Supplementary Material

(ω-Ammonioalkyl)cyclopentadienides by Rhodium-Catalyzed Vinylcarbene Transfer to Semicyclic Enaminocarbonyl Compounds

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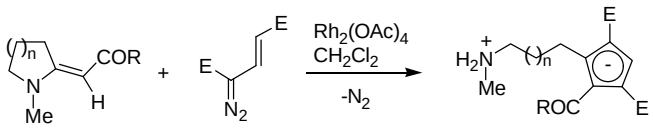
ABSTRACT



1 **2** **3**

R = aryl, hetaryl, OMe, O^{t}Bu
n = 1, 2, 3
E = COOMe

The rhodium(II)-catalyzed reaction of vinyldiazoacetate 2 **with semicyclic ß-enaminocarbonyl compounds** 1 **provides (ω-methylammonioalkyl)cyclopentadienides** 3**. This transformation represents a novel reaction cascade which combines carbenoid addition at a C=C bond with a ring-chain transformation. In some cases, products resulting from vinylcarbene insertion into the enaminic C–H bond of** 1 **are also isolated. These dienamines undergo subsequent isomerization to furnish betaines** 3**.**

EXPERIMENTAL

General Information. NMR spectra: Bruker AC 200 (^{1}H: 200.13 MHz; ^{13}C: 50.32 MHz) and Bruker AMX 500 (^{1}H: 500.14 MHz; ^{13}C: 125.77 MHz). Unless stated otherwise, all spectra were recorded with the latter instrument. TMS was always applied as the internal standard. IR spectra: Perkin-Elmer IR-Spectrophotometer 883; wavenumbers [cm^{-1}] are given. Elemental analyses: Perkin Elmer EA 240. Mass spectra: Varian MAT 711. Column chromatography was performed under hydrostatic pressure (silica gel Si 60, Macherey-Nagel, 0.063–0.2 mm) and under medium-pressure conditions (Merck Lobar columns, Lichroprep Si 60, particle size 40-63 μm, two columns (240x10 mm and 310x25 mm) connected; gradient pump Merck-Hitachi L6200).

All reactions were carried out in rigorously dried glassware under an argon atmosphere. Solvents were dried according to standard methods and stored under an argon atmosphere.

The following ß-enaminocarbonyl compounds were prepared by literature methods: **1a–e,j–l**;[1] **1f**;[2] **1g**;[3] **1h**,**i**.[4]

Dimethyl (*E*)-3-Diazo-1-propene-1,3-dicarboxylate (2). This compound was prepared from dimethyl glutaconate (12.33 g, 78 mmol) and *p*-acetamidobenzenesulfonyl azide (16.35 g, 0.78 mmol) according to the procedure for the diethyl ester:[5] yellow solid (12.78 g, 89 %); mp 58 °C; IR (KBr) 2105 (s, CN_2), 1720 (s, C=O), 1198 (vs) cm^{-1}; ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 3.75 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 5.73 (d, J = 15.8, 1H, CH), 7.34 (d, J = 15.8, 1H, CH); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 51.34 (OCH_3), 52.41 (OCH_3), 65.02 (CN_2), 111.00 (CH=), 130.81 (CH=), 163.25 (C=O), 166.22 (C=O). Anal. Calcd for $C_7H_8N_2O_4$ (184.1): C, 45.67; H, 4.38; N, 15.22; found C, 45.70; H, 4.39; N, 14.77.

Catalytic Decomposition of Vinyldiazoacetate 2 in the Presence of Enaminocarbonyl Compounds 1; General Procedure. A solution of **1** (1.2 equiv with respect to the enaminocarbonyl compound) in dichloromethane (5 mL) was added during 10 h with the help of an infusion pump to a stirred solution of enaminocarbonyl compound **1** (1.5–3.5 mmol) and $Rh_2(OAc)_4$ (3–4 mol%). Stirring was continued until evolution of nitrogen had ceased or until the IR absorption of the diazo group had disappeared (normally 1–2 h). In some cases, most of the betaine **3** crystallized from the mixture and was collected by filtration. An additional small portion of product was then obtained by column chromatography of the mother liquor (silica gel, elution with ethyl acetate). If the product did not crystallize from the reaction mixture, the

solvent was removed at rt/0.01 mbar and the residue was fractionated by column chromatography over silica gel. Elution with ethyl acetate furnished the following fractions: a) a small amount of unidentified products; b) a mixture of dienamine **4** (if formed) and catalyst which was separated by a second column chromatography (Merck Lobar columns, silica gel, elution with ethyl acetate). Further elution with methanol yielded betaine **3** which was purified further by chromatography (Merck Lobar columns, silica gel, elution with ethyl acetate).

