

Pyrazol-containing catalysts for the alternating copolymerization of CO/4-*tert*-butylstyrene

Abstract

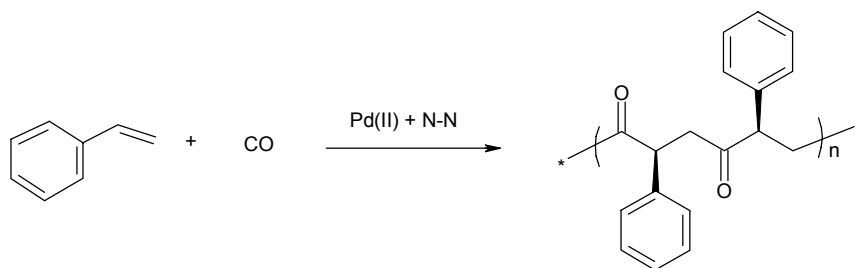
The activity of new cationic palladium (II) complexes, containing bisnitrogen ligands with a pyrazol moiety, in the copolymerization of 4-*tert*-butylstyrene with CO, is studied. The C_S-symmetry of the ligands leads to the synthesis of copolymers with syndiotactic microstructure. The molecular weight and the polydispersity of the obtained polymers are among the best reported for bisnitrogen planar ligands when mild reaction conditions are used.

4.1. Introduction

The copolymerization of carbon monoxide and alkenes using palladium catalyst is providing much interest.¹⁻³ Ethylene/carbon monoxide copolymerization has been widely studied and results have been best with diphosphine ligands. The high activity of these systems has raised industrial interest in the process.⁴⁻⁹ Several groups are reporting on the exploration of new systems.¹⁰⁻¹⁵

Chiral ligands have been successfully used for the copolymerization of carbon monoxide with propene^{16,17} and styrene.¹⁸⁻²¹ With styrene, however, only oligomers with low molecular weight are obtained with phosphine ligands. This has been attributed to a favoured β -hydride elimination.¹

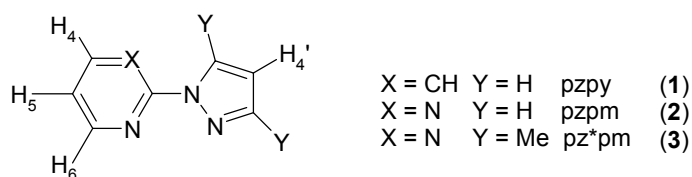
The first systems studied with styrene were Pd (II) catalyst based on planar 2,2'-bipyridine or 1,10-phenanthroline to give syndiotactic poly(styrene-alt-CO) (Scheme 1).²²⁻²⁴ This high stereochemical control (>90%) has been attributed to a chain-end control due to the interaction of the growing chain with the incoming styrene unit, which inserts exclusively in the 2,1-fashion.^{3,25}



Scheme 1. Syndiotactic polyketones are obtained using bipy or phen as N-N ligands

Chiral N-N ligands have also been successfully explored to yield isotactic copolymers,^{18,19,25,26} although in some cases the chain-end control is more efficient than the enantioselective control caused by the ligand and this results in the formation of syndiotactic polymers.²⁵ C_1 -symmetric chiral P-N ligands have been used to yield isotactic polymers due to the site-selective coordination of the alkene in the chiral environment generated by the ligand.^{21,25} For these systems, using P-N ligands, high CO pressures and moderate temperatures are required.

Since planar N-N ligands are efficient and since there is an interest in exploring new types of ligands, we report on the synthesis of new well-defined cationic Pd(II) catalyst using the unsymmetrical chelate ligands 2-(1-pyrazolyl)pyridine (pzpy, **1**), 2-(1-pyrazolyl)pyrimidine (pzpm, **2**) and 2-(1-(3,5-dimethyl)pyrazolyl)pyrimidine (pz^{*}pm, **3**), which yield syndiotactic alternating copolymers of *tert*-butylstyrene and CO at mild pressure and temperature.



