Furans Versus 4*H*-Pyrans: Catalyst-Controlled Regiodivergent Tandem Michael Addition/Cyclization Reaction of 2-(1-Alkynyl)-2-alken - 1- ones with 1, 3-dicarbonyl Compounds

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1.0 General information

NMR spectra were recorded on a NMR spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C with complete proton decoupling. Solvent DMF and $ClCH_2CH_2Cl$ were distilled from CaH_2. Petroleum ether refers to the fraction of Petroleum ether having a boiling point between 60 – 90 ^{o}C. The starting materials 2-(1-alkynyl)-alken-1-ones **1** were prepared according to known procedures.[1] $[Pd(L)(H_2O)_2]^{2+}(OTf^-)_2$, (L=dppp, dppe, dppb, dppf)were synthesized following the literature procedures.[2, 3] Unless otherwise stated, all reagents were obtained from commercial sources and used as received.

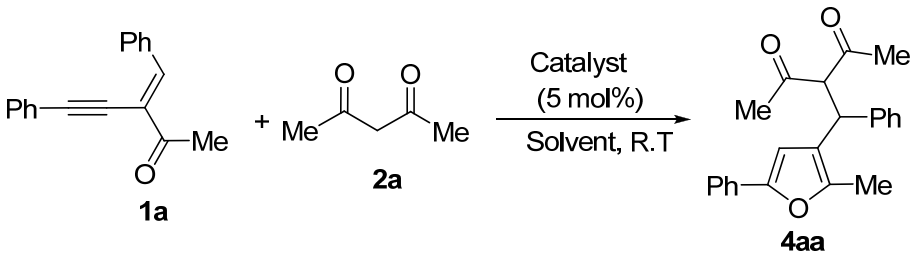
2.0 General procedure for synthesis of 4H-Pyran 3

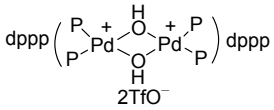
A solution of (E)-3-benzylidene-5-phenylpent-4-yn-2-one 1 (0.25 mmol, 1.0 equiv), β-keto compounds 2, (0.375 mmol, 1.5equiv) and 1, 8-diazabicyclo [5.4.0] undecen-7-ene (DBU) (0.0125 mmol, 5% mol) in 1.0 mL DMF was stirred at $100^{0}C$, After the reaction was complete which was determined by TLC analysis, the reaction was cooled down to r.t, 5.0 mL of water was added and the mixture was extracted by ether three times. The combined organic layers were washed by saturated brine solution and dried over $MgSO_4$. After filtration and evaporation, the residue was purified by column chromatography on silica gel (petroleum ether: ethyl ether = 3:1) to afford 4H-Pyran 3.

3.0 General procedure for synthesis of Furan 4

A solution of (*E*)-3-benzylidene-5-phenylpent-4-yn-2-one 1 (0.25mmol, 1.5equiv), β-keto compounds 2, (0.375 mmol, 1.5equiv) and $[Pd(dppp)(H_2O)_2]^{2+}(OTf^-)_2$ (0.0125 mmol, 5% mol) in 1.0 mL $ClCH_2CH_2Cl$ was stirred at r.t, After the reaction was complete which was determined by TLC analysis, the reaction was then concentrated in vacuo, the residue was purified by column chromatography on silica gel (petroleum ether: ethyl ether = 5:1) to afford Furan 4.

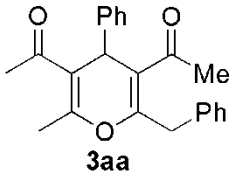
4.0 Optimization of the reaction conditions for direct synthesis of furan 4aa from (*E*)-3-benzylidene-5-phenylpent-4-yn-2-one 1a with acetylacetone 2a[a]



Entry	Catalyst (5 mol%)	Solvent	Time (h)	Yield (%)
1	$AuCl_3$	DCE	20	58
2	$PdCl_2(CH_3CN)_2$	DCE	10	0
3	$[Pd(dppp)(H_2O)_2](OTf)_2$	toluene	10	trace
4	$[Pd(dppp)(H_2O)_2](OTf)_2$	1,4-dioxane	10	0
5	$[Pd(dppp)(H_2O)_2](OTf)_2$	CH_3CN	24	60
6	$[Pd(dppp)(H_2O)_2](OTf)_2$	DMF	10	0
7	$[Pd(dppp)(H_2O)_2](OTf)_2$	DCE	7	99
8	$[Pd(dppp)(H_2O)_2](OTf)_2$	DCE	7	0[b]
9	$[Pd(dppe)(H_2O)_2](OTf)_2$	DCE	7	96
10	$[Pd(dppb)(H_2O)_2](OTf)_2$	DCE	10	89
11	$[Pd(dppf)(H_2O)_2](OTf)_2$	DCE	8	70
12		DCE	10	0

[a] The reaction was carried out by using **1a** (0.25 mmol), **2a** (0.375 mmol, 1.5 equivalents) and catalyst (5 mol%) in 1 mL of solvent at room temperature; [b] *molecular sieve (1.5 equivalents) was added.*

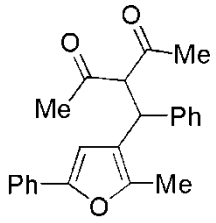
5.0 The characterization data for the newly synthesized compounds as well as the copies of the ^{1}H NMR、^{13}C NMR spectra of all products are given below.