3-[5-Benzoyl-2,4-di(methoxycarbonyl)cyclopentadienide]propyl(methyl)ammonium (3a). Prepared from **2** (469 mg, 2.55 mmol), $Rh_2(OAc)_4$ (45 mg, 0.10 mmol, 4 mol%), and **1a** (500 mg, 2.12 mmol). Crystallization from ethyl acetate gave a beige powder (191 mg, 23 %); mp 180 ^{o}C; IR (KBr) 3442 (m, br, NH_2^+), 1739 (sh), 1643 (s), 1485 (s), 1239 (s) cm^{-1}; ^{1}H NMR (CD_3OD): δ 2.22 (m_c, 2H, CH_2), 2.70 (s, 3H, NCH_3), 2.96 (m_c, 2H, CH_2), 3.09 (t, *J* = 6.3, 2H, NCH_2), 3.12 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 7.24 (s, 1H, CH), 7.37–7.48 (m, 3H, H_{Ph}), 7.66 (d, *J* =7.2, 2H, H_{Ph}), 9.19 (br, 2H, NH_2^+); ^{13}C NMR (CD_3OD) δ = 24.24 (CH_2), 27.24 (CH_2), 33.08 (NCH_3), 49.0 ppm (NCH_2, covered by solvent signal), 50.75 (OCH_3), 50.76 (OCH_3), 114.04 (C_{cp}), 117.82 (C_{cp}), 125.09 (CH_{cp}), 125.57 (C_{cp}), 128.80 (meta-C_{Ph}), 130.38 (ortho-C_{Ph}), 132.02 (para-C_{Ph}), 136.83 (C_{cp}), 144.82 (ipso-C_{Ph}), 169.40 (C=O), 169.70 (C=O), 197.97 (C=O). Anal. Calcd for $C_{20}H_{23}NO_5$ (357.4): C, 67.22; H, 6.49; N, 3.92; found C, 66.76; H, 6.46; N, 3.92.

3-[5-(4-Methoxybenzoyl)-2,4-di(methoxycarbonyl)cyclopentadienide]propyl-(methyl)ammonium (3b). Prepared from **2** (478 mg, 2.59 mmol), $Rh_2(OAc)_4$ (34 mg, 0.08 mmol, 3 mol%), and **1b** (500 mg, 2.16 mmol); yellow foam (600 mg, 72 %): IR (film) 3449 (br, w) and 3200–2400 (br, NH_2^+), 1710 (sh), 1642 (s), 1603 (s), 1541 (m), 1483 (s), 1443 (s), 1406 (m), 1303 (m), 1241 (s), 1205 (s), 1168 (s), 1145 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.19 (m_c, 2H, CH_2), 2.42 (s, 3H, NCH_3), 2.81 (m_c, 2H, CH_2), 3.00 (m_c, 2H, NCH_2), 3.38 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 7.31 (s, 1H, 3-H_{cp}), 6.86, 7.76 (AA'BB' system, 4H, C_6H_4), 9.23 (br s, 2H, NH_2^+); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 23.06 (CH_2), 24.22 (CH_2), 31.89 (NCH_3), 47.95 (NCH_2), 50.27 (OCH_3), 50.60 (OCH_3), 55.37 (OCH_3), 113.15 (C_{cp}), 113.71 (C_{cp}), 124.06 (C_{cp}), 124.50 (CH_{cp}), 128.14 (C_{Ar}), 131.59 (C_{cp}), 131.97, 134.97, 135.49, 162.43 (C_{Ar}-OCH_3), 167.18 (C=O), 167.65 (C=O), 195.23 (C=O). Anal. Calcd for $C_{21}H_{25}NO_6$ (387.4): C, 65.11; H, 6.50; N, 3.62; found C, 66.20; H, 6.25; N, 4.08.

