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Reactions of Manganese Pentadienoyl Complexes. Synthesis of (η^4-allyl–amide)Mn(CO)$_3$ Complexes: (η^4-oxapentadienyl)Mn(CO)$_3$ Complexes

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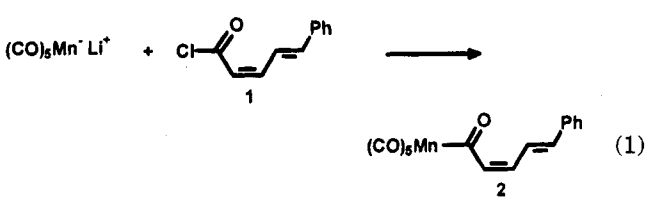
*Summary: (η^1-(2Z,4E)-5-phenylpentadienoyl)Mn(CO)$_5$ (**2**) was prepared by the reaction of Li(CO)$_5$Mn and (2Z,4E)-5-phenylpentadienoyl chloride. Introduction of **2** to N-methylmorpholine N-oxide in the presence of selected amines gives the amine-substituted η^4-oxapentadienyl complexes **3a–d**, which may also be described as (η^4-allyl–amide)Mn(CO)$_3$ complexes. Reaction of **2** with trimethylamine N-oxide in the absence of nucleophiles gives the dimethylamine–η^4-oxapentadienyl complex **3e**. X-ray crystallographic analysis of this complex corroborates that the oxapentadienyl ligand is bonded in an η^4 fashion. Addition of CH$_3$OH and N-methylmorpholine N-oxide to **2** forms the carbomethoxy ester substituted η^3-allyl complex **6**.*

We here report (1) the synthesis of amine-substituted (η^4-oxapentadienyl)Mn(CO)$_3$ complexes from the reaction of an (η^1-pentadienoyl)Mn(CO)$_5$ complex with selected amines and *N*-methylmorpholine *N*-oxide, (2) the reaction of an (η^1-pentadienoyl)Mn(CO)$_5$ complex with trimethylamine *N*-oxide to give a dimethylamine-substituted (η^4-oxapentadienyl)Mn(CO)$_3$ species, and (3) the reaction of an (η^1-pentadienoyl)Mn(CO)$_5$ complex with *N*-methylmorpholine *N*-oxide and methanol to give a carbomethoxy ester substituted (η^3-allyl)Mn(CO)$_3$ complex. To our knowledge, these reported oxapentadienyl complexes contain the first examples of η^4-coordinated pentadienyl ligands.

Recently we reported the characterization of (η^5-C$_5$H$_5$)Fe(pentadienoyl) complexes where a terminal carbon of a pentadienyl ligand incorporated a cumulated carbonyl moiety.[1] These complexes exhibit an enhanced reactivity over pentadienyl complexes where electrocyclic ring closure followed by keto–enol tautomerization led to formation of hydroxyferrocenes.[2] In our efforts to initiate a study of the synthesis and chemistry of pentadienoyl complexes of manganese, we prepared (CO)$_5$-Mn(η^1-(2Z,4E)-5-phenylpentadienoyl) (**2**) in 80% yield as red needles by the reaction of Li(CO)$_5$Mn[3] with (2Z,4E)-5-phenylpentadienoyl chloride[4] (**1**), as shown in eq 1.



(1)

Thermal and photochemical reaction attempts to affect loss of terminal carbonyl ligands from complex **2** to give η^3- and η^5-pentadienoyl complexes[5] did not meet

[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1994.

(1) (a) Yongskulrote, W.; Bramlett, J. M.; Mike, C. A.; Durham, B.; Allison, N. T. *Organometallics* **1989**, *8*, 556. (b) Dawson, D. P.; Yongskulrote, W.; Bromlett, J. M.; Wright, J. B.; Durham, B.; Allison, N. T. *Organometallics*, in press.

(2) (a) Ernst, R. D. *Chem. Rev.* **1988**, *88*(7), 1255–1291. (b) Powell, P. *Adv. Organomet. Chem. 26*, 125–64; **1986**, *6*(6), 1367–1369. (c) Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*(2), 56–62. (d) Ernst, R. D. *Struct. Bonding (Berlin)* **1984**, *57*, 1–53.