3aa

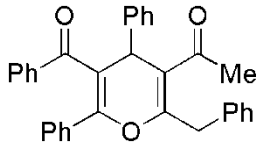
(**3aa**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23-7.11 (m, 10 H), 4.79 (s, 1H), 3.98 (d, J = 14.4 Hz, 1 H), 3.91 (d, J = 14.4 Hz, 1 H), 2.16 (s, 3 H), 2.15 (s, 3 H), 2.13 (s, 3 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.69, 197.99, 157.15, 156.92, 143.95, 136.80, 128.67(2C), 128.46, 128.03, 127.07, 126.67, 117.25, 117.18, 39.20, 37.06, 30.52, 29.92, 19.29; MS (EI) *m/z* (%): 346 (M^+,100); HRMS calcd for $C_{23}H_{22}O_3$: 346.1569, found: 346.1570.



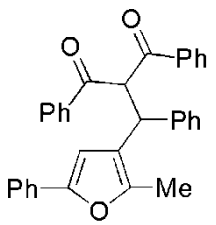
4aa

(**4aa**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 7.5 Hz, 2 H), 7.34-7.16 (m, 8 H), 6.55 (s, 1 H), 4.67 (d, *J* = 12.0 Hz, 1 H), 4.60 (d, *J* = 12.0 Hz, 1 H), 2.35 (s, 3 H), 2.10 (s, 3 H), 1.98 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.68, 202.46, 152.02, 147.49, 140.89, 130.46, 128.87, 128.48, 127.40, 126.99, 126.97, 123.21, 121.29, 104.32, 74.08, 41.89, 29.66, 29.60, 11.68 ppm; MS (70 eV): *m/z* (%): 346 (M^+, 15.24); 43 (100); HRMS calcd for $C_{23}H_{22}O_3$: 346.1569, found: 346.1579.



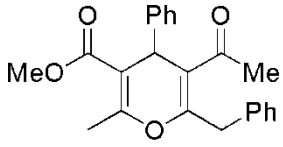
3ab

(**3ab**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 7.5 Hz, 2 H), 7.31-6.85 (m, 18 H), 5.00(s, 1 H), 4.26 (d, *J* = 14.1 Hz, 1 H), 3.98 (d, *J* = 14.1Hz, 1 H), 2.14(s, 3 H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.94, 197.26, 158.81, 152.10, 143.09, 137.66, 137.34, 132.52, 132.06, 129.67, 129.14, 128.91, 128.81, 128.68, 128.49, 128.11, 127.76, 127.63, 127.23, 126.69, 115.92, 114.82, 42.27, 37.30, 29.63 ppm; MS (70 eV): *m/z* (%): 470 (M^+, 13.94); 105 (100); HRMS calcd for $C_{33}H_{26}O_3$: 470.1882, found: 470.1901.



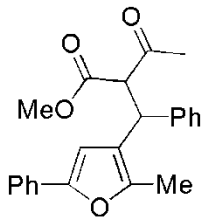
4ab

(**4ab**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.8 Hz, 2 H), 7.79(d, *J* = 7.8 Hz, 2 H), 7.41-7.00 (m, 16 H), 6.46 (s, 1 H), 6.12 (d, *J* = 11.4 Hz, 1 H), 5.08 (d, *J* = 11.4 Hz, 1 H), 2.12(s, 3 H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.04, 193.88, 151.71, 147.95, 141.58, 136.81, 136.79, 133.29, 133.27, 130.72, 128.58(4C), 128.51, 128.41, 127.76, 126.78, 126.63, 123.23, 121.41, 105.29, 62.23, 42.92, 11.57 ppm; MS (70 eV): *m*/*z* (%): 470 (M^+, 14.98); 105 (100); HRMS calcd for $C_{33}H_{26}O_3$: 470.1882, found: 470.1898.



3ac

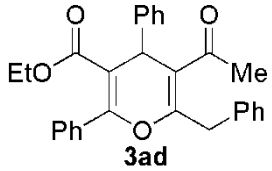
(**3ac**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28-7.09 (m, 10 H), 4.71(s, 1 H), 4.01 (d, *J* = 14.1 Hz, 1 H), 3.95 (d, *J* = 14.1Hz, 1 H), 3.59(s, 3 H), 2.18(s, 3 H), 2.11(s, 3 H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.85, 166.93, 158.48, 157.72, 144.22, 137.06, 128.83, 128.50, 128.40, 128.12, 126.99, 126.61, 116.13, 108.34, 51.40, 39.17, 36.95, 29.68, 18.70 ppm; MS (70 eV): *m*/*z* (%): 362 (M^+, 95.74); 285 (100); HRMS calcd for $C_{23}H_{22}O_4$: 362.1518, found: 362.1504.



