Electronic Supplementary Information

C-Methylenation of anilines and indoles with CO_2 and hydrosilane using a pentanuclear zinc complex catalyst

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1. General information

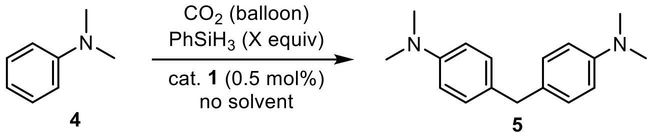
Instrumentation. Melting points were measured on a Yanaco melting point apparatus (uncorrected). NMR spectra were recorded on a JEOL JNM-ECS400 or a JEOL JEM-ECZ600R. Data are reported as follows: chemical shifts in ppm using the residual solvent peak as an internal standard, integration, multiplicity (s = singlet, d = doublet, t = triplet, sext = sextet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of double doublets, br = broadened), and coupling constants (Hz). High-resolution mass spectra were performed on a Bruker micrOTOF. TLC analyses were carried out on glass sheets coated with Merck Silica gel 60 F_{254} (0.25 mm), and visualization was accomplished with UV light. Column chromatography was performed on silica gel (Fuji Silysia BW-127 ZH, 100−270 mesh) or aluminum oxide 90 active basic (Merck 01799-11, 70−230 mesh). Preparative GPC was performed on a LC-5060 HPLC system (Japan Analytical Industry) using a JAIGEL-1HH (ø 20 mm × 600 mm) and a JAIGEL-2HH (ø 20 mm × 600 mm) (Japan Analytical Industry). GC was measured on a GC-8A (Shimadzu) with a packed column, Shincarbon-ST 50/80 (ø 3 mm × 6 m) (Shinwa Chemical Industries).

Materials. Most reagents were purchased and used without further purification unless otherwise specified. Dry solvents were purchased from Kanto Chemical Co., Inc. Phenylsilane was dried over 3A molecular sieves. Aniline was purified by distillation under reduced pressure and dried over 3A molecular sieves. $^{13}CO_2$ (99%) was purchased from Taiyo Nippon Sanso Corporation.

The full citation of reference 14: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *GAUSSIAN 16 (Revision C.01)*, Gaussian, Inc., Wallingford CT, 2019.

2. Synthesis of diarylmethanes

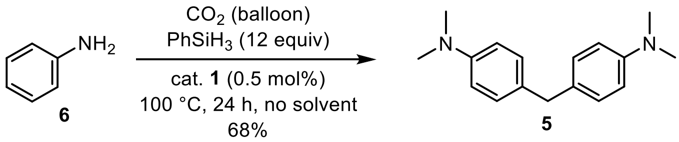
General procedure for the synthesis of bis[4-(*N*,*N*-dimethylamino)phenyl]methane (5) from *N*,*N*-dimethylaniline (4)



Catalyst **1** (3.0 mg, 1.3 μmol, 0.5 mol% based on **4**) was put in a dry Schlenk flask (30 mL), and then *N*,*N*-dimethylaniline (**4**) (32 μL, 0.25 mmol) was added. A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. The reaction mixture under CO_2 (1 atm) was stirred at reaction temperature for 10 min, and $PhSiH_3$ (3–6 equiv) was added via a syringe. The reaction mixture was stirred for reaction time. The yield was determined by using mesitylene as an internal standard after passing through a column (basic aluminum oxide, $CHCl_3$), or the product was purified by GPC ($CHCl_3$). Product **5** was characterized according to the literature.[S1]

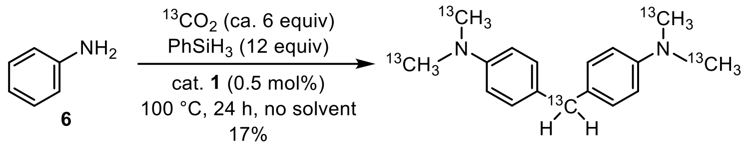
^{1}H NMR (600 MHz, $CDCl_3$) δ 2.90 (s, 12H), 3.81 (s, 2H), 6.68 (d, *J* = 8.6 Hz, 4H), 7.05 (d, *J* = 8.6 Hz, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 40.0, 41.1, 113.2, 129.5, 130.4, 148.2.

Procedure for the synthesis of bis[4-(*N*,*N*-dimethylamino)phenyl]methane (5) from aniline (6)



Catalyst **1** (3.0 mg, 1.3 μmol, 0.5 mol%) was put in a dry two-necked flask (10 mL), and then aniline (**6**) (23 μL, 0.25 mmol) was added. A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. The reaction mixture under CO_2 (1 atm) was stirred at 100 °C for 5 min, and $PhSiH_3$ (369 μL, 3.00 mmol) was added via a syringe. The reaction mixture was stirred at 100 °C for 24 h. The mixture was diluted with a mixed solvent of hexane/EtOAc (3/1). After the insoluble components were filtered off, the filtrate was evaporated to give a residue. The product was purified by column chromatography (SiO_2, hexane/EtOAc (3:1)) to afford **5** (21.7 mg, 85.3 μmol, 68%) as a colorless solid.

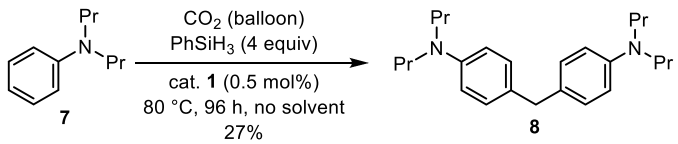
Procedure for the synthesis of ^{13}C-labeled bis[4-(*N*,*N*-dimethylamino)phenyl]methane (5')



Catalyst **1** (3.0 mg, 1.3 μmol, 0.5 mol%) was put in a dry Schlenk flask (30 mL), and then aniline (**6**) (23 μL, 0.25 mmol) was added. A $^{13}CO_2$ balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with $^{13}CO_2$ (ca. 30 mL). The reaction mixture under $^{13}CO_2$ was stirred at 100 °C for 5 min, and $PhSiH_3$ (369 μL, 3.00 mmol) was added via a syringe. The reaction mixture was stirred at 100 °C for 24 h. The mixture was passed through a basic aluminum oxide column ($CHCl_3$) and then purified by silica gel column chromatography (hexane/EtOAc (9:1)) to afford **5'** (5.4 mg, 21 μmol, 17%) as a colorless solid.

mp 78–80 °C; **IR** (KBr) 3009, 2916, 2855, 1612, 1520, 1477, 1439, 1335, 1223, 1188, 1061, 934, 826, 795 cm^{-1}; ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 2.90 (dd, *J* = 134.9, 4.3 Hz, 12H), 3.81 (d, *J* = 125.9 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 4H), 7.05 (dd, *J* = 8.7, 4.0 Hz, 4H); ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 40.0, 41.1, 113.2, 129.6 (d, *J* = 2.9 Hz), 130.5 (d, *J* = 44.8 Hz), 150.3 (d, *J* = 320.9 Hz); **HR MS** (ESI$^+$) Calcd for $^{12}C_{12}{}^{13}C_5H_{23}N_2$: 260.2023 [M + H]$^+$. Found: 260.2018.

Procedure for the synthesis of bis[4-(*N*,*N*-dipropylamino)phenyl]methane (8) from *N*,*N*-dipropylaniline (7)



Catalyst **1** (3.0 mg, 1.3 μmol, 0.5 mol%) was put in a dry Schlenk flask (30 mL), and then *N*,*N*-dipropylaniline (**7**) (48 μL, 0.25 mmol) was added. A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. The reaction mixture under CO_2 (1 atm) was stirred at 80 °C for 5 min, and $PhSiH_3$ (123 μL, 1.00 mmol) was added via a syringe. The reaction mixture was stirred at 80 °C for 96 h. The mixture was passed through a basic aluminum oxide column ($CHCl_3$) and then purified by silica gel column chromatography (hexane/EtOAc (20:1)) to afford **8** (12.3 mg, 33.6 μmol, 27%) as a colorless oil.

IR (neat) 3093, 2959, 2932, 2874, 1748, 1516, 1458, 1366, 1234, 1192, 1153, 1103, 799 cm^{-1}; ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.4 Hz, 12H), 1.58 (sext, *J* = 7.5 Hz, 8H), 3.18 (t, *J* = 7.7 Hz, 8H), 3.76 (s, 2H), 6.56 (dt, *J* = 2.6, 8.8 Hz, 4H), 7.01 (dt, *J* = 2.7, 8.8 Hz, 4H); ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 11.6, 20.6, 39.8, 53.2, 112.0, 128.9, 129.6, 146.5; **HR MS** (ESI$^+$) Calcd for $C_{25}H_{39}N_2$: 367.3108 [M + H]$^+$. Found: 367.3100.

General procedure for the synthesis of diindolylmethanes 10

Catalyst **1** (0.5 mol% based on **9**) was put in a dry Schlenk flask (30 mL), and then indole **9** (0.25 mmol) was added. A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. The reaction mixture under CO_2 (1 atm) was stirred at reaction temperature for 10 min, and $PhSiH_3$ (184 μL, 1.5 mmol) was added via a syringe. The reaction mixture was stirred for 24 h. The yield was determined by using mesitylene as an internal standard after short column chromatography (basic aluminum oxide, $CHCl_3$), or the product was purified by GPC ($CHCl_3$). Products **10a**[S2], **10b**[S3], **10c**[S2], **10d**[S4], **10e**[S3], **10f**[S2], and **10g**[S2] were characterized according to the literature.

10a: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.71 (s, 6H), 4.22 (s, 2H), 6.79 (s, 2H), 7.09 (ddd, *J* = 0.9, 7.0, 7.9 Hz, 2H), 7.22 (ddd, *J* = 1.1, 7.0, 8.3 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 21.1, 32.7, 109.2, 114.4, 118.7, 119.4, 121.5, 127.1, 128.0, 137.2.

10b: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.45 (s, 6H), 3.69 (s, 6H), 4.16 (s, 2H), 6.73 (s, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.42 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 21.0, 21.7, 32.8, 108.9, 113.9, 119.1, 123.1, 127.2, 127.9, 128.2, 135.7.

10c: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.68 (s, 6H), 3.83 (s, 6H), 4.14 (s, 2H), 6.76 (s, 2H), 6.89 (dd, *J* = 2.4, 8.7 Hz, 2H), 7.07 (d, *J* = 2.4 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 21.1, 32.9, 56.2, 101.2, 110.0, 111.7, 113.8, 127.7, 128.2, 132.7, 153.7.

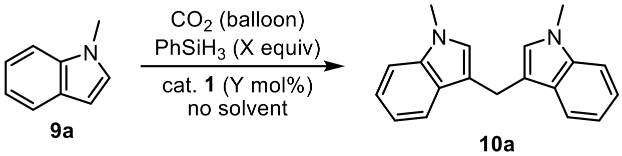
10d: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.71 (s, 6H), 4.11 (s, 2H), 6.81 (s, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.54 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 20.9, 33.0, 110.4, 113.6, 118.7, 121.9, 124.6, 128.3, 128.8, 135.7.

10e: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.71 (s, 6H), 4.10 (s, 2H), 6.78 (s, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 7.29 (dd, *J* = 1.7, 8.6 Hz, 2H), 7.70 (d, *J* = 1.8 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 20.9, 33.0, 110.8, 112.3, 113.6, 121.8, 124.5, 128.2, 129.5, 136.0.

10f: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.3 Hz, 6H), 1.83 (sext, *J* = 7.3 Hz, 4H), 4.01 (t, *J* = 7.0 Hz, 4H), 4.24 (s, 2H), 6.85 (s, 2H), 7.07 (t, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 11.7, 21.3, 23.8, 48.1, 109.4, 114.5, 118.6, 119.6, 121.4, 126.2, 128.4, 136.8.

10g: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.38 (s, 6H), 3.65 (s, 6H), 4.15 (s, 2H), 6.96 (t, *J* = 7.4 H, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 10.5, 20.2, 29.6, 108.5, 110.6, 118.6, 118.7, 120.4, 128.4, 132.8, 136.9.

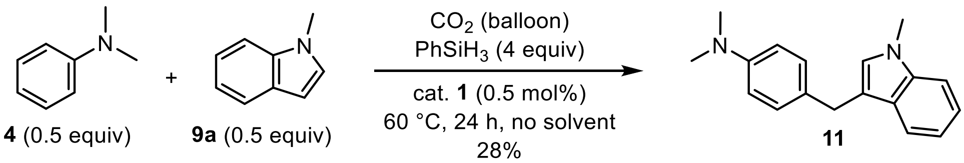
Table S1 Optimization of the synthesis of diindolylmethane **10a**[a]



Entry	X (equiv)	Y (mol%)	Temp (°C)	Yield (%)[b]
1	6	0.5	100	74
2	6	0.5	90	92
3	6	0.5	80	95 (94)[c]
4	6	0.5	70	89
5	6	0.5	60	85
6	6	0.5	40	0
7	4	0.5	80	73
8	6	0.2	80	10

[a] Conditions: **9a** (0.25 mmol), CO_2 (1 atm, balloon), $PhSiH_3$ (amount indicated above), cat. **1** (amount indicated above), 24 h. [b] Determined by ^{1}H NMR using mesitylene as an internal standard. [c] Isolated yield.

