Hydroacylation of Activated Ketones Catalyzed by *N*-Heterocyclic Carbenes

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General Information. All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring. THF, Et₂O, CH₂Cl₂, DMF and toluene were purified by passage through a bed of activated alumina.¹ Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.² Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and anisaldehyde, ceric ammonium nitrate stain, potassium permanganate, or phosphomolybic acid followed by heating. Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer. ¹H-NMR spectra were recorded on a Varian Inova 500 (500 MHz) or Mercury 400 (400 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 7.26 ppm). Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ¹³C-NMR spectra were recorded on a Varian

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1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometal.* **1996**, *15*, 1518-1520.
 2. Perrin, D. D. and Armarego, W. L. *Purification of Laboratory Chemicals*; 3rd Ed., Pergamon Press, Oxford. 1988.

Inova 500 (125 MHz) or Mercury 400 (100 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl_3 at 77.0 ppm). Mass spectra data were obtained on a Varian 1200 Quadrupole Mass Spectrometer and Micromass Quadro II Spectrometer.

Ethyl 2-(4-bromophenyl)-2-oxoacetate was prepared according to Imoto³ and ethyl 2-(4-chlorophenyl)-2-oxoacetate was prepared according to Mills⁴. Ethyl 2-(naphthalene-6-yl)-2-oxoacetate and ethyl 2-(3-methoxyphenyl)-2-oxoacetate were prepared according to procedure analogous to Seebach⁵. Ethyl 2-oxo-2-(thiophen-2-yl)acetate was purchased from Alfa Aesar Chemical Company. Methyl benzoyl formate, benzil, 9-fluorenone and all aldehydes were commercially available from Sigma-Aldrich Chemical Company and all aldehydes were purified before use.

General Procedure for triazolium-catalyzed reaction with protic solvent:

A screw-capped tube was charged with the triazolium salt (25 mg, 0.111 mmol) in a nitrogen-filled dry box. The tube was removed from the box and placed under a positive pressure of nitrogen. The tube was charged with methanol (1.5 mL), DBU (17 μL , 0.111 mmol), distilled benzaldehyde (75 μL , 0.74 mmol) and lastly, methyl benzoyl formate (213 mg, 1.3 mmol). The reaction was stirred at 23 °C for 24 hours until benzaldehyde was consumed (as judged by GC). The reaction mixture was concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel.

Ethyl 2-(4-bromophenyl)-2-hydroxyacetate (15): Purified with 20% EtOAc/hexanes yielding 153 mg (80%) of **15** as a white solid. R_f = 0.35 (1:3 EtOAc/hexanes); IR (film) 3460, 2982, 1734, 1477, 1396, 1256, 763 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.49 (d, J = 8.3, 2H); 7.31 (d, J = 8.3, 2H); 5.11 (d, J = 5.2, 1H); 4.22 (dq, J = 33.3, 7.0, 2H); 3.49 (d, J = 5.2, 1H); 1.23 (t, J = 7.0, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.2, 137.3, 131.6, 128.2, 122.4, 72.1, 62.5, 14.0.

Methyl 2-hydroxy-2-phenylacetate (17): Purified with 20% EtOAc/hexanes yielding 118 mg (75%) of **17** as a white solid. R_f = 0.36 (1:3 EtOAc/hexanes); IR (film) 3458, 2983, 1736, 1400, 1257, 768 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.38-7.33 (m, 4H); 5.13 (d, J = 5.2, 1H); 4.12 (dq, J = 32.1, 7.3, 2H); 3.48 (d, J = 5.5, 1H); 1.23 (t, J = 7.0, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.8, 137.3, 134.7, 129.2, 128.3, 72.6, 62.9, 14.5.

Ethyl-2-hydroxy-2-(3-methoxyphenyl)acetate (19): Purified with 20% EtOAc/hexanes yielding 131 mg (84%) of **19** as a light tan solid. R_f = 0.31 (1:3 EtOAc/hexanes); IR (film) 3472, 2938, 2935, 1734, 1369, 1261, 782, 738 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.28 (t, J = 7.9, 1H); 7.01 (d, J = 7.6, 1H); 6.98 (s, 1H); 6.86 (m, 1H); 5.13 (s, 1H); 4.22 (dq, J

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= 36.9, 7.3, 2H); 3.81 (s, 3H); 3.51 (s, 1H); 1.24 (t, $J = 7.0$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.8, 159.9, 140.1, 129.8, 119.1, 114.3, 112.0, 72.9, 62.5, 55.4, 14.1; LRMS (electrospray): Mass calculated for $\text{C}_{11}\text{H}_{14}\text{O}_4$ $[2\text{M}+\text{Na}]^+$ 443.5. Found 443.3.

