

Supporting Information
for

**Tetracoordinate silicon complexes of 1,2-bis(indol-2-yl)benzene as blue-emitting
dyes in the solid state**

Takayuki Tanaka* and Atsuhiko Osuka*

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502 (Japan)

E-mail: taka@kuchem.kyoto-u.ac.jp; osuka@kuchem.kyoto-u.ac.jp

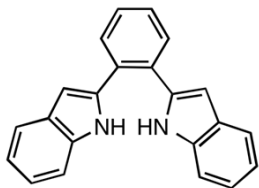
Contents

1. Instrumentation and Materials
2. Experimental Section
3. NMR Spectra
4. Mass Spectra
5. X-Ray Crystallographic Details
6. Optical Properties
7. DFT Calculations
8. Supporting References

1. Instrumentation and Materials

Commercially available solvents and reagents were used without further purification unless otherwise noted. The spectroscopic grade solvents were used as solvents for all spectroscopic studies. Silica gel column chromatography was performed on Wakogel C-300. Alumina column chromatography was performed on Sumitomo γ -Alumina. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F254 (Merck 5554). UV/Visible absorption spectra were recorded on Shimadzu UV-3600 spectrometers. Fluorescence spectra were recorded on a Shimadzu RF-5300PC spectrometer. Absolute fluorescence quantum yields were determined on a HAMAMATSU C9920-02S. ^1H , ^{13}C and ^{29}Si NMR spectra were recorded on a JEOL ECA-600 spectrometer (operating as 600 MHz for ^1H , 151 MHz for ^{13}C , and 119 MHz for ^{29}Si) using the residual solvents as the internal references for ^1H ($\delta = 7.26$ ppm in CDCl_3 and $\delta = 2.08$ ppm in toluene- d_8) and for ^{13}C ($\delta = 77.16$ ppm in CDCl_3) and tetramethylsilane as the external reference for ^{29}Si ($\delta = 0.00$ ppm in toluene- d_8). High-resolution atmospheric-pressure- chemical-ionization time-of-flight mass-spectroscopy (HR-APCI-TOF-MS) was recorded on a BRUKER micrOTOF model using positive mode. Mass spectra were recorded on a Shimadzu AXIMA-CFRplus using positive-MALDI-TOF method with matrix. Single-crystal diffraction analysis data were collected at -180 °C with a Rigaku XtaLAB P200 by using graphite monochromated Cu- $K\alpha$ radiation ($\lambda = 1.54187$ Å). The structures were solved by direct methods (SHELXS-97) and refined with full-matrix least square technique (SHELXL-97).

2. Experimental Section



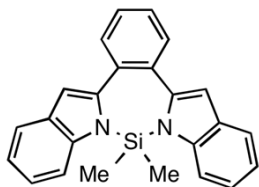
1,2-Bis(indol-2-yl)benzene (1).

To a dry Schlenk tube, indole-2-boronic acid pinacolate ester (1.40 g, 5.74 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (141 mg, 7.5 mol%), and dry dioxane (5.0 mL) were added. Degassed K_2CO_3 aq. (1.0 mL, 4.59 mmol) and 1,2-diiodobenzene (0.30 mL, 2.30 mmol) were then added, and the mixture was deoxygenated through freeze–pump–thaw cycle. The mixture was stirred at 90 °C for 24 h. After cooling to room temperature, the reaction was quenched by addition of water, extracted with ethyl acetate and washed by brine. The organic phase was dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica with dichloromethane as an eluent. Recrystallization from dichloromethane/*n*-hexane afforded 1,2-bis(indol-2-yl)benzene (**1**) as a white solid (492 mg, 1.59 mmol, 70%).

1; 1H NMR ($CDCl_3$) δ (ppm): 7.96 (s, 2H, NH), 7.68 (dd, $J = 3.2, 5.5$ Hz, 2H, benzene-H), 7.62 (m, 2H, indole-H), 7.45 (dd, $J = 3.2, 5.5$ Hz, 2H, benzene-H), 7.14–7.09 (m, 6H, indole-H) and 6.71 (d, 2H, $J = 2.3$ Hz, indole-H); ^{13}C NMR ($CDCl_3$) δ (ppm): 137.16, 136.67, 130.95, 130.90, 128.57, 128.47, 122.57, 120.72, 120.32, 111.24, and 102.78; HR-APCI-TOF-MS $m/z = 309.1375$, calcd. for $C_{22}H_{16}N_2 = 309.1386$ $[M+H]^+$. UV-vis (CH_2Cl_2) λ_{max} ($[M^{-1}cm^{-1}]$) = 293 (23000) nm; Fluorescence (CH_2Cl_2 , $\lambda_{ex} = 340$ nm) $\lambda_{max} = 422$ nm, $\phi_F = 0.58$; Fluorescence (powder, $\lambda_{ex} = 330$ nm) $\lambda_{max} = 440$ and 471 nm, $\phi_F = 0.09$.

General procedure for the synthesis of silicon complexes

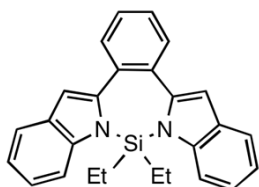
Potassium bis(trimethylsilyl)amide (0.5 M in toluene, 2.4 equiv.) was added to a solution of **1** in THF at 0 °C. After 15 min, dialkyl/diaryldichlorosilane (1.2 equiv.) was added dropwise, and the solution was allowed to gradually warm to room temperature over 12 h, at which time the reaction was quenched with a mixture of water and ethyl acetate. The organic extracts were washed with water and brine, dried over anhydrous Na_2SO_4 , and evaporated under reduced pressure. The residue was purified by column chromatography on silica with a mixture of dichloromethane and *n*-hexane as eluent to yield silicon complexes as off-white solids.



According to the general procedure, dimethyldichlorosilane (0.046 mL, 0.39 mmol) was reacted with **1** (100 mg, 0.32 mmol). Yield; 69 mg (0.19 mmol, 58%).

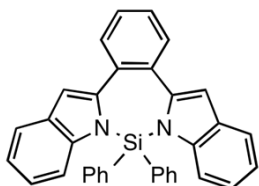
2a; 1H NMR (toluene- d_8 , -80 °C) δ (ppm): 7.70 (d, $J = 7.8$ Hz, 2H, indole-H), 7.45 (dd, $J = 5.5, 3.7$ Hz, 2H, phenyl-H), 7.37 ($J = 8.7$ Hz, 2H, indole-H), 7.33 (t, $J = 7.3$ Hz, 2H, indole-H), 7.25 (t, $J = 7.3$ Hz, 2H,

indole-H), 7.10 (dd, $J = 5.5, 3.7$ Hz, 2H, phenyl-H), 6.57 (s, 2H, indole-H), 0.68 (s, 3H, Me), and -0.18 (s, 3H, Me); ^{13}C NMR (CDCl_3 , 60°C) δ (ppm): 144.19, 141.39, 133.31, 131.69, 131.48, 128.90, 122.51, 120.97, 120.90, 112.89, 108.47 and 2.87; $^{29}\text{Si}\{^1\text{H}\}$ (toluene- d_8 , -80°C) 1.51 ppm; HR-APCI-TOF-MS $m/z = 365.1488$, calcd. for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{Si}_1 = 365.1469$ $[M+H]^+$; UV-vis (CH_2Cl_2) λ_{max} ($[\text{M}^{-1}\text{cm}^{-1}]$) = 293 (26000) nm; Fluorescence (CH_2Cl_2 , $\lambda_{\text{ex}} = 330$ nm) $\lambda_{\text{max}} = 395$ nm, $\phi_F = 0.58$; Fluorescence (powder, $\lambda_{\text{ex}} = 330$ nm) $\lambda_{\text{max}} = 379$ nm, $\phi_F = 0.55$.



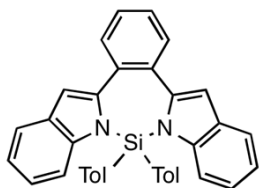
According to the general procedure, diethyldichlorosilane (0.12 mL, 0.78 mmol) was reacted with **1** (200 mg, 0.65 mmol). Yield; 103 mg (0.26 mmol, 40%).

2b; ^1H NMR (toluene- d_8 , -80°C) δ (ppm): 7.70 (d, $J = 7.8$ Hz, 2H, indole-H), 7.48 (dd, $J = 5.5, 3.7$ Hz, 2H, phenyl-H), 7.35 ($J = 8.7$ Hz, 2H, indole-H), 7.32 (t, $J = 7.6$ Hz, 2H, indole-H), 7.27 (t, $J = 7.6$ Hz, 2H, indole-H), 7.11 (dd, $J = 5.5, 3.7$ Hz, 2H, phenyl-H), 6.55 (s, 2H, indole-H), 1.34 (br, 2H, Et), 0.87 (t, $J = 7.3$ Hz, 3H, Et), 0.52 (br, 2H, Et) and 0.45 (t, $J = 7.3$ Hz, 3H, Et); ^{13}C NMR (CDCl_3 , 60°C) δ (ppm): 144.25, 141.42, 133.56, 131.49, 131.33, 128.85, 122.56, 120.91, 120.84, 112.98, 108.57, 6.80 and 6.76; $^{29}\text{Si}\{^1\text{H}\}$ (toluene- d_8 , -80°C) 3.03 ppm; HR-APCI-TOF-MS $m/z = 393.1783$, calcd. for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{Si}_1 = 393.1782$ $[M+H]^+$; UV-vis (CH_2Cl_2) λ_{max} ($[\text{M}^{-1}\text{cm}^{-1}]$) = 294 (27000) nm; Fluorescence (CH_2Cl_2 , $\lambda_{\text{ex}} = 330$ nm) $\lambda_{\text{max}} = 394$ nm, $\phi_F = 0.58$; Fluorescence (powder, $\lambda_{\text{ex}} = 330$ nm) $\lambda_{\text{max}} = 390$ nm, $\phi_F = 0.49$.



According to the general procedure, diphenyldichlorosilane (0.30 mL, 1.17 mmol) was reacted with **1** (300 mg, 0.97 mmol). Yield; 461 mg (0.94 mmol, 97%).

2c; ^1H NMR (CDCl_3 , 50°C) δ (ppm): 7.60 (d, $J = 7.8$ Hz, 2H, indole-H), 7.53 (d, $J = 6.9$ Hz, 4H, Si-Ph), 7.51 (d, $J = 7.8$ Hz, 2H, Si-Ph), 7.40 (dd, $J = 5.5, 3.7$ Hz, 2H, phenyl-H), 7.34 (t, $J = 7.8$ Hz, 4H, Si-Ph), 7.19 (dd, $J = 5.5, 3.7$ Hz, 2H, phenyl-H), 7.06 (t, $J = 7.8$ Hz, 2H, indole-H), 6.88 (s, 2H, indole-H), 6.78 (t, $J = 7.4$ Hz, 2H, indole-H), and 6.43 (d, $J = 7.8$ Hz, 2H, indole-H); ^{13}C NMR (CDCl_3) δ (ppm): 145.20, 142.88, 136.91, 132.41, 132.32, 132.03, 131.99, 129.79, 128.47, 128.35, 121.45, 120.96, 120.33, 115.36, and 109.30; $^{29}\text{Si}\{^1\text{H}\}$ (toluene- d_8 , -80°C) -22.09 ppm; HR-APCI-TOF-MS $m/z = 489.1785$, calcd. for $\text{C}_{34}\text{H}_{24}\text{N}_2\text{Si}_1 = 489.1782$ $[M+H]^+$; UV-vis (CH_2Cl_2) λ_{max} ($[\text{M}^{-1}\text{cm}^{-1}]$) = 294 (25000) nm; Fluorescence (CH_2Cl_2 , $\lambda_{\text{ex}} = 350$ nm) $\lambda_{\text{max}} = 421$ nm, $\phi_F = 0.65$; Fluorescence (powder, $\lambda_{\text{ex}} = 330$ nm) $\lambda_{\text{max}} = 388$ nm, $\phi_F = 0.54$.



