Supplementary Material

Rhodium-Catalyzed Dynamic Kinetic Resolution of Racemic Internal Allenes Towards Chiral Allylated Triazoles and Tetrazoles

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General & Materials

All reactions were performed using Schlenk technique in flame dried glassware under argon (Argon 5.0, *Sauerstoffwerk Friedrichshafen).* Catalysis reactions were performed in 3-10 ml screw-capped tubes. Chemicals were purchased from commercial suppliers and used without further purification, unless mentioned. Solvents were purchased in p.a. grade and, if not stated otherwise, used without further purification. Solvents employed for work-up and column chromatography were purchased in technical grade quality and distilled by rotary evaporator before use.

Chromatography

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 (λ_{max} = 254 nm) and/or by staining with 1% w/v $KMnO_4$ in 0.5 M aqueous K_2CO_3.
Chiral HPLC was performed on a AGILENT TECHNOLOGIES 1290 INFINITY II apparatus (pump: G1311B-1260 Quat pump, detector: G7117A-1290 DAD FS, column oven: G7116B-1290 MCT; columns: *Chiralcel* OD-H, 250 mm x 4.6 mm x 5 µm; *Lux* Cellulose-1, 150 mm x 4.6 mm x 3 µm; *Lux* Cellulose-2, 150 mm x 4.6 mm x 3 µm; *Lux* Cellulose-3, 150 mm x 4.6 mm x 3 µm, *Lux* Cellulose-4, 150 mm x 4.6 mm x 3 µm, *Lux* Amylose-1, 150 mm x 4.6 mm x 3 µm; *Lux* Amylose-2, 150 mm x 4.6 mm x 3 µm; chiralPAK AD-3, 150 mm x 4.6 mm x 3 µm; *Chiralcel* OD-3, 150 mm x 4.6 mm x 3 µm).

Nuclear Magnetic Resonance

NMR (Nuclear Magnetic Resonance) spectra were acquired on a BRUKER AVANCE 400 spectrometer (400.13 MHz and 100.61 MHz for ^{1}H and ^{13}C respectively) and/or on a BRUKER AVANCE III HD 500 (500.32 MHz, 125.81 MHz and 376.76 MHz for ^{1}H, ^{13}C and ^{19}F respectively). All ^{1}H-NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signal at 7.26 ppm ($CHCl_3$), 7.16 ppm (C_6H_6), 2.50 ppm (DMSO) or 2.05 (acetone). All ^{13}C-NMR spectra are reported in ppm relative to residual $CHCl_3$ (77.16 ppm), C_6H_6 (128.06 ppm), DMSO (39.51 ppm) or acetone (206.68 ppm) and were obtained with ^{1}H-decoupling. Data for ^{1}H-NMR are described as following: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sx, sextet; sept, septet; m, multiplet; m_c, centered 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).

Mass Spectrometry

High-resolution mass spectra (HR-MS) were obtained on a THERMO SCIENTIFIC ADVANTAGE and a THERMO SCIENTIFIC EXACTIVE instrument (APCI/MeOH: spray voltage 4-5 kV, ion transfer tube: 250-300 °C, vaporizer: 300-400 °C).

Materials

Solvents: Toluene and THF were freshly distilled over Sodium/Benzophenone and degassed with argon prior to use. Solvents employed for work-up and column chromatography were purchased in technical grade quality and distilled by rotary evaporator before use.

Ligand and Rhodium catalyst: The ligands were purchased from Sigma-Aldrich, ABCR, Alfa Aesar and TAKASAGO and used without further purification. $[Rh(COD)Cl]_2$ was purchased from Sigma-Aldrich.

Specific Rotation

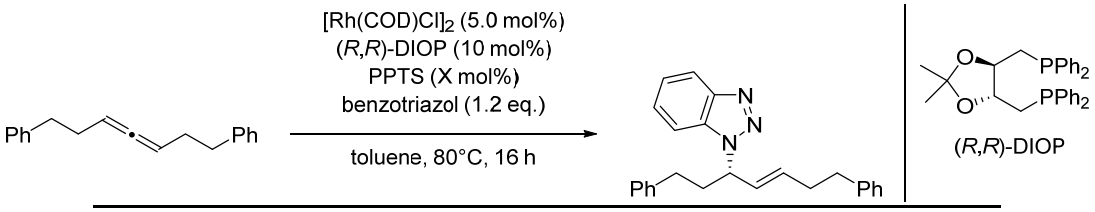
Angles of rotation of enantioenriched compounds were measured with a 241 Polarimeter from Perkin-Elmer Inc. The light source was a sodium vapor lamp, which emitted plan-polarized light at a wavelength of 589 nm. The specific rotation was calculated with the following equation,

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

where *T* is the temperature in °C, D is the sodium D-line emission, α is the angle of rotation, *c* is the concentration of the solution in g per 100 ml and *d* is the length of the polarimeter tube in dm (here 1 dm).

Screening Tables

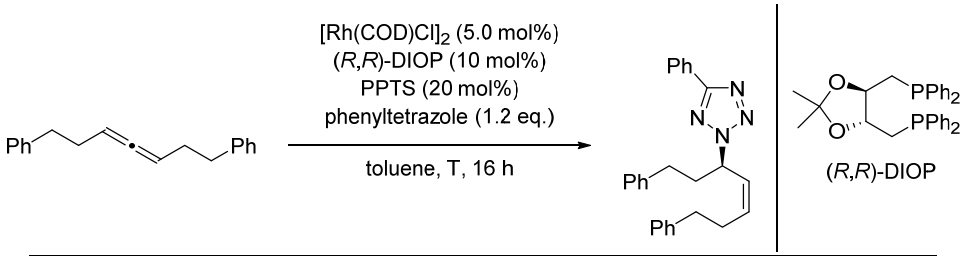
Table S1: Rhodium-catalyzed addition of triazoles to internal allenes.[a]



Entry	PPTS [%]	Yield [%][b]	N^1:N^2 [c]	*E*:*Z* [c]	*ee* [%][d]
1	20	90	93:7	79:21	*E*: 92, *Z*: 42
2	0	84	92:8	29:71	*E*: 54, *Z*: 70
3	50	71	92:8	92:8	*E*: 94, *Z*: *rac*
4	100	62	95:5	90:10	*E*: 94, *Z*: 10
5[e]	50	78	89:11	88:12	*E*: 89, *Z*: 18
6[f]	50	76	94:6	92:8	*E*: 95
7[f,g]	50	96	93:7	95:5	*E*: 96

[a] Reactions were performed on 0.25 mmol scales. Shown isomer is the N^1-isomer. [b] Yield of isolated product. [c] N^1:N^2- and *E*:*Z*-selectivites were determined by ^{1}H-NMR analysis of the crude reaction mixture. [d] The *ee* was determined by HPLC analysis using a chiral stationary phase. [e] Reaction was performed at 100 °C. [f] Reaction was performed at 60°C.[g] 2 eq. of benzotriazole were used.

Table S2: Rhodium-catalyzed addition of triazoles to internal allenes.[a]

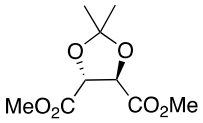


Entry	T [°C]	Yield [%][b]	*ee* [%][c]
1	80	96	83
2	60	91	85
3	40	93	85
4	rt	72[d]	79
5	100	76[e]	n.d.
6[f]	40	89	83
7[f,g]	40	92	83

[a] Reactions were performed on 0.25 mmol scales. Unless otherwise stated product was obtained in perfect *Z*- and N^2-selectivity. [b] Yield of isolated product. [c] The *ee* was determined by HPLC analysis using a chiral stationary phase. [d] ^{1}H-NMR analysis of the crude reaction mixture showed 73% conversion. [e] *E*:*Z*-selectivity of 54:46. [f] 2 eq. of phenyltetrazole were used. [g] 50 mol% of PPTS were used

Preparation of Ligand

(*R*,*R*)-diethyl 2,3-O-isopropylidentartrate



$C_9H_{14}O_6$
(218.21)

Prepared in analogy to a literature procedure.[1]

A solution of (*R*,*R*)-dimethyl tartrate (20.4 g, 115 mmol, 1.0 eq.), 2,2-dimethoxypropane (31.2 ml, 26.3 g, 253 mmol, 2.2 eq.) and (±)-10-camphorsulfonic acid (13.6 g, 57.5 mmol, 0.5 eq.) in acetone (140 ml) was stirred for 20 h at rt. The reaction was neutralized by addition of sat. aq. $NaHCO_3$ (50 ml). H_2O (50 ml) was added. The aq. layer was extracted with EtOAc (3 x 100 ml), the combined org. layers were dried over Na_2SO_4 and the solvent removed under vacuum. The crude product was distilled under vacuum (bp. 80 °C, 0.4 mbar) to give the acetal as colorless liquid (19.0 g, 77.2 mmol, 67 %).

^{1}H-NMR (400.13 MHz, $CDCl_3$):

δ = 1.49 (s, 6H), 3.82 (s, 6H), 4.80 (s, 2H).

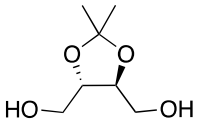
^{13}C-NMR (100.61 MHz, $CDCl_3$):

δ = 26.5, 52.9, 77.2, 114.0, 170.2.

HR-MS ($C_9H_{15}O_6$; $[M+H]^+$, pos. APCI): calcd: 219.0863, found: 219.0861.

The analytical data of the compound was in complete agreement with the literature.[1]

(*S*,*S*)-1,4-dihydroxy 2,3-O-isopropylidenbutane



$C_7H_{14}O_4$
(162.19)

Prepared in analogy to a literature procedure.[1]

A solution of (*R*,*R*)-diethyl 2,3-O-isopropylidentartrate (19.0 g, 77.2 mmol, 1.0 eq.) was added slowly to a suspension of $LiAlH_4$ (7.32 g, 193 mmol, 2.5 eq.) in THF (200 ml) at 0 °C. The reaction mixture was heated to reflux for 3 h, cooled to 0 °C, and quenched by addition of H_2O (15 ml) and 6 N NaOH (15 ml). The resulting suspension was filtered through a plug of silica gel, washed with Et_2O and dried over Na_2SO_4. The solvent was removed to give the diol as colorless liquid (9.03 g, 55.7 mmol, 72 %).

^{1}H-NMR (400.13 MHz, $CDCl_3$):

δ = 1.43 (s, 6H), 2.10 (s, 2H), 3.70 (ddd, *J* = 11.8, 2.4, 1.3 Hz, 2H), 3.81 (ddd, *J* = 11.8, 2.5, 1.4 Hz, 2H), 4.00-4.02 (m, 2H).

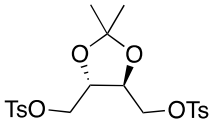
^{13}C-NMR (100.61 MHz, $CDCl_3$):

δ = 27.2, 62.2, 78.1, 109.4.

HR-MS ($C_7H_{15}O_4$; $[M+H]^+$, pos. APCI): calcd: 163.0965, found: 163.0966.

The analytical data of the compound was in complete agreement with the literature.[1]

(*S*,*S*)-1,4-ditosyl 2,3-O-isopropylidenbutane



$C_{21}H_{26}O_8S_2$
(470.55)

Prepared in analogy to a literature procedure.[2]

Tosyl chloride (32.8 g, 172 mmol, 3.1 eq.) was added to a solution of (*S*,*S*)-1,4-dihydroxy 2,3-O-isopropylidenbutane (9.03 g, 55.7 mmol, 1.0 eq.) in pyridine (70 ml) at -20 °C. The mixture was allowed to warm to rt and stirred for 20 h. H_2O (600 ml) was added and the mixture was cooled to 0 °C for several hours. The resulting precipitate was filtered off, washed with H_2O and EtOH and dried under vacuum. The ditosylate was obtained as colorless solid (15.1 g, 32.1 mmol, 58 %).

^{1}H-NMR (500.10 MHz, $CDCl_3$):

δ = 1.30 (s, 6H), 2.46 (s, 6H), 3.98-4.02 (m, 2H), 4.06-4.12 (m, 4H), 7.34-7.38 (m, 4H), 7.76-7.81 (m, 4H).

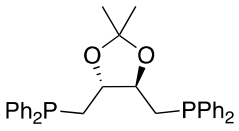
^{13}C-NMR (125.75 MHz, $CDCl_3$):

δ = 21.8, 26.9, 68.6, 75.2, 111.0, 128.2, 130.1, 132.6, 145.4.

HR-MS ($C_{21}H_{27}O_8S_2$; $[M+H]^+$, pos. APCI): calcd: 471.1142, found: 471.1140.

The analytical data of the compound was in complete agreement with the literature.[2]

(*R*,*R*)-DIOP



$C_{31}H_{32}O_2P_2$
(498.54)

Prepared in analogy to a literature procedure.[3]

n-BuLi (2.5 m, 26.9 ml, 67.1 mmol, 3.0 eq.) was added dropwise to a solution of diphenylphosphine (10.0 g, 53.7 mmol, 2.4 eq.) in abs THF (72 ml) at -78 °C. The reaction mixture was allowed to warm to rt and stirred for 2 h during which the color changed from yellow over orange to dark red. A solution of (*S*,*S*)-1,4-ditosyl 2,3-O-isopropylidenbutane (10.5 g, 22.4 mmol, 1.0 eq.) in abs. THF (70 ml) was added dropwise and the mixture stirred at rt for 16 h before it was quenched by addition of degassed MeOH (1.5 ml). The solvent was removed under reduced pressure and a degassed *n*-pentane/DCM mixture (1:1 150 ml) and degassed H_2O (50 ml) were added, the aq. layer was extracted with a degassed *n*-pentane/DCM mixture (1:1 3x 50 ml), the combined org. layers were dried over Na_2SO_4 and the solvent removed under vacuum. After recrystallization from EtOH the ligand was obtained as colorless solid (8.97 g, 18.0 mmol, 80 %).

^{1}H-NMR (400.13 MHz, $CDCl_3$):

δ = 1.35 (s, 6H), 2.31-2.45 (m, 4H), 3.92 (m_c, 2H), 7.29-7.34 (m, 12H), 7.37-7.47 (m, 8H).

^{13}C-NMR (100.61 MHz, $CDCl_3$):

δ = 27.4, 32.5 (dd, *J* = 15.7, 3.4 Hz), 79.8 (m_c), 109.6, 128.5, 128.6, 128.6, 128.7, 128.9, 133.0 (dd, *J* = 34.3, 19.4 Hz), 138.6 (dd, *J* = 28.7, 13.0 Hz).

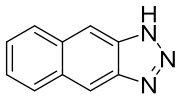
HR-MS ($C_{31}H_{32}O_2P_2$; $[M+H]^+$, pos. APCI): calcd: 498.1878, found: 498.1880.

The analytical data of the compound was in complete agreement with the literature.[4]

Preparation of Substrates

Synthesis and characterization of triazoles

1*H*-naphtho[2,3-d][1,2,3]triazole



$C_{10}H_7N_3$
(169.06)

Naphthalene-2,3-diamine (500 mg, 3.16 mmol, 1.0 eq.) was suspended in AcOH (0.36 mL, 380 mg, 6.50 mmol, 2.0 eq.) and H_2O (14 mL). After cooling to 0 °C a solution of $NaNO_2$ (240 mg, 3.48 mmol, 1.10 eq.) in H_2O (7 mL) was added. The heterogeneous reaction mixture was allowed to warm to rt and stirred overnight. After adding excess saturated aqueous sodium bicarbonate solution it was then extracted with DCM (3 × 50 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by recrystallization in hexanes/toluene to yield the product as a burgundy red solid (342 mg, 2.02 mmol, 64 %).

^{1}H-NMR (400.13 MHz, DMSO-d_6, 343K):

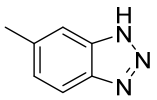
δ = 7.46-7.53 (m, 2H), 8.10-8.16 (m, 2H), 8.52 (br s, 2H), 15.80 (br s, 1H).

^{13}C-NMR (100.61 MHz, DMSO-d_6, 343K):

δ = 124.8 (br s), 128.2 (br s), 131.0 (br s).

HR-MS ($C_{10}H_8N_3$; $[M+H]^+$, pos. ESI): calcd: 170.0713, found: 170.0712.

6-methyl-1*H*-benzo[d][1,2,3]triazole



$C_7H_7N_3$
(133.06)

4-methylbenzene-1,2-diamine (1.00 g, 7.52 mmol, 1.0 eq.) was suspended in AcOH (0.93 mL, 901 mg, 15.0 mmol, 2.0 eq.) and H_2O (32 mL). After cooling to 0 °C a solution of $NaNO_2$ (254 mg, 7.86 mmol, 1.10 eq.) in H_2O (16 mL) was added. The heterogeneous reaction mixture was allowed to warm to rt and stirred overnight. After adding excess saturated sodium bicarbonate solution, it was then extracted with DCM (3 × 50 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 3:1) to give the title product as a brownish solid (914 mg, 6.87 mmol, 91%).

TLC (SiO_2): R_f (hexanes:AcOEt = 1:1) = 0.45.

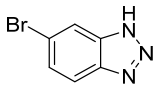
^{1}H-NMR (499.98 MHz, $CDCl_3$):

δ = 2.51 (s, 3H), 7.24 (br s, 1H), 7.63 (br s, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 14.00 (br s, 1H).

Despite a large number of scans, no 13C NMR signal was visible.

HR-MS ($C_7H_8N_3$; $[M+H]^+$, pos. ESI): calcd: 134.0713, found: 134.0713.

6-bromo-1*H*-benzo[d][1,2,3]triazole



$C_6H_4BrN_3$
(196.96)

4-bromobenzene-1,2-diamine (650 mg, 3.49 mmol, 1.0 eq.) was suspended in AcOH (0.40 mL, 387 mg, 6.45 mmol, 1.84 eq.) and H_2O (14 mL). After cooling to 0 °C a solution of $NaNO_2$ (265 mg, 3.84 mmol, 1.10 eq.) in H_2O (7 mL) was added. The heterogeneous reaction mixture was allowed to warm to rt and stirred overnight. After adding excess saturated sodium bicarbonate solution it was then extracted with DCM (3 × 50 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 3:1) to give the title product as a brownish solid (493 mg, 2.51 mmol, 72%).

TLC (SiO_2): R_f (hexanes:AcOEt = 1:1) = 0.47.

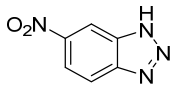
^{1}H-NMR (499.98 MHz, DMSO-d_6):

δ = 7.57 (d, *J* = 8.6 Hz, 1H), 7.90 (br s, 1H), 8.19 (br s, 1H), 15.89 (s, 1H).

Despite a large number of scans, no 13C NMR signal was visible.

HR-MS ($C_6H_5BrN_3$; $[M+H]^+$, pos. ESI): calcd:197.9661, found: 197.9662.

6-nitro-1*H*-benzo[*d*][1,2,3]triazole



$C_6H_4N_4O_2$
(164.03)

4-nitrobenzene-1,2-diamine (1.00 g, 6.53 mmol, 1.00 eq.) was suspended in AcOH (0.74 mL, 784 mg, 13.1 mmol, 2.00 eq.) and H_2O (32 mL). After cooling to 0 °C a solution of $NaNO_2$ (491 mg, 7.01 mmol, 1.10 eq.) in H_2O (16 mL) was added. The heterogeneous reaction mixture was allowed to warm to rt and stirred overnight. After adding excess saturated sodium bicarbonate-solution it was then extracted with DCM (3 × 50 mL) and the combined organic phases were dried over mgSO_4. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 3:1) to give the title product as a brownish solid (238 mg, 1.45 mmol, 22%).

^{1}H-NMR (400.13 MHz, DMSO-d_6):

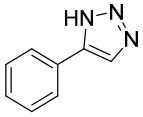
δ = 8.08 (d, *J* = 9.1 Hz, 1H), 8.29 (dd, *J* = 9.1, 2.1 Hz, 1H), 8.94 (d, *J* = 2.1 Hz, 1H).

^{13}C-NMR (100.61 MHz, DMSO-d_6):

δ = 114.1, 114.4, 120.8, 139.0, 140.5, 144.6.

HR-MS ($C_6H_3O_2N_4$; $[M-H]^-$, neg. ESI): calcd: 163.0261, found: 163.0261.

5-phenyl-1*H*-1,2,3-triazole



$C_8H_7N_3$
(145.06)

Ethynylbenzene (2.00 mL, 1.86 g, 18.2 mmol, 1.00 eq.), azidotrimethylsilane (3.83 mL, 3.15 g, 27.3 mmol, 1.50 eq.) and CuI (0.17 g, 0.91 mmol, 0.05 eq.) were dissolved in DMF/MeOH (9:1, 14 mL). The reaction mixture was stirred at 100 °C for 12 h. The mixture was cooled to room temperature, filtered through a short Florisil pad and concentrated. The residue was purified by flash column chromatography (SiO_2, hexanes/EtOAc, 3:1) to afford the desired product (1.31 g, 9.02 mmol, 50 %).

TLC (SiO_2): R_f (hexanes:AcOEt = 1:1) = 0.55.

^{1}H-NMR (499.98 MHz, DMSO-d_6):

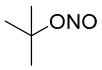
δ = 7.32-7.38 (m, 1H), 7.43-7.48 (m, 2H), 7.83-7.89 (m, 2H), 8.32 (br s, 1H), 15.06 (br s, 1H).

^{13}C-NMR (125.72 MHz, DMSO-d_6):

δ = 125.5, 128.1, 128.9, 130.6, 145.9.

HR-MS ($C_8H_8N_3$; $[M+H]^+$, pos. ESI): calcd: 146.0713, found: 146.0713.

tert-butyl nitrite



$C_4H_9NO_2$
(103.06)

Tert-butyl alcohol (74.0 g, 1.00 mmol, 1.00 eq.) and sodium nitrite (76.0 g, 1.10 mmol, 1.10 eq.) were dissolved in H_2O (440 mL) and cooled to 0 °C. Concentrated hydrochloric acid (90 mL) was added so that the solution temperature did not rise above 5 °C. The organic phase was washed with H_2O (400 ml), 5% sodium bicarbonate (3x) and with more H_2O (3x), then dried over calcium chloride and distilled (ϑ_b = 62 - 64 °C) to yield the desired product (31.6 g, 31 mmol, 31 %) as a colorless liquid.

Boiling point: ϑ_{bp} = 62 - 64 °C.

^{1}H NMR (400.13 MHz, $CDCl_3$):

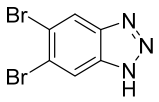
δ = 1.59 (s, 9H).

^{13}C NMR (100.61 MHz, $CDCl_3$)

δ = 29.2, 82.7.

HR-MS ($C_4H_{10}NO_2$; $[M+H]^+$, pos. ESI): calcd: 104.0706, found: 104.0706.

5,6-dibromo-1*H*-benzo[d][1,2,3]triazole



$C_6H_3Br_2N_3$
(274.87)

4,5-dibromobenzene-1,2-diamine (500 mg, 1.89 mmol, 1.00 eq.) was dissolved in acetonitrile (25 mL) to which tert-butyl nitrite (390 mg, 7.78 mmol, 2.00 eq.) was added at room temperature. After 2 h acetonitrile was evaporated, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, concentrated and recrystallized from hexanes/toluene/chloroform to yield the desired product (383.2 mg, 1.39 mmol, 74 %) as a brownish solid.

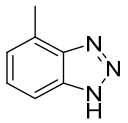
^{1}H NMR (400.13 MHz, acetone-d_6/DMSO-d_6 - 7:1)

δ = 8.35 (s,2H).

Despite a large number of scans, no 13C NMR signal was visible.

HR-MS ($C_6H_2{}^{79}Br^{81}BrN_3$; $[M+H]^+$, neg. ESI): calcd: 275.8600, found: 275.8600.

4-methyl-1H-benzo[d][1,2,3]triazole



$C_7H_7N_3$
(133.06)

3-methylbenzene-1,2-diamine (500 mg, 4.10 mmol, 1.0 eq.) was suspended in AcOH (0.37 mL, 392 mg, 6.01 mmol, 2.00 eq.) and H_2O (16 mL). After cooling to 0 °C a solution of $NaNO_2$ (246 mg, 3.51 mmol, 1.10 eq.) in H_2O (8 mL) was added. The heterogeneous reaction mixture was allowed to warm to rt and stirred overnight. After adding excess saturated sodium bicarbonate-solution it was then extracted with DCM (3 × 50 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by recrystallization from hexanes/$CHCl_3$ to yield the title product (416 mg, 3.13 mmol, 76%). as a brownish solid.

^{1}H NMR (400.13 MHz, $CDCl_3$):

δ = 2.76 (s, 3H), 7.18 (d, *J* = 7.1 Hz, 1H), 7.33 (dd, *J* = 8.3, 7.1 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 1H) 11.32 (br s, 1H).

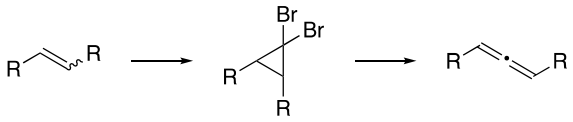
^{13}C NMR (100.61 MHz, $CDCl_3$):

δ = 17.4, 111.5, 125.7, 126.7, 137.8, 140.4.

HR-MS ($C_7H_8N_3$; $[M+H]^+$, pos. APCI): calcd: 134.0713, found: 134.0712.

Synthesis and characterization of triazoles

General Procedure A

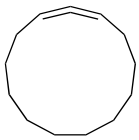


Reagents and conditions: *a) $CHBr_3$, TEBA, KOH EtOH/H_2O, 16 h, 0 °C, then RT; b) MeLi, Et_2O, -78 °C then RT, 1 h.*

Alkene (20.0 mmol, 1.0 equiv.), bromoform (5.20 mL, 15.0 g, 60 mmol, 3.0 equiv.), benzyltriethylammonium chloride (TEBA, 145 mg, 0.637 mmol, 3 mol%) and EtOH (1 mL) were added to the flask. The solution was cooled to 0 °C and the flask was wrapped in aluminum foil. A solution of KOH in H_2O (50 %, 10 mL) was added dropwise. The reaction mixture was warmed to RT and was stirred overnight. Water (20 mL) was added and the layers were separated. The aqueous layer was extracted with DCM (2 × 20 mL). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure. The product was used without further purification.

Dibromide (20 mmol, 1.0 equiv) was dissolved in Et_2O (abs., 20 mL). The solution was cooled to -78 °C and MeLi (1.0 M in Et_2O, 24 mL, 24 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was stirred for 20 min at -78 °C, was warmed to RT and was stirred for 1 h. The solution was cooled to 0 °C and water (20 mL) was added. The layers were separated and the organic layer was washed with concentrated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) and was then dried over Na_2SO_4. The solvent was removed and the crude product was purified by flash column chromatography.

cyclotrideca-1,2-diene



$C_{13}H_{22}$
(178.32)

The reaction was performed according to **general procedure A** with cyclododecene (3.85 mL, 3.33 g). The crude product was purified by flash column chromatography (SiO_2, hexanes) to afford the desired product as colorless oil (3.53 g, 19.8 mmol, 99 %).

TLC (SiO_2): R_f = 0.9 (hexanes).

^{1}H-NMR (400.13 MHz, $CDCl_3$):

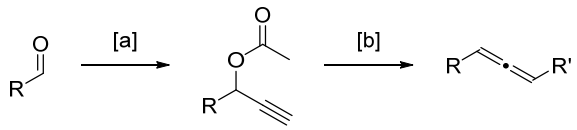
δ = 1.28-1.58 (m, 16H), 1.97-2.10 (m, 4H), 5.09 (m_c, 2H).

^{13}C-NMR (100.61 MHz, $CDCl_3$):

δ = 26.7, 26.9, 27.3, 27.3, 27.6, 91.5, 204.5.

HR-MS ($C_{13}H_{23}$; $[M+H]^+$, pos. APCI): calcd: 179.1794, found: 179.1747.

General procedure B for allene synthesis



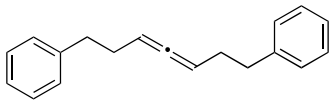
Reagents and conditions: a) HCCMgBr, AcCl, THF, 1 h, 0 °C, then rt; b) R'MgBr, CuBr, THF, 0 °C then rt, 2h.

Ethynylmagnesium bromide solution (0.5 M in THF, 33 ml, 16.5 mmol, 1.1 equiv.) was cooled to 0 °C. Aldehyde (15.0 mmol, 1.0 equiv.) was added dropwise. The solution was stirred for 1 h at RT and cooled to 0 °C again. Acetyl chloride (1.18 ml, 1.30 g, 16.5 mmol,1.1 equiv.) was added dropwise. The solution then was warmed to RT and stirred up to 1 h. The reaction was quenched with H_2O (50 ml) and the aqueous phase was extracted with Et_2O (3 × 50 ml). The combined organic phases were dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting crude product was purified by flash column chromatography (SiO_2, hexanes:Et_2O = 5:1) to afford the desired acetate.

Mg (437 mg ,18.0 mmol, 1.2 equiv.) and THF (30 mL) were added to the flask. Bromide (15.0 mmol, 1.0 equiv.) was added dropwise. The mixture was refluxed for 30 min and then cooled to RT.

CuBr (215 mg, 1.50 mmol, 10 mol%), THF (20 mL) and acetate (15.0 mmol, 1.0 equiv.) were added to a new flask. The suspension was cooled to 0 °C. Then the freshly prepared Grignard reagent was added slowly to this suspension and the mixture was stirred for 5 min at 0 °C. The reaction mixture was allowed to warm to RT and was stirred for 2 h at RT. NH_4Cl_{aq} (sat., 50 mL) was added to the reaction mixture. The organic layer was washed with brine (30 mL) and was dried over Na_2SO_4. The solvent was removed and the crude product was purified by flash column chromatography (SiO_2, hexanes) to obtain the internal allene.

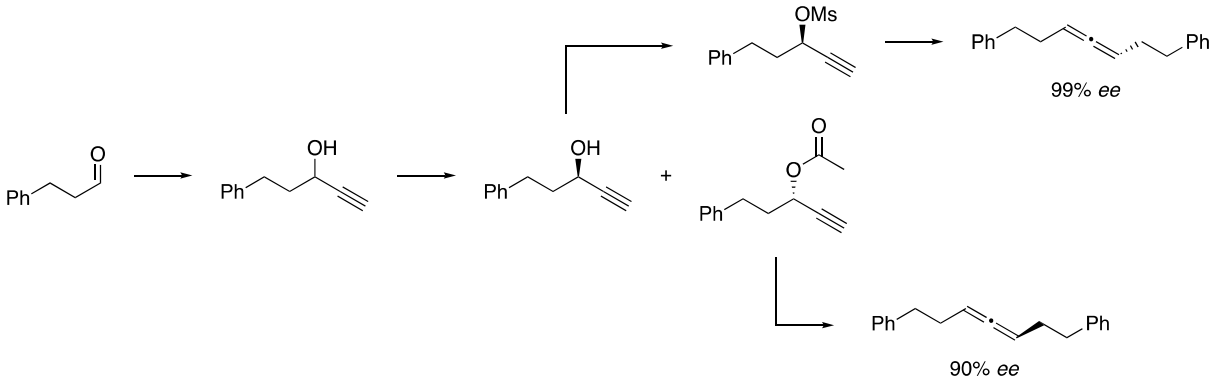
1,7-diphenylhepta-3,4-diene (1)



$C_{19}H_{20}$
(248.37)

3-Phenylpropanal (4.30 mL, 4.30 g, 32.0 mmol, 1.0 equiv.) was added dropwise to an ethynylmagnesium bromide solution (0.5 M in THF, 76.0 mL, 38.0 mmol, 1.2 equiv.) at 0 °C. The reaction mixture was warmed to RT and was stirred for 2 h. After complete conversion the solution was again cooled to 0 °C and acetyl chloride (2.70 mL, 3.00 g, 38.0 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was warmed to RT and was stirred for 2 h. After complete conversion the solution was cooled to 0 °C and water (40 mL) was added. The aqueous layer was extracted with Et_2O (2 × 20 mL) and the combined organic layers were washed with brine (2 × 20 mL) and dried over Na_2SO_4. The solvent was removed and the crude 5-phenylpent-1-yn-3-yl acetate was obtained as yellowish liquid (6.4 g, quant.). The product was used without further purification.

Mg (437 mg, 18.0 mmol, 1.2 equiv.) and THF (30 mL) were added to the flask. (2-Bromoethyl)benzene (2.05 mL, 2.78 g, 15.0 mmol, 1.0 equiv.) was added dropwise. The mixture was refluxed for 30 min and then cooled to RT.
CuBr (215 mg, 1.50 mmol, 10 mol%), THF (20 mL) and 5-phenylpent-1-yn-3-yl acetate (3.03 g, 15.0 mmol, 1.0 equiv.) were added to a new flask. The suspension was cooled to 0 °C. Then the freshly prepared Grignard reagent was added slowly to this suspension and the mixture was stirred for 5 min at 0 °C. The reaction mixture was allowed to warm to RT and was stirred for 2 h at RT. NH_4Cl_{aq} (sat., 50 mL) was added to the reaction mixture. The organic layer was washed with brine (30 mL) and was dried over Na_2SO_4. The solvent was removed and the crude product was purified by flash column chromatography (SiO_2, hexanes) to obtain 1,7-diphenylhepta-3,4-diene as colorless liquid (1.64 g, 6.6 mmol, 44% over 2 steps).



3-Phenylpropanal (4.30 mL, 4.30 g, 32.0 mmol, 1.0 equiv.) was added dropwise to ethynylmagnesium bromide (0.5 M in THF, 76.0 mL, 38.0 mmol, 1.2 equiv.) at 0 °C. The reaction mixture was warmed to RT and was stirred for 2 h. After complete conversion water (40 mL) was added. The aqueous layer was extracted with Et_2O (2 × 20 mL) and the combined organic layers were washed with brine (2 × 20 mL) and dried over Na_2SO_4. The solvent was removed and the crude 5-phenylpent-1-yn-3-ol was obtained as yellowish liquid (5.13 g, quant.). The product was used without further purification.

5-Phenylpent-1-yn-3-ol (6.60 g, 50.0 mmol, 1.0 equiv.), Candida Antarctica Lipase (Novozyme 435) resin, vinyl acetate (4.60 mL, 4.30 g, 50.0 mmol, 110 equiv.) and toluene (300 mL) were added to the flask. The reaction mixture was stirred for 16 h at RT. Then the conversion was checked by ^{1}H-NMR (50 % conversion). The mixture was filtered through a plug of celite. The solvent was removed under reduced pressure. The ester and the remaining alcohol were separated by column chromatography (SiO_2, hexanes:Et_2O = 5:1) to afford the pure products (alcohol: R_f = 0.10 (hexanes:Et_2O = 5:1), ester: R_f = 0.20 (hexanes:Et_2O = 5:1).[4]

The received enantiomerically enriched (*S*)-5-phenylpent-1-yn-3-yl acetate was submitted to the reaction conditions as stated above to afford enantiomerically enriched *(R)*-1,7-diphenylhepta-3,4-diene.

Remaining enantiomerically enriched *(R)*-5-phenylpent-1-yn-3-ol (2.56 g, 19.4 mmol, 1.0 equiv.) was dissolved in DCM (10.0 mL). The solution was cooled to 0 °C and triethylamin (2.95 mL, 2.16 g, 21.3 mmol, 1.1 equiv.) was added. Then MsCl (1.65 mL, 2.44 g, 21.3 mmol, 1.1 equiv.) was added dropwise at 0 °C. The reaction mixture was stirred for 10 min at 0 °C and was then allowed to warm to RT and was stirred for 3.5 h. After complete conversion the solution was cooled to 0 °C and water (40 mL) was added. The aqueous layer was extracted with Et_2O (2 × 20 mL) and the combined organic layers were washed with brine (2 × 20 mL) and dried over Na_2SO_4. The solvent was removed to afford *(R)*-5-phenylpent-1-yn-3-yl methanesulfonate.

The received enantiomerically enriched *(R)*-5-phenylpent-1-yn-3-yl methanesulfonate was submitted to the reaction conditions as stated above to afford enantiomerically enriched *(S)*-1,7-diphenylhepta-3,4-diene.

Analytical Data of **1**:

TLC (SiO_2): R_f = 0.20 (hexanes).

^{1}H-NMR (400.13 MHz, $CDCl_3$):

δ = 2.31-2.24 (m, 4H), 2.67 (t, *J* = 7.7 Hz, 4H), 5.14 (m_c, 2H), 7.15-7.22 (m, 6H), 7.27-7.30 (m, 4H).

^{13}C-NMR (100.61 MHz, $CDCl_3$):

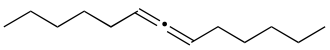
δ = 30.8, 35.5, 91.0, 126.0, 128.4, 128.7, 142.0, 204.3.

HR-MS ($C_{19}H_{24}N$; $[M+NH_4]^+$, pos. APCI): calcd: 266.1903, found: 266.1903.

$[\alpha]_D^{25}$ 63.2° (c = 1.1, CH_2Cl_2).

HPLC (Lux C-4, λ = 212 nm, *n*-heptane, 0.5 mL/min, 22 °C): t_R = 11.5 min (major peak), 12.8 min (minor peak); 99 % *ee*.

trideca-6,7-diene



$C_{13}H_{24}$
(180.34)

The reaction was performed according to **general procedure B**. The crude product was purified by flash column chromatography (SiO_2, hexanes) to afford the desired product as yellow oil (2.39 g, 13.3 mmol, 53 % over 2 steps).

TLC (SiO_2): R_f = 0.9 (hexanes).

^{1}H-NMR (400.13 MHz, $CDCl_3$):

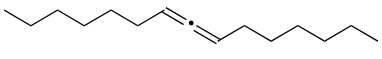
δ = 0.89 (t, *J* = 7.0 Hz, 6H), 1.30-1.32 (m, 8H), 1.38-1.42 (m, 4H), 1.95-2.00 (m, 4H), 5.06 (m_c, 2H).

^{13}C-NMR (100.61 MHz, $CDCl_3$):

δ = 14.2, 14.3, 22.7, 22.9, 29.1, 29.2, 29.5, 29.8, 31.5, 32.1, 91.1, 204.0.

HR-MS ($C_{25}H_{49}$; $[M+H]^+$, pos. ESI): calcd: 180.3350, found: 180.3356.

pentadeca-7,8-diene



$C_{15}H_{28}$
(208.39)

The reaction was performed according to **general procedure B**. The crude product was purified by flash column chromatography (SiO_2, hexanes) to afford the desired product as colorless oil (1.16 g, 5.56 mmol, 37 % over 2 steps).

TLC (SiO_2): R_f = 0.88 (hexanes).

^{1}H-NMR (400.13 MHz, $CDCl_3$):

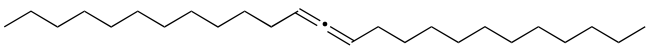
δ = 0.89 (t, *J* = 7.0 Hz, 6H), 1.24-1.35 (m, 12H), 1.36-1.44 (m, 4H), 1.95-2.00 (m, 4H), 5.04-5.08 (m, 2H).

^{13}C-NMR (100.61 MHz, $CDCl_3$):

δ = 14.2, 22.8, 29.0, 29.2, 29.4, 31.9, 91.1, 204.0.

HR-MS ($C_{15}H_{32}N$; $[M+NH_4]^+$, pos. ESI): calcd: 226.2529, found: 226.2529.

pentacosa-12,13-diene



$C_{25}H_{48}$
(348.66)

The reaction was performed according to **general procedure B**. The crude product was purified by flash column chromatography (SiO_2, hexanes) to afford the desired product as colorless oil (1.24 g, 3.54 mmol, 24 % over 2 steps).

TLC (SiO_2): R_f = 0.9 (hexanes).

^{1}H-NMR (400.13 MHz, $CDCl_3$):

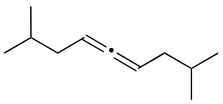
δ = 0.88 (t, *J* = 6.9 Hz, 6H), 1.26-1.31 (m, 36H), 1.95-2.00 (m, 4H), 5.06 (m_c, 2H).

^{13}C-NMR (100.61 MHz, $CDCl_3$):

δ = 14.3, 22.9, 29.2, 29.3, 29.4, 29.5, 29.7, 29.8, 29.9, 32.1, 91.1, 204.0.

HR-MS ($C_{25}H_{49}$; $[M+H]^+$, pos. ESI): calcd: 348.3756, found: 348.3753.

2,8-dimethylnona-4,5-diene



$C_{11}H_{20}$
(152.28)

The reaction was performed according to **general procedure B**. The crude product was purified by flash column chromatography (SiO_2, hexanes) to afford the desired product as colorless oil (1.36 g, 8.93 mmol, 47 % over 2 steps).

TLC (SiO_2): R_f = 0.9 (hexanes).

^{1}H-NMR (400.13 MHz, $CDCl_3$):

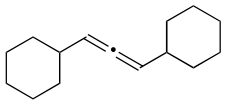
δ = 0.92 (d, *J* = 6.6 Hz, 12H), 1.65 (tsept, *J* = 6.7, 6.7 Hz, 2H), 1.85-1.91 (m, 4H), 5.00 (m_c, 2H).

^{13}C-NMR (100.61 MHz, $CDCl_3$):

δ = 22.3, 22.4, 28.7, 38.7, 88.9, 205.2.

HR-MS ($C_{11}H_{21}$; $[M+H]^+$, pos. ESI): calcd: 152.1565, found: 152.1566.

1,3-dicyclohexylpropa-1,2-diene



$C_{15}H_{24}$
(204.36)

The reaction was performed according to **general procedure B**. The crude product was purified by flash column chromatography (SiO_2, hexanes) to afford the desired product as colorless oil (2.65 g, 12.9 mmol, 38 % over 2 steps).

TLC (SiO_2): R_f = 0.9 (hexanes).

^{1}H-NMR (400.13 MHz, $CDCl_3$):

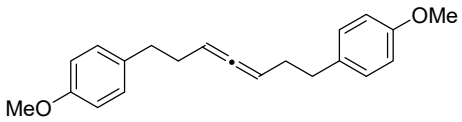
δ = 1.15-1.29 (m, 10H), 1.69-1.76 (m, 10H), 1.94 (m_c, 2H), 5.11 (m_c, 2H).

^{13}C-NMR (100.61 MHz, $CDCl_3$):

δ = 26.3, 26.4, 27.1, 30.4, 33.4, 33.4, 37.5, 43.7, 98.1, 201.6.

HR-MS ($C_{15}H_{25}$; $[M+H]^+$, pos. APCI): calcd: 205.1951, found: 205.1949.

1,7-bis(4-methoxyphenyl)hepta-3,4-diene



$C_{21}H_{24}O_2$
(308.42)

The reaction was performed according to **general procedure B**. The crude product was purified by flash column chromatography (SiO_2, hexanes) to afford the desired product as colorless oil (508 mg, 1.65 mmol, 27 % over 2 steps).

TLC (SiO_2): R_f = 0.33 (hexanes:Et_2O = 20:1).

^{1}H-NMR (400.13 MHz, $CDCl_3$):

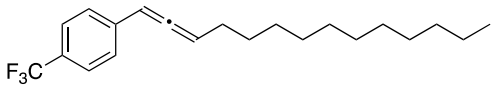
δ = 2.19-2.18 (m, 4H), 2.60 (t, *J* = 7.7 Hz, 4H), 3.77 (s, 6H), 5.12 (m_c, 2H), 6.82 (m_c, 4H), 7.09 (m_c, 4H).

^{13}C-NMR (100.61 MHz, $CDCl_3$):

δ = 31.0, 34.7, 55.4, 90.9, 113.9, 129.5, 134.2, 158.0, 204.3.

HR-MS ($C_{21}H_{25}O_2$; $[M+H]^+$, pos. APCI): calcd: 309.1849, found: 309.1846.

1-(tetradeca-1,2-dien-1-yl)-4-(trifluoromethyl)benzene



$C_{21}H_{29}F_3$
(338.46)

The reaction was performed according to **general procedure B** with 4-(trifluoromethyl)benzaldehyde and 1-bromoundecane. The crude product was purified by flash column chromatography (SiO_2, hexanes) to afford the desired product as colorless oil (2.24 g, 6.62 mmol, 44 % over 2 steps).

TLC (SiO_2): R_f = 0.45 (hexanes:Et_2O = 5:1).

^{1}H-NMR (400.41 MHz, $CDCl_3$):

δ = 0.88 (t, *J* = 6.9 Hz, 3H), 1.25 (s, 14H), 1.33-1.38 (m, 2H), 1.44-1.52 (m, 2H), 2.14 (dtd, *J* = 7.0, 6.9, 3.0 Hz, 2H), 5.63 (dt, *J* = 6.7, 6.7 Hz, 1H), 6.14 (dt, *J* = 6.4, 3.1 Hz, 1H), 7.35-7.39 (m, 2H), 7.51-7.55 (m, 2H).

^{13}C-NMR (100.68 MHz, $CDCl_3$):

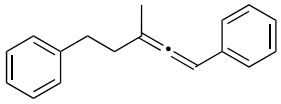
δ = 14.3, 22.8, 28.7, 29.2, 29.3, 29.5, 29.6, 29.8, 31.1, 32.1, 93.9, 95.9, 124.4 (q, *J* = 271.7 Hz), 125.5, 125.6, 125.6, 125.7, 128.6 (q, *J* = 32.4 Hz), 139.3, 206.2.

^{19}F-NMR (376.76 MHz, $CDCl_3$, unified scale):

δ = -62.2.

HR-MS ($C_{21}H_{30}F_3$; $[M+H]^+$, pos. ESI): calcd: 339.2300, found: 339.2298.

(3-methylpenta-1,2-diene-1,5-diyl)dibenzene



$C_{18}H_{18}$
234.34

The reaction was performed according to **general procedure B** with 4-phenylbutan-2-one and bromobenzene. The crude product was purified by flash column chromatography (SiO_2, hexanes) to afford the desired product as colorless oil (2.14 g, 9.15 mmol, 61 % over 2 steps).

TLC (SiO_2): R_f = 0.36 (hexanes).

^{1}H-NMR (400.13 MHz, $CDCl_3$):

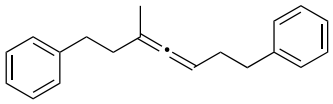
δ = 1.86 (d, *J* = 2.9 Hz, 3H), 2.40-2.46 (m, 2H), 2.80-2.85 (m, 2H), 6.08 (tq, *J* = 2.9, 2.9 Hz, 1H), 7.15-7.23 (m, 6H), 7.25-7.30 (m, 4H).

^{13}C-NMR (100.68 MHz, $CDCl_3$):

δ = 19.0, 34.0, 36.0, 94.6, 103.2, 126.0, 126.6 126.7, 128.5, 128.6, 128.6, 135.9, 142.1, 203.0.

HR-MS ($C_{18}H_{19}$; $[M+H]^+$, pos. ESI): calcd: 235.1481, found: 235.1478.

(3-methylhepta-3,4-diene-1,7-diyl)dibenzene



$C_{20}H_{22}$
(262.40)

The reaction was performed according to **general procedure B** with 4-phenylbutan-2-one and (2-bromoethyl)benzene. The crude product was purified by flash column chromatography (SiO_2, hexanes) to afford the desired product as colorless oil (3.03 g, 11.6 mmol, 77 % over 2 steps).

TLC (SiO_2): R_f = 0.41 (hexanes:).

^{1}H-NMR (400.13 MHz, $CDCl_3$):

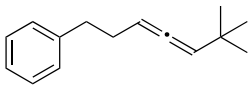
δ = 1.67 (d, *J* = 2.9 Hz, 3H), 2.19-2.29 (m, 4H), 2.63-2.72 (m, 4H), 5.09 (m_c, 1H), 7.15-7.20 (m, 6H), 7.26-7.30 (m, 4H).

^{13}C-NMR (100.61 MHz, $CDCl_3$):

δ = 19.5, 31.0, 34.1, 35.7, 35.8, 90.4, 99.6, 125.8, 125.8, 125.9, 128.3, 128.4, 128.4, 128.5, 128.7, 142.2, 142.5, 201.7.

HR-MS ($C_{20}H_{26}N$; $[M+NH_4]^+$, pos. ESI): calcd: 280.2060, found: 260.2062.

(6,6-dimethylhepta-3,4-dien-1-yl)benzene



$C_{15}H_{20}$
(200.33)

The reaction was performed according to **general procedure B** with pivalaldehyde and (2-bromoethyl)benzene. The crude product was purified by flash column chromatography (SiO_2, hexanes) to afford the desired product as colorless oil (1.40 g, 7.01 mmol, 47 % over 2 steps).

TLC (SiO_2): R_f = 0.53 (hexanes).

^{1}H-NMR (400.13 MHz, $CDCl_3$):

δ = 1.02 (s, 9H), 2.28-2.35 (m, 2H), 2.73 (t, *J* = 7.9 Hz, 2H), 5.12 (dt, *J* = 6.2, 3.1 Hz, 1H), 5.21 (dt, *J* = 6.4, 6.4 Hz, 1H), 7.16-7.22 (m, 3H), 7.26-7.31 (m, 2H).

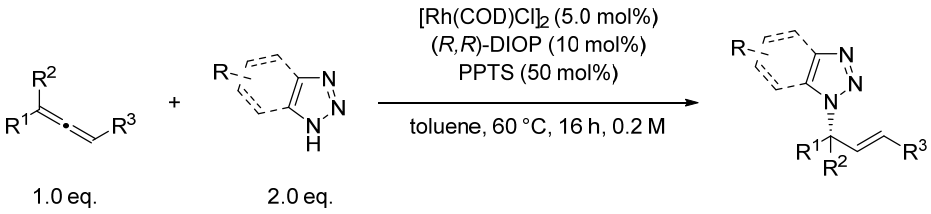
^{13}C-NMR (100.61 MHz, $CDCl_3$):

δ = 30.4, 31.1, 31.8, 35.7, 92.3, 103.7, 125.9, 128.4, 128.6, 142.2, 201.3.

HR-MS ($C_{15}H_{24}N$; $[M+NH_4]^+$, pos. ESI): calcd: 218.1903, found: 218.1901.

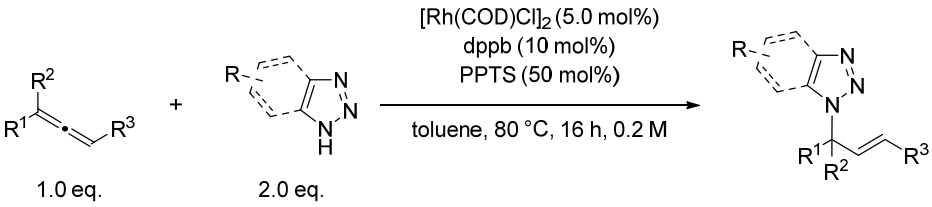
General Procedure for Catalysis

General procedure C: *N*-allylated triazoles (GP C)



A 20 ml screw-cap Schlenk tube was dried under vacuum, backfilled with argon (Argon 5.0 Sauerstoffwerke Friedrichshafen) and cooled to room temperature using a standard Schlenk line apparatus. The tube was filled with $[Rh(COD)Cl]_2$ (6.2 mg, 0.013 mmol, 5.0 mol%), (*R,R*)-DIOP (12.5 mg, 0.025 mmol, 10.0 mol%), PPTS (31.5 mg, 0.125 mmol, 50.0 mol%) and triazole (0.500 mmol, 2.0 equiv.). The tube was put on vacuum and backfilled with argon again. Freshly distilled toluene (1.25 ml) and allene (0.25 mmol, 1.0 equiv.) were added by syringe under a flow of argon, and then the tube was sealed by a screw cap. The mixture was stirred at 60 °C for 16 hours. The tube was cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography using AcOEt and hexanes as eluent on silica gel.

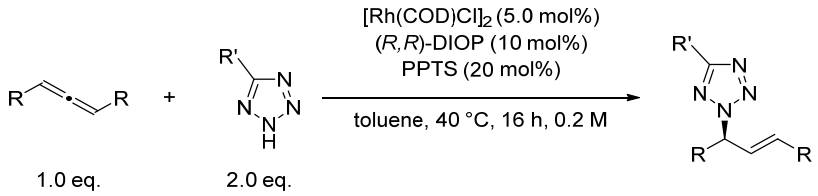
General procedure D: Racemic *N*-Allylated triazoles



A 20 ml screw-cap Schlenk tube was dried under vacuum, backfilled with argon (Argon 5.0 Sauerstoffwerke Friedrichshafen) and cooled to room temperature using a standard Schlenk line apparatus. The tube was filled with $[Rh(COD)Cl]_2$ (6.2 mg, 0.013 mmol, 5.0 mol%), dppb (10.7 mg, 0.025 mmol, 10.0 mol%), PPTS (31.5 mg, 0.125 mmol, 50.0 mol%) and triazole (0.500 mmol, 2.0 equiv.). The tube was put on vacuum and backfilled with argon again. Freshly distilled toluene (1.25 ml) and allene (0.25 mmol, 1.0 equiv.) were added by syringe under a flow of argon, and then the tube was sealed by a screw cap. The mixture was stirred at 80 °C for 16 hours. The tube was cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography using AcOEt and hexanes as eluent on silica gel.

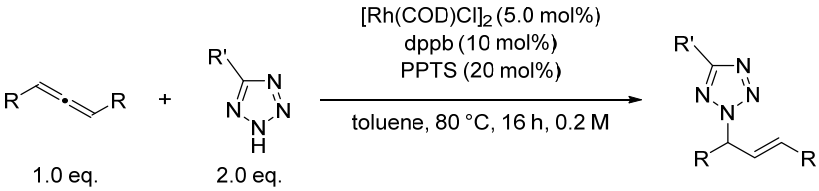
General Procedure for the coupling towards N-allylated triazoles

General Procedure E: *N*-allylated tetrazoles (GP E)



A 20 ml screw-cap Schlenk tube was dried under vacuum, backfilled with argon (Argon 5.0 Sauerstoffwerke Friedrichshafen) and cooled to room temperature using a standard Schlenk line apparatus. The tube was filled with $[Rh(COD)Cl]_2$ (6.2 mg, 0.0125 mmol, 5.0 mol%), (*R,R*)-DIOP (12.5 mg, 0.025 mmol, 10.0 mol%), PPTS (12.6 mg, 0.05 mmol, 20.0 mol%) and tetrazole (0.30 mmol, 1.2 equiv.). The tube was put on vacuum and backfilled with argon again. Freshly distilled toluene (1.25 ml) and allene (0.25 mmol, 1.0 equiv.) were added by syringe under a flow of argon, and then the tube was sealed by a screw cap. The mixture was stirred at 40 °C for 16 h. The tube was cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography using Et_2O and hexanes as eluent on silica gel.

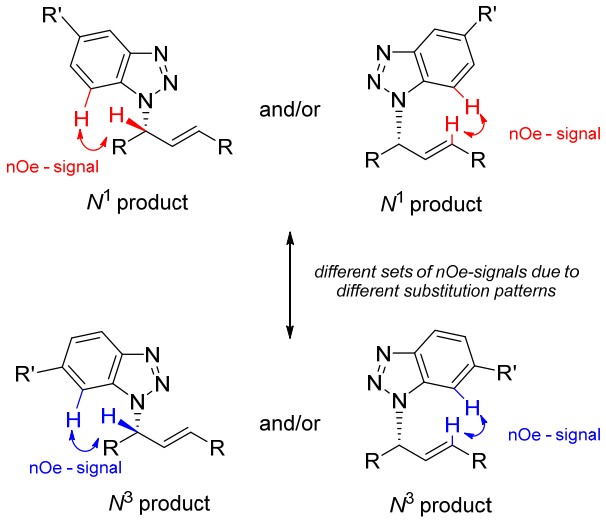
General Procedure F: Racemic *N*-allylated tetrazoles (GP F)



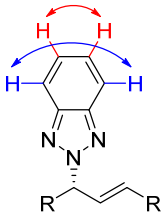
A 20 ml screw-cap Schlenk tube was dried under vacuum, backfilled with argon (Argon 5.0 Sauerstoffwerke Friedrichshafen) and cooled to room temperature using a standard Schlenk line apparatus. The tube was filled with $[Rh(COD)Cl]_2$ (6.2 mg, 0.0125 mmol, 5.0 mol%), dppb (10.7 mg, 0.025 mmol, 10.0 mol%), PPTS (12.6 mg, 0.05 mmol, 20.0 mol%) and tetrazole (0.30 mmol, 1.2 equiv.). The tube was put on vacuum and backfilled with argon again. Freshly distilled toluene (1.25 ml) and allene (0.25 mmol, 1.0 equiv.) were added by syringe under a flow of argon, and then the tube was sealed by a screw cap. The mixture was stirred at 80 °C for 16 h. The tube was cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography using AcOEt and hexanes as eluent on silica gel.

Assignment to the N^1-, N^2- or N^3-products by NMR-experiments

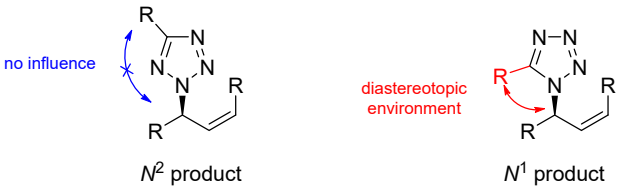
nOE-Experimets



The N^2 product could be assigned based on the symmetric NMR signals.

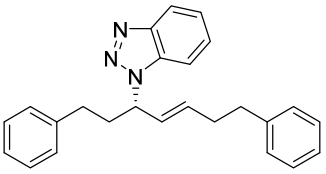


Only the reactions of the two tetrazoles **31**, **32** gave an N^2- / N^1-mixture. It was found that the tetrazole substituents of the N^1-product are in a diasteretopic environment due to their proximity to the stereocenter. The protons of the substituent of the N^2-products were not affected by the stereocenter. By comparison of NMR-spectra the remaining tetrazole-products could be assigned the N^2-products.



Analytical Data of Products

(*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 3)



$C_{25}H_{25}N_3$
(367.50)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 1*H*-benzo[*d*][1,2,3]triazole (59.6 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (82.9 mg, 0.226 mmol, 90 %). *N*^{1}/*N*^{2}-ratio = 96:4 and the *E*/*Z*-selectivity were determined by ^{1}H-NMR spectroscopy of the crude product.

Analytical data of ***3****:*

TLC (SiO_2): R_f = 0.46 (hexanes:Et_2O = 1:1).

***E/Z*:** 95:5.

^{1}H-NMR (400.13 MHz, $CDCl_3$):

δ = 2.32-2.46 (m, 3H), 2.47-2.59 (m, 2H), 2.60-2.74 (m, 3H), 5.15-5.27 (m, 1H), 5.67 (dt, *J* = 15.4, 6.6 Hz, 1H), 5.81 (ddt, *J* = 15.4, 7.0, 1.1 Hz, 1H), 7.05-7.10 (m, 4H), 7.11-7.29 (m, 6H), 7.32-7.45 (m, 3H), 8.05-8.10 (m, 1H).

^{13}C-NMR (100.61 MHz, $CDCl_3$):

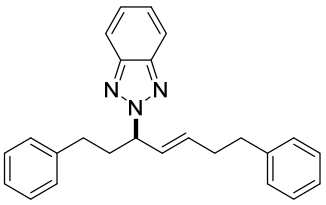
δ = 32.3, 33.9, 35.4, 35.7, 61.3, 110.2, 120.2, 124.1, 126.1, 126.4, 127.2, 128.5, 128.6, 128.6, 128,6 126.7, 132.6, 134.1, 140.6, 146.1.

HR-MS ($C_{25}H_{26}N_3$; $[M+H]^+$, pos. ESI): calcd: 368.2121, found: 368.2122

$[\alpha]_D^{25}$ -8.1° (c = 0.9, CH_2Cl_2).

HPLC (ChiralPAK AD-3, *λ* = 257 nm, *n*-heptane:EtOH = 90:10, 0,5 ml/min, 22°C): t_R = 20.7 min (major peak), 37.2 min (minor peak) min, 97 % *ee*.

(*E*)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-benzo[*d*][1,2,3]triazole (N^2-product, 3b)



$C_{25}H_{25}N_3$
(367.50)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 1*H*-benzo[*d*][1,2,3]triazole (59.6 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (5.6 mg, 0.015 mmol, 6 %). N^1/N^2-ratio = 96:4 and the *E/Z*-selectivity were determined by ^{1}H-NMR spectroscopy of the crude product.

Analytical data of **3b***:*

***E*/*Z*:** >95:5

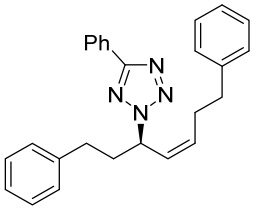
TLC (SiO_2): R_f = 0.76 (hexanes:Et_2O = 1:1).

^{1}H-NMR (500.10 MHz, $CDCl_3$): δ = 2.30-2.39 (m, 3H), 2.42-2.49 (m, 1H), 2.51-2.57 (m, 1H), 2.59-2.66 (m, 1H), 2.66-2.70 (m, 2H), 5.29-5.35 (m, 1H), 5.80 (dt, *J* = 15.5 Hz, 6.5 Hz, 1H), 5.89 (ddt, *J* = 15.4, 7.9, 1.2 Hz, 1H), 7.11-7.14 (m, 4H), 7.15-7.28 (m, 6H), 7.37-7.41 (m, 2H), 7.87-7.91 (m, 2H).

^{13}C-NMR (125.75 MHz, $CDCl_3$): δ = 32.2, 34.0, 35.3, 37.1, 68.9, 118.3, 126.1, 126.2, 126.3, 128.4, 128.6, 128,6, 128.6, 128.7, 134.8, 140.8, 141.4, 144.2.

HR-MS ($C_{25}H_{26}N_3$; $[M+H]^+$, pos. APCI): calculated: 368.2121, found: 368.2122.

(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-phenyl-2*H*-tetrazole (5)



$C_{26}H_{26}N_4$
(394.52)

The reaction was performed according to ***GP-E*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5-phenyl-2*H*-tetrazole (43.9 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:Et_2O = 5:1) to afford the desired product as a colorless oil (81.7 mg, 0.230 mmol, 92 %). *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the crude product.

***E*/*Z*:** <5:95

TLC (SiO_2): R_f = 0.41 (hexanes:Et_2O = 5:1).

^{1}H-NMR (500.10 MHz, C_6D_6): δ = 1.86-1.94 (m, 1H), 2.13-2.18 (m, 2H), 2.20-2.44 (m, 5H), 5.38 (dtd, J = 10.7, 7.6, 0.9 Hz, 1H), 5.46-5.52 (m, 1H), 5.67 (ddt, J = 10.8, 9.4, 1.5 Hz, 1H), 6.92-6.96 (m, 3H), 7.01-7.14 (m, 7H), 7.17-7.19 (m, 3H), 8.41-8.46 (m, 2H).

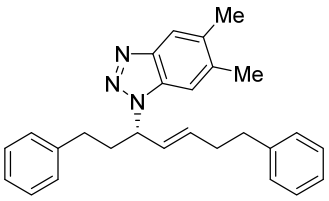
^{13}C-NMR (125.75 MHz, C_6D_6): δ = 29.7, 31.9, 35.5, 37.0, 60.8, 126.4, 126.5, 127.2, 127.4, 128.6, 128.7, 128.8, 129.2, 130.3, 134.5, 140.6, 141.3, 165.6.

HR-MS ($C_{26}H_{27}N_4$; $[M+H]^+$, pos. APCI): calculated: 395.2230, found: 395.2234.

$[\alpha]_D^{25}$ -95.1° (c = 1.1, CH_2Cl_2).

HPLC (LC-3, λ = 250 nm, n-heptane:EtOH = 95:5, 0.5 ml/min, 22°C): t_R = 25.4 min, 29.0 min (major peak); 85% *ee*.

(*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-5,6-dimethyl-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 6)



$C_{27}H_{29}N_3$
(395.55)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5,6-dimethyl-1*H*-benzo[*d*][1,2,3]triazole (65.3 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (87.3 mg, 0.221 mmol, 88 %). N^1/N^2-ratio = 94:6 and the *E/Z*-selectivity were determined by ^{1}H-NMR spectroscopy of the crude product.

Analytical data of **6***:*

TLC (SiO_2): R_f = 0.63 (hexanes:Et_2O = 1:1).

E/Z: 94:6.

^{1}H-NMR (400.13 MHz, $CDCl_3$):

δ = 2.32-2.41 (m, 3H), 2.41 (s, 6H), 2.49-2.54 8m, 2H), 2.59-2.69 (m, 3H) 5.13-5.20 (m, 1H), 5.65 (dt, *J* = 15.6, 6.7 Hz, 1H), 5.82 (ddt, *J* = 15.6, 7.1, 1.4 Hz, 1H), 7.06 - 7.11 (m, 4H), 7.12-7.32 (m, 7H), 7.81 (s, 1H).

^{13}C-NMR (100.61 MHz, $CDCl_3$)

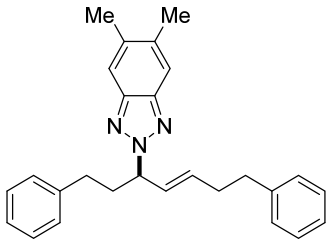
δ = 20.5, 21.1, 32.3, 33.9, 35.4, 35.8, 61.0, 109.6, 119.3, 126.1, 126.3, 128.4, 128.5, 128.6 128.7, 128.8, 131.6, 133.7, 133.7, 137.3, 140.8, 141.4, 145.7.

HR-MS ($C_{27}H_{30}N_3$; $[M+H]^+$, pos. ESI): calcd: 396.2434, found: 396.2438

$[\alpha]_D^{25}$ -2.2° (c = 1.2, CH_2Cl_2).

HPLC (ChiralPAK AD-3, λ = 212 nm, n-heptane:*i*PrOH = 60:40, 0,5 ml/min, 22°C): t_R = 12.3 min (major peak), 17.9 min, 92 % *ee*.

(*E*)-2-(1,7-diphenylhept-4-en-3-yl)-5,6-dimethyl-2*H*-benzo[*d*][1,2,3]triazole (N^2-product, 6b)



$C_{27}H_{29}N_3$
(395.55)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5,6-dimethyl-1*H*-benzo[*d*][1,2,3]triazole (65.3 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (5.6 mg, 0.014 mmol, 6 %). N^1/N^2-ratio = 94:6 and the *E/Z*-selectivity were determined by ^{1}H-NMR spectroscopy of the crude product.

Analytical data of **6b***:*

TLC (SiO_2): R_f = 0.83 (hexanes:Et_2O = 1:1).

E/Z: >95:5.

^{1}H-NMR (400.13 MHz, $CDCl_3$):

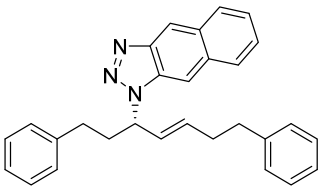
δ = 2.24 – 2.40 (m, 3H), 2.41 (s, 6H), 2.42-2.64 (m, 3H), 2.65-2.70 (m, 2H), 5.23-2.29 (m, 1H), 5.76 (dt, *J* = 15.5, 6.4 Hz, 1H), 5.87 (ddt, *J* = 15.4, 7.7, 1.3 Hz, 1H), 7.09 - 7.14 (m, 4H), 7.14-7.29 (m, 6H) 7.62 (s, 1H).

^{13}C-NMR (100.61 MHz, $CDCl_3$):

δ = 21.0, 29.9, 32.2, 34.1, 35.4, 37.1, 68.5, 116.8, 126.0, 126.2, 128.5, 128.6, 128.6, 129.0, 134.4, 136.7, 141.0, 141.5, 143.6.

HR-MS ($C_{27}H_{30}N_3$; $[M+H]^+$, pos. ESI): calcd: 396.2434, found: 396.2437

(*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole (*N*^{1}-product, 7)



$C_{29}H_{27}N_3$
(417.56)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 1*H*-naphtho[2,3-*d*][1,2,3]triazole (84.5 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (82.2 mg, 0.197 mmol, 79 %). *N*^{1}/*N*^{2}-ratio = 94:6 and the *E/Z*-selectivity were determined by ^{1}H-NMR spectroscopy of the crude product.

Analytical data of ***7****:*

TLC (SiO_2): R_f = 0.56 (hexanes:Et_2O = 1:1).

***E/Z*:** 95:5.

^{1}H-NMR (400.13 MHz, $CDCl_3$):

δ = 2.34-2.40 (m, 2H), 2.45-2.52 (m, 1H), 2.56-2.60 (m, 2H), 2,62-2.68 (m, 2H), 2.73-2.82 (m, 1H), 5.31-5.37 (m, 1H), 5.72 (dt, *J* = 15.5, 6.7 Hz, 1H), 5.87 (dd, *J* = 15.4, 7.1 Hz, 1H), 7.06-7.13 (m, 5H), 7.16-7.22 (m, 3H), 7.24-7.29 (m, 2H), 7.45 (dd, *J* = 8.3, 6.9 Hz, 1H), 7.51 (ddd, *J* = 8.3, 7.3 Hz, 1H), 7.80 (s, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 8.80 (d, *J* = 8.3 Hz, 1H), 8.66 (s, 1H).

^{13}C-NMR (125.72 MHz, $CDCl_3$):

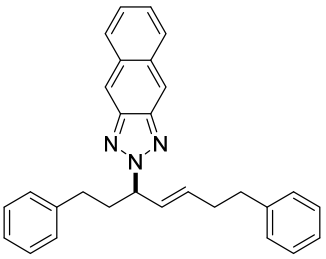
δ = 32.1, 33.9, 35.3, 35.6, 61.1, 105.8, 124.7, 126.0, 126.3, 126.5, 128.1, 128.4, 128.5, 128.5, 128.6, 128.6, 129.4, 130.7, 131.3, 132.7, 133.9, 140.6, 141.2, 145.6.

HR-MS ($C_{29}H_{28}N_3$; $[M+H]^+$, pos. ESI): calcd: 418.2278, found: 418.2282.

$[\alpha]_D^{25}$ -19.7° (c = 2.4, CH_2Cl_2).

HPLC (ChiralPAK AD-3, λ = 212 nm, *n*-heptane:*i*PrOH = 60:40, 0,5 ml/min, 22°C): t_R = 16.8 min (major peak), 24.4 min, 96 % *ee*.

(*E*)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-naphtho[2,3-*d*][1,2,3]triazole (N^2-product, 7b)



$C_{29}H_{27}N_3$
(417.56)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 1*H*-naphtho[2,3-*d*][1,2,3]triazole (84.5 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (3.7 mg, 0.009 mmol, 4 %). N^1/N^2-ratio = 94:6 and the *E/Z*-selectivity were determined by ^{1}H-NMR spectroscopy of the crude product.

Analytical data of **7b***:*

TLC (SiO_2): R_f = 0.72 (hexanes:Et_2O = 1:1).

***E/Z*: >**95:5.

^{1}H-NMR (400.13 MHz, $CDCl_3$):

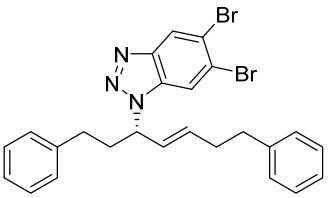
δ = 2.37-2.45 (m, 3H), 2.46-2.50 (m, 1H) 2.54-2.60 (m, 1H), 2.67-2.74 (m, 3H), 5.44-5.48 (m, 1H), 5.86 (dt, *J* = 15.4, 6.5 Hz, 1H), 5.97 (dd, *J* = 15.4, 8.1 Hz, 1H), 7.10-7.15 (m, 5H), 7.16-7.22 (m, 3H), 7.25-7.29 (m, 2H), 7.35 (m_c, 2H), 7.95 (m_c, 2H), 8.46 (s, 2H).

^{13}C-NMR (125.72 MHz, $CDCl_3$):

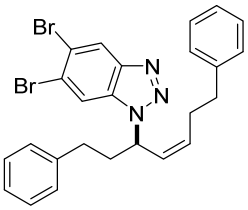
δ = 29.8, 32.1, 34.0, 35.2, 37.2, 69.9, 115.2, 124.9, 126.0, 126.2, 128.4, 128.5, 128.5, 128.5, 128.6, 128.8, 132.7, 135.2, 141.3, 143.4.

HR-MS ($C_{29}H_{28}N_3$; $[M+H]^+$, pos. ESI): calcd: 418.2278, found: 418.2280.

(*S*,*E*)-5,6-dibromo-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (N^1-, *E*-product, 8) & (*Z*)-5,6-dibromo-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (N^1-, *Z*-product, 8b)



$C_{25}H_{23}Br_2N_3$
(525.29)



$C_{25}H_{23}Br_2N_3$
(525.29)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5,6-dibromo-1*H*-benzo[*d*][1,2,3]triazole (137.4 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (91.4 mg, 0.174 mmol, 70 %). N^1/N^2-ratio = 91:9 and the *E/Z*-selectivity were determined by ^{1}H-NMR spectroscopy.

Analytical data of **8** *and* **8b***:*

TLC (SiO_2): R_f = 0.65 (hexanes:Et_2O = 1:1).

***N*^{1}*/N*^{2}** 91:9.

E:Z 58:42.

^{1}H NMR (499.98 MHz, C_6D_6)

δ = 1.92-2.09 (m, 3H), 2.14-2.27 (m, 3H), 2.29-2.39 (m, 2H), 5.23-5.33 (m, 1H), 6.82-6.92 (m, 4H), 6.96-7.13 (m, 6H).

Characteristic *E*-product signals*:* δ = 4.57-4.63 (m, 1H), 5.14 (dt, *J* = 15.6, 6.7f Hz, 1H), 7.38 (s, 1H), 8.13 (s, 1H).

Characteristic *Z*-product signals*:* δ = 1.79-1.88 (m, 1H), 5.04-5.10 (m, 1H), 5.44 (dd, *J* = 10.6, 8.9 Hz, 1H), 7.40 (s, 1H), 8.11 (s, 1H).

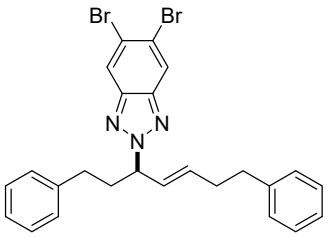
^{13}C NMR (125.72 MHz, C_6D_6)

δ = 29.9, 32.1, 32.2, 33.8, 35.4, 35.4, 35.6, 36.5, 55.6, 31.3, 114.5, 114.6, 119.7, 132.8, 124.9, 125.0, 126.4, 126.5, 126.6, 126.6, 127.6, 128.5, 128.7, 128.7, 128.7, 128.8, 128.8, 128.9, 132.4, 132.7, 134.0, 134.4, 140.4, 145.6, 141.0, 141.2, 146.7, 146.7.

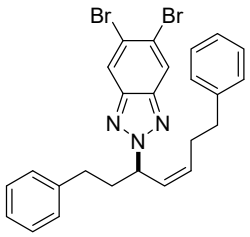
HR-MS ($C_{25}H_{24}N_3Br^{81}Br$; $[M+H]^+$, pos. ESI): calcd. 526.0311, found 526.0305.

HPLC (ChiralPAK AD-3, λ = 228 nm, *n*-heptane:*i*PrOH = 70:30, 0,5 ml/min, 22°C):
E-product: t_R = 10.2 min (major peak), 11.3 min; 94 % *ee*.
Z-product: t_R = 7.8 min, 9.0 min (major peak); 83 % *ee*.

(*E*)-5,6-dibromo-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-benzo[*d*][1,2,3]triazole (N^2-, *E*-product, 8c) & (*Z*)-5,6-dibromo-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-benzo[*d*][1,2,3]triazole (N^2-, *Z*-product, 8d)



$C_{25}H_{23}Br_2N_3$
(525.29)



$C_{25}H_{23}Br_2N_3$
(525.29)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5,6-dibromo-1*H*-benzo[*d*][1,2,3]triazole (137.4 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (9.1 mg, 0.017 mmol, 7 %). N^1/N^2-ratio = 91:9 and the *E/Z*-selectivity were determined by ^{1}H-NMR spectroscopy.

Analytical data of **8c** *and* **8d***:*

TLC (SiO_2): R_f = 0.80 (hexanes:Et_2O = 1:1).

N¹/N² 91:9.

E:Z 85:15.

^{1}H NMR (499.98 MHz, C_6D_6)

δ = 2.04-2.13 (m, 3H), 2.20-2.34 (m, 2H), 2.36-2.45 (m. 2H), 2.48-2.56 (m, 1H), 5.36-5.44 (m, 1H), 6.90-6.94 (m, 2H), 6.97-7.16 (m, 8H).

Characteristic *E*-product signals*:* δ = 5.13-5.20 (m, 1H), 5.70 (ddt, *J* = 15.5, 8.1, 1.2 Hz, 1H), 8.03 (s, 2H).

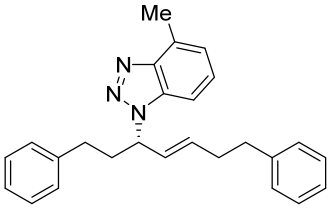
Characteristic *Z*-product signals*:* δ = 1.90-1.97 (m, 2H), 5.52-5.57 (m, 1H), 5.80 (ddt, *J* = 10.8, 9.4, 1.4 Hz, 1H), 8.00 (s, 2H).

^{13}C NMR (125.72 MHz, C_6D_6)

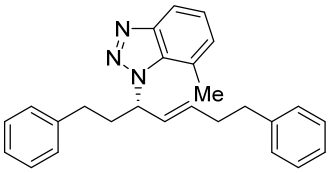
δ = 14.4, 23.2, 30.2, 30.2, 32.1, 32.2, 32.3, 34.0, 35.4, 35.6, 37.3, 37.5, 64.1, 69.4, 122.7, 123.0, 123.0, 126.3, 126.4, 126.6, 126.6, 128.6, 128.7, 128.7, 128.8, 128.8, 128.8, 134.1, 134.9, 140.7, 140.8, 141.3, 141.4, 144.4, 144.4.

HR-MS ($C_{25}H_{24}N_3Br^{81}Br$; $[M+H]^+$, pos. ESI): calcd. 526.0311, found 526.0306.

(*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-4-methyl-1*H*-benzo[*d*][1,2,3]triazole (N^1-product, 9) & (*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-7-methyl-1*H*-benzo[*d*][1,2,3]triazole (N^3-product, 9b)



$C_{26}H_{27}N_3$
(381.22)



$C_{26}H_{27}N_3$
(381.22)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 4-methyl-1*H*-benzo[*d*][1,2,3]triazole (66.5 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford a mixture of the desired products as a colorless oil (77.0 mg, 0.202 mmol, 81 %). $N^1/N^2/N^3$-ratio = 75:6:19 and the *E*/*Z*-selectivity were determined by ^{1}H-NMR spectroscopy.

Analytical data of **9** *and* **9b***:*

TLC (SiO_2): R_f = 0.61 (hexanes:Et_2O = 1:1).

$N^1/N^2/N^3$ 73:6:21.

E:Z N^1*:* 93:7, N^3: >95:5.

^{1}H NMR (499.98 MHz, $CDCl_3$)

δ = 2.30-2.34 (m, 1H), 2.36-2.45 (m, 2H), 2.46-2.59 (m, 2H), 2.61-2.70 (m, 3H), 6.99-7.10 (m, 4H), 7.12-7.33 (m, 9H).

N^1-*E*-product*:* δ = 2.82 (s, 3H), 5.17-5.25 (m, 1H), 5.66 (dt, *J* = 15.3, 6.7 Hz, 1H), 5.81 (dd, *J* = 15.4, 7.1 Hz, 1H).

N^3-*E*-product*:* δ = 2.35 (s, 3H), 5.26-5.33 (m, 1H), 5.40 (dt, *J* = 15.2, 6.8 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H).

N^1-*Z*-product*:* δ = 2.81 (s, 3H), 5.45-5.51 (m, 1H), 5.89 (ddt, *J* = 10.8, 9.1, 1.5 Hz, 1H).

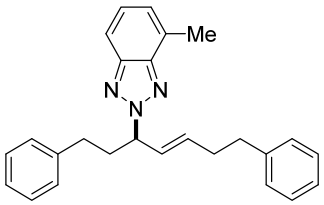
^{13}C NMR (125.72 MHz, $CDCl_3$)

δ = 16.5, 18.8, 32.2, 32.3, 33.9, 33.9, 35.4, 35.7, 36.7, 60.9, 61.2, 76.9, 107.5, 117.9, 120.9, 123.8, 124.0, 126.0, 126.1, 126.3, 126.4, 127.1, 128.4, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.7, 128.9, 130.7, 131.1, 132.4, 132.7, 133.8, 140.7, 141.3, 146.1, 146.3.

HR-MS ($C_{26}H_{28}N_3$; $[M+H]^+$, pos. ESI): calcd. 382.2278, found 382.2277.

HPLC (ChiralPAK AD-3, λ = 212 nm, *n*-heptane:*i*PrOH = 85:15, 0,5 ml/min, 22°C):
N^3-*E*-product: t_R = 9.9 (major peak), 11.5 (minor peak) min, 97 % *ee.*
N^1-*E*-product: t_R = 14.8 (minor peak), 15.6 (major peak) min, 97 % *ee.*

(*E*)-2-(1,7-diphenylhept-4-en-3-yl)-4-methyl-2*H*-benzo[*d*][1,2,3]triazole (N^2-product, 9c)



$C_{26}H_{27}N_3$
(381.22)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 4-methyl-1*H*-benzo[*d*][1,2,3]triazole (66.5 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (5.2 mg, 0.014 mmol, 5 %). $N^1/N^2/N^3$-ratio = 75:6:19 and the *E/Z*-selectivity were determined by ^{1}H-NMR spectroscopy.

Analytical data of **9c**:*:*

TLC (SiO_2): R_f = 0.83 (hexanes:Et_2O = 1:1).

$N^1/N^2/N^3$ 73:6:21.

E:Z >95:5.

^{1}H NMR (499.98 MHz, $CDCl_3$)

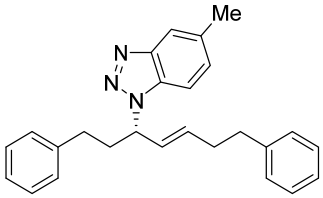
δ = 2.30-2.40 (m, 3H), 2.41-2.48 (m, 1H), 2.52-2.63 (m. 2H), 2.64-2.71 (m, 5H), 5.29-5.35 (m, 1H), 5.79 (dt, *J* = 15.5, 6.7 Hz, 1H), 5.90 (dd, *J* = 15.5, 7.9 Hz, 1H), 7.11-7.14 (m, 5H), 7.15-7.30 (m, 7H), 7.70 (d, *J* = 8.5 Hz, 1H).

^{13}C NMR (125.72 MHz, $CDCl_3$)

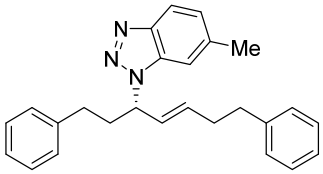
δ = 17.4, 29.9, 32.2, 34.1, 35.4, 37.1, 68.9, 115.4, 125.3, 126.0, 126.2, 128.4, 128.6, 128.6, 128.6, 128.9, 128.9, 134.6, 140.9, 141.5, 144.2, 144.6.

HR-MS ($C_{26}H_{28}N_3$; $[M+H]^+$, pos. ESI): calcd. 382.2278, found 382.2277.

(*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-5-methyl-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 10b) & (*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-6-methyl-1*H*-benzo[*d*][1,2,3]triazole (*N*^{3}-product, 10)



$C_{26}H_{27}N_3$
(381.52)



$C_{26}H_{27}N_3$
(381.52)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5-methyl-1*H*-benzo[*d*][1,2,3]triazole (66.5 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford a mixture of the desired products as a colorless oil (86.6 mg, 0.227 mmol, 91 %). *N*^{1}/*N*^{2}/*N*^{3}-ratio = 53:6:43 and *E*/*Z*-selectivity were determined by ^{1}H-NMR spectroscopy.

Analytical data of **10** *and* **10b***:*

TLC (SiO_2): R_f = 0.47 (hexanes:Et_2O = 1:1).

***N*^{1}/*N*^{2}/*N*^{3}** 53:6:43.

***E*/*Z*:** *N*^{1}-product 94:6, *N*^{3}-product 93:7

^{1}H-NMR (499.98 MHz, C_6D_6):

shared signals between isomers:
δ = 1.99-2.04 (m, 2H), 2.07-2.19 (m, 4H), 2.26-2.38 (m, 4H), 2.49-2.61 (m, 1H), 4.91-4.98 (m, 1H), 5.25-5.32 (m, 1H), 6.88-7.13 (m, 12H).

N^1*-signals:* 5.48 (ddt, *J* = 15.4, 6.9, 1.4 Hz, 1H), 7.84 (s, 1H).

N^3*-signals*: 5.53 (ddt, *J* = 15.4, 7.0, 1.4 Hz, 1H), 6.82 (d, *J* = 8.5, 1.4 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H).

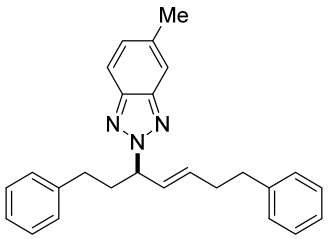
^{13}C-NMR (125.72 MHz, C_6D_6):

δ = 21.3, 21.9, 32.4, 33.9, 35.5, 35.8, 36.0, 60.7, 61.0, 109.3, 109.7, 119.8, 120.2, 126.0, 126.3, 126.3, 126.4, 128.6, 128.6, 128.7, 128.7, 128.8, 128.9, 128.9, 129.2, 129.3, 131.5, 133.2, 133.2, 133.5, 133.6, 137.1, 141.1, 141.5, 145.9, 147.9.

HR-MS ($C_{26}H_{28}N_3$; $[M+H]^+$, pos. ESI): calcd: 382.2278, found: 382.2278.

HPLC (ChiralPAK AD-3, λ = 278 nm, *n*-heptane:EtOH = 90:10, 0,5 ml/min, 22°C):
N^1: t_R = 13.3 min (major peak), 28.7 min, 95 % *ee*.
N^3: t_R = 17.4 min (major peak), 23.9 min, 94 % *ee*.

(*E*)-2-(1,7-diphenylhept-4-en-3-yl)-5-methyl-2*H*-benzo[*d*][1,2,3]triazole (*N*^{2}-product, 10c)



$C_{26}H_{27}N_3$
(381.52)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5-methyl-1*H*-benzo[*d*][1,2,3]triazole (66.5 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired products as a colorless oil (3.8 mg, 0.010 mmol, 4 %). $N^1/N^2/N^3$-ratio = 53:6:43 and *E/Z*-selectivity were determined by ^{1}H-NMR spectroscopy.

Analytical data of **10c***:*

TLC (SiO_2): R_f = 0.71 (hexanes:Et_2O = 1:1).

***N*^{1}*/N*^{2}*/N*^{3}** 53:6:43.

***E/Z*:** >95:5.

^{1}H-NMR (499.98 MHz, C_6D_6):

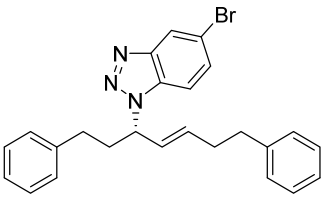
δ = 2.03-2.09 (m, 2H), 2.13 (s, 3H), 2.15-2.2 (m, 1H), 2.31-2.44 (m, 4H), 2.64-2.73 (m, 1H), 5.30-5.35 (m, 1H), 5.46 (dt, *J* = 15.4, 6.8 Hz, 1H), 5.84 (ddt, *J* = 15.4, 8.0, 1.5 Hz, 1H), 6.90-6.94 (m, 3H), 6.99-7.14 (m, 8H), 7.68 (s, 1H), 7.80 (d, *J* = 9.0 Hz, 1H).

^{13}C-NMR (125.72 MHz, C_6D_6):

δ = 21.9, 30.2, 32.4, 34.1, 35.4, 37.5, 68.8, 117.1, 118.1, 126.2, 126.4, 128.6, 128.7, 128.7, 128.9, 129.1, 129.5, 134.1, 136.1, 141.3, 141.7, 143.6, 145.5.

HR-MS ($C_{26}H_{28}N_3$; $[M+H]^+$, pos. ESI): calcd: 382.2278, found: 382.2278.

(*S*,*E*)-5-bromo-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[d][1,2,3]triazole (*N*^{1}-product, 11)



$C_{25}H_{24}BrN_3$
(446.39)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 4-phenyl-1*H*-1,2,3-triazole (98.5 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (32.3 mg, 0.072 mmol, 29 %). *N*^{1}/*N*^{2}/*N*^{3}-ratio = 35:5:60 and *E*/*Z*-selectivity were determined by ^{1}H-NMR spectroscopy.

Analytical data of **11***:*

TLC (SiO_2): R_f = 0.67 (hexanes:Et_2O = 1:1).

E:Z: 86:14.

^{1}H NMR (499.98 MHz, C_6D_6)

δ = 1.96-2.04 (m, 2H), 2.05-2.12 (m, 1H), 2.22-2.30 (m, 2H), 2.31-2.36 (m, 2H), 2.36-2.45 (m, 1H), 4.78-4.84 (m, 1H), 5.21 (dt, *J* = 15.4, 6.8 Hz, 1H), 5.36 (ddt, *J* = 15.4, 7.1, 1.4 Hz, 1H), 6.59-6.62 (m, 2H), 6.85-6.93 (m, 4H), 6.98-7.14 (m, 6H), 7.20 (dd, *J* = 8.8, 1.7 Hz, 1H), 8.17 (d, *J* = 1.5 Hz, 1H).

Significant *Z*-product signals: δ = 5.30 (dt, *J* = 10.7, 7.5 Hz, 4H), 5.51 (ddt, *J* = 10.7, 9.0, 1.6 Hz, 1H).

^{13}C NMR (125.72 MHz, C_6D_6)

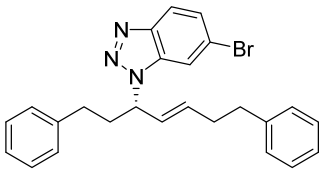
δ = 32.3, 33.8, 35.4, 35.6, 61.1, 111.3, 117.0, 123.3, 126.4, 126.6, 128.6, 128.7, 128.7, 128.8, 128.8, 128.8, 130.1, 131.7, 133.7, 140.8, 141.3, 148.2.

HR-MS ($C_{25}H_{25}N_3Br$; $[M+H]^+$, pos. ESI): calcd. 446.1226, found 446.1226.

$[\alpha]_D^{25}$ -16.5° (c = 0.9, CH_2Cl_2).

HPLC (ChiralPAK AD-3, *λ* = 228 nm, *n*-heptane:*i*PrOH = 70:30, 0,5 ml/min, 22°C):
N^1: t_R = 10.8 min (major peak), 14.4 min, 96 % *ee*.

(*S*,*E*)-6-bromo-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[d][1,2,3]triazole (N^3-product, 11b)



$C_{25}H_{24}BrN_3$
(446.39)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 4-phenyl-1*H*-1,2,3-triazole (98.5 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (54.2 mg, 0.121 mmol, 49 %). $N^1/N^2/N^3$-ratio = 35:5:60 and *E/Z*-selectivity were determined by ^{1}H-NMR spectroscopy.

Analytical data of **11b***:*

TLC (SiO_2): R_f = 0.68 (hexanes:Et_2O = 1:1).

E:Z: 93:7.

^{1}H NMR (499.98 MHz, C_6D_6)

δ = 1.95-2.01 (m, 2H), 2.01-2.10 (m, 1H), 2.26 (t, *J* = 7.6 Hz, 2H), 2.30-2.35 (m, 2H), 2.36-2.45 (m, 1H), 4.68-4.75 (m, 1H), 5.18 (dt, *J* = 15.3, 6.8 Hz, 1H), 5.35 (ddt, *J* = 15.4, 7.1, 1.4 Hz, 1H), 6.85-6.92 (m, 4H), 6.98-7.14 (m, 7H), 7.38 (d, *J* = 1.7 Hz, 1H), 7.64 (dd, *J* = 8.8 Hz, 1H).

Significant *Z*-product signals: δ = 5.29 (dtd, *J* = 10.8, 7.5, 1.2 Hz, 4H), 5.50 (ddt, *J* = 10.6, 9.0, 1.6 Hz, 1H).

^{13}C NMR (125.72 MHz, C_6D_6)

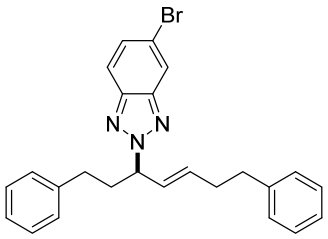
δ = 32.2, 33.8, 35.4, 35.7, 61.1, 113.2, 121.3, 121.8, 126.3, 126.5, 127.4, 128.6, 128.6, 128.7, 128.7, 128.8, 133.8, 134.0, 140.6, 141.3, 145.8.

HR-MS ($C_{25}H_{25}N_3{}^{81}Br$; $[M+H]^+$, pos. ESI): calcd. 448.1206, found 448.1206.

$[\alpha]_D^{25}$ -14.1° (c = 1.5, CH_2Cl_2).

HPLC (ChiralPAK AD-3, λ = 228 nm, *n*-heptane:*i*PrOH = 70:30, 0,5 ml/min, 22°C):
N^3: t_R = 9.4 min (major peak), 13.7 min, 97 % *ee*.

(*S*,*E*)-5-bromo-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-benzo[d][1,2,3]triazole (N^2-product, 11c)



$C_{25}H_{24}BrN_3$
(446.39)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 4-phenyl-1*H*-1,2,3-triazole (98.5 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (4.0 mg, 0.009 mmol, 4 %). $N^1/N^2/N^3$-ratio = 35:5:60 and *E*/*Z*-selectivity were determined by ^{1}H-NMR spectroscopy.

Analytical data of **11c***:*

TLC (SiO_2): R_f = 0.84 (hexanes:Et_2O = 1:1).

E:Z 95:5

^{1}H NMR (499.98 MHz, C_6D_6)

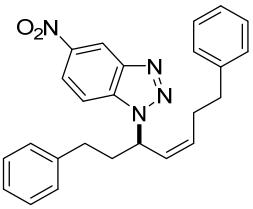
δ = 2.02-2.08 (m, 2H), 2.08-2.15 (m, 1H), 2.20-2.43 (m, 4H), 2.53-2.62 (m, 1H), 5.20-5.26 (m, 1H), 5.41 (dt, *J* = 15.2, 6.7 Hz, 1H), 5.74 (ddt, *J* = 15.4, 8.1, 1.5 Hz, 1H), 6.90-6.94 (m, 2H), 6.97-7-16 (m, 9H), 7.47 (dd, *J* = 9.0 Hz, 1H), 8.05 (d, *J* = 1.8 Hz, 1H).

^{13}C NMR (125.72 MHz, C_6D_6)

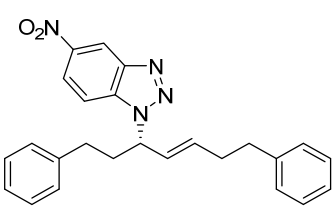
δ = 32.3, 34.0, 35.3, 37.3, 69.2, 120.0, 120.1, 121.2, 126.3, 126.5, 128.6, 128.6, 128.7, 128.8, 128.8, 128.9, 130.1, 134.6, 141.0 ,143.4, 145.7.

HR-MS ($C_{25}H_{25}N_3{}^{81}BrCl$; $[M+Cl]^+$, pos. ESI): calcd. 482.0816, found 482.0814.

(*Z*)-1-(1,7-diphenylhept-4-en-3-yl)-5-nitro-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}, *Z*-product, 12) & (*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-5-nitro-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}, *E*-product, 12b)



$C_{25}H_{24}N_4O_2$
(412.49)



$C_{25}H_{24}N_4O_2$
(412.49)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5-nitro-1*H*-benzo[*d*][1,2,3]triazole (67.0 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (33.2 mg, 0.080 mmol, 32 %). $N^1/N^2/N^3$-ratio = 45:9:46 and *E/Z*-selectivity were determined by ^{1}H-NMR spectroscopy.

Analytical data of **12** *and* **12b***:*

TLC (SiO_2): R_f = 0.54 (hexanes:Et_2O = 1:1).

$N^1/N^2/N^3$ 45:9:46.

E:Z 21:79.

^{1}H NMR (499.98 MHz, C_6D_6)

δ = 1.86-1.94 (m, 1H), 1.97-2.04 (m, 1H), 2.05-2.14 (m, 1H), 2.20-2.38 (m, 5H), 5.11-5.17 (m, 1H), 5.31 (dt, *J* = 10.7, 7.5 Hz, 1H); 5.46 (ddt, *J* = 10.7, 9.1, 1.5 Hz, 1H). 6.51 (d, *J* = 9.0 Hz, 1H), 6.84-6.89 (m, 4H), 6.97-7.01 (m, 1H), 7.02-7.12 (m, 5H), 7.86 (dd, *J* = 9.0, 2.0 Hz, 1H), 8.74 (d, *J* = 2.0 Hz, 1H).

Characteristic *E*-product signals: δ = 4.72-4.78 (m, 1H), 5.21 (dt, *J* = 15.4, 6.6 Hz, 1H), 8.76 (d, *J* = 2.0 Hz, 1H).

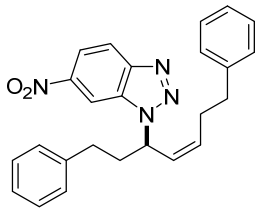
^{13}C NMR (125.72 MHz, C_6D_6)

δ = 29.9, 32.1, 35.4, 36.3, 56.8, 110.0, 117.6, 121.8, 126.6, 126.7, 127.7, 128.7, 128.7, 128.7, 128.9, 134.4, 134.8, 140.3, 141.0, 144.8, 145.6.

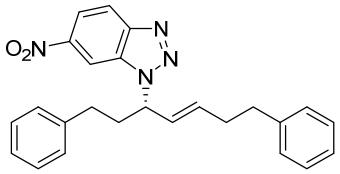
HR-MS ($C_{26}H_{25}O_2N_4$; $[M+H]^+$, pos. ESI): calcd. 413.1972, found 413.1974.

HPLC (ChiralPAK AD-3, λ = 240 nm, *n*-heptane:*i*PrOH = 90:10, 0,5 ml/min, 22°C):
t_R(*Z*-product) = 18.2 min, 19.5 min (major peak), 87 % *ee*.

(*Z*)-1-(1,7-diphenylhept-4-en-3-yl)-6-nitro-1*H*-benzo[d][1,2,3]triazole (N^3,*Z*-product, 12c) & (*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-6-nitro-1*H*-benzo[d][1,2,3]triazole (N^3,*E*-product, 12d)



$C_{25}H_{24}N_4O_2$
(412.49)



$C_{25}H_{24}N_4O_2$
(412.49)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5-nitro-1*H*-benzo[*d*][1,2,3]triazole (67.0 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford a mixture of the desired product as a colorless oil (35.1 mg, 0.085 mmol, 34%). $N^1/N^2/N^3$-ratio = 45:9:46 and *E*/*Z*-selectivity were determined by ^{1}H-NMR spectroscopy.

Analytical data of **12c** *and* **12d***:*

TLC (SiO_2): R_f = 0.52 (hexanes:Et_2O = 1:1).

$N^1/N^2/N^3$ 45:9:46.

E:Z 31:69.

^{1}H NMR (499.98 MHz, C_6D_6)

Shared peaks: δ = 1.85-1.94 (m, 1H), 1.99-2.13 (m, 2H), 2.18-2.42 (m, 5H), 5.28-5.35 (m, 1H), 6.84-6.91 (m, 4H), 6.93-7.14 (m, 6H).

Characteristic *Z*-product signals: δ = 5.12-5.20 (m, 1H), 5.47 (ddt, *J* = 10.6, 9.0, 1.6 Hz, 1H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.74 (dd, *J* = 9.0, 1.9 Hz, 1H), 8.03 (d, *J* = 1.9 Hz, 1H).

Characteristic *E*-product signals: δ = 4.66-4.72 (m, 1H), 5.18-5.25 (m, 1H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.75 (dd, *J* = 9.0, 2.0 Hz, 1H), 8.01 (d, *J* = 2.0 Hz, 1H).

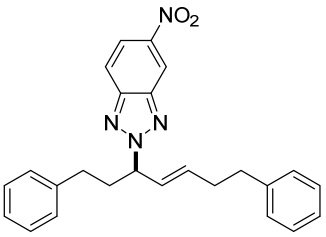
^{13}C NMR (125.72 MHz, C_6D_6)

δ = 29.9, 32.1, 32.2, 33.7, 35.2, 35.3, 35.5, 35.7, 36.4, 37.1, 61.4, 61.8, 107.1, 107.2, 118.8, 120.9, 121.0, 126.4, 126.5, 126.7, 127.4, 128.6, 128.7, 128.7, 128.7, 128.9, 128.9, 131.6, 132.0, 134.6, 134.7, 140.3, 140.4, 140.9, 148.6, 148.6.

HR-MS ($C_{26}H_{25}O_2N_4$; $[M+H]^+$, pos. ESI): calcd. 413.1972, found 413.1975.

HPLC (ChiralPAK AD-3, λ = 240 nm, *n*-heptane:*i*PrOH = 90:10, 0,5 ml/min, 22°C):
t_R (*Z*-product) = 11.1 min, 15.0 (major peak) min, 85 % *ee*.

(*E*)-2-(1,7-diphenylhept-4-en-3-yl)-5-nitro-2*H*-benzo[*d*][1,2,3]triazole (*N*^{2},*E*-product, 12e)



$C_{25}H_{24}N_4O_2$
(412.49)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5-nitro-1*H*-benzo[*d*][1,2,3]triazole (67.0 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (2.6 mg, 0.006 mmol, 3 %). *N*^{1}/*N*^{2}/*N*^{3}-ratio = 45:9:46 and *E/Z*-selectivity were determined by ^{1}H-NMR spectroscopy.

Analytical data of **12e**

TLC (SiO_2): R_f = 0.71 (hexanes:Et_2O = 1:1).

N^1/*N*^{2}/*N*^{3} 45:9:46.

E:Z 41:59.

