Supporting Information to

Two-Step One-Pot Ni-Catalyzed Neopentylglycolborylation and Complementary Pd/Ni-Catalyzed Cross-Coupling with Aryl Halides, Mesylates and Tosylates

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1. Materials

Borane dimethylsulfide complex, 3,5-dimethoxy-1-bromobenzene, 4-(benyzyloxy)phenol, 1-bromonapthalene, 4-iodoanisole, hydrocinnamic acid, 1,3-bis(diphenylphosophino)propane and 1,2-bis(diphenphosophino)ethane were used as received from Aldrich. 1,1'-bis(diphenylphosphino)ferrocene, 99%, 2-(dicyclohexylphosphino)biphenyl, 98% and Ni(COD)$_2$ were used as received from Strem Chemicals. 4-chlorotoluene and 4-bromoanisole were used as received from Lancaster. $NiCl_2•6H_2O$ was used as received from Acros. (i-Pr)$_2$EtN, CsF and P(Cy)$_3$ were used as received from Aldrich. $MgSO_4$, NaCl, $NaHCO_3$, dichloromethane, acetone, ethyl acetate, hexanes, and methanol were all used as received from Fischer. K_3PO_4 (tribasic) from Fischer was dried at 40 °C prior to use. Neopentylglycol from Acros was recrystallized from dichloromethane prior to use. Dioxane and THF (ACS Reagent grade) from Fischer were dried over sodium ketyl prior use. Toluene and triethylamine (ACS reagent grade) from Fischer were distilled over CaH_2 and stored under nitrogen prior to use. Deuterated solvents were obtained from Cambridge Isotope Labs. Ni-based catalysts $NiCl_2$(dppp)[1], $NiCl_2$(dppe)[2], $NiCl_2$(dppf)[3], $NiCl_2(PPh_3)_2$,[4] $NiCl_2(Et_3N)_2$,[5] $NiCl_2$(bpy)[6] and Pd catalyst $PdCl_2$(dppf)[7] were synthesized according to the original procedures.

2. Instrumentation

^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker DRX 500, using TMS as internal standard. High-resolution mass spectra of new compounds were obtained on an Autospec high resolution double focusing chemical ionization spectrometer. Agilent GC 6890 coupled with an FID detector gas chromatograph and column HP 19091J-413 (5%-phenyl)-methylpolysiloxane 30m Length 0.32mm internal diameter was used to follow the reaction conversions and to assess purity of final compounds complementary to the NMR technique. The crude reaction mixtures were diluted with THF stabilized with BHT (3%), which was used as internal standard. Inert atmosphere for air sensitive reagents and reactions (Ni(COD)$_2$-catalized cross-coupling) was provided by Innovative Technology System 1, Glove Box.

3. List of Abbreviations

BH_3•DMS borane dimethylsulfide complex
CI chemical ionization
DCM dichloromethane
dppe 1,2-bis(diphenylphosphino)ethane
dppf 1,1'-bis(diphenylphosphino)ferrocene
dppp 1,3-bis(diphenylphosphino)propane
$NiCl_2$(dppe) (1,2-bis(diphenylphosphino)ethane)nickel(II) chloride
$NiCl_2$(dppp) (1,3-bis(diphenylphosphino)propane)nickel(II) chloride
Ni(COD)$_2$ bis (1,5-cyclopentadiene)nickel (0)

4. Synthesis

All reactions were performed in oven dried two neck round-bottom flasks or Schlenk tubes with rubber septa tops under an inert atmosphere of N_2. Commercially available air sensitive reagents and dialkoxyboranes generated *in-situ* were transferred via syringe. Silica Gel Chromatography (Flash Chromatography) was performed using silica gel (60 Å pore size, 230-400 Mesh, 40-64 µm particle size, SiliCycle). Thin Layer Chromatography was carried out on pre-coated aluminum plates (silicagel with F254 indicator; layer thickness 200 µm; particle size, 2-25 µm; pore size 60 Å, from SIGMA-Aldrich).

4.1. General Procedure for Two-Step Sequential Neopentylglycolborylation

a. Fresh Preparation of Neopentylglycolborane

To a cooled solution of neopentylglycol (10.0 mmol, 2.0 equiv) dissolved in toluene (5 mL) and maintained at 0 °C was slowly added BH_3•DMS (10.0 mmol, 2.0 equiv) via syringe under nitrogen. After 30 min of stirring at 0 °C, the reaction mixture was allowed to warm to rt and left stirring at rt until the gas evolution ceased (60-90 min). Neopentylglycolborane was used directly without further purification.

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b. Sequential Neopentylglycolborylation

A round-bottom flask charged with the aryl halide (5.0 mmol, 1.0 equiv), Ni[8] ($NiCl_2(L)_x$, $Ni(COD)_2$) or Pd[9] catalysts ($PdCl_2(dppf)$) (0.5 mmol, 0.1 to 0.02 equiv), ligand (L: dppp, dppe, dppf, PPh_3, Et_3N, bpy, PCy_3) (0.5 mmol, 0.1 equiv), and a Teflon coated stir bar was evacuated three times for 10 min under high vacuum and backfilled with N_2. Toluene (5 mL) and base (Et_3N or (i-Pr)$_2$EtN (15.0 mmol, 3.0 equiv) were added to the reaction mixture at rt. Freshly prepared neopentylglycolborane (10.0 mmol, 2.0 equiv in 5 ml toluene) was added to the red colored suspension via syringe at 23 °C. The reaction mixture was heated to 100 °C and the conversion was followed by GC. After 2 h-12 h[10], the reaction mixture was quenched via slow addition of saturated aqueous ammonium chloride (10 mL). The quenched reaction mixture was three times washed with saturated aqueous ammonium chloride and extracted with ethyl acetate (50 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was purified by silica gel chromatography or recrystallization.

4.2. General Procedure for Two-Step One-Pot Neopentylglycolborylation

To a round-bottom flask, aryl halide (5.0 mmol, 1.0 equiv), neopentylglycol (10.0 mmol, 2.0 equiv), Ni catalyst ($NiCl_2(dppp)$ or $NiCl_2(dppe)$ (0.5 mmol, 0.1 equiv), ligand (L: dppp or dppe) (0.5 mmol, 0.1 equiv), and Teflon coated stir bar was added. The flask was evacuated three times for 10 min under high vacuum and backfilled with N_2. Freshly distilled toluene was added under nitrogen via syringe and the reaction flask was then cooled to 0 °C. BH_3•DMS complex (10.0 mmol, 2.0 equiv) was added slowly under N_2 to the suspension. After 30 min of stirring at 0 °C, the reaction mixture was allowed to warm to rt and left stirring for 1h when the gas evolution ceased. Et_3N (15.0 mmol, 3.0 equiv) was added at rt and the reaction mixture was than heated to 100 °C. After complete conversion (GC) the reaction was quenched with saturated solution of NH_4Cl and extracted with ethyl acetate. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was purified by silica gel chromatography or recrystallization.

