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# Palladium complex with tetrahydronaphthyl-substituted diimine ligand as a catalyst for polymerization of norbornenes and diazoacetates

**Ivan V. Nazarov, Evgeniya V. Bermesheva, Konstantin V. Potapov, Zoya B. Khesina, Mikhail M. Il’in, Elizaveta K. Melnikova and Maxim V. Bermeshev**

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# General information

## *Materials*

(*S*)-(+)-1,2,3,4-Tetrahydro-1-naphthylamine, palladium chloride (II), glyoxal solution (40 wt. % in $H_2O$), tetramethyltin, cycloocta-1,5-diene, racemic 1-phenylethylamine, *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (*exo*-NDA) and $AgSbF_6$ were used as purchased (Sigma-Aldrich). 2-(2-Tosylhydrazono)acetic acid were prepared according to previously reported procedure [S1]. Dihydroxybenzoic acid (DHB) and α-cyano-4-hydroxycinnanic acid (CHCA) were purchased from Bruker Daltonics, Germany. (COD)Pd(Me)Cl was synthesized from palladium(II) chloride, cycloocta-1,5-diene and tetramethyltin according to literature [S2]. Dichloromethane, THF, benzene and hexane were distilled over molecular sieve (4Å) under argon. For the analysis, 2 typical MALDI matrices were used 2,5-dihydroxybenzoic acid (DHB) and α-cyano-4-hydroxycinnanic acid (CHCA). Before the analysis the solutions of studied samples were mixed with the matrix (DHB or CHCA) in 1:10 molar ratio, then was applied onto a stainless steel support and dried in air atmosphere at room temperature. Mass spectra were registered under the conditions of either positive or negative ion detection in the reflectron mode in a mass range of 90—2000 Da, and the laser power was 50% of the maximum value.

## *Methods*

NMR spectra were recorded using a Bruker “Avance 600” spectrometer (Bremen, Germany) at 600 MHz ($^1H$ NMR) and 151 MHz ($^{13}C$ NMR) in $CDCl_3$ solution. Chemical shifts (δ) are reported in parts per million (ppm) relative to a reference (residual $CHCl_3$ signal). Calorimetric measurements were conducted using a “Mettler” TA-4000 differential scanning calorimeter (Giesen, Germany) at a heating rate of 20 deg/min under argon. The molecular masses of polymers were estimated by means of gel permeation chromatography (GPC, Milford, MA, USA) using a “Water`s” high-pressure chromatograph with a refractometric detector and a Microgel mix 1–5 μm, 500 mm × 7.7 mm Chropack column; the solvent was chloroform, the sample volume was 100 μl, and the concentration was 1 mg/ml. Wide-angle X-ray diffraction (WAXD) data were obtained using a two-coordinate AXS detector (Bruker, Bremen, Germany) and Cu Kα emission (wavelength of 0.154 nm). The conditions of MALDI-MS analysis are described in detail in [S3]. Mass spectra were registered on a Bruker UltraFlex II MALDI TOF mass-spectrometer (Germany), equipped with a time-of-flight analyzer and modified nitrogen-cooled solid-state laser operating on the basis of Smartbeam technology with the working wavelength 337 nm and the maximum power of 110 μJ per impulse. Data acquisition and processing were performed using the flexControl 1.1 and flexAnalysis 2.2 software. Specific rotation was measured using KRÜSS P3000 polarimeter in $CH_2Cl_2$ (hplc grade). Concentration in measurement is 2.5 g/100ml (*c* = 2.5).

## *Experimental data*

### (1*S*,1'*S*,NZ,N'*Z*)-*N*,*N'*-(Ethane-1,2-diylidene)bis(1,2,3,4-tetrahydronaphthalen-1-amine) 1

In a 25-mL, two necked, round bottomed flask equipped with Ar inlet, septum and a magnetic stirring bar is introduced methylene chloride (10 ml) and an aqueous glyoxal solution (0.493 g, 3.40 mmol, 0.5 eq.) was added by syringe the septum. After that, the septum was temporarily removed and solid sodium sulfate (2.84 g) was added, while the mixture was stirred at room temperature. The resulting suspension was stirred for additional 15 minutes. The suspension was cooled to 0°C. Then (*S*)-(+)-1,2,3,4-tetrahydro-1-naphthylamine (1.0 g, 6.80 mmol, 1 eq.) was syringed dropwise within 2 minutes. The mixture was stirred at room temperature for 18 h. Sodium sulfate was removed by filtration and rinsed with $CH_2Cl_2$ (2x5 ml). The filtrate was concentrated in vacuum. The crude yellow oil was redissolved in minimum amount of $CH_2Cl_2$ (room temperature), then *n*-hexane was added, and the mixture was cooled to crystalize **1**. The pale yellow crystals were twice washed with small amounts of *n*-hexane. The product was stored under Ar at -40°C. Diimine **1** was obtained in 65% yield (0.697 g).

$[\alpha]_d^{22}$ = -297.2° ($CH_2Cl_2$, C=2.5). The NMR spectra are consistent with literature [S4].

$^1$H NMR (δ, $CDCl_3$, J (Hz)): 1.80-1.88 (m, 2H); 1.98-2.10 (m, 6H); 2.78-2.93 (m, 4H); 4.52-4.56 (m, 2H); 6.96-7.01 (m, 2H, ArH); 7.10-7.20 (m, 6H, ArH); 8.09 (s, 2H, R-C(H)=N-R).

$^{13}$C NMR (δ, $CDCl_3$, J (Hz)): 19.46 ($CH_2$); 29.30 ($CH_2$); 31.05 ($CH_2$); 67.92 (CH); 125.96 (Ar); 127.25 (Ar); 128.96 (Ar); 129.32 (Ar); 135.86 (Ar); 137.15 (Ar); 161.39 (R-C(H)=N-R).

DEPT 135 NMR (δ, m.d., $CDCl_3$, J (Hz)): 19.46 ($CH_2$); 29.30 ($CH_2$); 31.05 ($CH_2$); 67.92 (CH); 125.96 (Ar); 127.25 (Ar); 128.96 (Ar); 129.32 (Ar); 161.39 (R-C(H)=N-R).

