60 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:3, $R_f$ = 0.35) to afford the product as a white solid (53.8 mg, 72%).

**m.p.**: 113 – 114 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ = 8.14 - 8.11 (m, 2 H), 7.85 - 7.81 (m, 2 H), 7.73 - 7.69 (m, 2 H), 7.49 - 7.44 (m, 3 H), 6.20 - 6.09 (m, 1 H), 5.48 - 5.41 (m, 1 H), 5.37 - 5.31 (m, 2 H), 3.82 - 3.67 (m, 2 H), 2.38 - 2.24 (m, 1 H), 2.10 (tdd, *J* = 6.1, 10.5, 14.0 Hz, 1 H), 1.82 - 1.57 (m, 2 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 168.4, 165.1, 134.5, 134.1, 132.1, 130.3, 128.9, 127.6, 127.0, 123.4, 119.7, 66.6, 37.1, 31.7, 25.0; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{21}H_{20}O_2N_5$, 374.16170; found, 374.16170. **HPLC (**CHIRALCEL® L-C2, *n*-heptane / $^{i}$PrOH = 50:50, 0.5 mL/min) $t_R$ = 14.12 min (minor), $t_R$ = 26.35 min (major), 86% *ee* (***S***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = + 33.9 (c = 0.585, $CH_2Cl_2$).

**2** Enantioselective Formation of Quaternary Allylic C-N Bonds (**2a-f**)

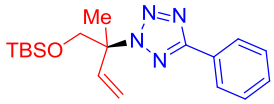
**2.1** (*S*)-2-(2-(adamantan-1-yl)but-3-en-2-yl)-5-phenyl-2H-tetrazole **(2a)**



The reaction was performed with 5-phenyl-1*H*-tetrazole (29.2 mg, 0.2 mmol) and 1-(penta-3,4-dien-2-yl)adamantane (80.9 mg, 0.4 mmol) at 100 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:15, $R_f$ = 0.43) to afford the product as a white solid (68.2 mg, 99%).

**m.p.**: 116 – 117 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ = $^{1}$H NMR (400MHz ,CHLOROFORM-d) d = 8.23 - 8.15 (m, 2 H), 7.53 - 7.41 (m, 3 H), 6.94 (dd, *J* = 11.1, 17.6 Hz, 1 H), 5.40 (dd, *J* = 0.8, 11.1 Hz, 1 H), 5.25 (dd, *J* = 0.8, 17.6 Hz, 1 H), 1.97 (td, *J* = 3.3, 6.5 Hz, 3 H), 1.91 (s, 3 H), 1.71 - 1.60 (m, 6 H), 1.58 - 1.48 (m, 6 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 163.3, 137.1, 130.0, 128.8, 128.1, 126.9, 116.4, 77.3, 75.7, 40.3, 36.9, 36.7, 28.7, 18.0; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{21}H_{27}N_4$, 335.22357; found, 335.22360. **HPLC (**CHIRALCEL® OD-3, *n*-heptane / $^{i}$PrOH = 98:2, 1 mL/min) $t_R$ = 2.98 min (major), $t_R$ = 3.41 min (minor), 74% *ee* (***S***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = + 49.6 (c = 0.635, $CH_2Cl_2$).

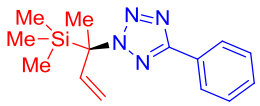
**2.2** (*R*)-2-(1-((tert-butyldimethylsilyl)oxy)-2-methylbut-3-en-2-yl)-5-phenyl-2*H*-tetrazole **(2b)**




The reaction was performed with 5-phenyl-1*H*-tetrazole (29.2 mg, 0.2 mmol) and *tert*-butyldimethyl((2-methylpenta-3,4-dien-1-yl)oxy)silane (85.0 mg, 0.4 mmol) at 100 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:15, $R_f$ = 0.47) to afford the product as a colorless oil (44.8 mg, 65%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.18 - 8.14 (m, 2 H), 7.50 - 7.42 (m, 3 H), 6.32 (dd, *J* = 10.9, 17.6 Hz, 1 H), 5.32 (d, *J* = 10.9 Hz, 1 H), 5.17 (d, *J* = 17.4 Hz, 1 H), 4.24 (d, *J* = 10.1 Hz, 1 H), 4.00 (d, *J* = 10.1 Hz, 1 H), 1.95 (s, 3 H), 0.77 (s, 9 H), -0.01 (s, 3 H), -0.06 (s, 3 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 164.5, 137.7, 130.1, 128.9, 127.9, 127.0, 116.7, 70.7, 69.0, 25.7, 21.0, 18.1, -5.5, -5.6; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{18}H_{29}ON_4Si$, 345.21107; found, 345.21120. **HPLC (**CHIRALCEL® L-C2, *n*-heptane / *i*PrOH = 200:1, 0.5 mL/min) $t_R$ = 8.19 min (minor), $t_R$ = 9.62 min (major), 79% *ee* (***R***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = - 11.2 (c = 0.525, $CH_2Cl_2$).

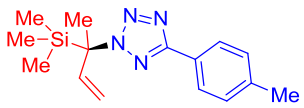
**2.3** (*S*)-5-phenyl-2-(2-(trimethylsilyl)but-3-en-2-yl)-2*H*-tetrazole **(2c)**




The reaction was performed with 5-phenyl-1*H*-tetrazole (29.2 mg, 0.2 mmol) and buta-2,3-dien-2-yltrimethylsilane (50.5 mg, 0.4 mmol) at 100 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:15, $R_f$ = 0.43) to afford the product as a colorless oil (46.1 mg, 85%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.19 - 8.12 (m, 2 H), 7.52 - 7.41 (m, 3 H), 6.34 (dd, *J* = 10.9, 17.4 Hz, 1 H), 5.20 (dd, *J* = 0.6, 10.9 Hz, 1 H), 4.91 (dd, *J* = 0.6, 17.3 Hz, 1 H), 1.87 (s, 3 H), 0.19 (s, 9 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 164.2, 138.8, 130.1, 128.9, 128.0, 126.9, 113.2, 77.3, 63.3, 20.2, -3.2; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{14}H_{21}N_4Si$, 273.15355; found, 273.15360. **HPLC (**CHIRALCEL® OD-3, *n*-heptane / $^i$PrOH = 300:1, 0.5 mL/min) $t_R$ = 8.87 min (major), $t_R$ = 10.07 min (minor), 94% *ee* (***S***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = + 36.6 (c = 0.550, $CH_2Cl_2$).

**2.4** (*S*)-5-(p-tolyl)-2-(2-(trimethylsilyl)but-3-en-2-yl)-2*H*-tetrazole **(2d)**

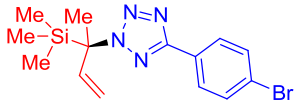



The reaction was performed with 5-phenyl-1*H*-tetrazole (29.2 mg, 0.2 mmol) and buta-2,3-dien-2-yltrimethylsilane (50.5 mg, 0.4 mmol) at 100 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:40, $R_f$ = 0.27) to afford the product as a colorless oil (49.9 mg, 87%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.07 - 8.02 (m, 2 H), 7.31 - 7.26 (m, 2 H), 6.33 (dd, *J* = 10.9, 17.3 Hz, 1 H), 5.20 (dd, *J* = 0.5, 11.0 Hz, 1 H), 4.91 (dd, *J* = 0.6, 17.4 Hz, 1 H), 2.41 (s, 3 H), 1.87 (s, 3 H), 0.19 (s, 9 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = $^{13}$C NMR (101MHz ,CHLOROFORM-d) d = 164.3, 140.2, 138.9, 129.6, 126.8, 125.2, 113.2, 63.2, 21.6, 20.2, -3.1; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{15}H_{23}N_4Si$, 287.16920; found,

287.1688. **HPLC (**CHIRALCEL® L-C1, *n*-heptane / $^{i}$PrOH = 300:1, 0.5 mL/min) $t_R$ = 9.67 min (major), $t_R$ = 11.59 min (minor), 96% *ee* (***S***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = + 40.0 (c = 0.520, $CH_2Cl_3$).

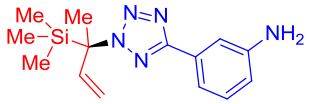
**2.5** (*S*)-5-(4-bromophenyl)-2-(2-(trimethylsilyl)but-3-en-2-yl)-2*H*-tetrazole **(2e)**




The reaction was performed with 5-phenyl-1*H*-tetrazole (29.2 mg, 0.2 mmol) and buta-2,3-dien-2-yltrimethylsilane (50.5 mg, 0.4 mmol) at 100 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:40, $R_f$ = 0.32) to afford the product as a white solid (63.3 mg, 90%).

**m.p.**: 60 – 61 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ = 8.05 - 8.01 (m, 2 H), 7.63 - 7.59 (m, 2 H), 6.33 (dd, *J* = 10.9, 17.4 Hz, 1 H), 5.21 (dd, *J* = 0.5, 10.9 Hz, 1 H), 4.92 (dd, *J* = 0.5, 17.3 Hz, 1 H), 1.87 (s, 3 H), 0.19 (s, 9 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 163.5, 138.7, 132.2, 128.4, 127.0, 124.5, 113.4, 63.5, 20.2, -3.2; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{14}H_{20}N_4{}^{79}BrSi$, 351.06406; found, 351.06380; calcd for $C_{14}H_{20}N_4{}^{81}BrSi$, 353.06201; found, 353.06170. **HPLC (**CHIRALCEL® 2*L-A2, *n*-heptane / EtOH = 98:2, 0.5 mL/min) $t_R$ = 14.37 min (major), $t_R$ = 15.54 min (minor), 95% *ee* (***S***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = + 39.8 (c = 0.530, $CH_2Cl_2$).

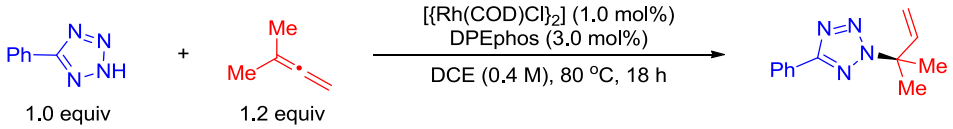
**2.6** (*S*)-3-(2-(2-(trimethylsilyl)but-3-en-2-yl)-2*H*-tetrazol-5-yl)aniline **(2f)**




The reaction was performed with 5-phenyl-1*H*-tetrazole (29.2 mg, 0.2 mmol) and buta-2,3-dien-2-yltrimethylsilane (50.5 mg, 0.4 mmol) at 100 °C. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:5, $R_f$ = 0.17) to afford the product as a yellowish oil (42.0 mg, 73%).

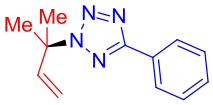
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ = 7.55 (ddd, *J* = 1.0, 1.5, 7.7 Hz, 1 H), 7.49 (qd, *J* = 0.7, 2.4 Hz, 1 H), 7.28 - 7.23 (m, 1 H), 6.76 (ddd, *J* = 1.0, 2.5, 8.0 Hz, 1 H), 6.33 (dd, *J* = 10.9, 17.4 Hz, 1 H), 5.20 (dd, *J* = 0.5, 10.9 Hz, 1 H), 4.90 (dd, *J* = 0.6, 17.4 Hz, 1 H), 1.86 (s, 3 H), 0.19 (s, 9 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 164.3, 146.9, 138.8, 129.9, 128.8, 117.2, 116.8, 113.2, 63.3, 20.2, -3.2; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{14}H_{22}N_5Si$, 228.16445; found, 288.16410. **HPLC (**CHIRALCEL® AD-3, *n*-heptane / EtOH = 95:5, 1 mL/min) $t_R$ = 11.22 min (minor), $t_R$ = 12.18 min (major), 97% *ee* (***S***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = + 35.6 (c = 0.530, $CHCl_3$).

## Gram Scale Prenylation of Phenyltetrazole




The reaction was performed in a 25 ml Schlenk tube under argon. $[Rh(COD)Cl]_2$ (28.6 mg, 0.058 mmol, 1.0 mol%), DPEphos (93.7 mg, 0.174 mmol, 3.0 mol%), phenyltetrazole (847.7 mg, 5.8 mmol, 1.0 equiv) were dissolved in DCE (14.5 mL), then allene (474.1 mg, 6.96 mmol, 1.2 equiv.) was added and the tube was sealed. The reaction mixture was stirred at 80 °C for 18 hours. After cooling to room temperature, the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:20, $R_f$ = 0.33) to afford the product as a colorless oil (1.22 g, 98%).

2-(2-methylbut-3-en-2-yl)-5-phenyl-2*H*-tetrazole **(3)**

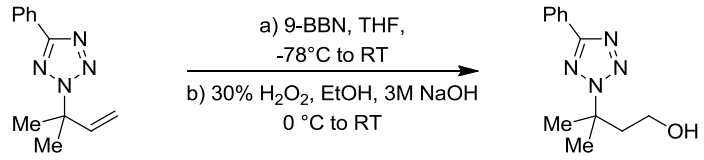



The crude product was purified by flash column chromatography on silica gel (EA / CH = 1:30, $R_f$ = 0.35) to afford the product as a yellowish oil (43.0 mg, 80%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.14 - 8.21 (m, 2 H), 7.44 - 7.52 (m, 3 H), 6.29 (dd, *J*=17.3, 10.7 Hz, 1 H), 5.25 (d, *J*=10.7 Hz, 1 H), 5.19 (d, *J*=17.3 Hz, 1 H), 1.93 (s, 6 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 164.7, 141.1, 130.2, 128.9, 127.9, 127.0, 114.7, 66.8, 27.3; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{12}H_{15}N_4$, 215.12912; found, 215.12924.

## Derivatization of $N^2$-allylated Tetrazoles

**1** Synthesis of 3-methyl-3-(5-phenyl-2*H*-tetrazol-2-yl)butan-1-ol **(4a)**

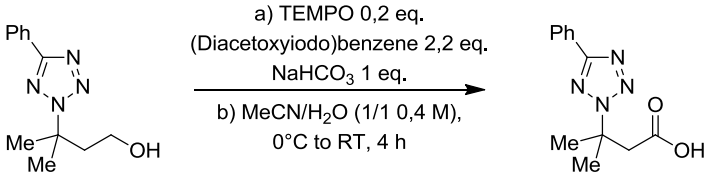



**3** **4a**

Compound **3** (144.8 mg, 0.6 mmol, 1.00 equiv) was dissolved in dry, degassed THF (3.0 ml, 0.2 M) and cooled to -78 ℃. Then 9-BBN (1.5 mmol, 3.00 ml, 2.5 equiv, 0.5 M solution in THF) was added to the reaction vessel. The reaction mixture was stirred for 1 h at -78 ℃, then allowed to slowly warm to room temperature and stirred overnight. The resulting solution was cooled to 0 ℃, at which time EtOH (1.8 ml, 3 mL/mmol), 3 M NaOH (0.9 ml, 1.5 mL/mmol), and 30% $H_2O_2$ (0.9 ml, 1.5 mL/mmol) were added in the specified order. The reaction was allowed to warm to room temperature and was stirred for an additional 6 h. The reaction was diluted with ether, then washed with 1 M NaOH and saturated aqueous $NH_4Cl$. The organic layer was dried over $MgSO_4$, filtered and concentrated.[4] The crude product was purified by flash column silica gel chromatography (CH/EE = 2/1, $R_f$ = 0.23) to give **4a** (139.2 mg, 99% yield) as a colorless oil.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.10 - 8.19 (m, 2 H), 7.40 - 7.55 (m, 3 H), 3.67 (t, *J*=6.7 Hz, 2 H), 2.36 (t, *J*=6.6 Hz, 2 H), 1.84 (s, 6 H), 1.75 (br. s., 1 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 164.6, 130.3, 128.9, 127.8, 127.0, 65.7, 58.6, 44.3, 27.9; **HRMS-APCI** (m/z): $[M+H]^+$ calcd for $C_{12}H_{17}ON_4$, 233.13969; found, 233.13983.

**2** Synthesis of 3-methyl-3-(5-phenyl-2*H*-tetrazol-2-yl)butanoic acid **(4b)**

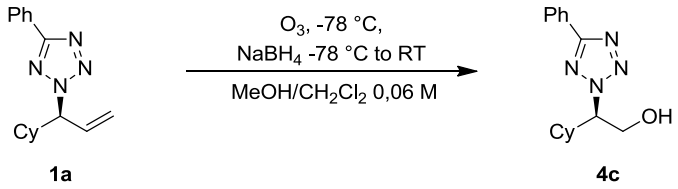



**4a** **4b**

Iodobenzene diacetate (425.2 mg, 1.32 mmol 2.2 eq.), TEMPO (18.8 mg, 0.12 mmol 20 mol%), $NaHCO_3$ (100.8 mg, 1.20 mmol, 2.0 eq.), and **4a** (144.8 g, 0.60 mmol) were added in a flask. To this mixture was added MeCN : $H_2O$ (0.75 mL : 0.75 mL). The reaction was cooled to 0 ℃ and stirred for 2 h, then warmed to room temperature and stirred for an additional 2 h. The reaction mixture was concentrated under reduced pressure.[4] The crude reaction mixture was initially purified by flash column chromatography (CH/EE/formic acid = 4/1/0.02, $R_f$ = 0.20) to give **4b** (145.5 mg, 99 % yield) as a white solid.

**m.p.:** 126-128 ºC; **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 10.77 (br. s., 1 H), 8.08 - 8.20 (m, 2 H), 7.41 - 7.53 (m, 3 H), 3.19 (s, 2 H), 1.91 (s, 6 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 174.6, 164.7, 130.3, 128.9, 127.7, 127.0, 64.0, 45.3, 27.6; **HRMS-APCI** (m/z): $[M+H]^+$ calcd for $C_{12}H_{15}ON_4$, 274.11895; found, 274.11893.

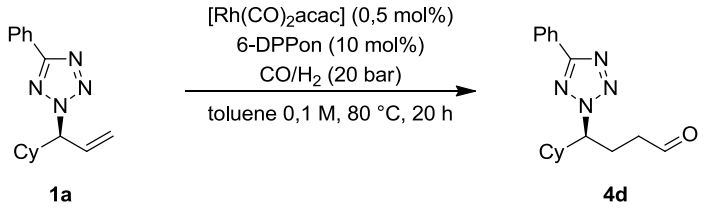
**3** Synthesis of (*R*)-2-cyclohexyl-2-(5-phenyl-2*H*-tetrazol-2-yl)ethanol **(4c)**




**1a** (134.2 mg, 0.50 mmol) was dissolved in MeOH : $CH_2Cl_2$ (5 ml : 5 ml, 0.05 M) and cooled to -78 ℃. Ozone was bubbled through the solution until a blue color persisted in the solution (approximately 5 min). Then, $NaBH_4$ (94.6 mg, 2.50 mmol, 5 eq.) was added to the reaction mixture. The cold bath was removed, and the reaction was allowed to gradually warm to room temperature. After stirring for two hours at room temperature, the reaction was quenched by adding 1 M HCl (15 mL). The resulting organic layer was separated. The aqueous layer was brought to neutral pH by addition of saturated aqueous $NaHCO_3$ and extracted with EtOAc (2 x 30 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated.[4] The resulting crude product was purified by flash column silica gel chromatography (CH/EE = 5/1, $R_f$ = 0.20) to give **4c** (120.8 mg, 0.44 mmol, 89%) as a white solid.

**m.p.**: 88-90 °C**; $^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.09 - 8.18 (m, 2 H), 7.44 - 7.52 (m, 3 H), 4.73 (ddd, *J*=8.6, 7.3, 3.0 Hz, 1 H), 4.30 (dd, *J*=12.3, 7.3 Hz, 1 H), 4.10 (dd, *J*=12.3, 3.0 Hz, 1 H), 2.49 (br. s, 1 H), 2.16 (ddddd, *J*=11.6, 11.6, 8.3, 3.4, 3.4 Hz, 1 H), 1.88 - 1.97 (m, 1 H), 1.75 - 1.85 (m, 1 H), 1.59 - 1.73 (m, 2 H), 0.94 - 1.38 (m, 6 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 165.0, 130.4, 129.0, 127.4, 127.0, 71.7, 62.2, 39.1, 29.8, 29.4, 26.1, 25.9, 25.7; **HRMS-APCI** (m/z): $[M+H]^+$ calcd for $C_{15}H_{21}ON_4$, 273.17099; found, 273.17099. **HPLC (**CHIRALCEL® AD-3, *n*-heptane / $^i$PrOH = 90:10, 1 mL/min) $t_R$ = 8.27 min (minor), $t_R$ = 9.70 min (major), 85% *ee* (***R***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = + 10.8 (c = 0.665, $CH_2Cl_2$).

**4** Synthesis of (*S*)-4-cyclohexyl-4-(5-phenyl-2*H*-tetrazol-2-yl)butanal **(4d)**

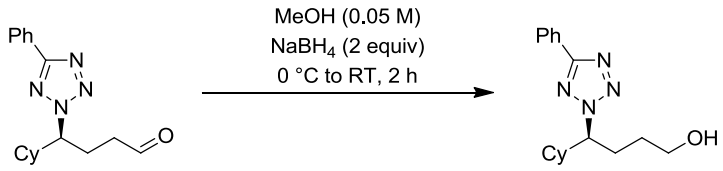



[$Rh(CO)_2$acac] (0.3 mg, 1 μmol, 0.5 mol%) and 6-DPPon (5.6 mg, 0.02 mmol, 10mol%) were added in a high-pressure autoclave and dissolved in toluene (2.0 mL 0.01 M) before **1a** (53.7 mg, 0.2 mmol, 1.0 equiv) was added. The mixture was stirred at 80 ℃ under $CO/H_2$ (20 bar) for 20 hours. The reaction mixture was filtrated over a short silica column, rinsed with ethyl acetate and concentrated by rotary evaporation.[6] The resulting crude product was purified by flash column silica gel chromatography (CH/EE = 10/1, $R_f$ = 0.11) to give **4d** (41.8 mg, 70%) as a colorless oil.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ = 9.69 (s, 1 H), 8.14 - 8.18 (m, 2 H), 7.45 - 7.52 (m, 3 H), 4.65 (ddd, *J*=10.5, 8.1, 3.7 Hz, 1 H), 2.33 - 2.50 (m, 2 H), 2.20 - 2.33 (m, 2 H), 1.91 - 2.07 (m, 2 H), 1.76 - 1.84 (m, 1 H), 1.60 - 1.73 (m, 2 H), 0.94 - 1.36 (m, 6 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 200.3, 165.1, 130.4, 129.0, 127.6, 127.0, 69.5, 42.5,

40.2, 29.8, 29.3, 26.1, 25.9, 25.7, 23.9; **HRMS-APCI** (m/z): $[M+H]^+$ calcd for $C_{17}H_{22}ON_4Na$, 321.16858; found, 321.16867.

**5** Synthesis of (*S*)-4-cyclohexyl-4-(5-phenyl-2*H*-tetrazol-2-yl)butan-1-ol **(4e)**



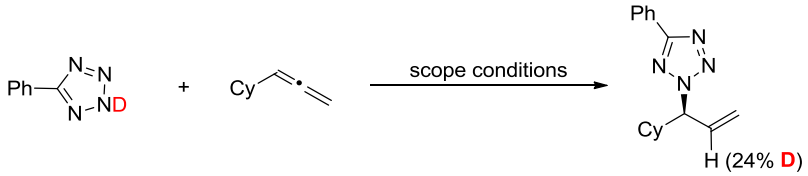

**4d** (15.0 mg, 0.05 mmol, 1.0 equiv) was dissolved in dry MeOH (1.0 ml, 0.05) and cooled to 0 ℃. Then $NaBH_4$ (3.8 mg, 0.1 mmol, 2.0 equiv) was added to the reaction vessel. The reaction mixture was stirred for 15 min at 0 ℃. Then, the ice bath was removed and the solution was stirred overnight at room temperature. The reaction mixture was quenched by adding saturated aqueous $NH_4Cl$ Solution (5 ml) and the resulting solution was extracted several times with $Et_2O$. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash column silica gel chromatography (CH/EE = 5/1, $R_f$ = 0.09) to give **4e** (13.1 mg, 87 % yield) as a colorless oil.

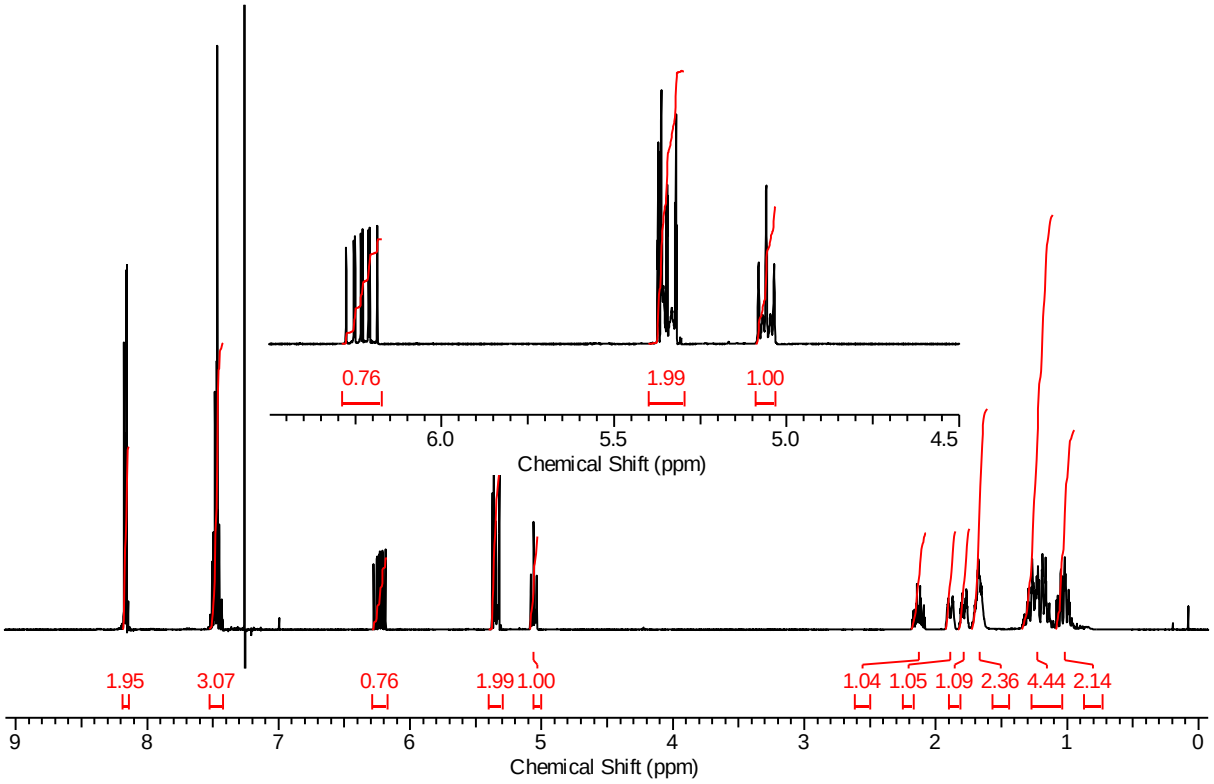
**$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.19 - 8.14 (m, 2 H), 7.52 - 7.43 (m, 3 H), 4.70 - 4.61 (m, 1 H), 3.68 - 3.54 (m, 2 H), 2.28 - 2.10 (m, 2 H), 2.04 - 1.90 (m, 2 H), 1.83 - 1.74 (m, 1 H), 1.72 - 1.61 (m, 2 H), 1.50 - 1.38 (m, 2 H), 1.35 - 0.94 (m, 7 H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 164.9, 130.3, 128.9, 127.8, 127.0, 70.4, 62.1, 42.6, 30.0, 29.3, 29.1, 28.0, 26.2, 26.0, 25.8; **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{17}H_{24}ON_4Na$, 323.18423; found, 323.18448. **HPLC (**CHIRALCEL® AD-3, *n*-heptane / $^i$PrOH = 93:7, 1 mL/min) $t_R$ = 12.03 min (minor), $t_R$ = 12.99 min (major), 87% *ee* (***S***); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = + 8.1 (c = 0.520, $CH_2Cl_2$).

## Deuterium Labeling Experiment

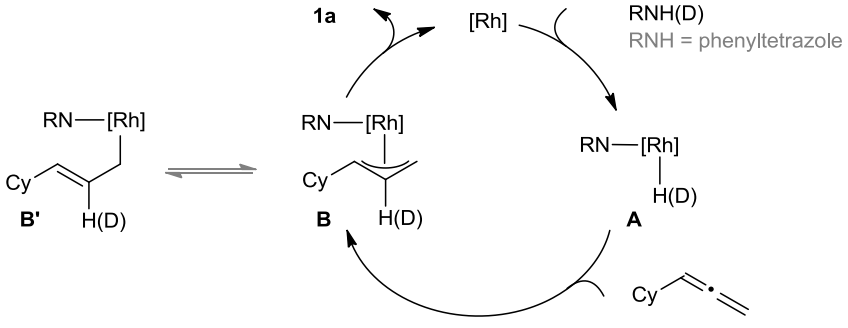
### Rhodium catalyzed coupling of [D]phenyltetrazole with cyclohexylallene

Experiment adapted the standard scope conditions, product **5** was isolated as a colorless oil, yield 59% (37.7 mg).




## Proposed Mechanism



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2 a) Taherirastgar, F.; Brandsma, L. *Synth. Commun.* **1997**, *27*, 4035–4040; b) Xu, K.; Thieme, N.; Breit, B. *Angew. Chem. Int. Ed.* **2014**, *53*, 2162-2165; c) Kuang, J.; Ma, S. *J. Org. Chem.* **1999**, *74*, 1763-1765; d) Danheiser, R. L.; Tsai, Y.; Fink, D. M. *Org. Synth.* **1988**, *66*, 1-7.

3 Deuterium exchange according to: T. Sakaizumi, H. Kikuchi, O. Ohashi, I. Yamaguchi, *Bull. Chem. Soc. Jpn*., **1987**, *60*, 3903-3909.

4 L. M. Stanley, J. F. Hartwig, *J. Am. Chem. Soc.* **2009**, *131*, 8971-8983.

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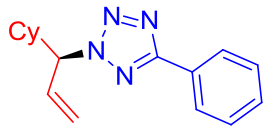
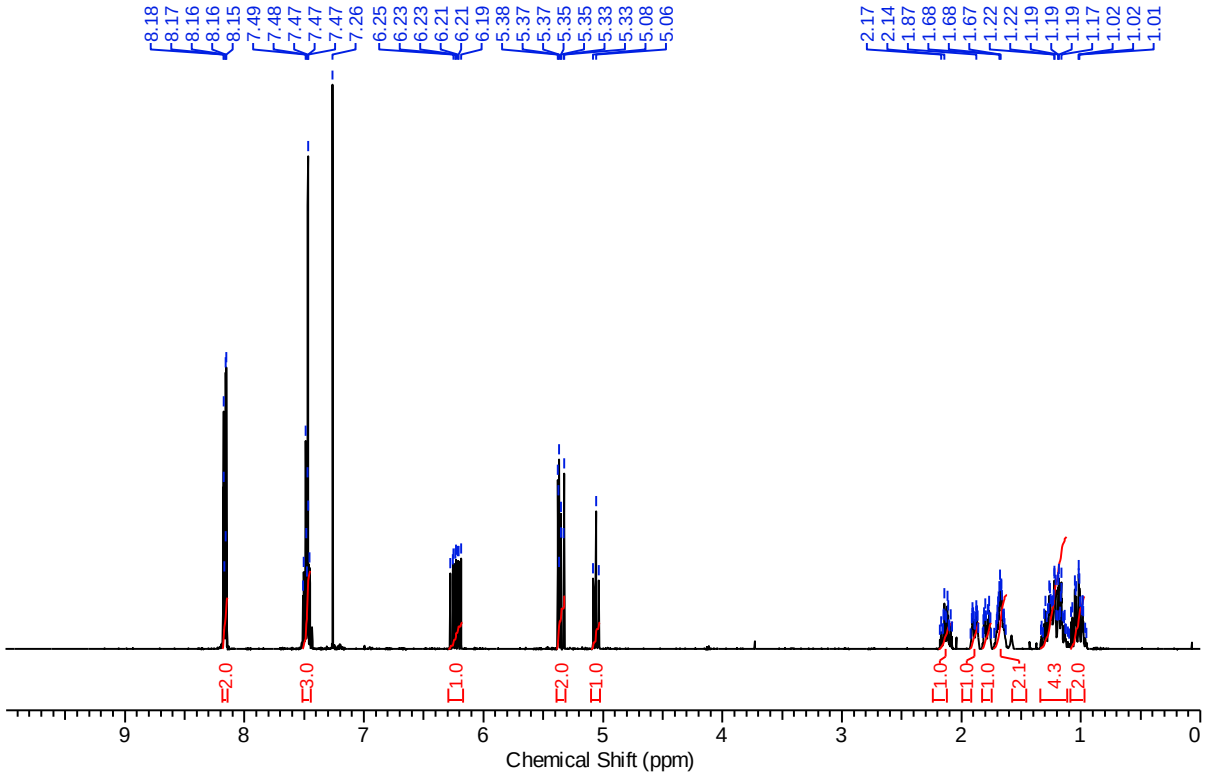
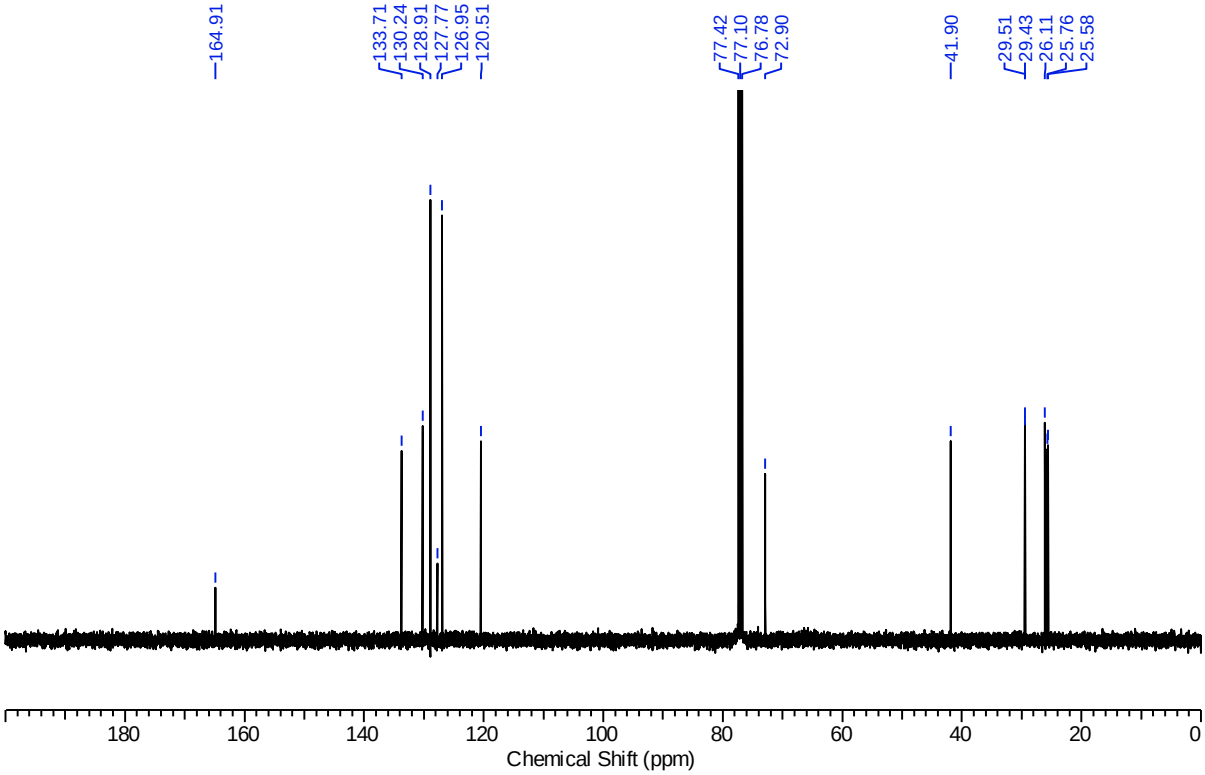
**$^{1}$H NMR and $^{13}$C NMR spectra**

