Supporting Information

for

Palladium-Catalyzed Regio- and Stereoselective Carbothiolation of Terminal Alkynes with Azolyl Sulfides

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1. General

Instrumentation

All the reactions were carried out under an Ar atmosphere using standard Schlenk techniques. Glassware was dried in an oven (150 °C) and heated under reduced pressure before use. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 F_{254}, 0.25 mm) were used. Silica gel column chromatography was carried out using Silica gel 60 (spherical, 40-100 μm) from Kanto Chemicals Co., Ltd. NMR spectra (^{1}H, ^{13}C{^{1}H}, and ^{19}F{^{1}H}) were recorded on Varian INOVA-600 (600 MHz), Mercury-400 (400 MHz) and 300-NMR ASW (300 MHz) spectrometers. Chemical shifts (δ) are in parts per million relative to $CDCl_3$ at 7.26 ppm for ^{1}H and at 77.0 ppm for ^{13}C{^{1}H} NMR spectra or DMSO-d_6 at 2.50 ppm for ^{1}H and at 39.5 ppm for ^{13}C{^{1}H} NMR spectra, respectively. The ^{19}F{^{1}H} NMR spectra were measured by using C_6H_5F (δ = –113.15) as an external standard. The NMR yields were determined using dibromomethane as internal standard. Infrared spectra were recorded on a Shimadzu IRPrestige-21 spectrophotometer and reported in wave numbers (cm^{-1}). LRMS analyses were carried out on a SHIMADZU GC-17A equipped with a SHIMADZU QP-5050 GC-MS system. HRMS were determined on a JEOL JMS-700 MStation. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN elemental analyzer.

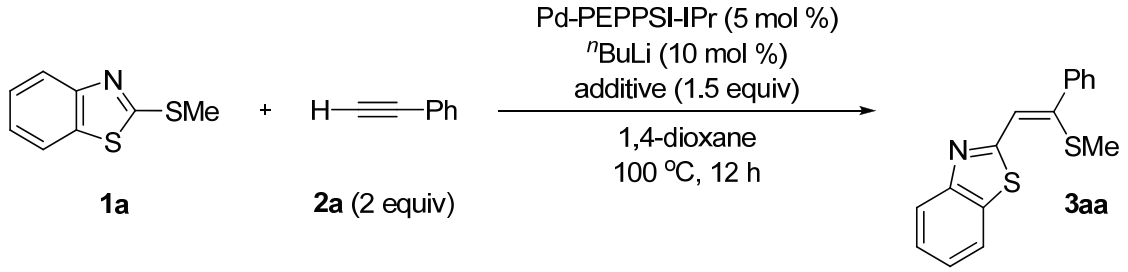
The reaction under microwave irradiation was carried out using a focused microwave unit (Biotage Initiator^{TM}). The maximum irradiation power is 400 W. Each reaction was run in a 20-mL glass pressure vial, which is a commercially available vial specifically for the Biotage Initiator^{TM}. It took 5 min to reach 160 ^{o}C. After reaching the indicated temperature, controlled microwave irradiation started and continued for 40 min, keeping the reaction temperature constant.

Chemicals

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Pd-PEPPSIs[1] was prepared according to the literature. Sulfides **1a** and **1d**–**1g** were prepared by the reaction of the corresponding thiol with iodomethane.[2] Sulfide **1b** was prepared from benzothiazole and diphenyl disulfide.[3] Sulfides **1a**,[4] **1b**,[5] **1d**,[6] **1e**,[7] **1f**,[8] and **1g**[9] were known compounds. Sulfide **1c** and alkynes **2** were commercially available.

2. *Optimization of Reaction Conditions*

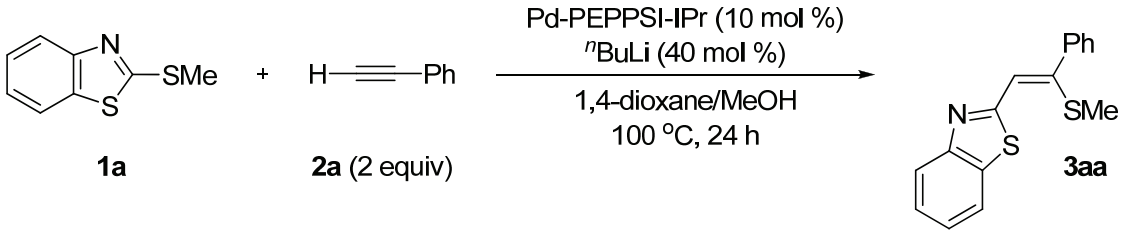
Additive Screening



entry	additive	NMR yield (%)
1	none	51
2	H_2O	57
3	MeOH	66
4	EtOH	45
5	^{t}BuOH	57
6	AcOH	0
7	pyridine	45

3. Experimental Procedures and Spectroscopic Data for New Compounds

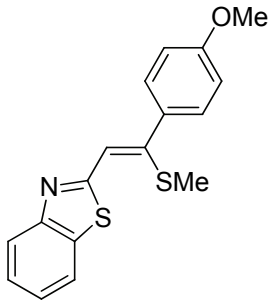
A Typical Procedure for Addition of Azolyl Sulfides 1 to Terminal Alkynes 2: Synthesis of (*Z*)-2-(2-Methylthio-2-phenylethenyl)benzothiazole (3aa).



Pd-PEPPSI-IPr (68 mg, 0.10 mmol) was placed in a 20-mL Schlenk tube under argon. *n*-Butyllithium (1.6 M hexane solution, 0.25 mL, 0.40 mmol) and 1,4-dioxane (8 mL) were added, and the mixture was stirred for 15 min. Phenylacetylene (**2a**, 220 μL, 2.0 mmol), 2-benzothiazolyl methyl sulfide (**1a**, 181 mg, 1.0 mmol), and methanol (250 μL) were sequentially added. The reaction mixture was heated at 100 °C for 24 h. After the mixture was cooled to 25 °C, the reaction was quenched with saturated NH_4Cl aqueous solution (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. Purification of the residue on silica gel column chromatography (hexane:ethyl acetate = 20:1) provided **3aa** (263 mg, 0.928 mmol) in 93% yield as a yellow viscous oil.

R_f = 0.21 (hexane:ethyl acetate = 20:1). B.p. 150 °C/9.8 Torr. FT-IR (neat, cm^{-1}): 3055 (w), 2920 (w), 2849 (w), 1427 (m), 1317 (w), 758 (s). ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 2.16 (s, 3H), 7.30 (s, 1H), 7.36–7.51 (m, 5H), 7.59–7.62 (m, 2H), 7.90–7.92 (m, 1H), 8.00–8.03 (m, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, rt): δ 16.9, 121.4, 122.8, 125.1, 125.2, 126.2, 128.4, 128.7, 129.0, 135.4, 138.7, 147.4, 152.3, 164.5. MS (EI, m/z (relative intensity)): 283 (M^+, 80), 268 (100), 251 (13), 250 (68), 236 (61), 223 (16), 134 (14), 109 (15). Anal. Calcd for $C_{16}H_{13}NS_2$: C, 67.81; H, 4.62; N, 4.94%. Found: C, 67.91; H, 4.66; N, 4.86%.

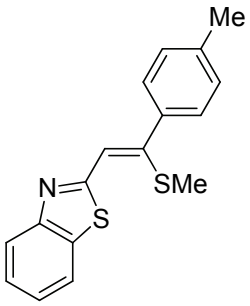
(*Z*)-2-{2-(*p*-Methoxyphenyl)-2-Methylthioethenyl}benzothiazole (3ab)



The title compound was obtained in 81% (253 mg, 0.807 mmol) as orange solid. R_f = 0.09 (hexane:ethyl acetate = 20:1). M.p. 55–56 °C. FT-IR (KBr, cm^{-1}): 2957 (w), 2924 (w), 2835 (w), 1603 (s), 1504 (s), 1250 (s), 760 (s). ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 2.16 (s, 3H), 3.85 (s, 3H), 6.94–6.97 (m, 2H), 7.25 (s, 1H), 7.36 (td, J = 8.0, 1.2 Hz, 1H), 7.46 (td, J = 8.0, 1.2 Hz, 1H), 7.54–7.56 (m, 2H), 7.87–7.89 (m, 1H), 7.97–7.99 (m,

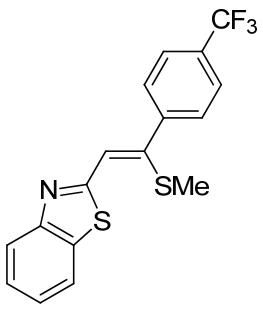
1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 16.8, 55.0, 113.9, 121.1, 122.4, 124.0, 124.8, 125.8, 129.4, 130.6, 135.1, 146.8, 152.0, 160.1, 164.6. MS (EI, m/z (relative intensity)): 313 (M^+, 100), 312 (38), 299 (18), 298 (99), 281 (30), 280 (92), 266 (46), 255 (16), 254 (17), 223 (49). Anal. Calcd for $C_{17}H_{15}NOS_2$: C, 65.14; H, 4.82; N, 4.47%. Found: C, 65.41; H, 5.13; N, 4.24%.

(*Z*)-2-{2-(*p*-Methylphenyl)-2-methylthioethenyl}benzothiazole (3ac)



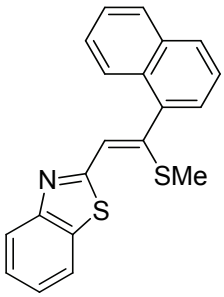
The title compound was obtained in 91% (270 mg, 0.908 mmol) as an orange oil. R_f = 0.24 (hexane:ethyl acetate = 20:1). B.p. 170 °C/7.1 Torr. FT-IR (neat, cm^{-1}): 3055 (m), 2922 (m), 1597 (m), 1574 (m), 1427 (s), 1317 (m,), 1200 (m), 820 (s), 760 (s), 729 (s). ^1H NMR (400 MHz, $CDCl_3$, rt): δ 2.13 (s, 3H), 2.37 (s, 3H), 7.21 (d, J = 8.0 Hz, 2H), 7.23 (s, 1H), 7.34 (td, J = 8.0, 1.6 Hz, 1H), 7.44 (td, J = 8.0, 1.6 Hz, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.85–7.88 (m, 1H), 7.96–7.99 (m, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 17.0, 21.3, 121.4, 122.6, 124.5, 125.1, 126.2, 128.3, 129.5, 135.3, 135.7, 139.3, 147.6, 152.2, 164.7. MS (EI, m/z (relative intensity)): 297 (M^+, 77), 296 (37), 283 (20), 282 (100), 265 (15), 264 (69), 250 (51), 249 (17), 223 (14), 115 (19). Anal. Calcd for $C_{17}H_{15}NS_2$: C, 68.65; H, 5.08; N, 4.71%. Found: C, 68.27; H, 4.84; N, 4.53%.

(*Z*)-2-[2-Methylthio-2-{*p*-(trifluoromethyl)phenyl}ethenyl]benzothiazole (3ad)



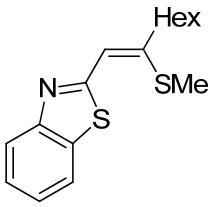
The title compound was obtained in 44% (77 mg, 0.219 mmol) as pale yellow solid. R_f = 0.27 (hexane:ethyl acetate = 20:1). M.p. 50–52 °C. FT-IR (KBr, cm^{-1}): 2928 (w), 1614 (m), 1325 (s), 1169 (s), 1121 (s), 723 (s), 540 (s). ^1H NMR (300 MHz, $CDCl_3$, rt): δ 2.15 (s, 3H), 7.34 (s, 3H), 7.40 (td, J = 8.1, 1.2 Hz, 1H), 7.50 (td, J = 8.1, 1.2 Hz, 1H), 7.72 (s, 4H), 7.92 (d, J = 8.1 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 16.9, 121.5, 122.9, 123.9 (q, J = 270 Hz), 125.6, 125.8 (q, J = 3.6 Hz), 126.4, 126.5, 128.7, 130.0, 130.8 (q, J = 33 Hz) 135.4, 142.3, 152.0, 164.0; ^{19}F NMR (300 MHz, $CDCl_3$, rt): 10.8. MS (EI, m/z (relative intensity)): 351 (M^+, 78), 350 (24), 337 (18), 336 (100), 318 (50), 304 (50), 223 (12), 109 (14), 108 (12), 69 (13). Anal. Calcd for $C_{17}H_{12}F_3NS_2$: C, 58.10; H, 3.44; N, 3.99%. Found: C, 57.70; H, 3.45; N, 3.85%.

(*Z*)-2-{2-Methylthio-2-(1-naphthyl)ethenyl}benzothiazole (3ae)



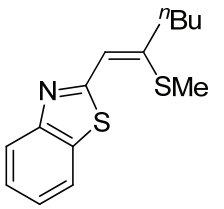
The title compound was obtained in 34% (56 mg, 0.169 mmol) as orange solid. R_f = 0.45 (hexane:ethyl acetate = 10:1). M.p. 50–51 °C. FT-IR (KBr, cm^{-1}): 3055 (s), 2922 (s), 2205 (w), 1942 (w), 1557 (m), 1427 (m), 1315 (m), 1117 (m), 1015 (m), 937 (w). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 1.87 (s, 3H), 7.08 (s, 1H), 7.38–7.41 (m, 1H), 7.46–7.47 (m, 1H), 7.49–7.55 (m, 5H), 7.89–7.94 (m, 3H), 8.09 (d, J = 7.8 Hz, 1H), 8.20–8.22 (m, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 15.8, 121.1, 121.4, 122.8, 124.9, 125.1, 125.2, 126.2, 126.4, 126.6, 126.9, 128.4, 129.0, 131.2, 133.4, 135.2, 136.2, 148.0, 152.8, 164.0. MS (EI, m/z (relative intensity)): 333 (M^+, 75), 318 (100), 300 (30), 286 (80), 152 (23). HRMS (FAB+): Calcd for $C_{20}H_{16}NS_2$: 334.0724. Found: 334.0716 $[M+H]^+$.

(*Z*)-2-(2-Methylthio-1-octenyl)benzothiazole (3af)



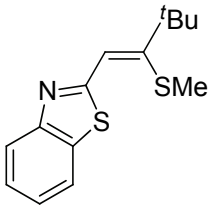
The title compound was obtained in 67% (195 mg, 0.669 mmol) as pale yellow solid. R_f = 0.27 (hexane:ethyl acetate = 20:1). M.p. 42 °C. FT-IR (KBr, cm^{-1}): 2928 (s), 2853 (s), 1574 (s), 1454 (s), 1427 (s), 1292 (m), 758 (s), 727 (s). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 0.90 (t, J = 6.9 Hz, 3H), 1.25–1.40 (m, 6H), 1.67 (quin, J = 7.5 Hz, 2H), 2.45 (s, 3H), 2.56 (t, J = 7.5 Hz, 2H), 6.95 (s, 1H), 7.34 (td, J = 8.1, 1.2 Hz, 1H), 7.45 (td, J = 8.1, 1.2 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rt): δ 14.0, 14.8, 22.5, 28.6, 28.9, 31.6, 36.9, 120.5, 121.2, 122.5, 124.6, 125.9, 135.2, 148.6, 152.4, 164.3. MS (EI, m/z (relative intensity)): 291 (M^+, 45), 276 (28), 245 (18), 244 (100), 234 (30), 188 (31), 187 (25), 186 (25), 174 (21), 173 (28). Anal. Calcd for $C_{16}H_{21}NS_2$: C, 65.93; H, 7.26; N, 4.81%. Found: C, 66.30; H, 7.13; N, 4.81%.

(*Z*)-2-(2-Methylthio-1-hexenyl)benzothiazole (3ag)



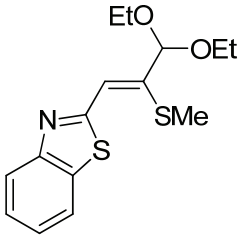
The title compound was obtained in 70% (184 mg, 0.699 mmol) as yellow solid. R_f = 0.17 (hexane:ethyl acetate = 20:1). M.p. 50–52 °C. FT-IR (KBr, cm^{-1}): 2945 (s), 2112 (w), 1782 (w), 1597 (s), 1015 (m), 748 (s). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 0.96 (t, J = 7.2 Hz, 3H), 1.43 (sex, J = 7.2 Hz, 2H), 1.65 (quin, J = 7.2 Hz, 2H), 2.45 (s, 3H), 2.56 (t, J = 7.2 Hz, 2H), 6.97 (s, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 13.9, 14.8, 22.1, 31.1, 36.6, 120.3, 121.3, 122.4, 124.7, 126.1, 135.1, 149.3, 151.9, 164.4. MS (EI, m/z (relative intensity)): 263 (M^+, 82), 248 (44), 234 (35), 230 (19), 216 (100), 188 (21), 187 (35), 186 (37), 174 (36), 173 (40). HRMS (FAB+): Calcd for $C_{14}H_{18}NS_2$: 264.0881. Found: 264.0901 $[M+H]^+$.

(*Z*)-2-(3,3-Dimethyl-2-methylthio-1-butenyl)benzothiazole (3ah)



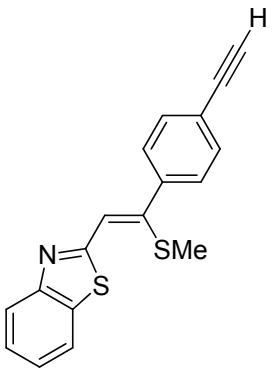
The title compound was obtained in 60% (79 mg, 0.300 mmol) as white solid. R_f = 0.36 (hexane:ethyl acetate = 20:1). M.p. 246–247 °C. FT-IR (KBr, cm^{-1}): 3057 (w), 2965 (m), 2290 (w), 1454 (m), 1427 (m), 970 (w), 883 (w), 760 (s), 729 (m). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.31 (s, 9H), 2.35 (s, 3H), 7.39 (td, J = 7.8, 1.2 Hz, 1H), 7.43 (s, 1H), 7.47 (td, J = 7.8, 1.2 Hz, 1H) 7.87–7.90 (m, 1H), 7.98–8.02 (m, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, rt): δ 21.5, 29.1, 41.3, 121.35, 121.37, 121.38, 122.8, 125.4, 126.1, 128.4, 157.4, 165.4. MS (EI, m/z (relative intensity)): 263 (M^+, 100), 248 (82), 230 (37), 201 (21), 200 (30), 192 (21), 174 (23). Anal. Calcd for $C_{14}H_{17}NS_2$: C, 63.83; H, 6.50; N, 5.32%. Found: C, 63.92; H, 6.72; N, 5.04%.

(*Z*)-2-(3,3-Diethoxy-2-methylthio-1-propenyl)benzothiazole (3ai)



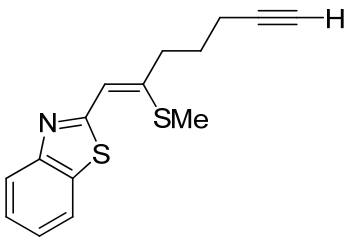
The title compound was isolated in 75% (232 mg, 0.750 mmol) as a pale yellow oil. R_f = 0.25 (hexane:ethyl acetate = 10:1). B.p. 200 °C/7.2 Torr. FT-IR (neat, cm^{-1}): 3057 (w), 2974 (m), 1578 (m), 1454 (m), 1429 (m), 1126 (s), 1059 (s), 760 (s). ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 1.28 (t, J = 7.2 Hz, 6H), 2.61 (s, 3H), 3.55–3.74 (m, 4H), 5.19 (s, 1H), 7.38 (td, J = 7.2, 1.2 Hz, 1H), 7.40 (s, 1H), 7.49 (td, J = 7.2 Hz, 1.2 Hz, 1H), 7.88–7.91 (m, 1H), 8.03–8.05 (m, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 15.1, 15.6, 61.9, 102.3, 121.4, 122.86, 122.94, 125.2, 126.2, 135.6, 142.9, 152.2, 163.6. MS (EI, m/z (relative intensity)): 309 (M^+, 4.6), 280 (83), 233 (55), 103 (53), 75 (100). Anal. Calcd for $C_{15}H_{19}NO_2S_2$: C, 58.22; H, 6.19; N, 4.53%. Anal. Calcd for $C_{15}H_{19}NO_2S_2$: C, 58.22; H, 6.19; N, 4.53%. Found: C, 58.40; H, 6.23; N, 4.45%.

