Supplementary Information

Aerobic Oxidative Synthesis of Benzimidazoles by Flavin Photocatalysis

Yuta Shiogai, Marina Oka, Hazuki Miyake, 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. The emission spectra were recorded on a JASCO FP-8300 fluorescence spectrometer (JASCO, Tokyo, Japan).

2. Materials

Riboflavin tetraacetate (**4**),[S1] 7-trifluoromethyl-1,3-dimethylalloxazine (**5**),[S2] 5-ethyl-10-(2-hydroxylethyl)-7,8-dimethylisoalloxazinium triflate (**6•TfO**),[S3] 7-trifluoromethyl-1,3-dimethylalloxazinium triflate (**7•TfO**)[S3] and 1,10-ethylene-3,7,8-trimethylisoalloxazinium triflate (**8•TfO**)[S3] were synthesized according to the previously reported methods. 2-((2-hydroxyethyl)amino)-5-(trifluoromethyl)-aniline (**2h**) was synthesized according to the previously reported method.[S4] 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 benzylamine (**1a**, 107 mg, 1.0 mmol), **4** (13.6 mg, 0.025 mmol), MeOH (10 mL) was stirred and irradiated (blue LED, 11 W, λ_{max} = 466 nm) under air at 40 °C for 2 h and then 2-aminodiphenylamine (**2a**, 92.1 mg, 0.50 mmol) was added into the reaction mixture. The mixture was stirred and irradiated (blue LED, 11 W, λ_{max} = 466 nm) under air at 40 °C for 30 h. In order to maintain a constant reaction temperature, the reaction was carried out in a water bath (Figure S1). After the solvent was removed by evaporation, the residue was purified by column chromatography (SiO_2, hexane/ethyl acetate = 3/1, v/v) to give **3aa** (120 mg, 89%) as a white solid. These results are summarized in Scheme 2, in which the yields were calculated based on *o*-phenylenediamines **2**.

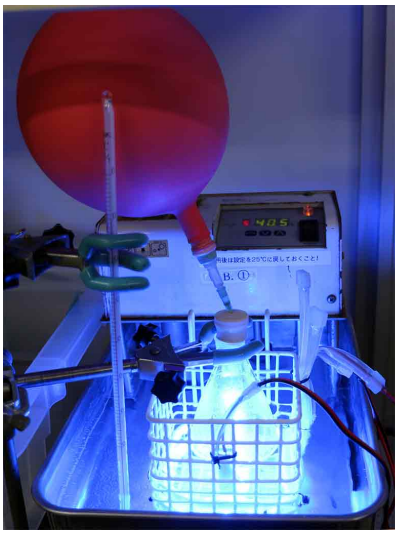
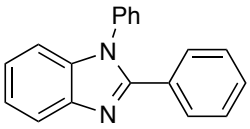
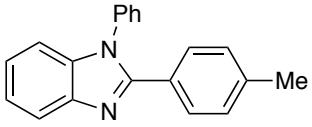


Figure S1. Reaction apparatus

Spectroscopic data of benzimidazoles

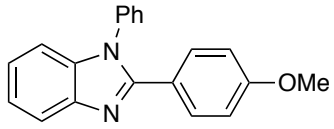


Spectroscopic data of 1,2-diphenyl-1*H*-benz[*d*]imidazole (**3aa**)[S5]: Columm chromatography (SiO_2, hexane/ethyl acetate=3/1, v/v) afforded the desired product (120 mg, 89%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.89 (d, J = 8.5 Hz, 1H), 7.58-7.55 (m, 2H), 7.50-7.40 (m, 3H), 7.35-7.23 (m, 8H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C, δ): 152.5, 143.1, 137.3, 137.1, 130.0, 129.9, 129.5, 128.6, 128.4, 127.5, 123.4, 123.1, 119.9, 110.5.

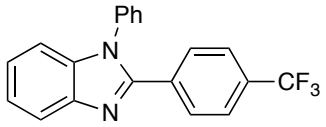


Spectroscopic data of 2-(4-methylphenyl)-1-phenyl-1*H*-benz[d]imidazole (**3ba**)[S6]: Columm chromatography (SiO_2, hexane/ethyl acetate=3/1, v/v) afforded the desired product (122 mg, 86%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.88 (d,

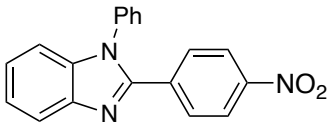
J = 8.1 Hz, 1H), 7.45-7.30 (m, 5H), 7.31-7.17 (m, 5H), 7.06 (d, *J* = 7.9 Hz, 2H), 2.29 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 25 °C, *δ*): 152.5, 143.0, 139.5, 137.2, 137.1, 129.8, 129.3, 129.0, 128.4, 127.4, 127.0, 123.1, 122.9, 119.7, 110.3, 21.3.



Spectroscopic data of 2-(4-methoxyphenyl)-1-phenyl-1*H*-benz[*d*]imidazole (**3ca**)[S6]: Columm chromatography (SiO_2, hexane/ethyl acetate=3/1, v/v) afforded the desired product (140 mg, 93%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, *δ*): 7.76 (d, *J* = 7.9 Hz, 1H), 7.41-7.33 (m, 5H), 7.21-7.17 (m, 3H), 7.13-7.08 (m, 2H), 6.70 (dt, J = 8.9, 2.5 Hz, 2H), 3.65 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 25 °C, *δ*): 160.5, 152.4, 143.1, 137.3, 137.2, 130.9, 129.9, 128.5, 127.5, 123.0, 122.9, 122.4, 119.6, 113.8, 110.3, 55.3.

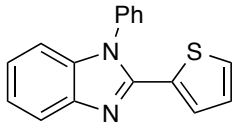


Spectroscopic data of 1-phenyl-2-(4-(trifluoromethyl)phenyl)-1*H*-benz[*d*]imidazole (**3da**)[S6]: Columm chromatography (SiO_2, hexane/ethyl acetate=3:1, v/v) afforded the desired product (104.4 mg, 62%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, *δ*): 7.90 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.57-7.47 (m, 5H), 7.38-7.24 (m, 5H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 25 °C, *δ*): 150.8, 143.1, 137.5, 136.8, 133.6, 131.3 (q, J = 32.8 Hz), 130.2, 129.8, 129.1, 127.5, 125.4, 124.1, 124.0 (q, J = 273.2 Hz), 123.5, 120.3, 110.8.

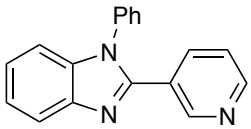


Spectroscopic data of 2-(4-nitrophenyl)-1-phenyl-1*H*-benz[*d*]imidazole (**3ea**):[S7] Column chromatography (SiO_2, hexane/ethyl acetate=10/1 to 3/1, v/v) afforded the desired product (50.0 mg, 32%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, *δ*): 8.14 (dt, J = 9.0, 2.2 Hz, 2H), 7.91 (d, J = 8.1 Hz, 1H), 7.75 (dt, J = 9.1, 2.2 Hz, 2H), 7.58-

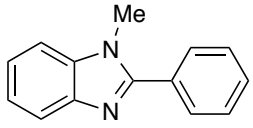
7.54 (m, 3H), 7.38 (td, J = 7.6, 1.2 Hz, 1H), 7.34-7.31 (m, 3H), 7.27 (d, J = 6.5 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 25 °C, δ): 149.8, 148.1, 143.0, 137.5, 136.5, 136.1, 130.4, 130.2, 129.4, 127.4, 124.5, 123.8, 123.6, 120.4, 110.9.



Spectroscopic data of 1-phenyl-2-(thiophen-2-yl)-1*H*-benz[*d*]imidazole (**3fa**)[S8]: Columm chromatography (SiO_2, hexane/ethyl acetate= 3:1, v/v) afforded the desired product (115.5 mg, 84%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.84 (d, J = 8.2 Hz, 1H), 7.56-7.53 (m, 3H), 7.39-7.35 (m, 2H), 7.30-7.26 (m, 2H), 7.19 (t, J = 7.7 Hz, 1H), 7.03 (d, J = 8.1 Hz, 1H), 6.86 (t, J = 4.4 Hz, 1H), 6.83 (d, J = 3.6 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 25 °C, δ): 147.3, 142.8, 137.7, 136.4, 132.6, 130.1, 129.6, 128.34, 128.27, 128.2, 127.5, 123.3, 123.0, 119.5, 110.1.

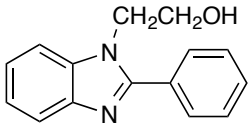


Spectroscopic data of 1-phenyl-2-(pyridine-3-yl)-1*H*-benz[*d*]imidazole (**3ga**)[S8]: Columm chromatography (SiO_2, hexane/ethyl acetate=1/5, v/v) afforded the desired product (70.3 mg, 72%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 8.78 (d, J = 1.6, 1H), 8.58 (dd, J = 4.9, 1.6 Hz, 1H), 7.94-7.89 (m, 2H), 7.54-7.48 (m, 3H), 7.38-7.24 (m, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 25 °C, δ): 150.3, 150.1, 149.6, 143.1, 137.4, 136.6, 136.5, 130.3, 129.2, 127.5, 126.4, 124.0, 123.4, 123.2, 120.1, 110.7.

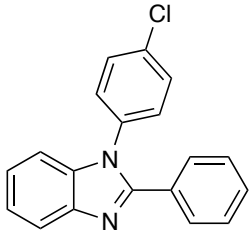


Spectroscopic data of 1-methyl-2-phenyl-1*H*-benz[*d*]imidazole (**3ab**)[S9]: Columm chromatography (SiO_2, hexane/ethyl acetate=2/1, v/v) afforded the desired product (85.4 mg, 86%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.83-7.81 (m, 1H), 7.73 (dd, J = 7.7, 1.7 Hz, 2H), 7.50-7.44 (m, 3H), 7.34-7.27 (m, 3H), 3.78 (s, 3H). $^{13}C\{^{1}H\}$

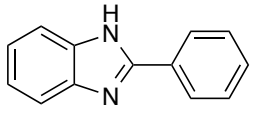
NMR (126 MHz, $CDCl_3$, 25 °C, δ): 153.7, 142.9, 136.6, 130.2, 129.7, 129.4, 128.7, 122.8, 122.4, 119.8, 109.7, 31.6.



Spectroscopic data of 1-(2-hydroxyethyl)-2-phenyl-1*H*-benz[*d*]imidazole (**3ac**): Columm chromatography (SiO_2, hexane/ethyl acetate= 2:1, v/v) afforded the desired product (99.6 mg, 84%) as a white solid. Mp: 141.2-143.2 °C. IR (KBr, cm^{-1}): 3162, 2844, 1656, 1346. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.78-7.76 (m, 2H), 7.67-7.66 (m, 1H), 7.46-7.40 (m, 4H), 7.27-7.20 (m, 3H), 4.37 (t, J = 5.5 Hz, 2H), 4.06 (t, J = 5.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C, δ): 154.2, 142.5, 135.4, 129.9, 129.8, 129.7, 128.6, 122.8, 122.7, 119.4, 110.3, 60.6, 47.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{14}N_2O$, 239.1179; found, 239.1176.

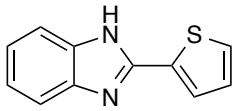


Spectroscopic data of 1-(4-chlorophenyl)-2-phenyl-1*H*-benz[*d*]imidazole (**3ad**)[S8]: Columm chromatography (SiO_2, hexane/ethyl acetate= 3:1, v/v) afforded the desired product (129 mg, 84%) as a white solid. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.88 (dt, J = 7.9, 0.9 Hz, 1H), 7.56-7.53 (m, 2H), 7.45 (dt, J = 8.7, 2.5 Hz, 2H), 7.37-7.29 (m, 4H), 7.28-7.19 (m, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C, δ): 152.4, 143.1, 137.0, 135.6, 134.5, 130.2, 129.7, 129.5, 128.7, 128.5, 123.6, 123.3, 120.1, 110.3.

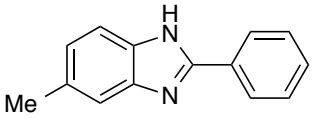


Spectroscopic data of 2-phenyl-1*H*-benz[*d*]imidazole (**3ae**)[S10]: Columm chromatography (SiO_2, hexane/ethyl acetate= 3:1, v/v) afforded the desired product (47.7 mg, 75%) as a white solid. ^1H NMR (500 MHz, DMSO-d_6, 25 °C, δ): 12.9 (br, s, 1H), 8.19 (dt, J = 8.1, 1.7 Hz, 2H), 7.64 (br, s, 1H), 7.57-7.53 (m, 2H), 7.49 (tt, J = 7.3, 1.6 Hz, 1H), 7.25-7.15

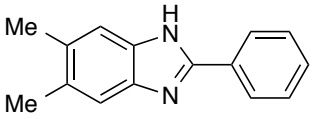
(m, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6, 25 °C, δ): 151.2, 143.8, 135.1, 130.2, 129.9, 129.0, 126.4, 122.5, 121.7, 118.9, 111.3.



Spectroscopic data of 2-(thiophen-2-yl)-1*H*-benzo[d]imidazole (**3ee**)[S10]: Columm chromatography (SiO_2, hexane/ethyl acetate=4/1 to 2/1, v/v) afforded the desired product (62.4 mg, 62%) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C, δ): 12.96 (br s, 1H), 7.84 (dd, J = 3.8, 1.1 Hz, 1H), 7.72 (dd, J = 5.0, 1.2 Hz, 1H), 7.60-7.50 (m, 2H), 7.23 (dd, J = 5.0, 3.8 Hz, 1H), 7.19 (td, J = 6.6, 3.7 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6, 25 °C, δ): 147.3, 143.8, 134.9, 133.9, 128.9, 128.5, 126.9, 122.8, 121.9, 118.7, 111.3.

