

Electronic Supplementary Information

for

Highly regio-, chemo- and diastereoselective synthesis of oxa-bridged spirocycles: A novel observation of reverse selectivity

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Experimental Section

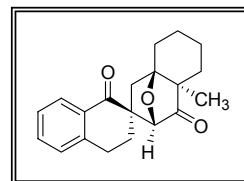
General Procedure. The melting points are uncorrected. The FT-IR spectra were recorded using KBr method. ^1H NMR and ^{13}C NMR spectra (200 MHz and 50.3 MHz, respectively) were referenced to TMS. Carbon types were determined from DEPT ^{13}C NMR experiments. Mass analyses were performed with an ionizing voltage of 70 eV method unless otherwise stated. High resolution mass analyses were performed using electrospray ionization technique. All reactions were carried out under an argon atmosphere and glasswares were dried in an oven before using for catalytic diazo decomposition reaction. Dry solvents have freshly been prepared for every reaction. Analytical thin layer chromatography (TLC) was performed on alumina plates and components were visualized by observation under iodine and UV-Light. Column chromatography was performed on a silica gel (100-200 mesh) column.

Typical Procedure, Method A: To an oven-dried flask, a solution containing the appropriate carbonyl compound (1 mmol) and 0.3 mol% of rhodium (II) acetate dimer in dry dichloromethane (dried over phosphorous pentoxide) was degassed using argon. To this reaction mixture, a solution of appropriate α -diazo ketone (1.1 mmol) **3** (R=H) or **7** (R₁=H) or **9** in dry dichloromethane was added very slowly over a period of 1 h. The progress of the reaction was monitored by TLC. The solvent was removed under reduced pressure and the resulting residue purified using silica gel column chromatography (hexane/EtOAc) to afford the respective oxa-bridged spirocycles.

Method B: Reactions utilizing α -diazo ketones **3** (R=COOEt) and **7** (R₁=COOEt) were performed in dry benzene (dried over sodium) at reflux conditions. The procedure was further followed as described above. All new compounds exhibited spectral data consistent with their structures. The requisite starting materials α -diazo ketones¹ and α -methylene² ketones were prepared according to the literature work.

- 1 S. Muthusamy, S. A. Babu, C. Gunanathan, E. Suresh, P. Dastidar, and R. V. Jasra, *Tetrahedron*, 2000, **56**, 6307.
2 J. -L. Gras, *Org. Synth, Coll. Vol. VII*, 1970, 332.

Compound 5a: A mixture of 2-methylene-3,4-dihydro-2H-naphthalen-1-one (**4**, 250 mg, 1.6 mmol) and α -diazo ketone **3a** (310 mg, 1.7 mmol) was allowed to react in the presence of $\text{Rh}_2(\text{OAc})_4$



(2.0 mg, 0.3 mol%) in dry dichloromethane (DCM, 15 mL) for 1.5 h to afford **5a** (437 mg, 89%) based on method A.

Colourless solid: mp 138-140 °C (chloroform/hexane).

^1H NMR (CDCl_3 , 200 MHz) δ 1.09 (s, 3H, CH_3), 1.62-1.21 (m, 8H), 2.18-1.71 (m, 3H), 2.57 (d, $J = 12.7$ Hz, 1H), 2.78 (dt, $J_1 = 17.1$ Hz, $J_2 = 4.0$ Hz, 1H), 3.20-3.12 (m, 1H), 4.32 (s, 1H, OCH), 7.28-7.15 (m, 2H), 7.42 (d, $J = 7.4$ Hz, 1H, ArH), 7.99 (d, $J = 7.7$ Hz, 1H, ArH).

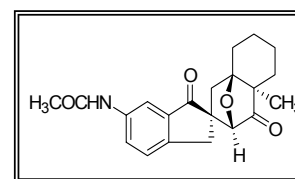
^{13}C NMR (CDCl_3 , 50.3 MHz) δ 16.3 (CH_3), 20.8 (CH_2), 22.7 (CH_2), 26.6 (CH_2), 28.9 (CH_2), 31.2 (CH_2), 31.6 (CH_2), 38.2 (CH_2) 50.5 (*quat-C*), 54.6 (*quat-C*), 86.1 (OCH_2), 89.1 (*quat-C*), 127.3 (=CH), 128.9 (=CH), 129.4 (=CH), 131.5 (*quat-C*), 134.0 (=CH), 143.4 (*quat-C*), 196.8 (C=O), 216.0 (C=O).

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2933, 1752, 1688, 1446, 1226, 961, 741.

MS (EI, 70 eV): m/z (%) 310 (M^+ , 8), 265 (10), 264 (100), 249 (25), 221 (18), 146 (40), 41 (22).

HRMS (ES^+ , LCMS) for $\text{C}_{20}\text{H}_{22}\text{O}_3$ [$(\text{M}+\text{Na})^+$] calcd 333.1467, Found 333.1489.

Compound 5b: A mixture of N-(2-methylene-3-oxoindan-5-yl)-acetamide (200 mg, 1.0 mmol) and α -diazo ketone **3a** (200 mg, 1.1 mmol) was allowed to react in the presence of $\text{Rh}_2(\text{OAc})_4$



(2.0 mg, 0.3 mol%) in dry DCM (15 mL) for 2.5 h to afford **5b** (234 mg, in 66%) based on

method A.

Colourless solid: mp 248-250 °C (chloroform/hexane).

^1H NMR (CDCl_3 , 200 MHz) δ 1.08 (s, 3H, CH_3), 1.65-1.29 (m, 8H), 2.09-1.74 (m, 2H), 2.14 (s, 3H, CH_3), 2.89 (d, $J = 17.4$ Hz, 1H), 3.15 (d, $J = 17.5$ Hz, 1H), 4.16 (s, 1H, OCH), 7.36 (d, $J = 8.2$ Hz, 1H, ArH) 7.56 (s, 1H, NH), 7.72 (d, $J = 1.6$ Hz, 1H, ArH), 8.01 (dd, $J_1 = 8.3$ Hz, $J_2 = 1.8$ Hz, 1H, ArH),

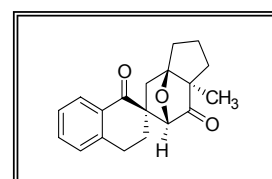
^{13}C NMR (CDCl_3 , 50.3 MHz) δ 16.9 (CH_3), 21.0 (CH_2), 22.8 (CH_2), 25.0 (CH_3), 28.9 (CH_2), 31.3 (CH_2), 35.8 (CH_2), 43.3 (CH_2), 50.4 (quat-C), 55.2 (quat-C), 86.1 (OCH), 89.4 (quat-C), 115.3 (=CH), 127.2 (=CH), 128.3 (=CH), 135.8 (quat-C), 139.1 (quat-C), 147.5 (quat-C), 169.7 (C=O), 206.9 (C=O), 215.5 (C=O),

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3348, 2932, 1752, 1700, 1680, 1603, 1545, 1495, 1441, 1371, 1275, 1170, 990, 714.

MS (EI, 70 eV): m/z (%) 353 (M^+ , 22), 307 (100), 217 (43), 189 (42), 147 (45), 119 (19), 43 (61).

Anal. Calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_4$: C, 71.37; H, 6.56; N, 3.96. Found: C, 71.33; H, 6.60; N, 3.98.

Compound 5c: A mixture of 2-methylene-3,4-dihydro-2H-naphthalen-1-one (175 mg, 1.10 mmol) and α -diazo ketone **3c** (200 mg, 1.20 mmol) was allowed to react in the presence of $\text{Rh}_2(\text{OAc})_4$



(2.0 mg, 0.3 mol%) in dry DCM (12 mL) for 2 h to afford **5c** (197 mg, 60%) based on method A.

