

Supporting Information

Calcium-mediated intermolecular hydroamination of diphenylbutadiyne with secondary anilines

Carsten Glock, Helmar Görls, Matthias Westerhausen

Friedrich Schiller University,
Institute of Inorganic and Analytical Chemistry,
Humboldtstrasse 8,
D-07743 Jena, Germany.
Fax: +49-3641-948132; Tel: +49-3641-948110;
e-mail: m.we@uni-jena.de

Experimental Procedures

General

Column chromatography was performed with aluminum oxide (Sigma-Aldrich, activated, neutral, type 507C). NMR spectra were recorded on Bruker AC 200/400 or 600 MHz spectrometers. All chemical shifts in NMR experiments are reported as ppm downfield from TMS. Mass spectra were performed on a Finnigan MAT SSQ 710 System, IR measurements were carried out using a Perkin-Elmer System 2000 FTIR. IR spectra were taken as Nujol mulls between KBr windows. Melting points were determined with a Reichert-Jung type 302102 apparatus and are uncorrected.

N-[(*E,Z*)-1,4-diphenylbut-1-en-3-ynyl]-*N*-phenyl-aniline (1)

1,4-diphenylbutadiyne (600 mg, 2.97 mmol) and diphenylamine (500 mg, 2.95 mmol) were dissolved in 15 ml of THF and then 2 ml of a THF-solution containing $[K_2Ca(NPh_2)_4]$ (4 mol-%) were added. During heating to reflux for about 6 hours the color of the reaction solution became intensively yellow. Following a standard workup procedure that includes hydrolysis with 10 ml of water, extraction with diethyl ether, drying with sodium sulfate, and recrystallization from pentane yielded the crystalline *Z*-isomer (hexagonal and cubic habitus) while the *E*-isomer only formed a yellow to brown oil.

Yield: *E/Z*-mixture > 90% out of NMR studies; *Z*-isomer: 40.4 % (isolated).

M.P.: 113.9 - 114.2°C.

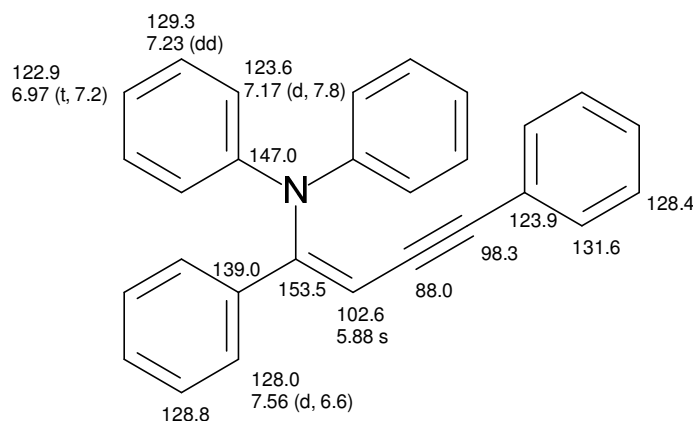
Elemental Analysis (calc.): C 90.58 (90.53), H 5.85 (5.70), N 3.57 (3.77).

DEI-MS: *m/z* (%) 372 (M+1, 30), 371 (M, 95), 180 (Ph₂NC, 100).

IR: 3421 (b, w), 3059 (m), 3033 (m), 2188 (w), 1946 (w), 1876 (w), 1801 (w), 1587 (vs), 1569 (m), 1492 (vs), 1445 (m), 1358 (m), 1310 (sh), 1290 (s), 1250 (m), 1179 (m), 1077 (m), 1028 (m), 753 (vs), 693 (vs), 507 (m) cm⁻¹.

NMR investigations:

Z-Isomer:

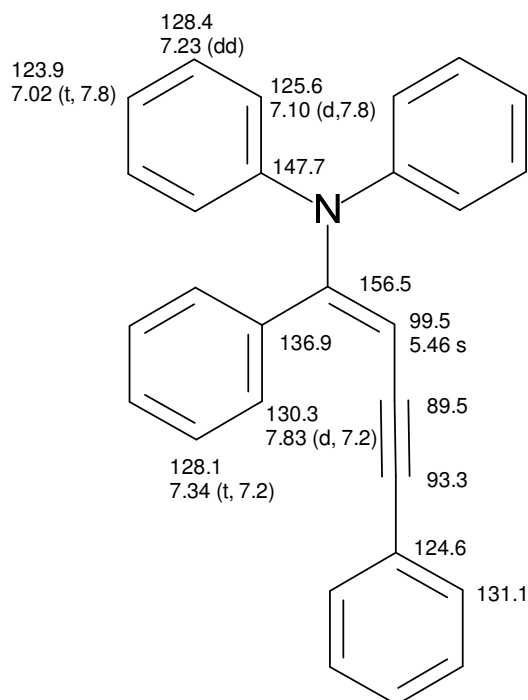


$^1\text{H-NMR}$ (CD_2Cl_2 , 600 MHz, 300 K): 5.88 (1H, s, =CH), 6.97 (2H, t, $J = 7.2$ Hz, p-Aniline), 7.02 (2H, d, o-≡-Ph), 7.17 (4H, d, $J = 7.8$ Hz, o-Aniline), 7.19-7.31 (20H, m, remaining protons), 7.23 (4H, m-Aniline), 7.28 (2H, t, $J = 7.2$ Hz, m-=-Ph), 7.56 (2H, t, $J = 7.2$ Hz, o-=-Ph) ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (CD_2Cl_2 , 150 MHz, 300 K): 88.0, 98.3, 102.6, 122.9, 123.6, 123.9, 128.0, 128.4, 128.8, 129.3, 131.6, 139.0, 147.0, 153.5 ppm.

$^1\text{H-NMR}$ (THF-d_8 , 200 MHz, 300 K): 5.95 (1H, s, =CH), 6.80-7.60 (20H, m, Ph) ppm.

***E*-Isomer:**



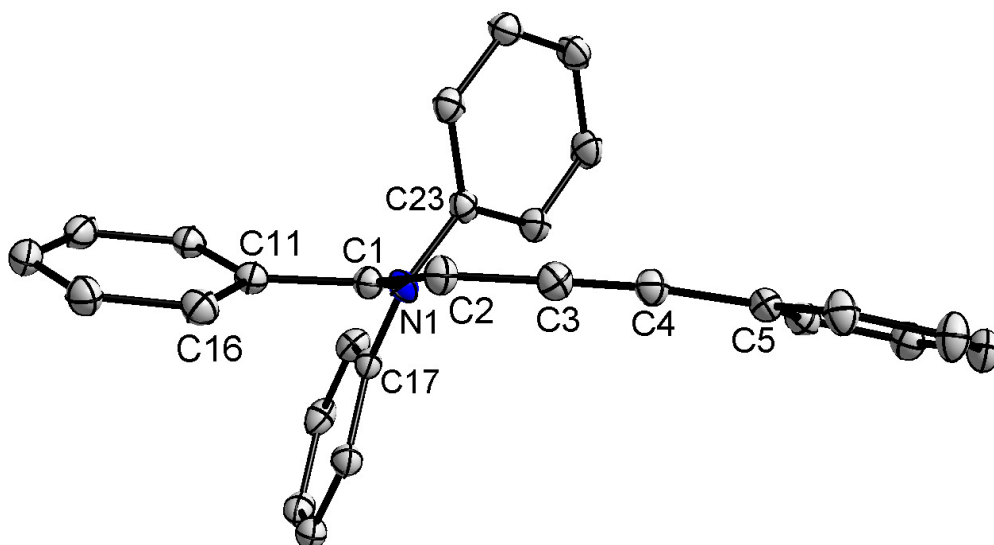
$^1\text{H-NMR}$ (CD_2Cl_2 , 600 MHz, 300 K): 5.46 (1H, s, =CH), 7.02 (2H, t, $J = 7.8$ Hz, p-aniline), 7.10 (4H, d, $J = 7.8$ Hz, o-aniline), 7.19-7.31 (20H, m, remaining protons), 7.23 (4H, m-aniline), 7.34 (2H, t, $J = 7.2$ Hz, m-=-Ph), 7.83 (2H, t, $J = 7.2$ Hz, o-=-Ph) ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (CD_2Cl_2 , 150 MHz, 300 K): 89.5, 93.3, 99.5, 123.9, 124.6, 125.6, 128.1, 128.4, 130.3, 131.1, 136.9, 147.7, 156.5 ppm.

These signals could not be related to a specific C-atom: 128.7, 128.1, 129.1, 127.8

$^1\text{H-NMR}$ (THF-d_8 , 200 MHz, 300 K): 5.44 (1H, s, =CH), 6.80-7.90 (20H, m, Ph) ppm.

Structural Data Z-1:



Selected bond lengths [pm]: C1-C2 135.3(2), C2-C3 141.9(2), C3-C4 120.1(2), C4-C5 143.5(2), N1-C1 142.4(2), N1-C17 141.8(2), N1-C23 142.0(2), C1-C11 148.1(2).

Selected bond angles [°]: C1-N1-C17 119.22(12), C17-N1-C23 121.33(12), C23-N1-C1 119.19(12), N1-C1-C2 120.41(13), C2-C1-C11 122.17(14), C11-C1-N1 117.23(13), C3-C4-C5 175.04(16).

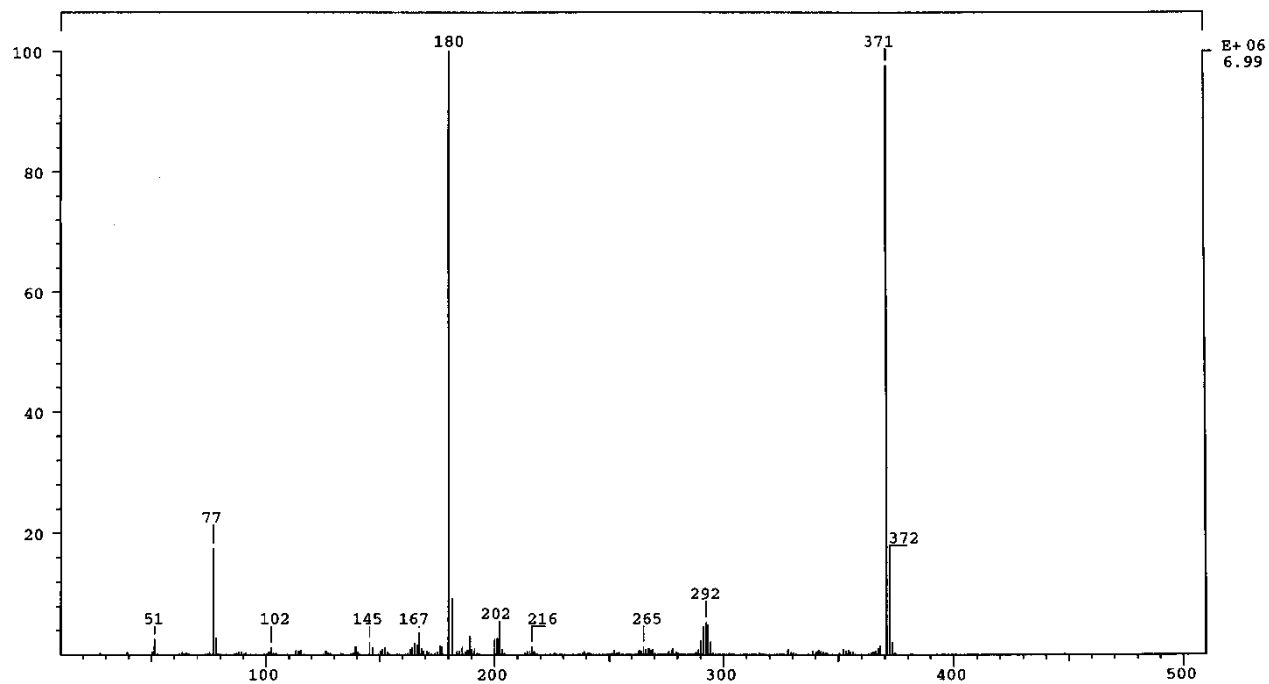
Selected torsion angles [°]: C2-C1-C11-C16 24.7, C2-C1-N1-C23 57.5.

Crystal Data Z-1:

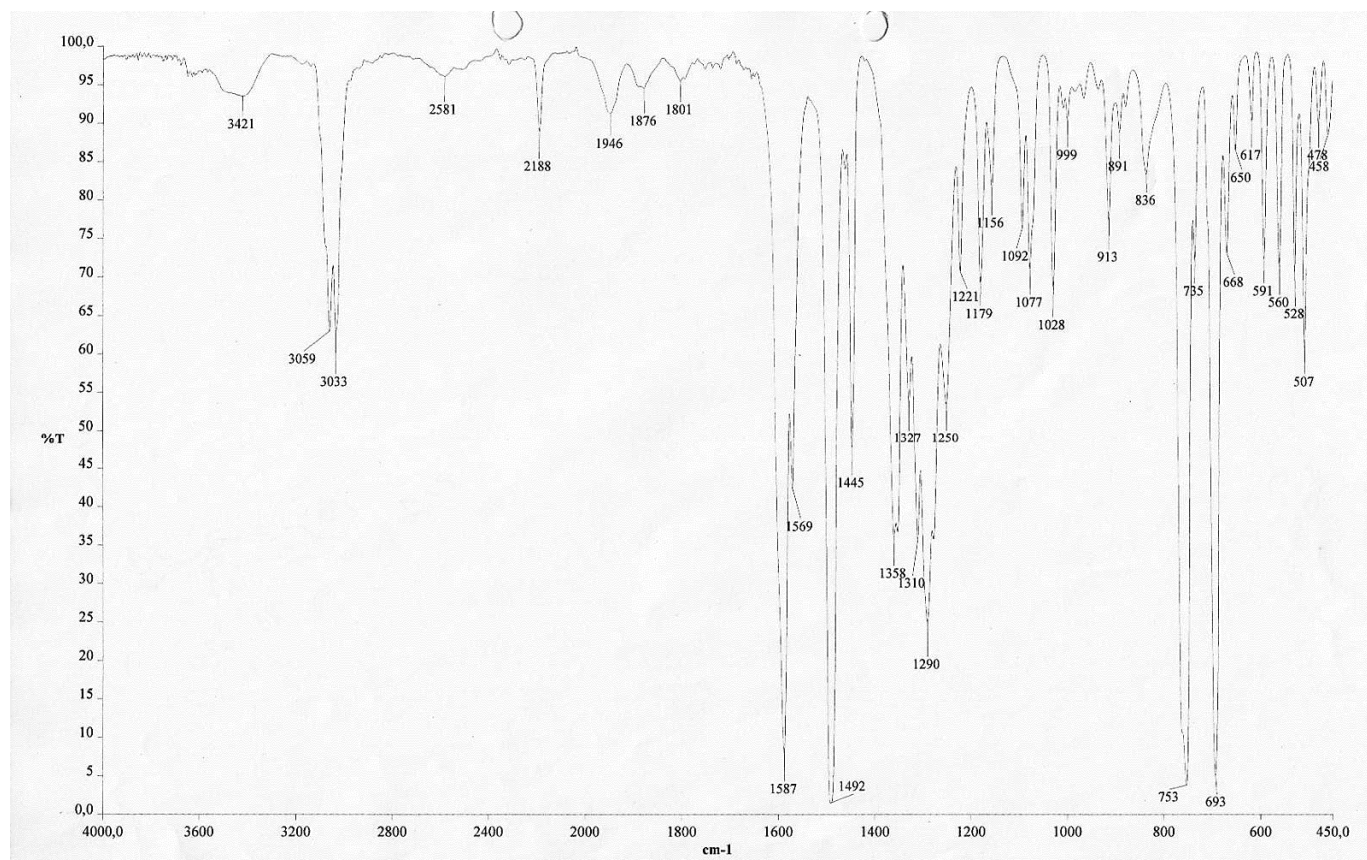
$C_{28}H_{21}N$, $M_r = 371.46 \text{ g mol}^{-1}$, light yellow prism, size $0.06 \times 0.05 \times 0.05 \text{ mm}^3$, monoclinic, space group $P 2_1/n$, $a = 11.0644(4)$, $b = 10.4214(5)$, $c = 17.6016(8) \text{ \AA}$, $\beta = 97.730(3)^\circ$, $V = 2011.14(15) \text{ \AA}^3$, $T = -140 \text{ }^\circ\text{C}$, $Z = 4$, $\rho_{\text{calcd.}} = 1.227 \text{ g cm}^{-3}$, $\mu (\text{Mo-K}\alpha) = 0.71 \text{ cm}^{-1}$, $F(000) = 784$, 11402 reflections in $h(-14/14)$, $k(-13/10)$, $l(-22/22)$, measured in the range $2.32^\circ \leq \Theta \leq 27.49^\circ$, completeness $\Theta_{\text{max}} = 98.7\%$, 4568 independent reflections, $R_{\text{int}} = 0.0337$, 3738 reflections with $F_o > 4\sigma(F_o)$, 346 parameters, 0 restraints, $R1_{\text{obs}} = 0.0481$, $wR^2_{\text{obs}} = 0.1078$, $R1_{\text{all}} = 0.0637$, $wR^2_{\text{all}} = 0.1183$, GOOF = 1.076, largest difference peak and hole: $0.227 / -0.199 \text{ e \AA}^{-3}$.