Ethyl-2-hydroxy-2-(naphthalen-3-yl)acetate (21): Purified with 15% EtOAc/hexanes yielding 151 mg (89%) of **21** as a white solid. $R_f = 0.26$ (1:3 EtOAc/hexanes); IR (film) 3462, 3051, 2982, 1734, 1367, 1258 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.91 (s, 1H); 7.85 (m, 3H); 7.51 (m, 3H); 5.33 (d, $J = 4.6$, 1H); 4.23 (dq, $J = 43.7, 7.0$, 2H); 3.85 (d, $J = 5.2$, 1H); 1.22 (t, $J = 7.0$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 174.2, 139.8, 136.2, 133.7, 133.6, 128.9, 128.6, 128.2, 126.8, 126.3, 124.6, 73.5, 62.9, 14.5; LRMS (electrospray): Mass calculated for $\text{C}_{14}\text{H}_{14}\text{O}_3$ $[2\text{M}+\text{Na}]^+$ 483.5. Found 483.4

Ethyl-2-hydroxy-2-(thiophen-2-yl)acetate (23): Purified with 15% EtOAc/hexanes yielding 98 mg (71%) of **23** as a light yellow oil. $R_f = 0.49$ (1:3 EtOAc/hexanes); IR (film) 3466, 3102, 2983, 1736, 1369, 1267, 706 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.29 (d, $J = 5.2$, 1H); 7.11 (s, 1H); 6.99 (m, 1H); 5.40 (s, 1H); 4.29 (m, 2H); 3.49 (s, 1H); 1.29 (t, $J = 7.3$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 172.7, 141.7, 127.2, 125.9, 125.5, 69.3, 62.8, 14.3; LRMS (electrospray): Mass calculated for $\text{C}_{13}\text{H}_{16}\text{O}_2$ $[2\text{M}]^+$ 372.4. Found 372.4.

9H-fluoren-9-ol (27): Purified with 12.5% EtOAc/hexanes yielding 102 mg (75%) of **27** as a light tan solid. $R_f = 0.42$ (1:3 EtOAc/hexanes); IR (film) 3199, 3054, 2986, 1265 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.65 (m, 4H); 7.40 (t, $J = 7.6$, 2H); 7.33 (t, $J = 7.3$, 2H); 5.60 (sb, 1H); 1.82 (d, $J = 5.8$, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 146.1, 140.5, 129.6, 128.3, 125.6, 120.5, 75.7.

General Procedure for triazolium-catalyzed reaction with aprotic solvent:

A screw-capped tube was charged with the triazolium salt (17 mg, 0.074 mmol) in a nitrogen-filled dry box. The tube was removed from the box and placed under a positive pressure of nitrogen. The tube was charged with CH_2Cl_2 (1.5 mL), DBU (11 μL , 0.074 mmol), distilled *p*-anisaldehyde (90 μL , 0.74 mmol) and lastly, methyl benzoyl formate (213 mg, 1.3 mmol). The reaction was stirred at 23 $^\circ\text{C}$ for 9 hours or until benzaldehyde was consumed (as judged by GC). The reaction mixture was concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel.

(Methoxycarbonyl)(phenyl)methyl benzoate (7): Purified with 30-50% CH_2Cl_2 /hexanes yielding 155 mg (78%) of **7** as a white solid. $R_f = 0.39$ (1:1 CH_2Cl_2 /hexanes); IR (film) 3035, 2951, 1753, 1719, 1259 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.13 (d, $J = 7.9$, 2H); 7.59 (m, 3H); 7.43 (m, 5H); 6.17 (s, 1H); 3.76 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.5, 166.1, 134.2, 133.7, 130.2, 129.5, 129.4, 129.1, 128.7, 128.9, 75.1, 52.9; LRMS (electrospray): Mass calculated for $\text{C}_{16}\text{H}_{14}\text{O}_4$ $[2\text{M}+\text{Na}]^+$ 563.6. Found 563.2.

(Methoxycarbonyl)(phenyl)methyl 4-methoxybenzoate (8):

Purified with 15% EtOAc/hexanes yielding 170 mg (77%) of **8** as a colorless oil. $R_f = 0.56$ (1:3 EtOAc/hexanes); IR (film) 2951, 1753, 1718, 1450, 1257, 845 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.08 (f, $J = 8.9$, 2H); 7.57 (m, 2H); 7.42 (m, 3H); 6.93 (d, $J = 8.6$, 2H); 6.014 (s, 1H); 3.87 (s, 3H); 3.75 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.5, 165.5, 163.8, 134.1, 132.1, 129.2, 128.8, 127.6, 121.5, 113.7, 74.6, 55.4, 52.6; LRMS (electrospray): Mass calculated for $\text{C}_{17}\text{H}_{16}\text{O}_5$ $[2\text{M}+\text{Na}]^+$ 623.6 Found 623.29.

(Methoxycarbonyl)(phenyl)methyl 4-fluorobenzoate (9):

Purified with 45% CH_2Cl_2 /hexanes yielding 152 mg (71%) of **9** as a white solid. $R_f = 0.39$ (1:1 CH_2Cl_2 /hexanes); IR (film) 2955, 1761, 1726, 1259, 849 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.14 (m, 2H); 7.58 (m, 2H); 7.45 (m, 4H); 7.13 (t, $J = 8.6$, 1H); 6.15 (s, 1H); 3.76 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.7, 165.4, 133.8, 133.1, 129.9, 129.4, 129.3, 128.9, 128.1, 116.2, 75.4, 53.2.