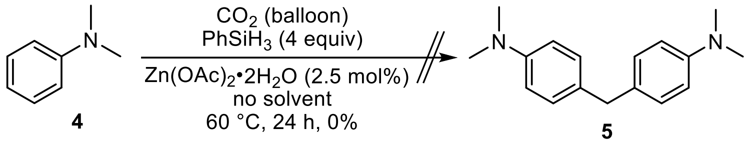
Procedure for the synthesis of unsymmetrical diarylmethane 11



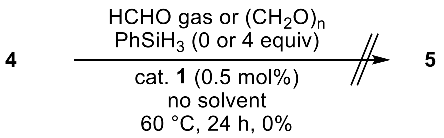
Catalyst **1** (3.0 mg, 1.3 μmol, 0.5 mol%) was put in a dry Schlenk flask (30 mL), and then *N*,*N*-dimethylaniline (**4**) (15.8 μL, 0.125 mmol) and 1-methylindole (**9a**) (15.6 μL, 0.125 mmol) were added. A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. The reaction mixture under CO_2 (1 atm) was stirred at 60 °C for 10 min, and $PhSiH_3$ (123 μL, 1.00 mmol) was added via a syringe. The reaction mixture was stirred at 60 °C for 24 h. The product was purified by column chromatography (basic aluminum oxide, $CHCl_3$) and GPC ($CHCl_3$) to afford **11** (9.3 mg, 0.041 mmol, 28%) as a yellow oil and **10a** (11.3 mg, 0.0352 mmol, 33%) as a pink solid. Product **11** was characterized according to the literature.[S5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.92 (s, 6H), 3.73 (s, 3H), 4.02 (s, 2H), 6.73 (br s, 3H), 7.07 (ddd, *J* = 1.0, 6.9, 7.9 Hz, 1H), 7.10–7.25 (m, 3H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 30.6, 32.7, 41.1, 109.2, 113.1, 115.4, 118.7, 119.4, 121.5, 127.1, 128.0, 129.4, 129.7, 137.3, 149.2.

Procedures for the control experiments (Scheme 5)

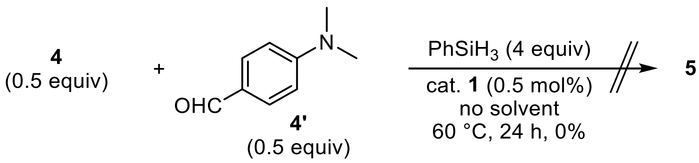


(a) $Zn(OAc)_2 \cdot 2H_2O$ (1.4 mg, 6.3 µmol, 2.5 mol% based on **4**) was put in a dry Schlenk flask (30 mL), and then **4** (32 µL, 0.25 mmol) was added. A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. The mixture under CO_2 (1 atm) was stirred at 60 °C for 10 min, and $PhSiH_3$ (123 µL, 1.00 mmol) was added via a syringe. The reaction mixture was stirred at 60 °C for 24 h. The ^1H NMR spectrum was measured after passing through a column (basic aluminum oxide, $CHCl_3$), and compound **5** was not detected.



(b) The method using a formaldehyde gas: paraformaldehyde (121 mg, 4.0 mmol based on formaldehyde) was put in a dry two-necked flask (5 mL) and maintained at 120 °C under N_2 atmosphere. The generated gas was guided to another dry two-necked flask (5 mL) containing a mixture of cat. **1** (3.0 mg, 1.3 µmol, 0.5 mol% based on **4**), **4** (32 µL, 0.25 mmol), and $PhSiH_3$ (123 µL, 1.00 mmol) by cannula transfer. The mixture was stirred at 60 °C for 24 h. The ^1H NMR spectrum was measured after passing through a column (basic aluminum oxide, $CHCl_3$), and compound **5** was not detected.

The method using paraformaldehyde: catalyst **1** (2.9 mg, 1.3 µmol, 0.5 mol% based on **4**) was put in a dry Schlenk flask (30 mL), and then **4** (32 µL, 0.25 mmol) and paraformaldehyde (30 mg, 1.0 mmol based on formaldehyde) was added. A N_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with N_2. The mixture was stirred at 60 °C for 10 min, and $PhSiH_3$ (0 or 4 equiv) was added via a syringe. The reaction mixture was stirred at 60 °C for 24 h. The ^1H NMR spectrum was measured after passing through a column (basic aluminum oxide, $CHCl_3$), and compound **5** was not detected.



(c) Catalyst **1** (2.9 mg, 1.3 µmol, 0.5 mol% based on **4** + **4'**) was put in a dry Schlenk flask (30 mL), and then **4** (16 µL, 0.13 mmol) and **4'** (19 mg, 0.13 mmol) were added. A N_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with N_2. The mixture was stirred at 60 °C for 10 min, and $PhSiH_3$ (123 µL, 1.0 mmol) was added via a syringe. The reaction mixture was stirred at 60 °C for 24 h. The ^1H NMR spectrum was measured after passing through a column (basic aluminum oxide, $CHCl_3$), and compound **5** was not detected.

3. H_2 and HD generation reactions

General procedure for the H_2 generation reaction

To a solution of hydrosilane (0.75 mmol based on a number of Si−H bonds) and cat. **1** (0–0.9 mol%) in DMSO (200 μL) was added ROH (3 equiv) at reaction temperature under N_2 atmosphere. The volume of the H_2 gas was measured by the water displacement method. The generation of H_2 gas was identified by ^{1}H NMR ($CDCl_3$, 4.62 (s) ppm)[S6] (Fig. S1), GC (Fig. S2), and olefin hydrogenation (Scheme S1).

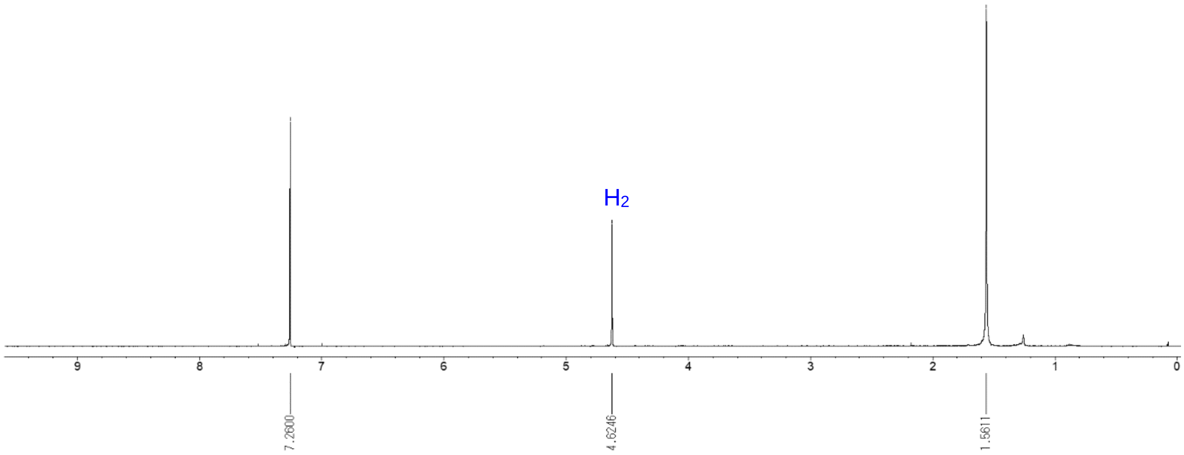


Fig. S1 ^{1}H NMR spectrum of the produced gas (H_2) (400 MHz, $CDCl_3$). Reaction conditions: $PhSiH_3$ (0.25 mmol), H_2O (3 equiv), cat. **1** (0.3 mol%), DMSO (200 μL), rt (ca. 20 °C), 5 min.

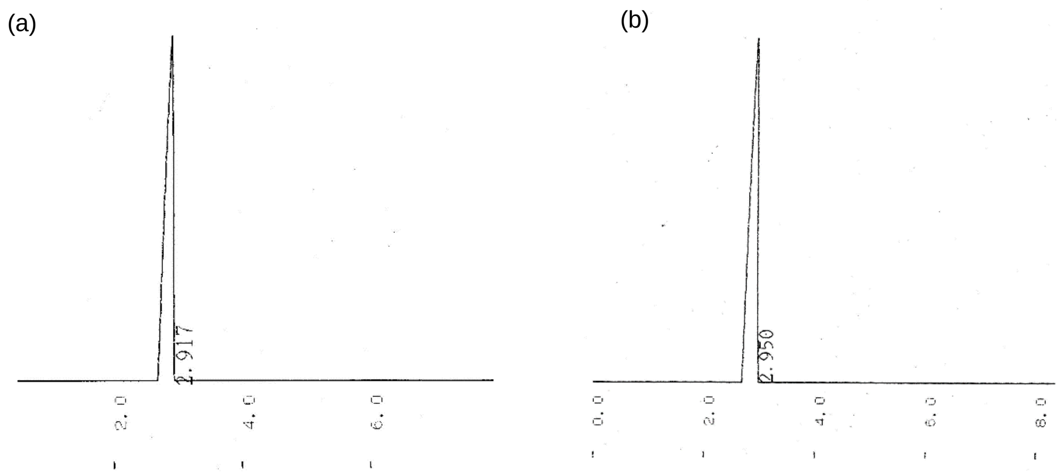
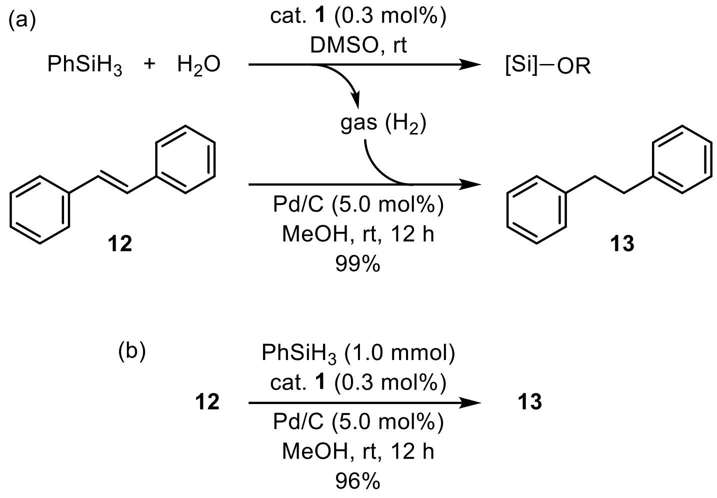


Fig. S2 GC charts of (a) the produced gas and (b) authentic sample of H_2. GC conditions: Shincarbon-ST 50/80 (Shinwa Chemical Industries), ϕ 3 mm × 6 m, Inj. 200 °C, Col. 70 °C, Det. (TCD) 200 °C, Ar. Reaction conditions: $PhSiH_3$ (0.25 mmol), H_2O (3 equiv), cat. **1** (0.3 mol%), DMSO (200 μL), rt (ca. 20 °C), 5 min.



Scheme S1 Synthesis of 1,2-diphenylethane (**13**) from *trans*-stilbene (**12**).

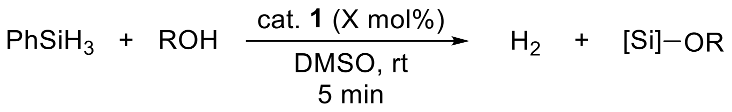
(a) To a solution of $PhSiH_3$ (126 μL, 1.02 mmol) and cat. **1** (24.1 mg, 11.0 μmol) in DMSO (800 μL), H_2O (180 μL, 10.0 mmol) was added at room temperature under N_2 atmosphere. The generated gas was guided to a flask containing a mixture of **12** (45.1 mg, 250 μmol) and 10% Pd/C (22.5 mg) in MeOH (1.5 mL) by cannula transfer. The mixture was stirred at room temperature for 5 h. After Pd/C was filtered off, the filtrate was evaporated to afford **13** as a colorless powder. The yield was determined by using mesitylene as an internal standard (>99%). The NMR data were in agreement with those reported previously.[S7]

(b) To a mixture of **12** (45.6 mg, 253 μmol), cat. **1** (24.0 mg, 10.9 μmol), and 10% Pd/C (22.5 mg) in MeOH (1.5 mL) was added $PhSiH_3$ (126 μL, 1.02 mmol) at room temperature (ca. 20 °C) under N_2 atmosphere. The reaction mixture was stirred at room temperature for 12 h. After Pd/C was filtered off, the filtrate was evaporated to give a residue. The residue was purified by column chromatography (SiO_2, $CHCl_3$) to afford **13** (44.3 mg, 243 μmol, 96%) as a colorless powder.

Screening of the H_2 generation reaction

We screened five reactants, ROHs, in the presence of 0.3 mol% of cat. **1** at room temperature for 5 min in DMSO (Table S2). When H_2O or MeOH was used, H_2 gas generated quantitatively (entries 1−2), and the reaction finished within two and one minutes, respectively (Fig. S3). The bulky alcohols and phenol gave lower yields (42−65%, entries 3−5). A catalyst loading of 0.1 mol% was sufficient, although the reaction rate became somewhat slower (entry 6 and Fig. S4). The reaction did not proceed without cat. **1** (entry 7). The catalyst was recyclable without lowering the catalytic activity for at least five cycles, which demonstrates the robustness of cat. **1** (entry 8 and Fig. S5). The reaction was sensitive to temperature, and interestingly, it did not proceed at −10 °C without solidification (entry 9 and Fig. S6). In addition, we screened various hydrosilanes and confirmed that phenylsilane was the best choice (Table S3).

