Ligand-Controlled Diastereoselective Cobalt-Catalysed Hydroalkynylation of Terminal Alkynes to E- or Z-1,3-Enynes

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Experimental Procedures

General Information

All reactions with water- and/or air-sensitive starting materials were carried out in pre-dried glass wares under Argon atmosphere utilizing standard Schlenk techniques. All used solvents were dried over molecular sieves (3 Å) and they were degassed prior to use. Thin layer chromatography (TLC) was carried out on prefabricated plates (silica gel 60, F254 with fluorescence indicator) by Macherey Nagel. Column Chromatography was carried out on silica gel 60 (40-63 µm, 230-400 mesh) by Macherey Nagel. Commercially available chemicals were used without further purification.

The alkyne substrates 1-ethynyl-4-fluorobenzene[1], 1-ethynyl-4-bromobenzene[2], 1-ethynyl-4-methylbenzene[2], 1-ethynyl-4-methoxybenzene[2], 1-ethynyl-4-(trifluoromethyl)benzene[3], methyl 4-ethynylbenzoate[4], (4-ethynylphenyl)methanol[5], 1-tert-butyl-4-ethynyl-benzene[5], 1-ethynyl-3-methylbenzene[5], 1-ethynyl-3-methoxybenzene[6], 1-ethynyl-2-methylbenzene[5], 1-ethynyl-2-methoxybenzene[6], 3-ethynylpyridine[4] and 2-ethylthiophene[3] were synthesized via Sonogashira cross-coupling[7], followed by protodesilylation with potassium carbonate in methanol. The analytical data of each substrate are in accordance with the literature.

Cobalt dibromide was dried at 150 °C in vacuo and stored under Argon atmosphere. Zinc iodide was dried at 230 °C in vacuo and stored under Argon atmosphere.

$^1$H and $^{13}$C NMR were either recorded on a Bruker Fourier 300HD or a Bruker Avance III 500HD spectrometer at room temperature utilizing preset pulse programs. The residual solvent signal (CDCl$_3$: $^1$H NMR: 7.26 ppm, $^{13}$C NMR: 77.16 ppm, DMSO-d$_6$: $^1$H NMR: 2.50 ppm, $^{13}$C NMR: 39.52 ppm) was used for calibration referred to tetramethylsilane.[8] The chemical shifts are given in parts per million (ppm). The multiplicity of each signal is reported as singulett (s), doublet (d), triplet (t), quartet (q), multiplet (m) or combinations thereof. Multiplicities are reported as they were measured, and they might disagree with the expected multiplicity of a signal. $^{19}$F NMR were recorded on a Bruker Avance III 500HD spectrometer at room temperature utilizing preset pulse programs. The chemical shifts are given in ppm. Hexafluorobenzene ($^{19}$F NMR: −164.9 ppm[9]) was used as an internal standard. Infrared spectra were recorded on a Shimadzu IR Spirit QATR-S spectrometer. The absorption bands are given in wave numbers (cm$^{-1}$). High resolution mass spectra (EI) were recorded on a Thermo Scientific DFS spectrometer. The ionization was accomplished by electron ionization (EI) at an energy of 70 eV. Electron spray ionization (ESI) spectra were recorded on a Waters Q-TOP Premier spectrometer.

GC/MS spectra were recorded on a Shimadzu GC QP2020 spectrometer, equipped with an Optima 5HT column (length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 µm), fabricated by Macherey Nagel. Ionization was accomplished by electron ionization (EI) at 70 eV. GC/FID spectra were recorded on a Shimadzu GC 2010 Plus gas chromatograph, equipped with an Optima 5 MS column (length: 15 m, inner diameter: 0.25 mm, film thickness: 0.25 µm), fabricated by Macherey Nagel. Melting points were measured on a Gallenkamp MPD 350 BM 2.5 device. All specified melting points are not corrected.

$(E)/(Z)$ ratios of the pure products were determined by the baseline separated signals in the corresponding $^1$H NMR spectra. 

Design of Experiments was performed using JMP13 software package by SAS (version 13.2.1, SAS Institute Inc., Cary, NC, USA, © 2016).
SUPPORTING INFORMATION

Synthesis of the cobalt pre-catalysts

Synthesis of [CoBr₂(dppp)]
Following a literature-known procedure anhydrous cobalt dibromide (1.04 g, 4.75 mmol, 1.00 equiv.) was added to a pre-dried reaction vessel and dried in vacuo for 15 min. The salt was dissolved in dry THF (40.0 mL). To the blue solution 1,3-bis(diphenylphosphino)propane (1.96 g, 4.75 mmol, 1.00 equiv.) was added and the resulting dark green suspension was stirred for 16 h. The mixture was concentrated under reduced pressure and the catalyst was precipitated by the addition of n-pentane (20 mL). The residue was filtered and washed with n-pentane and diethyl ether. The pre-catalyst was dried in vacuo and isolated as a blue-green amorphous solid (2.99 g, 4.75 mmol, quant.). The catalyst was used without further purification.

Synthesis of [CoBr₂(TriPhos)]
Under Argon atmosphere anhydrous cobalt dibromide (656 mg, 3.00 mmol, 1.00 equiv.) was added to a pre-dried reaction vessel and dried in vacuo for another 15 min. The salt was dissolved in dry THF (60.0 mL). To the blue solution bis(diphenylphosphinoethyl)phenylphosphine (1.60 g, 3.00 mmol, 1.00 equiv.) dissolved in THF (30.0 mL) was added slowly and the resulting dark red suspension was stirred for 16 h. Within the addition the suspension solidified for a short period of time. The solvent was removed under reduced pressure and the residue washed with n-pentane and diethyl ether. The pre-catalyst was dried in vacuo and isolated as a red-brown amorphous solid (2.25 g, 3.00 mmol, quant.). The catalyst was used without further purification.

Synthesis of (E)-But-1-en-3ynes

General Procedure 1:
Under Argon atmosphere [CoBr₂(dppp)] (2 mol%), zinc dust (4 mol%) and triphenylphosphine (4.5 mol%) were added to a pre-dried reaction vessel. The solids were dried 10 min in vacuo. The catalyst system was dissolved in dry acetonitrile (0.8 mL/mmol). The resulting dark suspension was shortly heated to approximately 80 °C, whereas a color change from dark blue/green to green appeared. The resulting solution was cooled to 0 °C and the corresponding alkyne (1.00 equiv.) was added. The reaction mixture was stirred until complete conversion was determined via GC/MS and TLC. The mixture was diluted with CH₂Cl₂ and filtered over a short plug of silica gel (eluent: n-pentane:CH₂Cl₂ = 3:1 or CH₂Cl₂, depending on the polarity of the substrate). The solvent was removed under reduced pressure. The crude product was purified via column chromatography (n-pentane:CH₂Cl₂ or n-pentane:ethyl acetate).

(E)-But-1-en-3yne-1,4-diylbenzene (2a)
According to General Procedure 1 the title compound was prepared using phenylacetylene (102 mg, 1.00 mmol, 1.00 equiv.), [CoBr₂(dppp)] (12.6 mg, 20.0 µmol, 0.02 equiv.), zinc dust (2.6 mg, 40.0 µmol, 0.04 equiv.) and triphenylphosphine (11.8 mg, 45.0 µmol, 0.05 equiv.) in acetonitrile (0.8 mL). The reaction mixture was stirred 2 h at 0 °C. The product was obtained after column chromatography (eluent: n-pentane:CH₂Cl₂ = 10:1) as a colorless solid (61.7 mg, 308 µmol, 62%).

melting point: 98 – 101 °C.

¹H NMR (300 MHz, CDCl₃) δ = 7.47 (ddd, J = 15.7, 7.7, 2.6 Hz, 4H), 7.39 – 7.28 (m, 6H), 7.06 (d, J = 16.2 Hz, 1H), 6.41 (d, J = 16.2 Hz, 1H) ppm.
The title compound was also synthesized on a 10 mmol scale following General Procedure 1. The product was obtained as a colorless solid (603 mg, 2.95 mmol, 59%).

\((E)-4,4'-(But-1-en-3-yne-1,4-diyl)bis(fluorobenzene)\) (2b)

According to General Procedure 1 the title compound was prepared using 1-ethynyl-4-fluorobenzene (120 mg, 1.00 mmol, 1.00 equiv.), [CoBr\(_2\)(dppp)] (12.6 mg, 20.0 \(\mu\)mol, 0.02 equiv.), zinc dust (2.6 mg, 40.0 \(\mu\)mol, 0.04 equiv.) and triphenylphosphine (11.8 mg, 45.0 \(\mu\)mol, 0.05 equiv.) in acetonitrile (0.8 mL). The reaction mixture was stirred 2 h at 0 °C. The product was obtained after column chromatography (eluent: n-pentane:CH\(_2\)Cl\(_2\) = 10:1) as a colorless solid (98.0 mg, 408 \(\mu\)mol, 82%).

**melting point**: 118 – 121 °C.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 7.45 \ (dd, \ J = 8.7, 5.5 \text{ Hz}, 2H), 7.39 \ (dd, \ J = 8.7, 5.4 \text{ Hz}, 2H), 7.06 – 7.01 \ (m, 4H), 6.99 \ (d, \ J = 16.8 \text{ Hz}, 1H), 6.27 \ (d, \ J = 16.2 \text{ Hz}, 1H) \text{ ppm.}\)

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta = 163.1 \ (d, \ J = 249.0 \text{ Hz}), 162.6 \ (d, \ J = 249.7 \text{ Hz}), 140.2, 133.5 \ (d, \ J = 8.3 \text{ Hz}, 2C), 132.7 \ (d, \ J = 3.4 \text{ Hz}), 128.1 \ (d, \ J = 8.2 \text{ Hz}, 2C), 119.6 \ (d, \ J = 3.6 \text{ Hz}), 116.0 \ (d, \ J = 16.5 \text{ Hz}, 2C), 115.8 \ (d, \ J = 17.0 \text{ Hz}, 2C), 107.9, 90.7, 88.5 \text{ ppm.}\)

\(^{19}\)F NMR (470 MHz, CDCl\(_3\)) \(\delta = -114.0, -115.5 \text{ ppm.}\)

IR (ATR): \(\tilde{\nu} = 3100, 3062, 3032, 1900, 1596, 1584, 1396, 1294, 1226, 1159, 1094, 1011, 960, 943, 856, 834, 814, 786, 670, 533 \text{ cm}^{-1}.\)

HRMS (EI): \(m/z\) for C\(_{16}\)H\(_{10}\)F\(_2\) [M]: calc.: 240.0745, found: 240.0744.

\((E)-4,4'-(But-1-en-3-yne-1,4-diyl)bis(chlorobenzene)\) (2c)

According to General Procedure 1 the title compound was prepared using 1-chloro-4-ethynylbenzene (137 mg, 1.00 mmol, 1.00 equiv.), [CoBr\(_2\)(dppp)] (12.6 mg, 20.0 \(\mu\)mol, 0.02 equiv.), zinc dust (2.6 mg, 40.0 \(\mu\)mol, 0.04 equiv.) and triphenylphosphine (11.8 mg, 45.0 \(\mu\)mol, 0.05 equiv.) in acetonitrile (0.8 mL). The reaction mixture was stirred 2 h at 0 °C. The product was obtained after column chromatography (eluent: n-pentane:CH\(_2\)Cl\(_2\) = 10:1) as a light-yellow solid (121 mg, 444 \(\mu\)mol, 89%).

**melting point**: 175 – 177 °C.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.43 – 7.25 \ (m, 8H), 7.00 \ (d, \ J = 16.2 \text{ Hz}, 1H), 6.34 \ (d, \ J = 16.2 \text{ Hz}, 1H) \text{ ppm.}\)

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 140.4, 134.8, 134.6, 134.5, 132.9 \ (2C), 129.1 \ (2C), 128.9 \ (2C), 127.6 \ (2C), 121.9, 108.6, 91.2, 89.7 \text{ ppm.}\)

IR (ATR): \(\tilde{\nu} = 3084, 3052, 3029, 1902, 1780, 1586, 1486, 1404, 1396, 1297, 1279, 1174, 1090, 1011, 954, 857, 824, 804, 763, 707, 690, 637, 631, 581, 523 \text{ cm}^{-1}.\)

HRMS (EI): \(m/z\) for C\(_{16}\)H\(_{10}\)Cl\(_2\) [M]: calc.: 272.0154, found: 272.0146.
According to General Procedure 1 the title compound was prepared using 1-bromo-4-ethynylbenzene (181 mg, 1.00 mmol, 1.00 equiv.), [CoBr$_2$(dppp)] (12.6 mg, 20.0 µmol, 0.02 equiv.), zinc dust (2.6 mg, 40.0 µmol, 0.04 equiv.) and triphenylphosphine (11.8 mg, 45.0 µmol, 0.05 equiv.) in acetonitrile (0.8 mL). The reaction mixture was stirred 2 h at 0 °C. The product was obtained after column chromatography (eluent: n-pentane:CH$_2$Cl$_2$ = 10:1) as a light-yellow solid (168 mg, 464 µmol, 93%).

