Efficient Nickel-Catalyzed [2+2+2] Cycloaddition of CO_2 and Diynes

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Supporting Information

General information. $Ni(COD)_2$ and 2,8-decadiyne (**9**) were purchased from Strem and TCI America, respectively, and used without further purification. Complexes $Ni(IPr)_2$ and ligand IPr were prepared as previously reported or under slightly modified procedures and handled in a N_2 filled drybox or using standard Schlenk techniques.[1] Diynes 2,2-di-but-2-ynyl-malonic acid dimethyl ester (**1**),[2] 2,2-di-pent-2-ynyl-malonic acid dimethyl ester (**2**), 2,2-bis-(4-methyl-pent-2-ynyl)-malonic acid dimethyl ester (**3**), 5,5-dibenzyloxymethyl-2,7-nonadiyne (**4**), 5,5-bis-(tert-butyl-dimethyl-silanyloxymethyl)-nona-2,7-diyne (**5**), 5,5-di-but-2-ynyl-2,2-dimethyl-[1,3]dioxane (**6**),[3] 2-but-2-ynyl-hex-4-ynoic acid methyl ester (**7**),[4] 2,3-di-but-2-ynyl-2,3-bis-ethoxycarbonyl-succinic acid diethyl ester (**8**), 2,2-bis-(4,4-dimethyl-pent-2-ynyl)-malonic acid dimethyl ester (**22**)**,** 1,8-bis-trimethylsilanyl-octa-1,7-diyne (**23**)[5] and 2-But-2-ynyl-2-(3-trimethylsilanyl-prop-2-ynyl)-malonic acid dimethyl ester (**24**) were prepared using literature procedures or under slightly modified procedures.[6]

^1H and ^{13}C NMR spectra were recorded on a GE-300 NMR and referenced to residual protiated solvent (resonances downfield to the standard are reported as positive). All ^{13}C NMR spectra were proton decoupled. Low-resolution mass spectra were obtained on a Hewlett Packard 5890 series II gas chromatograph interfaced with a Hewlett Packard 5989A mass spectrometer. IR spectra were recorded on a Mattson Polaris FT-IR spectrometer. Elemental analyses were performed at Midwest Microlab LLC., Indianapolis, IN. High-resolution mass spectra (HR-MS) (EI) were provided by the University of Utah Mass Spectrometry Facility.

2,2-Di-pent-2-ynyl-malonic acid dimethyl ester (2)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): 3.86 (s, 6H), 3.03 (t, 2.4 Hz, 4H), 2.24 (qt, 7.6 Hz, 2.4 Hz, 4H), 1.20 (t, 7.5 Hz, 6H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 169.4, 84.7, 73.2, 57.1, 52.6, 22.7, 13.8, 12.1.

2,2-Bis-(4-methyl-pent-2-ynyl)-malonic acid dimethyl ester (3)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): 3.74 (s, 6H), 2.90 (d, 2.2 Hz, 4H), 2.48 (sept of t, 6.9 Hz, 2.2 Hz, 2H), 1.11 (d, 6.9 Hz, 12H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 169.9, 89.6, 73.7, 57.8, 53.0, 23.4, 23.1, 20.7.

5,5-Dibenzyloxymethyl-2,7-nonadiyne (4)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.38-7.54 (m, 10H), 4.67 (s, 4H), 3.61 (s, 4H), 2.48 (q, 2.5 Hz, 4H), 1.90 (t, 2.5 Hz, 6H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 140.0, 130.4, 129.5, 128.3, 127.4, 76.6, 73.5, 43.5, 23.5, 4.8.

5,5-Bis-(tert-butyl-dimethyl-silanyloxymethyl)-nona-2,7-diyne5)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): 3.62 (s, 4H), 2.31 (q, 2.5 Hz, 4H), 1.91 (t, 2.5 Hz, 6H), 1.02 (s, 18H), 0.17 (s, 12H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 78.2, 77.1, 64.7, 44.8, 27.0, 22.3, 19.4, 4.8, -4.4.