3-[5-(4-Chlorobenzoyl)-2,4-di(methoxycarbonyl)cyclopentadienide]propyl(methyl)-ammonium (3c). Prepared from **2** (768 mg, 4.17 mmol), $Rh_2(OAc)_4$ (73 mg, 0.17 mmol, 4 mol%), and **1c** (700 mg, 3.48 mmol); yellow oil (432 mg, 35 %): IR (neat) 3438 (w, br) and 3080–2300 (m, br, NH_2^+), 1687 (vs), 1643 (vs), 1487 (vs), 1240 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.18 (m_c, 2H, CH_2), 2.54 (t, *J*=5.0 Hz, 3H, NCH_3), 2.83 (m_c, 2H, CH_2), 2.99 (m_c, 2H, NCH_2),), 3.31 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 7.25 (s, 1H, CH), 7.68 (AA'BB' system, 4H, C_6H_4), 9.19 (br s, 2H, NH_2^+); ^{13}C NMR ($CDCl_3$) δ = 22.97 (CH_2), 24.57 (CH_2), 32.23 (NCH_3), 50.47 (OCH_3), 50.95 (OCH_3), 113.86 (C_{cp}), 116.53 (C_{cp}), 118.05 (CH_2), 123.83 (C_{cp}), 124.84 (CH), 128.14 (C_{Ar}), 131.59 (C_{cp}), 130.92, 137.37, 140.82 (all C_{Ar}), 167.31 (C=O), 167.41 (C=O), 194.66 (C=O). Anal. Calcd for $C_{20}H_{22}ClNO_5$ (391.8): C, 61.30; H, 5.66; N, 3.57; found C, 61.6; H, 5.7; N, 3.7.

3-[5-(2-Furylcarbonyl)-2,4-di(methoxycarbonyl)cyclopentadienide]propyl(methyl)-ammonium (3d): Prepared from **2** (578 mg, 3.14 mmol), $Rh_2(OAc)_4$ (42 mg, 0.09 mmol, 3 mol%), and **1d** (500 mg, 2.61 mmol); yellow solid (825 mg, 91 %): mp 138 °C (ethyl acetate); IR (KBr) 3440 (m, br) and 3250–2250 (m, br, NH_2^+), 1739 (m), 1673 (vs, br), 1471 (vs), 1236 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.19 (m_c, 2H, CH_2), 2.58 (t, *J* = 5.0 Hz, 3H, NCH_3), 2.85 (m_c, 2H, CH_2), 3.00 (pseudo-t, 2H, CH_2), 3.48 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 6.45 (dd, *J* = 3.5, *J* = 1.8, 1H, CH), 6.85 (dd, *J* = 3.5, *J* = 0.8, 1H, CH), 7.27 (s, 1H, CH), 7.50 (dd, *J* = 1.8, *J* = 0.8, 1H, CH), 9.16 (br s, 2H, NH_2^+); ^{13}C NMR ($CDCl_3$) δ 23.00 (CH_2), 24.45 (CH_2), 32.38 (NCH_3), 48.45 (NCH_2), 50.05 (OCH_3), 50.13 (OCH_3), 112.22 (C_{cp}), 114.64 (C_{cp}), 117.11 (C_{cp}), 118.92 (CH_{furyl}), 122.80 (C_{cp}), 125.12 (CH_{cp}), 136.0 (CH_{furyl}), 145.18 (CH_{furyl}), 155.45 (C_{furyl}), 167.03 (C=O), 167.92 (C=O), 182.01 (C=O); MS (FD, 8 kV): *m/z* (%) 348 (42) [MH^+], 347 (43) [M^+], 283 (0.1), 315 (100). Anal. Calcd for $C_{18}H_{21}NO_6$ (347.3): C, 62.25; H, 6.09; N, 4.03; found C, 61.15; H, 6.24; N, 3.98.

Methyl{3-[2,4,5-tri(methoxycarbonyl)cyclopentadienide]propyl}ammonium (3f) and 1,2,4-Trimethyl 1-(1-Methyltetrahydro-1*H*-2-pyrrolidene)-2-butene-1,2,4-tricarboxylate (4f). Prepared from **2** (712 mg, 3.87 mmol), $Rh_2(OAc)_4$ (51 mg, 0.12 mmol, 3 mol%), and **1f** (500 mg, 3.10 mmol).

