Supplementary Information Lipids as Versatile Solvents for Chemical Synthesis

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Table of content:

General considerations	2
Description of oils from grocery	4
Drying and storage of vegetable oils	20
General experimental procedures for optimization of cross-couplings	23
Setup of high-throughput screening	30
Table S1. Suzuki-Miyaura coupling in rapeseed oil from Askim: optimization	39
Table S2. Suzuki-Miyaura coupling in oils: screening of solvents	40
Table S3. Suzuki-Miyaura coupling in rapeseed oil from Askim: screening of electrophiles	41
Table S4. Hiyama coupling in rapeseed oil from Askim: optimization	42
Table S5. Hiyama coupling in oils: screening of solvents	43
Table S6. Hiyama coupling in rapeseed oil from Askim: screening of electrophiles	44
Table S7. Stille coupling in rapeseed oil from Askim: optimization	45
Table S8. Stille coupling in oils: screening of solvents	46
Table S9. Stille coupling in rapeseed oil from Askim: screening of electrophiles	47
Table S10. Sonogashira coupling in rapeseed oil from Askim: optimization	48
Table S11. Sonogashira coupling in oils: screening of solvents	49
Table S12. Sonogashira coupling in oils: optimization for unactivated aryl bromides	50
Table S13. Sonogashira coupling in oils: optimization for aryl chlorides	52
Table S14. Heck coupling in rapeseed oil from Askim: optimization	53
Table S15. Heck coupling in oils: screening of solvents	54
Table S16. Heck coupling in rapeseed oil from Askim: screening of electrophiles	55
General experimental procedures for cross-couplings	56
Production and processing of waste rapeseed oil	67
Characterization of products	70
Copies of spectra	89

General considerations

Commercially available starting materials, reagents, catalysts and anhydrous and degassed solvents were used without further purification. Flash column chromatography was performed with Merck silica gel 60 (230-400 mesh). The solvents for column chromatography were distilled before use (in case of technical solvents). Thin layer chromatography was carried out using Merck TLC Silica gel 60 F₂₅₄ and visualized by short-wavelength ultraviolet light or by treatment with potassium permanganate (KMnO₄) stain. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Bruker Avance 400 MHz at 20 °C. All ¹H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signal for CHCl₃ (7.26 ppm). All ¹³C NMR spectra were reported in ppm relative to residual CDCl₃ (77.20 ppm) and were obtained with ¹H decoupling. Coupling constants, *J*, are reported in Hertz (Hz). High-resolution mass spectra (HRMS) were recorded from methanol solutions on an LTQ Orbitrap XL (Thermo Scientific) either in negative or in positive electrospray ionization (ESI) mode.

Triglycerides, phospholipids and related lipids possess a varying number of internal double bonds. The fact that we could develop highly efficient methodologies for a range of different cross-coupling reactions in vegetable oils, avoiding side processes involving the solvent (including the Heck coupling), is intriguing. The Heck cross-coupling reaction is known to be quite sensitive to steric hindrance, which can be one of the reasons for the efficiency of vegetable oils and related systems as solvents. Thus, control experiments with internal olefins or substituted styrenes, using the best conditions for Heck coupling, provided partial recovery of starting materials and reductive homocoupling of the aryl halide (Scheme 4, **11i**,**j**).

The solvent was not affected in a series of control experiments, where the best conditions for cross-couplings described above were run in rapeseed oil in the presence of only 3,5bis(trifluoromethyl)bromobenzene (**2a**). In all cases, we observed partial recovery of the starting aryl halide alongside the biaryl formed from the reductive homocoupling of the aryl halide. ¹H, ¹³C and ¹⁹F NMR spectra of the solvent before and after the control experiments were identical. As lipids/oils consist of esters, decomposition via saponification is another possible side reaction. In our work saponification was observed only in the presence of water or strong bases such as alkoxides. Considerable amount of saponification is easily detectable, as the liquid phase turns into a wax-like solid when a reaction mixture is cooled. This phenomenon was never seen for anhydrous conditions or bases like carbonates, fluorides, acetates and amines, which are commonly used for cross-coupling reactions, including the present work.

The following oils were bought from Sigma Aldrich and are available worldwide: Rapeseed oil from *Brassica rapa* (CAS: 8002-13-9); Sunflower seed oil from *Helianthus annuus* (CAS: 8001-21-6); Soybean oil from *Glycine max* (CAS: 8001-22-7); Fish oil from menhaden (CAS: 8002-50-4).

The rest of vegetable oils and butter were bought from local groceries (Norway) and are available in Nordic countries (for detailed descriptions see Figures S1-S16). Before use, all oils were treated with anhydrous CaCl₂ powder for 24h (butter and coconut oil were melted during the treatment), which was followed by hot filtration to remove CaCl₂ (along with NaCl in case of butter). The resulting oils were

degased and stored over activated molecular sieves (4Å) under Ar atmosphere (for detailed descriptions see Figures S17-S19).

Natural waxes are commercially available and were bought from the following international suppliers: Carnauba wax No. 1 yellow (Sigma Aldrich, CAS: 8015-86-9); Beeswax (Sigma Aldrich, CAS: 8012-89-3); Lanolin (Alfa Aesar, CAS: 8006-54-0). After the delivery, these waxes were stored under Ar atmosphere.

For the production of waste rapeseed oil, we fried potatoes in virgin rapeseed oil from the brand Coop. Frying was performed under air at 130 °C. After every 2 hours, a portion of waste rapeseed oil was separated and filtered through a short plug of silica gel. Accordingly, we generated four fractions of waste rapeseed oil, which were used for frying potatoes for 2, 4, 6 and 8 hours respectively. Obtained waste rapeseed oils were stored under air and used for Suzuki-Miyaura and Heck cross-couplings without additional tretment. Products obtained in waste rapeseed oils can be isolated using column chromatography. For more details on the production and processing of waste rapeseed oils, see Figures S30-S32.

Monoterpenes used for preparative column chromatography are commercially available and were bought from the following international suppliers: (–)- α -Pinene (Sigma Aldrich, CAS: 7785-26-4, Cat No: <u>W290203-8KG-K</u>); 3-Carene (Sigma Aldrich, CAS: 13466-78-9, Cat No: W382108-4KG</u>); Dipentene (Sigma Aldrich, CAS: 138-86-3, Cat No: 334111-4L); (*R*)-(+)-Limonene (Sigma Aldrich, CAS: 5989-27-5, Cat No: W263303-1KG-K); γ -Terpinene (Sigma Aldrich, CAS: 99-85-4, Cat No: W355909-1KG-K); α -Terpinene (Sigma Aldrich, CAS: 99-86-5, Cat No: W355801-4KG-K); Terpinolene (Sigma Aldrich, CAS: 586-62-9, Cat No: W304603-4KG-K); Sabinene (Sigma Aldrich, CAS: 3387-41-5, Cat No: W530597-1KG-K); Myrcene (Sigma Aldrich, CAS: 123-35-3, Cat No: W276200-1KG-K); α -Phellandrene (Sigma Aldrich, CAS: 99-83-2, Cat No: W285609-1KG-K). Monoterpenes were evaporated before use.

Description of oils from grocery



Figure S1. Rapeseed oils and rapeseed oil from the brand Askim.







Figure S2. Rapeseed oil from the brand Coop.



Figure S3. Rapeseed oil from the brand Odelia.



Figure S4. Rapeseed oil from the brand Rema.



Figure S5. Rapeseed oil from the brand Anglamark.







ND SOLSIKKEOLJE LITT OM VAREN: Innholdet av flerumettede fettsyrer er middels høyt i solsikkeolje. Et godt råd! La ikke oljen bli for sterkt oppvarmet og stek ikke maten for mye. Kast alltid stekoljen. Kan brukes til all slags matlaging, både kald og varm. INGREDIENSER: Raffinert vegetabilsk olje utvunnet av solsikkekjerner. OPBEVARING: Ved romtemperatur. Beskyttet mot lys og varme. PAKKET: 1 år før Best før. BEST FØR: Se øverst på flasken. EMBALLASJE: Sorteres som plast. ORBRUKERKONTAKT: www.coop.no

Figure S6. Sunflower oil.



Figure S7. Olive oil.



Figure S8. Soybean oil.



Figure S9. Corn oil.

COOP TRADING A/S. Fremstillet for/Produsert for Coop Trading A/S. Postiboks 255, DK-2630 Taastrup. PRODUCENT/PRODUSENT: Dielficio Zucchi S.p.A., Italien/Italia.
24230





Figure S10. Avocado oil.



Figure S11. Sesame oil.



Figure S12. Rice bran oil.



Figure S13. Mixture of oils consisting of rapeseed oil (60%), sunflower oil (25%) and olive oil (15%).



INGSINDHOLD/NÄRINGSINNEHÅLL/RAVINTOAR	/OT PR/PER.	100 G:
ai/Energiaa:	3/68 kJ/9001	Kcal
/Fett/Rasvaa:	100 g	
Mættede fedtsyrer/varav mättat fett/ josta tyydyttyneitä rasvahappoja	86,5 g	
Enkeltumættede fedtsyrer/en-umettede fettsyrer/ enkelomättet fett/kertatyydymättömia rasvahappoja	5,5 g	
Flerumættede fedtsyrer/flerumettet fettsyrer/	180	
fleromättade fett/monityydyttymättömiä rasvahappoja	1,0 9 	1
ulhydrat/Kolhydrat/Hiilihydraattia:	09	
heraf sukkerarter/varav sockerarter/	Da	1
josta sokereita:	Og	
lbre/Fibrer/Ravintokuitua:	09	
Protein Proteiinia: Salt/Suolaa;	0 g	
2014 2		

NL-BIO-O1 Ikke-EV-jordbruk Tuotettu EV:n ulkopuolella

Them



DK/ND/SE: ØKOLOGISK/EKOLOGISK KOKOSOLIE/-OLJE/-OLJA, SMAGSNEUTRAL/SMAKSMETTE AK NO/SE: BKOLOGISK/EKOLOGISK, KUKUSOLIE/-OLDE/-OLDA, SMAGSHEUHAL/SMASA MGREDENSER: 100% økologisk, raffineret/raffinert kokosolie/-olje/-olja ANVENDELSE/BRUK/ANVÄNDNING: Green Choice økologisk/ekologisk kokosolie/alje/dja n magneutal/smaksnøytral og fungerer derfor fortrinligt/perfekt/utmärkt til madaming/malagni, komng/bakning og til at stege/å steke i. Kokosolie/olje/olja bliver flydende/flytende ved ä gre PEEVARING/FÖRVARING/OPPBEVARING: Mørkt og køligt. HOLDBARHED/HÅLLBARHET EFTER ÅBNING/ÖPPNANDE: 3 måneder.

R: LUOMU KOOKOSÕLIY, NEUTRAALINMAKUINEN AMESOSAT: 100% luomu, raffinoitu kookosõljy. LÄTTÖ: Einen Choice luomu kookosõljy on maultaan neutraali ja soveltuu siten ruomier akunsaan ja paistamiseen. Kookosõljy muuttuu nestemäiseen muotoon 25 asteessa. SATTYS: kuivassa paikassa, poissa suoralta auringonvalolta. AVATUMA SÄLLYVYYS: 3 kuukautta.

BEDST FØR/BÄST FÖRE/PARASTA ENNEN: Se venligst låget/Se locket/Katso kansi.

en/Netrovikt/Netropaino: **400 g** e

Figure S14. Coconut oil.



Arte. En selvfølge i kjøleskapet. Smaksheveren du sauser, supper, til baking, steking og på brødskiva. smakene. for bruk, for
Q

Figure S15. Butter.



MÖLLER'S TRAN Tran inneholder viktige næringsstoffer, som omega-3 og vitaminer, som hjelper til å holde deg frisk. Omega-3 er essensielle fettsyrer kroppen trenger hele livet og som har en dokumentert positiv virkning på hjerte, hjerne og syn. Möller's tar ingen snarveier når det gjelder kvalitet. Tranen vår lages av norsk arktisk torsk fra Lofoten og Vesterålen og vi jobber kontinuerlig for å gi deg det aller beste for helsen din. Möller's - For hele kroppen. Hele livet. Hjelper til å holde deg frisk! En skje Möller's Tran gir deg 1,2 g naturlige omega-3 fettsyrer fra fisk og vitamin A, D og E, Fettsyrene EPA og DHA bidrar til hjertets normale funksjon*. Vitamin D bidrar til Immunsystemets normale funksjon. Vitamin D bidrar til immunsystemets normale funksjon. Vitamin A bidrar til å opprettholde normalt syn og til immunsystemets normale funksjon. Vitamin A bidrar til å opprettholde normale av Og til immunsystemets normale funksjon. Vitamin & bidrar til å beskytte cellene mot oksidativt stress. Støtter god utvikling Möller's tran er spesielt rik på DHA. DHA bidrar til å opprettholde normal hjernefunksjon og syn**. Vitamin D er nødvendig for at barns bein skal vokse og utvikles normalt. * Gunstig effekt oppnås ved et daglig inntak av 250 mg EPA og DHA ** Gunstig effekt oppnås ved et daglig inntak av 250 mg DHA ^{Anbefalt} dagsdose for barn fra 3 år og voksne: 5 ml ega-3-fettsyrer totalt 1,2 g Ingredienser: Tran, dl-α-tokoferylacetat (vitamin E), antioksidant (Dokosaheksaensyre) 0,6 g (Eikosapentaensyre) 0,4 g (tokoferolrik ekstrakt). 10 µg (200%*) 250 µg (31%*) 500 ml 3 mg (25%*) dagsdose bør ikke overskrides nes utilgen bler brei oversidnoss udd erstendelig for barn. udd erstatter ikke et variert kosthold. tike ber lagres kjelig i maks 3 måneder beskyttende atmosfære. Orkla (800 80 555 mollers.no 11.2020 09:54 84442273

Figure S16. Fish oil.

Drying and storage of vegetable oils



Figure S17. Treatment of oils with anhydrous CaCl₂ powder.



Figure S18. Hot filtration of corn oil from CaCl₂.



Figure S19. Degased oils over activated molecular sieves (4Å) and under Ar atmosphere.

General experimental procedures for optimization of cross-couplings

Optimization of Suzuki-Miyaura coupling in rapeseed oil from Askim. For general setup, see Figures S20-S27.



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with 4-tolylboronic acid (1 equiv., 0.368 mmol), corresponding Pd-complex (0.4-5 mol%), ligand (0-12 mol%) and the base (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (2 mL), corresponding additive (0-0.3 mL) and 3,5-bis(trifluoromethyl)bromobenzene (1.5 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 20-110 °C for 6-24 h. Afterwards, the reaction mixture was cooled down, which was followed by addition of 1,3,5-trimethoxybenzene (1 equiv., internal standard), 20 drops of CHCl₃ and 2 mL of CDCl₃ (or CCl₄). The resulting mixture was thoroughly shaked for 2 minutes than centrifuged. This was followed by NMR analysis of an aliquot taken from the resulting mixture.

Screening of solvents for Suzuki-Miyaura coupling. For general setup, see Figures S20-S27.



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with 4-tolylboronic acid (1 equiv., 0.368 mmol), Pd(PPh₃)₄ (5 mol%) and CsF (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added corresponding solvent (2 mL)¹ and 3,5-bis(trifluoromethyl)bromobenzene (1.5 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 80-90 °C for 6 h. Afterwards, the reaction mixture was cooled down, which was followed by addition of 1,3,5-trimethoxybenzene (1 equiv., internal standard), 20 drops of CHCl₃ and 2 mL² of CDCl₃ (or CCl₄). In case of 2MeTHF, acetal, dioxane, toluene or DMF, the solvent was evaporated before addition of the internal standard and chloroform. The resulting mixture was thoroughly shaked for 2 minutes than centrifuged. This was followed by NMR analysis of an aliquot taken from the resulting mixture.

¹ Beeswax and Carnauba wax where weighed inside of glove box like other solids (2g). Lanolin, Butter and coconut oil were melted before addition (80 °C). In general, vegetable oils are viscous liquids. The transfer of vegetable oils from the main container into the reaction vessel with the syringe can be greatly facilitated by heating the oil to 50-80 °C.

² In case of Beeswax and Carnauba wax, the mixture was diluted with 6 mL of CDCl₃ (CCl₄).

Screening of electrophiles for Suzuki-Miyaura coupling. For general setup, see Figures S20-S27.



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with 4-tolylboronic acid (1 equiv., 0.368 mmol), Pd₂dba₃ (2 mol%), DavePhos (8 mol%) and CsF (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (2 mL) and corresponding aryl halide/sulfonate ester³ (1.5 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 80 °C for 24 h. Afterwards, the reaction mixture was cooled down, which was followed by addition of 1,3,5-trimethoxybenzene (1 equiv., internal standard), 20 drops of CHCl₃ and 2 mL of CDCl₃ (or CCl₄). The resulting mixture was thoroughly shaked for 2 minutes than centrifuged. This was followed by NMR analysis of an aliquot taken from the resulting mixture.

Optimization of Hiyama coupling in rapeseed oil from Askim. For general setup, see Figures S20-S27.



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with corresponding Pd-complex (0.4-4 mol%), ligand (0-10 mol%) and the base (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (2 mL), corresponding additive (0-0.2 mL), phenyltriethoxysilane (1 equiv., 0.333 mmol) and 3,5-bis(trifluoromethyl)bromobenzene (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 20-110 °C for 6-24 h. Afterwards, the reaction mixture was cooled down, which was followed by addition of 1,3,5-trimethoxybenzene (1 equiv., internal standard), 20 drops of CHCl₃ and 2 mL of CDCl₃ (or CCl₄). The resulting mixture was thoroughly shaked for 2 minutes than centrifuged. This was followed by NMR analysis of an aliquot taken from the resulting mixture.

Screening of solvents for Hiyama coupling. For general setup, see Figures S20-S27.



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with $Pd(OAc)_2$ (4 mol%), Ad₂BuPHI (10 mol%) and TBAFx3H₂O (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added corresponding solvent (2 mL),¹ phenyltriethoxysilane (1 equiv., 0.333 mmol) and 3,5-

³ Solid electrophiles were weighed in the glove box.

bis(trifluoromethyl)bromobenzene (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 80-90 °C for 24 h. Afterwards, the reaction mixture was cooled down, which was followed by addition of 1,3,5-trimethoxybenzene (1 equiv., internal standard), 20 drops of CHCl₃ and 2 mL² of CDCl₃ (or CCl₄). In case of 2MeTHF, acetal, dioxane, toluene or DMF, the solvent was evaporated before addition of the internal standard and chloroform. The resulting mixture was thoroughly shaked for 2 minutes than centrifuged. This was followed by NMR analysis of an aliquot taken from the resulting mixture.

Screening of electrophiles for Hiyama coupling. For general setup, see Figures S20-S27.



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with $Pd(OAc)_2$ (4 mol%), Ad₂BuPHI (10 mol%) and TBAFx3H₂O (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (2 mL), trimethoxy(*p*-tolyl)silane (1 equiv., 0.471 mmol) and corresponding aryl halide/sulfonate ester³ (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 80 °C for 24 h. Afterwards, the reaction mixture was cooled down, which was followed by addition of 1,3,5-trimethoxybenzene (1 equiv., internal standard), 20 drops of CHCl₃ and 2 mL of CDCl₃ (or CCl₄). The resulting mixture was thoroughly shaked for 2 minutes than centrifuged. This was followed by NMR analysis of an aliquot taken from the resulting mixture.