5,5-Di-but-2-ynyl-2,2-dimethyl-[1,3]dioxane (6)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): 3.88 (s, 4H), 2.46 (q, 2.5 Hz, 4H), 1.92 (t, 2.5 Hz, 6H), 1.55 (s, 6H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 99.1, 79.5, 75.7, 67.2, 36.5, 25.0, 24.2, 4.7.

2-But-2-ynyl-hex-4-ynoic acid methyl ester (7)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): 3.72 (s, 3H), 2.66 (m, 1H), 2.53 (m, 4H), 1.77 (t, 2.5 Hz, 6H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 183.1, 87.1, 84.8, 61.2, 53.4, 29.8, 13.0.

2,3-Di-but-2-ynyl-2,3-bis-ethoxycarbonyl-succinic acid diethyl ester (8)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): 4.36 (m, 8H), 3.20 (q, 2.5 Hz, 4H), 1.86 (t, 2.5 Hz, 6H), 1.41 (t, 7.0 Hz, 12H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 169.9, 79.1, 75.8, 62.9, 23.8, 23.2, 15.6, 5.0.

2,2-Bis-(4,4-dimethyl-pent-2-ynyl)-malonic acid dimethyl ester (22)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): 3.73 (s, 6H), 2.86 (s, 4H), 1.16 (s, 18H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 169.9, 92.4, 73.0, 58.0, 52.9, 31.3, 27.5, 23.0.

2-But-2-ynyl-2-(3-trimethylsilanyl-prop-2-ynyl)-malonic acid dimethyl ester (24)

^{41}H NMR (300 MHz, $CDCl_3$, ppm): 3.73 (s, 6H), 2.96 (s, 2H), 2.89 (q, 2.7 Hz, 2H), 1.74 (t, 2.4 Hz, 3H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 169.4, 101.1, 88.2, 79.1, 73.0, 57.1, 52.9, 24.0, 23.0, 3.5, -0.1.

General [2+2+2] Cycloaddition Procedure. An oven dried two-neck Round Bottom flask equipped with a magnetic stir bar, septum, gas adapter and balloon is evacuated and filled with CO_2. A solution of diyne is added and the flask is submerged into a 60 °C oil bath. To the stirring solution, a solution of $Ni(COD)_2$ and IPr is added. The dark greenish-black reaction mixture is then heated for 2 hours (or until complete consumption of starting material was observed as judged by GC), cooled to ambient temperature, concentrated, and purified by silica gel column chromatography.

1,4-Dimethyl-3-oxo-3,5-dihydro-7H-cyclopenta[c]pyran-6,6-dicarboxylic acid dimethyl ester (10). The general procedure was used with 2,2-di-but-2-ynyl-malonic acid dimethyl ester (**1**, 200 mg, 0.85 mmol), $Ni(COD)_2$ (12 mg, 0.04 mmol), IPr (31 mg, 0.08 mmol), and 3.3 mL of toluene. The reaction mixture was purified by recrystallization in CH_2Cl_2 and hexanes to afford the desired product (228 mg, 96%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 3.72 (s, 6H), 3.28 (s, 2H), 3.22 (s, 2H), 2.11 (s, 3H), 1.94 (s, 3H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 170.7, 164.3, 155.0, 151.8, 115.9, 115.5, 59.4, 53.2, 38.6, 35.4, 17.4, 12.7; IR (KBr pellet): 3025, 2952, 2924, 1757, 1728, 1714, 1671, 1601, 1429, 1389, 1369, 1325, 1300, 1255, 1201, 1176, 1072, 1030, 968, 862, 816, 758, 675, 656, 588; HR-MS calcd. for $C_{14}H_{16}O_6$ (M+): 280.0947, found 280.0938; Anal. calcd for $C_{14}H_{16}O_6$: C, 59.99; H, 5.75, found: C, 59.64; H, 5.77.

