SUPPORTING INFORMATION

Designing Homogeneous Copper-Free Sonogashira Reaction through a Prism of Pd-Pd Transmetallation

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1. GENERAL INFORMATION

Starting materials were used as obtained from the commercial sources (Merck, Fluorochem, abcr). Anhydrous solvents, used in solvent screening experiments (1,4-dioxane, dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), ethyl acetate (EtOAc), methanol (MeOH), isopropanol (*i*-PrOH)), were used as received. Acetonitrile (MeCN) was freshly distilled from calcium hydride (CaH_2) under argon atmosphere. Pentane, tetrahydrofuran (THF), and toluene were freshly distilled from sodium wire under argon atmosphere. Palladium oxidative adducts **4a** and **4b** were prepared using standard Schlenk line techniques.

Melting points were determined on a Kofler micro hot stage and are uncorrected.

IR spectra were obtained with a Perkin-Elmer Spectrum 100, equipped with a Specac Golden Gate Diamond ATR as a solid sample support.

NMR spectra were recorded with a Bruker Avance III 500 MHz NMR instrument operating at 500 MHz (^{1}H), 471 MHz (^{19}F), 202 MHz (^{31}P), 160 MHz (^{11}B), and 126 (^{13}C) MHz at 296 K. Proton spectra were recorded in $CDCl_3$ and DMSO-d_6 and are referenced to the residual signals of $CHCl_3$ (at δ 7.26 ppm) and DMSO-d_5 (at δ 2.50 ppm). Carbon chemical shifts are given against the central line of the solvent signal: $CDCl_3$ (at δ 77.16 ppm), DMSO-d_6 (at δ 39.52 ppm). ^{19}F NMR and ^{11}B NMR spectra were referenced to CCl_3F and 15% BF_3 etherate in $CDCl_3$, respectively, as external standards at δ 0. ^{31}P NMR spectra were referenced to external 85% phosphoric acid (at δ 0 ppm) and were acquired with a Bruker ^{31}P composite pulse decoupling (CPD) program. Chemical shifts are given on δ scale (ppm). Coupling constants (*J*) are given in Hertz. Multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or br (broadened).

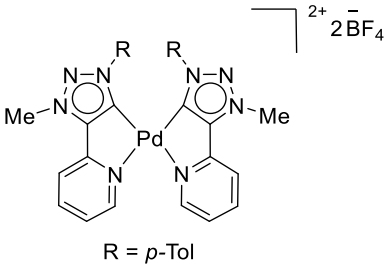
An Agilent 6224 time-of-flight (TOF) mass spectrometer equipped with a double orthogonal electrospray source at atmospheric pressure ionization (ESI) coupled to an Agilent 1260 HLPC was used for recording HRMS spectra. Mobile phase composed of two solvents: A was 0.1% formic acid in Milli-Q water, and B was 0.1% formic acid in acetonitrile mixed in the ratio of 1:1. Compounds were prepared by dissolving the samples in acetonitrile. 0.1–10 μL of each sample and injected into the LC-MS. Flow rate was 0.4 mL/min. Fragmentor voltage was 150 V. Capillary voltage 4000 V. Mass range 100–1700.

Analytical thin-layer chromatography (TLC) was carried out on Fluka Silica Gel TLC cards, visualized with a UV lamp (254 nm and/or 366 nm).

Purification of products was achieved by column chromatography using silica gel 60N.

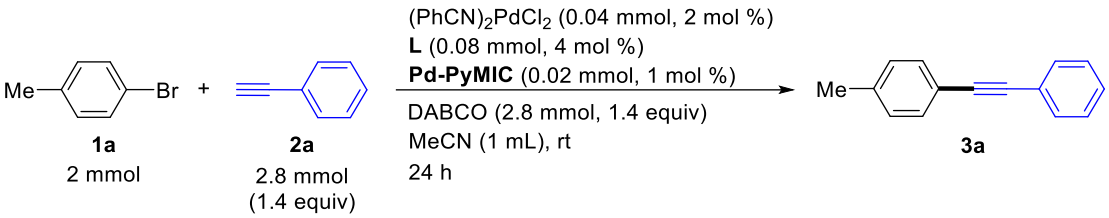
2. EXPERIMANTAL

2.1. Preparation of palladium complex Pd-PyMIC

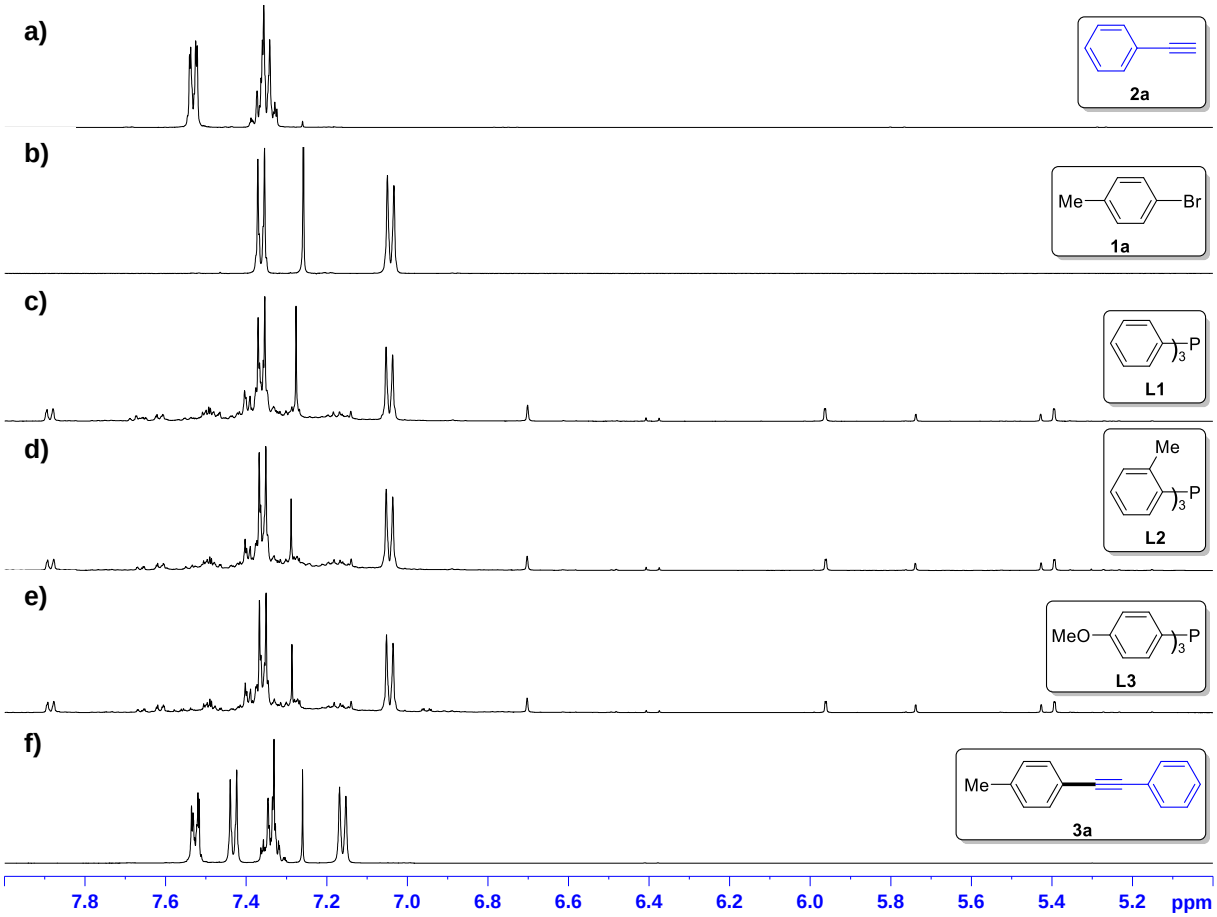


Palladium complex **Pd-PyMIC** was prepared by the previously reported procedure.[1,2] White solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.82–8.75 (m, 2H), 8.54–8.46 (m, 2H), 8.27–8.19 (m, 2H), 7.75–7.69 (m, 2H), 7.54–7.44 (m, 4H), 7.38–7.33 (m, 4H), 4.43 (s, 6H), 2.41 (s, 6H). NMR data are in agreement with those from the literature.[1,2]

2.2. Formation of enyne-like side products in phosphine ligand screening experiments (Table 1, L1–L3)

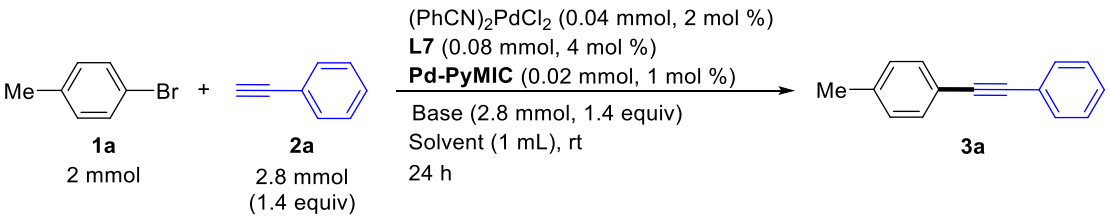


Procedure: An oven-dried (130 °C for 3 hour) 5 mL round-bottom flask, equipped with magnetic stir bar and septum, was charged with acetonitrile (1 mL), $(PhCN)_2PdCl_2$ (0.04 mmol, 2 mol %) and ligand **L** (0.08 mmol, 4 mol %) under continuous flow of argon. The reaction mixture was stirred for 5 min at room temperature, then **Pd-PyMIC** (0.02 mmol, 1 mol %), DABCO (2.8 mmol, 1.4 equiv), 4-bromotoluene (**1a**, 2 mmol) and phenylacetylene (**2a**, 2.8 mmol, 1.4 equiv) were added. The argon flow was removed and the reaction mixture was stirred at room temperature for 24 hours. The conversions were determined by ^{1}H NMR of aliquots (20 µL) of the crude reaction mixture, dissolved in $CDCl_3$ (0.7 mL). Each experiment was performed at least in duplicate and the results are collected in Table 1 and Supplementary Figure S1.



Supplementary Figure S1. Selected regions of ^{1}H NMR spectra of a) alkyne **2a**, b) bromide **1a**, c) crude reaction mixture using **L1** as a ligand, d) crude reaction mixture using **L2** as a ligand, e) crude reaction mixture using **L3** as a ligand, and f) tolane **3a** in $CDCl_3$, 500 MHz.

2.3. Solvent and base screening experiments (Supplementary Table S1)



Procedure: An oven-dried (130 °C for 3 hours) 5 mL round-bottom flask, equipped with magnetic stir bar and septum was charged with Solvent (1 mL), $(PhCN)_2PdCl_2$ (0.04 mmol, 2 mol %) and Cata*CX*ium A (**L7**, 0.08 mmol, 4 mol %) under continuous flow of argon. The reaction mixture was stirred for 5 min at room temperature, then **Pd-PyMIC** (0.02 mmol, 1 mol %), Base (2.8 mmol, 1.4 equiv), 4-bromotoluene (**1a**, 2 mmol) and phenylacetylene (**2a**, 2.8 mmol, 1.4 equiv) were added. The argon flow was removed and the reaction mixture was stirred at room temperature for 24 hours. The conversions were determined by ^{1}H NMR of

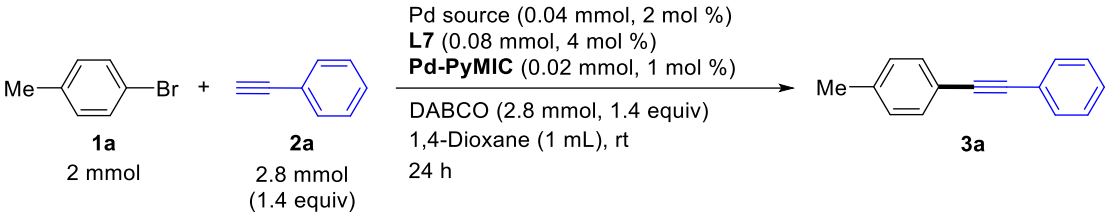
aliquots (20 µL) of the crude reaction mixture, dissolved in $CDCl_3$ (0.7 mL). Each experiment was performed at least in duplicate and the results are collected in Supplementary Table S1.

Supplementary Table S1. Results from the solvent and base screening experiments.

Entry	Solvent	Base	Yield (%)[a]
1	MeCN	DABCO	20
2	NMP	DABCO	13
3	DMF	DABCO	17
4	MeOH	DABCO	15
5	*i*-PrOH	DABCO	14
6	EtOAc	DABCO	22
7	THF	DABCO	19
8	1,4-Dioxane	DABCO	35, 50[b]
9	Toluene	DABCO	<1
10	1,4-Dioxane	Pyrolidine	<1
11	1,4-Dioxane	*t*-$BuNH_2$	<1
12	1,4-Dioxane	NEt_3	11
13	1,4-Dioxane	*i*-Pr_2NEt	10
14	1,4-Dioxane	Cy_2NMe	12
15	1,4-Dioxane	DBU	<1
16	1,4-Dioxane	DBN	<1
17	1,4-Dioxane	TMG	<1
18	1,4-Dioxane	K_2CO_3	38, 70[b]
19	1,4-Dioxane	Cs_2CO_3	10
20	1,4-Dioxane	K_3PO_4	22
21	1,4-Dioxane	KOAc	9
22	1,4-Dioxane	KOPiv	13
23	1,4-Dioxane	KOH	<1

[a] NMR yield determined from at least two consecutive runs. [b] Reaction time was 72 h.

2.4. Palladium source screening experiments (Supplementary Table S2)



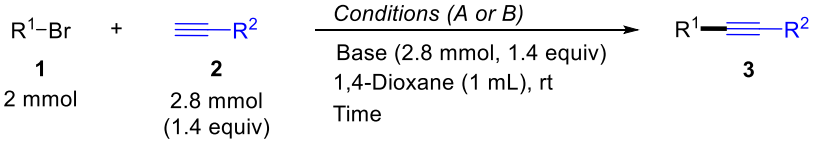
Procedure: An oven-dried (130 °C for 3 hours) 5 mL round-bottom flask, equipped with magnetic stir bar and septum was charged with 1,4-dioxane (1 mL), Pd source (0.04 mmol, 2 mol %) and Cata*CX*ium A (**L7**, 0.08 mmol, 4 mol %) under continuous flow of argon. The reaction mixture was stirred for 5 min at room temperature, then **Pd-PyMIC** (0.02 mmol, 1 mol %), DABCO (2.8 mmol, 1.4 equiv), 4-bromotoluene (**1a**, 2 mmol) and phenylacetylene (**2a**, 2.8 mmol, 1.4 equiv) were added. Argon flow was removed and the reaction mixture was stirred at room temperature for 24 hours. The conversions were determined by ^{1}H NMR of aliquots (20 µL) of the crude reaction mixture, dissolved in $CDCl_3$ (0.7 mL). Each experiment was performed at least in duplicate and the results are collected in Supplementary Table S2.

Supplementary Table S2. Results from palladium source screening experiments.

Entry	Pd source	Yield (%)[a]
1	$(PhCN)_2PdCl_2$	38[b]
2	$(MeCN)_2PdCl_2$	7
3	$(PhCN)_2PdBr_2$	17
4	$Pd(OAc)_2$	22
5	$Pd(TFA)_2$	29
6	$Pd(dba)_2$	10

[a] NMR yield determined from at least two consecutive runs. [b] For comparison reasons, the result is taken from Supplementary Table S1.

2.5. Synthesis and characterization of products from Table 3

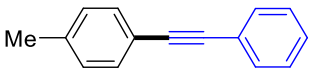


***Conditions A*:** An oven-dried (130 °C for 3 hours) 5 mL round-bottom flask, equipped with magnetic stir bar and septum, was charged with anhydrous 1,4-dioxane (1 mL), $(PhCN)_2PdCl_2$

(0.04 mmol, 2 mol %) and Cata*CX*ium A (**L7**, 0.08 mmol, 4 mol %) under continuous flow of argon. The reaction mixture was stirred for 5 min at room temperature, then **Pd-PyMIC** (0.02 mmol, 1 mol %), Base (2.8 mmol, 1.4 equiv), bromide **1** (2 mmol) and acetylene **2** (2.8 mmol, 1.4 equiv) were added. Argon flow was removed and the reaction mixture was stirred at room temperature for the time indicated below and in Table 3, during which milky, yellowish to brownish coloured mixture started forming. After completion the reaction mixture was diluted with ethyl acetate (150 mL) and washed with brine (2 × 100 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporation to give a crude brown solid/oil. Product **3** was additionally purified by SiO_2 column chromatography.

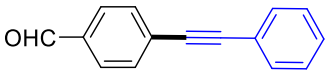
***Conditions B*:** An oven-dried (130 °C for 3 hours) 5 mL round-bottom flask, equipped with magnetic stir bar and septum was charged with anhydrous 1,4-dioxane (1 mL), $(PhCN)_2PdCl_2$ (0.005 mmol, 0.25 mol %) and Cata*CX*ium A (**L7**, 0.01 mmol, 0.5 mol %) under continuous flow of argon. The reaction mixture was stirred for 5 min at room temperature, then **Pd-PyMIC** (0.005 mmol, 0.25 mol %), Base (2.8 mmol, 1.4 equiv), bromide **1** (2 mmol) and acetylene **2** (2.8 mmol, 1.4 equiv) were added. Argon flow was removed and the reaction mixture was stirred at room temperature for the time indicated below and in Table 3, during which milky, yellowish to brownish coloured mixture started forming. After completion the reaction mixture was diluted with ethyl acetate (150 mL) and washed with brine (2 × 100 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporation to give a crude brown solid/oil. Product **3** was additionally purified by SiO_2 column chromatography.

1-Methyl-4-(phenylethynyl)benzene (3a; Table 3)



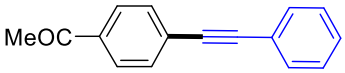
Prepared according to *Conditions A*, using $(PhCN)_2PdCl_2$ (15.3 mg, 0.04 mmol), Cata*CX*ium A (**L7**, 28.7 mg, 0.08 mmol), complex **Pd-PyMIC** (15.6 mg, 0.02 mmol), K_2CO_3 (387 mg, 2.8 mmol), 4-bromotoluene (**1a**, 342 mg, 2 mmol), phenylacetylene (**2a**, 286 mg, 2.8 mmol), reaction time 72 h. The title product **3a** (242 mg, 63%) was obtained after column chromatography purification (petroleum ether, R_f = 0.28) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.50 (m, 2H), 7.45–7.41 (m, 2H), 7.37–7.31 (m, 3H), 7.18–7.13 (m, 2H), 2.37 (s, 3H). NMR data are in agreement with those from the literature.[3,4]

4-(Phenylethynyl)benzaldehyde (3b; Table 3)



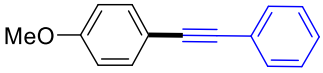
Prepared according to *Conditions B*, using $(PhCN)_2PdCl_2$ (1.9 mg, 0.005 mmol), Cata*CX*ium A (**L7**, 3.6 mg, 0.01 mmol), complex **Pd-PyMIC** (3.9 mg, 0.005 mmol), DABCO (314 mg, 2.8 mmol), 4-bromobenzaldehyde (**1b**, 370 mg, 2 mmol), phenylacetylene (**2a**, 286 mg, 2.8 mmol), reaction time 24 h. The title product **3b** (355 mg, 86%) was obtained after column chromatography purification (petroleum ether/ethyl acetate = 20 : 1, R_f = 0.20) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.89–7.85 (m, 2H), 7.70–7.65 (m, 2H), 7.57–7.55 (m, 2H), 7.40–7.37 (m, 3H). NMR data are in agreement with those from the literature.[5,6]

1-(4-(Phenylethynyl)phenyl)ethan-1-one (3c; Table 3)



Prepared according to *Conditions B*, using $(PhCN)_2PdCl_2$ (1.9 mg, 0.005 mmol), Cata*CX*ium A (**L7**, 3.6 mg, 0.01 mmol), complex **Pd-PyMIC** (3.9 mg, 0.005 mmol), DABCO (314 mg, 2.8 mmol), 4-bromoacetophenone (**1c**, 398 mg, 2 mmol), phenylacetylene (**2a**, 286 mg, 2.8 mmol), reaction time 72 h. The title product **3c** (419 mg, 95%) was obtained after column chromatography purification (petroleum ether/ethyl acetate = 20 : 1, R_f = 0.26) as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96–7.92 (m, 2H), 7.63–7.59 (m, 2H), 7.57–7.53 (m, 2H), 7.39–7.35 (m, 3H), 2.61 (s, 3H). NMR data are in agreement with those from the literature.[7,8]

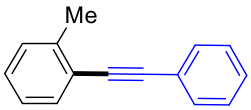
1-Methoxy-4-(phenylethynyl)benzene (3d; Table 3)



Prepared according to *Conditions A*, using $(PhCN)_2PdCl_2$ (15.3 mg, 0.04 mmol), Cata*CX*ium A (**L7**, 28.7 mg, 0.08 mmol), complex **Pd-PyMIC** (15.6 mg, 0.02 mmol), DABCO (314 mg,

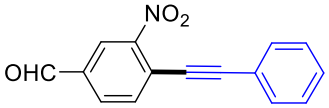
2.8 mmol), 4-bromoanisole (**1d**, 374 mg, 2 mmol), phenylacetylene (**2a**, 286 mg, 2.8 mmol), reaction time 48 h. The title product **3d** (162 mg, 39%) was obtained after column chromatography purification (petroleum ether/ethyl acetate = 100 : 1, R_f = 0.18) as a light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.49 (m, 2H), 7.49–7.46 (m, 2H), 7.36–7.30 (m, 3H), 6.90–6.86 (m, 2H), 3.83 (s, 3H). NMR data are in agreement with those from the literature.[8,9]

1-Methyl-2-(phenylethynyl)benzene (3e; Table 3)



Prepared according to *Conditions A*, using $(PhCN)_2PdCl_2$ (15.3 mg, 0.04 mmol), Cata*CX*ium A (**L7**, 28.7 mg, 0.08 mmol), complex **Pd-PyMIC** (15.6 mg, 0.02 mmol), DABCO (314 mg, 2.8 mmol), 1-bromo-2-methylbenzene (**1e**, 342 mg, 2 mmol), phenylacetylene (**2a**, 286 mg, 2.8 mmol), reaction time 72 h. The title product **3e** (135 mg, 35%) was obtained after column chromatography purification (petroleum ether, R_f = 0.36) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58–7.54 (m, 2H), 7.53–7.50 (m, 1H), 7.39–7.33 (m, 3H), 7.26–7.23 (m, 2H), 7.21–7.16 (m, 1H), 2.54 (s, 3H). NMR data are in agreement with those from the literature.[10,11]

