# A novel oxidative alkylation–nitration of 1,3-dicarbonyl compounds to dicyclopentadiene and norbornene †

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A one-pot CAN-mediated oxidative alkylation–nitration of *endo*-dicyclopentadiene and norbornene with 1,3-dicarbonyl compounds is described. The key step involves the Wagner–Meerwein rearrangement of **2** which leads to the *exo*-dicyclopentadienyl nitrate **4**.

Oxidative addition reactions of 1,3-dicarbonylalkyl radicals to alkenes have received a lot of attention over the years. Oxidative methods mediated by salts of $Mn^{III}$, $Cu^{II}$, $Ag^{I}$, $V^{V}$, $Fe^{III}$, *etc.* have been explored.[1] Recently, cerium(IV) ammonium nitrate (CAN)-mediated addition of 1,3-dicarbonyl compounds to various alkenes was reported.[2] Also, a general and convenient synthesis of carbohydrate 2-*C*-analogs was achieved by the CAN-mediated addition of malonate to glycals.[3] Nevertheless, a practical and high-yielding alkylation–nitration of 1,3-dicarbonyl radicals to *polycyclic alkenes* has never been realized.[4]

The tricyclo[5.2.1.$0^{2,6}$]decane system is present in naturally occurring compounds[5] and has also served as a useful building block for the synthesis of a variety of natural and synthetic compounds.[6] Our goal has been to develop a novel synthesis of this system. Initially, we studied the 1,3-dicarbonyl addition to dicyclopentadiene.[7] In our hands, addition of a $CH_3CN$ solution of CAN to *endo*-dicyclopentadiene and acetylacetone in $CH_3CN$ at room temperature, followed by stirring for 1 h, provided the alkylated *exo*-dicyclopentadienyl nitrate **4** as a *ca.* 1 : 1 mixture of inseparable isomers **4a** and **4b**.[8] The structures of **4a** and **4b** were established by $^1$H NMR, $^{13}$C NMR, COSY, DEPT, HMQC, MS and elemental analysis. Furthermore, single crystal X-ray analysis of **4** revealed 1 : 1 ratio of **4a** and **4b** in the solid state (Fig. 1).[9] This ratio is supported by the nearly equal bond length measurements for C3–C4 and C4–C5 (1.410 and 1.385 Å respectively).

A plausible mechanism for the CAN-induced oxidative addition of dicarbonyl compounds to dicyclopentadiene is illustrated in Scheme 1. The 1,3-diketoalkyl radical attacks one of the double bonds in dicyclopentadiene from the *exo* direction, generating the norbornyl radical **1a** (path A). Oxidation of the radical **1a** by CAN provides the norbornyl cation **2**, which undergoes a Wagner–Meerwein rearrangement[10] to **3**. Cation **3** is trapped by CAN, affording the nitrate product **4a**.[11] Alternatively, path B provides **4b** *via* **1b**. Under the same reaction conditions, homologous dicarbonyl compounds afforded the *exo*-dicyclopentadiene adducts **5**–**9** (entries 2–6, Table 1). To further extend the scope of this reaction to other bicyclo-[2.2.1]alkane systems, norbornene was employed and allowed to react with the 1,3-diketoalkyl radical. This led to the formation of a single adduct **10**. Other diketones reacted similarly to afford **11** and **12** (entries 8, 9, Table 1).