Spectra of 1

- DEI-MS:

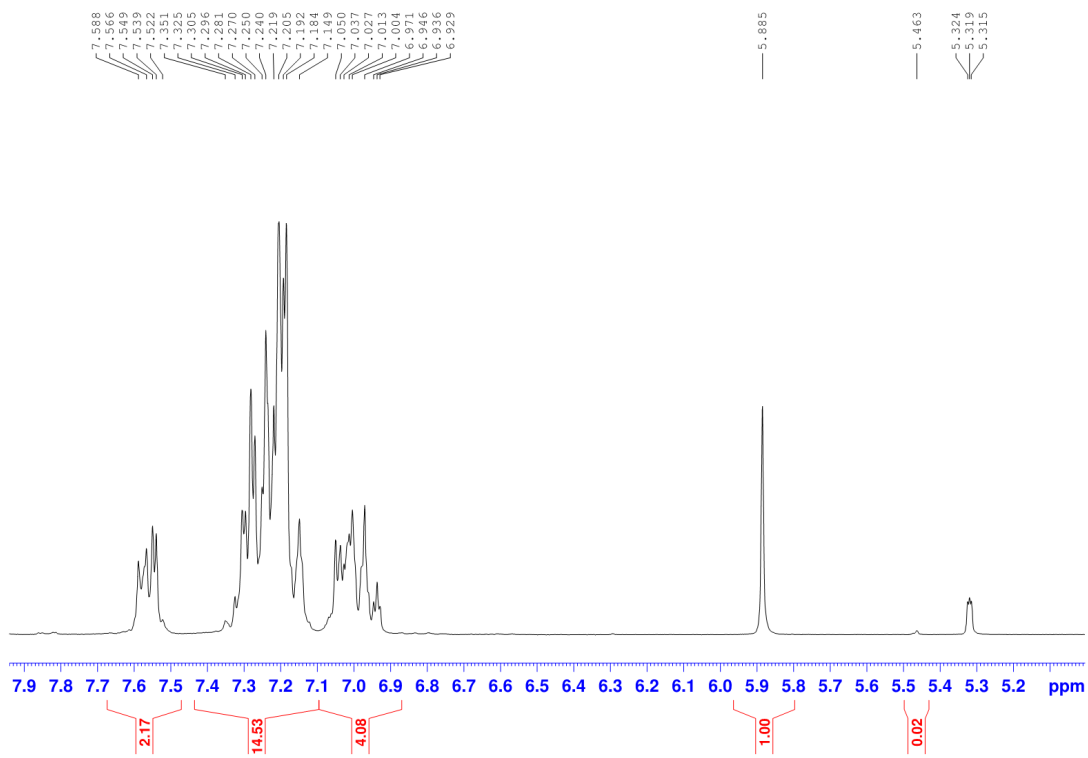


- IR (KBr)

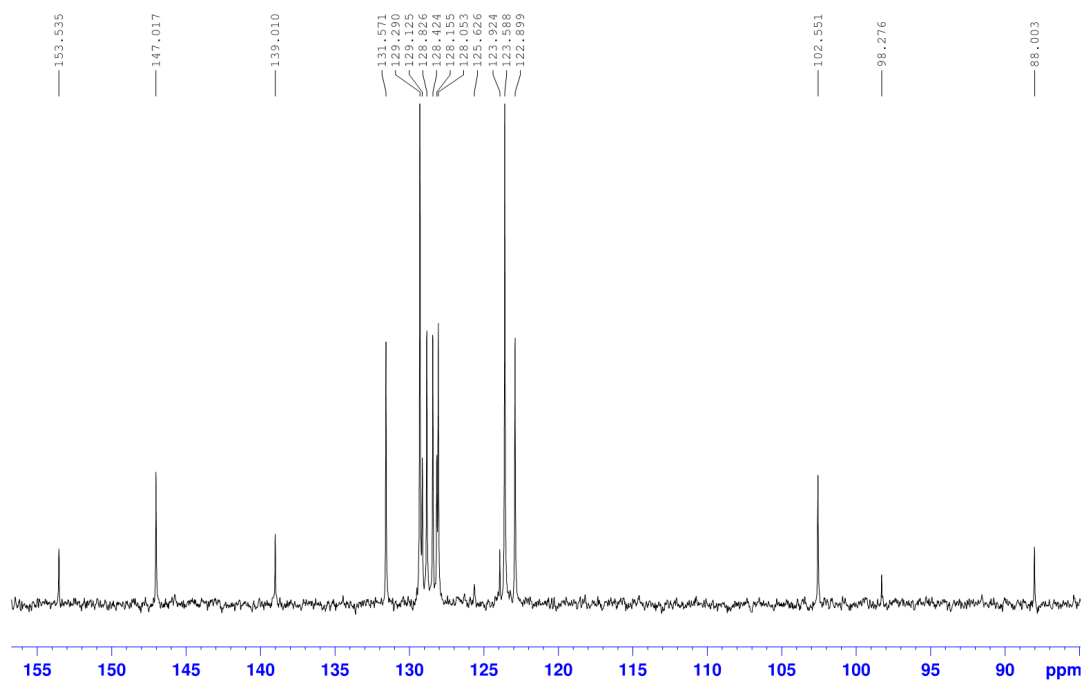


- NMR-Spectra of Z-1 (200MHz, CD₂Cl₂, 300K):

¹H-NMR:

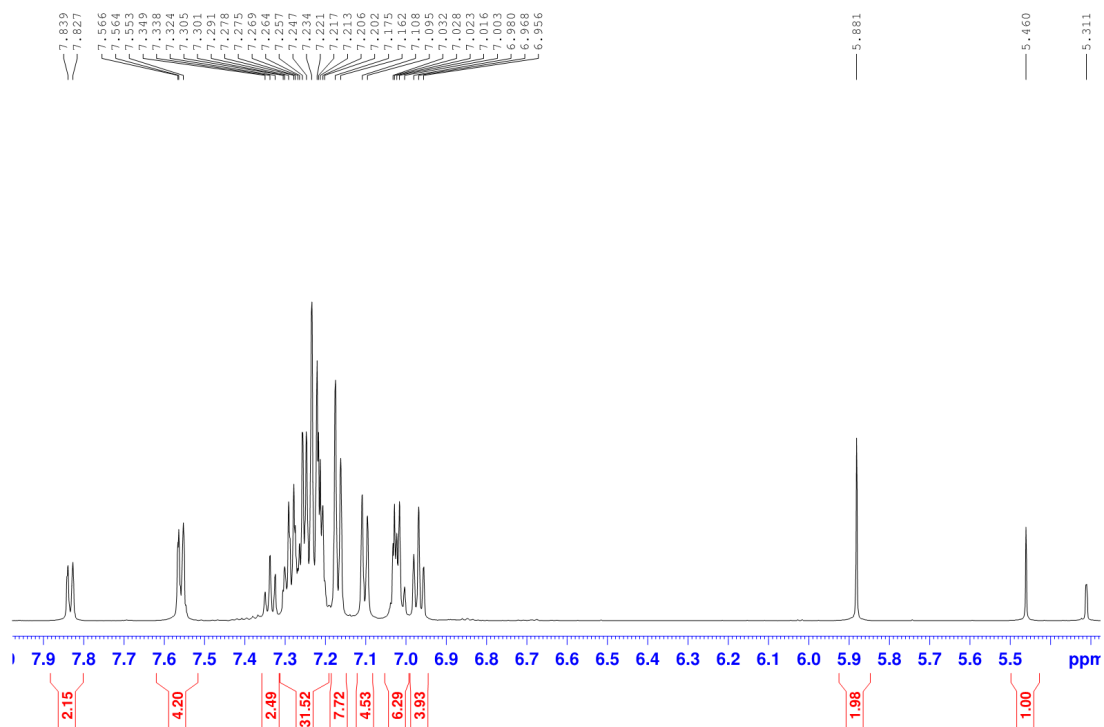


¹³C-NMR:

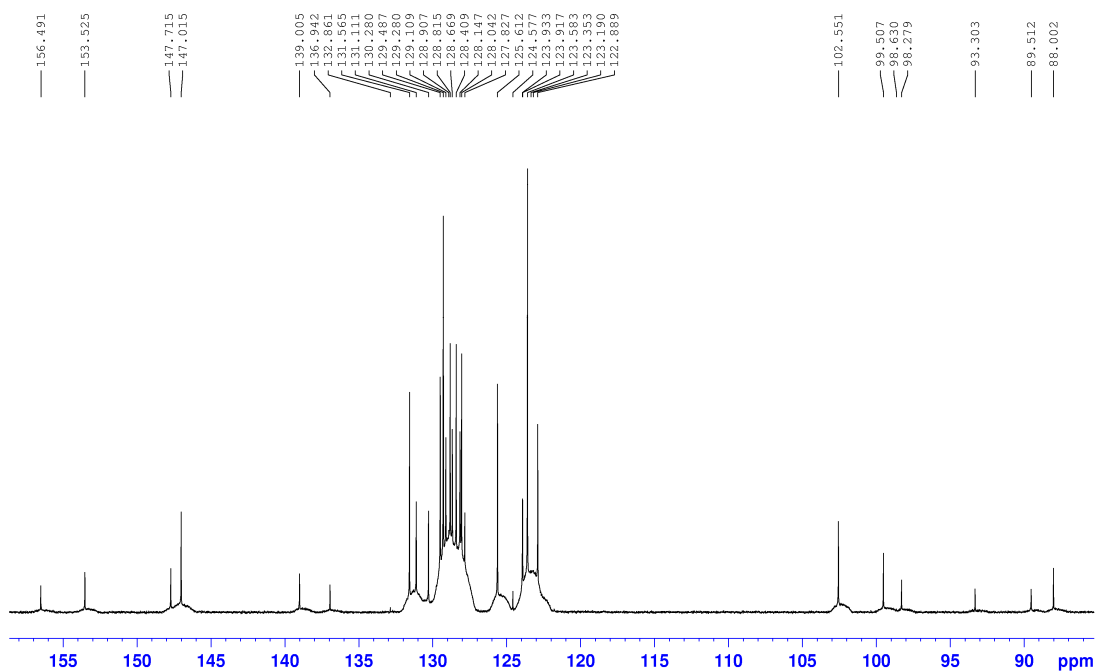


- NMR-Spectra of a *E/Z*-mixture of **1** (600MHz, CD₂Cl₂, 300K):

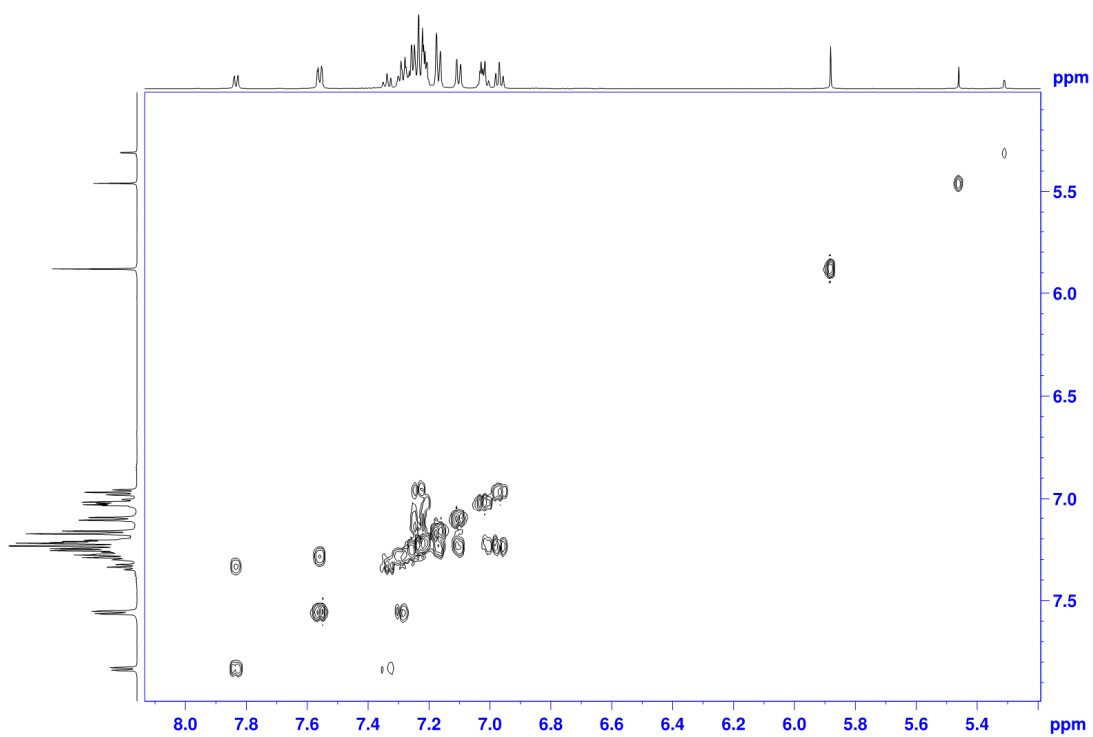
¹H-NMR:



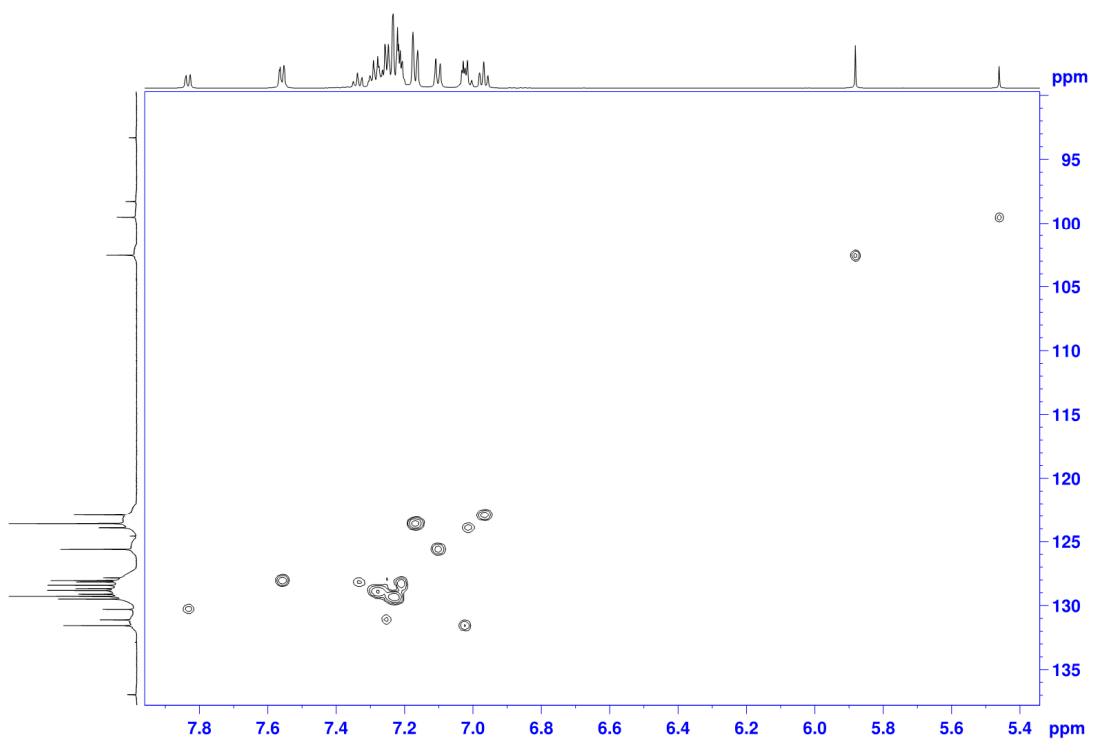
¹³C-NMR:



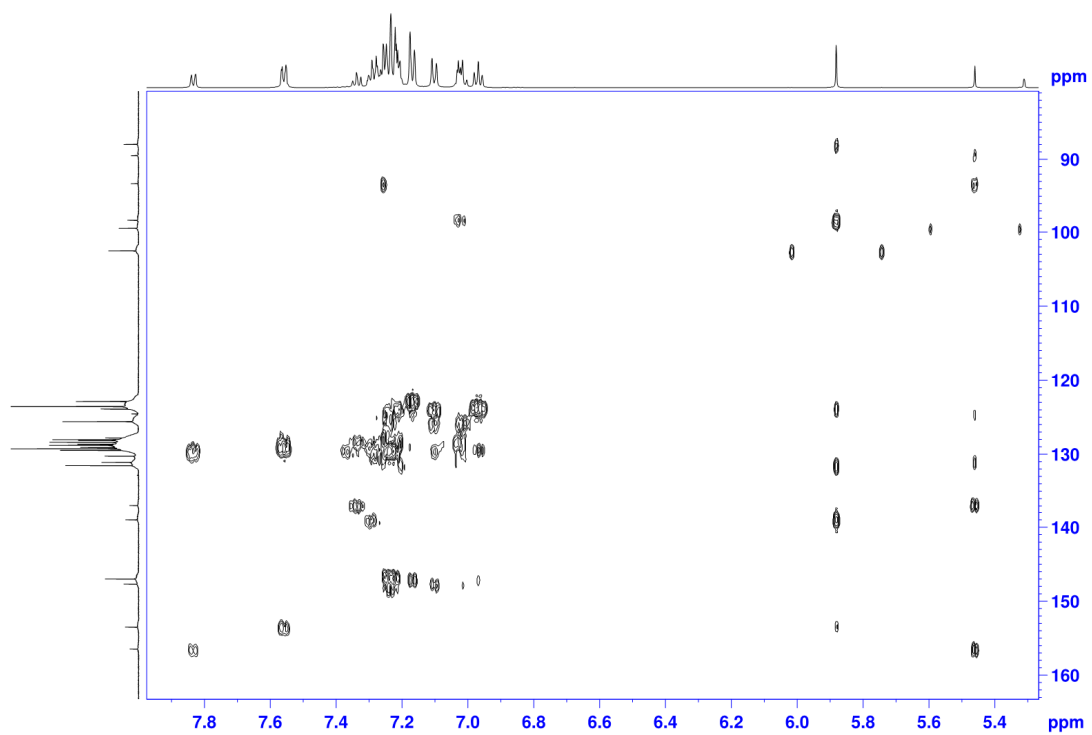
HH-COSY:



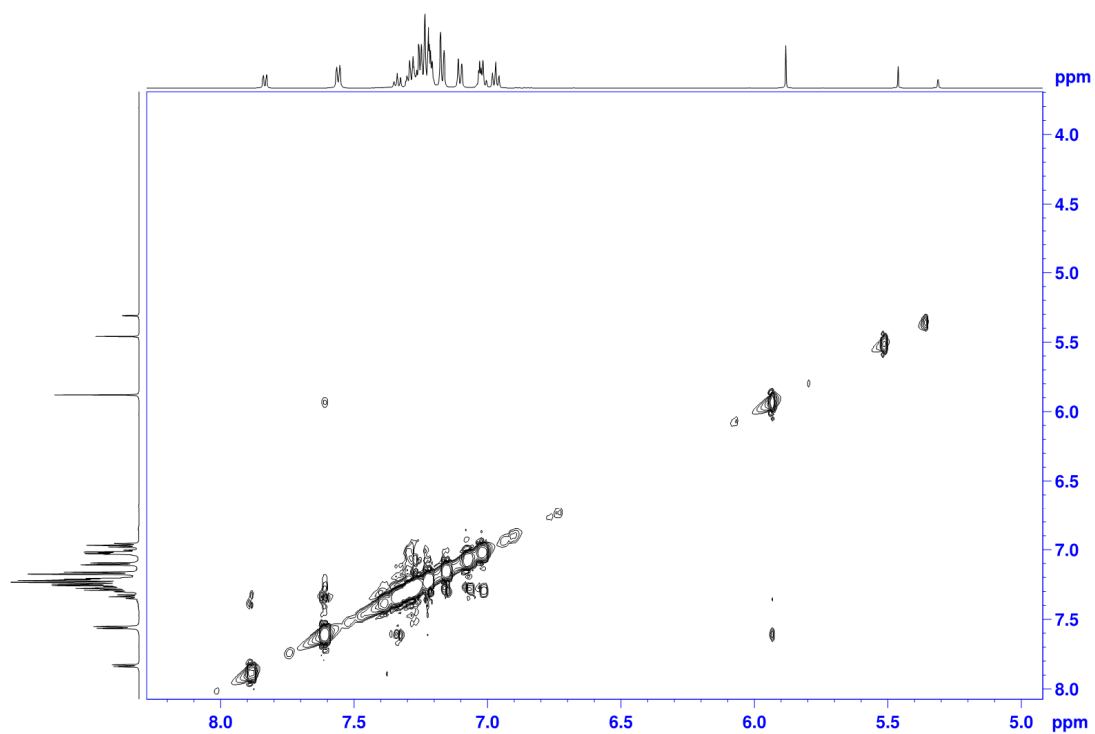
HSQC:



HMBC:



NOESY:



N-[(*E,Z*)-1,4-diphenylbut-1-en-3-ynyl]-*N*-isopropyl-aniline (2)

An equimolar mixture of 1,4-diphenylbutadiyne (556 mg, 2.75 mmol) and *N*-isopropylaniline (0.4 ml, 2.76 mmol) in 10 ml of THF was heated to reflux for 5 h with 4 mol% of [(thf)₄K₂Ca{N(Ph)*i*Pr}₄]. Standard hydrolytic workup and recrystallization from pentane yielded crystalline *E*-isomer while the *Z*-isomer remained as a dark yellow oil.

Yield of *E/Z*-mixture: 91% (isolated).

M.P. of *E*-isomer: 103.8 - 104.3°C.

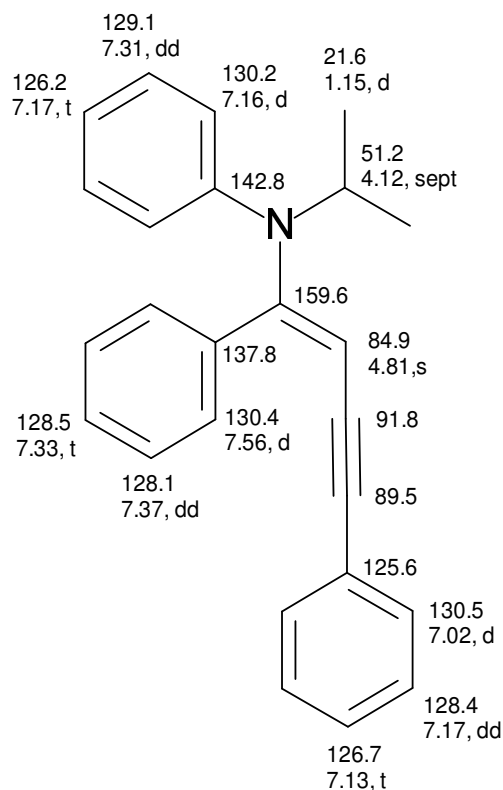
Elemental Analysis (calc.): C 88.80 (88.98), H 6.93 (6.87), N 3.86 (4.15).

DEI-MS: *m/z* (%) 337 (M, 100), 322 (M - CH₃, 53), 294 (M - *i*Pr, 18).

IR: 3434 (w, b), 3057 (m), 3023 (w), 2978 (s), 2181 (vs), 1959 (w), 1888 (w), 1812 (w), 1579 (m), 1550 (vs), 1485 (vs), 1441 (m), 1403 (vs), 1365 (m), 1315 (vs), 1264 (m), 1238 (m), 1118 (vs), 754 (s), 704 (s), 532 (m) cm⁻¹.

NMR investigations:

E-Isomer:

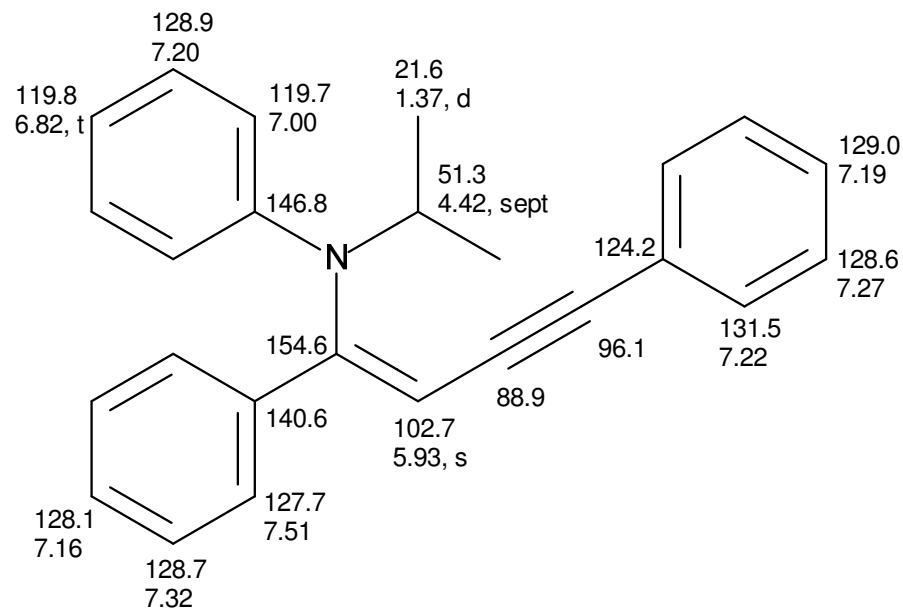


¹H-NMR (CD₂Cl₂, 600 MHz, 300 K): 1.15 (6H, d, *J* = 6.6Hz), 4.12 (1H, sept, *J* = 6.6Hz), 4.81 (1H, s), 7.12 - 7.19 (6H, m), 7.30 - 7.33 (3H, m), 7.37 (2H, t, *J* = 7.8Hz), 7.56 (2H, d, *J* = 7.2Hz) ppm.

¹³C{¹H}-NMR (CD₂Cl₂, 150 MHz, 300 K): 21.6, 51.2, 84.9, 89.5, 91.8, 125.6, 126.2, 126.7, 128.1, 128.4, 128.5, 129.1, 130.2, 130.4, 130.5, 137.8, 142.8, 159.6 ppm.

$^1\text{H-NMR}$ ($[\text{D}_8]$ THF, 200 MHz, 300 K): 1.17 (6H, d, $J = 6.3\text{Hz}$), 4.10 (1H, sept, $J = 6.6\text{Hz}$), 4.80 (1H, s), 6.97-7.60 (15H, m, Ph) ppm

Z-Isomer:

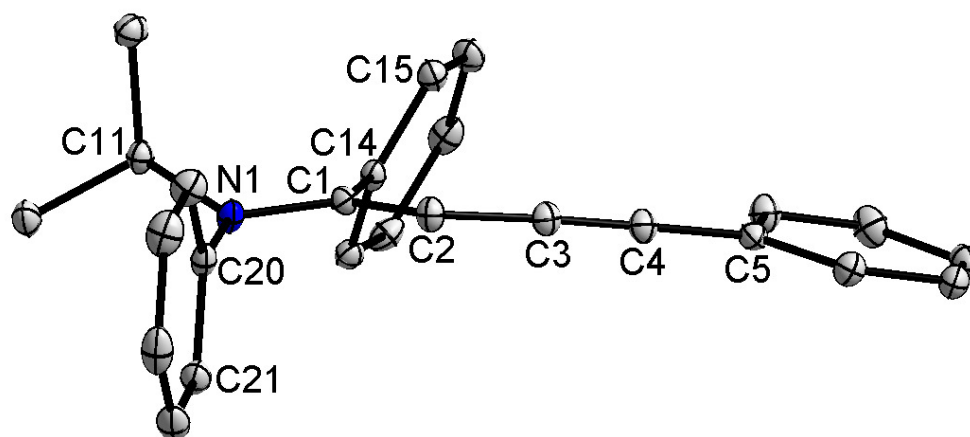


$^1\text{H-NMR}$ (CD_2Cl_2 , 400 MHz, 300 K): 1.37 (6H, d, $J = 6.4\text{Hz}$), 4.42 (1H, sept, $J = 6.4\text{Hz}$), 5.93 (1H, s), 6.82 (1H, t, $J = 7.2$), 7.00 (2H, d, $J = 7.8\text{Hz}$), 7.13 - 7.39 (10 H, m), 7.51 (2H, d, $J = 7.2\text{Hz}$) ppm.

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (CD_2Cl_2 , 150 MHz, 300 K): 21.6, 51.3, 88.9, 96.1, 102.7, 119.7, 119.8, 124.2, 127.7, 128.1, 128.6, 128.7, 128.9, 129.0, 131.5, 140.6, 146.8, 154.6 ppm.