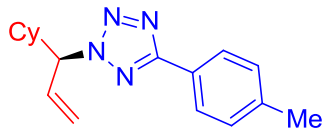
(*S*)-2-(1-cyclohexylallyl)-5-phenyl-2*H*-tetrazole **(1a)**

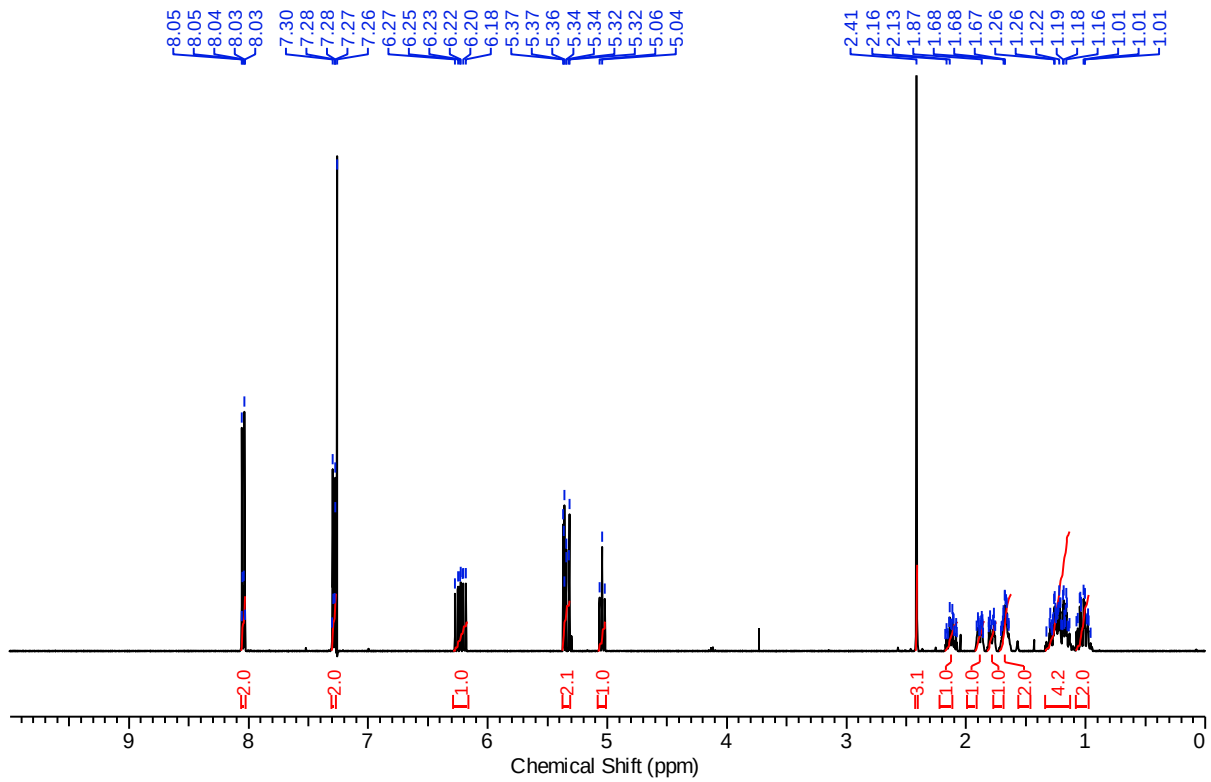


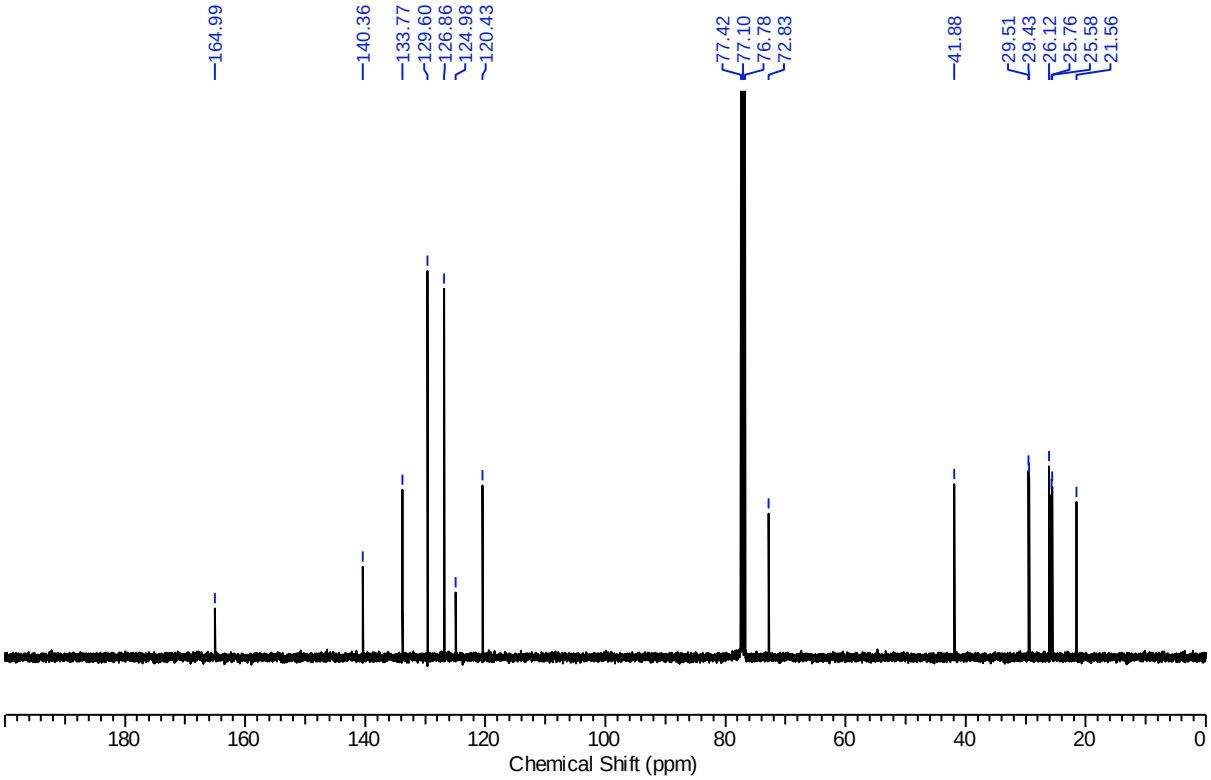



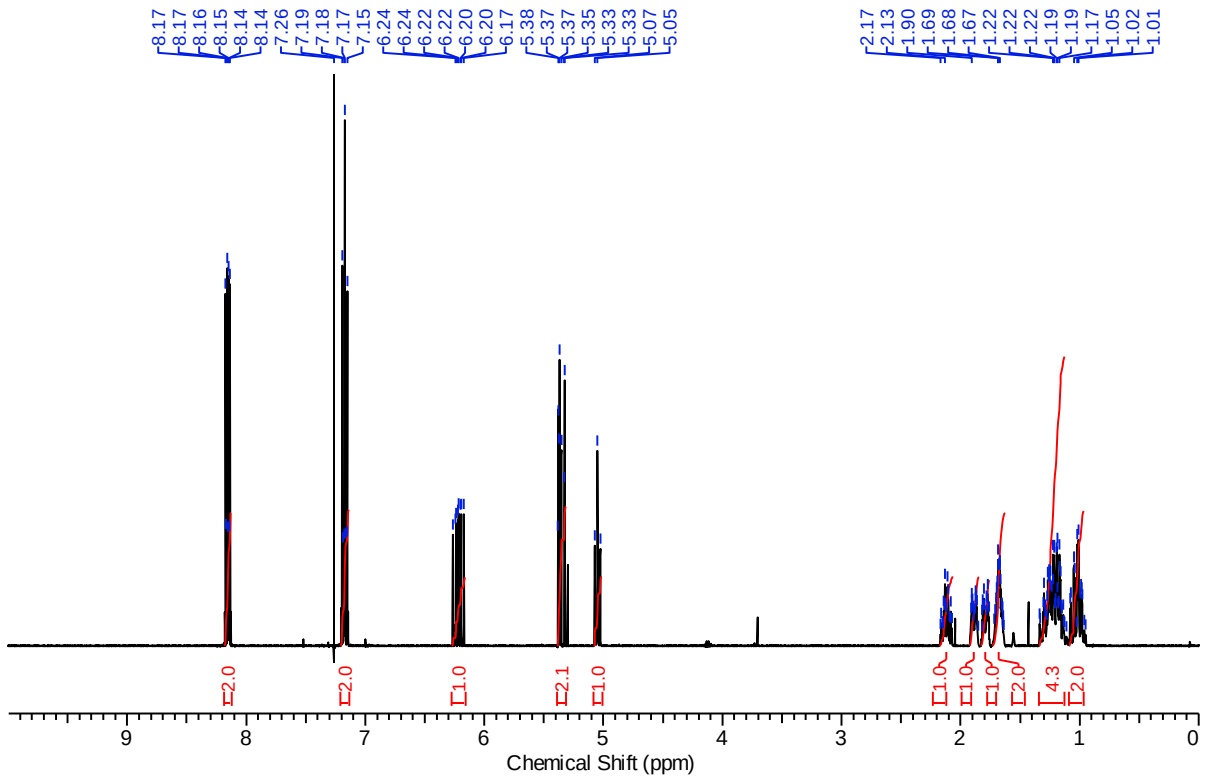
(*S*)-2-(1-cyclohexylallyl)-5-(p-tolyl)-2*H*-tetrazole **(1b)**

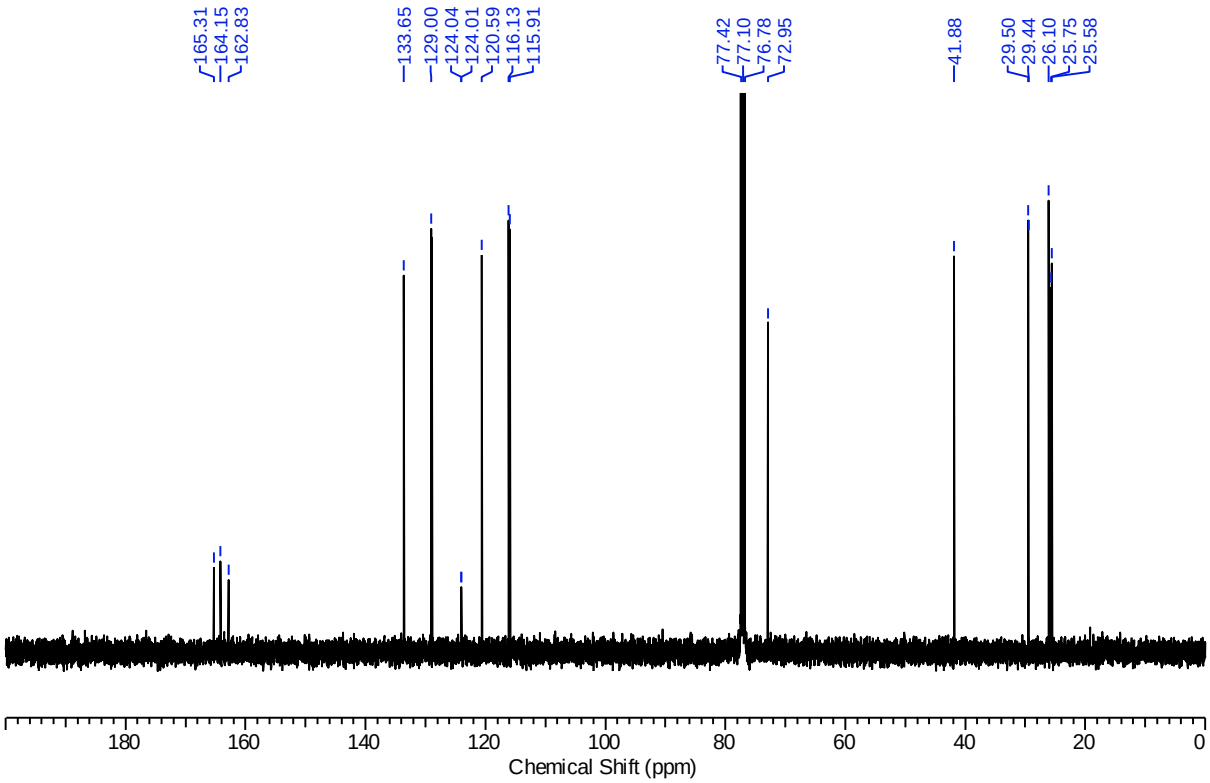


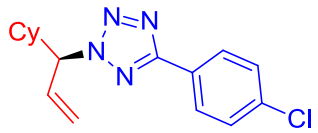



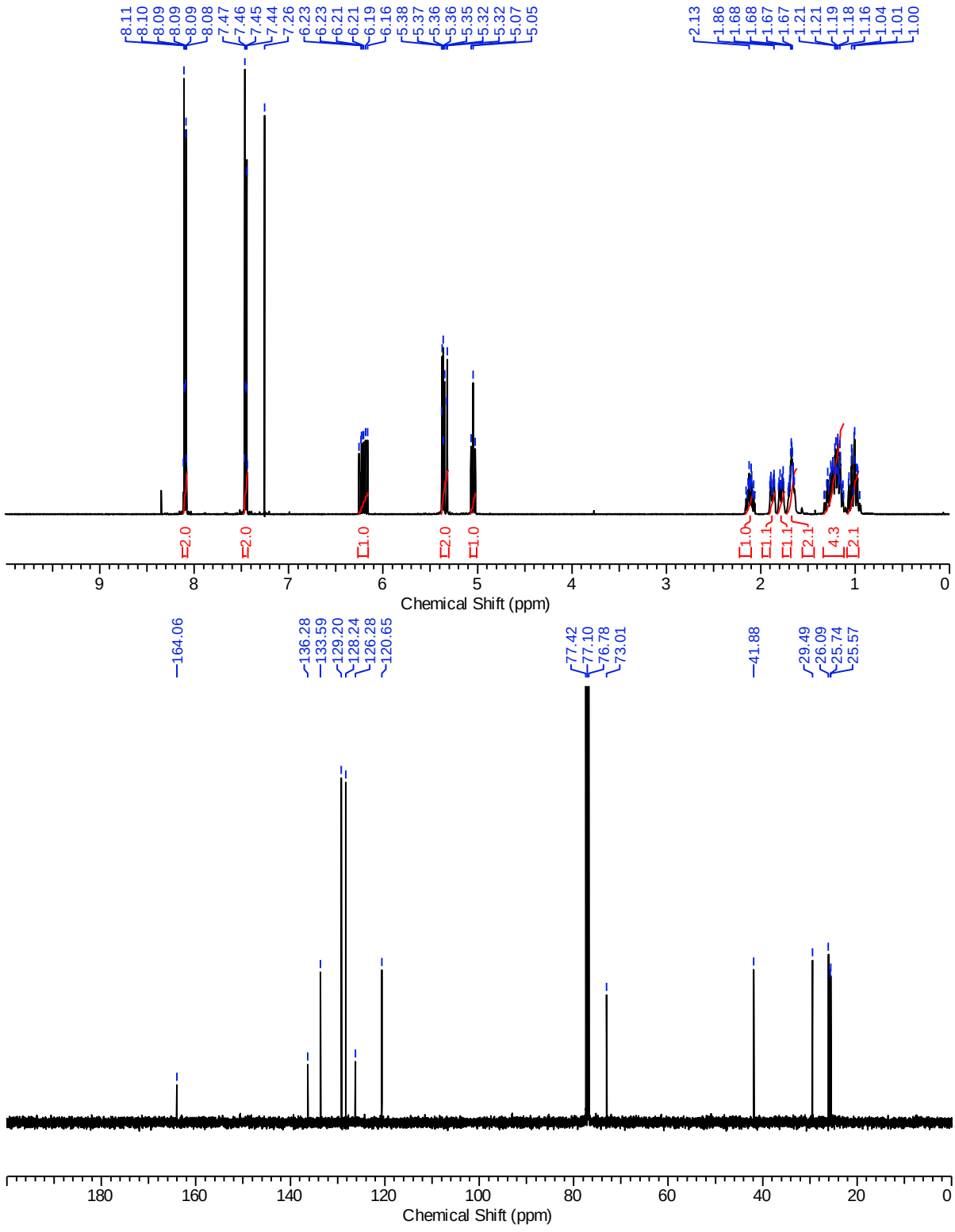
(*S*)-2-(1-cyclohexylallyl)-5-(4-fluorophenyl)-2*H*-tetrazole **(1c)**

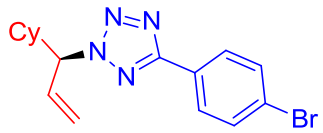



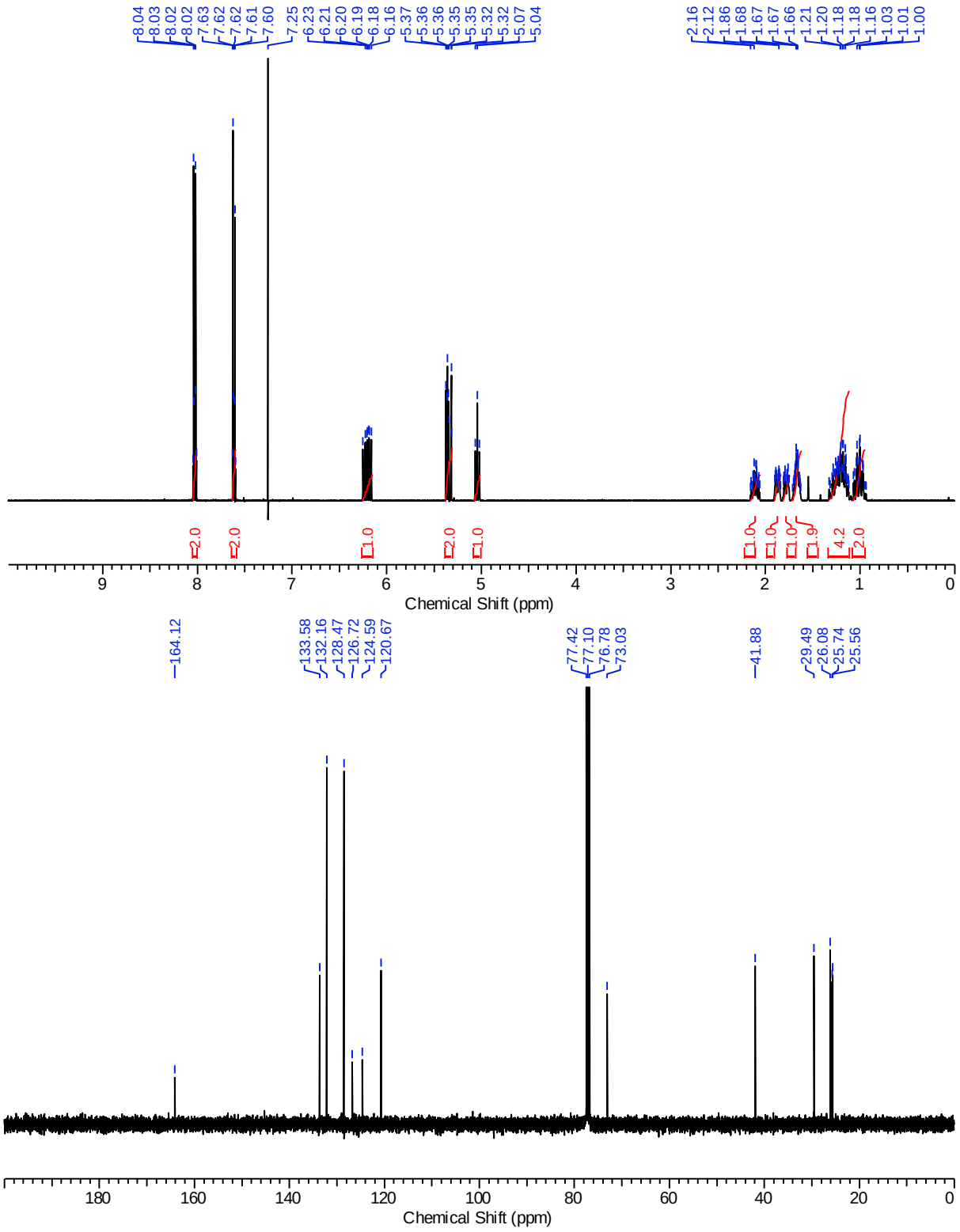
(*S*)-5-(4-chlorophenyl)-2-(1-cyclohexylallyl)-2*H*-tetrazole **(1d)**



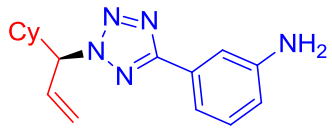



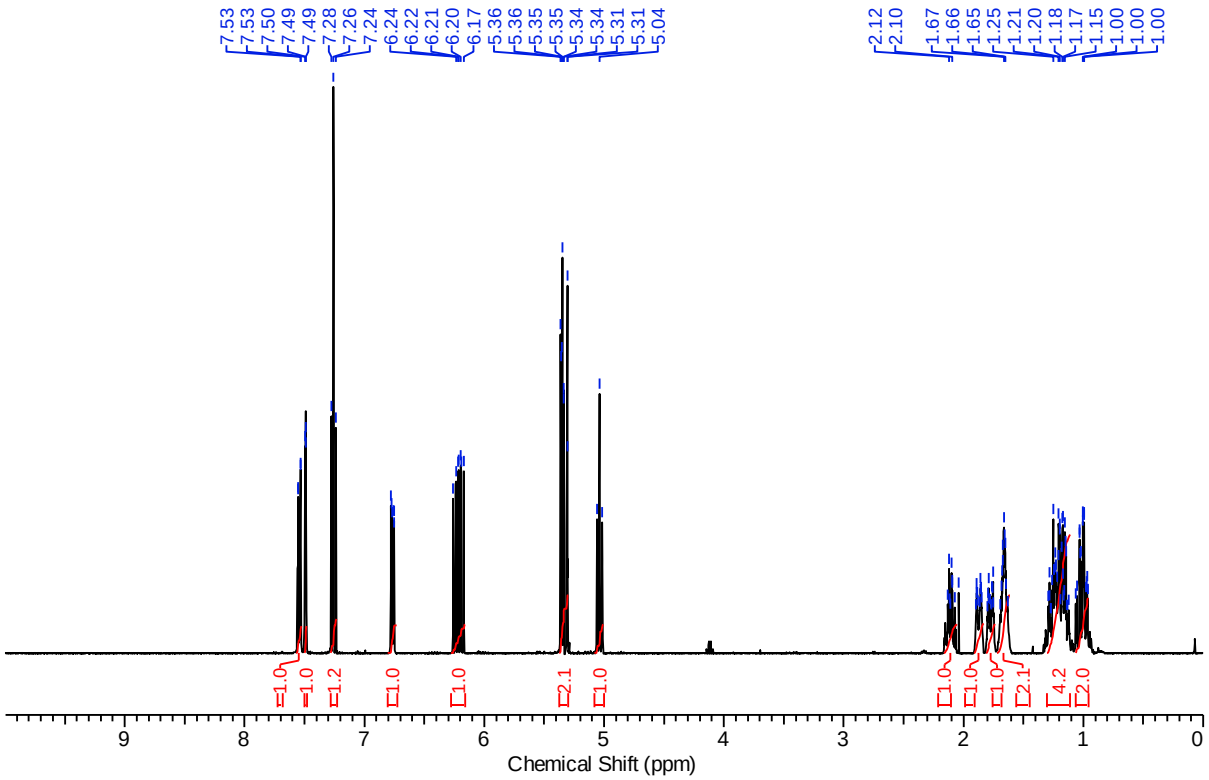
(*S*)-5-(4-bromophenyl)-2-(1-cyclohexylallyl)-2*H*-tetrazole **(1e)**

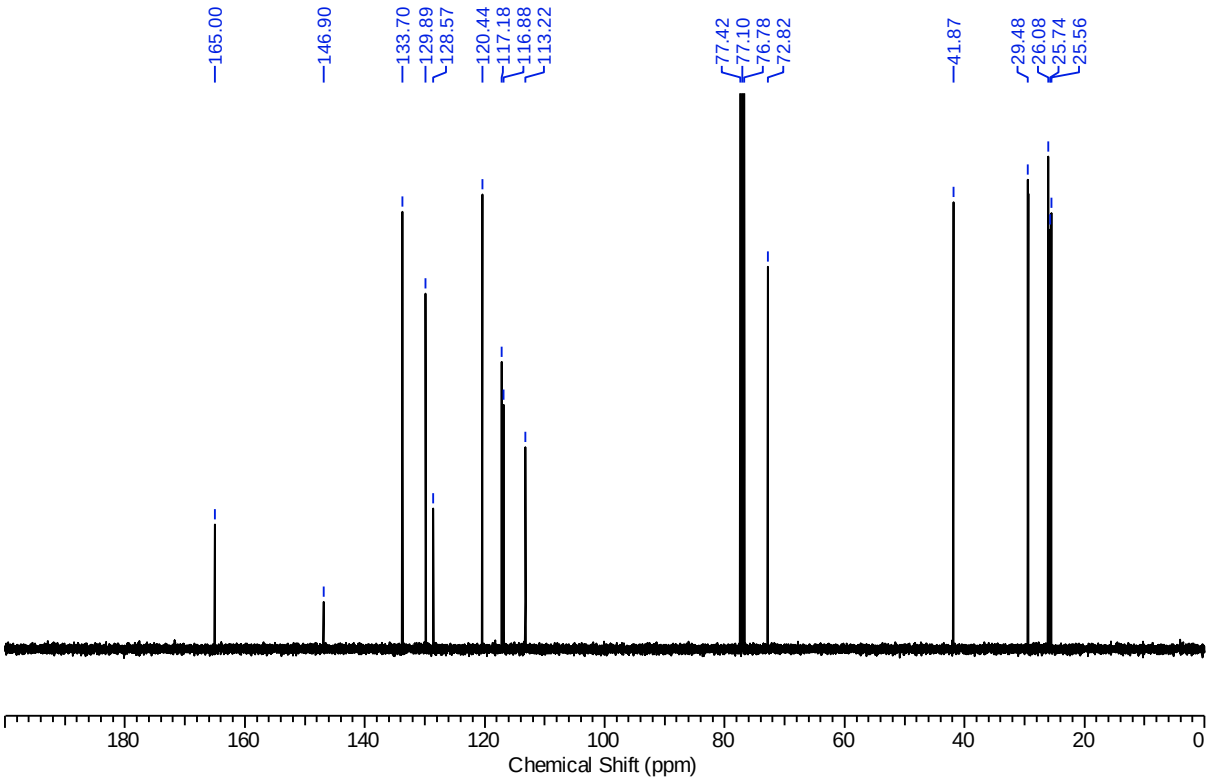


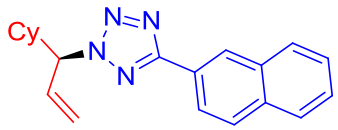
(*S*)-3-(2-(1-cyclohexylallyl)-2*H*-tetrazol-5-yl)aniline **(1f)**

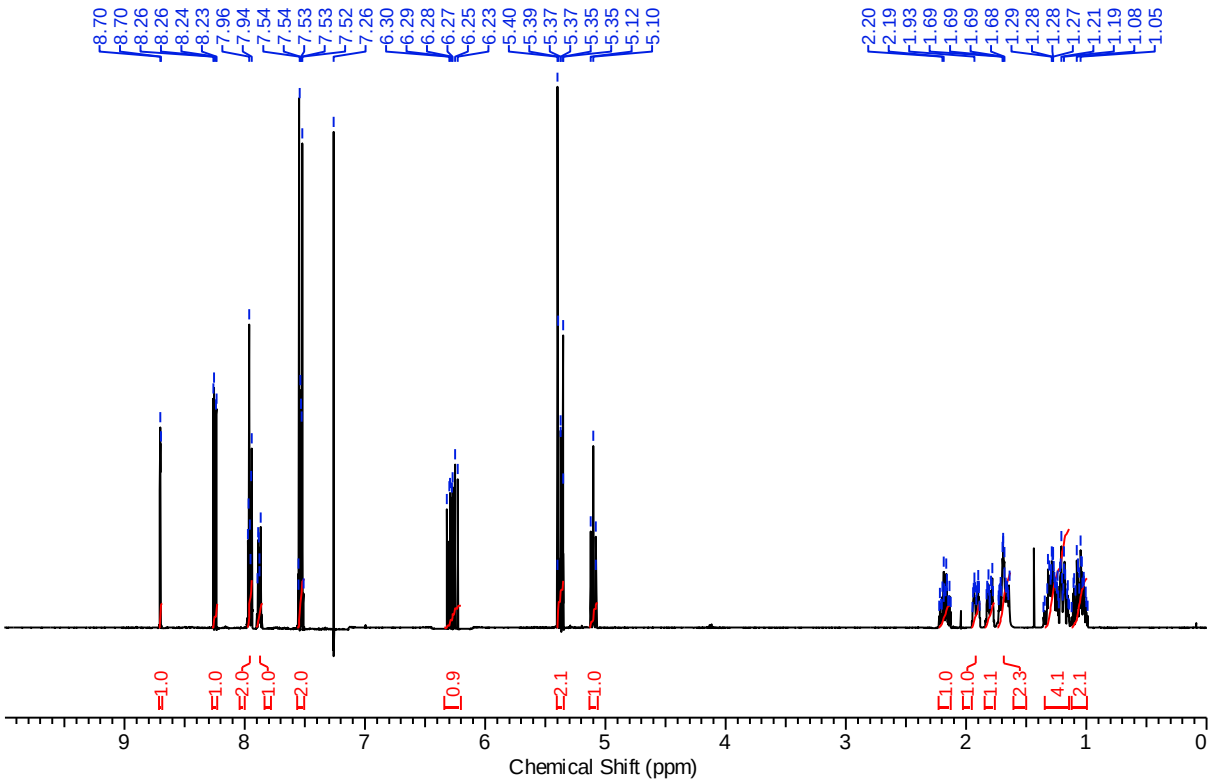


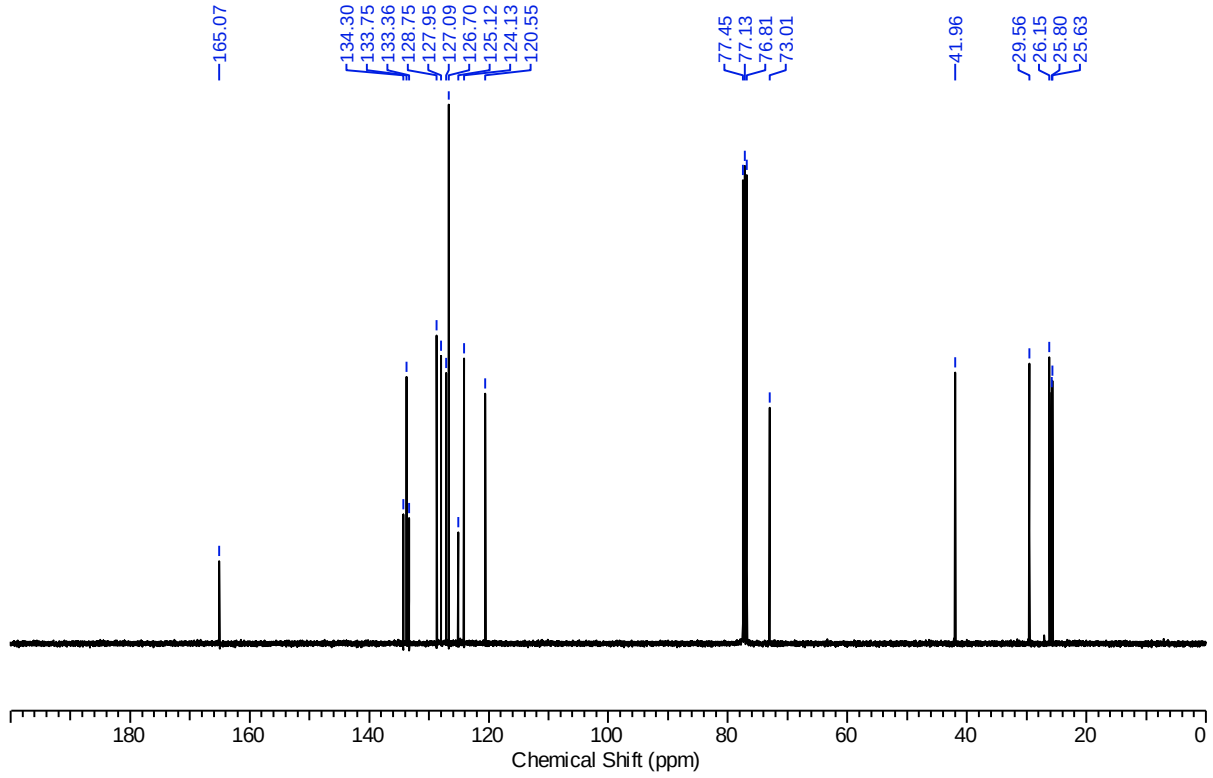



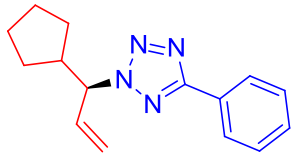
(*S*)-2-(1-cyclohexylallyl)-5-(naphthalen-2-yl)-2*H*-tetrazole **(1g)**