3f: Colorless powder (727 mg, 73 %), mp 173 °C (dec); IR (KBr) 3125 (s, br, NH_2^+), 1706 (vs), 1641 (vs), 1481 (vs), 1272 (vs), 1239 (vs), 1211 (vs) cm^{-1}; ^1H NMR (DMSO) δ 1.81 (m_c, 2H, CH_2), 2.49 (s, 3H, NCH_3), 2.79 (t, *J* = 7.2, 2H, CH_2), 2.85 (t, *J* = 6.7, 2H, CH_2),

3.51 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 6.73 (s, 1H, CH), 8.18 (br s, 2H, NH_2^+); ^{13}C NMR (DMSO) δ 23.03 (CH_2), 27.12 (CH_2), 32.35 (NCH_3), 48.06 (CH_2), 49.26 (OCH_3), 49.56 (OCH_3), 49.96 (OCH_3), 109.63 (C_{cp}), 112.97 (C_{cp}), 114.27 (C_{cp}), 120.71 (CH_{cp}), 132.66 (C_{cp}), 165.79 (C=O), 166.01 (C=O), 168.29 (C=O). Anal. Calcd for $C_{15}H_{21}NO_6$ (311.2): C, 57.88; H, 6.80; N, 4.50, found C, 58.30; H, 6.97; N, 4.51.

4f: Crystallization from ether (-10 °C) gave yellow crystals (38 mg, 4 %): mp 58 °C; IR (KBr) 1712 (C=O), 1676 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.88 and 2.02 (2 m_c, 2H, CH_2), 2.66 (s, 3H, NCH_3), 2.88 and 3.00 (AB part of ABX system, $|^2J_{AB}|$ = 18.3, $^3J_{AX}$ = $^3J_{BX}$ = 6.5, 2H, CH_2), 3.23 (m_c, 2H, NCH_2), 3.39 (m_c, 2H, CH_2,), 3.56, 3.69, 3.75 (all s, 3H, 3 OCH_3), 6.93 (X part of ABX system, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 21.39 (NCH_2CH_2), 34.78 (CH_2CO), 34.98 (CH_2), 37.06 (NCH_3), 50.62, 51.92, 52.06 (all OCH_3), 56.69 (NCH_2), 87.22 (N-C=*C*), 132.45 (*C*H-CH_2), 133.51 (*C*-$COOCH_3$), 165.02 (N-*C*=C), 168.61, 168.70, 171.09 (all C=O); MS (FD, 8 kV) *m/z* (%) 311 (100) [M^+]. Anal. Calcd for $C_{15}H_{21}NO_6$ (311.3): C, 57.87; H, 6.80; N, 4.50, found C, 57.69; H, 6.86; N, 4.56.

When the reaction mixture was allowed to stir for 2-3 days, only **3f** was obtained which crystallized from the mixture.

3-[5-(tert-Butyloxycarbonyl)cyclopentadienide]propyl(methyl)ammonium (3g) and 1-(tert-Butyl) 2,4-Dimethyl 1-(1-Methyltetrahydro-1*H*-2-pyrrolidene)-2-butene-1,2,4-tricarboxylate (4g). Prepared from **2** (560 mg, 3.04 mmol), $Rh_2(OAc)_4$ (40 mg, 0.09 mmol, 3 mol%), and **1g** (500 mg, 2.53 mmol). A mixture of **3g** and **4g** was obtained.. When stirring was continued for 7 days, complete isomerization **4g**→**3g** occurred.

3g: Pale-yellow oil (336 mg, 37 %); IR (neat) 3465 (s, br, NH_2^+) 1643 (vs), 1604 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.52 (s, 9H, $C(CH_3)_3$), 2.01 (m_c, 2H, CH_2), 2.51 (s, 3H, NCH_3), 2.68 (m_c, 2H, CH_2), 2.99 (m_c, 2H, CH_2), 3.69 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 7.11 (s, 1H, CH), 8.20 (br s, 2H, NH_2^+); ^{13}C NMR($CDCl_3$) δ 22.25 (CH_2), 26.42 (CH_2), 28.34 ($C(CH_3)_3$), 33.45 (NCH_3), 48.48 (NCH_2), 50.35 (OCH_3), 50.68 (OCH_3), 79.71 ($C(CH_3)_3$), 111.97 (C_{cp}), 114.32 (C_{cp}), 115.97 (C_{cp}), 122.10 ($C_{cp}H$), 132.51 (C_{cp}), 168.21 (C=O), 168.38 (C=O), 169.32 (C=O). Anal. Calcd for $C_{18}H_{27}NO_6$ (353.4): C, 61.18; H, 7.70; N, 3.96; found C, 60.94; H, 7.78; N, 4.31.