According to the general procedure, di(*p*-tolyl)dichlorosilane (0.15 mL, 0.58 mmol) was reacted with **1** (150 mg, 0.49 mmol). Yield; 155 mg (0.30 mmol, 62%).

2d; ^1H NMR (CD_2Cl_2 , r.t.) δ (ppm): 7.56 (d, $J = 7.8$ Hz, 2H, indole-H), 7.40 (dd, $J = 5.7, 3.5$ Hz, 2H, phenyl-H), 7.34 (d, $J = 7.8$ Hz, 4H, tolyl-H), 7.21 (dd, $J = 5.7, 3.5$ Hz, 2H, phenyl-H), 7.15 (d, $J = 7.8$ Hz, 4H, tolyl-H), 7.01 (t, $J = 7.3$ Hz, 2H, indole-H), 6.86 (s, 2H), 6.74 (t, $J = 7.3$ Hz, 2H, indole-H), 6.42 (d, $J = 8.7$ Hz, 2H, indole-H) and 2.36 (s, 6H, tolyl-Me); ^{13}C NMR (CDCl_3) δ (ppm): 145.27, 142.92, 142.21, 136.92, 132.47, 132.25, 131.93, 129.13, 128.39, 126.34, 121.33, 120.82, 120.23, 115.48, 109.14, and 21.95; $^{29}\text{Si}\{^1\text{H}\}$ (toluene- d_8 , -80 °C) -22.21 ppm; HR-APCI-TOF-MS $m/z = 517.2105$, calcd. for $\text{C}_{36}\text{H}_{28}\text{N}_2\text{Si}_1 = 517.2095$ [$M+\text{H}$] $^+$; UV-vis (CH_2Cl_2) λ_{max} ($[\text{M}^{-1}\text{cm}^{-1}]$) = 295 (26000) nm; Fluorescence (CH_2Cl_2 , $\lambda_{\text{ex}} = 340$ nm) $\lambda_{\text{max}} = 419$ nm, $\phi_F = 0.62$; Fluorescence (powder, $\lambda_{\text{ex}} = 330$ nm) $\lambda_{\text{max}} = 386$ nm, $\phi_F = 0.71$.

3. NMR Spectra

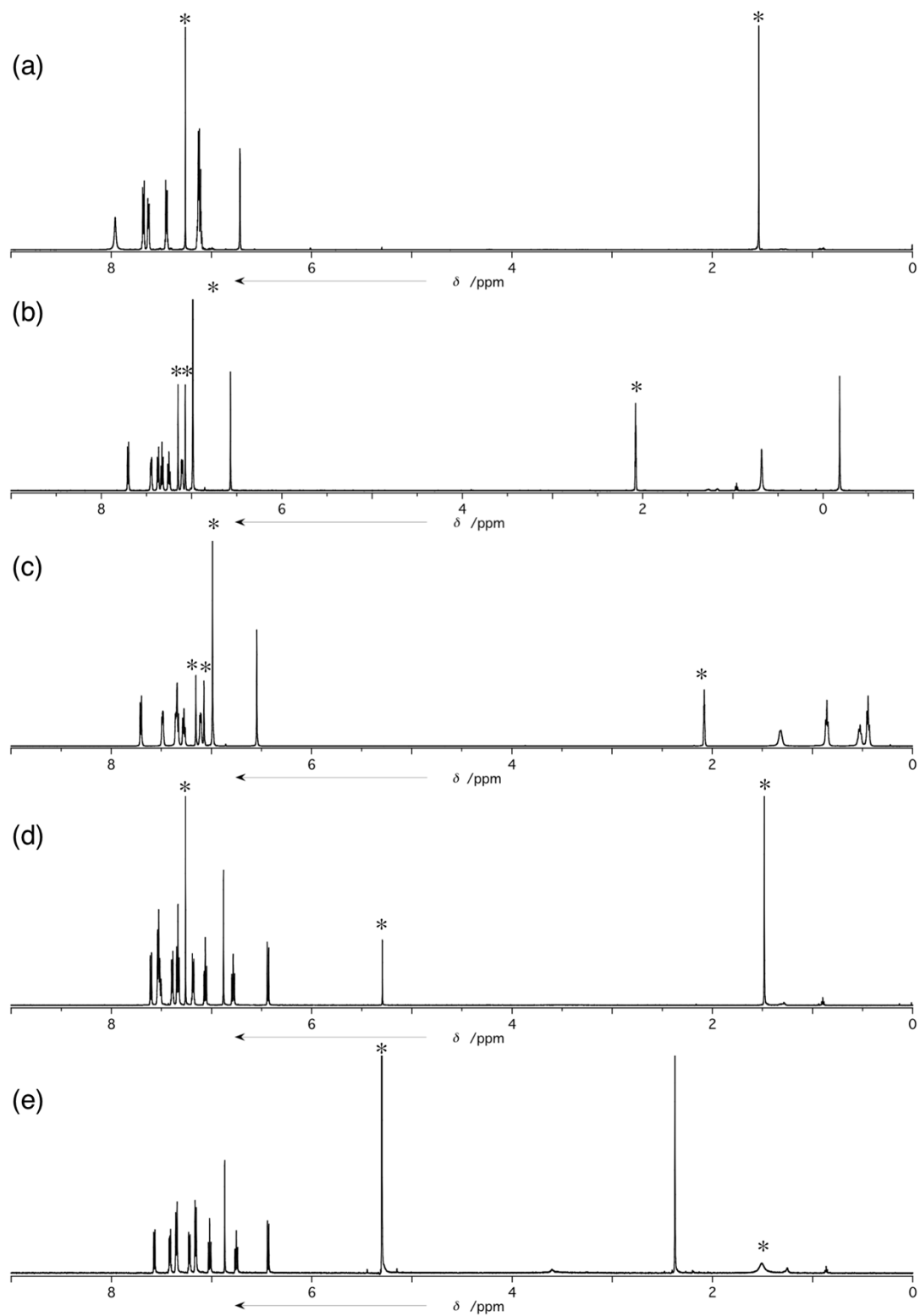


Figure S1. ^1H NMR spectra of (a) **1** at r.t. in CDCl_3 , (b) **2a** at -80°C in $\text{toluene-}d_8$, (b) **2b** -80°C in $\text{toluene-}d_8$, (d) **2c** at 50°C in CDCl_3 , and (e) **2d** at r.t. in CD_2Cl_2 . * means residual solvent peaks.

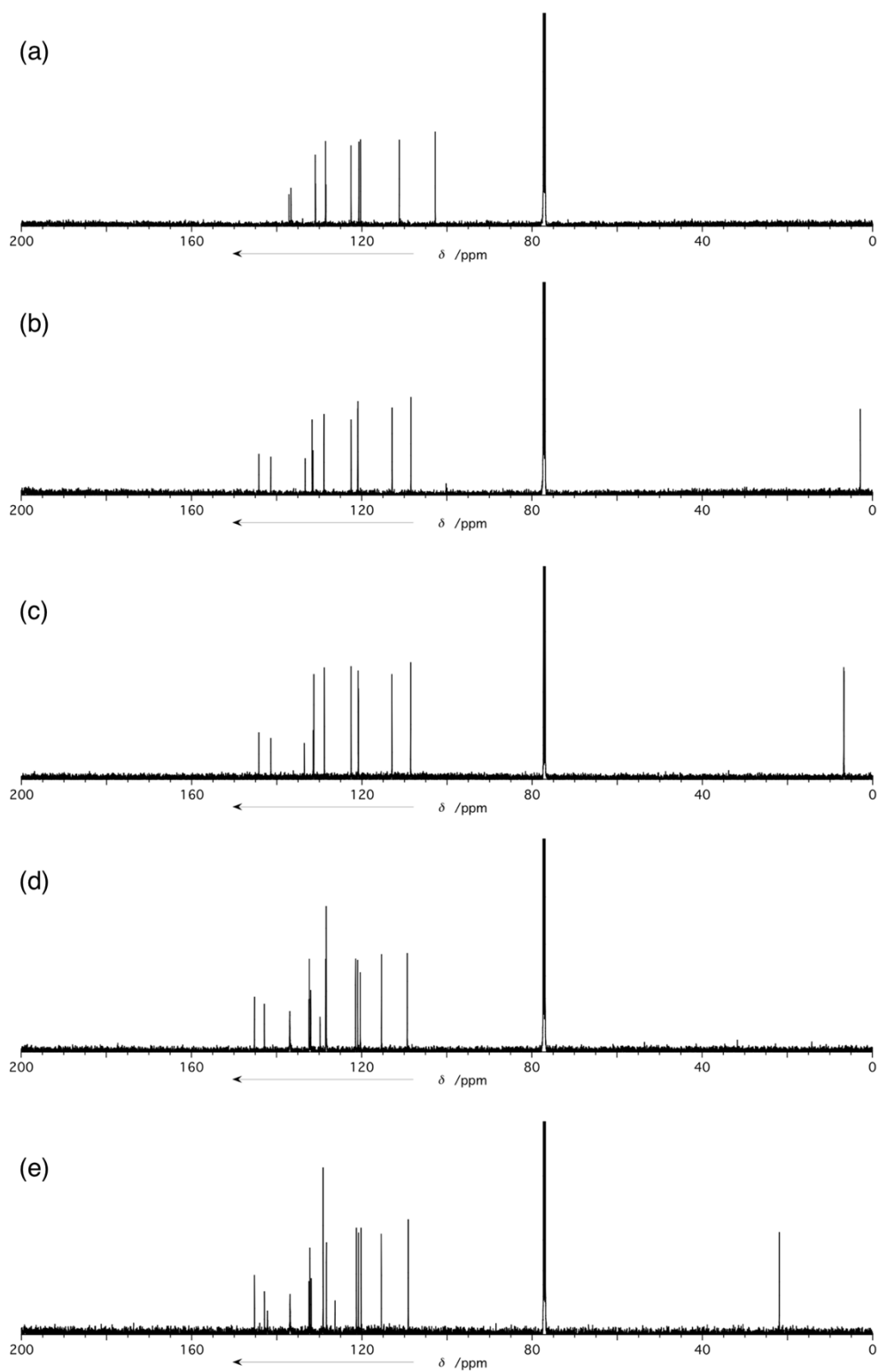


Figure S2. ^{13}C NMR spectra of (a) **1** at r.t., (b) **2a** at 60 °C, (b) **2b** at 60 °C, (d) **2c** at r.t., and (c) **2d** at r.t. in CDCl_3 .

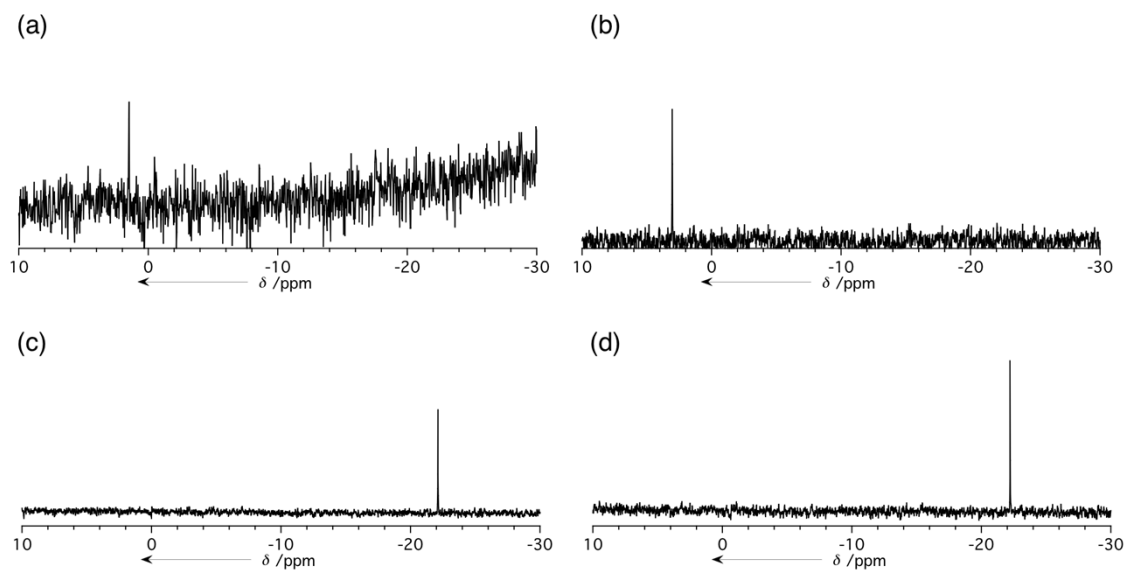


Figure S3. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of (a) **2a**, (b) **2b**, (c) **2c**, and (d) **2d** at $-80\text{ }^\circ\text{C}$ in toluene- d_8 .