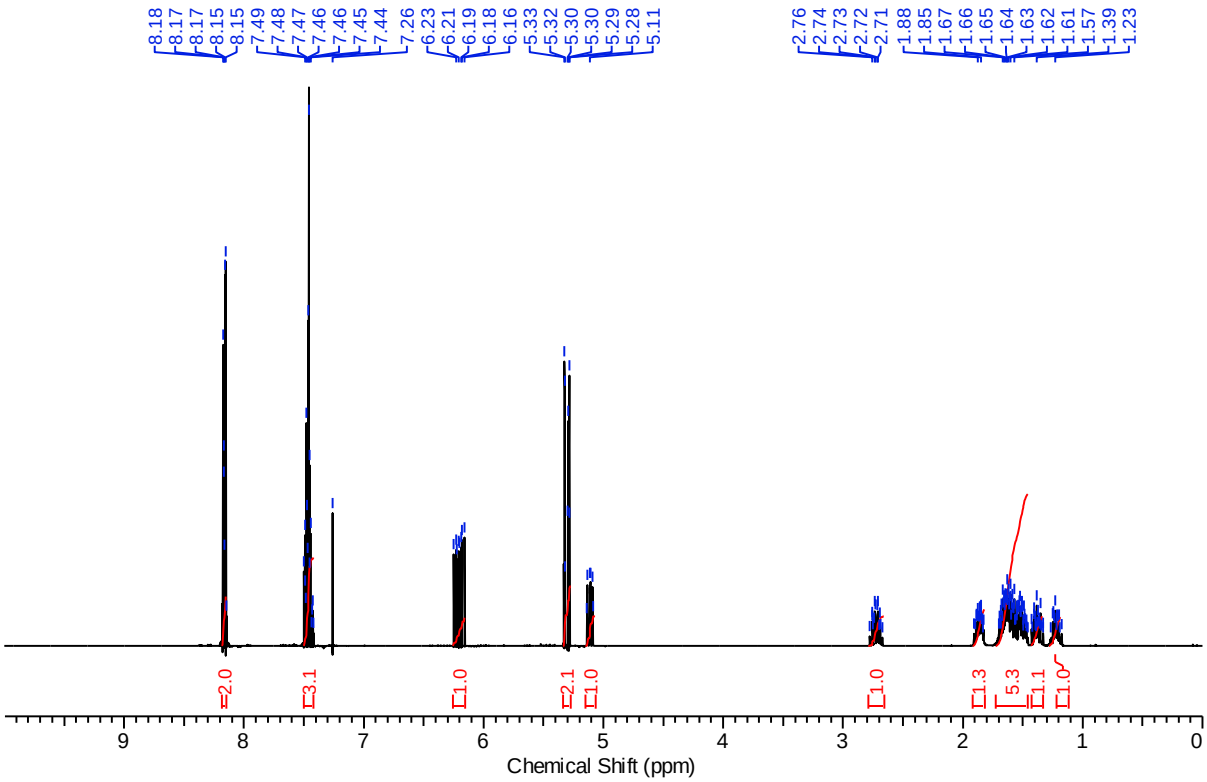


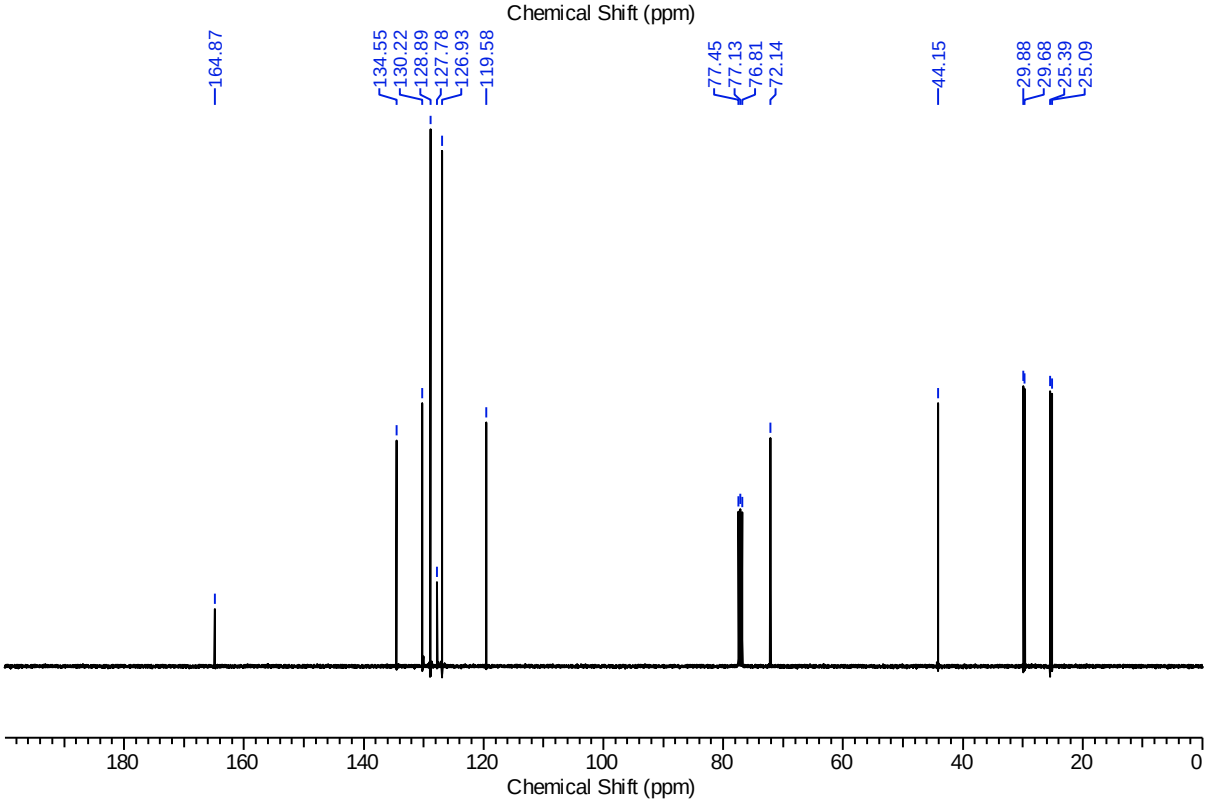



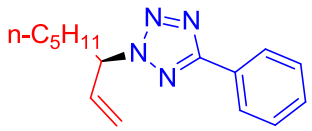
(*S*)-2-(1-cyclopentylallyl)-5-phenyl-2*H*-tetrazole **(1h)**

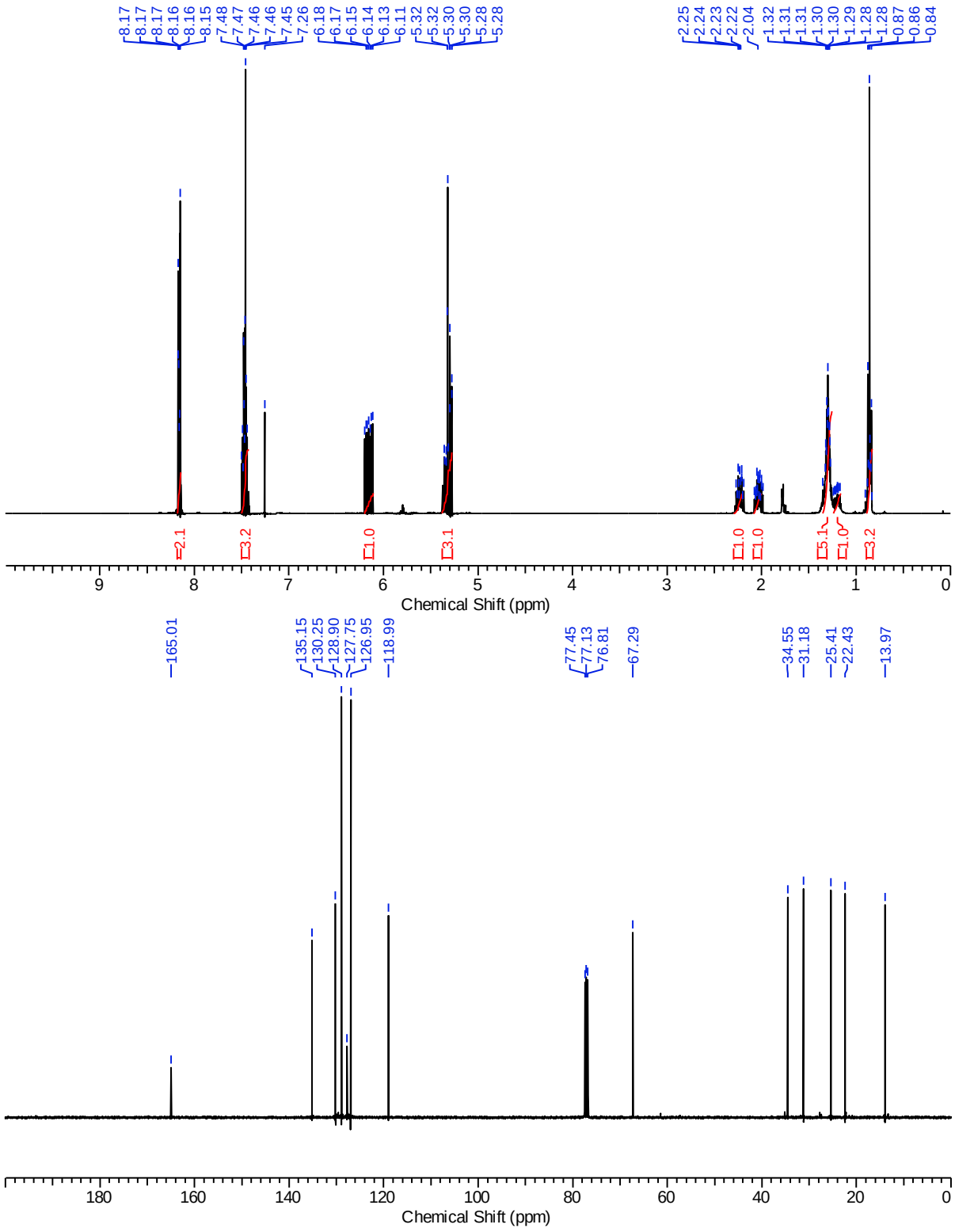




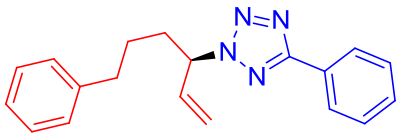



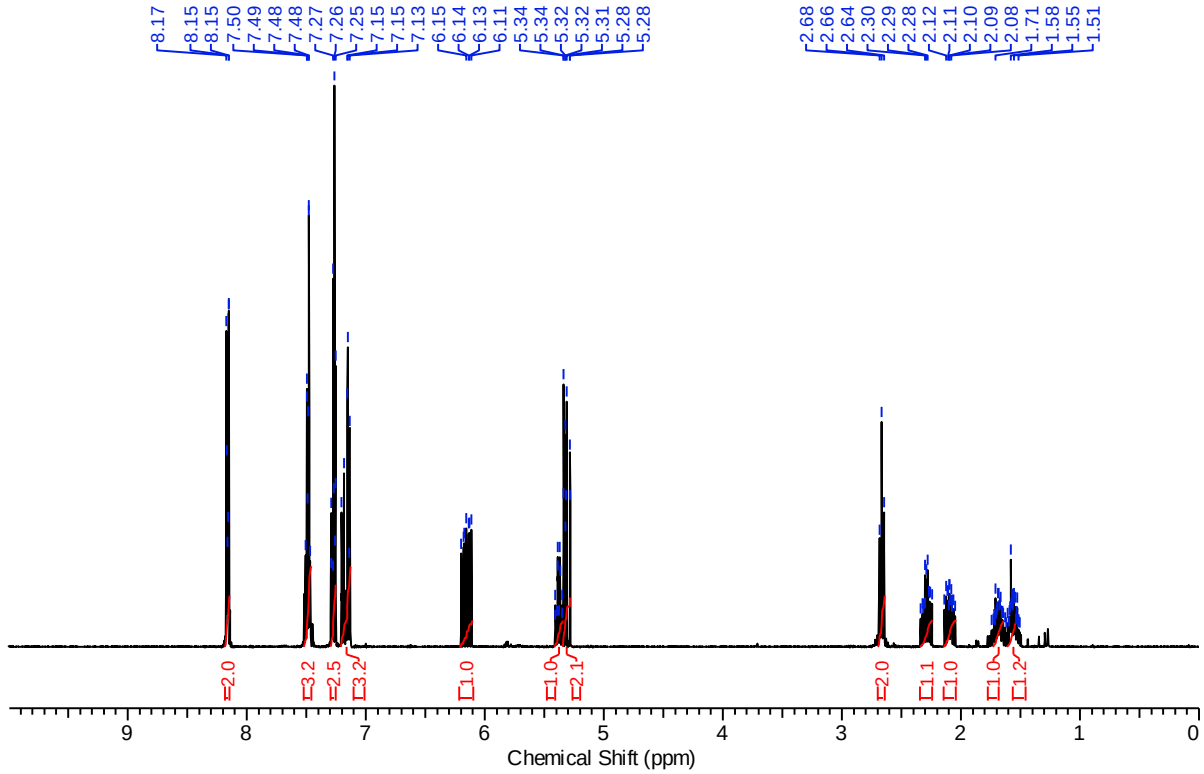
(*R*)-2-(oct-1-en-3-yl)-5-phenyl-2*H*-tetrazole **(1i)**

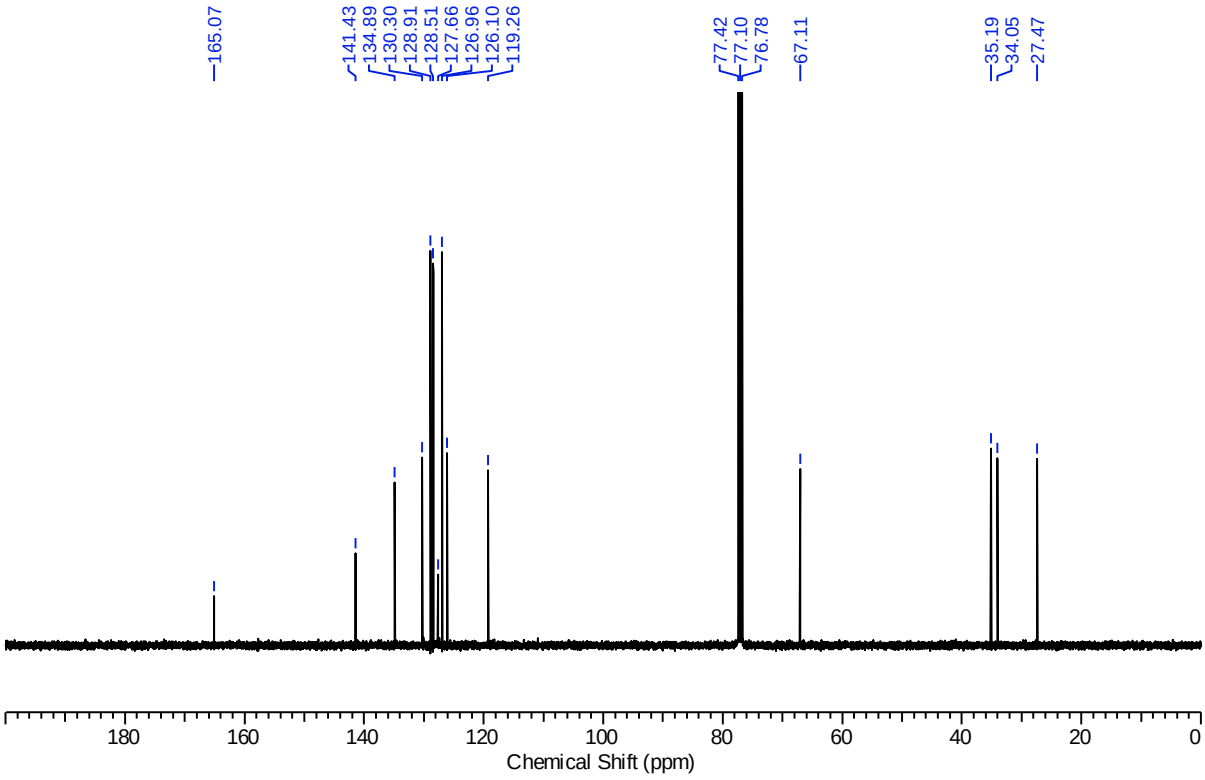


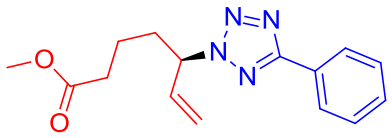
(*R*)-5-phenyl-2-(6-phenylhex-1-en-3-yl)-2*H*-tetrazole **(1j)**

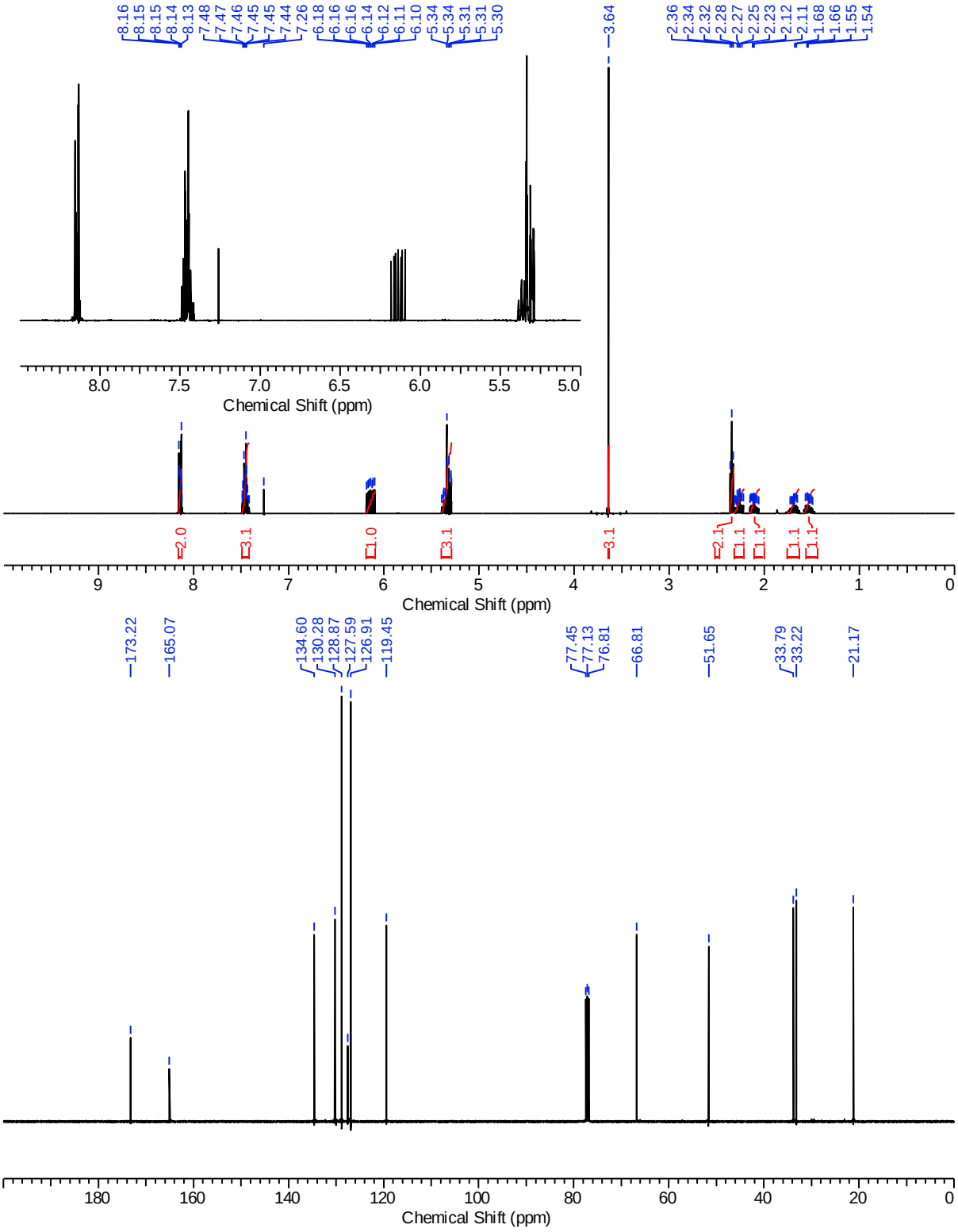




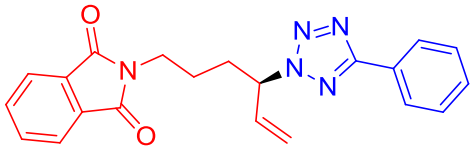



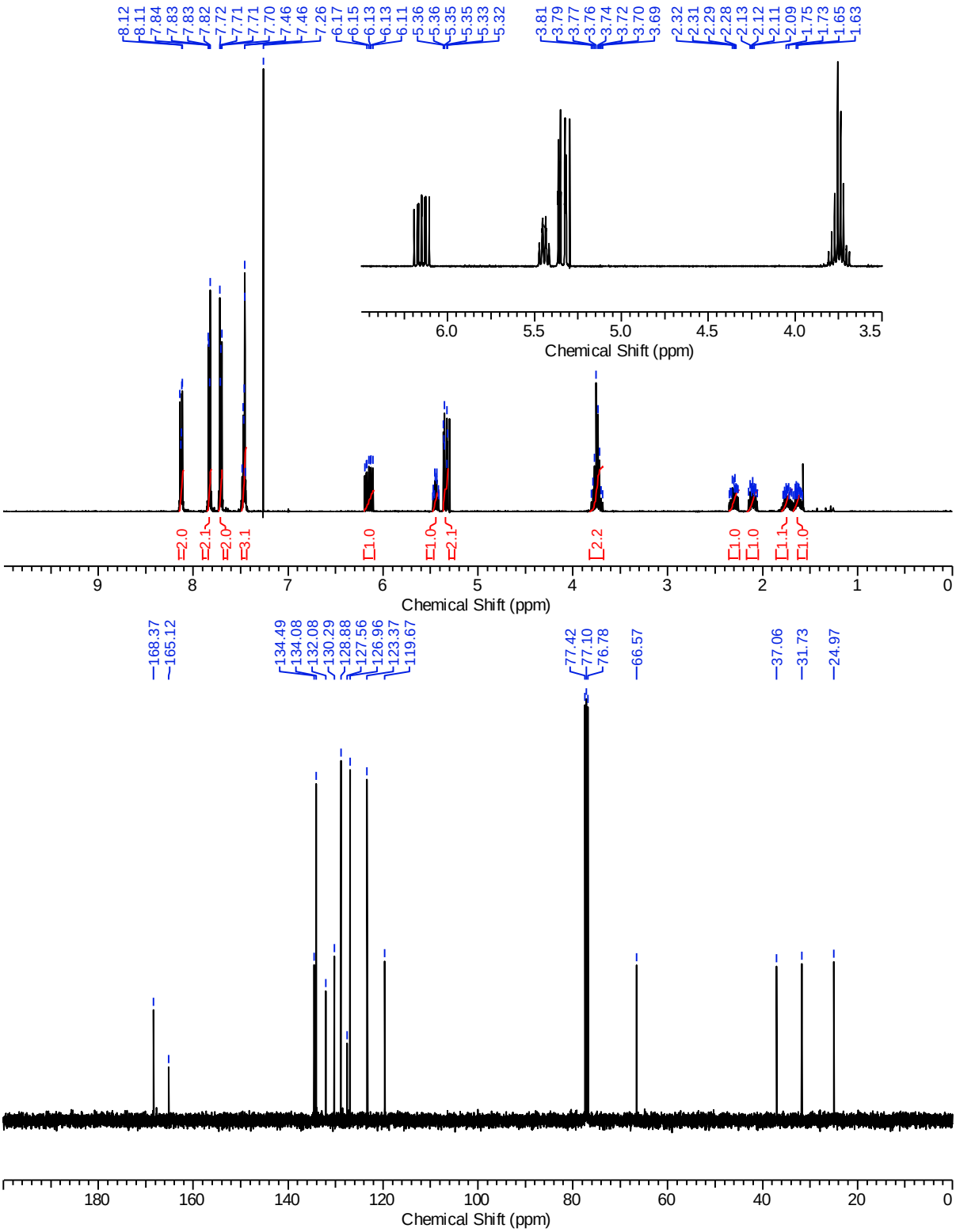
(*R*)-methyl 5-(5-phenyl-2*H*-tetrazol-2-yl)hept-6-enoate **(1k)**



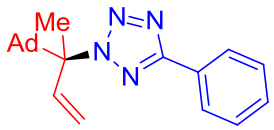


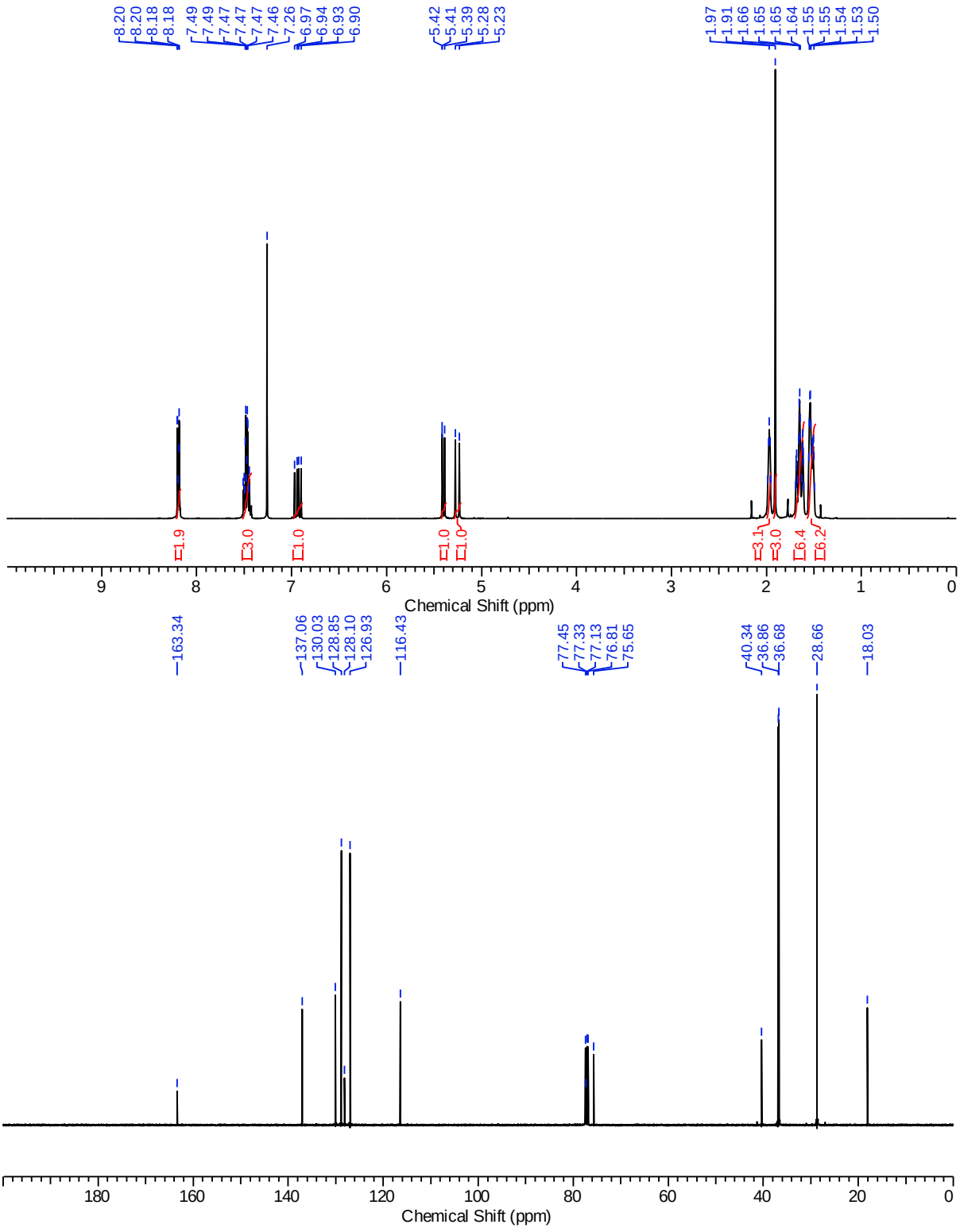
(*R*)-2-(4-(5-phenyl-2*H*-tetrazol-2-yl)hex-5-en-1-yl)isoindoline-1,3-dione **(1l)**



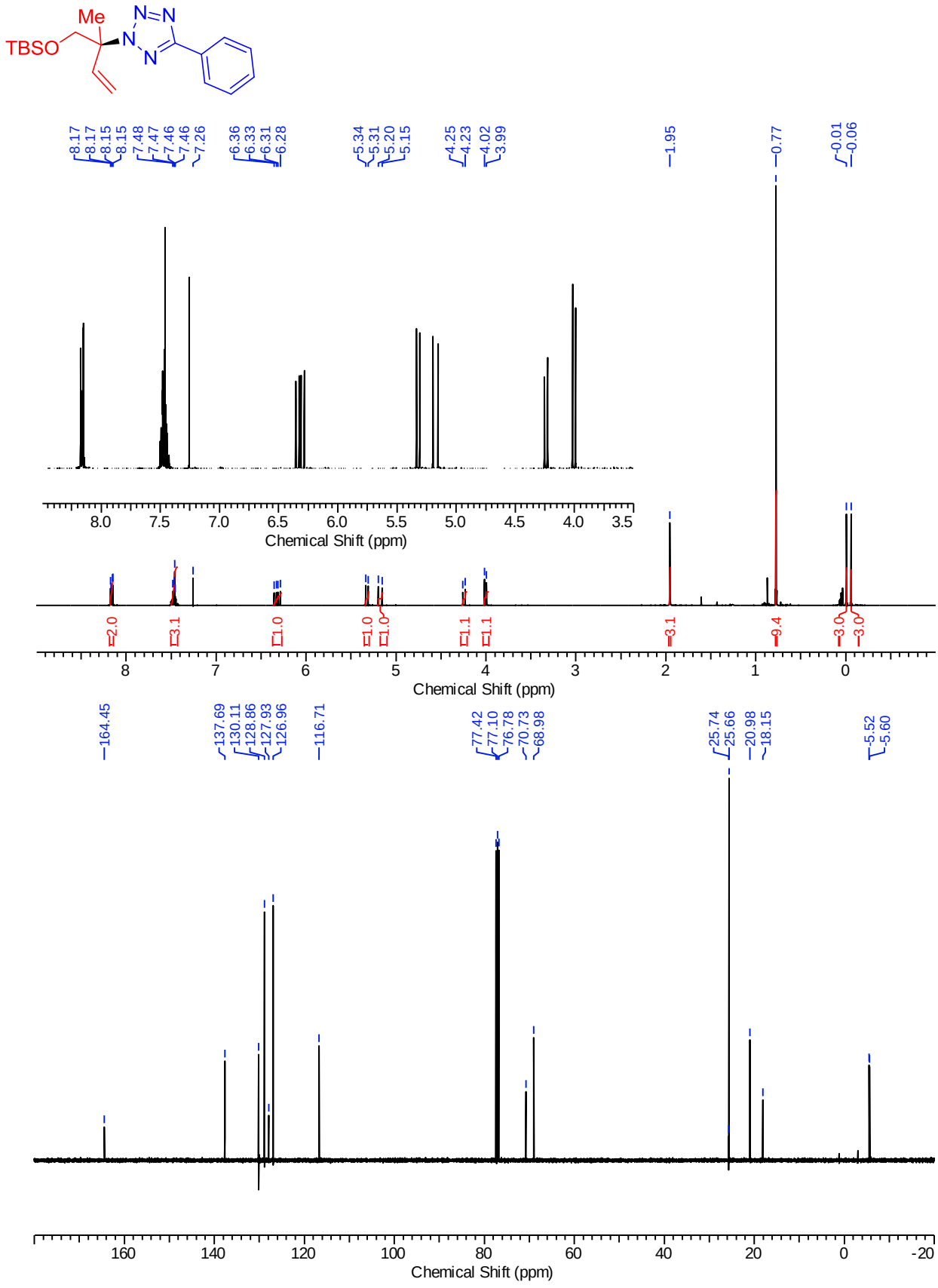


(*S*)-2-(2-(adamantan-1-yl)but-3-en-2-yl)-5-phenyl-2*H*-tetrazole **(2a)**

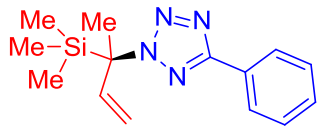


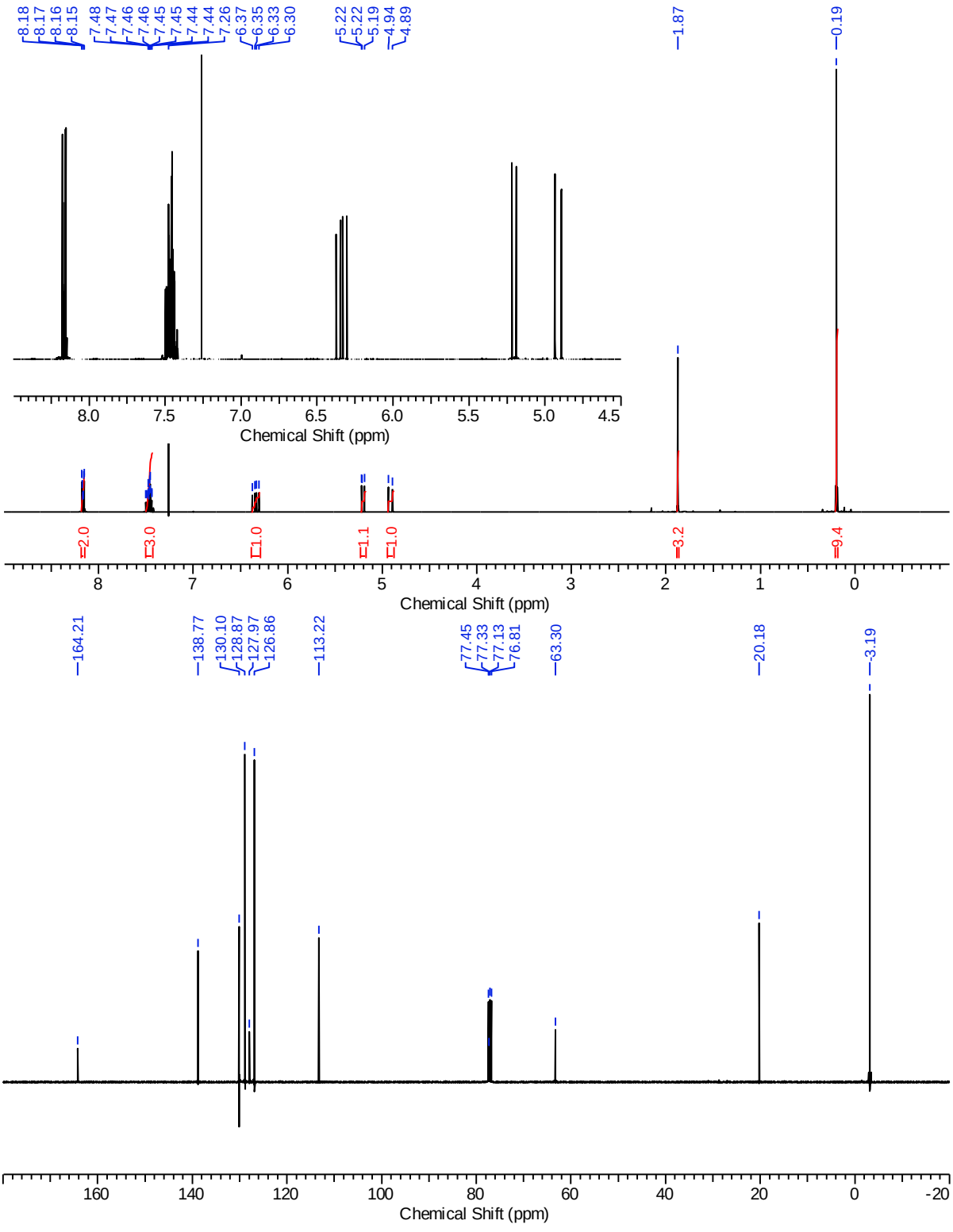



(*R*)-2-(1-((tert-butyldimethylsilyl)oxy)-2-methylbut-3-en-2-yl)-5-phenyl-2*H*-tetrazole **(2b)**