***(Z)*-2-{2-(*p*-Ethynylphenyl)-2-methylthioethenyl}benzothiazole (3aj)**



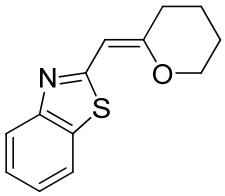
The title compound was obtained in 52% (80 mg, 0.260 mmol) as pale yellow solid. R_f = 0.20 (hexane:ethyl acetate = 20:1). M.p. 128–130 °C. FT-IR (KBr, cm^{-1}): 3264 (s), 2920 (m), 1954 (w), 1425 (m), 851 (s), 752 (s). ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 2.17 (s, 3H), 3.18 (s, 1H), 7.35 (s, 1H), 7.40 (td, J = 8.0, 1.2 Hz, 1H), 7.50 (td, J = 8.0, 1.2 Hz, 1H), 7.58–7.59 (m, 4H), 7.90–7.92 (m, 1H), 8.02–8.04 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rt): δ 16.9, 78.7, 83.0, 121.3, 122.79, 122.82, 125.3, 125.9, 126.2, 128.2, 132.4, 135.4, 139.0, 146.0, 152.2, 164.2. MS (EI, m/z (relative intensity)): 307 (M^+, 84), 292 (100), 274 (68), 260 (62). Anal. Calcd for $C_{18}H_{13}NS_2$: C, 70.32; H, 4.26; N, 4.56%. Found: C, 70.00; H, 3.86; N, 4.38%.

(*Z*)-2-(2-Methylthio-1-hepten-6-ynyl)benzothiazole (3ak)



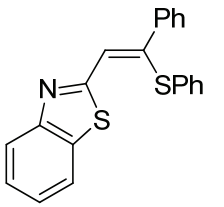
The title compound was obtained in 30% (82 mg, 0.300 mmol) as pale yellow solid. R_f = 0.06 (hexane:ethyl acetate = 20:1). M.p. 30–31 °C. FT-IR (KBr, cm^{-1}): 2955 (s), 1601 (s), 1454 (s), 1314 (m), 1144 (m), 758 (s). ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 1.90 (quin, J = 7.2 Hz, 2H), 2.02 (t, J = 2.8 Hz, 1H), 2.32 (td, J = 7.2, 2.8 Hz, 2H), 2.47 (s, 3H), 2.71 (t, J = 7.2 Hz, 2H), 6.99 (s, 1H), 7.34 (td, J = 7.6, 1.2 Hz, 1H), 7.45 (td, J = 7.6, 1.2 Hz, 1H), 7.86–7.88 (m, 1H), 7.98–8.00 (m, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, rt): δ 14.9, 17.6, 27.6, 35.5, 69.3, 83.4, 121.29, 121.33, 122.6, 124.8, 126.1, 135.2, 147.4, 152.3, 164.1. MS (EI, m/z (relative intensity)): 273 (M^+, 40), 258 (45), 240 (23), 234 (100), 226 (76), 224 (24), 187 (73), 186 (46), 173 (30), 109 (25). Anal. Calcd for $C_{15}H_{15}NS_2$: C, 65.89; H, 5.53; N, 5.12%. Found: C, 66.22; H, 5.43; N, 5.03%.

(*Z*)-2-{(2-Tetrahydropyranylidene)methyl}benzothiazole (3al')



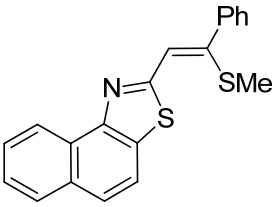
The title compound was obtained in 74% (171 mg, 0.739 mmol) as pale yellow solid. R_f = 0.09 (hexane:ethyl acetate = 10:1). M.p. 118–119 °C. FT-IR (KBr, cm^{-1}): 3055 (m), 2953 (s), 2862 (m), 1942 (w), 1697 (s), 1587 (m), 1306 (s), 1094 (m), 1067 (s). ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 1.81–1.92 (m, 4H), 2.50 (t, J = 6.0 Hz, 2H), 4.27 (t, J = 5.6 Hz, 2H), 6.09 (s, 1H), 7.28 (td, J = 7.6, 1.2 Hz, 1H), 7.40 (td, J = 7.6, 1.2 Hz, 1H), 7.81–7.83 (m, 1H), 7.90–7.92 (m, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 20.9, 24.1, 29.2, 68.9, 102.7, 121.1, 121.8, 124.0, 125.7, 134.9, 151.8, 162.4, 163.7. MS (EI, m/z (relative intensity)): 231 (M^+, 87), 230 (34), 203 (21), 202 (100). HRMS (FAB+): Calcd for $C_{13}H_{15}NOS$: 232.0796. Found: 232.0807 $[M+H]^+$.

(*Z*)-2-(2-Phenyl-2-phenylthioethenyl)benzothiazole (3ba)



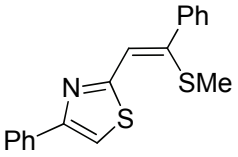
The title compound was obtained in 82% (283 mg, 0.819 mmol) as orange solid. R_f = 0.13 (hexane:ethyl acetate = 20:1). M.p. 134–135 °C. FT-IR (KBr, cm^{-1}): 3057 (w), 3017 (w), 1479 (m), 1204 (m), 762 (s), 691 (s). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 7.08–7.17 (m, 3H), 7.25–7.30 (m, 5H), 7.38 (td, J = 8.1, 1.2 Hz, 1H), 7.49 (td, J = 8.1, 1.2 Hz, 1H), 7.67–7.70 (m, 2H), 7.73 (s, 1H), 7.86 (d, J = 8.1 Hz, 1H), 8.05 (d, J = 8.1 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 121.4, 123.0, 125.6, 126.3, 126.9, 128.3, 128.4, 129.0, 129.1, 129.4, 130.0, 133.2, 135.5, 138.8, 142.7, 152.3, 164.5. MS (EI, m/z (relative intensity)): 345 (M^+, 100), 344 (73), 312 (46), 269 (15), 268 (83), 236 (44), 210 (31), 121 (19), 109 (17), 77 (15). Anal. Calcd for $C_{21}H_{15}NS_2$: C, 73.01; H, 4.38; N, 4.05%. Found: C, 73.01; H, 4.25; N, 3.99.

(*Z*)-2-(2-Methylthio-2-phenylethenyl)naphtho[1,2-*d*]thiazole (3ca)



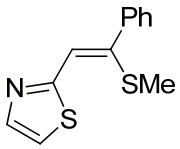
The title compound was obtained in 75% (125 mg, 0.375 mmol) as a brown viscous oil. R_f = 0.40 (hexane:ethyl acetate = 20:1). B.p. 210 °C/7.1 Torr. FT-IR (neat, cm^{-1}): 3053 (s), 3024 (m), 2922 (m), 2826 (w), 1954 (w), 1746 (w), 1568 (m), 1487 (s), 1215 (s), 1078 (s), 1024 (m), 905 (m), 806 (s). ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 2.18 (s, 3H), 7.41–7.48 (m, 4H), 7.60 (td, J = 8.4, 1.2 Hz, 1H), 7.65–7.67 (m, 2H), 7.70 (td, J = 8.4 Hz, 1.2 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.95–7.97 (m, 1H), 8.87–8.89 (m, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 16.9, 118.8, 123.8, 125.1, 125.9, 126.0, 126.8, 128.0, 128.27, 128.35, 128.6, 128.8, 132.0, 132.1, 138.7, 145.8, 148.7, 163.5. MS (EI, m/z (relative intensity)): 333 (M^+, 100), 318 (50), 300 (80), 207 (39), 159 (38). HRMS (FAB+): Calcd for $C_{20}H_{16}NS_2$: 334.0724. Found: 334.0720 $[M+H]^+$.

(*Z*)-2-(2-Methylthio-2-phenylethenyl)-4-phenylthiazole (3da)



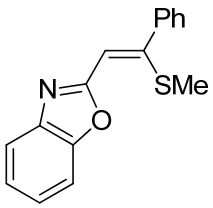
The title compound was obtained in 79% (122 mg, 0.394 mmol) as a brown viscous oil. R_f = 0.37 (hexane:ethyl acetate = 20:1). B.p. 190 °C/6.9 Torr. FT-IR (neat, cm^{-1}): 3059 (m), 3024 (m), 2922 (m), 1952 (w), 1587 (m), 1574 (m), 1470 (s), 1445 (s), 1072 (m), 1059 (m). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 2.15 (s, 3H), 7.33 (s, 1H), 7.35–7.41 (m, 2H), 7.42–7.46 (m, 4H), 7.54 (d, J = 1.2 Hz, 1H), 7.59–7.62 (m, 2H), 7.94–7.97 (m, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 16.7, 113.6, 124.7, 126.4, 128.1, 128.3, 128.6, 128.65, 128.69, 134.3, 138.7, 143.8, 154.7, 164.2. MS (EI, m/z (relative intensity)): 309 (M^+, 61), 294 (61), 276 (100), 134 (51). Anal. Calcd for $C_{18}H_{16}NS_2$: C, 69.86; H, 4.89; N, 4.53%. Found: C, 70.12; H, 5.13; N, 4.23.

(*Z*)-2-(2-Methylthio-2-phenylethenyl)thiazole (3ea)



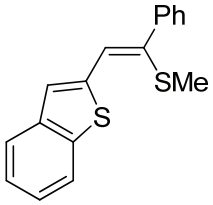
The title compound was obtained in 57% (66 mg, 0.283 mmol) as an orange oil. R_f = 0.23 (hexane:ethyl acetate = 10:1). B.p. 205 °C/6.8 Torr. FT-IR (neat, cm^{-1}): 3111 (w), 3057 (w), 2963 (w), 2207 (w), 1734 (w), 1572 (w), 1491 (m), 1470 (m), 1445 (m), 1142 (m), 1092 (m), 876 (w), 760 (s). ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 2.12 (s, 3H), 7.25 (s, 1H), 7.37–7.45 (m, 4H), 7.56–7.58 (m, 2H), 7.87 (d, J = 4.8 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 16.7, 119.4, 124.1, 127.1, 128.4, 128.7, 128.8, 138.6, 141.7, 164.6. MS (EI, m/z (relative intensity)): 233 (M^+, 88), 232 (94), 217 (90), 200 (100), 186 (92). HRMS (FAB+): Calcd for $C_{12}H_{12}NS_2$: 234.0411. Found: 234.0397 $[M+H]^+$.

(*Z*)-2-(2-Methylthio-2-phenylethenyl)benzoxazole (3fa)



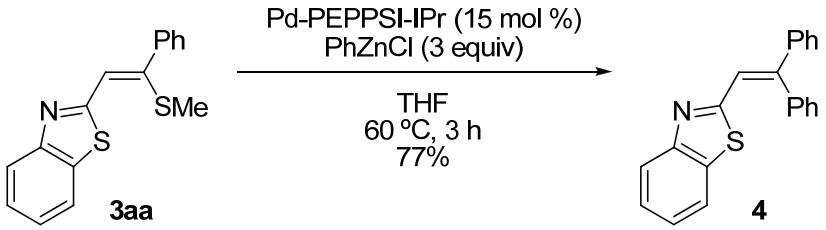
The title compound was obtained in 43% (115 mg, 0.430 mmol) as a pale yellow oil. R_f = 0.12 (hexane:ethyl acetate = 20:1). B.p. 160 °C/5.7 Torr. FT-IR (neat, cm^{-1}): 3019 (m), 2955 (s), 2928 (s), 2859 (s), 1601 (s), 1576 (s), 1495 (m), 1454 (s), 1377 (w), 1314 (m), 1142 (m). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.90 (s, 3H), 6.38 (s, 1H), 7.08 (s, 1H), 7.13–7.16 (m, 2H), 7.22–7.27 (m, 4H), 7.32–7.35 (m, 1H), 7.62–7.65 (m, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, rt): δ 16.6, 110.2, 111.7, 120.0, 124.3, 124.9, 128.3, 128.6, 128.8, 138.8, 142.3, 149.7, 153.8, 161.5. MS (EI, m/z (relative intensity)): 267 (M^+, 100), 266 (55), 220 (42), 252 (27), 234 (24). HRMS (FAB+): Calcd for $C_{16}H_{14}NOS$: 268.0796. Found: 268.0786 $[M+H]^+$.

(*Z*)-2-(2-Methylthio-2-phenylethenyl)benzothiophene (3ga)



The reaction was conducted on 1 mmol scale. The title compound was obtained in 12% (34 mg, 0.120 mmol) as white solid. R_f = 0.44 (hexane:ethyl acetate= 20:1). M.p. 81 °C. FT-IR (KBr, cm^{-1}): 3046 (w), 2990 (w), 2922 (m), 1427 (m), 1310 (w), 746 (s). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 2.14 (s, 3H), 7.13 (s, 1H), 7.31–7.37 (m, 3H), 7.42–7.45 (m, 3H), 7.63 (d, J = 7.8 Hz, 2H), 7.73 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 16.8, 122.1, 123.2, 124.3, 124.7, 125.7, 126.7, 128.17, 128.17, 128.6, 138.2, 138.6, 139.8, 140.6, 140.9. MS (EI, m/z (relative intensity)): 282 (M^+, 100), 268 (18), 267 (96), 266 (14), 235 (24), 234 (89), 221 (10), 202 (13), 189 (11), 117 (25). Anal. Calcd for $C_{17}H_{14}S_2$: C, 72.30; H, 5.00%. Found: C, 72.45; H, 4.98%.

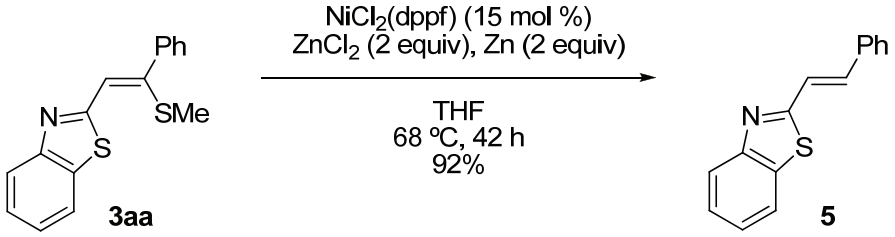
Negishi Coupling of Sulfide 3aa: Synthesis of 2-(2,2-Diphenylethenyl)benzothiazole (4)



Pd-PEPPSI-IPr (20 mg, 0.030 mmol) and **3aa** (57 mg, 0.20 mmol) were placed in a 20-mL Schlenk tube under argon. THF (3 mL) and PhZnCl (0.15 M THF solution, 4.0 mL, 0.60 mmol) were added. The reaction mixture was stirred at 60 °C for 3 h. The mixture was poured into saturated NH_4Cl aqueous solution (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried over anhydrous sodium sulfate and concentrated in vacuo. Purification by column chromatography on silica gel (hexane:ethyl acetate = 20:1) provided 2-(2,2-diphenylethenyl)benzothiazole (**4**, 48 mg, 0.153 mmol, 77%) as yellow solid.

R_f = 0.37 (hexane:ethyl acetate = 20:1). M.p. 104–105 °C. FT-IR (KBr, cm^{-1}): 3057 (w), 3030 (w), 1740 (w), 1597 (w), 1491 (m), 1445 (m), 1431 (m), 1350 (m), 1317 (m), 1256 (w), 874 (w). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 7.28 (td, J = 8.0, 0.8 Hz, 1H), 7.33–7.37 (m, 5H), 7.39–7.45 (m, 3H), 7.54–7.57 (m, 3H), 7.63 (d, J = 8.0 Hz, 1H), 7.67 (s, 1H), 7.98 (d, J = 8.0 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, rt): δ 121.1, 122.3, 122.7, 125.1, 126.0, 127.37, 127.38, 128.5, 128.9, 129.0, 129.5, 130.0, 135.5, 137.9, 140.4, 149.3, 152.1. MS (EI, m/z (relative intensity)): 313 (M^+, 29), 312 (100), 235 (19), 206 (50). Anal. Calcd for $C_{21}H_{15}NS$: C, 80.48; H, 4.82; N, 4.47%. HRMS (FAB+): Calcd for $C_{21}H_{15}NS$: 313.0925. Found: 313.0897 [M^+].

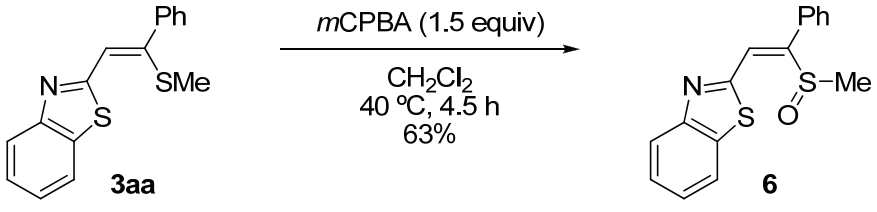
Reduction of Sulfide 3aa: Synthesis of (*E*)-2-(2-Phenylethenyl)benzothiazole (5)[10]



In a 20-mL Schlenk tube, sulfide **3aa** (102 mg, 0.36 mmol), $NiCl_2$(dppf) (37 mg, 0.054 mmol), $ZnCl_2$ (1 M THF solution, 0.72 mL, 0.72 mmol,), and Zn powder (47 mg, 0.72 mmol) were placed under argon. The reaction mixture was stirred at reflux for 42 h. The mixture was filtered through a pad of silica gel. The filtrate was evaporated to yield a crude oil. Purification by column chromatography on silica gel (hexane:ethyl acetate = 20:1) provided (*E*)-2-(2-phenylethenyl)benzothiazole (**5**, 79 mg, 0.333 mmol, 92%) as an orange oil. The spectroscopic data of **5** can be found in the literature.[11]

^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 7.37–7.52 (m, 7H), 7.57–7.61 (m, 2H), 7.86 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H).

Oxidation of Sulfide 3aa: Synthesis of (*Z*)-2-(2-Methylsulfinyl-2-phenylethenyl)benzothiazole (6)

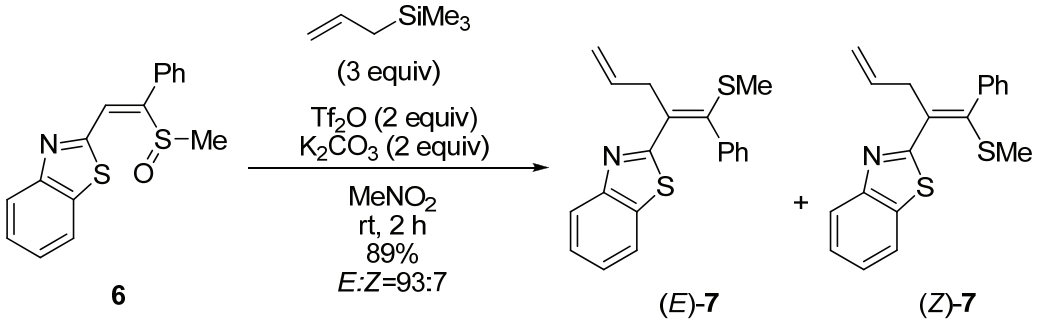


In a 20-mL Schlenk tube, sulfide **3aa** (283 mg, 1.0 mmol) was dissolved in dichloromethane (10 mL). *m*-Chloroperoxybenzoic acid (77%, 336 mg, 1.5 mmol) was added portionwise to the solution. The reaction mixture was stirred at 40 °C for 4.5 h. The mixture was cooled to room temperature and then poured into saturated $NaHCO_3$ aqueous solution (10 mL). The product was

extracted with dichloromethane (10 mL × 3). The combined organic layers were dried over anhydrous sodium sulfate and concentrated in vacuo. Purification by column chromatography on silica gel (hexane:ethyl acetate = 5:1) afforded sulfoxide **6** (190 mg, 0.635 mmol, 63%) as yellow solid.

