Photochemical Preparation of Highly Functionalized 1-Indanones

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Supporting information

General. The following reagents were commercially available: 2-methylbenzaldehyde **4**, 2-methylbenzonitrile **5**, 2-methylacetophenone **8**, 2-iodophenyl-acetic acid, 1-bromo-2-ethylbenzene **17**. The following reagents were prepared according to literature procedures: hydroxy-mesyloxy-iodobenzene (HMIB) [9b], methyl 2-(2-iodophenylacetate) **13** [13]. THF and Et₂O were dried over Na metal in the presence of benzophenone as an indicator of dryness and distilled at atmospheric pressure. CH₂Cl₂ was dried by heating to reflux over P₂O₅ and distilled at atmospheric pressure. All moisture-sensitive reagents were transferred via syringe under N₂ or Ar atmosphere; moisture-sensitive reactions were carried out under N₂ or Ar atmosphere. Flash column chromatography (FCC): silica gel, 230-400 mesh (*Fluka*). Anal. TLC: *Merck* silica gel 60 F₂₅₄ plates; detection by UV light. M.p.: *Büchi 530*, uncorrected. NMR: CDCl₃, CD₂Cl₂ and d₆-DMSO solutions; *Bruker DPX300* equipment; chemical shifts δ in ppm; calibration: CDCl₃ (¹H: 0.00 ppm = Me₄Si; ¹³C: 77.0 ppm), d₆-DMSO (¹H: 2.49 ppm; ¹³C: 39.5 ppm); IR: *Perkin-Elmer-881*, solids as KBr pastilles, liquids and oils on NaCl crystals as film, in cm⁻¹. EI-MS: *Hewlett-Packard 5995 A*, 70eV at 293-593 K, m/z (%). HR-EI-MS: *MSI Concept 1H*. Elemental Analysis were carried out by the analytical laboratory of the Institute of Chemistry of the Humboldt-University Berlin. Photochemistry: prep. irradiations with a 150-W high pressure Hg-arc lamp (*Hanau*); anal. irradiation with a 500-W high pressure Hg-arc lamp (*OSRAM HBO-500*), UV cuvet 1 x 1 cm, filter *WG 295* (*Schott*).

Quantum chemical calculations. The geometry optimization were performed with the program package Gaussian 98 [28] using the B3PW91 hybrid functional [29] and the 6-31G* basis set. At the same level of theory frequency calculations were carried out to characterize each structure as minimum (**23**, **24**, **26**, **28**, **30**, **33**, **35a**, **35b**, **37-40**) or transition state (**25**, **27**, **29**, **31**, **32**, **34**, **36**) respectively and to obtain the zero point vibrational energies. Afterwards,

single point calculations were performed with the same DFT functional using the extended basis set 6-311++G** basis set in order to obtain improved energies.

General Procedure I - 2-Mesyloxylation of ketones. To a stirred mixture of the appropriate ketone **1a-1e** (10.0 mmol) in MeCN or CH₂Cl₂ (25 ml) was added HMIB (3.16 g, 10.0 mmol). The reaction mixture was stirred at r.t. or heated to reflux until TLC indicated disappearance of the ketone. The reaction mixture was concentrated to an oil (if MeCN was used as solvent), diluted with CH₂Cl₂ (25 ml) and washed with brine (25 ml) and H₂O (25 ml), dried over anhydrous MgSO₄ and concentrated under reduced pressure. Purification of the residue by FCC (petroleum ether / ethyl acetate mixtures: 10:1-10:3) gave the 2-mesyloxy ketones.

General Procedure II - Synthesis of Hydroxy-ketones 12a-c. To a stirred solution of diisopropylamine (0.5 g, 5.02 mmol) in 10 ml abs. Et₂O was added 3.1 ml *n*-butyllithium (hexane, 1.6 M) at -78 °C under a nitrogen atmosphere and stirred for 45 min. To the resulting mixture a solution of **11** (1.0 g, 4.6 mmol) in 1 ml abs. Et₂O was dropped. After additional 45 min of stirring the corresponding aldehyde or ketone was added and the solution was stirred for 2 h. The mixture was quenched with sat. NH₄Cl (aq, 20 ml) and allowed to come to r.t. The layers were separated and the organic layer was washed with sat. NH₄Cl (aq, 3 x 10 ml). The combined aqueous layers were extracted with Et₂O (3 x 20 ml). The combined organic solutions were dried over MgSO₄ and concentrated in vacuo. The residue was dissolved in 10 ml acetonitrile, cooled to 0 °C and treated with 30 drops of HF (aq, 40 %). After 4 h of stirring 150 mg solid NaHCO₃ was added and the suspension was stirred for further 0.5 h. The solid was separated by filtering, the filtrate was diluted with Et₂O, washed with sat. NaHCO₃ (aq, 3 x 20 ml), dried over MgSO₄, and concentrated in vacuo. The crude residue was purified by flash chromatography (petrol ether : ethyl acetate = 100 : 3 – 100 : 5)

General Procedure III - Irradiation of ketones 1a-o. The irradiation of ketones **1a-o** was performed in the solvent specified in table 1 (200 or 400 ml) at concentrations of 0.01 mmol/ml in some cases in the presence of *N*-methylimidazole (2 equiv., see table 1), using a high pressure mercury arc lamp (150 W). Light of wavelength below 300 nm was absorbed using a Pyrex^{TM} glass jacket between the lamp and the reaction vessel. The reaction was monitored by TLC and aborted when the reactant had completely disappeared (1-3 h). The solution was concentrated *in vacuo* to 10% of the original volume. To the solution was added

silica gel (5 g), and the remaining solvent was removed under reduced pressure. The residue was purified immediately by FCC (petroleum ether / ethyl acetate mixtures: 100:5-100:20) to give indanones **20**, 1-alkylidene-1,3-dihydro-2-benzofuran **21** or 2-(1-alkoxyalkyl)-acetophenones **22**.

2-Mesyloxy-1-(2-methylphenyl)-1-ethanone 1a. Prepared from **8** (0.5 g, 3.7 mmol) and HMIB (1.5 g, 4.8 mmol) according to general procedure I. Purification by flash chromatography (petrol ether : ethyl acetate = 10 : 1) to give the ester **1a** (1.0 g, 92 %) as a yellow oil: IR (thin film) 1710, 1601, 1349, 1175, 956, 808, 721 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 2.47 (s, 3 H), 3.20 (s, 3 H), 5.29 (s, 1 H), 7.36-7.50 (m, 4 H); ^{13}C NMR (75,5 MHz, CDCl_3) δ 194.2, 139.5, 133.3, 132.8-126.0, 71.1, 39.2, 21.3; Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{O}_4\text{S}$: C, 52.62; H, 5.30; S, 14.05. Found: C, 52.64; H, 5.33; S, 13.69. HRMS (ESI, 70 eV) m/z calcd for $(\text{C}_{10}\text{H}_{12}\text{O}_4\text{S} + \text{Na})^+$ 251.0349, found 251.0349.

2-Mesyloxy-1-(2-methylphenyl)-1-propanone 1b. Prepared from **7a** (0.5 g, 3.4 mmol) and HMIB (3.2 g, 10.1 mmol) according to general procedure I. Purification by flash chromatography (petrol ether : ethyl acetate = 10 : 1) to give the ester **1b** (0.59 g, 72 % yield) as a yellow oil: IR (thin film) 1704, 1688, 1456, 1350, 1176, 922, 738 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.48 (d, $J = 7.2$, 3 H), 2.39 (s, 3 H), 3.06 (s, 3 H), 5.82 (q, $J = 7.1$, 1 H), 7.19-7.20 (m, 2 H), 7.22-7.24 (m, 1 H), 7.33-7.36 (m, 1 H); ^{13}C NMR (75,5 MHz, CDCl_3) δ 199.1, 138.7, 134.6, 132.8-125.9, 78.5, 39.4, 20.6, 17.8. Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_4\text{S}$: C, 54.53; H, 5.82; S, 13.23. Found: C, 54.54; H, 5.82; S, 13.08. HRMS (EI, 70 eV) m/z calcd for $(\text{C}_{11}\text{H}_{14}\text{O}_4\text{S})^+$ 242.06128, found 242.06126.

2-Mesyloxy-1-(2-methylphenyl)-1-butanone 1c. Prepared from **7b** (1.0 g, 6.2 mmol) and HMIB (4.9 g, 15.5 mmol) according to general procedure I. Purification by flash chromatography (petrol ether : ethyl acetate = 10 : 1) to give the ester **1c** (1.1 g, 70 % yield) as a white solid: mp. 43 $^\circ\text{C}$, IR (neat) 1703, 1362, 1221, 1174, 942, 777 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.97 (t, $J = 7.6$, 3 H), 1.73-1.89 (qd, $J = 7.6$, $J = 4.1$, 2 H), 2.39 (s, 3 H), 3.07 (s, 3 H), 5.68 (dd, $J = 4.1$, 1 H), 7.19-7.24 (m, 2 H), 7.34-7.38 (m, 1 H), 7.51-7.54 (m, 1 H); ^{13}C NMR (75,5 MHz, CDCl_3) δ 198.9, 138.6, 135.0, 132.1-123.9, 83.7, 39.3, 25.1, 20.5, 9.5; Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}$: C, 56.23; H, 6.29; S, 12.51. Found: C, 56.02; H, 6.27; S, 12.56.

2-Mesyloxy-1-(2-methylphenyl)-2-phenyl-ethanone 1d. Prepared from **7c** (0.3 g, 1.4 mmol) and HMIB (0.6 g, 1.86 mmol) according to general procedure I. Purification by flash chromatography (petrol ether : ethyl acetate = 20 : 1) to give the ester **1d** (0.3 g, 63 % yield): ^1H NMR (300 MHz, CDCl_3) δ 2.19 (s, 3 H), 3.06 (s, 3 H), 6.63 (s, 1 H), 7.10-7.29 (m, 8 H), 7.53-7.55 (m, 1 H); ^{13}C NMR (75,5 MHz, CDCl_3) δ 195.9, 138.8, 135.0, 132.0-131.8, 131.7, 129.9-125.7, 83.8, 39.7, 20.3; Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_4\text{S}$: C, 63.14; H, 5.30; S, 10.54. Found: C, 62.91; H, 5.50; S, 10.47.

