

Selective Oxygenation of Alkynes: A Direct Approach to Diketones and Vinyl Acetate

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General Remarks: Column chromatography was carried out on silica gel. Unless noted ^1H NMR spectra were recorded on 400 MHz in CDCl_3 and d -DMSO, ^{13}C NMR spectra were recorded on 100 MHz in CDCl_3 and d -DMSO. IR spectra were recorded on an FT-IR spectrometer and only major peaks are reported in cm^{-1} . Melting points were determined on a microscopic apparatus and were uncorrected. All new products were further characterized by HRMS (high resolution mass spectra), high resolution mass spectrometry (HRMS) spectra was obtained on a microTOF-Q instrument equipped with an ESI source; copies of their ^1H NMR and ^{13}C NMR spectra are provided. Commercially available reagents and solvents were used without further purification. The starting materials **1** were prepared according to the previous work.^[1]

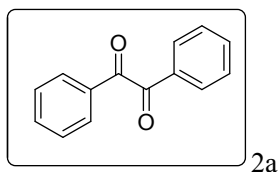
Typical procedure for the synthesis of product 2.

To a solution of 1,2-diphenylethyne (**1a**, 0.3 mmol, 53.4 mg) in HOAc/HFIP (V:V = 1:2, 2.0 mL) was added $\text{Cu}(\text{OTf})_2$ (10.9 mg, 10 mol%), $\text{PhI}(\text{OAc})_2$ (289 mg, 3 equiv.). The reaction mixture was then stirred for 12 h at room temperature in air. The resulting mixture was quenched with saturation $\text{Na}_2\text{S}_2\text{O}_3$ and extracted twice with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. Purification of the crude product by flash column chromatography afforded the product **2** (petroleum ether/ethyl acetate as eluent (30:1)).

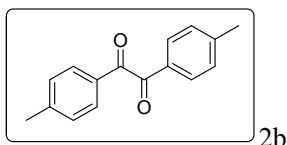
Typical procedure for the synthesis of product 3.

To a solution of 1,2-diphenylethyne (**1a**, 0.3 mmol, 53.4 mg) in HOAc/HFIP (V:V = 2:1, 2.0 mL) was added $n\text{-Bu}_4\text{NI}$ (132.8 mg, 1.2 equiv.), $\text{PhI}(\text{OAc})_2$ (231 mg, 2.4 equiv.). The reaction mixture was then stirred for 12 h at room temperature in air. The resulting mixture was quenched with saturation $\text{Na}_2\text{S}_2\text{O}_3$ and extracted twice with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. Purification of the crude product by flash column chromatography afforded the product **3** (petroleum ether/ethyl acetate as eluent (30:1)).

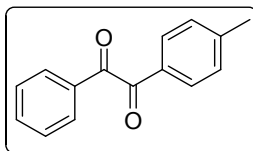
Characterization data of compounds 2 and 3.



m.p. = 87-89 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.96-7.98 (m, 4 H), 7.62-7.66 (m, 2 H), 7.48-7.51 (m, 4 H); ^{13}C NMR (100 MHz, CDCl_3): 194.5, 134.8, 132.9, 129.8, 128.9; IR(cm^{-1}): 3064, 2922, 1659, 1594, 1579, 1449, 1211, 1173, 875, 795, 718, 696, 642; MS ($\text{C}_{14}\text{H}_{10}\text{O}_2$): 210 (M^+);

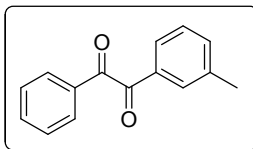


m.p. = 88-90 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.88-7.90 (m, 4 H), 7.31-7.33 (m, 4 H), 2.45 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3): 194.5, 146.0, 130.6, 129.9, 129.6, 21.8; IR(cm^{-1}): 2925, 1665, 1604, 1572, 1327, 1221, 1174, 886, 829, 781, 744, 693, 598; MS ($\text{C}_{16}\text{H}_{14}\text{O}_2$): 238 (M^+);