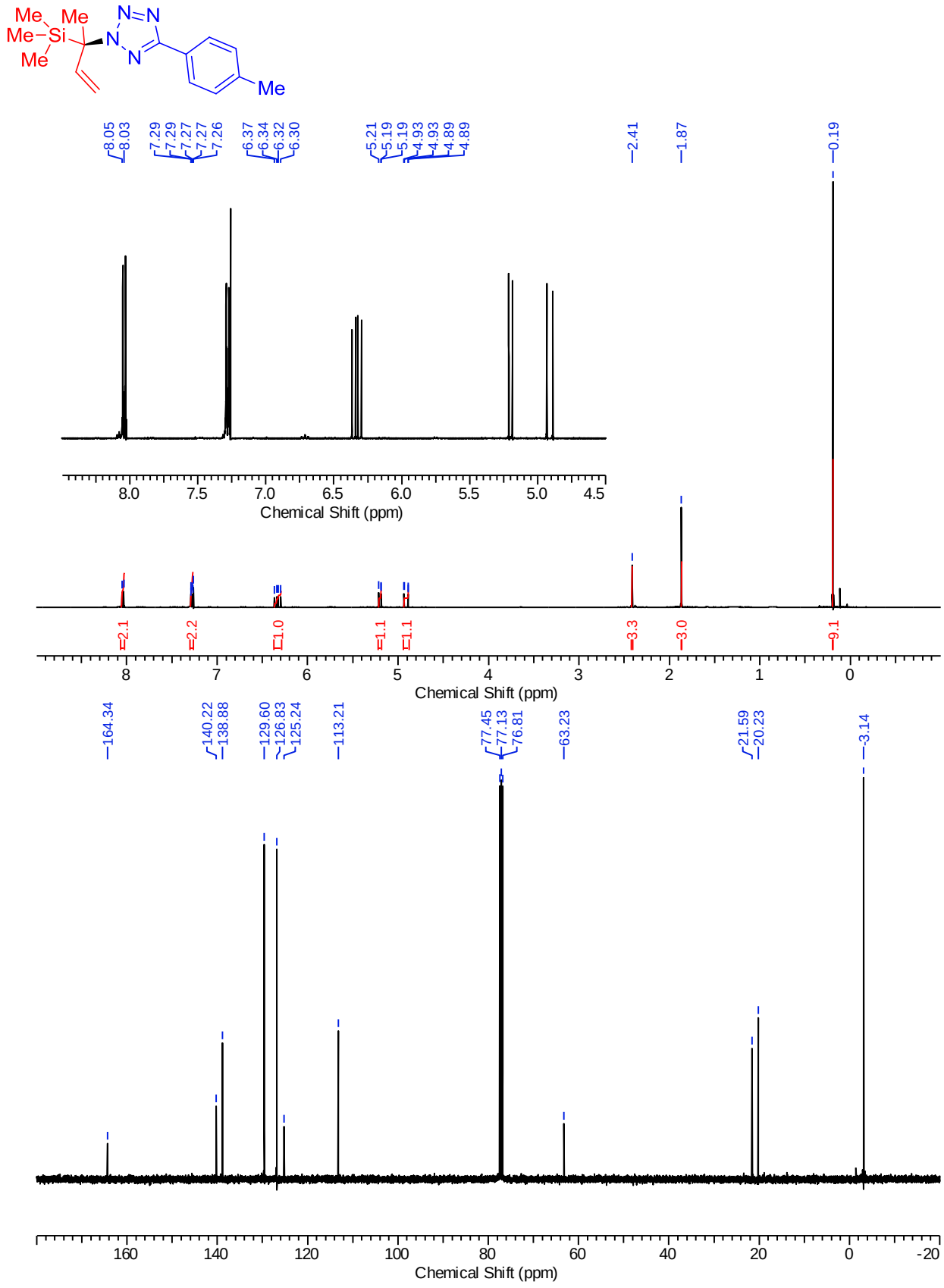


(*S*)-5-phenyl-2-(2-(trimethylsilyl)but-3-en-2-yl)-2*H*-tetrazole **(2c)**

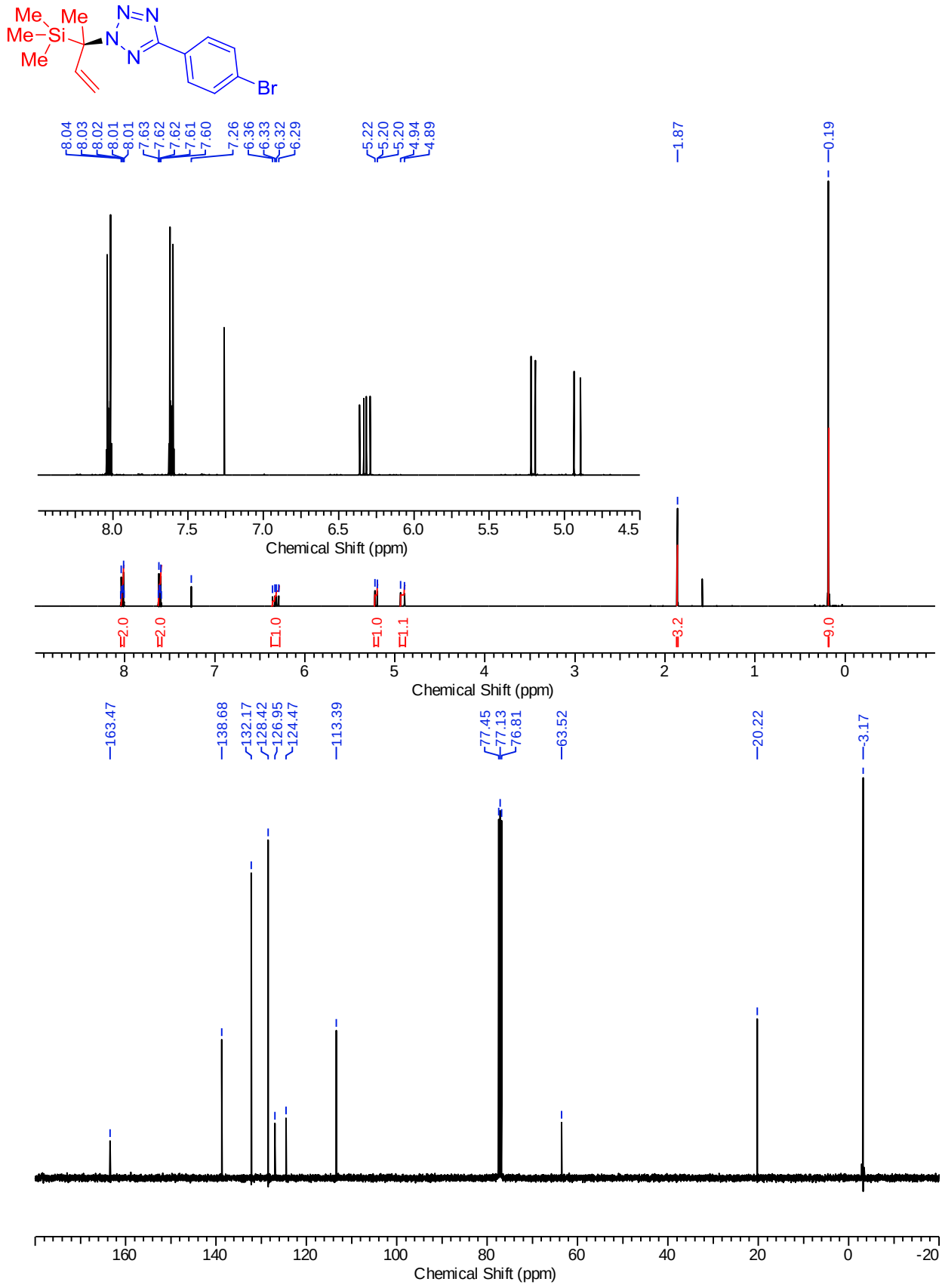


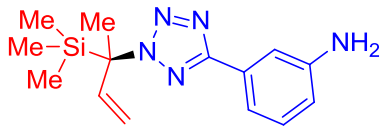
(*S*)-5-(p-tolyl)-2-(2-(trimethylsilyl)but-3-en-2-yl)-2*H*-tetrazole **(2d)**

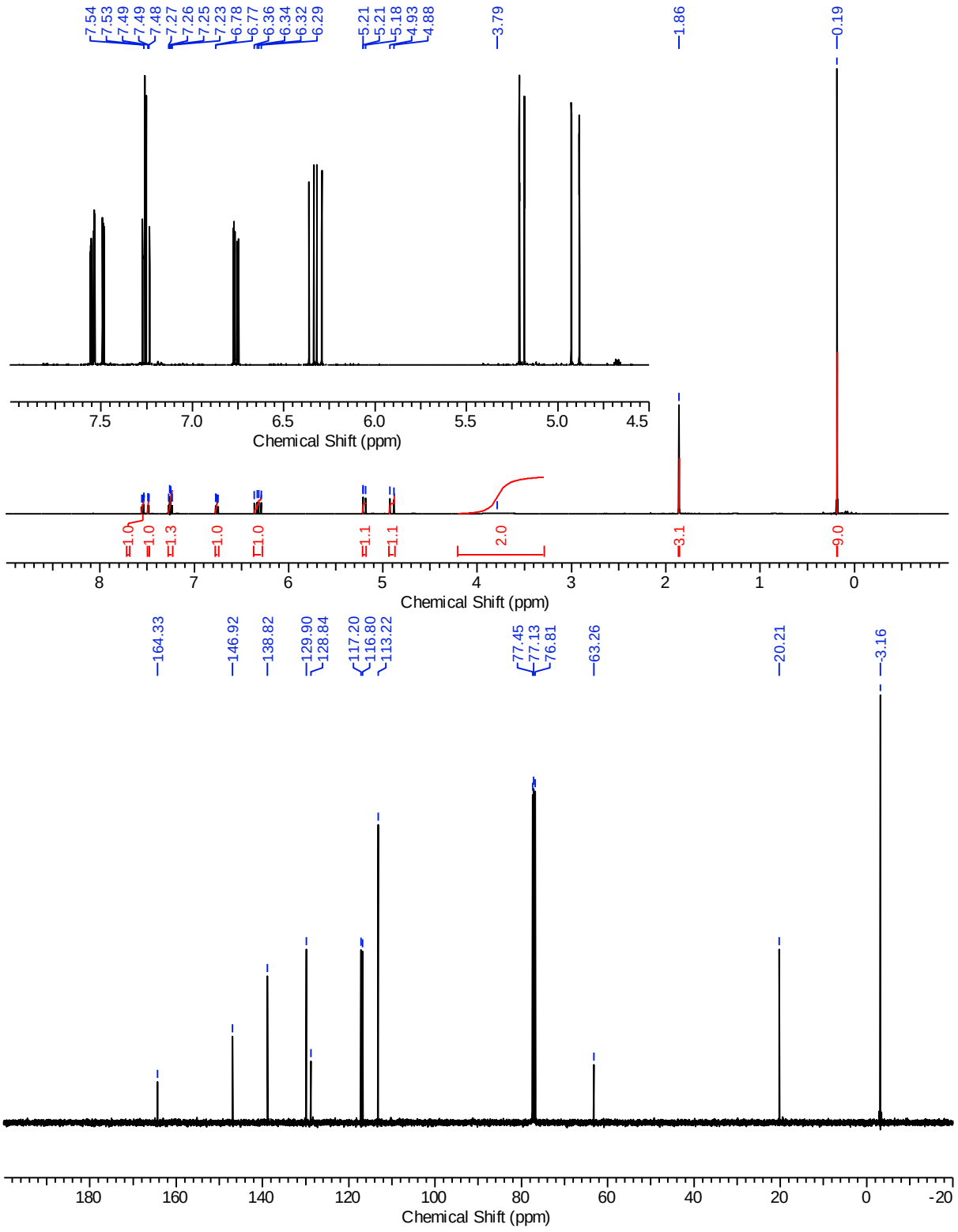


(*S*)-5-(4-bromophenyl)-2-(2-(trimethylsilyl)but-3-en-2-yl)-2*H*-tetrazole **(2e)**

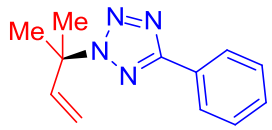


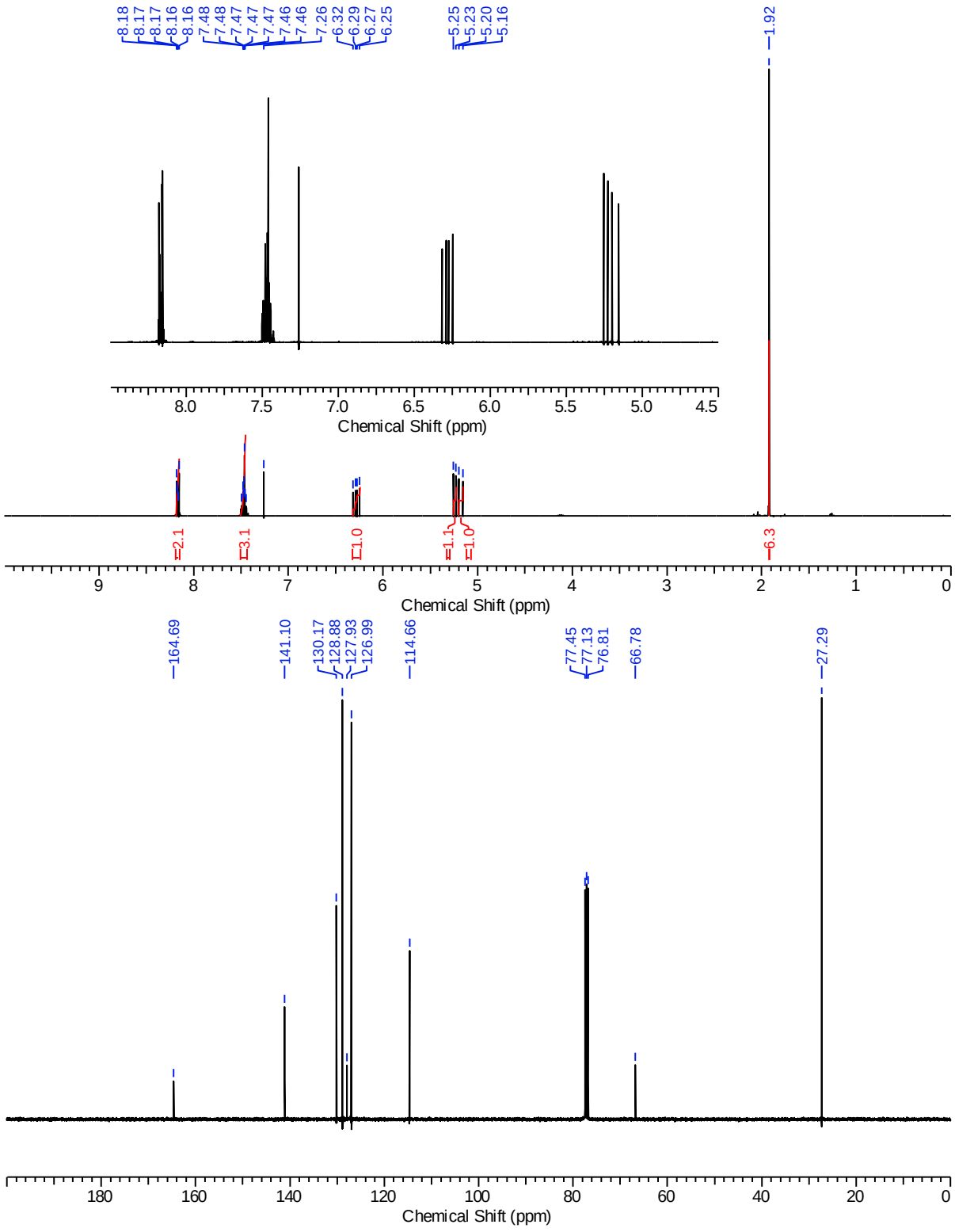
(*S*)-3-(2-(2-(trimethylsilyl)but-3-en-2-yl)-2*H*-tetrazol-5-yl)aniline **(2f)**



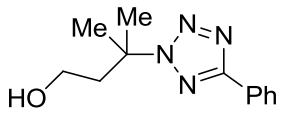



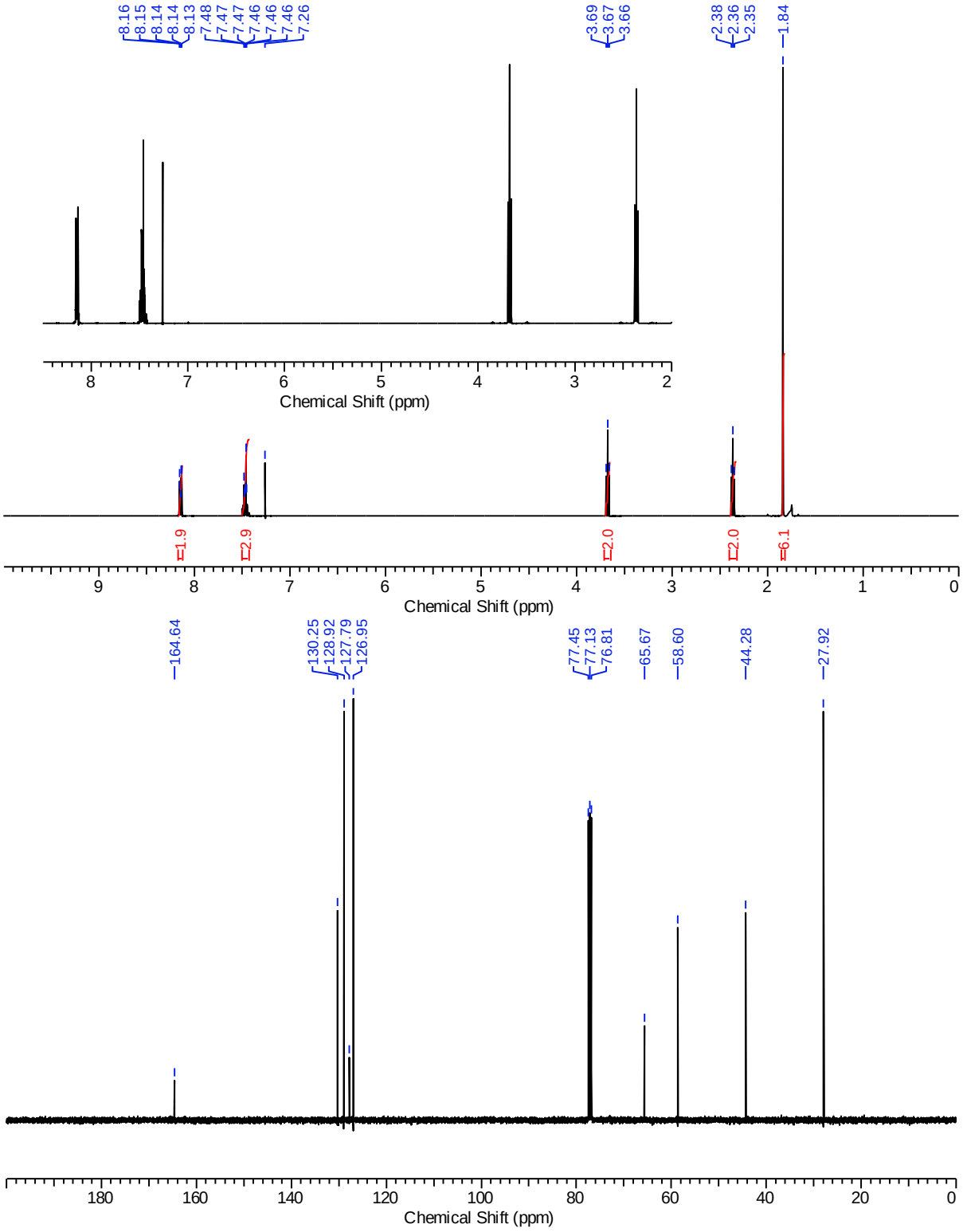
2-(2-methylbut-3-en-2-yl)-5-phenyl-2*H*-tetrazole **(3)**



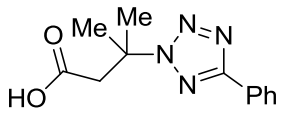



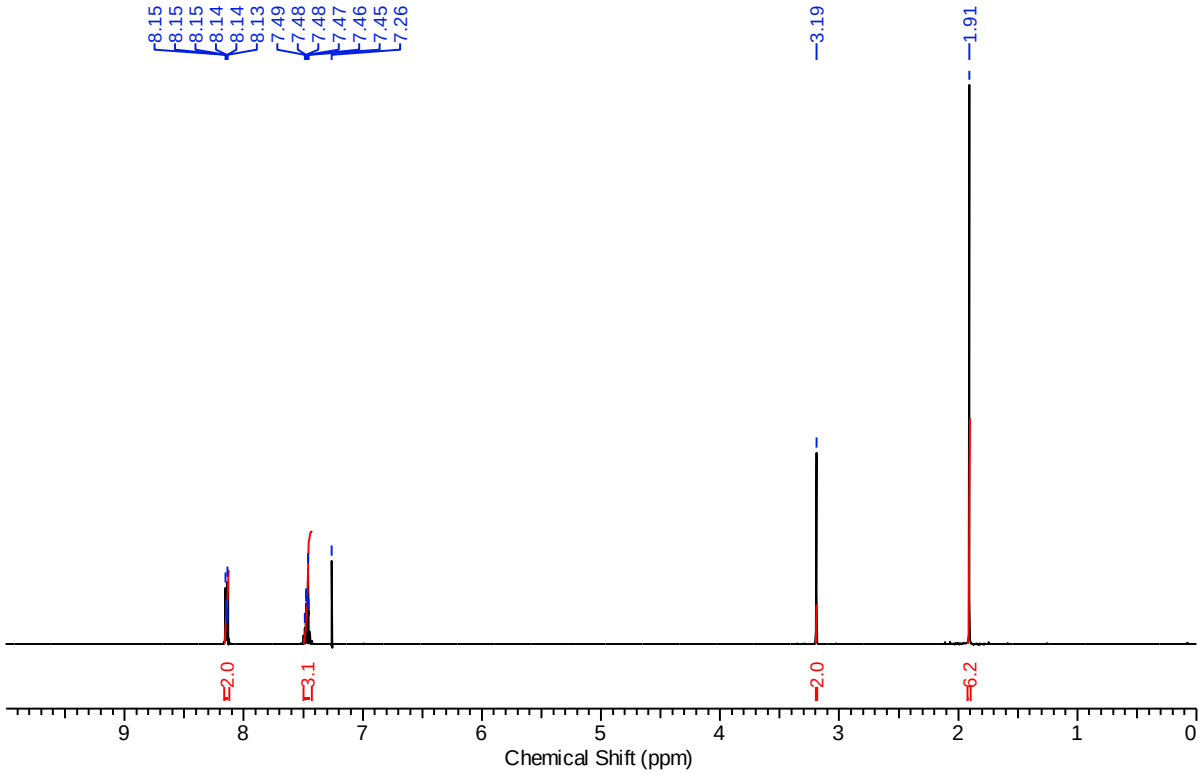
3-methyl-3-(5-phenyl-2*H*-tetrazol-2-yl)butan-1-ol **(4a)**

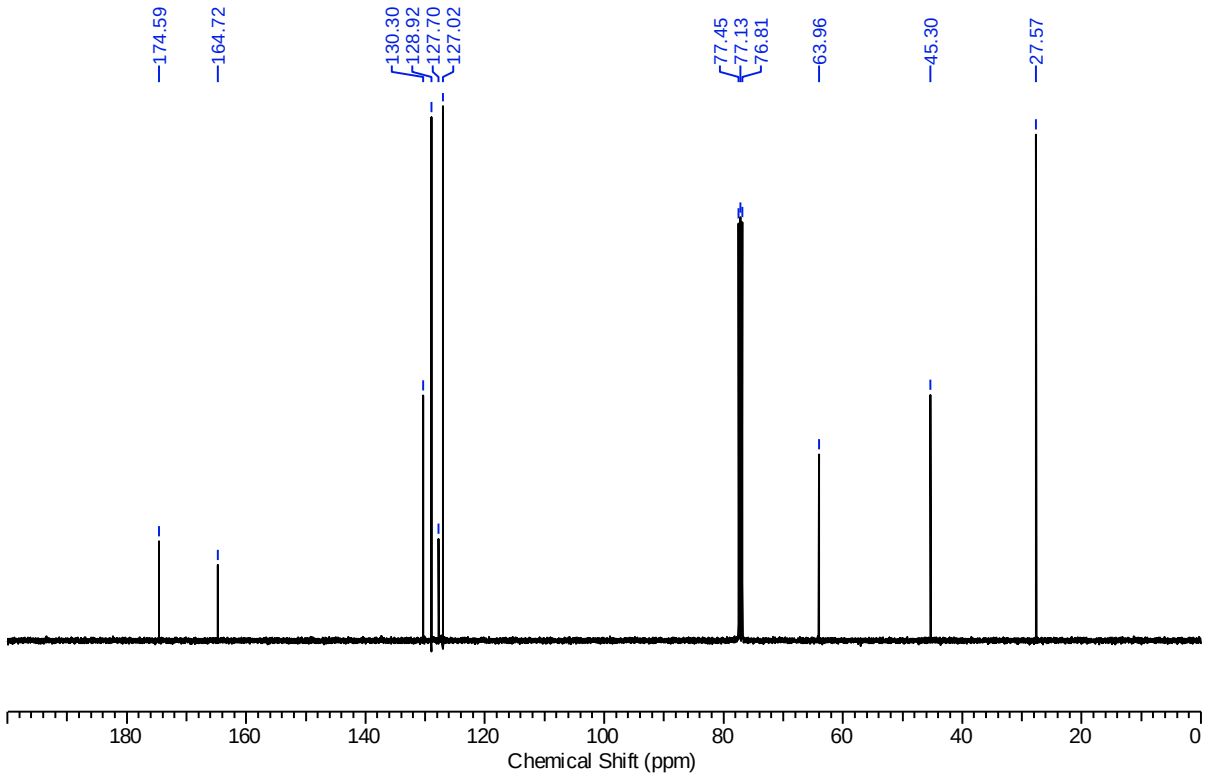


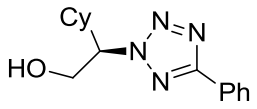
3-methyl-3-(5-phenyl-2*H*-tetrazol-2-yl)butanoic acid **(4b)**

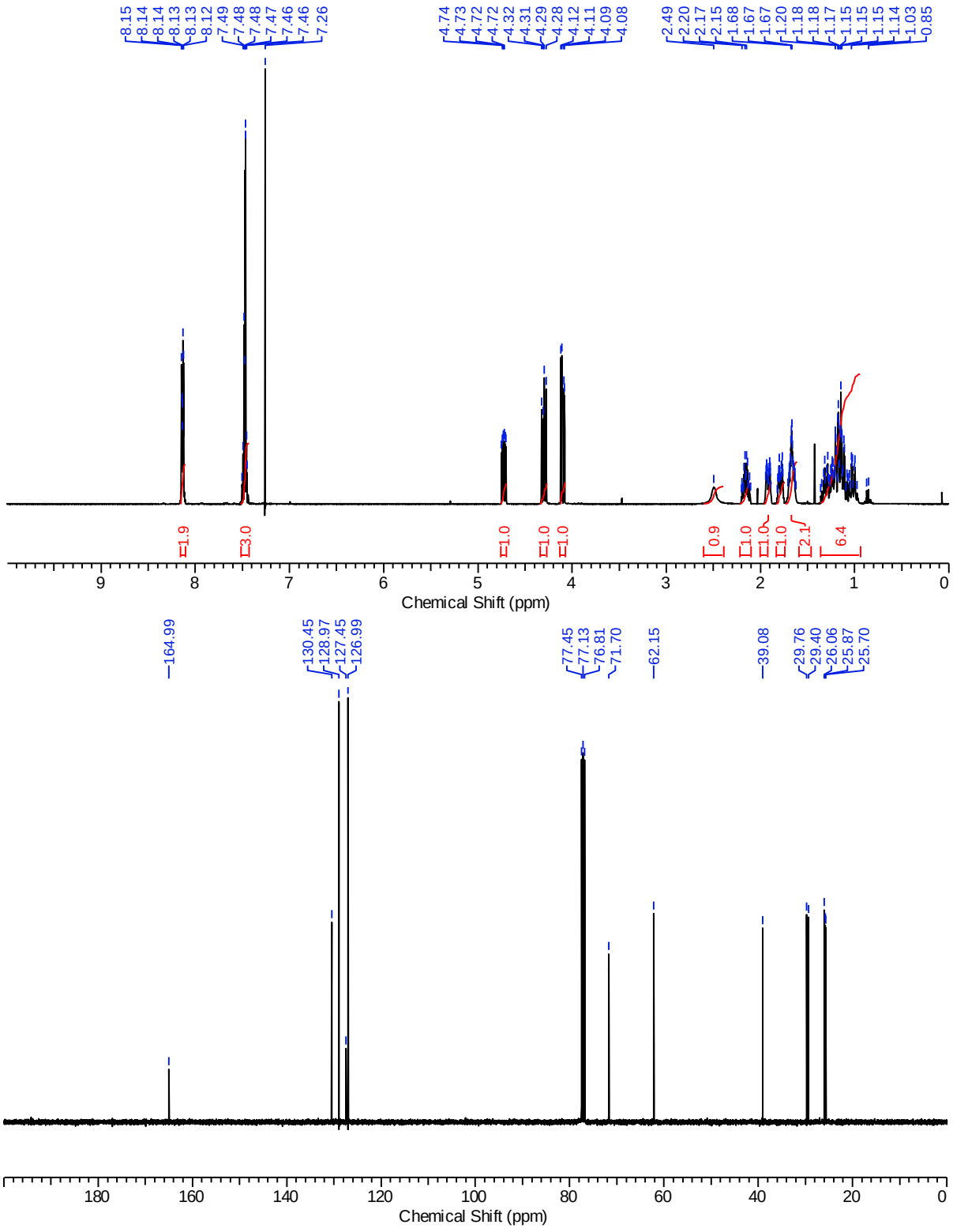


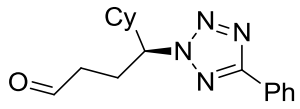



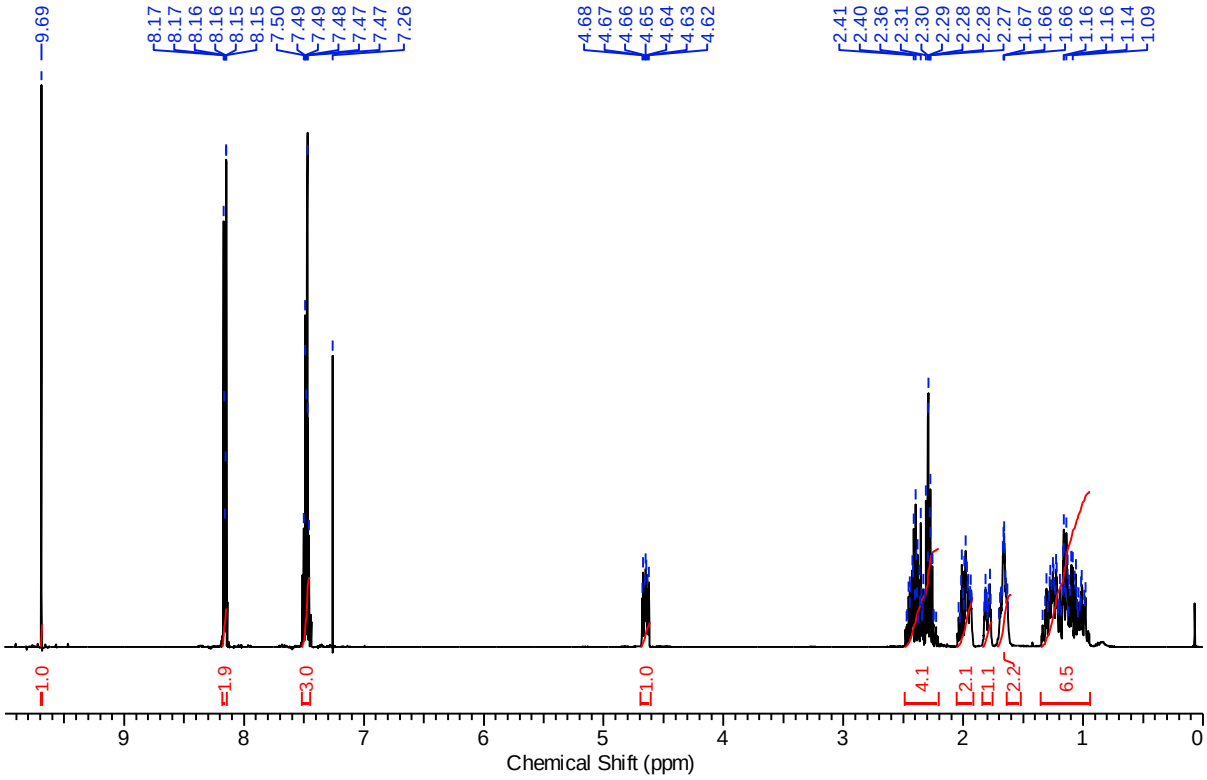
(*R*)-2-cyclohexyl-2-(5-phenyl-2*H*-tetrazol-2-yl)ethanol **(4c)**