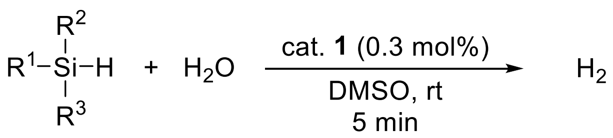
Table S2 Hydrogen generation from phenylsilane and water or alcohols[a]



Entry	ROH	X (mol%)	Yield of H_2 (%)[b]
1	H_2O	0.3	99
2	MeOH	0.3	99
3	*i*PrOH	0.3	65
4	*t*BuOH	0.3	42
5	PhOH	0.3	54
6	H_2O	0.1	99
7	H_2O	0	0
8[c]	H_2O	0.9	99
9[d]	H_2O	0.3	0

[a] Conditions: $PhSiH_3$ (0.25 mmol), ROH (3 equiv based on the number of Si−H bonds), cat. **1** (amount indicated above), DMSO (200 μL), rt (ca. 20 °C), 5 min, N_2 atmosphere. [b] Determined by volume of H_2 collected by the water displacement method. [c] After four-time recycling of the catalyst. [d] −10 °C.

Table S3 Hydrogen generation from various hydrosilanes and H_2O[a]



Entry	Silane	Yield of H_2 (%)[b]
1	$PhSiH_3$	99
2	Ph_2SiH_2	65
3	Ph_3SiH	0
4	$PhMe_2SiH$	0
5	Ph_2MeSiH	0
6	PMHS	0

[a] Conditions: Hydrosilane (0.25 mmol), H_2O (3 equiv based on the number of Si−H bonds), cat. **1** (0.3 mol%), DMSO (200 μL), rt (ca. 20 °C), 5 min, N_2 atmosphere. [b] Determined by volume of H_2 collected by the water displacement method.

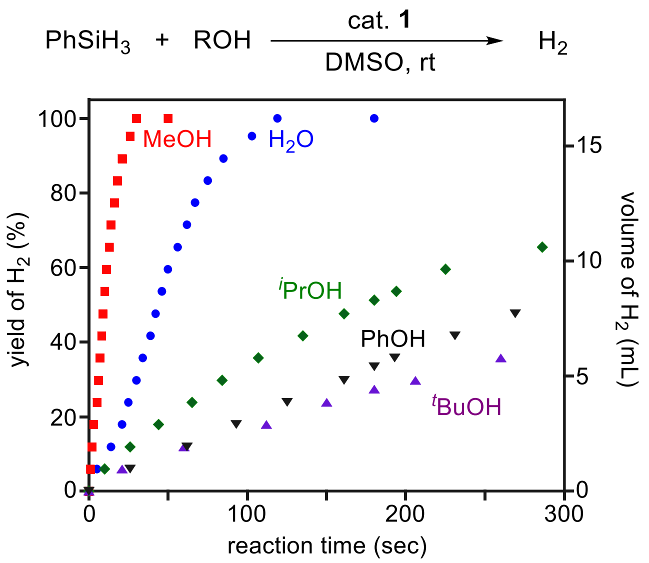


Fig. S3 H_2 generation by the reaction of $PhSiH_3$ with ROH (H_2O or alcohols). Conditions: $PhSiH_3$ (0.25 mmol), ROH (0.75 mmol), cat. **1** (0.3 mol%), DMSO (200 μL), rt (ca. 20 °C), N_2 atmosphere.

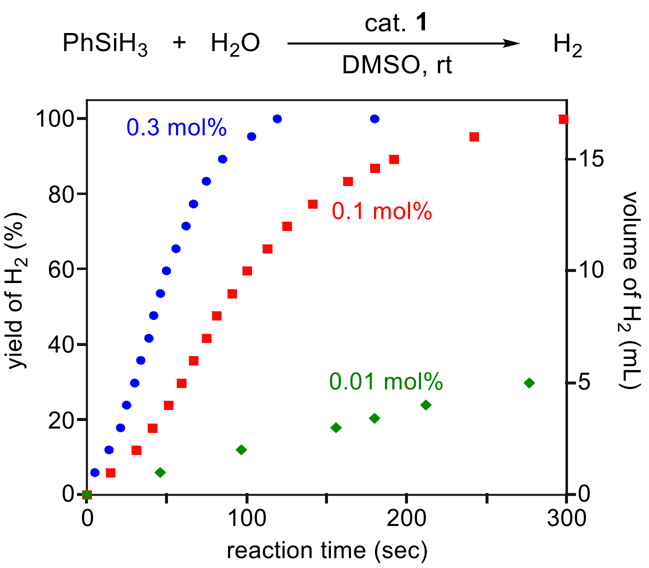


Fig. S4 H_2 generation by the reaction of $PhSiH_3$ with H_2O using various amounts of cat. **1**. Conditions: $PhSiH_3$ (0.25 mmol), H_2O (0.75 mmol), cat. **1** (amount indicated above), DMSO (200 μL), rt (ca. 20 °C), N_2 atmosphere.

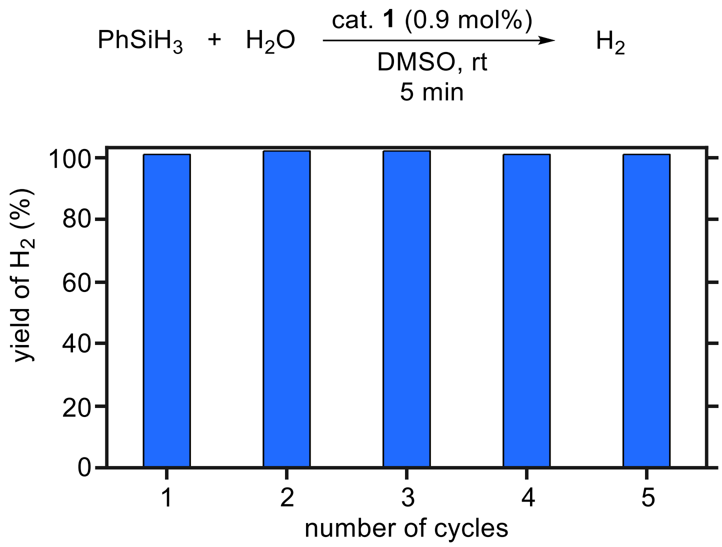


Fig. S5 Reuse of cat. **1**. Conditions: $PhSiH_3$ (0.25 mmol), H_2O (0.75 mmol), cat. **1** (0.9 mol%), DMSO (200 μL), rt (ca. 20 °C), 5 min, N_2 atmosphere.

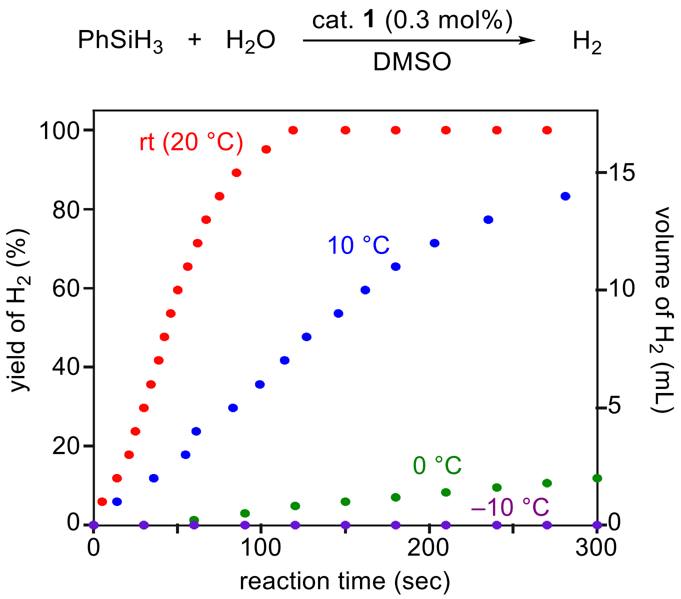


Fig. S6 H_2 generation by the reaction of $PhSiH_3$ with H_2O at various temperature. Conditions: $PhSiH_3$ (0.25 mmol), H_2O (0.75 mmol), cat. **1** (0.3 mol%), DMSO (200 μL), N_2 atmosphere.

General procedure for the HD gas generation reaction (Schemes 7b and 7c)

To a solution of $PhSiH_3$ (32 μL, 0.25 mmol) and cat. **1** (0.3 mol%) in DMSO (200 μL) was added ROD (D_2O (99.9% D) or CD_3OD (99.8% D), 10 equiv) at room temperature (ca. 20 °C) under N_2 atmosphere. The volume of the HD gas was measured by the water displacement method. The HD gas was identified by ^1H NMR (Fig. S7).[S8]

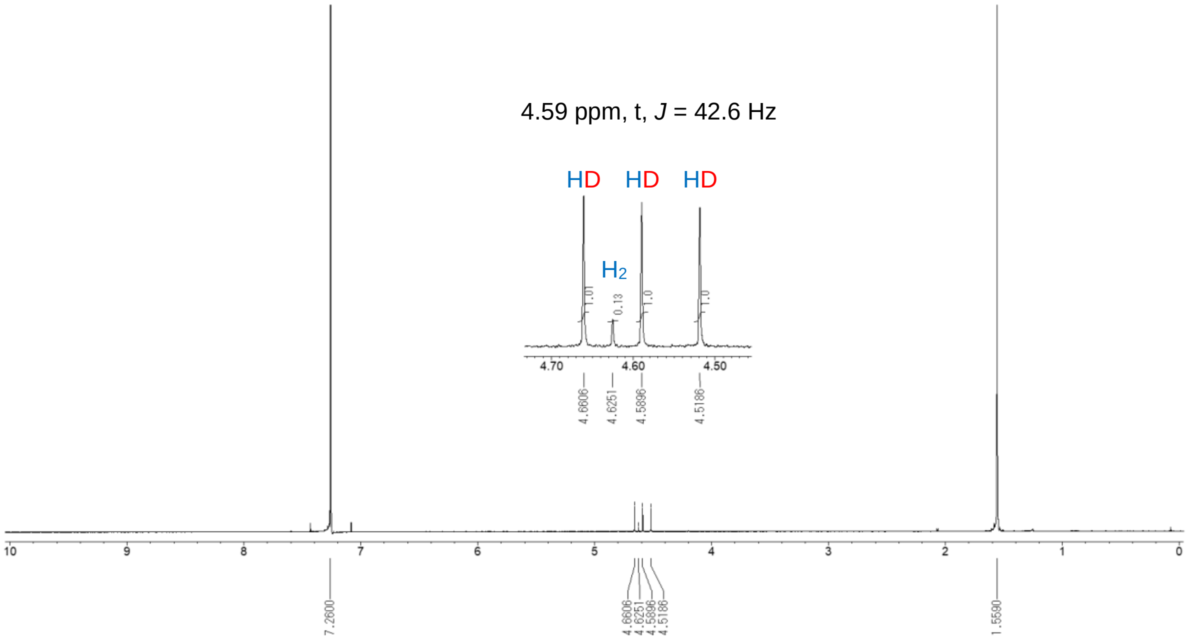


Fig. S7 ^1H NMR spectrum of the produced gas (600 MHz, $CDCl_3$). Reaction conditions: $PhSiH_3$ (0.25 mmol), D_2O (10 equiv), cat. **1** (0.3 mol%), DMSO (200 μL), rt (ca. 20 °C), 5 min, N_2 atmosphere.

Procedure for the temperature-controllable H_2 gas generation reaction (Fig. 1)

To a solution of cat. **1** (0.3 mol%) in DMSO (200 μL) and H_2O (45 μL, 2.5 mmol) at −10 °C under N_2 atmosphere, $PhSiH_3$ (32 μL, 0.25 mmol) was added, and the mixture solution was stirred for 15 min. The mixture was heated at 30 °C for 15 min. The volume of the H_2 gas was measured by the water displacement method.

General procedure for the stepwise H_2 gas generation reaction (Fig. S8 and S9)

To a solution of $PhSiH_3$ (246 µL, 2.0 mmol) and cat. **1** (0.2 mol%) in DMSO (1.6 mL) was added ROH (0.25 mmol) at room temperature (ca. 20 °C) under N_2 atmosphere. The volume of the H_2 gas was measured by the water displacement method. Additional portions of ROH (0.25 mmol) were added every 30 min (5 times).

We tried to control **1**-catalyzed H_2 generation by injection of H_2O (Fig. S8). The sequential injection of H_2O at 30 min intervals to a mixture of phenylsilane and cat. **1** in DMSO led to sequential and immediate H_2 generation at least five times. When MeOH was used instead of H_2O, injection-responsive H_2 generation was also achieved (Fig. S9).

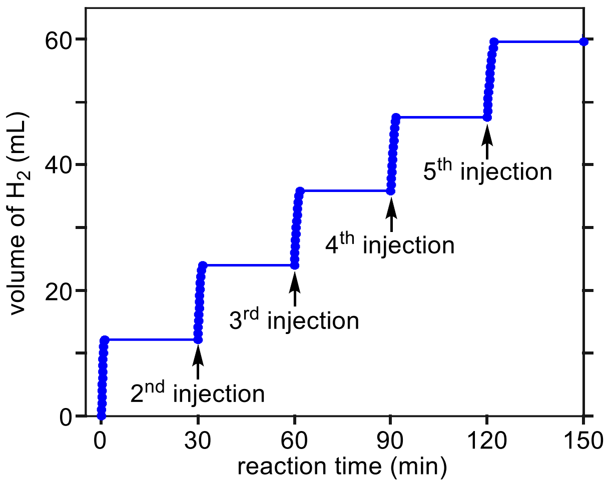


Fig. S8 Generation of H_2 by sequential injection of H_2O at 30 min intervals.