Scheme 2. (N-N') - ligand systems

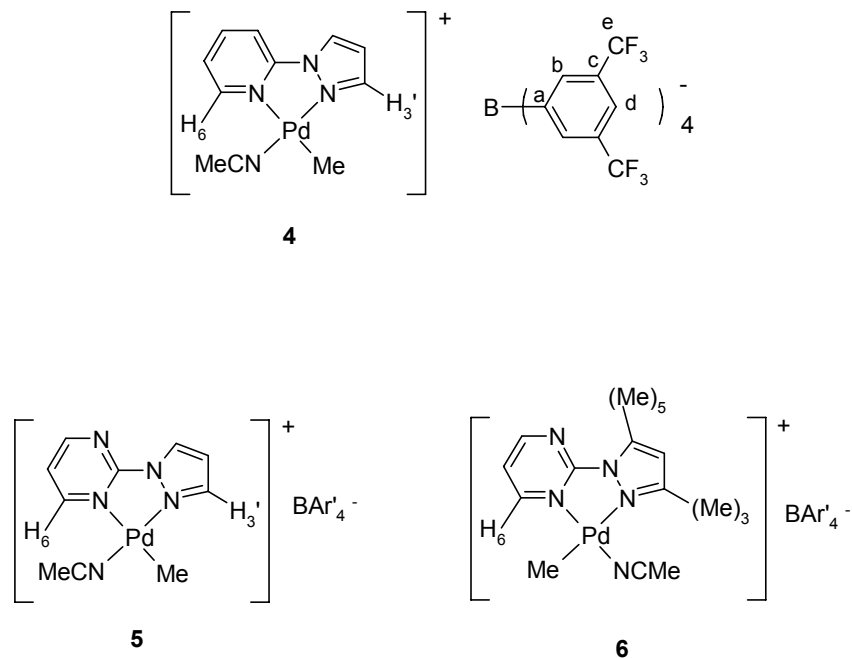
4.2. Results and discussion

4.2.1. Synthesis and characterization of the palladium catalyst precursors $[\text{PdMe}(\text{NCMe})(\text{N-N}')][\text{BAr}_4']$ (4-6)

The cationic complexes $[\text{PdMe}(\text{NCMe})(\text{N-N}')][\text{BAr}_4']$ were obtained by adding a previously prepared solution of the neutral complexes $[\text{PdClMe}(\text{N-N}')]$ ²⁷ to an equimolar solution of NaBAr_4' in MeCN.

NOE difference NMR experiments showed that cationic precursors **4** and **5** had the methyl group *trans* to pyridine and pyrimidine ring, respectively, while **6** had the methyl group *trans* to the pyrazole moiety (Scheme 3). Because of the large *trans* influence of the methyl group, we should expect it to be coordinated *trans* to the less basic ring (pyrazole in compound **4** and pyrimidine in compounds **5** and **6**). We therefore believe that this stereochemistry cannot be explained in terms of electronic effects. The sterical hindrance caused by the hydrogen H_6 in compounds **4** and **5** may be larger than the one caused by the $\text{H}_{3'}$ of the pyrazole fragment, which could force the methyl to be *cis* to the pyrazole in both molecules. This agrees with the stereochemistry observed in **6**, where the steric

demand of the methyl group (Me)₃ of the pyrazole ring is greater than the bulkiness of H₆, thus placing the methyl group *trans* to the pyrazole moiety.



Scheme 3. Stereochemistry around palladium of compounds **4**, **5** and **6**

Spectroscopic data suggest that these configurations are in agreement with the stereochemistry of the related [PdClMe(N-N)], although in the case of [PdClMe(pz*pm)] there is also a minor isomer with the methyl ligand *trans* to the pyrimidine ring.²⁷ In the case of **6**, it is also noteworthy the fluxional behaviour found for the pz*pm ligand (**3**). An NOE experiment carried out at low temperature (243 K) reflects the expected NOE interaction between the methyl group and H₆. However, at room temperature an NOE effect has been found not only with this proton

but also with H₄ being the observed percent of 2.4 % for H₆ and 0.6 % for H₄. This implies a process of Pd-N bond rupture, internal rotation of the ligand around the pz*-pm bond and reformation of the Pd-N bond. The two separated resonances for H₄ and H₆ at room temperature indicate that the process is in a slow exchange regime at this temperature. This Pd-N bond rupture is also observed in related Pd (II) complexes with this type of ligands.²⁸

4.2.2. Copolymerization experiments

Whereas C_{2v}-symmetric bipyridyl- or phenantroline- type ligands are a well-known class of planar ligands for the styrene/CO copolymerization reaction, few systems have been reported in which a non symmetrical N-N' planar ligand leads to similar activities and molecular weights.²⁹ The new complexes **4**, **5** and **6** were explored as catalysts in this reaction at mild conditions (room temperature and 1 atmosphere of CO) (Table 1).