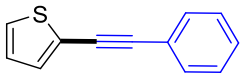
3-Nitro-4-(phenylethynyl)benzaldehyde (3f; Table 3)



Prepared according to *Conditions B*, using $(PhCN)_2PdCl_2$ (1.9 mg, 0.005 mmol), Cata*CX*ium A (**L7**, 3.6 mg, 0.01 mmol), complex **Pd-PyMIC** (3.9 mg, 0.005 mmol), DABCO (314 mg, 2.8 mmol), 4-bromo-3-nitrobenzaldehyde (**1f**, 460 mg, 2 mmol), phenylacetylene (**2a**, 286 mg, 2.8 mmol), reaction time 24 h. Due to low solubility of starting bromide **1f**, 2.5 mL of 1,4-dioxane was used. The title product **3f** (446 mg, 89%) was obtained after column chromatography purification (petroleum ether/ethyl acetate = 10 : 1, R_f = 0.25) as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.59–8.55 (m, 1H), 8.14–8.09 (m, 1H),

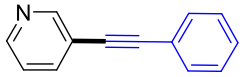
7.90–7.87 (m, 1H), 7.66–7.61 (m, 2H), 7.47–7.39 (m, 3H). NMR data are in agreement with those from the literature.[1]

2-(Phenylethynyl)thiophene (3g; Table 3)



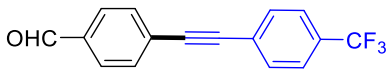
Prepared according to *Conditions A*, using $(PhCN)_2PdCl_2$ (15.3 mg, 0.04 mmol), Cata*CX*ium A (**L7**, 28.7 mg, 0.08 mmol), complex **Pd-PyMIC** (15.6 mg, 0.02 mmol), DABCO (314 mg, 2.8 mmol), 2-bromothiophene (**1g**, 326 mg, 2 mmol), phenylacetylene (**2a**, 286 mg, 2.8 mmol), reaction time 48 h. The title product **3g** (148 mg, 40%) was obtained after column chromatography purification (petroleum ether, R_f = 0.39) as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.50 (m, 2H), 7.37–7.32 (m, 3H), 7.31–7.28 (m, 2H), 7.04–6.99 (m, 1H). NMR data are in agreement with those from the literature.[8,12]

3-(Phenylethynyl)pyridine (3h; Table 3)



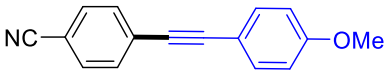
Prepared according to *Conditions A*, using $(PhCN)_2PdCl_2$ (15.3 mg, 0.04 mmol), Cata*CX*ium A (**L7**, 28.7 mg, 0.08 mmol), complex **Pd-PyMIC** (15.6 mg, 0.02 mmol), DABCO (314 mg, 2.8 mmol), 3-bromopyridine (**1h**, 316 mg, 2 mmol), phenylacetylene (**2a**, 286 mg, 2.8 mmol), reaction time 48 h. The title product **3h** (258 mg, 72 %) was obtained after column chromatography purification (petroleum ether/ethyl acetate = 5 : 1, R_f = 0.23) as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79–8.76 (m, 1H), 8.57–8.53 (m, 1H), 7.83–7.79 (m, 1H), 7.57–7.53 (m, 2H), 7.39-7.35 (m, 3H), 7.30–7.27 (m, 1H). NMR data are in agreement with those from the literature.[13,14]

4-((4-(Trifluoromethyl)phenyl)ethynyl)benzaldehyde (3i; Table 3)



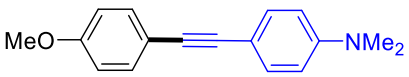
Prepared according to *Conditions A*, using $(PhCN)_2PdCl_2$ (15.3 mg, 0.04 mmol), Cata*CX*ium A (**L7**, 28.7 mg, 0.08 mmol), complex **Pd-PyMIC** (15.6 mg, 0.02 mmol), DABCO (314 mg, 2.8 mmol), 4-bromobenzaldehyde (**1b**, 370 mg, 2 mmol), 1-ethynyl-4-(trifluoromethyl)benzene (**2b**, 476 mg, 2.8 mmol), reaction time 48 h. The title product **3i** (466 mg, 85%) was obtained after column chromatography purification (petroleum ether/ethyl acetate = 20 : 1, R_f = 0.21) as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.92–7.87 (m, 2H), 7.72–7.68 (m, 2H) 7.67–7.62 (m, 4H). ^{19}F NMR (461 MHz, $CDCl_3$) δ –62.9. NMR data are in agreement with those from the literature.[15]

4-((4-Methoxyphenyl)ethynyl)benzonitrile (3j; Table 3)



Prepared according to *Conditions B*, using $(PhCN)_2PdCl_2$ (1.9 mg, 0.005 mmol), Cata*CX*ium A (**L7**, 3.6 mg, 0.01 mmol), complex **Pd-PyMIC** (3.9 mg, 0.005 mmol), DABCO (314 mg, 2.8 mmol), 4-bromobenzonitrile (**1i**, 364 mg, 2 mmol), 1-ethynyl-4-methoxybenzene (**2c**, 370 mg, 2.8 mmol), reaction time 24 h. The title product **3j** (438 mg, 94%) was obtained after column chromatography purification (petroleum ether/ethyl acetate = 10 : 1, R_f = 0.22) as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64–7.60 (m, 2H), 7.59–7.55 (m, 2H), 7.50–7.45 (m, 2H), 6.93–6.88 (m, 2H), 3.84 (s, 3H). NMR data are in agreement with those from the literature.[16,17]

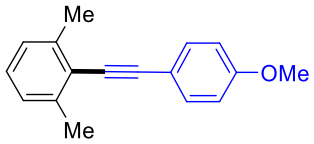
4-((4-Methoxyphenyl)ethynyl)-*N*,*N*-dimethylaniline (3k; Table 3)



Prepared according to *Conditions A*, using $(PhCN)_2PdCl_2$ (15.3 mg, 0.04 mmol), Cata*CX*ium A (**L7**, 28.7 mg, 0.08 mmol), complex **Pd-PyMIC** (15.6 mg, 0.02 mmol), DABCO (314 mg, 2.8 mmol), 4-bromoanisole (**1d**, 374 mg, 2 mmol), 4-ethynyl-*N*,*N*-dimethylaniline (**2d**, 407 mg, 2.8 mmol), reaction time 48 h. The title product **3k** (271 mg, 54%) was obtained after column chromatography purification (petroleum ether/ethyl acetate = 20 : 1, R_f = 0.22) as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.42 (m, 2H), 7.40–7.37 (m, 2H), 6.88–

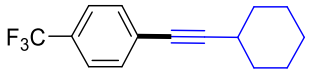
6.83 (m, 2H), 6.68–6.63 (m, 2H), 3.82 (s, 3H), 2.98 (s, 3H). NMR data are in agreement with those from the literature.[17,18]

2-((4-Methoxyphenyl)ethynyl)-1,3-dimethylbenzene (3l; Table 3)



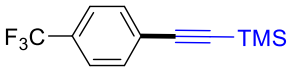
Prepared according to *Conditions A*, using $(PhCN)_2PdCl_2$ (15.3 mg, 0.04 mmol), Cata*CX*ium A (**L7**, 28.7 mg, 0.08 mmol), complex **Pd-PyMIC** (15.6 mg, 0.02 mmol), DABCO (314 mg, 2.8 mmol), 2-bromo-1,3-dimethylbenzene (**1j**, 370 mg, 2 mmol), 1-ethynyl-4-methoxybenzene (**2c**, 370 mg, 2.8 mmol), reaction time 48 h. The title product **3l** (151 mg, 32%) was obtained after column chromatography purification (petroleum ether/ethyl acetate = 100 : 1, R_f = 0.21) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.47 (m, 2H), 7.14–7.09 (m, 1H), 7.09–7.05 (m, 2H), 6.92–6.87 (m, 2H), 3.84 (s, 3H), 2.52 (s, 6H). NMR data are in agreement with those from the literature.[19]

1-(Cyclohexylethynyl)-4-(trifluoromethyl)benzene (3m; Table 3)



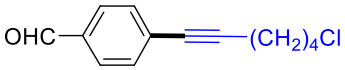
Prepared according to *Conditions A*, using $(PhCN)_2PdCl_2$ (15.3 mg, 0.04 mmol), Cata*CX*ium A (**L7**, 28.7 mg, 0.08 mmol), complex **Pd-PyMIC** (15.6 mg, 0.02 mmol), DABCO (314 mg, 2.8 mmol), 1-bromo-4-(trifluoromethyl)benzene (**1k**, 450 mg, 2 mmol), ethynylcyclohexane (**2e**, 303 mg, 2.8 mmol), reaction time 72 h. The title product **3m** (257 mg, 51%) was obtained after column chromatography purification (petroleum ether, R_f = 0.23) as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.50 (m, 2H), 7.50–7.46 (m, 2H), 2.65–2.56 (m, 1H), 1.93–1.85 (m, 2H), 1.81–1.71 (m, 2H), 1.60–1.50 (m, 3H), 1.40–1.30 (m, 3H). NMR data are in agreement with those from the literature.[20]

Trimethyl((4-(trifluoromethyl)phenyl)ethynyl)silane (3n; Table 3)



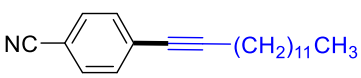
Prepared according to *Conditions A*, using $(PhCN)_2PdCl_2$ (15.3 mg, 0.04 mmol), Cata*CX*ium A (**L7**, 28.7 mg, 0.08 mmol), complex **Pd-PyMIC** (15.6 mg, 0.02 mmol), DABCO (314 mg, 2.8 mmol), 1-bromo-4-(trifluoromethyl)benzene (**1k**, 450 mg, 2 mmol), ethynyltrimethylsilane (**2f**, 275 mg, 2.8 mmol), reaction time 72 h. The title product **3n** (388 mg, 80%) was obtained after column chromatography purification (petroleum ether, R_f = 0.23) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57–7.54 (m, 4H), 0.26 (s, 9H). NMR data are in agreement with those from the literature.[21,22]

4-(6-Chlorohex-1-yn-1-yl)benzaldehyde (3o; Table 3)



Prepared according to *Conditions A*, using $(PhCN)_2PdCl_2$ (15.3 mg, 0.04 mmol), Cata*CX*ium A (**L7**, 28.7 mg, 0.08 mmol), complex **Pd-PyMIC** (15.6 mg, 0.02 mmol), DABCO (314 mg, 2.8 mmol), 4-bromobenzaldehyde (**1b**, 370 mg, 2 mmol), 6-chlorohex-1-yne (**2g**, 326 mg, 2.8 mmol), reaction time 48 h. The title product **3o** (309 mg, 70%) was obtained after column chromatography purification (petroleum ether/ethyl acetate = 40 : 1, R_f = 0.17) as a yellow solid. Mp 39.1–41.0 °C. IR (cm^{-1}): 2954, 1684, 1603, 1425, 1316, 1281, 1208, 933, 859, 831, 768, 650. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.82–7.77 (m, 2H), 7.55–7.50 (m, 2H), 3.60 (t, J = 6.6 Hz, 2H), 2.50 (t, J = 6.9 Hz, 2H), 2.00–1.92 (m, 2H), 1.82–1.75 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6, 135.2, 132.2, 130.3, 129.6, 94.1, 80.8, 44.6, 31.7, 25.8, 19.0. HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_{13}H_{14}ClO$, 221.0728; found, 221.0727.

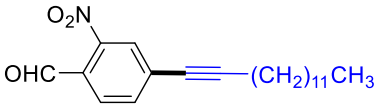
4-(Tetradec-1-yn-1-yl)benzonitrile (3p; Table 3)



Prepared according to *Conditions A*, using $(PhCN)_2PdCl_2$ (15.3 mg, 0.04 mmol), Cata*CX*ium A (**L7**, 28.7 mg, 0.08 mmol), complex **Pd-PyMIC** (15.6 mg, 0.02 mmol), DABCO (314 mg, 2.8 mmol), 4-bromobenzonitrile (**1i**, 364 mg, 2 mmol), 1-tetradecyne (**2h**, 544 mg, 2.8 mmol),

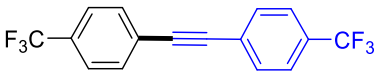
reaction time 24 h. The title product **3p** (547 mg, 93%) was obtained after column chromatography purification (petroleum ether/ethyl acetate = 100 : 1, R_f = 0.23) as a white solid. Mp 45.7–47.0 °C. IR (cm^{-1}): 2957, 2914, 2846, 2225, 1676, 1605, 1502, 1460, 1272, 1181, 837, 722. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58–7.54 (m, 2H), 7.47–7.43 (m, 2H), 2.42 (t, J = 7.1 Hz, 2H), 1.64–1.57 (m, 2H), 1.47–1.40 (m, 2H), 1.35–1.20 (m, 16H), 0.90–0.85 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.2, 132.0, 129.3, 118.8, 110.9, 95.9, 79.5, 32.0, 29.79, 29.77, 29.74, 29.6, 29.5, 29.2, 29.0, 28.6, 22.8, 19.6, 14.2. HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_{21}H_{30}N$, 296.2373; found, 296.2369.

2-Nitro-4-(tetradec-1-yn-1-yl)benzaldehyde (3r; Table 3)



Prepared according to *Conditions A*, using $(PhCN)_2PdCl_2$ (15.3 mg, 0.04 mmol), Cata*CX*ium A (**L7**, 28.7 mg, 0.08 mmol), complex **Pd-PyMIC** (15.6 mg, 0.02 mmol), DABCO (314 mg, 2.8 mmol), 4-bromo-2-nitrobenzaldehyde (**1l**, 460 mg, 2 mmol), 1-tetradecyne (**2h**, 544 mg, 2.8 mmol), reaction time 72 h. Due to low solubility of starting bromide **1l**, 2.5 mL of 1,4-dioxane was used. The title product **3r** (275 mg, 40%) was obtained after column chromatography purification (petroleum ether/ethyl acetate = 20 : 1, R_f = 0.33) as a yellow solid. Mp 39.1–40.3 °C. IR (cm^{-1}): 2953, 2915, 2849, 2224, 1690, 1611, 1526, 1470, 1344, 1191, 906, 851, 826, 745, 716. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.38–10.37 (m, 1H), 8.06–8.02 (m, 1H), 7.90–7.86 (m, 1H), 7.73–7.69 (m, 1H), 2.45 (t, J = 7.1 Hz, 2H), 1.66–1.59 (m, 2H), 1.48–1.40 (m, 2H), 1.36–1.22 (m, 16H), 0.90–0.86 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.6, 149.8, 136.5, 130.8, 129.6, 129.3, 127.3, 98.3, 78.4, 32.0, 29.79, 29.77, 29.75, 29.6, 29.5, 29.2, 29.1, 28.4, 22.8, 19.7, 14.3. HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_{21}H_{30}NO_3$, 344.2220; found, 344.2219.

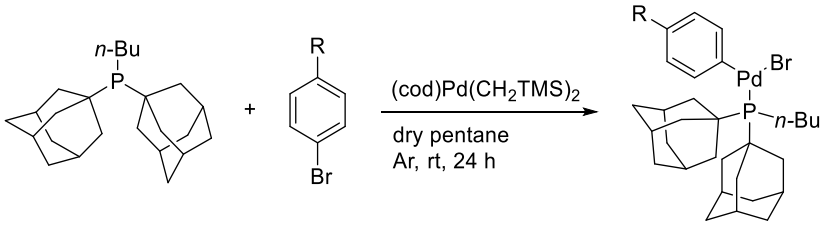
1,2-bis(4-(Trifluoromethyl)phenyl)ethyne (3s; Table 3)



Prepared according to *Conditions A*, using $(PhCN)_2PdCl_2$ (15.3 mg, 0.04 mmol), Cata*CX*ium A (**L7**, 28.7 mg, 0.08 mmol), complex **Pd-PyMIC** (15.6 mg, 0.02 mmol), DABCO (314 mg,

2.8 mmol), 1-bromo-4-(trifluoromethyl)benzene (**1k**, 450 mg, 2 mmol), 1-ethynyl-4-(trifluoromethyl)benzene (**2b**, 476 mg, 2.8 mmol), reaction time 96 h. The title product **3s** (289 mg, 46%) was obtained after column chromatography purification (petroleum ether, R_f = 0.43) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68–7.60 (m, 8H). ^{19}F NMR (461 MHz, $CDCl_3$) δ –62.9. NMR data are in agreement with those from the literature.[23,24]

2.6. Synthesis and characterization of palladium oxidative adducts 4

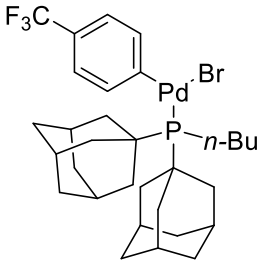


L7 (1 equiv) **1** (1.3 equiv) **4**

Compounds **4a** and **4b** were prepared by a modified literature procedure.[25]

General procedure: To a flame dried Schlenk flask Cata*CX*ium A (**L7**, 64.5 mg, 0.18 mmol), anhydrous pentane (5.0 mL) and aryl bromide **1** (0.24 mmol) were added under argon atmosphere, followed by addition of (cod)Pd($CH_2TMS)_2$ (70.0 mg, 0.18 mmol). The reaction mixture was stirred for 24 hours at room temperature. During the reaction an off-white precipitate was formed. The precipitate was collected by filtration, and washed with cold Et_2O (3 × 20 mL) and dried in vacuum to obtain desired products **4**.

(*p*-CF_3Ph)(Br)Pd(Cata*CX*ium A) (4a)

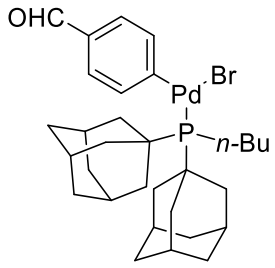


4a

Prepared according to *General procedure*, using Cata*CX*ium A (**L7**, 64.5 mg, 0.18 mmol), 1-bromo-4-(trifluoromethyl)benzene (**1k**, 54.0 mg, 0.24 mmol), (cod)Pd($CH_2TMS)_2$ (70.0 mg,

0.18 mmol), reaction time 24 h. The titled product **4a** (74 mg, 60%) was obtained as a white solid. The product was found to be unstable at ambient atmosphere and temperature (22 °C) for a prolonged time. Mp 201.5–202.1 °C (with decomposition). IR (cm^{-1}): 2954, 2902, 2851, 1587, 1450, 1326, 1302, 1155, 1111, 1097, 1069, 1008, 816, 726. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58–7.51 (m, 2H), 7.19–7.07 (m, 2H), 2.40–2.25 (m, 12H), 2.06–1.98 (m, 6H), 1.82–1.68 (m, 12H), 1.42–1.28 (m, 2H), 1.16–1.00 (m, 2H), 0.67–0.47 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.2 (m), 126.0, 123.9, 125.3 (q, J = 32.1 Hz), 122.8, 42.9 (d, J = 14.4 Hz), 40.8, 36.7, 29.0 (d, J = 8.6 Hz), 28.2, 25.6 (d, J = 11.8 Hz), 20.1 (d, J = 22.3 Hz), 13.6. Quartet resonance for CF_3 carbon atom could not be found in the ^{13}C NMR spectrum. ^{19}F NMR (471 MHz, $CDCl_3$) δ –61.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ 47.5. HRMS–ESI (*m/z*): $[M - Br + MeCN]^+$ calcd for $C_{33}H_{46}F_3NPPd$, 650.2355; found, 650.2356.

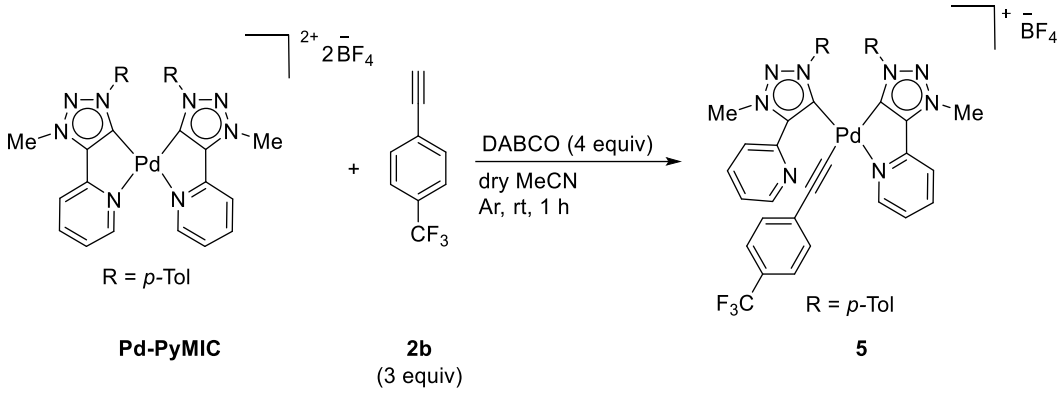
(*p*-CHOPh)(Br)Pd(Cata*CX*ium A) (4b)



4b

Prepared according to *General procedure*, using Cata*CX*ium A (**L7**, 64.5 mg, 0.18 mmol), 4-bromobenzaldehyde (**1b**, 44.4 mg, 0.24 mmol), (cod)Pd($CH_2TMS)_2$ (70.0 mg, 0.18 mmol), reaction time 24 h. The titled product **4b** (82 mg, 70%) was obtained as a white solid. The product was found to be unstable at ambient atmosphere and temperature (22 °C) for a prolonged time. Mp 190.0–192.1 °C (with decomposition). IR (cm^{-1}): 2954, 2903, 2849, 1701, 1572, 1552, 1453, 1343, 1299, 1213, 1167, 1043, 1006, 967, 814, 706. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.82 (brs, 1H), 7.71–7.63 (m, 2H), 7.43–7.33 (m, 2H), 2.42–2.24 (m, 12H), 2.08–1.98 (m, 6H), 1.83–1.68 (m, 12H), 1.43–1.31 (m, 2H), 1.20–1.05 (m, 2H), 0.62–0.51 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.8, 137.8, 132.3, 127.2, 43.0 (d, J = 14.1 Hz), 40.9, 36.7, 29.0 (d, J = 8.9 Hz), 28.2, 25.5 (d, J = 11.9 Hz), 20.4, 13.6. ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 47.8. HRMS–ESI (*m/z*): $[M - Br + MeCN]^+$ calcd for $C_{33}H_{47}NOPPd$, 610.2430; found, 610.2435.