1,4-Diethyl-3-oxo-3,5-dihydro-7H-cyclopenta[c]pyran-6,6-dicarboxylic acid dimethyl ester (11). The general procedure was used with 2,2-di-pent-2-ynyl-malonic acid dimethyl ester (**2**, 200 mg, 0.76 mmol), $Ni(COD)_2$ (10 mg, 0.04 mmol), IPr (30 mg, 0.08 mmol), and 7.6 mL of toluene. The reaction mixture was purified by column chromatography on silica gel (5% Et_2O in CH_2Cl_2) to afford the desired product (225 mg, 96%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 3.78 (s, 6H), 3.34 (s, 2H), 3.27 (s, 2H), 2.44 (q, 7.6 Hz, 2H), 2.43 (q, 7.6 Hz, 2H), 1.21 (t, 7.6 Hz, 3H), 1.12 (t, 7.6 Hz, 3H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 170.9, 164.0, 156.9, 154.8, 121.7, 115.2, 59.8, 53.3, 38.3, 35.2, 25.1, 21.1, 12.5, 11.4; IR (neat): 2972, 2877, 1736, 1712, 1673, 1604, 1435, 1377, 1259, 1203,

1169, 1101, 1070, 1034, 993, 964, 928, 872, 779; HR-MS calcd. for $C_{16}H_{20}O_6$ (M+): 308.1270, found 308.1260; Anal. calcd for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54, found: C, 62.30; H, 6.54.

1,4-Diisopropyl-3-oxo-3,5-dihydro-7H-cyclopenta[c]pyran-6,6-dicarboxylic acid dimethyl ester (12). The general procedure was used with 2,2-bis-(4-methyl-pent-2-ynyl)-malonic acid dimethyl ester (**3**, 50 mg, 0.17 mmol), $Ni(COD)_2$ (2.3 mg, 0.008 mmol), IPr (6.6 mg, 0.017 mmol), and 1.7 mL of toluene. The reaction mixture was purified by column chromatography on silica gel (8% Et_2O in hexanes) to afford the desired product (49 mg, 86%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$, ppm): 3.78 (s, 6H), 3.39 (s, 2H), 3.25 (s, 2H), 2.98 (sept, 7.1 Hz, 1H), 2.72 (sept, 7.1 Hz, 1H), 1.23 (d, 7.1 Hz, 6H), 1.22 (d, 7.1 Hz, 6H); ^{13}C {^1H} NMR (75 MHz, $CDCl_3$, ppm): 171.2, 160.0, 156.6, 154.3, 125.2, 114.3, 60.0, 53.5, 38.9, 35.0, 31.3, 28.9, 20.1, 19.9; IR (neat): 2972, 2937, 1738, 1709, 1664, 1603, 1500, 1439, 1261, 1205, 1173, 1074, 1032, 995, 949, 922, 872, 750, 694; HR-MS calcd. for $C_{18}H_{24}O_6$ (M+): 336.1573, found 336.1575.

6,6-Bis-benzyloxymethyl-1,4-dimethyl-6,7-dihydro-5H-cyclopenta[c]pyran-3-one (13). The general procedure was used with 5,5-dibenzyloxymethyl-2,7-nonadiyne (**4**, 200 mg, 0.76 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), IPr (22 mg, 0.06 mmol), and 5.5 mL of toluene. The reaction mixture was purified by column chromatography on silica gel (3% Et_2O in CH_2Cl_2) to afford the desired product (211 mg, 94%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$, ppm): 7.38-7.28 (m, ArH, 10H), 4.53 (s, 4H), 3.44 (s, 4H), 2.67 (s, 2H), 2.59 (s, 2H), 2.12 (s, 3H), 1.96 (s, 3H); ^{13}C {^1H} NMR (75 MHz, $CDCl_3$, ppm): 164.9, 158.4, 151.7, 138.3, 128.3, 127.6, 118.1, 115.6, 107.4, 73.3, 72.7, 48.4, 37.3, 33.7, 17.4, 12.8; IR (neat): 3097, 2995, 1711, 1664, 1603, 1452, 1363, 1271, 1101, 1028, 739, 698; HR-MS calcd. for $C_{26}H_{28}O_4$ (M+): 404.1988, found 404.1986.

