



## Photodecarboxylative additions of phenoxyacetates to *N*-methylphthalimide

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### ABSTRACT

Photoaddition of various phenoxyacetates to *N*-methylphthalimide affords the corresponding hydroxyphthalimidines in yields of 21–93%. The diastereoselectivity of the intermolecular addition is studied for a series of 2-substituted phenoxyacetates with low diastereoselectivities being observed. Comparison experiments with anisole and ether-containing phthalimide confirm that the crucial electron-transfer step occurs from the carboxylate functionality.

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As is apparent from several review articles, the phthalimide chromophore has attracted significant interest in synthetic organic photochemistry.<sup>1</sup> Among the numerous applications, addition reactions of alkenes, alcohols, ethers, thioethers, alkylbenzenes, and amines to the phthalimide system have been described.<sup>2</sup> We have intensively studied the photodecarboxylative addition of carboxylates,  $\alpha$ -keto carboxylates, and heteroatom-substituted carboxylates to phthalimides as a versatile alternative to Grignard-additions.<sup>3</sup> The developed method has been applied to the synthesis of arylmethylene-isoindolin-1-ones (**I**; Fig. 1),<sup>4</sup> and in particular to ‘open analogues’ of aristolactams (**II**).<sup>5</sup> In continuation of this medicinal chemistry application, we became interested in the synthesis of aryloxymethylene isosteres of arylmethylene-isoindolin-1-ones.

*N*-Methylphthalimide **1** was chosen as a model compound for this study and was irradiated ( $\lambda = 300 \pm 25$  nm) in aqueous acetone in the presence of three equivalents of phenoxyacetates **2a–j** (Scheme 1).<sup>6</sup> The reaction progress was monitored by TLC analysis or by passing the departing nitrogen stream through a saturated barium hydroxide solution until precipitation of barium carbonate ceased. Following this procedure, the corresponding addition products **3a–j** were isolated in poor to excellent yields of 21–93% (Table 1).

For all compounds **3**, the C–OH group appeared as a characteristic singlet at around 90 ppm in the <sup>13</sup>C NMR spectrum. In some cases (**2c**, **g**, **h**, and **j**), larger amounts of the corresponding ‘simple’ decarboxylation products ( $-\text{CO}_2\text{H} \leftrightarrow -\text{H}$  exchange), that is, anisole

derivatives, were identified in the crude NMR spectrum, but no attempt was made to isolate these products. The *O*-benzyl-derived carboxylate **2j** gave a somewhat lower yield of the corresponding addition product **3j**. In this case, H-abstraction from the benzylic position may compete with decarboxylation.

The photoreaction involving 2-(4-chloro-2-methylphenoxy)acetate **2e** gave a mixture of the desired compound **3e** and a second, minor product (30%). Both the <sup>1</sup>H and <sup>13</sup>C NMR gave two com-

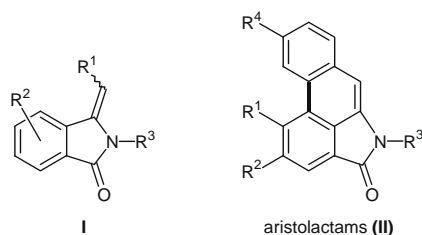
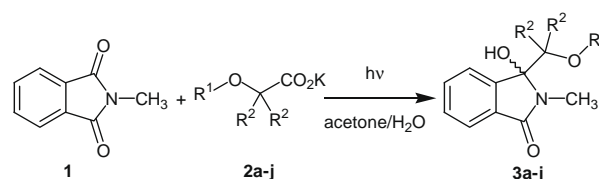


Figure 1. Examples of arylmethylene-isoindolin-1-ones.



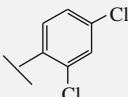
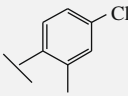
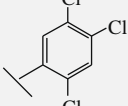
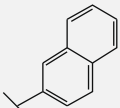
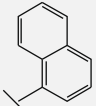
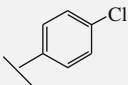


Scheme 1. Additions of phenoxyacetates **2** to *N*-methylphthalimide **1**.