**Melting point**: 196 – 199 °C.

**$^1$H NMR** (300 MHz, CDCl$_3$) δ = 7.48 (dd, $J$ = 8.5, 1.8 Hz, 4H), 7.40 – 7.23 (m, 4H), 6.98 (d, $J$ = 16.2 Hz, 1H), 6.35 (d, $J$ = 16.2 Hz, 1H) ppm.

**$^{13}$C NMR** (75 MHz, CDCl$_3$) δ = 140.5, 135.2, 133.1 (2C), 132.1 (2C), 131.8 (2C), 127.9 (2C), 122.9, 122.7, 122.3, 108.7, 91.4, 89.8 ppm.

**IR** (ATR): $\tilde{v}$ = 3027, 1909, 1579, 1394, 1320, 1279, 1253, 1176, 1099, 1009, 859, 823, 806, 753, 706, 664, 636, 541, 527, 516, 501 cm$^{-1}$.

**HRMS** (EI): $m/z$ for C$_{16}$H$_{10}$Br$_2$ [M$^+$]: calc.: 359.9144, found: 359.9135.

The title compound was also synthesized on an 8.00 mmol scale following General Procedure 1. The product was obtained as a light-yellow solid (1.25 g, 3.45 mmol, 86%).

**Melting point**: 157 – 159 °C.

**$^1$H NMR** (300 MHz, CDCl$_3$) δ = 7.35 (dd, $J$ = 14.8, 7.9 Hz, 4H), 7.15 (dd, $J$ = 8.0, 4.1 Hz, 4H), 7.01 (d, $J$ = 16.2 Hz, 1H), 6.34 (d, $J$ = 16.2 Hz, 1H), 2.37 (s, 6H) ppm.

**$^{13}$C NMR** (75 MHz, CDCl$_3$) δ = 141.0, 138.7, 138.4, 133.8, 131.5 (2C), 129.6 (2C), 129.2 (2C), 126.3 (2C), 120.6, 107.3, 91.7, 88.6, 21.6, 21.5 ppm.

**IR** (ATR): $\tilde{v}$ = 3029, 2914, 2853, 2190, 1910, 1609, 1580, 1506, 1483, 1283, 1180, 1109, 1072, 1040, 957, 944, 853, 817, 800, 773, 710, 530, 516 cm$^{-1}$.

**HRMS** (EI): $m/z$ for C$_{18}$H$_{16}$ [M$^+$]: calc.: 232.1247, found: 232.1242.

According to General Procedure 1 the title compound was prepared using 1-ethynyl-4-methoxybenzene (116 mg, 1.00 mmol, 1.00 equiv.), [CoBr$_2$(dppp)] (12.6 mg, 20.0 µmol, 0.02 equiv.), zinc dust (2.6 mg, 40.0 µmol, 0.04 equiv.) and triphenylphosphine (11.8 mg, 45.0 µmol, 0.05 equiv.) in acetonitrile (0.8 mL). The reaction mixture was stirred 2 h at 0 °C. The product was obtained after column chromatography (eluent: n-pentane:CH$_2$Cl$_2$ = 2:1) as a colorless solid (108 mg, 408 µmol, 82%).
melting point: 153 – 155 °C.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 7.43 – 7.39\) (m, 2H), 7.37 – 7.33 (m, 2H), 6.96 (d, \(J = 16.2\) Hz, 1H), 6.89 – 6.84 (m, 4H), 6.24 (d, \(J = 16.2\) Hz, 1H), 3.82 (s, 3H), 3.82 (s, 3H) ppm.

\(^1^3\)C NMR (126 MHz, CDCl\(_3\)) \(\delta = 160.1, 159.6, 140.2, 133.0\) (2C), 129.6, 127.7 (2C), 116.0, 114.3 (2C), 114.2 (2C), 106.2, 91.2, 88.1, 55.5, 55.4 ppm.

IR (ATR): \(\bar{\nu} = 2957, 2934, 2834, 2193, 1600, 1566, 1503, 1460, 1439, 1307, 1284, 1246, 1204, 1173, 1107, 1072, 1024, 1009, 964, 936, 851, 833, 821, 807, 769, 670, 640, 563, 539\) cm\(^{-1}\).

HRMS (EI): \(m/z\) for C\(_{18}\)H\(_{16}\)O\(_2\) [M\(^+\)]: calc.: 264.1145, found: 264.1139.

(E)-4,4‘-(But-1-en-3-yne-1,4-diyl)bis((trifluoromethyl)benzene) (2g)

![Diagram](image)

According to General Procedure 1 the title compound was prepared using 1-ethyl-4-(trifluoromethyl)benzene (170 mg, 1.00 mmol, 1.00 equiv.), [CoBr\(_2\)(dppp)] \((12.6\) mg, 20.0 \(\mu\)mol, 0.02 equiv.), triphenylphosphine \((11.8\) mg, 45.0 \(\mu\)mol, 0.05 equiv.) in acetonitrile \((0.8\) mL). The reaction mixture was stirred \(2\) h at 0 °C. The product was obtained after column chromatography (eluent: \(n\)-pentane:CH\(_2\)Cl\(_2\) = 10:1) as a colorless solid \((150\) mg, 440 \(\mu\)mol, 88%).

melting point: 138 – 141 °C.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 7.63 – 7.56\) (m, 6H), 7.53 (d, \(J = 8.2\) Hz, 2H), 7.10 (d, \(J = 16.3\) Hz, 1H), 6.47 (d, \(J = 16.3\) Hz, 1H) ppm.

\(^1^3\)C NMR (126 MHz, CDCl\(_3\)) \(\delta = 140.8, 139.5, 132.0\) (2C), 130.8 (q, \(J = 32.8\) Hz), 130.3 (q, \(J = 32.7\) Hz), 127.1, 126.7 (2C), 126.0 (q, \(J = 3.8\) Hz, 2C), 125.5 (q, \(J = 3.6\) Hz, 2C), 124.2 (q, \(J = 271.9\) Hz), 124.1 (q, \(J = 272.2\) Hz), 110.4, 91.7, 90.7 ppm.

\(^1^9\)F NMR (470 MHz, CDCl\(_3\)) \(\delta = -65.8, -66.0\) ppm.

IR (ATR): \(\bar{\nu} = 2197, 1929, 1612, 1409, 1317, 1174, 1127, 1104, 1064, 1013, 966, 950, 864, 843, 820, 763, 736, 720, 656, 636, 597, 543, 527\) cm\(^{-1}\).

HRMS (EI): \(m/z\) for C\(_{18}\)H\(_{10}\)F\(_6\) [M\(^+\)]: calc.: 340.0681, found: 340.0681.

(E)-4,4‘-(But-1-en-3-yne-1,4-diyl)dibenzaldehyde (2h)

According to General Procedure 1 the title compound was prepared using 4-ethynylbenzaldehyde \((130\) mg, 1.00 mmol, 1.00 equiv.), [CoBr\(_2\)(dppp)] \((12.6\) mg, 20.0 \(\mu\)mol, 0.02 equiv.), zinc dust \((2.6\) mg, 40.0 \(\mu\)mol, 0.04 equiv.) and triphenylphosphine \((11.8\) mg, 45.0 \(\mu\)mol, 0.05 equiv.) in acetonitrile \((0.8\) mL). The reaction mixture was stirred \(2\) h at 0 °C. The product was obtained after column chromatography (eluent: CH\(_2\)Cl\(_2\)) as a light-yellow solid \((107\) mg, 412 \(\mu\)mol, 82%).

melting point: 204 – 206 °C.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 10.01\) (s, 1H), 10.00 (s, 1H), 7.86 (dd, \(J = 8.2, 3.5\) Hz, 4H), 7.60 (dd, \(J = 11.4, 8.0\) Hz, 4H), 7.13 (d, \(J = 16.2\) Hz, 1H), 6.54 (d, \(J = 16.2\) Hz, 1H) ppm.

\(^1^3\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 191.6, 191.5, 141.8, 141.3, 136.4, 135.7, 132.2\) (2C), 130.4 (2C), 129.7 (2C), 129.3, 127.0 (2C), 111.2, 92.8, 92.4 ppm.

IR (ATR): \(\bar{\nu} = 2849, 2752, 2192, 1926, 1683, 1599, 1560, 1392, 1297, 1286, 107, 1159, 1100, 1009, 947, 866, 857, 827, 801, 721, 640, 570, 531, 514\) cm\(^{-1}\).

HRMS (EI): \(m/z\) for C\(_{18}\)H\(_{16}\)O\(_2\) [M\(^+\)]: calc.: 260.0832, found: 260.0825.
Dimethyl 4,4'-{(but-1-en-3-yn-1,4-diyl)(E)}-dibenzoate (2i)

According to General Procedure 1 the title compound was prepared using methyl 4-ethynylbenzoate (160 mg, 1.00 mmol, 1.00 equiv.), [CoBr$_2$(dppp)] (12.6 mg, 20.0 µmol, 0.02 equiv.), zinc dust (2.6 mg, 40.0 µmol, 0.04 equiv.) and triphenylphosphine (11.8 mg, 45.0 µmol, 0.05 equiv.) in acetonitrile (0.8 mL). The reaction mixture was stirred 2 h at 0 °C. The product was obtained after column chromatography (eluent: CH$_2$Cl$_2$) as a light-yellow solid (120 mg, 375 µmol, 75%).

melting point: 208 – 210 °C.

$^1$H NMR (300 MHz, CDCl$_3$) δ = 8.01 (dt, $J = 8.4, 1.9$ Hz, 4H), 7.66 – 7.38 (m, 4H), 7.09 (d, $J = 16.2$ Hz, 1H), 6.49 (dd, $J = 16.2, 1.5$ Hz, 1H), 3.92 (s, 6H) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$) δ = 166.7, 166.6, 141.2, 140.4, 131.6 (2C), 130.2 (3C), 129.7 (3C), 127.9, 126.4 (2C), 110.4, 92.4, 91.5, 52.4, 52.3 ppm.

IR (ATR): $\tilde{v} = 2959, 1716, 1603, 1502, 1432, 1410, 1309, 1274, 1190, 1174, 1106, 949, 861, 830, 814, 763, 696, 560, 531$ cm$^{-1}$.

HRMS (EI)$^+$: $m/z$ for C$_{20}$H$_{16}$O$_4$ [M]$^+$: calc.: 320.1043, found: 320,1040.

(E)-(But-1-en-3-yn-1,4-diylbis(4,1-phenylene))dimethanol (2j)

According to General Procedure 1 the title compound was prepared using (4-ethynylphenyl)methanol (132 mg, 1.00 mmol, 1.00 equiv.), [CoBr$_2$(dppp)] (12.6 mg, 20.0 µmol, 0.02 equiv.), zinc dust (2.6 mg, 40.0 µmol, 0.04 equiv.) and triphenylphosphine (11.8 mg, 45.0 µmol, 0.05 equiv.) in acetonitrile (0.8 mL). The reaction mixture was stirred 2 h at 0 °C. The product was obtained after column chromatography (eluent: CH$_2$Cl$_2$) as a light-yellow solid (102 mg, 388 µmol, 77%).

melting point: 202 – 205 °C.

$^1$H NMR (300 MHz, DMSO-d$_6$) δ = 7.53 (d, $J = 7.8$ Hz, 2H), 7.44 (d, $J = 7.9$ Hz, 2H), 7.33 (t, $J = 8.5$ Hz, 4H), 7.08 (d, $J = 16.3$ Hz, 1H), 6.60 (d, $J = 16.3$ Hz, 1H), 5.30 (t, $J = 5.8$ Hz, 1H), 5.24 (t, $J = 5.8$ Hz, 1H), 4.51 (t, $J = 5.7$ Hz, 4H) ppm.

$^{13}$C NMR (75 MHz, DMSO-d$_6$) δ = 143.5, 143.3, 141.2, 134.4, 131.0 (2C), 126.8 (2C), 126.7 (2C), 126.3 (2C), 120.8, 107.4, 91.7, 89.1, 62.6, 62.5 ppm.

IR (ATR): $\tilde{v} = 3262$ (bs), 2853, 1694, 1506, 1437, 1410, 1207, 1177, 1199, 1036, 1000, 960, 947, 849, 804, 783, 720, 599, 557, 531 cm$^{-1}$.

HRMS (EI)$^+$: $m/z$ for C$_{18}$H$_{16}$O$_2$ [M]$^+$: calc.: 264.1145, found: 264.1138.