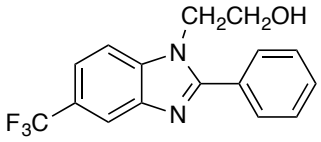


Spectroscopic data of 5-methyl-2-phenyl-1*H*-benzo[d]imidazole (**3af**)[S11]: Columm chromatography (SiO_2, hexane/ethyl acetate= 4:1 to 2/1, v/v) afforded the desired product (82.8 mg, 79%) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C, δ): 12.73 (br, s, 1H), 8.16 (d, J = 7.3 Hz, 2H), 7.54 (t, J = 7.5 Hz, 2H), 7.51-7.45 (m, 2H), 7.38 (s, 1H), 7.02 (d, J = 8.2 Hz, 1H), 2.43 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6, 25 °C, δ): 150.9, 131.3, 130.3, 129.7, 128.9, 126.3, 123.6, 21.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{12}N_2$, 209.1073; found, 209.1075.

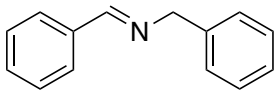


Spectroscopic data of 5,6-dimethyl-2-phenyl-1*H*-benzo[d]imidazole (**3ag**)[S10]: Columm chromatography (SiO_2, hexane/ethyl acetate=4/1 to 2/1, v/v) afforded the desired product (86.2 mg, 78%) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C, δ): 12.66 (br, s, 1H), 8.15 (d, J = 7.2 Hz, 2H), 7.52 (d, J = 7.5 Hz, 2H), 7.45 (tt, J = 7.4, 1.5 Hz, 1H), 7.37

(br, s, 2H), 2.32 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6, 25 °C, δ): 150.4, 142.5, 133.3, 130.5, 129.4, 128.9, 128.4, 128.0, 126.2, 118.9, 111.4, 20.0.



Spectroscopic data of 1-(2-hydroxyethyl)-2-phenyl-5-trifluoromethyl-1*H*-benzo[d]imidazole (**3ah**): Columm chromatography (SiO_2, hexane/ethyl acetate=2/1, v/v) afforded the desired product (82.4 mg, 54%) as an orange solid. Mp: 160.8-162.6 °C. IR (KBr, cm^{-1}): 3227, 2955, 2838, 1627, 1328. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 7.75 (dd, J = 8.3, 1.2 Hz, 2H), 7.67 (s, 1H), 7.42-7.32 (m, 3H), 7.29 (t, J = 7.7 Hz, 2H), 4.88 (br s, 1H), 4.33 (t, J = 5.0 Hz, 2H), 4.19 (t, J = 5.0 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 25 °C, δ): 156.2, 141.6, 137.0, 130.1, 130.0, 128.7, 128.6, 124.9 (q, J = 32.6 Hz), 124.6 (q, J = 272.3Hz), 119.8, 116.8, 110.4, 60.7, 47.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{14}F_3N_2O$, 307.1053; found, 307.1050.

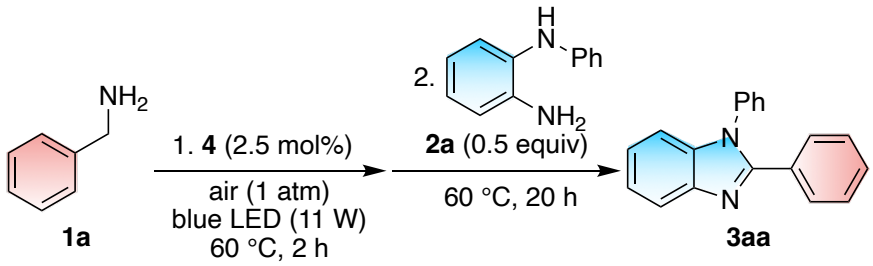


Spectroscopic data of *N*-benzylidenebenzylamine (**9a'**):[S12] ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ): 8.40 (s, 1H), 7.79-7.77 (m, 2H), 7.43-7.40 (m, 3H), 7.34 (d, J = 4.6 Hz, 4H), 7.28-7.24 (m, 1H), 4.83 (d, J = 1.4 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 25 °C, δ): 162.1, 139.4, 136.3, 130.9, 128.7, 128.6, 128.4, 128.1, 127.1, 65.2.

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	yield (%)
1	THF	72
2	CH_3CN	75
3	DMF	84
4	EtOH	80
5	tBuOH	90
6	MeOH	98

Reaction Conditions: a mixture of **1a** (0.1 M) and **4** (2.5 mol%) in solvent was placed under irradiation with blue LED lamps (11 W) while stirring under air (1 atm, balloon) at 60 °C for 2 h. **2a** (0.5 equiv) was then added into the reaction mixture, and the mixture was stirred under irradiation at 60 °C for 20 h. Yield was determined by GC using biphenyl as an internal standard, and calculated based on **2a**.

5. Quenching Experiment

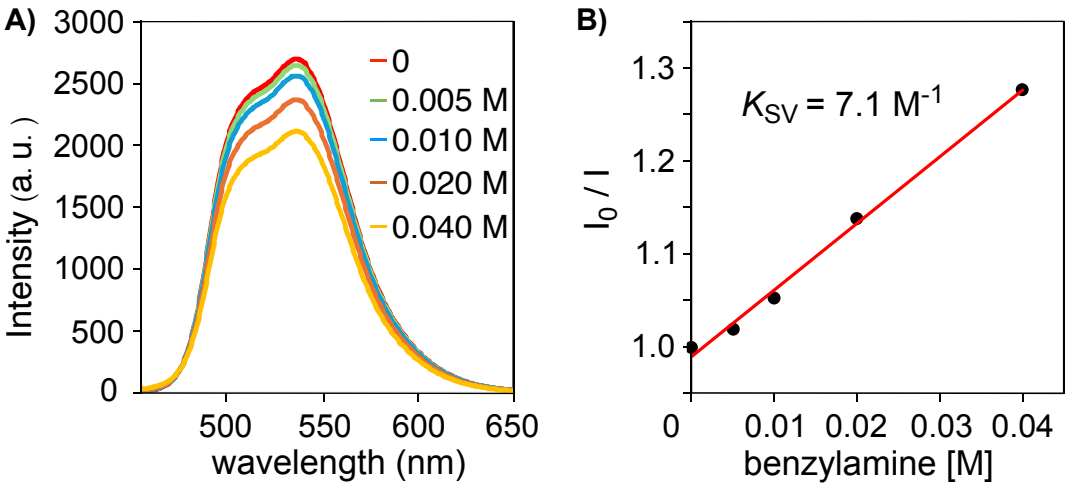
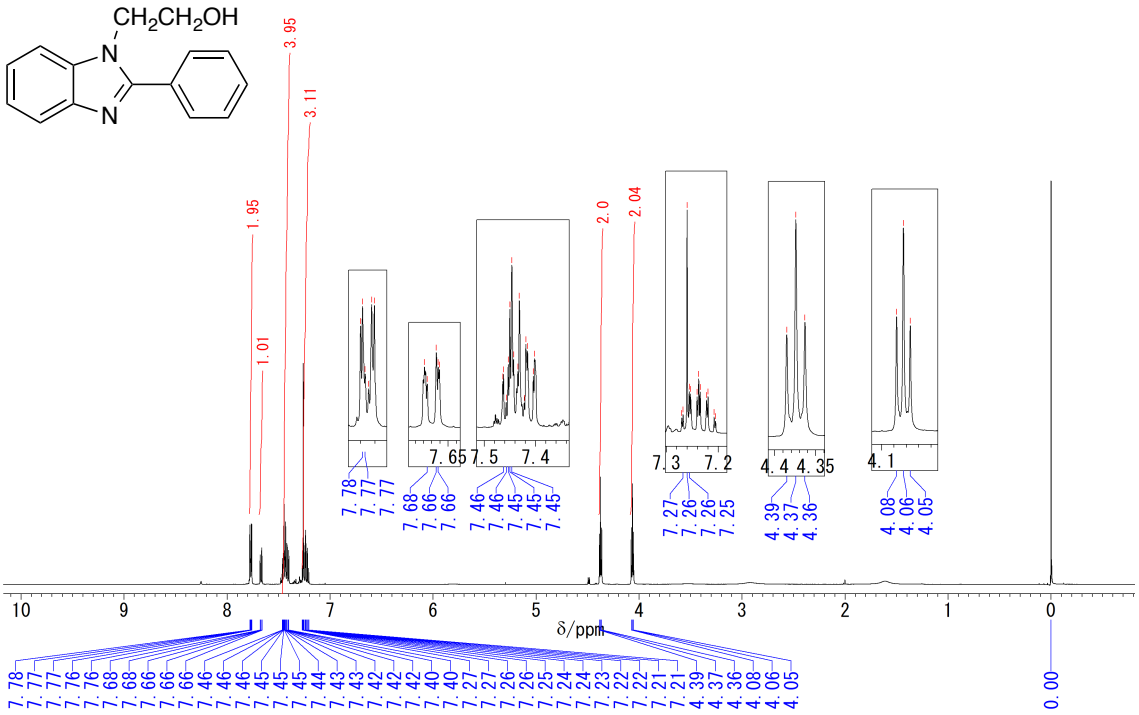
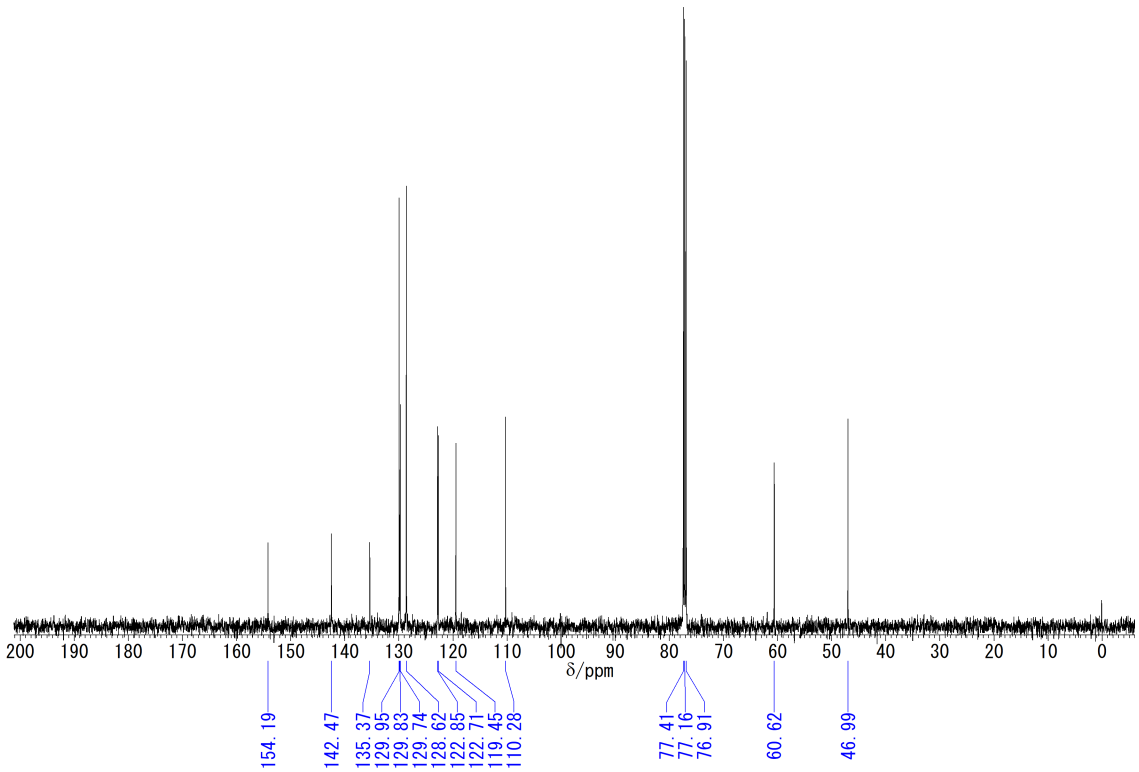


Figure S2. (A) Fluorescence quenching of **4** (1×10^{-6} M) by benzylamine in methanol. (B) Stern-Volmer plot of fluorescence quenching of **4** with benzylamine (**1a**) in methanol.

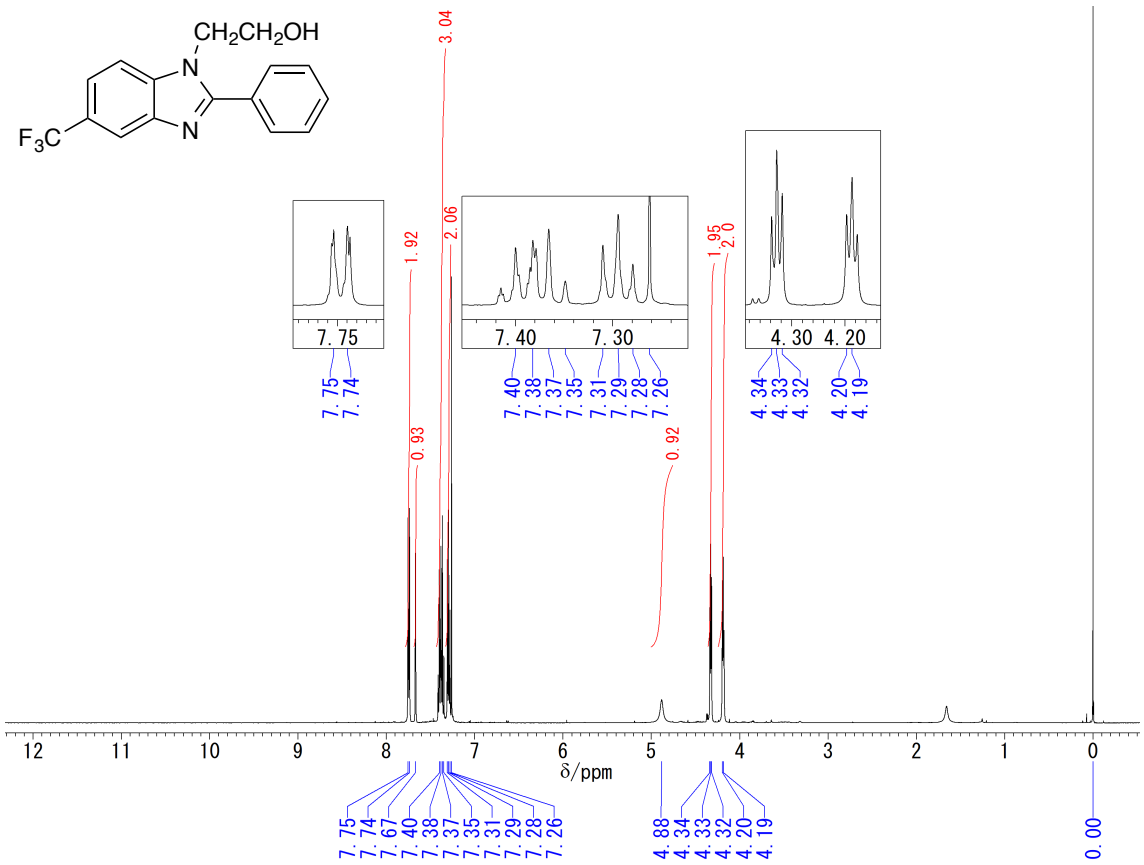
6. ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra of Novel Compounds



