Supporting Information

Palladium-Catalyzed Alkynylation and Concomitant *ortho*-Alkylation of Aryl Iodides

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Experimental procedures and NMR characterization of compounds

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I. General Information

All NMR spectra were acquired on Bruker 500 MHz, 400 MHz or 300 MHz NMR spectrometers. ^{1}H NMR chemical shifts were recorded relative to TMS (δ 0.00) or residual protiated solvents ($CDCl_3$: δ 7.26). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet), hept (heptet) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a *J* value in Hz. ^{13}C NMR spectra were obtained at 125 MHz on 500 MHz, 100 MHz on 400 MHz or 75 MHz on 300 MHz NMR instruments and chemical shifts were recorded relative to solvent resonance ($CDCl_3$: δ 77.16). ^{19}F NMR spectra were recorded at 376 MHz on 400 MHz NMR spectrometers, 282 MHz on 300 MHz NMR without any external standard. Proof of purity of new compounds was demonstrated with copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra.

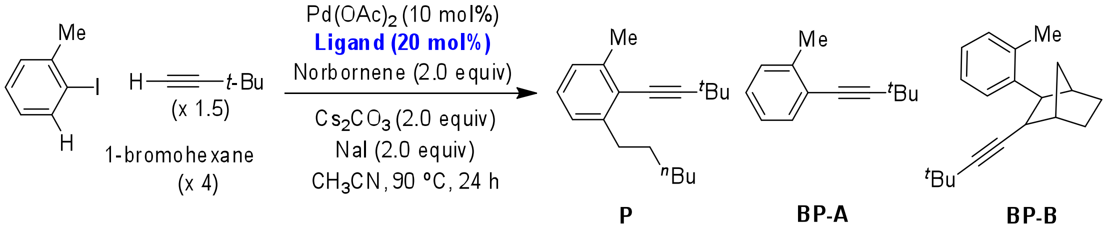
Glassware was dried at 120 °C for at least 3 hours before use. Anhydrous acetonitrile (Aldrich) was degassed by argon bubbling and then stored over activated 4 Å molecular sieve beads in the glove box before use. Dry NMP and DMA (Aldrich) were used without further purification and were stored in the glove box. Other solvents used in the solvent optimization were dried and purified according to the procedure from "Purification of Laboratory chemicals book". All of anhydrous solvents were stored in Schlenk tubes in the glove box. Unless noted otherwise, commercially available chemicals were used without further purification.

Flash chromatography was performed using Merck 40-63D 60 Å silica gel. The GC internal standard, *n*-dodecane was degassed and dried over activated 4 Å molecular sieve beads before use. GC analysis was performed on a Shimadzu GC-2010 instrument with Agilent J&W GC column DB-5MS-UI. GC/MS analysis was conducted on a Thermo Scientific DSQ II single quadruple GC/MS instrument with Agilent J & W GC column DB-5MS-UI. Microwave experiment was conducted with CEM Discover® microwave synthesis reactor.

II. Condition optimization

A typical procedure: In an argon-filled glove box, a 10-mL reaction tube containing a magnetic stir bar was charged with $Pd(OAc)_2$ (10 mol%, 2.2 mg, 0.01 mmol), P(2-furyl)$_3$ (20 mol%, 4.6 mg, 0.02 mmol) and 1 mL of dry acetonitrile. After stirring at room temperature for 10 minutes, *o*-iodotoluene (22 mg, 0.1 mmol), 1-bromohexane (66 mg, 0.4 mmol), 2-norbornene (19 mg, 0.2 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), *t*-butylacetylene (12 mg, 0.15 mmol) and a GC standard *n*-dodecane (10 μL) were then added sequentially. The tube was capped tightly and the reaction mixture was heated in an aluminum-heating block at 90 °C for 12 h. At the end of the reaction, the mixture was cooled to rt. Aliquots of the reaction mixture were passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC analysis to determine the conversion of *o*-iodotoluene and calibrated GC yields of products and byproducts.

Table S1. Effect of supporting ligands



Entry	Ligand	Conv. of ArI (%)	**P** (%)	**BP-A** (%)	**BP-B** (%)
1	No added ligand	75	59	11	5
2	PPh_3	100	83	6	3
3	P(2-furyl)$_3$	100	88	10	1
4	P(2-thienyl)$_3$	100	83	5	5
5	PCy_3	91	65	9	12
6	P^tBu_3	88	18	2	59
7	P^tBu_3•HBF_4	100	17	9	68

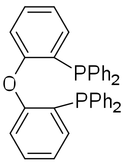
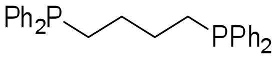
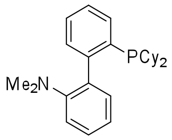
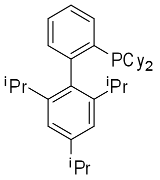
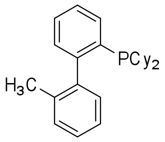
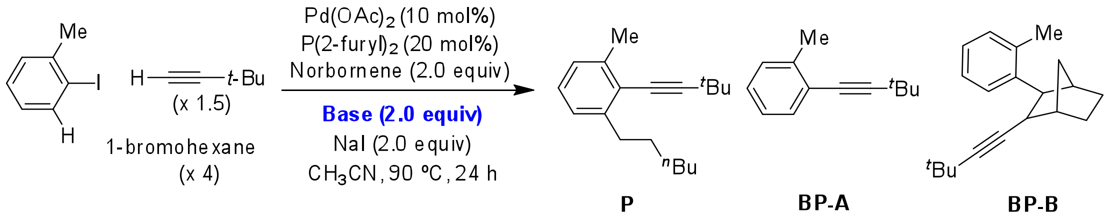
8		100	52	5	20
9	DPPF	82	18	2	36
10		100	40	3	7
11	BINAP	83	10	3	6
12		100	33	16	49
13		100	62	5	30
14		100	39	15	34

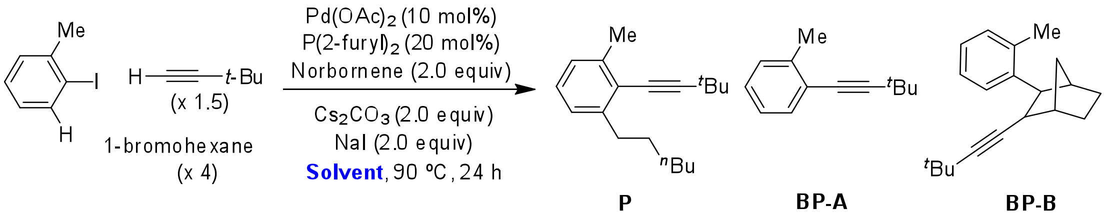
Table S2. Effect of bases



Entry	Base	Conv. of ArI (%)	**P** (%)	**BP-A** (%)	**BP-B** (%)
1	Cs_2CO_3	100	88	10	1
2	NaOH	90	42	9	2
3	KOH	93	36	3	2
4	Na_2CO_3	78	4	0	1
5	K_2CO_3	100	51	5	11

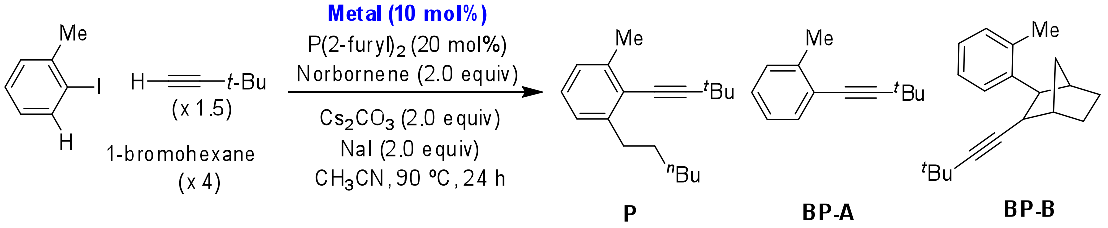
6	K_3PO_4	100	65	6	18
7	NaOPh	60	24	1	0
8	KOPh	76	17	4	0
9	NaHMDS	83	6	4	3
10	KHMDS	75	8	9	3
11	LiOAc	7	0	0	0
12	NaOAc	59	0	0	0
13	NaO^{t}Bu	100	14	72	9
14	KO^{t}Bu	62	5	8	4
15	NaOMe	100	12	61	17
16	$NaHCO_2$	85	0	0	0
17	$KHCO_3$	82	8	0	3
18	Proton sponge	60	0	0	0
19	Et_3N	35	0	0	0
20	DIPEA	71	0	0	0
21	No added base	15	0	0	0

Table S3. Effect of solvents



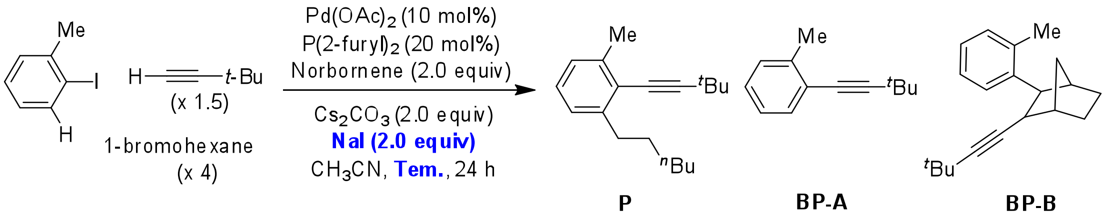
Entry	Solvent	Conv. of ArI (%)	**P** (%)	**BP-A** (%)	**BP-B** (%)
1	CH_3CN	100	88	10	1
2	Diglyme	100	11	5	33
3	DMF	100	38	1	1
4	1,4-Dioxane	100	3	23	56
5	THF	100	6	14	78
6	$PhCF_3$	100	3	11	80
7	Anisole	100	0	14	81
8	DME	100	56	0	38
9	DMSO	35	9	2	0
10	MeOH	100	12	53	29
11	NMP	90	32	1	6
12	Toluene	100	1	10	83

Table S4. Effect of palladium source



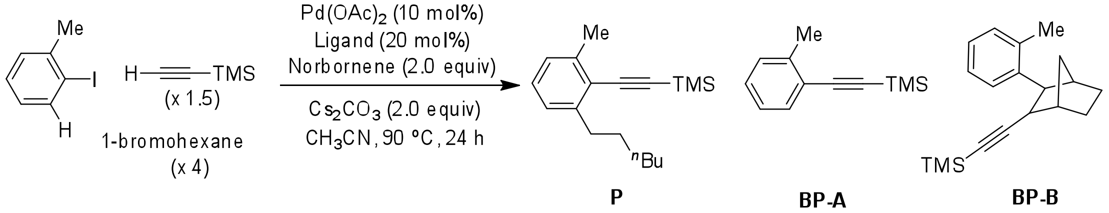
Entry	Metal	Conv. of ArI (%)	**P** (%)	**BP-A** (%)	**BP-B** (%)
1	Pd(OAc)$_2$	100	88	10	1
2	Pd(dba)$_2$	100	57	3	6
3	Pd(TFA)$_2$	100	54	4	10
4	PdCl$_2$	100	50	3	7
5	PdI$_2$	95	48	3	6
6	Pd(PPh$_3$)$_4$	100	31	3	33
7	K$_2$PdCl$_4$	100	12	1	80

Table S5. Effect of reaction temperature and additives



Entry	Temperature	Conv. of ArI (%)	**P** (%)	**BP-A** (%)	**BP-B** (%)
1	25 °C	3	1	0	0
2	50 °C	96	80	12	4
3	90 °C	100	88	10	1
4	90 °C NaI (none)	100	81	12	6