^{1}H NMR (499.98 MHz, C_6D_6)

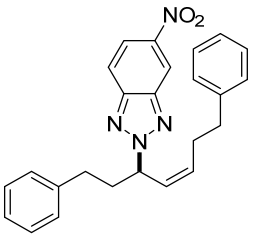
δ = 2.04-2.13 (m, 2H), 2.16-2.34 (m, 3H), 2.36-2.44 (m, 2H), 2.47-2.55 (m, 1H), 5.17-5.23 (m, 1H), 5.42 (dt, *J* = 15.5, 6.8 Hz, 1H), 5.70 (ddt, *J* = 15.4, 8.2, 1.4 Hz, 1H), 6.90-7.14 (m, 10H), 7.43 (d, *J* = 9.2 Hz, 1H), 7.81 (dd, *J* = 9.2, 2.1 Hz, 1H), 8.64 (d, *J* = 2.0 Hz, 1H).

^{13}C NMR (125.72 MHz, C_6D_6)

δ = 32.2, 34.0, 35.3, 37.2, 69.9, 116.3, 119.1, 120.7, 126.4, 126.6, 128.7, 128.7, 128.8, 128.8, 135.3, 140.6, 141.3, 143.0, 146.4, 146.7.

HR-MS ($C_{25}H_{25}O_2N_4$; $[M+H]^+$, pos. ESI): calcd. 413.1972, found 413.1977.

(*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-nitro-2*H*-benzo[*d*][1,2,3]triazole (*N*^{2},*Z*-product, 12f)



$C_{25}H_{24}N_4O_2$
(412.49)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5-nitro-1*H*-benzo[*d*][1,2,3]triazole (67.0 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (3.7 mg, 0.009 mmol, 4 %). *N*^{1}/*N*^{2}/*N*^{3}-ratio = 45:9:46 and *E/Z*-selectivity were determined by ^{1}H-NMR spectroscopy.

Analytical data of **12f***:*

:

TLC (SiO_2): R_f = 0.86 (hexanes:Et_2O = 1:1).

N^1/*N*^{2}/*N*^{3} 46:9:45.

E:Z 41:59.

^{1}H NMR (499.98 MHz, C_6D_6)

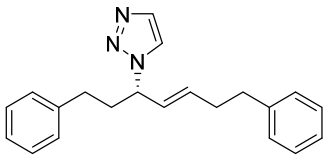
δ = 1.92-2.00 (m, 1H), 2.17-2.36 (m, 5H), 2.38-2.45 (m, 1H), 2.45-2.54 (m, 1H), 5.42 (dtd, *J* = 10.7, 7.6, 0.9 Hz, 1H), 5.55-5.62 (m, 1H), 5.79 (ddt, *J* = 10.7, 9.4, 1.5 Hz, 1H), 6.91-6.95 (m, 2H), 6.96-7.06 (m, 5H) 7.08-7.13 (m, 3H), 7.41 (d, *J* = 9.2 Hz, 1H), 7.80 (dd, *J* = 9.3, 2.1 Hz, 1H), 8.61 (d, *J* = 2.1 Hz, 1H).

^{13}C NMR (125.72 MHz, C_6D_6)

δ = 29.8, 32.1, 35.6, 37.5, 64.6, 116.3, 119.1, 120.7, 126.5, 126.6, 128.7, 128.7, 128.8 128.8, 140.6, 141.2, 143.0, 146.4.

HR-MS ($C_{25}H_{25}O_2N_4$; $[M+H]^+$, pos. ESI): calcd. 413.1972, found 413.1977.

(*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-1,2,3-triazole (*N*^{1}-product, 13)



$C_{21}H_{23}N_3$
(317.44)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 1*H*-1,2,3-triazole (34.5 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (61.2 mg, 0.192 mmol, 77 %). N^1/N^2-ratio = 94:6 and the *E/Z*-selectivity were determined by ^{1}H-NMR spectroscopy of the crude product.

Analytical data of **13***:*

TLC (SiO_2): R_f = 0.76 (hexanes:Et_2O = 1:1).

***E/Z*:** 92:8

^{1}H-NMR (400.13 MHz, $CDCl_3$):

δ = 2.16–2.26 (m, 1H), 2.33-2.44 (m,3H), 2.47-2.55 (m, 2H), 2.71 (t, *J* = 7.7 Hz, 2H), 4.96-5.03 (m,1H), 5.60–5.75 (m, 2H), 7.07–7.16 (m, 4H), 7.16-7.22 (m, 2H), 7.24-7.31 (m, 4H), 7.37 (s, 1H), 7.70 (s, 1H).

^{13}C-NMR (100.61 MHz, $CDCl_3$):

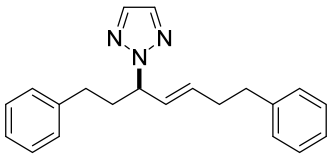
δ = 31.9, 33.8, 35.2, 36.6, 62.4, 121.9, 126.1, 126.3, 128.5, 128.5, 128.5, 128.6, 133.6, 134.7, 140.4, 141.1.

HR-MS ($C_{21}H_{24}N_3$; $[M+H]^+$, pos. ESI): calcd: 318.1965, found: 318.1961.

$[\alpha]_D^{25}$ +14.9° (c = 1.7, CH_2Cl_2).

HPLC (ChiralPAK AD-3, λ = 212 nm, *n*-heptane:*i*PrOH = 60:40, 0,5 ml/min, 22°C): t_R = 9.7 min, 10.2 (major peak) min, 83 % *ee*.

(*E*)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-1,2,3-triazole (N^2-product, 13b)



$C_{21}H_{23}N_3$
(317.44)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 1*H*-1,2,3-triazole (34.5 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired product as a colorless oil (4.0 mg, 0.013 mmol, 5 %). N^1/N^2-ratio = 94:6 and the *E/Z*-selectivity were determined by ^{1}H-NMR spectroscopy of the crude product.

Analytical data of **13b***:*

TLC (SiO_2): R_f = 0.84 (hexanes:Et_2O = 1:1).

***E/Z*:** 90:10

^{1}H-NMR (400.13 MHz, $CDCl_3$):

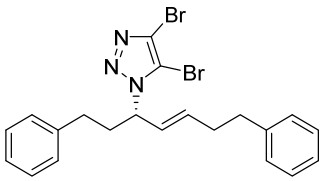
δ = 2.13-2.24 (m, 1H), 2.33-2.52 (m, 5H), 2.65-2.71 (m, 2H), 5.03-5.09 (m, 1H), 5.64-5.80 (m, 2H), 7.10-7.20 (m, 6H), 7.23-7.29 (m, 4H), 7.62 (s, 2H).

^{13}C-NMR (100.61 MHz, $CDCl_3$):

δ = 32.1, 34.0, 35.4, 36.7, 66.9, 126.0, 126.1, 128.4, 128.5, 128.6, 128.9, 133.8, 133.9, 141.0, 141.5.

HR-MS ($C_{21}H_{24}N_3$; $[M+H]^+$, pos. ESI): calcd: 318.1965, found: 318.1962.

(*S*,*E*)-2-(1,7-diphenylhept-4-en-3-yl)-5-methyl-2*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 14)



$C_{21}H_{21}Br_2N_3$
(475.23)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 4,5-dibromo-1*H*-1,2,3-triazole (112.4 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford the desired products as a colorless oil (110.0 mg, 0.231 mmol, 93%). N^1/N^2-ratio = >95:5 and the *E*/*Z*-selectivity were determined by ^{1}H-NMR spectroscopy.

Analytical data of **14***:*

TLC (SiO_2): R_f = 0.69 (hexanes:Et_2O = 1:1).

***E*/*Z*:** >95:5

^{1}H-NMR (499.98 MHz, C_6D_6):

δ = 1.73-1.82 (m, 1H), 1.98-2.12 (m, 2H), 2.14-2.23 (m, 2H), 2.25-2.40 (m, 3H), 4.89-4.95 (m, 1H), 5.26 (dt, *J* = 10.6, 7.7 Hz, 1H), 5.44 (ddt, *J* = 10.6, 9.3, 1.6 Hz, 1H), 6.81-6.85 (m, 2H), 6.90-6.94 (m, 2H), 7.02-7.07 (m, 2H) 7.08-7.15 (m, 4H).

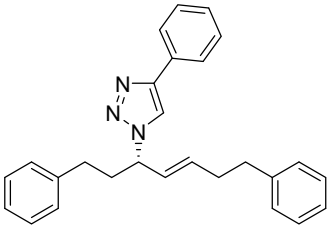
^{13}C-NMR (125.72 MHz, C_6D_6):
δ = 29.9, 31.8, 35.5, 36.0, 58.2, 111.7, 123.2, 126.5, 126.5, 127.4, 128.6, 128.7, 128.7, 128.7, 133.8, 140.2, 141.1.

HR-MS ($C_{21}H_{22}BrBr^{81}N_3$; $[M+H]^+$, pos. ESI): calcd. 476.0150, found 476.0155

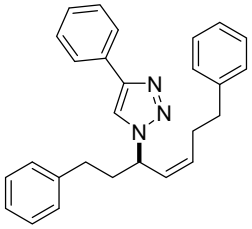
$[\alpha]_D^{25}$ -43.2° (c = 1.5, CH_2Cl_2).

HPLC (ChiralPAK AD-3, λ = 218 nm, *n*-heptane:EtOH = 95:5, 0,5 ml/min, 22°C): t_R = 7.5 min, 8.5 min (major peak), 84 % *ee*.

(*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-4-phenyl-1*H*-1,2,3-triazole (N^1-, *E*-product, 15) & (*Z*)-1-(1,7-diphenylhept-4-en-3-yl)-4-phenyl-1*H*-1,2,3-triazole (N^1-, *Z*-product, 15b)



$C_{27}H_{27}N_3$
(393.22)



$C_{27}H_{27}N_3$
(393.22)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 4-phenyl-1*H*-1,2,3-triazole (76.5 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford ta mixture of the desired products as a colorless oil (35.5 mg, 0.090 mmol, 36 %). N^1/N^2-ratio = 65:35 and the *E/Z*-selectivity were determined by ^{1}H-NMR spectroscopy.

Analytical data of **15** *and* **15b***:*

TLC (SiO_2): R_f = 0.50 (hexanes:Et_2O = 1:1).

***N*^{1}*/N*^{2}** 65:35.

***E/Z*:** 79:21

^{1}H-NMR (499.98 MHz, $CDCl_3$)

δ = 2.33-2.49 (m, 3H), 2.51-2.60 (m, 2H), 5.70-5.78 (m, 2H), 7.09-7.22 (m, 6H), 7.23-7.32 (m, 4H), 7.33-7.37 (m, 1H), 7.40-7.45 (m, 2H), 7.80-7.85 (m, 2H).

Characteristic *E*-product signals*:* δ = 2.20-2.29 (m, 1H), 2.70-2.75 (m, 2H), 5.67 (dd, *J* = 15.8, 7.2 Hz, 1H), 7.57 (s, 1H).

Characteristic *Z*-product signals*:* δ = 2.03-2.12 (m, 1H), 2.64-2.68 (m, 2H), 5.16-5.22 (m, 1H), 7.47 (s, 1H).

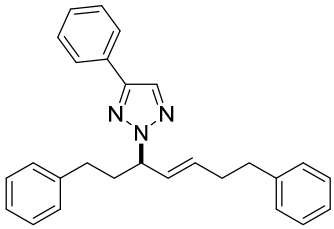
^{13}C-NMR (125.72 MHz, $CDCl_3$):

δ = 29.7, 31.9, 32.0, 33.9, 35.2, 35.3, 36.7, 37.4, 57.6, 62.6, 118.1, 118.2, 125.8, 125.9, 126.2, 126.3, 126.4, 126.4, 128.0 128.2, 128.2, 128.5, 128.5, 128.6, 128.6, 128.6, 128.7, 128.7, 128.9, 128.9, 130.9, 134.6, 137.8, 140.5, 140.5, 141.1, 141.1, 147.7.

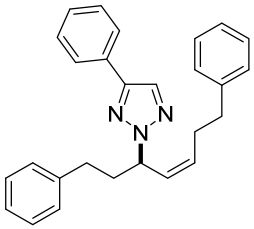
HR-MS ($C_{27}H_{28}N_3$; $[M+H]^+$, pos. ESI): calcd. 394.2278, found 394.2282.

HPLC (ChiralPAK AD-3, λ = 218 nm, *n*-heptane:*i*PrOH = 60:40, 0,5 ml/min, 22°C):
E-product: t_R = 15.6 min, 20.2 min (major peak); 92 % *ee*.

(*S*,*E*)-2-(1,7-diphenylhept-4-en-3-yl)-4-phenyl-2*H*-1,2,3-triazole (N^2-, *E*-product, 15c) & (*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-4-phenyl-2*H*-1,2,3-triazole (N^2-, *Z*-product, 15d)



$C_{27}H_{27}N_3$
(393.22)



$C_{27}H_{27}N_3$
(393.22)

The reaction was performed according to ***GP-C*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 4-phenyl-1*H*-1,2,3-triazole (76.5 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt = 5:1) to afford ta mixture of the desired products as a colorless oil (19.0 mg, 0.048 mmol, 19 %). N^1/N^2-ratio = 65:35 and the *E*/*Z*-selectivity were determined by ^{1}H-NMR spectroscopy.

Analytical data of **15c** *and* **15d***:*

TLC (SiO_2): R_f = 0.75 (hexanes:Et_2O = 1:1).

***E*/*Z*:** 71:29

^{1}H-NMR (499.98 MHz, $CDCl_3$)

δ = 2.43-2.57 (m, 3H), 5.66-5.76 (m, 1H), 5.77-5.86 (m, 1H), 7.13-7.21 (m, 6H), 7.23-7.30 (m, 4H), 7.33-7.38 (m, 1H), 7.41-7.46 (m, 2H), 7.79-7.83 (m, 2H).

Characteristic *E*-product signals*:* δ = 2.17-2.28 (m, 1H), 2.35-2.41 (m, 2H), 2.67-2.74 (m,2H), 5.03-5.09 (m, 1H), 7.86 (1H).

Characteristic *Z*-product signals*:* δ = 2.00-2.10 (m, 1H), 2.60-2.66 (m, 1H), 5.34-5.41 (m, 1H) 7.84 (s, 1H).

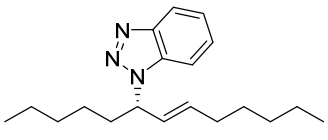
^{13}C-NMR (125.72 MHz, $CDCl_3$):

δ = 29.7, 32.1, 32.2, 34.1, 35.4, 35.6, 36.8, 37.3, 62.0, 67.2, 126.0, 126.1, 126.1, 126.2, 128.4, 128.4, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 129.0, 129.0, 129.0, 130.1, 130.1, 133.2, 133.8, 141.0, 141.1, 141.4, 141.5, 147.4, 147.5.

HR-MS ($C_{27}H_{28}N_3$; $[M+H]^+$, pos. ESI): calcd. 394.2278, found 394.2279.

HPLC (ChiralPAK AD-3, λ = 228 nm, *n*-heptane:EtOH = 95:5, 0,5 ml/min, 22°C):
E-product: t_R = 9.0 min (major peak), 20.2 min; 95 % *ee*.

(*S*,*E*)-1-(tridec-7-en-6-yl)-*1H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 16)



$C_{19}H_{29}N_3$
(299.24)

The reaction was performed according to ***GP-C*** with trideca-6,7-diene (45.1 mg) and 1*H*-benzo[*d*][1,2,3]triazole (59.6 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 20:1) to afford the desired product as a colorless oil (56.8 mg, 0.190 mmol, 76 %). N^1/N^2-ratio = >95:5 and *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the crude product.

Analytical data of **16***:*

TLC (SiO_2): R_f = 0.81 (hexanes:Et_2O = 1:1).

N^1/N^2: > 95:5.

E/Z: > 95:5.

^{1}H-NMR (400.13 MHz, C_6D_6):

δ = 0.75-0.80 (m, 3H), 0.83 (t, *J* = 7.4 Hz, 3H), 1.00-1.24 (m, 12H), 1.76-1.84 (m, 2H), 1.86-1.98 (m, 1H), 2.14-2.24 (m, 1H), 5.04-5.12 (m, 1H), 5.44 (dt, *J* = 15.5, 6.8 Hz, 1H), 5.64 (ddt, *J* = 15.4, 6.8, 1.4 Hz, 1H), 6.99 (ddd, *J* = 8.1, 6.7, 0.6 Hz, 1H), 7.10 (ddd, *J* = 8.1, 6.7, 0.8 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 1H), 8.04 (dt, *J* = 8.3 Hz, 1H).

^{13}C-NMR (100.61 MHz, C_6D_6):

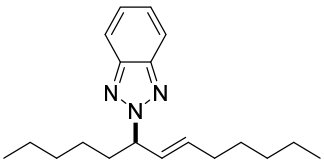
δ = 14.1, 14.2, 22.7, 22.8, 26.2, 28.9, 31.6, 32.4, 34.5, 62.3, 110.2, 123.6, 126.6, 128.6, 128.7, 133.0 134.4, 147.3.

HR-MS ($C_{19}H_{30}N_3$; $[M+H]^+$, pos. ESI): calcd: 300.2434, found: 300.2435.

$[\alpha]_D^{25}$ -5.8° (c = 1.6, CH_2Cl_2).

HPLC (ChiralPAK AD-3, λ = 212 nm, *n*-heptane:*i*-PrOH = 99.5:0.5, 0.5 ml/min, 22 °C):
t_R = 45.0 min (major peak), 49.5 min; 98 % ee.

(*E*)-2-(tridec-7-en-6-yl)-2*H*-benzo[*d*][1,2,3]triazole (N^2-product, 16b)



$C_{19}H_{29}N_3$
(299.24)

The reaction was performed according to ***GP-C*** with trideca-6,7-diene (45.1 mg) and 1*H*-benzo[*d*][1,2,3]triazole (59.6 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 20:1) to afford the desired product as a colorless oil (1.3 mg, 0.004 mmol, 2 %). N^1/N^2-ratio = >95:5 and *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **16b***:*

TLC (SiO_2): R_f = 0.92 (hexanes:Et_2O = 1:1).

N^1/N^2: > 95:5.

E/Z: >95:5.

^{1}H-NMR (499.98 MHz, C_6D_6):

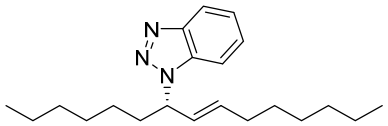
δ = 0.74-0.85 (m, 6H), 1.08-1.22 (m, 12H), 1.81-1.87 (m, 2H), 1.93-2.01 (m, 1H), 2.31-2.41 (m, 1H), 5.35-5.41 (m, 1H), 5.60 (dt, *J* = 15.3, 6.8 Hz, 1H), 5.98 (ddt, *J* = 15.3, 8.1, 1.5 Hz, 1H), 7.00-7.04 (m, 2H), 7.83-7.88 (m, 2H).

^{13}C-NMR (125.72 MHz, C_6D_6):

δ = 14.1, 14.2, 22.8, 22.8, 26.0, 28.9, 31.6, 31.7, 32.5, 35.1, 70.1, 118.6, 126.2, 128.6, 135.0, 144.9.

HR-MS ($C_{19}H_{30}N_3$; $[M+H]^+$, pos. ESI): calcd: 300.2434, found: 300.2437.

(*S*,*E*)-1-(pentadec-8-en-7-yl)-1*H*-benzo[d][1,2,3]triazole (*N*^{1}-product, 17)



$C_{21}H_{33}N_3$
(327.27)

The reaction was performed according to ***GP-C*** with pentadeca-7,8-diene (52.1 mg) and 1*H*-benzo[*d*][1,2,3]triazole (59.6 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 20:1) to afford the desired product as a colorless oil (70.1 mg, 0.214 mmol, 86 %). *N*^{1}/*N*^{2}-ratio = >95:5 and *E*/*Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the crude product.

Analytical data of **17***:*

TLC (SiO_2): R_f = 0.81 (hexanes:Et_2O = 1:1).

N^1/*N*^{2}: > 95:5.

E*/*Z: > 95:5.

^{1}H-NMR (400.13 MHz, C_6D_6):

δ = 0.83 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H), 1.04-1.24 (m, 16H), 1.77-1.85 (m, 2H), 1.88-2.00 (m, 1H), 2.15-2.27 (m, 1H), 5.06-5.13 (m, 1H), 5.45 (dt, *J* = 15.5, 6.7 Hz, 1H), 5.66 (ddt, *J* = 15.3, 6.9, 1.4 Hz, 1H), 6.99 (ddd, *J* = 8.4, 6.9, 1.0 Hz, 1H), 7.10 (ddd, *J* = 8.4, 6.9, 1.0 Hz, 1H), 7.24 (dt, *J* = 8.3, 1.0 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H).

^{13}C-NMR (100.61 MHz, C_6D_6):

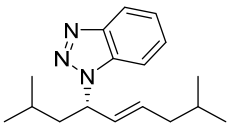
δ = 14.2, 14.3, 229., 23.0, 26.5, 29.1, 29.2, 29.2, 31.9, 32.0, 32.4, 34.5, 62.3, 110.2, 120.8, 123.6, 126.6, 128.6, 128.7, 133.0, 134.4, 147.3.

HR-MS ($C_{21}H_{34}N_3$; $[M+H]^+$, pos. ESI): calcd: 328.2747, found: 328.2749.

$[\alpha]_D^{25}$ -4.3° (c = 0.9, CH_2Cl_2).

HPLC (ChiralPAK AD-3, *λ* = 212 nm, *n*-heptane:*i*-PrOH = 99.5:0.5, 0.5 ml/min, 22 °C):
t_R = 31.3 min (major peak), 50.0 min (minor peak); 98 % ee.

(*S*,*E*)-1-(2,8-dimethylnon-5-en-4-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 18)



$C_{17}H_{25}N_3$
(271.20)

The reaction was performed according to ***GP-C*** with 2,8-dimethylnona-4,5-diene (38.1 mg) and 1*H*-benzo[*d*][1,2,3]triazole (59.6 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 20:1) to afford the desired product as a colorless oil (45.8 mg, 0.169 mmol, 68 %). *N*^{1}/*N*^{2}-ratio = >95:5 and *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **18***:*

TLC (SiO_2): R_f = 0.75 (hexanes:Et_2O = 1:1).

N^1/*N*^{2}: > 95:5

***E/Z*:** >95:5.

^{1}H-NMR (400.13 MHz, C_6D_6):

δ = 0.69 (d, *J* = 6.7 Hz, 3H), 0.72 (d, *J* = 6.8 Hz, 3H), 0.74 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.7 Hz, 3H), 1.25-1.41 (m, 2H), 1.65-1.70 (m, 2H), 1.75 (ddd, *J* = 14.1, 8.0, 6.5 Hz, 1H), 2.16 (ddd, *J* = 14.1, 9.2, 6.1 Hz, 1H), 5.24-5.31 (m, 1H), 5.40 (dt, *J* = 15.4, 7.1 Hz, 1H), 5.58 (ddt, *J* = 15.4, 6.9, 1.4 Hz, 1H), 6.98 (dd, *J* = 8.1, 7.2 Hz, 1H), 7.09 (dd, *J* = 8.1, 7.2 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 8.3 Hz, 1H).

^{13}C-NMR (100.61 MHz, C_6D_6):

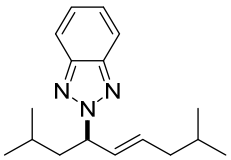
δ = 22.1, 22.3, 22.3, 22.5, 25.0, 28.3, 41.6, 43.2, 60.3, 110.1, 120.8, 123.6, 126.7, 130.0, 132.8, 147.3.

HR-MS ($C_{21}H_{30}N_3$; $[M+H]^+$, pos. ESI): calcd: 272.2121, found: 272.2121.

$[\alpha]_D^{25}$ -2.5° (c = 1.7, CH_2Cl_2).

HPLC (ChiralPAK AD-3, *λ* = 212 nm, *n*-heptane:*i*-PrOH = 95:5, 0.5 ml/min, 22 °C):
t_R = 8.8 min (major peak), 9.6 min (minor peak); 98 % ee.

(*E*)-2-(2,8-dimethylnon-5-en-4-yl)-2*H*-benzo[*d*][1,2,3]triazole (N^2-product, 18b)



$C_{17}H_{25}N_3$
(271.20)

The reaction was performed according to ***GP-C*** with 2,8-dimethylnona-4,5-diene (38.1 mg) and 1*H*-benzo[*d*][1,2,3]triazole (59.6 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 20:1) to afford the desired product as a colorless oil (1.3 mg, 0.005 mmol, 2 %). N^1/N^2-ratio = >95:5 and *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **18b***:*

TLC (SiO_2): R_f = 0.87 (hexanes:Et_2O = 1:1).

N^1/N^2: > 95:5

***E/Z*:** >95:5.

^{1}H-NMR (400.13 MHz, C_6D_6):

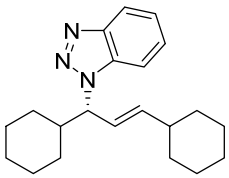
^{1}H NMR (400.13 MHz, $CDCl_3$) δ 0.71-0.77 (m, 9H), 0.87 (d, *J* = 6.6 Hz, 3H), 1.38-1.45 (m, 2H), 1.71-1.76 (m, 2H), 1.81 (ddd, *J* = 13.8, 7.9, 6.3 Hz, 1H), 2.35 (ddd, *J* = 13.8, 9.1, 6.2 Hz, 1H), 5.52-5.63 (m, 2H), 5.94 (ddt, *J* = 15.3, 8.1, 1.4 Hz, 1H), 7.00-7.06 (m, 2H), 7.82-7.88 (m, 2H).

^{13}C-NMR (100.61 MHz, C_6D_6):

δ = 22.2, 22.3, 22.3, 22.5, 25.1, 28.3, 41.7, 44.9, 68.2, 118.6, 126.1, 130.4, 133.5, 144.9.

HR-MS ($C_{21}H_{30}N_3$; $[M+H]^+$, pos. ESI): calcd: 272.2121, found: 272.2121.

(*S*,*E*)-1-(1,3-dicyclohexylallyl)-1*H*-benzo[d][1,2,3]triazole (*N*^{1}-product, 19)



$C_{21}H_{29}N_3$
(323.24)

The reaction was performed according to ***GP-C*** with 1,3-dicyclohexylpropa-1,2-diene (51.1 mg) and 1*H*-benzo[*d*][1,2,3]triazole (59.6 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 20:1) to afford the desired product as a colorless oil (71.4 mg, 0.221 mmol, 88 %). *N*^{1}/*N*^{2}-ratio = >95:5 and *E*/*Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **19***:*

TLC (SiO_2): R_f = 0.76 (hexanes:Et_2O = 1:1).

N^1/*N*^{2}: 93:7

E/*Z*: > 95:5.

^{1}H-NMR (400.13 MHz, C_6D_6):

δ = 0.73-1.23 (m, 11H), 1.38-1.78 (m, 9H), 1.83-1.92 (m, 1H), 2.17-2.29 (m, 1H), 4.76 (dd, *J* = 9.0, 9.0 Hz, 1H), 5.49 (dd, *J* = 15.5, 6.7 Hz, 1H), 5.85 (ddd, *J* = 15.5, 8.6, 1.4 Hz, 1H), 6.99 (ddd, *J* = 8.3, 6.9, 1.1 Hz, 1H), 7.10 (ddd, *J* = 8.2, 6.8, 1.0 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 1H), 8.03 (dt, *J* = 8.3, 1.0 Hz, 1H).

^{13}C-NMR (100.61 MHz, C_6D_6):

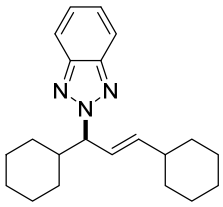
δ = 25.9, 26.2, 26.2, 26.2, 26.4, 26.5, 68.2, 110.0, 120.7, 123.5, 124.8, 126.7, 128.6, 133.3, 141.5, 147.0.

HR-MS ($C_{21}H_{30}N_3$; $[M+H]^+$, pos. ESI): calcd: 324.2434, found: 324.2433.

$[\alpha]_D^{25}$ 2.8° (c = 1.6, CH_2Cl_2).

HPLC (ChiralPAK AD-3, *λ* = 212 nm, *n*-heptane:*i*-PrOH = 95:5, 0.5 ml/min, 22 °C):
t_R = 13.7 min (minor peak), 14.9 min (major peak); 92 % ee.

(*E*)-2-(1,3-dicyclohexylallyl)-2*H*-benzo[*d*][1,2,3]triazole (N^2-product, 19b)



$C_{21}H_{29}N_3$
(323.24)

The reaction was performed according to ***GP-C*** with 1,3-dicyclohexylpropa-1,2-diene (51.1 mg) and 1*H*-benzo[*d*][1,2,3]triazole (59.6 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 20:1) to afford the desired product as a colorless oil (5.7 mg, 0.018 mmol, 7 %). N^1/N^2-ratio = >95:5 and *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **19b***:*

TLC (SiO_2): R_f = 0.89 (hexanes:Et_2O = 1:1).

N^1/N^2: 93:7

***E/Z*:** 94:6.

^{1}H-NMR (400.13 MHz, C_6D_6):

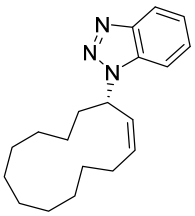
δ = 0.84-1.21 (m, 11H), 1.42-1.65 (m, 8H), 1.72-1.82 (m, 1H), 1.84-1.90 (m, 1H), 2.29-2.40 (m, 1H), 5.10 (dd, *J* = 9.3, 9.3 Hz, 1H), 5.60 (dd, *J* = 15.5, 6.6 Hz, 1H), 6.05 (ddd, *J* = 15.5, 9.2, 1.4 Hz, 1H), 7.01-7.07 (m, 2H), 7.84-7.89 (m, 2H).

^{13}C-NMR (100.61 MHz, C_6D_6):

δ = 26.0, 26.2, 26.2, 26.2, 26.4, 26.5, 30.0, 37.8, 32.9, 40.7, 43.1, 53.3, 75.8, 118.6, 125.4, 126.1, 128.6, 142.0, 144.8.

HR-MS ($C_{21}H_{30}N_3$; $[M+H]^+$, pos. ESI): calcd: 324.2434, found: 324.2434.

(*S*,*Z*)-1-(cyclotridec-2-en-1-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}, *Z*-product, 20)



$C_{19}H_{27}N_3$
(297.22)

The reaction was performed according to ***GP-C*** with cyclotrideca-1,2-diene (55.1 mg) and 1*H*-benzo[*d*][1,2,3]triazole (59.6 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 20:1) to afford a mixture of the desired product as a colorless oil (55.7 mg, 0.187 mmol, 75 %). *N*^{1}/*N*^{2} and *E*/*Z*-selectivities were determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **20***:*

TLC (SiO_2): R_f = 0.92 (hexanes:Et_2O = 1:1).

N^1/*N*^{2}: >95:5.

***Z*/*E*:** 85:15.

^{1}H-NMR (499.98 MHz, C_6D_6):

δ = 1.10-1.21 (m, 4H), 1.22-1.42 (m, 12H), 1.66-1.74 (m, 1H), 1.91-2.01 (m, 1H), 2.13-2.24 (m, 1H), 2.27-2.37 (m, 1H), 5.28 (td, *J* = 10.9, 4.1 Hz, 1H), 5.61 (td, *J* = 9.2, 5.1 Hz, 1H), 5.66 (ddd, *J* = 10.9, 9.2, 2.1 Hz, 1H), 6.98-7.03 (m, 1H), 7.08-7.12 (m, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H).

Significant E-product signals: δ = 4.77 (ddd, *J* = 11.3, 9.1, 3.3 Hz, 1H), 5.35 (ddd, *J* = 15.5, 9.9, 4.5 Hz, 1H), 5.53 (ddd, *J* = 15.3, 9.1, 1.3 Hz, 1H).

^{13}C-NMR (125.72 MHz, C_6D_6):
δ = 24.1, 24.4, 25.9, 26.0, 27.0, 27.2, 27.9, 28.6, 28.7, 34.4, 56.3, 110.1, 120.8, 123.6, 126.6, 128.6, 128.8, 135.7, 142.2.

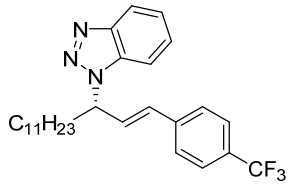
HR-MS ($C_{19}H_{28}N_3$; $[M+H]^+$, pos. ESI): calcd: 298.2278, found: 298.2275.

$[\alpha]_D^{25}$ -96.4° (c = 1.4, CH_2Cl_2).

HPLC (ChiralPAK AD-3, *λ* = 212 nm, *n*-heptane:EtOH = 90:10, 0.5 ml/min, 22 °C):
t_R = 8.4 min, 13.0 min (major peak); 88 % ee.

.

(*S*,*E*)-1-(1-(4-(trifluoromethyl)phenyl)tetradec-1-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}, *C*^{1}, *E*-product, 21)



$C_{27}H_{34}F_3N_3$
(457.59)

The reaction was performed according to ***GP-C*** with 1-(tetradeca-1,2-dien-1-yl)-4-(trifluoromethyl)benzene (84.6 mg) and 1*H*-benzo[*d*][1,2,3]triazole (59.6 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 5:1) to afford the desired product as a colorless oil (37.9 mg, 0.083 mmol, 33 %). *N*^{1}/*N*^{2}, *C*^{1}/*C*^{3} and *E*/*Z*-selectivities were determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **21***:*

TLC (SiO_2): R_f = 0.71 (hexanes:Et_2O = 1:1).

N^1/*N*^{2}: >95:5.

***C*^{1}/*C*^{3}:** 83:17.

***E/Z*:** *C*^{1}: 93:7, *C*^{3}: >95:5.

^{1}H-NMR (400.13 MHz, C_6D_6)

δ = 0.89-0.94 (m, 3H), 1.02-1.38 (m, 22H), 1.87-2.00 (m, 1H), 2.21-2.34 (m, 1H), 6.77-6.83 (m, 2H), 6.88-7.03 (m, 2H), 7.07-7-12 (m, 1H), 7.23-7.29 (m, 2H), 8.04-8.07 (m, 1H).

C^1*E*: δ = 5.10-5.19 (m, 1H), 6.11 (d, *J* = 16.0 Hz, 1H), 6.26 (dd, *J* = 16.0, 6.5 Hz,1H)

C^3*E*: δ = 5.44 (dt, *J* = 15.3, 6.8 Hz, 2H), 6.06 (ddt, *J* = 15.3, 7.3, 1.5 Hz, 1H), 6.16-6.22 (m, 1H).

C^{1}Z: δ = 5.51-i5.58 (m, 1H), 6.02 (dd, *J* = 11.5, 9.9 Hz, 1H).

^{13}C-NMR (100.61 MHz, C_6D_6)

δ = 14.4, 23.1, 26.5, 29.5, 29.7, 29.8, 30.0, 30.1, 30.1, 32.3, 34.4, 61.2, 109.8, 120.9, 124.0, 125.7 (q, *J* = 3.7 Hz), 127.1, 130.0 (q, *J* = 31.2 Hz), 130.5, 131.1, 133.0, 137.1, 139.6, 147.2.

^{19}F NMR (377 MHz, C_6D_6)

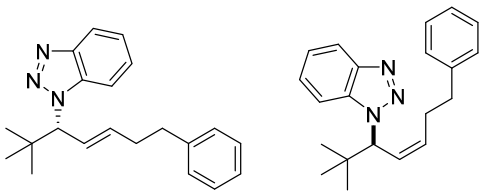
C^1*E*: δ = -62.24 (s, 3F).
C^3*E*: δ = -62.40 (s, 3F).
C^{1}Z: δ = -62.29 (s, 3F).

HR-MS ($C_{27}H_{35}N_3F_3$; $[M+H]^+$, pos. ESI): calcd. 458.2778, found 458.2777.

$[\alpha]_D^{25}$ -18.8° (c = 0.9, CH_2Cl_2).

HPLC (ChiralPAK AD-3, λ = 212 nm, *n*-heptane:EtOH = 90:10, 0.5 ml/min, 22 °C):
C[1]*E*-product: t_R = 12.5 min (major peak), 24.4 min; 42 % ee.

(*S*,*E*)-1-(2,2-dimethyl-7-phenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1},*C*^{1},*E*-product, 22) & (*Z*)-1-(2,2-dimethyl-7-phenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1},*C*^{1},*Z*-product, 22b)



$C_{21}H_{25}N_3$ (319.45) $C_{21}H_{25}N_3$ (319.45)

The reaction was performed according to ***GP-C*** with (6,6-dimethylhepta-3,4-dien-1-yl)benzene (50.0 mg) and 1*H*-benzo[*d*][1,2,3]triazole (59.6 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 5:1) to afford the desired product as a colorless oil (5.2 mg, 0. 016 mmol, 7 %). *N*^{1}/*N*^{2}, *C*^{1}/*C*^{3} and *E*/*Z*-selectivities were determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **22** *and* **22b***:*

TLC (SiO_2): R_f = 0.61 (hexanes:Et_2O = 1:1).

***N*^{1}/*N*^{2}:** 94:6.

***C*^{1}/*C*^{3}:** 93:7.

***E*/*Z*:** *C*^{1} 50:50, *C*^{3} >95:5.

^{1}H-NMR (499.98 MHz, C_6D_6):

Shared signals: δ = 0.85 (s, 9H), 2.00-2.28 (m, 3H), 2.33-2.46 (m, 1H), 6.84-6.87 (m, 1H), 6.90-6.94 (m, 1H), 6.94-7.14 (m, 6H), 7.99-8.03 (m, 1H).

C^1*E*-product: δ = 4.62 (d, *J* = 9.0, 1H), 5.38 (dt, *J* = 15.3, 6.8 Hz, 1H), 6.18 (ddt, *J* = 15.3, 8.9, 1.4 Hz, 1H).
C^1*Z*-product: δ = 5.14 (dd, *J* = 9.6, 0.9 Hz, 1H), 5.42-5.48 (m 1H), 6.16 (ddt, *J* = 11.0, 9.7, 1.6 Hz, 1H).
C^3*E*-product: δ = 0.79 (s, 9H), 5.02-5.08 (m, 1H), 5.58 (dd, *J* = 15.8, 6.9 Hz, 1H).

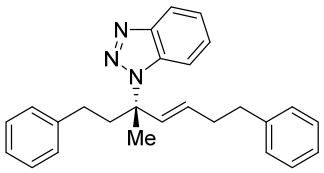
^{13}C-NMR (100.61 MHz, C_6D_6):

δ = 27.0, 27.2, 29.3, 29.9, 33.9, 35.4, 35.5, 36.6, 36.7, 36.8, 71.1, 110.1, 110.4, 120.5, 120.6, 123.4, 123.4, 125.4, 126.2, 126.3, 126.4, 126.7, 128.6, 128.6, 128.6, 128.7, 134.1, 134.7, 135.4, 141.4, 141.5, 146.3.

HR-MS ($C_{21}H_{26}N_3$; $[M+H]^+$, pos. ESI): calcd: 320.2121. found: 320.2121.

HPLC (ChiralPAK AD-3, λ = 212 nm, *n*-heptane:*i*-PrOH = 95:5, 0.5 ml/min, 22 °C):
C^1*E*-product: t_R = 12.8 min (major peak), 15.0 min (minor peak); 85 % ee.
C^1*Z*-product: t_R = 9.5 min (minor peak), 11.6 min (major peak); 75 % ee.

(*S*,*E*)-1-(3-methyl-1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1},*C*^{1},*E*-product, 23)



$C_{26}H_{27}N_3$
(381.22)

The reaction was performed according to ***GP-C*** with (3-methylhepta-3,4-diene-1,7-diyl)dibenzene (64.5 mg) and 1*H*-benzo[*d*][1,2,3]triazole (59.6 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 5:1) to afford the desired product as a colorless oil (42.3 mg, 0.111 mmol, 44 %). *N*^{1}/*N*^{2}, *C*^{1}/*C*^{3} and *E*/*Z*-selectivities were determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **23***:*

TLC (SiO_2): R_f = 0.73 (hexanes:Et_2O = 1:1).

N^1/*N*^{2}: 91:9.

C^1/C^3: >95:5

***E/Z*:** >95:5

^{1}H-NMR (499.98 MHz, C_6D_6):

^{1}H NMR (499.98 MHz, C_6D_6) δ = 1.65 (s, 3H), 2.07-2.17 (m, 3H), 2.29 – 2.37 (m, 1H), 2.34 (ddd, *J* = 13.7, 11.9, 4.7 Hz, 1H), 2.39-2.46 (m, 3H), 2.48-2.54 (m, 1H), 5.22 (dt, *J* = 15.8, 6.8 Hz, 1H), 5.44 (dt, *J* = 15.8, 1.4 Hz, 1H), 6.92-6.98 (m, 4H), 6.98-7.08 (m, 5H), 7.08-7.14 (m, 4H), 7.21 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H),

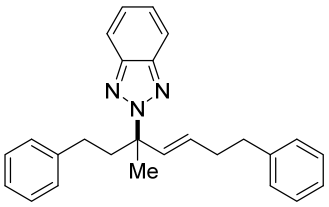
^{13}C-NMR (125.72 MHz, C_6D_6):
δ = 25.8, 30.1, 30.6, 34.1, 35.6, 42.5, 65.5, 112.6, 120.7, 123.4, 126.2, 126.4, 126.4, 128.7, 128.7, 128.7, 128.8, 130.4, 132.8, 134.4, 141.5, 141.9, 147.9.

HR-MS ($C_{21}H_{30}N_3$; $[M+H]^+$, pos. ESI): calcd: 382.2278. found: 382.2278.

$[\alpha]_D^{25}$ -0.5° (c = 1.2, CH_2Cl_2).

HPLC (Chiralcel OD-3, *λ* = 212 nm, *n*-heptane:EtOH = 99.5:0.5, 0.5 ml/min, 22 °C):
t_R = 29.2 min, 35.3 min (major peak); 24 % ee.

(*E*)-2-(3-methyl-1,7-diphenylhept-4-en-3-yl)-2*H*-benzo[*d*][1,2,3]triazole (*N*^{2},*C*^{1},*E*-product, 23b)



$C_{26}H_{27}N_3$
(381.22)

The reaction was performed according to ***GP-C*** with (3-methylhepta-3,4-diene-1,7-diyl)dibenzene (64.5 mg) and 1*H*-benzo[*d*][1,2,3]triazole (59.6 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 5:1) to afford the desired product as a colorless oil (4.2 mg, 0.011 mmol, 4 %). *N*^{1}/*N*^{2}, *C*^{1}/*C*^{3} and *E*/*Z*-selectivities were determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **23b***:*

TLC (SiO_2): R_f = 0.91 (hexanes:Et_2O = 1:1).

N^1/*N*^{2}: 91:9.

***E*/*Z*:** >95:5.

^{1}H-NMR (499.98 MHz, C_6D_6):

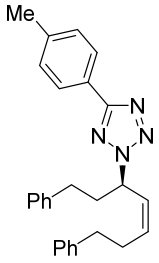
δ = 1.89 (s, 3H), 2.13-2.19 (m, 2H), 2.40-2.47 (m, 5H), 2.65-2.70 (m, 1H), 5.42 (dt, *J* = 15.7, 6.9 Hz, 1H), 6.07 (dt, *J* = 15.8, 1.5 Hz, 1H), 7.03-7.06 (m, 5H), 7.08-7.15 (m, 7H), 7.86-7.89 (m, 2H).

^{13}C-NMR (125.72 MHz, C_6D_6):

δ = 30.1, 30.8, 34.5, 35.7, 43.9, 70.3, 118.7, 126.2, 128.6, 128.7, 128.8, 128.8, 134.9, 142.0, 144.7.

HR-MS ($C_{26}H_{28}N_3$; $[M+H]^+$, pos. ESI): calcd: 382.2278. found: 382.2281.

(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-(p-tolyl)-2*H*-tetrazole (24)



$C_{27}H_{28}N_4$
(408.55)

The reaction was performed according to ***GP E*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5-(p-tolyl)-1*H*-tetrazole (48.1 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:Et_2O = 5:1) to afford the desired product as a colorless oil (98.0 mg, 0.240 mmol, 96 %). *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the crude product.

Analytical data of **25***:*

TLC (SiO_2): R_f = 0.43 (hexanes:Et_2O = 5:1).

Z/*E*: >95:5.

^{1}H-NMR (400.13 MHz, $CDCl_3$)

δ = 2.04-2.18 (m, 1H), 2.42 (s, 3H), 2.43-2.55 (m, 5H), 2.59-2.75 (m, 2H), 5.54-5.62 (m, 1H), 5.74 (dt, *J* = 10.8, 7.4 Hz, 1H), 5.83 (ddt, *J* = 10.8, 9.2, 1.3 Hz, 1H), 7.11-7.22 (m, 6 H), 7.24-7.32 (m, 6H), 8.02-8.07 (m, 2H).

^{13}C-NMR (100.61 MHz, $CDCl_3$):

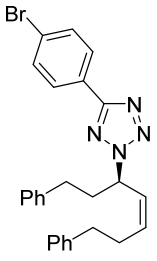
δ = 21.6, 29.7, 31.9, 35.4, 36.9, 60.8, 125.1, 126.3, 128.4, 127.0, 127.1, 128.5, 128.6, 128.6, 128.7, 129.7, 134.6, 140.4, 140.4, 165.1.

HR-MS ($C_{27}H_{29}N_4$; $[M+H]^+$, pos. ESI): calcd. 409.2387, found, 409.2390.

$[\alpha]_D^{25}$ -87.6° (c = 1.0, CH_2Cl_2).

HPLC (ChiralPAK AD-3, *λ* = 250 nm, *n*-heptane:EtOH = 90:10, 0.5 ml/min, 22°C):
t_R = 8.1 min(major peak), 9.5 min; 75 % *ee*.

(*R*,*Z*)-5-(4-bromophenyl)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazole (25)



$C_{26}H_{25}BrN_4$
(473.42)

The reaction was performed according to ***GP E* but at 80°C** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5-(4-bromophenyl)-1*H*-tetrazole (67.5 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:Et_2O = 5:1) to afford the desired product as a colorless oil (115.6 mg, 0.244 mmol, 98 %). *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **26***:*

TLC (SiO_2): R_f = 0.47 (hexanes:Et_2O = 5:1).

Z/*E*: 95:5.

^{1}H-NMR (500.42 MHz, C_6D_6)

δ = 1.84-1.93 (m, 1H), 2.12-2.19 (m, 2H), 2.19-2.35 (m, 4), 2.35-2.43 (m, 1H), 5.39 (dt, *J* = 10.8, 7.7 Hz, 1H), 5.43-5.49 (m, 1H), 5.64 (ddt, *J* = 10.8, 9.4, 1.6 Hz, 1H), 6.91-6.96 (m, 4H), 7.01-7.07 (m, 2H), 7.09-7.14 (m, 4H), 7.24-7.28 (m, 2H), 8.02-8.05 (m, 2H).

Characteristic *E*-product signals: δ = 5.05-5.11 (m, 1H), 5.33 (dt, *J* = 15.5, 6.7 Hz, 1H), 5.52 (ddt, *J* = 15.5, 8.0, 1.3 Hz, 1H).

^{13}C-NMR (125.83 MHz, C_6D_6):

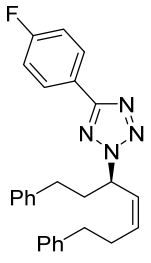
δ = 29.7, 31.9, 35.5, 36.9, 60.9, 124.8, 125.5, 126.6, 127.2, 127.4, 128.7, 128.7, 128.8, 128.8, 128.8, 132.4, 134.7, 140.5, 141.2, 164.7.

HR-MS ($C_{26}H_{26}N_4{}^{81}Br$; $[M+H]^+$, pos. ESI): calcd. 475.1315, found: 475.1317.

$[\alpha]_D^{25}$ -84.5° (c = 0.9, CH_2Cl_2).

HPLC (ChiralPAK AD-3, λ = 228 nm, *n*-heptane:EtOH = 90:10, 0.5 ml/min, 22°C):
t_R = 8.6 min (major-peak), 9.8 min; 81% *ee*.

(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-(4-fluorophenyl)-2*H*-tetrazole (26)



$C_{26}H_{25}FN_4$
(412.51)

The reaction was performed according to ***GP E*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5-(4-fluorophenyl)-1*H*-tetrazole (49.2 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:Et_2O = 5:1) to afford the desired product as a colorless oil (101.9 mg, 0.247 mmol, 99 %). *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **27**:

TLC (SiO_2): R_f = 0.38 (hexanes:Et_2O = 5:1).

Z/*E*: >95:5.

^{1}H-NMR (500.42 MHz, C_6D_6)

δ = 1.85-1.93 (m, 1H), 2.13-2.19 (m, 2H), 2.20-2.44 (m, 5H), 5.40 (dt, *J* = 10.9, 7.5 Hz, 1H), 5.45-5.51 (m, 1H), 5.66 (ddt, *J* = 10.9, 9.3, 1.6 Hz, 1H), 6.75-6.81 (m, 2H), 6.92-6.96 (m, 4H), 7.00-7.07 (m, 2H), 7.09-7.14 (m, 4H), 8.15-8.22 (m, 2H).

^{13}C-NMR (125.83 MHz, C_6D_6):

δ = 29.7, 31.9, 35.5, 36.9, 60.9, 116.2 (d, *J* = 22.1 Hz), 124.7, 126.4, 126.6, 127.3, 128.7, 128.8, 128.8, 128.8, 129.2, 129.2, 134.6, 140.5, 141.2, 164.3 (d, *J* = 249.6 Hz), 164.7.

^{19}F-NMR (376.76 MHz, C_6D_6, unified scale):

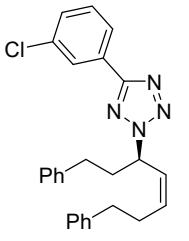
δ = -110.2.

HR-MS ($C_{26}H_{26}N_4F$; $[M+H]^+$, pos. ESI): calcd. 413.2136, found: 413.2139.

$[\alpha]_D^{25}$ -100.1° (c = 1.0, CH_2Cl_2).

HPLC (ChiralPAK AD-3, λ = 218 nm, *n*-heptane:EtOH = 90:10, 0.5 ml/min, 22°C):
t_R = 7.3 min (major peak), 8.3 min; 79 % ee.

(*R*,*Z*)-5-(3-chlorophenyl)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazole (27)



$C_{26}H_{25}ClN_4$
(428.96)

v

The reaction was performed according to ***GP E*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5-(3-chlorophenyl)-1*H*-tetrazole (54.2 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:Et_2O = 5:1) to afford the desired product as a colorless oil (109.1 mg, 0.246 mmol, 99 %). *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of**:28**:

TLC (SiO_2): R_f = 0.41 (hexanes:Et_2O = 5:1).

Z/*E*: >95:5.

^{1}H-NMR (500.42 MHz, C_6D_6)

δ = 1.83-1.92 (m, 1H), 2.12-2.18 (m, 2H), 2.19-2.35 (m, 4H), 2.36-2.43 (m, 1H), 5.39 (dt, *J* = 10.8, 7.6 Hz, 1H), 5.43-5.49 (m, 1H), 5.63 (ddt, *J* = 10.9, 9.4, 1.6 Hz, 1H), 6.83 (dd, *J* = 7.9, 7.9 Hz, 1H), 6.92-6.96 (m, 4H), 7.01-7.07 (m, 3H), 7.09-7.14 (m, 4H), 8.13 (ddd, *J* = 7.9, 1.3, 1.3 Hz, 1H), 8.13 (dd, *J* = 7.9, 1.8, 1.8 Hz, 1H),

^{13}C-NMR (125.83 MHz, C_6D_6):

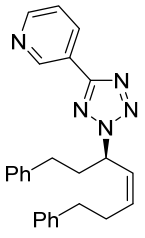
δ = 29.7, 31.9, 35.5, 36.9, 61.0, 125.2, 126.5, 126.6, 127.2, 127.3, 128.7, 128.8, 128.8, 128.8, 130.3, 130.3, 130.5, 134.7, 135.3, 141.2, 164.3.

HR-MS ($C_{26}H_{26}N_4Cl$; $[M+H]^+$, pos. ESI): calcd. 429.1841, found: 429.1842.

$[\alpha]_D^{25}$ -92.7° (c = 1.1, CH_2Cl_2).

HPLC (ChiralPAK AD-3, *λ* = 240 nm, *n*-heptane:EtOH = 98:2, 0.5 ml/min, 22°C):
t_R = 8.4 min (major peak), 9.0 min; 84 % ee.

(*R*,*Z*)-3-(2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazol-5-yl)pyridine (28)



$C_{25}H_{25}N_5$
(395.51)

The reaction was performed according to ***GP E* but at 80°C** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 3-(1*H*-tetrazol-5-yl)pyridine (44.2 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:Et_2O = 1:1) to afford the desired product as a colorless oil (77.3 mg, 0.195 mmol, 78 %). *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **29***:*

TLC (SiO_2): R_f = 0.33 (hexanes:Et_2O = 1:1).

Z/*E*: 91:9.

^{1}H-NMR (500.42 MHz, C_6D_6)

δ = 1.82-1.92 (m, 1H), 2.12-2.19 (m, 2H), 2.19-2.35 (m, 4H), 2.37-2.43 (m, 1H), 5.39 (dt, *J* = 10.7, 7.5 Hz, 1H), 5.43-5.49 (m, 1H), 5.63 (dt, *J* = 10.7, 9.4, 1.6 Hz, 1H), 6.70 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.91-6.96 (m, 4H), 7.00-7.07 (m, 2H), 7.09-7.14 (m, 4H), 8.28 (ddd, *J* = 7.9, 2.0, 2.0 Hz, 1H), 8.49 (dd, *J* = 4.9, 1.8 Hz, 1H), 9.77 (d, *J* = 2.0 Hz, 1H).

Characteristic *E*-product signals: δ = 5.05-5.11 (m, 1H), 5.51 (ddt, *J* = 15.5, 8.1, 1.3 Hz, 1H).

^{13}C-NMR (125.83 MHz, C_6D_6):

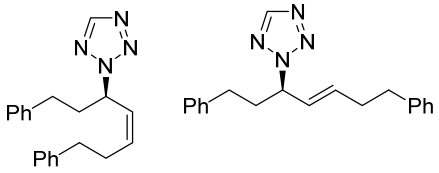
δ = 29.7, 31.9, 35.4, 36.9, 61.0, 123.6, 124.3, 126.5, 126.6, 127.1, 128.7, 128.8, 128.8, 128.8, 133.7, 134.7, 140.4, 141.2, 148.7, 151.5, 163.3.

HR-MS ($C_{25}H_{26}N_5$; $[M+H]^+$, pos. ESI): calcd. 396.2183, found: 333.2185.

$[\alpha]_D^{25}$ -65.9° (c = 0.9, CH_2Cl_2).

HPLC (ChiralPAK AD-3, *λ* = 228 nm, *n*-heptane:EtOH = 90:10, 0.5 ml/min, 22°C):
t_R = 12.0 min (major peak), 13.1 min (major peak); 56 % *ee*.

(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazole (29) & (*R*,*E*)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazole (29b)



$C_{20}H_{22}N_4$ (318.42) $C_{20}H_{22}N_4$ (318.42)

The reaction was performed according to ***GP E* but at 80°C** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 1*H*-tetrazole (21.0 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:Et_2O = 5:1) to afford the desired product as a colorless oil (49.9 mg, 0.157 mmol, 63 %). *E*/*Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **30** *and* **30b***:*

TLC (SiO_2): R_f = 0.31 (hexanes:Et_2O = 5:1).

Z/*E*: 50:50.

^{1}H-NMR (500.42 MHz, C_6D_6)

Shared signals: δ = 1.78-1.87 (m, 0.5H), 1.92-2.03 (m, 1.5H), 2.08-2.22 (m, 3H), 2.22-2.40 (m, 3H), 5.44-5.51 (m, 1H) 6.90-6.94 (m, 4H), 7.01-7.08 (m, 2H), 7.09-7.15 (m, 4H)

Z-product: δ = 5.34 (dt, *J* = 10.8, 7.6 Hz, 1H), 5.59 (ddt, *J* = 10.8, 9.4, 1.5 Hz, 1H), 8.14 (s, 1H).
E-product: δ = 5.05-5.11 (m, 1H) 5.30 (dt, *J* = 15.5, 6.7 Hz, 1H), 8.11 (s, 1H).

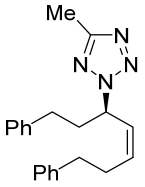
^{13}C-NMR (125.85 MHz, C_6D_6):

δ = 29.6, 31.9, 32.0, 33.9, 35.2, 35.4, 36.6, 36.9, 60.7, 65.9, 126.3, 126.4, 126.5, 126.6, 127.2, 127.8, 128.7, 128.7, 128.7, 128.7, 128.8, 128.8, 128.8, 128.8, 134.5, 135.2, 140.5, 140.6, 141.2, 141.4, 153.0, 153.0.

HR-MS ($C_{20}H_{23}N_4$; $[M+H]^+$, pos. ESI): calcd. 319.1917, found: 319.1918.

HPLC (ChiralPAK AD-3, *λ* = 212 nm, *n*-heptane:EtOH = 90:10, 0.5 ml/min, 22°C):
t_R = 7.1 min (*Z*-product), 7.6 min (*Z*-product, major-peak), 9.8 min(*E*-product), 11.0 min (*E*-product, major peak); 71% *ee* (*Z*-product), 86% *ee* (*E*-product).

(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-methyl-2*H*-tetrazole (30)



$C_{21}H_{24}N_4$
(332.45)

The reaction was performed according to ***GP E*** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5-methyl-1*H*-tetrazole (43.9 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes: Et_2O = 5:1) to afford the desired product as a colorless oil (45.7 mg, 0.142 mmol, 57 %). *E*/*Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **31***:*

TLC (SiO_2): R_f = 0.27 (hexanes:Et_2O = 5:1).

Z/*E*: 91:9.

^{1}H-NMR (500.42 MHz, C_6D_6)

δ = 1.82-1.89 (m, 1H), 2.12-2.18 (m, 2H), 2.18-2.27 (m, 2H), 2.27 (m, 3H), 2.28-2.43 (m, 3H), 5.36 (dt, *J* = 10.7, 7.5 Hz, 1H), 5.42-5.48 (m, 1H), 5.66 (ddt, *J* = 10.7, 9.3, 1.6 Hz, 1H), 6.91-6.97 (m, 4H), 7.02-7.06 (m, 2H), 7.09-7.14 (m, 4H).

Characteristic *E*-product signals: δ = 5.04-5.10 (m, 1H), 5.54 (ddt, *J* = 15.4, 8.0, 1.5 Hz, 1H).

^{13}C-NMR (125.83 MHz, C_6D_6):

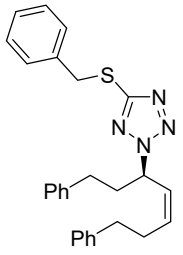
δ = 10.9, 29.7, 32.0, 35.5, 36.9, 60.4, 126.4, 126.5, 127.6, 128.7, 128.8, 128.8, 128.8, 134.2, 140.7, 141.3, 163.1.

HR-MS ($C_{21}H_{25}N_4$; $[M+H]^+$, pos. ESI): calcd. 333.2074, found: 333.2075.

$[\alpha]_D^{25}$ -75.0° (c = 1.3, CH_2Cl_2).

HPLC (ChiralPAK AD-3, *λ* = 212 nm, *n*-heptane:EtOH = 90:10, 0.5 ml/min, 22°C):
t_R = 6.0 min (minor peak), 6.5 min (major peak); 82 % ee.

(*R*,*Z*)-5-(benzylthio)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazole (31)



$C_{27}H_{28}N_4S$
(440.61)

The reaction was performed according to ***GP E* but at 80°C** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5-(benzylthio)-1*H*-tetrazole (67.7 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:Et_2O = 5:1) to afford the desired product as a colorless oil (80.6 mg, 0.183 mmol, 73 %). *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **32***:*

TLC (SiO_2): R_f = 0.41 (hexanes:Et_2O = 5:1).

N^2/N^1: 74:26

Z/*E*: >95:5.

^{1}H-NMR (500.42 MHz, C_6D_6)

δ = 1.72-1.82 (m, 1H), 2.05-2.11 (m, 2H), 2.11-2.18 (m, 2H), 2.19-2.24 (m, 1H), 2.24-2.29 (m, 1H), 2.32-2.39 (m, 1H), 4.23 (s, 2H), 5.30-5.37 (m, 2H), 5.53 (ddt, *J* = 10.8, 9.2, 1.6 Hz, 1H), 6.88-6.97 (m, 5H), 6.98-7.07 (m, 4H), 7.09-7.14 (m, 4H), 7.21-7.24 (m, 2H).

^{13}C-NMR (125.83 MHz, C_6D_6):

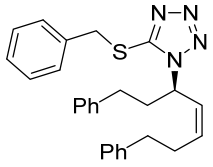
δ = 29.6, 31.8, 35.4, 36.5, 36.7, 61.1, 126.4, 126.5, 127.1, 127.6, 128.7, 128.7, 128.8, 128.8, 128.8, 134.6, 137.4, 140.5, 141.2, 164.0.

HR-MS ($C_{27}H_{29}N_4S$; $[M+H]^+$, pos. ESI): calcd. 441.2107, found: 441.2109.

$[\alpha]_D^{25}$ –101.1° (c = 0.9, CH_2Cl_2).

HPLC (ChiralPAK AD-3, λ = 218 nm, *n*-heptane:EtOH = 90:10, 0.5 ml/min, 22°C):
t_R = 9.1 min, 13.4 min (major peak); 84 % ee.

(*R*,*Z*)-5-(benzylthio)-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-tetrazole (31b)



$C_{27}H_{28}N_4S$
(440.61)

The reaction was performed according to ***GP E* but at 80°C** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5-(benzylthio)-1*H*-tetrazole (67.7 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:Et_2O = 5:1) to afford the desired product as a colorless oil (28.2 mg, 0.064 mmol, 26 %). *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **32b***:*

TLC (SiO_2): R_f = 0.21 (hexanes:Et_2O = 5:1).

N^2/N^1: 74:26

Z/*E*: >95:5.

^{1}H-NMR (500.42 MHz, C_6D_6)

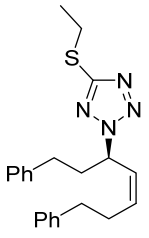
δ = 1.71-1.81 (m, 1H), 2.02-2.10 (m, 2H), 2.10-2.22 (m, 3H), 2.22-2.29 (m, 1H), 2.31-2.39 (m, 1H), 4.20 (d, *J* = 13.0 Hz, 1H), 4.28 (d, *J* = 13.0 Hz, 1H), 4.82-4.88 (m, 1H), 5.26 (dt, *J* = 10.9, 7.5 Hz, 1H), 5.38 (ddt, *J* = 10.9, 9.2, 1.6 Hz, 1H), 6.82-6.85 (m, 2H), 6.91-6.99 (m, 5H), 7.01-7.06 (m, 2H), 7.07-7.14 (m, 6H).

^{13}C-NMR (125.83 MHz, C_6D_6):

δ = 29.8, 31.8, 35.4, 36.0, 37.8, 55.6, 126.4, 126.5, 126.9, 128.6, 128.6, 128.7, 128.8, 129.3, 134.2, 136.5, 140.3, 141.2, 152.6.

HR-MS ($C_{27}H_{29}N_4S$; $[M+H]^+$, pos. ESI): calcd. 441.2107, found: 441.2110.

(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-(ethylthio)-2*H*-tetrazole (32)



$C_{22}H_{26}N_4S$
(378.54)

The reaction was performed according to ***GP E* but at 80°C** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5-(ethylthio)-1*H*-tetrazole (39.1 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:Et_2O = 5:1) to afford the desired product as a colorless oil (74.6 mg, 0.197 mmol, 79 %). *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the crude product.

Analytical data of **33***:*

TLC (SiO_2): R_f = 0.37 (hexanes:Et_2O = 5:1).

N^2/N^1: 79:21

Z/*E*: >95:5.

^{1}H-NMR (500.42 MHz, C_6D_6)

δ = 1.16 (t, *J* = 7.3 Hz, 3H), 1.76-1.85 (m, 1H), 2.07-2.14 (m, 2H), 2.14-2.23 (m, 2H), 2.23-2.30 (m, 2H), 2.33-2.40 (m, 1H), 2.96 (q, *J* = 7.3 Hz, 2H), 5.34 (dt, *J* = 10.8, 7.7 Hz, 1H), 5.36-5.42 (m, 1H), 5.57 (ddt, *J* = 10.8, 9.3, 1.6 Hz, 1H), 6.90-6.94 (m, 4H), 7.02-7.06 (m, 2H), 7.08-7.14 (m, 4H).

^{13}C-NMR (125.83 MHz, C_6D_6):

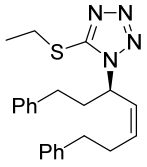
δ = 15.1, 26.3, 29.6, 31.8, 35.4, 36.7, 61.0, 126.3, 126.5, 127.1, 128.6, 128.7, 128.7, 134.5, 140.5, 141.2, 164.5.

HR-MS ($C_{22}H_{27}N_4S$ $[M+H]^+$, pos. ESI): calcd. 379.1951, found: 379.1954.

$[\alpha]_D^{25}$ -108.8° (c = 0.9, CH_2Cl_2).

HPLC (ChiralPAK AD-3, *λ* = 240 nm, *n*-heptane:EtOH = 98:2, 0.5 ml/min, 22°C):
t_R = 8.3 min, 8.9 min (major peak); 86 % *ee*.

(*R*,*Z*)-1-(1,7-diphenylhept-4-en-3-yl)-5-(ethylthio)-1*H*-tetrazole (32b)



$C_{22}H_{26}N_4S$
(378.54)

The reaction was performed according to ***GP E* but at 80°C** with 1,7-diphenylhepta-3,4-diene (62.1 mg) and 5-(ethylthio)-1*H*-tetrazole (39.1 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:Et_2O = 5:1) to afford the desired product as a colorless oil (19.3 mg, 0.051 mmol, 20 %). *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the crude product.

Analytical data of **33b***:*

TLC (SiO_2): R_f = 0.14 (hexanes:Et_2O = 5:1).

N^2/N^1: 79:21

Z/*E*: 87:13.

^{1}H-NMR (500.42 MHz, C_6D_6)

δ = 1.06 (t, *J* = 7.3 Hz, 3H), 1.79-1.87 (m, 1H), 2.11-2.17 (m, 2H), 2.18-2.35 (m, 4H), 2.35-2.45 (m, 1H), 2.88-2.94 (m, 2H), 4.88-4.94 (m, 1H), 5.31 (dt, *J* = 10.8, 7.6 Hz, 1H), 5.47 (ddt, *J* = 10.8, 9.3, 1.6 Hz, 1H), 6.86-6.91 (m, 2H), 6.94-6.98 (m, 2H), 7.02-7.07 (m, 2H), 7.10-7.16 (m, 4H).

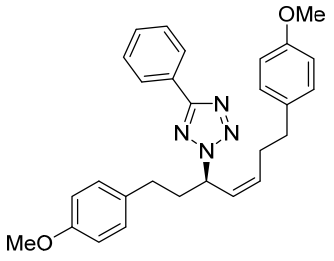
Characteristic *E*-product signals: δ = 4.49-4.55 (m, 1H).

^{13}C-NMR (125.83 MHz, C_6D_6):

δ = 27.8, 30.0, 32.0, 35.6, 36.1, 55.5, 126.5, 126.6, 127.2, 128.7, 128.7, 128.8, 128.8, 134.1, 140.4, 141.3, 153.0.

HR-MS ($C_{22}H_{27}N_4S$ $[M+H]^+$, pos. ESI): calcd. 379.1951, found: 379.1955.

(*R*,*Z*)-2-(1,7-bis(4-methoxyphenyl)hept-4-en-3-yl)-5-phenyl-2*H*-tetrazole (33)



$C_{28}H_{30}N_4O_2$
(454.57)

The reaction was performed according to ***GP E*** with 1,7-bis(4-methoxyphenyl)hepta-3,4-diene (77.1 mg) and 5-phenyl-2*H*-tetrazole (43.9 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 20:1) to afford the desired product as a colorless oil (109.1 mg, 0.240 mmol, 96 %). *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **34***:*

TLC (SiO_2): R_f = 0.18 (hexanes:Et_2O = 5:1).

Z/*E*: >95:5.

^{1}H-NMR (400.13 MHz, C_6D_6):

δ = 1.87-1.99 (m, 1H), 2.14-2.45 (m, 7H), 3.33 (s, 3H), 3.33 (s, 3H), 5.44 (dt. *J* = 10.7, 7.7 Hz, 1H), 5.52-5.60 (m, 1H), 5.73 (dd, *J* = 10.7, 9.3 Hz, 1H), 6.76-6.79 (m, 4H), 6.86-6.92 (m, 4H), 7.07-7.13 (m, 1H), 7.16-7.21 (m, 2H), 8.40-8.44 (m, 2H).

^{13}C-NMR (100.61 MHz, C_6D_6):

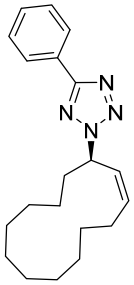
δ = 30.0, 31.1, 34.7, 37.3, 54.8, 54.8, 60.9, 114.3, 114.4, 127.3, 127.5, 128.7, 129.2, 129.7, 129.8, 130.3, 132.5, 133.2, 134.6, 158.7, 158.8, 165.6.

HR-MS ($C_{28}H_{31}O_2N_4$; $[M+H]^+$, pos. ESI): calcd. 455.2442, found 455.2443.

$[\alpha]_D^{25}$ -90.5° (c = 0.7, CH_2Cl_2).

HPLC (Lux Cellulose 4, λ = 212 nm, *n*-heptane:*i*-PrOH = 95:5 0.5 ml/min, 22 °C):
t_R = 13.1 (minor peak), 14.5 min (major peak); 82 % ee.

(*R*,*Z*)-2-(cyclotridec-2-en-1-yl)-5-phenyl-2*H*-tetrazole (34)



$C_{20}H_{28}N_4$
(324.47)

The reaction was performed according to ***GP E*** with cyclotrideca-1,2-diene (55.1 mg) and 5-phenyl-2*H*-tetrazole (43.9 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 20:1) to afford the desired product as a colorless oil (73.0 mg, 0.225 mmol, 90 %). *E*/*Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the products.

Analytical data of **35***:*

TLC (SiO_2): R_f = 0.30 (hexanes:Et_2O = 20:1).

Z*/*E: 95:5.

^{1}H-NMR (400.13 MHz, C_6D_6)

δ = 1.04-1.16 (m, 4H), 1.16-1.36 (m, 12H), 1.72-1.8 (m, 1H), 1.89-2.00 (m, 1H), 2.07-2.17 (m, 1H), 2.24-2.37 (m, 1H), 5.35 (ddd, *J* = 11.1, 9.8, 4.0 Hz, 1H), 5.63-5.75 (m, 2H), 7.08-7.13 (m, 1H), 7.16-7.20 (m, 2H), 8.40-8.45 (m, 2H).

^{13}C-NMR (100.61 MHz, C_6D_6):

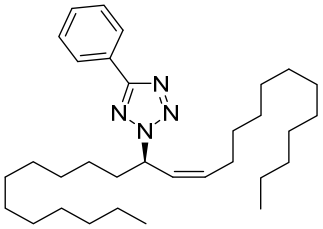
δ = 23.7, 24.4, 26.0, 26.1, 27.1, 27.1, 27.9, 28.5, 28.6, 34.8, 60.6, 127.2, 127.8, 129.1, 130.2, 136.8, 165.4.

HR-MS ($C_{20}H_{29}N_4$; $[M+H]^+$, pos. ESI): calcd. 325.2387, found, 325.2388.

$[\alpha]_D^{25}$ -188.1° (c = 0.9, CH_2Cl_2).

HPLC (ChiralPAK AD-3, λ = 218 nm, *n*-heptane:*i*-PrOH = 99.5:0.5, 0.5 ml/min, 22 °C):
t_R = 9.3 min, 12.2 min (major peak); 89 % ee.

(*R*,*Z*)-2-(pentacos-13-en-12-yl)-5-phenyl-2*H*-tetrazole (35)



$C_{32}H_{54}N_4$
(494.81)

The reaction was performed according to ***GP E*** with pentacosa-12,13-diene (87.1 mg) and 5-phenyl-2*H*-tetrazole (43.9 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 20:1) to afford the desired product as a colorless oil (91.3 mg, 0.185 mmol, 74 %). *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the crude product.

Analytical data of **36***:*

TLC (SiO_2): R_f = 0.47 (hexanes:Et_2O = 20:1).

Z/E: >95:5.

^{1}H-NMR (400.13 MHz, C_6D_6):

δ = 0.90-0.95 (m, 6H), 1.14-1.36 (m, 36H), 1.83-1.95 (m, 1H), 2.02-2.10 (m, 2H), 2.10-2.19 (m, 1H), 5.50 (dt, *J* = 10.7, 7.5 Hz, 1H), 5.66-5.73 (m, 1H), 5.80 (ddt, *J* = 10.8, 9.3, 1.6 Hz, 1H), 7.07-7.12 (m, 1H), 7.14-7.20 (m, 2H), 8.41-8.45 (m, 2H).

^{13}C-NMR (100.61 MHz, C_6D_6):

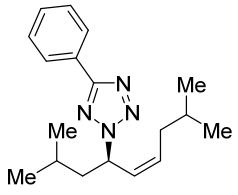
δ = 14.4, 23.1, 26.1, 28.0, 29.4, 29.6, 29.6, 29.8, 29.8, 29.8, 29.9, 30.0, 30.1, 30.1, 30.1, 32.4, 32.4, 35.8, 61.7, 127.2, 127.2, 129.1, 130.2, 135.6, 165.5.

HR-MS ($C_{32}H_{55}N_4$; $[M+H]^+$, pos. ESI): calcd. 495.4421, found 495.4424.

$[\alpha]_D^{25}$ -30.9° (c = 0.1, CH_2Cl_2).

HPLC (ChiralPAK AD-3, λ = 212 nm, *n*-heptane:*i*-PrOH = 99.5:0.5, 0.5 ml/min, 22 °C): t_R = 9.1 min (major peak), 9.7 min; 83 % ee.

(*R*,*Z*)-2-(2,8-dimethylnon-5-en-4-yl)-5-phenyl-2*H*-tetrazole (36)



$C_{18}H_{26}N_4$
(298.43)

The reaction was performed according to ***GP-E*** with 2,8-dimethylnona-4,5-diene (38.1 mg) and 5-phenyl-2*H*-tetrazole (43.9 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 20:1) to afford the desired product as a colorless oil (63.6 mg, 0.213 mmol, 85 %). *E*/*Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the product.

Analytical data of ***37****:*

TLC (SiO_2): R_f = 0.38 (hexanes:Et_2O = 20:1).

***Z*/*E*:** 94:6.

^{1}H-NMR (400.13 MHz, C_6D_6):

δ = 0.69 (d, *J* = 6.6 Hz, 3H), 0.75 (d, *J* = 6.6 Hz, 3H), 0.77 (d, *J* = 6.7 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H), 1.26-1.37 (m, 1H), 1.38-1.48 (m, 1H), 1.66 (ddd, *J* = 13.9, 7.7, 6.3 Hz, 1H), 1.91-1.97 (m, 2H), 2.09 (ddd, *J* = 13.9, 8.3, 6.4 Hz, 1H), 5.44 (dt, *J* = 9.9, 7.6 Hz, 1H), 5.75-5.86 (m, 2H), 7.06-7.11 (m, 1H), 7.13-7.19 (m, 2H), 8.40-8.44 (m, 2H).

^{13}C-NMR (100.61 MHz, C_6D_6):

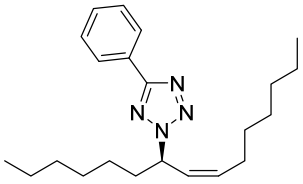
δ = 22.1, 22.2, 22.4, 22.5, 24.9, 28.6, 36.9, 44.5, 60.0, 127.2, 129.1, 130.2, 134.1, 165.5.

HR-MS ($C_{18}H_{27}N_4$; $[M+H]^+$, pos. ESI): calcd: 299.2230, found: 299.2229.

$[\alpha]_D^{25}$ -158.5° (c = 0.9, CH_2Cl_2).

HPLC (ChiralPAK AD-3, λ = 240 nm, *n*-heptane:*i*-PrOH = 99.6:0.4, 0.5 ml/min, 22 °C): t_R = 19.1 min (major peak), 21.0 min; 92 % ee.

(*R*,*Z*)-2-(pentadec-8-en-7-yl)-5-phenyl-2*H*-tetrazole (37)



$C_{22}H_{34}N_4$
(354.54)

The reaction was performed according to ***GP E*** with pentadeca-7,8-diene (52.1 mg) and 5-phenyl-2*H*-tetrazole (43.9 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 20:1) to afford the desired product as a colorless oil (81.7 mg, 0.230 mmol, 92 %). *E/Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the crude product.

Analytical data of **38***:*

TLC (SiO_2): R_f = 0.57 (hexanes:Et_2O = 20:1).

***Z*/*E*:** >95:5.

^{1}H-NMR (400.13 MHz, C_6D_6):

δ = 0.83 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H), 1.02-1.28 (m, 16H), 1.79-1.90 (m, 1H), 1.98-2.07 (m, 2H), 2.07-2.16 (m, 1H), 5.48 (dt, *J* = 10.7, 7.5 Hz, 1H), 5.62-5.70 (m, 1H), 5.77 (ddt, *J* = 10.7, 9.3 Hz, 1H), 7.06-7.12 (m, 1H), 7.13-7.19 (m, 2H), 8.41-8.45 (m, 2H).

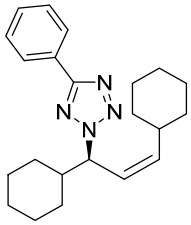
^{13}C-NMR (100.61 MHz, C_6D_6):
δ = 14.2, 14.3, 22.9, 23.0, 26.0, 28.0, 29.1, 29.2, 29.5, 31.9, 32.0, 35.7, 61.7, 127.2, 127.2, 129.1, 130.2, 135.5, 165.3.

HR-MS ($C_{22}H_{35}N_4$; $[M+H]^+$, pos. ESI): calcd. 355.2856, found 355.2856.

$[\alpha]_D^{25}$ -131.1° (c = 0.9, CH_2Cl_2).

HPLC (ChiralPAK AD-3, λ = 212 nm, *n*-heptane:*i*-PrOH = 98:2, 0.5 ml/min, 22 °C): t_R = 10.0 min (major peak), 12.1 min; 83 % ee.

(*R*,*Z*)-2-(1,3-dicyclohexylallyl)-5-phenyl-2*H*-tetrazole (38)



$C_{22}H_{30}N_4$
(350.51)

The reaction was performed according to ***GP E*** with 1,3-dicyclohexylpropa-1,2-diene (51.1 mg) and 5-phenyl-2*H*-tetrazole (43.9 mg). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 20:1) to afford the desired product as a colorless oil (80.9 mg, 0.231 mmol, 92 %). *E*/*Z*-selectivity was determined by ^{1}H-NMR spectroscopy of the products.
Analytical data of **:**

Analytical data of **39**:

TLC (SiO_2): R_f = 0.36 (hexanes:Et_2O = 20:1).

***Z*/*E*:** 82:18.

^{1}H-NMR (400.13 MHz, C_6D_6):
Shared signals: δ = 0.78-1.09 (m, 8H), 1.13-1.27 (m, 3H) 1.43-1.64 (m, 8H), 1.73-1.83 (m, 1H), 2.04-2.15 (m, 1H), 2.39-2.52 (m, 1H), 7.06-7.11 (m, 1H), 7.12-7.16 (m, 2H), 8.40-8.45 (m, 2H).

Z-product: δ = 5.41 (dd, *J* = 10.5, 10.5 Hz, 1H), 5.49 (dd, *J* = 9.8, 9.5 Hz, 1H), 5.75 (dd, *J* = 10.5, 10.2 Hz, 1H).
E-product: δ = 4.95 (dd, *J* = 9.2, 9.1 Hz, 1H), 5.83 (ddd, *J* = 15.5, 9.2, 1.3 Hz, 1H).

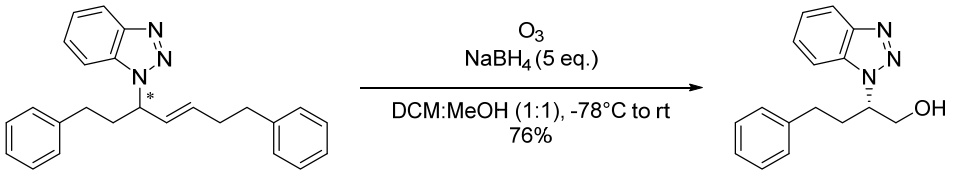
^{13}C-NMR (100.61 MHz, C_6D_6):
δ = 25.8, 25.9, 26.1, 26.1, 26.3, 29.6, 29.7, 33.1, 33.2, 66.9, 124.0, 127.3, 129.1, 130.2, 142.0, 165.5.

HR-MS ($C_{22}H_{31}N_4$; $[M+H]^+$, pos. ESI): calcd. 351.2543, found, 351.2544.

HPLC (ChiralPAK AD-3, *λ* = 218 nm, *n*-heptane:*i*-PrOH = 99.5:0.5, 0.5 ml/min, 22 °C):
Z-product: t_R = 9.0 (minor peak), 10.4 min (major peak); 91 % ee.
E-product: t_R = 11.2 (major peak), 11.6 min (minor peak); 97 % ee.

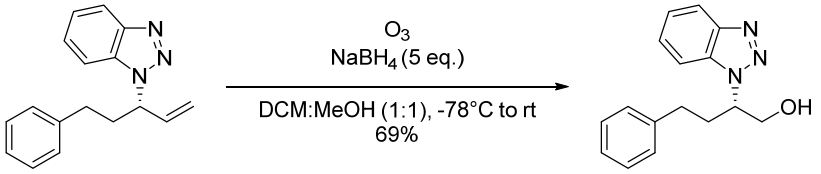
Determination of Absolute Configuration, Deuteration Experiments and Detailed mechanism

For determination of the absolute configuration of the triazoles compound **3** of this publication as well as an allylated benzotriazole with known absolute configuration[5] were cleaved by ozonolysis followed by reductive workup to receive the corresponding alcohols. Comparison of the values of optical rotation revealed the absolute configuration. Both alcohols showed a positive sign.



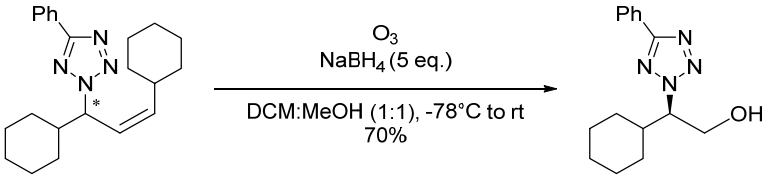
3

$[\alpha]_D^{25}$ = +2.39 (c = 1.34, CH_2Cl_2)



$[\alpha]_D^{25}$ = +2.31 (c = 1.30, CH_2Cl_2)

For determination of the absolute configuration of the tetrazoles compound **38** of this publication was cleaved by ozonolysis followed by reductive workup to receive the corresponding alcohol. Comparison of the value of optical rotation with the literature[6] revealed the absolute configuration.



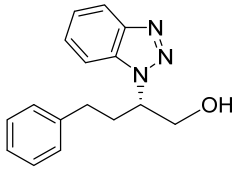
38

$[\alpha]_D^{25}$ = +15.1 (c = 0.37, CH_2Cl_2)

General procedure for ozonolysis with reductive work up

A solution of the alkene (1.0 eq) in DCM/MeOH (1:1, 0.1 M) was cooled to -78°C and O_3 was bubbled directly into the solution until a blue color appeared in the solution. N_2 was bubbled through the solution until the blue color disappeared. $NaBH_4$ (5.0 eq.) was added at -78°C and the mixture was allowed to warm to rt. After stirring it for 1 hour at rt an aq. solution of HCl (1 M) was added for quenching the reaction and the mixture was neutralized by aq. $NaHCO_3$ (sat.) The aqueous phase was extracted with DCM (3x) and the combined organic layers were washed with brine and dried over Na_2SO_4. The solvents were removed under reduced pressure and the crude product was purified by flash column chromatography (SiO_2, hexanes:AcOEt).

(*S*)-2-(1*H*-benzo[d][1,2,3]triazol-1-yl)-4-phenylbutan-1-ol



$C_{16}H_{17}N_3O$
(267.33)

The reaction was performed according to the general procedure above with compound **3** (367.5 mg, 1.0 mmol) and $NaBH_4$ (189.2 mg, 5.0 mmol, 5.0 eq.). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 5:1) to afford the desired product as a colorless oil (203.2 mg, 0.760 mmol, 76%).

Analytical data:

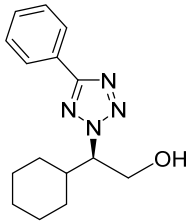
TLC (SiO_2): R_f = 0.44 (hexanes:Et_2O = 1:1).

^{1}H-NMR (400.13 MHz, $CDCl_3$):
δ = 2.32-2.41 (m, 1H), 2.44-2.66 (m, 3H), 4.10 (dd, *J* = 11.8, 3.7 Hz, 1H), 4.29 (dd, *J* = 11.8, 7.5 Hz, 1H), 4.72-4.80 (m, 1H), 7.02-7.06 (m, 2H), 7.16-7.21 (m, 1H), 7.22-7.32 (m, 3H), 7.37-7.46 (m, 2H), 7.84-7.89 (m, 1H).

^{13}C-NMR (100.61 MHz $CDCl_3$):
δ = 32.1, 32.4, 61.1, 65.2, 109.9, 119.8, 119.9, 124.2, 126.5, 127.4, 128.5, 128.7, 133.9, 134.0, 140.3, 145.6.

HR-MS ($C_{16}H_{18}ON_3$; $[M+H]^+$, pos. ESI): calcd. 268.1444, found, 268.1446.

(*R*)-2-cyclohexyl-2-(5-phenyl-2*H*-tetrazol-2-yl)ethan-1-ol



$C_{15}H_{20}N_4O$
(272.35)

The reaction was performed according to the general procedure above with compound **38** (13.4 mg, 0.038 mmol) and $NaBH_4$ (7.2 mg, 0.19 mmol, 5.0 eq.). The crude product was purified by flash column chromatography (SiO_2, hexanes:EtOAc = 10:1) to afford the desired product as a colorless oil (7.2 mg, 0.26 mmol, 70%).

Analytical data:

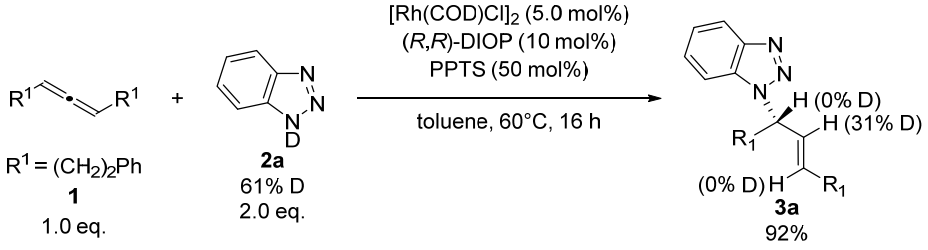
TLC (SiO_2): R_f = 0.36 (hexanes:Et_2O = 5:1).

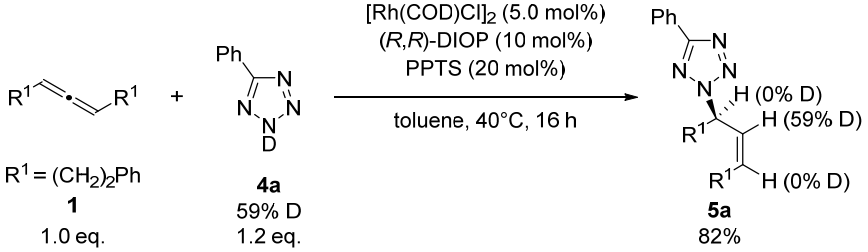
^{1}H-NMR (400.13 MHz, $CDCl_3$):
δ = 0.99-1.08 (m, 1H), 1.12-1.34 (m, 5H), 1.58 (br. s, 1H), 1.64-1.72 (m, 2H), 1.77-1.84 (m, 1H), 1.90-1.98 (m, 1H), 2.13-2.23 (m. 1H), 4.10 (dd, *J* = 12.3, 3.1 Hz, 1H), 4.31 (dd, *J* = 12.3, 7.2 Hz, 1H), 4.73 (ddd, *J* = 8.9, 7.2, 3.1 Hz, 1H), 7.46-7.53 (m, 3H), 8.14-8.19 (m, 2H).

^{13}C-NMR (100.61 MHz $CDCl_3$):
δ = 25.7, 25.9, 26.1, 29.4, 29.7, 39.0, 62.1, 71.6, 127.0, 129.0, 130.5, 165.1.

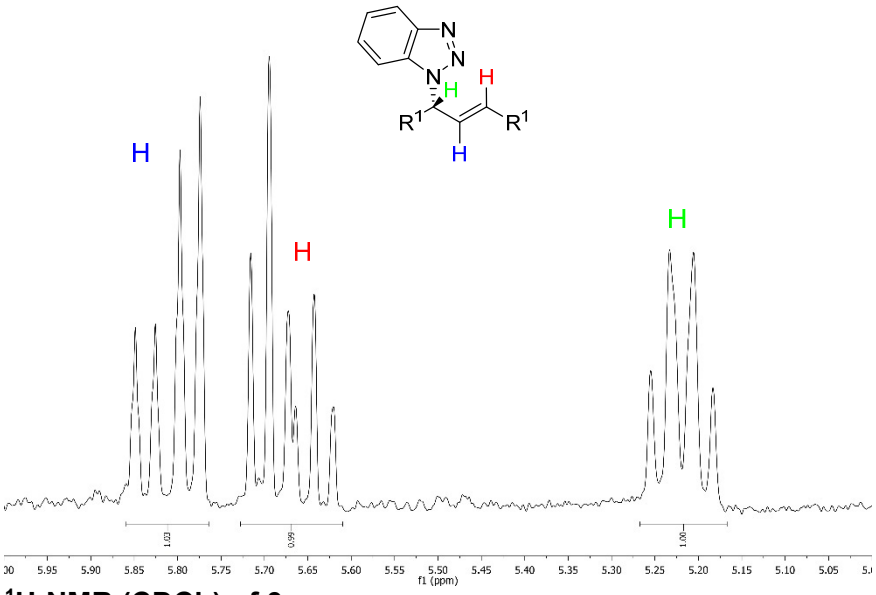
HR-MS ($C_{15}H_{21}ON_4$; $[M+H]^+$, pos. ESI): calcd. 273.1710, found, 273.1712.

Deuteration Experiments

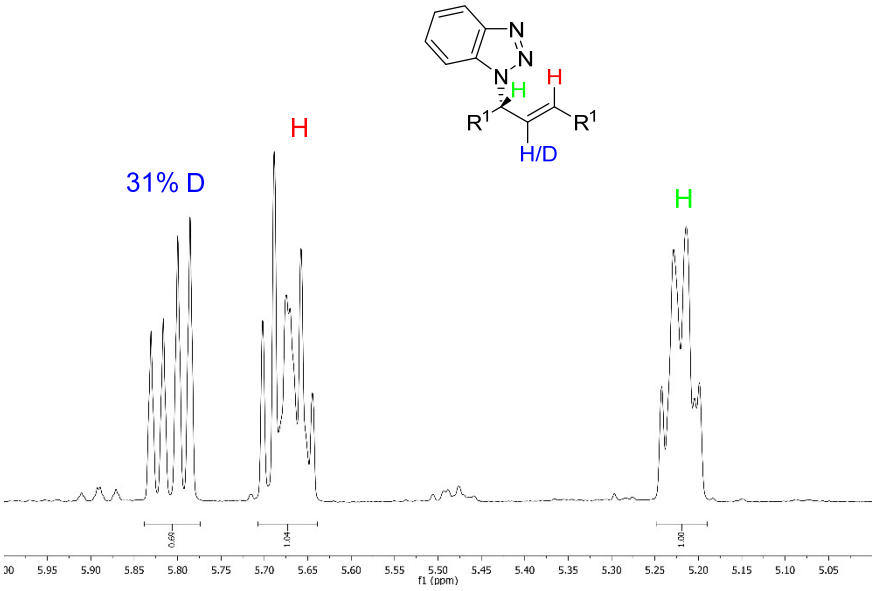




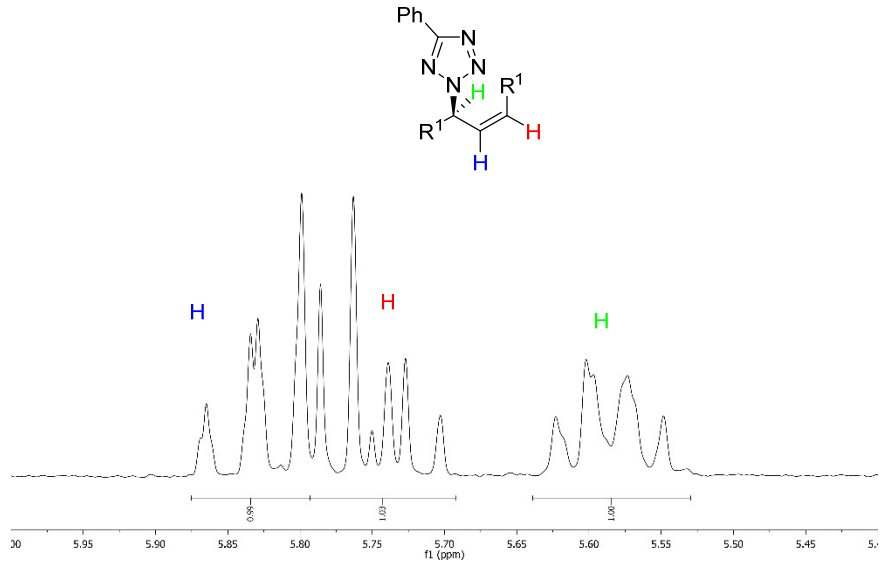
^{1}H-NMR ($CDCl_3$) of 3:



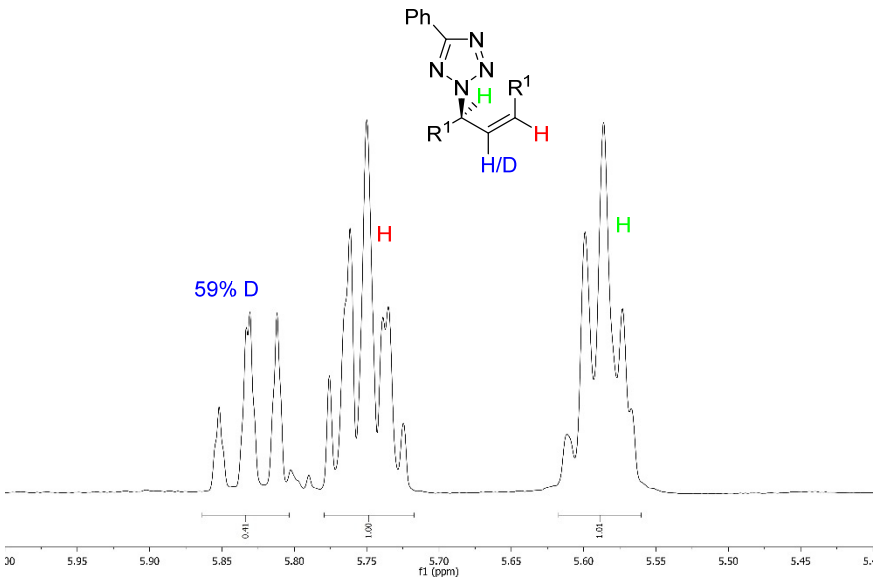
^{1}H-NMR ($CDCl_3$) of 3a:



^{1}H-NMR ($CDCl_3$) of 5:



^{1}H-NMR ($CDCl_3$) of 5a:



References

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[2] P. Kielbasinski, M. Albrycht, M. Mikolajczyk, M. W. Wieczorek, W. R. Majzner, A. Filipczak, P. Ciolkiewicz, *Heteroatom Chem.* **2005**, *16*, 93–103.

[3] C. F. Hobbs, W. S. Knowles, *J. Org. Chem.* **1981**, *46*, 4422–4427.

[4] M. J. Johansson, D. J. Gorin, S. T. Staben, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 18002–18003.

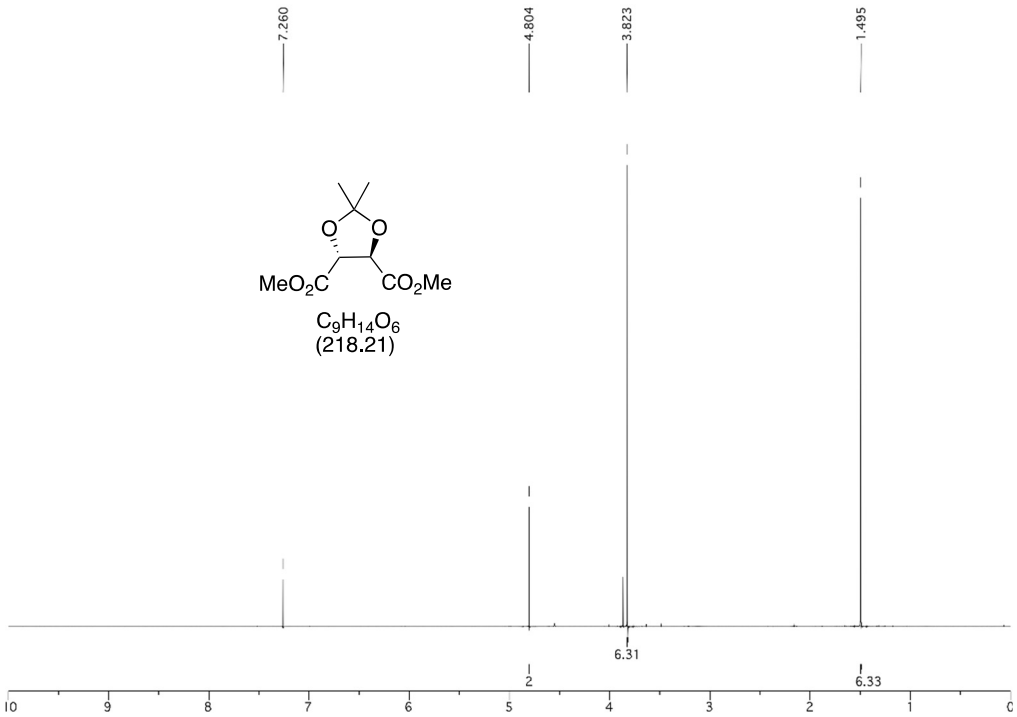
[5] D. Berthold, B. Breit, *Org. Lett.* **2018**, *20*, 598–601.

[6] K. Xu, W. Raimondi, T. Bury, B. Breit, *Chem. Commun.* **2015**, *51*, 10861–10863.