4g: Crystallization from ether (-10 °C) gave yellow crystals (447 mg, 50 %): mp 92 °C; IR (KBr) 1738, 1720, 1675 (all vs, C=O), 1572 (vs), 1265 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 9H, $C(CH_3)_3$), 1.82–2.10 (m, 2H, CH_2), 2.61 (s, 3H, NCH_3), 2.83 and 2.96 (AB part of ABX

system, $|^2J_{AB}|$ = 18.4, $^3J_{AX} = {}^3J_{BX}$ = 7.0, 2H, CH_2), 3.14–3.23 (m, 2H, CH_2), 3.30–3.43 (m, 2H, CH_2), 3.68 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 6.81 (X part of ABX system, 1H, =CH); ^{13}C NMR ($CDCl_3$) δ = 21.43 (NCH_2CH_2), 28.20 ($C(CH_3)_3$), 34.48 (CH_2CO), 34.64 (CH_2), 37.00 (NCH_3), 51.57 (OCH_3), 51.60 (OCH_3), 56.25 (NCH_2), 78.11 ($C(CH_3)_3$), 89.46 (N-C=*C*), 130.60 (CH), 133.99 (*C*=CH), 164.03 (N-*C*=C), 167.59 (C=O), 168.71 (C=O), 171.05 (C=O). Anal. Calcd for $C_{18}H_{27}NO_6$ (356.4): C, 61.18; H, 7.70; N, 3.96; found C, 61.02; H, 7.72; N, 4.25.

4-[5-(4-Chlorobenzoyl)-2,4-di(methoxycarbonyl)cyclopentadienide]butyl(methyl)-ammonium (3h). Prepared from **2** (442 mg, 2.4 mmol), $Rh_2(OAc)_4$ (32 mg, 0.07 mmol, 3 mol%), and **1h** (500 mg, 2 mmol). Crystallization from ethyl acetate gave a yellow powder (690 mg, 85 %): mp. 192 °C (dec); IR (KBr) 3436 (w, br, NH_2^+), 1674 (vs), 1646 (vs), 1442 (s), 1409 (s), 1223 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$/DMSO, 9:1) δ 1.79 (m_c, 4H, 2 CH_2), 2.65 (s, 3H, NCH_3), 2.89 (m_c, 2H, CH_2), 3.02 (m_c, 2H, CH_2), 3.19 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 7.11 (s, 1H, CH), 7.26 and 7.65 (AA'BB' system, 4H, C_6H_4Cl); ^{13}C NMR ($CDCl_3$/DMSO 9:1) δ 23.84 (CH_2), 24.48 (CH_2), 26.45 (CH_2), 32.48 (NCH_3), 47.90 (NCH_2), 48.75 (OCH_3), 48.95 (OCH_3), 110.97 (C_{cp}), 114.48 (C_{cp}), 121.37 ($C_{cp}H$), 122.71 (C_{cp}), 126.57 (C_{Ar}), 129.50 (C_{Ar}), 134.91 (C_{cp}), 136.81 (ipso-C), 141.21 (C-Cl), 165.61 (C=O), 166.36 (C=O), 192.42 (C=O). Anal. Calcd for $C_{21}H_{24}NO_5Cl$ (405.8): C, 62.15; H, 5.96; N, 3.45; found C, 61.52; H, 5.94; N, 3.44.