The catalyst precursor **5** seemed the most active after 24 h, with a productivity of 11.75 g/(g Pd. h), although the cationic system **4** behaved in a similar way (entries 1 and 2). Increasing the reaction time from 24 hours to 48 hours led, as expected, to higher conversions and molecular weights although the difference in activity between the two catalysts (**4** and **5**) narrowed, probably due to the combined effects of the increasing difficulty of the monomers to access the catalytic site and decomposition of catalyst **5** to palladium metal (entries 4 and 5). The molecular weights (20000 - 70000)

and the polydispersities (1.1 - 1.3) are in the order of the best ones reported for bisnitrogen systems using styrene derivatives.^{24,26} The activity and molecular weight obtained with catalyst precursor **6** were lower than those obtained with precursors **4** and **5** (entries 1-3). This lower productivity may be attributed to the sterically more demanding ligand pz*pm (**3**), as previously reported for other systems.²⁵ When the substrate / catalyst ratio is 620 for precursor **4**, productivity and molecular weight increased (entries 1 and 6).

We also studied the effect of CO pressure. When the CO pressure was increased to 5 atm., conversion and molecular weight decreased, although polydispersities remained stable (entries 7 and 8).

Table 1. Copolymerization of 4- tert- butylstyrene and CO with **4**, **5** and **6** at 1 atm. CO and RT

Entry	Catalyst precursor	pCO (atm.)	t (h)	% Conv. ^a	M _n (M _w /M _n) (g CP/g Pd.h)
1	4	1	24	38.45	21440 (1.1)
2	5	1	24	55	36353 (1.3)
3	6	1	24	25.78	15720 (1.5)
4	4	1	48	67.49	72360 (1.1)
5	5	1	48	68.88	70680 (1.2)
6 ^b	4	1	24	43.15	30380 (1.4)
7	4	5	24	14.59	15570 (1.1)
8	5	5	24	10.73	7155 (1.2)

Reaction conditions: Solvent: 5 mL chlorobenzene, alkene/catalyst = 310.

^aStyrene conversion calculated from the isolated polymer weight.

^balkene/catalyst = 620.

To compare the activity of the most active catalyst precursors **4** and **5**, we varied reaction times from 7 h to 72 h and plotted styrene conversion against reaction time (Fig. 1). With catalyst **5** the initial reaction rate was

higher but prolonged reaction time with **4**, however, resulted in similar conversions, as mention above.

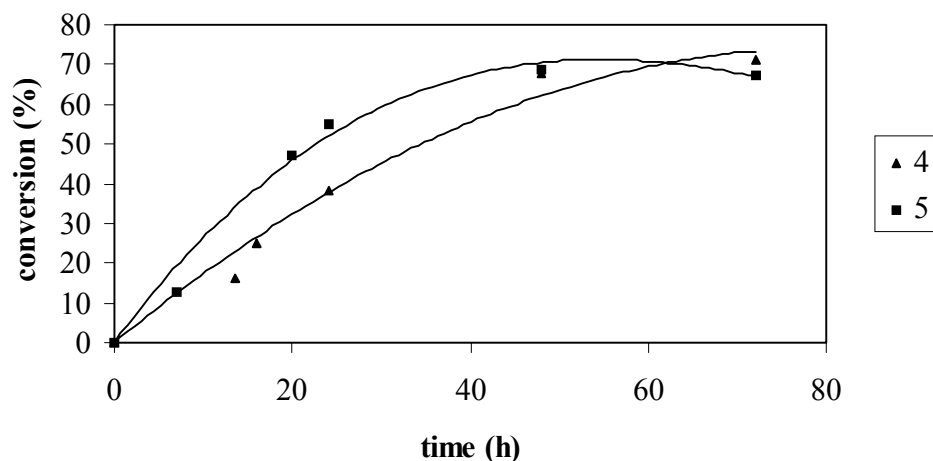


Fig.1. Compared activity of catalysts **4** and **5**, containing ligands pzpy and pzpm, respectively

All the systems we studied yield prevailing syndiotactic copolymers, which is indicative of a stereocontrol from the growing polymer chain (chain-control). Analysis of the decoupled ^{13}C spectra indicated a substantial degree of stereoregularity (ca. 92% of syndiotactic diads) by integration of the signals of the methylene carbon atoms. The greater resonance at 43.2 ppm was assigned to the syndiotactic *uu*- triad by comparison with the spectrum of the epimerized polymer and with literature values (Fig. 2).^{18,21}