Ethyl 2-mesyloxy-3-(2-methylphenyl)-3-oxopropanoate 1e. Prepared from **9** (0.30 g, 1.5 mmol) and HMIB (0.60 g, 1.9 mmol) according to general procedure I. Purification by flash chromatography (petrol ether : ethyl acetate = 10 : 1) to give the ester **1e** (0.4 g, 91 % yield): IR (KBr) 1761, 1702, 1362, 1178 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.14 (t, $J = 7.2$, 3 H), 2.43 (s, 3 H), 3.16 (s, 3 H), 4.19 (q, $J = 7.2$, 2 H), 6.09 (s, 1 H), 7.23-7.39 (m, 3 H), 7.65-7.67 (m, 1 H); ^{13}C NMR (75,5 MHz, CDCl_3) δ 190.8, 164.3, 140.2, 133.6, 125.9-132.9, 78.6, 62.9, 39.6, 21.1, 13.8; Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_6\text{S}$: C, 51.99; H, 5.37; S, 10.68. Found: C, 52.28; H, 5.49; S, 10.60.

1-{2-Mesyloxy-3-(2-methylphenyl)-3-oxopropanoyl}-pyrrolidine 1f. Prepared from **10** (0.30 g, 1.2 mmol) and HMIB (0.50 g, 1.6 mmol) according to general procedure I. Purification by flash chromatography (petrol ether : ethyl acetate = 10 : 4) to give the amid **1f** (0.40 g, 99 % yield): IR (KBr) 1707, 1662, 1646, 1434, 1355, 1171, 939, 774 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.61-1.98 (m, 4 H), 2.44 (s, 3 H), 3.15 (s, 3 H), 3.38-3.59 (m, 4 H), 6.16 (s, 1 H), 7.04-7.71 (m, 4 H); ^{13}C NMR (75,5 MHz, CDCl_3) δ 193.4, 161.5, 139.6, 137.4, 134.4-125.6, 79.9, 46.9-46.8, 39.8, 26.1-23.9, 20.7; Anal. Calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_5\text{S}$: C, 55.37; H, 5.89; S, 9.85. Found: C, 55.41; H, 5.81; S, 9.71.

3-Methyl-1-(2-methylphenyl)-2-mesyloxy-1-butanone 1g. To a stirred and cooled (0 °C) solution of **12b** (50 mg, 0.26 mmol) in 2 ml pyridine methanesulfonyl chloride (36 mg, 0.31 mmol) was added. The resulting solution was allowed to warm to r.t. and stirred for 16 h. Afterwards, the mixture was cooled to 0 °C, water (20 ml) was added, and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 20 ml), the combined organic layers were washed with half-concentrated HCl (aq, 3x 15 ml), NaHCO_3 (aq, 5 %, 3 x 15 ml), water (2 x 10 ml), brine (aq, 1 x 10 ml), dried over MgSO_4 , and concentrated in vacuo. The

residue was purified by flash chromatography (petrol ether : ethyl acetate = 20 : 3) to give the ester **1g** (70 mg, 99 % yield): IR (thin film) 1704, 1461, 1356, 1178, 1008, 936, 829, 752 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.83 (d, J = 6.8, 3 H), 1.02 (d, J = 7.1, 3 H), 2.12-2.21 (m, 1 H), 2.41 (s, 3 H), 3.08 (s, 3 H), 5.64 (d, J = 3.4, 1 H), 7.22-7.24 (m, 2 H), 7.34-7.36 (m, 1 H), 7.53-7.55 (m, 1 H); ^{13}C NMR (75,5 MHz, CDCl_3) δ 198.8, 138.6, 135.3, 132.3-125.3, 86.8, 39.3, 30.6, 20.6, 19.5, 16.1; Anal. Calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_4\text{S}$: C, 57.76; H, 6.71; S, 11.86. Found: C, 57.77; H, 6.94; S, 12.02.

2-Methyl-1-(2-methylphenyl)-2-tosyloxy-1-propanone 1h. 12c (100 mg, 0.56 mmol) and pyridine (133 mg, 1.68 mmol) were dissolved in 4 ml dichloromethane and toluene-4-sulfonic acid anhydride (548 mg, 1.68 mmol) was added. The resulting suspension was stirred for 2 d, then 10 ml water was added and the layers were separated. The organic layer was washed with sat. NaHCO_3 (aq, 5 ml) and sat. NH_4Cl (aq, 5 ml). The combined aqueous layers were extracted with dichloromethane (1 x 10 ml). The combined organic layers were dried over MgSO_4 and concentrated in vacuo. The residue was purified by flash chromatography (petrol ether : ethyl acetate = 20 : 1) to give the ester **1h** (40 mg, 21 % yield). IR (thin film) 1690, 1596, 1339, 1176, 1090, 915, 858, 738 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.81 (s, 6 H), 2.32 (s, 6 H), 6.99-7.28 (m, 7 H), 7.35-7.37 (m, 1 H); ^{13}C NMR (75,5 MHz, CDCl_3) δ 204.2, 144.3, 138.0, 136.5, 135.4, 131.5-124.7, 92.5, 26.5, 21.5, 20.5; Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_4\text{S}$: C, 65.04; H, 6.06; S, 9.65. Found: C, 64.29; H, 6.49; S, 9.32.

Phosphoric acid diethyl 1-(2-methylphenyl)-1-oxo-2-propyl ester 1i. Diethyl chlorophosphate (134 mg, 0.77 mmol) was added to a stirred and cooled (0 °C) solution of **12a** (100 mg, 0.61 mmol) in 2 ml pyridine. The resulting solution was allowed to warm to r.t. and stirred for 16 h. Afterwards, the mixture was cooled to 0 °C, water (10 ml) was added, and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 20 ml), the combined organic layers were washed with half-concentrated HCl (aq, 3x 15 ml), NaHCO_3 (aq, 5 %, 3 x 15 ml), water (2 x 10 ml), brine (aq, 1 x 10 ml), dried over MgSO_4 , and concentrated in vacuo. The residue was purified by flash chromatography (dichloromethane : MeOH = 100 : 1) to give the ester **1i** (162 mg, 89 % yield): ^1H NMR (300 MHz, CDCl_3) δ 1.11-1.29 (m, 6 H), 1.42 (d, J = 7.2, 3 H), 2.38 (s, 3 H), 3.90-4.11 (m, 4 H), 5.51 (q, J = 7.2, 1 H) 7.09-7.16 (m, 2 H), 7.29-7.32 (m, 1 H), 7.50-7.55 (m, 1 H); ^{13}C NMR (75,5 MHz, CDCl_3) δ 200.6, 138.3, 135.5, 131.5-125.6, 76.0, 64.0, 20.5, 18.6, 16.0; ^{31}P NMR (121.5 MHz,

CDCl_3) δ -0.55 (s); HRMS (EI, 70 eV) m/z calcd for $(\text{C}_{14}\text{H}_{21}\text{O}_5\text{P})^+$ 300.11266, found 300.11259.

Carbonic acid 1-(2-methylphenyl)-1-oxo-2-propyl isobutyl ester 1j. Isobutyl chloroformate (178 mg, 1.30 mmol) was added to a stirred and cooled (0 °C) solution of **12a** (102 mg, 0.62 mmol) in 2 ml pyridine. The resulting solution was heated to 80 °C for 1 h. After cooling to r.t. the mixture was treated with water (10 ml) and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 20 ml), the combined organic layers were washed with half-concentrated HCl (aq, 3x 15 ml), NaHCO_3 (aq, 5 %, 3 x 15 ml), water (2 x 10 ml), brine (aq, 1 x 10 ml), dried over MgSO_4 , and concentrated in vacuo. The residue was purified by flash chromatography (petrol ether : ethyl acetate = 100 : 3) to give the ester **1j** (164 mg, 99 % yield): IR (thin film) 1745, 1704, 1379, 1259, 1021, 961, 892, 791 cm^{-1} ; HRMS (ESI, 70 eV) m/z calcd for $(\text{C}_{15}\text{H}_{20}\text{O}_4 + \text{Na})^+$ 287.1259, found 287.1254; ^1H NMR (300 MHz, CDCl_3) δ 0.87 (t, J = 4.9, 3 H), 0.88 (t, J = 4.9, 3 H), 1.4 (d, J = 7.1, 3 H), 1.86-1.96 (m, 2 H), 2.38 (s, 3 H), 3.83 (q, J = 6.8, 2 H), 5.62 (q, J = 7.1, 1 H) 7.17-7.22 (m, 2 H), 7.29-7.35 (m, 1 H), 7.54-7.56 (m, 1 H); ^{13}C NMR (75,5 MHz, CDCl_3) δ 200.5, 154.8, 138.5, 135.3, 132.8-125.6, 75.9, 73.9, 27.8, 20.5, 18.9, 16.4.

Carbonic acid 1-methyl-2-(2-methylphenyl)-2-oxoethyl ethyl ester 1k. Prepared from **12a** (150 mg, 0.91 mmol) and ethyl chloroformate (203 mg, 1.87 mmol) according to the procedure described for preparation of **1j** to give the ester **1k** (167 mg, 77 % yield): IR (thin film) 1744, 1705, 1456, 1372, 1303, 1260, 1069, 862, 791 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.23 (t, J = 7.2, 3 H), 1.40 (d, J = 7.2, 3 H), 2.38 (s, 3 H), 4.14 (q, J = 7.2, 2 H), 5.63 (q, J = 7.2, 1 H), 7.17-7.19 (m, 2 H), 7.30-7.34 (m, 1 H), 7.56-7.59 (m, 1 H); ^{13}C NMR (75,5 MHz, CDCl_3) δ 200.4, 154.6, 138.5, 135.3, 131.8-125.6, 75.9, 64.4, 20.5, 16.4, 14.1; HRMS (ESI, 70 eV) m/z calcd for $(\text{C}_{13}\text{H}_{16}\text{O}_4 + \text{Na})^+$ 259.0946, found 259.0941.

1-Methyl-2-(2-methylphenyl)-2-oxoethyl acetate 1l. Prepared from **12a** (100 mg, 0.61 mmol) and acetylchloride (57 mg, 0.73 mmol) according to procedure described for preparation of **1i** to give the ester (167 mg, 77 % yield): IR (thin film) 1742, 1704, 1370, 1237, 1037, 735 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.69 (d, J = 7.1, 3 H), 2.38 (s, 3 H), 2.69 (s, 3 H), 6.04 (q, J = 7.1, 1 H) 7.49-7.53 (m, 2 H), 7.61-7.66 (m, 1 H), 7.90-7.92 (m, 1 H); ^{13}C

NMR (75,5 MHz, CDCl_3) δ 200.8, 170.5, 138.4, 135.5, 131.8–125.6, 73.2, 20.7, 20.5, 16.3;
HRMS (ESI, 70 eV) m/z calcd for $(\text{C}_{12}\text{H}_{14}\text{O}_3 + \text{Na})^+$ 229.0835, found 229.0833.