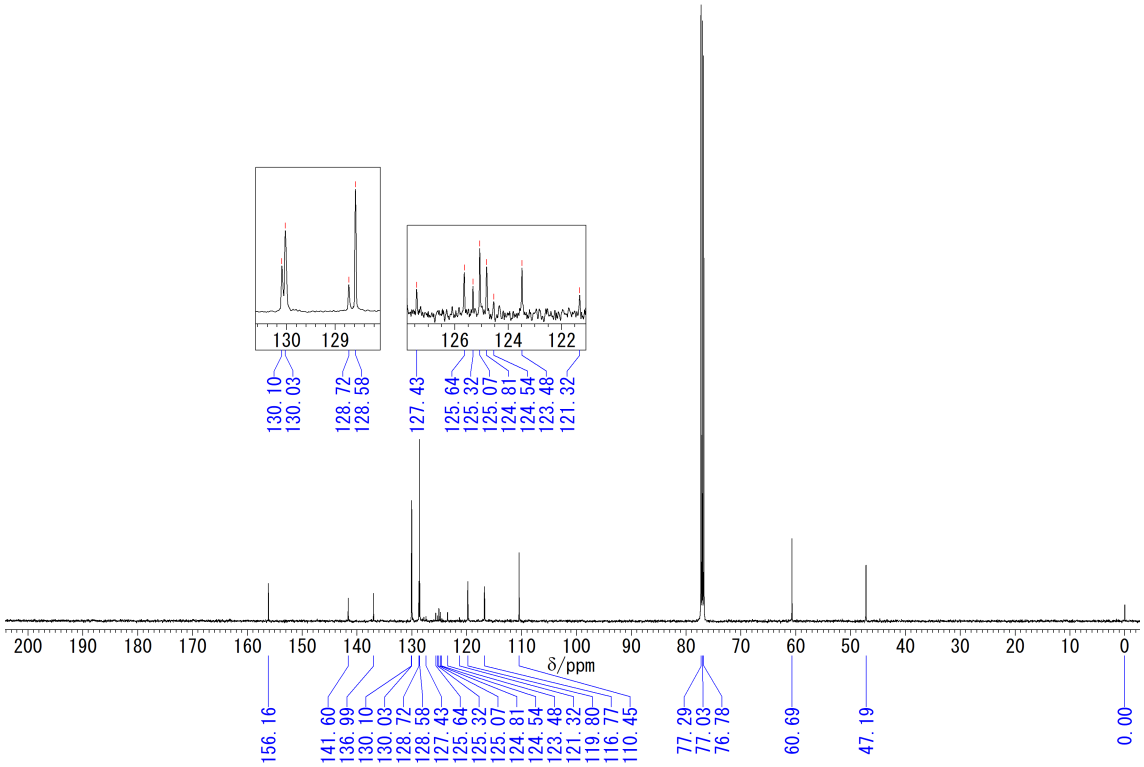
Spectrum S1. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ac**.



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

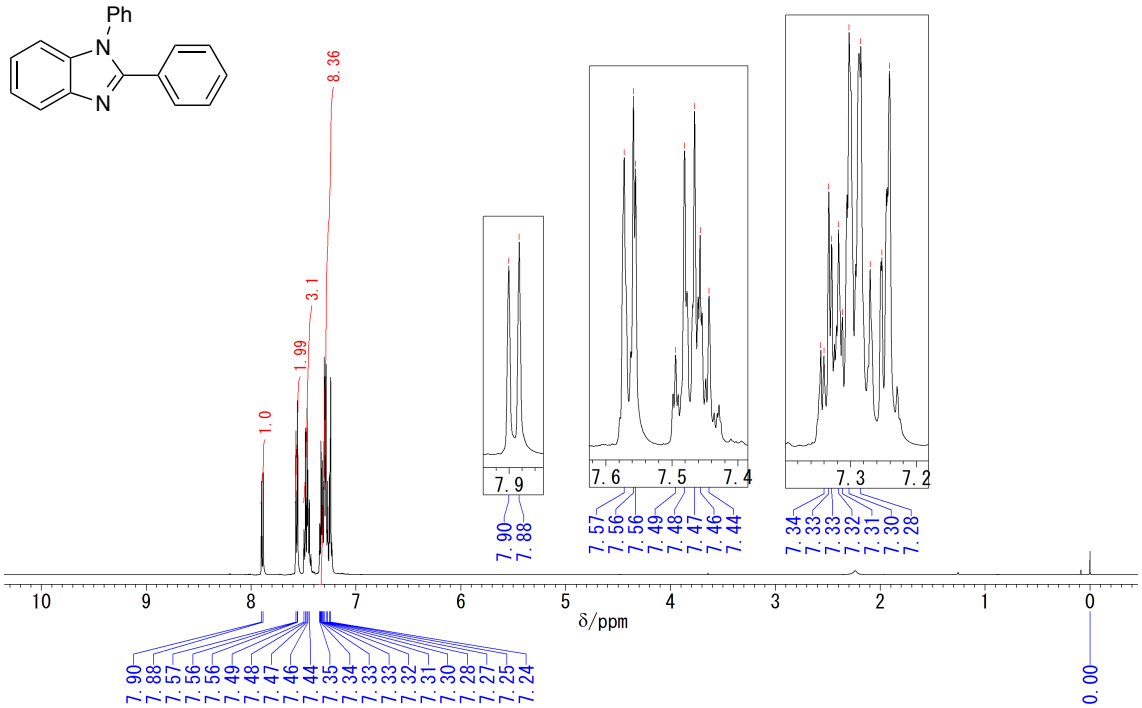


Spectrum S3. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ah**.

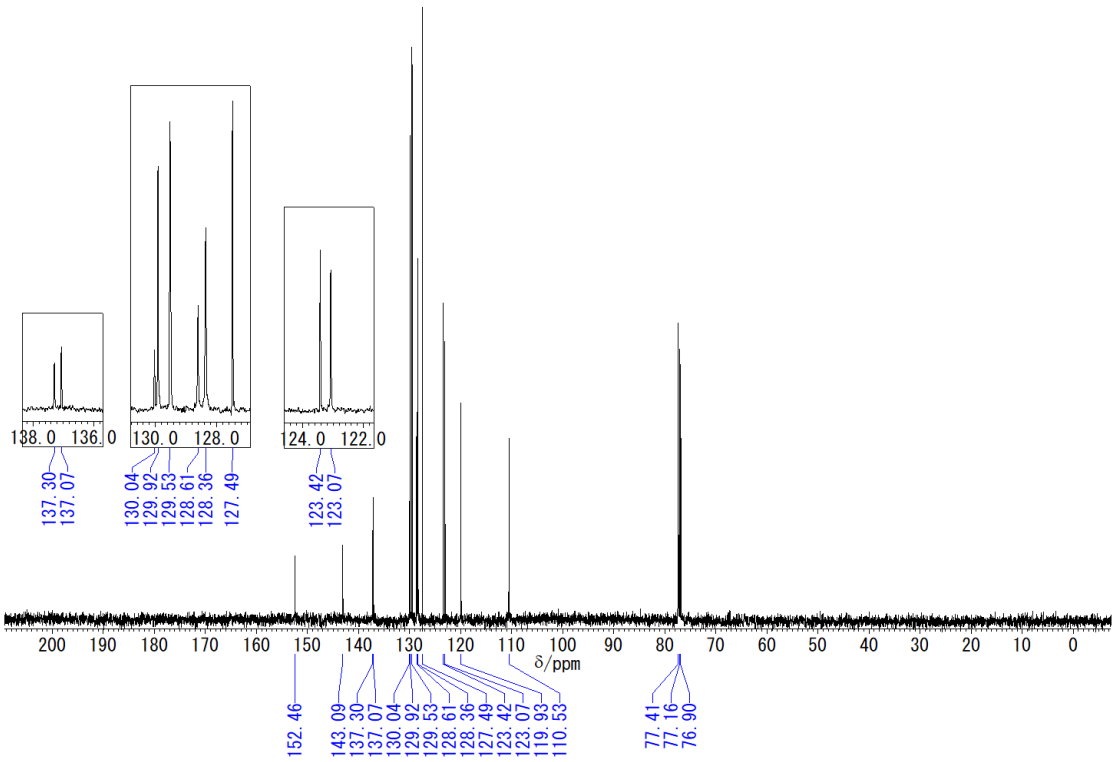


Spectrum S4. ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) spectrum of compound **3ah**.

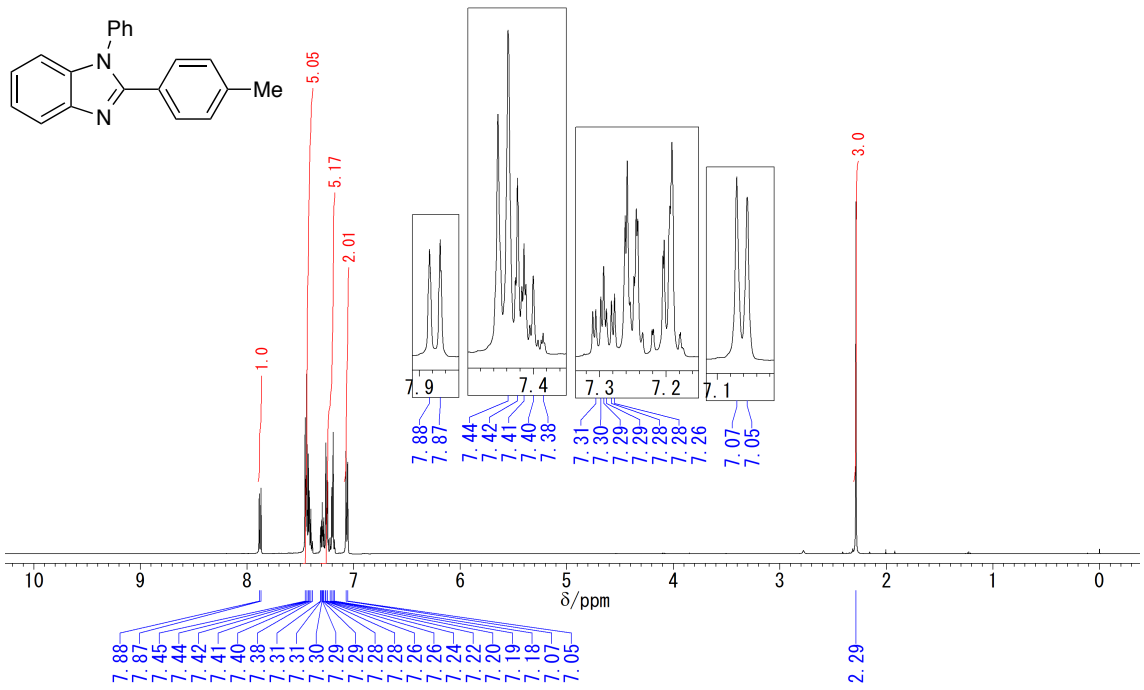
7. ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra of Known Compounds



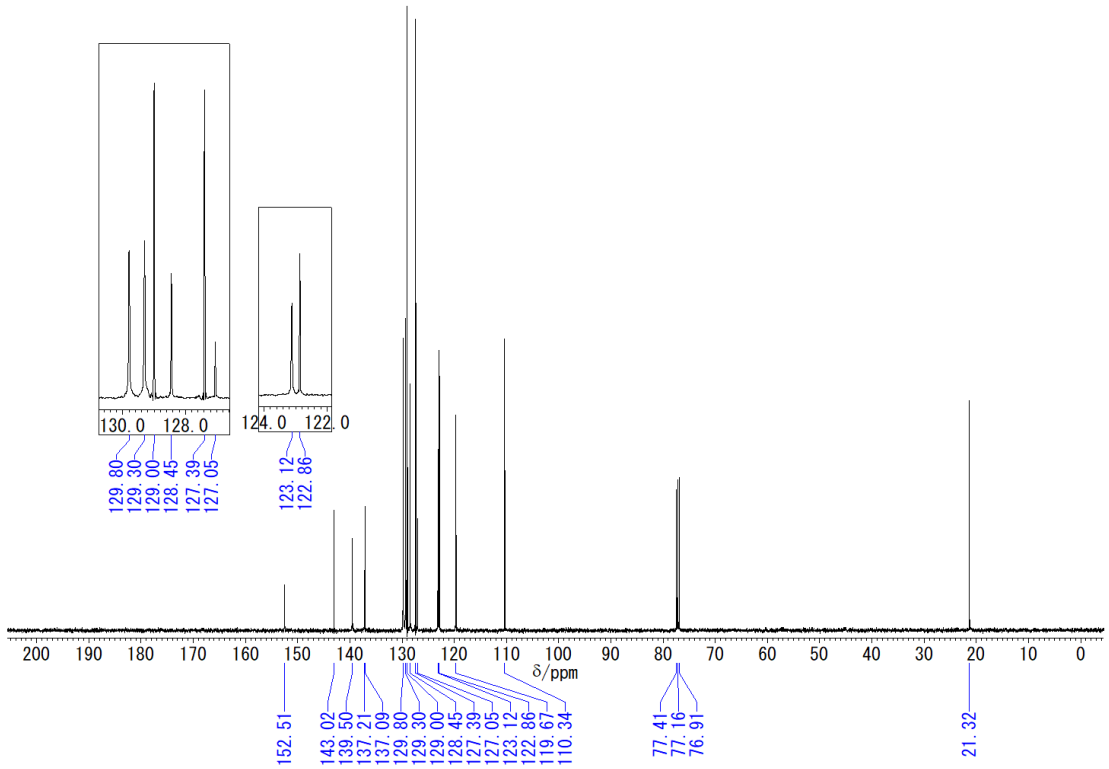
Spectrum S5. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3aa**.