4ac

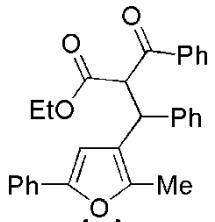
(**4ac**) Two diastereoisomers are hard to be separated by column chromatography on silica gel.^{1}H NMR (300 MHz, $CDCl_3$): δ = [7.48-7.46 (m, 2 H)]; [7.24-7.06 (m, 8 H)]; [6.50 (s, 0.39 H),6.46 (s, 0.61 H)]; [4.54 (d, *J* = 11.7 Hz, 1 H)]; [4.31 (d, *J* = 11.7 Hz, 1 H)]; [3.50(s, 1.16 H), 3.41 (s, 1.84 H)]; [2.26 (s, 3 H)]; [2.08(s, 1.83 H), 1.96 (s, 1.17 H)]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = (201.43, 201.24), (167.93, 167.82), (151.92, 151.61), 147.82, (141.10, 140.73), (130.65, 130.50), (128.76, 128.59), 128.45, 127.49, 127.26, (126.92, 126.80), (123.18, 123.13), (121.34, 121.02), (104.44, 104.31), (64.82, 64.46), (52.50, 52.35), (41.63, 41.47), (30.19, 30.14), (11.67, 11.64);

MS (70 eV): *m*/*z* (%): 362 (M^+, 52.96); 247 (100); HRMS calcd for $C_{23}H_{22}O_4$: 362.1518, found: 362.1533.



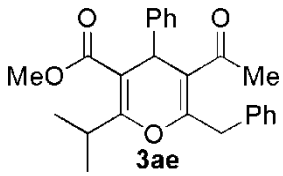
3ad

(**3ad**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30-7.07 (m, 15 H), 4.81 (s, 1H), 4.19 (d, *J* = 14.1 Hz , 1 H), 3.92 (d, *J* = 14.1 Hz, 1 H), 3.81 (q, 2 H), 2.16 (s, 3 H), 0.78 (t, *J* = 7.2 Hz, 3 H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.74, 166.52, 158.40, 156.86, 143.94, 137.03, 133.71, 129.67, 129.04, 128.82, 128.67, 128.43, 128.21, 127.60, 127.20, 126.69, 116.07, 109.29, 60.44, 40.10, 37.04, 29.73, 13.43 ppm; MS (70 eV): *m*/*z* (%): 438 (M^+, 21.20); 105 (100); HRMS calcd for $C_{29}H_{26}O_4$: 438.1831, found: 438.1849.



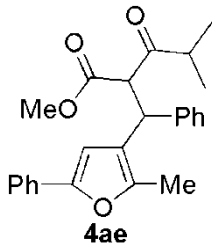
4ad

(**4ad)** Two diastereoisomers are hard to be separated by column chromatography on silica gel.^{1}H NMR (300 MHz, $CDCl_3$): δ = [7.96-7.91 (m, 2 H)]; [7.52-6.98 (m, 13 H)]; [6.61 (s, 0.35 H),6.36 (s, 0.65 H)]; [5.20 (d, *J* = 11.7 Hz, 0.35 H), 5.15 (d, *J* = 11.4 Hz, 0.65 H)]; [4.87 (d, *J* = 11.7 Hz, 0.35 H), 4.82 (d, *J* = 11.4 Hz, 0.65 H)]; [3.93-3.77 (m, 2 H)]; [2.31(s, 1.08H), 2.27 (s, 1.92 H)]; [0.92(t, *J* = 7.2 Hz, 1.05 H), 0.83(t, *J* = 7.2 Hz, 1.95 H)]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = (192.74, 192.64), (167.69, 167.56), (151.61, 151.52), (148.11, 147.93), (141.48, 141.26), 136.46, 133.53, (130.81, 130.66), (128.62, 128.59), (128.57, 128.53), (128.48, 128.36), (127.88, 127.45), (126.83, 126.79), (126.70, 126.55), (123.19, 123.12), (121.55, 121.51), (105.21, 104.47), (61.55, 61.44), (59.44, 59.35), (41.83, 41.53), (13.71, 13.63), 11.78; MS (70 eV): *m*/*z* (%): 438 (M^+, 35.24); 247 (100); HRMS calcd for $C_{29}H_{26}O_4$: 438.1831, found: 438.1837.



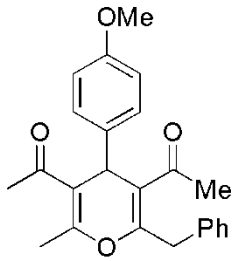
3ae

(**3ae**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23-7.08 (m, 10 H), 4.70 (s, 1H), 4.13 (d, *J* = 14.4 Hz , 1 H), 3.91 (d, *J* = 14.4 Hz, 1 H), 3.66-3.58 (m, 1 H), 3.59 (s, 3 H), 2.12 (s, 3 H), 0.97 (d, *J* = 6.9 Hz, 3 H), 0.78 (d, *J* = 6.6 Hz, 3 H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.78, 166.83, 165.25, 157.89, 144.51, 136.98, 128.98, 128.52, 128.32, 127.95, 126.93, 126.58, 116.17, 106.74, 51.41, 39.33, 37.01, 29.71, 29.17, 19.20, 19.17 ppm; MS (70 eV): *m*/*z* (%): 390 (M^+, 85.11); 313 (100); HRMS calcd for $C_{25}H_{26}O_4$: 390.1831, found: 390.1830



