

Air- and moisture-stable Xantphos-ligated palladium dialkyl complexes as precatalysts for cross-coupling reactions

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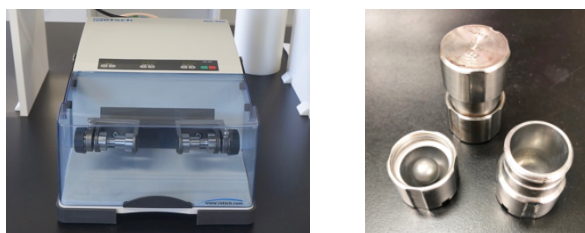
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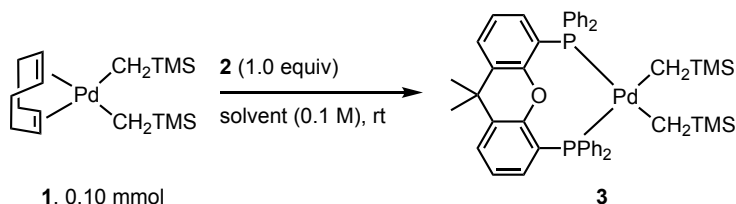
1. General and Materials.

The starting materials were obtained from commercial suppliers and used as received unless otherwise noted. Solvents were also purchased from commercial suppliers, and dried over molecular sieves (MS 4Å). Mechanochemical reaction was carried out using grinding vessels in a Retsch MM400 mill (Supplementary Figure 1). Both jar (25 mL) and ball (diameter: 10 mm) are made of stainless (Supplementary Figure 1). NMR spectra were recorded on JEOL JNM-ECX400P and JNM-ECS400 spectrometers (^1H : 392, 396, 400 or 401 MHz, ^{13}C : 99, 100 or 101 MHz, ^{31}P : 160 MHz). Tetramethylsilane (^1H), CDCl_3 (^1H , ^{13}C) and H_3PO_4 (^{31}P) were employed as external standards, respectively. Multiplicity was recorded as follows: s = singlet, br, s = broad singlet, d = doublet, t = triplet, quint = quintet, sext = sextet, sep = septet, m = multiplet. Dibromomethane or 1,2-diphenylethane were used as an internal standard to determine NMR yields. GLC analyses were conducted with a Shimadzu GC-2014 or GC-2025 equipped with ULBON HR-1 glass capillary column (Shinwa Chemical Industries) and a FID detector. High-resolution mass spectra were recorded at the Global Facility Center, Hokkaido University. Melting points were measured using an ATM-02, AS ONE melting point apparatus. Single crystal X-ray structural analyses were carried out on a Rigaku XtaLAB PRO MM007 diffractometer using graphite monochromated Mo-K_α radiation. The structure was solved by direct methods and expanded using Frontier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using Olex crystallographic software package except for refinement, which was performed using SHELXL.¹



Supplementary Figure 1. Retsch MM400 mill (left) and ball milling vessels (right).

2. General Procedure for Synthesis of Palladium Dialkyl Complex **3**.

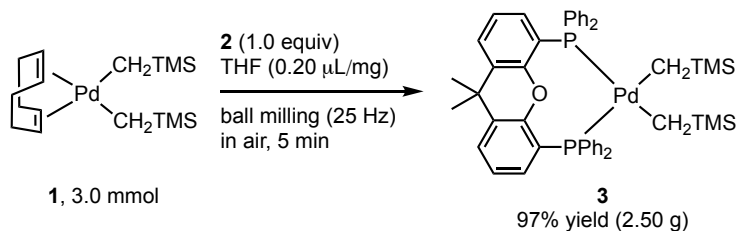


(COD)Pd(CH₂TMS)₂ **1** was prepared by according to the reported procedure.² The material **1** is thermo-sensitive and must be stored at a temperature of -20°C or lower to avoid decomposition, while the material can be stored out of glovebox and used in air.

1 (38.9 mg, 0.10 mmol) and Xantphos (**2**) (57.9 mg, 0.10 mmol, 1.0 equiv) were placed in an oven-dried reaction vial, then MeCN (1.0 mL) was added. The reaction mixture was stirred at room temperature for 20 minutes, then the solvent was removed under reduced pressure. The crude product was washed with pentane and Et₂O and dried under reduced pressure to afford the palladium complex **3** as a yellow solid (66.5 mg, 0.0773 mmol, 78% yield).

¹H NMR (396 MHz, CDCl₃, δ): -0.34 (s, 18H), 0.37 – 0.54 (m, 4H), 1.68 (s, 6H), 6.90 – 7.42 (m, 24H), 7.51 (dd, $J = 1.6, 7.1$ Hz, 2H). ¹³C NMR was not assigned due to poor resolution and peak broadening in several common NMR-solvents; spectrum recorded in CDCl₃ is shown in appendix. ³¹P NMR (160 MHz, CDCl₃, δ): 8.9. HRMS-ESI (m/z): $[\text{M}-\text{TMSCH}_2]^+$ calcd for C₄₃H₄₃OP₂PdSi, 771.1593; found, 771.1587.

*Gram-scale synthesis of palladium complex **3** by mechanochemistry*

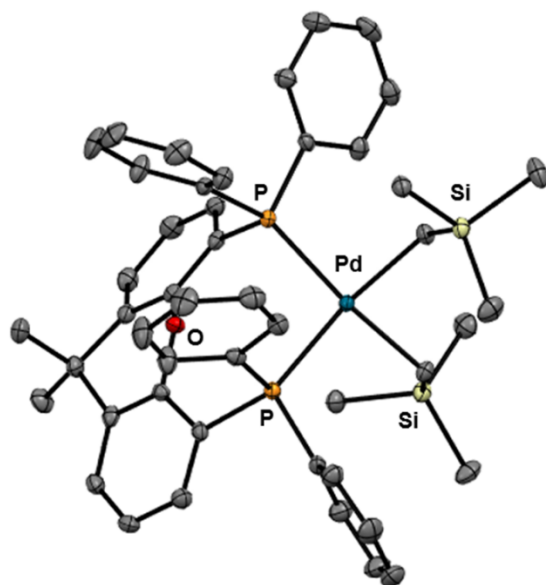


1 (3.0 mmol) and **2** (3.0 mmol, 1.0 equiv) were placed in a ball milling vessel (stainless, 25 mL) loaded with two grinding balls (stainless, diameter: 10 mm), then THF (0.58 mL, $0.20 \mu\text{L mg}^{-1}$) was added via syringe. After the vessel was closed in air without the purge with inert gas, the vessel was placed in the ball mill (Retch MM400, 5 min at 25Hz). The crude product was washed with pentane and Et₂O and dried under reduced pressure to afford the corresponding palladium complex **3** as a yellow solid (2.50 g, 2.9 mmol, 97% yield).

3. Single Crystal X-Ray Analysis of 3.

Supplementary Table 1. Summary of X-ray crystallographic data for **3**.

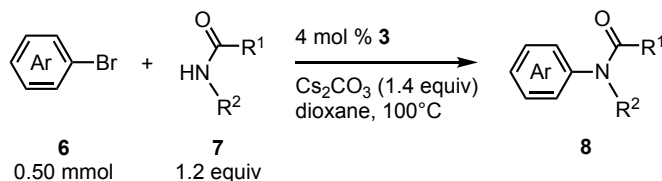
CCDC number	1938978
Empirical Formula	C ₄₇ H ₅₄ OP ₂ PdSi ₂
Formula Weight	859.42
Crystal System	monoclinic
Crystal Size / mm ³	0.55 × 0.08 × 0.09
a / Å	20.6034(4)
b / Å	11.5855(2)
c / Å	35.7054(8)
α / °	90
β / °	97.7204(19)
γ / °	90
V / Å ³	8445.6(3)
Space Group	C2/c
Z value	8
D _{calc} / g·cm ⁻³	1.352
Temperature / K	123(2)
No. of Reflections	53737
Measured	7717 (<i>R</i> _{int} = 0.0720)
Residuals: <i>R</i> ₁	0.0337
(<i>I</i> > 2.00σ(<i>I</i>)) / %	
Residuals: <i>wR</i> ₂	0.0821
(All reflections) / %	
Goodness of Fit (GOF)	1.075
Maximum peak in Final Diff. Map / Å ³	0.76 e ⁻
Minimum peak in Final Diff. Map / Å ³	-0.60 e ⁻



Supplementary Figure 2. Single-crystal structure of **3** (thermal ellipsoids set at 50% probability; hydrogen atoms have been omitted for clarity).

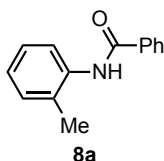
4. General Procedure for Cross-Coupling Reactions.

C–N Coupling with amides



3 (0.015 mmol), **6** (0.50 mmol), **7** (0.60 mmol) and Cs_2CO_3 (0.70 mmol) were placed in an oven-dried reaction vial. After being sealed with a screw cap containing a Teflon-coated rubber septum, the vial was connected to a nitrogen line through a needle. After 1,4-dioxane (1.0 mL) was added, the reaction mixture was heated to 100 °C for the specified time. After cooling to room temperature, the reaction mixture was passed through a short silica gel column. The crude mixture was purified by flash column chromatography (SiO_2 , EtOAc/hexane, 0:100–30:70).

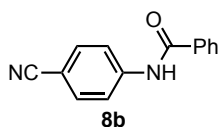
N-(o-Tolyl)benzamide (8a)



The reaction was carried out for 8 h with **3** (19.1 mg, 0.02 mmol), 1-bromo-2-methylbenzene (85.1 mg, 0.50 mmol), benzamide (72.7 mg, 0.60 mmol) and Cs_2CO_3 (135.1 mg, 0.70 mmol). The product **8a** was obtained in 86% yield (90.6 mg, 0.43 mmol) as a white solid (m.p. = 145–146 °C).

^1H NMR (401 MHz, CDCl_3 , δ): 2.35 (s, 3H), 7.13 (td, J = 1.1, 7.4 Hz, 1H), 7.21–7.31 (m, 2H), 7.48–7.54 (m, 2H), 7.58 (tt, J = 1.8, 7.3 Hz, 1H), 7.66 (br, s, 1H), 7.90 (d, J = 7.2 Hz, 2H), 7.98 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3 , δ): 17.8 (CH_3), 123.1 (CH), 125.3 (CH), 126.9 (CH), 127.0 (CH), 128.8 (CH), 129.3 (C), 130.5 (CH), 131.8 (CH), 135.0 (C), 135.7 (C), 165.6 (C). HRMS-EI (m/z): [M] calcd for $\text{C}_{14}\text{H}_{13}\text{NO}$, 211.0997; found, 211.1002.

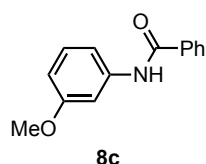
N-(4-Cyanophenyl)benzamide (**8b**)



The reaction was carried out for 7 h with **3** (21.5 mg, 0.025 mmol), 4-bromobenzonitrile (91.3 mg, 0.50 mmol), benzamide (72.5 mg, 0.60 mmol) and Cs₂CO₃ (134.7 mg, 0.70 mmol). The product **8b** was obtained in 95% yield (105.9 mg, 0.48 mmol) as a white solid (m.p. = 171–172 °C).

¹H NMR (392 MHz, CDCl₃, δ): 7.50–7.56 (m, 2H), 7.61 (tt, *J* = 1.6, 7.4 Hz, 1H), 7.68 (dt, *J* = 2.0, 9.0 Hz, 2H), 7.80 (dt, *J* = 2.2, 9.0 Hz, 2H), 7.85–7.90 (m, 2H), 7.94 (br, s, 1H). ¹³C NMR (100 MHz, CDCl₃, δ): 107.3 (C), 118.8 (C), 119.9 (CH), 127.1 (CH), 129.0 (CH), 132.5 (CH), 133.3 (CH), 134.1 (C), 142.0 (C), 165.9 (C). HRMS-EI (*m/z*): [M] calcd for C₁₄H₁₀N₂O, 222.0793; found, 222.0796.

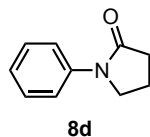
N-(3-Methoxyphenyl)benzamide (**8c**)



The reaction was carried out for 3 h with **3** (21.4 mg, 0.025 mmol), 1-bromo-2-methylbenzene (93.5 mg, 0.50 mmol), benzamide (72.7 mg, 0.65 mmol) and Cs₂CO₃ (135.2 mg, 0.70 mmol). The product **8c** was obtained in 65% yield (74.1 mg, 0.33 mmol) as a white solid (m.p. = 113–114 °C).

¹H NMR (392 MHz, CDCl₃, δ): 3.84 (s, 3H), 6.72 (dd, *J* = 2.4, 8.2 Hz, 1H), 7.09 (dt, *J* = 0.9, 8.0 Hz, 1H), 7.22–7.32 (m, 1H), 7.45 (t, *J* = 2.2 Hz, 1H), 7.47–7.59 (m, 3H), 7.78 (br, s, 1H), 7.87 (d, *J* = 8.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 55.2 (CH₃), 105.8 (CH), 110.4 (CH), 112.4 (CH), 127.0 (CH), 128.6 (CH), 129.6 (CH), 131.7 (CH), 134.8 (C), 139.2 (C), 160.0 (C), 166.0 (C). HRMS-EI (*m/z*): [M] calcd for C₁₄H₁₃NO₂, 227.0946; found, 227.0949.

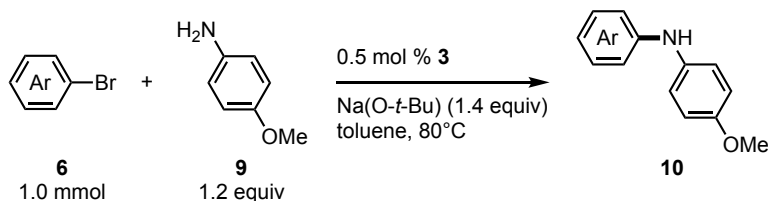
1-Phenylpyrrolidin-2-one (**8d**)



The reaction was carried out for 20 h with **3** (21.4 mg, 0.025 mmol), bromobenzene (78.1 mg, 0.50 mmol), pyrrolidin-2-one (51.1 mg, 0.60 mmol) and Cs₂CO₃ (135.4 mg, 0.70 mmol). The product **8d** was obtained in 63% yield (50.6 mg, 0.31 mmol) as a beige solid (m.p. = 67–68 °C).

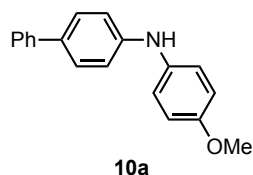
¹H NMR (396 MHz, CDCl₃, δ): 2.17 (quint, *J* = 7.6 Hz, 2H), 2.62 (t, *J* = 7.9 Hz, 2H), 3.87 (t, *J* = 6.9 Hz, 2H), 7.12–7.18 (m, 1H), 7.34–7.41 (m, 2H), 7.58–7.64 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 17.9 (CH₂), 32.6 (CH₂), 48.6 (CH₂), 119.8 (CH), 124.3 (CH), 128.7 (CH), 139.2 (C), 174.1 (C). HRMS-EI (*m/z*): [M] calcd for C₁₀H₁₁NO, 161.0841; found, 161.0847.

C–N Coupling with aryl amines



3 (0.005 mmol), **6** (1.0 mmol), **9** (1.2 mmol) and Na(O-*t*-Bu) (1.4 mmol) were placed in an oven-dried reaction vial. After being sealed with a screw cap containing a Teflon-coated rubber septum, the vial was connected to a nitrogen line through a needle. After toluene (2.0 mL) was added, the reaction mixture was heated to 80 °C for the specified time. After cooling to room temperature, the reaction mixture was passed through a short silica gel column. The crude mixture was purified by flash column chromatography (SiO₂, EtOAc/hexane, 0:100–10:90).

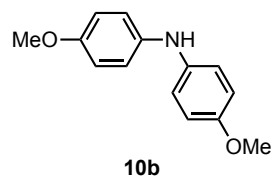
N-(4-Methoxyphenyl)-(1,1'-biphenyl)-4-amine (**10a**)



The reaction was carried out for 2 h with **3** (4.2 mg, 0.005 mmol), 4-bromo-1,1'-biphenyl (233.2 mg, 1.0 mmol), **9** (148.2 mg, 1.2 mmol) and Na(O-*t*-Bu) (134.2 mg, 1.4 mmol). The product **10a** was obtained in 89% yield (244.3 mg, 0.89 mmol) as a white solid (m.p. = 126 °C).

¹H NMR (401 MHz, CDCl₃, δ): 3.81 (s, 3H), 5.58 (s, 1H), 6.85–6.92 (m, 2H), 6.94–7.01 (m, 2H), 7.08–7.15 (m, 2H), 7.27–7.31 (m, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 55.6 (CH₃), 114.7 (CH), 115.7 (CH), 122.4 (CH), 126.3 (CH), 126.4 (CH), 127.9 (CH), 128.7 (CH), 132.3 (C), 135.4 (C), 141.0 (C), 144.6 (C), 155.4 (C). HRMS-EI (*m/z*): [*M*] calcd for C₁₉H₁₇NO, 275.1310; found, 275.1311.

Bis(4-methoxyphenyl)amine (**10b**)

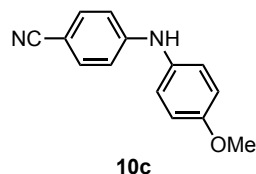


The reaction was carried out for 24 h with **3** (4.3 mg, 0.005 mmol), 1-bromo-4-methoxybenzene (187.1 mg, 1.0 mmol), **9** (148.1 mg, 1.2 mmol) and Na(O-*t*-Bu) (134.1 mg, 1.4 mmol). The product **10b** was

obtained in 64% yield (147.3 mg, 0.64 mmol) as an off-white solid (m.p. = 103–104 °C).

^1H NMR (396 MHz, CDCl_3 , δ): 3.78 (s, 6H), 5.28 (br, s, 1H), 6.82 (dt, J = 2.8, 9.8 Hz, 4H), 6.94 (dt, J = 2.9, 9.5 Hz, 4H). ^{13}C NMR (99 MHz, CDCl_3 , δ): 55.4 (CH_3), 114.6 (CH), 119.3 (CH), 137.8 (C), 154.0 (C). HRMS-EI (m/z): [M] calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_2$, 229.1103; found, 229.1106.

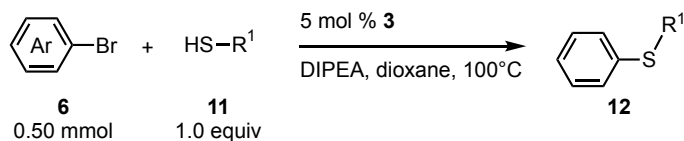
4-[(4-Methoxyphenyl)amino]benzonitrile (**10c**)



The reaction was carried out for 1 h with **3** (4.3 mg, 0.005 mmol), 4-bromobenzonitrile (182.2 mg, 1.0 mmol), **9** (148.4 mg, 1.2 mmol) and $\text{Na}(\text{O}-t\text{-Bu})$ (134.6 mg, 1.4 mmol). The product **10c** was obtained in 86% yield (210.7 mg, 0.86 mmol) as a white solid (m.p. = 102–103 °C).

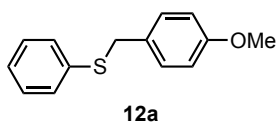
^1H NMR (396 MHz, CDCl_3 , δ): 3.82 (s, 3H), 5.87 (br, s, 1H), 6.79 (dt, J = 2.3, 9.1 Hz, 2H), 6.91 (dt, J = 2.8, 9.8 Hz, 2H), 7.12 (dt, J = 2.7, 9.7 Hz, 2H), 7.43 (dt, J = 2.3, 9.1 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3 , δ): 55.3 (CH_3), 99.6 (C), 113.5 (CH), 114.6 (CH), 120.2 (C), 124.6 (CH), 132.4 (C), 133.5 (CH), 149.6 (C), 156.7 (C). HRMS-EI (m/z): [M] calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}$, 224.0950; found, 224.0952.

C-S Coupling with thiols



3 (0.015 mmol), **6** (0.50 mmol) were placed in an oven-dried reaction vial. After being sealed with a screw cap containing a Teflon-coated rubber septum, the vial was connected to a nitrogen line through a needle. 1,4-Dioxane (1.0 mL), DIPEA (174 μ L, 2.0 mmol) and **11** (0.50 mmol) were added to the mixture, then the reaction mixture was heated to 100 $^\circ$ C for 1 h. After cooling to room temperature, the reaction mixture was passed through a short silica gel column. The crude mixture was purified by flash column chromatography (SiO₂, EtOAc/hexane, 0:100–10:90).

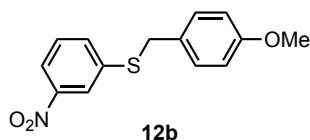
(4-Methoxybenzyl)(phenyl)sulfane (**12a**)



The reaction was carried out for 1 h with **3** (21.4 mg, 0.025 mmol), bromobenzene (79.5 mg, 0.50 mmol) and (4-methoxyphenyl)methanethiol (69 μ L, 0.50 mmol). The product **12a** was obtained in 95% yield (110.2 mg, 0.48 mmol) as a white solid (m.p. = 86–87 $^\circ$ C).

¹H NMR (396 MHz, CDCl₃, δ): 3.79 (s, 3H), 4.08 (s, 2H), 6.82 (dt, J = 2.6, 9.2 Hz, 2H), 7.15–7.34 (m, 7H). ¹³C NMR (100 MHz, CDCl₃, δ): 38.4 (CH₂), 55.2 (CH₃), 113.8 (CH), 126.2 (CH), 128.8 (CH), 129.3 (C), 129.7 (CH), 129.9 (CH), 136.5 (C), 158.7 (C). HRMS-EI (m/z): [M] calcd for C₁₄H₁₄OS, 230.0765; found, 230.0769.

(4-Methoxybenzyl)(3-nitrophenyl)sulfane (**12b**)

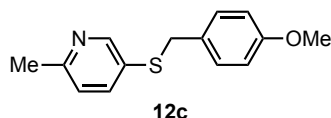


The reaction was carried out for 1 h with **3** (21.5 mg, 0.025 mmol), 1-bromo-3-nitrobenzene (101.0 mg, 0.50 mmol) and (4-methoxyphenyl)methanethiol (69 μ L, 0.50 mmol). The product **12b** was obtained in 97% yield (133.2 mg, 0.48 mmol) as a yellow solid (m.p. = 58–59 $^\circ$ C).

¹H NMR (396 MHz, CDCl₃, δ): 3.79 (s, 3H), 4.17 (s, 2H), 6.84 (dt, J = 2.4, 9.4 Hz, 2H), 7.21–7.29 (m, 2H), 7.40 (t, J = 7.9 Hz, 1H), 7.54 (dt, J = 1.0, 7.7 Hz, 1H), 7.99 (dd, J = 2.2, 8.1 Hz, 1H), 8.12 (t, J = 2.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, δ): 37.5 (CH₂), 55.1 (CH₃), 114.0 (CH), 120.5 (CH),

122.8 (CH), 127.7 (C), 129.3 (CH), 129.9 (CH), 134.3 (CH), 139.5 (C), 148.2 (C), 158.9 (C). HRMS-EI (m/z): [M] calcd for C₁₄H₁₃NO₃S, 275.0616; found, 275.0616.