R_f = 0.07 (hexane:ethyl acetate = 5:1). M.p. 160–161 °C. FT-IR (KBr, cm^{-1}): 3044 (m), 3036 (m), 2073 (w), 1782 (w), 1583 (s), 1493 (s), 1325 (s), 1040 (s). ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 2.92 (s, 3H), 7.47–7.54 (m, 5H), 7.58–7.63 (m, 3H), 8.11–8.13 (m, 1H), 8.18–8.20 (m, 1H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6, rt): δ 34.5, 122.5, 123.4, 125.2, 126.2, 127.0, 128.0, 129.3, 129.7, 132.5, 135.9, 152.9, 154.4, 160.9. MS (FAB$^+$): 300 ([M+H]$^+$). Anal. Calcd for $C_{16}H_{13}NOS_2$: C, 64.18; H, 4.38; N, 4.68%. Found: C, 64.16; H, 4.27; N, 4.53%.

Allylation of Sulfoxide 6: Synthesis of 2-(1-Methylthio-1-phenyl-1,4-pentadien-2-yl)benzothiazole (7)[12]



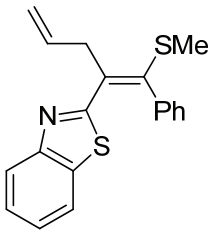
6 (*E*)-**7** (*Z*)-**7**

A mixture of nitromethane (1 mL), **6** (90 mg, 0.30 mmol), potassium carbonate (83 mg, 0.60 mmol), and allyltrimethylsilane (0.14 mL, 0.90 mmol) was placed in a 20-mL Schlenk tube under an atmosphere of argon. Trifluoromethanesulfonic anhydride (169 mg, 0.60 mmol) was added to the solution at 0 °C, and the mixture was stirred at room temperature for 2 h. The mixture was poured into saturated $NaHCO_3$ aqueous solution (10 mL) and the product was extracted with dichloromethane (10 mL × 3). The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. Purification by silica gel column chromatography (hexane:ethyl acetate = 20:1) afforded **7** (86 mg, 0.266 mmol, 89%, *E*/*Z* = 93/7) as a pale yellow oil.

R_f = 0.45 (hexane:ethyl acetate = 20:1). B.p. 170 °C/7.5 Torr. MS (EI, m/z (relative intensity)): 323 (M+, 21), 308 (100), 276 (39), 274 (25), 121 (33). Anal. Calcd for $C_{19}H_{17}NS_2$: C, 70.55; H, 5.30; N, 4.33%. Found: C, 70.56; H, 5.13; N, 4.28%.

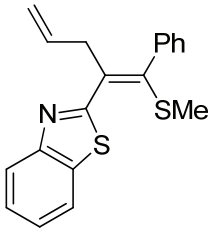
Stereoisomers (*E*/*Z*)-**7** were separated by gel-permeation chromatography ($CHCl_3$).

(*E*)-2-(1-Methylthio-1-phenyl-1,4-pentadien-2-yl)benzothiazole ((*E*)-7)



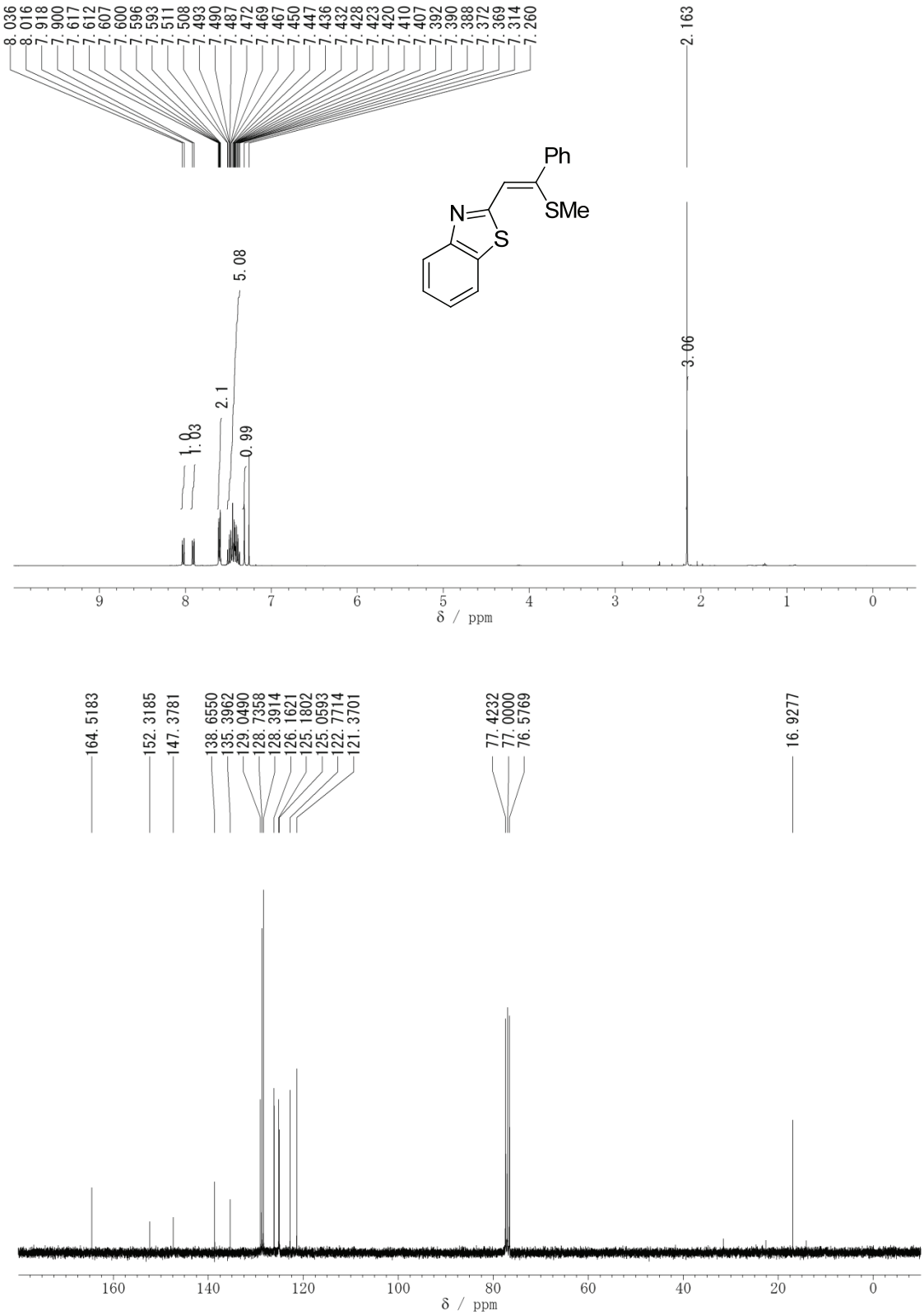
FT-IR (neat, cm^{-1}): 3075 (w), 2922 (w), 2363 (w), 1636 (w), 1570 (m), 1485 (m), 1431 (s), 1315 (w), 910 (m), 758 (s). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 1.86 (s, 3H), 4.00 (dd, J = 6.0, 3.6 Hz, 2H), 5.07 (dd, J = 10, 1.8 Hz, 1H), 5.21 (dtd, J = 17, 3.6, 1.8 Hz, 1H), 5.97–6.03 (m, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.29–7.31 (m, 2H), 7.36 (t, J = 7.8 Hz, 1H), 7.41–7.43 (m, 3H), 7.56 (d, J = 7.8 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 15.4, 38.2, 115.6, 120.8, 122.8, 124.6, 125.6, 128.9, 129.1, 129.9, 130.4, 134.6, 135.8, 136.6, 146.1, 152.0, 167.0.

(*Z*)-2-(1-Methylthio-1-phenyl-1,4-pentadien-2-yl)benzothiazole ((*Z*)-7)

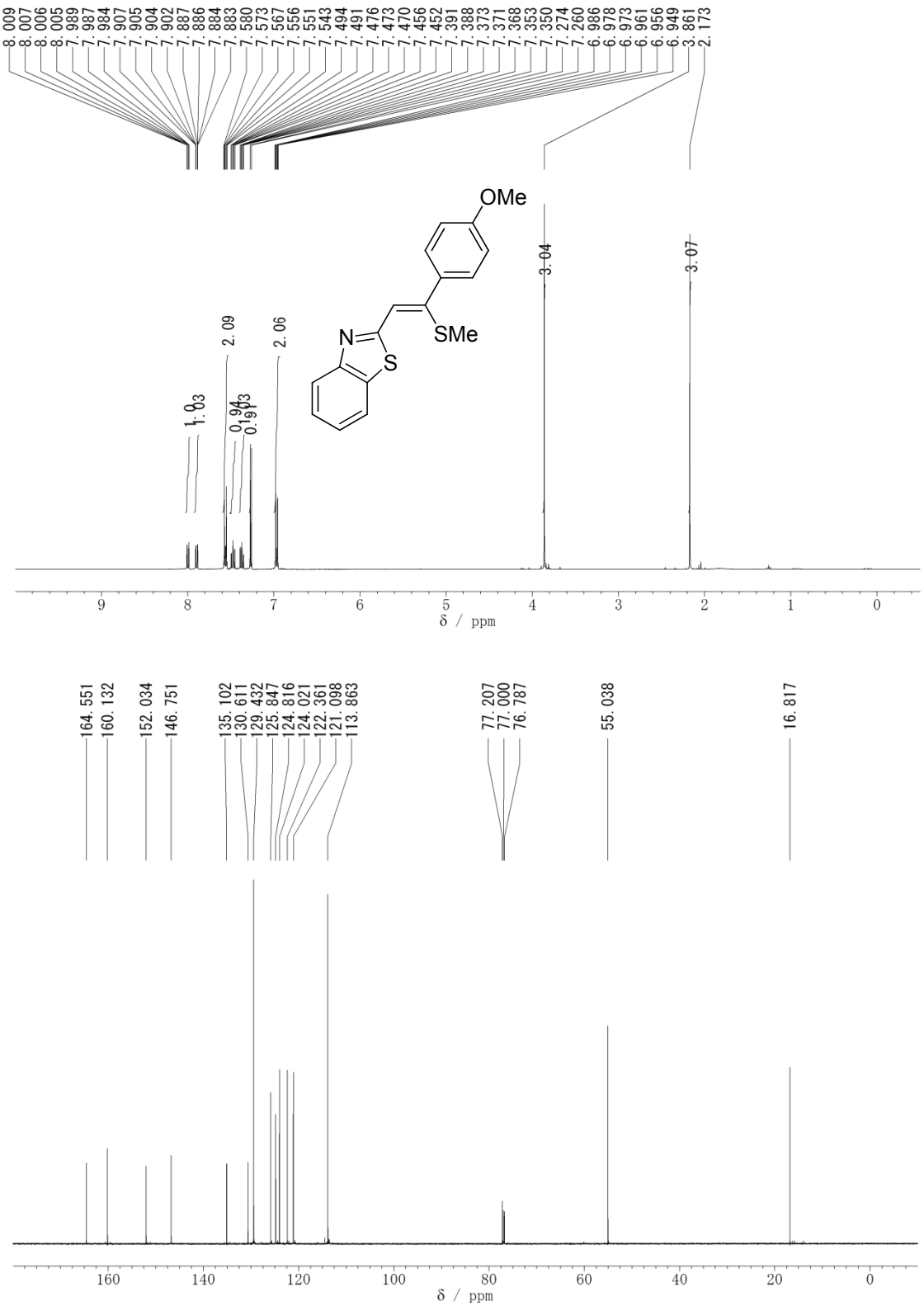


FT-IR (neat, cm^{-1}): 3075 (w), 2922 (w), 2363 (w), 1717 (w), 1431 (m), 1315 (w), 760 (m). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 1.84 (s, 3H), 3.30 (dd, J = 6.0, 1.2 Hz, 2H), 4.91–4.95 (m, J = 2H), 5.77–5.83 (m, 1H), 7.31 (d, J = 7.8 Hz, 2H), 7.35–7.39 (m, 2H), 7.43–7.49 (m, 3H), 7.89 (d, J = 7.8 Hz, 1H), 8.09 (d, J = 7.8 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 16.5, 39.3, 116.2, 121.3, 123.1, 125.0, 125.9, 128.0, 128.1, 128.5, 128.8, 135.2, 135.7, 137.8, 145.0, 152.5, 166.8.

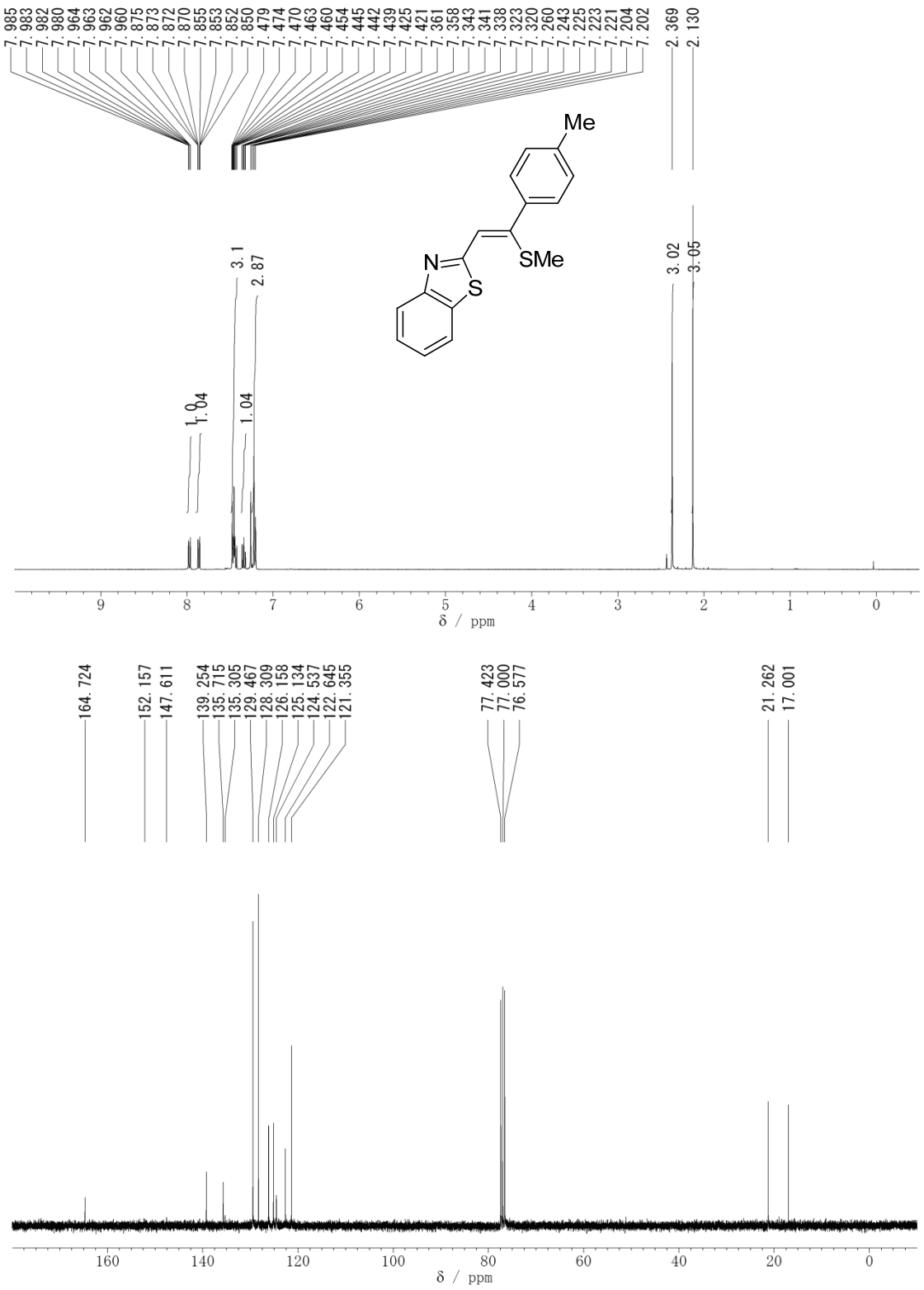
4. Copies of ^{1}H and ^{13}C NMR Charts of the New Compounds



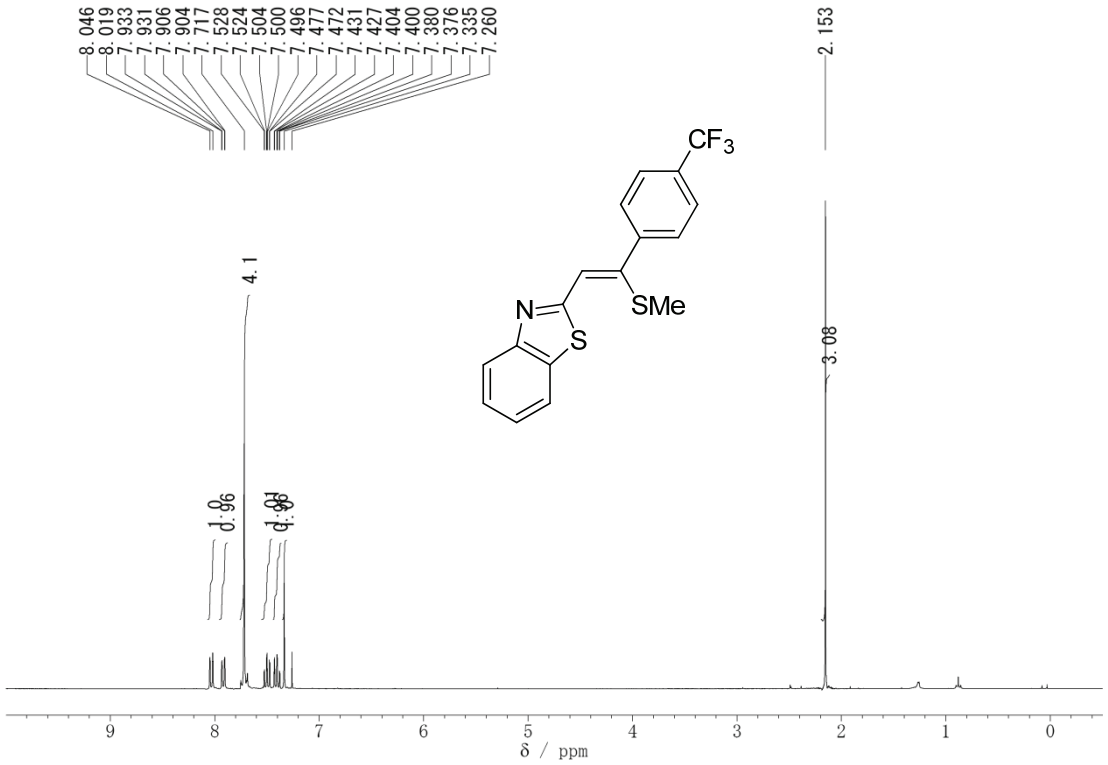
^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (75 MHz) spectra of **3aa** (rt, $CDCl_3$).