(E)-4,4'-(But-1-en-3-yn-1,4-diyl)bis(tert-butylbenzene) (2k)

According to General Procedure 1 the title compound was prepared using methyl 1-(tert-butyl)ethynylbenzene (158 mg, 1.00 mmol, 1.00 equiv.), [CoBr$_2$(dppp)] (12.6 mg, 20.0 µmol, 0.02 equiv.), zinc dust (2.6 mg, 40.0 µmol, 0.04 equiv.) and triphenylphosphine (11.8 mg, 45.0 µmol, 0.05 equiv.) in acetonitrile (0.8 mL). The reaction mixture was stirred 2 h at 0 °C. The product was obtained after column chromatography (eluent: n-pentane:CH$_2$Cl$_2$ = 10:1) as a light yellow solid (146 mg, 462 µmol, 92%).

melting point: 176 – 179 °C.

$^1$H NMR (500 MHz, CDCl$_3$) δ = 7.45 – 7.40 (m, 2H), 7.40 – 7.33 (m, 6H), 7.02 (d, $J = 16.1$ Hz, 1H), 6.36 (d, $J = 16.2$ Hz, 1H), 1.34 (s, 9H), 1.33 (s, 9H) ppm.
According to General Procedure 1 the title compound was prepared using 1-ethynyl-3-
-methylbenzene (140 mg, 1.21 mmol, 1.00 equiv.), \([\text{CoBr}_2(dppp)]\) (12.6 mg, 20.0 \(\mu\)mol, 0.02 equiv.), zinc dust (2.6 mg, 40.0 \(\mu\)mol, 0.04 equiv.) and triphenylphosphine (11.8 mg, 45.0 \(\mu\)mol, 0.05 equiv.) in acetonitrile (0.8 mL). The reaction mixture was stirred 2 h at 0 °C.

The product was obtained after column chromatography (eluent: \(n\)-pentane:CH\(_2\)Cl\(_2\) = 15:1) as a colorless oil (67.5 mg, 291 \(\mu\)mol, 48%).

\(1^H\) NMR (500 MHz, CDCl\(_3\)) \(\delta = 7.37\) (s, 1H), 7.35 (dd, \(J = 7.9, 1.6\) Hz, 1H), 7.32 – 7.28 (m, 4H), 7.21 – 7.14 (m, 2H), 7.06 (d, \(J = 16.2\) Hz, 1H), 6.43 (d, \(J = 16.2\) Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H) ppm.

\(13^C\) NMR (126 MHz, CDCl\(_3\)) \(\delta = 141.4, 138.5, 138.1, 136.5, 132.2, 129.6, 129.2, 128.8 (2C), 128.4, 127.1, 123.6, 123.5, 108.2, 92.0, 88.8, 21.5, 21.4 ppm.

IR (ATR): \(\tilde{v} = 2953, 2902, 2866, 1502, 1462, 1407, 1392, 1363, 1267, 1203, 1106, 1026, 1014, 957, 943, 853, 834, 814, 760, 836, 697, 559, 523, 513\) cm\(^{-1}\).

HRMS (EI): \(m/z\) for C\(_{18}\)H\(_{16}\)[M]+: calc.: 232.1247, found: 232.1252.

\(13^C\) NMR (126 MHz, CDCl\(_3\)) \(\delta = 141.4, 138.5, 138.1, 136.5, 129.6, 129.2, 128.8 (2C), 128.4, 127.1, 123.6, 123.5, 108.2, 92.0, 88.8, 21.5, 21.4 ppm.

IR (ATR): \(\tilde{v} = 3024, 2919, 2193, 1942, 1599, 1579, 1482, 1452, 1377, 1297, 1167, 1089, 1040, 949, 904, 876, 774, 687, 521\) cm\(^{-1}\).

HRMS (EI): \(m/z\) for C\(_{18}\)H\(_{16}\)O\(_2\)[M]+: calc.: 264.1145, found: 264.1137.

According to General Procedure 1 the title compound was prepared using 1-ethynyl-3-
-methoxybenzene (132 mg, 1.00 mmol, 1.00 equiv.), \([\text{CoBr}_2(dppp)]\) (12.6 mg, 20.0 \(\mu\)mol, 0.02 equiv.), zinc dust (2.6 mg, 40.0 \(\mu\)mol, 0.04 equiv.) and triphenylphosphine (11.8 mg, 45.0 \(\mu\)mol, 0.05 equiv.) in acetonitrile (0.8 mL). The reaction mixture was stirred 2 h at 0 °C. The product was obtained after column chromatography (eluent: \(n\)-pentane:CH\(_2\)Cl\(_2\) = 2:1) as a light-yellow waxy oil (72.2 mg, 273 \(\mu\)mol, 55%).

\(1^H\) NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.26\) (dd, \(J = 7.7, 2.2\) Hz, 2H), 7.12 – 6.94 (m, 5H), 6.87 (ddd, \(J = 8.8, 7.7, 2.6\) Hz, 2H), 6.38 (d, \(J = 16.2\) Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H) ppm.

\(13^C\) NMR (75 MHz, CDCl\(_3\)) \(\delta = 160.0, 159.5, 141.4, 137.8, 129.9, 129.5, 124.5, 124.2, 119.2, 116.4, 115.1, 114.4, 111.7, 108.5, 92.0, 88.8, 55.4 (2C) ppm.

IR (ATR): \(\tilde{v} = 2956, 2937, 2833, 2193, 1593, 1573, 1463, 1427, 1320, 1283, 1269, 1243, 1206, 1153, 1080, 1044, 993, 950, 851, 773, 684, 564, 521\) cm\(^{-1}\).

HRMS (EI): \(m/z\) for C\(_{18}\)H\(_{16}\)O\(_2\)[M]+: calc.: 264.1145, found: 264.1137.
afterwards for 14 h at ambient temperature. The product was obtained after column chromatography (eluent: n-pentane:CH₂Cl₂ = 10:1) as a colorless solid (81.4 mg, 350 µmol, 70%).

**melting point:** 54 – 57 °C.

**1H NMR** (500 MHz, CDCl₃) δ = 7.52 (dd, J = 6.7, 2.3 Hz, 1H), 7.47 (dt, J = 7.5, 1.1 Hz, 1H), 7.29 (d, J = 16.1 Hz, 1H), 7.24 – 7.15 (m, 6H), 6.36 (d, J = 16.1 Hz, 1H), 2.51 (s, 3H), 2.42 (s, 3H) ppm.

**13C NMR** (126 MHz, CDCl₃) δ = 140.2, 138.8, 135.9, 135.5, 132.0, 130.7, 129.6, 128.6, 128.4, 126.4, 125.7, 125.1, 123.4, 109.5, 93.2, 90.5, 20.9, 19.9 ppm.

**IR** (ATR): ṽ = 3062, 3016, 2944, 1953, 1614, 1597, 1476, 1457, 1379, 1290, 1272, 1116, 1102, 1046, 950, 868, 811, 743, 713, 553, 544 cm⁻¹.

**HRMS** (EI): m/z for C₁₈H₁₆Cl₁₂: calc.: 232.1247, found: 232.1241.

(E)-2,2'-([But-1-en-3-yne-1,4-diyl]bis(methoxybenzene)) (2o)

According to General Procedure 1 the title compound was prepared using 1-ethynyl-2-methoxybenzene (132 mg, 1.00 mmol, 1.00 equiv.), [CoBr₂(dppp)] (12.6 mg, 20.0 µmol, 0.02 equiv.), zinc dust (2.6 mg, 40.0 µmol, 0.04 equiv.) and triphenylphosphine (11.8 mg, 45.0 µmol, 0.05 equiv.) in acetonitrile (0.8 mL). The reaction mixture was stirred 2 h at 0 °C and afterwards for 14 h at ambient temperature. The product was obtained after column chromatography (eluent: n-pentane:CH₂Cl₂ = 2:1) as a light-yellow waxy oil (94.5 mg, 357 µmol, 72%).

**melting point:** 54 – 57 °C.

**1H NMR** (300 MHz, CDCl₃) δ = 7.47 (dd, J = 7.5, 1.6 Hz, 2H), 7.38 (d, J = 16.4 Hz, 1H), 7.33 – 7.23 (m, 2H), 6.99 – 6.85 (m, 4H), 6.55 (d, J = 16.4 Hz, 1H), 3.93 (s, 3H), 3.88 (s, 3H) ppm.

**13C NMR** (75 MHz, CDCl₃) δ = 159.9, 157.1, 136.5, 133.6, 129.6 (2C), 127.0, 125.7, 120.8, 120.6, 113.0, 111.1, 110.7, 109.2, 93.9, 87.7, 56.0, 55.6 ppm.

**IR** (ATR): ṽ = 3003, 2936, 2834, 1593, 1572, 1492, 1484, 1463, 1433, 1291, 1272, 1240, 1177, 1162, 1119, 1106, 1049, 1023, 956, 803, 779, 744, 711, 616, 581, 524 cm⁻¹.

**HRMS** (EI): m/z for C₁₈H₁₆O₂: calc.: 264.1145, found: 264.1136.

(E)-3,3'-(But-1-en-3-yne-1,4-diyl)dipyridine (2p)

According to General Procedure 1 the title compound was prepared using 3-ethynylpyridine (103 mg, 1.00 mmol, 1.00 equiv.), [CoBr₂(dppp)] (12.6 mg, 20.0 µmol, 0.02 equiv.), zinc dust (2.6 mg, 40.0 µmol, 0.04 equiv.) and triphenylphosphine (11.8 mg, 45.0 µmol, 0.05 equiv.) in acetonitrile (0.8 mL). The reaction mixture was stirred 2 h at 0 °C and then 46 h at ambient temperature. The product was obtained after column chromatography (eluent: ethyl acetate) as a light-brown solid (58.5 mg, 284 µmol, 56%).

**melting point:** 92 – 95 °C.

**1H NMR** (300 MHz, CDCl₃) δ = 8.71 (d, J = 16.6 Hz, 2H), 8.56 (d, J = 4.1 Hz, 2H), 7.77 (d, J = 7.9 Hz, 2H), 7.30 (dt, J = 7.9, 4.8 Hz, 2H), 7.08 (d, J = 16.3 Hz, 1H), 6.47 (d, J = 16.3 Hz, 1H) ppm.

**13C NMR** (75 MHz, CDCl₃) δ = 152.3, 149.9, 148.8, 148.4, 138.6, 138.5, 132.6, 132.0, 123.9, 123.3, 120.5, 109.9, 91.5, 89.4 ppm.

**IR** (ATR): ṽ = 3056, 3039, 2922, 2852, 1619, 1567, 1559, 1474, 1439, 1420, 1409, 1314, 1269, 1186, 1120, 1020, 963, 951, 855, 847, 814, 800, 754, 720, 699, 653, 626, 539 cm⁻¹.

**HRMS** (ESI): m/z for C₁₄H₁₀N₂H: calc.: 207.0922, found: 207.0920.
**SUPPORTING INFORMATION**

### (E)-2,2'-(But-1-ene-3-yne-1,4-diyl)dipyridine (2q)

According to General Procedure 1 the title compound was prepared using 2-ethynylpyridine (103 mg, 1.00 mmol, 1.00 equiv.), [CoBr₂(dppp)] (12.6 mg, 20.0 µmol, 0.02 equiv.), zinc dust (2.6 mg, 40.0 µmol, 0.04 equiv.) and triphenylphosphine (11.8 mg, 45.0 µmol, 0.05 equiv.) in acetonitrile (0.8 mL). The reaction mixture was stirred 2 h at 0 °C and then 46 h at ambient temperature. The product was obtained after column chromatography (eluent: ethyl acetate) as a light-brown solid (57.4 mg, 278 µmol, 56%).

**melting point**: 57 – 60 °C.

**¹H NMR** (300 MHz, CDCl₃) δ = 8.69 – 8.61 (m, 2H), 7.71 (tt, J = 7.7, 2.0 Hz, 2H), 7.53 (dt, J = 7.8, 1.1 Hz, 1H), 7.40 – 7.17 (m, 4H), 7.03 (d, J = 15.9 Hz, 1H) ppm.

**¹³C NMR** (75 MHz, CDCl₃) δ = 153.9, 150.2, 150.0, 143.5, 141.9, 136.8, 136.3, 127.4, 123.4, 122.9, 122.8, 111.8, 92.5, 88.5 ppm.

**IR (ATR):** ν = 3074, 3052, 3003, 2923, 2852, 2197, 1619, 1577, 1562, 1470, 1460, 1427, 1303, 1260, 1150, 1120, 1094, 1050, 1029, 986, 963, 900, 767, 737, 696, 627, 617, 539 cm⁻¹.