Optimization of Stille coupling in rapeseed oil from Askim. For general setup, see Figures S20-S27.



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with corresponding Pd-complex (0.5-2 mol%), ligand (2-8 mol%), CuI (0-4 mol%) and the base (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (2 mL), absolute ethanol (0-0.3 mL), tributylphenylstannane (1 equiv., 0.545 mmol) and 3,5-bis(trifluoromethyl)bromobenzene (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 20-100 °C for 6-24 h. Afterwards, the reaction mixture was cooled down, which was followed by addition of 1,2,4,5-tetramethylbenzene (1 equiv., internal standard), 20 drops of CHCl₃ and 2 mL of CDCl₃ (or CCl₄). The resulting mixture was thoroughly shaked for 2 minutes than centrifuged. This was followed by NMR analysis of an aliquot taken from the resulting mixture.

Screening of solvents for Stille coupling. For general setup, see Figures S20-S27.



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with Pd_2dba_3 (2 mol%), AsPh₃ (8 mol%) and CsF (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added corresponding solvent (2 mL),¹ tributylphenylstannane (1 equiv., 0.545 mmol) and 3,5-bis(trifluoromethyl)bromobenzene (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 100 °C for 6 h. Afterwards, the reaction mixture was cooled down, which was followed by addition of 1,2,4,5-tetramethylbenzene (1 equiv., internal standard), 20 drops of CHCl₃ and 2 mL² of CDCl₃ (or CCl₄). In case of 2MeTHF, acetal, dioxane, toluene or DMF, the solvent was evaporated before addition of the internal standard and chloroform. The resulting mixture was thoroughly shaked for 2 minutes than centrifuged. This was followed by NMR analysis of an aliquot taken from the resulting mixture.

Screening of electrophiles for Stille coupling. For general setup, see Figures S20-S27.



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with Pd₂dba₃ (2 mol%), XPhos (8 mol%) and CsF (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (2 mL), 2-(tributylstannyl)thiophene (1 equiv., 0.536 mmol) and corresponding aryl halide/sulfonate ester³ (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 100 °C for 24 h. Afterwards, the reaction mixture was cooled down, which was followed by addition of 1,2,4,5-tetramethylbenzene (1 equiv., internal standard), 20 drops of CHCl₃ and 2 mL of CDCl₃ (or CCl₄). The resulting mixture was thoroughly shaked for 2 minutes than centrifuged. This was followed by NMR analysis of an aliquot taken from the resulting mixture.

Optimization of Sonogashira coupling in rapeseed oil from Askim. For general setup, see Figures S20-S27.



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with corresponding Pd-complex (0.75-3 mol%), ligand (0-6 mol%), CuI (0-5 mol%), phenylacetylene (1 equiv., 0.783 mmol, degassed), 3,5-bis(trifluoromethyl)bromobenzene (1.5 equiv., degassed), rapeseed oil from Askim (2 mL, degassed) and DIPEA (1.5 equiv., degassed). The flask was sealed with a rubber septa, removed

from the glove box and stirred at 20-80 °C for 6-24 h. Afterwards, the reaction mixture was cooled down, which was followed by addition of 1,3,5-trimethoxybenzene (0.5 equiv., internal standard), 20 drops of CHCl₃ and 2 mL of CDCl₃ (or CCl₄). The resulting mixture was thoroughly shaked for 2 minutes than centrifuged. This was followed by NMR analysis of an aliquot taken from the resulting mixture.

Screening of solvents for Sonogashira coupling. For general setup, see Figures S20-S27.



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with Pd₂dba₃ (0.75 mol%), XantPhos (2 mol%), CuI (5 mol%), phenylacetylene (1 equiv., 0.783 mmol, degassed), 3,5bis(trifluoromethyl)bromobenzene (1.5 equiv., degassed), corresponding solvent (2 mL, degassed)¹ and DIPEA (1.5 equiv., degassed). The flask was sealed with a rubber septa, removed from the glove box and stirred at 80-90 °C for 6 h. Afterwards, the reaction mixture was cooled down, which was followed by addition of 1,3,5-trimethoxybenzene (0.5 equiv., internal standard), 20 drops of CHCl₃ and 2 mL² of CDCl₃ (or CCl₄). In case of 2MeTHF, acetal, dioxane, toluene or DMF, the solvent was evaporated before addition of the internal standard and chloroform. The resulting mixture was thoroughly shaked for 2 minutes than centrifuged. This was followed by NMR analysis of an aliquot taken from the resulting mixture.

Optimization of Sonogashira coupling for unactivated aryl halides. For general setup, see Figures S20-S27.



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with corresponding Pd-complex (2-5 mol%), ligand (0-8 mol%), CuI (5 mol%), 4-ethynyltoluene (1 equiv., 0.689 mmol, degassed), 4-bromoanisole (1.5 equiv., degassed), rapeseed oil from Askim (2 mL, degassed) and appropriate base (1.5 equiv., degassed). The flask was sealed with a rubber septa, removed from the glove box and stirred at 80 °C for 24 h. Afterwards, the reaction mixture was cooled down, which was followed by addition of 1,3,5-trimethoxybenzene (0.5 equiv., internal standard), 20 drops of CHCl₃ and 2 mL of CDCl₃ (or CCl₄). The resulting mixture was thoroughly shaked for 2 minutes than centrifuged. This was followed by NMR analysis of an aliquot taken from the resulting mixture.

Optimization of Heck coupling in rapeseed oil from Askim. For general setup, see Figures S20-S27.



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with corresponding Pd-complex (0.5-5 mol%), ligand (0-12 mol%) and the base (2 equiv.).⁴ The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (3 mL), 4-methylstyrene (1 equiv., 0.846 mmol) and 3,5-bis(trifluoromethyl)bromobenzene (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 80-140 °C for 24-48 h. Afterwards, the reaction mixture was cooled down, which was followed by addition of methyl 3,5-dinitrobenzoate (0.5 equiv., internal standard), 20 drops of CHCl₃ and 3 mL of CDCl₃ (or CCl₄). The resulting mixture was thoroughly shaked for 2 minutes than centrifuged. This was followed by NMR analysis of an aliquot taken from the resulting mixture.

Screening of solvents for Heck coupling. For general setup, see Figures S20-S27.



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with Pd₂dba₃ (0.5 mol%), tBu₃PHBF₄ (2 mol%) and Bu₄NOAc (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added mL),¹ 4-methylstyrene (1 corresponding solvent (3 equiv., 0.846 mmol) and 3.5bis(trifluoromethyl)bromobenzene (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 120 °C for 30 h. Afterwards, the reaction mixture was cooled down, which was followed by addition of methyl 3,5-dinitrobenzoate (0.5 equiv., internal standard), 20 drops of CHCl₃ and 3 mL² of CDCl₃ (or CCl₄). In case of 2MeTHF, acetal, dioxane, toluene or DMF, the solvent was evaporated before addition of the internal standard and chloroform. The resulting mixture was thoroughly shaked for 2 minutes than centrifuged. This was followed by NMR analysis of an aliquot taken from the resulting mixture.

Screening of electrophiles for Heck coupling. For general setup, see Figures S20-S27.



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with Pd₂dba₃ (0.5-2 mol%), corresponding ligand (2-8 mol%) and Bu₄NOAc (2 equiv.). The flask was sealed with a rubber

⁴ Liquid bases were added outside of the glove box following the addition of rapeseed oil.

septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (3 mL), 4-methylstyrene (1 equiv., 0.846 mmol) and corresponding aryl halide/sulfonate ester³ (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 120 °C for 30 h. Afterwards, the reaction mixture was cooled down, which was followed by addition of methyl 3,5-dinitrobenzoate (0.5 equiv., internal standard), 20 drops of CHCl₃ and 3 mL of CDCl₃ (or CCl₄). The resulting mixture was thoroughly shaked for 2 minutes than centrifuged. This was followed by NMR analysis of an aliquot taken from the resulting mixture.

Setup of high-throughput screening



Figure S20. Charging of reaction vials with solid reactants and catalyst in the glove box.



Figure S21. Addition of vegetable oil and liquid reaction components.



Figure S22. Stirring of the reaction mixture at appropriate temperature.



Figure S23. Addition of an internal standard to the reaction mixture at room temperature.



Figure S24. Addition of 20 drops of CHCl₃ and CDCl₃ (or CCl₄).



Figure S25. Shaking of the reaction mixture to dissolve all organic matter.



Figure S26. Centrifugation to precipitate inorganic matter.


Figure S27. Taking an aliquot for crude ¹H NMR analysis.



Figure S28. Miscibility of rapeseed oil with common organic solvents.

Me OH +		Br CF ₃	Catalyst (mol%), Ligand (mol%), Base (equiv.) Rapeseed oil (Askim), Additive, °C, h		CF ₃ CF ₃		
Entry	Catalyst (mol%)	Ligand (mol%)	Base (equiv.)	Additive (mL)	°C, h	Yield % ^a	
1	$Pd_2dba_3(2)$	XPhos (8)	$K_2CO_3(2)$	-	80, 24	60	
2	Pd ₂ dba ₃ (2)	tBuXPhos (8)	K ₂ CO ₃ (2)	-	80, 24	33	
3	$Pd_2dba_3(2)$	DavePhos (8)	K ₂ CO ₃ (2)	_	80, 24	82	
4	$Pd_2dba_3(2)$	DavePhos (8)	CsF (2)	_	80, 24	100	
5	$Pd_2dba_3(2)$	SPhos (8)	K ₂ CO ₃ (2)	_	80, 24	77	
6	$Pd_2dba_3(2)$	BrettPhos (8)	K ₂ CO ₃ (2)	-	80, 24	80	
7	$Pd_2dba_3(2)$	RuPhos (8)	K ₂ CO ₃ (2)	-	80, 24	63	
8	XPhos Pd G3 (0.4)	XPhos (0.4)	K ₂ CO ₃ (2)	-	80, 24	63	
9	$Pd_2dba_3(2)$	XantPhos (4)	K ₂ CO ₃ (2)	-	80, 24	58	
10	$Pd_2dba_3(2)$	Ad ₂ BuPHI (8)	K ₂ CO ₃ (2)	-	80, 24	37	
11	$Pd(OAc)_2(3)$	tBu ₃ PHBF ₄ (6)	K ₂ CO ₃ (2)	-	80, 24	57	
12	[PdCl(allyl)] ₂ (2)	IPrHCl (5)	K ₂ CO ₃ (2)	-	80, 24	8	
13	$Pd_2dba_3(2)$	$AsPh_3(8)$	K ₂ CO ₃ (2)	-	80, 24	67	
14	$Pd(OAc)_2(3)$	P(2-furyl) ₃ (12)	K ₂ CO ₃ (2)	-	80, 24	82	
15	$Pd(PPh_3)_4(5)$	-	K ₂ CO ₃ (2)	-	80, 24	90	
16	$Pd(PPh_3)_4(5)$	-	$K_2CO_3(2)$	-	110, 24	89	
17	$Pd(PPh_3)_4(5)$	-	$K_2CO_3(2)$	-	20, 24	0	
18	Pd(PPh ₃) ₄ (2.5)	-	K ₂ CO ₃ (2)	-	80, 24	78	
19	$Pd(PPh_3)_4(5)$	-	$K_2CO_3(2)$	EtOH (0.3)	80, 24	100	
20	$Pd(PPh_3)_4(5)$	-	$K_2CO_3(2)$	EtOH (0.3)	20, 24	100	
21	$Pd(PPh_3)_4(5)$	-	$K_{2}CO_{3}(2)$	EtOH (0.3)	80, 6	100	
22	$Pd(PPh_3)_4(5)$	-	$K_2CO_3(2)$	EtOH (0.1)	80, 6	89	
23	$Pd(PPh_3)_4(5)$	-	$K_2CO_3(2)$	EtOH (0.3)	20, 6	34	
24	Pd(PPh ₃) ₄ (2.5)	-	$K_2CO_3(2)$	EtOH (0.3)	20, 24	48	
25	$Pd(PPh_3)_4(5)$	-	$K_2CO_3(2)$	Glycerol (0.3)	80, 24	60	
26	$Pd(PPh_3)_4(5)$	-	K ₃ PO ₄ (2)	-	80, 24	67	
27	$Pd(PPh_3)_4(5)$	-	Bu ₄ NOAc (2)	-	80, 24	0	
28	$Pd(PPh_3)_4(5)$	-	$Cs_2CO_3(2)$	-	80, 24	92	
29	$Pd(PPh_3)_4(5)$	-	CsOAc (2)	-	80, 24	83	
30	$Pd(PPh_3)_4(5)$	-	CsF (2)	-	80, 24	100	
31	$Pd(PPh_3)_4(5)$	-	CsF (2)	-	80, 6	100/92 ^b	

Table S1. Suzuki-Miyaura coupling in rapeseed oil from Askim: optimization

^a Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard. ^b Isolated yield.

Table S2. Suzuki-Miyaura coupling in oils: screening of solvents



^a Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard. ^b Isolated yield. ^c The reaction was performed in the presence of DavePhos/Pd₂dba₃-based catalytic system. ^d The reaction was performed at 90 °C.



Table S3. Suzuki-Miyaura coupling in rapeseed oil from Askim: screening of electrophiles

^a Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard. ^b Isolated yield.

	Si(OEt) ₃ +	CF ₃ CF ₃ Ca L CF ₃ CF ₃ Ca	atalyst (mol%), igand (mol%), Additive (mL) Base (equiv.), eseed oil (Askim), °C, h		CF ₃ CF ₃	
Entry	Catalyst (mol%)	Ligand (mol%)	Base (2 equiv.)	Additive (mL)	°C, h	Yield % ^a
1	$Pd_2dba_3(2)$	XPhos (10)	TBAFx3H ₂ O	-	80, 24	72
2	$Pd(OAc)_2(4)$	XPhos (10)	TBAFx3H ₂ O	-	80, 24	60
3	$Pd(OAc)_2(4)$	XPhos (10)	TBAFx3H ₂ O	-	80, 24	58 ^b
4	$Pd(OAc)_2(4)$	XPhos (10)	TBAFx3H ₂ O	MS 4 Å ^c	80, 24	32
5	$Pd_2dba_3(2)$	tBuXPhos (10)	TBAFx3H ₂ O	-	80, 24	69
6	$Pd_2dba_3(2)$	DavePhos (10)	TBAFx3H ₂ O	-	80, 24	65
7	$Pd_2dba_3(2)$	SPhos (10)	TBAFx3H ₂ O	-	80, 24	80
8	$Pd_2dba_3(2)$	BrettPhos (10)	TBAFx3H ₂ O	-	80, 24	51
9	$Pd_2dba_3(2)$	RuPhos (10)	TBAFx3H ₂ O	-	80, 24	60
10	tBuXPhos Pd G3 (0.4)	tBuXPhos (0.4)	TBAFx3H ₂ O	-	80, 24	20
11	$Pd_2dba_3(2)$	XantPhos (5)	TBAFx3H ₂ O	-	80, 24	44
12	$Pd_2dba_3(2)$	<i>t</i> Bu ₃ PHBF ₄ (10)	TBAFx3H ₂ O	-	80, 24	57
13	$Pd_2dba_3(2)$	tBu ₂ MePHBF ₄ (10)	TBAFx3H ₂ O	-	80, 24	46
14	$Pd_2dba_3(2)$	Ad ₂ BuPHI (10)	TBAFx3H ₂ O	-	80, 24	93
15	$Pd(OAc)_2(4)$	Ad ₂ BuPHI (10)	TBAFx3H ₂ O	-	80, 24	96/79 ^d
16	$Pd(OAc)_2(4)$	DABCO (8)	TBAFx3H ₂ O	-	80, 24	62
17	$Pd(OAc)_2(4)$	IPrHCl (4)	TBAFx3H ₂ O	-	80, 24	60
18	$PdCl_2[P(o-Tol)_3]_2(4)$	-	TBAFx3H ₂ O	-	80, 24	36
19	$Pd(OAc)_2(4)$	Ad ₂ BuPHI (10)	TBAFx3H ₂ O	-	110, 24	60
20	$Pd(OAc)_2(2)$	$Ad_2BuPHI(5)$	TBAFx3H ₂ O	-	80, 24	89
21	$Pd(OAc)_2(4)$	Ad ₂ BuPHI (10)	TBAFx3H ₂ O	EtOH (0.2)	80, 24	97
22	$Pd(OAc)_2(4)$	Ad ₂ BuPHI (10)	TBAFx3H ₂ O	EtOH (0.2)	20, 24	0
23	$Pd(OAc)_2(4)$	Ad ₂ BuPHI (10)	TBAFx3H ₂ O	EtOH (0.2)	80, 6	90
24	$Pd(OAc)_2(4)$	XPhos (10)	TBAFx3H ₂ O	EtOH (0.2)	80, 24	99/90 ^d
25	$Pd(OAc)_2$ (4)	XPhos (10)	TBAFx3H ₂ O	EtOH (0.1)	80, 24	89
26	$Pd(OAc)_2(4)$	XPhos (10)	TBAFx3H ₂ O	Glycerol (0.2)	80, 24	20
27	$Pd(OAc)_2(4)$	XPhos (10)	CsF	-	80, 24	0
28	$Pd(OAc)_2(4)$	XPhos (10)	CsF/TBAB (0.5)	-	80, 24	9

Table S4. Hiyama coupling in rapeseed oil from Askim: optimization

^a Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard. ^b Silane used in 2 equiv.. ^c 80 mg. ^d Isolated yield.

Table S5. Hiyama coupling in oils: screening of solvents

Br

CF₃

 CF_3









Entry	Solvent (2 mL)	Yield % ^a
1	Triacetin	93
2	Tributyrin	96
3	Rapeseed oil (Askim)	96/79 ^b
4	Rapeseed oil (Coop)	86
5	Rapeseed oil (Odelia)	93
6	Rapeseed oil (Rema)	86
7	Rapeseed oil (Anglamark)	92
8	Rapeseed oil (Sigma)	86
9	Sunflower oil	86
10	Sunflower oil (Sigma)	72/88 ^c
11	Olive oil	84
12	Soybean oil	93
13	Soybean oil (Sigma)	82
14	Corn oil	93
15	Avocado oil	91
16	Sesame oil	74/92 ^c
17	Rice bran oil	79
18	Mixture of oils	85
19	Coconut oil	78
20	Butter	88
21	Fish oil	88
22	Fish oil (Sigma)	92
23	Carnauba wax No. 1 yellow	100 ^d
24	Beeswax, refined	86
25	Lanolin	79
26	2MeTHF	98
27	Acetal	85
28	Dioxane	88
29	Toluene	91
30	DMF	67

^a Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard. ^b Isolated yield. ^c The reaction was performed in the presence of ethanol (0.2 mL). ^d The reaction was performed at 90 °C.





^a Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard.

