Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Gold(I)–NHC-catalysed synthesis of benzofurans via migratory cyclization of 2-alkynylaryl benzyl ethers

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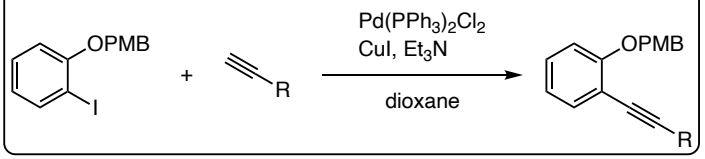
Contents

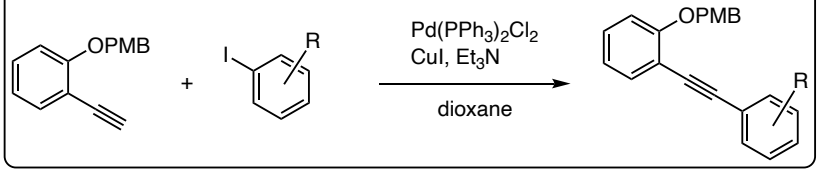
General reaction schemes

Synthesis of substrates

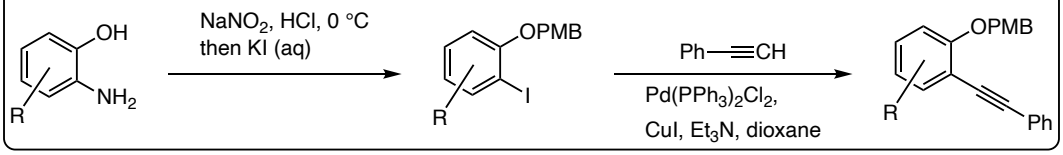
Method A (used to prepare alkynes **9a–c**, **9h**, **9k**, and **9o–q**)



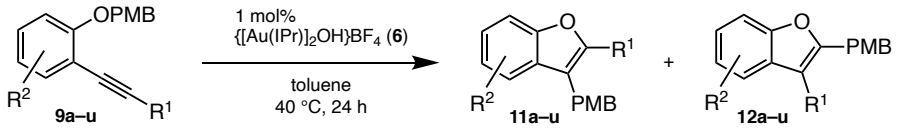
Method B (used to prepare alkynes **9d–h** and **9i–n**)

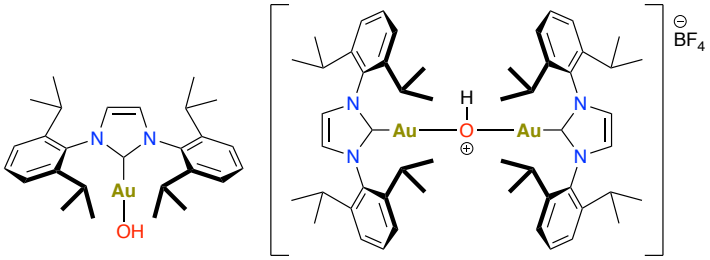


Method C (used to prepare alkynes **9r–u**)



Synthesis of benzofurans





Materials and methods

Instrumentation

Nuclear magnetic resonance spectra (NMR) were acquired on Bruker FOURIER300 spectrometer. Chemical shifts are measured relative to residual solvent peaks as an internal standard set to δ 7.26 and δ 77.0 ($CDCl_3$) or δ 2.50 and δ 39.52 (DMSO-d_6) for ^{1}H and ^{13}C, respectively. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q) or combinations thereof while higher coupling patterns are not abbreviated. Quantitative ^{1}H NMR measurements were performed using relative "100%" or by internal calibration method using methyl-2,5-dinitrobenzoate (Sigma–Aldrich, TraceCERT) as the standard.[1] Carbon–proton decoupled ^{13}C NMR was acquired using the following decoupling parameters: O2 = 5.00 ppm; CPDPRG 2 = waltz16; PCPD2 = 80 μsec; PLW2 = 20 W; PLW12 = 0.6 W; PLW13 = 0.4 W.

Accurate mass measurements were conducted at MS Facility at UC Irvine. Component spectra for $[M+H]^+$ or $[M+Na]^+$ were lock mass calibrated to the nearest Na.PEG or Na.MePEH standards.

IR spectra were recorded on a Thermo Smart Orbit spectrophotometer and are reported in wavenumbers (cm^{-1}).

Preparative methods

Unless otherwise noted, all reactions were magnetically stirred under inert gas (N_2) atmosphere using standard Schlenk techniques. Glassware was dried by placing in an oven (200 °C) for 24 h or flame-dried under vacuum. Drying over Na_2SO_4 implies stirring with an appropriate amount of anhydrous salt for minimum 30 minutes followed by filtration through a glass frit and rinsing of the filter cake with additional solvent. For reactions below room temperature, the reaction vessel was cooled using a mixture of ice and water (0 °C), acetone and dry ice (−78 °C) or a slurry of acetone and liquid N_2 (−94 °C). Stated reaction temperatures refer to the external bath temperature. Cannulas and syringes were used for the transfer of air- and moisture-sensitive reagents and solvents under inert gas atmosphere.

Chromatographic purification was performed under elevated pressure (flash column chromatography)[2] or under reduced pressure (DCVC).[3] Alternatively, purification was carried out using Biotage Isolera Prime semi-automated flash chromatography instrument. After flash column chromatography, the concentrated fractions were filtered once through a glass frit. To visualize the analytes, TLC plates were irradiated with UV light (254 nm) and/or treated with a staining solution of potassium permanganate or phosphomolybdic acid followed by heating.

Chemicals

Reagents with purity of >95% or higher were purchased from Fisher Scientific, TCI America, Alfa Aesar, Acros Organics, Sigma Aldrich, or Oakwood Chemical were used without further purification. Purchased solvents in HPLC- and analytical-grade quality were used without further purification. The expression "hexanes" refers to a mixture of hexane isomers with a boiling point between 40–80 °C. Unless otherwise noted, reactions were performed using dry solvents. Toluene (PhMe) and triethylamine (Et_3N) were dried by distillation over CaH_2. Other dry solvents were dried and stored over 4 Å molecular sieves.[4] For running extra dry reactions with synthetic compounds, stock solutions were prepared in PhMe, the respective amounts transferred into oven-dried glassware and the solvent was removed by stirring under high vacuum (<1 mbar). This procedure was followed by freeze-drying the compound to ensure that H_2O was azeotropically removed.

Alkyne substrates **9a**–**9u** were prepared via Sonogashira cross-coupling of aryl iodide and terminal alkyne according to the literature procedure[5]. Aryl iodide **S1** was prepared from 2-iodophenol as previously reported.[6] Alkyne **S3** was prepared by a Sonogashira reaction of aryl iodide **S1** with trimethylsilylacetylene, followed by removal of the TMS group with potassium fluoride.[7] Aryl acetylenes needed for the synthesis of alkynes **9a**–**c**, **9h**, **9k**, and **9o**–**q** (Method A) and aryl iodides needed for the synthesis of **9d**–**g**, and **9i**–**n** (Method B) were purchased from commercial sources

and used as received. Aryl iodides needed for the synthesis of alkynes **9r–u** (Method C) were synthesized from corresponding 2-aminophenols via the Sandmeyer reaction according to published procedures.[8]

Thin layer chromatography (TLC) was performed using glass-backed silica gel (250 μm) plates and flash chromatography utilized 230–400 mesh silica gel from SiliCycle. UV light, and/or the use of potassium permanganate or phosphomolybdic acid solutions were used to visualize products. Flash chromatography was performed using SiliaFlash® P60, 60Å, 40–63 μm silica gel purchased from SiliCycle.[2]

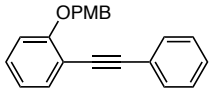
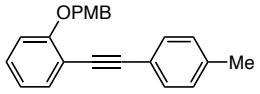
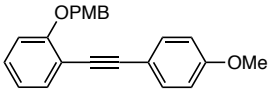
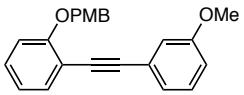
DFT Calculations

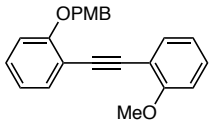
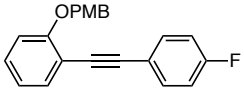
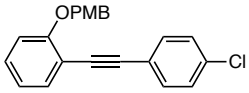
All calculations were performed using a development version of Q-Chem 5.1.{Shao, 2015 #889} The geometry of each isomer was optimized with the B3LYP functional and def2-SVP as the basis. Harmonic frequencies were calculated at the same level of theory indicating that a minimum energy structure was achieved. The 12 highest intensity vibrational peaks above 1400 cm^{-1} were reported. These are the unscaled harmonic frequencies and are known to be overestimates of the true vibrational frequencies.{Merrick, 2007 #890;Kesharwani, 2015 #891} NMR spectral shifts were also computed at the optimized geometries with HF/6-31G** relative to THF. Only the shifts for the three most shielded carbon atoms are reported.

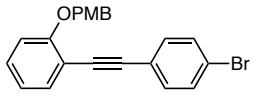
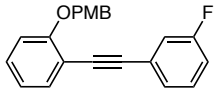
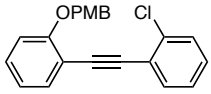
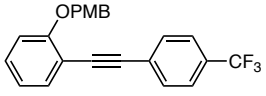
Experimental procedures

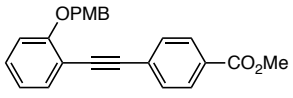
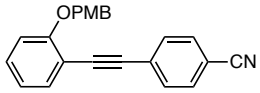
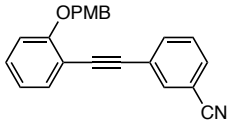
Synthesis of substrates via Sonogashira cross-coupling (general procedure)

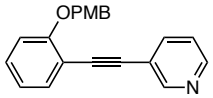
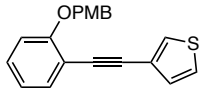
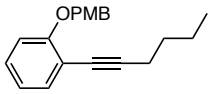
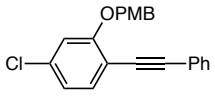
Aryl iodide (1.00 equiv.), $Pd(PPh_3)_2Cl_2$ (0.03 equiv.) and CuI (0.02 equiv.) were added to a dry, argon flushed flask and dissolved in dry dioxane–Et_3N (1:1 v/v, 0.3 M). The flask was flushed with argon and a solution of alkyne (1.1 equiv.) in dioxane–Et_3N (1 mL) was added dropwise via syringe. The reaction was stirred under argon at room temperature or heated at 45–50 °C until starting materials were consumed (TLC analysis, 4 h–overnight). The reaction mixture was filtered through Celite®, the solids were washed with ethyl acetate, the collected liquid was concentrated, and the residue was purified via flash chromatography (SiO_2, ethyl acetate in hexanes).