4.3. General Procedure for $Ni(COD)_2$-Catalyzed Cross-Coupling of Neopentylglycolboronate Esters and Aryl Chlorides, Mesylates and Tosylates

In a glove box with N_2 atmosphere, a Schlenk tube was charged with aryl halide, tosylate or mesylate (1.0 equiv), aryl neopentylglycolboronate (1.5 equiv), potassium phosphate (0.9 mmol, 3.0 equiv), $Ni(COD)_2$ (0.018 mmol, 0.06 equiv), tricyclohexylphosphine (0.11 mmol, 0.18 equiv), and a Teflon coated stirbar. Dry THF (2 ml) was added and reaction was left stirring for 8 h at rt. The reaction mixture was diluted with DCM (10 mL) and filtered. The filtrated solid was washed with DCM (100 mL) and the organic solvent concentrated. The coupling products were precipitated in MeOH and the white crystals were filtrated and washed with cold MeOH.

4.4. General Procedure for Pd-Catalyzed Cross-Coupling of Neopentylglycolboronate Esters and Aryl Halides

A Schlenk tube was charged with aryl halide (0.67 mmol, 1.0 equiv), aryl boronate ester (0.81 mmol, 1.2 equiv), potassium phosphate or CsF (3.0 equiv), Pd catalyst (0.1 equiv), 2-(dicyclohexylphosphino)biphenyl (0.2 equiv)[11] and a Teflon coated stirbar. The reaction mixture was evacuated three times for ten minutes under high vacuum and backfilled with N_2. Dry dioxane was added via the T-neck and the reaction mixture was heated to 110 °C for 18 h. The reaction mixture was cooled to room temperature and diluted with DCM (10 mL). The solution was filtered and the filtrated washed with DCM (100 mL). The filtrate was concentrated and purified by silica gel chromatography.

4.5. General Procedure for Three-step One-Pot Neopentylglycolborylation and Cross-coupling

The same conditions for one-pot borylations are used. After complete conversion (determined by GC) the solvent is removed under vacuum and the $PdCl_2(dppf)$ catalyst (0.1eq), aryl halide, and base are added. The reaction vessel is evacuated three times for 15 min and backfilled with N_2. Dry dioxane is added and the reaction mixture is heated to 110 °C. After 18 h the flask is cooled to rt and the salt is filtrated and washed 5 times with DCM. The organic solvent is concentrated and the compound is purified by column chromatography.

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[8] For exact amount of catalyst and co-ligand see Table 1 in the manuscript; 10% loading was used for Ni catalysts not specified in Table 1.

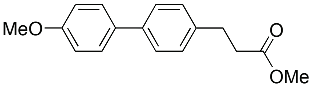
[9] No co-ligand was used for Pd catalyst.

[10] Reaction time depends on the type of the aryl halide; iodo derivatives were found to react faster, in 2-4 h , while bromo derivatives in 8-12h

[11] Co-ligand was used in the presence of $Pd(OAc)_2$ as catalyst and CsF as base (see Table 1, entries 13-15); reaction was performed at rt

Neopentylglycolboronate esters of methyl 4-iodohydrocinnamate, 4-iodoanisole, 4-bromomethylbenzoate, dimethyl biphenyl -4,4'-dicarboxylate, methyl 4'-methylbiphenyl-4carboxylate, methyl 4'-mehoxybiphenyl-4-carboxylate[12] and cross-coupling products of methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate with 1-bromonaphthalene[13] and 2-bromotoluene[14] have been reported. The NMR spectra of these compounds are in agreement with those reported in the literature. Aryl tosylates[15] and mesylates[16] have been synthesized in accordance with the literature procedures. The NMR spectra of these compounds agree with those reported in the literature. Only the synthesis and characterization by NMR of new compounds is presented in this manuscript.

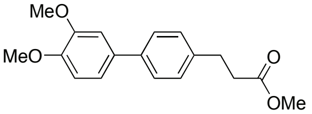
4.6. Methyl 3-(4'-methoxybiphenyl-4-yl)propanoate



The crude product was passed through a short silica gel column with (DCM) and recrystalyzed from MeOH to yield the product as white crystals (93% yield); mp 115 °C.

^{1}H NMR (Acetone-d$_6$, δ, ppm TMS): 2.66 (t, 2H, J = 7.70Hz, Ar-CH$_2$ 1 position), 2.95 (t, 2H, J = 7.70 Hz, CH$_2$COO), 3.63 (s, 3H, COOMe, Ar 4 position), 3.94 (s, 3H, OMe, Ar 3 position), 7.01 (d, 2H, J = 8.80 Hz, Ar 2',6' positions) 7.30 (d, 2H, J = 8.25Hz, Ar 2,6 positions), 7.52 (d, 2H, J = 8.25 Hz, Ar 3,5 positions), 7.57 (d, 2H, J = 8.80 Hz, Ar 3'5' positions);^{13}C NMR (Acetone-d$_6$, δ, ppm TMS): 31.94, 36.86, 52.38, 56.43, 115.95, 128.11, 129.41, 130.45, 134.97, 140.23, 141.01, 160.94, 174.14; HRMS (CI) calcd. For $C_{17}H_{18}O_3$ (M+): 270.1256, Found: 270.1238.

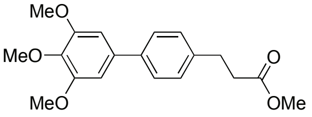
4.7. Methyl 3-(3',4'-dimethoxybiphenyl-4-yl)propanoate



The crude product was purified by silica gel chromatography (hexane:ethyl acetate 4:1), and recrystalyzed from MeOH to yield the product as white crystals (92% yield); mp 75 °C.

^{1}H NMR (CDCl$_3$, δ, ppm TMS): 2.66 (t, 2H, J = 7.70 Hz, Ar-CH$_2$ 1 position), 2.98 (t, 2H, J = 7.70 Hz, CH$_2$COO), 3.69 (s, 3H, COOMe), 3.92 (s, 3H, OMe), 3.94 (s, 3H, OMe), 6.94 (d, 1H, J = 8.25 Hz, Ar 5' position), 7.09 (d, 1H, J = 2.20 Hz, Ar 2' position), 7.13 (dd, 1H, J = 8.25 Hz, J = 2.20 Hz, Ar 6' position), 7.25 (d, 2H, Ar 2,6 positions), 7.48 (d, 2H, Ar 3,5 positions); ^{13}C NMR (CDCl$_3$, δ, ppm TMS): 30.77, 35.87, 56.15, 56.24, 110.80, 111.90, 119.51, 127.17, 128.87, 134.29, 136.27, 139.33, 148.87, 149.40, 173.46; HRMS (CI) calcd. For $C_{18}H_{20}O_4$ (M+): 300.1362, Found: 300.1348

4.8. Methyl 3-(3',4',5'-trimethoxybiphenyl-4-yl)propanoate



The crude product was purified by silica gel chromatography (DCM) to yield the product as white crystals (93% yield); mp 73 °C.

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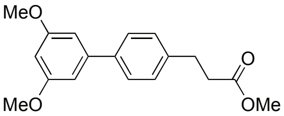
^{1}H NMR ($CDCl_3$, δ, ppm TMS): 2.66 (t, 2H, J = 7.70 Hz, Ar-CH_2 1 position), 2.99 (t, 2H, J = 7.70 Hz, CH_2COO), 3.69 (s, 3H, COOMe), 3.88 (s, 3H, Ar-OMe 4'-position), 3.91 (s, 6H, Ar-OMe 3',5' positions), 6.76 (s, 2H, Ar 2',6' positions), 7.25 (d, 2H, J = 8.25 Hz, Ar 2,6 positions), 7.47 (d, 2H, J = 8.25Hz, Ar 3,5 positons); ^{13}C NMR ($CDCl_3$, δ, ppm TMS): 31.34, 36.56, 52.23, 56.62, 99.42, 105.02, 115.87, 133.54 125.31, 129.26, 133.23, 161.71, 173.43; HRMS (CI) calcd. For $C_{19}H_{22}O_5$ (M^+): 330.1467, Found: 331.1551.

