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Electronic Supplementary Information

TEMPO-immobilized metal-organic frameworks for efficient oxidative coupling of 2-aminophenols and aldehydes to benzoxazoles

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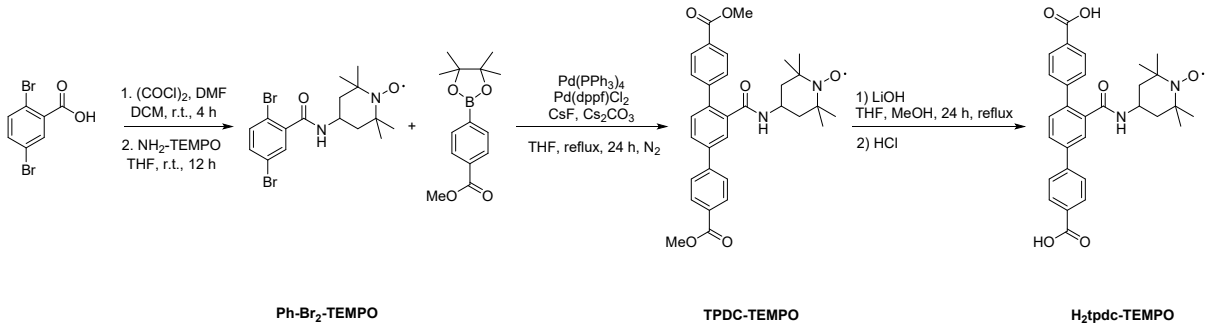
1. General Materials and Methods

All reagents, solvents, and NMR solvents used in this study were obtained from reputable chemical companies, namely Sigma-Aldrich, TCI, Alfa-Aesar, Acros, and BLDpharm, without the need for additional purification. Thin-layer chromatography (TLC) analysis was conducted on precoated silica gel 60 F254 plates, which were visualized using 254 nm UV light. Flash column chromatography was performed on silica gel (400-630 mesh) to separate the desired compounds using a mixture of ethyl acetate and *n*-hexane as main eluent.

The ^{1}H NMR (Nuclear Magnetic Resonance) and ^{13}C NMR spectra were acquired using a Bruker AVANCE 500 NMR spectrometer operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C, respectively. Chemical shifts were reported in parts per million (ppm) relative to the appropriate solvent peak and/or tetramethylsilane (TMS) as the reference standard. When appropriate, peak patterns were indicated using the following abbreviations: s (singlet), d (doublet), dd (doublet of doublet), ddd (doublet of doublet of doublet), dt (doublet of triplet), t (triplet), q (quartet), quin (quintet), and m (multiplet). Coupling constants (J) were expressed in Hertz (Hz).

2. Synthesis of H_2tpdc-TEMPO Ligands



Scheme S1. Preparation of H_2tpdc-TEMPO.

Ph-Br$_2$-TEMPO:[S1] 2,5-Dibromobenzoic acid (2.22 g, 8 mmol) was added in dichloromethane (DCM, 20 mL), and oxalyl chloride (1.03 mL, 12 mmol) were added to the solution. *N*,*N*-dimethylformamide (DMF, 8 drops) was added into the mixture, and stirred at room temperature for 4 h under nitrogen atmosphere. After conversion of carboxylic acid to acid chloride, remaining oxalyl chloride and solvent were evaporated. Then, the acid chloride intermediate was dissolved in anhydrous THF (20 mL), and a solution of 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (2.06 g, 12.0 mmol) and triethylamine (2.6 mL) in anhydrous THF (20 mL) was slowly added to acid chloride solution by dropwise under ice-bath condition. The mixture was additionally stirred for 12 h at room temperature under nitrogen atmosphere. After completion (monitored by TLC), the solvent was evaporated, and the mixture was extracted with DCM and washed with brine. The organic portions were collected and dried over $MgSO_4$. The organic solvent and volatile residue were removed in vacuo. The crude product was purified by silica gel column chromatography (EtOAc:*n*-hexane = 1:3). And target product, Ph-Br$_2$-TEMPO (2.95 g, 6.8 mmol, 85%) was obtained as an orange solid.

^{1}H NMR (500 MHz, $CDCl_3$ with phenylhydrazine) δ 7.49 (d, J = 2.3 Hz, 1H), 7.32 (d, J = 8.5 Hz, 1H), 7.28 (d, J = 2.5 Hz, 1H), 4.38 – 4.28 (m, 1H), 1.94 (dd, J = 13.0, 4.0 Hz, 2H), 1.71 (t, J = 12.9 Hz, 2H), 1.29 (s, 6H), 1.24 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 139.5, 134.8, 134.3, 132.4, 121.6, 118.0, 44.7, 41.9, 31.8, 20.0.

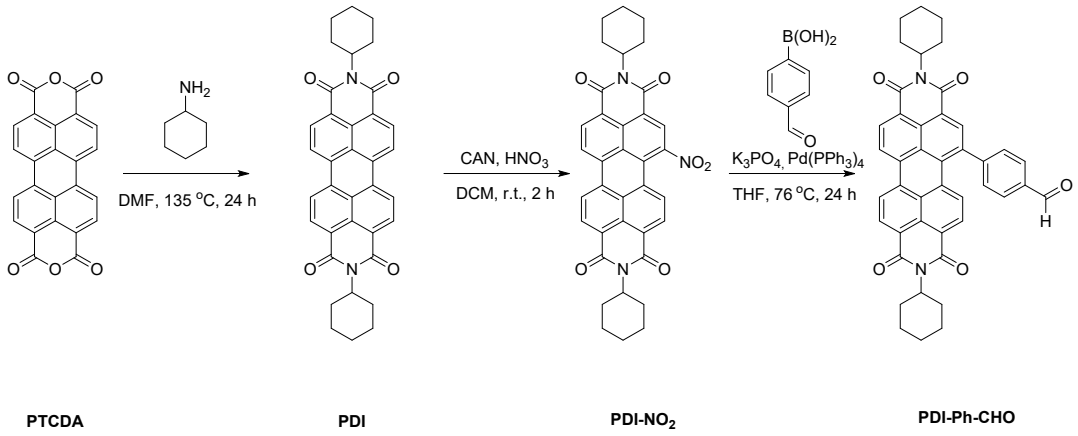
TPDC-TEMPO:[S1] Ph-Br_2-TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidin-1-yl)oxyl, 3.5 g, 8.0 mmol), 4-methoxycarbonylphenylboronic acid pinacol ester (4.8 g, 18.0 mmol), $Pd(PPh_3)_4$(277 mg, 0.24 mmol) and $Pd(dppf)Cl_2$ (653 mg, 0.8 mmol) were dissolved in anhydrous THF (80 mL). Cs_2CO_3 (7.9 g, 24.0 mmol) and CsF (604 mg, 4.0 mmol) were dissolved in H_2O (4 mL), and this base solution was added to reaction solution. The mixture was heated to 75 °C and stirred in heating mantle for 24 h under nitrogen atmosphere. After cooling to room temperature, the insoluble solids were removed by Celite filtration. Then the mixture was extracted with DCM, and washed with brine. And the organic portions were dried over $MgSO_4$, and the organic solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (EtOAc:*n*-hexane = 1:3). And target product, TPDC-TEMPO (2.2 g, 4.0 mmol, 50%) was obtained as a red solid.

^{1}H NMR (400 MHz, DMSO 0.05% v/v TMS with phenylhydrazine) δ 8.13 (d, *J* = 7.9 Hz, 1H), 8.12 – 8.06 (m, 2H), 8.03 – 7.98 (m, 2H), 7.96 – 7.87 (m, 3H), 7.79 (d, *J* = 2.0 Hz, 1H), 7.60 – 7.53 (m, 3H), 4.04 – 3.93 (m, 1H), 3.89 (s, 4H), 3.88 (s, 3H), 1.59 – 1.50 (m, 2H), 1.23 – 1.14 (m, 2H), 1.06 – 0.98 (m, 12H); ^{13}C NMR (101 MHz, DMSO with phenylhydrazine) δ 167.66, 166.13, 166.03, 144.57, 143.41, 138.20, 138.15, 138.11, 130.51, 129.95, 129.03, 128.88, 128.82, 128.34, 127.80, 127.07, 126.19, 57.77, 52.24, 52.20, 44.33, 40.69, 32.63, 19.62.

H_2tpdc-TEMPO:[S1] TPDC-TEMPO (2.2 g, 4.0 mmol) was dissolved in THF (60 mL) and MeOH (10 mL). LiOH (0.7 g, 29.3 mmol) was dissolved in H_2O (27 mL), and LiOH solution was added to the mixture. The mixture was heated to 75 °C and stirred in heating mantle for 24 h under nitrogen atmosphere. After cooling to room temperature, the organic solvents were removed by evaporation, and insoluble solids were removed by Celite filtration with H_2O. The aqueous phase was adjusted to pH 3 with aqueous 1M HCl solution. The precipitates were collected by filtration, washed with H_2O and dried under vacuo. Target product, H_2tpdc-TEMPO (1.9 g, 3.8 mmol, 95%) was obtained as a pale-pink solid.

^{1}H NMR (500 MHz, DMSO with phenylhydrazine) δ 8.12 (d, *J* = 7.9 Hz, 1H), 8.09 – 8.04 (m, 2H), 8.02 – 7.94 (m, 2H), 7.93 – 7.86 (m, 3H), 7.77 (d, *J* = 2.1 Hz, 1H), 7.59 – 7.51 (m, 3H), 4.05 – 3.91 (m, 1H), 1.55 (dd, *J* = 12.6, 3.8 Hz, 2H), 1.21 (t, *J* = 12.4 Hz, 2H), 1.04 (d, *J* = 12.1 Hz, 12H); ^{13}C NMR (101 MHz, DMSO with phenyhydrazine) δ 167.81, 167.50, 167.37, 144.02, 142.91, 138.31, 138.19, 130.50, 130.11, 129.20, 128.62, 128.36, 127.76, 126.87, 126.11, 58.23, 44.19, 40.60, 32.33, 19.67.

3. Synthesis of PDI substrate



Scheme S2. Preparation of PDI-Ph-CHO.

PDI (Perylenediimide):[S2] Perylene-3,4:9,10-tetracarboxylic acid dianhydride (PTCDA, 785 mg, 2 mmol) was added in DMF(40 mL), and the 5 mL of cyclohexylamine was added to a suspension. The mixture was stirred at 135 °C for 24 h. After cooling, 1 M HCl (15 mL) was added, then MeOH (40 mL) was added to the mixture. The precipitate was filtered, and washed with MeOH. The precipitate was dried at 70 °C under vacuum overnight (1.3 g, 85%). Red solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, J = 8.0 Hz, 4H), 8.60 (d, J = 8.1 Hz, 4H), 5.09 – 5.01 (m, 2H), 2.63 – 2.51(m, 4H), 1.92 (d, J = 13.1 Hz, 4H), 1.78 (d, J = 13.7 Hz, 6H), 1.53 – 1.40 (m, 6H).

PDI-NO_2 (Perylenediimide-NO_2):[S2] PDI (1.0 g, 1.8 mmol) and CAN (ceric ammonium nitrate, 1.2 g, 2.2 mmol) were dissolved in DCM (150 mL). Nitric acid (2.0 g, 31.7 mmol) was slowly added at 25 °C under N_2 for 2 h with stirring. The solution was neutralized with 10% KOH and was extracted with DCM. The mixture was dried over anhydrous $MgSO_4$, and the organic solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (DCM) (971 mg, 90%). Red solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, J = 8.0 Hz, 1H), 8.74 – 8.66 (m, 4H), 8.59 (d, J = 8.1 Hz, 1H), 8.24 (d, J = 8.2 Hz, 1H), 5.03 (t, J = 12.3 Hz, 2H), 2.59 – 2.49 (m, 4H), 1.92 (d, J = 12.8 Hz, 4H), 1.76 (d, J = 11.0 Hz, 6H), 1.52 – 1.42 (m, 4H), 1.40 – 1.28 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 163.3, 163.2, 162.3, 147.7, 135.5, 132.9, 131.4, 131.2, 129.4, 129.3, 129.0, 128.0, 127.8, 127.5, 126.6, 126.5, 126.4, 125.5, 125.5, 124.7, 124.6, 124.1, 123.7, 54.6, 54.4, 29.2, 29.2, 26.6, 26.6, 25.5, 25.5.

PDI-Ph-CHO (Perylenediimide-phenylaldehyde):[S2] PDI-NO_2 (600 mg, 1.0 mmol), K_3PO_4 (637 mg, 3.0 mmol), 4-formylphenyl boronic acid (200 mg, 1.33 mmol), and $Pd(PPh_3)_4$ (116 mg, 0.10 mmol) were dissolved in dry THF under N_2. The mixture was stirred at 75 °C for 48 h under N_2. After cooling, the organic solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (DCM), and recrystallized in DCM/*n*-hexane condition (527 mg, 80%). Red solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.70 (d, J = 7.9 Hz, 3H), 8.67 – 8.57 (m, 1H), 8.51 (s, 1H), 8.14 – 8.01 (m, 3H), 7.76 – 7.63 (m, 3H), 5.08 – 4.96 (m, 2H), 2.61 – 2.48 (m, 4H), 1.99 – 1.85 (m, 4H), 1.83 – 1.67 (m, 4H), 1.53 – 1.39 (m, 4H), 1.39 – 1.25 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.5, 163.9, 163.7, 163.6, 148.9, 140.0, 136.2, 135.3, 134.8, 134.1, 133.9, 132.7, 131.7, 131.3, 131.1, 130.3, 130.0, 129.9, 129.6, 129.0, 128.6, 128.0, 127.4, 124.0, 123.7, 123.3, 123.2, 123.1, 123.0, 54.3, 54.1, 29.2, 29.2, 26.7, 26.6, 25.6, 25.5.

4. Detailed Procedures for MOF Preparation

UiO-68-(TEMPO)$_{1.0}$:[S1] H_2tpdc-TMEPO (214 mg, 0.42 mmol), $ZrCl_4$ (96 mg, 0.42 mmol), and benzoic acid (BzOH, 760 mg, 6.2 mmol) were charged in a round bottom flask (250 mL) with a magnetic stirring bar (3 mm x 6 mm), and the mixtures were dissolved in DMF (16 mL). The mixture was stirred (300 rpm) at 120 °C in heating mantle for 48 h. After cooling to room temperature, the microcrystalline powder was isolated by centrifugation (3600 rpm). and washed 3 times with fresh DMF (3 x 10 mL), washed 3 times with MeOH (3 x 10 mL), and washed 3 times with acetone (3 x 10 mL). The solids were dried under vacuum for 24 h yielded the activated UiO-68-TEMPO.

UiO-68-(TEMPO)$_{0.75}$(Me$_2$)$_{0.25}$: H_2tpdc-TMEPO (160 mg, 0.31 mmol) and H_2tpdc-Me_2 (36 mg, 0.10 mmol) were used for UiO-68-(TEMPO)$_{0.75}$(Me$_2$)$_{0.25}$ preparation.

UiO-68-(TEMPO)$_{0.75}$(Me$_2$)$_{0.25}$: H_2tpdc-TMEPO (108 mg, 0.21 mmol) and H_2tpdc-Me_2 (72 mg, 0.21 mmol) were used for UiO-68-(TEMPO)$_{0.75}$(Me$_2$)$_{0.25}$ preparation.

UiO-68-(TEMPO)$_{0.25}$(Me$_2$)$_{0.75}$: H_2tpdc-TMEPO (53 mg, 0.10 mmol) and H_2tpdc-Me_2 (108 mg, 0.31 mmol) were used for UiO-68-(TEMPO)$_{0.25}$(Me$_2$)$_{0.75}$ preparation.

UiO-68-(Me$_2$)$_{1.0}$: H_2tpdc-Me_2 (145 mg, 0.42 mmol) were used for UiO-68-(Me$_2$)$_{1.0}$ preparation.

5. General procedure of MOF Characterizations.

MOF digestion for NMR measurement: approximately 10 mg of MOFs were dried under vacuum and digested with sonication in 590 μL of DMSO-d_6 and 10 μL of HF (48% aqueous solution). Phenylhydrazine was employed together for TEMPO-based molecules as a reducing agent for the paramagnetic nitroxide radicals to the corresponding hydroxylamine.

PXRD (Powder X-ray diffraction): PXRD data was collected at ambient temperature on a Rigaku Miniflex at 40 kV, 15 mA for CuKa (λ = 1.5406 Å), with a scan speed of 1 sec/step, a step size of 0.02 ° in 2θ, and a 2θ range of 3-30 °.

N_2 full isotherms for MOF-TEMPO: The N_2 full sorption isotherms were obtained using a ASAP2020 at 77K. Prior to the sorption measurements, the sample was activated as following steps. Approximately 30-60 mg of MOF sample was evacuated under vacuum for a moment at room temperature. Samples were then transferred to a pre-weighed sample tube and degassed at 150 °C on an ASAP2020 for a minimum of 24 h or until the outgas rate was < 5 μm Hg/min. The sample tube was re-weighted to obtain a consistent mass for the degassed MOF materials.

6. General Procedure of the Obtained Products

Optimization Condition

General Procedure A (See Table 1): 2-Aminophenol (1.0mmol) and benzaldehyde (1.0 mmol) were placed in the 4 mL vial and dissolved in 2 mL of solvent. The mixture was stirred for 30 min at room temperature and the UiO-68-$(TEMOPO)_{1.0}$ (63 mg, 10 mol% of TEMPO) was added. The mixture was heated to temperature, and kept stirred for time under oxygen atmosphere. After cooling to room temperature, MOF catalyst was removed by centrifugation, and washed with DCM and acetone three times each. The desired product was isolated by a silica gel column chromatography with ethyl acetate-hexane as the eluent.

Reaction Condition for Effects of Immobilization amounts in UiO-68-TEMPO

General Procedure B (See Table S2): 2-Aminophenol (0.5 mmol) and benzaldehyde (0.5 mmol) were placed in the 4 mL vial and dissolved in 1 mL of *p*-xylene. The mixture was stirred for 30 min at room temperature and the UiO-66-$(TEMOPO)_{1.0}$ (16 mg, 5 mol% of TEMPO), UiO-66-$(TEMOPO)_{0.75}(Me_2)_{0.25}$ (20 mg, 5 mol% of TEMPO), UiO-66-$(TEMOPO)_{0.5}(Me_2)_{0.5}$ (27 mg, 5 mol% of TEMPO) , UiO-66-$(TEMOPO)_{0.25}(Me_2)_{0.75}$ (50 mg, 5 mol% of TEMPO) was added. The mixture was heated to100 °C, and kept stirred for time under oxygen atmosphere. After cooling to room temperature, MOF catalyst was removed by centrifugation, and washed with DCM and acetone three times each. The desired product was isolated by a silica gel column chromatography with ethyl acetate-hexane as the eluent.

Oxidative Coupling Reactions with Various Substrate Scopes

General Procedure C (See Fig. 3): 2-Aminophenol (0.5 mmol) and benzaldehyde (0.5 mmol) were placed in the 4 mL vial and dissolved in 1 mL of *p*-xylene. The mixture was stirred for 30 min at room temperature and the UiO-66-$(TEMOPO)_{1.0}$ (32 mg, 10 mol% of TEMPO) was added. The mixture was heated to 100 °C, and kept stirred for 24 h under oxygen atmosphere. After cooling to room temperature, MOF catalyst was removed by

centrifugation, and washed with DCM and acetone three times each. The desired product was isolated by a silica gel column chromatography with ethyl acetate-hexane as the eluent.

Reaction Condition for Heterogeneous and Homogeneous Conditions

General Procedure D (See in Scheme 3): PDI-Ph-CHO (Perylenediimide-phenylaldehyde) **1j** (65.9 mg, 0.1 mmol) and 2-Aminophenol **1a** (5.5 mg, 0.1 mmol) were placed in the 4 mL vial and dissolved in 1 mL of *p*-xylene. The mixture was stirred for 30 min at room temperature and the TEMPO-catalyst (10 mol%; 6.4 mg of UiO-66-(TEMPO)$_{1.0}$ or 5.4 mg of TPDC-TEMPO) was added. The mixture was heated to 100 ^{o}C, and kept stirred for 24 h under oxygen atmosphere. After cooling to room temperature, MOF catalyst was removed by centrifugation, and washed with DCM and acetone three times each. The desired product was isolated by a silica gel column chromatography with ethyl acetate-hexane as the eluent (Ethyl acetate: Hexane = 1:5, 1:3)

Reaction Condition for One-pot Sequential Aerobic Oxidation-oxidative cyclization

General Procedure E (See Scheme 4) : Benzyl alcohol (0.5 mmol), UiO-66-(TEMOPO)$_{1.0}$ (32 mg, 10 mol% of TEMPO) and *t*-BuCN 1 mL were added to the 4 mL vial. *tert*-butyl nitrite (5 mg, 0.05 mmol) was added to the mixture, and then the mixture was stirred for 3 h at 80 ^{o}C under oxygen atmosphere. After 3 h, cooled the mixture to room temperature and monitored full conversion of benzyl alcohol by thin-layer chromatography. After conversion of benzyl alcohol to aldehyde was complete, 2-Phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide (12 mg, 0.05 mmol) and 2-aminophenol (55 mg, 0.5 mmol) was added in to mixture and added 1 mL of *p*-xylene. The mixture was heated to 100 ^{o}C, and kept stirred for 48 h under oxygen atmosphere. After cooling to room temperature, MOF catalyst was removed by centrifugation, and washed with DCM and acetone three times each. The desired product was isolated by a silica gel column chromatography with ethyl acetate-hexane (1:50 v/v) as the eluent, obtained as a colorless solid.