6,6-Bis-(tert-butyl-dimethyl-silanyloxymethyl)-1,4-dimethyl-6,7-dihydro-5H-cyclopenta[c]pyran-3-one (14). The general procedure was used with 5,5-bis-(tert-butyl-dimethyl-silanyloxymethyl)-nona-2,7-diyne (**5**, 200 mg, 0.49 mmol), $Ni(COD)_2$ (6 mg, 0.02 mmol), IPr (15 mg, 0.04 mmol), and 5 mL of toluene. The reaction mixture was purified by column chromatography on silica gel (3% Et_2O in CH_2Cl_2) to afford the desired product (208 mg, 94%) as a white solid. ^1H NMR (300 MHz, $CDCl_3$, ppm): 3.48 (s, 4H), 2.54 (s, 2H),

2.46 (s, 2H), 2.14 (s, 3H), 1.98 (s, 3H), 0.88 (s, 18H), 0.03 (s, 12H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 165.1, 158.9, 151.5, 118.5, 115.5, 65.1, 50.6, 36.3, 32.7, 25.8, 18.2, 17.3, 12.8, -5.6; IR (KBr pellet): 2951, 2862, 1701, 1603, 1259, 1053, 1018, 839, 777, 669; HR-MS calcd. for $C_{24}H_{44}O_4Si_2$ (M+): 453.2856, found 453.2834. Anal. calcd for $C_{24}H_{44}O_4Si_2$: C, 63.66; H, 9.80, found: C, 63.90; H, 9.59.

11,11-Dimethyl-10,12-dioxa-spiro[4.5]decyl-3,6-dimethyl-pyran-2-one (15). The general procedure was used with 5,5-di-but-2-ynyl-2,2-dimethyl-[1,3]dioxane (**6**, 200 mg, 0.91 mmol), $Ni(COD)_2$ (12 mg, 0.04 mmol), IPr (31 mg, 0.08 mmol), and 3.6 mL of toluene. The reaction mixture was purified by column chromatography on silica gel (5% Et_2O in CH_2Cl_2) to afford the desired product (236 mg, 98%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 3.61 (s, 4H), 2.58 (s, 2H), 2.51 (s, 2H), 2.06 (s, 3H), 1.88 (s, 3H), 1.37 (s, 6H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 164.5, 156.9, 152.1, 117.0, 115.9, 98.0, 67.9, 41.9, 38.0, 34.5, 23.6, 17.3, 12.7; IR (KBr pellet): 2943, 2864, 2833, 1720, 1664, 1599, 1452, 1371, 1257, 1201, 1105, 1053, 1024, 827, 756, 521; HR-MS calcd. for $C_{15}H_{20}O_4$ (M+): 264.1362, found 264.1349.

1,4-Dimethyl-3-oxo-3,5,6,7-tetrahydro-cyclopenta[c]pyran-6-carboxylic acid methyl ester (16). The general procedure was used with 2-but-2-ynyl-hex-4-ynoic acid methyl ester (**7**, 100 mg, 0.56 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), IPr (21 mg, 0.05 mmol), and 5.6 mL of toluene. The reaction mixture was purified by column chromatography on silica gel (5% Et_2O in CH_2Cl_2) to afford the desired product (103 mg, 82%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 3.28 (s, 3H), 2.80 (quint, 8.3 Hz, 1H), 2.56-2.47 (m, 4H), 1.71 (s, 3H), 1.53 (s, 3H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 174.2, 164.5, 156.9, 151.5, 117.3, 115.2, 52.0, 42.6, 34.3, 31.1, 17.3, 12.7; IR (KBr pellet): 2939, 2864, 2831, 1697, 1655, 1603, 1439, 1221, 1176, 1053, 1022, 760; HR-MS calcd. for $C_{12}H_{14}O_4$ (M+): 222.0892, found 222.0900.