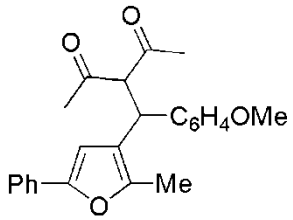
4ae

(**4ae**) Two diastereoisomers are hard to be separated by column chromatography on silica gel.^{1}H NMR (300 MHz, $CDCl_3$): δ = [7.51 (d, *J* = 8.1 Hz, 0.92 H), 7.46 (d, *J* = 7.8 Hz, 1.08 H)]; [7.23-7.08 (m, 8 H)]; [6.60 (s, 0.45 H), 6.41 (s, 0.55 H)]; [4.60 (d, *J* = 3.6 Hz, 0.34 H), 4.56 (d, *J* = 3.6 Hz, 0.66 H)]; [4.48 (d, *J* = 12.0 Hz, 0.66 H), 4.44 (d, *J* = 12.3 Hz, 0.34 H)]; [3.49(s, 1.34H), 3.40 (s, 1.66 H)]; [2.56-2.47(m, 0.55 H), 2.38-2.28(m, 0.45H)]; [2.25(s, 1.62H), 2.22 (s, 1.38 H)]; [0.96(d, *J* = 6.9 Hz, 1.65 H), 0.88(d, *J* = 6.9 Hz, 1.35 H)]; [0.77(d, *J* = 6.9 Hz, 1.65 H), 0.62(d, *J* = 6.9 Hz, 1.35 H)]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = (206.91, 206.82), (167.91, 167.83), (151.86, 151.54), (148.09, 147.86), (141.26, 140.97), (130.74, 130.59), (128.58, 128.45), 127.87, 127.29, (126.88, 126.81), (126.78, 126.74), (123.18, 123.16), (121.26, 121.17), (104.63, 104.52), (62.81, 61.70), (52.42, 52.26), (42.21, 42.08), (41.98, 41.71), (17.70, 17.55), (17.38, 17.17), (11.68, 11.55); MS (70 eV): *m*/*z* (%): 390 (M^+, 20.41); 43 (100); HRMS calcd for $C_{25}H_{26}O_4$: 390.1831, found: 390.1848.



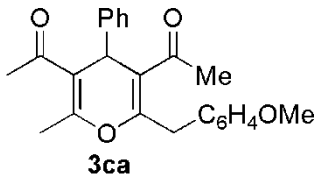
3ba

(**3ba**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27-7.23(m, 5H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 4.81(s, 1 H), 4.04 (d, *J* = 14.7Hz, 1 H), 3.98(d, *J* = 14.7Hz, 1 H), 3.76(s, 3 H), 2.23(s, 6 H), 2.22(s, 3 H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.91, 198.21, 158.52, 156.87, 156.64, 136.90, 136.23, 129.15, 128.71, 128.48, 126.68, 117.43, 117.36, 114.02, 55.16, 38.40, 37.09, 30.53, 29.92, 19.31 ppm; MS (70 eV): *m*/*z* (%): 376 (M^+, 100); HRMS calcd for $C_{24}H_{24}O_4$: 376.1675, found: 376.1680.



4ba

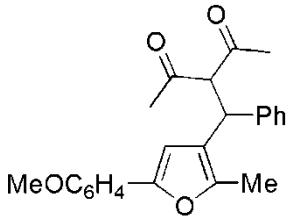
(**4ba**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.4 Hz, 2H), 7.34-7.16 (m, 5H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.54(s, 1 H), 4.62 (d, *J* = 12.3Hz, 1 H), 4.55 (d, *J* = 12.0Hz, 1 H), 3.73(s, 3 H), 2.35(s, 3 H), 2.09(s, 3 H), 1.99(s, 3 H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.84, 202.54, 158.34, 151.97, 147.32, 132.94, 130.49, 128.46, 128.41, 126.95, 123.19, 121.60, 114.19, 104.30, 74.33, 55.05, 41.14, 29.64, 29.59, 11.65 ppm; MS (70 eV): *m*/*z* (%): 376 (M^+, 41.25); 277 (100); HRMS calcd for $C_{24}H_{24}O_4$: 376.1675, found: 376.1689.



3ca

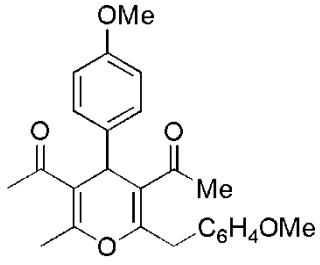
(**3ca**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26-7.18 (m, 7 H), 6.85 (d, *J* = 8.4 Hz, 2H), 4.86 (s, 1 H), 3.98 (d, *J* = 14.4 Hz, 1 H), 3.85 (d, *J* = 14.4 Hz, 1 H), 3.80 (s, 3 H), 2.25 (s, 3 H), 2.22(s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.81, 198.08, 158.43,

157.64, 157.02, 144.05, 129.77, 128.88, 128.72, 128.08, 127.11, 117.25, 117.01, 113.91, 55.23, 39.26, 36.26, 30.58, 30.00, 19.38 ppm; MS (70 eV): *m*/*z* (%): 376 (M^+, 100); HRMS calcd for $C_{24}H_{24}O_4$: 376.1675, found: 376.1667.



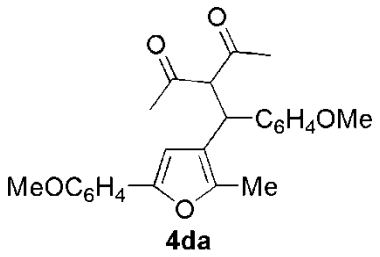
4ca

(**4ca**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.7 Hz, 2 H), 7.27-7.16 (m, 5 H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.41(s, 1 H), 4.65 (d, *J* = 12.0 Hz, 1 H), 4.59 (d, *J* = 12.0 Hz, 1 H), 3.78 (s, 3 H), 2.34 (s, 3 H), 2.10 (s, 3 H), 1.97 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.73, 202.51, 158.74, 152.08, 146.64, 140.99, 128.84, 127.40, 126.92, 124.68, 123.63, 121.09, 113.93, 102.71, 74.07, 55.15, 41.95, 29.66, 29.58, 11.62 ppm; MS (70 eV): *m*/*z* (%): 376 (M^+, 86.71); 43 (100); HRMS calcd for $C_{24}H_{24}O_4$: 376.1675, found: 376.1669.