(Methoxycarbonyl)(phenyl)methyl 4-methylbenzoate (10):

Purified with 40-50% CH_2Cl_2 /hexanes yielding 155 mg (72%) of **10** as a white solid. $R_f = 0.34$ (1:1 CH_2Cl_2 /hexanes); IR (film) 2954, 1753, 1723, 1261, 840 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.01 (d, $J = 8.3$, 2H); 7.59 (m, 2H); 7.42 (m, 3H); 7.25 (m, 2H); 6.15 (s, 1H); 3.75 (s, 3H); 2.42 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.7, 166.2, 144.6, 134.3, 133.8, 130.3, 129.5, 129.4, 129.1, 127.9, 75.0, 52.9, 22.0; LRMS (electrospray): Mass calculated for $\text{C}_{17}\text{H}_{16}\text{O}_4$ $[\text{M}+\text{H}]^+$ 591.6. Found 591.2.

(Methoxycarbonyl)(phenyl)methyl 2-naphthoate (11):

Purified with 45% CH_2Cl_2 /hexanes yielding 171 mg (70%) of **11** as a colorless oil. $R_f = 0.31$ (1:1 CH_2Cl_2 /hexanes); IR (film) 3051, 2947, 1753, 1721, 1263 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.71 (s, 1H); 8.13 (m, 2H); 7.97 (d, $J = 8.3$, 1H); 7.89 (m, 1H); 7.59 (m, 3H); 7.45 (m, 4H); 6.24 (s, 1H); 3.78 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.6, 166.3, 136.0, 133.7, 132.6, 129.7, 129.6, 129.1, 129.0, 128.7, 128.6, 128.5, 128.0, 127.9, 127.8, 127.0, 75.2, 52.9; LRMS (electrospray): Mass calculated for $\text{C}_{20}\text{H}_{16}\text{O}_4$ $[2\text{M}+\text{Na}]^+$ 663.7. Found 663.9.

(Methoxycarbonyl)(phenyl)methyl furan-2-carboxylate (12):

Purified with 10% EtOAc/hexanes yielding 138 mg (73%) of **12** as a colorless oil. $R_f = 0.57$ (1:3 EtOAc/hexanes); IR (film) 3136, 2956, 1753, 1730, 1285 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.57 (m, 2H); 7.41 (m, 4H); 7.31 (m, 1H); 6.53 (sb, 1H); 6.15 (s, 1H); 3.76 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.3, 158.0, 147.2, 144.0, 133.8, 129.6, 129.1, 128.0, 119.5,

112.3, 74.8, 53.0; LRMS (electrospray): Mass calculated for $C_{14}H_{12}O_5$ $[2M+Na]^+$ 543.4. Found 543.2.

(Ethoxycarbonyl)(4-bromophenyl)methyl 4-methoxybenzoate (14): Purified with 7.5% EtOAc/hexanes yielding 251 mg (87%) of **14** as a colorless oil. R_f = 0.58 (1:3 EtOAc/hexanes); IR (film) 2974, 1746, 1719, 1257, 837, 770 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 8.9, 2H); 73.55 (d, J = 8.6, 2H); 7.46 (d, J = 8.6, 2H); 6.93 (d, J = 8.9, 2H); 6.07 (s, 1H); 4.21 (dq, J = 25.0, 7.0, 2H); 3.87 (s, 3H); 1.23 (t, J = 7.3, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 165.9, 164.3, 133.8, 132.5, 129.7, 123.8, 121.9, 114.2, 74.5, 62.3, 55.9, 14.5; LRMS (electrospray): Mass calculated for $C_{18}H_{17}BrO_5$ $[2M+Na]^+$ 809.4. Found 808.7.

(Ethoxycarbonyl)(4-chlorophenyl)methyl 4-methoxybenzoate (16): Purified with 10% EtOAc/hexanes yielding 206 mg (81%) of **16** as a colorless oil. R_f = 0.54 (1:3 EtOAc/hexanes); IR (film) 2974, 1753, 1719, 1257, 837, 770 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 8.9, 2H); 7.52 (d, J = 8.3, 2H); 7.39 (d, J = 8.3, 2H); 6.93 (d, J = 8.9, 2H); 6.08 (s, 1H); 4.21 (dq, J = 24.1, 7.0, 2H); 3.87 (s, 3H); 1.23 (t, J = 7.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 165.9, 164.3, 135.6, 133.3, 132.5, 129.5, 121.9, 114.2, 74.5, 62.3, 55.9, 14.5; LRMS (electrospray): Mass calculated for $C_{18}H_{17}ClO_5$ $[2M+Na]^+$ 719.5. Found 719.1.