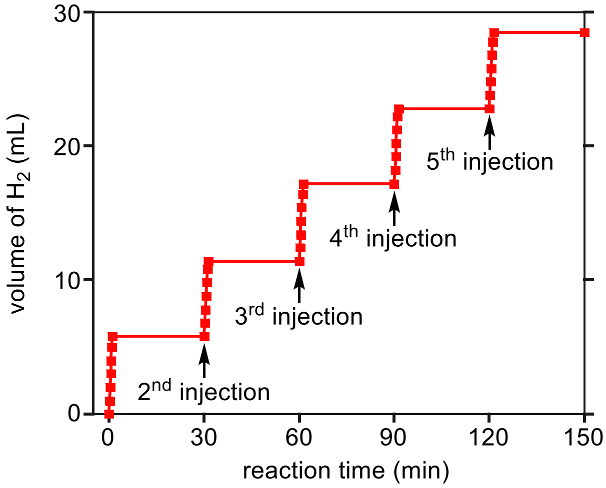


Fig. S9 Generation of H_2 by sequential injection of MeOH at 30 min intervals.

4. DFT calculations

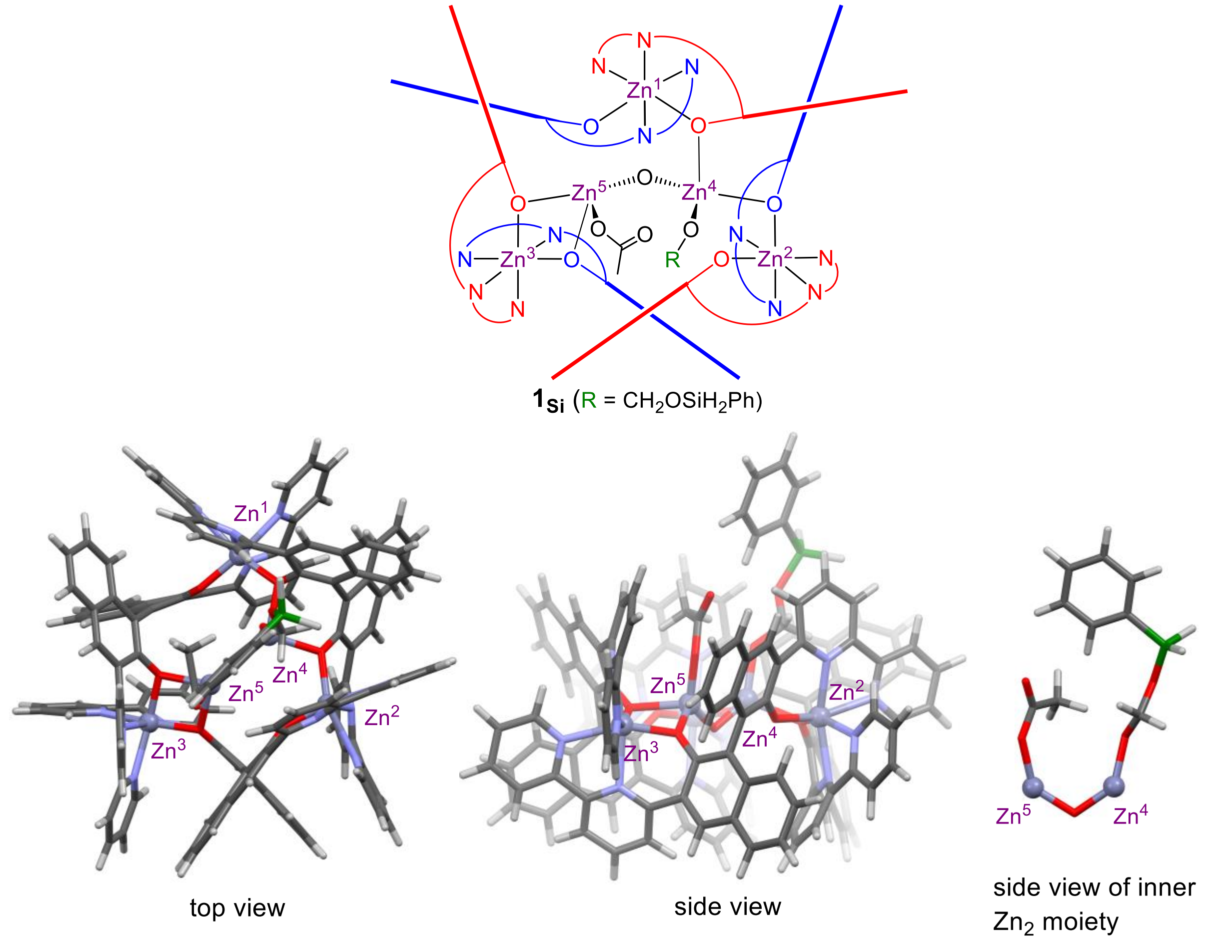
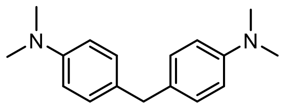


Fig. S10 DFT-optimized structures of Zn^{II} complex $\mathbf{1_{Si}}$ at the B3LYP/6-31G(d) level for the H, C, N, O, and Si atoms and at the B3LYP/LanL2DZ level for the Zn atoms.

5. ¹H and ¹³C NMR spectra



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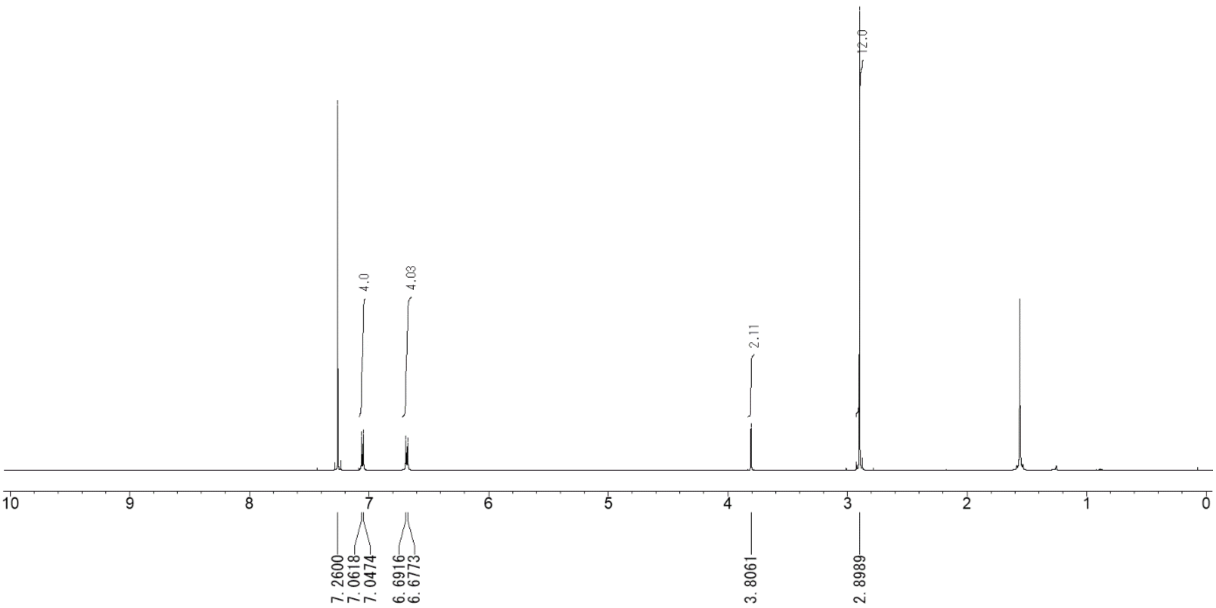
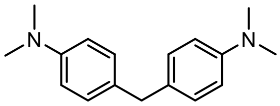


^{1}H NMR spectrum of **5** (600 MHz, $CDCl_3$)



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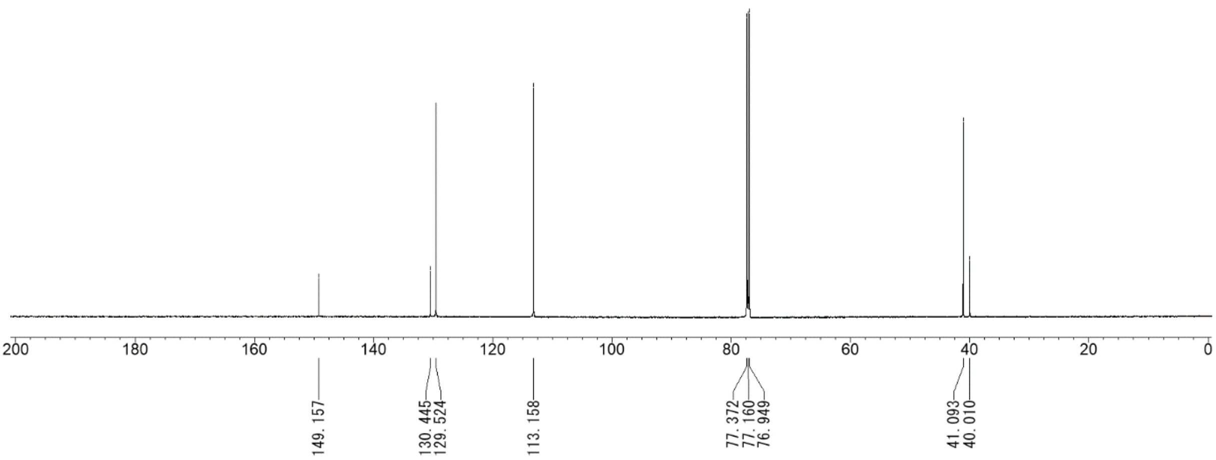
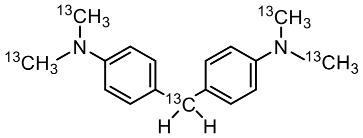
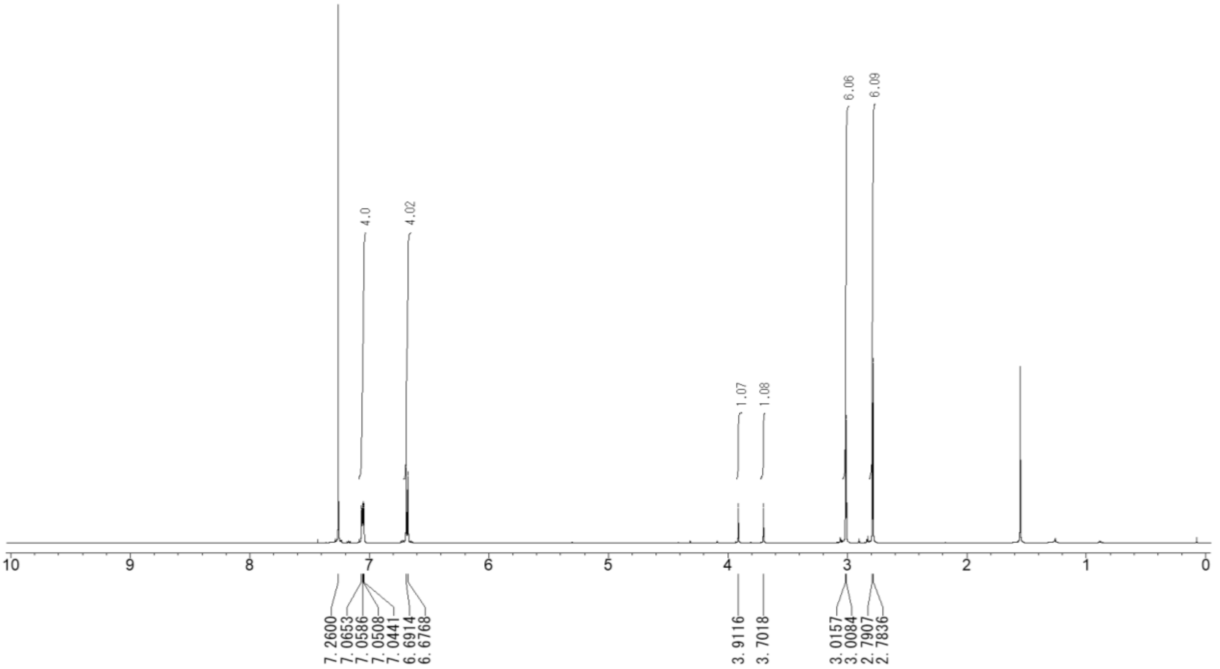


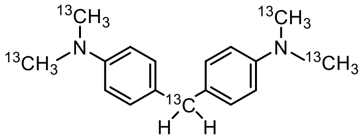
^{13}C NMR spectrum of **5** (151 MHz, $CDCl_3$)