4.9. Methyl 3-(3',5'-dimethoxybiphenyl-4-yl)propanoate



The crude product was purified by silica gel chromatography (hexane:ethyl acetate 7:1) to yield the product as colorless oil (94% yield); mp 73 ºC.

^{1}H NMR ($CDCl_3$, δ, ppm TMS): 2.66 (t, 2H, J = 7.70 Hz, Ar-CH_2 1 position), 2.98 (t, 2H, J = 7.70 Hz, CH_2COO), 3.69 (s, 3H, COOMe), 3.84 (s, 6H, OMe), 3.94 (s, 3H, COOMe), 6.45 (t, 1H, J = 2.20 Hz Ar 4' position), 6.71 (d, 2H, J = 2.20 Hz, Ar 2',6' positions), 7.25 (d, 2H, J = 8.25 Hz, Ar, 2,6 positions), 7.50 (d, 2H, J = 8.25 Hz, Ar 3,5 positions). ^{13}C NMR ($CDCl_3$, δ, ppm TMS): 30.62, 35.63, 51.62, 55.43, 99.31, 105.44, 127.32, 128.67, 139.31, 139.99, 143.26, 161.59, 173.28. LRMS (MALDI-TOF) calcd. For $C_{18}H_{20}O_4$ ($M^+ + H$): 301.14, Found: 301.37

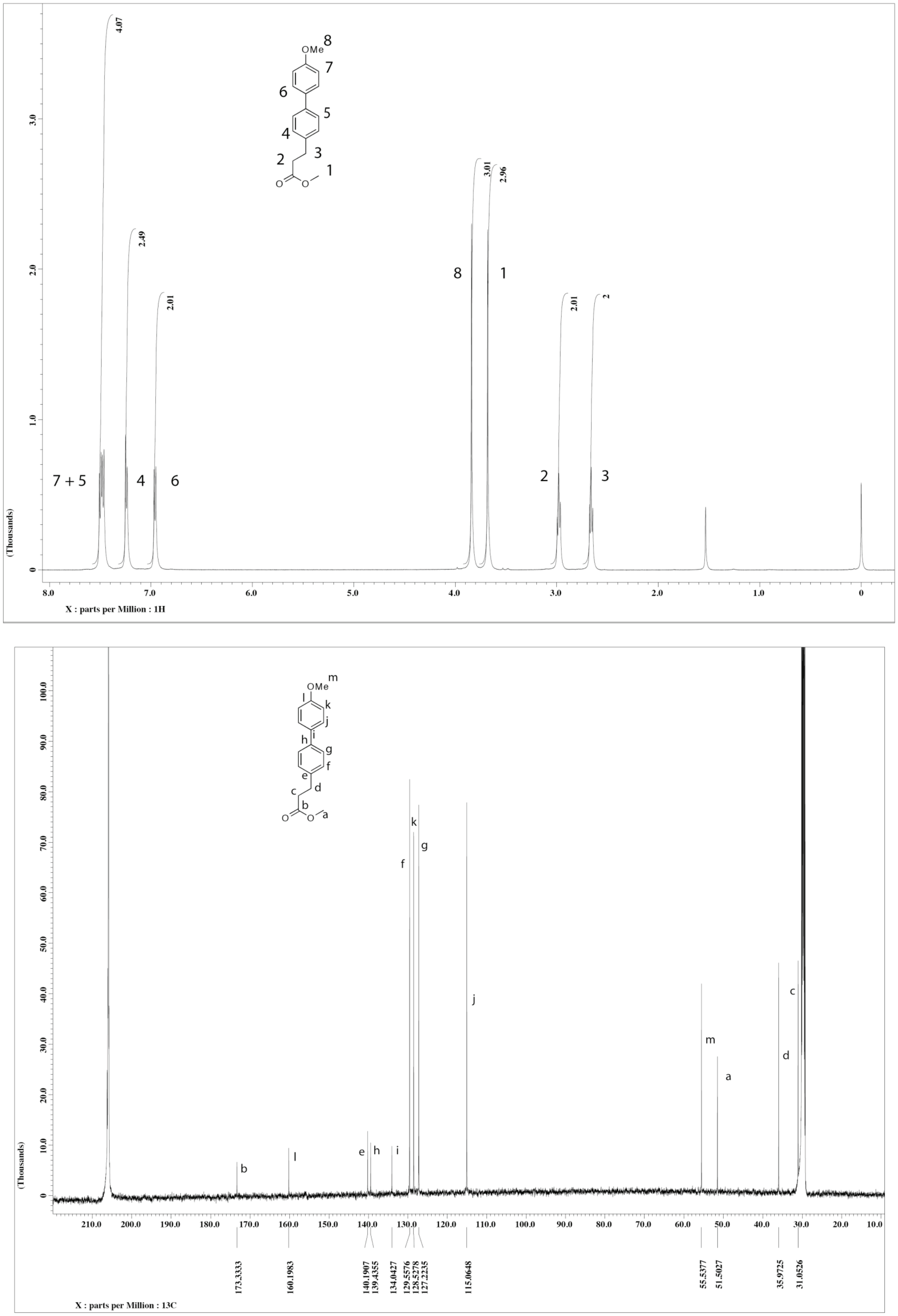


Figure SF1. ^{1}H-NMR and ^{13}C-NMR spectrum of methyl 3-(4'-dimethoxybiphenyl-4-yl)propanoate in C*D*Cl$_3$ and acetone-d$_6$ (500 MHz)