	SnBu ₃ +	Br Cl CF ₃	F ₃ Catal <u>y</u> Ligar <u>Additive</u> Bas Rapesee	yst (mol%), nd (mol%), <u>e (mol%/mL)</u> e (equiv.), ed oil (Askim), °C, h	CF ₃	CF3
Entry	Catalyst (mol%)	Ligand (mol%)	Base (2 equiv.)	Additive	°C, h	Yield % ^a
1	$Pd_2dba_3(2)$	XPhos (8)	KF	-	100, 24	98
2	$Pd_2dba_3(2)$	XPhos (8)	TBAFx3H ₂ O	-	100, 24	89
3	$Pd_2dba_3(2)$	XPhos (8)	CsF	-	100, 24	99
4	$Pd_2dba_3(2)$	XPhos (8)	K ₂ CO ₃	-	100, 24	95
5	$Pd_2dba_3(2)$	XPhos (8)	Cs ₂ CO ₃	-	100, 24	84
6	$Pd(OAc)_2(2)$	XPhos (3)	CsF	-	100, 24	93
7	$Pd(OAc)_2(2)$	XPhos (3)	CsF	EtOH (0.3 mL)	100, 24	97
8	$Pd_2dba_3(2)$	tBuXPhos (8)	CsF	-	100, 24	4
9	$Pd_2dba_3(2)$	DavePhos (8)	CsF	-	100, 24	100
10	$Pd_2dba_3(2)$	SPhos (8)	CsF	-	100, 24	91
11	$Pd_2dba_3(2)$	BrettPhos (8)	CsF	-	100, 24	95
12	$Pd_2dba_3(2)$	RuPhos (8)	CsF	-	100, 24	95
13	$Pd_2dba_3(2)$	XantPhos (5)	CsF	-	100, 24	100
14	Pd ₂ dba ₃ (1.5)	Ad ₂ BuPHI (8)	CsF	-	100, 24	90
15	$Pd_2dba_3(2)$	$tBu_3PHBF_4(8)$	CsF	-	100, 24	37
16	$Pd_2dba_3(2)$	$tBu_3PHBF_4(8)$	CsF	CuI (4 mol%)	100, 24	1
17	$Pd_2dba_3(2)$	<i>t</i> Bu ₃ PHBF ₄ (8)	CsF	CuI (4 mol%)/EtOH (0.3 mL)	100, 24	68
18	$Pd(OAc)_2(2)$	IPrHCl (3)	CsF	-	100, 24	98
19	$Pd_2dba_3(2)$	P(2-furyl) ₃ (8)	CsF	-	100, 24	98
20	$Pd_2dba_3(2)$	AsPh ₃ (8)	CsF	-	100, 24	99
21	$Pd_2dba_3(2)$	$AsPh_3(8)$	CsF	-	20, 24	16
22	$Pd_2dba_3(2)$	AsPh ₃ (8)	CsF	-	100, 6	100/99 ^b
23	Pd_2dba_3 (0.5)	AsPh ₃ (2)	CsF	-	100, 6	92

Table S7. Stille coupling in rapeseed oil from Askim: optimization

^a Yields determined by ¹H NMR using 1,2,4,5-tetramethylbenzene as internal standard. ^b Isolated yield.

Table S8. Stille coupling in oils: screening of solvents



^a Yields determined by ¹H NMR using 1,2,4,5-tetramethylbenzene as internal standard. ^b Isolated yield.

Table S9. Stille coupling in rapeseed oil from Askim: screening of electrophiles



^a Yields determined by ¹H NMR using 1,2,4,5-tetramethylbenzene as internal standard. ^b Isolated yields.

	Br	CF ₃ F	Catalyst (mol%), Ligand (mol%), Additive (mol%) Base (equiv.), Capeseed oil (Askim), °C, h		=-{	
Entry	Catalyst (mol%)	Ligand (mol%)	Additive (mol%)	Base (equiv.)	°C, h	Yield % ^a
1	Pd_2dba_3 (1.5)	XPhos (6)	CuI (5)	DIPEA (1.5)	80, 24	57
2	$Pd_2dba_3(1.5)$	tBuXPhos (6)	CuI (5)	DIPEA (1.5)	80, 24	73
3	Pd ₂ dba ₃ (1.5)	DavePhos (6)	CuI (5)	DIPEA (1.5)	80, 24	27
4	Pd_2dba_3 (1.5)	SPhos (6)	CuI (5)	DIPEA (1.5)	80, 24	8
5	Pd_2dba_3 (1.5)	BrettPhos (6)	CuI (5)	DIPEA (1.5)	80, 24	73
6	Pd ₂ dba ₃ (1.5)	RuPhos (6)	CuI (5)	DIPEA (1.5)	80, 24	11
7	Pd_2dba_3 (1.5)	tBu_3PHBF_4 (6)	CuI (5)	DIPEA (1.5)	80, 24	21
8	Pd_2dba_3 (1.5)	$Ad_2BuP(6)$	CuI (5)	DIPEA (1.5)	80, 24	23
9	Pd_2dba_3 (1.5)	XantPhos (4)	CuI (5)	DIPEA (1.5)	80, 24	100
10	Pd ₂ dba ₃ (0.75)	XantPhos (2)	CuI (5)	DIPEA (1.5)	80, 6	100/86 ^b
11	Pd ₂ dba ₃ (1.5)	XantPhos (4)	CuI (5)	DIPEA (1.5)	20, 24	100
12	$PdCl_2(PPh_3)_2(3)$	-	CuI (5)	DIPEA (1.5)	80, 24	99/96 ^b
13	$PdCl_2(PPh_3)_2(3)$	-	CuI (5)	DIPEA (1.5)	20, 24	98
14	$PdCl_2(PPh_3)_2(3)$	-	CuI (5)	DIPEA (1.5)	20, 6	36
15	$PdCl_2(PPh_3)_2(3)$	-	CuI (5)	DIPEA (1.5)	80, 6	98
16	$PdCl_{2}(PPh_{3})_{2}(1.5)$	-	CuI (5)	DIPEA (1.5)	20, 24	89
17	PdCl ₂ (PPh ₃) ₂ (1.5)	-	CuI (5)	DIPEA (1.5)	80, 6	96
18	$PdCl_2(PPh_3)_2(3)$	-	-	DIPEA (1.5)	80, 24	91
19	Pd_2dba_3 (1.5)	$Ad_2BuP(6)$	-	DIPEA (1.5)	80, 24	24
20	Pd ₂ dba ₃ (1.5)	tBu ₃ PHBF ₄ (6)	-	DIPEA (1.5)	80, 24	44
21	$Pd_2dba_3(1.5)$	XPhos (6)	-	DIPEA (1.5)	80, 24	63
22	$Pd_{2}dba_{3}(1.5)$	XantPhos (4)	-	DIPEA (1.5)	80, 24	45

Table S10. Sonogashira coupling in rapeseed oil from Askim: optimization

^a Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard. ^b Isolated yield.



ĊF₃

Br

.CF₃



Pd₂dba₃ (0.75 mol%), XantPhos (2 mol%), Cul (5 mol%) DIPEA (1.5 equiv.), **Solvent**, 80°C, 6h



Entry	Solvent (2 mL)	Yield % ^a
1	Triacetin	100
2	Tributyrin	100
3	Rapeseed oil (Askim)	100/86 ^b
4	Rapeseed oil (Coop)	100
5	Rapeseed oil (Odelia)	100
6	Rapeseed oil (Rema)	100
7	Rapeseed oil (Anglamark)	100
8	Rapeseed oil (Sigma)	100
9	Sunflower oil	100
10	Sunflower oil (Sigma)	100
11	Olive oil	100
12	Soybean oil	100
13	Soybean oil (Sigma)	100
14	Corn oil	100
15	Avocado oil	99
16	Sesame oil	100
17	Rice bran oil	100
18	Mixture of oils	100
19	Coconut oil	100
20	Butter	100
21	Fish oil	100
22	Fish oil (Sigma)	100
23	Carnauba wax No. 1 yellow	100 ^c
24	Beeswax, refined	99
25	Lanolin	99
26	2MeTHF	100
27	Acetal	97
28	Dioxane	100
29	Toluene	96
30	DMF	95

^a Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard. ^b Isolated yield. ^c The reaction was performed at 90 °C.

Table S12. Sonogashira	coupling in	oils: of	ptimization	for unactivated	aryl bromides







Entry	Catalyst (mol%)	Ligand (mol%)	Base	Yield % ^a
1	$Pd_2dba_3(2)$	XantPhos (5)	DIPEA	28
2	$Pd_2dba_3(2)$	XantPhos (5)	TEA	59
3	$Pd_2dba_3(2)$	XantPhos (5)	Cy ₂ NMe	67
4	$Pd_2dba_3(2)$	XantPhos (5)	Bu4NOAc	51
5	$Pd_2dba_3(2)$	XantPhos (5)	Cs ₂ CO ₃	61
6	$Pd_2dba_3(2)$	<u>DPEPhos</u> (5)	Cy ₂ NMe	29
7	$Pd_2dba_3(2)$	<u>tBu-Xantphos</u> (5)	Cy ₂ NMe	0
8	$Pd_2dba_3(2)$	<u>N-XantPhos</u> (5)	Cy ₂ NMe	25
9	$Pd_2dba_3(2)$	<u>dppBz</u> (5)	Cy ₂ NMe	0
10	$Pd_2dba_3(2)$	<u>dppf</u> (5)	Cy ₂ NMe	27
11	$Pd_2dba_3(2)$	<u>dippf</u> (5)	Cy ₂ NMe	21
12	$Pd_2dba_3(2)$	<u>1-Diphenylphosphino-1'-(di-tert-</u> <u>butylphosphino)ferrocene</u> (5)	Cy ₂ NMe	18
13	$Pd_2dba_3(2)$	<u>dppb</u> (5)	Cy ₂ NMe	0
14	XantPhos Pd G3 (4)	-	Cy ₂ NMe	47
15	$\underline{PdCl_2(dtbpf)}(4)$	-	Cy ₂ NMe	13
16	$Pd_2dba_3(2)$	XPhos (8)	Cy ₂ NMe	31
17	$Pd_2dba_3(2)$	tBuXPhos (8)	Cy ₂ NMe	46
18	$Pd_2dba_3(2)$	BrettPhos (8)	Cy ₂ NMe	36
19	$Pd_2dba_3(2)$	Ad ₂ BuPHI (8)	Cy ₂ NMe	14
20	$Pd_2dba_3(2)$	tBu_3PHBF_4 (8)	Cy ₂ NMe	0
21	$PdCl_2(PPh_3)_2(5)$	-	Cy ₂ NMe	34
22	$Pd_2dba_3(2)$	XantPhos (5)	<u><i>i</i>PrN(Me)<i>t</i>Bu</u>	53
23	$Pd_2dba_3(2)$	XantPhos (5)	2-(Diethylamino)ethanol	58
24	$Pd_2dba_3(2)$	XantPhos (5)	<u>Triethanolamine</u>	61
25	$Pd_2dba_3(2)$	XantPhos (5)	<u>Hexamethyldisilazane</u>	8
26	$Pd_2dba_3(2)$	XantPhos (5)	<u>TMEDA</u>	88
27	$Pd_2dba_3(2)$	XantPhos (5)	2,6-Lutidine	0
28	$Pd_2dba_3(2)$	XantPhos (5)	DMAP	57
29	$Pd_2dba_3(2)$	XantPhos (5)	2,2,6,6-Tetramethylpiperidine	87
30	$Pd_2dba_3(2)$	XantPhos (5)	<u>Pempidine</u>	77
31	$Pd_2dba_3(2)$	XantPhos (5)	1,1,3,3-Tetramethylguanidine	66
32	$Pd_2dba_3(2)$	XantPhos (5)	DBU	100

33	$Pd_2dba_3(2)$	XantPhos (5)	TBD	61

^a Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard.

Me	+ CI + CI CI CI CI CI CI CI CI CI CI	Me-	OMe
Entry	Catalyst (mol%)	Cu-catalyst (5 mol%)	Yield % ^a
1	$Pd_2dba_3(2)$	CuI	12
2	$Pd_2dba_3(2)$	<u>Cu(TC)</u>	6
3	$Pd_2dba_3(2)$	[(MeCN) ₄ Cu]PF ₆	2
4	PdCl ₂ (4)	CuI	0
5	$Pd(OAc)_2$ (4)	CuI	0
6	[PdCl(allyl)] ₂ (2)	CuI	0
7	$[(\eta^{3}-1-tert-Butylindenyl)(\mu-Cl)Pd]_{2} (2)$	CuI	0
8	$[(Cinnamy1)PdC1]_2 (2)$	CuI	0
0	Di-µ-chlorobis[2-[(dimethylamino)methyl]phenyl-	CuI	0
9	<u>C,N]dipalladium(II)</u> (2)	Cui	U
10	Di-µ-mesylbis[2'-(amino-N)[1,1'-biphenyl]-2-yl-	CuI	0
10	<u>C]dipalladium(II)</u> (2)	Cui	U
11	cataCXium [®] C (2)	CuI	20

Table S13. Sonogashira coupling in oils: optimization for aryl chlorides

^a Yields determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard.

Table S14. Heck coupling in rapeseed oil from Askim: optimization

	\bigcirc	+ Br	CF ₃ CF ₃ CF ₃ CF ₃ Crataly Ligar Base	yst (mol%), nd (mol%), e (equiv.)	~ ~	CF ₃	
Me		 Cl	= ₃	°C, h M	e	× × ·c	F3
	Entry	Catalyst (mol%)	Ligand (mol%)	Base (2 equiv.)	°C, h	Yield % ^a	
	1	Pd_2dba_3 (3)	XPhos (12)	TEA	120°C, 48h	12	
	2	Pd_2dba_3 (3)	tBuXPhos (12)	TEA	120°C, 48h	71	
	3	Pd_2dba_3 (3)	tBuXPhos (12)	Bu ₄ NOAc	120°C, 30h	100	
	4	Pd_2dba_3 (3)	DavePhos (12)	TEA	120°C, 48h	64	
	5	Pd_2dba_3 (3)	SPhos (12)	TEA	120°C, 48h	20	
	6	$Pd_2dba_3(3)$	BrettPhos (12)	TEA	120°C, 48h	0	
	7	$Pd_2dba_3(3)$	RuPhos (12)	TEA	120°C, 48h	16	
	8	$Pd_2dba_3(3)$	JohnPhos (12)	TEA	120°C, 48h	56	
	9	XPhos Pd G3 (1)	XPhos (1)	TEA	120°C, 48h	21	
	10	<i>t</i> BuXPhos Pd G3 (1)	tBuXPhos (1)	TEA	120°C, 48h	50	
	11	$Pd_2dba_3(3)$	XantPhos (7)	TEA	120°C, 48h	0	
	12	$Pd_2dba_3(3)$	Ad ₂ BuPHI (12)	TEA	120°C, 48h	7	
	13	$Pd_2dba_3(3)$	$tBu_3PHBF_4(12)$	TEA	120°C, 48h	82	
	14	[PdCl(allyl)] ₂ (3)	IPrHCl (7)	TEA	120°C, 48h	17	
	15	PdCl ₂ (PPh ₃) ₂ (5)	-	TEA	120°C, 48h	13	
	16	$Pd_2dba_3(3)$	$tBu_3PHBF_4(12)$	TEA	80°C, 48h	8	
	17	$Pd_2dba_3(3)$	$tBu_3PHBF_4(12)$	TEA	140°C, 30h	83	
	18	$Pd_2dba_3(3)$	<i>t</i> Bu ₃ PHBF ₄ (12)	TEA	120°C, 24h	82	
	19	Pd_2dba_3 (3)	tBu_3PHBF_4 (12)	TEA	120°C, 30h	82	
	20	$Pd_2dba_3(3)$	$tBu_3PHBF_4(12)$	Cs ₂ CO ₃	120°C, 30h	14	
	21	Pd_2dba_3 (3)	tBu_3PHBF_4 (12)	DIPEA	120°C, 30h	90	
	22	$Pd_2dba_3(3)$	$tBu_3PHBF_4(12)$	DIPEA	120°C, 30h	63 ^b	
	23	Pd_2dba_3 (3)	<i>t</i> Bu ₃ PHBF ₄ (12)	Cy ₂ NMe	120°C, 30h	93	
	24	$Pd_2dba_3(3)$	tBu_3PHBF_4 (12)	Bu ₄ NOAc	120°C, 30h	100	
	25	$Pd_2dba_3(2)$	tBu ₃ PHBF ₄ (8)	Bu ₄ NOAc	120°C, 30h	100	
	26	Pd ₂ dba ₃ (1.5)	tBu ₃ PHBF ₄ (6)	Bu ₄ NOAc	120°C, 30h	100	
	27	Pd ₂ dba ₃ (0.5)	tBu ₃ PHBF ₄ (2)	Bu ₄ NOAc	120°C, 30h	100/94 ^c	

^a Yields determined by ¹H NMR using methyl 3,5-dinitrobenzoate as internal standard. ^b 4-Methylstyrene used in 2 equiv.. ^c Isolated yield.





^a Yields determined by ¹H NMR using methyl 3,5-dinitrobenzoate as internal standard. ^b The catalyst loading was Pd₂dba₃ (3 mol%), *t*Bu₃PHBF₄ (12 mol%). ^c Isolated yield. ^d We have used 2 g of corresponding solvent.

Me		+ X	Catalyst (mol%) Ligand (mol%), Bu₄NOAc (2 equi Rapeseed oil (Asŀ 120ºC, 30h), , v.) kim) , M	e	
	Entry	Catalyst (mol%)	Ligand (mol%)	Х	Yield % ^a	
	1	Pd_2dba_3 (0.5)	$tBu_3PHBF_4(2)$	X = Br	67	
	2	$Pd_2dba_3(2)$	tBu_3PHBF_4 (8)	X = Br	100/99 ^b	
	3	$Pd_2dba_3(2)$	tBu_3PHBF_4 (8)	X = Cl	41	
	4	$Pd_2dba_3(2)$	tBuXPhos (8)	X = Cl	0	
	5	$Pd_2dba_3(2)$	tBu_3PHBF_4 (8)	X = OTf	37	
	6	$Pd_2dba_3(2)$	tBuXPhos (8)	X = OTf	0	
	7	$Pd_2dba_3(2)$	tBu_3PHBF_4 (8)	X = OTs	0	
	8	$Pd_2dba_3(2)$	tBu_3PHBF_4 (8)	$\overline{X} = OMs$	0	

Table S16. Heck coupling in rapeseed oil from Askim: screening of electrophiles

^a Yields determined by ¹H NMR using methyl 3,5-dinitrobenzoate as internal standard. ^b Isolated yield.

General experimental procedures for cross-couplings

Suzuki-Miyaura coupling, Method A (Figure S29).