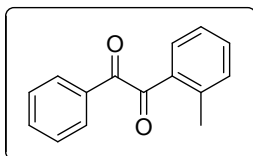
2c

m.p. = 94-96 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.94-7.96 (m, 2 H), 7.84-7.86 (m, 2 H), 7.58-7.60 (m, 1 H), 7.44-7.48 (m, 2 H), 7.26-7.28 (m, 2 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 194.6, 194.1, 146.1, 134.6, 132.9, 130.4, 129.8, 129.6, 128.8, 21.7; IR(cm^{-1}): 3066, 1776, 1671, 1603, 1214, 1175, 879, 828, 747, 716, 686; MS ($\text{C}_{15}\text{H}_{12}\text{O}_2$): 224 (M^+);



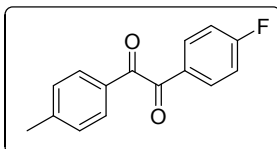
2d

m.p. = 73-75 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.96-7.98 (m, 2 H), 7.76-7.78 (m, 2 H), 7.63-7.67 (m, 1 H), 7.41-7.52 (m, 3 H), 7.37-7.39 (m, 1 H), 2.40 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 194.8, 194.7, 138.9, 135.7, 134.8, 132.9, 130.1, 129.8, 128.9, 128.8, 127.2, 21.2; IR(cm^{-1}): 3061, 2924, 1671, 1598, 1583, 1449, 1233, 1164, 837, 791, 772, 740, 710; MS ($\text{C}_{15}\text{H}_{12}\text{O}_2$): 224 (M^+);



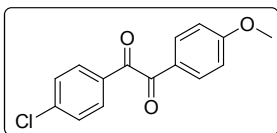
2e

m.p. = 53-55 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.96-7.98 (m, 2 H), 7.63-7.65 (m, 2 H), 7.46-7.53 (m, 3 H), 7.33-7.35 (m, 1 H), 7.24-7.25 (m, 1 H), 2.71 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 196.7, 194.8, 141.3, 134.7, 133.7, 133.0, 132.5, 132.4, 131.7, 129.9, 128.9, 128.4, 125.9, 21.9; IR(cm^{-1}): 1969, 1777, 1676, 1597, 1449, 1206, 880, 761, 736, 720; MS ($\text{C}_{15}\text{H}_{12}\text{O}_2$): 224 (M^+);



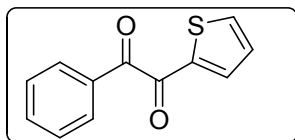
2f, oil

^1H NMR (400 MHz, CDCl_3): δ 8.00-8.04 (m, 2 H), 7.87-7.89 (m, 2 H), 7.31-7.33 (m, 2 H), 7.16-7.21 (m, 2 H), 2.45 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 193.8, 192.9, 167.9, 165.4, 146.3, 130.0, 129.7, 129.6, 129.2, 128.5, 116.4, 116.2, 21.8; IR(cm^{-1}): 2961, 2924, 1779, 1672, 1598, 1506, 1414, 1231, 1211, 1156, 885, 847, 756, 598; MS ($\text{C}_{15}\text{H}_{11}\text{FO}_2$): 242 (M^+);



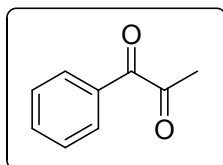
2g

m.p. = 109-111 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.91-7.95 (m, 4 H), 7.47-7.49 (m, 2 H), 6.97-6.99 (m, 2 H), 3.89 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 193.3, 192.4, 165.1, 141.3, 132.4, 131.2, 129.3, 125.8, 114.4, 55.6; IR(cm^{-1}): 1660, 1596, 1263, 1215, 1166, 1020, 836, 744; MS ($\text{C}_{15}\text{H}_{11}\text{ClO}_3$): 274 (M^+);