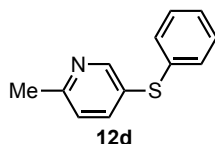
5-[(4-Methoxybenzyl)thio]-2-methylpyridine (**12c**)



The reaction was carried out for 1 h with **3** (21.5 mg, 0.025 mmol), 5-bromo-2-methylpyridine (85.9 mg, 0.50 mmol) and (4-methoxyphenyl)methanethiol (69 μ L, 0.50 mmol). The product **12c** was obtained in 92% yield (112.4 mg, 0.46 mmol) as a white solid (m.p. = 58–59 °C).

¹H NMR (396 MHz, CDCl₃, δ): 2.51 (s, 3H), 3.78 (s, 3H), 4.00 (s, 2H), 6.80 (dt, J = 2.5, 9.2 Hz, 2H), 7.02 (d, J = 8.2 Hz, 1H), 7.14 (dt, J = 2.6, 9.4 Hz, 2H), 7.45 (dd, J = 2.3, 8.2 Hz, 1H), 8.41 (d, J = 2.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, δ): 24.0 (CH₃), 39.3 (CH₂), 55.2 (CH₃), 113.8 (CH), 123.1 (CH), 129.1 (C), 129.9 (CH), 139.4 (CH), 151.3 (CH), 156.9 (C), 158.8 (C). HRMS-EI (m/z): [M] calcd for C₁₄H₁₅NOS, 245.0874; found, 245.0875.

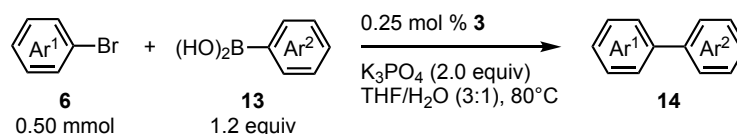
2-Methyl-5-(phenylthio)pyridine (**12d**)



The reaction was carried out for 1 h with **3** (21.5 mg, 0.025 mmol), 5-bromo-2-methylpyridine (85.7 mg, 0.50 mmol) and benzenethiol (51 μ L, 0.50 mmol). The product **12d** was obtained in 81% yield (81.0 mg, 0.40 mmol) as a pale yellow liquid.

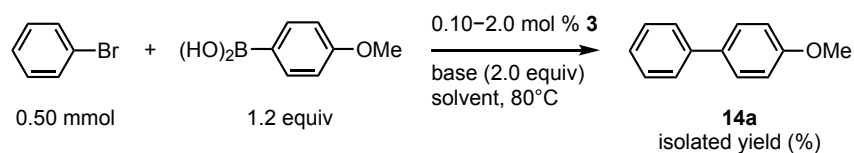
¹H NMR (396 MHz, CDCl₃, δ): 2.55 (s, 3H), 7.11 (d, J = 8.3 Hz, 1H), 7.21–7.31 (m, 5H), 7.57 (dd, J = 2.2, 8.1 Hz, 1H), 8.51 (d, J = 2.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, δ): 24.0 (CH₃), 123.6 (CH), 127.0 (CH), 128.8 (C), 129.2 (CH), 130.2 (CH), 135.4 (C), 139.6 (CH), 151.6 (CH), 157.5 (C). HRMS-EI (m/z): [M] calcd for C₁₂H₁₁NS, 201.0612; found, 201.0618.

Suzuki-Miyaura Cross-Coupling Reaction



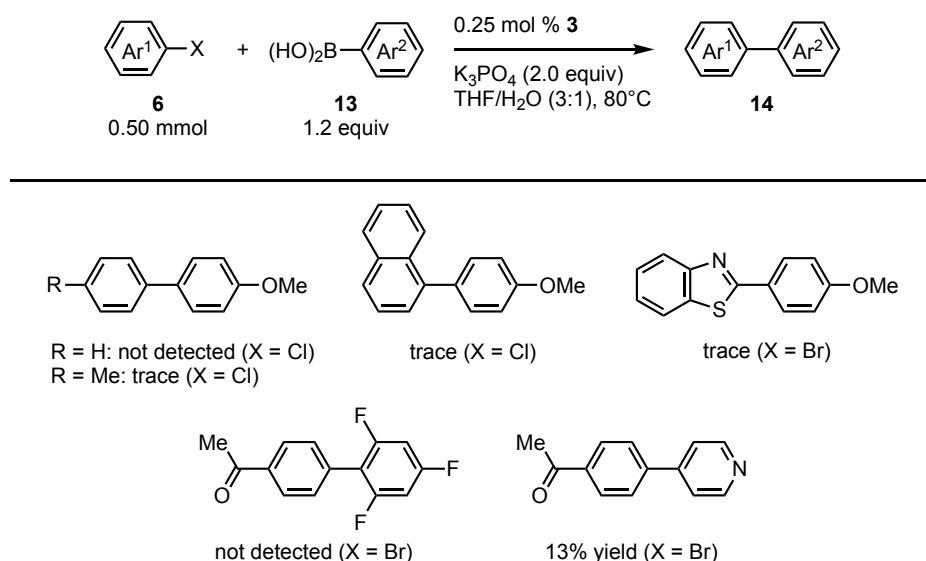
3 (1.25 μmol), **6** (0.50 mmol), **13** (0.60 mmol) and K_3PO_4 (1.0 mmol) were placed in an oven-dried reaction vial. After being sealed with a screw cap containing a Teflon-coated rubber septum, the vial was connected to a nitrogen line through a needle. THF (1.0 mL) and H_2O (0.33 mL) were added, then the reaction mixture was heated to 80 $^\circ\text{C}$ for 3–24 h. After cooling to room temperature, the reaction mixture was extracted three times with CH_2Cl_2 , washed with brine and dried over MgSO_4 . The crude mixture was purified by flash column chromatography.

Supplementary Table 2. Optimization of reaction conditions for Suzuki-Miyaura cross-coupling reaction.



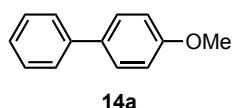
Entry	Base	Solvent (mL)	Catalyst (mol %)	Time (h)	Yield of 14a (%)
1	K_2CO_3	DMF (1.0)	2.0	6	78
2	K_3PO_4	DMF (1.0)	2.0	24	92
3	K_3PO_4	THF (1.0)	2.0	1	88
4	K_3PO_4	THF (1.0)	1.0	1	94
5	K_3PO_4	THF (1.0)	0.50	7	92
6	K_3PO_4	THF (1.0) + H_2O (0.33)	0.50	1.5	94
7	K_3PO_4	THF (1.0) + H_2O (0.33)	0.25	1	95
8 ^a	K_3PO_4	THF (3.0) + H_2O (1.0)	0.10	6	96

^aThe reaction was conducted in 1.5 mmol scale.



Supplementary Figure 3. Unsuccessful substrates in C-C coupling reaction.

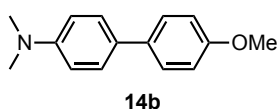
4-Methoxy-1,1'-biphenyl (**14a**)



The reaction was carried out for 1 h with **3** (1.1 mg, 1.25 μ mol), 1-bromo-4-methoxybenzene (78.9 mg, 0.50 mmol), (4-methoxyphenyl)boronic acid (91.2 mg, 0.60 mmol) and K_3PO_4 (212.5 mg, 1.0 mmol). The product **14a** was obtained in 95% yield (88.3 mg, 0.48 mmol) as a white solid (m.p. = 89 °C) by flash chromatography (SiO_2 , hexane/ CH_2Cl_2 , 100:0 to 80:20).

1H NMR (396 MHz, $CDCl_3$, δ): 3.85 (s, 3H), 6.98 (dt, J = 2.4, 9.2 Hz, 2H), 7.30 (tt, J = 1.4, 7.3 Hz, 1H), 7.42 (tt, J = 1.7, 7.7 Hz, 2H), 7.54 (tt, J = 2.1, 8.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 55.2 (CH₃), 114.1 (CH), 126.59 (CH), 126.65 (CH), 128.1 (CH), 128.7 (CH), 133.6 (C), 140.7 (C), 159.1 (C). HRMS-EI (m/z): [M] calcd for $C_{13}H_{12}O$, 184.0888; found, 184.0887.

4'-Methoxy-*N,N*-dimethyl-(1,1'-biphenyl)-4-amine (**14b**)

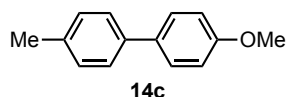


The reaction was carried out for 24 h with **3** (4.3 mg, 5.0 μ mol), 4-bromo-*N,N*-dimethylaniline (100.2 mg, 0.50 mmol), (4-methoxyphenyl)boronic acid (91.5 mg, 0.60 mmol) and K_3PO_4 (211.4 mg, 1.0 mmol). The product **14b** was obtained in 86% yield (97.4 mg, 0.43 mmol) as a white solid (m.p. = 158–159 °C) by flash chromatography (SiO_2 , hexane/ CH_2Cl_2 , 90:10 to 0:100).

1H NMR (400 MHz, $CDCl_3$, δ): 2.98 (s, 6H), 3.84 (s, 3H), 6.80 (dt, J = 2.7, 9.2 Hz, 2H), 6.95 (dt, J =

2.3, 9.3 Hz, 2H), 7.43–7.51 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3 , δ): 40.6 (CH_3), 55.2 (CH_3), 112.8 (CH), 114.0 (CH), 127.2 (CH), 129.0 (C), 133.8 (C), 149.5 (C), 158.1 (C). HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{18}\text{NO}$, 228.1383; found, 228.1381.

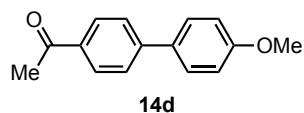
4-Methoxy-4'-methyl-1,1'-biphenyl (**14c**)



The reaction was carried out for 3 h with **3** (1.1 mg, 1.25 μmol), 1-bromo-4-methylbenzene (85.9 mg, 0.50 mmol), (4-methoxyphenyl)boronic acid (91.6 mg, 0.60 mmol) and K_3PO_4 (212.3 mg, 1.0 mmol). The product **14c** was obtained in 72% yield (71.6 mg, 0.36 mmol) as a white solid (m.p. = 110–111 $^\circ\text{C}$) by flash chromatography (SiO_2 , hexane/ CH_2Cl_2 , 50:50).

^1H NMR (400 MHz, CDCl_3 , δ): 2.39 (s, 3H), 3.85 (s, 3H), 6.97 (dt, $J = 2.7, 9.5$ Hz, 2H), 7.23 (d, $J = 7.6$ Hz, 2H), 7.45 (dt, $J = 1.8, 8.3$ Hz, 2H), 7.51 (dt, $J = 2.7, 9.5$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3 , δ): 21.0 (CH_3), 55.2 (CH_3), 114.1 (CH), 126.5 (CH), 127.9 (CH), 129.4 (CH), 133.6 (C), 136.3 (C), 137.9 (C), 158.8 (C). HRMS-EI (m/z): $[\text{M}]$ calcd for $\text{C}_{14}\text{H}_{14}\text{O}$, 198.1045; found, 198.1043.

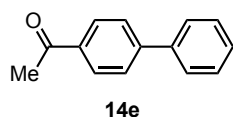
1-[4'-Methoxy-(1,1'-biphenyl)-4-yl]ethan-1-one (**14d**)



The reaction was carried out for 3 h with **3** (1.1 mg, 1.25 μmol), 1-(4-bromophenyl)ethan-1-one (99.2 mg, 0.50 mmol), (4-methoxyphenyl)boronic acid (91.0 mg, 0.60 mmol) and K_3PO_4 (212.0 mg, 1.0 mmol). The product **14d** was obtained in 92% yield (104.3 mg, 0.46 mmol) as a white solid (m.p. = 158–159 $^\circ\text{C}$) by flash chromatography (SiO_2 , hexane/ EtOAc , 97:3 to 60:40).

^1H NMR (400 MHz, CDCl_3 , δ): 2.64 (s, 3H), 3.87 (s, 3H), 7.01 (dt, $J = 2.5, 9.5$ Hz, 2H), 7.59 (dt, $J = 2.7, 9.5$ Hz, 2H), 7.65 (dt, $J = 1.9, 8.5$ Hz, 2H), 8.01 (dt, $J = 1.5, 8.8$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3 , δ): 26.6 (CH_3), 55.3 (CH_3), 114.3 (CH), 126.5 (CH), 128.3 (CH), 128.9 (CH), 132.1 (C), 135.1 (C), 145.2 (C), 159.8 (C), 197.7 (C). HRMS-EI (m/z): $[\text{M}]$ calcd for $\text{C}_{15}\text{H}_{14}\text{O}_2$, 226.0994; found, 226.0994.

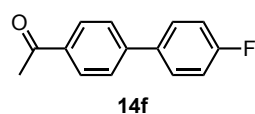
1-[(1,1'-Biphenyl)-4-yl]ethan-1-one (14e)



The reaction was carried out for 3 h with **3** (1.1 mg, 1.25 μ mol), 1-(4-bromophenyl)ethan-1-one (99.6 mg, 0.50 mmol), phenylboronic acid (73.2 mg, 0.60 mmol) and K_3PO_4 (212.3 mg, 1.0 mmol). The product **14e** was obtained in 92% yield (90.6 mg, 0.46 mmol) as a white solid (m.p. = 122–123 °C) by flash chromatography (SiO_2 , hexane/EtOAc, 100:0 to 85:15).

1H NMR (400 MHz, $CDCl_3$, δ): 2.65 (s, 3H), 7.41 (tt, J = 1.6, 7.3 Hz, 1H), 7.48 (tt, J = 1.7, 7.3 Hz, 2H), 7.61–7.66 (m, 2H), 7.70 (dt, J = 1.9, 8.5 Hz, 2H), 8.04 (dt, J = 1.9, 8.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 26.5 (CH_3), 127.06 (CH), 127.13 (CH), 128.1 (CH), 128.80 (CH), 128.83 (CH), 135.7 (C), 139.7 (C), 145.6 (C), 197.6 (C). HRMS-EI (m/z): [M] calcd for $C_{14}H_{12}O$, 196.0888; found, 196.0889.

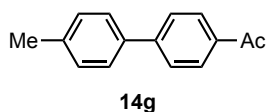
1-[4'-Fluoro-(1,1'-biphenyl)-4-yl]ethan-1-one (14f)



The reaction was carried out for 24 h with **3** (1.1 mg, 1.25 μ mol), 1-(4-bromophenyl)ethan-1-one (99.3 mg, 0.50 mmol), (4-fluorophenyl)boronic acid (83.2 mg, 0.60 mmol) and K_3PO_4 (212.2 mg, 1.0 mmol). The product **14f** was obtained in 85% yield (79.4 mg, 0.43 mmol) as a white solid (m.p. = 105–106 °C) by flash chromatography (SiO_2 , hexane/EtOAc, 98:2 to 60:40).

1H NMR (400 MHz, $CDCl_3$, δ): 2.65 (s, 3H), 7.17 (tt, J = 2.4, 9.1 Hz, 2H), 7.57–7.62 (m, 2H), 7.64 (dt, J = 2.0, 8.5 Hz, 2H), 8.03 (dt, J = 1.9, 8.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 26.5 (CH_3), 115.8 (d, J = 21.2 Hz, CH), 126.9 (CH), 128.8 (CH), 128.9 (CH), 135.7 (d, J = 13.5 Hz, C), 144.5 (C), 161.6 (C), 164.1 (C), 197.6 (C). HRMS-EI (m/z): [M] calcd for $C_{14}H_{11}FO$, 214.0794; found, 214.0794.

1-[4'-Methyl-(1,1'-biphenyl)-4-yl]ethan-1-one (14g)

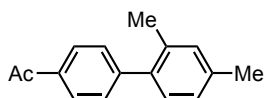


The reaction was carried out for 24 h with **3** (1.1 mg, 1.25 μ mol), 1-bromo-4-methylbenzene (85.1 mg, 0.50 mmol), (4-acetylphenyl)boronic acid (98.6 mg, 0.60 mmol) and K_3PO_4 (212.3 mg, 1.0 mmol).

The product **14g** was obtained in 84% yield (88.3 mg, 0.42 mmol) as a white solid (m.p. = 122–123 °C) by flash chromatography (SiO₂, hexane/ CH₂Cl₂, 100:0 to 0:100).

¹H NMR (400 MHz, CDCl₃, δ): 2.42 (s, 3H), 2.64 (s, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃, δ): 21.0 (CH₃), 26.5 (CH₃), 126.8 (CH), 126.9 (CH), 128.8 (CH), 129.6 (CH), 135.4 (C), 136.7 (C), 138.1 (C), 145.5 (C), 197.6 (C). HRMS-EI (*m/z*): [M] calcd for C₁₅H₁₄O, 210.1045; found, 210.1043.

1-[2',4'-Dimethyl-(1,1'-biphenyl)-4-yl]ethan-1-one (**14h**)

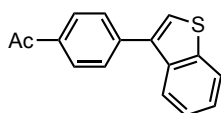


14h

The reaction was carried out for 24 h with **3** (1.1 mg, 1.25 μmol), 1-(4-bromophenyl)ethan-1-one (99.8 mg, 0.50 mmol), (2,4-dimethylphenyl)boronic acid (90.0 mg, 0.60 mmol) and K₃PO₄ (212.4 mg, 1.0 mmol). The product **14h** was obtained in 94% yield (105.7 mg, 0.47 mmol) as a colorless liquid by flash chromatography (SiO₂, hexane/CH₂Cl₂, 100:0 to 0:100).

¹H NMR (400 MHz, CDCl₃, δ): 2.25 (s, 3H), 2.38 (s, 3H), 2.65 (s, 3H), 7.06–7.15 (m, 3H), 7.42 (dt, *J* = 1.9, 8.3 Hz, 2H), 8.00 (dt, *J* = 2.0, 8.4 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃, δ): 20.2 (CH₃), 21.0 (CH₃), 26.5 (CH₃), 126.6 (CH), 128.1 (CH), 129.35 (CH), 129.39 (CH), 131.2 (CH), 134.8 (C), 135.2 (C), 137.5 (C), 137.7 (C), 146.8 (C), 197.7 (C). HRMS-EI (*m/z*): [M] calcd for C₁₆H₁₆O, 224.1201; found, 224.1201.

1-[4-(Benzo[*b*]thiophen-3-yl)phenyl]ethan-1-one (**14i**)

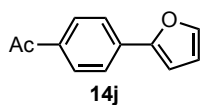


14i

The reaction was carried out for 24 h with **3** (1.1 mg, 1.25 μmol), 1-(4-bromophenyl)ethan-1-one (99.8 mg, 0.50 mmol), benzo[*b*]thiophene-3-boronic acid (106.7 mg, 0.60 mmol) and K₃PO₄ (212.3 mg, 1.0 mmol). The product **14i** was obtained in 98% yield (124.6 mg, 0.49 mmol) as a pale pink solid (m.p. = 92–93 °C) by flash chromatography (SiO₂, hexane/CH₂Cl₂, 90:10 to 0:100).

¹H NMR (400 MHz, CDCl₃, δ): 2.67 (s, 3H), 7.39–7.46 (m, 2H), 7.51 (s, 1H), 7.71 (dt, *J* = 1.9, 8.7 Hz, 2H), 7.89–7.97 (m, 2H), 8.09 (dt, *J* = 1.8, 8.4 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃, δ): 26.5 (CH₃), 122.5 (CH), 122.9 (CH), 124.49 (CH), 124.54 (CH), 124.7 (CH), 128.5 (CH), 128.7 (CH), 135.8 (C), 136.7 (C), 137.2 (C), 140.5 (C), 140.6 (C), 197.5 (C). HRMS-EI (*m/z*): [M] calcd for C₁₆H₁₂OS, 252.0609; found, 252.0602.

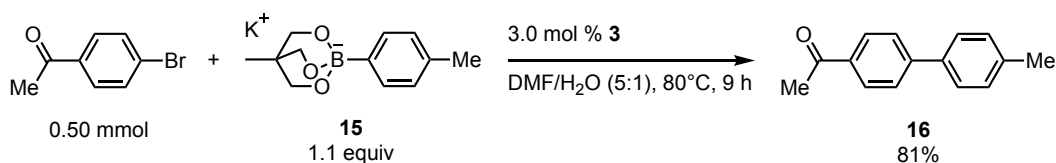
1-[4-(Furan-2-yl)phenyl]ethan-1-one (**14j**)



The reaction was carried out for 24 h at 40 °C with **3** (12.9 mg, 0.015 mmol), 1-(4-bromophenyl)ethan-1-one (99.2 mg, 0.50 mmol), 2-furylboronic acid (67.1 mg, 0.60 mmol) and K₃PO₄ (212.0 mg, 1.0 mmol). The product **14j** was obtained in 79% yield (73.5 mg, 0.39 mmol) as a white solid (m.p. = 104–105 °C) by flash chromatography (SiO₂, hexane/ CH₂Cl₂, 90:10 to 0:100).

¹H NMR (400 MHz, CDCl₃, δ): 2.62 (s, 3H), 6.52 (q, *J* = 1.7 Hz, 1H), 6.81 (dd, *J* = 0.8, 3.6 Hz, 1H), 7.54 (dd, *J* = 0.8, 2.0 Hz, 1H), 7.75 (dt, *J* = 1.9, 8.7 Hz, 2H), 7.98 (dt, *J* = 1.8, 8.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃, δ): 26.4 (CH₃), 107.4 (CH), 112.0 (CH), 123.4 (CH), 128.8 (CH), 134.7 (C), 135.3 (C), 143.2 (CH), 152.7 (C), 197.2 (C). HRMS-EI (*m/z*): [*M*] calcd for C₁₂H₁₀O₂, 186.0681; found, 186.0675.

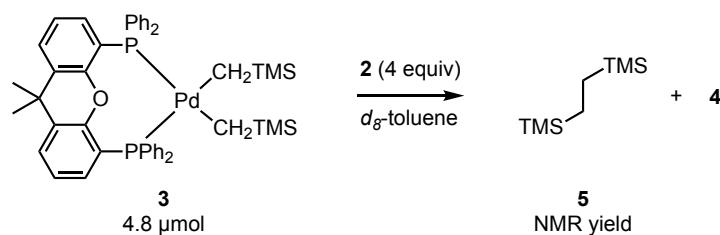
Base-Free Suzuki-Miyaura Cross-Coupling



3 (13.0 mg, 0.015 mmol), 1-(4-bromophenyl)ethan-1-one (99.6 mg, 0.50 mmol) and **15** (142.0 mg, 0.55 mmol) were placed in an oven-dried reaction vial. After being sealed with a screw cap containing a Teflon-coated rubber septum, the vial was connected to a nitrogen line through a needle. DMF (1.25 mL) and water (0.25 mL) were added, then the reaction mixture was heated to 80 °C for 9 hours. After cooling to room temperature, the reaction mixture was extracted three times with EtOAc, washed with brine and dried over MgSO₄. The crude mixture was purified by flash column chromatography (SiO₂, EtOAc/hexane, 0:100–6:94). The product **16** was obtained in 81% yield (85.7 mg, 0.41 mmol) as a white solid (m.p. = 122–123 °C).