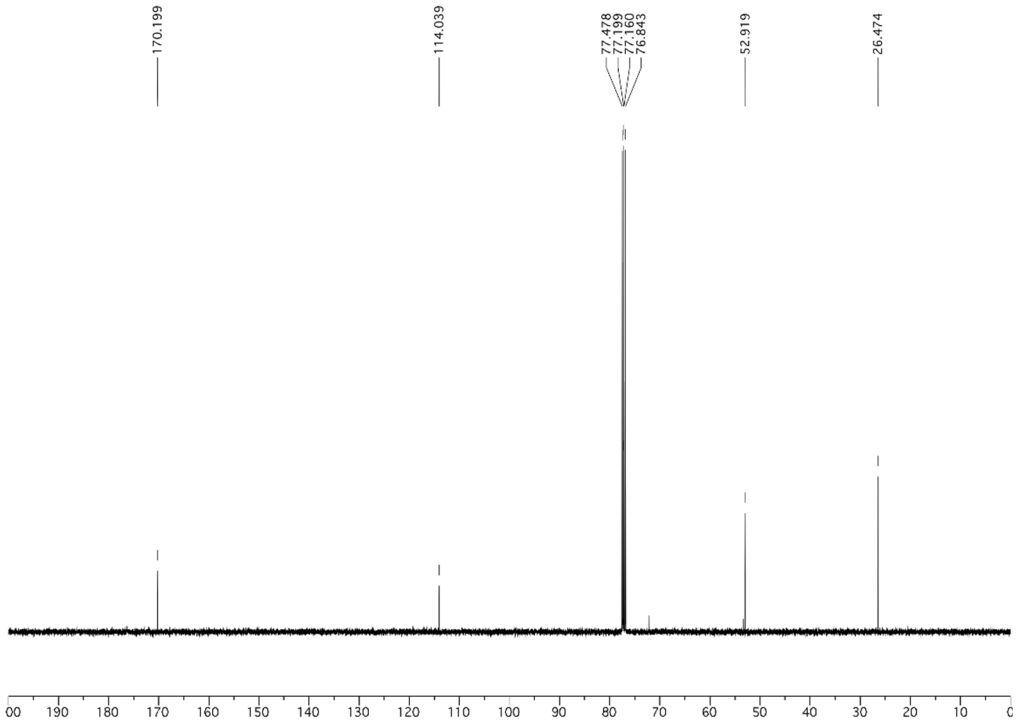
NMR spectra & HPLC chromatograms

(*R*,*R*)-diethyl 2,3-O-isopropylidentartrate

^{1}H-NMR (400.13 MHz, $CDCl_3$):

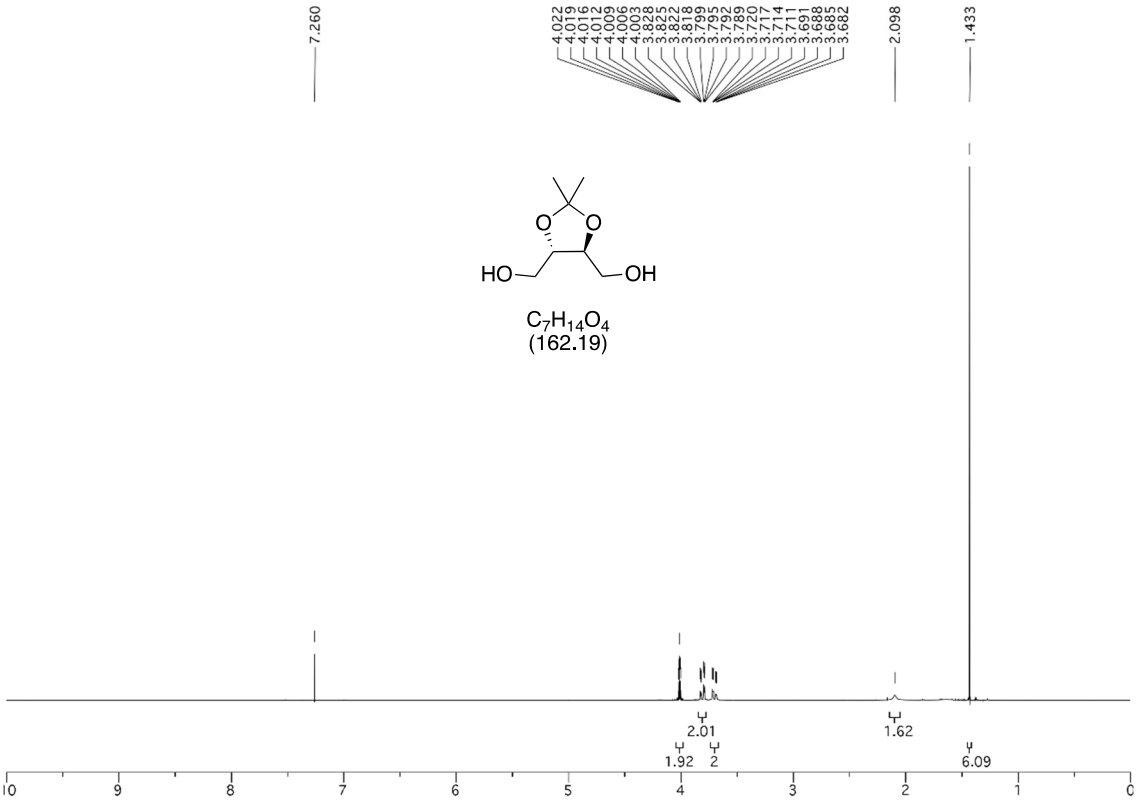


^{13}C-NMR (100.61 MHz, $CDCl_3$):

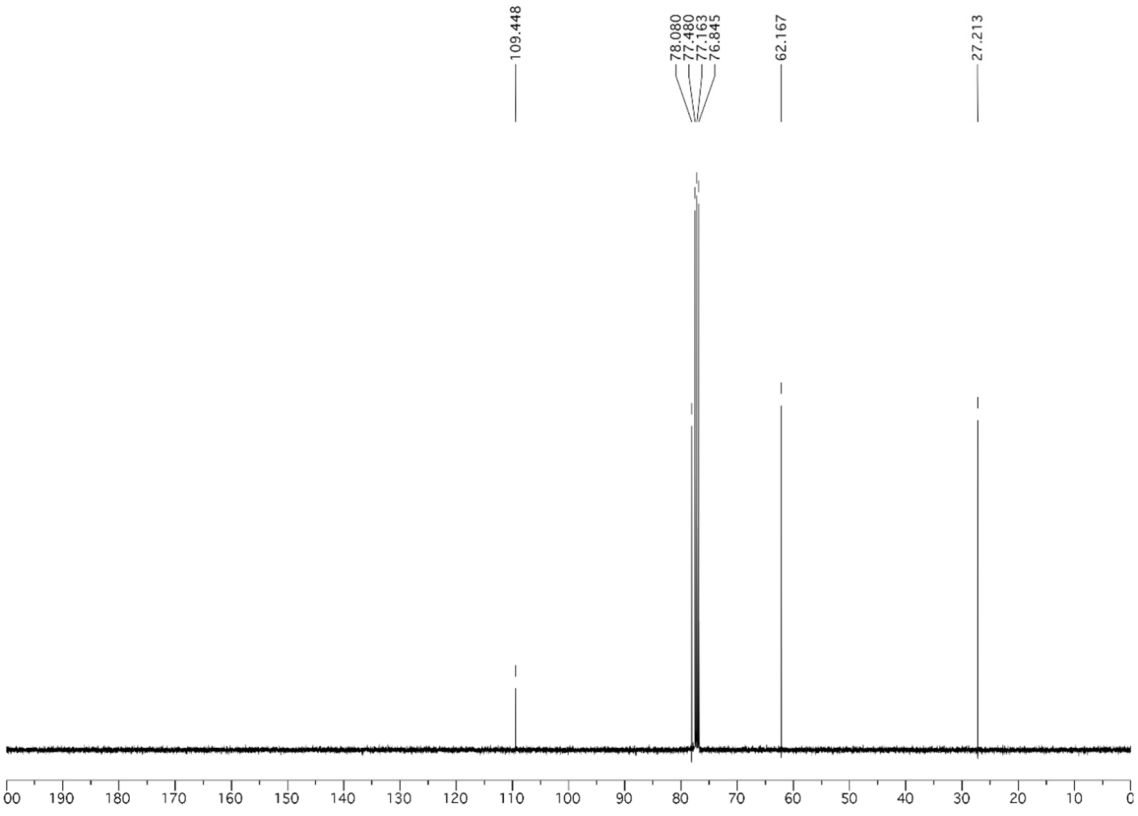


(*S*,*S*)-1,4-dihydroxy 2,3-O-isopropylidenbutane

^{1}H-NMR (400.13 MHz, $CDCl_3$):

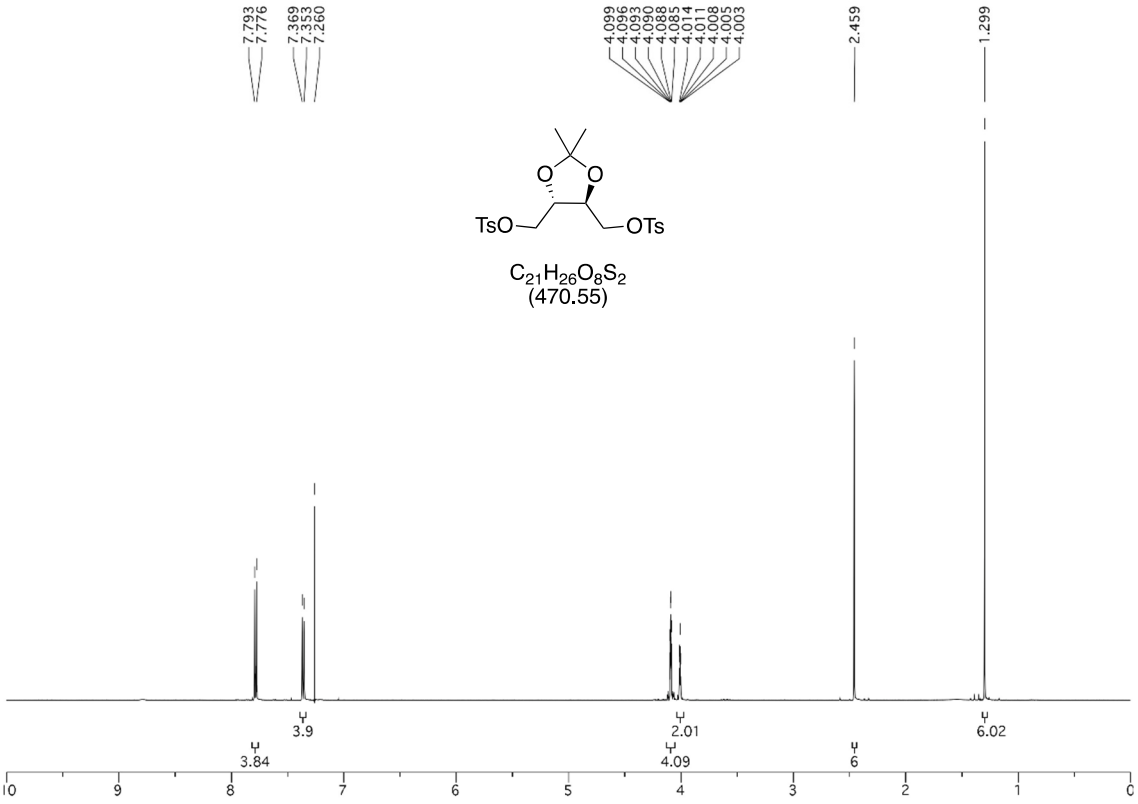


^{13}C-NMR (100.61 MHz, $CDCl_3$):

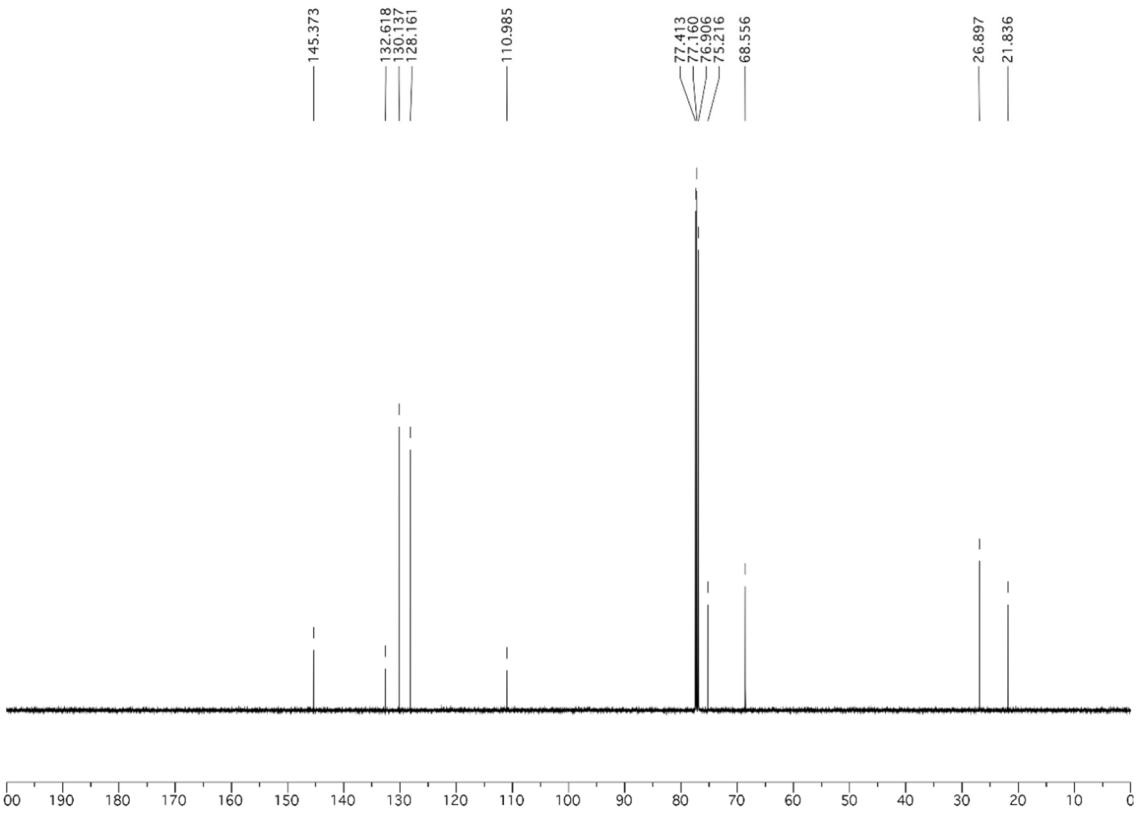


(*S*,*S*)-1,4-ditosyl 2,3-O-isopropylidenbutane

^{1}H-NMR (500.10 MHz, $CDCl_3$):

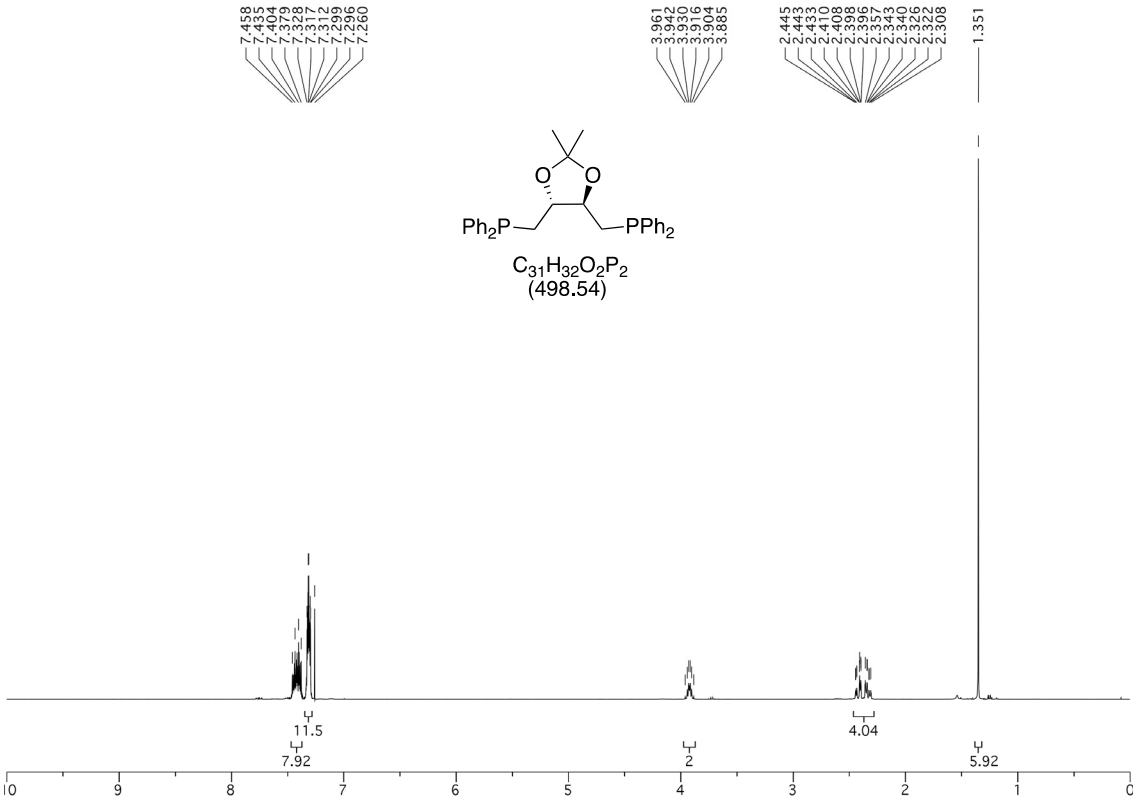


^{13}C-NMR (125.75 MHz, $CDCl_3$):

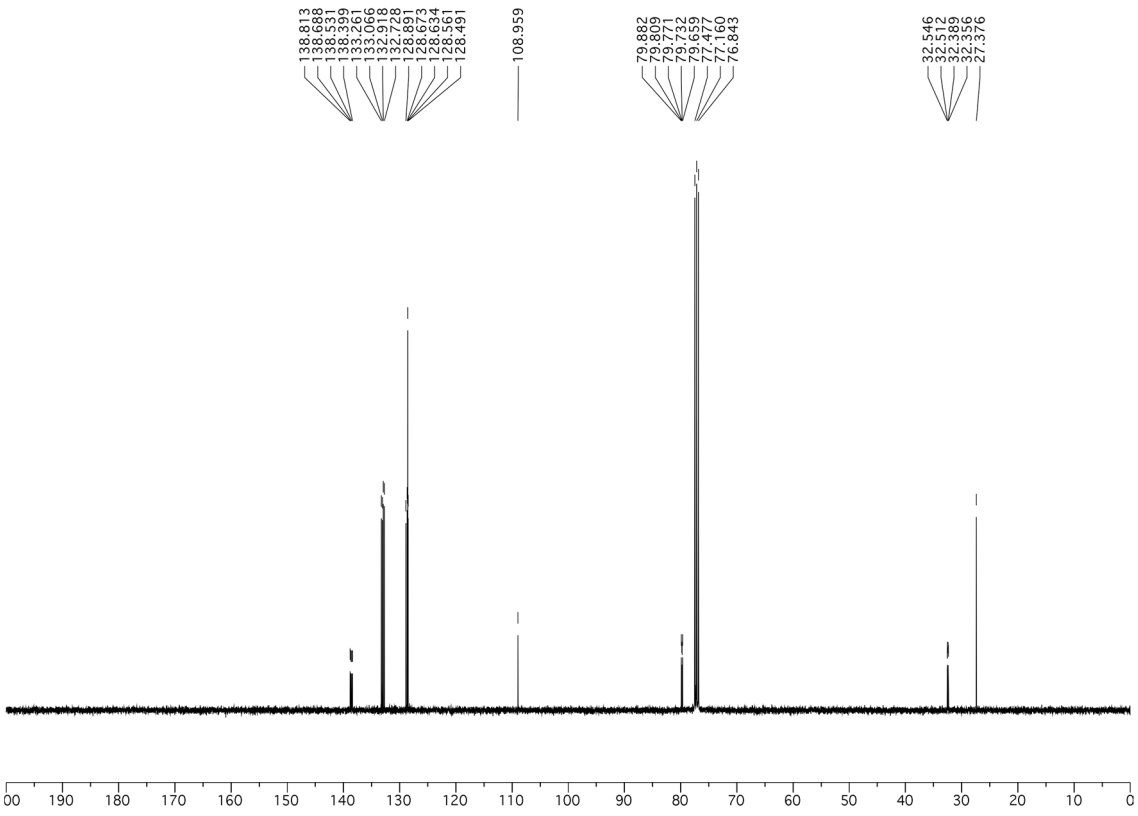


(*R*,*R*)-DIOP

^{1}H-NMR (400.13 MHz, $CDCl_3$):

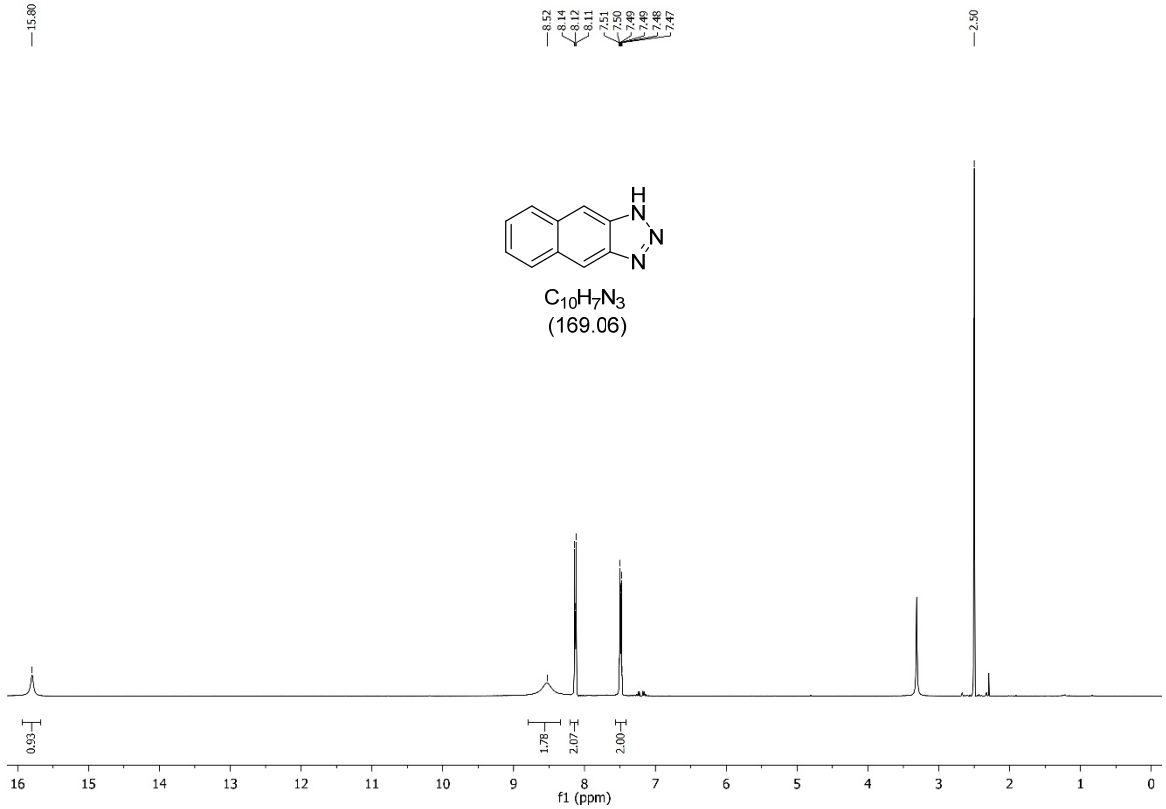


^{13}C-NMR (100.61 MHz, $CDCl_3$):

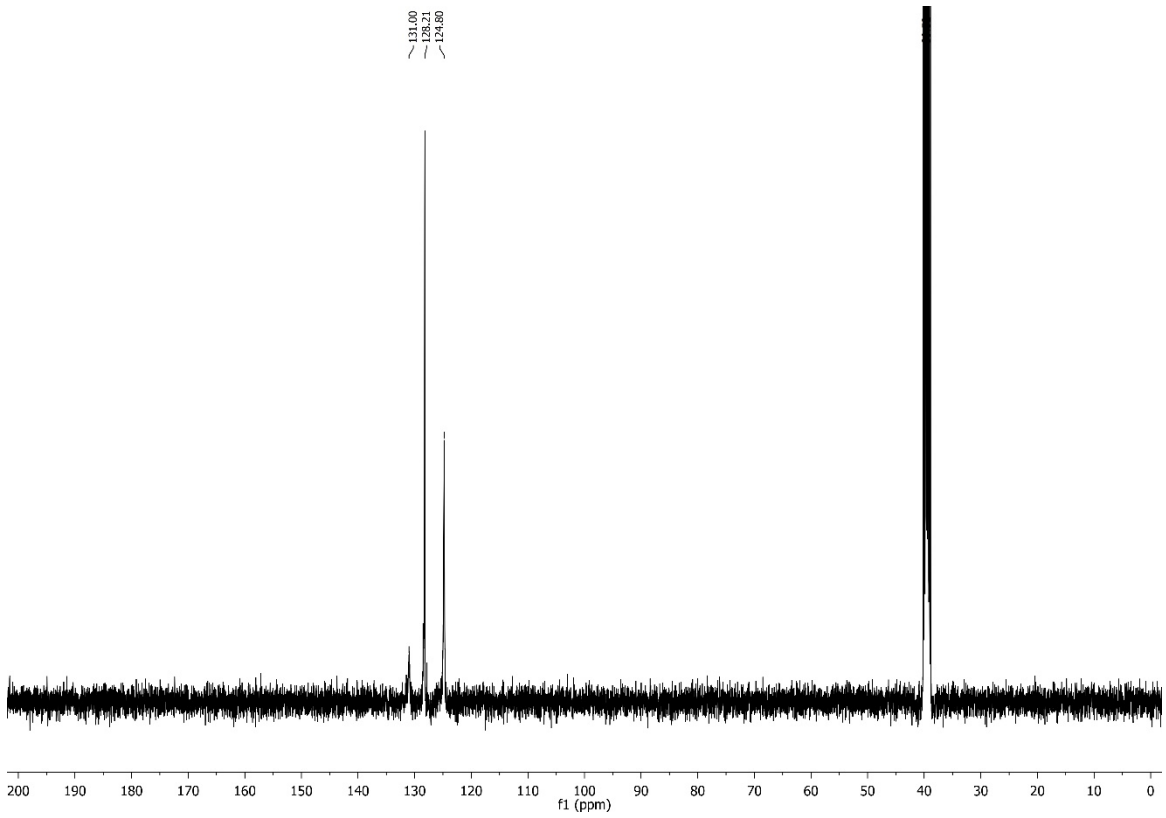


1*H*-naphtho[2,3-d][1,2,3]triazole

^{1}H-NMR (400.13 MHz, 343K, DMSO-d_6):

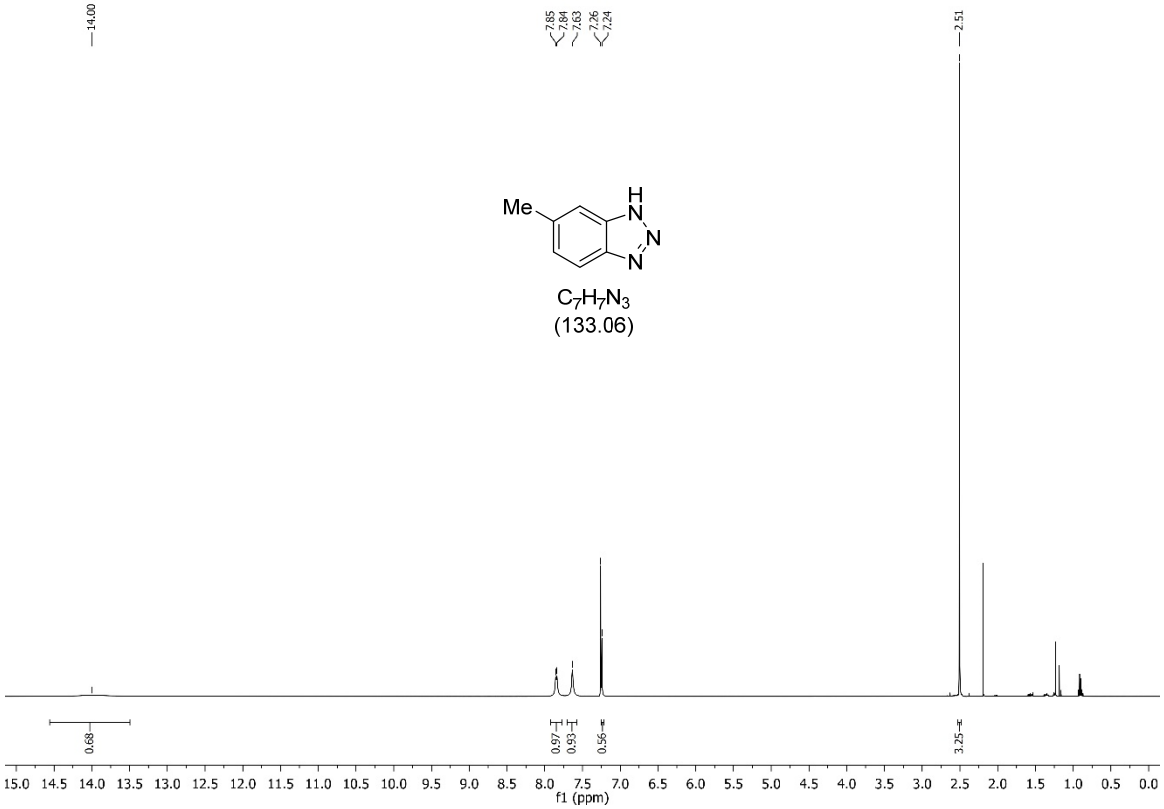


^{13}C-NMR (100.61 MHz, $CDCl_3$):



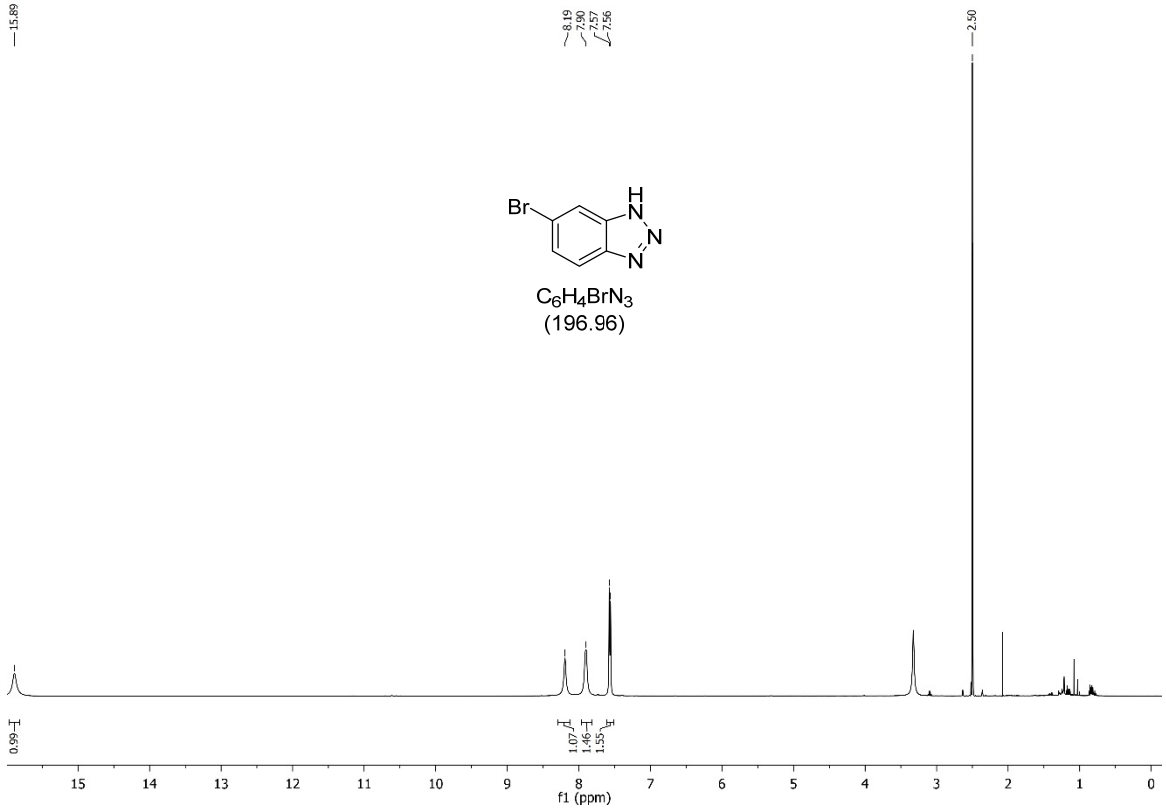
6-methyl-1*H*-benzo[d][1,2,3]triazole

^{1}H-NMR (499.98 MHz, $CDCl_3$):



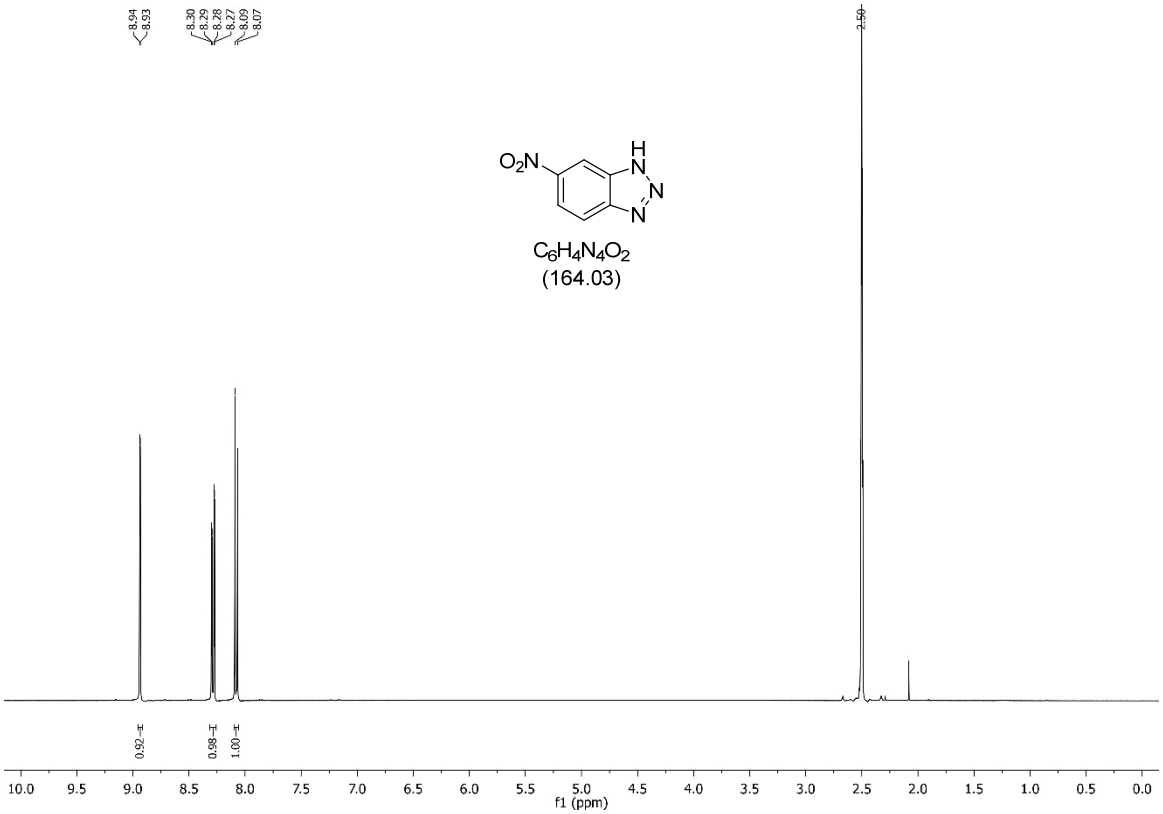
6-bromo-1*H*-benzo[d][1,2,3]triazole

^{1}H-NMR (499.98 MHz, DMSO-d_6):

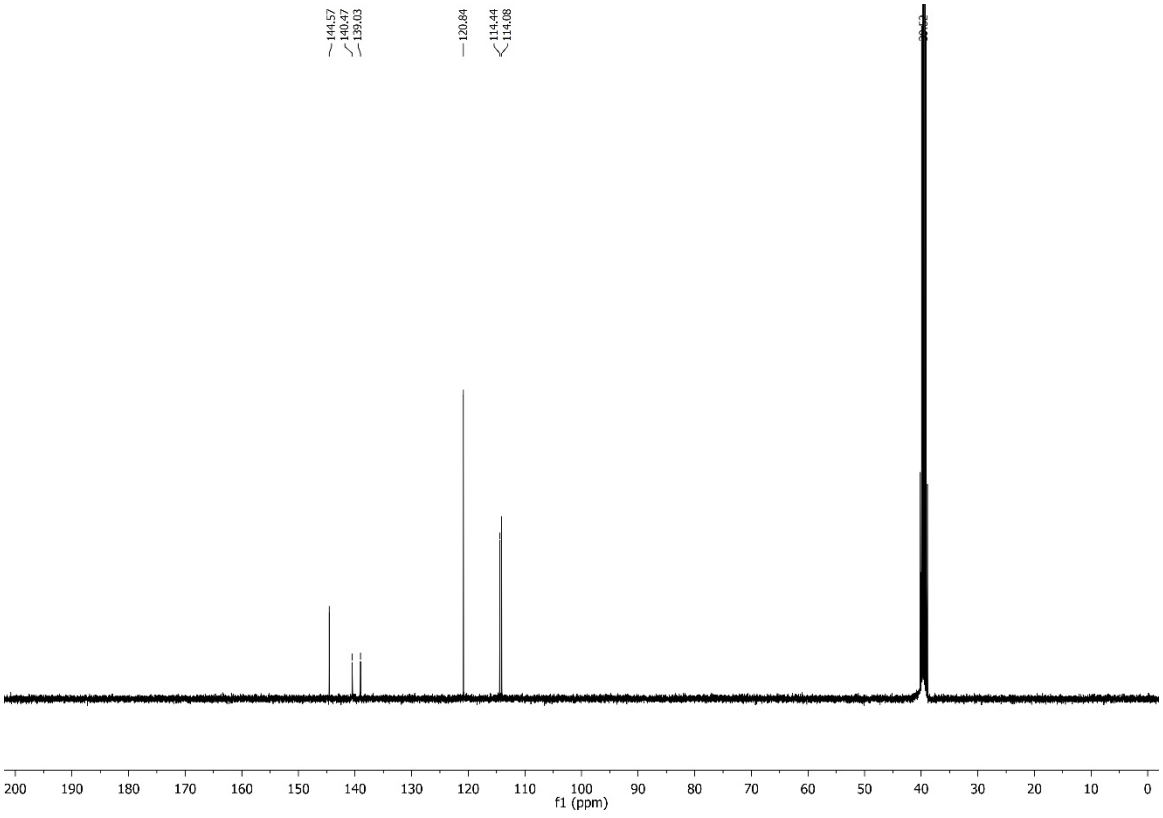


6-nitro-1*H*-benzo[*d*][1,2,3]triazole

^{1}H-NMR (400.13 MHz, DMSO-d_6):

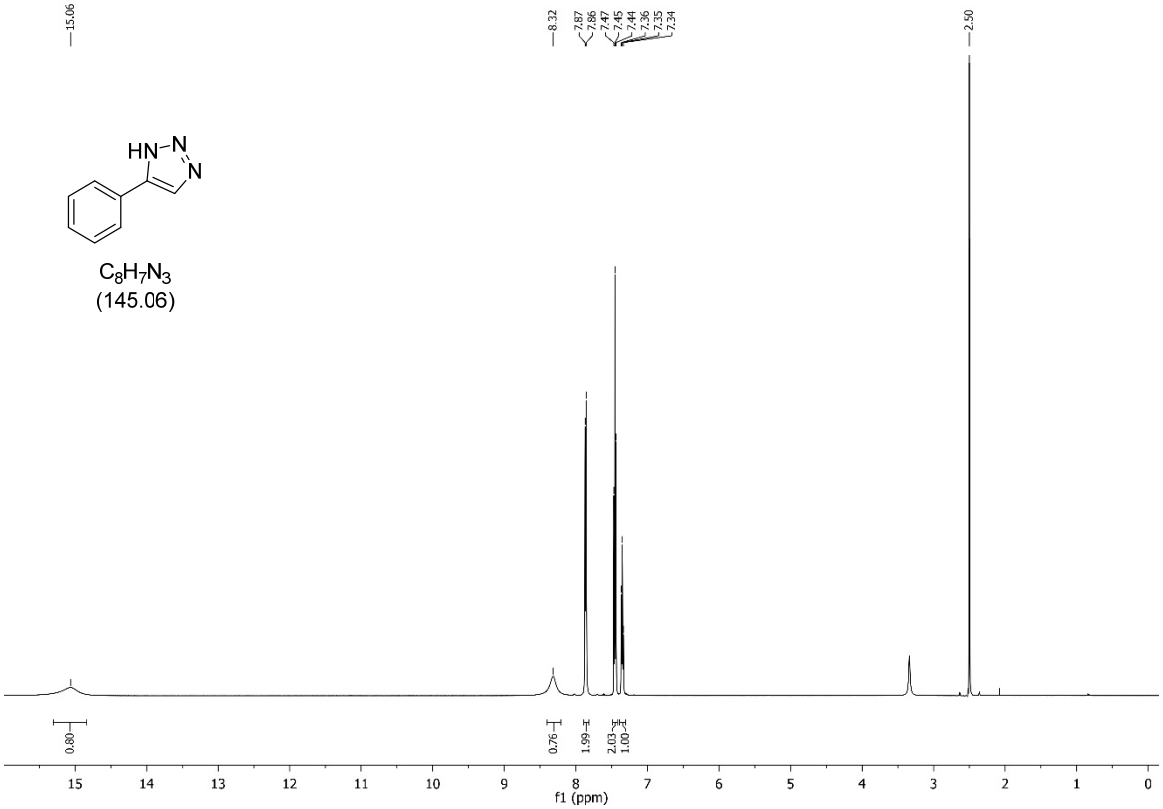


^{13}C-NMR (100.61 MHz, , DMSO-d_6):

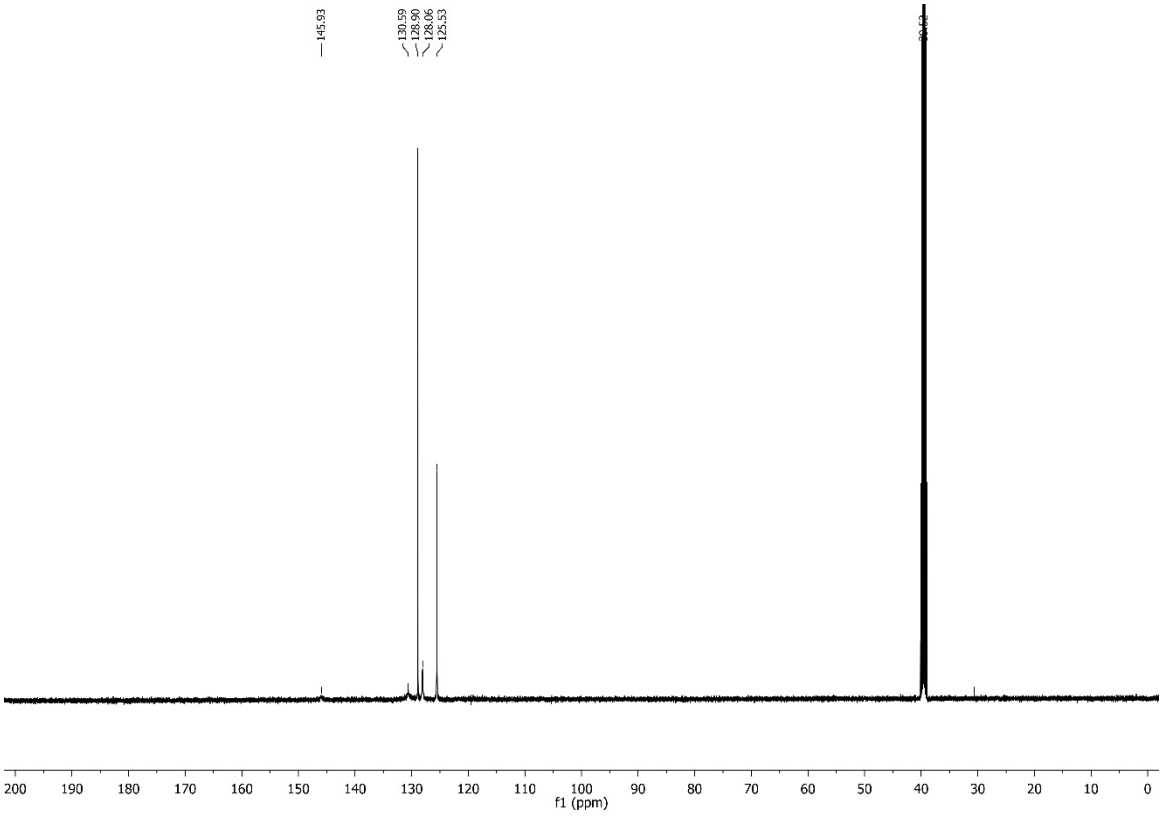


5-phenyl-1*H*-1,2,3-triazole

^{1}H-NMR (499.98 MHz, DMSO-d6):

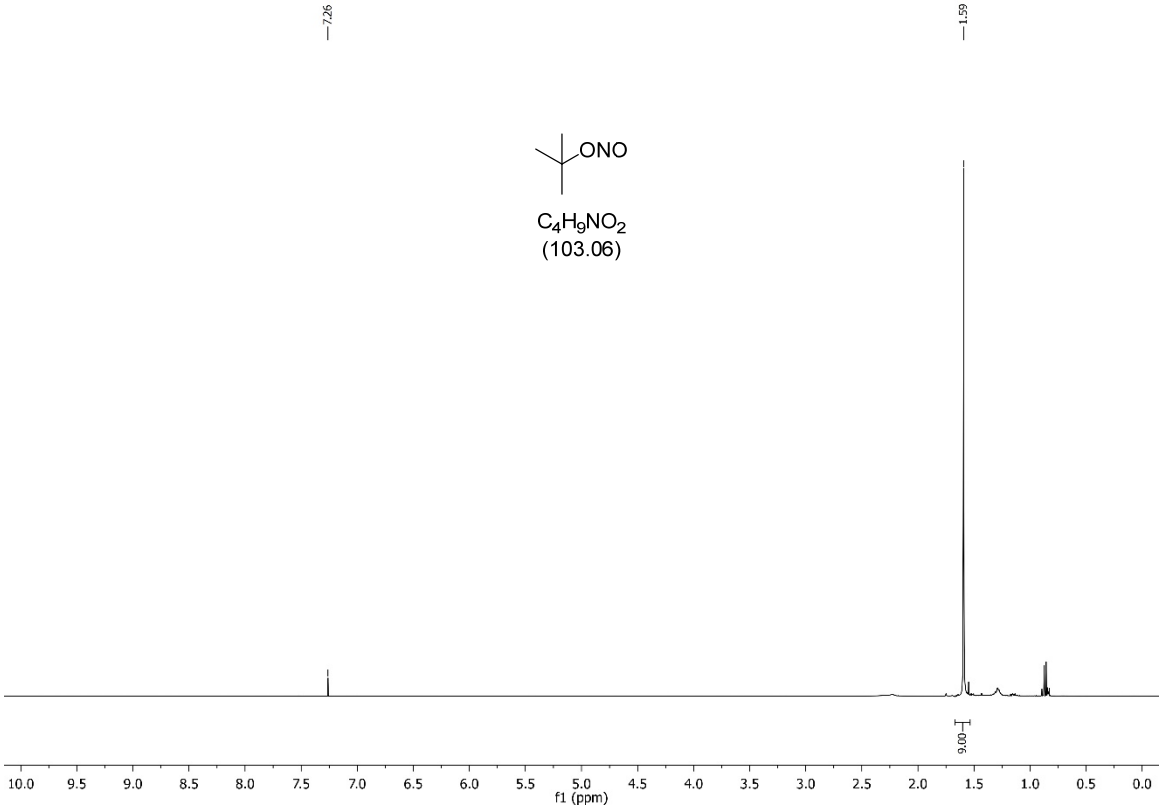


^{13}C-NMR (125.72 MHz, DMSO-d6):

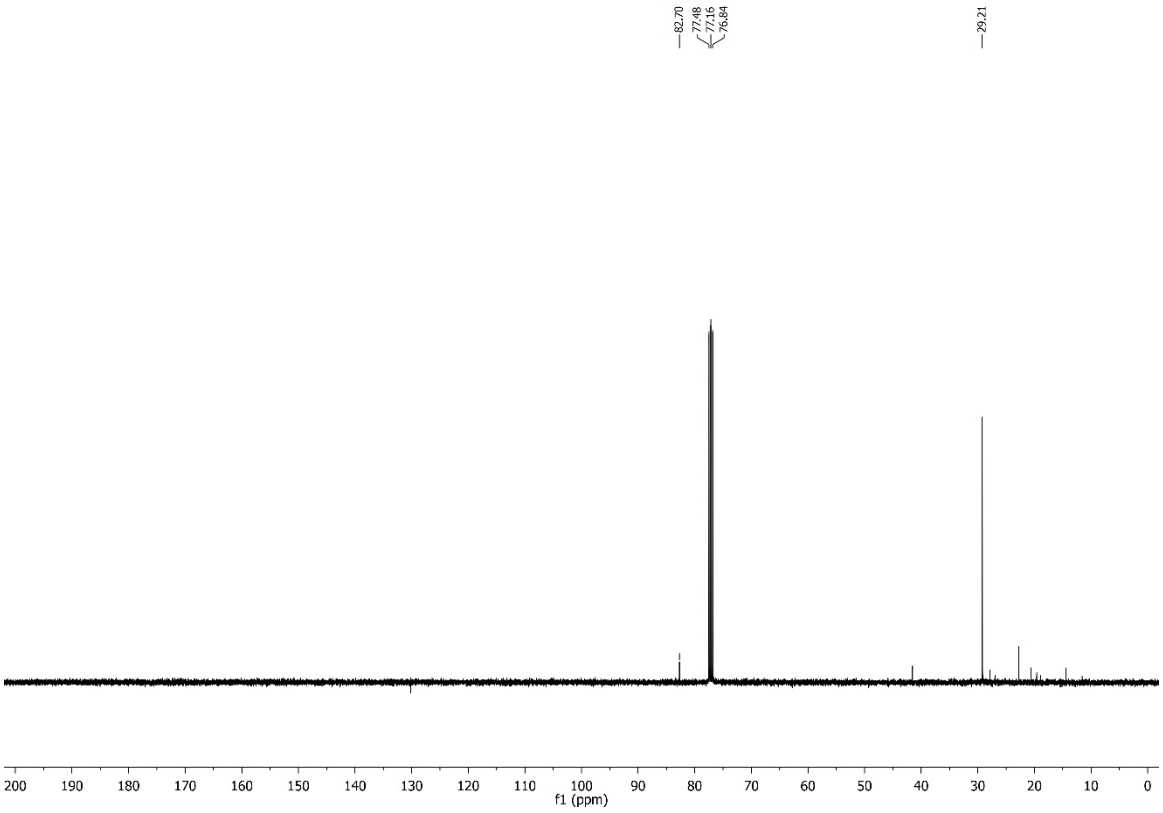


tert-butyl nitrite

^{1}H-NMR (400.13 MHz, $CDCl_3$):

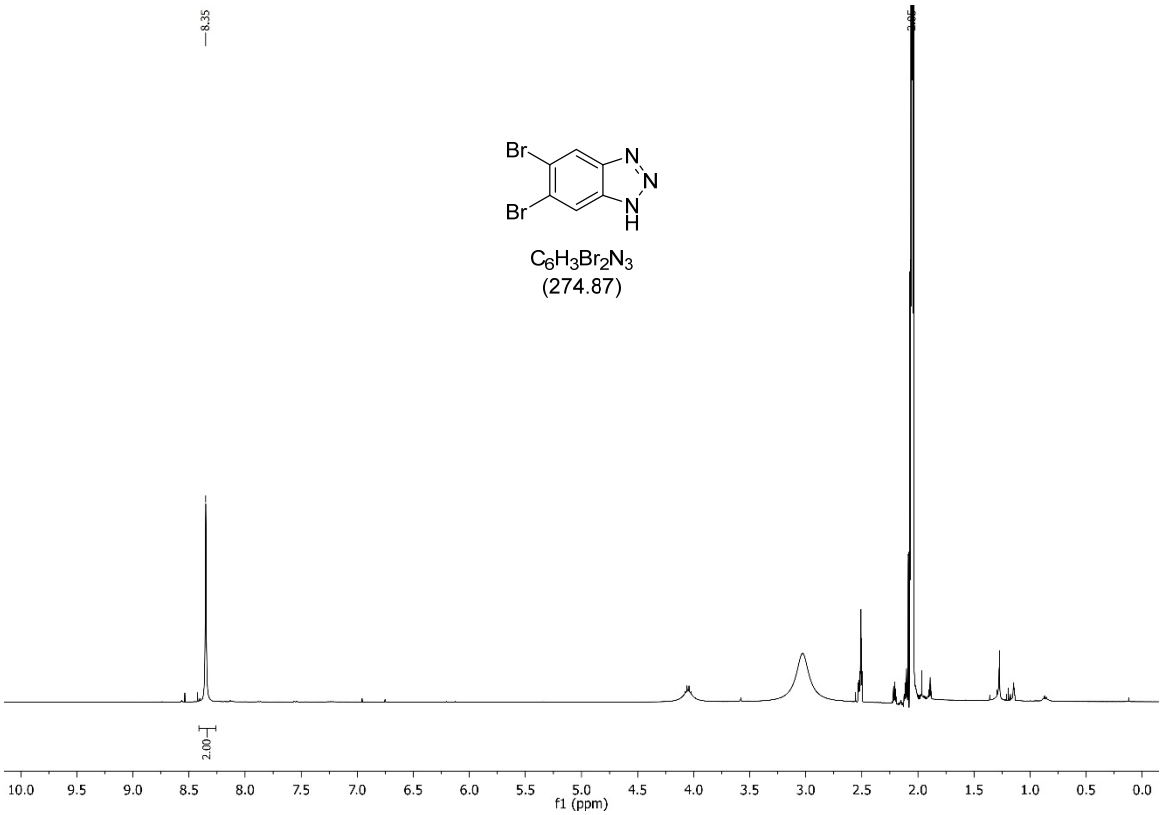


^{13}C-NMR (100.61 MHz, $CDCl_3$):



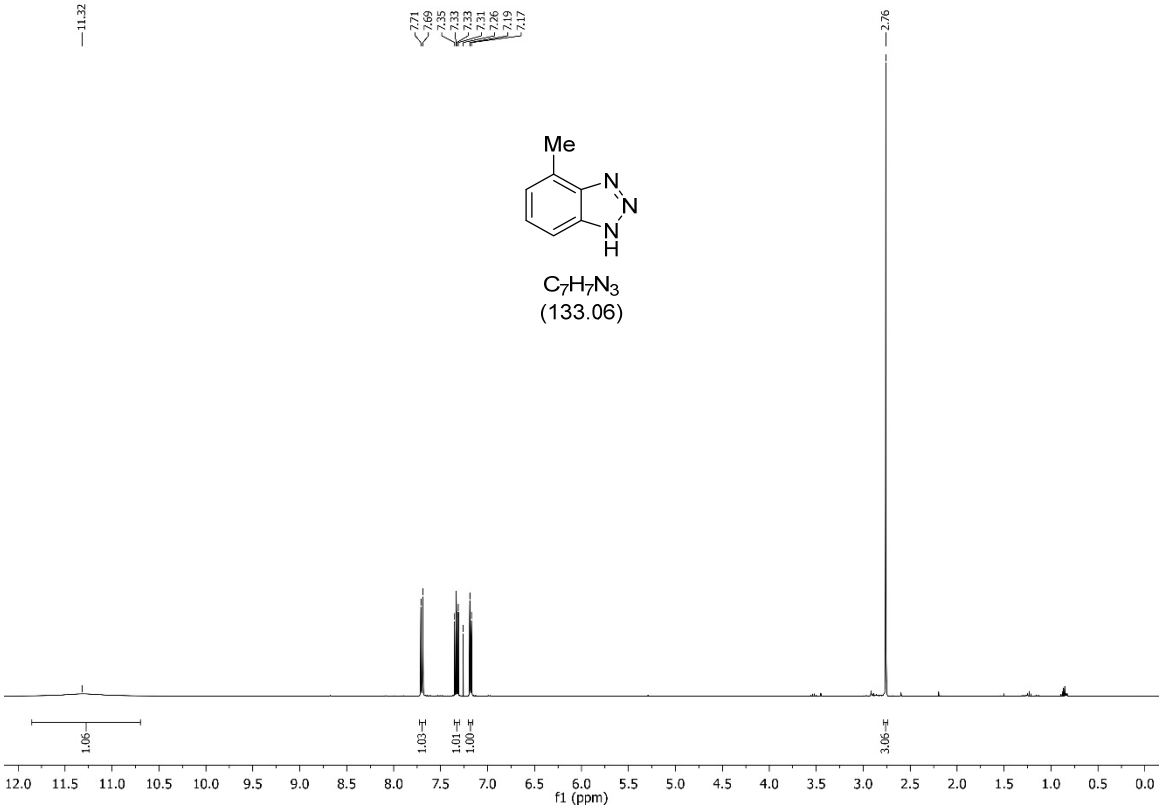
5,6-dibromo-1*H*-benzo[d][1,2,3]triazole

^{1}H-NMR (400.13 MHz, acetone-d_6/DMSO-d_6 - 7:1):

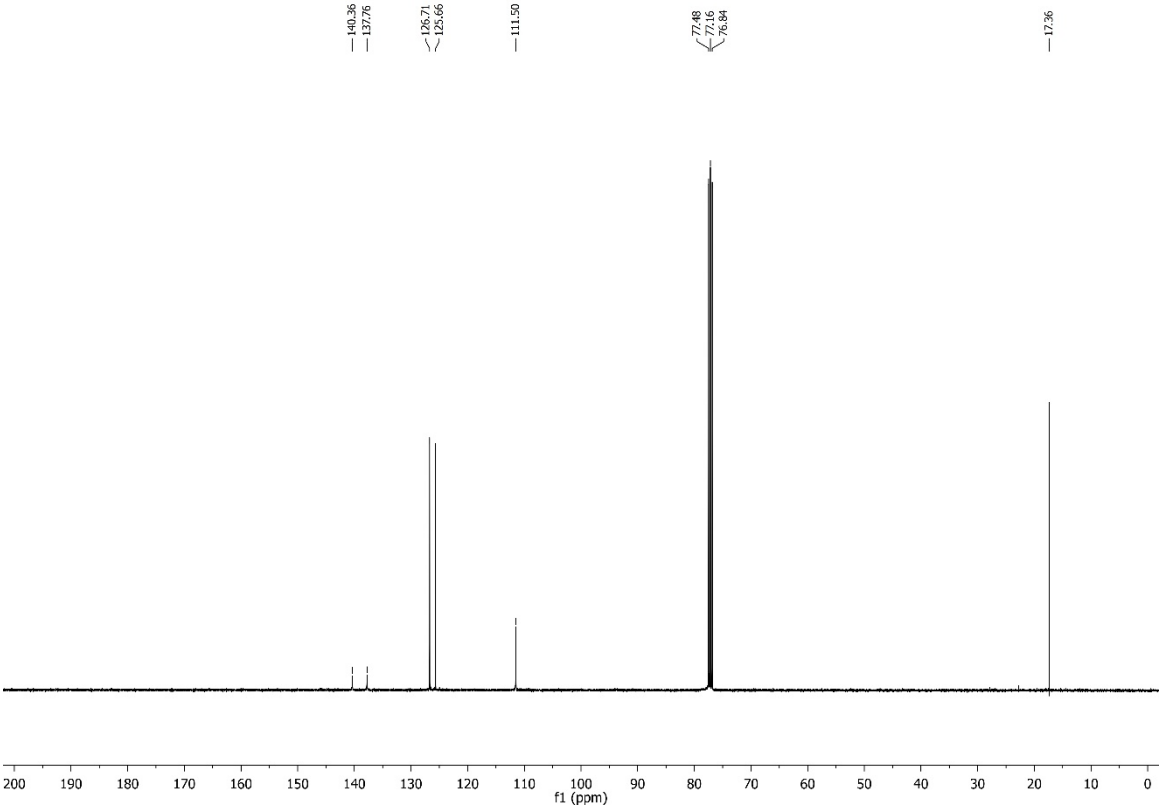


4-methyl-1*H*-benzo[d][1,2,3]triazole

^{1}H-NMR (400.13 MHz, $CDCl_3$):

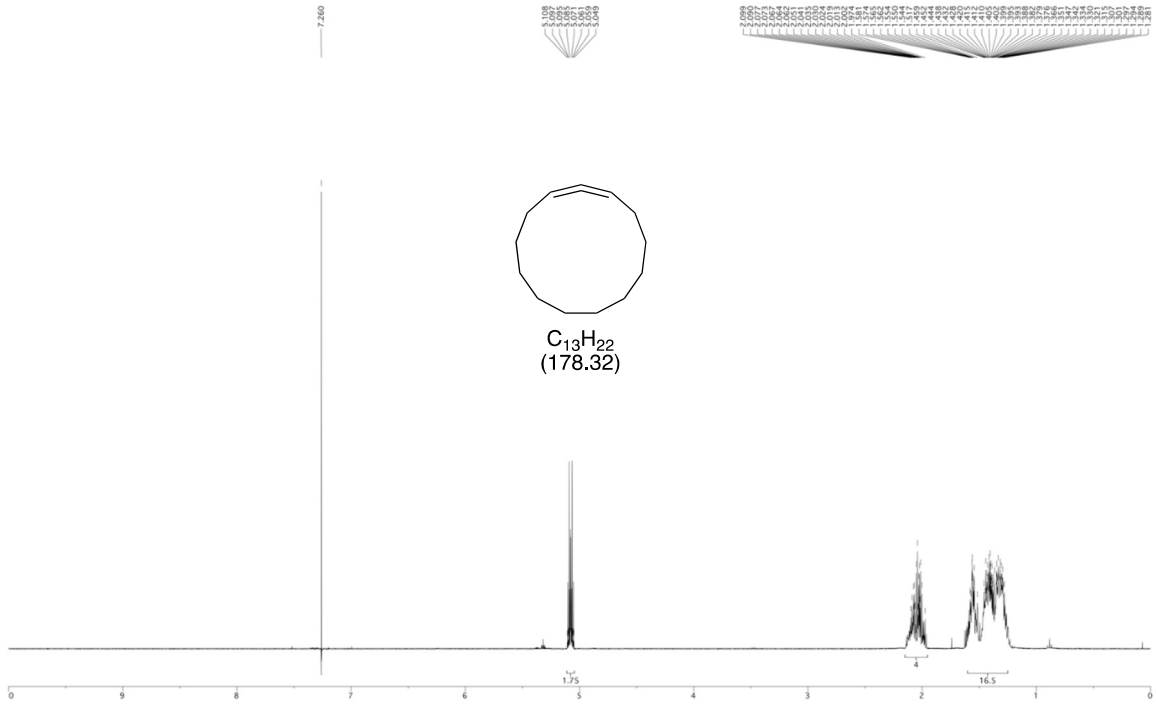


^{13}C-NMR (100.61 MHz, $CDCl_3$):

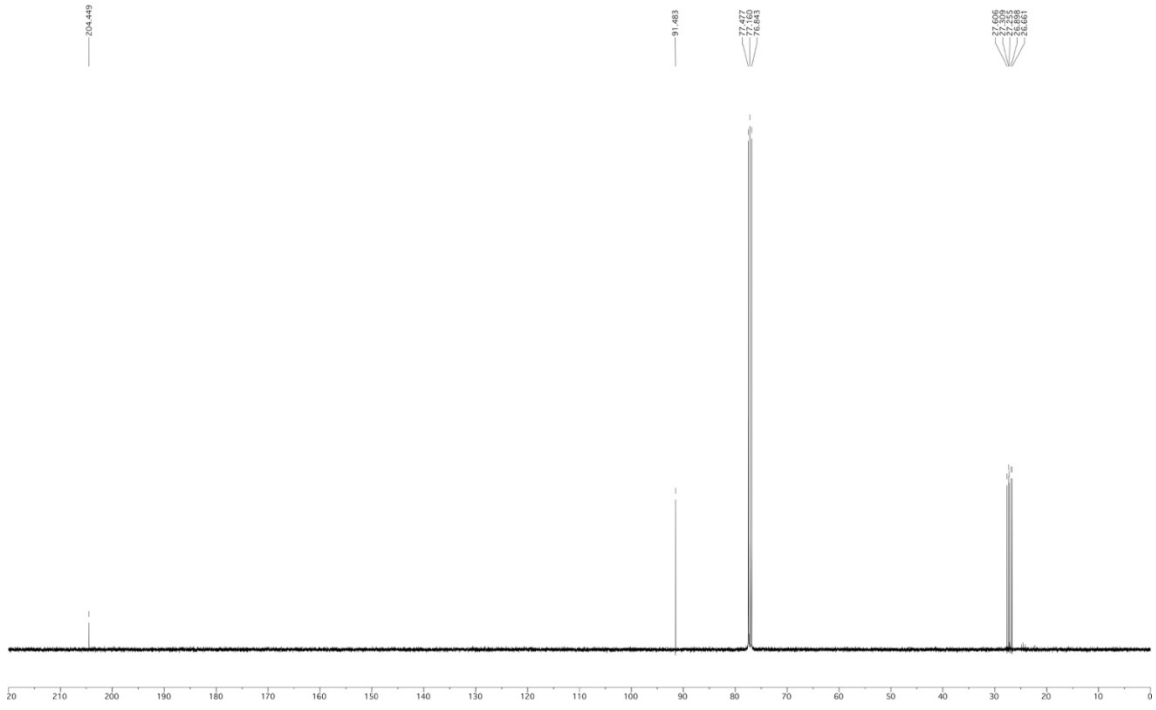


cyclotrideca-1,2-diene

^{1}H-NMR (400.13 MHz, $CDCl_3$):

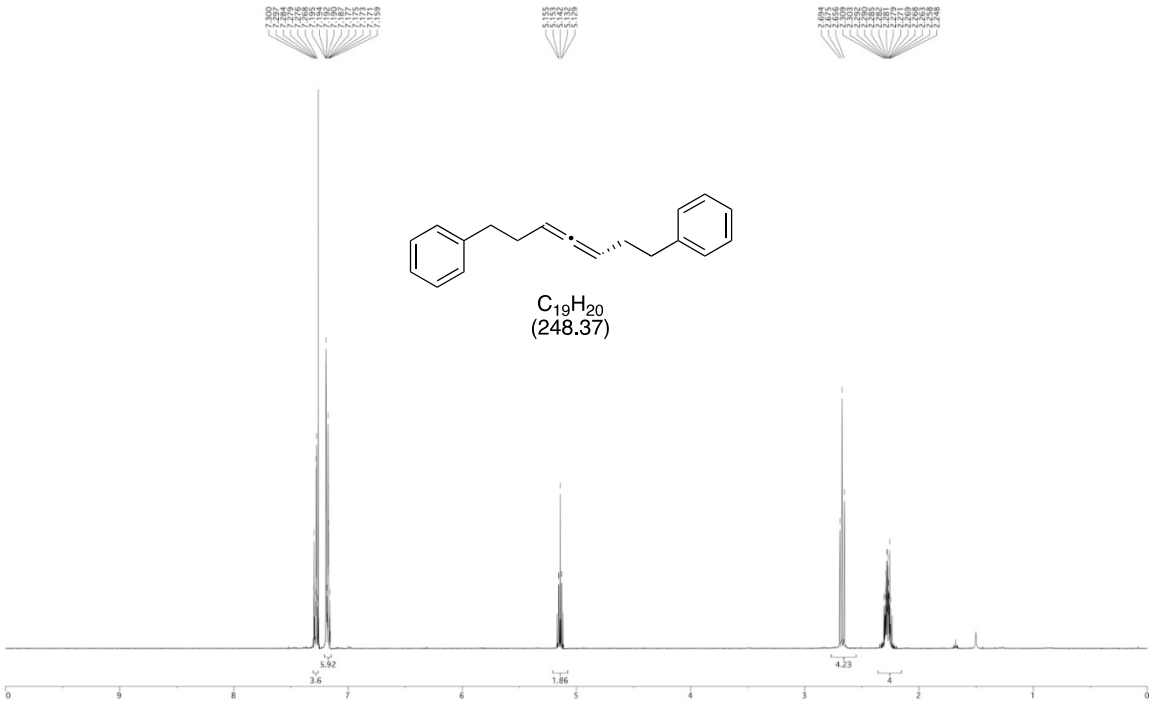


^{13}C-NMR (100.61 MHz, $CDCl_3$):

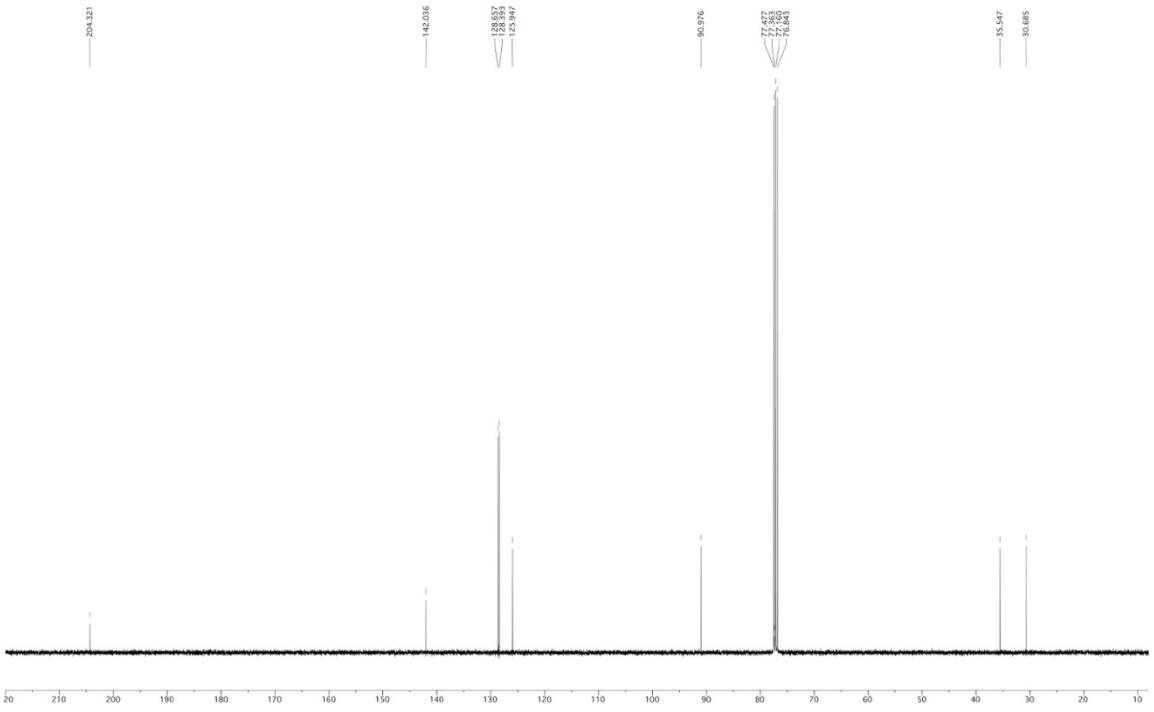


1,7-diphenylhepta-3,4-diene (1)

^{1}H-NMR (400.13 MHz, $CDCl_3$):

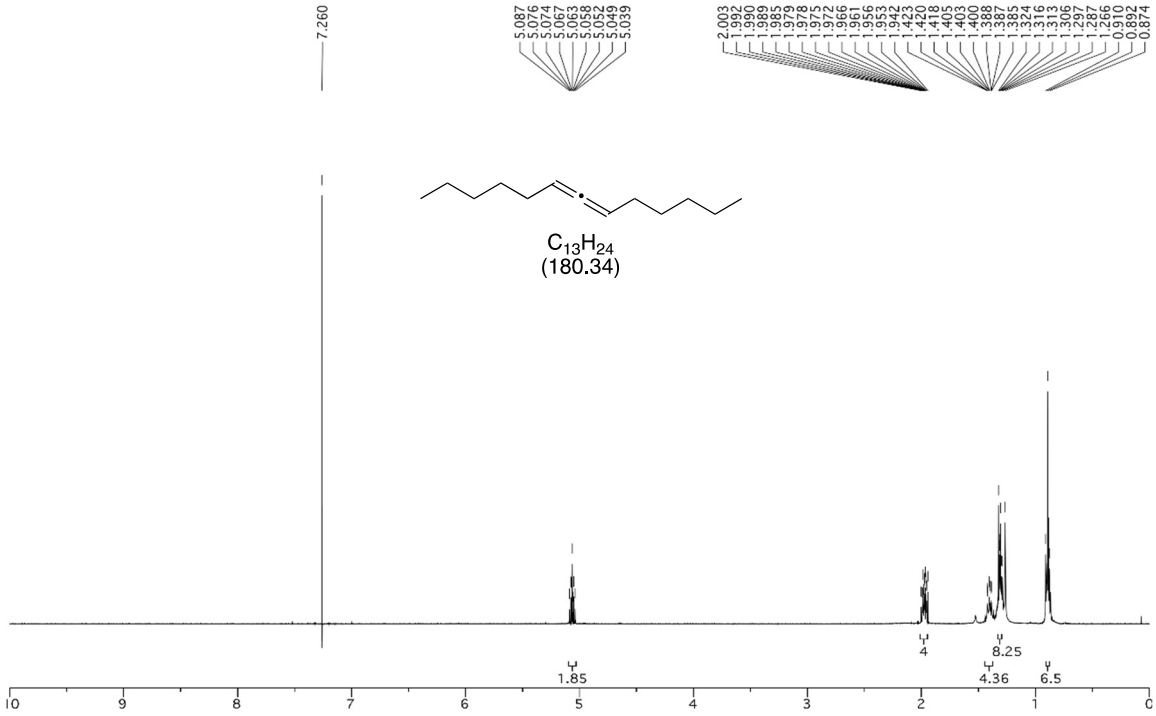


^{13}C-NMR (100.61 MHz, $CDCl_3$):

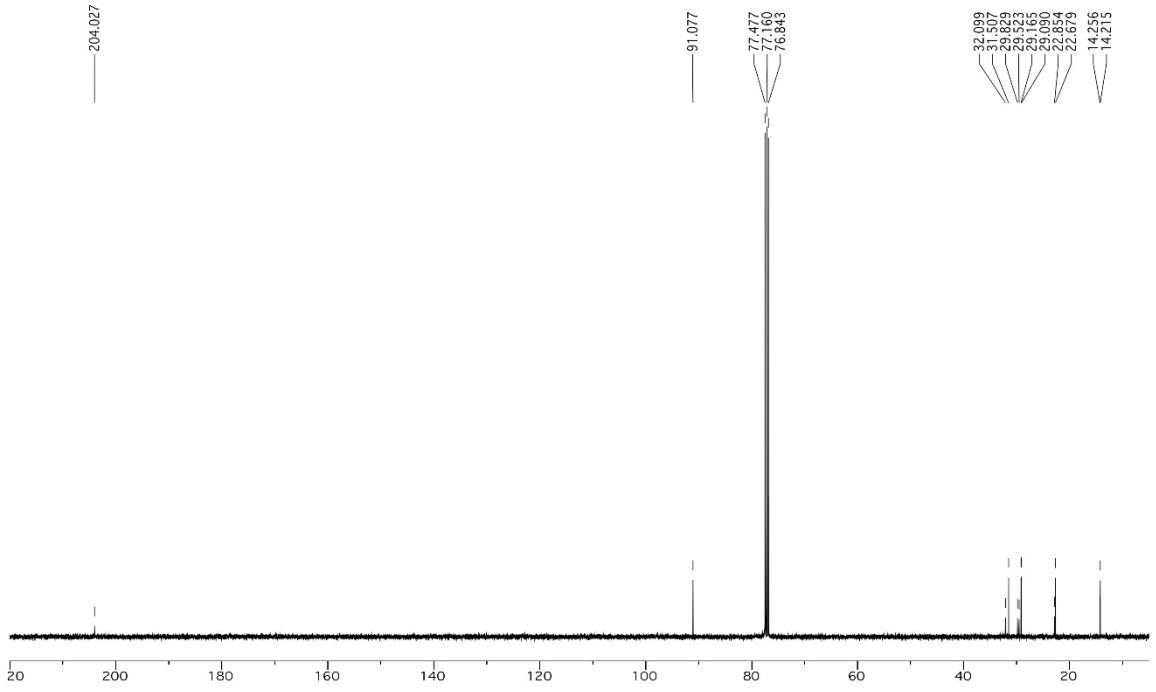


trideca-6,7-diene

^{1}H-NMR (400.13 MHz, $CDCl_3$):

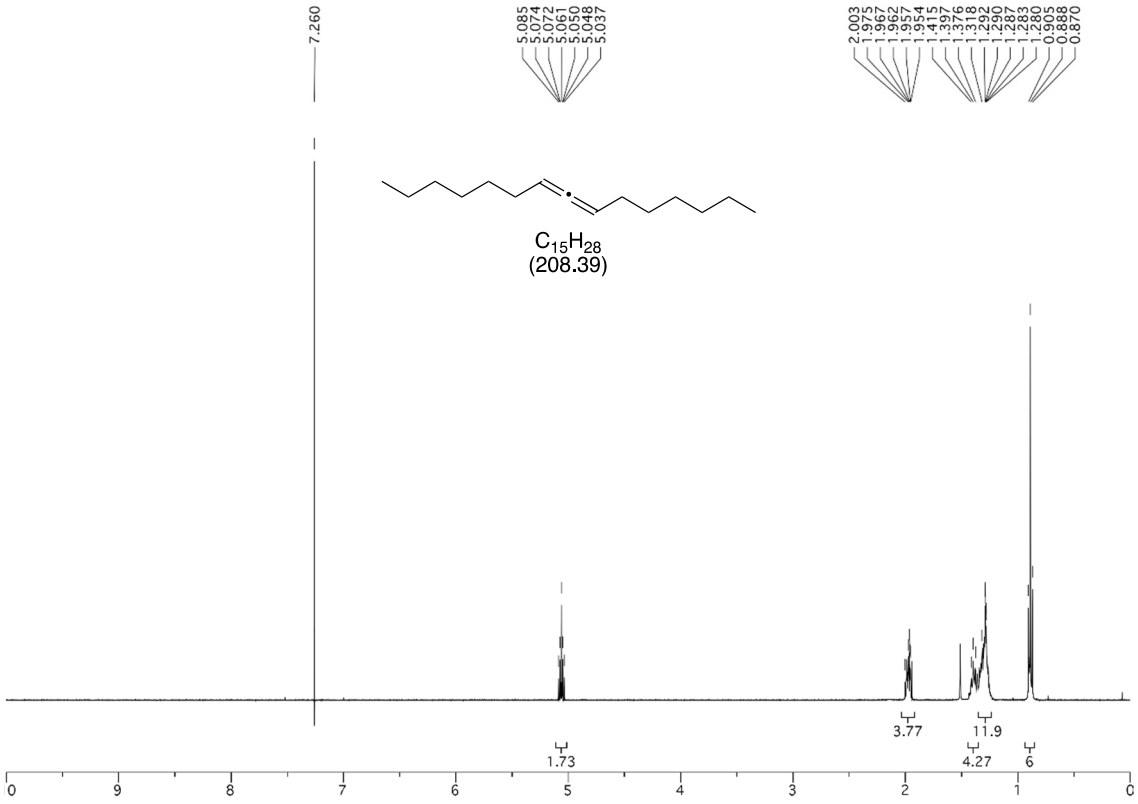


^{13}C-NMR (100.61 MHz, $CDCl_3$):

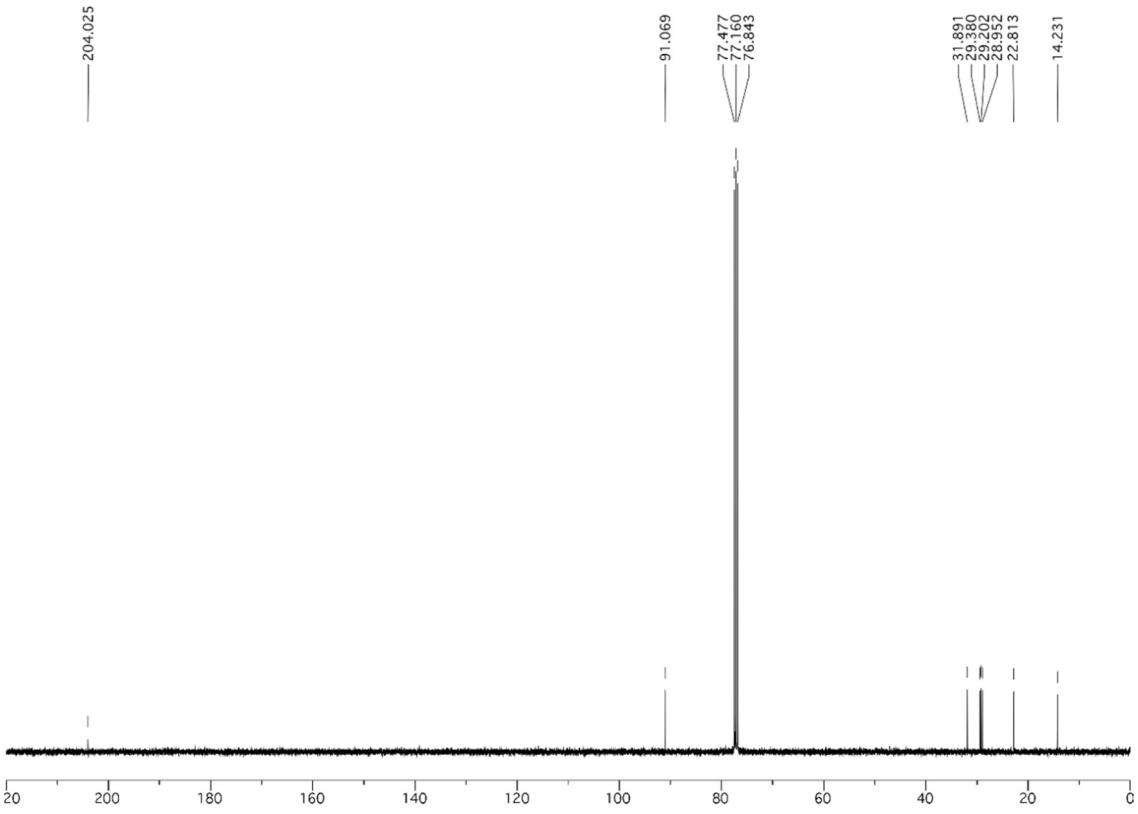


pentadeca-7,8-diene

^{1}H-NMR (400.13 MHz, $CDCl_3$):

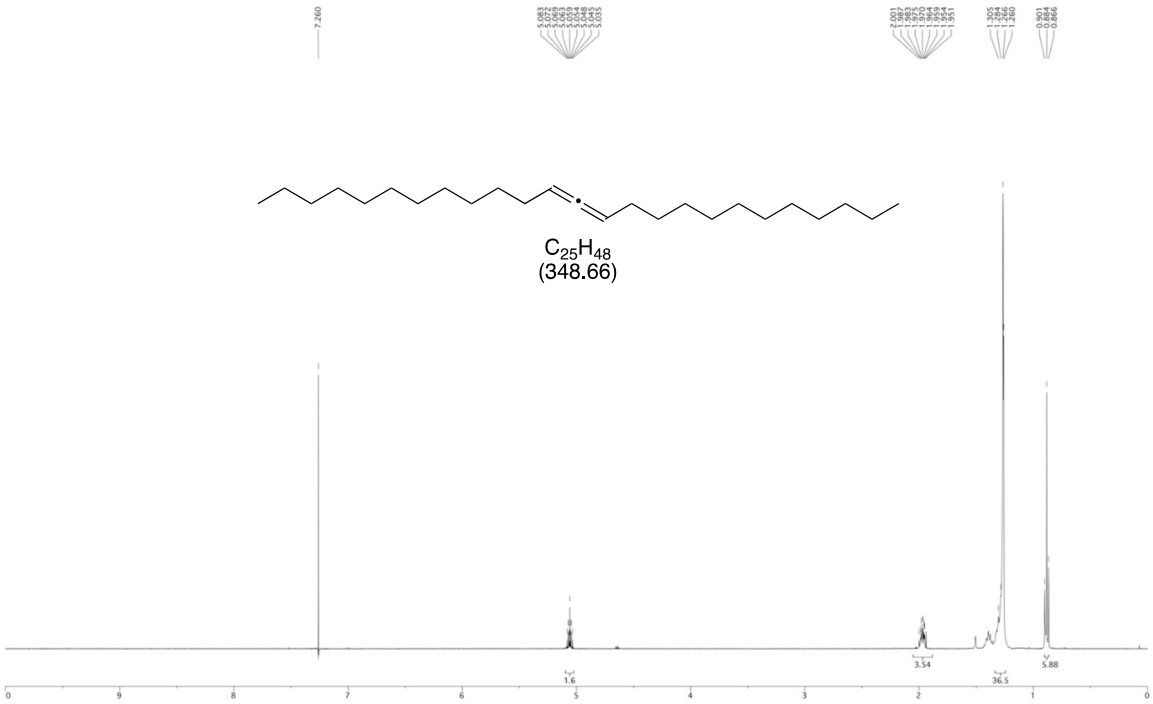


^{13}C-NMR (100.61 MHz, $CDCl_3$):

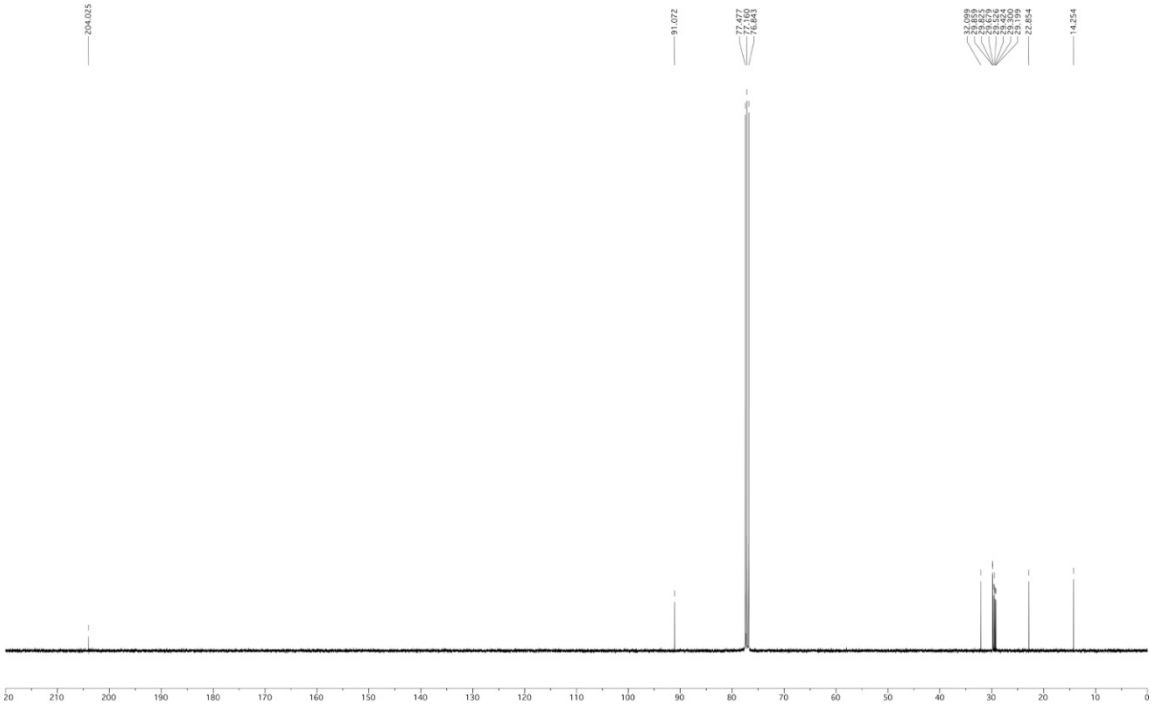


pentacosa-12,13-diene

^{1}H-NMR (400.13 MHz, $CDCl_3$):

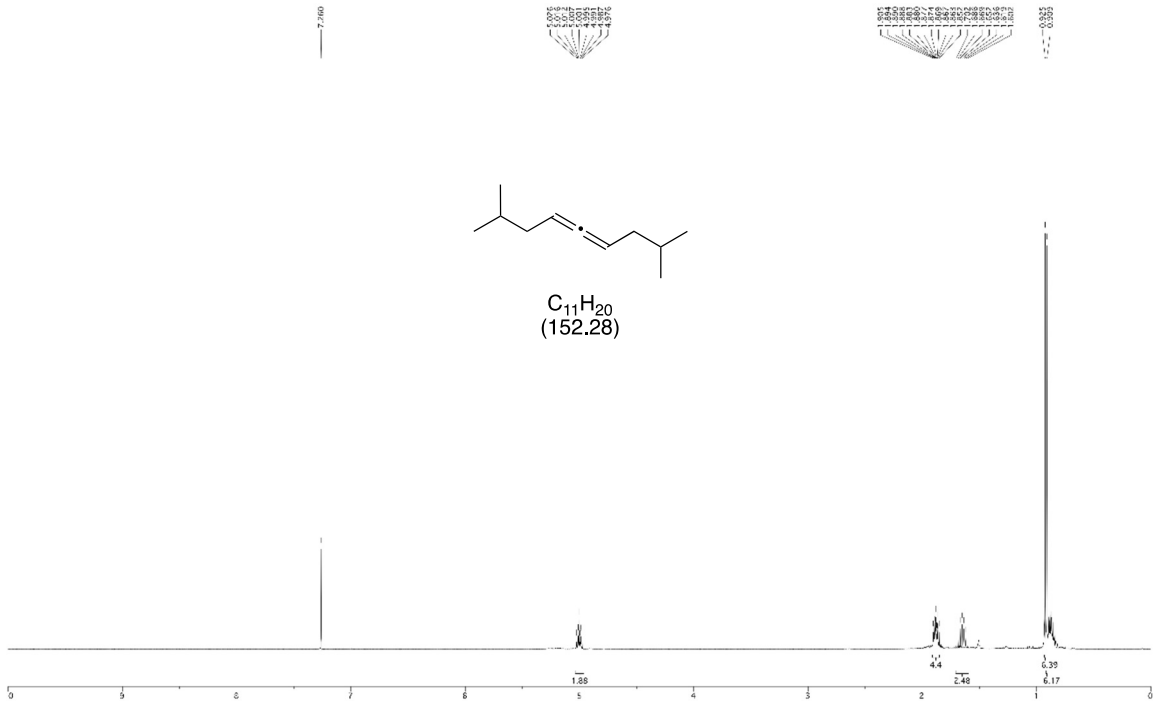


^{13}C-NMR (100.61 MHz, $CDCl_3$):



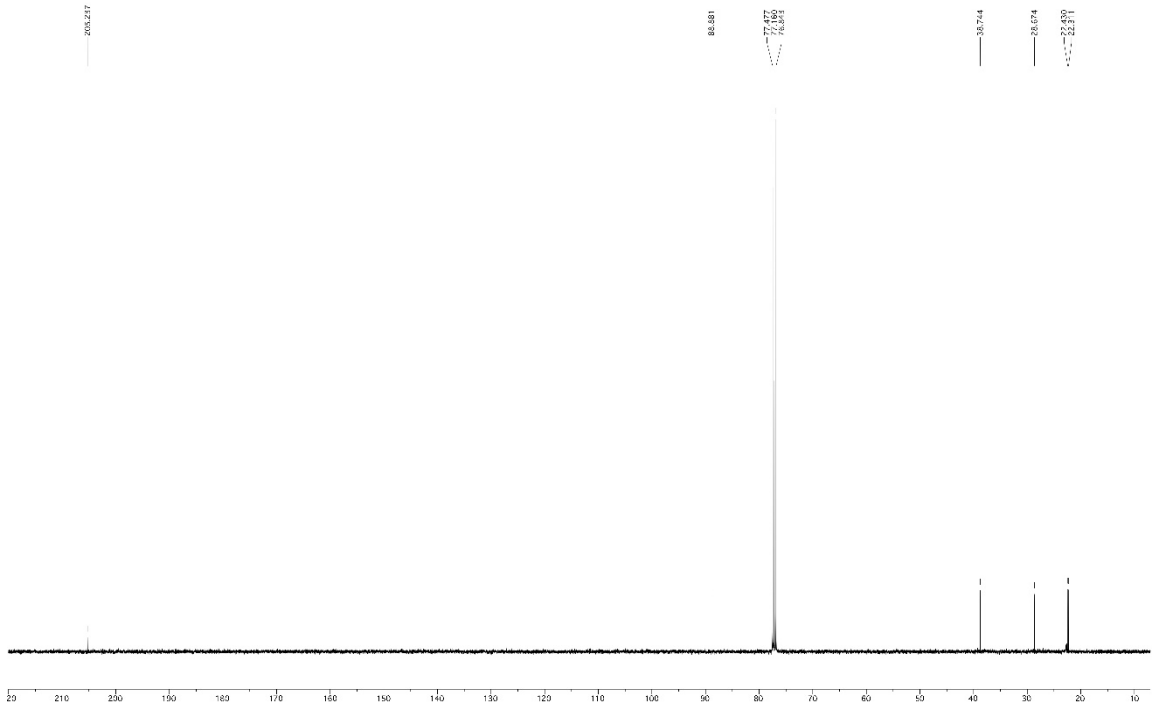
2,8-dimethylnona-4,5-diene

^{1}H-NMR (400.13 MHz, $CDCl_3$):



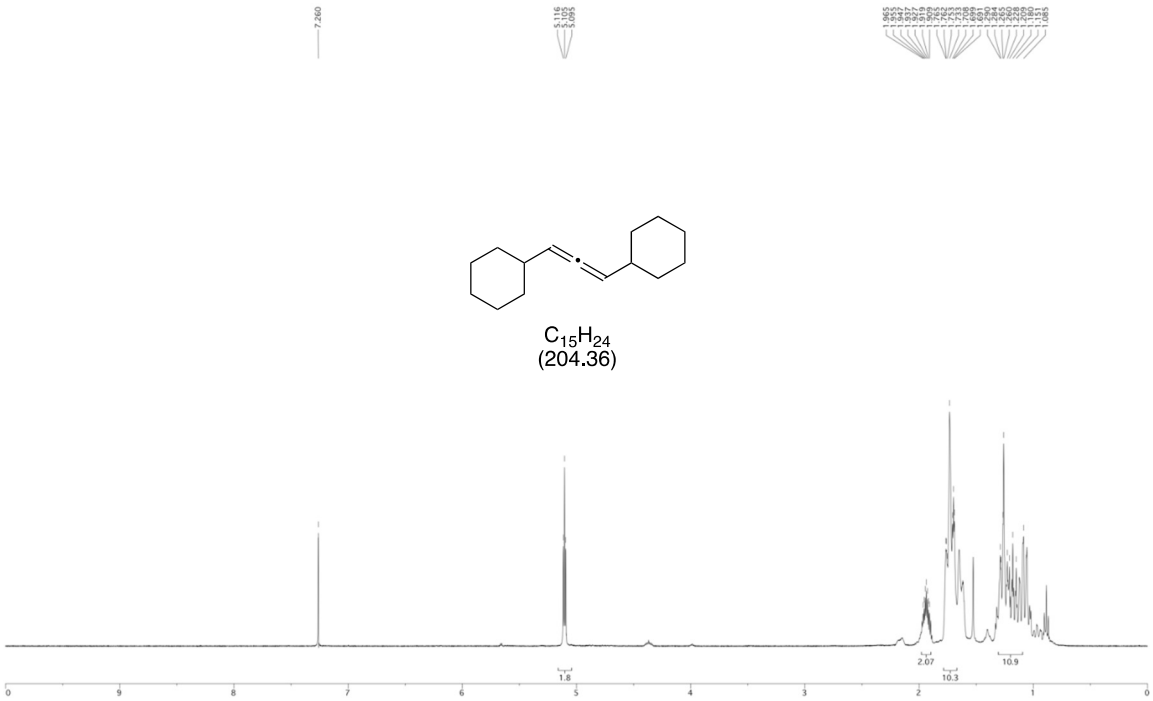
$C_{11}H_{20}$
(152.28)

^{13}C-NMR (100.61 MHz, $CDCl_3$):



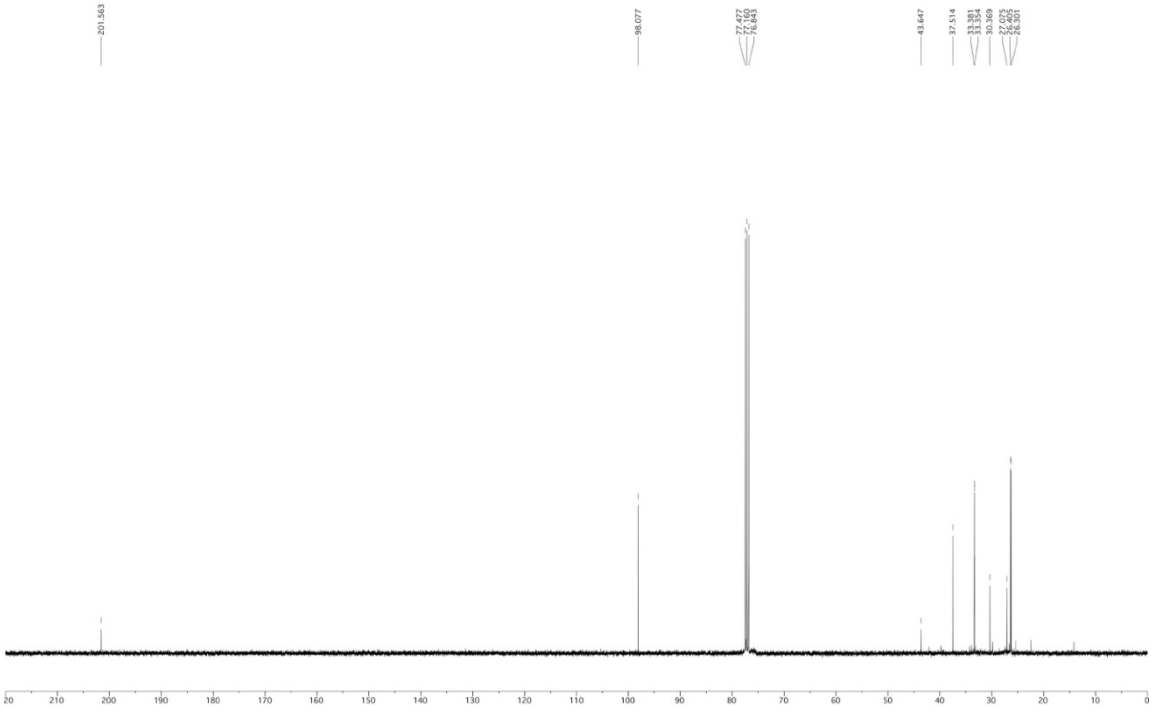
1,3-dicyclohexylpropa-1,2-diene

^{1}H-NMR (400.13 MHz, $CDCl_3$):



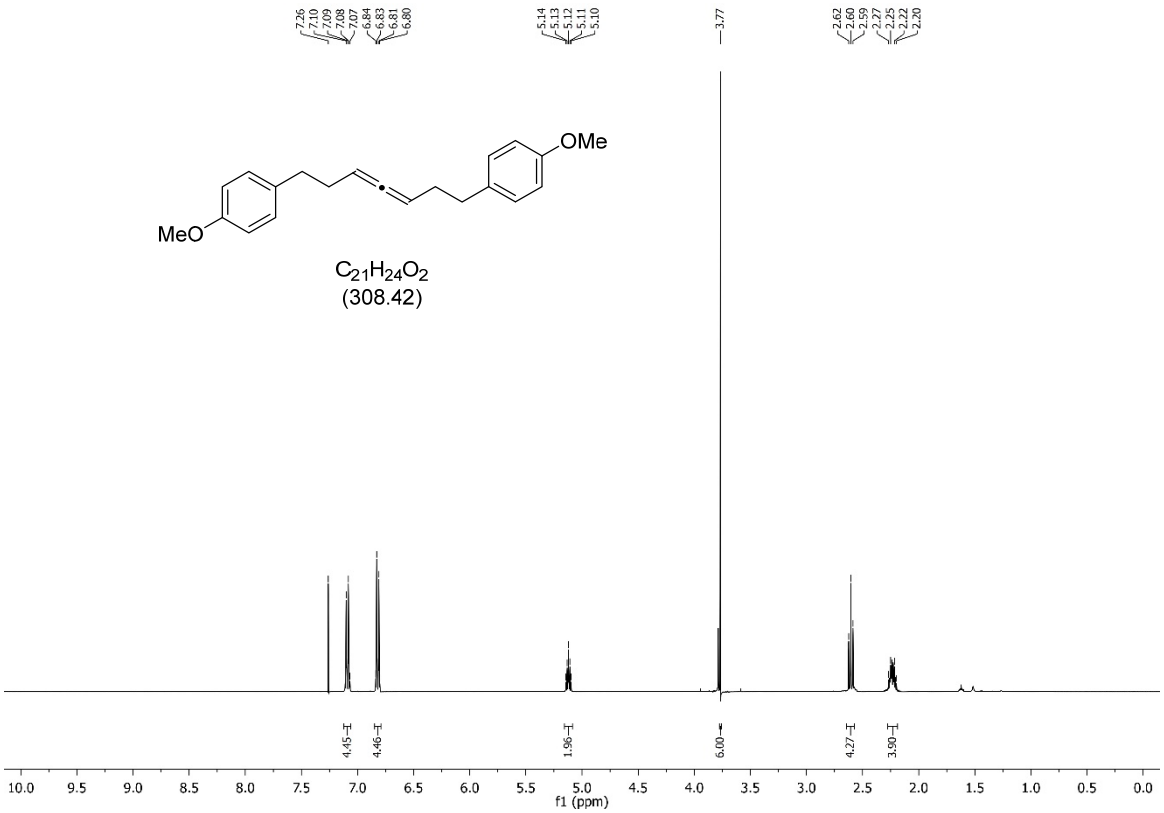
$C_{15}H_{24}$
(204.36)

^{13}C-NMR (100.61 MHz, $CDCl_3$):

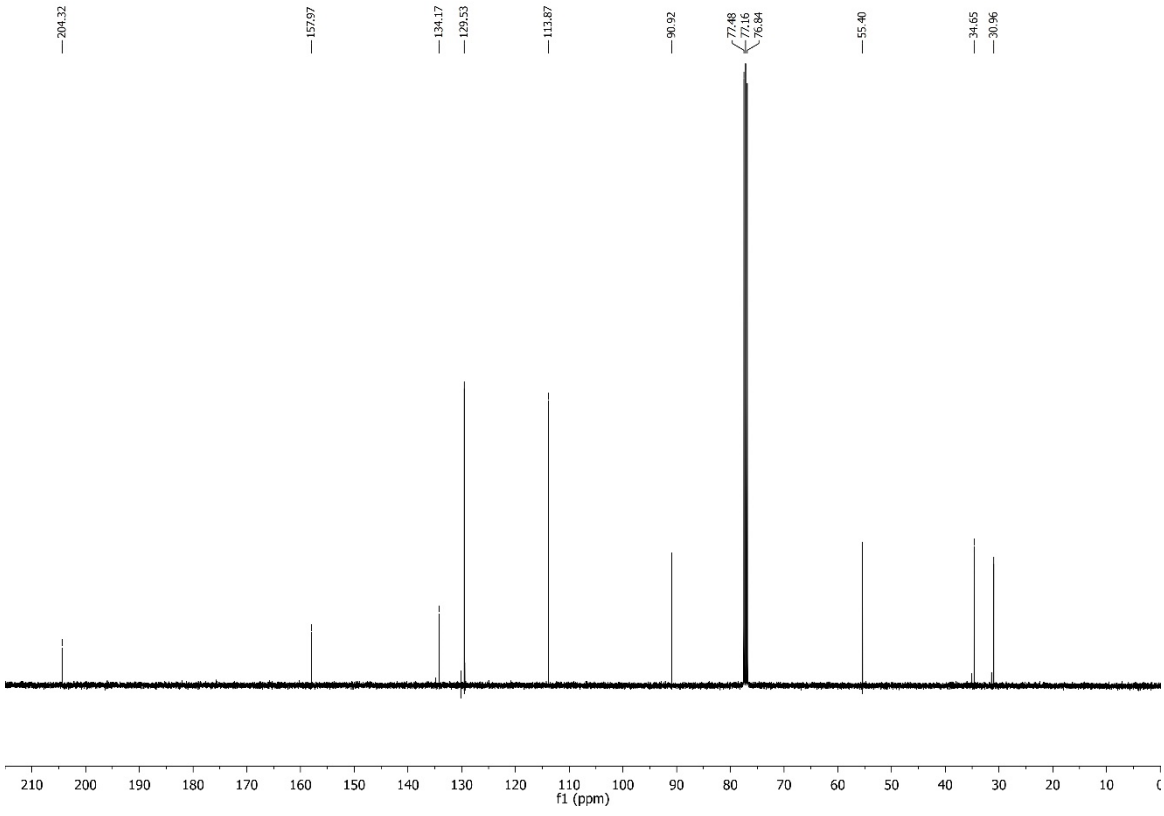


1,7-bis(4-methoxyphenyl)hepta-3,4-diene

^{1}H-NMR (400.13 MHz, $CDCl_3$):