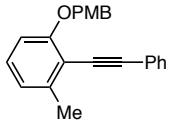
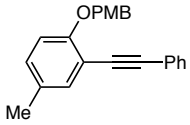
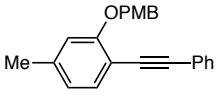
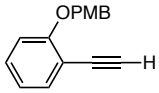
Compound	Characterization data
	**1-((4-methoxybenzyl)oxy)-2-(phenylethynyl)benzene (9a):** Method A, isolated yield 1.51 g (91%), white solid; mp 69–72 °C; R_f = 0.44 (10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61–7.52 (m, 3H), 7.52–7.43 (m, 2H), 7.43–7.24 (m, 4H), 7.05–6.86 (m, 4H), 5.16 (s, 2H), 3.84 (s, 3H). The analytical data is in agreement with the literature.[9]
	**1-[(4-methoxyphenyl)methoxy]-2-[2-(4-methylphenyl)ethynyl]-benzene (9b):** Method A, isolated yield 1.16 g (99%), white solid; mp 91–94 °C; R_f = 0.42 (15% EtOAc/hexanes); IR (ATR) 3026, 2969, 2938, 2881, 2841, 2157, 1906, 1888, 1610, 1590, 1574, 1514, 1488, 1469, 1443, 1422, 1404 cm^{-1}; ^{1}H NMR (300 MHz, CDCl3) δ 7.54 – 7.37 (m, 5H), 7.32 – 7.20 (m, 1H), 7.19 – 7.10 (m, 2H), 6.99 – 6.87 (m, 4H), 5.14 (s, 2H), 3.82 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, CDCl3) δ 159.39, 138.28, 133.36, 131.60, 129.54, 129.33, 129.18, 128.72, 121.05, 120.79, 113.98, 113.87, 113.28, 94.01, 85.41, 70.55, 55.49, 21.68. HRMS (CI): Exact mass calcd for $C_{23}H_{20}O_2$ $[M]^+$ 328.1463, found 328.1474.
	**1-[2-(4-methoxyphenyl)ethynyl]-2-[(4-methoxyphenyl)methoxy]-benzene (9c):** Method A, isolated yield 0.75 g (69%), red-orange solid (color intensifies upon exposure to light); mp 80-82 °C; R_f = 0.32 (15% EtOAc/hexanes); IR (ATR) 2963, 2962, 2834, 2211, 1913, 1891, 1605, 1589, 1566, 1510, 1488, 1464 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.40 (m, 5H), 7.26 (ddd, *J* = 8.4, 7.3, 1.7 Hz, 1H), 7.00 – 6.83 (m, 6H), 5.13 (s, 2H), 3.83 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.61, 159.37, 159.30, 133.17, 133.10, 129.34, 128.75, 128.69, 121.03, 116.01, 114.05, 113.98, 113.96, 113.26, 93.81, 84.73, 70.53, 55.46, 55.36; HRMS (CI): Exact mass calcd for $C_{23}H_{20}O_3$ $[M]^+$ 344.1412, found 344.1415.
	**1-[2-(3-methoxyphenyl)ethynyl]-2-[(4-methoxyphenyl)methoxy]-benzene (9d):** Method B, isolated yield 0.83 g (77%), white solid; mp 94–95 °C; R_f = 0.32 (15% EtOAc/hexanes);

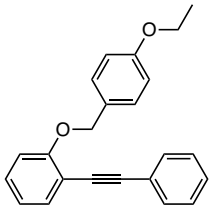
Compound	Characterization data
	IR (ATR) 3073, 3004, 2952, 2908, 2872, 2834, 2210, 2157, 1930, 1615, 1592, 1581, 1574, 1517, 1497, 1485, 1466, 1445, 1418 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.34 – 7.17 (m, 2H), 7.12 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.04 (dd, *J* = 2.7, 1.4 Hz, 1H), 7.01 – 6.83 (m, 5H), 5.13 (s, 2H), 3.82 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.56, 159.46, 159.44, 133.43, 129.80, 129.45, 129.28, 128.79, 124.88, 124.29, 121.06, 116.38, 114.99, 114.01, 113.60, 113.26, 93.77, 85.95, 70.60, 55.41. HRMS (CI): Exact mass calcd for $C_{23}H_{20}O_3$ $[M]^+$ 344.1412, found 344.1410.
	**1-[2-(2-methoxyphenyl)ethynyl]-2-[(4-methoxyphenyl)methoxy]-benzene (9e):** Method B, isolated yield 0.94 g (86%), tan solid; mp 72–74 °C; R_f = 0.34 (15% EtOAc/hexanes); IR (ATR) 3003, 2932, 2839, 2354, 2327, 1891, 1610, 1579, 1570, 1512, 1497, 1464, 1455, 1444 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.52 – 7.42 (m, 3H), 7.35 – 7.19 (m, 2H), 7.01 – 6.81 (m, 6H), 5.14 (s, 2H), 3.83 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.07, 159.42, 159.37, 133.70, 133.57, 129.64, 129.56, 129.45, 128.88, 121.02, 120.58, 114.07, 113.96, 113.39, 113.21, 110.95, 90.22, 90.16, 70.61, 56.00, 55.44. HRMS (CI): Exact mass calcd for $C_{23}H_{20}O_3$ $[M]^+$ 344.1412, found 344.1414.
	**1-fluoro-4-(2-{2-[(4-methoxyphenyl)methoxy]phenyl}ethynyl)benzene (9f):** Method B, isolated yield 1.15 g (82%), white solid; mp 43–45 °C; R_f = 0.28 (10% EtOAc/hexanes); IR (ATR) 3067, 3037, 3006, 2955, 2923, 2870, 2834, 2211, 1613, 1596, 1508, 1486 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.44 (m, 5H), 7.31 (ddd, *J* = 8.2, 7.5, 1.7 Hz, 1H), 7.13 – 7.01 (m, 2H), 7.01 – 6.85 (m, 4H), 5.13 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, CDCl3) δ 162.37 (d, J = 249.2 Hz), 159.37, 133.46, 133.36, 133.19, 129.74, 129.04, 128.65, 120.87, 119.87 (d, J = 3.4 Hz), 115.56 (d, J = 22.0 Hz), 113.84, 113.07 (d, J = 22.3 Hz), 92.65, 85.85 (d, J = 1.5 Hz), 70.28, 55.23; HRMS (CI): Exact mass calcd for $C_{22}H_{17}FO_2$ $[M]^+$ 332.1212, found 332.1211.
	**1-chloro-4-(2-{2-[(4-methoxyphenyl)methoxy]phenyl}ethynyl)-benzene (9g):** Method B, isolated yield 0.44 g (60%), white solid; mp 85–87 °C; R_f = 0.30 (10% EtOAc/hexanes); IR (ATR) 3070, 3007, 2957, 2927, 2866, 2832, 1610, 1585, 1573, 1516, cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.49 – 7.37 (m, 4H), 7.36 – 7.22 (m, 3H), 7.01 – 6.86 (m, 4H), 5.13 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.54, 159.48, 134.14, 133.38, 132.89, 129.99, 129.19, 128.75, 122.40, 121.06, 114.02, 113.29, 113.18, 92.66, 87.14, 70.57, 55.46; HRMS (CI): Exact mass calcd for $C_{22}H_{17}ClO_2$ $[M]^+$ 366.1261, found 366.1253.

Compound	Characterization data
	**1-bromo-4-(2-{2-[(4-methoxyphenyl)methoxy]phenyl}ethynyl)-benzene (9h):** Method A, isolated yield 1.12 g (70%), brown solid; mp 102-104 °C; R_f = 0.40 (10% EtOAc/hexanes); IR (ATR) 3074, 3010, 2958, 2929, 2870, 2832, 2157, 1612, 1594, 1584, 1572, 1516, 1496, 1482, 1450, 1425 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.22 (m, 8H), 7.01 – 6.86 (m, 4H), 5.12 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.50, 159.44, 133.36, 133.09, 131.65, 130.02, 129.13, 128.74, 122.82, 122.33, 121.03, 113.98, 113.20, 113.11, 92.70, 87.31, 70.50, 55.46. HRMS (CI): Exact mass calcd for $C_{22}H_{17}BrO_2$ $[M]^+$ 392.0412, found 392.0413.
	**1-fluoro-3-(2-{2-[(4-methoxyphenyl)methoxy]phenyl}ethynyl)benzene (9i):** Method B, isolated yield 1.25 g (90%), white solid; mp 31-33 °C; R_f = 0.35 (10% EtOAc/hexanes); IR (ATR) 3064, 2998, 2971, 2934, 2890, 2853, 2210, 2157, 1945, 1890, 1606, 1591, 1573, 1514, 1481, 1497, 1461, 1443, 1424 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.44 (d, *J* = 8.9 Hz, 2H), 7.34 – 7.24 (m, 3H), 7.19 (ddt, *J* = 9.7, 2.9, 0.8 Hz, 1H), 7.11 – 6.87 (m, 5H), 5.13 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.39 (d, *J* = 246.1 Hz), 159.42 (d, *J* = 13.7 Hz), 133.29, 129.96, 129.78 (d, *J* = 8.8 Hz), 129.01, 128.61, 127.38 (d, *J* = 2.6 Hz), 125.60 (d, *J* = 9.4 Hz), 120.89, 118.41, 118.19, 115.30 (d, *J* = 21.4 Hz), 113.90, 113.01, 92.38 (d, *J* = 3.6 Hz), 86.96, 70.42, 55.29. HRMS (CI): Exact mass calcd for $C_{22}H_{17}FO_2$ $[M]^+$ 332.1212, found 332.1200.
	**1-chloro-2-(2-{2-[(4-methoxyphenyl)methoxy]phenyl}ethynyl)-benzene (9j):** Method B, isolated yield 1.29 g (87%), white solid; mp 48–50 °C; R_f = 0.29 (10% EtOAc/hexanes); IR (ATR) 3076,2995, 2960, 2934, 2874, 2831, 2217, 1607, 1590, 1564, 1511, 1493 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 2H), 7.48 – 7.42 (m, 2H), 7.43 – 7.37 (m, 1H), 7.29 (ddd, *J* = 8.4, 7.5, 1.7 Hz, 1H), 7.25 – 7.17 (m, 2H), 7.01 – 6.93 (m, 2H), 6.93 – 6.85 (m, 2H), 5.12 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.54, 159.44, 135.86, 133.72, 133.41, 130.16, 129.34, 129.11, 129.04, 129.01, 126.46, 123.79, 120.95, 113.95, 113.15, 113.02, 91.36, 90.48, 70.51, 55.44 HRMS (CI): Exact mass calcd for $C_{22}H_{17}ClO_2$ $[M]^+$ 348.0917, found 348.0925.
	**1-[(4-methoxyphenyl)methoxy]-2-{2-[4-(trifluoromethyl)phen-yl]ethynyl}benzene (9k):** Method A, isolated yield 1.48 g (92%), white solid; mp 91–93 °C; R_f = 0.30 (10% EtOAc/hexanes); IR (ATR) 3079, 3000, 2951, 2936, 2908, 2838, 2215, 1611, 1594, 1582, 1510, 1487 cm^{-1};

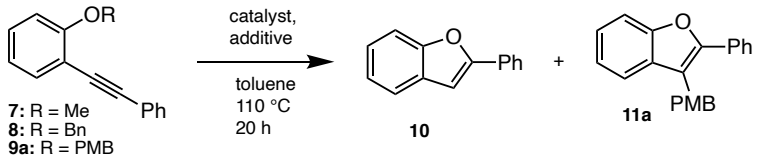
Compound	Characterization data
	^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (s, 4H), 7.54s – 7.49 (m, 1H), 7.53 – 7.39 (m, 2H), 7.37 – 7.24 (m, 1H), 7.02 – 6.86 (m, 4H), 5.13 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.73, 159.54, 133.55, 131.87, 130.40, 129.81 (q, *J* = 32.0 Hz), 129.11, 128.79, 127.74, 125.35 (q, *J* = 3.7 Hz), 123.97 (q, *J* = 272.0 Hz), 121.08, 114.06, 113.15, 112.90, 92.38, 88.68, 70.59, 55.46. HRMS (CI): Exact mass calcd for $C_{23}H_{17}F_3O_2$ $[M]^+$ 328.1181, found 328.1183.
	**methyl 4-(2-{2-[(4-methoxyphenyl)methoxy]phenyl}ethynyl)benzoate (9l):** Method B, isolated yield 0.70 g (45%), brown solid, mp 94-96 °C. R_f = 0.31 (10% EtOAc/hexanes); IR (ATR) 3079, 2874, 2839, 2211, 1718, 1604, 1593, 1511, 1431 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 – 7.92 (m, 2H), 7.63 – 7.48 (m, 3H), 7.48 – 7.40 (m, 2H), 7.36 – 7.23 (m, 1H), 7.03 – 6.86 (m, 4H), 5.14 (s, 2H), 3.93 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.79, 159.70, 159.52, 133.54, 131.57, 130.33, 129.61, 129.38, 129.13, 128.76, 128.65, 121.07, 114.05, 113.17, 113.06, 93.07, 89.30, 70.58, 55.47, 52.34; HRMS (CI): Exact mass calcd for $C_{24}H_{20}O_4$ $[M]^+$ 372.1362, found 372.1344.
	**4-(2-{2-[(4-methoxyphenyl)methoxy]phenyl}ethynyl)benzonitrile (9m):** Method B, isolated yield 0.71 g (66%), yellow solid; mp 105–106 °C; R_f = 0.25 (15% EtOAc/hexanes); IR (ATR) 3097, 3043, 3008, 2959, 2932, 2879, 2825, 2220, 1615, 1601, 1570, 1518, 1488, 1449 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 – 7.48 (m, 5H), 7.46 – 7.39 (m, 2H), 7.33 (ddd, *J* = 8.4, 7.5, 1.7 Hz, 1H), 7.03 – 6.94 (m, 2H), 6.94 – 6.87 (m, 2H), 5.13 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.81, 159.58, 133.57, 132.12, 130.73, 129.00, 128.88, 128.82, 121.08, 118.78, 114.06, 113.06, 112.52, 111.31, 92.16, 90.84, 70.57, 55.47; HRMS (CI): Exact mass calcd for $C_{23}H_{17}NO_2$ $[M]^+$ 339.1259, found 339.1269.
	**3-(2-{2-[(4-methoxyphenyl)methoxy]phenyl}ethynyl)benzonitrile (9n):** Method B, isolated yield 0.88 g (82%), light yellow solid; mp 76–78 °C; R_f = 0.33 (20% EtOAc/hexanes); IR (ATR) 3061, 3034, 3003, 2914, 2874, 2834, 2231, 2202, 1611, 1591 1566, 1513, 1491, 1478, 1450, 1464, 1422 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (td, *J* = 1.7, 0.6 Hz, 1H), 7.68 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.57 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.50 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.37 – 7.27 (m, 1H), 7.03 – 6.87 (m, 4H), 5.12 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.82, 159.63, 135.63, 135.04, 133.47, 131.25, 130.56, 129.34, 129.00, 128.82, 125.57, 121.06, 118.33, 114.10, 113.06, 112.97, 112.59, 91.32, 88.79, 70.59, 55.49; HRMS (CI): Exact mass calcd for $C_{23}H_{17}NO_2$ $[M]^+$ 339.1259, found 339.1247.