**HRMS (ESI)**: m/z for C₁₄H₁₀N₂H [M+H]: calc.: 207.0922, found: 207.0922.

### (E)-4,4'-(But-1-ene-3-yne-1,4-diyl)dithiophene (2r)

According to General Procedure 1 the title compound was prepared using 2-ethynylthiophene (108 mg, 1.00 mmol, 1.00 equiv.), [CoBr₂(dppp)] (12.6 mg, 20.0 µmol, 0.02 equiv.), zinc dust (2.6 mg, 40.0 µmol, 0.04 equiv.) and triphenylphosphine (11.8 mg, 45.0 µmol, 0.05 equiv.) in acetonitrile (0.8 mL). The reaction mixture was stirred 2 h at 0 °C. The product was obtained after column chromatography (eluent: n-pentane:CH₂Cl₂ = 10:1) as a yellow solid (56.2 mg, 260 µmol, 52%).

**melting point**: 102 – 105 °C.

**¹H NMR** (500 MHz, CDCl₃) δ = 7.27 (dd, J = 5.2, 1.2 Hz, 1H), 7.22 (td, J = 4.4, 3.7, 1.1 Hz, 2H), 7.12 (d, J = 15.9 Hz, 1H), 7.06 (d, J = 3.4 Hz, 1H), 7.00 (td, J = 5.2, 3.6 Hz, 2H), 6.19 (d, J = 15.9 Hz, 1H) ppm.

**¹³C NMR** (126 MHz, CDCl₃) δ = 141.5, 134.1, 131.9, 127.9, 127.4, 127.4, 125.8, 123.6, 107.0, 92.7, 85.4 ppm.

**IR (ATR):** ν = 3102, 3074, 3040, 2184, 1800, 1652, 1602, 1503, 1419, 1359, 1277, 1489, 1217, 1202, 1194, 1041, 907, 934, 846, 830, 809, 757, 694, 577, 540, 531, 524, 514, 507 cm⁻¹.

**HRMS (EI)**: m/z for C₁₂H₂₆S₂ [M]: calc.: 216.0062, found: 216.0058.

### (E)-2,7-Dimethylocta-1,3,7-trien-5-yne (2s)

According to General Procedure 1 the title compound was prepared using 2-methylbut-1-ene-3-yne (95.2 µL, 1.00 mmol, 1.00 equiv.), [CoBr₂(dppp)] (12.6 mg, 20.0 µmol, 0.02 equiv.), zinc dust (2.6 mg, 40.0 µmol, 0.04 equiv.) and triphenylphosphine (11.8 mg, 45.0 µmol, 0.05 equiv.) in acetonitrile (0.8 mL). The reaction mixture was stirred 2 h at 0 °C. The product was obtained after column chromatography (eluent: n-pentane) as a colorless liquid (19.0 mg, 143 µmol, 29%).

**¹H NMR** (500 MHz, CDCl₃) δ = 6.69 (d, J = 16.1 Hz, 1H), 5.71 (d, J = 16.0 Hz, 1H), 5.32 – 5.27 (m, 1H), 5.23 (p, J = 1.6 Hz, 1H), 5.09 – 5.04 (m, 2H), 1.95 – 1.90 (m, 3H), 1.85 – 1.85 (m, 3H) ppm.

**¹³C NMR** (126 MHz, CDCl₃) δ = 144.2, 141.6, 127.2, 121.7, 119.0, 108.4, 93.1, 88.0, 23.6, 18.0 ppm.

**IR (ATR):** ν = 2976, 2952, 2923, 1793, 1610, 18586, 1454, 1373, 1297, 1215, 954, 907, 840, 757, 733, 669, 650, 530 cm⁻¹.

**HRMS (EI)**: m/z for C₁₀H₁₂ [M]: calc.: 132.0934, found: 132.0934.
Synthesis of (Z)-But-1-en-3-yne

**General Procedure 2:**

Under Argon atmosphere [CoBr₂(TriPhos)] (10 mol%), zinc dust (20 mol%) and zinc iodide (46 mol%) were added to a pre-dried reaction vessel. The solids were dried 10 min in vacuo. The catalyst system was dissolved in dry acetonitrile (0.67 mL mmol⁻¹) and the resulting dark red suspension was heated to 37 °C and stirred for 15 min. Then the corresponding alkyne (1.00 equiv.) was added at 37 °C. The reaction mixture was stirred until complete conversion was determined via GC/MS and TLC. The mixture was diluted with CH₂Cl₂ and filtered over a short plug of silica gel (eluent: n-pentane:CH₂Cl₂ = 3:1 or CH₂Cl₂, depending on the polarity of the substrate). The solvent was removed under reduced pressure. The crude product was purified via column chromatography (n-pentane:CH₂Cl₂ or n-pentane:ethyl acetate).

(Z)-But-1-en-3-yne,1,4-diyldibenzo([Z])

According to General Procedure 2 the title compound was prepared using phenylacetylene (102 mg, 1.00 mmol, 1.00 equiv., [CoBr₂(TriPhos)] (75.3 mg, 100 µmol, 0.10 equiv.), zinc dust (13.1 mg, 200 µmol, 0.20 equiv.) and zinc iodide (147 mg, 460 µmol, 0.46 equiv.) in acetonitrile (0.67 mL). The reaction mixture was stirred 2.5 h at 37 °C. The product was obtained after column chromatography (eluent: n-pentane:CH₂Cl₂ = 10:1) as a colorless liquid (65.6 mg, 321 µmol, 64%, E:Z = 6:94).

**1H NMR** (500 MHz, CDCl₃) δ = 7.95 (dd, J = 8.3, 1.4 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.43 – 7.39 (m, 2H), 7.38 – 7.31 (m, 4H), 6.72 (d, J = 11.9 Hz, 1H), 5.94 (d, J = 11.9 Hz, 1H) ppm.

**13C NMR** (126 MHz, CDCl₃) δ = 138.8, 136.7, 131.6 (2C), 128.9 (2C), 128.6 (3C), 128.5, 128.4 (2C), 123.7, 107.6, 96.0, 88.4 ppm.

**IR** (ATR): ν = 3060, 3020, 2190, 1949, 1880, 1594, 1569, 1489, 1442, 1410, 1184, 1157, 1070, 953, 914, 834, 780, 686, 563, 523 cm⁻¹.

**HRMS** (EI): m/z for C₁₆H₁₂ [M]+: calc.: 204.0934, found: 204.0933.

(Z)-4,4′-(But-1-en-3-yne,1,4-diyldiyl)bis(fluorobenzene) (3b)

According to General Procedure 2 the title compound was prepared using 4-fluorophenylacetylene (120 mg, 1.00 mmol, 1.00 equiv., [CoBr₂(TriPhos)] (75.3 mg, 100 µmol, 0.10 equiv.), zinc dust (13.1 mg, 200 µmol, 0.20 equiv.) and zinc iodide (147 mg, 460 µmol, 0.46 equiv.) in acetonitrile (0.67 mL). The reaction mixture was stirred 2.5 h at 37 °C. The product was obtained after column chromatography (eluent: n-pentane:CH₂Cl₂ = 10:1) as a colorless liquid (78.0 mg, 325 µmol, 65%, E:Z = 5:95).

**1H NMR** (500 MHz, CDCl₃) δ = 7.93 – 7.85 (m, 2H), 7.45 (ddd, J = 8.3, 5.3, 2.6 Hz, 2H), 7.09 – 7.03 (m, 4H), 6.67 (d, J = 11.9 Hz, 1H), 5.88 (d, J = 11.9 Hz, 1H) ppm.

**13C NMR** (126 MHz, CDCl₃) δ = 162.8 (d, J = 250.3 Hz), 162.7 (d, J = 249.3 Hz), 137.6, 133.5 (d, J = 8.3 Hz, 2C), 132.9 (d, J = 3.4 Hz, 2C), 130.6 (d, J = 8.1 Hz, 2C), 119.6 (d, J = 3.6 Hz, 2C), 116.0 (d, J = 22.2 Hz), 115.4 (d, J = 21.6 Hz), 107.0 (d, J = 1.8 Hz), 94.8, 87.8 ppm.

**IR** (ATR): ν = 3023, 2360, 2332, 2192, 1890, 1599, 1582, 1503, 1422, 1402, 1313, 1296, 1229, 1173, 1154, 1093, 1013, 977, 954, 937, 830, 814, 787, 754, 669, 640, 609, 560, 526 cm⁻¹.
HRMS (El): m/z for C\textsubscript{16}H\textsubscript{10}F\textsubscript{2} [M]\textsuperscript{+}: calc.: 240.0745, found: 240.0752.

General Procedure 3:

![Chemical Structure Diagram]

Under Argon atmosphere [CoBr\textsubscript{2}(TriPhos)] (10 mol%), zinc dust (20 mol%) and zinc iodide (46 mol%) were added to a pre-dried reaction vessel. The solids were dried 10 min in vacuo. The catalyst system was dissolved in dry acetonitrile (0.67 mL mmol\textsuperscript{-1}) and the resulting dark red suspension was heated to 37 °C and stirred for 15 min. Then the corresponding alkyne (1.00 equiv.) was added at 0 °C. The reaction mixture was stirred 1 h at 0 °C. Afterwards the mixture was stirred at ambient temperature until complete conversion was determined via GC/MS and TLC. The mixture was diluted with CH\textsubscript{2}Cl\textsubscript{2} and filtered over a short plug of silica gel (eluent: n-pentane:CH\textsubscript{2}Cl\textsubscript{2} = 3:1 or CH\textsubscript{2}Cl\textsubscript{2}, depending on the polarity of the substrate). The solvent was removed under reduced pressure. The crude product was purified via column chromatography (n-pentane:CH\textsubscript{2}Cl\textsubscript{2} or n-pentane:ethyl acetate).

(Z)-4,4'-(But-1-en-3-yn-1,4-diyl)bis(chlorobenzene) (3c)

According to General Procedure 3 the title compound was prepared using 4-chlorophenylacetylene (136 mg, 1.00 mmol, 1.00 equiv.), [CoBr\textsubscript{2}(TriPhos)] (75.3 mg, 100 \textmu mol, 0.10 equiv.), zinc dust (13.1 mg, 200 \textmu mol, 0.20 equiv.) and zinc iodide (147 mg, 460 \textmu mol, 0.46 equiv.) in acetonitrile (0.67 mL). The alkyne was added at 0 °C, the mixture was warmed to room temperature and stirred for 4 h. The product was obtained after column chromatography (eluent: n-pentane:CH\textsubscript{2}Cl\textsubscript{2} = 10:1) as a light-yellow solid (94.1 mg, 345 \textmu mol, 69%, E:Z < 1:99).

Melting point: 99 – 101 °C.

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ = 7.83 (d, J = 8.4 Hz, 2H), 7.46 – 7.29 (m, 6H), 6.67 (d, J = 11.9 Hz, 1H), 5.92 (d, J = 11.9 Hz, 1H) ppm.

\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ = 137.8, 135.0, 134.8, 134.3, 132.8 (2C), 130.1 (2C), 129.0 (2C), 128.7 (2C), 121.8, 107.9, 95.4, 88.9 ppm.

IR (ATR): \textbar{v} = 3017, 2187, 1896, 1587, 1559, 1486, 1422, 1343, 1313, 1269, 1223, 1113, 1090, 1013, 967, 956, 834, 823, 813, 759, 851, 726, 703, 686, 637, 604, 556, 534, 519 cm\textsuperscript{-1}.

HRMS (El): m/z for C\textsubscript{16}H\textsubscript{10}Cl\textsubscript{2} [M]\textsuperscript{+}: calc.: 272.0154, found: 272.0154.

(Z)-4,4'-(But-1-en-3-yn-1,4-diyl)bis(bromobenzene) (3d)

According to General Procedure 3 the title compound was prepared using 4-bromophenylacetylene (136 mg, 1.00 mmol, 1.00 equiv.), [CoBr\textsubscript{2}(TriPhos)] (75.3 mg, 100 \textmu mol, 0.10 equiv.), zinc dust (13.1 mg, 200 \textmu mol, 0.20 equiv.) and zinc iodide (147 mg, 460 \textmu mol, 0.46 equiv.) in acetonitrile (0.67 mL). The alkyne was added at 0 °C, the mixture was warmed to room temperature and stirred for 4 h. The product was obtained after column chromatography (eluent: n-pentane:CH\textsubscript{2}Cl\textsubscript{2} = 10:1) as a light-yellow solid (114 mg, 315 \textmu mol, 63%, E:Z = 1:99).

Melting point: 106 – 109 °C.

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ = 8.80 – 8.72 (m, 2H), 8.54 – 8.46 (m, 4H), 8.36 – 8.30 (m, 2H), 7.66 (d, J = 11.9 Hz, 1H), 6.93 (d, J = 11.9 Hz, 1H) ppm.
SUPPORTING INFORMATION

\( ^{13}C\text{ NMR}\) (126 MHz, CDCl\(_3\)) \(\delta = 137.9, 135.4, 133.0\) (2C), 131.9 (2C), 131.6 (2C), 130.3 (2C), 123.0, 122.6, 122.3, 108.1, 95.5, 89.1 ppm.