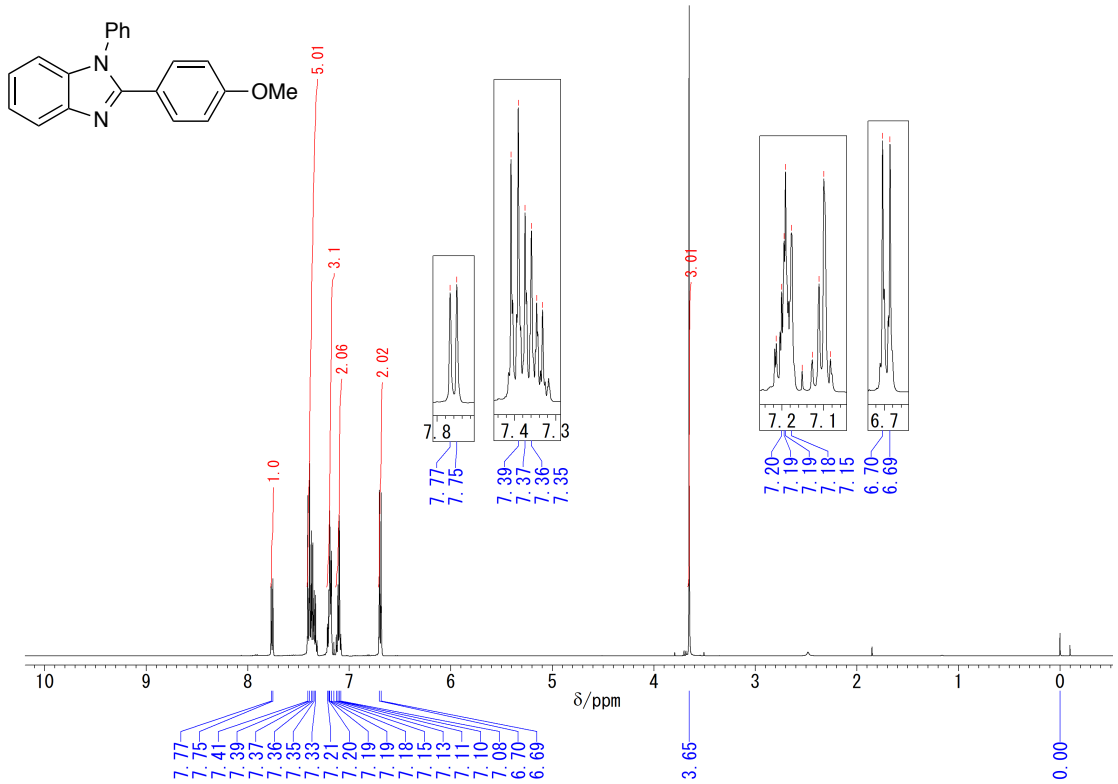
Spectrum S6. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **3aa**.



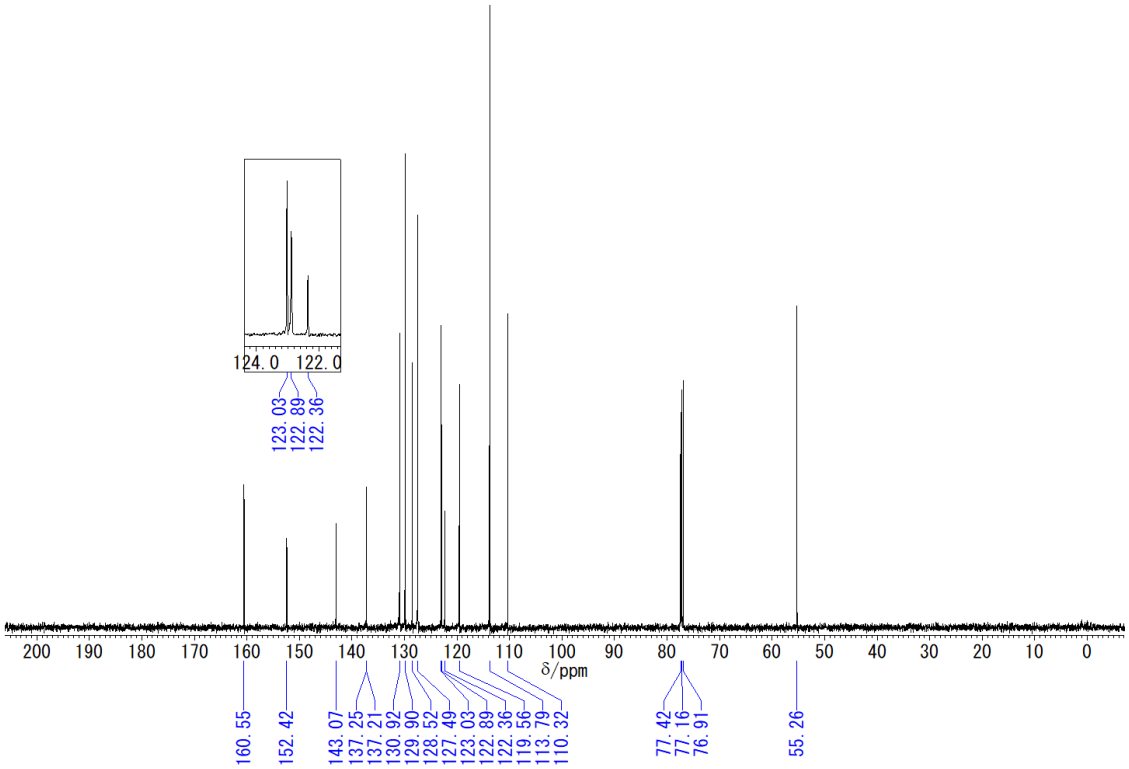
Spectrum S7. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ba**.



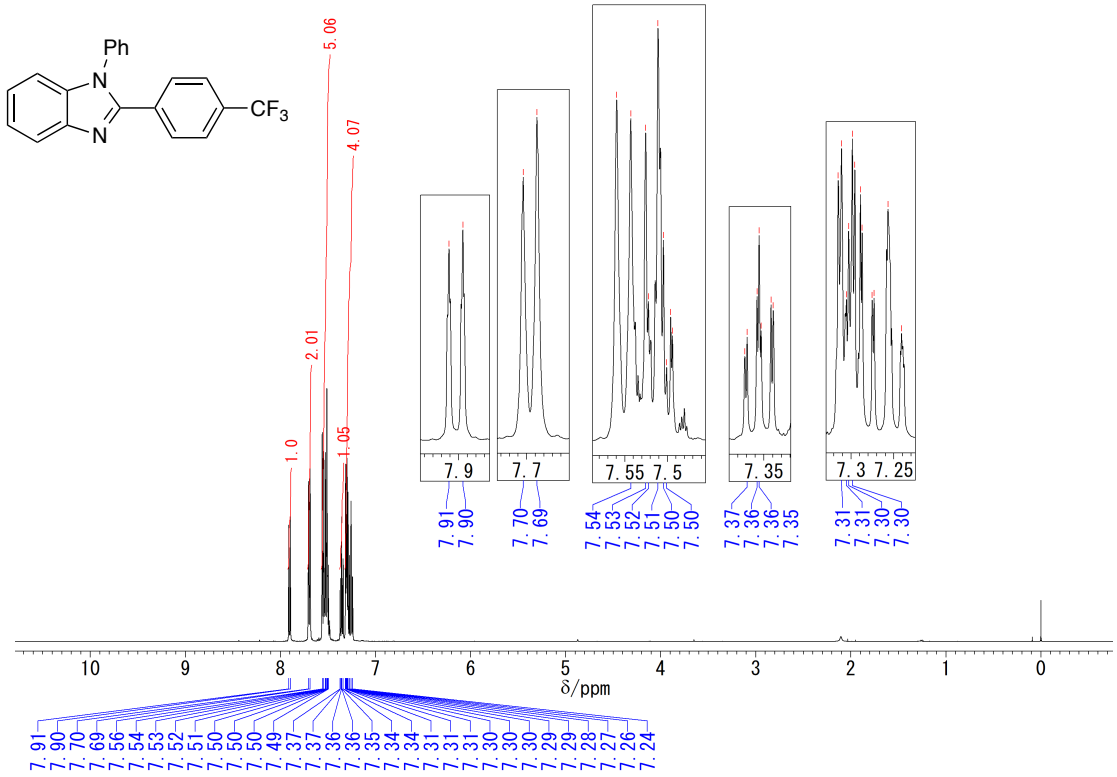
Spectrum S8. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **3ba**.



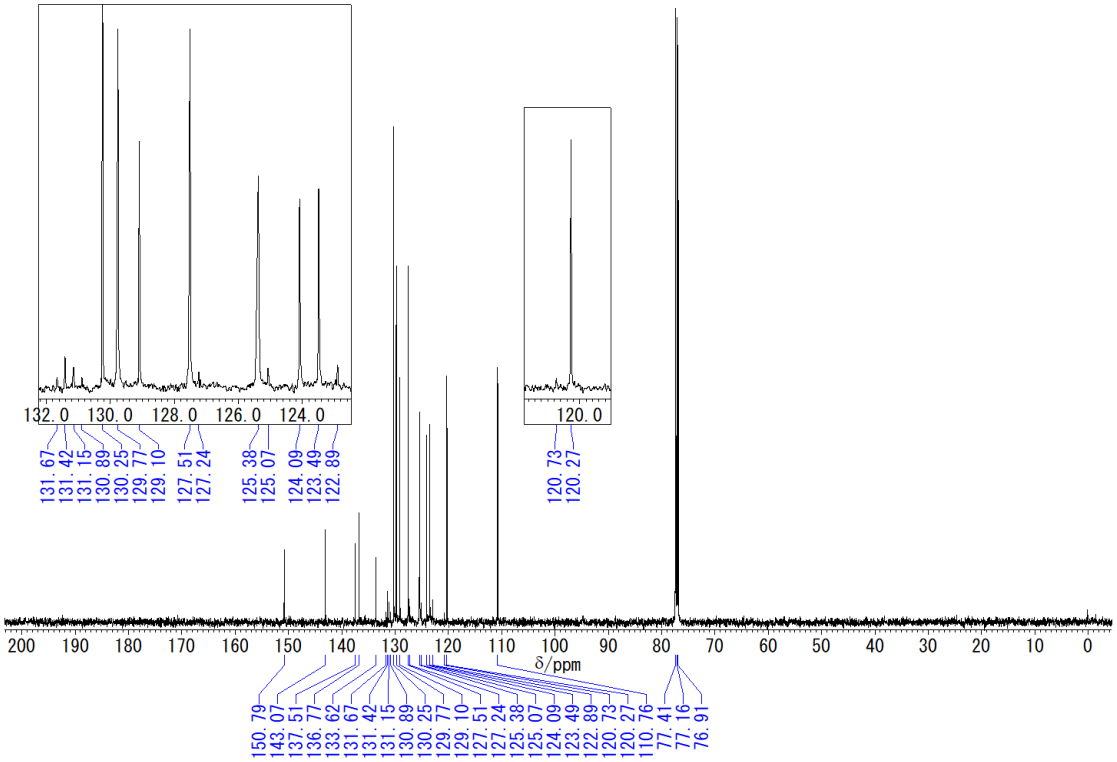
Spectrum S9. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ca**.



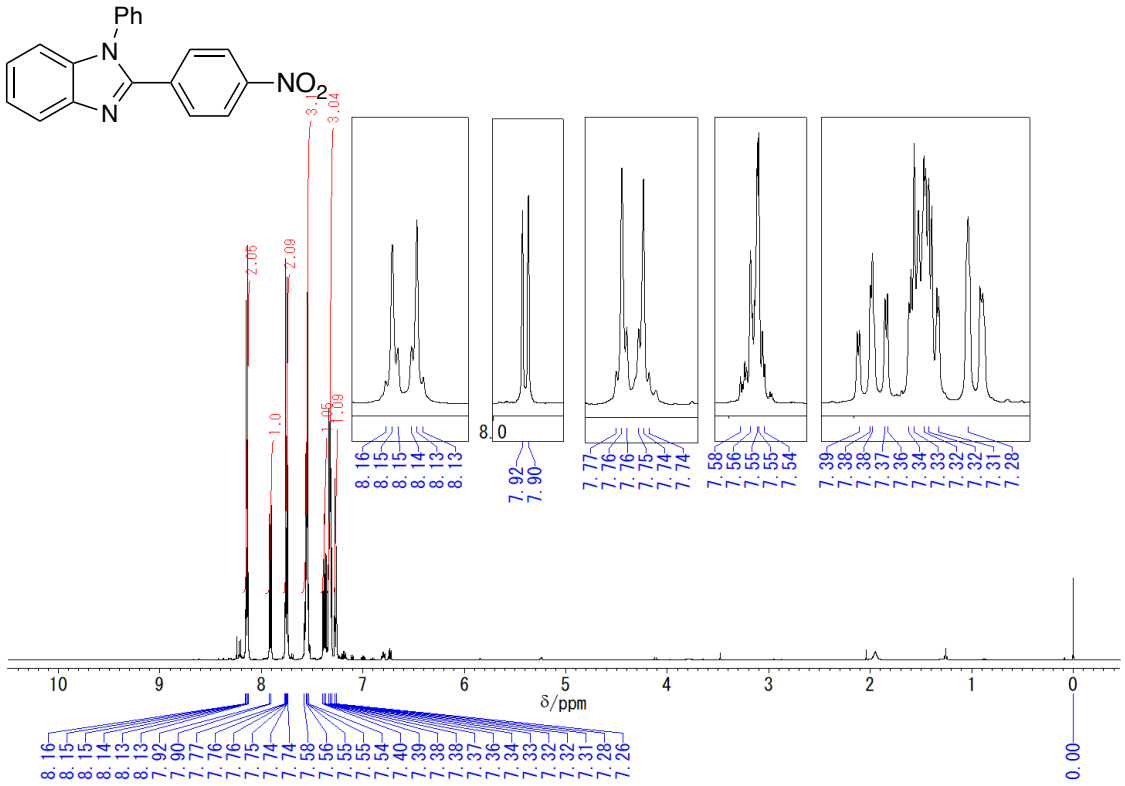
Spectrum S10. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **3ca**.