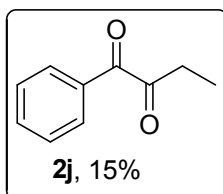
2h, oil

^1H NMR (400 MHz, CDCl_3): δ 7.95-7.97 (m, 2 H), 7.75-7.77 (m, 1 H), 7.72-7.73 (m, 1 H), 7.56-7.60 (m, 1 H), 7.42-7.46 (m, 2 H), 7.10-7.12 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3): 192.0, 185.6, 139.8, 136.9, 136.7, 134.8, 132.6, 130.2, 129.6, 128.9, 128.8; IR(cm^{-1}): 3106, 2964, 1652, 1511, 1414, 1215, 1065, 729, 649; MS ($\text{C}_{12}\text{H}_8\text{SO}_2$): 216 (M^+);



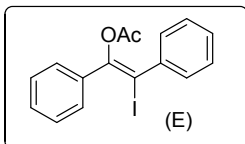
2i, oil

^1H NMR (400 MHz, CDCl_3): δ 8.00-8.03 (m, 2 H), 7.63-7.66 (m, 1 H), 7.48-7.52 (m, 2 H), 2.53 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 200.5, 191.4, 134.6, 131.7, 130.3, 128.8, 26.4; IR(cm^{-1}): 2959, 2927, 1736, 1715, 1675, 1206, 1076, 968, 763, 701; MS ($\text{C}_9\text{H}_8\text{O}_2$): 148 (M^+);



2j, 15%

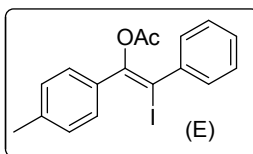
^1H NMR (400 MHz, CDCl_3): δ 7.96-7.98 (m, 2 H), 7.62-7.66 (m, 1 H), 7.47-7.52 (m, 2 H), 2.91 (dd, J = 16.0, 8.0 Hz, 2 H), 1.19 (t, J = 6.0 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 203.8, 192.6, 147.1, 134.5, 128.8, 123.9, 119.1, 34.8, 6.8; IR(cm^{-1}): 2961, 2926, 1764, 1714, 1673, 1493, 1449, 1188, 1081, 968, 697;



3a

m.p. = 144-146 $^{\circ}\text{C}$ (lit. m.p. = 146-146.5 $^{\circ}\text{C}$).^[3] ^1H NMR (400 MHz, CDCl_3): δ 7.63-7.65 (m, 2 H), 7.32-7.43 (m, 7 H), 7.26-7.27 (m, 1 H), 1.81 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 168.5, 147.2, 140.7, 137.1, 129.6, 129.3, 128.4, 128.3, 128.2, 128.0, 89.0, 20.4; IR(cm^{-1}): 1748, 1648, 1545, 1191, 759, 705;

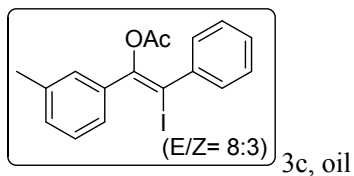
HRMS (ESI) m/z : calcd for $\text{C}_{16}\text{H}_{13}\text{INaO}_2$: $\text{M}+\text{Na}$ = 386.9858; found: 386.9851.



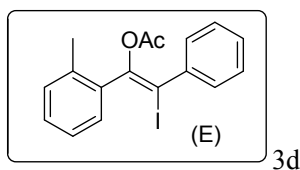
3b

m.p. = 77-79 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.44-7.46 (m, 2 H), 7.32-7.34 (m, 2 H), 7.21-7.23 (m, 2 H), 7.15-7.17 (m, 1 H), 7.10-7.12 (m, 2 H), 2.28 (s, 3 H), 1.71 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 168.4, 147.2, 140.7, 139.2, 134.1, 129.4, 128.6, 128.4, 128.1, 88.4, 21.3, 20.3; IR(cm^{-1}): 3028, 2923, 1760, 1672, 1443, 1368, 1177, 1044, 819, 750, 725, 697;

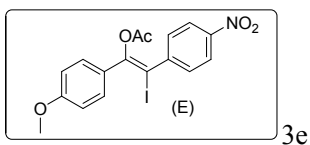
HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{15}\text{INaO}_2$: $\text{M}+\text{Na}$ = 401.0014; found: 401.0011.