4-[2,4-Di(methoxycarbonyl)-5-(2-thienylcarbonyl)cyclopentadienide]butyl(methyl)-ammonium (3i): Prepared from **2** (499 mg, 2.7 mmol), $Rh_2(OAc)_4$ (36 mg, 0.08 mmol, 3 mol%), and **1i** (500 mg, 2.26 mmol). Crystallization from ethyl acetate gave yellow crystals 486 mg, 57 %): mp 154 °C (dec); IR (KBr) 3430 (w, br, NH_2^+), 1738 (w), 1686 (s), 1442 (s), 1411 (s), 1392 (s), 1230 (s), 1201 (s) cm^{-1}; ^{1}H NMR($CDCl_3$) δ 1.81 (m_c, 2H, CH_2), 1.95 (m_c, 2H, CH_2), 2.29 (s, 3H, NCH_3), 2.78 (m_c, 2H, CH_2), 2.98 (pseudo-t, 2H, CH_2), 3.60 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 7.01 (dd, *J* = 4.9, *J* = 3.8, 1H, CH), 7.20 (s, 1H, CH), 7.45 (dd, *J* = 3.7, *J* = 1.1, 1H, CH), 7.46 (dd, *J* = 5.0, *J* = 1.2, 1H, CH), 7.93 (br s, NH_2^+); ^{13}C NMR ($CDCl_3$) δ 24.29 (CH_2), 24.97 (CH_2), 26.28 (CH_2), 34.32 (NCH_3), 47.69 (NCH_2), 50.30 (OCH_3), 51.34 (OCH_3), 113.99 (C_{cp}), 115.15 (C_{cp}), 122.04 (C_{cp}), 122.83 (CH_{cp}), 127.68 ($CH_{thienyl}$), 131.88 (C_{cp}), 133.42 ($CH_{thienyl}$), 140.20 ($CH_{thienyl}$), 148.31($C_{thienyl}$), 167.24 (C=O), 169.83 (C=O), 186.00 (C=O). Anal. Calcd for $C_{19}H_{23}NO_5S$ (377.4): C, 60.46; H, 6.14; N, 3.71; found C, 60.02; H, 6.34; N, 3.63.

5-[5-Benzoyl-2,4-di(methoxycarbonyl)cyclopentadienide]pentyl(methyl)-ammonium (3j) and Dimethyl 2-[1-(1-Methyl-2-azepanylidene)-2-oxo-2-phenylethyl]-2-pentenedioate (4j). Prepared from **2** (297 mg, 1.61 mmol), $Rh_2(OAc)_4$ (29 mg, 0.06 mmol, 4 mol%), and **1j** (500 mg, 1.47 mmol).

3j: Yellow resin (13 mg, 5 %); IR (neat) 3458 (s, br, NH_2^+), 1737 (vs), 1711 (vs), 1528 (vs), 1265 (vs) cm^{-1}; ^1H NMR (DMSO) δ 1.22–1.28 (m, 2H, CH_2), 1.42–1.47 (m, 2H, CH_2), 1.48–1.54 (m, 2H, CH_2), 2.50 (s, 3H, NCH_3), 2.72–2.75 (m, 2H, CH_2), 2.78–2.82 (m, 2H, NCH_2), 2.99 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 6.80 (s, 1H, CH), 7.27–7.36 (m, 3H, H_{Ph}), 7.52–7.55 (m, 2H, H_{Ph}), NH_2 exchanging with H_2O in solvent; ^{13}C NMR (DMSO) δ 25.15 (CH_2), 25.94 (CH_2), 26.27 (CH_2), 31.25 (CH_2), 32.47 (NCH_3), 48.42 (NCH_2), 48.81 (OCH_3), 49.17 (OCH_3), 110.52 (C_{cp}), 113.57(C_{cp}), 120.42 (CH),123.99 (C_{cp}), 128.25 (C_{Ar}), 129.68 (C_{Ar}), 135.45 (ipso-C), 165.55 (C=O), 165.98 (C=O), 193.89 (C=O). Anal. Calcd for $C_{22}H_{27}NO_5$ (385.7): C, 68.55; H, 7.06; N, 3.63; found C, 67.98, H, 7.02; N, 3.65.

