Supplementary Information

Aerobic Cross-Dehydrogenative Coupling of Toluenes and *o*-Phenylenediamines by Flavin Photocatalysis for Facile Synthesis of Benzimidazoles

Yuta Shiogai, Marina Oka, Hiroki Iida*

Department of Chemistry, Graduate School of Natural Science and Technology,
Shimane University, 1060 Nishikawatsu, Matsue, 690-8504, Japan

E-mail address: iida@riko.shimane-u.ac.jp

1. General

The IR spectra were recorded on a JASCO FT/IR-660plus spectrophotometer (JASCO, Tokyo, Japan). The NMR spectra were measured using JEOL JNM-L400 and JNM ECX-500 spectrometers (JEOL, Akishima, Japan) operating at 400 and 500 MHz, respectively, for ^{1}H and 100 and 126 MHz, respectively, for ^{13}C using tetramethylsilane (TMS) or a solvent residual peak as the internal standard. The electrospray ionization mass (ESI-MS) spectra were recorded on a Bruker microTOFII mass spectrometer (Bruker, Billerica, MA) using the positive or negative mode ESI-TOF method for acetonitrile solutions and sodium formate as the reference. The GC measurements were performed on a Shimadzu GC-2014 gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector (FID) using a Supelco Equity-5 (30 m x 0.25 mm) column.

2. Materials

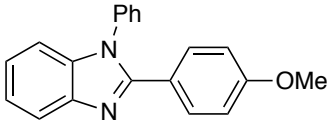
Riboflavin tetraacetate (**4a**),[S1] 1,3-dimethylalloxazine (**5a**),[S2] 7-trifluoromethyl-1,3-dimethylalloxazine (**5b**),[S2] 5-ethyl-10-(2-hydroxylethyl)-7,8-dimethylisoalloxazinium triflate (**6•TfO**),[S3] 5-ethyl-1,3,7,8-tetramethylalloxazinium triflate (**7•TfO**),[S3] and 1,10-ethylene-3,7,8-trimethylisoalloxazinium triflate (**8•TfO**),[S3] were synthesized according to the previously reported methods. 1-Methyl-4-phenoxybenzene (**1c**) and 4-methyl-*N*-phenylbenzene-1,2-diamine (**2f**) were synthesized according to the previously reported methods.[S4,5] Other starting materials were purchased from Sigma-Aldrich (St. Louis, USA), FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan), Nacalai tesque (Kyoto, Japan), and Tokyo Kasei (TCI, Tokyo, Japan) and were used as received.

3. Experimental Procedures

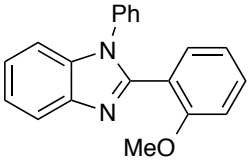
Typical procedure for synthesis of 3aa. A mixture of 4-methoxytoluene (**1a**, 122 mg, 1.0 mmol), **4a** (13.6 mg, 0.025 mmol), MeOH (12.5 mL), and H_2O (12.5 mL) was irradiated using blue LED lamps (11 W) while stirring under air (1 atm, balloon) at 25 °C for 6 h. A solution of 2-aminodiphenylamine (**2a**, 92.1 mg, 0.50 mmol) in MeOH (25 mL) was then

added into the reaction mixture, and the mixture was stirred under irradiation at 60 ˚C for 15 h. After the solvent was removed by evaporation, the residue was purified by column chromatography (SiO_2, hexane/ethyl acetate = 4/1, v/v) to give **3aa** (120 mg, 80%) as a white solid. These results are summarized in Scheme 3.

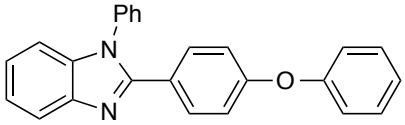
Spectroscopic data of benzimidazoles



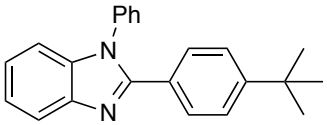
Spectroscopic data of 2-(4-methoxyphenyl)-1-phenyl-1*H*-benz[*d*]imidazole (**3aa**):[S6] Column chromatography (SiO_2, hexane/ethyl acetate=4/1, v/v) afforded the desired product (120 mg, 80%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.86 (d, J = 8.1 Hz, 1H), 7.52-7.42 (m, 5H), 7.33-7.28 (m, 3H), 7.24-7.18 (m, 2H), 6.81 (dt, J = 8.9, 2.5 Hz, 2H), 3.78 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C, δ): 160.6, 152.5, 143.1, 137.30 137.26, 131.0, 129.9, 128.6, 127.5, 123.1, 122.9, 122.4, 119.6, 113.8, 110.4, 55.3.



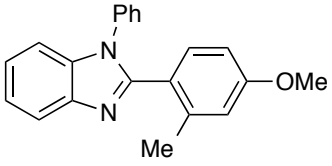
Spectroscopic data of 2-(2-methoxyphenyl)-1-phenyl-1*H*-benz[*d*]imidazole (**3ba**): Column chromatography (SiO_2, hexane/ethyl acetate=9/1 to 3/1, v/v) afforded the desired product (58.9 mg, 60%) as a white solid. Mp: 153.1-154.4 °C. IR (KBr, cm^{-1}): 3049, 2834, 1260, 1032. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.89 (d, J = 8.0 Hz, 1H), 7.66 (dd, J = 7.6, 1.7 Hz, 1H), 7.39-7.21 (m, 9H), 7.03 (td, J = 7.5, 0.9 Hz, 1H), 6.72 (d, J = 8.1 Hz, 1H), 3.31 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C, δ): 157.0, 151.4, 143.3, 137.4, 136.1, 132.3, 131.5, 129.1, 127.7, 126.0, 123.2, 122.6, 120.8, 120.1, 120.0, 110.9, 110.4, 54.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}N_2O$, 301.1335; found, 301.1339.



Spectroscopic data of 2-(4-phenoxyphenyl)-1-phenyl-1*H*-benz[*d*]imidazole (**3ca**): Column chromatography (SiO_2, hexane/ethyl acetate=9/1 to 4:1, v/v) afforded the desired product (85.3 mg, 72%) as a white solid. Mp: 148.2-150.3 °C. IR (KBr, cm^{-1}): 3060, 3015, 1241. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.87 (d, J = 8.0 Hz, 1H), 7.55-7.43 (m, 5H), 7.36-7.29 (m, 5H), 7.26-7.20 (m, 2H), 7.13 (t, J = 7.4 Hz, 1H), 7.02 (dd, J = 8.7, 1.1 Hz, 2H), 6.90 (dt, J = 8.8, 2.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C, δ): 158.8, 156.2, 152.1, 143.1, 137.4, 137.1, 131.1, 130.03, 129.99, 128.7, 127.6, 124.6, 124.1, 123.3, 123.1, 119.8, 118.0, 110.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{19}N_2O$, 363.1492; found, 363.1500.

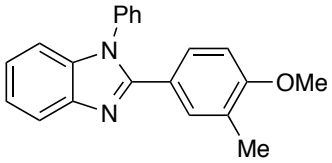


Spectroscopic data of 2-(4-(*tert*-butyl)phenyl)-1-phenyl-1*H*-benz[*d*]imidazole (**3da**):[S7] Column chromatography (SiO_2, hexane/ethyl acetate=9/1 to 4:1, v/v) afforded the desired product (38.8 mg, 36%) as a white solid. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.88 (d, J = 8.0 Hz, 1H), 7.53-7.47 (m, 5H), 7.34-7.29 (m, 5H), 7.24-7.20 (m, 2H), 1.29 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C, δ): 152.8, 152.6, 143.2, 137.5, 137.3, 130.0 129.2, 128.7, 127.7, 127.1, 125.4, 123.2, 123.0, 119.8, 110.5, 34.9, 31.3.

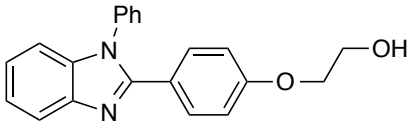


Spectroscopic data of 2-(4-methoxy-2-methylphenyl)-1-phenyl-1*H*-benz[*d*]imidazole (**3ga**): Column chromatography (SiO_2, hexane/ethyl acetate= 4:1, v/v) afforded the desired product (69.4 mg, 67%) as a white solid. Mp: 144.2-145.8 °C. IR (KBr, cm^{-1}): 3053, 2954,

1242, 1046. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.88 (d, J = 7.9 Hz, 1H), 7.39-7.24 (m, 6H), 7.21-7.18 (m, 3H), 6.69 (d, J = 2.6 Hz, 1H), 6.66 (dd, J = 8.4, 2.6 Hz, 1H), 3.76 (s, 3H), 2.17 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C, δ): 160.4, 153.1, 143.2, 139.6, 136.6, 135.8, 132.3, 129.5, 127.9, 126.7, 123.1, 122.8, 122.7, 120.0, 115.7, 111.1, 110.5, 55.2, 20.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{19}N_2O$, 315.1492; found, 315.1498.

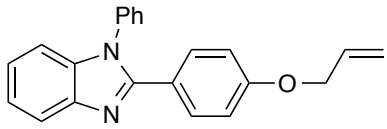


Spectroscopic data of 2-(4-methoxy-3-methylphenyl)-1-phenyl-1*H*-benz[*d*]imidazole (**3ha**): Column chromatography (SiO_2, hexane/ethyl acetate= 4:1, v/v) afforded the desired product (75.2 mg, 73%) as a pale pink solid. Mp: 136.6-138.9 °C. IR (KBr, cm^{-1}) 3052, 2987, 1250, 1031. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.86 (d, J = 8.0 Hz, 1H), 7.53-7.47 (m, 4H), 7.34-7.30 (m, 3H), 7.25-7.19 (m, 3H), 6.68 (d, J = 8.4 Hz, 1H), 3.80 (s, 3H), 2.15 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C, δ): 158.9, 152.7, 143.1, 137.44, 137.37, 132.0, 129.9, 128.6, 128.3, 127.7, 126.9, 123.0, 122.9, 121.9, 119.6, 110.4, 109.4, 55.4, 16.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{19}N_2O$, 315.1492; found, 315.1498.

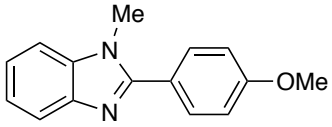


Spectroscopic data of 2-(4-(2-hydroxy)ethoxyphenyl)-1-phenyl-1*H*-benz[*d*]imidazole (**3ia**): Column chromatography (SiO_2, hexane/ethyl acetate= 4:1 to 1:1, v/v) afforded the desired product (65.3 mg, 66%) as a white solid. Mp: 179.4-181.9 °C. IR (KBr, cm^{-1}): 3292, 2947, 2858, 1254, 1055. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.86 (d, J = 8.0 Hz, 1H), 7.52-7.43 (m, 5H), 7.34-7.28 (m, 3H), 7.26-7.20 (m, 2H), 6.79 (dt, J = 9.0, 2.5 Hz, 2H), 4.02 (t, J = 4.6 Hz, 2H), 3.94 (t, J = 4.6 Hz, 2H), 2.99 (br, s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C, δ): 158.8, 151.4, 142.0, 136.3, 136.2, 130.1, 129.0, 127.7, 126.6, 122.2,

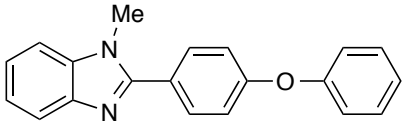
122.1, 121.7, 118.6, 113.5, 109.5, 68.4, 60.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{19}N_2O_2$, 331.1455; found, 331.1441.