7. Characterization of the Obtained Products

2-Phenylbenzoxazole (**3aa**):[S3] Benzaldehyde **1a** (51 μL, 0.5 mmol) was reacted with aminophenol **2a** (54.5 mg, 0.5 mmol) following the general procedure **C**. After purification by column chromatography (Ethyl acetate: Hexane = 1: 50), 2-Phenylbenzoxazole **3aa** was obtained as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 – 8.24 (m, 2H), 7.81 – 7.77 (m, 1H), 7.61 – 7.57 (m, 3H), 7.55 – 7.52 (m, 1H), 7.39 – 7.33 (m, 1H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 163.2, 150.9, 142.2, 131.7, 129.1, 127.8, 127.3, 125.3, 124.8, 120.2, 110.8.

2-(*p*-Tolyl)benzoxazole (**3ba**):[S4] 4-Methylbenzaldehyde **1b** (59 μL, 0.5 mmol) was reacted with aminophenol **2a** (54.5 mg, 0.5 mmol) following the general procedure **C**. After purification by column chromatography (Ethyl acetate: Hexane = 1: 50), 2-(*p*-Tolyl)benzoxazole **3ba** was obtained as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.2 Hz, 2H), 7.80 – 7.73 (m, 1H), 7.61 – 7.54 (m, 1H), 7.36 – 7.31 (m, 4H), 2.44 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) : δ 163.4, 150.8, 142.3, 142.2, 129.8, 127.7, 125.0, 124.6, 124.5, 112.0, 110.6, 21.8.

2-(*m*-Tolyl)benzoxazole (**3ca**):[S4] 3-Methylbenzaldehyde **1c** (59 μL, 0.5 mmol) was reacted with aminophenol **2a** (54.5 mg, 0.5 mmol) following the general procedure **C**. After purification by column chromatography (Ethyl acetate: Hexane = 1: 50), 2-(*m*-Tolyl)benzoxazole **3ca** was obtained as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.61 – 7.55 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.39 – 7.33 (m, 3H), 2.46 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) : δ 163.4, 150.9, 142.3, 138.9, 132.5, 129.0, 128.3, 127.2, 125.2, 124.9, 124.7, 120.1, 110.7, 21.5.

2-(*o*-Tolyl)benzoxazole (**3da**):[S3] 2-Methylbenzaldehyde **1d** (58 μL, 0.5 mmol) was reacted with aminophenol **2a** (54.5 mg, 0.5 mmol) following the general procedure **C**. After purification by column chromatography (Ethyl

acetate: Hexane = 1: 50), 2-(*o*-Tolyl)benzoxazole **3da** was obtained as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.84 – 7.79 (m, 1H), 7.62 – 7.58 (m, 1H), 7.44 – 7.40 (m, 1H), 7.39 – 7.34 (m, 4H), 2.82 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) : δ 163.6, 150.4, 142.3, 139.0, 131.9, 131.1, 130.1, 126.4, 126.2, 125.2, 124.5, 120.3, 110.6, 22.4.

2-(4-Methoxyphenyl)benzoxazole (**3ea**):[S3] 4-Methoxylbenzaldehyde **1e** (60 μL, 0.5 mmol) was reacted with aminophenol **2a** (54.5 mg, 0.5 mmol) following the general procedure **C**. After purification by column chromatography (Ethyl acetate: Hexane = 1: 50), 2-(4-Methoxyphenyl)benzoxazole **3ea** was obtained as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 – 8.18 (m, 2H), 7.77 – 7.69 (m, 1H), 7.58 – 7.52 (m, 1H), 7.36 – 7.29 (m, 2H), 7.06 – 7.00 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) : δ 163.3, 162.5, 150.8, 142.4, 129.5, 124.7, 124.6, 119.8, 119.8, 114.5, 110.5, 55.6.

2-(4-Chlorophenyl)benzoxazole (**3fa**):[S3] 4-Chlorobenzaldehyde **1f** (70.2 mg, 0.5 mmol) was reacted with aminophenol **2a** (54.5 mg, 0.5 mmol) following the general procedure **C**. After purification by column chromatography (Ethyl acetate: Hexane = 1: 60), 2-(4-Chlorophenyl)benzoxazole **3fa** was obtained as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.6 Hz, 2H), 7.80 – 7.73 (m, 1H), 7.61 – 7.55 (m, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.39 – 7.35 (m, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) : δ 162.2, 150.9, 142.2, 137.9, 129.4, 129.0, 125.8, 125.5, 124.9, 120.2, 110.8.

4-(Benzoxazol-2-yl)benzonitrile (**3ga**):[S4] 4-Formylbenzonitrile **1g** (65.6 mg, 0.5 mmol) was reacted with aminophenol **2a** (54.5 mg, 0.5 mmol) following the general procedure **C**. After purification by column chromatography (Ethyl acetate: Hexane = 1: 50), 4-(Benzoxazol-2-yl)benzonitrile **3ga** was obtained as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.4 Hz, 2H), 7.85 – 7.77 (m, 3H), 7.66 – 7.59 (m, 1H), 7.46 – 7.37 (m, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) : δ 161.1, 151.0, 142.0, 132.8, 131.3, 128.1, 126.3, 125.3, 120.7, 118.3, 114.9, 111.01.

2-(4-Nitrophenyl)benzoxazole (**3ha**):[S3] 4-Nitrobenzaldehyde **1h** (75.6 mg, 0.5 mmol) was reacted with aminophenol **2a** (54.5 mg, 0.5 mmol) following the general procedure **C**. After purification by recrystalization DCM and hexane, 4-(Benzoxazol-2-yl)benzonitrile **3ha** was obtained as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 – 8.37 (m, 4H), 7.85 – 7.81 (m, 1H), 7.65 – 7.62 (m, 1H), 7.43 (tt, *J* = 7.4, 5.8 Hz, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) : δ 160.81, 151.18, 149.55, 142.07, 132.96, 128.55, 126.49, 125.38, 124.38, 120.84, 111.10.

2-(*tert*-Butyl)benzoxazole (**3ia**):[S3] Pivalaldehyde **1i** (54 μL, 0.5 mmol) was reacted with aminophenol **2a** (54.5 mg, 0.5 mmol) following the general procedure **C**. After purification by column chromatography (Ethyl acetate: Hexane = 1: 50), 2-(*tert*-Butyl)benzoxazole **3ia** was obtained as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.66 (m, 1H), 7.52 – 7.46 (m, 1H), 7.35 – 7.27 (m, 2H), 1.50 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 150.9, 141.2, 124.6, 124.1, 119.8, 110.5, 34.3, 28.6.

4-Methyl-2-phenylbenzoxazole (**3ab**):[S4] Benzaldehyde **1a** (51 μL, 0.5 mmol) was reacted with 2-Amino-3-methylphenol **2b** (61.6 mg, 0.5 mmol) following the general procedure **C**. After purification by column chromatography (Ethyl acetate: Hexane = 1: 100, 1: 30), 4-Methyl-2-phenylbenzoxazole **3ab** was obtained as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.21 (m, 3H), 7.61 – 7.47 (m, 4H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.21 (m, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 2.69 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 150.6, 141.5, 131.4, 130.7, 129.0, 127.7, 127.5, 125.2, 124.9, 108.0, 16.7.

5-Methyl-2-phenylbenzoxazole (**3ac**):[S4] Benzaldehyde **1a** (51 μL, 0.5 mmol) was reacted with 2-Amino-4-methylphenol **2c** (61.6 mg, 0.5 mmol) following the general procedure **C**. After purification by column chromatography (Ethyl acetate: Hexane = 1: 30), 5-Methyl-2-phenylbenzoxazole **3ac** was obtained as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 – 8.19 (m, 2H), 7.56 (s, 1H), 7.52 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3, 149.1, 142.4,

6-Methyl-2-phenylbenzoxazole (**3ad**):[S4] Benzaldehyde **1a** (51 μL, 0.5 mmol) was reacted with 2-Amino-5-methylphenol **2d** (61.6 mg, 0.5 mmol) following the general procedure **C**. After purification by column chromatography (Ethyl acetate: Hexane = 1: 50), 6-Methyl-2-phenylbenzoxazole **3ad** was obtained as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 – 8.21 (m, 2H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.39 (s,

1H), 7.18 (d, J = 8.0 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7, 151.1, 139.8, 135.8, 131.5, 129.0, 127.6, 127.3, 126.0, 119.4, 110.9, 22.0.

2,5-Diphenylbenzoxazole (**3ae**):[S5] Benzaldehyde **1a** (51 μL, 0.5 mmol) was reacted with 3-Amino-[1,1'-biphenyl]-4-ol **2e** (92.6 mg, 0.5 mmol) following the general procedure **C**. After purification by column chromatography (Ethyl acetate: Hexane = 1: 30), 2,5-Diphenylbenzoxazole **3ae** was obtained as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 – 8.25 (m, 2H), 7.98 (d, J = 1.7 Hz, 1H), 7.68 – 7.62 (m, 3H), 7.59 (dd, J = 8.5, 1.8 Hz, 1H), 7.58 – 7.52 (m, 3H), 7.48 (t, J = 7.7 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 150.5, 142.9, 141.2, 138.6, 131.7, 129.1, 129.0, 127.8, 127.6, 127.4, 127.3, 124.9, 118.6, 110.7.

5-Nitro-2-phenylbenzoxazole (**3af**):[S3] Benzaldehyde **1a** (51 μL, 0.5 mmol) was reacted with 2-Amino-4-nitrophenol **2f** (77.1 mg, 0.5 mmol) following the general procedure **C**. After purification by column chromatography (Ethyl acetate: Hexane = 1: 30), 5-Nitro-2-phenylbenzoxazole **3af** was obtained as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, J = 2.2 Hz, 1H), 8.33 (dd, J = 8.9, 2.3 Hz, 1H), 8.31 – 8.24 (m, 2H), 7.69 (d, J = 8.9 Hz, 1H), 7.65 – 7.54 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 154.5, 145.6, 142.7, 132.8, 129.3, 128.2, 126.1, 121.3, 116.5, 110.9.

2-Phenylbenzothiazole (**3ag**):[S4] Benzaldehyde **1a** (51 μL, 0.5 mmol) was reacted with 2-Aminothiophenol **2g** (62.6 mg, 0.5 mmol) following the general procedure **C**. After purification by column chromatography (Ethyl acetate: Hexane = 1: 50), 2-Phenylbenzothiazole **3ag** was obtained as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 – 8.06 (m, 3H), 7.91 (d, J = 7.9 Hz, 1H), 7.55 – 7.46 (m, 4H), 7.43 – 7.36 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 154.3, 135.2, 133.7, 131.1, 129.2, 127.7, 126.5, 125.3, 123.4, 121.8.

2-Pheny-1H-benzoimidazole (**3ah**):[S4] Benzaldehyde **1a** (51 μL, 0.5 mmol) was reacted with Benzene-1,2-diamine **2h** (54.1 mg, 0.5 mmol) following the general procedure **C**. After purification by column chromatography (Ethyl acetate: Hexane = 1: 3), 2-Pheny-1H-benzoimidazole **3ah** was obtained as a yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.90 (s, 1H), 8.25 – 8.12 (m, 2H), 7.67 (d, J = 7.6 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.53 – 7.46 (m, 1H), 7.28 – 7.13 (m, 2H); ^{13}C NMR (126 MHz, DMSO d_6) δ 151.20, 143.8, 135.0, 130.2, 129.8, 128.9, 126.4, 122.5, 121.6, 118.8, 111.3, 39.5.

PDI-Ph-Benzox (Perylenediimide-phenylbenzoxazole) (**3ja**): PDI-Ph-CHO (Perylenediimide-phenylaldehyde) **1j** (65.9 mg, 0.1 mmol) was reacted with 2-aminophenol **1a** (5.5 mg, 0.1 mmol) following the general procedure **D**. After purification by column chromatography (Ethyl acetate: Hexane = 1: 3), PDI-Ph-Benzox (Perylenediimide-phenylbenzoxazole) **3ja** was obtained as a red solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 – 8.59 (m, 4H), 8.58 (s, 1H), 8.46 – 8.41 (m, 2H), 8.12 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.69 – 7.62 (m, 3H), 7.45 – 7.38 (m, 2H), 5.02 (dtt, J = 28.4, 12.1, 3.7 Hz, 2H), 2.63 – 2.46 (m, 4H), 1.90 (t, J = 16.4 Hz, 4H), 1.82 – 1.68 (m, 4H), 1.53 – 1.38 (m, 4H), 1.38 – 1.29 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 163.7, 163.6, 162.3, 151.0, 145.9, 142.0, 140.3, 135.5, 134.8, 134.1, 134.1, 132.6, 131.1, 131.1, 130.3, 130.1, 129.6, 129.4, 129.0, 128.6, 128.0, 127.4, 127.4, 125.7, 125.0, 123.9, 123.7, 123.7, 123.2, 123.1, 122.9, 120.3, 110.9, 54.3, 54.1, 29.2, 29.2, 26.7, 26.6, 25.6, 25.5, 22.8.

8. Role of TEMPO species in each step of sequential reaction from the reported references

In the first step of the sequential reaction, based on the reported mechanism of the oxidation of alcohols (Fig. S1),[S1] TEMPO species participates the oxidation of alcohol in the form of TEMPO oxoammonium.[S11, S12] Thermally unstable TBN releases NO_x radicals, which in turn oxidize the TEMPO radical to form TEMPO oxoammonium.[S13] This oxoammonium species is reduced to the hydroxylamine species by oxidizing the alcohol moiety to aldehyde. Afterwards, hydroxylamine species can be regenerated into oxoammonium species through NO_x radicals and continue to participate in the catalytic cycle.

In the second step of the sequential reaction, based on the previously proposed mechanism of the oxidative cyclization (Fig. S2),[S3] TEMPO radical instead of the TEMPO oxoammonium participates the oxidative cyclization. Therefore, the presence of NO_x radicals which able to change TEMPO species from radical to oxoammonium could suppress the oxidative cyclization and adding PTIO, which is known to quench NO_x radicals, could resulting higher conversion rate.

In order to confirm the role of the additives in the second steps, control experiments were conducted (Table S5). Based on entry 1 and 2, oxidative cyclization was suppressed by the presence of the TBN addictive, which thermolyzed by NO_x radical and tert-butoxyl radical or tert-butyl alcohol.[S14, S15] However, *tert*-butyl alcohol (entry 3) and di-*tert*-butylperoxide (DTBP) (entry 4) did not significantly affect reactivity. Therefore, we thought that NO_x radicals generated due to thermolysis of TBN may have influenced the oxidative cyclization in the second reaction. This is further supported by entry 5, which shows that the oxidative cyclization reaction increases from 16% (entry 1) to 77% (entry 5) by adding PTIO, which is known to quench NO_x radicals,[S16-S18] to the second reaction. Note that the presence of PTIO solely showed minor effects in oxidative cyclization (entry 6).

9. Supplementary Tables and Figures

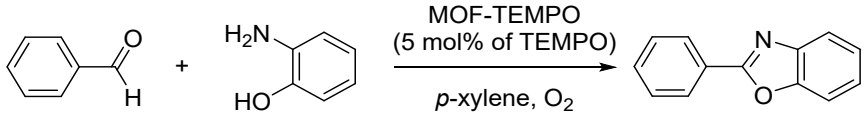
Table S1 BET values of UiO-68-$(TEMPO)_x(Me_2)_{1-x}$ (x = 1.0, 0.75, 0.25, and 0) from N_2 isotherm at 77 K.

Sample	BET surface area
UiO-68-$(TEMPO)_{1.0}$	2,155 m^2/g
UiO-68-$(TEMPO)_{0.75}(Me_2)_{0.25}$	2,529 m^2/g
UiO-68-$(TEMPO)_{0.50}(Me_2)_{0.50}$	2,686 m^2/g
UiO-68-$(TEMPO)_{0.25}(Me_2)_{0.75}$	3,071 m^2/g
UiO-68-$(Me_2)_{1.0}$	3,751 m^2/g

Table S2 Total mass of TEMPO-immobilized MOFs and mol fraction of TEMPO.

Sample	Molecular formula $[Zr_6O_4(OH)_4(H_2tpdc\text{-}TEMPO)_x](H_2tpdc\text{-}Me_2)_{6-X}]$	Molecular weight of MOF (g/mol)	TEMPO loading (mmol/g)
UiO-68-$(TEMPO)_{1.0}$	$[Zr_6O_4(OH)_4(C_{30}H_{31}N_2O_6)_6]$	3760.6	1.60
UiO-68-$(TEMPO)_{0.75}(Me_2)_{0.25}$	$[Zr_6O_4(OH)_4(C_{30}H_{31}N_2O_6)_{4.5}(C_{22}H_{18}O_4)_{1.5}]$	3506.9	1.28
UiO-68-$(TEMPO)_{0.50}(Me_2)_{0.50}$	$[Zr_6O_4(OH)_4(C_{30}H_{31}N_2O_6)_{3.0}(C_{22}H_{18}O_4)_{3.0}]$	3252.9	0.92
UiO-68-$(TEMPO)_{0.25}(Me_2)_{0.75}$	$[Zr_6O_4(OH)_4(C_{30}H_{31}N_2O_6)_{1.5}(C_{22}H_{18}O_4)_{4.5}]$	2999.5	0.50
UiO-68-$(Me_2)_{1.0}$	$[Zr_6O_4(OH)_4\ (C_{22}H_{18}O_4)_{6.0}]$	2745.6	-

Table S3 Effects of immobilization amounts in UiO-68-TEMPO for the oxidative cyclization of **1a** and **2a** to **3aa**.[a]



1a **2a** **3aa**

Entry	Time (h)	**X** in UiO-68-$(TEMPO)_x(Me_2)_{1-x}$			
		1.0	0.75	0.5	0.25
1[b]	24	87	-	86	-
2	6	50	40	32	31
3	12	69	63	62	39
4	16	81	77	75	51
5	24	86	86	85	73
6	48	89	88	88	85
TOF_{6h} of catalysts		0.83	0.66	0.54	0.51
TON_{6h} of catalysts		5.00	4.00	3.25	3.08

[a] Reaction conditions: 1a (0.5 mmol), 2a (0.5 mmol), catalyst and solvent (1 mL) were used for the reaction optimization. [b] MOF-TEMPO (10 mol% of TEMPO) was used.

Table S4 Correlations between the maximum yields and catalyst-loading in various MOF-based catalysts from literature.

Target reaction	MOF	Catalyst in MOF	Yield from optimized cat. loading (%)	Yield from maximum cat. loading (%)	Ref.
Henry reaction	UiO-67	Urea	**67%** yield with 36% loading	**19%** yield with 100% loading	S6
Henry reaction	PCN-56	Urea	**90%** yield with 50% loading	**41%** yield with 100% loading	S7
Friedel-Craft reaction	UiO-67	Squaramide	**78%** yield with 50% loading	**22%** yield with 100% loading	S8
Aerobic oxidation	UiO-67	TEMPO	**99%** yield with 38% loading	**60%** yield with 100% loading	S9
H_2 generation	MIL-125	Pt and sulfide	**3814.0 μmolg^{-1}h^{-1}** with 20% loading	**2972.4 μmolg^{-1}h^{-1}** yield with 50% loading	S10

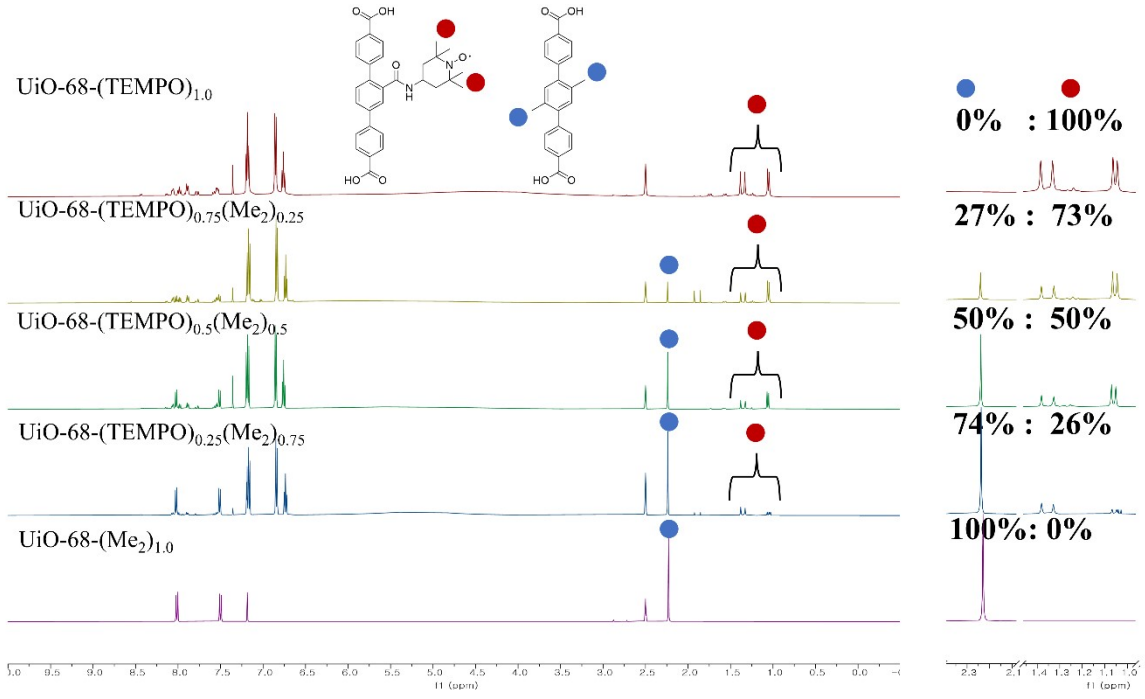


Fig. S1 ^{1}H NMR spectra of UiO-68-(TEMPO)$_x$(Me$_2$)$_{1-x}$ (x = 1.0, 0.75, 0.25, and 0) after digestion (stabilized with phenylhydrazine).