Compound	Characterization data
	**3-(2-{2-[(4-methoxyphenyl)methoxy]phenyl}ethynyl)pyridine (9o):** Method A, isolated yield 0.805 g (93%), yellow oil; R_f = 0.34 (40% EtOAc/hexanes); IR (ATR) 3029, 3002, 2955, 2933, 2908, 2834, 2218, 1612, 1596, 1584, 1574, 1560 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.71 (brs, 2H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.36 – 7.14 (m, 2H), 7.01 – 6.86 (m, 4H), 5.11 (s, 2H), 3.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.55, 159.44, 151.98, 148.09, 138.39, 133.44, 130.31, 128.92, 128.67, 120.96, 113.98, 112.99, 112.68, 90.23, 89.58, 70.44, 55.34; HRMS (CI): Exact mass calcd for $C_{21}H_{17}NO_2$ $[M]^+$ 315.1259, found 316.1327.
	**3-(2-{2-[(4-methoxyphenyl)methoxy]phenyl}ethynyl)thiophene (9p):** Method A, isolated yield 1.09 g (80%), brown solid; mp 86–88 °C; R_f = 0.33 (10% EtOAc/hexanes); IR (ATR) 3108, 2954, 2872, 2833, 1611, 1591, 1575, 1515, 1488, 1464 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 2H), 7.52 – 7.43 (m, 2H), 7.36 – 7.27 (m, 1H), 7.28 – 7.20 (m, 1H), 7.05 – 6.91 (m, 4H), 5.14 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.28, 159.25, 133.20, 129.93, 129.61, 129.07, 128.59, 128.34, 125.30, 122.75, 120.90, 113.84, 113.37, 113.03, 88.83, 85.57, 70.30, 55.23; HRMS (CI): Exact mass calcd for $C_{20}H_{16}O_2S$ $[M]^+$ 320.0871, found 320.0867.
	**1-(hex-1-yn-1-yl)-2-[(4-methoxyphenyl)methoxy]benzene (9q):** Method A, isolated yield 0.72 g (83%), yellow oil; R_f = 0.32 (5% EtOAc/hexanes); IR (ATR) 2998, 2955, 2930, 2870, 2835, 1613, 1595, 1574, 1514, 1490, 1464 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 3H), 7.29 – 7.14 (m, 1H), 6.97 – 6.84 (m, 4H), 5.09 (s, 2H), 3.82 (s, 3H), 2.47 (t, *J* = 6.9 Hz, 2H), 1.69 – 1.54 (m, 2H), 1.54 – 1.39 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.33, 159.32, 133.52, 129.31, 128.79, 120.86, 114.29, 113.89, 113.06, 94.83, 70.41, 55.38, 31.02, 22.07, 19.55, 13.81. HRMS (CI): Exact mass calcd for C20H22O2 $[M]^+$ 294.1620, found 294.1632.
	**4-chloro-2-[(4-methoxyphenyl)methoxy]-1-(2-phenylethynyl)benzene (9r):** Method A, isolated yield 0.52 g (80%), white solid; mp 87–90 °C; R_f = 0.22 (1% EtOAc/hexanes); IR (ATR) 3005, 2930, 2831, 1613, 1587, 1557, 1493 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.47 – 7.39 (m, 3H), 7.38 – 7.28 (m, 3H), 7.00 – 6.87 (m, 4H), 5.10 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.89, 135.06, 133.86, 131.67, 128.79, 128.51, 128.44, 128.37, 123.54, 121.23, 114.06, 113.70, 112.22, 94.58, 85.10, 70.71, 55.43. HRMS (CI): Exact mass calcd for C22H17ClO2 $[M]^+$ 348.0917, found 348.0919.

Compound	Characterization data
	**1-[(4-methoxyphenyl)methoxy]-3-methyl-2-(2-phenylethynyl)benzene (9s):** Method A, isolated yield 0.70 g (75%), yellow solid; mp 48–49 °C; R_f = 0.18 (5% EtOAc/hexanes); IR (ATR) 3052, 2994, 2910, 2825, 2211, 1891, 1613, 1586, 1569, 1513, 1491, 1457, 1441 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 2H), 7.49 – 7.42 (m, 2H), 7.39 – 7.28 (m, 3H), 7.16 (t, *J* = 7.9 Hz, 1H), 6.95 – 6.89 (m, 2H), 6.87 (dt, *J* = 7.6, 0.9 Hz, 1H), 6.83 – 6.76 (m, 1H), 5.12 (s, 2H), 3.82 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.69, 159.37, 142.23, 131.61, 129.50, 128.88, 128.68, 128.41, 128.07, 124.20, 122.36, 113.98, 113.55, 110.31, 98.16, 84.97, 70.53, 55.43, 20.98. HRMS (CI): Exact mass calcd for C23H20O2 $[M]^+$ 328.1463, found 328.1458.
	**1-[(4-methoxyphenyl)methoxy]-4-methyl-2-(2-phenylethynyl)benzene (9t):** Method A, isolated yield 0.51 g (32%), brown solid; mp 61–63 °C; R_f = 0.24 (5% EtOAc/hexanes); IR (ATR) 3034, 2901, 2830, 2207, 1748, 1695, 1612, 1513,1499, 1488, 1450, 1437 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 2H), 7.54 – 7.45 (m, 2H), 7.45 – 7.32 (m, 4H), 7.15 – 7.06 (m, 1H), 7.03 – 6.92 (m, 2H), 6.89 (d, *J* = 8.4 Hz, 1H), 5.13 (s, 2H), 3.84 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.25, 157.36, 133.70, 131.59, 130.28, 130.23, 129.33, 128.69, 128.33, 128.04, 123.84, 113.83, 113.33, 113.23, 93.42, 86.36, 70.62, 55.27, 20.39; HRMS (CI): Exact mass calcd for C23H20O2 $[M]^+$ 328.1463, found 328.1465.
	**2-[(4-methoxyphenyl)methoxy]-4-methyl-1-(2-phenylethynyl)benzene (9u):** Method A, isolated yield 0.80 g (87%), white solid; mp 74–75 °C; R_f = 0.29 (10% EtOAc/hexanes); IR (ATR) 3048, 1994, 2910, 2861, 2834, 2216, 1613, 1594, 1564, 1510, 1485, 1459, 1415 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.39 (m, 5H), 7.39 – 7.30 (m, 3H), 6.99 – 6.88 (m, 2H), 6.83 – 6.76 (m, 2H), 5.12 (s, 2H), 3.83 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.39, 140.29, 133.10, 131.60, 129.34, 128.73, 128.67, 128.36, 127.97, 124.03, 121.87, 114.07, 113.93, 110.56, 93.12, 86.32, 70.44, 55.44, 22.00; HRMS (CI): Exact mass calcd for C23H20O2 $[M]^+$ 328.1463, found 328.1473.
	**1-ethynyl-2-[(4-methoxyphenyl)methoxy]benzene (S1):** Isolated yield: 0.44 g (56%); white solid; mp 54–56 °C; R_f = 0.38 (10% EtOAc/hexanes); IR (ATR) 3296, 2927, 2829, 2095, 1611, 1592, 1571, 1517, 1488, 1462, 1440 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.34 (m, 4H), 7.32 – 7.21 (m, 1H), 6.96 – 6.85 (m, 5H), 5.12 (s, 3H), 3.81 (s, 3H), 3.29 (s, 1H);

Compound	Characterization data
	^{13}C NMR (75 MHz, CDCl3) δ 159.98, 159.44, 134.30, 130.22, 129.00, 128.73, 120.86, 114.07, 113.04, 112.25, 81.41, 81.39, 80.26, 70.42, 55.42; HRMS (CI): Exact mass calcd for $C_{16}H_{14}O_2$ [M]$^+$ 238.0994, found 238.0996.
	**1-ethoxy-4-[2-(2-phenylethynyl)phenoxymethyl]benzene (13):** Yield: 1.51 g (81%); yellow oil R_f = 0.26 (5% EtOAc/hexanes); IR (ATR) 3060, 3032, 2978, 2928, 2870, 1612, 1593, 1512, 1496 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 2H), 7.54 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.46 (ddt, *J* = 8.2, 6.6, 1.1 Hz, 2H), 7.42 – 7.34 (m, 2H), 7.31 (ddd, *J* = 8.3, 7.2, 1.4 Hz, 1H), 7.23 – 7.14 (m, 3H), 6.90 – 6.78 (m, 2H), 4.26 (s, 2H), 4.01 (q, *J* = 7.0 Hz, 2H), 1.41 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.50, 158.78, 133.41, 131.71, 129.74, 129.13, 128.72, 128.40, 128.16, 123.89, 121.03, 114.56, 113.65, 113.27, 93.80, 86.14, 70.59, 63.59, 14.98; HRMS (CI): Exact mass calcd for $C_{23}H_{20}O_2$ [M]$^+$ 328.1463, found 328.1451.

Optimization of reaction conditions



To a 2-dram vial was added the catalyst, alkyne **9a** (250 μmol), additive (250 μL), and toluene (500 μL). The vial was capped and the mixture stirred at 110 °C for 20 h. The mixture was then cooled to room temperature and solvent was evaporated in a stream of nitrogen and the residue was dissolved in $CDCl_3$, filtered, and analyzed by ^{1}H NMR.

Table 1

Entry	Substrate	Catalyst	Cat (mol%)	Additive	Solvent	Temp (°C)	Time (h)	Conv.[a] (%)	10a:11a[a]
1	**7**	**5**	5	AcOH	toluene	110	20	<5	—
2	**8**	**5**	5	AcOH	toluene	110	20	<5	—
3	**9a**	**5**	5	AcOH	toluene	110	20	>95	1:1
4	**9a**	**6**	5	AcOH	toluene	110	20	>95	1:4
5	**9a**	**6**	5		toluene	110	20	>95	1:20
6	**7**	**6**	5		toluene	110	20	<5	—
7	**8**	**6**	5		toluene	110	20	<5	—
8	**9a**	**6**	0.25		toluene	110	1	>95	10:1
9	**9a**	**6**	0.10		toluene	110	4	83	10:1
10	**9a**	**6**	0.05		toluene	110	4	12	10:1
11	**9a**	**6**	1.0		toluene	rt	24	>95	10:1
12	**9a**	Au(IPr)Cl	2.0		toluene	110	24	<5	—
13	**9a**	$Au(PPh_3)Cl$	2.0		toluene	110	24	<5	—
14	**9a**	Au(IPr)OH	2.0		toluene	110	24	<5	—
15	**9a**	$Au(IPr)Cl + AgBF_4$	2.0		toluene	rt	24	>95	—[b]
16	**9a**	$Au(PPh_3)Cl + AgSbF_6$	2.0		toluene	rt	24	>95	—[b]
17	**9a**	$Au(PPh_3)Cl + AgBF_4$	2.0		toluene	rt	24	>95	—[b]
18	**9a**	$Au(PPh_3)Cl + AgPF_6$	2.0		toluene	rt	24	>95	4:1
19	**9a**	$Au(IPr)NTf_2$	2.0		toluene	rt	24	>95	10:1
20	**9a**	**6**	1.0		CH_2Cl_2	rt	24	>95	10:1
21	**9a**	**6**	1.0		THF	rt	24	>95	10:1
22	**9a**	**6**	1.0		MTBE	rt	24	40	10:1
23	**9a**	**6**	1.0		1,2-DCE	rt	24	>95	10:1
24	**9a**	**6**	1.0		EtOAc	rt	24	>95	10:1
25	**9a**	**6**	1.0		CH_3CN	rt	24	68	10:1
26	**9a**	**6**	1.0		EtOH	rt	24	>95[c]	10:1
27	**9a**	**6**	1.0		*n*-BuOH	rt	24	>95[c]	10:1
28	**9a**	**6**	1.0		CH_2Cl_2	rt	72[d]	>95	10:1

[a]Determined by ^{1}H NMR; [b]Complex mixture of products was obtained; [c]Approximately 30% of benzofuran **10** was also observed [d]After 24 h and 48 h an additional equivalent of **9a** was added to the reaction mixture.