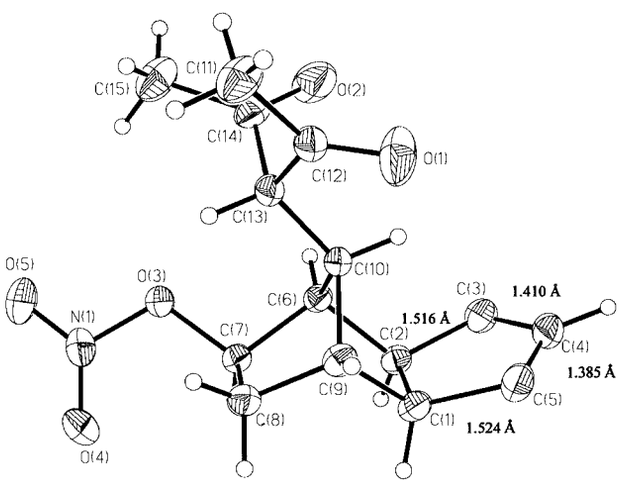


**Fig. 1** ORTEP plot of the X-ray crystal structure of **4**.

In summary, this manuscript reports the novel and practical oxidative alkylation–nitration of bicyclo[2.2.1]alkene systems in the presence of 1,3-dicarbonyl compounds and CAN. The reaction constitutes the first example of a CAN-mediated Wagner–Meerwein rearrangement followed by oxidative alkylation. Further exploration of the scope of this reaction and its application to organic synthesis is underway in our laboratories.

## Experimental

$^1$H and $^{13}$C NMR spectra were obtained using a Bruker Avance DPX-400 spectrometer, IR spectra were recorded using a Perkin-Elmer 682 spectrometer, and mass spectra were obtained using either a Fison VG Trio-2000 or Fison VG-702505 instrument.

### General procedure for the oxidative addition

To a solution of *endo*-dicyclopentadiene (1.19 g, 9.0 mmol) and acetylacetone (0.99 g, 9.9 mmol) in $CH_3CN$ (100 mL) was slowly added a solution of CAN (10.4 g, 18.9 mmol) in $CH_3CN$ (20 mL) at 25 °C under Ar. The reaction mixture was stirred at 25 °C for 1 h. The reaction was quenched with $H_2O$ (100 mL) and the resulting solution was diluted with $CH_2Cl_2$ (100 mL).

† The IUPAC name for dicyclopentadiene is 3a,4,7,7a-tetrahydro-4,7-methanoindene and for norbornene is bicyclo[2.2.1]hept-2-ene.
‡ Correspondence regarding the X-ray structural data should be addressed to this author.