4j: Crystallization from ether (-10 °C) gave yellow crystals (407 mg, 72 %; 1:1 mixture of 2 isomers): mp 82 °C; IR (KBr) 1732 (vs), 1713 (vs), 1630 (s), 1526 (vs) cm^{-1} ;^1H NMR ($CDCl_3$) δ 1.41–1.77 (m, 12H, 4'-, 5'-, 6'-CH_2), 2.40–2.62 (m_c, 4H, 3'-CH_2), 2.77 (s, 3H, NCH_3) 2.93–2.96 (s, 3H, NCH_3, and m, 4H, *C*H_2CO), 3.05–3.40 (m, 4H, NCH_2), 3.58, 3.62, 3.68, 3.70 (all s, each 3H, OCH_3), 6.83 (t, *J* = 6.5, 1H, CH), 6.91 (t, *J* = 6.0, 1H, CH), 7.31 (m_c, 6H, H_{Ph}), 7.55 (m_c, 4H, H_{Ph}); ^{13}C NMR ($CDCl_3$) δ 24.93, 25.70, 26.02, 26.16, 28.55, 29.36 (NCH_2*C*H_2*C*H_2*C*H_2, both isomers), 33.24 (*C*H_2CO) 35.24 (3'-CH_2), 43.82 (NCH_3), 45.77 (NCH_3), 51.95, 52.05, 52.75, 52.75 (4 x OCH_3, both isomers), 100.91, 105.99 (all N-C=*C*) , 127.63, 127.77, 128.72, 129.65, 129.88, 130.32 (all C_{Ph}), 131.66, 136.26 (both *C*=C-$COOCH_3$), 136.85 (C=*C*-$COOCH_3$), 142.89 (ipso-C_{Ph}), 168.14 (N-*C*=C), 168.74, 169.92, 170.72, 171.06, 189.25, 196.22 (all C=O). Anal. Calcd for $C_{22}H_{27}NO_5$ (385.5): C, 68.55; H, 7.06; N, 3.63; found C, 68.09; H, 7.00; N, 3.64.

5-[5-(4-Methoxybenzoyl)-2,4-di(methoxycarbonyl)cyclopentadienide]pentylmethyl)-ammonium (3k): Prepared from **2** (427 mg, 2.31 mmol), $Rh_2(OAc)_4$ (31 mg, 0.07 mmol, 3 mol%), and **3k** (500 mg, 1.93 mmol). Crystallization from methanol gave yellow needles (601 mg, 75 %): mp 169 °C (dec); IR (KBr) 3428 (m, br) and 3100-2400 (w, br, NH_2^+), 1741 (m), 1654 (vs), 1604 (s), 1483 (vs), 1306 (s), 1253 (s), 1213 (s) cm-$^{-1}$; ^1H NMR (DMSO) δ 1.23 (quin, 2H, CH_2), 1.40 (quin, 2H, CH_2), 1.49 (quin, 2H, CH_2), 2.50 (s, 3H, NCH_3), 2.68 (dd,

2H, CH_2), 2.78 (dd, 2H, CH_2), 3.09 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 6.80 (s, 1H, CH), 6.83 and 7.53 (AA'BB' system, 4H, $C_6H_4OCH_3$), 8.14 (br s, 2H, NH_2^+); ^{13}C NMR (DMSO) δ 25.09 (CH_2), 25.88 (CH_2), 26.22 (CH_2), 31.21 (CH_2), 32.42 (NCH_3), 48.36 (NCH_2), 48.91 (OCH_3), 49.07 (OCH_3), 55.08 (OCH_3), 110.18 (C_{cp}), 112.38 (C_{Ar}), 112.92 (C_{cp}), 120.04 (CH_{cp}), 124.41 (C_{cp}), 130.29 (C_{cp}), 134.08 (C_{Ar}), 135.08 (ipso-C_{Ar}), 160.70 (C_{ar}-OCH_3), 165.43 (C=O), 165.93 (C=O), 193.41 (C=O). Anal. Calcd for $C_{23}H_{29}NO_6$ (415.4): C, 66.50; H, 7.04; N, 3.37; found C, 66.4; H, 7.1; N, 3.4.