(Ethoxycarbonyl)(naphthalene-3-yl)methyl 4-methoxybenzoate (18): Purified with 9% EtOAc/hexanes yielding 183 mg (72%) of **18** as a colorless oil. R_f = 0.41 (1:3 EtOAc/hexanes); IR (film) 2951, 1753, 1718, 1260, 849, 771, 687 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 8.6, 2H); 7.33 (m, 1H); 7.16 (m, 1H); 7.12 (s, 1H); 6.93 (d, J = 8.6, 2H); 6.08 (s, 1H); 4.21 (m, 2H); 3.86 (s, 3H); 3.84 (s, 3H); 1.24 (t, J = 7.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 165.8, 163.9, 160.0, 135.8, 132.2, 130.0, 121.8, 120.1, 114.8, 113.9, 113.3, 74.9, 61.9, 55.7, 55.5, 14.2; LRMS (electrospray): Mass calculated for $C_{19}H_{20}O_6$ $[2M+Na]^+$ 711.7. Found 711.1.

(Ethoxycarbonyl)(naphthalene-3-yl)methyl 4-methoxybenzoate (20): Purified with 10% EtOAc/hexanes yielding 208 mg (78%) of **20** as a colorless oil. R_f = 0.57 (1:3 EtOAc/hexanes); IR (film) 2972, 2911, 1746, 1717, 1258, 747 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 8.6, 2H); 8.05 (s, 1H); 7.88 (d, J = 7.9, 1H); 7.53 (m, 2H); 6.94 (d, J = 8.6, 2H); 4.22 (dq, J = 34.2, 7.0, 2H); 3.87 (s, 3H); 1.23 (d, J = 7.33, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 165.9, 164.0, 133.8, 133.4, 132.4, 131.9, 128.9, 128.5, 128.0, 127.6, 127.0, 126.8, 125.0, 121.9, 114.0, 75.2, 62.0, 55.7, 14.3; LRMS (electrospray): Mass calculated for $C_{22}H_{20}O_5$ $[2M+Na]^+$ 751.7. Found 751.1

(Ethoxycarbonyl)(thiophen-2-yl)methyl 4-methoxybenzoate

(22): Purified with 5.0% EtOAc/hexanes yielding 170 mg (73%) of **22** as a light yellow oil. R_f = 0.67 (1:3 EtOAc/hexanes); IR (film) 2974, 1742, 1718, 1259, 849, 709 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.07 (d, J = 8.6, 2H); 7.38

(d, J = 4.9, 1H); 7.25 (d, J = 4.3, 1H); 7.04 (t, J = 4.3, 1H); 6.93 (d, J = 8.6, 2H); 6.38 (s, 1H); 4.26 (m, 2H); 3.87 (s, 3); 1.27 (t, J = 7.0, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 128.6, 165.8, 164.3, 136.4, 132.6, 128.0, 127.4, 121.8, 114.2, 71.0, 62.5, 55.9, 14.5; LRMS (electrospray): Mass calculated for $\text{C}_{16}\text{H}_{16}\text{O}_5\text{S}$ $[\text{2M}+\text{Na}]^+$ 663.7. Found 663.1.

2-oxo-1,2-diphenylethyl benzoate (24): Purified with 45% CH_2Cl_2 /hexanes yielding 195 mg (83%) of **24** as a white solid. R_f = 0.44 (1:1 CH_2Cl_2 /hexanes); IR (film) 3064, 1711, 1696, 1277, 1251 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.13 (d, J = 7.3, 2H); 8.00 (d, J = 7.3, 2H); 7.57 (m 3H); 7.54 (t, J = 7.3, 1H); 7.43 (m, 7H); 7.09 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 194.2, 166.5, 135.2, 134.2, 134.0, 133.9, 133.8,

130.5, 129.9, 129.8, 129.6, 129.3, 129.2, 128.9, 78.4; LRMS (electrospray): Mass calculated for $\text{C}_{21}\text{H}_{16}\text{O}_3$ $[\text{2M}+\text{Na}]^+$ 655.7. Found 655.0.

General Procedure for triazolium-catalyzed intramolecular hydroacylation reaction:

A flame-dried 10 mL round bottom flask equipped with stir bar was charged with the triazolium salt (54 mg, 0.238 mmol) and placed under a positive pressure of nitrogen. Into the flask was then added 1,2-diacylbenzene⁶ (50 mg, 0.238 mmol) and purged with nitrogen followed by addition of THF (1.2 mL) and DBU (36 μL , 0.238 mmol) via syringe. The reaction was stirred at 23 $^\circ\text{C}$ for 24 hours until the 1,2-diacylbenzene was consumed (as judged by GC). The reaction was diluted with ethyl acetate (10 mL) and washed with water (2x10 mL). The aqueous layer was washed with ethyl acetate (2x10 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel.