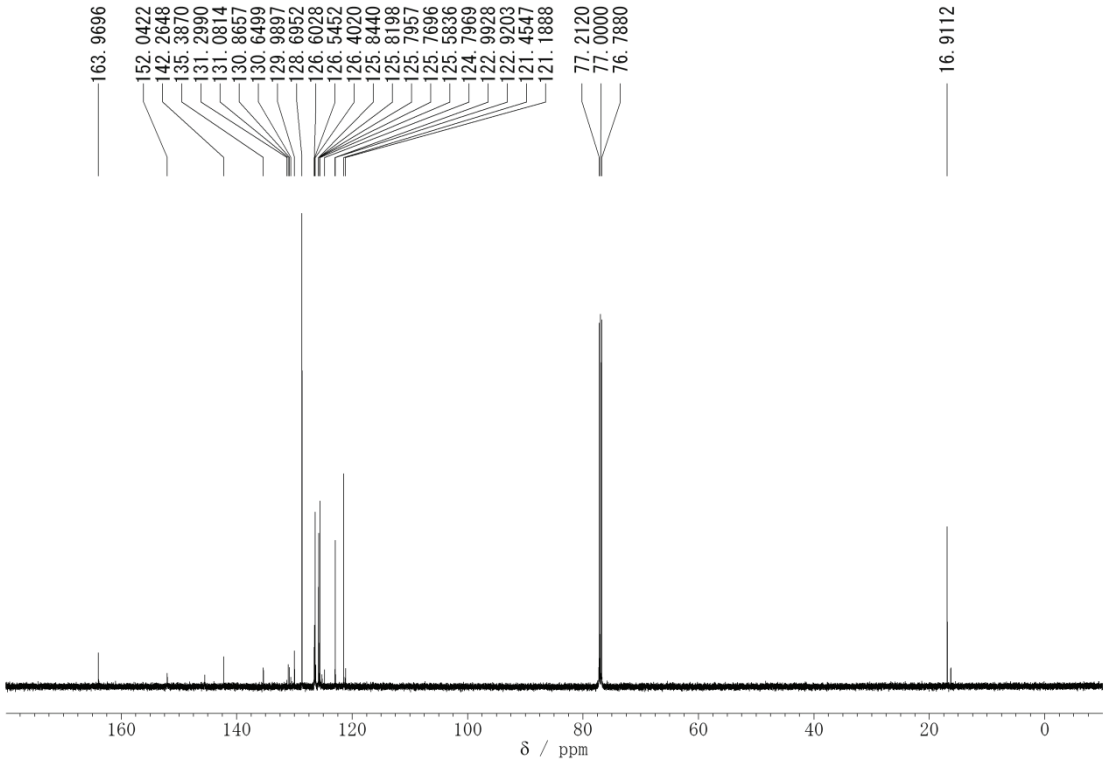


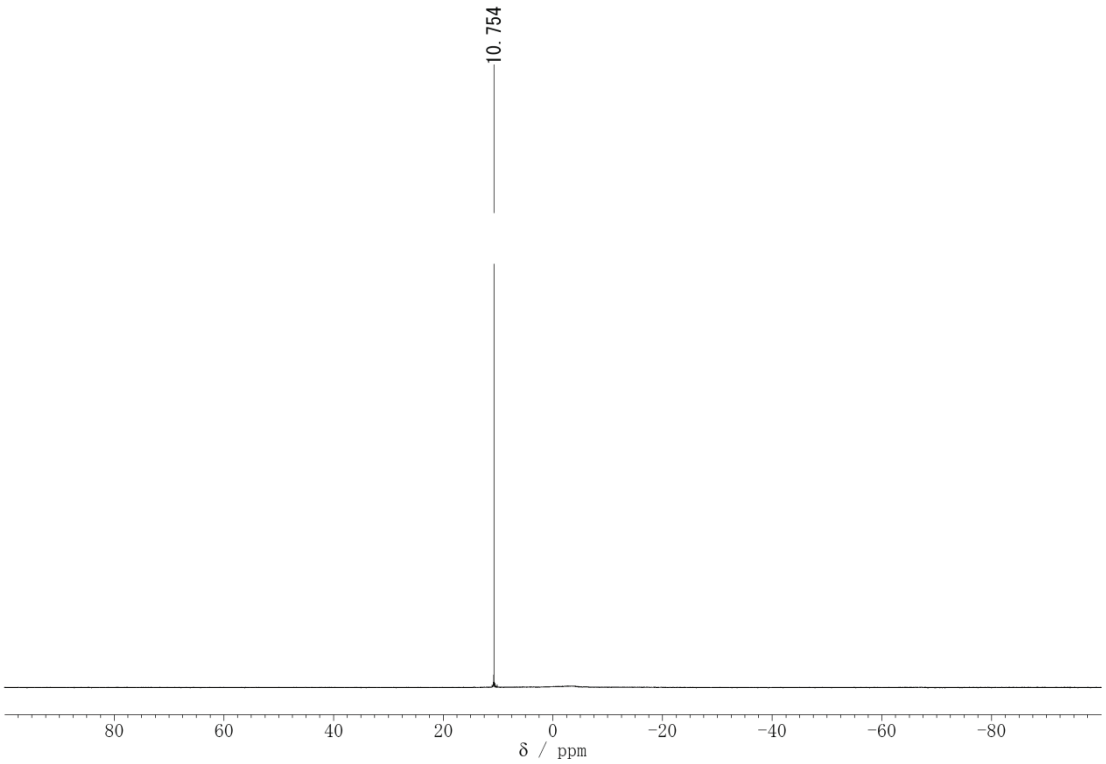
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3ab** (rt, $CDCl_3$).



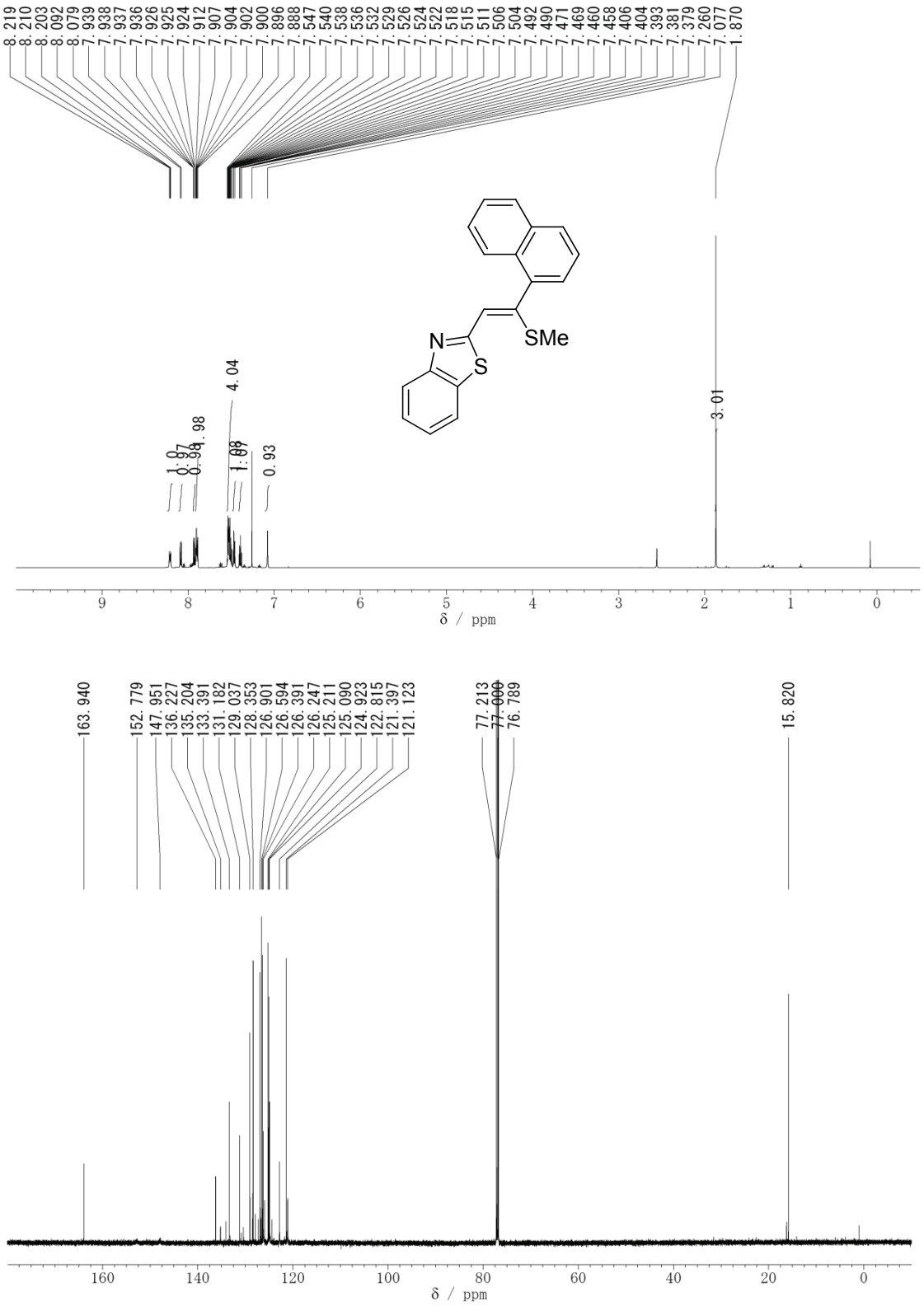
^{1}H NMR (400 MHz) and ^{13}C{1H} NMR (75 MHz) spectra of **3ac** (rt, $CDCl_3$).


8.046
8.019
7.933
7.931
7.906
7.904
7.717
7.528
7.524
7.504
7.500
7.496
7.477
7.472
7.431
7.427
7.404
7.400
7.380
7.376
7.335
7.260
2.153
4.1
3.08
CF3
SMe
N
S
δ / ppm

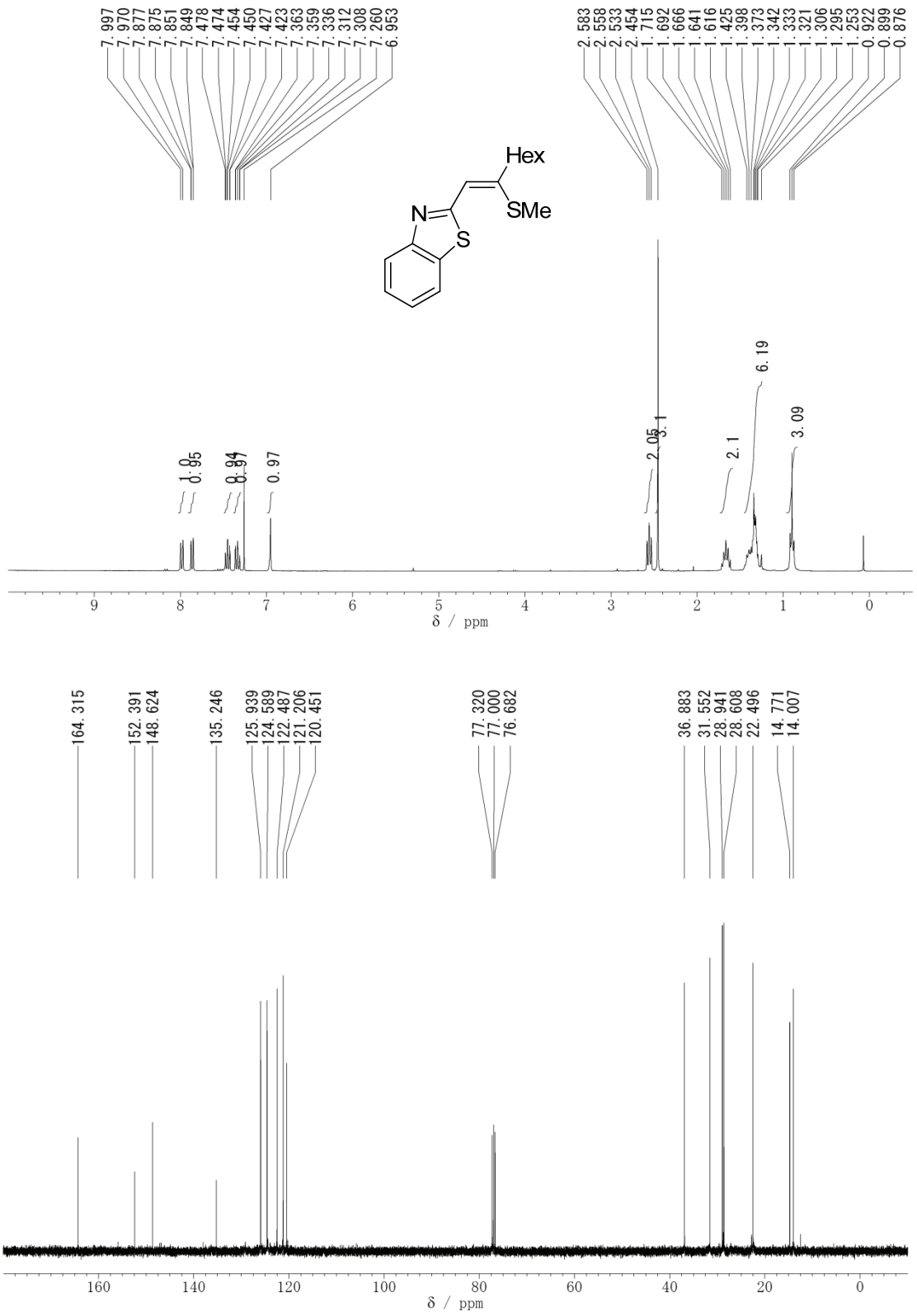

163.9696
152.0422
142.2648
135.3870
131.2990
131.0814
130.8657
130.6499
129.9897
128.6952
126.6028
126.5452
126.4020
125.8440
125.8198
125.7957
125.7696
125.5836
124.7969
122.9928
122.9203
121.4547
121.1888
77.2120
77.0000
76.7880
16.9112
δ / ppm



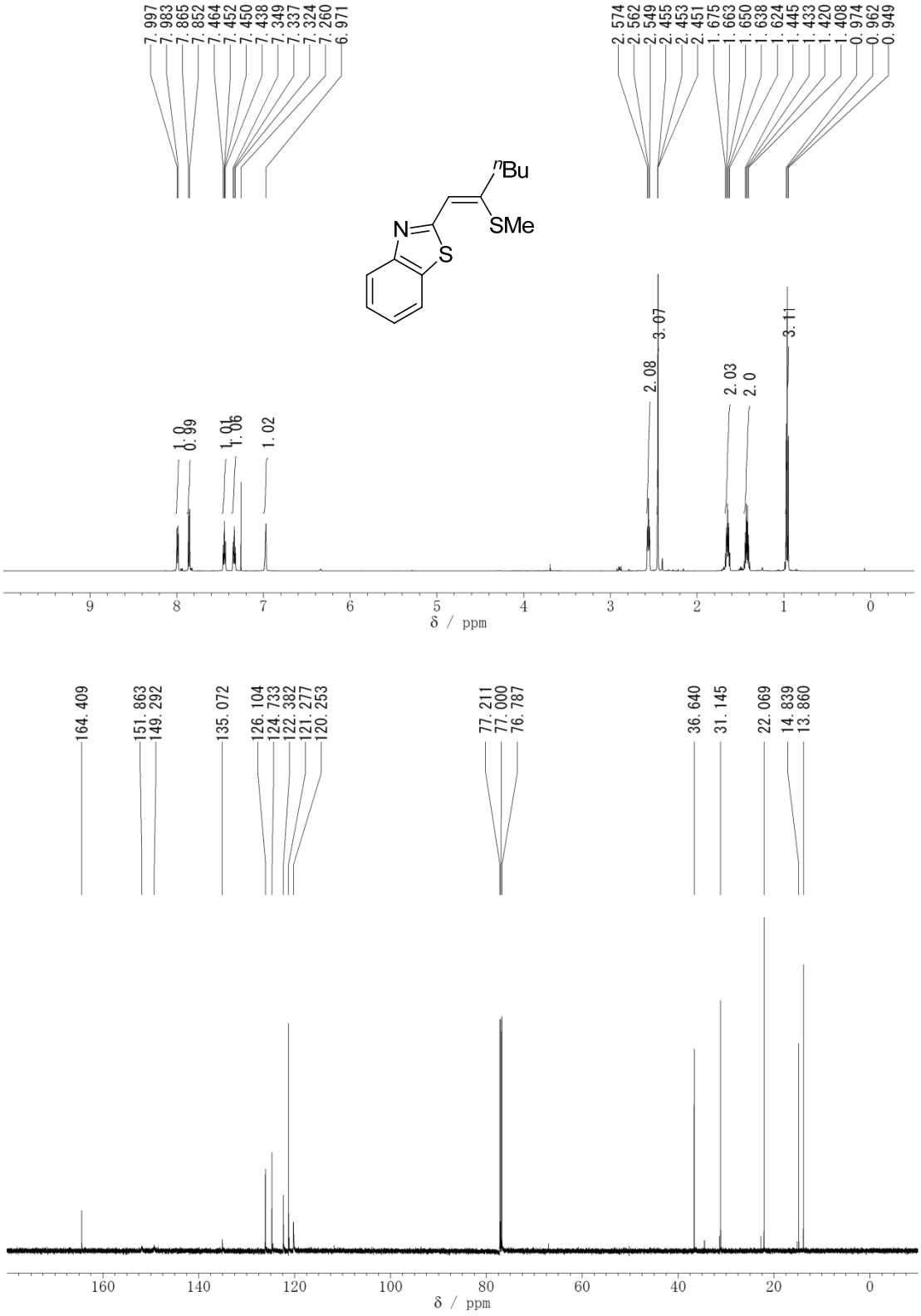
^{1}H NMR (300 MHz), ^{13}C{^{1}H} NMR (150 MHz), and ^{19}F{^{1}H} NMR (300 MHz) spectra of **3ad** (rt, $CDCl_3$).



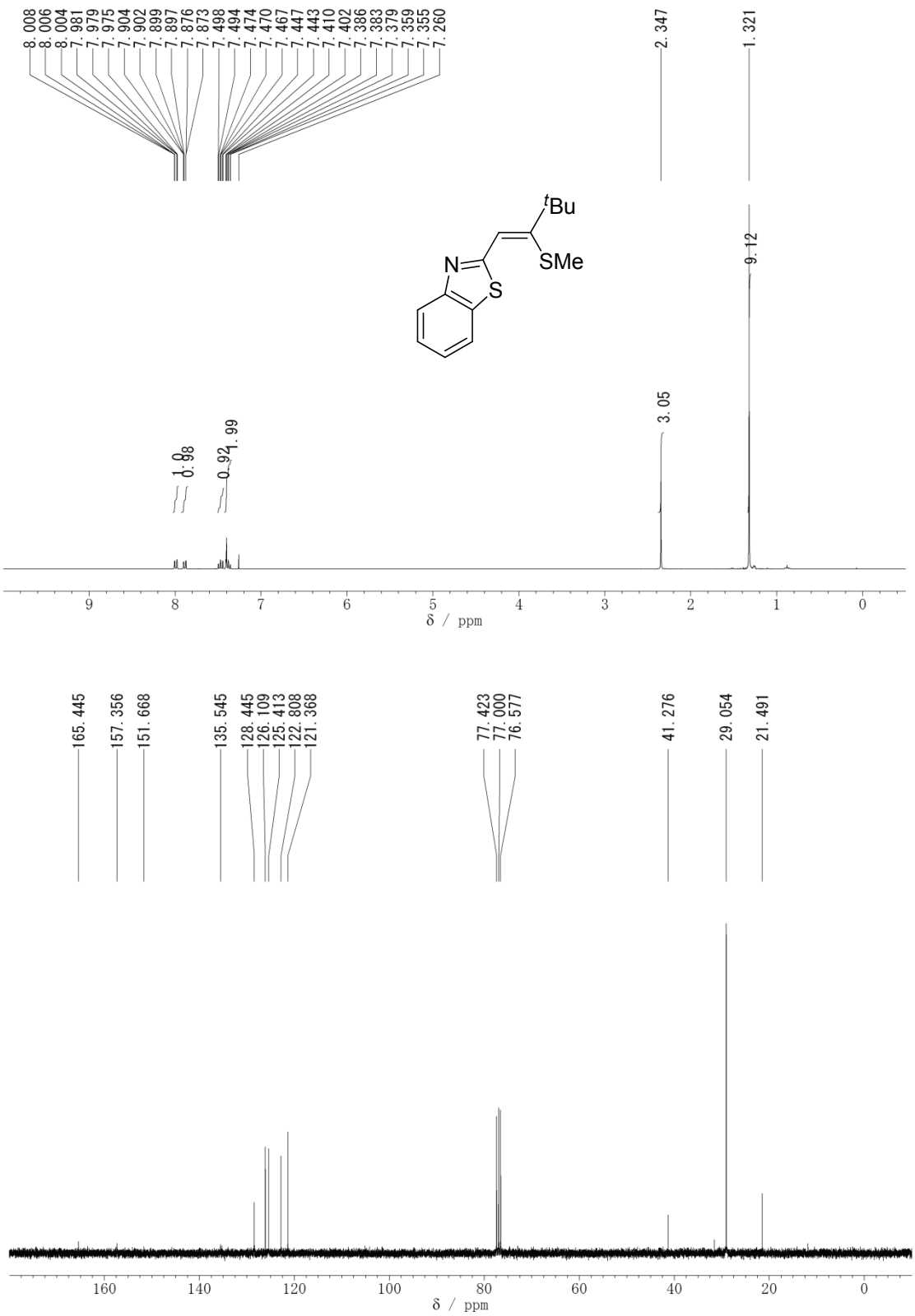
^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3ae** (rt, $CDCl_3$).