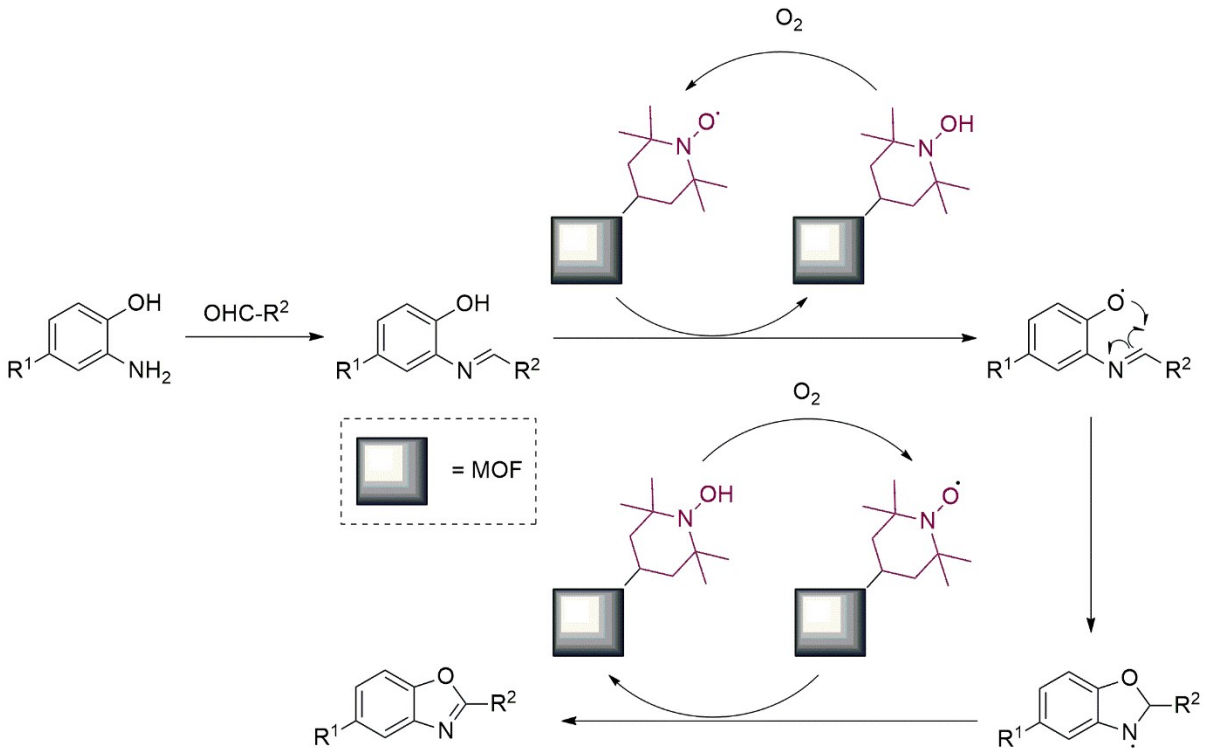
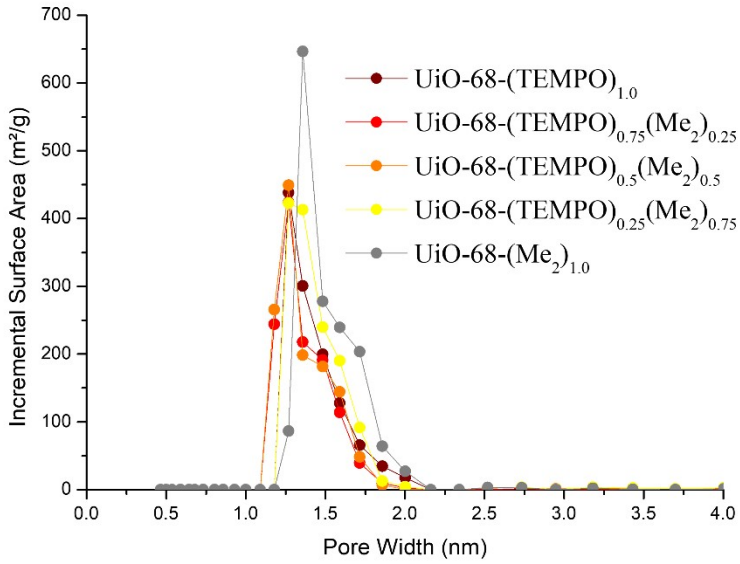


Fig. S2 A proposed mechanism of MOF-TEMPO-catalyzed aerobic oxidative cyclization toward 2-substituted benzoxazoles.[S3]

a)



b)

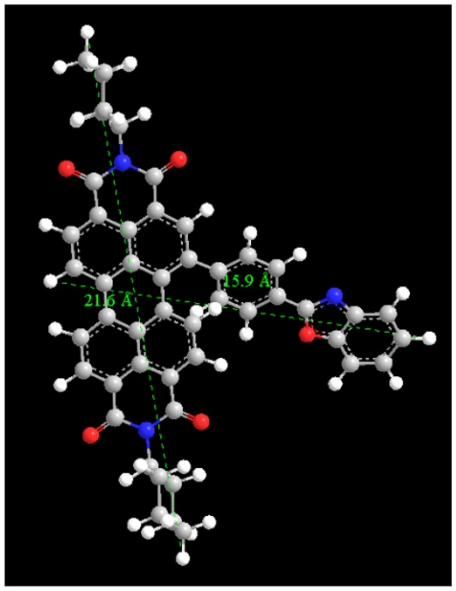


Fig. S3 (a) DFT pore size distribution of UiO-68-$(TEMPO)_x(Me_2)_{1-x}$ (x = 1.0, 0.75, 0.25, and 0). (b) Molecular size of PDI-benzoxazole (**3ja**) optimized by MM2 calculation.

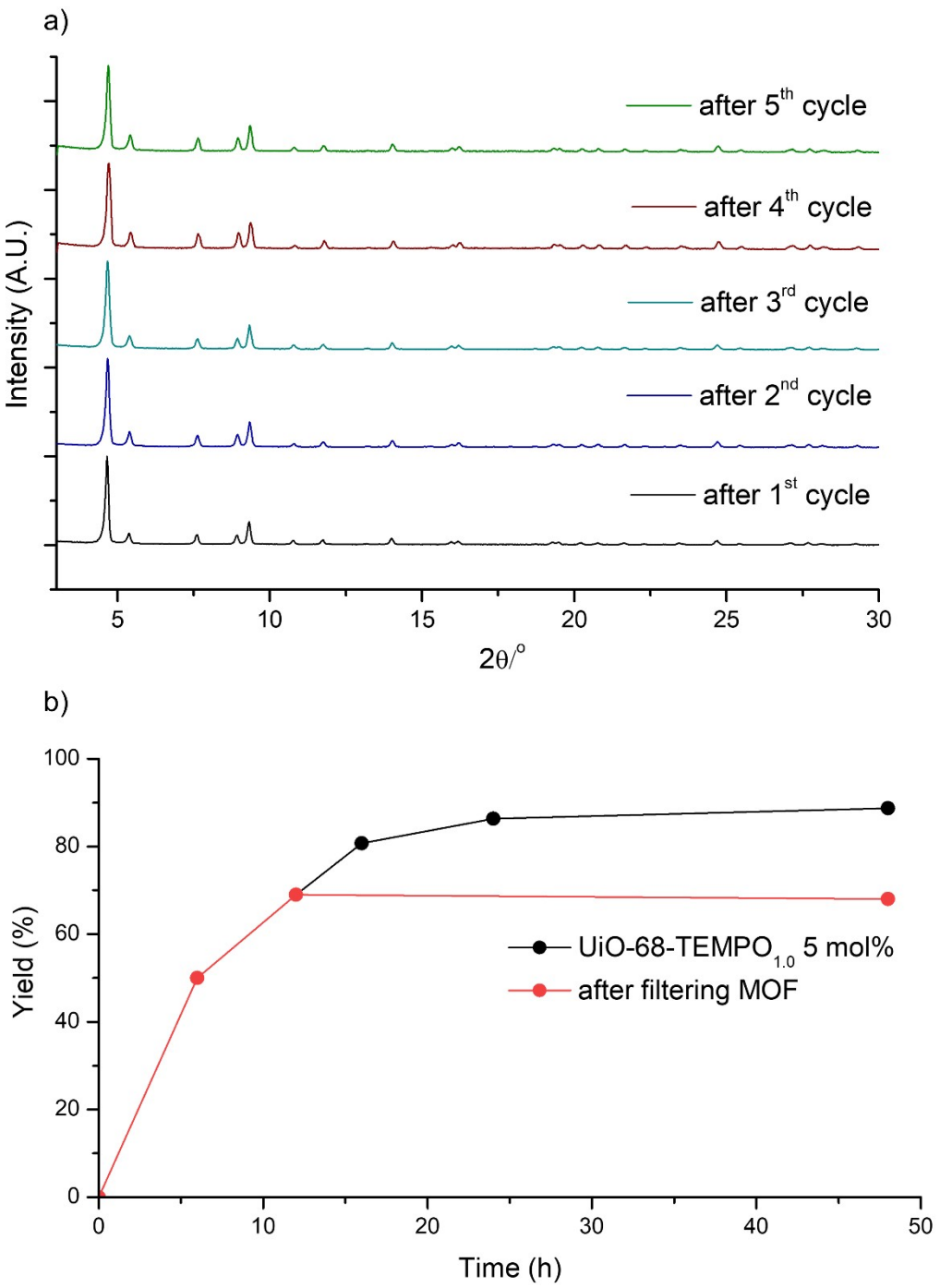


Fig. S4 (a) PXRD patterns of the recovered UiO-68-$(TEMPO)_{1.0}$ from oxidative cyclization. (b) Hot filtration test (12 h) to proof heterogeneity of UiO-68-$(TEMPO)_{1.0}$ catalyzed oxidative cyclization.

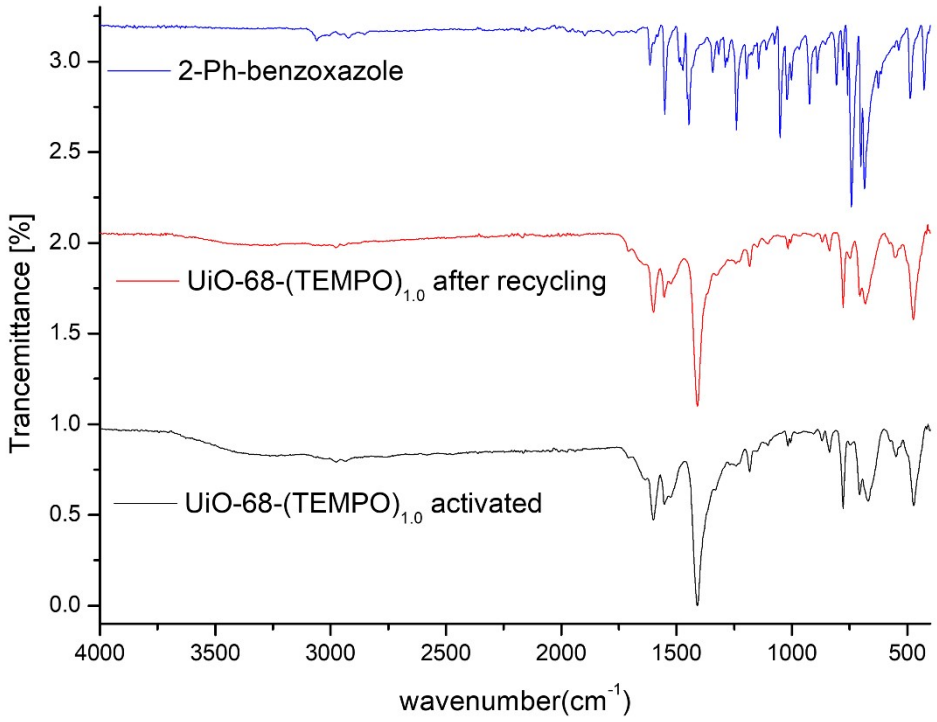


Fig. S5 FT-IR spectra of the 2-Ph-benzoxazole (**3aa**), UiO-68-(TEMPO)$_{1.0}$, and UiO-68-(TEMPO)$_{1.0}$ after 5 cycling from oxidative cyclization.

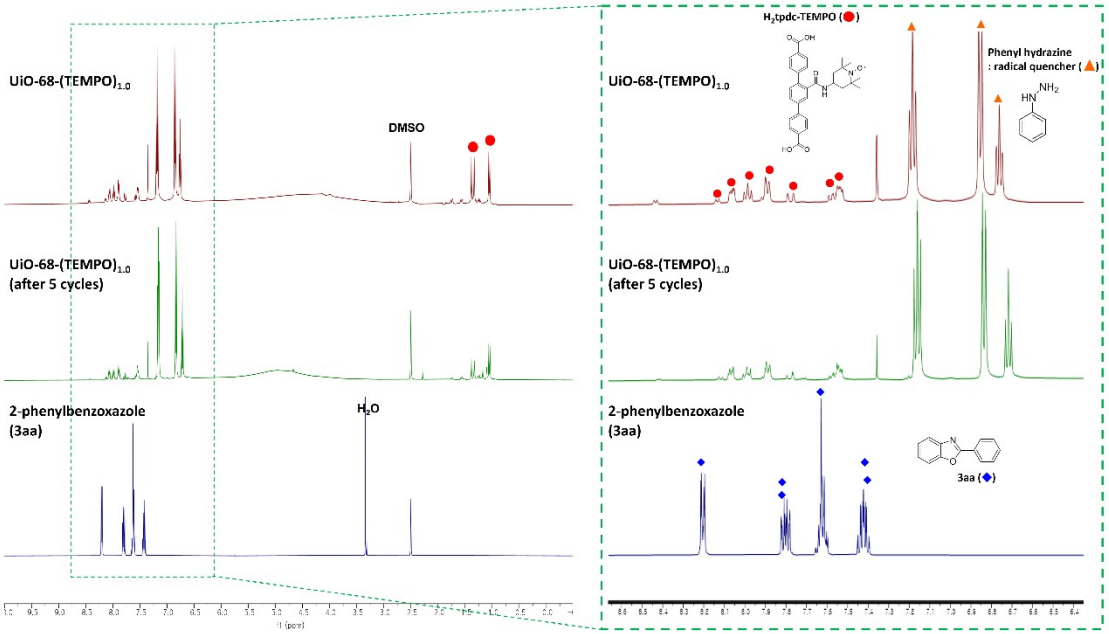


Fig. S6 ^{1}H-NMR spectra of the 2-Ph-benzoxazole (**3aa**), UiO-68-(TEMPO)$_{1.0}$, and UiO-68-(TEMPO)$_{1.0}$ after 5 cycling from oxidative cyclization. The spectra in the green lined box are the enlargement of the high chemical shift region in the ^{1}H-NMR spectra (DMSO-d_6 was used for NMR solvent).

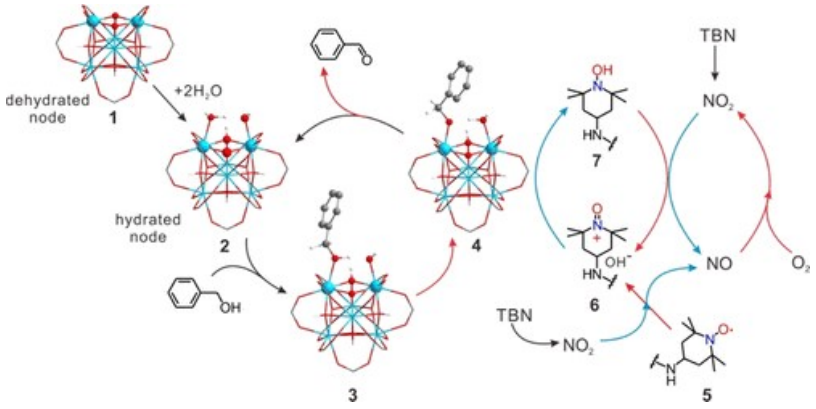


Fig. S7 Proposed catalytic cycle of oxidation of benzyl alcohol in UiO-68-TEMPO. TEMPO moiety participates the catalytic cycle as TEMPO oxoammonium species in alcohol oxidation.

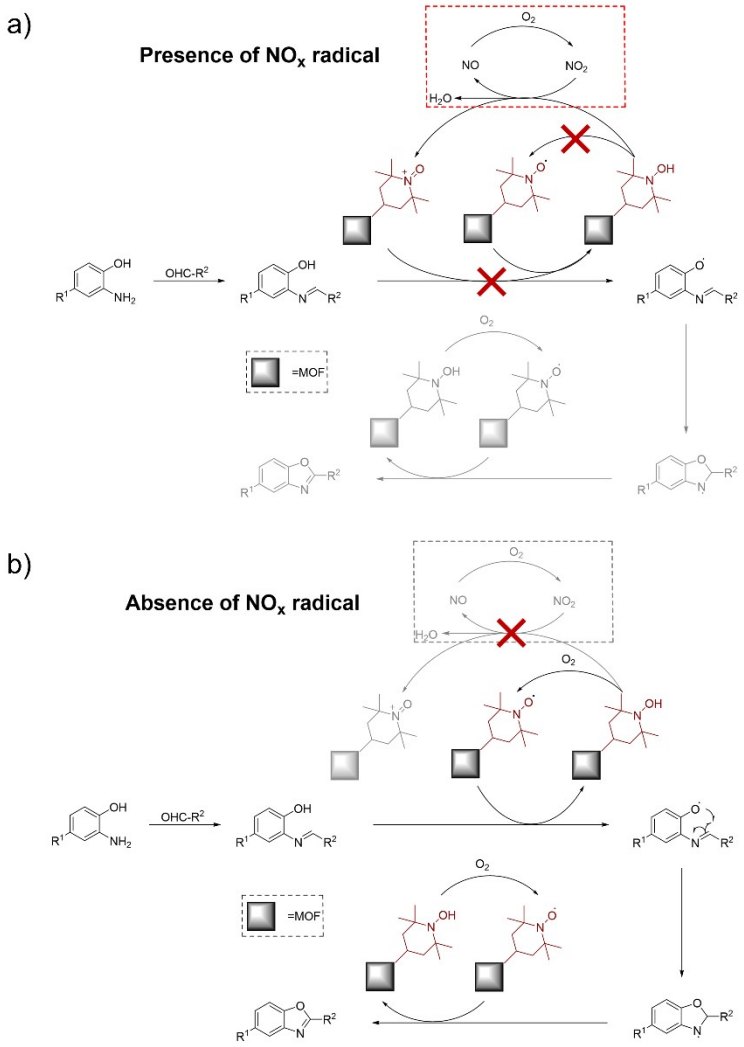


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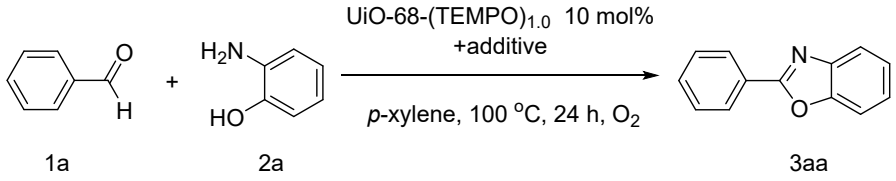
Fig. S8 Proposed catalytic cycle of mechanism of oxidative cyclization presence (a)/absence

(b) of NO_x species.

Table S5 Oxidative cyclization with various additives. Reaction conditions: 10 mol% of UiO-68-(TEMPO)$_{1.0}$, 100 °C, reaction time 24 h, *p*-xylene solvent system, and additives.



