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Electronic Supplementary Information

Highly emissive planarized *B*,*N*-diarylated benzonaphthoazaborine compounds for narrowband blue fluorescence

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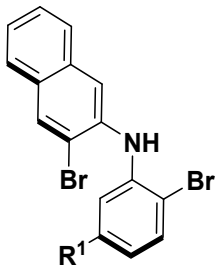
General considerations

All operations were performed under an inert nitrogen atmosphere using standard Schlenk and glovebox techniques. Anhydrous grade solvents were used after drying over activated molecular sieves (5Å). Spectrophotometric-grade toluene was used for photophysical measurements. Commercial reagents were used without further purification after purchase. Deuterated solvents from Eurisotop were used. NMR spectra were recorded on a Bruker AM 300 (300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C) or a Bruker AVANCE III HD 400 (128.38 MHz for ^{11}B) spectrometer at ambient temperature. Chemical shifts (in ppm) are referenced against external Me_4Si (^{1}H, ^{13}C) and $BF_3{\cdot}OEt_2$ (^{11}B). Mass spectra were obtained using a JEOL JMS700 high-resolution EI-mass spectrometer (HR EI-MS) at the Korea Basic Science Institute (KBSI), Daegu, Korea. Cyclic voltammetry experiments were carried out on a CHI600E system. The photophysical analysis was done by using an FS5 spectrophotometer (Edinburgh Instruments) and PLQY spectrophotometer (Quantaurus-QY C11347-11, Hamamatsu Photonics) at total-period analysis center for Ulsan chemical industry of KBSI.

Synthesis



1a, R^1 = H
4a, R^1 = Me
5a, R^1 = ^{t}Bu

3-Bromo-*N*-(2-bromophenyl)naphthalen-2-amine (1a)

The mixture of 2,3-dibromonaphthalene (3.00 g, 10.50 mmol), 2-bromoaniline (1.20 g, 7.00 mmol), tris-(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$, 0.19 g, 0.21 mmol), bis[(2-diphenylphosphino)phenyl] ether (DPEPhos, 0.23 g, 0.42 mmol), and sodium *tert*-butoxide ($NaO^{t}Bu$, 1.00 g, 10.5 mmol) in dry toluene (30 mL) was heated at 80 °C for 12 h. After cooling down, the mixture was diluted with CH_2Cl_2 (30 mL), filtered through celite pad, and concentrated under reduced pressure. The crude product was subjected to silica gel column chromatography using CH_2Cl_2/hexane (1:10, v/v) as an eluent to give **1a** as a white solid (yield: 1.40 g, 53%). ^{1}H NMR ($CDCl_3$): δ 8.13 (s, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.64–7.60 (m, 3H), 7.45 (ddd, J = 13.8, 8.2, 6.8 Hz, 2H), 7.36 (dd, J = 8.1, 1.2 Hz, 1H), 7.30 (dd, J =

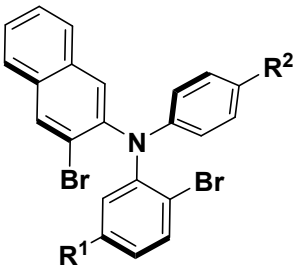
7.3, 1.4 Hz, 1H), 6.92–6.86 (m, 1H), 6.62 (br, 1H). ^{13}C NMR ($CDCl_3$): δ 140.1, 137.5, 133.4, 133.4, 132.2, 129.9, 128.3, 127.0, 126.8, 126.6, 124.7, 122.9, 118.6, 115.6, 114.7, 112.7.

3-Bromo-*N*-(2-bromo-5-methylphenyl)naphthalen-2-amine (4a)

This compound was prepared in a manner analogous to the synthesis of **1a** using $Pd_2(dba)_3$ (0.23 g, 0.25 mmol), DPEPhos (0.27 g, 0.5 mmol), NaO^{t}Bu (1.21 g, 12.58 mmol), 2,3-dibromonaphthalene (2.4 g, 8.39 mmol), and 2-bromo-5-methylaniline (1.04 g, 5.59 mmol) to give **4a** as a white powder (yield: 1.10 g, 51%). ^{1}H NMR ($CDCl_3$): δ 8.13 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.60 (s, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.46–7.40 (m, 1H), 7.35 (m, 1H), 7.28 (d, J = 1.7 Hz, 1H), 6.72 (dd, J = 8.2, 1.9 Hz, 1H), 6.54 (br, 1H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.8, 138.5, 137.7, 133.4, 133.0, 132.2, 129.9, 126.9, 126.8, 126.6, 124.6, 124.1, 119.4, 115.6, 112.8, 111.6, 21.5.

3-Bromo-*N*-(2-bromo-5-(*tert*-butyl)phenyl)naphthalen-2-amine (5a)

This compound was prepared in a manner analogous to the synthesis of **1a** using $Pd_2(dba)_3$ (0.09 g, 0.10 mmol), DPEPhos (0.11 g, 0.21 mmol), NaO^{t}Bu (0.50 g, 5.25 mmol), 2,3-dibromonaphthalene (2.0 g, 7.0 mmol), and 2-bromo-5-(*tert*-butyl)aniline (0.79 g, 3.50 mmol) to give **5a** as a white powder (yield: 1.20 g, 79%). ^{1}H NMR ($CDCl_3$): δ 8.13 (s, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.61–7.52 (m, 4H), 7.42 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.33 (ddd, J = 8.0, 6.9, 1.2 Hz, 1H), 6.95 (dd, J = 8.4, 2.3 Hz, 1H), 6.60 (s, 1H), 1.31 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 151.8, 139.2, 138.0, 133.4, 132.8, 132.2, 129.6, 127.0, 126.8, 126.5, 124.4, 120.7, 117.1, 115.2, 112.1, 111.3, 34.9, 31.3.



1b, $R^1 = R^2 = H$
3b, $R^1 = H$, $R^2 = {}^t$Bu
4b, $R^1 = Me$, $R^2 = {}^t$Bu
5b, $R^1 = {}^t$Bu, $R^2 = {}^t$Bu

3-Bromo-*N*-(2-bromophenyl)-*N*-phenylnaphthalen-2-amine (1b)

The mixture of **1a** (1.40 g, 3.71 mmol), iodobenzene (3.80 g, 18.60 mmol), copper iodide (0.35 g, 1.86 mmol), and potassium carbonate (1.50 g, 11.13 mmol) was refluxed at 200 °C for 24 h. After cooling to room temperature, CH_2Cl_2 (30 mL) and water (50 mL) were added to the mixture. The organic layer

was separated and the aqueous layer was extracted with CH_2Cl_2 three times (30 mL × 3). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using CH_2Cl_2/hexane (1:10, v/v) as an eluent to give **1b** as a white solid (yield: 1.45 g, 86%). ^{1}H NMR ($CDCl_3$): δ 8.16 (s, 1H), 7.77–7.71 (m, 1H), 7.64 (d, J = 7.0 Hz, 2H), 7.52 (s, 1H), 7.45 (dd, J = 6.0, 3.2 Hz, 2H), 7.23 (dt, J = 19.4, 7.3 Hz, 4H), 7.07 (t, J = 7.5 Hz, 1H), 7.00 (t, J = 7.2 Hz, 1H), 6.78 (d, J = 7.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 147.8, 146.2, 143.2, 134.8, 133.6, 133.2, 132.2, 129.5, 129.1, 128.5, 127.4, 127.1, 126.8, 126.7, 126.5, 126.4, 122.2, 122.0, 121.4, 121.3.

3-Bromo-*N*-(2-bromophenyl)-*N*-(4-(*tert*-butyl)phenyl)naphthalen-2-amine (3b)

This compound was prepared in a manner analogous to the synthesis of **1b** using **1a** (2.0 g, 5.3 mmol), copper iodide (0.50 g, 2.65 mmol), potassium carbonate (2.19 g, 15.90 mmol), and 1-(*tert*-butyl)-4-iodobenzene (6.9 g, 26.52 mmol) to give **3b** as a white powder (yield: 1.90 g, 72%). ^{1}H NMR ($CDCl_3$): δ 8.13 (s, 1H), 7.73 (dd, J = 6.0, 3.2 Hz, 1H), 7.64–7.59 (m, 2H), 7.46–7.40 (m, 3H), 7.22 (d, J = 8.5 Hz, 3H), 7.14 (dd, J = 8.0, 1.5 Hz, 1H), 7.07–7.01 (m, 1H), 6.71 (d, J = 8.7 Hz, 2H), 1.30 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 146.6, 145.3, 145.1, 143.6, 134.7, 133.5, 133.2, 132.0, 129.2, 128.4, 127.3, 126.8, 126.6, 126.2, 126.1, 125.9, 122.0, 122.0, 121.5, 121.4, 34.4, 31.6.

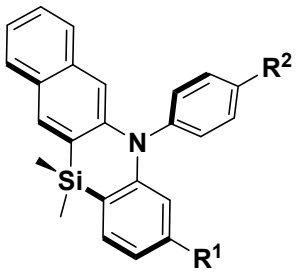
3-Bromo-*N*-(2-bromo-5-methylphenyl)-*N*-(4-(*tert*-butyl)phenyl)naphthalen-2-amine (4b)

This compound was prepared in a manner analogous to the synthesis of **1b** using **4a** (1.1 g, 2.81 mmol), copper iodide (0.26 g, 1.40 mmol), potassium carbonate (1.16 g, 8.43 mmol), and 1-(*tert*-butyl)-4-iodobenzene (3.65 g, 14.06 mmol) to give **4b** as a white powder (yield: 0.90 g, 61%). ^{1}H NMR ($CDCl_3$): δ 8.13 (s, 1H), 7.73 (dd, J = 6.2, 3.2 Hz, 1H), 7.63 (dd, J = 6.0, 3.4 Hz, 1H), 7.49–7.40 (m, 4H), 7.22 (d, J = 8.7 Hz, 2H), 6.94 (s, 1H), 6.86 (d, J = 8.1 Hz, 1H), 6.68 (d, J = 8.7 Hz, 2H), 2.23 (s, 3H), 1.30 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 146.0, 145.3, 144.8, 143.6, 138.5, 134.3, 133.5, 133.2, 132.0, 129.8, 127.3, 127.3, 126.8, 126.7, 126.6, 126.1, 125.9, 121.6, 121.1, 118.7, 34.3, 31.6, 21.1.

3-Bromo-*N*-(2-bromo-5-(*tert*-butyl)phenyl)-*N*-(4-(*tert*-butyl)phenyl)naphthalen-2-amine (5b)

This compound was prepared in a manner analogous to the synthesis of **1b** using **5a** (1.2 g, 2.77 mmol), copper iodide (0.26 g, 1.38 mmol), potassium carbonate (1.15 g, 8.31 mmol), and 1-(*tert*-butyl)-4-iodobenzene (3.60 g, 13.85 mmol) to give **5b** as a white powder (yield: 1.20 g, 75%). ^{1}H NMR ($CDCl_3$): δ 8.14 (s, 1H), 7.73 (dd, J = 5.8, 3.1 Hz, 1H), 7.64 (dd, J = 6.1, 3.1 Hz, 1H), 7.55–7.49 (m, 2H), 7.43 (dd, J = 5.8, 2.7 Hz, 2H), 7.21 (d, J = 9.2 Hz, 3H), 7.07 (d, J = 8.4 Hz, 1H), 6.66 (d, J = 8.2 Hz, 2H),

1.30 (s, 9H), 1.20 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 152.0, 145.8, 145.2, 144.5, 143.4, 134.0, 133.5, 133.2, 132.0, 127.4, 126.8, 126.8, 126.7, 126.5, 126.1, 125.8, 123.6, 121.6, 120.6, 118.8, 34.7, 34.3, 31.6, 31.3.



1c, $R^1 = R^2 = H$
3c, $R^1 = H$, $R^2 = {}^t$Bu
4c, $R^1 = Me$, $R^2 = {}^t$Bu
5c, $R^1 = R^2 = {}^t$Bu

12,12-Dimethyl-5-phenyl-5,12-dihydrobenzo[b]naphtho[2,3-e][1,4]azasiline (1c)

To a solution of **1b** (1.50 g, 3.31 mmol) in dry THF (30 mL) was added dropwise *n*-BuLi (2.5 M in hexane, 2.65 mL, 6.62 mmol) at −78 °C. The mixture was stirred at −78 °C for 1 h and then Me_2SiCl_2 (0.43 g, 3.31 mmol) was slowly added. After stirring at room temperature overnight, the resulting white turbid mixture was quenched by saturated aqueous NH_4Cl solution (50 mL) and extracted with diethyl ether (30 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using CH_2Cl_2/hexane (1:10, v/v) as an eluent to give **1c** as a white powder (yield: 0.97 g, 83%). ^{1}H NMR ($CDCl_3$): δ 8.10 (s, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.70 (dd, J = 10.3, 4.7 Hz, 2H), 7.63–7.54 (m, 2H), 7.43 (d, J = 8.0 Hz, 1H), 7.39–7.35 (m, 2H), 7.33–7.24 (m, 2H), 7.16 (ddd, J = 8.8, 7.2, 1.8 Hz, 1H), 6.99 (dt, J = 7.1, 3.6 Hz, 1H), 6.62 (s, 1H), 6.38 (d, J = 8.6 Hz, 1H), 0.62 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 149.8, 146.9, 144.0, 135.3, 134.8, 134.4, 131.3, 131.2, 130.2, 128.1, 128.0, 127.3, 127.2, 126.7, 123.5, 122.8, 119.8, 119.0, 117.2, 112.1, 0.4.

5-(4-(*Tert*-butyl)phenyl)-12,12-dimethyl-5,12-dihydrobenzo[b]naphtho[2,3-e][1,4]azasiline (3c)

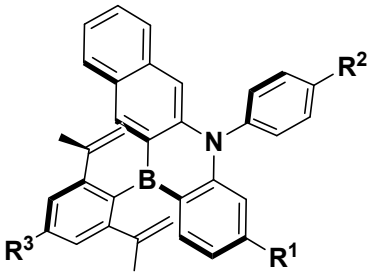
This compound was prepared in a manner analogous to the synthesis of **1c** using **3b** (1.94 g, 3.82 mmol) to give **3c** as a white powder (yield: 1.14 g, 73%). ^{1}H NMR ($CDCl_3$): δ 8.08 (s, 1H), 7.76 (dd, J = 8.0, 1.3 Hz, 1H), 7.69–7.65 (m, 2H), 7.59 (dd, J = 7.1, 1.8 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.33–7.22 (m, 4H), 7.16 (ddd, J = 8.9, 7.2, 1.9 Hz, 1H), 6.96 (t, J = 6.9 Hz, 1H), 6.62 (s, 1H), 6.38 (d, J = 8.4 Hz, 1H), 1.47 (s, 9H), 0.60 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 151.1, 150.0, 147.1, 141.2, 135.2, 134.8, 134.3, 130.6, 130.2, 128.1, 128.0, 127.3, 127.2, 126.6, 123.4, 122.7, 119.6, 118.8, 117.1, 112.0, 35.0, 31.7, 0.5.

5-(4-(*Tert*-butyl)phenyl)-3,12,12-trimethyl-5,12-dihydrobenzo[b]naphtho[2,3-e][1,4]azasiline (4c)

This compound was prepared in a manner analogous to the synthesis of **1c** using **4b** (0.90 g, 1.72 mmol) to give **4c** as a white powder (yield: 0.54 g, 75%). ^{1}H NMR ($CDCl_3$): δ 8.05 (s, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.68–7.63 (m, 2H), 7.48 (d, J = 7.3 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.30 (dd, J = 6.7, 1.3 Hz, 1H), 7.26–7.20 (m, 3H), 6.80 (d, J = 7.3 Hz, 1H), 6.56 (s, 1H), 6.19 (s, 1H), 2.17 (s, 3H), 1.47 (s, 9H), 0.57 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 151.0, 150.1, 147.2, 141.2, 140.2, 135.2, 134.8, 134.3, 130.5, 128.0, 127.9, 127.3, 127.2, 126.6, 123.3, 123.0, 120.8, 117.7, 115.5, 112.1, 35.0, 31.7, 22.3, 0.6.

3-(*Tert*-butyl)-5-(4-(*tert*-butyl)phenyl)-12,12-dimethyl-5,12-dihydrobenzo[b]naphtho[2,3-e][1,4]azasiline (5c)

This compound was prepared in a manner analogous to the synthesis of **1c** using **5b** (1.1 g, 1.95 mmol) to give **5c** as a white powder (yield: 0.75 g, 83%). ^{1}H NMR ($CDCl_3$): δ 8.06 (s, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.69–7.64 (m, 2H), 7.51 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 8.1 Hz, 1H), 7.33–7.26 (m, 2H), 7.26–7.20 (m, 2H), 6.99 (dd, J = 7.6, 1.6 Hz, 1H), 6.70 (s, 1H), 6.31 (d, J = 1.5 Hz, 1H), 1.46 (s, 9H), 1.09 (s, 9H), 0.57 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 153.1, 151.0, 150.1, 147.1, 141.4, 135.3, 134.9, 134.0, 130.5, 127.9, 127.9, 127.3, 127.2, 126.5, 123.2, 122.9, 117.0, 115.6, 114.6, 111.9, 35.0, 34.9, 31.6, 31.0, 0.6.