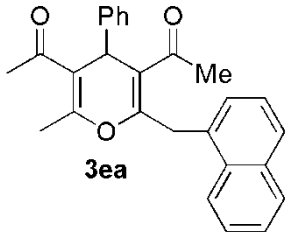
3da

(**3da**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 4.80(s, 1 H), 3.96 (d, *J* = 15.0 Hz, 1 H), 3.91 (d, *J* = 14.7Hz, 1 H), 3.79 (s, 3 H), 3.75 (s, 3 H), 2.24 (s, 3 H), 2.22 (s, 3 H), 2.21 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.92, 198.18, 158.48, 158.35, 157.26, 156.66, 136.26, 129.72, 129.12, 128.89, 117.34, 117.09, 113.98, 113.84, 55.17, 55.14, 38.36, 36.19, 30.50, 29.90, 19.32 ppm; MS (70 eV): *m*/*z* (%): 406 (M^+, 45.40); 298 (100); HRMS calcd for $C_{25}H_{26}O_5$: 406.1780, found: 406.1771.



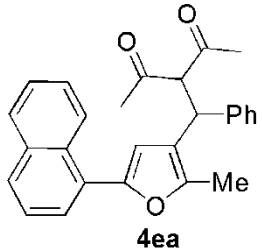
4da

(**4da**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.7 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.40(s, 1 H), 4.61 (d, *J* = 12.0 Hz, 1 H), 4.56 (d, *J* = 12.0 Hz, 1 H), 3.79 (s, 3 H), 3.74 (s, 3 H), 2.34 (s, 3 H), 2.10 (s, 3 H), 1.99 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.94, 202.64, 158.72, 158.33, 152.04, 146.47, 133.06, 128.42, 124.67, 123.68, 121.40, 114.18, 113.92, 102.69, 74.34, 55.15, 55.06, 41.22, 29.66, 29.59, 11.61 ppm; MS (70 eV): *m*/*z* (%): 406 (M^+, 58.19); 307 (100); HRMS calcd for $C_{25}H_{26}O_5$: 406.1780, found: 406.1794.



3ea

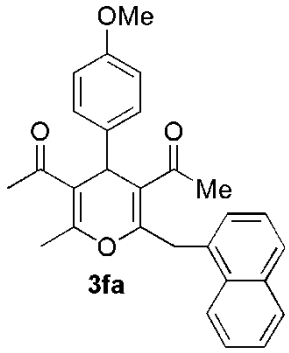
(**3ea**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 5.4 Hz, 1 H), 7.87 (d, *J* = 5.4 Hz, 1 H), 7.78 (d, *J* = 7.8 Hz, 1 H), 7.52 (d, *J* = 3.3 Hz, 1 H), 7.52-7.35 (m, 3 H), 7.30-7.21 (m, 5 H), 4.94 (s, 1 H), 4.52 (s, 2 H), 2.25 (s, 3 H), 2.20 (s, 3 H), 2.10(s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.93, 198.05, 157.22, 143.95, 133.76, 132.78, 132.10, 128.72(2C), 128.14(2C), 127.50, 127.14, 126.30, 126.12, 125.70, 125.47, 123.68, 118.01, 117.13, 39.29, 34.53, 30.55, 29.99, 19.19 ppm; MS (70 eV): *m*/*z* (%): 396 (M^+, 82.38); 43 (100); HRMS calcd for $C_{27}H_{24}O_3$: 396.1725, found: 396.1728.



4ea

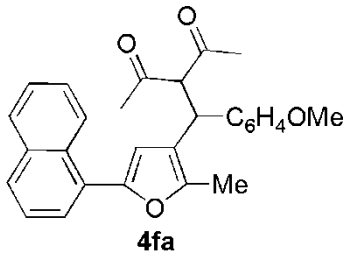
(**4ea**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 8.1 Hz, 1 H), 7.85 (d, *J* = 7.8 Hz, 1 H), 7.77 (d, *J* = 8.1 Hz, 1 H), 7.64 (d, *J* = 7.2 Hz, 1 H), 7.56-7.42 (m, 3H), 7.32-7.30

(m, 4 H), 7.24-7.18 (m, 1 H), 6.64 (s, 1 H), 4.73 (d, *J* = 12.0 Hz, 1 H), 4.66 (d, *J* = 12.0 Hz, 1 H), 2.43(s, 3 H), 2.17 (s, 3 H), 2.00(s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.77, 202.55, 151.58, 147.91, 141.00, 133.92, 129.98, 128.97, 128.51, 128.28, 128.20, 127.54, 127.06, 126.52, 125.83, 125.61, 125.30, 125.21, 121.04, 108.76, 74.39, 42.11, 29.85, 29.61, 11.83 ppm; MS (70 eV): *m*/*z* (%): 396 (M^+, 72.27); 43 (100); HRMS calcd for $C_{27}H_{24}O_3$: 396.1725, found: 396.1721.