Colourless solid: mp 116-118 °C (chloroform/hexane).

^1H NMR (CDCl_3 , 200 MHz) δ 1.12 (s, 3H, CH_3), 1.61-1.22 (m, 3H), 2.71-1.99 (m, 6H), 2.93-2.81 (m, 2H), 3.31-3.17 (m, 1H), 4.31 (s, 1H, OCH), 7.34-7.20 (m, 2H, ArH), 7.48 (d, $J = 7.3$ Hz, 1H), 8.05 (d, $J = 7.6$ Hz, 1H, ArH).

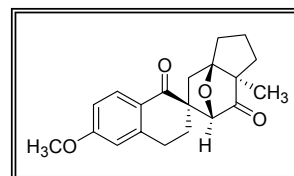
^{13}C NMR (CDCl_3 , 50.3 MHz) δ 18.2 (CH_3), 23.2 (CH_2), 26.4 (CH_2), 29.8 (CH_2), 31.6 (CH_2), 33.0 (CH_2), 35.1 (CH_2), 56.7 (*quat-C*), 58.9 (*quat-C*), 86.0 (OCH), 101.1 (*quat-C*), 127.3 (=CH), 129.0 (=CH), 129.3 (=CH), 131.5 (*quat-C*), 134.0 (=CH), 143.4 (*quat-C*), 196.7 (C=O), 214.7 (C=O).

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2960, 1754, 1680, 1454, 1228, 949, 746.

MS (GCMS): m/z (%) 296 (M^+ , 10), 267 (30), 174 (65), 108 (80), 84 (50), 49 (100), 41 (62).

Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{O}_3$: C, 77.00; H, 6.80. Found: C, 77.09; H, 6.78.

Compound 5d: A mixture of 6-methoxy-2-methylene-3,4-dihydro-2H-naphthalen-1-one (380 mg, 2.02 mmol) and α -diazo ketone **3c** (350 mg, 2.10 mmol) was allowed to react in the



presence of $\text{Rh}_2(\text{OAc})_4$ (2.0 mg, 0.3 mol%) in dry DCM (20 mL) for 1 h to afford **5d** (336 mg, 51%) based on method A.

Colourless solid: mp 179-181 °C (chloroform/hexane).

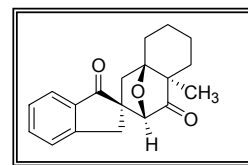
^1H NMR (CDCl_3 , 200 MHz) δ 1.11 (s, 3H, CH_3), 1.56-1.44 (m, 2H), 2.29-1.79 (m, 7H), 2.93-2.76 (m, 2H), 3.28-3.13 (m, 1H), 3.84 (s, 3H, CH_3), 4.31 (s, 1H, OCH), 6.66 (s, 1H, ArH), 6.83 (d, $J = 8.08$ Hz, 1H, ArH), 8.07 (d, $J = 8.6$ Hz, 1H, ArH).

^{13}C NMR (CDCl_3 , 50.3 MHz) δ 18.3 (CH_3), 23.3 (CH_2), 26.9 (CH_2), 29.9 (CH_2), 31.8 (CH_2), 33.1 (CH_2), 35.2 (CH_2), 56.0 (OCH $_3$), 56.4 (*quat-C*), 59.0 (*quat-C*), 86.4 (OCH), 101.2 (*quat-C*), 113.0 (=CH), 114.2 (=CH), 125.0 (*quat-C*), 131.5 (=CH), 145.8 (*quat-C*), 164.2 (*quat-C*), 195.7 (C=O), 214.9 (C=O).

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2935, 1752, 1680, 1602, 1452, 1270, 1241, 1115, 1032, 950, 825. MS (CI^+ , SP): m/z (%) 327 ($(\text{M}+\text{H})^+$, 100), 328 (M+2, 28), 280 (20), 205 (19), 95 (8).

HRMS (CI^+ , SP) for $\text{C}_{20}\text{H}_{22}\text{O}_4$ [$(\text{M}+\text{H})^+$] calcd 327.1596, Found 327.1602.

Compound 5e: A mixture of 2-methyleneindan-1-one (140 mg, 1.0 mmol) and α -diazo ketone **3a** (200 mg, 1.1 mmol) was allowed to react in the presence of $\text{Rh}_2(\text{OAc})_4$ (2.0 mg, 0.3 mol%) in dry DCM (12 mL) for 2 h to afford **5e** (271 mg, 94%) based on method A.



Colourless solid: mp 155-157 °C (chloroform/hexane).

^1H NMR (CDCl_3 , 200 MHz) δ 1.15 (s, 3H, CH_3), 1.41-1.26 (m, 2H), 1.73-1.69 (m, 5H), 1.93-1.87 (m, 1H), 2.16-2.04 (m, 2H), 3.00 (d, $J = 17.5$ Hz, 1H), 3.25 (d, $J = 17.5$ Hz, 1H), 4.21 (s, 1H, OCH), 7.41-7.38 (m, 2H, ArH), 7.59 (d, $J = 7.1$ Hz, 1H, ArH), 7.76 (d, $J = 7.5$ Hz, 1H, ArH).

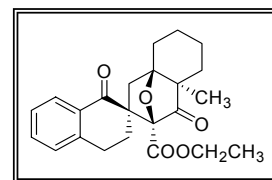
^{13}C NMR (CDCl_3 , 50.3 MHz) δ 16.7 (CH_3), 20.8 (CH_2), 22.7 (CH_2), 28.7 (CH_2), 31.0 (CH_2), 36.0 (CH_2), 42.9 (CH_2), 50.1 (quat-C), 54.3 (quat-C), 85.9 (OCH), 89.1 (quat-C), 124.8 (=CH), 126.6 (=CH), 128.2 (=CH), 135.2 (quat-C), 135.5 (=CH), 151.7 (quat-C), 206.2 (C=O), 215.3 (C=O).

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2968, 2938, 2860, 1754, 1702, 1603, 1461, 1436, 1282, 1214, 997, 795, 743.

MS (CI+, SP): m/z (%) 297 ((M+H) $^+$, 100), 298 (M+2, 30), 279 (41), 250 (48), 161 (11).

HRMS (CI, SP) for $\text{C}_{19}\text{H}_{20}\text{O}_3$ [(M+H) $^+$] calcd 297.1491, Found 297.1487.

Compound 5f: A mixture of 2-methylene-3,4-dihydro-2H-naphthalen-1-one (200 mg, 1.3 mmol) and α -diazo ketone **3b** (350 mg, 1.4 mmol) was allowed to react in the presence of $\text{Rh}_2(\text{OAc})_4$ (2.0 mg, 0.3 mol%) in dry benzene (20 mL) for 3 h to afford **5f** (450 mg, 93%) based on method B.



Colourless solid: mp 212-214 °C (chloroform/hexane).

^1H NMR (CDCl_3 , 200 MHz) δ 1.09 (s, 3H, CH_3), 1.18 (t, $J = 7.3$ Hz, 3H, CH_3), 1.88-1.29

(m, 10H), 2.15 (d, $J = 12.9$ Hz, 1H), 2.67-2.52 (m, 1H), 2.96-2.92 (m, 2H), 4.17 (q, $J = 5.7$ Hz, 2H, OCH₂), 7.22-7.10 (m, 2H, ArH), 7.36 (t, $J = 6.9$ Hz, 1H, ArH), 7.87 (d, $J = 7.4$ Hz, 1H, ArH).