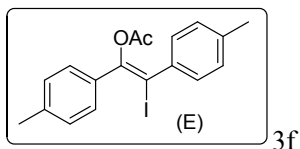
^1H NMR (400 MHz, CDCl_3): δ 7.62-7.64 (m, 1 H), 7.21-7.32 (m, 10 H), 7.16-7.18 (m, 1 H), 2.38 (s, 3 H), 2.34 (s, 1.5 H), 1.80 (s, 4 H); ^{13}C NMR (100 MHz, CDCl_3): 168.5, 147.3, 140.7, 136.9, 130.0, 129.2, 129.1, 128.4, 128.2, 128.0, 127.9, 126.7, 125.3, 89.3, 88.7, 21.4, 20.3; IR (cm^{-1}): 3029, 1756, 1369, 1043, 750, 726, 696; HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{15}\text{INaO}_2$: $M+\text{Na} = 401.0014$; found: 401.0015.



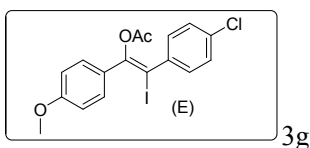
^1H NMR (400 MHz, CDCl_3): δ 7.43-7.45 (m, 1 H), 7.28-7.38 (m, 2 H), 7.20-7.24 (m, 2 H), 7.16-7.19 (m, 4 H), 2.41 (s, 3 H), 1.72 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 168.2, 147.5, 139.9, 136.9, 136.8, 130.8, 130.0, 129.3, 128.5, 128.3, 128.2, 125.5, 92.0, 20.3, 19.5; IR (cm^{-1}): 3066, 2925, 1750, 1369, 1188, 1031, 905, 749, 728, 696. HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{15}\text{INaO}_2$: $M+\text{Na} = 401.0014$; found: 401.0009.



m.p. = 119-121 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 8.19-8.22 (m, 2 H), 7.57-7.60 (m, 4 H), 6.92-6.95 (m, 2 H), 3.84 (s, 3 H), 1.87 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 168.3, 160.4, 148.8, 147.5, 130.9, 129.7, 123.4, 113.5, 84.1, 55.3, 20.4; IR (cm^{-1}): 2933, 2839, 1763, 1599, 1514, 1345, 1253, 1188, 1172, 1110, 913, 747, 694; HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{14}\text{INNaO}_5$: $M+\text{Na} = 461.9814$; found: 461.9809.

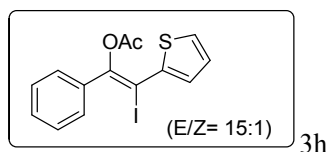


m.p. = 190-192 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.43-7.45 (m, 2 H), 7.22-7.24 (m, 2 H), 7.10-7.12 (m, 2 H), 7.03-7.05 (m, 2 H), 2.28 (s, 3 H), 2.25 (s, 3 H), 1.74 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 168.6, 146.9, 139.2, 138.1, 137.9, 134.4, 130.6, 130.1, 129.9, 129.7, 129.5, 128.8, 128.7, 128.4, 88.9, 21.4, 21.2, 20.4; IR (cm^{-1}): 3027, 2923, 2865, 1762, 1669, 1605, 1511, 1367, 1192, 1177, 1042, 915, 819, 753; HRMS (ESI) m/z : calcd for $\text{C}_{18}\text{H}_{17}\text{INaO}_2$: $M+\text{Na} = 415.0171$; found: 415.0169.