**Diimine methylpalladium(II) chloride complex 2** A solution of diimine **1** (0.200 g, 0.63 mmol) in $CH_2Cl_2$ (10 ml) was syringed into a solution of (COD)Pd(Me)Cl (0.160 g, 0.60 mmol) in a Schlenk tube with stirring at room temperature under argon for 1 h. The resulting solution was slowly evaporated and dried for 3 h *in vacuo*. After that, the residue was redissolved by the addition of the solution of **1** (60 mg, 0.19 mmol) in $CH_2Cl_2$ (8 ml) with stirring at room temperature under an argon atmosphere for 1 h. The product was precipitated from the solution by addition of *n*-hexane (60 ml). The precipitate was filtered and washed with *n*-hexane (3 x 20 ml). The orange powder was dried *in vacuo*; yield: 0.22 g (79%). Found, %: C, 58.75; H, 6.00; Cl, 7.55. Calculated for $C_{23}H_{27}N_2Cl$, %: C, 58.36; H, 5.75; Cl, 7.49.

$^1$H NMR (δ, m.d., $CDCl_3$, J (Hz)): 1.40 (s, 3H, $CH_3$); 1.28-1.46 (m, 2H, $CH_2$); 1.72-1.82 (m, 2H, $CH_2$); 2.07-2.19 (m, 2H, $CH_2$); 2.62-2.69 (m, 1H, $CH_2$); 2.67-2.8 (m, 5H, $CH_2$); 5.30 (s, 1H, $CH_3$); 5.64 (s, 1H, $CH_3$); 6.97-7.03 (m, 2H, ArH); 7.08-7.13 (m, 3H, ArH); 7.16-7.19 (m, 2H, ArH); 7.18 (s, 1H, R-CH=N-R); 7.21-7.23 (m, 1H, ArH) 7.35-7.41 (s, 1H, R-CH=N-R).

$^{13}$C NMR (δ, m.d., $CDCl_3$, J (Hz)): -0.66 ($CH_3$); 16.57 ($CH_2$); 28.13 ($CH_2$); 28.46 ($CH_2$); 28.61 ($CH_2$); 28.73 ($CH_2$); 62.80 (CH); 64.01 (CH) 126.54 (Ar); 126.93 (Ar); 128.21 (Ar); 128.68 (Ar); 129.19 (Ar); 129.31 (Ar); 130.03 (Ar); 130.17 (Ar); 132.29 (Ar); 132.70 (Ar); 138.74 (Ar); 139.00 (Ar); 158.16 (R-C(H)=N-R); 163.41 (R-C(H)=N-R).

DEPT 135 NMR (δ, m.d., $CDCl_3$, J (Hz)): -0.54 ($CH_3$); 16.69 ($CH_2$); 28.26 ($CH_2$); 28.74 ($CH_2$); 28.86 ($CH_2$); 28.86 ($CH_2$); 62.67 (CH); 63.86 (CH) 126.67 (Ar); 127.06 (Ar); 128.34 (Ar); 128.81 (Ar); 129.33 (Ar); 129.44 (AR); 130.16 (Ar); 130.30 (Ar); 158.30 (R-C(H)=N-R); 163.54 (R-C(H)=N-R).

### (1*R*,2*R*,6*S*,7*S*)-4-[(1*RS*)-1-Phenylethyl]-4-azatricyclo[5.2.1.0$^{2,6}$]dec-8-ene-3,5-dione (3)

A 250 ml round bottom flask was filled with *exo*-NDA (6.450 g, 0.040 mol), toluene )100 ml), *rac*-1-phenylethylamine (5.236 g, 0.0495 mol), magnetic stirring bar, fitted with Dean-Stark trap, and refluxed for 5 h. The mixture was cooled to room temperature. Then it was washed twice with the solution of 10% HCl (30 ml) and with $H_2O$ (30 ml). The organic layer was dried with $Na_2SO_4$. Toluene was evaporated using a rotary evaporator. Molten yellow solid was dissolved in $CH_2Cl_2$ and was filtered through a pad of silica. The final solution was evaporated using a rotary evaporator, and the residue was recrystallized from MeOH. Monomer **3** was obtained as a white crystal powder (6.99 g, 61%). M. p. 75-79 °C. MS (EI): 70% (267, $M^+$), 96% (201, $C_{12}H_{11}NO_2^+$), 100% (66, $C_5H_6^+$). $^1$H NMR spectrum is consistent with one published for **3**, which was obtained from *S*-phenylethylamine [S5].

$^1$H NMR ($CDCl_3$, δ, ppm): 0.97 (d, 1H, $CH_2$, $^2$J=9.8 Hz); 1.28 (d, 1H, $CH_2$, $^2$J=9.8 Hz) 1.68 (d, 3H, $C(H)_3$-CH, $^3$J=7.6 Hz); 2.49 (s, 2H, C(H)-CH=CH); 3.09 (s, 1H, C(H)-C(O)); 3.14 (s, 1H, C(H)-C(O)); 5.27 (q, 1H, C(H)-$CH_3$, $^3$J=7.6 Hz); 6.14 (s, 2H, R-C(H)=C(H)-R); 7.23-7.38 (m, 3H, ArH); 7.40-7.50 (m, 2H, ArH).

$^{13}$C NMR ($CDCl_3$, δ, ppm): 16.39 ($CH_3$); 42.53 (CH); 45.39 (CH); 45.43 (CH); 47.39 (CH); 50.11($CH_2$); 127.52 (Ar); 127.40 (Ar); 128.34 (Ar); 137.91 (R-C(H)=C(H)-R); 137.93 (R-C(H)=C(H)-R); 139.52 (Ar); 177.56 (C(O)); 177.80 (C(O)).