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with appropriate boronic acid (1 equiv., 0.724-0.786 mmol), Pd(PPh₃)₄ (5 mol%) and CsF (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim or waste rapeseed oil (3 mL) and corresponding aryl halide³ (1.5 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 80 °C for 6 h. Afterwards, the reaction mixture was cooled down, which was followed by isolation of the product according to one of the following methods:

(I) The reaction mixture was transferred onto the top of a column, filled with silica gel, using a disposable Pasteur pipette. The reaction vial was washed with 1 mL of DCM that was diluted with 1 mL of heptane and transferred onto the top of the column. This was followed by a classical column separation using mixtures of heptane as eluent. Rapeseed oil can be washed out from the column using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(II) The flask containing the reaction mixture was attached to the short-path vacuum distillation apparatus (Kugelrohr) and heated to 200 °C under reduced pressure. The product is being condensed in the receiving bulb within 40-60 minutes. If necessary, the condensed product can be further purified by column chromatography. Rapeseed oil from the flask containing the reaction mixture can be filtered through a short pad of silica gel using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(III) The reaction mixture was transferred into a 250 mL round bottom flask. The reaction vial was washed using EtOAc or THF and transferred into the 250 mL flask containing the reaction mixture. Afterwards, volatiles were removed using rotary evaporator that was followed by addition of 40 mL of 5M NaOH solution. The flask was equipped with a condenser and stirred under reflux for 4 h. The resulting mixture was treated with 100 mL of saturated NaCl solution, transferred into a 500 mL separating funnel and extracted with DCM (3 x 50 mL).⁵ Organic factions were collected, evaporated to dryness and further purified using a column chromatography.

Suzuki-Miyaura coupling, Method B (Figure S29).



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with appropriate boronic acid (1 equiv., 1.011-1.103 mmol), Pd₂dba₃ (2 mol%), DavePhos (8 mol%) and CsF (2 equiv.).

⁵ DCM can be substituted with 2MeTHF, Et₂O or EtOAc.

The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (3 mL) and corresponding aryl halide/sulfonate ester³ (1.5 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 80 °C for 24 h. Afterwards, the reaction mixture was cooled down, which was followed by isolation of the product according to one of the following methods:

(I) The reaction mixture was transferred onto the top of a column, filled with silica gel, using a disposable Pasteur pipette. The reaction vial was washed with 1 mL of DCM that was diluted with 1 mL of heptane and transferred onto the top of the column. This was followed by a classical column separation using mixtures of heptane as eluent. Rapeseed oil can be washed out from the column using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(II) The flask containing the reaction mixture was attached to the short-path vacuum distillation apparatus (Kugelrohr) and heated to 200 °C under reduced pressure. The product is being condensed in the receiving bulb within 40-60 minutes. If necessary, the condensed product can be further purified by column chromatography. Rapeseed oil from the flask containing the reaction mixture can be filtered through a short pad of silica gel using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(III) The reaction mixture was transferred into a 250 mL round bottom flask. The reaction vial was washed using EtOAc or THF and transferred into the 250 mL flask containing the reaction mixture. Afterwards, volatiles were removed using rotary evaporator that was followed by addition of 40 mL of 5M NaOH solution. The flask was equipped with a condenser and stirred under reflux for 4 h. The resulting mixture was treated with 100 mL of saturated NaCl solution, transferred into a 500 mL separating funnel and extracted with DCM (3 x 50 mL).⁵ Organic factions were collected, evaporated to dryness and further purified using a column chromatography.

Hiyama coupling, Method C (Figure S29).



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with $Pd(OAc)_2$ (4 mol%), Ad₂BuPHI (10 mol%) and TBAFx3H₂O (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (3 mL), appropriate alkoxysilane (1 equiv., 0.725-0.848 mmol) and corresponding aryl halide/triflate³ (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 80 °C for 24 h. Afterwards, the reaction mixture was cooled down, which was followed by isolation of the product according to one of the following methods:

(I) The reaction mixture was transferred onto the top of a column, filled with silica gel, using a disposable Pasteur pipette. The reaction vial was washed with 1 mL of DCM that was diluted with 1 mL of heptane and transferred onto the top of the column. This was followed by a classical column separation using mixtures of heptane as eluent. Rapeseed oil can be washed out from the column using ethyl acetate,

dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(II) The flask containing the reaction mixture was attached to the short-path vacuum distillation apparatus (Kugelrohr) and heated to 200 °C under reduced pressure. The product is being condensed in the receiving bulb within 40-60 minutes. If necessary, the condensed product can be further purified by column chromatography. Rapeseed oil from the flask containing the reaction mixture can be filtered through a short pad of silica gel using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(III) The reaction mixture was transferred into a 250 mL round bottom flask. The reaction vial was washed using EtOAc or THF and transferred into the 250 mL flask containing the reaction mixture. Afterwards, volatiles were removed using rotary evaporator that was followed by addition of 40 mL of 5M NaOH solution. The flask was equipped with a condenser and stirred under reflux for 4 h. The resulting mixture was treated with 100 mL of saturated NaCl solution, transferred into a 500 mL separating funnel and extracted with DCM (3 x 50 mL).⁵ Organic factions were collected, evaporated to dryness and further purified using a column chromatography.

Hiyama coupling, Method D (Figure S29).



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with $Pd(OAc)_2$ (4 mol%), XPhos (10 mol%) and TBAFx3H₂O (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (3 mL), absolute ethanol (0.2 mL), appropriate alkoxysilane (1 equiv., 0.725-0.848 mmol) and corresponding aryl halide³ (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 80 °C for 24 h. Afterwards, the reaction mixture was cooled down, which was followed by isolation of the product according to one of the following methods:

(I) The reaction mixture was transferred onto the top of a column, filled with silica gel, using a disposable Pasteur pipette. The reaction vial was washed with 1 mL of DCM that was diluted with 1 mL of heptane and transferred onto the top of the column. This was followed by a classical column separation using mixtures of heptane as eluent. Rapeseed oil can be washed out from the column using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(II) The flask containing the reaction mixture was attached to the short-path vacuum distillation apparatus (Kugelrohr) and heated to 200 °C under reduced pressure. The product is being condensed in the receiving bulb within 40-60 minutes. If necessary, the condensed product can be further purified by column chromatography. Rapeseed oil from the flask containing the reaction mixture can be filtered through a short pad of silica gel using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(III) The reaction mixture was transferred into a 250 mL round bottom flask. The reaction vial was washed using EtOAc or THF and transferred into the 250 mL flask containing the reaction mixture.

Afterwards, volatiles were removed using rotary evaporator that was followed by addition of 40 mL of 5M NaOH solution. The flask was equipped with a condenser and stirred under reflux for 4 h. The resulting mixture was treated with 100 mL of saturated NaCl solution, transferred into a 500 mL separating funnel and extracted with DCM (3 x 50 mL).⁵ Organic factions were collected, evaporated to dryness and further purified using a column chromatography.

Stille coupling, Method E (Figure S29).



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with Pd_2dba_3 (2 mol%), AsPh₃ (8 mol%) and CsF (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (3 mL), appropriate organotin reagent (1 equiv., 0.634-0.716 mmol) and corresponding aryl halide³ (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 100 °C for 6 h. Afterwards, the reaction mixture was cooled down, which was followed by isolation of the product according to one of the following methods:

(I) The reaction mixture was transferred onto the top of a column, filled with silica gel, using a disposable Pasteur pipette. The reaction vial was washed with 1 mL of DCM that was diluted with 1 mL of heptane and transferred onto the top of the column. This was followed by a classical column separation using mixtures of heptane as eluent. Rapeseed oil can be washed out from the column using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(II) The flask containing the reaction mixture was attached to the short-path vacuum distillation apparatus (Kugelrohr) and heated to 200 °C under reduced pressure. The product is being condensed in the receiving bulb within 40-60 minutes. If necessary, the condensed product can be further purified by column chromatography. Rapeseed oil from the flask containing the reaction mixture can be filtered through a short pad of silica gel using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(III) The reaction mixture was transferred into a 250 mL round bottom flask. The reaction vial was washed using EtOAc or THF and transferred into the 250 mL flask containing the reaction mixture. Afterwards, volatiles were removed using rotary evaporator that was followed by addition of 40 mL of 5M NaOH solution. The flask was equipped with a condenser and stirred under reflux for 4 h. The resulting mixture was treated with 100 mL of saturated NaCl solution, transferred into a 500 mL separating funnel and extracted with DCM (3 x 50 mL).⁵ Organic factions were collected, evaporated to dryness and further purified using a column chromatography.

Stille coupling, Method F (Figure S29).



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with Pd_2dba_3 (2 mol%), XPhos (8 mol%) and CsF (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (3 mL), appropriate organotin reagent (1 equiv., 0.634-0.716 mmol) and corresponding aryl halide/triflate³ (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 100 °C for 24 h. Afterwards, the reaction mixture was cooled down, which was followed by isolation of the product according to one of the following methods:

(I) The reaction mixture was transferred onto the top of a column, filled with silica gel, using a disposable Pasteur pipette. The reaction vial was washed with 1 mL of DCM that was diluted with 1 mL of heptane and transferred onto the top of the column. This was followed by a classical column separation using mixtures of heptane as eluent. Rapeseed oil can be washed out from the column using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(II) The flask containing the reaction mixture was attached to the short-path vacuum distillation apparatus (Kugelrohr) and heated to 200 °C under reduced pressure. The product is being condensed in the receiving bulb within 40-60 minutes. If necessary, the condensed product can be further purified by column chromatography. Rapeseed oil from the flask containing the reaction mixture can be filtered through a short pad of silica gel using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(III) The reaction mixture was transferred into a 250 mL round bottom flask. The reaction vial was washed using EtOAc or THF and transferred into the 250 mL flask containing the reaction mixture. Afterwards, volatiles were removed using rotary evaporator that was followed by addition of 40 mL of 5M NaOH solution. The flask was equipped with a condenser and stirred under reflux for 4 h. The resulting mixture was treated with 100 mL of saturated NaCl solution, transferred into a 500 mL separating funnel and extracted with DCM (3 x 50 mL).⁵ Organic factions were collected, evaporated to dryness and further purified using a column chromatography.

Sonogashira coupling, Method G (Figure S29).



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with Pd_2dba_3 (0.75 mol%), XantPhos (2 mol%), CuI (5 mol%), suitable acetylene (1 equiv., 0.947-0.999 mmol, degassed), corresponding aryl halide (1.5 equiv., degassed), rapeseed oil from Askim (3 mL, degassed) and DIPEA (1.5 equiv., degassed). The flask was sealed with a rubber septa, removed from the glove box and stirred at 60-80 °C for 6-24 h. Afterwards, the reaction mixture was cooled down, which was followed by isolation of the product according to one of the following methods:

(I) The reaction mixture was transferred onto the top of a column, filled with silica gel, using a disposable Pasteur pipette. The reaction vial was washed with 1 mL of DCM that was diluted with 1 mL of heptane and transferred onto the top of the column. This was followed by a classical column separation

using mixtures of heptane as eluent. Rapeseed oil can be washed out from the column using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(II) The flask containing the reaction mixture was attached to the short-path vacuum distillation apparatus (Kugelrohr) and heated to 250 °C under reduced pressure. The product is being condensed in the receiving bulb within 40-60 minutes. If necessary, the condensed product can be further purified by column chromatography. Rapeseed oil from the flask containing the reaction mixture can be filtered through a short pad of silica gel using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(III) The reaction mixture was transferred into a 250 mL round bottom flask. The reaction vial was washed using EtOAc or THF and transferred into the 250 mL flask containing the reaction mixture. Afterwards, volatiles were removed using rotary evaporator that was followed by addition of 40 mL of 5M NaOH solution. The flask was equipped with a condenser and stirred under reflux for 4 h. The resulting mixture was treated with 100 mL of saturated NaCl solution, transferred into a 500 mL separating funnel and extracted with DCM (3 x 50 mL).⁵ Organic factions were collected, evaporated to dryness and further purified using a column chromatography.

Sonogashira coupling, Method H (Figure S29).



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with Pd₂dba₃ (2 mol%), XantPhos (5 mol%), CuI (5 mol%), suitable acetylene (1 equiv., 0.979 mmol, degassed), corresponding aryl halide/sulfonate ester (1.5 equiv., degassed), rapeseed oil from Askim (3 mL, degassed) and DBU (1.5 equiv., degassed). The flask was sealed with a rubber septa, removed from the glove box and stirred at 80 °C for 24 h. Afterwards, the reaction mixture was cooled down, which was followed by isolation of the product according to one of the following methods:

(I) The reaction mixture was transferred onto the top of a column, filled with silica gel, using a disposable Pasteur pipette. The reaction vial was washed with 1 mL of DCM that was diluted with 1 mL of heptane and transferred onto the top of the column. This was followed by a classical column separation using mixtures of heptane as eluent. Rapeseed oil can be washed out from the column using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(II) The flask containing the reaction mixture was attached to the short-path vacuum distillation apparatus (Kugelrohr) and heated to 250 °C under reduced pressure. The product is being condensed in the receiving bulb within 40-60 minutes. If necessary, the condensed product can be further purified by column chromatography. Rapeseed oil from the flask containing the reaction mixture can be filtered through a short pad of silica gel using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(III) The reaction mixture was transferred into a 250 mL round bottom flask. The reaction vial was washed using EtOAc or THF and transferred into the 250 mL flask containing the reaction mixture. Afterwards, volatiles were removed using rotary evaporator that was followed by addition of 40 mL of 5M NaOH solution. The flask was equipped with a condenser and stirred under reflux for 4 h. The resulting mixture was treated with 100 mL of saturated NaCl solution, transferred into a 500 mL separating funnel and extracted with DCM (3 x 50 mL).⁵ Organic factions were collected, evaporated to dryness and further purified using a column chromatography.

Heck coupling, Method I (Figure S29).



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with Pd_2dba_3 (0.5 mol%), tBu_3PHBF_4 (2 mol%) and Bu_4NOAc (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (3 mL), appropriate olefin (1 equiv., 0.819-0.894 mmol) and corresponding aryl halide³ (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 120 °C for 30 h. Afterwards, the reaction mixture was cooled down, which was followed by isolation of the product according to one of the following methods:

(I) The reaction mixture was transferred onto the top of a column, filled with silica gel, using a disposable Pasteur pipette. The reaction vial was washed with 1 mL of DCM that was diluted with 1 mL of heptane and transferred onto the top of the column. This was followed by a classical column separation using mixtures of heptane as eluent. Rapeseed oil can be washed out from the column using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(II) The flask containing the reaction mixture was attached to the short-path vacuum distillation apparatus (Kugelrohr) and heated to 250 °C under reduced pressure. The product is being condensed in the receiving bulb within 40-60 minutes. If necessary, the condensed product can be further purified by column chromatography. Rapeseed oil from the flask containing the reaction mixture can be filtered through a short pad of silica gel using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(III) The reaction mixture was transferred into a 250 mL round bottom flask. The reaction vial was washed using EtOAc or THF and transferred into the 250 mL flask containing the reaction mixture. Afterwards, volatiles were removed using rotary evaporator that was followed by addition of 40 mL of 5M NaOH solution. The flask was equipped with a condenser and stirred under reflux for 4 h. The resulting mixture was treated with 100 mL of saturated NaCl solution, transferred into a 500 mL separating funnel and extracted with DCM (3 x 50 mL).⁵ Organic factions were collected, evaporated to dryness and further purified using a column chromatography.

Heck coupling, Method J (Figure S29).



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with Pd_2dba_3 (2 mol%), tBu_3PHBF_4 (8 mol%) and Bu_4NOAc (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (3 mL), appropriate olefin (1 equiv., 0.819-0.894 mmol) and corresponding aryl halide³ (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 120 °C for 30 h. Afterwards, the reaction mixture was cooled down, which was followed by isolation of the product according to one of the following methods:

(I) The reaction mixture was transferred onto the top of a column, filled with silica gel, using a disposable Pasteur pipette. The reaction vial was washed with 1 mL of DCM that was diluted with 1 mL of heptane and transferred onto the top of the column. This was followed by a classical column separation using mixtures of heptane as eluent. Rapeseed oil can be washed out from the column using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(II) The flask containing the reaction mixture was attached to the short-path vacuum distillation apparatus (Kugelrohr) and heated to 250 °C under reduced pressure. The product is being condensed in the receiving bulb within 40-60 minutes. If necessary, the condensed product can be further purified by column chromatography. Rapeseed oil from the flask containing the reaction mixture can be filtered through a short pad of silica gel using ethyl acetate, dried and applied for another experiment. NMR spectra of rapeseed oil before and after the reaction are identical.

(III) The reaction mixture was transferred into a 250 mL round bottom flask.⁶ The reaction vial was washed using EtOAc or THF and transferred into the 250 mL flask containing the reaction mixture. Afterwards, volatiles were removed using rotary evaporator that was followed by addition of 40 mL of 5M NaOH solution. The flask was equipped with a condenser and stirred under reflux for 4 h. The resulting mixture was treated with 100 mL of saturated NaCl solution, transferred into a 500 mL separating funnel and extracted with DCM (3 x 50 mL).⁵ Organic factions were collected, evaporated to dryness and further purified using a column chromatography.

Gram-scale Hiyama coupling.



Inside of an Ar filled glove box an oven dried 50 mL round bottom flask was sequentially charged with $Pd(OAc)_2$ (4 mol%), Ad₂BuPHI (8 mol%) and TBAFx3H₂O (1.5 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were

⁶ This method of separation is not applicable for the product **11h**.

added rapeseed oil from Askim (15 mL), triethoxyphenylsilane (1 equiv., 6.240 mmol) and 1-bromo-4fluorobenzene (1.5 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 80 °C for 24 h. Afterwards, the flask containing the reaction mixture was attached to the short-path vacuum distillation apparatus (Kugelrohr) and heated to 200 °C under reduced pressure. The product is being condensed in the receiving bulb within 60 minutes. The condensed product was further purified by column chromatography.

Gram-scale Sonogashira coupling.



Inside of an Ar filled glove box an oven dried 50 mL round bottom flask was sequentially charged with Pd₂dba₃ (2 mol%), XantPhos (5 mol%), CuI (5 mol%), phenylacetylene (1 equiv., 9.790 mmol, degassed), 1-bromo-4-fluorobenzene (1.5 equiv., degassed), rapeseed oil from Askim (20 mL, degassed) and DBU (1.5 equiv., degassed). The flask was sealed with a rubber septa, removed from the glove box and stirred at 80 °C for 24 h. Afterwards, the reaction mixture was transferred onto the top of a column, filled with silica gel, using a disposable Pasteur pipette. The reaction vial was washed with 5 mL of DCM that was diluted with 5 mL of heptane and transferred onto the top of the column. This was followed by a classical column separation using mixtures of heptane as eluent.

Gram-scale Heck coupling.



Inside of an Ar filled glove box an oven dried 50 mL round bottom flask was sequentially charged with Pd₂dba₃ (2 mol%), *t*Bu₃PHBF₄ (8 mol%) and Bu₄NOAc (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (20 mL), 4-chlorostyrene (1 equiv., 7.216 mmol) and bromobenzene (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 120 °C for 30 h. Afterwards, the reaction mixture was transferred onto the top of a column, filled with silica gel, using a disposable Pasteur pipette. The reaction vial was washed with 5 mL of DCM that was diluted with 5 mL of heptane and transferred onto the top of the column. This was followed by a classical column separation using mixtures of heptane as eluent.

Substitution of heptane with other renewable solvents for column chromatography on the instance of Heck cross-coupling.