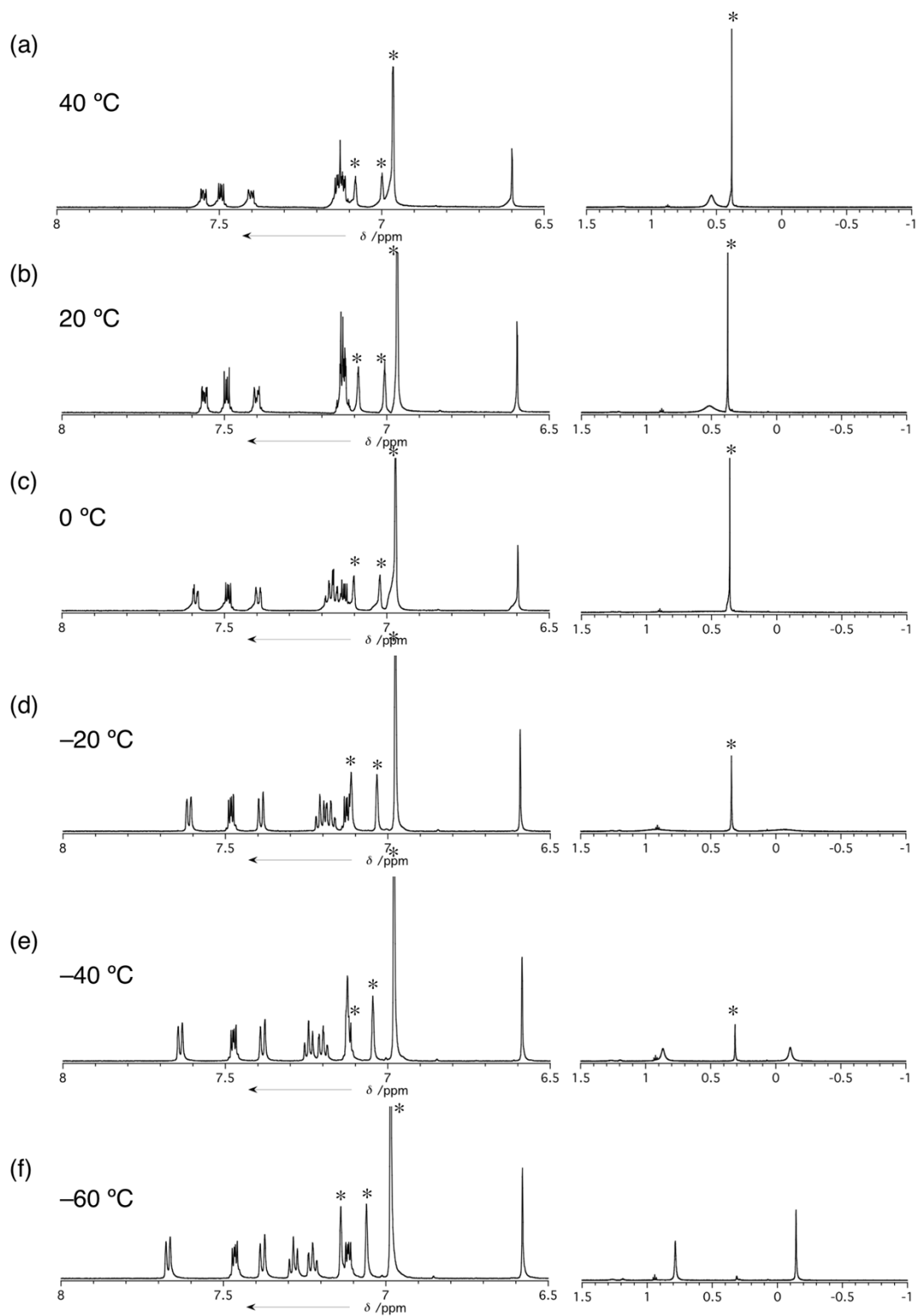


Figure S4. Variable-temperature ^1H NMR spectra of **2a** in $\text{toluene-}d_8$. * means residual solvent peaks.

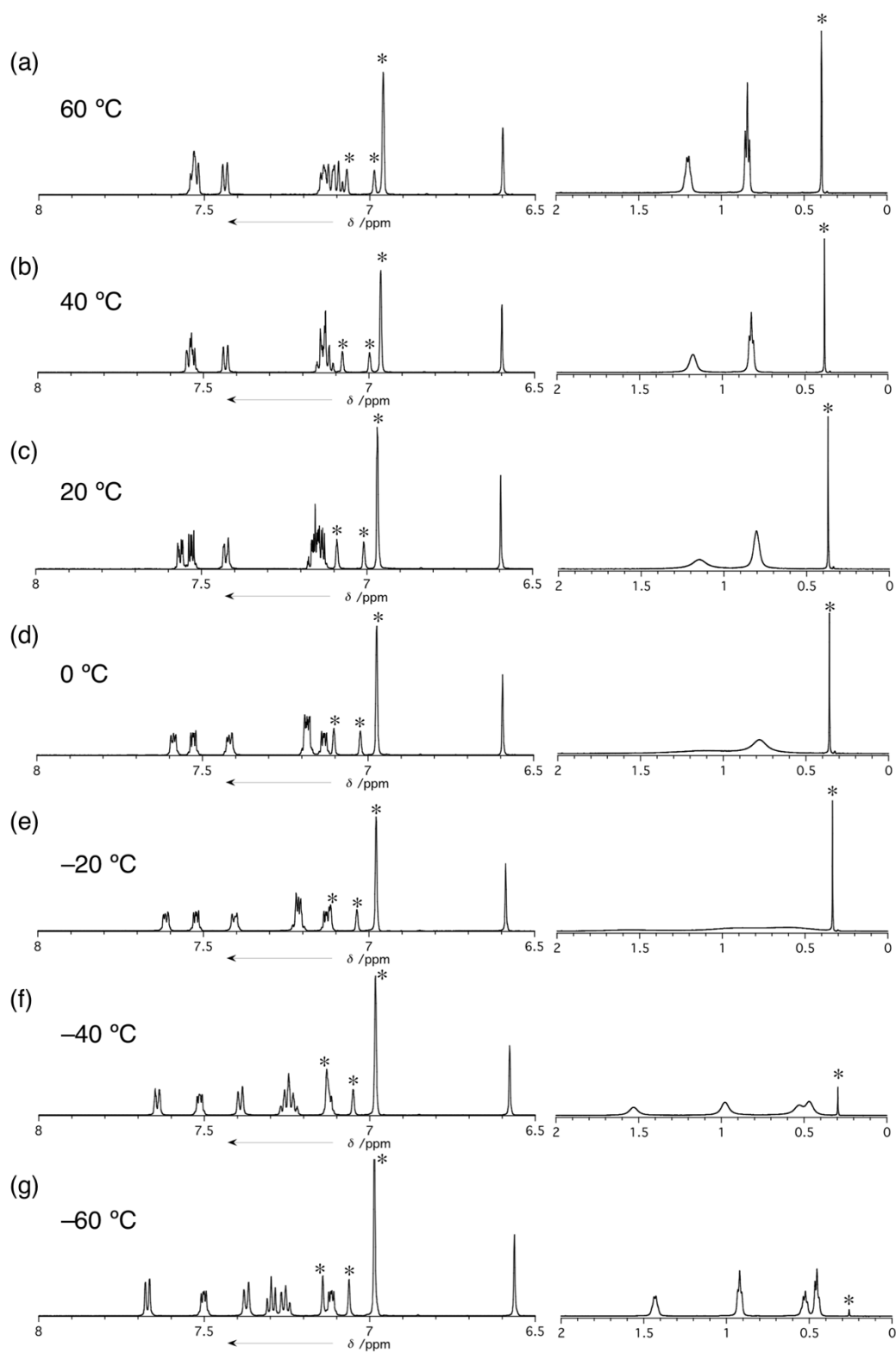


Figure S5. Variable-temperature ^1H NMR spectra of **2b** in toluene- d_8 . * means residual solvent peaks.

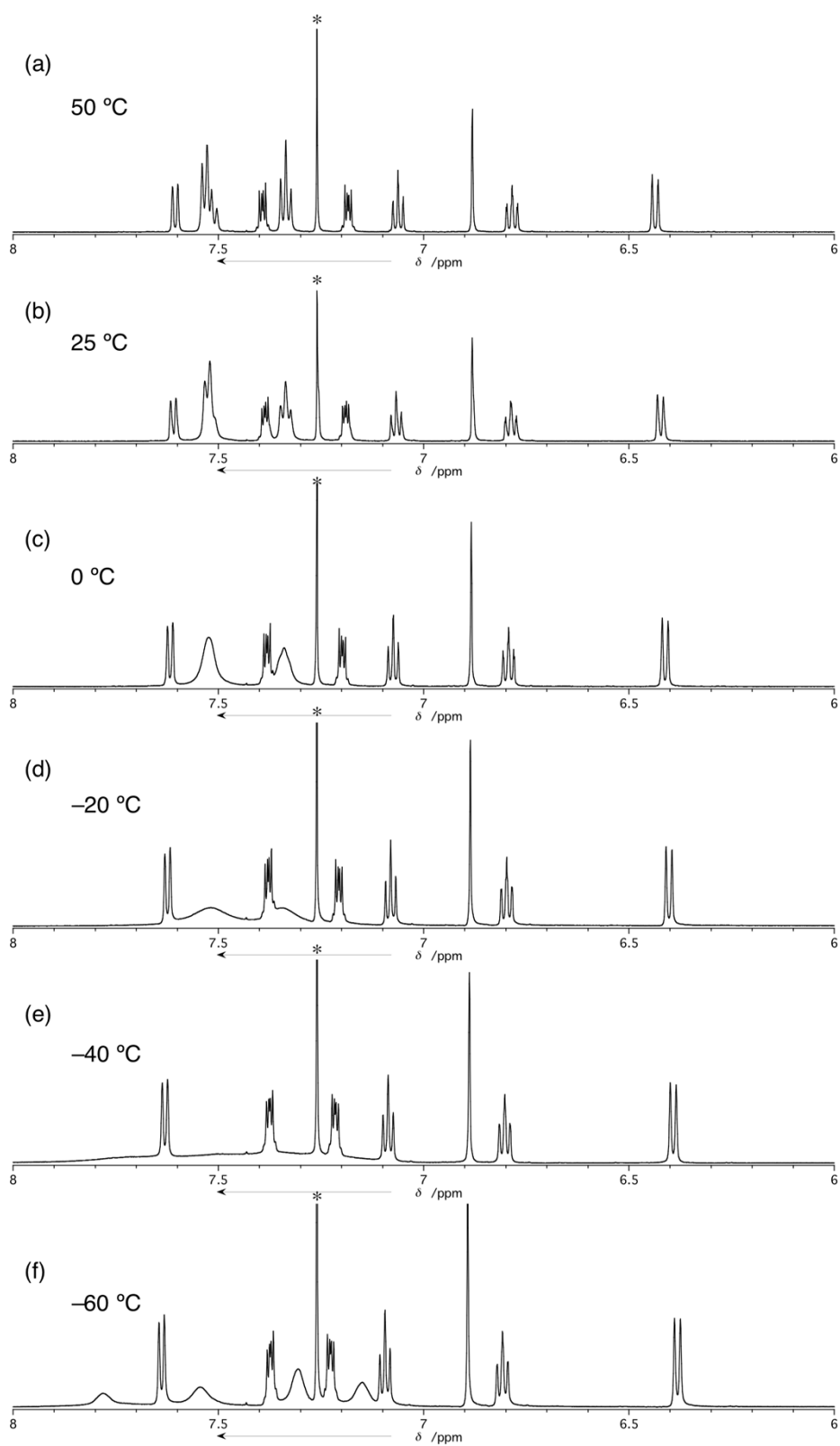


Figure S6. Variable-temperature ^1H NMR spectra of **2c** in CDCl_3 . * means residual solvent peaks.