1d, $R^1 = R^2 = R^3 = H$
2d, $R^1 = R^2 = H$, $R^3 = {}^t$Bu
3d, $R^1 = H$, $R^2 = R^3 = {}^t$Bu
4d, R^1 = Me, $R^2 = R^3 = {}^t$Bu
5d, $R^1 = R^2 = R^3 = {}^t$Bu

12-(2,6-Di(prop-1-en-2-yl)phenyl)-5-phenyl-5,12-dihydrobenzo[b]naphtho[2,3-e][1,4]azaborinine (1d)

Boron tribromide (BBr_3, 0.53 g, 2.10 mmol) was added carefully to the flask containing **1c** (0.25 g, 0.70 mmol) at room temperature. After stirring at 60 °C for 3 h, the volatiles were removed under reduced pressure at the same temperature for 2 h. The crude mixture was dissolved in anhydrous toluene (10 mL), into which a toluene solution of (2,6-di(prop-1-en-2-yl)phenyl)lithium was added at 0 °C. The

latter solution was prepared by the addition of *n*-BuLi (2.5 M in hexane, 0.4 mL, 1 mmol) into a toluene solution of 2-bromo-1,3-di(prop-1-en-2-yl)benzene (0.20 g, 0.84 mmol) at 0 °C. After stirring at room temperature for 12 h, the mixture was quenched with saturated NH_4Cl solution and extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was subjected to silica gel column chromatography using CH_2Cl_2/hexane (1:6, v/v) to give **1d** as a yellow solid (yield: 0.10 g, 40%). ^{1}H NMR (CD_2Cl_2): δ 8.47 (s, 1H), 7.84 (d, J = 7.7 Hz, 2H), 7.78 (t, J = 7.3 Hz, 2H), 7.72–7.66 (m, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.45 (m, 7H), 7.31–7.25 (m, 1H), 7.08–7.00 (m, 2H), 6.70 (d, J = 8.7 Hz, 1H), 4.65 (s, 2H), 4.53 (s, 2H), 1.91 (s, 6H). ^{13}C NMR (CD_2Cl_2): δ 148.2, 148.0, 147.8, 144.5, 142.5, 138.9, 137.6, 136.2, 133.2, 131.5, 129.2, 129.1, 127.9, 127.8, 127.4, 127.3, 125.9, 123.6, 119.4, 117.3, 116.7, 112.3, 112.3, 24.7. ^{11}B NMR (CD_2Cl_2): δ 55.3.

12-(4-(*Tert*-butyl)-2,6-di(prop-1-en-2-yl)phenyl)-5-phenyl-5,12-dihydrobenzo[b]naphtho[2,3-e][1,4]azaborinine (2d)

This compound was prepared in a manner analogous to the synthesis of **1d** using **1c**, BBr_3, and (4-(*tert*-butyl)-2,6-di(prop-1-en-2-yl)phenyl)lithium to give **2d** as a yellow powder (yield: 0.19 g, 40%). ^{1}H NMR (CD_2Cl_2): δ 8.50 (s, 1H), 7.85 (dd, J = 7.5, 1.9 Hz, 2H), 7.80–7.74 (m, 2H), 7.71–7.65 (m, 1H), 7.59 (d, J = 8.1 Hz, 1H), 7.45–7.37 (m, 6H), 7.28 (ddd, J = 8.0, 6.7, 1.2 Hz, 1H), 7.05–6.99 (m, 2H), 6.69 (d, J = 8.6 Hz, 1H), 4.64 (s, 2H), 4.52 (s, 2H), 1.93 (s, 6H), 1.48 (s, 9H). ^{13}C NMR (CD_2Cl_2): δ 150.2, 148.7, 147.8, 147.7, 144.5, 142.5, 138.9, 137.6, 136.2, 133.1, 131.5, 131.1, 129.1, 129.1, 127.8, 127.8, 127.2, 123.6, 123.0, 119.3, 117.0, 116.7, 112.2, 35.0, 31.7, 24.8. ^{11}B NMR (CD_2Cl_2): δ 55.3.

12-(4-(*Tert*-butyl)-2,6-di(prop-1-en-2-yl)phenyl)-5-(4-(*tert*-butyl)phenyl)-5,12-dihydrobenzo[b]naphtho[2,3-e][1,4]azaborinine (3d)

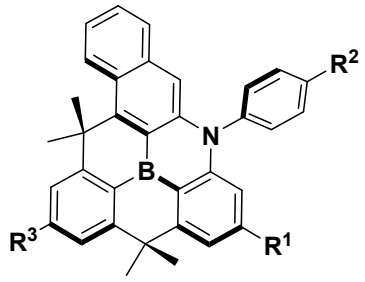
This compound was prepared in a manner analogous to the synthesis of **1d** using **3c**, BBr_3, and (4-(*tert*-butyl)-2,6-di(prop-1-en-2-yl)phenyl)lithium to give **3d** as a yellow powder (yield: 0.29 g, 43%). ^{1}H NMR (CD_2Cl_2): δ 8.49 (s, 1H), 7.87–7.82 (m, 2H), 7.77 (d, J = 8.5 Hz, 2H), 7.60 (s, 1H), 7.44–7.37 (m, 4H), 7.33 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 6.8 Hz, 1H), 7.07 (s, 1H), 7.01 (t, J = 6.8 Hz, 1H), 6.71 (d, J = 8.7 Hz, 1H), 4.64 (s, 2H), 4.52 (s, 2H), 1.92 (s, 6H), 1.51 (s, 9H), 1.48 (s, 9H). ^{13}C NMR (CD_2Cl_2): δ 152.3, 150.1, 148.7, 148.0, 147.8, 144.7, 139.7, 138.9, 137.6, 136.2, 133.0, 130.3, 129.1, 128.4, 127.8, 127.2, 123.5, 123.0, 119.2, 117.0, 116.8, 112.2, 35.3, 35.0, 31.7, 24.8. ^{11}B NMR (CD_2Cl_2): δ 52.4.

12-(4-(*Tert*-butyl)-2,6-di(prop-1-en-2-yl)phenyl)-5-(4-(*tert*-butyl)phenyl)-3-methyl-5,12-dihydrobenzo[b]naphtho[2,3-e][1,4]azaborinine (4d)

This compound was prepared in a manner analogous to the synthesis of **1d** using **4c**, BBr_3, and (4-*(tert*-butyl)-2,6-di(prop-1-en-2-yl)phenyl)lithium to give **4d** as a yellow powder (yield: 0.37 g, 52%). ^{1}H NMR (CD_2Cl_2): δ 8.45 (s, 1H), 7.86–7.70 (m, 4H), 7.59 (d, J = 8.4 Hz, 1H), 7.43–7.35 (m, 3H), 7.29 (dd, J = 12.4, 8.3 Hz, 3H), 7.01 (s, 1H), 6.85 (d, J = 7.8 Hz, 1H), 6.52 (s, 1H), 4.63 (d, J = 1.5 Hz, 2H), 4.52 (s, 2H), 2.29 (s, 3H), 1.91 (s, 6H), 1.51 (s, 9H), 1.48 (s, 9H). ^{13}C NMR (CD_2Cl_2): δ 152.2, 150.0, 148.7, 148.1, 147.7, 143.9, 139.6, 138.6, 137.6, 136.1, 130.3, 129.0, 128.3, 127.7, 127.6, 127.3, 123.4, 123.0, 120.9, 116.8, 116.7, 112.2, 35.3, 34.9, 31.7, 2.8, 22.6. ^{11}B NMR (CD_2Cl_2): δ 55.4.

3-(*Tert*-butyl)-12-(4-(*tert*-butyl)-2,6-di(prop-1-en-2-yl)phenyl)-5-(4-(*tert*-butyl)phenyl)-5,12-dihydrobenzo[b]naphtho[2,3-e][1,4]azaborinine (5d)

This compound was prepared in a manner analogous to the synthesis of **1d** using **5c**, BBr_3, and (4-(*tert*-butyl)-2,6-di(prop-1-en-2-yl)phenyl)lithium to give **5d** as a yellow powder (yield: 0.19 g, 40%). ^{1}H NMR (CD_2Cl_2): δ 8.45 (s, 1H), 7.86–7.70 (m, 4H), 7.59 (d, J = 8.4 Hz, 1H), 7.43–7.35 (m, 3H), 7.29 (dd, J = 12.4, 8.3 Hz, 3H), 7.01 (s, 1H), 6.85 (d, J = 7.8 Hz, 1H), 6.52 (s, 1H), 4.63 (d, J = 1.5 Hz, 2H), 4.52 (s, 2H), 2.29 (s, 3H), 1.91 (s, 6H), 1.51 (s, 9H), 1.48 (s, 9H). ^{13}C NMR (CD_2Cl_2): δ 152.3, 150.0, 148.8, 148.0, 147.7, 144.7, 139.7, 138.7, 137.2, 136.1, 130.4, 129.1, 128.2, 127.7, 127.6, 127.5, 123.3, 123.0, 117.3, 116.8, 113.4, 112.1, 35.5, 35.3, 35.0, 31.7, 31.6, 31.2, 31.0, 24.8. ^{11}B NMR (CD_2Cl_2): δ 55.2.



BzNp (1), $R^1 = R^2 = R^3 = H$
BuBzNp (2), $R^1 = R^2 = H$, $R^3 = {}^t$Bu
Bu_2BzNp (3), $R^1 = H$, $R^2 = R^3 = {}^t$Bu
Bu_2BzMeNp (4), $R^1 = Me$, $R^2 = R^3 = {}^t$Bu
Bu_2BzBuNp (5), $R^1 = R^2 = R^3 = {}^t$Bu

4,4,14,14-Tetramethyl-8-phenyl-8,14-dihydro-4H-8-aza-3a2-boraphenaleno[2,1,9,8-defg]tetracene (BzNp, 1)

The mixture of **1d** (0.10 g, 0.22 mmol) and scandium(III) triflate ($Sc(OTf)_3$, 0.22 g, 0.44 mmol) in anhydrous 1,2-dichloroethane (50 mL) was refluxed for 12 h. After cooling down, a saturated aqueous

solution of $NaHCO_3$ was added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified through silica gel chromatography using CH_2Cl_2/hexane (1:6, v/v) to give **1** as a yellow solid (yield: 0.04 g, 36%). ^{1}H NMR (CD_2Cl_2): δ 8.75 (m, 1H), 7.77 (m, 4H), 7.72–7.65 (m, 3H), 7.54 (t, J = 8.1 Hz, 1H), 7.47–7.39 (m, 5H), 6.97 (s, 1H), 6.48 (d, J = 8.4 Hz, 1H), 2.23 (s, 6H), 1.83 (s, 6H). ^{13}C NMR (CD_2Cl_2): δ 160.3, 156.9, 154.8, 154.1, 147.5, 144.0, 142.5, 138.5, 133.8, 132.6, 131.5, 131.0, 130.1, 129.0, 128.5, 126.4, 124.8, 123.9, 122.5, 117.9, 112.6, 111.9, 44.8, 43.0, 35.0, 33.6. ^{11}B NMR (CD_2Cl_2): δ 43.1. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{34}H_{28}BN$: 461.2315; found: 461.2313.

2-(*Tert*-butyl)-4,4,14,14-tetramethyl-8-phenyl-8,14-dihydro-4H-8-aza-3a2-boraphenaleno[2,1,9,8-defg]tetracene (BuBzNp, 2)

This compound was prepared in a manner analogous to the synthesis of **1** using **2d** (0.19 g, 0.32 mmol) to give **2** as a yellow solid (yield: 0.07 g, 36%). ^{1}H NMR (CD_2Cl_2): δ 8.78–8.71 (m, 1H), 7.82–7.73 (m, 4H), 7.71–7.64 (m, 2H), 7.54 (t, J = 8.1 Hz, 1H), 7.48–7.38 (m, 5H), 6.95 (s, 1H), 6.46 (d, J = 8.1 Hz, 1H), 2.23 (s, 6H), 1.83 (s, 6H), 1.51 (s, 9H). ^{13}C NMR (CD_2Cl_2): δ 160.0, 157.1, 155.7, 154.4, 154.3, 147.5, 144.0, 142.6, 138.5, 133.6, 131.5, 131.1, 130.1, 129.0, 128.5, 126.3, 125.4, 122.4, 121.9, 121.1, 117.9, 112.5, 111.8, 45.1, 43.2, 36.1, 35.1, 33.7, 31.8. ^{11}B NMR (CD_2Cl_2): δ 44.6. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{38}H_{36}BN$: 517.2941; found: 517.2936.

2-(*Tert*-butyl)-8-(4-(*tert*-butyl)phenyl)-4,4,14,14-tetramethyl-8,14-dihydro-4H-8-aza-3a2-boraphenaleno[2,1,9,8-defg]tetracene (Bu_2BzNp, 3)

This compound was prepared in a manner analogous to the synthesis of **1** using **3d** (0.29 g, 0.51 mmol) to give **3** as a yellow solid (yield: 0.14 g, 48%). ^{1}H NMR (CD_2Cl_2): δ 8.74 (m, 1H), 7.79 (dd, J = 5.5, 1.7 Hz, 2H), 7.75 (dd, J = 4.4, 1.7 Hz, 2H), 7.70 (dd, J = 6.4, 3.4 Hz, 1H), 7.54 (t, J = 8.1 Hz, 1H), 7.47–7.38 (m, 3H), 7.38–7.33 (m, 2H), 6.99 (s, 1H), 6.48 (d, J = 8.1 Hz, 1H), 2.23 (s, 6H), 1.83 (s, 6H), 1.51 (s, 9H), 1.50 (s, 9H). ^{13}C NMR (CD_2Cl_2): δ 159.9, 157.1, 155.6, 154.3, 154.3, 152.1, 147.6, 144.1, 139.7, 138.5, 133.6, 130.2, 130.1, 128.5, 128.4, 126.2, 125.3, 122.4, 121.9, 121.1, 117.8, 112.6, 111.8, 45.0, 43.2, 36.1, 35.2, 35.1, 33.7, 31.8, 31.7. ^{11}B NMR (CD_2Cl_2): δ 41.2. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{42}H_{44}BN$: 573.3567; found: 573.3569.

2-(*Tert*-butyl)-8-(4-(*tert*-butyl)phenyl)-4,4,6,14,14-pentamethyl-8,14-dihydro-4H-8-aza-3a2-boraphenaleno[2,1,9,8-defg]tetracene (Bu_2BzMeNp, 4)

This compound was prepared in a manner analogous to the synthesis of **1** using **4d (**0.3 g, 0.51 mmol) to give **4** as a yellow solid (yield: 0.11 g, 32%). ^{1}H NMR (CD_2Cl_2): δ 8.73 (dd, J = 6.8, 3.5 Hz, 1H), 7.80–7.72 (m, 4H), 7.68 (dd, J = 6.5, 3.4 Hz, 1H), 7.44–7.39 (m, 2H), 7.36–7.31 (m, 2H), 7.24 (s, 1H), 6.93 (s, 1H), 6.33 (s, 1H), 2.39 (s, 3H), 2.22 (s, 6H), 1.82 (s, 6H), 1.51 (d, J = 2.9 Hz, 18H). ^{13}C NMR (CD_2Cl_2): δ 159.9, 157.0, 155.6, 154.2, 152.1, 147.6, 144.3, 144.1, 139.6, 138.4, 133.5, 130.2, 130.0, 128.5, 128.4, 126.2, 125.2, 122.3, 121.8, 121.1, 117.7, 112.5, 111.7, 45.0, 43.1, 36.0, 35.2, 35.1, 33.6, 31.8, 31.6, 21.1. ^{11}B NMR (CD_2Cl_2): δ 44.7. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{43}H_{46}BN$: 587.3723; found: 587.3722.

2,6-Di-*tert*-butyl-8-(4-(*tert*-butyl)phenyl)-4,4,14,14-tetramethyl-8,14-dihydro-4H-8-aza-3a2-boraphenaleno[2,1,9,8-defg]tetracene (Bu_2BzBuNp, 5)

This compound was prepared in a manner analogous to the synthesis of **1** using **5d** (0.2 g, 0.32 mmol) to give **5** as a yellow solid (yield: 0.06 g, 35%). ^{1}H NMR (CD_2Cl_2): δ 8.74 (dd, J = 6.5, 3.6 Hz, 1H), 7.76 (dd, J = 8.5, 5.7 Hz, 4H), 7.70 (dd, J = 6.3, 3.5 Hz, 1H), 7.46 (d, J = 1.0 Hz, 1H), 7.44–7.39 (m, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.02 (s, 1H), 6.48 (d, J = 1.0 Hz, 1H), 2.23 (s, 6H), 1.83 (s, 6H), 1.51 (d, J = 0.8 Hz, 18H), 1.25 (s, 9H). ^{13}C NMR (CD_2Cl_2): δ 159.8, 157.2, 156.3, 155.4, 154.5, 154.1, 152.1, 147.7, 144.3, 139.7, 138.5, 130.3, 130.1, 128.5, 128.2, 126.1, 125.2, 122.3, 121.8, 121.2, 115.6, 111.7, 109.7, 45.1, 43.3, 36.0, 36.0, 35.2, 33.6, 31.8, 31.6, 31.3. ^{11}B NMR (CD_2Cl_2): δ 45.7. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{46}H_{52}BN$: 629.4193; found: 629.4193.