¹H NMR (392 MHz, CDCl₃, δ): 2.41 (s, 3H), 2.64 (s, 3H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.54 (dt, *J* = 2.0, 8.4 Hz, 2H), 7.68 (dt, *J* = 1.9, 8.7 Hz, 2H), 8.02 (dt, *J* = 1.9, 8.4 Hz, 2H). ¹³C NMR (99 MHz, CDCl₃, δ): 21.1 (CH₃), 26.5 (CH₃), 126.8 (CH), 127.0 (CH), 128.8 (CH), 129.6 (CH), 135.4 (C), 136.8 (C), 138.1 (C), 145.5 (C), 197.6 (C). HRMS-EI (*m/z*): [*M*] calcd for C₁₅H₁₄O, 210.1045; found, 210.1037.

5. Monitoring the Progress of the Reductive Elimination from **3**.



2 (11.0 mg, 19 μmol), **3** (4.1 mg, 4.8 μmol) and 1,2-diphenylethane (3.0 mg) as an internal standard were placed in the NMR test tube, then d_8 -toluene was added. The mixture was heated to 40, 60 or 80 $^{\circ}\text{C}$ and the yield of **5** was determined by ^1H NMR analysis.

Supplementary Table 3. Monitoring the reductive elimination at different reaction temperatures.

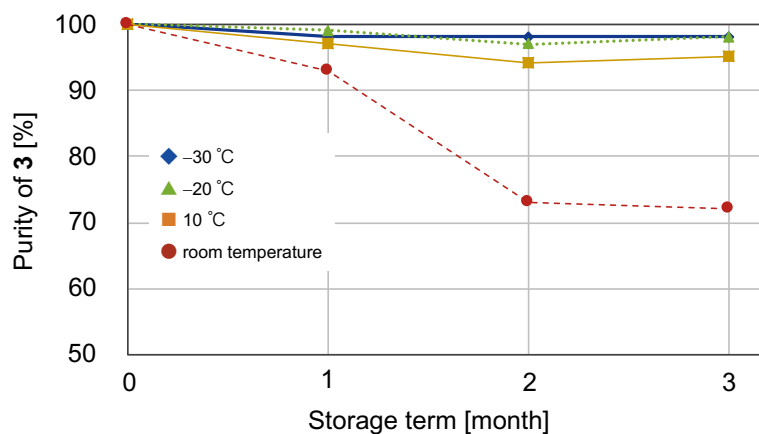
Temperature	NMR yield of 5 (%)					
	10 min	20 min	30 min	40 min	50 min	60 min
40 $^{\circ}\text{C}$	9	14	18	22	28	32
60 $^{\circ}\text{C}$	47	71	81	88	91	94
80 $^{\circ}\text{C}$	98	102	-	-	-	-

6. Stability of **3** for the Long-Term Storage.

3 in the nitrogen purged vials were stored at room temperature (desiccator), 10 °C (refrigerator), –20 °C and –30 °C (freezer) respectively. The purity of them were determined by ¹H NMR analysis using dibromomethane as an internal standard.

Supplementary Table 4. Purity of **3 for three months from the synthesis.**

Storage conditions	Purity of 3 (%)		
	1 month	2 months	3 months
–30 °C	98	98	98
–20 °C	99	97	98
10 °C	97	94	95
room temperature	93	73	72



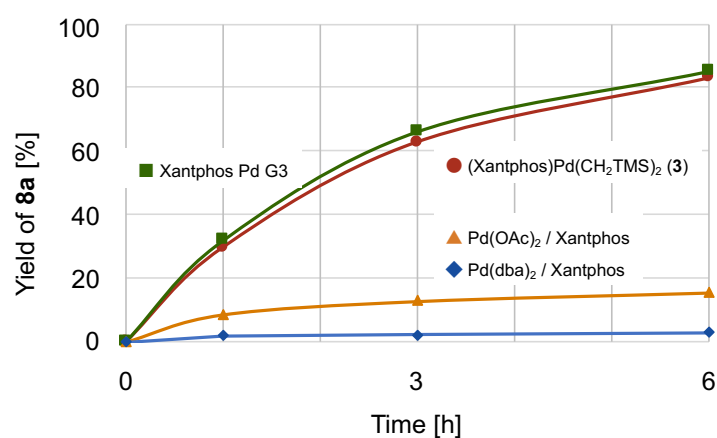
Supplementary Figure 4. Monitoring the purity of **3 depending on the storage temperature.**

7. Comparison of the Catalytic Performance of **3** with Those of Other Catalyst Precursors.

Supplementary Table 5. Results of C–N coupling with various catalyst precursors.

<chem>Cc1ccccc1Br</chem> + <chem>Nc1ccccc1=O</chem> 0.50 mmol 1.2 equiv				$\xrightarrow[\text{Cs}_2\text{CO}_3, \text{ dioxane, } 100^\circ\text{C}]{4.0 \text{ mol \% Pd/Xantphos}}$	<chem>Cc1ccccc1NC(=O)c2ccccc2</chem> 8a GC yield
Precursor	GC yield of 8a (%) ^a				
	1 h	3 h	6 h		
3	30	63	83		
Xantphos Pd G3	32	66	85		
Pd(OAc) ₂ / Xantphos	9	13	16		
Pd(dba) ₂ / Xantphos	4	6	5		

^aDetermined by GC analysis using 4,4'-di-tert-butyl-1,1'-biphenyl as an internal standard.

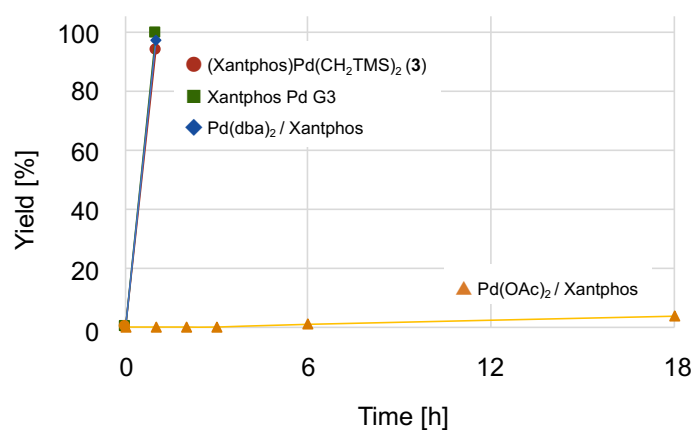


Supplementary Figure 5. Comparison of the catalytic performance of **3 with those of other catalyst precursors in C–N coupling.**

Supplementary Table 6. Results of C–N coupling with various catalyst precursors.

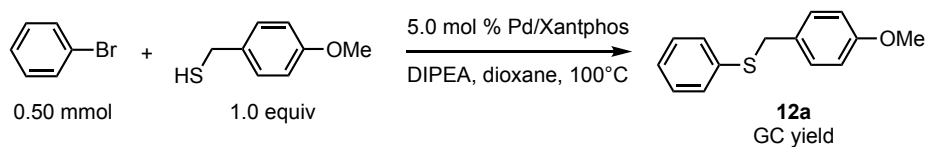
Precursor	GC yield of 10a (%) ^a			
	1 h	3 h	6 h	18 h
3	94	-	-	-
Xantphos Pd G3	99	-	-	-
Pd(OAc) ₂ / Xantphos	0	0	1	4
Pd(dba) ₂ / Xantphos	97		-	-

^aDetermined by GC analysis using 1,4-di-*tert*-butylbenzene as an internal standard.



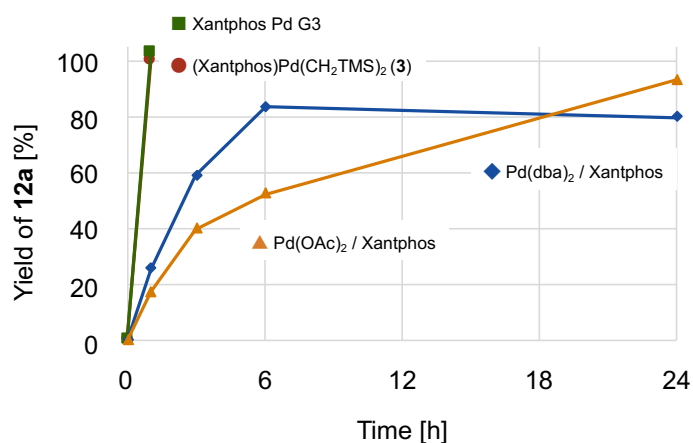
Supplementary Figure 6. Comparison of the catalytic performance of **3 with those of other catalyst precursors in C–N coupling.**

Supplementary Table 7. Result of C-S coupling of with various catalyst precursors.



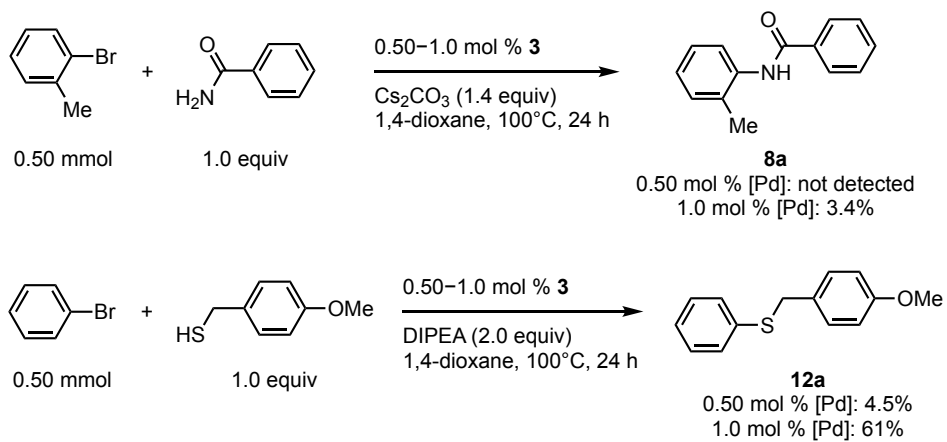
Precursor	GC yield of 12a (%) ^a			
	1 h	3 h	6 h	24 h
3	100	-	-	-
Xantphos Pd G3	103	-	-	-
Pd(OAc) ₂ / Xantphos	17	40	52	93
Pd(dba) ₂ / Xantphos	26	59	84	80

^aDetermined by GC analysis using 4,4'-di-tert-butyl-1,1'-biphenyl as an internal standard.



Supplementary Figure 7. Comparison of the catalytic performance of 3 with those of other catalyst precursors in C-S coupling.

8. Investigation of C-Heteroatom Cross-coupling Reaction with Low Catalyst Loading^a.

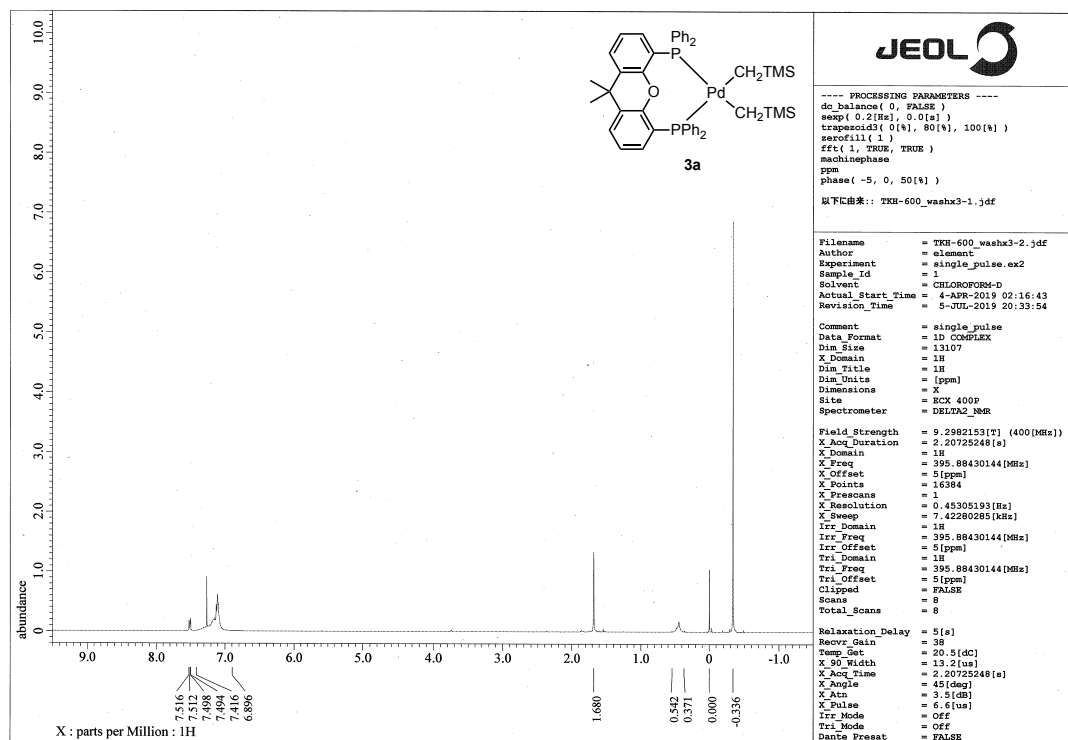


^aYields were determined by ¹H NMR analysis using dibromomethane as an internal standard.

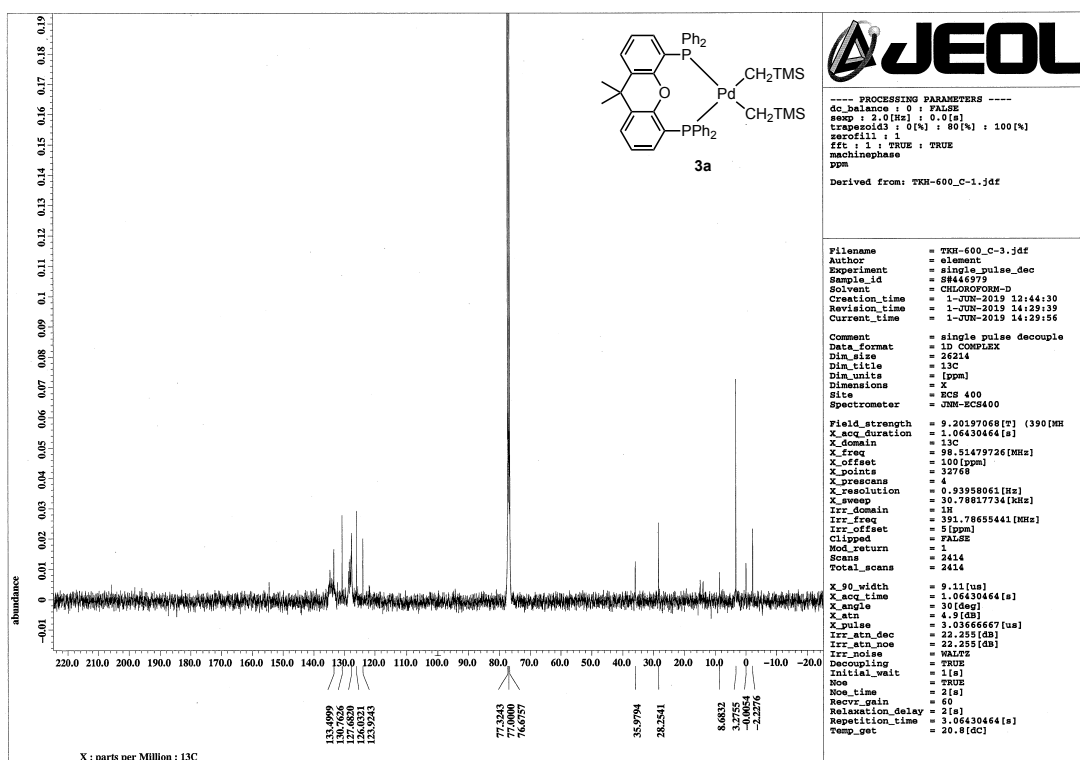
9. References

- 1) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.
- 2) Kubota, K.; Dai, P.; Pentelute, B. L.; Buchwald, S. L. *J. Am. Chem. Soc.* **2018**, *140*, 3128–3133.
- 3) Andersen, T. L.; Kramer, S.; Overgaard, J.; Skrydstrup, T. *Organometallics* **2017**, *36*, 2058–2066.

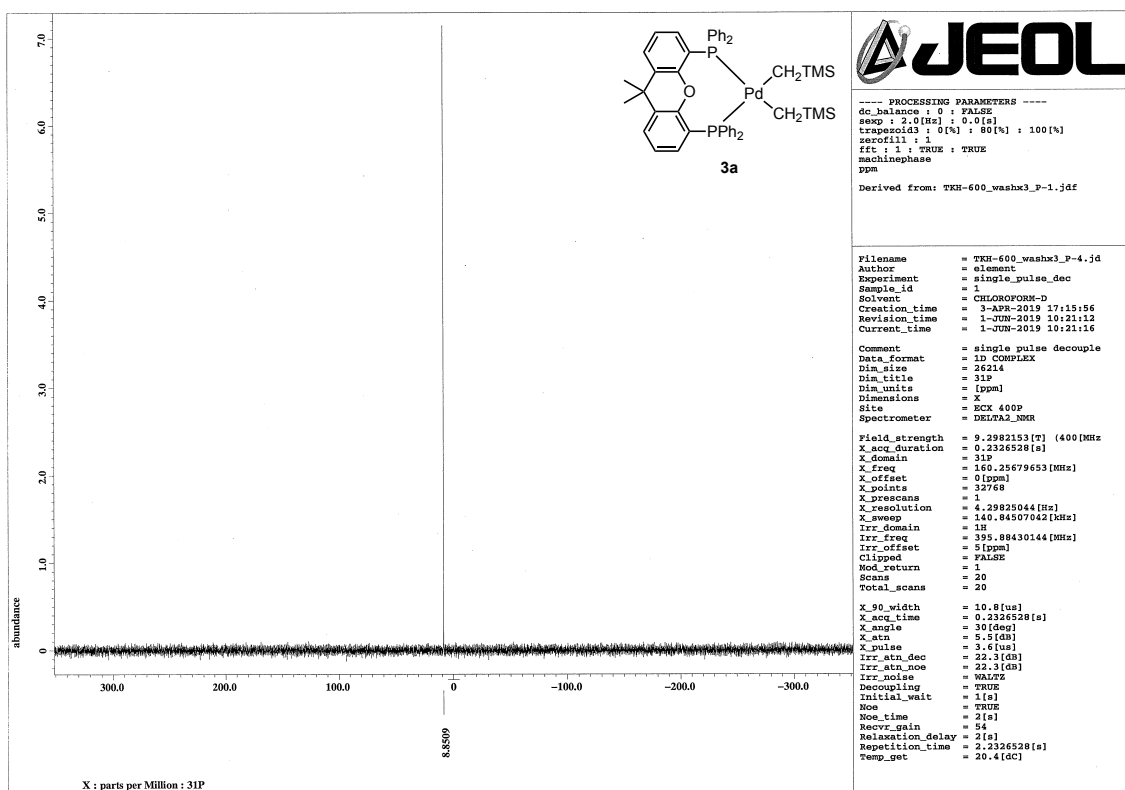
10. NMR Spectra



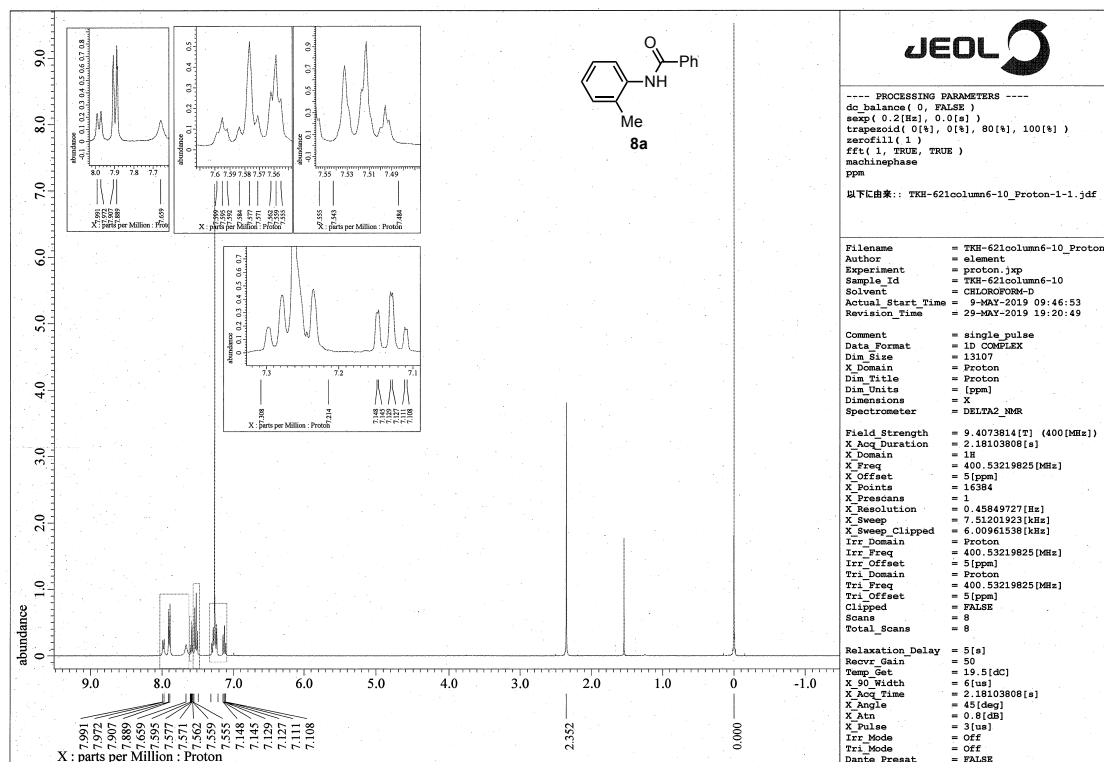
Supplementary Figure 8. ¹H NMR spectrum of 3a.