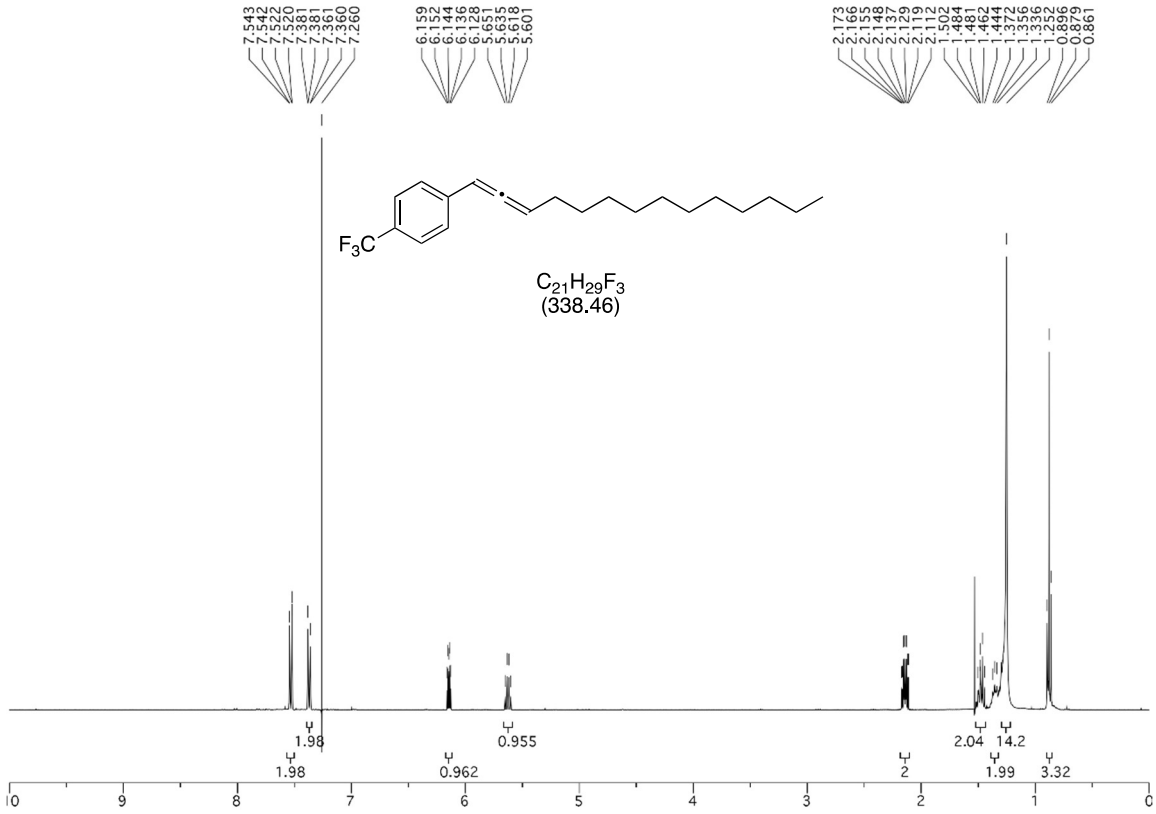


^{13}C-NMR (100.61 MHz, $CDCl_3$):

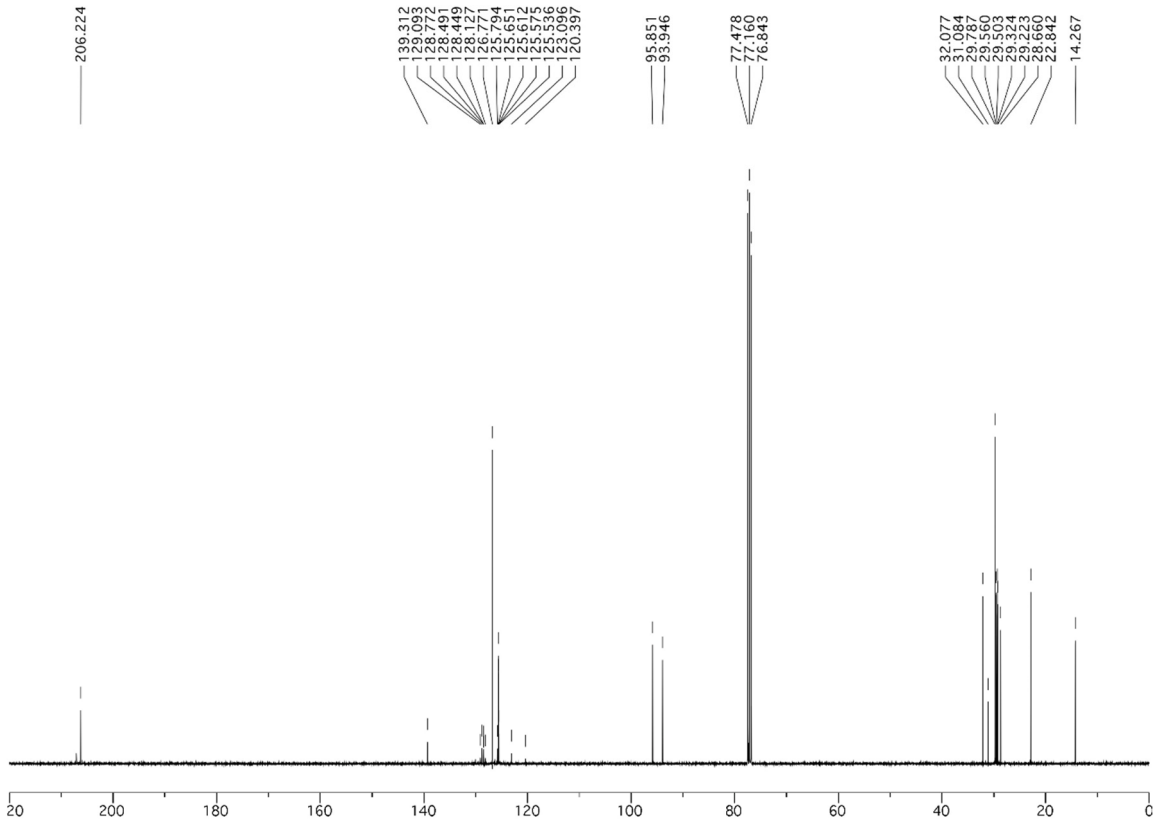


1-(tetradeca-1,2-dien-1-yl)-4-(trifluoromethyl)benzene

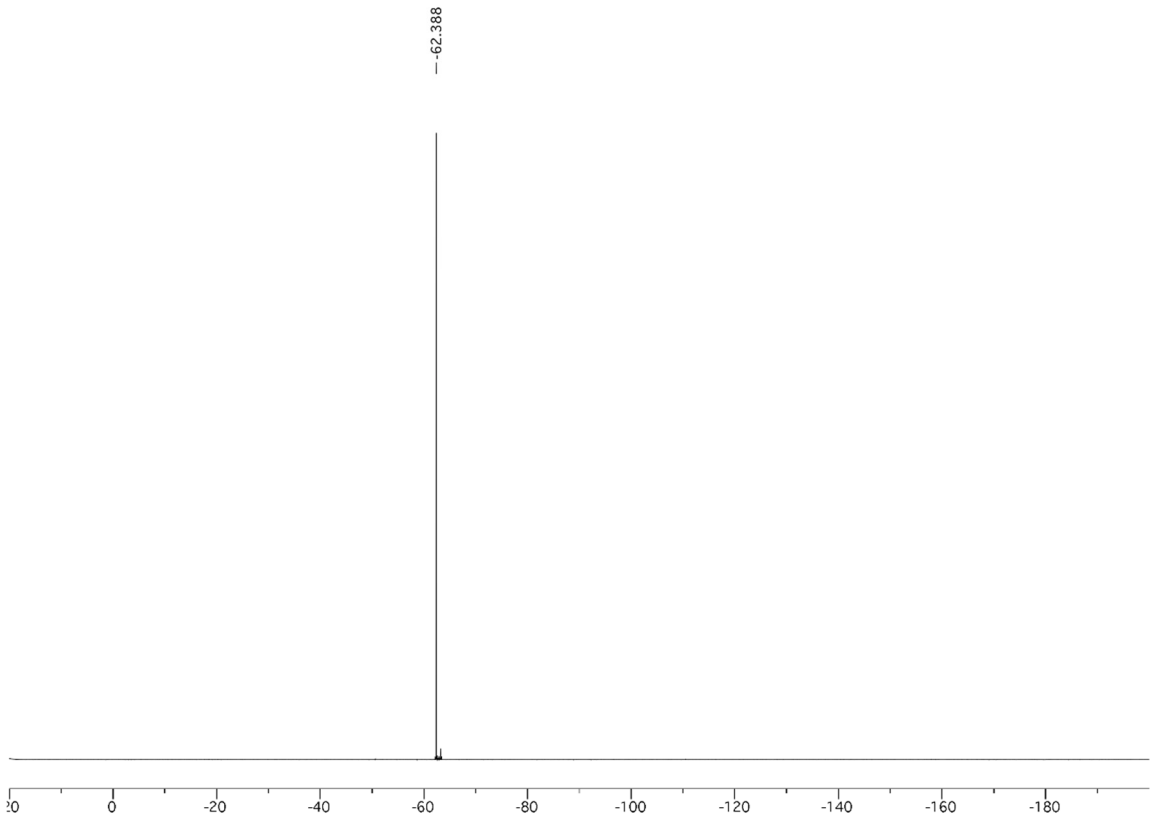
^{1}H-NMR (400.13 MHz, $CDCl_3$):



^{13}C-NMR (100.61 MHz, $CDCl_3$):

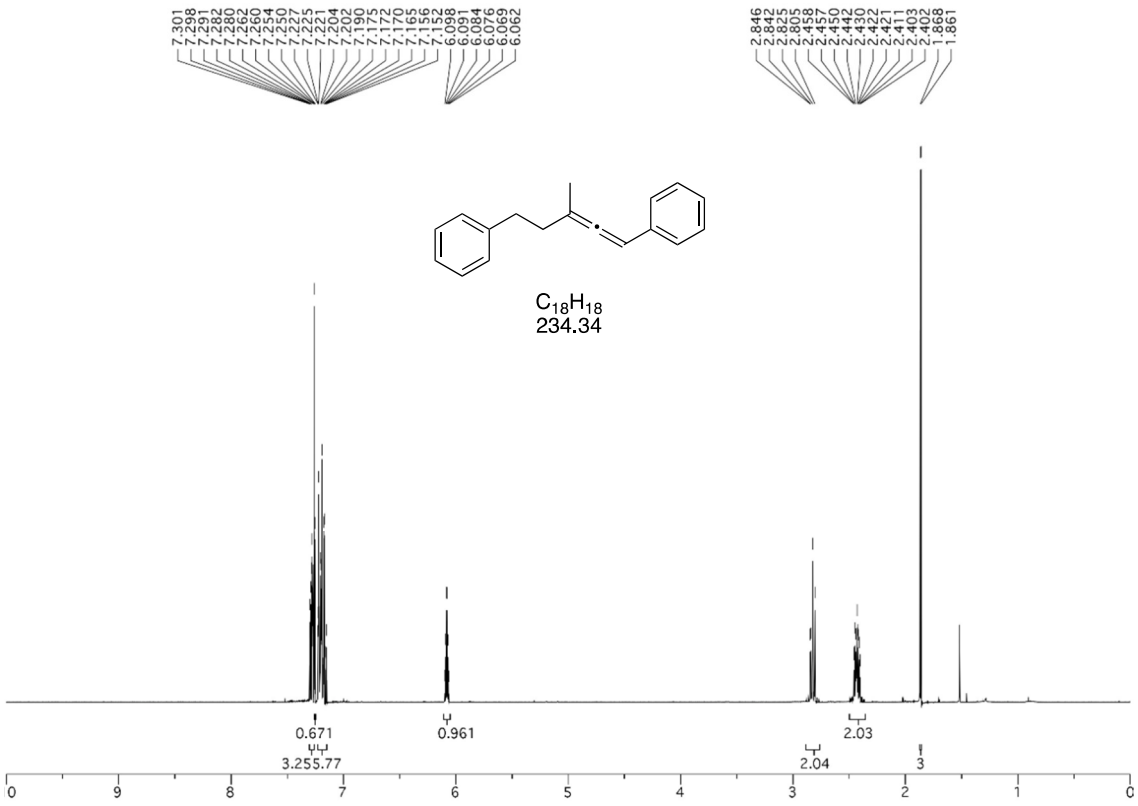


^{19}F-NMR (376.76 MHz, $CDCl_3$, unified scale):

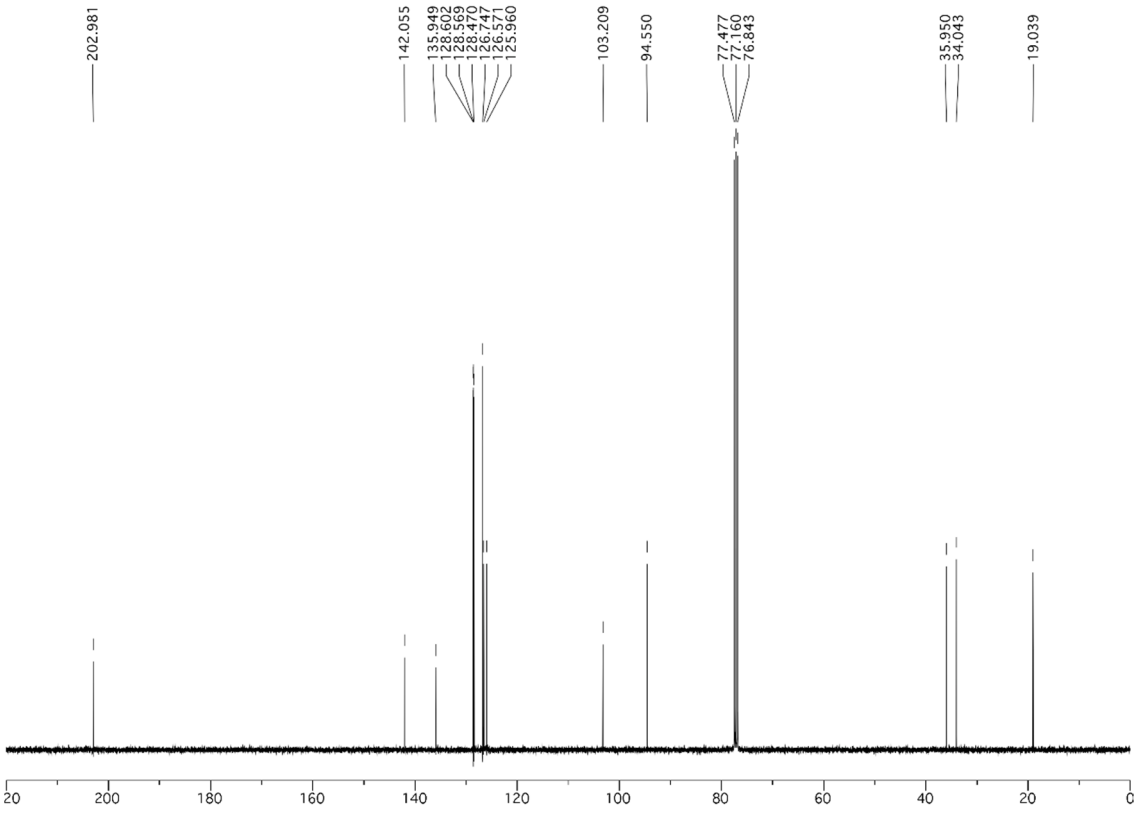


(3-methylpenta-1,2-diene-1,5-diyl)dibenzene

^{1}H-NMR (400.13 MHz, $CDCl_3$):

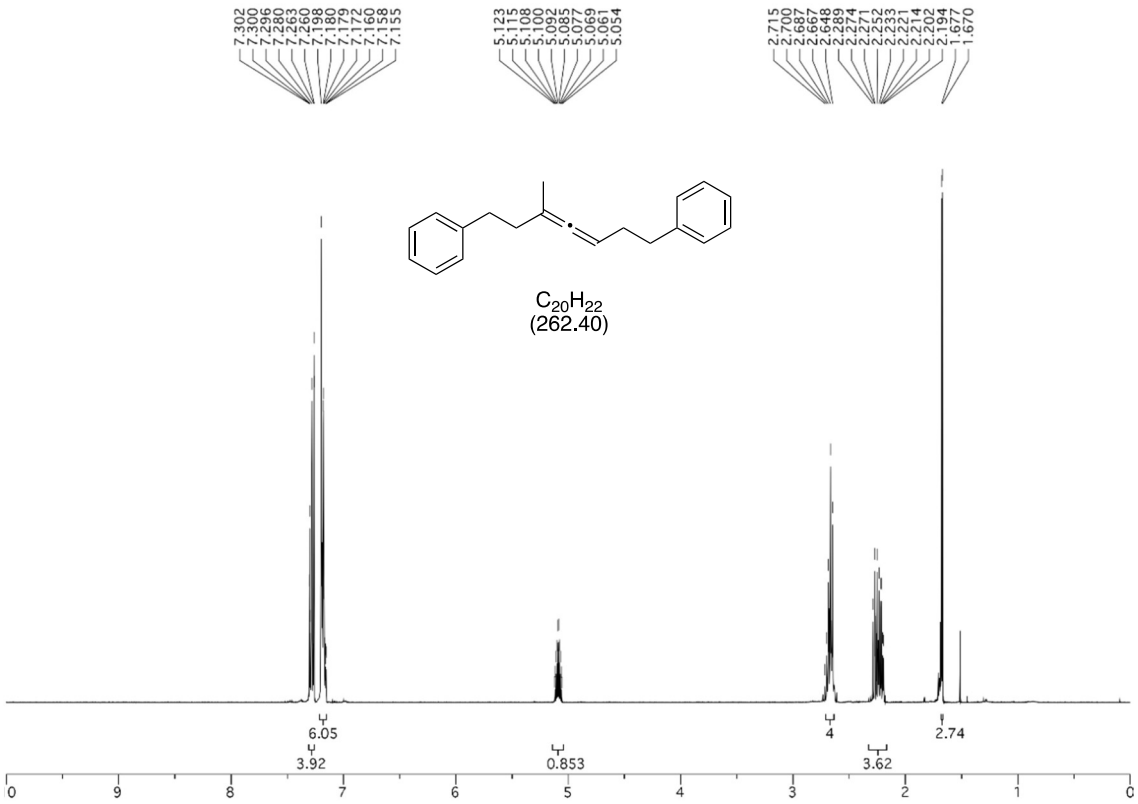


^{13}C-NMR (100.61 MHz, $CDCl_3$):

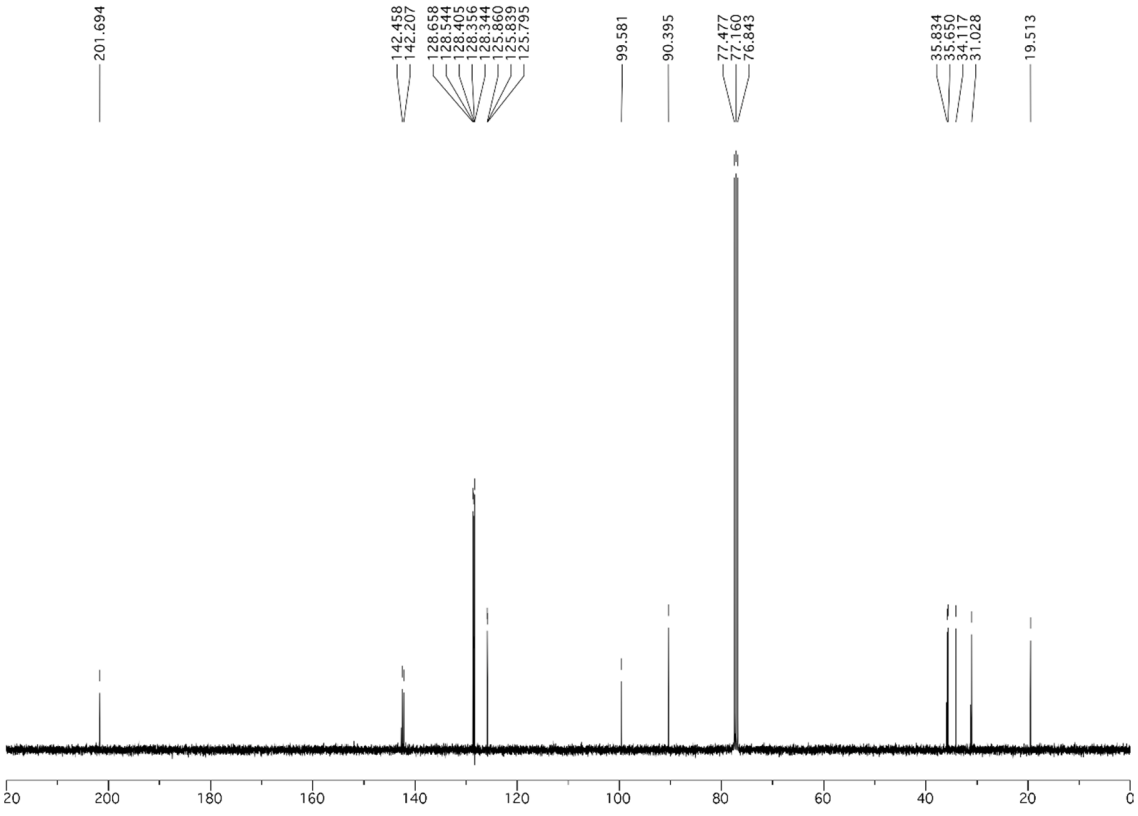


(3-methylhepta-3,4-diene-1,7-diyl)dibenzene

^{1}H-NMR (400.13 MHz, $CDCl_3$):

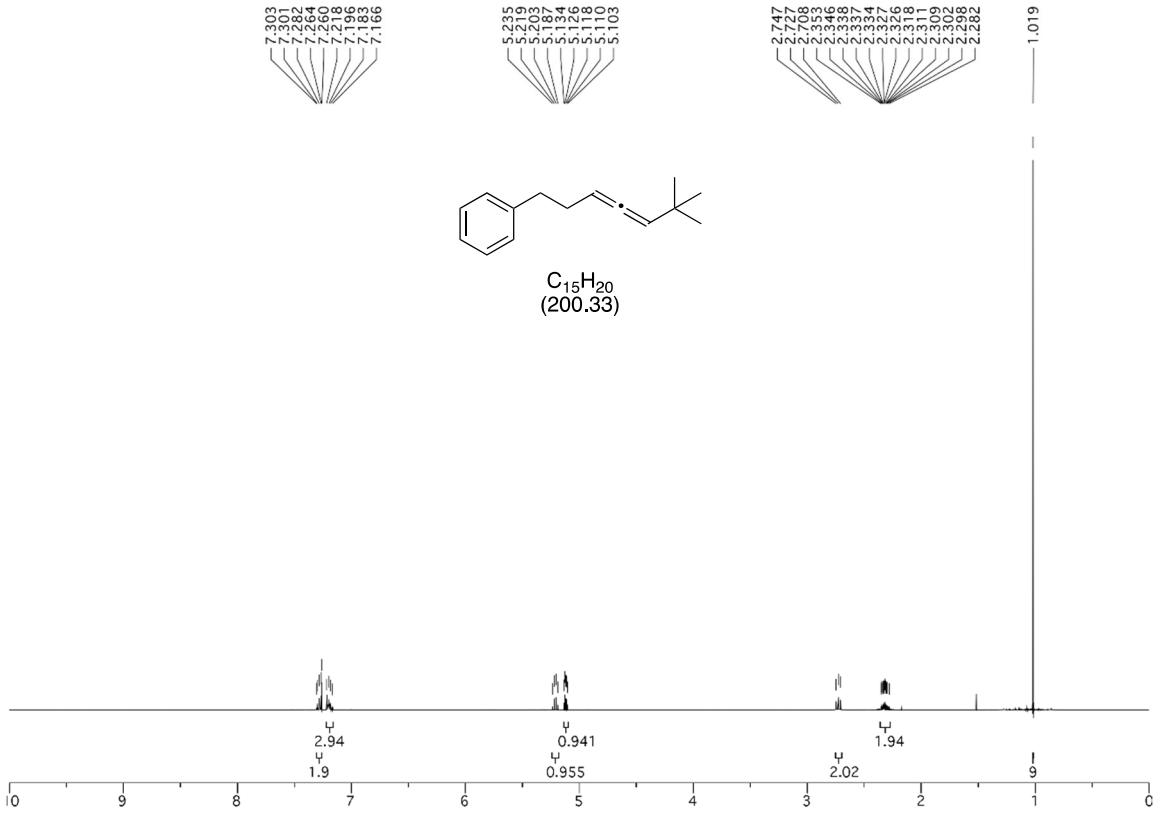


^{13}C-NMR (100.61 MHz, $CDCl_3$):

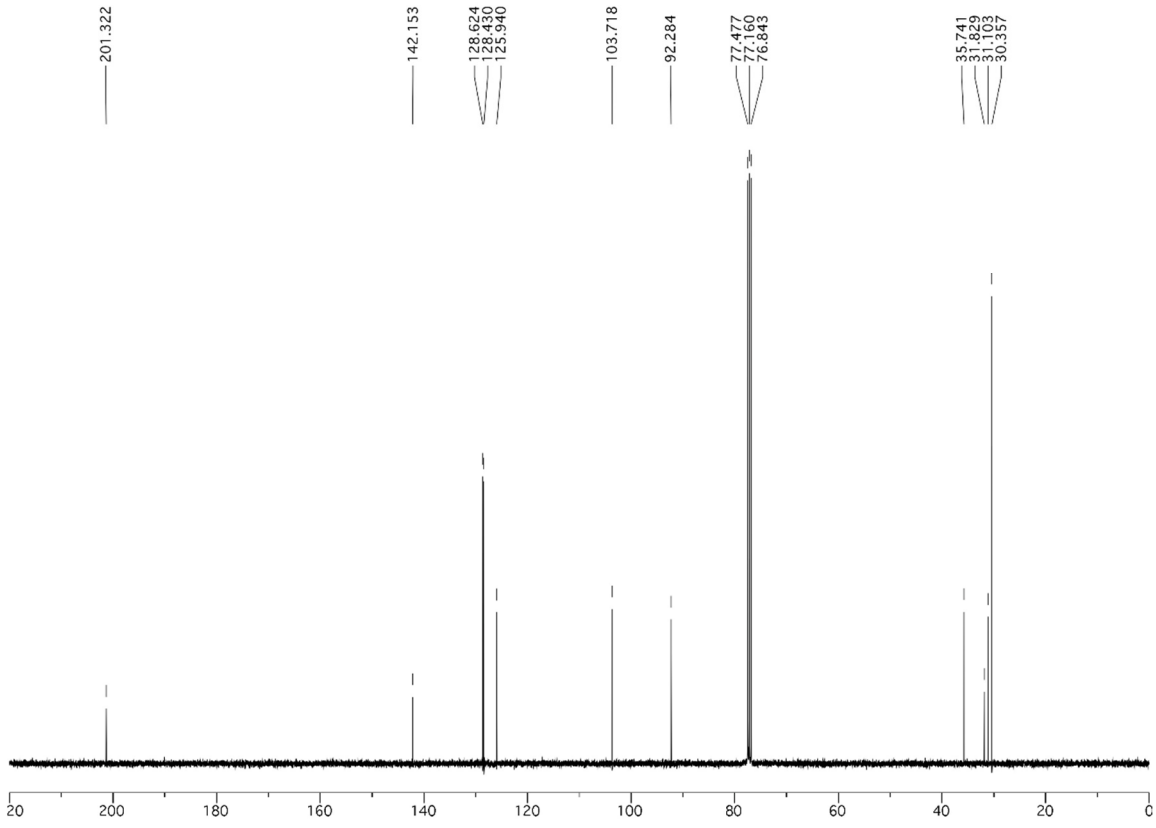


(6,6-dimethylhepta-3,4-dien-1-yl)benzene

^{1}H-NMR (400.13 MHz, $CDCl_3$):

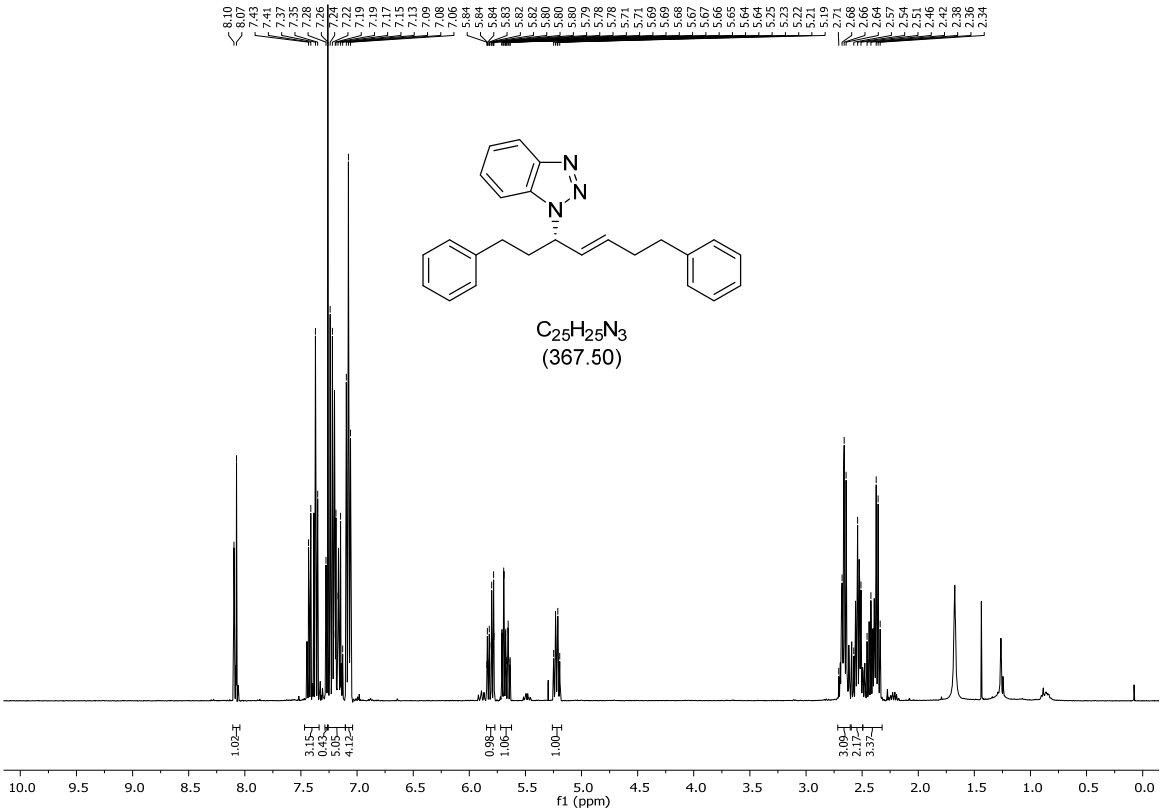


^{13}C-NMR (100.61 MHz, $CDCl_3$):

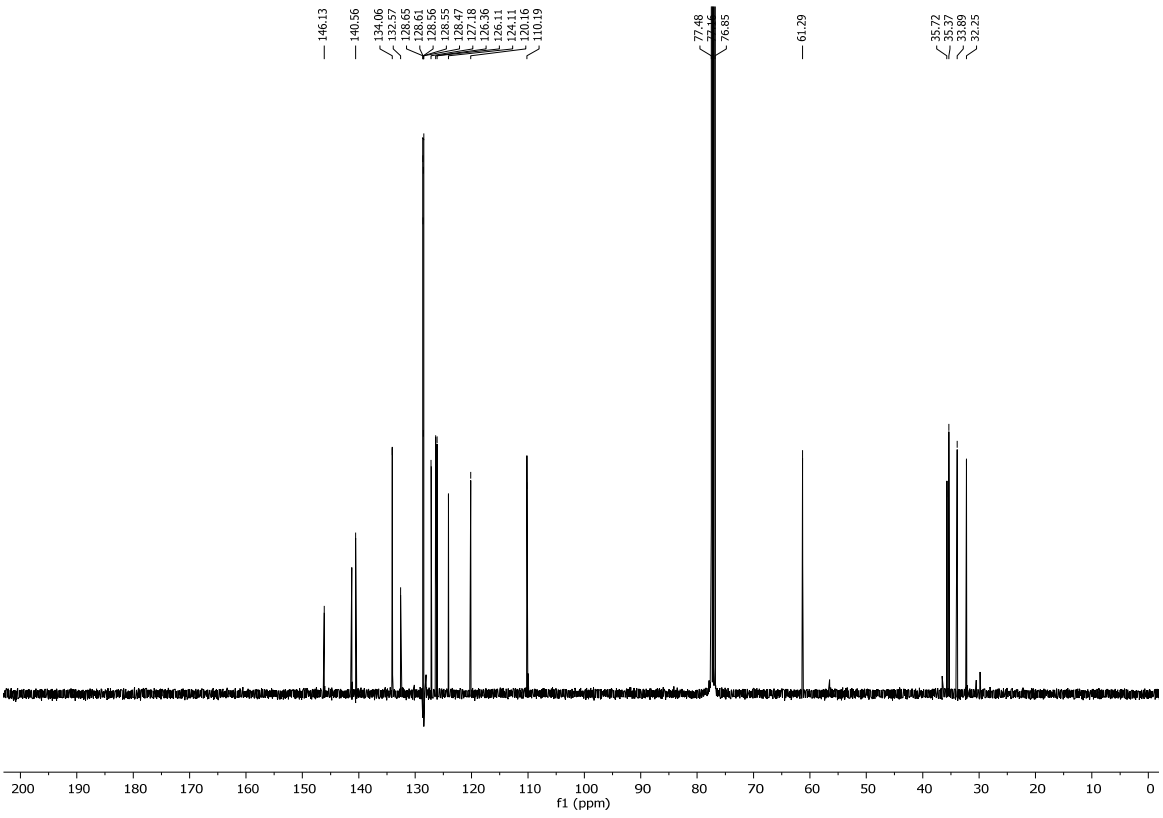


(*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 3)

^{1}H-NMR (400.13 MHz, $CDCl_3$):

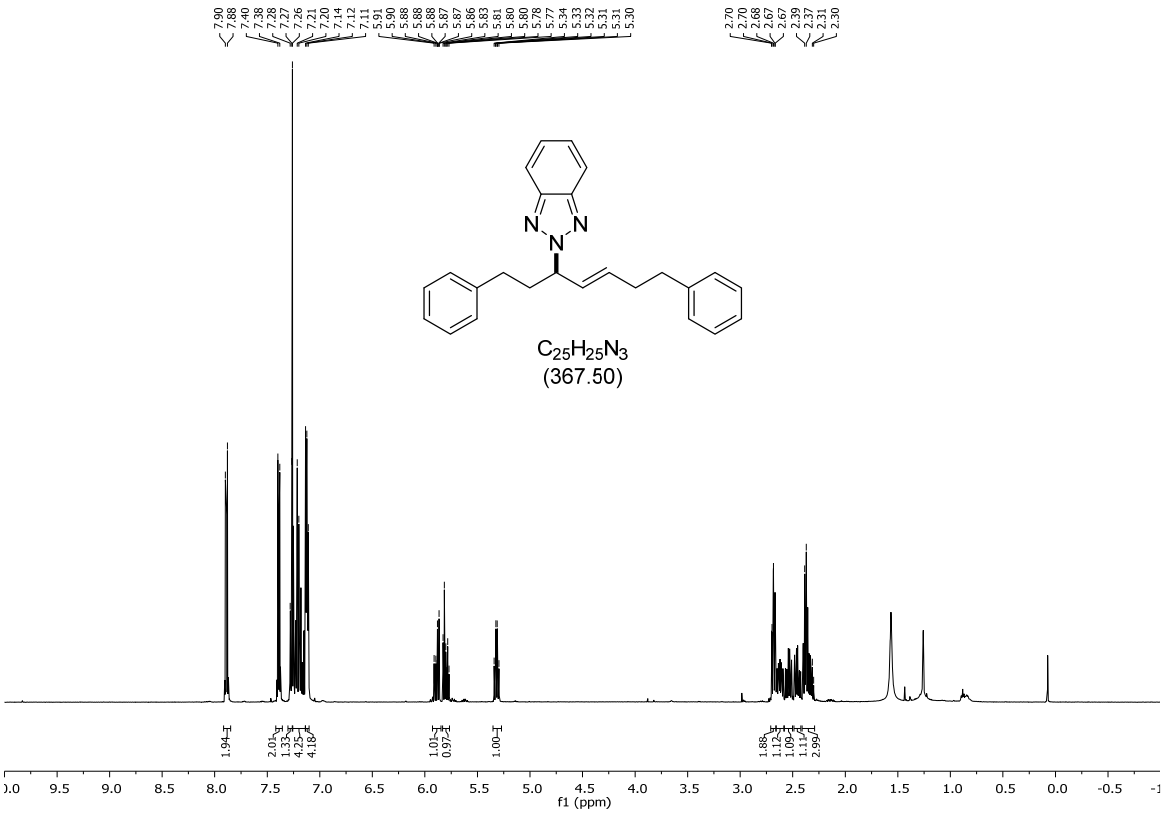


^{13}C-NMR (100.61 MHz, $CDCl_3$):

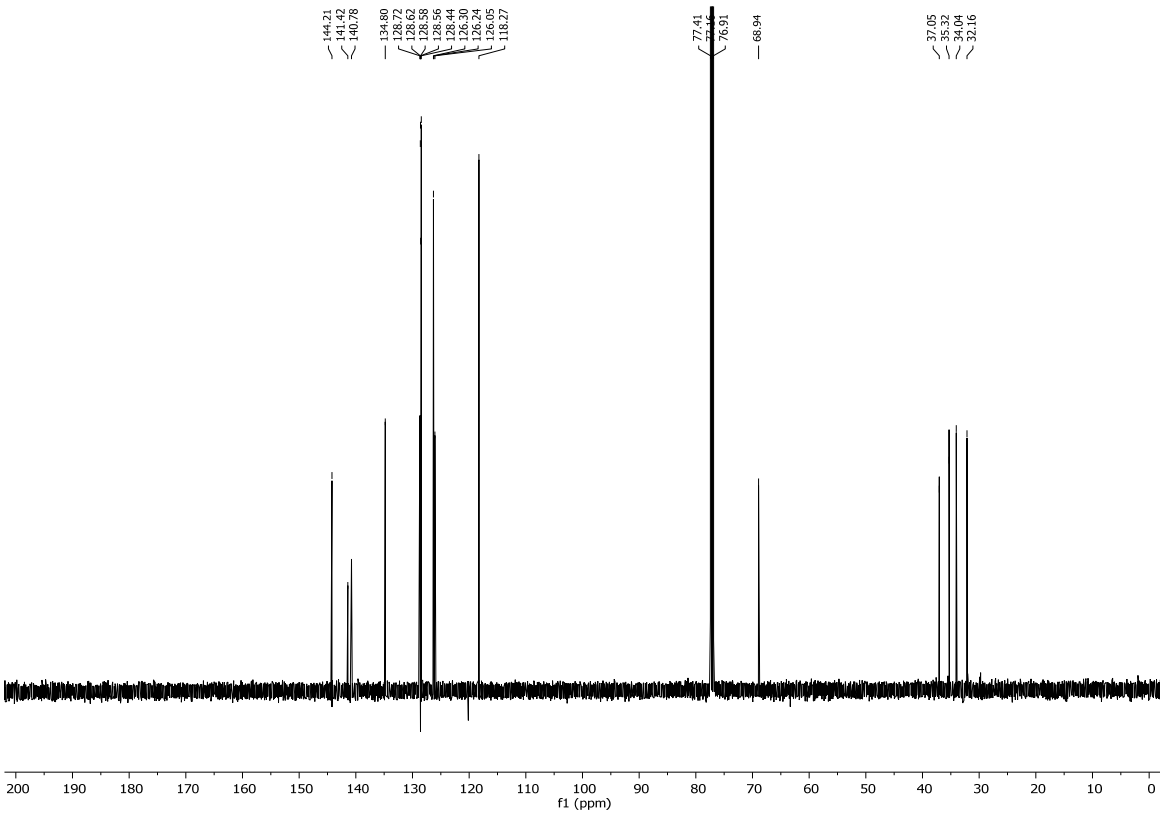


(*E*)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-benzo[*d*][1,2,3]triazole (*N*^{2}-product, 3b)

^{1}H-NMR (500.10 MHz, $CDCl_3$):

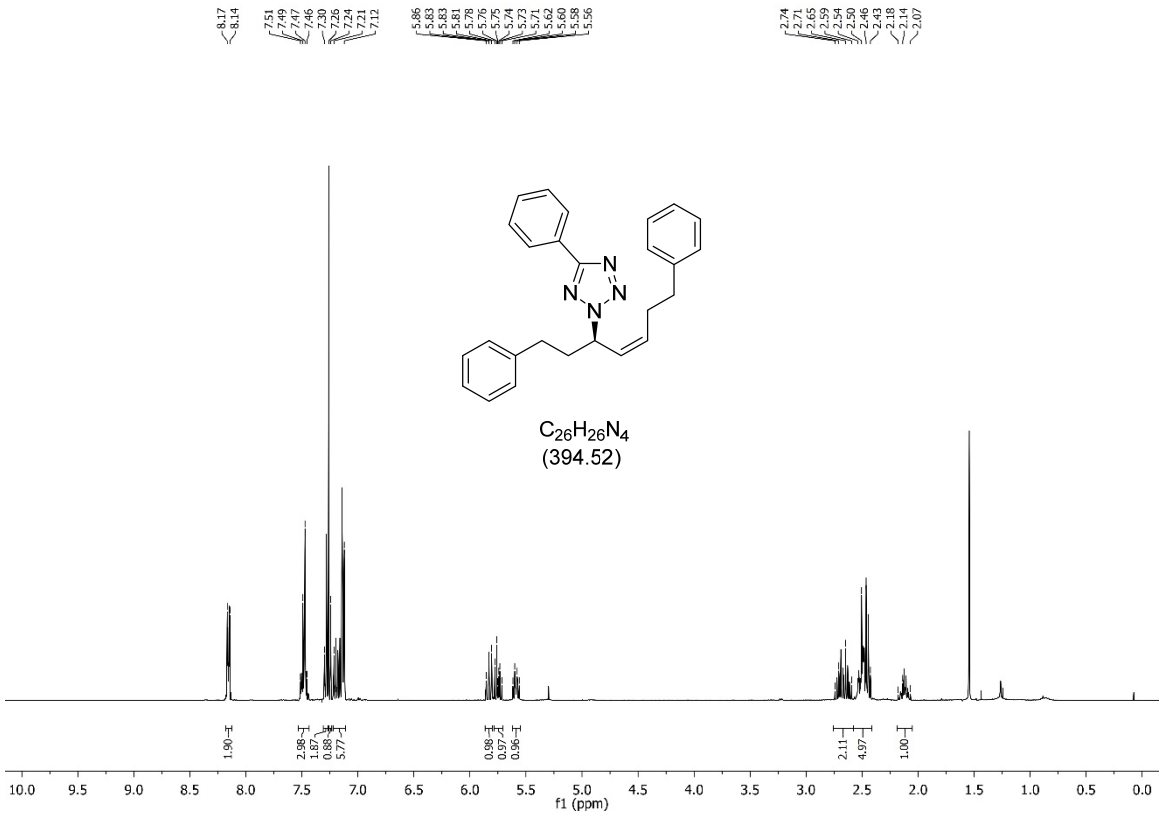


^{13}C-NMR (125.75 MHz, $CDCl_3$):

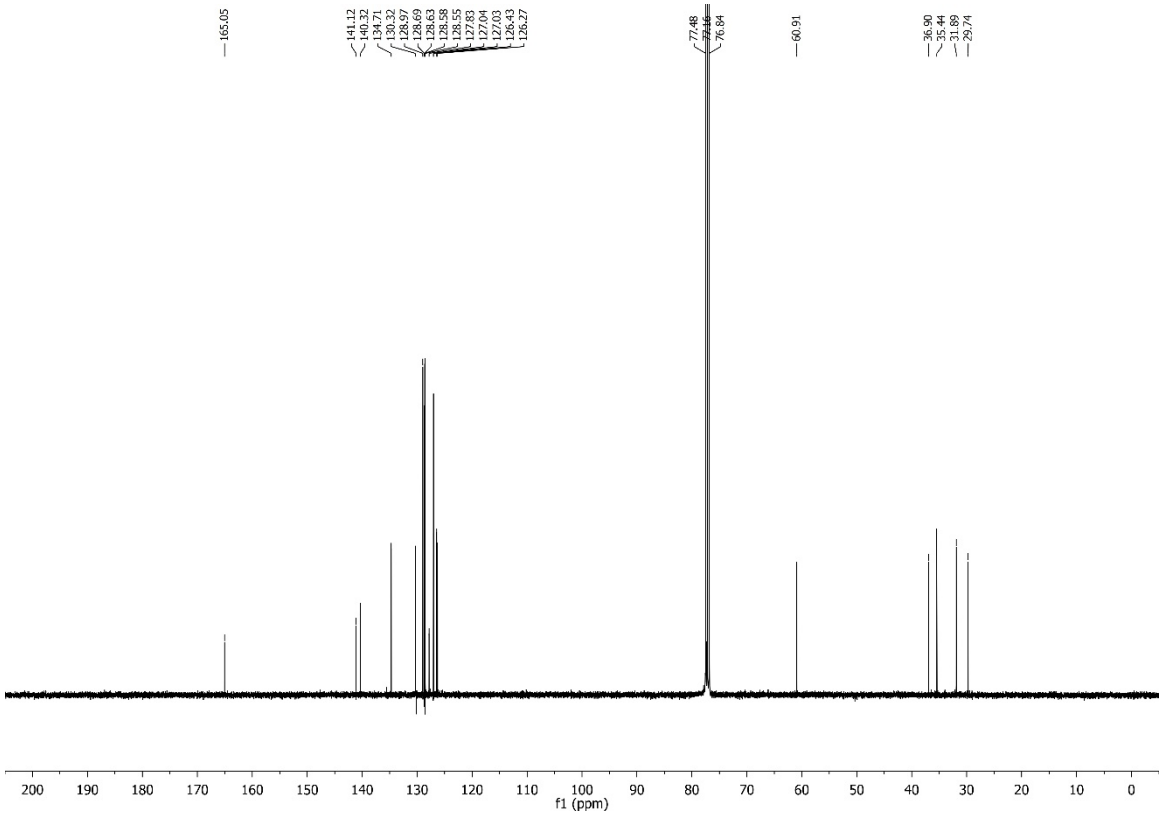


(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-phenyl-2*H*-tetrazole (5)

^{1}H-NMR (400.13 MHz, $CDCl_3$):

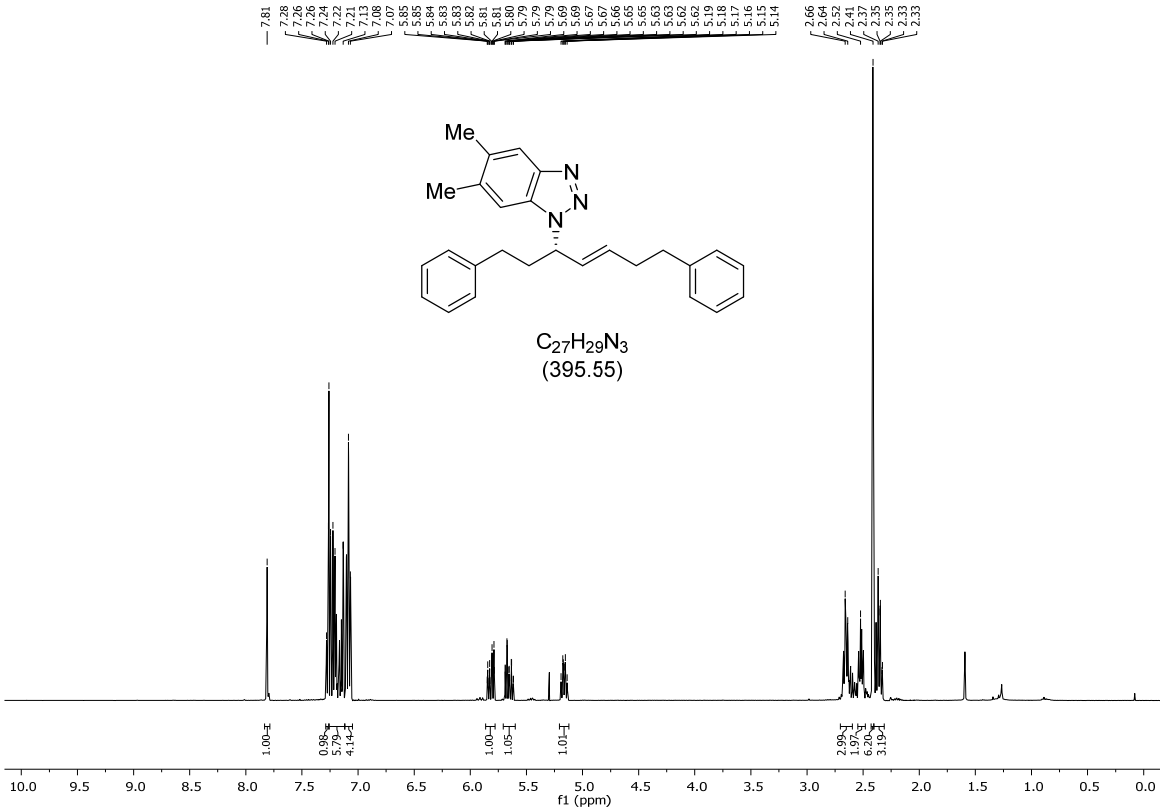


^{13}C-NMR (100.61 MHz, $CDCl_3$):

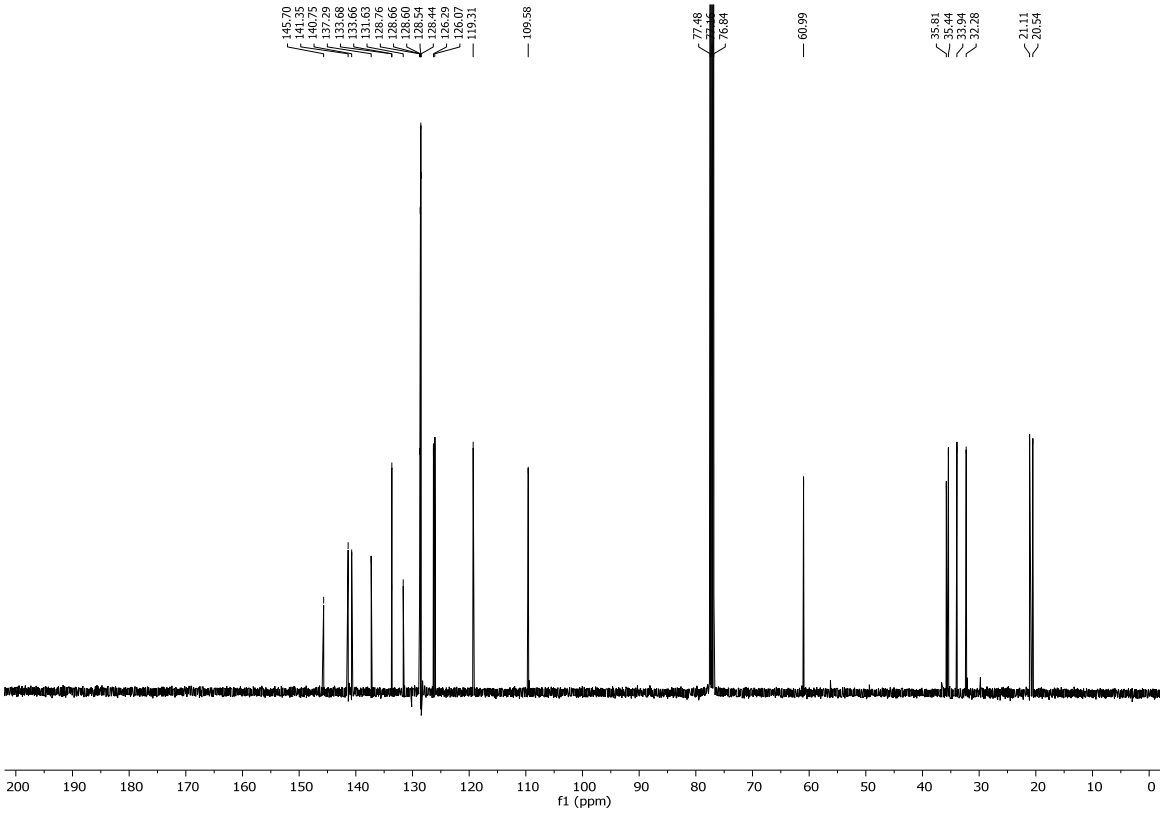


(*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-5,6-dimethyl-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 6)

^{1}H-NMR (400.13 MHz, $CDCl_3$):

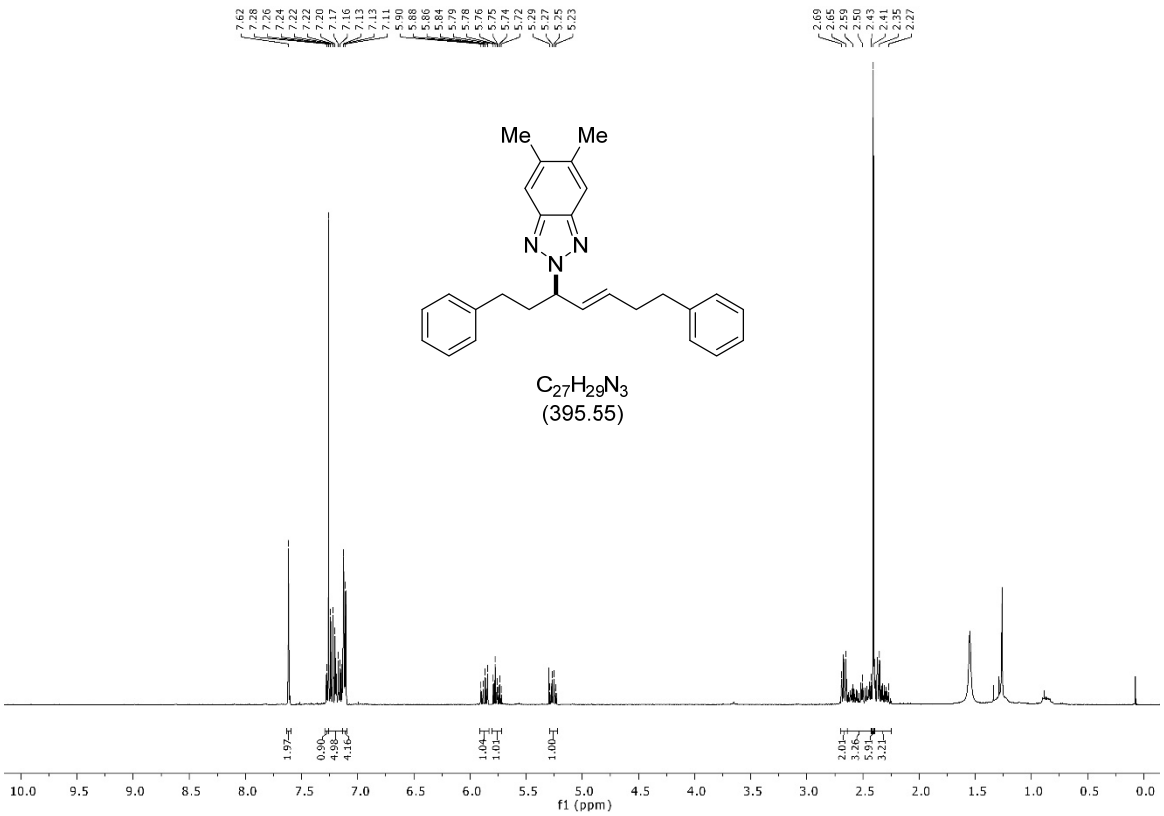


^{13}C-NMR (100.61 MHz, $CDCl_3$):

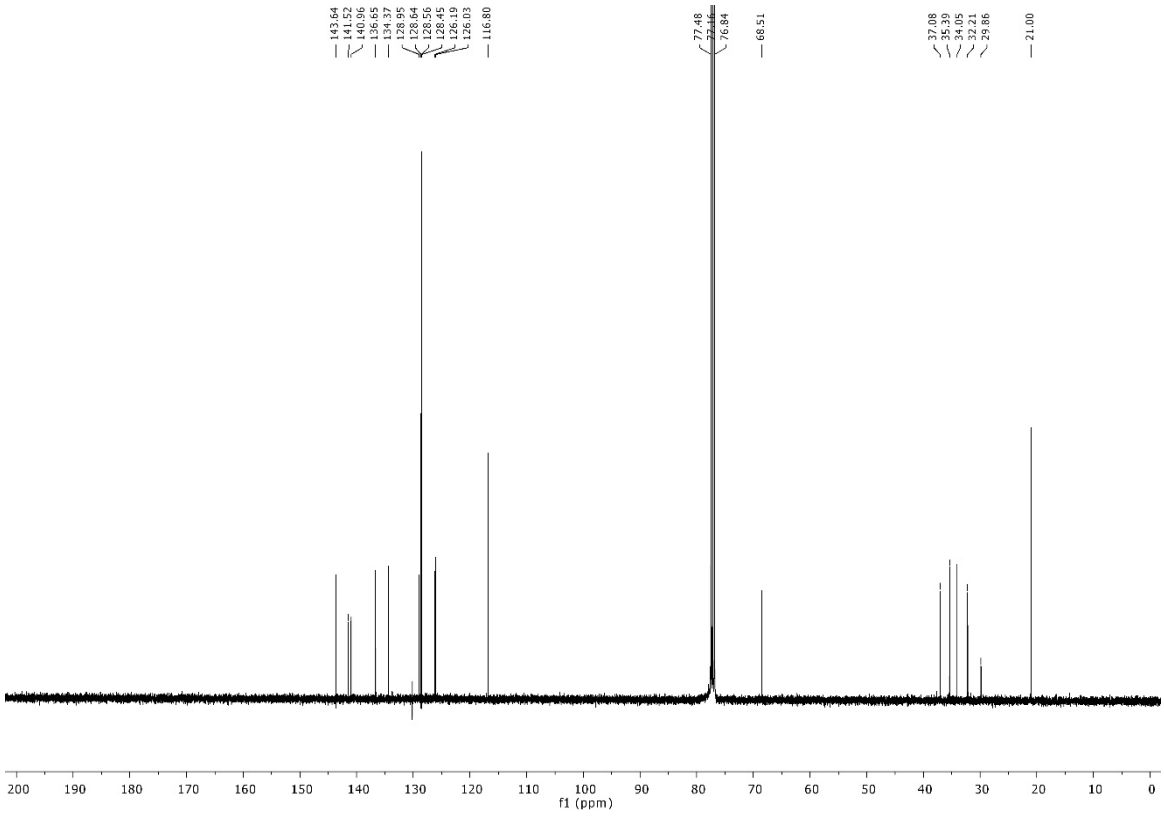


(*E*)-2-(1,7-diphenylhept-4-en-3-yl)-5,6-dimethyl-2*H*-benzo[*d*][1,2,3]triazole (N^2-product, 6b)

^{1}H-NMR (400.13 MHz, $CDCl_3$):

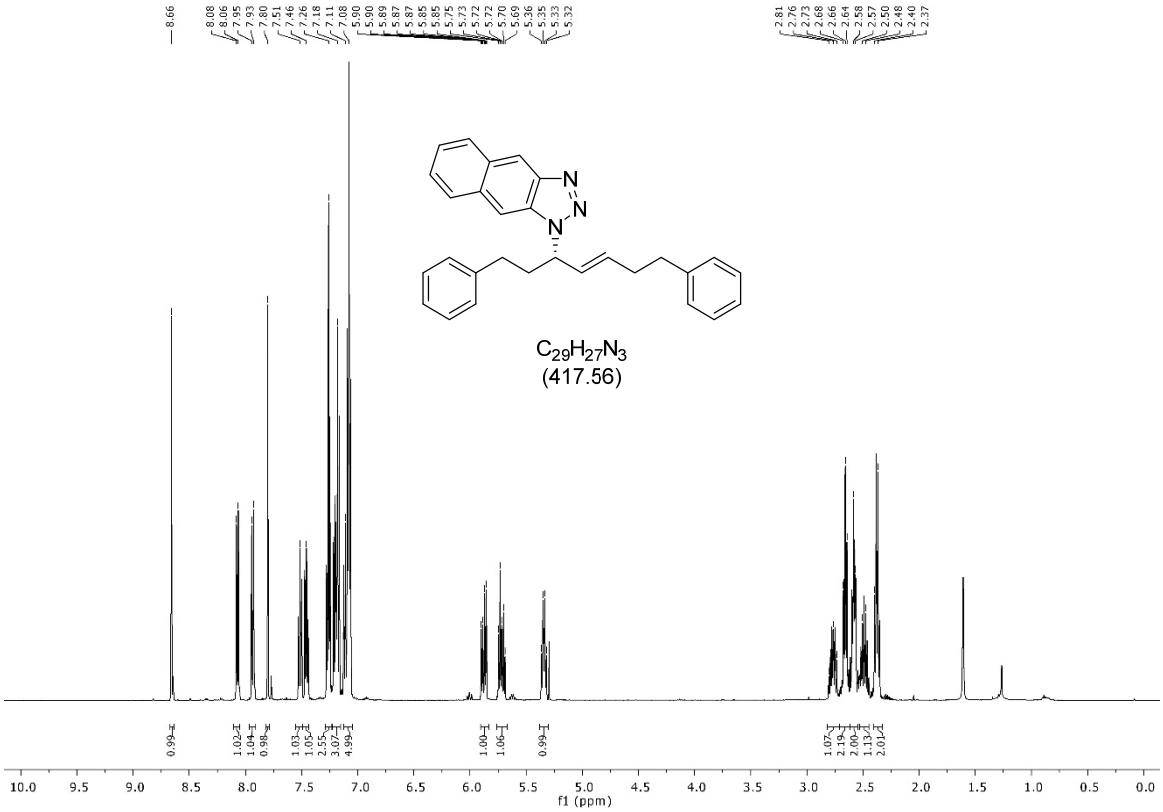


^{13}C-NMR (100.61 MHz, $CDCl_3$):

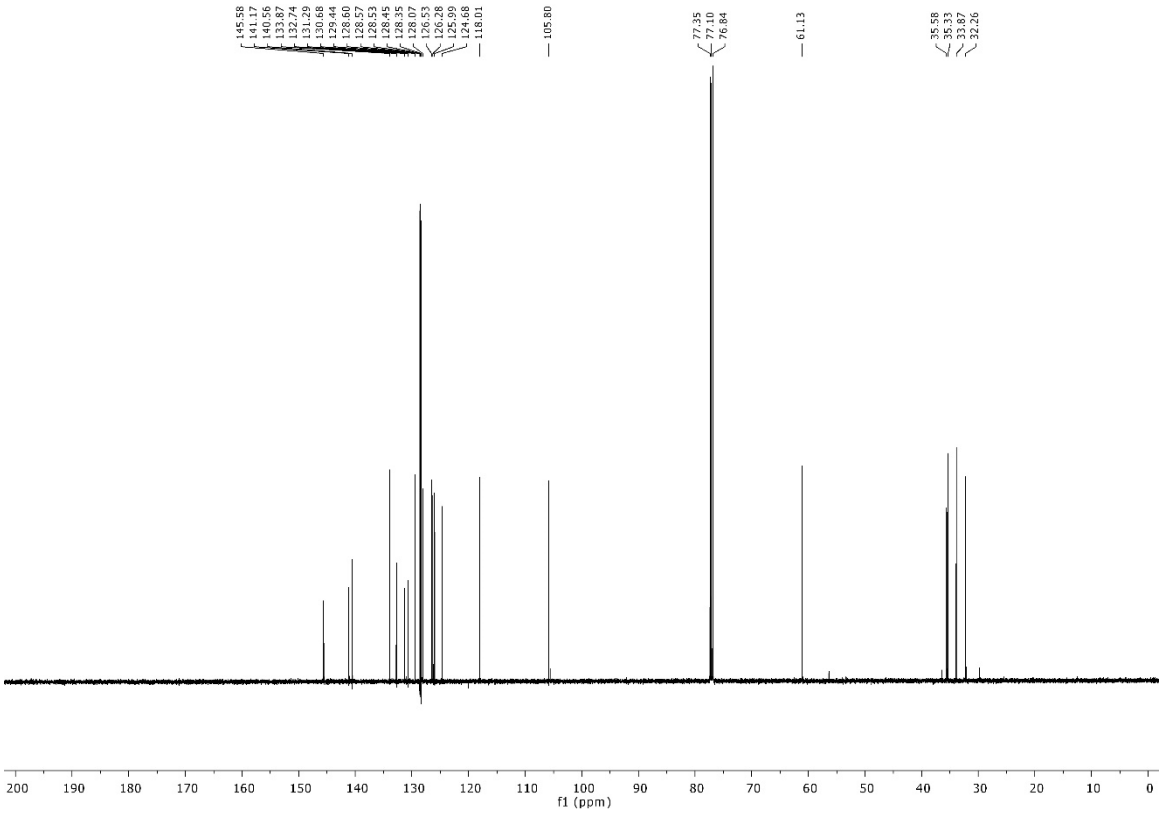


(*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole (*N*^{1}-product, 7)

^{1}H-NMR (400.13 MHz, $CDCl_3$):

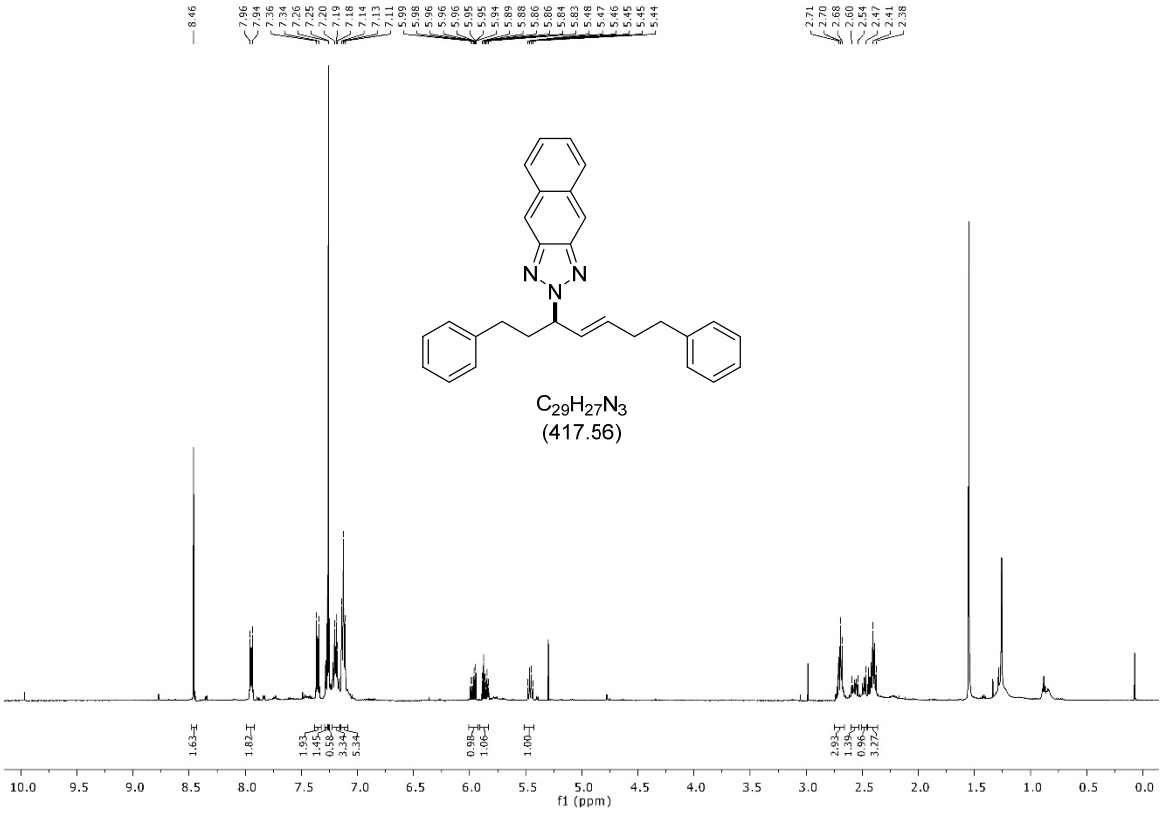


^{13}C-NMR (100.61 MHz, $CDCl_3$):

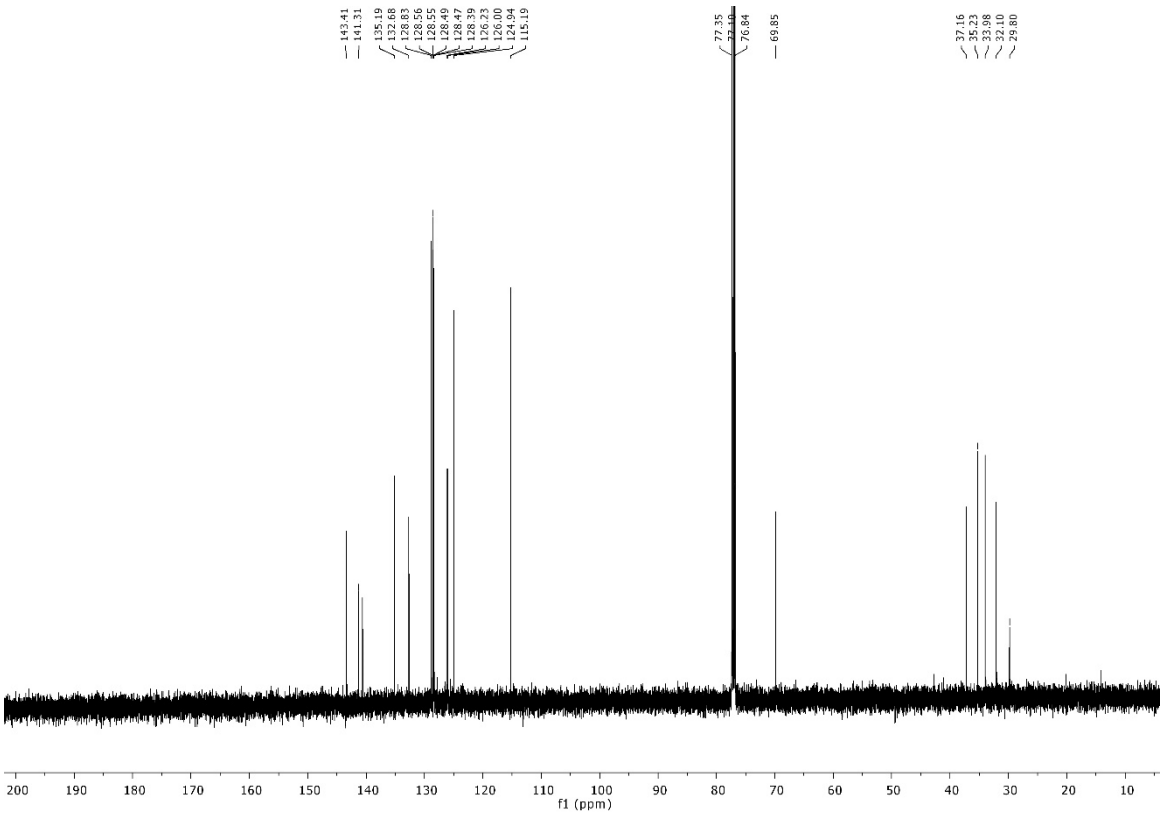


(*E*)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-naphtho[2,3-*d*][1,2,3]triazole (N^2-product, 7b)

^{1}H-NMR (400.13 MHz, $CDCl_3$):

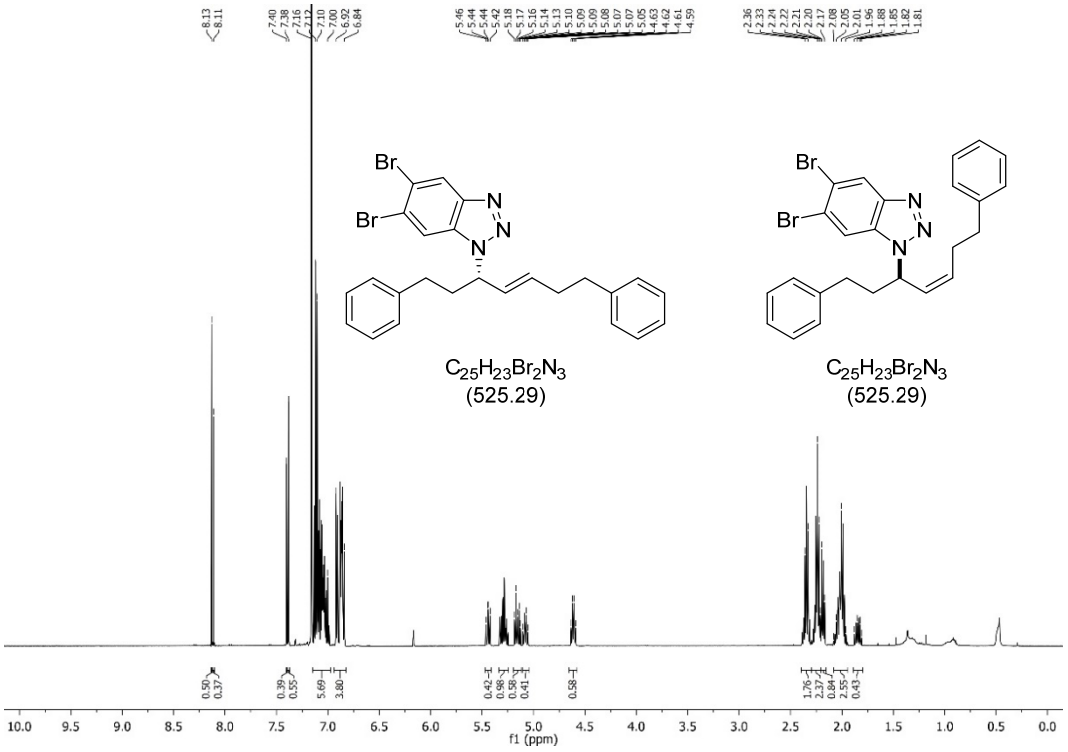


^{13}C-NMR (100.61 MHz, $CDCl_3$):

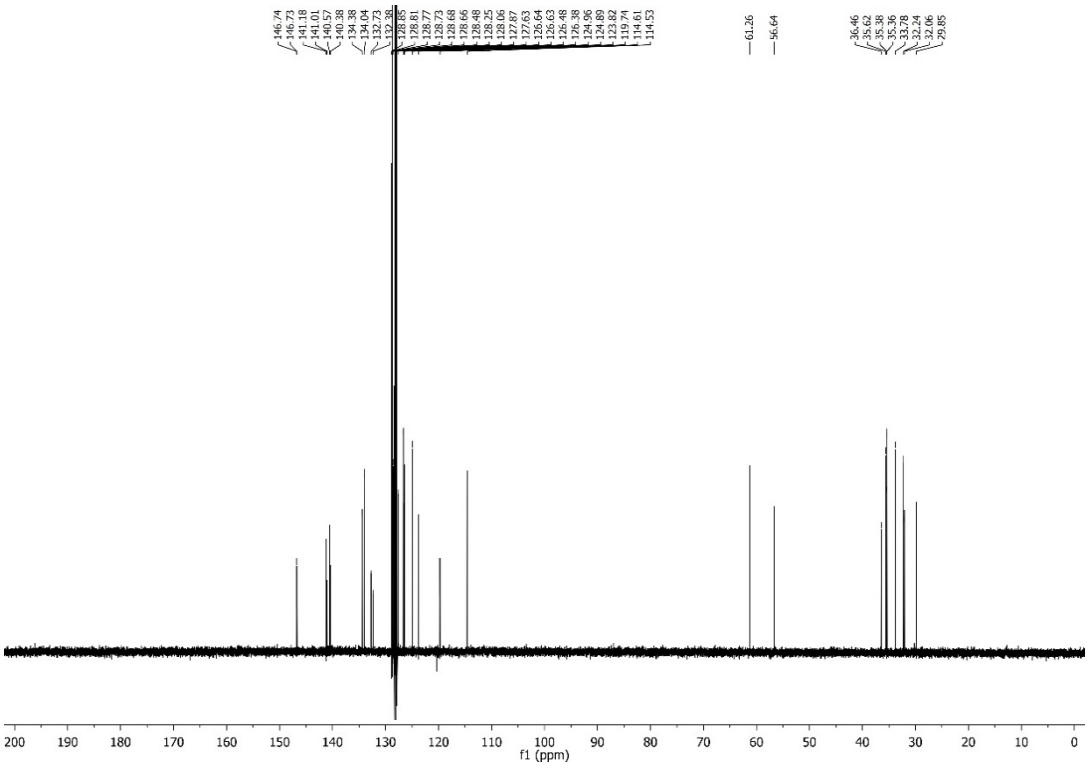


(*S*,*E*)-5,6-dibromo-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-, *E*-product, 8) & (*Z*)-5,6-dibromo-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-, *Z*-product, 8b)

^{1}H-NMR (499.98 MHz, C_6D_6):

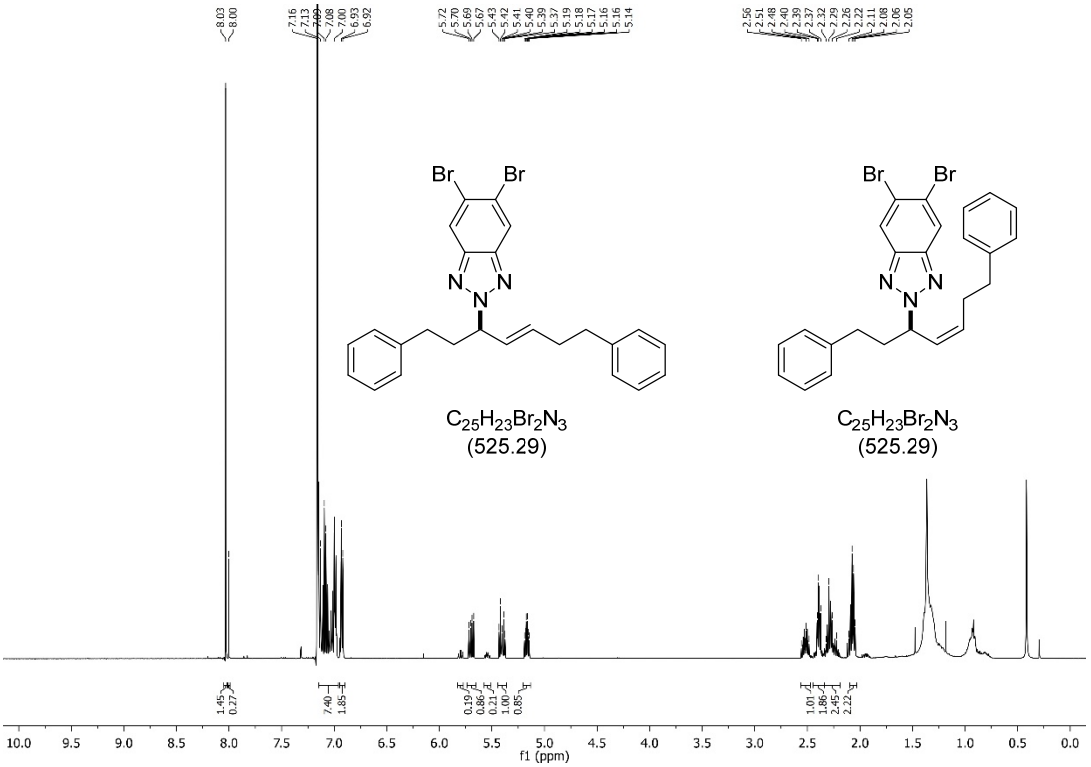


^{13}C-NMR (125.72 MHz, C_6D_6):

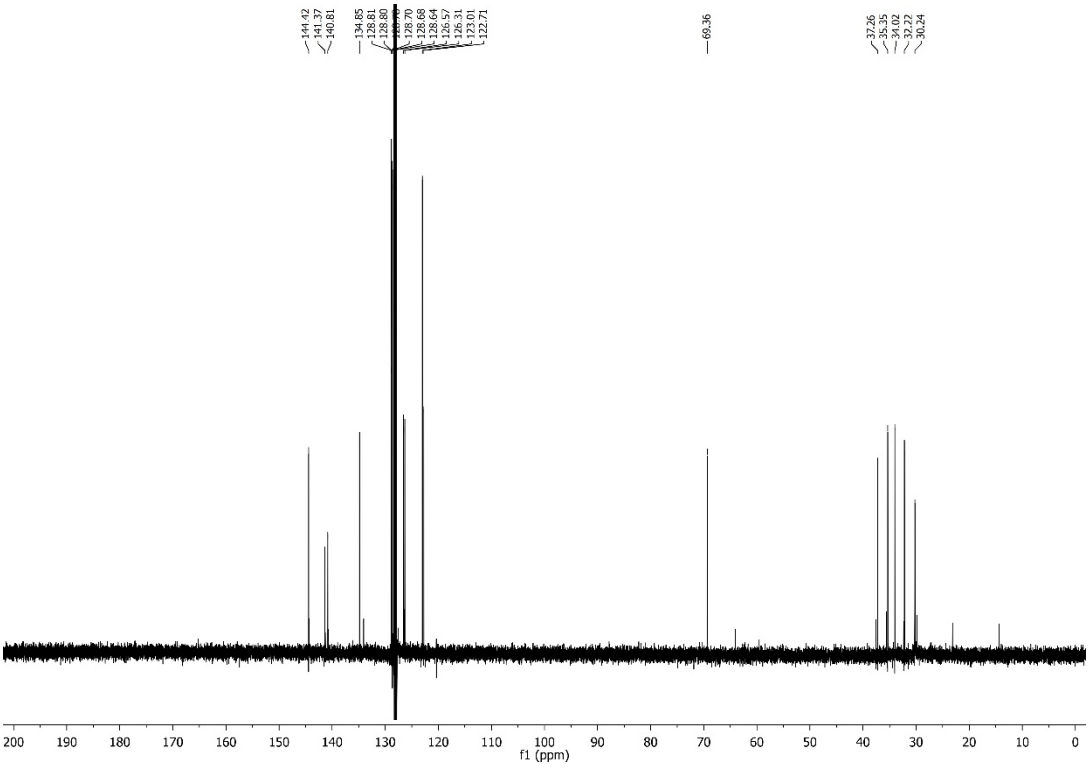


(*E*)-5,6-dibromo-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-benzo[*d*][1,2,3]triazole (N^2-, *E*-product, 8c) & (*Z*)-5,6-dibromo-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-benzo[*d*][1,2,3]triazole (N^2-, *Z*-product, 8d)

^{1}H-NMR (499.98 MHz, C_6D_6):



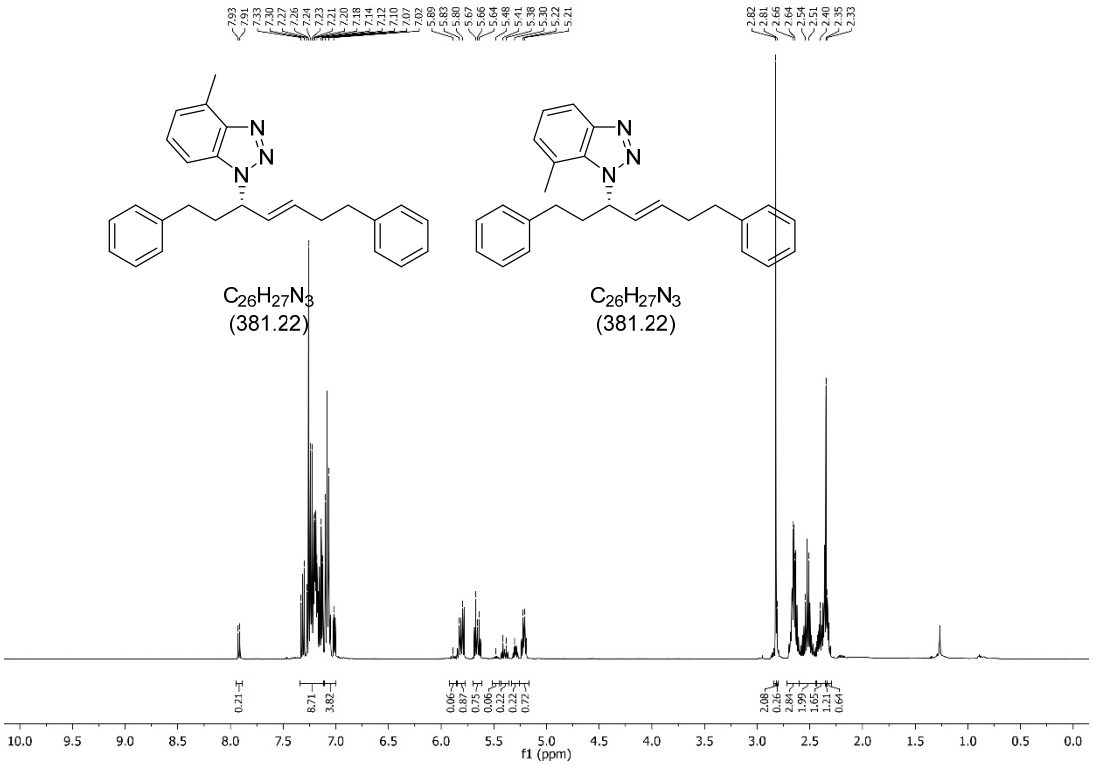
^{13}C-NMR (125.72 MHz, C_6D_6):



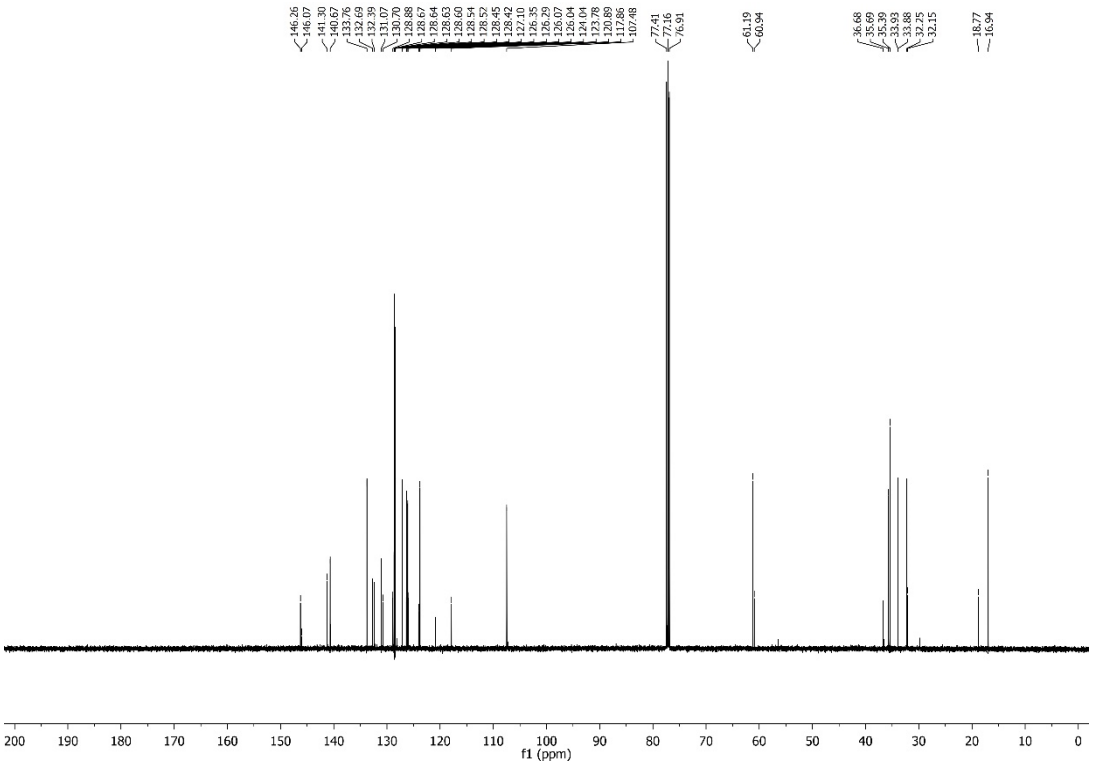
(*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-4-methyl-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 9) &

(*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-7-methyl-1*H*-benzo[*d*][1,2,3]triazole (*N*^{3}-product, 9b)

^{1}H-NMR (499.98 MHz, $CDCl_3$):

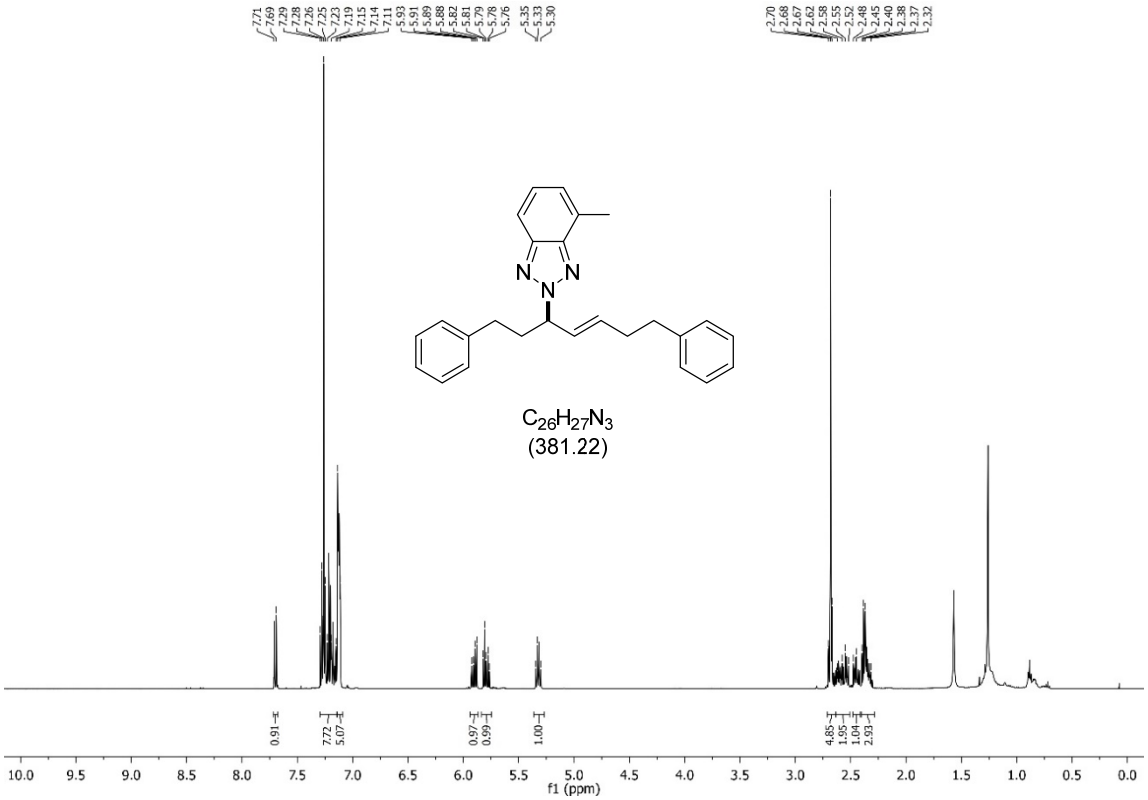


^{13}C-NMR (125.72 MHz, $CDCl_3$):

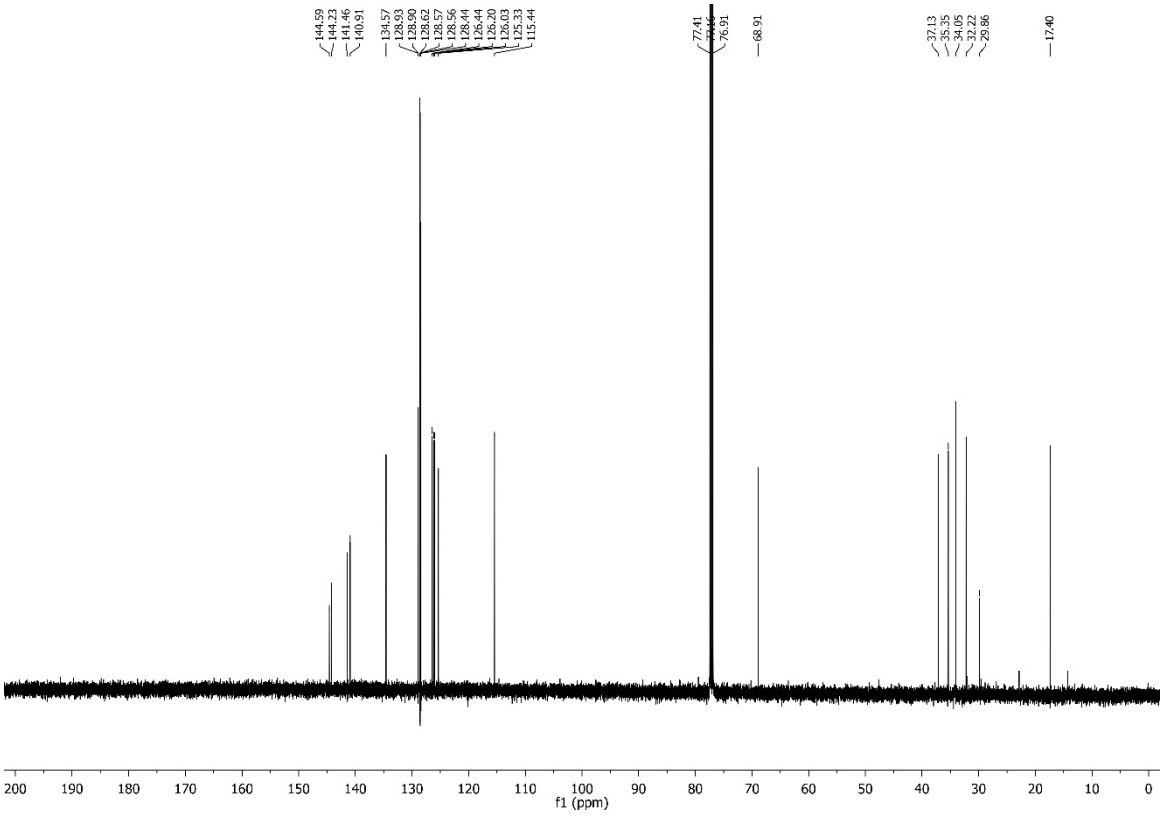


(*E*)-2-(1,7-diphenylhept-4-en-3-yl)-4-methyl-2*H*-benzo[*d*][1,2,3]triazole (N^2-product, 9c)

^{1}H-NMR (499.98 MHz, $CDCl_3$):

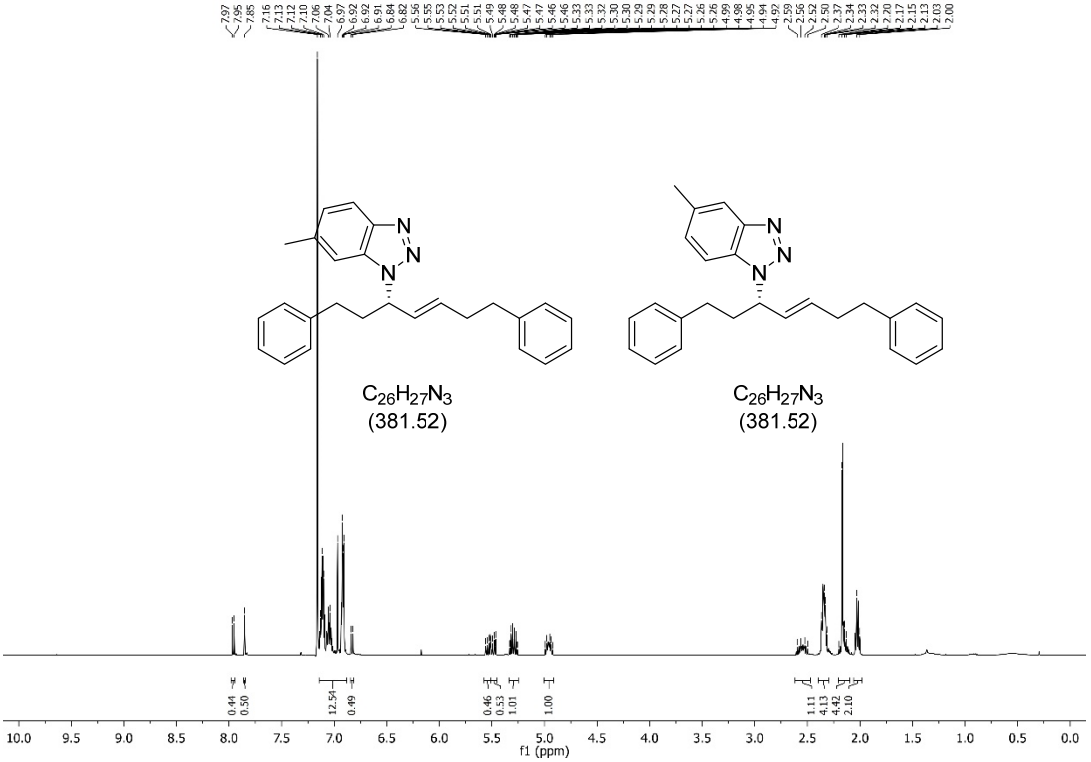


^{13}C-NMR (125.72 MHz, $CDCl_3$):

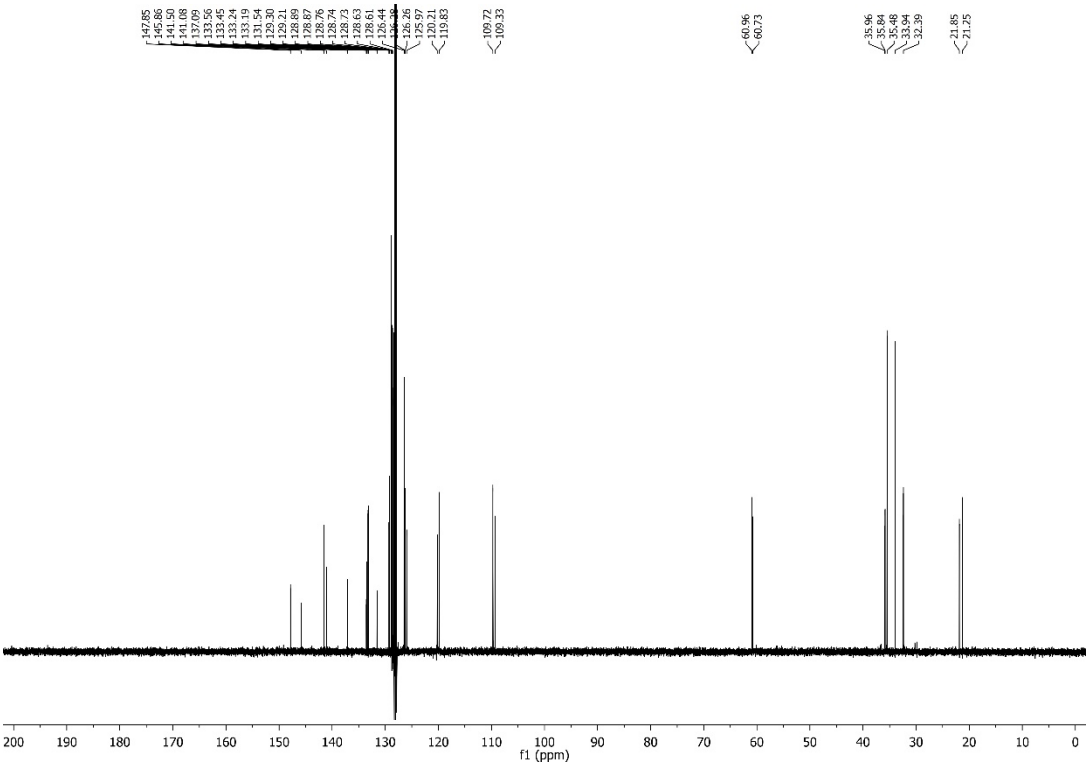


(*E*)-1-(1,7-diphenylhept-4-en-3-yl)-6-methyl-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 10) & (*E*)-1-(1,7-diphenylhept-4-en-3-yl)-5-methyl-1*H*-benzo[*d*][1,2,3]triazole (*N*^{3}-product, 10b)

^{1}H-NMR (499.98 MHz, C_6D_6):

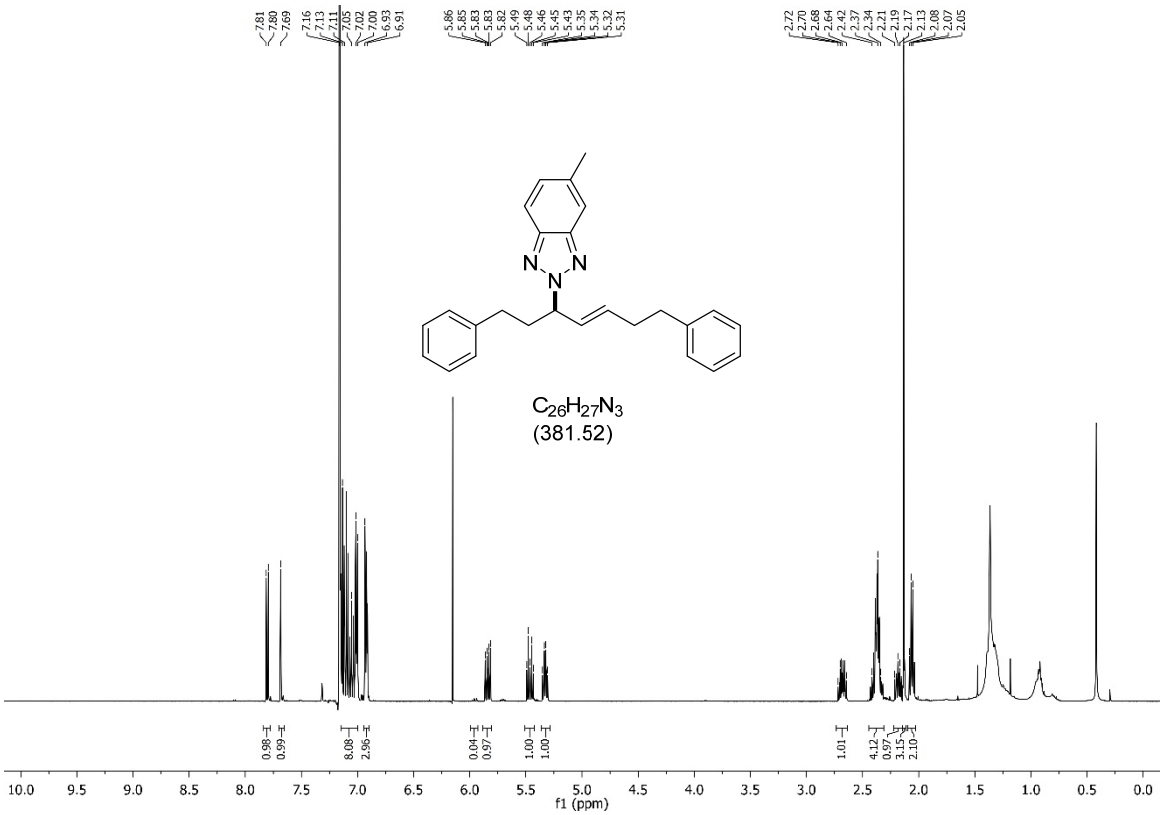


^{13}C-NMR (125.72 MHz, C_6D_6):