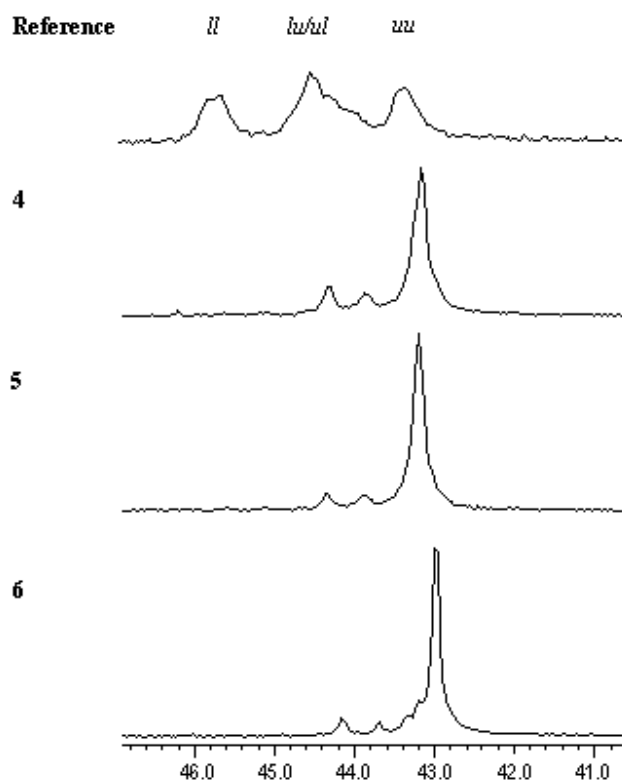


Fig.2. Methylene carbon atom-region of the copolymers obtained with precursors **4**, **5** and **6**. The reference spectrum is epimerized poly (4-*tert*-butylstyrene- alt- CO)

4.3. Conclusions

This study shows that new cationic palladium(II) compounds containing the bisnitrogen ligands pzpy (**1**), pzpm (**2**) and pz*pm (**3**) are active as catalyst precursors in the alternating CO/4-*tert*-butylstyrene

copolymerization. The C_s -symmetry of the ligands did not seem to affect stereocontrol, which was determined by the chain end. These systems behave similar to the previously studied C_{2v} -symmetric bipyridyl and phenantroline ligands that yield readily syndiotactic copolymers.

4.4. Experimental

4.4.1. General procedure

All reactions were carried out in a nitrogen atmosphere at room temperature using standard Schlenk techniques. Solvents were distilled and deoxygenated prior to use unless otherwise stated. The salt $NaBAr'_4$ ($Ar' = 3, 5-(CF_3)_2-C_6H_3$) was prepared according to reported methods.³⁰ Ligands **1** and **2** were prepared according to published methods.²⁸ **3** was prepared in a similar way.

1H and ^{13}C NMR spectra were recorded on a Varian Gemini spectrometer with a 1H resonance frequency of 300 MHz and on a Varian Mercury VX spectrometer with a 1H resonance frequency of 400 MHz. Chemical shifts were reported relative to tetramethylsilane for 1H and ^{13}C . Some assignments in NMR spectra were determined by $^1H - ^{13}C$ COSY, DEPT and NOE experiments. IR spectra (range 4000-400 cm^{-1}) were recorded on a Midac Grams/386 spectrophotometer in KBr pellets. Elemental analyses were carried out on a Carlo Erba Microanalyser EA 1108. The molecular weight of the copolymers and molecular weight distributions were determined by gel permeation chromatography (GPC - MALLS) measurements made in THF on a Waters 510 gel-permeation

chromatography device using a three-serial column system (SHODEX K80M and PLGEL MIXED-D and MIXED-E linear columns) with a Wyatt mini-DAWN Light Scattering and a SHIMADZU RID-6A refractive index detector.