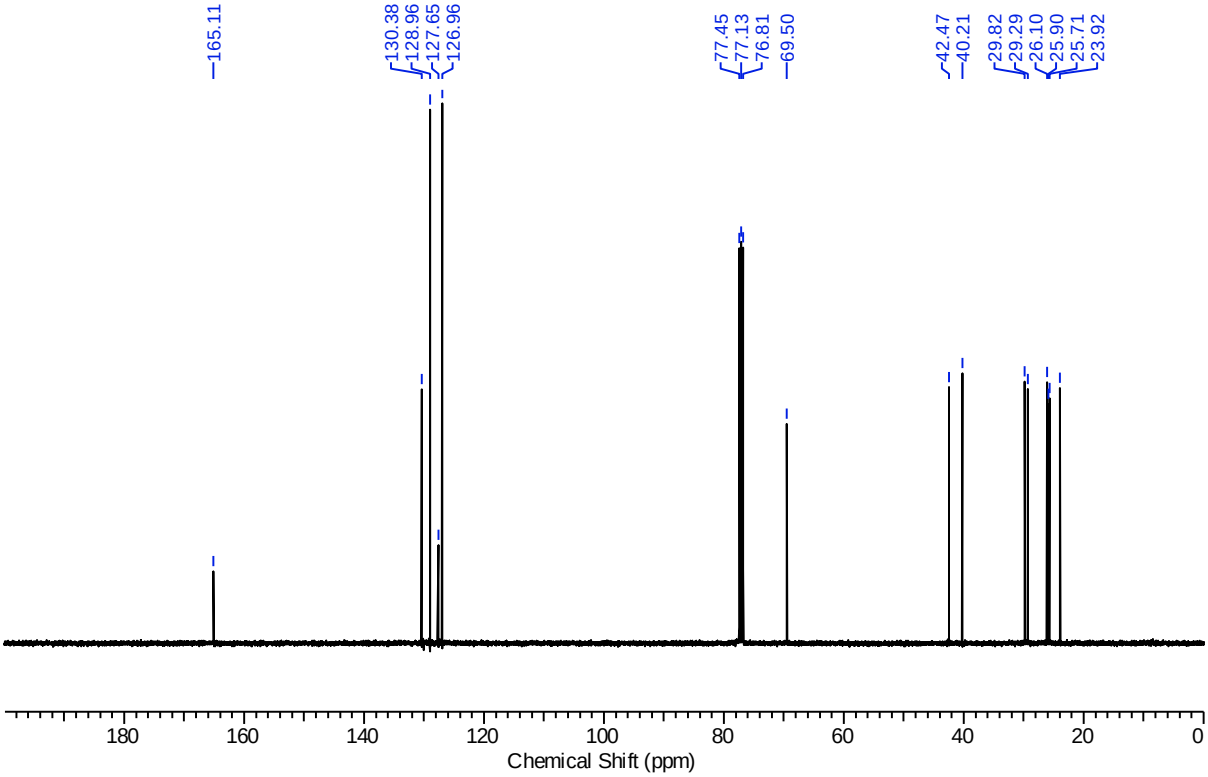


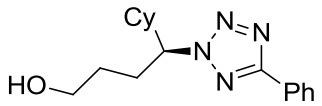
(*S*)-4-cyclohexyl-4-(5-phenyl-2*H*-tetrazol-2-yl)butanal **(4d)**

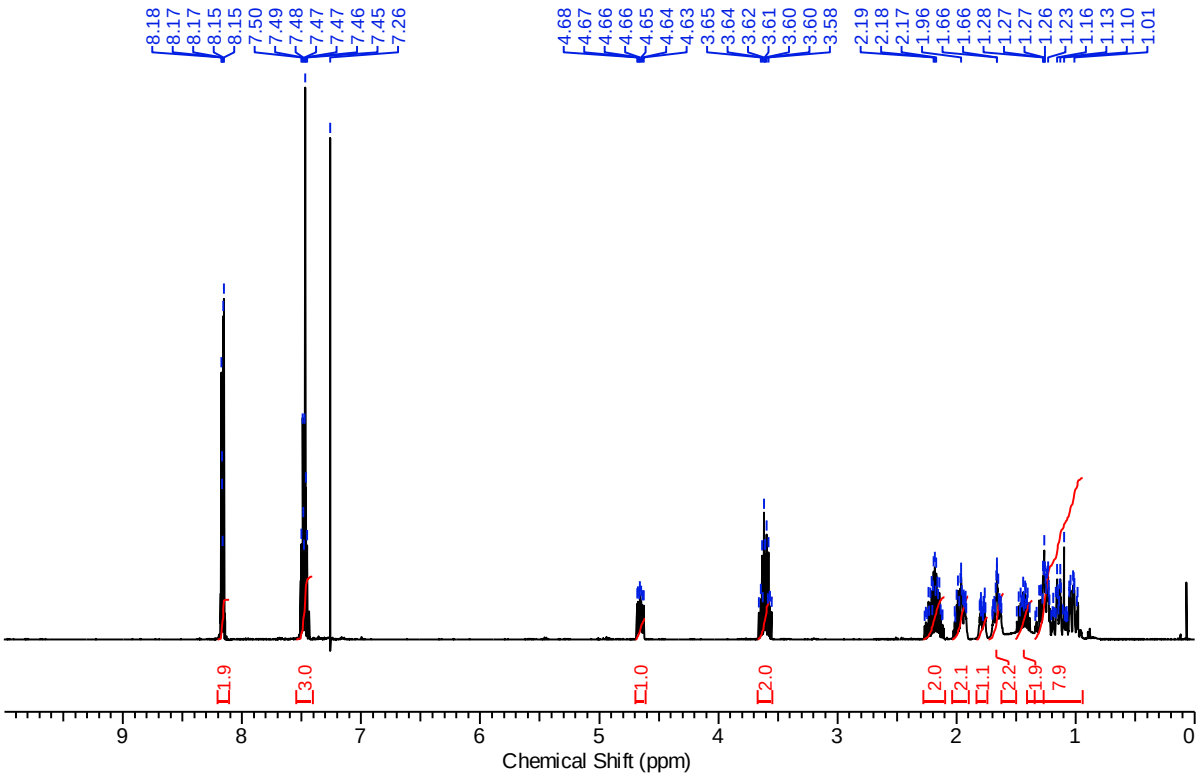


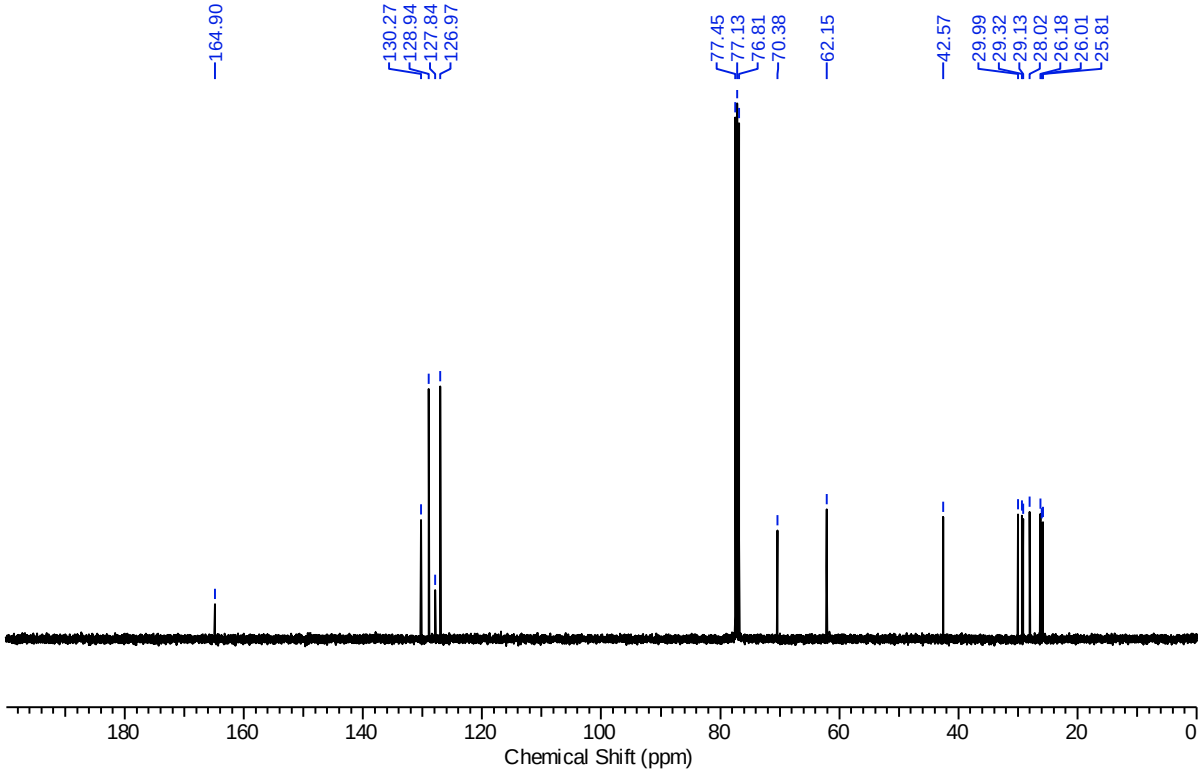



(*S*)-4-cyclohexyl-4-(5-phenyl-2*H*-tetrazol-2-yl)butan-1-ol **(4e)**



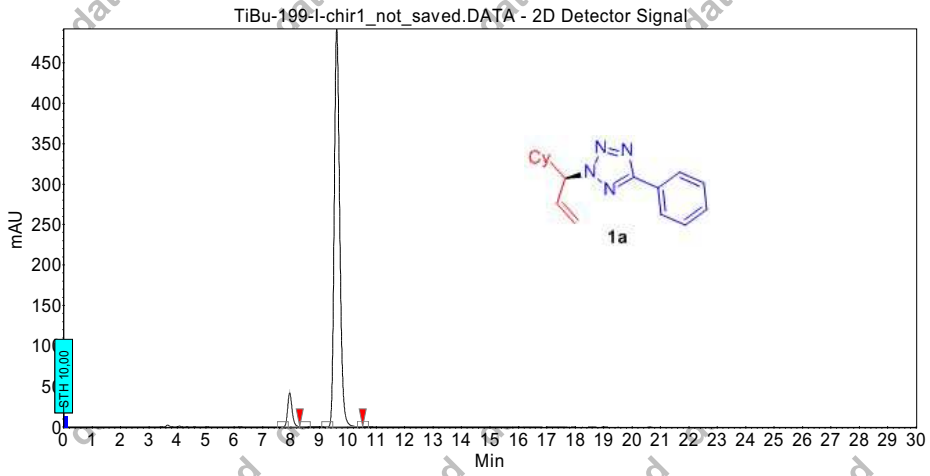



## Chromatogram :L-C2 Hep_IPA 100_1 0,5ml 220nm

Method : L-C2 Hep_IPA 100_1 0,5ml 220nm
User : Timm Bury
07.04.2015 08:40:12
Timm Bury
TiBu-199-l-chir1

Acquired : 07.04.2015 08:40:12
Processed : 08.04.2015 05:08:15
Printed : 08.04.2015 05:08:47
System 2 (RP / NP Anlage)




### Peak results :

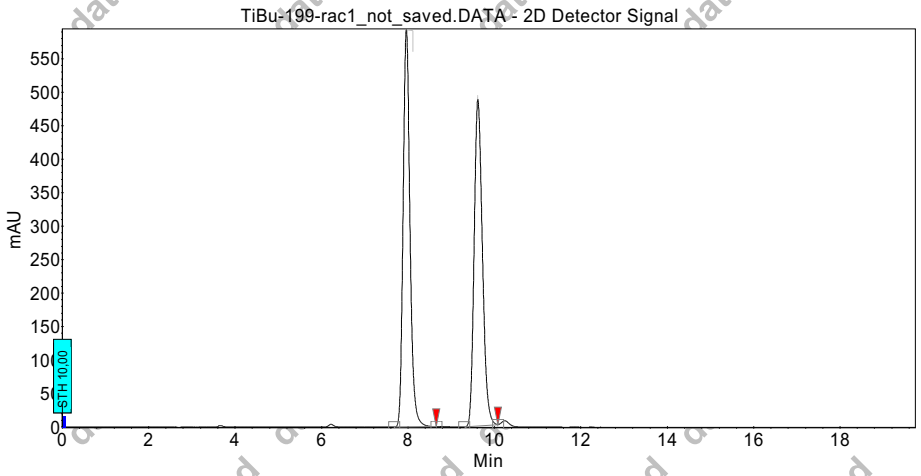
| Index | Name | Time [Min] | Quantity [% Area] | Height [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | | 7,95 | 6,46 | 42,4 | 7,6 | 6,465 |
| 2 | UNKNOWN | 9,61 | 93,54 | 492,0 | 110,3 | 93,535 |
| | | | | | | |
| Total | | | 100,00 | 534,3 | 118,0 | 100,000 |



## Chromatogram :L-C2 Hep_IPA 100_1 0,5ml 220nm

Method : L-C2 Hep_IPA 100_1 0,5ml 220nm
User : Timm Bury
07.04.2015 08:18:35
Timm Bury
TiBu-199-rac1

Acquired : 07.04.2015 08:18:35
Processed : 08.04.2015 05:03:24
Printed : 08.04.2015 05:04:03
System 2 (RP / NP Anlage)




### Peak results :

| Index | Name | Time [Min] | Quantity [% Area] | Height [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | | 7,96 | 50,25 | 594,7 | 109,3 | 50,254 |
| 2 | | 9,62 | 49,75 | 488,1 | 108,2 | 49,746 |
| | | | | | | |
| Total | | | 100,00 | 1082,8 | 217,5 | 100,000 |

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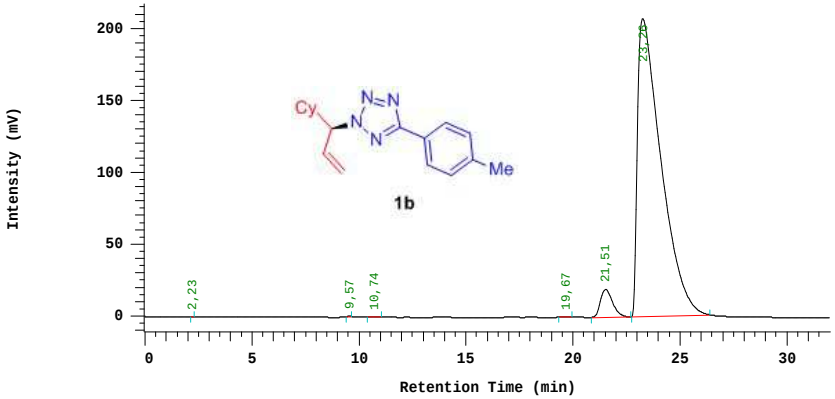
**Inst. für Organische Chemie und Biochemie**

Analyzed: 07.04.14 14:13 Reported: 08.04.15 11:04
Processed: 07.04.14 14:45
Data Path: C:\PROGRAMME\HSM\Rainondi\DATA\0032\
Processing Method: AD-3 Hep/IPA 400/1 1ml 245nm
System(acquisition): Sys 2 Series:0032
Application: Rainondi Vial Number: 1
Sample Name: wil01086-c Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 1,0 ul
Sample Description:

Chrom Type: HPLC Channel : 1




Acquisition Method: AD-3 Hep/IPA 400/1 1ml 245nm
Column Type: WHELK-02 Developed by: fehrenbach
Pump A Type: L-7100
Solvent A: Heptan Solvent B: i-Propanol
Solvent C: Hep/IPA 100/1 Solvent D: Äthanol
Method Description: n-Heptan / IPA 400/1, 245nm, 1ml/min

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

| No. | RT | Area % | Area | BC |
|---|---|---|---|---|
| 1 | 2,23 | 0,008 | 1322 | BB |
| 2 | 9,57 | 0,039 | 6279 | BB |
| 3 | 10,74 | 0,018 | 2817 | BB |
| 4 | 19,67 | 0,018 | 2957 | BB |
| 5 | 21,51 | 4,501 | 722746 | BB |
| 6 | 23,26 | 95,416 | 15321921 | BB |
| | | 100,000 | 16058042 | |

Peak rejection level: 0





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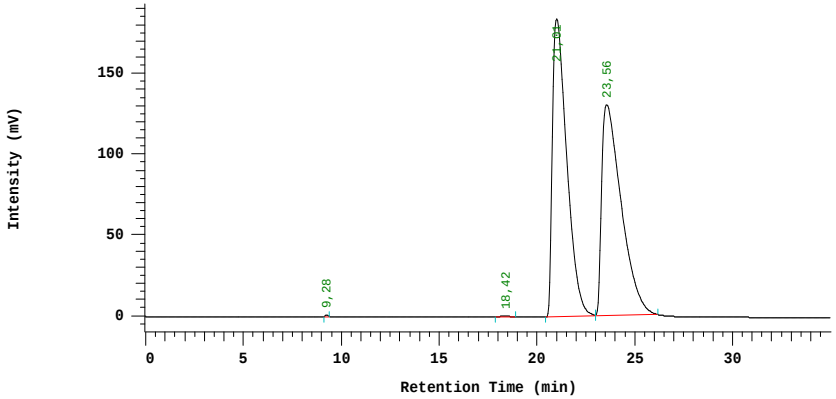
Analyzed: 07.04.14 13:35 Reported: 08.04.15 11:04
Processed: 07.04.14 14:10
Data Path: C:\PROGRAMME\HSM\Rainondi\DATA\0031\
Processing Method: AD-3 Hep/IPA 400/1 1ml 245nm
System(acquisition): Sys 2 Series:0031
Application: Rainondi Vial Number: 1
Sample Name: kx-5065e rac Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 1,0 ul
Sample Description:

Chrom Type: HPLC Channel : 1




Acquisition Method: AD-3 Hep/IPA 400/1 1ml 245nm
Column Type: WHELK-02 Developed by: fehrenbach
Pump A Type: L-7100
Solvent A: Heptan Solvent B: i-Propanol
Solvent C: Hep/IPA 100/1 Solvent D: Äthanol
Method Description: n-Heptan / IPA 400/1, 245nm, 1ml/min

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

| No. | RT | Area % | Area | BC |
|---|---|---|---|---|
| 1 | 9,28 | 0,048 | 8619 | BB |
| 2 | 18,42 | 0,060 | 10665 | BB |
| 3 | 21,01 | 50,512 | 8983621 | BV |
| 4 | 23,56 | 49,379 | 8782168 | VB |
| | | 100,000 | 17785073 | |

Peak rejection level: 0

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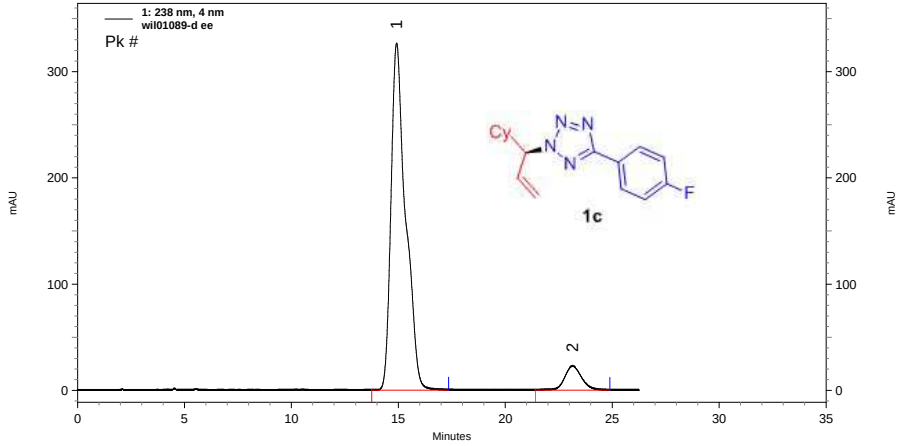
**Institut für Organische Chemie und Biochemie**

wil01089-d ee {Data Description}

E:\EZDatenOC\Raidondi\Method\L-C4, Hep_IPA 600_1, 22°C, 1ml.met

Vial: 194 Injection Volume (µl): 2
Run Time: 07.04.2014 15:51:49 Analysis Time: 08.04.2015 11:00:38




**1: 238 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 14,920 | 92,569 | 241 |
| **2** | 23,147 | 7,431 | 241 |

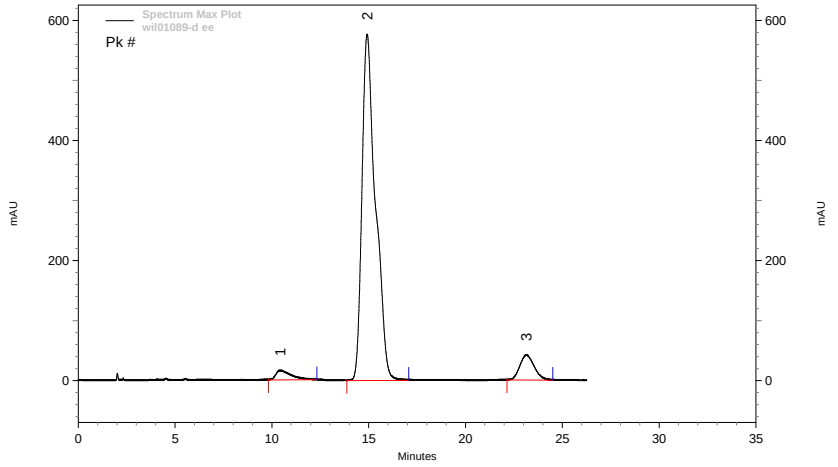
**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 10,433 | 2,657 | 225 |
| **2** | 14,920 | 90,382 | 241 |
| **3** | 23,147 | 6,960 | 241 |

**DAD-250 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 14,920 | 92,585 | 241 |
| **2** | 23,147 | 7,415 | 241 |





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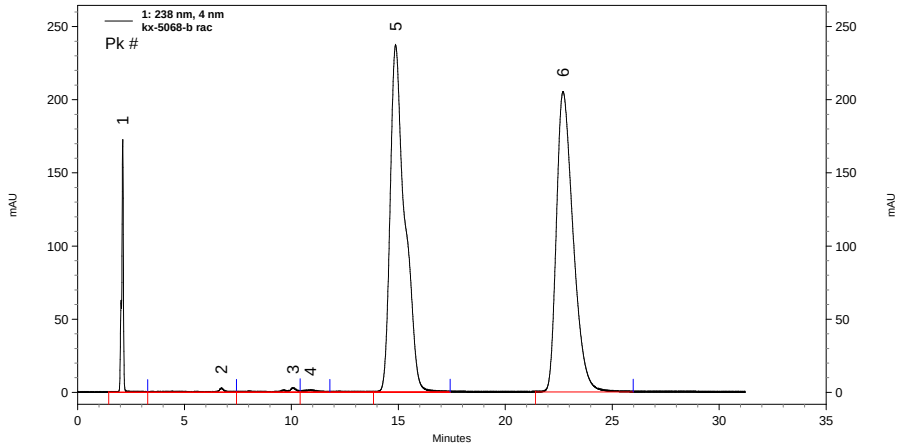
kx-5068-b rac {Data Description}

E:\EZDatenOC\Raidondi\Method\L-C4, Hep_IPA 600_1, 22°C, 1ml.met

Vial: 193 Injection Volume (µl): 2
Run Time: 07.04.2014 15:17:35 Analysis Time: 08.04.2015 11:01:08




**1: 238 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,113 | 4,151 | 236 |
| 2 | 6,727 | 0,187 | 272 |
| 3 | 10,073 | 0,317 | 238 |
| 4 | 10,893 | 0,199 | 236 |
| 5 | 14,873 | 47,783 | 241 |
| 6 | 22,700 | 47,364 | 241 |

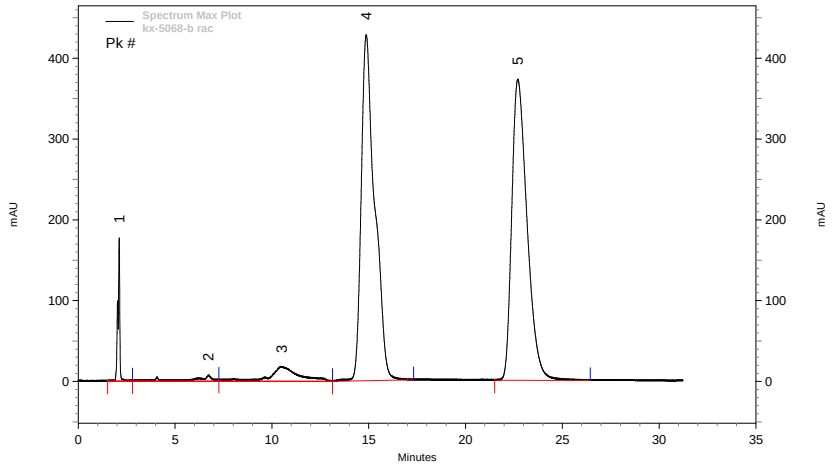
**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,113 | 2,687 | 236 |
| 2 | 6,727 | 0,881 | 272 |
| 3 | 10,493 | 3,884 | 274 |
| 4 | 14,873 | 46,537 | 241 |
| 5 | 22,700 | 46,012 | 241 |

**DAD-250 nm Results**



| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,113 | 2,455 | 236 |
| 2 | 6,727 | 0,208 | 272 |
| 3 | 10,073 | 0,325 | 238 |
| 4 | 10,900 | 0,180 | 235 |
| 5 | 14,873 | 48,679 | 241 |
| 6 | 22,700 | 48,153 | 241 |



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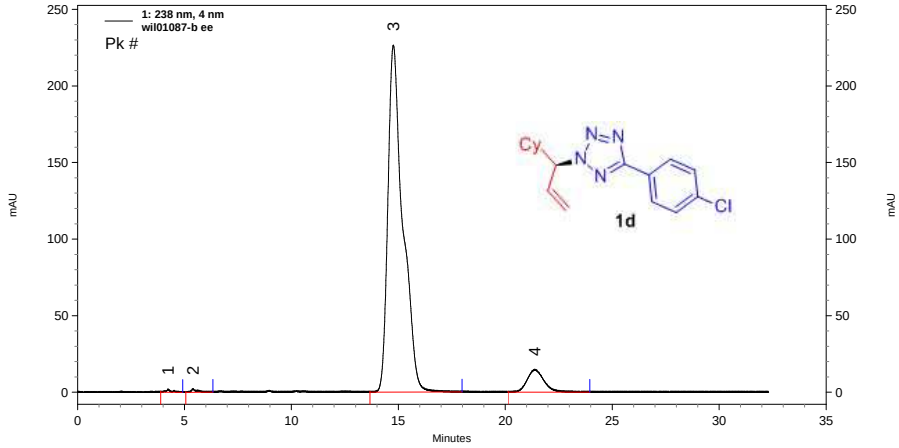
**Institut für Organische Chemie und Biochemie**

wil01087-b ee {Data Description}

E:\EZDatenOC\Raidondi\Method\L-C4, Hep_IPA 600_1, 22°C, 1ml.met

Vial: 192 Injection Volume (µl): 2
Run Time: 07.04.2014 14:42:10 Analysis Time: 08.04.2015 11:00:14




**1: 238 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 4,233 | 0,212 | 204 |
| **2** | 5,400 | 0,284 | 201 |
| **3** | 14,767 | 92,904 | 203 |
| **4** | 21,387 | 6,599 | 203 |

**Spectrum Max Plot Results**

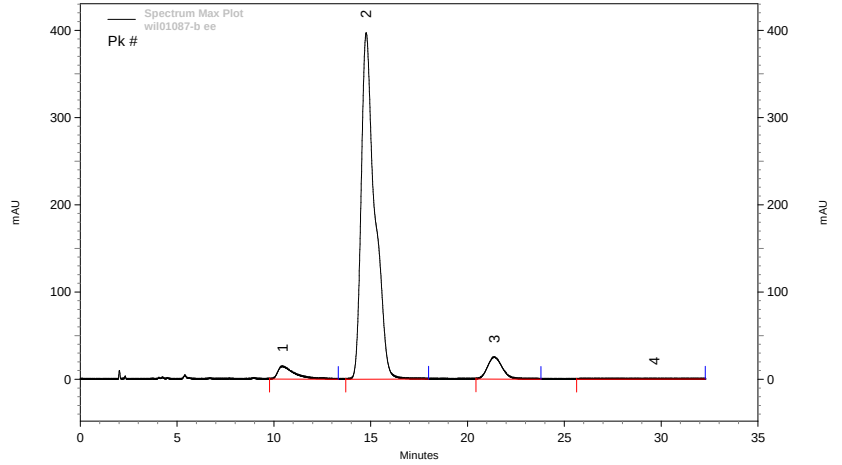
| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 10,447 | 3,940 | 226 |
| **2** | 14,767 | 89,868 | 203 |
| **3** | 21,387 | 6,089 | 203 |
| **4** | 29,647 | 0,103 | 212 |

**DAD-250 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 4,233 | 0,164 | 204 |
| **2** | 5,400 | 0,240 | 201 |



| | | | |
|---|---|---|---|
| **3** | 14,767 | 93,019 | 203 |
| **4** | 21,387 | 6,578 | 203 |



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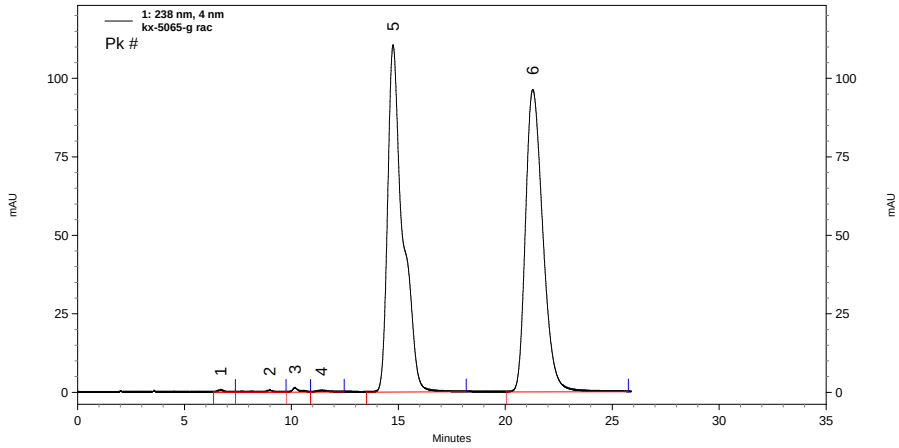
**Institut für Organische Chemie und Biochemie**

kx-5065-g rac {Data Description}

E:\EZDatenOC\Raidondi\Method\L-C4, Hep_IPA 600_1, 22°C, 1ml.met

Vial: 191 Injection Volume (µl): 2
Run Time: 07.04.2014 14:13:21 Analysis Time: 08.04.2015 10:59:50




**1: 238 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 6,700 | 0,114 | 276 |
| **2** | 8,993 | 0,130 | 265 |
| **3** | 10,173 | 0,250 | 247 |
| **4** | 11,407 | 0,129 | 249 |
| **5** | 14,753 | 49,712 | 202 |
| **6** | 21,287 | 49,664 | 202 |

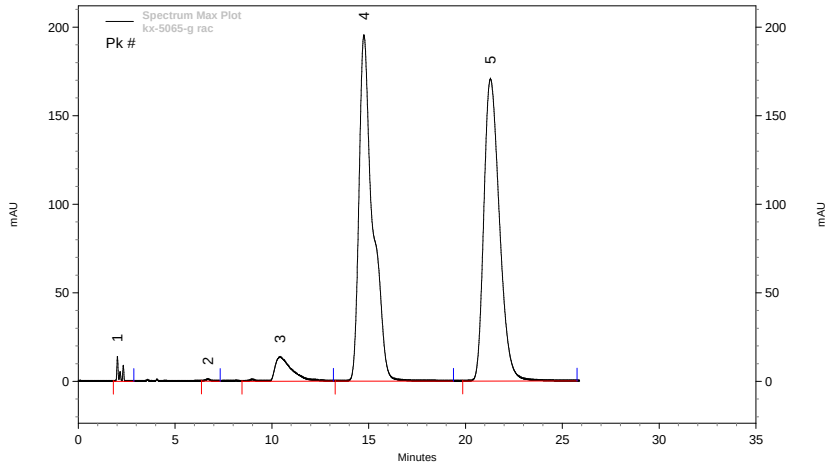
**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,020 | 0,599 | 290 |
| **2** | 6,700 | 0,083 | 276 |
| **3** | 10,420 | 4,083 | 230 |
| **4** | 14,753 | 47,685 | 202 |
| **5** | 21,287 | 47,551 | 202 |

**DAD-250 nm Results**



| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 6,707 | 0,093 | 276 |
| **2** | 8,987 | 0,101 | 265 |
| **3** | 10,167 | 0,174 | 247 |
| **4** | 11,393 | 0,117 | 250 |
| **5** | 14,753 | 49,823 | 202 |
| **6** | 21,287 | 49,693 | 202 |



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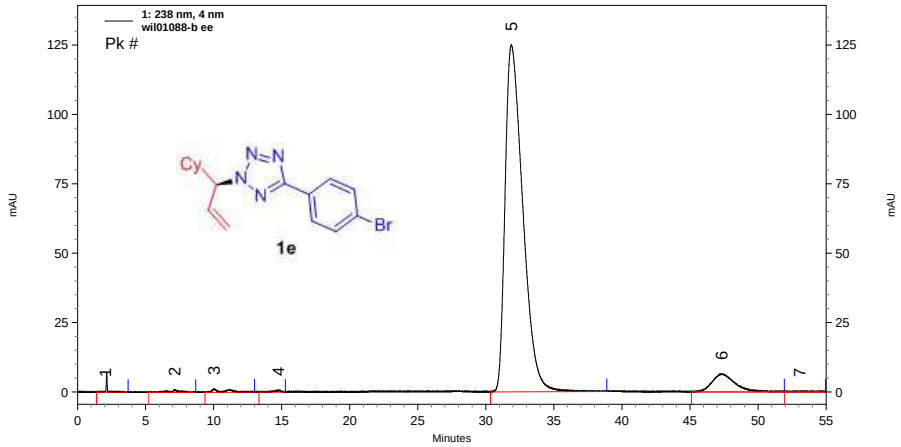
## Institut für Organische Chemie und Biochemie

wil01088-b ee {Data Description}

E:\EZDatenOC\Raidondi\Method\L-C4, Hep_IPA 1000_1, 22°C, 1ml.met

Vial: 196 Injection Volume (µl): 2
Run Time: 08.04.2014 11:57:26 Analysis Time: 08.04.2015 10:58:12




**1: 238 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,033 | 0,260 | 279 |
| 2 | 7,140 | 0,238 | 255 |
| 3 | 10,033 | 0,445 | 203 |
| 4 | 14,767 | 0,140 | 227 |
| 5 | 31,873 | 92,911 | 204 |
| 6 | 47,333 | 5,966 | 204 |
| 7 | 53,053 | 0,039 | 276 |

**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 14,873 | 3,809 | 226 |
| 2 | 31,880 | 90,730 | 204 |
| 3 | 47,360 | 5,460 | 204 |

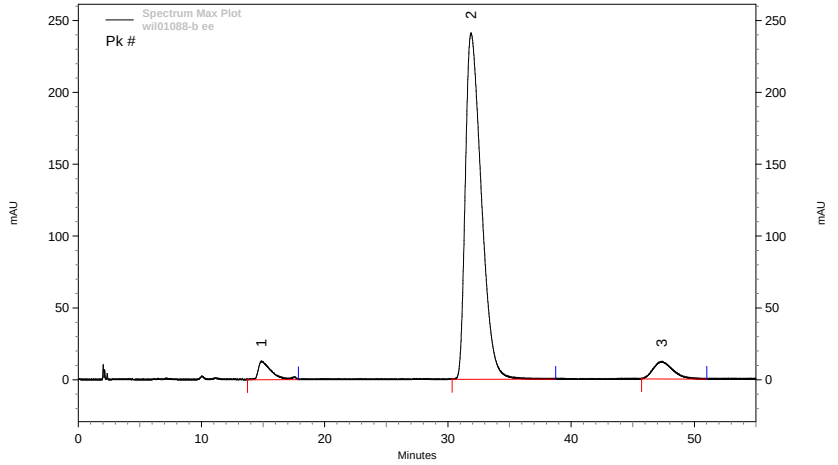
**DAD-253 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|





| | | | |
|---|---|---|---|
| 1 | 7,147 | 0,170 | 255 |
| 2 | 10,040 | 0,335 | 203 |
| 3 | 31,873 | 93,509 | 204 |
| 4 | 47,320 | 5,986 | 204 |