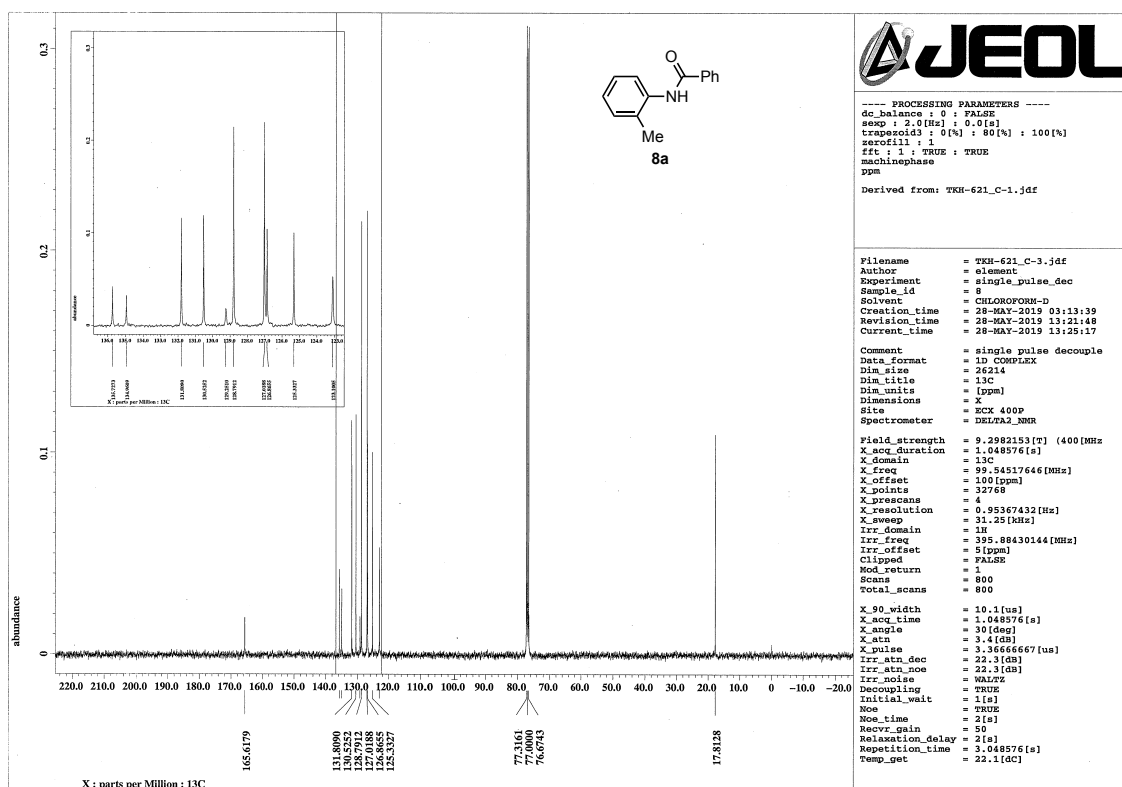
Supplementary Figure 9. ¹³C NMR spectrum of 3a.



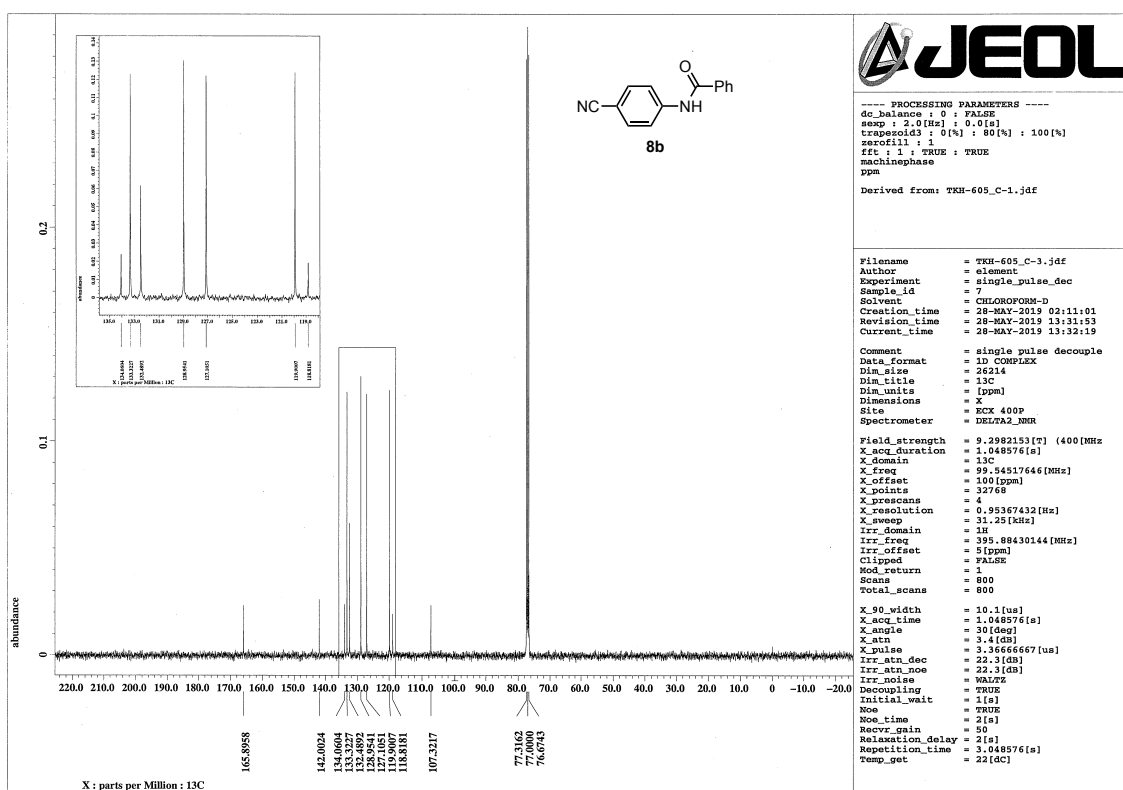
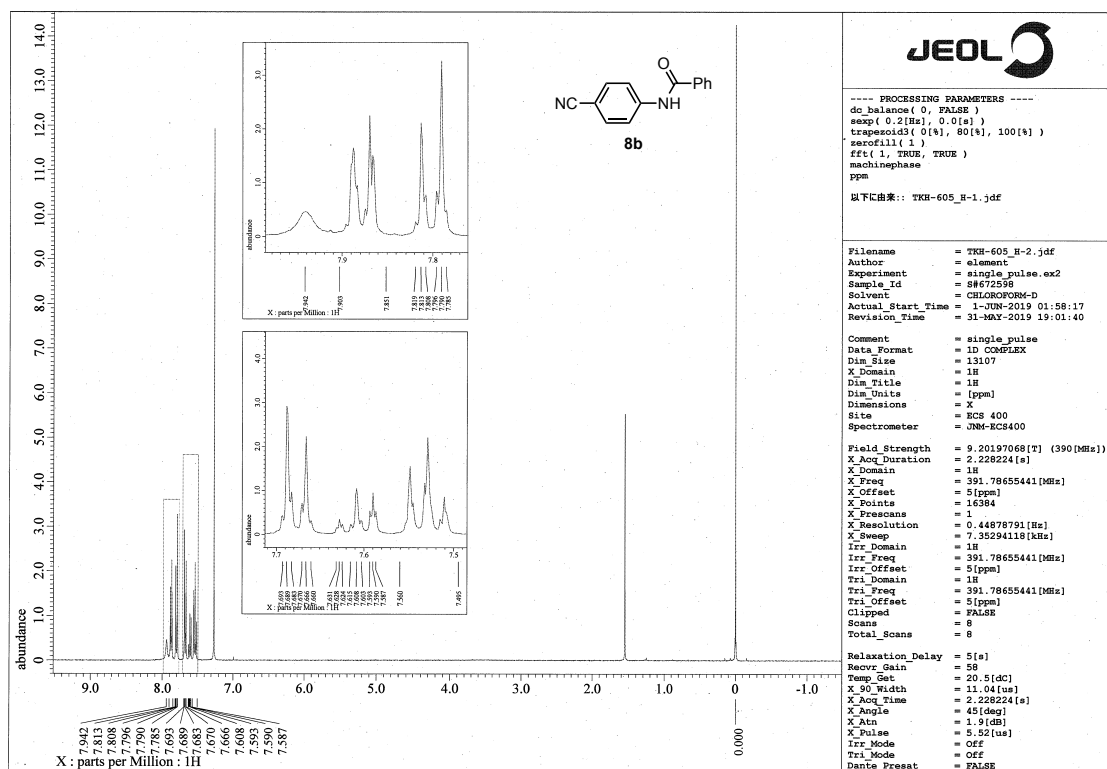
Supplementary Figure 10. ³¹P NMR spectrum of 3a.

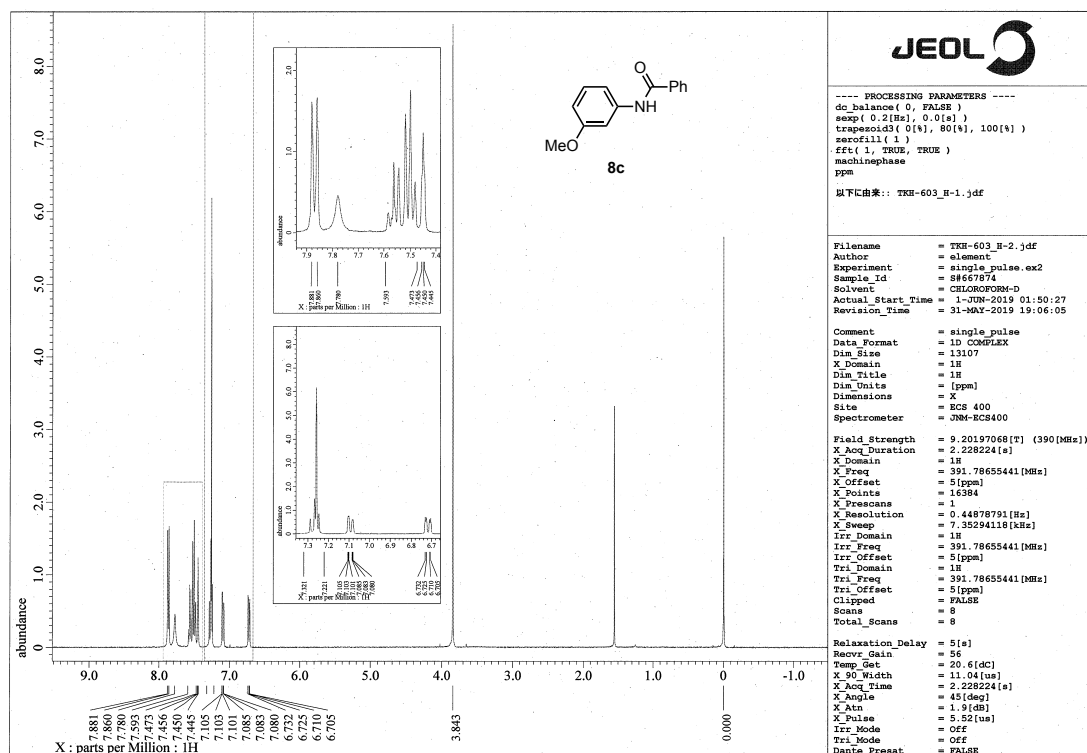


Supplementary Figure 11. ¹H NMR spectrum of 8a.

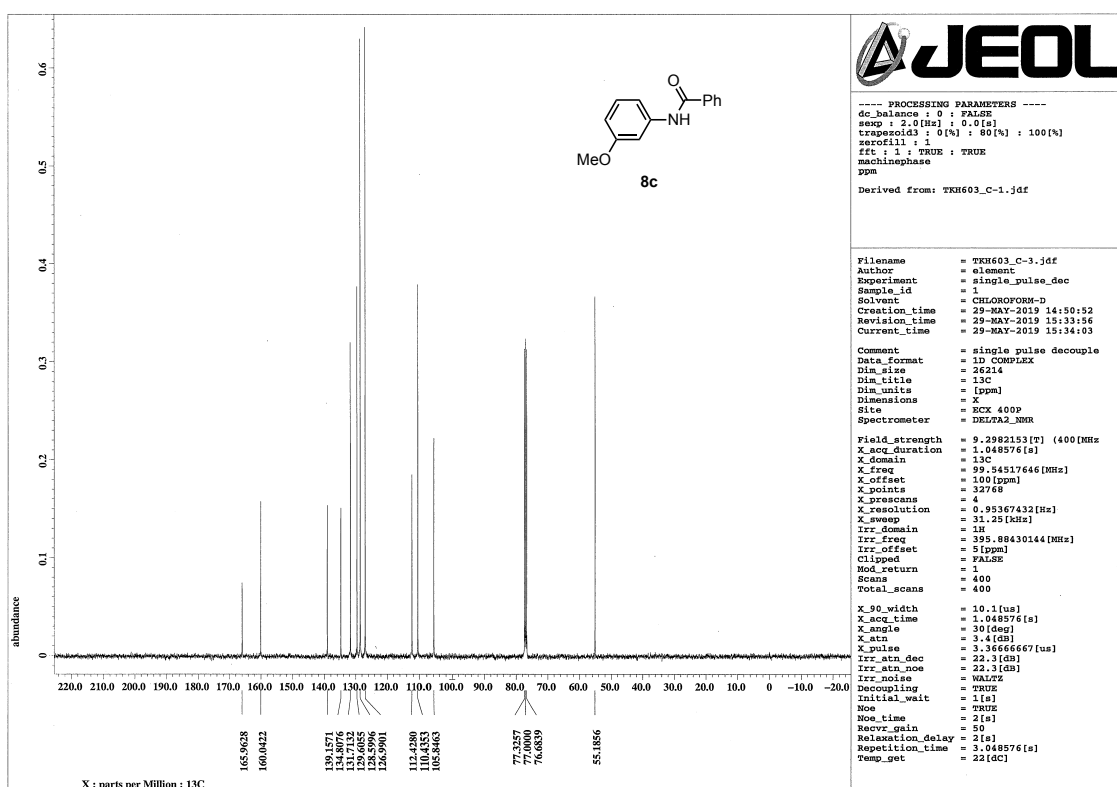


Supplementary Figure 12. ¹³C NMR spectrum of 8a.

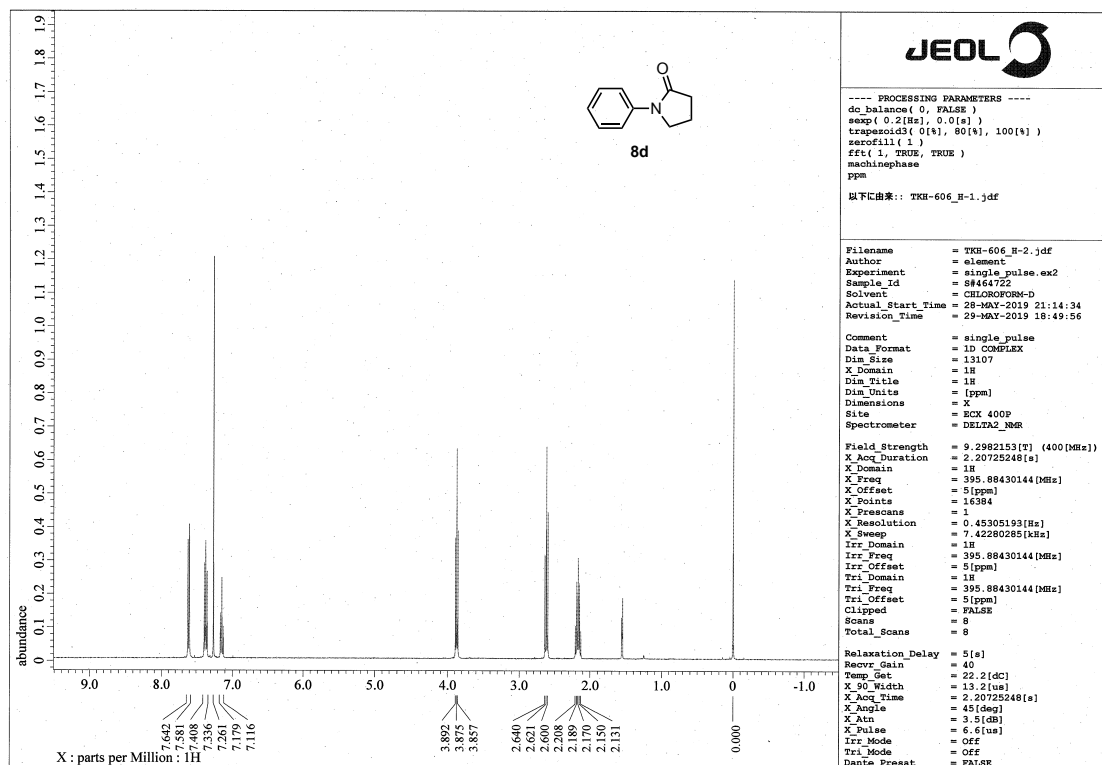




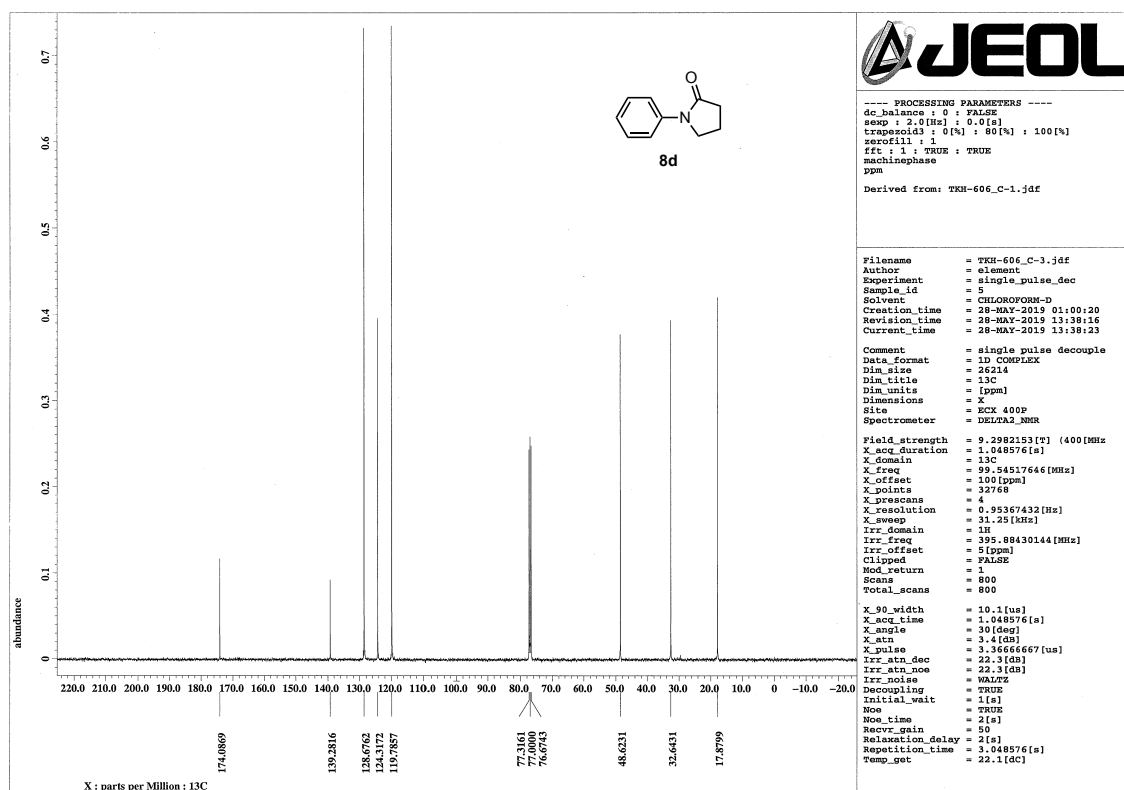
Supplementary Figure 15. ¹H NMR spectrum of 8c.



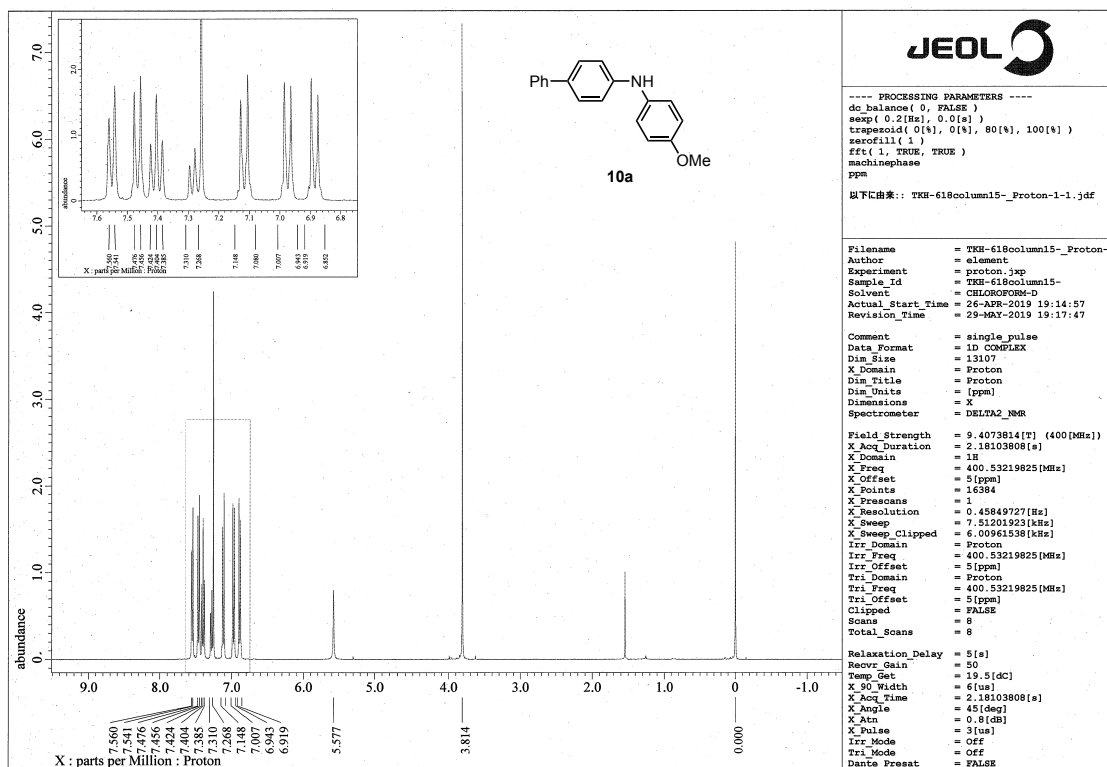
Supplementary Figure 16. ¹³C NMR spectrum of 8c.



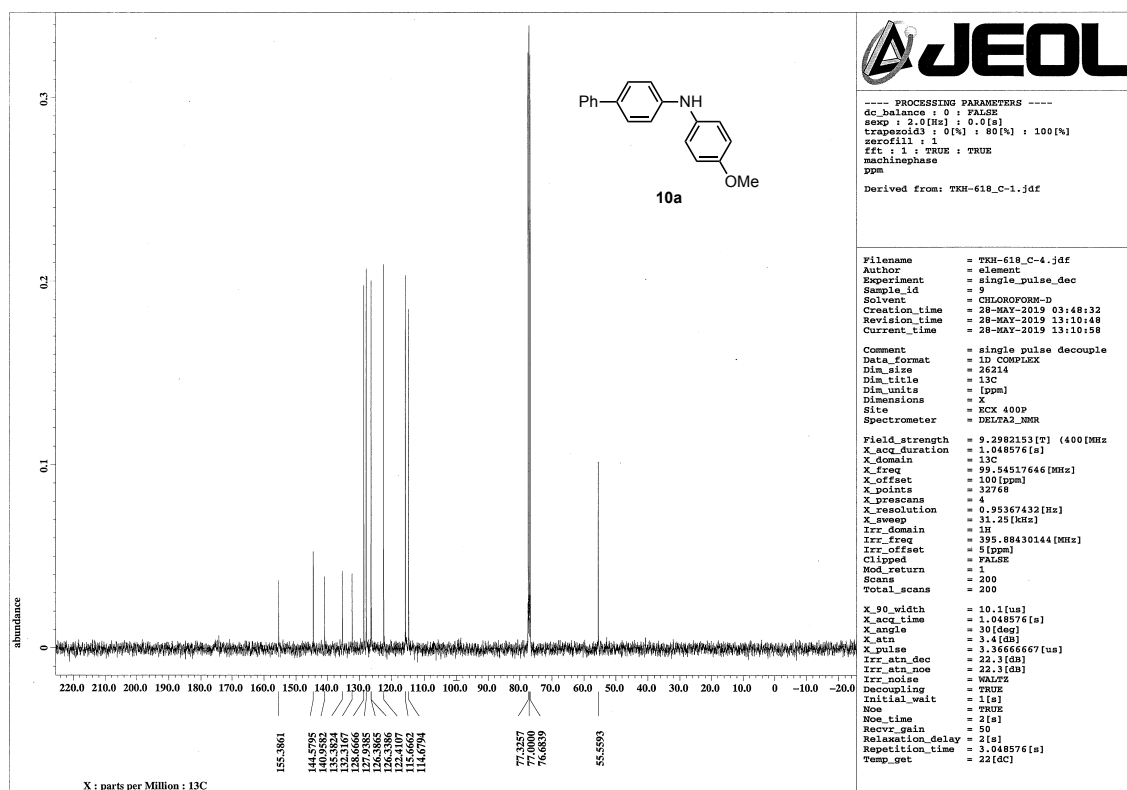
Supplementary Figure 17. ^1H NMR spectrum of 8d.