NMR results (Table 1, entry 3)

Parameter	Value
Title	CCD2-028.1.fid
Origin	Bruker BioSpin GmbH
Owner	NMR-Student
Instrument	FOURIER300
Author	
Solvent	CDCl3
Temperature	1013.9
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm DUL 13C-1H/ D Z-GRD Z111650/ 0010
Number of Scans	16
Receiver Gain	16.2
Relaxation Delay	1.0000
Pulse Width	11.7500
Presaturation Frequency	
Acquisition Time	5.3687
Acquisition Date	2020-08-26T18:28:00
Modification Date	2020-08-26T18:29:56
Spectrometer Frequency	300.18
Spectral Width	6103.5
Lowest Frequency	-1203.1
Nucleus	1H
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.09

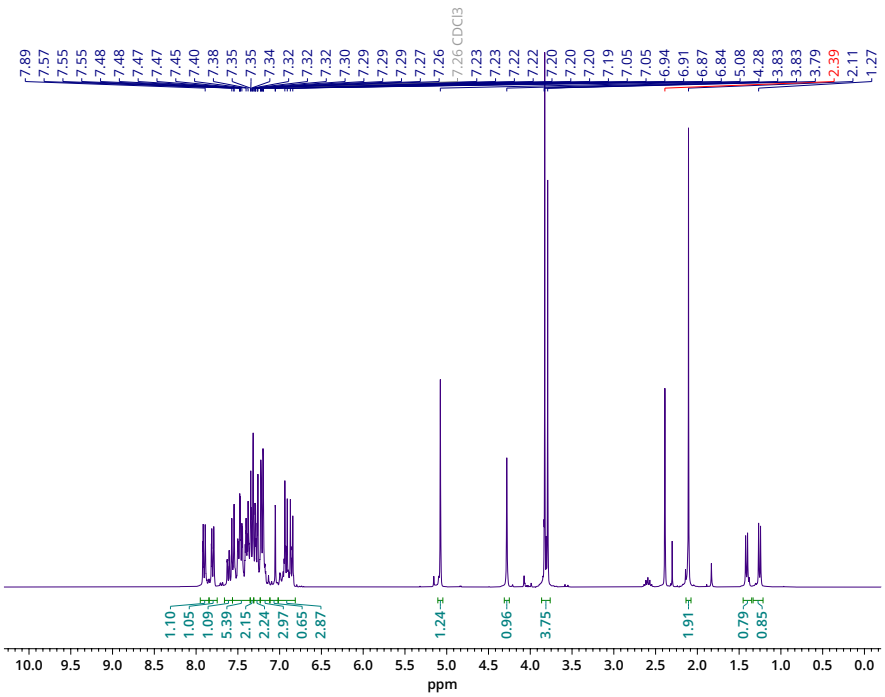


Figure 1. ^{1}H NMR ($CDCl_3$) of the crude reaction mixture

Parameter	Value
Title	CCD2-028.11.fid
Origin	Bruker BioSpin GmbH
Owner	NMR-Student
Instrument	FOURIER300
Author	
Solvent	CDCl3
Temperature	1013.9
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm DUL 13C-1H/ D Z-GRD Z111650/ 0010
Number of Scans	16
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	11.7500
Presaturation Frequency	
Acquisition Time	5.3687
Acquisition Date	2020-08-27T18:42:00
Modification Date	2020-08-27T18:43:38
Spectrometer Frequency	300.18
Spectral Width	6103.5
Lowest Frequency	-1203.2
Nucleus	1H

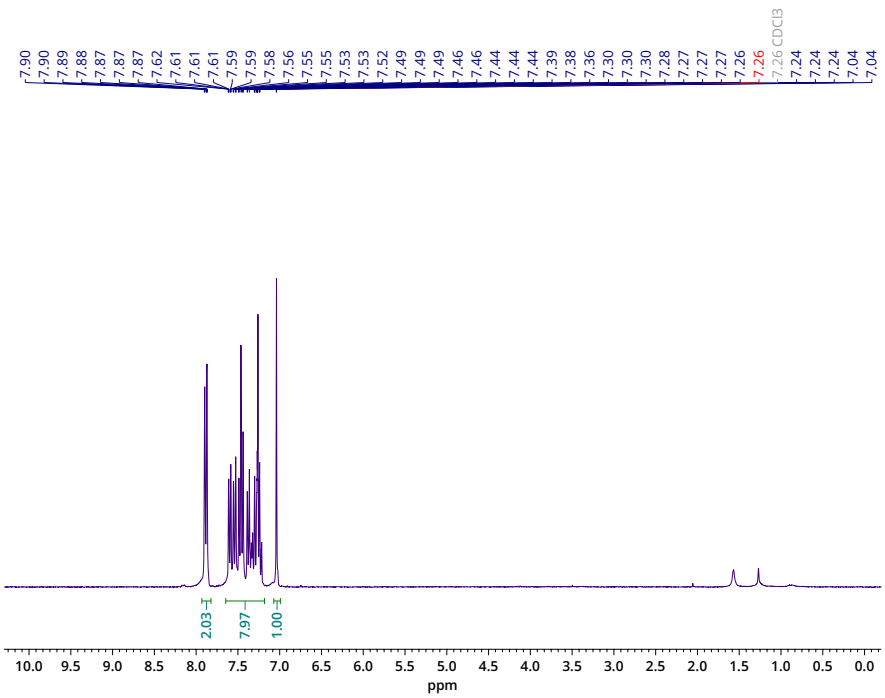


Figure 2. ^{1}H NMR ($CDCl_3$) of debenzylated benzofuran **10**

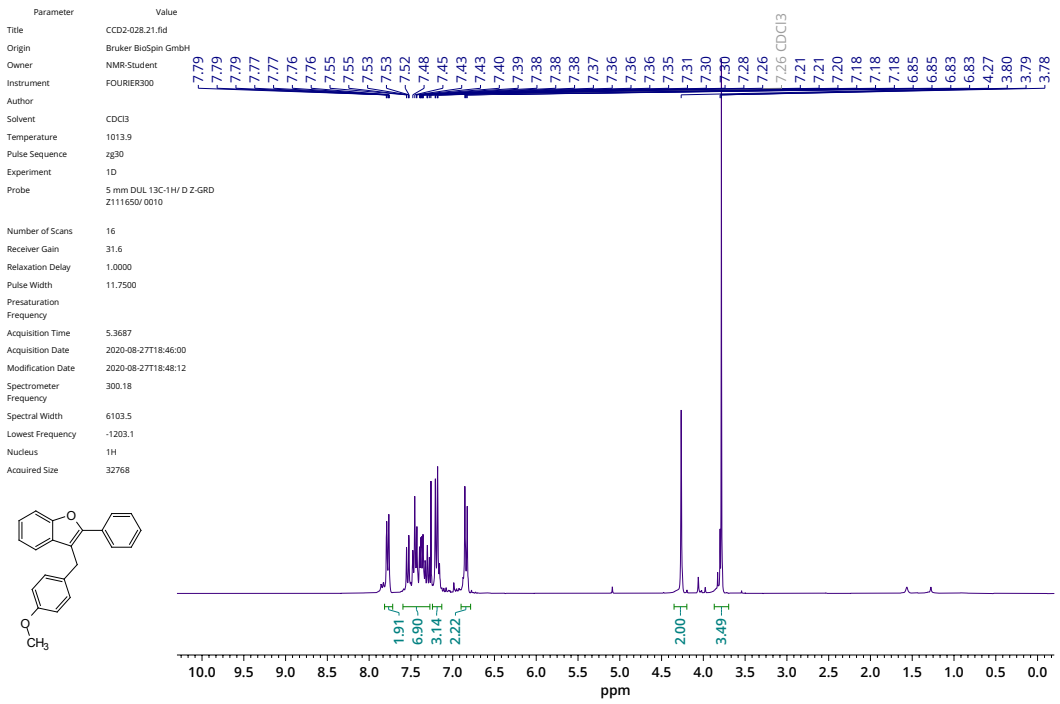


Figure 3. ^{1}H NMR ($CDCl_3$) of cyclodimerization product **11a**

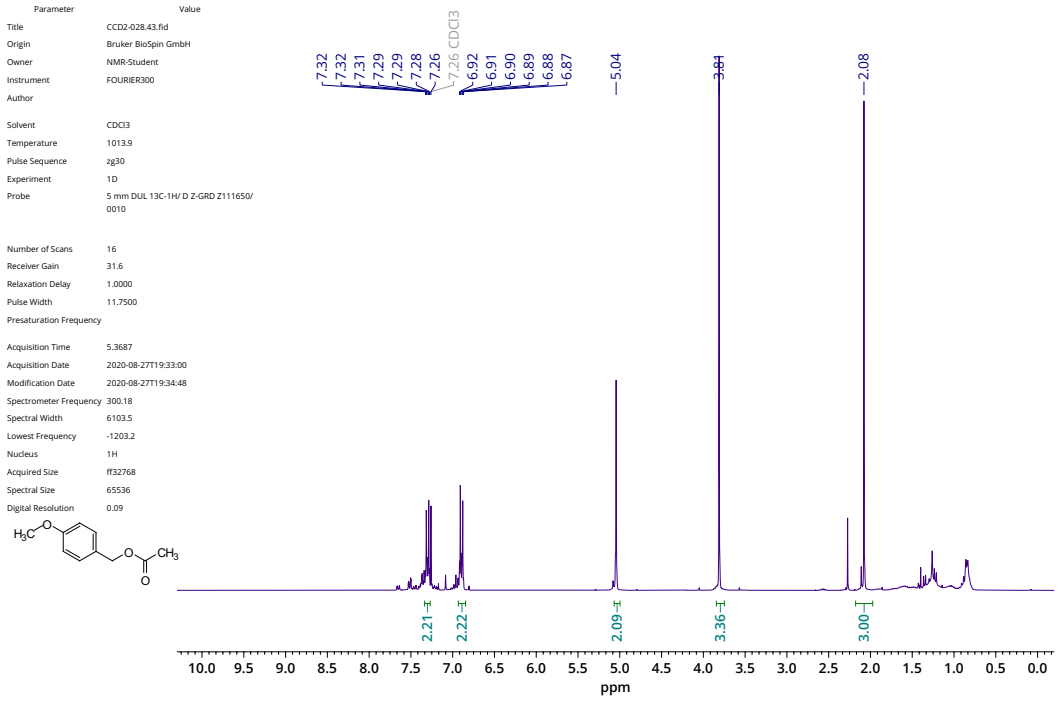
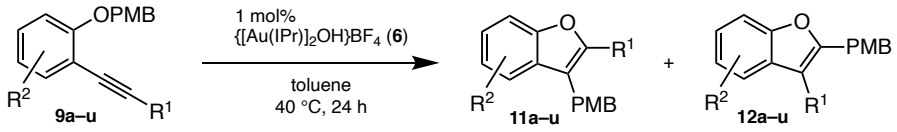
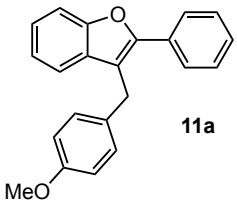
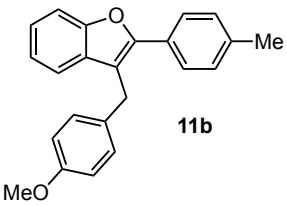
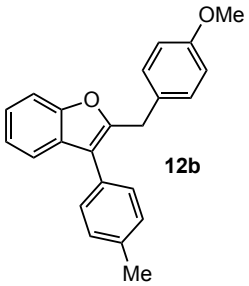


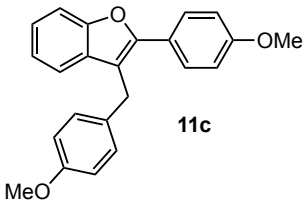
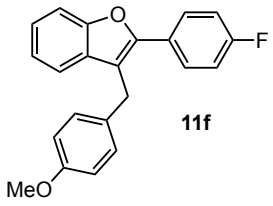
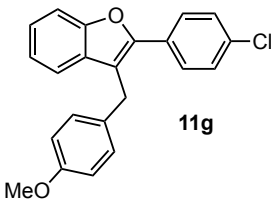
Figure 4. ^{1}H NMR ($CDCl_3$) of benzyl acetate.