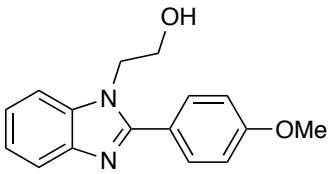
Spectroscopic data of 2-(4-(allyloxy)phenyl)-1-phenyl-1*H*-benz[*d*]imidazole (**3ja**): Column chromatography (SiO_2, hexane/ethyl acetate= 4:1, v/v) afforded the desired product (103 mg, 63%) as a colorless oil. IR (neat, cm^{-1}): 3063, 2985, 1650, 1178, 1074, 1015. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.86 (d, J = 8.0 Hz, 1H), 7.52-7.43 (m, 5H), 7.33-7.29 (m, 3H), 7.25-7.19 (m, 2H), 6.82 (dt, J = 9.0, 2.5 Hz, 2H), 6.02 (ddt, J = 17.3, 10.4, 5.2 Hz, 1H), 5.39 (ddd, J = 17.3, 3.1, 1.6 Hz, 1H), 5.27 (ddd, J = 10.6, 2.7, 1.3 Hz, 1H), 4.52 (t, J = 1.5 Hz, 1H), 4.51 (t, J = 1.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C, δ): 159.7, 152.5, 143.1, 137.32, 137.28, 132.9, 131.0, 130.0, 128.6, 127.6, 123.1, 123.0, 122.6, 119.7, 118.0, 114.6, 110.4, 68.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}N_2O$, 327.1492; found, 327.1508.



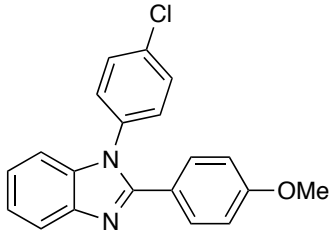
Spectroscopic data of 2-(4-methoxyphenyl)-1-methyl-1*H*-benz[*d*]imidazole (**3ab**):[S8] Column chromatography (SiO_2, hexane/ethyl acetate=3/1, v/v) afforded the desired product (90.3 mg, 76%) as a white solid. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.82-7.79 (m, 1H), 7.69 (dt, J = 8.5, 2.5 Hz, 2H), 7.35-7.26 (m, 3H), 7.02 (dt, J = 8.5, 2.5 Hz, 2H), 3.85 (s, 3H), 3.80 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C, δ): 160.8, 153.8, 143.0, 136.6, 130.9, 122.6, 122.5, 122.3, 119.6, 114.2, 109.6, 55.4, 31.7.



Spectroscopic data of 1-methyl-2-(4-phenoxyphenyl)-1*H*-benz[*d*]imidazole (**3cb**): Column chromatography (SiO_2, hexane/ethyl acetate= 4:1, v/v) afforded the desired product (66.9 mg, 66%) as a white solid. Mp: 129.8-131.2 °C. IR (KBr, cm^{-1}): 3041, 2946, 1237. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.83-7.80 (m, 1H), 7.74 (dt, J = 8.7, 2.5 Hz, 2H), 7.41-7.36 (m, 3H), 7.34-7.28 (m, 2H), 7.17 (t, J = 7.4 Hz, 1H), 7.13 (dt, J = 8.7, 2.5 Hz, 2H), 7.10 (m, 2H), 3.87 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C, δ): 159.1, 156.4, 153.5, 143.1, 136.7, 131.2, 130.1, 125.0, 124.2, 122.8, 122.6, 119.9, 119.7, 118.5, 109.7, 31.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}N_2O$, 301.1335; found, 301.1338.

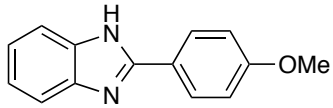


Spectroscopic data of 1-(2-hydroxyethyl)-2-(4-methoxyphenyl)-1*H*-benz[*d*]imidazole (**3ac**): Column chromatography (SiO_2, hexane/ethyl acetate= 2:1, v/v) afforded the desired product (57.6 mg, 65%) as a white solid. Mp: 134.5-135.7 °C. IR (KBr, cm^{-1}): 3160, 2935, 2837, 1255, 1026. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.66 (dt, J = 8.9, 2.5 Hz, 2H), 7.33 (d, J = 7.8 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.08 (td, J = 7.6, 1.1 Hz, 1H), 7.01 (td, J = 7.6, 1.0 Hz, 1H), 6.77 (dt, J = 8.9, 2.6 Hz, 2H), 4.23 (t, J = 5.3 Hz, 2H), 4.10 (t, J = 5.3 Hz, 2H), 3.80 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C, δ): 160.6, 154.1, 142.2, 135.1, 131.5, 122.6, 122.5, 121.9, 118.9, 113.9, 110.0, 60.5, 55.3, 47.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{17}N_2O_2$, 269.1285; found, 269.1287.

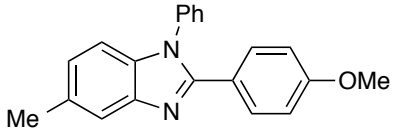


Spectroscopic data of 1-(4-chlorophenyl)-2-(4-methoxyphenyl)-1*H*-benz[*d*]imidazole (**3ad**):[S9] Column chromatography (SiO_2, hexane/ethyl acetate=4/1, v/v) afforded the desired

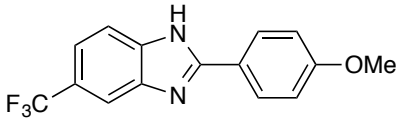
product (72.9 mg, 66%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.86 (d, J = 8.0 Hz, 1H), 7.51-7.46 (m, 4H), 7.35-7.31 (m, 1H), 7.28-7.22 (m, 3H), 7.20 (d, J = 8.1 Hz, 1H), 6.85 (dt, J = 8.8, 2.5 Hz, 2H), 3.82 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C, δ): 160.8, 152.4, 143.2, 137.0, 135.8, 134.4, 131.0, 130.3, 128.8, 123.3, 123.2, 122.1, 119.8, 114.0, 110.2, 55.4.



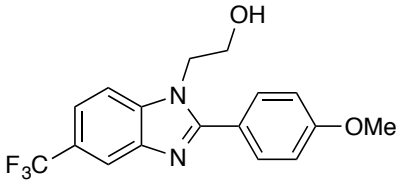
Spectroscopic data of 2-(4-methoxyphenyl)-1*H*-benz[*d*]imidazole (**3ae**):[S10] Column chromatography (SiO_2, hexane/ethyl acetate=3/1, v/v) afforded the desired product (76.7 mg, 77%) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C, δ): 12.7 (br s, 1H), 8.13 (dt, J = 8.9, 2.5 Hz, 2H), 7.62 (d, J = 6.0 Hz, 1H), 7.50 (d, J = 5.5 Hz, 1H), 7.17 (d, J = 4.3 Hz, 2H), 7.11 (dt, J = 8.9, 2.5 Hz, 2H), 3.84 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C, δ): 160.6, 151.4, 143.9, 135.0, 128.0, 122.7, 122.1, 121.5, 118.5, 114.4, 110.0, 55.3.



Spectroscopic data of 2-(4-methoxyphenyl)-5-methyl-1-phenyl-1*H*-benz[*d*]imidazole (**3af**): Column chromatography (SiO_2, hexane/ethyl acetate=4/1, v/v) afforded the desired product (80.8 mg, 78%) as a white solid. Mp: 141.6-143.2 °C. IR (KBr, cm^{-1}): 3006, 2839, 1254, 1028. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.64 (s, 1H), 7.50-7.40 (m, 5H), 7.28 (dt, J = 7.0, 1.6 Hz, 2H), 7.09 (d, J = 8.3 Hz, 1H), 7.04 (dd, J = 8.2, 1.1 Hz, 1H), 6.80 (dt, J = 8.9, 2.5 Hz, 2H), 3.78 (s, 3H), 2.50 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C, δ): 160.5, 152.4, 143.4, 137.4, 135.5, 132.6, 130.9, 129.9, 128.4, 127.5, 124.5, 122.6, 119.4, 113.8, 109.9, 55.3, 21.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{19}N_2O$, 315.1500; found, 315.1492.



Spectroscopic data of 2-(4-methoxyphenyl)-5-trifluoromethyl-1*H*-benz[*d*]imidazole (**3ag**):[S11] Column chromatography (SiO_2, hexane/ethyl acetate=1/5, v/v) afforded the desired product (70.3 mg, 74%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 8.10 (dt, J = 8.9, 2.4 Hz, 2H), 7.78 (s, 1H), 7.58 (d, J = 8.3 Hz, 1H), 7.43 (dd, J = 8.7, 1.5 Hz, 1H), 6.91 (dt, J = 8.9, 2.5 Hz, 2H), 3.80 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C, δ): 161.8, 154.6, 128.7, 125.0 (q, J = 32 Hz), 124.9 (q, J = 273 Hz), 121.9, 119.7, 114.7, 55.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{12}F3N_2O$, 293.0896; found, 293.0894.

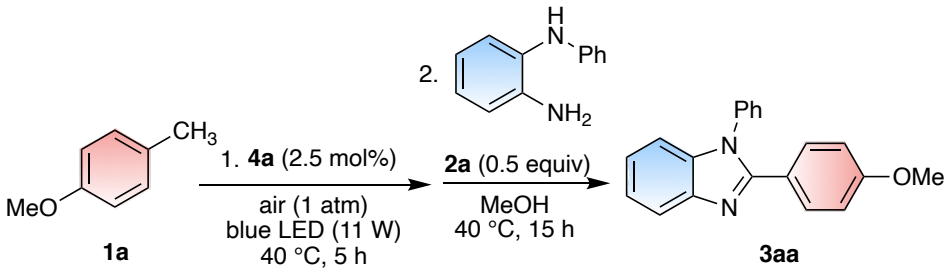


Spectroscopic data of 1-(2-hydroxyethyl)-2-(4-methoxyphenyl)-5-trifluoromethyl-1*H*-benz[*d*]imidazole (**3ah**): Column chromatography (SiO_2, hexane/ethyl acetate=2/1, v/v) afforded the desired product (66.2 mg, 60%) as a white solid. Mp: 148.1-149.6 °C. IR (KBr, cm^{-1}): 3180, 3016, 2846, 1610, 1338, 1327, 1257, 1025. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.75 (dt, J = 8.8, 2.5 Hz, 2H), 7.58 (s, 1H), 7.33 (dd, J = 8.5, 1.4 Hz, 1H), 7.28 (d, J = 8.5 Hz, 1H), 6.79 (dt, J = 9.0, 2.5 Hz, 2H), 4.31 (t, J = 4.7 Hz, 2H), 4.24 (t, J = 4.7 Hz, 2H), 3.85 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C, δ): 161.0, 156.2, 141.3, 136.7, 131.9, 124.8 (q, J = 33 Hz) 124.7 (q, J = 278 Hz), 120.8, 119.6, 116.1, 113.9, 110.1, 60.5, 55.3, 47.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{16}F_3N_2O_2$, 337.1158; found, 337.1158.

4. Optimization of Reaction Condition

The solvent effect on the flavin-catalyzed reaction of **1a** with **2a** was investigated as shown in Table S1.

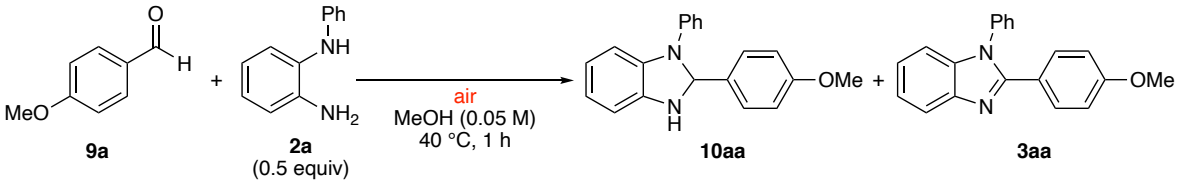
Table S1. Solvent effect.



entry	solvent (v/v)	yield (%)	entry	solvent (v/v)	yield (%)
1	MeOH	trace	7	THF/H_2O (1:1)	2
2	$MeOH/H_2O$ (99:1)	9	8	$CHCl_3/H_2O$ (1:1)	2
3	$MeOH/H_2O$ (9:1)	19	9	DMF/H_2O (1:1)	28
4	$MeOH/H_2O$ (4:1)	36	10	CH_3CN/H_2O (1:1)	25
5	$MeOH/H_2O$ (1:1)	64	11	$MeOH/H_2O$ (1:1)	64
6	$MeOH/H_2O$ (1:2)	51	12	*t*-$BuOH/H_2O$ (1:1)	56

Reaction Conditions: a mixture of **1a** (0.05 M) and **4a** (2.5 mol%) in solvent was placed under irradiation with blue LED lamps (11 W) while stirring under air (1 atm, balloon) at 40 °C for 5 h. A solution of **2a** in MeOH (0.025 M) was then added into the reaction mixture, and the mixture was stirred under irradiation at 40 °C for 15 h. Yield was determined by GC using biphenyl as an internal standard.