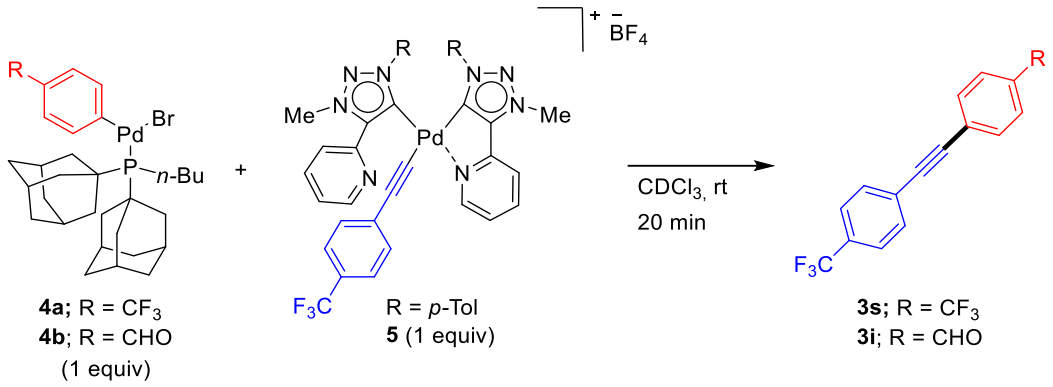
2.7. Synthesis and characterization of palladium acetylide 5



Pd-PyMIC **2b** (3 equiv) **5**

To a 100 mL round-bottom flask, equipped with a magnetic stir bar and septum anhydrous MeCN (40 mL), DABCO (53.8 mg, 0.48 mmol), 1-ethynyl-4-(trifluoromethyl)benzene (**2b**, 61.2 mg, 0.36 mmol) and palladium complex **Pd-PyMIC** (93.7 mg, 0.12 mmol) were added under continuous flow of argon. The reaction mixture was stirred for 1 hour under argon atmosphere at room temperature. Then, the reaction mixture was filtered through a pad of Celite. The solvent from the filtrate was removed under reduced pressure and the residue was subjected to column chromatography (DCM/MeCN = 5 : 1, with the addition of 1 vol % of Et_3N; R_f = 0.32) to afford title product **5** (74 mg, 71%) as an off-white solid. Product **5** was not stable under prolonged time if exposed to ambient atmosphere and temperature (22 °C). Mp 105.3–107.0 °C (with decomposition). IR (cm^{-1}): 3374, 2925, 2104, 1611, 1512, 1453, 1320, 1160, 1102, 1061, 1013, 823, 791, 747, 700. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.54–9.49 (m, 1H), 9.35–9.30 (m, 1H), 8.73–8.67 (m, 1H), 8.32–8.24 (m, 2H), 8.05–8.00 (m, 2H), 7.94–7.89 (m, 1H), 7.54–7.49 (m, 1H), 7.44–7.36 (m, 3H), 7.33–7.27 (m, 4H), 7.16–7.11 (m, 2H), 6.81–6.76 (m, 2H), 4.57 (s, 3H), 4.36 (s, 3H), 2.49 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.03, 154.5, 149.7, 149.0, 148.4, 148.1, 147.0, 142.0, 141.5, 140.9, 140.7, 137.6, 136.6, 134.9, 131.4, 130.9, 130.0, 129.3, 127.6 (q, J = 32.3 Hz), 125.9, 125.7, 125.0 (q, J = 3.6 Hz), 124.7, 124.4, 123.7, 122.2, 115.2, 105.5, 40.4, 39.6, 21.5, 21.4. Quartet resonance for CF_3 carbon atom could not be located in the ^{13}C NMR spectrum. ^{19}F NMR (471 MHz, $CDCl_3$) δ –62.4, –153.1 (d, J = 24.7 Hz). ^{11}B NMR (160 MHz, $CDCl_3$) δ –1.05. HRMS–ESI (*m/z*): $[M]^+$ calcd for $C_{39}H_{32}F_3N_8Pd$, 775.1731; found, 775.1737.

2.8. Transmetalation reaction between oxidative adducts 4 and palladium monoacetylide 5



4a; R = CF_3
4b; R = CHO
(1 equiv)

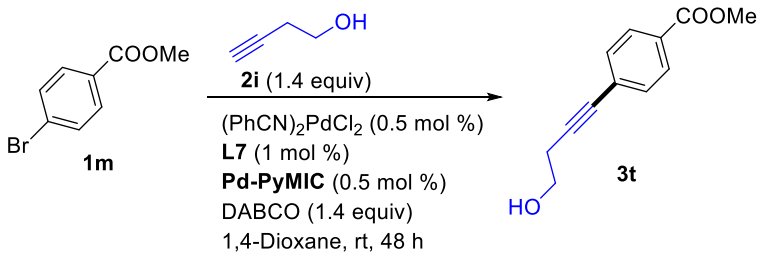
R = *p*-Tol
5 (1 equiv)

3s; R = CF_3
3i; R = CHO

An oven-dried (130 °C for 30 minutes) NMR tube was cooled in continuous flow of argon and charged with palladium oxidative adduct **4a** (3.2 mg, 4.6 µmol) and palladium monoacetylide (**5**, 4.0 mg, 4.6 µmol), followed by the addition of 0.7 mL of $CDCl_3$. NMR tube was sealed with parafilm and left at room temperature (22 °C) for 20 minutes before ^1H and $^{19}F\{H\}$ NMR spectrum were recorded. ^1H and $^{19}F\{H\}$ NMR spectra showed the formation of the cross-coupled product **3s** (Figure 1 and Supplementary Figures S37 and S38).

Reaction was repeated under the same reaction conditions as above, using palladium oxidative adduct **4b** (3.0 mg, 4.6 µmol) and palladium monoacetylide (**5**, 4.0 mg, 4.6 µmol) in $CDCl_3$ (0.7 mL). After standing at room temperature (22 °C) for 20 minutes ^1H and $^{19}F\{H\}$ NMR spectra were measured, showing the formation of the cross-coupled product **3i** (Supplementary Figures S39 and S40).

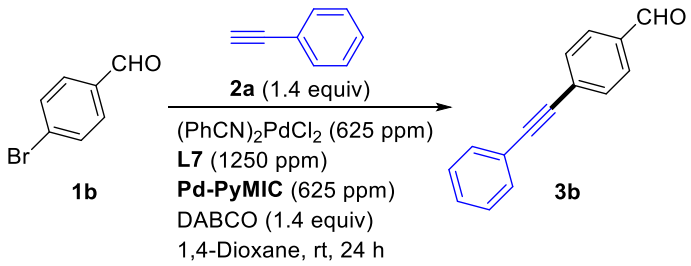
2.9. Synthesis of methyl 4-(4-hydroxybut-1-yn-1-yl)benzoate (3t)



An oven-dried (130 °C for 3 hours) 5 mL round-bottom flask, equipped with magnetic stir bar and septum was charged with anhydrous 1,4-dioxane (1 mL), $(PhCN)_2PdCl_2$ (3.8 mg, 0.01 mmol) and Cata*CX*ium A (**L7**, 7.2 mg, 0.02 mmol) under continuous flow of argon. The

reaction mixture was stirred for 5 min at room temperature, then **Pd-PyMIC** (7.8 mg, 0.01 mmol), DABCO (314 mg, 2.8 mmol), methyl 4-bromobenzoate (**1m**, 430 mg, 2 mmol) and but-3-yn-1-ol (**2i**, 196 mg, 2.8 mmol) were added. Argon flow was removed and the reaction mixture was stirred at room temperature for 48 hours, during which milky mixture started forming. The reaction mixture was then diluted with ethyl acetate (150 mL) and washed with brine (2 × 100 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give a brown solid. The title product **3t** (367 mg, 90%) was obtained after column chromatography purification (petroleum ether/ethyl acetate = 2 : 1, R_f = 0.22) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99–7.94 (m, 2H), 7.49–7.44 (m, 2H), 3.91 (s, 3H), 3.84 (q, J = 6.2 Hz, 2H), 2.72 (t, J = 6.2 Hz, 2H), 1.81 (t, J = 6.2 Hz, 1H). NMR data are in agreement with those from the literature.[26,27]

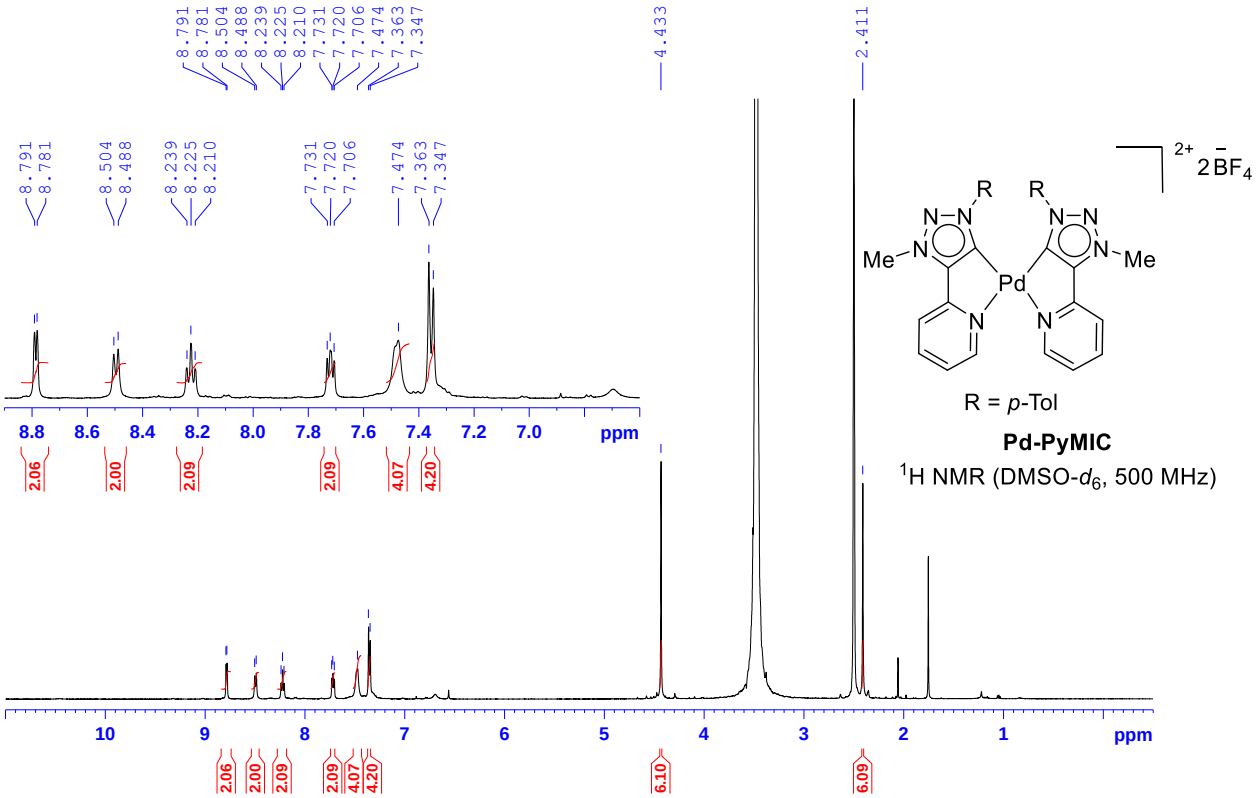
2.10. Multi-gram synthesis of 4-(phenylethynyl)benzaldehyde (3b)



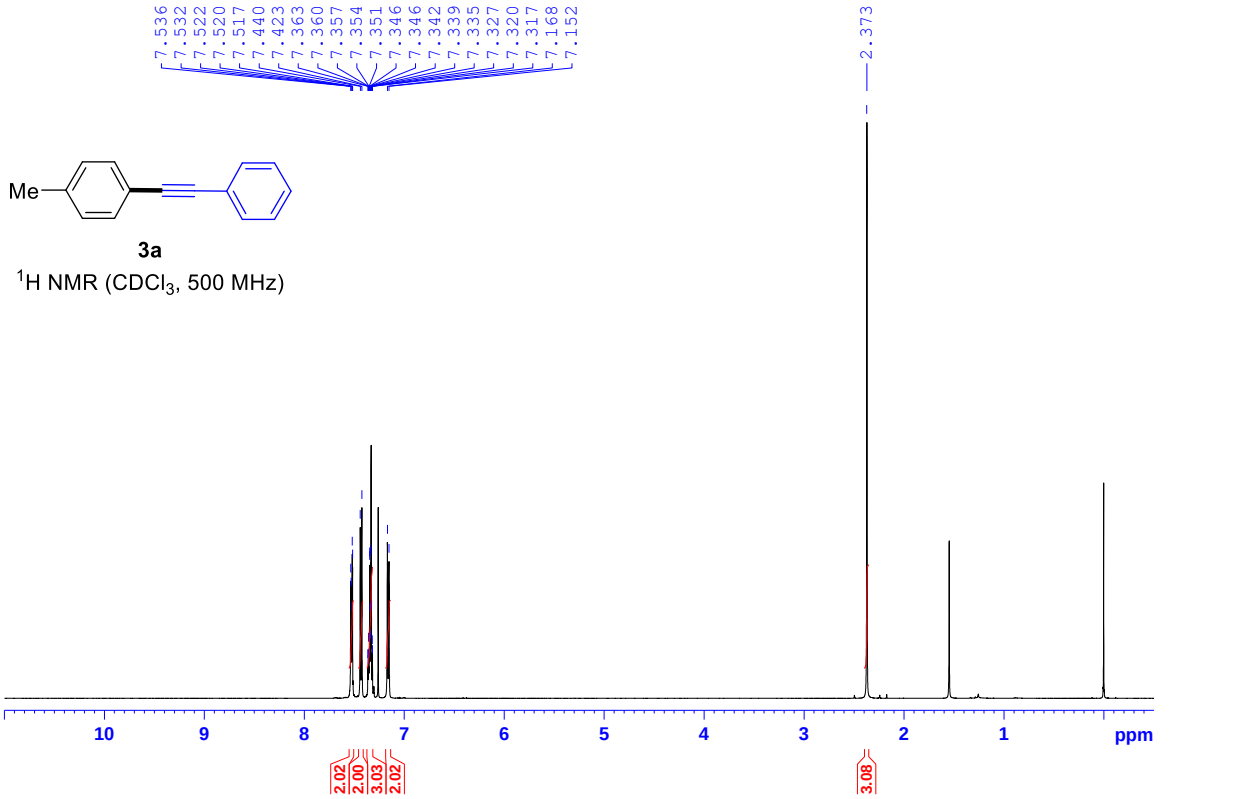
An oven-dried (130 °C for 3 hours) 25 mL round-bottom flask, equipped with magnetic stir bar and septum was charged with anhydrous 1,4-dioxane (12.5 mL), $(PhCN)_2PdCl_2$ (6.0 mg, 15.6 µmol) and Cata*CX*ium A (**L7**, 11.2 mg, 31.2 µmol) under continuous flow of argon. The reaction mixture was stirred for 5 min at room temperature, then **Pd-PyMIC** (12.2 mg, 15.6 µmol), DABCO (3.926 g, 35 mmol), 4-bromobenzaldehyde (**1b**, 4.626 g, 25 mmol) and phenylacetylene (**2a**, 3.575 g, 35 mmol) were added. Argon flow was removed and the reaction mixture was stirred at room temperature for 24 hours. The reaction the mixture was filtered and the filtered solids were additionally washed with ethyl acetate (300 mL) and the combined organic layer was washed with brine (2 × 200 mL). Anhydrous Na_2SO_4 (70 g) and silica gel (30 g) were added to this organic solution and the resulting slurry mixture was stirred for 30 minutes at room temperature. The mixture was filtered and the filter cake was washed with ethyl acetate (200 mL). The filtrate was concentrated under reduced pressure to give crude solid material that was dissolved in hot methanol (200 mL) and filtered. To the hot filtrate water (800 mL) was added under vigorous stirring, causing crystallization of the

product. The mixture was placed in the refrigerator (4 °C) overnight. The crystals were filtered, thoroughly washed with cold water and dried under high vacuum to afford the desired 4-(phenylethynyl)benzaldehyde (**3b**, 4.692 g, 91%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.89–7.85 (m, 2H), 7.70–7.65 (m, 2H), 7.57–7.55 (m, 2H), 7.40–7.37 (m, 3H). NMR data are in agreement with those from the literature.[5,6]

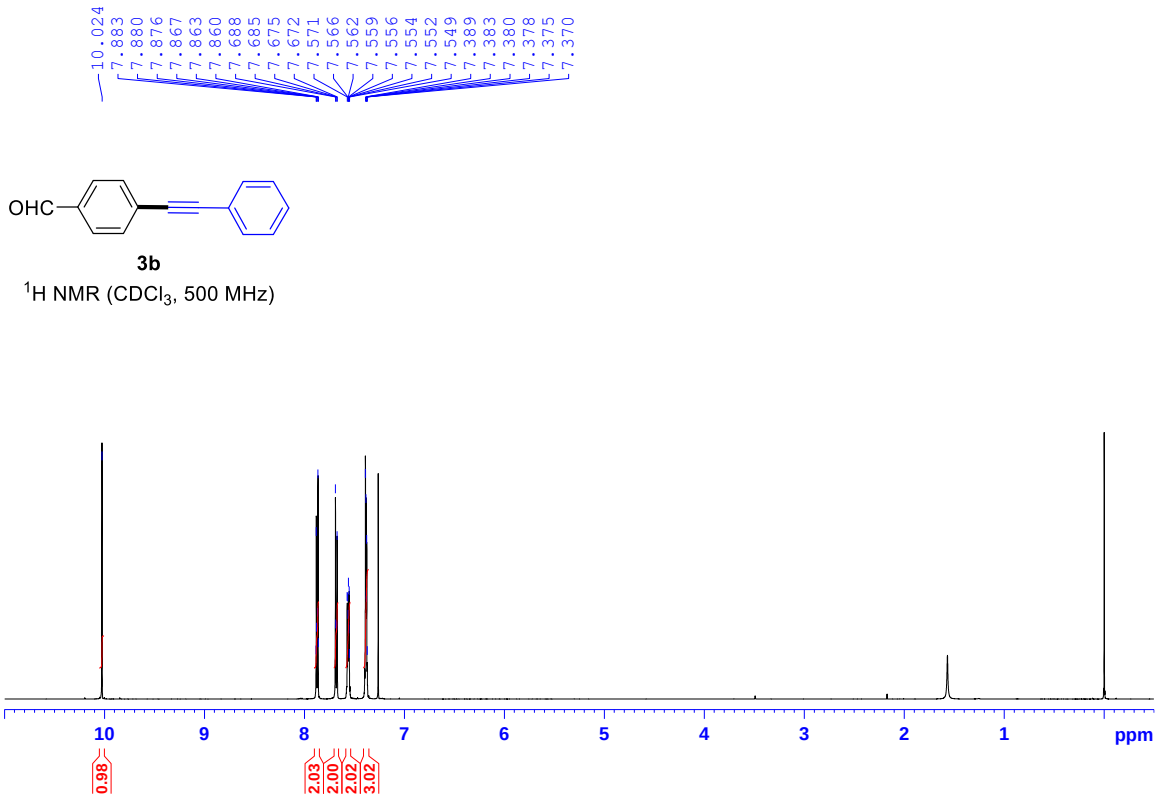
3. COPIES OF NMR SPECTRA



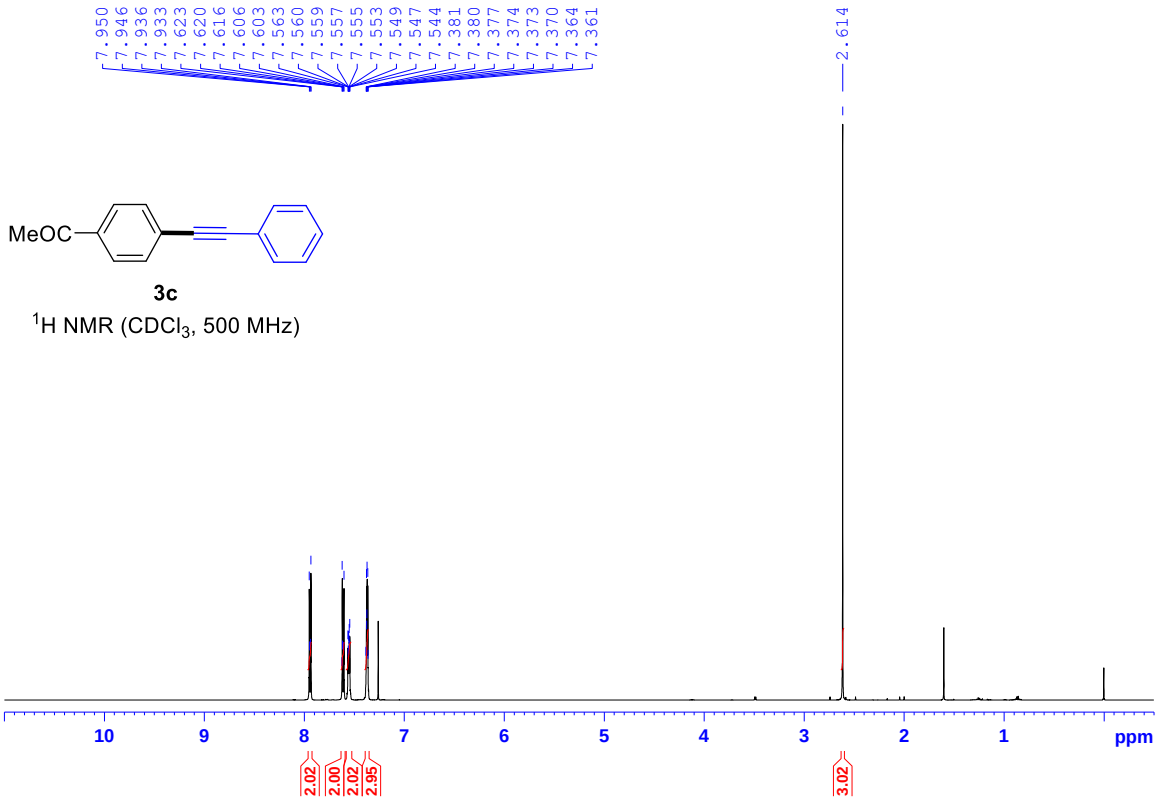
Supplementary Figure S2. ^{1}H NMR spectrum of compound **Pd-PyMIC** in DMSO-d_6, 500 MHz.