4.4.2. Synthesis of catalyst precursors

[PdMe(NCMe)(pzpy)][BAr'₄] (4)

A previously prepared solution of [PdClMe(pzpy)]²⁷ (0.05 g, 0.17 mmol) in 3 mL of CH₂Cl₂ was added to a solution of NaBAr'₄ (Ar' = 3,5-(CF₃)₂C₆H₃) (0.147 g, 0.17 mmol) in the minimum amount of MeCN. The light orange solution formed was stirred for about an hour, filtrated through Kieselghur and evaporated to dryness. The white-brownish compound was crystallised from CH₂Cl₂ / hexane. Yield: 75%. Anal. Found: C, 44.71; H, 2.11; N, 4.75%. Calc. for C₄₃H₂₅BF₂₄N₄Pd: C, 44.10; H, 2.14; N, 4.78%. ¹H NMR (400 MHz, CDCl₃, RT): δ 8.15 (ddd, ³J = 5.2 Hz, ⁴J = 1.6 Hz, ⁵J = 0.8 Hz, 1H, H₆), 8.08 (d, ³J = 3.2 Hz, 1H, H₅), 7.9 (ddd, ³J = 8.4 Hz, ³J = 7.6 Hz, ⁴J = 1.6 Hz, 1H, H₄), 7.8 (d, ³J = 2.0 Hz, 1H, H₃), 7.71 (s, 8H, H_b), 7.52 (s, 4H, H_d), 7.45 (td, ³J = 8.4 Hz, ⁴J = 0.8 Hz, ⁵J = 0.8 Hz, 1H, H₃), 7.23 (ddd, ³J = 7.6 Hz, ³J = 5.2 Hz, ⁴J = 0.8 Hz, 1H, H₅), 6.7 (dd, ³J = 3.2 Hz, ³J = 2 Hz, 1H, H₄), 2.38 (s, 3H, Pd-CH₃CN), 1.21 (s, 3H, Pd-CH₃). ¹³C NMR (100.5 MHz, CDCl₃, RT): δ 161.9 (q, J_{C-B} = 198.3 Hz, C_a), 147.5 (s, C₆), 142.4 (s, C₃' or C₄), 142.3 (s, C₄ or C₃'), 135 (s, C_b), 129.5 (s, C₅'), 129.1 (m, C_e), 126 (s, C_c), 124.4 (s, C₅), 123.3 (s, Pd-CH₃CN), 117.7 (s, C_d), 111.2 (s, C₄' or C₃), 111.1 (s, C₃ or C₄'), 3.3 (s, Pd-CH₃CN), -0.8 (s, Pd-CH₃).

[PdMe(NCMe)(pzpm)][BAR'₄] (5)

Compound **5** was obtained from [PdClMe(pzpm)]²⁷ as a white-brownish solid in a similar way to compound **4**, although it does not analyse as a pure solid. Yield: 72%. Anal. Found: C, 43.29; H, 2.22; N, 6.07%. Calc. for C₄₃H₂₄BF₂₄N₅Pd: C, 43.03; H, 3.59; N, 5.98%. ¹H NMR (300 MHz, CDCl₃, RT): δ 8.74 (dd, ³J = 4.8 Hz, ⁴J = 2.4 Hz, 1H, H₄), 8.57 (dd, ³J = 3.2 Hz, ⁴J = 0.8 Hz, 1H, H₅), 8.33 (dd, ³J = 5.2 Hz, ⁴J = 2.4 Hz, 1H, H₆), 7.84 (dd, ³J = 2.4 Hz, ⁴J = 0.8 Hz, 1H, H₃'), 7.71 (s, 1H, H_b), 7.52 (s, 1H, H_d), 7.14 (dd, ³J = 5.2 Hz, ³J = 4.8 Hz, 1H, H₅), 6.76 (dd, ³J = 3.2 Hz, ³J = 2.4 Hz, 1H, H₄'), 2.32 (s, 3H, Pd-CH₃CN), 1.3 (s, 3H, Pd-CH₃). ¹³C NMR (100.5 MHz, CDCl₃, RT): δ 161.9 (q, J_{C-B} = 198.3 Hz, C_a), 161.6 (s, C₆), 156.3 (s, C₄), 143.8 (s, C₃'), 135 (s, C_b), 132.3 (s, C₅'), 129.2 (m, C_e), 126 (s, C_c), 123.3 (s, Pd-CH₃CN), 120.8 (s, C₅), 117.7 (s, C_d), 111.2 (s, C₄'), 3.2 (s, Pd-CH₃CN), -0.1 (s, Pd-CH₃).