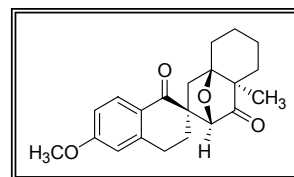
¹³C NMR (CDCl₃, 50.3 MHz) δ 14.4 (CH₃), 16.6 (CH₃), 20.5 (CH₂), 22.2 (CH₂), 27.0 (CH₂), 28.8 (CH₂), 30.2 (CH₂), 31.4 (CH₂), 40.1 (CH₂), 50.7 (quat-C), 56.0 (quat-C), 61.9 (CH₂), 85.7 (quat-C), 93.5 (quat-C), 127.2 (=CH), 129.0 (=CH), 131.6 (quat-C), 134.0 (=CH), 142.9 (quat-C), 166.3 (COO), 196.2 (C=O), 210.7 (C=O).

ν_{\max} (KBr)/cm⁻¹ 2940, 1767, 1732, 1688, 1451, 1287, 1231, 1137, 1081, 860.

MS (EI, 70 eV): m/z (%) 382 (M⁺, 23), 383 (M+1, 9), 336 (20), 290 (100), 262 (60), 225 (31), 173 (65), 55 (35).

Anal. Calcd for C₂₃H₂₆O₅: C, 72.23; H, 6.85. Found: C, 72.40; H, 6.79.

Compound 5g: A mixture of 6-methoxy-2-methylene-3,4-dihydro-2H-naphthalen-1-one (190 mg, 1.0 mmol) and α -diazo ketone **3a** (200 mg, 1.1 mmol) was allowed to react in the



presence of Rh₂(OAc)₄ (2.0 mg, 0.3 mol%) in dry DCM (15 mL) for 2.5 h to afford **5g** (326 mg, 95%) based on method A.

Colourless solid: mp 143-145 °C (chloroform/hexane).

¹H NMR (CDCl₃, 200 MHz) δ 1.04 (s, 3H, CH₃), 1.79-1.16 (m, 9H), 2.18-1.95 (m, 2H), 2.73-2.47 (m, 2H), 3.18-3.05 (m, 1H), 3.74 (s, 3H, OCH₃), 4.27 (s, 1H, OCH), 6.56 (s, 1H, ArH), 6.72 (d, $J = 8.6$ Hz, 1H, ArH), 7.91 (d, $J = 8.7$ Hz, 1H, ArH).

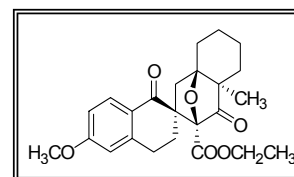
¹³C NMR (CDCl₃, 50.3 MHz) δ 16.2 (CH₃), 20.8 (CH₂), 22.6 (CH₂), 27.0 (CH₂), 28.8 (CH₂), 31.1 (CH₂), 31.6 (CH₂), 38.1 (CH₂), 50.4 (quat-C), 54.1 (quat-C), 55.8 (OCH₃), 86.3 (OCH), 89.0 (quat-C), 112.8 (=CH), 114.0 (=CH), 124.8 (quat-C), 131.2 (=CH), 145.7 (quat-C), 164.0 (quat-C), 195.6 (C=O), 216.0 (C=O).

$\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2937, 1752, 1675, 1600, 1447, 1269, 1239, 1095, 959, 840.

MS (EI, 70 eV): m/z (%) 340 (M^+ , 17), 289 (48), 257 (58), 203 (56), 120 (52), 83 (70), 57 (100).

HRMS (ES^+ , LCMS) for $\text{C}_{21}\text{H}_{24}\text{O}_4$ [$(M+\text{Na})^+$] calcd 363.1572, Found 363.1607.

Compound 5h: A mixture of 6-methoxy-2-methylene-3,4-dihydro-2H-naphthalen-1-one (250 mg, 1.3 mmol) and α -diazo ketone **3b** (360 mg, 1.4 mmol) was allowed to react in the



presence of $\text{Rh}_2(\text{OAc})_4$ (2.0 mg, 0.3 mol%) in dry benzene (20 mL) for 3.5 h to afford **5h** (493 mg, 90%) based on method B.

Colourless solid: mp 143-145 (C (chloroform/hexane)).

^1H NMR (CDCl_3 , 200 MHz) δ 1.17 (s, 3H, CH_3), 1.27 (t, $J = 7.12$ Hz, 3H, CH_3), 2.04-1.44 (m, 9H), 2.32-2.13 (m, 2H), 2.74-2.59 (m, 1H), 3.03-2.98 (m, 2H), 3.84 (s, 3H, OCH_3), 4.26 (q, $J = 7.0$ Hz, 2H, OCH_2), 6.65 (s, 1H, ArH), 6.81 (dd, $J_1 = 8.7$ Hz, $J_2 = 2.2$ Hz, 1H, ArH), 7.95 (d, $J = 8.8$ Hz, 1H, ArH).

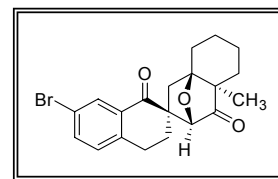
^{13}C NMR (CDCl_3 , 50.3 MHz) δ 14.6 (CH_3), 16.8 (CH_3), 20.7 (CH_2), 22.4 (CH_2), 27.6 (CH_2), 29.0 (CH_2), 30.6 (CH_2), 31.6 (CH_2), 40.7 (CH_2), 50.8 (*quat-C*), 55.9 (*quat-C*), 56.0 (OCH_3), 62.0 (OCH_2), 85.8 (*quat-C*), 93.8 (*quat-C*), 112.7 ($=\text{CH}$), 114.1 ($=\text{CH}$), 125.3 (*quat-C*), 131.6 ($=\text{CH}$), 145.5 (*quat-C*), 164.3 (*quat-C*), 166.5 (COO), 195.1 ($\text{C}=\text{O}$), 211.0 ($\text{C}=\text{O}$).

$\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2951, 2931, 1768, 1721, 1670, 1598, 1445, 1261, 1236, 1116, 1028, 854.

MS (EI, 70 eV): m/z (%) 412 (M^+ , 20), 320 (35), 292 (71), 203 (66), 148 (47), 91 (68), 55 (100).

Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{O}_6$: C, 69.88; H, 6.84. Found: C, 69.72; H, 6.79.

Compound 5i: A mixture of 7-bromo-2-methylene-3,4-dihydro-2H-naphthalen-1-one (250 mg, 1.1 mmol) and α -diazo ketone **3a** (210 mg, 1.2 mmol) was allowed to react in the presence of



$\text{Rh}_2(\text{OAc})_4$ (2.0 mg, 0.3 mol%) in dry DCM (15 mL) for 2 h to afford **5i** (258 mg, 63%) based on method A.

Colourless solid: mp 202-204 °C (chloroform/hexane).

^1H NMR (CDCl_3 , 200 MHz) δ 1.08 (s, 3H, CH_3), 1.72-1.16 (m, 8H) 1.82 (dt, $J_1 = 13.9$ Hz, $J_2 = 6.7$ Hz, 1H), 2.23-1.99 (m, 2H), 2.53 (d, $J = 12.8$ Hz, 1H), 2.80-2.69 (m, 1H), 3.21-3.04 (m, 1H), 4.29 (s, 1H, OCH), 7.06 (d, $J = 8.2$ Hz, 1H, ArH), 7.52 (dd, $J_1 = 6.7$ Hz, $J_2 = 1.5$ Hz, 1H, ArH), 8.10 (d, $J = 1.3$ Hz, 1H, ArH).