2-(2-Ethylphenyl)-2-oxoethyl methanesulfonate 1m: *N*-Butyllithium (0.84 ml, 1.34 mmol, 1.6 M in hexane) was added dropwise to a cold (-78°C) solution of **19** in dry diethyl ether and stirred for 30 min at -78°C . Then methanesulfonyl chloride (0.1 ml, 1.34 mmol) was added and the mixture was warmed to room temperature and stirred for 1.5 h. The crude product obtained by typical work-up procedure was purified by flash chromatography to give the analytical pure product **1m** (121 mg, 0.5 mmol, 41 %). IR (thin film): 3025, 2972, 1708, 1599, 1571, 1447, 1355, 1220, 1177, 1055, 954 cm^{-1} . ^1H -NMR (300 MHz, CDCl_3) δ : 1.20 (t, $J = 6.0$ Hz, 3H), 2.85 (q, $J = 6.0$ Hz), 3.24 (s, 3H), 5.30 (s, 2H), 7.25–7.47 (m, 4H); ^{13}C -NMR (75 MHz, CDCl_3) δ : 15.8, 28.9, 39.2, 71.2, 125.9, 127.9, 130.9, 132.7, 133.2, 145.2, 194.8; Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_4\text{S}$: C, 54.53; H, 5.82; S, 13.23; Found: C, 54.47; H, 5.86; S, 12.34.

Methyl 2-(2-{2-[(methylsulfonyl)oxy]acetyl}phenyl)acetate 1n. Prepared from **16a** and HMIB according to general procedure I (yield: 66%); mp. $97\text{--}100^\circ\text{C}$; IR (KBr): 3028, 2947, 1737, 1697, 1527, 1436, 1347, 1334, 1234, 1174, 970 cm^{-1} . ^1H -NMR (300 MHz, CDCl_3) δ : 3.23 (s, 3H), 3.68 (s, 3H), 3.96 (s, 2H), 5.41 (s, 2H), 7.29–7.32 (m, 1H), 7.39–7.45 (m, 1H), 7.56–7.57 (m, 1H), 7.63–7.65 (m, 1H); ^{13}C -NMR (75 MHz, CDCl_3) δ : 39.1, 39.3, 52.1, 70.8, 127.7, 128.3, 132.9, 133.0, 134.0, 134.6, 171.6, 194.6; Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_6\text{S}$: C, 50.34; H, 4.93; S, 11.20 Found: C, 50.39; H, 4.99; S, 11.28.

2-[2-(Cyanomethyl)phenyl]-2-oxoethyl methanesulfonate 1o. Prepared from **16b** and HMIB according to general procedure I (yield: 63%); ^1H -NMR (300 MHz, CDCl_3) δ : 3.26 (s, 3H), 4.14 (s, 2H), 5.43 (s, 2H), 7.49–7.54 (m, 1H), 7.65–7.67 (m, 2H), 7.74–7.76 (m, 1H); ^{13}C -NMR (75 MHz, CDCl_3) δ : 23.0, 39.2, 70.5, 117.4, 128.7, 129.3, 131.2, 131.5, 134.2, 193.2; HRMS calcd for $\text{C}_{11}\text{H}_{11}\text{NO}_4\text{S}$: 253.04088 Found: 253.04085.

1-(2-Methylphenyl)-2-phenylethanol 6a. To a stirred suspension of 1.9 g (78.0 mmol) magnesium turnings and a grain of iodine in 15 ml of abs. Et_2O , cooled to -5°C and flushed with nitrogen, were slowly added some drops of a solution of benzylbromide (8.9 g, 52.0 mmol) in 25 ml abs. Et_2O . After starting the reaction, recognisable by warming and becoming

muddy, the rest of the benzylbromide solution was slowly added. To the resulting solution a mixture of 9.4 g (78.0 mmol) 2-methyl-benzaldehyde **4** in 5 ml abs. Et₂O was dropped and then stirred for 1 h. The solution was quenched with 100 ml of 2 N HCl at 0 °C. The layers were separated and the aqueous phase was extracted with Et₂O (3 x 20 ml). The combined organic solutions were washed with sat. NaHSO₃ (aq, 20 ml), 10 % NaOH (aq, 20 ml) brine (aq, 20 ml), dried over MgSO₄ and concentrated. The residue was purified by flash chromatography (petrol ether : ethyl acetate = 100 : 4) to give the alcohol **6a** (8.4 g, 95 % yield). Analytical data are identical to those described in ref. [S1].

1-(2-Methylphenyl)-1-propanone 7a. To suspension of 2.6 g (106.7 mmol) magnesium turnings and a grain of iodine in 15 ml of abs. Et₂O, stirred under an atmosphere of nitrogen, were slowly added some drops of a solution of iodoethane (17.5 g, 112.1 mmol) in 25 ml abs. Et₂O. After starting the reaction, the rest of the iodoethane solution was slowly added and then heated to reflux for 1.5 h and then cooled to r.t. To the resulting solution was dropped a solution of 2-methyl-benzonitril **5** (5 g, 42.7 mmol) in 5 ml abs. Et₂O and the mixture was stirred and heated to reflux for 2 h. The solution was quenched with 100 ml of 2 N HCl at 0 °C. The layers were separated and the aqueous phase were extracted with Et₂O (3 x 20 ml). The combined organic solutions were washed with sat. NaHSO₃ (aq, 20 ml), 10 % NaOH (aq, 20 ml) brine (aq, 20 ml), dried over MgSO₄, and concentrated. The residue was purified by high vacuum distillation to give the ketone **7a** (6.1 g, 97 % yield) as a colorless oil. Analytical data are identical to those described in ref. [S2].

1-(2-Methylphenyl)-1-butanone 7b. Prepared from **5** according to the procedure described above for preparation of **7a**, to give the ketone **7b** (4.9 g, 71 % yield). Analytical data are identical to those described in ref. [S3].

1-(2-Methylphenyl)-2-phenyl-1-ethanone 7c. A solution of **6a** in 10 ml abs. dichloromethane was added to a stirred suspension of PDC (4.5 g, 14.1 mmol) in 40 ml abs. dichloromethane. The reaction was monitored by TLC (petrol ether : ethyl acetate = 10 : 1). The suspension was filtered through a plug of silica (eluent: dichloromethane) and evaporated to give 1.8 g (89 % yield) **7c**. Analytical data are identical to those described in ref. [S1].

Ethyl 3-oxo-3-(2-methylphenyl)-propanoate 9. Sodium (0.5 g, 22.4 mmol) was slowly dissolved in a double-necked flask equipped with a dropping funnel and distillation assembly with a 10 cm column in 15 ml abs. EtOH. Surplus EtOH was removed by distillation under reduced pressure (70 °C, 200 mbar, then 20 mbar). After cooling to r.t., 20 ml of diethyl carbonate followed by **8** (3.0 g, 22.4 mmol) were dropped to the residue. The resulting suspension was stirred for 10 min and then heated to 50 °C and EtOH was removed under reduced pressure (100 mbar). After 3 h the solution was cooled to r.t., then 30 ml half-concentrated acetic acid was added and the layers were separated. The aqueous layer was extracted with Et₂O (3 x 20 ml). The combined organic solutions were washed with water (3 x 10 ml), dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by flash chromatography (petrol ether : ethyl acetate = 100 : 2) to give the β -keto-ester **9** (3.1 g, 67 % yield). Analytical data are identical to those described in ref. [S4].

1-{3-(2-Methylphenyl)-3-oxo-propanoyl}-pyrrolidine 10. A solution of **9** (1.0 g, 4.85 mmol), pyrrolidine (0.69 g, 9.70 mmol) and DMAP (177 mg, 1.45 mmol) in toluol was heated to reflux for 3 h. After cooling to r.t., the solvent was removed in vacuo and the crude residue was purified by flash chromatography (petrol ether : ethyl acetate = 10 : 2) to give the β -keto-amide **10** (960 mg, 86 % yield): IR (thin film) 1727, 1460, 1284, 1123, 1073, 743; HRMS (ESI, 70 eV) m/z calcd for (C₁₄H₁₇NO₂ + Na)⁺ 254.1157, found 254.1152. ¹H NMR (300 MHz, CDCl₃) δ 1.85-1.91 (m, 4 H), 2.40 (s, 3 H), 3.39-3.48 (m, 4 H), 3.94 (s, 2 H), 7.13-7.74 (m, 4 H); ¹³C NMR (75,5 MHz, CDCl₃) δ 196.3, 174.1, 136.4, 135.9, 132.2-125.6, 49.2, 45.9, 24.5, 20.4.

2-(2-Methylphenyl)-2-trimethylsilyloxy-acetonitrile 11. Trimethylsilyl cyanide (2.4 g, 24.0 mmol) was slowly dropped to a stirred and cooled (0 °C) suspension of 2-methylbenzaldehyde **4** (2 g, 16.6 mmol) and 0.4 g Montmorillonite-K 10 in 30 ml Et₂O. After stirring for 3 d the solid was separated by filtration and washed with dichloromethane. The solvent was removed in vacuo to give the nitrile **11** (3.6 g, 99 % yield) as a yellow oil. The analytical data are identical to those described in ref. [S5]

2-Hydroxy-1-(2-methylphenyl)-1-propanone 12a. [S6] Prepared from **11** (1.00 g, 4.6 mmol) and acetaldehyde (0.20 g, 4.6 mmol) according to general procedure III. Purification

by flash chromatography (petrol ether : ethyl acetate = 100 : 5) to give **12a** as a yellow oil (0.45 g, 61 % yield). The analytical data are identical to those described in ref. [S6].

2-Hydroxy-3-methyl-1-(2-methylphenyl)-1-butanone 12b. Prepared from **11** (1.0 g, 4.6 mmol) and 2-methylpropanal (0.3 g, 4.6 mmol) according to general procedure II. Purification by flash chromatography (petrol ether : ethyl acetate = 100 : 5) to give **12b** as a yellow oil (0.46 g, 52 % yield): IR (thin film) 1680, 1456, 1383, 1253, 1123, 1030, 985, 761 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.57 (d, J = 6.8, 3 H), 1.02 (d, J = 6.8, 3 H), 1.97 (dq, J = 2.6, J = 6.8, 1 H), 2.43 (s, 3 H), 3.65 (s, 1 H), 4.82 (d, J = 2.6, 1 H), 7.17-7.23 (m, 2 H), 7.82 (m, 1 H), 7.46-7.48 (m, 1 H); ^{13}C NMR (75,5 MHz, CDCl_3) δ 205.3, 138.9, 134.3, 132.2-125.7, 78.3, 32.1, 20.9, 20.2, 14.6; Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_2$: C, 74.97; H, 8.39. Found: C, 74.15; H, 8.40.