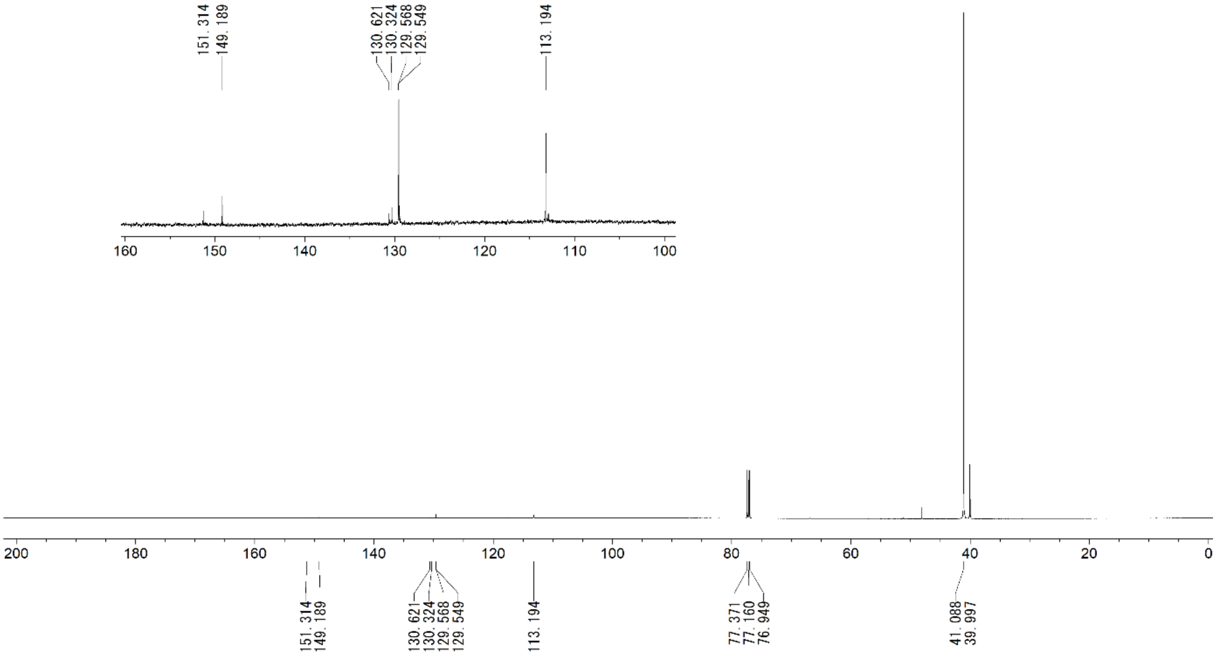
5'



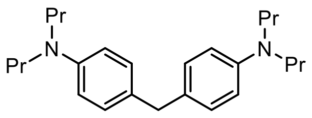
^{1}H NMR spectrum of **5'** (600 MHz, $CDCl_3$)



5'



^{13}C NMR spectrum of **5’** (151 MHz, $CDCl_3$)



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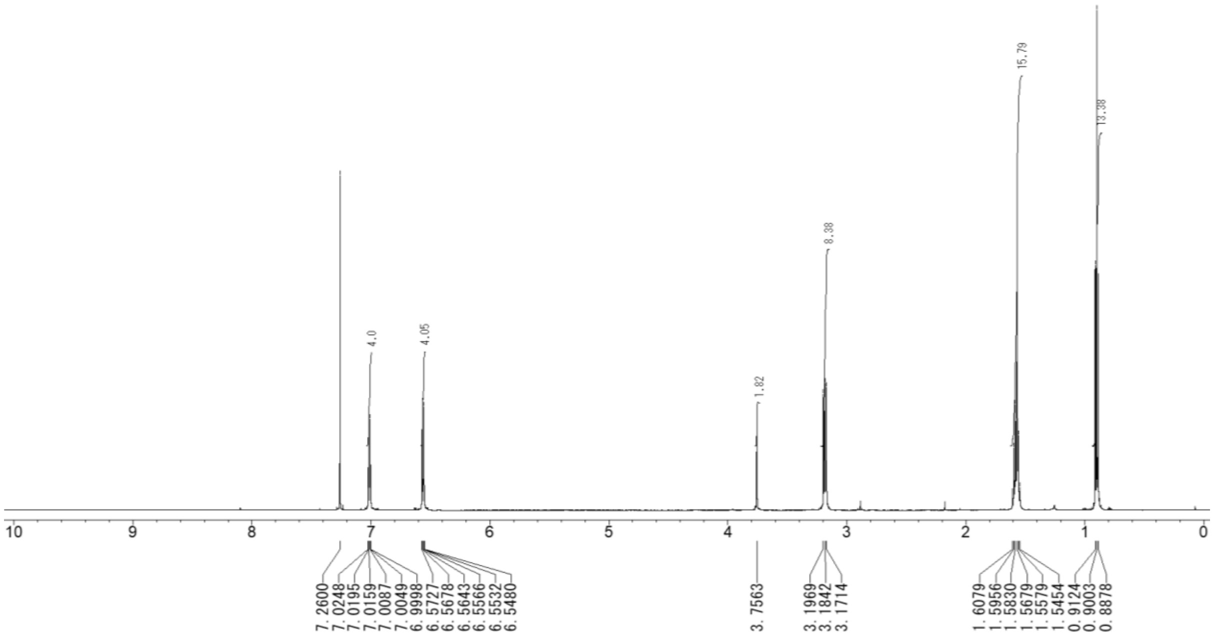
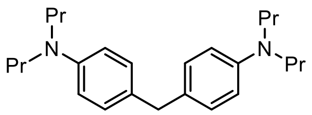


^{1}H NMR spectrum of **8** (600 MHz, $CDCl_3$)



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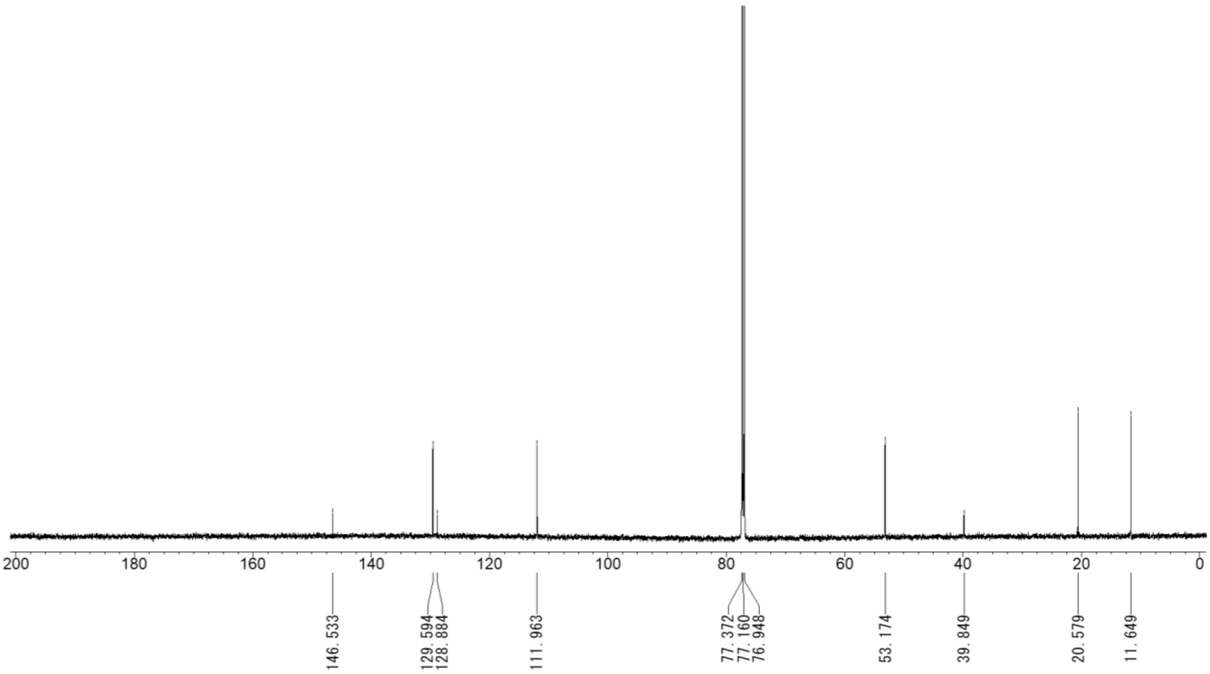
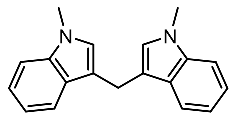
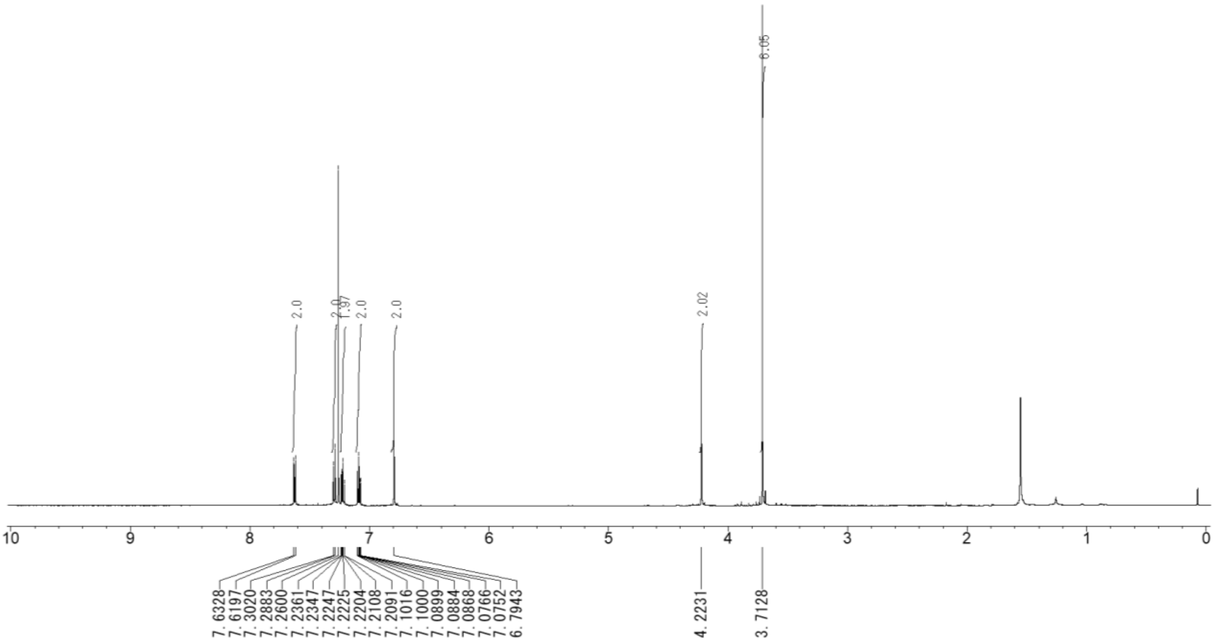


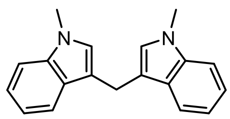
^{13}C NMR spectrum of **8** (151 MHz, $CDCl_3$)



10a



^{1}H NMR spectrum of **10a** (600 MHz, $CDCl_3$)



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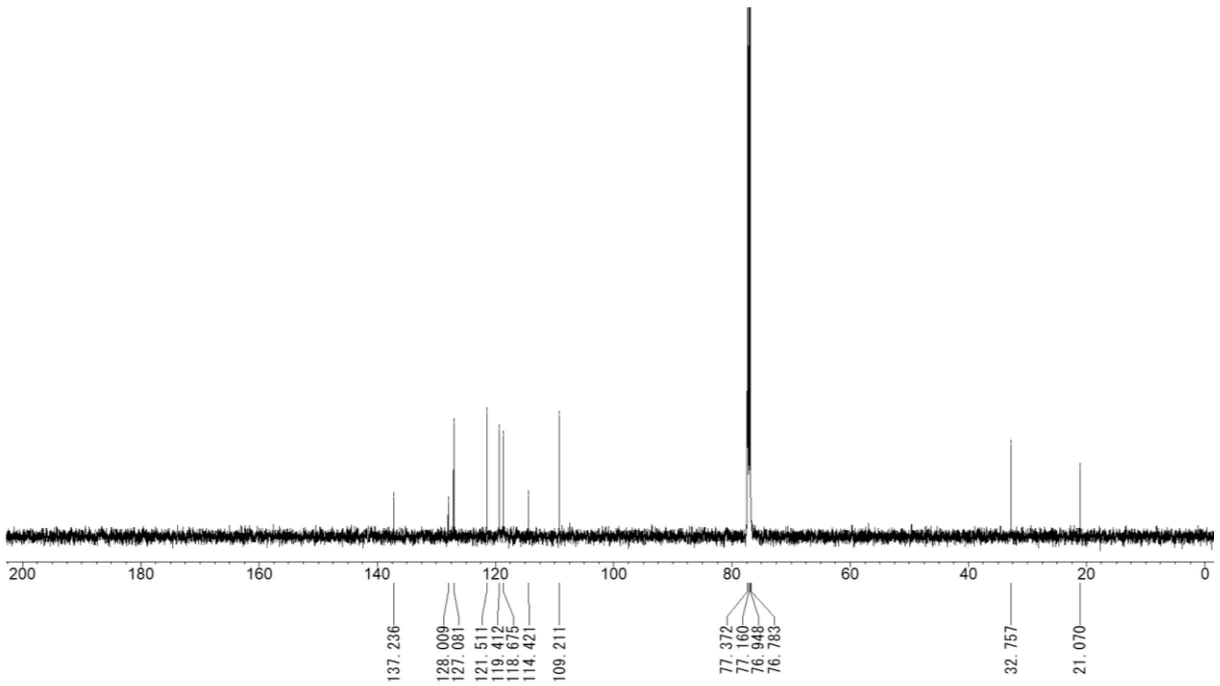
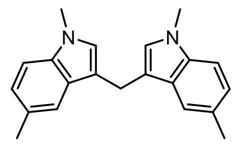


^{13}C NMR spectrum of **10a** (151 MHz, $CDCl_3$)