1,4-Dimethyl-3-oxo-3,5-dihydro-8H-isochromene-6,6,7,7-tetracarboxylic acid tetraethyl ester (17). The general procedure was used with 2,3-di-but-2-ynyl-2,3-bis-ethoxycarbonyl-succinic acid diethyl ester (**8**, 200 mg, 0.48 mmol), $Ni(COD)_2$ (6 mg, 0.02 mmol), IPr (20 mg, 0.05 mmol), and 5 mL of toluene. The reaction mixture was purified by column chromatography on silica gel (7% Et_2O in CH_2Cl_2) to afford the desired product (212 mg,

96%) as a cream-colored oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 4.27-4.20 (m, 8H), 3.25 (s, 2H), 3.12 (s, 2H), 2.21 (s, 3H), 2.03 (s, 3H), 1.27 (t, 6.3 Hz, 12H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 169.3, 163.4, 154.4, 147.3, 117.7, 108.8, 62.3, 62.2, 56.8, 56.6, 32.9, 29.6, 17.1, 13.8, 11.9; IR (neat): 2985, 2906, 2873, 1722, 1639, 1557, 1470, 1446, 1387, 1367, 1256, 1206, 1095, 1051, 935, 863, 787, 769; HR-MS calcd. for $C_{23}H_{30}O_{10}$ (M+): 466.1839, found 466.1819. Anal. calcd for $C_{23}H_{30}O_{10}$: C, 59.22; H, 6.48, found: C, 59.25; H, 6.44.

1,4-Dimethyl-5,6,7,8-tetrahydro-isochromen-3-one (18). The general procedure was used with 2,8-decadiyne (**9**, 200 mg, 1.5 mmol), $Ni(COD)_2$ (20 mg, 0.07 mmol), IPr (60 mg, 0.15 mmol), and 15 mL of toluene. The reaction mixture was purified by column chromatography on silica gel (5% Et_2O in CH_2Cl_2) to afford the desired product (206 mg, 77%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 2.54 (bt, 6 Hz, 2H), 2.41 (bt, 6 Hz, 2H), 2.17 (s, 3H), 1.99 (s, 3H), 1.72-1.68 (m, 4H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 164.0, 154.0, 151.8, 117.6, 112.1, 27.7, 24.3, 22.2, 22.0, 16.8, 11.7; IR (KBr pellet): 2949, 2868, 2831, 1685, 1630, 1545, 1454, 1371, 1319, 1194, 1053, 1020, 760, 663; HR-MS calcd. for $C_{11}H_{14}O_2$ (M+): 178.0994, found 178.0995. Anal. calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92, found: C, 73.84; H, 7.94.

4-Methyl-3-oxo-1-trimethylsilanyl-3,5-dihydro-7H-cyclopenta[c]pyran-6,6-dicarboxylic acid dimethyl ester (25). The general procedure was used with 2-But-2-ynyl-2-(3-trimethylsilanyl-prop-2-ynyl)-malonic acid dimethyl ester (**24**, 100 mg, 0.34 mmol), $Ni(COD)_2$ (5 mg, 0.02 mmol), IPr (13 mg, 0.03 mmol), and 3.4 mL of benzene. The reaction mixture was purified by column chromatography on silica gel (3:1 hexanes:EtOAc) to afford the desired product (95 mg, 83%) as a cream solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 3.78 (s, 6H), 3.38 (s, 2H), 3.21 (bq, 1Hz, 2H), 2.17 (bt, 1Hz, 3H), 0.31 (s, 9H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 171.0, 166.6, 165.3, 155.6, 116.9, 116.3, 59.4, 53.3, 41.1, 34.6, 17.9, -0.1; IR (KBr pellet): 2956, 2922, 1736, 1709, 1664, 1552, 1433, 1290, 1265, 1203, 1163, 1122, 1072, 1053, 980, 945, 874, 843, 775, 692, 640, 565; HR-MS calcd. for $C_{16}H_{22}O_6Si$ (M+): 338.1186, found 338.1186. Anal. calcd for $C_{16}H_{22}O_6Si$: C, 56.78; H, 6.55, found: C, 56.61; H, 6.64.

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