Inside of an Ar filled glove box an oven dried 10 mL flask was sequentially charged with Pd₂dba₃ (2 mol%), *t*Bu₃PHBF₄ (8 mol%) and Bu₄NOAc (2 equiv.). The flask was sealed with a rubber septa, removed from the glove box and equipped with an Ar balloon. Next, sequentially were added rapeseed oil from Askim (3 mL), 4-methylstyrene (1 equiv., 0.846 mmol) and 1-bromo-3,5-dimethylbenzene (2 equiv.). The Ar balloon was removed and the resulting mixture was stirred at 120 °C for 30 h. Afterwards, the reaction mixture was transferred onto the top of a column, filled with silica gel (suspended in suitable monoterpene), using a disposable Pasteur pipette. The reaction vial was washed with 1 mL of DCM that was diluted with 1 mL of appropriate monoterpene and transferred onto the top of the column. This was followed by a classical column separation using mixtures of corresponding monoterpene as eluent.

(A) Separation using a Kugelrohr



(B) Separation with column chromatography



(C) Separation based on hydrolysis and extraction





Figure S29. Overview of separation methods.

Production and processing of waste rapeseed oil

(A) Frying potatoes in rapeseed oil



Figure S30. Production and processing of waste rapeseed oil.

(B) Filtration of waste rapeseed oil



(C) Waste rapeseed oil after filtration





Figure S31. Rapeseed oil from Coop before and after frying potatoes at 130 °C for 8h.



Figure S32. Waste rapeseed oils used for frying potatoes for 2, 4, 6 and 8 hours respectively.

Characterization of products



4'-Methyl-3,5-bis(trifluoromethyl)-1,1'-biphenyl, 3a.⁷ Starting from 0.736 mmol of corresponding boronic acid the product was obtained as a white solid, yield 92% (0.205 g, method A). For the reaction performed in waste rapeseed oil, used for frying at 130 °C for 8h, starting from 0.736 mmol of corresponding boronic acid the product was obtained as a white solid, yield 93% (0.207 g, method A). ¹H NMR (400 MHz, CDCl₃): δ = 2.46 (s, 3H, Me), 7.34 (d, *J* = 7.9 Hz, 2H, Ar), 7.53-7.55 (m, 2H, Ar),

7.88 (s, 1H, Ar), 8.03 (s, 2H, Ar). ¹³**C NMR** (101 MHz, CDCl₃): $\delta = 21.3$, 120.8 (p, J = 3.9 Hz), 123.7 (q, J = 271 Hz), 127.0-127.1 (m), 127.2, 130.2, 132.3 (q, J = 33.2 Hz), 135.5, 139.2, 143.5.



2-Methyl-3',5'-bis(trifluoromethyl)-1,1'-biphenyl, 3b.⁸ Starting from 0.736 mmol of corresponding boronic acid the product was obtained as a colourless oil, yield 91% (0.203 g, method A). ¹**H NMR** (400 MHz, CDCl₃): δ = 2.31 (s, 3H, Me), 7.25-7.27 (m, 1H, Ar), 7.31-7.40 (m, 3H, Ar), 7.84 (s, 2H, Ar), 7.92 (s, 1H, Ar). ¹³**C NMR** (101 MHz, CDCl₃): δ = 20.4, 121.0 (hept, *J* = 3.9 Hz), 123.6 (q, *J* = 272.6 Hz), 126.5, 128.9, 129.6 (q, *J* = 3.8 Hz), 129.8, 131.0, 5.4, 120.1, 144.2

131.8 (q, *J* = 33.2 Hz), 135.4, 139.1, 144.2.



3,5-Bis(trifluoromethyl)-1,1'-biphenyl, 3c.⁹ Starting from 0.738 mmol of corresponding boronic acid the product was obtained as a white solid, yield 61% (0.131 g, method A). Starting from 1.066 mmol of corresponding boronic acid the product was obtained as a white solid, 94% (0.291 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 7.44-7.49 (m, 1H, Ar), 7.50-7.54 (m, 2H, Ar), 7.60-7.63 (m, 2H, Ar), 7.88 (s, 1H, Ar), 8.03 (s, 2H, Ar). ¹³C NMR (101 MHz,

CDCl₃): δ = 121.1 (p, *J* = 3.8 Hz), 123.6 (q, *J* = 271 Hz), 127.4, 129.1, 129.5, 132.3 (q, *J* = 33.2 Hz), 138.4, 143.5.



2-(3,5-Bis(trifluoromethyl)phenyl)naphthalene, **3d.**¹⁰ Starting from 0.756 mmol of corresponding boronic acid the product was obtained as a white solid, yield 97% (0.249 g, method A). ¹H NMR (400 MHz, CDCl₃): δ = 7.59 (td, *J* = 5.7, 4.8, 3.3 Hz, 2H, Ar), 7.71 (dd, *J* = 8.5, 1.9 Hz, 1H, Ar), 7.90-7.98 (m, 4H, Ar), 8.05 (s, 1H, Ar), 8.17 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 121.1 (hept, *J* = 3.9 Hz), 123.7 (q, *J*

= 271 Hz), 124.8, 126.7, 127.0, 127.1, 127.5 (q, *J* = 3.5 Hz), 127.9, 128.6, 129.3, 132.4 (q, *J* = 33.2 Hz), 133.4, 133.7, 135.5, 143.4.

⁷ F. D'Accriscio, A. Ohleier, E. Nicolas, M. Demange, O. T. D. Boullay, N. Saffon-Merceron, M. Fustier-Boutignon, E. Rezabal, G. Frison, N. Nebra and N. Mezailles, *Organometallics*, 2020, **39**, 1688-1699.

⁸ Y. Uozumi and Y. Nakai, Org. Lett., 2002, 4, 2997-3000.

⁹ S. Ichii, G. Hamasaka and Y. Uozumi, *Chem. Asian J.*, 2019, 14, 3850-3854.

¹⁰ Y.-N. Wang, X.-Q. Guo, X.-H. Zhu, R. Zhong, L.-H. Cai and X.-F. Hou, Chem. Commun., 2012, 48, 10437-10439.



4'-Methoxy-3,5-bis(trifluoromethyl)-1,1'-biphenyl, 3e.¹¹ Starting from 0.724 mmol of corresponding boronic acid the product was obtained as a white solid, yield 95% (0.219 g, method A). ¹H NMR (400 MHz, CDCl₃): δ = 3.88 (s, 3H, OMe), 7.02-7.05 (m, 2H, Ar), 7.54-7.58 (m, 2H, Ar), 7.82 (s, 1H, Ar), 7.98 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 55.6, 114.9, 120.4 (p, *J* = 3.8 Hz), 123.7 (q, *J* = 271 Hz), 126.8 (q, *J* = 3.8 Hz), 128.6, 130.8, 132.2 (q, *J* = 33.1 Hz), 143.1, 160.6.



4'-Fluoro-3,5-bis(trifluoromethyl)-1,1'-biphenyl, 3f.¹² Starting from 0.786 mmol of corresponding boronic acid the product was obtained as a white solid, yield 42% (0.102 g, method A). Starting from 1.072 mmol of corresponding boronic acid the product was obtained as a white solid, 94% (0.311 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 7.18-7.23 (m, 2H, Ar), 7.57-7.62 (m, 2H, Ar), 7.88 (s, 1H, Ar), 7.98 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 116.5 (d, *J* = 21.8 Hz), 121.2 (hept, *J* = 3.9 Hz),

123.6 (q, *J* = 271 Hz), 127.3 (q, *J* = 3.8 Hz), 129.2 (d, *J* = 8.4 Hz), 132.5 (q, *J* = 33.3 Hz), 134.6 (d, *J* = 3.3 Hz), 142.5, 163.6 (d, *J* = 249.2 Hz).



3-(3,5-Bis(trifluoromethyl)phenyl)benzo[b]thiophene, 3g.¹³ Starting from 1.011 mmol of corresponding boronic acid the product was obtained as a white solid, yield 99% (0.345 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 7.45-7.52 (m, 2H, Ar), 7.55 (s, 1H, Ar), 7.83-7.87 (m, 1H, Ar), 7.96-8.00 (m, 2H, Ar), 8.09 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 121.5 (p, J = 3.8 Hz), 122.2, 123.4, 123.6 (q, J = 271 Hz),

125.2, 125.3, 125.9, 128.9 (q, *J* = 3.6 Hz), 132.4 (q, *J* = 33.4 Hz), 135.1, 137.2, 138.3, 141.0.



1-Butyl-3,5-bis(trifluoromethyl)benzene, **3h.**¹⁴ Starting from 1.079 mmol of corresponding boronic acid the product was obtained as a colourless oil, yield 18% (0.052 g, method B). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.96$ (t, J = 7.3 Hz, 3H, Me), 1.39 (dq, J = 14.7, 7.3 Hz, 2H, CH₂), 1.61-1.69 (m, 2H, CH₂), 2.72-2.76 (m, 2H, CH₂), 7.63 (s, 2H, Ar),

7.70 (s, 1H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 14.0, 22.5, 33.4, 35.6, 120.0$ (hept, J = 4.0 Hz), 123.7 (q, J = 270 Hz), 128.7 (dd, J = 5.6, 2.7 Hz), 131.7 (q, J = 33.0 Hz), 145.4.

¹¹ A. D. Zotto, F. Amoroso, W. Baratta and P. Rigo, Eur. J. Org. Chem., 2009, 110-116.

¹² M. Butters, J. N. Harvey, J. Jover, A. J. J. Lennox, G. C. Lloyd-Jones and P. M. Murray, *Angew. Chem. Int. Ed.*, 2010, **49**, 5156-5160.

¹³ C. Colletto, J. Bures and I. Larrosa, *Chem. Commun.*, 2017, **53**, 12890-12893.

¹⁴ T. Agrawal and S. P. Cook, Org. Lett., 2013, 15, 96-99.



4-Methyl-1,1'-biphenyl, 3i.¹⁵ Starting from 1.103 mmol of corresponding boronic acid the product was obtained as a white solid, yield 99% (0.184 g, X = Br, method B), 49% (0.091 g, X = Cl, method B), 99% (0.185 g, X = OTf, method B). ¹**H NMR** (400 MHz, CDCl₃): δ = 2.53 (s, 3H, Me), 7.38 (d, *J* = 7.9 Hz, 2H, Ar), 7.44-7.48 (m, 1H, Ar), 7.54-7.58 (m, 2H, Ar), 7.63-7.65 (m, 2H, Ar), 7.65-7.65 (m, 2H, Ar), 7.65-7.65 (m, 2H,

Ar), 7.71-7.74 (m, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 21.2$, 127.1, 127.2, 128.9, 129.6, 137.1, 138.5, 141.3.



3,4',5-Trimethyl-1,1'-biphenyl, 3j.¹⁶ Starting from 1.103 mmol of corresponding boronic acid the product was obtained as a white solid, yield 99% (0.216 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 2.47-2.48 (m, 9H, 3xMe), 7.07 (s, 1H, Ar), 7.30-7.33 (m, 4H, Ar), 7.56-7.59 (m, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 21.3, 21.6, 125.1, 127.2, 128.8, 129.5, 136.9, 138.3, 138.7, 141.4.

Me

2,4'-Dimethyl-1,1'-biphenyl, 3k.¹⁷ Starting from 1.103 mmol of corresponding boronic acid the product was obtained as a colourless oil, yield 99% (0.201 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 2.43-2.45 (m, 3H, Me), 2.55-2.56 (m, 3H, Me), 7.37-7.42 (m, 8H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 20.7, 21.3, 125.9, 127.2, 128.9, 129.2, 130.0, 130.4, 135.5, 136.5, 139.2, 142.1.



3-Methoxy-4'-methyl-1,1'-biphenyl, **31**.¹⁸ Starting from 1.103 mmol of corresponding boronic acid the product was obtained as a white solid, yield 98% (0.215 g, X = Br, method B), 80% (0.175 g, X = Cl, method B). ¹H NMR (400 MHz, CDCl₃): δ = 2.48-2.49 (m, 3H, Me), 3.93-3.94 (m, 3H, OMe), 6.95-6.99 (m, 1H, Ar), 7.21-7.24 (m, 1H, Ar), 7.25-7.28

(m, 1H, Ar), 7.32-7.35 (m, 2H, Ar), 7.40-7.45 (m, 1H, Ar), 7.57-7.61 (m, 2H, Ar). ¹³C **NMR** (101 MHz, CDCl₃): $\delta = 21.2$, 55.4, 112.5, 112.9, 119.6, 127.2, 129.6, 129.8, 137.3, 138.4, 142.8, 160.1.



4'-Methyl-3-(trifluoromethyl)-1,1'-biphenyl, 3m.¹⁹ Starting from 0.736 mmol of corresponding boronic acid the product was obtained as a white solid, yield 80% (0.139 g, method A). ¹H NMR (400 MHz, CDCl₃): δ = 2.48 (s, 3H, Me), 7.34 (d, *J* = 7.8 Hz, 2H, Ar), 7.55-7.60 (m, 3H, Ar), 7.64-7.66 (m, 1H, Ar), 7.80 (d, *J* = 7.7 Hz, 1H, Ar), 7.91 (s, 1H, Ar). ¹³C

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¹⁶ B. R. Barnett, L. A. Labios, J. M. Stauber, C. E. Moore, A. L. Rheingold and J. S. Figueroa, *Organometallics*, 2017, **36**, 944-954.

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¹⁸ X. Zhou, X. Guo, F. Jian and G. Wei, *ACS Omega*, 2018, **3**, 4418-4422.

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NMR (101 MHz, CDCl₃): $\delta = 21.1$, 123.7 (dq, J = 7.6, 3.8 Hz), 124.4 (q, J = 271 Hz), 127.1, 129.2, 129.8, 130.2-130.3 (m), 131.2 (q, J = 32.1 Hz), 136.9, 138.0, 142.0.



Pentafluoro(4'-methyl-[1,1'-biphenyl]-3-yl)- λ^6 -sulfane, 3n. Starting from 1.103 mmol of corresponding boronic acid the product was obtained as a white solid, yield 99% (0.324 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 2.48 (s, 3H, Me), 7.33-7.35 (m, 2H, Ar), 7.52-7.56 (m, 3H, Ar), 7.73-7.78 (m, 2H, Ar), 8.03 (p, J = 2.0 Hz, 1H, Ar). ¹³C

NMR (101 MHz, CDCl₃): $\delta = 21.2$, 124.6 (dp, J = 20.5, 4.6 Hz), 127.2, 129.2, 130.0, 130.2, 136.7, 138.4, 142.5, 154.7 (p, J = 16.8 Hz). **HRMS-EI** (m/z) [M+H]⁺ calcd. for C₁₃H₁₂F₅S 295.0574 found 295.0570.



2-(*p*-*Tolyl*)*benzo[b]thiophene*, **30**.²⁰ Starting from 1.103 mmol of corresponding boronic acid the product was obtained as a white solid, yield 62% (0.154 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 2.41 (s, 3H, Me), 7.24-7.27 (m, 2H, Ar), 7.30-7.39 (m, 2H, Ar), 7.50-7.53 (m, 1H, Ar), 7.62-7.65 (m, 2H, Ar), 7.76-7.79 (m, 1H, Ar), 7.83-7.85 (m, 1H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 21.4, 119.0, 122.4, 123.6, 124.3, 124.6,

126.5, 129.8, 131.7, 138.4, 139.5, 141.0, 144.6.



(4-Methylphenyl)ferrocene, **3p.** Starting from 1.103 mmol of corresponding boronic acid the product was obtained as a dark red solid, yield 51% (0.154 g, method B). ¹H NMR (400 MHz, CDCl₃): $\delta = 2.40$ (s, 3H, Me), 4.11 (s, 5H, ferrocene), 4.35 (t, J = 1.9 Hz, 2H, ferrocene), 4.68 (t, J = 1.9 Hz, 2H, ferrocene), 7.17 (d, J = 7.8 Hz, 2H, Ar), 7.45 (d, J = 7.9 Hz, 2H, Ar). ¹³C

NMR (101 MHz, CDCl₃): δ = 21.3, 66.5, 68.8, 69.7, 85.9, 126.2, 129.2, 135.6, 136.2. **HRMS-EI** (m/z) [M+H]⁺ calcd. for C₁₇H₁₇Fe 277.0674 found 277.0674.



3,5-Bis(trifluoromethyl)-1,1'-biphenyl, 5a.²¹ Starting from 0.832 mmol of corresponding silane the product was obtained as a colourless solid, yield 79% (0.190 g, method A), 90% (0.218 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 7.46-7.55 (m, 3H, Ar), 7.62-7.64 (m, 2H, Ar), 7.90 (s, 1H, Ar), 8.05 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 121.1 (hept, *J* = 3.9 Hz), 123.6 (q, *J* = 271 Hz), 127.4, 129.1, 129.5, 132.4 (q, *J* = 33.2 Hz), 138.5, 143.6.

²⁰ A. E. Purta, S. Ichiia, A. Tazawa and Y. Uozumi, *Synlett*, 2020, **31**, 1634-1638.

²¹ S. Ichii, G. Hamasaka and Y. Uozumi, *Chem. Asian J.*, 2019, **14**, 3850-3854.



4'-Methyl-3,5-bis(trifluoromethyl)-1,1'-biphenyl, 5b.²² Starting from 0.848 mmol of corresponding silane the product was obtained as a colourless solid, yield 82% (0.211 g, method A). ¹H NMR (400 MHz, CDCl₃): δ = 2.47 (s, 3H, Me), 7.34-7.36 (m, 2H, Ar), 7.52-7.55 (m, 2H, Ar), 7.89 (s, 1H, Ar), 8.04 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 21.3, 120.8 (hept, *J* = 3.9 Hz), 123.7 (q, *J* = 271 Hz), 127.1-127.2 (m), 127.2, 130.2, 132.3 (q, *J* = 33.2 Hz), 135.5, 139.2, 143.5.



1-(3,5-Bis(trifluoromethyl)phenyl)naphthalene, **5c.**²³ Starting from 0.725 mmol of corresponding silane the product was obtained as a colourless solid, yield 75% (0.185 g, method A), 78% (0.192 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 7.44-7.46 (m, 1H, Ar), 7.49-7.60 (m, 3H, Ar), 7.72-7.76 (m, 1H, Ar), 7.96-8.06 (m, 5H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 119.5, 121.4 (p, *J* = 3.8 Hz), 122.3, 125.0, 125.5, 126.0, 126.5, 127.2,

127.6, 127.7, 128.1, 128.9, 129.3, 130.4 (d, *J* = 3.9 Hz), 131.2, 132.0 (q, *J* = 33.2, 32.7 Hz), 134.0, 137.1, 143.1.



4'-Chloro-3,5-bis(trifluoromethyl)-1,1'-biphenyl, 5d.²⁴ Starting from 0.728 mmol of corresponding silane the product was obtained as a colourless solid, yield 95% (0.224 g, method A). ¹H NMR (400 MHz, CDCl₃): δ = 7.46-7.50 (m, 2H, Ar), 7.53-7.57 (m, 2H, Ar), 7.89 (s, 1H, Ar), 7.99 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 121.4 (hept, *J* = 3.8 Hz), 123.5 (q, *J* = 271 Hz), 127.2 (q, *J* = 3.9 Hz), 128.7, 129.7, 132.5 (q, *J* = 33.3 Hz), 135.5, 136.8, 142.3.