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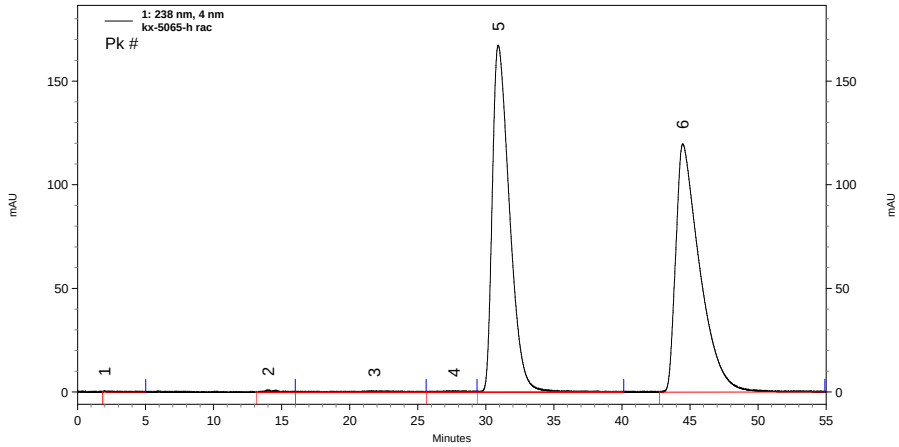
**Institut für Organische Chemie und Biochemie**

kx-5065-h rac {Data Description}

E:\EZDatenOC\Raidondi\Method\L-C4, Hep_IPA 1000_1, 22°C, 1ml.met

Vial: 195 Injection Volume (µl): 2
Run Time: 08.04.2014 10:59:24 Analysis Time: 08.04.2015 10:57:39




**1: 238 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 1,987 | 0,040 | 275 |
| **2** | 14,020 | 0,151 | 277 |
| **3** | 21,827 | 0,217 | 259 |
| **4** | 27,667 | 0,156 | 259 |
| **5** | 30,913 | 49,780 | 204 |
| **6** | 44,473 | 49,656 | 204 |

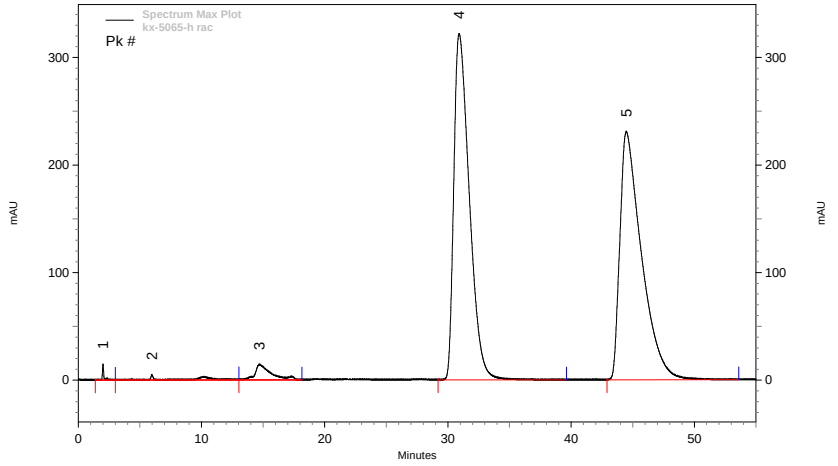
**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,013 | 0,192 | 275 |
| **2** | 5,980 | 0,477 | 278 |
| **3** | 14,707 | 2,205 | 228 |
| **4** | 30,913 | 48,671 | 204 |
| **5** | 44,480 | 48,455 | 204 |

**DAD-253 nm Results**



| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 13,980 | 0,112 | 277 |
| **2** | 21,780 | 0,124 | 260 |
| **3** | 27,713 | 0,096 | 259 |
| **4** | 30,913 | 49,866 | 204 |
| **5** | 44,480 | 49,801 | 204 |



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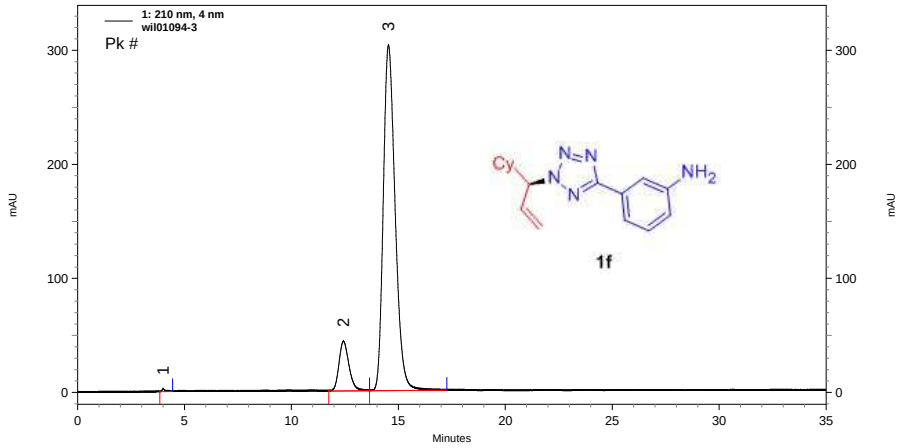
wil01094-3 {Data Description}

E:\EZDatenOC\Raidondi\Method\OD-H, Hep_IPA 80_20, 22°C, 1ml.met

Vial: 192 Injection Volume (µl): 2
Run Time: 05.02.2014 11:14:33 Analysis Time: 08.04.2015 10:56:10




**DAD-228 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 4,007 | 0,024 | 205 |
| 2 | 9,567 | 0,052 | 205 |
| 3 | 10,987 | 0,039 | 205 |
| 4 | 12,433 | 10,704 | 228 |
| 5 | 14,540 | 89,182 | 228 |

**Spectrum Max Plot Results**

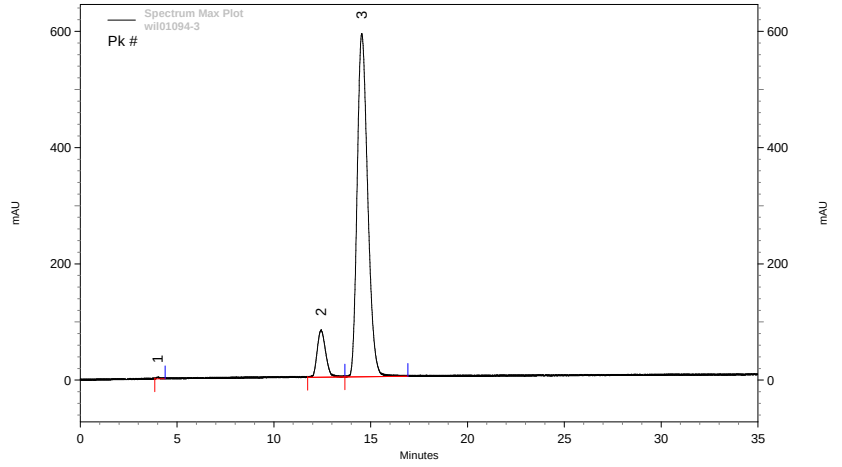
| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 4,007 | 0,106 | 205 |
| 2 | 12,433 | 9,862 | 228 |
| 3 | 14,540 | 90,032 | 228 |

**1: 210 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 4,000 | 0,166 | 206 |
| 2 | 12,433 | 10,747 | 228 |



| | | | |
|---|---|---|---|
| 3 | 14,540 | 89,086 | 228 |



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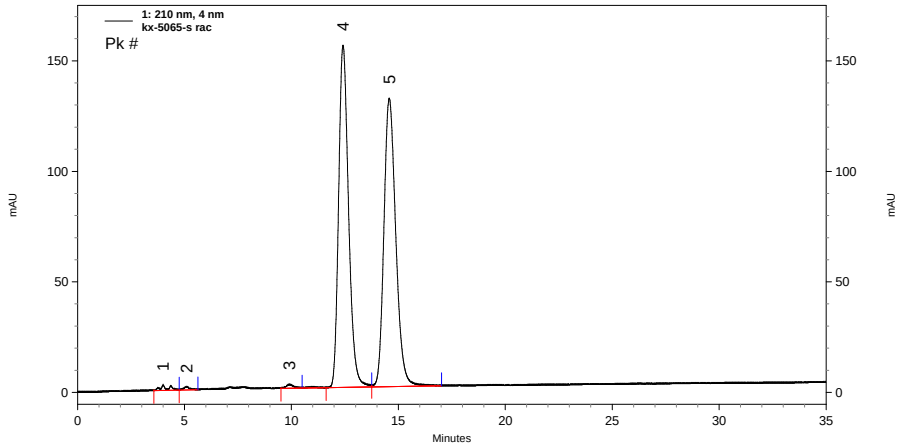
kx-5065-s rac {Data Description}

E:\EZDatenOC\Raidondi\Method\OD-H, Hep_IPA 80_20, 22°C, 1ml.met

Vial: 191 Injection Volume (µl): 2
Run Time: 05.02.2014 10:36:31 Analysis Time: 08.04.2015 10:56:46




**1: 210 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 4,000 | 0,559 | 205 |
| **2** | 5,100 | 0,238 | 204 |
| **3** | 9,907 | 0,344 | 204 |
| **4** | 12,413 | 49,243 | 228 |
| **5** | 14,573 | 49,615 | 228 |

**Spectrum Max Plot Results**

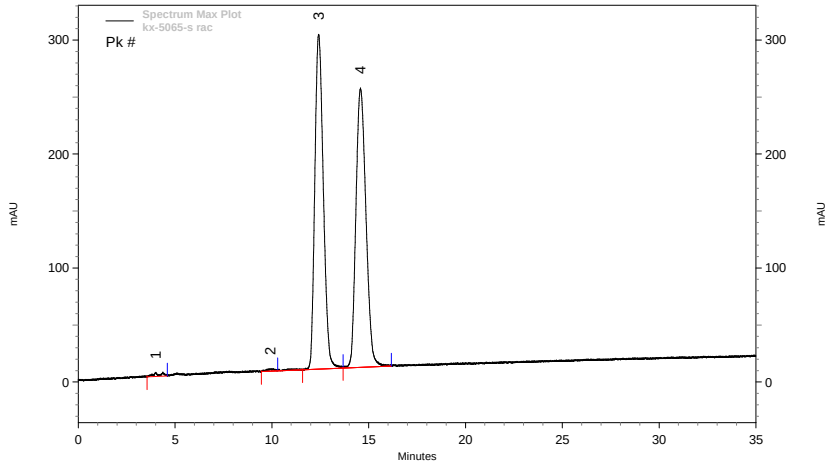
| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 3,987 | 0,432 | 205 |
| **2** | 9,920 | 0,214 | 204 |
| **3** | 12,413 | 50,136 | 228 |
| **4** | 14,573 | 49,218 | 228 |

**DAD-228 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 5,100 | 0,229 | 204 |



| | | | |
|---|---|---|---|
| **2** | 7,120 | 0,426 | 204 |
| **3** | 9,907 | 0,253 | 204 |
| **4** | 12,413 | 49,250 | 228 |
| **5** | 14,573 | 49,843 | 228 |



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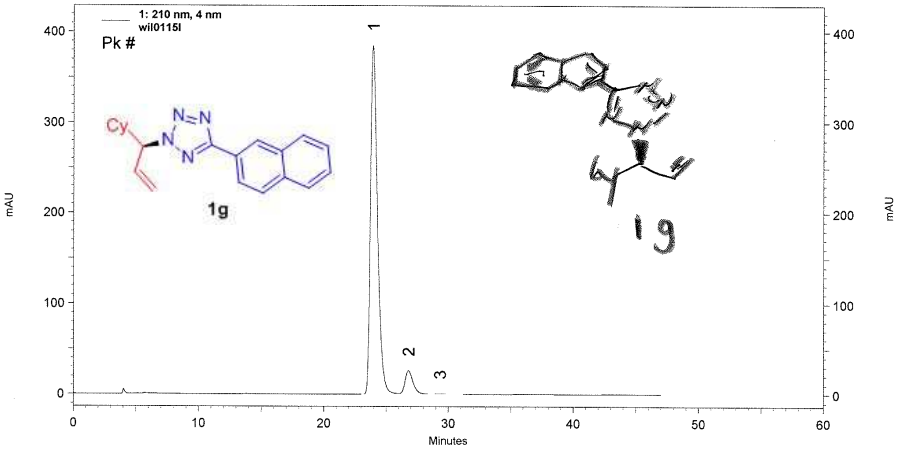
**Institut für Organische Chemie und Biochemie**

wil01151l {Data Description}

E:\EZDatenOC\Raidondi\Method\OD-3, Hep_IPA 300_1, 22°C, 0,5ml.met

Vial: 192 Injection Volume (µl): 2
Run Time: 14.05.2014 15:32:47 Analysis Time: 14.05.2014 16:03:57




**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 13,813 | 0,927 | 224 |
| 2 | 23,913 | 91,687 | 242 |
| 3 | 26,793 | 7,243 | 242 |
| 4 | 29,247 | 0,142 | 241 |

**DAD-241 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 4,013 | 0,018 | 295 |
| 2 | 5,773 | 0,012 | 288 |
| 3 | 23,913 | 92,461 | 242 |
| 4 | 26,793 | 7,350 | 242 |
| 5 | 29,247 | 0,159 | 241 |

**1: 210 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 23,913 | 92,534 | 242 |





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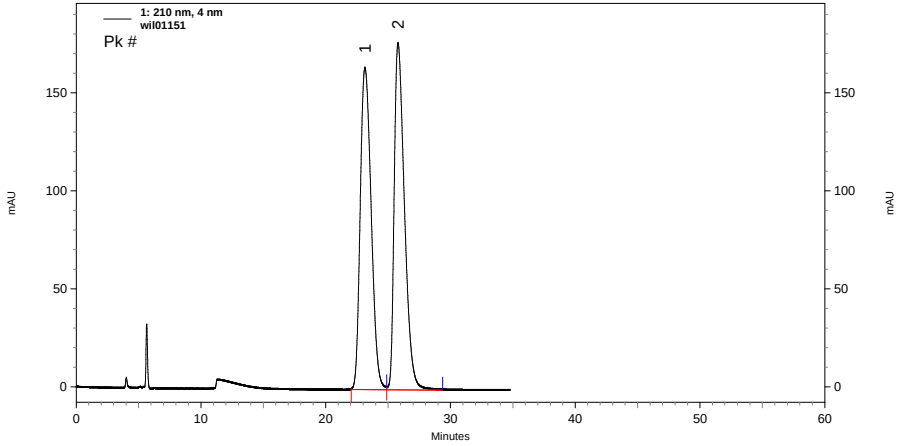
**Institut für Organische Chemie und Biochemie**

wil01151 {Data Description}

E:\EZDatenOC\Raidondi\Method\OD-3, Hep_IPA 300_1, 22°C, 0,5ml.met

Vial: 191 Injection Volume (µl): 2
Run Time: 14.05.2014 14:55:10 Analysis Time: 08.04.2015 16:01:37




**1: 210 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 23,147 | 49,657 | 242 |
| 2 | 25,800 | 50,343 | 242 |

**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 23,147 | 49,752 | 242 |
| 2 | 25,800 | 50,248 | 242 |

**DAD-241 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 23,147 | 49,754 | 242 |
| 2 | 25,800 | 50,246 | 242 |

**Universität Freiburg**
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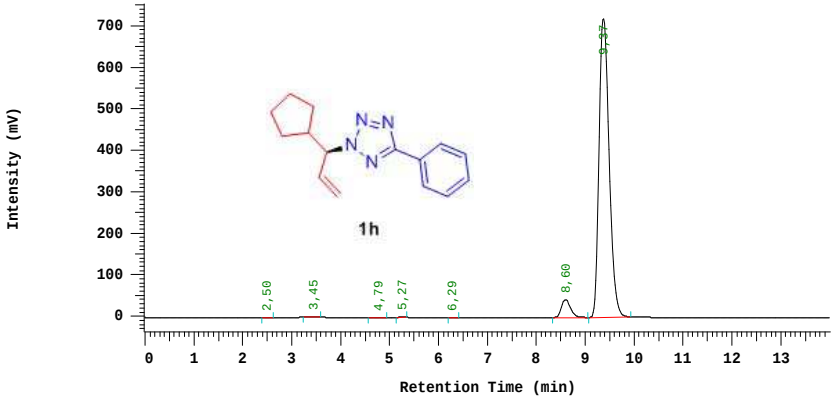
**Biochemie**

Analyzed: 03.07.14 11:20
Reported: 08.04.15 11:05
Processed: 03.07.14 11:35
Data Path: C:\PROGRAMME\HSM\Rainondi\DATA\0052\
Processing Method: AD-3 Hep/IPA 98/2 1ml 240nmAS

System(acquisition): Sys 2
Series:0052
Application: Rainondi
Vial Number: 114
Sample Name: wil01154 ee
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 1,0 ul
Sample Description:

Chrom Type: HPLC Channel : 1




Acquisition Method: AD-3 Hep/IPA 98/2 1ml 240nmAS
Column Type: WHELK-02
Developed by: fehrenbach
Pump A Type: L-7100
Solvent A: Heptan
Solvent B: i-Propanol
Solvent C: Hep/IPA 100/1
Solvent D: Äthanol
Method Description: n-Heptan / IPA 98/2, 240nm, 1ml/min

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

| No. | RT | Area % | Area | BC |
|---|---|---|---|---|
| 1 | 2,50 | 0,013 | 1325 | BB |
| 2 | 3,45 | 0,059 | 6046 | BB |
| 3 | 4,79 | 0,015 | 1484 | BB |
| 4 | 5,27 | 0,039 | 4000 | BB |
| 5 | 6,29 | 0,008 | 781 | BB |
| 6 | 8,60 | 5,110 | 520756 | BB |
| 7 | 9,37 | 94,756 | 9656753 | BB |
| | | 100,000 | 10191145 | |

Peak rejection level: 0





Channel 1 Noise: Not Measured
Channel 1 Drift: Not Measured

Configuration parameters:
Interface Module: D-7000
Gradient Mode: Low
Channel 1 Detector: L-7400
Channel 2 Detector: None
Column Oven: None
Autosampler: L-7250
Pump A: L-7100
Pump B: None
Number of Solvents pump A: 4
Number of Solvents pump B: 1
External Instrument Software: None
Column Name: WHELK-02

Method Information:
Method Name: AD-3 Hep/IPA 98/2 1ml 240nmAS
Developed by: fehrenbach
Description:
n-Heptan / IPA 98/2, 240nm, 1ml/min

Method History

| Date | User | Comment |
|---|---|---|
| 01.10.12 15:35 | test | Method originated from OD3 n-Heptan/IPA 90/10 254nm |
| 01.10.12 15:35 | test | |

Pump Setup:
Main Pump (A) Pressure Limit: 10 to 150 bar

Pump A (L-7100):
Solvent A: Heptan
Solvent B: i-Propanol
Solvent C: Hep/IPA 100/1
Solvent D: Äthanol

Pump A (L-7100):
Pump Solvent and Event Table

| Time (min) | %Hepta | %i-Pro | %Hep/I | %Äthan | Flow (ml/min) | Event 1 | Event 2 | Event 3 | Event 4 |
|---|---|---|---|---|---|---|---|---|---|
| 0,0 | 98,0 | 2,0 | 0,0 | 0,0 | 1,000 | | | | |

Autosampler Setup (L-7250):
Syringe Speed: 5
Needle Down Speed: Fast
Syringe Volume: 500 ul
Injection Method: Cut
Lead Volume: 100,00 ul
Rear Volume: 100,00 ul
Needle Wash Strokes: 1
Needle Wash Speed: 5
Injection Port Wash Stroke: 1
Injection Port Wash Speed: 5

Channel 1 Detector (L-7400):
Response Time: 2.0 sec
Absorbance Range: 1 AU
Offset: 0,000 AU
Stop Time: 14,00 min
Auto Data Sampling Mode: YES
Initial Sampling Period: 200 msec
Doubling Time: 10,00 min

Detector Table

| Time(min) | WL(nm) | Baseline |
|---|---|---|
| 0,0 | 240 | Auto Zero |

Sampling Period Table

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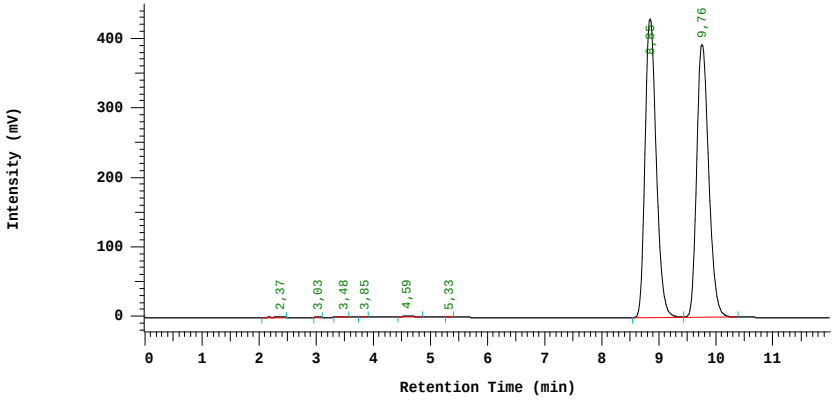
Analyzed: 02.07.14 16:42 Reported: 08.04.15 11:05
Processed: 02.07.14 16:55
Data Path: C:\PROGRAMME\HSM\Rainondi\DATA\0047\
Processing Method: AD-3 Hep/IPA 98/2 1ml 240nmAS

System(acquisition): Sys 2 Series:0047
Application: Rainondi Vial Number: 106
Sample Name: wil01153 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 1,0 ul
Sample Description:

Chrom Type: HPLC Channel : 1




Acquisition Method: AD-3 Hep/IPA 98/2 1ml 240nmAS
Column Type: WHELK-02 Developed by: fehrenbach
Pump A Type: L-7100
Solvent A: Heptan Solvent B: i-Propanol
Solvent C: Hep/IPA 100/1 Solvent D: Äthanol
Method Description: n-Heptan / IPA 98/2, 240nm, 1ml/min

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

| No. | RT | Area % | Area | BC |
|---|---|---|---|---|
| 1 | 2,37 | 0,016 | 1763 | BB |
| 2 | 3,03 | 0,008 | 870 | BB |
| 3 | 3,48 | 0,048 | 5372 | BB |
| 4 | 3,85 | 0,015 | 1677 | BB |
| 5 | 4,59 | 0,212 | 23552 | BB |
| 6 | 5,33 | 0,007 | 788 | BB |
| 7 | 8,85 | 49,877 | 5528856 | BV |
| 8 | 9,76 | 49,816 | 5522054 | VB |
| | | 100,000 | 11084932 | |

Peak rejection level: 0





Channel 1 Noise: Not Measured
Channel 1 Drift: Not Measured

Configuration parameters:
Interface Module: D-7000 Gradient Mode: Low
Channel 1 Detector: L-7400 Channel 2 Detector: None
Column Oven: None Autosampler: L-7250
Pump A: L-7100 Pump B: None
Number of Solvents pump A: 4 Number of Solvents pump B: 1
External Instrument Software: None Column Name: WHELK-02

Method Information:
Method Name: AD-3 Hep/IPA 98/2 1ml 240nmAS
Developed by: fehrenbach
Description:
n-Heptan / IPA 98/2, 240nm, 1ml/min

Method History

| Date | User | Comment |
|---|---|---|
| 01.10.12 15:35 | test | Method originated from OD3 n-Heptan/IPA 90/10 254nm |
| 01.10.12 15:35 | test | |

Pump Setup:
Main Pump (A) Pressure Limit: 10 to 150 bar

Pump A (L-7100):
Solvent A: Heptan Solvent B: i-Propanol
Solvent C: Hep/IPA 100/1 Solvent D: Äthanol

Pump A (L-7100):
Pump Solvent and Event Table

| Time (min) | %Hepta | %i-Pro | %Hep/I | %Äthan | Flow (ml/min) | Event 1 | Event 2 | Event 3 | Event 4 |
|---|---|---|---|---|---|---|---|---|---|
| 0,0 | 98,0 | 2,0 | 0,0 | 0,0 | 1,000 | | | | |

Autosampler Setup (L-7250):
Syringe Speed: 5 Needle Down Speed: Fast
Syringe Volume: 500 ul Injection Method: Cut
Lead Volume: 100,00 ul Rear Volume: 100,00 ul
Needle Wash Strokes: 1 Needle Wash Speed: 5
Injection Port Wash Stroke: 1 Injection Port Wash Speed: 5

Channel 1 Detector (L-7400):
Response Time: 2.0 sec Absorbance Range: 1 AU
Offset: 0,000 AU Stop Time: 17,00 min
Auto Data Sampling Mode: YES Initial Sampling Period: 200 msec
Doubling Time: 10,00 min

Detector Table

| Time(min) | WL(nm) | Baseline |
|---|---|---|
| 0,0 | 240 | Auto Zero |

Sampling Period Table

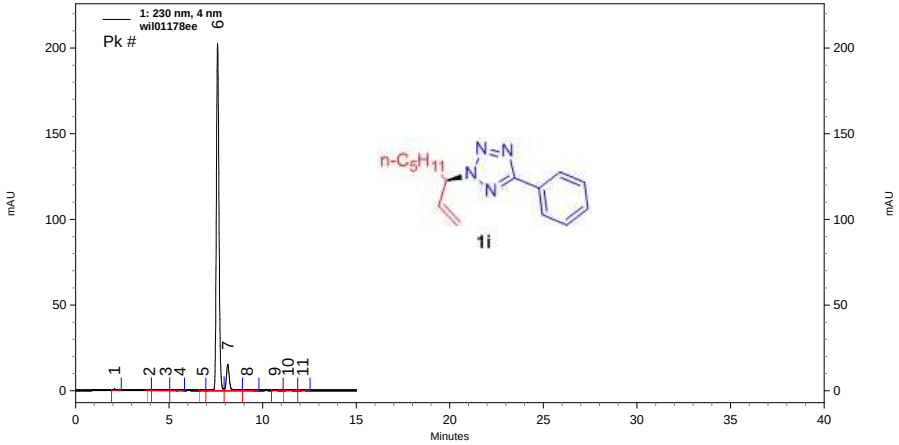
Albert-Ludwigs-Universität Freiburg

**Institut für Organische Chemie und Biochemie**

wil01178ee {Data Description}

E:\EZDatenOC\KunXu\Method\AD-3, Hept_IPA, 200_1,200-400nm, 22°C, 1 ml.met

Vial: 8 Injection Volume (µl): 1
Run Time: 12.09.2014 19:13:04 Analysis Time: 08.04.2015 10:47:33




**1: 230 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,073 | 0,172 | 385 |
| 2 | 3,947 | 0,021 | 248 |
| 3 | 4,827 | 0,075 | 240 |
| 4 | 5,580 | 0,080 | 269 |
| 5 | 6,787 | 0,035 | 232 |
| 6 | 7,593 | 91,502 | 201 |
| 7 | 8,133 | 7,780 | 200 |
| 8 | 9,167 | 0,144 | 233 |
| 9 | 10,647 | 0,051 | 232 |
| 10 | 11,367 | 0,088 | 237 |
| 11 | 12,153 | 0,052 | 238 |

**2: 250 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,073 | 0,025 | 385 |
| 2 | 3,947 | 0,023 | 248 |
| 3 | 4,827 | 0,034 | 240 |
| 4 | 5,573 | 0,082 | 269 |



| | | | |
|---|---|---|---|
| 5 | 6,793 | 0,029 | 232 |
| 6 | 7,147 | 0,035 | 232 |
| 7 | 7,593 | 91,759 | 201 |
| 8 | 8,140 | 7,800 | 200 |
| 9 | 9,180 | 0,070 | 233 |
| 10 | 10,213 | 0,018 | 236 |
| 11 | 10,640 | 0,029 | 232 |
| 12 | 11,393 | 0,061 | 237 |
| 13 | 12,207 | 0,035 | 238 |

**4: 210 nm, 4 nm Results**

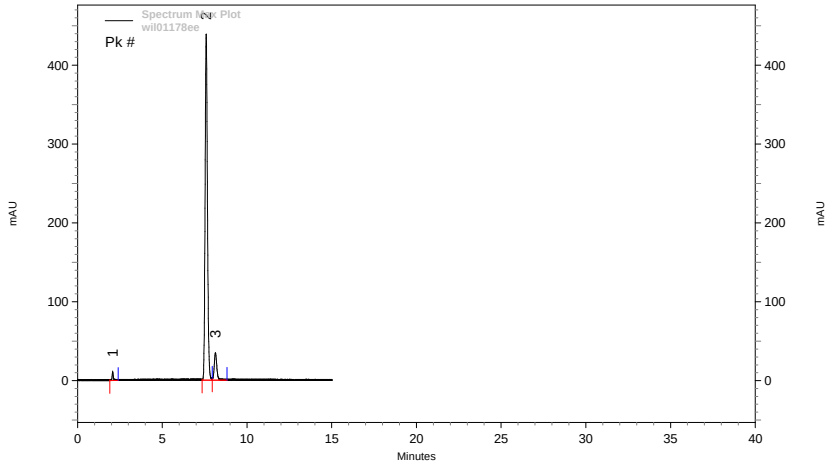
| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,067 | 1,236 | 385 |
| 2 | 2,360 | 0,020 | 385 |
| 3 | 3,940 | 0,034 | 248 |
| 4 | 4,827 | 0,039 | 240 |
| 5 | 5,173 | 0,009 | 384 |
| 6 | 5,573 | 0,086 | 269 |
| 7 | 6,047 | 0,008 | 230 |
| 8 | 6,780 | 0,041 | 232 |
| 9 | 7,160 | 0,043 | 234 |
| 10 | 7,593 | 90,412 | 201 |
| 11 | 8,133 | 7,752 | 200 |
| 12 | 9,180 | 0,139 | 233 |
| 13 | 9,587 | 0,014 | 234 |
| 14 | 10,187 | 0,036 | 236 |
| 15 | 10,660 | 0,044 | 233 |
| 16 | 11,367 | 0,067 | 237 |
| 17 | 12,207 | 0,021 | 238 |

**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,067 | 1,187 | 385 |
| 2 | 7,593 | 90,999 | 201 |
| 3 | 8,133 | 7,813 | 200 |

**DAD-241 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,067 | 0,031 | 385 |
| 2 | 7,593 | 92,040 | 201 |
| 3 | 8,133 | 7,739 | 200 |
| 4 | 11,373 | 0,048 | 237 |
| 5 | 12,193 | 0,048 | 238 |
| 6 | 13,193 | 0,058 | 239 |
| 7 | 13,700 | 0,029 | 239 |
| 8 | 14,647 | 0,008 | 239 |



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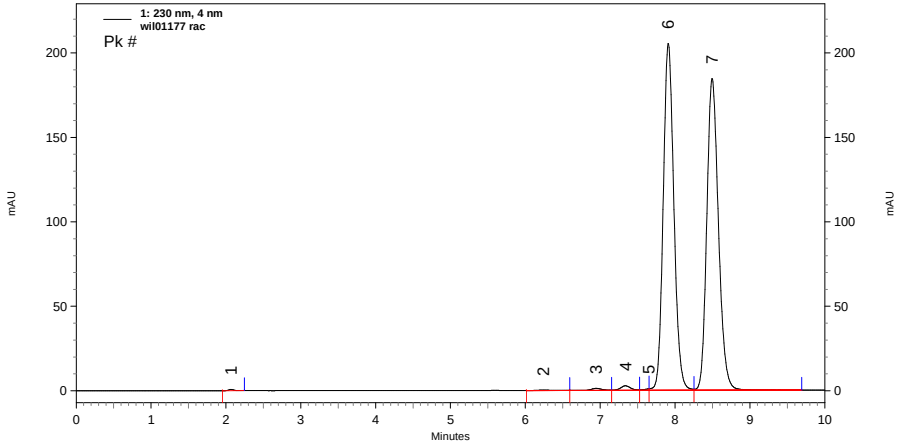
**Institut für Organische Chemie und Biochemie**

wil01177 rac {Data Description}

E:\EZDatenOC\KunXu\Method\AD-3, Hept_IPA, 200_1,200-400nm, 22°C, 1 ml.met

Vial: 3 Injection Volume (µl): 1
Run Time: 12.09.2014 15:42:32 Analysis Time: 08.04.2015 10:48:06




**1: 230 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,067 | 0,090 | 276 |
| **2** | 6,240 | 0,063 | 233 |
| **3** | 6,947 | 0,280 | 236 |
| **4** | 7,340 | 0,614 | 240 |
| **5** | 7,647 | 0,093 | 235 |
| **6** | 7,907 | 49,882 | 201 |
| **7** | 8,493 | 48,978 | 201 |

**2: 250 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,073 | 0,013 | 276 |
| **2** | 2,360 | 0,002 | 276 |
| **3** | 4,053 | 0,004 | 277 |
| **4** | 4,507 | 0,027 | 233 |
| **5** | 4,807 | 0,003 | 276 |
| **6** | 6,947 | 0,280 | 236 |
| **7** | 7,340 | 0,613 | 240 |
| **8** | 7,687 | 0,161 | 237 |

| | | | |
|---|---|---|---|
| **9** | 7,913 | 49,848 | 201 |
| **10** | 8,493 | 49,047 | 201 |
| **11** | 9,773 | 0,003 | 232 |

**4: 210 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,067 | 0,663 | 276 |
| **2** | 2,360 | 0,010 | 276 |
| **3** | 6,947 | 0,297 | 236 |
| **4** | 7,340 | 0,639 | 240 |
| **5** | 7,660 | 0,118 | 236 |
| **6** | 7,907 | 49,554 | 201 |
| **7** | 8,493 | 48,719 | 201 |

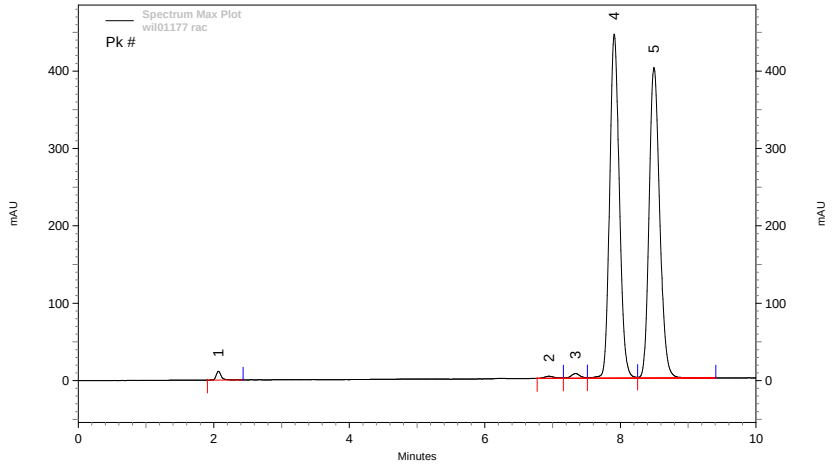
**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,067 | 0,654 | 276 |
| **2** | 6,947 | 0,336 | 236 |
| **3** | 7,333 | 0,661 | 240 |
| **4** | 7,907 | 49,613 | 201 |
| **5** | 8,493 | 48,736 | 201 |