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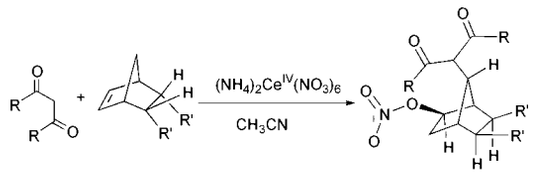
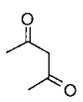
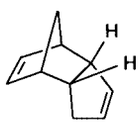
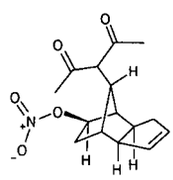
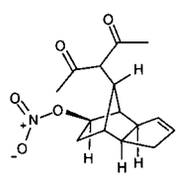
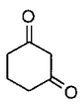
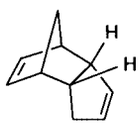
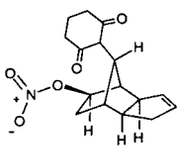
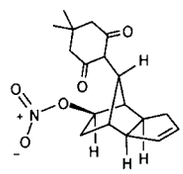
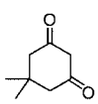
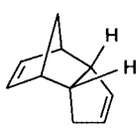
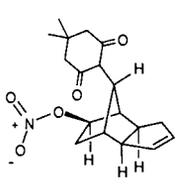
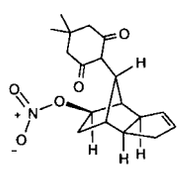
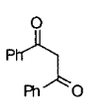
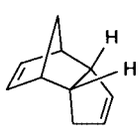
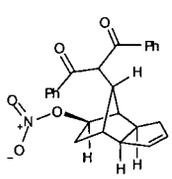
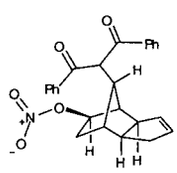
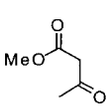
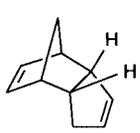
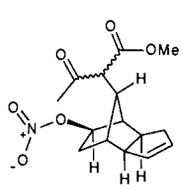
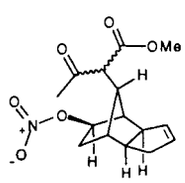
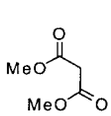
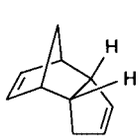
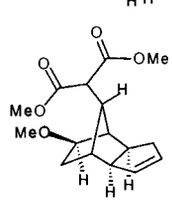
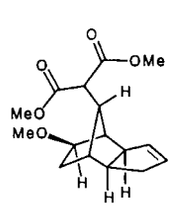
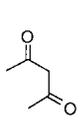
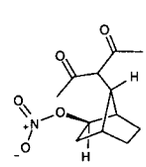
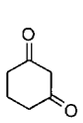
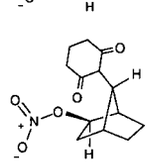
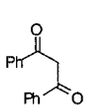
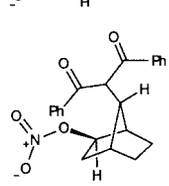
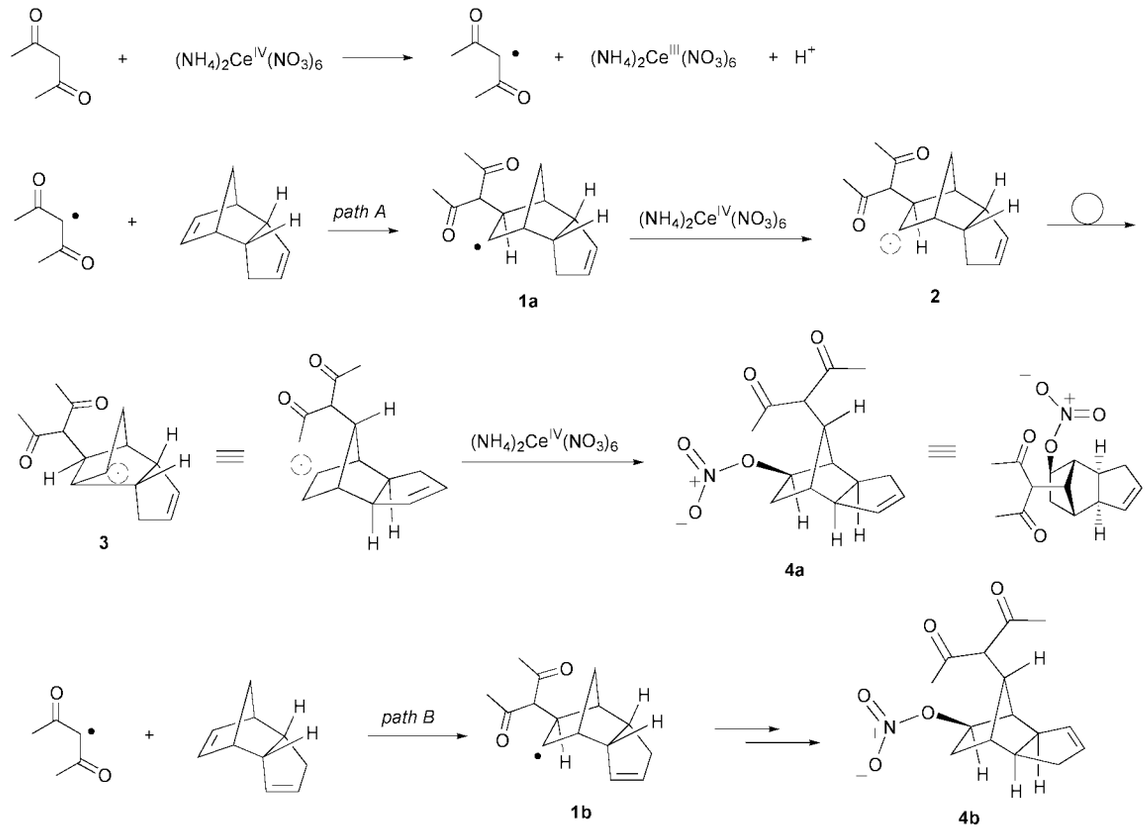
**Table 1** Oxidative addition of dicarbonyl compounds to alkenes