\(^\text{IR (ATR):}\) \(\tilde{\nu} = 3014, 2186, 1894, 1582, 1557, 1482, 1392, 1313, 1269, 1176, 1110, 1094, 1070, 977, 967, 956, 834, 823, 747, 701, 693, 636, 627, 556, 517\ cm\(^{-1}\).

\(\text{HRMS (EI):}\) \(m/z\) for C\(_{16}\)H\(_{10}\)Br\(_2\) [M\(^+\)]: calc.: 359.9144, found: 359.9139.

(Z)-4,4’-(But-1-en-3-yne-1,4-diyli)bis(methylbenzene) (3e)

According to General Procedure 3 the title compound was prepared using 4-methylphenylacetylene (116 mg, 1.00 mmol, 1.00 equiv.), [CoBr\(_2\)(TriPhos)] (75.3 mg, 100 \(\mu\)mol, 0.10 equiv.), zinc dust (13.1 mg, 200 \(\mu\)mol, 0.20 equiv.) and zinc iodide (147 mg, 460 \(\mu\)mol, 0.46 equiv.) in acetonitrile (0.67 mL). The alkyne was added at 0 °C, the mixture was warmed to room temperature and stirred for 4 h. The product was obtained after column chromatography (eluent: \(n\)-pentane:CH\(_2\)Cl\(_2\) = 10:1) as a colorless solid (78.8 mg, 339 \(\mu\)mol, 68%, \(E:Z = 5:95\)).

\(1^H\text{ NMR}\) (500 MHz, CDCl\(_3\)) \(\delta = 7.85\) (d, \(J = 8.2\) Hz, 2H), 7.40 (d, \(J = 8.1\) Hz, 2H), 7.21 (d, \(J = 8.0\) Hz, 2H), 7.17 (d, \(J = 7.8\) Hz, 2H), 6.66 (d, \(J = 11.8\) Hz, 1H), 5.87 (d, \(J = 11.9\) Hz, 1H), 2.39 (s, 6H) ppm.

\(^{13}C\text{ NMR}\) (126 MHz, CDCl\(_3\)) \(\delta = 138.6, 138.4, 134.1, 131.5\) (2C), 129.3, 129.2 (2C), 129.1 (2C), 128.9 (2C), 120.7, 106.7, 96.1, 88.1, 21.7, 21.5 ppm.

\(\text{IR (ATR):}\) \(\tilde{\nu} = 3016, 2914, 2184, 1896, 1623, 1582, 1556, 1506, 1480, 1392, 1269, 1176, 1107, 1070, 1037, 1009, 964, 834, 823, 749, 706, 646, 560, 517\ cm\(^{-1}\).

\(\text{HRMS (EI):}\) \(m/z\) for C\(_{18}\)H\(_{16}\) [M\(^+\)]: calc.: 232.1247, found: 232.1244.

\(1^H\text{ NMR}\) (500 MHz, CDCl\(_3\)) \(\delta = 7.93\) – 7.86 (m, 2H), 7.46 – 7.40 (m, 2H), 6.93 – 6.87 (m, 4H), 6.60 (d, \(J = 11.9\) Hz, 1H), 5.79 (d, \(J = 11.9\) Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H) ppm.

\(^{13}C\text{ NMR}\) (126 MHz, CDCl\(_3\)) \(\delta = 159.8\) (2C), 137.5, 133.0 (2C), 130.3 (2C), 130.0, 116.0, 114.3 (2C), 113.8 (2C), 105.4, 95.6, 87.6, 55.5 (2C) ppm.

\(\text{IR (ATR):}\) \(\tilde{\nu} = 3007, 2967, 2930, 2836, 2183, 2049, 1892, 1717, 1603, 1563, 1503, 1460, 1437, 1409, 1306, 1289, 1259, 1243, 1106, 1027, 959, 853, 830, 813, 781, 760, 714, 686, 647, 636, 610, 561, 533, 516\ cm\(^{-1}\).

\(\text{HRMS (EI):}\) \(m/z\) for C\(_{16}\)H\(_{16}\)O\(_2\) [M\(^+\)]: calc.: 264.1145, found: 264.1144.
**SUPPORTING INFORMATION**

### (Z)-4,4′-(But-1-en-3-yn-1,4-diy)bis(trifluoromethylbenzene) (3g)

According to General Procedure 3 the title compound was prepared using 4-trifluoromethylphenylacetylene (132 mg, 1.00 mmol, 1.00 equiv.), [CoBr₂(TriPhos)] (75.3 mg, 100 μmol, 0.10 equiv.), zinc dust (13.1 mg, 200 μmol, 0.20 equiv.) and zinc iodide (147 mg, 460 μmol, 0.46 equiv.) in acetonitrile (0.67 mL). The alkyne was added at 0 °C and the mixture was warmed to room temperature and stirred for 4 h. The product was obtained after column chromatography (eluent: n-pentane:CH₂Cl₂ = 10:1) as a colorless oil (91.2 mg, 268 μmol, 54%, E:Z = 3:97).

**1H NMR** (500 MHz, CDCl₃) δ = 7.99 (d, J = 8.1 Hz, 2H), 7.68 – 7.61 (m, 4H), 7.58 (d, J = 8.2 Hz, 2H), 6.80 (d, J = 12.0 Hz, 1H), 6.06 (d, J = 11.9 Hz, 1H) ppm.

**13C NMR** (126 MHz, CDCl₃) δ = 139.7, 138.3, 131.9, 130.6 (q, J = 32.9 Hz, 2C), 130.51 (q, J = 32.6 Hz, 2C), 129.0, 126.9, 125.6 (q, J = 3.6 Hz, 2C), 126.15 (q, J = 33.6 Hz, 2C), 124.9 (<J = 7.8 Hz, 2H), 7.86 (m, 4H), 7.62 (d, J = 11.9 Hz, 2H) ppm.

**19F NMR** (470 MHz, CDCl₃) δ = –62.7, –62.9 ppm.

**IR (ATR):** ν = 3359, 2722, 1924, 1804, 1684, 1597, 1559, 1429, 1689, 1207, 1162, 1103, 1011, 949, 824, 807, 724, 710, 686, 639, 579, 561, 547, 531, 523 cm⁻¹.

**HRMS (EI):** m/z for C₁₇H₁₂F₆ [M⁺]: calc.: 340.0681, found: 340.0675.

### (Z)-4,4′-(But-1-en-3-yn-1,4-diy)bis(methylbenzene) (3h)

According to General Procedure 3 the title compound was prepared using 4-ethynylbenzaldehyde (130 mg, 1.00 mmol, 1.00 equiv.), [CoBr₂(TriPhos)] (75.3 mg, 100 μmol, 0.10 equiv.), zinc dust (13.1 mg, 200 μmol, 0.20 equiv.) and zinc iodide (147 mg, 460 μmol, 0.46 equiv.) in acetonitrile (0.67 mL). The alkyne was added at 0 °C, the mixture was warmed to 37 °C and stirred for 24 h. The product was obtained after column chromatography (eluent: CH₂Cl₂) as a light-yellow solid (17.9 mg, 68.7 μmol, 14%, E:Z = 9:91).

**1H NMR** (300 MHz, CDCl₃) δ = 10.03 (s, 2H), 8.04 (d, J = 8.2 Hz, 2H), 7.93 – 7.86 (m, 4H), 7.62 (d, J = 8.1 Hz, 2H), 6.84 (d, J = 12.0 Hz, 1H), 6.11 (d, J = 11.9 Hz, 1H) ppm.

**13C NMR** (75 MHz, CDCl₃) δ = 191.7, 191.4, 142.1, 134.1, 136.1, 135.9, 132.2 (2C), 129.9 (2C), 129.8 (2C), 129.4 (2C), 129.2, 110.4, 96.3, 91.5 ppm.

**IR (ATR):** ν = 3359, 2722, 1924, 1804, 1684, 1597, 1559, 1429, 1389, 1302, 1207, 1162, 1103, 1011, 949, 824, 807, 724, 710, 686, 639, 579, 561, 547, 531, 523 cm⁻¹.

**HRMS (EI):** m/z for C₁₇H₁₂O₂ [M⁺]: calc.: 260.0832, found: 260.0831.

### (Z)-4,4′-(But-1-en-3-yn-1,4-diy)bis(tert-butylbenzene) (3i)

According to General Procedure 3 the title compound was prepared using methyl 4-ethynyl benzoate (160 mg, 1.00 mmol, 1.00 equiv.), [CoBr₂(TriPhos)] (75.3 mg, 100 μmol, 0.10 equiv.), zinc dust (13.1 mg, 200 μmol, 0.20 equiv.) and zinc iodide (147 mg, 460 μmol, 0.46 equiv.) in acetonitrile (0.67 mL). The alkyne was added at 0 °C, the mixture was warmed to room temperature and stirred for 4 h. The product was obtained after column chromatography (eluent: CH₂Cl₂) as a yellow waxy oil (108 mg, 337 μmol, 67%, E:Z = 2:98).

**1H NMR** (500 MHz, CDCl₃) δ = 8.08 – 8.04 (m, 2H), 8.04 – 8.02 (m, 2H), 7.95 (d, J = 8.4 Hz, 2H), 7.57 – 7.50 (m, 2H), 6.79 (d, J = 11.9 Hz, 1H), 6.05 (d, J = 11.9 Hz, 1H), 3.93 (s, 3H), 3.93 (s, 3H) ppm.
SUPPORTING INFORMATION

$^{13}$C NMR (126 MHz, CDCl$_3$) δ = 166.8, 166.6, 140.7, 138.7 (2C), 131.6 (2C), 130.0, 129.8 (4C), 128.8 (2C), 127.8, 109.6, 96.1, 90.7, 52.4, 52.3 ppm.

IR (ATR): $\tilde{v}$ = 3039, 3019, 2964, 1719, 1604, 1559, 1504, 1467, 1436, 1404, 1312, 1273, 1183, 1104, 1014, 954, 854, 840, 810, 781, 763, 739, 689, 519 cm$^{-1}$.

HRMS (EI)+: $m/z$ for C$_{20}$H$_{16}$O$_4$ [M]$^+$: calc.: 320.1043, found: 320.1034.

(Z)-4,4'-((But-en-3-yn-1,4-diyl)bis(tert-butylbenzene) (3k)

According to General Procedure 3 the title compound was prepared using 4-tert-butylphenylacetylene (158 mg, 1.00 mmol, 1.00 equiv.), [CoBr$_2$(TriPhos)] (75.3 mg, 100 µmol, 0.10 equiv.), zinc dust (13.1 mg, 200 µmol, 0.20 equiv.) and zinc iodide (147 mg, 460 µmol, 0.46 equiv.) in acetonitrile (0.67 mL). The alkyne was added at 0 °C, the mixture was warmed to room temperature and stirred for 4 h. The product was obtained after column chromatography (eluent: n-pentane:CH$_2$Cl$_2$ = 10:1) as a yellow waxy oil (94.6 mg, 299 µmol, 60%, E:Z = 1:99).

$^1$H NMR (500 MHz, CDCl$_3$) δ = 7.94 – 7.87 (m, 2H), 7.48 – 7.44 (m, 2H), 7.45 – 7.37 (m, 4H), 6.66 (d, $J$ = 11.9 Hz, 1H), 5.88 (d, $J$ = 11.9 Hz, 1H), 1.36 (s, 9H), 1.35 (s, 9H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$) δ = 151.8, 151.7, 138.2, 134.1, 131.3 (2C), 128.7 (2C), 125.6 (2C), 125.4 (2C), 120.8, 106.8, 96.1, 88.1, 35.0, 34.9, 31.4 (3C), 31.3 (3C) ppm.

IR (ATR): $\tilde{v}$ = 3020, 2960, 2903, 2867, 2190, 1909, 1787, 1669, 1606, 1503, 1462, 1420, 1394, 1363, 1322, 1267, 1230, 1200, 1107, 1017, 923, 833, 763, 726, 577, 559, 523, 513 cm$^{-1}$.

HRMS (EI)+: $m/z$ for C$_{24}$H$_{28}$ [M]$^+$: calc.: 316.2186, found: 316.2181.

(Z)-3,3'-(But-en-3-yn-1,4-diyl)bis(methylbenzene) (3l)

According to General Procedure 3 the title compound was prepared using 3-methylphenylacetylene (116 mg, 1.00 mmol, 1.00 equiv.), [CoBr$_2$(TriPhos)] (75.3 mg, 100 µmol, 0.10 equiv.), zinc dust (13.1 mg, 200 µmol, 0.20 equiv.) and zinc iodide (147 mg, 460 µmol, 0.46 equiv.) in acetonitrile (0.67 mL). The alkyne was added at 0 °C, the mixture was warmed to room temperature and stirred for 24 h. The product was obtained after column chromatography (eluent: n-pentane:CH$_2$Cl$_2$ = 15:1) as a yellow oil (64.7 mg, 279 µmol, 56%, E:Z = 4:96).