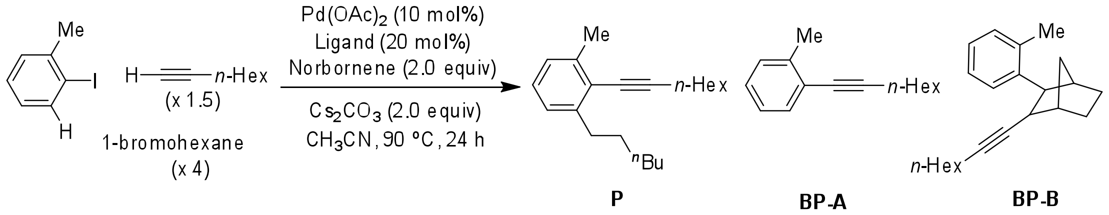
Table S6. Effect of ligands for coupling of trimethylsilyl acetylene



Entry	Ligand	Conv. of ArI (%)	**P** (%)	**BP-A** (%)[a]	**BP-B** (%)[a]
1	P(2-furyl)$_3$	100	14	<10	40
2	P(4-tolyl)$_3$	100	61	<10	21
3	PPh$_3$	100	38	<10	31
4	P(4-F-phenyl)$_3$	100	43	<10	37
5	P(4-CF$_3$-phenyl)$_3$	100	14	<10	65
6	P(3-MeO-phenyl)$_3$	100	52	<10	19
7	P(3-Cl-phenyl)$_3$	100	22	<10	58

[a] Estimated yields based on response factors in Table S1

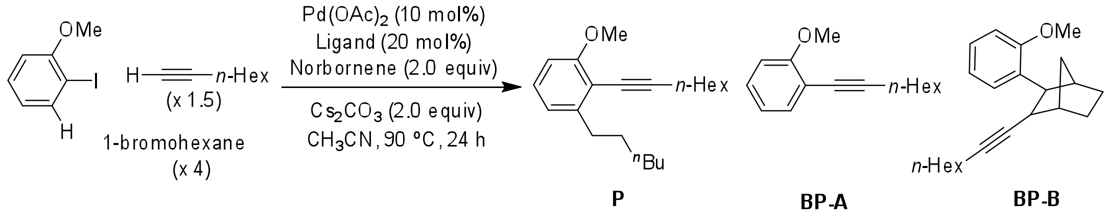
Table S7. Effect of ligands for coupling of *o*-iodotoluene and 1-octyne



Entry	Ligand	Conv. of ArI (%)	**P** (%)	**BP-A** (%)[a]	**BP-B** (%)[a]
1	PPh_3	100	48	46	6
2	$P(2\text{-furyl})_3$	100	28	48	18
3	$P(2\text{-tolyl})_3$	100	11	78	9
4	$P(3\text{-tolyl})_3$	100	43	50	7
5	$P(4\text{-tolyl})_3$	100	35	50	7
6	$P(3\text{-MeO-phenyl})_3$	100	42	48	4
7	$P(4\text{-MeO-phenyl})_3$	100	37	48	5
8	$P(4\text{-F-phenyl})_3$	100	45	38	12
9	$P(4\text{-Cl-phenyl})_3$	100	37	45	15
10	No added ligand	100	17	27	21
11	Catellani-type conditions[b]	100	10	11	25

[a] Estimated yields based on response factors in Table S1. [b] $Pd(OAc)_2$ (10 mol%, 0.01 mmol), aryl iodide (0.1 mmol), 1-bromohexane (0.4 mmol), 2-norbornene (0.2 mmol), KOAc (0.6 mmol), alkyne (0.15 mmol) and a GC standard *n*-dodecane (10 μL) in dry DMA (1 mL). 90 °C for 12 h (without slow addition).

Table S8. Effect of ligands for coupling of 2-iodoanisole and 1-octyne

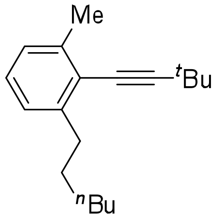


Entry	Ligand	Conv. of ArI (%)	**P** (%)	**BP-A** (%)[a]	**BP-B** (%)[a]
1	PPh_3	100	34	21	15
2	P(2-furyl)$_3$	100	13	19	24
3	P(2-tolyl)$_3$	100	8	43	21
4	P(3-tolyl)$_3$	100	30	20	15
5	P(4-tolyl)$_3$	100	37	19	12
6	P(3-OMe-phenyl)$_3$	100	42	16	17
7	P(4-OMe-phenyl)$_3$	100	33	19	9
8	P(4-F-phenyl)$_3$	100	30	27	14
9	P(4-Cl-phenyl)$_3$	100	21	19	32
10	No added ligand	100	9	24	28
11	Catellani-type conditions[b]	100	19	5	13

[a] Estimated yields based on response factors in Table S1. [b] Pd(OAc)$_2$ (10 mol%, 0.01 mmol), aryl iodide (0.1 mmol), 1-bromohexane (0.4 mmol), 2-norbornene (0.2 mmol), KOAc (0.6 mmol), alkyne (0.15 mmol) and a GC standard *n*-dodecane (10 μL) in dry DMA (1 mL). 90 °C for 12 h (without slow addition).

III. Couplings with *ortho*-substituted aryl halides

A typical procedure: In an argon-filled glove box, a 10-mL Schlenk tube containing a magnetic stir bar was charged with $Pd(OAc)_2$ (10 mol%, 6.6 mg, 0.03 mmol), $P(2\text{-furyl})_3$ (20 mol%, 13.9 mg, 0.06 mmol) and 3 mL of dry acetonitrile. After stirring at room temperature for 10 minutes, *o*-iodotoluene (65 mg, 0.3 mmol), 1-bromohexane (198 mg, 1.2 mmol, 4 equiv), 2-norbornene (57 mg, 0.6 mmol, 2 equiv), Cs_2CO_3 (195 mg, 0.6 mmol, 2 equiv), NaI (90 mg, 0.6 mmol, 2 equiv), *t*-butylacetylene (37 mg, 0.45 mmol) and GC standard *n*-dodecane (30 μL) were then added sequentially. The tube was capped tightly and the reaction mixture was heated on an oil bath maintained at 90 °C for 24 h. At the end of the reaction, the mixture was cooled to room temperature. Aliquots of the reaction mixture were passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC analysis for determination of the conversion of *o*-iodotoluene. The desired products were purified by flash chromatography over silica gel using hexane as elute.



2-*t*-Butylacetylenyl-1-*n*-hexyl-3-methylbenzene.

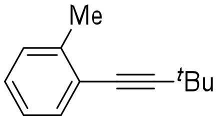
Yellow oil. 64 mg, 83% yield. When RI was used in the absence of NaI, 79% yield.

When 1-chlorohexane was used in the presence of *n*-Bu_4NI (1 equiv), 77% yield of the product was produced. Without *n*-Bu_4NI, only 39% yield was obtained.

^1H NMR (400 MHz, $CDCl_3$): δ 7.08 (ψt, *J* = 7.5 Hz, 1H), 7.03 – 6.99 (m, 2H), 2.76 – 2.73 (m, 2H), 2.41 (s, 3H), 1.67 – 1.60 (m, 2H), 1.38 – 1.33 (m, 15H), 0.90 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 140.1, 127.0, 126.7, 126.0, 123.3, 106.9, 76.6, 35.4, 32.0, 31.4, 30.9, 29.6, 28.6, 22.8, 21.2, 14.3.

MS (EI) Calcd for $C_{19}H_{28}$: 256.2; found: 256.1.

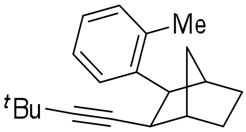


1-*t*-Butylacetylenyl-2-methylbenzene (minor byproduct)

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.35 (d, *J* = 7.2 Hz, 1H), 7.18 – 7.15 (m, 2H), 7.13 – 7.07 (m, 1H), 2.40 (s, 3H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 140.0, 131.7, 129.4, 127.5, 125.5, 123.9, 103.0, 78.0, 31.3, 28.3, 20.8.

MS (EI) Calcd for $C_{13}H_{16}$: 172.3; found: 172.1.

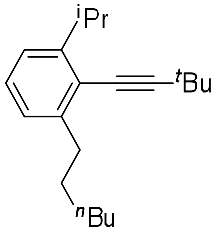


***exo,exo*-2-*t*-Butylacetylenyl-3-(*o*-tolyl)norbornane (minor byproduct)**

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.25 (d, *J* = 7.4 Hz, 1H), 7.17 – 7.03 (m, 3H), 2.94 (d, *J* = 8.8 Hz, 1H), 2.85 (d, *J* = 8.8 Hz, 1H), 2.62 (br s, 1H), 2.37 (br s, 1H), 2.26 (s, 3H), 2.03 – 2.00 (m, 1H), 1.65 – 1.62 (m, 2H), 1.36 – 1.31 (m, 3H), 0.75 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 142.4, 137.4, 129.7, 126.1, 125.5, 125.3, 91.9, 79.5, 49.0, 44.5, 40.8, 40.5, 36.2, 31.0, 30.9, 28.4, 27.0, 20.2.

MS (EI): Calcd for $C_{20}H_{26}$: 266.2; found: 266.1.



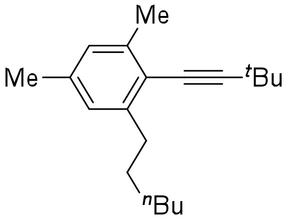
2-*t*-Butylacetylenyl-1-*n*-hexyl-3-isopropylbenzene.

Yellow oil. 73 mg, 85% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.16 (ψt, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 5.9 Hz, 1H), 3.51 – 3.44 (m, 1H), 2.78 – 2.74 (m, 2H), 1.68 – 1.60 (m, 2H), 1.41 – 1.39 (m, 2H), 1.37 (s, 9H), 1.35 – 1.32 (m, 4H), 1.27 (d, *J* = 6.9 Hz, 6H), 0.91 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 150.4, 145.0, 127.3, 126.0, 122.3, 122.1, 106.5, 76.2, 35.6, 32.0, 31.8, 31.2, 30.9, 29.7, 28.5, 23.1, 22.8, 14.3.

MS (EI): Calcd for $C_{21}H_{32}$: 284.3; found: 284.2.



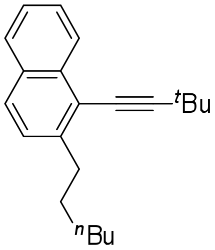
2-*t*-Butylacetylenyl-1,5-dimethyl-3-*n*-hexyl-benzene.

Yellow oil. 64 mg, 79% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.84 (s, 1H), 6.82 (s, 1H), 2.73 – 2.68 (m, 2H), 2.37 (s, 3H), 2.28 (s, 3H), 1.65 – 1.57 (m, 2H), 1.41 – 1.28 (m, 15H), 0.91 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 144.8, 139.9, 136.7, 127.6, 126.9, 120.3, 105.9, 76.6, 35.4, 32.0, 31.4, 31.0, 29.7, 28.5, 22.8, 21.5, 21.1, 14.3.

MS (EI): Calcd for $C_{20}H_{30}$: 270.2; found: 270.2.



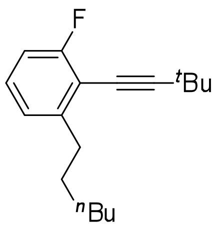
1-*t*-Butylacetylenyl-2-*n*-hexyl-naphthalene.

1-Iodonaphthalene was used. Yellow oil. 59 mg, 67% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.55 (ψt, *J* = 7.5 Hz, 1H), 7.45 (ψt, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 3.00 – 2.96 (m, 2H), 1.77 – 1.70 (m, 2H), 1.48 (s, 9H), 1.44 – 1.35 (m, 6H), 0.93 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 133.8, 131.8, 128.0, 127.5, 127.4, 126.5, 126.3, 125.4, 119.8, 107.7, 75.9, 35.6, 32.0, 31.4, 31.0, 29.5, 28.7, 22.8, 14.3.