| Entry | Dicarbonyl | Alkenes | Product | | Yields (%)[a] |
|---|---|---|---|---|---|
| 1 |  |  |  |  **4** | 80 |
| 2 |  |  |  |  **5** | 73 |
| 3 |  |  |  |  **6** | 62 |
| 4 |  |  |  |  **7** | 74 |
| 5 |  |  |  |  **8** | 71 |
| 6 |  |  |  |  **9** | 78[b] |
| 7 |  |  |  | **10** | 75 |
| 8 |  |  |  | **11** | 70 |
| 9 |  |  |  | **12** | 78 |

[a] Isolated yield based on starting alkenes. [b] The reaction was carried out in MeOH. Reaction in $CH_3CN$ gave a complicated mixture.




**Scheme 1**

The organic solution was dried over $MgSO_4$ and concentrated *in vacuo* to give the crude product as an oil. The crude product was purified by flash column chromatography (silica gel) with 5% EtOAc–hexane ($R_f = 0.43$ in 10% EtOAc–hexane) to give nitrate **4** as a colorless solid (2.11 g, 80% yield); mp 133–135 °C; IR (neat) $\nu$ 2967, 1696, 1627, 1360, 1272 $cm^{-1}$; $^1H$ NMR ($C_6D_6$, 400 MHz, 5 : 4 isomeric forms, * denotes minor isomer) $\delta$ 5.56–5.52 (m, 2 H), 5.24–5.23* (m, 1 H), 5.18–5.17 (m, 1 H), 4.31–4.29* (m, 1 H), 4.23–4.20 (m, 1 H), 3.83 (d, $J = 12.2$ Hz, 1H), 3.81* (d, $J = 12.2$ Hz, 1 H), 2.50–2.45 (m, 2 H), 2.35–2.20 (m, 2 H), 2.12–2.02 (m, 2 H), 1.94 (s, 3 H), 1.93* (s, 3 H), 2.00–1.90 (m, 2 H), 1.74 (s, 3 H), 1.73* (s, 3 H), 1.80–1.70 (m, 1 H), 1.60–1.55 (2 H), 1.45–1.25 (m, 7 H); $^{13}C$ NMR ($C_6D_6$, 100 MHz, 5 : 4 isomeric forms, * denotes minor isomer) $\delta$ 203.24 (C), 202.87* (C), 202.35 (C), 202.27* (C), 134.91* (CH), 134.53 (CH), 131.47 (CH), 131.00* (CH), 87.58* (CH), 86.82 (CH), 67.38 (CH), 67.25* (CH), 55.17 (CH), 52.46* (CH), 49.40 (CH), 46.90* (CH), 44.72* (CH), 43.33* (CH), 42.71* (CH), 42.59 (CH), 42.41 (CH), 40.39 (CH), 39.85* ($CH_2$), 39.62 ($CH_2$), 36.27 ($CH_2$), 36.07* ($CH_2$), 31.00 ($CH_3$), 30.70* ($CH_3$), 28.63* ($CH_3$), 28.03 ($CH_3$); MS (*m*/*z*, relative intensity) 293 ($M^+$, 51%), 251 (19), 205 (14), 187 (44), 161 (35), 145 (35), 131 (100); exact mass calculated for $C_{15}H_{19}NO_5$ ($M^+$): 293.1263; found 293.1264. Anal. calcd for $C_{15}H_{19}NO_5$: C, 61.42; H 6.53; N, 4.78; O, 27.27; found C, 61.27; H, 6.50; N, 4.75; O, 27.48%.