5-[2,4-Di(methoxycarbonyl)-5-(2-thienylcarbonyl)cyclopentadienide]pentyl(methyl)-ammonium (3l): Prepared from **2** (468 mg, 2.55 mmol), $Rh_2(OAc)_4$ (34 mg, 0.08 mmol, 3 mol%), and **1l** (500 mg, 2.12 mmol): yellow powder (539 mg, 65 %); mp 160-161°C (dec); IR (KBr) 3438 (m, br, NH_2^+), 1693 (s), 1655 (vs), 1622 (s), 1485 (vs), 1398 (s), 1214 (vs) cm^{-1}; ^{1}H NMR (DMSO) δ 1.25 (quin, 2H, CH_2), 1.44 (quin, 2H, CH_2), 1.52 (quin, 2H, CH_2), 2.51 (s, 3H, NCH_3), 2.71 (t, *J* = 7.5, 2H, CH_2), 2.80 (t, *J* = 7.6, 2H, CH_2), 3.18 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 6.79 (s, 1H, CH), 6.98 (dd, *J* = 6.1, *J* = 3.7, 1H, CH), 7.14 (dd, *J*= 3.7, *J* = 1.4, 1H, CH), 7.59 (dd, *J* = 6.1, *J* = 1.2, 1H, CH), 8.20 (br s, 2H, NH_2^+); ^{13}C NMR (DMSO) δ 25.1 (CH_2), 25.86 (CH_2), 26.2 (CH_2), 31.14 (CH_2), 32.42 (NCH_3), 48.36 (NCH_2), 49.05 (OCH_3), 49.10 (OCH_3), 110.51 (C_{cp}), 113.28 (C_{cp}), 120.52 (CH_{cp}), 124.04 (C_{cp}), 126.83 ($CH_{thienyl}$), 129.93 ($CH_{thienyl}$), 130.18 ($CH_{thienyl}$), 134.80 (C_{cp}), 150.10 ($C_{thienyl}$), 165.70 (C=O), 165.87 (C=O), 185.77 (C=O). Anal. Calcd for $C_{20}H_{25}NO_5S$ (391.4): C 61.37, H 6.44, N 3.56, found C 61.25, H 6.62, N 3.45.

Methyl 2-(2-Methyl-3-oxocyclopent-1-en-1-yl)-3-(1-methyltetrahydro-1*H*-pyrrol-2-ylidene)-4-oxo-4-(2-thienyl)butanoate (**11**). This compound was prepared from enaminoketone **1e** (500 mg, 2.41 mmol), $Rh_2(OAc)_4$ (53.3 mg, 0.08 mmol, 5 mol%), and diazoacetate **10**[6] (468 mg, 2.41 mmol) in dichloromethane at ambient temperature. After 12 h, the diazo compound was consumed (IR control), and the mixture was separated by column chromatography. Elution with ethyl acetate furnished several fractions containing unidentified minor by-products and the catalyst. With ethyl acetate/methanol (2:1), compound **11** was isolated as a sticky red oil (430 mg, 48 %): IR (KBr) 1741 (vs), 1698 (s), 1410 (s), 1374 (vs), 1242 (vs), 1047 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.76 (t, *J* = 2.0, 3H, CH_3-cyclopentene), 2.00–2.07 (m, 2H, CH_2-pyrrolidine), 2.32 and 2.41 (2 x ddd, $|^2J|$ = 18.9, ^3J= 7.0, $|^4J|$= 2.3, 2H, 5-CH_2-cyclopentene), 2.47 (broad signal, 3H, NCH_3), 2.45–2.53 (m, 1H, 4-CH-

cyclopentene), 2.57–2.62 (m, 1H, 3-CH-pyrrolidine), 2.82–2.92 (m, 2H, 3-CH-pyrrolidine and 4-CH-cyclopentene), 3.36 (m_c, 2H, NCH_2), 3.69 (s, 3H, OCH_3), 4.63 (s, 1H, CH), 7.01 (ddd, ^3J = 5.0, J = 3.7, 1H, $CH_{thienyl}$), 7.37 (dd, ^3J = 5.0, $|^4J|$ = 1.2, 1H, $CH_{thienyl}$), 7.45 (dd, ^3J = 5.0, $|^4J|$ = 1.2, 1H, $CH_{thienyl}$); ^{13}C NMR ($CDCl_3$): δ = 8.59 (CH_3-cyclopentene), 20.58 (NCH_2CH_2), 27.42 (C-5, cyclopentene), 33.62 (C-3, pyrrolidine, broadened by a dynamic process), 34.10 (C-4, cyclopentene), 39.39 (NCH_3), 48.79 (*C*HCOOCH_3), 52.57 (OCH_3), 56.55 (NCH_2), 98.86 (N-C=*C*, broadened by a dynamic process), 127.34 ($C_{thienyl}$), 129.06 ($C_{thienyl}$), 130.51 ($C_{thienyl}$), 136.23 (C-2, cyclopentene), 146.40 ($C_{thienyl}$), 164.20 (N-*C*=C, broadened by a dynamic process), 170.41 (C-1, cyclopentene), 171.02 (C=O, ester), 184.12 (C=O, thienyl), 211.65 (C=O, cyclopentene). Anal. Calcd for $C_{20}H_{23}NO_4S$ (373.4): C, 64.32; H, 6.21; N, 3.75; found C, 64.42; H, 6.26; N, 3.96.

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