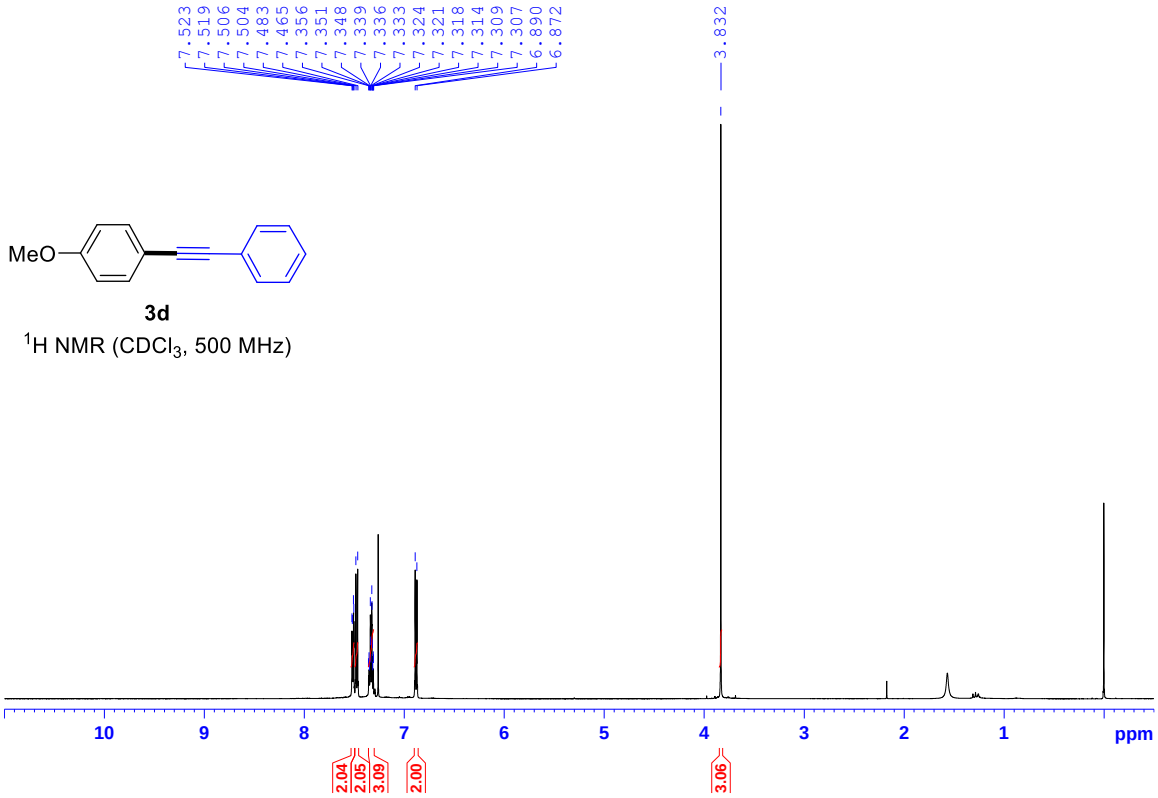
Supplementary Figure S3. ^{1}H NMR spectrum of compound **3a** in $CDCl_3$, 500 MHz.



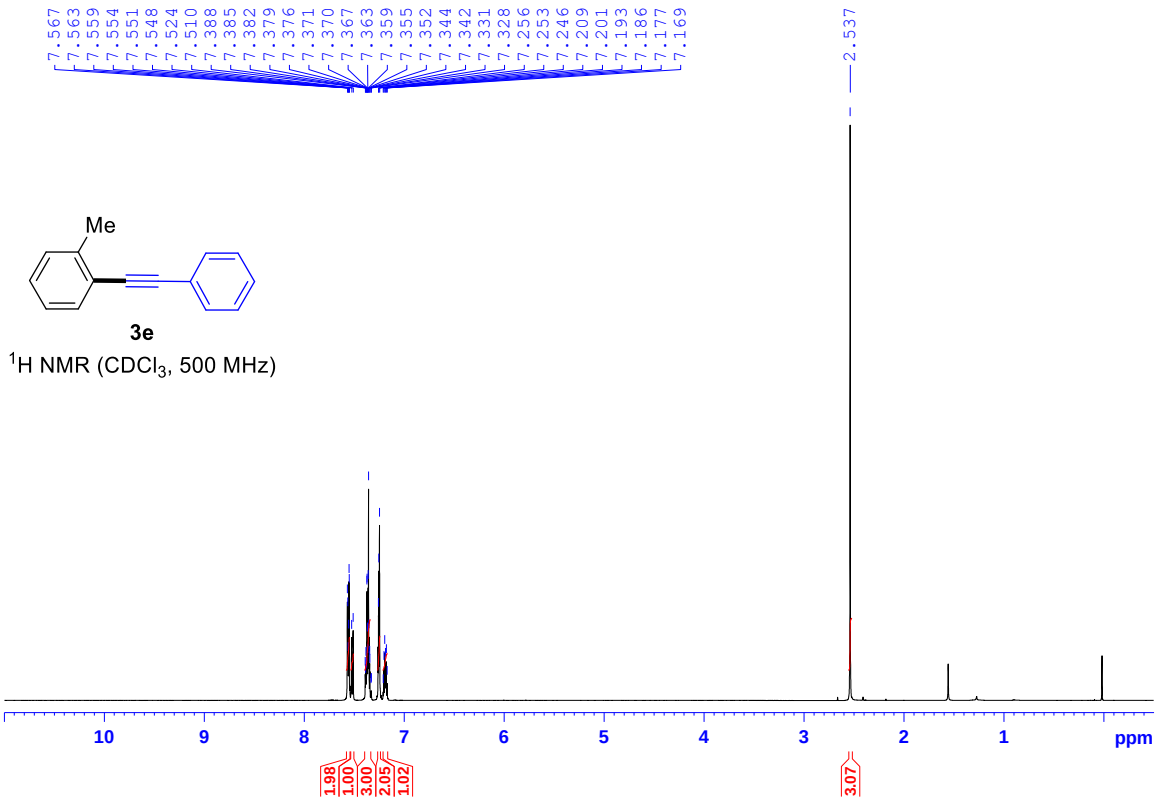
Supplementary Figure S4. ^{1}H NMR spectrum of compound **3b** in $CDCl_3$, 500 MHz.



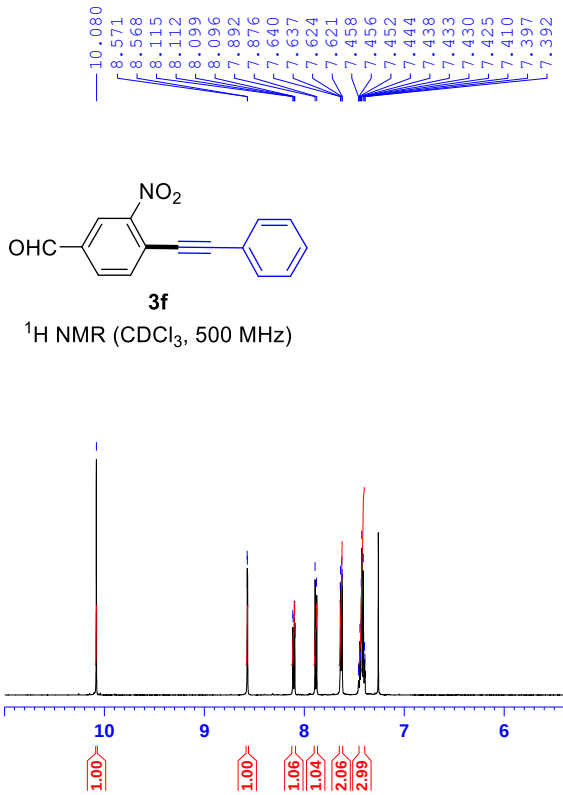
Supplementary Figure S5. ^{1}H NMR spectrum of compound **3c** in $CDCl_3$, 500 MHz.



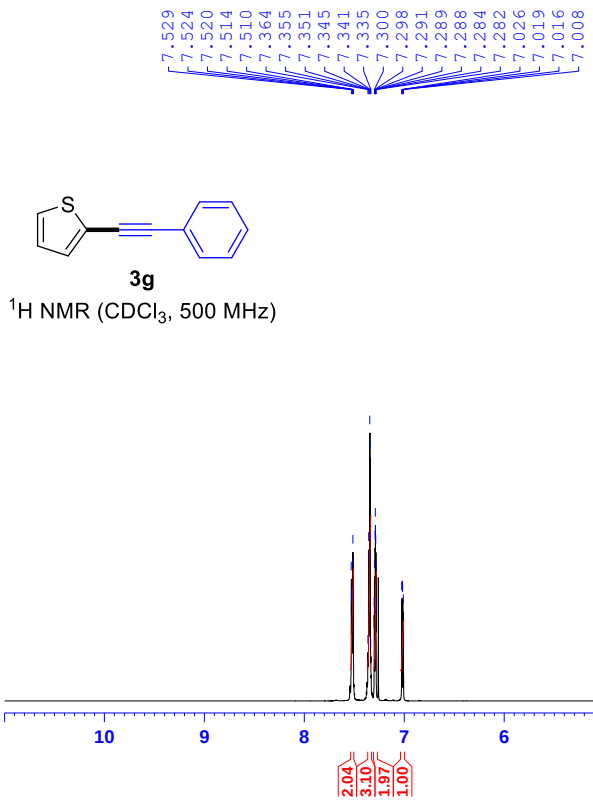
Supplementary Figure S6. ^{1}H NMR spectrum of compound **3d** in $CDCl_3$, 500 MHz.



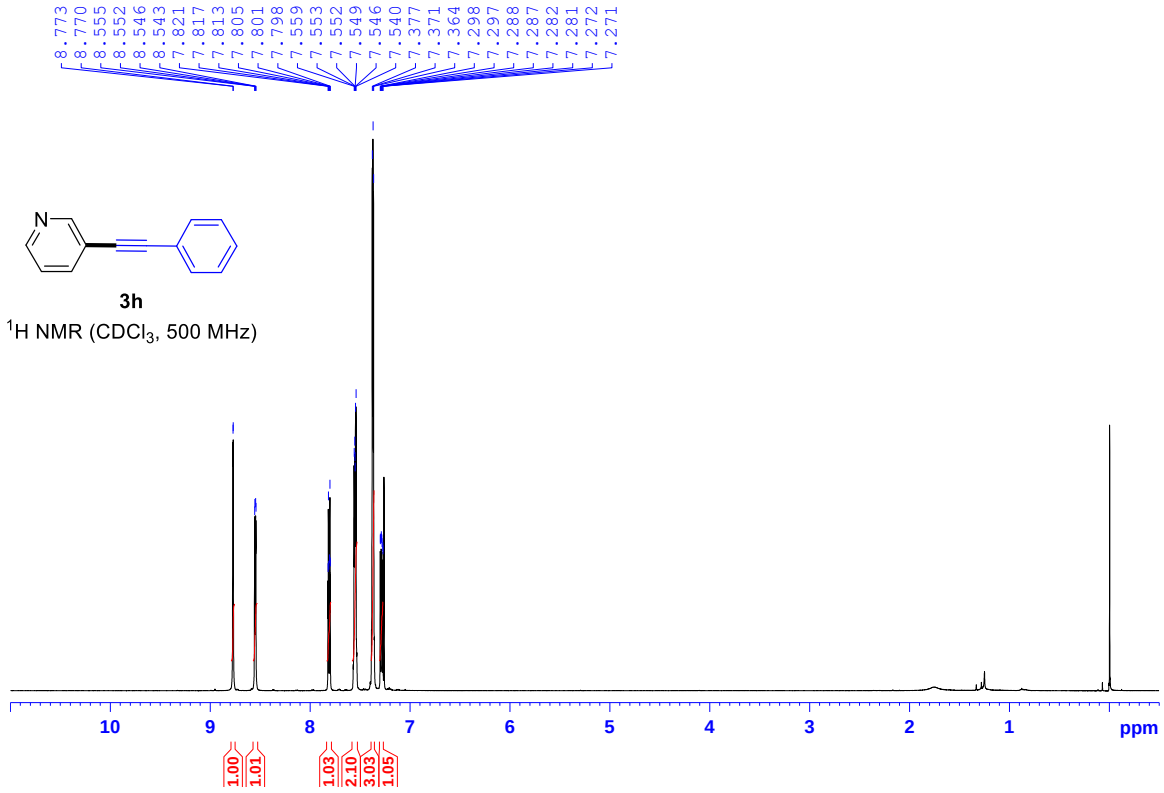
Supplementary Figure S7. ^{1}H NMR spectrum of compound **3e** in $CDCl_3$, 500 MHz.



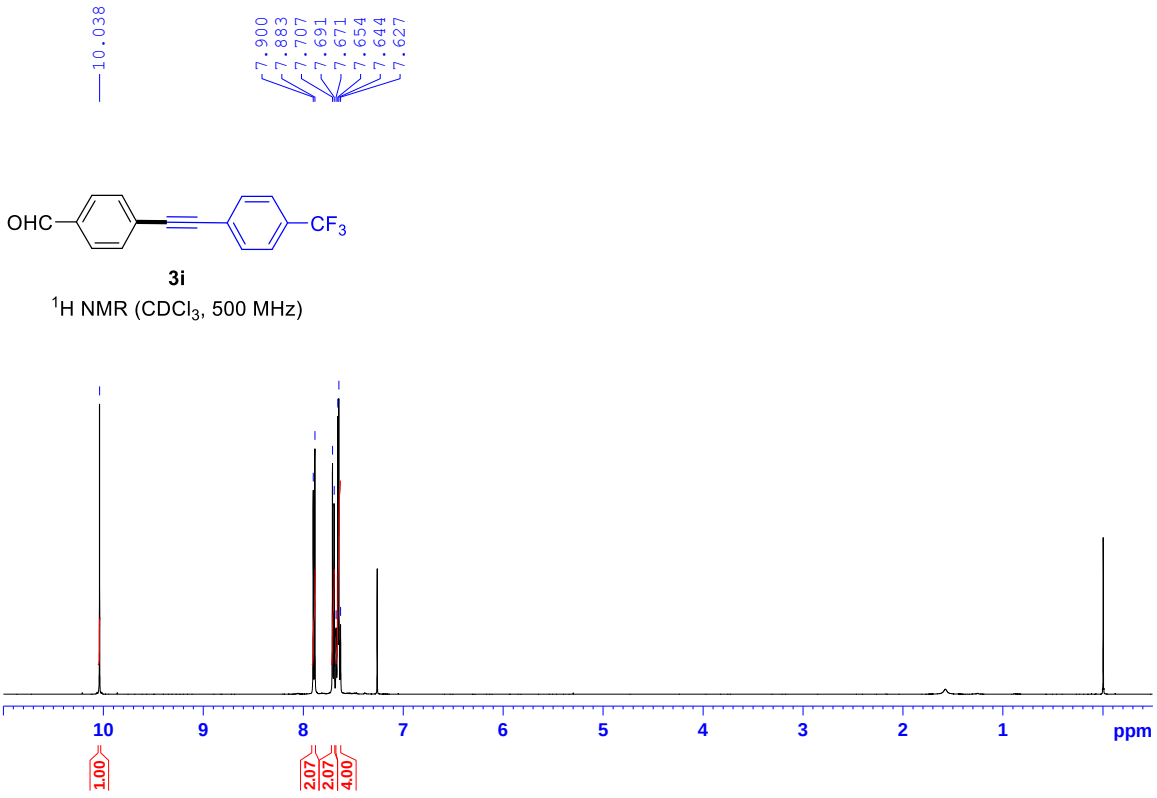
Supplementary Figure S8. ^{1}H NMR spectrum of compound **3f** in $CDCl_3$, 500 MHz.



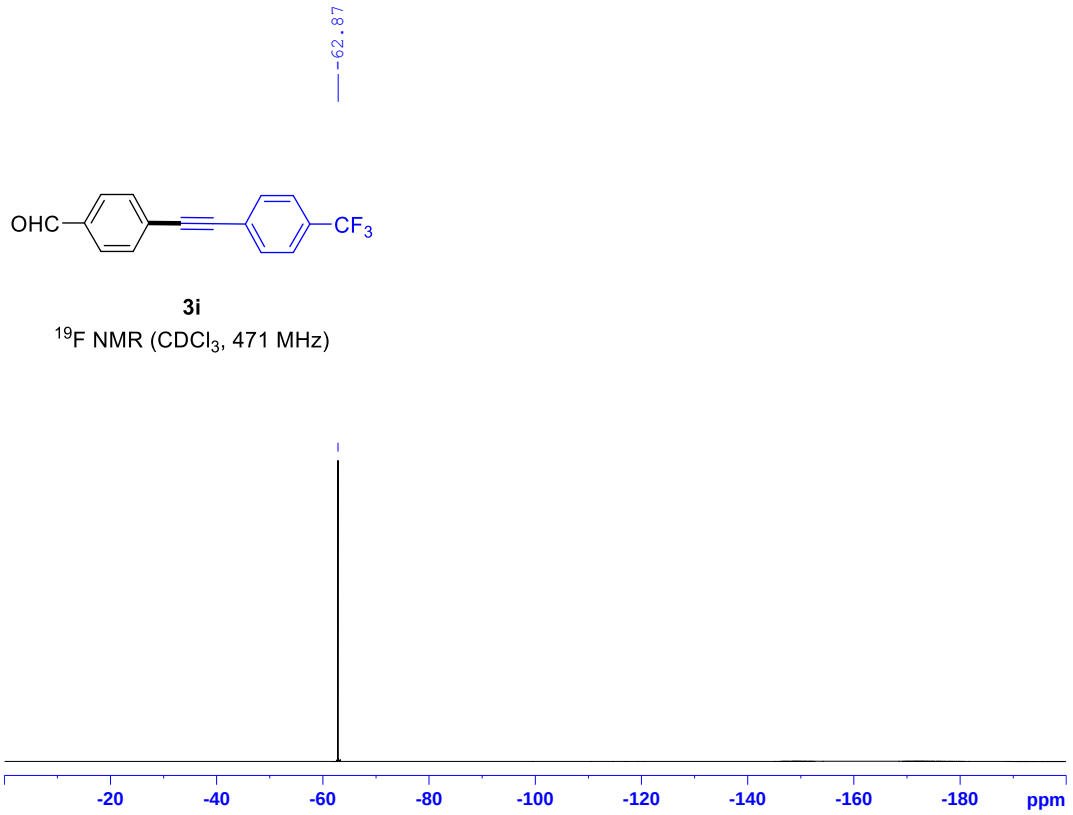
Supplementary Figure S9. ^{1}H NMR spectrum of compound **3g** in $CDCl_3$, 500 MHz.



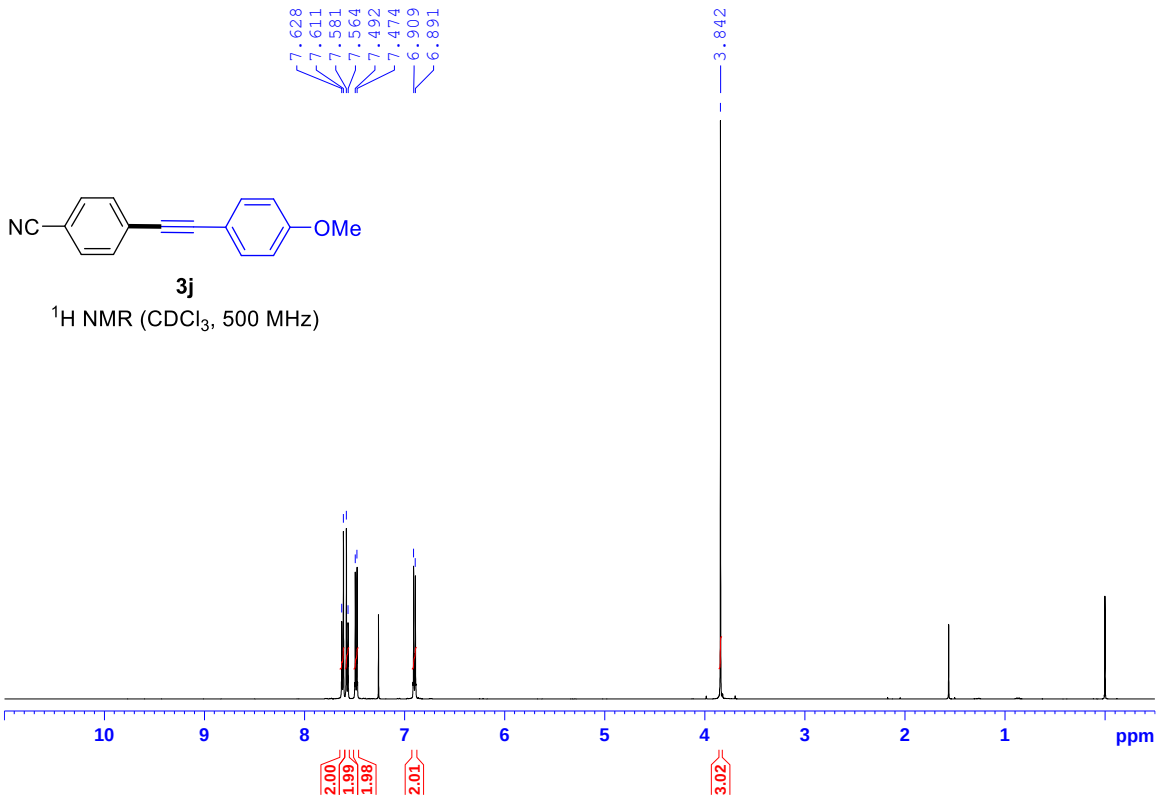
Supplementary Figure S10. ^{1}H NMR spectrum of compound **3h** in $CDCl_3$, 500 MHz.