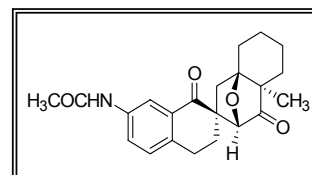
^{13}C NMR (CDCl_3 , 50.3 MHz) δ 16.4 (CH_3), 20.9 (CH_2), 22.7 (CH_2), 26.3 (CH_2), 29.0 (CH_2), 31.3 (CH_2), 31.4 (CH_2), 38.3 (CH_2), 50.7 (*quat-C*), 54.6 (*quat-C*), 86.0 (OCH), 89.4 (*quat-C*), 121.4 (*quat-C*), 131.3 (=CH), 131.8 (=CH), 133.1 (*quat-C*), 136.9 (=CH), 142.2 (*quat-C*), 195.7 (C=O), 216.0 (C=O).

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2948, 2928, 2856, 1751, 1688, 1589, 1445, 1214, 994, 811.

MS (EI, 70 eV): m/z (%) 388 (M^+ , 15), 390 ($\text{M}+2$, 13), 345 (24), 344 (100), 343 (25), 342 (95), 254 (19), 252 (20), 224 (17), 170 (18), 146 (41), 144 (15), 95 (19), 93 (55), 55 (58), 53 (25).

Anal. Calcd for $\text{C}_{20}\text{H}_{21}\text{BrO}_3$: C, 61.71; H, 5.44. Found: C, 61.84; H, 5.48.

Compound 5j: A mixture of *N*-(7-methylene-8-oxo-5,6,7,8-tetrahydronaphthalen-2-yl)acetamide (250 mg, 1.1 mmol) and α -diazo ketone **3a** (220 mg, 1.2 mmol) was allowed to react in



the presence of $\text{Rh}_2(\text{OAc})_4$ (2.0 mg, 0.3 mol%) in dry DCM (12 mL) for 2.5 h to afford **5j** (273 mg, 64%) based on method A.

Colourless solid: mp 224-226 °C (chloroform/hexane).

^1H NMR (CDCl_3 , 200 MHz) δ 1.15 (s, 3H, CH_3), 1.92-1.26 (m, 9H), 2.15 (s, 3H, CH_3), 2.64-2.51 (m, 2H), 2.93-2.78 (m, 2H), 3.18-3.11 (m, 1H), 3.91 (s, 1H, NH), 4.39 (s, 1H, OCH), 7.22 (d, $J = 6.7$ Hz, 1H, ArH), 7.85 (s, 1H, ArH), 8.01 (d, $J = 5.8$ Hz, 1H, ArH).

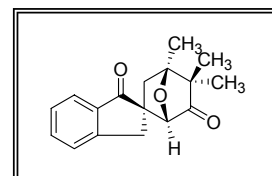
^{13}C NMR (CDCl_3 , 50.3 MHz) δ 16.1 (CH_3), 20.6 (CH_2), 22.5 (CH_2), 24.1 (CH_3), 25.9 (CH_2), 28.7 (CH_2), 31.1 (CH_2), 31.5 (CH_2), 38.2 (CH_2), 50.5 (*quat-C*), 54.5 (*quat-C*), 86.0 (OCH), 89.3 (*quat-C*), 119.1 ($=\text{CH}$), 126.5 ($=\text{CH}$), 130.0 ($=\text{CH}$), 131.9 (*quat-C*), 137.9 (*quat-C*), 139.0 (*quat-C*), 170.5 ($\text{C}=\text{O}$), 197.3 ($\text{C}=\text{O}$), 216.3 ($\text{C}=\text{O}$).

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3368, 2941, 2862, 1745, 1681, 1611, 1593, 1536, 1498, 1370, 1314, 1176, 996, 845.

MS (EI, 70 eV): m/z (%) 367 (M^+ , 5), 355 (10), 216 (15), 203 (95), 161 (98), 123 (50), 105 (45), 57 (47), 43 (100).

Anal. Calcd for $\text{C}_{22}\text{H}_{25}\text{NO}_4$: C, 71.91; H, 6.86; N, 3.81. Found: C, 72.08; H, 6.81; N, 3.86.

Compound 8a: A mixture of 2-methyleneindan-1-one (**4**, 150 mg, 1.0 mmol) and the appropriate α -diazo ketone **7** (175 mg, 1.1 mmol) was allowed to react in the presence of $\text{Rh}_2(\text{OAc})_4$ (2.0 mg,



0.3 mol%) in dry DCM (12 mL) for 2 h to afford **8a** (259 mg, 92%) based on method A.

Colourless solid: mp 140-142 °C (chloroform/hexane).

^1H NMR (CDCl_3 , 200 MHz) δ 0.98 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.95 (d, $J = 12.8$ Hz, 1H), 2.14 (d, $J = 12.7$ Hz, 1H), 2.93 (d, $J = 17.4$ Hz, 1H), 3.13 (d, $J = 17.4$ Hz, 1H), 4.02 (s, 1H, OCH), 7.32-7.25 (m, 2H, ArH), 7.49 (d, $J = 7.1$ Hz, 1H, ArH), 7.66 (d, $J = 7.4$ Hz, 1H, ArH).

^{13}C NMR (CDCl_3 , 50.3 MHz) δ 16.9 (CH_3), 19.7 (CH_3), 21.3 (CH_3), 35.9 (CH_2), 43.1 (CH_2), 51.1 (*quat-C*), 54.8 (*quat-C*), 85.6 (OCH), 89.8 (*quat-C*), 124.8 ($=\text{CH}$), 126.6

(=CH), 128.3 (=CH), 135.2 (*quat*-C), 135.5 (=CH), 151.7 (*quat*-C), 206.0 (C=O), 215.6 (C=O),

$\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2978, 2968, 1754, 1711, 1612, 1455, 1288, 1000, 740.

MS (EI, 70 eV): m/z (%) 270 (M^+ , 34), 224 (32), 209 (50), 195 (26), 185 (14), 160 (100), 132 (78), 115 (40), 70 (18), 55 (38).

HRMS (ES^+ , LCMS) for $C_{17}H_{18}O_3$ [$(M+Na)^+$] calcd 293.1154, Found 293.1159.

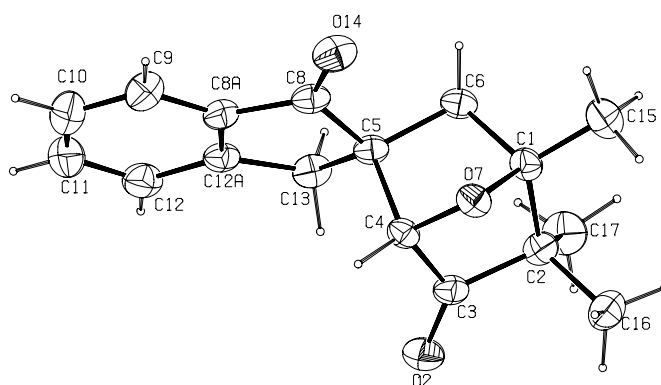
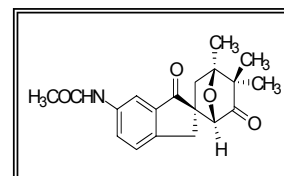


Fig. 1 ORTEP view of the compound **8a**.

Compound 8b: A mixture of N-(2-methylene-3-oxoindan-5-yl)-acetamide (200 mg, 1.0 mmol) and the appropriate α -diazo ketone **7** (170 mg, 1.1 mmol) was allowed to react in the



presence of $Rh_2(OAc)_4$ (2.0 mg, 0.3 mol%) in dry DCM (10 mL) for 3 h to afford **8b** (253 mg, 78%) based on method A.

Colourless solid: mp 217-219 °C (chloroform/hexane).