(3) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553–558.

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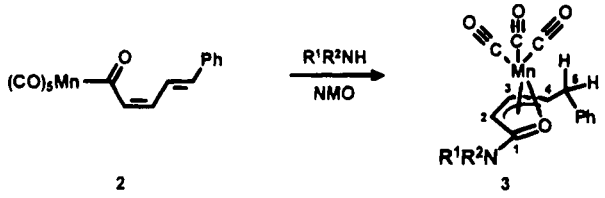
with success; however, slow addition of *N*-methylmorpholine *N*-oxide (NMO) and selected amines to acyl complex **2** gave η^4-coordinated oxapentadienyl complexes **3** as yellow solids, as shown in Table 1.[6,7]

Table 1. (η^4-oxapentadienyl)Mn(CO)$_3$ Products 3 and Yields from the Reaction of 2 with NMO and Selected Amines

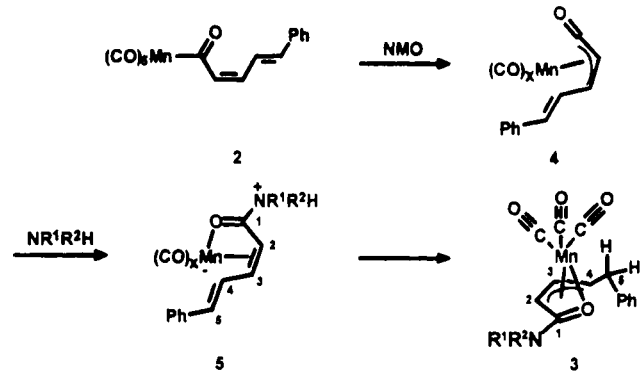


product	R^1	R^2	yield, %
3a	$-(CH_2)_3CH_3$	$-H$	15
3b	$-CH_2CH_3$	$-CH_2CH_3$	56
3c	$-CH_2C_6H_5$	$-H$	27
3d	$-(CH_2)_4-$		24

The oxapentadienyl ligand's ^{1}H NMR resonances in **3a** are typical for all complexes **3** and appear at δ 7.33 (m, 4H, Ph), 7.23 (m, 1H, Ph), 5.16 (dd, J_{23} = 7.05 Hz, J_{34} = 12.27 Hz, 1H, HC(3)), 4.25 (d, J_{23} = 7.05 Hz, 1H, HC(2)), 3.08 (ddd, J_{34} = 12.27 Hz, J_{45} = 4.83 Hz, $J_{45'}$ = 8.51 Hz, HC(4)), 3.76 (dd, J_{45} = 4.83 Hz, $J_{55'}$ = −14.80 Hz, 1H, HC(5)), 3.22 (dd, $J_{45'}$ = 8.51 Hz, $J_{55'}$ = −14.80 Hz, 1H, HC(5′)). Other resonances include an N−H absorption at δ 5.24 (broad s) and diastereotopic proton absorptions attributed to the CH_2−N moiety at δ 2.98 (ddt, J_{gem} = −13.6 Hz, J_{HNCH} = 6.9 Hz, J_{HCCH} = 6.8 Hz,1H), and 2.89 (ddt, J_{gem} = −13.6 Hz, J_{HNCH} = 6.9 Hz, J_{HCCH} = 6.5 Hz, 1H). Other multiplets appearing at δ 1.375 (N−C−CH_2), 1.275 (N−C−C−CH_2), and 0.878 (t, J = 7.2 Hz, CH_3) are observed.[8,9]

The ^{13}C NMR spectrum of **3a** gave resonances at δ 225, 224, and 223 (terminal CO) and 168.60 (amide C=O), with allyl resonances at δ 51.17 (C(2)), 106.02 (C(3)), and 80.17 (C(4)). Other resonances appear at δ 40.71 and 39.02 (*C*-Ph and *C*-N), 142.50 (Ph_{ipso}), 129.17 and 129.03 (Ph_{ortho}, Ph_{meta}), 126.79 (Ph_{para}), 31.37 (*C*−CN), 19.80 (*C*−CCN), and 13.49 (*C*−CCCN). The IR spectrum (CH_2Cl_2) of **3a** gave strong terminal carbonyl resonances at ν 2019, 1936, and 1909 cm^{-1}. The absorption observed at 1573 cm^{-1} is consistent with that of a coordinated amide moiety.