3-phenylisobenzofuran-1(3H)-one (32): Purified with 0.5:3.5:6 EtOAc/ CH_2Cl_2 /hexanes yielding 29.4 mg (59%) of **32** as a white solid. R_f = 0.45 (0.5:3.5:6 EtOAc/ CH_2Cl_2 /hexanes); IR (film) 3033, 2920, 1765, 1285 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.97 (d, J = 7.6, 1H); 7.65 (t, J = 7.3, 1H); 7.56 (t, J = 7.3, 1H); 7.38 (m, 3H); 7.34 (d, J = 7.6, 1H); 7.28 (m, 2H); 6.41 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 149.9, 136.6, 134.5, 129.6, 129.5, 129.2, 127.3,

127.2, 125.9, 125.8, 123.1, 82.9. LRMS (electrospray): Mass calculated for $\text{C}_{14}\text{H}_{10}\text{O}_2$ $[\text{2M}+\text{Na}]^+$ 443.5. Found 443.4.

6. Kotali, A.; Papapetrou, M.; Dimos, V.; Harris, P.A. *Org. Prep. and Proc. Int.* **1998**, 30 (2), 177-181.

General Procedure for the crossover experiment:

Into a 25 mL sealed-tube equipped with stir bar was added 4Å molecular sieves and flame-dried under vacuum and purged with N₂ (3x). Into it was charged with the triazolium salt (22 mg, 0.1 mmol) in a nitrogen-filled dry box. The tube was removed from the box and placed under a positive pressure of nitrogen. The tube was charged with CH₂Cl₂ (2.0 mL), DBU (15 µL, 0.1 mmol), benzaldehyde-α-d₁ (50 µL, 0.49 mmol), *p*-tolualdehyde (58 µL, 0.49 mmol) and lastly, methyl benzoyl formate (245 µL, 1.7 mmol). The reaction was stirred at 23 °C for 24 hours (as judged by GC). The reaction mixture was concentrated *in vacuo*. The resulting residue was purified by flash chromatography on silica gel and the 4 products were isolated.

Crossover experiment products and mass spectrum:

01272006-01 47 (3.238) Cn (Top,4, Ht); Sm (Mn, 1x1.00); Sb (1.40.00); Cm (46:54)

Scan ES+
7.68e6

Selected NMR Spectra

Structural Analysis with crystal structures:**2-oxo-1,2-diphenylethyl benzoate (24)** Table 1. Crystal data and structure refinement for **24**.

Identification Code	s08tm	
Empirical formula	C ₂₁ H ₁₆ O ₃	
Formula weight	316.34	
Temperature	153 (2) K	
Wavelength	0.71073 Å	
Crystal System	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.6694 (7) Å	$\alpha = 90.00^\circ$.
	b = 22.1068(17) Å	$\beta = 100.1520 (10)^\circ$.
	c = 8.7642(7) Å	$\chi = 90.00^\circ$.
Volume	1653.4 (2) Å ³	
Z	4	
Absorption coefficient	0.084 mm ⁻¹	

F(000)	664
Crystal size	4.3 x 3.5 x 2.3 mm ³
Theta range for data collection	2.52 to 28.40°
Index ranges	-11<=h<=11, -29<=k<=28, -11<=l<=11
Reflections collected	4808
Independent reflections	4032
Completeness of theta = 28.40°	98.7%
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data/ restraints/ parameters	4032/0/281
Goodness-of-fit on F ²	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0412, wR2 = 0.1141
R indices (all data)	R1 = 0.0488, wR2 = 0.1212

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for **24**.

	x	y	z	U(eq)
H3	0.150(2)	0.2255(8)	0.2479(19)	0.052(5)
H11	0.6660(19)	0.2928(7)	0.6754(19)	0.045(4)
H13	0.6504(19)	0.3119(7)	1.1341(19)	0.046(4)
H20	1.301(2)	0.4856(8)	0.806(2)	0.063(5)
H5	0.035(2)	0.3653(8)	-0.055(2)	0.054(5)
H6	0.231(2)	0.4258(8)	0.0939(19)	0.049(4)
H21	1.302(2)	0.3955(8)	0.664(2)	0.056(5)
H4	-0.007(2)	0.2653(8)	0.0211(19)	0.051(4)
H19	1.0666(18)	0.5362(7)	0.8212(18)	0.042(4)
H22	1.0601(18)	0.3579(7)	0.5258(18)	0.039(4)
H12	0.6712(19)	0.2485(8)	0.9186(19)	0.049(4)
H14	0.6189(19)	0.4169(7)	1.0986(18)	0.044(4)
H18	0.8192(18)	0.4967(6)	0.6905(17)	0.035(3)
H2	0.340(2)	0.2853(7)	0.3984(19)	0.046(4)
H15	0.6081(16)	0.4590(7)	0.8519(15)	0.032(3)
H9	0.6010(15)	0.4486(6)	0.5782(14)	0.025(3)
O3	0.49728(9)	0.37280(3)	0.48279(9)	0.02805(19)
O1	0.46023(10)	0.45033(4)	0.31423(9)	0.0324(2)
O2	0.77319(11)	0.36059(4)	0.40442(10)	0.0394(2)
C10	0.63502(12)	0.37935(5)	0.73999(12)	0.0246(2)
C7	0.42781(12)	0.39972(5)	0.35068(12)	0.0254(2)
C17	0.92108(13)	0.42253(5)	0.59669(12)	0.0268(2)
C1	0.30613(13)	0.36040(5)	0.25949(12)	0.0276(2)
C9	0.62288(12)	0.40537(5)	0.57829(12)	0.0250(2)
C15	0.62324(13)	0.41608(5)	0.86601(13)	0.0288(2)
C16	0.77395(13)	0.39415(5)	0.51380(12)	0.0274(2)