[PdMe(NCMe)(pz*pm)][BAR'₄] (6)

Compound **6** was synthesised from [PdClMe(pz*pm)]²⁷ following a similar procedure to compound **4** and isolated as a light grey solid. Yield: 82.1%. Anal. Found: C, 44.6; H, 2.3; N, 5.6%. Calc. for C₄₄H₂₈BF₂₄N₅Pd: C, 44.1; H, 2.3; N, 5.8%. ¹H NMR (400MHz, CDCl₃, RT): δ 8.80 (dd, ³J = 4.8 Hz, ⁴J = 2.2 Hz, 1H, H₄), 8.48 (dd, ³J = 6 Hz, ⁴J = 2.2 Hz, 1H, H₆), 7.71 (s, 8H, H_b), 7.53 (s, 4H, H_d), 7.29 (dd, ³J = 6 Hz, ³J = 4.8 Hz, 1H, H₅), 6.19 (s, 1H, H₄'), 2.7 (s, 3H, (Me)₃ or (Me)₅), 2.35 (s, 3H, Pd-CH₃CN), 2.23 (s, 3H, (Me)₅ or (Me)₃), 1 (s, 3H, Pd-CH₃). ¹³C NMR (75.4 MHz, CDCl₃, RT): δ 161.9 (q, J_{C-B} = 198.2 Hz, C_a), 160.6 (s, C₆), 156 (s, C₄), 135 (s, C_b), 129.1 (m, C_e), 126.5 (s, C_c), 122.9 (s, Pd-CH₃CN), 119.3 (s, C₅), 117.7 (s, C_d), 113.5 (s, C₄'), 15.4 (s, (Me)₃ or (Me)₅), 13.3 (s, (Me)₅ or (Me)₃), 5.5 (s, Pd-CH₃CN), 3.4 (s, Pd-CH₃).

4.4.3. Copolymerization reactions- General Procedure

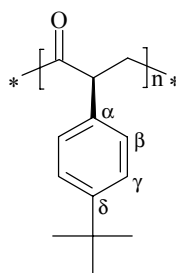
The 4-*tert*-butylstyrene was passed through a small column of Al₂O₃ prior to use. Chlorobenzene was used as purchased from Aldrich.

In a typical procedure the cationic precursor **4**, **5** or **6** (0.0125 mmol) was dissolved in 5 mL of chlorobenzene in a previously flushed Schlenk and the N₂ atmosphere replaced with CO. 4-*tert*-butylstyrene (0.7 mL, 3.875 mmol) was then introduced and the reaction was allowed to take place at room temperature and 1 atm. of CO. The experiments under 5 atm. of CO pressure were carried out in a 100 mL stainless steel Berghoff autoclave. The reaction mixture was introduced into the autoclave by suction and the pressure level was kept constant by continuous feeding from a gas reservoir. Reaction times varied from 7 hours to 96 hours. Workup included filtration of the reaction mixture through Kieselghur and precipitation of the polymeric material by adding the reaction solution dropwise into 100 mL of rapidly stirring methanol. The off-white powder was collected by filtration, washed with methanol and dried in a vacuum oven at 70° C overnight. Percentage conversions were calculated from the weight of the isolated polymeric material.

The polymers were purified by reprecipitation and then polymer weights were measured. The copolymers were dissolved in the minimum amount of THF, the solutions were filtered over a 0.22 μm filter and added dropwise to stirring methanol. The solid was then filtered and dried as previously stated.

4.4.4. Copolymer characterization

^1H NMR (300 MHz, CDCl_3 , RT): δ 7.0 (d, $^3J = 8.1$ Hz, 2H, H_β or H_γ), 6.59 (d, $^3J = 8.1$ Hz, 2H, H_γ or H_β), 4.11 (t, $^3J = 6.9$ Hz, 1H, CH), 3 (dd, $^2J = 18.1$ Hz, $^3J = 6.9$ Hz, 1H, CH_2), 2.64 (dd, $^2J = 18.1$ Hz, $^3J = 6.9$ Hz, 1H, CH_2), 1.23 (s, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (75.4 MHz, CDCl_3 , RT): δ 206.9 ($-\text{C}(\text{O})-$), 149.8 (C_δ), 134.3 (C_α), 128.2 (C_γ), 125.6 (C_β), 52.9 (CH), 43.2 (CH_2), 34.5 ($\text{C}(\text{CH}_3)_3$), 31.5 ($\text{C}(\text{CH}_3)_3$). IR (KBr, cm^{-1}): ν 1709 (C = O).



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4.5. References

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