$^1\text{H-NMR}$ ($[\text{D}_8]$ -THF, 200 MHz, 300 K): 1.26 (6H, d, $J = 6.7\text{Hz}$), 4.42 (1H, sept, $J = 6.7\text{Hz}$), 6.01 (1H, s), 6.71-7.60 (15H, m, Ph) ppm

Structural Data of the E-2:



Selected bond lengths [pm]: C1-C2 136.4(1), C2-C3 142.0(1), C3-C4 120.4(2), C4-C5 143.3(1), N1-C1 138.0(1), N1-C11 148.7(1), N1-C20 143.9(1), C1-C14 149.3(1).

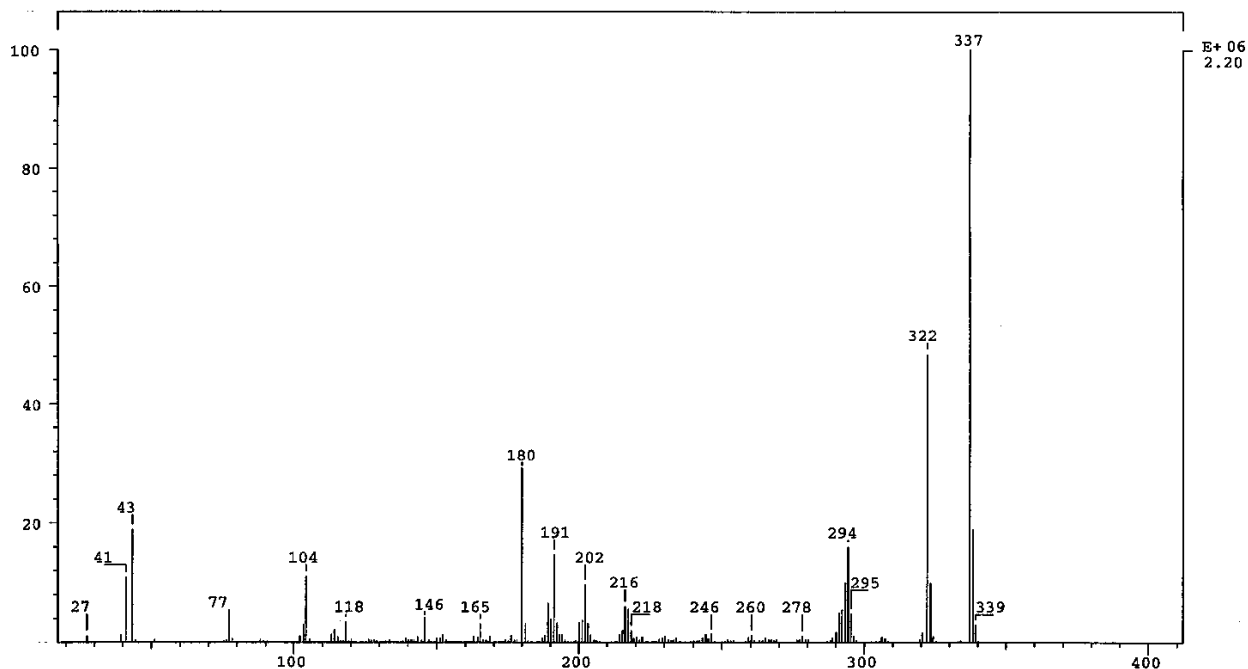
Selected bond angles [°]: C1-N1-C20 117.65(8), C20-N1-C11 119.07(8), C11-N1-C1 120.43(8), N1-C1-C14 117.54(8), C14-C1-C2 118.83(9), C2-C1-N1 123.49(9), C3-C4-C5 174.26(11).

Selected torsion angles [°]: C2-C1-C14-C15 61.8, C1-N1-C20-C21 90.2.

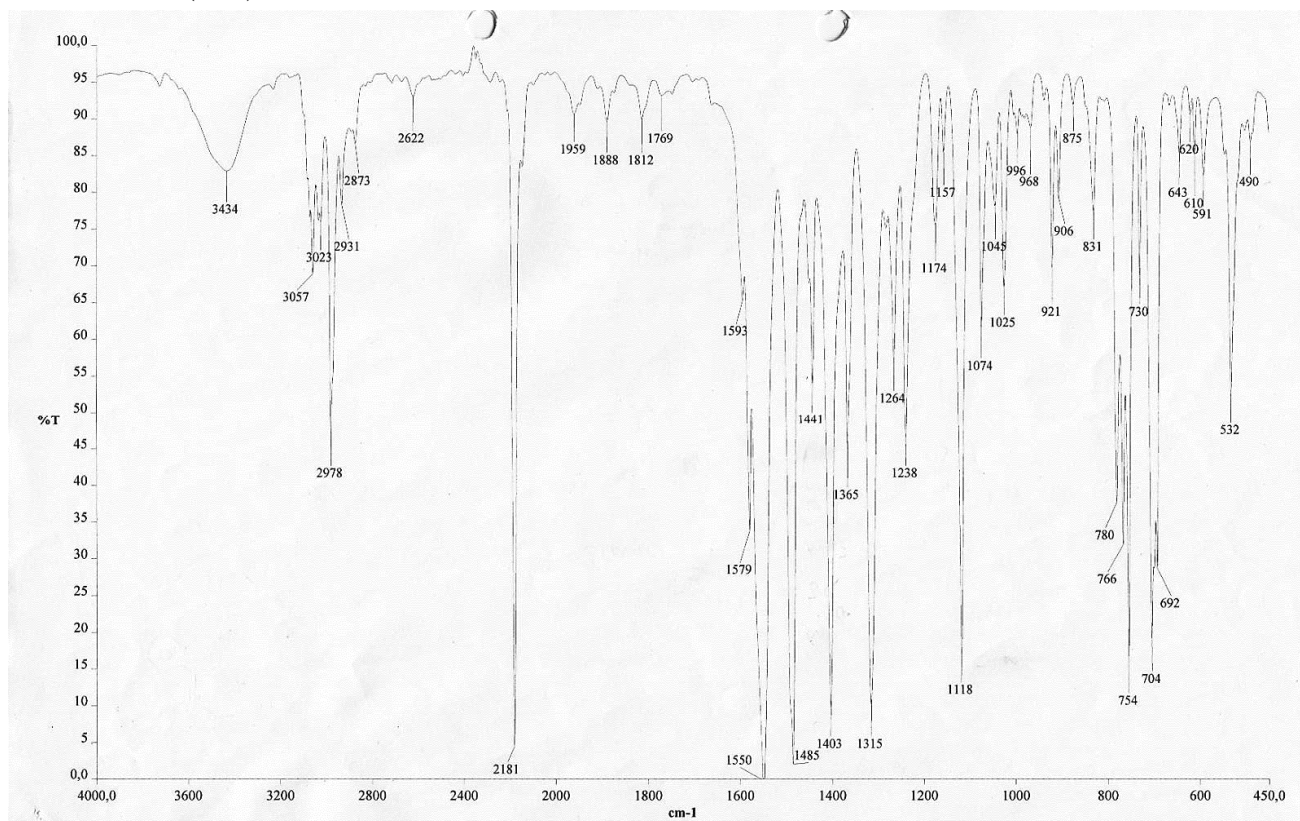
Crystal Data for E-2: C₂₅H₂₃N, Mr = 337.44 gmol⁻¹, light yellow prism, size 0.06 x 0.06 x 0.04 mm³, monoclinic, space group P 2₁/c, a = 9.7453(2), b = 11.3478(2), c = 17.3880(2) Å, β = 94.617(1)°, V = 1916.66(6) Å³, T = -140 °C, Z = 4, ρ_{calcd.} = 1.169 gcm⁻³, μ (Mo-K_α) = 0.67 cm⁻¹, F(000) = 720, 11729 reflections in h(-10/12), k(-14/14), l(-22/21), measured in the range 2.93° ≤ Θ ≤ 27.45°, completeness Θ_{max} = 99.2%, 4345 independent reflections, R_{int} = 0.0208, 3894 reflections with F_o > 4σ(F_o), 327 parameters, 0 restraints, R_{1obs} = 0.0389, wR²_{obs} = 0.0946, R_{1all} = 0.0444, wR²_{all} = 0.0994, GOOF = 1.012, largest difference peak and hole: 0.257 / -0.168 e Å⁻³.

Spectra of 2

- DEI-MS:

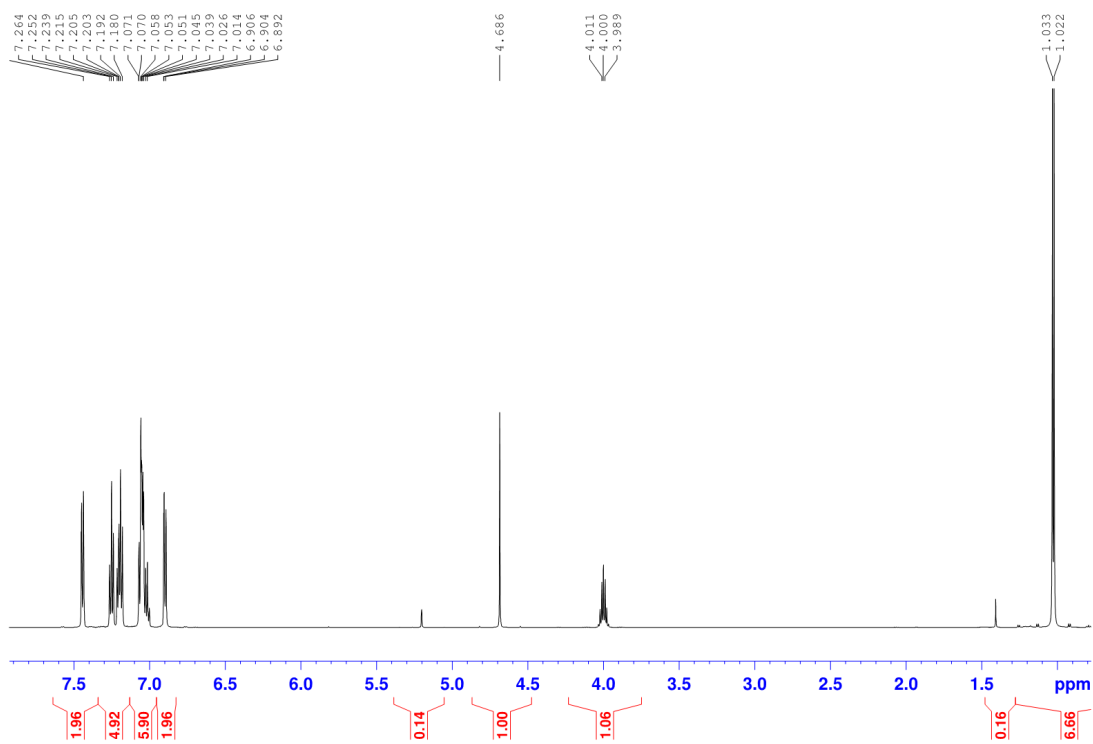


• IR (KBr):

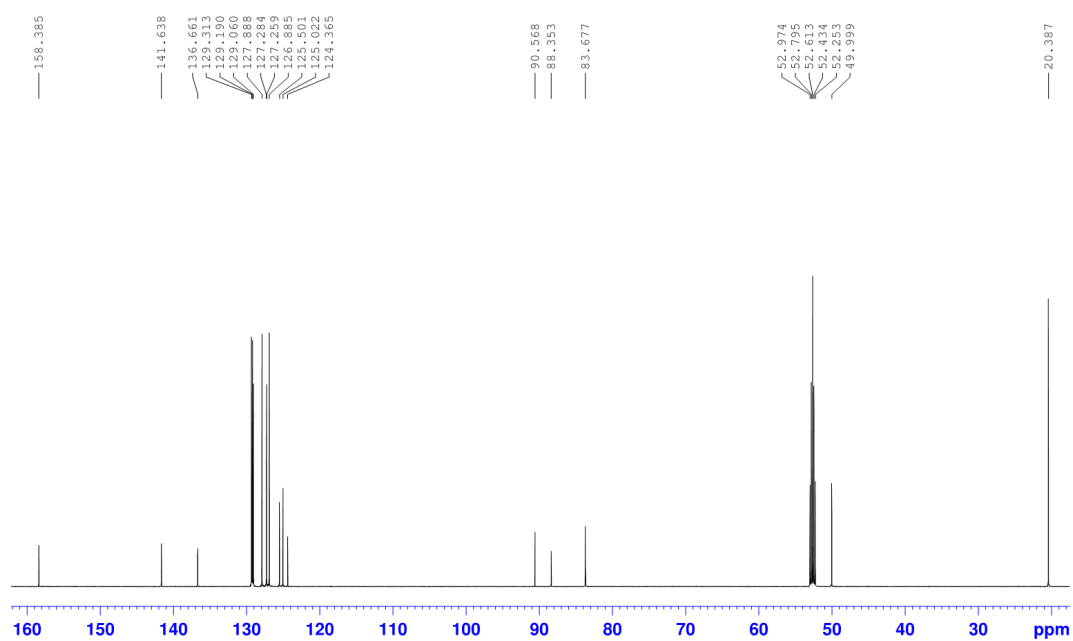


• NMR-Spectra of *E-2* (600MHz, CD₂Cl₂, 294K):

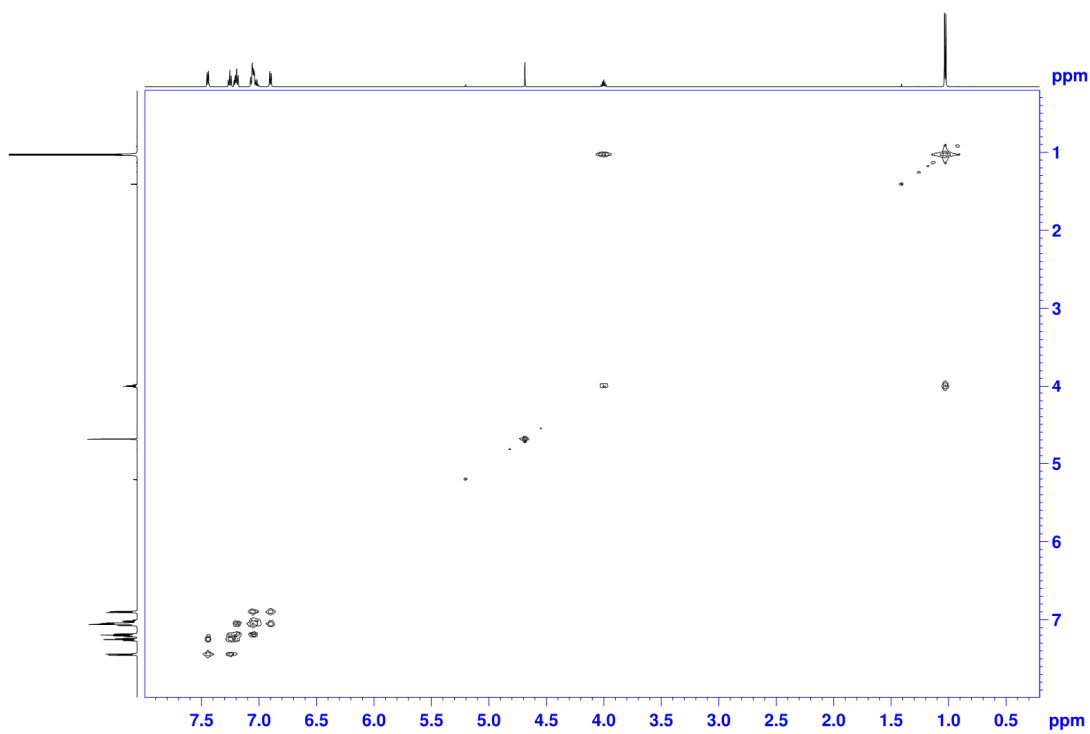
¹H-NMR:



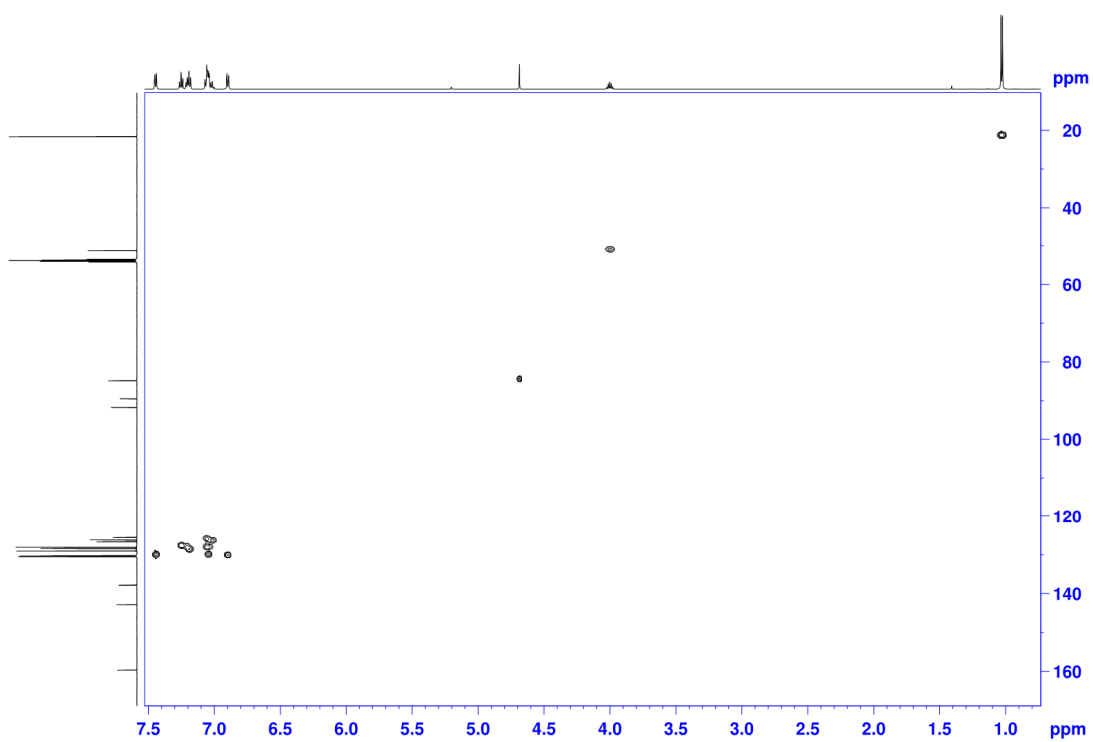
^{13}C -NMR:



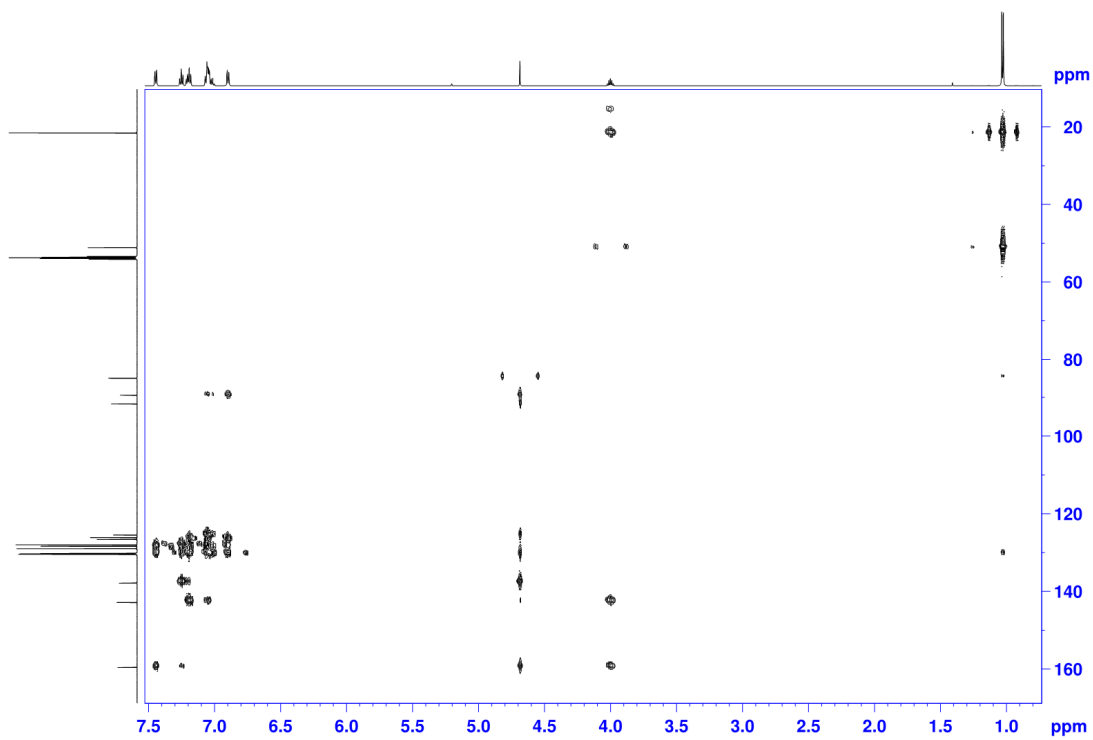
HH-COSY:



HSQC:

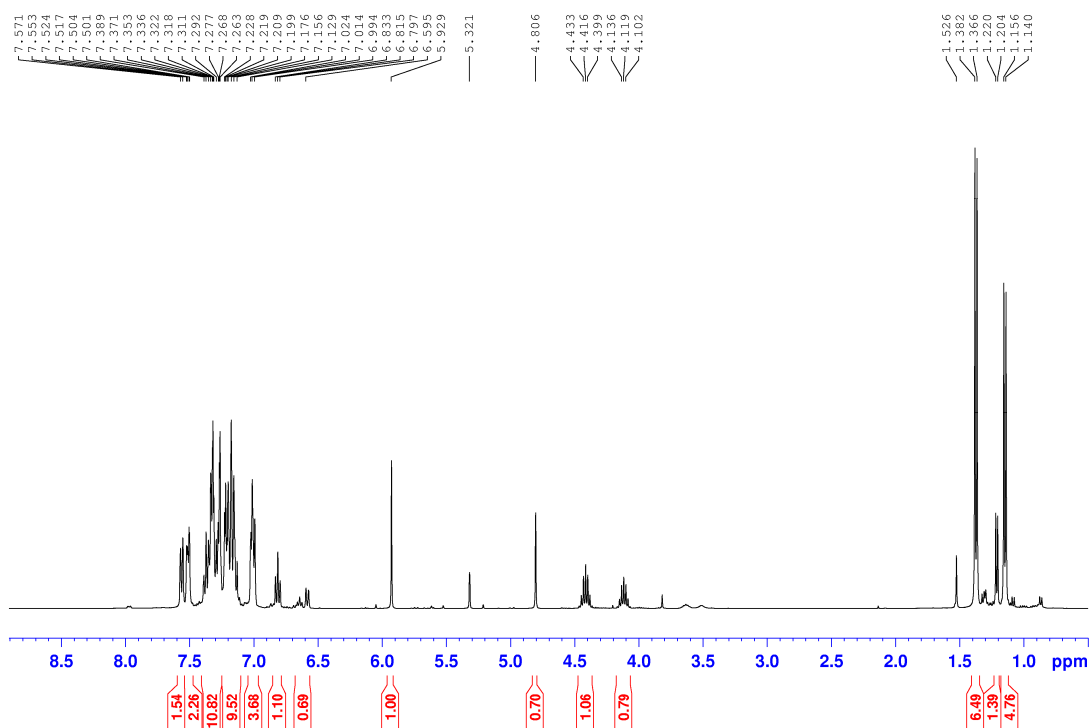


HMBC:

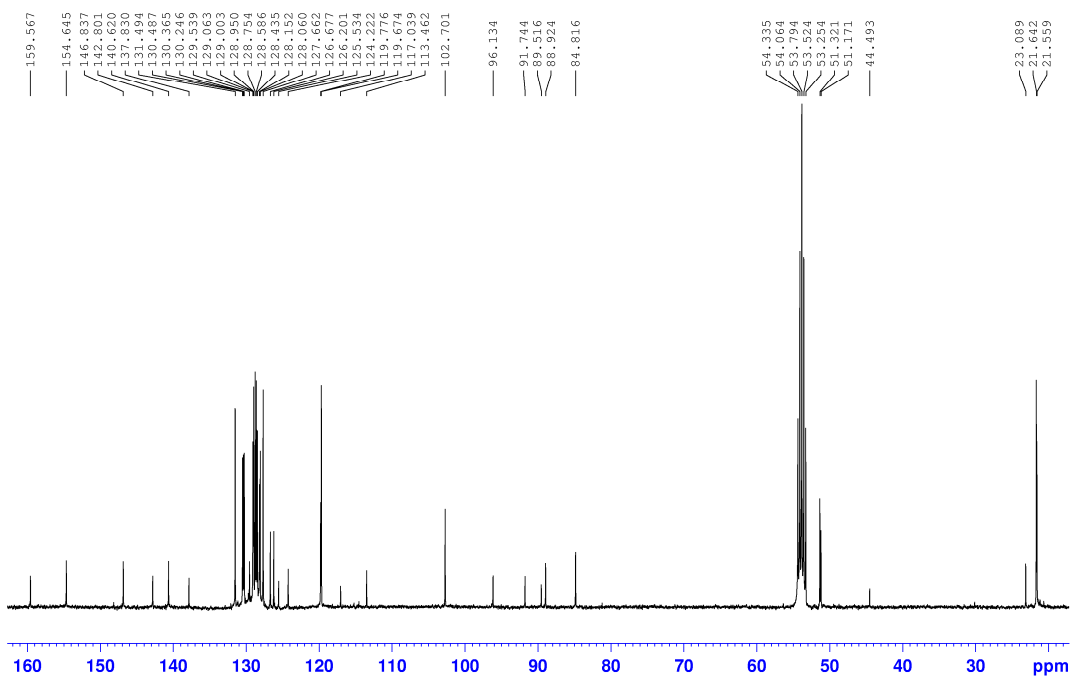


- NMR-Spectra of a *E/Z*-mixture of **2** (400MHz, CD₂Cl₂, 300K):

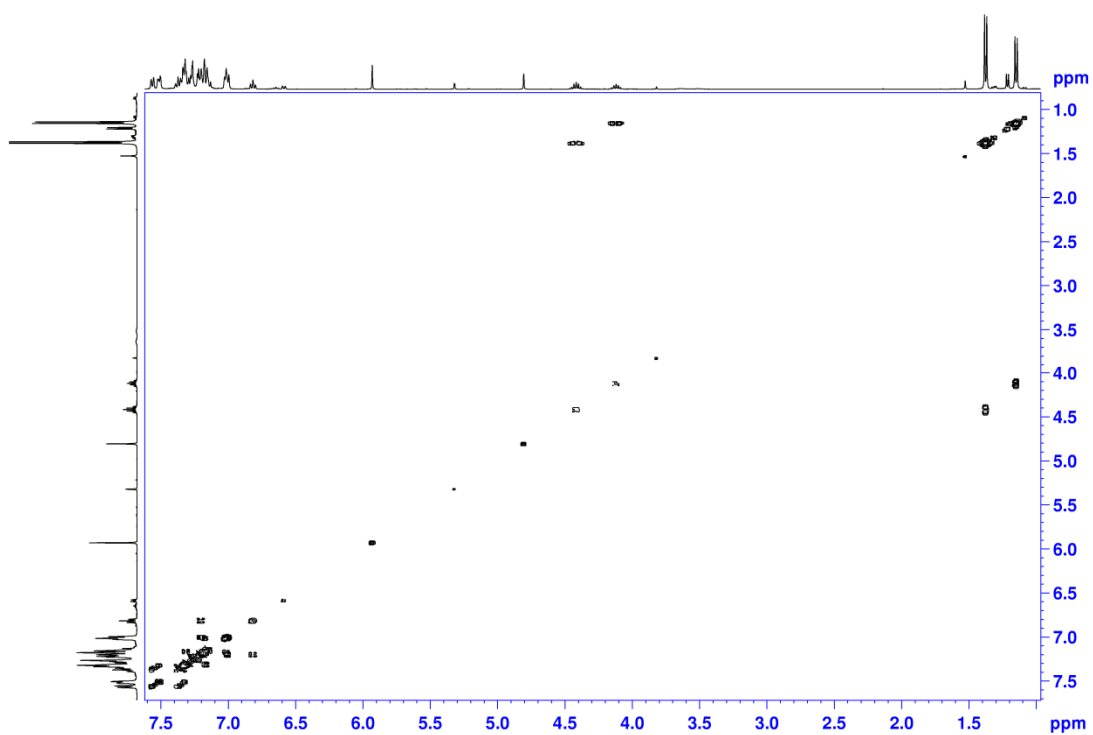
¹H-NMR:



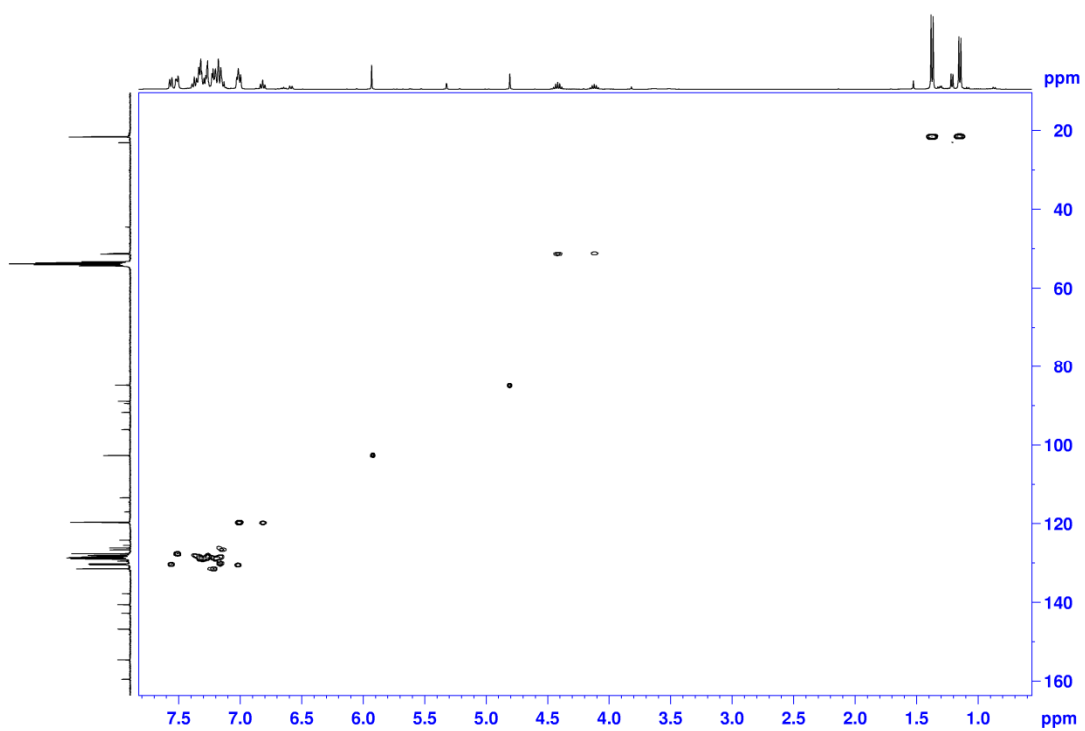
¹³C-NMR:



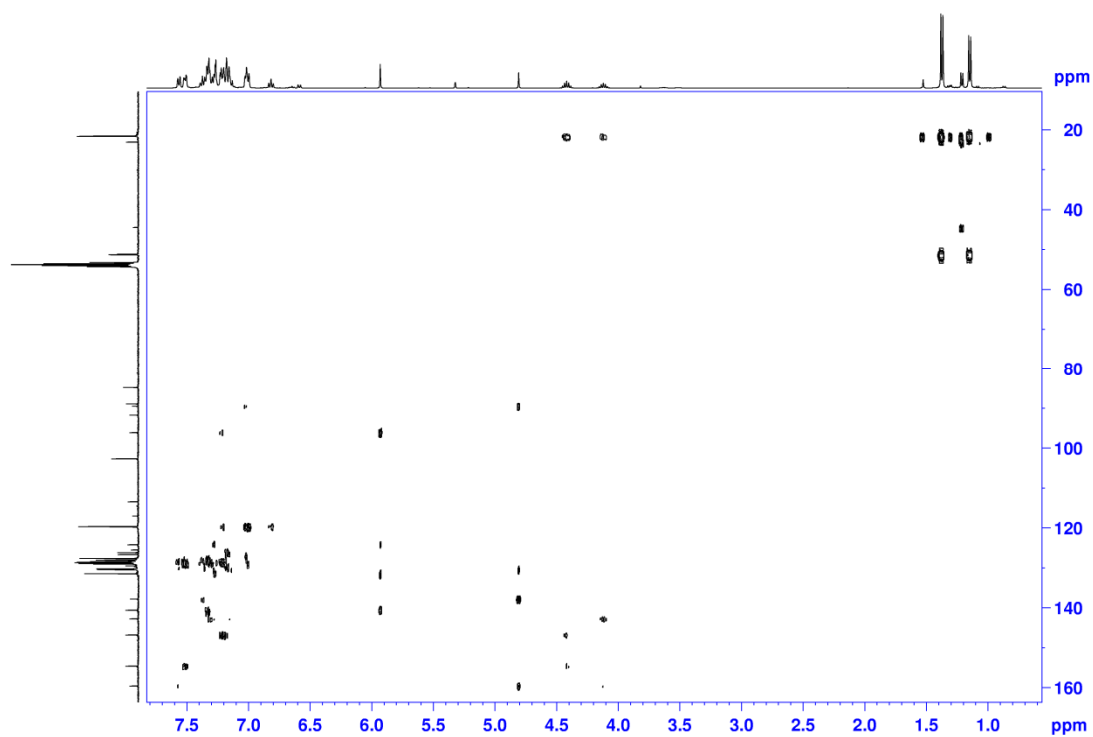
HH-COSY:



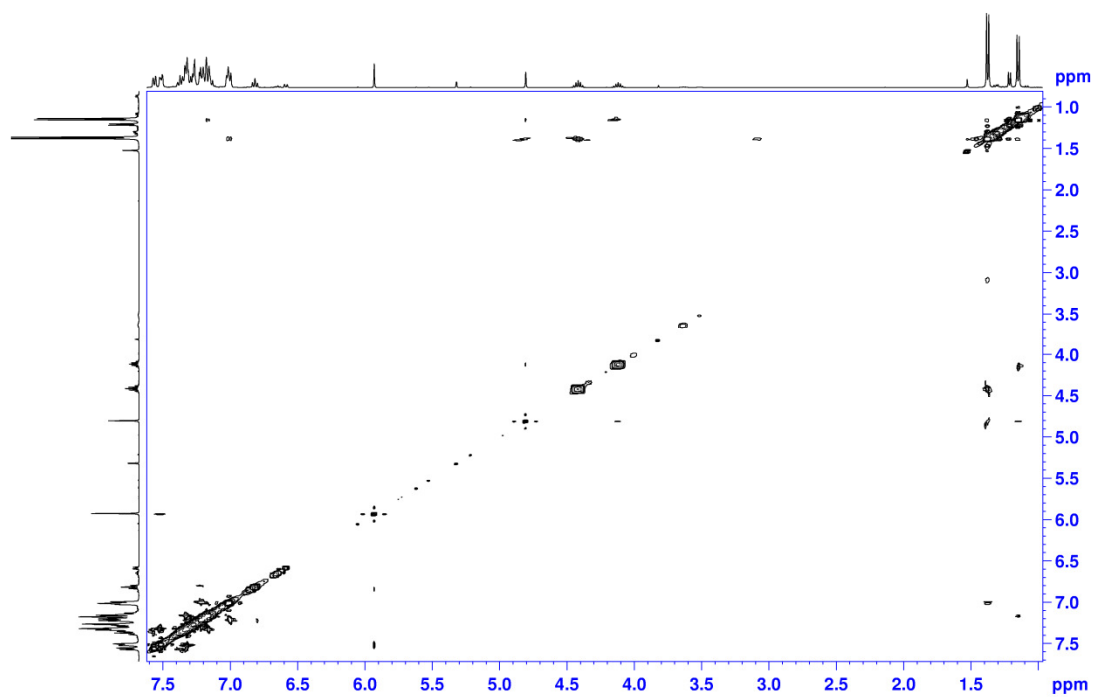
HSQC:



HMBC:



NOESY:



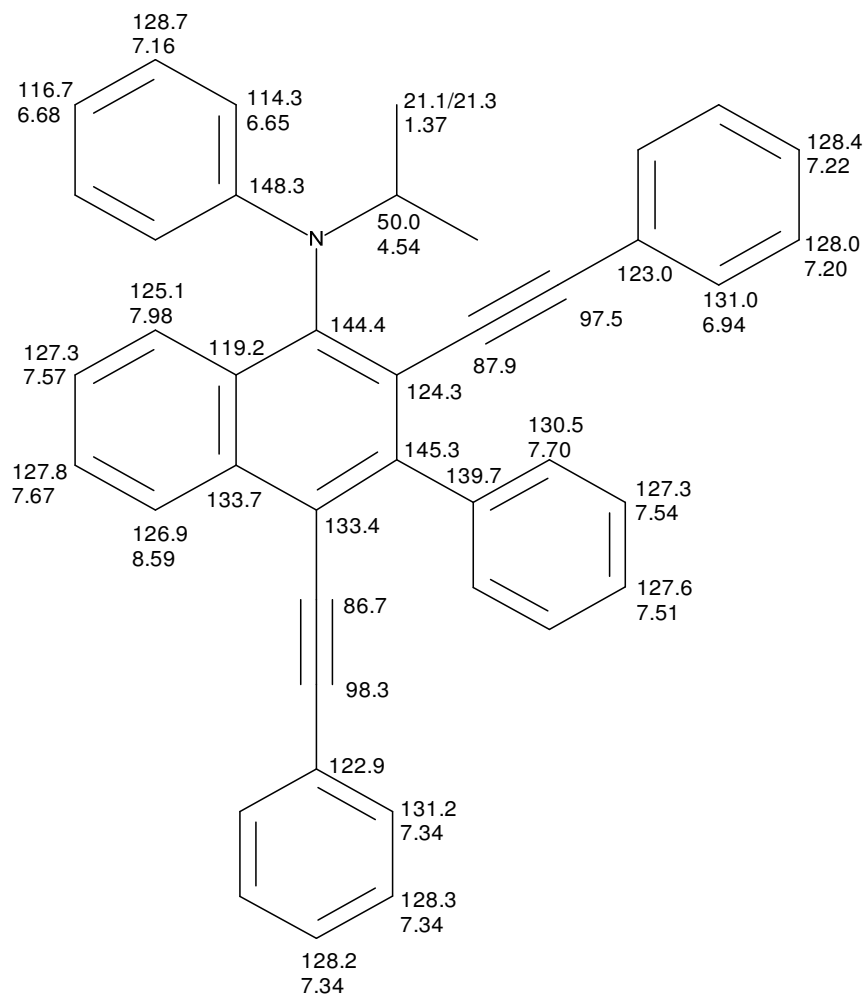
***N*-isopropyl-*N*,3-diphenyl-2,4-bis(2-phenylethynyl)naphthalen-1-amine (3)**

An equimolar mixture of 1,4-diphenylbutadiyne (200 mg, 1.0 mmol) and *N*-Isopropylaniline (135 mg, 145 µl, 1.0 mmol) in 5 ml of THF was heated to reflux for 5 h after addition of 20 mol-% of KN(Ph)*i*Pr (30 mg, 0.2 mmol) to give a dark solution and a black residue. Standard hydrolytic workup procedures including column chromatography over aluminium oxide with heptane/ethyl acetate (40:1) yielded yellow **3**. Crystals suitable for SCXRD could be obtained from a pentane solution.

Yield: 16mg (0.03mmol, 14.6%)

DEI-MS: m/z (%) 537 (M^+ , 1.5), 522 ($M^+ - \text{CH}_3$, 10), 43 (*i*Pr, 100).

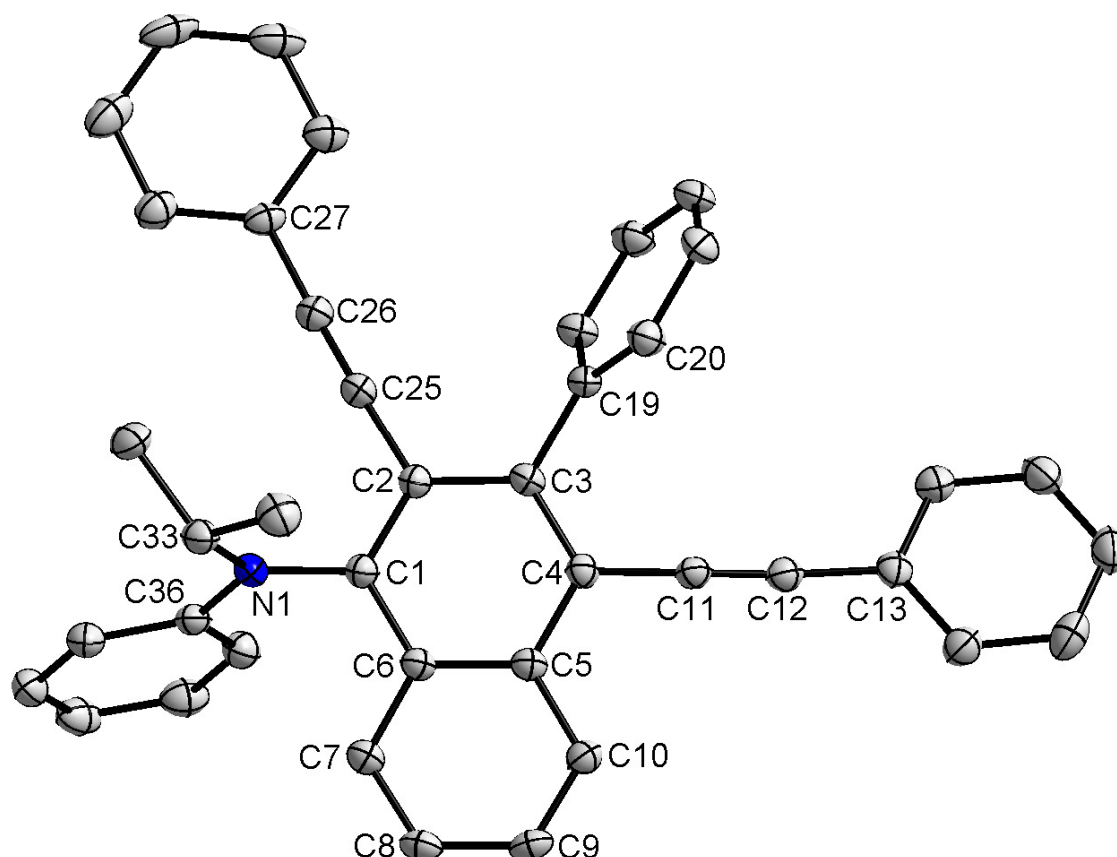
NMR investigations:



$^1\text{H-NMR}$ (CD_2Cl_2 , 400 MHz, 300 K): 1.34 (6H, 2 d), 4.54 (1H, sept, $J = 5.6\text{Hz}$), 6.65 (2H, d, $J = 8.4\text{ Hz}$), 6.68 (1H, t, $J = 7.3\text{Hz}$), 6.93 (2H, d, $J = 6.7\text{ Hz}$), 7.13 - 7.25 (5H, m), 7.34 (5H, m), 7.49 - 7.57 (4H, m), 7.67 (1H, t, $J = 7.6\text{ Hz}$), 7.70 (2H, d, $J = 7.6\text{ Hz}$), 7.98 (1H, d, $J = 8.4\text{ Hz}$), 8.59 (1H, d, $J = 8.4\text{Hz}$) ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (CD_2Cl_2 , 100 MHz, 300 K): 21.1, 21.3, 50.0, 86.7, 87.9, 97.5, 98.3, 114.2, 116.7, 119.2, 122.9, 123.0, 124.3, 125.1, 126.9, 127.3 (2C), 127.6, 127.8, 128.0, 128.2, 128.3, 128.4, 128.7, 130.5, 131.0, 131.2, 133.4, 133.7, 139.7, 144.4, 145.3, 148.3 ppm.