C14	0.63138(16)	0.39061(6)	1.01198(13)	0.0356(3)
C2	0.28014(16)	0.30161(6)	0.30521(15)	0.0372(3)
C6	0.21617(16)	0.38401(6)	0.12491(14)	0.0362(3)
C18	0.92192(13)	0.47510(5)	0.68457(14)	0.0310(2)
C13	0.64911(17)	0.32900(6)	1.03285(14)	0.0385(3)
C12	0.66038(18)	0.29219(5)	0.90725(14)	0.0403(3)
C11	0.65469(16)	0.31746(5)	0.76164(13)	0.0352(3)
C5	0.10043(17)	0.34884(7)	0.03784(16)	0.0447(3)
C20	1.20253(15)	0.46970(6)	0.75162(16)	0.0407(3)
C22	1.06255(14)	0.39417(6)	0.58571(14)	0.0344(3)
C19	1.06337(15)	0.49912(6)	0.76054(15)	0.0378(3)
C21	1.20210(15)	0.41722(6)	0.66529(16)	0.0410(3)
C3	0.16546(18)	0.26647(7)	0.21666(17)	0.0468(3)
C4	0.07510(18)	0.29042(7)	0.08347(17)	0.0475(3)

Table 3. Anisotropic displacement parameters for **24**.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
O3	0.0314(4)	0.0274(4)	0.0229(4)	0.0022(3)	-0.0022(3)	-0.0039(3)
O1	0.0417(5)	0.0269(4)	0.0267(4)	0.0027(3)	0.0008(3)	-0.0009(3)
O2	0.0441(5)	0.0445(5)	0.0303(4)	-0.0118(4)	0.0084(4)	0.0040(4)
C10	0.0250(5)	0.0262(5)	0.0218(5)	0.0012(4)	0.0017(4)	0.0011(4)
C7	0.0281(5)	0.0269(5)	0.0210(5)	-0.0003(4)	0.0039(4)	0.0033(4)
C17	0.0299(5)	0.0284(5)	0.0226(5)	0.0029(4)	0.0056(4)	-0.0008(4)
C1	0.0280(5)	0.0312(5)	0.0230(5)	-0.0027(4)	0.0025(4)	0.0012(4)
C9	0.0282(5)	0.0234(5)	0.0219(5)	0.0001(4)	0.0002(4)	-0.0019(4)
C15	0.0346(6)	0.0245(5)	0.0279(5)	-0.0004(4)	0.0072(4)	0.0005(4)
C16	0.0341(6)	0.0263(5)	0.0215(5)	0.0015(4)	0.0044(4)	-0.0008(4)
C14	0.0502(7)	0.0334(6)	0.0250(5)	-0.0047(4)	0.0113(5)	-0.0038(5)
C2	0.0423(7)	0.0347(6)	0.0314(6)	0.0010(5)	-0.0020(5)	-0.0050(5)
C6	0.0415(7)	0.0358(6)	0.0279(6)	-0.0007(5)	-0.0028(5)	0.0028(5)
C18	0.0294(6)	0.0301(5)	0.0335(6)	-0.0013(4)	0.0052(4)	-0.0011(4)
C13	0.0571(8)	0.0350(6)	0.0227(5)	0.0042(4)	0.0054(5)	-0.0058(5)
C12	0.0664(9)	0.0245(6)	0.0288(6)	0.0026(4)	0.0051(6)	0.0004(5)
C11	0.0553(7)	0.0261(5)	0.0234(5)	-0.0020(4)	0.0050(5)	0.0014(5)
C5	0.0451(7)	0.0495(8)	0.0334(6)	-0.0051(5)	-0.0098(5)	0.0028(6)
C20	0.0292(6)	0.0475(7)	0.0439(7)	-0.0021(6)	0.0022(5)	-0.0067(5)
C22	0.0363(6)	0.0358(6)	0.0321(6)	-0.0018(5)	0.0091(5)	0.0027(5)
C19	0.0353(6)	0.0346(6)	0.0428(7)	-0.0058(5)	0.0045(5)	-0.0056(5)
C21	0.0293(6)	0.0487(7)	0.0458(7)	-0.0009(6)	0.0085(5)	0.0040(5)
C3	0.0547(8)	0.0391(7)	0.0430(7)	-0.0017(6)	-0.0012(6)	-0.0144(6)
C4	0.0439(8)	0.0528(8)	0.0413(7)	-0.0118(6)	-0.0049(6)	-0.0103(6)

Table 4. Bond lengths for **24**.