**DAD-241 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 4,060 | 0,003 | 277 |
| **2** | 4,493 | 0,024 | 233 |
| **3** | 5,587 | 0,013 | 275 |
| **4** | 6,240 | 0,058 | 233 |
| **5** | 6,947 | 0,278 | 236 |
| **6** | 7,340 | 0,608 | 240 |
| **7** | 7,907 | 50,000 | 201 |
| **8** | 8,493 | 49,015 | 201 |





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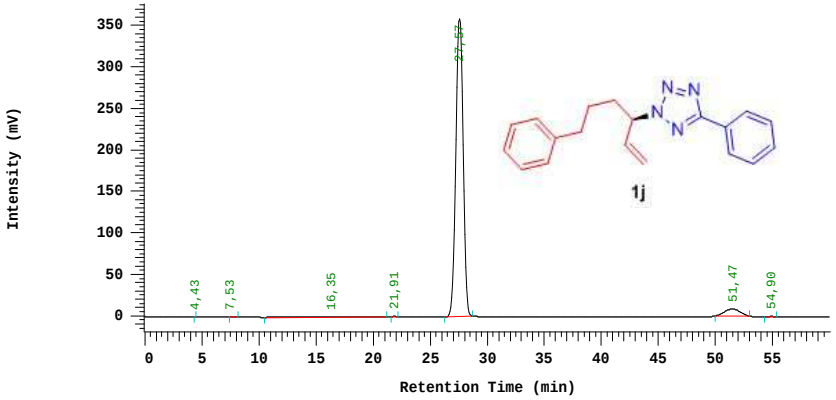
Analyzed: 24.09.14 15:00 Reported: 08.04.15 11:06
Processed: 24.09.14 16:01

Data Path: D:\HSM\KunXu\DATA\0701\
Processing Method: L-C2 Hep/IPA 200/1 240nm 0,5ml

System(acquisition): Sys 1 Series:0701
Application: KunXu Vial Number: 1
Sample Name: wil01109-b ee Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 1,0 ul
Sample Description:

Chrom Type: HPLC Channel : 1




Acquisition Method: L-C2 Hep/IPA 200/1 240nm 0,5ml
Column Type: Chiralpak AD-H Developed by: fehrenbach
Pump A Type: L-7100
Solvent A: Heptan Solvent B: i-Propanol
Solvent C: Hep/IPA 100/1 Solvent D: Äthanol
Method Description: n-Heptan/IPA 200/1, 240nm, 0,5ml/min

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

| No. | RT | Area % | Area | BC |
|---|---|---|---|---|
| 1 | 4,43 | 0,016 | 2457 | BB |
| 2 | 7,53 | 0,036 | 5629 | BB |
| 3 | 16,35 | 1,020 | 157454 | BB |
| 4 | 21,91 | 0,059 | 9168 | BB |
| 5 | 27,57 | 93,749 | 14471544 | BB |
| 6 | 51,47 | 5,066 | 782067 | BB |
| 7 | 54,90 | 0,053 | 8154 | BB |
| | | 100,000 | 15436473 | |

Peak rejection level: 0







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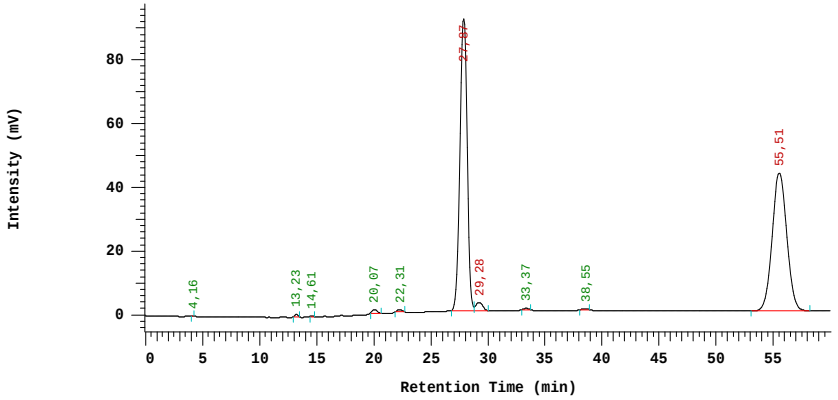
Analyzed: 24.09.14 12:58 Reported: 08.04.15 11:06
Processed: 24.09.14 14:59

Data Path: D:\HSM\KunXu\DATA\0700\
Processing Method: L-C2 Hep/IPA 200/1 240nm 0,5ml

System(acquisition): Sys 1 Series:0700
Application: KunXu Vial Number: 1
Sample Name: kx-5067-a rac Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 1,0 ul
Sample Description:

Chrom Type: HPLC Channel : 1




Acquisition Method: L-C2 Hep/IPA 200/1 240nm 0,5ml
Column Type: Chiralpak AD-H Developed by: fehrenbach
Pump A Type: L-7100
Solvent A: Heptan Solvent B: i-Propanol
Solvent C: Hep/IPA 100/1 Solvent D: Äthanol
Method Description: n-Heptan/IPA 200/1, 240nm, 0,5ml/min

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

| No. | RT | Area % | Area | BC |
|---|---|---|---|---|
| 1 | 4,16 | 0,011 | 825 | BB |
| 2 | 13,23 | 0,185 | 14020 | BB |
| 3 | 14,61 | 0,055 | 4164 | BB |
| 4 | 20,07 | 0,430 | 32534 | BB |
| 5 | 22,31 | 0,228 | 17224 | BB |
| 6 | 27,87 | 48,680 | 3681514 | MC |
| 7 | 29,28 | 1,360 | 102872 | MC |
| 8 | 33,37 | 0,152 | 11466 | BB |
| 9 | 38,55 | 0,143 | 10841 | BB |
| 10 | 55,51 | 48,756 | 3687284 | MC |
| | | 100,000 | 7562744 | |

Peak rejection level: 0

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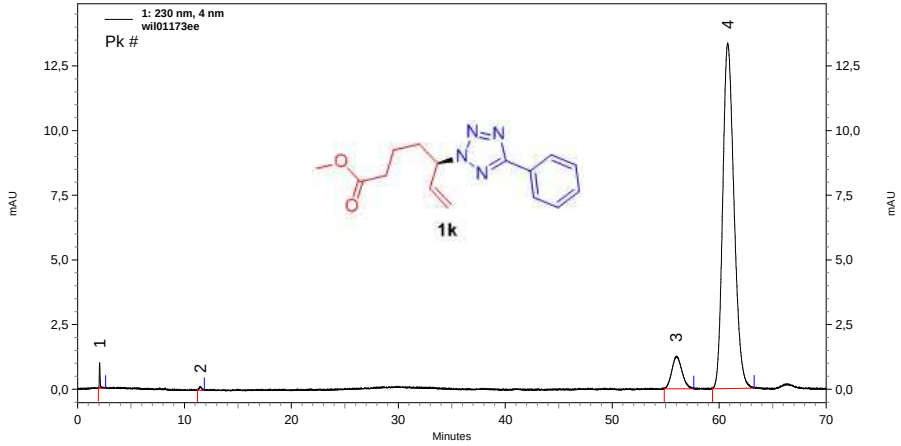
wil01173ee {Data Description}

E:\EZDatenOC\KunXu\Method\AD-3, Hept_IPA, 200_1,200-400nm, 22°C, 1 ml.met

Vial: 7 Injection Volume (µl): 1
Run Time: 12.09.2014 17:59:55 Analysis Time: 08.04.2015 10:45:57




**1: 230 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,073 | 0,493 | 391 |
| 2 | 11,473 | 0,197 | 236 |
| 3 | 55,980 | 7,665 | 200 |
| 4 | 60,807 | 91,644 | 200 |

**2: 250 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,073 | 0,064 | 391 |
| 2 | 7,633 | 0,012 | 234 |
| 3 | 8,160 | 0,030 | 234 |
| 4 | 11,493 | 0,192 | 236 |
| 5 | 56,027 | 7,669 | 240 |
| 6 | 60,807 | 92,033 | 200 |

**4: 210 nm, 4 nm Results**



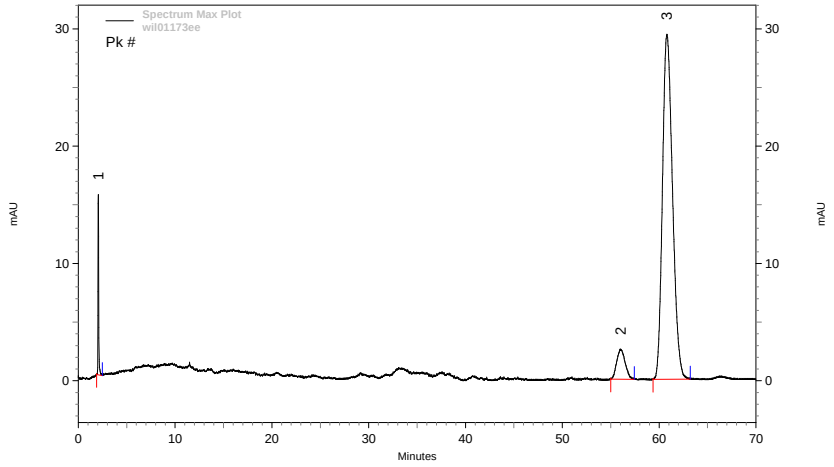
| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,073 | 3,330 | 391 |
| 2 | 56,047 | 7,452 | 200 |
| 3 | 57,540 | 0,027 | 238 |
| 4 | 60,800 | 88,296 | 200 |
| 5 | 66,367 | 0,873 | 239 |
| 6 | 67,260 | 0,023 | 239 |

**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,073 | 3,353 | 391 |
| 2 | 56,040 | 6,531 | 200 |
| 3 | 60,807 | 90,116 | 200 |

**DAD-241 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,067 | 0,138 | 390 |
| 2 | 56,007 | 7,944 | 200 |
| 3 | 58,127 | 0,065 | 239 |
| 4 | 60,807 | 90,495 | 200 |
| 5 | 63,553 | 0,022 | 239 |
| 6 | 64,500 | 0,025 | 239 |
| 7 | 66,420 | 1,281 | 239 |
| 8 | 67,767 | 0,030 | 239 |



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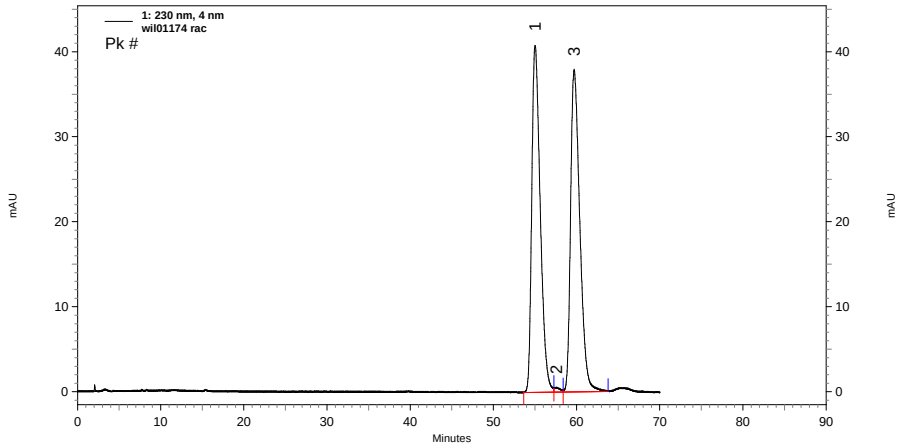
**Institut für Organische Chemie und Biochemie**

wil01174 rac {Data Description}

E:\EZDatenOC\KunXu\Method\AD-3, Hept_IPA, 200_1,200-400nm, 22°C, 1 ml.met

Vial: 5 Injection Volume (µl): 1
Run Time: 12.09.2014 16:23:37 Analysis Time: 08.04.2015 10:46:35




**1: 230 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 55,020 | 49,590 | 201 |
| 2 | 57,593 | 0,411 | 237 |
| 3 | 59,713 | 49,999 | 201 |

**2: 250 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 55,013 | 49,612 | 201 |
| 2 | 57,533 | 0,423 | 237 |
| 3 | 59,713 | 49,965 | 201 |

**4: 210 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 55,013 | 49,608 | 201 |
| 2 | 57,513 | 0,356 | 237 |
| 3 | 59,713 | 50,035 | 201 |



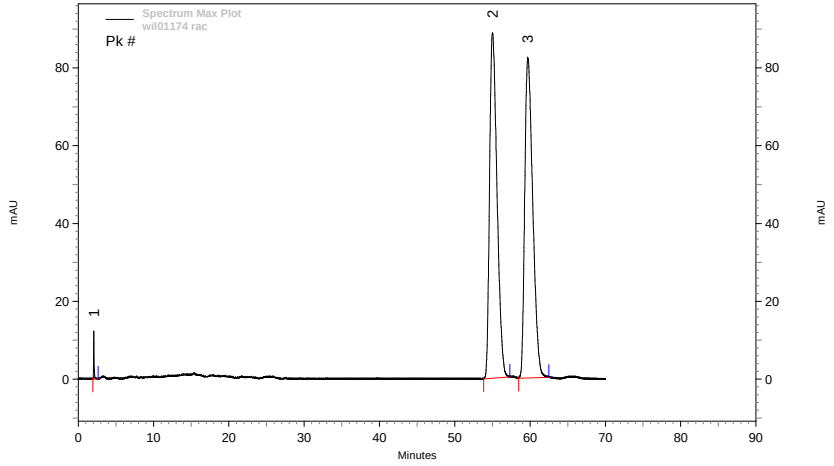


**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,067 | 0,511 | 268 |
| 2 | 55,020 | 49,763 | 201 |
| 3 | 59,700 | 49,726 | 201 |

**DAD-241 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 15,407 | 0,042 | 232 |
| 2 | 39,740 | 0,077 | 233 |
| 3 | 48,460 | 0,025 | 263 |
| 4 | 55,013 | 48,652 | 201 |
| 5 | 57,540 | 0,474 | 237 |
| 6 | 59,707 | 49,553 | 201 |
| 7 | 65,367 | 1,086 | 236 |
| 8 | 67,700 | 0,081 | 234 |
| 9 | 69,400 | 0,008 | 261 |



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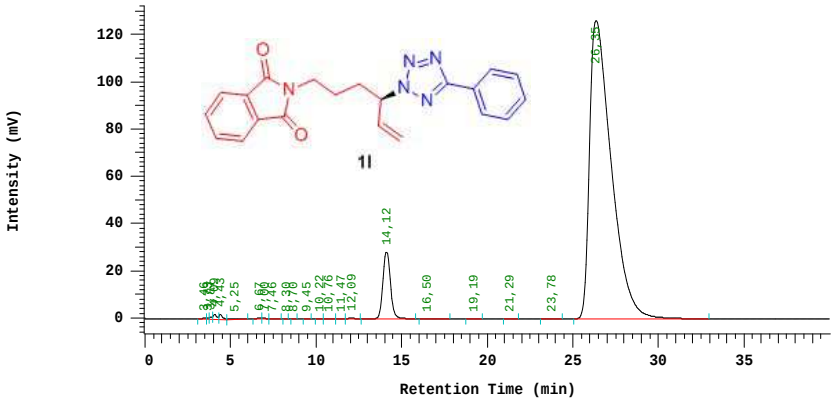
Analyzed: 07.10.14 13:03 Reported: 08.04.15 11:07
Processed: 07.10.14 13:45

Data Path: D:\HSM\KunXu\DATA\0723\
Processing Method: L-C2 Hep/IPA 50/50 235nm 0,5ml

System(acquisition): Sys 1 Series:0723
Application: KunXu Vial Number: 1
Sample Name: wil01097-B ee Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 1,0 ul
Sample Description:

Chrom Type: HPLC Channel : 1




Acquisition Method: L-C2 Hep/IPA 50/50 235nm 0,5ml
Column Type: Chiralpak AD-H Developed by: fehrenbach
Pump A Type: L-7100
Solvent A: Heptan Solvent B: i-Propanol
Solvent C: Hep/IPA 100/1 Solvent D: Äthanol
Method Description: n-Heptan/IPA 50/50, 235nm, 0,5ml/min

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

| No. | RT | Area % | Area | BC |
|---|---|---|---|---|
| 1 | 3,46 | 0,049 | 5693 | BV |
| 2 | 3,73 | 0,041 | 4752 | VV |
| 3 | 3,87 | 0,078 | 9154 | VV |
| 4 | 4,09 | 0,207 | 24194 | VV |
| 5 | 4,43 | 0,219 | 25646 | VB |
| 6 | 5,25 | 0,087 | 10200 | BB |
| 7 | 6,67 | 0,039 | 4522 | BV |
| 8 | 7,00 | 0,028 | 3258 | VV |
| 9 | 7,46 | 0,027 | 3133 | VB |
| 10 | 8,30 | 0,005 | 528 | BB |
| 11 | 8,70 | 0,005 | 546 | BB |
| 12 | 9,45 | 0,009 | 1060 | BB |
| 13 | 10,22 | 0,007 | 825 | BB |
| 14 | 10,76 | 0,025 | 2978 | BB |
| 15 | 11,47 | 0,008 | 896 | BB |
| 16 | 12,09 | 0,072 | 8385 | BB |





| | | | | |
|---|---|---|---|---|
| 17 | 14,12 | 6,945 | 811917 | BB |
| 18 | 16,50 | 0,042 | 4938 | BB |
| 19 | 19,19 | 0,009 | 1030 | BB |
| 20 | 21,29 | 0,007 | 824 | BB |
| 21 | 23,78 | 0,038 | 4446 | BB |
| 22 | 26,35 | 92,054 | 10762364 | BB |
| | | 100,000 | 11691289 | |

Peak rejection level: 0

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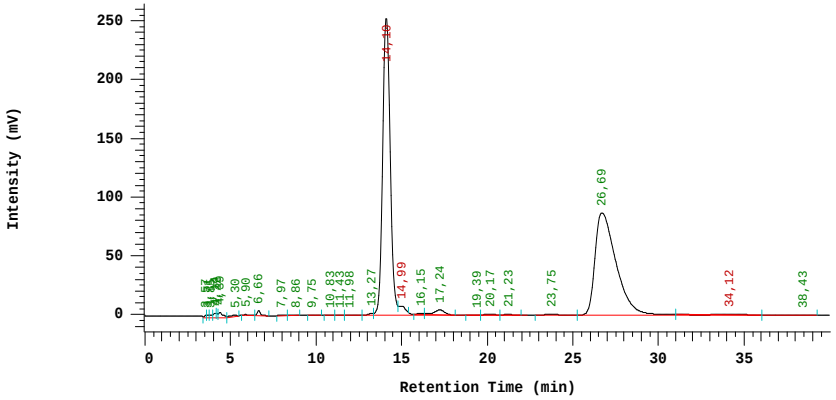
**Biochemie**

Analyzed: 07.10.14 12:02 Reported: 08.04.15 11:07
Processed: 07.10.14 12:58
Data Path: D:\HSM\KunXu\DATA\0722\
Processing Method: L-C2 Hep/IPA 50/50 235nm 0,5ml
System(acquisition): Sys 1 Series:0722
Application: KunXu Vial Number: 1
Sample Name: kx-5067-D rac Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 1,0 ul
Sample Description:

Chrom Type: HPLC Channel : 1




Acquisition Method: L-C2 Hep/IPA 50/50 235nm 0,5ml
Column Type: Chiralpak AD-H Developed by: fehrenbach
Pump A Type: L-7100
Solvent A: Heptan Solvent B: i-Propanol
Solvent C: Hep/IPA 100/1 Solvent D: Äthanol
Method Description: n-Heptan/IPA 50/50, 235nm, 0,5ml/min

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

| No. | RT | Area % | Area | BC |
|---|---|---|---|---|
| 1 | 3,57 | 0,075 | 11409 | BV |
| 2 | 3,71 | 0,143 | 21845 | VV |
| 3 | 3,85 | 0,141 | 21621 | VV |
| 4 | 4,14 | 0,224 | 34307 | VV |
| 5 | 4,22 | 0,132 | 20174 | VV |
| 6 | 4,39 | 0,424 | 64826 | VB |
| 7 | 5,30 | 0,156 | 23915 | BB |
| 8 | 5,90 | 0,063 | 9582 | BV |
| 9 | 6,66 | 0,283 | 43352 | VB |
| 10 | 7,97 | 0,061 | 9375 | BV |
| 11 | 8,86 | 0,008 | 1279 | VB |
| 12 | 9,75 | 0,005 | 720 | BB |
| 13 | 10,83 | 0,005 | 693 | BB |
| 14 | 11,43 | 0,036 | 5487 | BV |
| 15 | 11,98 | 0,032 | 4937 | VB |
| 16 | 13,27 | 0,214 | 32663 | BV |





| | | | | |
|---|---|---|---|---|
| 17 | 14,10 | 46,729 | 7148917 | MC |
| 18 | 14,99 | 2,088 | 319372 | MC |
| 19 | 16,15 | 0,101 | 15500 | TBV |
| 20 | 17,24 | 1,053 | 161037 | TVB |
| 21 | 19,39 | 0,039 | 5923 | TBV |
| 22 | 20,17 | 0,230 | 35180 | TVV |
| 23 | 21,23 | 0,125 | 19154 | TVB |
| 24 | 23,75 | 0,247 | 37735 | BV |
| 25 | 26,69 | 47,141 | 7211922 | VV |
| 26 | 34,12 | 0,212 | 32500 | MC |
| 27 | 38,43 | 0,035 | 5316 | VB |
| | | 100,000 | 15298741 | |

Peak rejection level: 0

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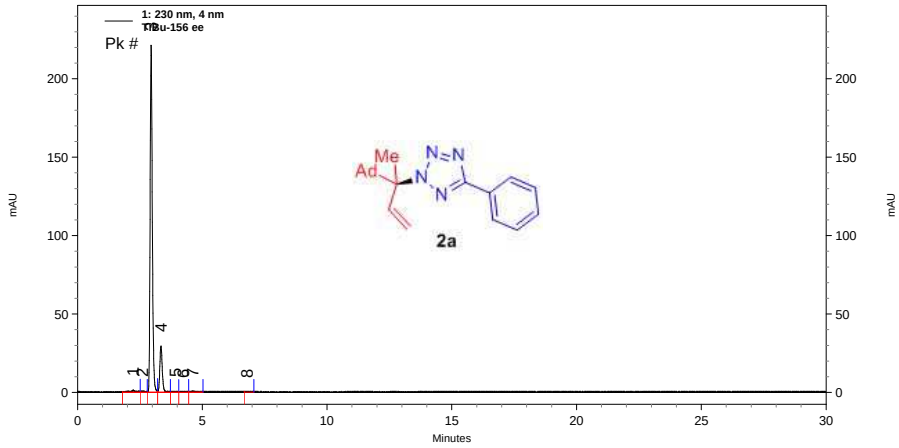
**Institut für Organische Chemie und Biochemie**

TiBu-156 ee {Data Description}

E:\EZDatenOC\Thieme\Method\OD-3, Hept_IPA, 98_2, 22°C, 1ml.met

Vial: 195 Injection Volume (µl): 1
Run Time: 11.08.2014 13:24:55 Analysis Time: 08.04.2015 10:07:16




**1: 230 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,227 | 0,897 | 201 |
| **2** | 2,593 | 0,294 | 204 |
| **3** | 2,947 | 85,601 | 205 |
| **4** | 3,347 | 12,736 | 204 |
| **5** | 3,920 | 0,135 | 203 |
| **6** | 4,240 | 0,062 | 201 |
| **7** | 4,620 | 0,232 | 202 |
| **8** | 6,800 | 0,043 | 227 |

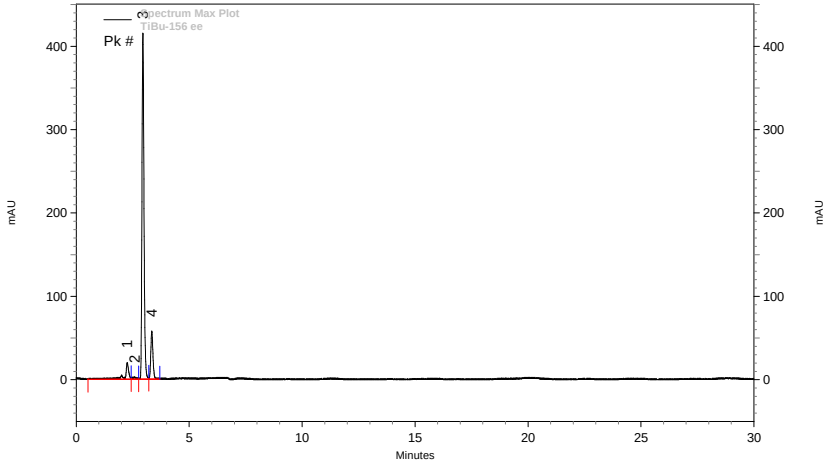
**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,253 | 6,523 | 201 |
| **2** | 2,593 | 0,737 | 204 |
| **3** | 2,947 | 80,658 | 205 |
| **4** | 3,340 | 12,082 | 204 |



**DAD-242 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,213 | 0,409 | 201 |
| **2** | 2,593 | 0,254 | 204 |
| **3** | 2,947 | 86,634 | 205 |
| **4** | 3,347 | 12,697 | 204 |
| **5** | 3,667 | 0,005 | 202 |



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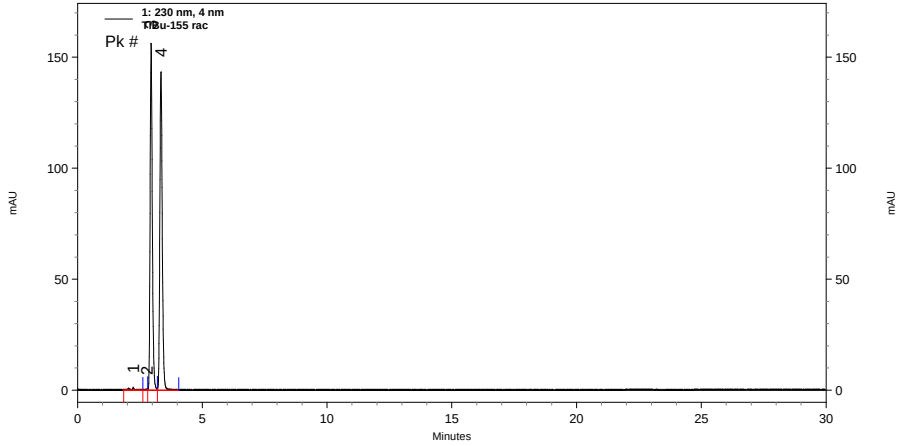
TiBu-155 rac {Data Description}

E:\EZDatenOC\Thieme\Method\OD-3, Hept_IPA, 98_2, 22°C, 1ml.met

Vial: 193 Injection Volume (µl): 1
Run Time: 11.08.2014 13:58:04 Analysis Time: 08.04.2015 10:06:29




**1: 230 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,233 | 0,577 | 201 |
| **2** | 2,780 | 0,120 | 242 |
| **3** | 2,947 | 49,466 | 204 |
| **4** | 3,347 | 49,837 | 204 |

**Spectrum Max Plot Results**

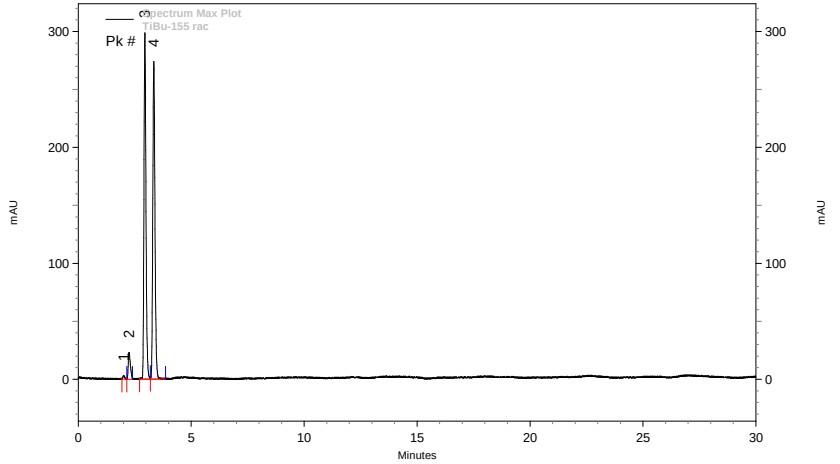
| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,007 | 0,410 | 204 |
| **2** | 2,247 | 3,954 | 201 |
| **3** | 2,947 | 47,801 | 204 |
| **4** | 3,347 | 47,835 | 204 |

**DAD-242 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,227 | 0,112 | 201 |
| **2** | 2,780 | 0,076 | 242 |



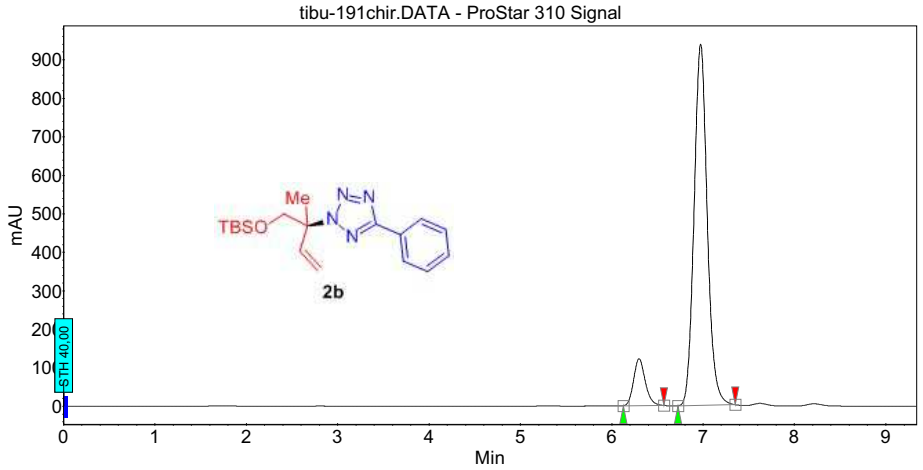
| | | | |
|---|---|---|---|
| **3** | 2,947 | 49,816 | 204 |
| **4** | 3,347 | 49,996 | 204 |



## Chromatogram :L-C2; Hep_IPA 200_1; 0,5ml; 240nm

Method : L-C2; Hep_IPA 200_1; 0,5ml; 240nm
User : AMH
26.11.2014 22:27:16
AMH
tibu-191chir

Acquired : 26.11.2014 22:27:16
Processed : 26.11.2014 22:37:23
Printed : 26.11.2014 22:37:45
ORGPC119
Project1
System 1 (Normal Phase)




### Peak results :

| Index | Name | Time [Min] | Quantity [% Area] | Height [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 6,30 | 10,27 | 122,0 | 18,0 | 10,268 |
| 2 | UNKNOWN | 6,97 | 89,73 | 939,2 | 157,2 | 89,732 |
| | | | | | | |
| Total | | | 100,00 | 1061,2 | 175,2 | 100,000 |

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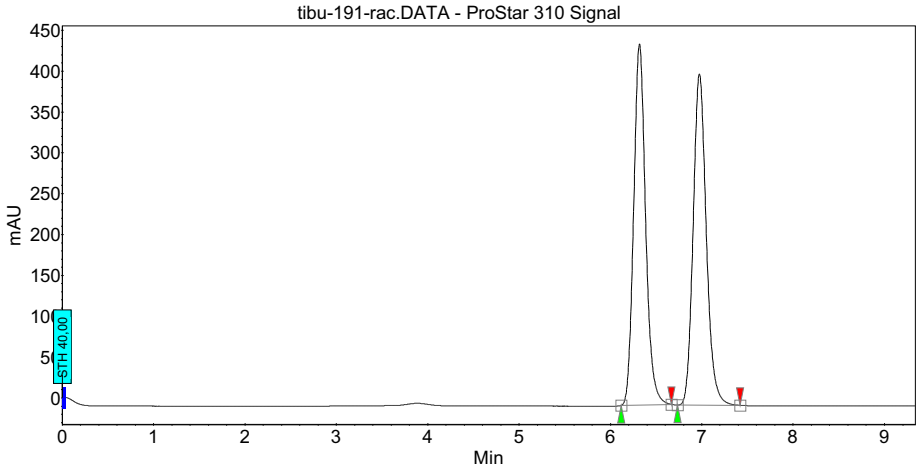
AGECOUNT

## Chromatogram :L-C2; Hep_IPA 200_1; 0,5ml; 240nm

Method : L-C2; Hep_IPA 200_1; 0,5ml; 240nm
User : AMH
26.11.2014 22:16:11
AMH
tibu-191-rac

Acquired : 26.11.2014 22:16:11
Processed : 26.11.2014 22:34:24
Printed : 26.11.2014 22:34:32
ORGPC119
Project1
System 1 (Normal Phase)




### Peak results :

| Index | Name | Time [Min] | Quantity [% Area] | Height [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 6,32 | 49,82 | 442,3 | 67,1 | 49,817 |
| 2 | UNKNOWN | 6,97 | 50,18 | 405,8 | 67,6 | 50,183 |
| | | | | | | |
| Total | | | 100,00 | 848,1 | 134,6 | 100,000 |

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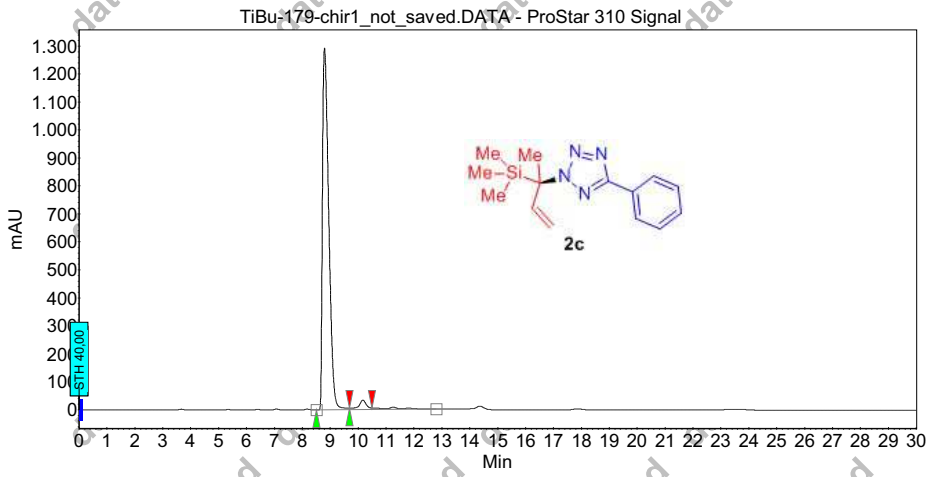
AGECOUNT

## Chromatogram :L-C1; Hep_IPA 300_1; 0,5ml; 215nm

Method : L-C1; Hep_IPA 300_1; 0,5ml; 215nm
User : TiBu
09.10.2014 18:48:18
TiBu
TiBu-179-chir1

Acquired : 09.10.2014 18:48:18
Processed : 23.10.2014 13:37:00
Printed : 23.10.2014 13:37:38
ORGPC119
Project1
System 1 (Normal Phase)




### Peak results :

| Index | Name | Time [Min] | Quantity [% Area] | Height [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 8,79 | 96,86 | 1293,6 | 338,1 | 96,856 |
| 2 | UNKNOWN | 10,17 | 3,14 | 33,8 | 11,0 | 3,144 |
| | | | | | | |
| Total | | | 100,00 | 1327,4 | 349,1 | 100,000 |