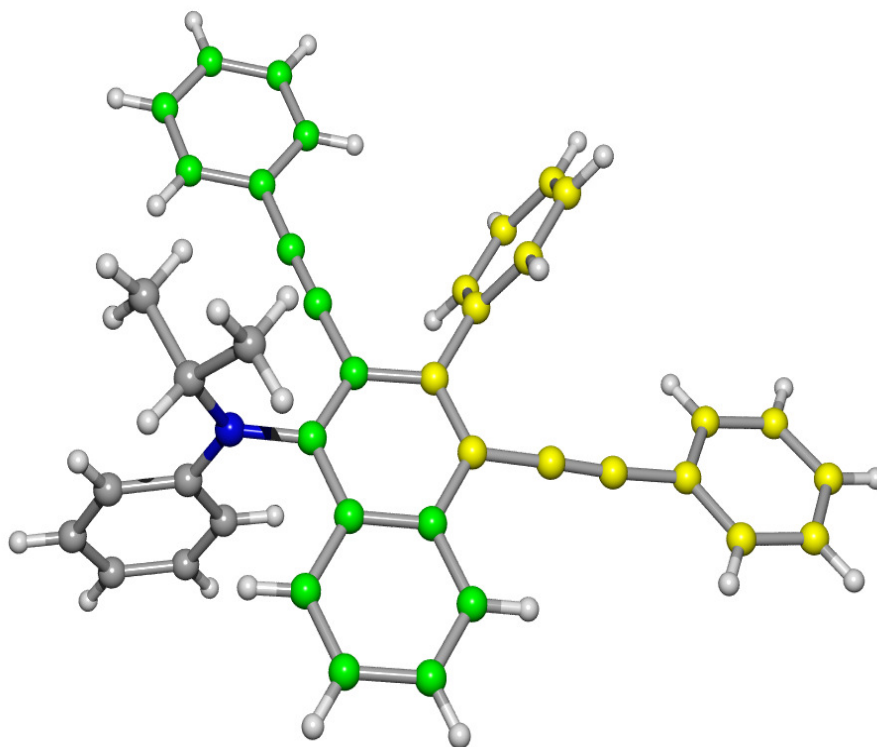
Structural Data:



Selected bond lengths [pm]: N1-C1 142.4(2), N1-C33 148.1(2), N1-C36 139.4(2), C1-C2 138.7(2), C2-C3 143.3(2), C3-C4 139.2(2), C4-C5 143.2(2), C5-C6 142.1(2), C6-C1 142.8(2), C6-C7 141.9(2), C7-C8 137.3(3), C8-C9 140.7(3), C9-C10 136.9(3), C10-C5 142.1(2), C4-C11 143.2(2), C11-C12 120.0(3), C12-C13 143.3(2), C3-C19 149.0(2), C2-C25 143.3(2), C25-C26 120.0(3), C26-C27 143.2(2).

Selected bond angles [°]: C1-N1-C36 118.68(14), C36-N1-C33 120.38(14), C33-N1-C1 119.76(14).

Selected torsion angles [°]: C2-C1-N1-C33 86.7, C4-C3-C19-C20 63.7.



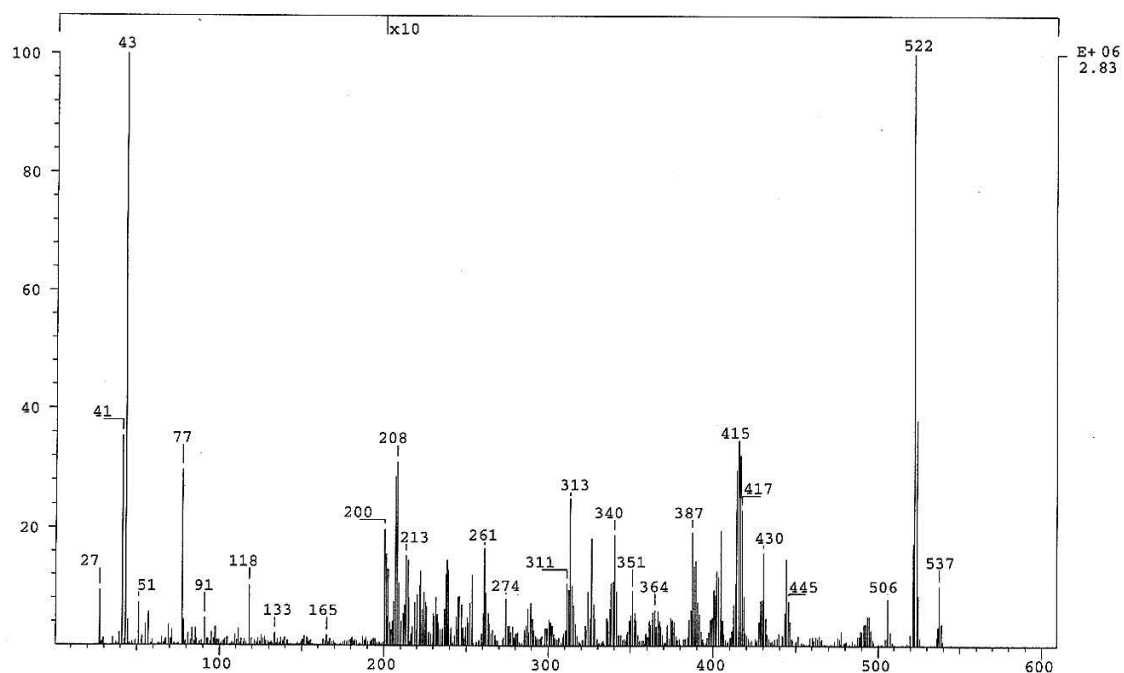
This Figure clarifies the combination of two butadiyne units (yellow and green) and one isopropylamine (C grey, N blue) forming a substituted naphthalene.

Crystal Data for 3 :

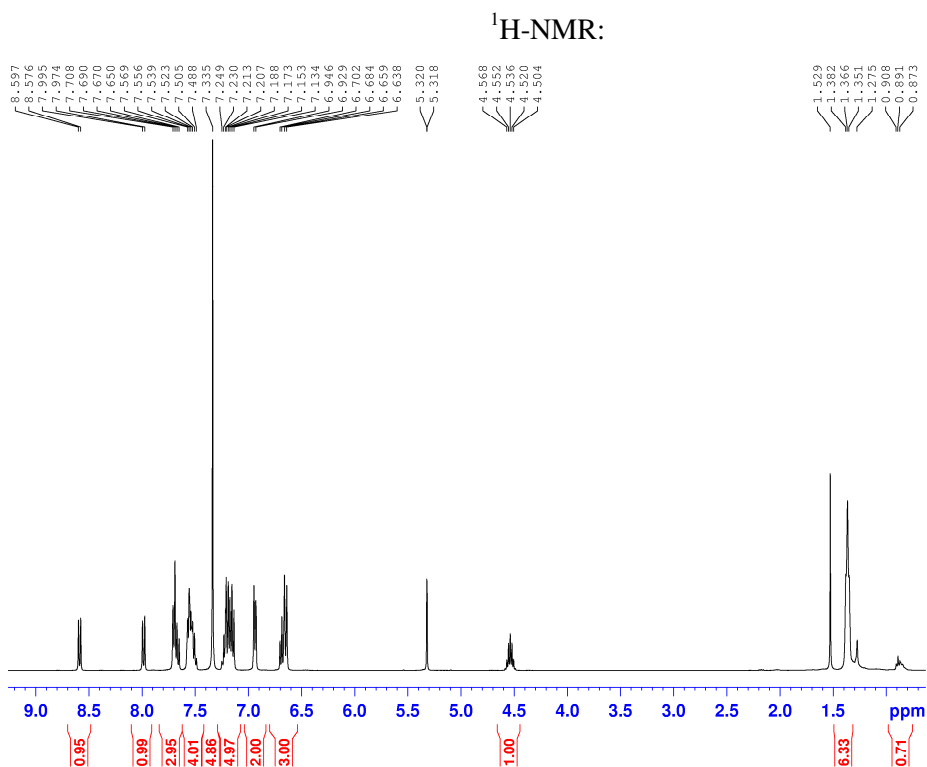
$C_{41}H_{31}N$, Mr = 537.67 g mol^{-1} , light yellow prism, size 0.07 x 0.06 x 0.05 mm^3 , triclinic, space group $P\bar{1}$, a = 10.0932(3), b = 11.9758(3), c = 13.0546(3) Å, $\alpha = 78.709(2)$, $\beta = 71.546(2)$, $\gamma = 89.447(1)^\circ$, V = 1465.53(7) Å³, T = -140 °C, Z = 2, $\rho_{\text{calcd.}} = 1.218 \text{ g cm}^{-3}$, $\mu (\text{Mo-K}\alpha) = 0.7 \text{ cm}^{-1}$, F(000) = 568, 9330 reflections in h(-11/13), k(-15/15), l(-16/16), measured in the range $2.67^\circ \leq \Theta \leq 27.52^\circ$, completeness $\Theta_{\text{max}} = 97.6\%$, 6589 independent reflections, $R_{\text{int}} = 0.0266$, 5588 reflections with $F_o > 4\sigma(F_o)$, 381 parameters, 0 restraints, $R1_{\text{obs}} = 0.0624$, $wR^2_{\text{obs}} = 0.1335$, $R1_{\text{all}} = 0.0757$, $wR^2_{\text{all}} = 0.1410$, GOOF = 1.077, largest difference peak and hole: 0.382 / -0.234 $e \text{ \AA}^{-3}$.

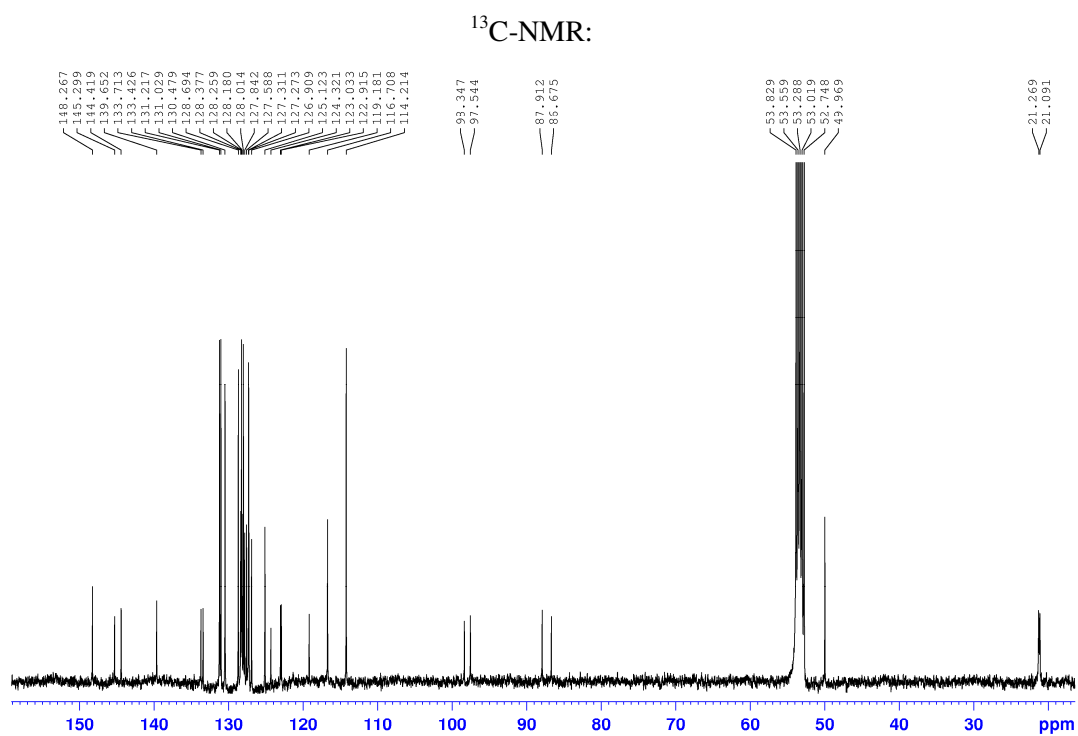
Spectra of 3

- DEI-MS:

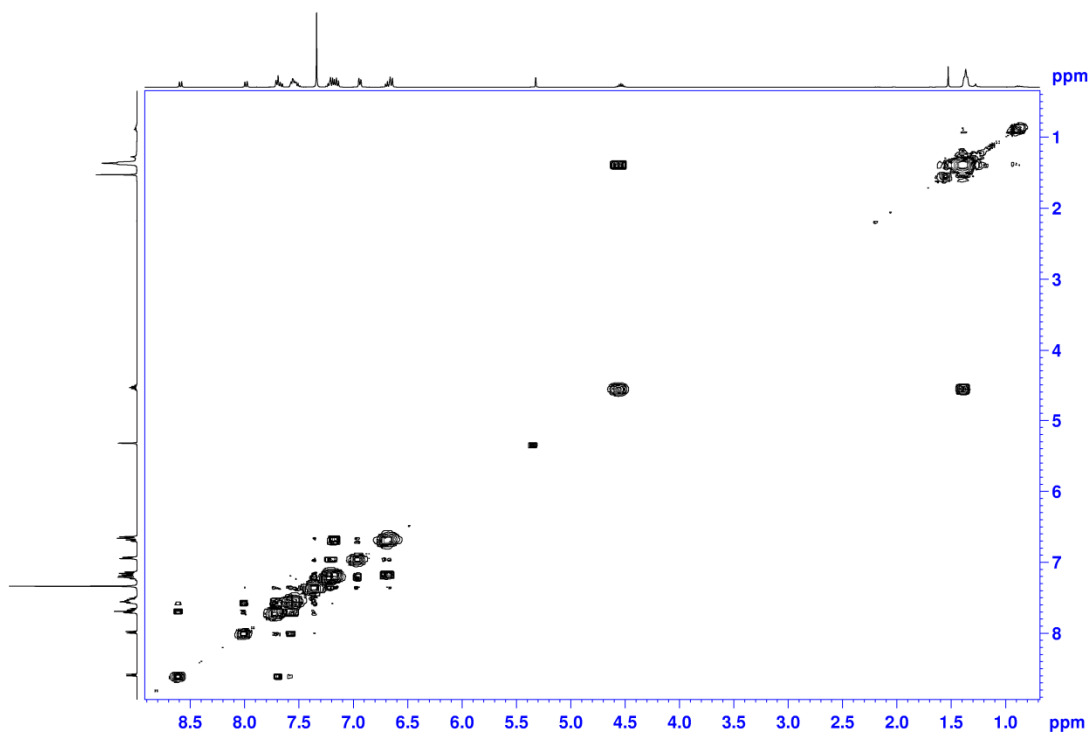


- NMR-Spectra of 3 (400MHz, CD₂Cl₂, 300K):