5. ESI-MS Analysis of Reaction Mixture



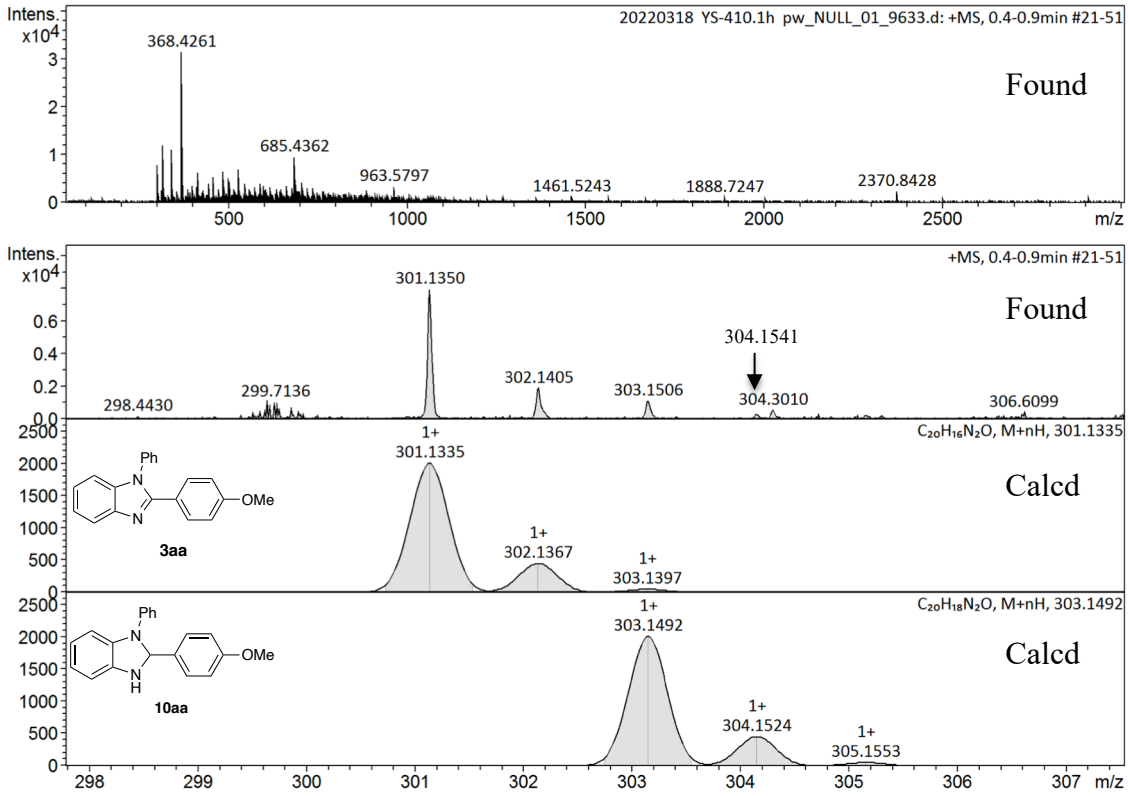
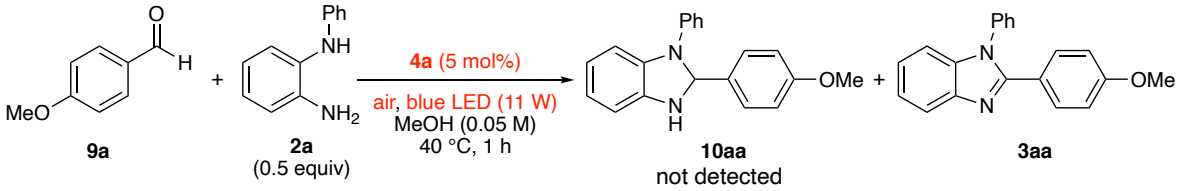


Figure S1. ESI-TOF mass spectra of the reaction mixture.



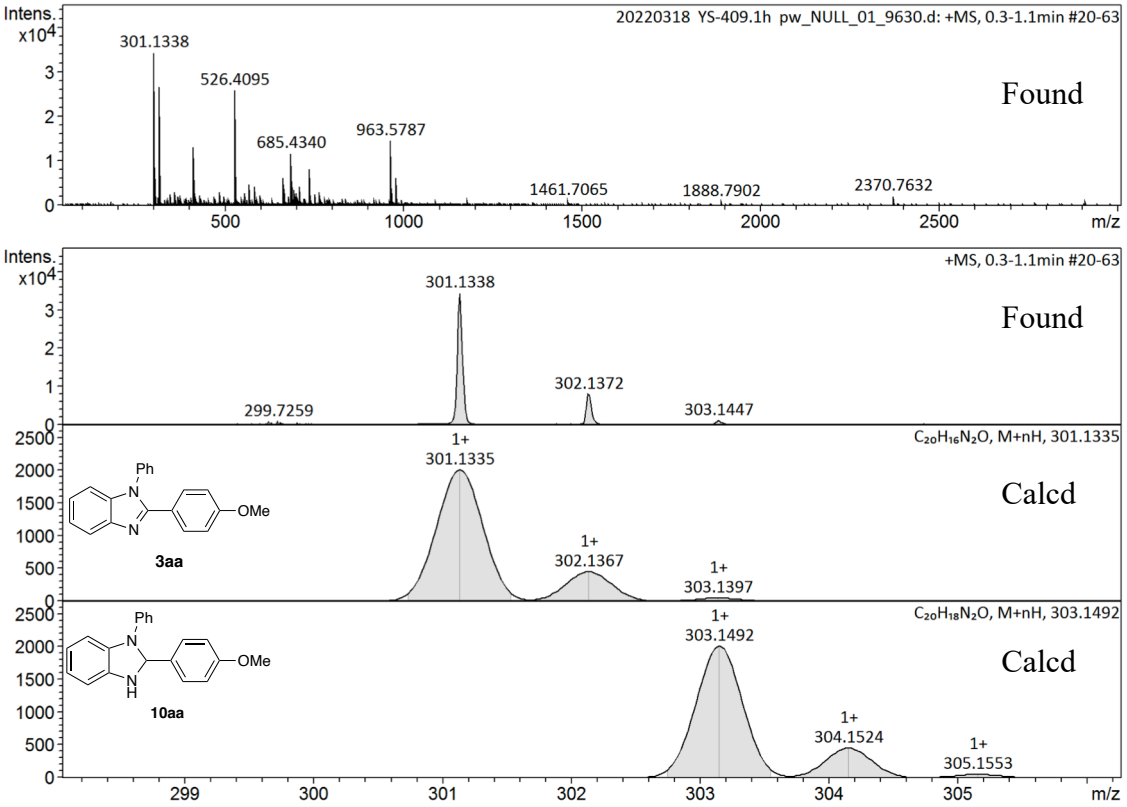
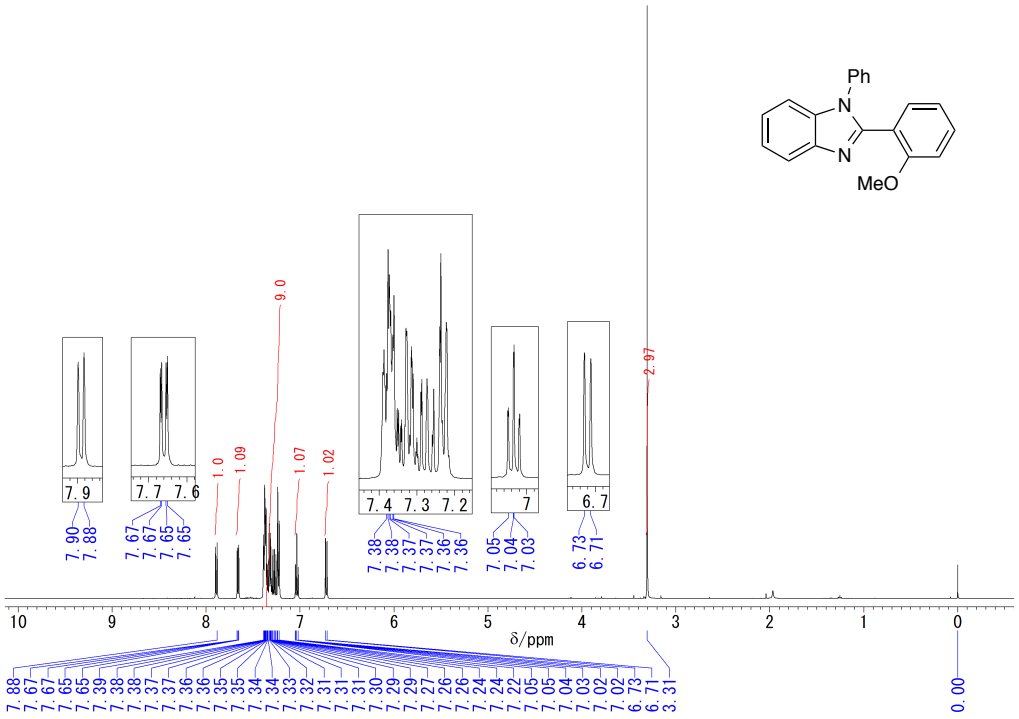
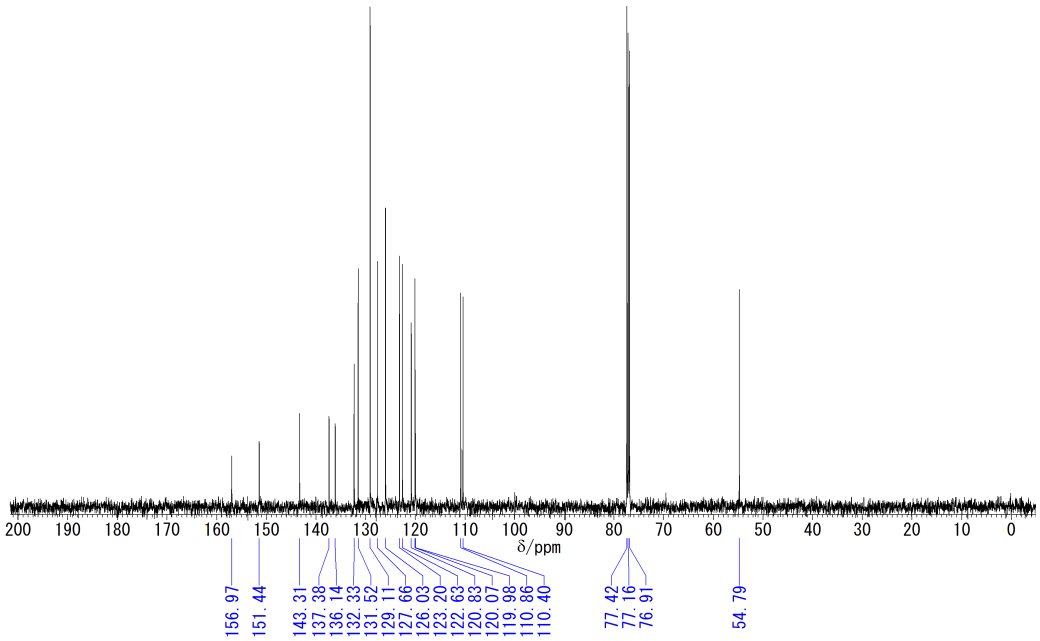


Figure S2. ESI-TOF mass spectra of the reaction mixture.