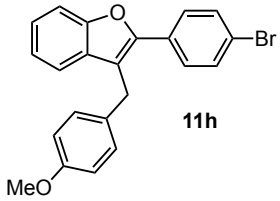
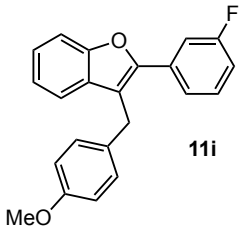
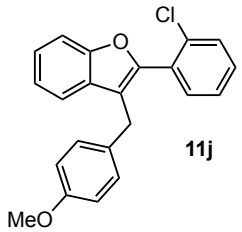
Synthesis of benzofurans via gold(I)-catalyzed cycloisomerization

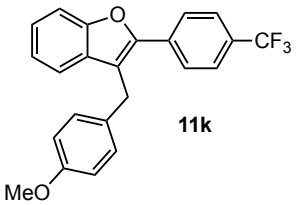
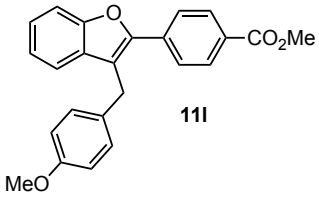
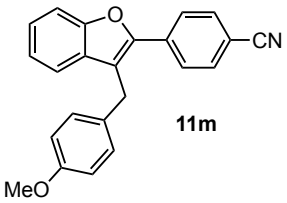


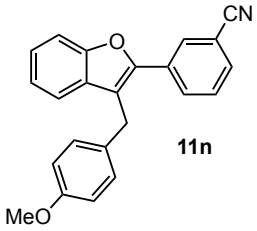
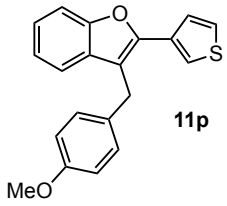
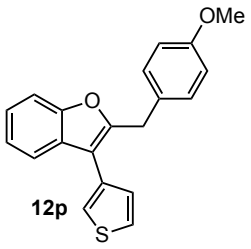
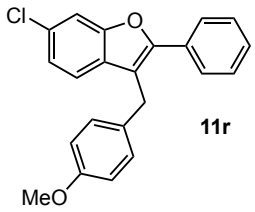
To a 2-dram vial was added the catalyst **6** (5.0 μmol), alkyne (0.50 mmol), and toluene (1.0 mL). The vial was capped and the mixture heated at 40 °C with stirring for 20 hours. The mixture was then cooled to room temperature and solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, EtOAc/hexanes) yielded the products as an inseparable mixture of regioisomers.

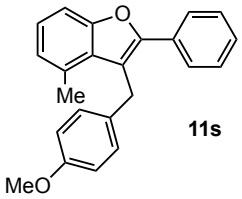
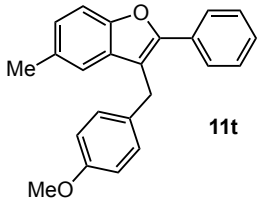
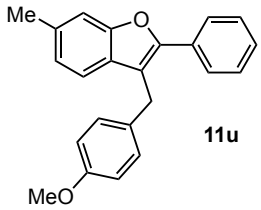
Compound	Characterization data
 **11a**	**3-[(4-methoxyphenyl)methyl]-2-phenyl-1-benzofuran (11a):** Yield: 0.1290 g (82%), white solid; R_f = 0.42 (5% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.73 (m, 2H), 7.58 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.52 – 7.30 (m, 5H), 7.27 – 7.17 (m, 3H), 6.94 – 6.82 (m, 2H), 4.30 (s, 2H), 3.81 (s, 3H); spectroscopic data are in agreement with previously published NMR data.[9]
 **11b**	**3-[(4-methoxyphenyl)methyl]-2-(4-methylphenyl)-1-benzofuran (11b):** Yield: 0.132 g (81%), white solid; mp 66–68 °C; R_f = 0.30 (5% EtOAc/hexanes); IR (ATR) 3058, 3030, 2997, 2952, 2932, 2914, 2836, 1610, 1583, 1508, 1474, 1452 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.34 – 7.24 (m, 3H), 7.24 – 7.14 (m, 3H), 6.88 – 6.82 (m, 2H), 4.26 (s, 2H), 3.80 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.22, 154.16, 152.31, 138.48, 131.52, 130.73, 129.57, 129.24, 128.25, 126.98, 124.31, 122.60, 119.97, 114.13, 113.63, 111.11, 55.39, 29.37, 21.49. HRMS (CI): Exact mass calcd for $C_{23}H_{20}O_2$ $[M]^+$ 328.1463, found 328.1448.
 **12b**	**8-[2-(4-methoxyphenyl)-1-(4-methylphenyl)ethylidene]-7-oxabicyclo[4.2.0]octa-1,3,5-triene (12b):** Yield: 11.2 mg (7%), colorless oil; R_f = 0.27 (5% EtOAc/hexanes); IR (ATR) 3030, 3000, 2953, 2929, 2902, 2831, 1611, 1583, 1505, 1474, 1449, 1431 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 2H), 7.46 (dd, *J* = 7.9, 0.6 Hz, 1H), 7.33 – 7.21 (m, 3H), 7.19 – 7.11 (m, 2H), 7.07 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.92 (d, *J* = 1.0 Hz, 1H), 6.88 – 6.81 (m, 2H), 4.04 (s, 2H), 3.79 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.16, 156.13, 155.35, 138.54, 138.32, 133.60, 130.03, 129.60, 128.03, 127.53, 124.88, 124.18, 120.58, 114.08, 111.39, 100.54, 55.43, 41.36, 21.51. HRMS (CI): Exact mass calcd for $C_{23}H_{20}O_2$ $[M]^+$ 328.1463, found 328.1458.

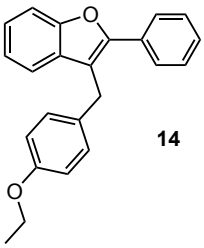
Compound	Characterization data
 **11c**	**2-(4-methoxyphenyl)-3-[(4-methoxyphenyl)methyl]-1-benzofuran (11c):** Yield: 0.130 g (75%); white solid mp 84–86 °C; R_f = 0.17 (5% EtOAc/hexanes); IR (ATR) 3035, 2998, 2952, 2931, 2905, 2834, 1610, 1584, 1572, 1506, 1453, 1440, 1418 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 2H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.37 (ddd, *J* = 7.7, 1.4, 0.7 Hz, 1H), 7.29 (ddd, *J* = 8.2, 7.2, 1.4 Hz, 1H), 7.26 – 7.13 (m, 3H), 7.08 – 6.93 (m, 2H), 6.92 – 6.81 (m, 2H), 4.24 (s, 2H), 3.86 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.83, 158.20, 154.05, 152.20, 131.53, 130.80, 129.19, 128.49, 128.43, 124.10, 123.71, 122.57, 119.80, 114.31, 114.12, 112.80, 111.01, 55.38, 29.30; HRMS (CI): Exact mass calcd for $C_{23}H_{20}O_3$ $[M]^+$ 344.1412, found 344.1401.
 **11f**	**2-(4-fluorophenyl)-3-[(4-methoxyphenyl)methyl]-1-benzofuran (11f):** Yield: 0.1142 g (69%); white solid; mp 58–60 °C; R_f = 0.34 (5% EtOAc/hexanes); IR (ATR) 3062, 2996, 2952, 2932, 2908, 2834, 1610, 1600, 1583, 1504, 1475, 1453 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.66 (m, 2H), 7.51 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.36 (ddd, *J* = 7.7, 1.4, 0.7 Hz, 1H), 7.29 (ddd, *J* = 8.3, 7.2, 1.4 Hz, 1H), 7.24 – 7.03 (m, 5H), 6.86 – 6.78 (m, 2H), 4.20 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.77 (d, *J* = 248.8 Hz), 158.30, 154.16, 151.19, 131.16, 130.56, 129.15, 128.87 (d, *J* = 8.1 Hz), 127.26 (d, *J* = 3.3 Hz), 124.60, 122.77, 120.07, 115.92 (d, *J* = 21.8 Hz), 114.20, 114.03, 111.15, 55.32, 29.23; HRMS (CI): Exact mass calcd for $C_{22}H_{17}FO_2$ [M]+ 332.1212, found 332.1200.
 **11g**	**2-(4-chlorophenyl)-3-[(4-methoxyphenyl)methyl]-1-benzofuran] (11g):** Yield: 79.0 mg (79%); white solid; mp 83–85 °C; R_f = 0.26 (2% EtOAc/hexanes); IR (ATR) 3039, 2996, 2933, 2836, 1610, 1582, 1510, 1489, 1452 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 – 7.67 (m, 2H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.34 (ddd, *J* = 8.3, 7.2, 1.4 Hz, 1H), 7.29 – 7.15 (m, 3H), 6.92 – 6.81 (m, 2H), 4.25 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.34, 154.21, 150.89, 134.32, 131.02, 130.54, 129.51, 129.15, 129.09, 128.16, 124.84, 122.84, 120.15, 114.80, 114.23, 111.21, 55.36, 29.29; HRMS (CI): Exact mass calcd for $C_{22}H_{21}ClNO_2$ $[M+NH_4]^+$ 366.1261, found 366.1253.

Compound	Characterization data
 **11h**	**2-(4-bromophenyl)-3-[(4-methoxyphenyl)methyl]-1-benzofuran (11h):** Yield: 0.128 g (79%); white solid; mp 103–104 °C; R_f = 0.38 (5% EtOAc/hexanes); IR (ATR) 3036, 2995, 2956, 2930, 2834, 1612, 1582, 1511, 1488, 1477, 1461, 1452 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.73 – 7.46 (m, 5H), 7.39 (ddd, *J* = 7.7, 1.3, 0.7 Hz, 1H), 7.32 (ddd, *J* = 8.3, 7.2, 1.4 Hz, 1H), 7.25 – 7.11 (m, 3H), 6.91 – 6.79 (m, 2H), 4.23 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.31, 154.20, 150.90, 132.03, 130.97, 130.54, 129.93, 129.15, 128.39, 124.88, 122.86, 122.56, 120.15, 114.91, 114.22, 111.23, 55.37, 29.29; HRMS (CI): Exact mass calcd for $C_{22}H_{17}BrO_2$ $[M]^+$ 392.0412, found 392.0402.
 **11i**	**2-(3-fluorophenyl)-3-[(4-methoxyphenyl)methyl]-1-benzofuran (11i):** Yield: 0.127 g (76%); white solid; mp 73–75 °C; R_f = 0.24 (5% EtOAc/hexanes); IR (ATR) 3072, 3039, 3012, 2961, 2935, 2913, 2838, 1612, 1574, 1509, 1490, 1474, 1464 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 3H), 7.40 (td, *J* = 8.0, 6.1 Hz, 2H), 7.34 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1H), 7.25 – 7.16 (m, 3H), 7.07 (tdd, *J* = 8.4, 2.6, 1.1 Hz, 1H), 6.90 – 6.82 (m, 2H), 4.27 (s, 2H), 3.79 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.92 (d, *J* = 245.7 Hz), 158.17, 154.05, 150.45 (d, *J* = 2.7 Hz), 132.91 (d, *J* = 8.5 Hz), 130.80, 130.32, 130.23 (d, *J* = 8.4 Hz), 129.00, 124.81, 122.68, 122.38 (d, *J* = 3.0 Hz), 120.09, 115.18, 115.10 (d, *J* = 21.1 Hz), 114.07, 113.67 (d, *J* = 23.5 Hz), 111.09, 55.20, 29.13; HRMS (CI): Exact mass calcd for $C_{22}H_{17}FO_2$ $[M]^+$ 332.1212, found 332.1207.
 **11j**	**2-(2-chlorophenyl)-3-[(4-methoxyphenyl)methyl]-1-benzofuran (11j):** Yield: 0.088 g (50%); colorless oil R_f = 0.31 (5% EtOAc/hexanes); IR (ATR) 3058, 3033, 2995, 2952, 2931, 2908, 2834, 1611, 1559, 1510, 1449 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (ddd, *J* = 10.5, 7.8, 1.8 Hz, 1H), 7.46 – 7.29 (m, 1H), 7.24 – 7.11 (m, 1H), 6.86 – 6.79 (m, 1H), 4.04 (s, 1H), 3.79 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.10, 154.81, 150.18, 134.76, 132.43, 131.38, 130.65, 130.24, 129.98, 129.44, 129.11, 126.73, 124.58, 122.58, 120.66, 117.20, 113.91, 111.36, 55.32, 29.49. HRMS (CI): Exact mass calcd for $C_{22}H_{21}ClNO_2$ $[M+NH_4]^+$ 366.1261, found 366.1269.