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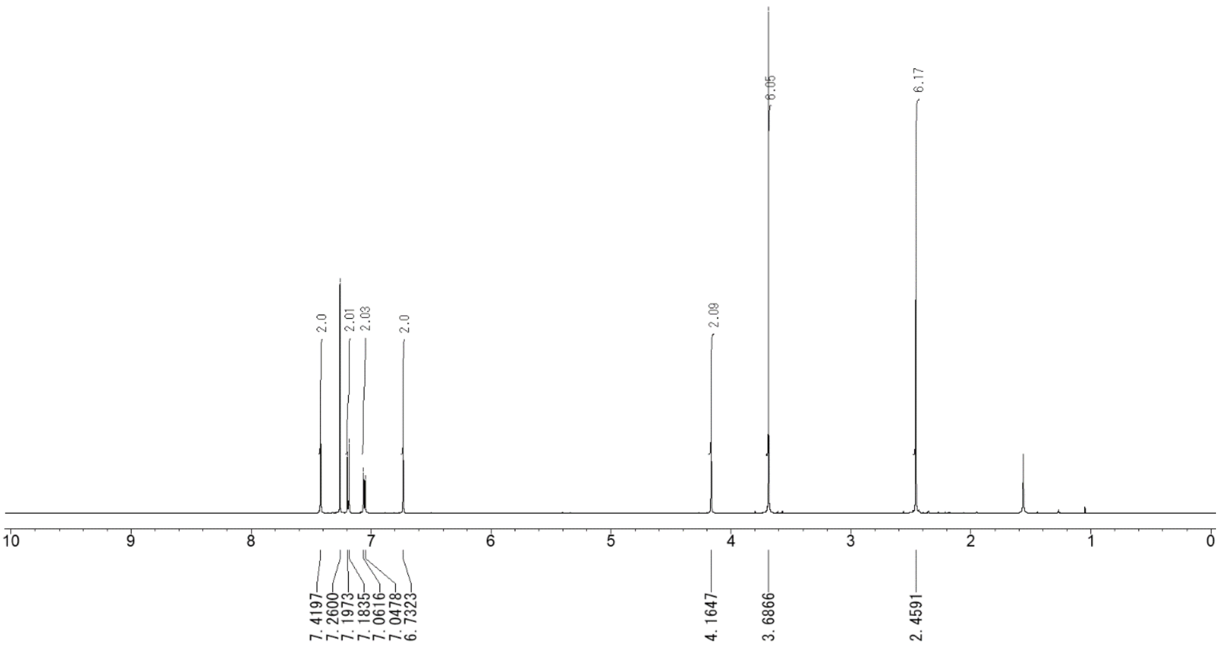
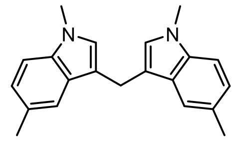


^{1}H NMR spectrum of **10b** (600 MHz, $CDCl_3$)



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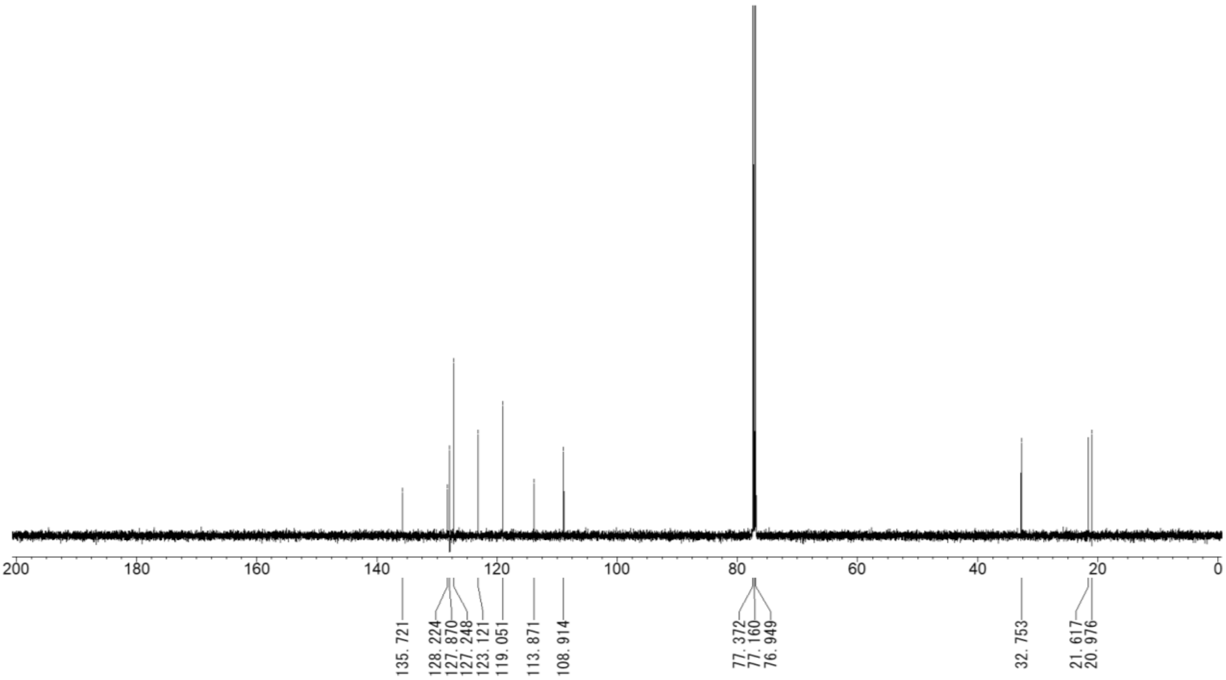
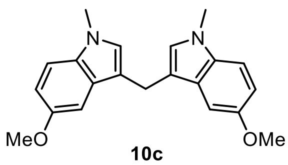


^{13}C NMR spectrum of **10b** (151 MHz, $CDCl_3$)



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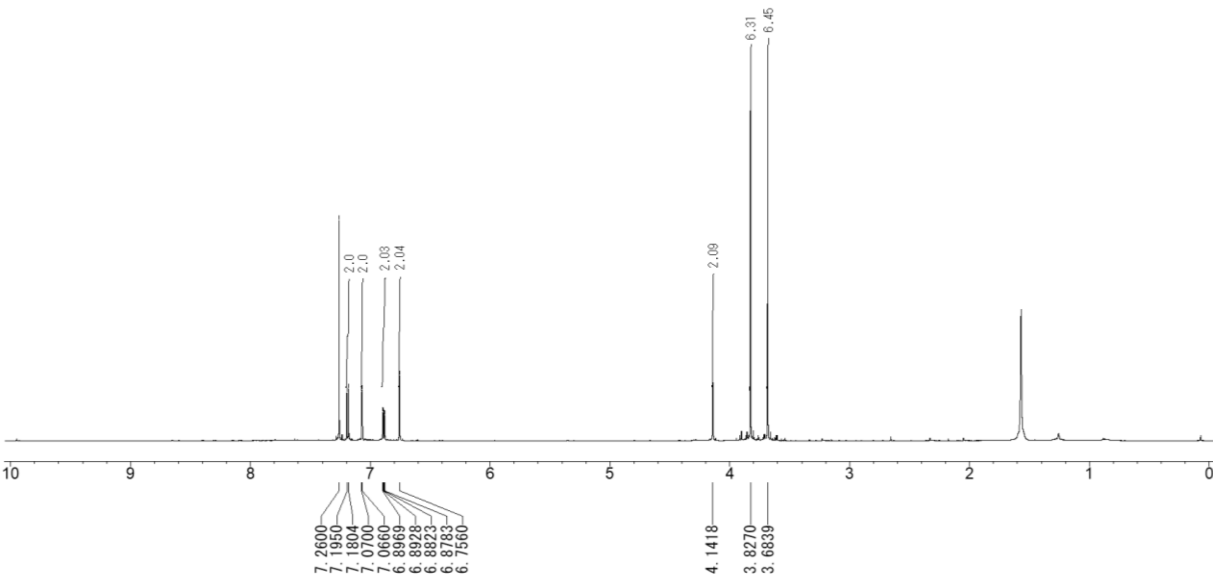
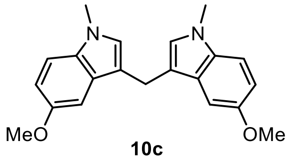
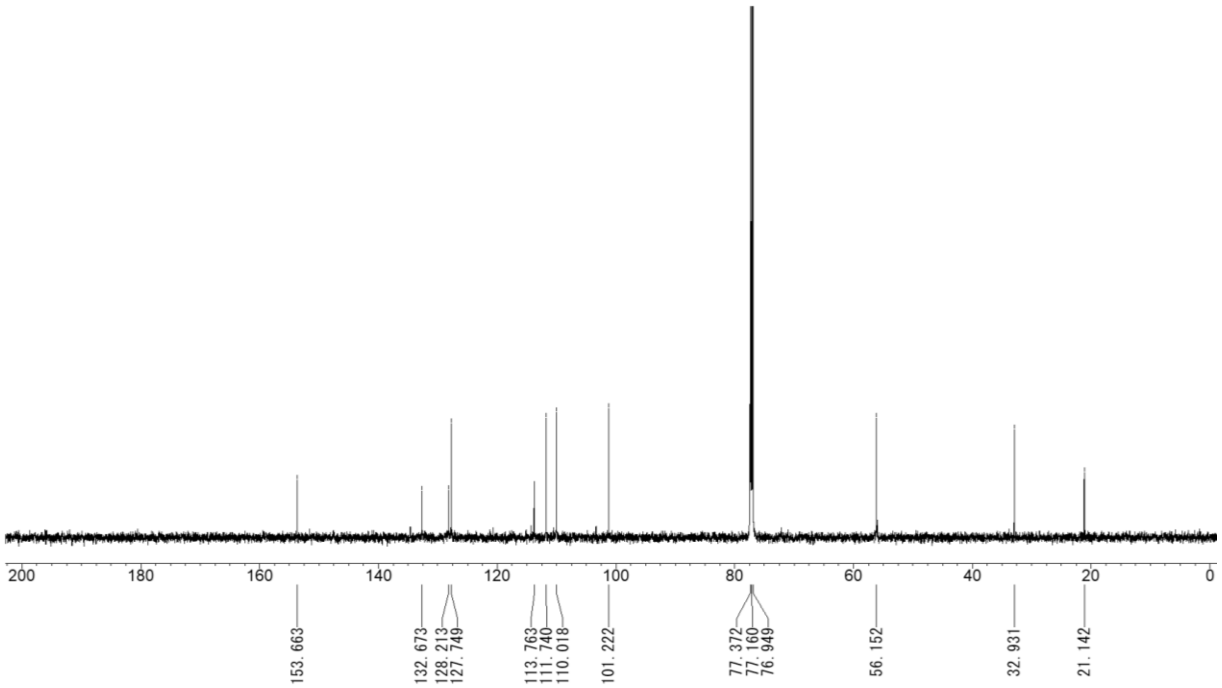


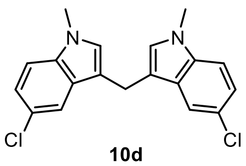
^{1}H NMR spectrum of **10c** (600 MHz, $CDCl_3$)



10c



^{13}C NMR spectrum of **10c** (151 MHz, $CDCl_3$)



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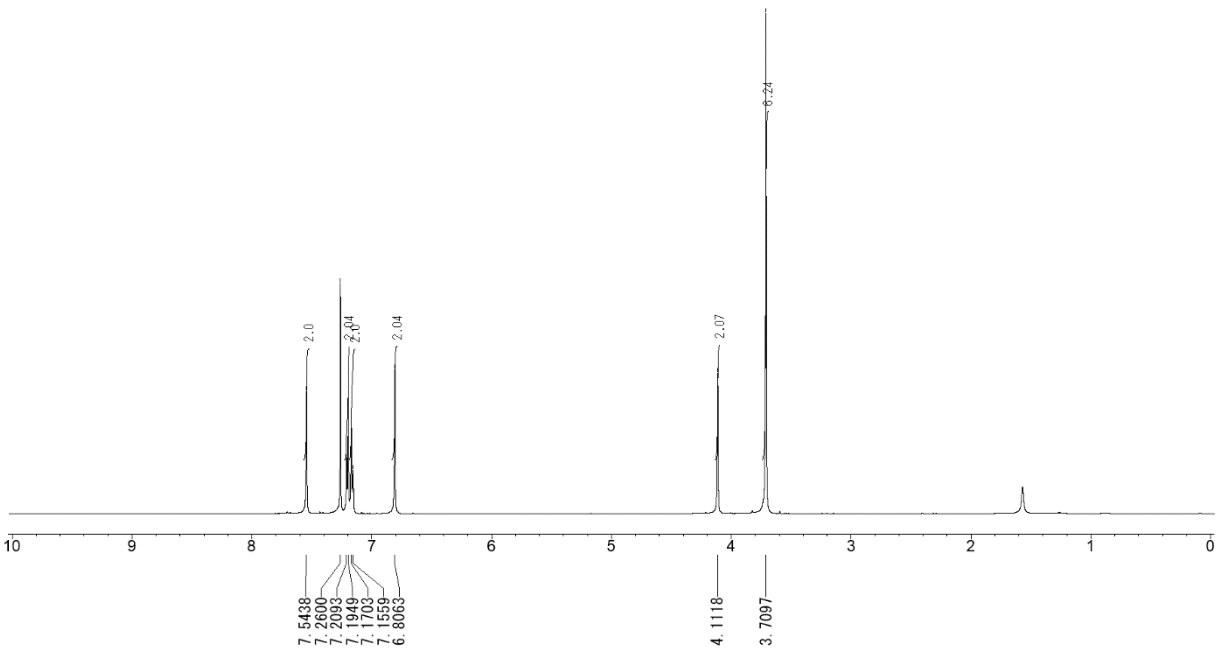
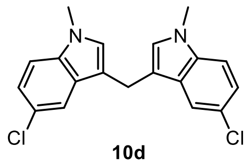