Cyclic voltammetry

Cyclic voltammetry measurements were carried out at room temperature in CH_2Cl_2 or THF (5×10^{-4} M) with a three-electrode cell configuration comprising platinum working and counter electrodes and an $Ag/AgNO_3$ (0.01 M in CH_3CN) reference electrode at room temperature. Tetra-*n*-butylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. The oxidation potentials were recorded at a scan rate of 100–200 mV/s and are reported against the ferrocene/ferrocenium (Fc/Fc^+) redox couple. The HOMO and LUMO energy levels were determined from the electrochemical oxidation and reduction ($E_{1/2}$) peaks of cyclic voltammograms.

Computational details

The computational study was carried out using the PBE0 hybrid functional[1] and 6-31+G(d,p) basis set implemented in GAUSSIAN 16 software package.[2] The ground (S_0) and lowest singlet (S_1) excited states of compounds **1**–**5** were optimized using density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations, respectively, with the same functional and basis set. Natural transition

orbitals (NTOs) were utilized to examine the characteristics for their electronic transitions from S_0 to S_1 state.[3] The polarizable continuum model using the integral equation formalism (IEFPCM) was employed to take account for the influence of solvent medium (toluene) on molecular geometric and electronic structures.[4] Nucleus-independent chemical shift (NICS) values were computed to identify the influence of increased conjugation length on the spectral wavelength at the PBE0/6-311++G(d,p)//PBE0/6-31G(d,p) level of theory.[5] The NICS(1) values obtained at 1 Å above the ring centers were utilized to reduce the local effects of sigma bonds.[6] The root-mean-square displacement values of structural deviation during transtion between S_0 and S_1 states were computed using Multiwfn programs.[7]

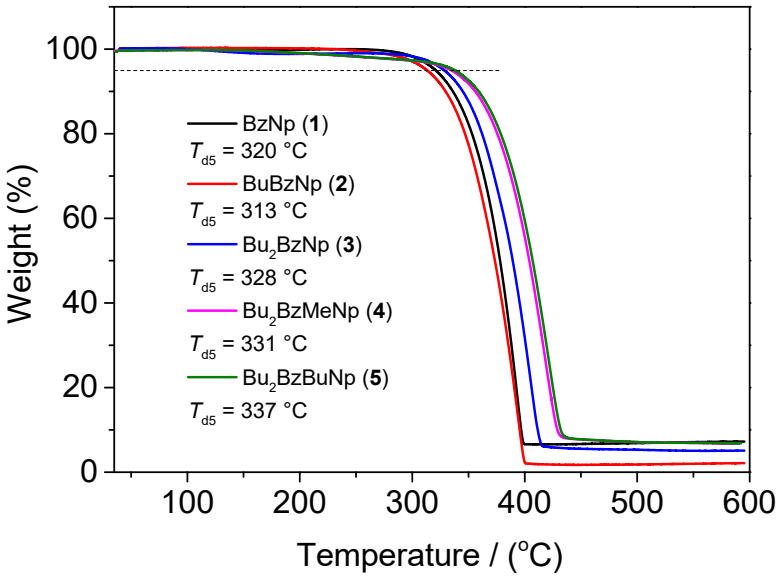


Fig. S1. TGA curves of **1**–**5**.

Table S1. Oxidation and reduction potentials, optical bandgaps, and HOMO/LUMO energy levels of **1**–**5**.

compd	E_{ox} (V)[a]	E_{red} (V)[a]	E_g (eV)	HOMO (eV)	LUMO (eV)
1	0.52	−2.48	3.00	−5.32	−2.32
2	0.51	−2.49	3.00	−5.31	−2.31
3	0.48	−2.50	2.98	−5.28	−2.30
4	0.46	−2.59	3.05	−5.26	−2.21
5	0.44	−2.62	3.06	−5.24	−2.18

[a]Half-wave potential ($E_{1/2}$).

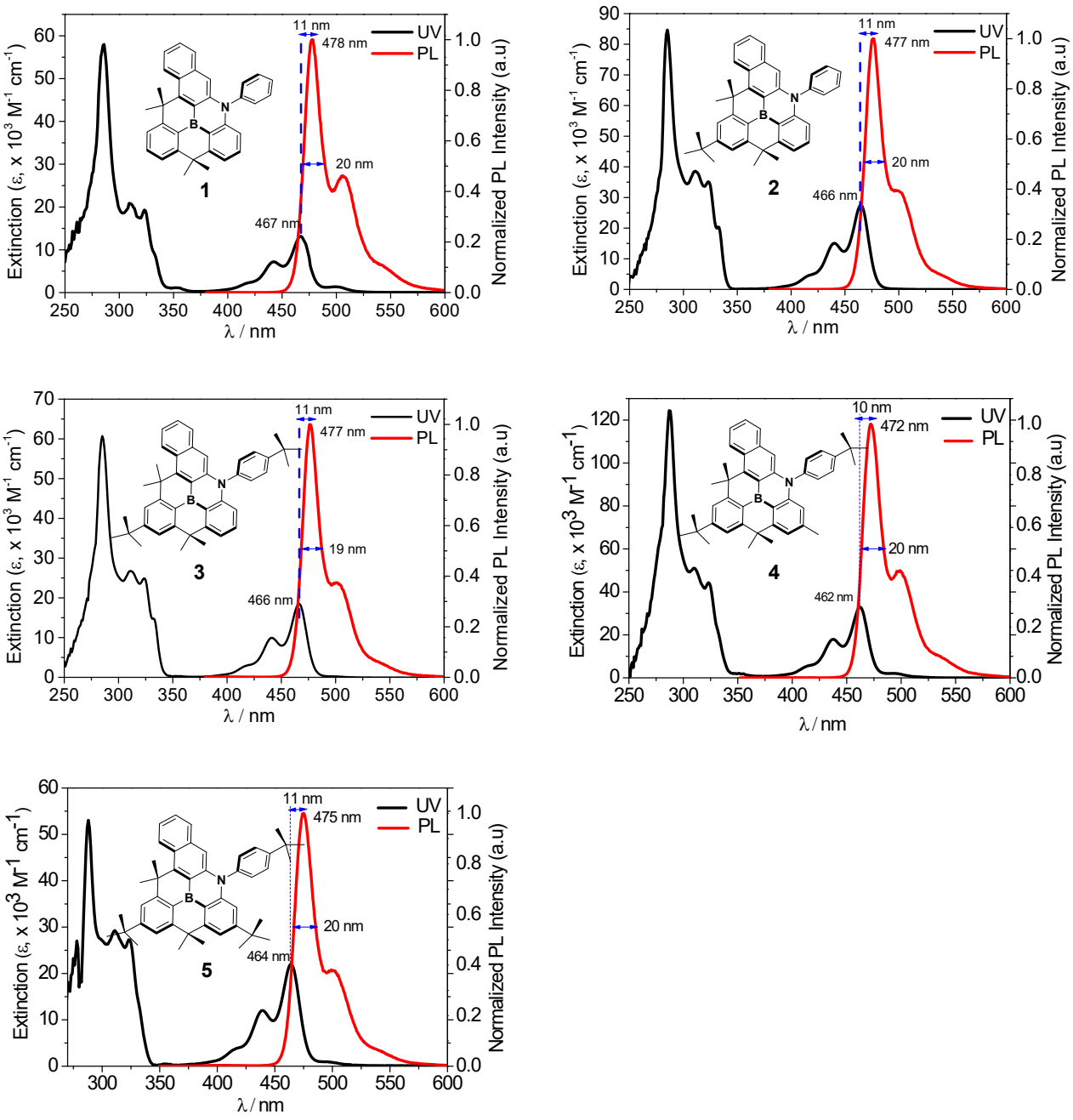


Fig. S2. UV/Vis absorption and PL spectra of **1**–**5** in toluene (2.0×10^{-5} M) at 298 K. The absorption and emission maximum wavelengths, Stokes shifts, and FWHMs are given.

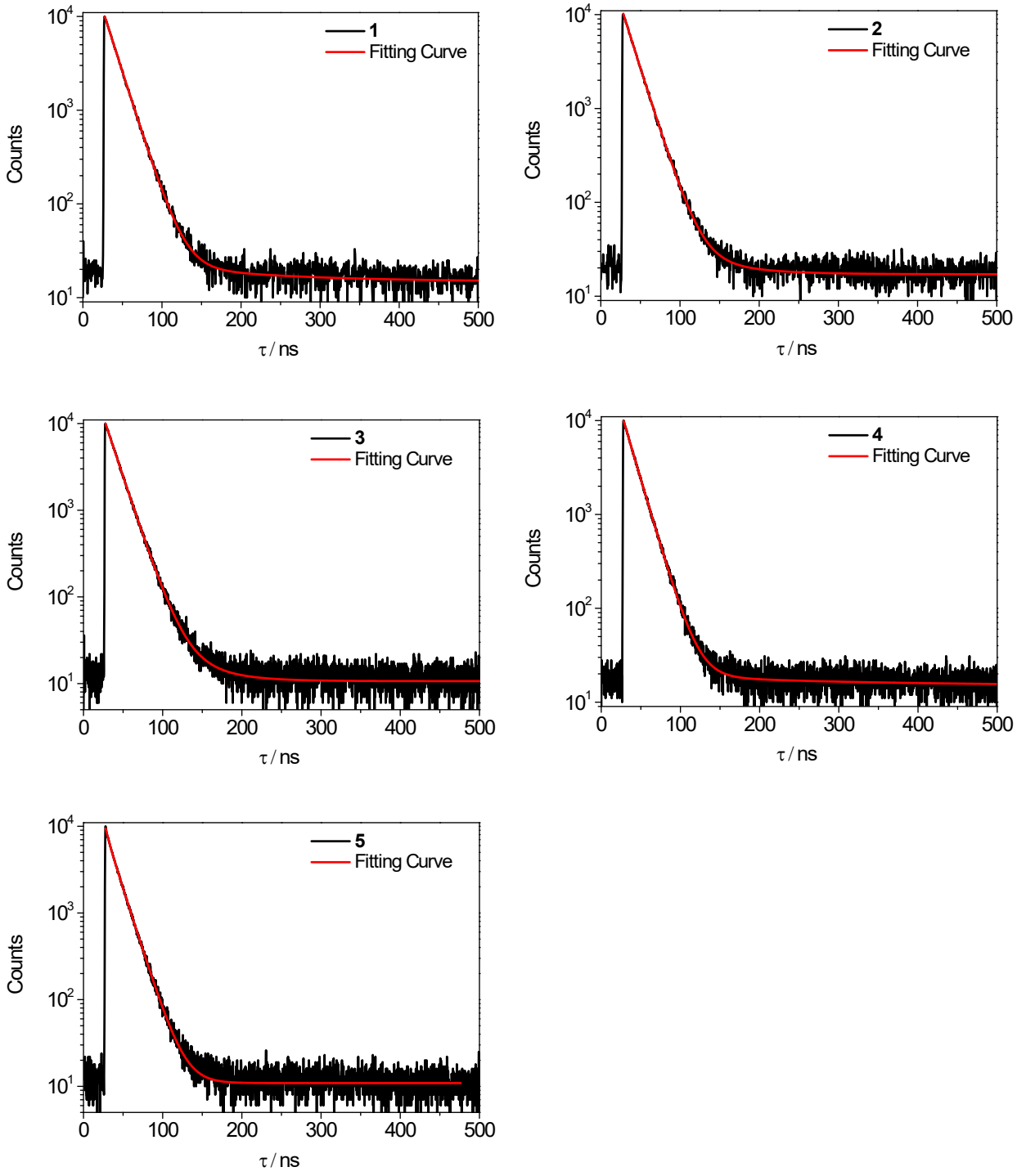
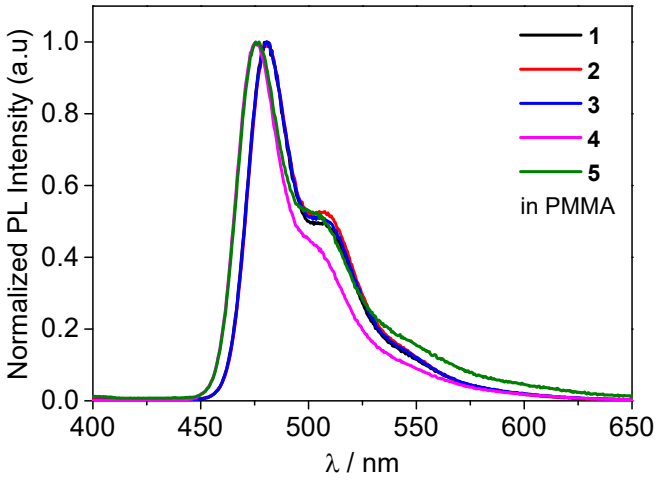


Fig. S3. Transient PL decay curves of **1**–**5** in toluene at 298 K.



compd	λ_{PL} (nm)	PLQY (%)
1	481	~100
2	480	~100
3	480	~100
4	475	~100
5	478	~100

Fig. S4. PL spectra of PMMA films doped with 1 wt% **1**–**5** (λ_{exc} = 335 nm).

Table S2. The absorption wavelength (λ_{abs} in nm) and corresponding oscillator strength (*f*) for the lowest energy electronic excitation, i.e., S_0 to S_1 transition, of compounds **1**–**5** obtained using the TDDFT calculations at the PBE0/6-31+g(d,p) level of theory.

compd	λ_{abs}	*f*	Major contribution
1	430	0.1711	HOMO → LUMO (98.3%)
2	427	0.1950	HOMO → LUMO (98.2%)
3	429	0.2033	HOMO → LUMO (98.2%)
4	425	0.2055	HOMO → LUMO (98.1%)
5	429	0.1947	HOMO → LUMO (98.2%)

Table S3. The emission wavelength (λ_{em} in nm) and corresponding oscillator strength (*f*) for the lowest energy electronic de-excitation, i.e., S_1 to S_0 transition, of compounds **1**–**5** obtained using the TDDFT calculations at the PBE0/6-31+g(d,p) level of theory.

compd	λ_{em}	*f*	Major contribution
1	456	0.1552	HOMO → LUMO (98.5%)
2	452	0.1760	HOMO → LUMO (98.4%)
3	454	0.1831	HOMO → LUMO (98.5%)
4	452	0.1791	HOMO → LUMO (98.4%)
5	454	0.1752	HOMO → LUMO (98.5%)

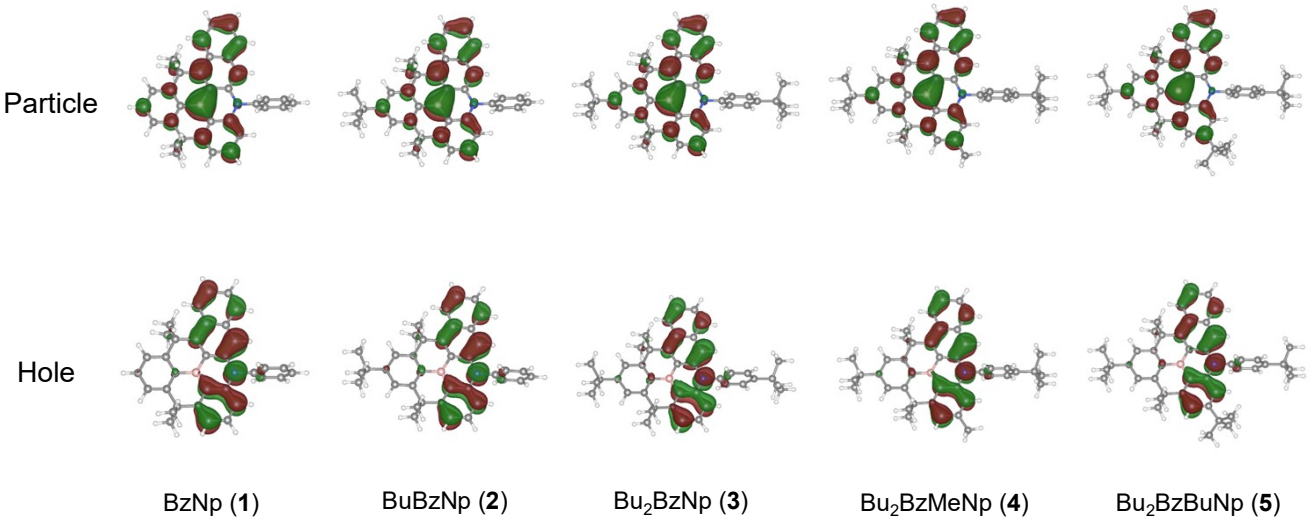


Fig. S5. Natural transition orbitals (NTO) of compounds **1**–**5** for the transitions from S_0 to S_1 state obtained using the TDDFT calculations at the PBE0/6-31+g(d,p) level of theory.