2-(3,5-Bis(trifluoromethyl)phenyl)thiophene, **5e.**²⁵ Starting from 0.812 mmol of corresponding silane the product was obtained as a colourless solid, yield 18% (0.043 g, method A), 60% (0.143 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 7.14-7.16 (m, 1H, thiophene), 7.41-7.45 (m, 2H, thiophene), 7.78 (s, 1H, Ar), 8.00 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 120.9 (dt, *J* = 7.7, 3.9 Hz), 123.4 (q, *J* = 271 Hz), 125.5, 125.8-125.9 (m), 127.2, 128.8, 132.5

(q, *J* = 33.4 Hz), 136.7, 140.6, 141.1.

²² F. D'Accriscio, A. Ohleier, E. Nicolas, M. Demange, O. T. D. Boullay, N. Saffon-Merceron, M. Fustier-Boutignon, E. Rezabal, G. Frison, N. Nebra and N. Mezailles, *Organometallics*, 2020, **39**, 1688-1699.

²³ Z. Zhou, H. Liang, W. Xia, H. Chen, Y. Zhang, X. He, S. Yu, R. Cao and L. Qiu, *New J. Chem.*, 2018, **42**, 5967-5971.

²⁴ Y. Uozumi and Y. Nakai, Org. Lett., 2002, 4, 2997-3000.

²⁵ J. Yang, S. Liu, J.-F. Zheng and J. Zhou, Eur. J. Org. Chem., 2012, 6248-6259.



1-(1-Phenylvinyl)-3,5-bis(trifluoromethyl)benzene, **5f.**²⁶ Starting from 0.751 mmol of corresponding silane the product was obtained as a colourless oil, yield 31% (0.073 g, method A), 73% (0.173 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 5.58 (s, 1H, olefin), 5.67 (s, 1H, olefin), 7.29-7.35 (m, 2H, Ar), 7.38-7.43 (m, 3H, Ar), 7.80 (s, 2H, Ar), 7.86 (s, 1H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 117.3, 121.7 (dt, *J* = 7.7, 3.9 Hz),

123.5 (q, *J* = 271 Hz), 128.2, 128.5 (q, *J* = 4.0 Hz), 128.8, 128.9, 131.9 (q, *J* = 33.3 Hz), 139.9, 143.9, 148.0.



4-Fluoro-1,1'-biphenyl, 5h.²⁷ Starting from 0.832 mmol of corresponding silane the product was obtained as a colourless oil, yield 87% (0.125 g, X = Br, method A), 57% (0.081 g, X = Cl, method A). For gram-scale experiment starting from 6.240 mmol (1.5 g) of corresponding silane the product was obtained as a colourless oil, yield 85% (0.914 g). ¹H NMR (400 MHz, CDCl₃): δ = 7.14-7.19

(m, 2H, Ar), 7.36-7.42 (m, 1H, Ar), 7.46-7.51 (m, 2H, Ar), 7.56-7.61 (m, 4H, Ar). ¹³**C NMR** (101 MHz, CDCl₃): $\delta = 115.8$ (d, J = 21.4 Hz), 127.2, 127.4, 128.9 (d, J = 8.1 Hz), 129.0, 137.5 (d, J = 3.3 Hz), 140.4, 162.6 (d, J = 246.3 Hz).



4-(*Trifluoromethyl*)-1,1'-biphenyl, 5i.²⁸ Starting from 0.832 mmol of corresponding silane the product was obtained as a colourless oil, yield 81% (0.150 g, X = Br, method A), 87% (0.161 g, X = Cl, method A). ¹H NMR (400 MHz, CDCl₃): δ = 7.45-7.49 (m, 1H, Ar), 7.51-7.56 (m, 2H, Ar), 7.64-7.67 (m, 2H, Ar), 7.72-7.77 (m, 4H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 124.6

(q, *J* = 270 Hz), 125.9 (q, *J* = 3.8 Hz), 127.4, 127.6, 128.4, 129.2, 129.5 (q, *J* = 32.4 Hz), 139.9, 144.9 (q, *J* = 1.4 Hz).



141.4, 141.5.

3-Methyl-1,1'-biphenyl, **5j**.²⁹ Starting from 0.832 mmol of corresponding silane the product was obtained as a colourless solid, yield 86% (0.120 g, method A). ¹H NMR (400 MHz, CDCl₃): δ = 2.54 (s, 3H, Me), 7.28-7.30 (m, 1H, Ar), 7.43-7.48 (m, 2H, Ar), 7.52-7.57 (m, 4H, Ar), 7.70-7.73 (m, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 21.7, 124.4, 127.3, 127.4, 128.1, 128.2, 128.8, 128.9, 138.5,

²⁶ F. Berthiol, H. Doucet and M. Santelli, Eur. J. Org. Chem., 2003, 1091-1096.

²⁷ R. N. Dhital, A. Sen, T. Sato, H. Hu, R. Ishii, D. Hashizume, H. Takaya, Y. Uozumi and Y. M. A. Yamada, *Org. Lett.*, 2020, **22**, 4797-4801.

²⁸ A. Ohno, T. Sato, T. Mase, Y. Uozumi and Y. M. A. Yamad, Adv. Synth. Catal., 2020, 362, 4687-4698.

²⁹ S. Yang and S. H. Hong, Asian J. Org. Chem., 2020, 9, 1846-1851.



1,1'-Biphenyl, 5k.³⁰ Starting from 0.832 mmol of corresponding silane the product was obtained as a colourless solid, yield 86% (0.110 g, X = Br, method A), 58% (0.074 g, X = OTf, method A). ¹H NMR (400 MHz, CDCl₃): δ = 7.42-7.46 (m, 2H, Ar), 7.51-7.56 (m, 4H, Ar), 7.68-7.71 (m, 4H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 127.3, 127.4, 128.9, 141.4.



3-(Trifluoromethoxy)-1,1'-biphenyl, **51.**³¹ Starting from 0.832 mmol of corresponding silane the product was obtained as a colourless oil, yield 85% (0.169 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 7.25-7.29 (m, 1H, Ar), 7.42-7.46 (m, 1H, Ar), 7.47-7.53 (m, 4H, Ar), 7.56-7.59 (m, 1H, Ar), 7.61-7.65 (m, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 119.7, 119.9, 120.8

(q, *J* = 255 Hz), 125.7, 127.3, 128.2, 129.1, 130.2, 139.9, 143.6, 149.9 (q, *J* = 1.8 Hz).



5-Phenyl-2,2'-bithiophene, 5m.³² Starting from 0.832 mmol of corresponding silane the product was obtained as a yellow solid, yield 50% (0.100 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 7.04-7.07 (m, 1H, Ar), 7.17-7.18 (m, 1H, Ar), 7.22-7.25 (m, 3H, Ar), 7.29-7.34 (m, 1H, Ar), 7.39-7.43 (m, 2H, Ar), 7.62-7.65 (m, 2H, Ar). ¹³C NMR (101 MHz,

CDCl₃): δ = 123.8, 123.9, 124.5, 124.8, 125.8, 127.7, 128.0, 129.1, 134.2, 136.9, 137.6, 143.3.



4'-Chloro-3,5-dimethyl-1,1'-biphenyl, 5n.³³ Starting from 0.728 mmol of corresponding silane the product was obtained as a colourless solid, yield 95% (0.150 g, method A). ¹H NMR (400 MHz, CDCl₃): δ = 2.44 (s, 6H, 2xMe), 7.07 (s, 1H, Ar), 7.23 (s, 2H, Ar), 7.42-7.45 (m, 2H, Ar), 7.54-7.56 (m, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 21.5, 125.1, 128.5, 128.9, 129.2, 129.4, 133.3, 138.6, 140.0, 140.1.



1-(4-Chlorophenyl)naphthalene, **50.**³⁴ Starting from 0.728 mmol of corresponding silane the product was obtained as a colourless solid, yield 84% (0.145 g, method A). ¹H NMR (400 MHz, CDCl₃): δ = 7.39-7.54 (m, 7H, Ar), 7.64-7.66 (m, 1H, Ar), 7.83-7.93 (m, 3H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 125.4, 125.5, 125.9, 126.1, 126.3, 126.4, 126.7, 127.1, 127.9,

128.2, 128.4, 128.6, 128.7, 128.8, 129.2, 131.5, 131.6, 132.9, 133.5, 133.7, 133.8, 134.0, 137.5, 139.1, 139.4, 139.8.

³⁰ M. Xiaojing, L. Gao, Z. Weng, H. Yang and X. Sun, New J. Chem., 2020, 44, 20525-20529.

³¹ M. Zhou, C. Ni, Z. He and J. Hu, Org. Lett., 2016, **18**, 3754-3757.

³² M. M. Martinez, M. Pena-Lopez, J. P. Sestelo and L. A. Sarandeses, Org. Biomol. Chem., 2012, 10, 3892-3898.

³³ P. Pattanayak, D. Patra, P. Brandao, D. Mal and V. Felix, *Inorg. Chem. Commun.*, 2015, **53**, 68-71.

³⁴ P.-F. Li, C.-B. Yi, S.-J. Ren and J. Qu, Adv. Synth. Catal., 2016, **358**, 2088-2092.



3,5-Bis(trifluoromethyl)-1,1'-biphenyl, 7a.²¹ Starting from 0.681 mmol of corresponding organothin reagent the product was obtained as a colourless solid, yield 99% (0.197 g, method C). ¹H NMR (400 MHz, CDCl₃): δ = 7.45-7.55 (m, 3H, Ar), 7.62-7.66 (m, 2H, Ar), 7.89 (s, 1H, Ar), 8.04 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 121.1 (p, *J* = 3.9 Hz), 123.6 (q, *J* = 271 Hz), 127.4-127.5 (m), 129.1, 129.5, 132.4 (q, *J* = 33.3 Hz), 138.5, 143.6.



4'-(*Benzyloxy*)-3,5-*bis*(*trifluoromethyl*)-1,1'-*biphenyl*, 7b. Starting from 0.634 mmol of corresponding organothin reagent the product was obtained as a colourless solid, yield 85% (0.213 g, method C). ¹H NMR (400 MHz, CDCl₃): δ = 5.17 (s, 2H, CH₂), 7.13-7.16 (m, 2H, Ar), 7.38-7.42 (m, 1H, Ar), 7.43-7.48 (m, 2H, Ar), 7.50-7.53 (m, 2H, Ar), 7.56-7.59 (m, 2H, Ar), 7.87 (s, 1H, Ar), 8.01 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 70.3, 120.4

(hept, J = 3.9 Hz), 123.7 (q, J = 271 Hz), 126.8 (q, J = 3.7 Hz), 127.7, 128.3, 128.6, 128.9, 131.0, 132.2 (q, J = 33.1 Hz), 136.8, 143.0, 159.7. **HRMS-EI** (m/z) [M+H]⁺ calcd. for C₂₁H₁₅F₆O 397.1022 found 397.1028.



4'-Chloro-3,5-bis(trifluoromethyl)-1,1'-biphenyl, 7c.²⁴ Starting from 0.697 mmol of corresponding organothin reagent the product was obtained as a colourless solid, yield 93% (0.210 g, method C). ¹H NMR (400 MHz, CDCl₃): δ = 7.47-7.50 (m, 2H, Ar), 7.54-7.57 (m, 2H, Ar), 7.89 (s, 1H, Ar), 7.99 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 121.4 (hept, *J* = 3.9 Hz), 123.5 (q, *J* = 271 Hz), 127.2 (q, *J* = 3.8 Hz), 128.7, 129.7, 132.5 (q, *J* = 33.4 Hz), 135.5, 136.8, 142.3.



2-(3,5-Bis(trifluoromethyl)phenyl)thiophene, **7d.**²⁵ Starting from 0.670 mmol of corresponding organothin reagent the product was obtained as a colourless solid, yield 99% (0.198 g, method D). ¹H NMR (400 MHz, CDCl₃): δ = 7.15 (dd, *J* = 5.1, 3.7 Hz, 1H, thiophene), 7.41-7.44 (m, 2H, thiophene), 7.79 (s, 1H, Ar), 8.01 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 120.9 (hept, *J* = 3.8 Hz), 123.4 (q, *J* = 271 Hz), 125.4, 125.8 (q, *J* = 3.9 Hz), 127.2, 128.7, 132.5

(q, *J* = 33.4 Hz), 136.7, 141.1.



2-(3,5-Bis(trifluoromethyl)phenyl)benzo[b]thiophene, **7e.**²⁴ Starting from 0.709 mmol of corresponding organothin reagent the product was obtained as a colourless solid, yield 99% (0.245 g, method D). ¹H NMR (400 MHz, CDCl₃): δ = 7.36-7.43 (m, 2H, Ar), 7.62 (s, 1H, Ar), 7.78-7.85 (m, 3H, Ar), 8.08 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 121.6 (hept, *J* = 3.8 Hz), 122.0, 122.6, 123.4 (q, *J* = 271 Hz), 124.4, 125.2, 125.6, 126.2 (q, *J* = 3.8 Hz), 132.6 (q, *J* = 33.4 Hz), 136.6, 140.0,

140.4, 140.5.



1-Styryl-3,5-bis(trifluoromethyl)benzene, **7f.**³⁵ Starting from 0.712 mmol of corresponding organothin reagent the product was obtained as a colourless oil, yield 82%, E/Z = 10/1.2 (0.185 g, method C). ¹H NMR (400 MHz, CDCl₃): $\delta = 6.60$ (d, J = 12.1 Hz, 0.12H, olefin, minor isomer), 6.85 (d, J = 12.2 Hz, 0.12H, olefin, minor isomer), 7.13 (d, J = 16.4 Hz, 1H, olefin, major isomer), 7.18-7.30 (m, 1.84H, Ar, minor

isomer/olefin, major isomer), 7.33-7.38 (m, 1H, Ar, major isomer), 7.40-7.44 (m, 2H, Ar, major isomer), 7.50-7.52 (m, 0.14H, Ar, minor isomer), 7.54-7.57 (m, 2H, Ar, major isomer), 7.67-7.70 (m, 0.40H, Ar, minor isomer), 7.77 (s, 1H, Ar, major isomer), 7.92 (s, 2H, Ar, major isomer), 8.02 (s, 0.17H, Ar, minor isomer), 8.04 (s, 0.34H, Ar, minor isomer). ¹³**C NMR** (101 MHz, CDCl₃): δ = 120.7-120.8 (m), 120.9 (p, *J* = 3.9 Hz), 123.2 (q, *J* = 271 Hz), 123.6 (q, *J* = 271 Hz), 125.7, 126.3 (q, *J* = 3.7 Hz), 127.1, 127.2, 127.3, 127.6, 127.7, 127.9, 128.1, 128.3, 128.8, 129.0, 129.1, 132.2 (q, *J* = 33.0 Hz), 132.7, 133.1 (q, *J* = 33.0 Hz), 134.1, 135.9, 136.2, 138.1, 139.4, 139.6, 140.6, 142.6.



1-(*Phenylethynyl*)-3,5-bis(trifluoromethyl)benzene, 7g.³⁶ Starting from 0.716 mmol of corresponding organothin reagent the product was obtained as a colourless solid, yield 77% (0.173 g, method C). ¹H NMR (400 MHz, CDCl₃): δ = 7.38-7.43 (m, 3H, Ar), 7.56-7.61 (m, 2H, Ar), 7.83 (s, 1H, Ar), 7.97 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 86.5, 93.0, 121.7 (p, *J* = 3.8 Hz), 122.1, 123.2 (q, *J* = 271 Hz), 125.9, 128.8, 129.5, 131.6 (q, *J* = 3.9 Hz), 132.0, 132.2 (q, *J* = 33.0 Hz).



4-Methyl-1,1'-biphenyl, 7i.³⁷ Starting from 0.681 mmol of corresponding organothin reagent the product was obtained as a colourless solid, yield 83% (0.095 g, X = Br, method D), 94% (0.108 g, X = Cl, method D). ¹H NMR (400 MHz, CDCl₃): δ = 2.49 (s, 3H, Me), 7.33-7.36 (m, 2H, Ar), 7.40-7.44 (m, 1H, Ar), 7.50-7.54 (m, 2H, Ar), 7.58-7.62 (m, 2H, Ar), 7.67-7.70 (m, 2H, Ar). ¹³C

NMR (101 MHz, CDCl₃): δ = 21.3, 127.1, 127.2, 128.9, 129.7, 137.2, 138.5, 141.3.



3,5-Dimethyl-1,1'-biphenyl, 7j.³⁸ Starting from 0.681 mmol of corresponding organothin reagent the product was obtained as a colourless solid, yield 99% (0.124 g, method D). ¹H NMR (400 MHz, CDCl₃): δ = 2.49 (s, 6H, 2xMe), 7.10 (s, 1H, Ar), 7.33 (s, 2H, Ar), 7.41-7.45 (m, 1H, Ar), 7.50-7.55 (m, 2H, Ar), 7.68-7.71 (m, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 21.6, 125.3, 127.2, 127.4, 128.8, 129.1, 138.4, 141.4, 141.6.

³⁵ A. N. Baumann, A. Music, J. Dechent, N. Meller, T. C. Jagau and D. Didier, *Chem. Eur. J.*, 2020, 26, 8382-8387.

³⁶ R. Zhou, W. Wang, Z.-j. Jiang, H.-y. Fu, X.-l. Zheng, C.-c. Zhang, H. Chen and R.-x. Li, *Catal. Sci. Technol.*, 2014, **4**, 746-751.

³⁷ J. Ishida, M. Nakatsuji, T. Nagata, H. Kawasaki, T. Suzuki and Y. Obora, ACS Omega, 2020, 5, 9598-9604.

³⁸ D. Kim, G. Choi, W. Kim, D. Kim, Y. K. Kang and S. H. Hong, *Chem. Sci.*, 2021, **12**, 363-373.



2-PhenyInaphthalene, **7k.**³⁹ Starting from 0.681 mmol of corresponding organothin reagent the product was obtained as a colourless solid, yield 99% (0.138 g, method D). ¹H NMR (400 MHz, CDCl₃): δ = 7.44-7.48 (m, 1H, Ar), 7.53-7.60 (m, 4H, Ar), 7.79-7.85 (m, 3H, Ar), 7.92-7.99 (m, 3H, Ar), 8.13 (d, J = 1.9 Hz, 1H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 125.8, 126.0, 126.1, h = 120.4, 120.6, 120.0, 122.0, 120.7, 141.2

 $126.4,\,127.5,\,127.6,\,127.8,\,128.4,\,128.6,\,129.0,\,132.8,\,133.9,\,138.7,\,141.3.$



2,4,6-Trimethyl-1,1'-biphenyl, 7l.⁴⁰ Starting from 0.681 mmol of corresponding organothin reagent the product was obtained as a colourless oil, yield 38% (0.051 g, method D). ¹H NMR (400 MHz, CDCl₃): δ = 2.08 (s, 6H, 2xMe), 2.40 (s, 3H, Me), 7.01 (s, 2H, Ar), 7.19-7.22 (m, 2H, Ar), 7.36-7.42 (m, 1H, Ar), 7.45-7.51 (m, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 20.9, 21.2,

126.7, 127.3, 127.4, 128.2, 128.5, 128.9, 129.5, 136.1, 136.7, 139.2, 141.3.