Scheme 1



A mechanism consistent with the formation of complexes **3** from acyl complex **2** is shown in Scheme 1. Decarbonylation of **2** leads to the η^3-allylketene complex **4**. Nucleophilic attack of **4** with an amine results in formation of the coordinated amide complex **5**. Hydrogen migration from N to C(5) with concomitant coordination of the π system gives the η^4-oxapentadienyl product **3**.[10]

To explore the effectiveness of a second decarbonylating reagent, we introduced trimethylamine *N*-oxide to acyl complex **2** *without* added amines.[11] In this case, we isolated the dimethyl complex **3e** as a yellow solid in 19% yield (eq 2). This complex was recrystallized in pentane to give yellow needles of X-ray crystallographic quality.[12]

X−ray crystallographic analysis of **3e** produced the structure shown in Figure 1.[13] The planarity of the C(1), N(1), C(15), and C(16) atoms and the fact that C(1) is out of plane from the remaining coordinated pentadienyl ligand atoms are consistent with an amide moiety being incorporated in the oxapentadienyl structure. As is typical for amides, π donation from the nitrogen atom

(4) The acid chloride **1** can be prepared from its corresponding carboxylic acid using oxalyl chloride. The carboxylic acid is generated from addition of CO_2 to 1-lithio-4-phenylbutadiene generated by lithium−halogen exchange (Seebach, D.; Neumann, H. *Tetrahedron Lett.* **1976**, *18*, 4839−4842) from 1-bromo-4-phenylbutadiene (Matsumoto, M.; Kuroda, K. *Tetrahedron Lett.* **1980**, *21*, 4021−4024).

(5) Lee, T. W.; Liu, R. S. *J. Organomet. Chem.* **1987**, *320*(2), 211−216.

(6) No reactions are observed when **2** is introduced to amines in the absence of amine oxides.

(7) The general procedure is as follows: A Schlenk tube equipped with magnetic stirrer and septum was charged with 0.223 g (0.6 mmol) of ((2*Z*,4*E*)-5-phenylpentadienoyl)Mn(CO)$_5$ and 10 mL of CH_2Cl_2. Two solutions, a solution of 0.16 g (1.4 mmol) of *N*-methylmorpholine *N*-oxide in 10 mL of CH_2Cl_2 and a solution of amine (0.7 mmol) in 10 mL of CH_2Cl_2, were simultaneously added over 3 h. After addition, the reaction mixture was then refluxed for 5 h. The products were purified by column chromatography (silica gel, CH_2Cl_2−hexane 1:2).

(8) Computer simulation of spectral data with the LAOCOON3 computer program gave the coupling constant and shift data. For LAOCOON3 cf.: Bothner-By, A. A.; Castellano, S. In *Computer Programs for Chemistry*; DeTar, D. F., Ed.; Benjamin: New York, 1968; Vol. 1, Chapter 3; Program QCPE 111 from Quantum Chemistry Program Exchange, Bloomington, IN. The IBM-PC modified program by M. Clark and J. S. Thrasher, QCMP 013, was used.