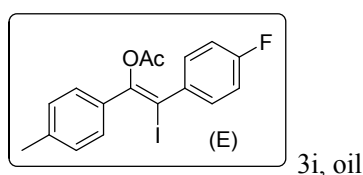


m. p. = 77-79 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.56-7.58 (m, 2 H), 7.29-7.35 (m, 4 H), 6.90-6.92

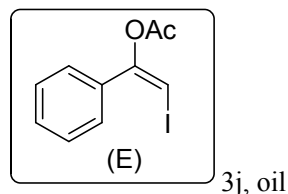
(m, 2 H), 3.81 (s, 3 H), 1.84 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 168.5, 160.2, 147.6, 139.4, 133.9, 131.0, 129.9, 128.4, 113.4, 86.4, 55.2, 20.4;
 IR(cm^{-1}): 2955, 2930, 1763, 1669, 1599, 1509, 1252, 1191, 1171, 1030, 833, 774, 608;
 HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{14}\text{ClINaO}_3$: $M+\text{Na} = 450.9574$; found: 450.9560.



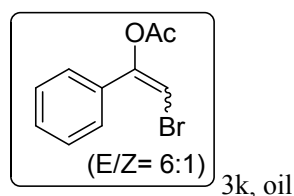
m.p. = 66-68 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.62 (s, 0.6 H), 7.30-7.40 (m, 5 H), 7.21-7.24 (m, 1.6 H), 7.06-7.08 (m, 0.6 H), 2.34 (s, 0.2 H), 1.84 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 168.2, 141.7, 141.3, 136.6, 131.1, 130.1, 128.4, 128.2, 128.1, 127.4, 126.8, 88.3, 87.7, 20.2;
 IR(cm^{-1}): 1765, 1606, 1418, 1366, 1019, 894, 747, 698;
 HRMS (ESI) m/z : calcd for $\text{C}_{14}\text{H}_{11}\text{SiNaO}_2$: $M+\text{Na} = 392.9422$; found: 392.9399.



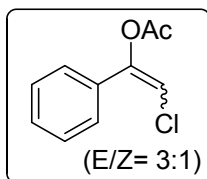
^1H NMR (400 MHz, CDCl_3): δ 7.51-7.53 (m, 2 H), 7.38-7.41 (m, 2 H), 7.19-7.21 (m, 2 H), 6.99-7.03 (m, 2 H), 2.37 (s, 3 H), 1.82 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 168.4, 163.4, 160.9, 147.7, 139.4, 136.8, 133.9, 130.4, 130.3, 129.4, 128.7, 115.2, 115.0, 87.0, 21.4, 20.3;
 IR(cm^{-1}): 1763, 1672, 1649, 1598, 1507, 1225, 1191, 1043, 915, 826, 760;
 HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{14}\text{FINaO}_2$: $M+\text{Na} = 418.9920$; found: 418.9915.



^1H NMR (400 MHz, CDCl_3): δ 7.59-7.61 (m, 2 H), 7.37-7.39 (m, 3 H), 6.34 (s, 1 H), 2.15 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 168.5, 151.2, 134.4, 129.5, 128.8, 128.1, 67.0, 20.8; IR(cm^{-1}): 2956, 2925, 1761, 1594, 1443, 1368, 1195, 1044, 894, 796, 694;
 HRMS (ESI) m/z : calcd for $\text{C}_{10}\text{H}_9\text{INaO}_2$: $M+\text{Na} = 310.9545$; found: 310.9539.



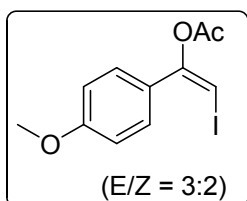
^1H NMR (400 MHz, CDCl_3): δ 8.08-8.10 (m, 0.5 H), 7.62-7.64 (m, 2 H), 7.49-7.53 (m, 0.6 H), 7.37-7.41 (m, 3 H), 6.72 (s, 0.3 H), 6.56 (s, 0.2 H), 6.32 (s, 1 H), 2.35 (s, 0.6 H), 2.18 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 168.5, 148.7, 134.3, 132.9, 128.1, 124.8, 97.6, 20.7; IR(cm^{-1}): 1767, 1698, 1544, 1371, 1200, 1056, 769, 697;
 HRMS (ESI) m/z : calcd for $\text{C}_{10}\text{H}_9\text{BrNaO}_2$: $M+\text{Na} = 262.9684$; found: 262.9678.