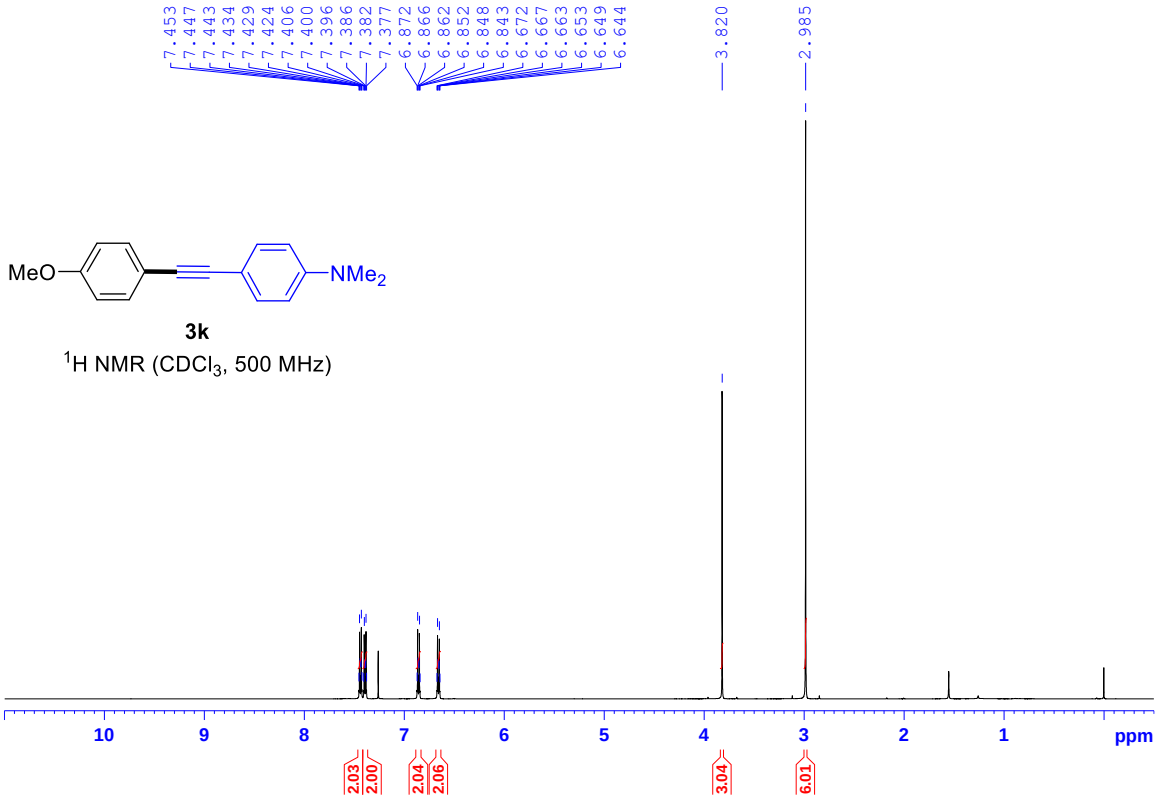
Supplementary Figure S11. ^{1}H NMR spectrum of compound **3i** in $CDCl_3$, 500 MHz.



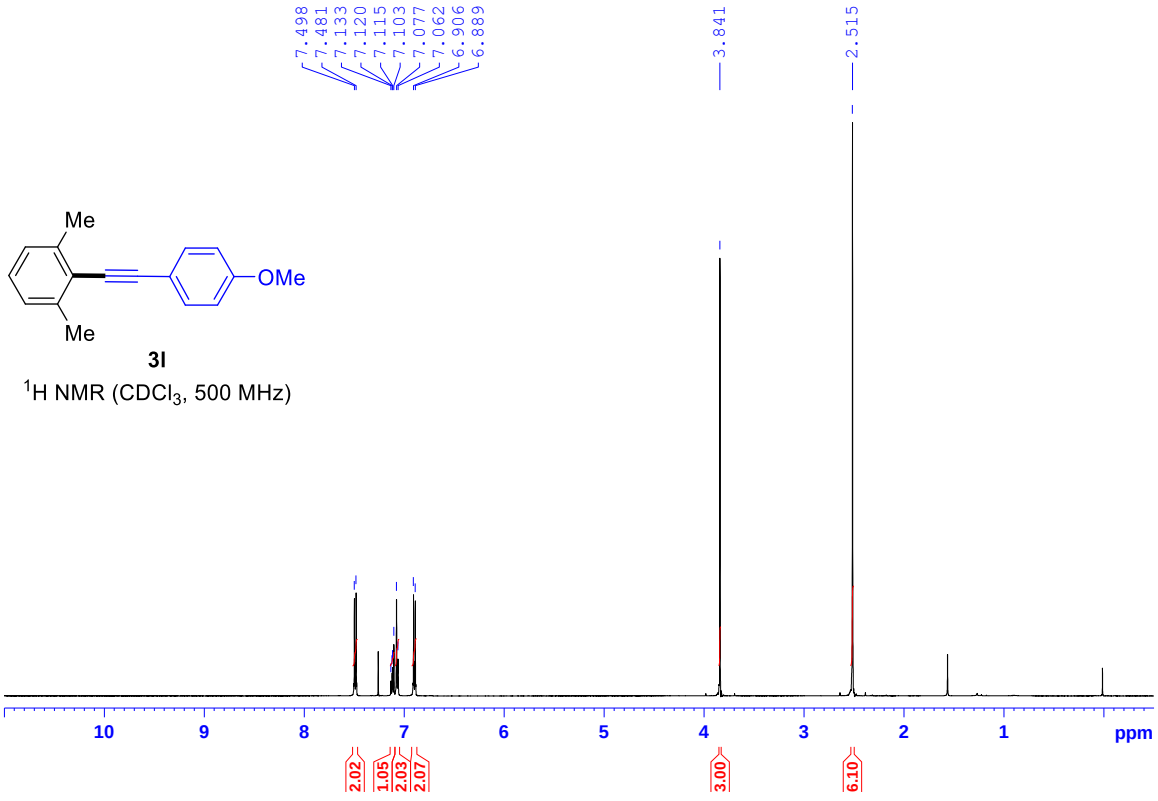
Supplementary Figure S12. ^{19}F NMR spectrum of compound **3i** in $CDCl_3$, 471 MHz.



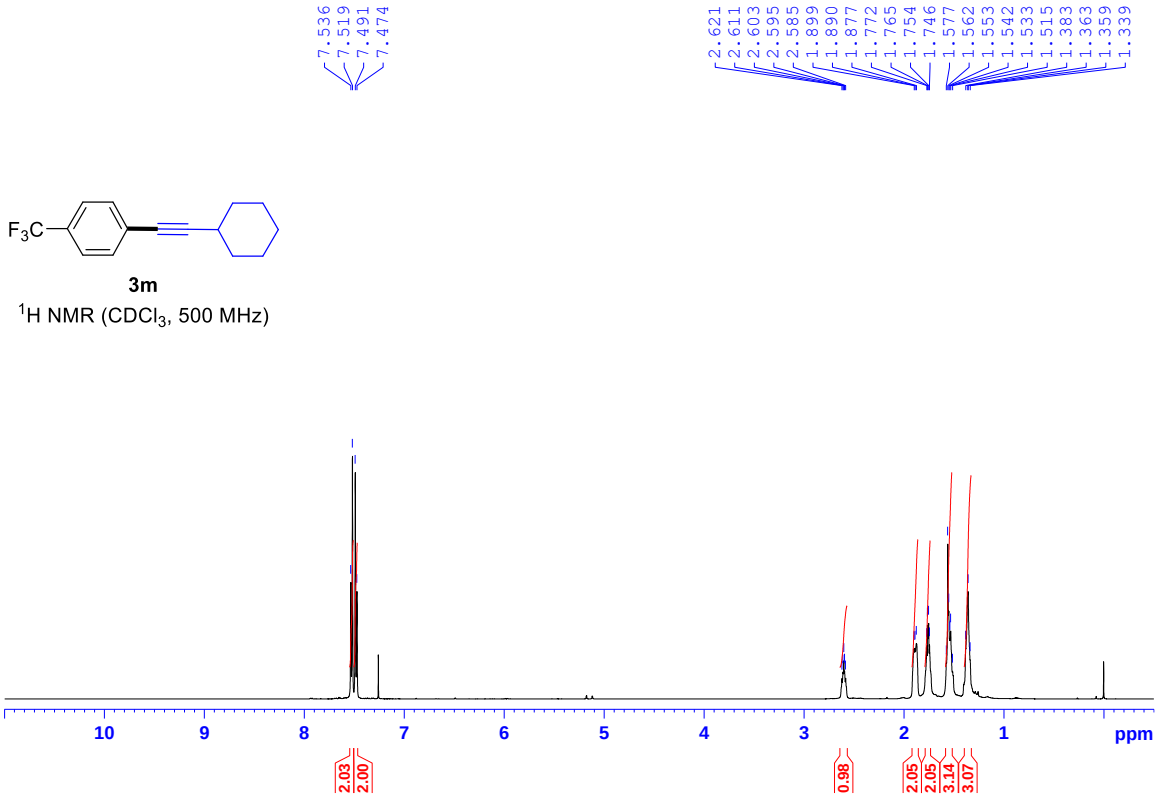
Supplementary Figure S13. ^{1}H NMR spectrum of compound **3j** in $CDCl_3$, 500 MHz.



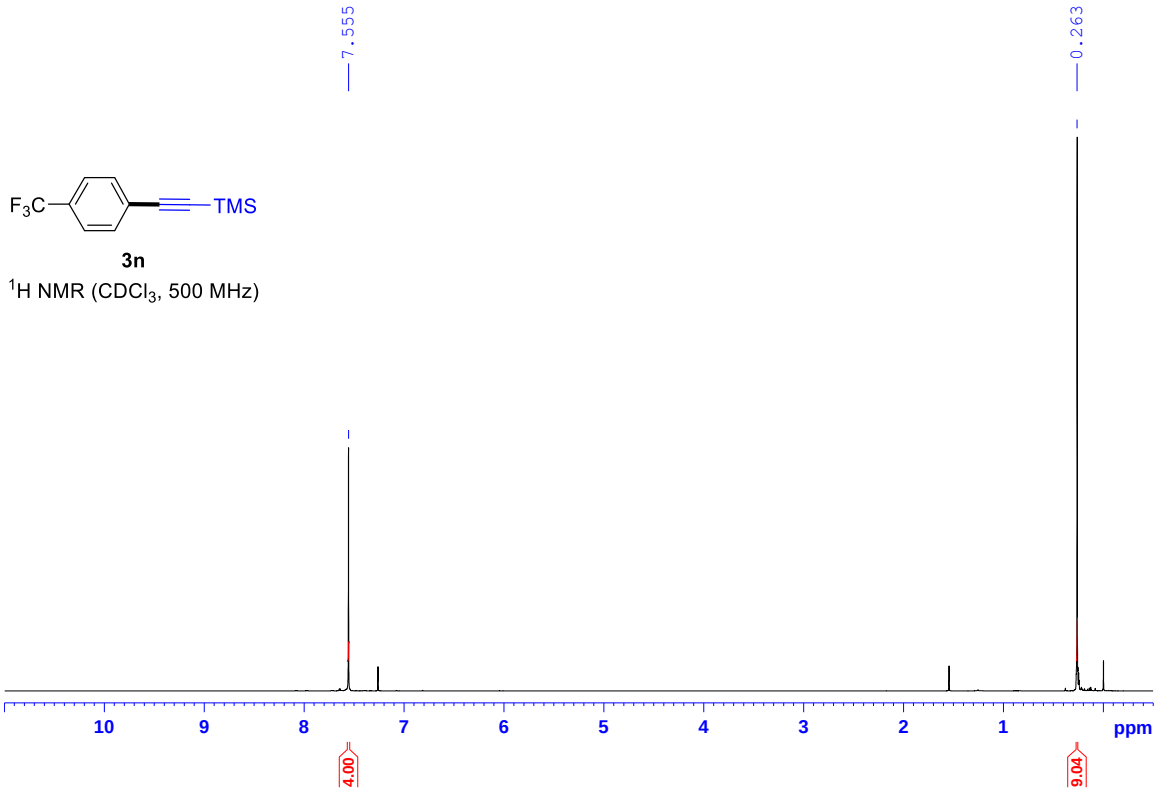
Supplementary Figure S14. ^{1}H NMR spectrum of compound **3k** in $CDCl_3$, 500 MHz.



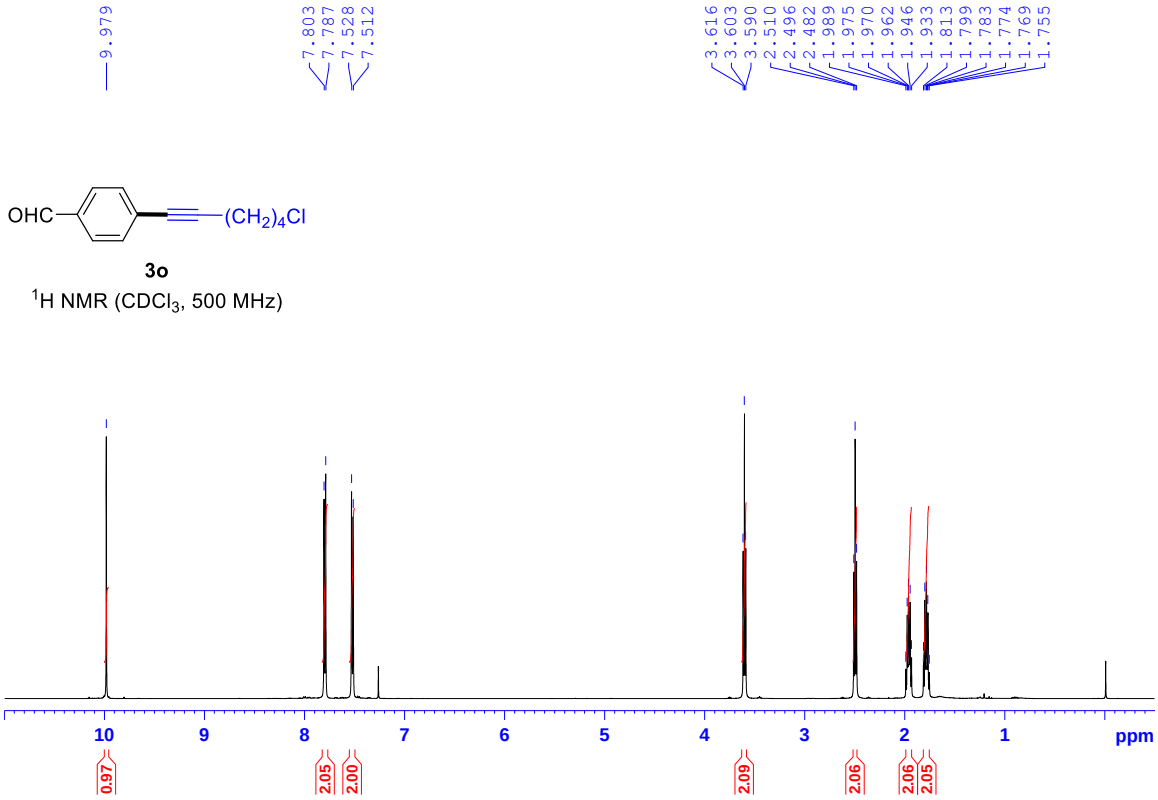
Supplementary Figure S15. ^{1}H NMR spectrum of compound **3l** in $CDCl_3$, 500 MHz.



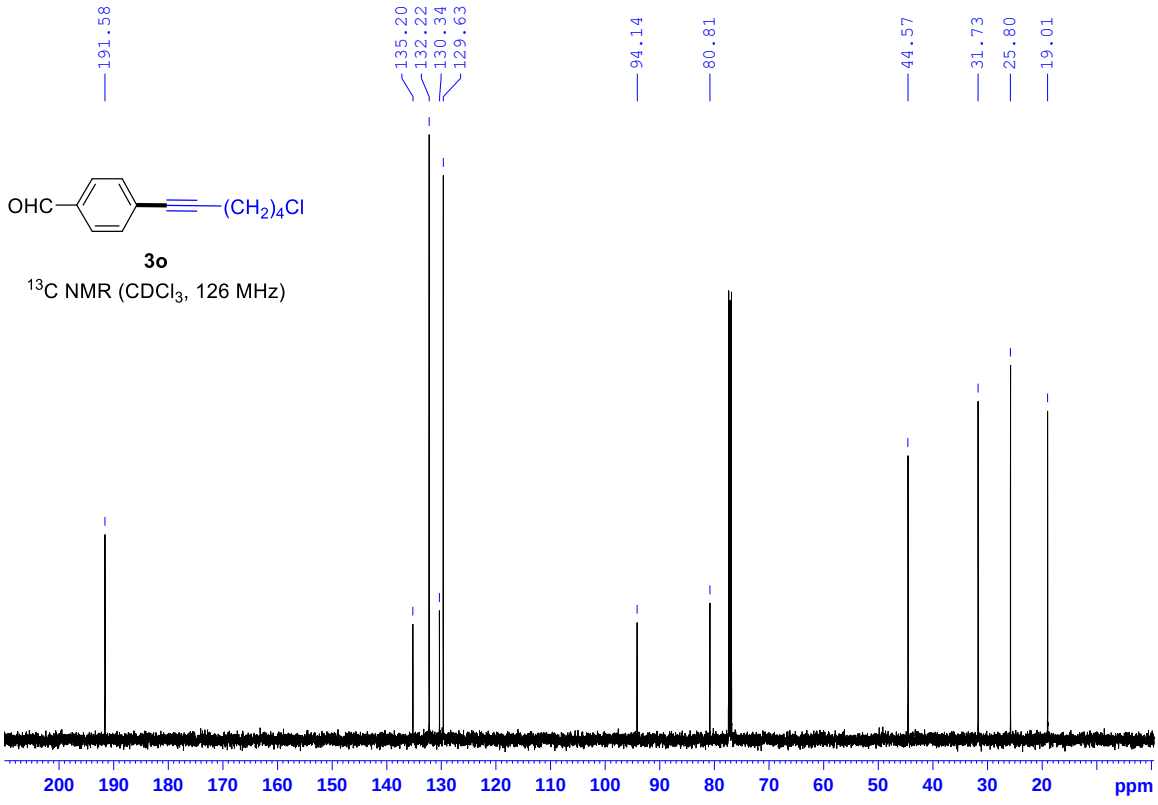
Supplementary Figure S16. ^{1}H NMR spectrum of compound **3m** in $CDCl_3$, 500 MHz.



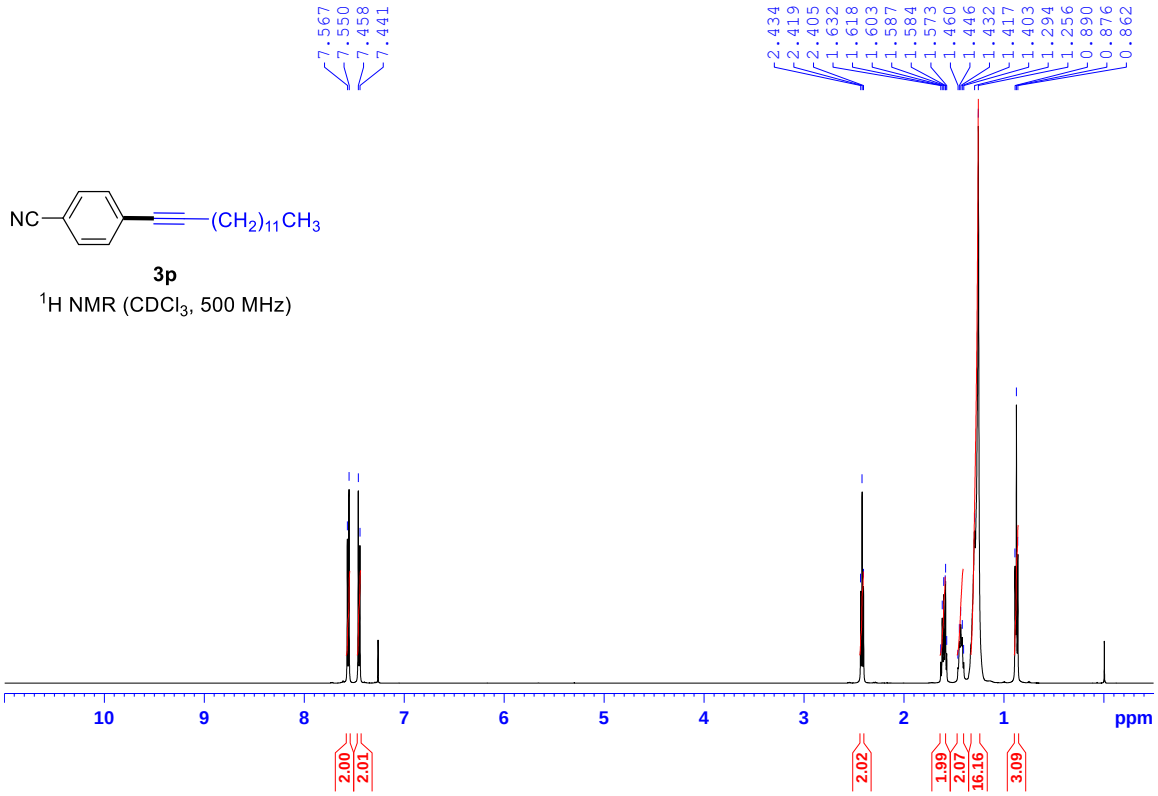
Supplementary Figure S17. ^{1}H NMR spectrum of compound **3n** in $CDCl_3$, 500 MHz.



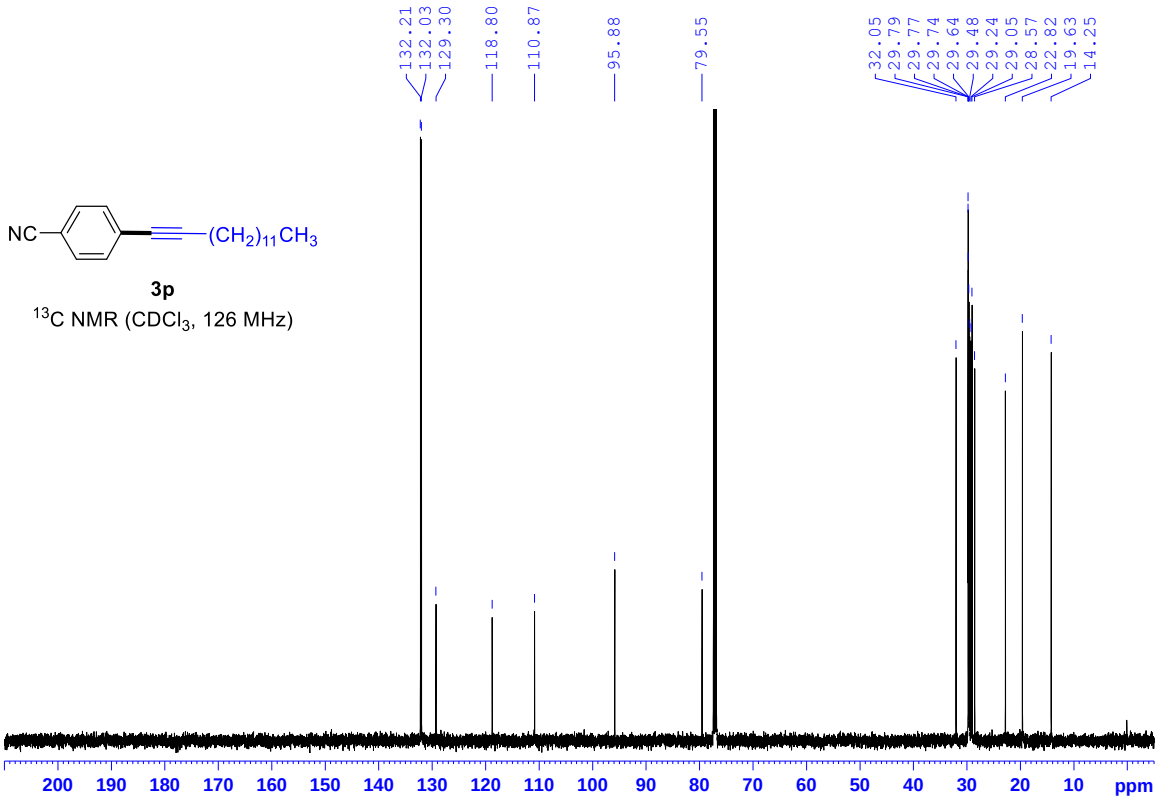
Supplementary Figure S18. ^{1}H NMR spectrum of compound **3o** in $CDCl_3$, 500 MHz.