MS (EI): Calcd for $C_{22}H_{28}$: 292.2; found: 292.2.



2-*t*-Butylacetylenyl-1-fluoro-3-*n*-hexylbenzene.

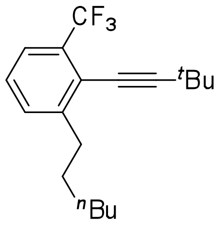
Yellow oil. 67 mg, 86% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.15 – 7.10 (m, 1H), 6.95 (d, J = 7.5 Hz, 1H), 6.87 (ψt, J = 8.7 Hz 1H), 2.77 – 2.73 (m, 2H), 1.68 – 1.60 (m, 2H), 1.37 (s, 9H), 1.34 – 1.33 (m, 6H), 0.91 (t, J = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 163.1 (d, J_{C-F} = 248.7 Hz), 147.5, 128.2 (d, J_{C-F} = 8.8 Hz), 124.2 (d, J_{C-F} = 3.1 Hz), 112.5 (d, J_{C-F} = 21.6 Hz), 112.1 (d, J_{C-F}= 15.4 Hz), 107.6 (d, J_{C-F} = 3.5 Hz), 71.3 (d, J_{C-F} = 1.9 Hz), 34.8 (d, J_{C-F}= 2.4 Hz), 31.9, 31.1, 30.6, 29.4, 28.6, 22.8, 14.2.

^{19}F {^{1}H} NMR (376 MHz, CDCl$_3$): δ -110.8.

MS (EI): Calcd for $C_{18}H_{25}F$: 260.2; found: 260.2.



2-*t*-Butylacetylenyl-3-*n*-hexyl-1-trifluoromethylbenzene.

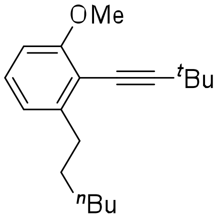
Yellow oil. 80 mg, 86% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.45 (d, J = 7.8 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.22 (ψt, J = 7.8 Hz, 1H), 2.81 – 2.77 (m, 2H), 1.66 – 1.59 (m, 2H), 1.37 – 1.30 (m, 15H), 0.90 (t, J = 3.5 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 146.8, 132.1 (q, J_{C-F} = 29.4 Hz), 132.0,126.9, 124.0 (q, J_{C-F} = 273.4 Hz), 123.3 (q, J_{C-F} = 5.3 Hz), 121.6 (q, J_{C-F} = 1.7 Hz), 108.6, 74.0, 35.0, 31.9, 30.7, 30.6, 29.5, 28.5, 22.8, 14.2.

^{19}F {^{1}H} NMR (376 MHz, CDCl$_3$): δ -62.4.

MS (EI): Calcd for $C_{19}H_{25}F_3$: 310.2; found: 310.2.



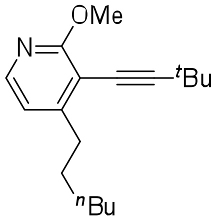
2-*t*-Butylacetylenyl-3-*n*-hexyl-1-methoxybenzene.

Yellow oil. 69 mg, 84% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.12 (ψt, *J* = 7.9 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 6.68(d, *J* = 8.2 Hz, 1H), 3.85 (s, 3H), 2.75 – 2.71 (m, 2H), 1.66 – 1.56 (m, 2H), 1.36 (s, 9H), 1.32 – 1.28 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 160.1, 147.1, 128.1, 121.3, 112.6, 108.1, 106.9, 73.7, 56.1, 35.1, 32.0, 31.3, 30.7, 29.5, 28.6, 22.8, 14.3.

MS (EI): Calcd for $C_{19}H_{28}O$: 272.2; found: 272.2.



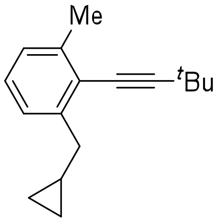
3-*t*-Butylacetylenyl-4-*n*-hexyl-2-methoxypyridine.

Yellow oil. 60 mg, 73% yield.

^{1}H NMR (300 MHz, CDCl$_3$): δ 7.92 (d, *J* = 5.2 Hz, 1H), 6.70 (d, *J* = 5.2 Hz, 1H), 3.96 (s, 3H), 2.72 – 2.67 (m, 2H), 1.67 – 1.56 (m, 2H), 1.35 (s, 9H), 1.31 – 1.24 (m, 6H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, CDCl$_3$): δ 164.0, 156.4, 144.5, 117.4, 108.0, 107.2, 72.5, 54.1, 34.3, 31.8, 31.2, 29.7, 29.4, 28.6, 22.7, 14.2.

MS (EI): Calcd for $C_{18}H_{27}NO$: 273.2; found: 273.2.



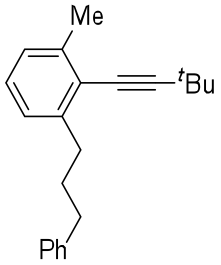
2-*t*-Butylacetylenyl-1-cyclopropylmethyl-3-methylbenzene.

Yellow oil. 57 mg, 84% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.16 – 7.10 (m, 2H), 7.07 – 7.05 (m, 1H), 2.71 (d, *J* = 6.9 Hz, 2H), 2.43 (s, 3H), 1.37 (s, 9H), 1.14 – 1.08 (m, 1H), 0.53 – 0.48 (m, 2H), 0.28 – 0.24 (m, 2H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 144.0, 140.1, 127.1, 126.9, 125.8, 123,3, 107.2, 76.8, 39.2, 31.3, 28.6, 21.3, 11.4, 4.7.

MS (EI): Calcd for $C_{17}H_{22}$: 226.2; found: 226.1.



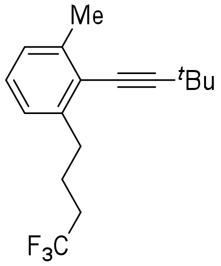
2-*t*-Butylacetylenyl-1-methyl-3-(3-phenylpropyl)benzene.

Yellow oil. 64 mg, 73% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.30 – 7.27 (m, 2H), 7.22 – 7.16 (m, 3H), 7.10 – 7.07 (m, 1H), 7.04 – 7.00 (m, 2H), 2.84 – 2.80 (m, 2H), 2.72 – 2.68 (m, 2H), 2.41 (s, 3H), 2.03 – 1.95 (m, 2H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 144.2, 142.7, 140.2, 128.6, 128.4, 127.1, 126.9, 126.0, 125.8, 123.4, 107.1, 76.5, 36.2, 35.0, 32.3, 31.4, 28.6, 21.2.

MS (EI): Calcd for $C_{22}H_{26}$: 290.2; found: 290.2.



2-*t*-Butylacetylenyl-1-methyl-3-(4,4,4-trifluorobutyl)benzene.

Yellow oil. 68 mg, 81% yield.

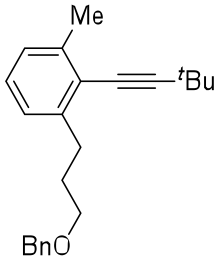
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.10 (ψt, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 6.4 Hz, 1H), 6.98 (d, *J* = 7.3

Hz, 1H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 2.18 – 2.06 (m, 2H), 1.97 – 1.89 (m, 2H), 1.36 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 142.6, 140.5, 127.42 (q, *J* = 276.2 Hz), 127.41, 127.2, 126.1, 123.5, 107.4, 76.3, 34.1, 33.6 (q, *J* = 28.3 Hz), 31.3, 28.6, 22.9 (q, *J* = 2.9 Hz), 21.2.

^{19}F {^{1}H} NMR (376 MHz, CDCl$_3$): δ -66.2.

MS (EI): Calcd for $C_{17}H_{21}F_3$: 282.2; found: 282.1.



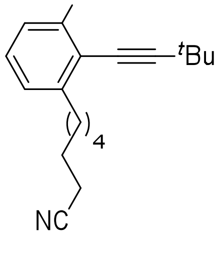
1-(3-Benzyloxypropyl)-2-*t*-butylacetylenyl-3-methylbenzene.

Yellow oil. 63 mg, 65% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.39 – 7.34 (m, 4H), 7.32 – 7.28 (m, 1H), 7.10 – 7.00 (m, 3H), 4.54 (s, 2H), 3.53 (t, *J* = 6.5 Hz, 2H), 2.89 – 2.85 (m, 2H), 2.42 (s, 3H), 2.04 – 1.96 (m, 2H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 143.8, 140.2, 138.9, 128.5, 127.8, 127.6, 127.0, 126.9, 126.2, 123.4, 107.2, 76.4, 73.0, 70.2, 31.8, 31.3, 30.4, 28.5, 21.2.

MS (EI): Calcd for $C_{23}H_{28}O$: 320.2; found: 320.2.



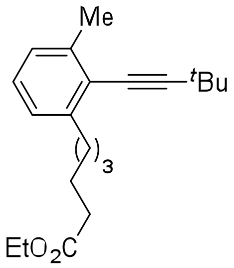
2-*t*-Butylacetylenyl-1-(6-cyanohexyl)-3-methylbenzene.

Yellow oil. 56 mg, 66% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.10 – 6.98 (m, 3H), 2.78 – 2.74 (m, 2H), 2.41 (s, 3H), 2.32 (t, *J* = 7.1 Hz, 2H), 1.71 – 1.63 (m, 4H), 1.54 – 1.50 (m, 2H), 1.49 – 1.42 (m, 2H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 144.2, 140.2, 127.0, 126.9, 126.0, 123,2, 119.8, 106.9, 76.5, 35.1, 31.3, 30.3, 28.8, 28.7, 28.5, 25.5, 21.2, 17.2.

MS (EI): Calcd for $C_{20}H_{27}N$: 281.2; found: 281.2.



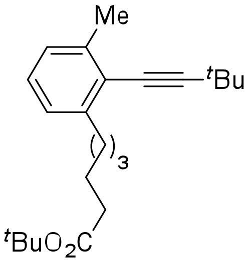
2-*t*-Butylacetylenyl-1-(5-ethoxycarbonylpentyl)-3-methylbenzene.

Yellow oil. 51 mg, 54% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.08 – 7.02 (m, 2H), 6.99 (ψt, *J* = 7.0 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.76 – 2.72 (m, 2H), 2.39 (s, 3H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.71 – 1.61 (m, 4H), 1.43 – 1.37 (m, 2H), 1.35 (s, 9H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 174.0, 144.4, 140.2, 127.0, 126.8, 126.0, 123.3, 106.9, 76.5, 60.3, 35.1, 34.6, 31.4, 30.4, 29.3, 28.5, 25.1, 21.2, 14.4.

MS (EI): Calcd for $C_{21}H_{30}O_2$: 314.2; found: 314.2.



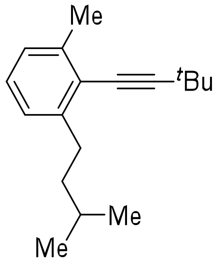
2-*t*-Butylacetylenyl-1-(5-*t*-butyloxycarbonylpentyl)-3-methylbenzene.

Yellow oil. 72 mg, 70% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.07 (ψt, *J* = 7.4 Hz, 1H), 7.02 – 6.98 (m, 2H), 2.77 – 2.73 (m, 2H), 2.40 (s, 3H), 2.22 (t, *J* = 7.5 Hz, 2H), 1.68 – 1.60 (m, 4H), 1.44 (s, 9H), 1.41 – 1.39 (m, 2H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 173.4, 144.5, 140.1, 127.0, 126.8, 126.0, 123.3, 106.9, 80.0, 76.5, 35.8, 35.1, 31.4, 30.4, 29.3, 28.5, 28.2, 25.2, 21.2.