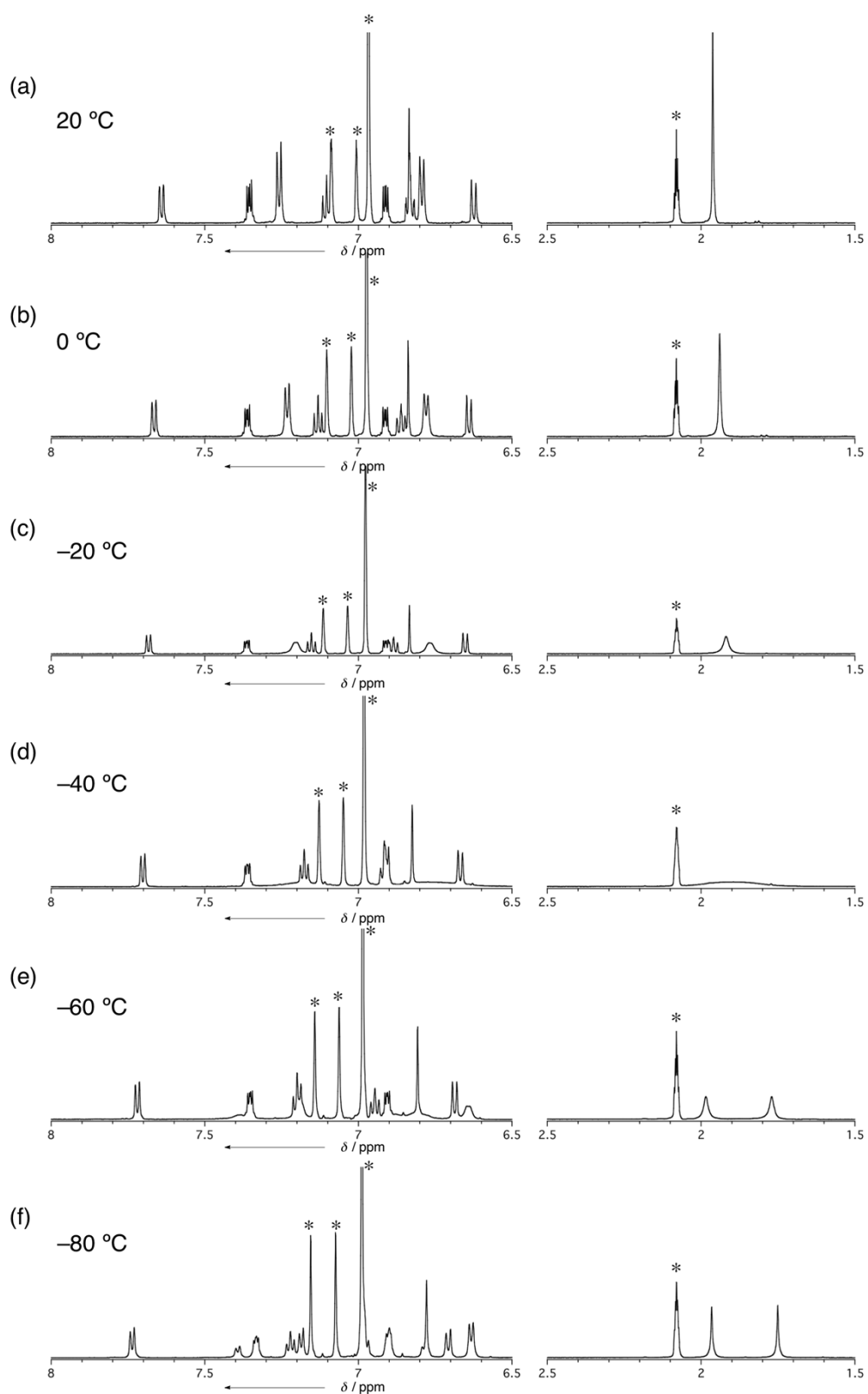


Figure S7. Variable-temperature ^1H NMR spectra of **2d** in $\text{toluene-}d_8$. * means residual solvent peaks.

Table S1. Simulated exchange rate constants (k) for **2a** and **2d** at various temperatures.^[a]

(a) 2a in toluene- d_8		(b) 2d in toluene- d_8	
T [K]	k [s^{-1}]	T (K)	k [s^{-1}]
303	54000	263	16000
298	32000	253	4400
293	18000	243	1450
283	4700	238	800
273	1300	233	500
263	550	228	290
258	350	223	180
253	200	218	80
248	45	213	41
		203	6.0

[a] The rate constants (k) were determined by simulations of singlet peaks observed at 0.54 ppm at 313 K for **2a**, and at 2.36 ppm at 273 K for **2d** by the DNMR program.^{S1}

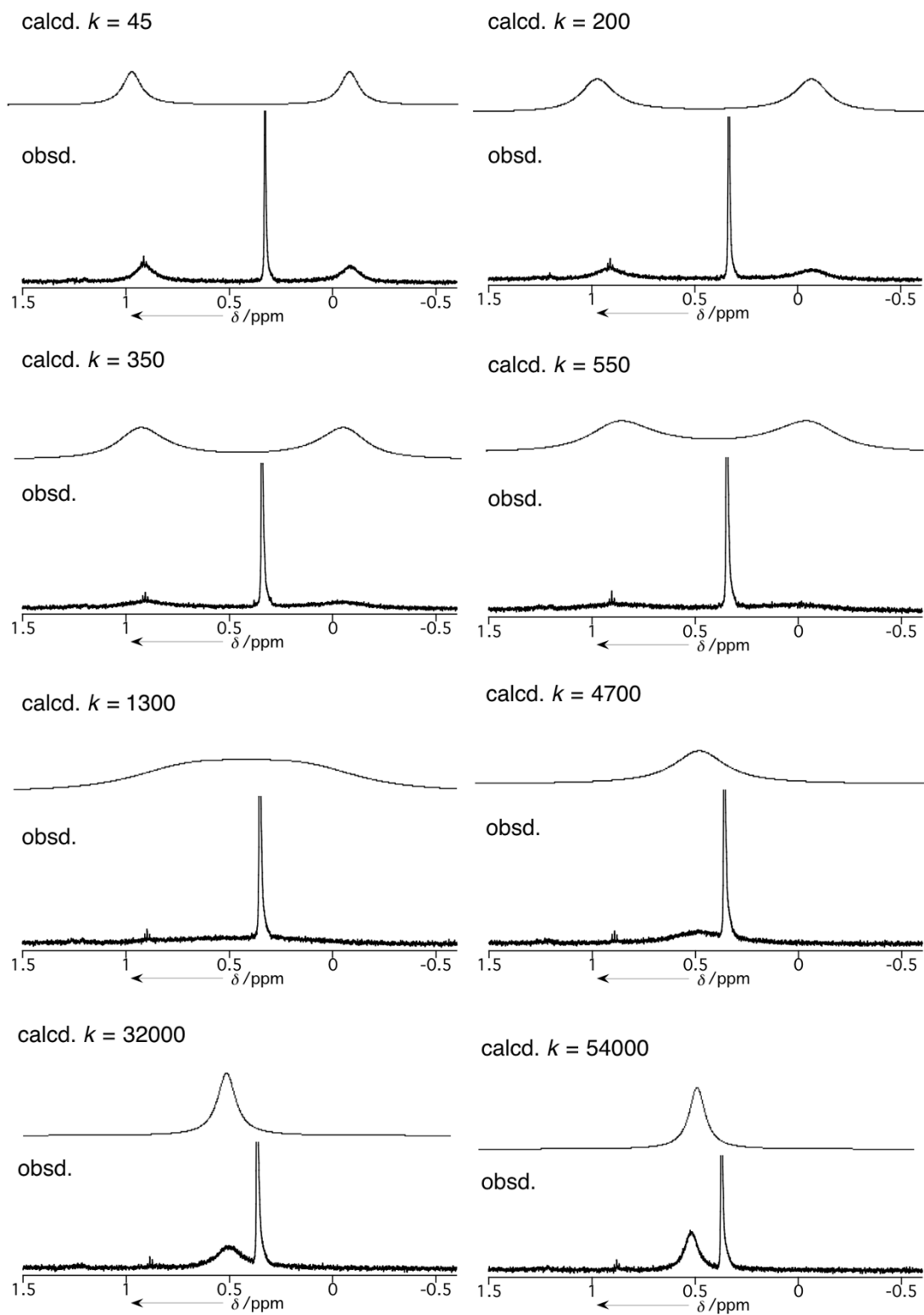


Figure S8. Observed (bottom) and simulated (top) ^1H NMR spectra of **2a** at various temperature.

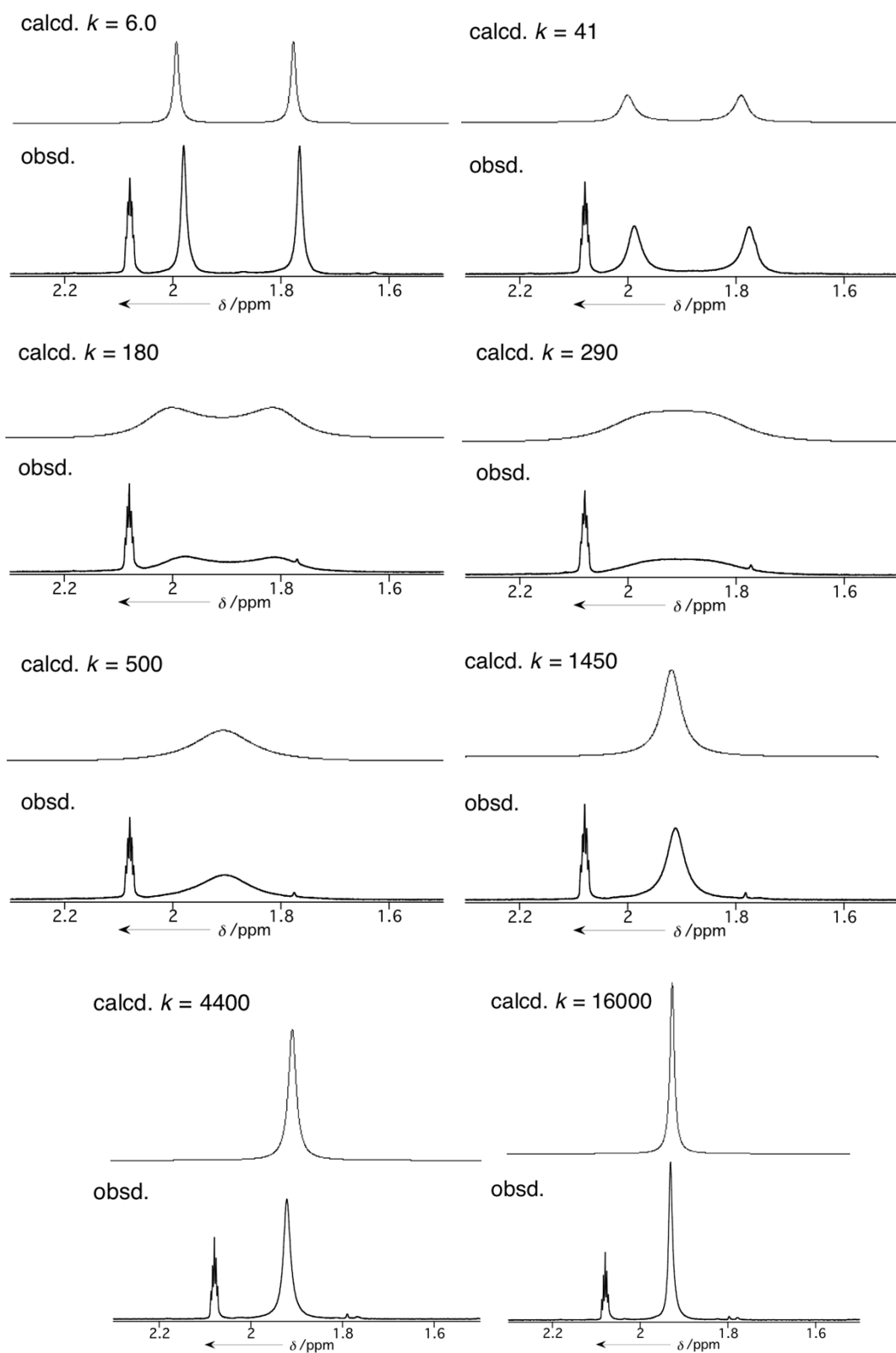


Figure S9. Observed (bottom) and simulated (top) ^1H NMR spectra of **2d** at various temperature.