1a 2a 3aa

entry	additive	quantity	Catalyst (mol%)	Yield (%)
1	Benzyl alcohol	10 mol%	10	82%
2	TBN	10 mol%	10	19%
3	*t*-BuOH	10 mol%	10	83%
4	DTBP	10 mol%	10	89%
5	TBN+PTIO	10 mol%	10	76%
6	PTIO	10 mol%	10	79%

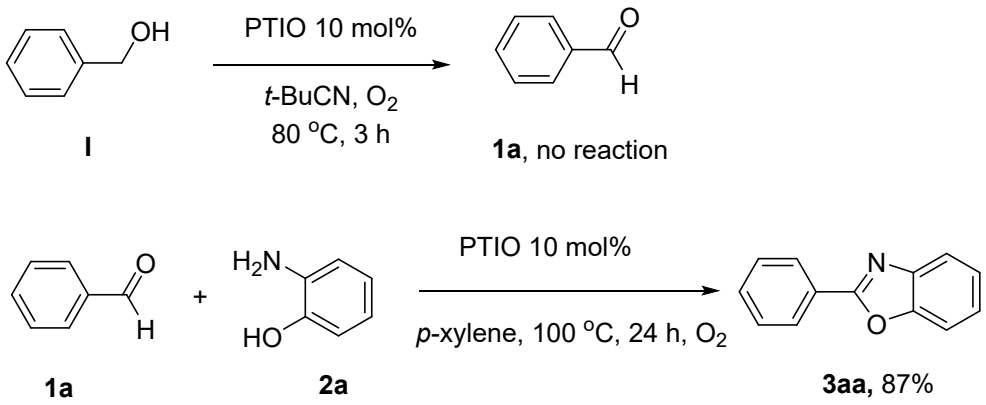


Fig. S9 Catalytic activity of PTIO for the aerobic oxidation of **I** to **1a** and oxidative cyclization between **1a** and **2a**.

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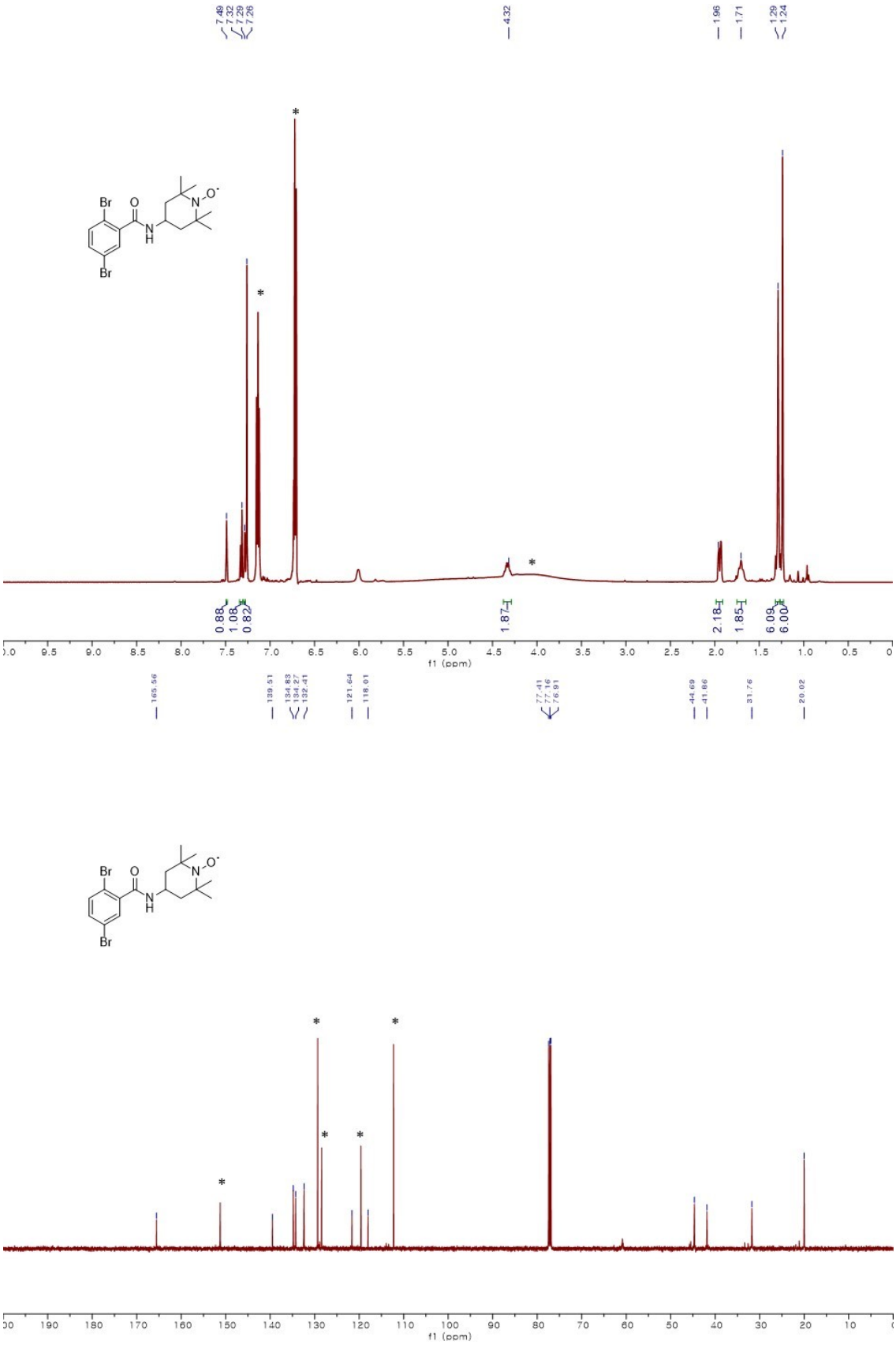
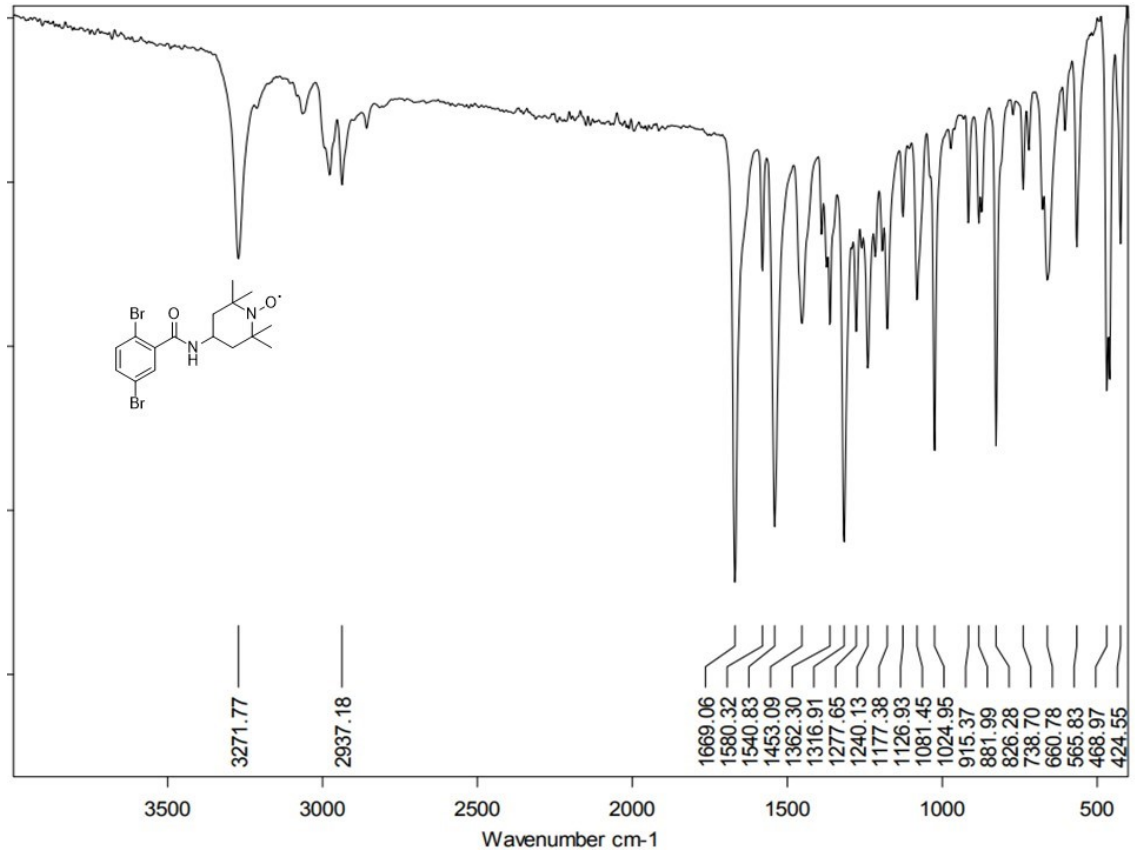
APPENDIX I

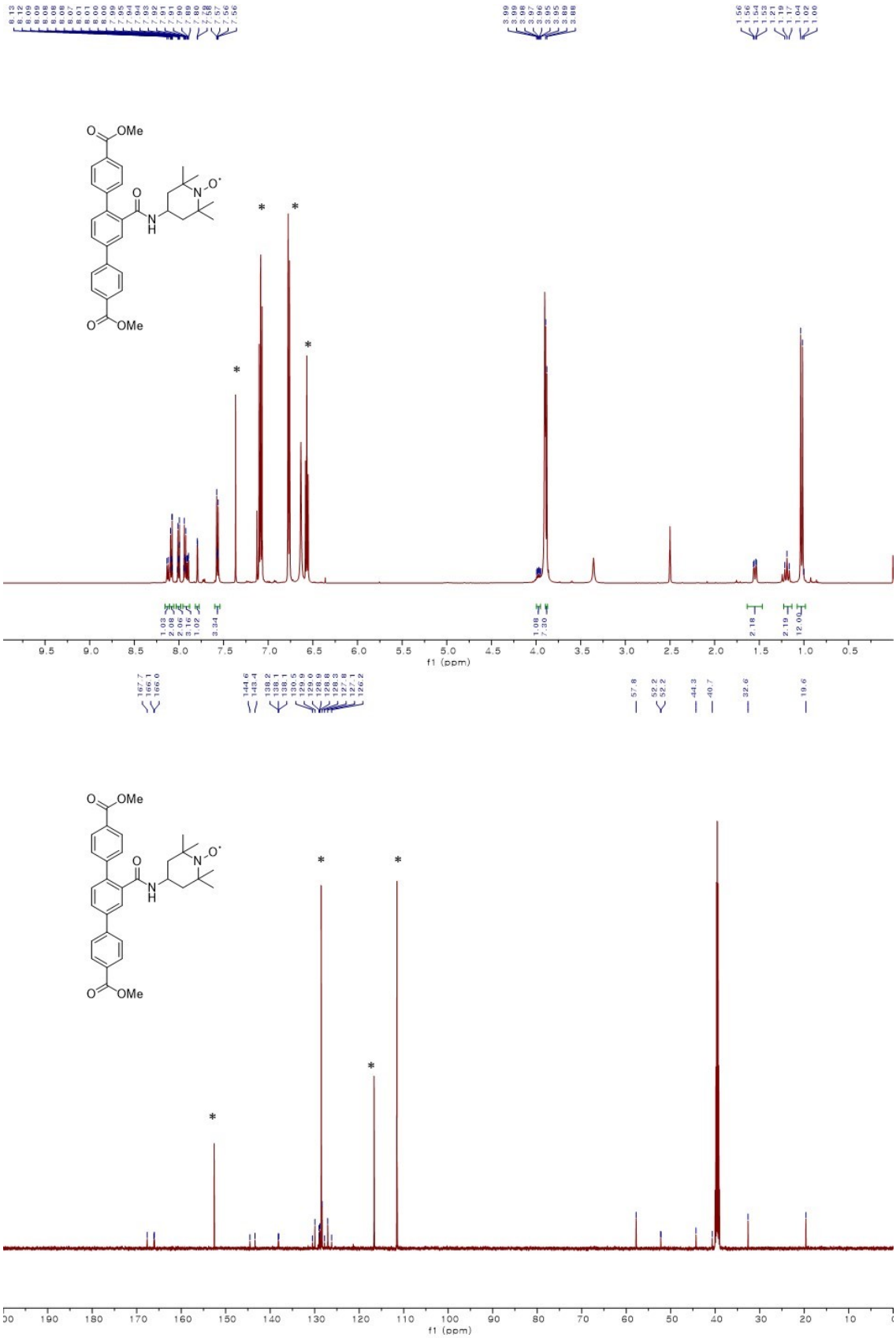
^{1}H NMR, ^{13}C NMR, and FT-IR of the obtained molecules

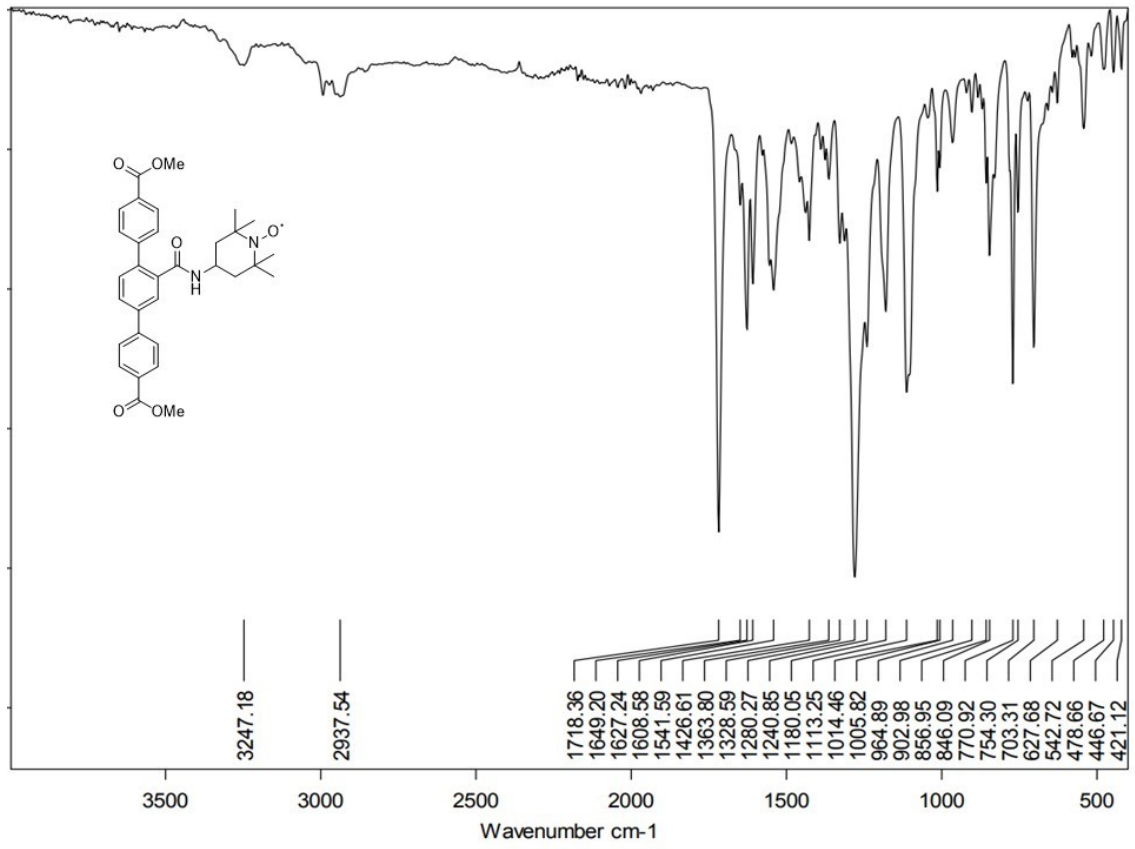
Ph-Br_2-TEMPO (* from phenylhydrazine)



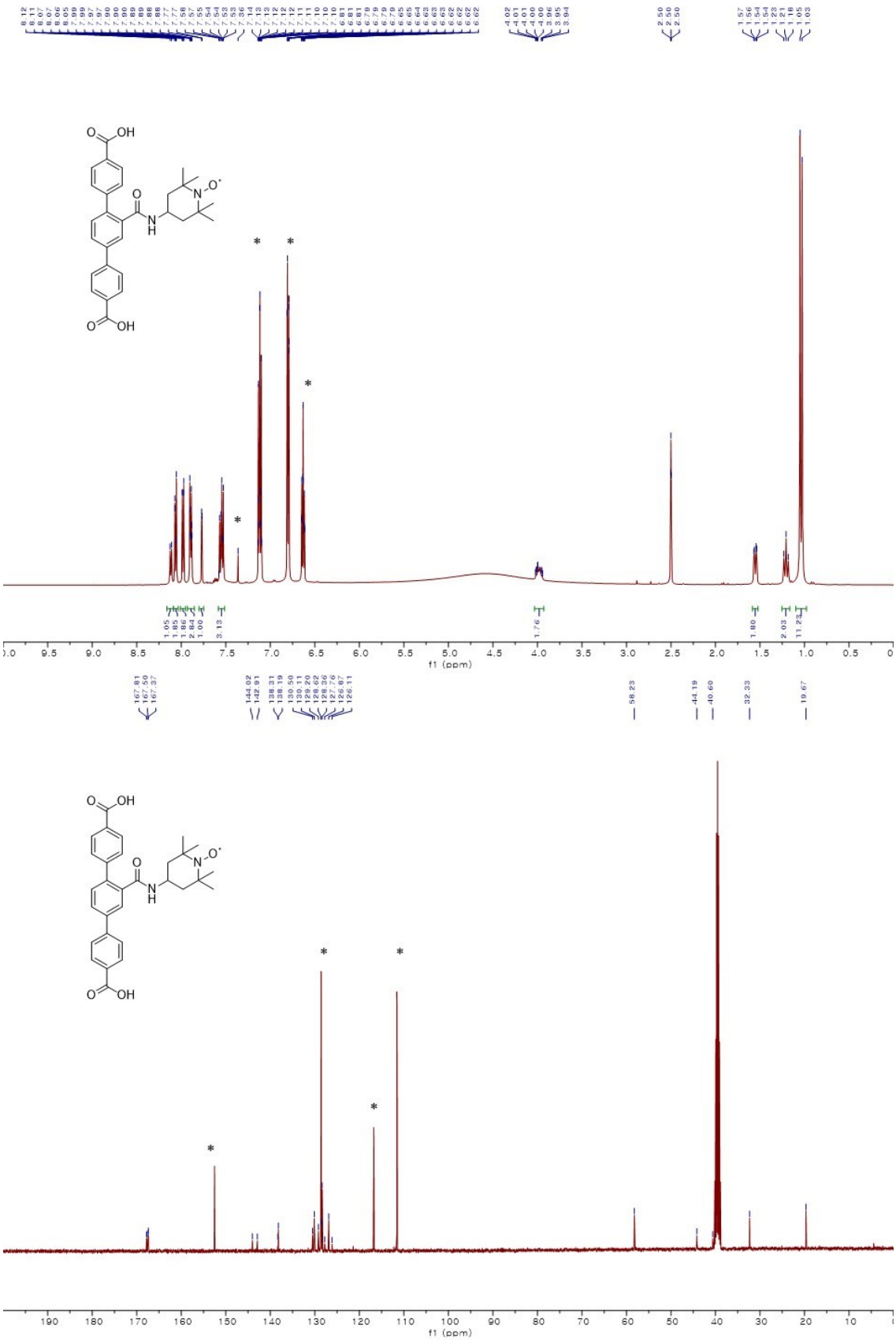

Br
O
N
O
H
Br
3271.77
2937.18
1669.06
1580.32
1540.83
1453.09
1362.30
1316.91
1277.65
1240.13
1177.38
1126.93
1081.45
1024.95
915.37
881.99
826.28
738.70
660.78
565.83
468.97
424.55
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