2-Hydroxy-2-methyl-1-(2-methylphenyl)-1-propanone 12c. Prepared from **11** (1.0 g, 4.6 mmol) and acetone (0.26 g, 4.6 mmol) according to general procedure II. Purification by flash chromatography (petrol ether : ethyl acetate = 100 : 3) to give **12c** as a yellow oil (0.42 g, 51 % yield). The analytical data are identical to those described in ref. [S7].

Methyl (2-ethynylphenyl)-acetate 14. To a stirred solution of methyl (2-iodo-phenyl)-acetate **13** [13] (2 g, 7.24 mmol) in 50 ml dioxane were added $\text{PdCl}_2(\text{PPh}_3)_2$ (159 mg, 290 μmol), CuI (138 mg, 725 μmol), diisopropyl amine (1.2 ml, 8.7 mmol) and ethinyl trimethyl silane (1.5 ml, 10.87 mmol). The reaction mixture stirred for 8 h at room temperature and was then filtered through a pad of silica gel using ethyl acetate as solvent, washed twice with water, dried over MgSO_4 and concentrated. Purification by flash chromatography afforded (2-trimethylsilanylethynyl-phenyl)-acetic acid methyl ester. (1.75 g, 7.1 mmol, 98 %). ^1H -NMR (300 MHz, CDCl_3) δ : 0.20 (s, 9H), 3.65 (s, 3H), 3.78 (s, 2H), 7.08-7.21 (m, 3H), 7.39-7.43 (m, 1H); ^{13}C -NMR (75 MHz, CDCl_3) δ : -0.1, 39.7, 51.9, 99.1, 102.8, 123.4, 127.0, 128.7, 129.7, 132.2, 136.5, 172.5. To remove the TMS-group the (2-ethynyl-phenyl)-acetic acid methyl ester (1.68 g, 6.82 mmol) was dissolved in 50 ml dioxane and 200 μl water. Potassium fluoride (396 mg, 6.82 mmol) and 18-crown-6 (1.8 g, 6.82 mmol) were added to this mixture and stirred for 1 h at room temperature. Then diethylether was added and the mixture was washed with water, NaHCO_3 solution and NaCl solution, dried over MgSO_4 and concentrated.

Purification by flash chromatography afforded **14** (1.03 g, 5.9 mmol, 87 %) as nearly colourless oil. The analytical data are identical to those described in ref. [S8].

[2-(2-Methyl-[1,3]dioxolan-2-yl)-phenyl]-acetonitrile 15. 2-(2-Bromomethyl-phenyl)-2-methyl-[1,3]dioxolane was prepared in two steps from 2-methyl acetophenone **8** according to the literature. [30] Potassium cyanide (2.3 g, 35.4 mmol) was dissolved in 150 ml of an ethanol/water mixture (2:1) and heated to reflux. 2-(2-Bromomethyl-phenyl)-2-methyl-[1,3]dioxolane (3.5 g, 13.6 mmol) dissolved in 10 ml ethanol and the solution was added dropwise during 20 min, thereafter the mixture was stirred another 50 min to reflux. It was then poured into 100 ml of an ice/water mixture. The product was extracted with chloroform and the organic layer was washed for 5 min with 5 % sulphuric acid to remove the formed isonitriles, then with NaHCO₃ solution and NaCl solution and dried over MgSO₄. The removal of the solvent afforded **15** (2.65 g, 13 mmol, 96 %) as a colorless oil. The analytical data are identical to those described in ref. [S9].

(2-Acetyl-phenyl)-acetic acid methyl ester 16a. To a stirred solution of (2-ethynyl-phenyl)-acetic acid methyl ester **14** (200 mg, 1.14 mmol) in 600 µl water and 3 ml methanol were added trifluoromethane sulfonic acid (58 µl, 574 µmol) and PPh₃AuCH₃ in catalytic amounts. The mixture was stirred for 18 h at 70°C. Then 20 ml methylene chloride was added, washed with water, dried over MgSO₄ and concentrated. Purification by flash chromatography afforded **16a** (108 mg, 562 µmol, 49 %). The analytical data are identical to those described in ref. [S10].

(2-Acetylphenyl)-acetonitrile 16b. [2-(2-Methyl-[1,3]dioxolan-2-yl)-phenyl]-acetonitrile **15** (1.2 g, 5.16 mmol) was dissolved in THF / 5% HCl-mixture (2:1), heated to reflux and controlled by thin layer chromatography. After finishing (about 1h) the THF was removed and the product was extracted with diethylether. The organic layer was washed with NaHCO₃ solution and NaCl-solution and concentrated. Purification by flash chromatography afforded (2-Acetyl-phenyl)-acetonitrile **16b** (780 mg, 4.9 mmol, 95%). The analytical data are identical to those described in ref. [S9].

2-[Dimethyl-(1,1,2-trimethyl-propyl)-silanyloxy]-N-methoxy-N-methyl-acetamide 18. To a stirred solution of ethyl glucolate (10 g, 84.65 mmol) and imidazole (11.5 g, 169.3 mmol) in

60 ml dimethylformamide was added (16.65 g, 93.12 mmol) hexyl dimethyl silylchloride at room temperature and stirred over night. 100 ml water were added to the mixture and the product was extracted with petrol ether. The organic layer was washed with water, dried over MgSO_4 , to give [Dimethyl-(1,1,2-trimethyl-propyl)-silanyloxy]-acetic acid ethyl ester as a colorless oil (20.6 g, 83.8 mmol, 99 %). IR (thin film): 2960, 1698, 1465, 1251, 1163, 1068, 610 cm^{-1} . $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 0.00 (s, 6H), 0.74 (s, 6H), 0.76 (d, $J = 6.8\text{ Hz}$, 6H), 1.14 (t, $J = 7.1\text{ Hz}$, 3H), 1.51 (m, 1H), 4.06 (q, $J = 7.2\text{ Hz}$, 2H), 4.08 (s, 2H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ : -3.5, 14.1, 18.4, 20.2, 25.2, 34.1, 60.7, 61.6, 171.8. A solution N,O-dimethyl hydroxylamine (5.9 g, 60.87 mmol) in dry THF was cooled to 0°C and AlMe_3 (30.4 ml, 2M in Hexan, 60.87 mmol) was added dropwise. The mixture stirred for 30 min at room temperature and was then canulated into an ice-cold mixture of [dimethyl-(1,1,2-trimethyl-propyl)-silanyloxy]-acetic acid ethyl ester in dry THF. The reaction mixture was stirred 10 min at 0°C , warmed to room temperature and stirred another 3 h. The mixture was treated carefully under cooling in an icebath with 5 M HCl. Water and diethyl ether were added and the organic layer was separated, washed with NaHCO_3 -solution and NaCl-solution and dried over MgSO_4 . The removal of the solvent gave **18** as colorless oil (8.04 g, 30.75 mmol, 76 %). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 0.00 (s, 6H), 0.73 (s, 6H), 0.75 (d, $J = 6.8\text{ Hz}$, 6H), 1.50 (m, 1H), 3.02 (s, 3H), 3.25 (s, 3H), 4.26 (s, 2H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ : -3.4, 18.5, 20.3, 25.4, 32.3, 34.2, 61.3, 61.6.

1-(2-Ethylphenyl)-2-hydroxy-ethanone 19. The highly reactive magnesium was prepared according to the procedure of *Rieke* [11]. To the freshly prepared suspension of highly reactive magnesium in THF (prepared from 1.4 g, 35.8 mmol potassium and 1.87 g, 19.7 mmol magnesium chloride) was added 2-bromo ethyl benzene (3.3 g, 17.8 mmol) at 0°C and stirred for 2 h to complete the formation of the *Grignard* reagent. The *Weinreb* amide **18** was dissolved in dry THF, cooled to 0°C and the prepared *Grignard* solution was canulated into the mixture, stirred 30 min at 0°C and than another 3h at room temperature. The reaction mixture was treated with 5 M HCl in diethylether, the organic layer was separated and washed with NaHCO_3 solution and NaCl solution, dried over MgSO_4 and concentrated. Purification by flash chromatography afforded the analytical pure product (4.15 g, 13.55 mmol, 86 %) as colourless oil. IR (thin film): 2961, 1709, 1464, 1251, 1158, 1126, 972, 834, 779, 754 cm^{-1} . $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 0.14 (s, 6H), 0.85 (s, 6H), 0.97 (d, $J = 7.2\text{ Hz}$, 6H), 1.22 (t, $J = 7.5\text{ Hz}$, 3H), 1.62 (heptett, $J = 7.2\text{ Hz}$, 1H), 2.80 (q, $J = 7.5\text{ Hz}$, 2H), 4.69 (s, 2H), 7.19-7.30

(m, 2H), 7.37-7.46 (m, 2H); ^{13}C -NMR (75 MHz, CDCl_3) δ : -3.4, 16.1, 18.4, 20.2, 25.3, 26.6, 34.0, 68.8, 125.3, 127.7, 130.0, 131.1, 136.1, 143.8, 202.9; Anal. Calcd for $\text{C}_{18}\text{H}_{30}\text{O}_2\text{Si}$: C, 70.53; H, 9.87 Found: C, 70.04; H, 9.88. To remove the hexyl dimethylsilyl group the product of the procedure above (1 g, 3.26 mmol) was solved in acetonitrile and treated with 0.5 ml HF (40 %) and monitored by thin layer chromatography. After complete reaction some solid KHCO_3 was added. The mixture was filtrated, dried over MgSO_4 and concentrated. Purification by flash chromatography afforded **19** as analytical pure product (480 mg, 2.92 mmol, 89 %, nearly colorless oil). IR (thin film): 3445, 1969, 1699, 1692, 1687, 1451, 1294, 1092 cm^{-1} . ^1H -NMR (300MHz, CDCl_3) δ : 1.12 (t, $J = 7.5$ Hz, 3H), 2.81 (q, $J = 7.5$ Hz, 2H), 3.46 (board s, 1H), 4.63 (s, 2H), 7.15-7.17 (m, 2H), 7.19-7.21 (m, 1H), 7.22-7.23 (m, 1H); ^{13}C -NMR (75 MHz, CDCl_3) δ : 15.7, 27.2, 66.7, 125.9, 128.2, 130.8, 132.7, 133.1, 145.5, 201.4; Anal Calcd for $\text{C}_{10}\text{H}_{12}\text{O}_2$: C, 73.15; H, 7.37 Found: C, 72.62; H, 7.39.