### 1-Phenylethyl 2-diazoacetate 5

To the suspension of 2-(2-tosylhydrazono)acetic acid (2.00 g, 8.26 mmol) in dry benzene (12 ml), $SOCl_2$ (1.97 g, 16.52 mmol) was added dropwise. The mixture was refluxed for 3 h, cooled, filtered through a Celite and evaporated under reduced pressure. The residual solid was dissolved in dry $CH_2Cl_2$ (10 ml) and added dropwise to an ice-cooled solution of 1-phenylethanol (0.71 g, 5.78 mmol) in dry $CH_2Cl_2$ (15 ml) under argon. Dimethylaniline (1.00 g, 8.26 mmol) was added, and mixture was stirred at 0 °C for 15 minprior to injection of $Et_3N$ (2.26

g, 22.30 mmol). The resulting suspension was stirred for more 10 min at 0°C and concentrated *in vacuo*. Saturated aqueous citric acid (30 ml) and 10% solution of EtOAc in petroleum ether (50 ml) were added. The organic layer was separated, and the aqueous one was extracted with 10% EtOAc-petroleum ether. The combined organic layers were washed twice with saturated aqueous citric acid, dried over $MgSO_4$ and evaporated to dryness to give a crude product. Silica gel column chromatography (eluent: petrol ether/EtOAc/triethylamine, 15:1:0.3, v/v) gave 0.72 g (65%) of the desired product as a pale yellow oil.

$^1$H NMR ($CDCl_3$, $\delta$, ppm): 1.56 (d, 3H, $C(\underline{H})_3$-CHPh, $^3J$ = 6.6 Hz,), 4.76 (s, 1H, $C(H)=N_2$), 5.97 (q, 1H, $C(\underline{H})-CH_3$, $^3J$ = 6.6 Hz), 7.40 – 7.23 (m, 5H, ArH).

$^{13}$C NMR ($CDCl_3$, $\delta$, ppm): 22.36 ($CH_3$), 46.47(CH), 72.81 (CH), 126.01 (Ar), 127.95 (Ar), 128.53 (Ar), 141.54 (Ar), 166.19 (C(O)).

**Synthesis of polymer 4** The catalytic system solution (complex **2**/$AgSbF_6$ at molar ratio 1:3) in $CH_2Cl_2$ was stirred for 1 h before the polymerization. The solution of catalytic system (0.01 M, 0.74 ml) was introduced into a vial with monomer **3** (0.20 g, 0.74 mmol), which was preliminary purged in vacuum and filled with argon. The solution was stirred to dissolve the monomer in the catalytic system solution for several minutes. After that, the vial was sealed and allowed to stay at 45°C for 48 h. Then the polymerization mixture was precipitated by methanol. The polymer was separated, washed several times with methanol, and dried in vacuum. The polymer was twice reprecipitated by methanol from $CH_2Cl_2$ solution and dried in vacuum at 50°C up to a constant weight. Yield: 0.090 g (45%). $M_w=76\cdot10^3$, $M_n=26\cdot10^3$, PDI=2.9.

$^1$H NMR ($CDCl_3$, $\delta$, ppm): 0.50-3.37 (m, 11H); 5.20-5.62 (m, 1H, Ph-$C(\underline{H})-CH_3$); 6.90-7.73 (m, 5H, ArH).

**Synthesis of polymer 6** A solution of complex **2** in THF (0.048 ml, 0.2750 M, $1.3\cdot10^{-2}$ mmol) was added to a solution of 1-phenylethyl 2-diazoacetate (300 mg, 1.578 mmol) in THF (0.25 ml) at 25 °C. The concentrations of the monomer and the catalyst were 5.295 M and 0.044 M, respectively. The initial feed ratio of monomer to the catalyst was 121:1. After the polymerization solution was stirred for 3 min at 25 °C, it was precipitated into a large amount of *n*-hexane. The precipitated solid was collected by centrifugation and dried in vacuum at room temperature overnight, afforded substance **6** as a yellow solid (38.4 mg).

$^1$H NMR ($CDCl_3$, $\delta$, ppm): 0.28-1.78 (m, 3H, $CH_3$); 5.55-6.07 (m, 1H, Ph-$C(\underline{H})-CH_3$); 6.79-7.54 (m, 5H, ArH).