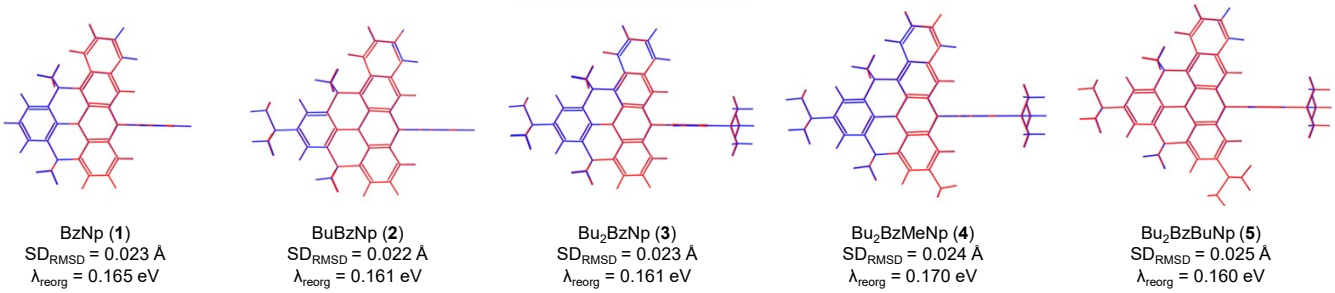


Fig. S6. Structural overlap of the ground (S_0, red) and lowest singlet excited (S_1, blue) states for the compounds **1**–**5**. The root-mean-square displacement values of structural deviation (SD_{RMSD}) and corresponding reorganization energies (λ_{reorg}) are provided.

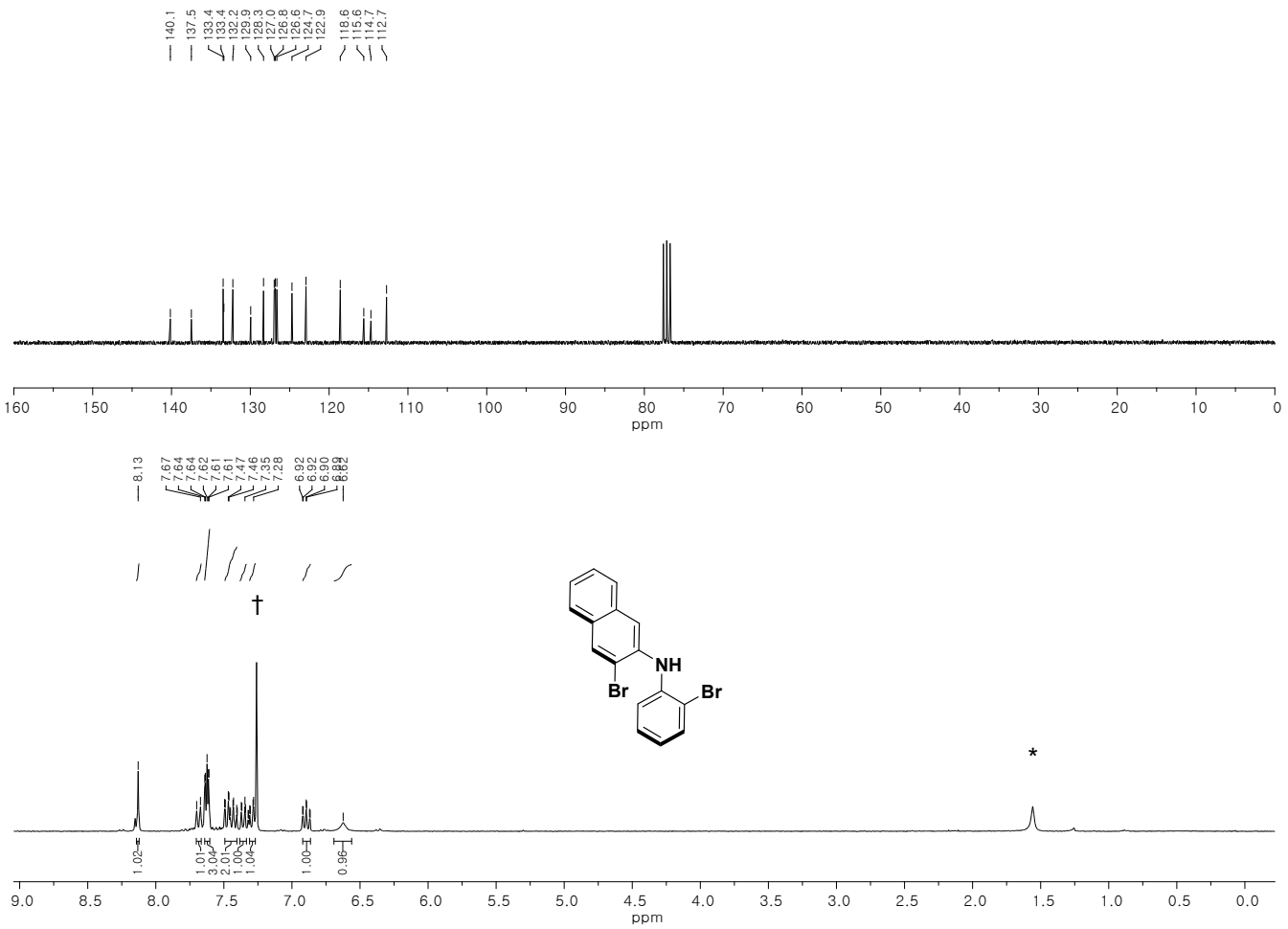


Fig. S7. ^{13}C (top) and ^{1}H (bottom) NMR spectra of **1a** in $CDCl_3$ (∗ from water and † from residual $CHCl_3$).

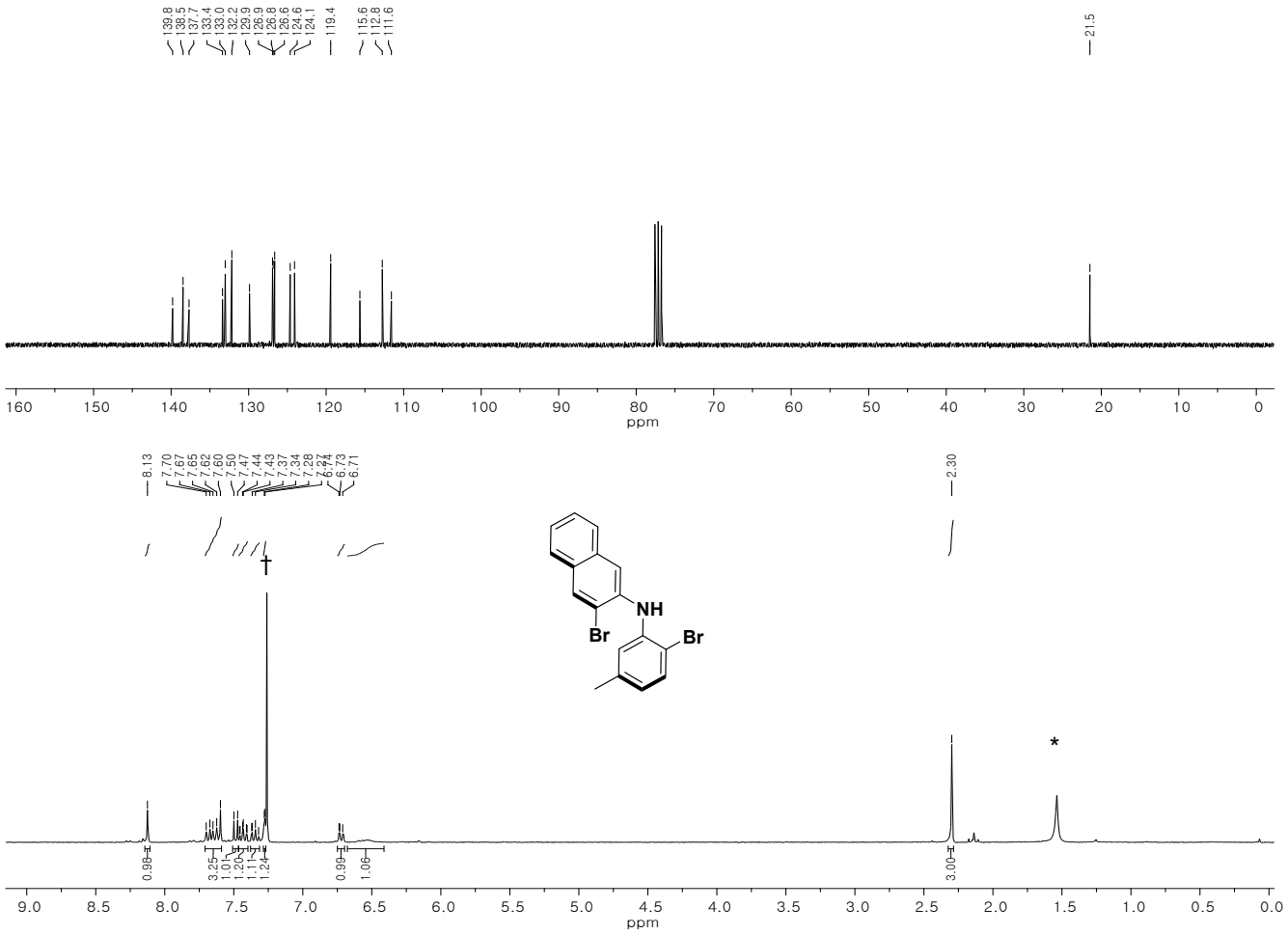


Fig. S8. ^{13}C (top) and ^{1}H (bottom) NMR spectra of **4a** in $CDCl_3$ (∗ from water and † from residual $CHCl_3$).

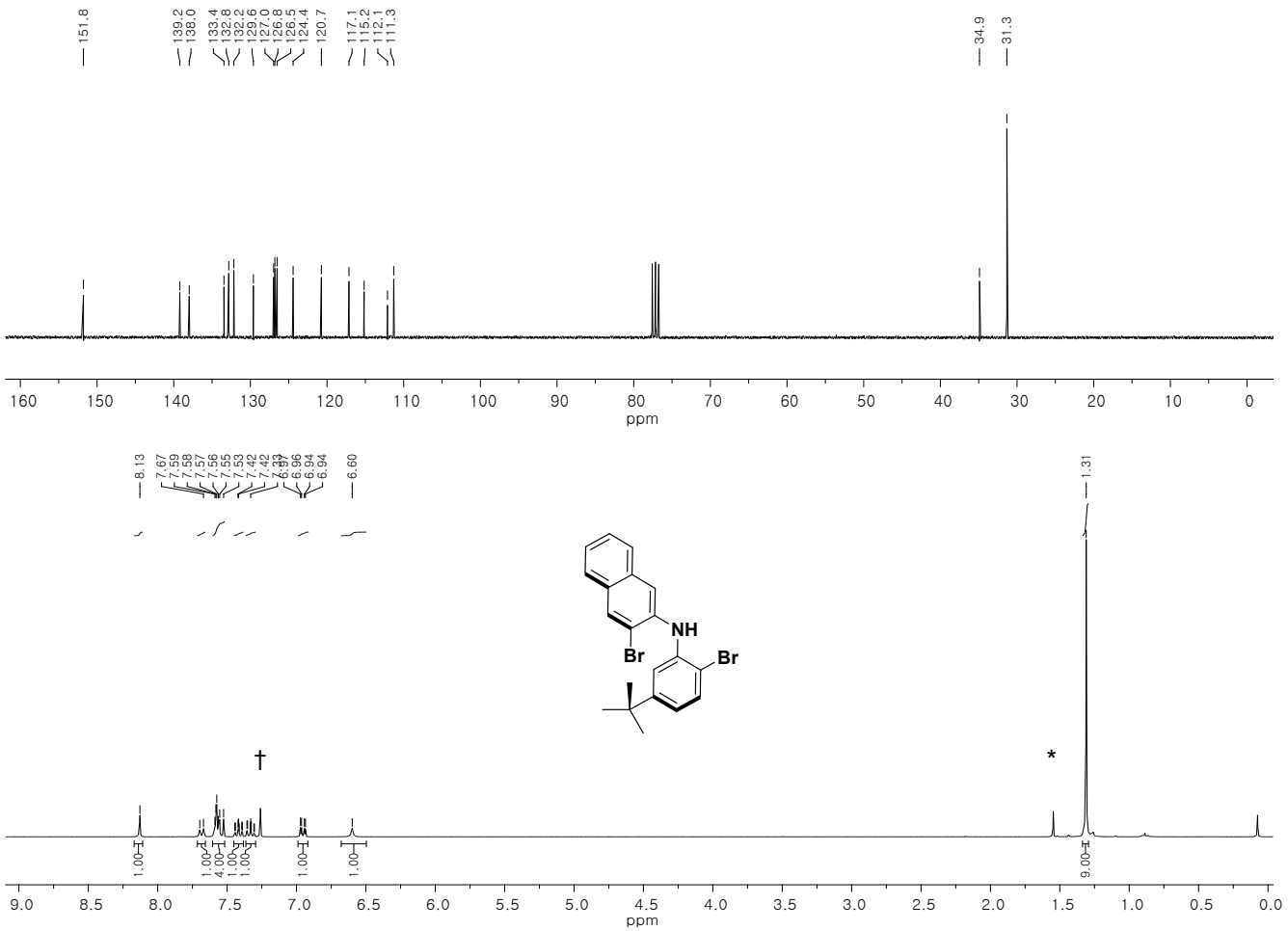


Fig. S9. ^{13}C (top) and ^{1}H (bottom) NMR spectra of **5a** in $CDCl_3$ (∗ from water and † from residual $CHCl_3$).

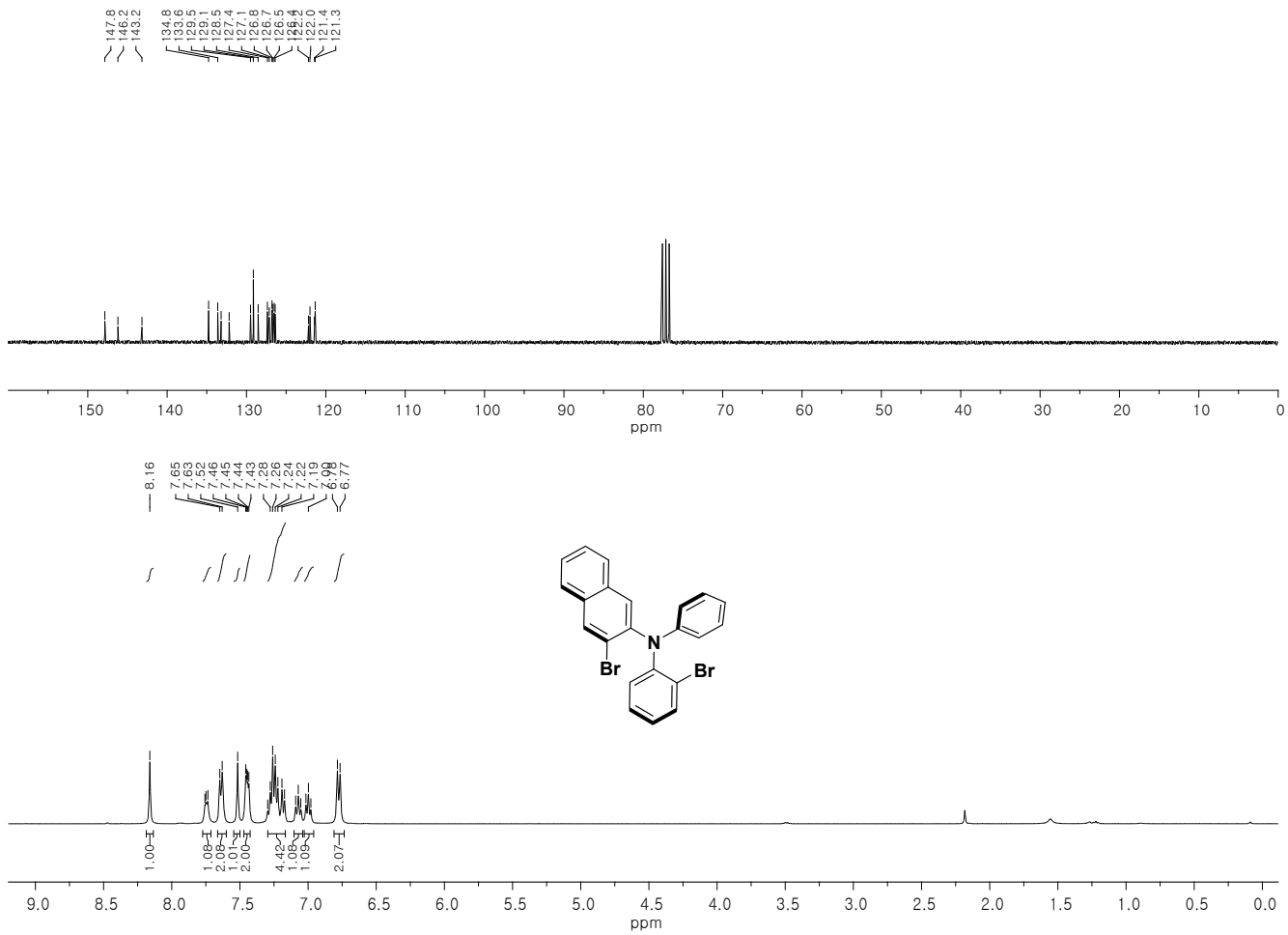


Fig. S10. ^{13}C (top) and ^{1}H (bottom) NMR spectra of **1b** in $CDCl_3$.