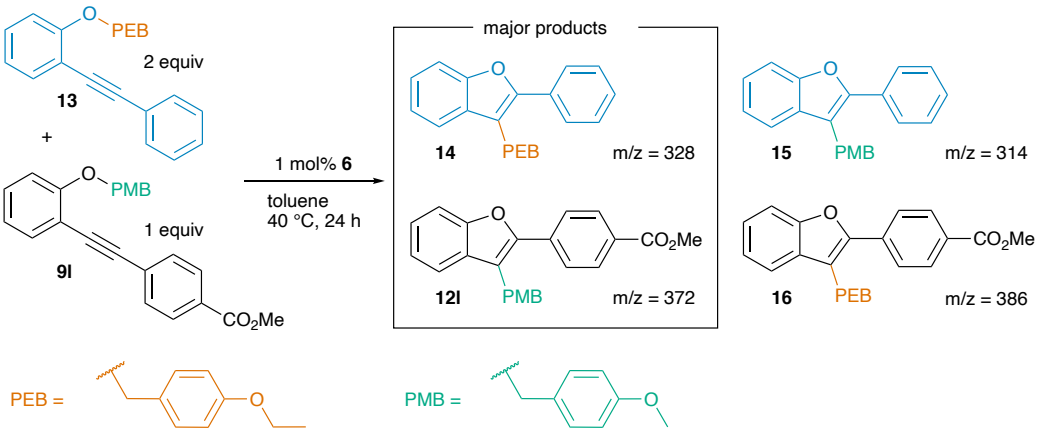
Compound	Characterization data
 **11k**	**3-[(4-methoxyphenyl)methyl]-2-[4-(trifluoromethyl)phenyl]-1-benzofuran (11k):** Yield: 0.0877 g (50%); colorless oil R_f = 0.31 (5% EtOAc/hexanes); IR (ATR) 3064, 3010, 2992, 2939, 2915, 2842,1616, 1584, 1511, 1452 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.41 (d, *J* = 6.8 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.24 – 7.12 (m, 2H), 6.83 (d, *J* = 8.6 Hz, 1H), 4.27 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.44, 154.43, 150.38, 134.42, 130.80, 130.46, 130.04 (q, J = 32.6 Hz), 129.16, 127.01, 125.82 (q, J = 3.5 Hz), 125.35, 124.21 (q, J = 273.0 Hz), 123.03, 120.40, 116.28, 114.33, 55.41, 29.34; HRMS (CI): Exact mass calcd for $C_{23}H_{17}F_3O_2$ $[M]^+$ 382.1181, found 382.1166.
 **11l**	**methyl 4-{3-[(4-methoxyphenyl)methyl]-1-benzofuran-2-yl}benzoate (11l):** Yield: 0.125 g (67%); white solid; mp 118–120 °C; R_f = 0.36 (15% EtOAc/hexanes); IR (ATR) 3075, 3036, 2999, 2951, 2836, 1723, 1610, 1580, 1509 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 – 8.04 (m, 2H), 7.87 – 7.80 (m, 2H), 7.54 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.41 (ddd, *J* = 7.7, 1.4, 0.7 Hz, 1H), 7.33 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1H), 7.24 – 7.12 (m, 3H), 6.88 – 6.78 (m, 2H), 4.28 (s, 2H), 3.94 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.85, 158.40, 154.45, 150.78, 135.26, 130.90, 130.54, 130.13, 129.57, 129.21, 126.62, 125.31, 122.97, 120.38, 116.47, 114.29, 111.36, 55.41, 52.34, 29.45; HRMS (CI): Exact mass calcd for $C_{24}H_{20}O_4$ $[M]^+$ 372.1362, found 372.1344.
 **11m**	**4-{3-[(4-methoxyphenyl)methyl]-1-benzofuran-2-yl}benzonitrile (11m):** Yield: 0.100 g (59%); white solid; mp 125–128 °C; R_f = 0.38 (15% EtOAc/hexanes); IR (ATR) 3067, 3040, 3001, 29334, 2938, 2223, 1607, 1509 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.80 (m, 1H), 7.75 – 7.65 (m, 1H), 7.55 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.43 (ddd, *J* = 7.8, 1.4, 0.7 Hz, 0H), 7.36 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 0H), 7.23 (ddd, *J* = 8.1, 7.2, 1.0 Hz, 0H), 7.15 (dt, *J* = 8.9, 0.8 Hz, 1H), 4.27 (s, 1H), 3.78 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.45, 154.45, 149.64, 135.17, 132.60, 130.37, 130.34, 129.09, 126.98, 125.77, 123.18, 120.49, 118.86, 117.39, 114.33, 111.42, 111.39, 55.37, 29.33.; HRMS (CI): Exact mass calcd for $C_{23}H_{21}N_2O_2$ $[M+NH_4]^+$ 357.1603, found 357.1600.

Compound	Characterization data
 **11n**	**3-{3-[(4-methoxyphenyl)methyl]-1-benzofuran-2-yl}benzonitrile (11n):** Yield: 0.126 g (74%), yellow oil; R_f = 0.38 (15% EtOAc/hexanes); IR (ATR) 3062, 2996, 2930, 2834, 2230, 1610, 1499, 1453 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 1.8 Hz, 1H), 7.99 – 7.91 (m, 1H), 7.61 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.58 – 7.48 (m, 2H), 7.42 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.35 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.27 – 7.12 (m, 3H), 6.88 – 6.80 (m, 2H), 4.25 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.41, 154.27, 149.23, 132.24, 131.37, 130.65, 130.43, 130.25, 130.18, 129.63, 129.09, 125.45, 123.09, 120.39, 118.58, 116.41, 114.30, 113.16, 111.34, 55.32, 29.20; HRMS (CI): Exact mass calcd for $C_{23}H_{21}N_2O_2$ $[M+NH4]^+$ 357.1603, found 357.1587.
 **11p**  **12p**	**3-[(4-methoxyphenyl)methyl]-2-(thiophen-3-yl)-1-benzofuran (11p/12p):** Yield: 115 mg (77%); yellow oil; R_f = 0.38 (5 EtOAc/hexanes), mixture of isomers (2:3 ratio); IR (ATR) 3038, 2995, 2933, 2836, 1610, 1582, 1510, 1490, 1452 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) isomer 1: δ 7.65 – 7.11 (m, 9H), 6.92 – 6.71 (m, 2H), 4.42 (s, 2H), 3.77 (s, 3H); isomer 2: ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 – 7.11 (m, 9H), 6.92 – 6.71 (m, 2H), 4.22 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.43, 158.20, 154.26, 153.93, 152.87, 148.92, 142.06, 132.07, 131.97, 131.13, 130.42, 129.81, 129.13, 129.07, 127.77, 127.27, 126.32, 126.07, 124.39, 124.11, 123.49, 122.98, 122.68, 120.86, 119.81, 114.13, 114.07, 113.44, 111.11, 111.04, 102.68, 55.30, 34.44, 29.09; (inseparable mixture of isomers) HRMS (CI): Exact mass calcd for $C_{20}H_{16}O_2S$ [M]+ 320.0871, found 320.0880.
 **11r**	**6-chloro-3-[(4-methoxyphenyl)methyl]-2-phenyl-1-benzofuran(11r):** Yield: 0.132 g (76%); yellow oil R_f = 0.40 (2% EtOAc/hexanes); IR (ATR) 3061, 2998, 2953, 2905, 2931, 2834, 1610, 1583, 1509, 1494, 1465, 1447, 1421 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 2H), 7.60 – 7.35 (m, 4H), 7.28 – 7.12 (m, 4H), 6.94 – 6.82 (m, 2H), 4.24 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.30, 154.23, 152.77, 130.88, 130.55, 130.24, 129.26, 129.13, 128.87, 128.69, 126.97, 123.36, 120.62, 114.17, 114.11, 111.69, 55.28, 29.22; HRMS (CI): Exact mass calcd for $C_{22}H_{17}ClO_2$ $[M]^+$ 348.0917, found 348.0908.

Compound	Characterization data
 **11s**	**3-[(4-methoxyphenyl)methyl]-4-methyl-2-phenyl-1-benzofuran (11s):** Yield: 0.102 g (62%), yellow oil; R_f = 0.31 (2% EtOAc/hexanes); IR (ATR) 3027, 2997, 2951, 2930, 2907, 2833, 1610, 1582, 1508, 1492, 1460, 1441, 1418 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.68 (m, 2H), 7.51 – 7.36 (m, 4H), 7.29 – 7.15 (m, 3H), 6.98 (dt, *J* = 7.4, 0.9 Hz, 1H), 6.97 – 6.86 (m, 2H), 4.39 (s, 2H), 3.83 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.19, 154.70, 152.55, 132.30, 132.08, 130.99, 129.01, 128.79, 128.67, 128.43, 127.19, 124.51, 124.40, 114.25, 114.21, 109.06, 55.33, 30.15, 19.17; HRMS (CI): Exact mass calcd for $C_{23}H_{20}O_2$ [M]+ 328.1463, found 328.1451.
 **11t**	**3-[(4-methoxyphenyl)methyl]-5-methyl-2-phenyl-1-benzofuran (11t):** Yield: 0.128 g (78%); yellow oil R_f = 0.38 (5% EtOAc/hexanes); IR (ATR) 3026, 2914, 2836, 1610, 1583, 1508 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 2H), 7.57 – 7.48 (m, 3H), 7.47 – 7.34 (m, 1H), 7.34 – 7.25 (m, 3H), 7.25 – 7.13 (m, 1H), 6.93 (dd, *J* = 9.0, 2.5 Hz, 2H), 4.31 (s, 2H), 3.84 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.19, 152.64, 152.17, 132.08, 131.39, 131.14, 130.73, 129.13, 128.79, 128.31, 126.88, 125.85, 119.78, 114.13, 113.95, 110.68, 55.29, 29.21, 21.49; HRMS (CI): Exact mass calcd for $C_{23}H_{20}O_2$ [M]+ 328.1463, found 328.1449.
 **11u**	**3-[(4-methoxyphenyl)methyl]-6-methyl-2-phenyl-1-benzofuran (11u):** Yield: 0.139 g (85%); white solid, mp 66–68 °C; R_f = 0.49 (10% EtOAc/hexanes); IR (ATR) 3032, 2998, 2952, 2911, 2834, 1611, 1584, 1490, 1462, 1440 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (dt, *J* = 7.6, 1.3 Hz, 2H), 7.52 – 7.33 (m, 4H), 7.28 – 7.15 (m, 3H), 7.02 (ddd, *J* = 7.9, 1.4, 0.7 Hz, 1H), 6.90 – 6.78 (m, 2H), 4.25 (s, 2H), 3.79 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.20, 154.66, 151.47, 134.85, 131.48, 131.23, 129.78, 129.21, 128.81, 128.22, 126.88, 124.07, 119.61, 114.20, 114.12, 111.45, 55.37, 29.38, 21.88; HRMS (CI): Exact mass calcd for $C_{23}H_{20}O_2$ [M]+ 328.1463, found 328.1453.