**NMR spectra**

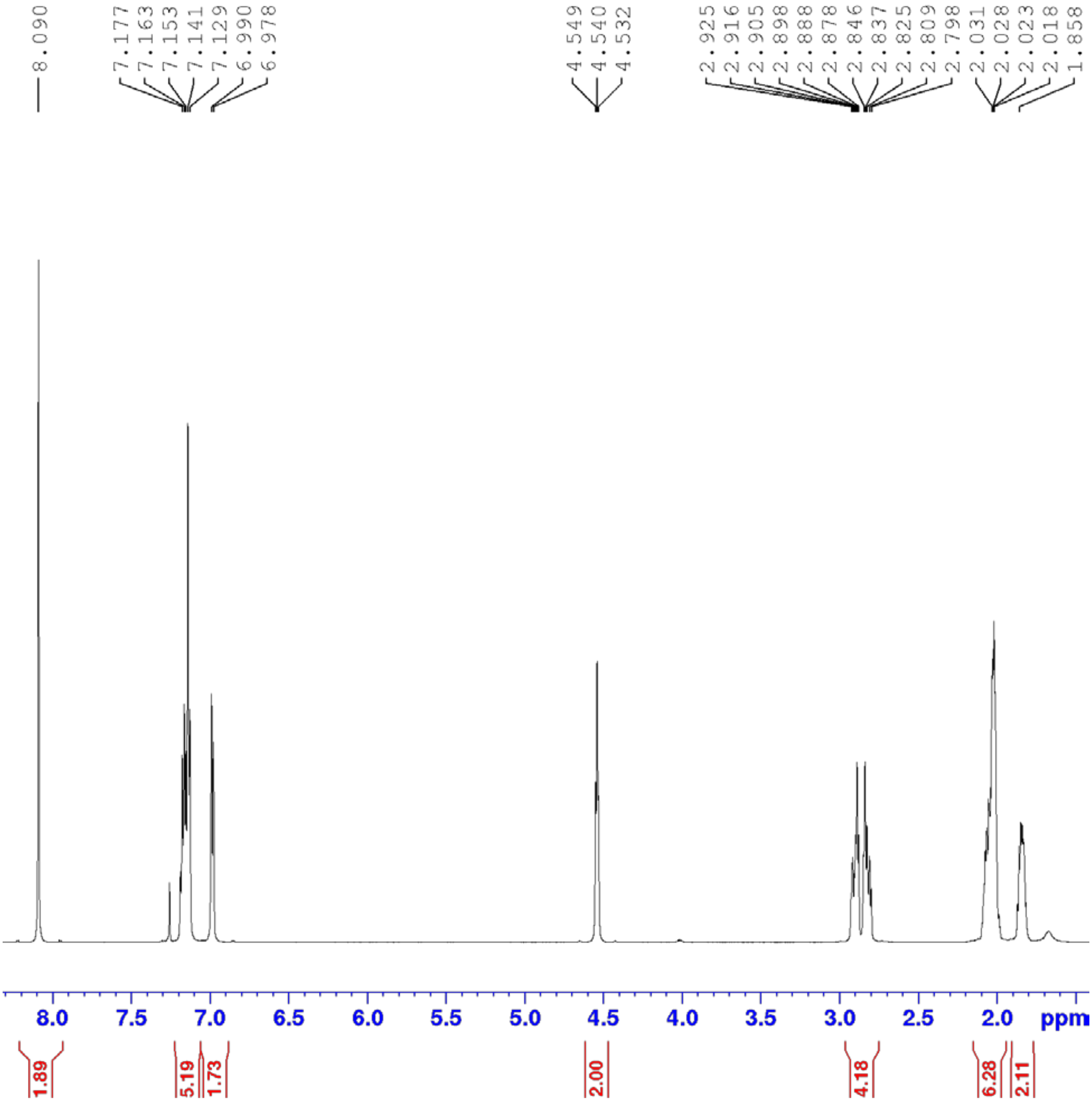

**Figure S1.** $^1$H NMR spectrum of **1** ($CDCl_3$).

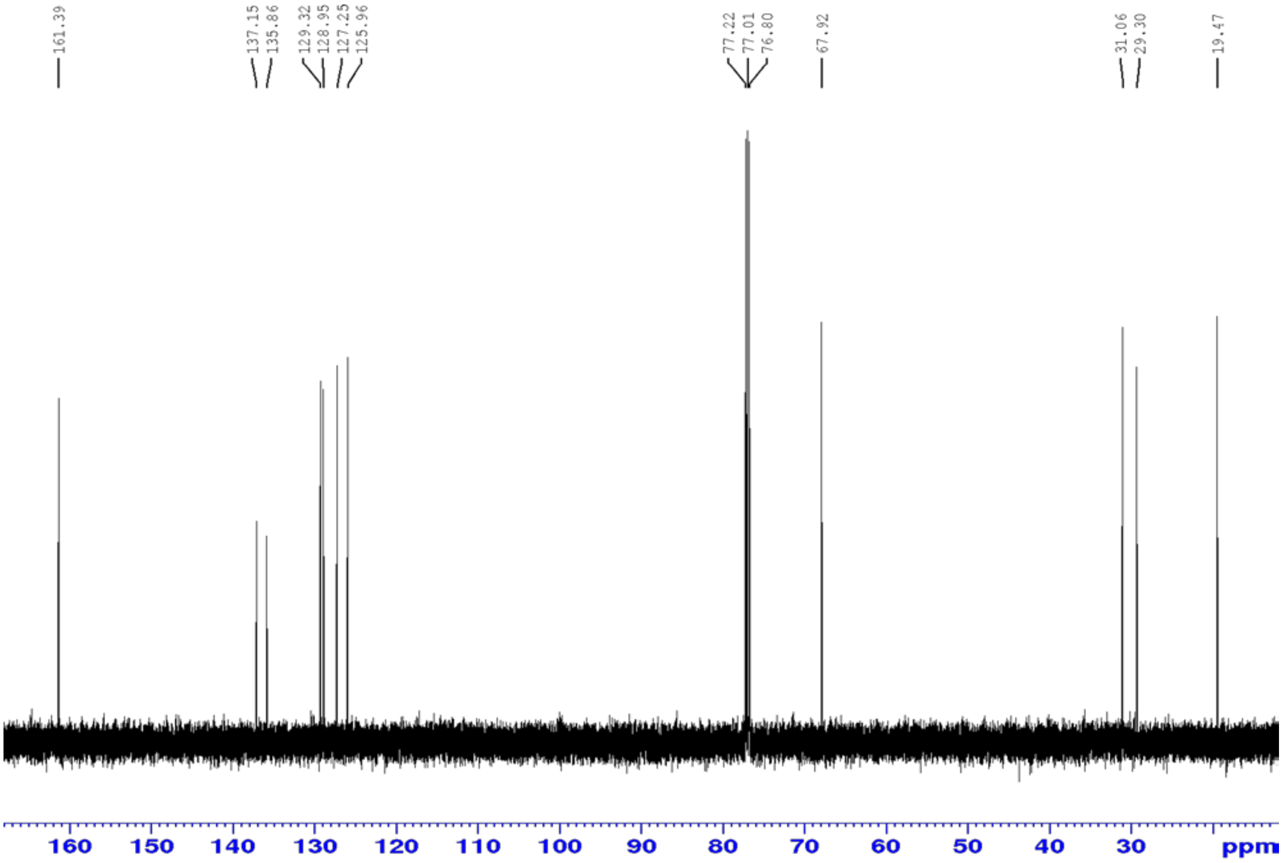

**Figure S2.** $^{13}$C NMR spectrum of **1** ($CDCl_3$).

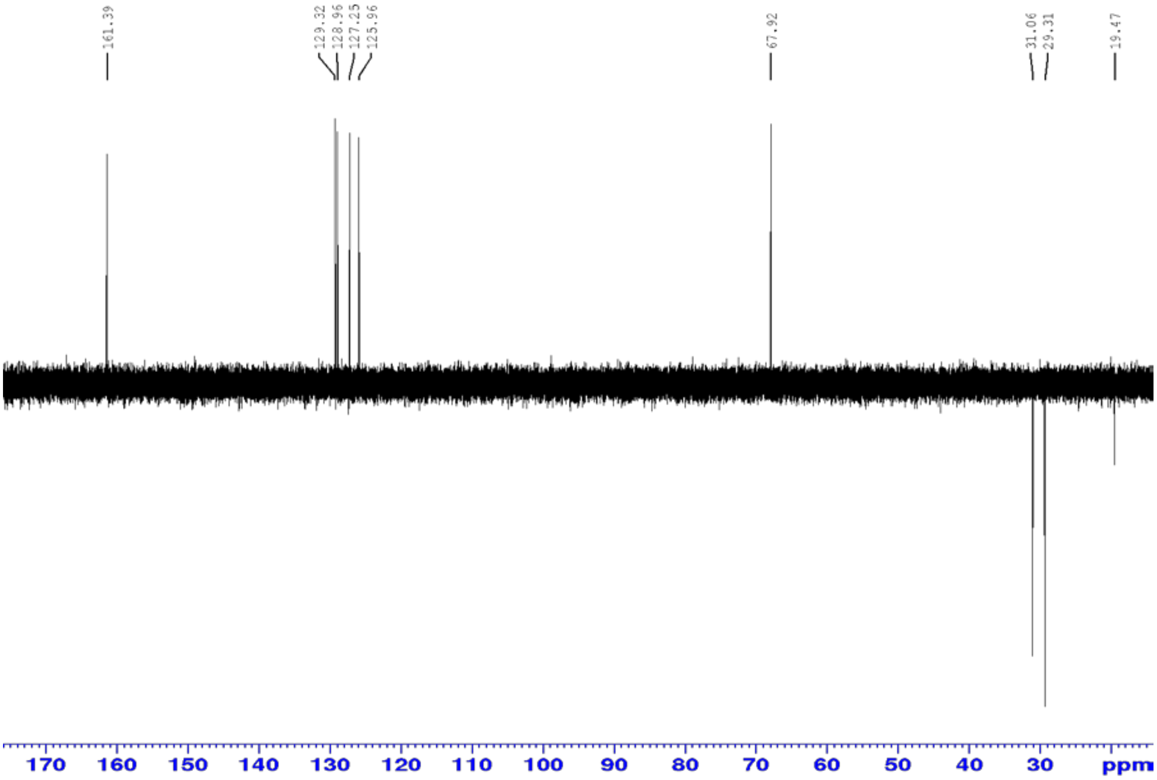

**Figure S3.** DEPT135 spectrum of **1** ($CDCl_3$).

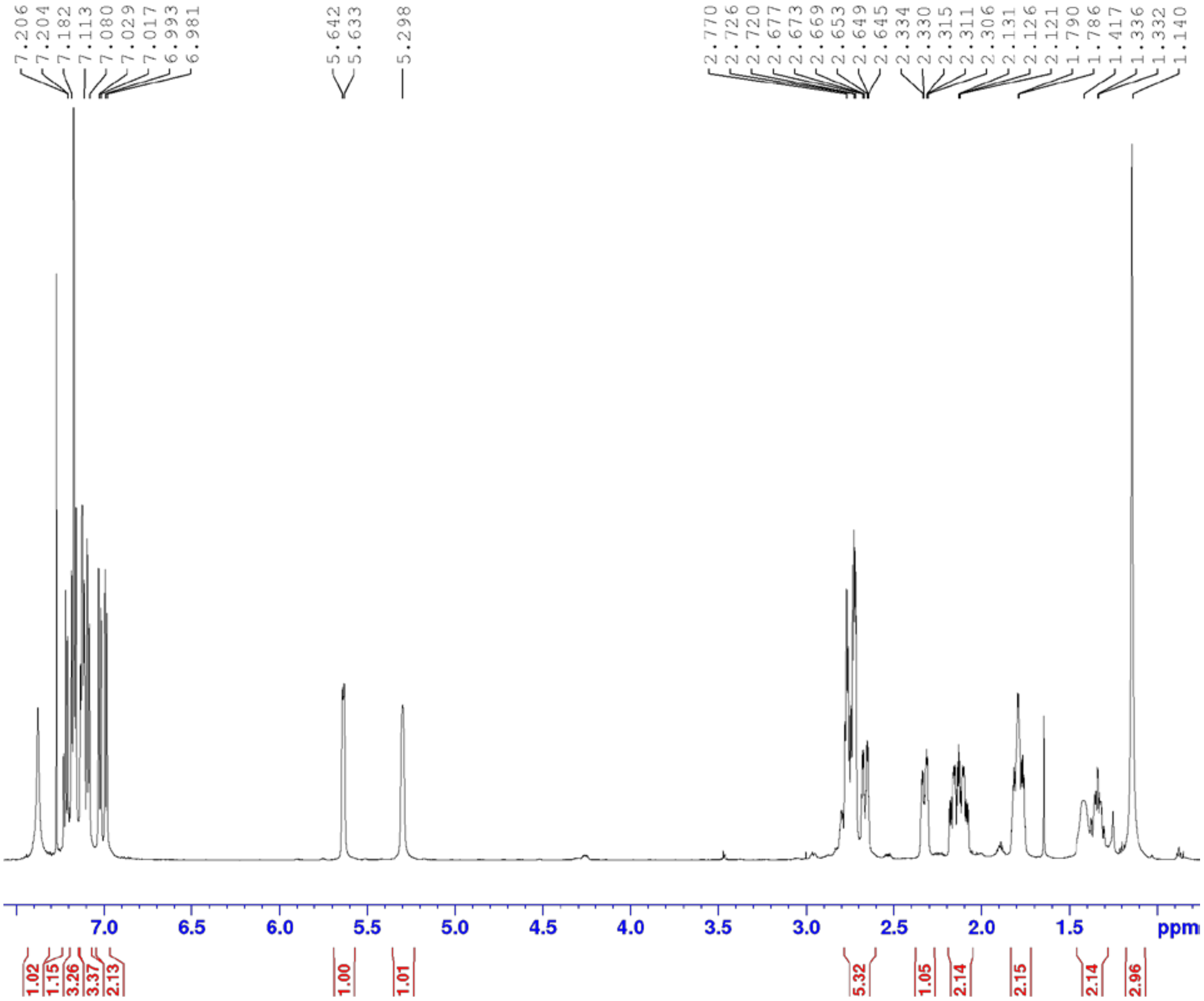

**Figure S4.** $^1$H NMR spectrum of **2** ($CDCl_3$).

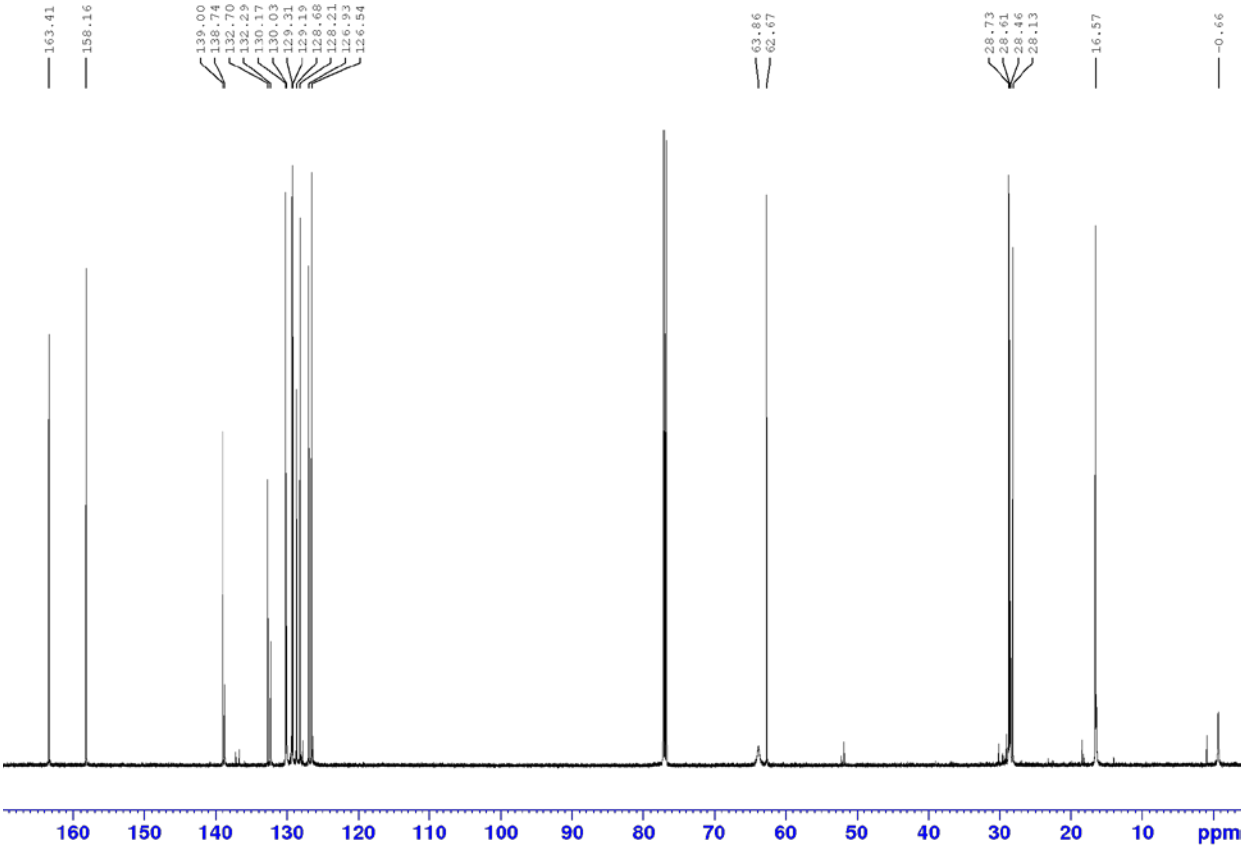

**Figure S5.** $^{13}$C NMR spectrum of **2** ($CDCl_3$).

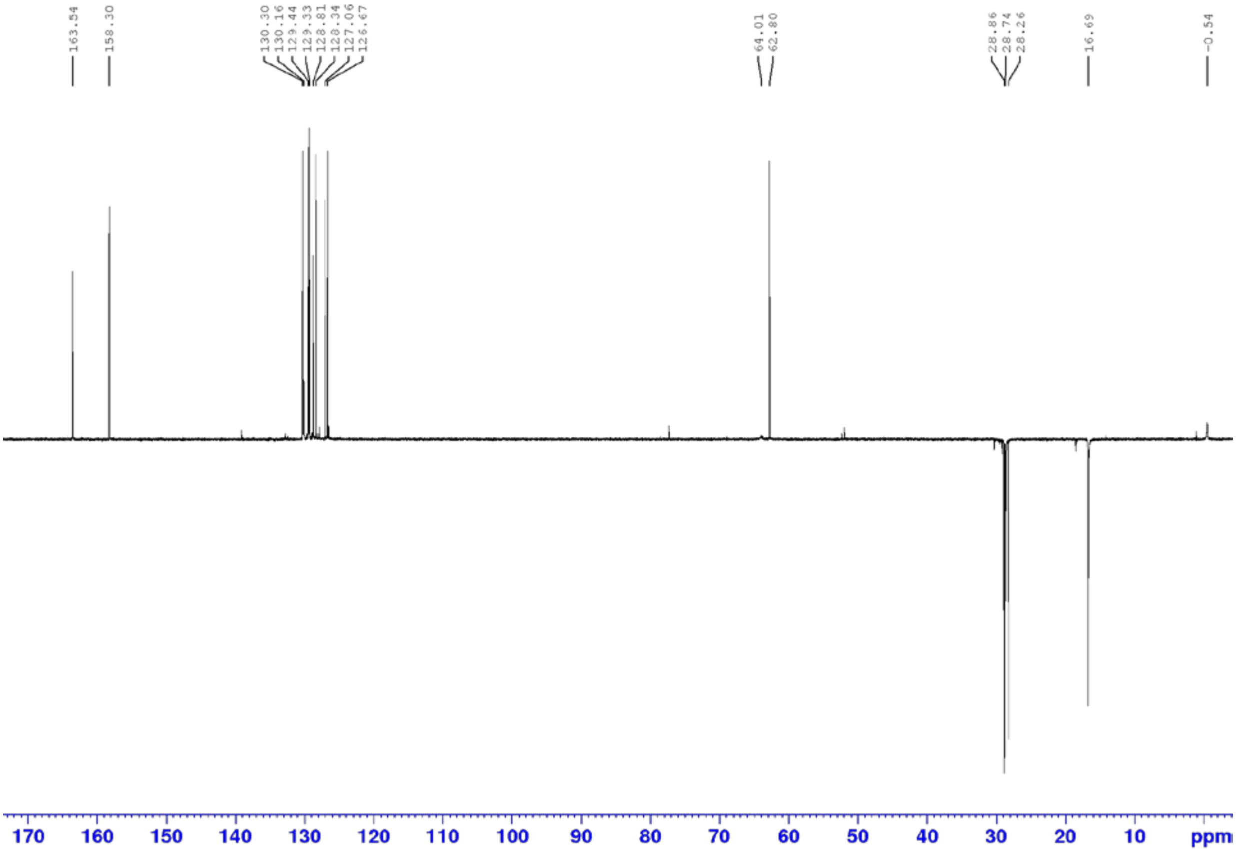