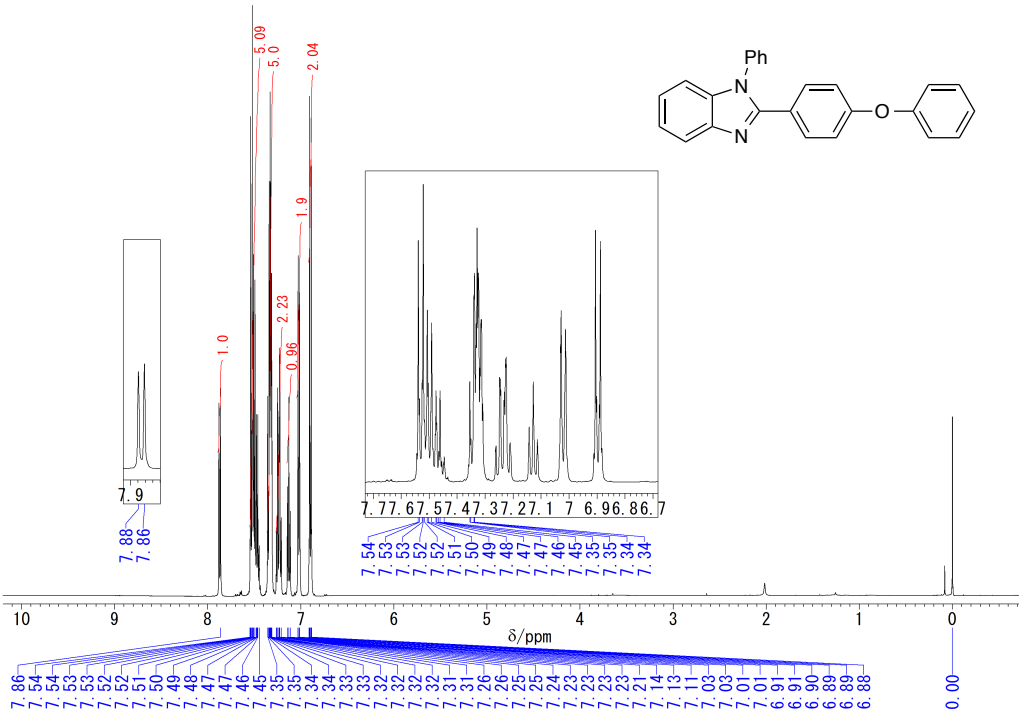
6. ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra of Novel Compounds



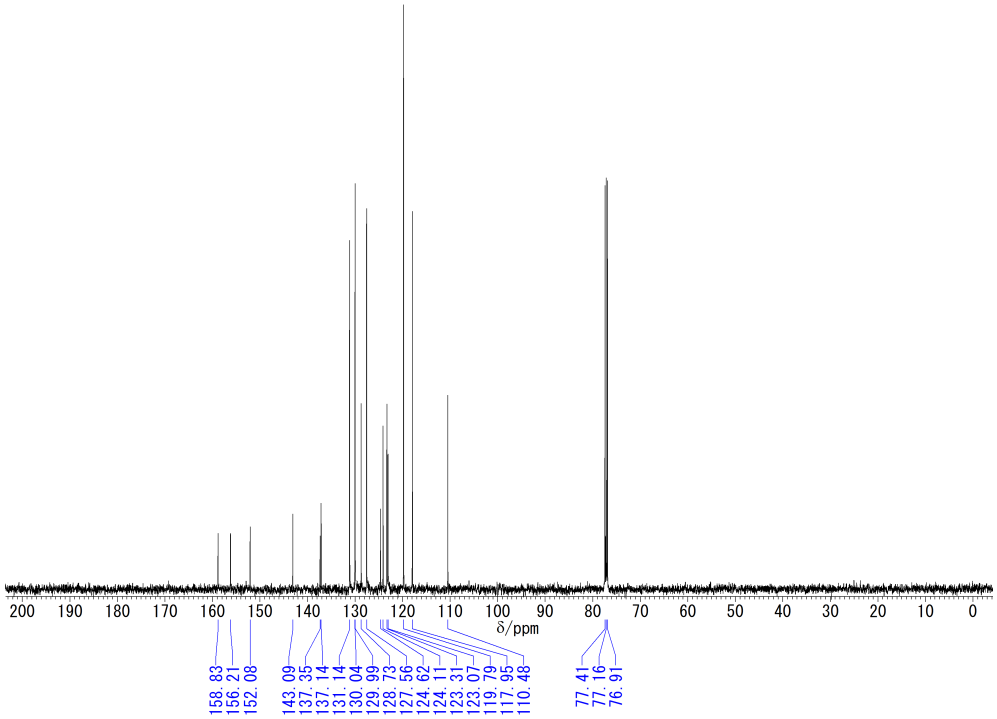
Spectrum S1. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ba**.



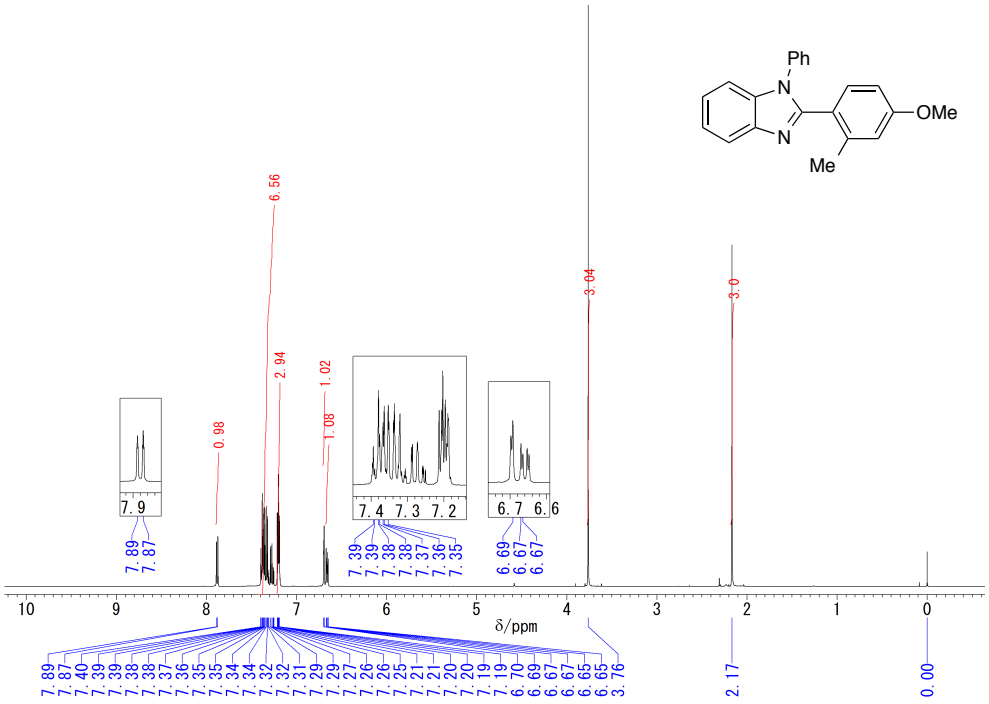
Spectrum S2. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **3ba**.



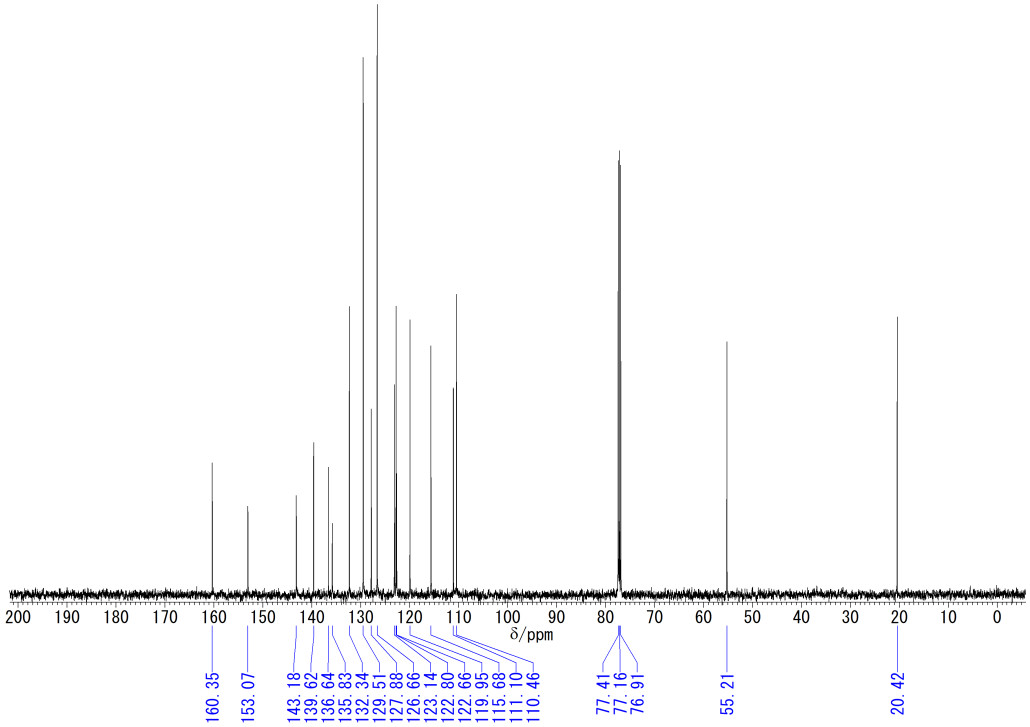
Spectrum S3. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ca**.



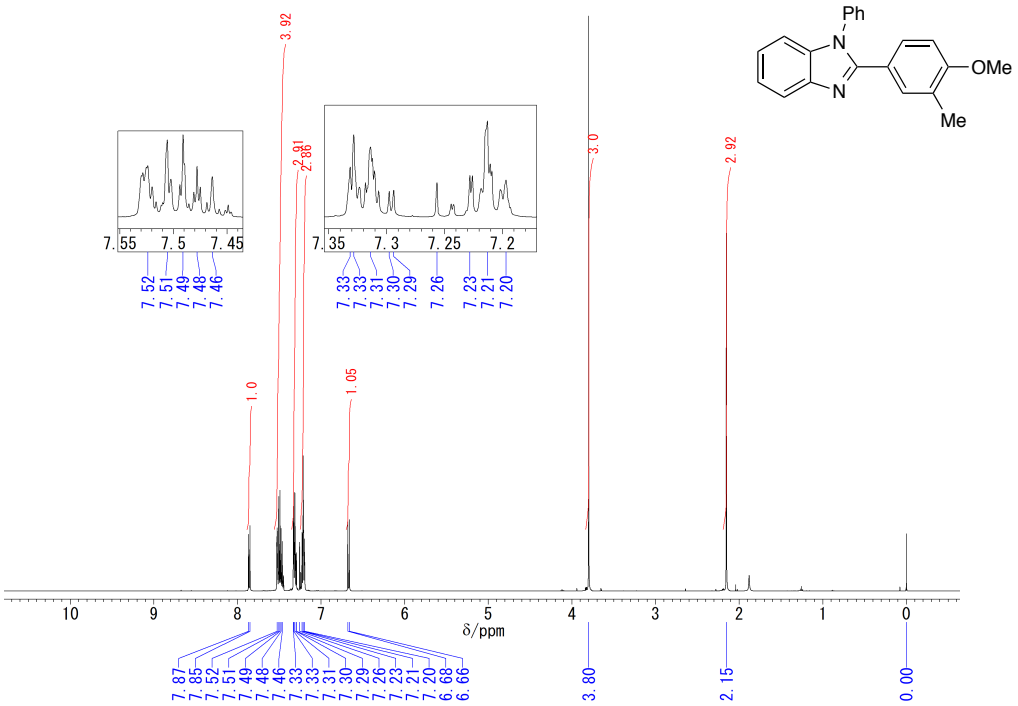
Spectrum S4. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **3ca**.