1H NMR ($CDCl_3$, 200 MHz) δ 1.08 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 2.06 (d, $J = 12.7$ Hz, 1H), 2.18 (s, 3H, CH_3), 2.21 (d, $J = 12.6$ Hz, 1H), 2.99 (d, $J = 17.3$ Hz, 1H), 3.17 (d, $J = 17.3$ Hz, 1H), 3.58 (s, 1H, NH), 4.13 (s, 1H, OCH), 7.35 (d, $J = 7.9$ Hz, 1H, ArH), 7.79 (s, 1H, ArH), 7.99 (d, $J = 8.0$ Hz, 1H, ArH).

^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 16.8 (CH_3), 19.7 (CH_3), 21.3 (CH_3), 24.3 (CH_3), 35.6

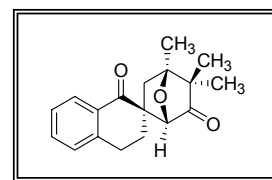
(CH₂), 43.3 (CH₂), 51.2 (*quat*-C), 55.5 (*quat*-C), 85.7 (OCH), 90.1 (*quat*-C), 115.1 (=CH), 126.9 (=CH), 128.2 (=CH), 135.4 (*quat*-C), 139.1 (*quat*-C), 147.3 (*quat*-C), 170.4 (C=O), 206.9 (C=O), 215.9 (C=O).

$\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3352, 2995, 1758, 1698, 1601, 1542, 1495, 1384, 1333, 1304, 1000, 873, 728.

MS (EI, 70 eV): *m/z* (%) 327 (M⁺, 18), 281 (17), 252 (15), 217 (62), 175 (19), 55 (25), 43 (100), 25 (35).

Anal. Calcd for C₁₉H₂₁NO₄: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.80; H, 6.44; N, 4.25.

Compound 8c: A mixture of 2-methylene-3,4-dihydro-2H-naphthalen-1-one (200 mg, 1.3 mmol) and the appropriate α -diazo ketone **7** (200 mg, 1.3 mmol) was allowed to react in the presence



of Rh₂(OAc)₄ (2.0 mg, 0.3 mol%) in dry DCM (15 mL) for 2 h to afford **8c** (291 mg, 81%) based on method A.

Colourless solid: mp 75-77 °C (chloroform/hexane).

¹H NMR (CDCl₃, 200 MHz) δ 0.98 (s, 3H, CH₃), 1.03 (s, 3H, CH₃), 1.38 (s, 3H, CH₃), 1.54 (d, *J* = 12.8 Hz, 1H), 1.83-1.76 (m, 1H), 2.22-2.06 (m, 1H), 2.79-2.59 (m, 2H), 3.24-3.07 (m, 1H), 4.21 (s, 1H, OCH), 7.25-7.11 (m, 2H, ArH), 7.38 (d, *J* = 7.2 Hz, 1H, ArH), 7.96 (d, *J* = 7.6 Hz, 1H, ArH).

¹³C NMR (CDCl₃, 50.3 MHz) δ 17.1 (CH₃), 19.1 (CH₃), 21.5 (CH₃), 26.6 (CH₂), 31.5 (CH₂), 38.4 (CH₂), 51.5 (*quat*-C), 54.9 (*quat*-C), 85.7 (OCH), 89.7 (*quat*-C), 127.3 (=CH), 128.9 (=CH), 129.3 (=CH), 131.4 (*quat*-C), 133.9 (=CH), 143.3 (*quat*-C), 196.7 (C=O), 216.5 (C=O).

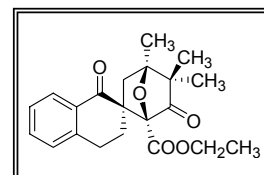
$\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2953, 1755, 1684, 1599, 1450, 1301, 1226, 1018, 946, 756.

MS (EI, 70 eV): *m/z* (%) 284 (M⁺, 79), 285 (M+1, 21), 227 (57), 184 (67), 174 (100), 146

(56), 91 (45), 55 (75).

HRMS (ES⁺, LCMS) for C₁₈H₂₀O₃ [(M+Na)⁺] calcd 307.1310, Found 307.1335.

Compound 8d: A mixture of 2-methylene-3,4-dihydro-2H-naphthalen-1-one (200 mg, 1.3 mmol) and the appropriate α -diazo ketone **7** (320 mg, 1.4 mmol) was allowed to react in the presence



of Rh₂(OAc)₄ (2.0 mg, 0.3 mol%) in dry benzene (15 mL) for 3.5 h to afford **8d** (338 mg, 75%) based on method B.

Colourless solid: mp 145-147 °C (chloroform/hexane).

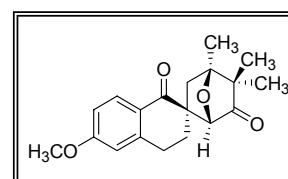
¹H NMR (CDCl₃, 200 MHz) δ 1.12 (s, 3H, CH₃), 1.22 (s, 3H, CH₃), 1.26 (t, *J* = 7.2 Hz, 3H, CH₃), 1.43 (s, 3H, CH₃), 1.87-1.77 (m, 2H), 2.39 (d, *J* = 13.1 Hz, 1H), 2.77-2.61 (m, 1H), 3.08-3.05 (m, 2H), 4.26 (q, *J* = 6.8 Hz, 2H, OCH₂), 7.33-7.20 (m, 2H, ArH), 7.47 (d, *J* = 7.0 Hz, 1H, ArH), 7.98 (d, *J* = 7.6 Hz, 1H, ArH).

¹³C NMR (CDCl₃, 50.3 MHz) δ 14.5 (CH₃), 17.3 (CH₃), 19.6 (CH₃), 21.9 (CH₃), 27.1 (CH₂), 30.1 (CH₂), 40.4 (CH₂), 51.8 (*quat*-C), 56.4 (*quat*-C), 62.0 (OCH₂), 86.6 (*quat*-C), 93.2 (*quat*-C), 127.3 (=CH), 129.0 (=CH), 131.6 (*quat*-C), 134.1 (=CH), 142.9 (=CH), 166.2 (COO), 196.1 (C=O), 211.1 (C=O).

ν_{\max} (KBr)/cm⁻¹ 2972, 1773, 1731, 1688, 1453, 1371, 1294, 1231, 1110, 860, 750. MS (EI, 70 eV): *m/z* (%) 356 (M⁺, 11), 310 (13), 264 (13), 246 (20), 227 (64), 214 (21), 209 (40), 173 (100), 90 (69), 55 (82).

HRMS (ES⁺, LCMS) for C₂₁H₂₄O₅ [(M+Na)⁺] calcd 379.1521, Found 379.1533.

Compound 8e: A mixture of 6-methoxy-2-methylene-3,4-dihydro-2H-naphthalen-1-one (250 mg, 1.3 mmol) and the appropriate α -diazo ketone **7** (220 mg, 1.4 mmol) was allowed to



react in the presence of $\text{Rh}_2(\text{OAc})_4$ (2.0 mg, 0.3 mol%) in dry DCM (15 mL) for 2.5 h to afford **8e** (313 mg, 75%) based on method A.

Colourless solid: mp 131-133 °C (chloroform/hexane).

^1H NMR (CDCl_3 , 200 MHz) δ 0.98 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.55 (d, $J = 12.8$ Hz, 1H), 1.88-1.73 (m, 1H), 2.20-2.05 (m, 1H), 2.75-2.59 (m, 2H), 3.18-3.06 (m, 1H), 3.75 (s, 3H, OCH_3), 4.21 (s, 1H, OCH), 6.57 (s, 1H, ArH), 6.74 (d, $J = 8.3$ Hz, 1H, ArH), 7.93 (d, $J = 8.6$ Hz, 1H, ArH).