**Figure S6.** DEPT135 spectrum of **2** ($CDCl_3$).

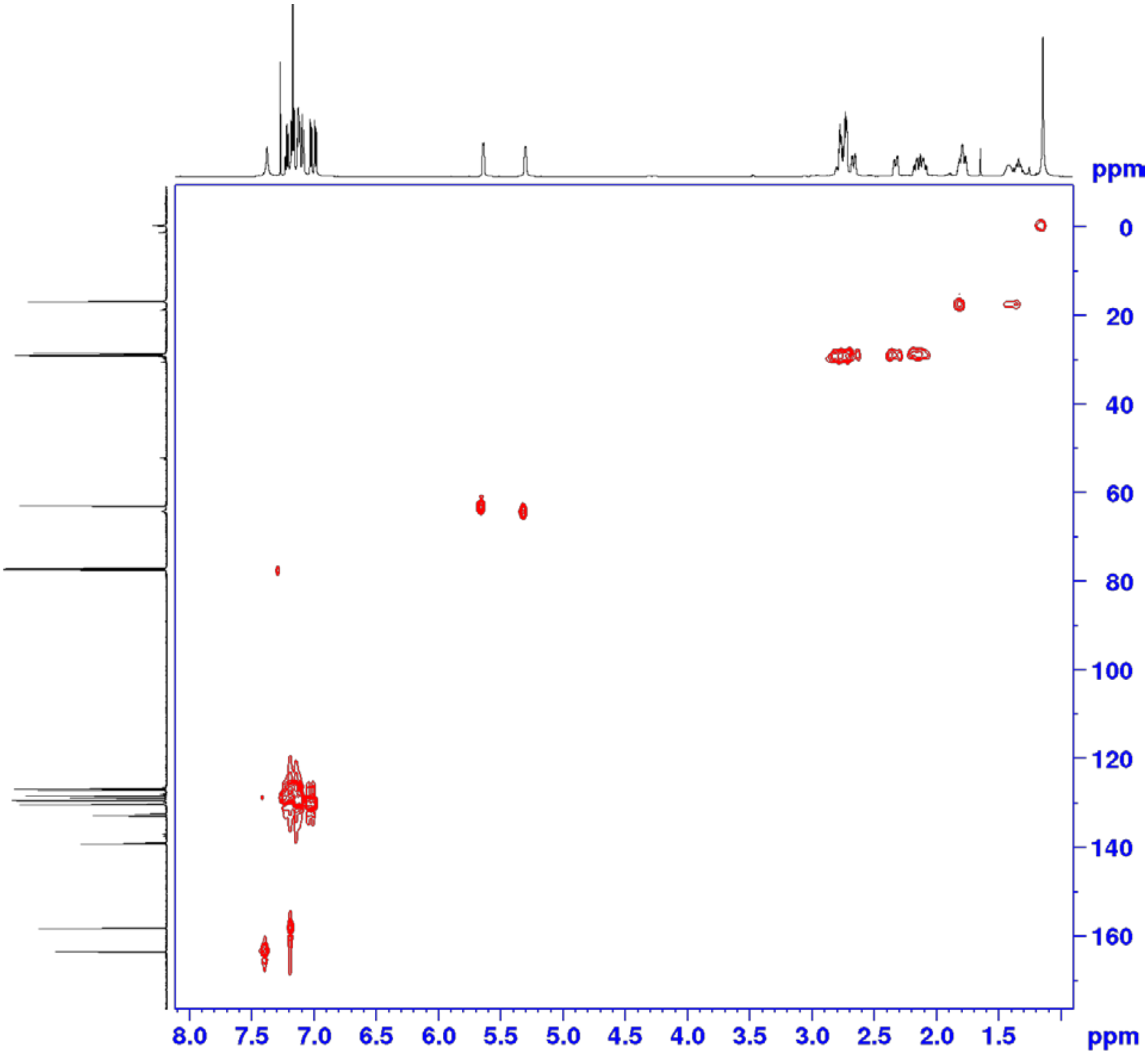

**Figure S7.** HSQC spectrum of **2** ($CDCl_3$).

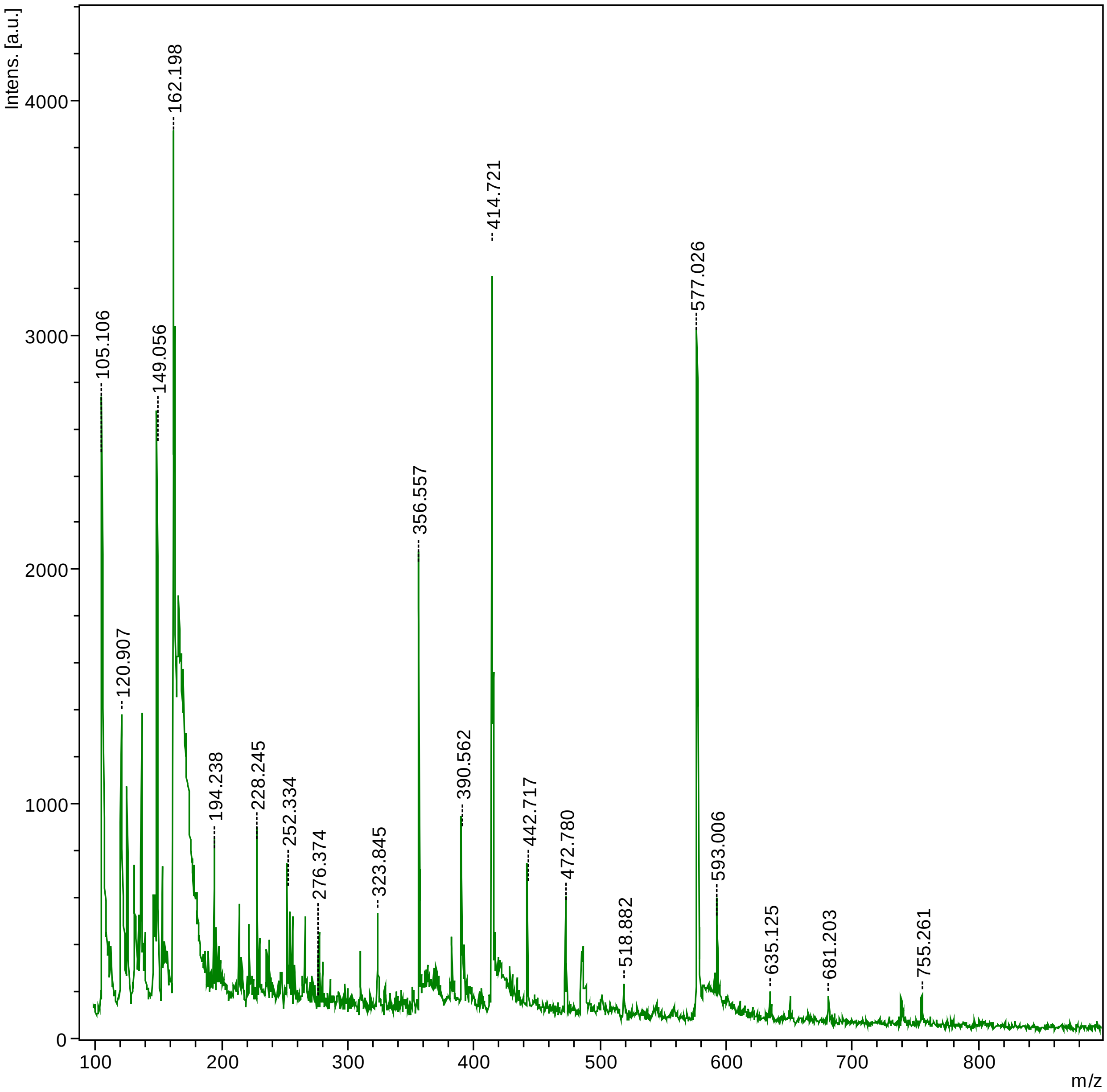

**Figure S8.** MALDI TOF mass spectrum of **6**.

***Crystallographic data***

Crystals of **1** ($C_{22}H_{24}N_2$, M = 1265.72) are monoclinic, space group $P2_1$, at 120 K: a = 13.968(3), b = 15.128(3), c = 16.682(4) Å, β = 90.244(4)°, V = 3525.0(13) $Å^3$, Z = 8 (Z’ = 