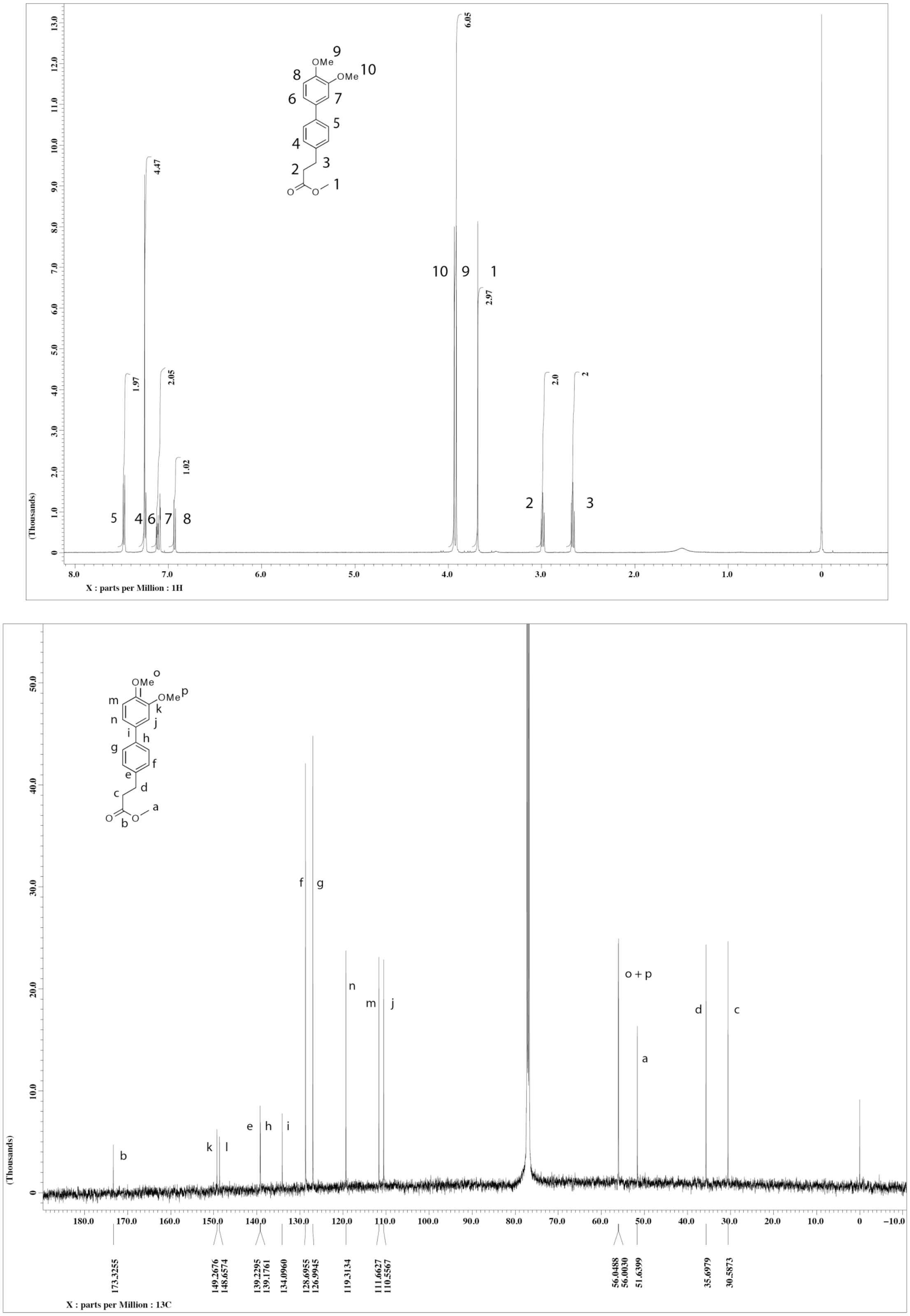


Figure SF2. ^{1}H-NMR and ^{13}C-NMR spectrum of methyl 3-(3',4'-dimethoxybiphenyl-4-yl)propanoate in C*D*Cl$_3$ (500 MHz)

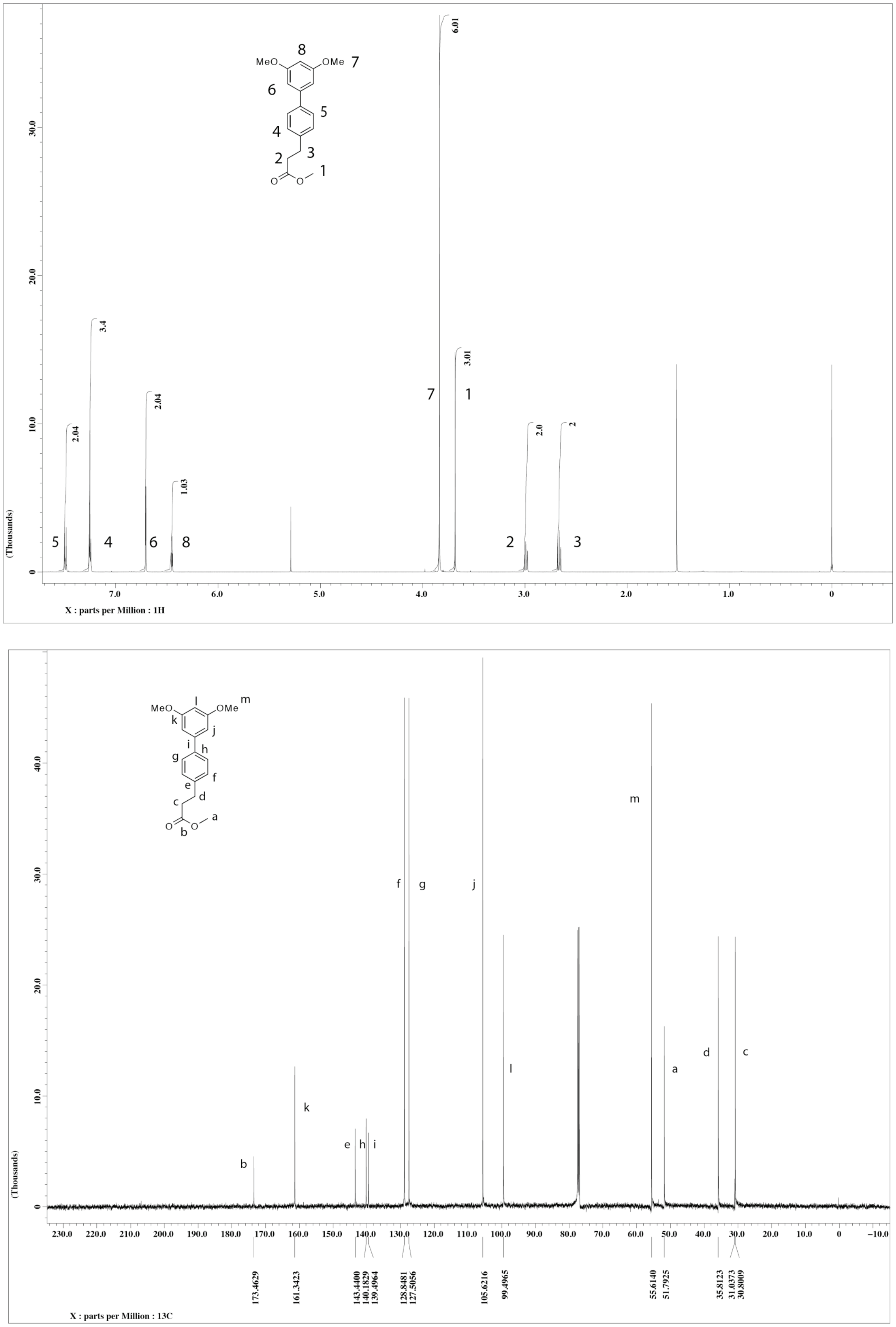


Figure SF3. ^{1}H-NMR and ^{13}C-NMR spectrum of methyl 3-(3',5'-dimethoxybiphenyl-4-yl)propanoate in C*D*Cl$_3$ (500 MHz)