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**Table 1**  
Product yields for the photodecarboxylative additions of **2** to **1**

Entry	R <sup>1</sup>	R <sup>2</sup>	Time (h)	Conversion <sup>a</sup> (%)	Yield (%)
a	Ph	H	1.5	100	85
b		H	1	100	93
c		H	11	61 <sup>b</sup>	53 (87 <sup>c</sup> )
d		H	1	100	71
e		H	1	91	55 (61 <sup>c,d</sup> )
f		H	3	87	51 (64 <sup>c</sup> )
g		H	4	65 <sup>b</sup>	48 (74 <sup>c</sup> )
h		H	10	29 <sup>b</sup>	21 (72 <sup>c</sup> )
i		Me	2	73	51 (70 <sup>c</sup> )
j	Bn	H	5	100 <sup>b</sup>	38

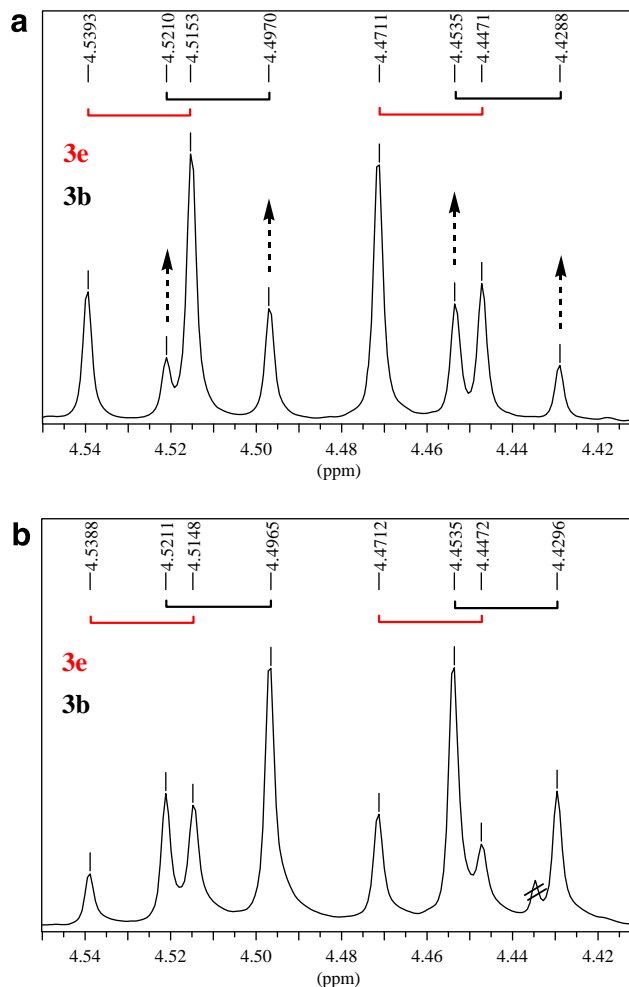
<sup>a</sup> Conversion determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture.

<sup>b</sup> Larger amounts of 'simple' photodecarboxylation (PDC) products identified in the crude NMR spectrum.

<sup>c</sup> Yield based on conversion.

<sup>d</sup> Contains 30% of **3b**.