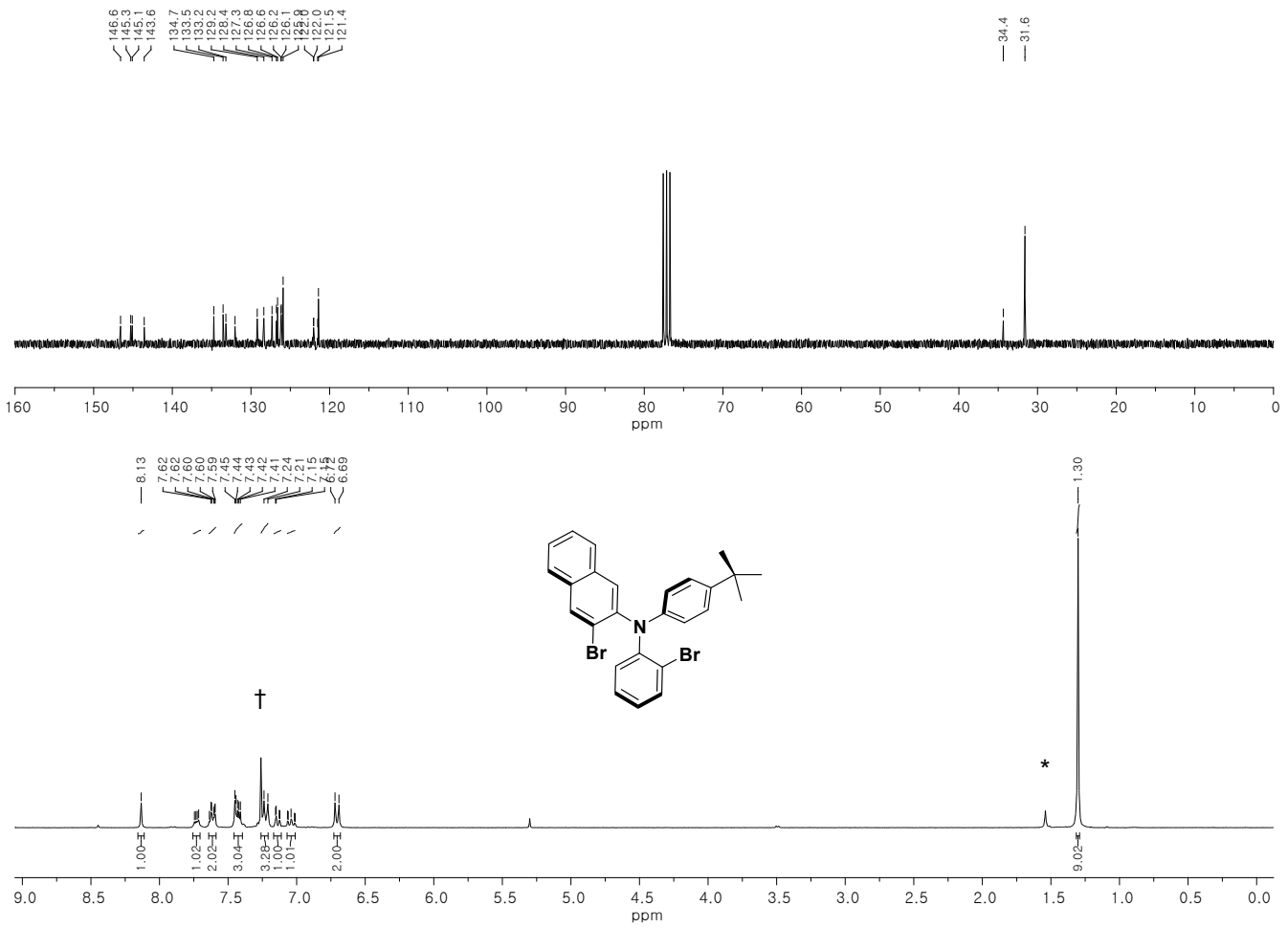


Fig. S11. ^{13}C (top) and ^{1}H (bottom) NMR spectra of **3b** in $CDCl_3$ (∗ from water and † from residual $CHCl_3$).

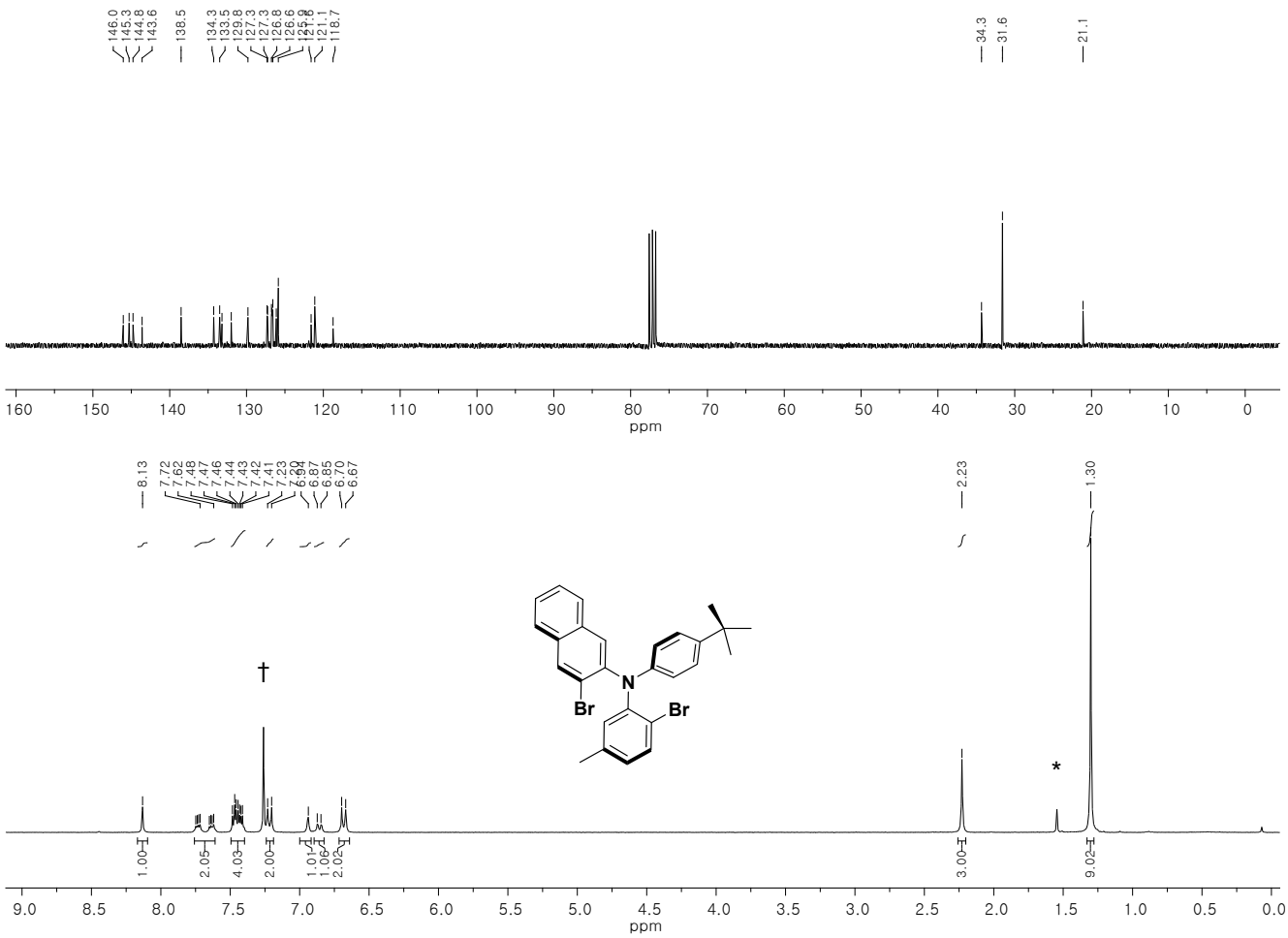


Fig. S12. ^{13}C (top) and ^{1}H (bottom) NMR spectra of **4b** in $CDCl_3$ (∗ from water and † from residual $CHCl_3$).

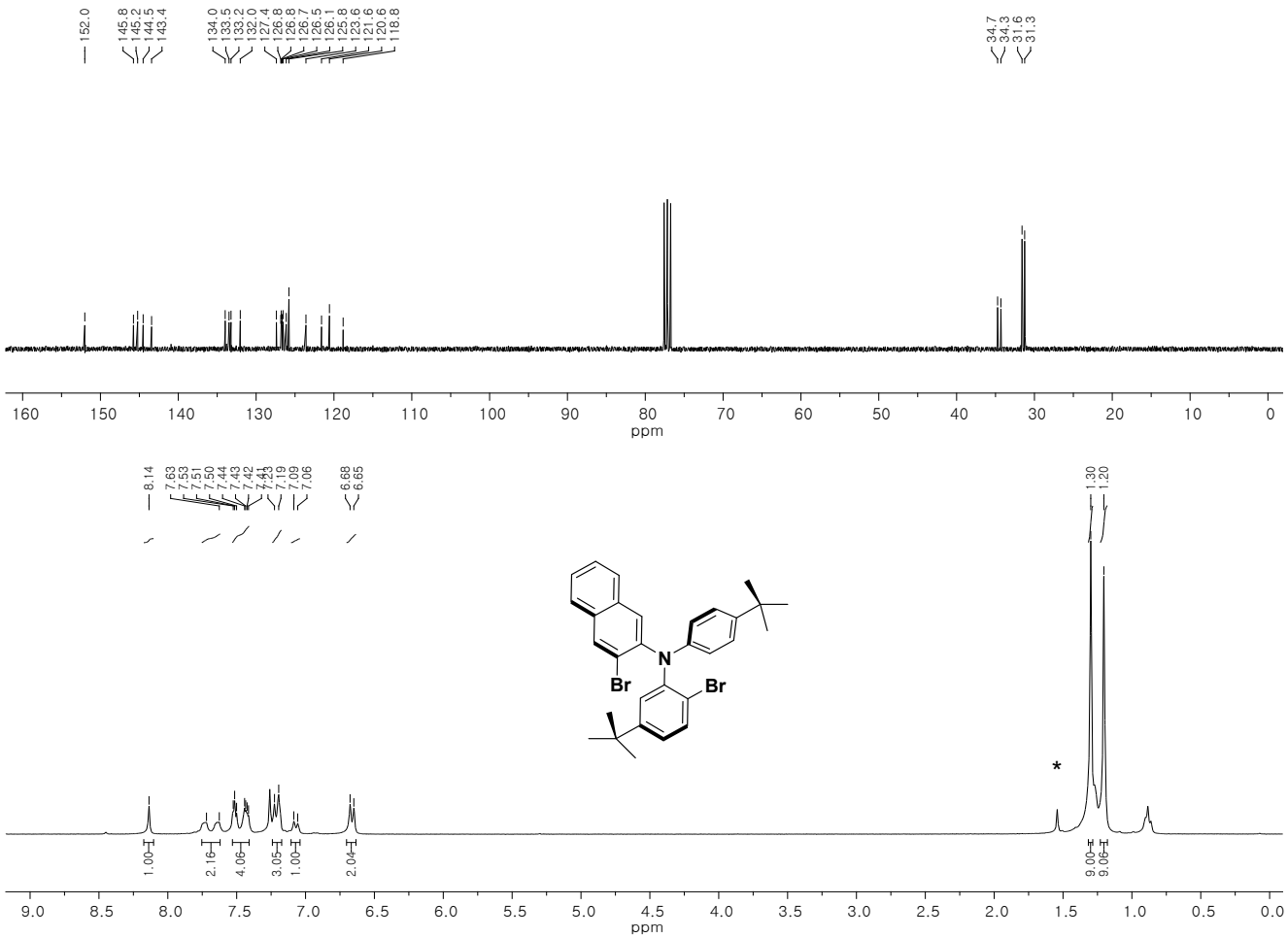


Fig. S13. ^{13}C (top) and ^{1}H (bottom) NMR spectra of **5b** in $CDCl_3$ (∗ from water).

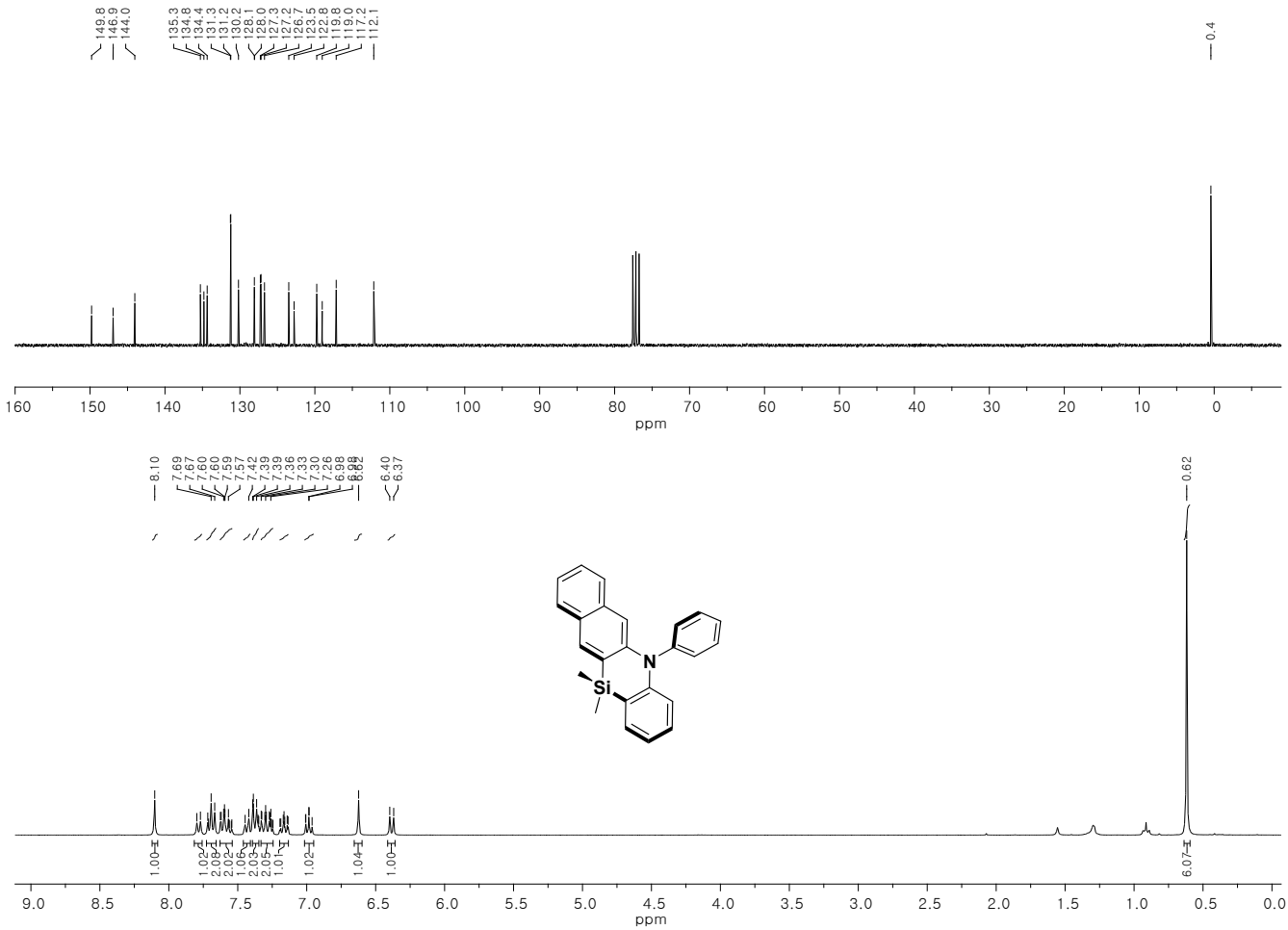


Fig. S14. ^{13}C (top) and ^{1}H (bottom) NMR spectra of **1c** in $CDCl_3$.