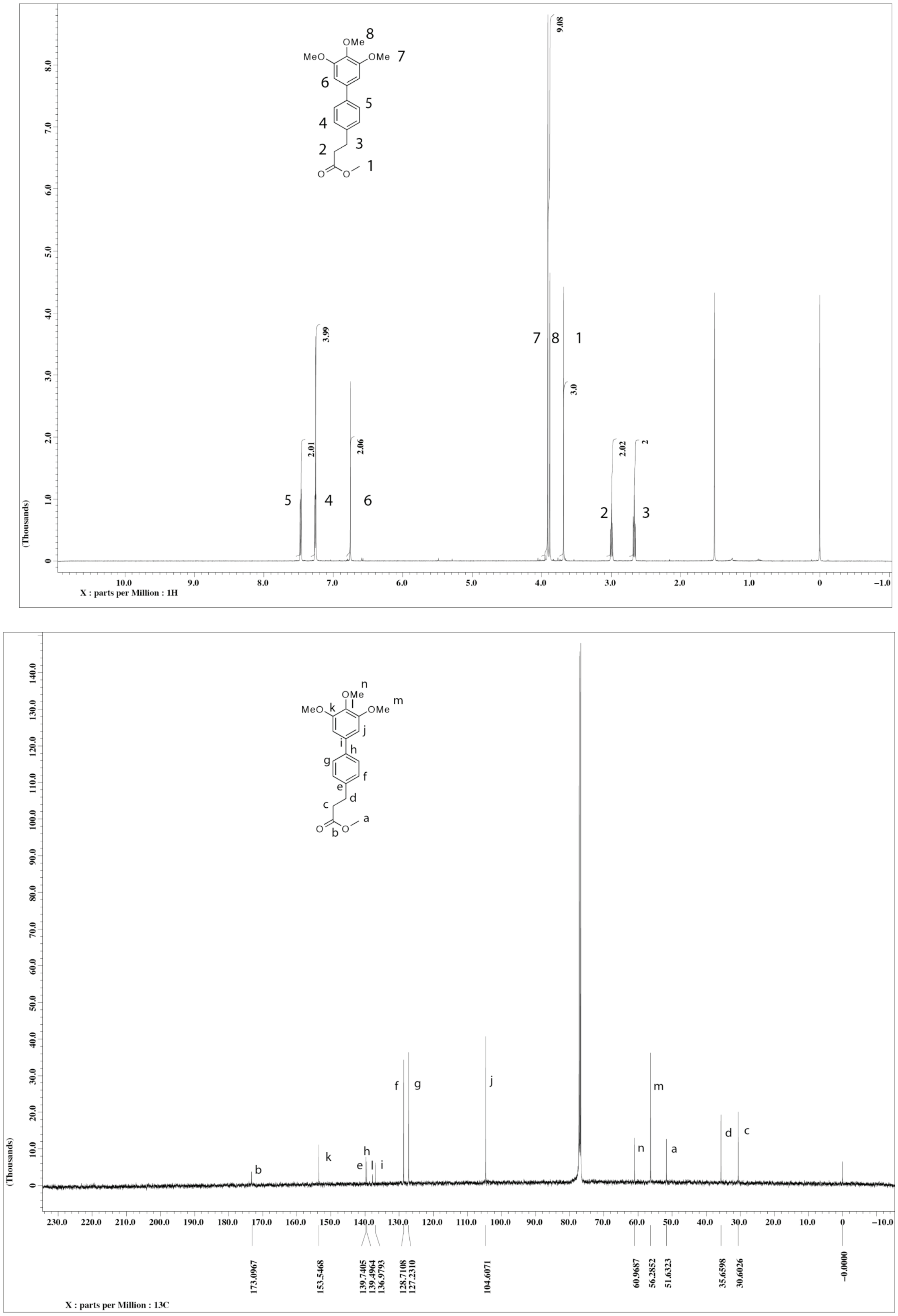


Figure SF4. ^{1}H-NMR and ^{13}C-NMR spectrum of methyl 3-(3',4',5'-dimethoxybiphenyl-4-yl)propanoate in C*D*Cl$_3$ (500 MHz)

GC Analysis of Sequential and One-Pot Neopentylglycolborylations and Cross-Coupling

GC analysis was carried out using an Agilent 6890 GC equipped with splitless injector, FID detector, and column HP 19091J-413 (5%-phenyl)-methylpolysiloxane 30m Length 0.32mm internal diameter. The GC oven method is shown schematically below.

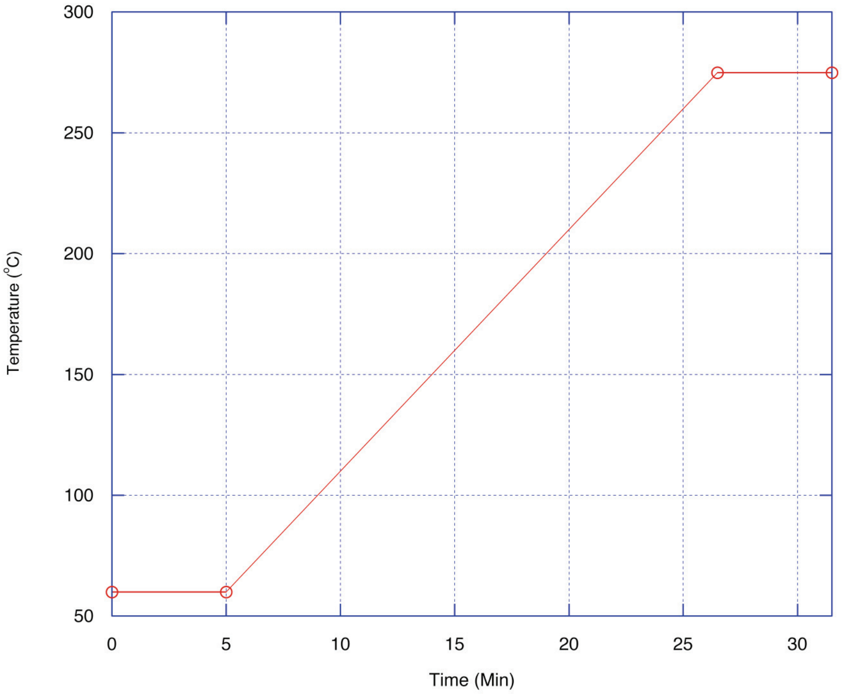


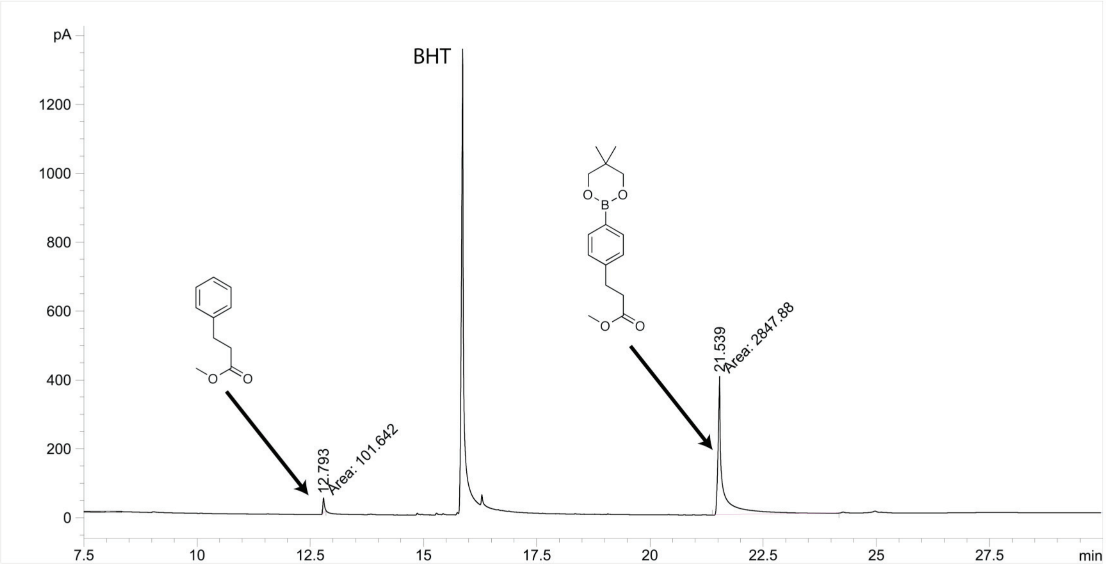
Figure SF5. GC oven method

In order to obtain more information regarding the retention time of the final neopentylglycolboronate esters and cross-coupling products, GC chromatograms were run for each starting material including the corresponding dehalogenated byproducts.