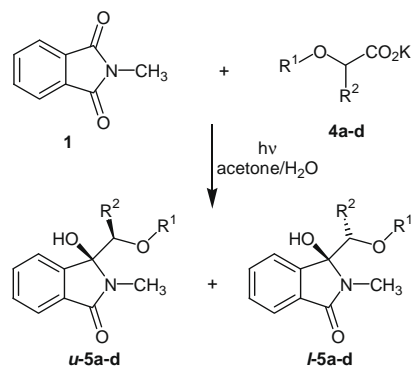
plete sets of signals, although overlap within the <sup>1</sup>H NMR made a definite assignment difficult. The purity of the corresponding carboxylic acid of **2e** was confirmed by NMR spectroscopy, and therefore the by-product must have been formed during irradiation. Based on the <sup>1</sup>H NMR spectrum, in particular the aromatic region, it was assumed that partial dehalogenation (–Cl → –H exchange) of **3e** to **3b** had occurred. A mixed NMR was subsequently recorded with independently synthesized **3b**. Following this strategy, all signals from the by-product in **3e** increased in height (Fig. 2 shows the pair of doublets for the methylene bridge –CH<sub>2</sub>Ar protons), thus unambiguously proving that it was indeed identical with **3b**. The reason for the partial dehalogenation of **3e** remains unclear at present. However, since this reaction was not observed for the related 2,4-dichlorinated carboxylic acid **2d**, the electronic nature of the *ortho*-substituent may play a crucial role in photodehalogenation. The electron-donating methyl group may thus favor dehalo-



**Figure 2.** <sup>1</sup>H NMR comparison: (a) original crude mixture (top), and (b) after addition of authentic **3b** (bottom).

genation, whereas the chloro-substituent shows no effect. Similar photodehalogenation reactions have been described in the literature.<sup>7</sup>

The photoreactions involving branched carboxylates **4a–d** furnished diastereoisomeric product mixtures **5a–d** (Scheme 2).<sup>8</sup> In all cases, two sets of signals were observed in the <sup>1</sup>H NMR spectra which were assigned to the two diastereoisomers. The diastereoisomeric ratio (de) was determined by integration of baseline separated signals in the <sup>1</sup>H NMR spectra. Selectivities were low for compounds **5a–c** being 6%; for **5d** a higher de of 28% was achieved



**Scheme 2.** Additions of branched phenoxyacetates **4** to *N*-methylphthalimide **1**.

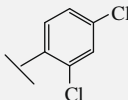
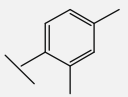
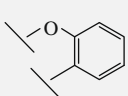
(Table 2). An assignment of the *like*- and *unlike*-diastereoisomers was not made.

Since phthalimides are known to react with ethers via H-abstraction,<sup>9</sup> *N*-methylphthalimide **1** was irradiated in the presence of five equivalents of anisole **6** (Scheme 3). Even after prolonged irradiation of 20 h, no addition product **3a** or photoreduction product was observed. Instead, **1** was recovered in 98% yield.

In order to establish the nature of the crucial photoinduced electron transfer (PET) step,<sup>10</sup> that is, whether it occurs from the carboxylate or the ether functionality, *N*-methoxymethylphthalimide **7** was irradiated in the presence of potassium propionate **8** (Scheme 4). Photodecarboxylative addition occurred smoothly and after 2 h of irradiation, compound **9** was isolated in a moderate yield of 51%.<sup>11</sup> No cyclization or photoreduction products arising from competing *intramolecular* CH-activations were detected.<sup>12</sup>

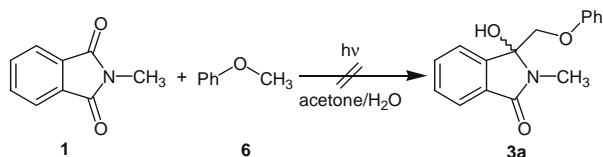
Although product formation for phenoxyacetates **2** and **4** can be explained by two competing electron transfer routes (Scheme 5), the high oxidation potentials of dialkyl ethers ( $E_{\text{Ox}} > 2.5$  V vs SCE<sup>13</sup>) makes electron transfer from the heteroatom (path A) unlikely.<sup>14,15</sup> Instead, electron transfer most likely occurs from the carboxylate functionality (path B), generating an unstable carboxy

**Table 2**  
Product yields and de ratios for photodecarboxylative additions of **4** to **1**

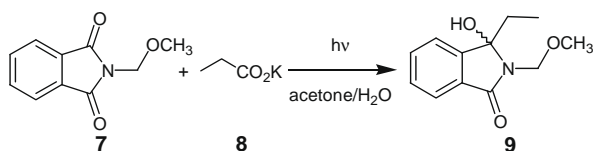
Entry	R <sup>1</sup>	R <sup>2</sup>	Time (h)	Conversion <sup>a</sup> (%)	de <sup>a</sup> (%)	Yield (%)
a	Ph	Me	2	100	6	87
b		Me	11	99	6	61 (62 <sup>b</sup> )
c		Me	1	100	6	80
d			1	95	28	83 (87 <sup>b</sup> )

<sup>a</sup> Conversion and de determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture.