MS (EI): Calcd for $C_{23}H_{34}O_2$: 342.3; found: 342.2.



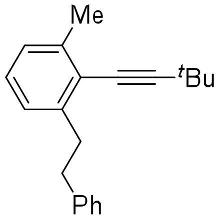
2-*t*-Butylacetylenyl-1-(3-methylbutyl)-3-methylbenzene.

RI was used in the absence of NaI. Yellow oil. 52 mg, 71% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.07 (ψt, *J* = 7.5 Hz, 1H), 7.01 – 6.98 (m, 2H), 2.76 – 2.72 (m, 2H), 2.40 (s, 3H), 1.66 – 1.59 (m, 1H), 1.53 – 1.48 (m, 2H), 1.35 (s, 9H), 0.96 (d, *J* = 6.5 Hz, 6H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 145.0, 140.2, 127.1, 126.7, 125.9, 123.2, 106.8, 76.5, 40.2, 33.3, 31.4, 28.54, 28.50, 22.8, 21.2.

MS (EI): Calcd for $C_{18}H_{26}$: 242.2; found: 242.2.



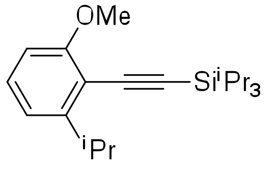
2-*t*-Butylacetylenyl-1-methyl-3-(2-phenylethyl)benzene.

RI was used in the absence of NaI. Yellow oil. 59 mg, 72% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.32 – 7.28 (m, 2H), 7.26 – 7.14 (m, 3H), 7.10 – 7.04 (m, 2H), 6.99 – 6.97 (m, 1H), 3.07 – 3.03 (m, 2H), 2.94 – 2.90 (m, 2H), 2.43 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 143.6, 142.5, 140.4, 128.6, 128.4, 127.2, 127.1, 126.2, 125.9, 123.3, 107.1, 76.5, 37.6, 37.2, 31.4, 28.6, 21.2.

MS (EI): Calcd for $C_{21}H_{24}$: 276.2; found: 276.2.



3-Isopropyl-1-methoxy-2-triisopropylsiylacetylenylbenzene

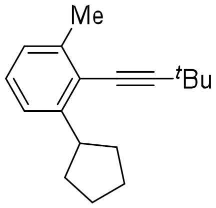
RI was used in the absence of NaI. Yellow oil. 38 mg, 38% yield, with a lot of norbornene-retained byproduct **B**.

If *t*-butylacetylene was used as the alkyne, the desired product was detected by GCMS but it was too volatile for isolation.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.23 (ψt, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 3.85 (s, 3H), 3.55 (hept, *J* = 6.9 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H), 1.16 (br s, 21H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 161.3, 153.0, 129.2, 117.1, 112.1, 108.2, 101.4, 99.7, 56.0, 31.7, 23.1, 18.8, 11.6.

MS (EI): Calcd for $C_{21}H_{34}OSi$: 330.2; found: 330.2.



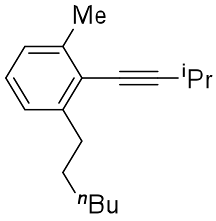
2-*t*-Butylacetylenyl-1-cyclopentyl-3-methylbenzene.

RI was used in the absence of NaI. Yellow oil. 46 mg, 64% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.14 – 7.08 (m, 2H), 7.03 – 7.01 (m, 1H), 3.56 – 3.47 (m, 1H), 2.42 (s, 3H), 2.13 – 2.06 (m, 2H), 1.84 – 1.78 (m, 2H), 1.76 – 1.66 (m, 2H), 1.64 – 1.58 (m, 2H), 1.37 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 147.9, 140.1, 127.2, 126.7, 123.5, 122.6, 107.4, 76.8, 44.2, 33.5, 31.3, 28.6, 25.7, 21.4.

MS (EI): Calcd for $C_{18}H_{24}$: 240.2; found: 240.2.



1-*n*-Hexyl-3-methyl-2-*i*-propylacetylenylbenzene.

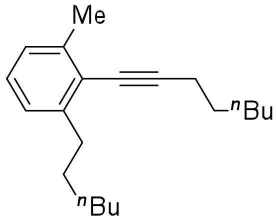
Tri(*p*-tolyl)phosphine (18 mg, 0.06 mmol) was used as ligand. NaI was not added. Yellow oil. 31

mg, 42% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.08 (ψt, *J* = 7.4 Hz, 1H), 7.03 – 6.99 (m, 2H), 2.87 (hept, *J* = 6.8 Hz, 1H), 2.77 – 2.73 (m, 2H), 2.42 (s, 3H), 1.67 – 1.60 (m, 2H), 1.40 – 1.32 (m, 6H), 1.31 (d, *J* = 6.9 Hz), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 145.0, 140.2, 127.0, 126.7, 126.0, 123.3, 104.0, 77.3, 35.3, 31.9, 30.8, 29.5, 23.5, 22.8, 21.7, 21.3, 14.3.

MS (EI): Calcd for $C_{18}H_{26}$: 242.2; found: 242.2.



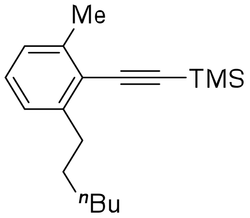
1-*n*-Hexyl-3-methyl-2-(oct-1-yn-1-yl)benzene.

Triphenylphosphine (16 mg, 0.06 mmol) was used as ligand in the absence of NaI. Yellow oil. 41 mg, 48% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.07 (ψt, *J* = 7.5 Hz, 1H), 7.02 – 6.99 (m, 2H), 2.77 – 2.73 (m, 2H), 2.49 (t, *J* = 6.9 Hz, 2H), 2.41 (s, 3H), 1.65 – 1.58 (m, 4H), 1.52 – 1.48 (m, 2H), 1.39 – 1.26 (m, 10H), 0.93 – 0.87 (m, 6H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 145.0, 140.3, 127.0, 126.7, 126.0, 123.4, 98.5, 78.1, 35.2, 31.9, 31.6, 30.8, 29.5, 29.2, 28.8, 22.81, 22.77, 21.4, 19.9, 14.3, 14.2.

MS (EI): Calcd for $C_{21}H_{32}$: 284.3; found: 284.2.



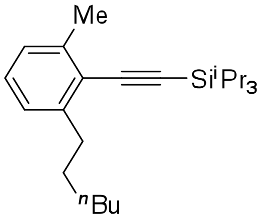
3-*n*-Hexyl-1-methyl-2-(trimethylsilylacetylenyl)benzene

Tri(*p*-tolyl)phosphine (18 mg, 0.06 mmol) was used as ligand. Yellow oil. 50 mg, 61% yield.

^{1}H NMR (300 MHz, CDCl$_3$): δ 7.12 (ψt, *J* = 7.5 Hz, 1H), 7.03 – 6.99 (m, 2H), 2.79 – 2.74 (m, 2H), 2.44 (s, 3H), 1.68 – 1.58 (m, 2H), 1.40 – 1.26 (m, 6H), 0.90 (t, *J* = 6.8 Hz, 3H), 0.27 (s, 9H).

^{13}C NMR (75 MHz, CDCl$_3$): δ 145.8, 140.9, 128.0, 126.8, 126.1, 122.6, 102.8, 102.3, 35.3, 31.9, 30.9, 29.5, 22.8, 21.2, 14.3, 0.3.

MS (EI): Calcd for $C_{28}H_{28}Si$: 272.2; found: 272.2.



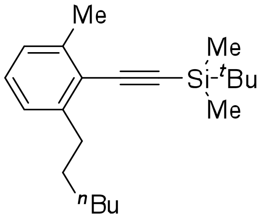
3-*n*-Hexyl-1-methyl-2-(triisopropylsilylacetylenyl)benzene

Tri(*p*-tolyl)phosphine (18 mg, 0.06 mmol) was used as ligand. Yellow oil. 85 mg, 79% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.14 (ψt, *J* = 7.5 Hz, 1H), 7.06 – 7.03 (m, 2H), 2.85 – 2.81 (m, 2H), 2.49 (s, 3H), 1.70 – 1.62 (m, 2H), 1.42 – 1.30 (m, 6H), 1.18 (br s, 21H), 0.91 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 145.7, 141.1, 127.9, 126.8, 126.1, 123.0, 104.4, 98.7, 35.6, 32.0, 31.2, 29.6, 22.9, 21.6, 18.9, 14.3, 11.6.

MS (EI): Calcd for $C_{24}H_{40}Si$: 356.3; found: 356.2.



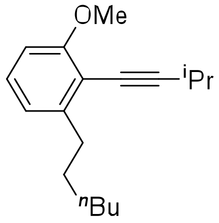
3-*n*-Hexyl-1-methyl-2-(*t*-butyldimethylsilylacetylenyl)benzene

Tri(*p*-tolyl)phosphine (18 mg, 0.06 mmol) was used as ligand. Yellow oil. 69 mg, 73% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.14 (ψt, *J* = 7.5 Hz, 1H), 7.06 – 7.02 (m, 2H), 2.83 – 2.79 (m, 2H), 2.47 (s, 3H), 1.70 – 1.62 (m, 2H), 1.41 – 1.31 (m, 6H), 1.04 (s, 9H), 0.93 (t, *J* = 6.9 Hz, 3H), 0.23 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 145.8, 141.0, 128.0, 126.8, 126.1, 122.7, 103.3, 100.7, 35.4, 32.0, 31.0, 29.6, 26.3, 22.8, 21.4, 16.8, 14.3, -4.3.

MS (EI): Calcd for $C_{21}H_{34}Si$: 314.2; found: 314.2.



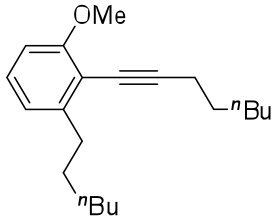
1-*n*-Hexyl-3-methyloxy-2-(*i*-propylacetylenyl)benzene.

Tri(*p*-tolyl)phosphine (18 mg, 0.06 mmol) was used as ligand in the absence of NaI. Yellow oil. 36 mg, 46% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.13 (ψt, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 3.86 (s, 3H), 2.89 (hept, *J* = 6.9 Hz, 1H), 2.77 – 2.72 (m, 2H), 1.68 – 1.56 (m, 2H), 1.39 – 1.30 (m, 12H), 0.89 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 160.1, 147.2, 128.1, 121.3, 112.5, 107.9, 104.1, 74.5, 56.0, 35.0, 32.0, 30.6, 29.5, 23.4, 22.8, 21.8, 14.3.

MS (EI): Calcd for $C_{18}H_{26}O$: 258.2; found: 258.2.



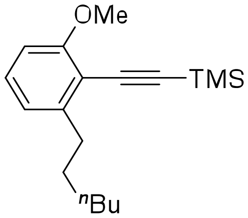
1-*n*-Hexyl-3-methoxy-2-(oct-1-yn-1-yl)benzene.

Tri(*m*-anisyl)phosphine (21 mg, 0.06 mmol) was used as ligand in the absence of NaI. Yellow oil. 36 mg, 40% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (ψt, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 1H), 3.86 (s, 3H), 2.77 – 2.73 (m, 2H), 2.52 (t, *J* = 7.0 Hz, 2H), 1.68 – 1.58 (m, 4H), 1.53 – 1.46 (m, 2H), 1.39 – 1.26 (m, 10H), 0.92 – 0.87 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 147.2, 128.1, 121.2, 112.6, 107.8, 98.8, 75.2, 56.0, 34.9, 31.9, 31.6, 30.6, 29.5, 29.1, 28.8, 22.79, 22.76, 20.1, 14.3, 14.2.