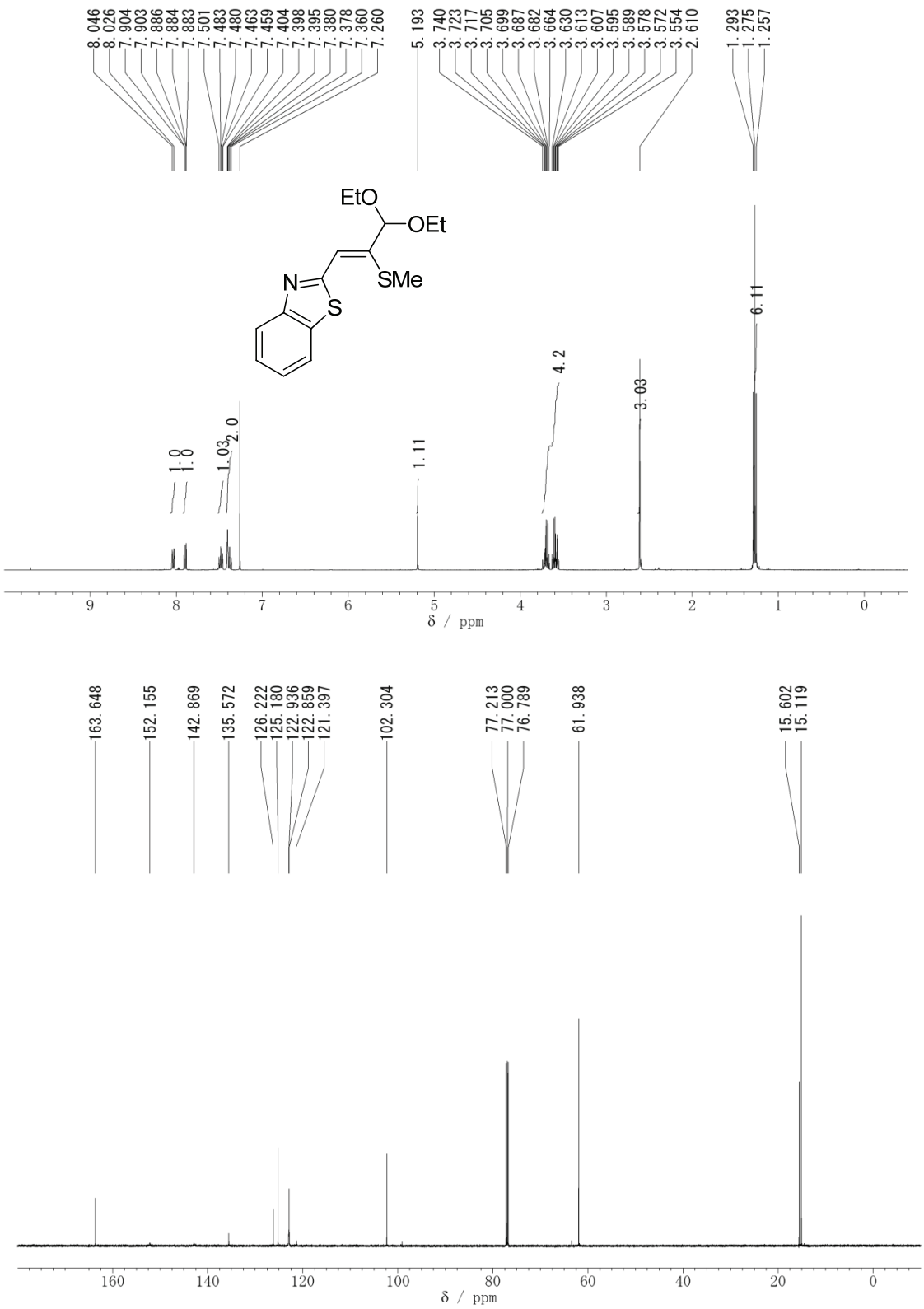
^{1}H NMR (300 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **3af** (rt, $CDCl_3$).



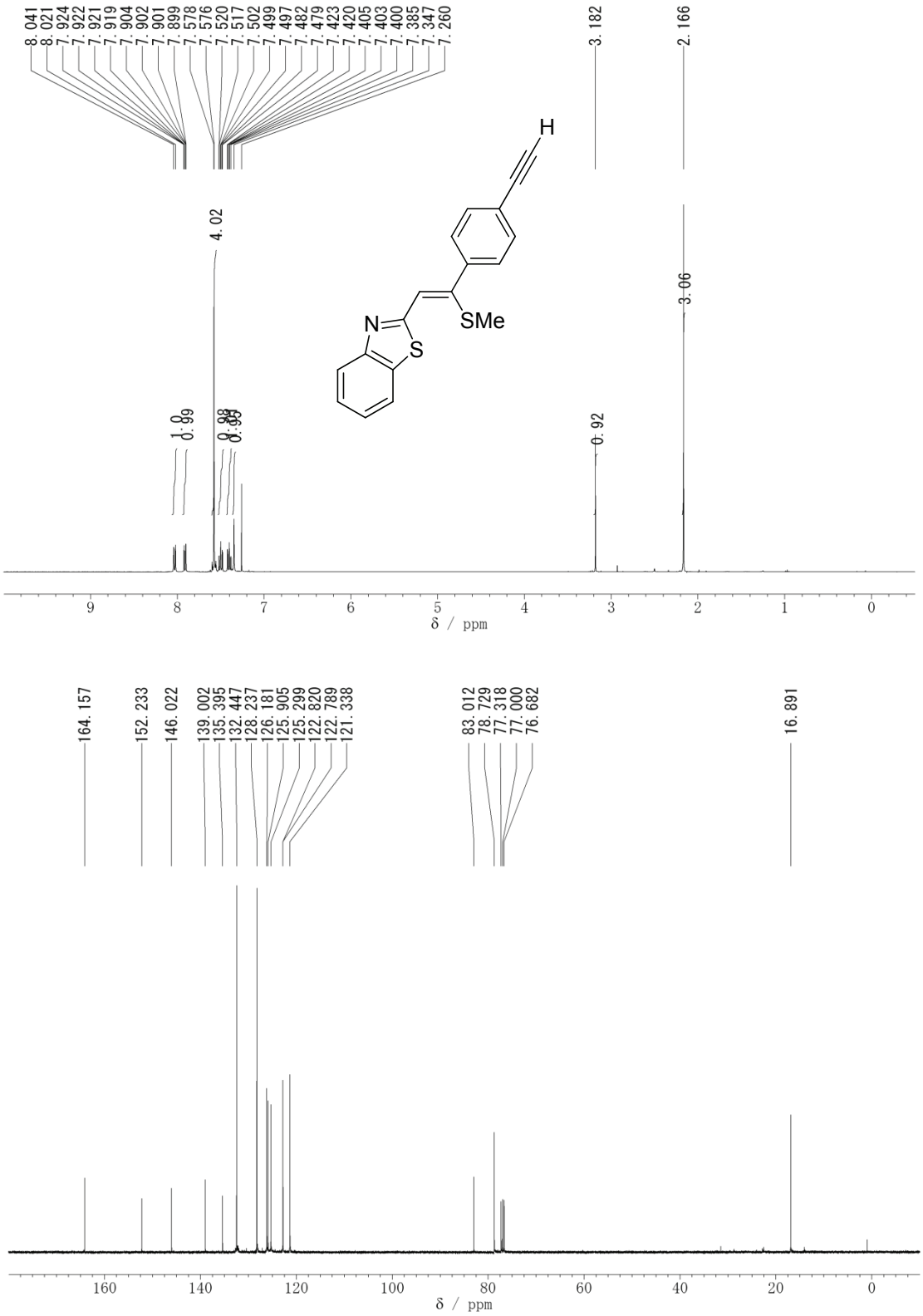
^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3ag** (rt, $CDCl_3$).



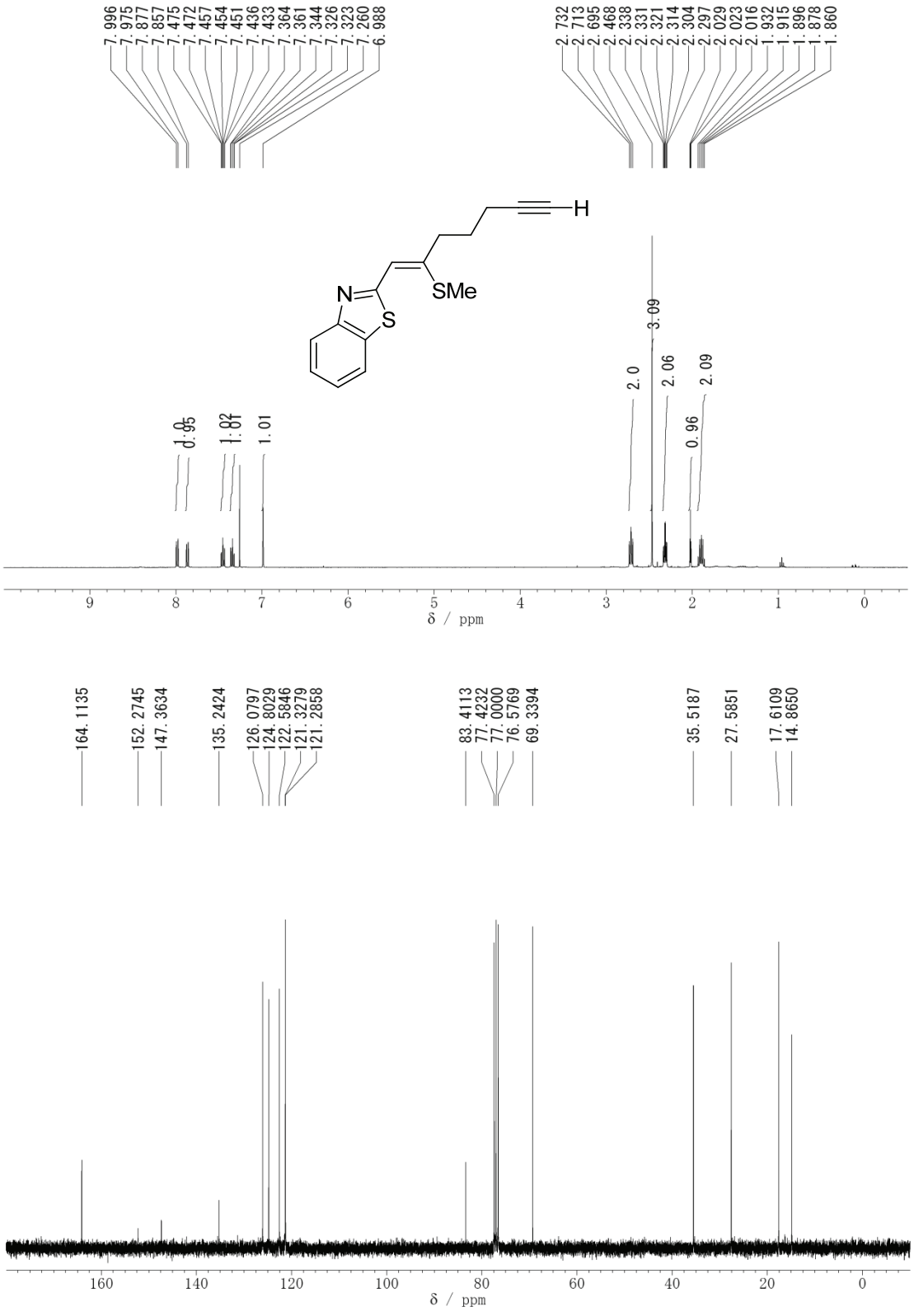
^{1}H NMR (300 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra of **3ah** (rt, $CDCl_3$).



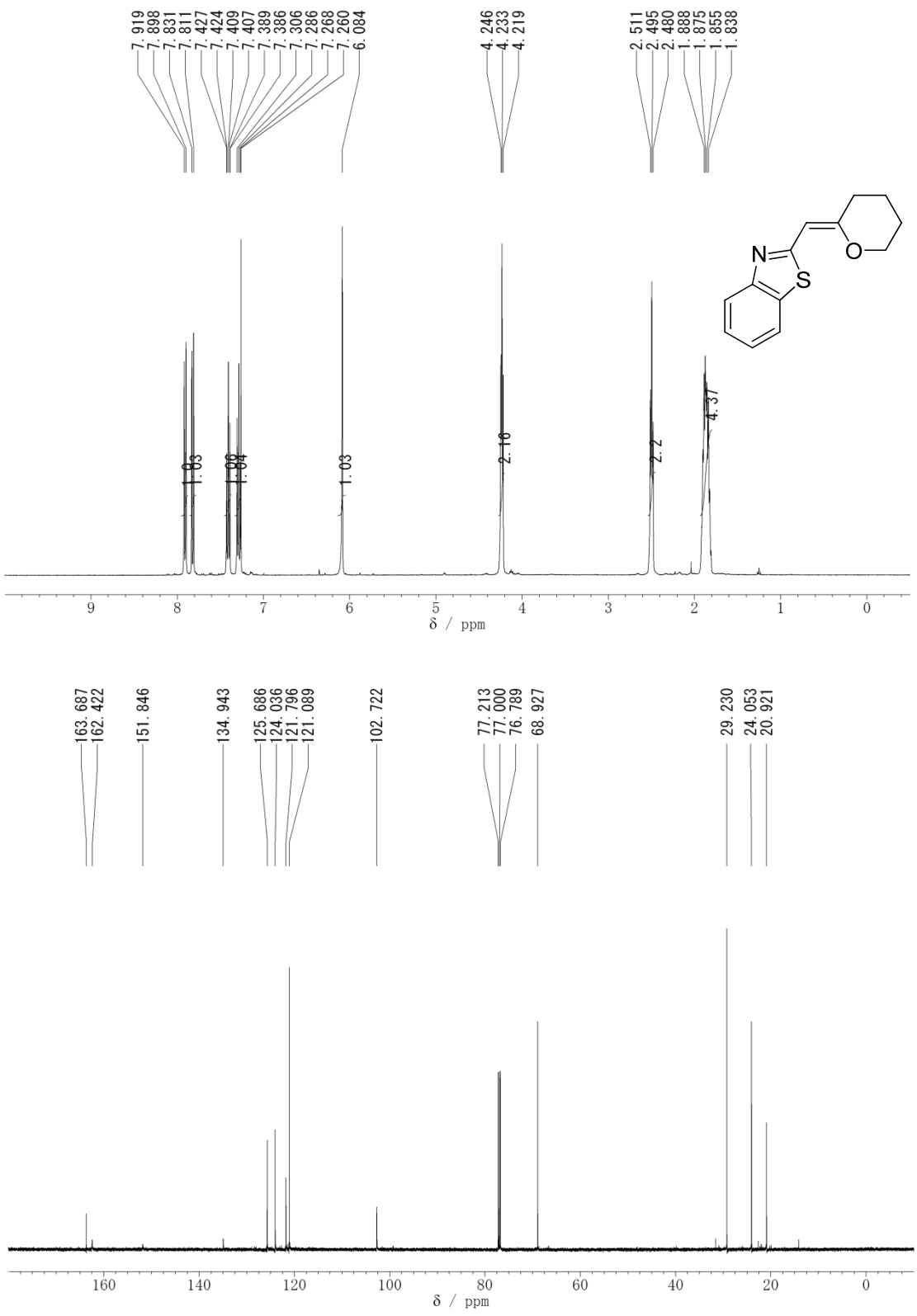
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3ai** (rt, $CDCl_3$).



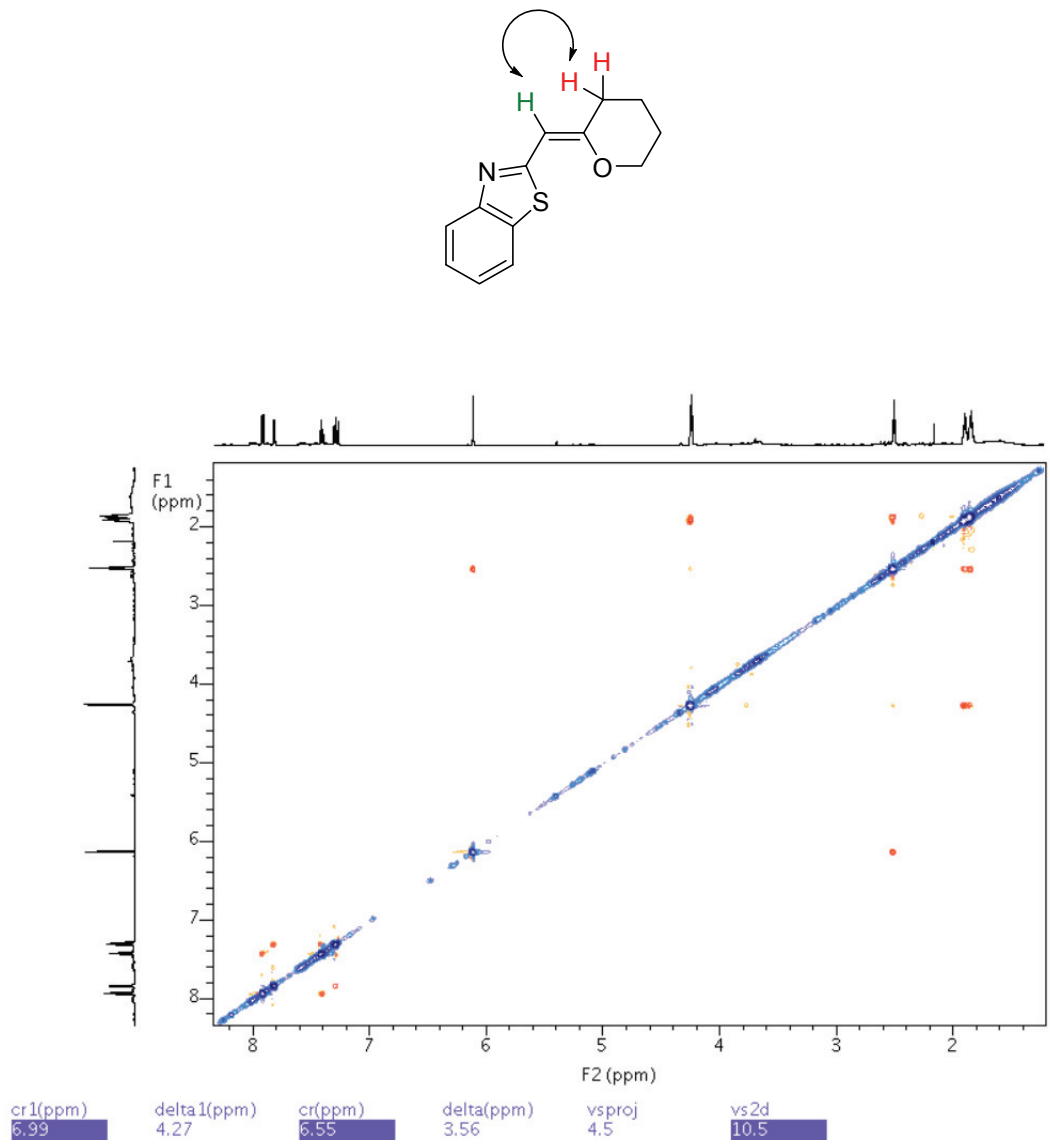
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra of **3aj** (rt, $CDCl_3$).