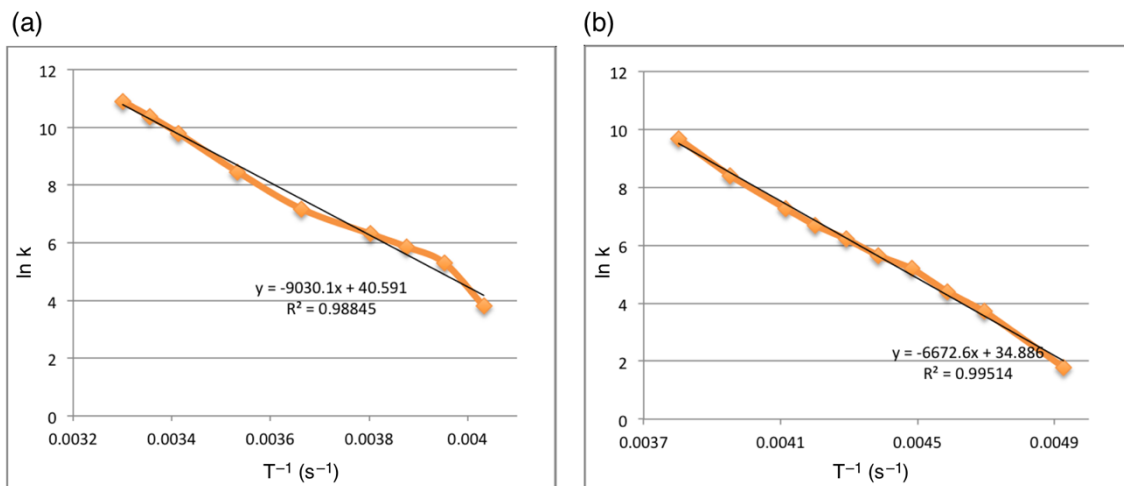


Figure S10. Arrhenius plots for (a) **2a** and (b) **2d**.

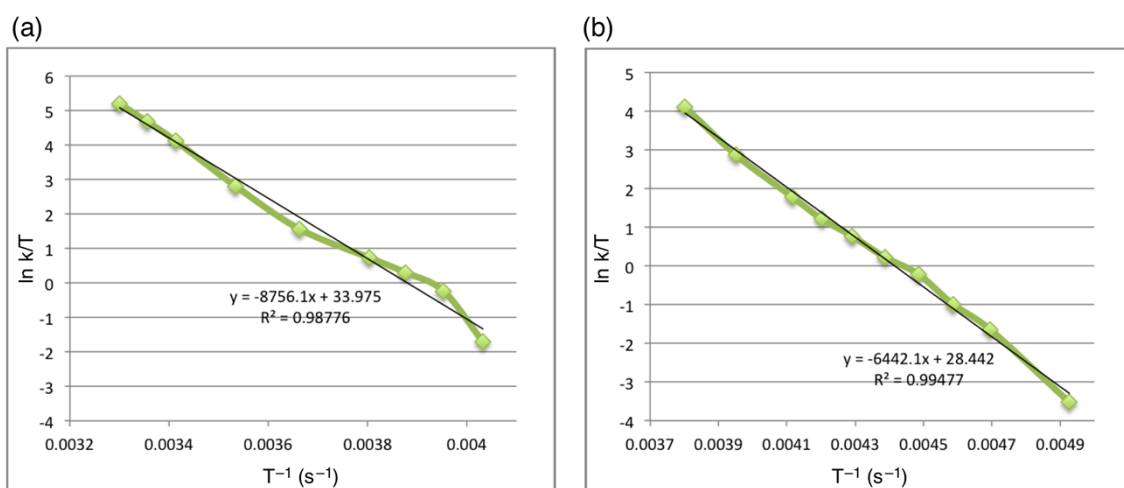


Figure S11. Eyring plots for (a) **2a** and (b) **2d**.

Table S2. Summary of the activation parameters.

	2a	2d
E_a [kcal mol ⁻¹]	17.94 ± 0.73	13.26 ± 0.33
ΔH^\ddagger [kcal mol ⁻¹]	17.40 ± 0.73	12.80 ± 0.33
ΔS^\ddagger [cal mol ⁻¹ K ⁻¹]	20.30 ± 2.69	9.30 ± 1.43
ΔG^\ddagger_{298} [kcal mol ⁻¹]	11.35 ± 0.73	10.03 ± 0.33

4. Mass Spectra

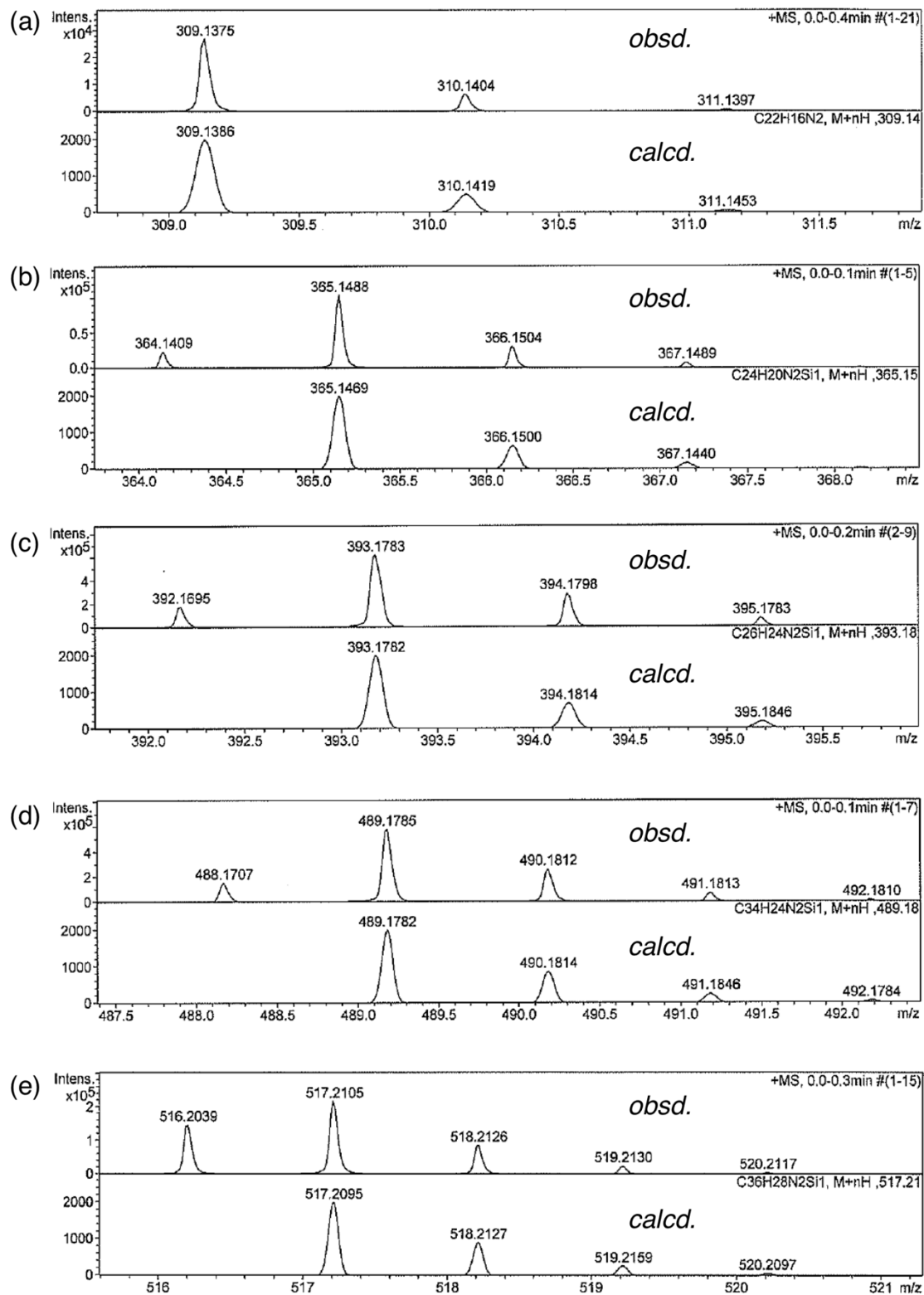


Figure S12. HR-APCI-TOF-MS of (a) **1**, (b) **2a**, (c) **2b**, (d) **2c**, and (e) **2d**. Top: observed, bottom: calculated.

5. X-Ray Crystallographic Details

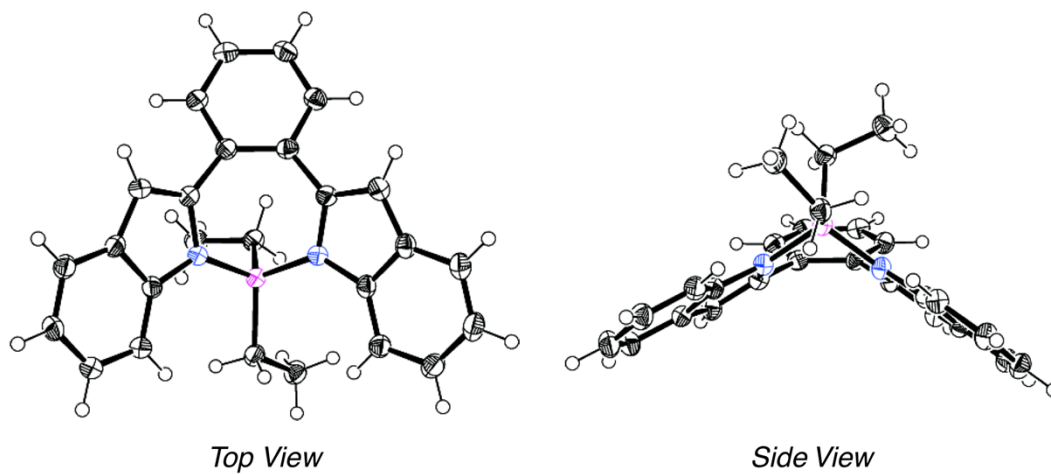


Figure S13. X-ray crystal structure of **2b**. Thermal ellipsoids were scaled to 50% probability.