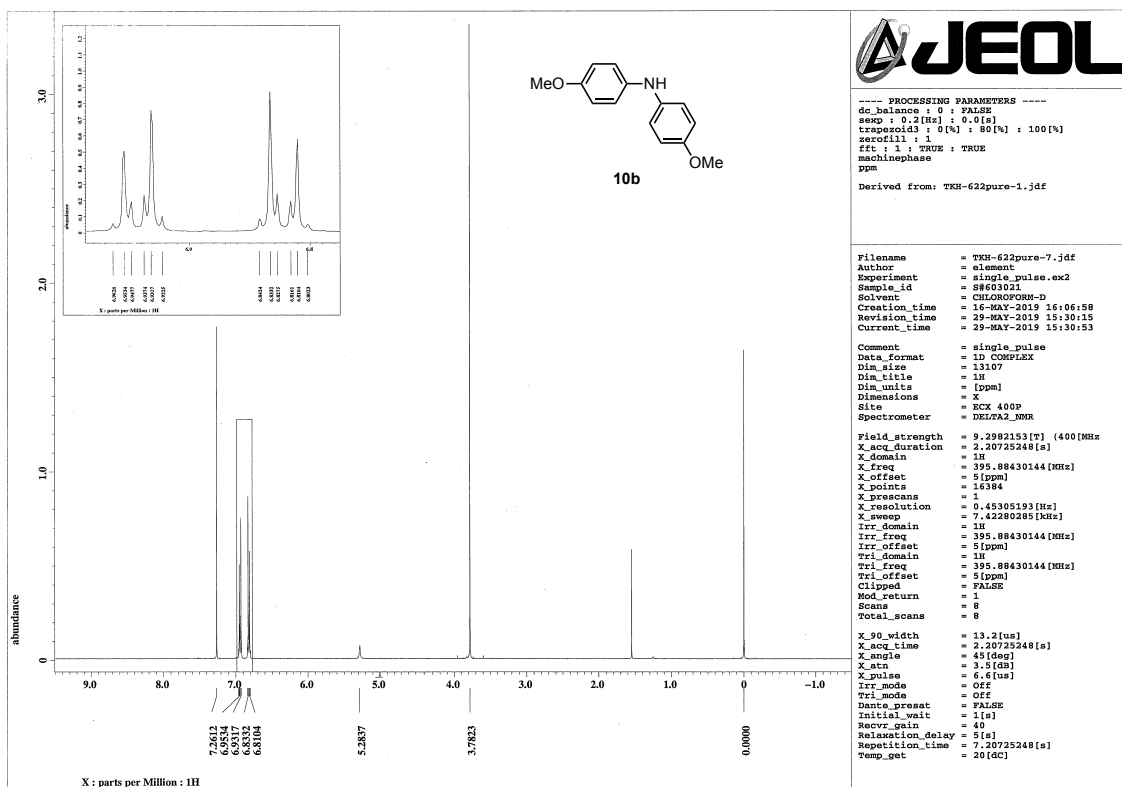
Supplementary Figure 18. ^{13}C NMR spectrum of 8d.



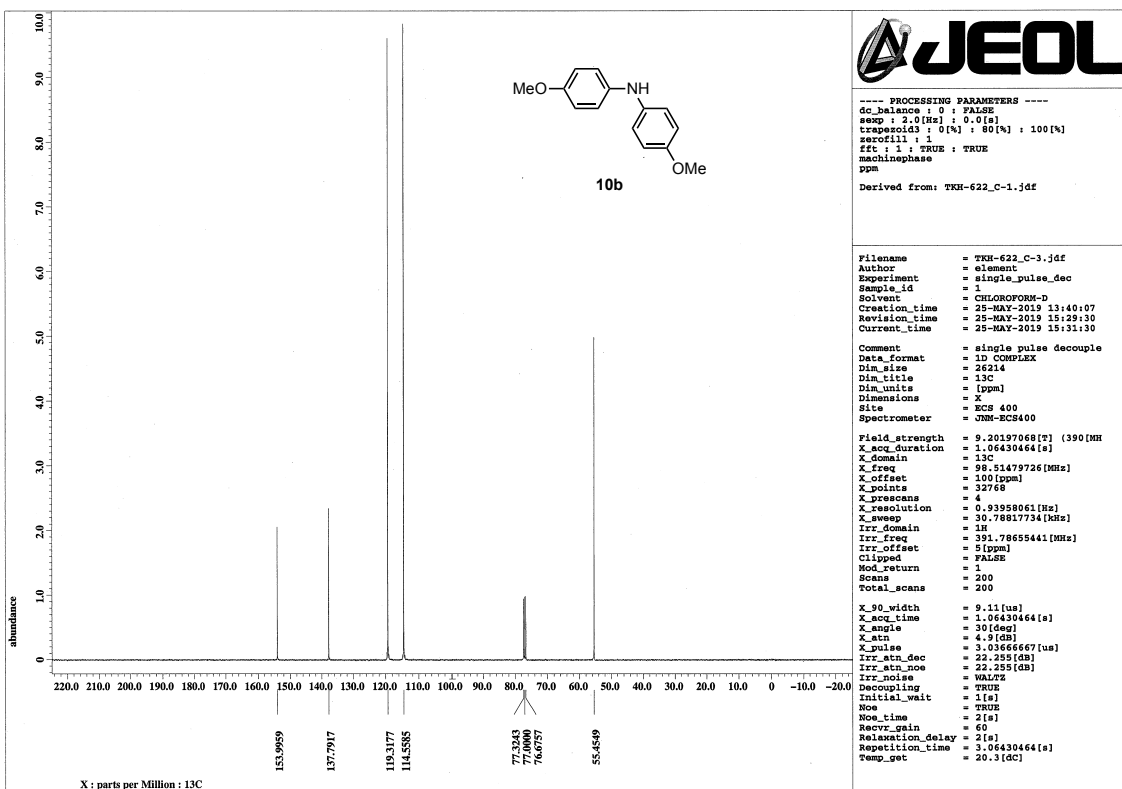
Supplementary Figure 19. ^1H NMR spectrum of 10a.



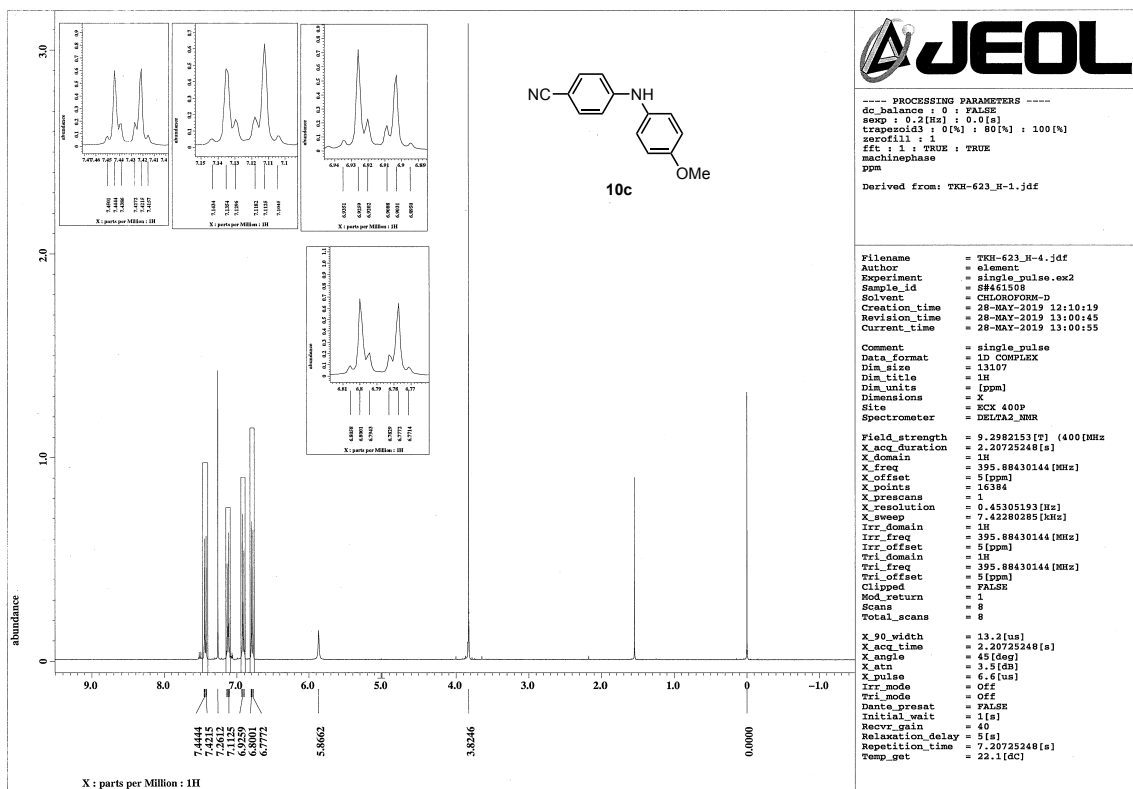
Supplementary Figure 20. ^{13}C NMR spectrum of 10a.



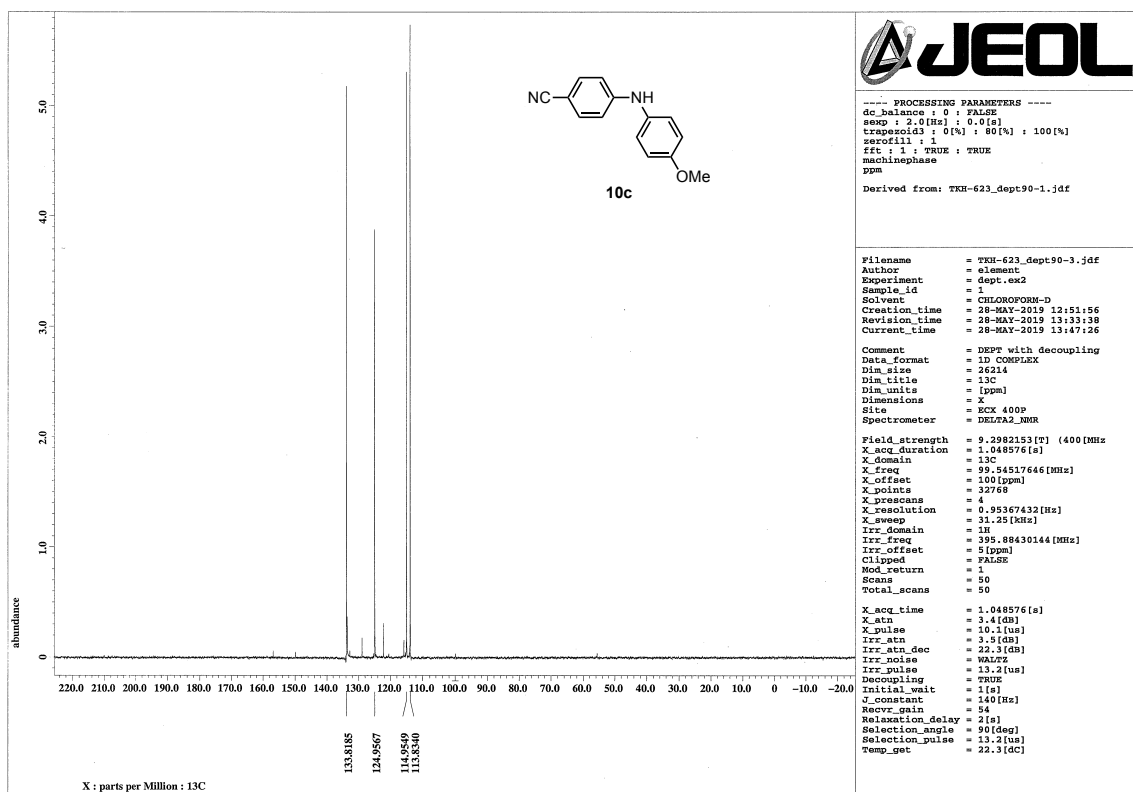
Supplementary Figure 21. ¹H NMR spectrum of 10b.



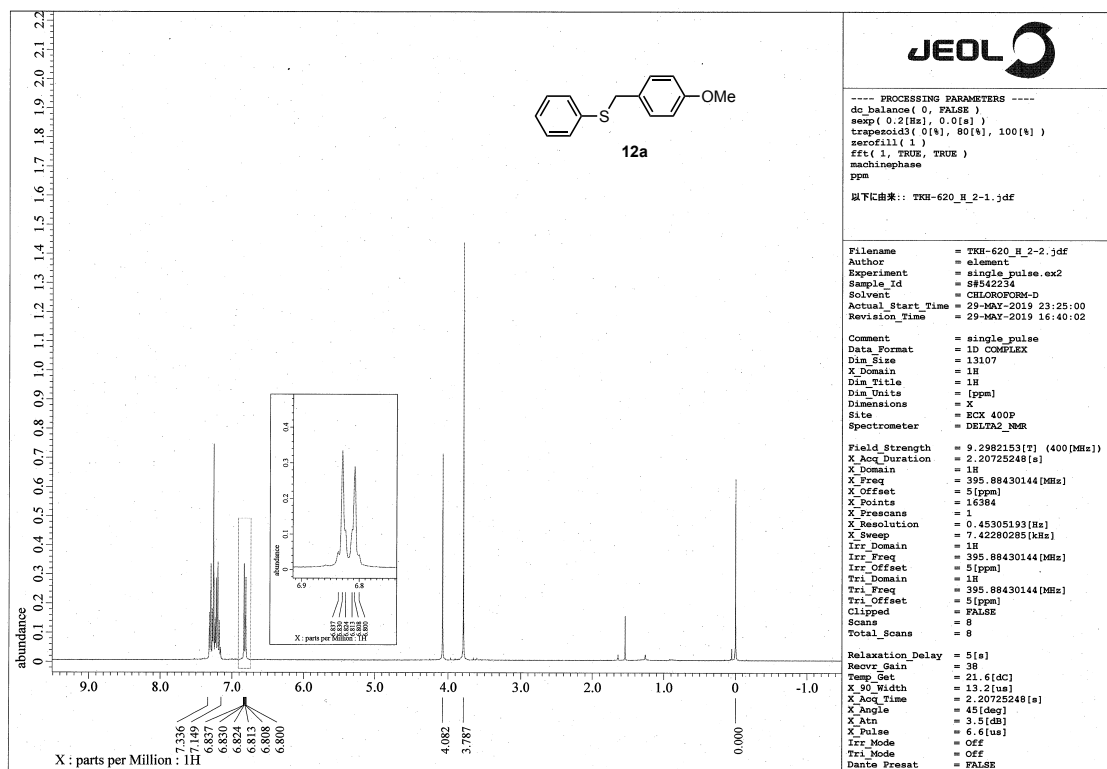
Supplementary Figure 22. ¹³C NMR spectrum of 10b.



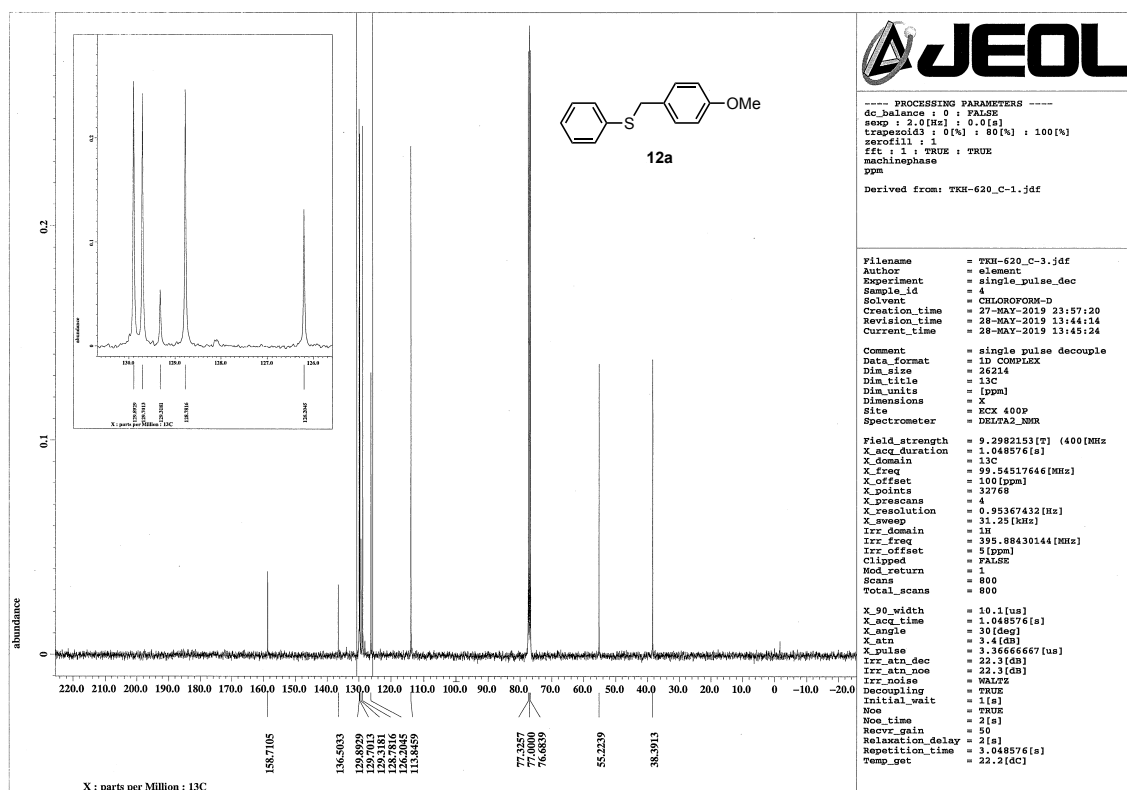
Supplementary Figure 23. ¹H NMR spectrum of 10c.



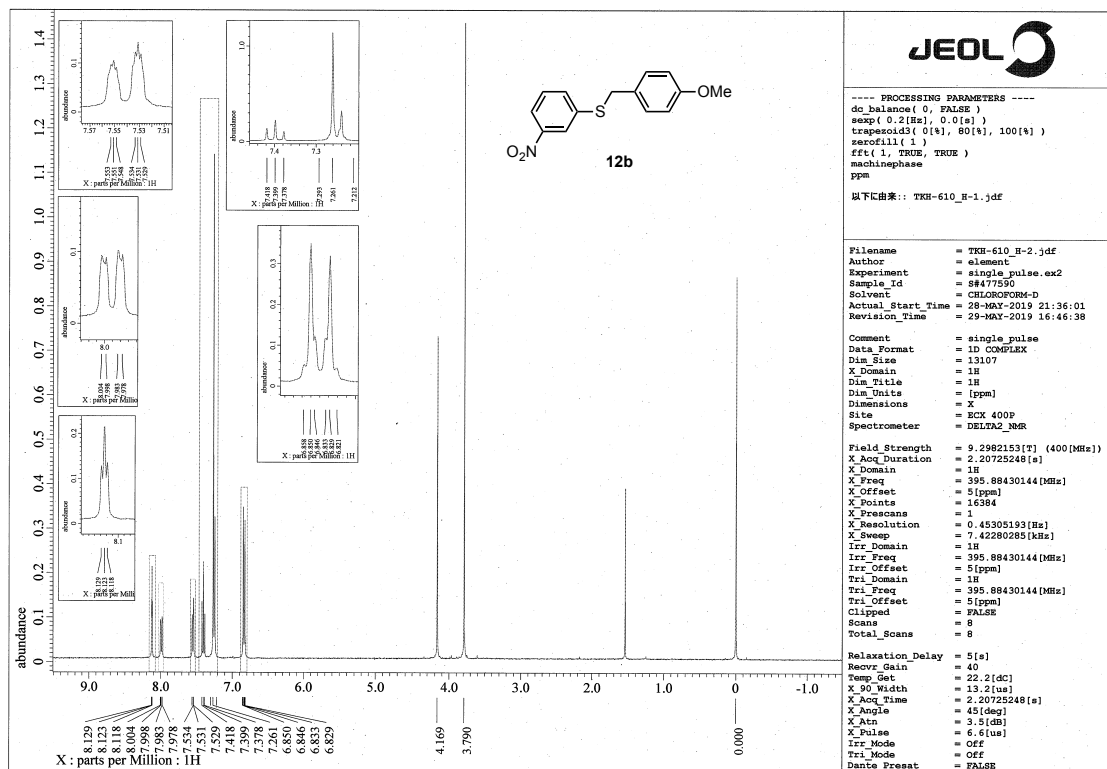
Supplementary Figure 24. ¹³C NMR spectrum of 10c.



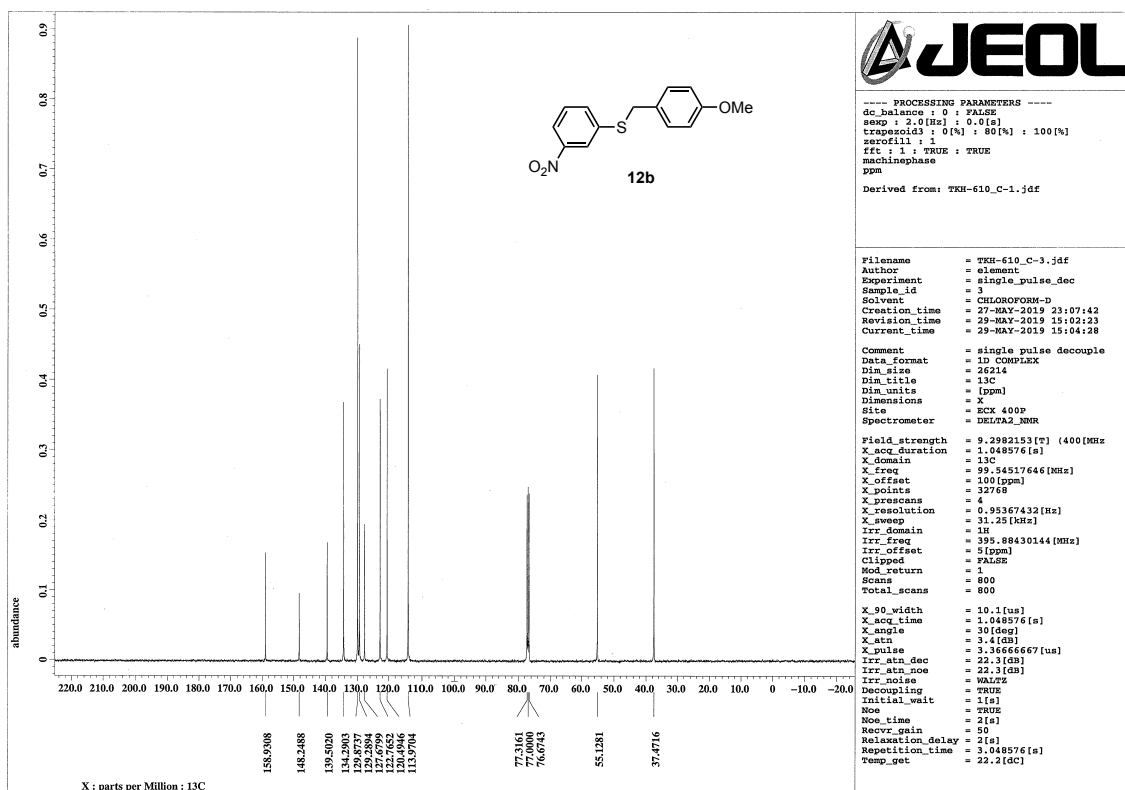
Supplementary Figure 25. ¹H NMR spectrum of 12a.