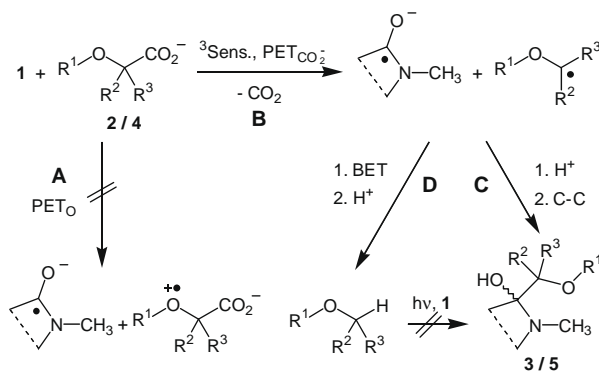
<sup>b</sup> Yield based on conversion.



**Scheme 3.** Attempted addition of anisole **6** to **1**.



**Scheme 4.** Addition of propionate **8** to *N*-methoxymethylphthalimide **7**.



**Scheme 5.** Mechanistic scenario.

radical that subsequently undergoes decarboxylation.<sup>16</sup> The resulting carbon-centered radical furnishes the observed addition products **3** and **5** (path C). The detected 'simple' decarboxylation products are formed through back electron transfer (BET) and subsequent protonation of the corresponding carbanions (path D).<sup>17</sup> This pathway was only competitive for carboxylates **2c**, **g**, **h**, and **j**, and consequently, the isolated yields for the desired addition products **3c**, **g**, **h**, and **j** remained low due to complete consumption of the carboxylate. Based on the unsuccessful addition of anisole to **1** it can be concluded that 'simple' decarboxylation products, if formed, do not contribute to the formation of addition products **3** or **5**, respectively.

The photoreactivity of *N*-methoxymethylphthalimide **7** correlates well with photoaddition reactions involving simple carboxylates.<sup>3b,d</sup> Incorporation of an ether group into the *N*-side chain has no influence on the ethylation and therefore electron transfer must occur exclusively from the propionate. In contrast, thioether-derived phthalimides are known to completely suppress photodecarboxylative additions.<sup>18</sup>

In conclusion, phenoxyacetates readily undergo photodecarboxylative addition to *N*-methylphthalimide **1**. The simple and general procedure developed offers a versatile access to 3-alkyl- and 3-arylmethylene-isoindolin-1-one isosteres and this potential application is currently being investigated. This application is also currently being transferred to 'micro-photochemistry', that is, photochemical transformations in micro-structured devices.<sup>19</sup>