$^1$H NMR (500 MHz, CDCl$_3$) δ = 7.83 (d, $J$ = 2.0 Hz, 1H), 7.72 (dt, $J$ = 7.7, 1.3 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.25 (d, $J$ = 7.6 Hz, 1H), 7.19 – 7.13 (m, 2H), 6.68 (d, $J$ = 11.9 Hz, 1H), 5.91 (d, $J$ = 11.9 Hz, 1H), 2.41 (s, 3H), 2.37 (s, 3H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$) δ = 138.8, 138.2, 137.9, 136.7, 132.2, 129.6, 129.4 (2C), 128.7, 128.5, 128.3, 126.2, 123.6, 107.4, 96.2, 88.3, 21.6, 21.4 ppm.

IR (ATR): $\tilde{v}$ = 3020, 2919, 2860, 2732, 2187, 1942, 1697, 1599, 1577, 1483, 1447, 1377, 1300, 1283, 1144, 1090, 1039, 953, 904, 879, 797, 780, 687, 586, 564, 523 cm$^{-1}$.

HRMS (EI)+: $m/z$ for C$_{18}$H$_{16}$ [M]+: calc.: 232.1247, found: 232.1242.
**SUPPORTING INFORMATION**

### (Z)-3,3′-(But-1-en-3-yn-1,4-diy)bis(methoxybenzene) (3m)

According to General Procedure 3 the title compound was prepared using 3-methoxyphenylacetlene (132 mg, 1.00 mmol, 1.00 equiv.). [CoBr2(TriPhos)] (75.3 mg, 100 µmol, 0.10 equiv.), zinc dust (13.1 mg, 200 µmol, 0.20 equiv.) and zinc iodide (147 mg, 460 µmol, 0.46 equiv.) in acetonitrile (0.67 mL). The alkyne was added at 0 °C, the mixture was warmed to room temperature and stirred for 4 h. The product was obtained after column chromatography (eluent: n-pentane:CH2Cl2 = 2:1) as a colorless oil (89.5 mg, 339 µmol, 68%, E:Z = 1:99).

### 1H NMR (500 MHz, CDCl3) δ = 7.68 (t, J = 2.0 Hz, 1H), 7.39 (dt, J = 7.5, 1.2 Hz, 1H), 7.30 (t, J = 7.9 Hz, 1H), 7.26 (t, J = 7.9 Hz, 1H), 7.10 (dt, J = 7.6, 1.2 Hz, 1H), 7.04 (dd, J = 2.6, 1.3 Hz, 1H), 6.93 – 6.86 (m, 2H), 6.69 (d, J = 12.0 Hz, 1H), 5.93 (d, J = 11.9 Hz, 1H), 3.82 (s, 6H) ppm.

### 13C NMR (126 MHz, CDCl3) δ = 159.6, 159.5, 138.8, 137.9, 129.6, 129.4, 124.5, 124.1, 121.9, 116.3, 115.2, 114.9, 113.4, 107.7, 96.3, 88.2, 55.4 (2C) ppm.

### IR (ATR): δ = 3002, 2956, 2937, 2833, 2189, 1929, 1843, 1706, 1594, 1572, 1484, 1460, 1429, 1317, 1289, 1257, 1236, 1203, 1162, 1082, 1040, 991, 854, 779, 706, 684, 564, 523 cm⁻¹.

### HRMS (EI): m/z for C26H16O2 [M⁺]: calc.: 264.1145, found: 264.1145.

### (Z)-2,2′-(But-1-en-3-yn-1,4-diy)bis(methylbenzene) (3n)

According to General Procedure 3 the title compound was prepared using 2-methylphenylacetylene (116 mg, 1.00 mmol, 1.00 equiv.). [CoBr2(TriPhos)] (75.3 mg, 100 µmol, 0.10 equiv.), zinc dust (13.1 mg, 200 µmol, 0.20 equiv.) and zinc iodide (147 mg, 460 µmol, 0.46 equiv.) in acetonitrile (0.67 mL). The alkyne was added at 0 °C, the mixture was warmed to room temperature and stirred for 24 h. The product was obtained after column chromatography (eluent: n-pentane:CH2Cl2 = 10:1) as a yellow oil (53.0 mg, 228 µmol, 46%, E:Z = 41:59).

### 1H NMR (500 MHz, CDCl3) δ = 8.32 (dd, J = 5.0, 3.8 Hz, 1H), 7.45 (dd, J = 7.5, 1.2 Hz, 1H), 7.29 – 7.23 (m, 6H), 6.96 (d, J = 11.7 Hz, 1H), 6.09 (d, J = 11.9 Hz, 1H), 2.47 (s, 3H), 2.43 (s, 3H) ppm.

### 13C NMR (126 MHz, CDCl3) δ = 140.3, 136.7, 136.5, 135.5, 132.2, 130.2, 129.6, 128.5, 128.4 (2C), 125.7 (2C), 123.5, 108.7, 94.1, 91.8, 20.9, 19.9 ppm.

### IR (ATR): δ = 3019, 2946, 2920, 2735, 2322, 2187, 1952, 1916, 1804, 1694, 1599, 1483, 1456, 1379, 1197, 1159, 1114, 1044, 987, 950, 866, 839, 811, 790, 750, 711, 667, 623, 514 cm⁻¹.

### HRMS (EI): m/z for C22H14 [M⁺]: calc.: 232.1247, found: 232.1245.

### (Z)-2,2′-(But-1-en-3-yn-1,4-diy)bis(methoxybenzene) (3o)

According to General Procedure 3 the title compound was prepared using 2-methoxyphenylacetylene (132 mg, 1.00 mmol, 1.00 equiv.). [CoBr2(TriPhos)] (75.3 mg, 100 µmol, 0.10 equiv.), zinc dust (13.1 mg, 200 µmol, 0.20 equiv.) and zinc iodide (147 mg, 460 µmol, 0.46 equiv.) in acetonitrile (0.67 mL). The alkyne was added at 0 °C, the mixture was warmed to room temperature and stirred for 18 h. The product was obtained after column chromatography (eluent: n-pentane:CH2Cl2 = 2.1) as a light-yellow waxy oil (81.4 mg, 308 µmol, 62%, E:Z = 30:70).

### 1H NMR (500 MHz, CDCl3) δ = 8.70 (dd, J = 7.8, 1.7 Hz, 1H), 7.42 (dd, J = 7.6, 1.7 Hz, 1H), 7.33 – 7.25 (m, 2H), 7.13 (d, J = 12.2 Hz, 1H), 7.05 – 6.97 (m, 1H), 6.96 – 6.89 (m, 1H), 6.89 (d, J = 8.3 Hz, 2H), 5.99 (d, J = 12.1 Hz, 1H), 3.93 (s, 3H), 3.86 (s, 3H) ppm.
**SUPPORTING INFORMATION**

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta = 160.3, 157.1, 133.4, 132.3, 129.8, 129.7, 129.0, 125.8, 120.5, 120.6, 120.3, 113.1, 110.5, 110.6, 107.2, 92.8, 92.3, 55.9, 55.7 \text{ ppm.}

IR (ATR): \(\tilde{\nu} = 3003, 2960, 2936, 2834, 2186, 1594, 1572, 1487, 1462, 1433, 1316, 1292, 1269, 1240, 1179, 1162, 1119, 1107, 1047, 1023, 957, 934, 853, 831, 801, 746, 671, 580 \text{ cm}^{-1}.

HRMS (EI): \(m/z\) for C\(_{18}\)H\(_{16}\)O\(_2\) [M]+: calc.: 264.1145, found: 264.1143.

(Z)-3,3'-(But-1-en-3-ynyl)naphtyl (3p)

![Diagram of (Z)-3,3'-(But-1-en-3-ynyl)dipyridine (3p)]

According to General Procedure 3 the title compound was prepared using 3-ethynylpyridine (103 mg, 1.00 mmol, 1.00 equiv.), [CoBr\(_2\)(TriPhos)] (75.3 mg, 100 \mu\text{mol}, 0.10 equiv.), zinc dust (13.1 mg, 200 \mu\text{mol}, 0.20 equiv.) and zinc iodide (147 mg, 460 \mu\text{mol}, 0.46 equiv.) in acetonitrile (0.67 mL). The alkyne was added at 0 °C, the mixture was warmed to room temperature and stirred for 28 h. The product was obtained after column chromatography (eluent: ethyl acetate) as a light-brown oil (18.8 mg, 91.2 \mu\text{mol}, 18%, \(E:Z = 10:90\)).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 8.95 (d, J = 2.3 \text{ Hz}, 1H), 8.72 (d, J = 2.1 Hz, 1H), 8.59 – 8.51 (m, 2H), 8.34 (dt, J = 8.1, 1.9 Hz, 1H), 7.80 – 7.70 (m, 1H), 7.31 (td, J = 7.7, 3.9 Hz, 2H), 7.05 (d, J = 11.9 Hz, 1H), 6.06 (d, J = 11.9 Hz, 1H) \text{ ppm.}

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 152.2, 150.5, 149.6, 149.1, 138.5, 136.1, 135.1, 132.2, 123.4, 123.3, 120.2, 109.5, 93.4, 90.6 \text{ ppm.}

IR (ATR): \(\tilde{\nu} = 3023, 2963, 1586, 1563, 1479, 1426, 1407, 1216, 1024, 907, 804, 753, 731, 704, 669, 650, 626 \text{ cm}^{-1}.

HRMS (EI): \(m/z\) for C\(_{14}\)H\(_{10}\)N\(_2\) [M]+: calc.: 206.0838, found: 206.0832.

(Z)-3,3'-But-1-en-3-ynyl)dithiophene (3r)

![Diagram of (Z)-3,3'-But-1-en-3-ynyl)dithiophene (3r)]

According to General Procedure 3 the title compound was prepared using 3-ethynylthiophene (108 mg, 1.00 mmol, 1.00 equiv.), [CoBr\(_2\)(TriPhos)] (75.3 mg, 100 \mu\text{mol}, 0.10 equiv.), zinc dust (13.1 mg, 200 \mu\text{mol}, 0.20 equiv.) and zinc iodide (147 mg, 460 \mu\text{mol}, 0.46 equiv.) in acetonitrile (0.67 mL). The alkyne was added at 0 °C, the mixture was warmed to room temperature and stirred for 4 h. The product was obtained after column chromatography (eluent: n-pentane:CH\(_2\)Cl\(_2\) = 10:1) as a yellow solid (47.5 mg, 220 \mu\text{mol}, 44%, \(E:Z = 3:97\)).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 7.37 (dt, J = 5.1, 1.0 \text{ Hz}, 1H), 7.33 (td, J = 4.9, 1.1 \text{ Hz}, 2H), 7.30 – 7.28 (m, 1H), 7.05 (ddd, J = 5.2, 3.6, 2.1 Hz, 2H), 6.96 (dt, J = 11.5, 0.7 Hz, 1H), 5.77 (d, J = 11.3 \text{ Hz}, 1H) \text{ ppm.}

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta = 141.0, 132.4, 131.9, 129.8, 127.9, 127.4, 123.7, 123.6, 104.4, 92.6, 92.3 \text{ ppm.}

IR (ATR): \(\tilde{\nu} = 3100, 3076, 2182, 1900, 1794, 1730, 166, 1660, 1582, 1537, 1516, 1499, 1433, 1419, 1393, 1350, 1334, 1267, 1212, 1197, 1116, 1077, 1043, 980, 941, 899, 847, 829, 764, 746, 727, 707, 693, 590, 569, 544, 526, 504 \text{ cm}^{-1}.

HRMS (EI): \(m/z\) for C\(_{12}\)H\(_8\)S\(_2\) [M]+: calc.: 216.0062, found: 216.0054.
**SUPPORTING INFORMATION**

**Reaction Optimization for the Synthesis of E-1,3-Enynes**

**Determination of categorical parameters**

Table S1. Optimization of the cobalt source for the E-selective dimerization of terminal alkynes.

| Entry | Cobalt salt      | Zinc iodide | Conversion | Yield[a] |
|-------|------------------|-------------|------------|----------|
| 1     | CoBr₂            | no          | 100%       | 52%      |
| 2     | CoBr₂            | yes         | 100%       | 49%      |
| 3     | Co(OAc)₂         | no          | 100%       | 50%      |
| 4     | CoCl₂            | no          | 0%         | 0%       |
| 5     | Co(ClO₄)₂·6H₂O   | no          | 0%         | 0%       |
| 6     | Co(BF₄)₂·6H₂O    | no          | 0%         | 0%       |

[a] All reactions were carried out on a 0.5 mmol scale using phenylacetylene as test substrate in 0.5 mL MeCN. For all reactions 5 mol% cobalt salt, 5 mol% dppp as ligand, 10 mol% zinc dust and 0.55 equiv. triethylamine were used. The yields were determined via GC/FID using mesitylene (1.0 M in CH₂Cl₂, 0.5 mL, 0.5 mmol, 1.00 equiv.) as internal standard. The internal standard was added after 16 h reaction time.