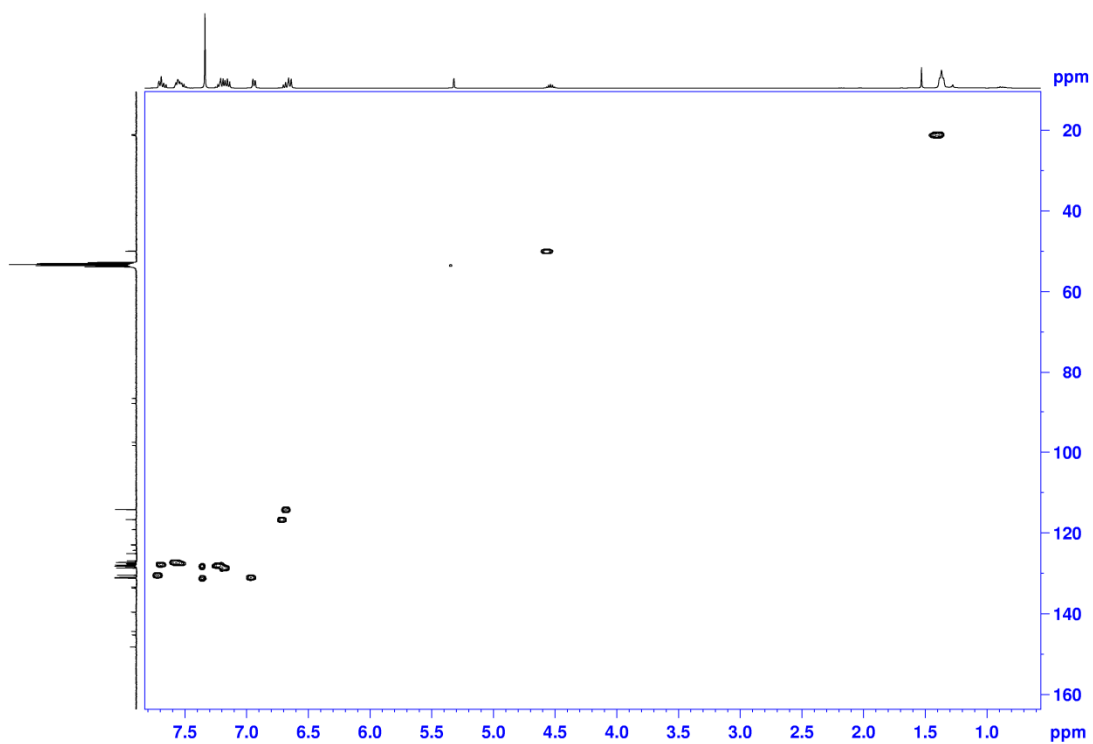




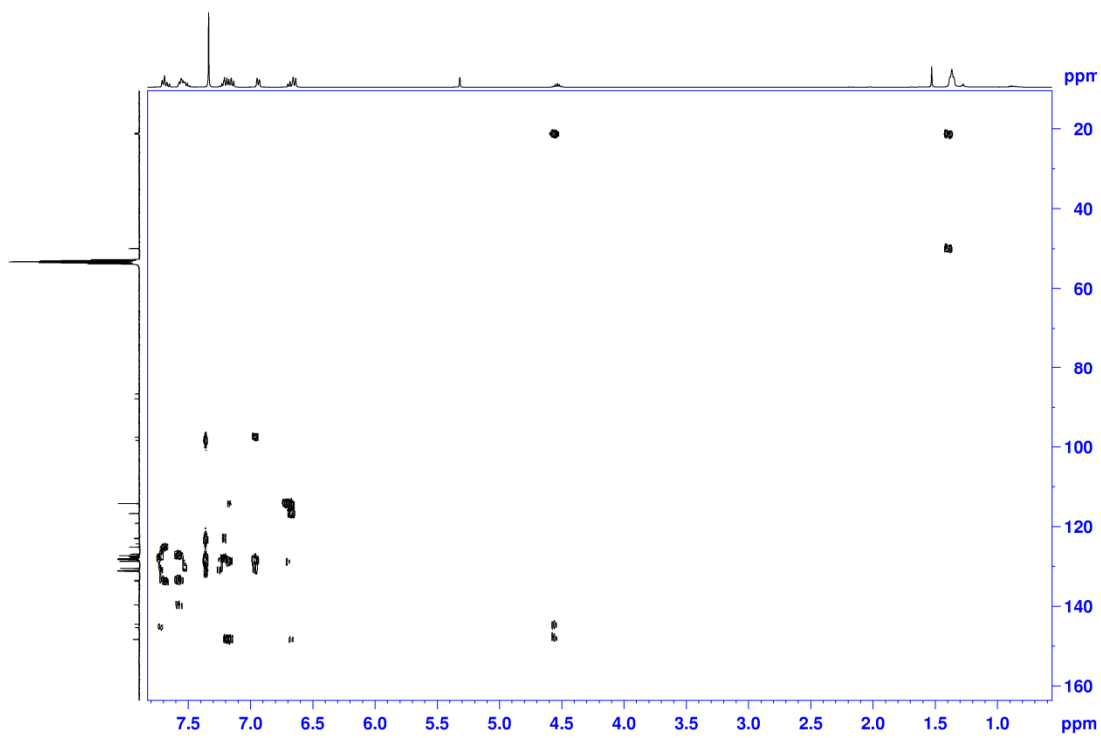
HH-COSY:



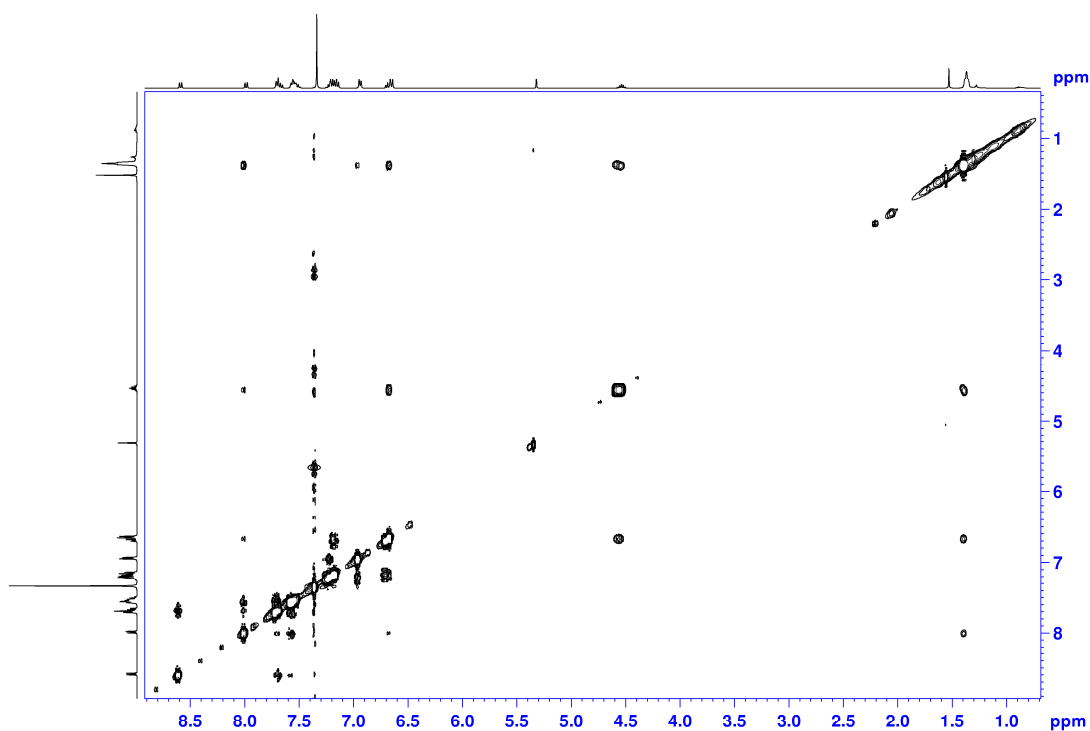
HSQC:



HMBC:



NOESY:



Investigations on NMR-scale:

General Procedure:

A sealable NMR-tube was charged with the metal complexes before a solution of starting materials in deuterated THF was added. Heating was performed by either direkt heating in the spectrometer (50°C) or by storage in a drying oven (60-65°C).

Yields were calculated by setting the aromatic area of the ¹H-NMR (consisting of starting material signals, product signals and metal complex signals) in relation to the product C=CH-protons under consideration of the metal complexes concentration.

Table 1:

Intermolecular hydroamination of diphenylbutadiyne with HNPh₂ (equimolar ratio) in THF at 65 °C yielding *E/Z*-1.

Catalyst	Mol-%	Time/h	Yield/%	Z/E ratio
KNPh ₂	8	regardless	0	-
Ca(NPh ₂) ₂	15	regardless	0	-
K ₂ Ca(NPh ₂) ₄	1	8	0	-
K ₂ Ca(NPh ₂) ₄	2	2	20.2	1:1.40
K ₂ Ca(NPh ₂) ₄	2	8	66.3	1:1.06
K ₂ Ca(NPh ₂) ₄	2	14	72.8	1:0.76
K ₂ Ca(NPh ₂) ₄	5	2	56.9	1:1.18
K ₂ Ca(NPh ₂) ₄	5	8	86.7	1:0.60
K ₂ Ca(NPh ₂) ₄	5	14	81.3	1:0.44
K ₂ Ca(NPh ₂) ₄	9	2	30.8	1:1.39
K ₂ Ca(NPh ₂) ₄	9	8	75.3	1:0.93

- Example of a NMR-spectrum showing product signals:

conditions: 5 mol% K₂Ca(NPh₂)₄ after 8h at 65°C (200MHz, [D₈]THF, 300K)

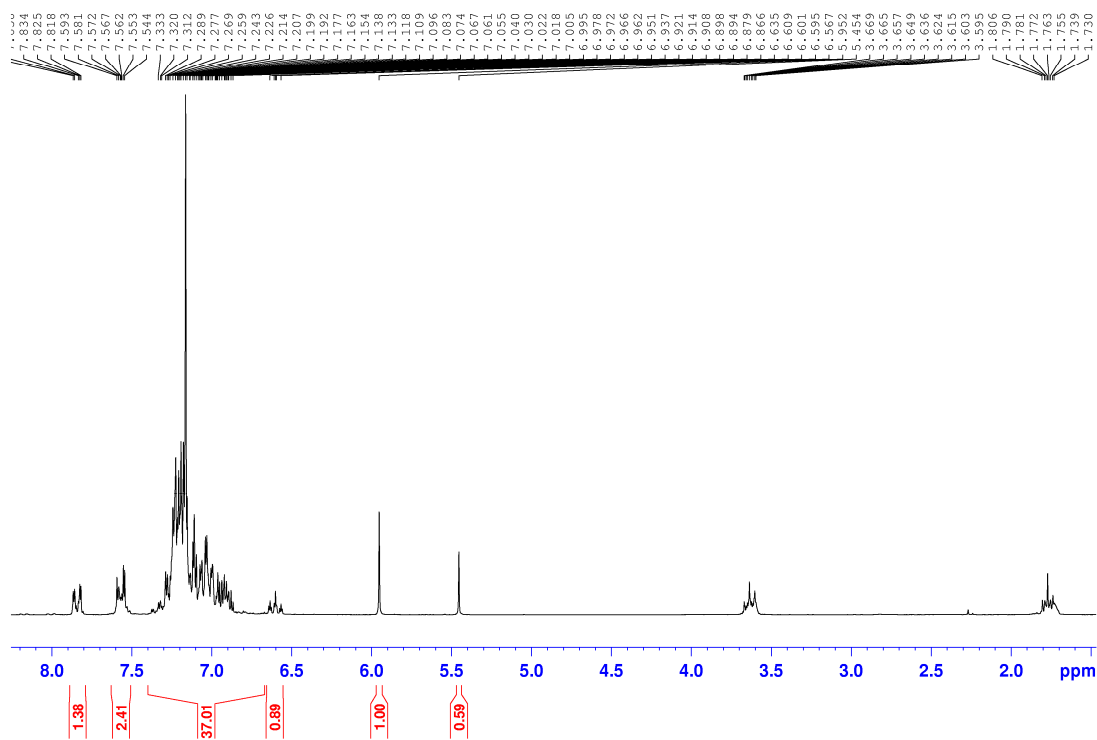


Table 2:

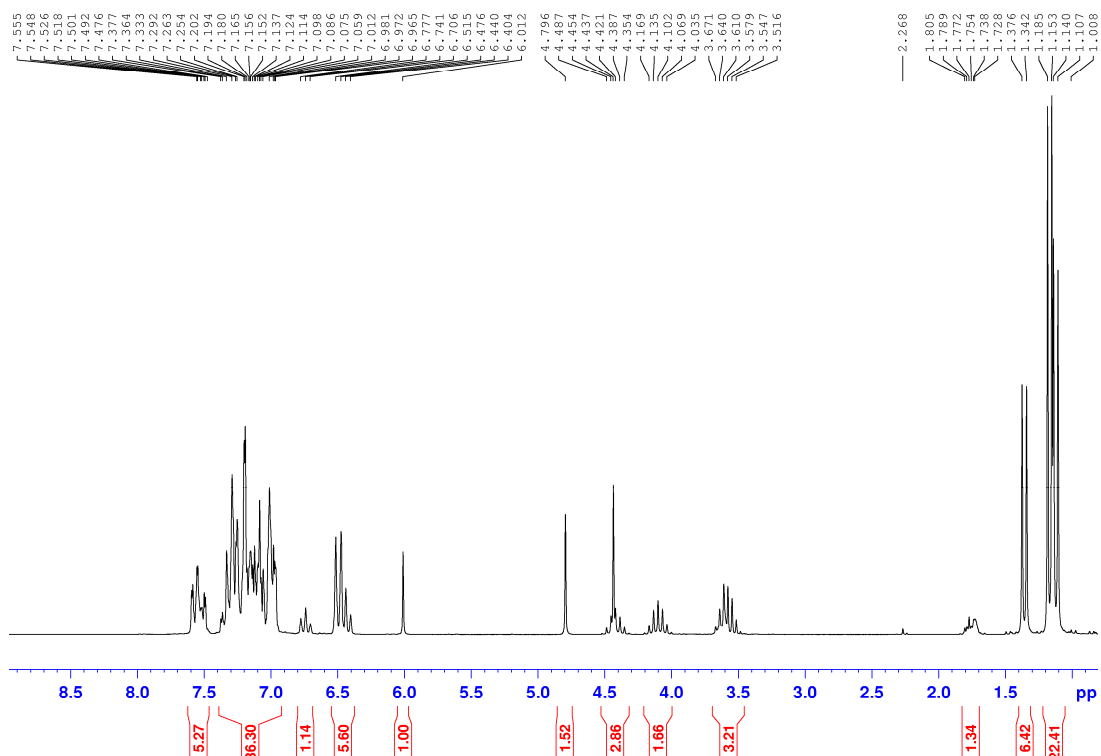
Intermolecular hydroamination of diphenylbutadiyne **A** with N-isopropylaniline **B** in THF at 65 °C yielding E/Z-**2** (R = iPr). Regardless of the reaction conditions an isomer ratio of 1.5:1 was found.

Catalyst	Mol-%	A/B ratio	Time	Yield/%
NaNRPh	12	1:2	7.5 h	0
	28	1:2	3 h	35.6
	28	1:2	10.5 h	88.8
	39	1:2	1.5 h	57.3
	39	1:2	8 h	88.5
KOtBu	20	1:2	6 h	83.5
	20	1:2	13 h	85.1
	28	1:6	4 h	78.4
	28	1:6	8.5 h	80.4
	28	1:6	14 h ^a	24.1
Ca(NRPh) ₂	7	1:1.6	3.5 h	89.0
	7	1:1.6	9 h	94.7
K ₂ Ca(NRPh) ₄	5	1:4	0.5 h	7.7
	5	1:4	1.5 h	52.6
	5	1:4	2.5 h	64.3
	5	1:4	3.5 h	83.2
	5	1:4	4.5 h	91.4
	5	1:4	5.5 h	96.7
	5	1:4	17.5 h	99.9
K ₂ Ca(NRPh) ₄	10	1:4	20 min ^b	45.0
	10	1:4	30 min ^b	77.9
	10	1:4	40 min ^b	89.1
	10	1:4	50 min ^b	94.5
	10	1:4	60 min ^b	97.3
	10	1:4	70 min ^b	97.8
	10	1:4	80 min ^b	98.2

^a) Catalysis was performed at r.t.; ^b) Catalysis at 50 °C.

- Example of a NMR-spectrum showing product signals and excess of **B**:

conditions: 4 mol% $K_2Ca\{N(Ph)iPr\}_4$ after 4.5h at 65°C (200MHz, $[D_8]THF$, 300K)



- NMR-spectrum after heating stoichiometric amounts of $K_2Ca(NPh_2)_4$ and diphenylbutadiyne:

conditions: after 2.5h at 65°C (200MHz, $[D_8]THF$, 300K)