Neopentylglycolborylation was monitored in time and both NMR and GC confirmed dehalogenation as the major byproduct resulted in the Ni(dppp) and Ni(dppe) – catalyzed borylation. No homocoupling product of the aryl halide was observed by GC or NMR.

By correlating the data obtained from running the starting materials and byproducts with the data obtained from the crude compounds each peak from chromatograms was identified and assigned. Additionally, each reaction was monitored in time by calculating the % conversion, yield, unreacted halogenated starting material and by product. The crude reaction mixtures were dilute with THF stabilized with BHT, which was used as internal standard.

Final products were also purified by column chromatography and their retention time was checked and confirmed with the one detected from the crude mixture. Some examples of the crude GC chromatograms are presented below:



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Dilution              :      1.0000


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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  12.793 MM    0.0389  101.64230   43.58814  3.44606
   2  21.539 MM    0.1180 2847.87744  402.25726 96.55394

Totals :                  2949.51974  445.84541
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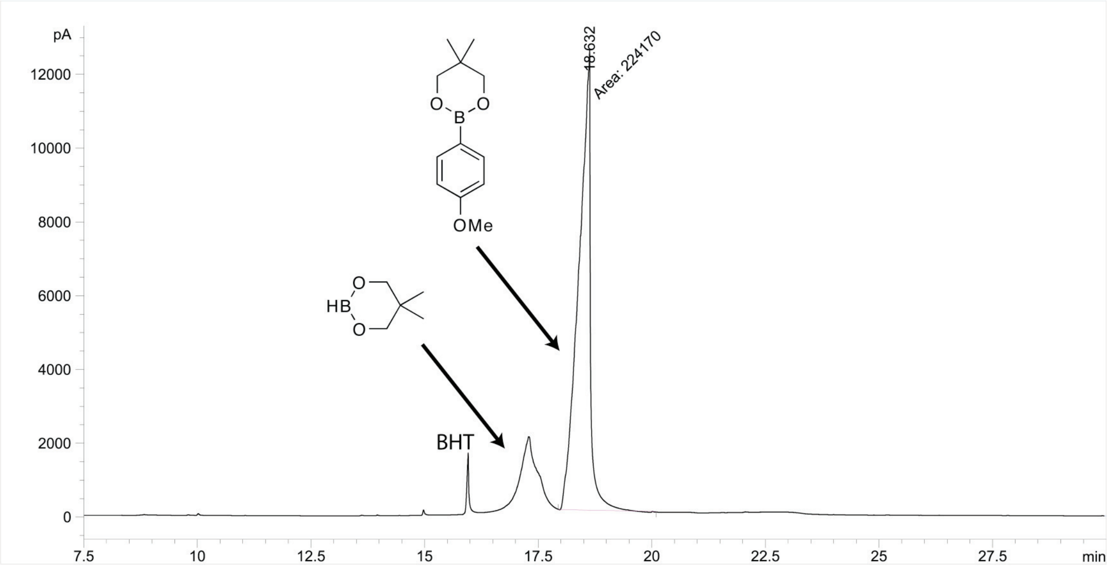
Figure SF6. GC chromatogram of two-step sequential neopentylglycoborylation of methyl 4-iodohydroxycinnamate (Table 1, entry 2)



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Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  18.632 MM    0.2995 2.24170e5  1.24756e4  1.000e2

Totals :                  2.24170e5  1.24756e4
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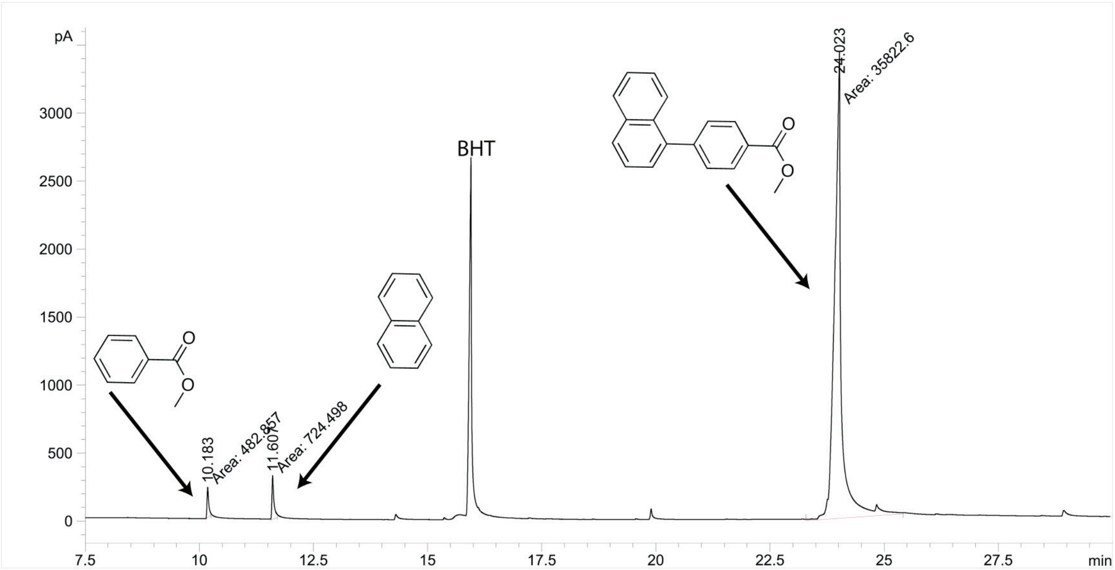
Figure SF7. GC chromatogram of two-step one-pot neopentylglycoborylation of iodoanisole (Table 2, entry 1)



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                         Area Percent Report
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Sorted By             :      Signal
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Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  10.183 MM    0.0379  482.85742  212.34065  1.30396
   2  11.607 MM    0.0414  724.49847  291.93744  1.95652
   3  24.023 MM    0.1734 3.58226e4  3443.57300 96.73951