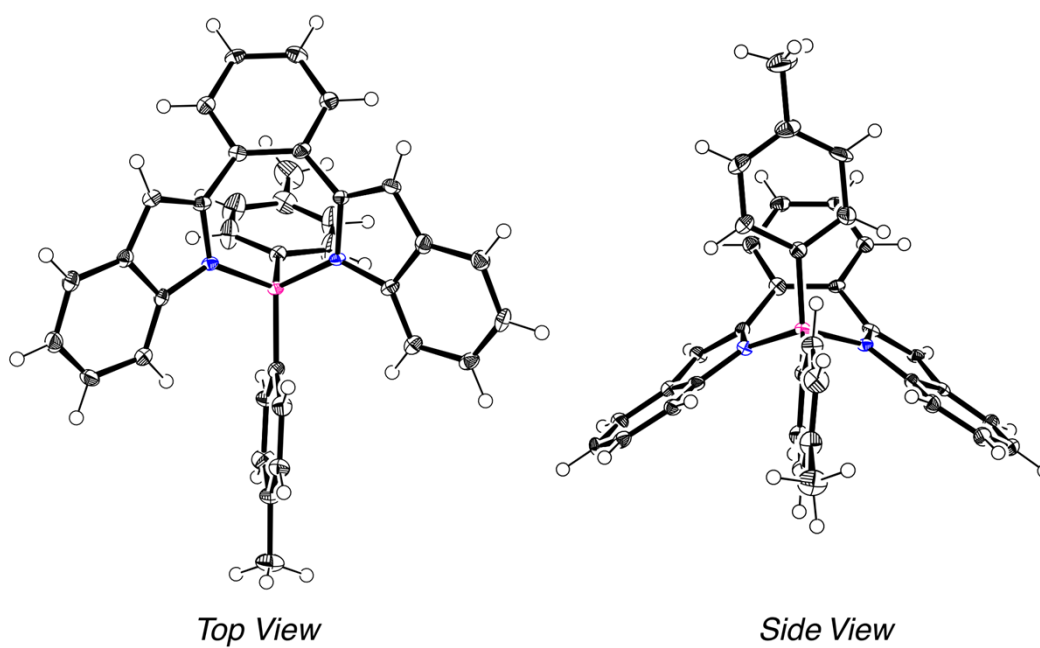
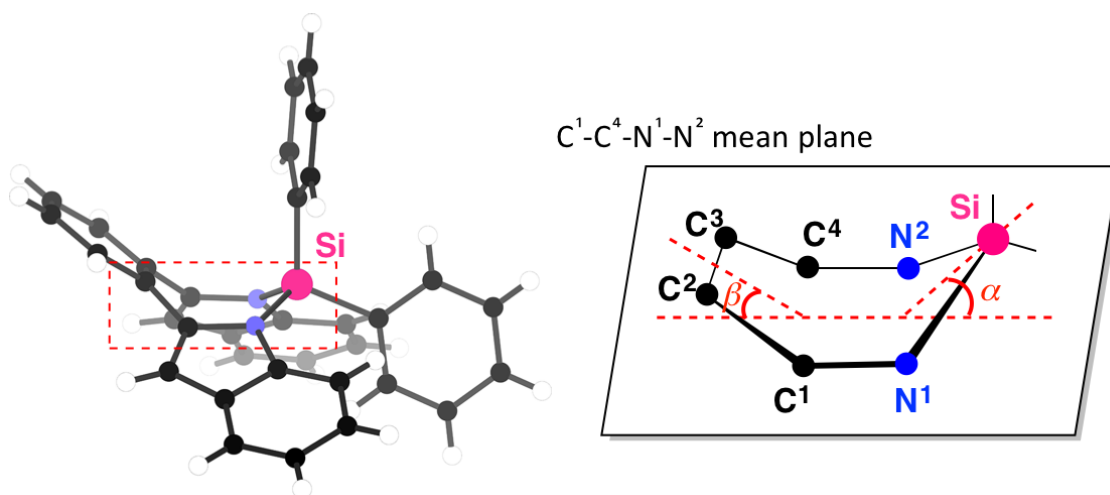


Figure S14. X-ray crystal structure of **2d**. Solvent molecules were omitted for clarity. Thermal ellipsoids were scaled to 50% probability.



	$\alpha^{[a]}$ (X-ray)	$\alpha^{[a]}$ (DFT) ^[b]	$\beta^{[a]}$ (X-ray)	$\beta^{[a]}$ (DFT) ^[b]	N—Si bonds (X-ray) [Å]	N—Si bonds (DFT) ^[b] [Å]
2a	46.11	45.37	42.81	38.31	1.772, 1.765	1.782
2b	47.81	47.40	37.20	37.67	1.763, 1.761	1.786
2c	35.04	36.26	41.37	39.40	1.761, 1.761	1.783
2d	38.82	37.11	38.98	39.49	1.767, 1.761	1.784

[a] The angles α and β are defined as the angles between C¹-C⁴-N¹-N² mean-plane and N¹-N²-Si plane, and between C¹-C⁴-N¹-N² mean-plane and C¹-C²-C³-C⁴ mean-plane, respectively.

[b] The optimized structures of **2a-d** have been calculated at the B3LYP/6-31G(d,p) level.

Figure S15. Selected bond lengths and structural details of **2a-d** in comparison with those of DFT optimized structures.

* While the α angles in the crystal structures are in consistent with those of calculated ones, the β angles are not in good agreement with calculated values probably due to the crystal packing forces.

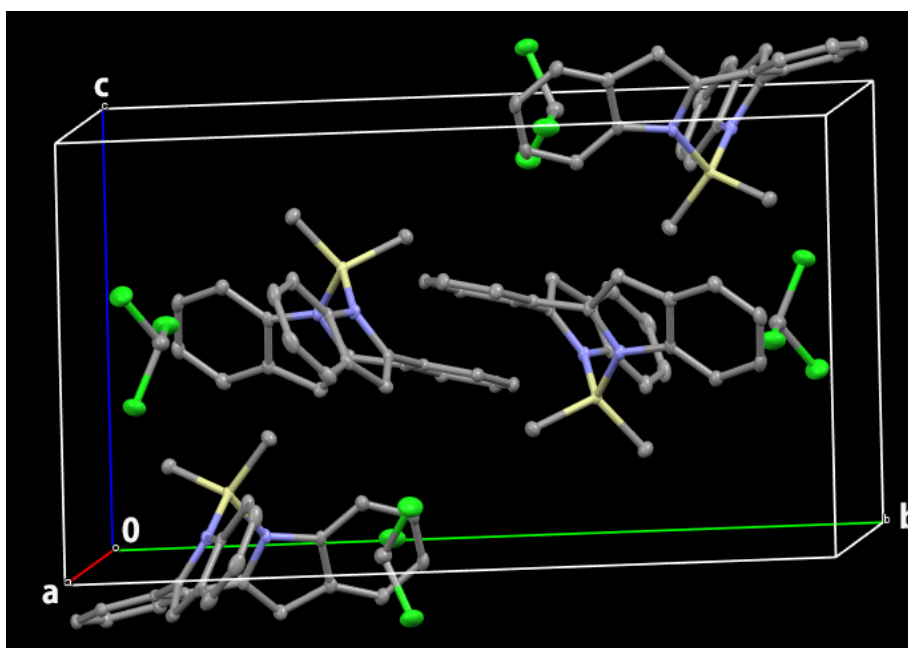


Figure S16. Crystal packing of **2a**. (atom colours, C: gray, N: blue, Si: yellow, Cl: green. Hydrogen atoms are omitted for clarity.)

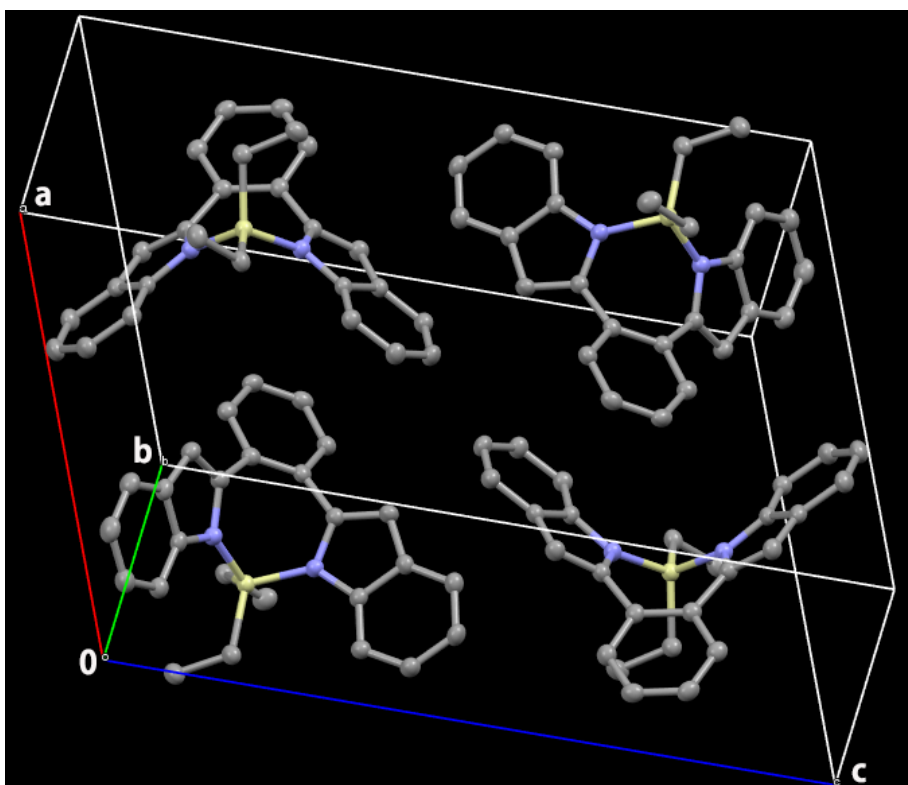


Figure S17. Crystal packing of **2b**. (atom colours, C: gray, N: blue, Si: yellow. Hydrogen atoms are omitted for clarity.)

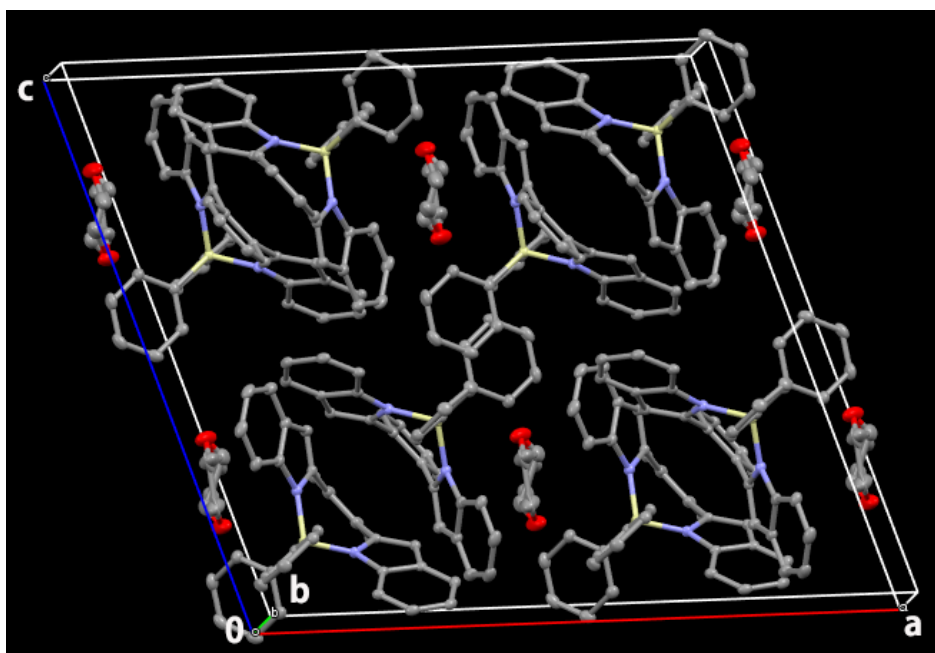


Figure S18. Crystal packing of **2c**. (atom colours, C: gray, N: blue, Si: yellow, O: red. Hydrogen atoms are omitted for clarity.)