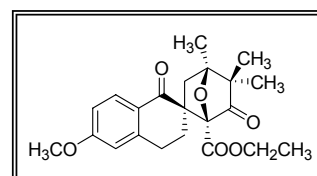
^{13}C NMR (CDCl_3 , 50.3 MHz) δ 17.1 (CH_3), 19.2 (CH_3), 21.6 (CH_3), 27.1 (CH_2), 31.7 (CH_2), 38.5 (CH_2), 51.5 (*quat-C*), 54.6 (*quat-C*), 55.9 (OCH_3), 86.1 (OCH), 89.7 (*quat-C*), 112.9 ($=\text{CH}$), 114.1 ($=\text{CH}$), 124.9 (*quat-C*), 131.3 ($=\text{CH}$), 145.8 (*quat-C*), 164.1 (*quat-C*), 195.6 ($\text{C}=\text{O}$), 216.7 ($\text{C}=\text{O}$).

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2932, 1756, 1673, 1599, 1453, 1275, 1236, 1132, 1030, 947, 828.

MS (EI, 70 eV): m/z (%) 314 (M^+ , 59), 315 ($\text{M}+1$, 21), 271 (32), 257 (57), 204 (87), 176 (100), 148 (55), 55 (57).

HRMS (ES^+ , LCMS) for $\text{C}_{19}\text{H}_{22}\text{O}_4$ [$\text{M}+\text{Na}$] $^+$ calcd 337.1416, Found 337.1411.

Compound 8f: A mixture of 6-methoxy-2-methylene-3,4-dihydro-2*H*-naphthalen-1-one (200 mg, 1.1 mmol) and the appropriate α -diazo ketone **7** (250 mg, 1.1 mmol) was allowed



to react in the presence of $\text{Rh}_2(\text{OAc})_4$ (2.0 mg, 0.3 mol%) in dry benzene (18 mL) for 4 h to afford **8f** (357 mg, 87%) based on method B.

Colourless solid: mp 144-146 °C (chloroform/hexane).

^1H NMR (CDCl_3 , 200 MHz) δ 1.11 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.26 (t, $J = 6.7$ Hz, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.86-1.76 (m, 2H), 2.34 (d, $J = 13.1$ Hz, 1H), 2.75-2.59 (m, 1H), 3.02-2.99 (m, 2H), 3.84 (s, 3H, OCH_3), 4.26 (q, $J = 5.7$ Hz, 2H, OCH_2), 6.64 (s, 1H,

ArH), 6.81 (d, $J = 8.4$ Hz, 1H, *ArH*), 7.96 (d, $J = 8.6$ Hz, 1H, *ArH*).

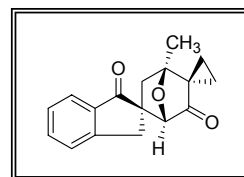
^{13}C NMR (CDCl_3 , 50.3 MHz) δ 14.5 (CH₃), 17.3 (CH₃), 19.7 (CH₃), 22.0 (CH₃), 27.5 (CH₂), 30.4 (CH₂), 40.8 (CH₂), 51.7 (*quat-C*), 55.9 (OCH₃), 56.1 (*quat-C*), 61.9 (OCH₂), 86.5 (*quat-C*), 93.4 (*quat-C*), 112.6 (=CH), 114.1 (=CH), 125.0 (*quat-C*), 131.4 (=CH), 145.4 (*quat-C*), 164.2 (*quat-C*), 166.2 (COO), 194.9 (C=O), 211.2 (C=O).

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2972, 2949, 1775, 1721, 1666, 1598, 1445, 1364, 1298, 1263, 1238, 1107, 1030, 854.

MS (EI, 70 eV): m/z (%) 386 (M^+ , 15), 358 (13), 340 (10), 285 (16), 257 (80), 203 (100), 148 (42), 55 (65).

HRMS (ES^+ , LCMS) for $\text{C}_{22}\text{H}_{26}\text{O}_6$ [$\text{M}+\text{Na}$] $^+$ calcd 409.1627, Found 409.1609.

Compound 8g: A mixture of 2-methyleneindan-1-one (300 mg, 2.1 mmol) and the appropriate α -diazo ketone **7** (340 mg, 2.2 mmol) was allowed to react in the presence of $\text{Rh}_2(\text{OAc})_4$ (2.0 mg, 0.3 mol%) in



dry DCM (20 mL) for 1.5 h to afford **8g** (502 mg, 90%) based on method A.

Colourless solid: mp 139-141 °C (chloroform/hexane).

^1H NMR (CDCl_3 , 200 MHz) δ 0.84-0.73 (m, 2H), 1.36-1.06 (m, 2H), 1.39 (s, 3H, CH₃), 1.89 (d, $J = 11.8$ Hz, 1H), 2.38 (d, $J = 11.8$ Hz, 1H), 3.09 (d, $J = 17.5$ Hz, 1H), 3.27 (d, $J = 17.5$ Hz, 1H), 4.30 (s, 1H, OCH), 7.39 (t, $J = 6.9$ Hz, 2H, *ArH*), 7.64-7.56 (m, 1H, *ArH*), 7.78 (d, $J = 7$ Hz, 1H, *ArH*).

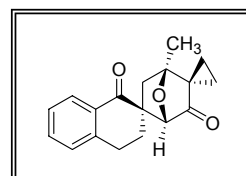
^{13}C NMR (CDCl_3 , 50.3 MHz) δ 12.8 (CH₂), 14.6 (CH₂), 17.3 (CH₃), 36.8 (CH₂), 39.0 (*quat-C*), 47.5 (CH₂), 55.0 (*quat-C*), 86.0 (OCH), 86.1 (*quat-C*), 124.9 (=CH), 126.7 (=CH), 128.4 (=CH), 135.5 (=CH), 135.6 (*quat-C*), 151.9 (*quat-C*), 206.5 (C=O), 210.9 (C=O).

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3012, 1745, 1710, 1607, 1434, 1329, 1005, 737.

MS (EI, 70 eV): m/z (%) 268 (M^+ , 18), 264 (32), 236 (17), 183 (19), 129 (21), 97 (29), 83 (50), 55 (100).

HRMS (ES^+ , LCMS) for $C_{17}H_{16}O_3$ [$(M+Na)^+$] calcd 291.0997, Found 291.1024.

Compound 8h: A mixture of 2-methylene-3,4-dihydro-2H-naphthalen-1-one (250 mg, 1.6 mmol) and the appropriate α -diazo ketone **7** (260 mg, 1.7 mmol) was allowed to react in the presence of



$Rh_2(OAc)_4$ (2.0 mg, 0.3 mol%) in dry DCM (18 mL) for 2 h to afford **8h** (348 mg, 78%) based on method A.

Colourless solid: mp 109-111 °C (chloroform/hexane).

1H NMR ($CDCl_3$, 200 MHz) δ 0.79-0.71 (m, 1H), 1.33-1.06 (m, 3H), 1.35 (s, 3H, CH_3), 1.49 (d, $J = 11.8$ Hz, 1H), 2.02-1.92 (m, 1H), 2.32-2.26 (m, 1H), 2.92-2.81 (m, 2H), 3.31-3.21 (m, 1H), 4.44 (s, 1H, OCH), 7.35-7.21 (m, 2H, ArH), 7.52-7.44 (m, 1H, ArH), 8.08 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.3$ Hz, 1H, ArH).

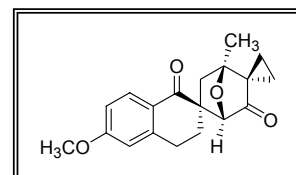
^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 12.8 (CH_2), 14.82 (CH_2), 17.5 (CH_3), 26.7 (CH_2), 32.6 (CH_2), 39.3 (quat-C), 43.1 (CH_2), 54.9 (quat-C), 86.1 (quat-C), 86.2 (OCH), 127.4 (=CH), 129.5 (=CH), 129.4 (=CH), 131.6 (quat-C), 134.1 (=CH), 143 (quat-C), 197.0 (C=O), 211.6 (C=O).