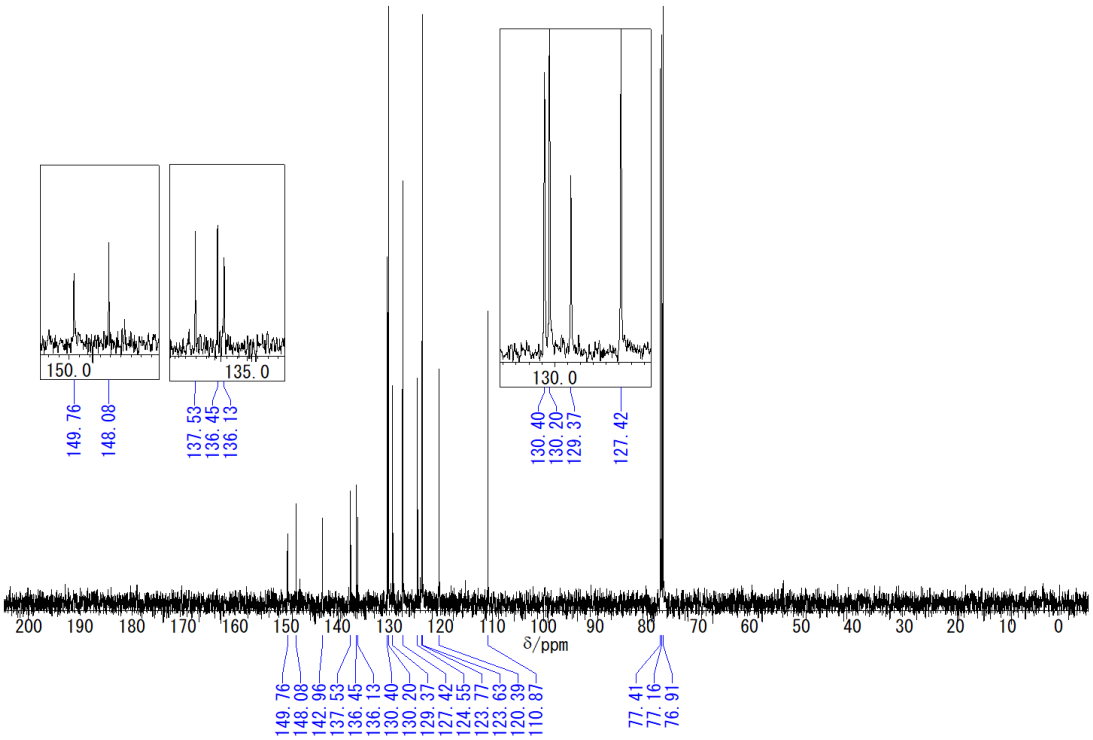
Spectrum S11. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3da**.



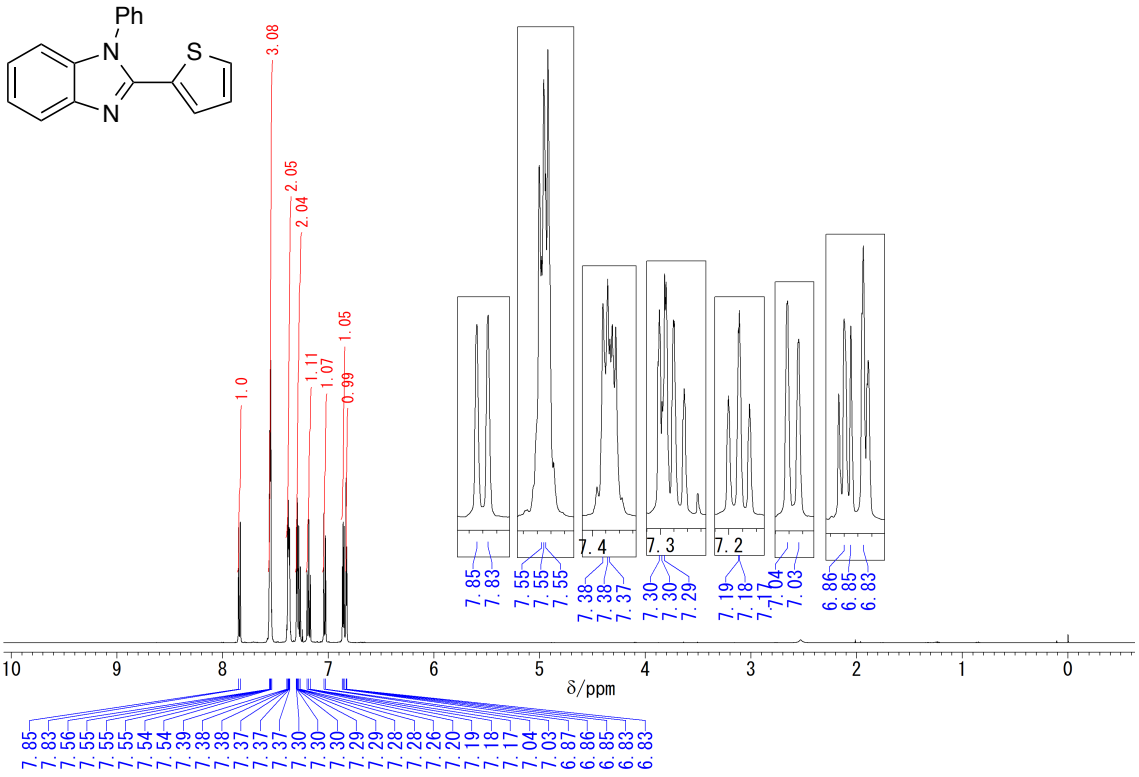
Spectrum S12. ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) spectrum of compound **3da**.



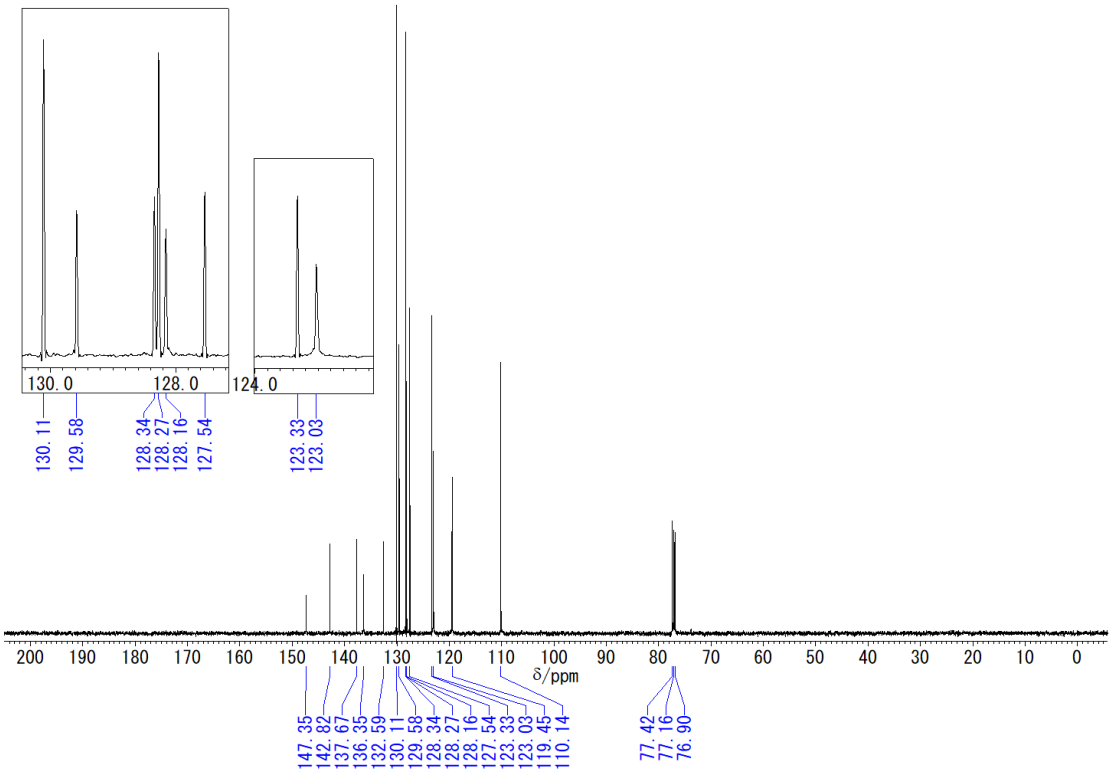
Spectrum S13. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ea**.



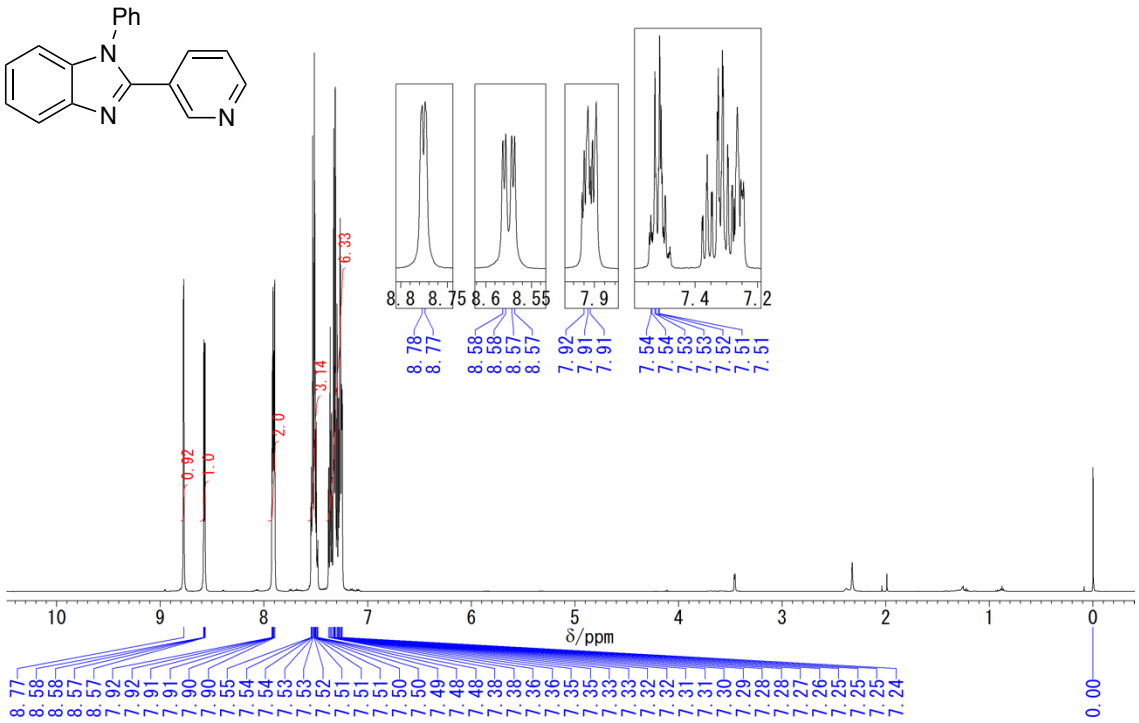
Spectrum S14. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **3ea**.



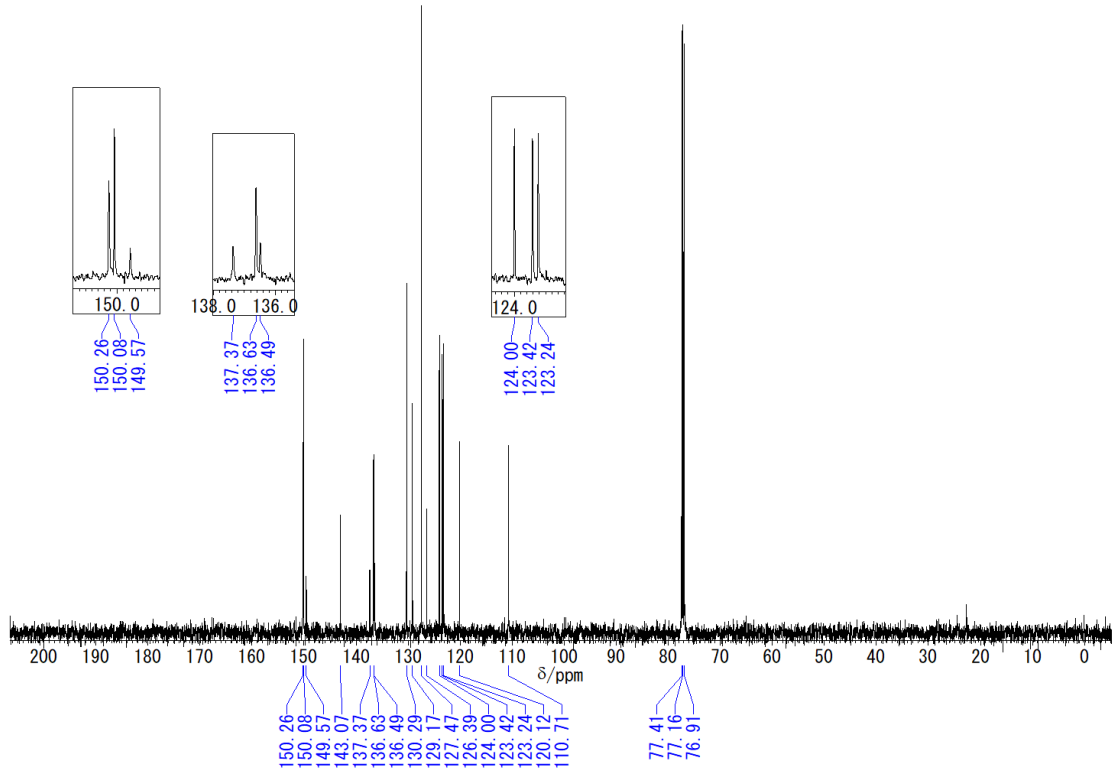
Spectrum S15. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3fa**.