3l, oil

^1H NMR (400 MHz, CDCl_3): δ 7.62-7.64 (m, 2 H), 7.34-7.37 (m, 5 H), 6.44 (s, 0.3 H), 6.24 (s, 0.8 H), 2.33 (s, 1 H), 2.19 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 168.8, 167.3, 148.4, 147.7, 129.3, 128.7, 128.2, 127.9, 124.6, 110.4, 107.9, 20.7, 20.4; IR (cm^{-1}): 1769, 1646, 1541, 1515, 1202, 1064, 749, 694;

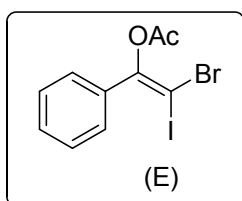
HRMS (ESI) m/z : calcd for $\text{C}_{10}\text{H}_9\text{ClNaO}_2$: $M+\text{Na} = 219.0189$; found: 219.0183.



3m, oil

^1H NMR (400 MHz, CDCl_3): δ 7.55-7.58 (m, 2 H), 7.46-7.48 (m, 1.4 H), 7.32-7.38 (m, 1.7 H), 7.19-7.23 (m, 1.2 H), 6.86-6.91 (m, 5.3 H), 6.23 (s, 1 H), 3.82 (s, 8.8 H), 2.17 (s, 2 H), 2.15 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 168.5, 167.0, 160.3, 160.2, 150.9, 133.7, 130.8, 130.2, 129.0, 126.8, 126.7, 113.5, 65.8, 55.3, 55.2, 20.8; IR (cm^{-1}): 1746, 1648, 1511, 1252, 1187, 827, 694;

HRMS (ESI) m/z : calcd for $\text{C}_{11}\text{H}_{12}\text{IO}_3$: $M+\text{H} = 318.9831$; found: 318.9826.



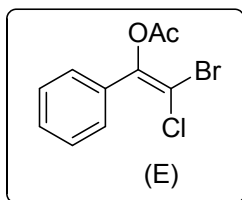
3n, oil

^1H NMR (400 MHz, CDCl_3): δ 7.52-7.54 (m, 2 H), 7.38-7.40 (m, 3 H), 2.18 (s, 3 H);

^{13}C NMR (100 MHz, CDCl_3): 166.9, 151.0, 134.9, 129.7, 129.3, 128.2, 47.7, 20.5;

IR (cm^{-1}): 1769, 1744, 1648, 1541, 1188, 894, 690;

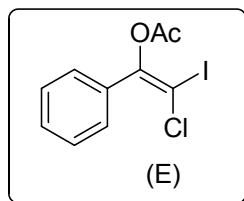
HRMS (ESI) m/z : calcd for $\text{C}_{10}\text{H}_8\text{BrNaO}_2$: $M+\text{Na} = 388.8650$; found: 388.8645.



3o, oil

^1H NMR (400 MHz, CDCl_3): δ 7.54-7.56 (m, 2 H), 7.37-7.39 (m, 3 H), 2.2 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 167.1, 146.1, 133.2, 129.7, 128.9, 128.2, 113.9, 101.6, 20.4; IR (cm^{-1}): 1769, 1744, 1648, 1541, 1514, 1188, 1058, 757, 690;

HRMS (ESI) m/z : calcd for $\text{C}_{10}\text{H}_8\text{BrClNaO}_2$: $M+\text{Na} = 296.9294$; found: 296.9288.

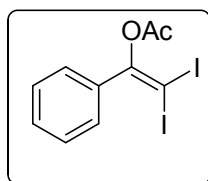


3p, oil

^1H NMR (400 MHz, CDCl_3): δ 7.50-7.53 (m, 2 H), 7.37-7.39 (m, 3 H), 2.17 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 167.1, 149.3, 134.8, 129.7, 129.4, 128.2, 65.9, 20.3;

IR (cm^{-1}): 1769, 1745, 1648, 1541, 1515, 1188, 1058, 765, 694;

HRMS (ESI) m/z : calcd for $\text{C}_{10}\text{H}_8\text{IClNaO}_2$: $M+\text{Na}$ = 344.9155; found: 344.9150.