^{1}H NMR spectrum of **10d** (600 MHz, $CDCl_3$)



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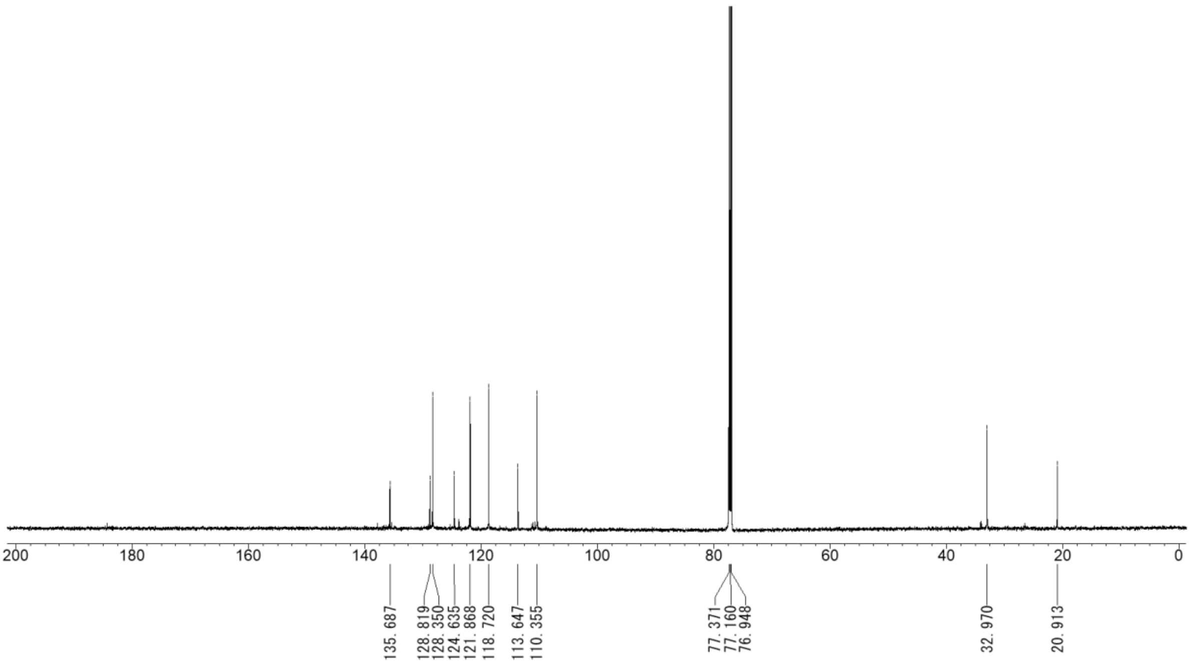
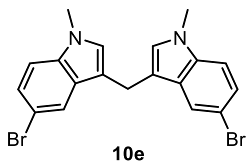


^{13}C NMR spectrum of **10d** (151 MHz, $CDCl_3$)



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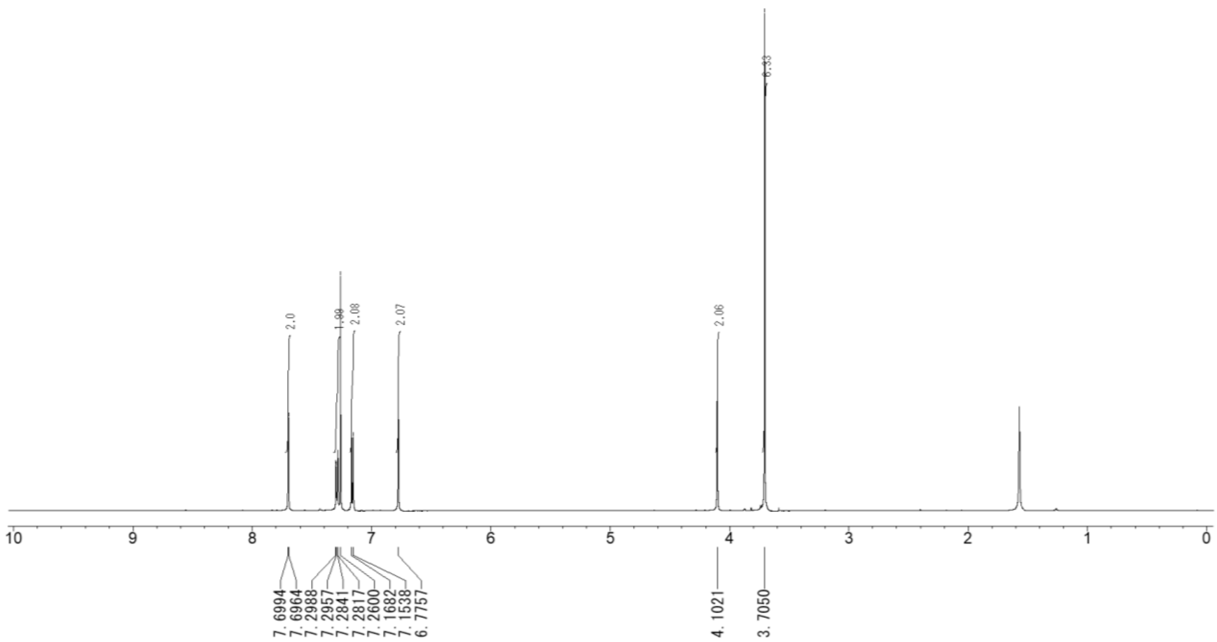
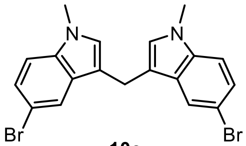


^{1}H NMR spectrum of **10e** (600 MHz, $CDCl_3$)



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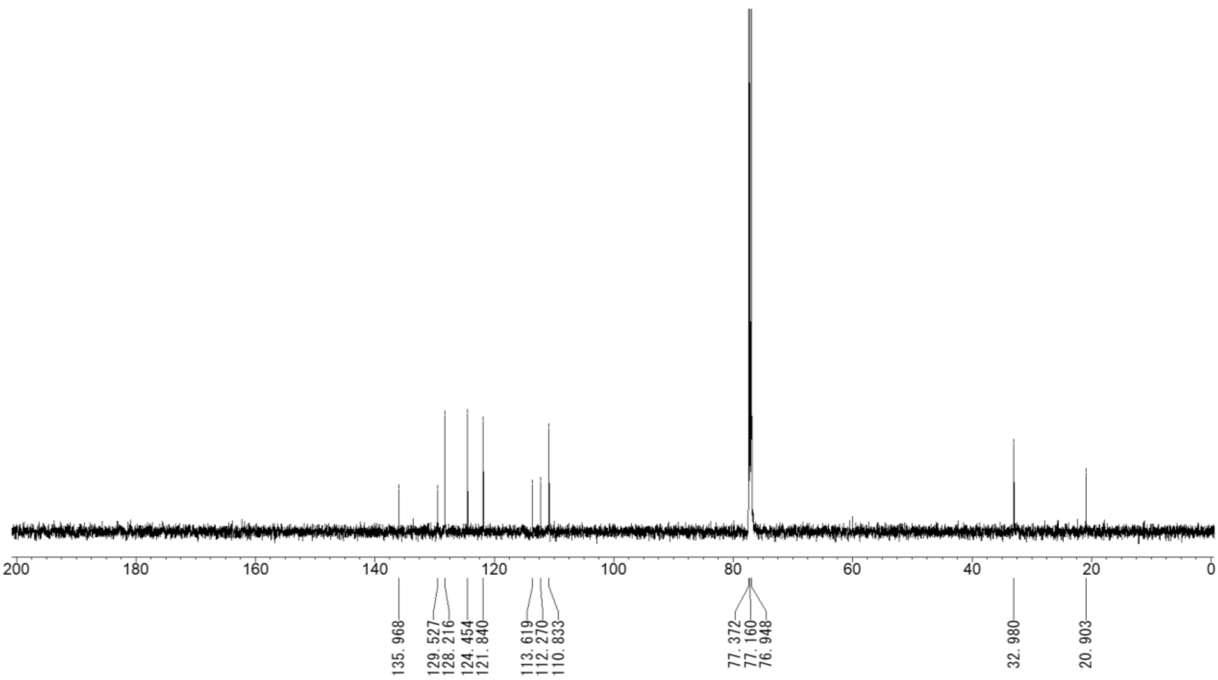
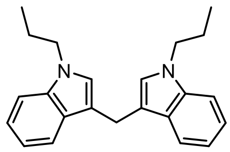


^{13}C NMR spectrum of **10e** (151 MHz, $CDCl_3$)



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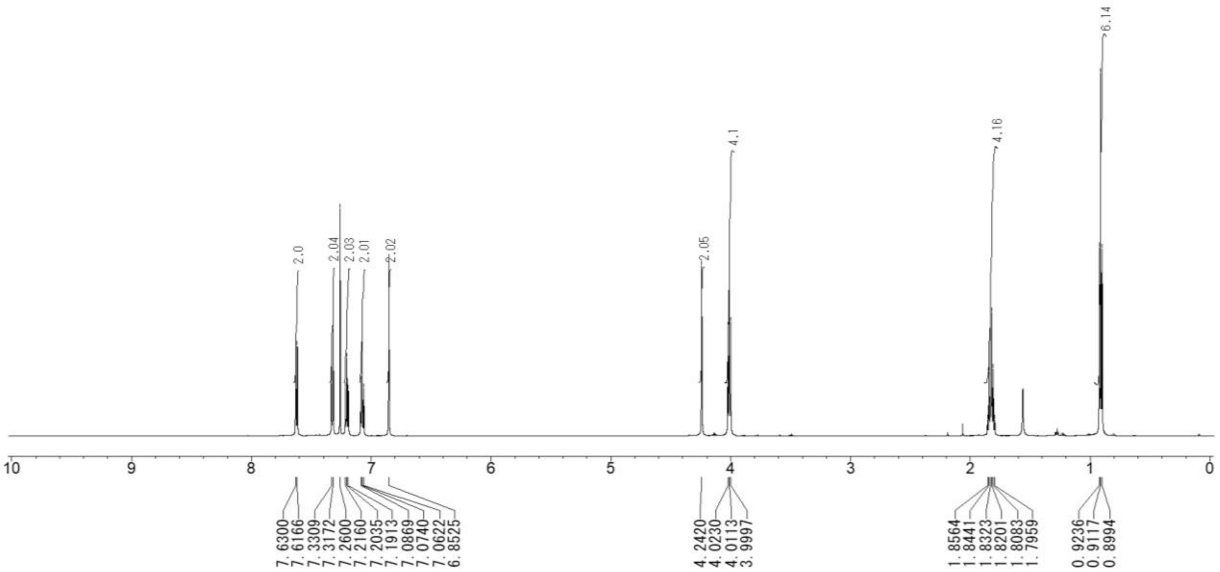
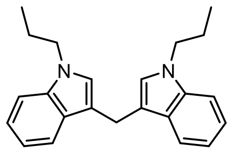


^1H NMR spectrum of **10f** (600 MHz, $CDCl_3$)