Totals :                  3.70299e4  3947.85109
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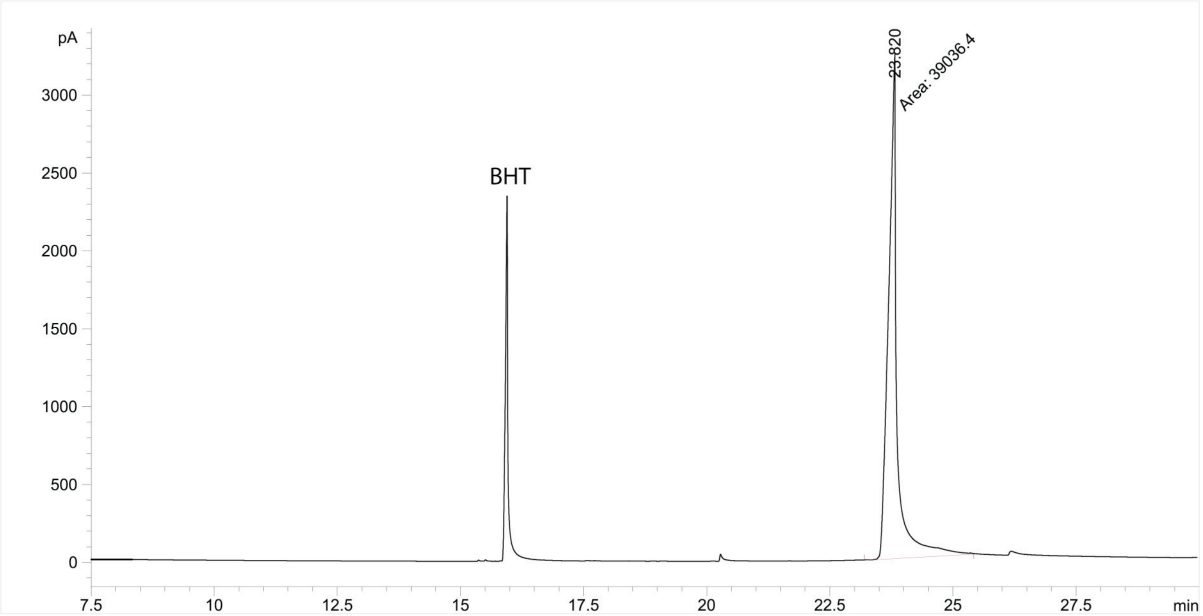
Figure SF8. GC chromatogram of the Pd-catalyzed cross-coupling after 12h (Table 4, entry 13)



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Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  23.820 MM    0.1979 3.90364e4  3287.39258 1.000e2

Totals :                  3.90364e4  3287.39258
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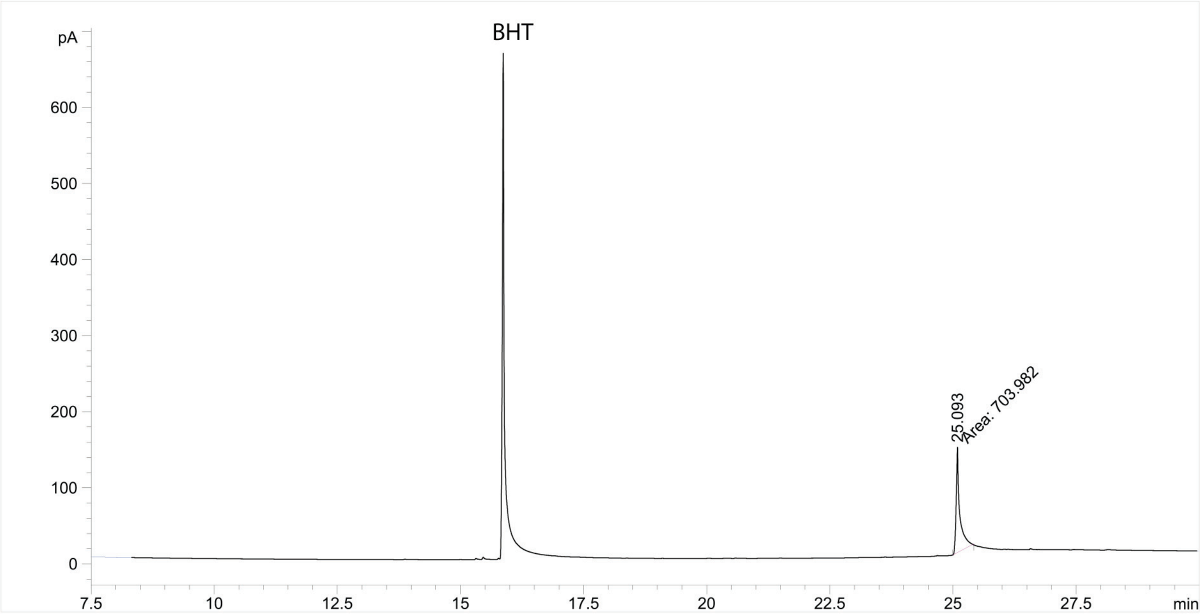
Figure SF9. GC chromatogram of methyl 3-(4’-methoxybiphenyl-4-yl)propanoate



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                         Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  25.093 MM    0.0845  703.98169  138.92401 1.000e2

Totals :                   703.98169  138.92401
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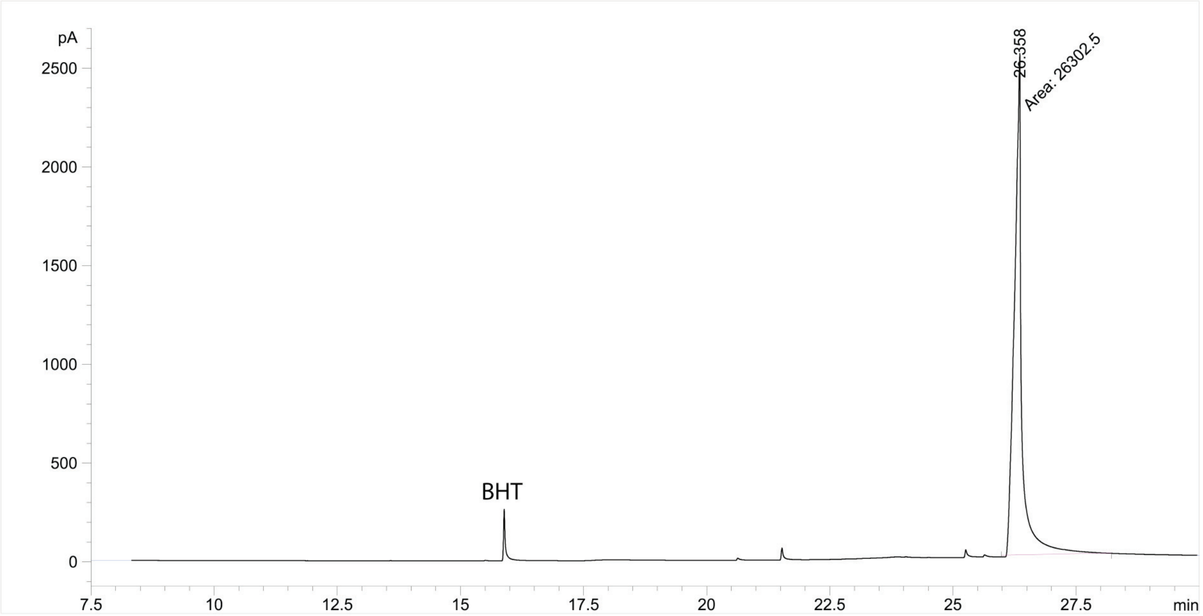
Figure SF10. GC chromatogram of methyl 3-(3’,4’-methoxybiphenyl-4-yl)propanoate