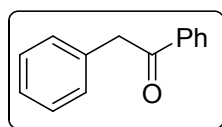


3q, oil

^1H NMR (400 MHz, CDCl_3): δ 7.51-7.53 (m, 2 H), 7.36-7.38 (m, 3 H), 2.17 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 166.9, 154.3, 134.7, 129.6, 129.3, 128.2, 20.8;

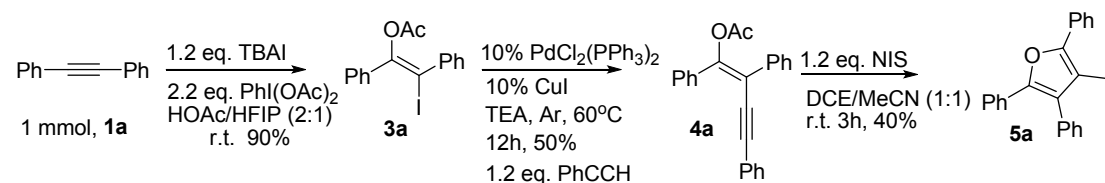
IR (cm^{-1}): 1645, 1544, 1514, 1187, 1050, 769, 690;

HRMS (ESI) m/z : calcd for $\text{C}_{10}\text{H}_8\text{I}_2\text{NaO}_2$: $M+\text{Na}$ = 436.8511; found: 436.8506.



^1H NMR (400 MHz, CDCl_3): δ 7.99-8.02 (m, 2 H), 7.52-7.54 (m, 1 H), 7.42-7.46 (m, 2 H), 7.23-7.33 (m, 5 H), 4.27 (s, 2 H); ^{13}C NMR (100 MHz, CDCl_3): 197.5, 136.5, 134.5, 133.1, 129.4, 128.6, 128.5, 126.8, 45.4;

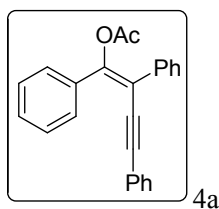
Synthetic Transformations



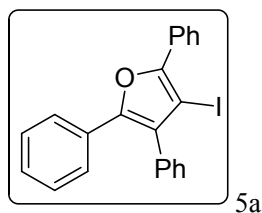
To a test tube equipped with a magnetic stir bar was charged with **3a** (327.6 mg, 0.9 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (63.1 mg, 10 mol%), CuI (17.2 mg, 10 mol%). The tube was sealed with a septum, evacuated and backfilled with Ar three times. Freshly degassed Et_3N was then added to the tube. Then ethynylbenzene (110 mg, 1.2 equiv.) was added to the tube via syringe. After stirring at 60 $^\circ\text{C}$ for 12 h, saturated solution NH_4Cl was added to quench the reaction and extracted twice with EtOAc . The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. Purification of the crude product by flash column chromatography afforded the product **4a** (petroleum ether/ethyl acetate as eluent (30:1)).

To a solution of **4a** (0.45 mmol, 152.1 mg) in DCE/MeCN (V:V = 1:1, 6.0 mL) was added NIS (121.5 mg, 1.2 equiv.). The reaction mixture was then stirred for 3 h at room temperature in air. The resulting mixture was quenched with saturation $\text{Na}_2\text{S}_2\text{O}_3$ and extracted twice with EtOAc .

The combined organic extracts were washed with brine, dried over Na₂SO₄ and concentrated. Purification of the crude product by flash column chromatography afforded the product **5a** (petroleum ether/ethyl acetate as eluent (30:1)).