MS (EI): Calcd for $C_{21}H_{32}O$: 300.2; found: 300.2.



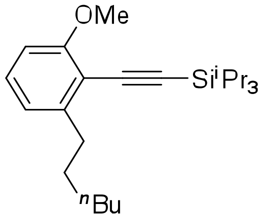
3-*n*-Hexyl-1-methoxy-2-(trimethylsilylacetylenyl)benzene

Tri(*p*-tolyl)phosphine (18 mg, 0.06 mmol) was used as ligand. Yellow oil. 52 mg, 60% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.17 (ψt, J = 8.0 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 6.68 (d, J = 8.3 Hz, 1H), 3.86 (s, 3H), 2.77-2.73 (m, 2H), 1.66 – 1.58 (m, 2H), 1.37 – 1.26 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H), 0.27 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 160.6, 147.9, 129.1, 121.2, 111.7, 107.8, 102.6, 100.0, 55.9, 34.9, 31.8, 30.5, 29.4, 22.7, 14.1, 0.1.

MS (EI): Calcd for $C_{18}H_{28}OSi$: 288.2; found: 288.2.



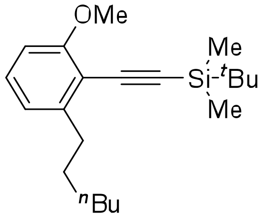
3-*n*-Hexyl-1-methoxy-2-(triisopropylsilylacetylenyl)benzene

Tri(*p*-tolyl)phosphine (18 mg, 0.06 mmol) was used as ligand. Yellow oil. 90 mg, 80% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.16 (ψt, J = 8.0 Hz, 1H), 6.78 (d, J = 7.6 Hz, 1H), 6.68 (d, J = 8.3 Hz, 1H), 3.83 (s, 3H), 2.81 – 2.77 (m, 2H), 1.67 – 1.59 (m, 2H), 1.37 – 1.31 (m, 2H), 1.30 – 1.26 (m, 4H), 1.15 (br s, 21H), 0.87 (t, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 161.4, 147.5, 128.9, 121.2, 112.7, 108.3, 101.7, 99.0, 56.0, 35.2, 32.0, 31.0, 29.6, 22.8, 18.9, 14.2, 11.6.

MS (EI): Calcd for $C_{24}H_{40}OSi$: 372.3; found: 372.2.



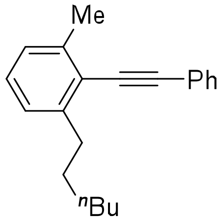
3-*n*-Hexyl-1-methoxy-2-(*t*-butyldimethylsilylacetylenyl)benzene

Tri(*p*-tolyl)phosphine (18 mg, 0.06 mmol) was used as ligand. Yellow oil. 65 mg, 65% yield.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.17 (ψt, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 3.85 (s, 3H), 2.79 – 2.76 (m, 2H), 1.65 – 1.59 (m, 2H), 1.37 – 1.26 (m, 6H), 1.02 (s, 9H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.20 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 161.1, 147.8, 129.1, 121.2, 112.2, 108.1, 100.9, 100.5, 56.0, 35.1, 32.0, 30.8, 29.5, 26.4, 22.8, 16.9, 14.3, -4.3.

MS (EI): Calcd for $C_{21}H_{34}OSi$: 330.2; found: 330.2.



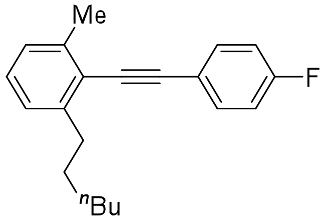
1-*n*-Hexyl-3-methyl-2-(phenylacetylenyl)benzene.

Dry NMP (3 mL) was used as solvent and KOAc (177 mg, 1.8 mmol) as base, in the absence of added ligand and NaI. Yellow oil. 48 mg, 58% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.55 – 7.52 (m, 2H), 7.39 – 7.32 (m, 3H), 7.16 (ψt, *J* = 7.5 Hz, 1H), 7.09 – 7.06 (m, 2H), 2.89 – 2.85 (m, 2H), 2.53 (s, 3H), 1.75 – 1.67 (m, 2H), 1.44 – 1.38 (m, 2H), 1.37 – 1.27 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 145.3, 140.6, 131.5, 128.5, 128.2, 128.0, 126.9, 126.2, 124.1, 122.6, 97.4, 87.2, 35.3, 31.9, 30.9, 29.5, 22.8, 21.3, 14.3.

MS (EI): Calcd for $C_{21}H_{24}$: 276.2; found: 276.1.



2-[(4-Fluorophenyl)acetylenyl]-1-*n*-hexyl-3-methylbenzene.

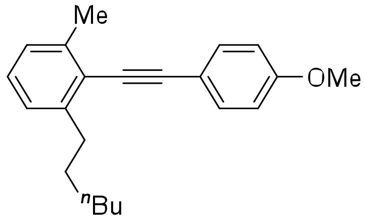
Dry NMP (3 mL) was used as solvent and KOAc (177 mg, 1.8 mmol) as base, in the absence of added ligand and NaI. Yellow oil. 44 mg, 50% yield.

^{1}H NMR (300 MHz, CDCl$_3$): δ 7.54 – 7.47 (m, 2H), 7.16 (ψt, *J* = 7.5 Hz, 1H), 7.09 – 7.02 (m, 4H), 2.87 – 2.82 (m, 2H), 2.52 (s, 3H), 1.75 – 1.65 (m, 2H), 1.43 – 1.31 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, CDCl$_3$): δ 162.6 (d, J_{C-F} = 249.1 Hz), 145.3, 140.5, 133.3 (d, J_{C-F} = 8.3 Hz), 128.0, 127.0, 126.2, 122.4, 120.2 (d, J_{C-F} = 3.6 Hz), 115.8 (d, J_{C-F} = 22.3 Hz), 96.3, 86.9, 35.3, 31.9, 30.9, 29.5, 22.8, 21.3, 14.3.

^{19}F {^{1}H} NMR (282 MHz, CDCl$_3$): δ -111.4.

MS (EI): Calcd for $C_{21}H_{23}$ F: 294.2; found: 294.2.



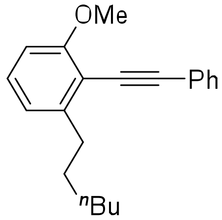
1-*n*-Hexyl-2-[(4-methoxyphenyl)acetylenyl]-3-methylbenzene.

Dry NMP (3 mL) was used as solvent and KOAc (177 mg, 1.8 mmol) as base, in the absence of added ligand and NaI. Yellow oil. 62 mg, 68% yield.

^{1}H NMR (125 MHz, CDCl$_3$): δ 7.48 (d, *J* = 8.7 Hz, 2H), 7.14 (ψt, *J* = 7.5 Hz, 1H), 7.07 (ψt, *J* = 7.2 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 2.88 – 2.84 (m, 2H), 2.53 (s, 3H), 1.74 – 1.68 (m, 2H), 1.44 – 1.39 (m, 2H), 1.37 – 1.33 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 159.7, 145.1, 140.3, 132.9, 127.6, 126.9, 126.2, 123.0, 116.4, 114.2, 97.4, 86.0, 55.5, 35.3, 32.0, 30.9, 29.5, 22.8, 21.3, 14.2.

MS (EI): Calcd for $C_{22}H_{26}O$: 306.2; found: 306.2.



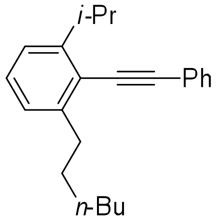
1-*n*-Hexyl-3-methoxy-2-(phenylacetylenyl)benzene.

Dry NMP (3 mL) was used as solvent and KOAc (177 mg, 1.8 mmol) as base, in the absence of added ligand and NaI. Yellow oil. 46 mg, 53% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.54 (m, 2H), 7.37 – 7.29 (m, 3H), 7.21 (ψt, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.75(d, *J* = 8.2 Hz, 1H), 3.91 (s, 3H), 2.87 – 2.83 (m, 2H), 1.74 – 1.66 (m, 2H), 1.41 – 1.26 (m, 6H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 147.4, 131.7, 129.1, 128.4, 128.1, 124.1, 121.4, 112.0, 108.0, 97.5, 84.6, 56.1, 35.0, 31.9, 30.7, 29.4, 22.8, 14.2.

MS (EI): Calcd for $C_{21}H_{24}O$: 292.2; found: 292.1.



1-*n*-Hexyl-3-isopropyl-2-(phenylacetylenyl)benzene.

Dry NMP (3 mL) was used as solvent and KOAc (177 mg, 1.8 mmol) as base, in the absence of added ligand and NaI. Yellow oil. 72 mg, 79% yield.

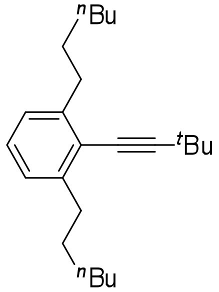
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 – 7.50 (m, 2H), 7.38 – 7.30 (m, 3H), 7.22 – 7.19 (m, 1H), 7.13 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.06 (dd, *J* = 7.4, 1.1 Hz, 1H), 3.60 (hept, *J* = 6.9 Hz, 1H), 2.89 – 2.84 (m, 2H), 1.75 – 1.65 (m, 2H), 1.47 – 1.21 (m, 12H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 150.9, 145.5, 131.4, 128.5, 128.3, 128.1, 126.3, 124.2, 122.3, 121.5, 97.2, 87.0, 35.5, 32.00, 31.96, 31.0, 29.6, 23.4, 22.8, 14.3.

MS (EI): Calcd for $C_{23}H_{28}$: 304.2; found: 304.2.

IV. Couplings with PhI and *para*-substituted aryl halides

A typical procedure (0.3 mmol scale): In an argon-filled glove box, a 10-mL Schlenk tube containing a magnetic stir bar was charged with $Pd(OAc)_2$ (10 mol%, 6.6 mg, 0.03 mmol), $P(2\text{-furyl})_3$ (20 mol%, 13.9 mg, 0.06 mmol) and 3 mL of dry acetonitrile. After stirring at room temperature for 10 minutes, aryl iodide (0.3 mmol), 1-bromohexane (297 mg, 1.8 mmol, 6 equiv), 2-norbornene (57 mg, 0.6 mmol, 2 equiv), Cs_2CO_3 (391 mg, 1.2 mmol, 4 equiv), NaI (90 mg, 0.6mmol), *t*-butylacetylene (37 mg, 0.45 mmol, 1.5 equiv) and GC standard *n*-dodecane (30 μL) were added sequentially. The tube was capped tightly and the reaction mixture was heated in an oil bath maintained at 90 °C for 24 h. At the end of the reaction, the mixture was cooled to room temperature. Aliquots of the reaction mixture were passed through a short plug of silica gel with ethyl acetate washings to determine the conversion. The desired products were purified by flash chromatography over silica gel using hexane as elute.



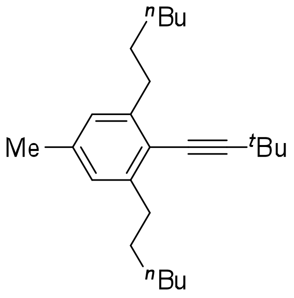
2-*t*-Butylacetylenyl-1,3-di-*n*-hexylbenzene.

Yellow oil. 69 mg, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 – 7.08 (m, 1H), 7.02 – 7.00 (m, 2H), 2.78 – 2.74 (m, 4H), 1.68 – 1.61 (m, 4H), 1.41 – 1.28 (m, 21H), 0.91 (t, J = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 127.1, 126.1, 122.8, 105.9, 76.4, 35.5, 32.0, 31.3, 30.9, 29.7, 28.5, 22.8, 14.3.