$\nu_{max}(KBr)/cm^{-1}$ 2935, 1749, 1681, 1598, 1452, 1333, 1309, 1230, 1017, 949.

MS (EI, 70 eV): m/z (%) 282 (M^+ , 51), 254 (21), 226 (54), 212 (31), 118 (68), 90 (100), 65 (47), 51 (29).

HRMS (ES^+ , LCMS) for $C_{18}H_{18}O_3$ [$(M+Na)^+$] calcd 305.1154, Found 305.1174.

Compound 8i: A mixture of 6-methoxy-2-methylene-3,4-dihydro-2H-naphthalen-1-one (300 mg, 1.6 mmol) and the



appropriate α -diazo ketone **7** (260 mg, 1.7 mmol) was allowed to react in the presence of $\text{Rh}_2(\text{OAc})_4$ (2.0 mg, 0.3 mol%) in dry DCM (18 mL) for 1 h to afford **8i** (334 mg, 67%) based on method A.

Colourless solid: mp 173-175 °C (chloroform/hexane).

^1H NMR (CDCl_3 , 200 MHz) δ 0.77-0.68 (m, 1H), 1.20-1.05 (m, 2H), 1.28-1.23 (m, 1H), 1.35 (s, 3H, CH_3), 1.46 (d, $J = 11.8$ Hz, 1H), 1.94 (dt, $J_1 = 14.0$ Hz, $J_2 = 4.3$ Hz, 1H), 2.30 (td, $J_1 = 13.8$ Hz, $J_2 = 4.8$ Hz, 1H), 2.89-2.74 (m, 2H), 3.31-3.16 (m, 1H), 3.85 (s, 3H, OCH_3), 4.45 (s, 1H, OCH), 6.68 (s, 1H, ArH), 6.85 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.1$ Hz, 1H, ArH), 8.08 (d, $J = 8.8$ Hz, 1H, ArH).

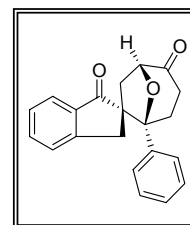
^{13}C NMR (CDCl_3 , 50.3 MHz) δ 12.7 (CH_2), 14.7 (CH_2), 17.4 (CH_3), 27.1 (CH_2), 32.6 (CH_2), 39.2 (*quat-C*), 43.0 (CH_2), 54.4 (*quat-C*), 55.9 (CH_3), 86.0 (*quat-C*), 86.4 (OCH), 112.9 ($=\text{CH}$), 114.1 ($=\text{CH}$), 125.0 (*quat-C*), 131 ($=\text{CH}$), 146.0 (*quat-C*), 164.1 (*quat-C*), 195.8 ($\text{C}=\text{O}$), 211.7 ($\text{C}=\text{O}$).

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2933, 1747, 1674, 1600, 1275, 1239, 1031, 950.

MS (EI, 70 eV): m/z (%) 312 (M^+ , 70), 284 (59), 255 (73), 227 (48), 148 (78), 120 (54), 91 (100), 77 (90), 53 (51).

HRMS (ES^+ , LCMS) for $\text{C}_{19}\text{H}_{20}\text{O}_4$ [$(\text{M}+\text{Na})^+$] calcd 335.1259, Found 335.1284.

Compound 10a: A mixture of 2-methyleneindan-1-one (**4**, 250 mg, 1.7 mmol) and the appropriate α -diazo ketone **9** (370 mg, 1.8 mmol) was allowed to react in the presence of $\text{Rh}_2(\text{OAc})_4$ (2.0 mg, 0.3 mol%) in dry DCM (20 mL) for 2 h to afford **10a** (420 mg, 76%) based on method A.



Colourless solid: mp 135-137 °C (chloroform/hexane).

^1H NMR (CDCl_3 , 200 MHz) δ 2.17-2.01 (m, 1H), 2.58-2.40 (m, 2H), 2.83-2.67 (m, 3H), 3.08 (d, $J = 17.5$ Hz, 1H), 3.29-3.11 (m, 1H), 4.48 (dd, $J_1 = 7.1$ Hz, $J_2 = 1.7$ Hz, 1H,

OCH), 6.84 (d, $J = 7.5$ Hz, 1H, ArH), 6.97 (d, $J = 7.1$ Hz, 2H, ArH), 7.36-7.14 (m, 5H, ArH), 7.69 (d, $J = 7.1$ Hz, 1H, ArH).

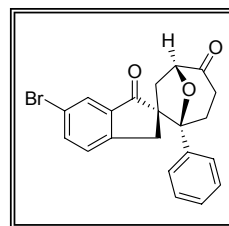
^{13}C NMR (CDCl_3 , 50.3 MHz) δ 33.3 (CH_2), 34.2 (CH_2), 42.8 (CH_2), 43.8 (CH_2), 62.8 (*quat*-C), 80.7 (OCH), 89.6 (*quat*-C), 124.2 (=CH), 124.6 (=CH), 126.1 (=CH), 127.6 (=CH), 128.0 (=CH), 135.7 (=CH), 137.6 (*quat*-C), 141.6 (*quat*-C), 153.2 (*quat*-C), 206.7 (C=O), 207.6 (C=O).

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2954, 1738, 1698, 1603, 1462, 1438, 1286, 1038, 764, 701.

MS (EI, 70 eV): m/z (%) 318 (M^+ , 56), 300 (20), 275 (21), 213 (40), 185 (58), 173 (95), 145 (100), 115 (42), 105 (65), 55 (38).

Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_3$: C, 79.22; H, 5.70. Found: C, 79.29; H, 5.74.

Compound 10b: A mixture of 6-bromo-2-methyleneindan-1-one (250 mg, 1.1 mmol) and the appropriate α -diazo ketone **9** (250 mg, 1.2 mmol) was allowed to react in the presence of $\text{Rh}_2(\text{OAc})_4$ (2.0 mg, 0.3 mol%) in dry DCM (18 mL) for 3 h to afford **10b** (401 mg, 90%)



based on method A. Colourless solid: mp 174-176 °C (chloroform/hexane).

^1H NMR (CDCl_3 , 200 MHz) δ 2.21-2.03 (m, 1H), 2.83-2.42 (m, 5H), 3.03 (d, $J = 17.7$ Hz, 1H), 3.35-3.15 (m, 1H), 4.59 (dd, $J_1 = 7.3$ Hz, $J_2 = 1.5$ Hz, 1H, OCH), 6.85 (d, $J = 8.1$ Hz, 2H, ArH), 7.75-7.08 (m, 3H, ArH), 7.53 (dd, $J_1 = 8.1$ Hz, $J_2 = 1.9$ Hz, 2H, ArH), 7.92 (d, $J = 1.7$ Hz, 1H, ArH).

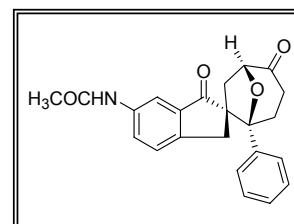
^{13}C NMR (CDCl_3 , 50.3 MHz) δ 33.3 (CH_2), 34.0 (CH_2), 42.9 (CH_2), 43.5 (CH_2), 63.4 (*quat*-C), 80.8 (OCH), 89.7 (*quat*-C), 122.3 (*quat*-C), 124.7 (*quat*-C), 127.2 (=CH), 127.8 (=CH), 127.9 (=CH), 128.4 (*quat*-C), 138.5 (=CH), 139.5 (*quat*-C), 141.5 (*quat*-C), 151.8 (*quat*-C), 205.4 (C=O), 207.4 (C=O).