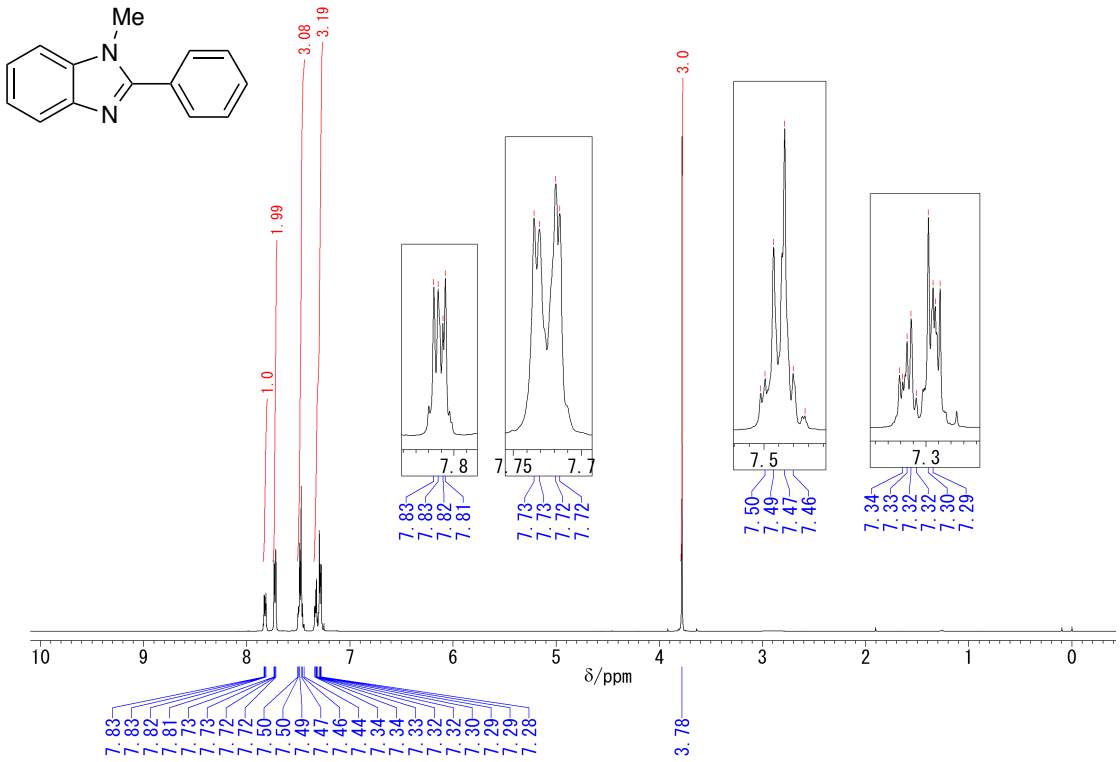
Spectrum S16. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **3fa**.



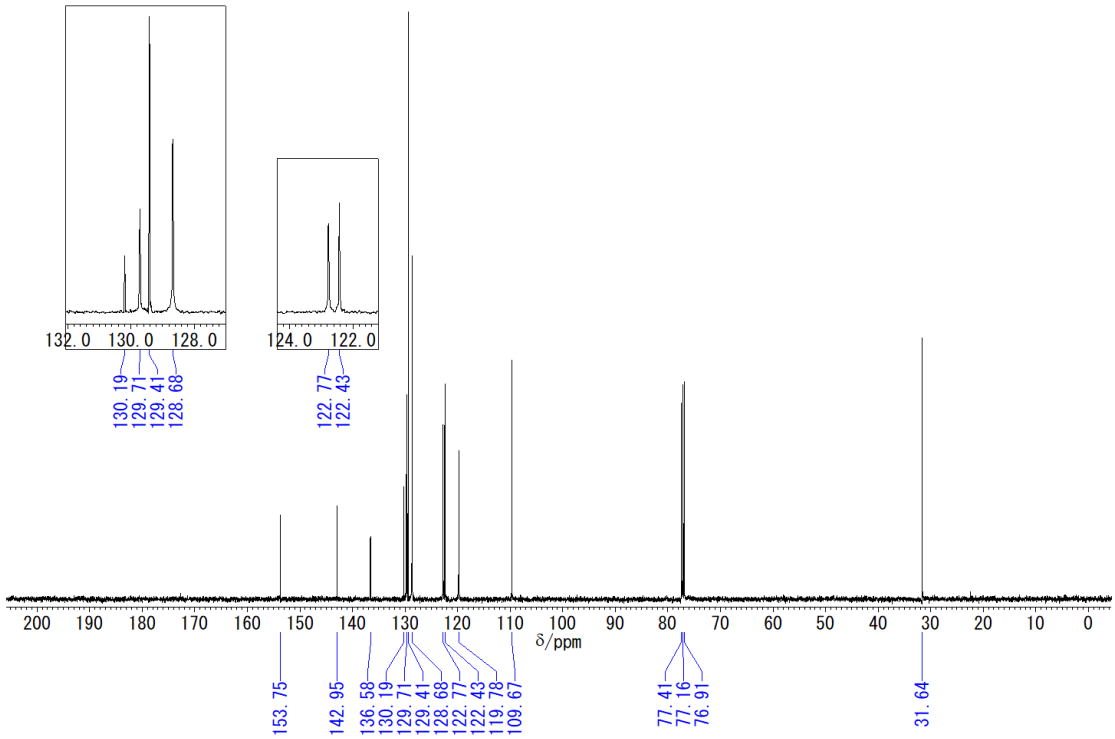
Spectrum S17. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ga**.



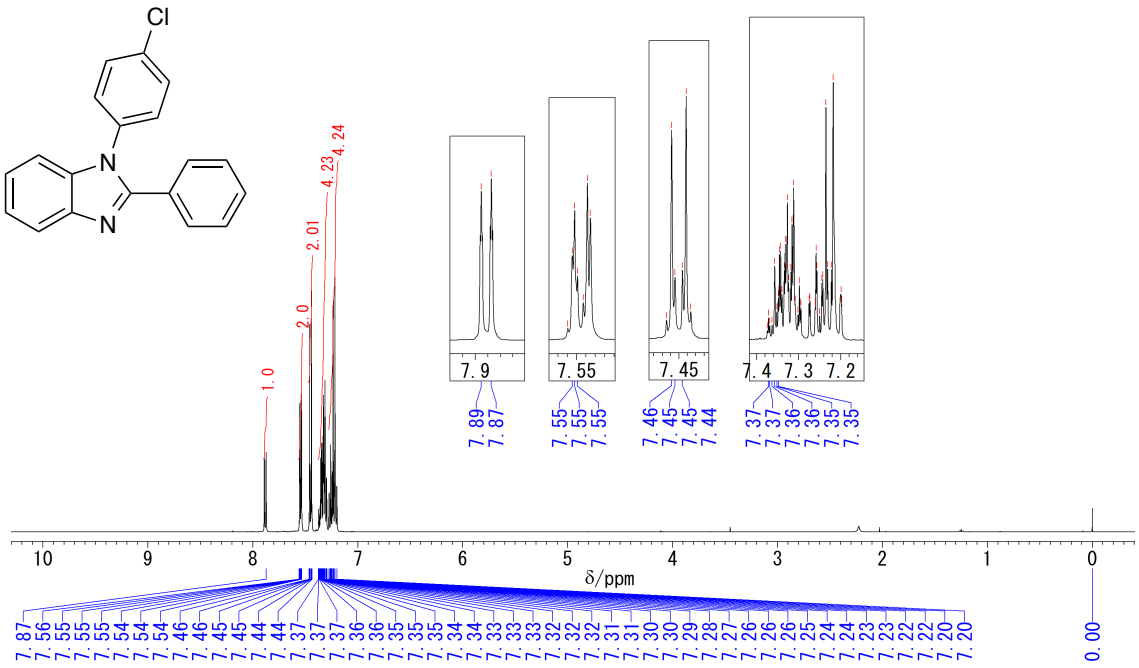
Spectrum S18. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **3ga**.



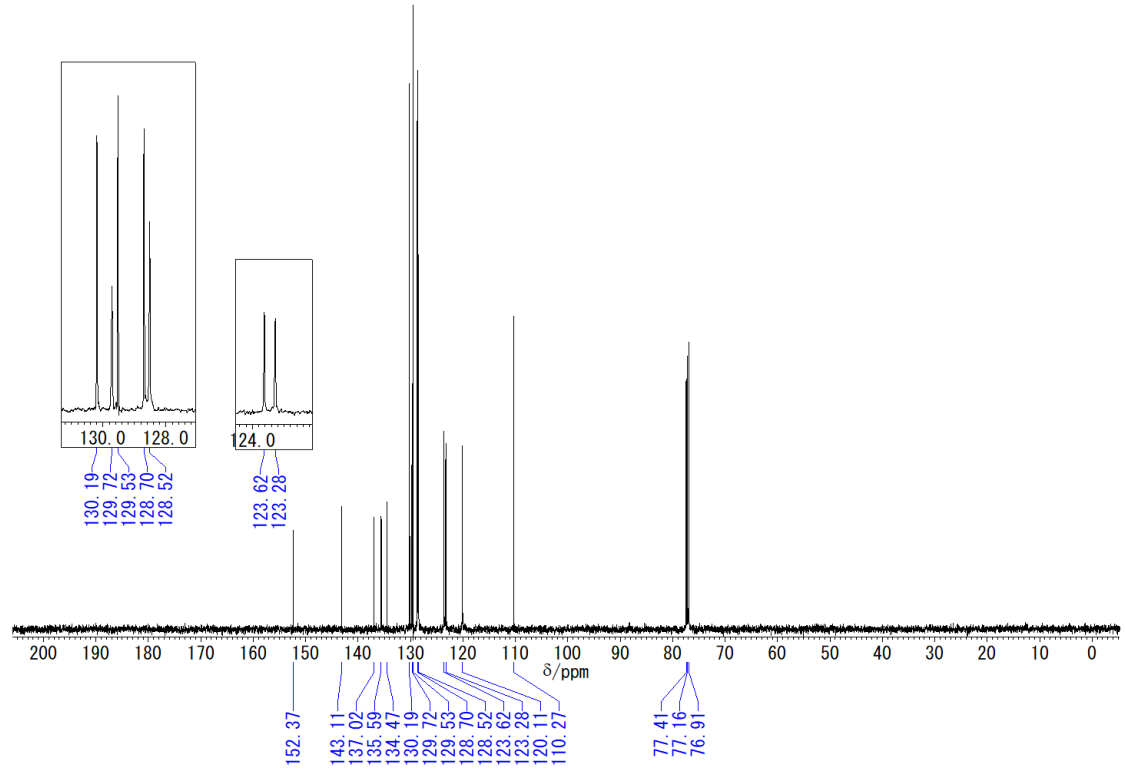
Spectrum S19. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ab**.



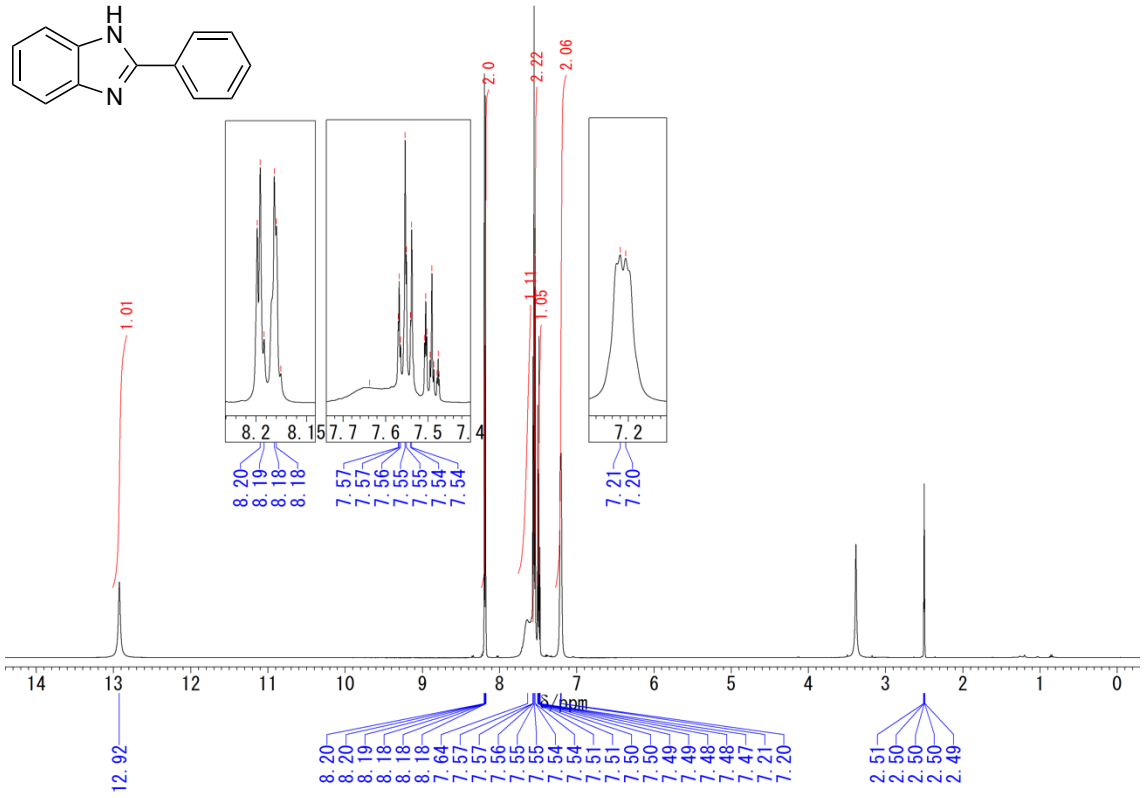
Spectrum S20. ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) spectrum of compound **3ab**.