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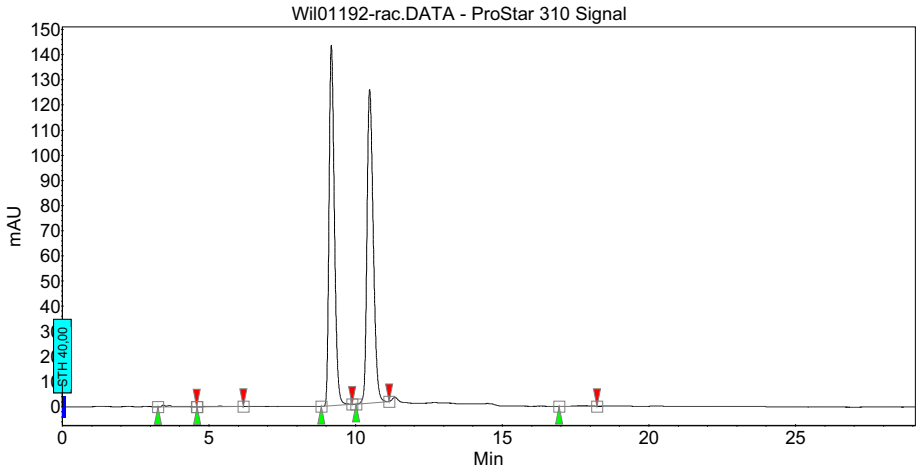
AGECOUNT

## Chromatogram :L-C1; Hep_IPA 300_1; 0,5ml; 215nm

Method : L-C1; Hep_IPA 300_1; 0,5ml; 215nm
User : Administrator
09.10.2014 17:04:32
TiBu
Wil01192-rac

Acquired : 09.10.2014 17:04:32
Processed : 10.10.2014 10:02:35
Printed : 10.10.2014 10:02:45
ORGPC119
Project1
System 1 (Normal Phase)




### Peak results :

| Index | Name | Time [Min] | Quantity [% Area] | Height [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 3,44 | 0,41 | 0,8 | 0,3 | 0,412 |
| 2 | UNKNOWN | 5,38 | 0,25 | 0,3 | 0,2 | 0,251 |
| 4 | UNKNOWN | 9,17 | 49,00 | 143,5 | 30,2 | 49,003 |
| 5 | UNKNOWN | 10,48 | 50,12 | 124,8 | 30,9 | 50,124 |
| 3 | UNKNOWN | 17,72 | 0,21 | 0,3 | 0,1 | 0,210 |
| | | | | | | |
| Total | | | 100,00 | 269,6 | 61,7 | 100,000 |



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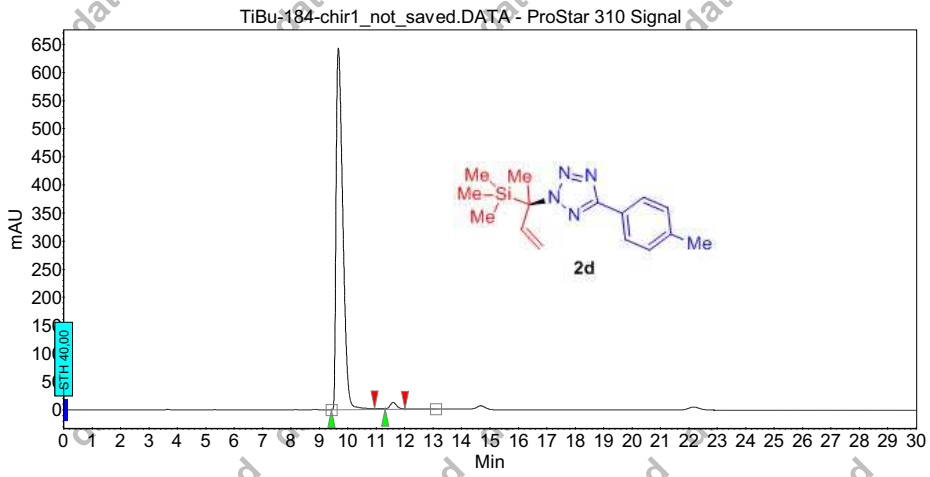
AGECOUNT

## Chromatogram :L-C1; Hep_IPA 300_1; 0,5ml; 215nm

Method : L-C1; Hep_IPA 300_1; 0,5ml; 215nm
User : TiBu
09.10.2014 19:19:30
TiBu
TiBu-184-chir1

Acquired : 09.10.2014 19:19:30
Processed : 23.10.2014 13:32:43
Printed : 23.10.2014 13:33:36
ORGPC119
Project1
System 1 (Normal Phase)




**Peak results :**

| Index | Name | Time [Min] | Quantity [% Area] | Height [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 9,67 | 98,01 | 643,6 | 176,9 | 98,012 |
| 2 | UNKNOWN | 11,59 | 1,99 | 12,4 | 3,6 | 1,988 |
| | | | | | | |
| Total | | | 100,00 | 655,9 | 180,4 | 100,000 |

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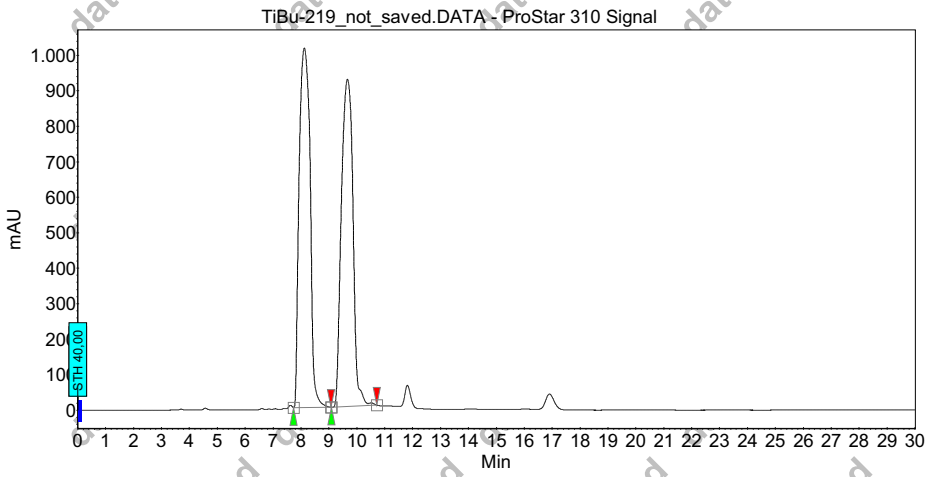
AGECOUNT

## Chromatogram :L-C1; Hep_IPA 300_1; 0,5ml; 215nm

Method : L-C1; Hep_IPA 300_1; 0,5ml; 215nm
User : TiBu
01.12.2014 16:58:18
TiBu
TiBu-219

Acquired : 01.12.2014 16:58:18
Processed : 01.12.2014 19:24:32
Printed : 01.12.2014 19:24:58
ORGPC119
Project1
System 1 (Normal Phase)




**Peak results :**

| Index | Name | Time [Min] | Quantity [% Area] | Height [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 8,12 | 50,84 | 1013,4 | 459,1 | 50,843 |
| 2 | UNKNOWN | 9,66 | 49,16 | 922,7 | 443,9 | 49,157 |
| | | | | | | |
| Total | | | 100,00 | 1936,1 | 903,1 | 100,000 |

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AGECOUNT

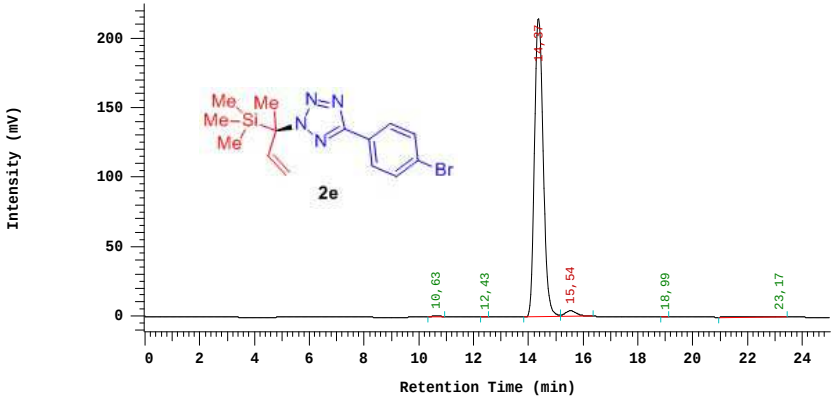
# D-7000 HPLC System Manager Report

Analyzed: 07.10.14 17:30
Reported: 08.04.15 11:08
Processed: 07.10.14 17:58

Data Path: D:\HSM\Alexander\DATA\0455\
Processing Method: 2*L-A2 Hep/Et 98/2 0,5ml 220nm

System(acquisition): Sys 2
Series:0455
Application: Alexander
Vial Number: 1
Sample Name: TiBu-185 ee
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 1,0 ul
Sample Description: Racemat

Chrom Type: HPLC Channel : 1




Acquisition Method: 2*L-A2 Hep/Et 98/2 0,5ml 220nm
Column Type: Chiralcel OD-H
Developed by: Alexander
Pump A Type: L-7100
Solvent A: n-Heptan
Solvent B: i-RrOH
Solvent C: Hept/IPA 100/1
Solvent D: Ethanol
Method Description: L-A2+L-A2, Hept/EtOH 98/2 0,5ml/min, 220 nm

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

| No. | RT | Area | Area % | BC |
|---|---|---|---|---|
| 1 | 10,63 | 9964 | 0,215 | BB |
| 2 | 12,43 | 1874 | 0,040 | BB |
| 3 | 14,37 | 4451400 | 96,165 | MC |
| 4 | 15,54 | 120947 | 2,613 | MC |
| 5 | 18,99 | 1861 | 0,040 | BB |
| 6 | 23,17 | 42862 | 0,926 | BB |
| | | 4628908 | 100,000 | |

Peak rejection level: 0





Channel 1 Noise: Not Measured
Channel 1 Drift: Not Measured

Configuration parameters:
Interface Module: D-7000
Gradient Mode: Low
Channel 1 Detector: L-7400
Channel 2 Detector: None
Column Oven: None
Autosampler: Manual
Pump A: L-7100
Pump B: None
Number of Solvents pump A: 4
Number of Solvents pump B: 1
External Instrument Software: None
Column Name: Chiralcel OD-H

Method Information:
Method Name: 2*L-A2 Hep/Et 98/2 0,5ml 220nm
Developed by: Alexander
Description:
L-A2+L-A2, Hept/EtOH 98/2 0,5ml/min, 220 nm

Method History

| Date | User | Comment |
|---|---|---|
| 14.06.13 11:21 | test | Method originated from ADH Hep/EtOH 10/90 0,5ml 280nm |
| 14.06.13 11:21 | test | |

Pump Setup:
Main Pump (A) Pressure Limit: 10 to 150 bar

Pump A (L-7100):
Solvent A: n-Heptan
Solvent B: i-RrOH
Solvent C: Hept/IPA 100/1
Solvent D: Ethanol

Pump A (L-7100):
Pump Solvent and Event Table

| Time (min) | %n-Hep | %i-RrO | %Hept/ | %Ethan | Flow (ml/min) | Event 1 | Event 2 | Event 3 | Event 4 |
|---|---|---|---|---|---|---|---|---|---|
| 0,0 | 98,0 | 0,0 | 0,0 | 2,0 | 0,500 | | | | |

Channel 1 Detector (L-7400):
Response Time: 2.0 sec
Absorbance Range: 1 AU
Offset: 0,000 AU
Stop Time: 60,00 min
Auto Data Sampling Mode: YES
Initial Sampling Period: 200 msec
Doubling Time: 10,00 min

Detector Table

| Time(min) | WL(nm) | Baseline |
|---|---|---|
| 0,0 | 220 | Auto Zero |

Sampling Period Table

| Time(min) | Period(msec) |
|---|---|
| 0,00 | 200 |
| 10,00 | 400 |
| 30,00 | 800 |
| 70,00 | 1600 |
| 150,00 | 3200 |

---

Method DP for channel 1

Calculation Method: Peak Quantitation: Area
  Calculation Method: AREA% Concentration data from method.
  Peak identification Window: % Time
  UNK peaks identification rule: Closest peak
  Update RT in component Table: YES Do blank subtraction: NO
  Do library search: NO

Component Table

| RT (min) | Window (%) | Func1 | Func2 | Func3 | E-Conc | Tolerance (%) |
|---|---|---|---|---|---|---|
| 0,01 | 10,00 | | | | | |

Integration Table

| Time (min) | Function | Value/Status |
|---|---|---|
| 0,00 | NOISE | 10 |
| 0,00 | SMOOTHING | OFF |
| 0,00 | SENSITIVITY | 20 |
| 0,00 | N-METHOD | 0 |

Perform system suitability test : NO
Perform module performance test : NO
Perform data diagnosis : NO

Chromatogram Display Format: Autoscale: YES
  Autoscale Time Range: 0,00 to 600,00 min
  Use alternate scale: NO Auto zero: NO
  Scale to Full Chrom Time Range: YES Peak rejection level: 0 uV * sec
  Baseline overlay: YES Peak start-end markers: YES
  Marker-In Signals: NO Peak labels: Time, None
  Show integration time table: NO Show sampling period time table: NO
  Show gradient curves: NO
  Report channel 1 labels in the chromatogram ovelay graph.
  Picture in picture: None

Report Format: Reported peaks: All Peaks
  Use primary layout: YES Use secondary layout: NO
  Print primary layout report: YES Print secondary layout report: NO
  Acquisition DDE: NO Acquisition macro name:
  Reprocess DDE: NO Reprocess macro name:
  Concentration 1 Unit: Other Concentration 1 name:
  Concentration 1 scale factor: 1,0000
  Concentration 1 divide by sample amount: NO
  Concentration 2 Unit: Other Concentration 2 name:
  Concentration 2 scale factor: 1,0000
  Concentration 2 use component multiplier: NO
  Injection report column 1 header: PK-NUM
  Injection report column 2 header: RT
  Injection report column 3 header: AREA
  Injection report column 4 header: AREA%
  Injection report column 5 header: BC





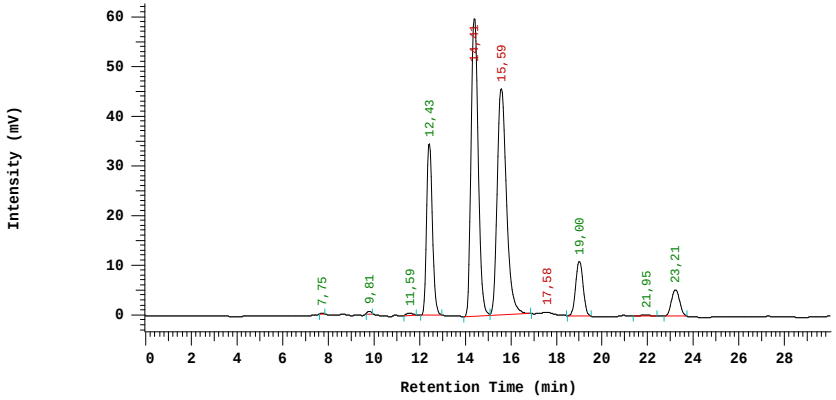
# D-7000 HPLC System Manager Report

Analyzed: 07.10.14 16:55 Reported: 08.04.15 11:08
Processed: 07.10.14 17:29

Data Path: D:\HSM\Alexander\DATA\0454\
Processing Method: 2*L-A2 Hep/Et 98/2 0,5ml 220nm

System(acquisition): Sys 2 Series:0454
Application: Alexander Vial Number: 1
Sample Name: TiBu-181 rac Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 1,0 ul
Sample Description: Racemat

Chrom Type: HPLC Channel : 1




Acquisition Method: 2*L-A2 Hep/Et 98/2 0,5ml 220nm
Column Type: Chiralcel OD-H Developed by: Alexander
Pump A Type: L-7100
  Solvent A: n-Heptan Solvent B: i-RrOH
  Solvent C: Hept/IPA 100/1 Solvent D: Ethanol
Method Description: L-A2+L-A2, Hept/EtOH 98/2 0,5ml/min, 220 nm

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

| No. | RT | Area | Area % | BC |
|---|---|---|---|---|
| 1 | 7,75 | 2033 | 0,061 | BB |
| 2 | 9,81 | 4873 | 0,147 | BB |
| 3 | 11,59 | 7568 | 0,228 | BB |
| 4 | 12,43 | 544682 | 16,431 | BB |
| 5 | 14,41 | 1198834 | 36,164 | MC |
| 6 | 15,59 | 1200553 | 36,216 | MC |
| 7 | 17,58 | 0 | 0,000 | |
| 8 | 19,00 | 226080 | 6,820 | BB |
| 9 | 21,95 | 6553 | 0,198 | BB |
| 10 | 23,21 | 123803 | 3,735 | BB |
| | | 3314979 | 100,000 | |

Peak rejection level: 0

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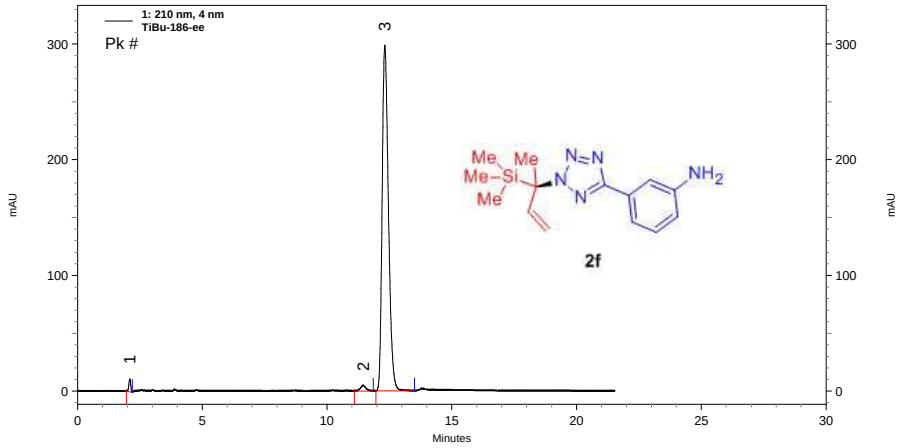
TiBu-186-ee {Data Description}

E:\EZDatenOC\Doktorand 1\Method\AD-3, Hept_EtOH, 95_5, 22°C, 1ml.met

Vial: 196 Injection Volume (µl): 2
Run Time: 17.10.2014 14:24:51 Analysis Time: 08.04.2015 10:38:34




**1: 210 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,093 | 1,066 | 204 |
| 2 | 11,447 | 1,324 | 229 |
| 3 | 12,313 | 97,610 | 229 |

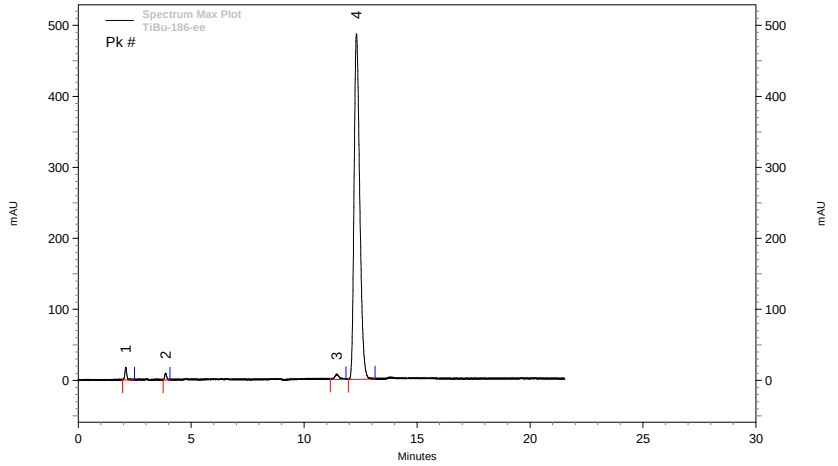
**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,107 | 1,217 | 204 |
| 2 | 3,867 | 0,664 | 202 |
| 3 | 11,447 | 1,001 | 229 |
| 4 | 12,313 | 97,118 | 229 |

**DAD-229 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 11,447 | 1,351 | 229 |
| 2 | 12,313 | 98,649 | 229 |





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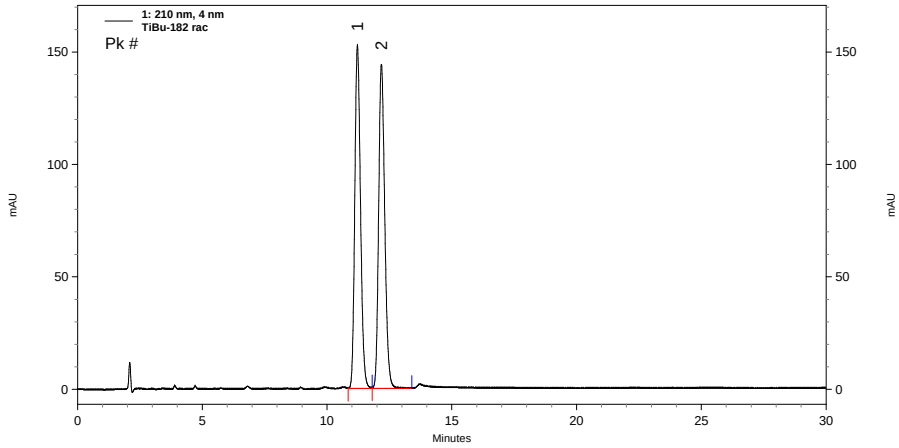
TiBu-182 rac {Data Description}

E:\EZDatenOC\Doktorand 1\Method\AD-3, Hept_EtOH, 95_5, 22°C, 1ml.met

Vial: 194 Injection Volume (µl): 2
Run Time: 17.10.2014 12:23:08 Analysis Time: 08.04.2015 10:38:02




**1: 210 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 11,220 | 49,787 | 229 |
| 2 | 12,180 | 50,213 | 229 |

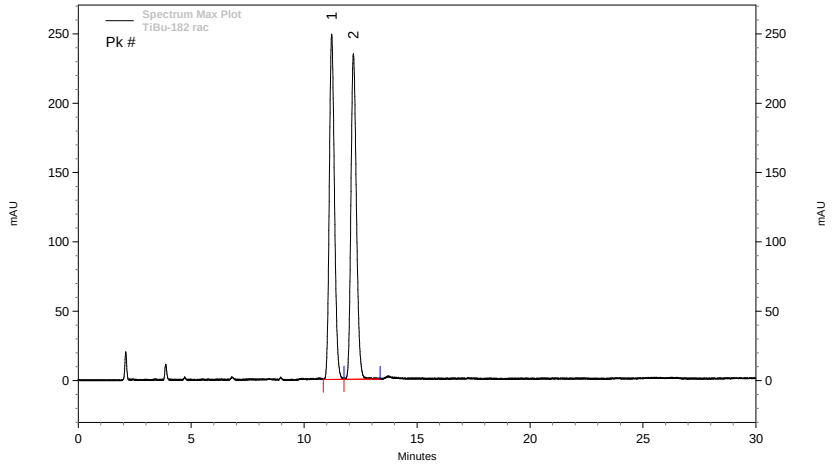
**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 11,220 | 49,864 | 229 |
| 2 | 12,180 | 50,136 | 229 |

**DAD-229 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 11,220 | 49,819 | 229 |
| 2 | 12,180 | 50,181 | 229 |





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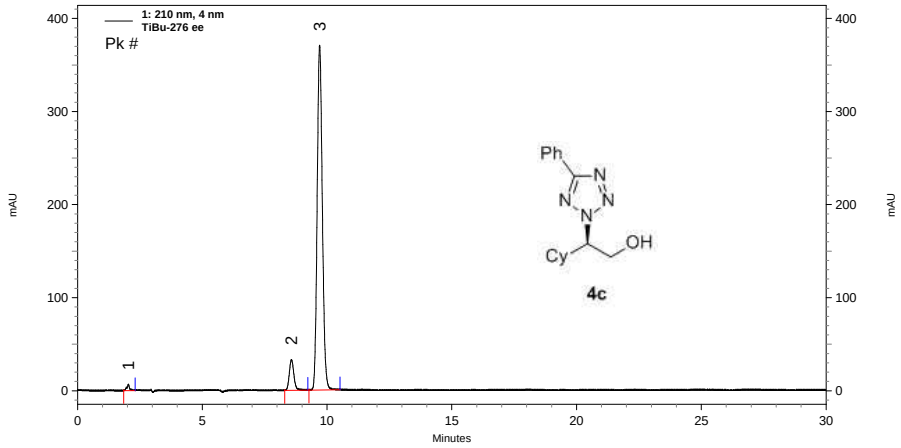
TiBu-276 ee {Data Description}

E:\EZDatenOC\Doktorand 1\Method\AD-3, Hept_IPA, 90_10, 22°C, 1ml.met

Vial: 195 Injection Volume (µl): 2
Run Time: 25.02.2015 12:30:11 Analysis Time: 08.04.2015 10:40:15




**1: 210 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,040 | 0,883 | 205 |
| **2** | 8,573 | 7,271 | 205 |
| **3** | 9,700 | 91,846 | 206 |

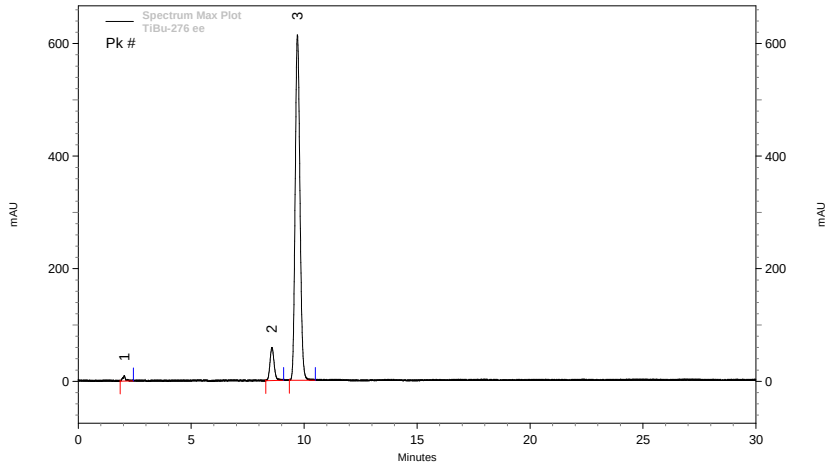
**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,040 | 0,791 | 205 |
| **2** | 8,573 | 7,556 | 205 |
| **3** | 9,700 | 91,653 | 206 |

**DAD-241 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 1,947 | 0,073 | 204 |
| **2** | 8,573 | 7,208 | 205 |
| **3** | 9,700 | 92,719 | 206 |





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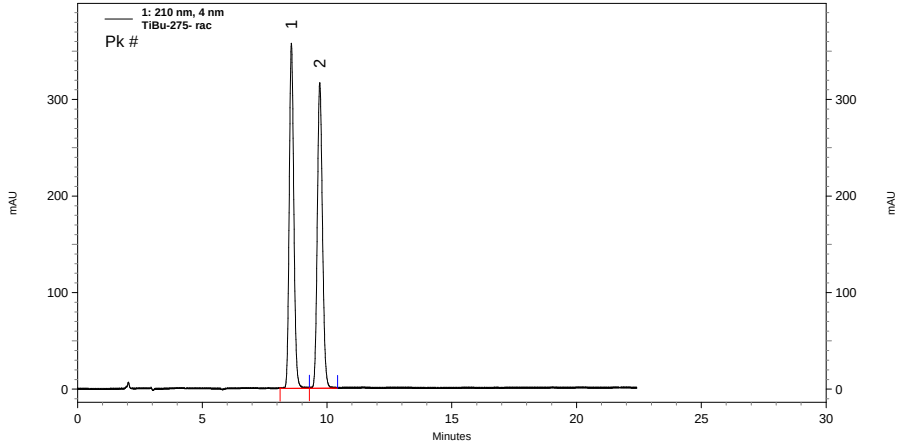
TiBu-275- rac {Data Description}

E:\EZDatenOC\Doktorand 1\Method\AD-3, Hept_IPA, 90_10, 22°C, 1ml.met

Vial: 192 Injection Volume (µl): 2
Run Time: 25.02.2015 10:57:23 Analysis Time: 08.04.2015 10:39:47




**1: 210 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 8,573 | 50,048 | 205 |
| 2 | 9,707 | 49,952 | 205 |

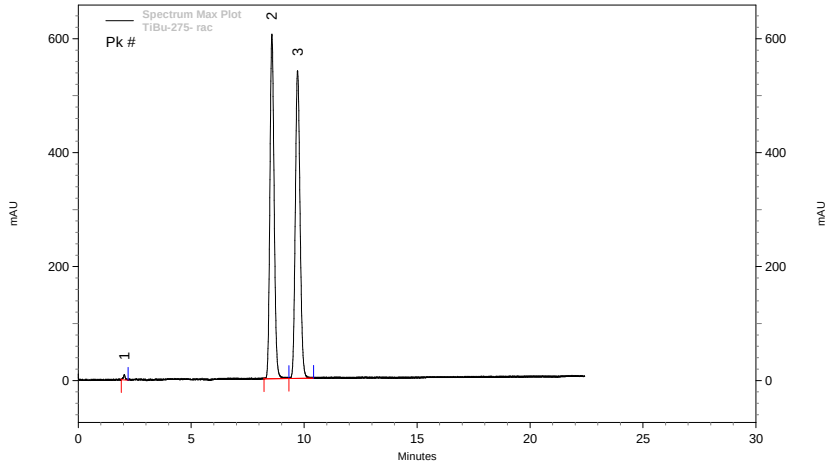
**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 2,040 | 0,341 | 205 |
| 2 | 8,573 | 49,726 | 205 |
| 3 | 9,707 | 49,933 | 205 |

**DAD-241 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| 1 | 8,573 | 50,050 | 205 |
| 2 | 9,707 | 49,950 | 205 |





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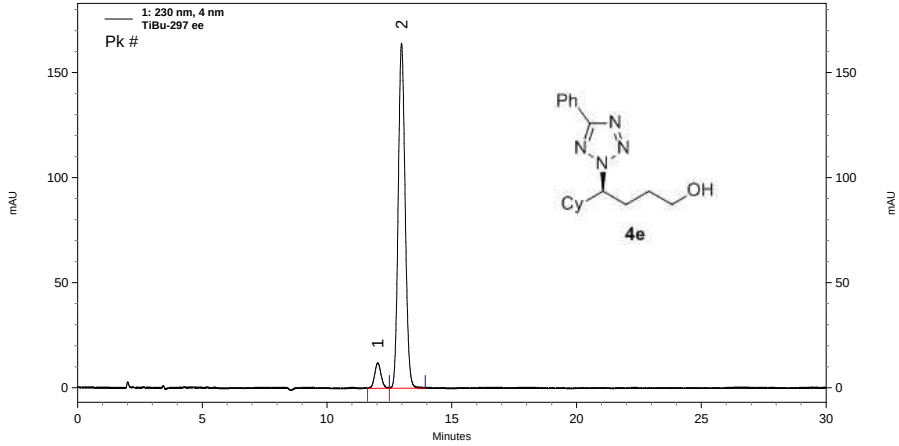
TiBu-297 ee {Data Description}

E:\EZDatenOC\Bury\Method\AD-3, Hept_IPA, 93_7, 22°C, 1ml.met

Vial: 192 Injection Volume (µl): 2
Run Time: 17.03.2015 11:03:27 Analysis Time: 08.04.2015 10:41:23




**1: 230 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 12,033 | 6,309 | 205 |
| **2** | 12,987 | 93,691 | 206 |

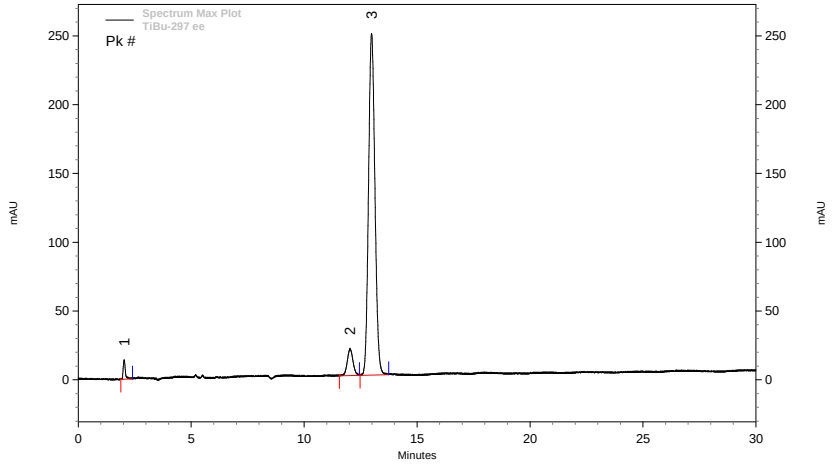
**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,033 | 1,718 | 206 |
| **2** | 12,033 | 6,318 | 205 |
| **3** | 12,987 | 91,965 | 206 |

**DAD-241 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,007 | 0,176 | 205 |
| **2** | 12,033 | 6,272 | 205 |
| **3** | 12,987 | 93,552 | 206 |





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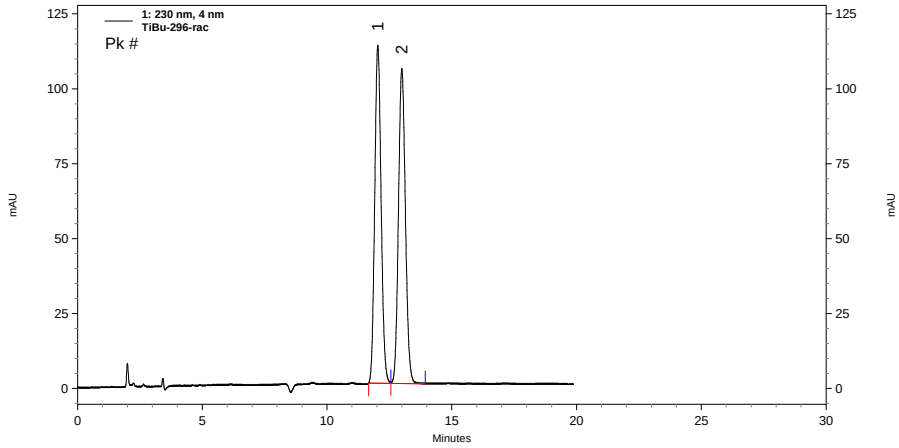
TiBu-296-rac {Data Description}

E:\EZDatenOC\Bury\Method\AD-3, Hept_IPA, 93_7, 22°C, 1ml.met

Vial: 191 Injection Volume (µl): 2
Run Time: 17.03.2015 10:40:04 Analysis Time: 08.04.2015 10:41:01




**1: 230 nm, 4 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 12,033 | 49,723 | 206 |
| **2** | 13,000 | 50,277 | 206 |

**Spectrum Max Plot Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 2,007 | 2,731 | 205 |
| **2** | 12,033 | 48,384 | 206 |
| **3** | 12,993 | 48,885 | 206 |

**DAD-241 nm Results**

| Pk # | Retention Time | Area Percent | Lambda Max |
|---|---|---|---|
| **1** | 12,033 | 49,812 | 206 |
| **2** | 13,000 | 50,188 | 206 |