4), $d_{calc}$ = 1.192 g $cm^{-3}$, μ(MoKα) = 0.70 $cm^{-1}$, F(000) = 1360. Crystals of **3** ($C_{17}H_{17}NO_2$, M = 267.31) are triclinic, space group P-1, at 120 K: a = 5.4838(17), b = 10.566(3), c = 11.825(4) Å, α = 99.867(4)°, β = 94.797(5)°, γ = 98.248(5)°, V = 663.9(4) $Å^3$, Z = 2, $d_{calc}$ = 1.337 g $cm^{-3}$, μ(MoKα) = 0.88 $cm^{-1}$, F(000) = 284. Intensities of 8499 and 37502 reflections were measured for **1** and **3**, respectively, with a Bruker APEX2 DUO CCD diffractometer [λ(MoKα) = 0.71073 Å, ω-scans, 2θ<60°]; 3987 and 15371 independent reflections [$R_{int}$ 0.0608 and 0.0978] were used in further refinement. Using Olex2 [S6], the structure was solved with the ShelXT [S7] structure solution program using Intrinsic Phasing and refined with the XL [S7] refinement package using Least-Squares minimisation. Positions of hydrogen atoms were calculated. All hydrogen atoms were refined in the isotropic approximation within the riding model. For **3,** the refinement converged to wR2 = 0.1777 and GOF = 0.912 for all the independent reflections (R1 = 0.0616 was calculated against F for 2191 observed reflections with $I>2\sigma(I)$). For **1**, the refinement converged to wR2 = 0.1358 and GOF = 0.985 for all the independent reflections (R1 = 0.0595 was calculated against F for 10645 observed reflections with $I>2\sigma(I)$)**.** CCDC 2065346 and 2065347 contain the supplementary crystallographic information for **3** and **1**, respectively.

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