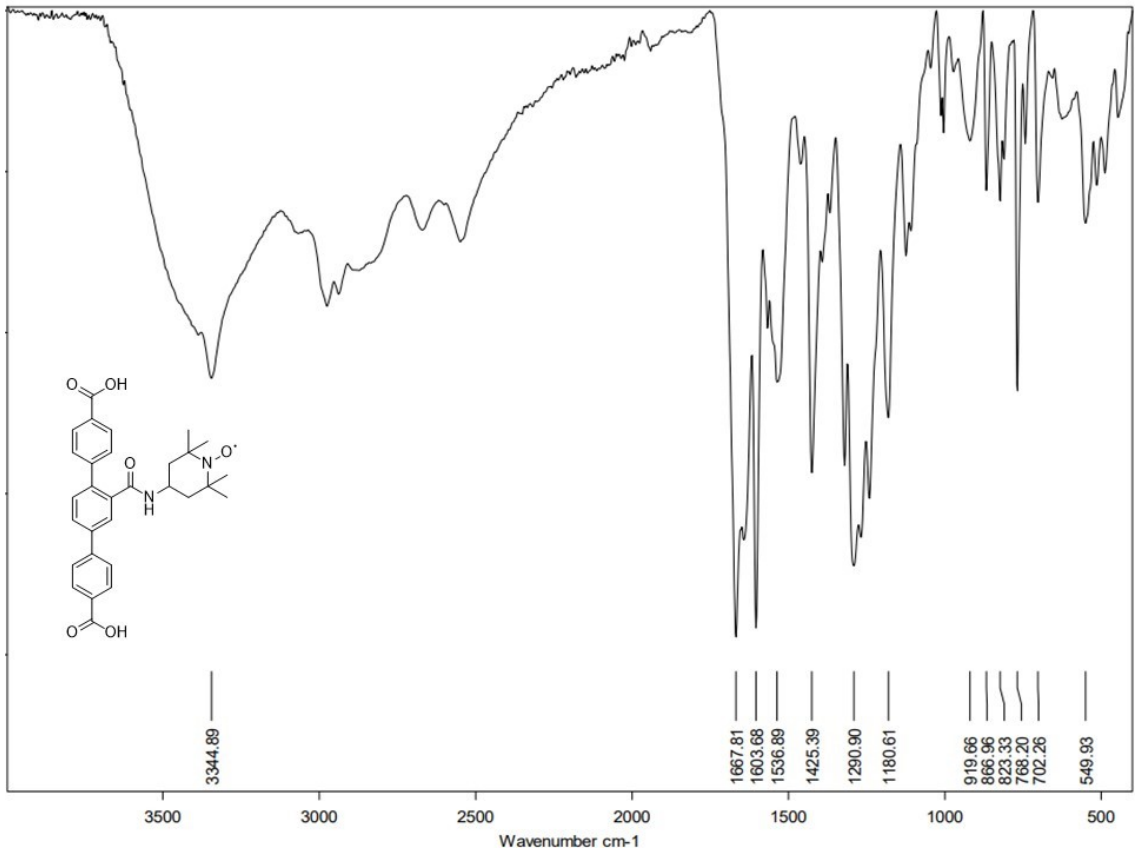
TPDC-TEMPO (* from phenylhydrazine)



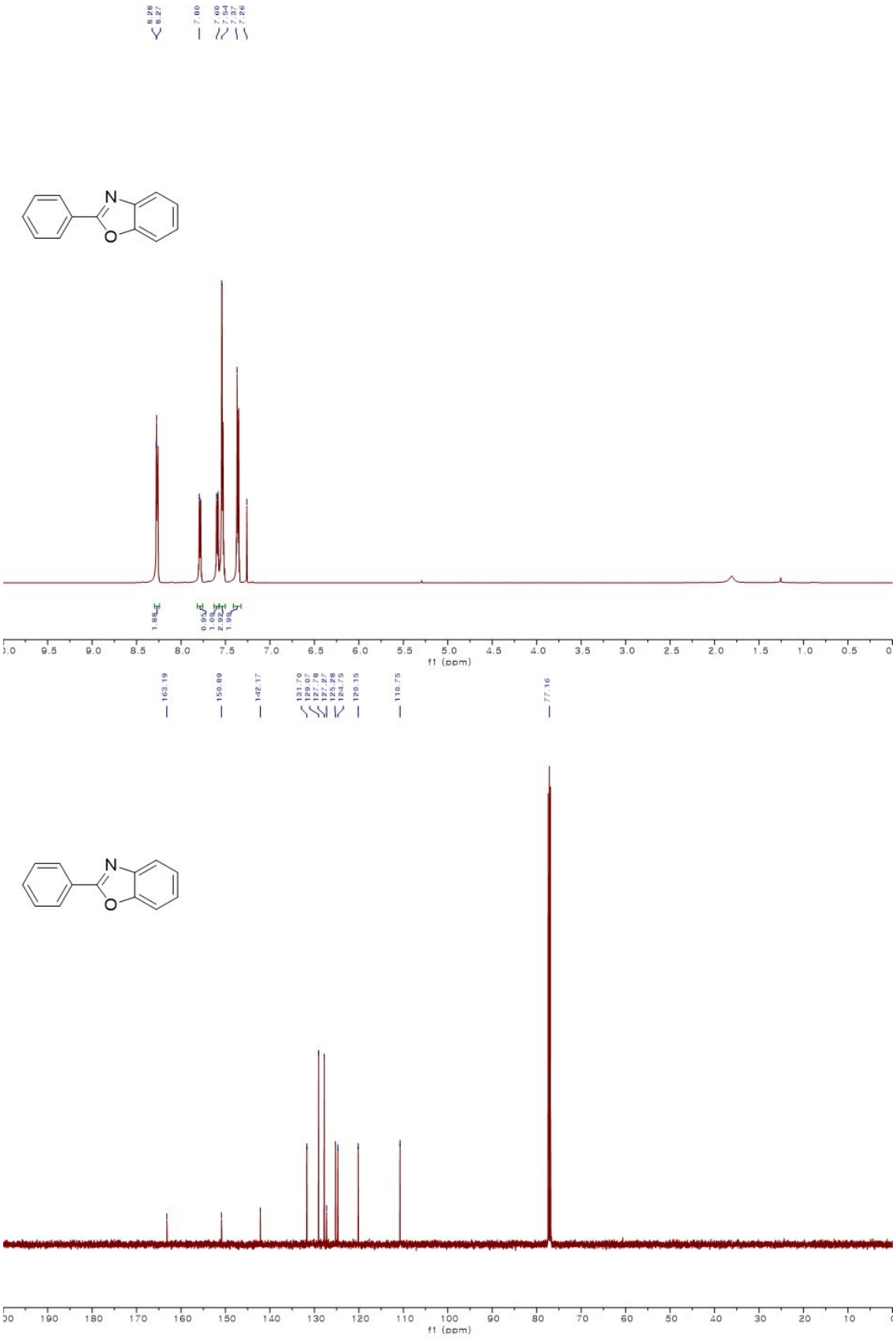

OMe
O
O
N
H
N
O
OMe
3247.18
2937.54
1718.36
1649.20
1627.24
1608.58
1541.59
1426.61
1363.80
1328.59
1280.27
1240.85
1180.05
1113.25
1014.46
1005.82
964.89
902.98
856.95
846.09
770.92
754.30
703.31
627.68
542.72
478.66
446.67
421.12
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

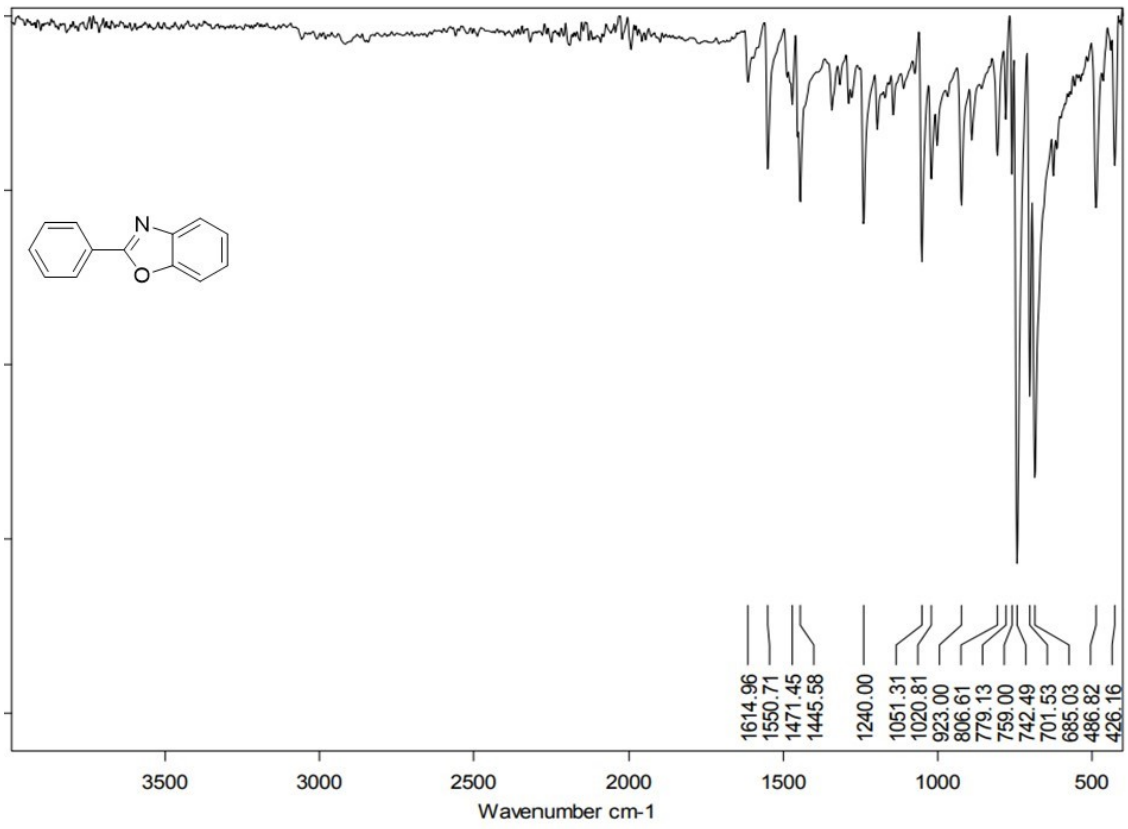
H_2tpdc-TEMPO (* from phenylhydrazine)



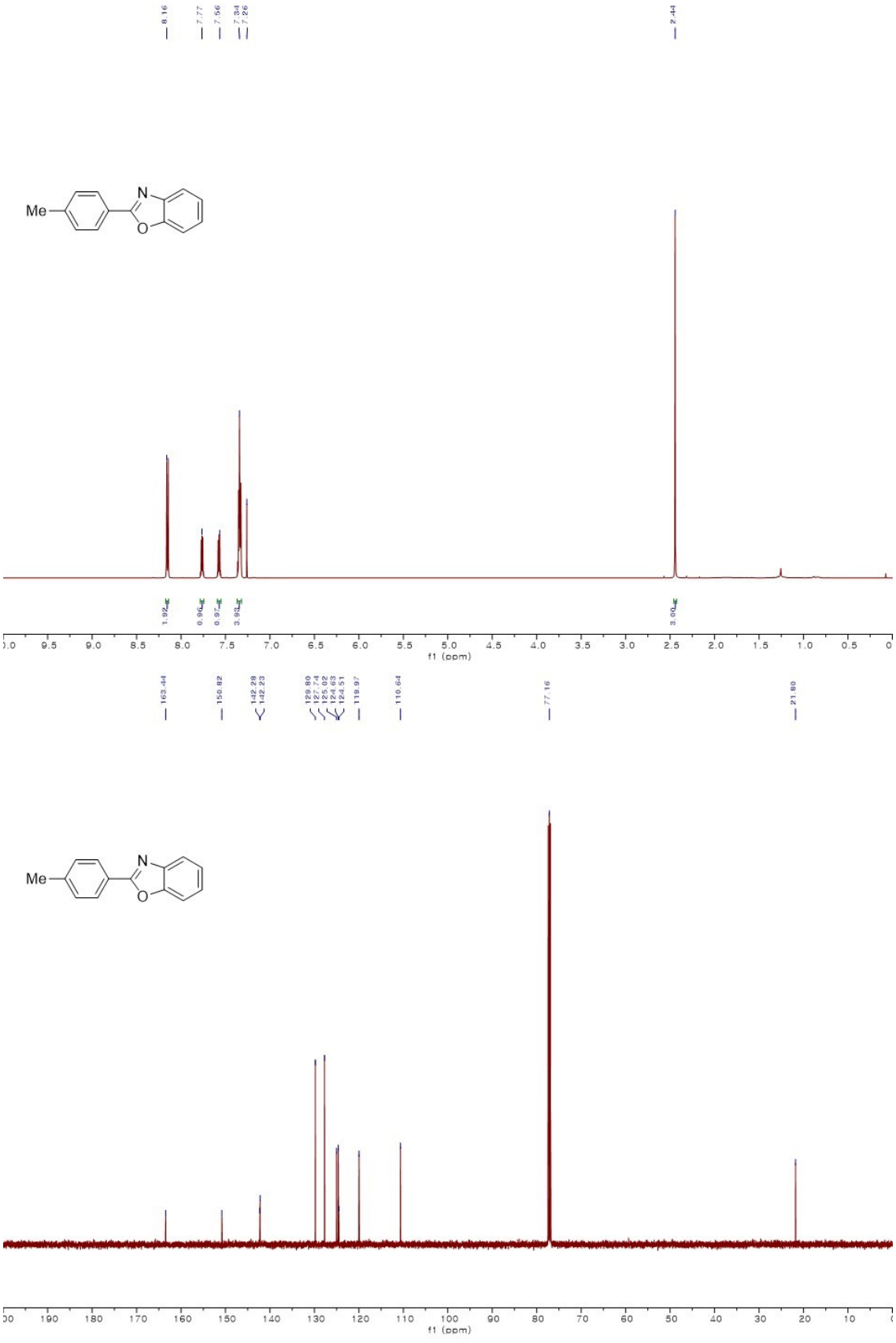

3344.89
1667.81
1603.68
1536.89
1425.39
1290.90
1180.61
919.66
866.96
823.33
768.20
702.26
549.93
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

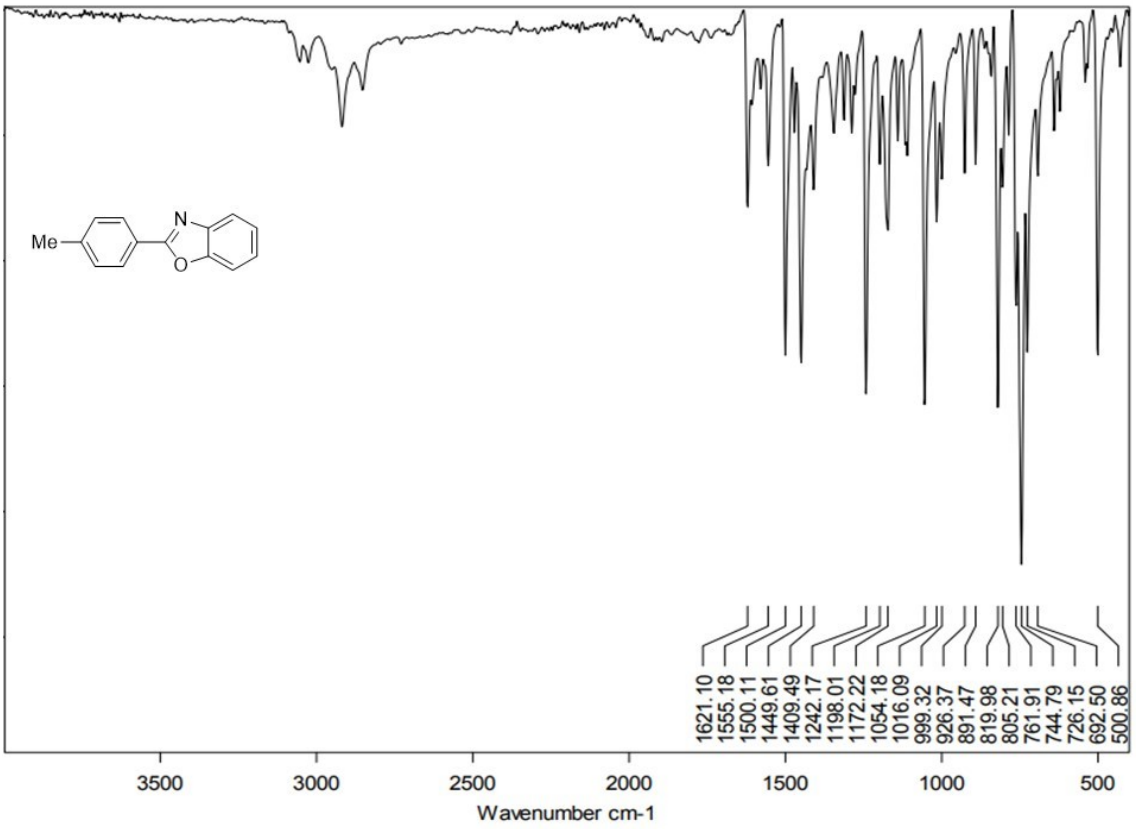
2-Phenylbenzoxazole (**3aa**)



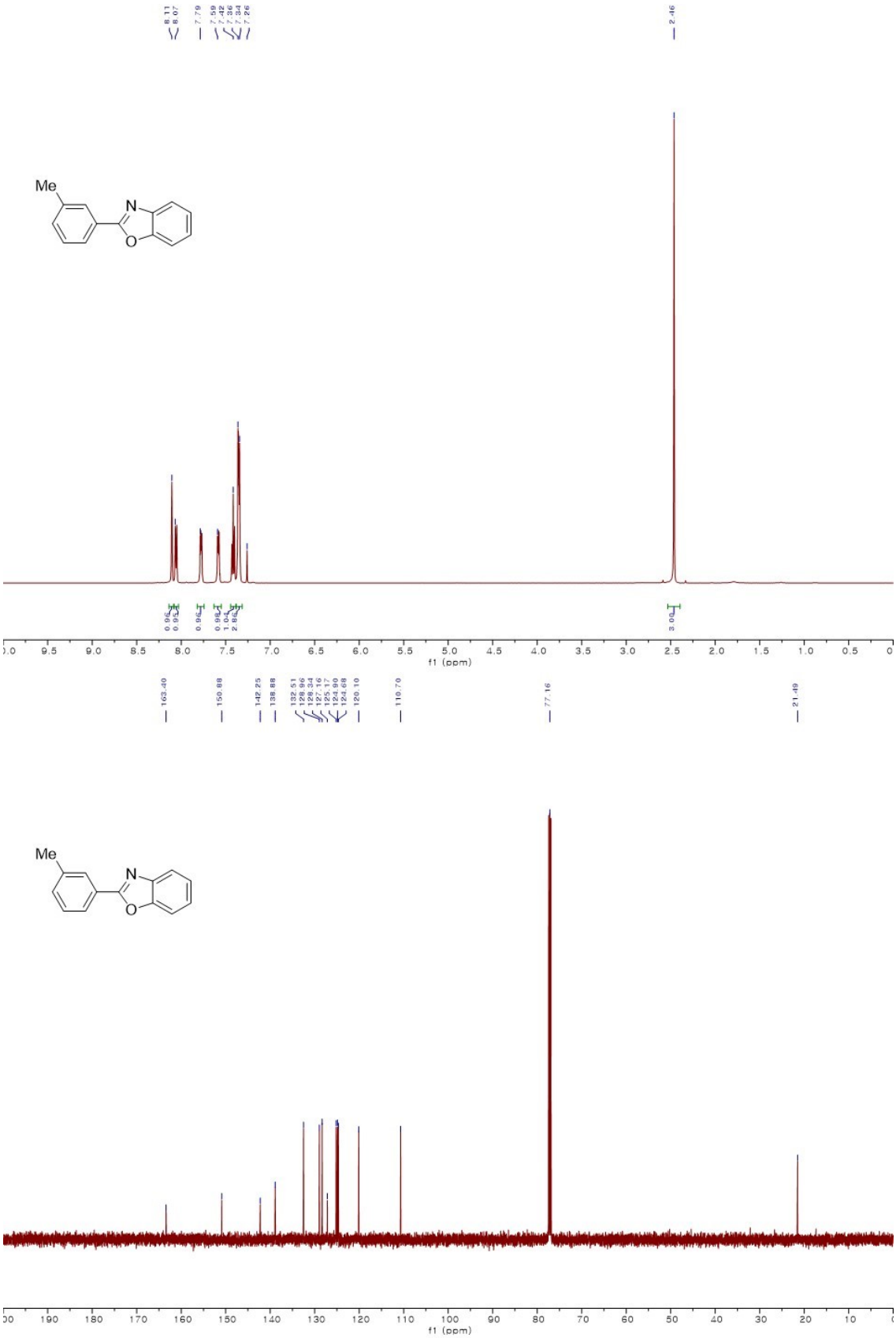

N
O
1614.96
1550.71
1471.45
1445.58
1240.00
1051.31
1020.81
923.00
806.61
779.13
759.00
742.49
701.53
685.03
486.82
426.16
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