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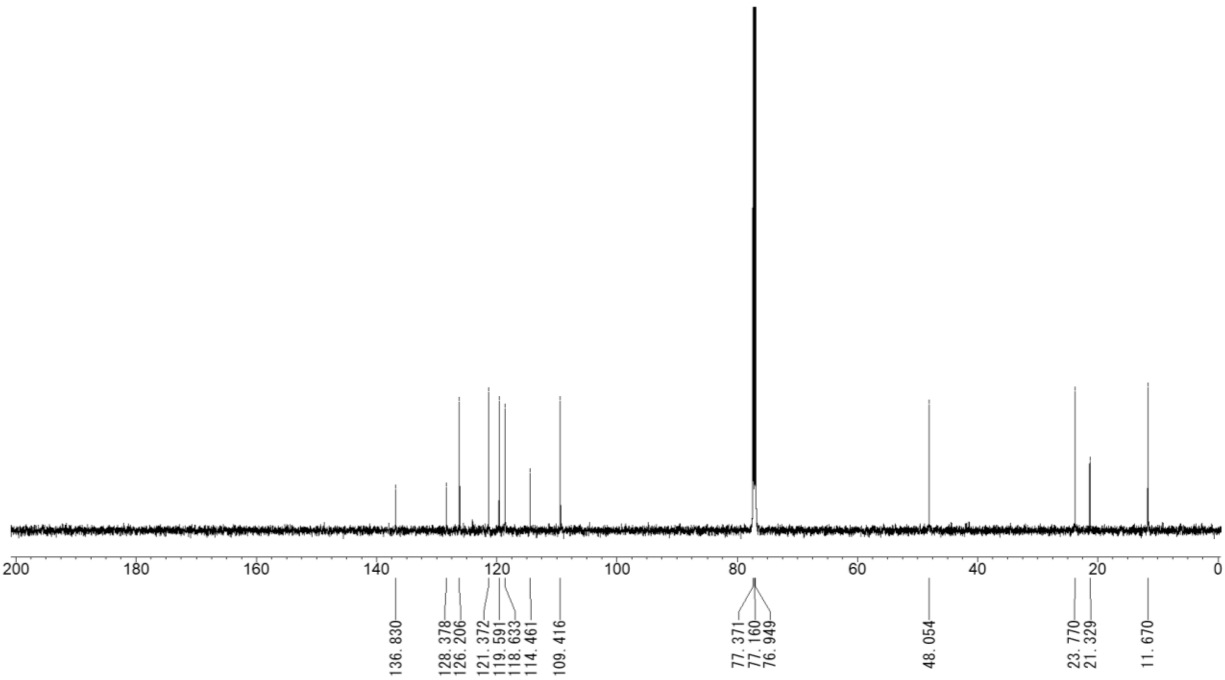
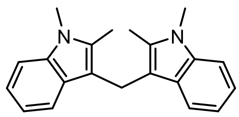
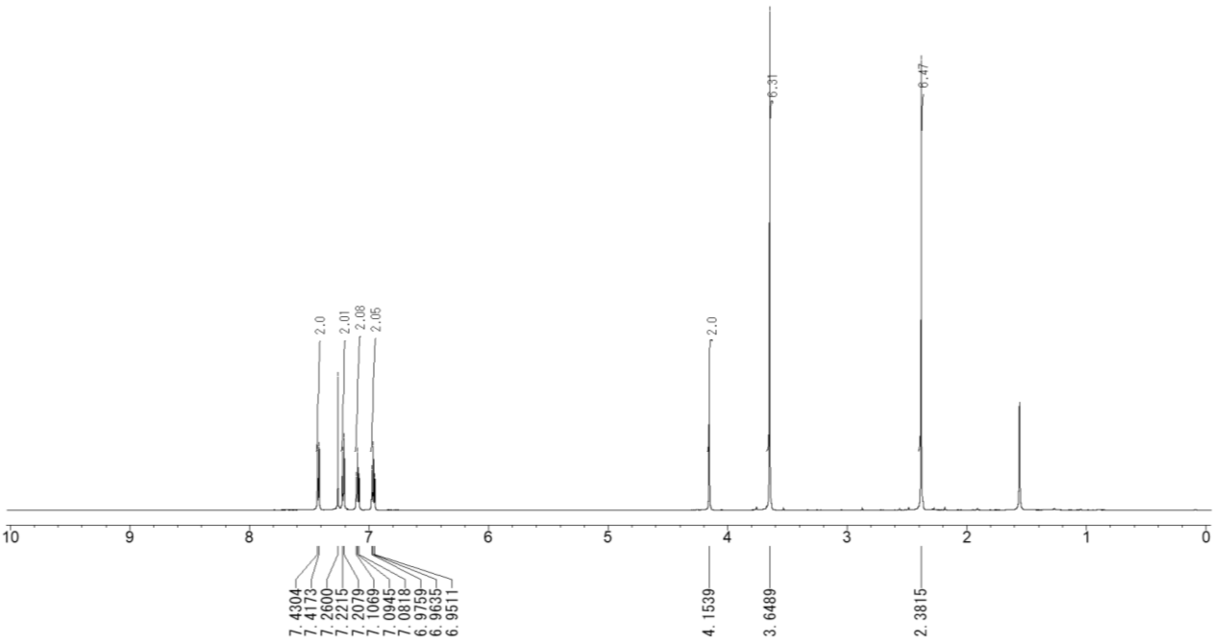


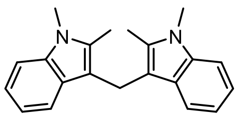
^{13}C NMR spectrum of **10f** (151 MHz, $CDCl_3$)



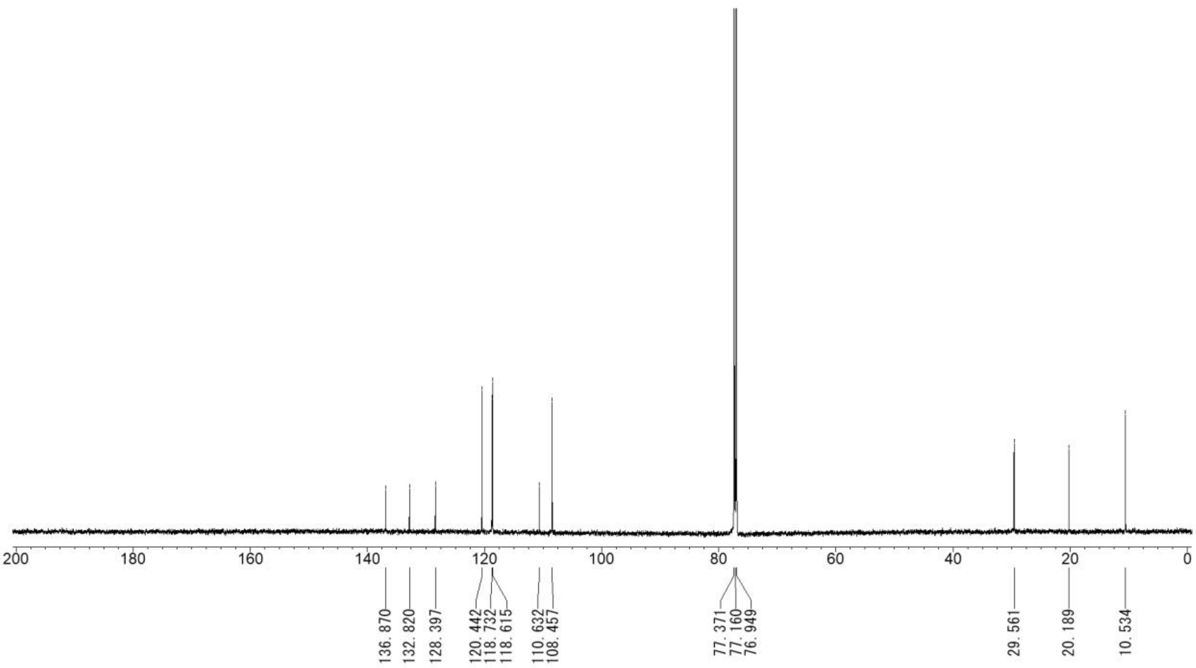
10g



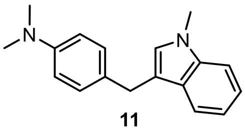
^{1}H NMR spectrum of **10g** (600 MHz, $CDCl_3$)



10g



^{13}C NMR spectrum of **10g** (151 MHz, $CDCl_3$)



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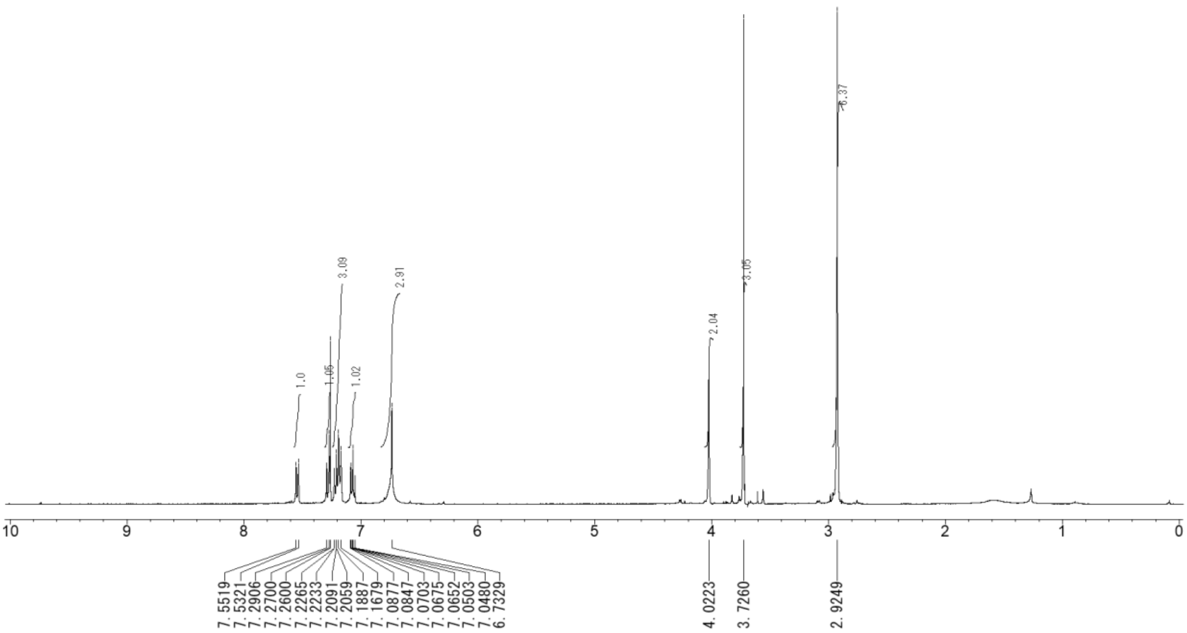
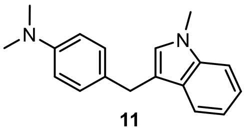


[1]H NMR spectrum of **11** (400 MHz, $CDCl_3$)



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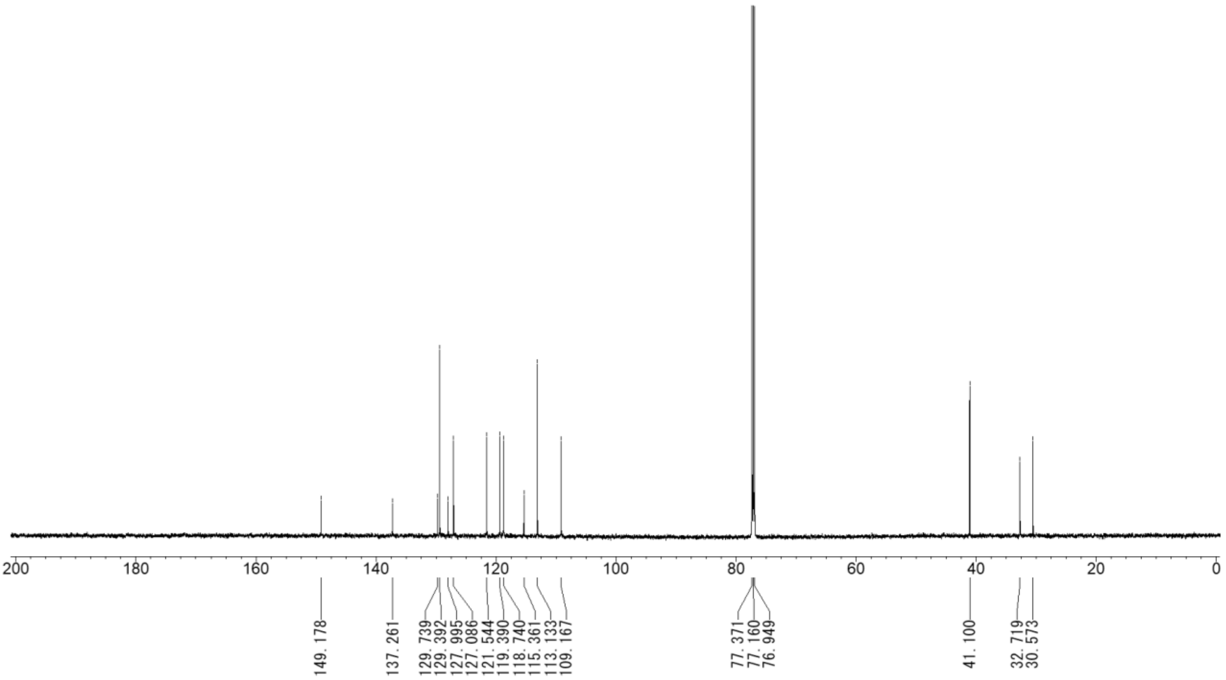

^{13}C NMR spectrum of **11** (151 MHz, $CDCl_3$)

6. Coordinates of optimized structures

Coordinates of Zn^{II} complex $\mathbf{1}_{\mathbf{Si}}$ in Fig. S10.

Zn	-4.624220	0.255814	-0.074613
Zn	-1.496302	-0.140358	0.299474
Zn	2.139647	3.611482	-0.423999
Zn	1.587425	0.084914	0.076406
Zn	1.854601	-3.385646	-0.797451
O	-3.044155	1.418332	0.440946
O	0.155824	3.401488	-0.069152
O	2.926662	1.715411	-0.360226
O	2.728748	-1.449440	-0.975207
O	-0.112621	-3.116297	-0.613425
O	-3.172808	-1.089632	-0.645763
O	-0.047957	0.272157	-0.779525
N	-4.942539	0.093820	2.159423
N	-6.257125	-1.249995	0.199522
N	1.705114	3.795541	-2.594440
N	4.102844	4.296652	-1.493725
N	3.068408	3.925523	1.584258
N	1.822500	5.821318	0.139809
N	1.863802	-3.418731	-3.069095
N	1.408343	-5.614546	-1.549178
N	1.838405	-4.203531	1.283495
N	3.927361	-4.154653	-0.403959
N	-4.895841	0.561908	-2.315756
N	-6.193650	1.871152	-0.325346
C	-2.475426	3.619303	1.145035
C	-3.018479	2.343073	1.393598
C	-3.545861	2.039569	2.709705
C	-3.477859	2.992787	3.711890
C	-2.904600	4.264767	3.501433
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