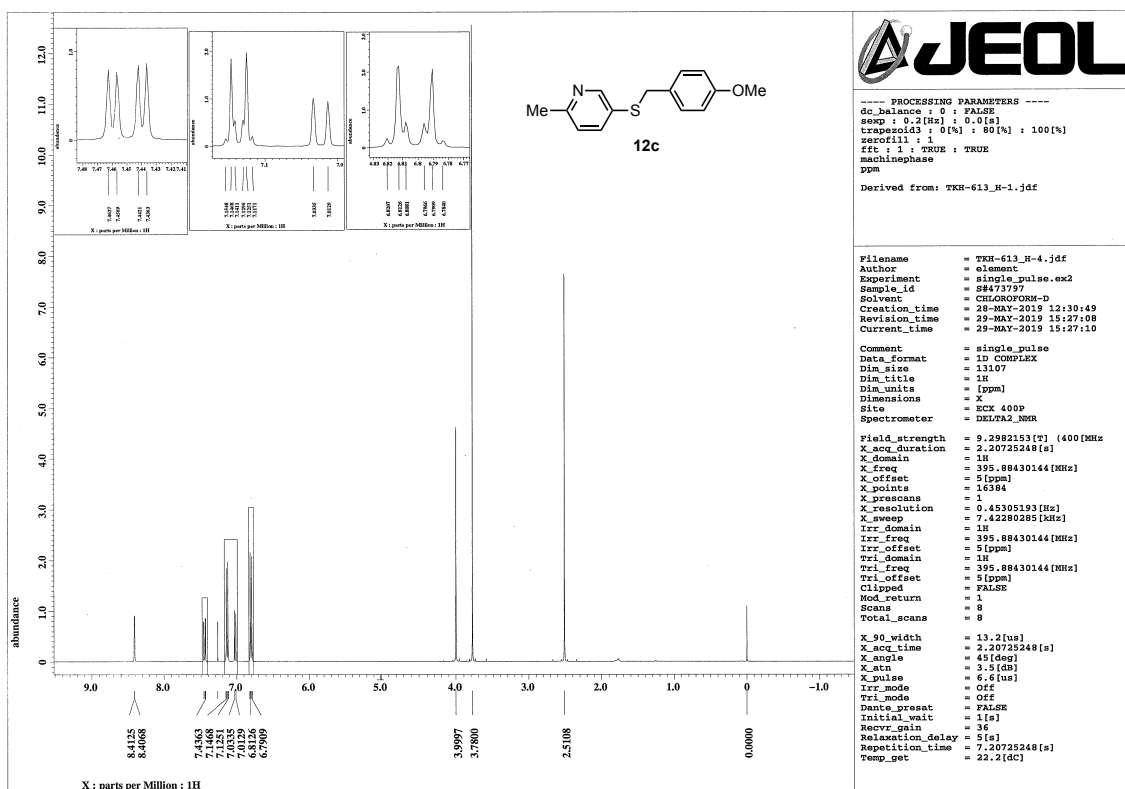
Supplementary Figure 26. ¹³C NMR spectrum of 12a.



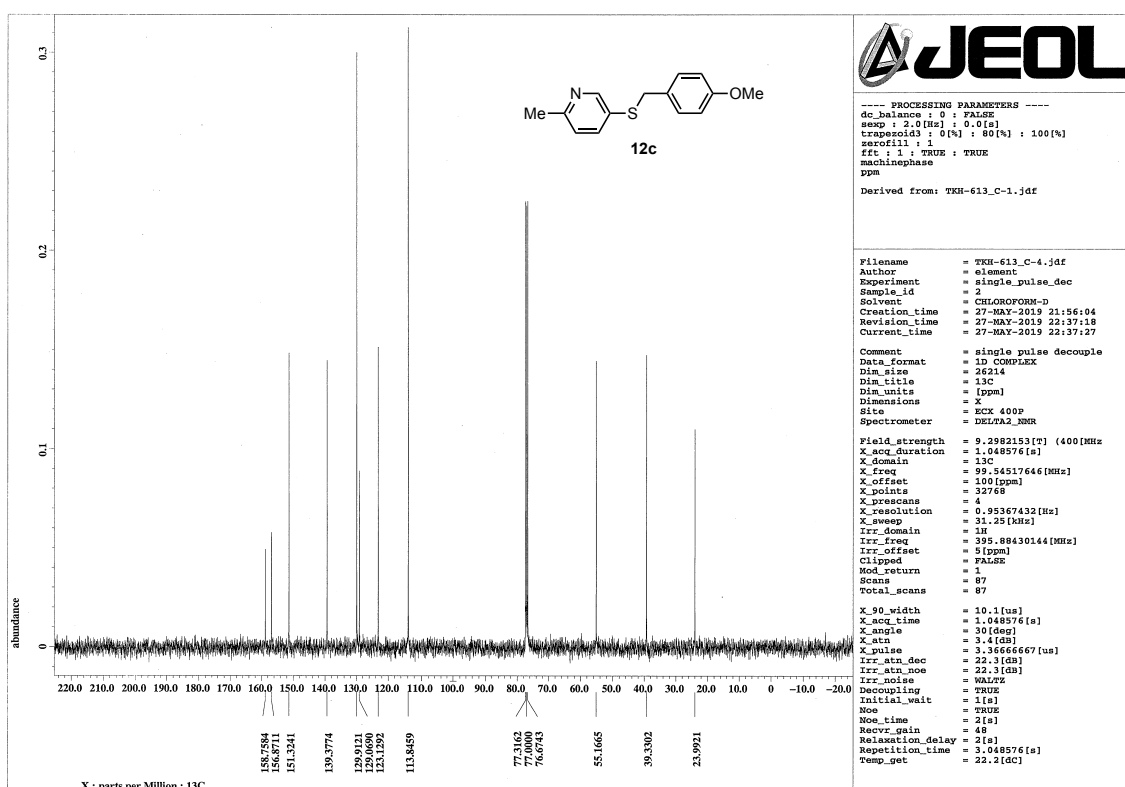
Supplementary Figure 27. ¹H NMR spectrum of 12b.



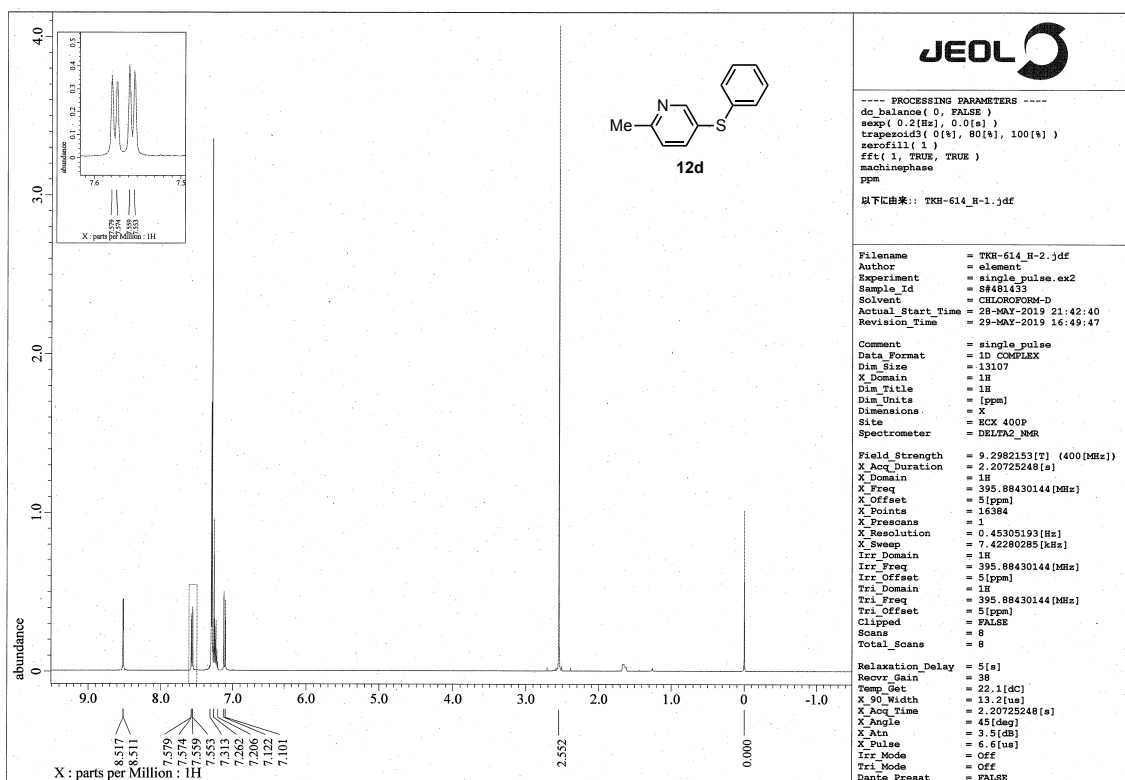
Supplementary Figure 28. ¹³C NMR spectrum of 12b.



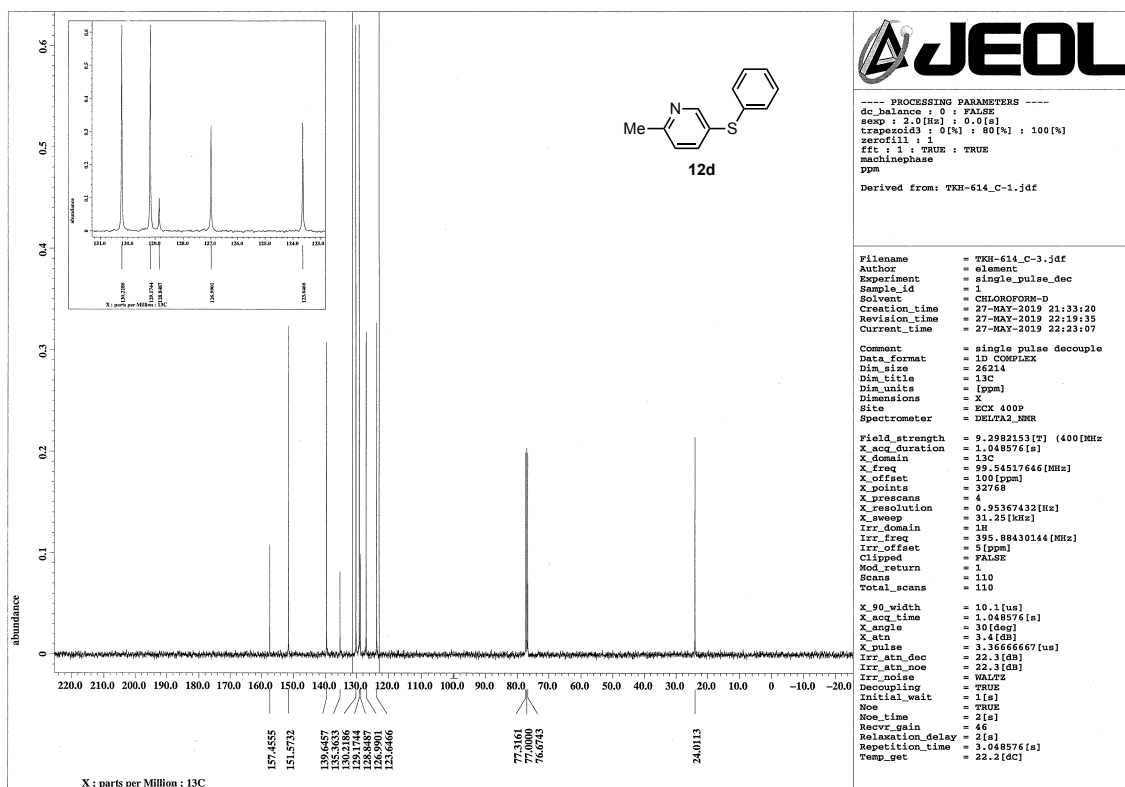
Supplementary Figure 29. ¹H NMR spectrum of 12c.



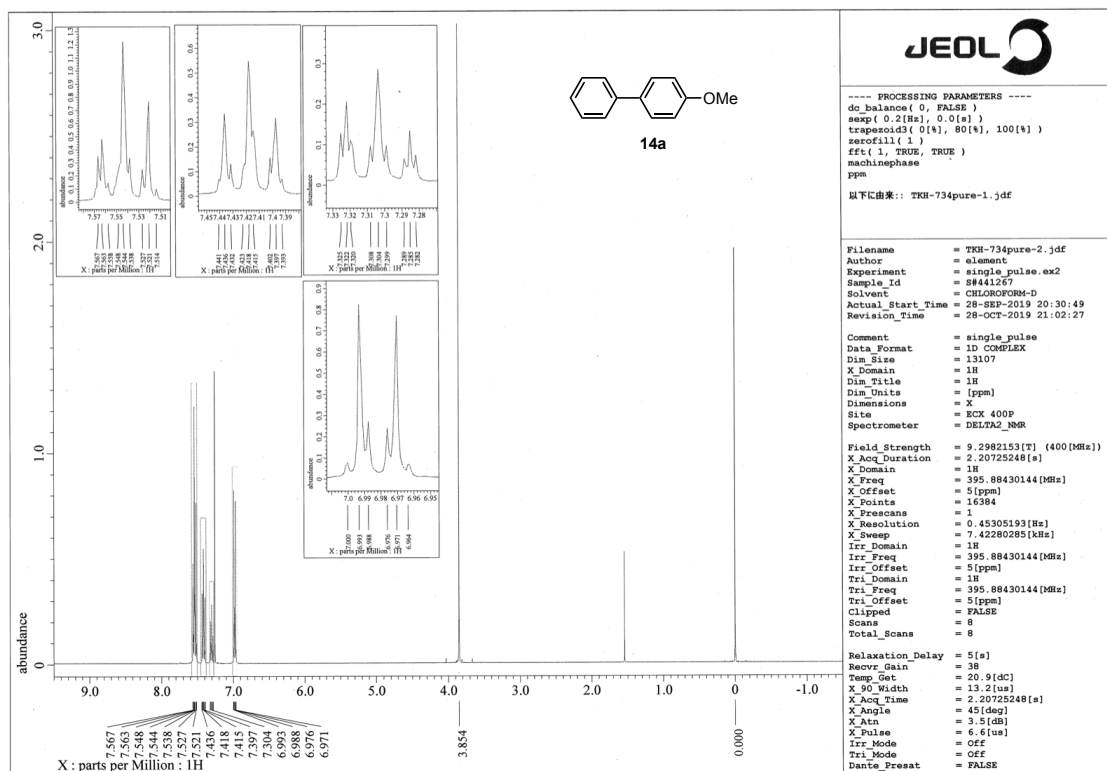
Supplementary Figure 30. ¹³C NMR spectrum of 12c.



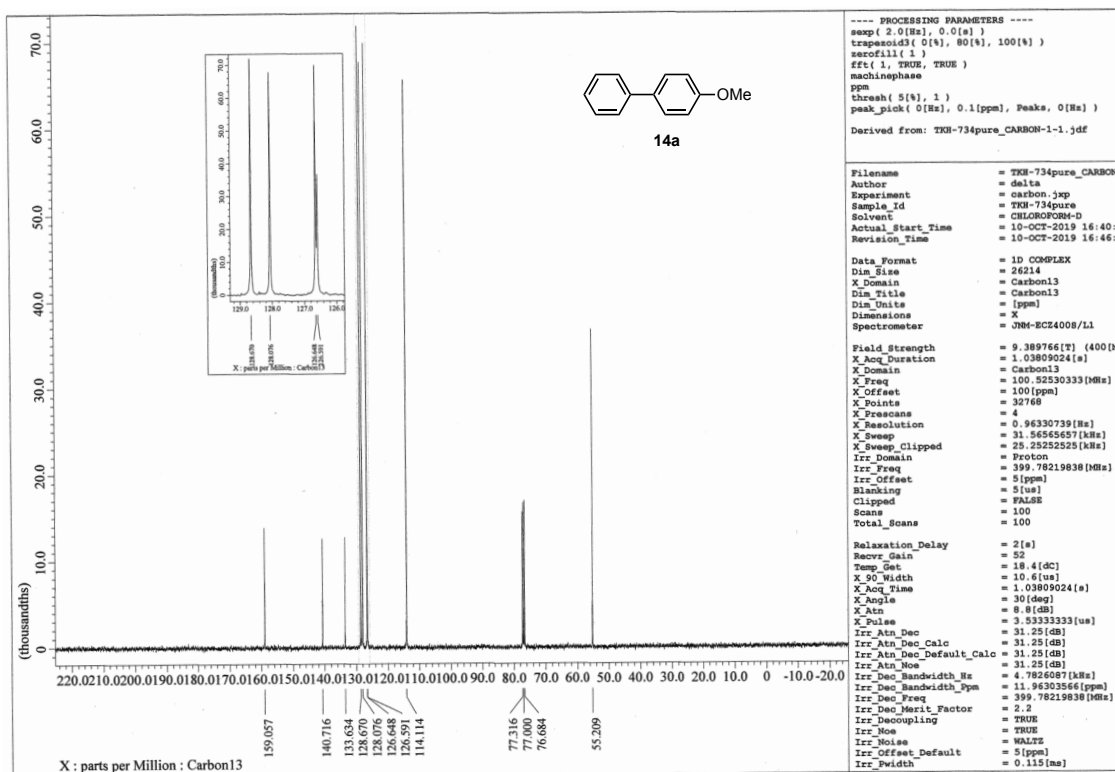
Supplementary Figure 31. ¹H NMR spectrum of 12d.



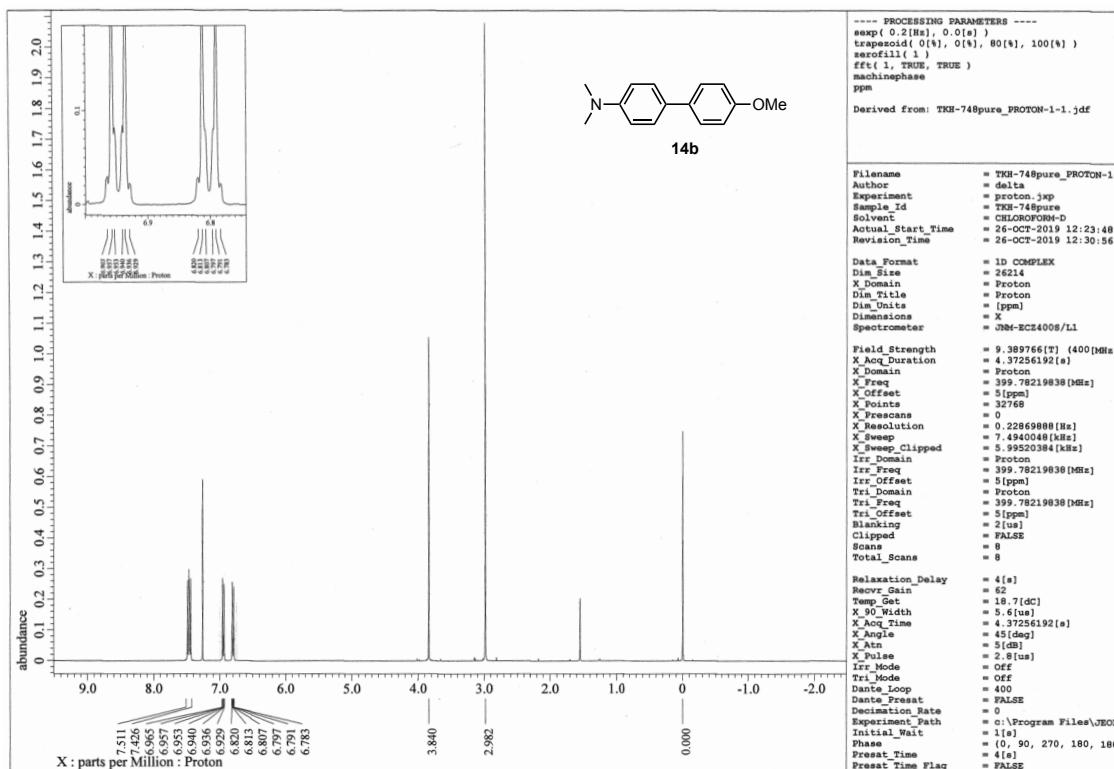
Supplementary Figure 32. ¹³C NMR spectrum of 12d.



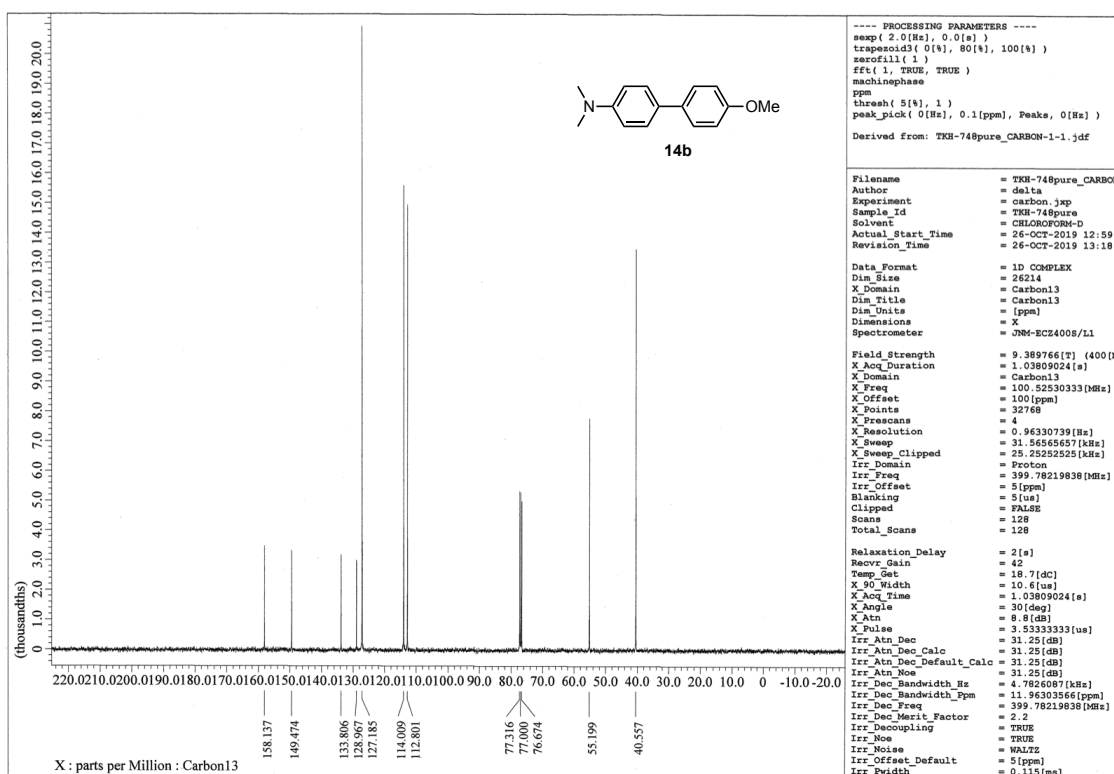
Supplementary Figure 33. ¹H NMR spectrum of 14a.