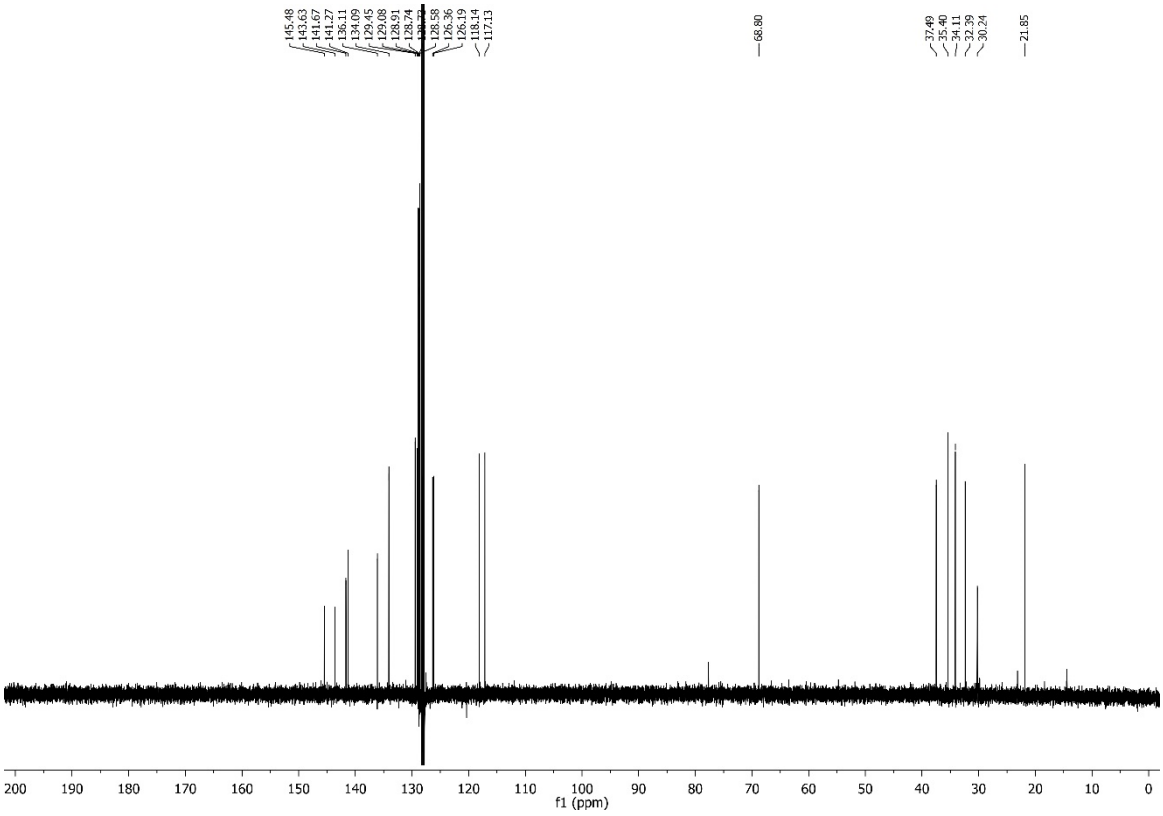


(*E*)-2-(1,7-diphenylhept-4-en-3-yl)-5-methyl-2*H*-benzo[*d*][1,2,3]triazole (*N*^{2}-product, 10c)

^{1}H-NMR (499.98 MHz, C_6D_6):

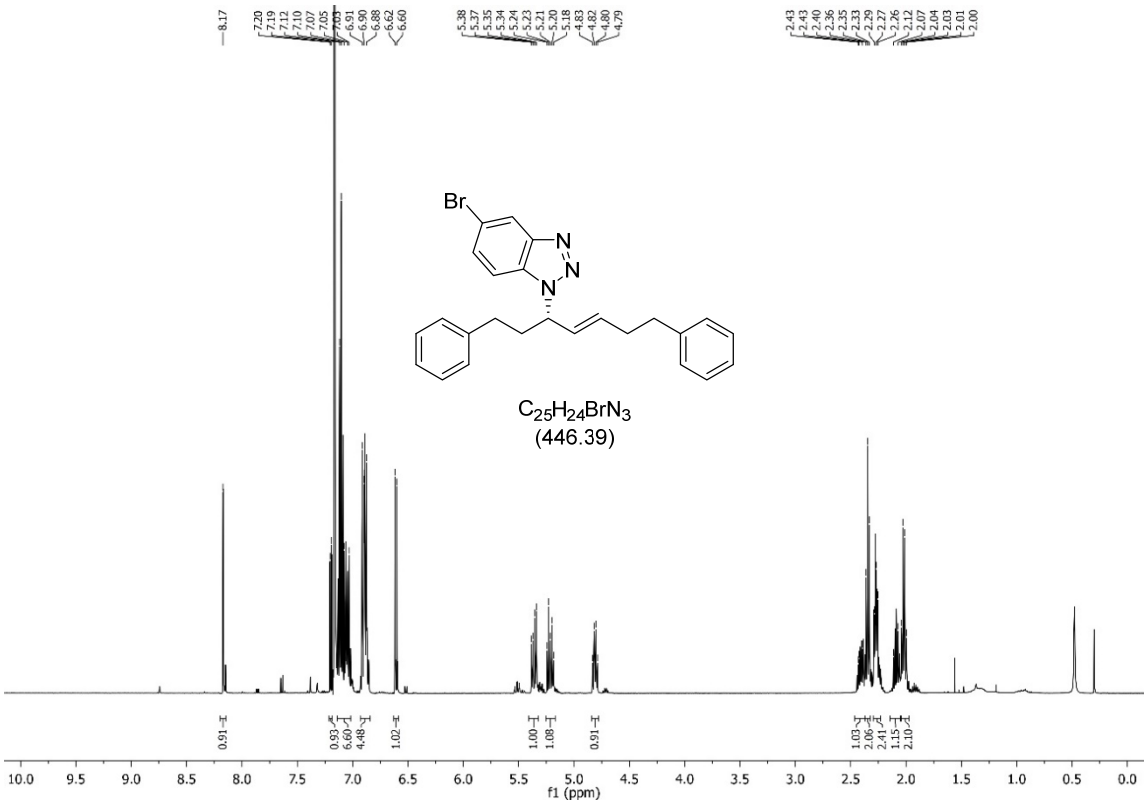


^{13}C-NMR (125.72 MHz, C_6D_6):

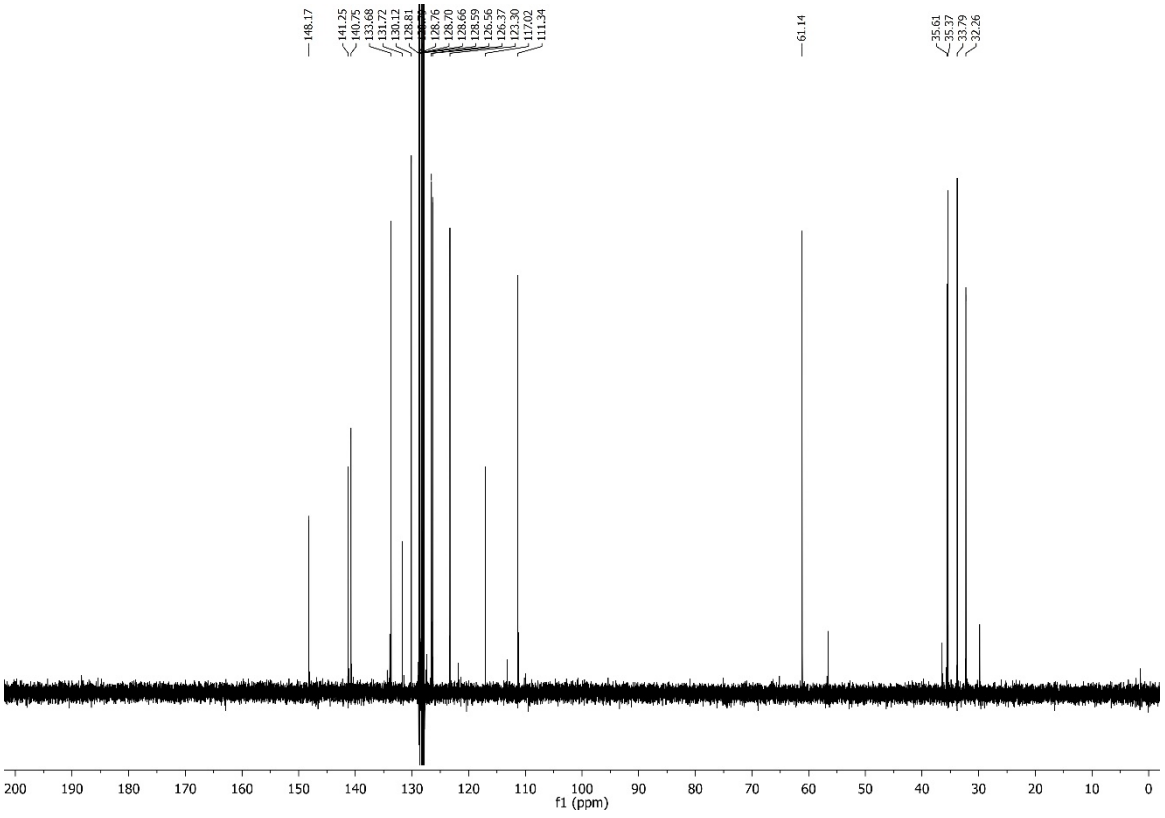


(*S*,*E*)-5-bromo-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[d][1,2,3]triazole (*N*[1]-product, 11)

^{1}H-NMR (499.98 MHz, C_6D_6):

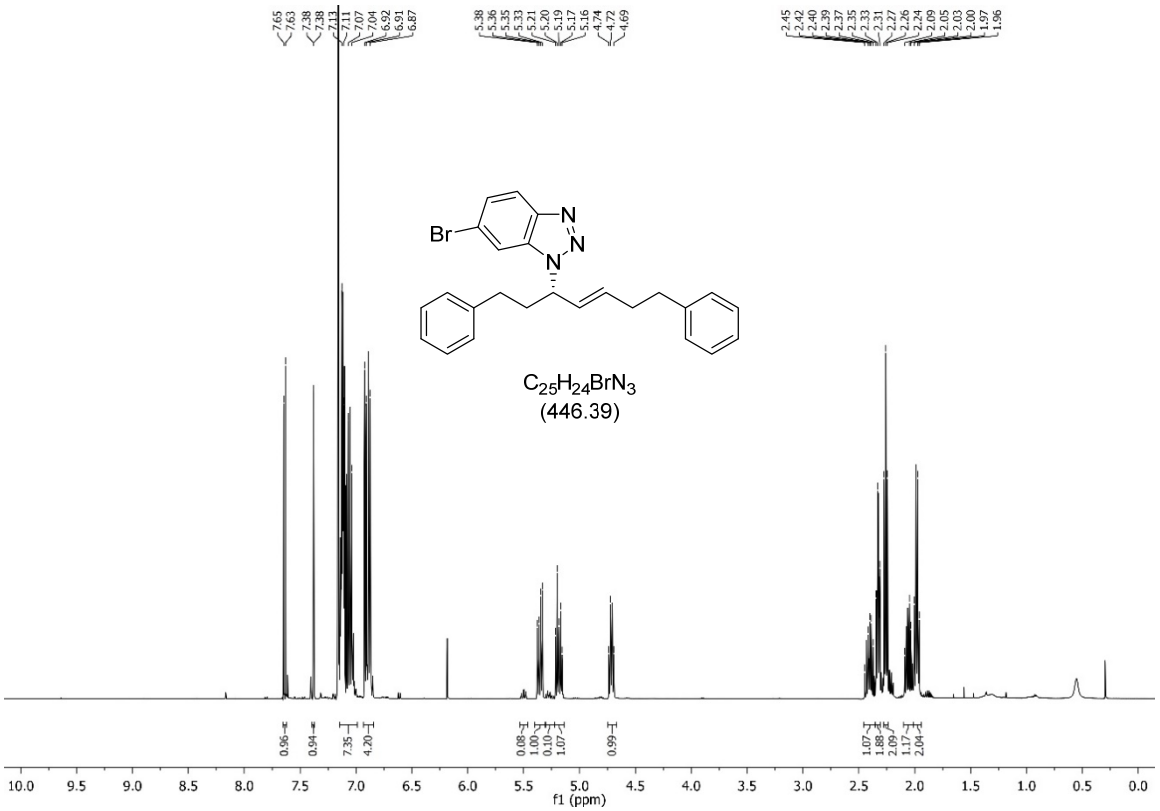


^{13}C-NMR (125.72 MHz, C_6D_6):

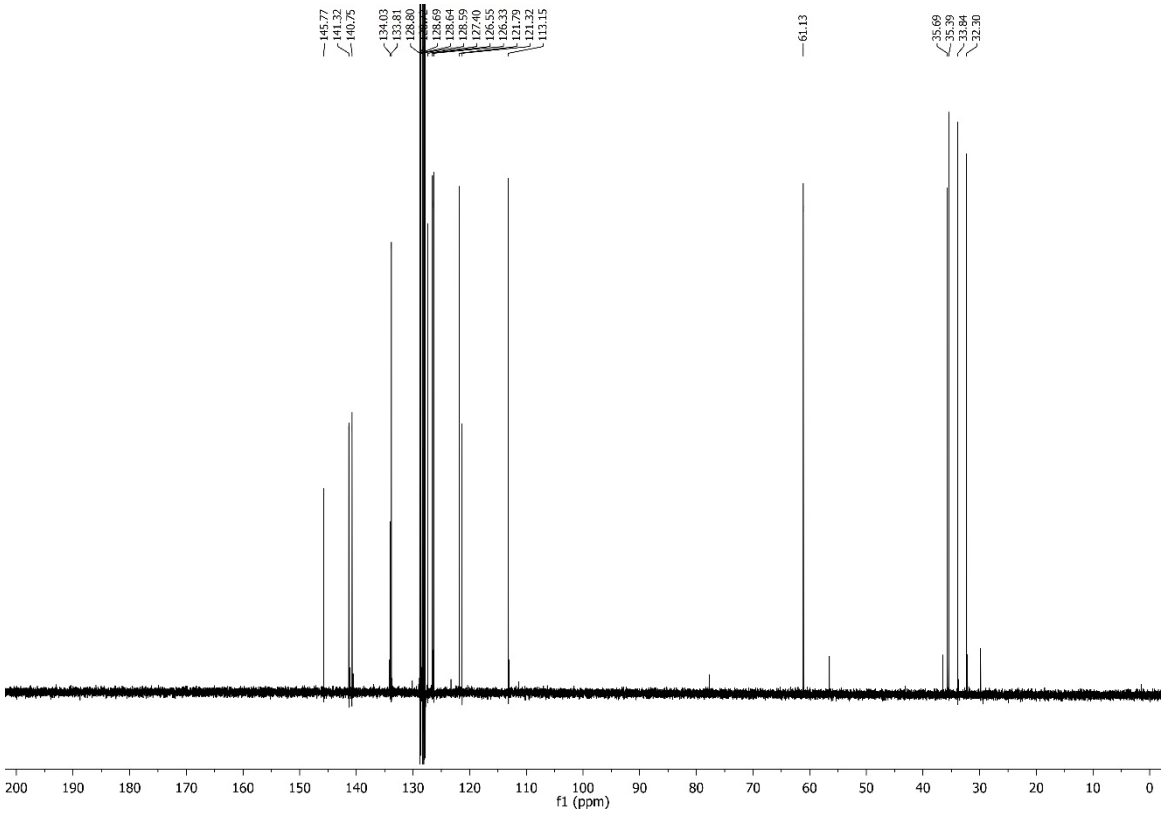


(*S*,*E*)-6-bromo-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[d][1,2,3]triazole (*N*^{3}-product, 11b)

^{1}H-NMR (499.98 MHz, C_6D_6):

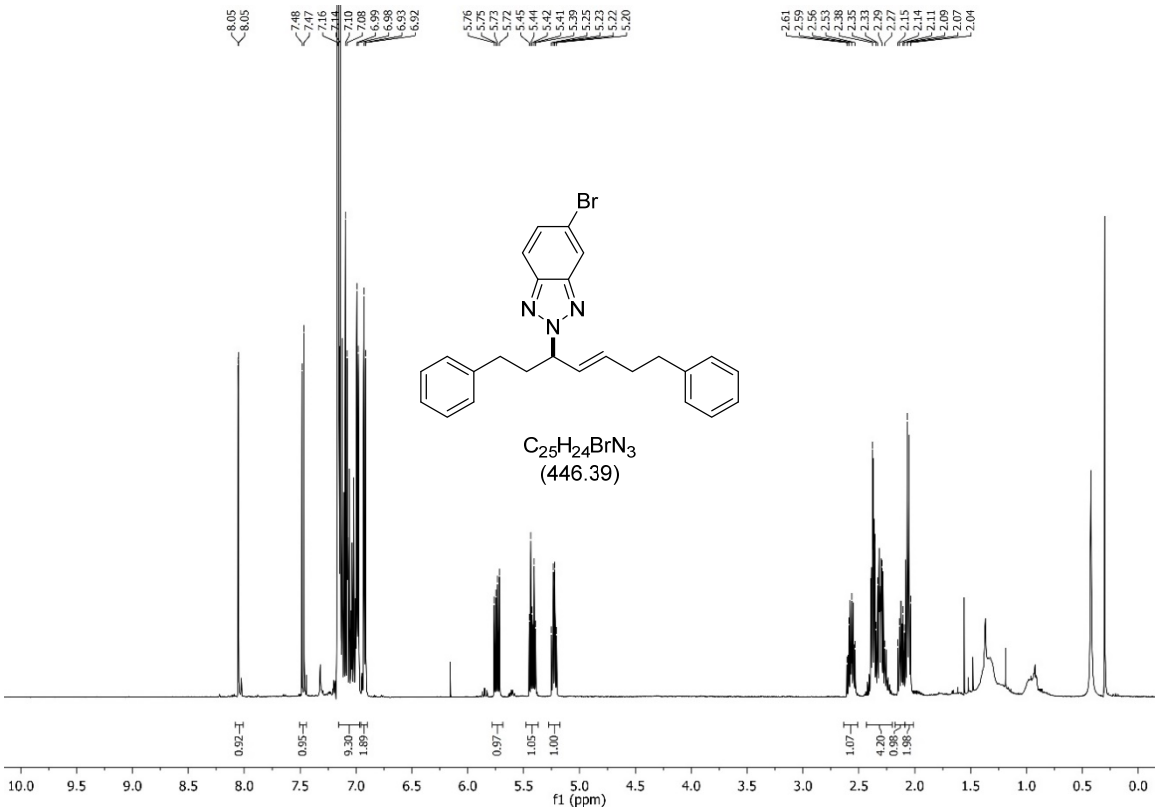


^{13}C-NMR (125.72 MHz, C_6D_6):

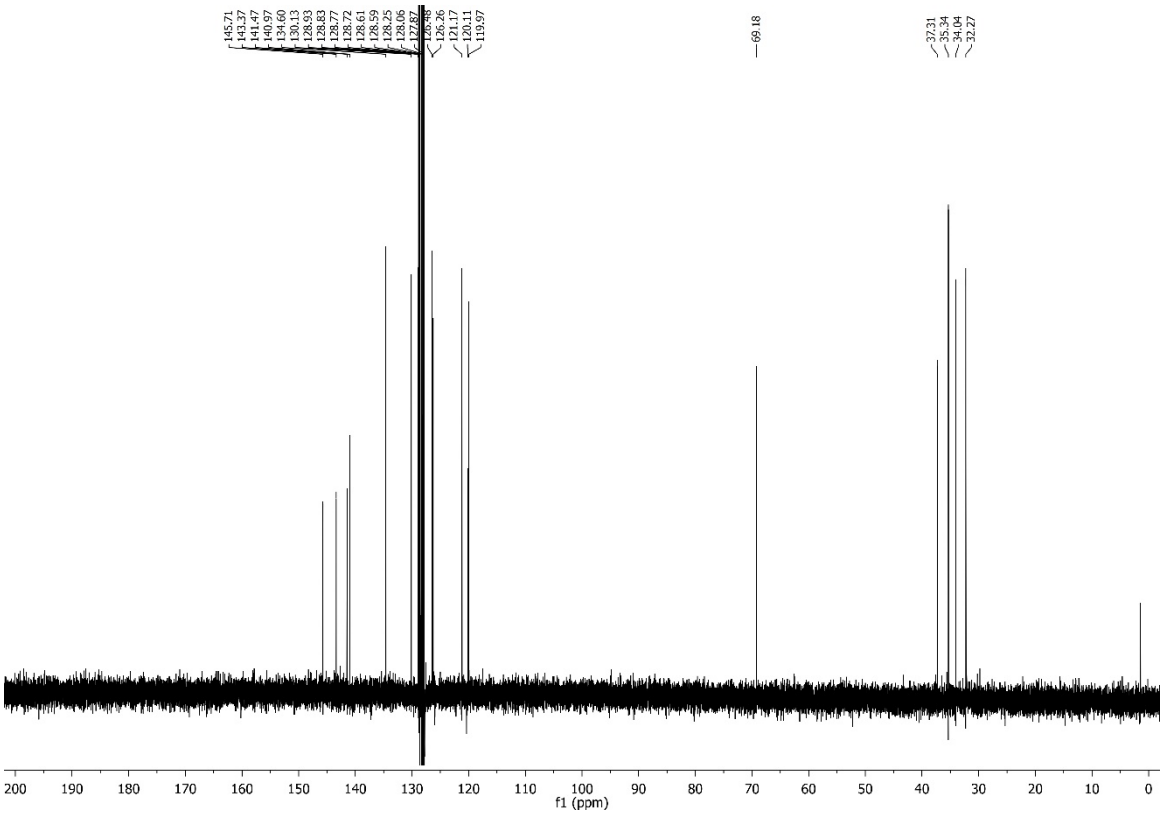


(*E*)-5-bromo-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-benzo[d][1,2,3]triazole (*N*^{2}-product, 11c)

^{1}H-NMR (499.98 MHz, C_6D_6):

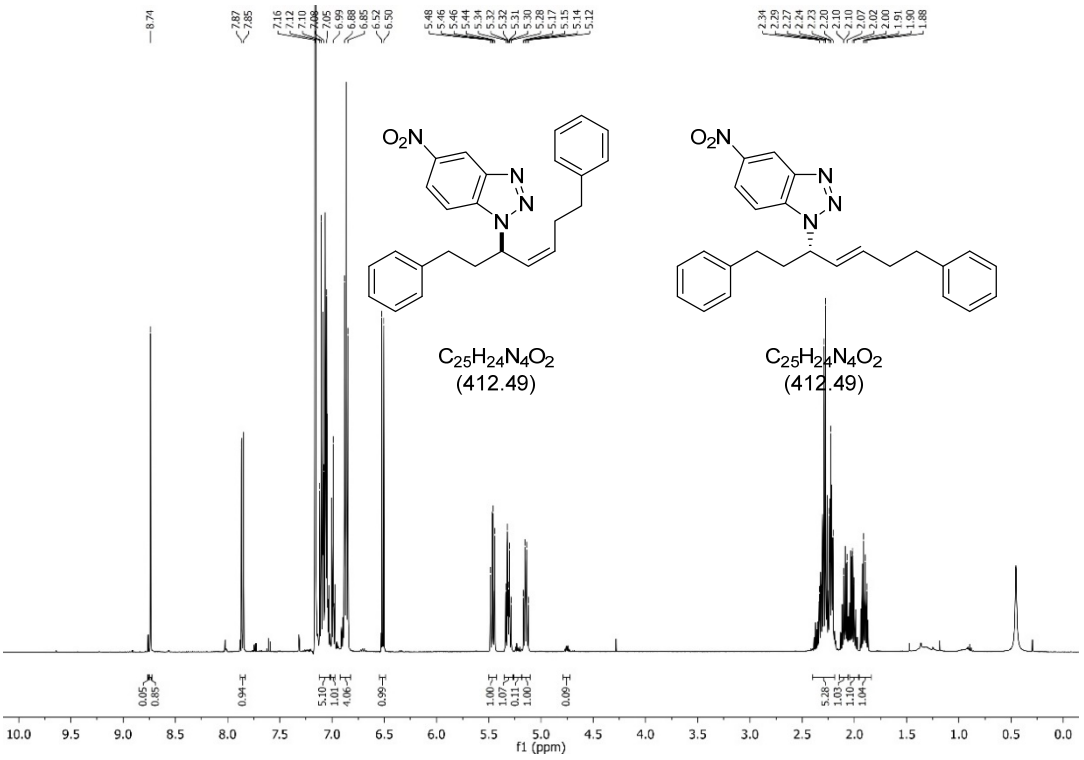


^{13}C-NMR (125.72 MHz, C_6D_6):

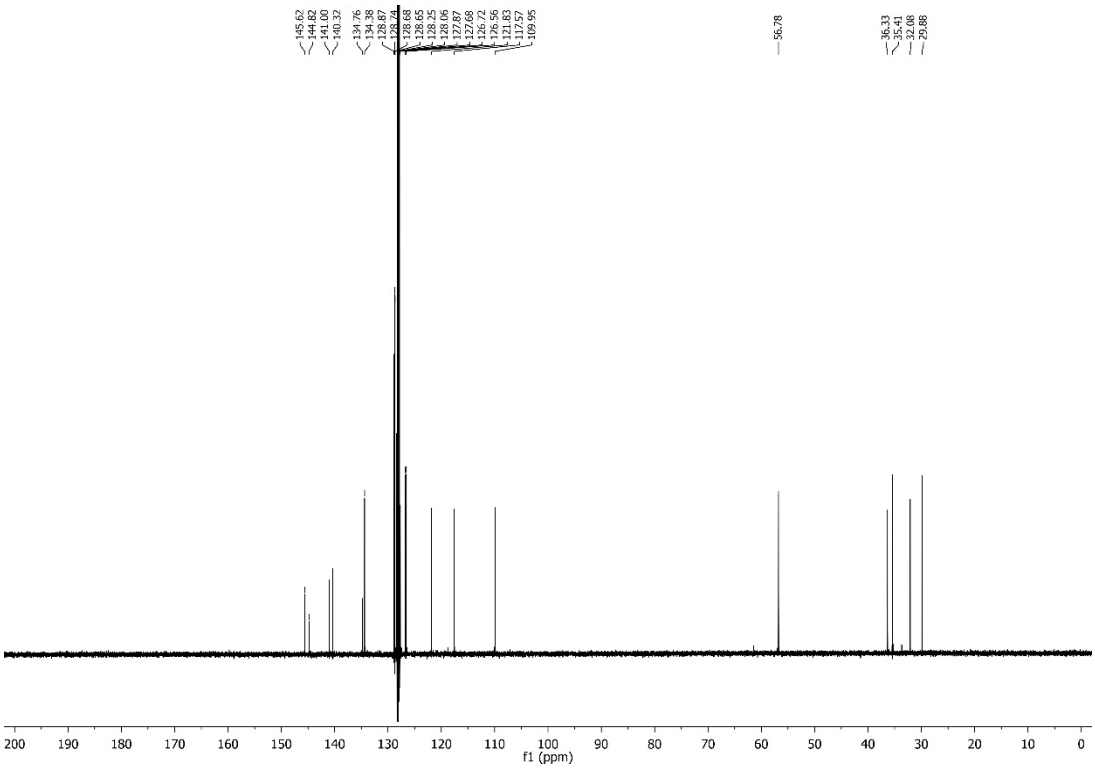


(*Z*)-1-(1,7-diphenylhept-4-en-3-yl)-5-nitro-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1},*Z*-product, 12) & (*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-5-nitro-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1},*E*-product, 12b)

^{1}H-NMR (499.98 MHz, C_6D_6):

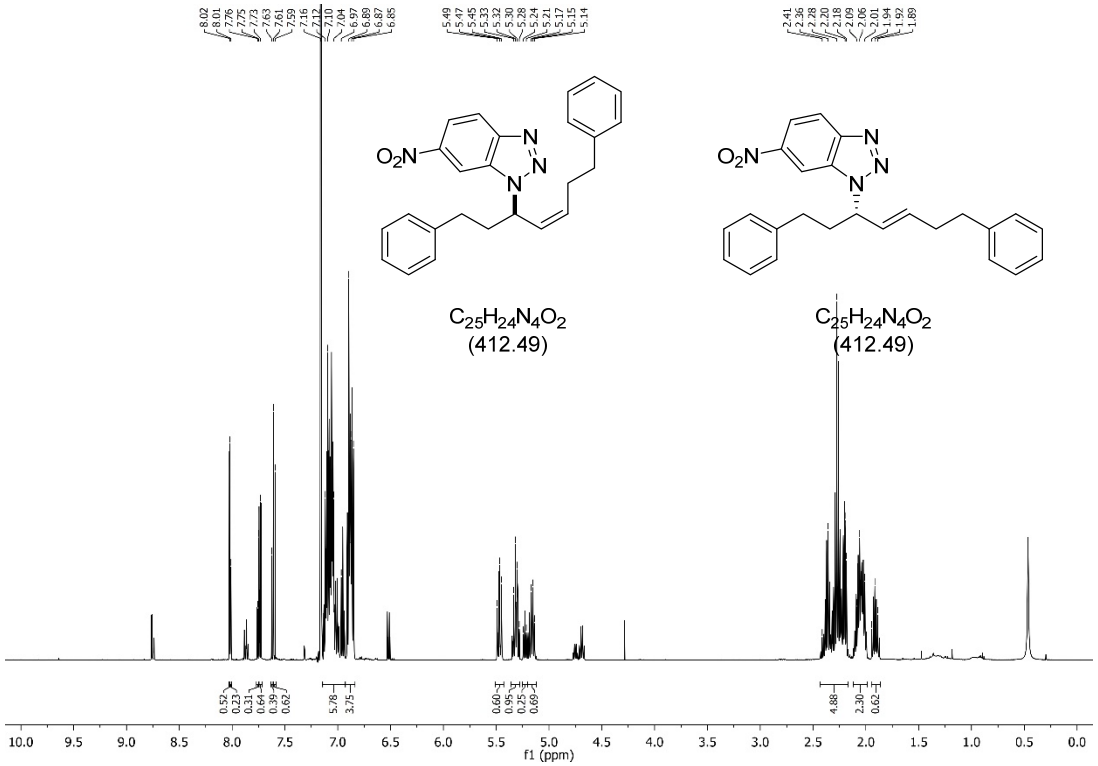


^{13}C-NMR (125.72 MHz, C_6D_6):

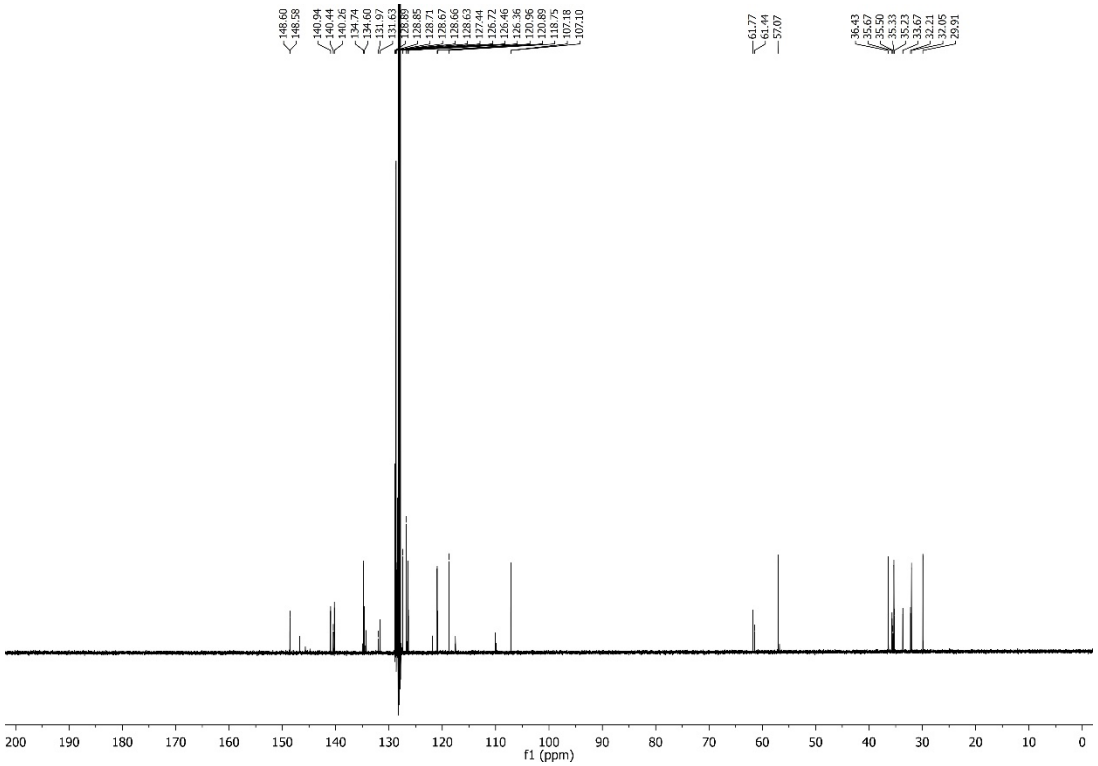


(*Z*)-1-(1,7-diphenylhept-4-en-3-yl)-6-nitro-1*H*-benzo[d][1,2,3]triazole (*N*^{3},*Z*-product, 12c) & (*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-6-nitro-1*H*-benzo[d][1,2,3]triazole (*N*^{3},*E*-product, 12d)

^{1}H-NMR (499.98 MHz, C_6D_6):

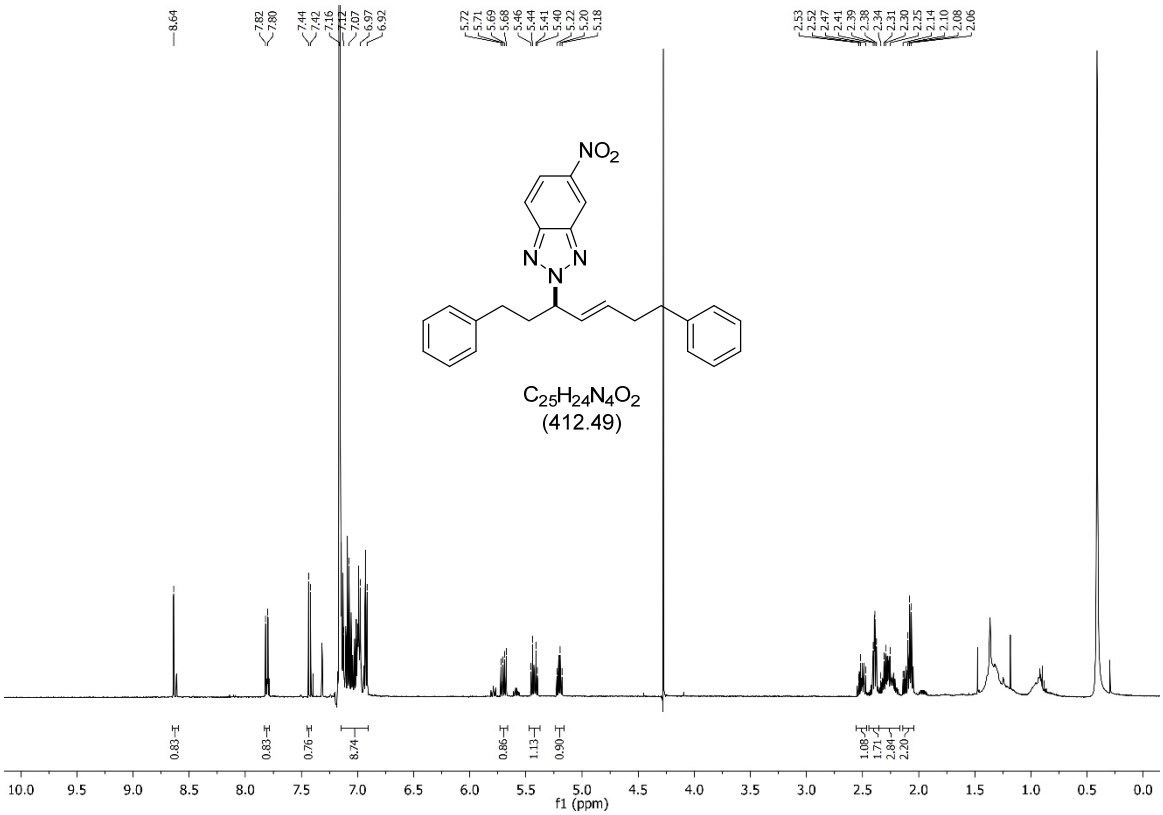


^{13}C-NMR 125.72 MHz, C_6D_6):

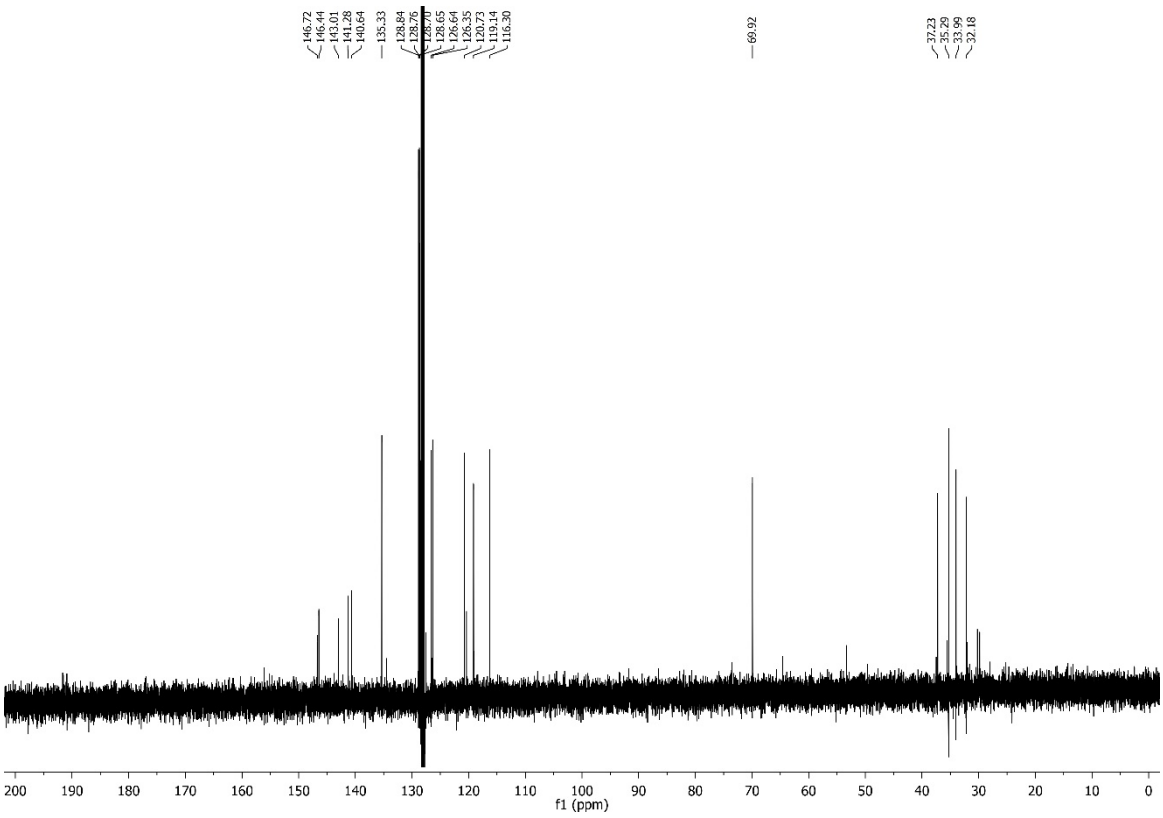


(*E*)-2-(1,7-diphenylhept-4-en-3-yl)-5-nitro-2*H*-benzo[*d*][1,2,3]triazole (*N*^{2},*E*-product, 12e)

^{1}H-NMR (499.98 MHz, C_6D_6):

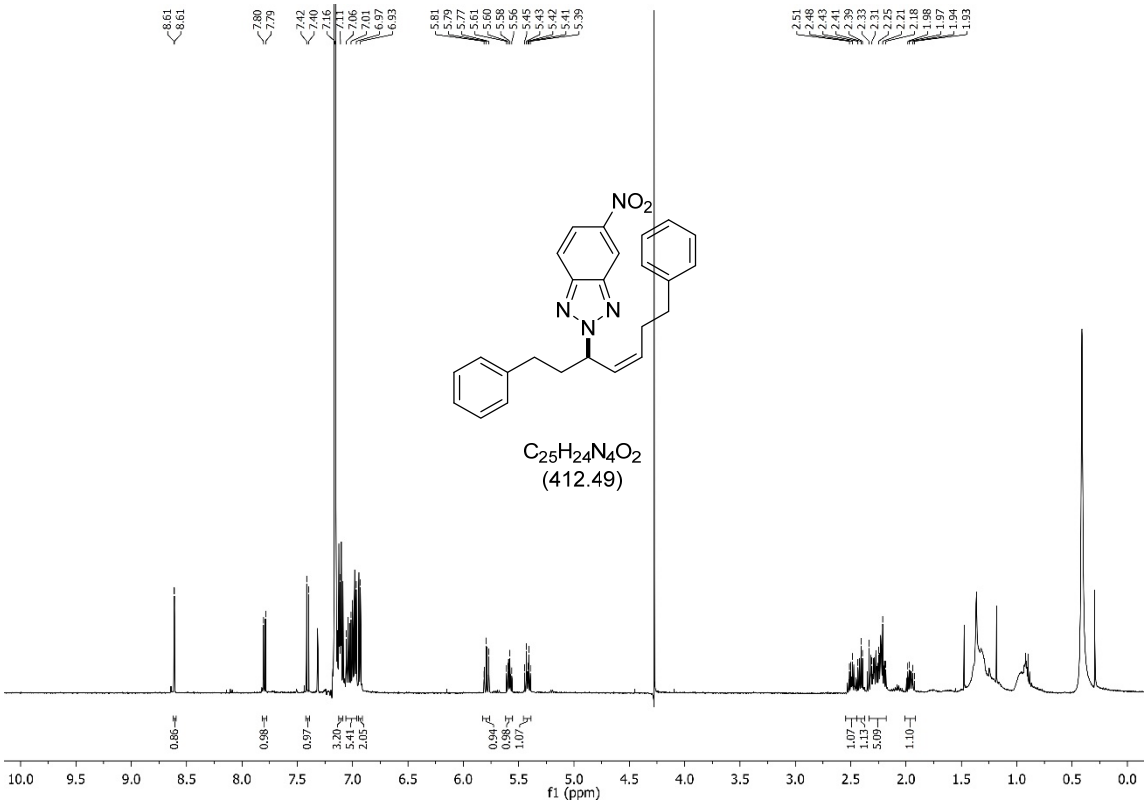


^{13}C-NMR (125.72 MHz, C_6D_6):

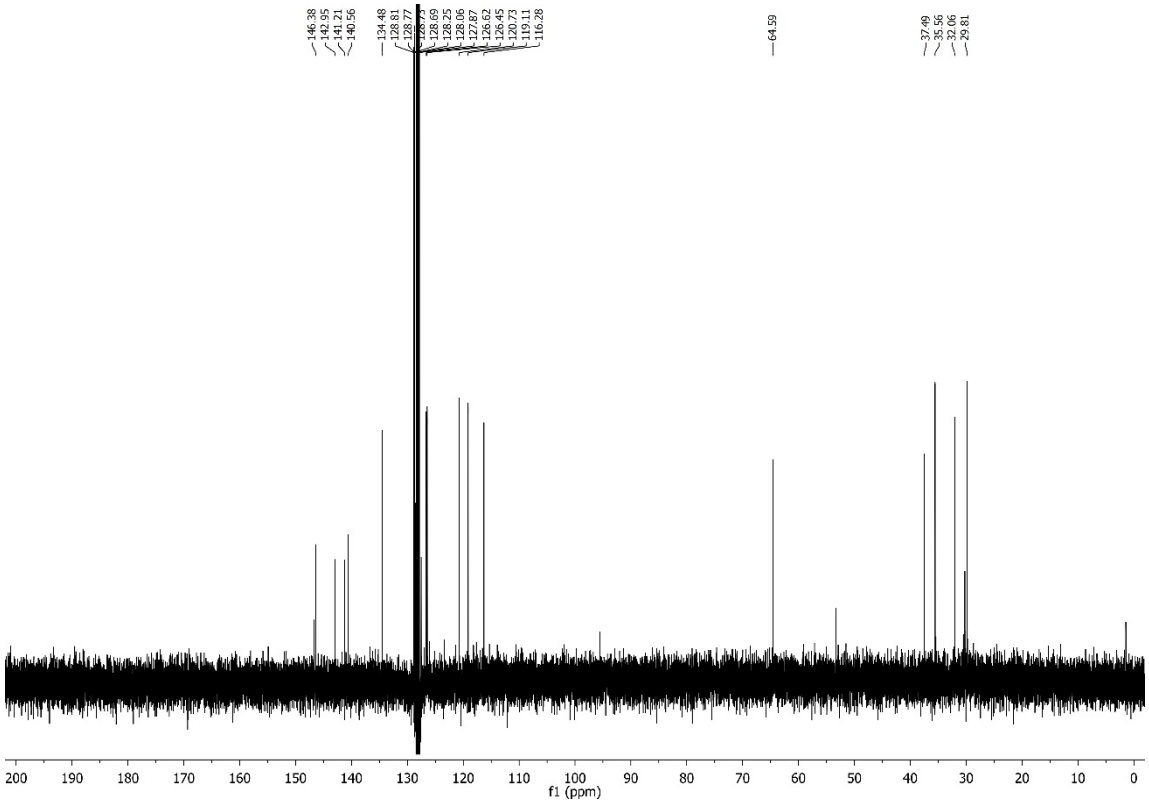


(*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-nitro-2*H*-benzo[*d*][1,2,3]triazole (*N*^{2},*Z*-product, 12f)

^{1}H-NMR (499.98 MHz, C_6D_6):

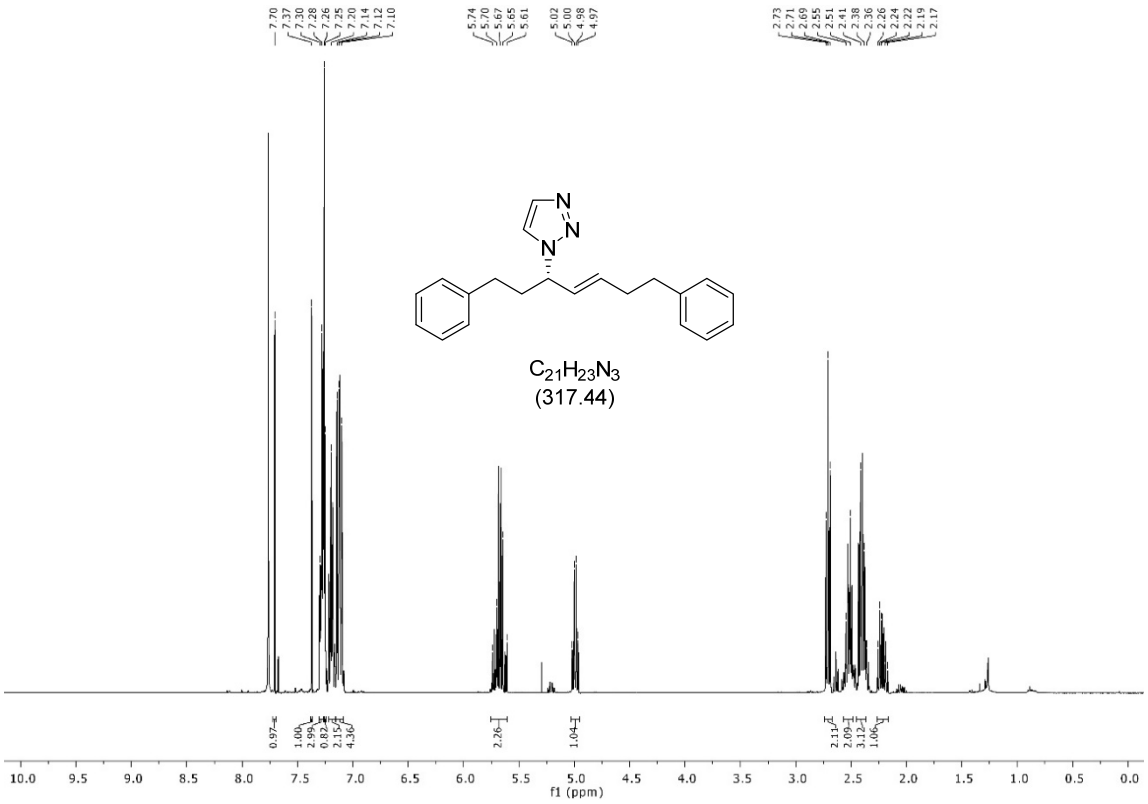


^{13}C-NMR (125.72 MHz, C_6D_6):

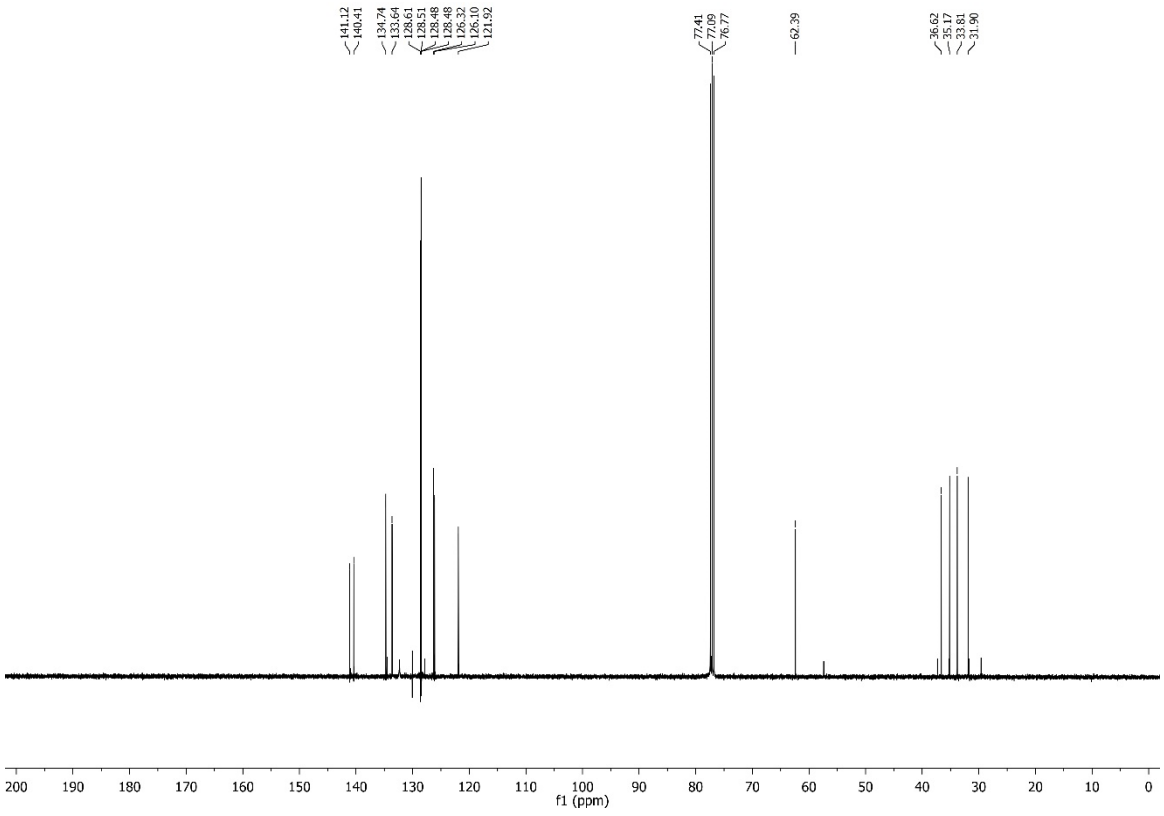


(*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-1,2,3-triazole (*N*^{1}-product, 13)

^{1}H-NMR (400.13 MHz, $CDCl_3$):

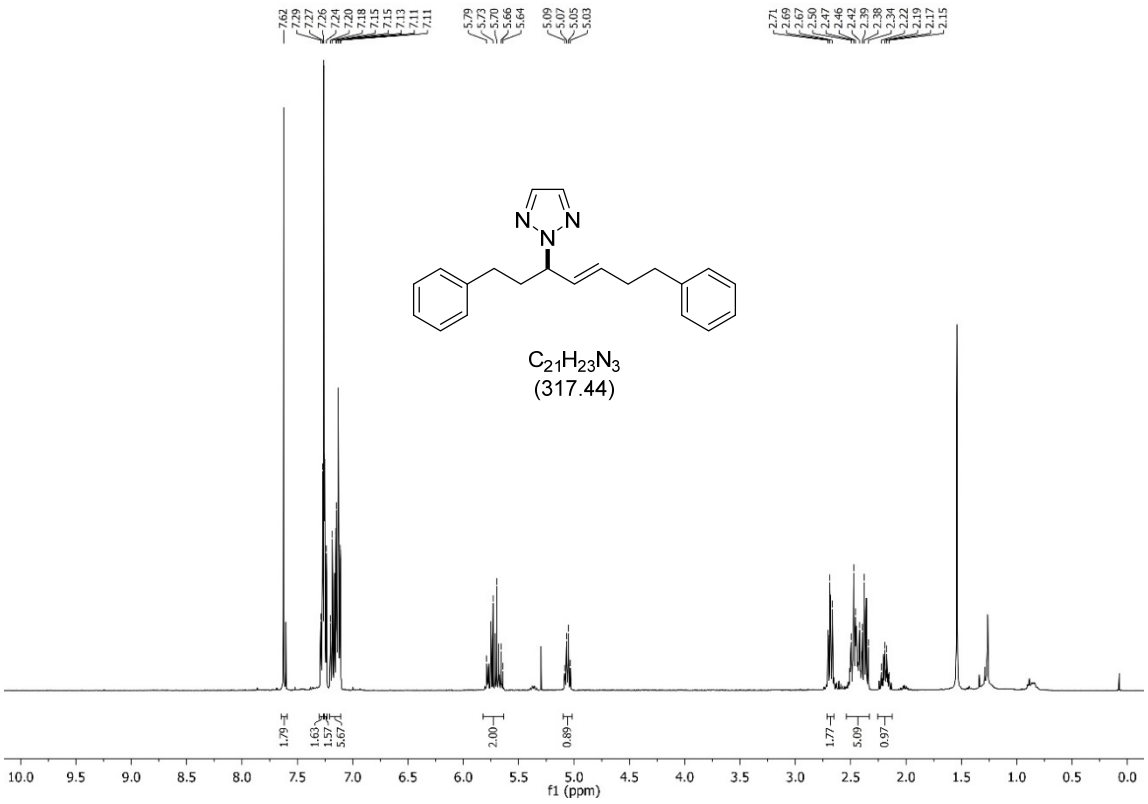


^{13}C-NMR (100.61 MHz, $CDCl_3$):



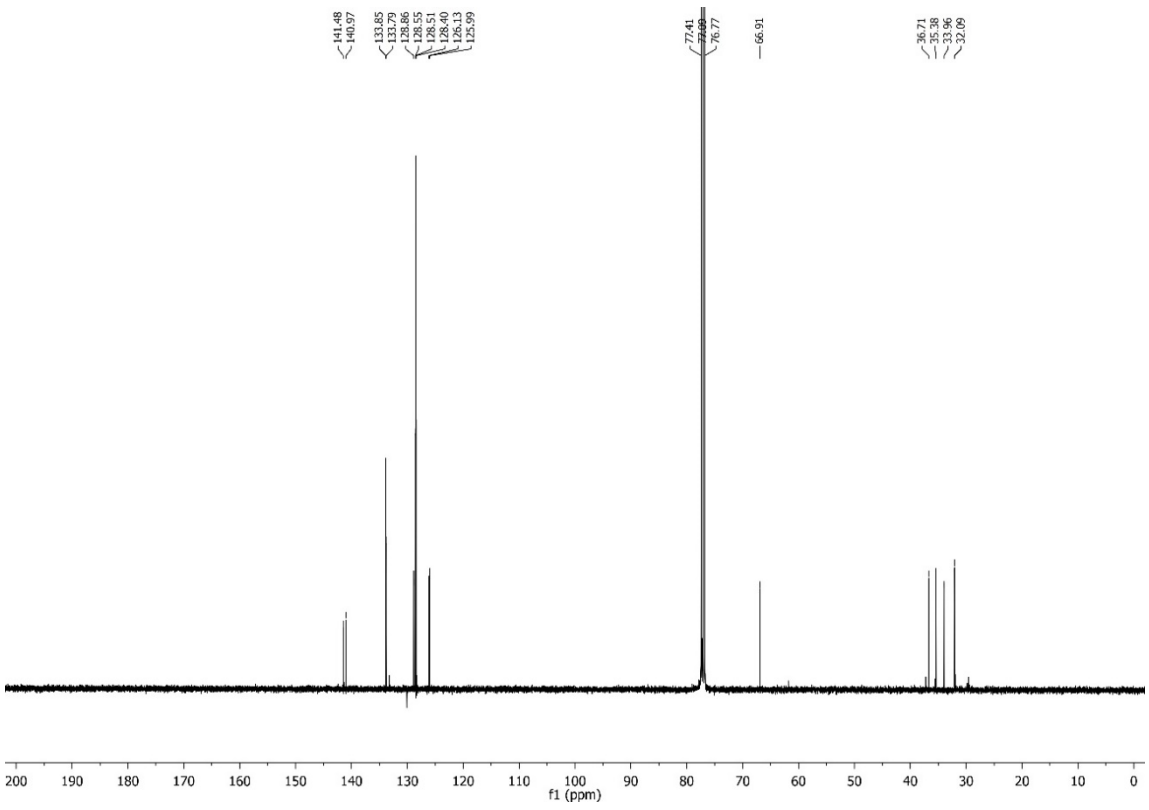
(*E*)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-1,2,3-triazole (*N*^{2}-product, 13b)

^{1}H-NMR (400.13 MHz, $CDCl_3$):



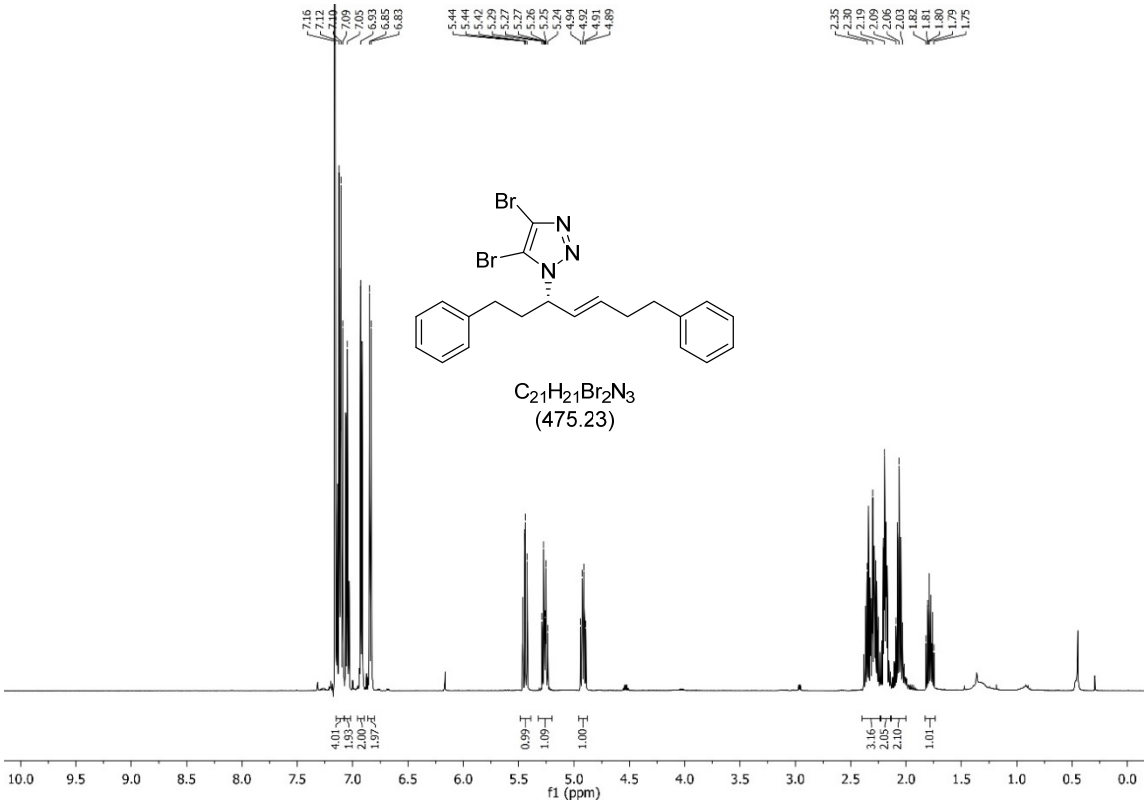
$C_{21}H_{23}N_3$
(317.44)

^{13}C-NMR (100.61 MHz, $CDCl_3$):

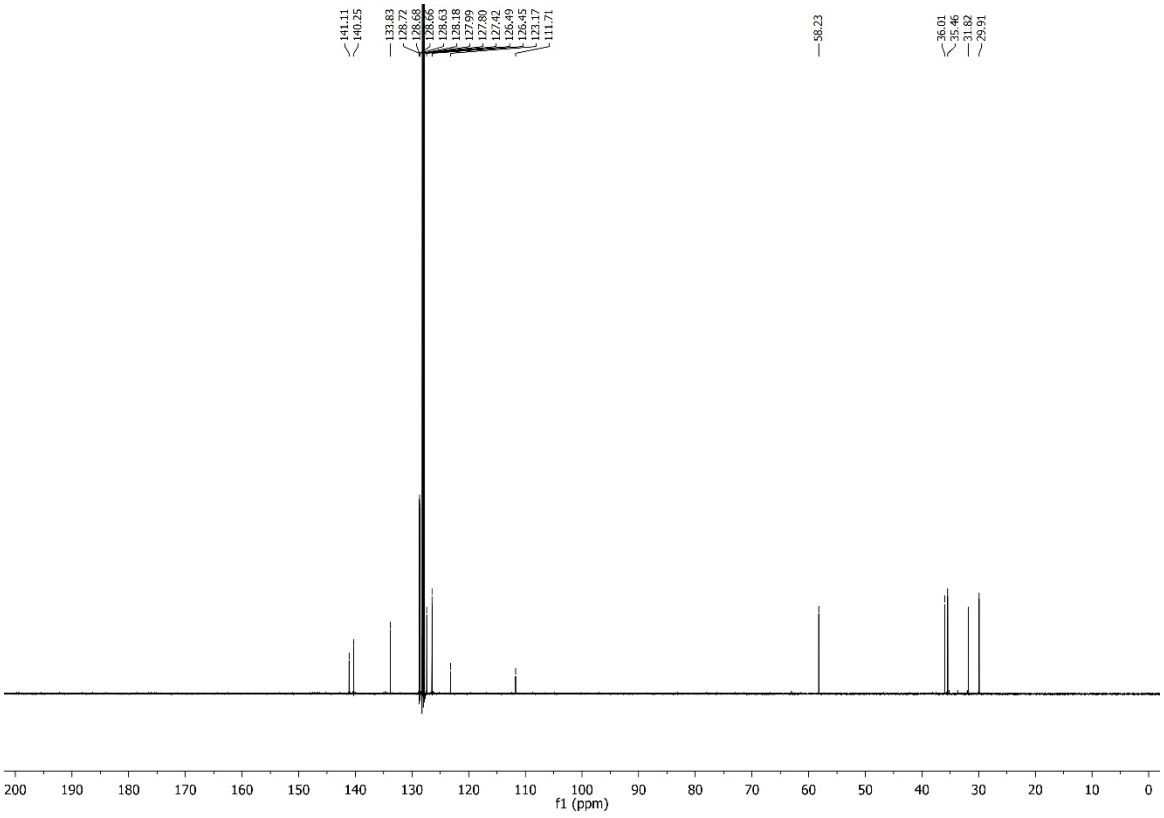


(*S*,*E*)-2-(1,7-diphenylhept-4-en-3-yl)-5-methyl-2*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 14)

^{1}H-NMR (499.98 MHz, C_6D_6):

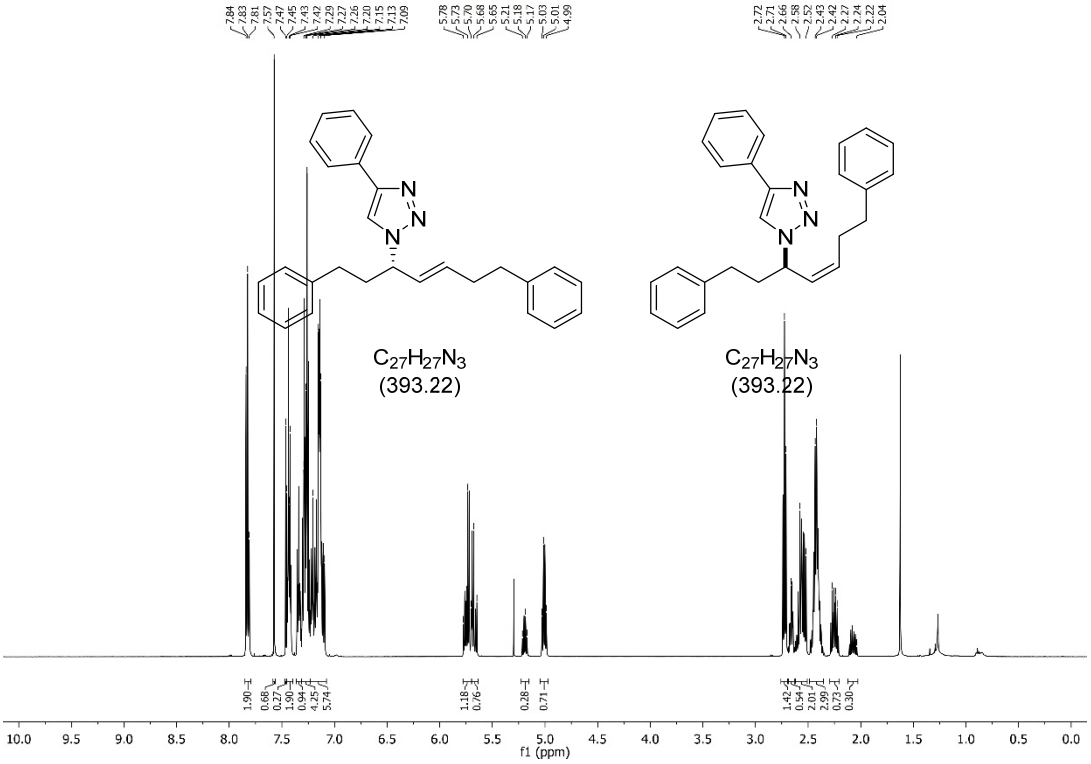


^{13}C-NMR (125.72 MHz, C_6D_6):

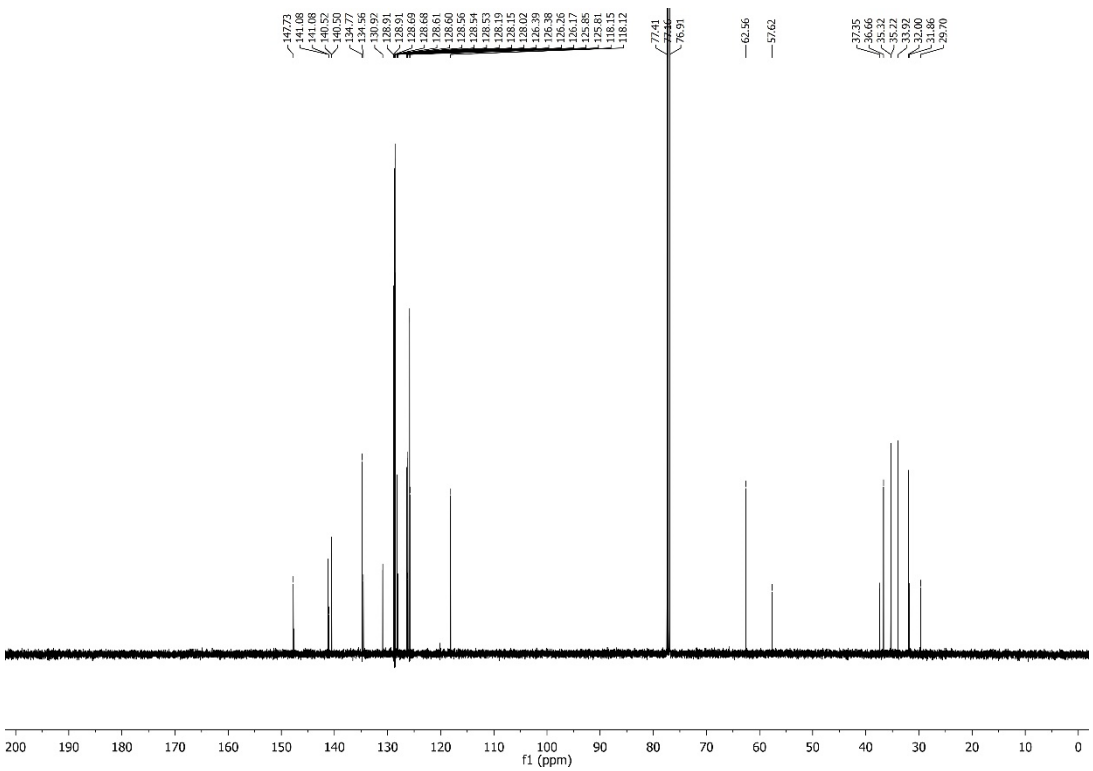


(*S*,*E*)-1-(1,7-diphenylhept-4-en-3-yl)-4-phenyl-1*H*-1,2,3-triazole (*N*^{1}-, *E*-product, 15) & (Z)-1-(1,7-diphenylhept-4-en-3-yl)-4-phenyl-1*H*-1,2,3-triazole (*N*^{1}-, *Z*-product, 15b)

^{1}H-NMR (499.98 MHz, $CDCl_3$):

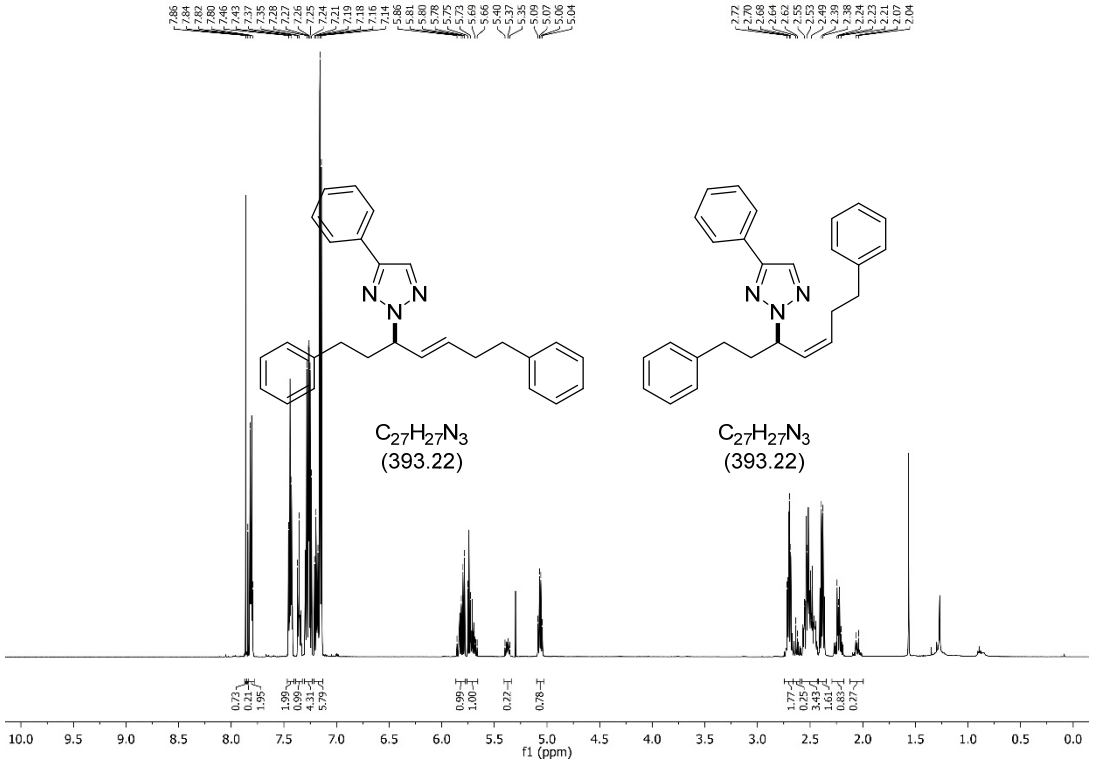


^{13}C-NMR (125.72 MHz, $CDCl_3$):

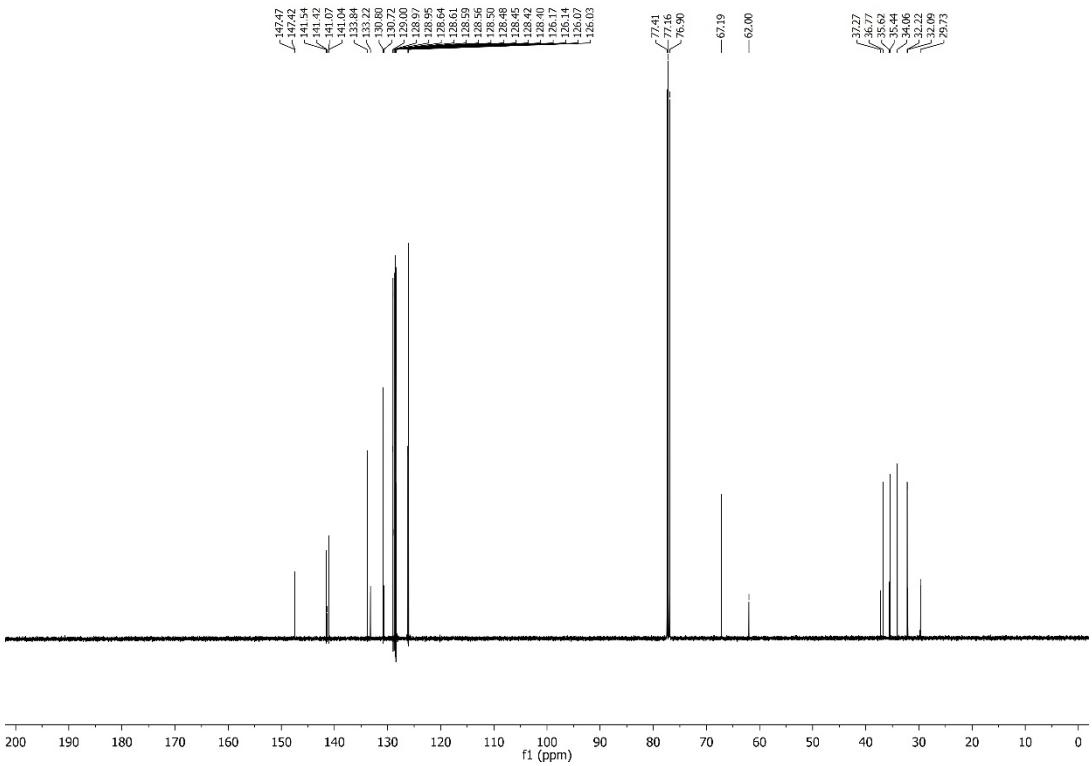


(*E*)-2-(1,7-diphenylhept-4-en-3-yl)-4-phenyl-2*H*-1,2,3-triazole (*N*^{2}-, *E*-product, 15c) & (*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-4-phenyl-2*H*-1,2,3-triazole (*N*^{2}-, *Z*-product, 15d)

^{1}H-NMR (499.98 MHz, $CDCl_3$):

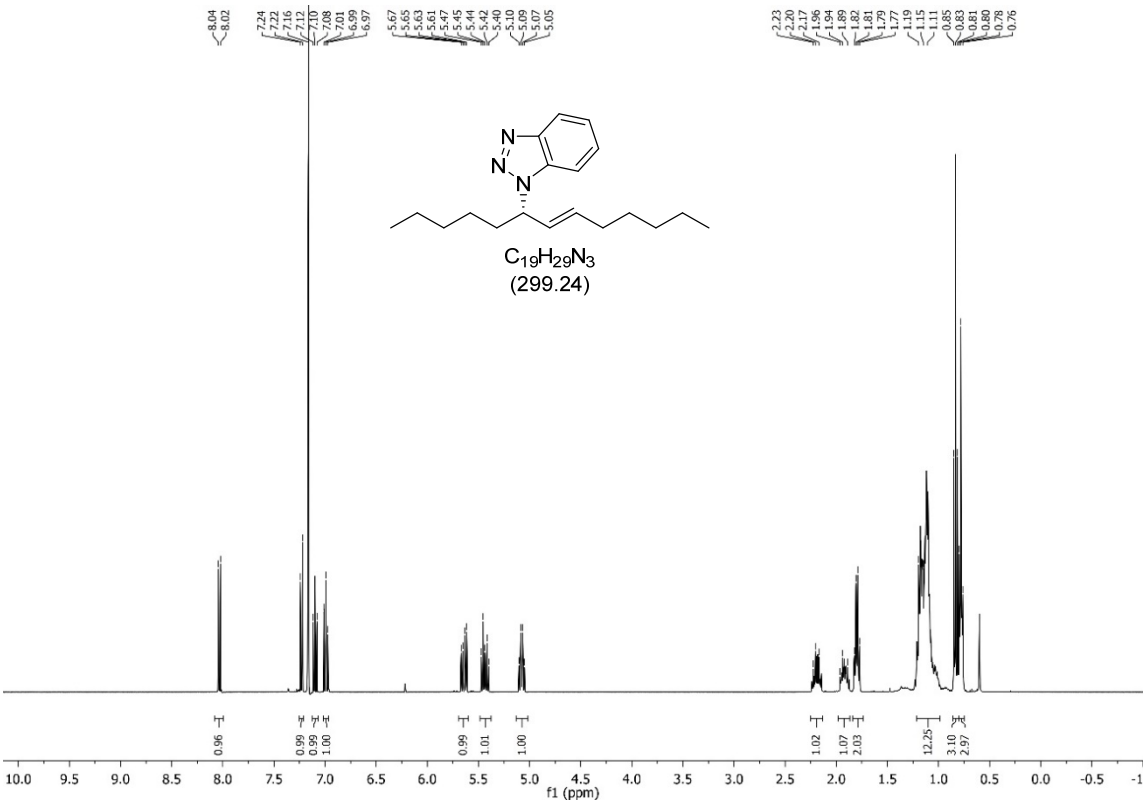


^{13}C-NMR (125.72 MHz, $CDCl_3$):

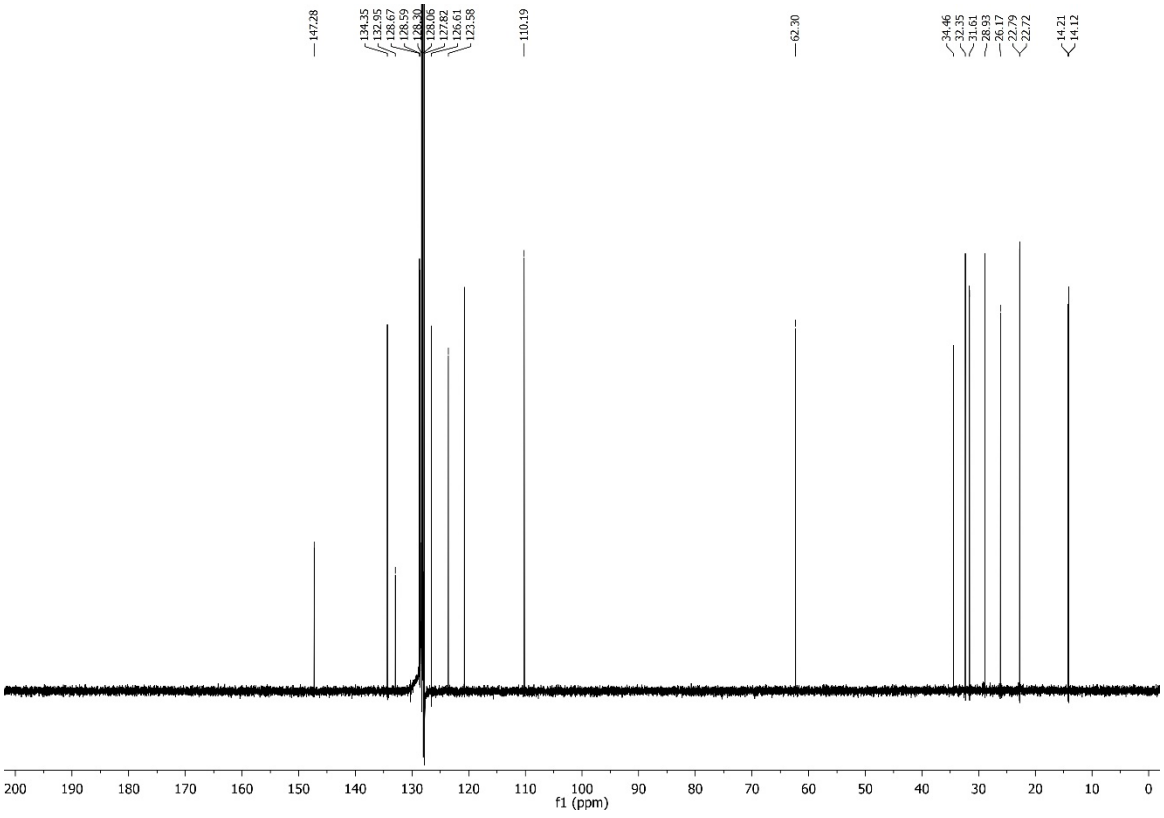


(*S*,*E*)-1-(tridec-7-en-6-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 16)

^{1}H-NMR (400.13 MHz, C_6D_6):

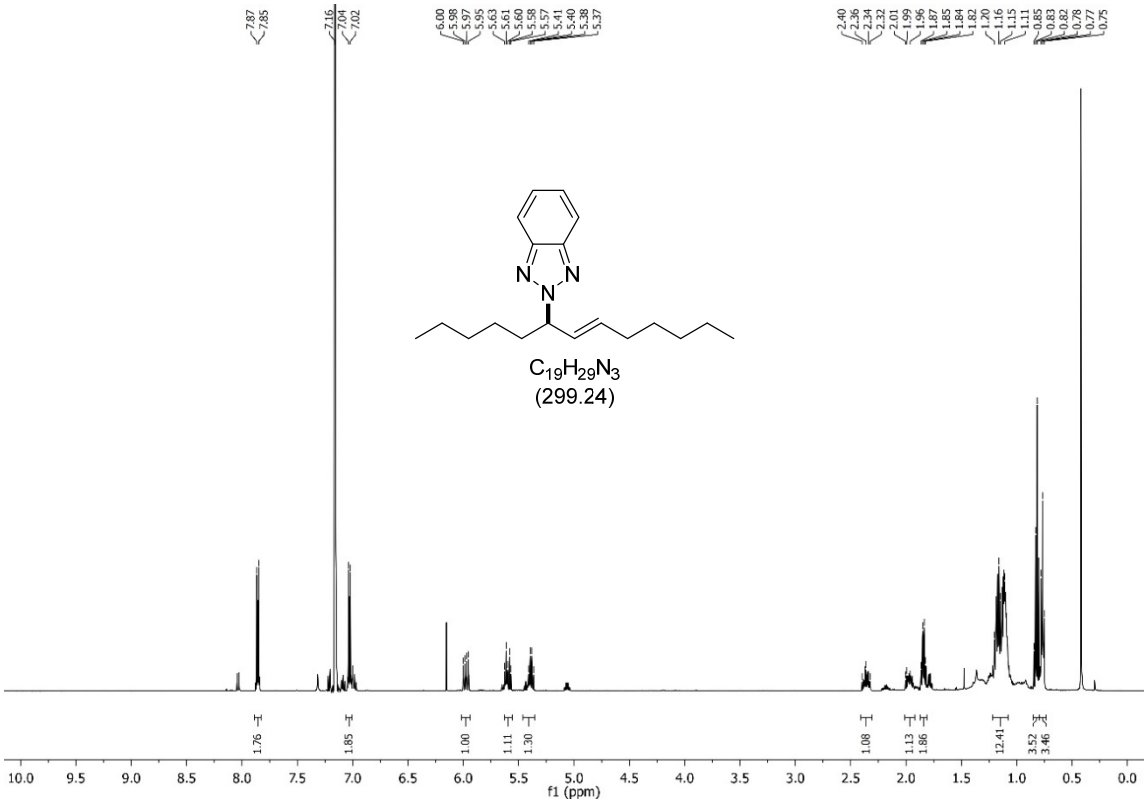


^{13}C-NMR (100.61 MHz, C_6D_6):

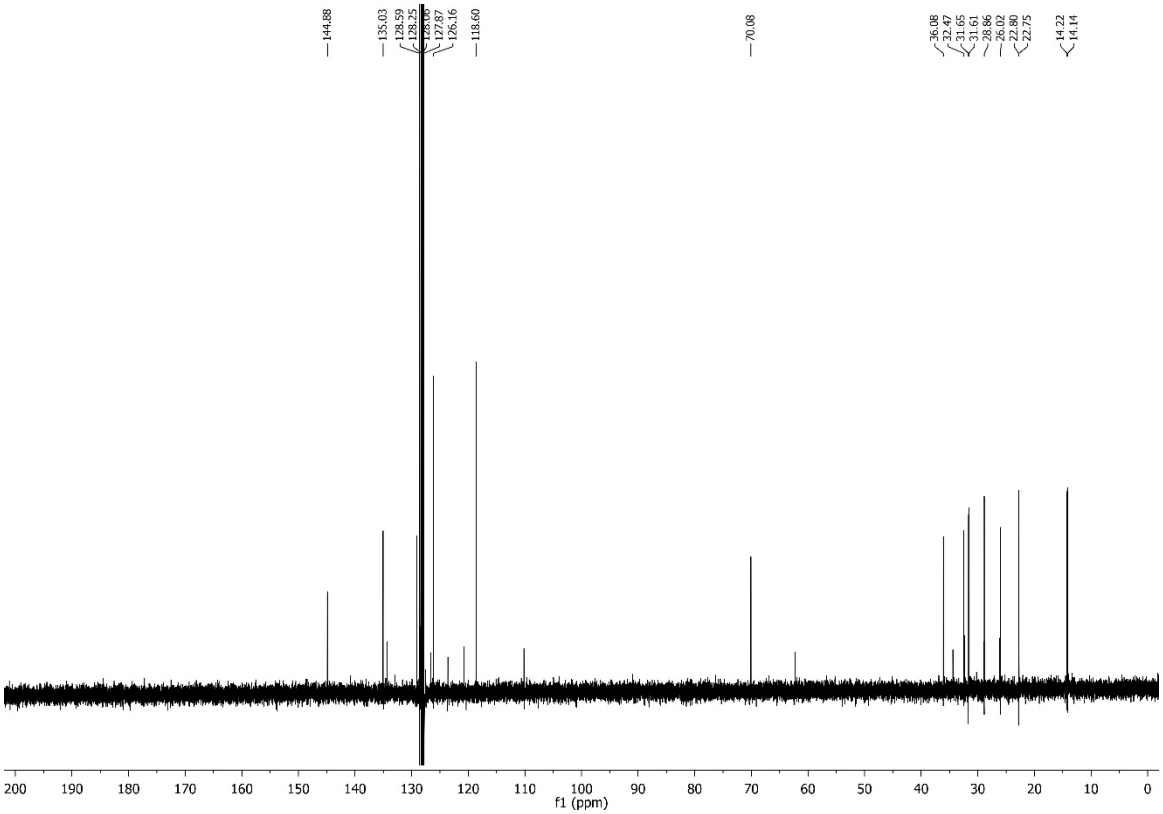


(*E*)-2-(tridec-7-en-6-yl)-2*H*-benzo[*d*][1,2,3]triazole (N^2-product, 16b)

^{1}H-NMR (499.98 MHz, C_6D_6):

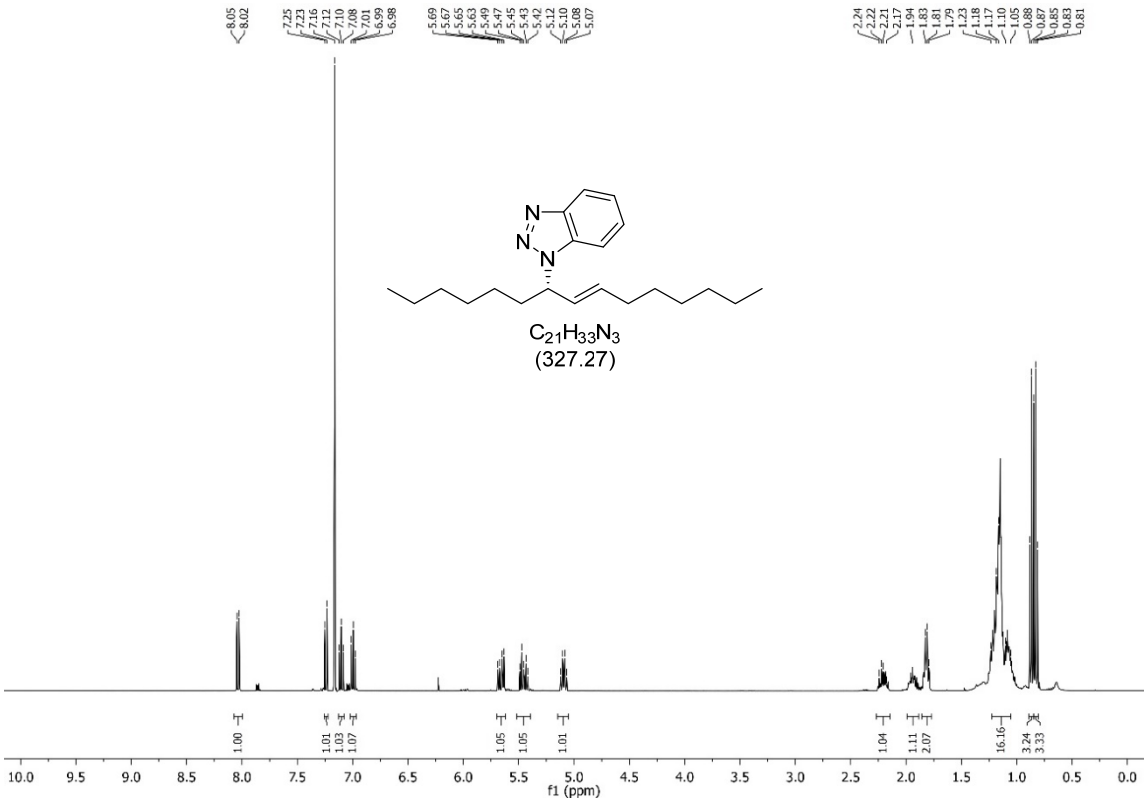


^{13}C-NMR (125.72 MHz, C_6D_6):

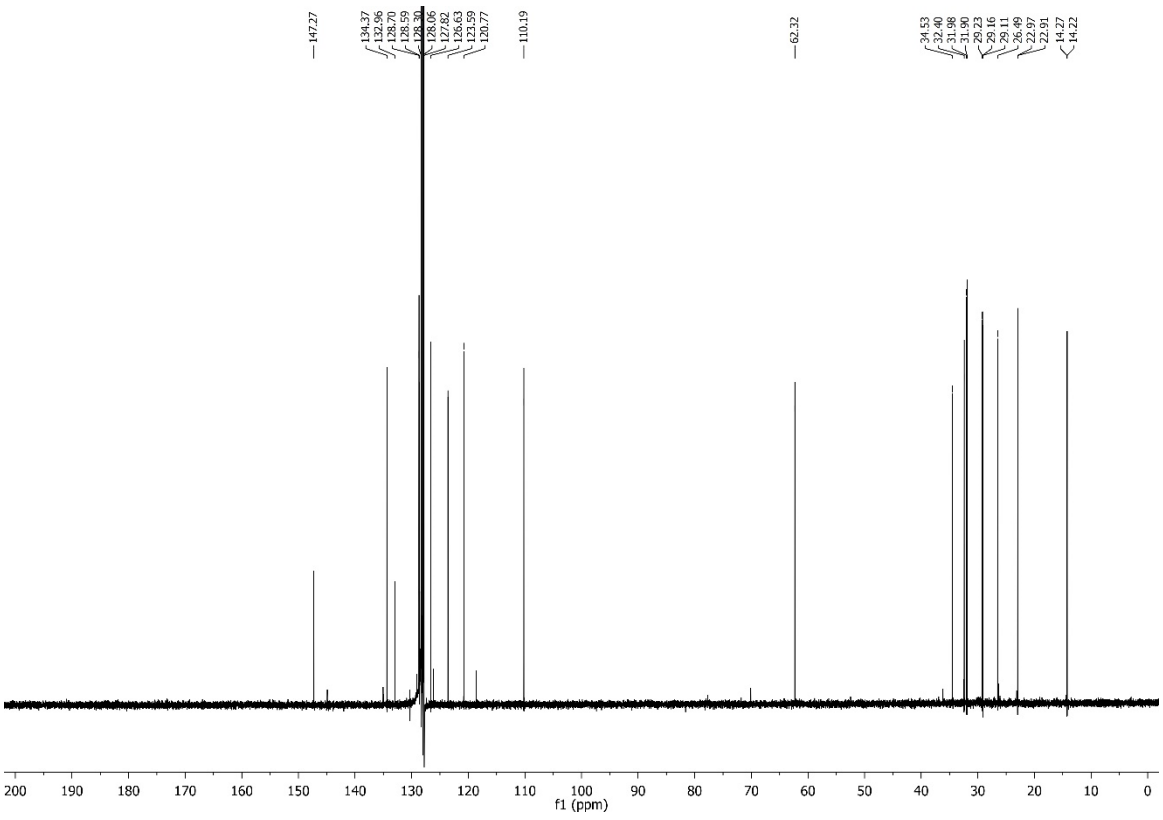


(*S*,*E*)-1-(pentadec-8-en-7-yl)-1*H*-benzo[d][1,2,3]triazole (*N*^{1}-product, 17)

^{1}H-NMR (400.13 MHz, C_6D_6):

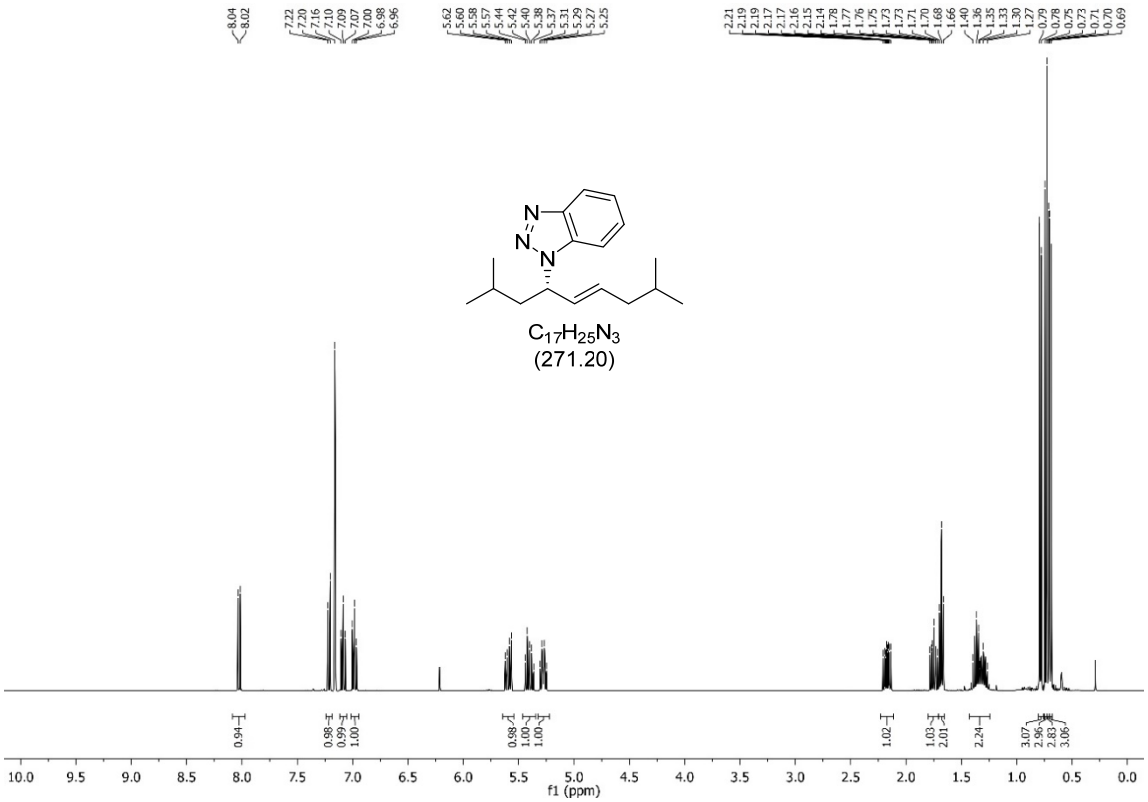


^{13}C-NMR (100.61 MHz, C_6D_6):

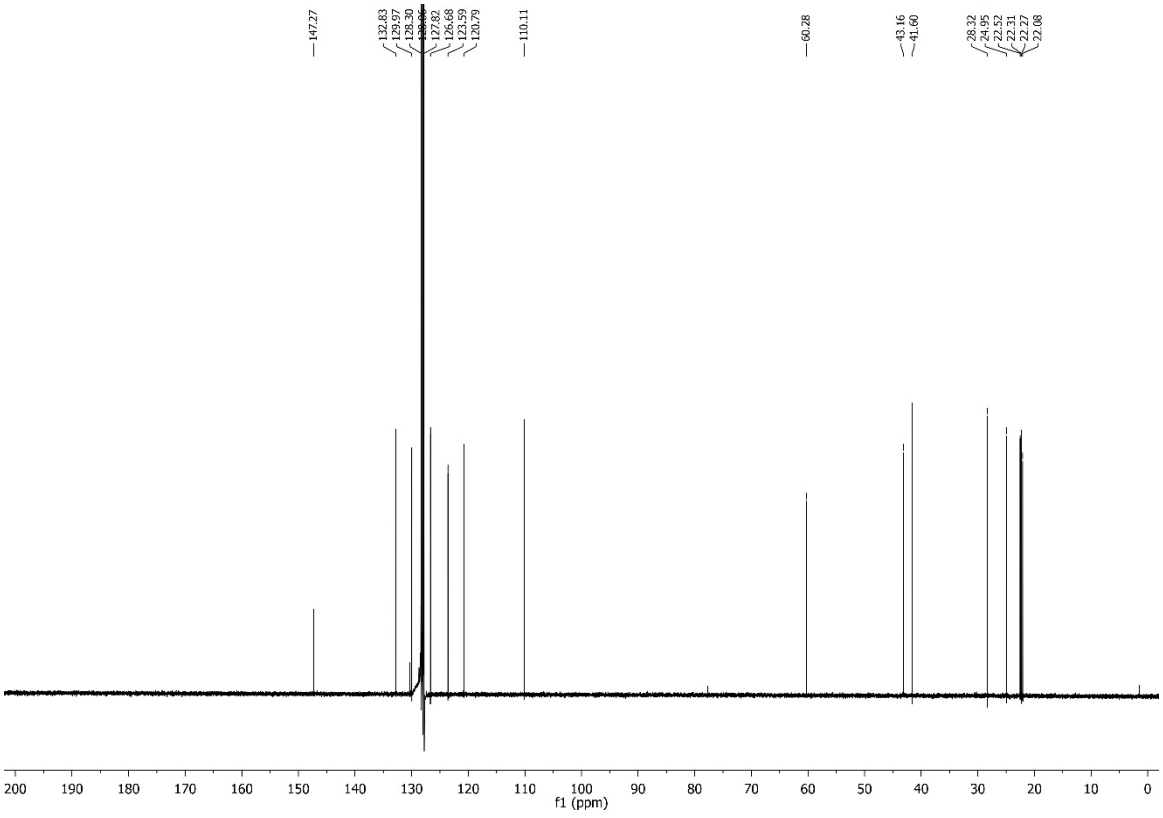


(*S*,*E*)-1-(2,8-dimethylnon-5-en-4-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 18)

^{1}H-NMR (400.13 MHz, C_6D_6):