O3-C7	1.3460(12)
O3-C9	1.4434(12)
O1-C7	1.2103(13)
O2-C16	1.2113(13)
C10-C11	1.3877(15)
C10-C15	1.3889(15)
C10-C9	1.5159(14)
C7-C1	1.4865(15)
C17-C18	1.3935(16)
C17-C22	1.3958(16)
C17-C16	1.4905(15)
C1-C2	1.3902(17)
C1-C6	1.3956(16)
C9-C16	1.5353(16)
C15-C14	1.3881(16)
C14-C13	1.3793(18)
C2-C3	1.3865(18)
C6-C5	1.3870(18)
C18-C19	1.3932(17)
C13-C12	1.3861(17)
C12-C11	1.3860(16)
C5-C4	1.381(2)
C20-C21	1.385(2)
C20-C19	1.3849(19)
C22-C21	1.3829(18)
C3-C4	1.391(2)

Table 5. Bond angles for **24**.

C7-O3-C9	117.11(8)
C11-C10-C15	119.48(10)
C11-C10-C9	119.24(9)
C15-C10-C9	121.26(9)
O1-C7-O3	123.11(10)
O1-C7-C1	125.06(10)
O3-C7-C1	111.81(9)
C18-C17-C22	119.59(10)
C18-C17-C16	122.76(10)
C22-C17-C16	117.65(10)
C2-C1-C6	119.90(11)
C2-C1-C7	121.83(10)
C6-C1-C7	118.27(10)

O3-C9-C10	105.89(8)
O3-C9-C16	108.13(8)
C10-C9-C16	111.08(9)
C14-C15-C10	119.80(10)
O2-C16-C17	121.89(10)
O2-C16-C9	120.28(10)
C17-C16-C9	117.70(9)
C13-C14-C15	120.60(11)
C3-C2-C1	119.95(12)
C5-C6-C1	119.85(12)
C17-C18-C19	120.02(11)
C14-C13-C12	119.75(11)
C11-C12-C13	119.90(11)
C12-C11-C10	120.46(11)
C4-C5-C6	120.10(12)
C21-C20-C19	120.39(12)
C21-C22-C17	120.06(12)
C20-C19-C18	119.75(12)
C22-C21-C20	120.15(12)
C2-C3-C4	119.91(13)
C5-C4-C3	120.29(12)

3-phenylisobenzofuran-1(3H)-one (32): Table 1. Crystal data and structure refinement for **32**.

Identification Code	s12tm	
Empirical formula	C14H9O2	
Formula weight	209.21	
Temperature	153 (2) K	
Wavelength	0.71073 Å	
Crystal System	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 6.0122 (8) Å	$\alpha = 90.00^\circ$.
	b = 7.4709 (10) Å	$\beta = 91.549 (2)^\circ$.

	c = 23.148 (3) Å	$\chi = 90.00^\circ$.
Volume	1039.4 (2) Å ³	
Z	4	
Absorption coefficient	0.089	
F(000)	664	
Crystal size	4.1 x 1.9 x 1.4 mm ³	
Theta range for data collection	2.73 to 28.53°	
Index ranges	-8<=h<=7, -9<=k<=9, -29<=l<=30	
Reflections collected	4320	
Independent reflections	2479	
Completeness of theta = 28.53°	99.5%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data/ restraints/ parameters	2479/0/185	
Goodness-of-fit on F ²	1.095	
Final R indices [I>2sigma(I)]	R1 = 0.1557, wR2 = 0.0572	
R indices (all data)	R1 = 0.1648, wR2 = 0.0731	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for **32**.

	x	y	z	U(eq)
O1	1.0687(2)	0.79527(18)	0.39428(6)	0.0302(3)
O2	1.3960(2)	0.7632(2)	0.44171(7)	0.0368(4)
C9	0.8118(3)	0.6933(2)	0.31753(8)	0.0261(4)
C4	0.8682(3)	0.6889(3)	0.38136(8)	0.0261(4)
C1	1.2222(3)	0.6967(3)	0.42504(8)	0.0288(4)
C10	0.6130(3)	0.7687(3)	0.29772(9)	0.0291(4)
C14	0.9561(3)	0.6183(3)	0.27803(9)	0.0314(5)
C2	1.1359(3)	0.5144(3)	0.43131(8)	0.0271(4)
C12	0.7010(4)	0.6948(3)	0.20033(9)	0.0353(5)
C13	0.9012(4)	0.6200(3)	0.21965(9)	0.0340(5)
C5	0.8042(4)	0.3514(3)	0.40499(9)	0.0323(5)
C3	0.9262(3)	0.5080(3)	0.40546(8)	0.0264(4)
C6	0.8998(4)	0.2019(3)	0.43104(10)	0.0378(5)
C7	1.1128(4)	0.2084(3)	0.45673(9)	0.0385(5)
C8	1.2327(4)	0.3655(3)	0.45772(9)	0.0329(5)
C11	0.5574(4)	0.7685(3)	0.23904(10)	0.0356(5)
H4	0.754(4)	0.745(3)	0.4028(10)	0.027(5)
H7	1.172(4)	0.102(3)	0.4724(10)	0.037(6)
H10	0.521(4)	0.826(3)	0.3252(10)	0.027(5)
H12	0.667(4)	0.684(4)	0.1597(12)	0.047(7)
H14	1.088(4)	0.571(3)	0.2913(10)	0.036(6)
H6	0.812(4)	0.094(4)	0.4269(11)	0.045(7)