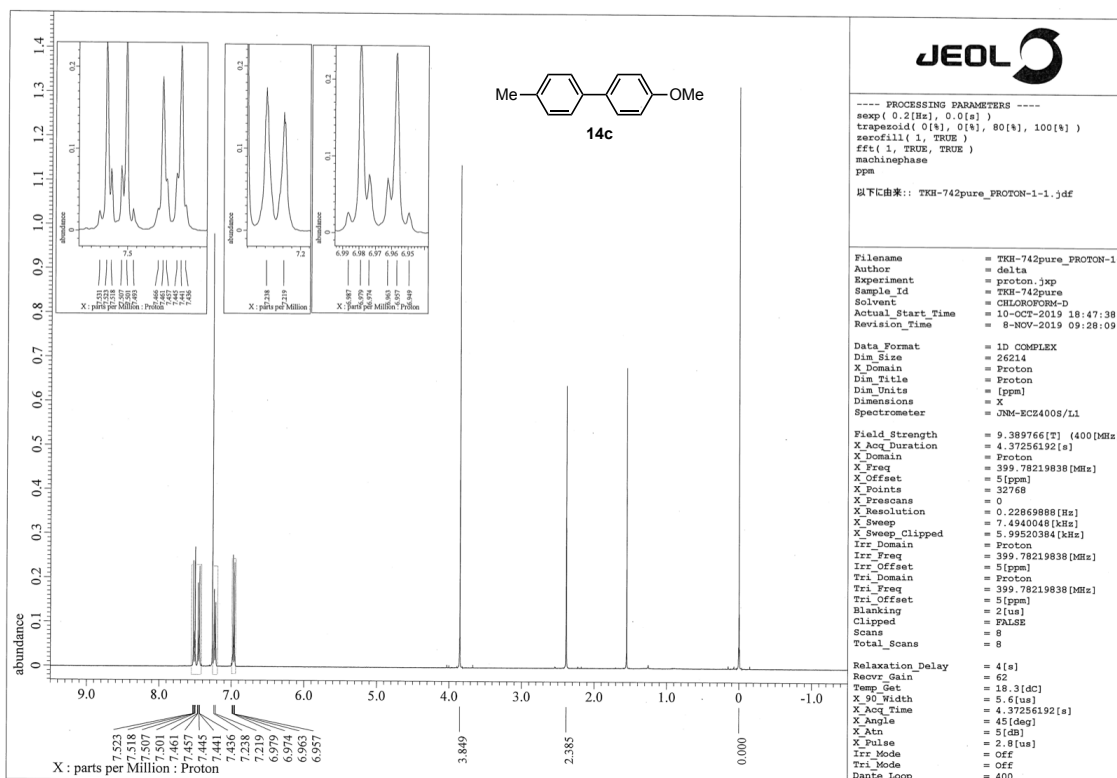
Supplementary Figure 34. ¹³C NMR spectrum of 14a.



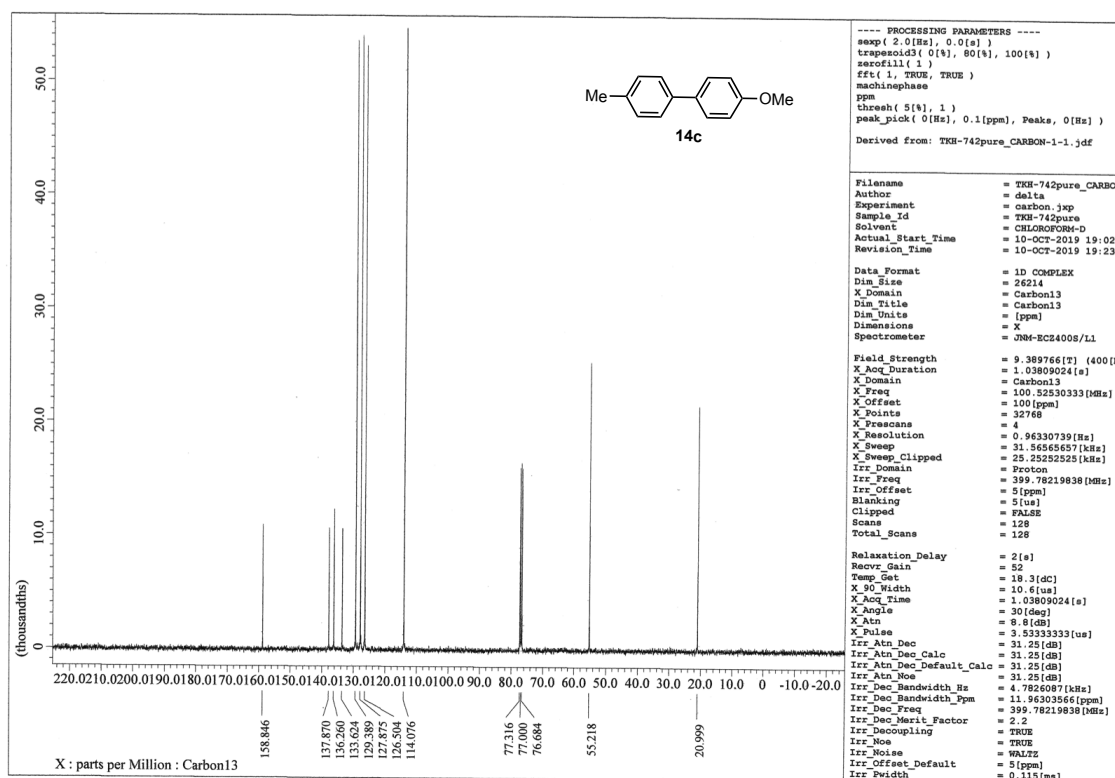
Supplementary Figure 35. ¹H NMR spectrum of 14b.



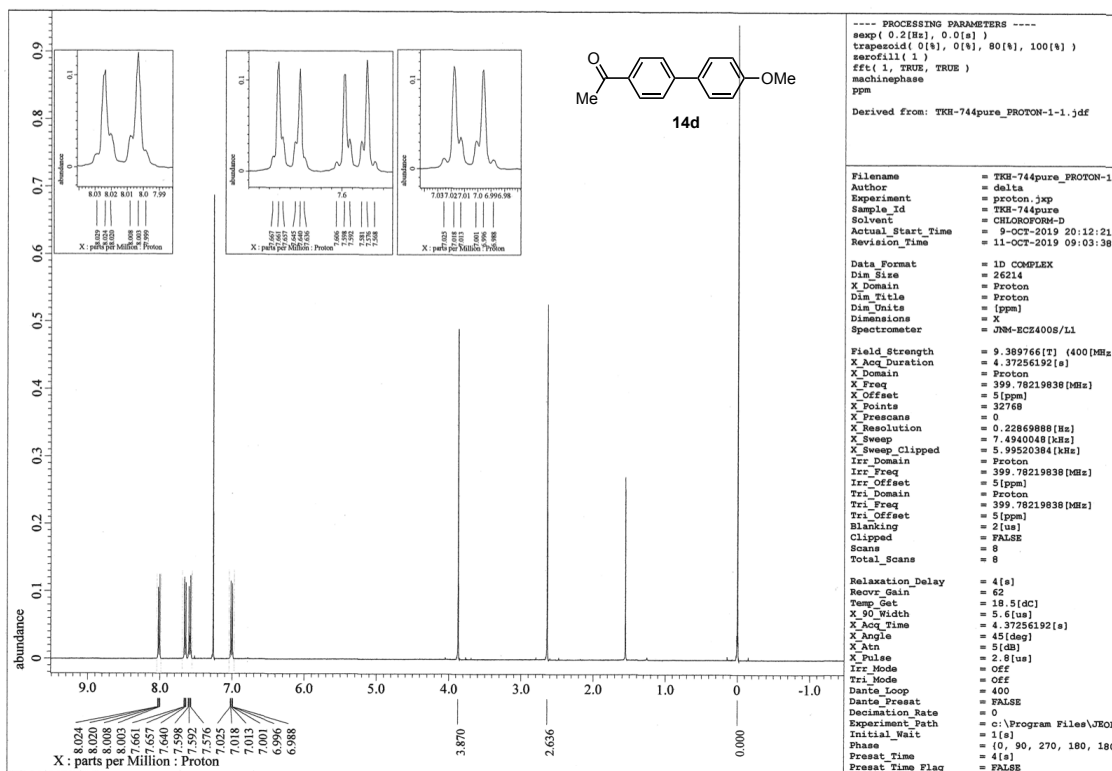
Supplementary Figure 36. ¹³C NMR spectrum of 14b.



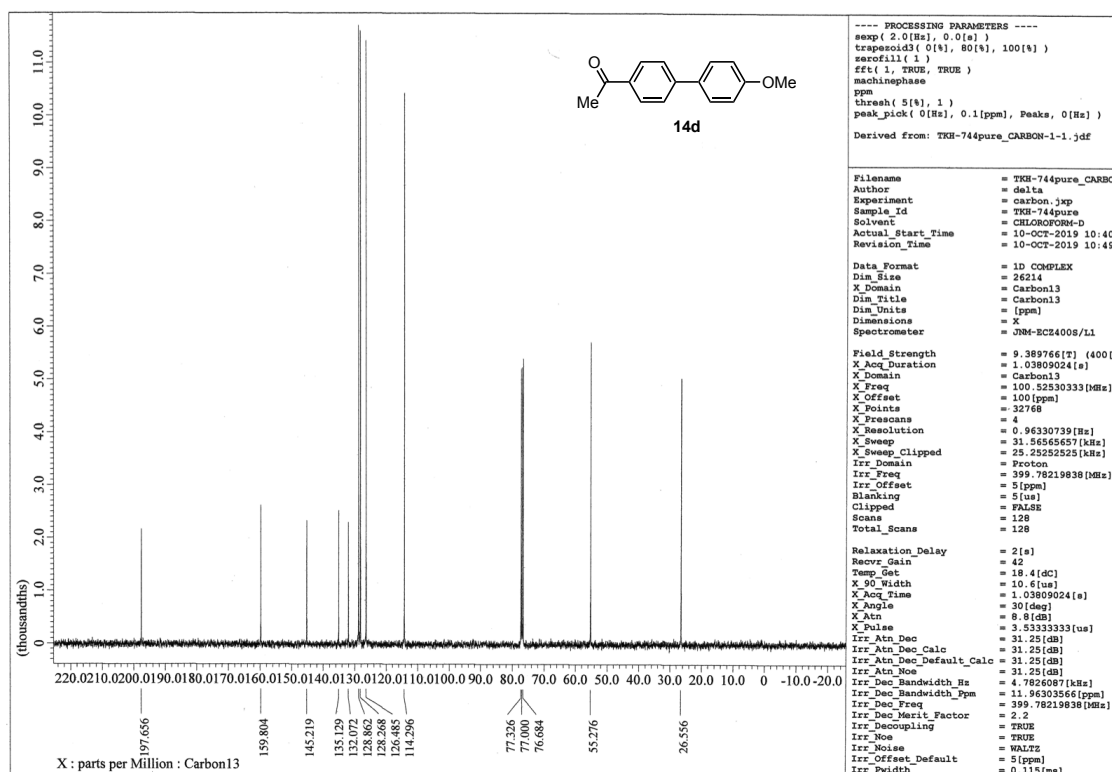
Supplementary Figure 37. ^1H NMR spectrum of 14c.



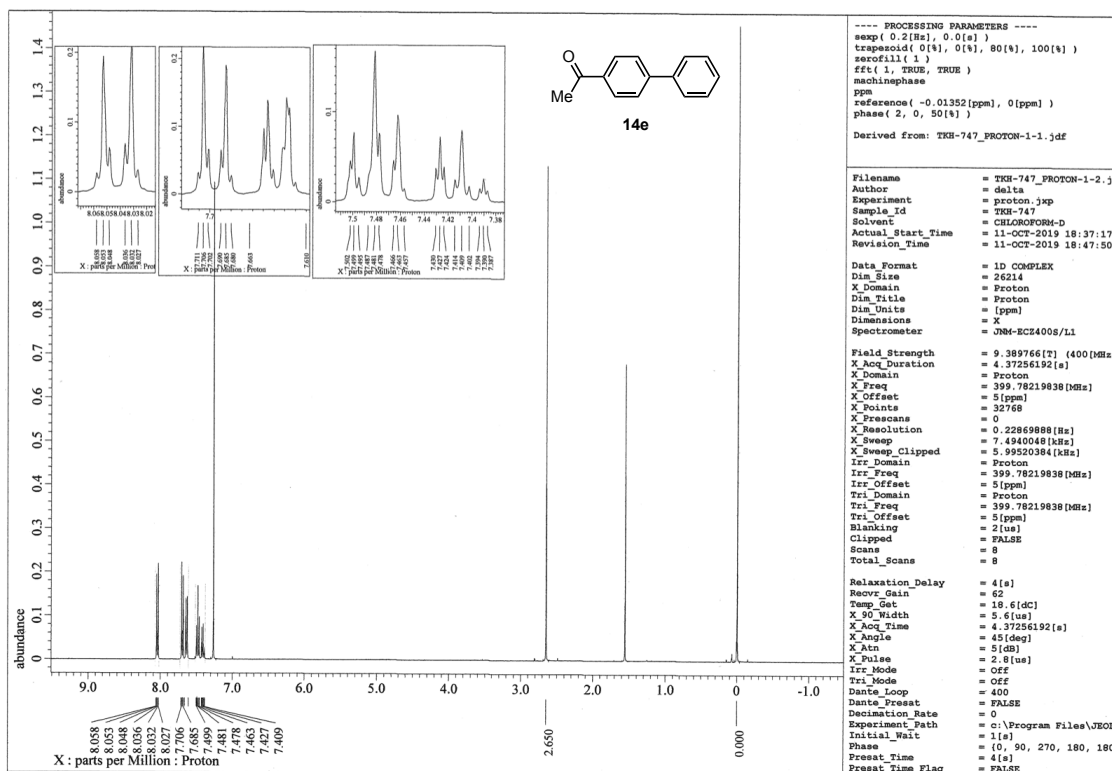
Supplementary Figure 38. ^{13}C NMR spectrum of 14c.



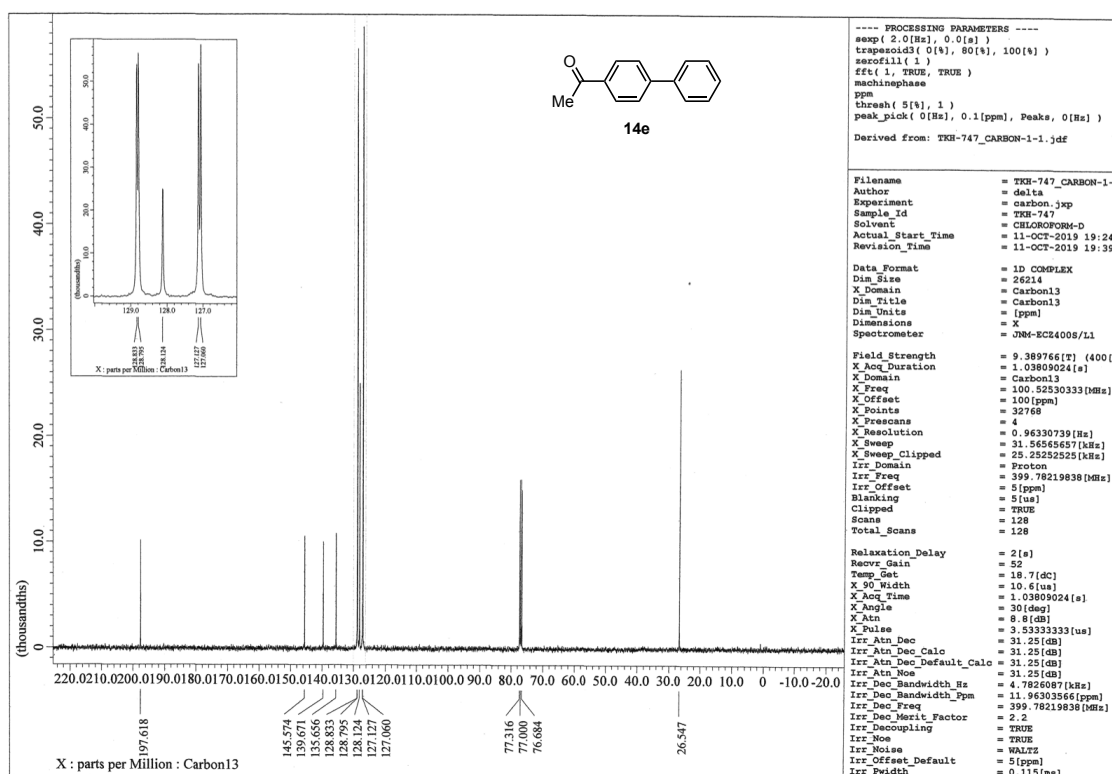
Supplementary Figure 39. ¹H NMR spectrum of 14d.



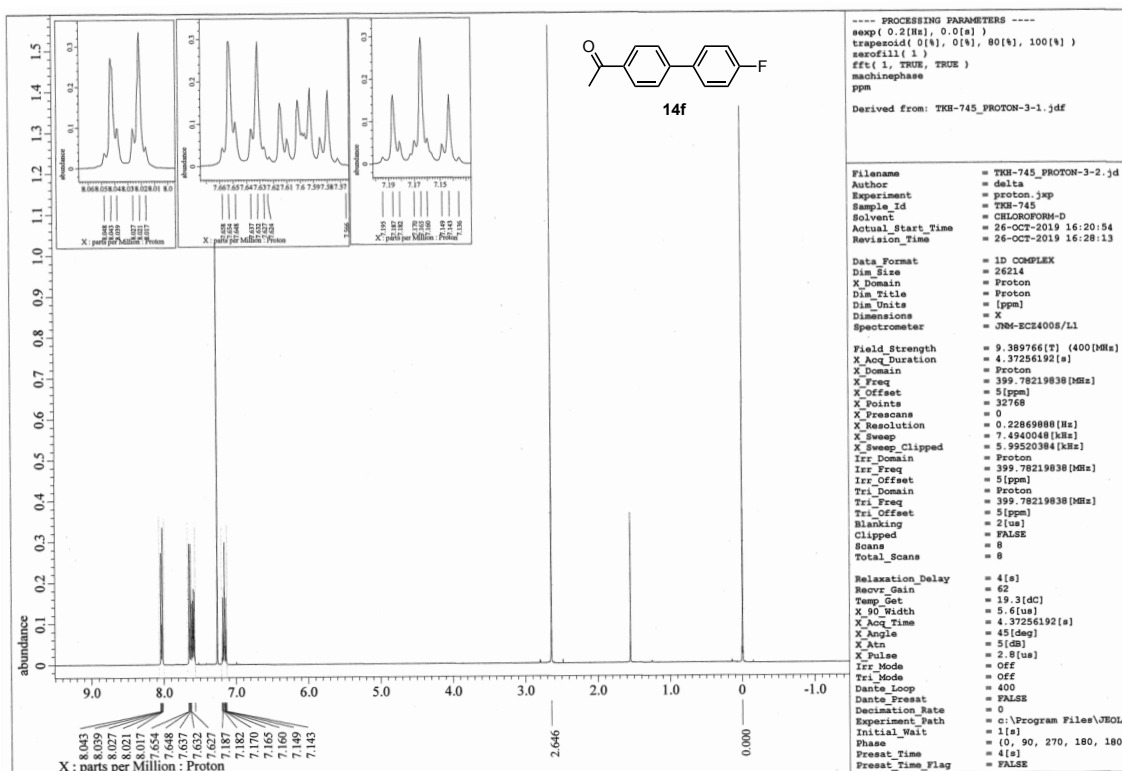
Supplementary Figure 40. ¹³C NMR spectrum of 14d.



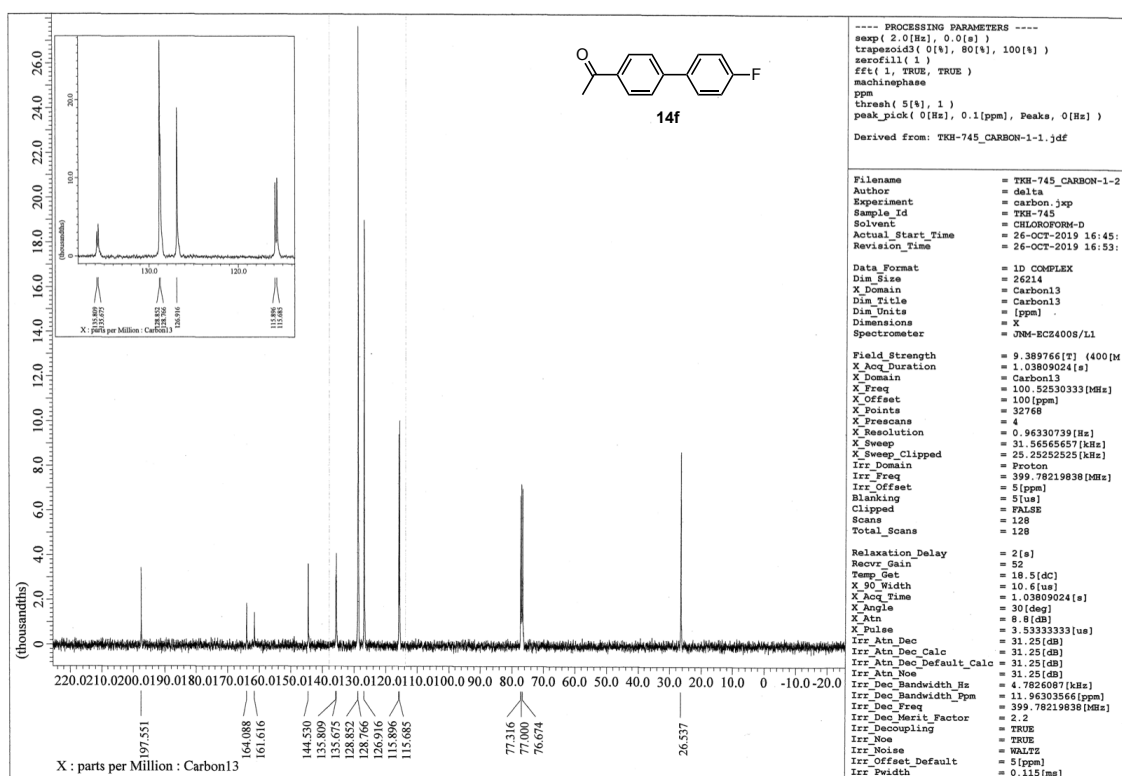
Supplementary Figure 41. ¹H NMR spectrum of 14e.