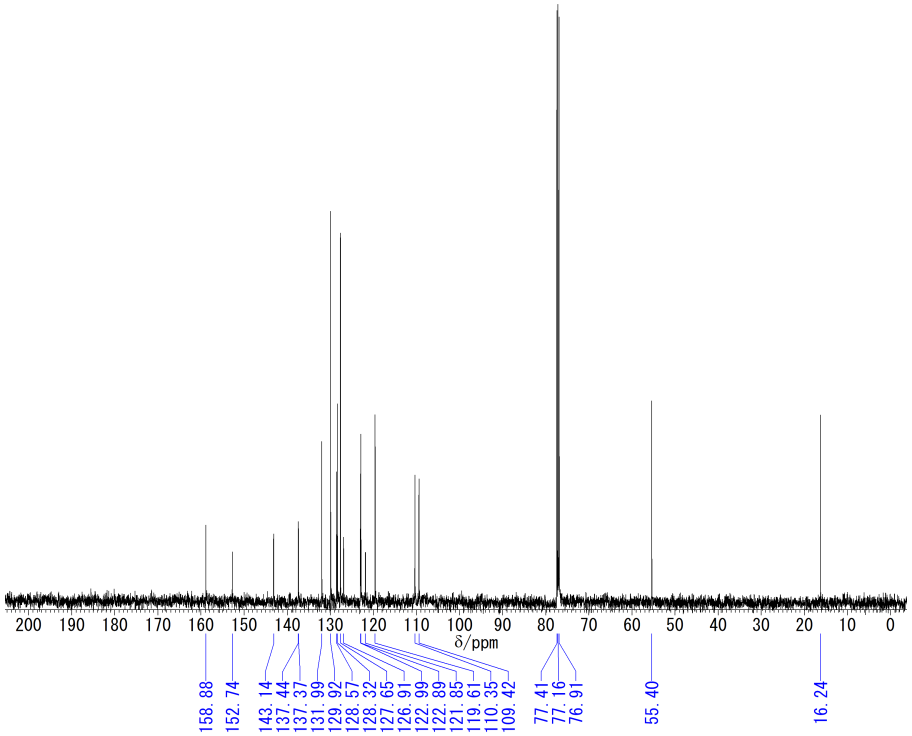
Spectrum S5. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ga**.



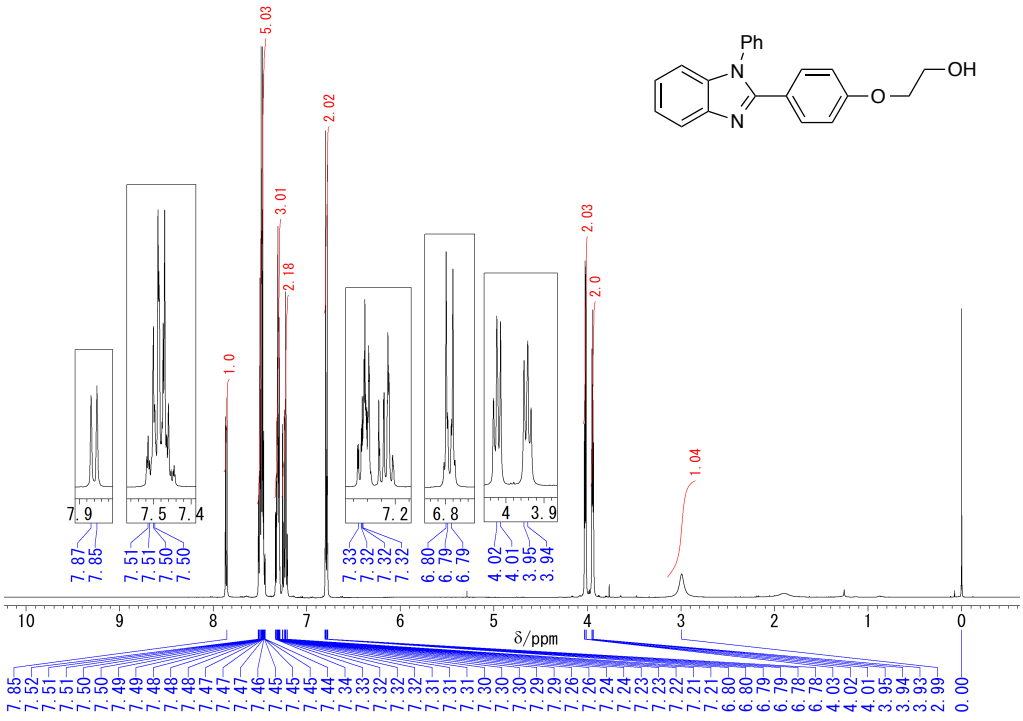
Spectrum S6. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **3ga**.



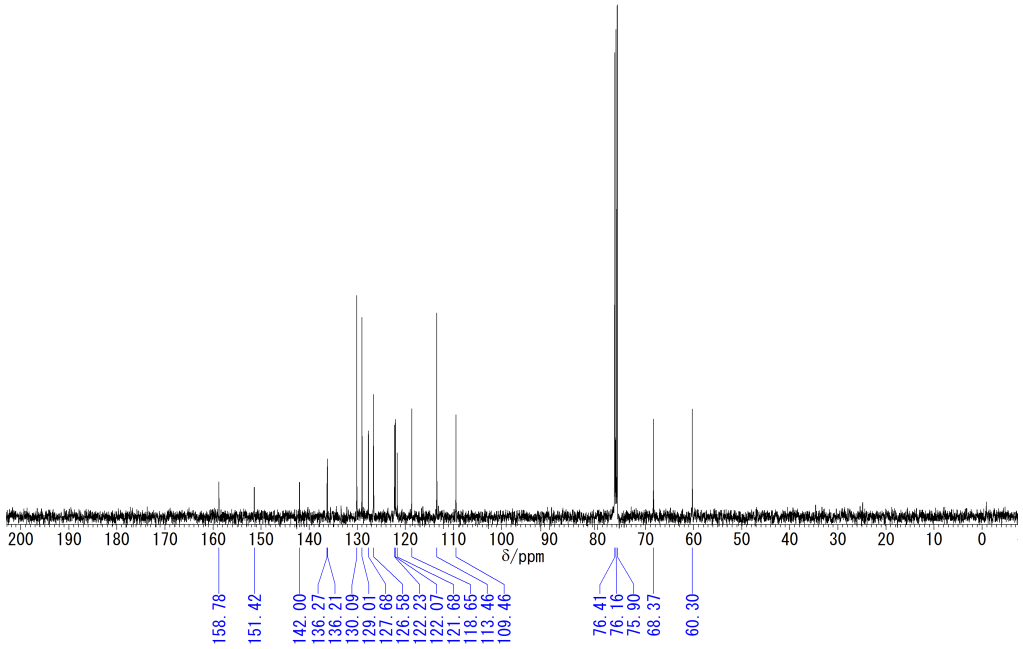
Spectrum S7. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ha**.



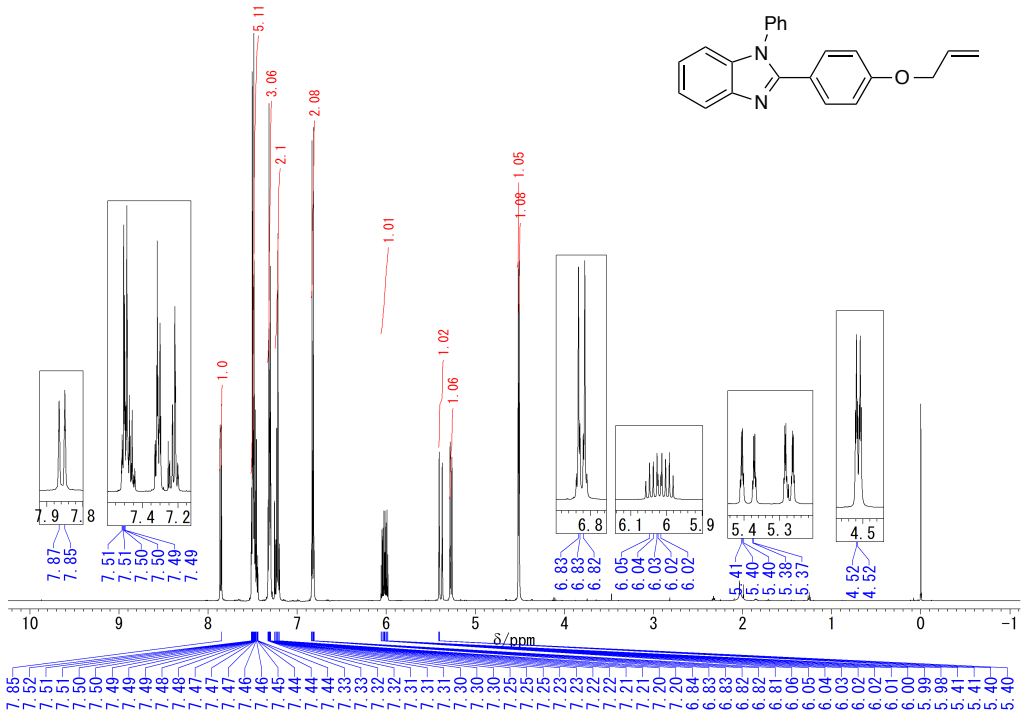
Spectrum S8. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **3ha**.



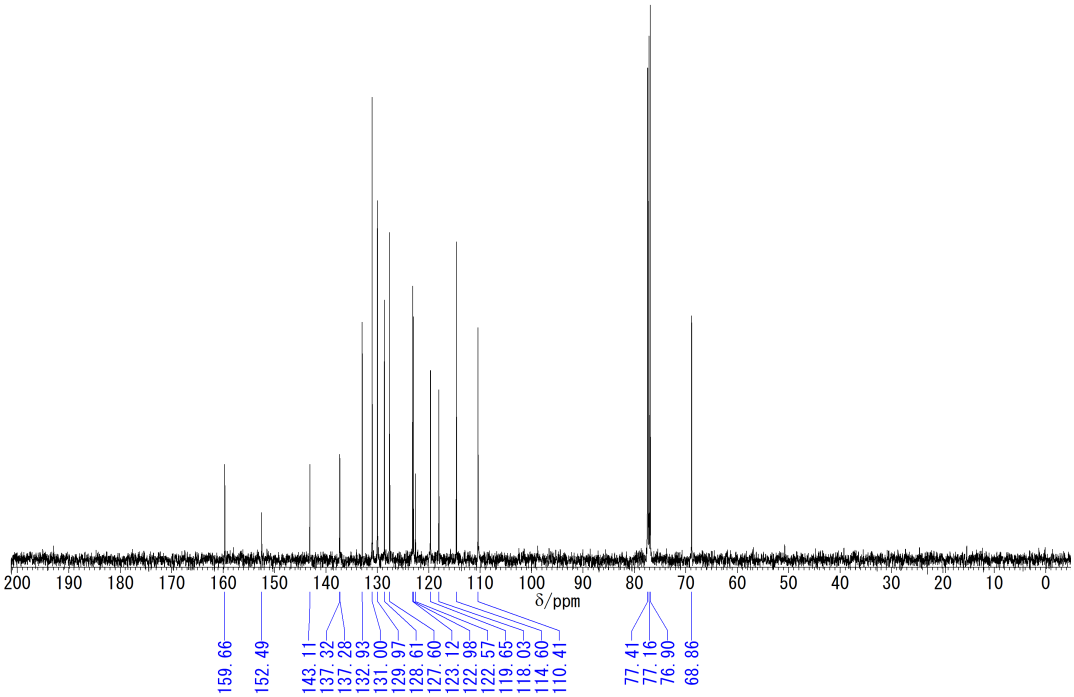
Spectrum S9. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ia**.