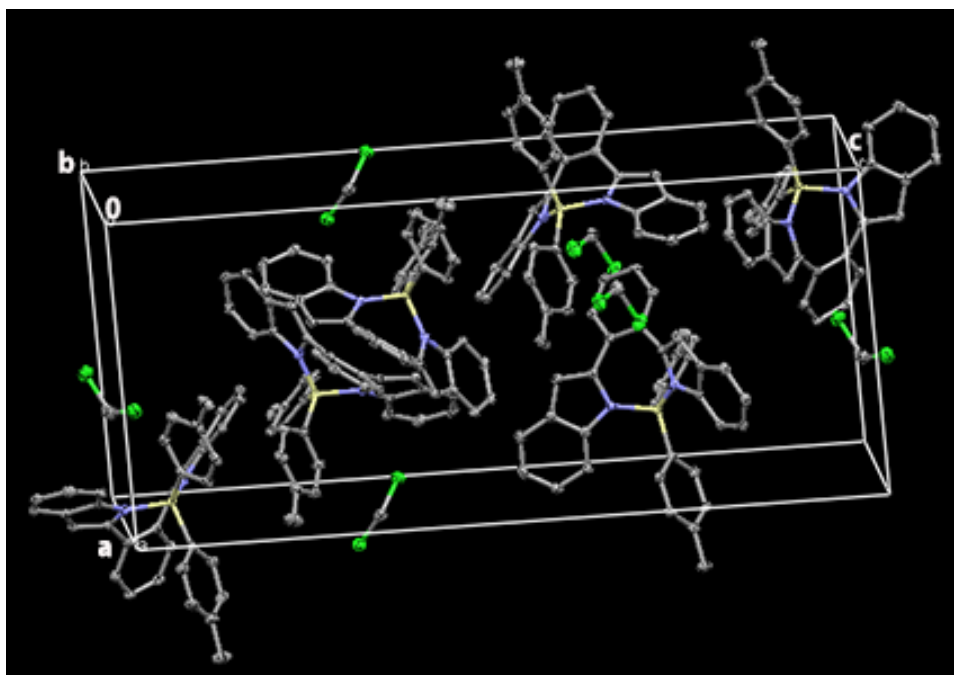


Figure S19. Crystal packing of **2d**. (atom colours, C: gray, N: blue, Si: yellow, Cl: green. Hydrogen atoms are omitted for clarity.)

Table S3. Crystal data and structure refinements for **2a-d**.

Compound	2a	2b	2c	2d
Empirical Formula	C ₂₄ H ₂₀ N ₂ Si ₁ ·(CHCl ₃)	C ₂₆ H ₂₄ N ₂ Si ₁	2(C ₃₄ H ₂₄ N ₂ Si ₁), ·(C ₄ H ₈ O)	2(C ₃₆ H ₂₈ N ₂ Si ₁), (CH ₂ Cl ₂)
<i>M_w</i>	483.88	392.56	1049.39	1118.31
Crystal System	Monoclinic	Monoclinic	Monoclinic	Trigonal
Space Group	<i>P</i> 2 ₁ / <i>c</i> (No.14)	<i>P</i> 2 ₁ / <i>a</i> (No.14)	<i>C</i> 2/ <i>c</i> (No.15)	<i>P</i> 3 ₂ 21 (No.154)
<i>a</i> [Å]	10.6810(19)	14.1331(3)	21.767(4)	13.156(3)
<i>b</i> [Å]	19.442(4)	7.81330(10)	12.983(2)	13.156(3)
<i>c</i> [Å]	11.152(2)	18.4958(3)	19.854(4)	28.415(8)
α [deg]	90	90	90	90
β [deg]	101.368(4)	102.1861(10)	108.480(4)	90
γ [deg]	90	90	90	120
Volume [Å ³]	2270.4(7)	1996.68(6)	5321.4(17)	4259.2(18)
<i>Z</i>	4	4	4	3
Density [Mg/m ³]	1.416	1.306	1.011	1.308
Completeness	0.973	0.997	0.985	0.994
Goodness-of-fit	1.039	1.073	1.034	1.030
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0277	0.0461	0.0348	0.0269
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0751	0.1035	0.0919	0.0275
<i>R</i> ₁ (all data)	0.0290	0.0592	0.365	0.0716
<i>wR</i> ₂ (all data)	0.0758	0.1126	0.0939	0.0719
Solvent System	CHCl ₃ / <i>n</i> -hexane	THF/heptane	THF/heptane	CH ₂ Cl ₂ /MeOH
CCDC	1050753	1050754	1050755	1050756

6. Optical Properties

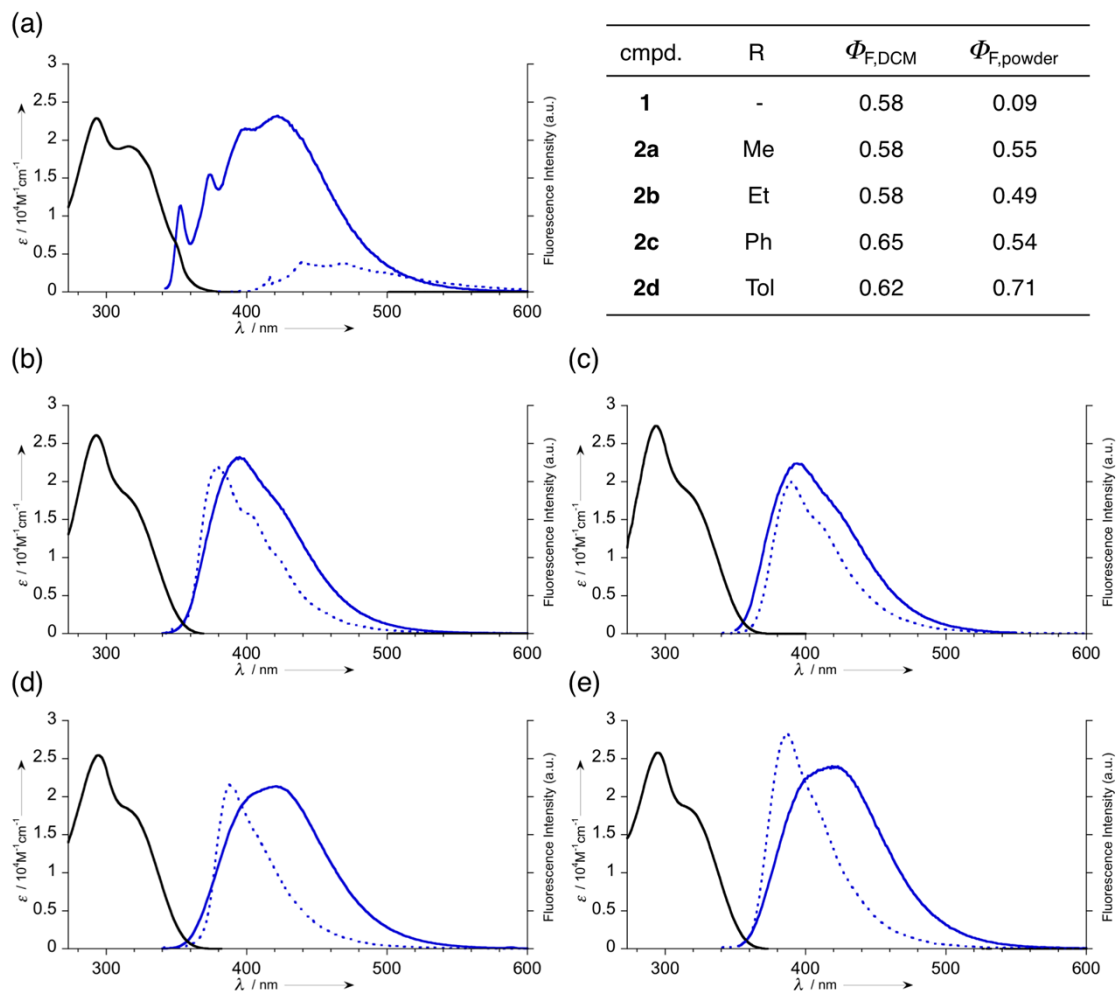


Figure S20. UV/vis absorption and emission spectra of (a) **1**, (b) **2a**, (c) **2b**, (d) **2c**, and (e) **2d** in CH_2Cl_2 (solid lines) and in the solid state (dashed lines).

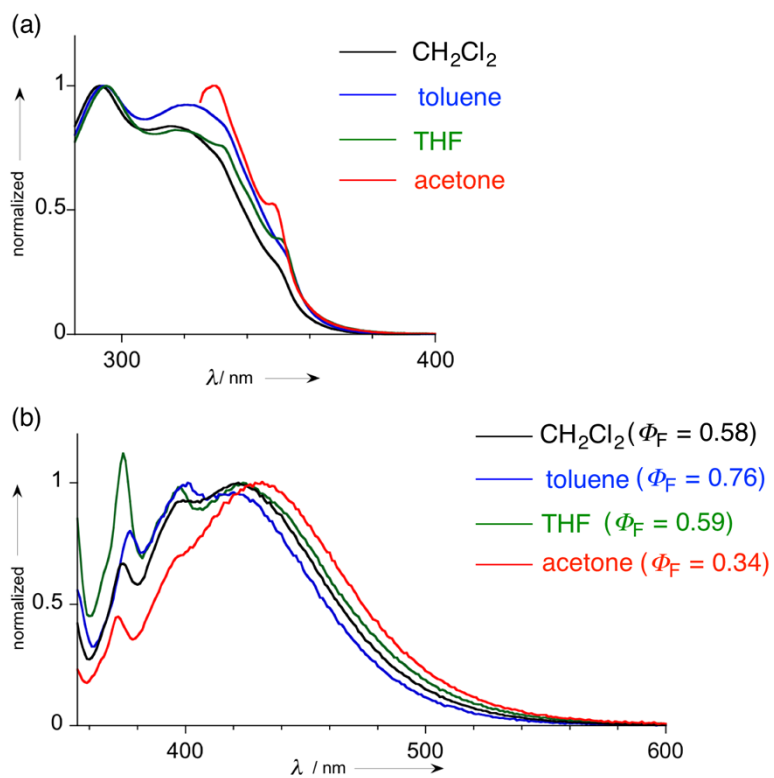


Figure S21. UV/vis absorption (a) and emission (b) spectra of **1** in various solvents.

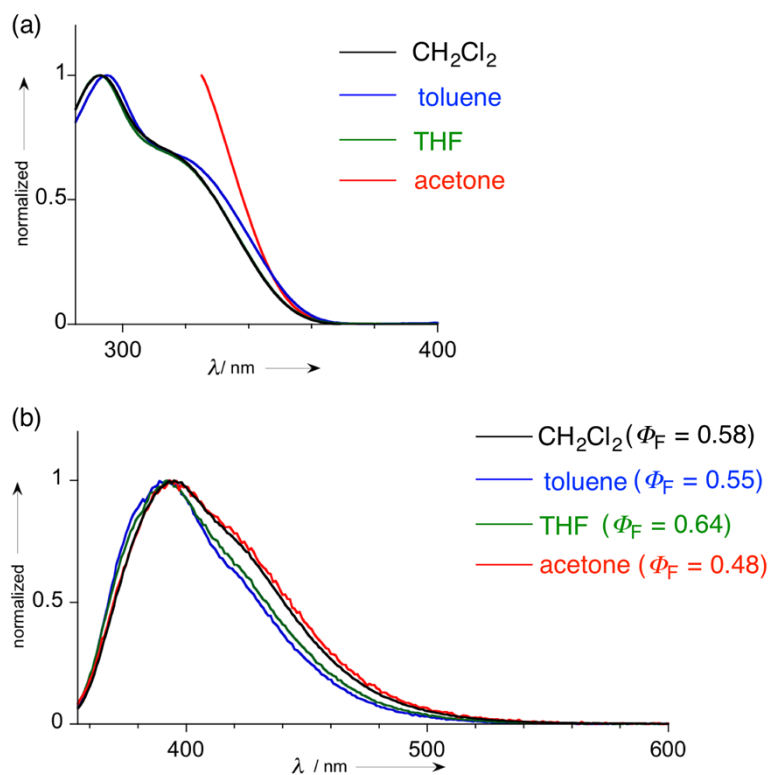


Figure S22. UV/vis absorption (a) and emission (b) spectra of **2a** in various solvents.