## Acknowledgements

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  - General procedure for irradiation:** *N*-methylphthalimide (1.5 mmol) was dissolved in acetone (50 mL). A solution of the potassium carboxylate (4.5 mmol) in water (50 mL) was added, and the mixture was irradiated (Rayonet Photochemical Reactor RPR-200;  $\lambda = 300 \pm 20$  nm) at 15–20 °C in a Pyrex tube ( $\lambda \geq 300$  nm) while purging with a slow stream of nitrogen. The progress of the reaction was monitored by TLC analysis or by passing the departing gas stream through a saturated barium hydroxide solution until precipitation of barium carbonate ceased. Most of the acetone was evaporated and the remaining solution was extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  50 mL). The combined organic layers were washed with 5%  $\text{NaHCO}_3$  (50 mL) and brine (50 mL), dried over  $\text{MgSO}_4$ , and evaporated. The products were purified by column chromatography (eluent: *n*-hexane/EtOAc = 1:1). In some cases, the pure product precipitated upon evaporation of acetone and was isolated by vacuum filtration and drying in vacuo instead.  
Selected physical and spectral data for 3-hydroxy-2-methyl-3-[(naphthalene-1-yloxy)methyl]isoindolin-1-one **3h**: yellow solid, mp 177–182 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 2.91 (s, 3H,  $\text{NCH}_3$ ), 4.17 (s, 1H, OH), 4.47 (d,  $^2J = 9.6$  Hz, 1H,  $\text{CH}_2$ ), 4.55 (d,  $^2J = 9.6$  Hz, 1H,  $\text{CH}_2$ ), 6.79 (d,  $^3J = 7.3$  Hz, 1H,  $\text{H}_{\text{arom}}$ ), 7.32 (m, 2H,  $\text{H}_{\text{arom}}$ ), 7.42 (m, 2H,  $\text{H}_{\text{arom}}$ ), 7.46 (ddd,  $^3J = 7.3$ ,  $^4J = 7.3$ ,  $^4J = 1.0$  Hz, 1H,  $\text{H}_{\text{arom}}$ ), 7.55 (ddd,  $^3J = 7.3$ ,  $^3J = 7.3$ ,  $^4J = 1.0$  Hz, 1H,  $\text{H}_{\text{arom}}$ ), 7.69 (m, 4H,  $\text{H}_{\text{arom}}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 24.2, 68.8, 89.2, 105.3, 121.6, 121.8, 122.4, 123.6, 125.5, 125.8, 125.9, 126.9, 127.7, 130.4, 131.9, 132.8, 134.7, 145.6, 153.9, 168.3. IR (KBr):  $\nu = 3295$ , 2945, 2347, 1676, 1618, 1070, 874  $\text{cm}^{-1}$ . MS (EI, 70 eV):  $m/z$  (%) = 319 ( $\text{M}^+$ , 6), 301 ( $\text{M}^+ - \text{H}_2\text{O}$ , 100), 272 (301-COH, 18), 244 ( $\text{M}^+ - \text{C}_6\text{H}_4$ , 7), 162 ( $\text{M}^+ - \text{C}_{11}\text{H}_9\text{O}$ , 84), 77 ( $\text{C}_6\text{H}_5$ , 23). MS (ESI, positive ions):  $m/z = 320$  ( $\text{M} + \text{H}^+$ ), 639 ( $\text{M}_2 + \text{H}^+$ ). HR-MS (ESI, positive ions): calcd [ $\text{M} + \text{H}$ ] $^+$ : 320.12812 for  $\text{C}_{20}\text{H}_{17}\text{NO}_3 + \text{H}^+$ . Found [ $\text{M} + \text{H}$ ] $^+$ : 320.12783. calcd [ $\text{M} + \text{Na}$ ] $^+$ : 342.11006 for  $\text{C}_{20}\text{H}_{17}\text{NO}_3 + \text{Na}^+$ . Found [ $\text{M} + \text{Na}$ ] $^+$ : 342.10988.