Irradiation of 2-Mesyloxy-1-(2-methylphenyl)-1-ethanone 1a. Conversion of **1a** (95 mg, 0.42 mmol) in 100 ml dichloromethane and in the presence of NMI (68 mg, 0.83 mmol) according to general procedure III led after FC (petrol ether : ethyl acetate = 20 : 1) to indan-1-one **20a** (23 mg, 42 % yield). The conversion of **1a** (99 mg, 0.43 mmol) in 100 ml MeOH and in the presence of NMI (71 mg, 0.87 mmol) according to general procedere III led after FC (petrol ether : ethyl acetate = 100 : 3) to a mixture of 56 mg indan-1-one **20a** (39 % yield) and 1-[2-(methoxymethyl)phenyl]-1-ethanone **22a** (47 % yield). The accurate ratio of both products was determined from ^1H NMR spectrum.

The analytical data of **20a** [S11] and **22a** [S12] are identical to those described in the literature.

2-Methyl-indan-1-one 20b. Conversion of **1b** (300 mg, 1.24 mmol) in 300 ml dichloromethane and in the presence of NMI (203 mg, 2.48 mmol) according to the general procedure III led after FC (petrol ether : ethyl acetate = 10 : 1) afforded **20b** (132 mg, 73 %).

Conversion of **1b** (92 mg, 0.38 mmol) in 100 ml MeOH and in the precense of NMI (62 mg, 0.76 mmol) according to general procedure III afforded **20b** (39 mg, 71 %).

Conversion of **1i** (70 mg, 0.23 mmol) in 100 ml MeOH and in the presence of NMI (38 mg, 0.46 mmol) according to general procedere III afforded **20b** (21 mg, 62 %).

Conversion of **1j** (85 mg, 0.32 mmol) in 100 ml MeOH according to general procedure III afforded **20b** (19 mg, 40 %).

Conversion of **1k** (88 mg, 0.37 mmol) in 100 ml MeOH according to general procedure III afforded **20b** (29 mg, 54 %)

The analytical data are identical to those described in ref. [S13].

Irradiation of 2-mesyloxy-1-(2-methylphenyl)-1-butanone 1c. Conversion of **1c** (96 mg, 0.38 mmol) in 100 ml dichloromethane and in the presence of NMI (62 mg, 0.76 mmol) according to general procedure III led after FC (petrol ether : ethyl acetate = 20 : 1) to 2-ethyl-indan-1-one **20c** (21 mg, 35 %) and indan-1-one **20a** (10 mg, 20 % yield). Conversion of **1c** (98 mg, 0.39 mmol) in 100 ml MeOH according to general procedure III led to 2-ethyl-indan-1-one **20c** (43 mg, 69 %) and indan-1-one **20a** (1 mg, 3 % yield). The analytical data of **20a** [S11] and **20c** [S14] are identical to those described in the literature.

Irradiation of 3-methyl-1-(2-methylphenyl)-2-mesyloxy-1-butanone 1g. Conversion of **1g** (224 mg, 0.83 mmol) in 300 ml dichloromethane and in the presence of NMI (136 mg, 1.66 mmol) according to general procedure III led after FC (petrol ether : ethyl acetate = 20 : 3) to 2-isopropyl-indan-1-one **20g** (6 mg, 5 %) and indan-1-one **20a** (35 mg, 32 % yield). Conversion of **1c** (94 mg, 0.35 mmol) in 100 ml MeOH and in the presence of NMI (57 mg, 0.70 mmol) according to general procedure III led after FC (petrol ether : ethyl acetate = 20 : 3) to 2-isopropyl-indan-1-one **20g** (28 mg, 46 %) and indan-1-one **20a** (13 mg, 27 % yield). The analytical data of **20a** [S11] and **20g** [S14] are identical to those described in the literature.

2-Phenyl-indan-1-one 20d. Conversion of **1d** (85 mg, 0.28 mmol) in 100 ml dichloromethane and in the presence of NMI (46 mg, 0.56 mmol) according to general procedure III led after FC (petrol ether : ethyl acetate = 20 : 3) to the indanone **20d** (11 mg, 20 %). Conversion of **1d** (28 mg, 0.09 mmol) in 100 ml MeOH according to general procedure III led the indanone **20d** (10 mg, 52 %). The analytical data are identical to those described in the ref. [S14].

Irradiation of Ethyl 2-mesyloxy-3-(2-methylphenyl)-3-oxopropanoate 1e. Conversion of **1e** (80 mg, 0.27 mmol) in 100 ml dichloromethane and in the presence of NMI (44 mg, 0.53 mmol) according to general procedure III led after FC (petrol ether : ethyl acetate = 20 : 1) to ethyl indane-1-one-2-carboxylate **20e** (15 mg, 30 % yield) and 2-[1(3*H*)-isobenzofuranylidene]-acetic acid ethyl ester **21a** (20 mg, 67 % yield). Conversion of **1e** (103 mg, 0.34 mmol) in 100 ml *tert.*-butanol according to general procedure III led only to the indanone **20e** (58 mg, 82 % yield). The analytical data of **21a** [S19] and **20e** [S15] are identical to those described in the literature.

Irradiation of 1-{2-Mesyloxy-3-(2-methylphenyl)-3-oxopropanoyl}-pyrrolidine 1f.

Conversion of **1f** (405 mg, 1.25 mmol) in 300 ml dichloromethane and in the presence of NMI (204 mg, 2.49 mmol) according to general procedure III led after FC (DCM : MeOH = 20 : 1) to 2-(1-pyrrolidinylcarbonyl)-indan-1-one **20f** (130 mg, 46 % yield) and 1-[2-[1(3*H*)-isobenzofuranylidene]acetyl]-pyrrolidine **21b** (122 mg, 43 % yield). Conversion of **1f** (102 mg, 0.31 mmol) in 100 ml *tert.*-butanol according to general procedure III led to **20f** (50 mg, 70 % yield) and **21b** (15 mg, 21 % yield). **20f**: ^1H NMR (300 MHz, CDCl_3) δ 1.80-2.02 (m, 4 H), 3.44-3.53 (m, 3 H), 3.67-3.73 (m, 1 H), 3.85-3.89 (m, 1 H), 4.05-4.13 (m, 1 H), 7.28-7.52 (m, 3 H), 7.63-7.66 (m, 1 H); ^{13}C NMR (75,5 MHz, CDCl_3) δ 202.2, 166.6, 154.8, 139.4-124.3, 52.7, 47.2, 46.3, 30.2, 26.0, 24.5; HRMS (EI, 70 eV) m/z calcd for $(\text{C}_{14}\text{H}_{15}\text{NO}_2)^+$ 229.1103, found 229.1103. LRMS (EI, 70 eV): 229 (13), 159 (100), 131 (37), 77 (47). **21b**: ^1H NMR (300 MHz, CDCl_3) δ 1.77-1.91 (m, 4 H), 3.46-3.51 (m, 4 H), 5.46 (s, 2 H), 5.55 (s, 1 H), 7.23-7.36 (m, 3 H), 7.49-7.52 (m, 1 H); ^{13}C NMR (75,5 MHz, CDCl_3) δ 164.8, 164.2, 140.8, 133.5, 130.5-120.8, 87.5, 75.8, 46.9, 45.3, 26.1, 24.4; HRMS (EI, 70 eV) m/z calcd for $(\text{C}_{14}\text{H}_{15}\text{NO}_2)^+$ 229.1103, found 229.1103. LRMS (EI, 70 eV): 229 (10), 159 (8), 131 (13), 118 (12), 91 (21), 77 (47).

3-Methyl-indan-1-one 20h. Obtained from **1m** according to general procedure III. For yields and conditions see table 1. The analytical data are identical to those described in ref. [S16].

Methyl indan-3-one-1-carboxylate 20i. Obtained from **1n** according to general procedure III. For yields and conditions see table 1. The analytical data are identical to those described in ref. [S17].

3-Oxo-indan-1-carbonitrile 20j. Obtained from **1o** according to general procedure III. For yields and conditions see table 1. The analytical data are identical to those described in ref. [S18].

1-[2-(1-Methoxy-ethyl)-phenyl]-ethanone 22b. Obtained from **1m** according to general procedure III. For yields and conditions see table 1. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 1.36 (d, $J = 6$ Hz, 3H), 2.53 (s, 2H), 3.13 (s, 3H), 4.85 (q, $J = 6$ Hz, 1H), 7.27-7.68 (m, 4H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ : 23.6, 29.6, 29.8, 56.6, 65.8, 126.5, 126.8, 127.8, 128.7, 131.1, 132.0, 205.9; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2$: 178.09938, Found: 178.09938.

1-[2-(1-tert-Butoxy-ethyl)-phenyl]-ethanone 22c. Obtained from **1m** according to general procedure III. For yields and conditions see table 1. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 1.10 (s, 9H), 1.33 (d, $J = 6.4$, 3H), 2.60 (s, 3H), 5.39 (q, $J = 6.4$ Hz, 1H), 7.24-7.97 (m, 4H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ : 26.4, 28.3, 29.8, 66.1, 74.1, 126.1, 127.6, 128.7, 131.8, 134.9, 148.9, 202.0. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{20}\text{O}_2$: 220.14633. Found: 220.14633.

Cartesian coordinates and energies of calculated structures

o-Methylacetophenone 23

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	1	0	0.541576	2.561793	-0.871569
2	8	0	2.274169	0.978224	-0.002146
3	6	0	-0.088716	2.365634	0.000838
4	6	0	-2.585200	-0.494249	-0.000101
5	6	0	-1.775146	-1.626295	-0.000575
6	6	0	-0.395196	-1.468367	-0.000509
7	6	0	0.205964	-0.198789	-0.000106
8	6	0	-0.617655	0.956487	0.000308
9	6	0	-2.004607	0.770757	0.000392
10	6	0	1.697533	-0.098641	-0.000321
11	6	0	2.519851	-1.377494	0.001678
12	1	0	-3.667965	-0.592796	-0.000065
13	1	0	-2.211667	-2.621363	-0.000929
14	1	0	0.229931	-2.355597	-0.000829
15	1	0	-2.645130	1.649959	0.000823
16	1	0	2.309541	-1.990587	0.885685
17	1	0	2.312236	-1.990627	-0.883021
18	1	0	3.574829	-1.098231	0.003049
19	1	0	-0.921404	3.076961	0.002413
20	1	0	0.543735	2.560442	0.871985

Method B3PW91/6-311++G**//B3PW91/6-31G*
 Multiplicity 1
 Electronic energy -424.154256 a.u.
 Zero-point vibrational energy 104.74921 kcal/mol
 Number of imaginary frequencies 0
 Point group C₁

o-Methylacetophenone (Triplet) 24

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	1	0	-0.639116	2.498465	0.883417
2	8	0	-2.323602	0.943734	0.000506
3	6	0	-0.008024	2.334540	-0.000086
4	6	0	2.619092	-0.427989	-0.000071
5	6	0	1.831209	-1.581385	0.000151
6	6	0	0.450312	-1.484883	0.000251
7	6	0	-0.199413	-0.218614	0.000041
8	6	0	0.610980	0.964923	-0.000074
9	6	0	1.993072	0.823110	-0.000150
10	6	0	-1.617214	-0.171275	-0.000159
11	6	0	-2.526501	-1.382301	-0.000376
12	1	0	3.703158	-0.497046	-0.000141
13	1	0	2.297372	-2.563799	0.000322
14	1	0	-0.145275	-2.392979	0.000557
15	1	0	2.604176	1.723749	-0.000278
16	1	0	-2.349794	-1.996155	-0.892390
17	1	0	-2.351721	-1.995282	0.892638
18	1	0	-3.575204	-1.073758	-0.001651
19	1	0	0.763729	3.111929	-0.000375
20	1	0	-0.639576	2.498247	-0.883300

Method UB3PW91/6-311++G**//UB3PW91/6-31G*

Multiplicity 3

Electronic energy -424.0474018 a.u.