3fa

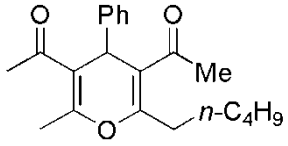
(**3fa**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09-8.06 (m, 1 H), 7.90-7.87 (m, 1 H), 7.79 (d, *J* = 7.8 Hz, 1 H), 7.55-7.38 (m, 4 H), 7.17 (d, *J* = 8.7 Hz, 2 H), 6.80 (d, *J* = 8.4 Hz, 2 H), 4.90 (s, 1 H), 4.53 (s, 2 H), 3.77 (s, 3 H), 2.26 (s, 3 H), 2.22 (s, 3 H), 2.11(s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.02, 198.13, 158.49, 156.84, 156.81, 136.16, 133.70, 132.79, 132.04, 129.18, 128.62, 127.42, 126.26, 126.05, 125.63, 125.42, 123.64, 118.07, 117.21, 113.97, 55.12, 38.39, 34.44, 30.45, 29.88, 19.11 ppm; MS (70 eV): *m*/*z* (%): 426 (M^+, 46.62); 43 (100); HRMS calcd for $C_{28}H_{26}O_4$: 426.1831, found: 426.1832.



4fa

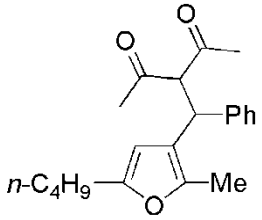
(**4fa**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (d, *J* = 8.4 Hz, 1 H), 7.84 (d, *J* = 8.1 Hz, 1 H), 7.77 (d, *J* = 8.1 Hz, 1 H), 7.64 (d, *J* = 6.9 Hz, 1 H), 7.56-7.42 (m, 3H), 7.23 (d, *J* = 8.4 Hz, 2 H), 6.83 (d, *J* = 8.4 Hz, 2 H), 6.64 (s, 1 H), 4.69 (d, *J* = 12.0 Hz, 1 H), 4.61 (d, *J* = 12.0 Hz, 1 H), 3.74 (s, 3 H), 2.42 (s, 3 H), 2.15(s, 3 H), 2.01(s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.93, 202.64, 158.41, 151.49, 147.70, 133.88, 133.02,

129.94, 128.52(2C), 128.48, 128.22, 126.49, 125.79, 125.56, 125.29, 125.19, 121.32, 114.27, 108.71, 74.58, 55.12, 41.33, 29.84, 29.59, 11.78 ppm; MS (70 eV): *m*/*z* (%): 426 (M^+, 0.28); 57 (100); HRMS calcd for $C_{28}H_{26}O_4$: 426.1831, found: 426.1839.



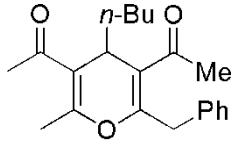
3ga

(**3ga**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27-7.17 (m, 5 H), 4.84 (s, 1 H), 2.63 (t, *J* = 7.2 Hz, 2 H), 2.31 (s, 3 H), 2.22 (s, 3 H), 2.20 (s, 3 H), 1.66-1.59 (m, 2 H), 1.37-1.32(m, 4 H), 0.91 (t, *J* = 6.3 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.63, 198.27, 159.90, 156.92, 144.25, 128.60, 127.97, 126.92, 116.94, 116.62, 39.10, 31.65, 31.44, 30.37, 30.14, 27.00, 22.32, 19.27, 13.91 ppm; MS (70 eV): *m*/*z* (%): 326 (M^+, 89.35); 249 (100); HRMS calcd for $C_{21}H_{26}O_3$: 326.1882, found: 326.1875.



4ga

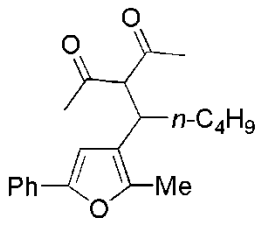
(**4ga**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29-7.16 (m, 5 H), 5.87 (s, 1 H), 4.58 (d, *J* = 12.0 Hz, 1 H), 4.51 (d, *J* = 12.3 Hz, 1 H), 2.47 (t, *J* = 7.5 Hz, 2 H), 2.23 (s, 3 H), 2.08 (s, 3 H), 1.95 (s, 3 H), 1.58-1.48 (m, 2 H), 1.34-1.27 (m, 2 H), 0.89 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.93, 202.72, 154.69, 145.33, 141.30, 128.76, 127.39, 126.78, 119.20, 103.93, 74.16, 42.15, 29.94, 29.71, 29.46, 27.62, 22.16, 13.70, 11.40 ppm; MS (70 eV): *m*/*z* (%): 326 (M^+, 24.66); 227 (100); HRMS calcd for $C_{21}H_{26}O_3$: 326.1882, found: 326.1881.



3ha

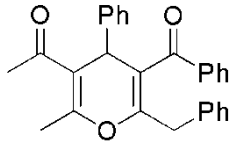
(**3ha**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20-7.14 (m, 5 H), 3.96 (d, *J* = 14.4 Hz, 1 H), 3.82 (d, *J* = 11.4 Hz, 1 H), 3.70 (t, *J* = 5.4 Hz, 1 H), 2.29 (s, 3 H), 2.27 (s, 3 H), 2.12

(s, 3 H), 1.29-1.01 (m, 6 H), 0.74 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.20, 198.34, 158.48, 158.28, 137.05, 128.61, 128.37, 126.54, 117.48, 116.91, 36.92(2C), 33.08, 29.87, 29.27, 26.96, 22.71, 19.05, 13.92 ppm; MS (70 eV): *m*/*z* (%): 326(M^+, 1.36); 269 (100); HRMS calcd for $C_{21}H_{26}O_3$: 326.1882, found: 326.1888.