3-Methoxy-1,1'-biphenyl, 7m.⁴¹ Starting from 0.681 mmol of corresponding organothin reagent the product was obtained as a colourless solid, yield 85% (0.106 g, X = Br, method D), 99% (0.125 g, X = Cl, method D). ¹H NMR (400 MHz, CDCl₃): δ = 3.90 (m, 3H, OMe), 6.93-6.97 (m, 1H, Ar), 7.18-7.20 (m, 1H, Ar), 7.22-7.25 (m, 1H, Ar), 7.37-7.43 (m, 2H, Ar), 7.46-7.50 (m, 2H,

Ar), 7.63-7.66 (m, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 55.4$, 112.8, 113.1, 119.8, 127.4, 127.6, 128.9, 129.9, 141.3, 142.9, 160.1.



3-(Trifluoromethyl)-1,1'-biphenyl, **7n.**⁴² Starting from 0.681 mmol of corresponding organothin reagent the product was obtained as a colourless oil, yield 64% (0.097 g, method C). ¹H NMR (400 MHz, CDCl₃): δ = 7.41-7.46 (m, 1H, Ar), 7.48-7.53 (m, 2H, Ar), 7.56-7.65 (m, 4H, Ar), 7.78-7.81 (m, 1H, Ar), 7.88 (s, 1H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 124.1 (qd, *J* = 3.8, 1.9

Hz), 124.4 (q, *J* = 271 Hz), 127.4, 128.1, 128.2, 129.2, 129.4, 130.6 (d, *J* = 1.5 Hz), 131.4 (q, *J* = 32.2 Hz), 136.7, 140.0, 142.2.



3-Phenylthiophene, **70.**⁴³ Starting from 0.681 mmol of corresponding organothin reagent the product was obtained as a colourless oil, yield 90% (0.098 g, method D). ¹H NMR (400 MHz, CDCl₃): δ = 7.35-7.40 (m, 1H, thiophene), 7.42-7.52 (m, 5H, Ar/thiophene), 7.66-7.70 (m, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 119.9, 120.4, 126.3, 126.5, 126.6, 127.3, 129.0, 136.0, 142.5.

³⁹ M. M. Talukder, J. M. O. Cue, J. T. Miller, P. L. Gamage, A. Aslam, G. T. McCandless, M. C. Biewer and M. C. Stefan, *ACS Omega*, 2020, **5**, 24018-24032.

⁴⁰ G. Pandey and B. Torok, *Green Chem.*, 2017, **19**, 5390-5395.

⁴¹ B. Liu, T. Xu, C. Li and J. Bai, New J. Chem., 2020, **44**, 3794-3801.

⁴² P. P. Mpungose, N. I. Sehloko, G. E. M. Maguire and H. B. Friedrich, New J. Chem., 2017, **41**, 13560-13566.

⁴³ J. Duczynski, A. N. Sobolev, S. A. Moggach, R. Dorta and S. G. Stewart, *Organometallics*, 2020, **39**, 105-115.



2-Phenylthiophene, **7p.**⁴⁴ Starting from 0.670 mmol of corresponding organothin reagent the product was obtained as a colourless solid, yield 88% (0.094 g, X = Cl, method D), 71% (0.076 g, X = OTf, method D). ¹H NMR (400 MHz, CDCl₃): δ = 7.12-7.15 (m, 1H, thiophene), 7.32-7.38 (m, 3H, Ar/thiophene), 7.41-7.46 (m, 2H, Ar), 7.67-7.70 (m, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 123.2, 124.9, 126.1,

127.6, 128.2, 129.0, 134.6, 144.6.



1-(Phenylethynyl)-3,5-bis(trifluoromethyl)benzene, 9a.⁴⁵ Starting from 0.979 mmol of corresponding acetylene the product was obtained as a colourless oil, yield 86% (0.264 g, method A). ¹H NMR (400 MHz, CDCl₃): δ = 7.39-7.44 (m, 3H, Ar), 7.59-7.62 (m, 2H, Ar), 7.85
(s, 1H, Ar), 7.97 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 86.5, 93.0, 121.7 (hept, J = 3.8 Hz), 122.2, 123.2 (q, J = 271 Hz), 125.9,

128.7, 129.5, 131.6 (q, *J* = 3.9 Hz), 132.1, 132.2 (q, *J* = 34 Hz).



1-((4-(tert-Butyl)phenyl)ethynyl)-3,5-

bis(trifluoromethyl)benzene, **9b.** Starting from 0.948 mmol of corresponding acetylene the product was obtained as a white solid, yield 93% (0.325 g, method A). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.37$ (s, 9H, *t*Bu), 7.44 (d, J = 8.8 Hz, 2H, Ar), 7.53 (d, J = 8.8 Hz, 2H, Ar), 7.83 (s, 1H, Ar), 7.97 (s, 2H, Ar). ¹³C

NMR (101 MHz, CDCl₃): δ = 31.3, 35.1, 86.0, 93.4, 119.1, 121.5 (p, *J* = 3.8 Hz), 123.3 (q, *J* = 272 Hz), 125.8, 126.2, 131.6 (q, *J* = 4.0 Hz), 131.8, 132.1 (q, *J* = 34 Hz), 153.0. **HRMS-EI** (m/z) [M+H]⁺ calcd. for C₂₀H₁₇F₆ 371.1229 found 371.1231.



I-(m-Tolylethynyl)-3,5-bis(trifluoromethyl)benzene, **9c.** Starting from 0.947 mmol of corresponding acetylene the product was obtained as a colourless oil, yield 92% (0.285 g, method A). ¹H NMR (400 MHz, CDCl₃): δ = 2.40 (s, 3H, Me), 7.23 (d, *J* = 7.7 Hz, 1H, Ar), 7.30 (t, *J* = 7.6 Hz, 1H, Ar), 7.39-7.42 (m, 2H, Ar), 7.83 (s, 1H, Ar), 7.96 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 21.4, 86.2,

93.3, 121.6 (hept, J = 3.9 Hz), 121.9, 123.2 (q, J = 271 Hz), 126.0, 128.6, 129.1, 130.4, 131.6 (q, J = 4.0 Hz), 132.1 (q, J = 33 Hz), 132.6, 138.5. **HRMS-EI** (m/z) [M+H]⁺ calcd. for C₁₇H₁₁F₆ 329.0759 found 329.0755.

⁴⁴ B. Karimi, M. Tavakolian, F. Mansouri and H. Vali, ACS Sustainable Chem. Eng., 2019, 7, 3811-3823.

⁴⁵ R. Zhou, W. Wang, Z.-j. Jiang, H.-y. Fu, X.-l. Zheng, C.-c. Zhang, H. Chen and R.-x. Li, *Catal. Sci. Technol.*, 2014, **4**, 746-751.

1-((4-Methoxyphenyl)ethynyl)-3,5-



bis(trifluoromethyl)benzene, 9d.⁴⁶ Starting from 0.984 mmol of corresponding acetylene the product was obtained as a white solid, yield 87% (0.295 g, method A). ¹H NMR (400 MHz, CDCl₃): δ = 3.84 (s, 3H, OMe), 6.92 (d, *J* = 8.4 Hz, 2H, Ar), 7.50-7.52 (m, 2H, Ar), 7.80 (s, 1H, Ar), 7.93 (s, 2H, Ar). ¹³C

NMR (101 MHz, CDCl₃): δ = 55.4, 85.5, 93.3, 114.1, 114.4, 121.3 (p, *J* = 3.9 Hz), 123.2 (q, *J* = 271 Hz), 126.3, 131.4 (q, *J* = 3.8 Hz), 132.1 (q, *J* = 33.6 Hz), 133.6, 160.6.



4-((3,5-bis(Trifluoromethyl)phenyl)ethynyl)-1,2dimethoxybenzene, 9e. Starting from 0.987 mmol of corresponding acetylene the product was obtained as a white solid, yield 97% (0.358 g, method A). ¹H NMR (400 MHz, CDCl₃): δ = 3.88 (d, *J* = 2.5 Hz, 6H, 2xOMe), 6.83 (d, *J* = 8.3 Hz, 1H, Ar), 7.03 (d, *J* = 1.8 Hz, 1H, Ar), 7.14 (dd, *J* = 8.3, 1.9

Hz, 1H, Ar), 7.76 (s, 1H, Ar), 7.90 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 55.9$, 56.0, 85.2, 93.3, 111.2, 114.1, 114.4, 121.2 (hept, J = 3.9 Hz), 123.1 (q, J = 272 Hz), 125.5, 126.1, 131.3 (q, J = 3.9 Hz), 132.0 (q, J = 33.6 Hz), 148.9, 150.5. HRMS-EI (m/z) [M+H]⁺ calcd. for C₁₈H₁₃F₆O₂ 375.0814 found 375.0807.



1-((4-Fluorophenyl)ethynyl)-3,5-bis(trifluoromethyl)benzene, **9f.** Starting from 0.999 mmol of corresponding acetylene the product was obtained as a white solid, yield 93% (0.307 g, method A). ¹H NMR (400 MHz, CDCl₃): δ = 7.06-7.11 (m, 2H, Ar), 7.55 (dd, *J* = 8.4, 5.3 Hz, 2H, Ar), 7.83 (s, 1H, Ar), 7.94 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 86.3, 91.9, 116.1 (d, *J* = 22.2 Hz),

118.3 (d, J = 3.5 Hz), 121.7-121.9 (m), 123.2 (q, J = 271 Hz), 125.8, 131.6 (q, J = 3.7 Hz), 132.2 (q, J = 33.7 Hz), 134.0 (d, J = 8.5 Hz), 163.4 (d, J = 251.4 Hz). **HRMS-EI** (m/z) [M+H]⁺ calcd. for C₁₆H₈F₇ 333.0509 found 333.0511.



1-(Non-1-yn-1-yl)-3,5-bis(trifluoromethyl)benzene, **9g.** Starting from 0.966 mmol of corresponding acetylene the product was obtained as a colourless oil, yield 72% (0.235 g, method A). ¹**H NMR** (400 MHz, CDCl₃): δ = 0.87-0.92 (m, 3H, Me), 1.28-1.39 (m, 6H, 3xCH₂), 1.46 (p, *J* = 6.7 Hz, 2H, CH₂), 1.63 (p, *J* = 7.2 Hz, 2H, CH₂), 2.44 (t, *J* = 7.1 Hz,

2H, CH₂), 7.75 (s, 1H, Ar), 7.81 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 14.2, 19.6, 22.9, 28.6, 29.0, 29.1, 31.9, 78.3, 94.9, 121.0 (p, *J* = 3.7 Hz), 123.3 (q, *J* = 271 Hz), 126.7, 131.7 (q, *J* = 3.9 Hz), 132.0 (q, *J* = 33 Hz). **HRMS-EI** (m/z) [M+H]⁺ calcd. for C₁₇H₁₉F₆ 337.1385 found 337.1383.

⁴⁶ J. He, K. Yang, J. Zhao and S. Cao, *Org. Lett.*, 2019, **21**, 9714-9718.



1-(Hex-1-yn-1-yl)-3,5-bis(trifluoromethyl)benzene, **9h.**⁴⁷ Starting from 0.974 mmol of corresponding acetylene the product was obtained as a colourless oil, yield 99% (0.286 g, method A). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.97$ (t, J = 7.3 Hz, 3H, Me), 1.45-1.54 (m, 2H, CH₂), 1.58-1.66 (m, 2H, CH₂), 2.44 (t, J = 7.0 Hz, 2H, CH₂), 7.74 (s, 1H, Ar), 7.81 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta =$

13.7, 19.2, 22.3, 30.7, 78.3, 94.8, 121.0 (hept, *J* = 3.9 Hz), 123.3 (q, *J* = 271 Hz), 126.7, 131.7 (q, *J* = 3.8 Hz), 132.0 (q, *J* = 33 Hz).



1-Methyl-2-(phenylethynyl)benzene, **9i.**⁴⁸ Starting from 0.979 mmol of corresponding acetylene the product was obtained as a white solid, yield 58% (0.109 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 2.58-2.59 (m, 3H, Me), 7.20-7.25 (m, 1H, Ar), 7.28-7.29 (m, 2H, Ar), 7.35-7.42 (m, 3H,

Ar), 7.55-7.62 (m, 3H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 88.5$, 93.5, 123.2, 123.7, 125.8, 128.3, 128.4, 128.5, 129.6, 131.7, 132.0, 140.3.



1,2-Diphenylethyne, **9**j.⁴⁹ Starting from 0.979 mmol of corresponding acetylene the product was obtained as a white solid, yield 99% (0.174 g, X = Br, method B), 90% (0.157 g, X = OTf, method B). ¹H NMR (400

MHz, CDCl₃): δ = 7.36-7.43 (m, 6H, Ar), 7.59-7.63 (m, 4H, Ar). ¹³**C** NMR (101 MHz, CDCl₃): δ = 89.6, 123.4, 128.4, 128.5, 131.8.



1-Methoxy-4-(phenylethynyl)benzene, **9k.**⁵⁰ Starting from 0.979 mmol of corresponding acetylene the product was obtained as a white solid, yield 97% (0.197 g, method B). ¹H NMR (400 MHz,

CDCl₃): $\delta = 3.83$ (s, 3H, OMe), 6.90-6.94 (m, 2H, Ar), 7.33-7.41 (m, 3H, Ar), 7.52-7.61 (m, 4H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 55.3$, 88.2, 89.6, 114.1, 115.5, 123.7, 128.1, 128.4, 131.6, 133.2, 159.7.



1-(Phenylethynyl)-4-(trifluoromethyl)benzene, 91.⁵¹ Starting from 0.979 mmol of corresponding acetylene the product was obtained as a white solid, yield 91% (0.220 g, X = Br, method A), 7% (0.018

g, X = Cl, method B). ¹**H NMR** (400 MHz, CDCl₃): δ = 7.39-7.42 (m, 3H, Ar), 7.59-7.68 (m, 6H, Ar). ¹³**C NMR** (101 MHz, CDCl₃): δ = 88.2, 92.0, 122.8, 124.2 (q, *J* = 270 Hz), 125.4 (q, *J* = 3.8 Hz), 127.3 (q, *J* = 1.5 Hz), 128.6, 129.0, 130.1 (q, *J* = 32.6 Hz), 131.9, 132.0.

⁴⁷ S. R. Chidipudi, I. Khan and H. W. Lam, Angew. Chem. Int. Ed., 2012, **51**, 12115-12119.

⁴⁸ F. Messa, G. Dilauro, F. M. Perna, P. Vitale, V. Capriati and A. Salomone, *ChemCatChem*, 2020, **12**, 1979-1984.

⁴⁹ S. Alapour, M. D. Farahani, D. Ramjugernath, N. A. Koorbanally and H. B. Friedrich, *ACS Sustainable Chem. Eng.*, 2019, **7**, 12697-12706.

⁵⁰ G. Hamasaka, D. Roy, A. Tazawa and Y. Uozumi, *ACS Catal.*, 2019, **9**, 11640-11646.

⁵¹ T. Tani, Y. Sawatsugawa, Y. Sano, Y. Hirataka, N. Takahashi, S. Hashimoto, T. Sugiura and T. Tsuchimoto, *Adv. Synth. Catal.*, 2019, **361**, 1815-1834.



1-Fluoro-4-(phenylethynyl)benzene, **9m.**⁵² Starting from 0.979 mmol of corresponding acetylene the product was obtained as a white solid, yield 70% (0.134 g, method A), 99% (0.191 g, method B). For

gram-scale experiment starting from 9.790 mmol (1 g) of corresponding acetylene the product was obtained as a white solid, yield 87% (1.673 g). ¹H NMR (400 MHz, CDCl₃): δ = 7.04-7.10 (m, 2H, Ar), 7.36-7.41 (m, 3H, Ar), 7.52-7.59 (m, 4H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 88.5, 89.2 (d, *J* = 1.5 Hz), 115.8 (d, *J* = 22.0 Hz), 119.5 (d, *J* = 3.4 Hz), 123.3, 128.4, 128.5, 131.7, 133.6 (d, *J* = 8.3 Hz), 162.6 (d, *J* = 249.5 Hz).



2-(*Phenylethynyl*)*naphthalene*, **9n.**⁵³ Starting from 0.979 mmol of corresponding acetylene the product was obtained as a yellow solid, yield 99% (0.223 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 7.40-7.48 (m, 3H, Ar), 7.54-7.59 (m, 2H, Ar), 7.68-7.72 (m, 3H, Ar),

7.87-7.90 (m, 3H, Ar), 8.16 (s, 1H, Ar). ¹³**C** NMR (101 MHz, CDCl₃): $\delta = 89.9$, 90.0, 120.7, 123.5, 126.7, 126.8, 127.9, 127.9, 128.2, 128.4, 128.5, 128.6, 131.6, 131.8, 132.9, 133.2.



9-(Phenylethynyl)anthracene, 90.⁵⁴ Starting from 0.979 mmol of corresponding acetylene the product was obtained as a yellow solid, yield 98% (0.268 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 7.49-7.61 (m, 5H, Ar), 7.72 (ddd, J = 8.5, 6.6, 1.3 Hz, 2H, Ar), 7.92-7.95 (m, 2H, Ar), 8.05 (d, J = 8.5 Hz, 2H, Ar), 8.41 (s, 1H, Ar), 8.83 (dd, J = 8.7, 1.2 Hz, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 86.6, 100.9, 117.3, 123.8, 125.7, 126.7, 126.8, 127.8, 128.5, 128.6, 128.8, 131.2, 131.8, 132.7.



3-(*Phenylethynyl*)*benzo*[*b*]*thiophene*, **9p.**⁵⁵ Starting from 0.979 mmol of corresponding acetylene the product was obtained as a white solid, yield 97% (0.223 g, method B). ¹H NMR (400 MHz, CDCl₃): δ = 7.37-7.50 (m, 4H, Ar), 7.51-7.56 (m, 1H, Ar), 7.66-7.70 (m, 2H, Ar), 7.73 (s, 1H, Ar), 7.90-7.92 (m, 1H, Ar), 8.11-8.14 (m, 1H, Ar). ¹³C NMR (101

MHz, CDCl₃): δ = 83.2, 92.0, 118.5, 122.8, 123.2, 123.3, 124.9, 125.2, 128.5, 128.6, 129.9, 131.8, 139.0, 139.3.

⁵² S. Ruengsangtongkul, N. Chaisan, C. Thongsornkleeb, J. Tummatorn and S. Ruchirawat, Org. Lett., 2019, 21, 2514-2517.

⁵³ A. Baralle, H. Yorimitsu and A. Osuka, *Chem. Eur. J.*, 2016, **22**, 10768-10772.

⁵⁴ Y. Thummala, A. K. Morri, G. V. Karunakar and V. R. Doddi, *Eur. J. Org. Chem.*, 2018, 6280-6285.

⁵⁵ S. Prateeptongkum, K. M. Driller, R. Jackstell, A. Spannenberg and M. Beller, *Chem. Eur. J.*, 2010, 16, 9606-9615.