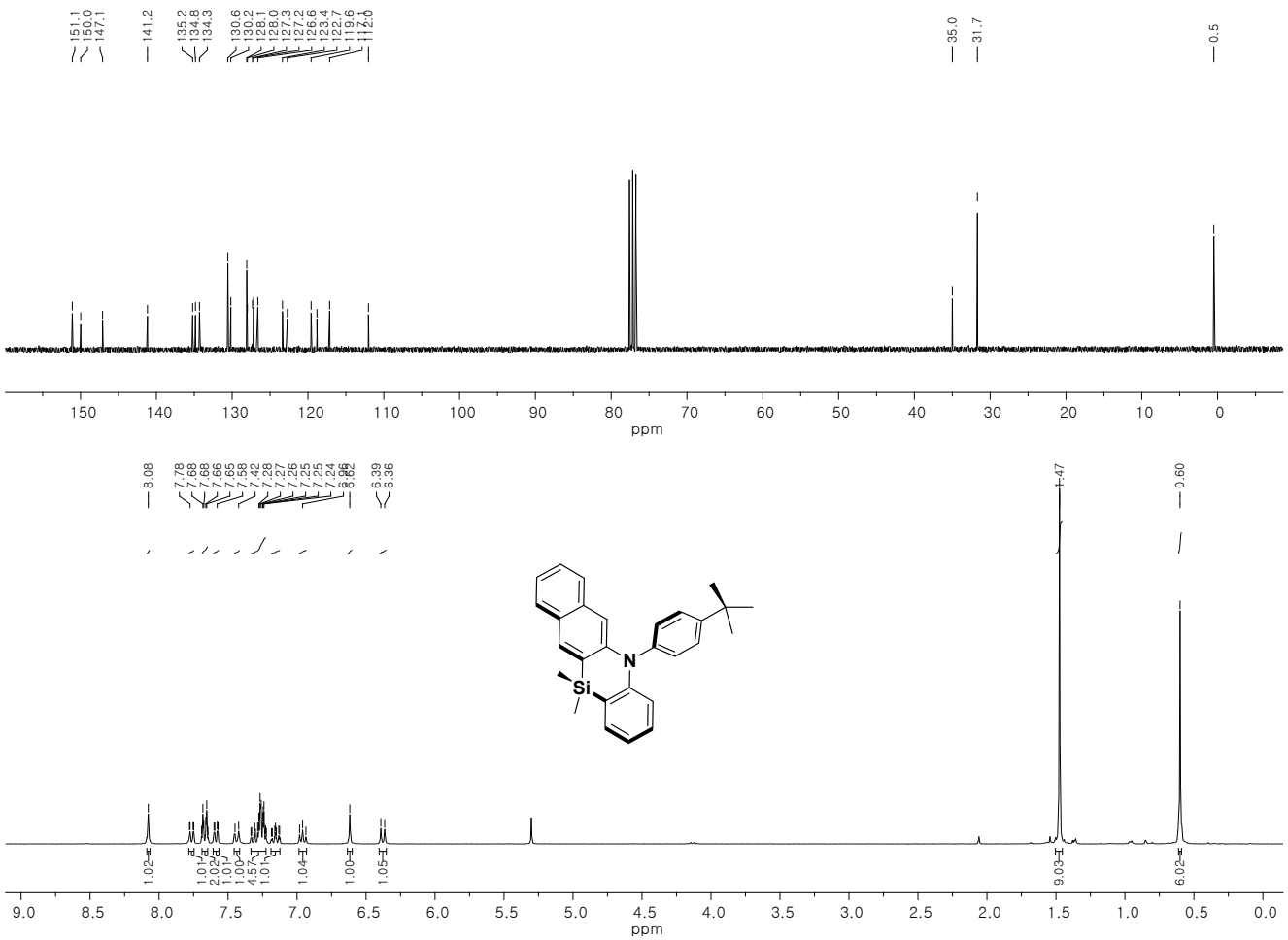


Fig. S15. ^{13}C (top) and ^{1}H (bottom) NMR spectra of **3c** in $CDCl_3$.

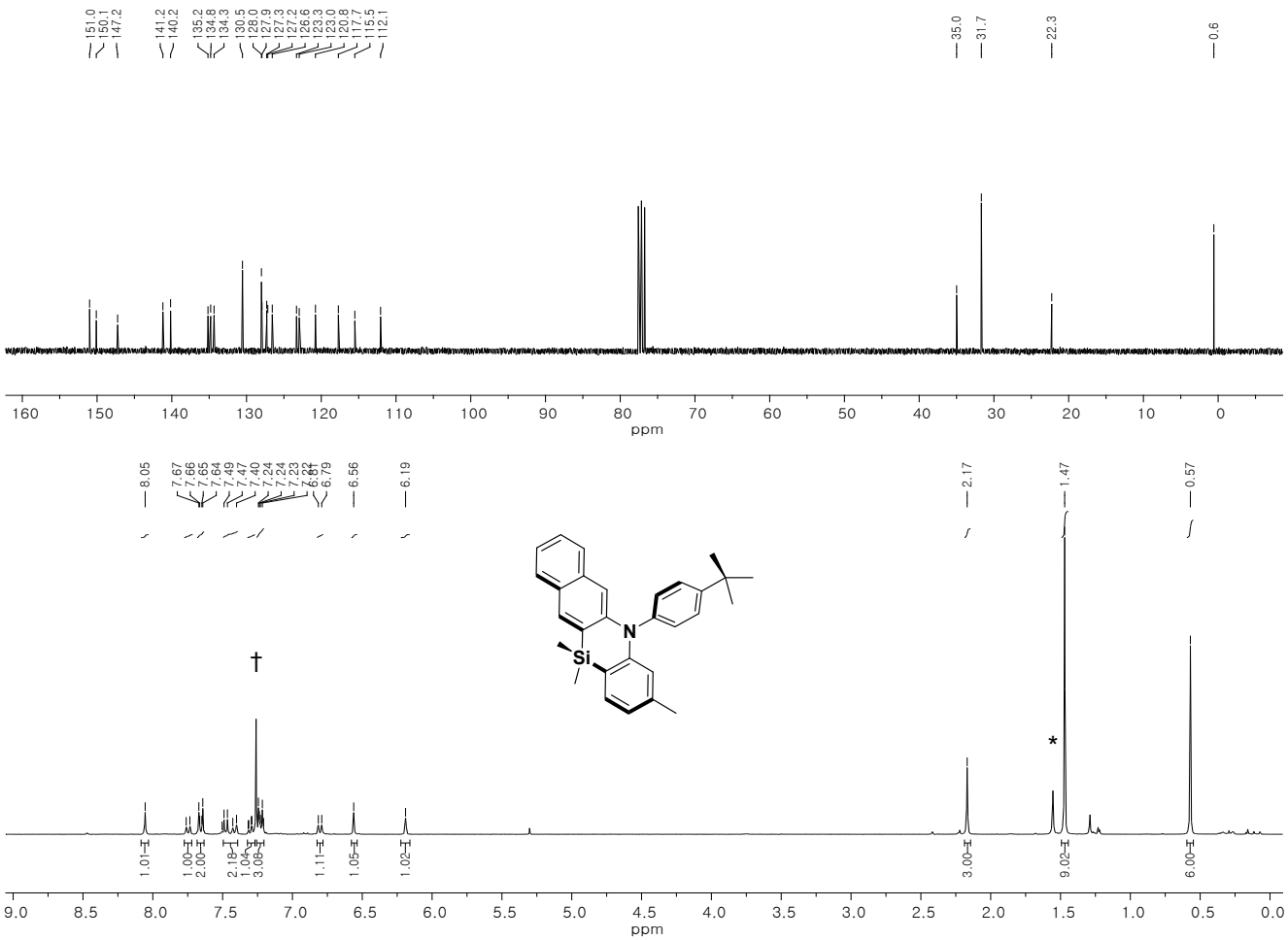


Fig. S16. ^{13}C (top) and ^{1}H (bottom) NMR spectra of **4c** in $CDCl_3$ (∗ from water and † from residual $CHCl_3$).

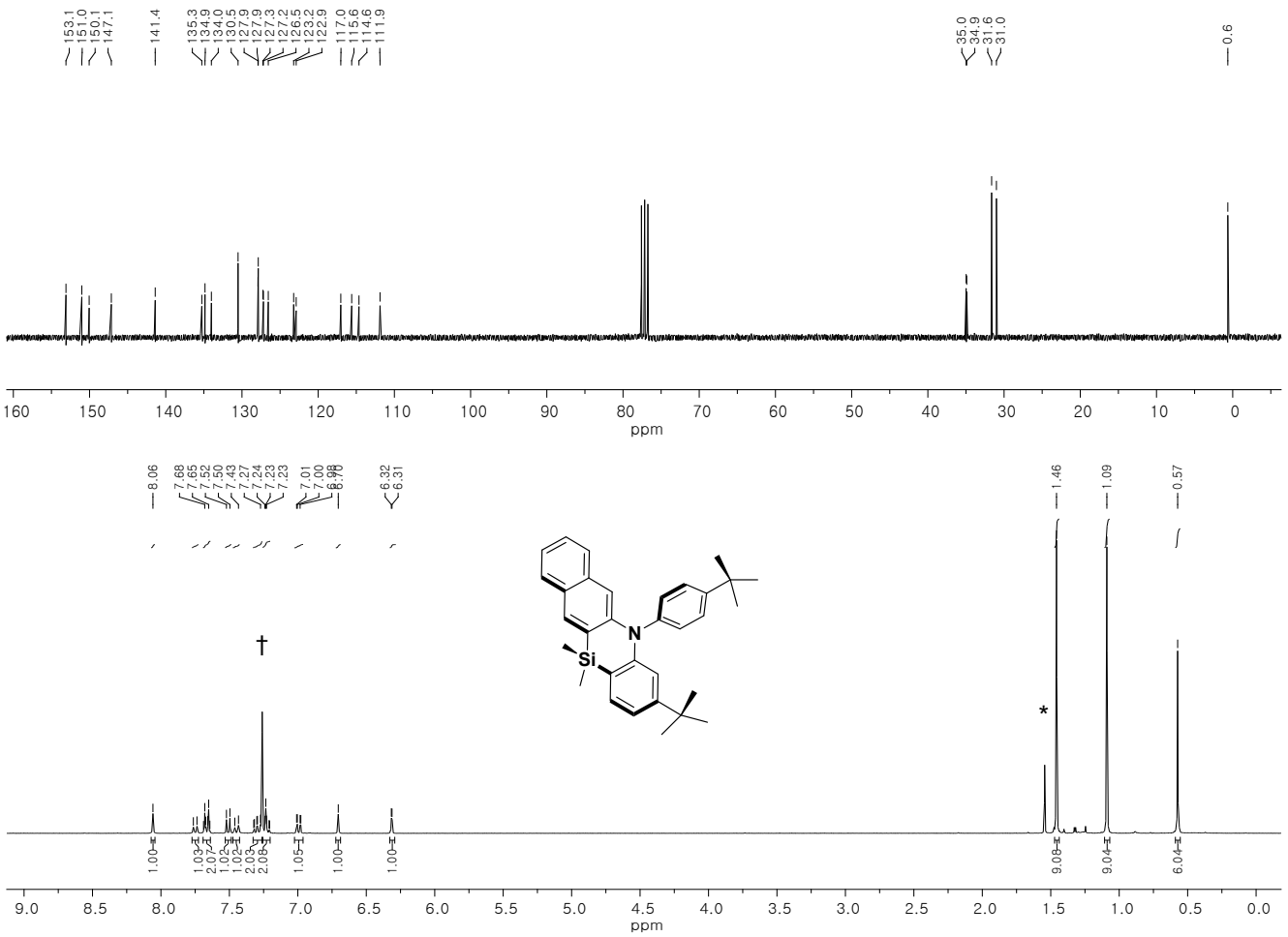


Fig. S17. ^{13}C (top) and ^{1}H (bottom) NMR spectra of **5c** in $CDCl_3$ (∗ from water and † from residual $CHCl_3$).

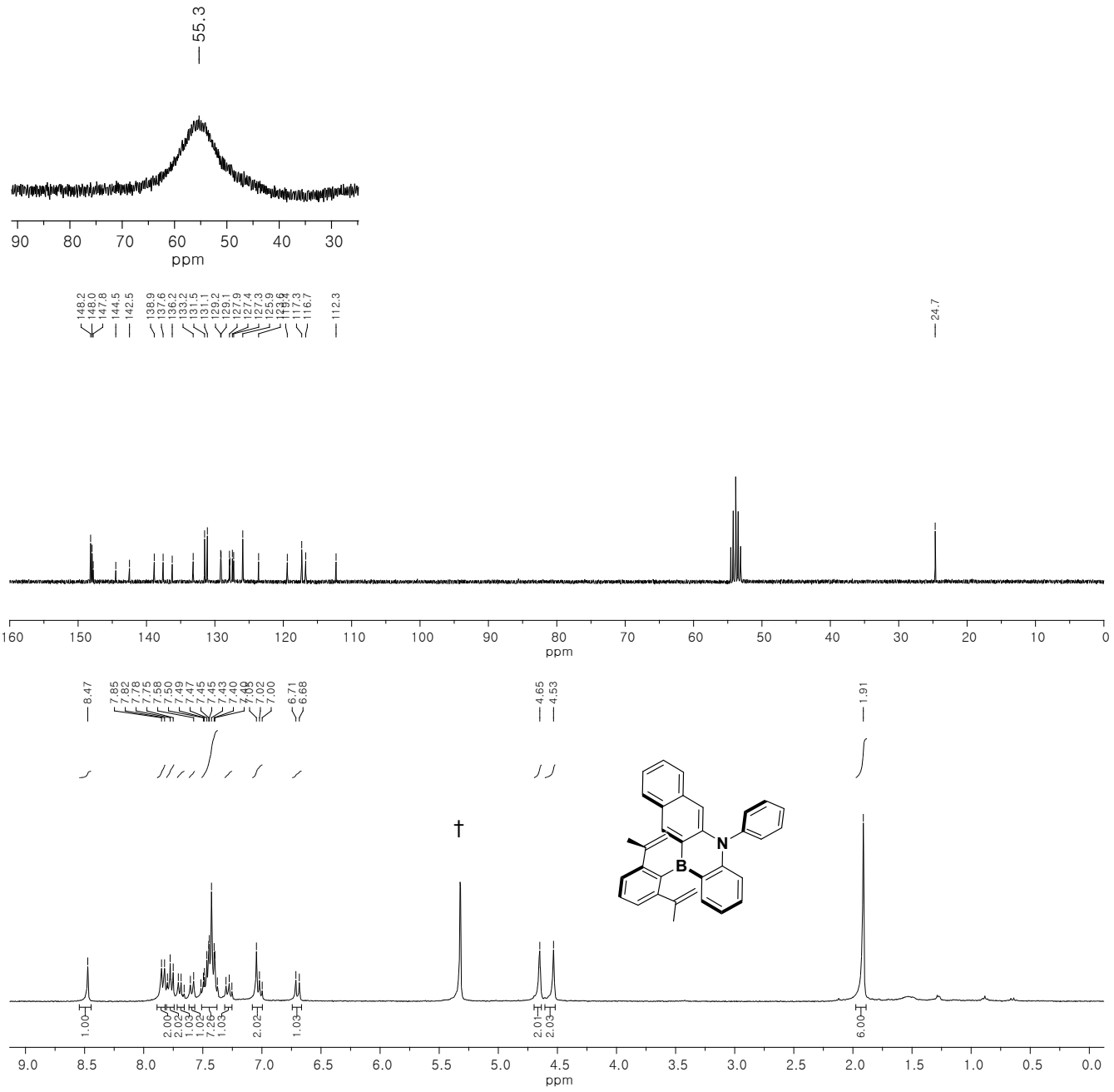


Fig. S18. ^{1}H (bottom), ^{13}C (middle), and ^{11}B (top) NMR spectra of **1d** in CD_2Cl_2 († from residual $CHDCl_2$).