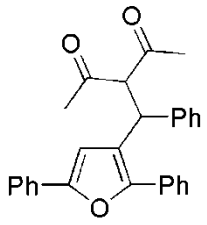
4ha

(**4ha**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.1 Hz, 2 H), 7.35 (dd, *J* = 7.8 Hz, 7.5 Hz , 2 H), 7.26-7.19 (m, 1 H), 6.42 (s, 1 H), 3.95 (d, *J* = 11.4 Hz, 1 H), 3.37-3.29 (m, 1 H), 2.31 (s, 3 H), 2.26 (s, 3 H), 1.94 (s, 3 H), 1.43-1.10 (m, 6 H), 0.84 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.48, 203.13, 152.10, 148.50, 130.69, 128.58, 126.98, 123.23, 120.38, 103.91, 75.28, 36.32, 33.49, 30.02, 29.51, 29.05, 22.32, 13.91, 11.69 ppm; MS (70 eV): *m*/*z* (%): 326 (M^+, 45.49); 43 (100); HRMS calcd for $C_{21}H_{26}O_3$: 326.1882, found: 326.1871.



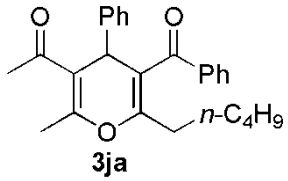
3ia

(**3ia**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 7.8 Hz, 2 H), 7.48 (dd, *J* = 7.5 Hz, 7.2 Hz, 1 H), 7.33 (dd, *J* = 7.5 Hz, 7.5 Hz, 2 H), 7.26-7.05 (m, 10 H), 4.93 (s, 1 H), 3.41 (d, *J* = 15.0 Hz, 1 H), 3.31 (d, *J* = 15.0 Hz, 1 H), 2.31 (s, 3 H), 2.07 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.94, 197.21, 158.17, 150.56, 143.24, 138.32, 136.34, 132.95, 128.86, 128.73, 128.60, 128.58, 128.36, 127.66, 127.18, 126.65, 117.16, 113.77, 41.80, 37.08, 29.64, 19.11 ppm; MS (70 eV): *m*/*z* (%): 408 (M^+, 89.32); 105 (100); HRMS calcd for $C_{28}H_{24}O_3$: 408.1725, found: 408.1729.



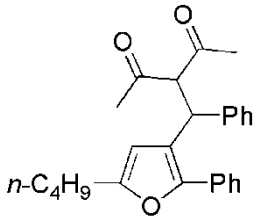
4ia

(**4ia**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73-7.68 (m, 4 H), 7.47-7.19 (m, 11 H), 6.86 (s, 1 H), 5.06 (d, *J* = 12.0 Hz, 1 H), 4.59 (d, *J* = 11.7 Hz, 1 H), 2.00 (s, 3 H), 1.94 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.87, 202.62, 153.16, 149.02, 140.69, 130.51, 130.14, 129.02, 128.74, 128.68, 127.93, 127.86, 127.71, 127.21, 126.55, 123.82, 122.49, 106.27, 75.69, 41.97, 30.99, 28.12 ppm; MS (70 eV): *m*/*z* (%): 408 (M^+,39.19); 105 (100); HRMS calcd for $C_{28}H_{24}O_3$: 408.1725, found: 408.1718.



3ja

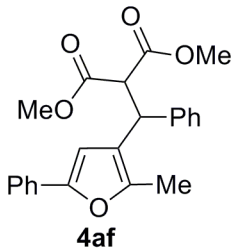
(**3ja**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50-7.44 (m, 3 H), 7.34-7.29 (m, 2 H), 7.24-7.10 (m, 5 H), 4.92 (s, 1 H), 2.40 (s, 3 H), 2.09 (s, 3 H), 1.96 (t, *J* = 7.8 Hz, 2 H), 1.50-1.37 (m, 2 H), 1.17-1.00 (m, 4 H), 0.78 (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.09, 197.54, 158.05, 152.81, 143.56, 138.84, 132.62, 128.76, 128.45, 128.39, 127.62, 126.99, 116.14, 113.70, 41.53, 31.09, 30.94, 29.57, 26.24, 22.03, 19.13, 13.75 ppm; MS (70 eV): *m*/*z* (%): 388 (M^+, 77.42); 105 (100); HRMS calcd for $C_{26}H_{28}O_3$: 388.2038, found: 388.2034.