Zero-point vibrational energy 102.28977 kcal/mol

Number of imaginary frequencies 0

Point group C_s

Transition state of hydrogen transfer 25

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	2.265514	0.919162	-0.079436
2	1	0	1.403756	1.803142	-0.084012
3	6	0	0.200944	2.235735	0.053456
4	6	0	-2.654773	-0.271531	-0.021111
5	6	0	-1.946571	-1.478958	0.000025
6	6	0	-0.562811	-1.487444	0.015674
7	6	0	0.174881	-0.272916	0.016873
8	6	0	-0.558709	0.957606	0.009695
9	6	0	-1.948916	0.935351	-0.020105
10	6	0	1.592166	-0.238878	0.002157
11	6	0	2.491796	-1.436934	0.020003
12	1	0	-3.740734	-0.267388	-0.041502
13	1	0	-2.485545	-2.423351	-0.007463
14	1	0	-0.033712	-2.435933	0.006993
15	1	0	-2.491826	1.878302	-0.031354
16	1	0	2.091806	-2.223671	0.668235
17	1	0	2.629475	-1.863109	-0.984442
18	1	0	3.478141	-1.151090	0.397225
19	1	0	0.042251	2.935978	-0.771875
20	1	0	0.254230	2.741633	1.023680

Method UB3PW91/6-311++G**//UB3PW91/6-31G*
 Multiplicity 3
 Electronic energy -424.0392636 a.u.
 Zero-point vibrational energy 98.92572 kcal/mol
 Number of imaginary frequencies 1
 Value of imaginary frequency -1435.2453 cm⁻¹
 Point group C₁

Z-1,4-Diradical **Z-26**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.867549	-1.544580	-0.066601
2	6	0	-2.644455	-0.395832	-0.102623
3	6	0	-0.469757	-1.451570	-0.011966
4	6	0	0.192158	-0.214868	0.029408
5	6	0	-0.619998	0.984376	0.084904
6	6	0	-2.014450	0.851900	-0.025478
7	6	0	1.628723	-0.171972	-0.014186
8	6	0	-0.067820	2.279089	0.328849
9	8	0	2.301319	0.897974	-0.525792
10	1	0	-2.333925	-2.525800	-0.106482
11	1	0	-3.726883	-0.456776	-0.169617
12	1	0	0.118183	-2.364088	-0.051291
13	1	0	-2.618185	1.756484	0.007611
14	6	0	2.525923	-1.315618	0.302576
15	1	0	0.911874	2.418369	0.773020
16	1	0	-0.715513	3.149764	0.290111
17	1	0	1.652585	1.549797	-0.843427
18	1	0	3.500213	-0.933262	0.626339
19	1	0	2.114122	-1.940508	1.101129
20	1	0	2.710327	-1.963311	-0.570355

Method UB3PW91/6-311++G**//UB3PW91/6-31G*
 Multiplicity 3
 Electronic energy -424.059172 a.u.
 Zero-point vibrational energy 102.33472 kcal/mol
 Number of imaginary frequencies 0
 Point group C₁

E-1,4-Diradical E-26

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.915609	-1.474149	0.152250
2	6	0	-2.657493	-0.299118	0.158059
3	6	0	-0.517649	-1.419451	0.054944
4	6	0	0.165842	-0.206618	-0.052163
5	6	0	-0.599882	1.012979	-0.117788
6	6	0	-2.001871	0.923438	0.022150
7	6	0	1.620285	-0.204557	-0.113015
8	6	0	-0.011002	2.274070	-0.388976
9	8	0	2.162137	-1.381118	-0.566862
10	1	0	-2.410115	-2.438800	0.233824
11	1	0	-3.740336	-0.327999	0.246521
12	1	0	0.059641	-2.338263	0.078999
13	1	0	-2.581021	1.843423	-0.022634
14	6	0	2.514766	0.646997	0.727075
15	1	0	1.028794	2.376645	-0.673101
16	1	0	-0.632420	3.162879	-0.440579
17	1	0	3.119574	-1.353007	-0.428331
18	1	0	2.832835	0.105157	1.635464
19	1	0	3.429208	0.940636	0.188684
20	1	0	2.012426	1.556730	1.060842

Method UB3PW91/6-311++G**//UB3PW91/6-31G*
 Multiplicity 3
 Electronic energy -424.0559236 a.u.
 Zero-point vibrational energy 102.27000 kcal/mol
 Number of imaginary frequencies 0
 Point group C₁

Transition state of bond rotation 27

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

1	6	0	1.797579	-1.573540	-0.065765
2	6	0	2.629813	-0.450488	0.010870
3	6	0	0.410571	-1.402277	-0.080448
4	6	0	-0.172782	-0.138635	-0.017644
5	6	0	0.670767	1.020119	0.055832
6	6	0	2.079976	0.816923	0.069962
7	6	0	-1.649507	-0.002924	-0.021667
8	6	0	0.139141	2.319874	0.119497
9	8	0	-2.195356	-0.051620	-1.287732
10	6	0	-2.480112	-0.516694	1.109398
11	1	0	2.224382	-2.571782	-0.116298
12	1	0	3.710134	-0.573318	0.023534
13	1	0	-0.234922	-2.275438	-0.146696
14	1	0	2.727870	1.688843	0.128251
15	1	0	0.792606	3.185188	0.173412
16	1	0	-0.932308	2.485286	0.106860
17	1	0	-3.485828	-0.069947	1.105940
18	1	0	-2.616164	-1.613559	1.079327
19	1	0	-2.016187	-0.272389	2.069832
20	1	0	-3.159410	-0.004084	-1.202512

Method	UB3PW91/6-311++G**//UB3PW91/6-31G*
Multiplicity	3
Electronic energy	-424.0508063 a.u.
Zero-point vibrational energy	101.99803 kcal/mol
Number of imaginary frequencies	1
Value of imaginary frequency	-64.3143 cm ⁻¹
Point group	C ₁

E-Xylenol E-28

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.884483	-1.488054	-0.044483
2	6	0	2.602881	-0.275360	0.262061
3	6	0	0.544072	-1.457605	-0.237622
4	6	0	-0.209514	-0.219727	-0.128713
5	6	0	0.559759	1.044912	-0.095823
6	6	0	1.969387	0.920317	0.255952
7	6	0	-1.569094	-0.289798	0.027763
8	6	0	0.076671	2.268676	-0.434049
9	8	0	-2.155621	-1.516679	-0.096003
10	1	0	2.423512	-2.430704	-0.090391
11	1	0	3.668052	-0.327772	0.475111
12	1	0	-0.007695	-2.374220	-0.415476
13	1	0	2.521262	1.840338	0.436223
14	6	0	-2.496908	0.822622	0.392239
15	1	0	-0.904495	2.422826	-0.866686
16	1	0	0.710358	3.147734	-0.349359
17	1	0	-3.096585	-1.436656	0.110242
18	1	0	-3.266622	0.452566	1.085612
19	1	0	-1.956352	1.640158	0.878526
20	1	0	-3.016887	1.243271	-0.479730

Method B3PW91/6-311++G**//B3PW91/6-31G*

Multiplicity 1

Electronic energy -424.0935826 a.u.

Zero-point vibrational energy 104.19660 kcal/mol

Number of imaginary frequencies 0

Point group C₁

Z-Xylenol Z-28

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

1	6	0	1.779739	-1.599694	-0.071110
2	6	0	2.561108	-0.435437	0.253304
3	6	0	0.443713	-1.481427	-0.273357
4	6	0	-0.228998	-0.202661	-0.182440
5	6	0	0.612190	1.014357	-0.109449
6	6	0	2.002726	0.799494	0.257640
7	6	0	-1.591060	-0.152176	0.026966
8	6	0	0.180781	2.285463	-0.370374
9	8	0	-2.237793	0.982346	0.335129
10	1	0	2.260550	-2.572387	-0.122435
11	1	0	3.619471	-0.552399	0.474551
12	1	0	-0.146538	-2.373164	-0.460094
13	1	0	2.609112	1.679920	0.458354
14	6	0	-2.530669	-1.316702	0.040882
15	1	0	-0.748791	2.509922	-0.886096
16	1	0	0.862941	3.121532	-0.243355
17	1	0	-1.564014	1.680702	0.506124
18	1	0	-3.500332	-0.996227	-0.352254
19	1	0	-2.172572	-2.156196	-0.556136
20	1	0	-2.694658	-1.667771	1.067931

Method B3PW91/6-311++G**//B3PW91/6-31G*

Multiplicity 1

Electronic energy -424.0999791 a.u.