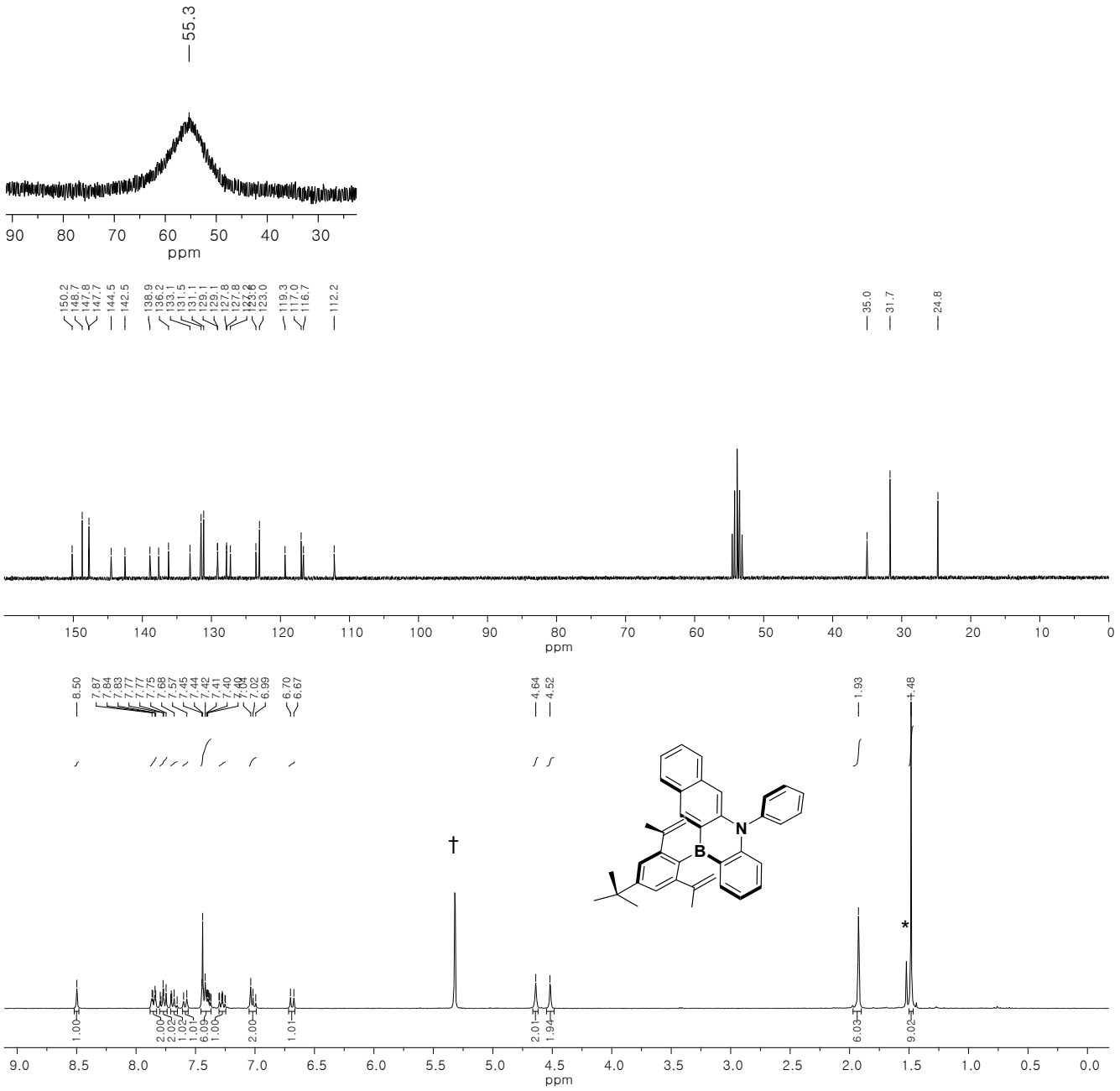


Fig. S19. ^{1}H (bottom), ^{13}C (middle), and ^{11}B (top) NMR spectra of **2d** in CD_2Cl_2 (∗ from water and † from residual $CHDCl_2$).

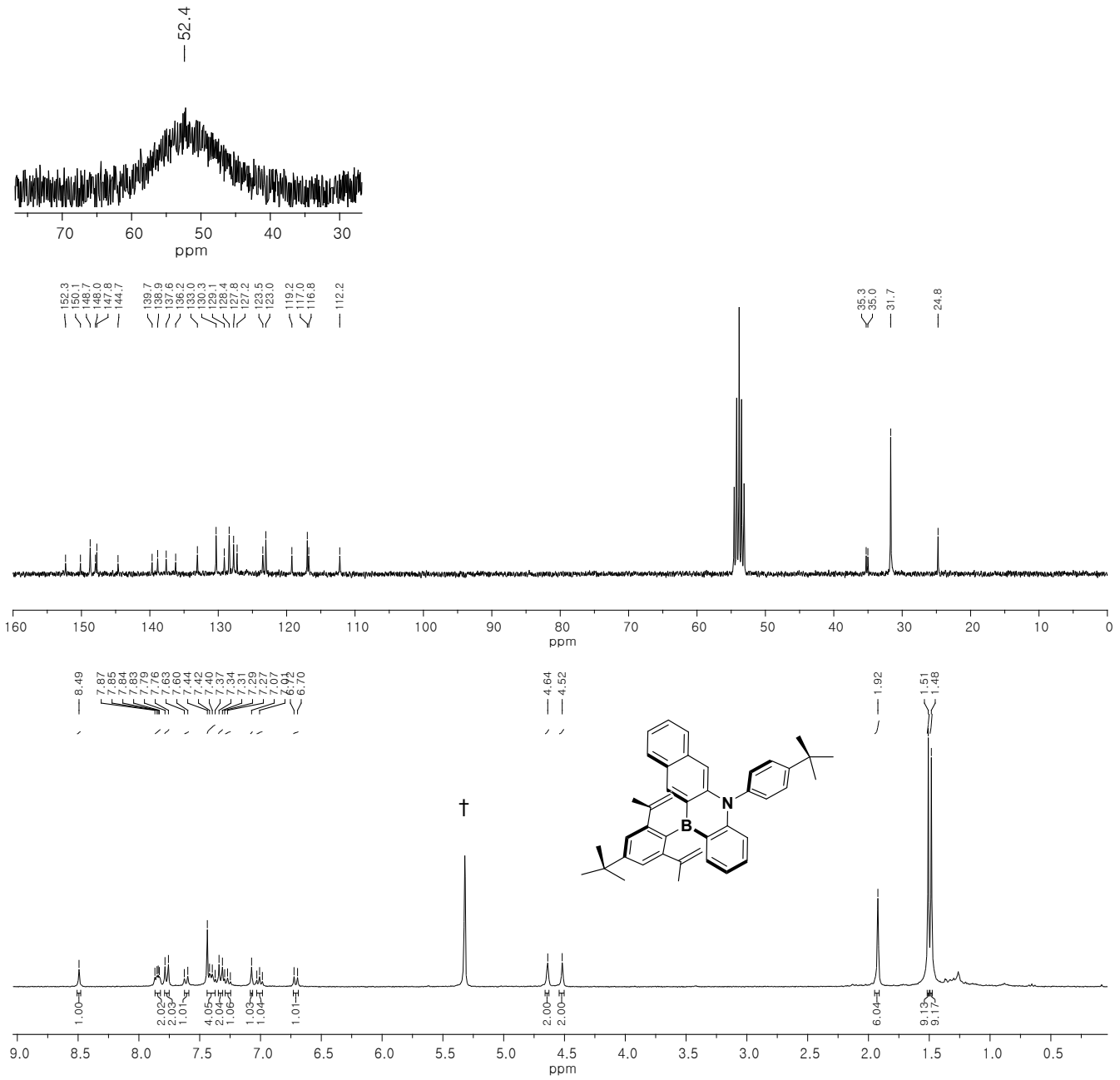


Fig. S20. ^{1}H (bottom), ^{13}C (middle), and ^{11}B (top) NMR spectra of **3d** in CD_2Cl_2 († from residual $CHDCl_2$).

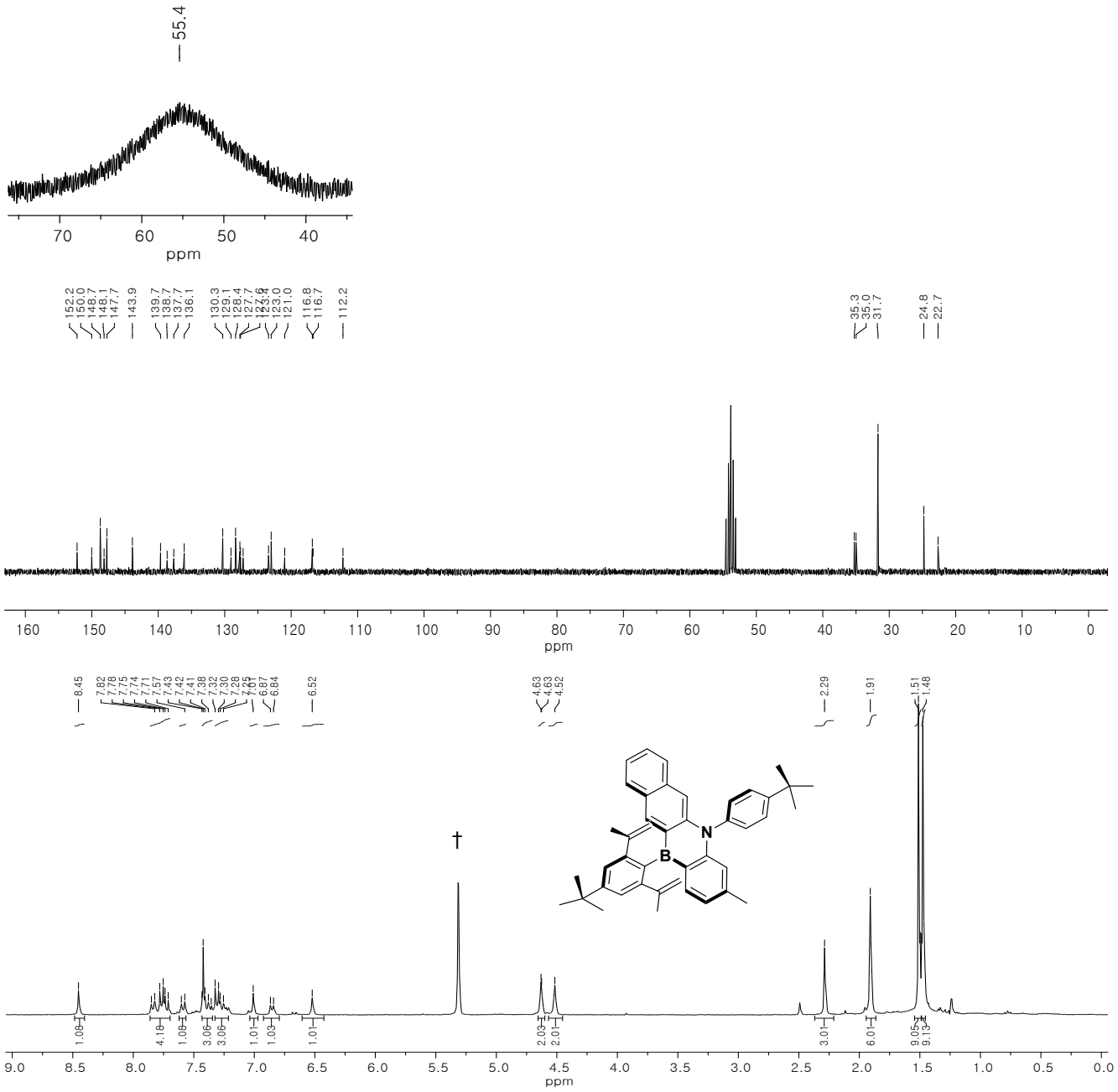


Fig. S21. ^{1}H (bottom), ^{13}C (middle), and ^{11}B (top) NMR spectra of **4d** in CD_2Cl_2 († from residual $CHDCl_2$).

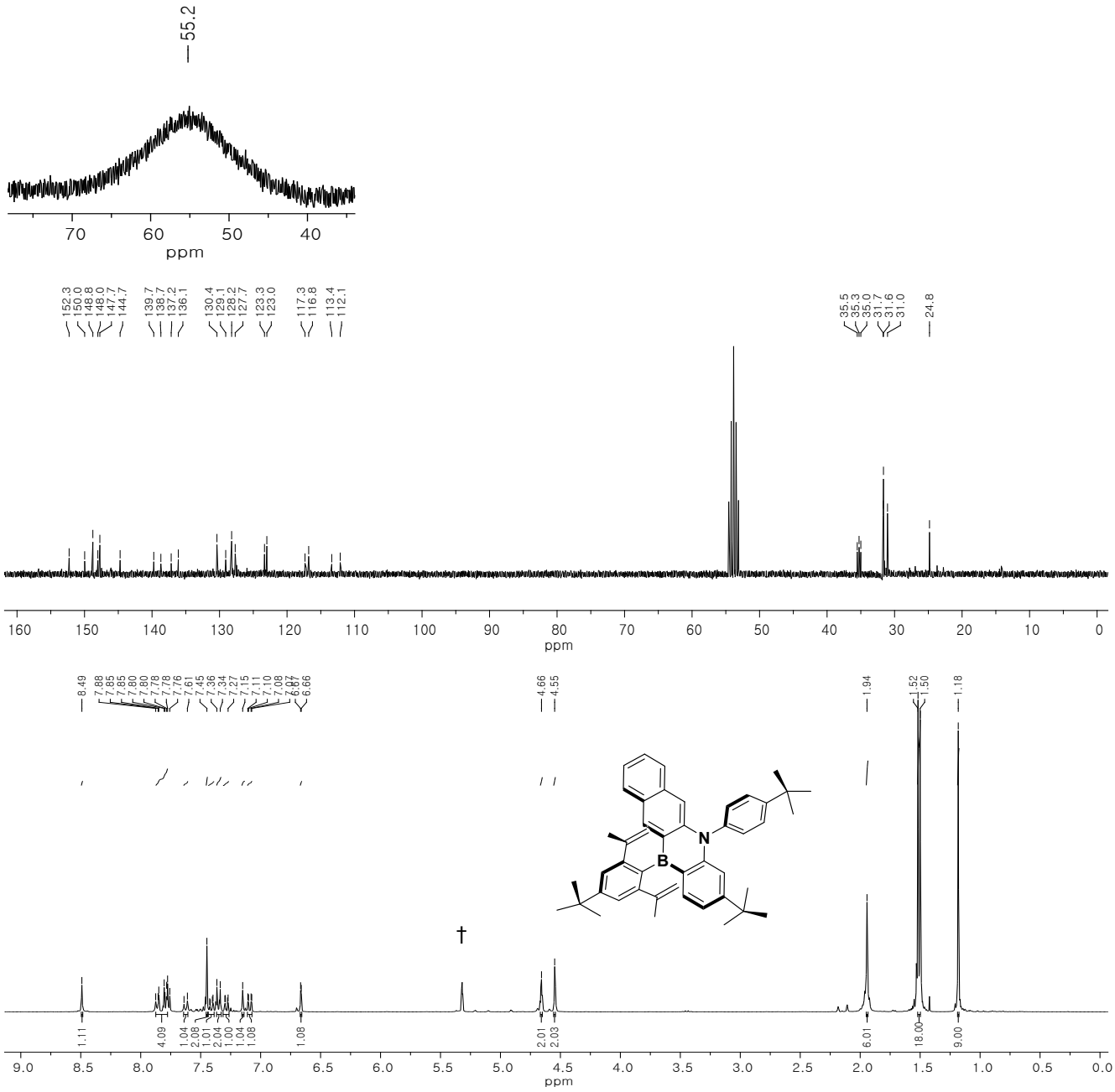


Fig. S22. ^{1}H (bottom), ^{13}C (middle), and ^{11}B (top) NMR spectra of **5d** in CD_2Cl_2 († from residual $CHDCl_2$).

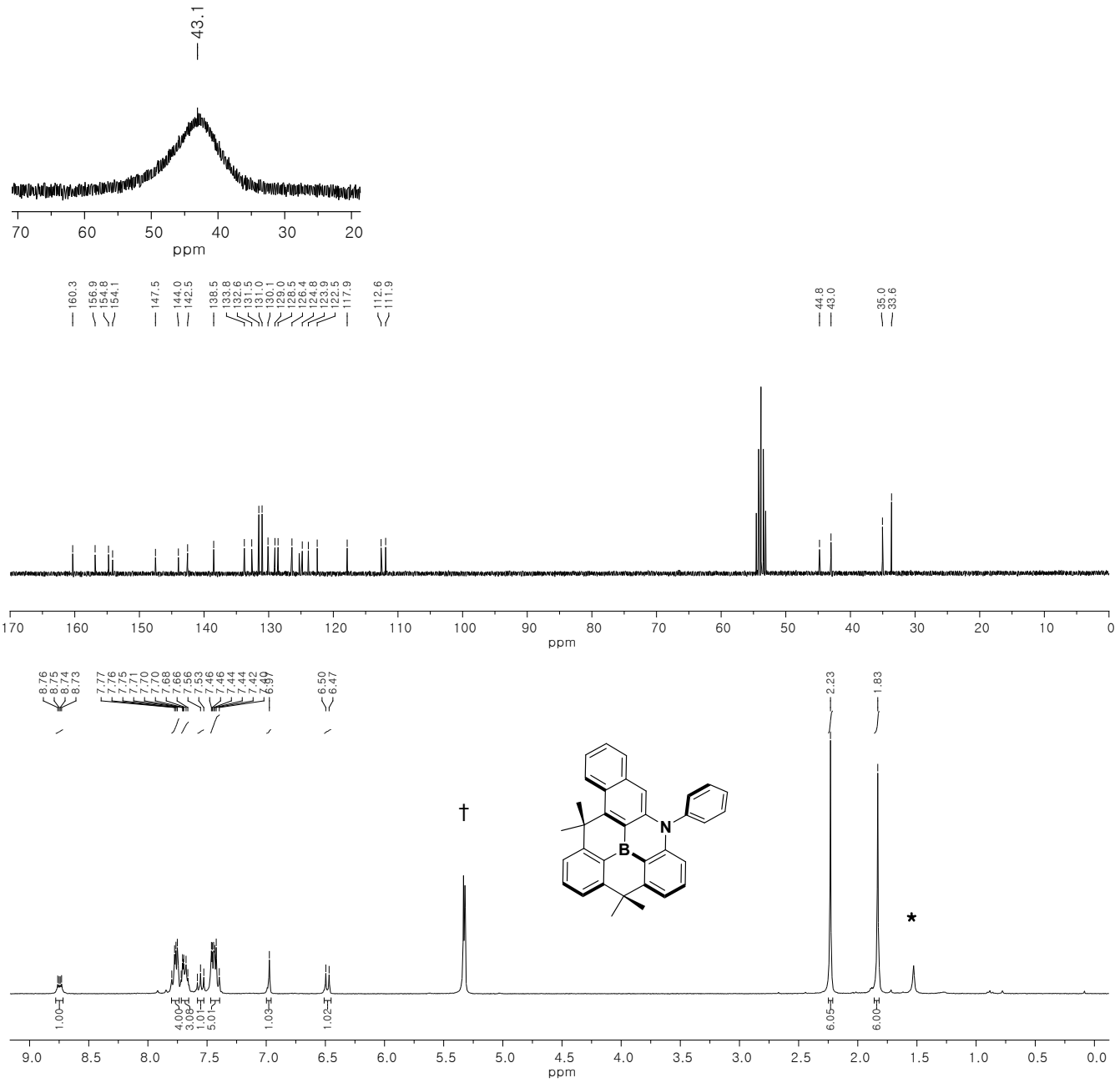


Fig. S23. ^{1}H (bottom), ^{13}C (middle), and ^{11}B (top) NMR spectra of **1** in CD_2Cl_2 (∗ from water and † from residual $CHDCl_2$).