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  - Selected physical and spectral data for 3-[1-(2,4-dichlorophenoxy)ethyl]-3-hydroxy-2-methylisoindolin-1-one **u-ll-5b**: yellow solid, mp (mixture) 115–125 °C. Main diastereoisomer:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 1.01 (d,  $^3J = 6.3$  Hz, 3H,  $\text{CH}_3$ ), 2.97 (s, 3H,  $\text{NCH}_3$ ), 4.52 (s, 1H, OH), 4.76 (q,  $^3J = 6.3$  Hz, 1H, CH), 6.90 (d,  $^3J = 8.8$  Hz, 1H,  $\text{H}_{\text{arom}}$ ), 7.13 (dd,  $^3J = 8.8$ ,  $^4J = 2.5$  Hz, 1H,  $\text{H}_{\text{arom}}$ ), 7.31 (d,  $^4J = 2.5$  Hz, 1H,  $\text{H}_{\text{arom}}$ ), 7.40 (m, 1H,  $\text{H}_{\text{arom}}$ ), 7.47–7.55 (m, 2H,  $\text{H}_{\text{arom}}$ ), 7.58 (d,  $^3J = 7.9$  Hz, 1H,  $\text{H}_{\text{arom}}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 14.8, 25.8, 80.1, 91.3, 116.8, 123.4, 123.9, 125.1, 127.6, 128.2, 130.7, 130.8, 132.4, 132.6, 144.2, 152.4, 168.4. Minor diastereoisomer:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 0.82 (d,  $^3J = 6.3$  Hz, 3H,  $\text{CH}_3$ ), 2.84 (s, 3H,  $\text{NCH}_3$ ), 3.15 (s, 1H, OH), 4.72 (q,  $^3J = 6.3$  Hz, 1H, CH), 6.98 (d,  $^3J = 8.9$  Hz, 1H,  $\text{H}_{\text{arom}}$ ), 7.14 (dd,  $^3J = 8.9$ ,  $^4J = 2.5$  Hz, 1H,  $\text{H}_{\text{arom}}$ ), 7.34 (d,  $^3J = 2.5$  Hz, 1H,  $\text{H}_{\text{arom}}$ ), 7.41 (m, 1H,  $\text{H}_{\text{arom}}$ ), 7.47–7.55 (m, 1H,  $\text{H}_{\text{arom}}$ ), 7.61 (d,  $^3J = 7.9$  Hz, 1H,  $\text{H}_{\text{arom}}$ ), 8.02 (d,  $^3J = 7.6$  Hz, 1H,  $\text{H}_{\text{arom}}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 14.9, 24.4, 78.7, 91.2, 116.9, 122.4, 125.3, 125.5, 127.3, 128.1, 130.3, 130.6, 132.0, 132.8, 144.1, 152.8, 168.2. IR (KBr, mixture):  $\nu = 3304$ , 2983, 2346, 1681, 1618, 1064, 750  $\text{cm}^{-1}$ . MS (EI, 70 eV, mixture):  $m/z$  (%) = 351 ( $\text{M}^+$ , <1), 333 ( $\text{M}^+ - \text{H}_2\text{O}$ , <1), 188 ( $\text{M}^+ - \text{C}_9\text{H}_8\text{NO}_2$ , 23), 162 ( $\text{M}^+ - \text{C}_8\text{H}_7\text{Cl}_2\text{O}^+$ , 100), 146 ( $\text{M}^+ - \text{C}_{11}\text{H}_{12}\text{NO}_3$ , 8), 77 ( $\text{C}_6\text{H}_5$ , 8). HR-MS (ESI, positive ions, mixture): calcd [ $\text{M} + \text{H}$ ] $^+$ : 352.05018 for  $\text{C}_{17}\text{H}_{15}\text{Cl}_2\text{NO}_3 + \text{H}^+$ . Found [ $\text{M} + \text{H}$ ] $^+$ : 352.05007.
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  - Physical and spectral data for 3-ethyl-3-hydroxy-2-(methoxymethyl)-isoindolin-1-one **9**: yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 0.59 (t,  $^3J = 7.6$  Hz, 3H,  $\text{CH}_3$ ), 2.24 (m, 2H,  $\text{CH}_2$ ), 3.40 (s, 3H,  $\text{OCH}_3$ ), 4.93 (m, 2H,  $\text{CH}_2$ ), 5.30 (s, 1H, OH), 7.58 (ddd,  $^3J = 7.6$ ,  $^3J = 7.6$ ,  $^4J = 1.0$  Hz, 1H,  $\text{H}_{\text{arom}}$ ), 7.65 (d,  $^3J = 7.6$  Hz, 1H,  $\text{H}_{\text{arom}}$ ), 7.71 (ddd,  $^3J = 7.6$ ,  $^3J = 7.6$ ,  $^4J = 1.0$  Hz, 1H,  $\text{H}_{\text{arom}}$ ), 7.75 (d,  $^3J = 7.2$  Hz, 1H,  $\text{H}_{\text{arom}}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.3, 31.2, 57.0, 70.5, 91.9, 123.1, 123.8, 130.1, 133.5, 144.0, 149.0, 166.0.
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