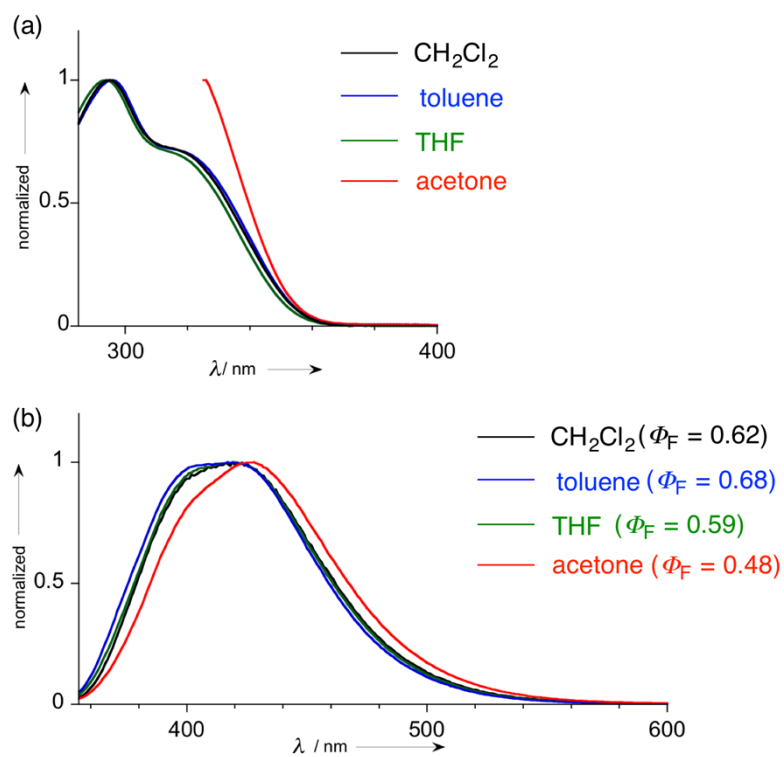


Figure S23. UV/vis absorption (a) and emission (b) spectra of **2c** in various solvents.

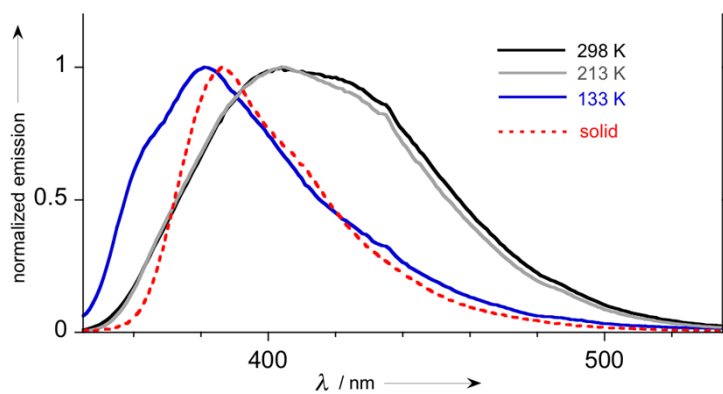


Figure S24. Variable-temperature emission spectra of **2c** in methylcyclohexane.

7. DFT Calculations

All calculations were carried out using the *Gaussian 09* program.^{S2} The structures were fully optimized without any symmetry restriction. Calculations were performed by the density functional theory (DFT) method with restricted B3LYP (Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional)^{S3} level, employing a basis sets 6-31G(d,p). Excitation energies and oscillator strengths were calculated with the TD-SCF method at the B3LYP level employing a basis sets 6-31G(d,p).

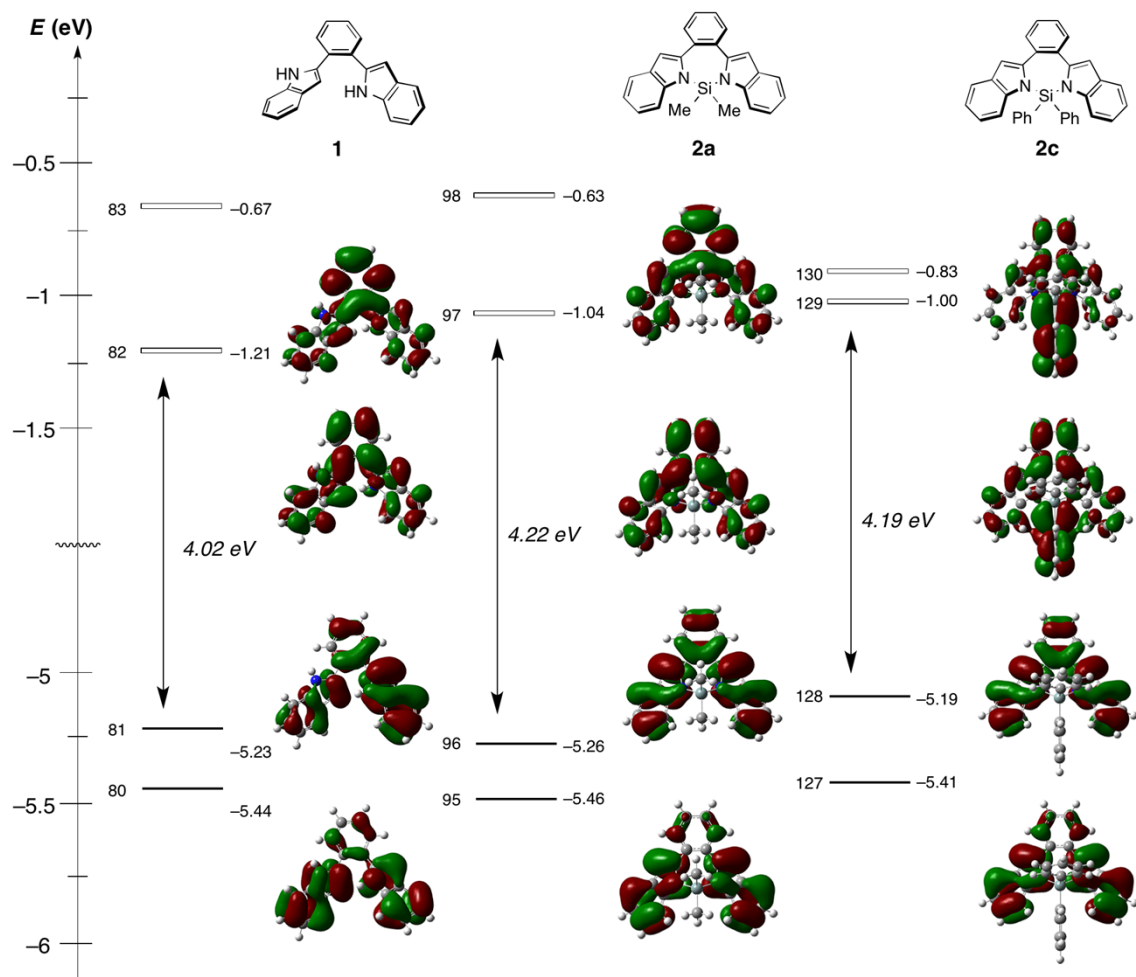


Figure S25. MO diagrams of **1**, **2a** and **2c**.

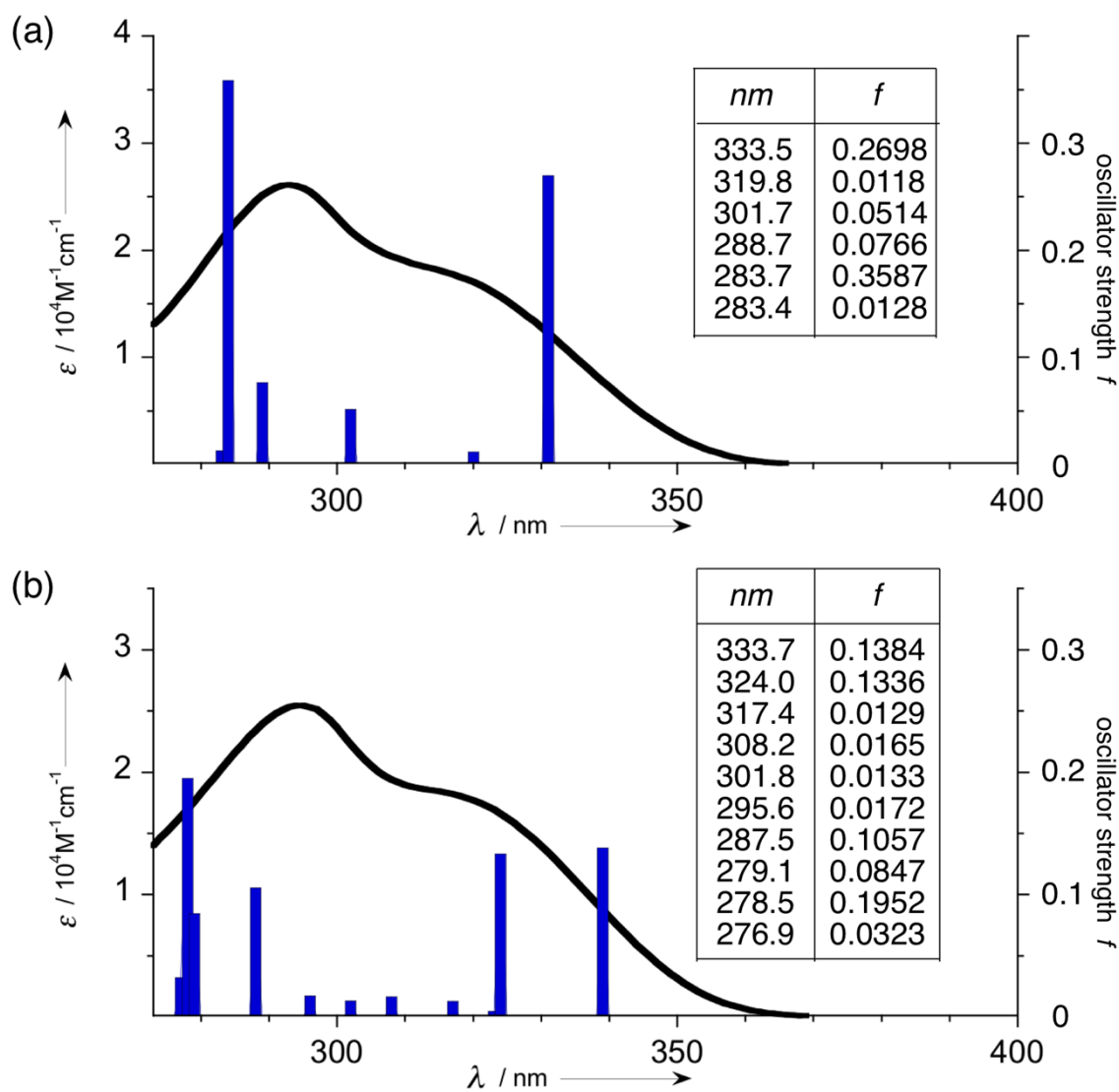


Figure S26. Calculated absorption spectra on the basis of optimized structures (bar) and observed absorption spectra (line) of (a) **2a** and (b) **2c** in CH_2Cl_2 .

8. Supporting References

[S1] DNMR3 simulation program: B. W. Tattershall, in DNMRUN and N3PLOT for Windows, Newcastle University, Newcastle, England, 2007; F. P. Gasparro and N. H. Kolodny, *J. Chem. Educ.*, 1977, **54**, 258.

[S2] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[S3] A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372; C. Lee, W. Yang and R. G. Parr *Phys. Rev. B*, 1998, **37**, 785.