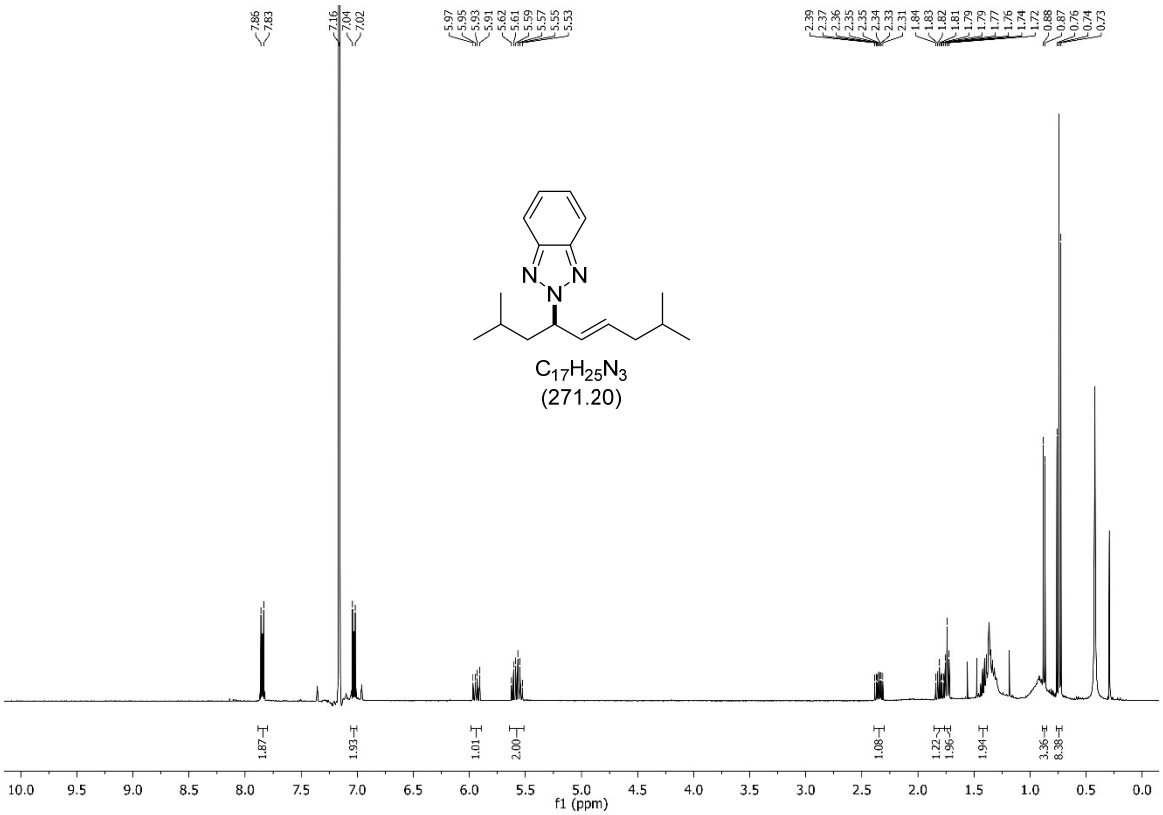


^{13}C-NMR (100.61 MHz, C_6D_6):

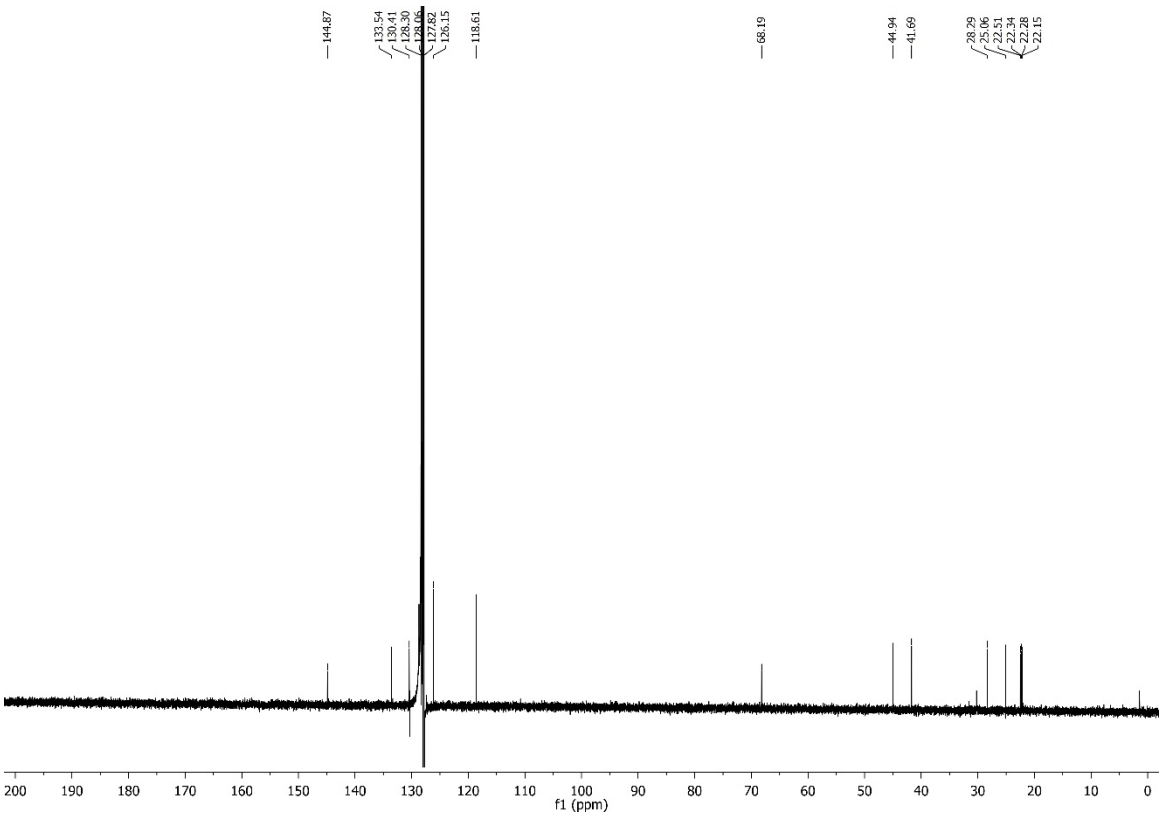


(*E*)-2-(2,8-dimethylnon-5-en-4-yl)-2*H*-benzo[*d*][1,2,3]triazole (N^2-product, 18b)

^{1}H-NMR (400.13 MHz, C_6D_6):

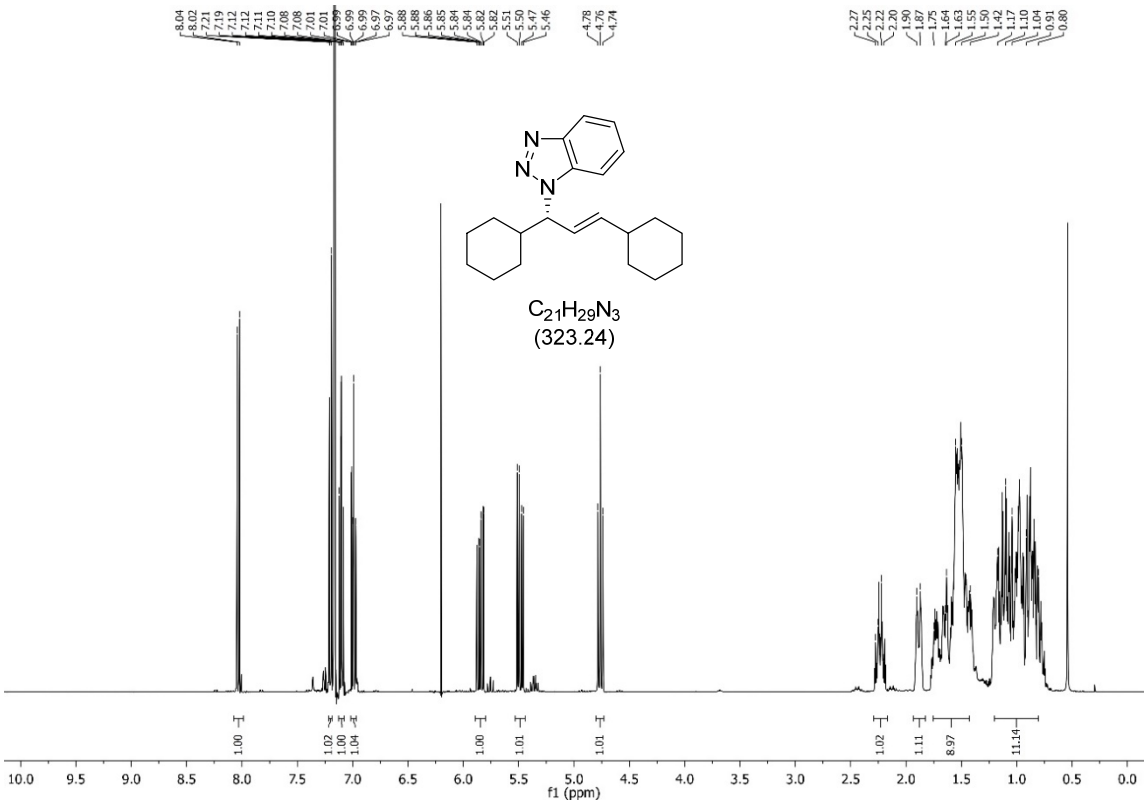


^{13}C-NMR (100.61 MHz, C_6D_6):

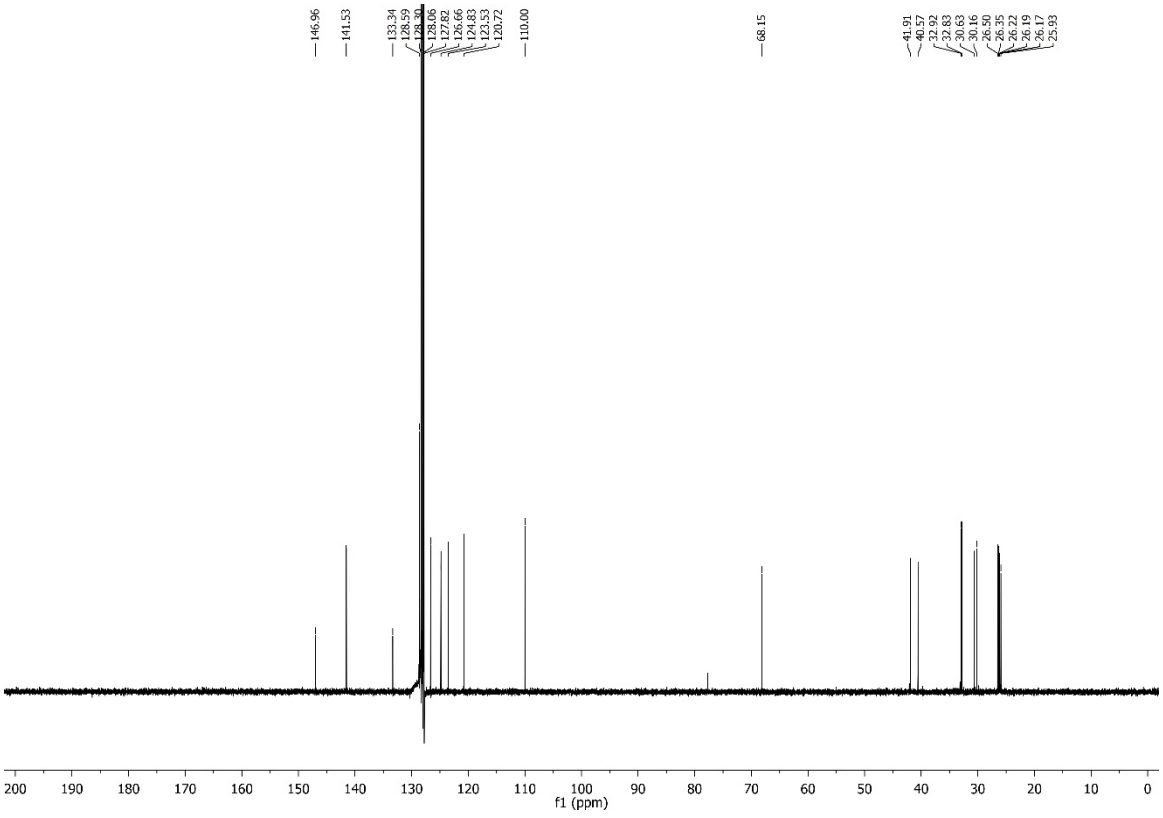


(*S*,*E*)-1-(1,3-dicyclohexylallyl)-1*H*-benzo[d][1,2,3]triazole (*N*[1]-product, 19)

^{1}H-NMR (400.13 MHz, C_6D_6):

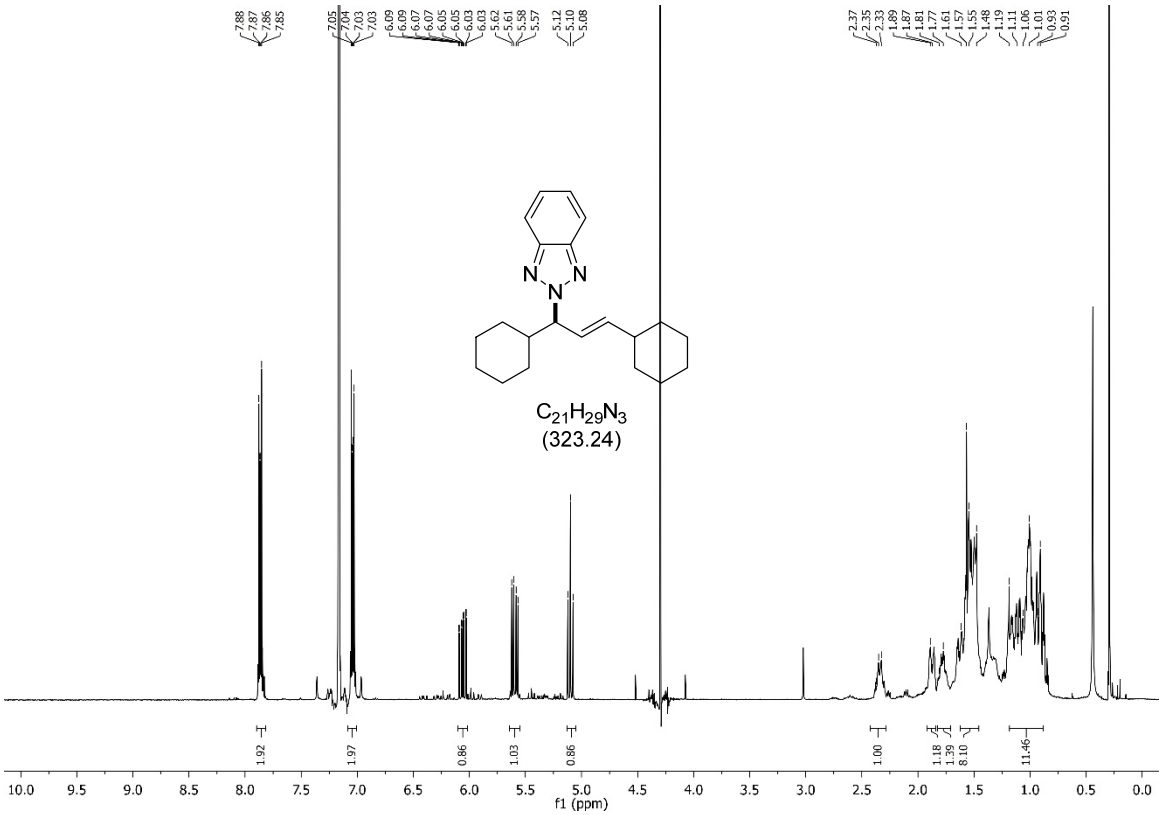


^{13}C-NMR (100.61 MHz, C_6D_6):

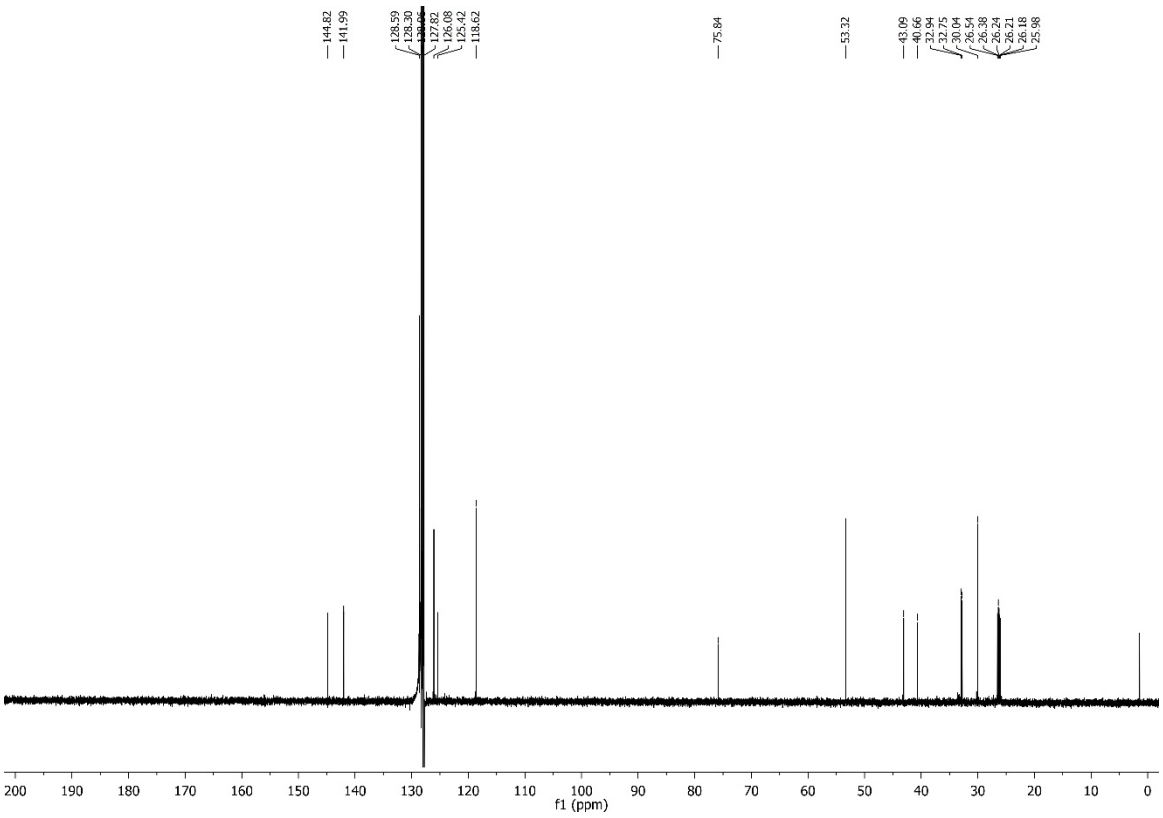


(*E*)-2-(1,3-dicyclohexylallyl)-2*H*-benzo[*d*][1,2,3]triazole (*N*^{2}-product, 19b)

^{1}H-NMR (400.13 MHz, C_6D_6):

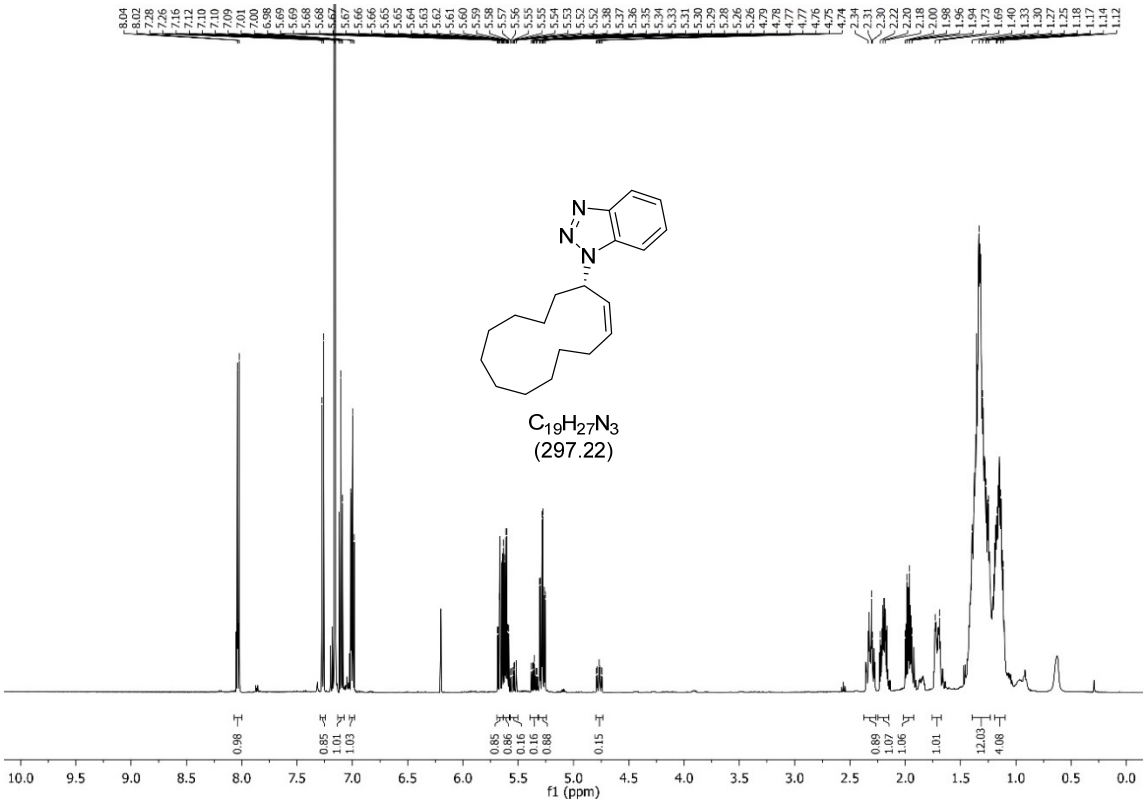


^{13}C-NMR (100.61 MHz, C_6D_6):

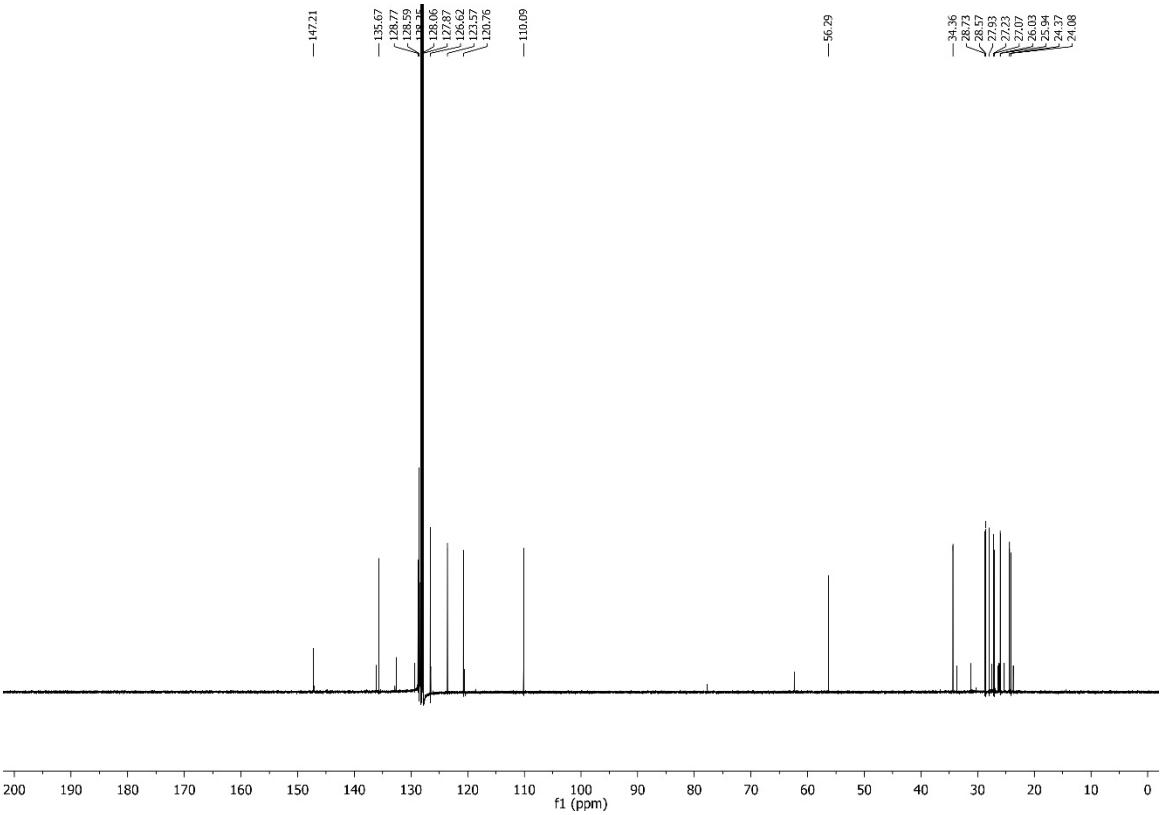


(*S*,*Z*)-1-(cyclotridec-2-en-1-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*[1], *Z*-product, 20)

^{1}H-NMR (499.98 MHz, C_6D_6):

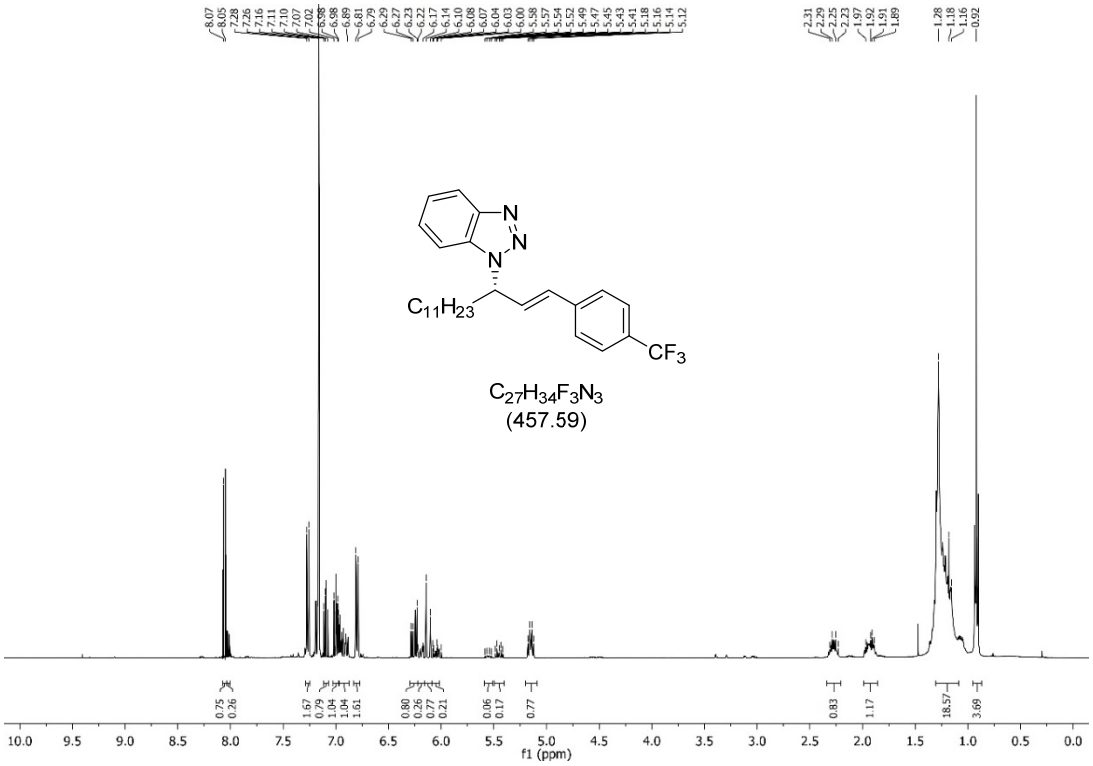


^{13}C-NMR (125.72 MHz, C_6D_6):

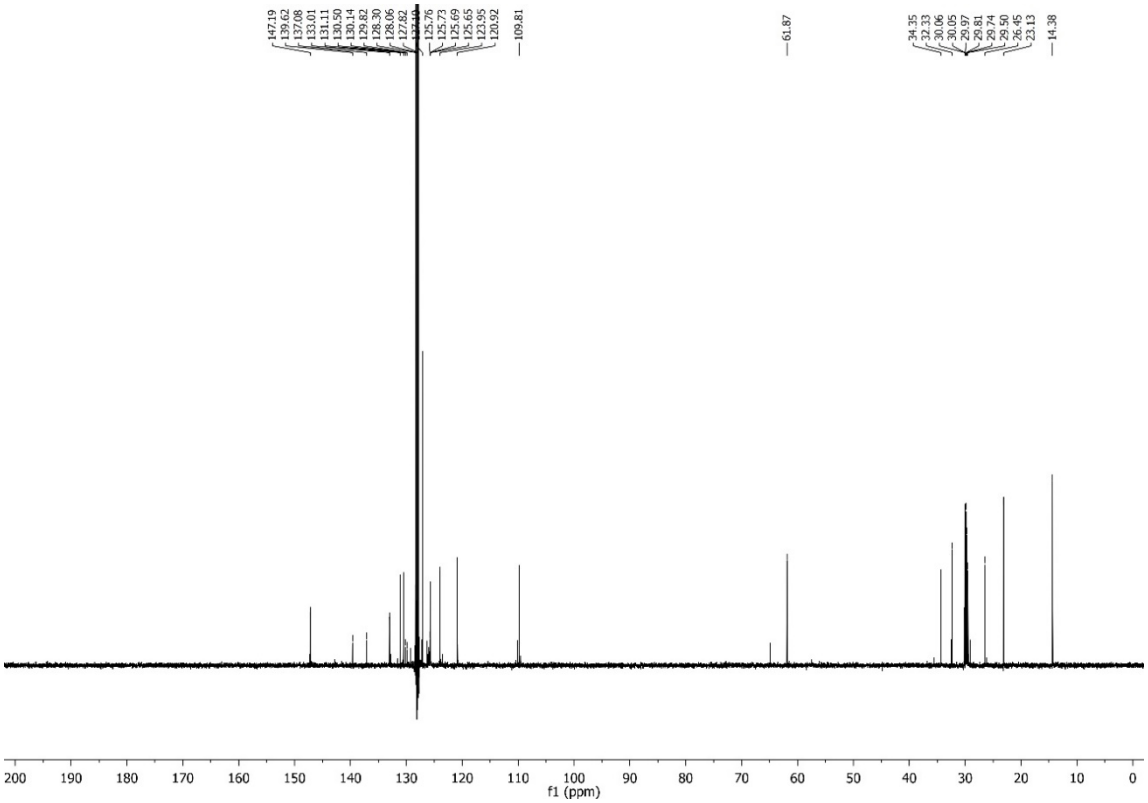


(*S*,*E*)-1-(1-(4-(trifluoromethyl)phenyl)tetradec-1-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}, *C*^{1}, *E*-product, 21)

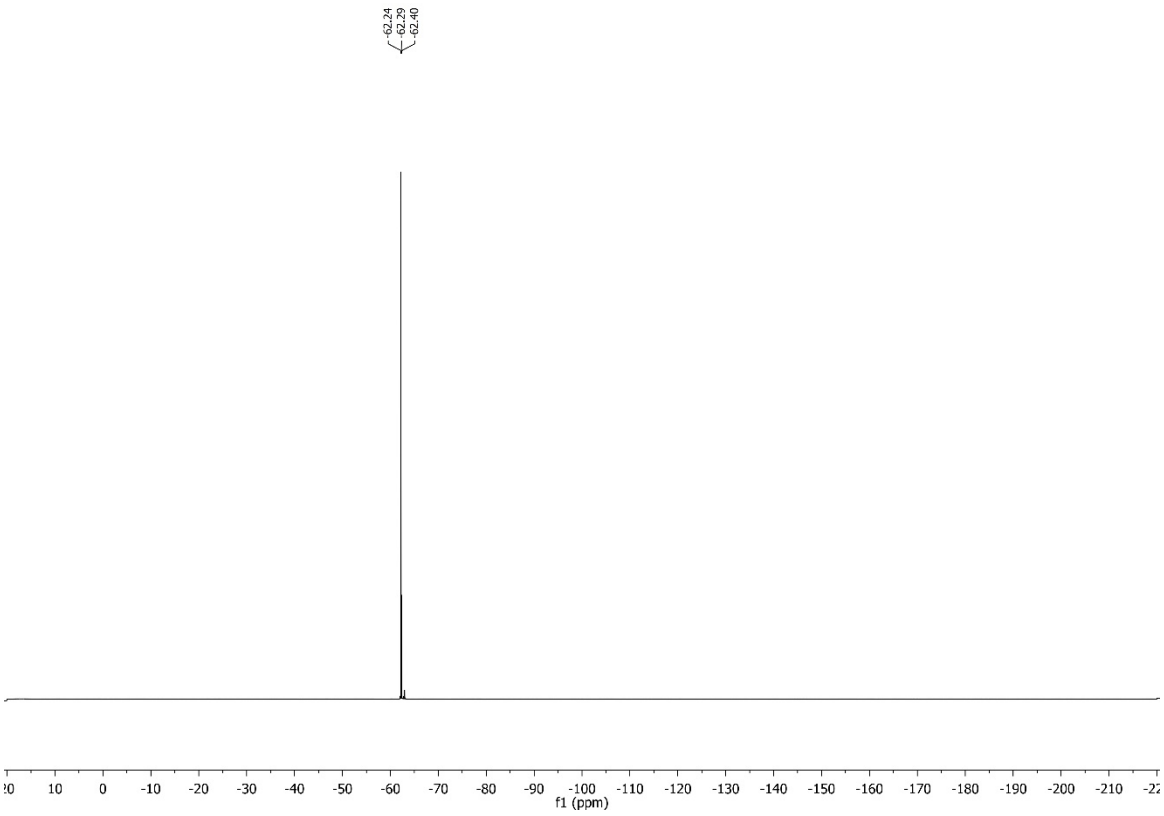
^{1}H-NMR (400.13 MHz, C_6D_6):



^{13}C-NMR (100.61 MHz, C_6D_6):

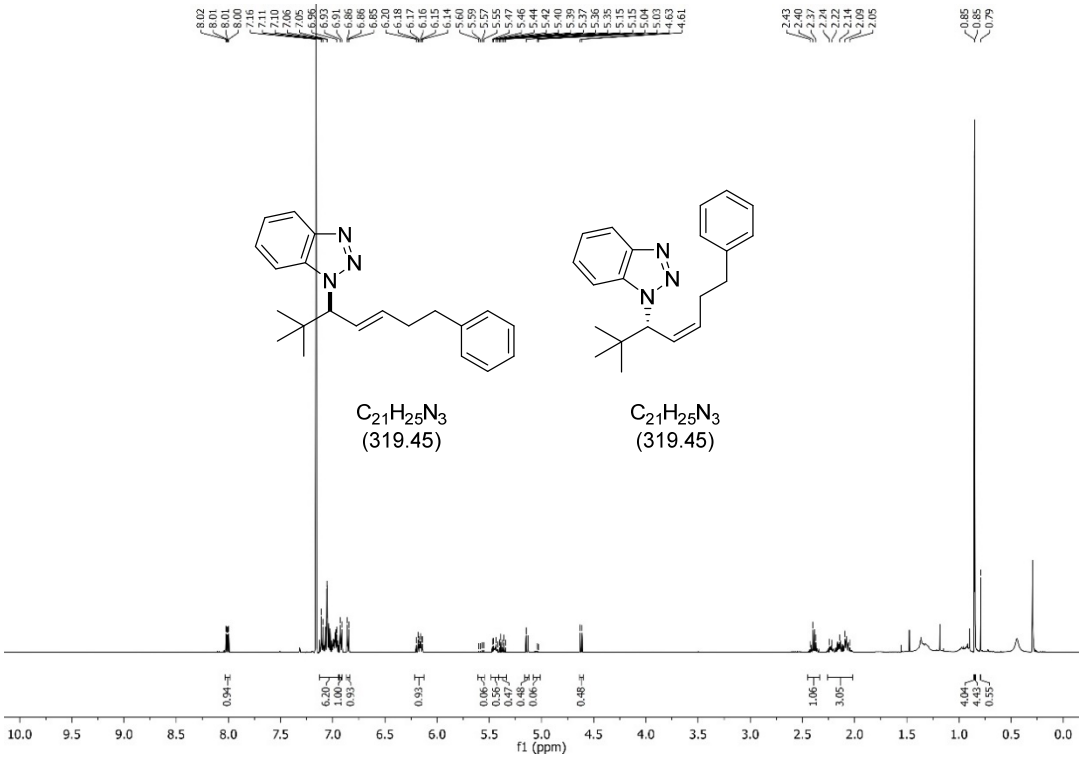


^{19}F-NMR (125.76 MHz, C_6D_6, unified scale):

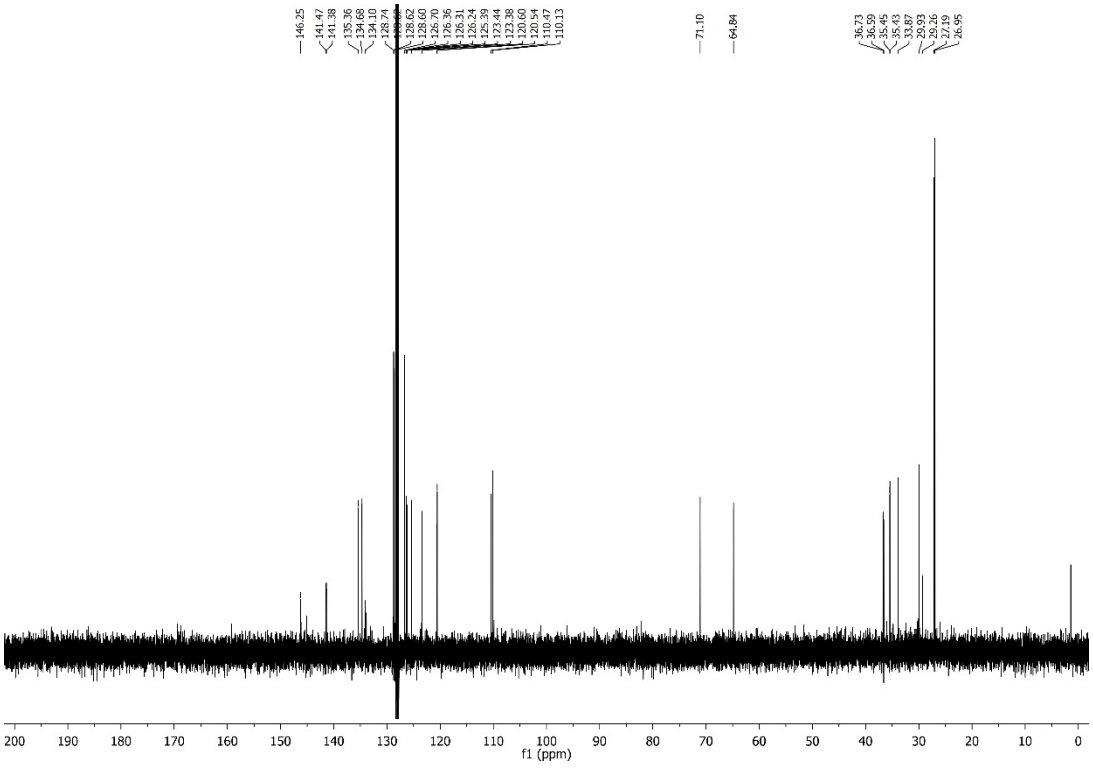

-62.24
-62.29
-62.40
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

(*S*,*E*)-1-(2,2-dimethyl-7-phenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1},*C*^{1},*E*-product, 22) & (*Z*)-1-(2,2-dimethyl-7-phenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1},*C*^{1},*Z*-product, 22b)

^{1}H-NMR (499.98 MHz, C_6D_6):

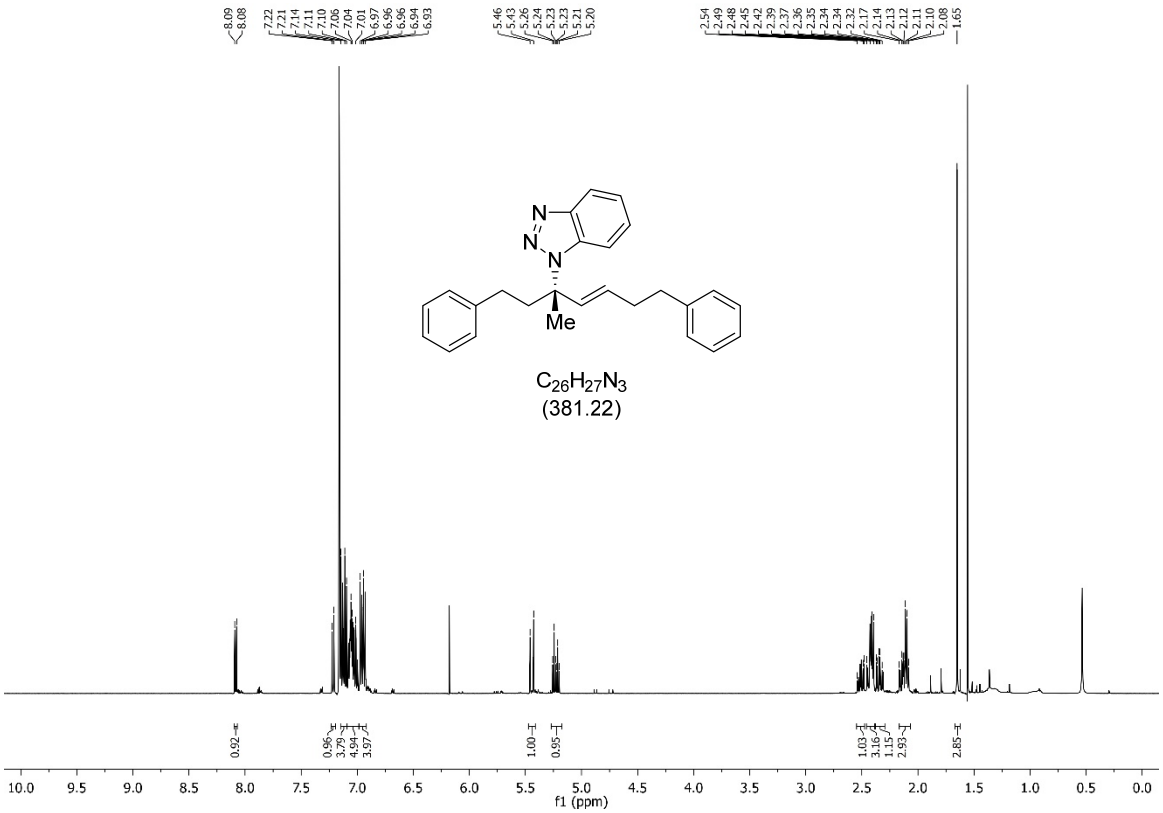


^{13}C-NMR (100.61 MHz, C_6D_6):

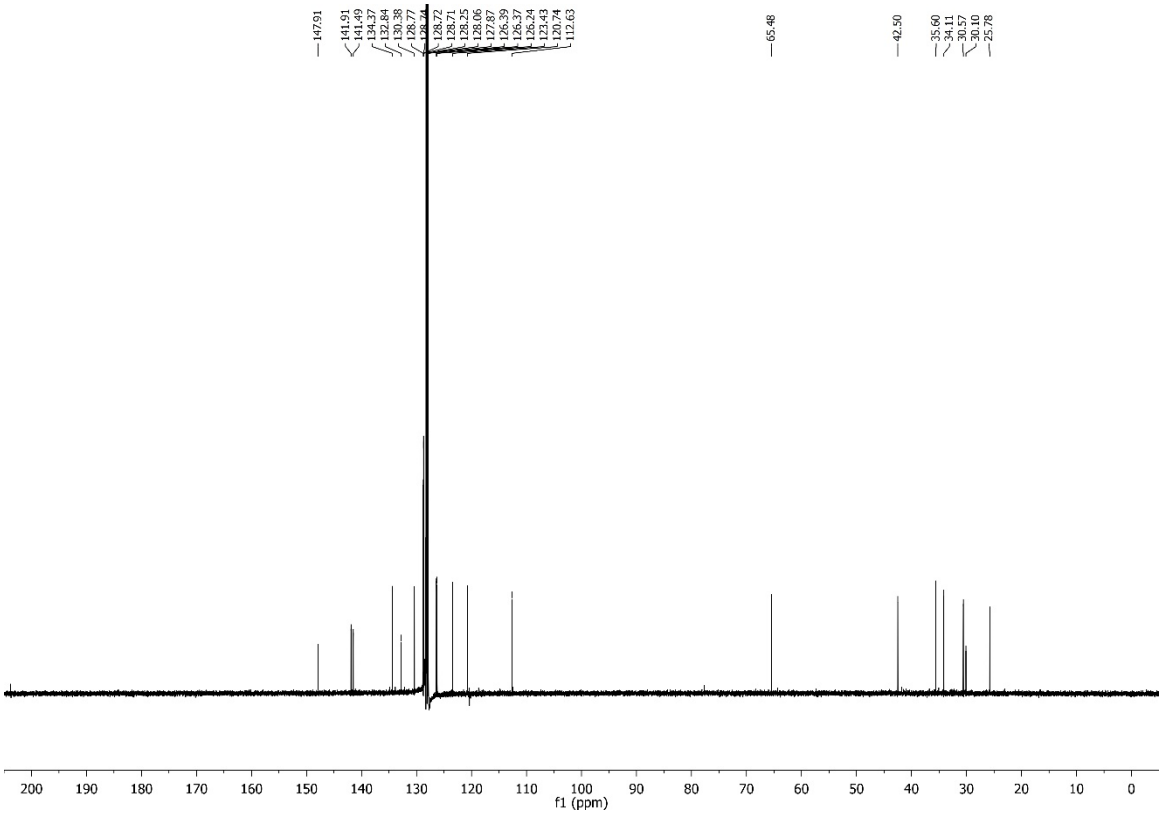


(*S*,*E*)-1-(3-methyl-1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1},*C*^{1},*E*-product, 23)

^{1}H-NMR (499.98 MHz, C_6D_6):

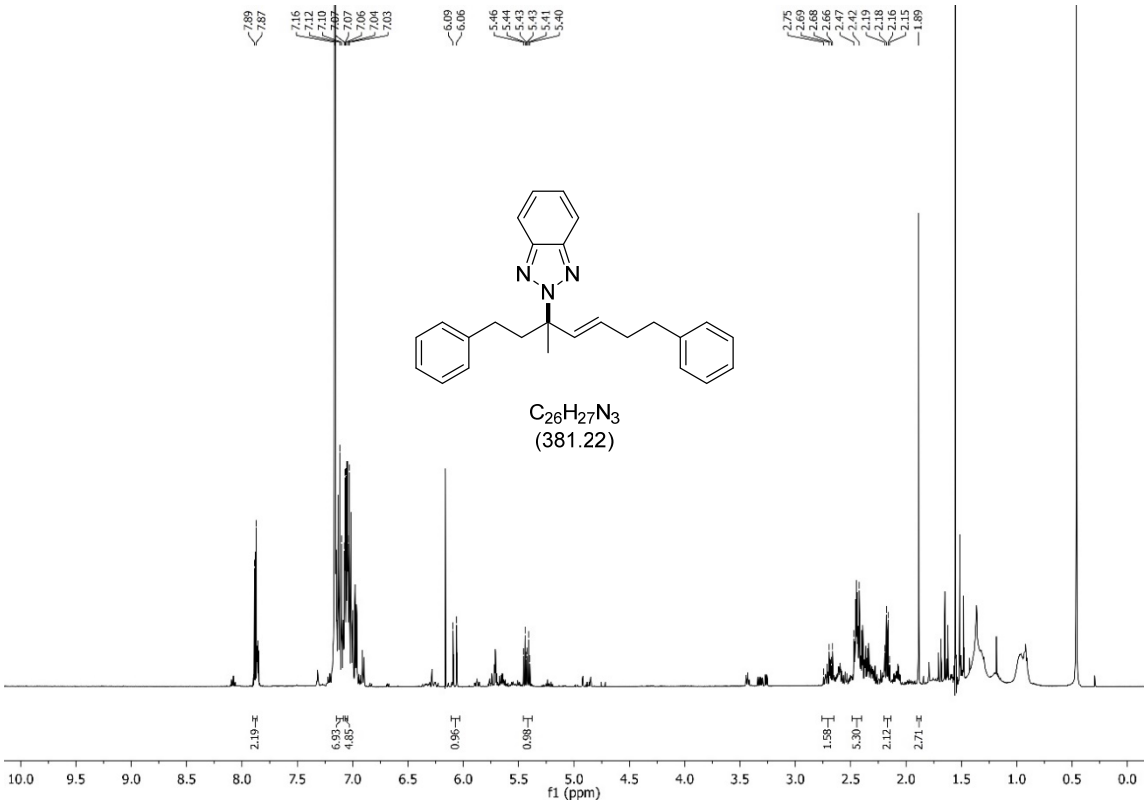


^{13}C-NMR (125.72 MHz, C_6D_6):

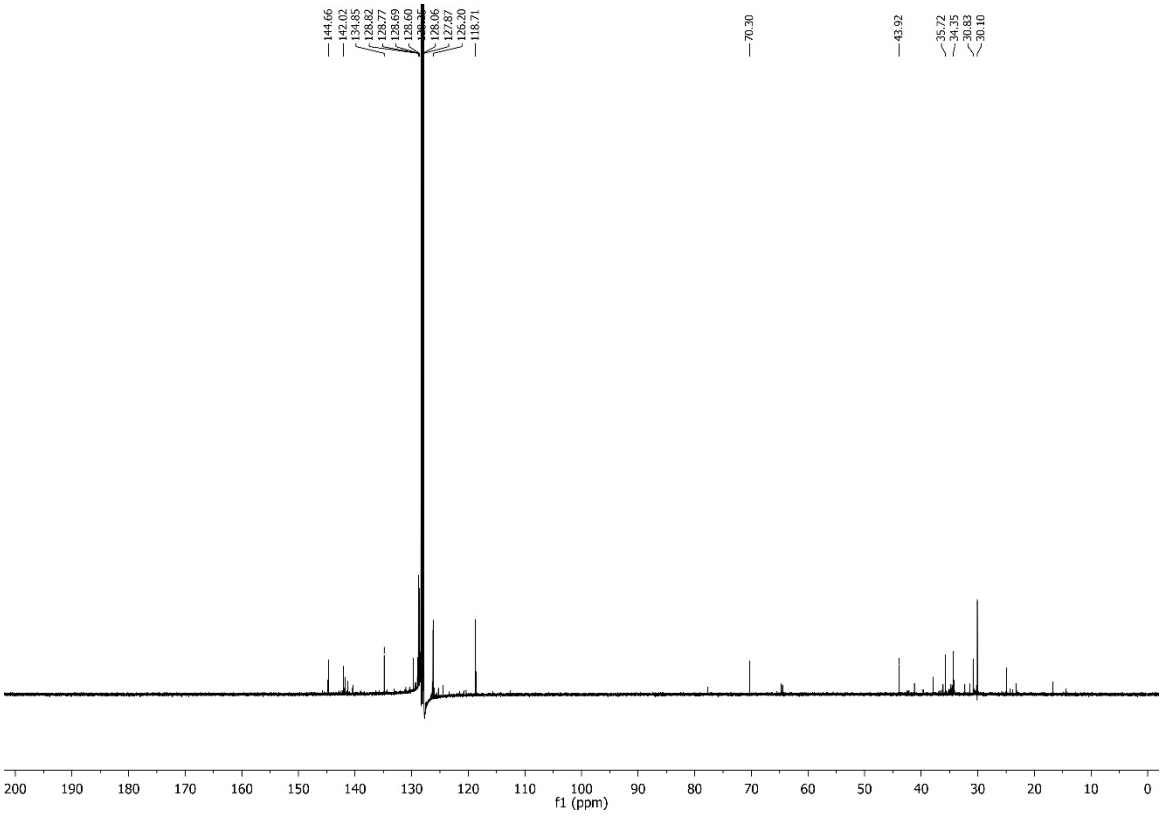


(*E*)-2-(3-methyl-1,7-diphenylhept-4-en-3-yl)-2*H*-benzo[*d*][1,2,3]triazole (*N*^{2},*C*^{1},*E*-product, 23b)

^{1}H-NMR (499.98 MHz, C_6D_6):

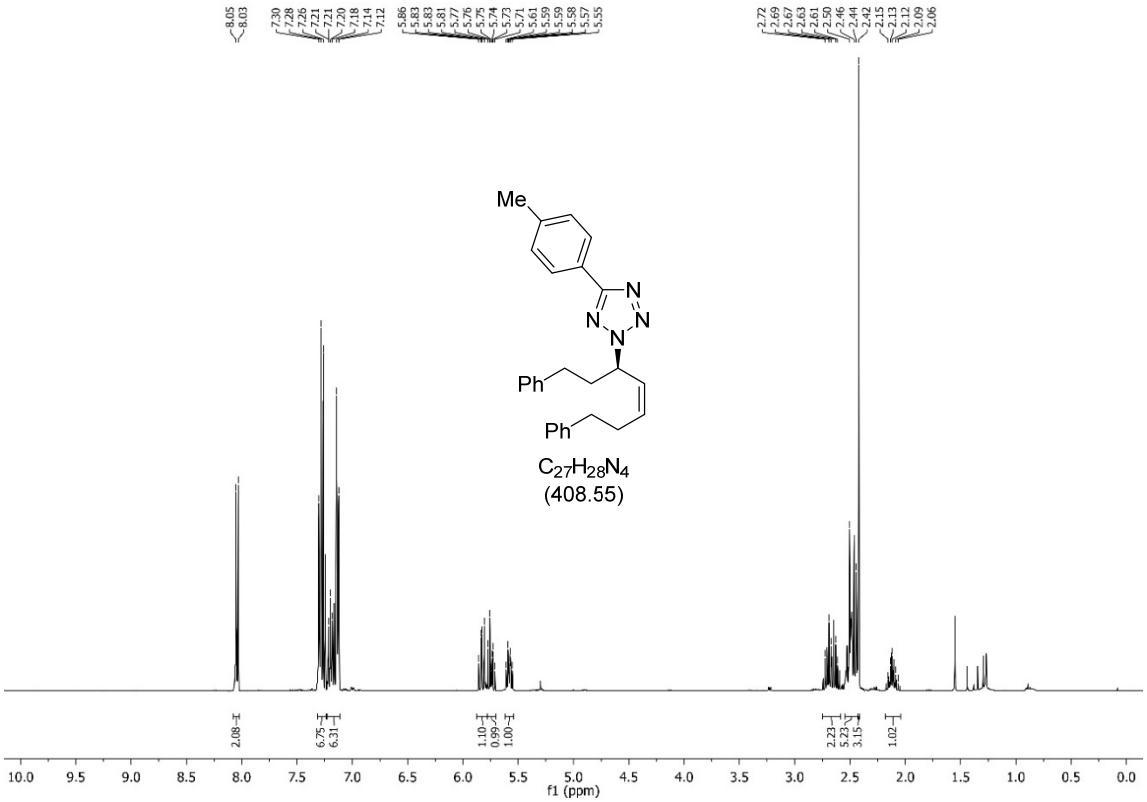


^{13}C-NMR (125.72 MHz, C_6D_6):

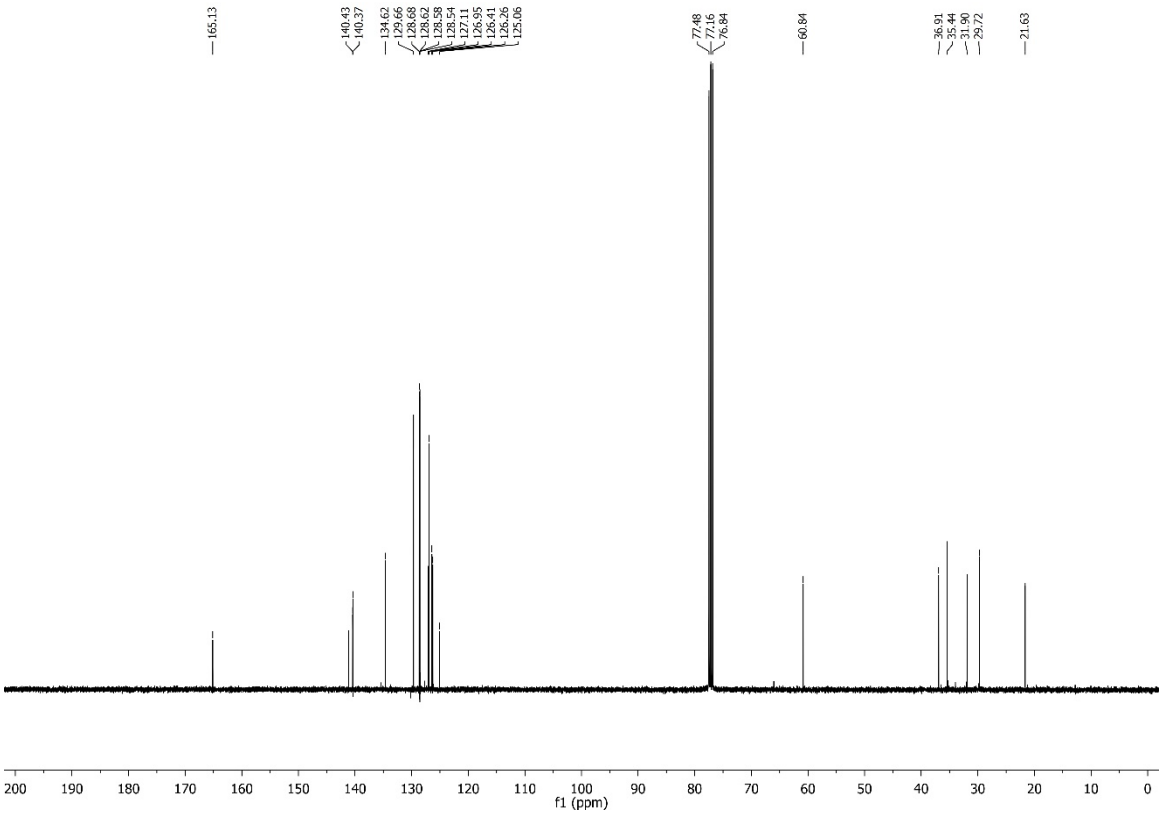


(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-(p-tolyl)-2*H*-tetrazole (24)

^{1}H-NMR (400.13 MHz, $CDCl_3$):

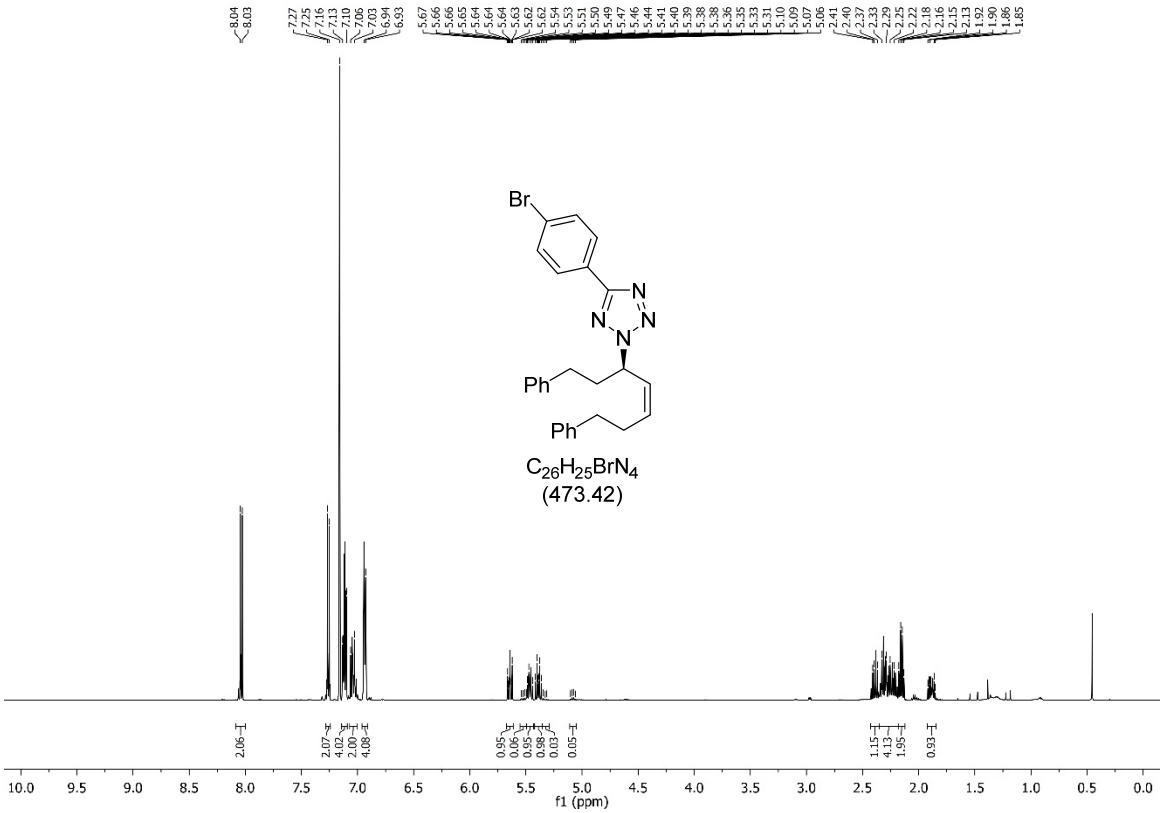


^{13}C-NMR (100.61 MHz, $CDCl_3$):

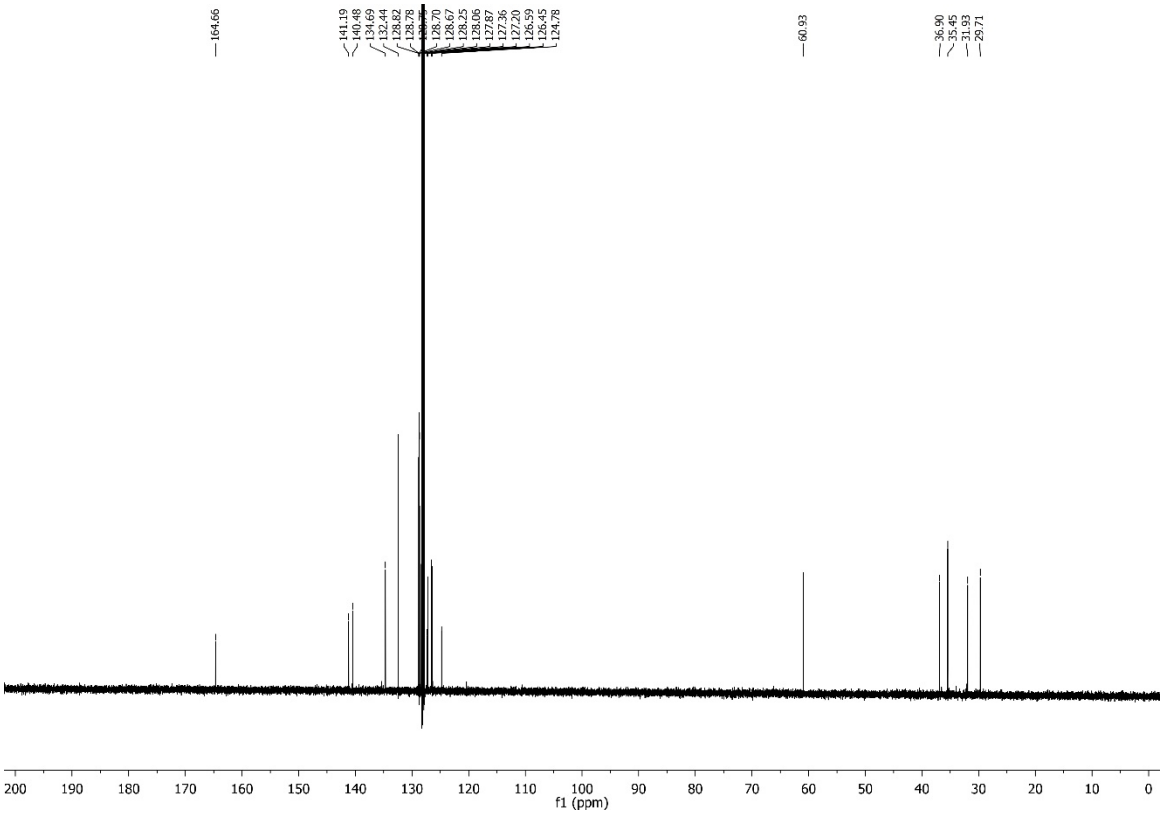


(*R*,*Z*)-5-(4-bromophenyl)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazole (25)

^{1}H-NMR (500.42 MHz, C_6D_6):

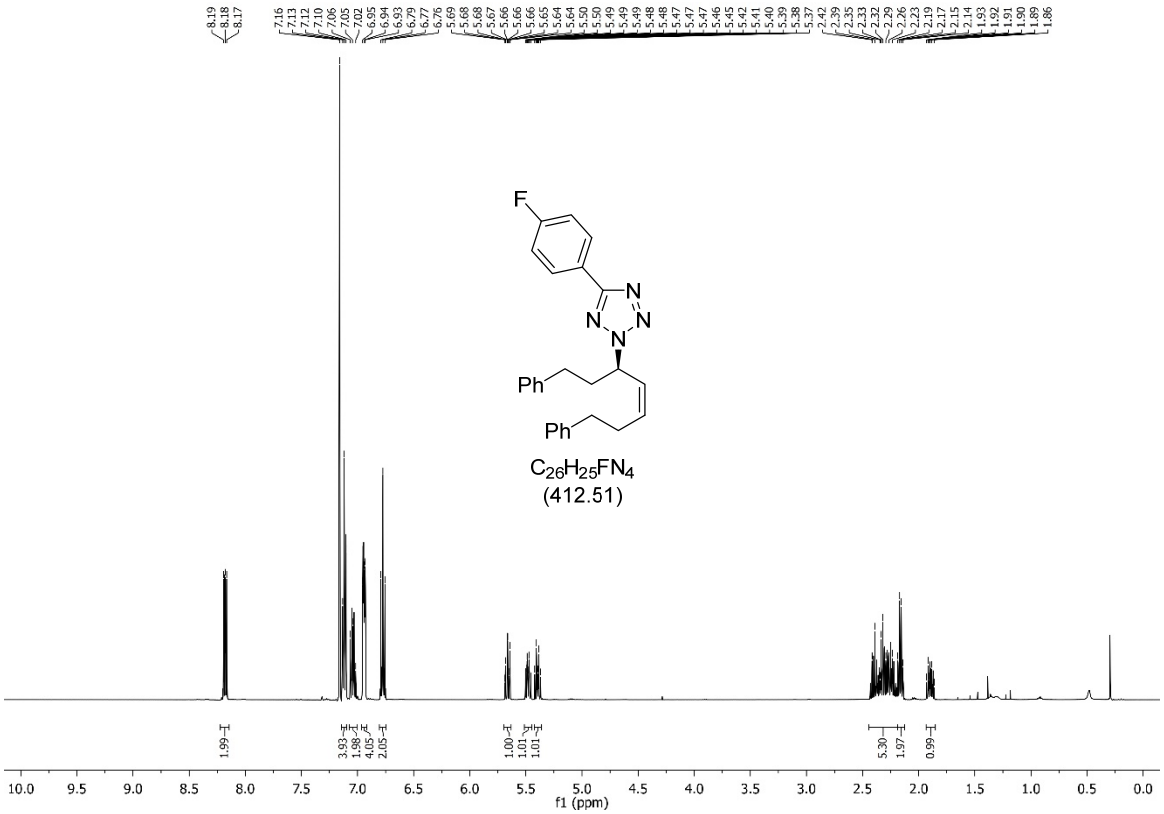


^{13}C-NMR (125.83 MHz, C_6D_6):

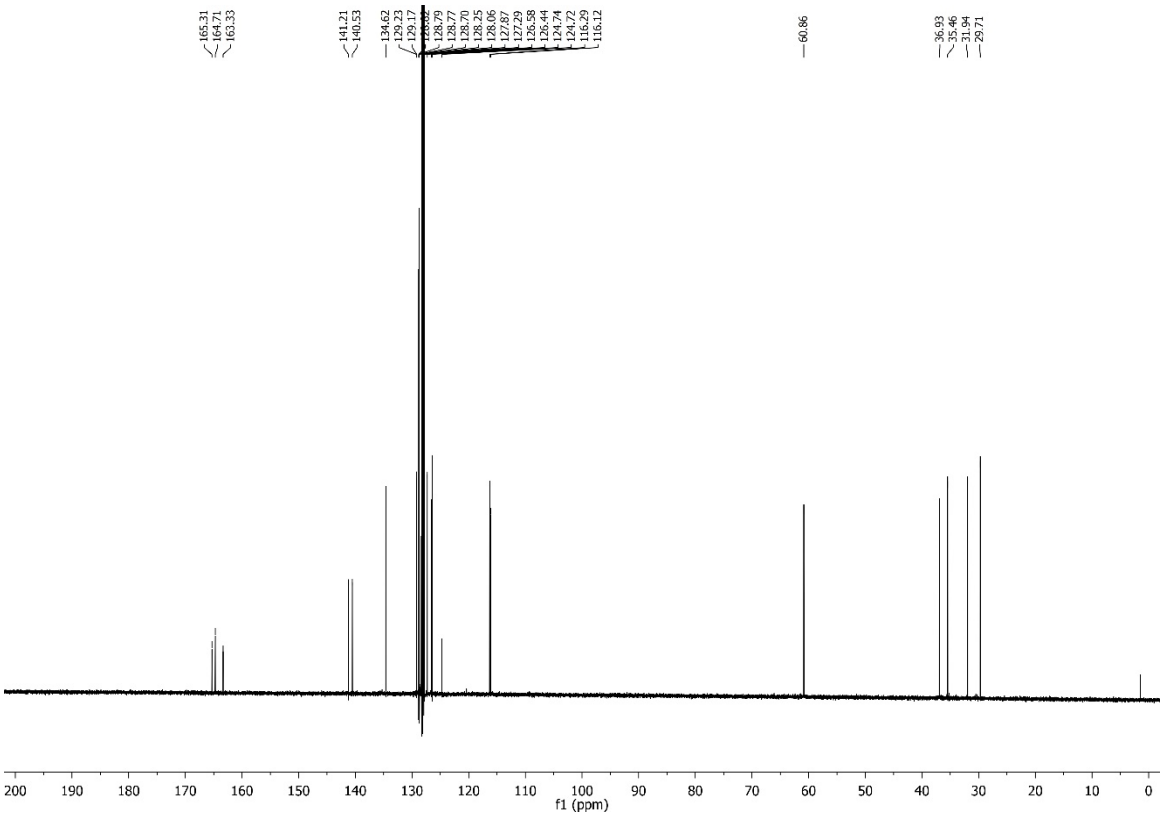


(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-(4-fluorophenyl)-2*H*-tetrazole (26)

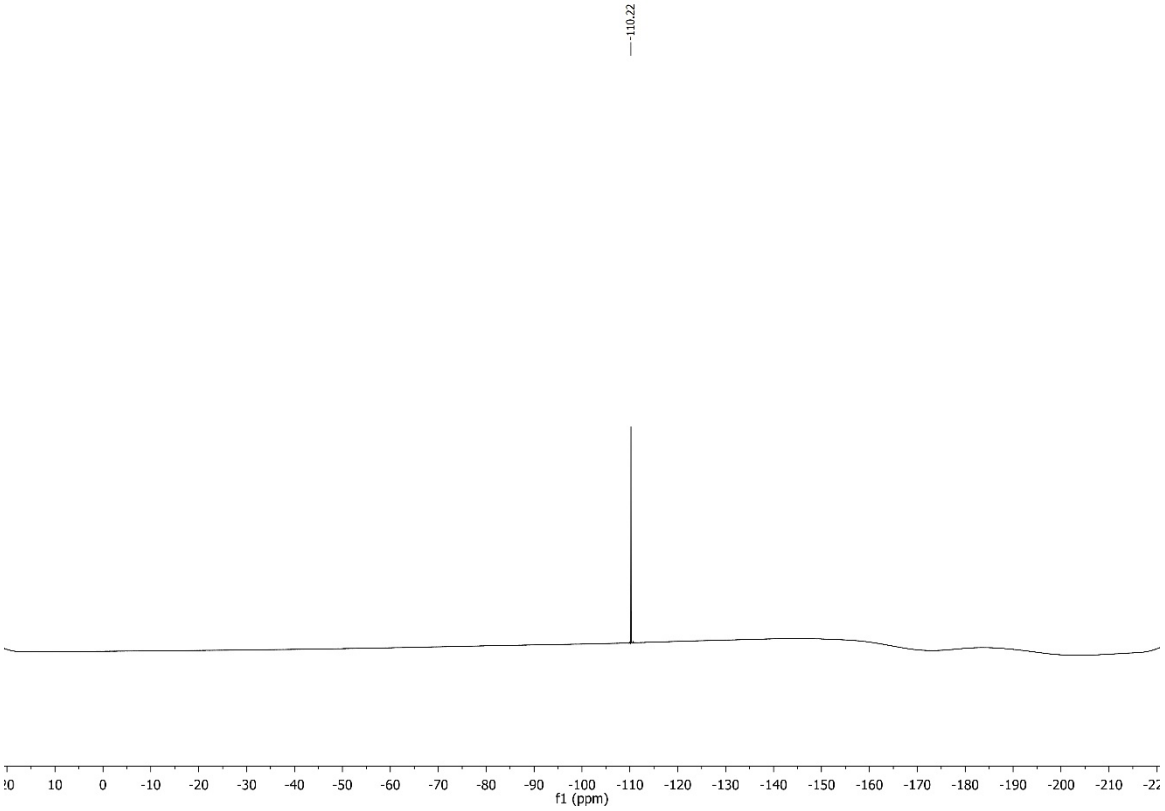
^{1}H-NMR (500.42 MHz, C_6D_6):



^{13}C-NMR (125.83 MHz, C_6D_6):

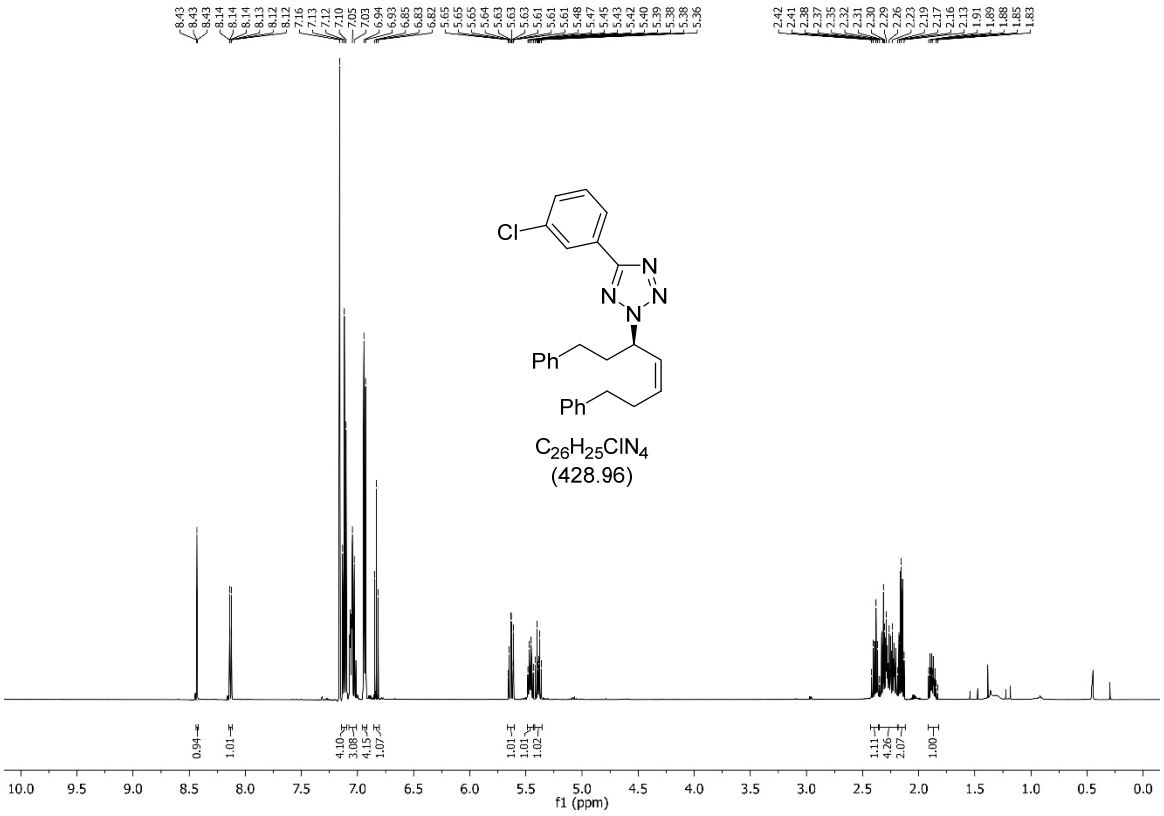


^{19}F-NMR (376.76 MHz, C_6D_6, unified scale):

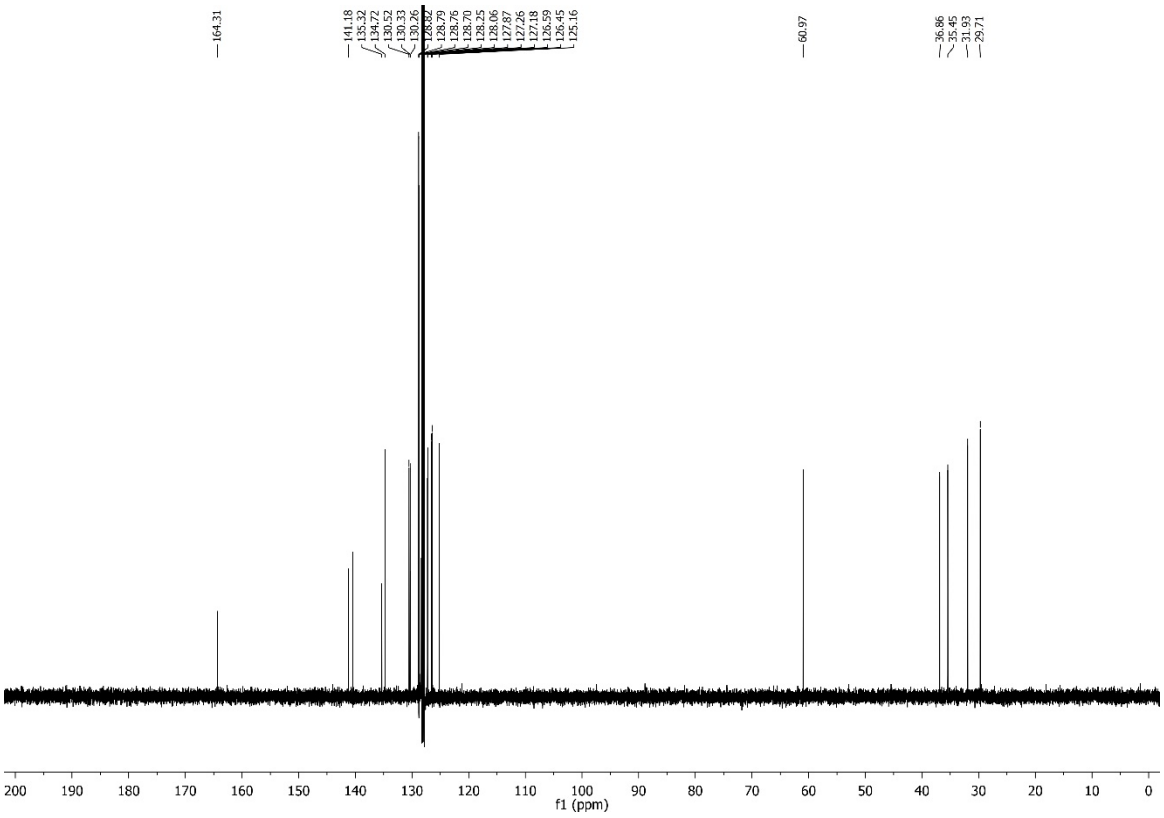


(*R*,*Z*)-5-(3-chlorophenyl)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazole (27)

^{1}H-NMR (500.42 MHz, C_6D_6):

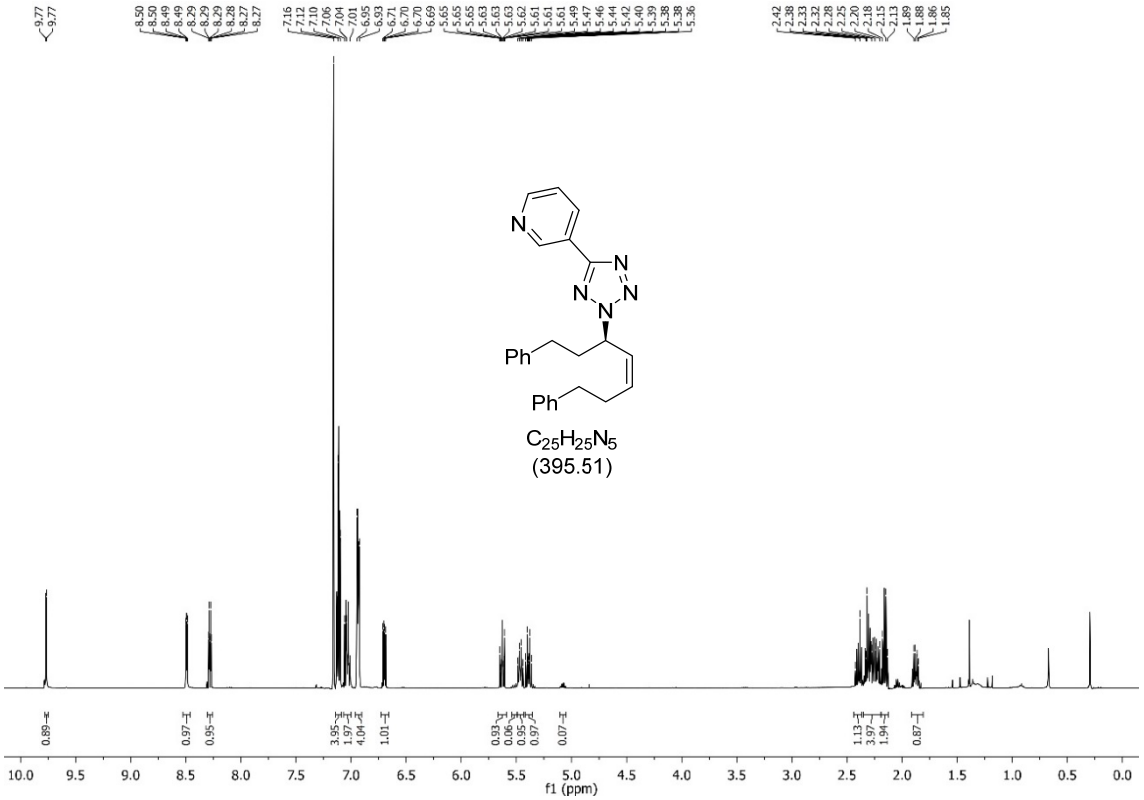


^{13}C-NMR (125.83 MHz, C_6D_6):

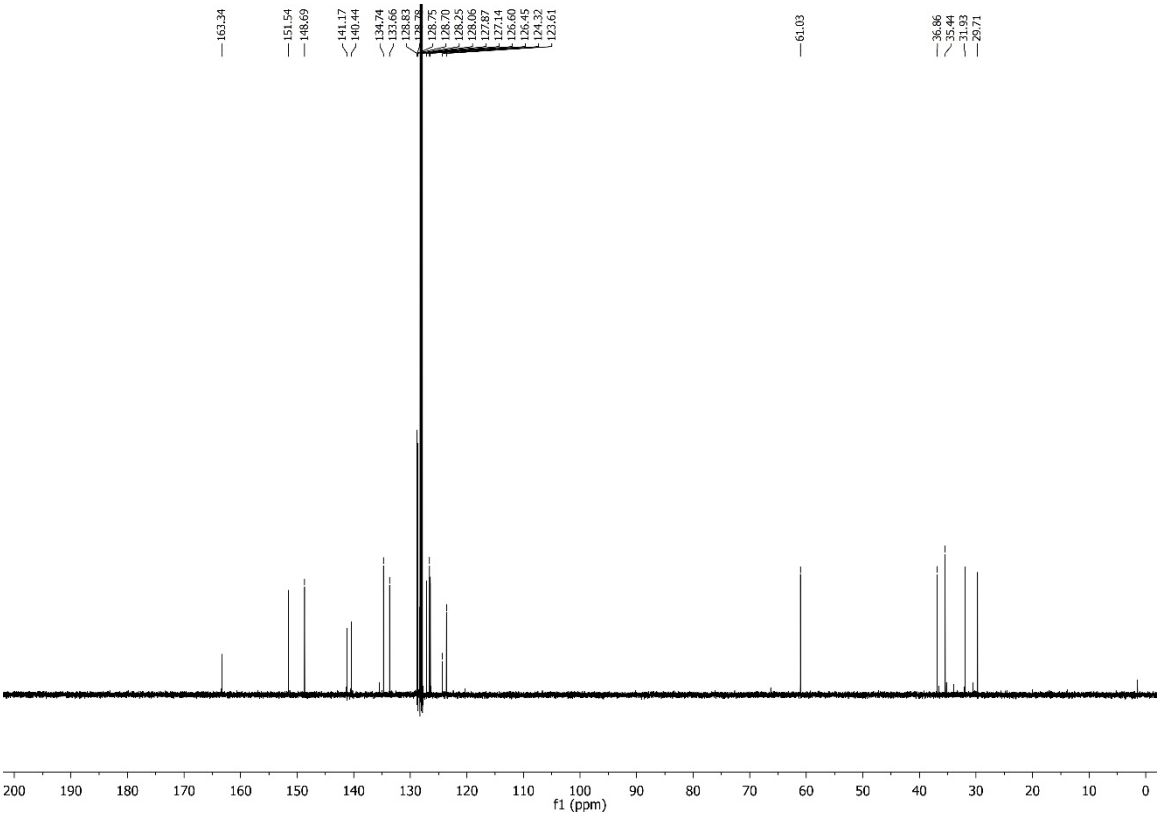


(*R*,*Z*)-3-(2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazol-5-yl)pyridine (28)

^{1}H-NMR (500.42 MHz, C_6D_6):

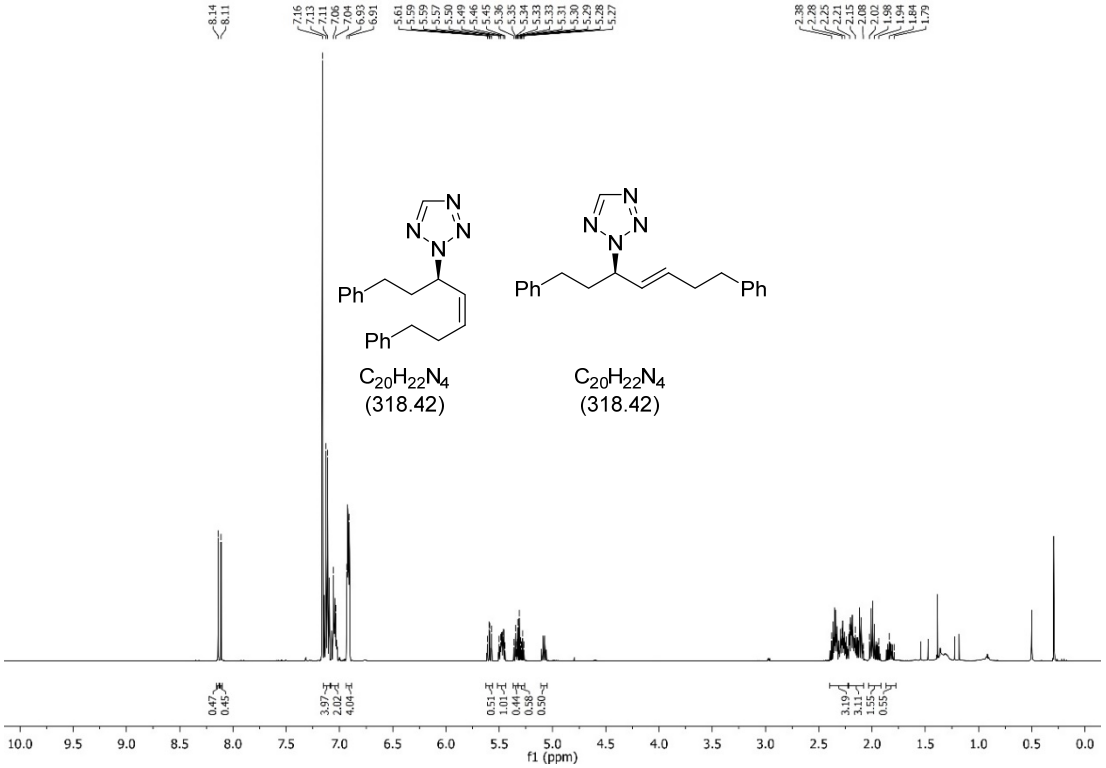


^{13}C-NMR (125.83 MHz, C_6D_6):

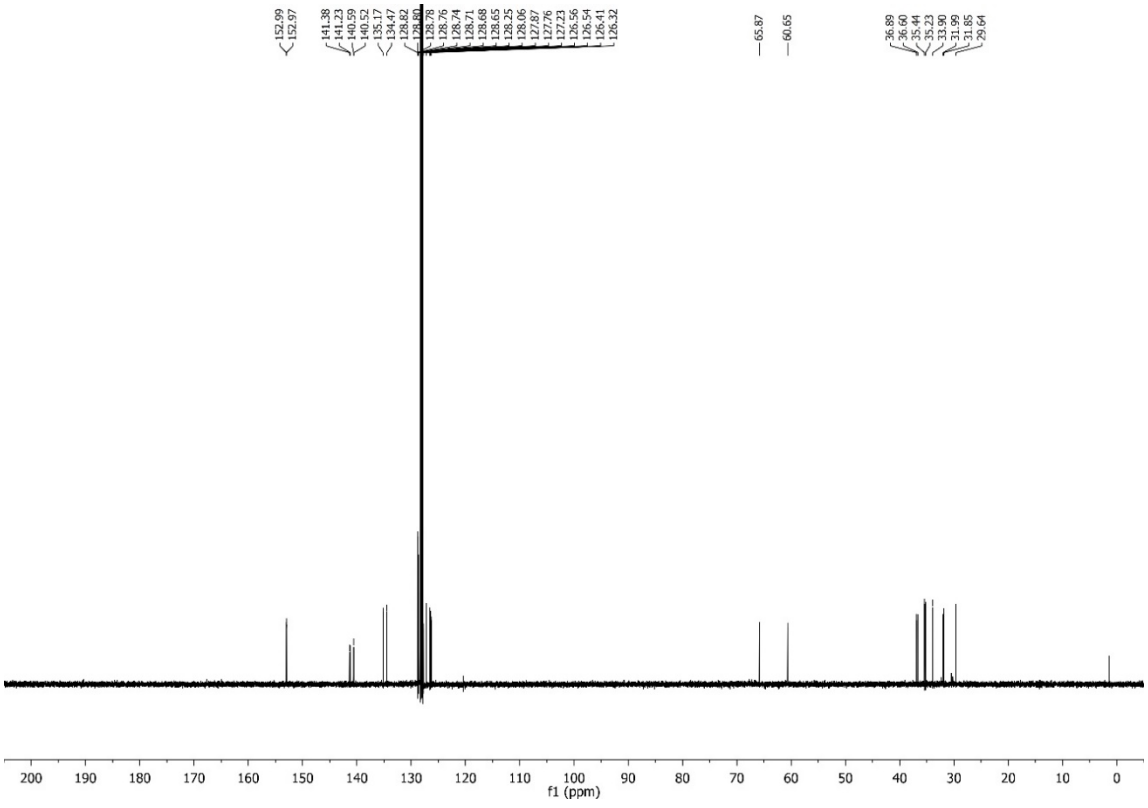


(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazole (29) & (*R*,*E*)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazole (29b)

^{1}H-NMR (500.42 MHz, C_6D_6):

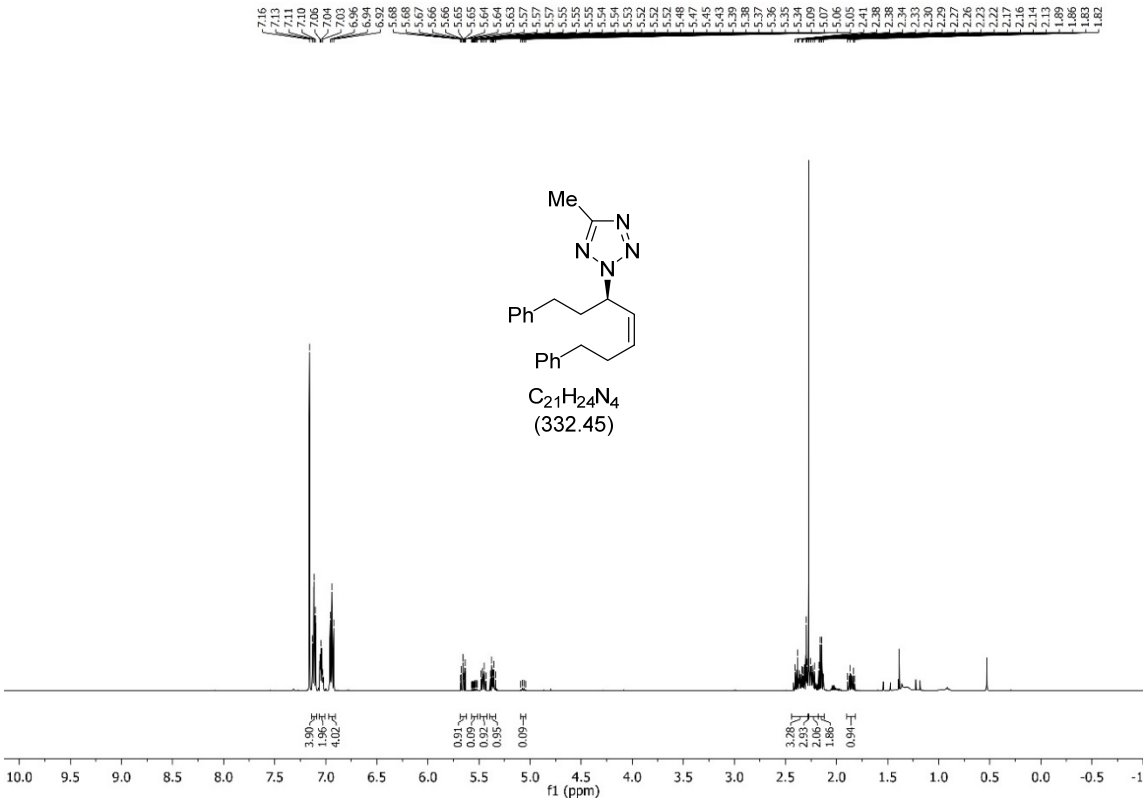


^{13}C-NMR (125.85 MHz, C_6D_6):

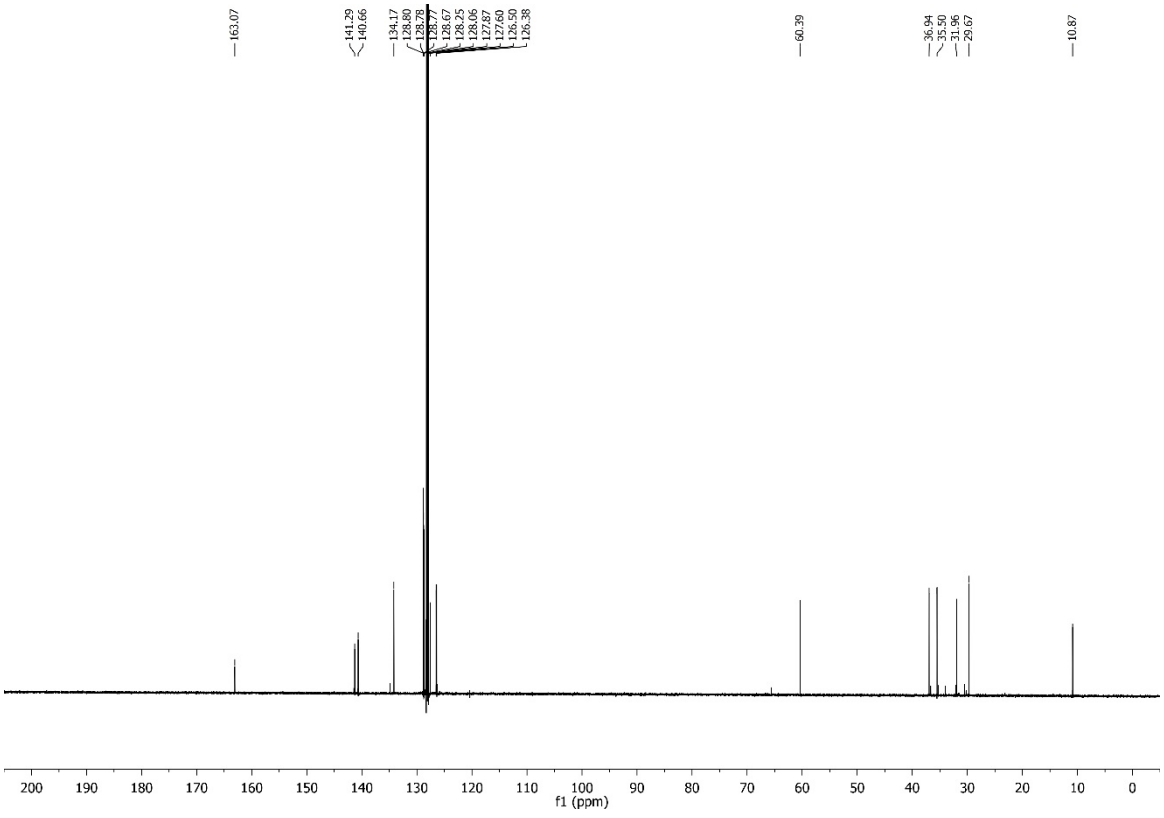


(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-methyl-2*H*-tetrazole (30)

^{1}H-NMR (500.42 MHz, C_6D_6):

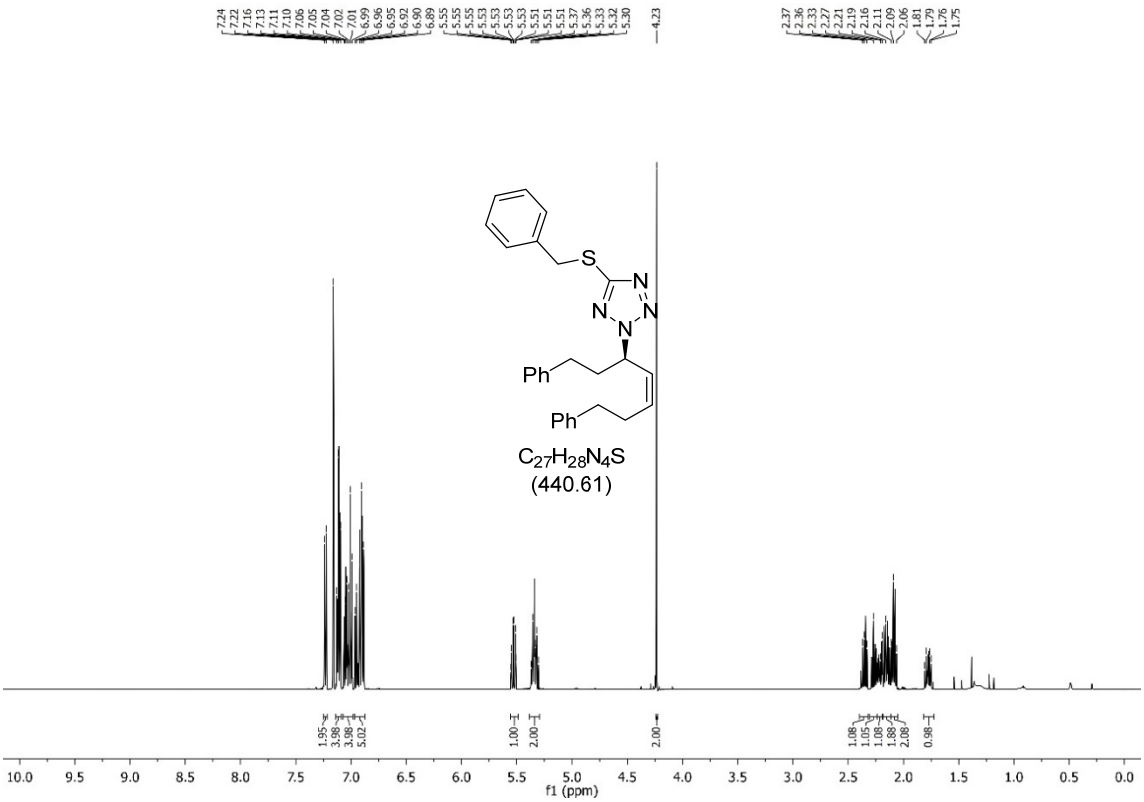


^{13}C-NMR (125.83 MHz, C_6D_6):