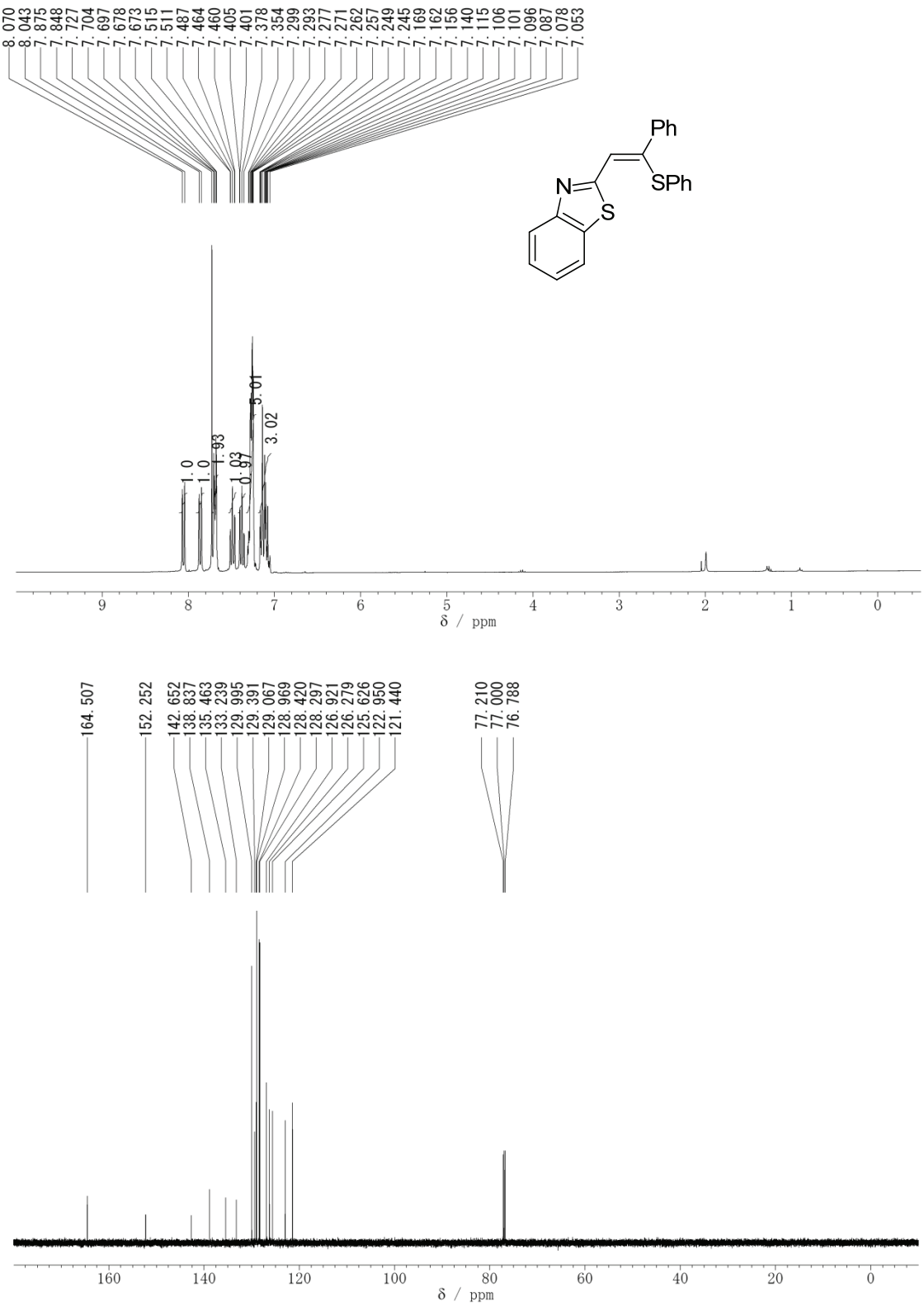
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra of **3ak** (rt, $CDCl_3$).



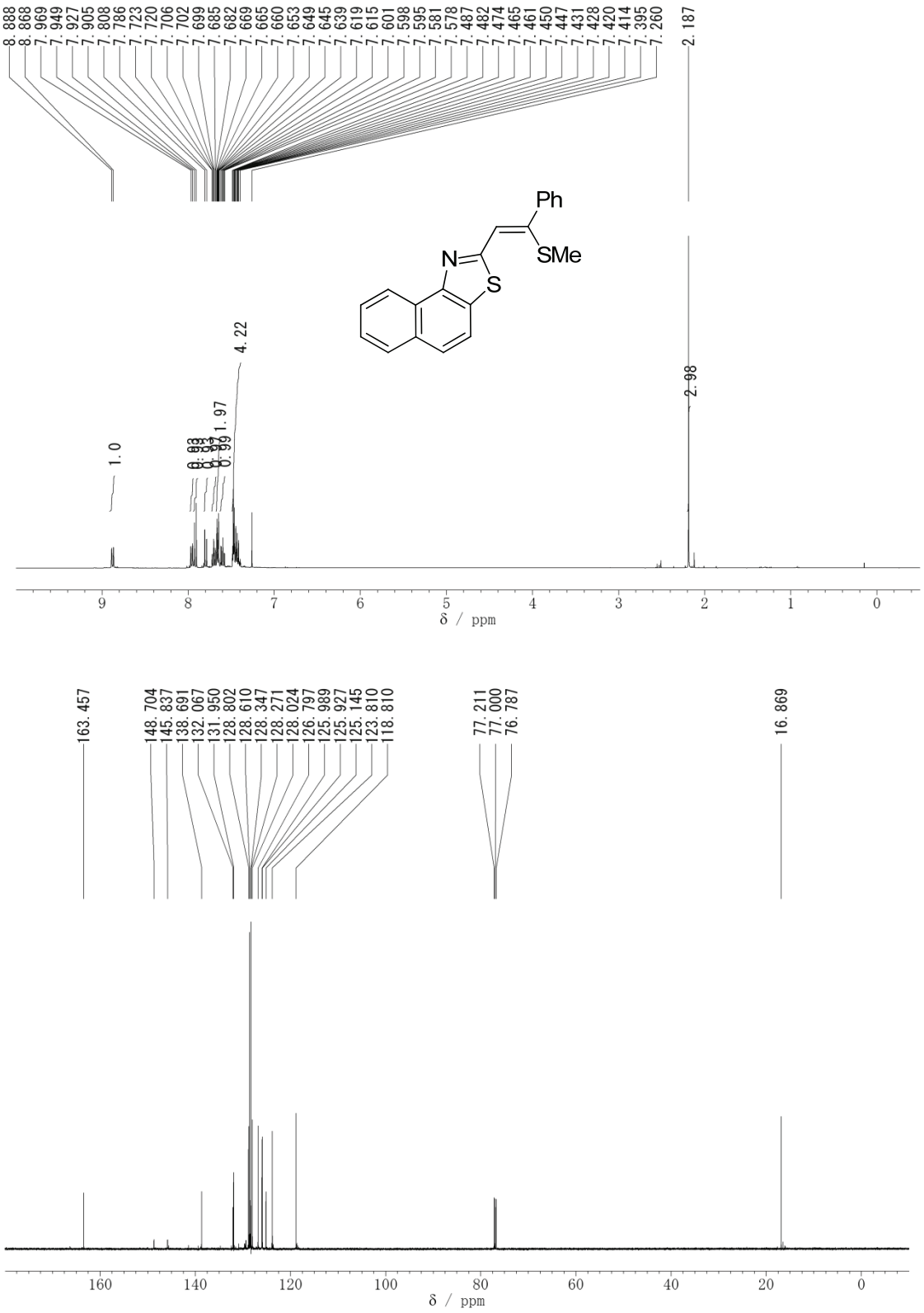
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3al'** (rt, $CDCl_3$).



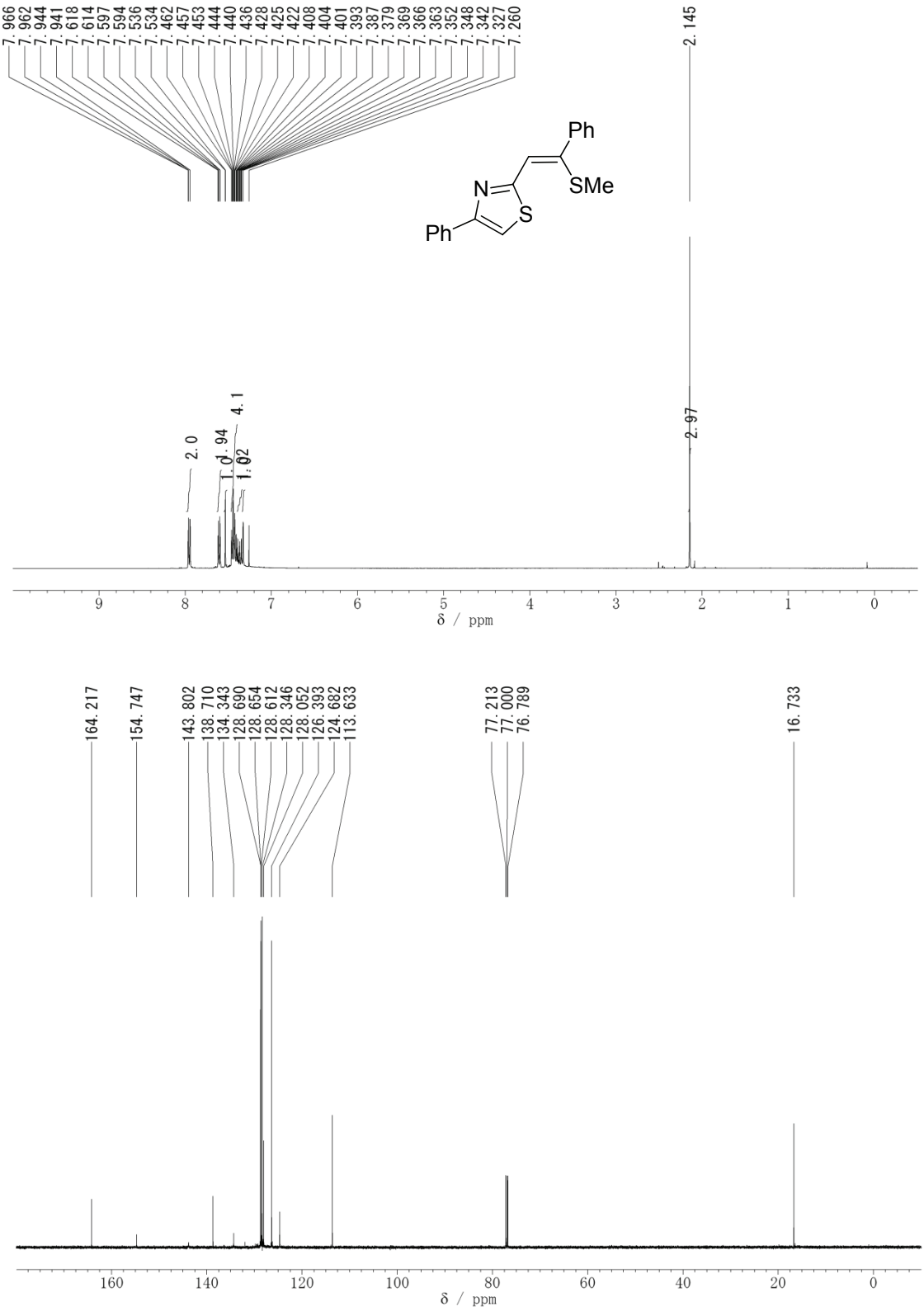
NOESY (600 MHz) spectrum of **3al'** (rt, $CDCl_3$) clearly showing the correlation between the allylic methylene protons and the vinyl proton (δ = 2.49 ppm and 6.08 ppm).



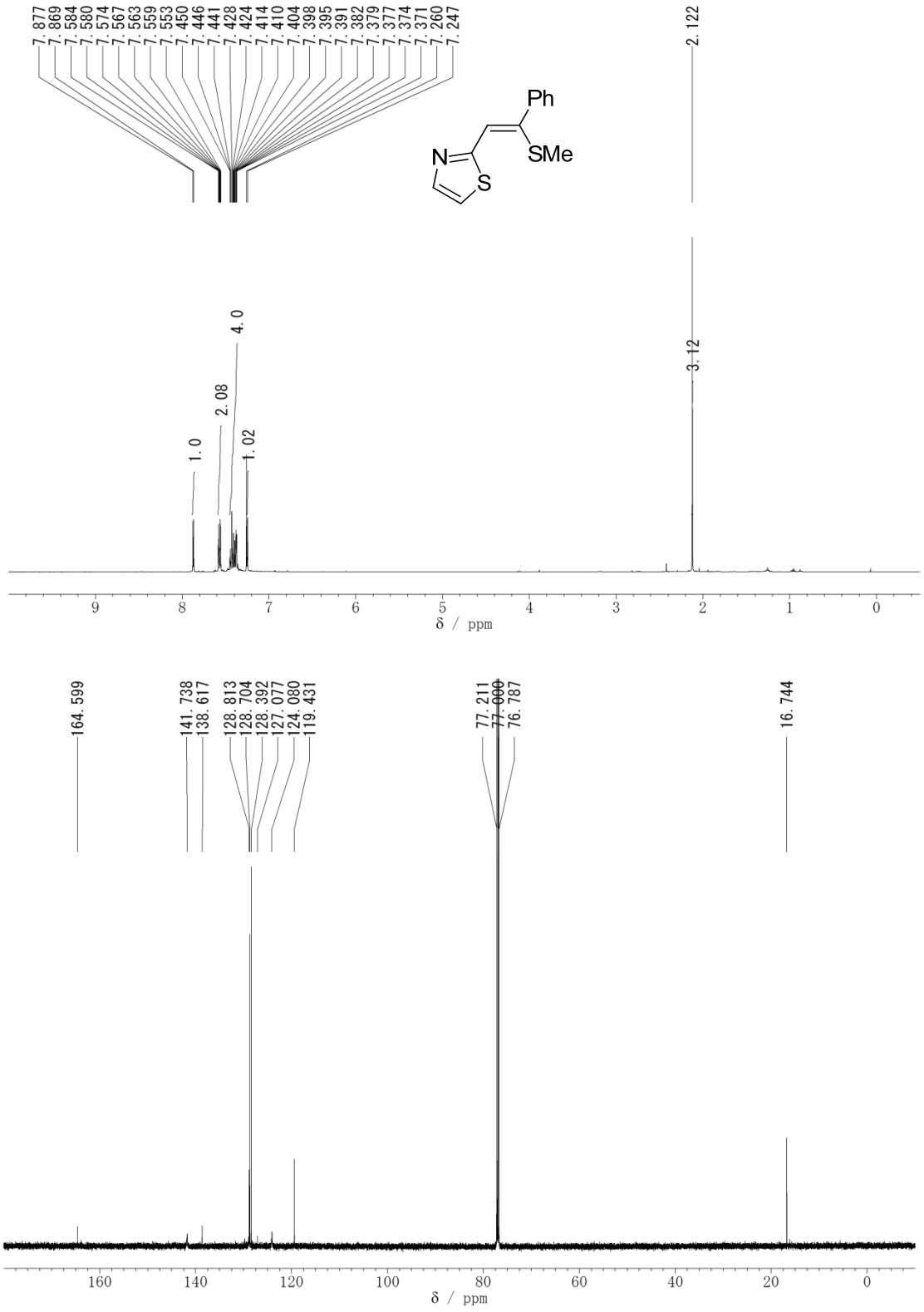
^{1}H NMR (300 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3ba** (rt, $CDCl_3$).



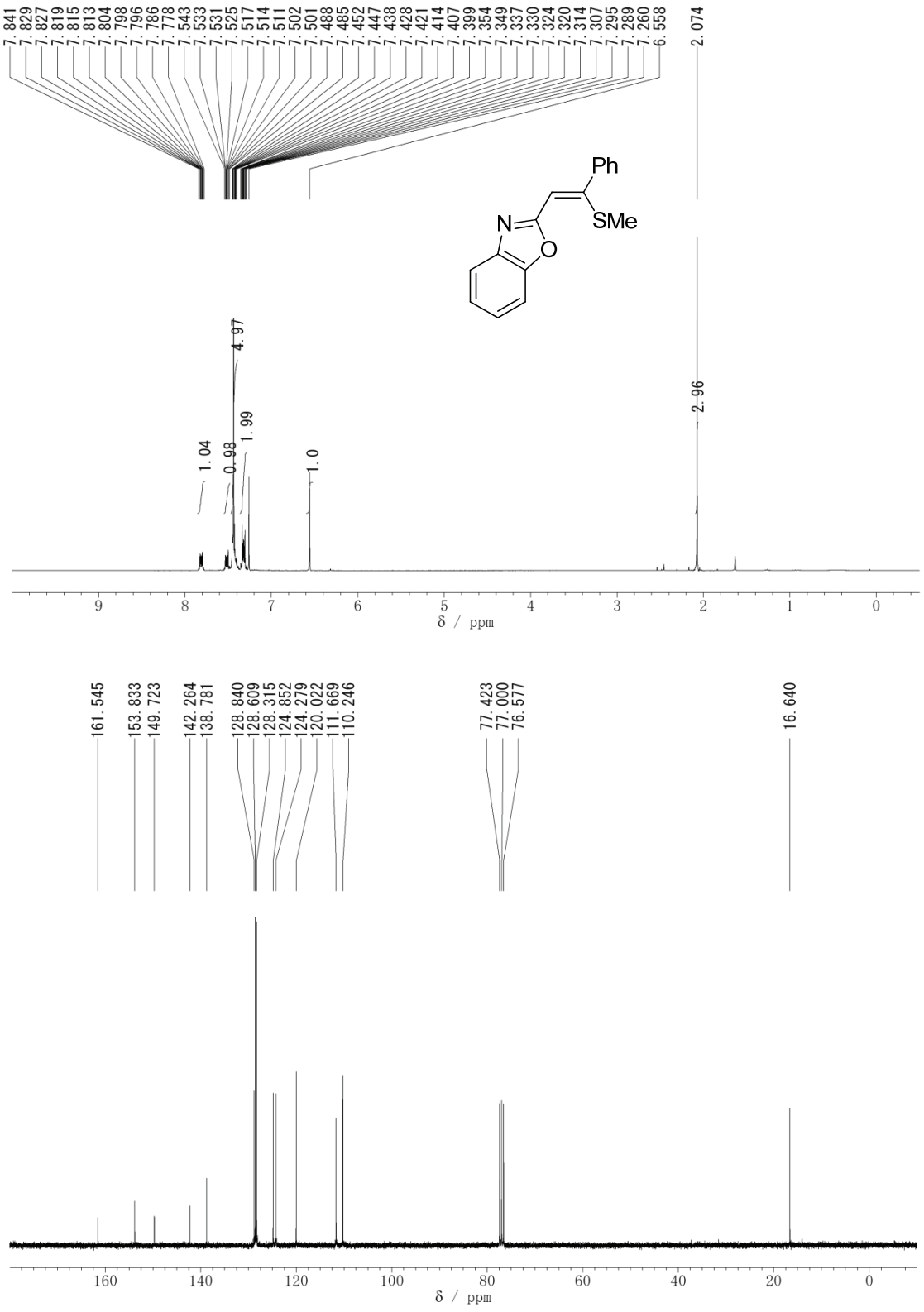
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3ca** (rt, $CDCl_3$).