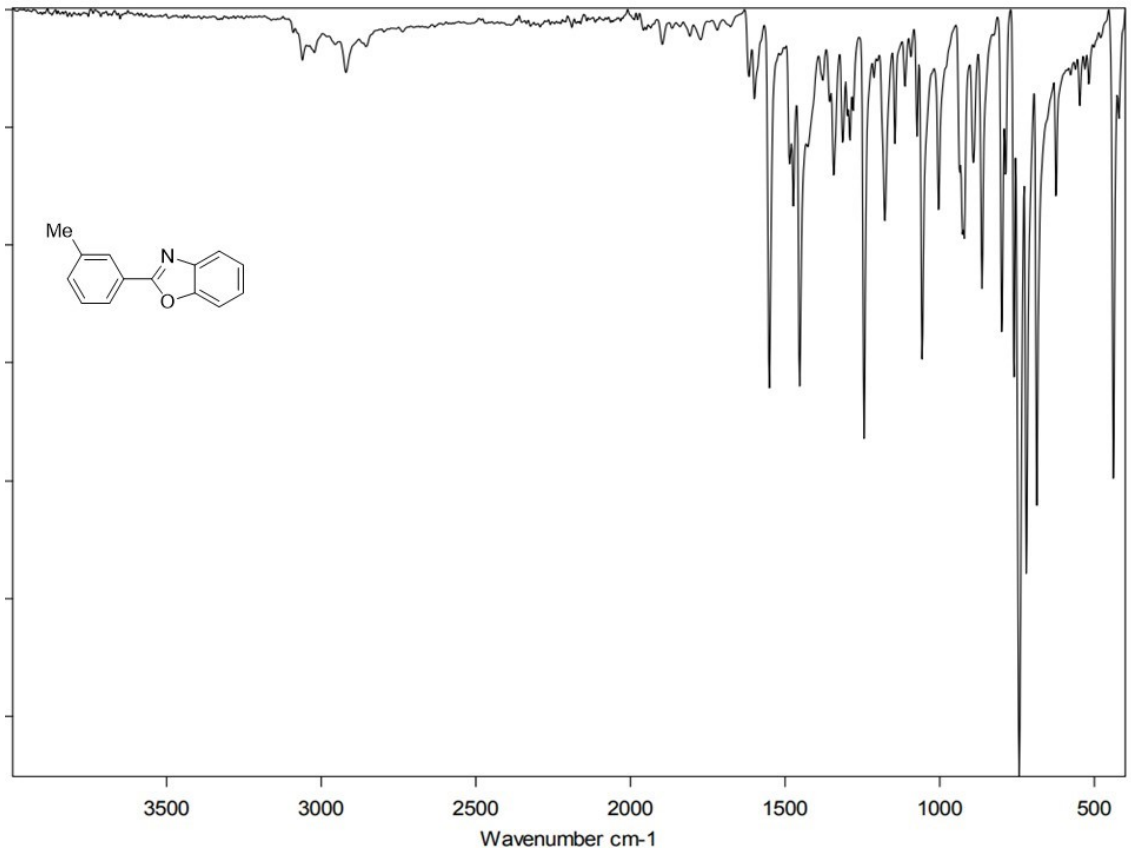
2-(*p*-Tolyl)benzoxazole (**3ba**)



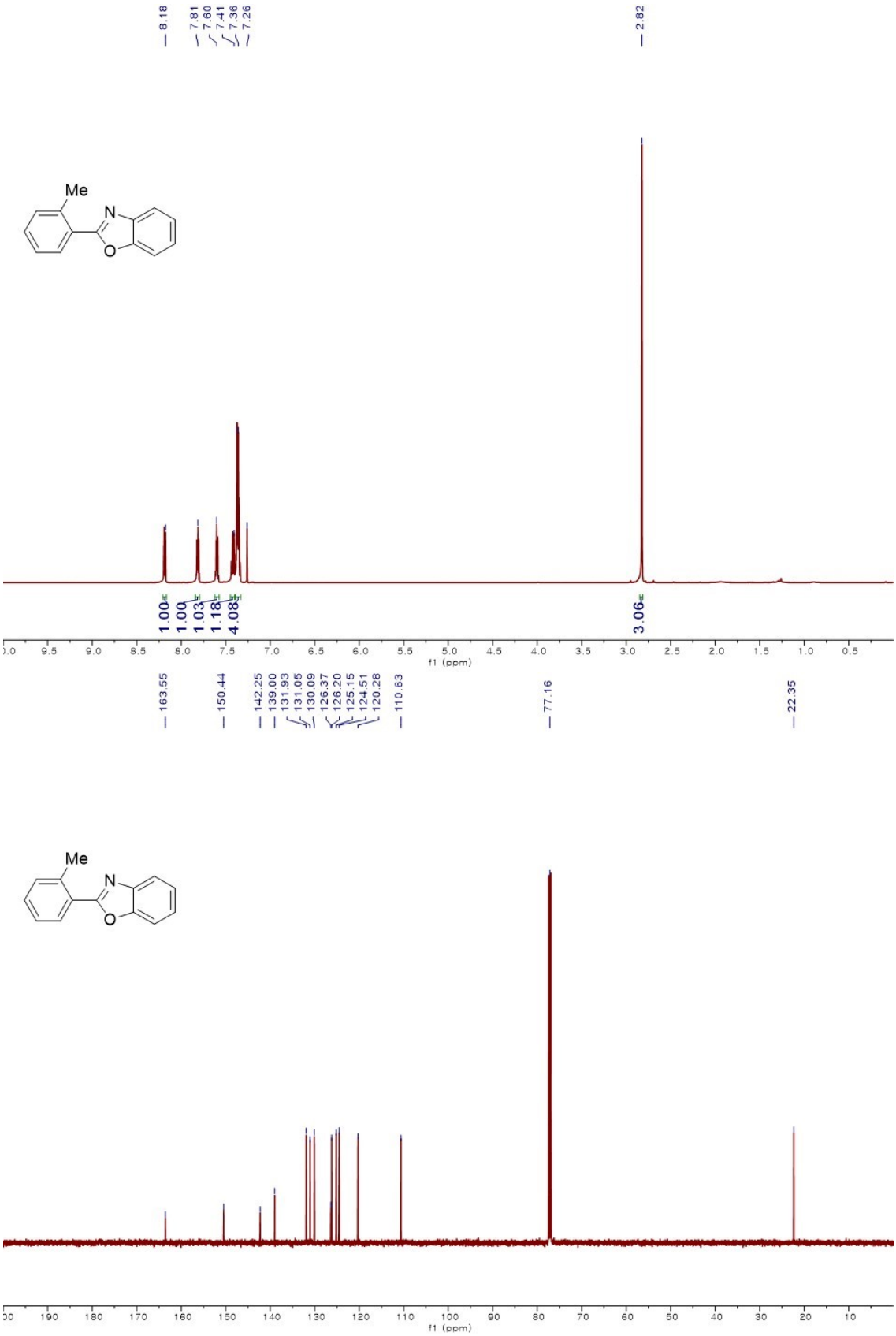

Me
N
O
1621.10
1555.18
1500.11
1449.61
1409.49
1242.17
1198.01
1172.22
1054.18
1016.09
999.32
926.37
891.47
819.98
805.21
761.91
744.79
726.15
692.50
500.86
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

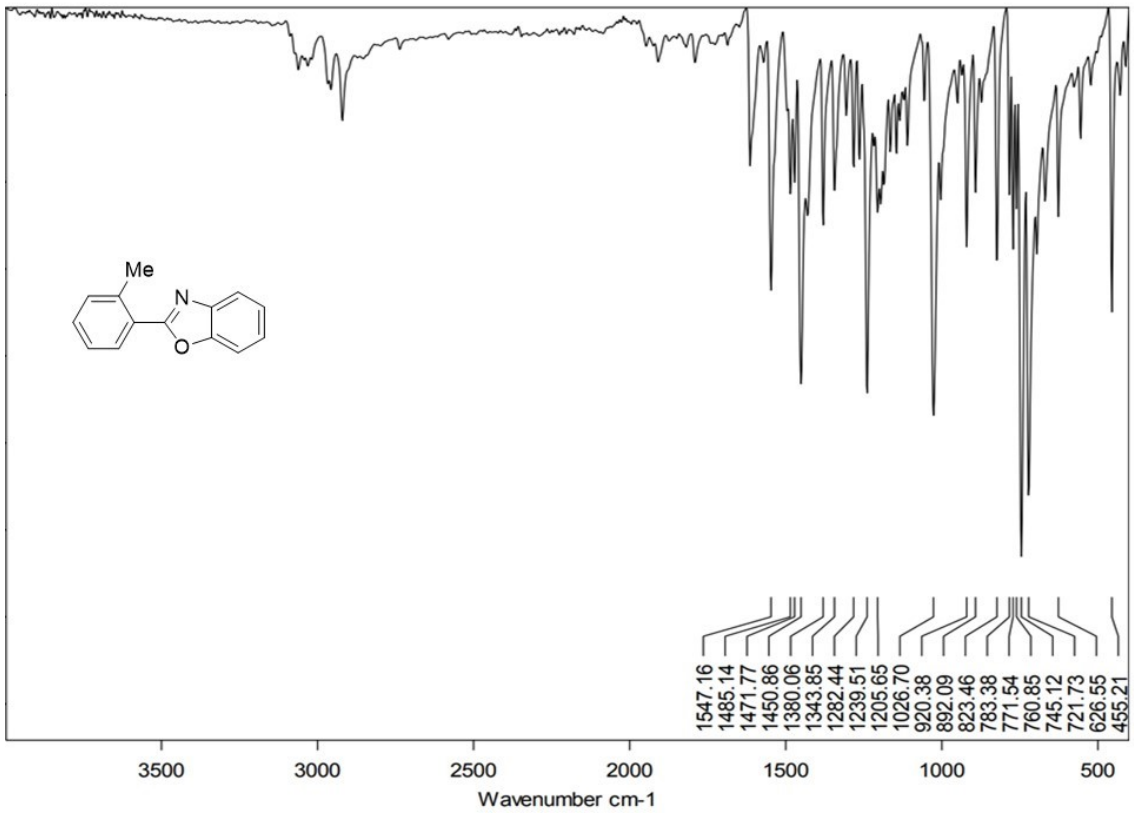
2-(*m*-Tolyl)benzoxazole (**3ca**)



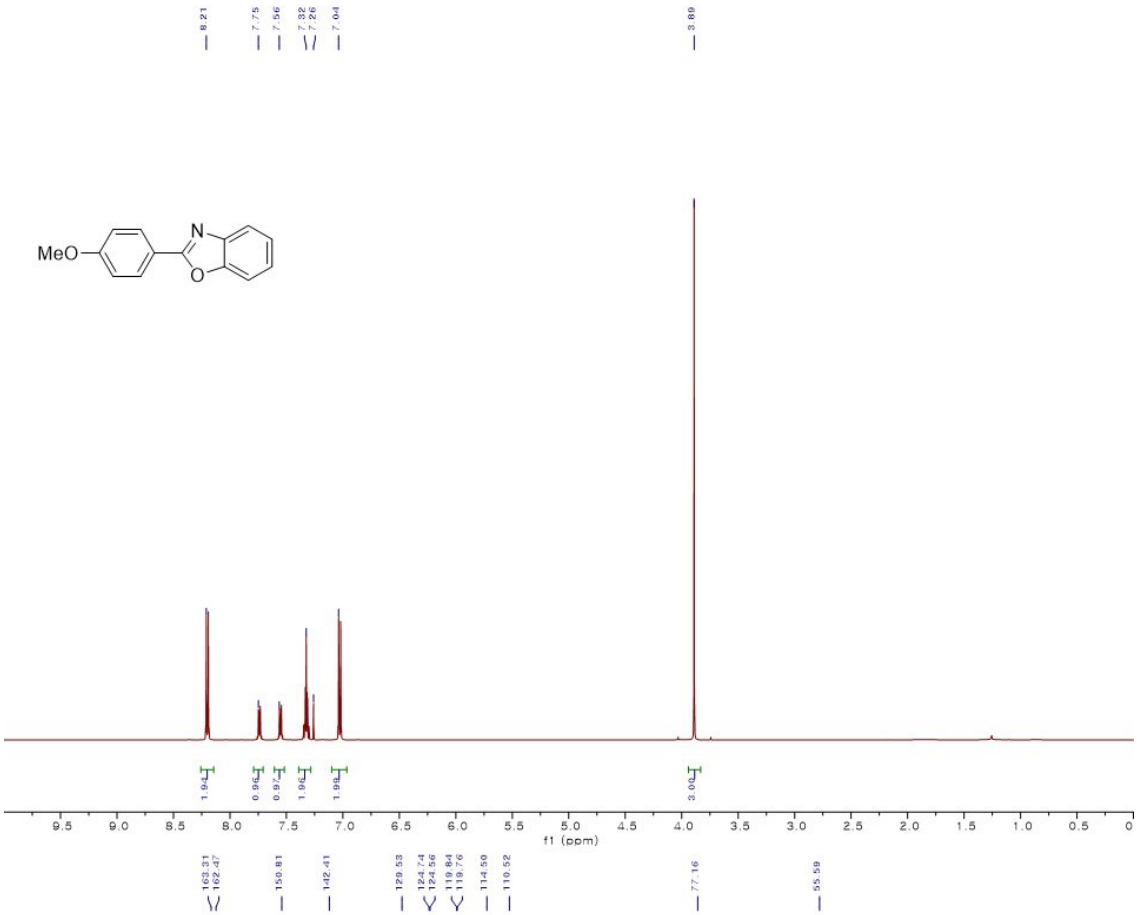

Me
N
O
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

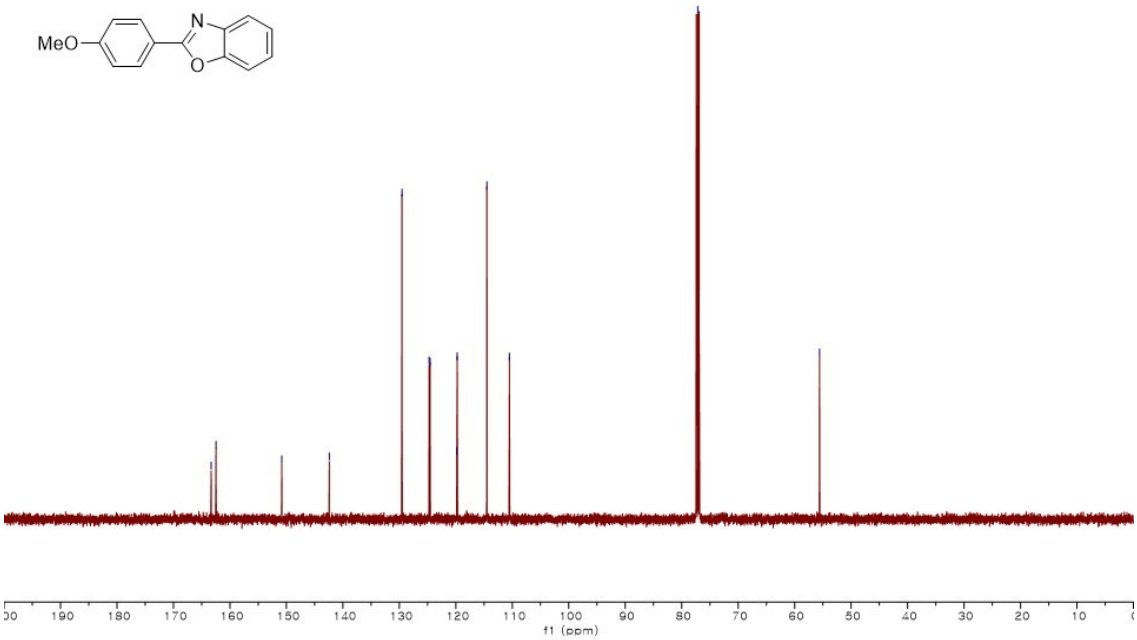
2-(*o*-Tolyl)benzoxazole (**3da**)

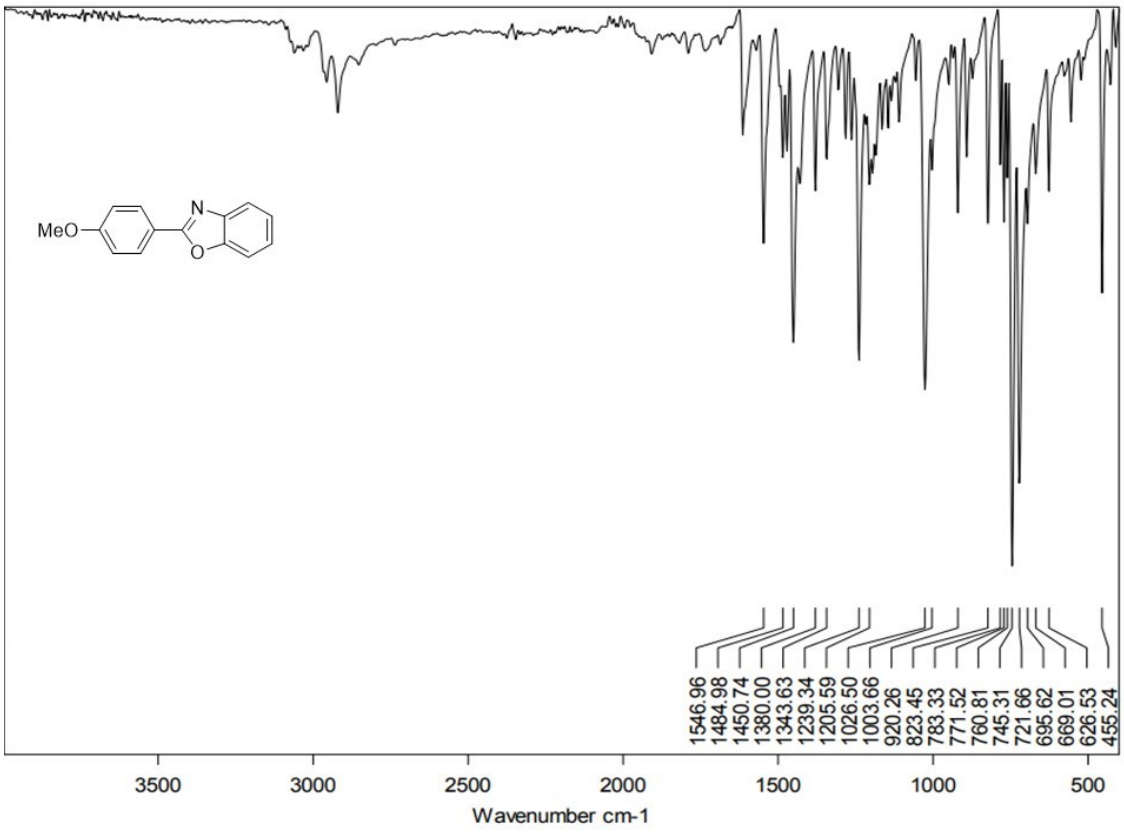



Me
N
O
1547.16
1485.14
1471.77
1450.86
1380.06
1343.85
1282.44
1239.51
1205.65
1026.70
920.38
892.09
823.46
783.38
771.54
760.85
745.12
721.73
626.55
455.21
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

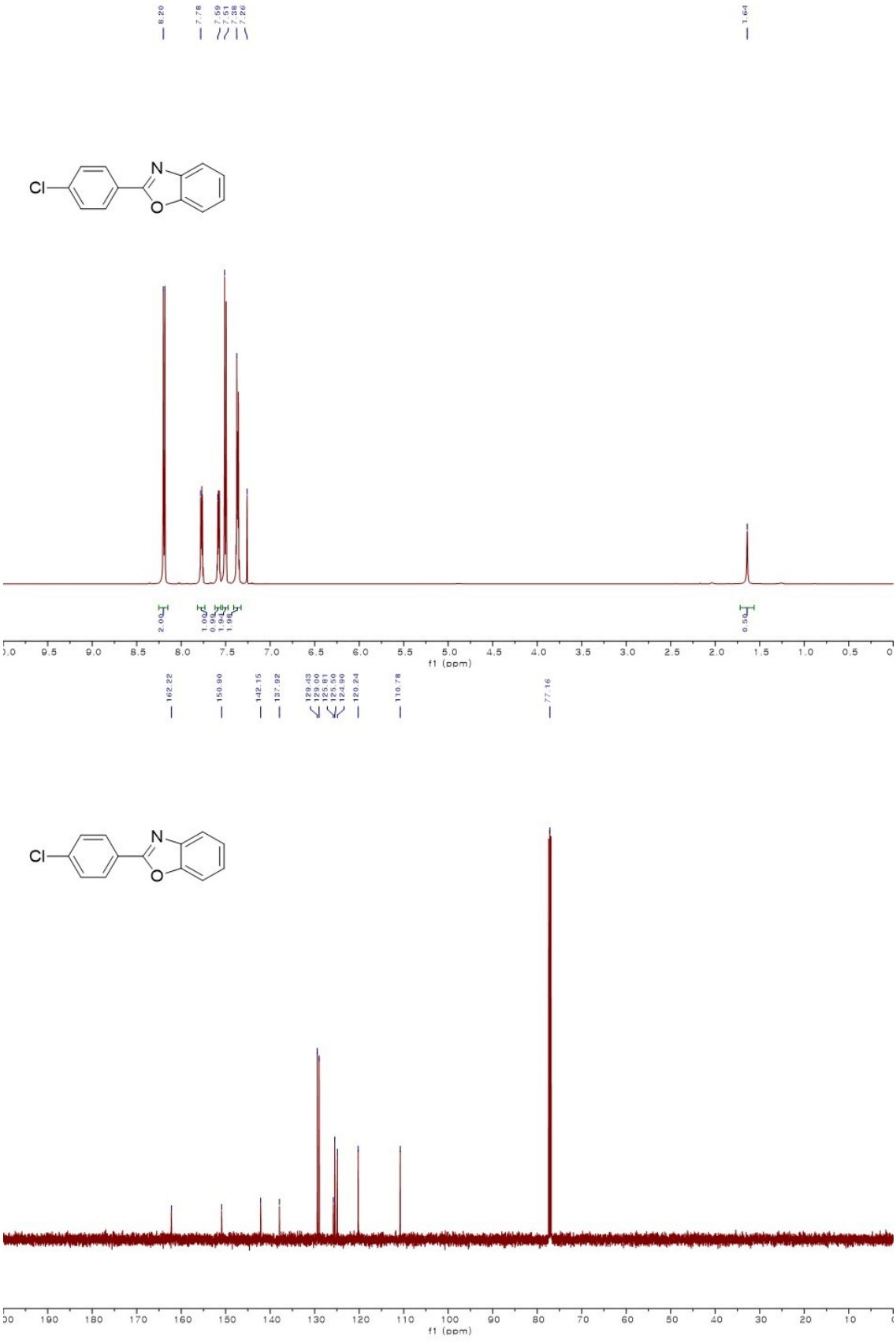
2-(4-Methoxyphenyl)benzoxazole (**3ea**)