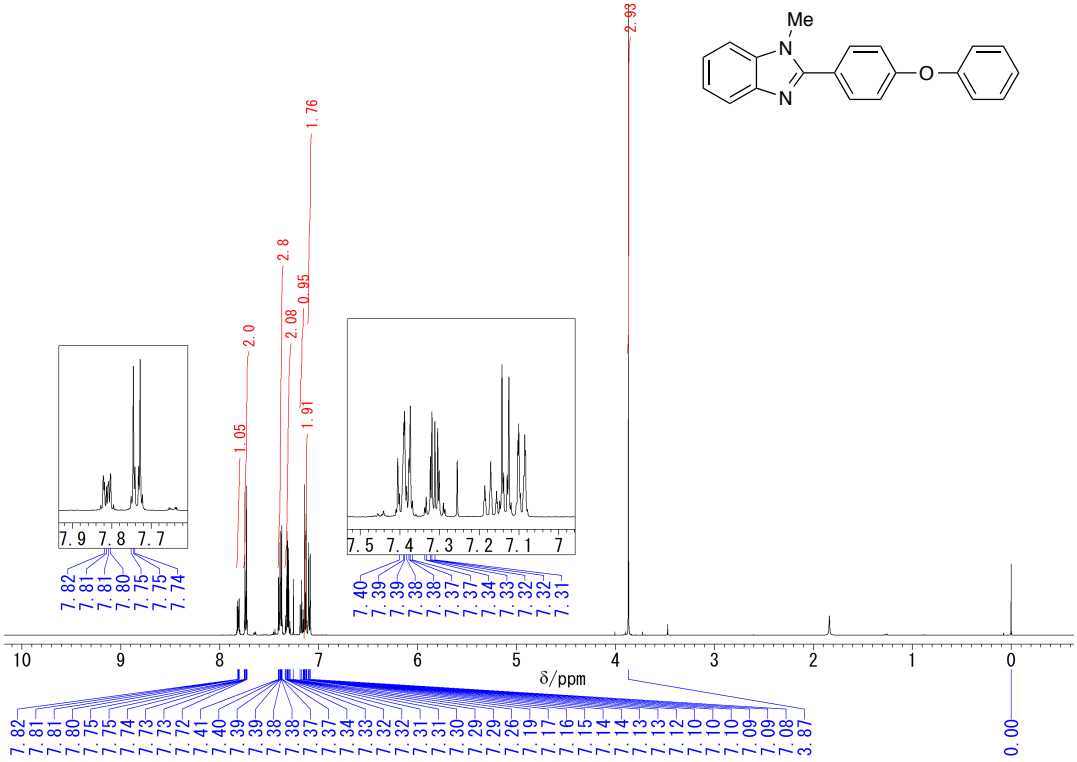
Spectrum S10. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **3ia**.



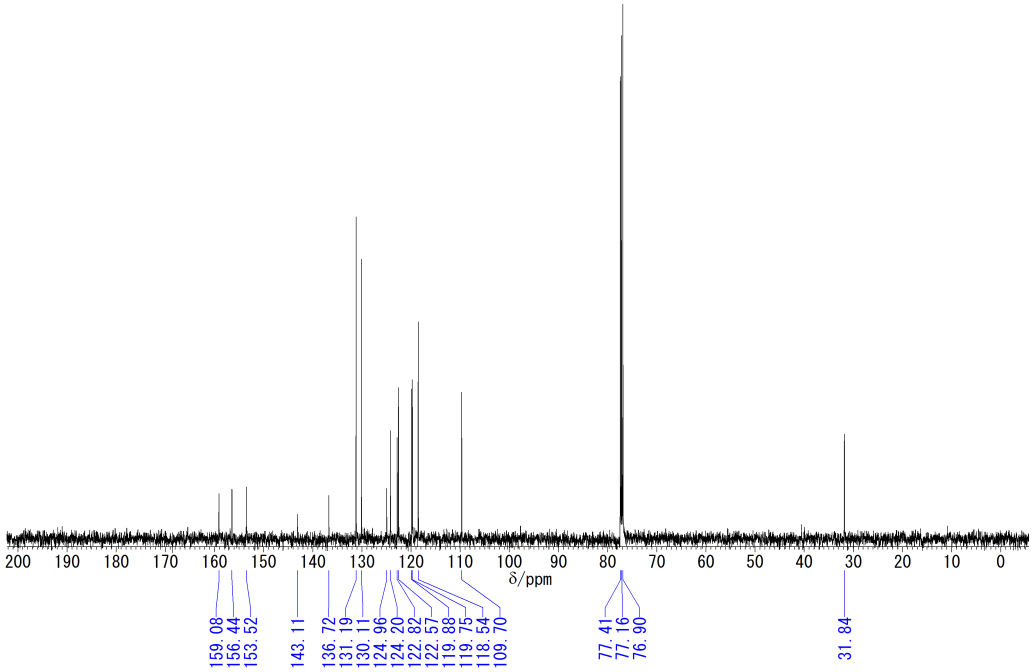
Spectrum S11. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ja**.



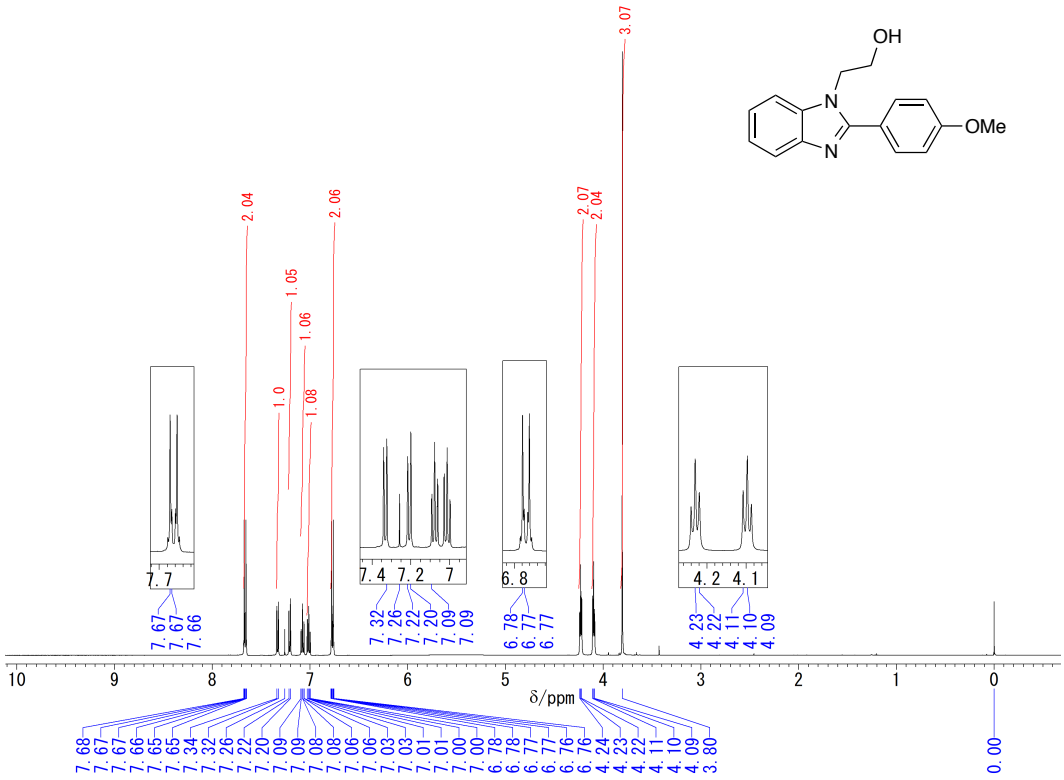
Spectrum S12. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **3ja**.



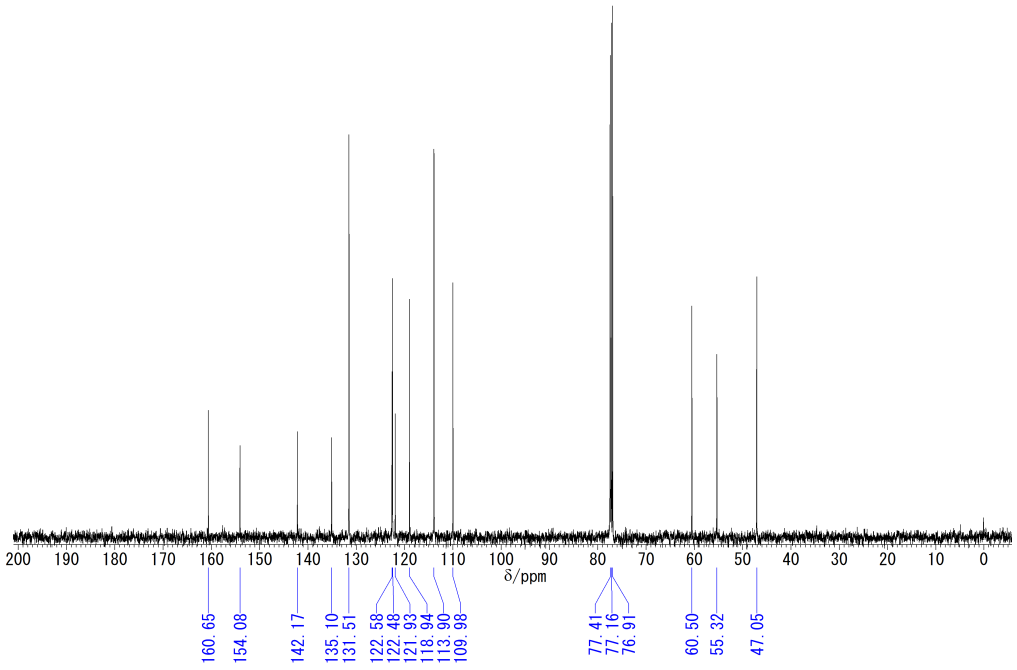
Spectrum S13. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3cb**.



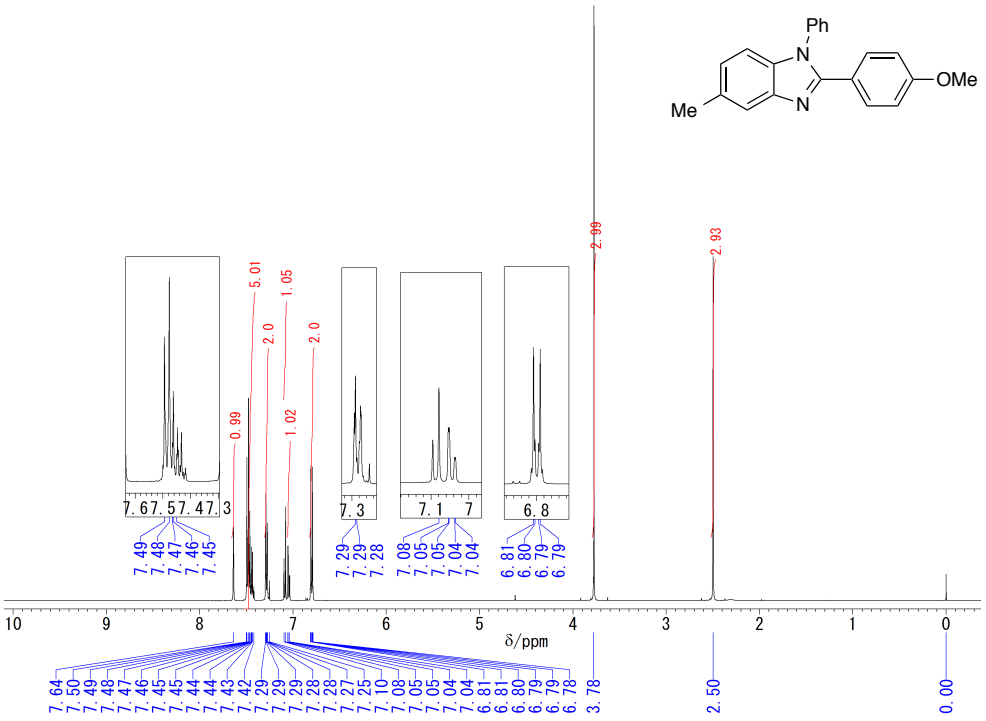
Spectrum S14. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **3cb**.