H8	1.384(4)	0.374(3)	0.4758(11)	0.045(7)
H13	1.006(5)	0.572(4)	0.1922(12)	0.062(8)
H5	0.652(5)	0.355(4)	0.3856(12)	0.051(7)
H11	0.414(4)	0.819(3)	0.2261(11)	0.039(6)

Table 3. Anisotropic displacement parameters for **32**.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
O1	0.0264(7)	0.0303(7)	0.0337(8)	0.0007(6)	-0.0037(6)	-0.0004(5)
O2	0.0239(7)	0.0499(9)	0.0363(9)	-0.0006(7)	-0.0033(6)	-0.0049(6)
C9	0.0237(9)	0.0239(9)	0.0306(10)	0.0022(7)	-0.0010(7)	0.0001(7)
C4	0.0199(8)	0.0283(9)	0.0299(10)	-0.0017(8)	-0.0007(7)	0.0019(7)
C1	0.0243(9)	0.0357(10)	0.0267(10)	-0.0007(8)	0.0028(7)	0.0037(8)
C10	0.0244(9)	0.0309(10)	0.0320(10)	0.0030(8)	0.0004(8)	0.0037(7)
C14	0.0292(10)	0.0296(10)	0.0356(11)	0.0039(8)	0.0014(8)	0.0073(8)
C2	0.0257(9)	0.0316(10)	0.0241(9)	-0.0018(7)	0.0029(7)	0.0029(7)
C12	0.0399(11)	0.0369(11)	0.0290(11)	0.0058(9)	-0.0036(9)	-0.0023(9)
C13	0.0401(11)	0.0299(10)	0.0322(11)	-0.0001(8)	0.0063(9)	0.0035(9)
C5	0.0346(10)	0.0348(11)	0.0276(10)	-0.0018(8)	0.0015(8)	-0.0036(8)
C3	0.0263(9)	0.0303(9)	0.0228(9)	-0.0001(7)	0.0040(7)	0.0030(7)
C6	0.0509(13)	0.0321(11)	0.0307(11)	-0.0001(9)	0.0062(9)	-0.0049(10)
C7	0.0548(14)	0.0335(11)	0.0275(11)	0.0041(9)	0.0054(9)	0.0114(10)
C8	0.0341(11)	0.0386(11)	0.0259(10)	0.0002(8)	0.0023(8)	0.0095(9)
C11	0.0283(10)	0.0410(12)	0.0371(12)	0.0099(9)	-0.0043(8)	0.0021(9)

Table 4. Bond lengths for **32**.

O1-C1	1.366(2)
O1-C4	1.468(2)
O2-C1	1.211(2)
C9-C10	1.387(3)
C9-C14	1.395(3)
C9-C4	1.508(3)
C4-C3	1.500(3)
C1-C2	1.465(3)
C10-C11	1.390(3)
C14-C13	1.382(3)
C2-C3	1.382(3)
C2-C8	1.390(3)
C12-C11	1.376(3)
C12-C13	1.390(3)
C5-C3	1.381(3)
C5-C6	1.386(3)

C6-C7	1.399(3)
C7-C8	1.377(3)

Table 5. Bond angles for **32**.

C1-O1-C4	110.73(15)
C10-C9-C14	119.46(18)
C10-C9-C4	120.11(17)
C14-C9-C4	120.41(17)
O1-C4-C3	103.33(14)
O1-C4-C9	110.48(15)
C3-C4-C9	115.35(16)
O2-C1- O1	120.63(19)
O2-C1-C2	130.90(19)
O1-C1-C2	108.47(16)
C9-C10-C11	120.32(19)
C13-C14-C9	120.06(19)
C3-C2-C8	121.95(19)
C3-C2 C1	108.10(17)
C8-C2-C1	129.96(18)
C11-C12-C13	120.3(2)
C14-C13-C12	119.98(19)
C3-C5-C6	117.7(2)
C5-C3-C2	120.73(18)
C5-C3-C4	129.99(18)
C2-C3-C4	109.28(17)
C5-C6-C7	121.4(2)
C8-C7-C6	120.7(2)
C7-C8-C2	117.5(2)
C12-C11-C10	119.86(19)