**Compound 5.** IR (neat) $\nu$ 2924, 2831, 1733, 1712, 1643, 1633, 1555, 1277, 857 $cm^{-1}$; $^1H$ NMR ($C_6D_6$, 400 MHz, 1 : 1 isomeric forms) $\delta$ 5.68–5.60 (m, 1 H), 5.58–5.50 (m, 1 H), 5.40–5.30 (m, 1 H), 5.18–5.10 (m, 1 H), 4.20–4.08 (m, 2 H), 3.15 (br s, 1 H), 3.09 (br s, 1 H), 2.85–2.65 (m, 2 H), 2.60–1.80 (m, 16 H), 1.70–1.30 (m, 12 H); $^{13}C$ NMR ($C_6D_6$, 100 MHz, 1 : 1 isomeric forms) $\delta$ 202.26, 202.14, 200.57, 200.05, 137.16, 134.77, 131.93, 129.85, 87.73, 87.04, 56.28, 52.28, 48.94 (two C), 48.83, 48.56, 46.37, 44.27, 41.99, 40.00, 39.88, 39.83, 39.19 (two C), 39.16, 39.08, 39.00, 38.98, 37.62, 37.49, 17.13, 17.07; MS (*m*/*z*, relative intensity) 305 ($M^+$, 11%), 281 (14), 260 (10), 248 (11), 207 (41), 131 (41), 117 (48), 105 (100); exact mass calculated for $C_{16}H_{19}NO_5$ ($M^+$): 305.1263; found 305.1252.

**Compound 6.** IR (neat) $\nu$ 2917, 2855, 1733, 1634, 1378, 1245, 1050, 856, 766 $cm^{-1}$; $^1H$ NMR ($C_6D_6$, 400 MHz, 1 : 1 isomeric forms) $\delta$ 5.70–5.50 (m, 2 H), 5.45–5.30 (m, 2 H), 4.85–4.60 (m, 2 H), 3.95–3.80 (m, 2 H), 2.90–1.50 (m, 26 H), 1.00 (s, 3 H), 0.95 (s, 3 H), 0.85 (s, 6 H); $^{13}C$ NMR ($C_6D_6$, 100 MHz, 1 : 1 isomeric forms) $\delta$ 193.46, 193.35, 177.88, 177.60, 133.26, 132.67, 131.26, 130.90, 90.75, 88.64, 53.18, 52.00, 51.97, 51.65, 49.80, 48.90, 48.09, 46.93, 46.02, 45.88, 45.09, 43.36, 42.49, 42.18, 40.95, 38.52, 38.45, 36.07, 35.55, 34.23, 33.22, 32.26, 29.48, 29.44, 28.75, 28.64; MS (*m*/*z*, relative intensity) 333 ($M^+$, 4%), 281 (5), 262 (4), 207 (15), 146 (47), 132 (79), 117 (100), 105 (76); exact mass calculated for $C_{18}H_{23}NO_5$ ($M^+$): 333.1576; found 333.1565.