(9) Data for **3a**: yellow solid, mp 50.5−51 °C. Anal. Calcd for $C_{18}H_{20}MnNO_4$·0.3C_5H_{12} (pentane from recrystallization): C, 59.69; H, 5.99. Found: C, 60.05; H, 5.73. Data for **3b**: yellow solid, mp 57.5−58 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (m, 4H, Ph), 7.23 (m, 1H, Ph), 5.20 (dd, J_{23} = 7.1 Hz, J_{34} = 12.2 Hz, 1H, C(3)H), 4.36 (d, J_{23} = 7.1 Hz, 1H, C(2)H), 3.77 (dd, J_{45} = 4.9 Hz, J_{55} = 14.6 Hz, 1H, C(5)H), 3.45 (m, 1H, NC*H*), 3.25 (complex m, 2H, C(5)H′ and NC*H*), 3.08 (complex multiplet, 3H, C(4)H, NCH_{syn}, NCH_{anti}), 1.287 (t, J = 7.2 Hz, NCC*H*, 3H), 0.964 (t, J = 7.2 Hz, NCC*H*, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 225, 224, and 221 (terminal CO), 168.19 (amide C=O), 143.3 (Ph_{ipso}), 129.28, 129.18 (Ph_{ortho}, Ph_{meta}), 126.87 (Ph_{para}), 106.24 (C(3)), 80.81 (C(4)), 49.19 (C(2)), 41.85, 41.02, 39.57 (C_{benzyl}, N−C_{cis}, N−C_{trans})), 13.64, 12.98 (N−C−C_{cis}, N−C−C_{trans}). IR (CH_2Cl_2): 2015, 1933, 1904 cm^{-1} (terminal CO), 1568 cm^{-1} (amide). Anal. Calcd for $C_{18}H_{20}MnNO_4$: C, 58.54; H, 5.46. Found: C, 58.65; H, 5.48. Data for **3c**: yellow solid, mp 94.5−95.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 7.25 (m, 10H, Ph), 5.52 (br s, 1H, NH), 5.20 (dd, J_{23} = 7.0 Hz, J_{34} = 12.1 Hz, 1H, C(3)H, 4.26 (d, J_{23} = 7.0 Hz, 1H, C(2)H) 4.17 (dd, J_{HCNH} = 6.2 Hz, J_{gem} = 14.5 Hz, 1H, NCH_{benzyl}), 4.05 (dd, $J_{H'CNH}$ = 5.5 Hz, J_{gem} = 14.7 Hz, 1H, NCH'_{benzyl}), 3.78 (dd, J_{45} = 4.76 Hz, $J_{55'}$ = 14.56 Hz, 1H, C(5)H), 3.24 (m, 1H, C(4)H), 3.24 (dd, $J_{45'}$ = 8.5 Hz, $J_{55'}$ = 14.6 Hz, 1H, C(5)H′), 3.15 (m, 1H, C(4)H. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 224.2, 223.1, 219.8 (terminal CO), 167.54 (amide C=O), 142.54 (Ph_{ipso}), 136.86 (Ph_{ipso}), 129.25, 128.91, 128.77, 128.22 (Ph_{ortho}, Ph_{ortho}, Ph_{meta}, Ph_{meta}), 128.38, 126.56 (Ph_{para}, Ph_{para}), 105.92 (C(3)), 80.55 (C(4)), 51.28 (C(2)), 43.48 ($C_{benzyl\text{-}N}$), 40.91 (C_{benzyl}). IR ($CDCl_3$): 2019.9, 1938.1, 1910.6 cm^{-1} (MCO), 1567.0 cm^{-1} (amide). Anal. Calcd for CHMnN: C, 62.54; H, 4.50. Found: C, 62.31; H, 4.75. Data for **3d**: yellow solid, mp 93−94.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (m, 5H, Ph), 5.20 (dd, J_{23} = 7.1 Hz, J_{34} = 12.1 Hz, 1H, C(3)H), 4.28 (d, J_{23} = 7.1 Hz, 1H, C(2)H), 3.78 (dd, J_{45} = 4.6 Hz, $J_{55'}$ = 14.6 Hz, 1H, C(5)H), 3.51 (complex m, 2H, NCH, NCH), 3.1 (complex m, 3H, C(4)H, NCH, NCH), 1.9 (complex m, 4H, NCCH). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 224.1, 222.8, 220.0 (terminal CO), 165.87 (amide C=O), 142.50 (Ph_{ipso}), 128.55, 128.42 (Ph_{ortho}, Ph_{meta}), 126.15 (Ph_{para}), 105.92 (C(3)), 80.02 (C(4)), 50.53 (C(2)), 46.16 (N−*C*), 44.71 (N−*C*), 40.72 (C(5)), 25.37 (NC−C), 25.35 (NC−*C*). IR ($CHCl_3$): 2016, 1933, 1906 cm^{-1} (terminal CO), 1573 cm^{-1} (amide).