Zero-point vibrational energy 104.29363 kcal/mol

Number of imaginary frequencies 0

Point group C₁

Transition state of $[2\pi, 2\pi]$ cycloaddition 29

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.510803	-0.206434	0.006603
2	6	0	0.560555	1.831443	-0.704057
3	6	0	-2.097212	-1.263850	0.107425
4	6	0	-2.617456	0.047608	0.240838
5	6	0	-1.819627	1.168084	0.098911
6	6	0	-0.456713	0.969679	-0.222956
7	6	0	0.084408	-0.334065	-0.110843
8	6	0	-0.741564	-1.474929	-0.075848
9	1	0	-2.768262	-2.112782	0.209800
10	1	0	-3.682039	0.169707	0.427908
11	1	0	-2.247268	2.167283	0.142869
12	1	0	-0.330636	-2.482749	-0.082103
13	1	0	0.579691	2.899890	-0.481885
14	1	0	1.084132	1.546176	-1.609236
15	8	0	2.317176	-1.094638	-0.631306
16	6	0	2.212772	0.362082	1.204376
17	1	0	1.816678	-1.490068	-1.362233
18	1	0	2.501227	-0.469822	1.867114
19	1	0	1.561970	1.045877	1.748499
20	1	0	3.131297	0.885885	0.923031

Method B3PW91/6-311++G**//B3PW91/6-31G*
 Multiplicity 1
 Electronic energy -424.0608475 a.u.
 Zero-point vibrational energy 103.57256 kcal/mol
 Number of imaginary frequencies 1
 Value of imaginary frequency -407.0193 cm^{-1}
 Point group C_1

Benzocyclobuten 30

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.260877	-1.116149	0.002633
2	6	0	-2.683230	0.219105	0.053384
3	6	0	-0.902913	-1.456192	-0.049196
4	6	0	-0.016056	-0.391147	-0.050715
5	6	0	-0.431736	0.935156	-0.017666
6	6	0	-1.772658	1.284167	0.045665
7	6	0	1.461378	-0.025443	-0.044311
8	6	0	0.977643	1.488567	-0.077555
9	8	0	2.119086	-0.477735	-1.211419
10	6	0	2.232929	-0.417246	1.209796
11	1	0	-3.009926	-1.904557	0.004336
12	1	0	-3.749399	0.430276	0.094936
13	1	0	-0.585451	-2.495008	-0.089455
14	1	0	-2.118777	2.314551	0.078123
15	1	0	1.237143	1.982616	-1.020329
16	1	0	1.300147	2.116877	0.762288
17	1	0	3.044363	-0.196756	-1.149749
18	1	0	2.364404	-1.503911	1.248936
19	1	0	3.227761	0.049788	1.213294
20	1	0	1.710170	-0.096898	2.116769

Method B3PW91/6-311++G**//B3PW91/6-31G*
 Multiplicity 1
 Electronic energy -424.1143012 a.u.
 Zero-point vibrational energy 105.06830 kcal/mol
 Number of imaginary frequencies 0
 Point group C₁

Transition state of bond rotation 31

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.798784	-1.573421	-0.060726
2	6	0	2.630270	-0.449515	0.014507
3	6	0	0.411878	-1.403140	-0.076945
4	6	0	-0.173440	-0.139600	-0.018602
5	6	0	0.669819	1.020283	0.051621
6	6	0	2.079460	0.817423	0.069582
7	6	0	-1.649754	-0.007233	-0.024302
8	6	0	0.140583	2.321128	0.106513
9	8	0	-2.197554	-0.073240	-1.288762
10	6	0	-2.480471	-0.496726	1.117147
11	1	0	2.226288	-2.571521	-0.108114
12	1	0	3.710643	-0.571576	0.029260
13	1	0	-0.233042	-2.276888	-0.140748
14	1	0	2.726712	1.689884	0.126844
15	1	0	0.796690	3.184573	0.159215
16	1	0	-0.929482	2.492303	0.086411
17	1	0	-3.484547	-0.046358	1.107653
18	1	0	-2.620624	-1.593458	1.107428
19	1	0	-2.013790	-0.236822	2.072112
20	1	0	-3.161191	-0.019419	-1.202739

Method UB3PW91/6-311++G**//UB3PW91/6-31G*
 Multiplicity 1
 Electronic energy -424.05089 a.u.
 Zero-point vibrational energy 101.88604 kcal/mol
 Number of imaginary frequencies 1
 Value of imaginary frequency -124.1993 cm⁻¹
 Point group C₁

Transition state of sigmatrope 1,5-hydrogen shift 32

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	2.213095	0.922236	-0.177006
2	6	0	0.081712	2.271152	0.205938
3	6	0	-1.856539	-1.524742	0.083136
4	6	0	-2.560337	-0.329919	-0.236916
5	6	0	-0.507977	-1.469055	0.301174
6	6	0	0.194275	-0.224223	0.262352
7	6	0	-0.550002	1.015704	0.113421
8	6	0	-1.928567	0.884687	-0.249648
9	6	0	1.582279	-0.195071	0.013185
10	1	0	-2.385910	-2.472258	0.124288
11	1	0	-3.625340	-0.382627	-0.452101
12	1	0	0.046026	-2.385298	0.486746
13	1	0	-2.488551	1.793051	-0.459375
14	6	0	2.411247	-1.430456	-0.193842
15	1	0	0.737740	2.464112	1.057646
16	1	0	-0.493393	3.143400	-0.099695
17	1	0	3.462078	-1.148307	-0.280919
18	1	0	2.299848	-2.123908	0.646398
19	1	0	2.111659	-1.963871	-1.103580
20	1	0	1.434541	1.709351	-0.296154

Method B3PW91/6-311++G**//B3PW91/6-31G*

Multiplicity 1

Electronic energy -424.092507 a.u.

Zero-point vibrational energy 101.76886 kcal/mol

Number of imaginary frequencies 1

Value of imaginary frequency -1021.1000 cm⁻¹

Point group C₁

2-Methyl-2'-mesyloxyacetophenone 33 (Triplet)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	1	0	-2.935749	-2.311856	1.237448
2	8	0	-0.904435	-2.419761	-0.061838
3	6	0	-3.477534	-1.836996	0.408951
4	6	0	-3.554376	1.957183	0.084132
5	6	0	-2.230170	2.251447	-0.244780
6	6	0	-1.297778	1.234275	-0.366024
7	6	0	-1.670367	-0.121559	-0.175607
8	6	0	-3.021255	-0.423519	0.178280
9	6	0	-3.926109	0.627753	0.294127
10	6	0	-0.689189	-1.149151	-0.351872
11	6	0	0.722548	-0.914776	-0.787848
12	1	0	-4.289019	2.751234	0.183823
13	1	0	-1.917164	3.280933	-0.398267
14	1	0	-0.266490	1.489900	-0.588828
15	1	0	-4.956494	0.396487	0.556103
16	1	0	0.742128	-0.128435	-1.549286
17	8	0	1.510112	-0.488402	0.365038
18	1	0	1.165302	-1.828094	-1.193490
19	1	0	-4.543883	-1.867193	0.656859
20	1	0	-3.328436	-2.464049	-0.479679
21	16	0	2.939848	0.217145	-0.016298
22	8	0	2.669717	1.471976	-0.711410
23	8	0	3.819700	-0.771399	-0.626543
24	6	0	3.452674	0.546398	1.659436
25	1	0	3.537923	-0.400897	2.193470
26	1	0	2.718150	1.201243	2.129945
27	1	0	4.424748	1.040770	1.597940

Method UB3PW91/6-311++G**//UB3PW91/6-31G*

Multiplicity 3

Electronic energy -1087.100361 a.u.

Zero-point vibrational energy 129.89531 kcal/mol

Number of imaginary frequencies 0

Point group C₁

Transition state of hydrogen transfer 34

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	-1.002189	-2.424573	-0.018942
2	6	0	-3.352401	-1.836501	0.370295
3	6	0	-3.551368	1.947708	0.117525
4	6	0	-2.242571	2.257503	-0.266518
5	6	0	-1.295381	1.258234	-0.419539
6	6	0	-1.639768	-0.098339	-0.202061
7	6	0	-2.978138	-0.409719	0.179563
8	6	0	-3.905412	0.616623	0.344751
9	6	0	-0.692804	-1.158767	-0.331685
10	6	0	0.715354	-0.978629	-0.766702
11	1	0	-4.289173	2.734639	0.245654
12	1	0	-1.955614	3.292684	-0.432211
13	1	0	-0.274473	1.524659	-0.677553
14	1	0	-4.922401	0.369422	0.641166
15	1	0	0.785902	-0.227500	-1.559827
16	8	0	1.510402	-0.519439	0.380400
17	1	0	1.135004	-1.924878	-1.115225
18	1	0	-3.756803	-2.115262	1.347505
19	1	0	-3.890422	-2.314956	-0.455223
20	16	0	2.905509	0.227545	-0.018998
21	8	0	2.592460	1.475656	-0.710760
22	8	0	3.814553	-0.727902	-0.640357
23	6	0	3.432186	0.576609	1.649045
24	1	0	3.553672	-0.366398	2.183660
25	1	0	2.684973	1.209516	2.129453
26	1	0	4.387791	1.100114	1.573426
27	1	0	-2.206596	-2.401031	0.292358

Method UB3PW91/6-311++G**//UB3PW91/6-31G*
 Multiplicity 3
 Electronic energy -1087.093918 a.u.
 Zero-point vibrational energy 126.68368 kcal/mol
 Number of imaginary frequencies 1
 Value of imaginary frequency -1392.4850 cm⁻¹
 Point group C₁

1,4-Diradical **35a** (without hydrogen bond)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	-0.827914	-2.338099	0.570126
2	6	0	-3.589519	-1.796107	-0.170924
3	6	0	-3.634295	1.925428	0.121596
4	6	0	-2.285281	2.238614	0.003203
5	6	0	-1.331262	1.214379	-0.074673
6	6	0	-1.701499	-0.132675	-0.069424
7	6	0	-3.104587	-0.466545	-0.020956
8	6	0	-4.030849	0.589428	0.112721
9	6	0	-0.674211	-1.160191	-0.094256
10	6	0	0.676942	-0.970343	-0.644182
11	1	0	-4.379168	2.711912	0.205603
12	1	0	-1.957561	3.274482	-0.006588
13	1	0	-0.277620	1.476601	-0.108497
14	1	0	-5.088788	0.340840	0.158549
15	1	0	0.664487	-0.262058	-1.476829
16	8	0	1.561654	-0.429093	0.417653
17	1	0	1.107524	-1.922499	-0.964603
18	1	0	-4.652803	-1.992031	-0.073971
19	1	0	-2.973726	-2.603469	-0.551057
20	16	0	2.937199	0.247732	-0.130452
21	8	0	2.631634	1.561169	-0.691241
22	8	0	3.671102	-0.723067	-0.934762
23	6	0	3.725968	0.444594	1.458494
24	1	0	3.870628	-0.540636	1.903513
25	1	0	3.097006	1.073866	2.089692
26	1	0	4.687852	0.928386	1.274630
27	1	0	-1.693252	-2.335860	1.012987

Method UB3PW91/6-311++G**//UB3PW91/6-31G*

Multiplicity 3

Electronic energy -1087.1153365 a.u.