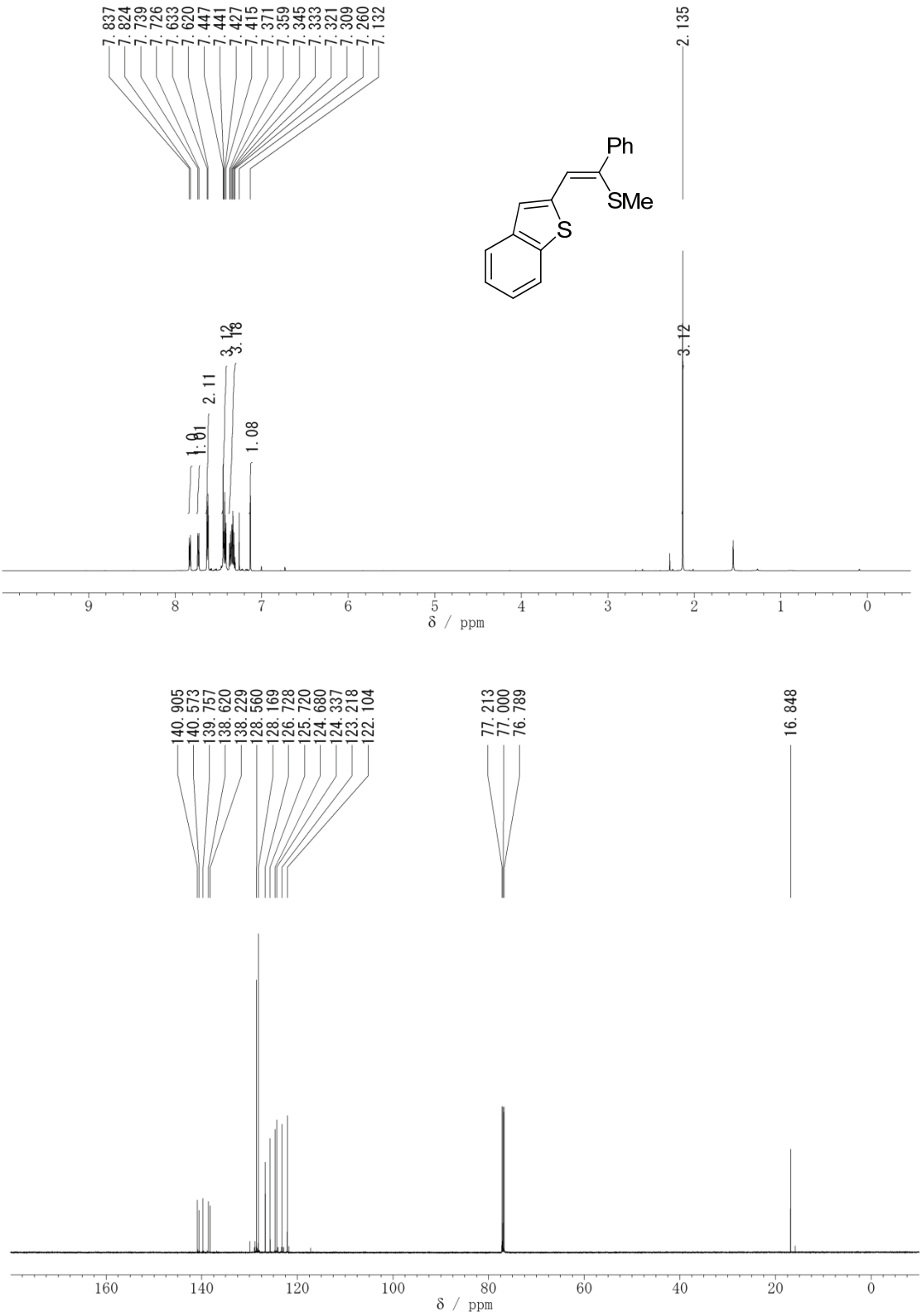
^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3da** (rt, $CDCl_3$).



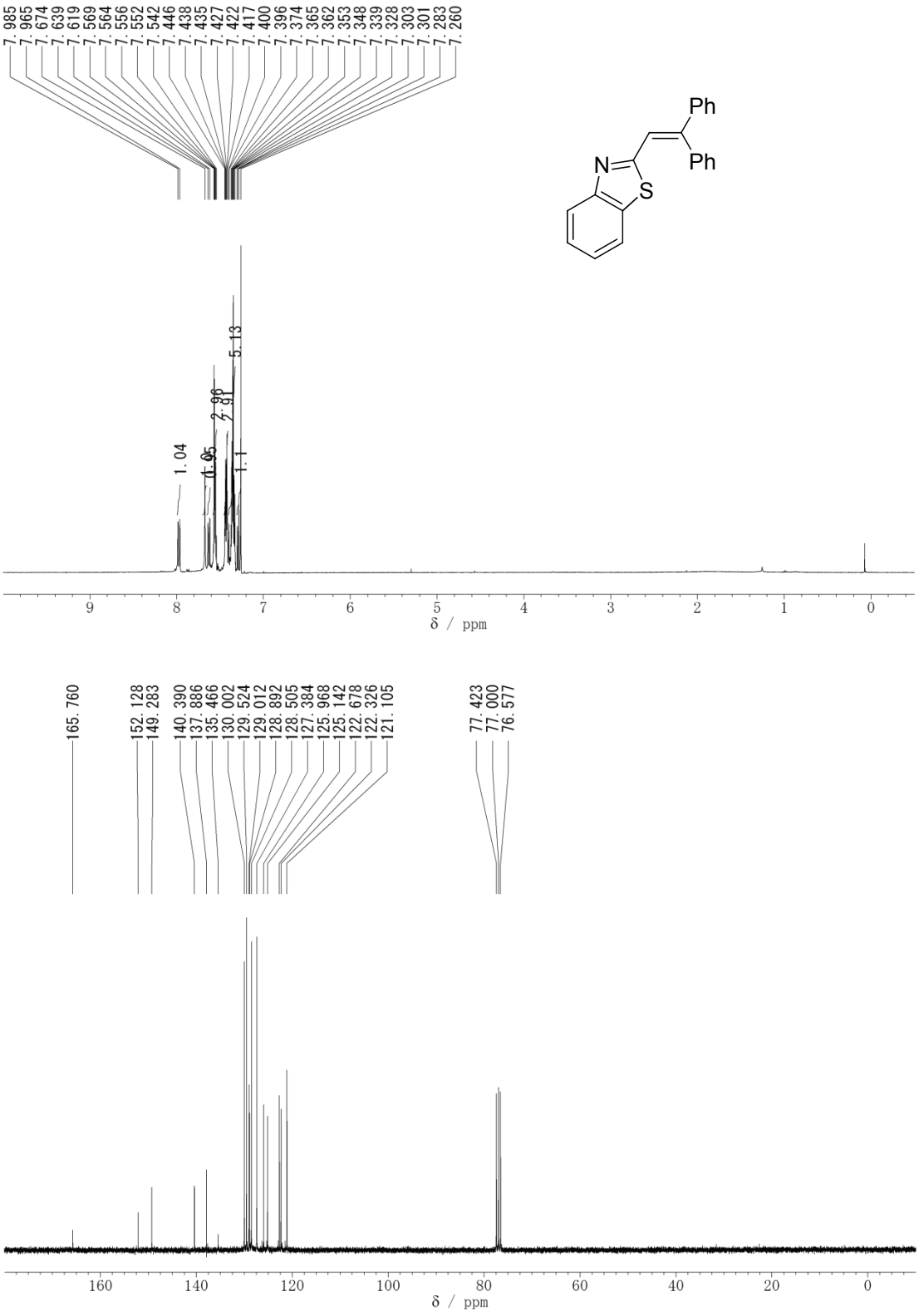
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3ea** (rt, $CDCl_3$).



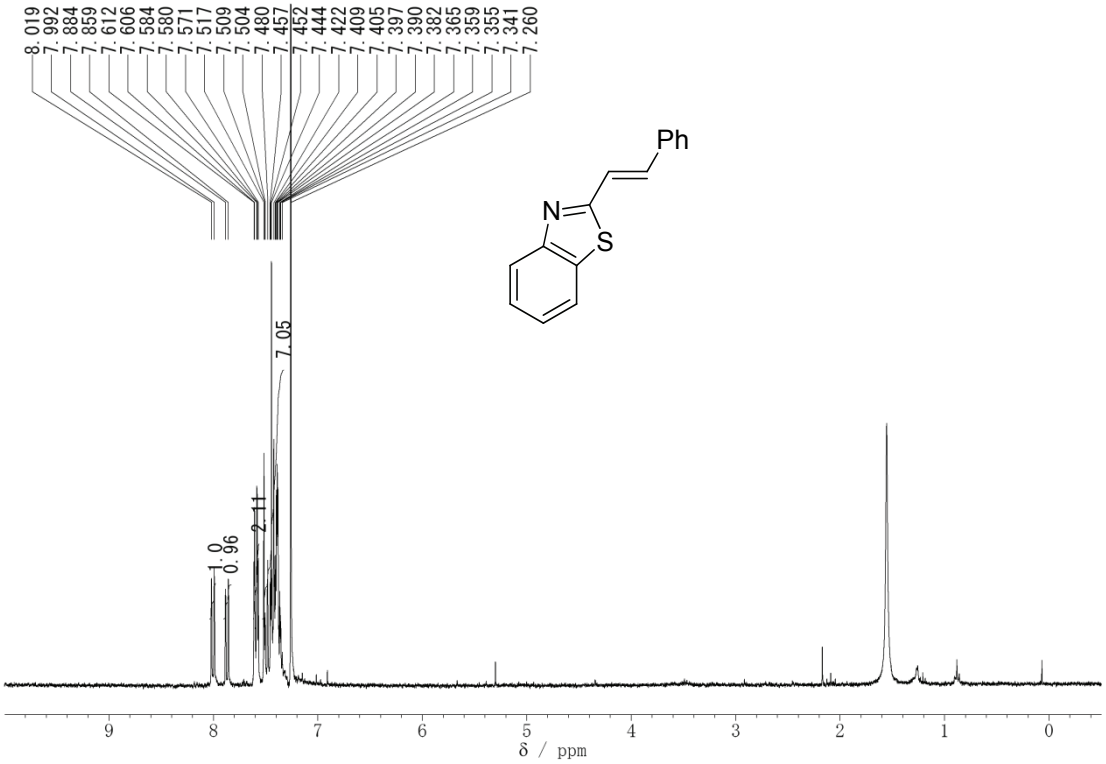
^{1}H NMR (300 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra of **3fa** (rt, $CDCl_3$).



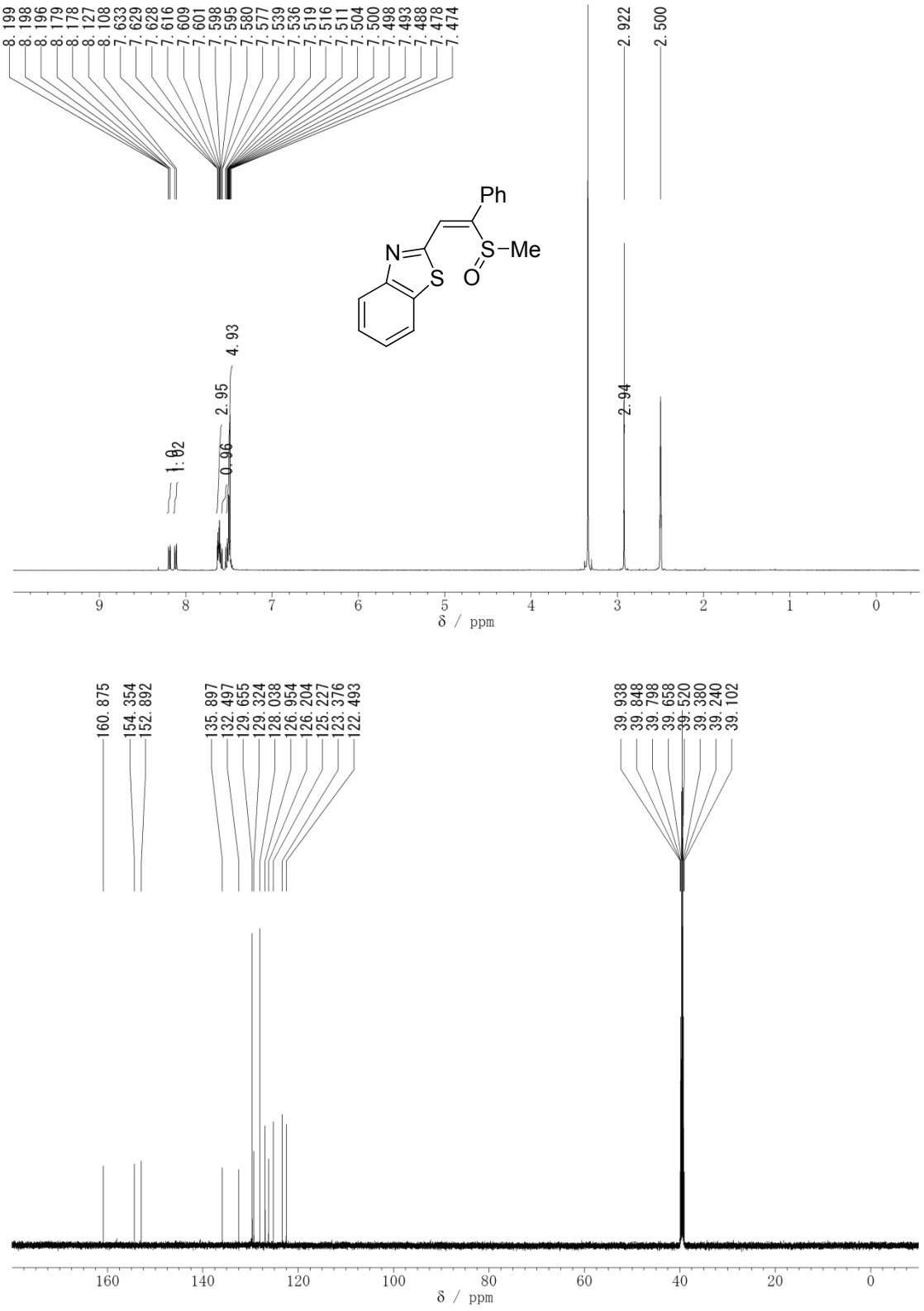
^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3ga** (rt, $CDCl_3$).



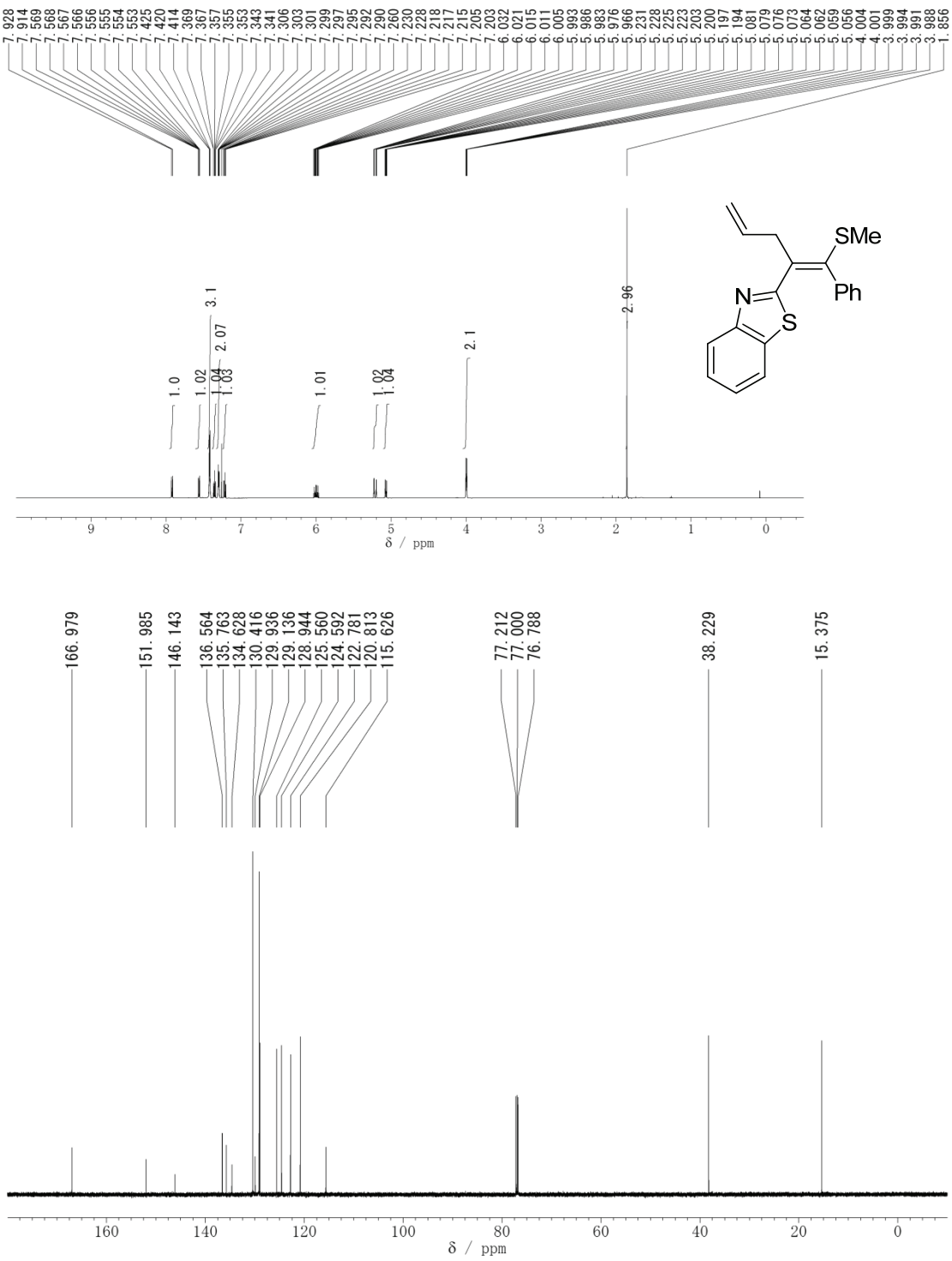
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra of **4** (rt, $CDCl_3$).