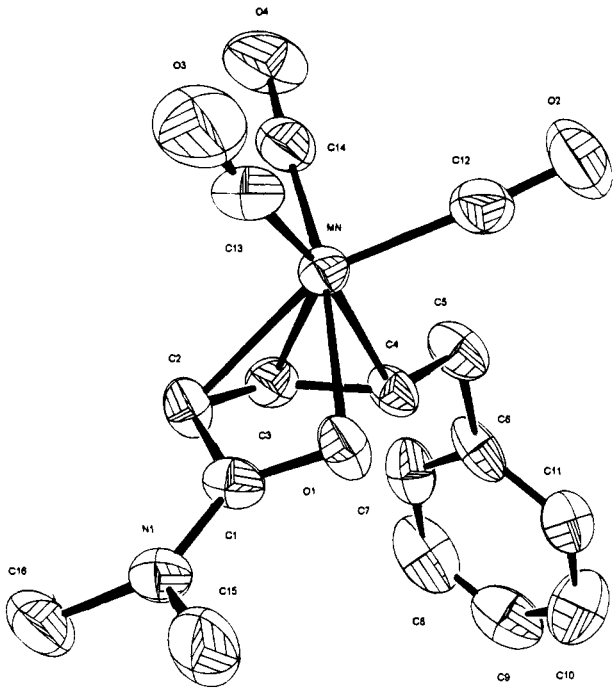
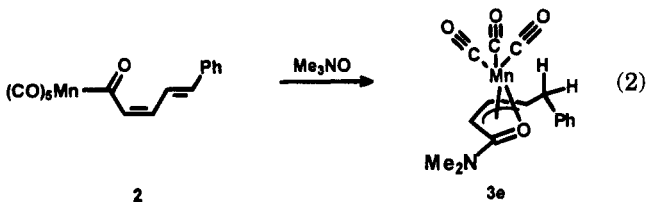


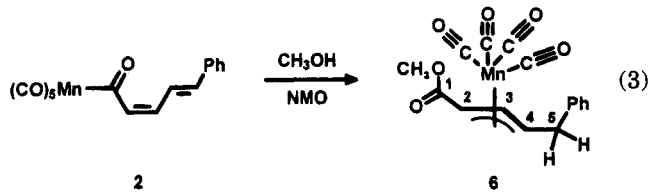
Figure 1. ORTEP drawing (30% probability ellipsoids) of the X-ray crystal structure of compound **3e**, and atomic labeling scheme. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) are as follows: Mn—O(1), 2.114(9); Mn—C(1), 2.49(2); Mn—C(2), 2.15(1); Mn—C(3), 2.07(1); Mn—C(4), 2.19(1); Mn—C(12), 1.82(2); Mn—C(13), 1.76(2); Mn—C(14), 1.75(2); C(1)—O(1), 1.27(2); C(1)—N(1), 1.29(2); C(1)—C(2), 1.48(2); C(2)—C(3), 1.42(2); C(3)—C(4), 1.38(2); C(4)—C(5), 1.53(2). C(1), N(1), C(15), and C(16) are within 0.02 Å of the least-squares plane. C(1) is displaced 0.48 Å from the least-squares plane defined within 0.03 Å by O(1), C(2), C(3), and C(4).



(2)

increases the basicity of the carbonyl, thus enhancing the observed dative coordination. This electronic effect contrasts sharply with the bonding of manganese η^5-oxapentadienyl complexes that are similarly substituted by —(OR groups.[14]

Initial attempts to investigate the scope of this reaction with other possible non-amine nucleophiles focused on the addition of methanol and NMO to acyl complex **2**. The resulting η^3-allyl complex **6** was isolated in a low (5%) yield (eq 3).[14,15]



(3)

Further work aimed at reactions of complexes **3** and other reactions of pentadienoyl complexes is being pursued.

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Supplementary Material Available: Tables of crystal and refinement data, atomic parameters for non-H atoms, anisotropic temperature factors, atomic parameters for H atoms, interatomic distances and angles and least-squares plane data (7 pages). Ordering information is given on any current masthead page.

OM940163U

(10) Zuniga Villarreal, N.; Paz-Sandoval, M. A.; Joseph-Nathan, P.; Esquivel, R. O. *Organometallics* **1991**, *10*, 2616–2125.