4ja

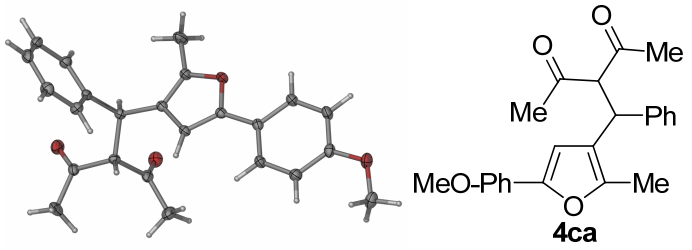
(**4ja**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.1 Hz, 2 H), 7.43(dd, *J* = 7.5 Hz, 7.8 Hz 2 H), 7.36-7.26 (m, 5 H), 7.24-7.18 (m, 1 H), 6.21 (s, 1 H), 4.99 (d, *J* = 11.7 Hz, 1 H), 4.52 (d, *J* = 12.0 Hz, 1 H), 2.64 (t, *J* = 7.5 Hz, 2 H), 1.98 (s, 3 H), 1.91(s, 3 H), 1.69-1.61 (m, 2 H), 1.43-1.36 (m, 2 H), 0.95 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75

MHz, $CDCl_3$): δ = 202.96, 202.76, 156.30, 147.58, 141.01, 130.89, 128.85, 128.55, 127.79, 127.33, 126.98, 126.19, 120.72, 106.25, 75.64, 42.05, 30.91, 29.86, 27.94, 27.73, 22.19, 13.73 ppm; MS (70 eV): *m/z* (%): 388 (M^+, 7.99); 69 (100); HRMS calcd for $C_{26}H_{28}O_3$: 388.2038, found: 388.2046.



4af

(**4af**)^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 7.2 Hz, 2 H), 7.33-7.17 (m, 8 H), 6.59 (s, 1 H), 4.63 (d, *J* = 11.7 Hz, 1 H), 4.20 (d, *J* = 12.0 Hz, 1 H), 3.63 (s, 3 H), 3.54 (s, 3 H), 2.36 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.01, 167.91, 151.75, 148.14, 140.85, 130.80, 128.65, 128.52, 127.52, 126.97, 126.90, 123.29, 121.14, 104.63, 57.37, 52.64, 52.51, 42.03, 11.75. ppm; MS (70 eV): *m/z* (%): 378 (M^+,32.34); 247 (100); HRMS calcd for $C_{23}H_{22}O_5$: 378.1467, found: 378.1469.



4ca

Figure 1. ORTEP depiction of compound **4ca** [4]

Reference:

1. a)T. Yao, X. Zhang, R. C. Larock, *J. Am. Chem. Soc*. **2004**, *126*, 11164; b) T. Yao, X. Zhang, R. C. Larock, *J. Org. Chem*. **2005**, *70*,7679.
2. P. J. Stang, D. H. Cao, G. T. Poulter, A. M. Arif, *Orgaometallics* **1995**, *14*, 1110.
3. S. Fallis, G. K. Anderson, N. P. Rath, *Organometallics* **1991**, *10*, 3180.
4. X-ray data for compound **4ca** (CH_2Cl_2/hexane)**:** $C_{24}H_{24}O_4$, Mw = 376.43, monoclinic, P2(1)/C space group, Mo-Kα(0.71073Å), R1(I > 2σ(I))= 0.0366, wR2 = 0.0985, a = 21.7484(4) Å, b = 8.3844(2) Å, c = 11.0805(2) Å, β = 101.215(1) °, V = 1981.92(7) Å^3, T = 173(2) K, Z = 4, reflections collected /unique: 17045/3476 (Rint = 0.0230), number of observations [I > 2σ(I)] 3025, parameters 254. CCDC 717871(**4ca**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge form The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

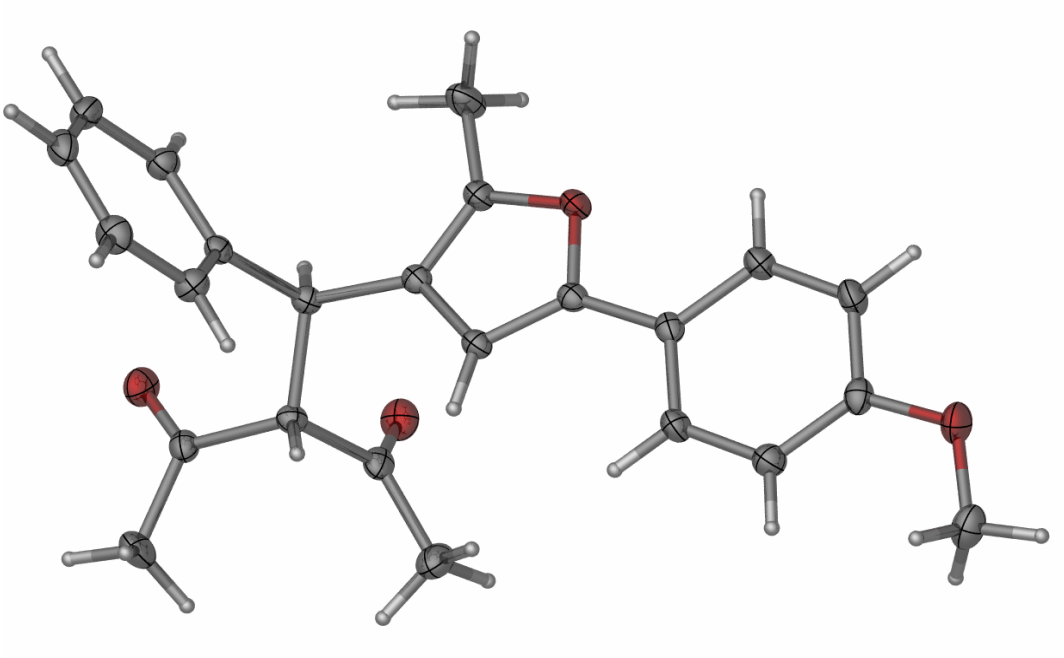


Figure 1. ORTEP depiction of compound **4ca**