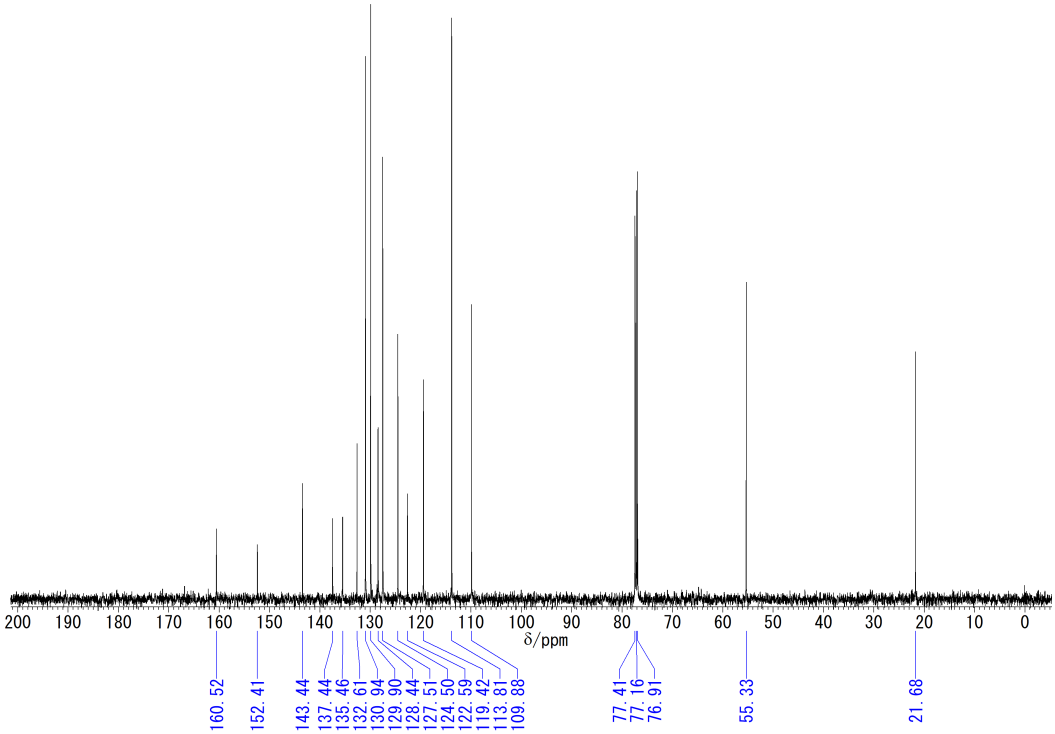
Spectrum S15. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ac**.



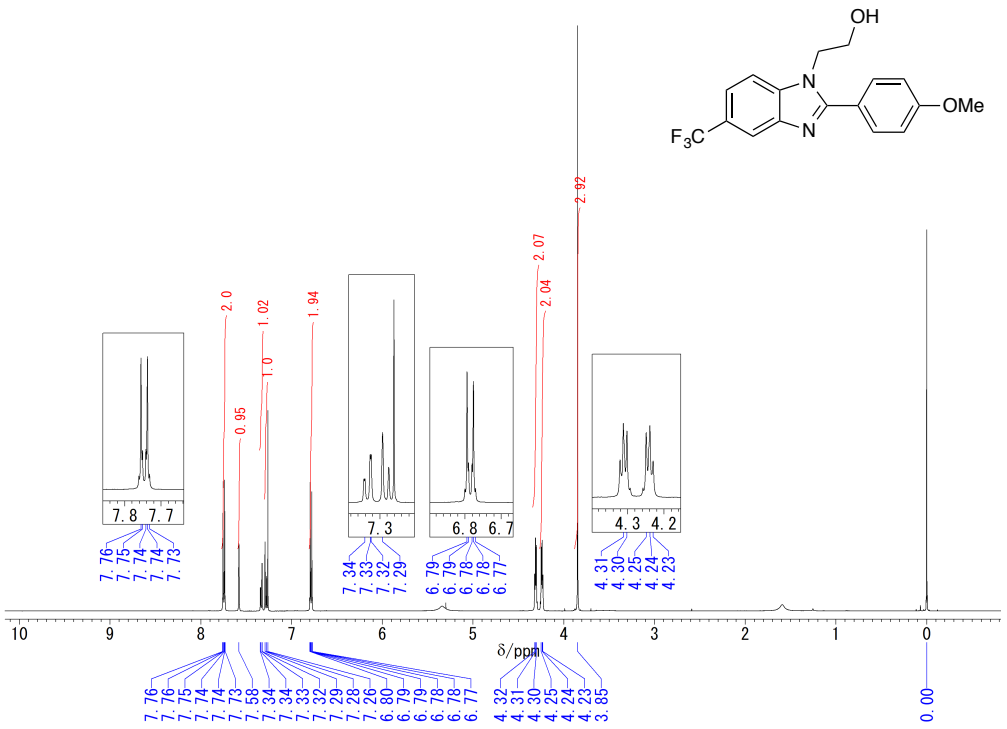
Spectrum S16. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **3ac**.



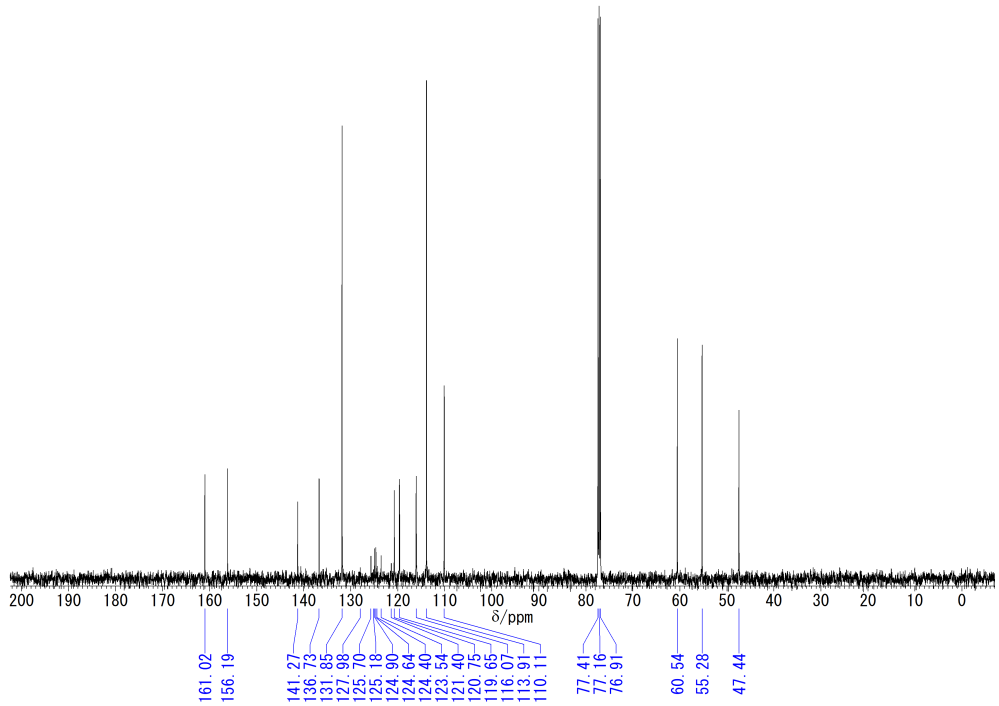
Spectrum S17. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3af**.



Spectrum S18. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **3af**.

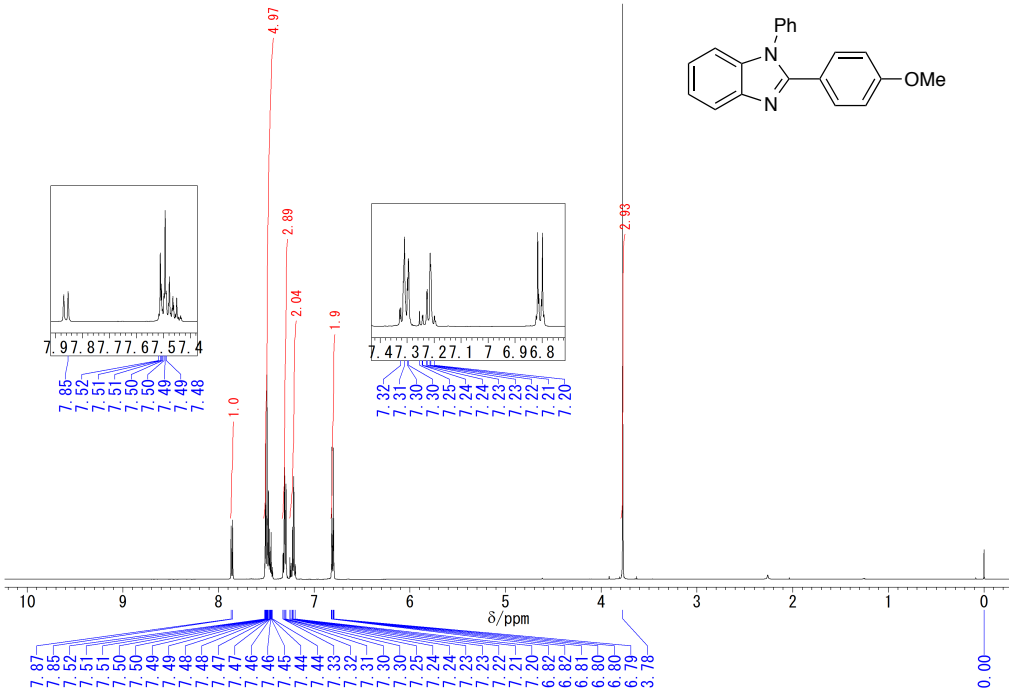


Spectrum S19. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ah.**

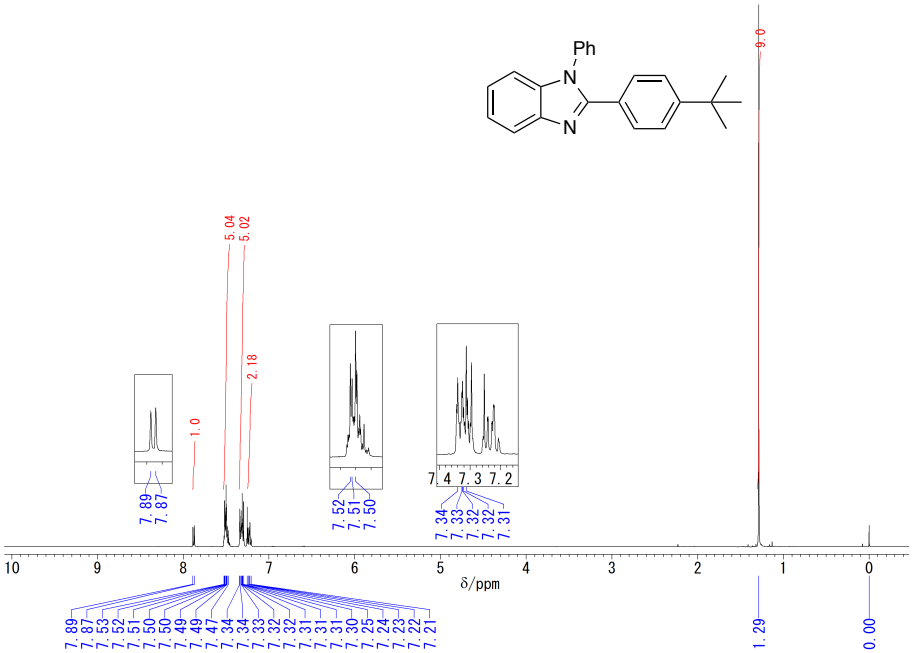


Spectrum S20. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **3ah**.