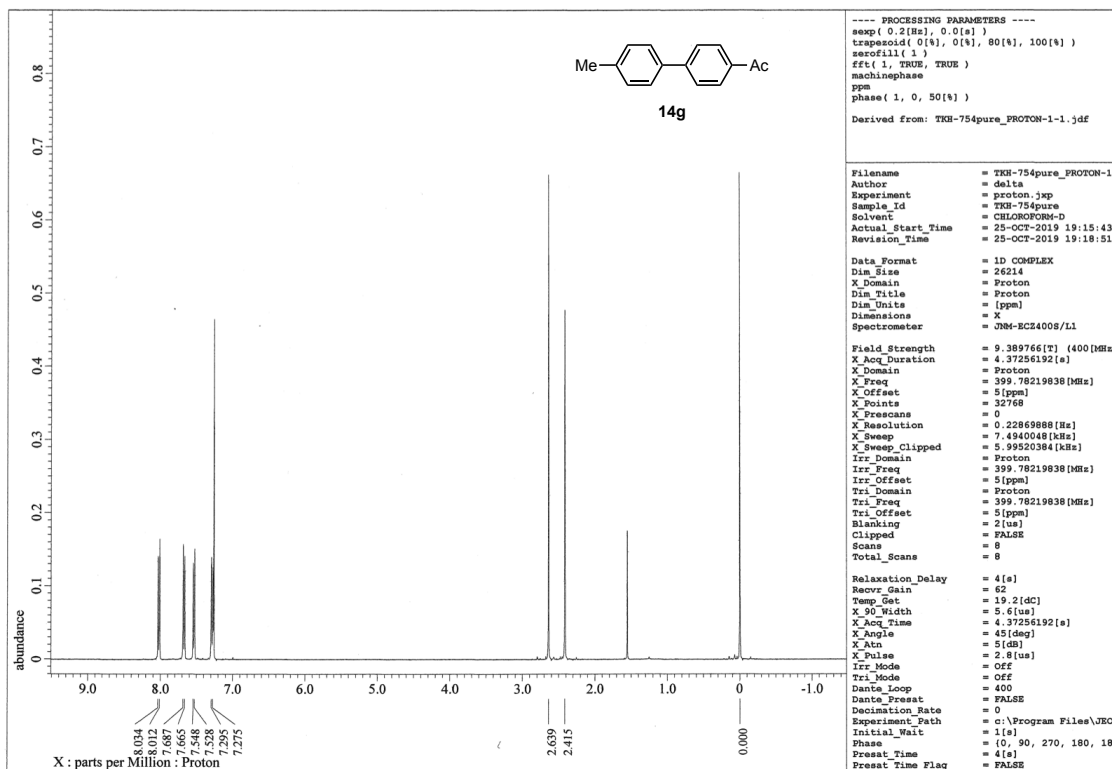
Supplementary Figure 42. ¹³C NMR spectrum of 14e.



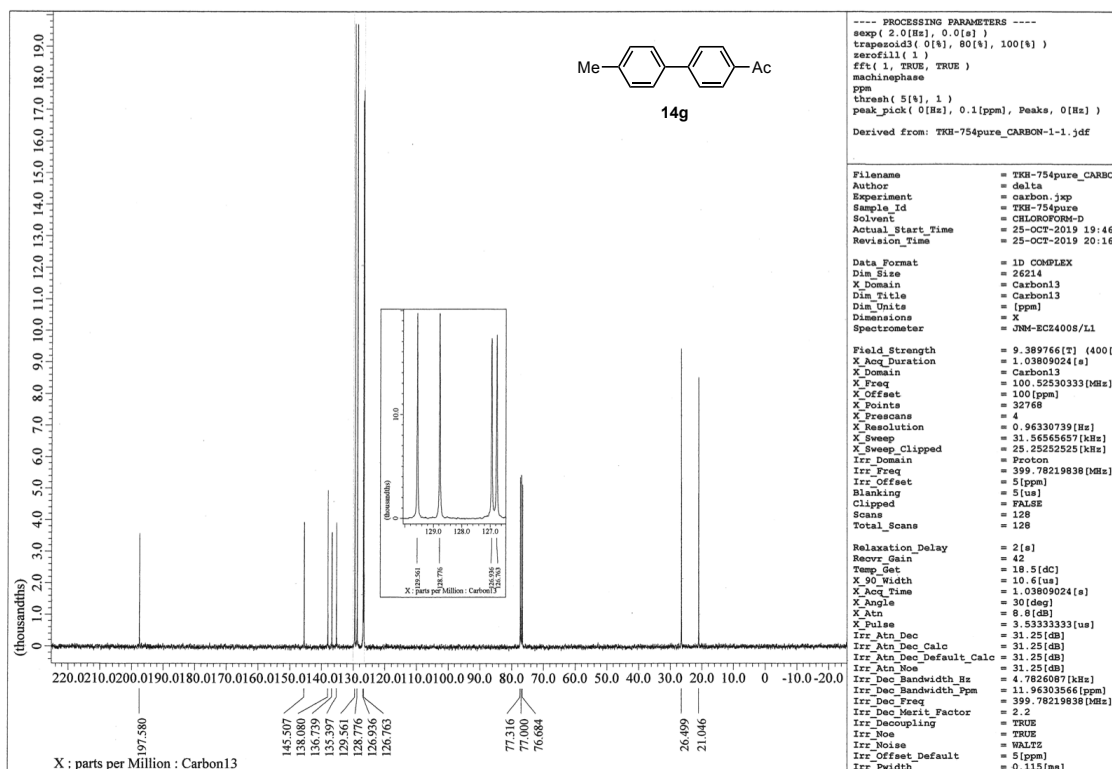
Supplementary Figure 43. ¹H NMR spectrum of 14f.



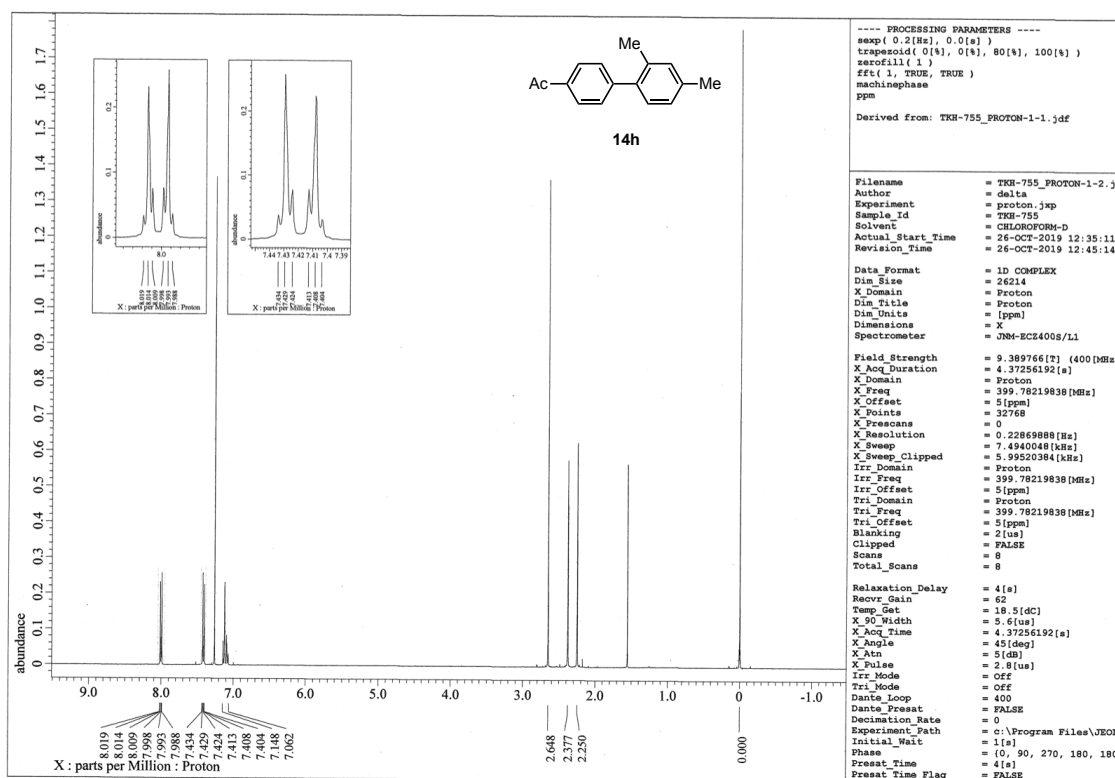
Supplementary Figure 44. ¹³C NMR spectrum of 14f.



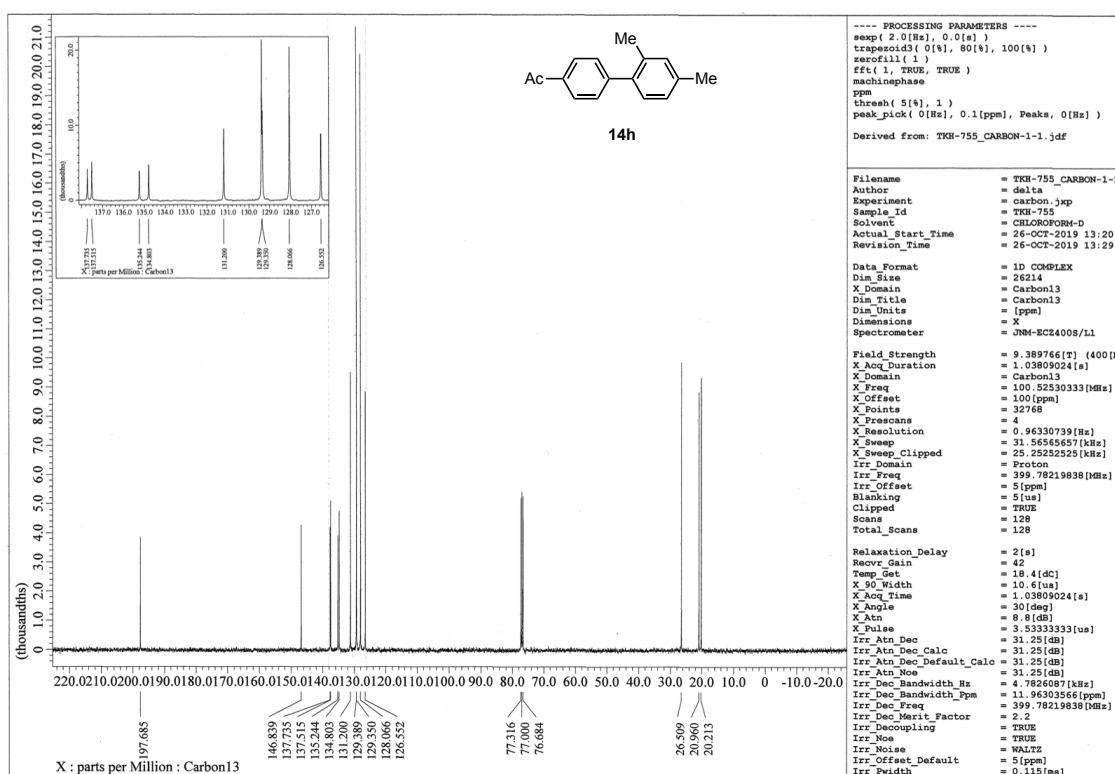
Supplementary Figure 45. ^1H NMR spectrum of 14g.



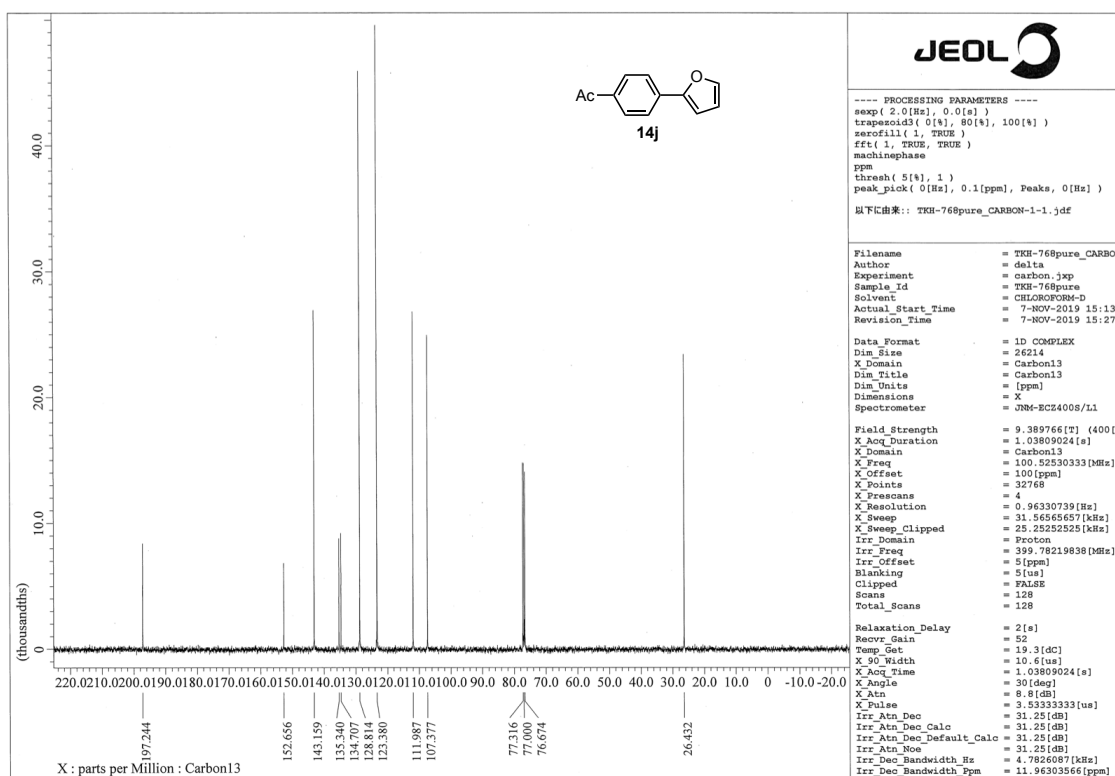
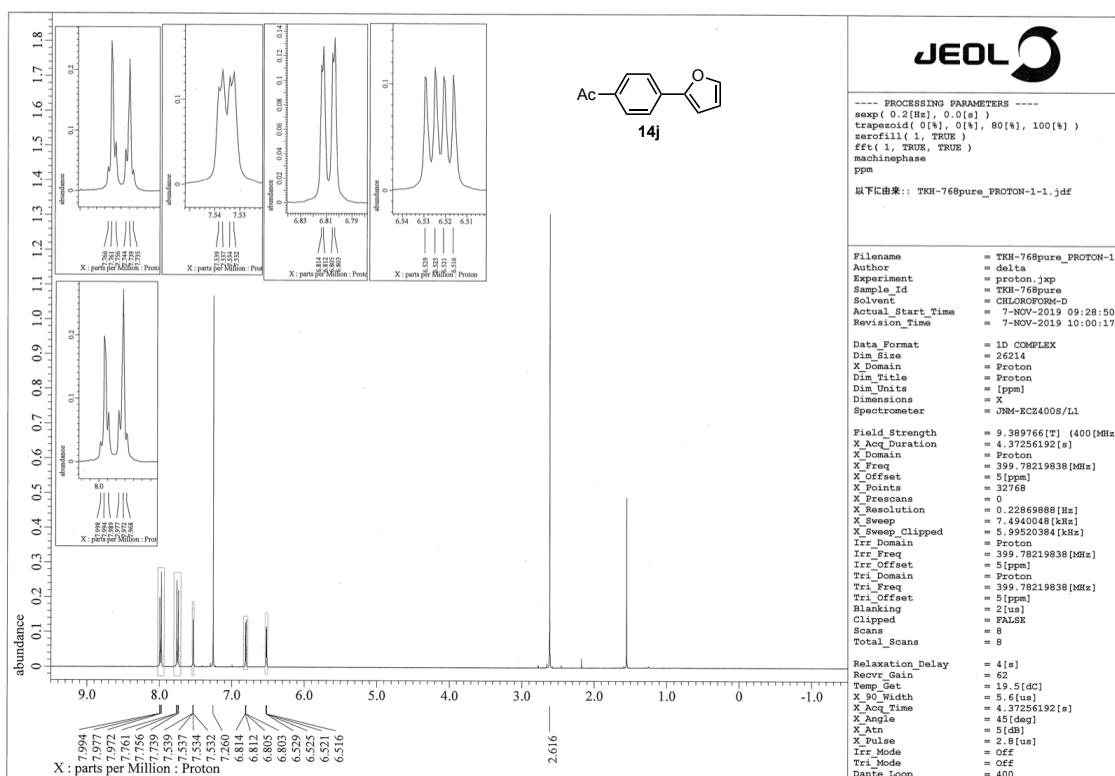
Supplementary Figure 46. ^{13}C NMR spectrum of 14g.

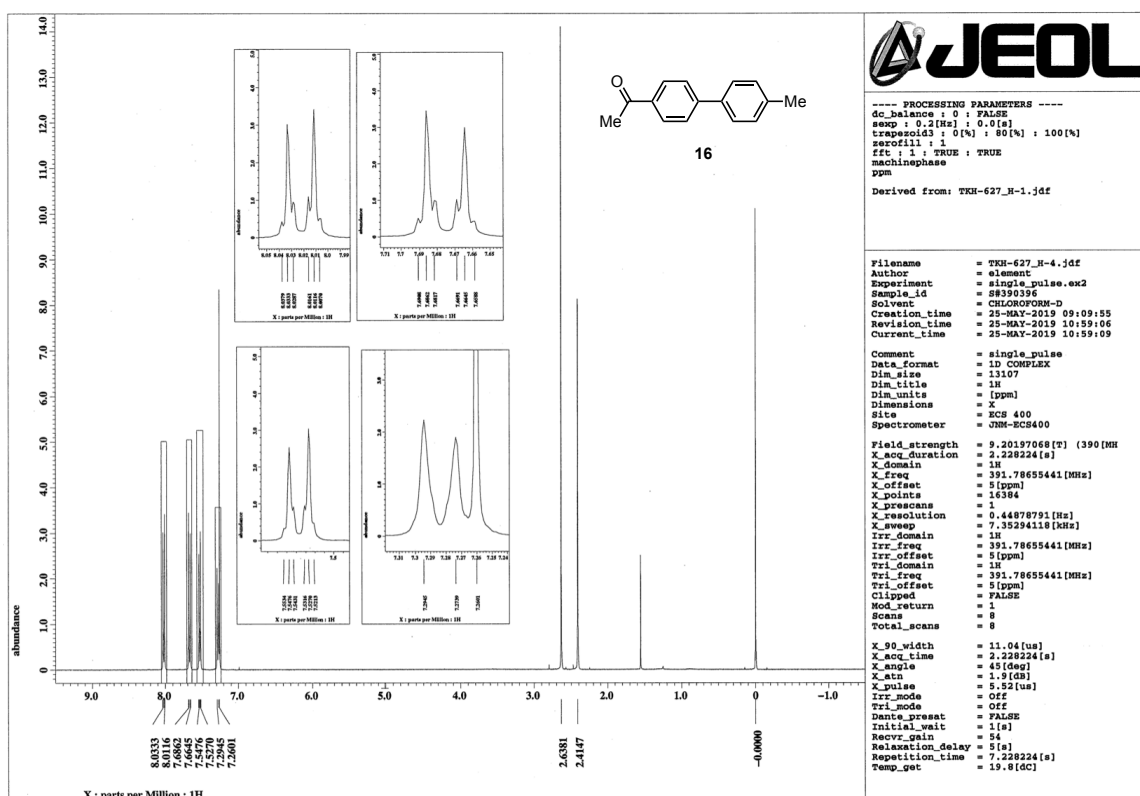


Supplementary Figure 47. ^1H NMR spectrum of 14h.

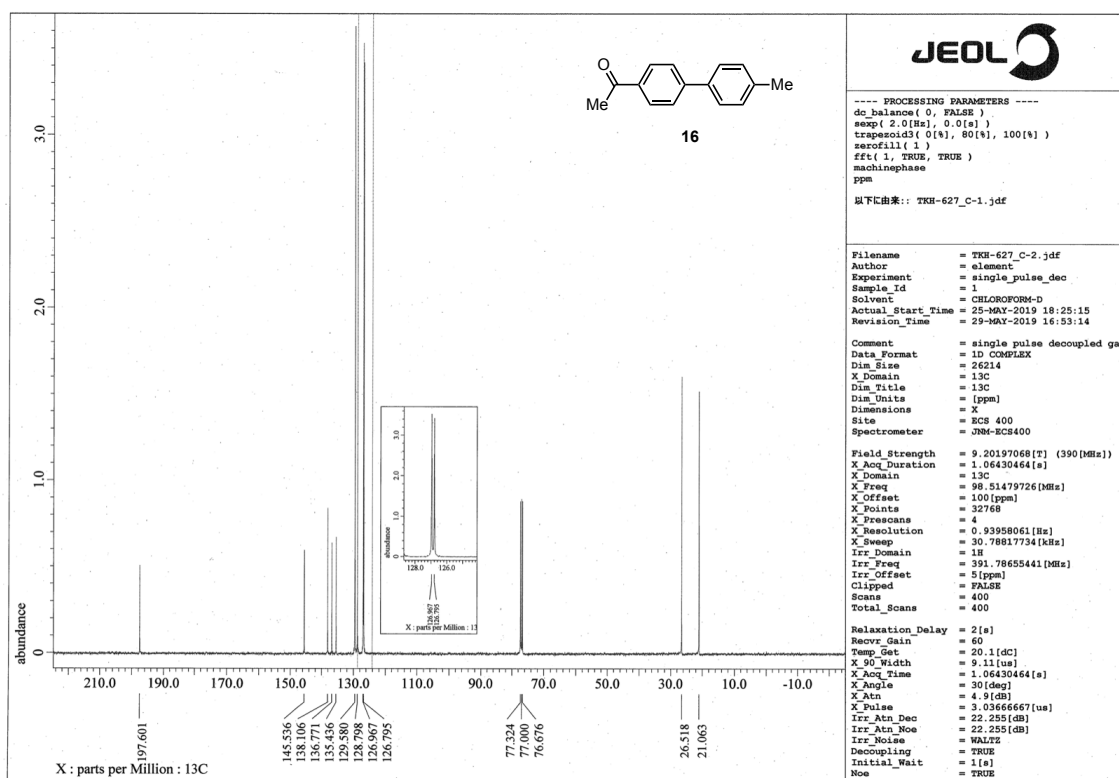


Supplementary Figure 48. ^{13}C NMR spectrum of 14h.





Supplementary Figure 53. ¹H NMR spectrum of 16.



Supplementary Figure 54. ¹³C NMR spectrum of 16.