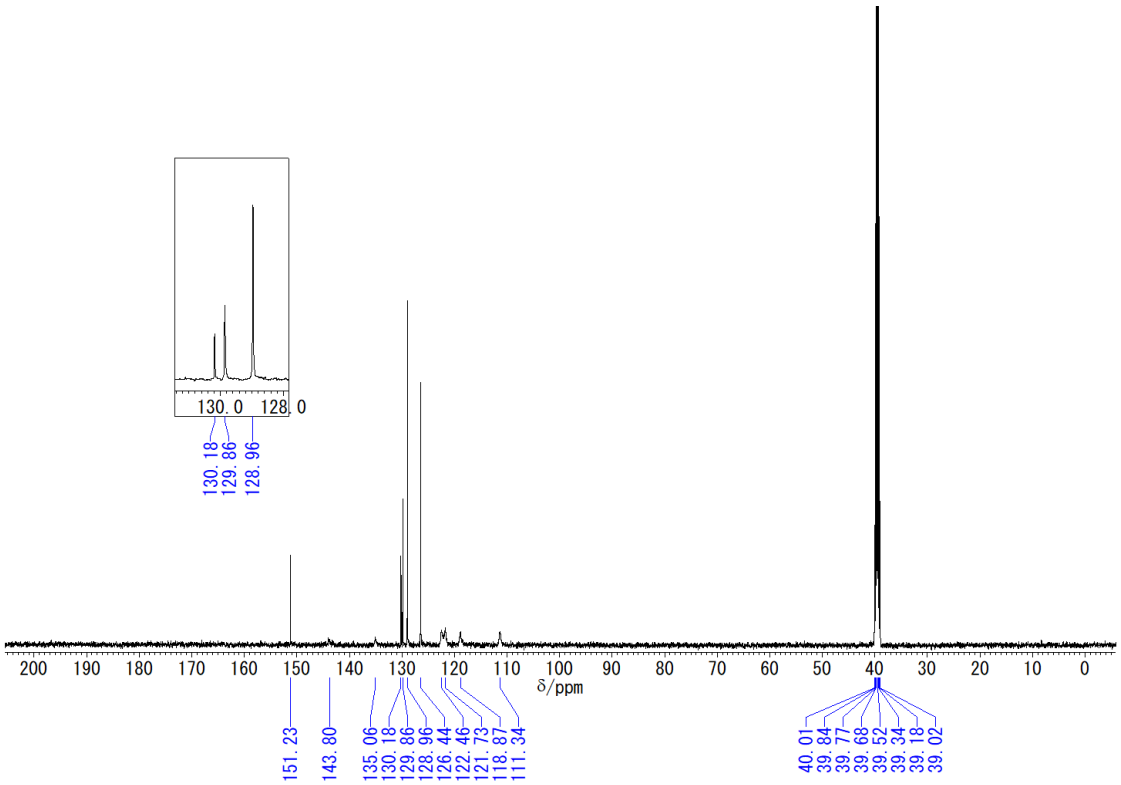
Spectrum S21. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3ad**.



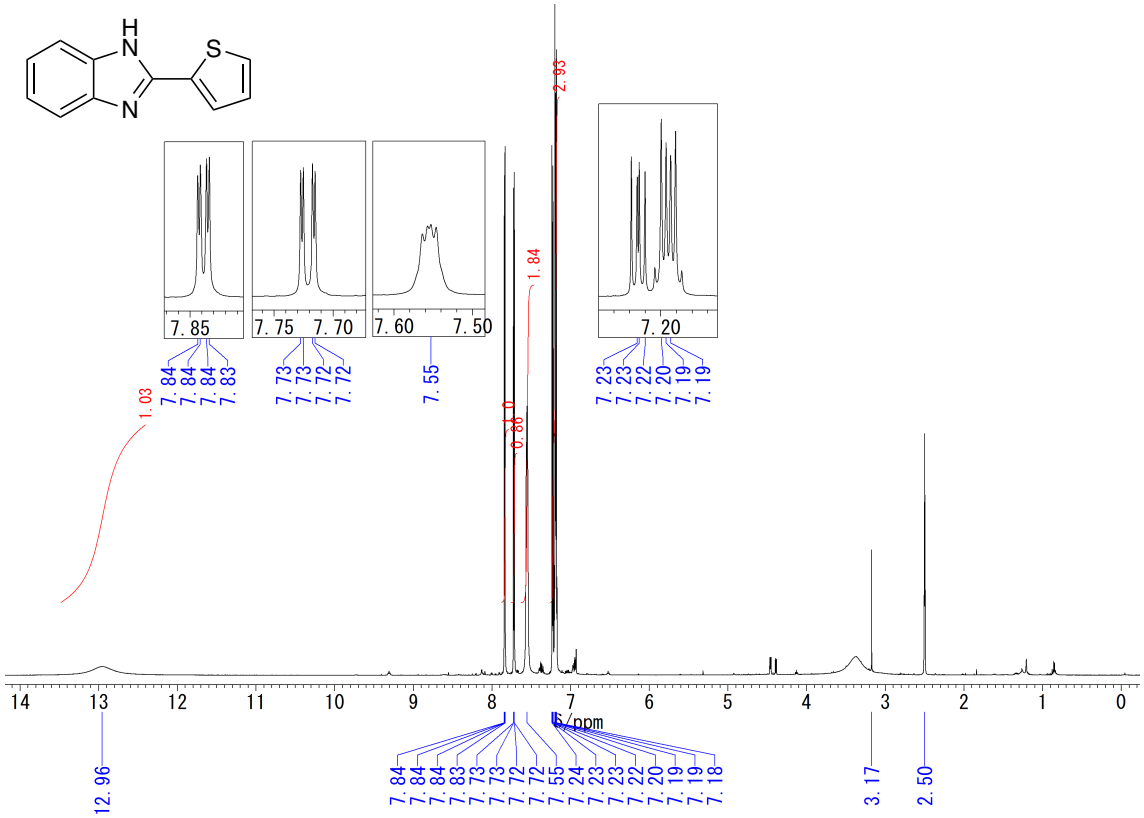
Spectrum S22. ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) spectrum of compound **3ad**.



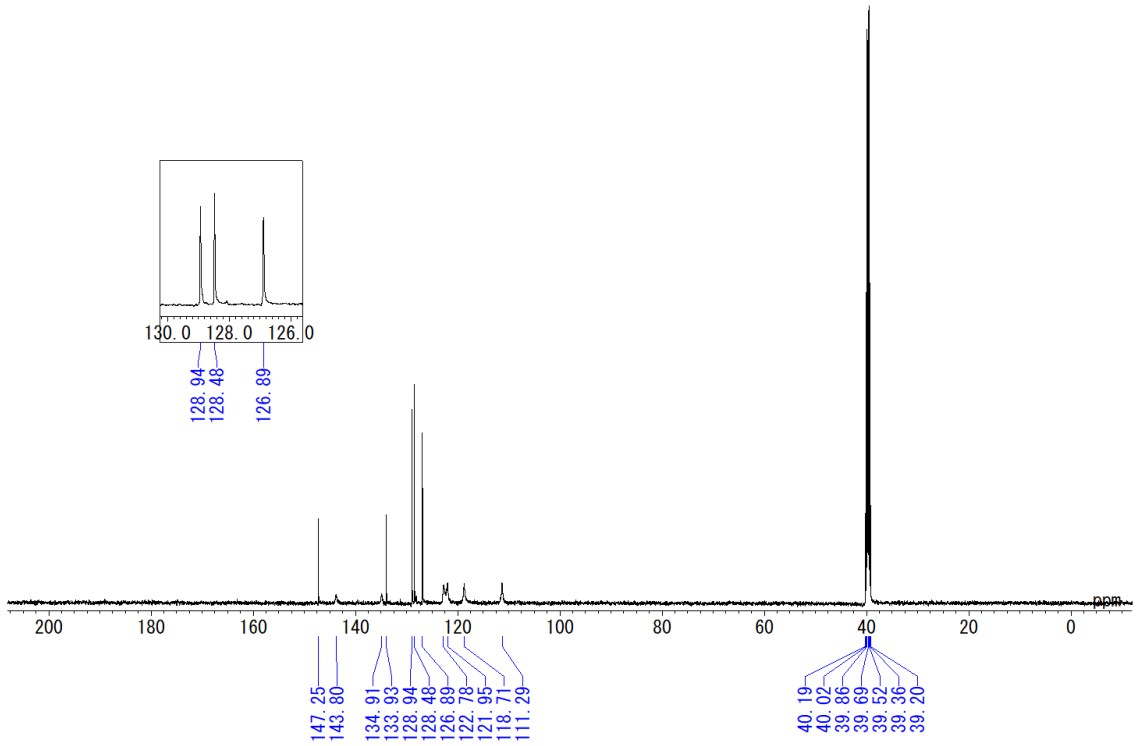
Spectrum S23. ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of compound **3ae**.



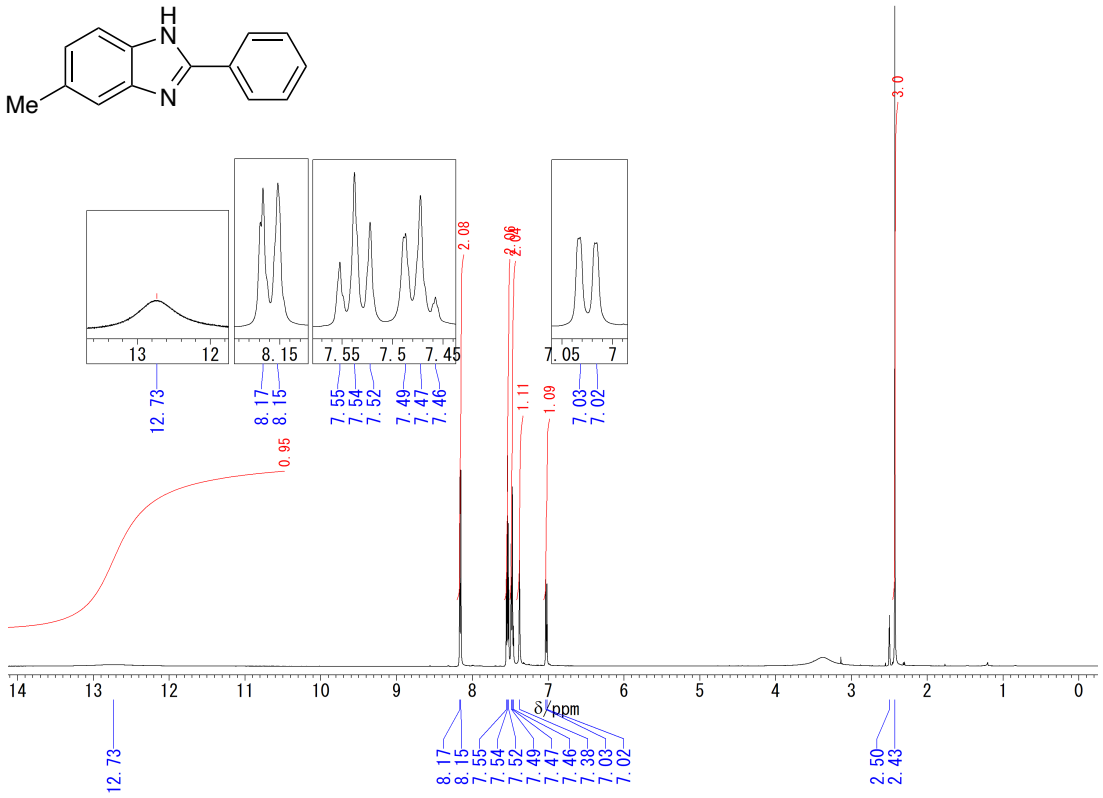
Spectrum S24. ^{13}C{^{1}H} NMR (DMSO-d_6, 126 MHz) spectrum of compound **3ae**.



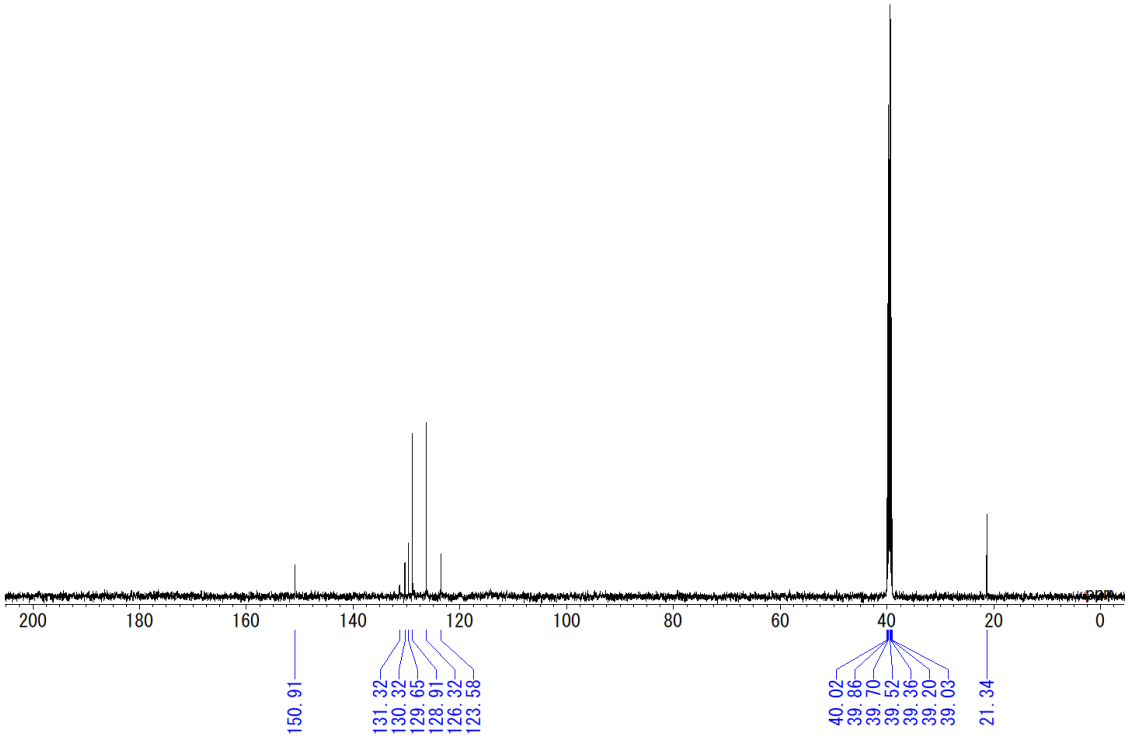
Spectrum S25. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz) spectrum of compound **3ee**.