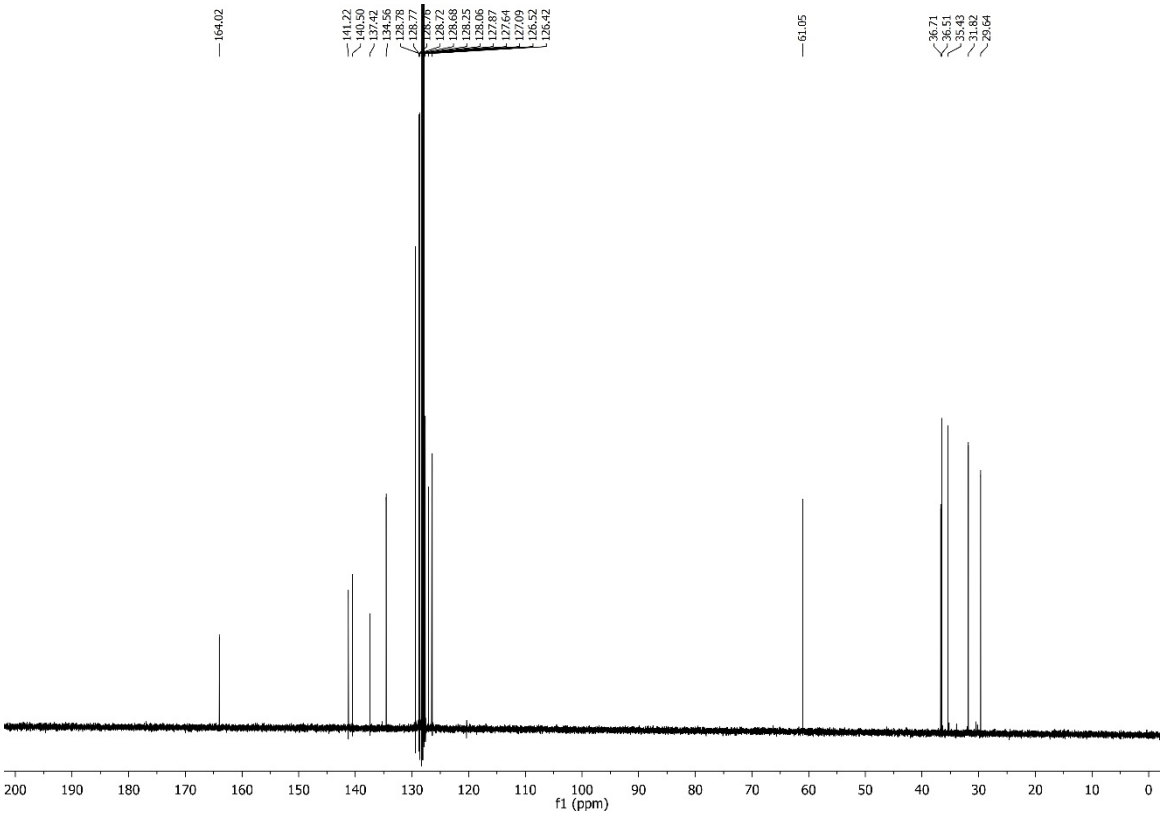


(*R*,*Z*)-5-(benzylthio)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazole (31)

^{1}H-NMR (500.42 MHz, C_6D_6):

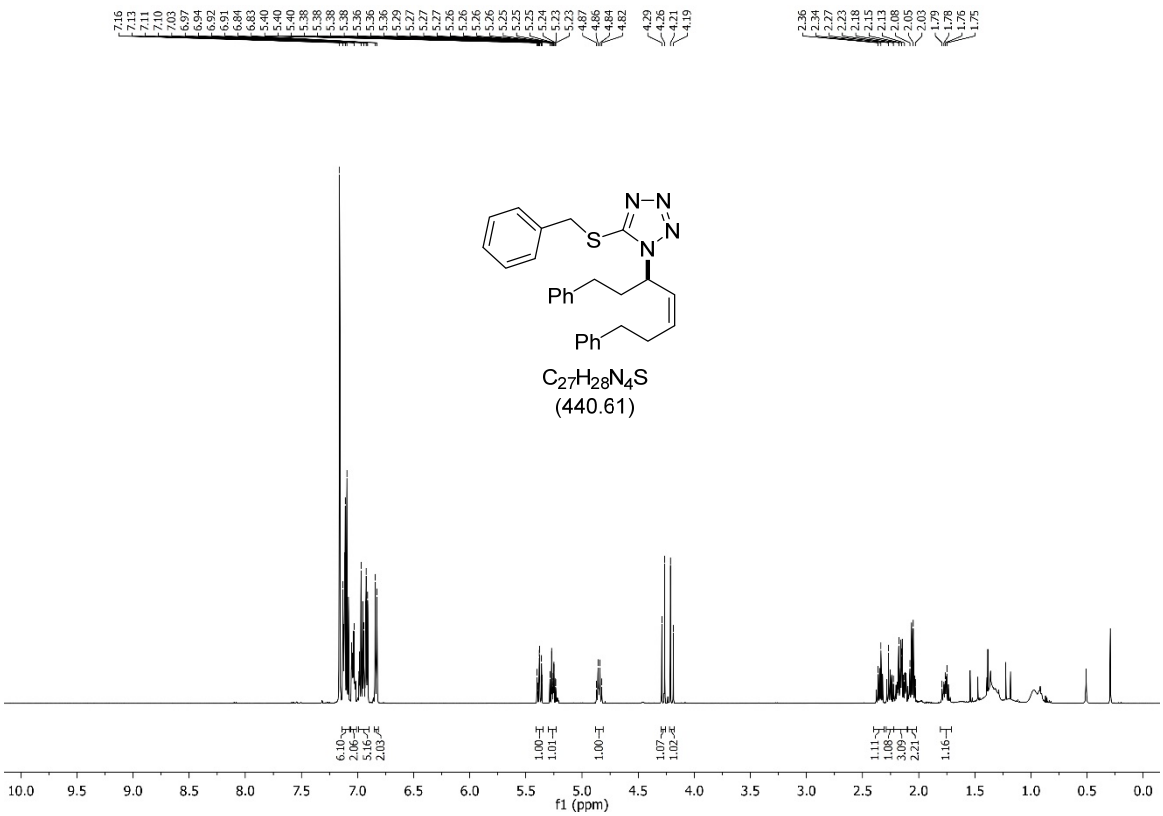


^{13}C-NMR (125.83 MHz, C_6D_6):

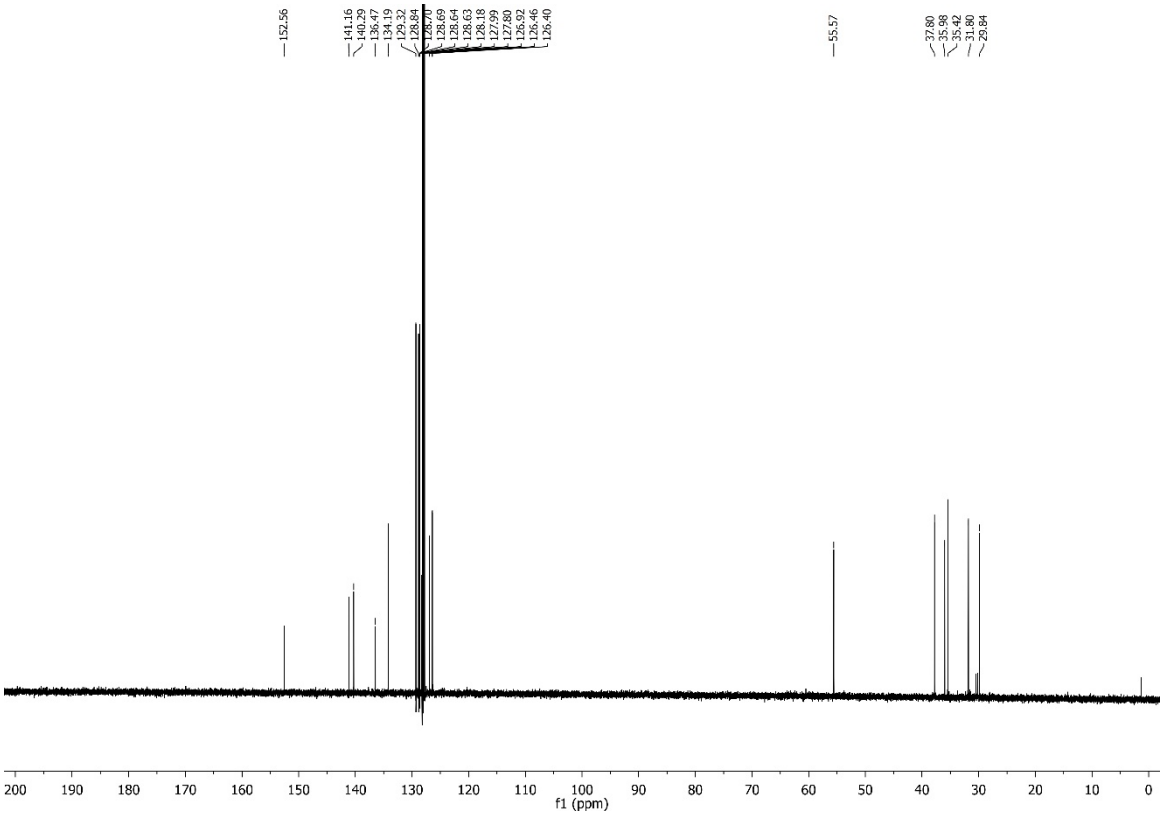


(*Z*)-5-(benzylthio)-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-tetrazole (31b)

^{1}H-NMR (500.42 MHz, C_6D_6):

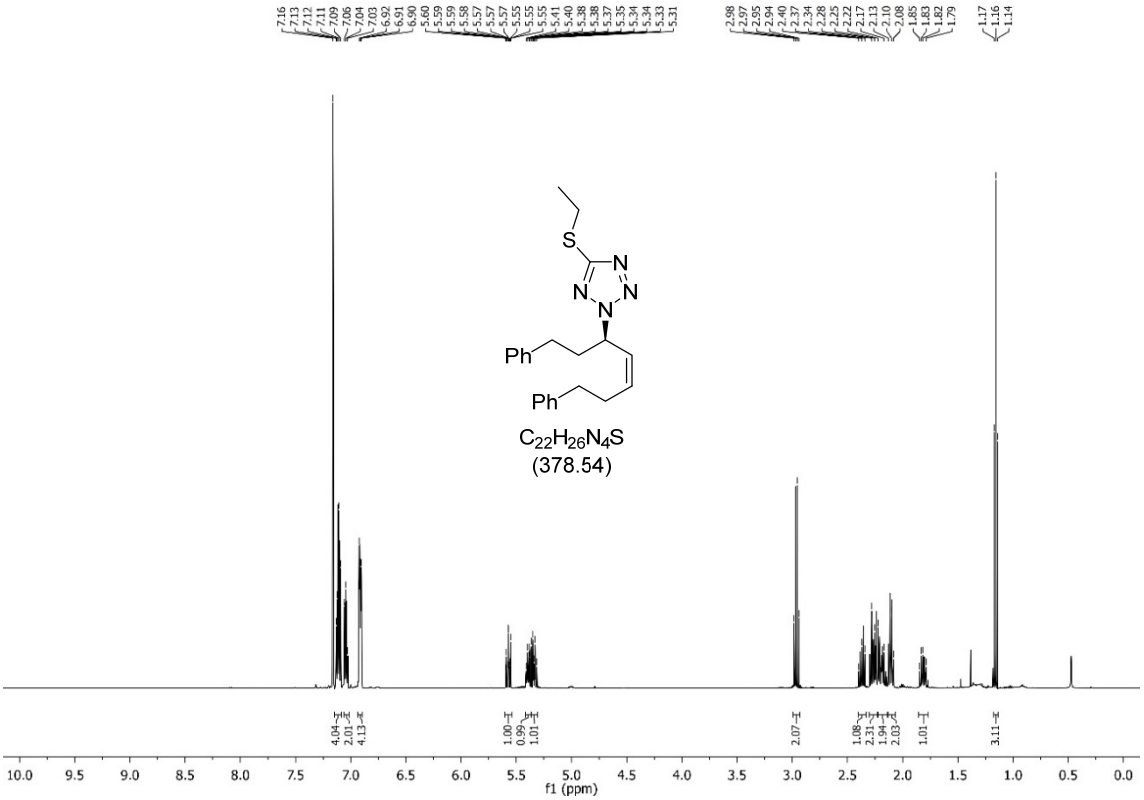


^{13}C-NMR (125.83 MHz, C_6D_6):

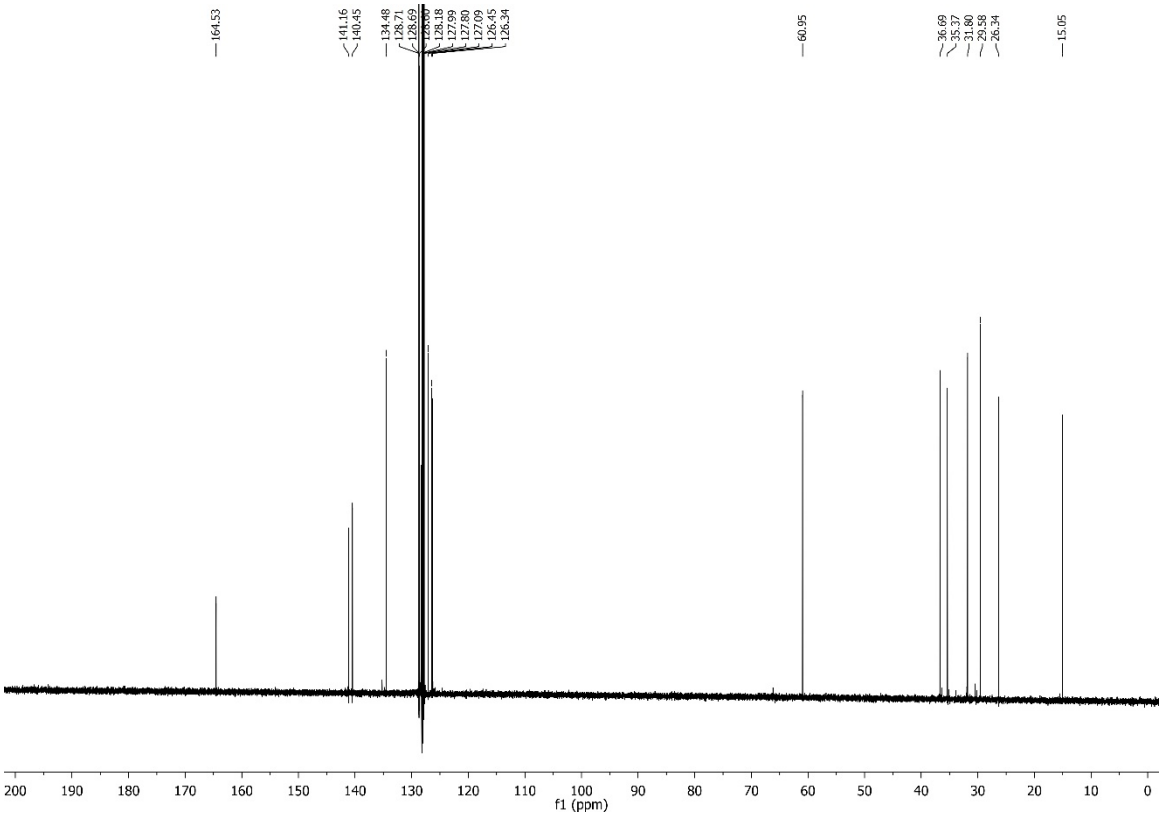


(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-(ethylthio)-2*H*-tetrazole (32)

^{1}H-NMR (500.42 MHz, C_6D_6):

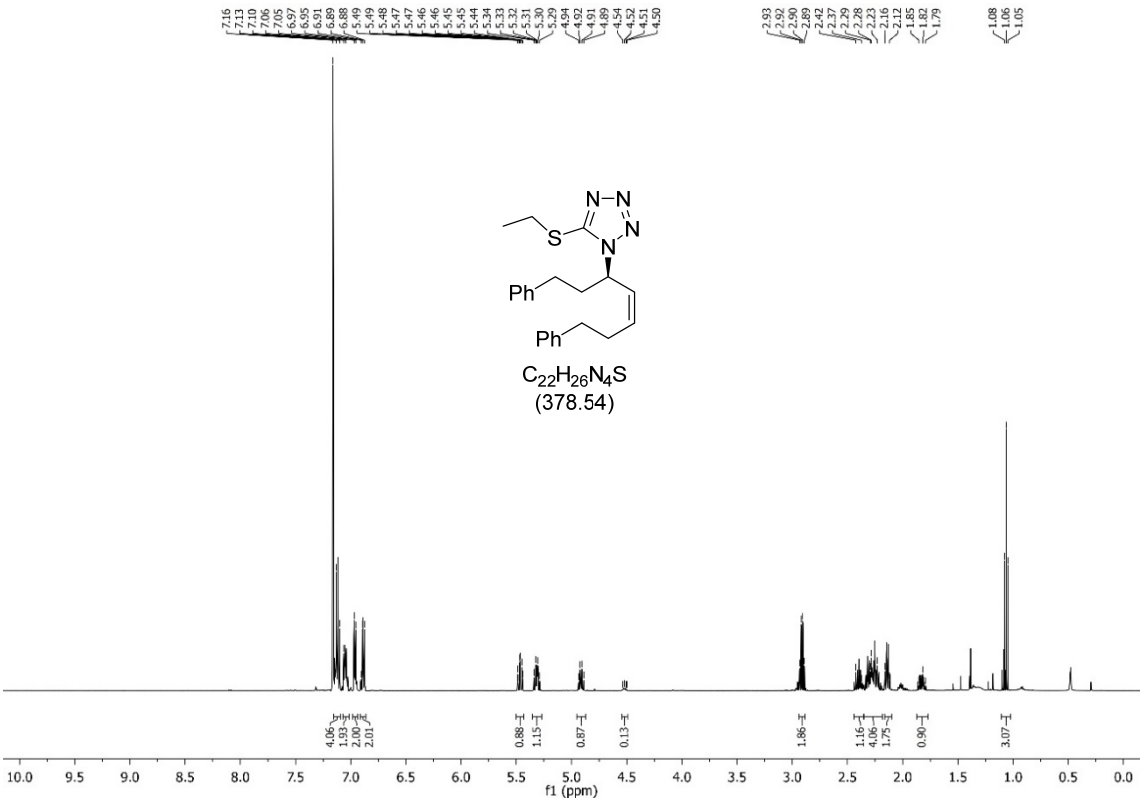


^{13}C-NMR (125.83 MHz, C_6D_6):

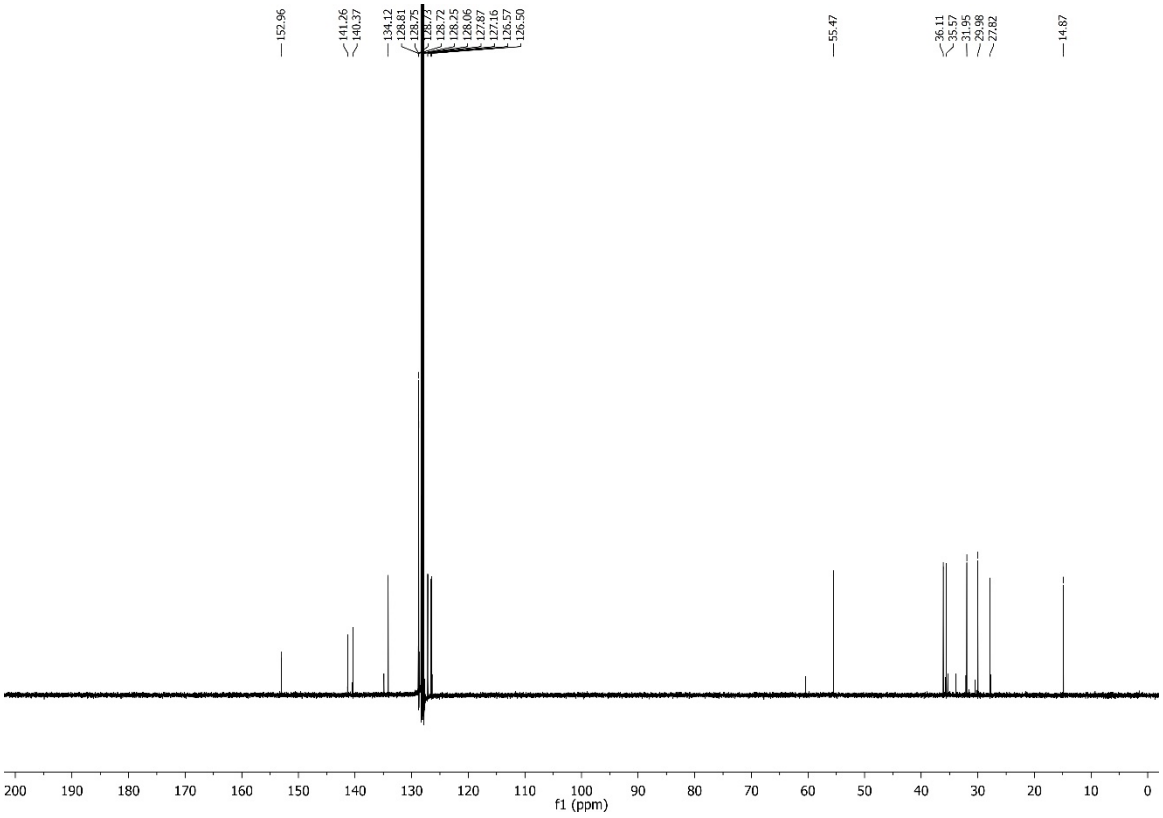


(*Z*)-1-(1,7-diphenylhept-4-en-3-yl)-5-(ethylthio)-1*H*-tetrazole (32b)

^{1}H-NMR (500.42 MHz, C_6D_6):

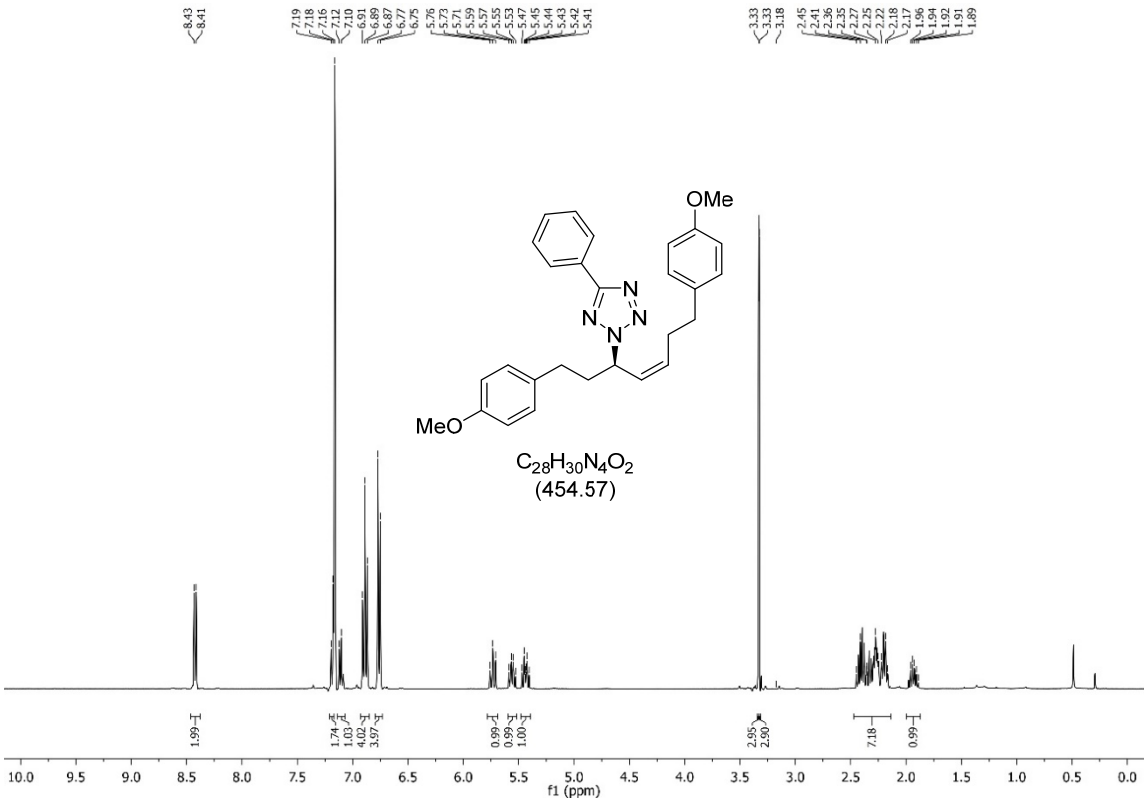


^{13}C-NMR (125.83 MHz, C_6D_6):

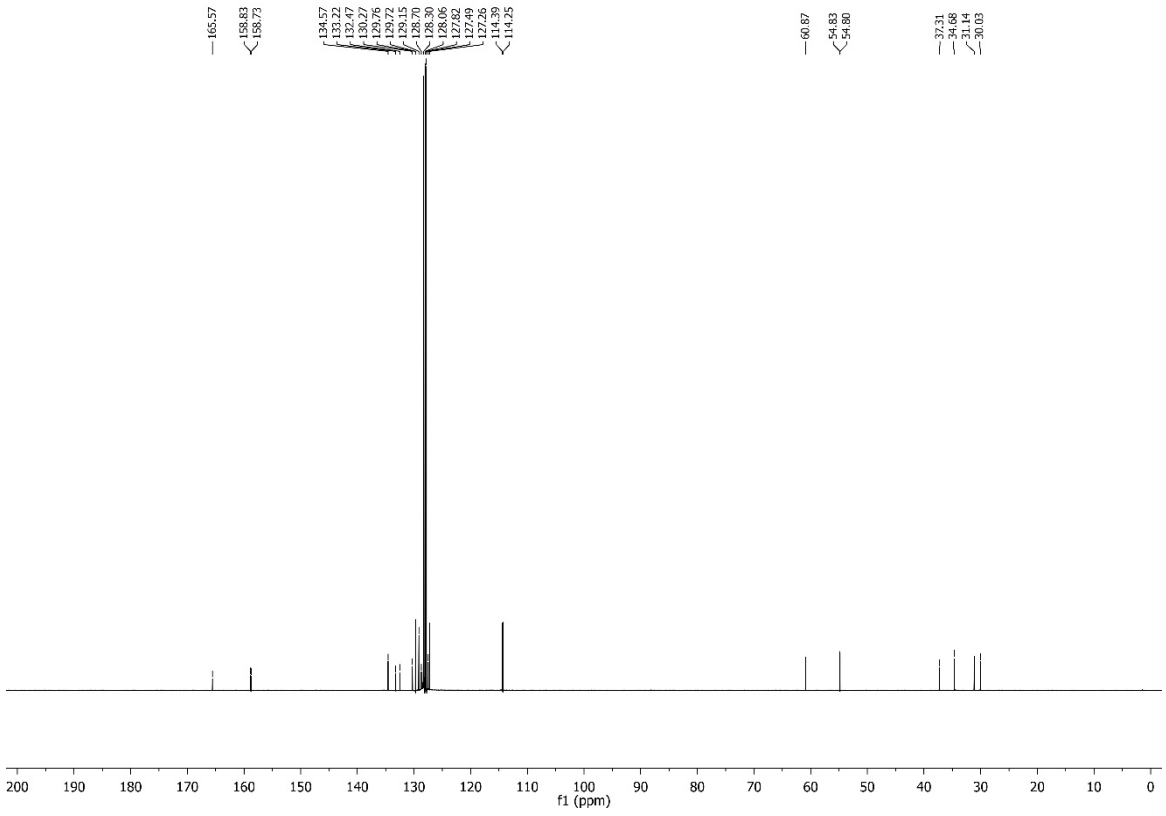


(*R*,*Z*)-2-(1,7-bis(4-methoxyphenyl)hept-4-en-3-yl)-5-phenyl-2*H*-tetrazole (33)

^{1}H-NMR (400.13 MHz, C_6D_6):

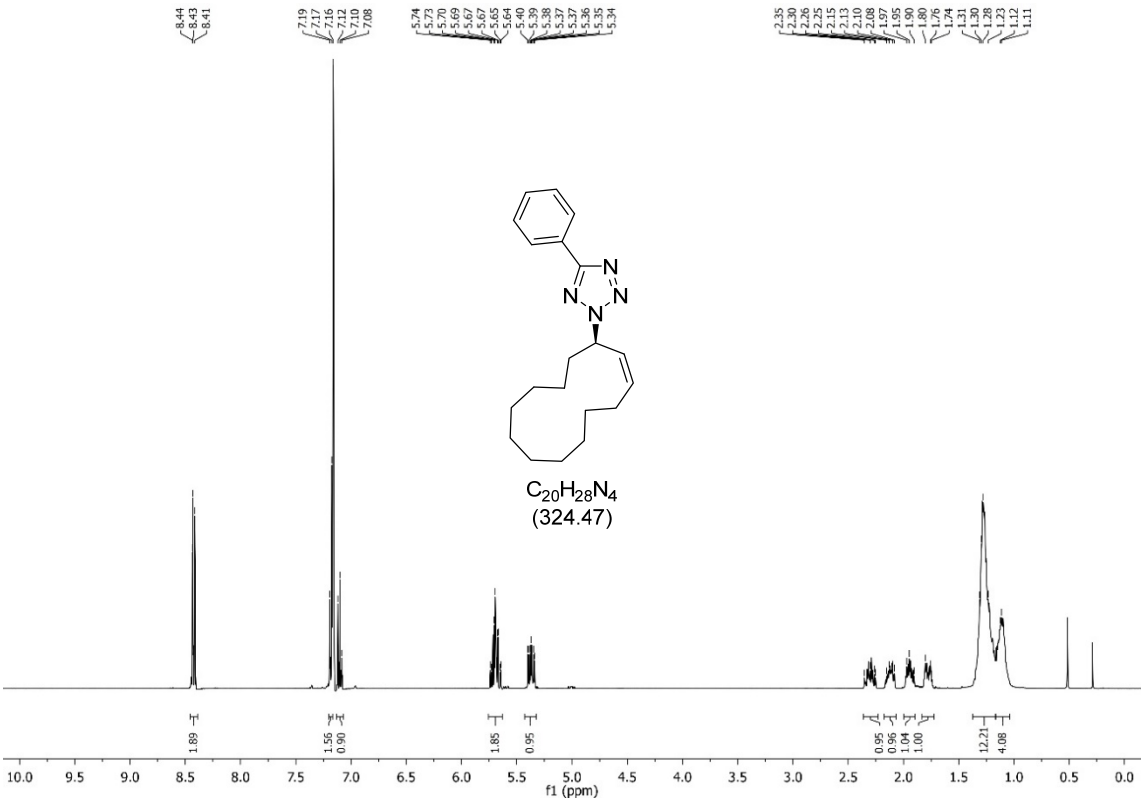


^{13}C-NMR (100.61 MHz, C_6D_6):

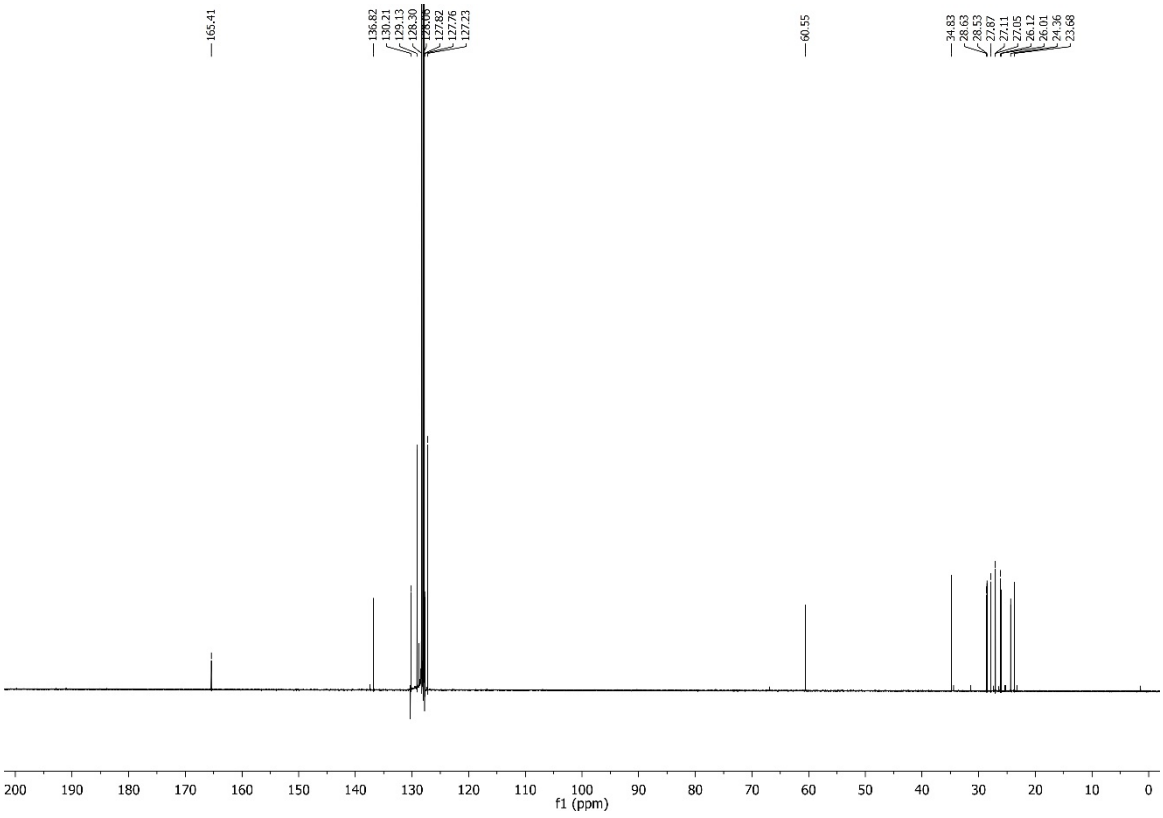


(*R*,*Z*)-2-(cyclotridec-2-en-1-yl)-5-phenyl-2*H*-tetrazole (34)

^{1}H-NMR (400.13 MHz, C_6D_6):

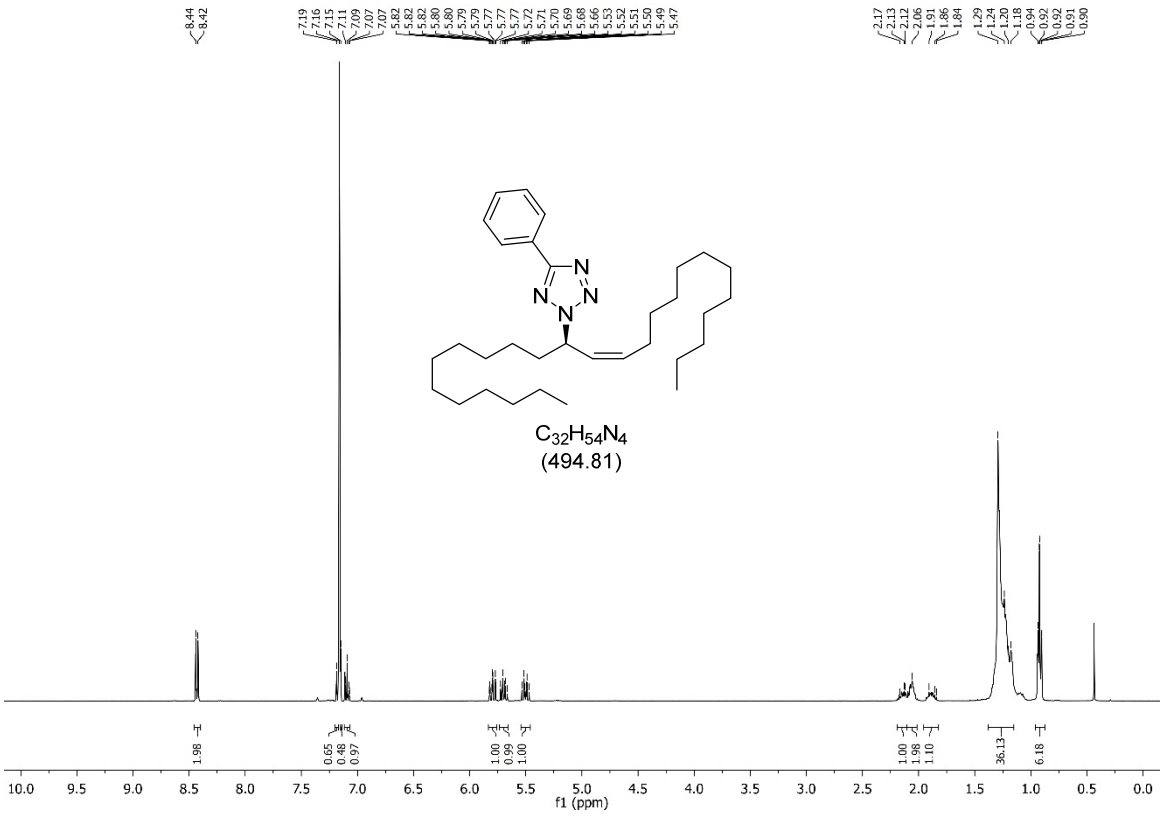


^{13}C-NMR (100.61 MHz, C_6D_6):

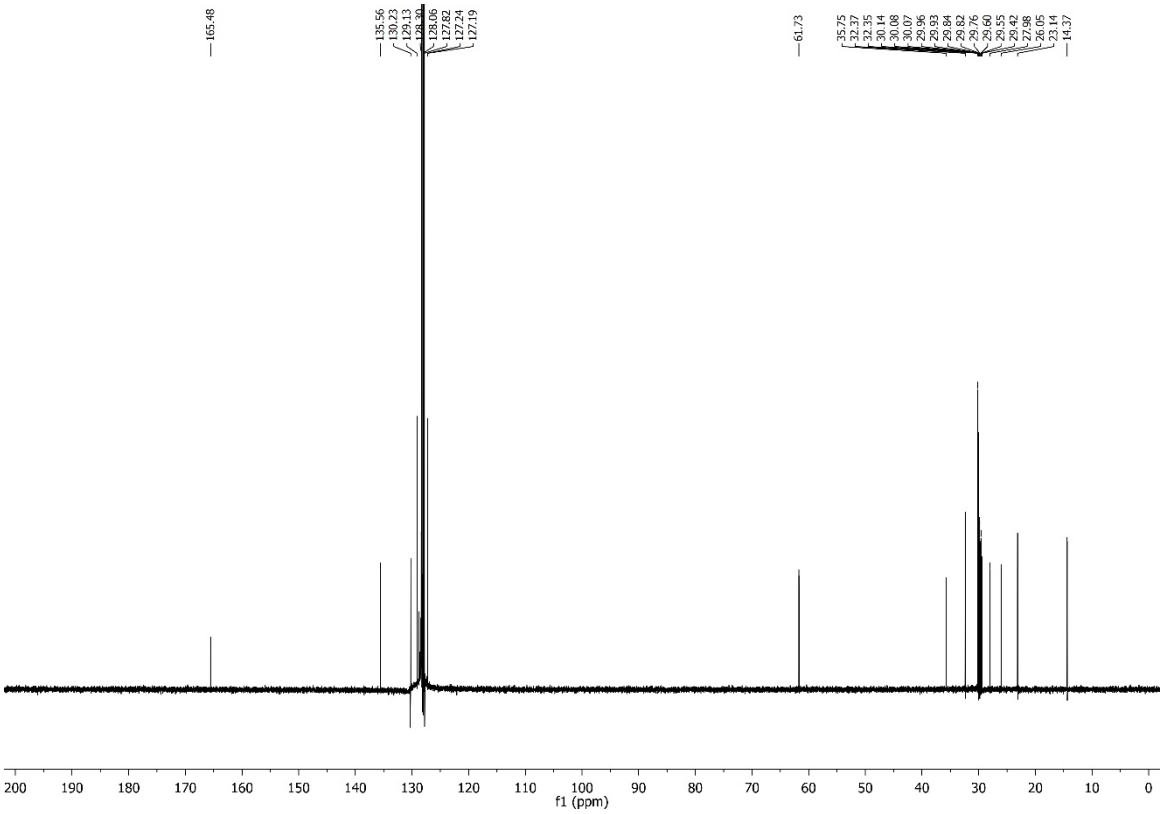


(*R*,*Z*)-2-(pentacos-13-en-12-yl)-5-phenyl-2*H*-tetrazole (35)

^{1}H-NMR (400.13 MHz, C_6D_6):

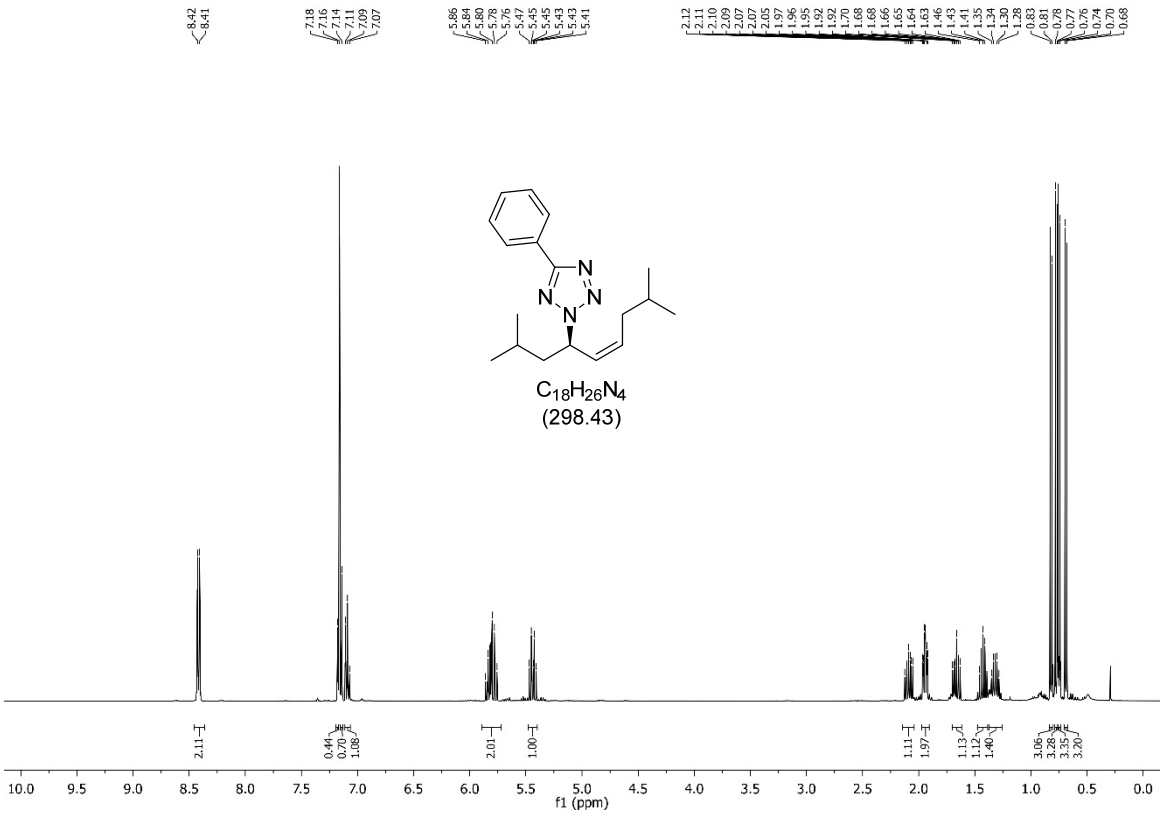


^{13}C-NMR (100.61 MHz, C_6D_6):

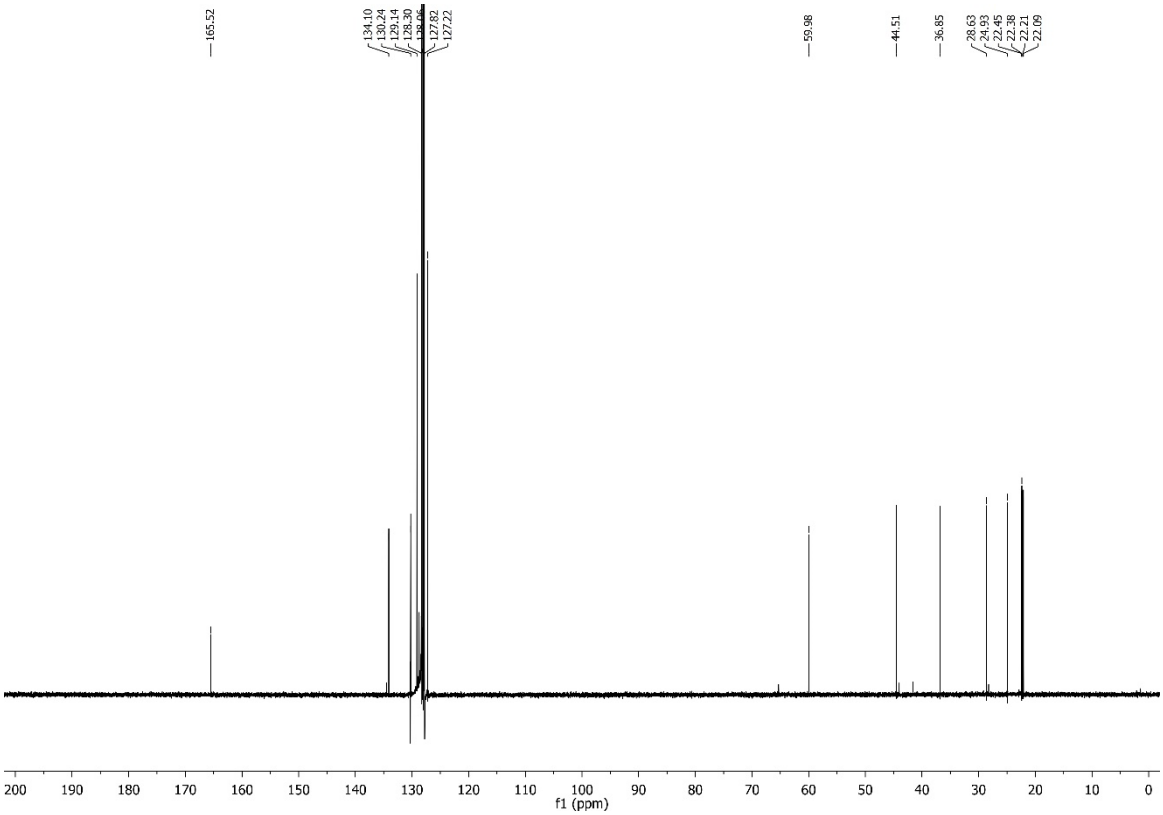


(*R*,*Z*)-2-(2,8-dimethylnon-5-en-4-yl)-5-phenyl-2*H*-tetrazole (36)

^{1}H-NMR (400.13 MHz, C_6D_6):

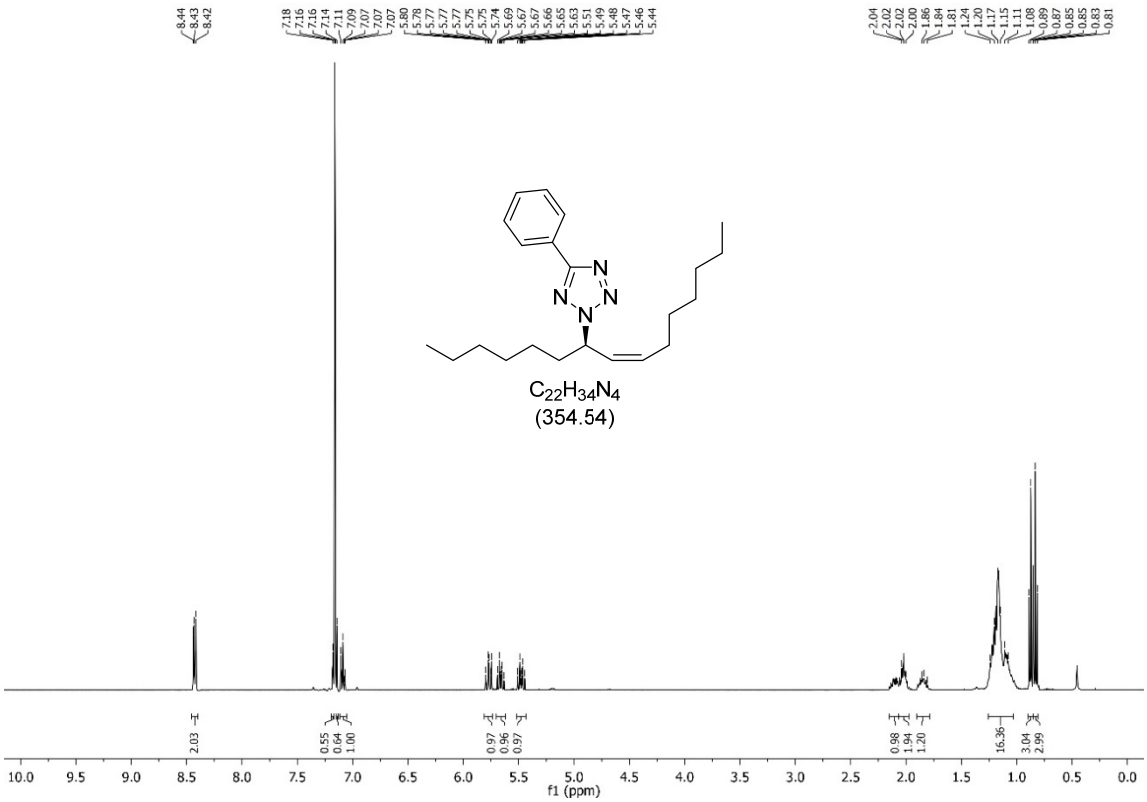


^{13}C-NMR (100.61 MHz, C_6D_6):

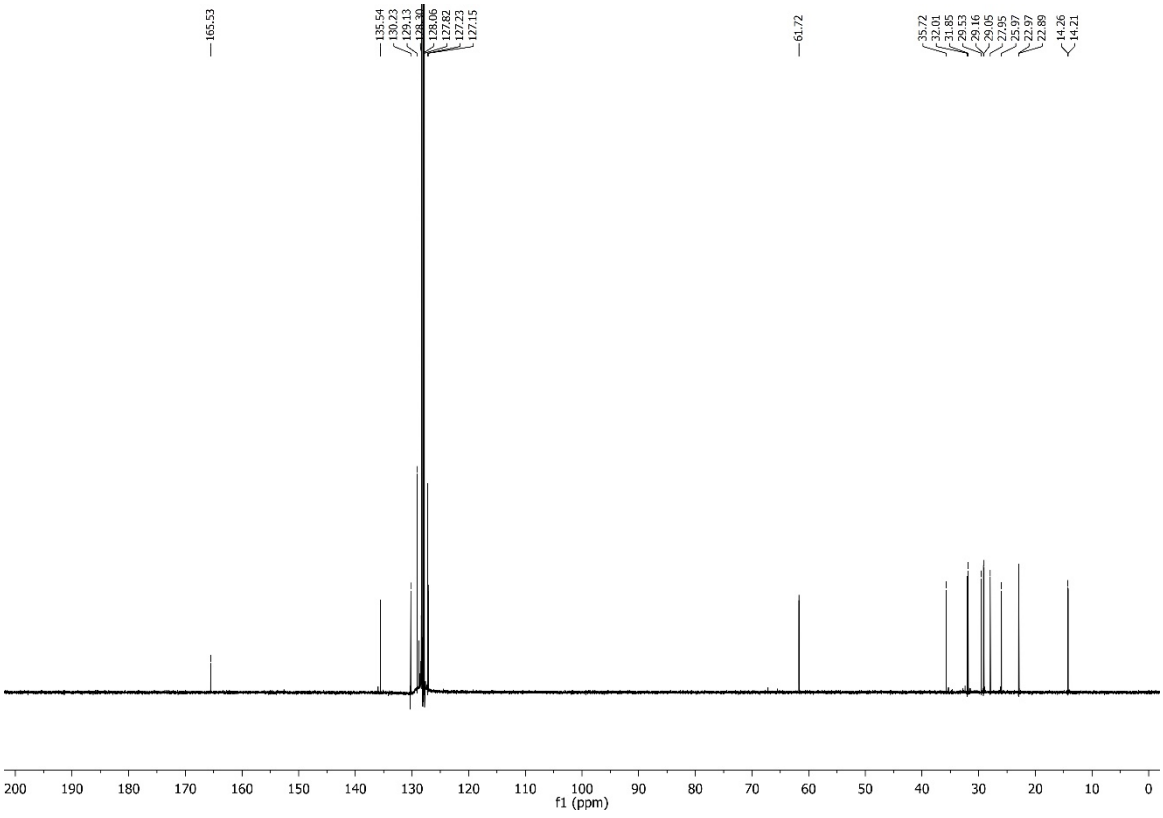


(*R*,*Z*)-2-(pentadec-8-en-7-yl)-5-phenyl-2*H*-tetrazole (37)

^{1}H-NMR (400.13 MHz, C_6D_6):

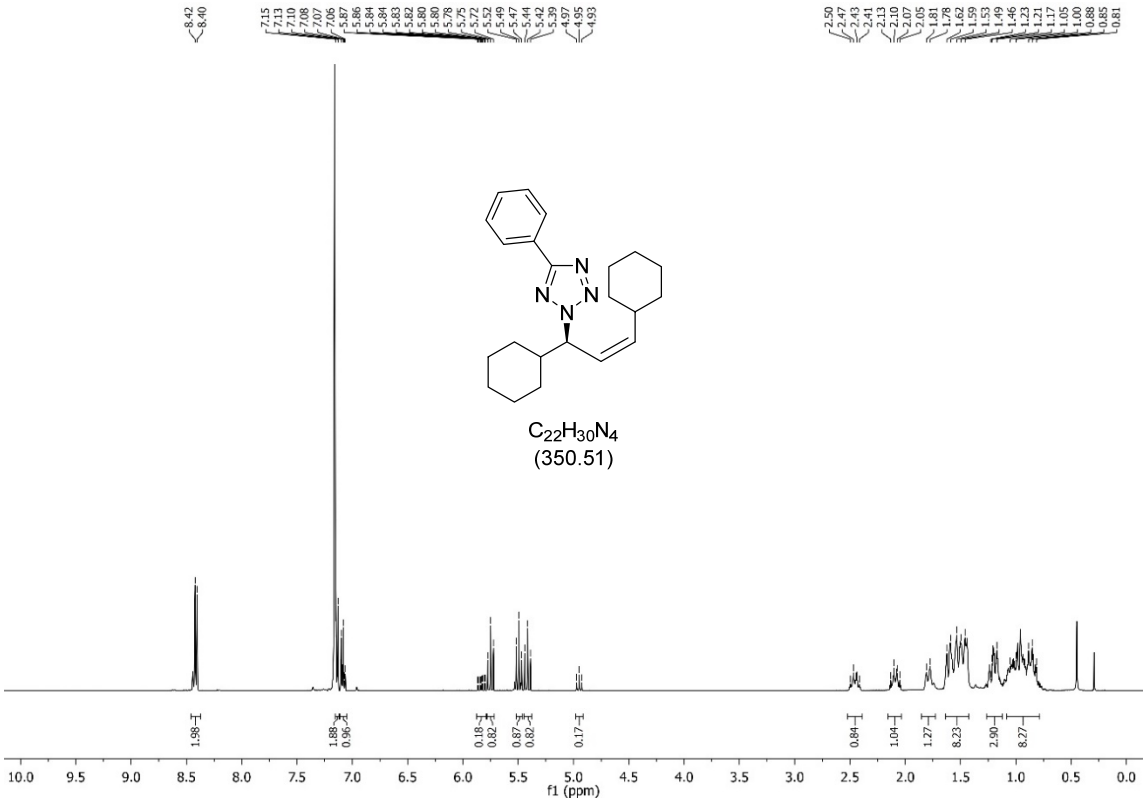


^{13}C-NMR (100.61 MHz, C_6D_6):

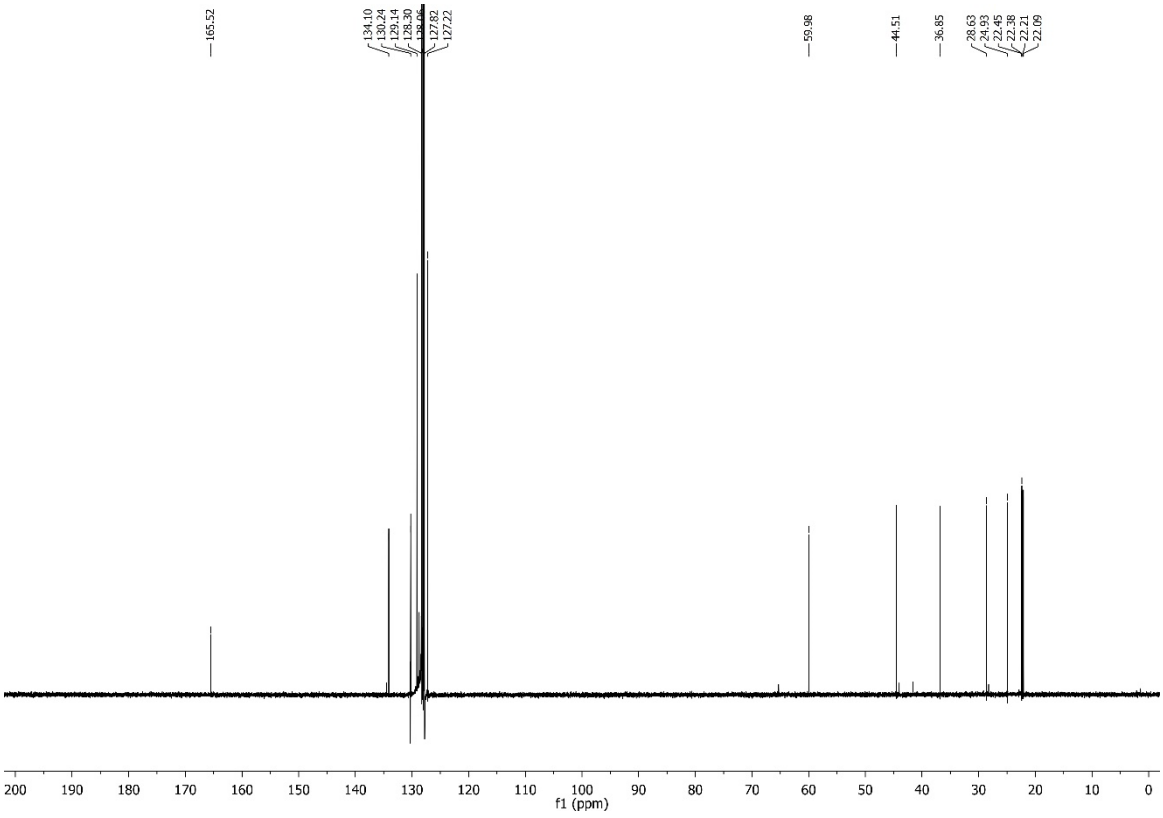


(*R*,*Z*)-2-(1,3-dicyclohexylallyl)-5-phenyl-2*H*-tetrazole (38)

^{1}H-NMR (400.13 MHz, C_6D_6):

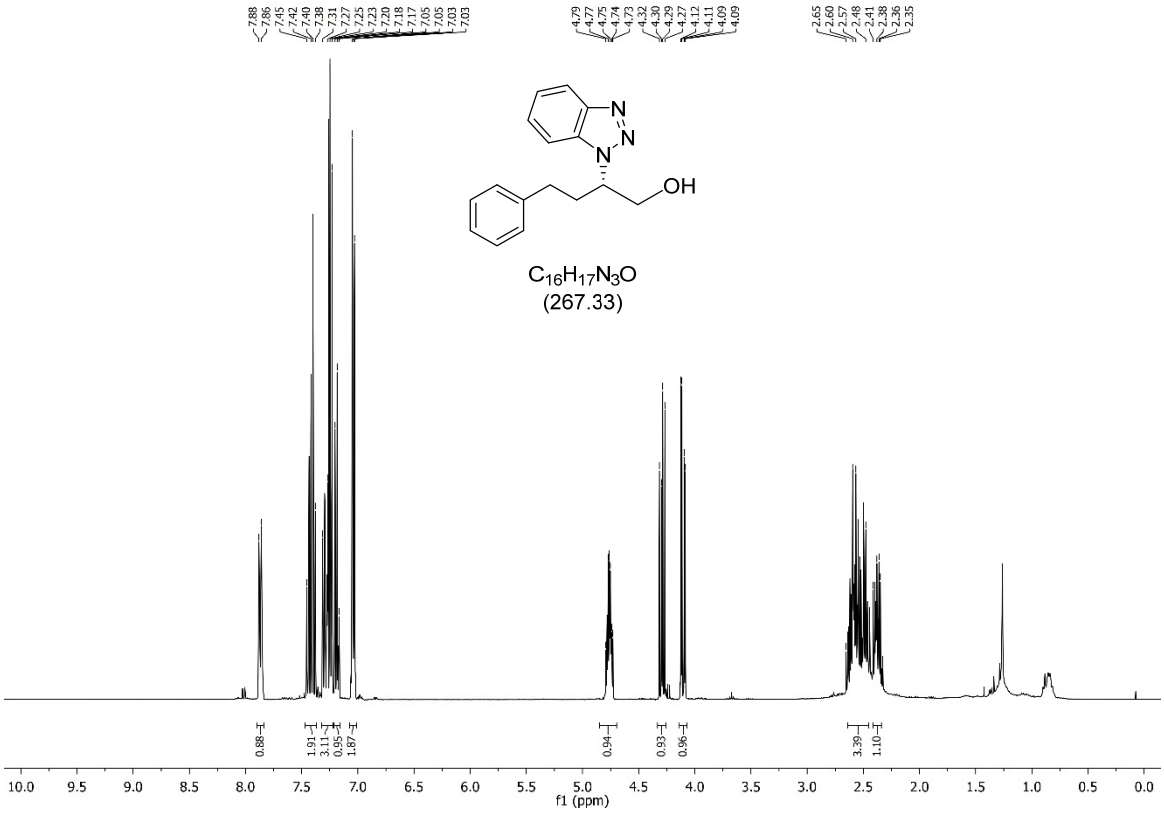


^{13}C-NMR (100.61 MHz, C_6D_6):

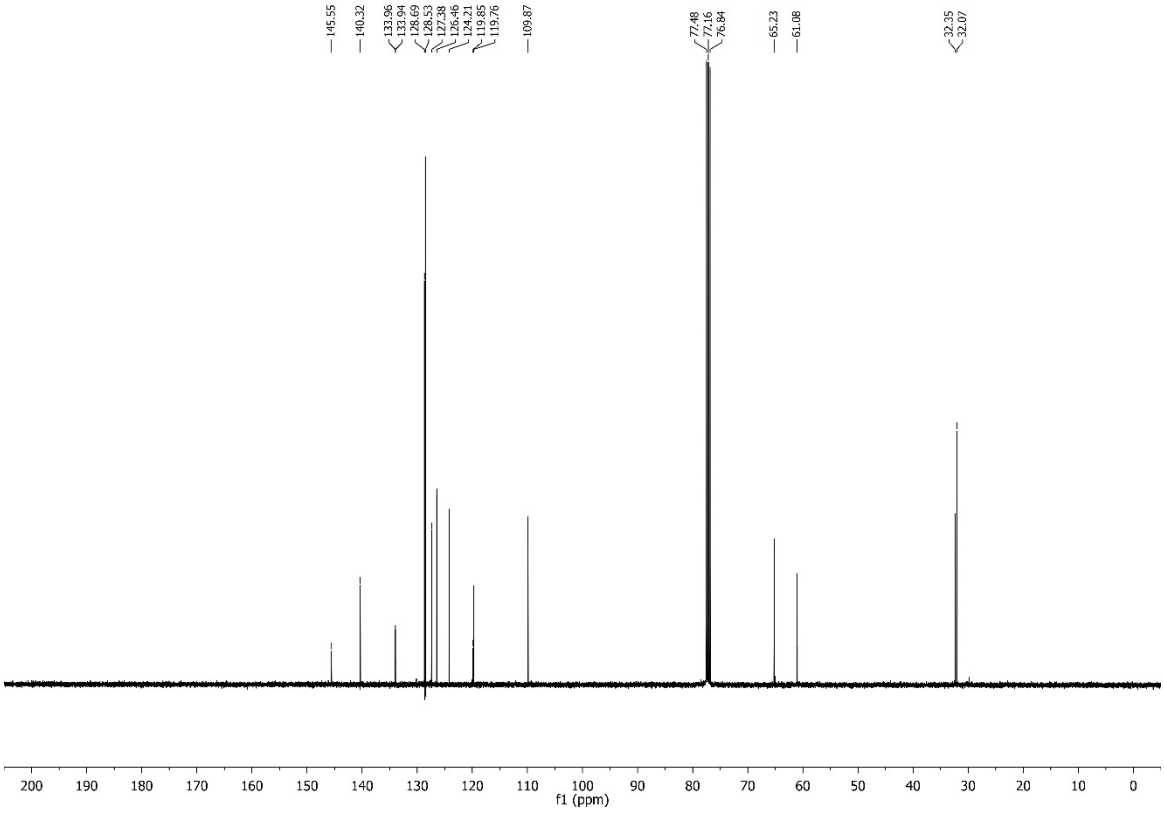


(*S*)-2-(1*H*-benzo[d][1,2,3]triazol-1-yl)-4-phenylbutan-1-ol

^{1}H-NMR (400.13 MHz, $CDCl_3$):

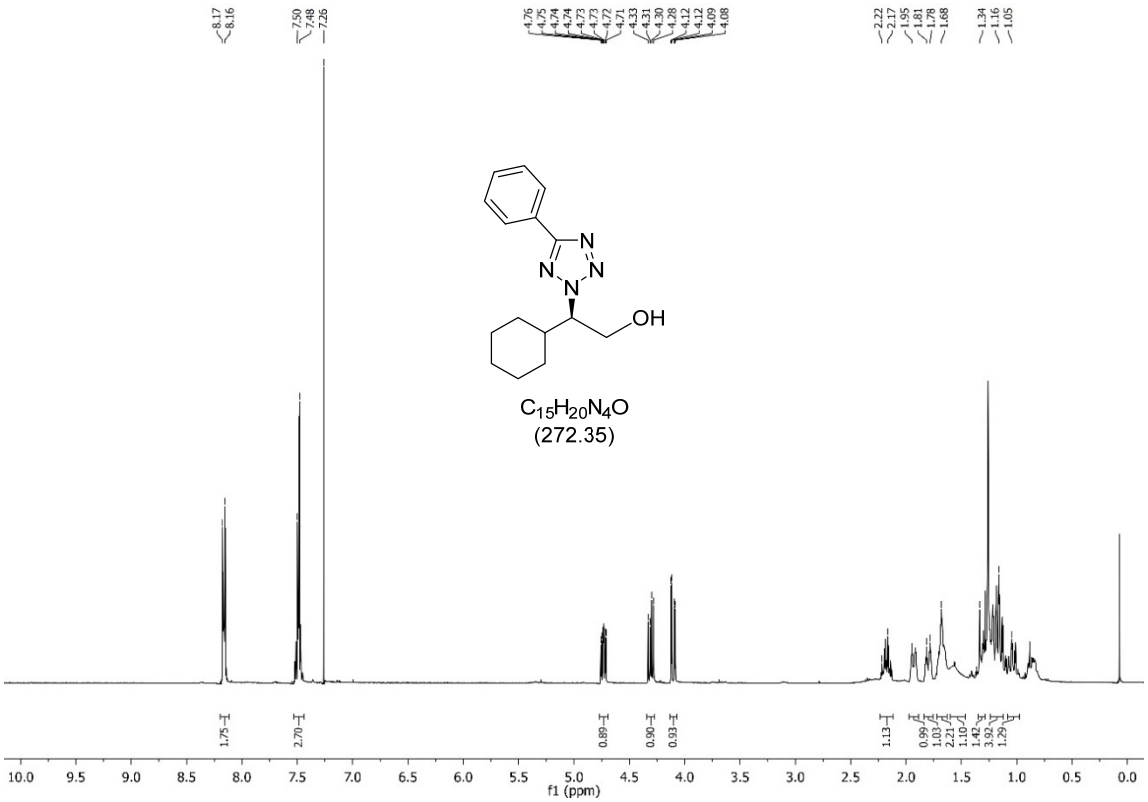


^{13}C-NMR (100.61 MHz, $CDCl_3$):

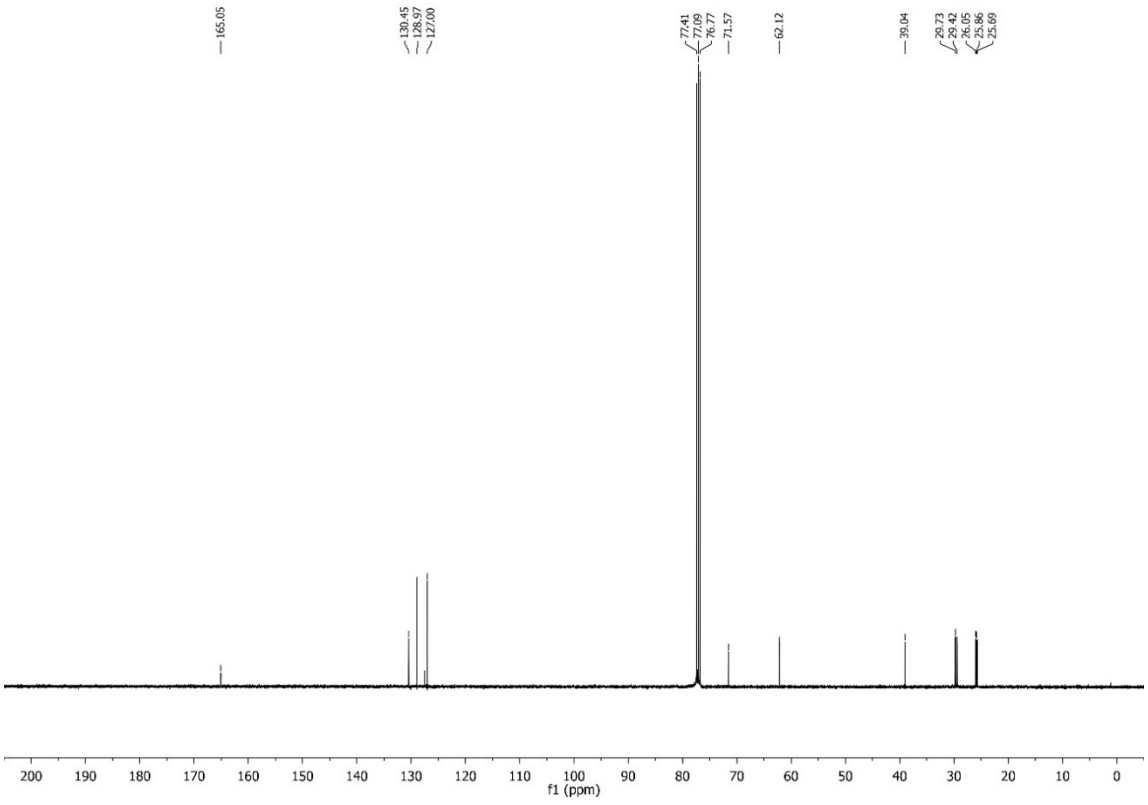


(*R*)-2-cyclohexyl-2-(5-phenyl-2*H*-tetrazol-2-yl)ethan-1-ol

^{1}H-NMR (400.13 MHz, $CDCl_3$):

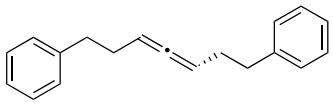


^{13}C-NMR (100.61 MHz, $CDCl_3$):

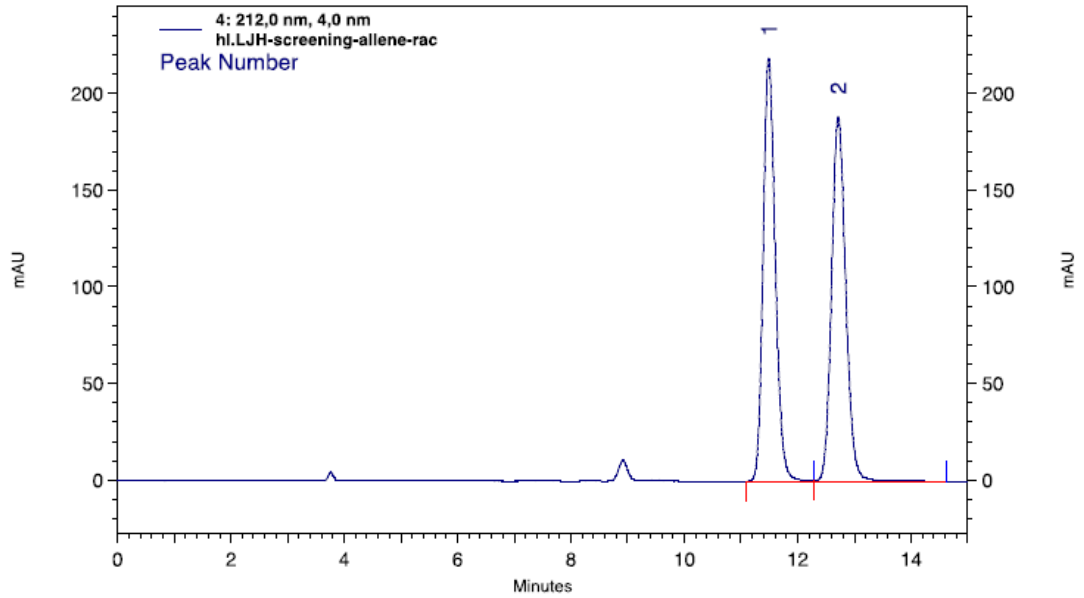


Appendix

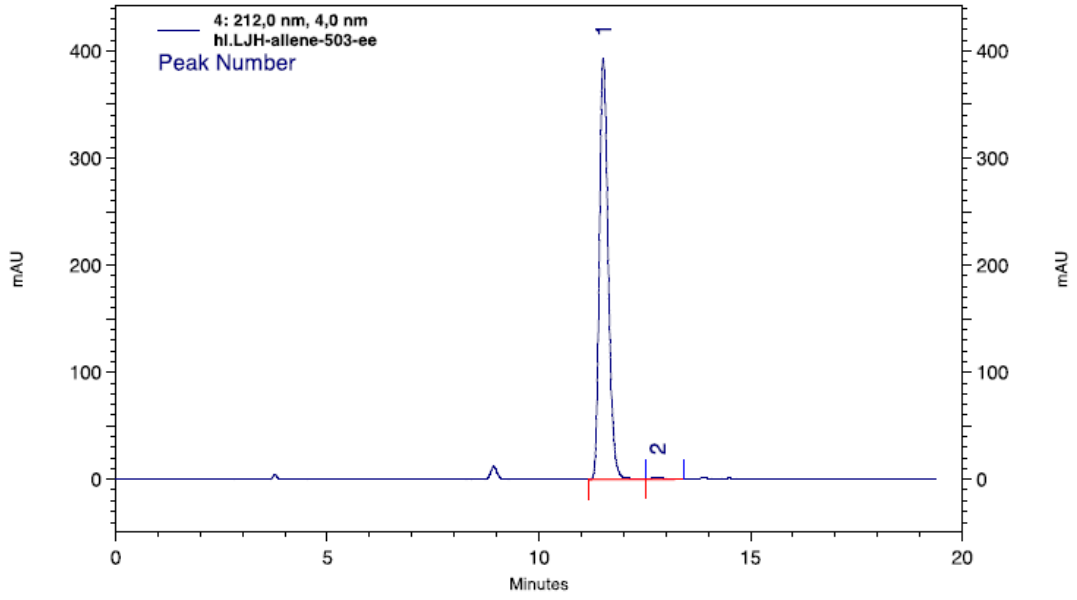
(*S*)-1,7-diphenylhepta-3,4-diene (1)



$C_{19}H_{20}$
(248.37)

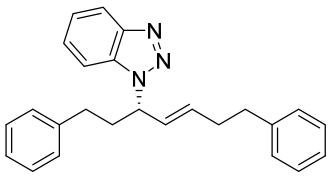


Peak Index	t [min]	Area [%]
1	11.5	49.941
2	12.7	50.059

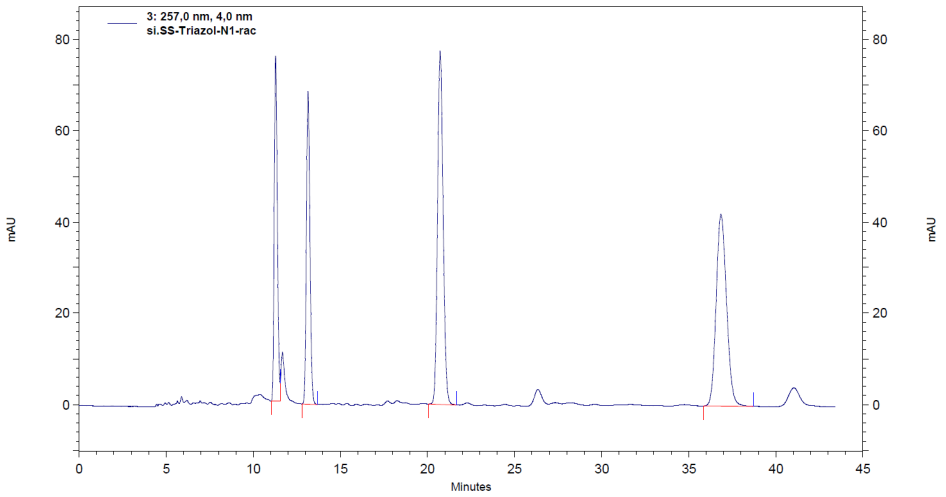


Peak Index	t [min]	Area [%]
1	11.5	99.892
2	12.8	0.108

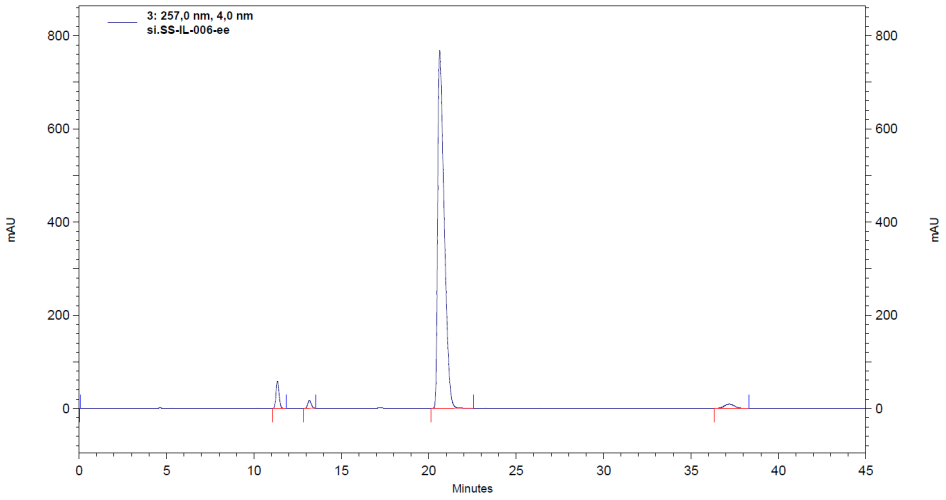
(*S,E*)-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 3)



$C_{25}H_{25}N_3$
(367.50)

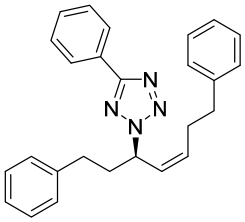


Peak Index	t [min]	area [%]
3	20.7	32.177
4	37.2	32.463

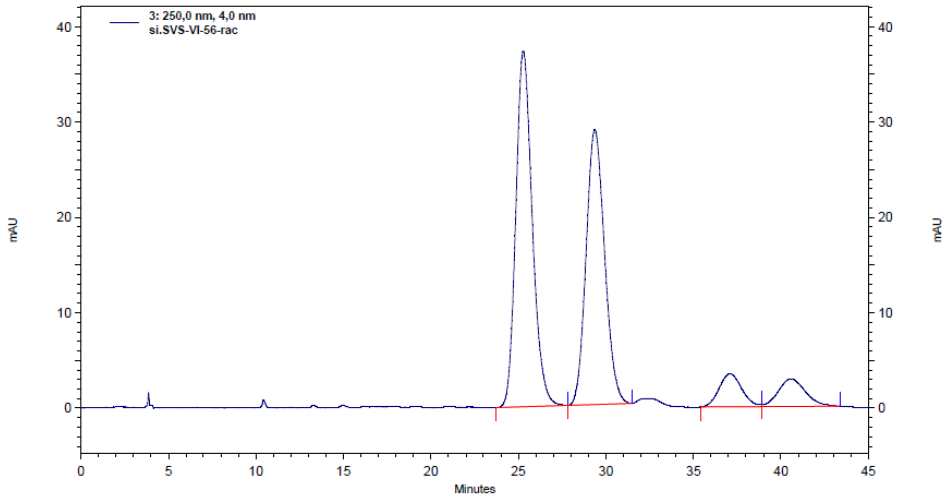


Peak Index	*t* [min]	area [%]
3	20.7	93.786
4	37.2	1.765

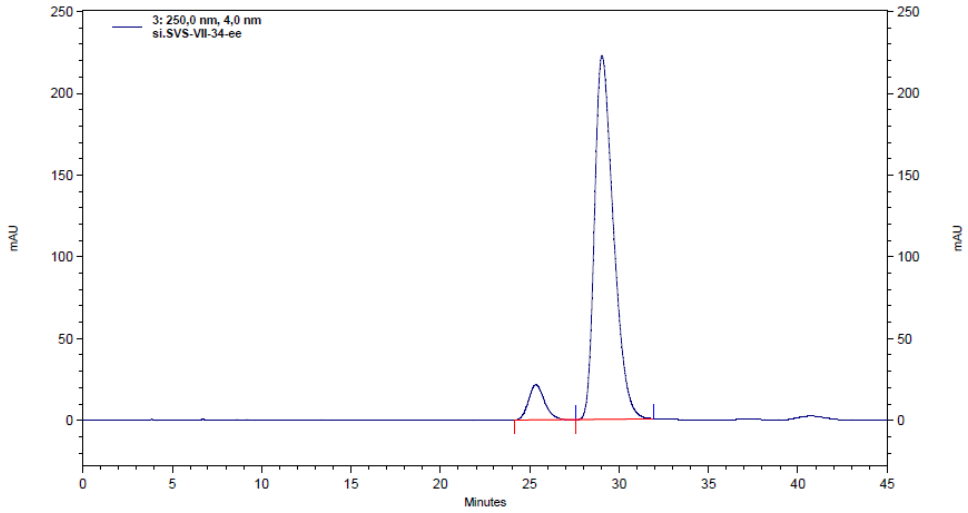
(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-phenyl-2*H*-tetrazole (5)



$C_{26}H_{26}N_4$
(394.52)

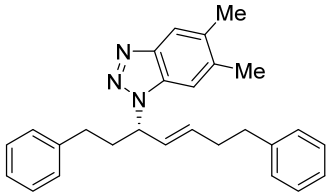


Peak Index	*t* [min]	area [%]
1	25.3	46.981
2	29.4	40.994

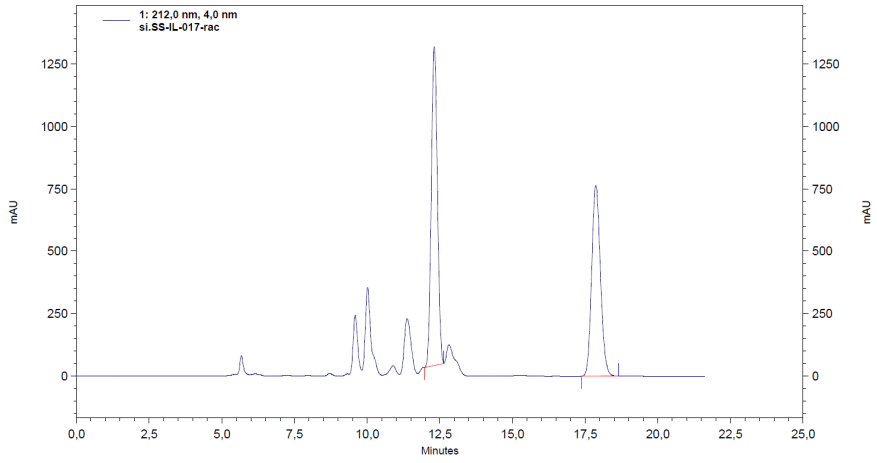


Peak Index	*t* [min]	area [%]
1	25.3	7.529
2	29.0	92.471

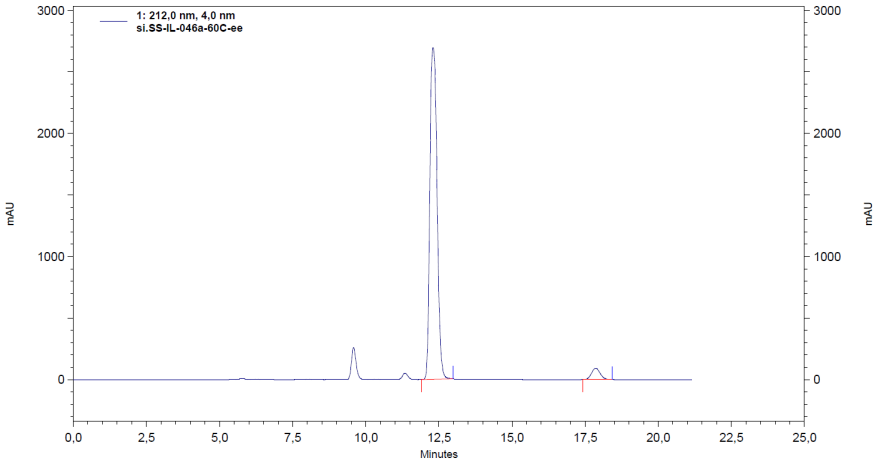
(*S,E*)-1-(1,7-diphenylhept-4-en-3-yl)-5,6-dimethyl-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 6)



$C_{27}H_{29}N_3$
(395.55)

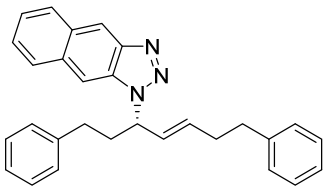


Peak Index	*t* [min]	area [%]
1	12.3	53.754
2	17.9	46.246

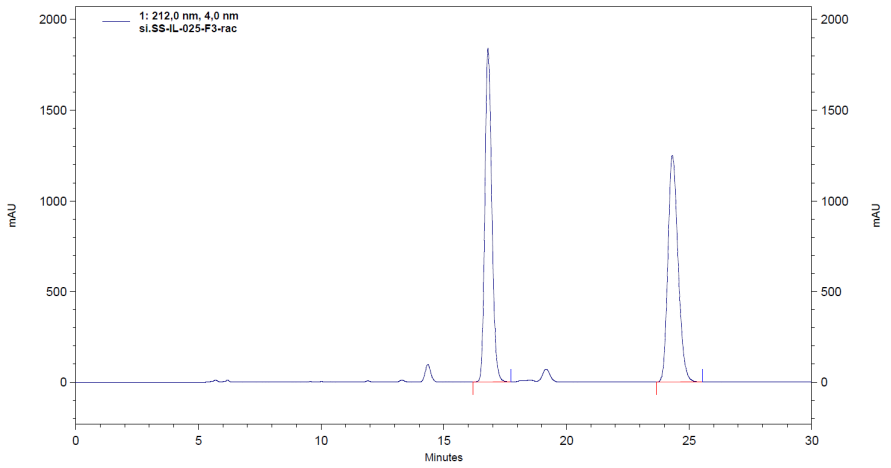


Peak Index	*t* [min]	area [%]
1	12.3	96.048
2	17.9	3.952

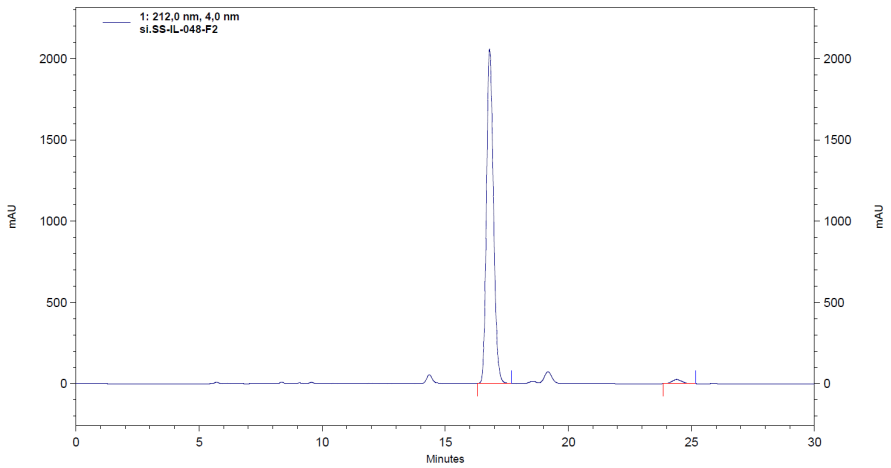
(*S,E*)-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole (*N*^{1}-product, 7)



$C_{29}H_{27}N_3$
(417.56)

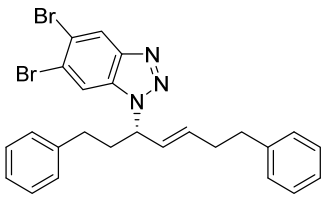


Peak Index	*t* [min]	area [%]
1	16.8	49.540
2	24.4	50.460

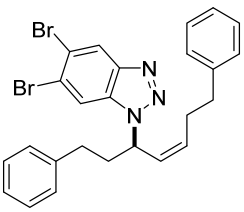


Peak Index	*t* [min]	area [%]
1	16.8	98.240
2	24.4	1.176

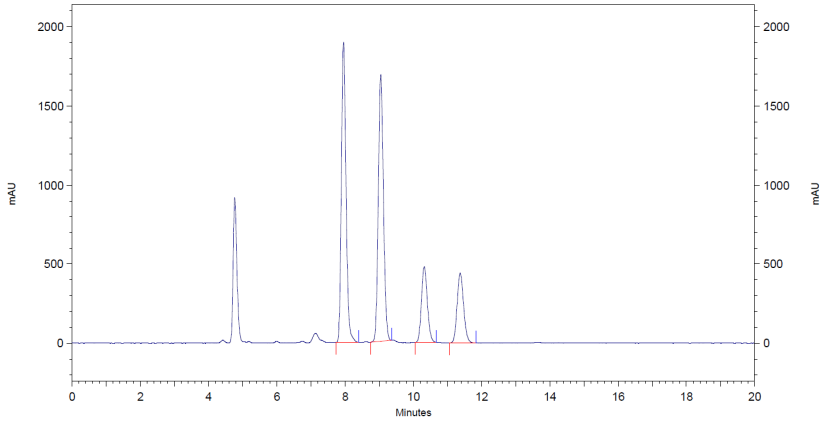
(*S,E*)-5,6-dibromo-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-, *E*-product, 8) & (*Z*)-5,6-dibromo-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-, *Z*-product, 8b)



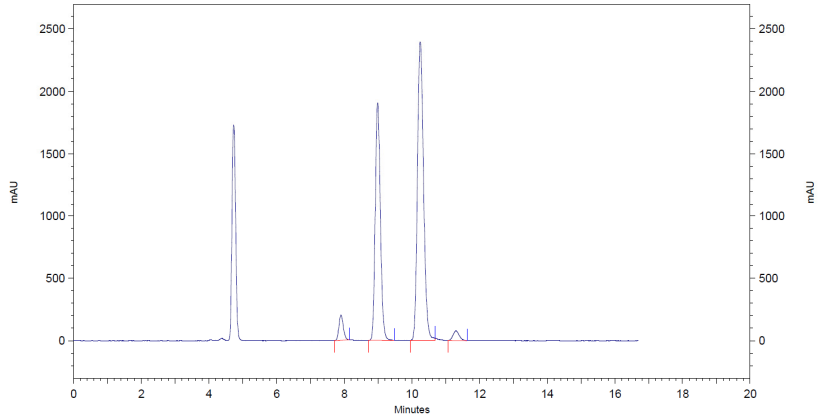
$C_{25}H_{23}Br_2N_3$
(525.29)



$C_{25}H_{23}Br_2N_3$
(525.29)

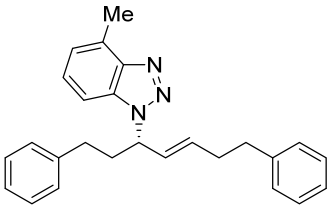


Peak Index	*t* [min]	area [%]
1	7.8	38.653
2	9.0	37.456
3	10.2	11.758
4	11.3	12.133

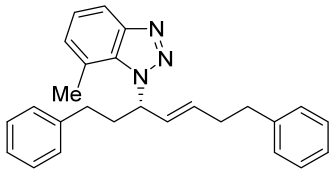


Peak Index	*t* [min]	area [%]
1	7.8 (*Z*)	3.446
2	9.0 (*Z*)	37.841
3	10.2 (*E*)	56.861
4	11.3 (*E*)	1.852

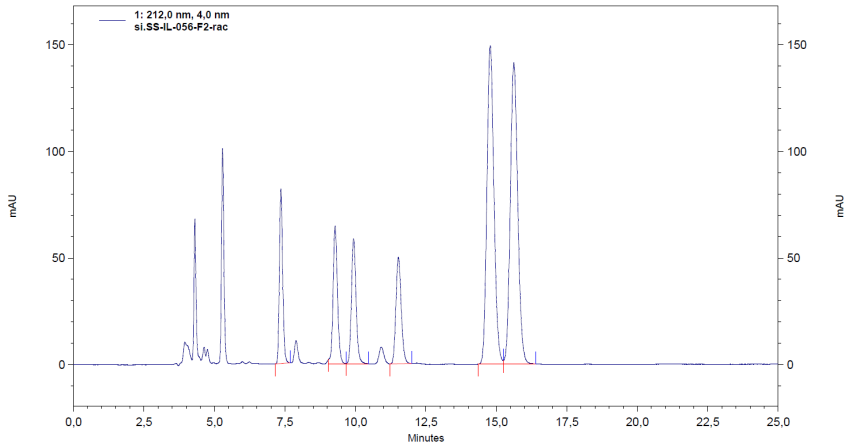
(*S,E*)-1-(1,7-diphenylhept-4-en-3-yl)-4-methyl-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 9) & (*S,E*)-1-(1,7-diphenylhept-4-en-3-yl)-7-methyl-1*H*-benzo[*d*][1,2,3]triazole (*N*^{3}-product, 9b)



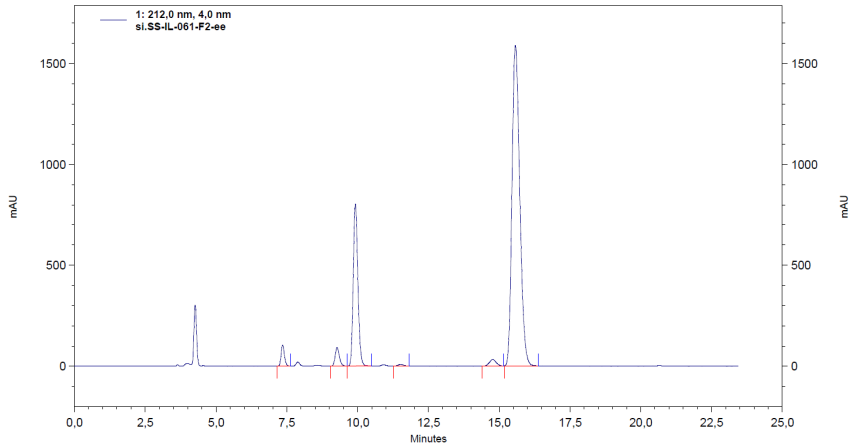
$C_{26}H_{27}N_3$
(381.22)



$C_{26}H_{27}N_3$
(381.22)

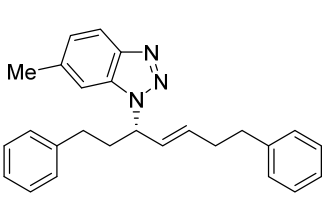


Peak Index	*t* [min]	area [%]
3	9.9 (*N*^{3}-*E*)	8.369
4	11.5 (*N*^{3}-*E*)	8.152
5	14.8 (*N*^{1}-*E*)	33.251
6	15.6 (*N*^{1}-*E*)	32.488

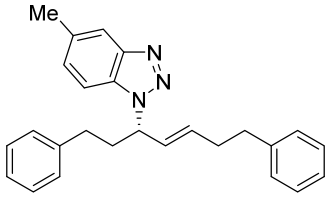


Peak Index	*t* [min]	area [%]
3	9.9 (*N*^{3}-*E*)	21.520
4	11.5 (*N*^{3}-*E*)	0.269
5	14.8 (*N*^{1}-*E*)	1.208
6	15.6 (*N*^{1}-*E*)	72.724

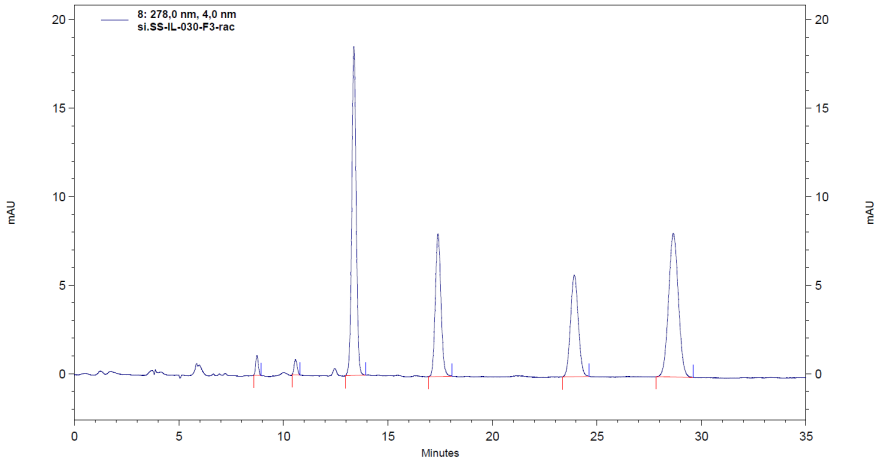
(*S,E*)-1-(1,7-diphenylhept-4-en-3-yl)-6-methyl-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 10) & (*S,E*)-1-(1,7-diphenylhept-4-en-3-yl)-5-methyl-1*H*-benzo[*d*][1,2,3]triazole (*N*^{3}-product, 10b)



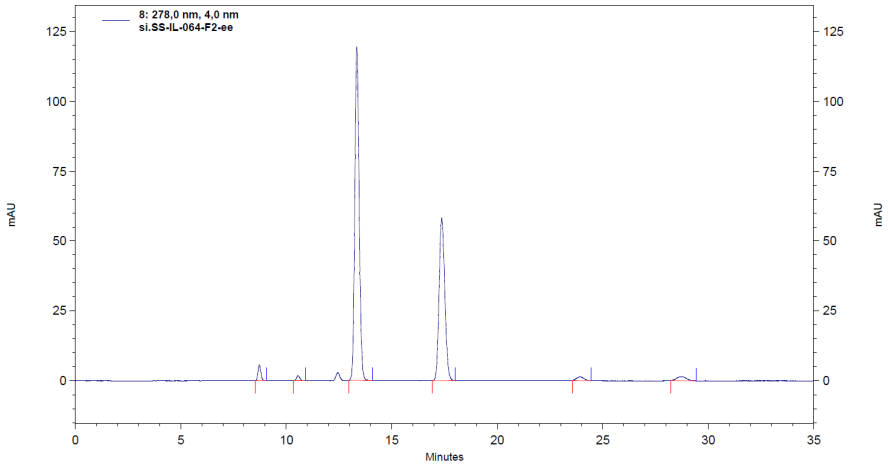
$C_{26}H_{27}N_3$
(381.52)



$C_{26}H_{27}N_3$
(381.52)

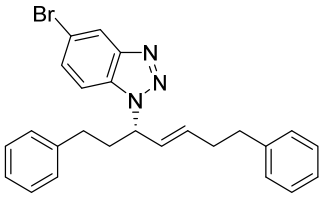


Peak Index	*t* [min]	area [%]
3	13.3 (*N*^{1})	25.271
4	17.4 (*N*^{3})	25.704
5	23.9 (*N*^{3})	24.949
6	28.7 (*N*^{1})	22.435

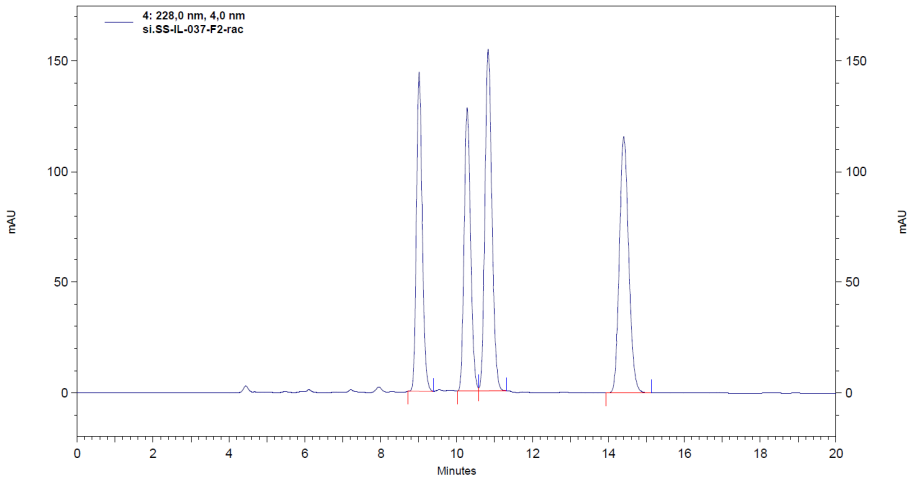


Peak Index	*t* [min]	area [%]
3	13.3 (*N*^{1})	58.074
4	17.4 (*N*^{3})	36.907
5	23.9 (*N*^{3})	1.069
6	28.7 (*N*^{1})	1.539

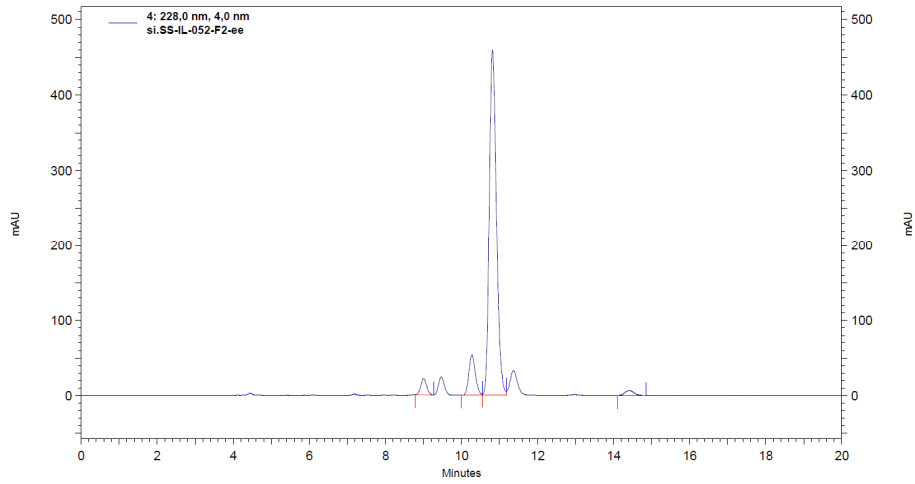
(*S,E*)-5-bromo-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[d][1,2,3]triazole (*N*^{1}-product, 11)