**Compound 7.** IR (neat) $\nu$ 2938, 2870, 1700, 1633, 1455, 1278, 858, 692 $cm^{-1}$; $^1H$ NMR ($C_6D_6$, 400 MHz, 1 : 1 isomeric forms) $\delta$ 8.22–8.00 (m, 8 H), 7.15–6.90 (m, 12 H), 5.78–5.68 (m, 2 H), 5.68–5.55 (m, 2 H), 5.35–5.30 (m, 1 H), 5.20–5.12 (m, 1 H), 4.42–4.30 (m, 2 H), 3.18 (d, $J = 11.7$ Hz, 2 H), 2.45–2.10 (m, 6 H), 1.85–1.30 (m, 10 H); $^{13}C$ NMR ($C_6D_6$, 100 MHz, 1 : 1 isomeric forms) $\delta$ 194.94, 194.79, 194.74 (two C), 137.36 (two C), 136.96 (two C), 134.03 (two C), 133.61 (two C), 133.17 (two C), 133.04 (two C), 130.68 (two C), 130.18 (two C), 128.77 (four C), 128.67 (two C), 128.03 (two C), 127.79 (two C), 127.55 (two C), 87.28, 86.57, 56.75, 56.45, 54.59, 51.70, 49.12, 46.66, 43.93, 43.87, 43.74, 42.59, 41.53, 39.53, 38.91, 38.74, 35.65, 35.40; MS (*m*/*z*, relative intensity) 417 ($M^+$, 35%), 373 (57), 334 (40), 281 (53), 257 (27), 207 (100), 185 (53), 155 (58); exact mass calculated for $C_{25}H_{23}NO_5$ ($M^+$): 417.1576; found 417.1576.

**Compound 8.** IR (neat) $\nu$ 2960, 2857, 1744, 1711, 1631, 1439, 1361, 1280, 858 $cm^{-1}$; $^1H$ NMR ($C_6D_6$, 400 MHz, four inseparable isomeric forms) $\delta$ 5.85–5.65 (m, 4 H), 5.62–5.45 (m, 4 H), 4.95–4.75 (m, 4 H), 4.10–4.00 (m, 4 H), 2.85 (br s, 12 H), 2.08

(s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3 H), 3.00–1.70 (m, 36 H); MS (*m*/*z*, relative intensity) 309 ($M^+$, 14%), 282 (13), 267 (12), 227 (11), 207 (46), 170 (20), 131 (32), 105 (100); exact mass calculated for $C_{15}H_{19}NO_6$ ($M^+$): 309.1212; found 309.1214.

**Compound 9.** IR (neat) *v* 2953, 2890, 1735, 1628, 1440, 1280, 857 $cm^{-1}$; $^1H$ NMR ($C_6D_6$, 400 MHz, 1:1 isomeric forms) $\delta$ 5.60–5.50 (m, 2 H), 5.38–5.28 (m, 2 H), 4.45–4.32 (m, 2 H), 3.89 (d, $J$ = 12.2 Hz, 1 H), 3.88 (d, $J$ = 12.2 Hz, 1 H), 3.40–3.28 (m, 6 H), 3.41 (s, 3 H), 3.39 (s, 3 H), 3.38 (s, 3 H), 3.35 (s, 3 H), 2.72–2.65 (m, 2 H), 2.45–1.90 (m, 8 H), 1.80–1.30 (m, 8 H); $^{13}C$ NMR ($C_6D_6$, 100 MHz, 1:1 isomeric forms) $\delta$ 169.89, 169.82, 169.73, 169.70, 134.83, 134.23, 131.34, 130.70, 87.41, 86.71, 55.36, 52.43, 52.35, 52.23 (two C), 50.12 (three C), 50.09, 49.76, 47.26, 45.15, 43.46, 43.15, 43.09, 42.89, 42.80, 40.19, 39.55, 39.47, 35.34, 34.92; MS (*m*/*z*, relative intensity) 294 ($M^+$, 10%), 262 (8), 234 (24), 196 (48), 162 (22), 130 (100); exact mass calculated for $C_{16}H_{22}O_5$ ($M^+$): 294.1467; found 294.1469.