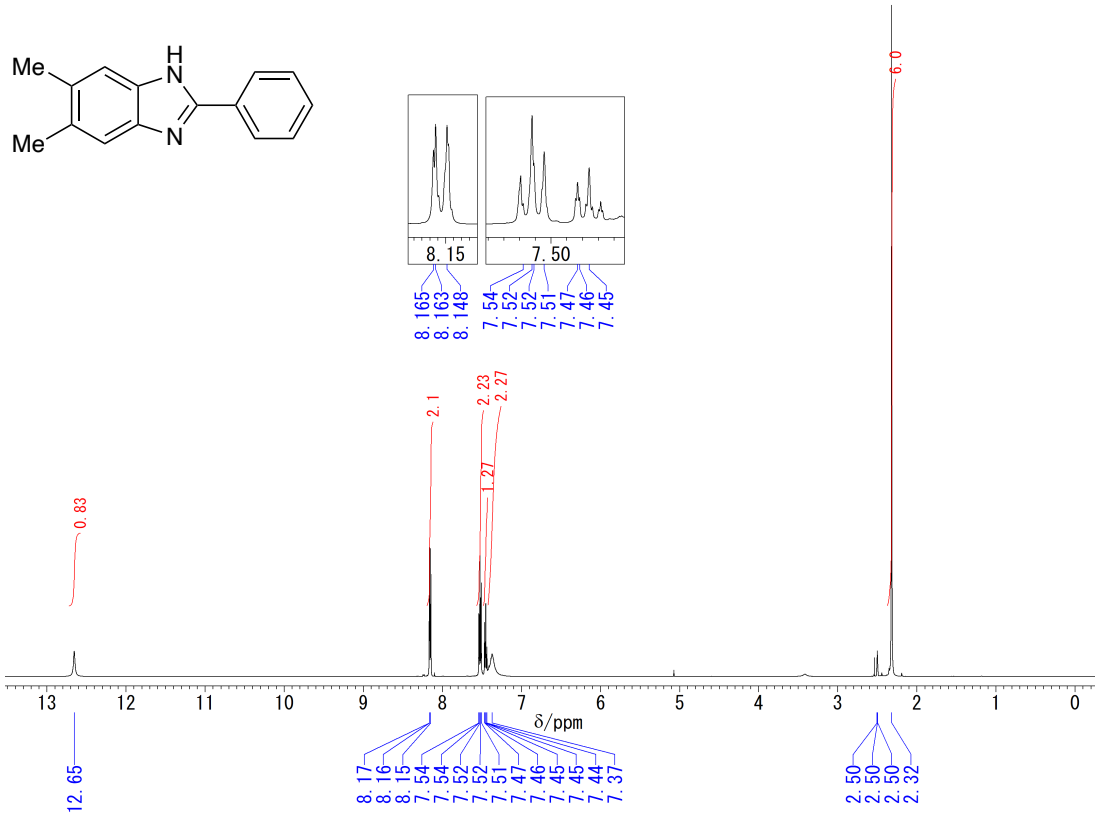
Spectrum S26. ^{13}C{^{1}H} NMR (DMSO-*d*$_6$, 126 MHz) spectrum of compound **3ee**.



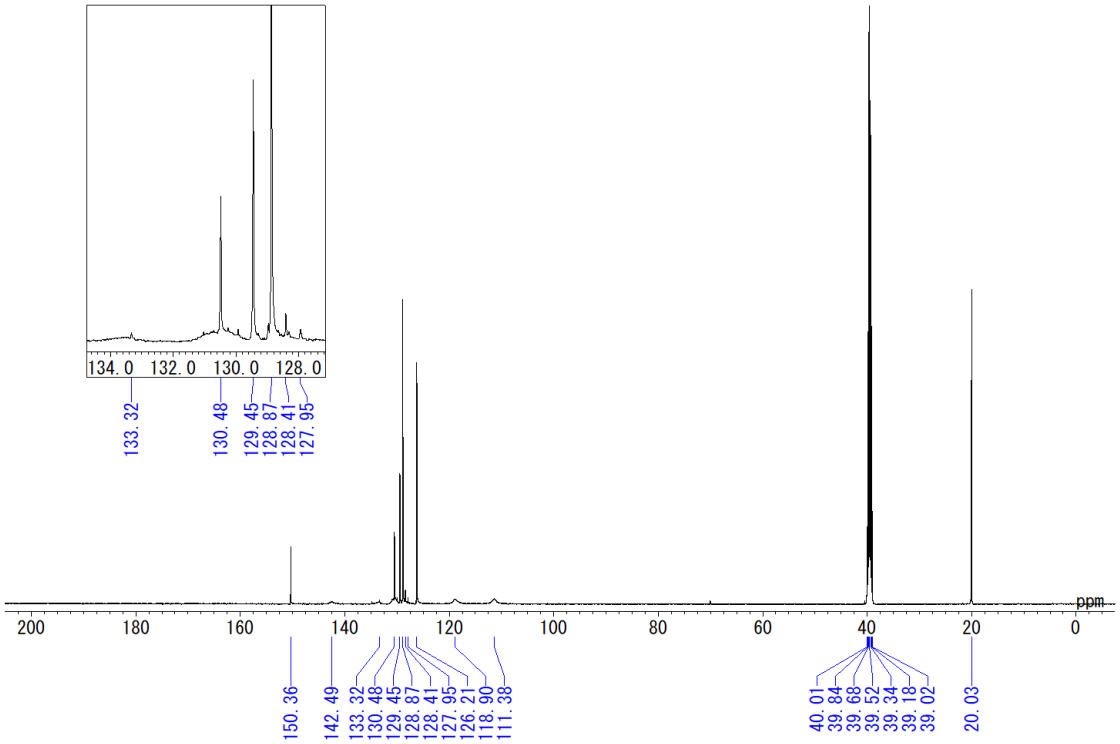
Spectrum S27. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz) spectrum of compound **3af**.



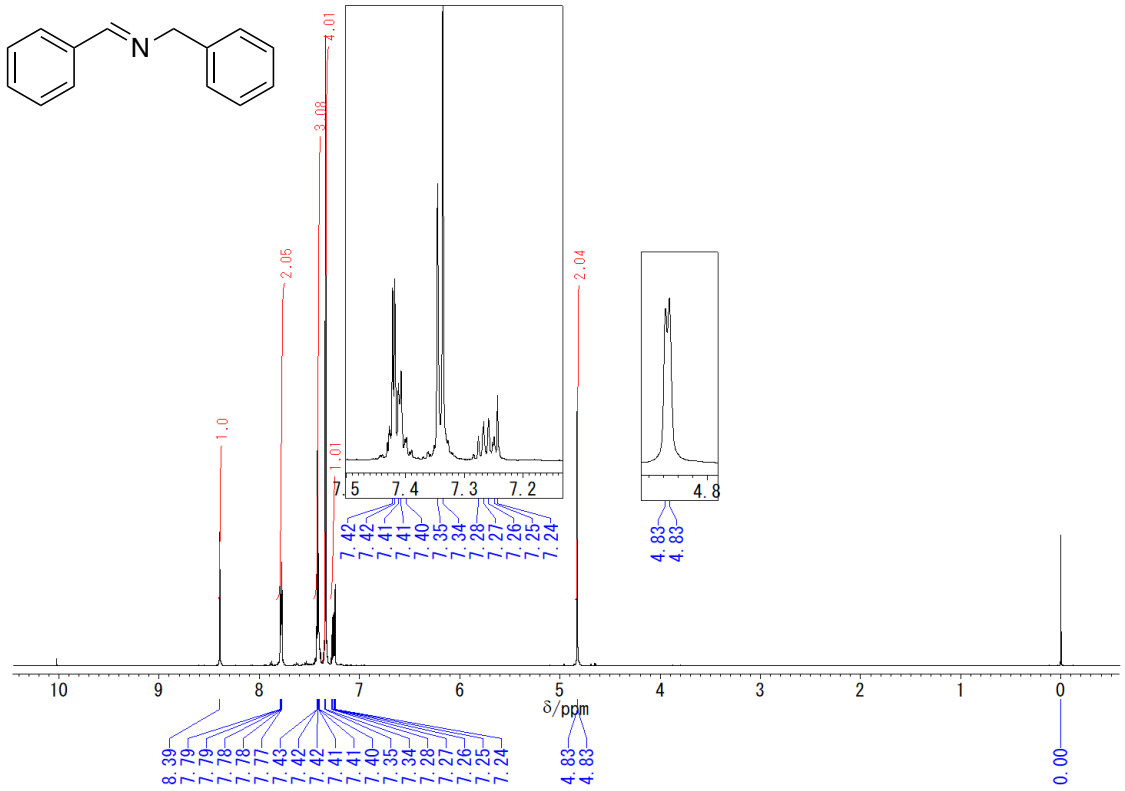
Spectrum S28. ^{13}C{^{1}H} NMR (DMSO-*d*$_6$, 126 MHz) spectrum of compound **3af**.



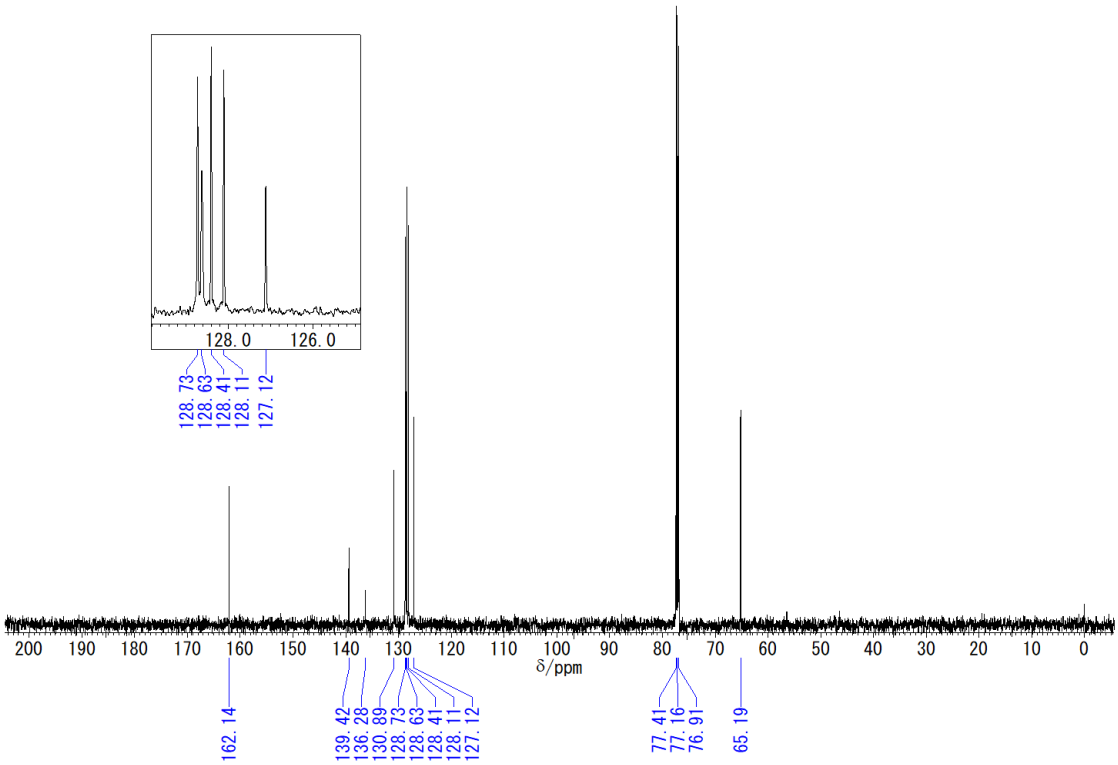
Spectrum S29. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz) spectrum of compound **3ag**.



Spectrum S30. ^{13}C{^{1}H} NMR (DMSO-*d*$_6$, 126 MHz) spectrum of compound **3ag**.



Spectrum S31. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **9a'**.



Spectrum S32. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of compound **9a'**.

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. W.-S. Li, N. Zhang and L. M. Sayre, *Tetrahedron*, 2001, **57**, 4507-4522.

S5. H. Baars, A. Beyer, S. V. Kohlhepp and C. Bolm, *Org. Lett.*, 2014, **16**, 536-539.

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

S7. D. Secci, A. Bolasco, M. D'Ascenzio, F. della Sala, M. Yáñez and S. Carradori, *J. Heterocycl. Chem*, 2012, **49**, 1187-1195.

S8. D. Zhao, J. Hu, N. Wu, X. Huang, X. Qin, J. Lan and J. You, *Org. Lett.*, 2011, **13**, 6516-6519.

S9. T. B. Nguyen, L. Ermolenko and A. Al-Mourabit, *Green Chem.*, 2013, **15**, 2713-2717.

S10. G. Naresh, R. Kant and T. Narender, *J. Org. Chem.*, 2014, **79**, 3821-3829.

S11. B. Chen, C. Zhang, L. Niu, X. Shi, H. Zhang, X. Lan and G. Bai, *Chem. –Eur. J.*, 2018, **24**, 3481-3487.

S12. P. F. Zhang, C. Y. Yu, Y. C. Yin, J. Droste, S. Klabunde, M. R. Hansen and Y. Y. Mai, *Chem. Eur. J.*, 2020, **26**, 16497-16503.