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                         Area Percent Report
=====================================================================

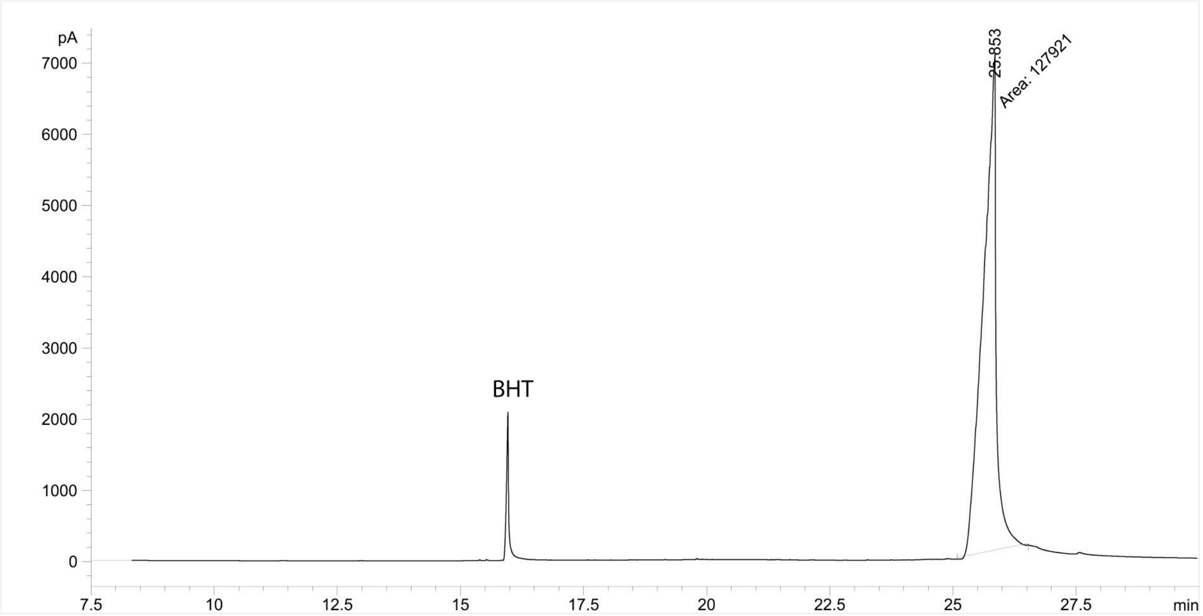
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  26.358 MM    0.1733 2.63025e4  2530.25171 1.000e2

Totals :                  2.63025e4  2530.25171
```

Figure SF11. GC chromatogram of methyl 3-(3’,4’,5’-methoxybiphenyl-4-yl)propanoate



```
=====================================================================
                         Area Percent Report
=====================================================================

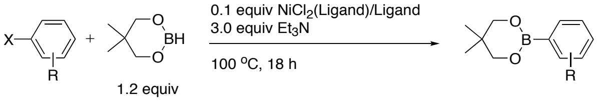
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

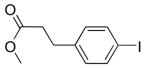
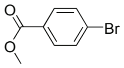
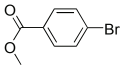
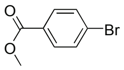
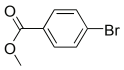
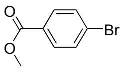
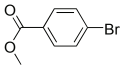
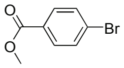
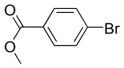
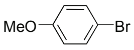
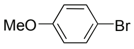
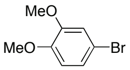
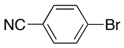
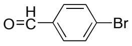
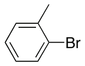
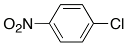
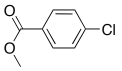

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  25.853 MM    0.3022 1.27921e5  7055.78418 1.000e2
```

Figure SF12. GC chromatogram of methyl 3-(3’, 5’-methoxybiphenyl-4-yl)propanoate

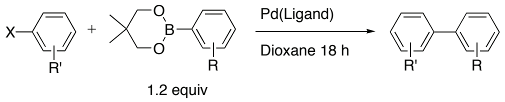
Table ST1. Two-Step Sequential Neopentylglycolborylation

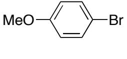
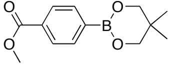
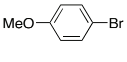
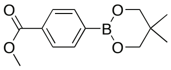
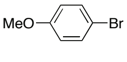
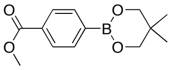
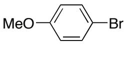
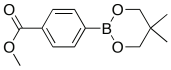
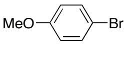
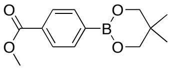
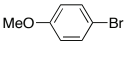
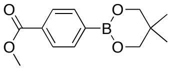
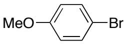
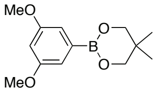


entry	substrate	catalyst[a] (%)	solvent	convn[b]:yield[c] (%)
1		$NiCl_2(dppf)$ (5)	toluene	94:37[d]
2		$NiCl_2(dppp)$ (5)	toluene	85:77
3		$NiCl_2(PPh_3)_2$[e] (5)	toluene	56:6
4		$NiCl_2(dppp)$ (10)	dioxane	64:55
5		$PdCl_2(dppf)$[f] (10)	toluene	45:9
6		$NiCl_2(dppe)$ (10)	anisole	34:34
7		$NiCl_2(dppe)$ (10)	dioxane	85:74
8		$NiCl_2(Et_3N)_2$	toluene	15:0
9		$NiCl_2(bpy)$	toluene	37:13
10		$NiCl_2(dppp)$ (10)	dioxane	48:48
11		$NiCl_2(dppe)$ (10)	dioxane	39:39
12		$NiCl_2(dppp)$[e] (5)	toluene	38:29
13		$NiCl_2(dppe)$ (10)	toluene	77:54
14		$NiCl_2(dppp)$ (5)	toluene	20:10
15		$NiCl_2(dppe)$ (10)	toluene	10:10
16		$NiCl_2(dppe)$ (10)	toluene	36:3
17		$NiCl_2(dppf)$ (10)	toluene	10:5

[a] Co-ligand added in 1:1 ratio to catalyst. [b] Conversion determined by GC. [c] GC yield. [d] major dehalogenated byproduct. [e] PPh_3 co-ligand 10%; reaction temperature 80 °C. [f] no co-ligand required.

Table ST2. Pd-Catalyzed Cross-Coupling of Aryl Halides



entry	aryl halide	boronate ester	catalyst (%)	base	temp (°C)	convn[a] : yield[b] (%)
1			$PdCl_2(dppf)$ (10%)	NEt_3	80	50:0
2			$PdCl_2(dppf)$ (10%)	K_3PO_4	110	100:92
3			$PdCl_2(MeCN)_2$ (10%)	K_3PO_4	110	100:57
4			$PdCl_2(dppf)$ (2%)	K_3PO_4	25	53:46
5			$PdCl_2(dppf)$ (1%)	K_3PO_4	110	100:93
6			$PdCl_2$ (10%)	K_3PO_4	110	100:81
7			$PdCl_2(dppf)$ (10%)	K_3PO_4	110	92:79

[a] Conversion determined by GC. [b] Isolated yield.