(*E*)-1-(4-Methylstyryl)-3,5-bis(trifluoromethyl)benzene, 11a.⁵⁶ Starting from 0.846 mmol of corresponding olefin the product was obtained as a colourless solid, yield 94% (0.262 g, method E). ¹H NMR (400 MHz, CDCl₃): $\delta = 2.53$ (s, 3H, Me), 7.20 (d, *J* = 16.5 Hz, 1H, olefin), 7.32-7.36 (m, 3H, Ar/olefin), 7.58 (d, *J* = 8.5 Hz, 2H, Ar), 7.88 (s, 1H, Ar), 8.03 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 21.4$, 120.7 (hept, *J* = 3.9 Hz), 123.6 (q, *J* =

271 Hz), 124.7, 126.2 (q, *J* = 3.7 Hz), 127.1, 127.7, 127.9, 129.5, 129.8, 132.2 (q, *J* = 33 Hz), 132.6, 133.4, 139.1, 139.8.



(*E*)-1-(4-Methoxystyryl)-3,5-bis(trifluoromethyl)benzene, 11b. Starting from 0.894 mmol of corresponding olefin the product was obtained as a colourless solid, yield 94% (0.291 g, method E). ¹H NMR (400 MHz, CDCl₃): $\delta = 3.85$ (s, 3H, OMe), 6.94-6.99 (m, 3H, Ar/olefin), 7.18 (d, J = 16.3 Hz, 1H, olefin), 7.47-7.51 (m, 2H, Ar), 7.73 (s, 1H, Ar), 7.87 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 55.4$, 114.5, 120.4 (hept, J = 3.8 Hz),

123.4, 123.6 (q, J = 271 Hz), 126.0 (q, J = 4.0 Hz), 128.5, 128.9, 132.1 (q, J = 33 Hz), 132.2, 140.0, 160.4. **HRMS-EI** (m/z) [M+H]⁺ calcd. for C₁₇H₁₃F₆O 347.0865 found 347.0862.



(*E*)-1-(4-Chlorostyryl)-3,5-bis(trifluoromethyl)benzene, 11c. Starting from 0.866 mmol of corresponding olefin the product was obtained as a colourless solid, yield 97% (0.295 g, method E). ¹H NMR (400 MHz, CDCl₃): δ = 7.07 (d, *J* = 16.6 Hz, 1H, olefin), 7.17 (d, *J* = 16.4 Hz, 1H, olefin), 7.35-7.38 (m, 2H, Ar), 7.45-7.47 (m, 2H, Ar), 7.77 (s, 1H, Ar), 7.90 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 121.2 (p, *J* = 3.9 Hz), 123.5 (q, *J* = 271 Hz),

126.2, 126.3 (q, J = 3.7 Hz), 128.2, 129.1, 129.2, 129.3, 131.3, 132.3 (q, J = 33.2 Hz), 134.7, 139.3. **HRMS-EI** (m/z) [M+H]⁺ calcd. for C₁₆H₁₀ClF₆ 351.0370 found 351.0377.



(*E*)-1-(4-Fluorostyryl)-3,5-bis(trifluoromethyl)benzene, 11d. Starting from 0.819 mmol of corresponding olefin the product was obtained as a colourless oil, yield 82% (0.225 g, method E). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.02$ (d, J = 16.3 Hz, 1H, olefin), 7.07-7.12 (m, 2H, Ar), 7.19 (d, J = 16.3 Hz, 1H, olefin), 7.49-7.53 (m, 2H, Ar), 7.76 (s, 1H, Ar), 7.89 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 116.1$ (d, J = 21.9 Hz), 121.0 (hept, J = 3.8 Hz), 123.6

(q, J = 271 Hz), 125.5 (d, J = 2.5 Hz), 126.2 (q, J = 3.8 Hz), 128.7 (d, J = 8.1 Hz), 131.4, 132.3 (q, J = 33 Hz),132.4, 139.5, 163.2 (d, J = 249.1 Hz). **HRMS-EI** (m/z) [M+H]⁺ calcd. for C₁₆H₁₀F₇ 335.0665 found 335.0670.

⁵⁶ M. S. M. Pearson and D. R. Carbery, J. Org. Chem., 2009, 74, 5320-5325.

(E)-1,3-Bis(trifluoromethyl)-5-(4-



(*trifluoromethyl*)*styryl*)*benzene*, **11e.**⁵⁷ Starting from 0.871 mmol of corresponding olefin the product was obtained as a colourless oil, yield 80% (0.269 g, method E). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.19$ (d, J = 16.3 Hz, 1H, olefin), 7.25 (d, J = 16.2 Hz, 1H, olefin), 7.61-7.67 (m, 4H, Ar), 7.79 (s, 1H, Ar), 7.94 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 121.6$ (p, J = 3.8

Hz), 123.9 (q, *J* = 271 Hz), 124.3 (q, *J* = 271 Hz), 126.1 (q, *J* = 3.8 Hz), 126.6 (q, *J* = 3.6 Hz), 127.2, 128.1, 130.7 (q, *J* = 33.4 Hz), 131.1, 132.5 (q, *J* = 33.4 Hz), 139.0, 139.6-139.7 (m).



(*E*)-2-(3,5-*Bis*(*trifluoromethyl*)*styryl*)*naphthalene*, **11f.** Starting from 0.843 mmol of corresponding olefin the product was obtained as a colourless solid, yield 93% (0.286 g, method E). ¹**H NMR** (400 MHz, CDCl₃): δ = 7.13 (d, *J* = 16.2 Hz, 1H, olefin), 7.32 (d, *J* = 16.4 Hz, 1H, olefin), 7.54-7.60 (m, 2H, Ar), 7.72 (d, *J* = 8.6 Hz, 1H, Ar), 7.87-7.90 (m, 5H, Ar), 7.94 (s, 2H, Ar). ¹³**C**

NMR (101 MHz, CDCl₃): $\delta = 120.8$ (p, J = 3.9 Hz), 123.3, 123.6 (q, J = 271 Hz), 125.6, 126.2 (q, J = 3.9 Hz), 126.7, 126.8, 127.9, 128.0, 128.4, 128.7, 132.1 (q, J = 33.4 Hz), 132.5, 133.6, 133.7, 139.5. **HRMS-EI** (m/z) [M+H]⁺ calcd. for C₂₀H₁₃F₆ 367.0916 found 367.0910.



Mixtureof1-(4-phenylbut-1-en-1-yl)-3,5-bis(trifluoromethyl)benzene,1-(4-phenylbut-2-en-1-yl)-3,5-bis(trifluoromethyl)benzene and 1-(4-phenylbut-3-en-1-yl)-3,5-bis(trifluoromethyl)benzene,11g.58Starting from 0.832 mmol ofcorresponding olefin the product was obtained as a colourless oil,yield 82% (0.235 g, method E).

Fraction 1: ¹**H** NMR (400 MHz, CDCl₃): $\delta = 2.57-2.62$ (m, 1.81H, CH₂), 2.78-2.87 (m, 2.45H, CH₂), 3.45 (dd, J = 27.6, 6.8 Hz, 0.27H, CH₂), 3.61 (d, J = 7.6 Hz, 0.31H, CH₂), 6.43-6.49 (m, 1.67H, olefin), 7.15-7.19 (m, 0.61H, olefin), 7.22-7.27 (m, 3.25H, Ar), 7.29-7.34 (m, 2.59H, Ar), 7.65-7.73 (m, 3H, Ar), 7.79-7.82 (m, 0.73H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 16.0$, 21.2, 34.7, 35.0, 35.3, 35.6, 37.0, 116.1, 120.5 (hept, J = 4.0 Hz), 121.2-121.3 (m), 122.3, 123.6 (q, J = 271 Hz), 125.0, 126.0 (q, J = 3.5 Hz), 126.3, 126.4, 126.5, 127.7, 127.8, 128.2, 128.3, 128.4, 128.6, 128.7, 128.8, 128.9, 130.5, 130.6, 131.5, 131.7, 132.0 (q, J = 33.4 Hz), 132.1, 132.4, 132.9, 133.0, 133.6, 134.5, 135.4, 140.0, 140.2, 141.2, 141.4, 143.6, 145.8.

Fraction 2: ¹**H** NMR (400 MHz, CDCl₃): $\delta = 3.03-3.10$ (m, 2.77H, CH₂), 3.19 (t, J = 7.5 Hz, 0.28H, CH₂), 3.32 (t, J = 7.8 Hz, 1H, CH₂), 3.41 (t, J = 7.8 Hz, 1.78H, CH₂), 3.49 (t, J = 7.6 Hz, 0.29H, CH₂), 3.94 (dd, J = 28.2, 6.8 Hz, 0.44H, CH₂), 6.65-6.73 (m, 0.89H, olefin), 6.90-6.94 (m, 1.81H, olefin), 7.67-7.72 (m, 3.28H, Ar), 7.77-7.83 (m, 4.91H, Ar), 8.13-8.23 (m, 4.57H, Ar), 8.38 (s, 0.44H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 32.3$, 34.3, 34.5, 35.0, 35.6, 35.7, 38.6, 39.1, 120.3 (p, J = 4.0 Hz), 120.5 (p, J = 5.0

⁵⁷ P. d. Medina, R. Casper, J.-F. Savouret and M. Poirot, J. Med. Chem., 2005, 48, 287-291.

⁵⁸ C.-C. Tseng, M. Li, B. Mo, S. A. Warren and A. C. Spivey, *Chem. Lett.*, 2011, **40**, 995-997.

3.8 Hz), 123.5 (q, *J* = 272 Hz), 123.6 (q, *J* = 271 Hz), 126.0 (q, *J* = 4.1 Hz), 126.2, 126.3, 126.4, 126.8, 127.5, 128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 128.8, 128.8-128.9 (m), 129.3, 131.7, 131.8 (q, *J* = 32 Hz), 132.0 (q, *J* = 33.4 Hz), 133.0, 134.5, 137.4, 139.0, 139.9, 140.0, 140.3, 141.4, 143.1, 143.4, 144.0, 144.2.



Butyl (E)-3-(3,5-bis(trifluoromethyl)phenyl)acrylate, **11h.**⁵⁹ Starting from 0.858 mmol of corresponding olefin the product was obtained as a colourless solid, yield 90% (0.262 g, method F). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.95$ (t, J = 7.4 Hz, 3H, Me), 1.44 (h, J = 7.4 Hz, 2H, CH₂), 1.69 (p, J = 6.4 Hz, 2H, CH₂), 4.23 (t, J = 7.4 Hz, 2H, CH₂), 6.58 (d, J= 16.0 Hz, 1H, olefin), 7.71 (d, J = 16.1 Hz, 1H, olefin), 7.85 (s, 1H,

Ar), 7.94 (s, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 13.8$, 19.3, 30.9, 65.1, 122.5, 123.2 (q, J = 272 Hz), 123.4 (hept, J = 3.8 Hz), 127.8 (q, J = 3.9 Hz), 132.6 (q, J = 33.6 Hz), 136.8, 141.0, 166.1.



(*E*)-1,3-Dimethyl-5-(4-methylstyryl)benzene, 11k.⁶⁰ Starting from 0.846 mmol of corresponding olefin the product was obtained as a colourless solid, yield 86% (0.161 g, method E), 86% (0.162 g, method F). For isolations based on the use of renewable monoterpenes starting from 0.846 mmol of corresponding olefin the product was obtained as a colourless solid, yield 90% (0.170 g, (–)- α -pinene), 91% (0.172 g, 3-carene), 86% (0.161 g, (*R*)-(+)-

limonene), 89% (0.167 g, γ-terpinene), 87% (0.163 g, sabinene). ¹H NMR (400 MHz, CDCl₃): δ = 2.65-2.67 (m, 9H, 3xMe), 7.21 (s, 1H, Ar), 7.32 (d, *J* = 16.4 Hz, 1H, olefin), 7.39 (d, *J* = 16.2 Hz, 1H, olefin), 7.45-7.48 (m, 4H, Ar), 7.72 (d, *J* = 7.8 Hz, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 21.4, 21.5, 124.5, 126.5, 128.0, 128.3, 129.4, 129.5, 134.9, 137.4, 137.6, 138.1.



(*E*)-1-Methyl-2-(4-methylstyryl)benzene, 111.⁶¹ Starting from 0.846 mmol of corresponding olefin the product was obtained as a colourless oil, yield 58% (0.102 g, method E), 95% (0.167 g, method F). ¹H NMR (400 MHz, CDCl₃): δ = 2.48 (s, 3H, Me), 2.55 (s, 3H, Me), 7.10 (d, *J* = 16.1 Hz, 1H, olefin), 7.28-7.35 (m, 5H, Ar), 7.42 (d, *J* = 16.1 Hz, 1H,

olefin), 7.54 (d, J = 8.4 Hz, 2H, Ar), 7.71 (d, J = 7.9 Hz, 1H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 20.1, 21.4, 125.4, 125.7, 126.3, 126.6, 127.5, 129.5, 130.1, 130.5, 135.1, 135.8, 136.7, 137.6.$

⁵⁹ M. Feuerstein, H. Doucet and M. Santelli, J. Org. Chem., 2001, 66, 5923-5925.

⁶⁰ K. Song, P. Liu, J. Wang, L. Pang, J. Chen, I. Hussain, B. Tan and T. Li, *Dalton Trans.*, 2015, 44, 13906-13913.

⁶¹ E. Shirakawa, X. Zhang and T. Hayashi, Angew. Chem. Int. Ed., 2011, 50, 4671-4674.



(*E*)-1-Methoxy-3-(4-methylstyryl)benzene, 11m.⁶² Starting from 0.846 mmol of corresponding olefin the product was obtained as a colourless solid, yield 87% (0.165 g, X = Br, method F), 71% (0.134 g, X = Cl, method F). ¹H NMR (400 MHz, CDCl₃): δ = 2.61 (s, 3H, Me), 4.08 (s, 3H, OMe), 7.06 (d, *J* = 8.2 Hz, 1H,

olefin), 7.30-7.36 (m, 4H, Ar/olefin), 7.42 (d, J = 7.8 Hz, 2H, Ar), 7.52 (t, J = 8.0 Hz, 1H, Ar), 7.66 (d, J = 7.1 Hz, 2H, Ar). ¹³**C NMR** (101 MHz, CDCl₃): $\delta = 21.4$, 55.3, 111.8, 113.2, 119.3, 126.6, 127.7, 129.1, 129.5, 129.7, 134.6, 137.7, 139.1, 160.0.



(*E*)-1-Methyl-4-styrylbenzene, 11n.⁶³ Starting from 0.846 mmol of corresponding olefin the product was obtained as a colourless solid, yield 99% (0.164 g, X = Br, method F), 0% (0 g, X = OTf, method F). ¹H NMR (400 MHz, CDCl₃): δ = 2.66 (s, 3H, Me), 7.34-7.43 (m, 2H, olefin), 7.47 (d, *J* = 7.8 Hz, 2H, Ar), 7.54-7.57 (m, 1H, Ar), 7.63-7.67

(m, 2H, Ar), 7.72 (d, J = 8.5 Hz, 2H, Ar), 7.81 (d, J = 7.7 Hz, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): $\delta = 21.4, 126.5, 126.6, 127.5, 127.8, 128.7, 128.8, 129.5, 134.7, 137.5, 137.6.$



(*E*)-1-Fluoro-4-(4-methylstyryl)benzene, 110.⁶⁴ Starting from 0.846 mmol of corresponding olefin the product was obtained as a colourless solid, yield 73% (0.131 g, X = Br, method F). ¹H NMR (400 MHz, CDCl₃): δ = 2.40 (s, 3H, Me), 7.00-7.10 (m, 4H, Ar/olefin), 7.20 (d, *J* = 7.8 Hz, 2H, Ar), 7.43 (d, *J* = 7.8 Hz, 2H, Ar),

7.49 (dd, J = 8.4, 5.4 Hz, 2H, Ar). ¹³**C NMR** (101 MHz, CDCl₃): $\delta = 21.4$, 115.6, 115.8, 126.5, 126.6, 128.0 (d, J = 7.9 Hz), 128.6 (d, J = 2.5 Hz), 129.6, 133.9 (d, J = 3.4 Hz), 134.6, 137.7, 162.4 (d, J = 246.8 Hz).



(*E*)-2-(4-Methylstyryl)naphthalene, 11p.⁶⁵ Starting from 0.846 mmol of corresponding olefin the product was obtained as a colourless solid, yield 64% (0.132 g, method F). ¹H NMR (400 MHz, CDCl₃): δ = 2.39 (s, 3H, Me), 7.18-7.23 (m, 4H, Ar/olefin), 7.42-7.51 (m, 4H, Ar), 7.75 (dd, *J* = 8.6, 1.8 Hz, 1H, Ar), 7.80-

7.86 (m, 4H, Ar). ¹³**C NMR** (101 MHz, CDCl₃): δ = 21.5, 123.7, 126.0, 126.5, 126.6, 126.7, 127.9, 128.0, 128.1, 128.4, 129.2, 129.6, 133.1, 133.9, 134.8, 135.2, 137.8.

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(*E*)-5-(4-Methylstyryl)benzofuran, 11q.⁶⁶ Starting from 0.846 mmol of corresponding olefin the product was obtained as a yellow solid, yield 69% (0.136 g, method F). ¹H NMR (400 MHz, CDCl₃): $\delta = 2.43$ (s, 3H, Me), 6.80 (d, J = 2.2 Hz, 1H, Ar), 7.13 (d, J = 16.3 Hz, 1H, olefin), 7.21-7.25 (m, 3H, Ar/olefin), 7.48-

7.50 (m, 2H, Ar), 7.54 (d, J = 1.3 Hz, 2H, Ar), 7.66 (d, J = 2.2 Hz, 1H, Ar), 7.75-7.76 (m, 1H, Ar). ¹³**C NMR** (101 MHz, CDCl₃): $\delta = 21.4$, 106.8, 111.6, 119.2, 123.1, 126.4, 127.8, 128.0, 128.1, 129.5, 132.8, 134.9, 137.4, 145.6, 154.8.



(*E*)-2-(4-Methylstyryl)thiophene, 11r.⁶⁷ Starting from 0.846 mmol of corresponding olefin the product was obtained as a colourless oil, yield 37% (0.062 g, method F). ¹H NMR (400 MHz, CDCl₃): δ = 2.39 (s, 3H, Me), 6.95 (d, *J* = 16.1 Hz, 1H, olefin), 7.03 (dd, *J* = 5.1, 3.5 Hz, 1H, thiophene), 7.07-7.08 (m, 1H, thiophene), 7.18-7.24 (m, 4H,

Ar/thiophene/olefin), 7.39-7.41 (m, 2H, Ar). ¹³**C NMR** (101 MHz, CDCl₃): $\delta = 21.4$, 121.0, 124.2, 125.9, 126.4, 127.7, 128.5, 129.6, 134.3, 137.7, 143.3.



(*E*)-1-Chloro-4-styrylbenzene, **11s.**⁶⁸ Starting from 7.216 mmol (1 g) of corresponding olefin the product was obtained as a colourless solid, yield 96% (1.496 g). ¹H NMR (400 MHz, CDCl₃): δ = 7.03-7.12 (m, 2H, olefin), 7.27-7.40 (m, 5H, Ar), 7.43-7.47 (m, 2H, Ar), 7.51-7.53 (m, 2H, Ar). ¹³C NMR (101 MHz, CDCl₃): δ = 126.7, 127.5, 127.8, 128.0, 128.9,

129.0, 129.5, 133.3, 136.0, 137.2.

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