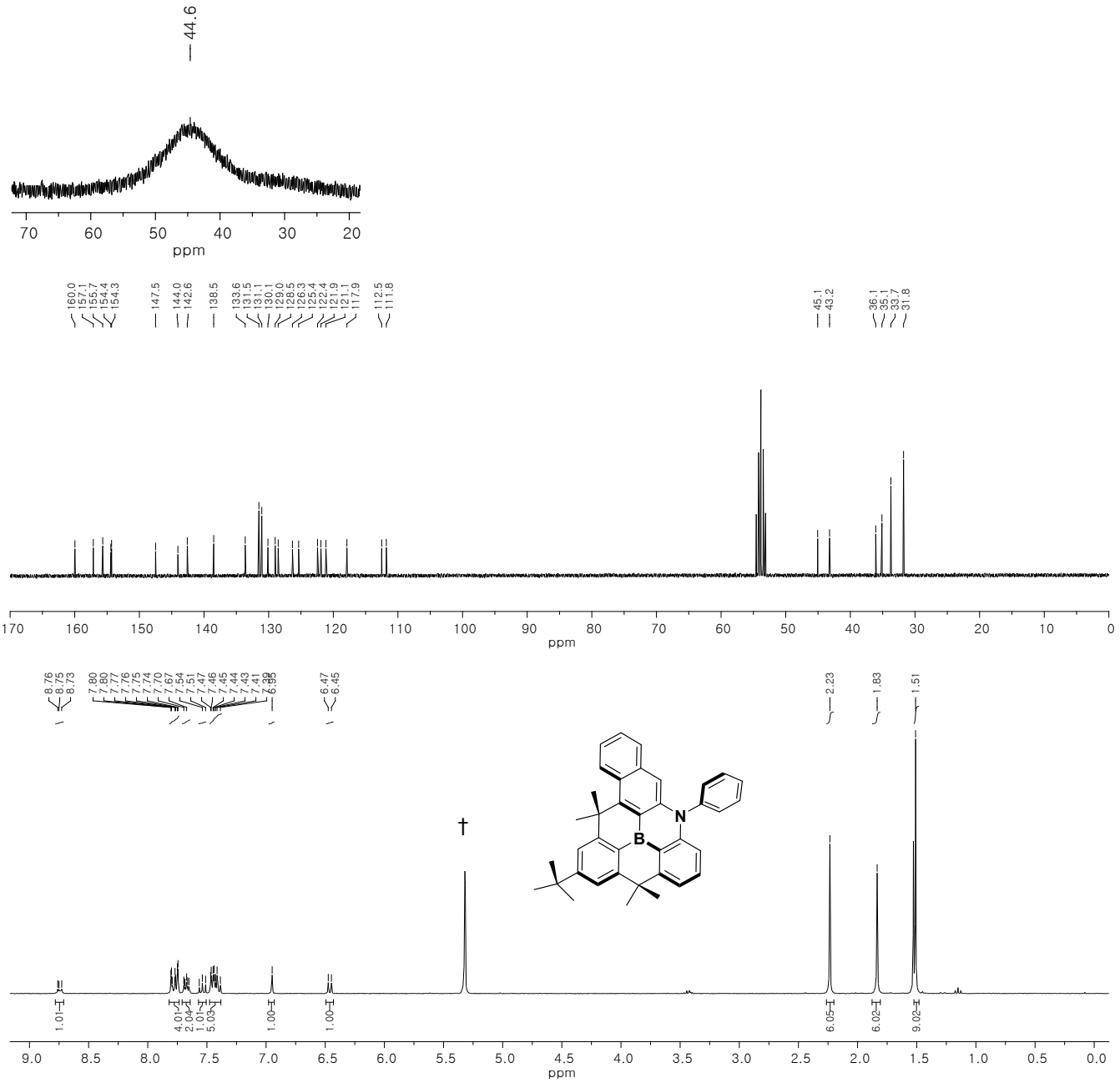


Fig. S24. ^{1}H (bottom), ^{13}C (middle), and ^{11}B (top) NMR spectra of **2** in CD_2Cl_2 († from residual $CHDCl_2$).

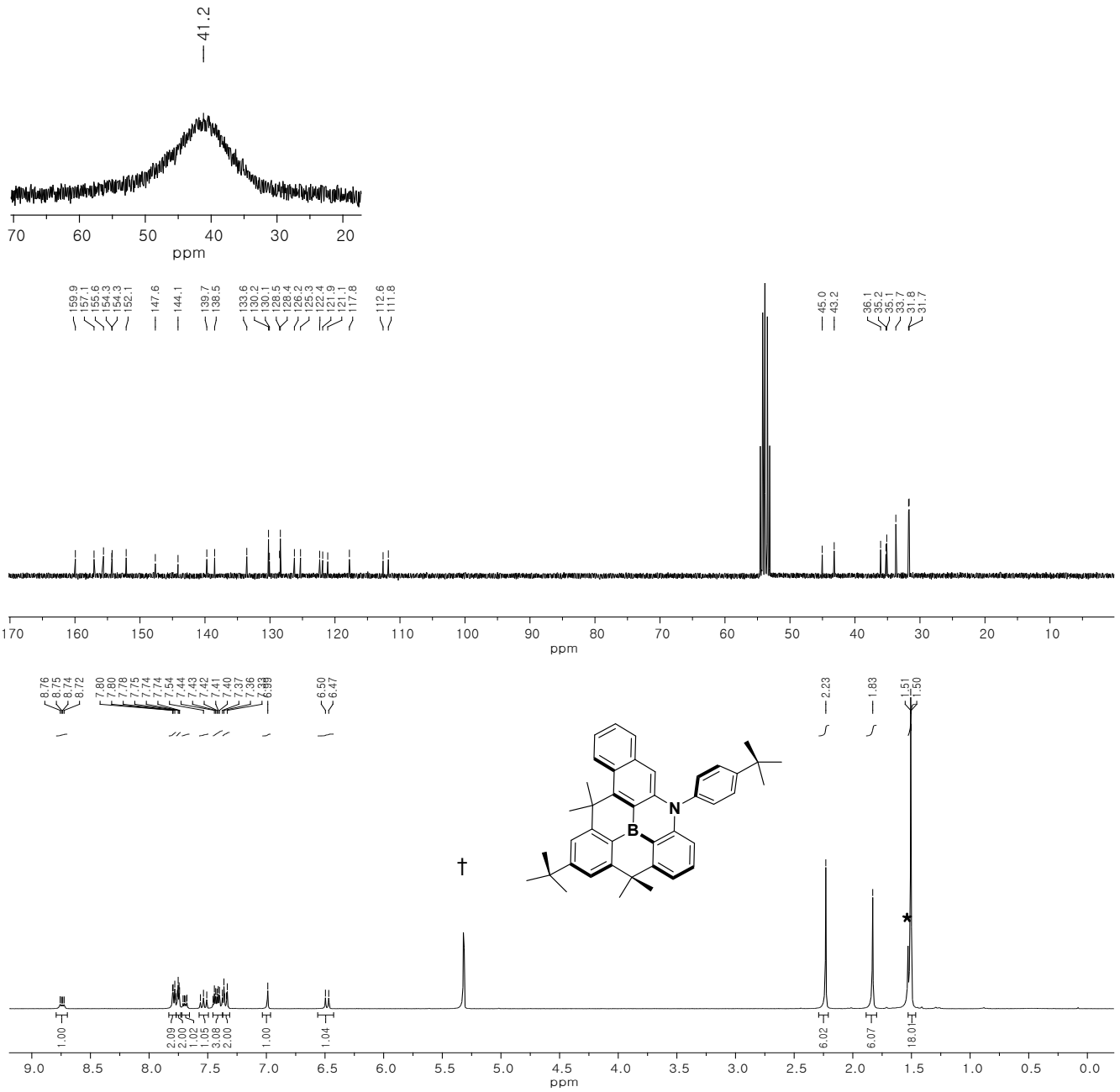


Fig. S25. ^{1}H (bottom), ^{13}C (middle), and ^{11}B (top) NMR spectra of **3** in CD_2Cl_2 (∗ from water and † from residual $CHDCl_2$).

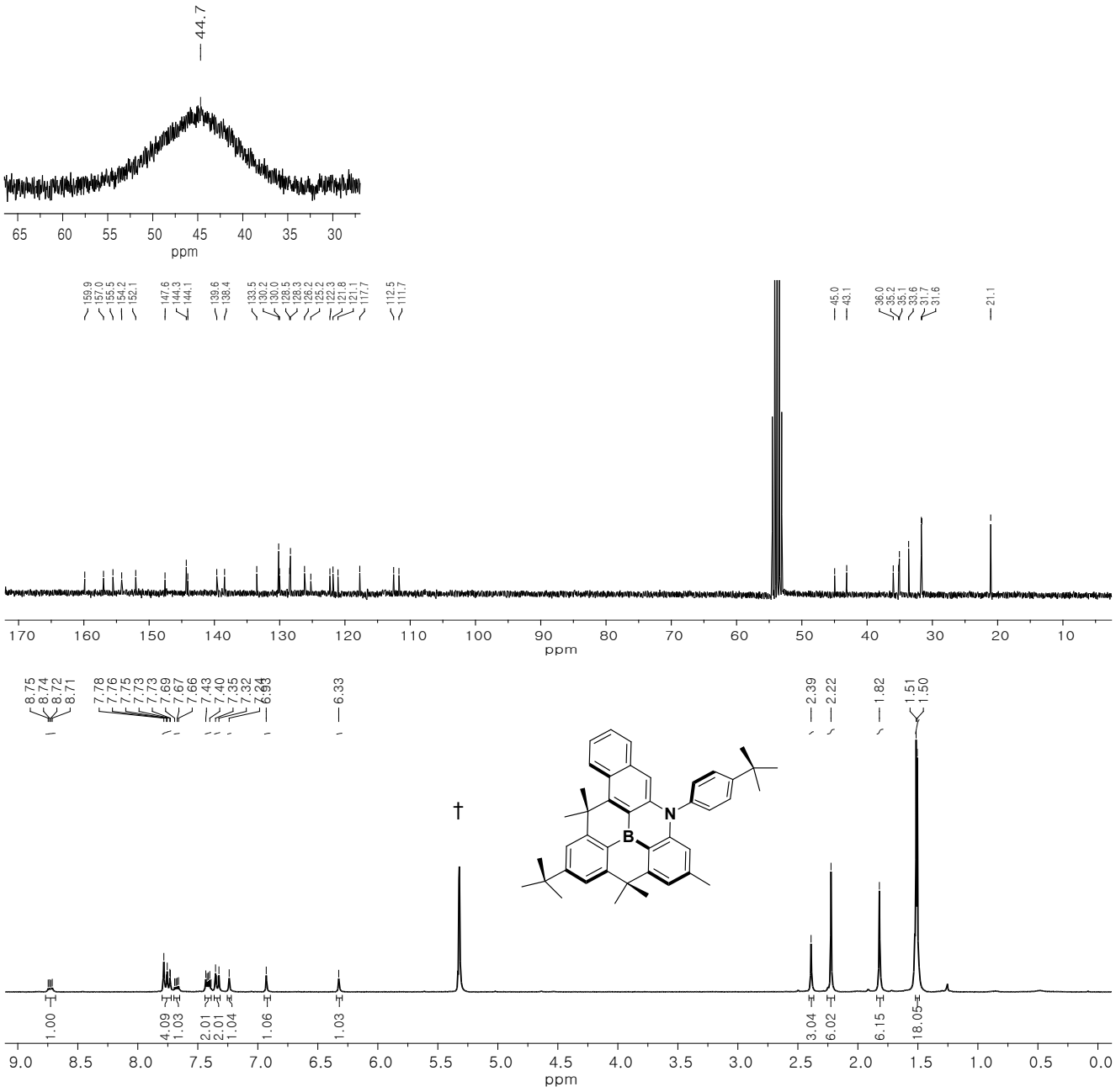


Fig. S26. ^{1}H (bottom), ^{13}C (middle), and ^{11}B (top) NMR spectra of **4** in CD_2Cl_2 († from residual $CHDCl_2$).

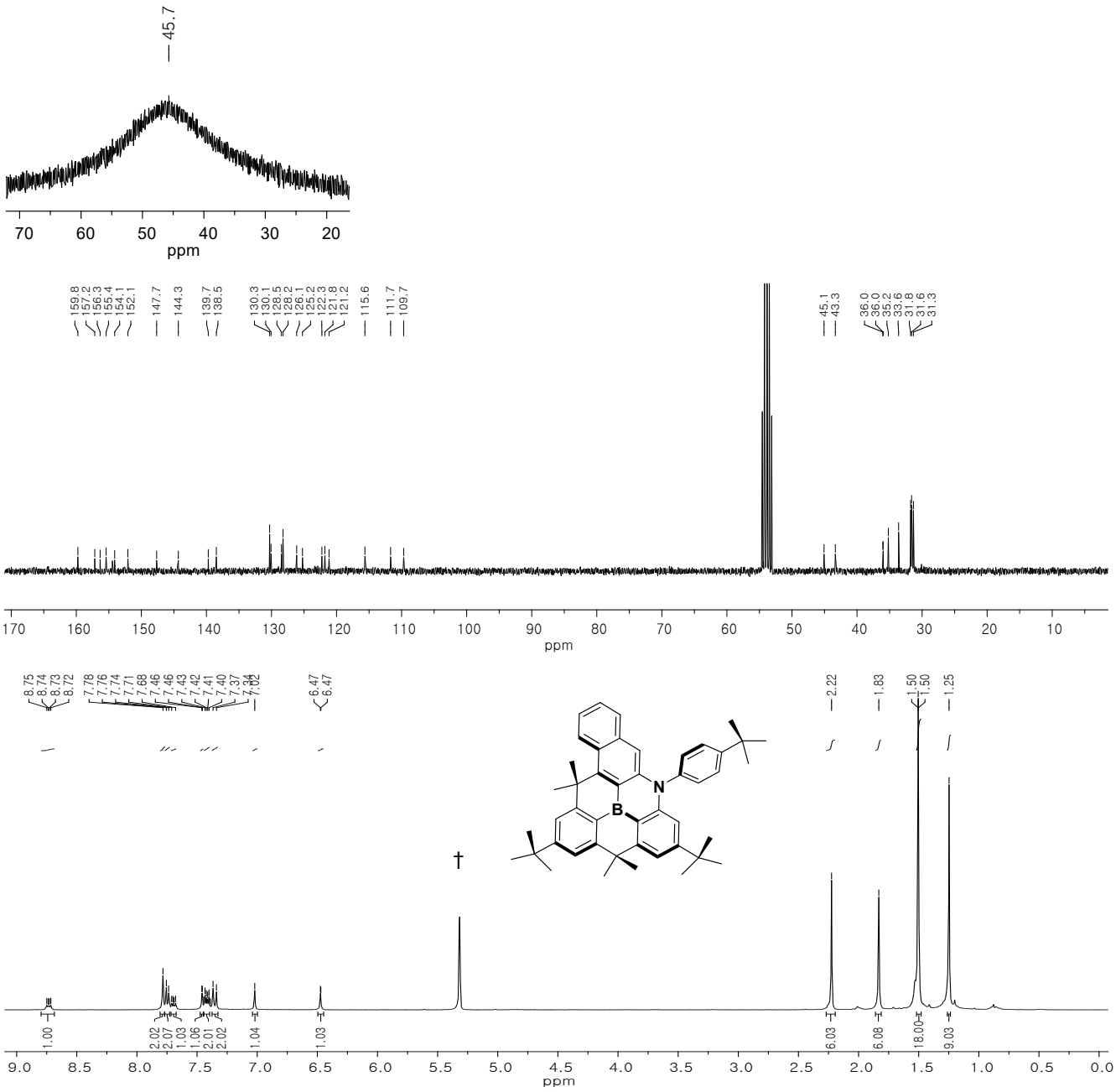


Fig. S27. ^{1}H (bottom), ^{13}C (middle), and ^{11}B (top) NMR spectra of **5** in CD_2Cl_2 († from residual $CHDCl_2$).

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