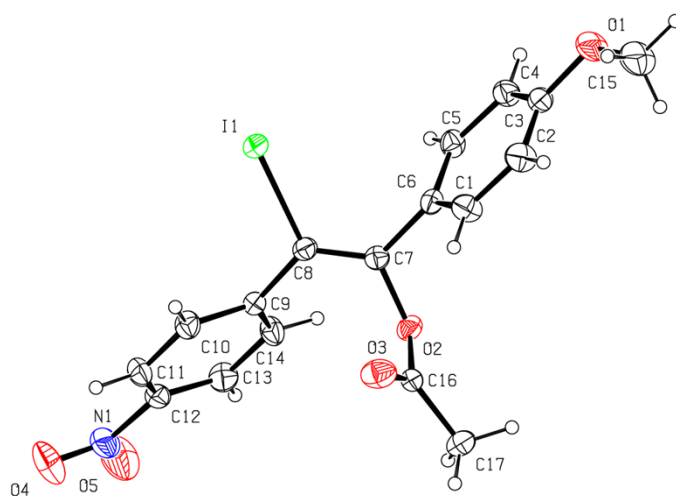
¹H NMR (400 MHz, CDCl₃): δ 7.92-7.94 (m, 2 H), 7.57-7.59 (m, 2 H), 7.31-7.37 (m, 8 H), 7.20-7.24 (m, 3 H), 1.95 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): 168.6, 151.0, 136.5, 134.7, 128.3, 127.7, 122.9, 113.7, 94.2, 88.4, 20.9; IR(cm⁻¹): 2927, 2927, 1749, 1648, 1544, 1517, 1192, 1054, 756, 701; HRMS (ESI) m/z: calcd for C₂₄H₁₈NaO₂: M+Na = 361.1204; found: 361.1199.



¹H NMR (400 MHz, *d*-DMSO): δ 8.10-8.11 (m, 2 H), 7.31-7.54 (m, 13 H); ¹³C NMR (100 MHz, *d*-DMSO): 149.9, 147.9, 133.4, 130.2, 129.7, 129.6, 129.3, 128.9, 128.8, 128.7, 128.3, 128.1, 127.9, 126.2, 125.2, 73.0; IR(cm⁻¹): 1645, 1548, 1517, 1459, 1393, 1187, 1117, 1003, 819, 765, 694; HRMS (ESI) m/z: calcd for C₂₂H₁₅IO₂: M⁺ = 422.0168; found: 422.0160.

Reference: [1] H. Xu, S. Gu, W. Chen, D. Li, and J. Dou. *J. Org. Chem.*, **2011**, 76, 2448–2458. [2] Y.-S. Feng, Z.-Q. Xu, L. Mao, F.-F. Zhang, and H.-J. Xu. *Org. Lett.*, **2013**, 15, 1472–1475. [3] Y. Ogata and I. Urasaki, *J. Org. Chem.*, **1971**, 36, 2164.

Crystal Data and Structure Refinement for **3e**.



No syntax errors found.

[CIF](#)

[dictionary](#)

Bond precision:	C-C = 0.0050 Å	Wavelength=0.71000	
Cell:	a=10.7835(4)	b=8.1115(3)	c=19.3202(7)
	alpha=90	beta=90.523(4)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	1689.87(11)	1689.87(11)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C17 H14 I N O5	C17 H14 I N O5	
Sum formula	C17 H14 I N O5	C17 H14 I N O5	
Mr	439.19	439.19	
Dx, g cm ⁻³	1.726	1.726	
Z	4	4	
Mu (mm ⁻¹)	1.921	1.921	
F000	864.0	864.0	
F000'	862.51		
h, k, lmax	13, 10, 23	13, 10, 23	
Nref	3322	3318	
Tmin, Tmax	0.526, 0.619	0.665, 1.000	
Tmin'	0.515		
Correction method=	MULTI-SCAN		
Data completeness=	0.999	Theta(max)= 25.990	
R(reflections)=	0.0321(2870)	wR2(reflections)= 0.0793(3318)	
S =	1.028	Npar= Npar = 219	