Table S2. Optimization of the solvent for the E-selective dimerization of terminal alkynes.

| Entry | Solvent | Conversion | Yield[a] |
|-------|---------|------------|----------|
| 1     | THF     | 100%       | 40%      |
| 2     | MeCN    | 100%       | 52%      |
| 3     | DMF     | 100%       | 50%      |
| 4     | DMA     | 100%       | 51%      |
| 5     | CH₂Cl₂  | 10%        | 3%       |

[a] All reactions were carried out on a 0.5 mmol scale using phenylacetylene as test substrate in 0.5 mL corresponding solvent. For all reactions 5 mol% cobalt salt, 5 mol% ligand, 10 mol% zinc dust and 0.55 equiv. triethylamine were used. The yields were determined via GC/FID using mesitylene (1.0 M in CH₂Cl₂, 0.5 mL, 0.5 mmol, 1.00 equiv.) as internal standard. The internal standard was added after 16 h reaction time. DMA: Dimethylacetamide

Table S3. Optimization of the bidentate ligand for the E-selective Dimerization of terminal alkynes.

| Entry | Ligand   | Conversion | Yield[a] |
|-------|----------|------------|----------|
| 1     | dppm     | 0%         | 0%       |
| 2     | dppe     | 44%        | 22%      |
| 3     | dppp     | 100%       | 52%      |
| 4     | dppb     | 0%         | 0%       |
| 5     | dppf     | 0%         | 0%       |
| 6     | PyImine  | 100%       | 0%[b]    |
| 7     | (IPrIm)₂Py | 100%     | 0%[b]    |

[a] All reactions were carried out on a 0.5 mmol scale using phenylacetylene as test substrate in 0.5 mL MeCN. For all reactions 5 mol% cobalt salt, 5 mol% ligand, 10 mol% zinc dust and 0.55 equiv. triethylamine were used. The yields were determined via GC/FID using mesitylene (1.0 M in CH₂Cl₂, 0.5 mL, 0.5 mmol, 1.00 equiv.) as internal standard. The internal standard was added after 16 h reaction time. dppm: Bis(diphenylphosphino)methane; dppe: 1,2-Bis(diphenylphosphino)ethane; dppp: 1,3-Bis(diphenylphosphino)propane; dppb: 1,4-Bis(diphenylphosphino)butane; dppf: 1,1'-Bis(diphenylphosphino)ferrocene, PyImine: N-mesityl-1-(pyridin-2-yl)methanimine; (IPrIm)₂Py: 1,1'-[pyridine-2,6-diy]bis[N-(2,6-disopropylphenyl)ethan-1-imine]. [b] Only cyclotrimerization product could be observed.
Table S4. Optimization of the additive for the E-selective dimerization of terminal alkynes.

| Entry | Additive | Conversion | Yield[a] |
|-------|----------|------------|----------|
| 1     | NEt$_3$  | 100%       | 52%      |
| 2     | Pyrrolidine | 100%       | 45%      |
| 3     | Pyridine | 7%         | 2%       |
| 4     | K$_2$CO$_3$ | 100%       | 43%      |
| 5     | KOPiv    | 0%         | 0%       |
| 6     | TMEDA    | 85%        | 38%      |
| 7     | Glycine  | 78%        | 34%      |
| 8     | PPh$_3$  | 100%       | 70%[b]   |

[a] All reactions were carried out on a 0.5 mmol scale using phenylacetylene as test substrate in 0.5 mL MeCN. For all reactions 5 mol% CoBr$_2$(dppp), 10 mol% zinc dust and 0.55 equiv. additive were used. The yields were determined via GC/FID using (1.0 M in CH$_2$Cl$_2$, 0.5 mL, 0.5 mmol, 1.00 equiv.) as internal standard. The internal standard was added after 16 h reaction time. [b] 4-Fluorophenylacetylene was used. The reaction mixture was quenched after 1 h reaction time.

Reaction Optimization for the E-selective hydroalkynylation of terminal alkynes using Design of Experiments

A D-optimal screening design was generated by using JMP 13 software package by SAS (version 13.2.1, SAS Institute Inc, Cary, NC, © 2016). The generated design considered all linear and quadratic terms of the numerical values. After running all initial experiments, the screening design was extended to consider possible cross interactions (temperature · substrate concentration, temperature · time, substrate concentration · time, catalyst loading · time, catalyst loading · zinc iodide). In this case only one cross interaction had a low p-value (temperature · substrate concentration). All other tested cross interactions did not have a big significance on the screening design. In total the design consisted of 25 reactions, excluding one verified outlier. For the lack of fit value three experiments were duplicated. At last three additional experiments were conducted for to gain a higher significance of the quadratic term of the triphenyl phosphate equivalents.

General Procedure 4:

Under Argon atmosphere all solids were added into a pre-dried reaction vessel. The solids were dried in vacuo for 15 min. Afterwards the catalyst system was dissolved in acetonitrile (0.33 - 2.50 mL) using standard single use syringes. The mixture was shortly heated up to approximately 80 °C. whereas a color-change from dark blue/green to dark green appeared. The resulting solution was cooled to the desired temperature and the test substrate (4-fluorophenylacetylene) was added (60.0 µL, 500 µmol, 1.00 equiv., via Eppendorf™ pipette) to the catalyst system. After the desired reaction time, mesitylene (1.0 M in CH$_2$Cl$_2$, 0.5 mL, 500 µmol, 1.00 equiv., via syringe) and hexafluorobenzene (57.7 µL, 500 µmol, 1.00 equiv., via Eppendorf™ pipette) were added. The yield of the product was determined via GC/FID and $^{19}$F NMR spectroscopy.
Table S5. Optimization reactions of DoE for the E-selective hydroalkynylation of terminal alkynes. All reactions were carried out on a 0.5 mmol scale, according to General Procedure 4. The predicted optimal reaction conditions were verified. Predicted yield: 85%, isolated yield: 82%.

| Entry | catalyst loading [mol%] | Equiv. PPh₃ | Temperature [°C] | Time [h] | zinc iodide | substrate concentration [M] | Yield [%] |
|-------|------------------------|-------------|-----------------|---------|------------|-----------------------------|-----------|
| 1     | 6                      | 1           | 55              | 6       | No         | 1.50                        | 3         |
| 2     | 2                      | 3           | 27.5            | 0.5     | No         | 1.43                        | 62        |
| 3     | 6                      | 2           | 55              | 6       | Yes        | 0.20                        | 3         |
| 4     | 2                      | 3           | 55              | 6       | Yes        | 0.20                        | 33        |
| 5     | 4                      | 3           | 55              | 3.25    | No         | 0.85                        | 37        |
| 6     | 2                      | 1           | 27.5            | 6       | Yes        | 0.85                        | 40        |
| 7     | 6                      | 1           | 27.5            | 3.25    | Yes        | 1.43                        | 20        |
| 8     | 6                      | 1           | 0               | 6       | Yes        | 0.85                        | 47        |
| 9     | 4                      | 1           | 0               | 0.5     | No         | 1.43                        | 75        |
| 10    | 2                      | 1           | 55              | 0.5     | No         | 0.20                        | 43        |
| 11    | 2                      | 2           | 55              | 0.5     | Yes        | 1.43                        | 29        |
| 12    | 2                      | 2           | 0               | 3.25    | No         | 0.20                        | 60        |
| 13    | 6                      | 1           | 55              | 0.5     | No         | 0.20                        | 24        |
| 14    | 6                      | 3           | 0               | 0.5     | Yes        | 0.20                        | 21        |
| 15    | 2                      | 1           | 55              | 6       | No         | 1.43                        | 19        |
| 16    | 4                      | 1           | 0               | 6       | No         | 0.20                        | 52        |
| 17    | 6                      | 2           | 0               | 0.5     | No         | 0.85                        | 71        |
| 18    | 6                      | 3           | 0               | 6       | No         | 1.50                        | 71        |
| 19    | 6                      | 3           | 27.5            | 6       | No         | 0.20                        | 46        |
| 20    | 6                      | 3           | 55              | 0.5     | Yes        | 1.43                        | 8         |
| 21    | 2                      | 3           | 0               | 6       | No         | 1.43                        | 76        |
| 22    | 4                      | 2           | 27.5            | 6       | Yes        | 1.43                        | 35        |
| 23    | 6                      | 2           | 27.5            | 2       | No         | 0.25                        | 48        |
| 24    | 3                      | 2           | 0               | 1       | No         | 0.50                        | 71        |
| 25    | 2                      | 1           | 15              | 3.25    | Yes        | 1.43                        | 52        |

Replication

| Entry | catalyst loading [mol%] | Equiv. PPh₃ | Temperature [°C] | Time [h] | zinc iodide | substrate concentration [M] | Yield [%] |
|-------|------------------------|-------------|-----------------|---------|------------|-----------------------------|-----------|
| 2     | 3                      | 27.5        | 0.5             | No      | 1.43       | 56                          | 56        |
| 4     | 1                      | 0           | 0.5             | No      | 1.43       | 73                          | 73        |
| 6     | 2                      | 0           | 0.5             | No      | 0.85       | 72                          | 72        |
| PPh₃-1| 2                      | 2           | 0               | 2       | No         | 1.25                        | 85        |
| PPh₃-2| 2                      | 2.5         | 0               | 2       | No         | 1.25                        | 77        |
| PPh₃-3| 2                      | 3           | 0               | 2       | No         | 1.25                        | 78        |
**Response yield**

**Actual by Predicted Plot**

![Actual by Predicted Plot](image)

**Effect Summary**

| Source                                    | LogWorth | PValue  |
|-------------------------------------------|----------|---------|
| temperature (0,55)                        | 10.239   | 0.00000 |
| zinc iodide                               | 5.597    | 0.00000 |
| temperature*substrate concentration       | 4.635    | 0.00002 |
| catalyst loading (2,6)                    | 4.535    | 0.0003  |
| substrate concentration*substrate concentration | 1.873   | 0.01338 |
| PPh$_3$ equivalents*PPh$_3$ equivalents    | 1.695    | 0.02019 |
| substrate concentration (0,2,1,5)         | 0.542    | 0.28719 |
| PPh$_3$ equivalents (1,4)                 | 0.430    | 0.37123 |

**Lack of Fit**

| Source          | DF | Sum of Squares | Mean Square | F Ratio   | Prob > F |
|-----------------|----|----------------|-------------|-----------|----------|
| Lack of Fit     | 20 | 935,32117      | 46,7661     | 6.8438    | 0.0690   |
| Pure Error      | 3  | 20,50000       | 6,8333      | 0.9989    |
| Total Error     | 23 | 955,82117      |             |           |

**Residual by Predicted Plot**

![Residual by Predicted Plot](image)
The results of the screening design were verified by $k$-fold cross validation ($k = 5$).
The higher $p$-value of the linear terms (substrate concentration and triphenylphosphine equivalents) could be a result of inaccuracies of the scale weighing small amounts of triphenylphosphine and inexact voluminal of the solvent using single-use syringes.
## Reaction Optimization for the Synthesis of Z-1,3-Enynes

### Determination of categorical parameters

**Table S6.** Optimization of the solvent for the Z-selective dimerization of terminal alkynes.

| Entry | Solvent | Yield$^{[a]}$ |
|-------|---------|--------------|
| 1     | THF     | 26%          |
| 2     | MeCN    | 41%          |
| 3     | EtOAc   | 12%          |
| 4     | Acetone | 19%          |
| 5     | DMF     | 22%          |
| 5     | CH$_2$Cl$_2$ | 3%       |

[a] All reactions were carried out on a 0.5 mmol scale using phenylacetylene as test substrate in 0.5 mL corresponding solvent. For all reactions 5 mol% [CoBr$_2$(TriPhos)], 10 mol% zinc dust and 1.00 equiv. triethylamine were used. The yields were determined via GC/FID using (1.0 M in CH$_2$Cl$_2$, 0.5 mL, 0.5 mmol, 1.00 equiv.) as internal standard. The internal standard was added after 16 h reaction time.