(11) For an excellent discussion of the reaction chemistry of trimethylamine *N*-oxide with metal carbonyls cf.: Pearson, A. J.; Shively, R. J., Jr. *Organometallics* **1994**, *13*, 578–584.

(12) Data for **3e**: yellow needles, mp 84.0–85.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (m, 4H, Ph), 7.23 (m, 1H, Ph), 5.20 (dd, J_{23} = 7.15 Hz, J_{34} = 12.2 Hz, 1H, C(3)H), 4.37 (d, J_{23} = 7 Hz, 1H, C(2)H), 3.78 (dd, J_{45} = 4.65 Hz, $J_{55'}$ = 14.6 Hz, 1H, C(5)H), 3.23 (dd, $J_{45'}$ = 8.12 Hz, $J_{55'}$ = 14.6 Hz, C(5)H'), 3.05 (m and s, 4H, NCH_3, and C(5)H), 2.63 (s, 3H, NCH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 224, 223, and 220 (terminal CO), 167.97 (amide C=O), 142.24 (Ph_{ipso}), 128.25, 128.10 (Ph_{ortho}, Ph_{meta}), 125.84 (Ph_{para}), 105.11 (C(3)), 79.65 (C(4)), 47.92 (C(2)), 39.90 (C_{benzyl}), 35.49, 32.98 (N—C_{cis}, N—C_{trans}). IR ($CDCl_3$): 2050, 1950, 1890 cm^{-1} (terminal CO), 1580 cm^{-1} (amide). Anal. Calcd for $C_{16}H_{16}MnNO_4$: C, 56.32; H, 4.73. Found: C, 56.17; H, 5.47.

(13) X-ray data for **3e**: monoclinic, space group $P2_1/c$, with a = 9.411(4) Å, b = 18.35(1) Å, c = 10.884(9) Å, β = 115.10(4)°, V = 1702(2) Å^3, d_{calc} = 1.45 g/cm^3, Z = 4, and μ = 7.7 cm^{-1}. Of 2356 reflections collected (Enraf-Nonius CAD-4, 293 K, Mo Kα), 813 had $I > 3\sigma(I)$. Least-squares refinement of 199 parameters converged at R_F = 0.057.

(14) Compound **6** was the only isolated product from this reaction using a procedure identical to the preparation of compounds **3a**–**d**[7] except that methanol was substituted for the amine. A carbomethoxy (η^3-allyl)Mn(CO)$_4$ complex has been reported. Under thermolytic conditions carbomethoxy (η^3-allyl)Mn(CO)$_4$ complexes can convert to oxapentadienyl complexes. Cf.: Cheng, M. H.; Cheng, C. Y.; Wang, S. L.; Peng, S. M.; Liu, R. S. *Organometallics* **1990**, *9*(6), 1853–1861.

(15) Data for **6**: yellow solid, mp 54–56 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3 (m, 5H, Ph), 5.52 (ddd, J_{23} = 10 Hz, J_{34} = 12 Hz, J_{35} = 0.7 Hz, 1H, C(3)H), 3.40 (m, 1H, C(4)H), 3.47 (dd, J_{45} = 2.8 Hz, $J_{55'}$ = 15 Hz, 1H, C(5)H), 3.2 (dd, J_{45} = 8 Hz, $J_{55'}$ = 15 Hz, 1H, C(5')H), 2.32 (d, J_{23} = 10 Hz, 1H, C(2)H), 3.75 (s, 3H, OCH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 216.7, 212.6, 211.0 (terminal CO), 172.5 (ester CO), 138.8 (Ph_{ipso}), 127.8, 127.4 (Ph_{ortho}, Ph_{meta}), 125.9 (Ph_{para}), 94.3, 69.8, 50.6 (allyl), 40.6, 39.3 (C_{benzyl}, CH_3O). IR (CH_2Cl_2) 2078, 1992, 1962 cm^{-1} (terminal CO), 1705 cm^{-1} (amide). MS: *m/z* 356 (M$^+$), 328 (M$^+$ − CO), 300 (M$^+$ − 2CO), 272 (M$^+$ − CO), 271, 244 (M$^+$ − 4CO).