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2966, 1740, 1704, 1457, 1438, 1256, 1208, 1032, 893, 764, 702.

MS (CI+, SP): m/z (%) 397 ((M+H)⁺, 57), 399 (M+2+H, 55), 379 (98), 381 (100), 302 (18), 301 (54), 105 (25).

HRMS (CI, SP) for C₂₁H₁₇O₃Br [(M+H)⁺] calcd 397.0439, Found 397.0436.

Compound 10c: A mixture of *N*-(2-methylene-3-oxoindan-5-yl)-acetamide (200 mg, 1.0 mmol) and the appropriate α -diazo ketone **9** (220 mg, 1.1 mmol) was allowed to react in the presence of Rh₂(OAc)₄ (2.0 mg, 0.3 mol%) in dry DCM (15 mL) for 2.5 h to afford **10c** (306 mg, 82%) based on method A.



Colourless solid: mp 180-182 °C (chloroform/hexane).

¹H NMR (CDCl₃, 200 MHz) δ 2.16-2.04 (m, 2H), (s, 3H, CH₃), 2.81-2.42 (m, 4H), 3.13-2.97 (m, 1H), 3.34-3.22 (m, 1H), 4.58 (d, J = 6.6 Hz, 1H, OCH), 6.90 (d, J = 8.1 Hz, 1H, ArH), 7.36-7.09 (m, 5H, ArH), 7.40 (s, 1H, NH), 7.70 (d, J = 7.8 Hz, 1H, ArH), 7.99 (s, 1H, ArH).

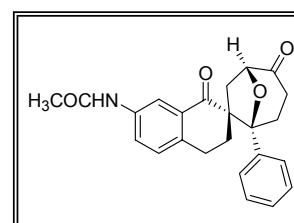
¹³C NMR (CDCl₃, 50.3 MHz) δ 24.0 (CH₃), 33.1 (CH₂), 34.0 (CH₂), 42.6 (CH₂), 43.2 (CH₂), 63.2 (quat-C), 80.6 (OCH), 89.6 (quat-C), 114.2 (=CH), 126.3 (quat-C), 127.6 (=CH), 127.9 (=CH), 128.0 (=CH), 128.8 (=CH), 137.8 (quat-C), 138.7 (quat-C), 141.4 (quat-C), 148.6 (quat-C), 170.4 (C=O), 206.9 (C=O), 208.6 (C=O).

ν_{\max} (KBr)/cm⁻¹ 3314, 2926, 1705, 1667, 1602, 1546, 1493, 1439, 1302, 1256, 1031, 899, 761, 701.

MS (EI, 70 eV): m/z (%) 375 (M⁺, 44), 270 (18), 242 (24), 202 (100), 173 (80), 105 (62), 77 (30), 43 (45).

Anal. Calcd for C₂₃H₂₁NO₄: C, 73.58; H, 5.64; N, 3.73. Found: C, 73.49; H, 5.69; N, 3.75.

Compound 10d: A mixture of *N*-(7-methylene-8-oxo-5,6,7,8-



tetrahydronaphthalen-2-yl)-acetamide (250 mg, 1.2 mmol) and the appropriate α -diazo ketone **9** (250 mg, 1.2 mmol) was allowed to react in the presence of $\text{Rh}_2(\text{OAc})_4$ (2.0 mg, 0.3 mol%) in dry DCM (15 mL) for 1.5 h to afford **10d** (249 mg, 55%) based on method A.

Colourless solid: mp 90-92 °C (chloroform/hexane).

^1H NMR (CDCl_3 , 200 MHz) δ 2.08-1.66 (m, 4H), 2.20 (s, 3H, CH_3), 2.63-2.33 (m, 4H), 2.94-2.83 (m, 1H), 3.23-3.05 (m, 1H), 4.50 (d, $J = 8.71$ Hz, 1H, OCH), 6.93 (d, $J = 8.2$ Hz, 1H, ArH), 7.54-7.22 (m, 5H, ArH), 7.78 (s, 1H, ArH), 7.91-7.88 (m, 2H, ArH).

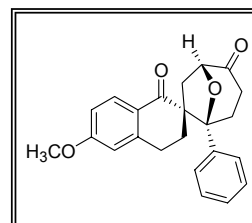
^{13}C NMR (CDCl_3 , 50.3 MHz) δ 24.8 (CH_3), 25.0 (CH_3), 33.5 (CH_2), 34.4 (CH_2), 36.4 (CH_2), 40.9 (CH_2), 58.2 (*quat*-C), 80.5 (OCH), 88.2 (*quat*-C), 118.7 (=CH), 125.4 (=CH), 126.6 (*quat*-C), 128.0 (=CH), 128.7 (=CH), 128.9 (=CH), 130.1 (=CH), 137.4 (*quat*-C), 140.3 (*quat*-C), 142.3 (*quat*-C), 169.3 (C=O), 199.2 (C=O), 208 (C=O).

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3305, 2927, 1729, 1671, 1595, 1538, 1497, 1411, 1307, 1178, 1030, 761, 701.

MS (EI, 70 eV): m/z (%) 389 (M^+ , 36), 371 (22), 256 (50), 216 (42), 186 (21), 161 (26), 105 (100), 77 (58), 43 (82).

Anal. Calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_4$: C, 77.49; H, 6.50; N, 3.61. Found: C, 77.54; H, 6.45; N, 3.64.

Compound 10e: A mixture of 2-methylene-3,4-dihydro-2H-naphthalen-1-one (200 mg, 1.1 mmol) and the appropriate α -diazo ketone **9** (230 mg, 1.1 mmol) was allowed to react in the presence of $\text{Rh}_2(\text{OAc})_4$ (2.0 mg, 0.3 mol%) in dry DCM (15 mL) for 2 h to afford **10e** (116 mg, 30%) based on method A.



Colourless solid: mp 109-111 °C (chloroform/hexane).

^1H NMR (CDCl_3 , 200 MHz) δ 2.24-1.67 (m, 5H), 2.50-2.32 (m, 2H), 2.66-2.58 (m, 1H),

3.00-2.88 (m, 1H), 3.24-3.10 (m, 1H), 3.81 (s, 3H, OCH₃), 4.49 (dd, $J_1 = 7.9$ Hz, $J_2 = 1.8$ Hz, OCH), 6.39 (d, $J = 2.4$ Hz, 1H, ArH), 6.84 (dd, $J_1 = 6.3$ Hz, $J_2 = 2.5$ Hz, 1H, ArH), 7.39-7.19 (m, 5H, ArH), 8.06 (d, $J = 8.8$ Hz, 1H, ArH).

¹³C NMR (CDCl₃, 50.3 MHz) δ 25.8 (CH₂), 33.6 (CH₂), 34.6 (CH₂), 36.6 (CH₂), 41.1 (CH₂), 56.0 (OCH₃), 58.0 (*quat*-C), 80.4 (OCH), 88.3 (*quat*-C), 112.6 (=CH), 114.1 (=CH), 125.4 (*quat*-C), 127.8 (=CH), 128.6 (=CH), 130.9 (=CH), 142.6 (*quat*-C), 147.1 (*quat*-C), 164.4 (OCH₃), 198.1 (C=O), 207.9 (C=O).

ν_{\max} (KBr)/cm⁻¹ 2939, 1729, 1664, 1600, 1494, 1447, 1346, 1265, 1234, 1032, 882, 738.

MS (CI+, SP): m/z (%) 363 ((M+H)⁺, 100), 345 (86), 301 (35), 189 (40), 161 (22).

HRMS (CI, SP) for C₂₃H₂₂O₄ [(M+H)⁺] calcd 363.1596, Found 363.1600.

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