**Compound 10.** Mp 69–70 °C; IR (neat) *v* 2949, 2857, 1738, 1696, 1627, 1365, 1291, 881 $cm^{-1}$; $^1H$ NMR ($C_6D_6$, 400 MHz) $\delta$ 4.32 (dd, $J$ = 3.3, 7.4 Hz, 1 H), 3.81 (d, $J$ = 12.1 Hz, 1 H), 2.18 (d, $J$ = 12.1 Hz, 1 H), 2.12–0.60 (m, 8 H), 1.97 (s, 3 H), 1.79 (s, 3 H); $^{13}C$ NMR ($C_6D_6$, 100 MHz) $\delta$ 203.23 (C), 202.54 (C), 87.52 (CH), 67.27 (CH), 49.00 (CH), 43.07 (CH), 38.33 (CH), 36.58 ($CH_2$), 31.06 ($CH_3$), 29.17 ($CH_3$), 28.32 ($CH_2$), 25.68 ($CH_2$); MS (*m*/*z*, relative intensity) 255 ($M^+$, 2%), 213 (34), 192 (35), 177 (26), 167 (56), 149 (100), 139 (71), 131 (22), 123 (33), 121 (38), 107 (43); exact mass calculated for $C_{12}H_{17}NO_5$ ($M^+$): 255.1107; found 255.1114.

**Compound 11.** Mp 81–82 °C; IR (neat) *v* 2958, 2857, 1627, 1401, 1180, 968 $cm^{-1}$; $^1H$ NMR ($C_6D_6$, 400 MHz) $\delta$ 4.28 (d, $J$ = 7.6 Hz, 1 H), 2.93 (d, $J$ = 7.6 Hz, 1 H), 2.52–2.49 (m, 1 H), 2.22–2.20 (m, 1 H), 2.10–2.00 (m, 2 H), 1.90–1.70 (m, 2 H), 1.50–1.30 (m, 3 H), 1.25–1.05 (m, 3 H), 1.05–0.80 (m, 2 H), 0.75–0.60 (m, 1 H); $^{13}C$ NMR ($C_6D_6$, 100 MHz) $\delta$ 194.04 (C), 178.51 (C), 91.98 (CH), 50.07 (CH), 43.20 (CH), 40.22 (two C of CH), 37.64 (CH), 32.58 (CH), 28.29 (CH), 24.36 (CH), 24.12 (CH), 22.57 (CH); MS (*m*/*z*, relative intensity) 204 ($M^+ - HNO_3$, 100%), 189 (10), 176 (58), 163 (10), 149 (20), 137 (40), 126 (42), 113 (40); exact mass calculated for $C_{13}H_{16}O_2$ ($M^+ - HNO_3$): 204.1150; found 204.1150.

**Compound 12.** Mp 128–130 °C; IR (neat) *v* 2986, 2893, 1705, 1645, 1599, 1470, 1290, 1217, 978, 849, 761, 706 $cm^{-1}$; $^1H$ NMR ($C_6D_6$, 400 MHz) $\delta$ 8.22–8.00 (m, 4 H), 7.10–6.95 (m, 6 H), 5.74 (d, $J$ = 11.5 Hz, 1 H), 4.37 (dd, $J$ = 7.7, 3.1 Hz), 2.90 (d, $J$ = 11.5 Hz, 1 H), 2.46 (d, $J$ = 4.9 Hz, 1 H), 1.95–1.60 (m, 2 H), 1.45–0.40 (m, 5 H); $^{13}C$ NMR ($C_6D_6$, 100 MHz) $\delta$ 195.82 (C), 195.66 (C), 138.26 (C), 137.89 (C), 134.26 (CH), 134.00 (CH), 129.81 (two C of CH), 129.59 (two C of CH), 129.51 (two C of CH), 128.94 (two C of CH), 88.00 (CH), 56.95 (CH), 51.08 (CH), 43.75 (CH), 38.31 (CH), 36.84 ($CH_2$), 28.50 ($CH_2$), 25.65 ($CH_2$); MS (*m*/*z*, relative intensity) 379 ($M^+$, 2%), 334 (24), 333 (100), 317 (12), 225 (6), 212 (93), 183 (8), 157 (9); exact mass calculated for $C_{22}H_{21}NO_5$ ($M^+$): 379.1420; found 379.1419.

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