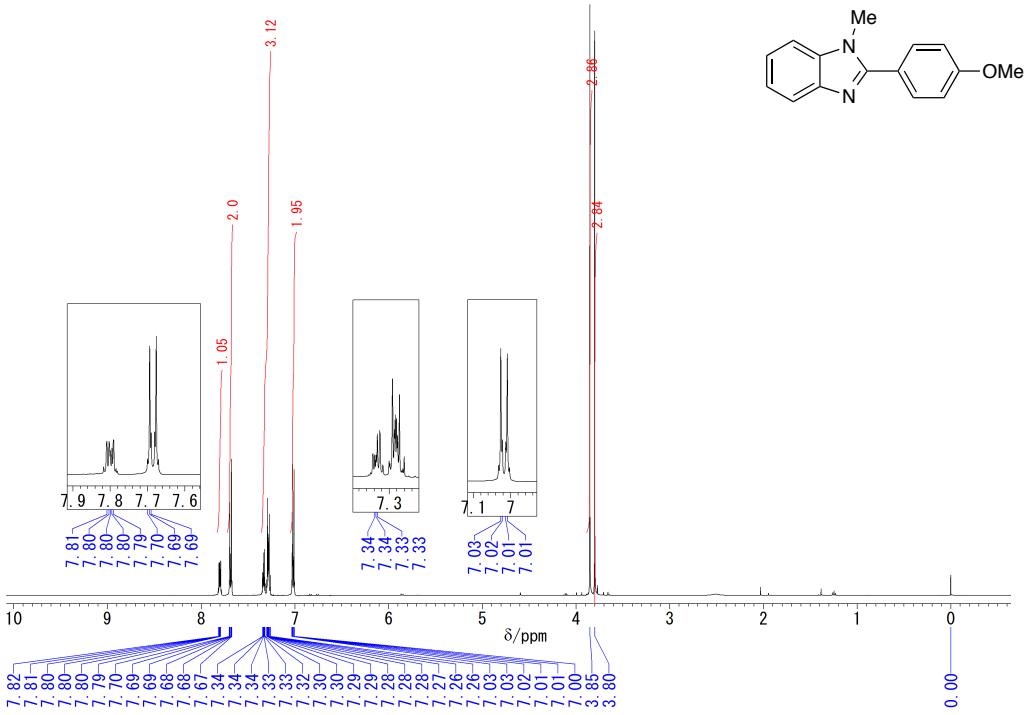
7. ^{1}H NMR Spectra of Known Compounds



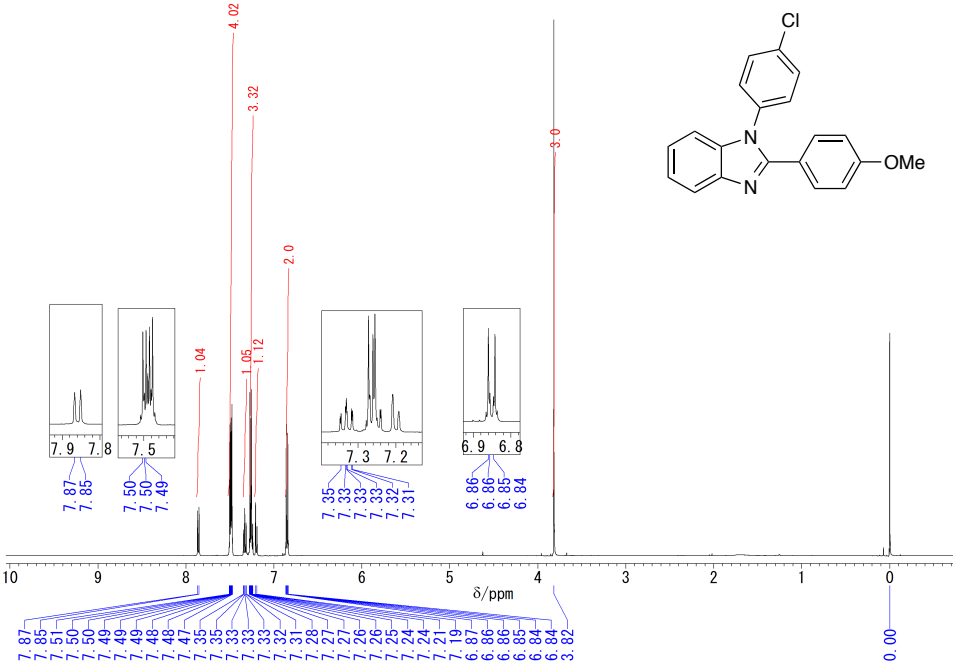
Spectrum S21. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3aa**.



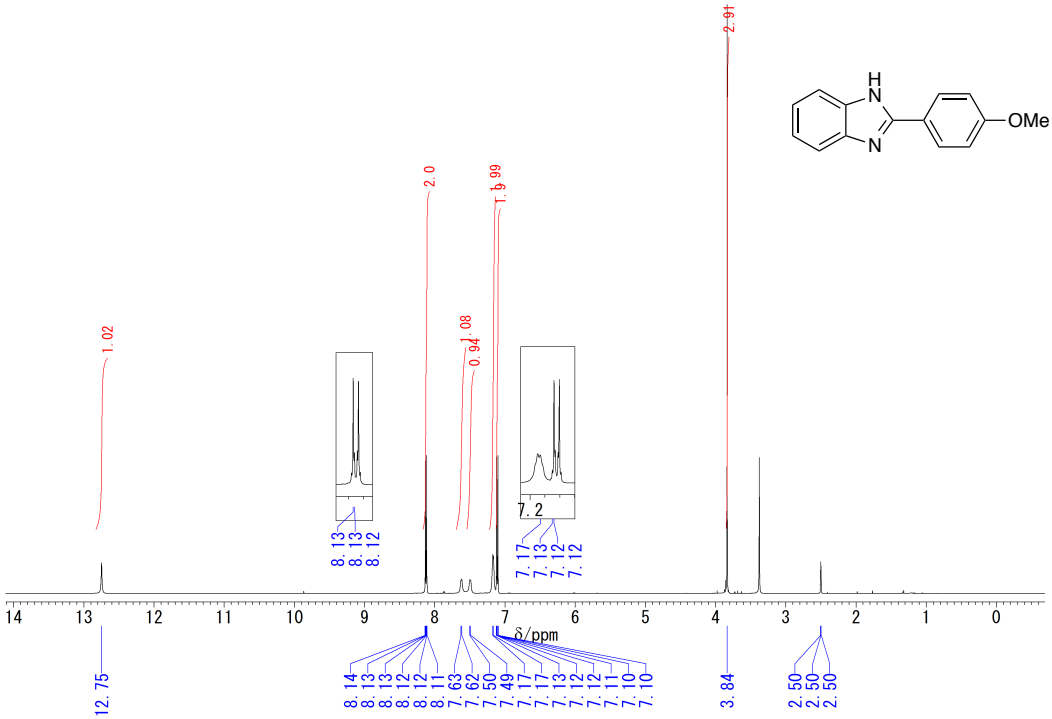
Spectrum S22. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3da**.



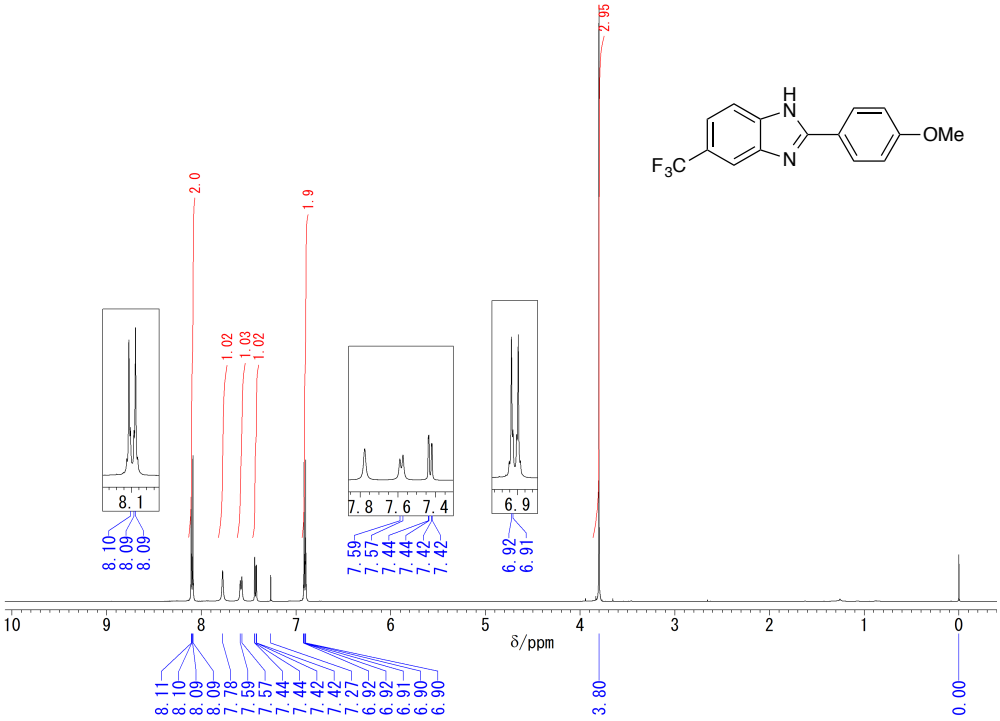
Spectrum S23. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ab**.



Spectrum S24. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ad**.



Spectrum S25. ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of compound **3ae**.



Spectrum S26. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ag**.

8. References

(S1) A. Takeda, H. Okai, K. Watabe and H. Iida, *J. Org. Chem.*, 2022, **87**, 10372-10376.

(S2) P. Ménová, H. Dvořáková, V. Eigner, J. Ludvík and R. Cibulka, *Adv. Synth. Catal.* 2013, **355**, 3451-3462.

(S3) T. Sakai, T. Kumoi, T. Ishikawa, T. Nitta and H. Iida, *Org, Biomol. Chem.*, 2018, **16**, 3999-4007.

(S4) S. Yang, C. Wu, M. Ruan, Y. Yang, Y. Zhao, J. Niu, W. Yang and J. Xu, *Tetrahedron Lett.*, 2012, **53**, 4288-4292.

(S5) a) S.-L. Qi, Y. Li, J.-F. Li, T. Zhang, Y.-X. Luan and M. Ye, *Org. Lett.*, 2021, **23**, 4034-4039. b) W.-S. Li, N. Zhang and L. M. Sayre, *Tetrahedron*, 2001, **57**, 4507-4522.

(S6) J. Jayabharathi, V. Thanikachalam and K. Jayamoorthy, *Photochem. Photobiol. Sci*, 2013, **12**, 1761-1773.

(S7) K. M. H. Nguyen and M. Largeron, *Chem. Eur. J*., 2015, **21**, 12606-12610.

(S8) X. Jin, Y. Liu, Q. Lu, D. Yang, J. Sun, S. Qin, J. Zhang, J. Shen, C. Chu and R. Liu, *Org. Biomol. Chem.,* 2013, **11**, 3776-3780.

(S9) P. Roy and A. Pramanik, *Tetrahedron Lett.*, 2013, **54**, 5243-5245.

(S10) O. Ravi, A. Shaikh, A. Upare, K. K. Singarapu and S. R. Bathela, *J. Org. Chem.*, 2017, **82**, 4422-4428.

(S11) B. M. Savall and J. R. Fontimayor, *Tetrahedron Lett.*, 2008, **49**, 6667-6669.