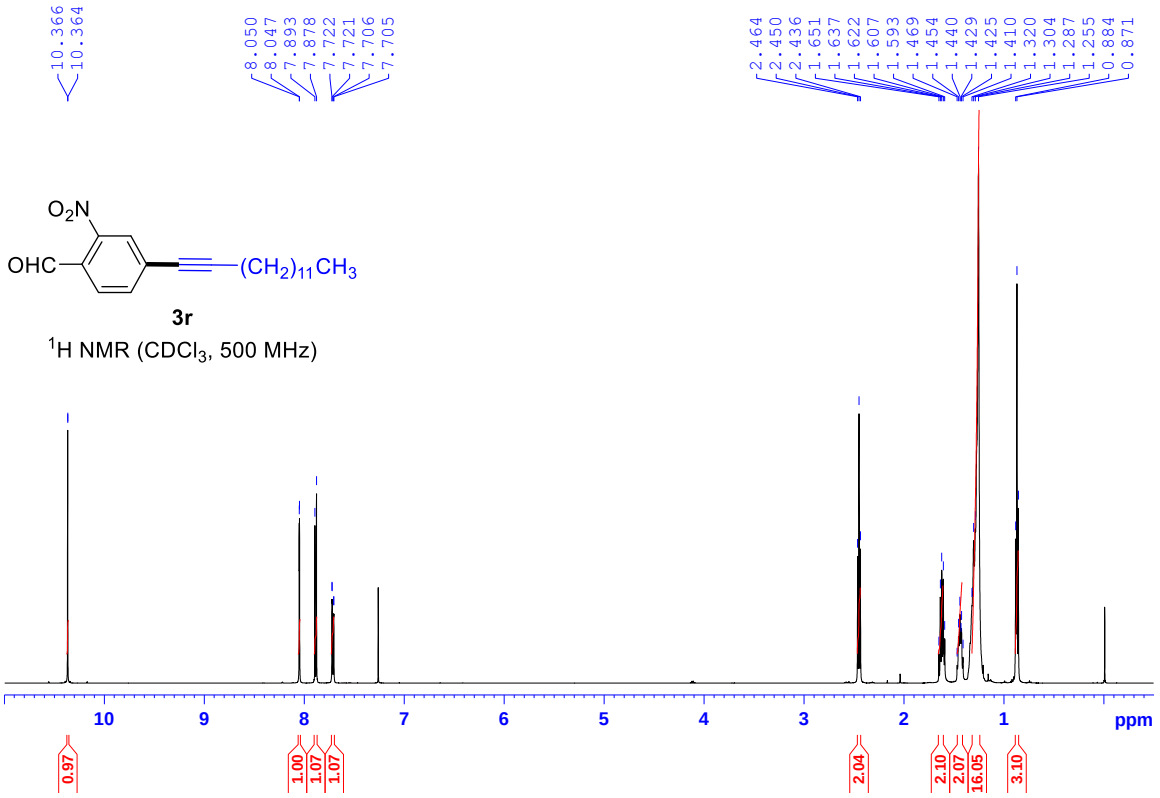
Supplementary Figure S19. ^{13}C NMR spectrum of compound **3o** in $CDCl_3$, 126 MHz.



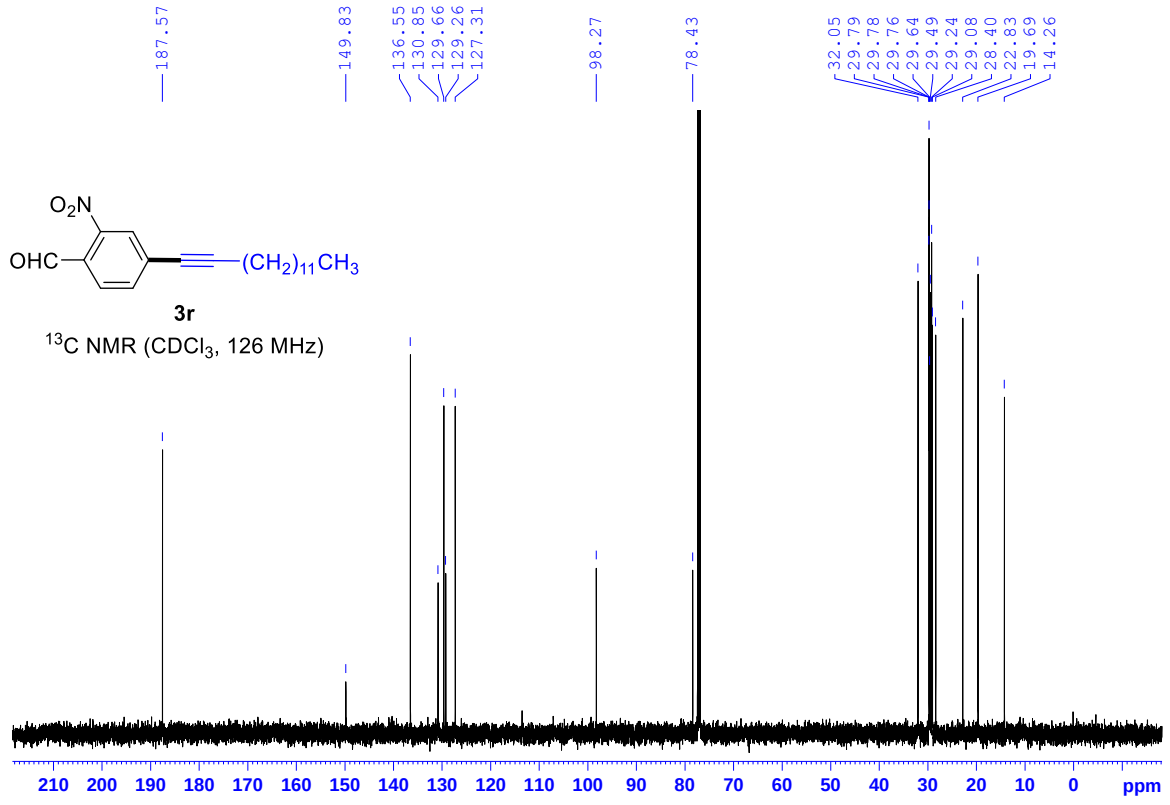
Supplementary Figure S20. ^{1}H NMR spectrum of compound **3p** in $CDCl_3$, 500 MHz.



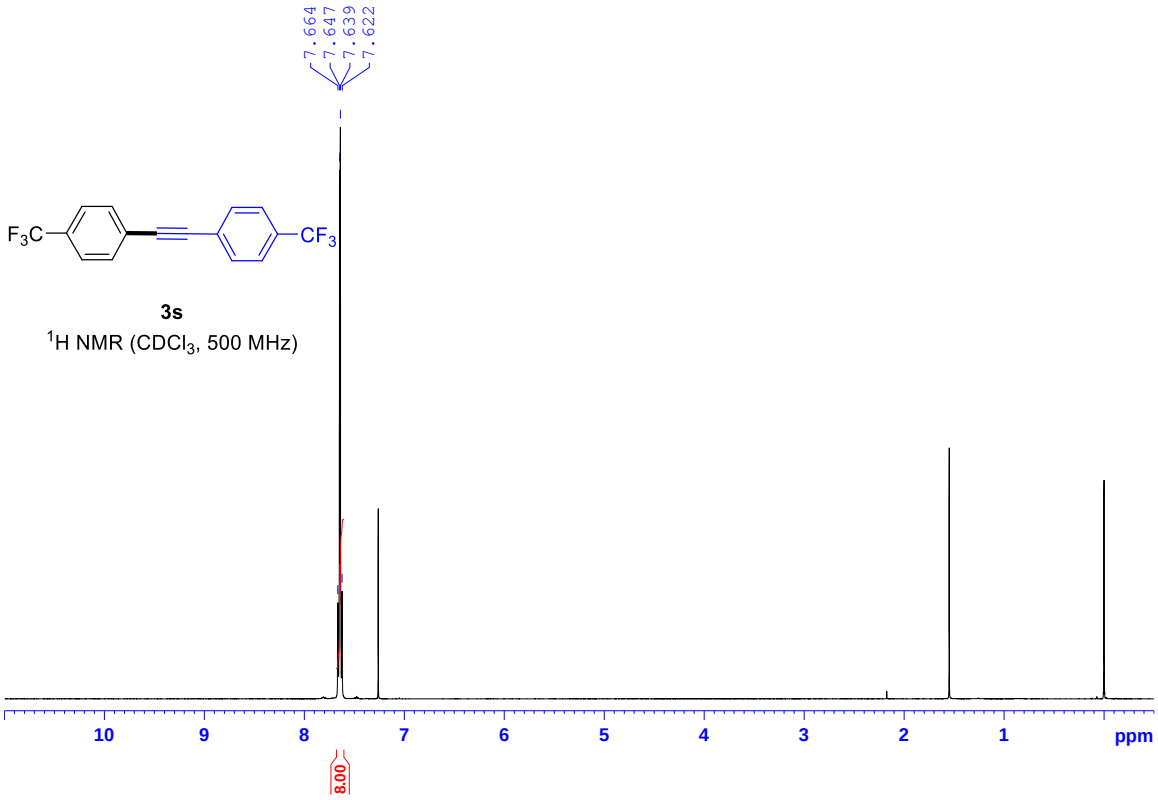
Supplementary Figure S21. ^{13}C NMR spectrum of compound **3p** in $CDCl_3$, 126 MHz.



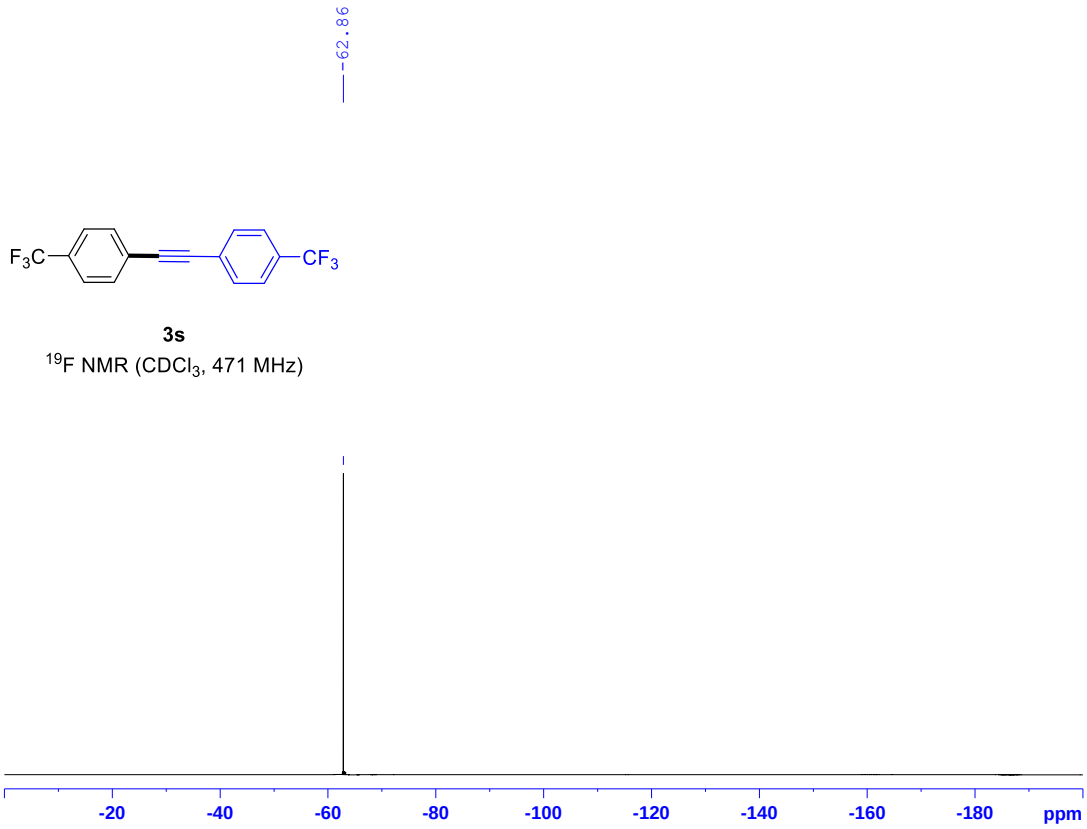
Supplementary Figure S22. ^{1}H NMR spectrum of compound **3r** in $CDCl_3$, 500 MHz.



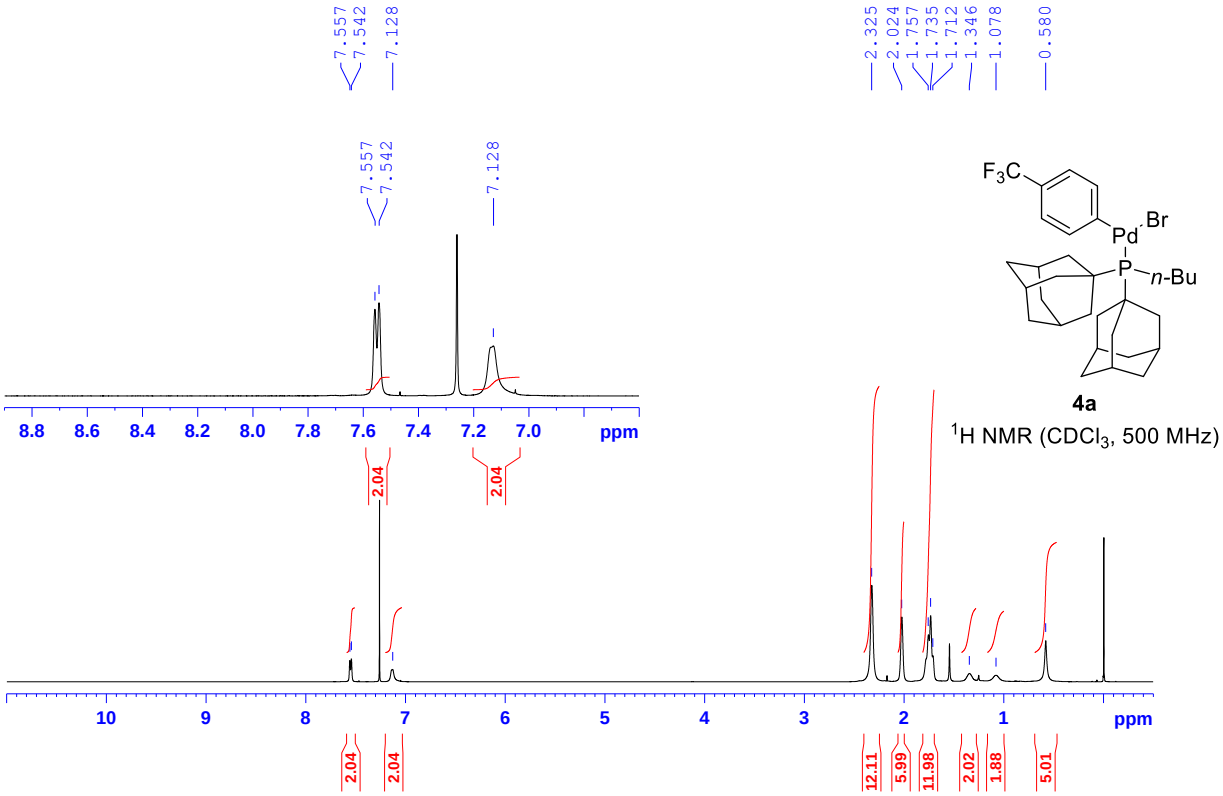
Supplementary Figure S23. ^{13}C NMR spectrum of compound **3r** in $CDCl_3$, 126 MHz.



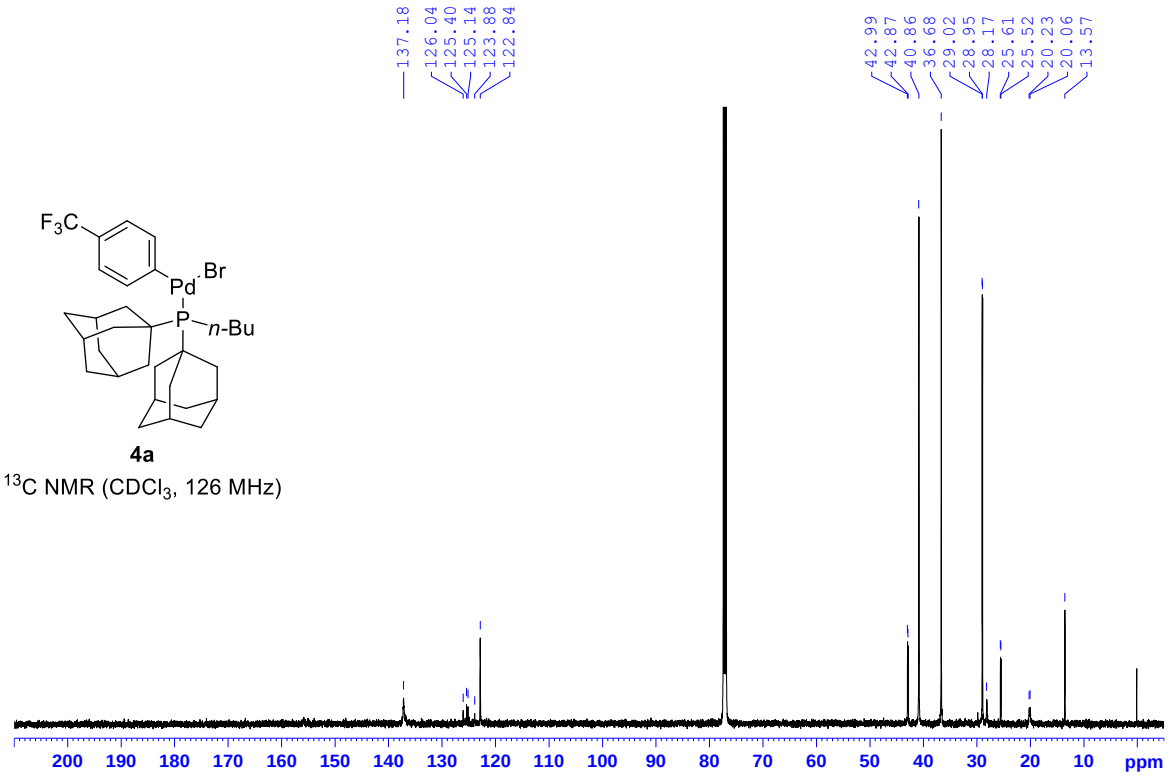
Supplementary Figure S24. ^{1}H NMR spectrum of compound **3s** in $CDCl_3$, 500 MHz.



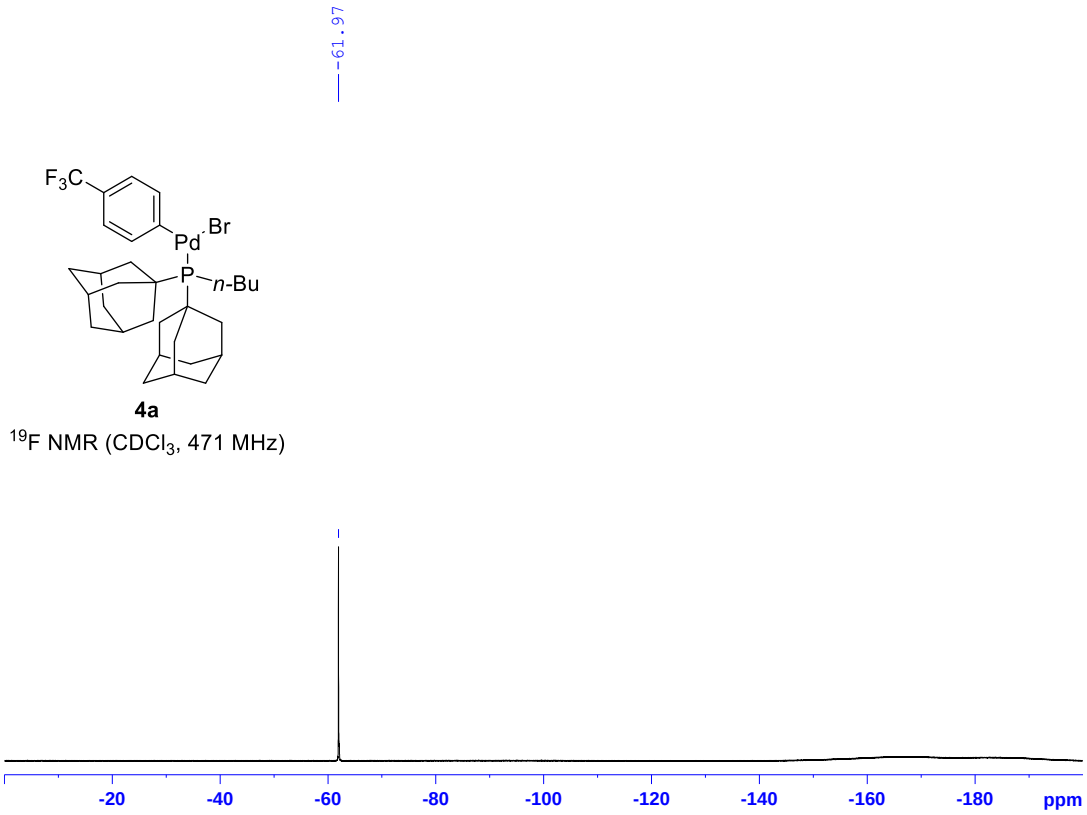
Supplementary Figure S25. ^{19}F NMR spectrum of compound **3s** in $CDCl_3$, 471 MHz.