Compound	Characterization data
 **14**	**3-[(4-ethoxyphenyl)methyl]-2-phenyl-1-benzofuran (14):** Yield: 0.126 g (89%), yellow oil; R_f = 0.33 (5% EtOAc/hexanes); IR (ATR) 3060, 3034, 2977, 2926, 2896, 1610, 1508, 1949 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 2H), 7.54 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.46 (ddt, *J* = 8.2, 6.6, 1.1 Hz, 2H), 7.42 – 7.34 (m, 2H), 7.31 (ddd, *J* = 8.3, 7.2, 1.4 Hz, 1H), 7.23 – 7.14 (m, 3H), 6.90 – 6.78 (m, 2H), 4.26 (s, 2H), 4.01 (q, *J* = 7.0 Hz, 2H), 1.41 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.61, 154.25, 152.06, 131.23, 131.06, 130.66, 129.21, 128.84, 128.46, 126.99, 124.53, 122.66, 120.15, 114.72, 114.32, 111.18, 63.51, 29.36, 15.01; HRMS (CI): Exact mass calcd for $C_{23}H_{20}O_2$ $[M]^+$ 328.1463, found 328.1451.

Cross-over experiment



To a 2-dram vial was added alkyne **13** (164.0 mg, 500 µmol), alkyne **9l** (93.0 mg, 250 µmol) and toluene (1.5 mL) and the mixture was stirred for 1 min at rt. An aliquot (40 µL) of the solution was taken and analyzed by ^{1}H NMR (Figure 5, top). The catalyst (9.5 mg, 7.5 µmol) was added to the mixture and the reaction was stirred at 60 °C for 20 h. The solvent was removed under reduced pressure and the mixture was analyzed by ^{1}H NMR (Figure 5, bottom) and GC/CI-MS.

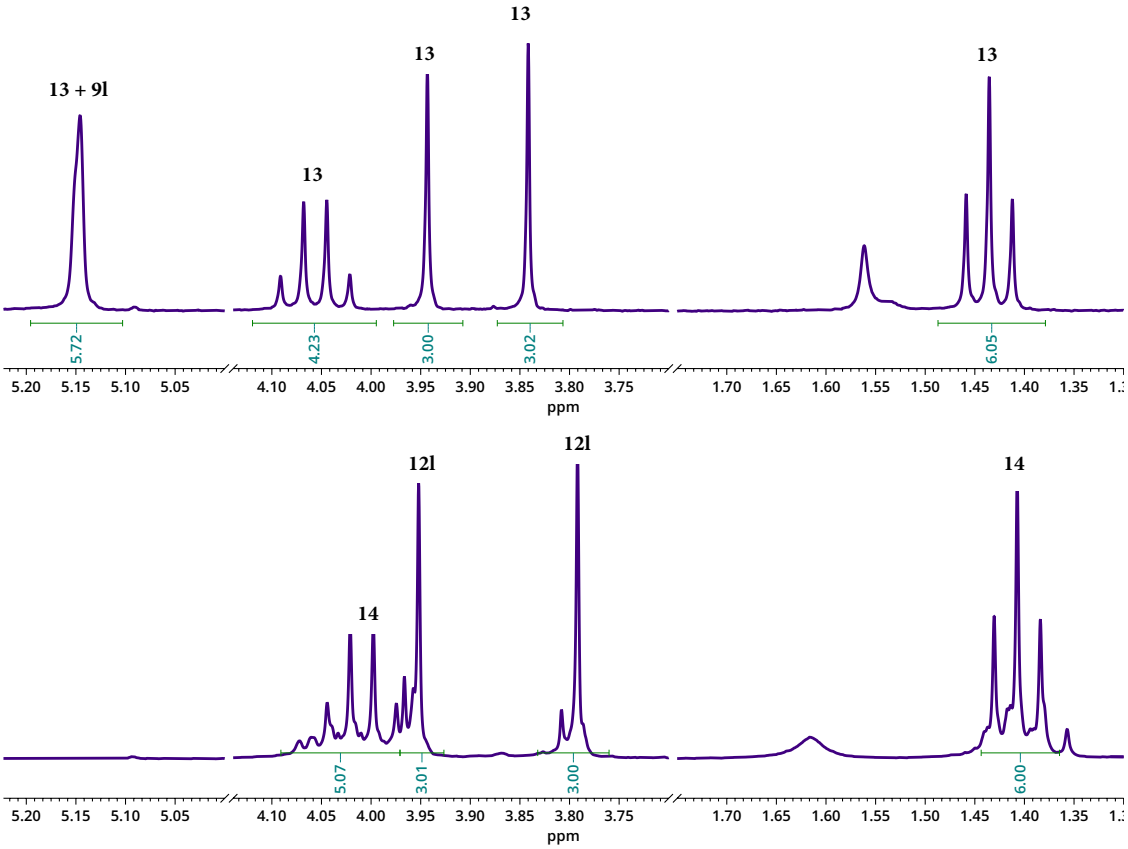


Figure 5 ^{1}H NMR spectrum of the pre-reaction mixture (top) and post-reaction mixture (bottom).

GC–MS analysis

- Instrument system: Agilent GC 7890A with Waters GCT Premier instrument operated in CI-MS mode.
- Software: Waters MassLynx 4.1
- GC conditions:
    - Column: Agilent DB-5MS UI, 30m x 0.32 mm x 0.25um;
    - Carrier gas: He @ 1.6 mL/min, constant flow;
    - Gradient: Initial temp = 50 C, ramp 20 °C/min —> final temp = 300 °C; hold time 4.5 mins. Total run time = 17.5 mins
    - Injection type: Splitless, 1 µL sample in dichloromethane @ 10 µM. Injector temp = 250 C. Purge flow = 40 mL/min, purge time = 2.0 min, septum purge flow 3.0 mL/min.
- CI-MS settings:
    - Detector V = 2600V
    - Source temp = 200 C
    - eV = 70 V
    - Emission current = 200 µA
    - CI gas flow = 10 % ammonia gas
    - Calibration standards = Heptacosatributylamine. 8-component calibration curve. Lockmass = nearest calibration peak.

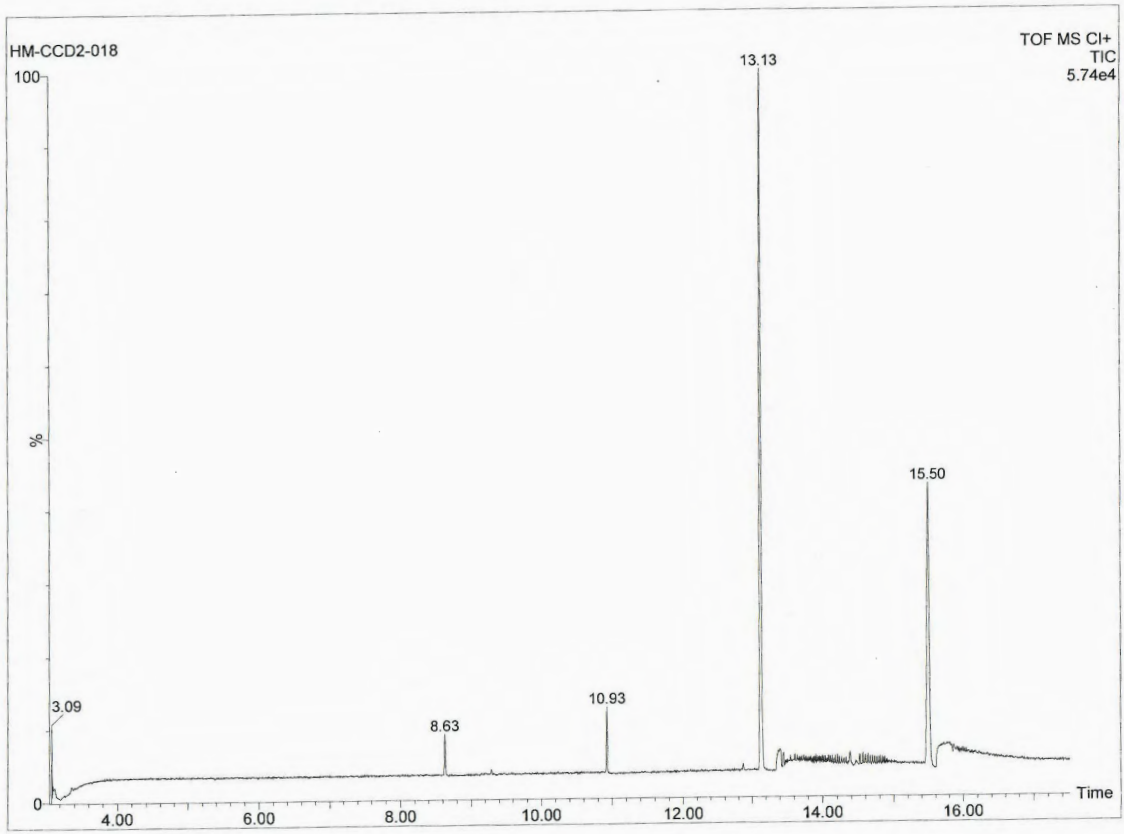


Figure 6. Gas chromatograph of the competition experiment.

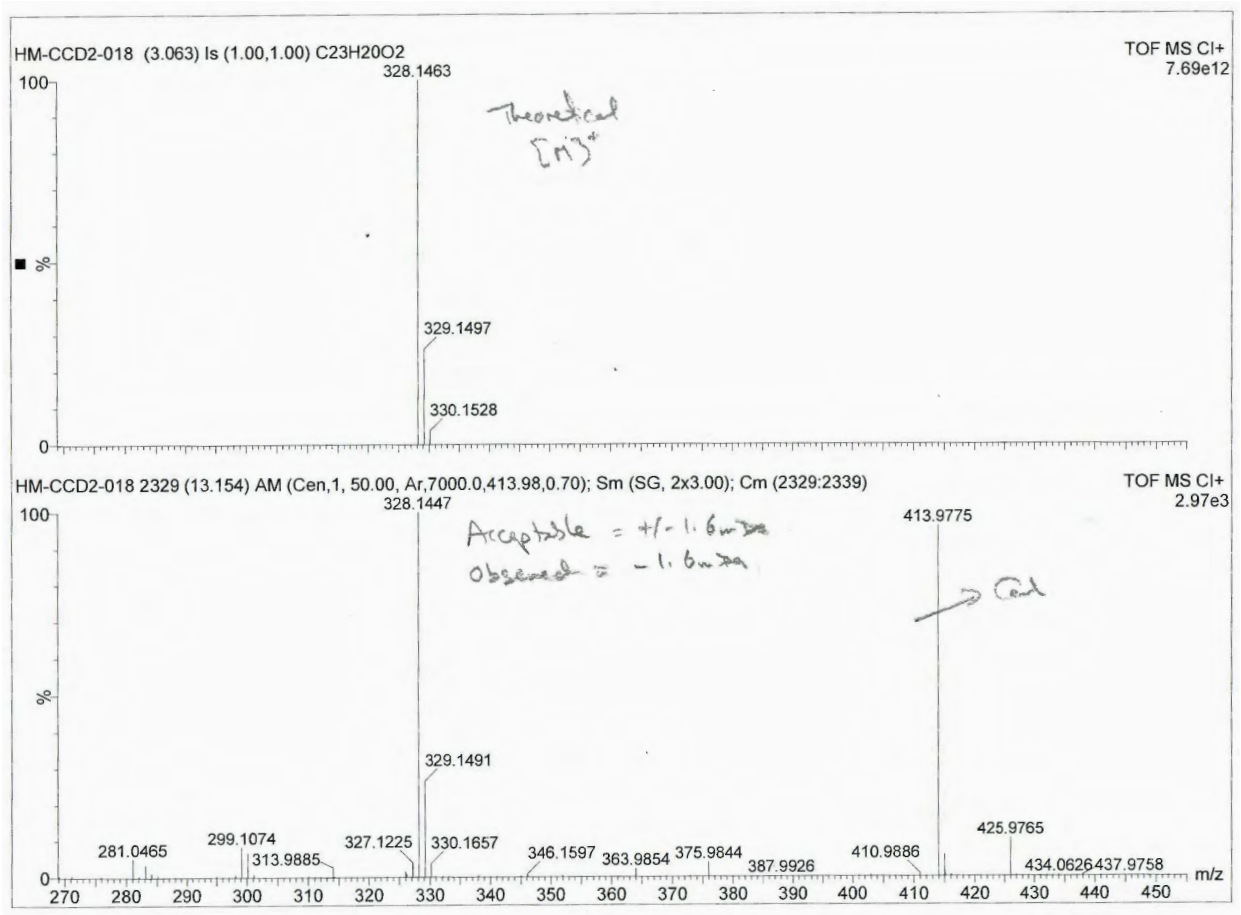


Figure 7. MS analysis of the major component (retention time 13.13 min).