Zero-point vibrational energy 130.07976 kcal/mol

Number of imaginary frequencies 0

Point group C₁

1,4-Diradical **35b** (with hydrogen bond)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	-1.641597	-.866731	-.525530
2	16	0	-2.810118	-.113150	.290628
3	8	0	-2.859960	-.643101	1.640354
4	8	0	-2.665871	1.337463	.073820
5	6	0	-4.255169	-.658531	-.604622
6	1	0	-5.127533	-.225454	-.110007
7	1	0	-4.188072	-.310105	-1.636456
8	1	0	-4.296631	-1.748158	-.561263
9	6	0	.398476	.607114	-.365224
10	6	0	-.610092	-.007632	-1.236334
11	8	0	.071180	1.727333	.319914
12	6	0	1.712274	.009444	-.130371
13	1	0	-1.180015	.741932	-1.793661
14	1	0	-.166525	-.728442	-1.921486
15	1	0	-.897063	1.874098	.244652
16	6	0	1.816627	-1.381275	-.095769
17	6	0	3.046668	-2.029974	.078942
18	6	0	4.203409	-1.274652	.240641
19	6	0	4.126246	.113911	.218845
20	6	0	2.904465	.802083	.029375
21	6	0	2.912670	2.215262	-.045525
22	1	0	.912239	-1.978957	-.178658
23	1	0	3.085294	-3.115615	.098997
24	1	0	5.164590	-1.761949	.382395
25	1	0	5.032327	.705343	.330712
26	1	0	3.849640	2.750850	.074165
27	1	0	2.010170	2.792644	-.187666

Method UB3PW91/6-311++G**//UB3PW91/6-31G*
 Multiplicity 3
 Electronic energy -1087.1177846 a.u.
 Zero-point vibrational energy 130.22254 kcal/mol
 Number of imaginary frequencies 0
 Point group C₁

Transition state of elimination of MsOH 36

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-.451675	.488827	.596378
2	6	0	.322045	-.100323	1.617373
3	8	0	.014796	1.490675	-.078751
4	6	0	-1.794680	-.011276	.261056
5	1	0	1.181714	.426914	2.006591
6	1	0	-.031767	-.973291	2.148802
7	1	0	1.096911	1.506755	-.001714
8	6	0	-1.980097	-1.394958	.253989
9	6	0	-3.204054	-1.963447	-.100588
10	6	0	-4.275578	-1.130447	-.434065
11	6	0	-4.116842	.245096	-.424289
12	6	0	-2.881446	.863023	-.088021
13	6	0	-2.802189	2.268047	-.068867
14	1	0	-1.136217	-2.042083	.476570
15	1	0	-3.314293	-3.043384	-.120671
16	1	0	-5.236247	-1.560332	-.705143
17	1	0	-4.955575	.887910	-.679568
18	1	0	-3.674745	2.855502	-.336537
19	1	0	-1.893874	2.798648	.181265
20	8	0	1.882307	-1.144481	.302552
21	16	0	2.835146	-.163037	-.338207
22	8	0	3.019102	-.352836	-1.775080
23	8	0	2.462214	1.256579	.073647
24	6	0	4.417180	-.409557	.459696
25	1	0	5.121284	.319634	.054335
26	1	0	4.303378	-.273210	1.536496
27	1	0	4.753755	-1.423870	.235961

Method UB3PW91/6-311++G**//UB3PW91/6-31G*
 Multiplicity 3
 Electronic energy -1087.1140435 a.u.
 Zero-point vibrational energy 127.52119 kcal/mol
 Number of imaginary frequencies 1
 Value of imaginary frequency -155.2749 cm⁻¹
 Point group C₁

1,5-Diradical **37** (solvated with MsOH)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.806539	-0.414002	-0.047582
2	6	0	-0.200995	-1.598569	0.499844
3	6	0	-2.283739	-0.256431	-0.020340
4	1	0	0.874391	-1.733147	0.414621
5	1	0	-0.780122	-2.331948	1.049878
6	6	0	-3.074077	-1.401690	-0.145461
7	6	0	-4.465772	-1.338319	-0.182935
8	6	0	-5.097951	-0.094372	-0.069139
9	6	0	-4.342950	1.054512	0.068081
10	6	0	-2.917838	1.032033	0.093006
11	6	0	-2.230902	2.244408	0.268318
12	1	0	-2.590719	-2.369138	-0.254688
13	1	0	-5.048898	-2.246676	-0.302301
14	1	0	-6.182755	-0.029947	-0.090022
15	1	0	-4.837471	2.018167	0.163462
16	1	0	-2.796851	3.166495	0.361376
17	1	0	-1.152616	2.302727	0.309129
18	8	0	-0.082170	0.485211	-0.534523
19	1	0	1.566081	0.553771	-0.758138
20	8	0	3.470028	0.783996	1.363681
21	16	0	3.450950	-0.014166	0.143834
22	8	0	3.095867	-1.433201	0.237844
23	8	0	2.540715	0.684557	-0.976556
24	6	0	5.016424	0.142880	-0.694040
25	1	0	4.969551	-0.399373	-1.639282
26	1	0	5.221956	1.201613	-0.859323
27	1	0	5.772767	-0.293085	-0.038153

Method UB3PW91/6-311++G**//UB3PW91/6-31G*
 Multiplicity 3
 Electronic energy -1087.1292858 a.u.
 Zero-point vibrational energy 127.83306 kcal/mol
 Number of imaginary frequencies 0
 Point group C₁

anti-1,5-Diradical **anti-38**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.570929	-.365618	-.016224
2	6	0	-1.798932	-1.527527	-.140120
3	6	0	-.408584	-1.426771	-.135906
4	6	0	.246815	-.198213	-.030963
5	6	0	-.533064	1.007388	.081631
6	6	0	-1.952111	.864152	.093662
7	6	0	1.739363	-.179226	-.071353
8	8	0	2.378517	.785850	-.525933
9	6	0	2.475263	-1.303402	.453603
10	6	0	.014380	2.294214	.209701
11	1	0	-3.656094	-.429157	-.011059
12	1	0	-2.274498	-2.498865	-.241657
13	1	0	.182557	-2.331970	-.250889
14	1	0	-2.552741	1.765669	.189700
15	1	0	3.552870	-1.298480	.328552
16	1	0	2.016762	-2.102016	1.027088
17	1	0	1.080360	2.470652	.192419
18	1	0	-.650551	3.147379	.309118

Method	UB3PW91/6-311++G**//UB3PW91/6-31G*
Multiplicity	3
Electronic energy	-422.8383387 a.u.
Zero-point vibrational energy	87.50086 kcal/mol
Number of imaginary frequencies	0
Point group	C ₁

syn-1,5-Diradical **syn-38**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.582230	-.237245	.115523
2	6	0	-1.874101	-1.446766	.136022
3	6	0	-.483446	-1.428281	.059218
4	6	0	.231677	-.233134	-.021598
5	6	0	-.479151	1.013950	-.097790
6	6	0	-1.902464	.958382	-.004432
7	6	0	1.722473	-.365323	-.024533
8	8	0	2.251907	-1.373728	-.527010
9	6	0	2.560172	.596371	.637912
10	6	0	.127648	2.260877	-.324829
11	1	0	-3.667278	-.238557	.181576
12	1	0	-2.402665	-2.392413	.217127
13	1	0	.081997	-2.355373	.076205
14	1	0	-2.454639	1.894019	-.054451
15	1	0	3.633994	.451105	.581522
16	1	0	2.164327	1.388925	1.264217
17	1	0	1.189391	2.373870	-.509031
18	1	0	-.483850	3.155272	-.394039

Method UB3PW91/6-311++G**//UB3PW91/6-31G*
 Multiplicity 3
 Electronic energy -422.8372139 a.u.
 Zero-point vibrational energy 87.53594 kcal/mol
 Number of imaginary frequencies 0
 Point group C₁

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.885065	-0.646494	0.004239
2	8	0	3.049641	0.109418	-0.289191
3	6	0	4.242915	-0.633602	-0.184585
4	1	0	2.052361	-1.215672	0.942461
5	1	0	1.682173	-1.380467	-0.790427
6	1	0	5.066669	0.050420	-0.401979
7	1	0	4.372831	-1.048553	0.826646
8	1	0	4.263569	-1.460257	-0.909656
9	6	0	-3.310579	-0.988983	-0.069502
10	6	0	-2.266269	-1.887006	0.071599
11	6	0	-0.946789	-1.413375	0.156730
12	6	0	-0.629469	-0.049536	0.082562
13	6	0	-1.718025	0.893416	-0.081641
14	6	0	-3.027303	0.379725	-0.140850
15	6	0	0.755860	0.333209	0.133986
16	8	0	1.132565	1.569743	0.547741
17	6	0	-1.528139	2.292306	-0.236524
18	1	0	-4.338895	-1.335225	-0.129116
19	1	0	-2.455588	-2.955678	0.130364
20	1	0	-0.151608	-2.139173	0.306264
21	1	0	-3.843089	1.087701	-0.271304
22	1	0	-2.397374	2.931835	-0.359196
23	1	0	-0.550724	2.750520	-0.226912
24	1	0	2.098425	1.603300	0.398371

Method UB3PW91/6-311++G**//UB3PW91/6-31G*
 Multiplicity 3
 Electronic energy -538.5626799 a.u.
 Zero-point vibrational energy 123.56350 kcal/mol
 Number of imaginary frequencies 0
 Point group C₁

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.862851	2.679054	0.002262
2	6	0	-2.098145	2.024307	-0.083217
3	6	0	-2.170603	0.642579	-0.066105
4	6	0	-0.995421	-0.153981	0.029689
5	6	0	0.256769	0.527393	0.148380
6	6	0	0.300394	1.916763	0.122093
7	6	0	-1.074156	-1.572057	-0.003507
8	8	0	-0.014003	-2.359625	0.038759
9	6	0	-2.370181	-2.341708	-0.074614
10	6	0	1.511608	-0.259258	0.351669
11	1	0	-0.808260	3.763546	-0.020151
12	1	0	-3.014071	2.603235	-0.176919
13	1	0	-3.138638	0.159278	-0.158275
14	1	0	1.268809	2.404417	0.200669
15	1	0	-2.173488	-3.410460	0.041430
16	1	0	-3.059563	-2.030683	0.720175
17	1	0	1.803720	-0.327232	1.416770
18	1	0	1.265636	-1.339325	0.070870
19	8	0	2.561204	0.229113	-0.418114
20	6	0	3.816973	-0.327817	-0.089648
21	1	0	-2.870929	-2.190476	-1.040471
22	1	0	4.559341	0.175809	-0.712485
23	1	0	4.061340	-0.169059	0.971269
24	1	0	3.842175	-1.406601	-0.300047

Method UB3PW91/6-311++G**//UB3PW91/6-31G*

Multiplicity 3

Electronic energy -538.5520367 a.u.

Zero-point vibrational energy 122.64357 kcal/mol

Number of imaginary frequencies 0

Point group C₁

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