MS (EI): Calcd for $C_{24}H_{38}$: 326.3; found: 326.3.



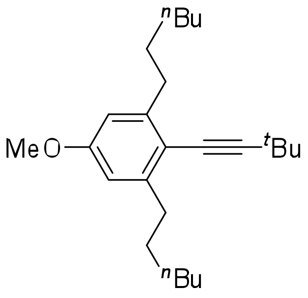
2-*t*-Butylacetylenyl-1,3-di-*n*-hexyl-4-methylbenzene.

Yellow oil. 47 mg, 46% yield.

^{1}H NMR (300 MHz, CDCl$_3$): δ 6.82 (s, 2H), 2.73 – 2.68 (m, 4H), 2.29 (s, 3H), 1.65 – 1.57 (m, 4H), 1.41 – 1.28 (m, 21H), 0.91 (t, *J* = 6.6 Hz, 6H).

^{13}C NMR (75 MHz, CDCl$_3$): δ 145.0, 136.8, 127.0, 119.8, 105.1, 76.5, 35.4, 32.0, 31.4, 31.0, 29.7, 28.5, 22.8, 21.5, 14.3.

MS (EI): Calcd for $C_{25}H_{40}$: 340.3; found: 340.3.



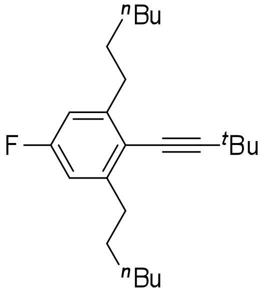
2-*t*-Butylacetylenyl-1,3-di-*n*-hexyl-4-methoxybenzene.

Yellow oil. 59 mg, 55% yield.

^{1}H NMR (500 MHz, CDCl$_3$): δ 6.56 (s, 2H), 3.78 (s, 3H), 2.74 – 2.70 (m, 4H), 1.66 – 1.60 (m, 4H), 1.40 – 1.31 (m, 21H), 0.90 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (125 MHz, CDCl$_3$): δ 158.6, 146.7, 115.3, 111.7, 104.3, 76.3, 55.2, 35.7, 32.0, 31.4, 30.8, 29.6, 28.5, 22.8, 14.3.

MS (EI): Calcd for $C_{25}H_{40}O$: 356.3; found: 356.3.



2-*t*-Butylacetylenyl-4-fluoro-1,3-di-*n*-hexylbenzene.

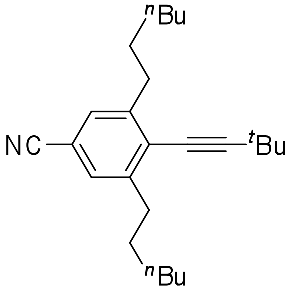
Yellow oil. 66 mg, 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (d, J = 9.5 Hz, 2H), 2.75 – 2.71 (m, 4H), 1.66 – 1.58 (m, 4H), 1.37 – 1.30 (m, 21H), 0.90 (t, J = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7 (d, $J_{C\text{-}F}$ = 246.6 Hz), 147.5 (d, $J_{C\text{-}F}$ = 7.8 Hz), 118.8 (d, $J_{C\text{-}F}$ = 2.9 Hz), 112.9 (d, $J_{C\text{-}F}$ = 21.3 Hz), 105.5, 75.6, 35.4 (d, $J_{C\text{-}F}$ = 1.2 Hz), 31.9, 31.3, 30.5, 29.5, 28.5, 22.8, 14.2.

^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$): δ -114.1.

MS (EI): Calcd for $C_{24}H_{37}F$: 344.3; found: 344.2.



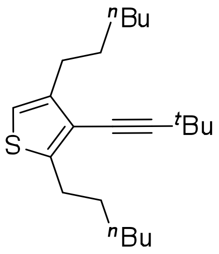
2-*t*-Butylacetylenyl-1,3-di-*n*-hexylbenzonitrile

Yellow oil. 53 mg, 50% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (s, 2H), 2.77 – 2.71 (m, 4H), 1.63 – 1.56 (m, 4H), 1.35 – 1.26 (m, 21H), 0.89 (t, J = 6.7 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 146.1, 129.5, 128.1, 119.5, 110.3, 110.2, 75.5, 35.1, 31.9, 31.0, 30.3, 29.4, 28.7, 22.8, 14.2.

MS (EI): Calcd for $C_{25}H_{37}N$: 351.3; found: 351.2.



3-(*t*-Butylacetylenyl)-2,4-di-*n*-hexylthiophene.

Yellow oil. 71 mg, 71% yield.

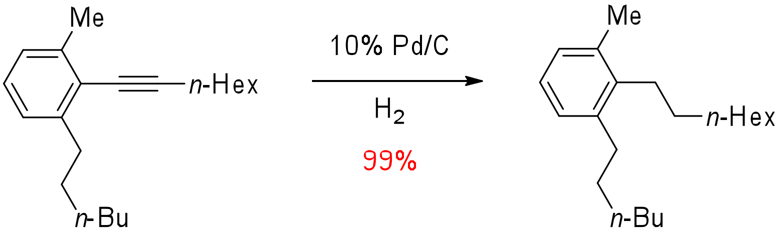
^{1}H NMR (400 MHz, CDCl$_3$): δ 6.62 (s, 1H), 2.86 – 2.82 (m, 2H), 2.59 – 2.55 (m, 2H), 1.71 – 1.59 (m, 4H), 1.40 –1.30 (m, 21H), 0.90 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 147.8, 144.1, 121.0, 116.1, 103.1, 73.5, 31.9, 31.7, 31.4, 31.2, 30.2, 29.7, 29.5, 29.3, 29.0, 28.4, 22.8, 22.7, 14.3, 14.2.

MS (EI): Calcd for $C_{22}H_{36}S$: 332.3; found: 332.2.

V. Product derivatization

(a) Hydrogenation by Pd/C



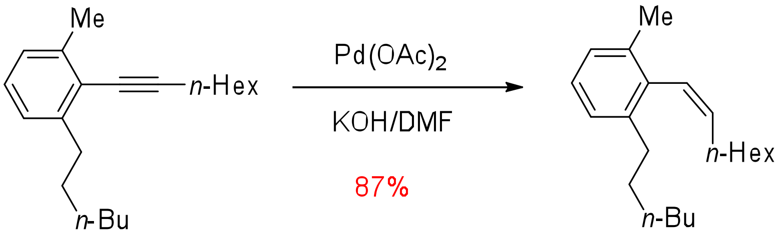
Under argon, to a solution of an alkyne (29 mg, 0.1 mmol) in 1 mL of analytic grade methanol was added 5% Pd/C (3 mg). The suspension was vigorously stirred at room temperature for 8 h in a Parr bomb pressurized with 10 atm of hydrogen. Then the hydrogen gas was released and the mixture was filtered through a pad of Celite and purified by silica gel chromatography using hexane as elute to get the desired product as light yellow oil (28 mg, 99% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.04 – 6.97 (m, 3H), 2.62 – 2.58 (m, 4H), 2.32 (s, 3H), 1.61 – 1.54 (m, 2H), 1.49 – 1.37 (m, 6H), 1.34 – 1.27 (m, 12H), 0.93 – 0.88 (m, 6H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 140.9, 139.3, 136.3, 128.1, 127.2, 125.6, 33.3, 32.1, 31.94, 31.89, 30.5, 30.3, 29.9, 29.7, 29.6, 29.46, 29.45, 22.84, 22.81, 20.1, 14.3.

MS (EI): Calcd for $C_{21}H_{36}$: 288.3; found: 288.1.

(b) $Pd(OAc)_2$-catalyzed semihydrogenation[1]



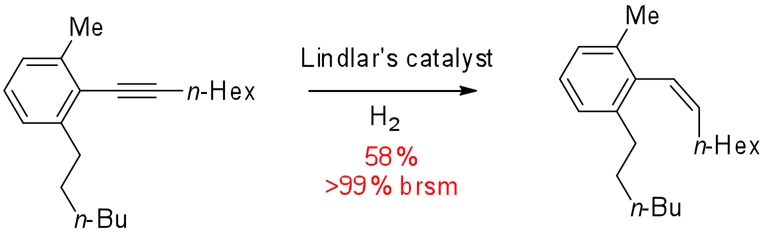
To a solution of an alkyne (29 mg, 0.1 mmol) in 1 mL of DMF was added $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) and KOH (17 mg, 0.3 mmol). The resulting suspension was vigorously stirred at room temperature for 3 days. Then the crude product was purified directly by silica gel chromatography using hexane as elute to give the desired product as light yellow oil (25 mg, 87% yield). DMF was the hydride source.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11-7.08 (m, 1H), 7.03 (ψd, *J* = 7.5 Hz, 2H), 6.30 (d, *J* = 11.2 Hz, 1H), 5.74 (dt, *J* = 11.3, 7.2 Hz, 1H), 2.53 (br s, 2H), 2.21 (s, 3H), 1.81 (ψq, *J* = 7.0 Hz, 2H), 1.52 – 1.47 (m, 2H), 1.33 – 1.19 (m, 14H), 0.90-0.84 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 141.1, 136.6, 136.2, 133.5, 127.12, 127.05, 126.5, 126.2, 33.9, 31.94, 31.88, 30.8, 29.9, 29.6, 29.2, 28.9, 22.79, 22.75, 20.6, 14.3, 14.2.

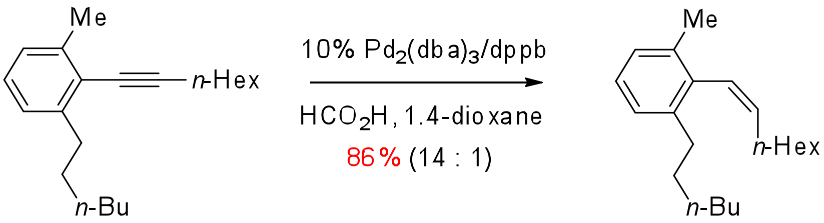
MS (EI): Calcd for $C_{21}H_{34}$: 286.3; found: 286.2.

(c) Hydrogenation by Lindlar catalyst



To a solution of an alkyne (29 mg, 0.1 mmol) in 2 mL of methanol was added 9 mg of 5% Lindlar catalyst. The resulting suspension was vigorously stirred at room temperature for 8 h in a Parr bomb under 10 atm of hydrogen. Then hydrogen gas was released and the mixture was filtered through a pad of Celite and washed with ethyl acetate (5 mL). The filtrate was purified by silica gel column chromatography using hexane as elute to get the desired product as light yellow oil (17 mg, 58% yield) with recovery of the unreacted alkyne (13 mg, 42% of starting material).

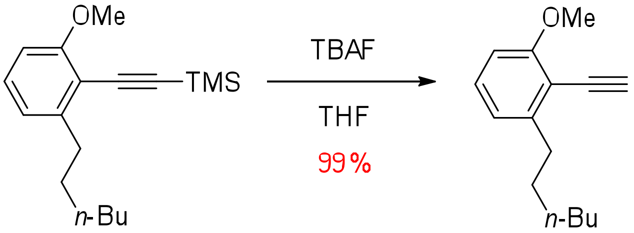
(d) Pd/dppb-catalyzed transfer semihydrogenation[2]



In an argon-filled glove box, a dry 10 mL Schlenk tube containing a magnetic stir bar was charged with $Pd_2(dba)_3$ (9 mg, 0.01 mmol), dppb (8.5 mg, 0.02 mmol), an alkyne (29 mg, 0.1 mmol) and 0.4 mL of 1,4-dioxane. After stirring at room temperature for 5 min, 25% aqueous HCO_2H (0.5 mmol, 96 μL) was added. The Schlenk tube was sealed and then heated at 80 °C for 20 h. At the end of the reaction, the residue was passed through a pad of Celite and purified by silica gel column chromatography using hexane as elute to afford the desired alkene (25 mg, 86%). The E/Z ratio in the crude mixture was to be 14:1 determined by GC and GCMS.