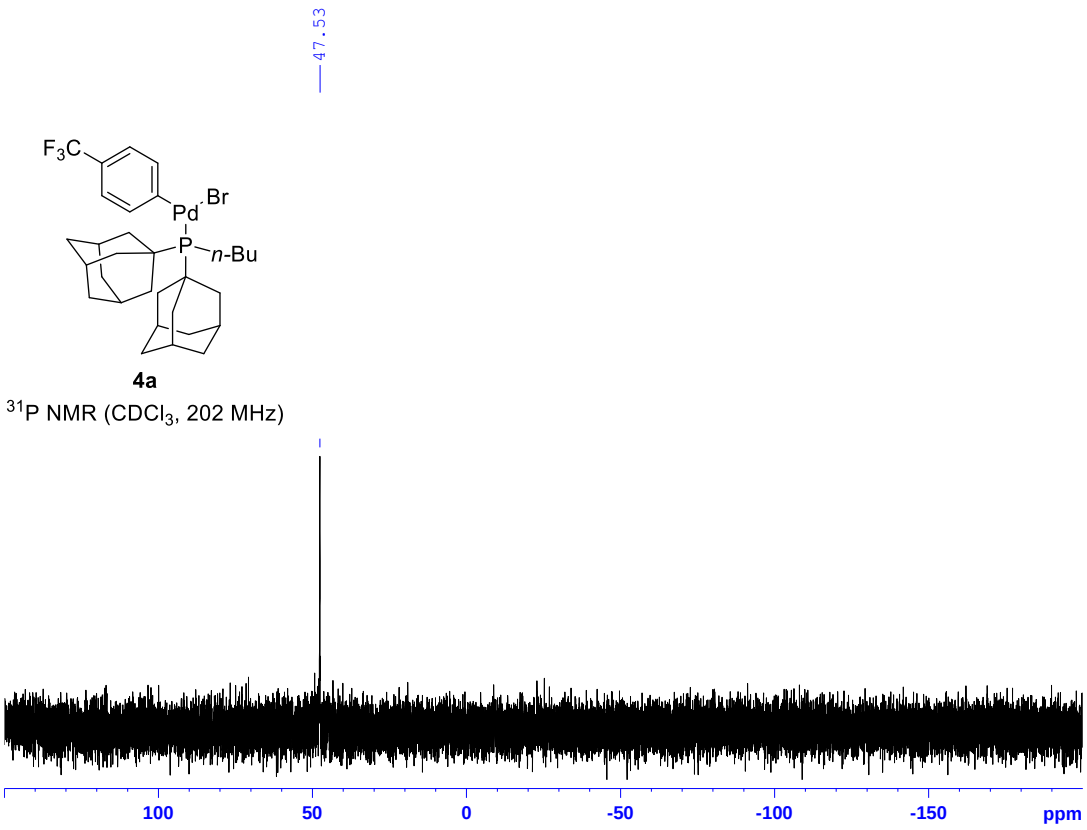
Supplementary Figure S26. ^{1}H NMR spectrum of compound **4a** in $CDCl_3$, 500 MHz.



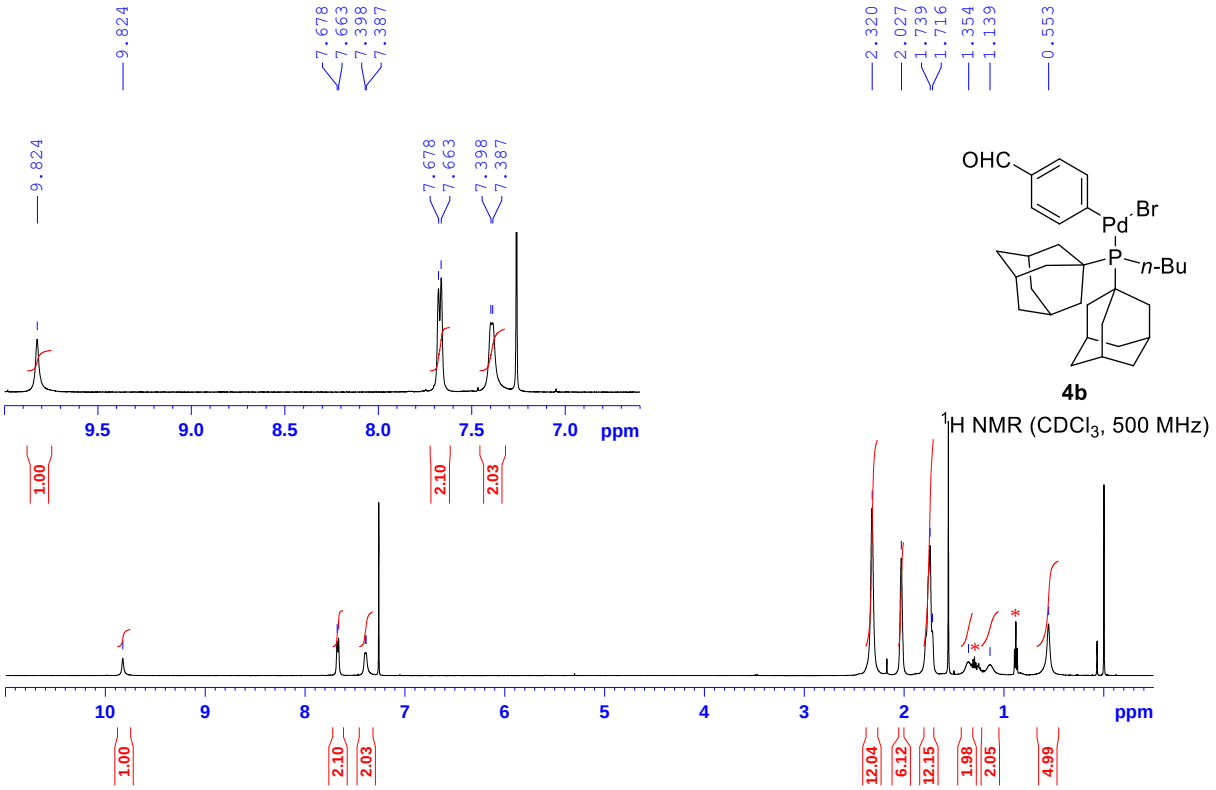
Supplementary Figure S27. ^{13}C NMR spectrum of compound **4a** in $CDCl_3$, 126 MHz with number of scans (NS) = 16384. Due to C–F and C–P coupling and low solubility of compound **4a** in $CDCl_3$, higher quality of spectra could not be obtained.



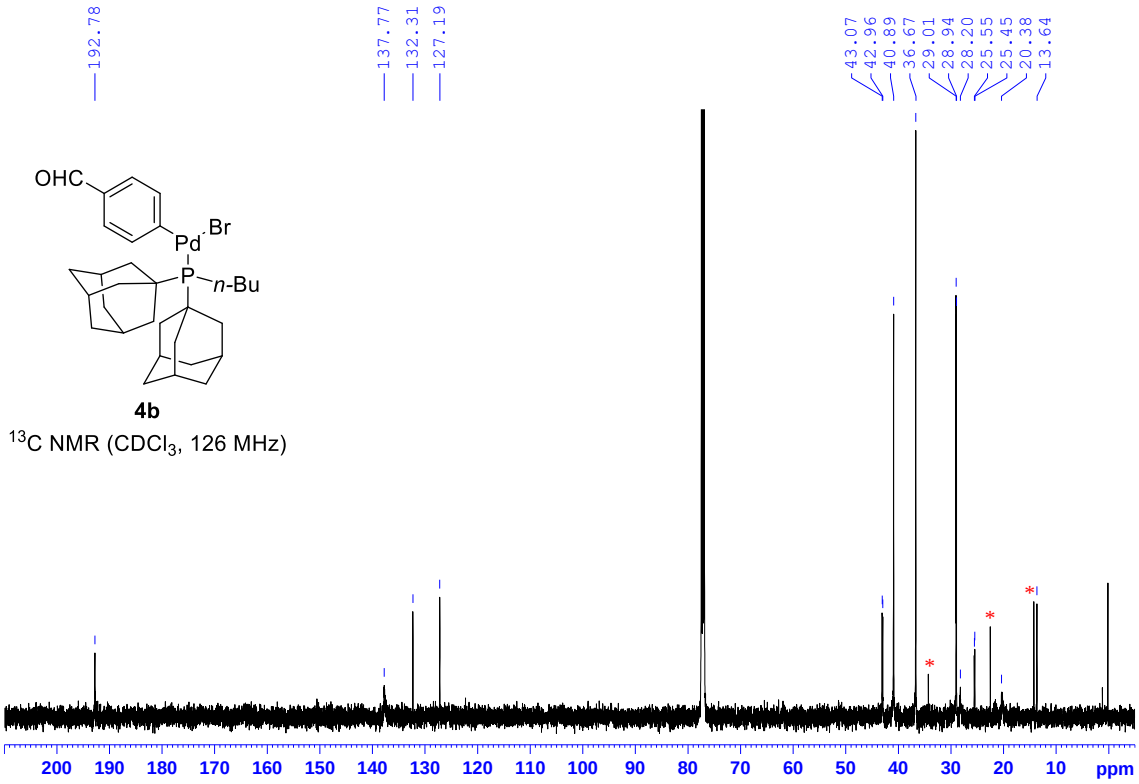
Supplementary Figure S28. ^{19}F NMR spectrum of compound **4a** in $CDCl_3$, 471 MHz.



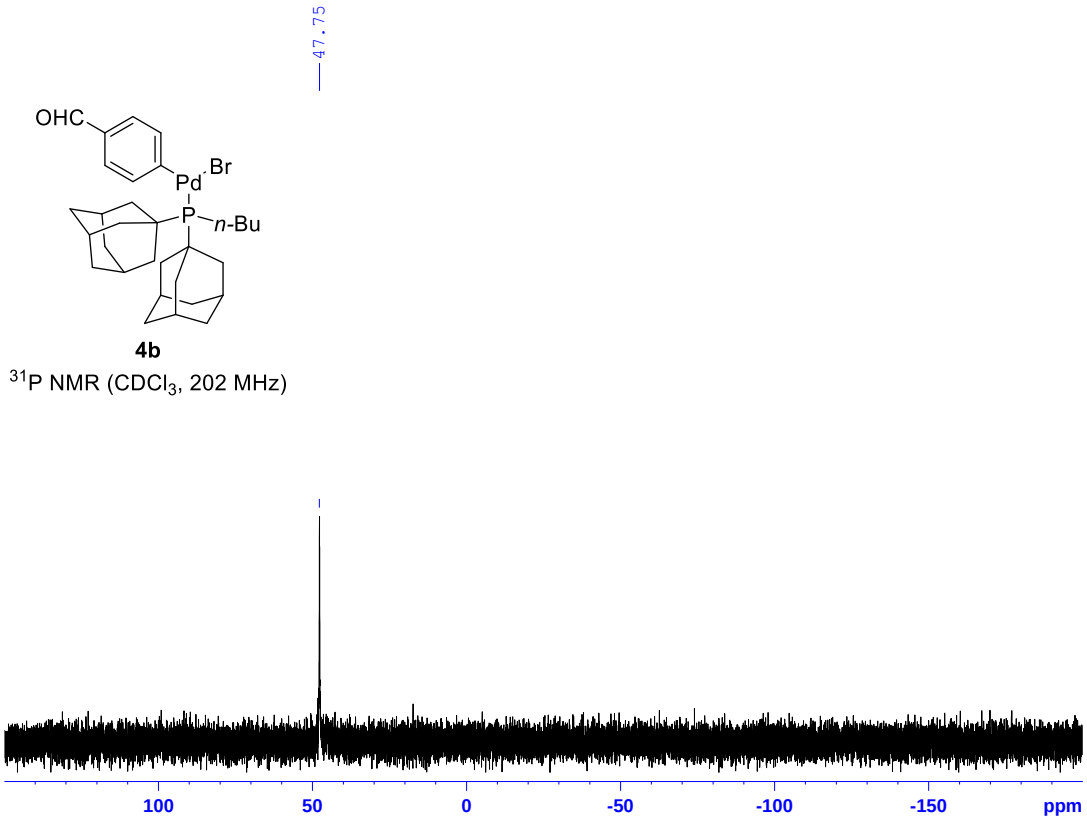
Supplementary Figure S29. ^{31}P NMR spectrum of compound **4a** in $CDCl_3$, 202 MHz.



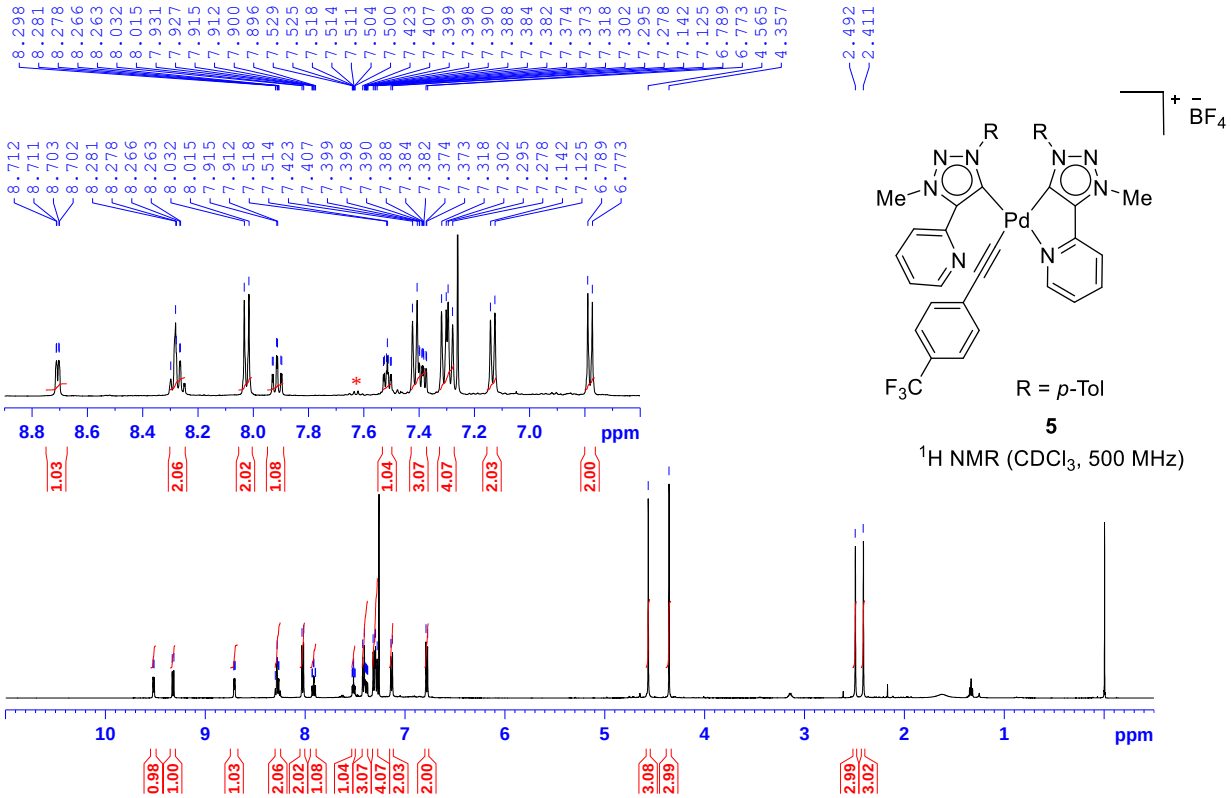
Supplementary Figure S30. ^{1}H NMR spectrum of compound **4b** in $CDCl_3$, 500 MHz. *Pentane residual resonances.



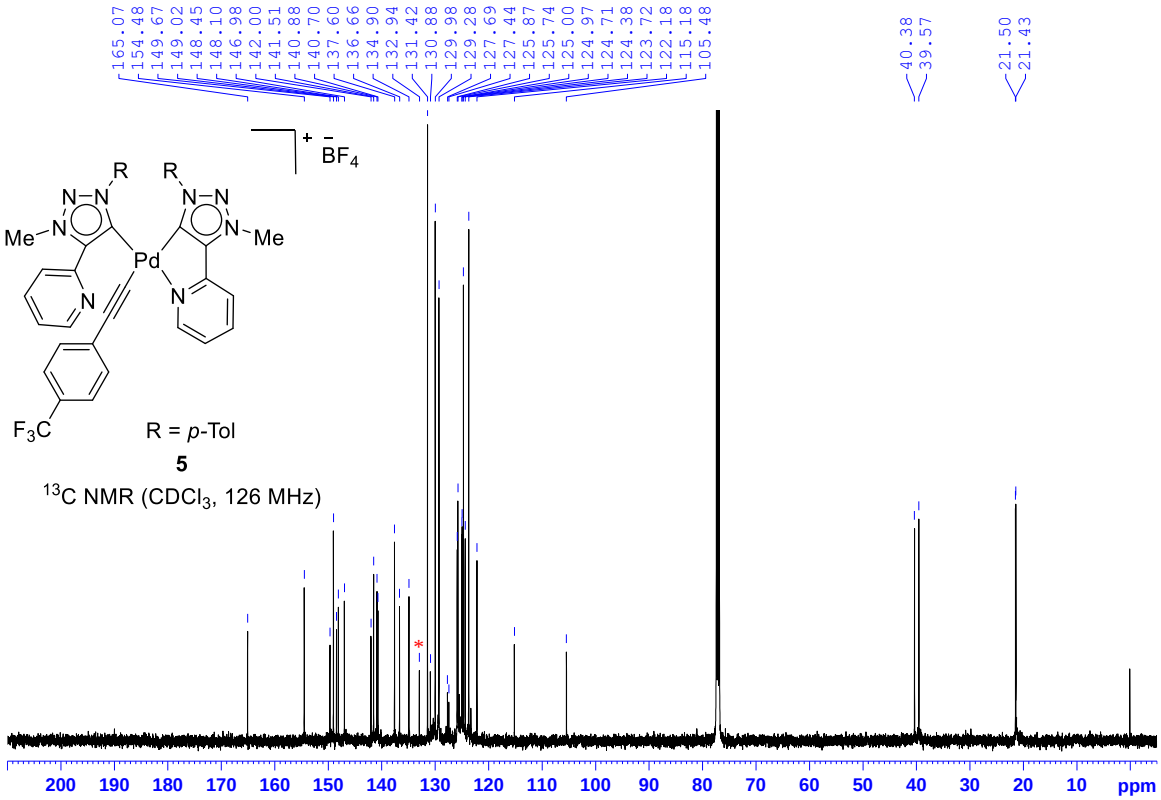
Supplementary Figure S31. ^{13}C NMR spectrum of compound **4b** in $CDCl_3$, 126 MHz with number of scans (NS) = 9216. Due to C–P coupling and low solubility of compound **4b** in $CDCl_3$, higher quality of spectra could not be obtained. *Pentane residual resonances.



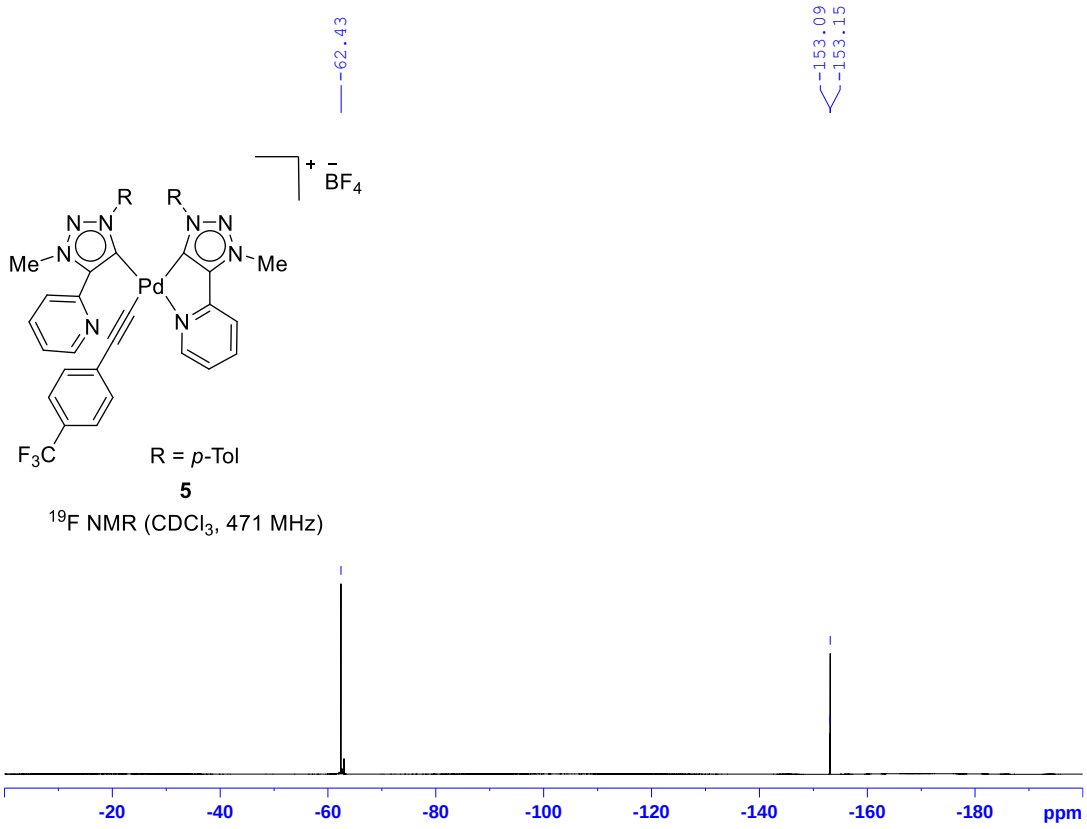
Supplementary Figure S32. ^{31}P NMR spectrum of compound **4b** in $CDCl_3$, 202 MHz.