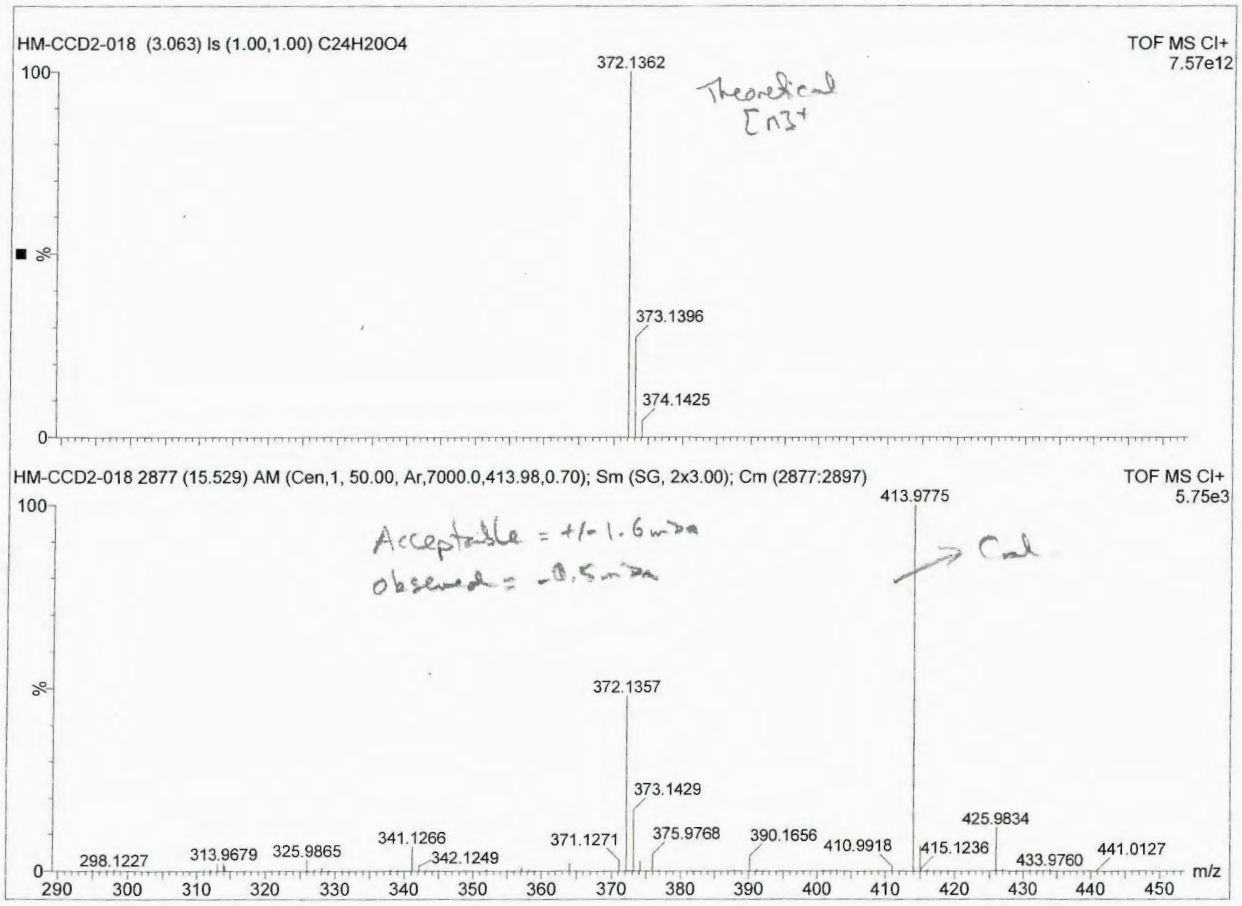
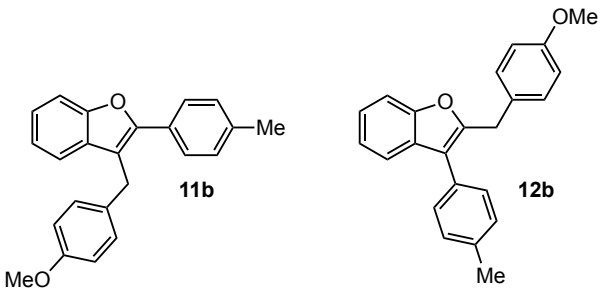


Figure 8. MS analysis of the major component (retention time 15.53 min).

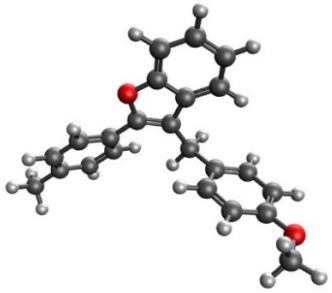
DFT Calculations



The energy difference in the optimized structures of **11b** and **12b** is less than 0.05 kJ/mol. Furthermore, these isomers are spectroscopically nearly indistinguishable at this level of theory. The minor product, **11b**, is slightly more polar and shows a slightly more deshielding of the methylene carbon. There is no significant differences in the IR frequencies or spectra. These results are qualitatively consistent with experimental characterization of these compounds and a higher level of theory would be required for numerical accuracy.

Compound 11b:

- Energy = -1038.198373 Eh
- Dipole = 1.925 D
- IR (12 highest intensity peaks over 1400 cm^{-1}): 3175, 3139, 3067, 3029, 3027, 2996, 1676, 1552, 1545, 1487, 1483, 1407
- ^{13}C NMR: 51.72, 30.56, 23.35



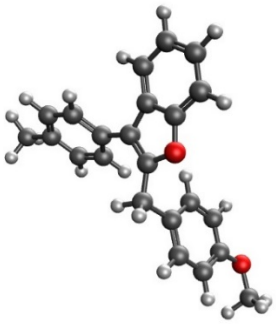
Standard Nuclear Orientation (Angstroms)

I	Atom	X	Y	Z
1	C	4.3785624300	-0.9435980904	1.3138111073
2	C	3.4566506127	0.0965842322	1.1574761837
3	C	3.2633649195	1.0652048247	2.1493133440
4	C	4.0319510320	0.9605479545	3.3206326314
5	C	4.9541622606	-0.0681642356	3.4960355170
6	C	5.1364214283	-1.0328101595	2.4917683610
7	C	2.2837822221	2.2132899419	1.9505780240
8	C	0.8942235697	1.7933326642	1.5497568873
9	C	0.0675501794	0.8271599975	2.2464449177
10	C	-1.1127691785	0.7120649790	1.4864851644
11	O	-1.0519774560	1.5295661635	0.4040564781
12	C	0.1592311611	2.1888658171	0.4536666611
13	C	0.1991976039	0.0539309155	3.4146977628
14	C	-0.8517474476	-0.7882438525	3.7763391627
15	C	-2.0225881351	-0.8769519931	2.9956288922
16	C	-2.1726461822	-0.1240817651	1.8288366118
17	C	0.4043552274	3.1085828294	-0.6618036925
18	C	1.1757533908	4.2792531912	-0.5194747931
19	C	1.4062068026	5.1194807611	-1.6073329783
20	C	0.8692743701	4.8407296585	-2.8754278698
21	C	0.0782353620	3.6892786160	-3.0068779623
22	C	-0.1540861180	2.8395791079	-1.9261007063
23	C	1.1275241550	5.7587917915	-4.0446547590
24	O	6.0546538302	-2.0014212085	2.7473203845
25	C	6.2888540649	-3.0007644162	1.7823572279
26	H	-3.0705100245	-0.1798627148	1.2103541855
27	H	1.1061601046	0.1052446090	4.0198609815
28	H	-0.7678405590	-1.3951472250	4.6815825852
29	H	-2.8268321009	-1.5483985459	3.3072025378
30	H	1.5727852968	4.5542157527	0.4588193344
31	H	2.0072321388	6.0227385438	-1.4641321567
32	H	-0.3629033863	3.4499158074	-3.9787150967
33	H	-0.7715957108	1.9492167699	-2.0563610637
34	H	2.2069288277	5.8511290676	-4.2521802591
35	H	0.7512453356	6.7766541232	-3.8466816352
36	H	0.6396162553	5.3935944519	-4.9602866422
37	H	2.2368445302	2.7984437174	2.8857705592
38	H	2.6882563610	2.8955149306	1.1869591328

39	H	2.8698056369	0.1472138126	0.2363596652
40	H	3.9058452678	1.7030050111	4.1146022704
41	H	5.5500165793	-0.1482288046	4.4076268571
42	H	4.4971436802	-1.6753163646	0.5143333665
43	H	7.0578712981	-3.6658094748	2.1988753290
44	H	6.6609278840	-2.5777964755	0.8311090598
45	H	5.3800404799	-3.5942297165	1.5725084295

Compound 12b:

- Energy = -1038.198389 Eh
- Dipole = 2.028 D
- IR (12 highest intensity peaks over 1400 cm-1): 3171, 3141, 3067, 3026, 2996, 1678, 1651, 1557, 1552, 1490, 1481, 1471
- ^{13}C NMR: 51.79, 32.47, 23.34



Standard Nuclear Orientation (Angstroms)

I	Atom	X	Y	Z
1	C	5.5007219024	-1.5573296672	1.2124100382
2	C	4.6301650515	-0.9984369668	0.2695210112
3	C	4.0059891095	0.2354434441	0.4804777768
4	C	4.2718762300	0.9017817158	1.6896818127
5	C	5.1314104734	0.3601285965	2.6407540844
6	C	5.7589954184	-0.8754571234	2.4104867868
7	C	3.1111649425	0.8363538821	-0.5977802656
8	C	2.0247977888	1.7311747026	-0.1044959000
9	O	1.0214964979	1.1127880240	0.5984754741
10	C	0.1156097336	2.0694846315	0.9371679485
11	C	0.5282799371	3.3230999029	0.4445470500
12	C	1.7916176128	3.0791384849	-0.2364087367
13	C	-0.2661849300	4.4510591453	0.7145245946
14	C	-1.4399180587	4.2780719163	1.4479854606
15	C	-1.8307103613	3.0081507056	1.9173660684
16	C	-1.0513845034	1.8757973483	1.6715980986
17	C	2.6292616784	4.0792146848	-0.9298827951
18	C	4.0233677513	4.1397615820	-0.7402622142
19	C	4.7993492990	5.0926824626	-1.4008459946
20	C	4.2212896161	6.0314912352	-2.2701870407
21	C	2.8314820260	5.9750309854	-2.4542629306
22	C	2.0499340853	5.0203921181	-1.8009382700
23	C	5.0706481812	7.0517303787	-2.9884917885
24	O	6.5842922994	-1.3243433846	3.3917940486
25	C	7.2485661469	-2.5546670205	3.2235930656
26	H	-1.3312510315	0.8852995651	2.0347466539
27	H	0.0319240892	5.4422852894	0.3663062694
28	H	-2.0698363166	5.1438607759	1.6670125173

29	H	-2.7573873310	2.9082833927	2.4879263919
30	H	4.5035531818	3.4467346172	-0.0455089134
31	H	5.8791037403	5.1156159974	-1.2249459881
32	H	2.3490217576	6.6907753728	-3.1264562260
33	H	0.9726963593	4.9933571122	-1.9813068812
34	H	5.5899779871	6.6026709523	-3.8535471990
35	H	5.8479398218	7.4658028912	-2.3266865756
36	H	4.4643217407	7.8883241161	-3.3670936989
37	H	3.7204456531	1.4119378695	-1.3139305513
38	H	2.6504588927	0.0132715989	-1.1709286660
39	H	4.4379601600	-1.5477492499	-0.6575990014
40	H	3.7897204314	1.8606680473	1.8979704981
41	H	5.3334081710	0.8772899096	3.5811223253
42	H	5.9639441943	-2.5216582745	1.0024074981
43	H	7.8637104772	-2.7048771637	4.1212517926
44	H	7.9077688704	-2.5507743148	2.3362569568
45	H	6.5399222232	-3.3983682904	3.1325924141

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