When a 25% HCO_2H solution in D_2O was used instead, 83% conversion of the alkyne was detected after 36 h at 80 °C and 37% of deuterium was incorporated in both olefinic CH bonds.

(e) Desilylation of silylalkyne



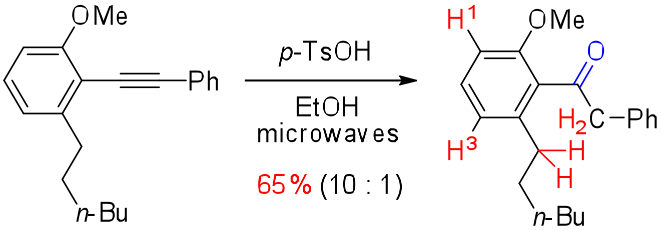
In air, to a solution of an alkyne (29 mg, 0.1 mmol) in THF/H_2O (1.0 mL/0.1 mL) was added 1 M TBAF in THF (0.15 mmol, 150 μL). After stirring at room temperature for 2 h, the reaction mixture was quenched with 2 mL of water and extracted with ethyl acetate (5 mL x 3). The crude product was purified by silica gel chromatography using 20:1 hexane/EA as elute to give the terminal alkyne as colorless oil (21 mg, 99%).

^1H NMR (400 MHz, $CDCl_3$): δ 7.22 (ψt, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 3.89 (s, 3H), 3.50 (s, 1H), 2.80 – 2.76 (m, 2H), 1.67–1.59 (m, 2H), 1.38 – 1.26 (m, 6H), 0.88 (t, *J* = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 148.0, 129.5, 121.3, 110.8, 107.9, 85.1, 78.8, 56.1, 34.7, 31.8, 30.6, 29.3, 22.8, 14.2.

MS (EI): Calcd for $C_{15}H_{20}O$: 216.2; found: 216.1.

(f) Acidic hydration of an alkyne[3]



To a 10 mL reaction tube was added an alkyne (29 mg, 0.1 mmol) and PTSA·H_2O (19 mg, 0.1 mmol) in absolute EtOH (1 mL). The reaction tube was then subjected to microwave irradiation at 130 °C for 1 h. After cooling to room temperature, 2 mL of H_2O was added, and the mixture was extracted with DCM (5 mL x 3). The organic layer was dried by Na_2SO_4, concentrated, and the crude product was purified by silica gel chromatography using 15:1 hexane/ethyl acetate as elute to get the desired product as colorless oil (20 mg, 65%) and 2 mg of its regioisomer (regioselectivity 10:1). The structure of main isomer was established on the basis of their spectroscopic data.

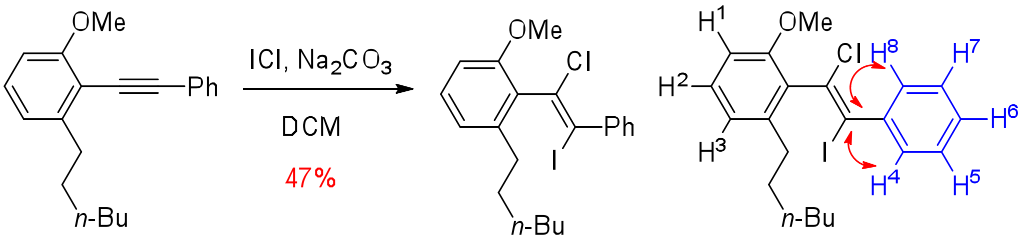
To confirm the position of the ketone group, H-H COSY and HMBC NMR experiments were conducted. The HMBC spectrum had clear $^4J_{C\text{-}H}$ couplings between the ketone carbon (205.1 ppm) and two aryl hydrogens (H1 and H3) and benzylic hydrogens.

^1H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.20 (m, 6H), 6.79 (d, J = 7.7 Hz, 1H), 6.75 (d, J = 8.3 Hz, 1H), 4.08 (s, 2H), 3.82 (s, 3H), 2.33 – 2.29 (m, 2H), 1.43 – 1.38 (m, 2H), 1.29 – 1.21 (m, 6H), 0.86 (t, J = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 205.1, 156.2, 141.2, 134.3, 130.7, 130.09, 130.05, 128.5, 127.0, 122.0, 108.2, 55.7, 51.8, 33.0, 31.8, 31.6, 29.4, 22.7, 14.2.

MS (ESI) Calcd for $C_{21}H_{26}O_2$ $[M+H]^+$: 311.2; found: 311.1.

(g) ICl addition to an internal alkyne[4]



In an argon-filled glove box, a dry 10 mL Schlenk tube containing a magnetic stir bar was charged with an alkyne (29 mg, 0.1 mmol), ICl (33 mg, 0.2 mmol) and Na_2CO_3 (21 mg, 0.2 mmol) in 2 mL of dry DCM. After stirring at room temperature for 2 h, 2 mL of H_2O was added to quench the reaction and the mixture was extracted with DCM (5 mL x 3). The reaction gave a complex mixture and no benzofuran product was detected by GCMS. The crude product was purified by silica gel chromatography using 30:1 hexane/ethyl acetate as elute to get the desired product as colorless oil (21mg, 47%).

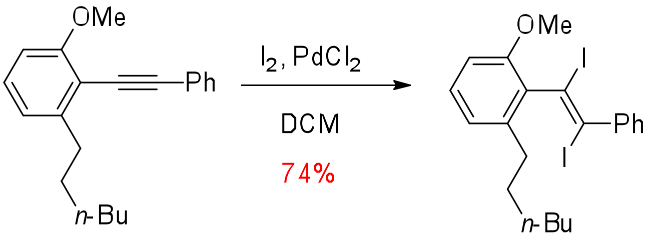
The position of the iodine was determined by HMBC-NMR spectroscopy. A cross signal was detected between the vinylic C(I) at high field (98.2 ppm) and two *ortho* hydrogens (H4 and H8) of the phenyl ring.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.49 (m, 2H), 7.43 – 7.39 (m, 2H), 7.35 – 7.30 (m, 2H), 6.92 (d, J = 7.7 Hz, 1H), 6.82 (d, J = 7.7 Hz, 1H), 3.93 (s, 3H), 2.76 – 2.72 (m, 2H), 1.80 – 1.72 (m, 2H), 1.47 – 1.32 (m, 6H), 0.91 (t, J = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 142.3, 142.1, 130.4, 130.3, 129.1, 128.6, 128.4, 127.6, 121.5, 108.8, 98.2, 56.3, 33.0, 31.9, 30.4, 29.8, 22.8, 14.3.

MS (EI): Calcd for $C_{21}H_{24}ClIO$: 454.1; found: 454.0.

(h) I_2 addition to an alkyne[4]



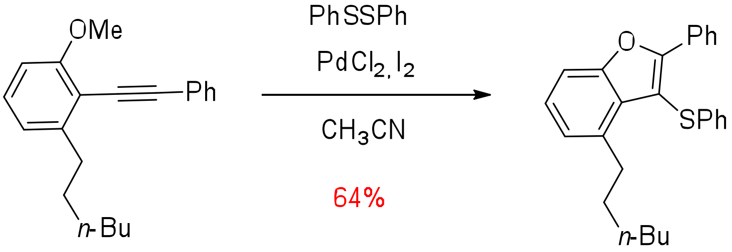
In an argon-filled glove box, a dry 10 mL Schlenk tube containing a magnetic stir bar was charged with an alkyne (29 mg, 0.1 mmol), I_2 (51 mg, 0.2 mmol), $PdCl_2$ (1.8 mg, 0.01 mmol) in 2 mL of dry DCM. After stirring at room temperature for 2 h, H_2O (2 mL) was added to quench the reaction, and the mixture was extracted with DCM (5 mL x 3). The reaction gave a complex mixture and no cyclization product was detected by GCMS. The crude product was purified by silica gel chromatography using 30:1 hexane/ethyl acetate as elute to get the desired product as light yellow oil (40 mg, 74%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 – 7.43 (m, 4H), 7.40 – 7.37 (m, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 3.97 (s, 3H), 2.75 – 2.72 (m, 2H), 1.87 – 1.80 (m, 2H), 1.55 – 1.49 (m, 2H), 1.46 – 1.37 (m, 4H), 0.97 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 147.3, 140.9, 134.9, 129.8, 128.7, 128.6, 121.5, 109.0, 100.1, 94.8, 56.2, 33.0, 32.0, 29.8, 29.4, 22.8, 14.3.

MS (EI): Calcd for $C_{21}H_{24}I_2O$: 546.0; found: 546.0.

(i) Pd-catalyzed cyclization to benzofuran[5]



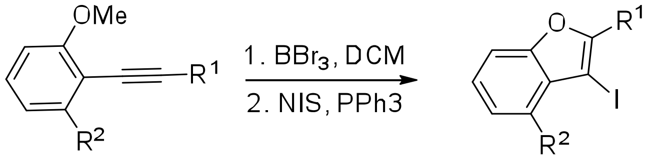
In an argon-filled glove box, to a 10 mL reaction tube was added an alkyne (29 mg, 0.1 mmol), phenyl disulfide (11 mg, 0.05 mmol), $PdCl_2$ (1.8 mg, 0.01 mmol) and I_2 (51 mg, 0.2 mmol) in 2 mL of dry CH_3CN. The reaction tube was stirred at 80 °C for 3 h. Then the mixture was diluted with EA (5 mL), washed with saturated NaS_2O_3 solution (10 mL) and extracted with EA (5 mL x 3). The crude mixture was purified by silica gel column chromatography using hexane as elute to afford the product as colorless oil (25 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 – 8.12 (m, 2H), 7.43 – 7.35 (m, 4H), 7.24 – 7.18 (m, 3H), 7.12 (d, *J* = 7.4 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 3.00 – 2.96 (m, 2H), 1.53 – 1.45 (m, 2H), 1.28 – 1.20 (m, 4H), 1.18 – 1.11 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 154.7, 138.6, 138.4, 130.0, 129.5, 129.3, 128.6, 128.0, 127.5, 125.5, 125.3, 125.2, 124.6, 109.2, 103.8, 32.7, 31.8, 31.6, 29.5, 22.8, 14.3.

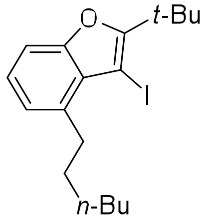
MS (ESI) Calcd for $C_{26}H_{26}OS$ $[M+H]^+$: 387.2; found: 387.1.

(j) Cyclization of *o*-anisyl alkynes to benzofurans[6]



A general procedure: Under argon, to a solution of an alkyne (0.1 mmol) in 2 mL of dry DCM was added of 1 M BBr_3 solution in DCM (0.15 mmol, 0.15 mL). The resulting solution immediately turned red and was then stirred for 30 minutes at room temperature. At the end of the reaction, the mixture was quenched with 20 μL of water and then stirred for 15 minutes. Next, the mixture was filtered through a short pad of silica gel and washed with DCM (10 mL) and the filtrate was concentrated under reduced pressure to dryness. The crude product was used directly in next step.

Under argon, to a 10 mL dry reaction tube was added the crude phenol (~0.1 mmol), NIS (34 mg, 0.15 mmol), and Ph_3P (3.9 mg, 0.015 mmol) in 3 mL of dry DCE. The reaction was stirred at room temperature for 30 minutes. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography using hexane as elute to obtain the benzofuran product.