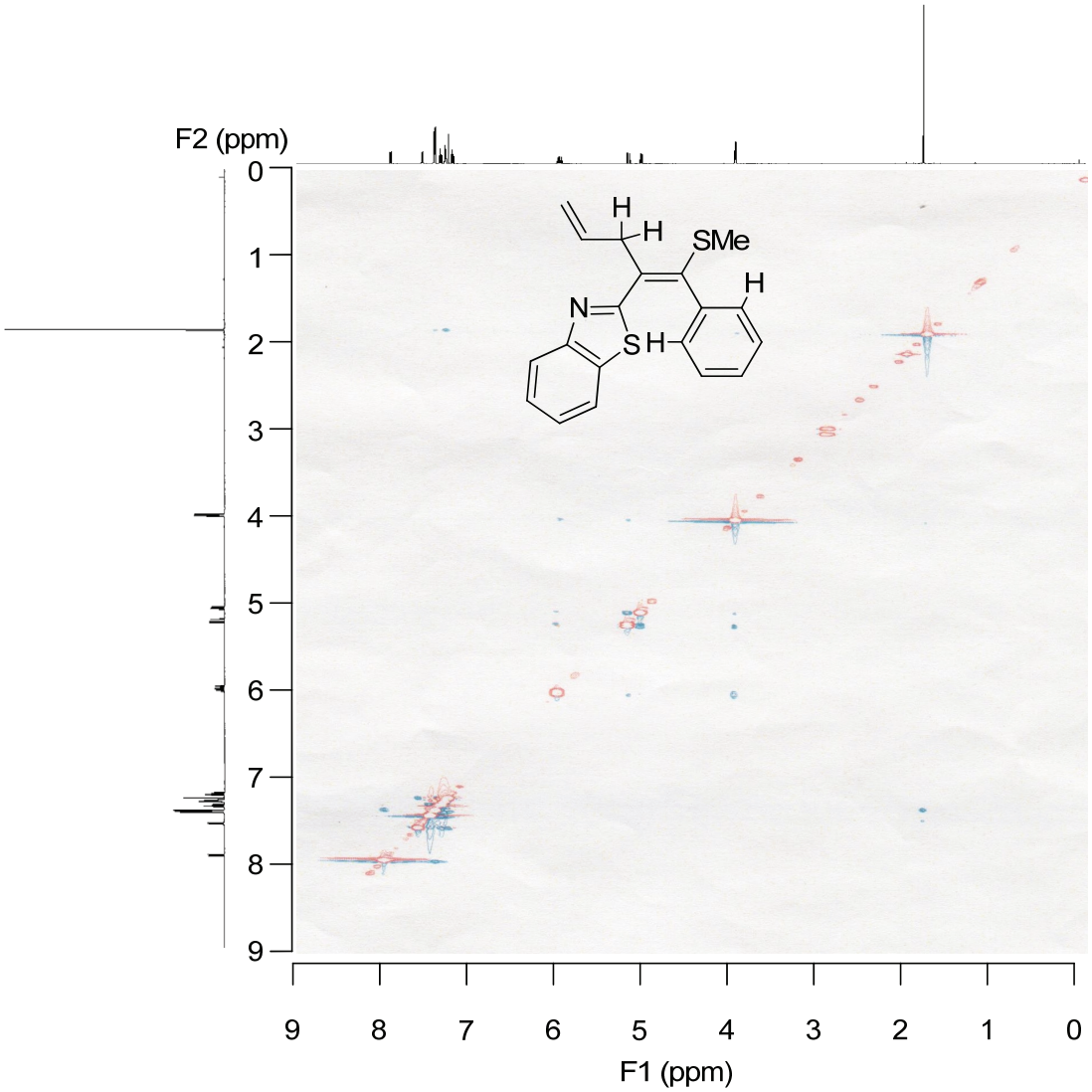
^{1}H NMR (300 MHz) spectrum of **5** (rt, $CDCl_3$).



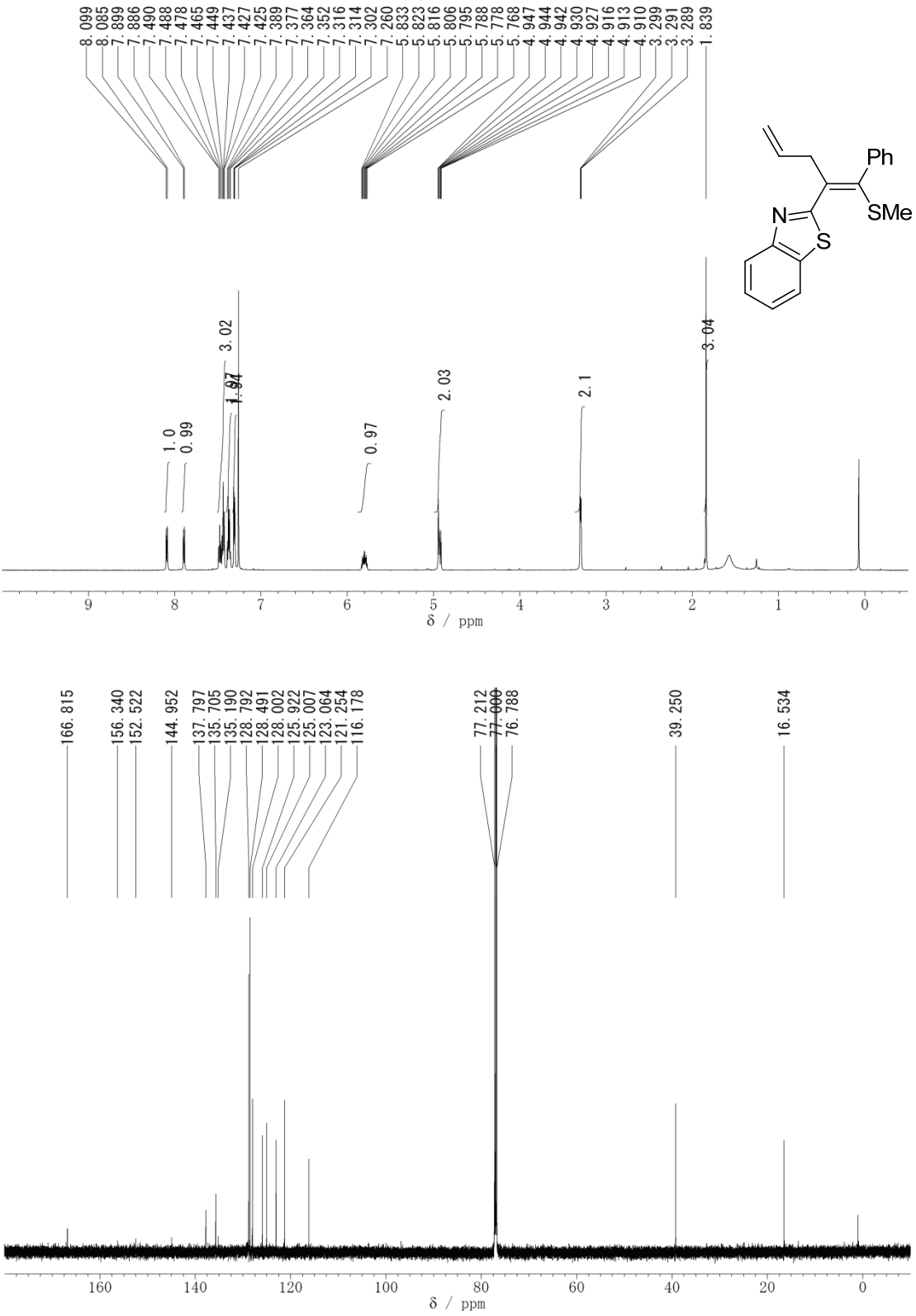
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **6** (rt, DMSO-d_6).



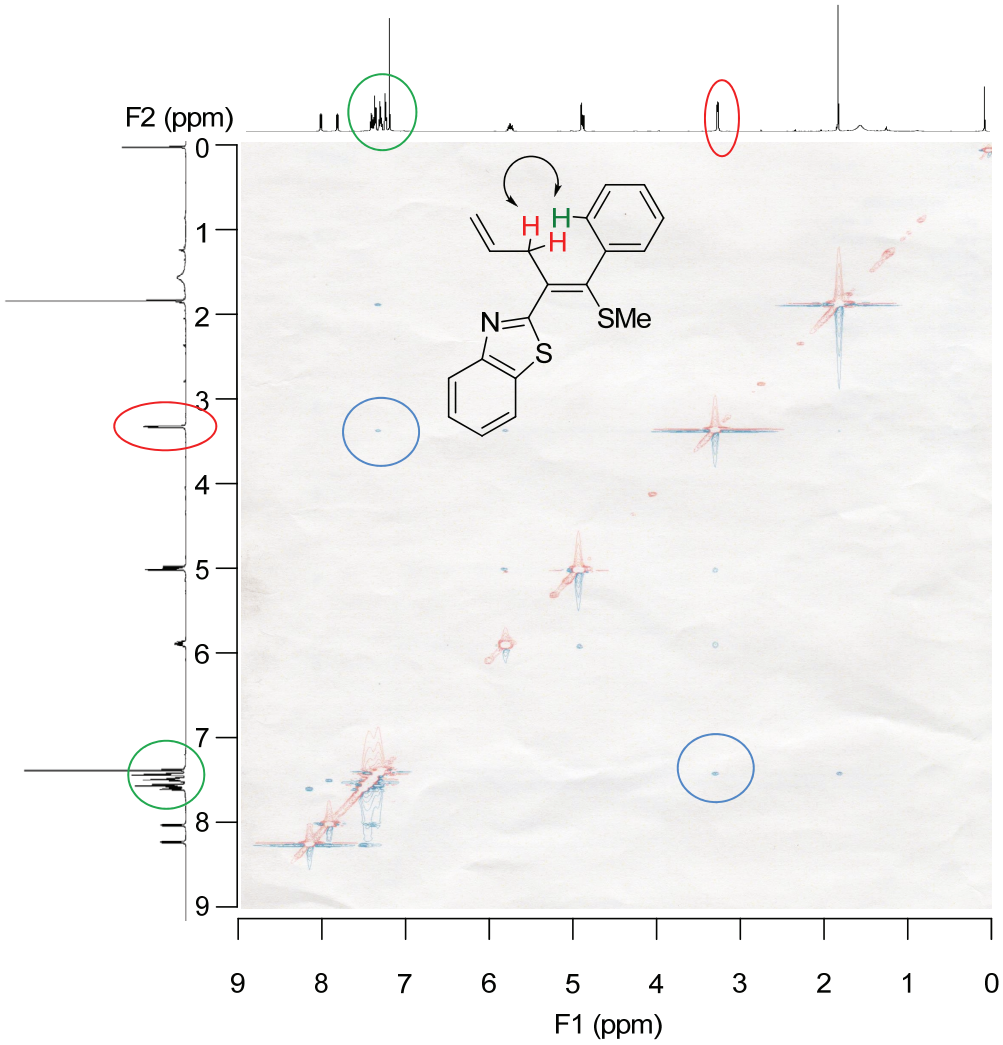
^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of (*E*)-**7** (rt, $CDCl_3$).



NOESY (600 MHz) spectrum of (*E*)-**7** (rt, $CDCl_3$) clearly showing no correlation between the allylic methylene protons and the aryl protons (δ = 4.00 ppm and 7.29–7.31 ppm).



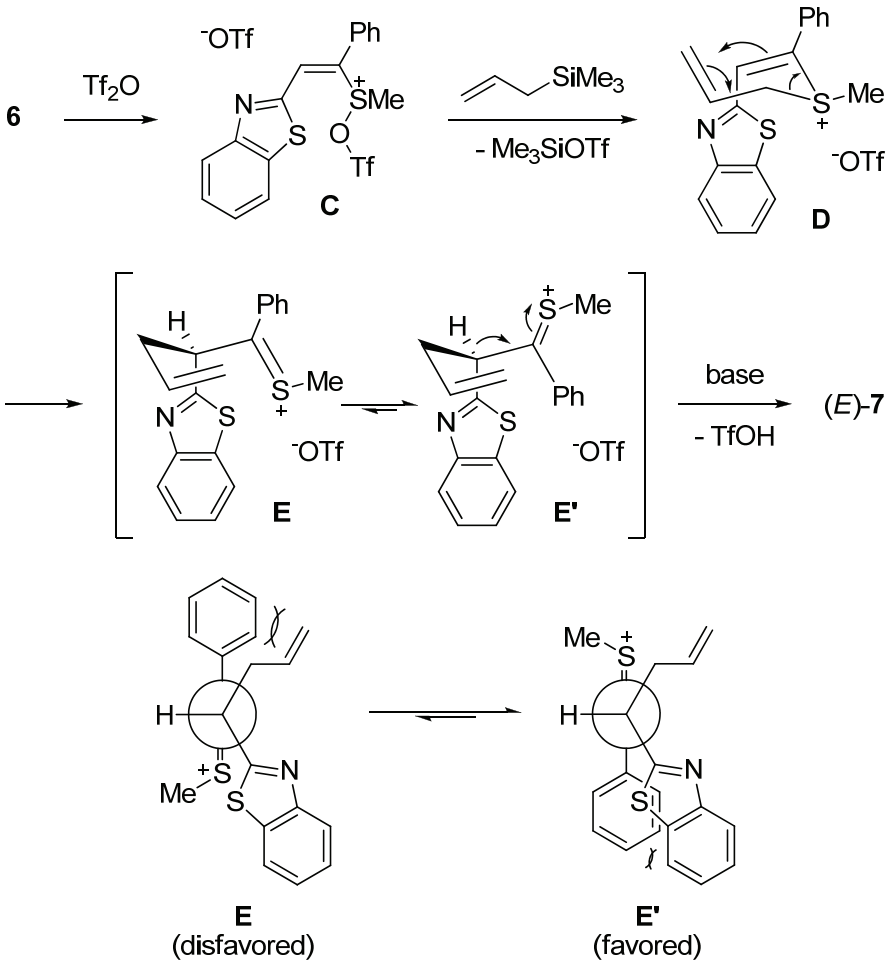
^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of (*Z*)-**7** (rt, $CDCl_3$).



NOESY (600 MHz) spectrum of (*Z*)-**7** (rt, $CDCl_3$) clearly showing the correlation between the allylic methylene protons and the aryl protons (δ = 3.30 ppm and 7.35–7.39 ppm).

5. A Plausible Reaction Mechanism of Allylation of Sulfoxide 6

The regio- and stereoselectivities of allylation would be rationalized as shown in Scheme S1. First, sulfonium salt **C** is generated by the reaction of sulfoxide **6** with trifluoromethanesulfonic anhydride (Tf_2O).[13] The subsequent nucleophilic attack of allylsilane on the cationic sulfur of **D** gives sulfonium salt **E** with a release of trimethylsilyl triflate.[12,14] Thio-Claisen rearrangement from **E** proceeds via a six-membered chair-like transition state, followed by deprotonation, affording the allylated product **7**.[15] During the stereodetermined deprotonation step, carbon–hydrogen bond should be placed at the perpendicular position of carbon–sulfur double bond from a stereoelectronic viewpoint. There are two possible conformations **E** and **E'** in the present reaction. The steric repulsion between the phenyl and allyl groups in **E** would retard the following deprotonation, while that between the phenyl and benzothiaolyl groups would be relatively smaller. The preferential deprotonation from **E'** provides (*E*)-**7** selectively.



Scheme S1. A plausible reaction mechanism of allylation.

6. *Structural Determination of Compounds by X-ray Analysis*

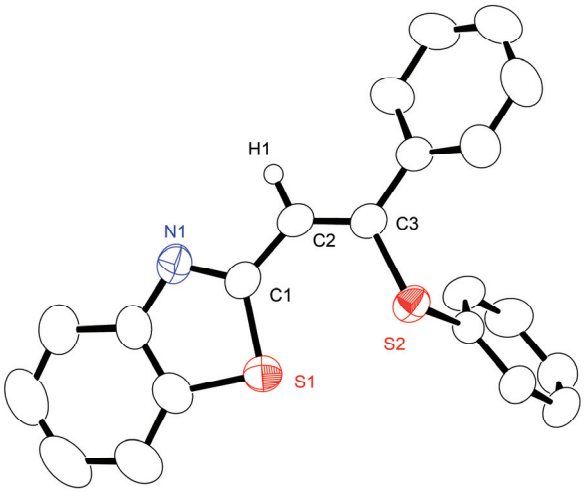


Figure S1. An ORTEP Drawing of **3ba**.

A. Crystal Data

Empirical Formula	$C_{21}H_{15}NS_2$
Formula Weight	345.48
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.50 × 0.20 × 0.20 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	7878 (6.4–55.0°)
Lattice Parameters	a = 9.1755(6) Å
	b = 10.6216(6) Å
	c = 10.7652(6) Å
	V = 865.79(9) Å^3
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.325 g/cm^3
F_{000}	360.00
μ(MoKα)	3.081 cm^{-1}

B. Intensity Measurements

Diffractometer	AFC7
Radiation	MoKα (λ = 0.71075 Å)

	graphite monochromated
Take-off Angle	2.8°
Detector Aperture	2.0–2.5 mm horizontal
	2.0 mm vertical
Crystal to Detector Distance	21 mm
Temperature	24.9 °C
Scan Type	w-2q
$2\theta_{max}$	55.0°
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.860–0.940)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma\, \omega\, (\|F_o\|-\|F_c\|)^2$
Least Squares Weights	1
$2\theta_{max}$ cutoff	55.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>2.00σ(I))	3946
No. Variables	277
Reflection/Parameter Ratio	14.25
Residuals: R (I>2.00σ(I))	0.0502
Residuals: R_w (I>2.00σ(I))	0.1105
Goodness of Fit Indicator	1.047
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.20 $e^-/Å^3$
Minimum peak in Final Diff. Map	–0.20 $e^-/Å^3$

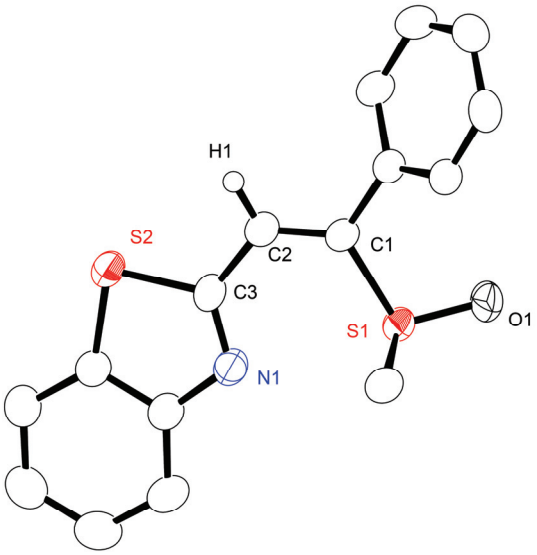


Figure S1. An ORTEP Drawing of **6**.

A. Crystal Data

Empirical Formula	$C_{16}H_{13}NOS_2$
Formula Weight	299.40
Crystal Color, Habit	yellow, prism
Crystal Dimensions	0.50 × 0.40 × 0.15 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	10855 (6.1–55.0°)
Lattice Parameters	a = 11.330(5) Å
	b = 7.224(3) Å
	c = 17.293(10) Å
	V = 1400.6(12) Å^3
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.420 g/cm^3
F_{000}	624.00
μ(MoKα)	3.734 cm^{-1}

B. Intensity Measurements

Diffractometer	AFC7
Radiation	MoKα (λ = 0.71075 Å)

	graphite monochromated
Take-off Angle	2.8°
Detector Aperture	2.0–2.5 mm horizontal
	2.0 mm vertical
Crystal to Detector Distance	21 mm
Temperature	24.9 °C
Scan Type	w-2θ
$2\theta_{max}$	55.0°
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.835–0.946)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma\, \omega\, (\|Fo\|-\|Fc\|)^2$
Least Squares Weights	1
$2\theta_{max}$ cutoff	55.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>2.00σ(I))	3170
No. Variables	233
Reflection/Parameter Ratio	13.61
Residuals: R (I>2.00σ(I))	0.0340
Residuals: R_w (I>2.00σ(I))	0.0946
Goodness of Fit Indicator	1.050
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.35 $e^-/Å^3$
Minimum peak in Final Diff. Map	–0.26 $e^-/Å^3$

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