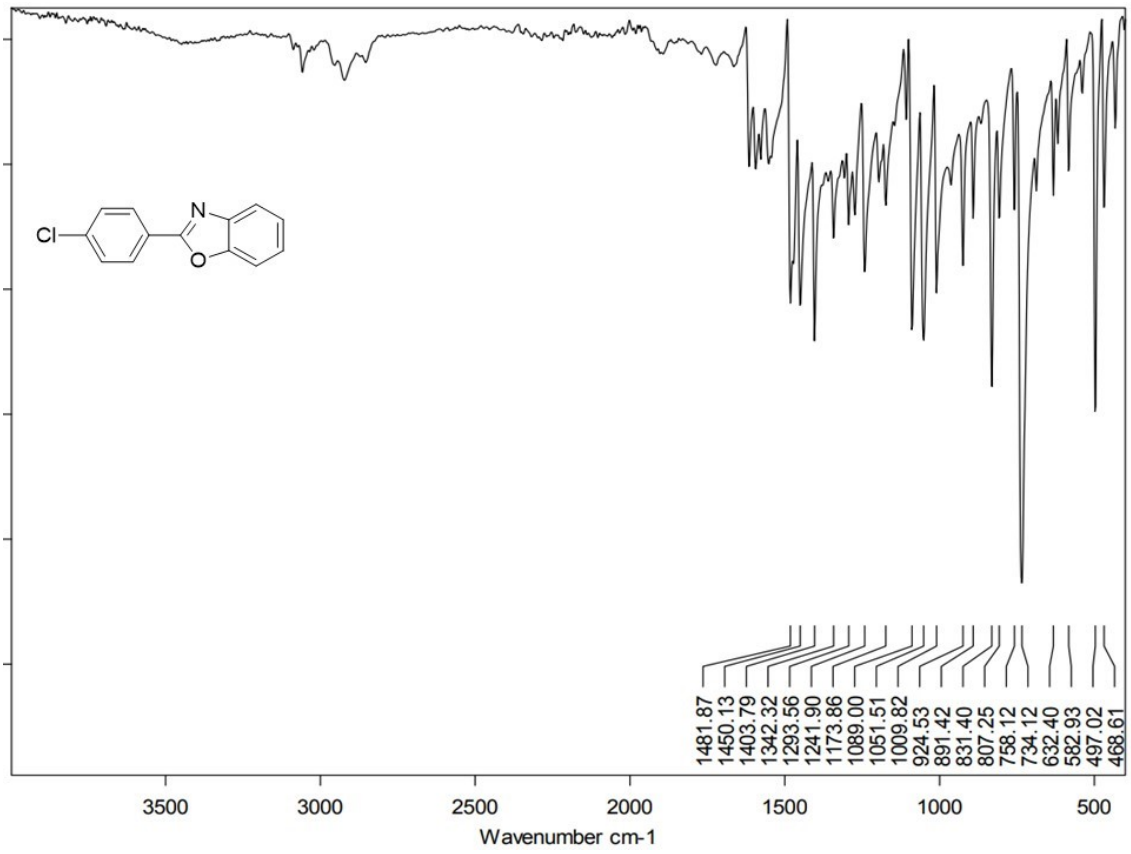




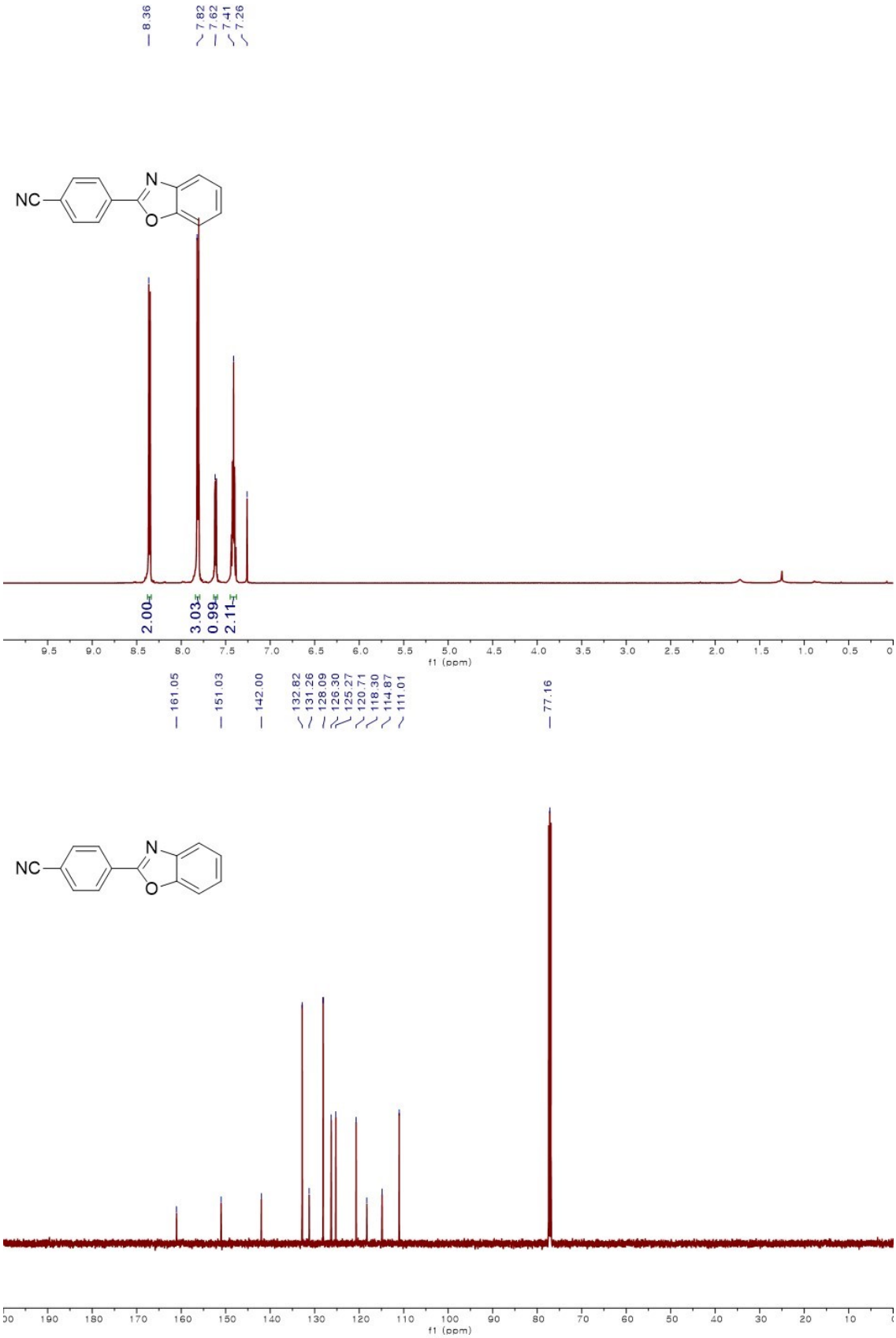

MeO
N
O
1546.96
1484.98
1450.74
1380.00
1343.63
1239.34
1205.59
1026.50
1003.66
920.26
823.45
783.33
771.52
760.81
745.31
721.66
695.62
669.01
626.53
455.24
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

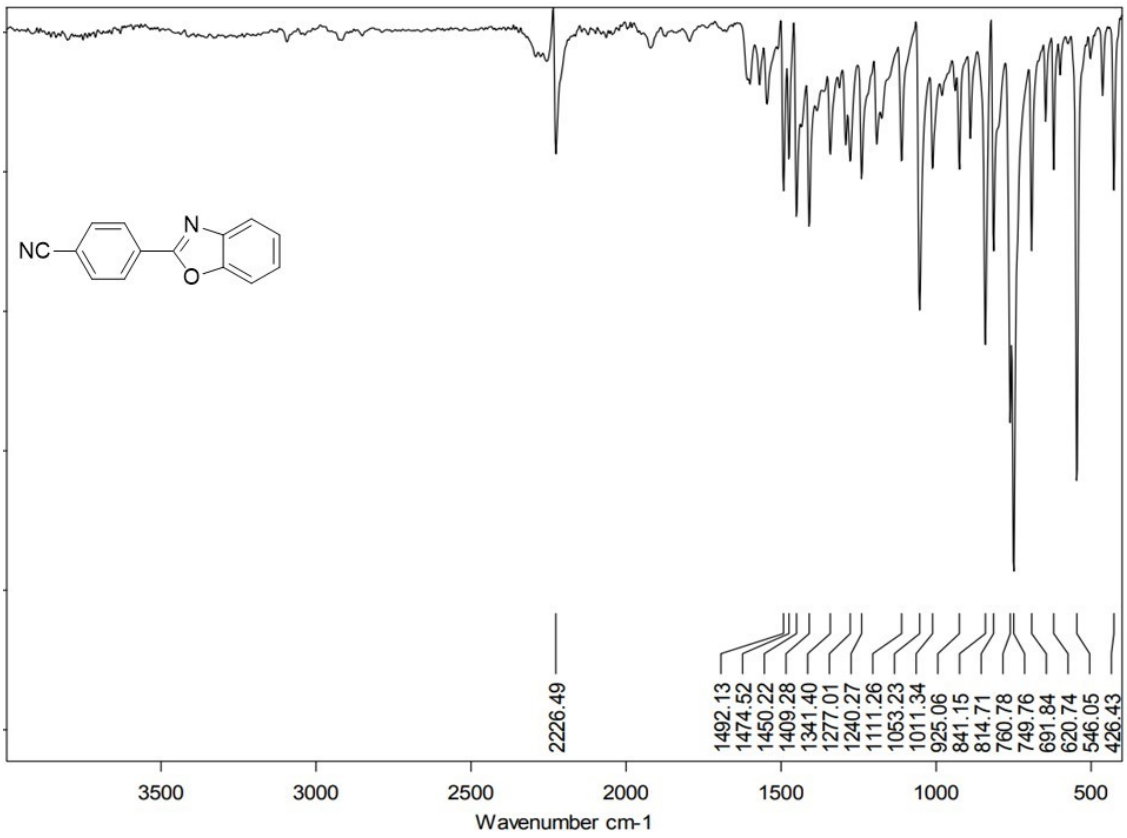
2-(4-Chlorophenyl)benzoxazole (**3fa**)



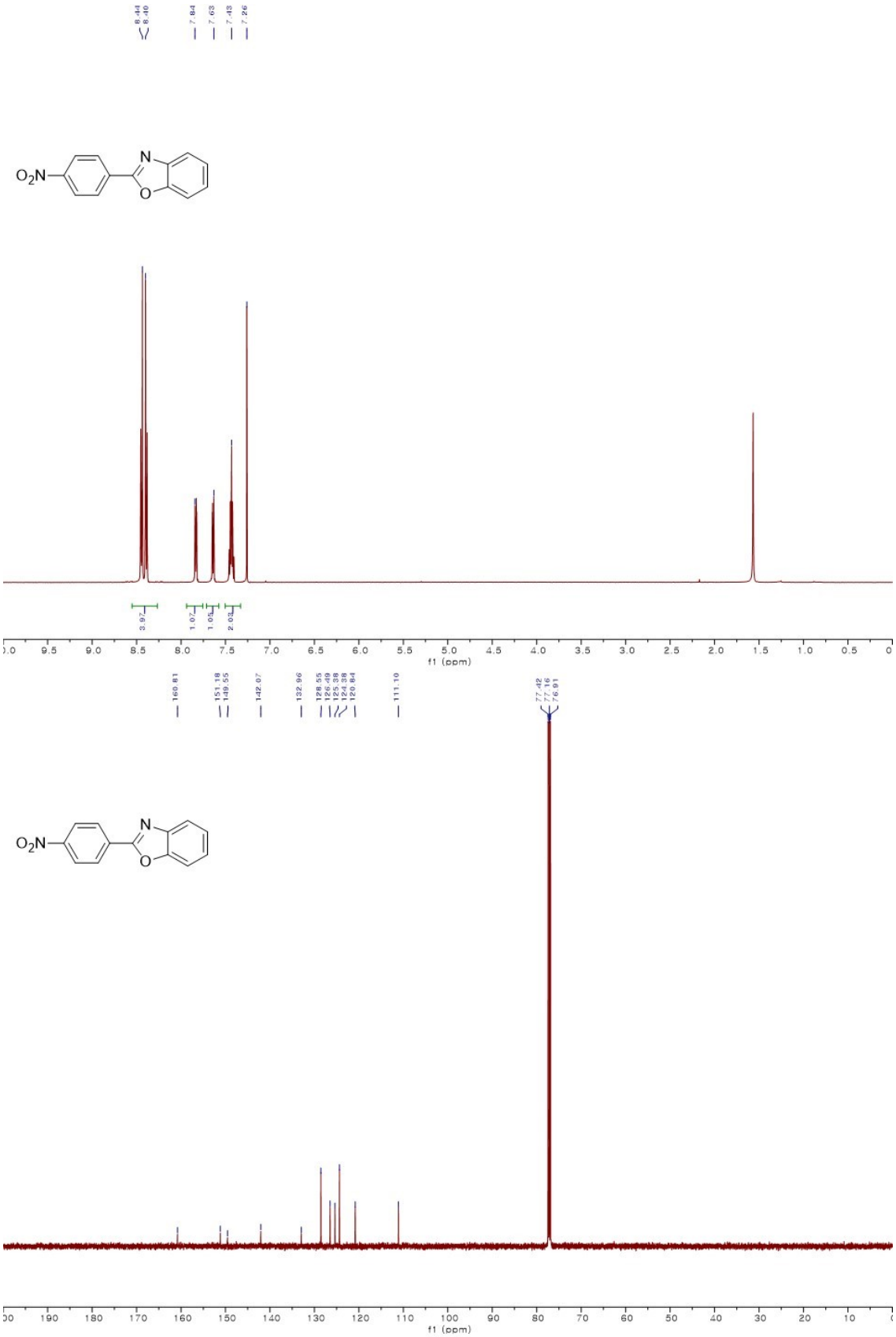

Cl
N
O
1481.87
1450.13
1403.79
1342.32
1293.56
1241.90
1173.86
1089.00
1051.51
1009.82
924.53
891.42
831.40
807.25
758.12
734.12
632.40
582.93
497.02
468.61
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

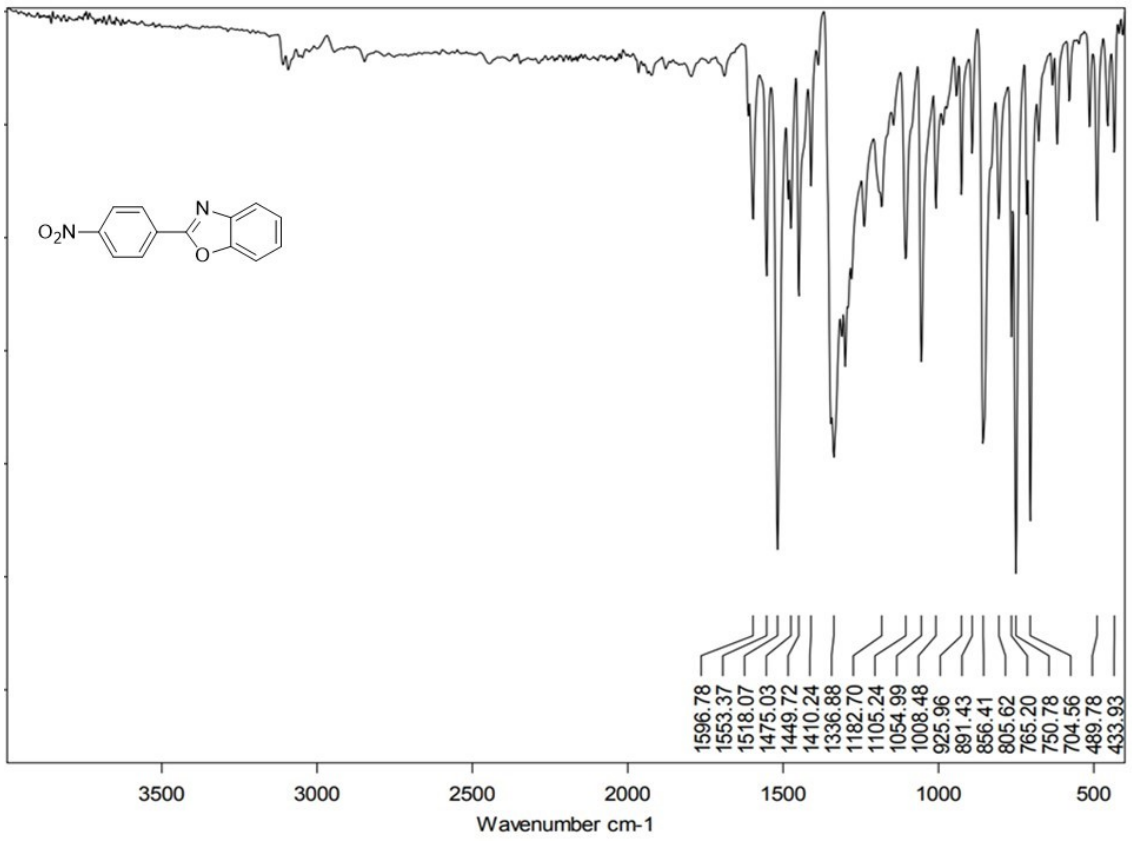
4-(Benzoxazol-2-yl)benzonitirle (**3ga**)



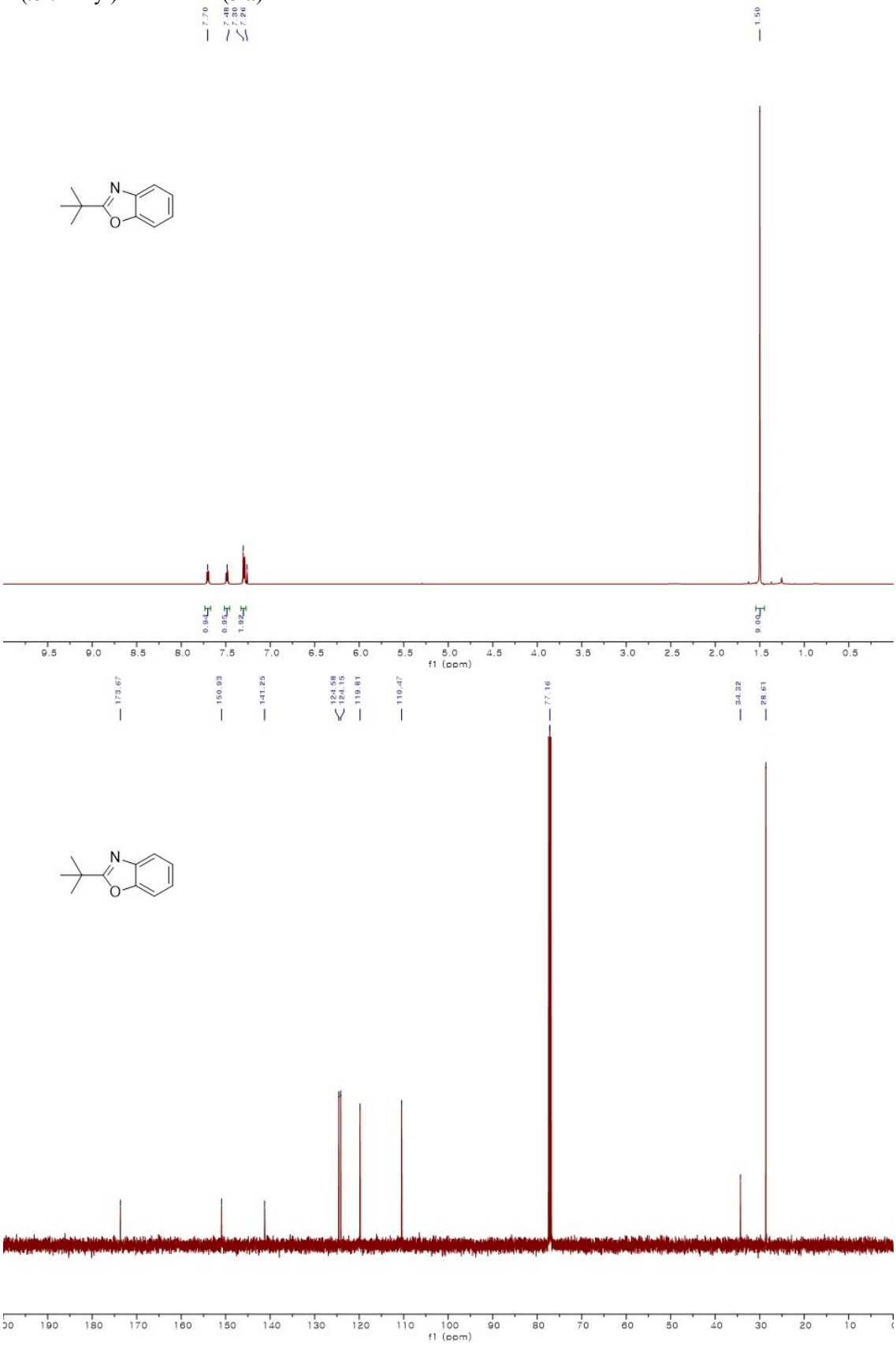

NC
N
O
2226.49
1492.13
1474.52
1450.22
1409.28
1341.40
1277.01
1240.27
1111.26
1053.23
1011.34
925.06
841.15
814.71
760.78
749.76
691.84
620.74
546.05
426.43
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