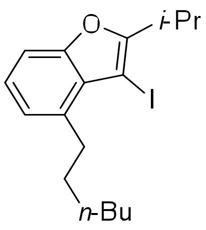
2-(*t*-Butyl)-4-*n*-hexyl-3-iodobenzofuran.

Yellow oil. 20 mg, 52% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.2, 1H), 7.15 (ψt, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 3.21 – 3.15 (m, 2H), 1.75 – 1.64 (m, 2H), 1.58 (s, 9H), 1.53 – 1.40 (m, 2H), 1.38 – 1.32 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 161.9, 153.2, 137.1, 127.1, 124.6, 123.7, 109.1, 54.6, 34.9, 33.3, 32.0, 31.5, 29.3, 29.2, 22.8, 14.3.

MS (EI): Calcd for $C_{18}H_{25}IO$: 384.1; found: 384.0.



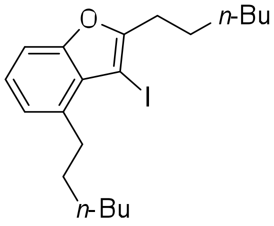
4-*n*-Hexyl-3-iodo-2-isopropylbenzofuran.

Yellow oil. 18 mg, 49% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.30 (d, *J* = 8.0 Hz, 1H), 7.14 (ψt, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 3.38 (hept, *J* = 6.9 Hz, 1H), 3.12 – 3.08 (m, 2H), 1.71 – 1.63 (m, 2H), 1.49 – 1.42 (m, 2H), 1.37 – 1.26 (m, 10H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 162.5, 154.4, 136.6, 126.0, 124.2, 123.7, 109.2, 57.2, 33.2, 32.0, 31.3, 29.2, 28.4, 22.8, 20.7, 14.3.

MS (EI): Calcd for $C_{17}H_{23}IO$: 370.1; found: 370.0.



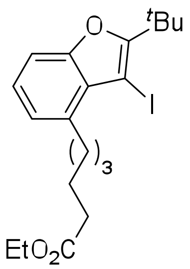
2,4-Di(*n*-hexyl)-3-iodobenzofuran.

Yellow oil. 19 mg, 46% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.28 (d, *J* = 8.2 Hz, 1H), 7.14 (ψt, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 3.12 – 3.08 (m, 2H), 2.86 (t, *J* = 7.6 Hz, 2H), 1.76 – 1.63 (m, 4H), 1.47 – 1.43 (m, 2H), 1.41 – 1.26 (m, 10H), 0.89 (ψt, *J* = 6.6 Hz, 6H).

^{13}C NMR (75 MHz, CDCl$_3$): δ 159.1, 154.5, 136.5, 126.2, 124.2, 123.8, 109.1, 59.0, 33.2, 32.0, 31.7, 31.2, 29.2, 29.0, 28.4, 27.9, 22.8, 22.7, 14.3, 14.2.

MS (EI): Calcd for $C_{20}H_{29}IO$: 412.1; found: 412.1.



2-*t*-Butyl-4-(5-ethoxycarbonylpentyl)-3-iodobenzofuran.

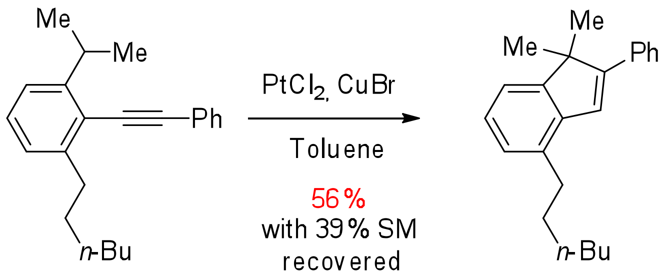
Yellow oil. 24 mg, 54% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.2 Hz, 1H), 7.13 (ψt, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 7.3 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.19 – 3.15 (m, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.74 – 1.67 (m, 4H), 1.56 (s, 9H), 1.52 – 1.44 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 162.0, 153.2, 136.6, 127.1, 124.6, 123.8, 109.2, 60.3, 54.5, 34.9, 34.5, 32.9, 31.2, 29.3, 28.9, 25.1, 14.4.

MS (EI): Calcd for $C_{20}H_{27}IO_3$: 442.1; found: 442.1.

(k) Cyclization of an *o*-isopropyl alkyne to an indene[7]



Under argon, to a 10 mL reaction tube was added an alkyne (31 mg, 0.1 mmol), $PtCl_2$ (5.4 mg, 0.02 mmol) and CuBr (29 mg, 0.2 mmol) in 1 mL of dry toluene. The reaction tube was stirred at 130 °C for 3 days. The reaction mixture was cooled to RT and then purified by silica gel column chromatography using hexane as elute to afford the product as yellow oil (17 mg, 56%) with recovery of starting material (12 mg, 39%)

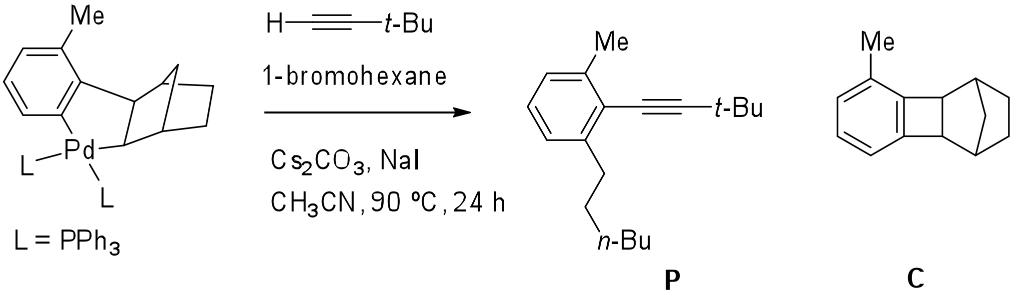
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.32 (m, 5H), 7.22 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.16 (ψt, *J* = 7.4 Hz, 1H), 7.02 – 7.00 (m, 1H), 6.17 (s, 1H), 2.33 – 2.29 (m, 2H), 1.38 (s, 6H), 1.33 – 1.22 (m, 2H), 1.19 – 1.12 (m, 2H), 1.05 – 0.98 (m, 2H), 0.93 – 0.85 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 146.2, 142.7, 139.9, 139.4, 137.5, 128.9, 128.5, 127.9, 127.1, 125.5, 119.2, 47.9, 32.8, 32.5, 31.7, 29.4, 25.1, 22.7, 14.2.

MS (EI): Calcd for $C_{23}H_{28}$: 304.2; found: 304.1.

VI. Mechanistic study

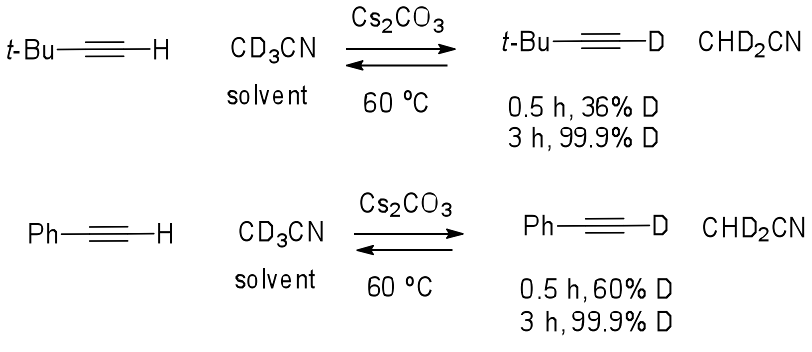
(a) Stoichiometric reactions of a palladacycle



P(2-furyl)$_3$ 0 mol% 33% P, 53% C
P(2-furyl)$_3$ 100 mol% 34% P, 27% C

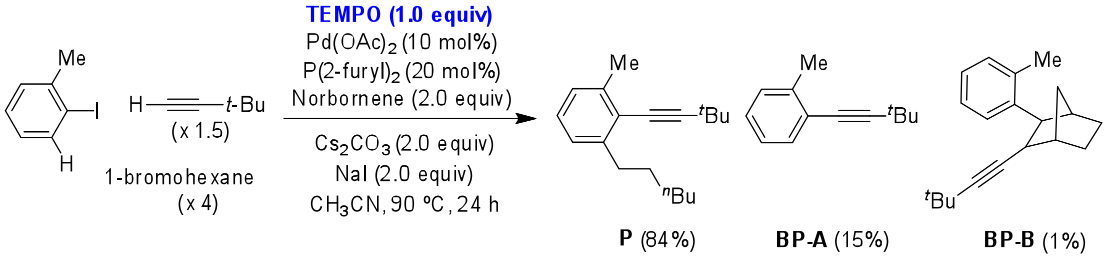
A typical procedure: In an argon-filled glove box, to a dry 25 mL Schlenk tube containing a magnetic stir bar was charged with the palladacycle (41 mg, 0.05 mmol), P(2-furyl)$_3$ (23 mg, 0.1 mmol) and 5 mL of dry acetonitrile. After stirring at room temperature for 2 min , 1-bromohexane (33 mg, 0.2 mmol), Cs_2CO_3 (33 mg, 0.1 mmol), NaI (15 mg, 0.1 mmol), *t*-butylacetylene (6 mg, 0.075 mmol, 1.5 equiv) and GC standard *n*-dodecane (5 μL) were added sequentially. The tube was capped tightly and the reaction mixture was heated in an oil bath maintained at 90 °C for 24 h. Aliquots of the reaction mixture were drawn from the reaction mixture in a glove box and passed through a short plug of silica gel with ethyl acetate washings. The filtrate was analyzed with GC to determine calibrated GC yields of the product. Scrambling of phenyl and furyl groups in two phosphines was observed by GCMS that resulted in significant amounts of PPh$_2$(2-furyl) and PPh(2-furyl)$_2$. The palladacycle was synthesized via reported procedures.[8]

(b) Base-promoted H/D exchange of alkynes



In an argon-filled glove box, to a 10 mL dry reaction tube was added *t*-butylacetylene (0.1 mmol, 8.2 mg) or phenylacetylene (10 mg, 0.1 mmol) and Cs_2CO_3 (65 mg, 0.1 mmol) in dry [D_3]-MeCN (0.6 mL, CIL). The suspension was vigorously stirred with a magnetic stir bar at 60 °C for 0.5 h or 3 h. The sample was transferred into a J. Young tube and the extent of deuteration was determined by quantitative ^{1}H NMR spectroscopy and the incorporation of deuterium was confirmed by ^{2}H NMR spectroscopy (*t*-butylacetylene: 2.29 ppm and phenylacetylene: 3.39 ppm).

(c) TEMPO trapping experiment



In an argon-filled glove box, a 10-mL reaction tube containing a magnetic stir bar was charged with $Pd(OAc)_2$ (10 mol%, 2.2 mg, 0.01 mmol), $P(2\text{-furyl})_3$ (20 mol%, 4.6 mg, 0.02 mmol) and 1 mL of dry acetonitrile. After stirring at room temperature for 10 minutes, *o*-iodotoluene (22 mg, 0.1 mmol), 1-bromohexane (66 mg, 0.4 mmol), 2-norbornene (19 mg, 0.2 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), *t*-butylacetylene (12 mg, 0.15 mmol), TEMPO (16 mg, 0.1 mmol) and a GC standard *n*-dodecane (10 mL) were then added sequentially. The tube was capped tightly and the reaction mixture was heated in an aluminum-heating block at 90 °C for 24 h. At the end of the reaction, the mixture was cooled to rt. Aliquots of the reaction mixture were passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC and GC-MS analysis to determine the conversion of *o*-iodotoluene and calibrated GC yields of products and byproducts.

VII. References

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