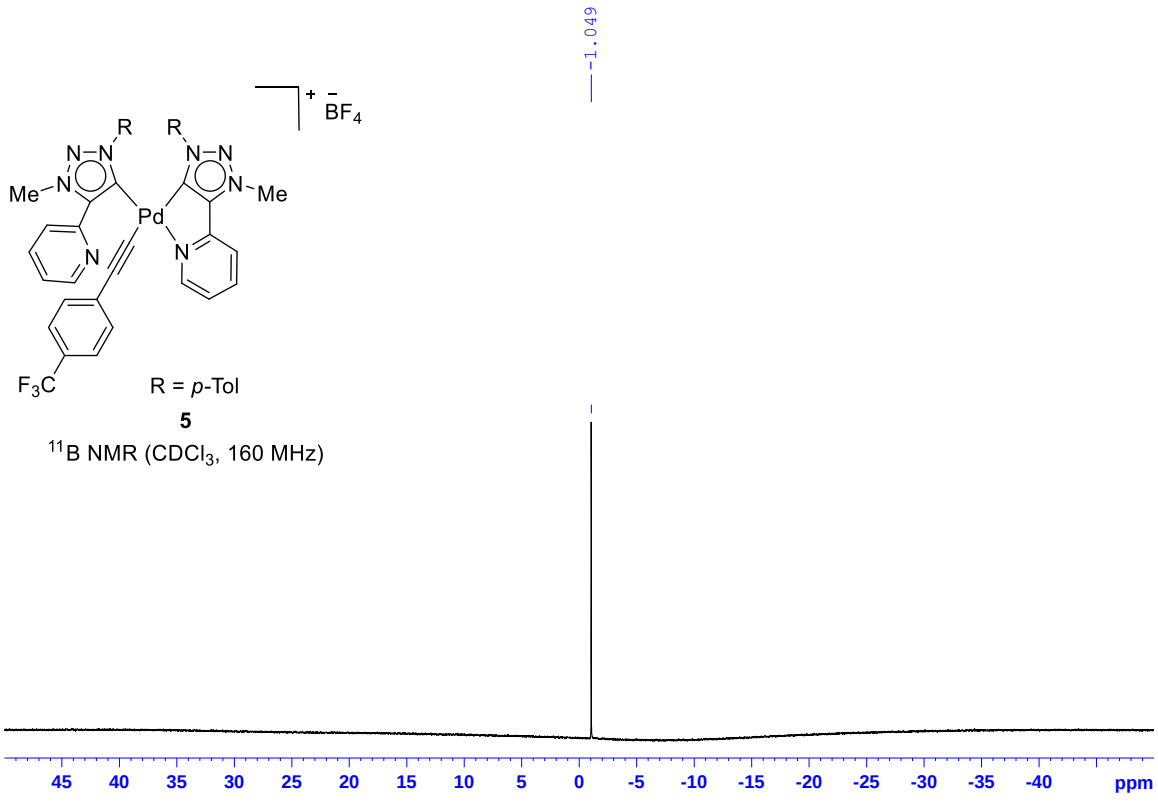
Supplementary Figure S33. ^{1}H NMR spectrum of compound **5** in $CDCl_3$, 500 MHz. *Resonance at δ 7.63 ppm is due to unidentified impurity, which correlates with the resonance at δ 132.9 ppm in ^{13}C NMR spectrum (based on ^{1}H–^{13}C *gs*-HSQC and ^{1}H–^{13}C *gs*-HMBC spectrum) shown in Supplementary Figure S34.



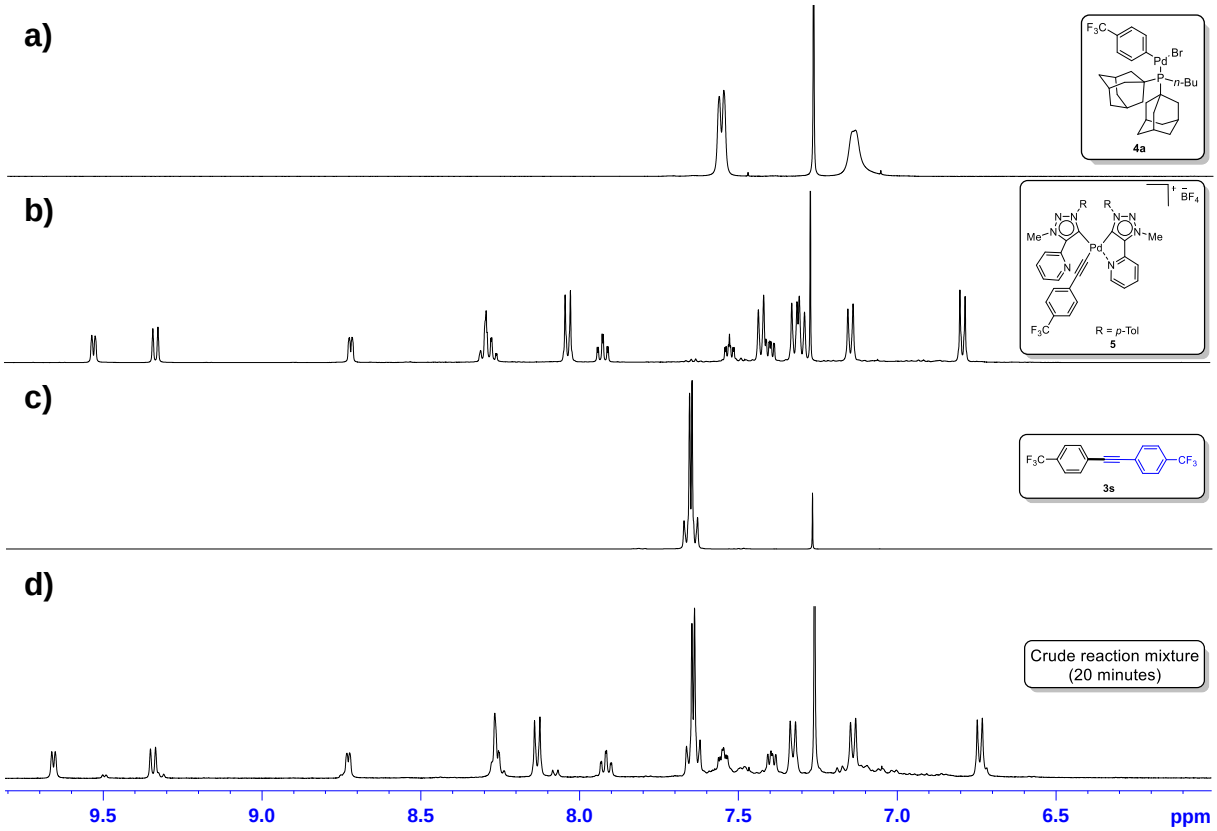
Supplementary Figure S34. ^{13}C NMR spectrum of compound **5** in $CDCl_3$, 126 MHz. *Resonance at δ 132.9 ppm is due to unidentified impurity, which correlates with peak at δ 7.63 ppm in ^{1}H NMR spectrum (based on ^{1}H–^{13}C *gs*-HSQC and ^{1}H–^{13}C *gs*-HMBC spectrum) shown in Supplementary Figure S33.



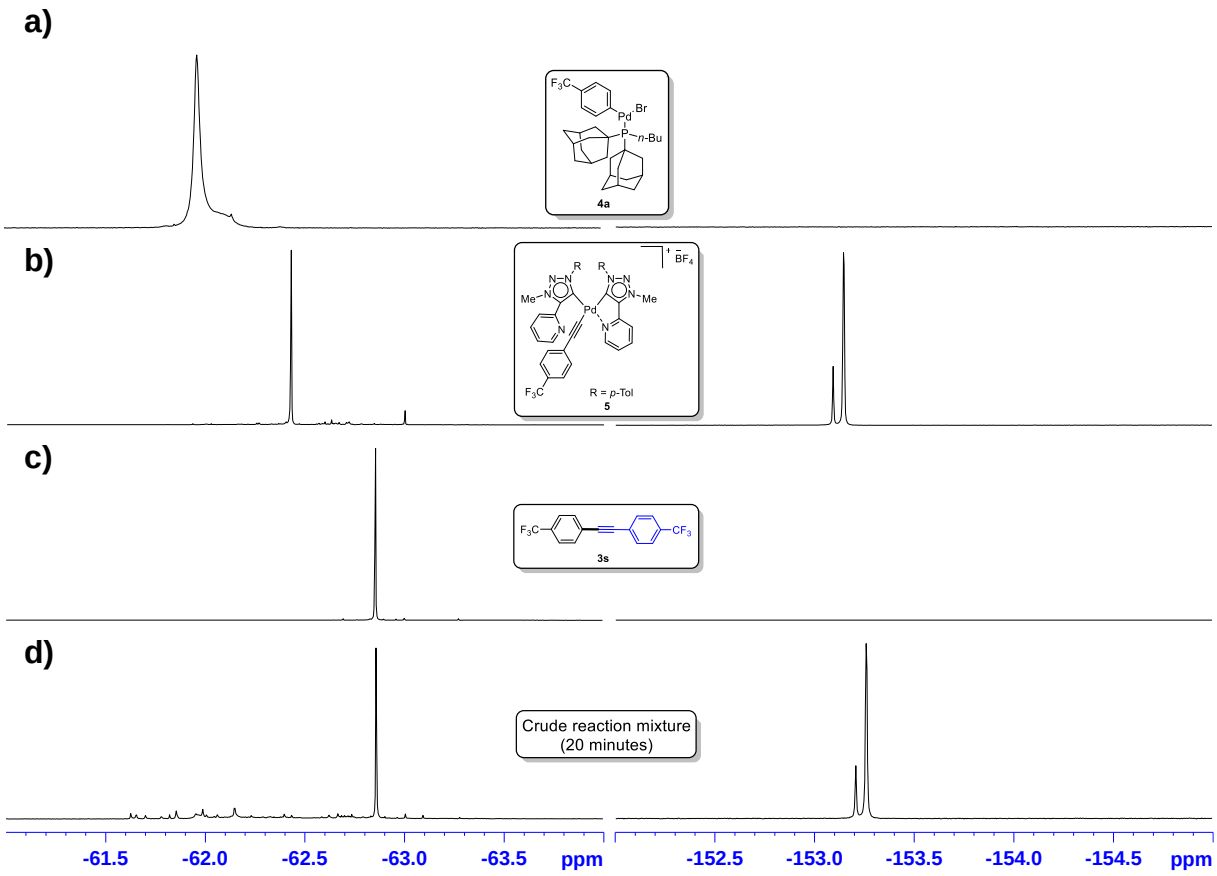
Supplementary Figure S35. ^{19}F NMR spectrum of compound **5** in $CDCl_3$, 471 MHz.



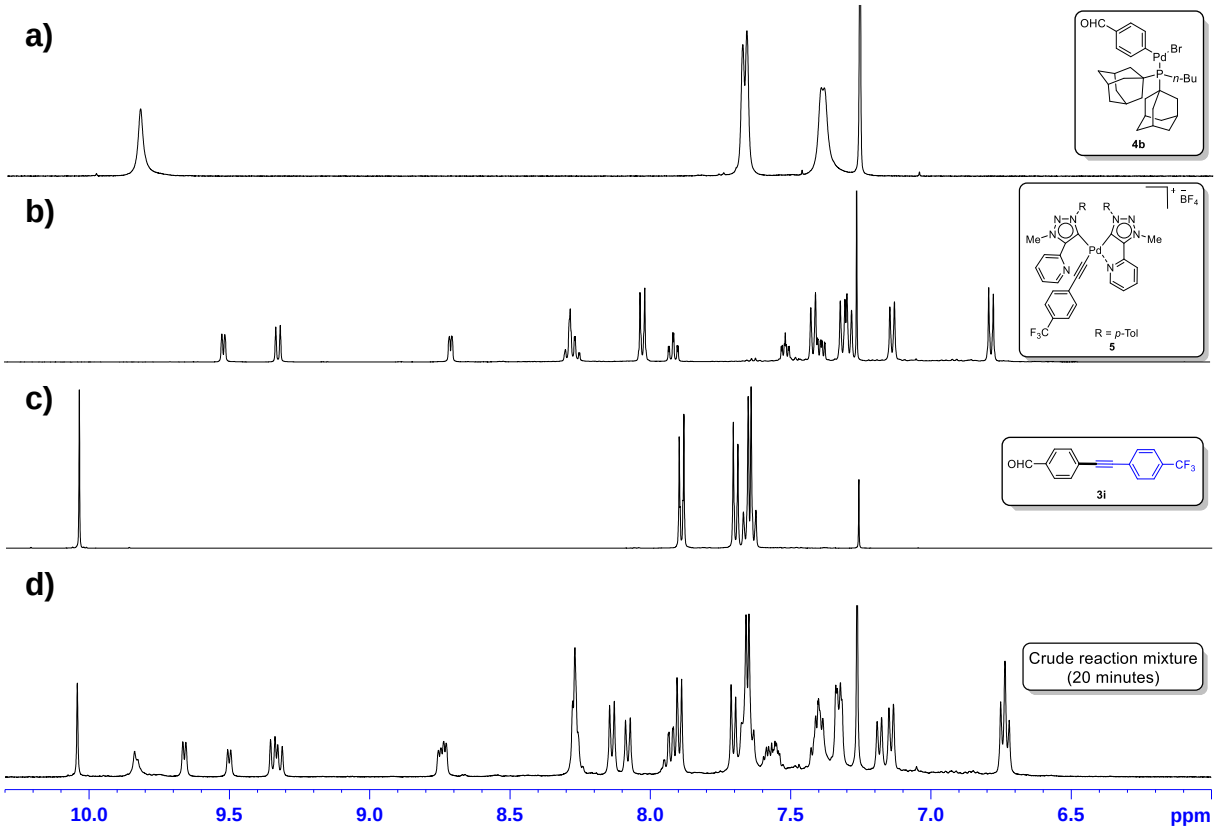
Supplementary Figure S36. ^{11}B NMR spectrum of compound **5** in $CDCl_3$, 160 MHz.



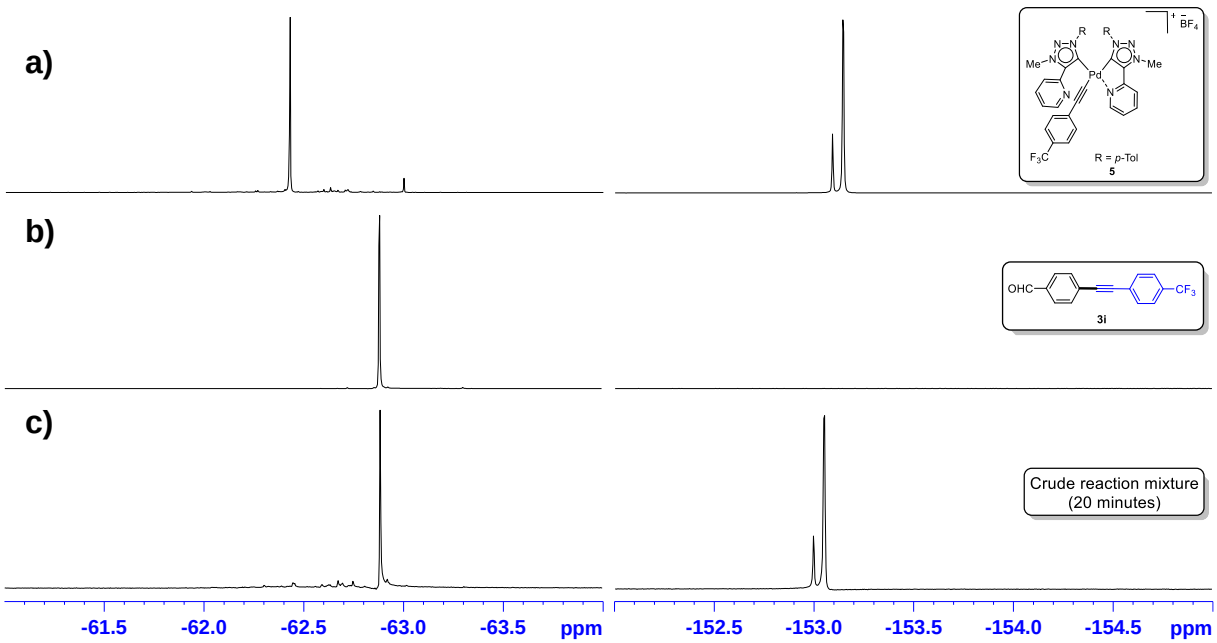
Supplementary Figure S37. Aromatic regions of ^{1}H NMR spectra of a) compound **4a**, b) compound **5**, c) product **3s**, and d) crude reaction mixture after 20 minutes, in $CDCl_3$, 500 MHz.



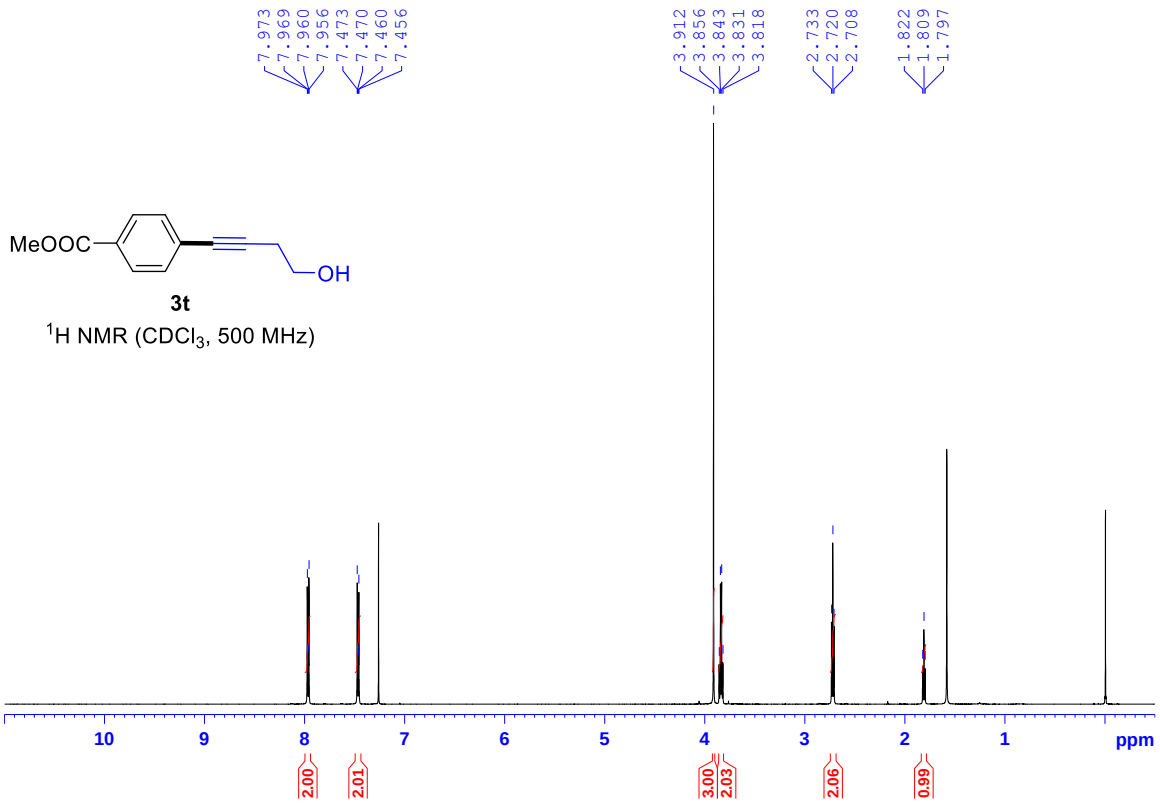
Supplementary Figure S38. $-CF_3$ (left) and BF_4^- (right) regions of $^{19}F\{H\}$ NMR spectra of a) compound **4a**, b) compound **5**, c) product **3s**, and d) crude reaction mixture after 20 minutes, in $CDCl_3$, 471 MHz.



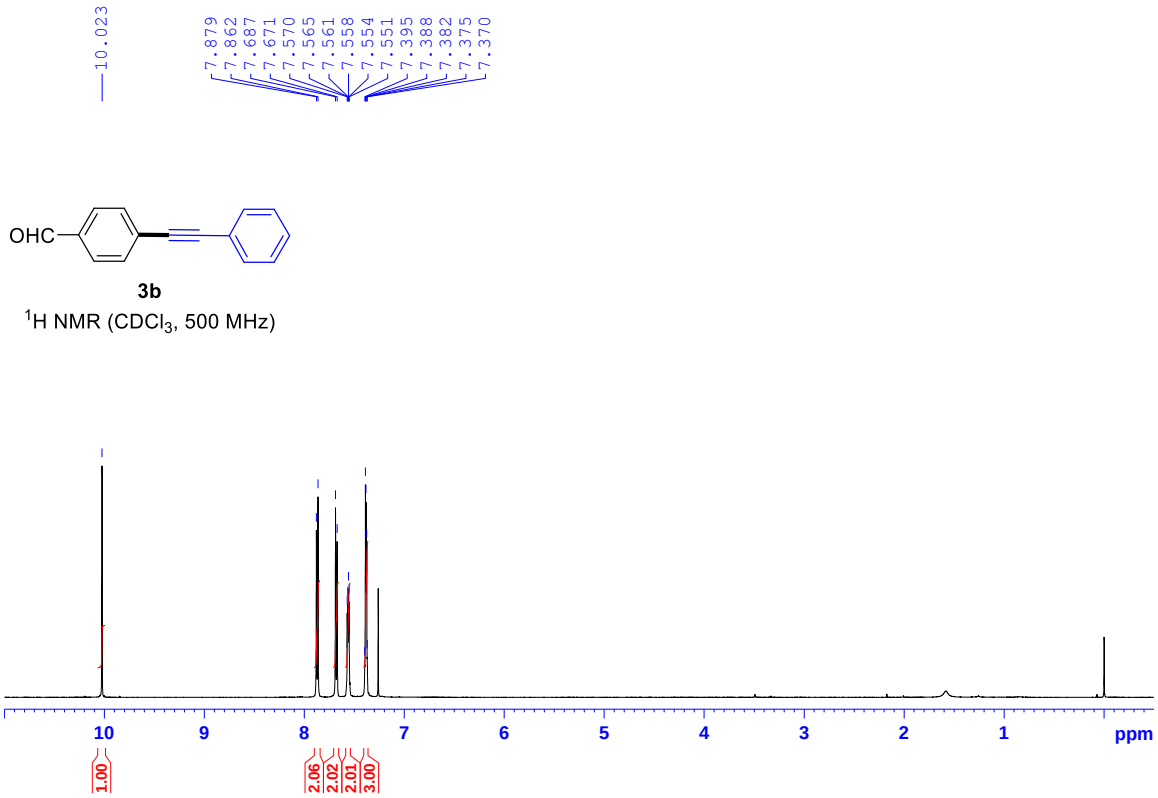
Supplementary Figure S39. Aromatic regions of ^{1}H NMR spectra of a) compound **4b**, b) compound **5**, c) product **3i**, and d) crude reaction mixture after 20 minutes, in $CDCl_3$, 500 MHz.



Supplementary Figure S40. $-CF_3$ (left) and BF_4^- (right) regions of $^{19}F\{H\}$ NMR spectra of a) compound **5**, b) product **3i**, and c) crude reaction mixture after 20 minutes, in $CDCl_3$, 471 MHz. The spectrum of compound **4b** is not shown as it does not contain fluorine atoms.



Supplementary Figure S41. ^1H NMR spectrum of compound **3t** in $CDCl_3$, 500 MHz.



Supplementary Figure S42. ^{1}H NMR spectrum of compound **3b** (multi-gram synthesis) in $CDCl_3$, 500 MHz..

4. REFERENCES AND NOTES

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