**Table S7: **Optimization of the Lewis acid for the Z-selective dimerization of terminal alkynes.

| Entry | Lewis Acid | Conversion | Yield$^{[a]}$ |
|-------|------------|------------|--------------|
| 1     | ZnI$_2$$^{[b]}$ | 95% | 52%          |
| 2     | ZnBr$_2$   | 87% | 44%          |
| 3     | ZnCl$_2$   | 84% | 36%          |
| 4     | AlCl$_3$   | 54% | 14%          |
| 5     | BF$_3$OEt$_2$ | 18% | 0%           |
| 6     | B(OiPr)$_3$ | 69% | 26%          |

[a] All reactions were carried out on a 0.5 mmol scale using (4-fluorophenyl)acetylene as test substrate in 0.5 mL acetonitrile. For all reactions 5 mol% [CoBr$_2$(TriPhos)], 10 mol% zinc dust and 10 mol% Lewis acid were used. The yields were determined via GC/FID using (1.0 M in CH$_2$Cl$_2$, 0.5 mL, 0.5 mmol, 1.00 equiv.) as internal standard. The internal standard was added after 16 h reaction time. [b] ZnI$_2$ (50 mol%) were used.

**Table S8: **Optimization of the counter ion and additives for the Z-selective dimerization of terminal alkynes.

| Entry | Cobalt salt | Zinc iodide | Additive | Conversion | Yield$^{[a]}$ | E/Z ratio |
|-------|-------------|-------------|----------|------------|--------------|-----------|
| 1     | CoBr$_2$    | Yes         | PPh$_3$ (5 mol%) | 76% | 41% | 5:95     |
| 2     | CoBr$_2$    | Yes         | PPh$_3$ (4 mol%) | 76% | 42% | 5:95     |
| 3     | CoBr$_2$    | Yes         | PPh$_3$ (10 mol%) | 71% | 26% | 50:50    |
| 4     | CoBr$_2$    | Yes         | None      | 80% | 44% | 5:95     |
| 5     | CoBr$_2$    | No          | PPh$_3$ (5 mol%) | 87% | 9%  | 12:88    |
| 6     | Co(OAc)$_2$ | No          | None      | 40% | 16% | 12:88    |
| 7     | CoCl$_2$    | No          | None      | 76% | 30% | 5:95     |
| 8     | CoCl$_2$    | Yes         | None      | 65% | 23% | 17:83    |
| 9     | Co(ClO$_4$)$_2$ | No      | NEt$_3$ | 60% | 23% | 6:94     |
| 10    | Co(BF$_4$)$_2$ | No      | None      | 54% | 7%  | 29:71    |
SUPPORTING INFORMATION

| Entry | Cobalt salt | Zinc iodide | Additive | Conversion | Yield[a] | E/Z ratio |
|-------|-------------|-------------|----------|------------|----------|-----------|
| 11    | Co(BF₄)₂·6H₂O | No          | PPh₃ (5 mol%) | 71%        | 14%      | 29:71     |
| 12    | CoBr₂       | Yes         | Pyridine (10 mol%) | 89%        | 40%      | 7:93      |
| 13    | CoBr₂       | Yes         | 2,6-Lutidine (10 mol%) | 90%        | 28%      | 7:93      |
| 14    | CoBr₂       | Yes         | 4-Chlorostyrene (10 mol%) | 86%        | 37%      | 5:95      |
| 15    | CoBr₂       | Yes         | Pyridine (10 mol%) | 89%        | 40%      | 7:93      |
| 16    | CoBr₂       | Yes         | Pcy₃ (5 mol%) | 81%        | 36%      | 3:97      |
| 17    | CoBr₂       | Yes         | tBu₃P (5 mol%) | 62%        | 10%      | 10:90     |
| 18    | CoBr₂       | Yes         | (2,6-MeO-C₆H₃)₃P (5 mol%) | 72%        | 29%      | 3:97      |

[a] All reactions were carried out on a 0.5 mmol scale using (4-fluorophenyl)acetylene as test substrate in 0.5 mL acetonitrile. For all reactions 5 mol% [CoBr₂(TriPhos)], 10 mol% zinc dust, 10 mol% zinc iodide and the corresponding additive were used. The yields were determined via GC/FID using (1.0 M in CH₂Cl₂, 0.5 mL, 0.5 mmol, 1.00 equiv.) as internal standard. The internal standard was added after 16 h reaction time.

Table S9: Investigations concerning the oxidation state of the cobalt central atom, the influence of additives and the relevance of each component.

| Entry | Reducing agent | ZnI₂ | Cobalt salt | Yield[a] |
|-------|----------------|------|-------------|----------|
| 1     | ---            | ---  | CoBr₂       | 10%      |
| 2     | ---            | Yes  | CoBr₂       | 5%       |
| 3     | ---            | Yes  | ---         | 0%       |
| 4     | Zn             | Yes  | ---         | 0%       |
| 5     | Zn             | Yes  | CoBr₂       | 50%      |
| 6     | ---            | Yes  | CoBr₂       | 0%[b]    |
| 7     | EtMgBr         | No   | CoBr₂       | 20%      |

[a] All reactions were carried out on a 0.5 mmol scale using (4-fluorophenyl)acetylene as test substrate in 0.5 mL acetonitrile. The yields were determined via GC/FID using (1.0 M in CH₂Cl₂, 0.5 mL, 0.5 mmol, 1.00 equiv.) as internal standard. The internal standard was added after 16 h reaction. [b] The reaction was performed under O₂-atmosphere.

Reaction Optimization for the Z-selective hydroalkynylation of terminal alkynes using Design of Experiments

A D-optimal screening design was generated by using JMP 13 software package by SAS (version 13.2.1, SAS Institute Inc, Cary, NC, © 2016). The generated design considered all linear and quadratic terms of the numerical parameters. After running all initial experiments, the screening design was extended to consider possible cross interactions and to expand the zinc iodide equivalents from 4 – 60 mol to 4 – 100 mol%. In this case no cross interaction had a low p-value. In total the design consisted of 30 reactions, excluding two verified outliers. For the lack of fit value six experiments were replicated. At last three experiments were run to verify the predicted optimum and reaction time.
**General Procedure 5:**

Under Argon atmosphere all solids were added into a pre-dried reaction vessel. The solids were dried *in vacuo* for 15 min. Afterwards the catalyst system was dissolved in acetonitrile (0.33 - 2.50 mL) using standard single use syringes. The mixture was stirred 15 min at 37 °C. The suspension was cooled or heated to the desired temperature and the test substrate (4-fluorophenylacetylene) was added via Eppendorf™ pipette (60.0 µL, 500 µmol, 1.00 equiv.) to the catalyst system. After the corresponding reaction time mesitylene (1.0 M in CH₂Cl₂, 0.5 mL, 500 µmol, 1.00 equiv., via syringe) and hexafluorobenzene (57.7 µL, 500 µmol, 1.00 equiv., via Eppendorf™ pipette) were added. The yield of the product was determined via GC/FID and ¹⁹F NMR spectroscopy.

**Table S10:** Optimization reactions of DoE for the Z-selective hydroalkynylation of terminal alkynes. All reactions were carried out on a 0.5 mmol scale, according to General Procedure 5. Predicted yield: 67%, isolated yield: 65%.

| Entry | catalyst loading [mol%] | Zinc iodide [mol%] | Temperature [°C] | Time [h] | substrate concentration [M] | Yield [%] |
|-------|--------------------------|--------------------|------------------|----------|-----------------------------|-----------|
| 1     | 10                       | 60                 | 25               | 13.5     | 0.20                        | 61        |
| 2     | 2                        | 22                 | 60               | 24       | 1.50                        | 51        |
| 3     | 10                       | 100                | 60               | 13.5     | 1.50                        | 26        |
| 4     | 2                        | 6.94               | 60               | 13.5     | 0.20                        | 24        |
| 5     | 10                       | 103                | -10              | 24       | 0.64                        | 0         |
| 6     | 10                       | 26.5               | 60               | 3        | 0.85                        | 59        |
| 7     | 2                        | 12                 | 25               | 3        | 1.50                        | 37        |
| 8     | 2                        | 12.7               | -10              | 13.5     | 0.85                        | 30        |
| 9     | 6                        | 60                 | 25               | 13.5     | 0.85                        | 56        |
| 10    | 6                        | 38.4               | 60               | 24       | 0.20                        | 40        |
| 11    | 2                        | 4.88               | 25               | 24       | 0.85                        | 28        |
| 12    | 10                       | 62.3               | -10              | 24       | 1.50                        | 58        |
| 13    | 6                        | 11.28              | -10              | 13.5     | 1.50                        | 39        |
| 14    | 6                        | 36                 | 60               | 3        | 0.85                        | 45        |
| 15    | 6                        | 12.22              | 25               | 3        | 0.20                        | 28        |
| 16    | 2                        | 100                | -10              | 24       | 0.20                        | 0         |
| 17    | 10                       | 4                  | -10              | 3        | 1.50                        | 30        |
| 18    | 2                        | 106                | 25               | 13.5     | 1.50                        | 11        |
| 19    | 10                       | 5                  | 25               | 24       | 1.50                        | 44        |
| 20    | 2                        | 97                 | 60               | 3        | 0.20                        | 11        |
| 21    | 10                       | 100                | 25               | 3        | 1.50                        | 44        |
| 22    | 2                        | 52                 | -10              | 24       | 1.50                        | 35        |
| 23    | 10                       | 4.9                | 60               | 24       | 0.85                        | 40        |
| 24    | 2                        | 4.6                | 60               | 3        | 1.50                        | 23        |
| 25    | 10                       | 52                 | 60               | 24       | 0.20                        | 41        |
| 26    | 10                       | 5.7                | 60               | 3        | 0.20                        | 42        |
| 27    | 6                        | 103                | 60               | 24       | 1.50                        | 27        |
## Response yield

### Actual by Predicted Plot

![Actual by Predicted Plot](image)

### Effect Summary

| Source                                      | LogWorth | PValue  |
|---------------------------------------------|----------|---------|
| zinc iodide mol%*zinc iodide mol%          | 10,514   | 0.0000  |
| substrate concentration(0,2,1,5)           | 4,382    | 0.0004  |
| catalyst loading(2,10)                     | 3,990    | 0.0010  |
| zinc iodide mol%(4,100)                     | 3,752    | 0.0018  |
| temperature (-10,60)                       | 3,190    | 0.0065  |
| temperature*temperature                    | 2,801    | 0.0015  |

### Lack of Fit

| Source         | DF  | Sum of Squares | Mean Square | F Ratio | Prob > F   |
|----------------|-----|----------------|-------------|---------|------------|
| Lack Of Fit    | 26  | 1366,1139      | 52,5428     | 3.2114  | Max RSq    |
| Pure Error     | 6   | 98,1667        | 16,3611     | 0.0748  | Max RSq    |
| Total Error    | 32  | 1464,2806      |             |         | 0.9930     |
SUPPORTING INFORMATION

Residual by Predicted Plot

Studentized Residuals

Externally Studentized Residuals with 95% Simultaneous Limits (Bonferroni)

Parameter Estimates

| Term                          | Estimate | Std Error | t Ratio | Prob>|t|   | VIF   |
|-------------------------------|----------|-----------|---------|--------|-------|
| Intercept                     | 54.354785| 2.292617  | 23.71   | <.0001*| 1     |
| catalyst loading(2,10)        | 5.7715943| 1.301911  | 4.43    | 0.0001*| 1.1017458|
| zinc iodide mol%(4,100)       | -6.271534| 1.47858   | -4.24   | 0.0002*| 1.0549539|
| temperature(-10,60)           | 5.3083966| 1.404013  | 3.78    | 0.0006*| 1.052395|
| substrate concentration(0,2,1.5)| 6.2179735| 1.310094  | 4.75    | <.0001*| 1.0305792|
| zinc iodide mol%*zinc iodide mol%| -25.97876| 2.630114  | -9.88   | <.0001*| 1.1923214|
| temperature*temperature       | -8.480181| 2.455669  | -3.45   | 0.0016*| 1.1097782|

Effect Tests

| Source                        | Nparm | DF | Sum of Squares | F Ratio | Prob > F |
|-------------------------------|-------|----|----------------|---------|----------|
| catalyst loading(2,10)        | 1     | 1  | 899.2979       | 19.6530 | 0.0001*  |
| zinc iodide mol%(4,100)       | 1     | 1  | 823.2513       | 17.9911 | 0.0002*  |
| temperature(-10,60)           | 1     | 1  | 654.1224       | 14.2950 | 0.0006*  |
| substrate concentration(0,2,1.5)| 1    | 1  | 1030.7835      | 22.5265 | <.0001*  |
| zinc iodide mol%*zinc iodide mol%| 1   | 1  | 4464.3882      | 97.5636 | <.0001*  |
| temperature*temperature       | 1     | 1  | 545.6884       | 11.9253 | 0.0016*  |
The results of the Screening design were verified by $k$-fold cross validation ($k = 5$).
SUPPORTING INFORMATION

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NMR spectra
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\[ \text{Chemical Structure: } 2b \]

![Chemical Structure](image)

![NMR Spectrum](image)