$C_{25}H_{24}BrN_3$
(446.39)

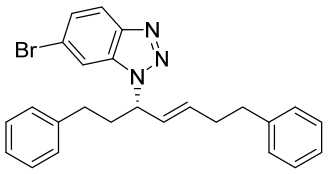


Peak Index	*t* [min]	area [%]
3	10.8	28.929
4	14.4	28.834

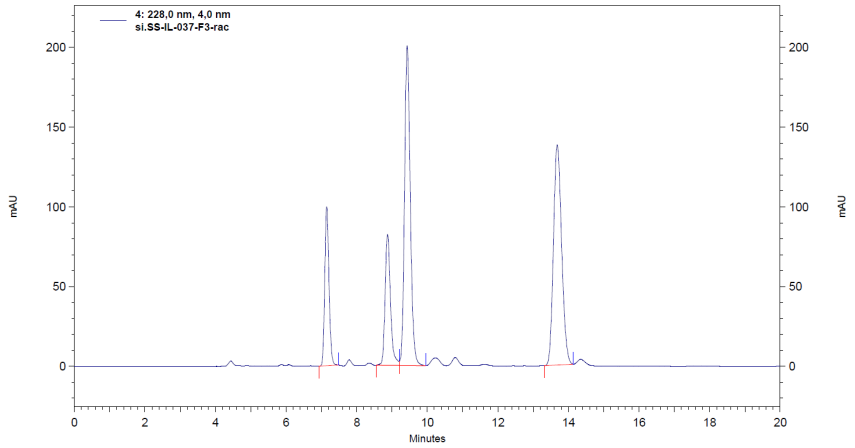


Peak Index	*t* [min]	area [%]
3	10.8	85.288
4	14.4	1.594

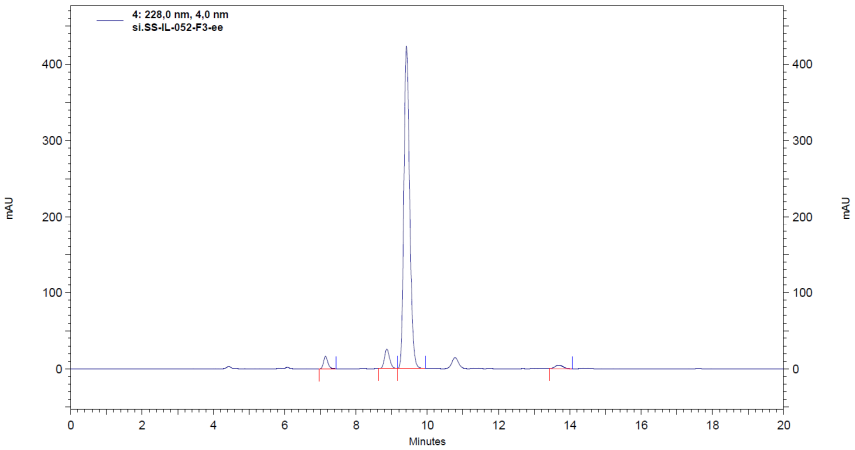
(*S*,*E*)-6-bromo-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[d][1,2,3]triazole (*N*^{3}-product, 11b)



$C_{25}H_{24}BrN_3$
(446.39)

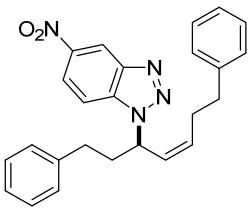


Peak Index	*t* [min]	area [%]
3	9.4	35.857
4	13.7	37.347

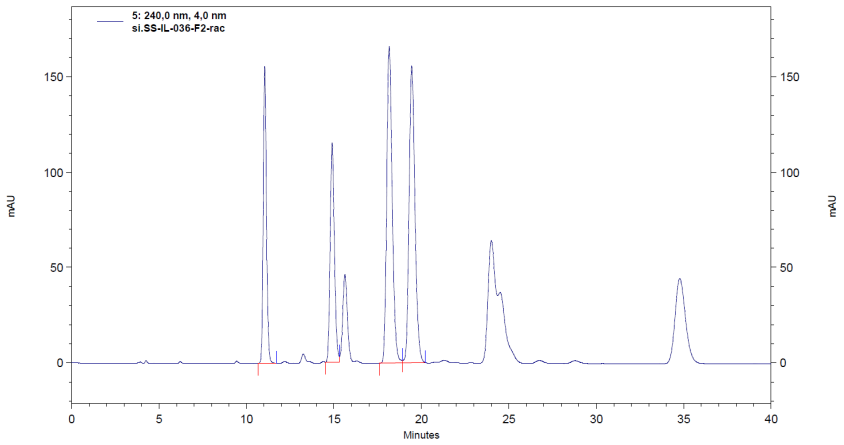


Peak Index	*t* [min]	area [%]
3	9.4	91.071
4	13.7	1.415

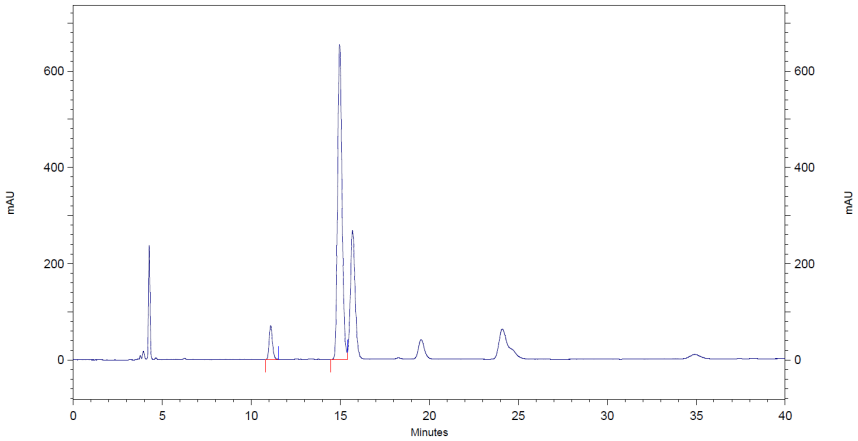
(*Z*)-1-(1,7-diphenylhept-4-en-3-yl)-5-nitro-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1},*Z*-product, 12)



$C_{25}H_{24}N_4O_2$
(412.49)

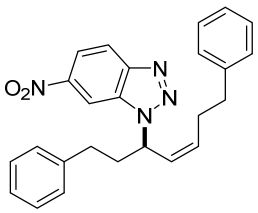


Peak Index	*t* [min]	area [%]
3	18.2	32.282
4	19.5	32.239

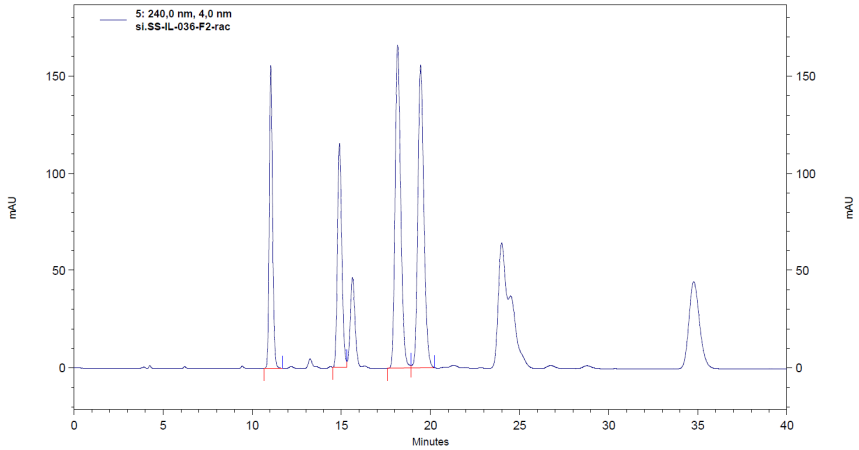


Peak Index	*t* [min]	area [%]
3	18.2	6.368
4	19.5	93.632

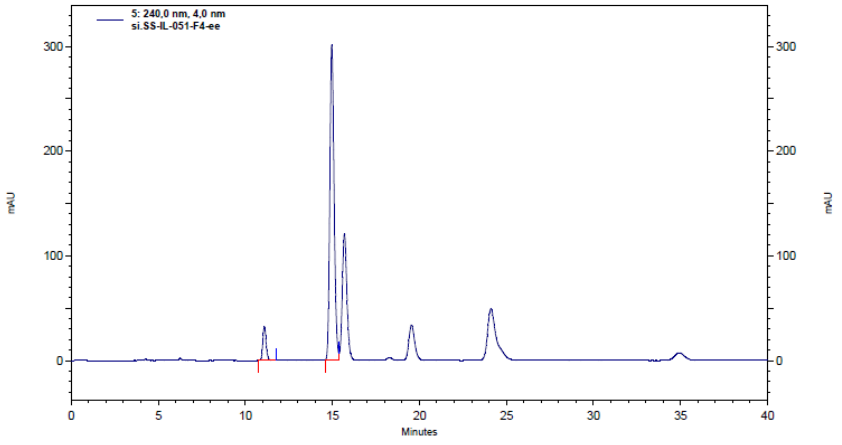
(*Z*)-1-(1,7-diphenylhept-4-en-3-yl)-6-nitro-1*H*-benzo[d][1,2,3]triazole (*N*^{3},Z-product, 11c)



$C_{25}H_{24}N_4O_2$
(412.49)

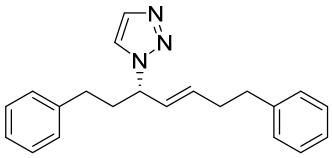


Peak Index	*t* [min]	area [%]
1	11.1	17.781
2	15.0	17.508

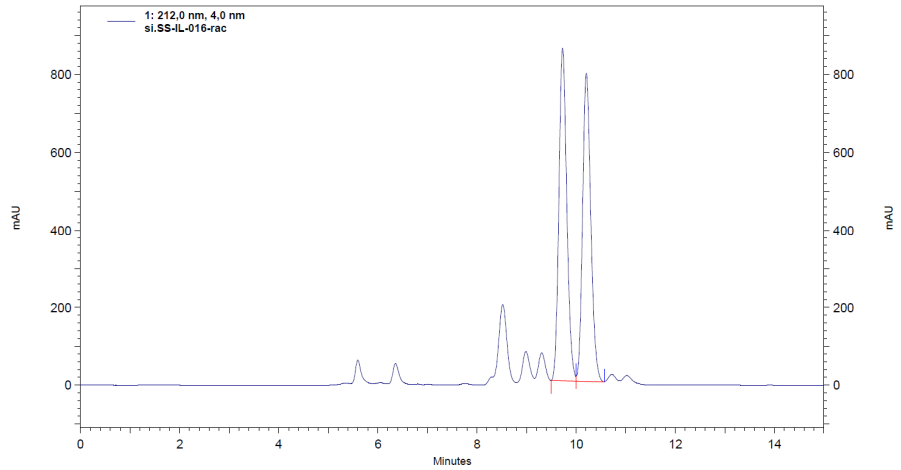


Peak Index	*t* [min]	area [%]
1	11.1	7.348
2	15.0	92.652

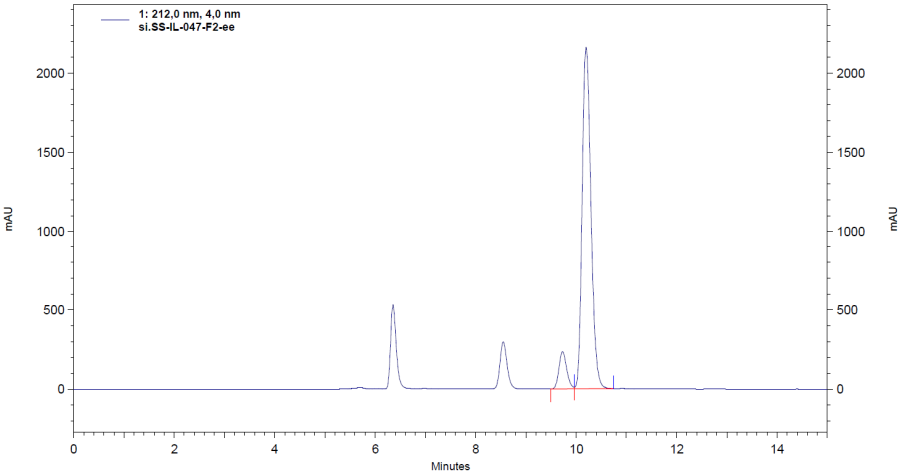
(*S,E*)-1-(1,7-diphenylhept-4-en-3-yl)-1*H*-1,2,3-triazole (*N*^{1}-product, 13)



$C_{21}H_{23}N_3$
(317.44)

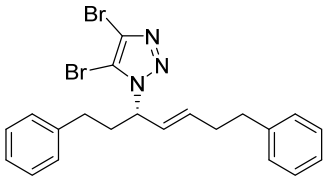


Peak Index	*t* [min]	area [%]
1	9.7	51.156
2	10.2	48.844

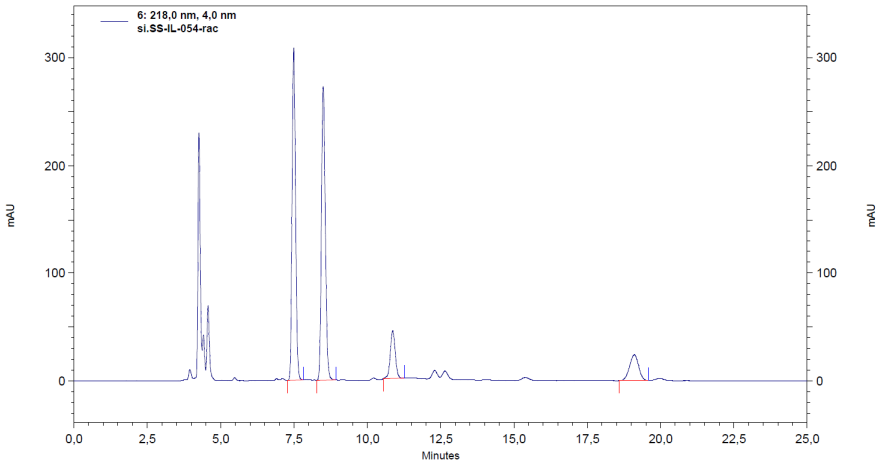


Peak Index	*t* [min]	area [%]
1	9.7	8.748
2	10.2	91.252

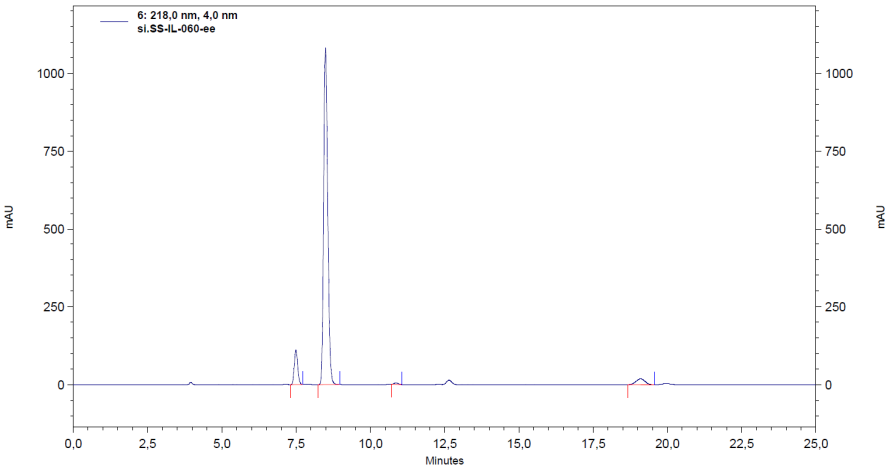
(*S,E*)-2-(1,7-diphenylhept-4-en-3-yl)-5-methyl-2*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 14)



$C_{21}H_{21}Br_2N_3$
(475.23)

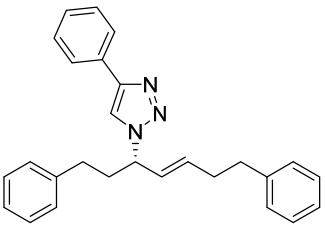


Peak Index	*t* [min]	area [%]
1	7.5	41.332
2	8.5	41.542

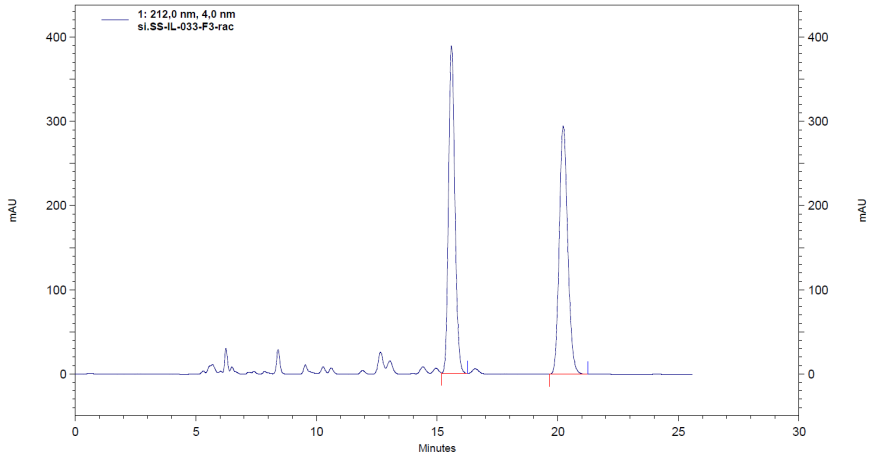


Peak Index	*t* [min]	area [%]
1	7.5	7.534
2	8.5	88.586

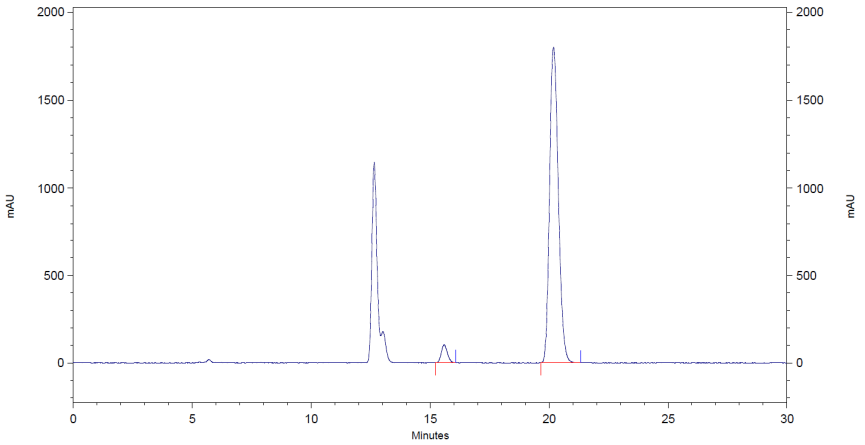
(*S,E*)-1-(1,7-diphenylhept-4-en-3-yl)-4-phenyl-1*H*-1,2,3-triazole (*N*^{1}-, *E*-product, 15)



$C_{27}H_{27}N_3$
(393.22)

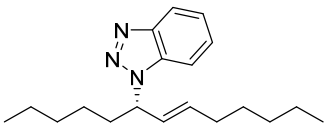


Peak Index	*t* [min]	area [%]
1	15.6	49.671
2	20.2	50.329

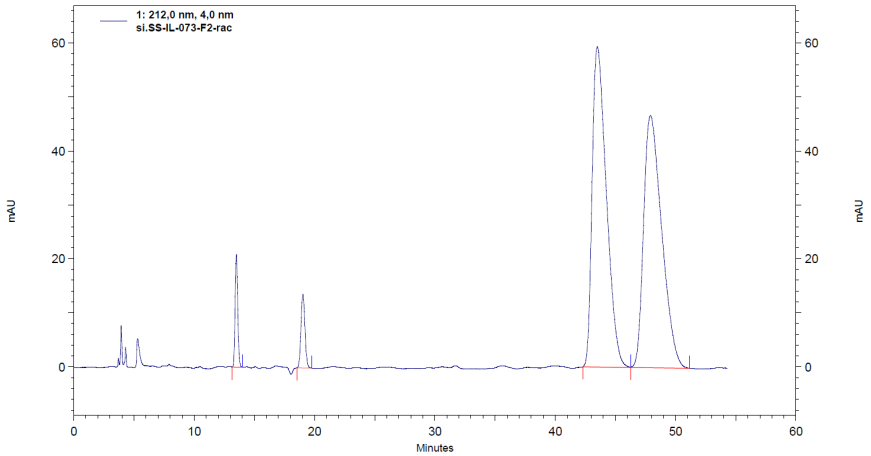


Peak Index	*t* [min]	area [%]
1	15.6	3.761
2	20.2	96.239

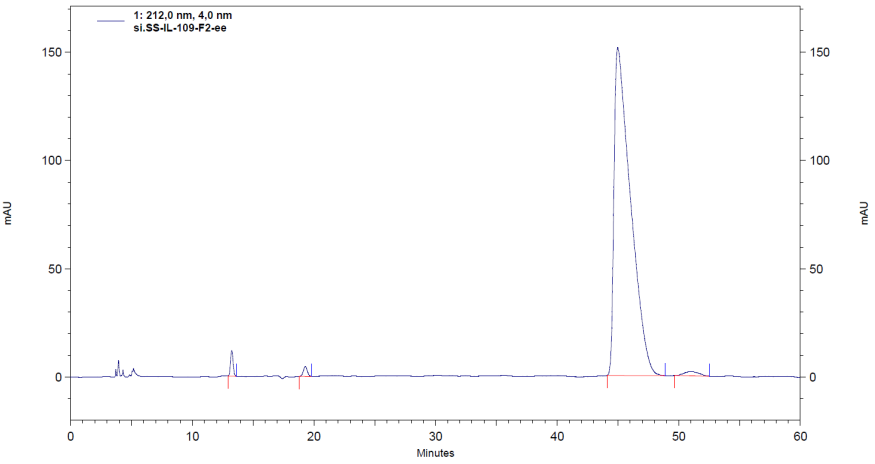
(*S*,*E*)-1-(tridec-7-en-6-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 16)



$C_{19}H_{29}N_3$
(299.24)

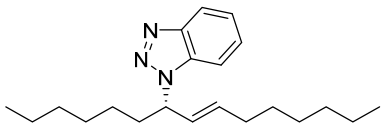


Peak Index	*t* [min]	area [%]
3	45.0	47.891
4	49.5	46.615

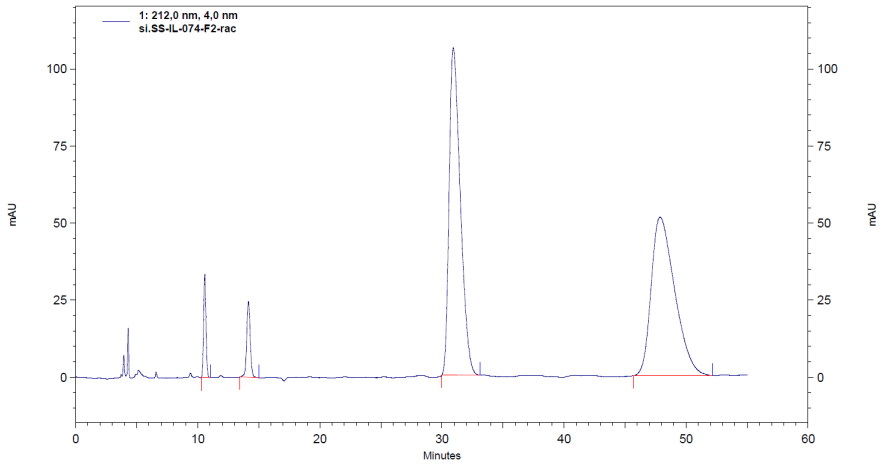


Peak Index	*t* [min]	area [%]
3	45.0	96.924
4	49.5	1.165

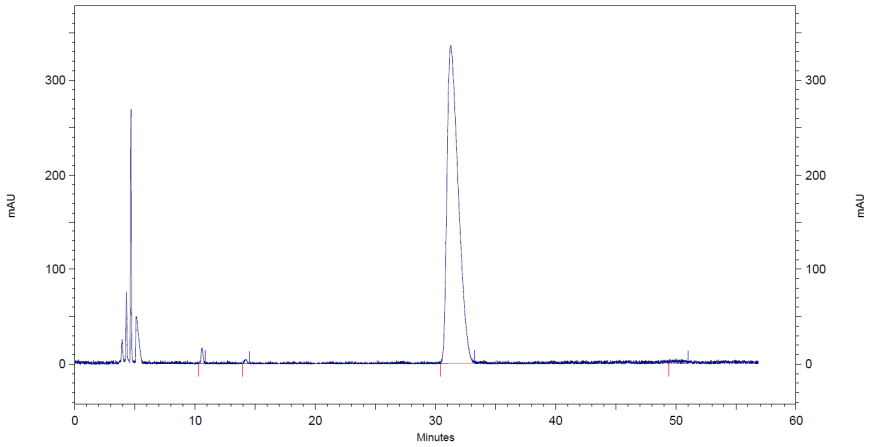
(*S*,*E*)-1-(pentadec-8-en-7-yl)-1*H*-benzo[d][1,2,3]triazole (*N*^{1}-product, 17)



$C_{21}H_{33}N_3$
(327.27)

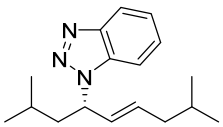


Peak Index	*t* [min]	area [%]
3	31.3	46.344
4	50.0	47.216

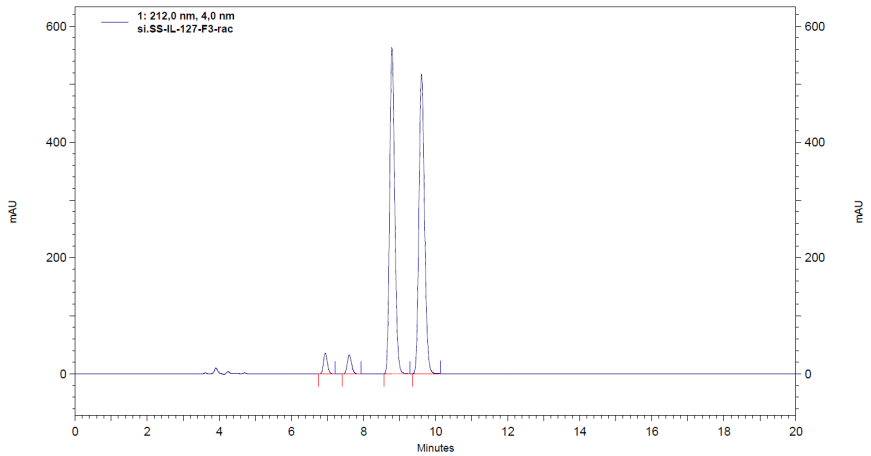


Peak Index	*t* [min]	area [%]
3	31.3	96.417
4	50.0	1.588

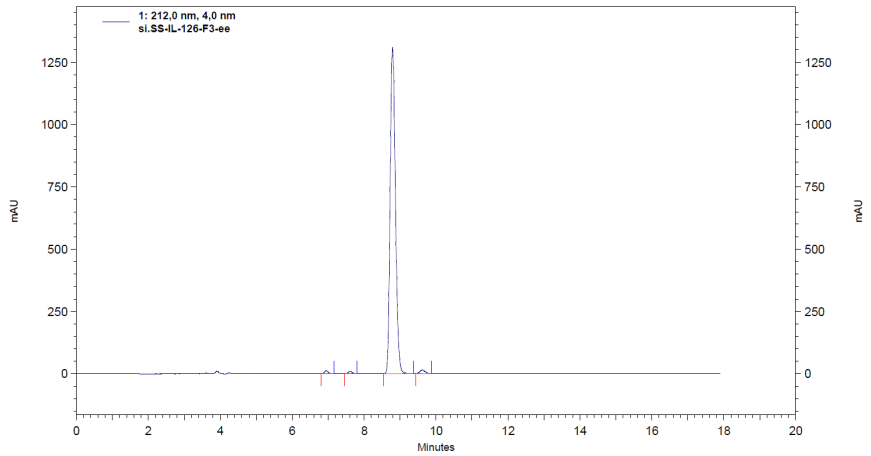
(*S*,*E*)-1-(2,8-dimethylnon-5-en-4-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}-product, 18)



$C_{17}H_{25}N_3$
(271.20)

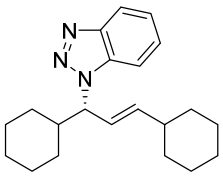


Peak Index	*t* [min]	area [%]
3	8.7	47.590
4	9.6	47.815

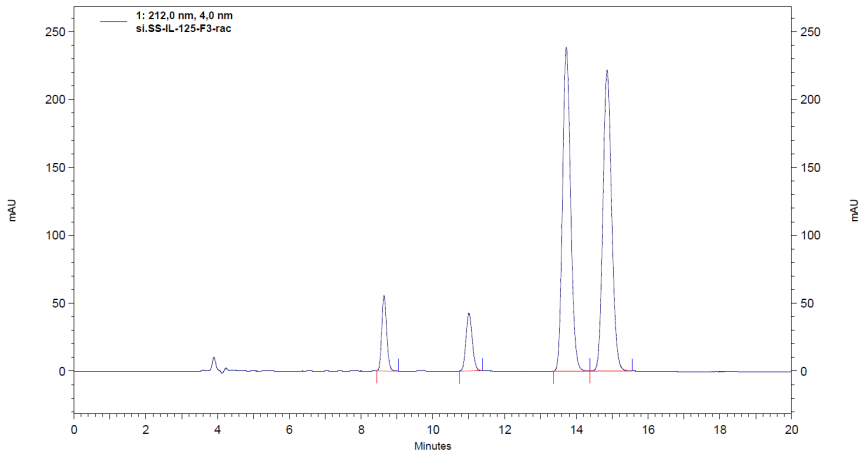


Peak Index	*t* [min]	area [%]
3	8.7	97.758
4	9.6	1.053

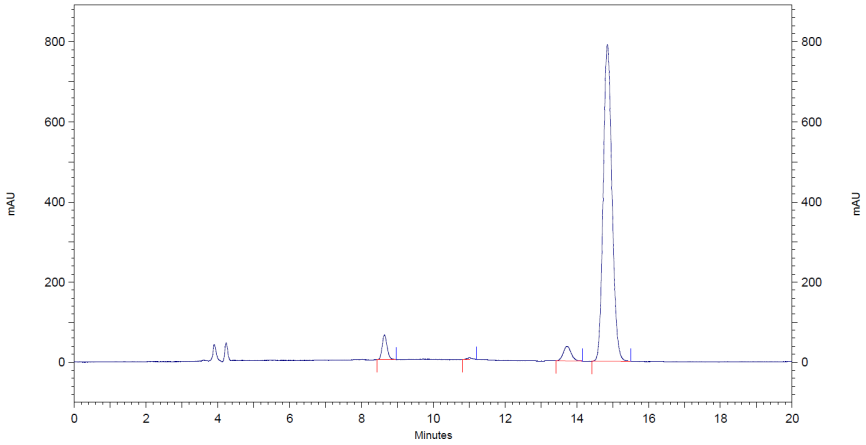
(*S*,*E*)-1-(1,3-dicyclohexylallyl)-1*H*-benzo[d][1,2,3]triazole (*N*^{1}-product, 19)



$C_{21}H_{29}N_3$
(323.24)

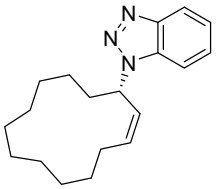


Peak Index	*t* [min]	area [%]
3	13.7	43.898
4	14.8	44.208

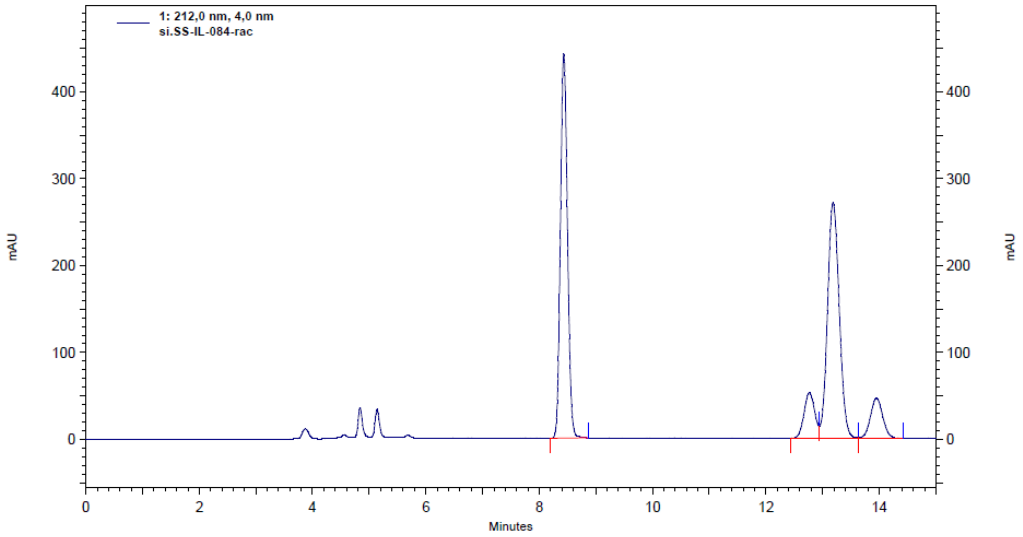


Peak Index	*t* [min]	area [%]
3	13.7	2.824
4	14.8	91.751

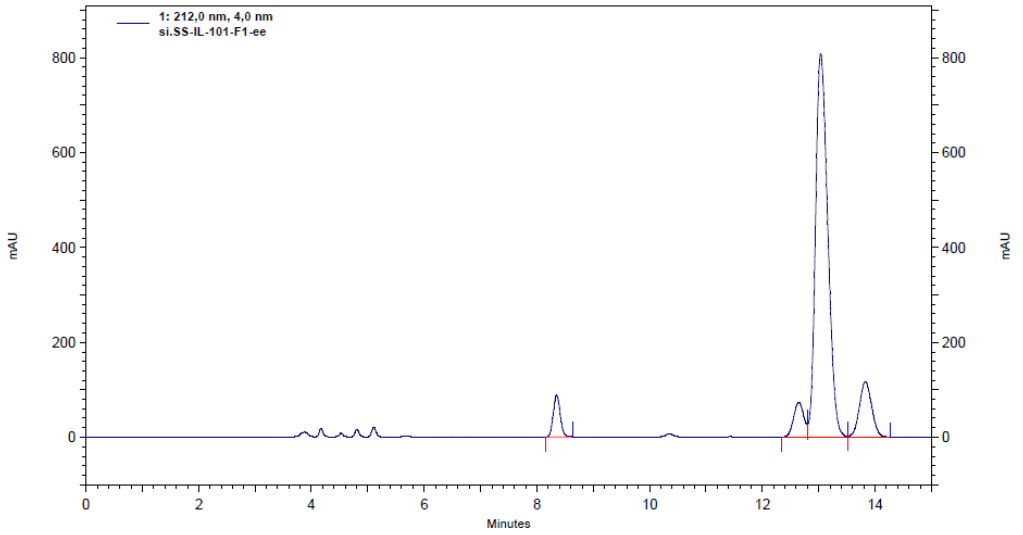
(*S*,*Z*)-1-(cyclotridec-2-en-1-yl)-1*H*-benzo[d][1,2,3]triazole (20)



$C_{19}H_{27}N_3$
297.45

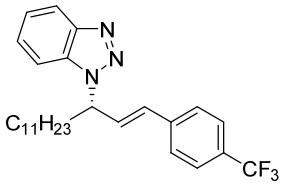


Peak Index	*t* [min]	area [%]
1	8.4	42.124
3	13.2	42.843

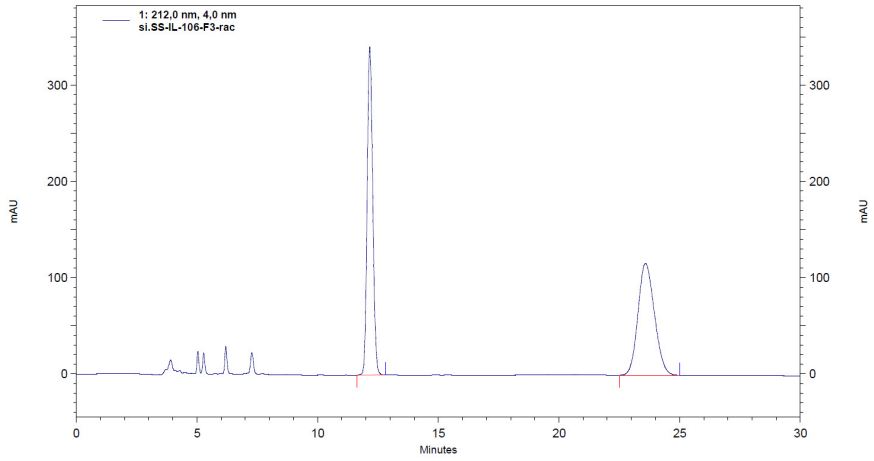


Peak Index	*t* [min]	area [%]
1	8.4	4.859
2	13.0	77.855

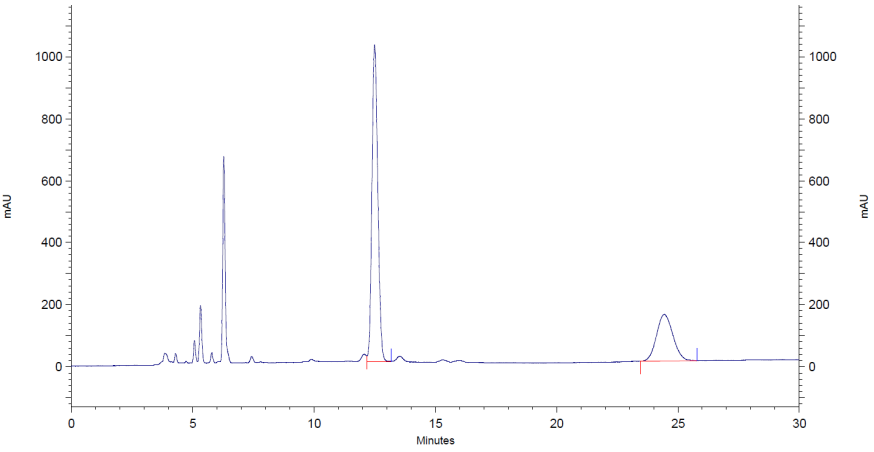
(*S,E*)-1-(1-(4-(trifluoromethyl)phenyl)tetradec-1-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1}, *C*^{1}, *E*-product, 21)



$C_{27}H_{34}F_3N_3$
(457.59)

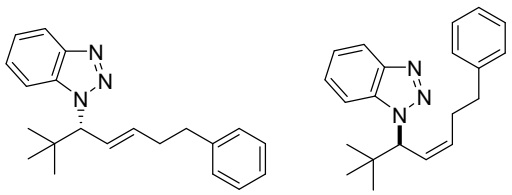


Peak Index	*t* [min]	area [%]
3	12.5	50.363
4	24.4	49.637



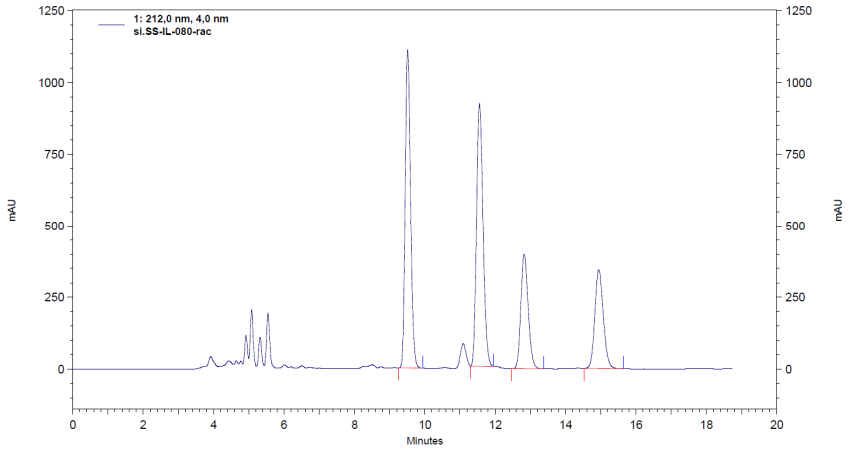
Peak Index	*t* [min]	area [%]
3	12.5	70.937
4	24.4	29.063

(*S*,*E*)-1-(2,2-dimethyl-7-phenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1},*C*^{1},*E*-product, 22) & (*Z*)-1-(2,2-dimethyl-7-phenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1},*C*^{1},*Z*-product, 22bb)

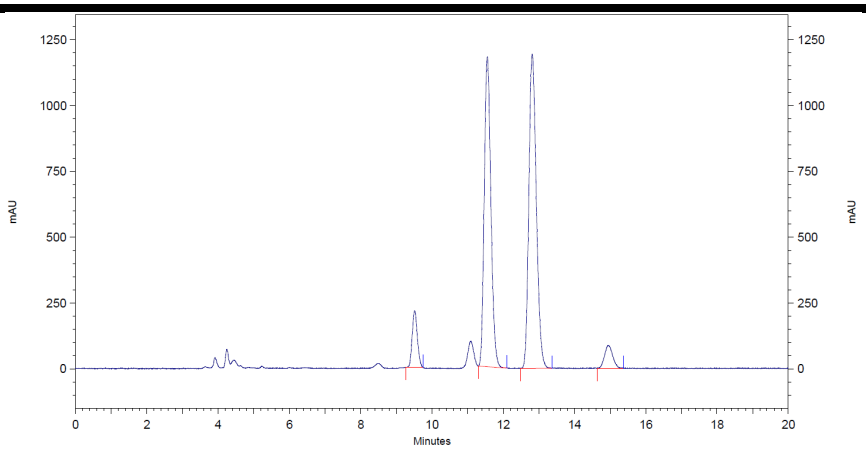


$C_{21}H_{25}N_3$ (319.45)

$C_{21}H_{25}N_3$ (319.45)

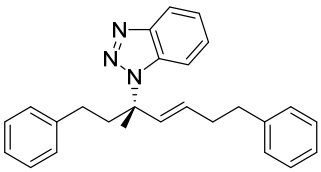


Peak Index	*t* [min]	area [%]
1	9.5 (*C*^{1}*Z*)	33.269
2	11.6 (*C*^{1}*Z*)	33.532
3	12.8 (*C*^{1}*E*)	16.636
4	15.0 (*C*^{1}*E*)	16.562

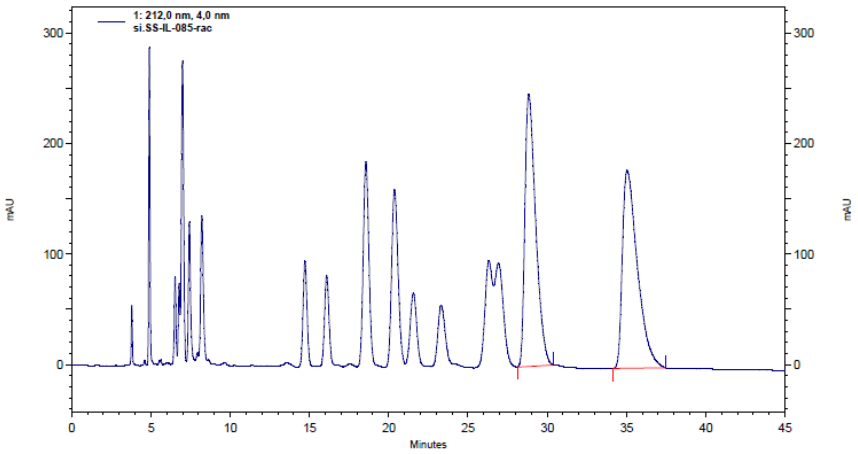


Peak Index	*t* [min]	area [%]
1	9.5 (*C*^{1}*Z*)	5.947
2	11.6 (*C*^{1}*Z*)	42.077
3	12.8 (*C*^{1}*E*)	48.149
4	15.0 (*C*^{1}*E*)	3.826

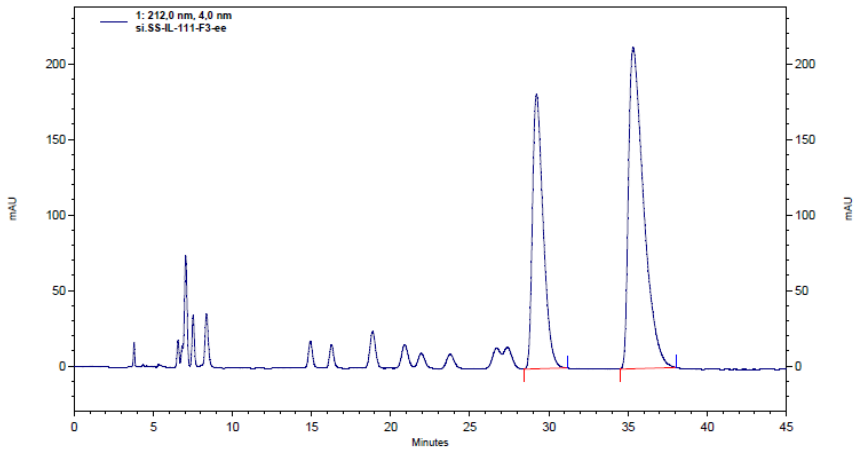
(*S*,*E*)-1-(3-methyl-1,7-diphenylhept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (*N*^{1},*C*^{1},*E*-product, 23)



$C_{26}H_{27}N_3$
(381.22)

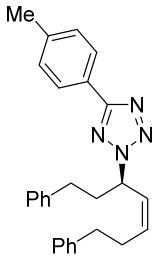


Peak Index	*t* [min]	area [%]
1	28.8	49.685
2	35.0	50.315

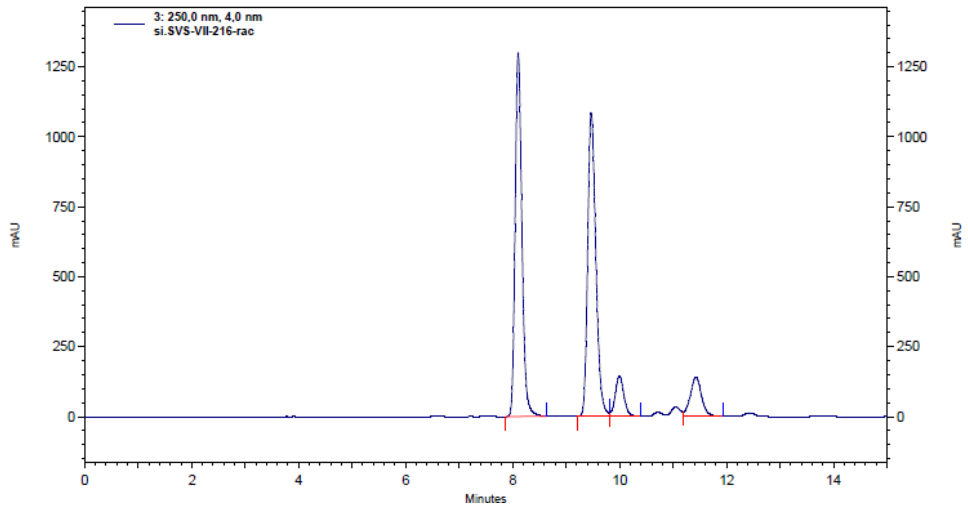


Peak Index	*t* [min]	area [%]
1	29.2	37.767
2	35.3	62.233

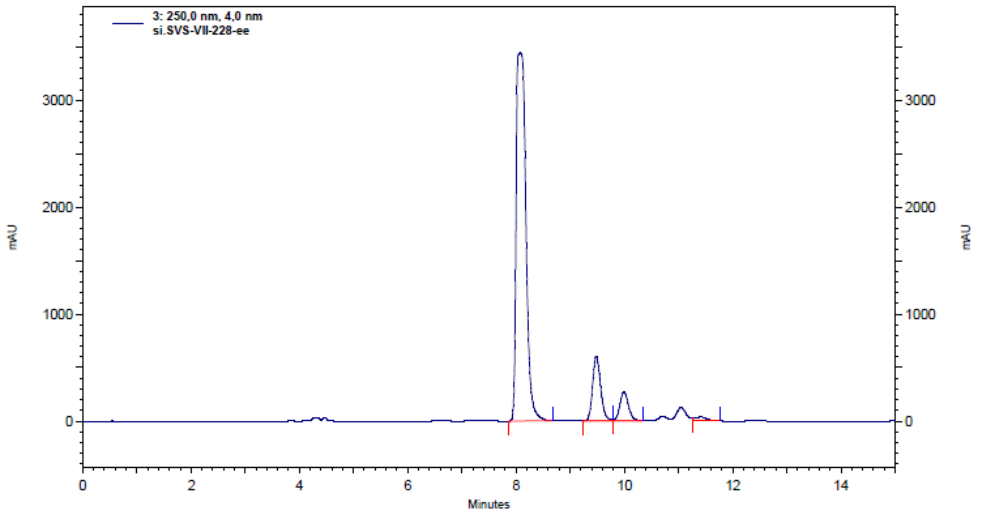
(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-(p-tolyl)-2*H*-tetrazole (24)



$C_{27}H_{28}N_4$
(408.55)

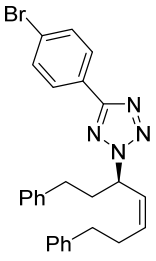


Peak Index	*t* [min]	area [%]
1	8.1	43.060
2	9.4	43.121

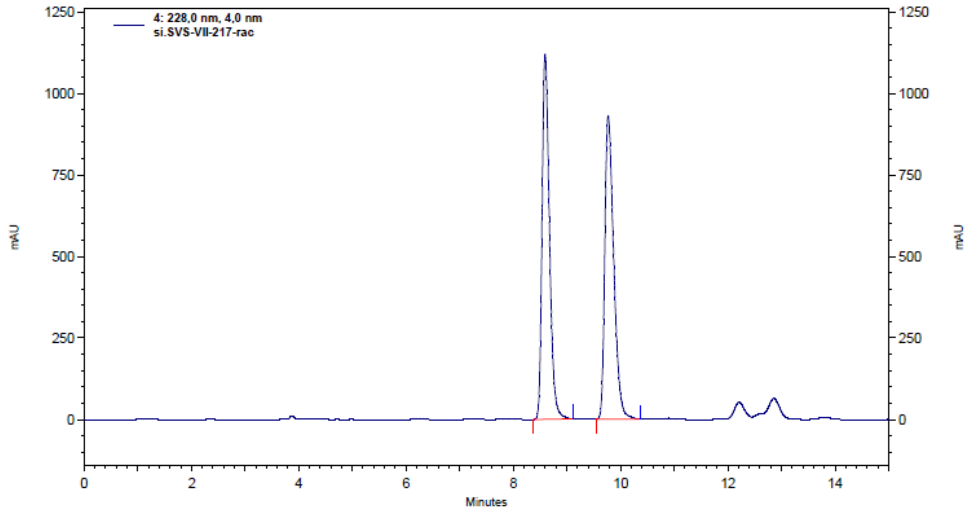


Peak Index	*t* [min]	area [%]
1	8.1	81.520
2	9.5	11.825

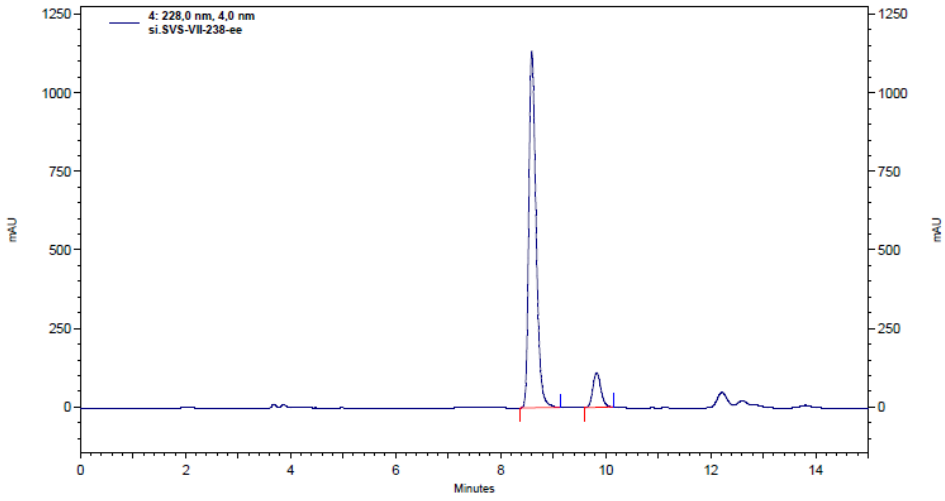
(*R*,*Z*)-5-(4-bromophenyl)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazole (25)



$C_{26}H_{25}BrN_4$
(473.42)

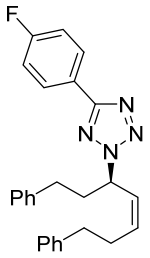


Peak Index	*t* [min]	area [%]
1	8.6	49.823
2	9.8	50.177

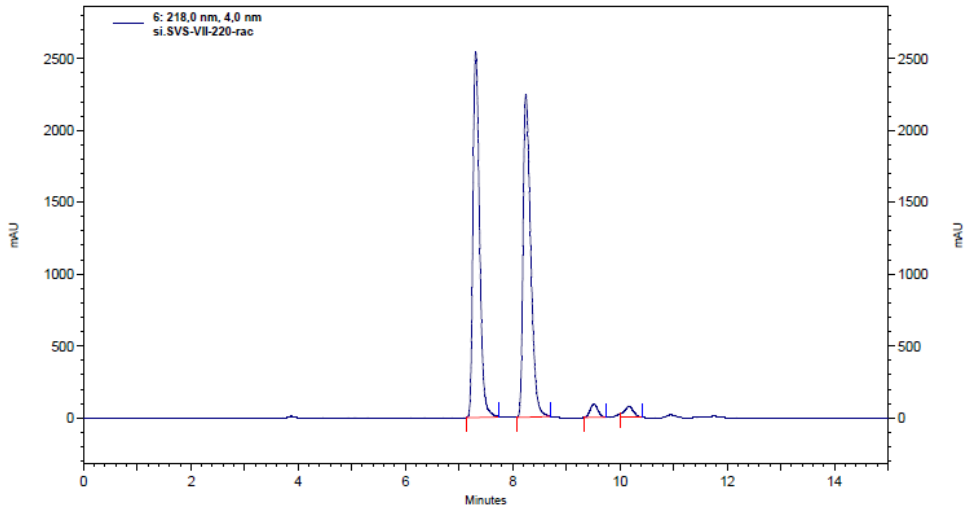


Peak Index	*t* [min]	area [%]
1	8.6	90.282
2	9.8	9.718

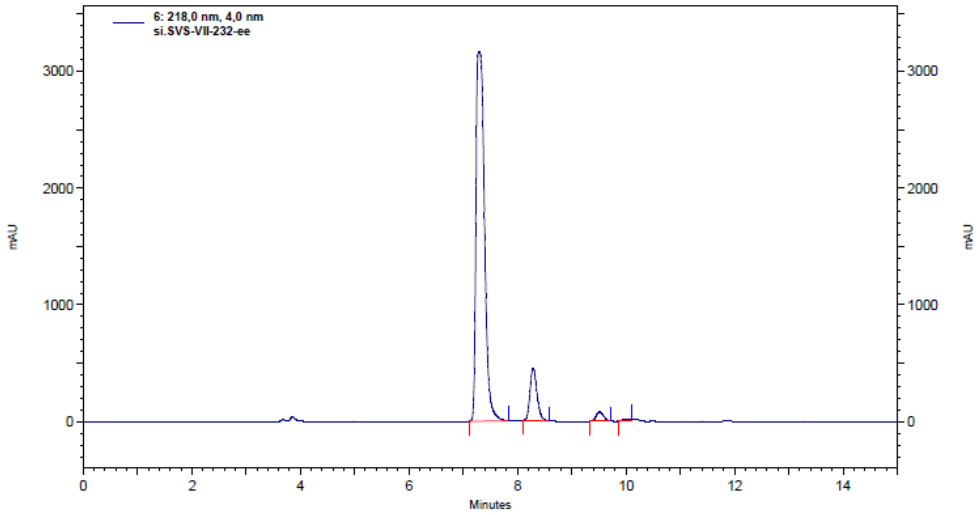
(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-(4-fluorophenyl)-2*H*-tetrazole (26)



$C_{26}H_{25}FN_4$
(412.51)

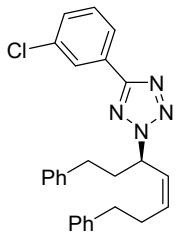


Peak Index	*t* [min]	area [%]
1	7.3	47.515
2	8.2	48.447

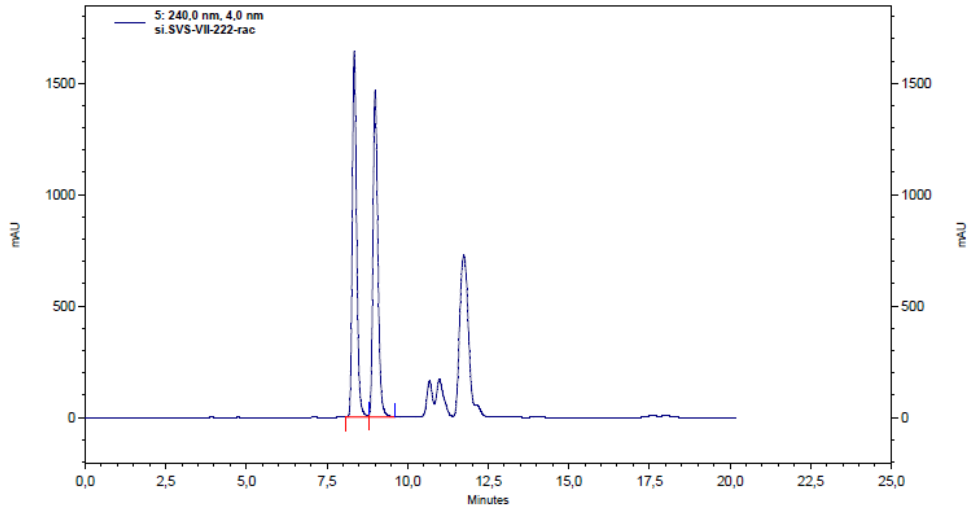


Peak Index	*t* [min]	area [%]
1	7.3	87.430
2	8.3	10.190

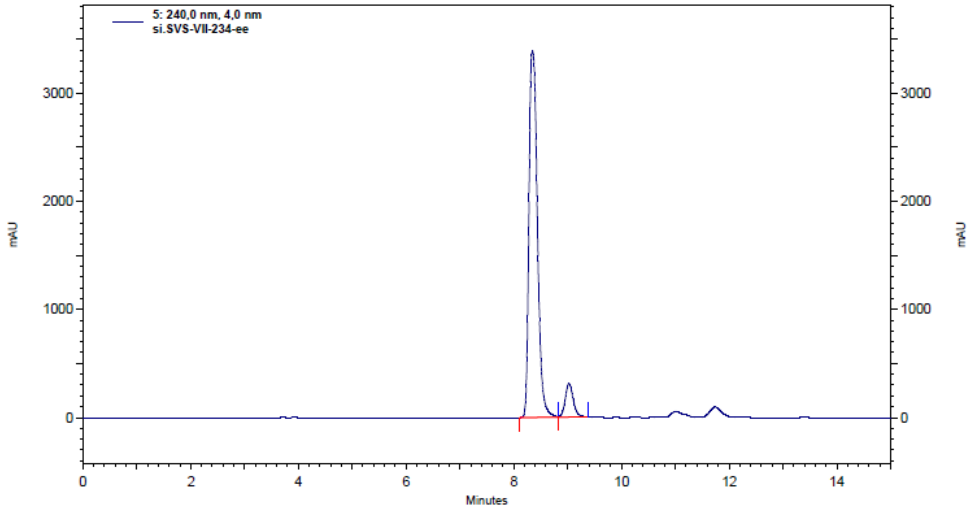
(*R*,*Z*)-5-(3-chlorophenyl)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazole (27)



$C_{26}H_{25}ClN_4$
(428.96)

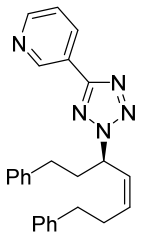


Peak Index	*t* [min]	area [%]
1	8.4	49.912
2	9.0	50.088

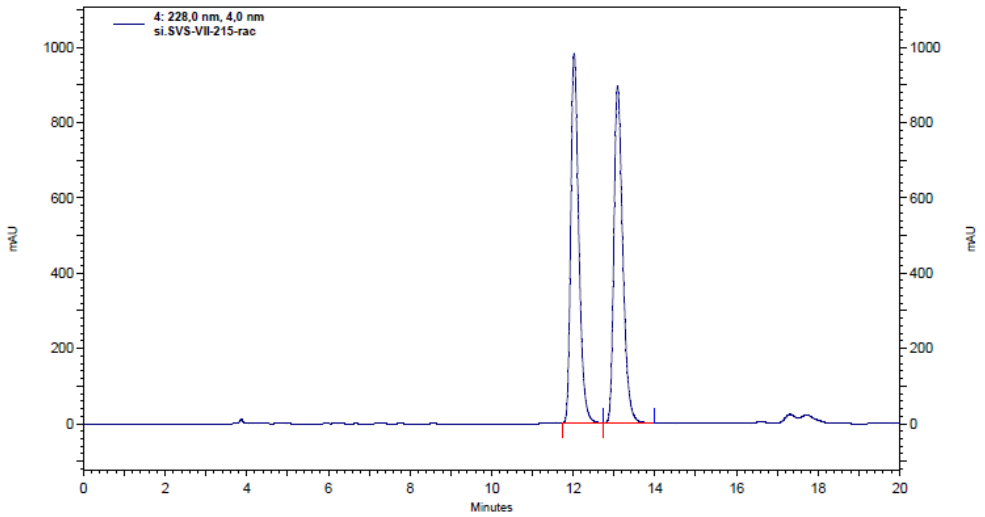


Peak Index	*t* [min]	area [%]
1	8.4	91.956
2	9.0	8.044

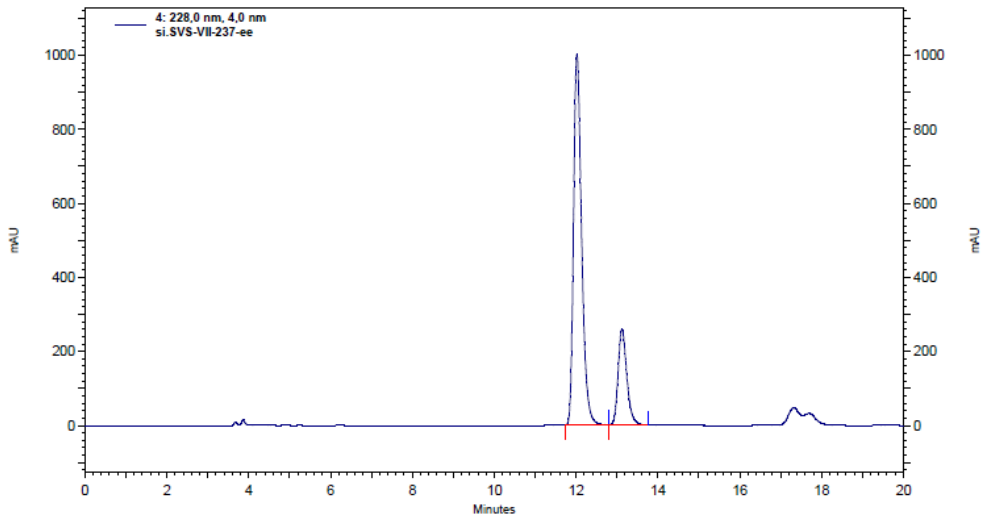
(*R*,*Z*)-3-(2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazol-5-yl)pyridine (28)



$C_{25}H_{25}N_5$
(395.51)

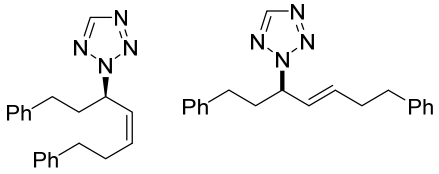


Peak Index	*t* [min]	area [%]
1	12.0	49.830
2	13.1	50.170



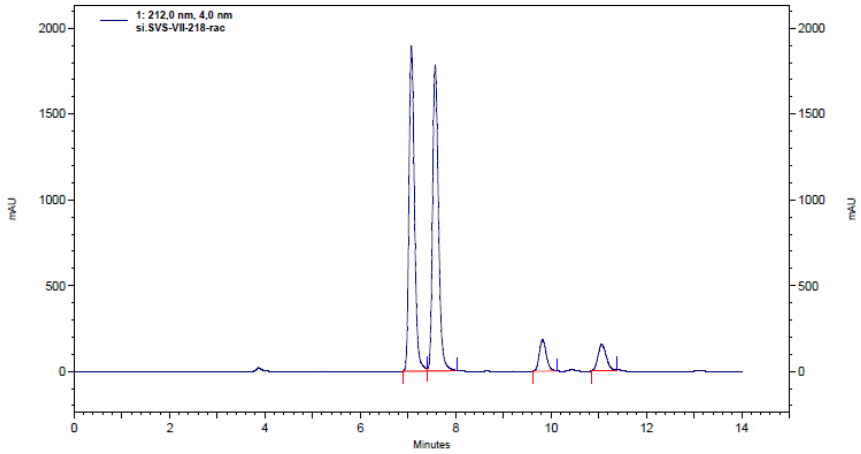
Peak Index	*t* [min]	area [%]
1	12.0	78.191
2	13.1	21.809

(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazole (29) & (*E*)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazole (29b)

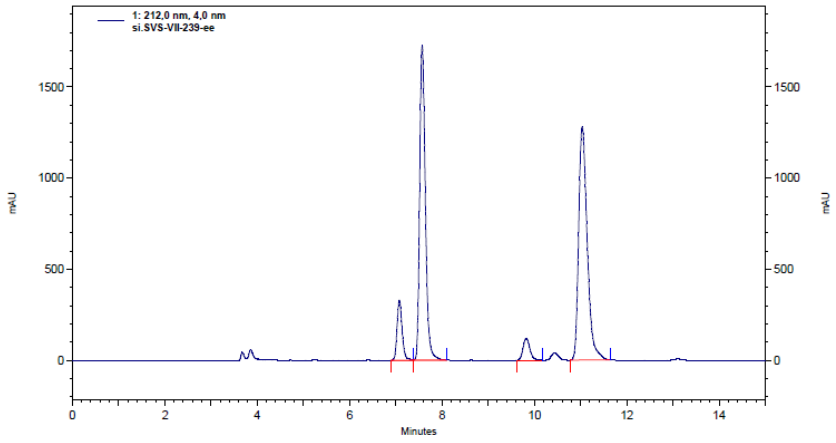


$C_{20}H_{22}N_4$
(318.42)

$C_{20}H_{22}N_4$
(318.42)

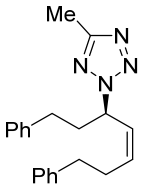


Peak Index	*t* [min]	area [%]
1	7.0 (*Z*)	44.186
2	7.6 (*Z*)	44.670
3	9.8 (*E*)	5.471
4	11.1 (*E*)	5.672

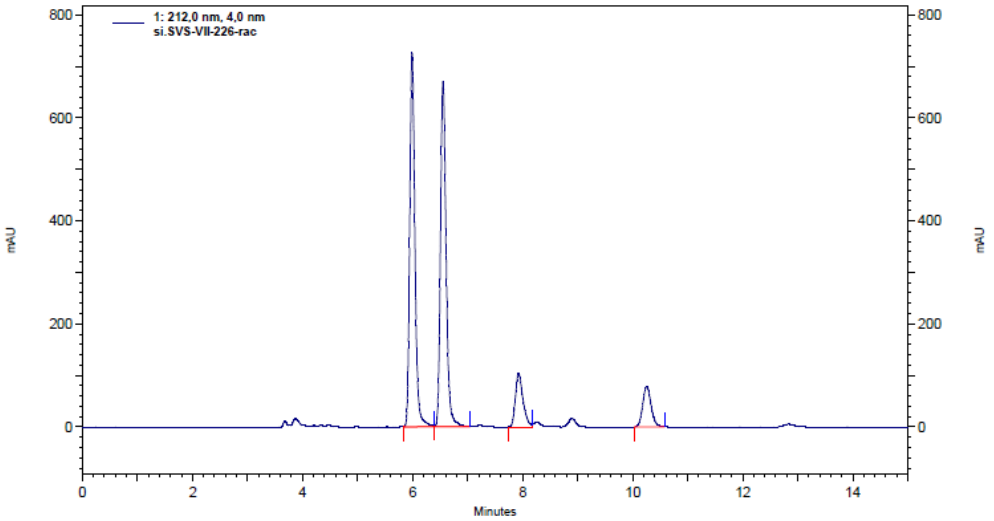


Peak Index	*t* [min]	area [%]
1	7.1 (*Z*)	7.166
2	7.6 (*Z*)	42.097
3	9.8 (*E*)	3.575
4	11.0 (*E*)	47.162

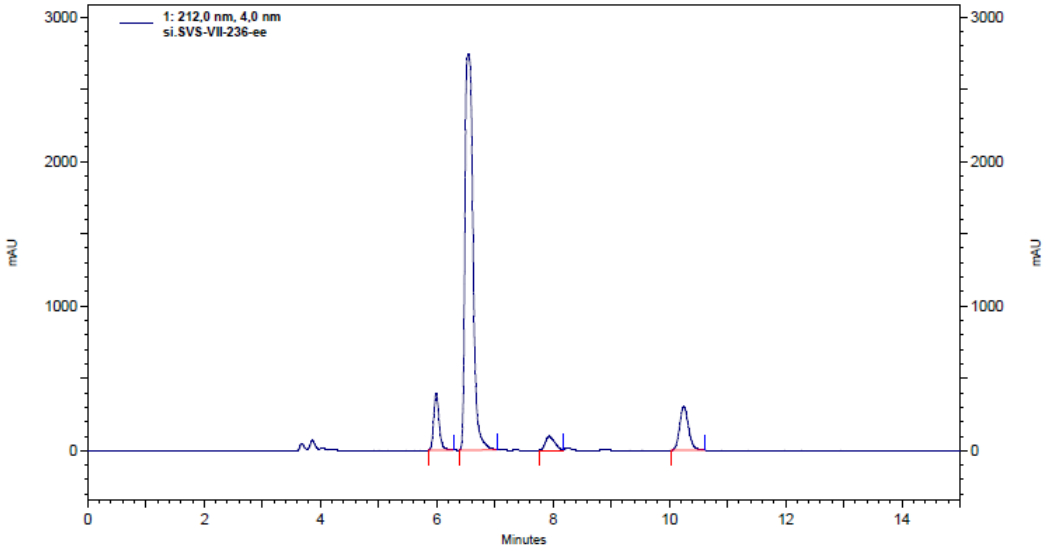
(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-methyl-2*H*-tetrazole (30)



$C_{21}H_{24}N_4$
(332.45)

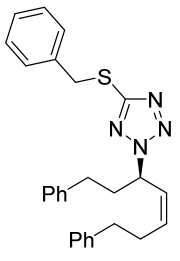


Peak Index	*t* [min]	area [%]
1	6.0	41.927
2	6.6	41.941

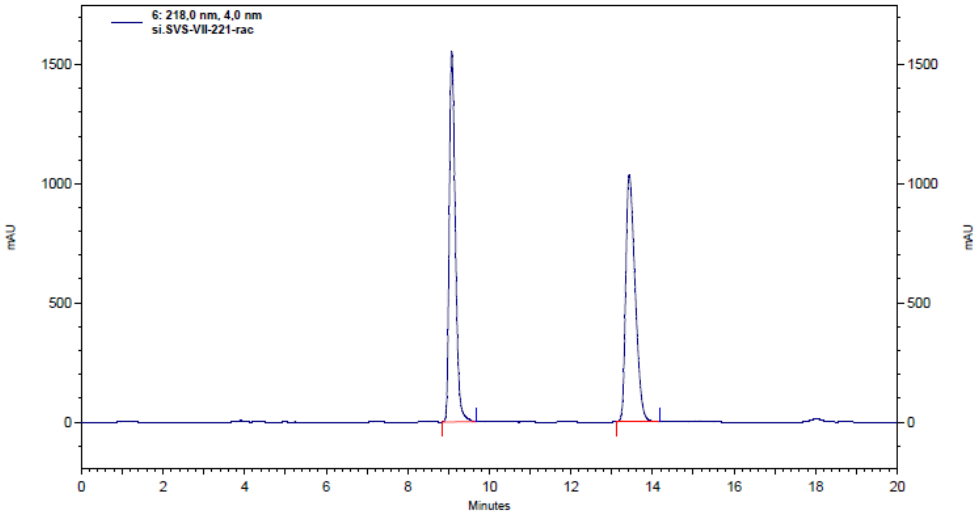


Peak Index	*t* [min]	area [%]
1	6.0	7.690
2	6.5	79.276

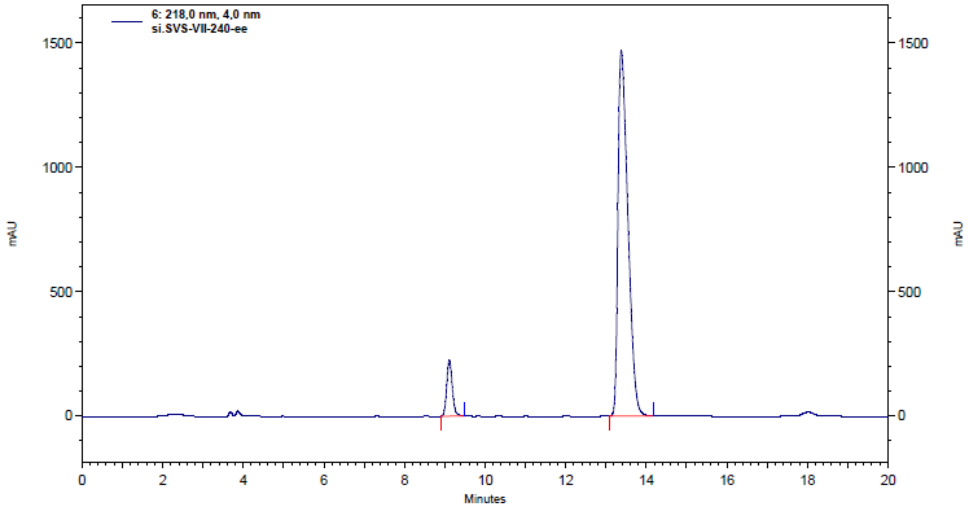
(*R*,*Z*)-5-(benzylthio)-2-(1,7-diphenylhept-4-en-3-yl)-2*H*-tetrazole (31)



$C_{27}H_{28}N_4S$
(440.61)

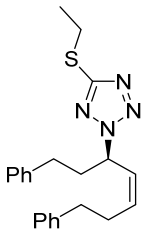


Peak Index	*t* [min]	area [%]
1	9.1	49.262
2	13.4	50.738

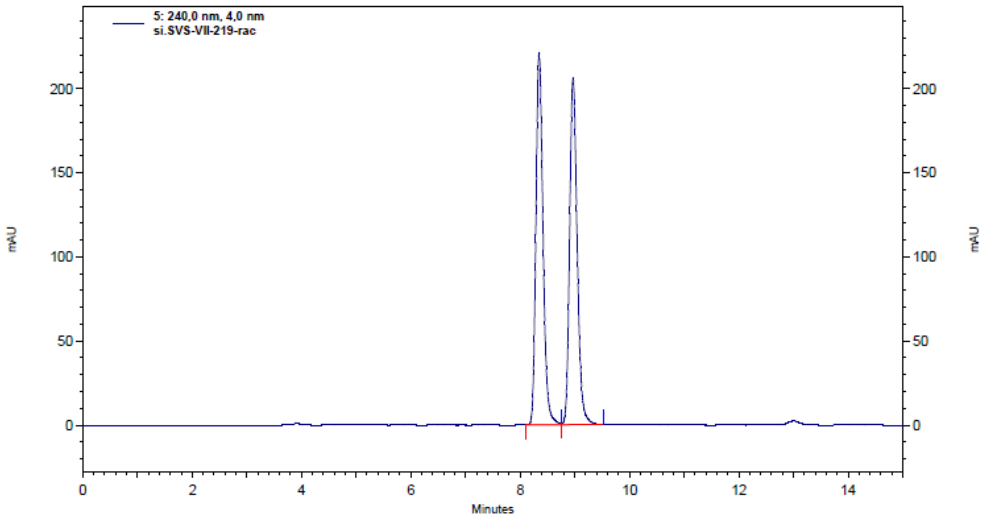


Peak Index	*t* [min]	area [%]
1	9.1	7.953
2	13.4	92.047

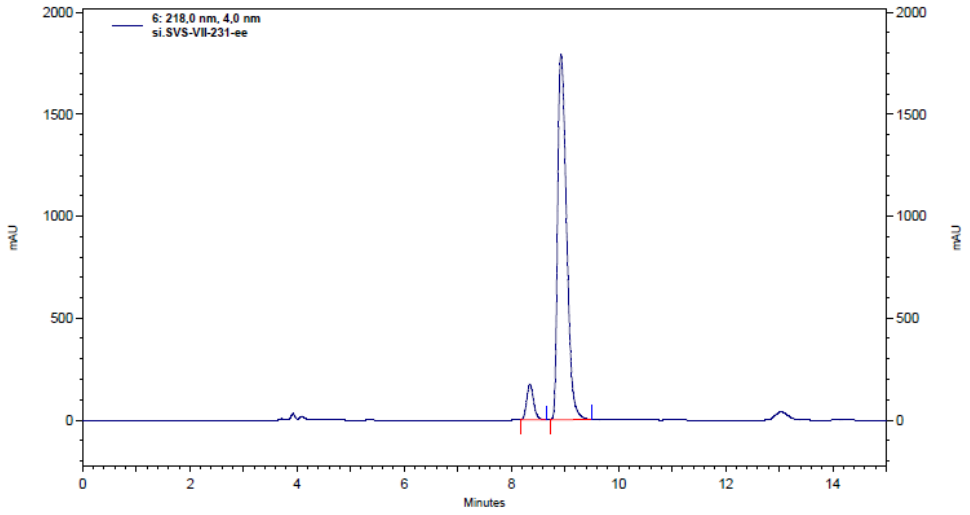
(*R*,*Z*)-2-(1,7-diphenylhept-4-en-3-yl)-5-(ethylthio)-2*H*-tetrazole (32)



$C_{22}H_{26}N_4S$
(378.54)

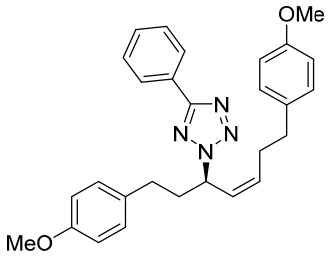


Peak Index	*t* [min]	area [%]
1	8.3	49.974
2	9.0	50.026

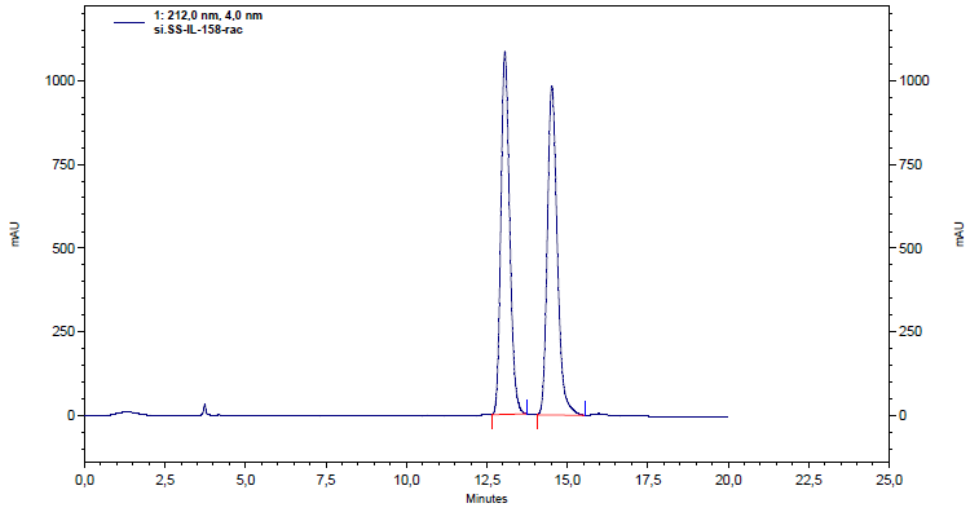


Peak Index	*t* [min]	area [%]
1	8.3	6.966
2	8.9	93.034

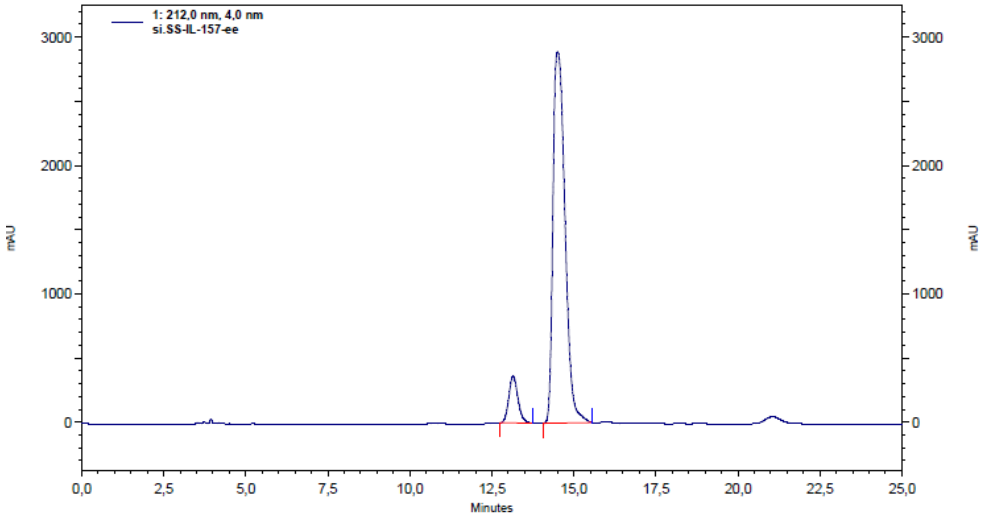
(*R*,*Z*)-2-(1,7-bis(4-methoxyphenyl)hept-4-en-3-yl)-5-phenyl-2*H*-tetrazole (33)



$C_{28}H_{30}N_4O_2$
(454.57)

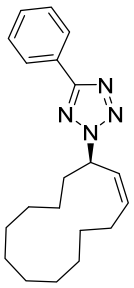


Peak Index	*t* [min]	area [%]
1	13.1	49.321
2	14.5	50.679

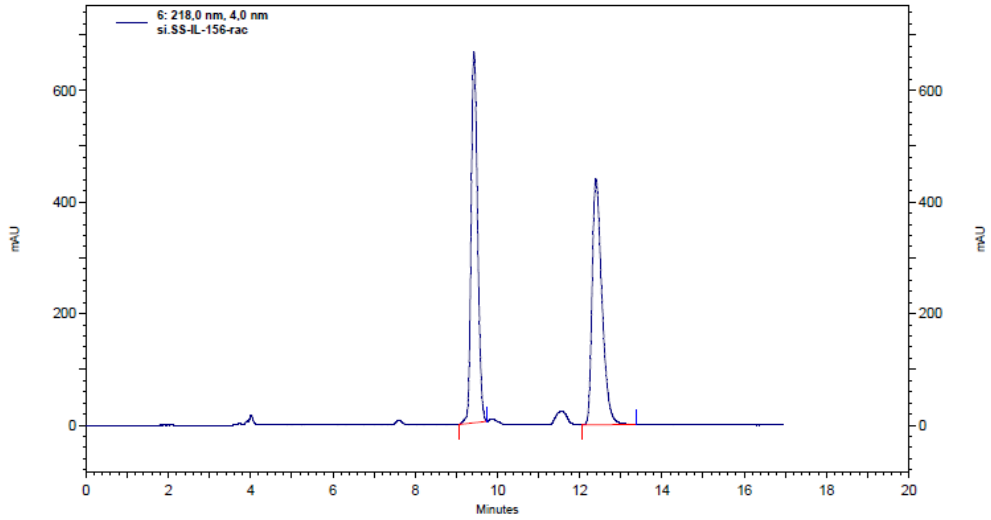


Peak Index	*t* [min]	area [%]
1	13.1	8.803
2	14.5	91.197

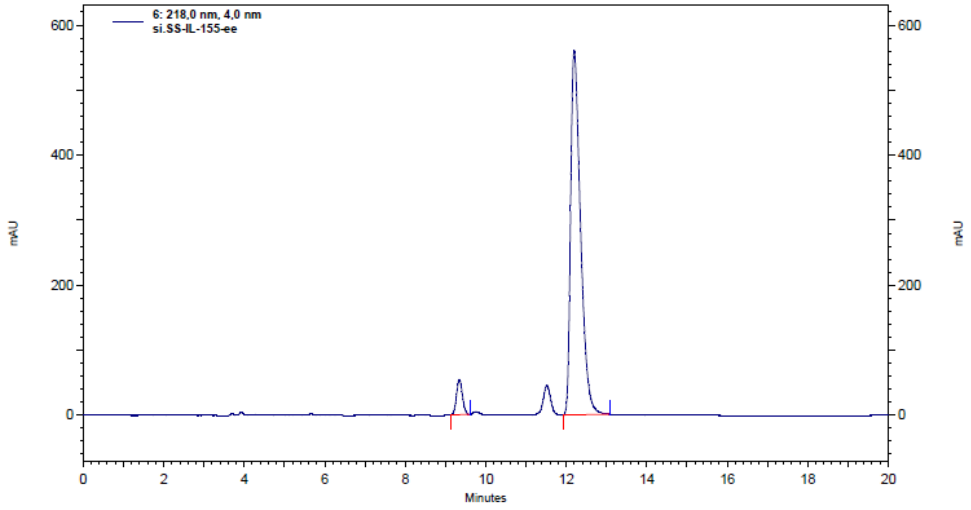
(*R*,*Z*)-2-(cyclotridec-2-en-1-yl)-5-phenyl-2*H*-tetrazole (34)



$C_{20}H_{28}N_4$
(324.47)

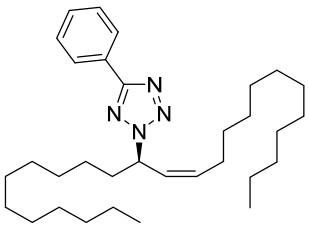


Peak Index	*t* [min]	area [%]
1	9.4	49.773
2	12.4	50.227

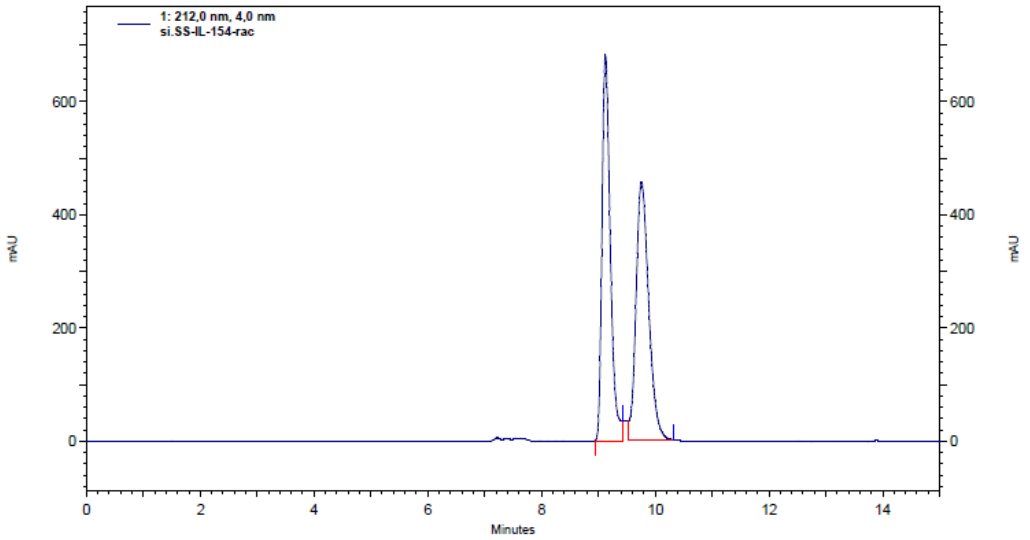


Peak Index	*t* [min]	area [%]
1	9.3	5.471
2	12.2	94.529

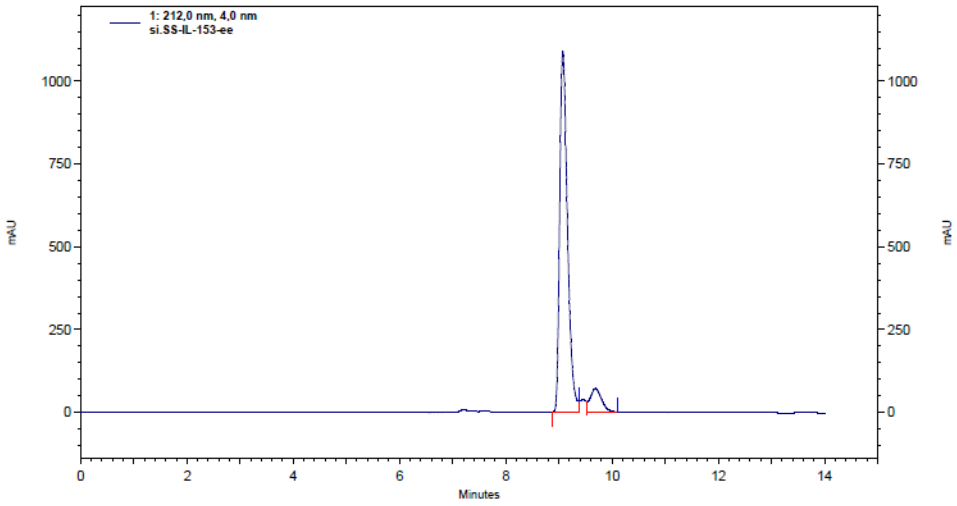
(*R*,*Z*)-2-(pentacos-13-en-12-yl)-5-phenyl-2*H*-tetrazole (35)



$C_{32}H_{54}N_4$
(494.81)

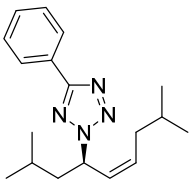


Peak Index	*t* [min]	area [%]
1	9.1	49.334
2	9.8	50.666

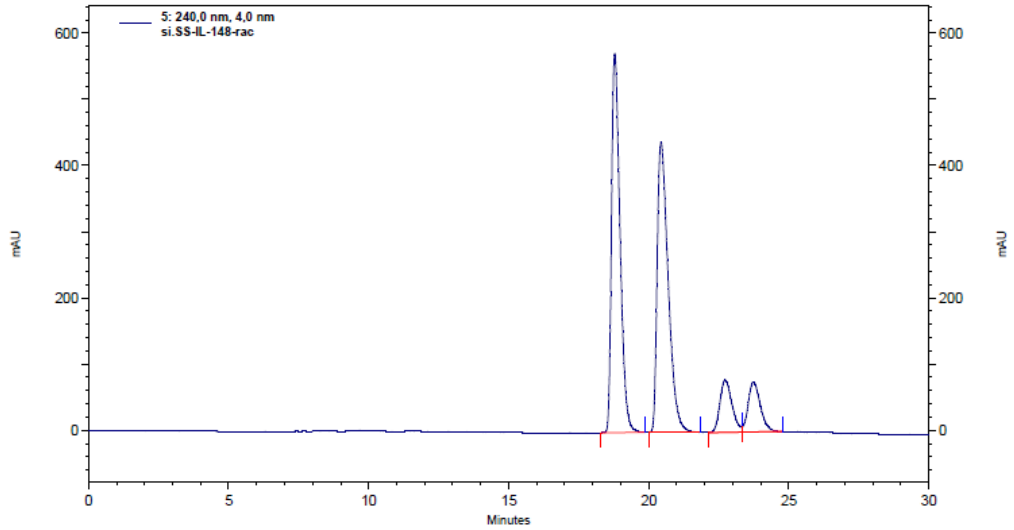


Peak Index	*t* [min]	area [%]
1	9.1	91.414
2	9.7	8.586

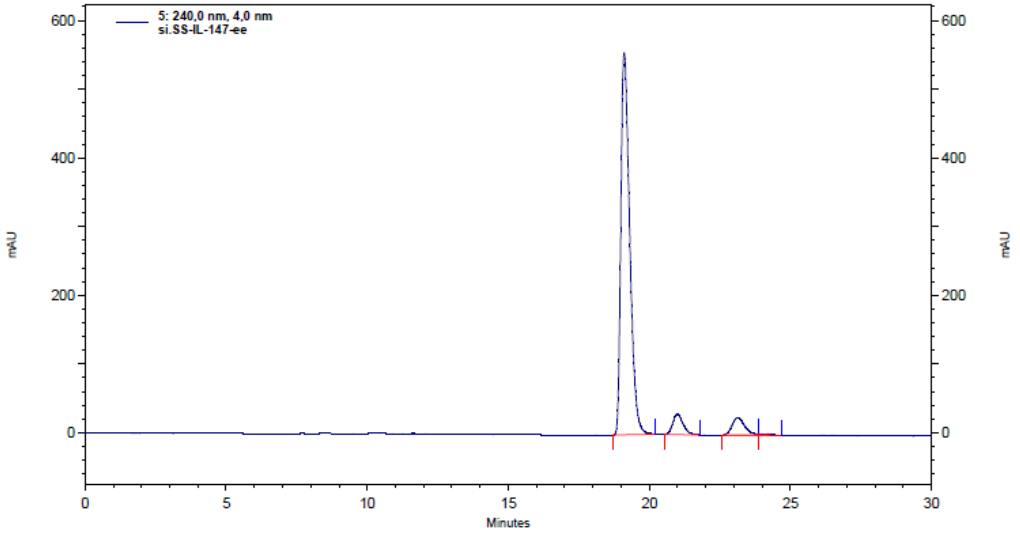
(*R*,*Z*)-2-(2,8-dimethylnon-5-en-4-yl)-5-phenyl-2*H*-tetrazole (36)



$C_{18}H_{26}N_4$
(298.43)

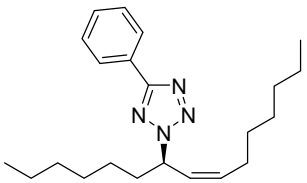


Peak Index	*t* [min]	area [%]
1	18.8	42.042
2	20.4	41.739

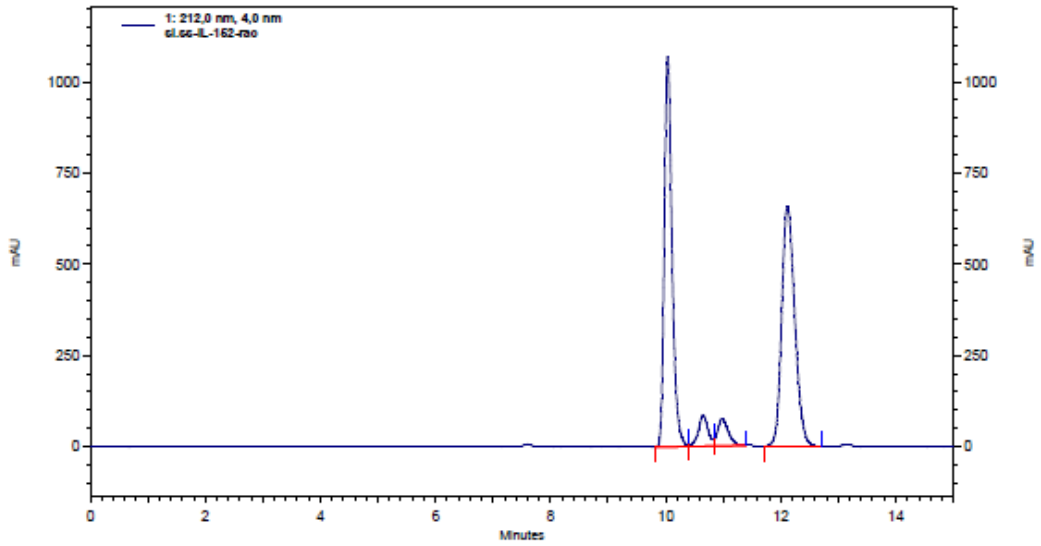


Peak Index	*t* [min]	area [%]
1	19.1	92.693
2	21.0	3.828

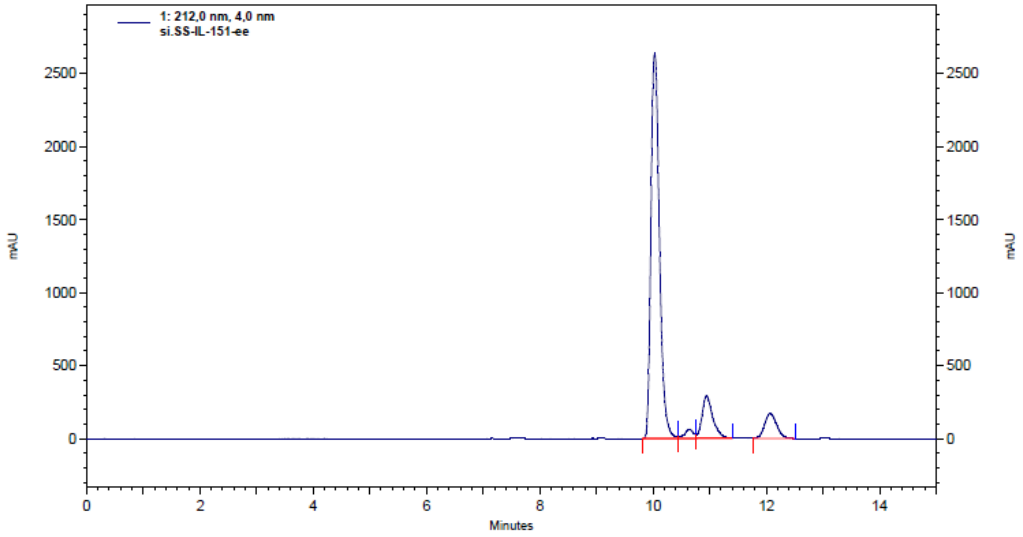
(*R*,*Z*)-2-(pentadec-8-en-7-yl)-5-phenyl-2*H*-tetrazole (37)



$C_{22}H_{34}N_4$
(354.54)

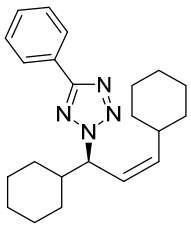


Peak Index	*t* [min]	area [%]
1	10.0	44.553
4	12.1	46.609

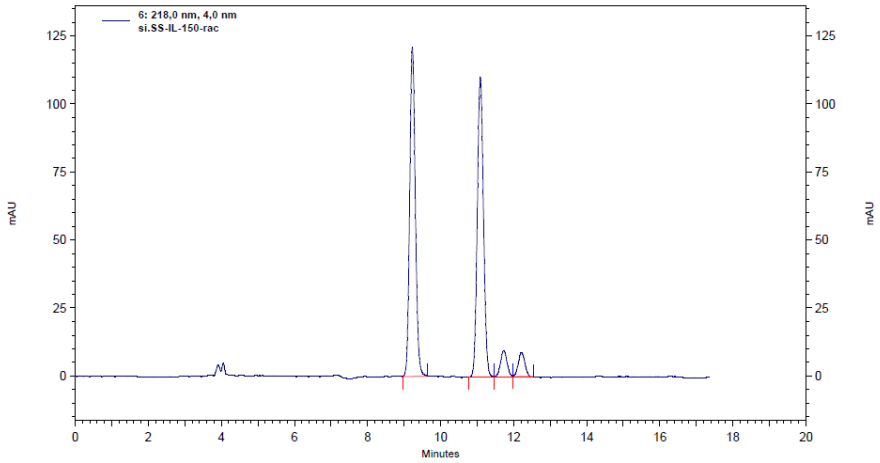


Peak Index	*t* [min]	area [%]
1	10.0	79.573
2	12.1	7.357

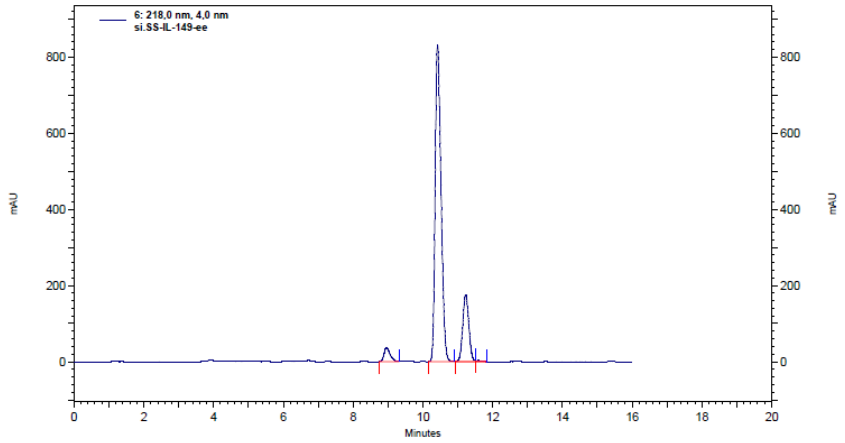
(*R*,*Z*)-2-(1,3-dicyclohexylallyl)-5-phenyl-2*H*-tetrazole (38)



$C_{22}H_{30}N_4$
(350.51)



Peak Index	*t* [min]	area [%]
1	9.3 (*Z*)	45.833
2	11.1 (*Z*)	45.818
3	11.7 (*E*)	4.295
4	12.2 (*E*)	4.054



Peak Index	*t* [min]	area [%]
1	9.0 (*Z*)	3.704
2	10.4 (*Z*)	78.767
3	11.2 (*E*)	17.294
4	11.6 (*E*)	0.236