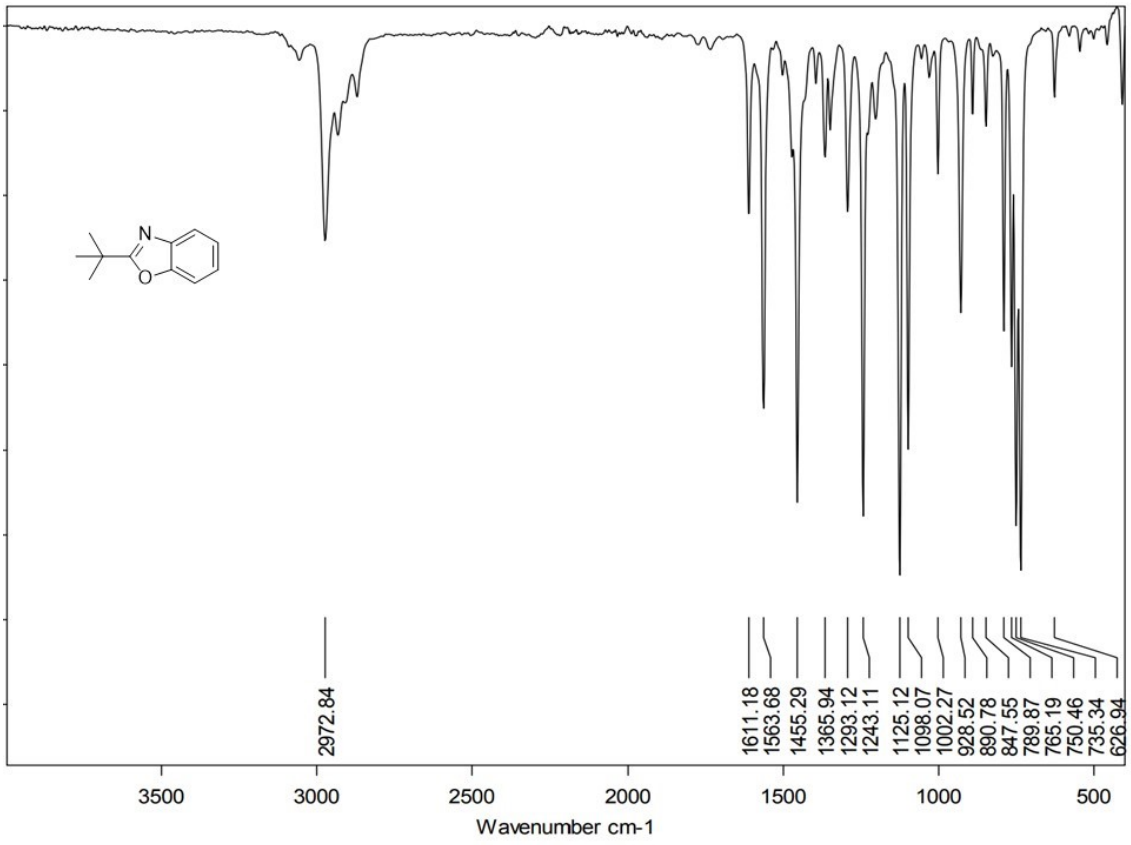
2-(4-Nitrophenyl)benzoxazole (**3ha**)



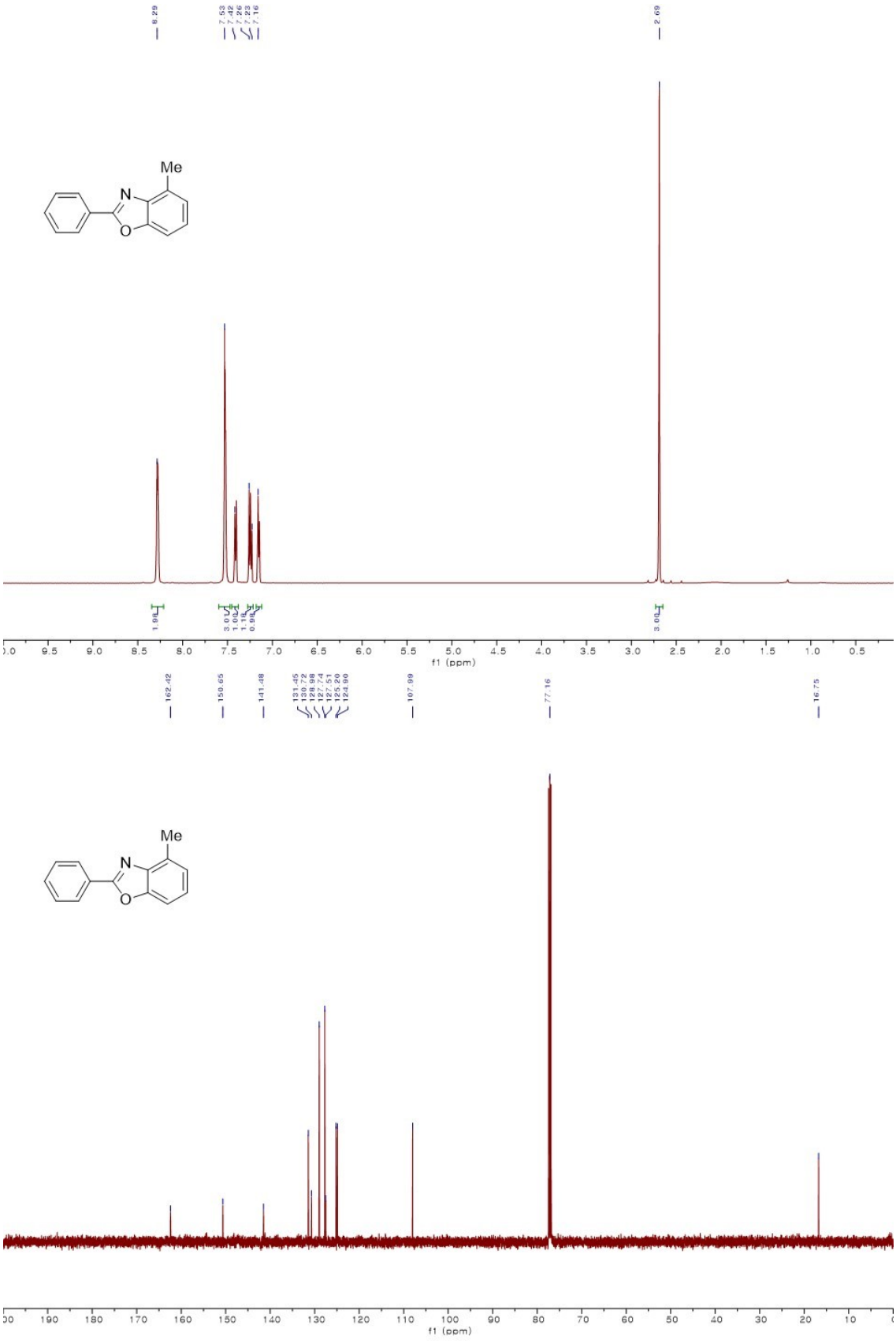

O2N
N
O
1596.78
1553.37
1518.07
1475.03
1449.72
1410.24
1336.88
1182.70
1105.24
1054.99
1008.48
925.96
891.43
856.41
805.62
765.20
750.78
704.56
489.78
433.93
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

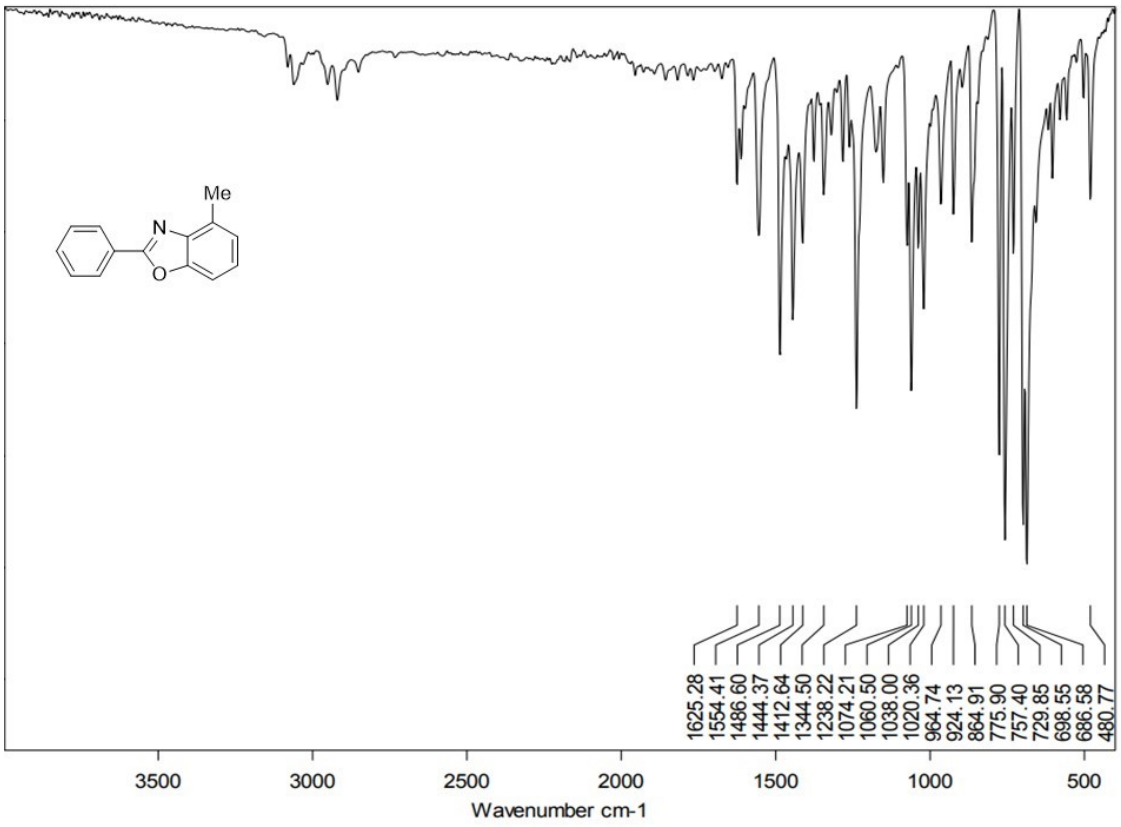
2-(*tert*-Butyl)benzoxazole(**3ia**)



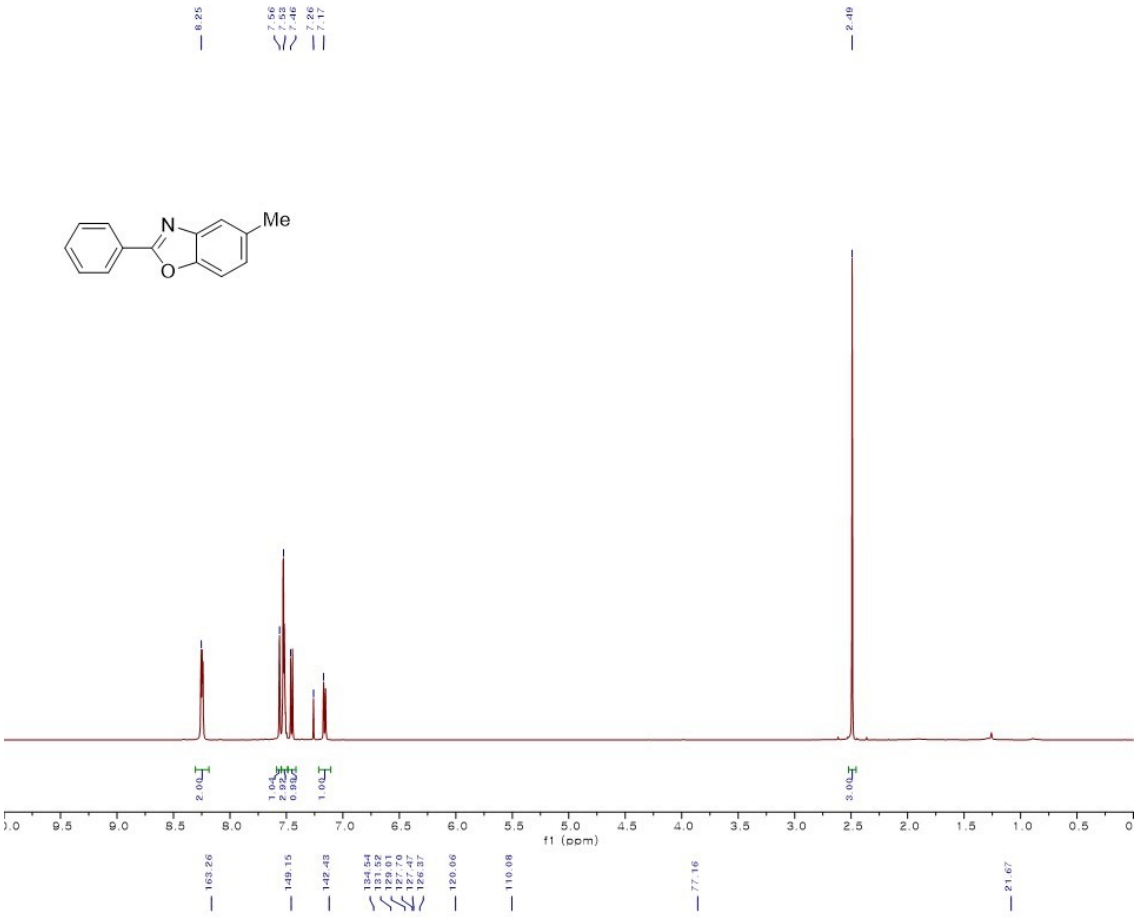

N
O
2972.84
1611.18
1563.68
1455.29
1365.94
1293.12
1243.11
1125.12
1098.07
1002.27
928.52
890.78
847.55
789.87
765.19
750.46
735.34
626.94
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

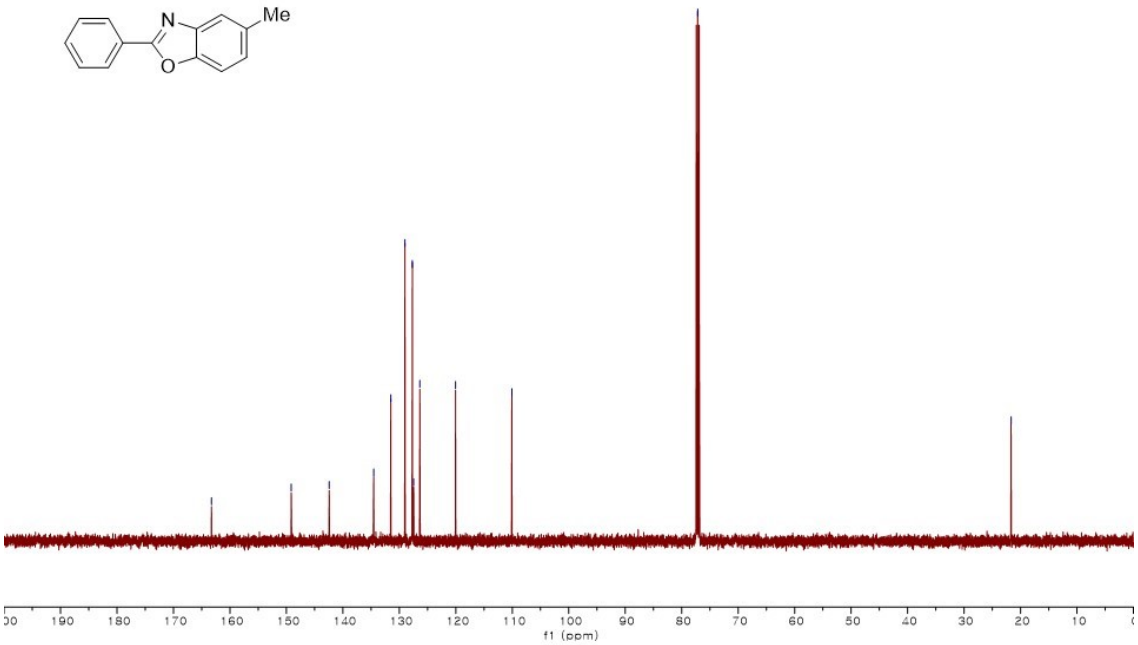
4-Methyl-2-phenylbenzoxazole (**3ab**)

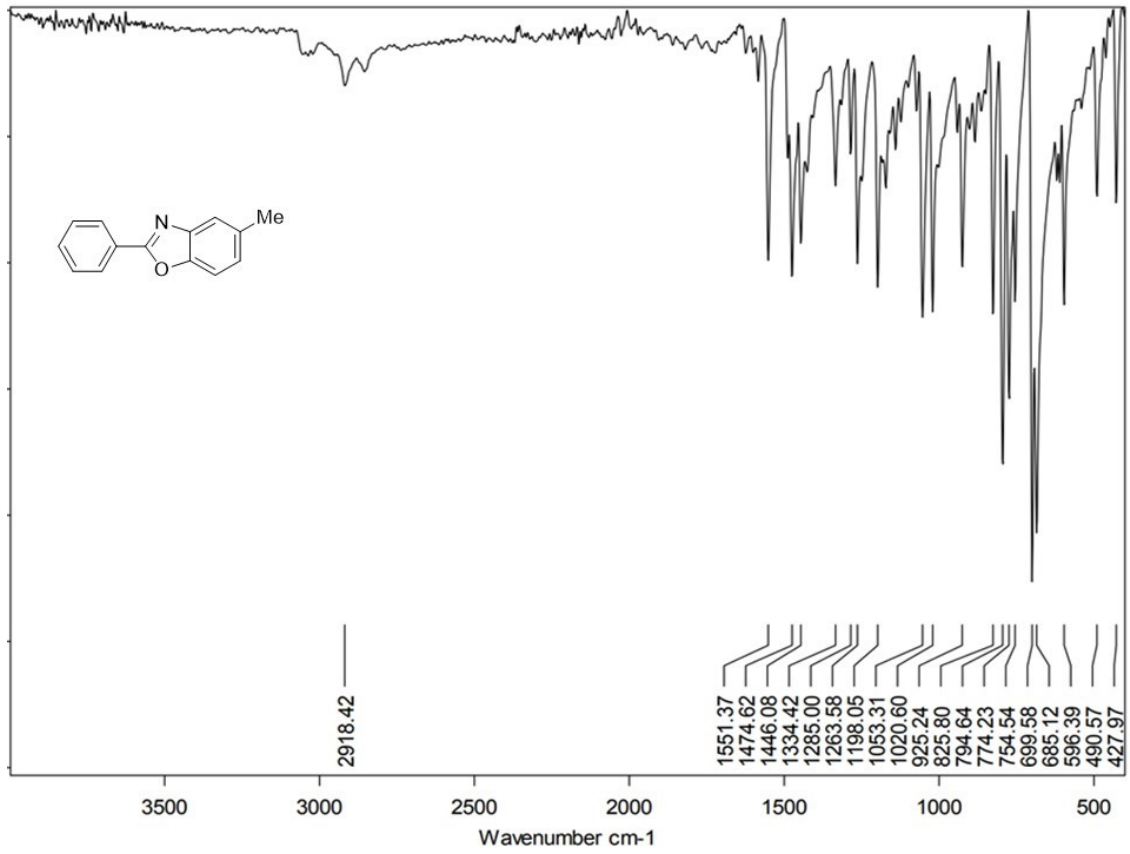



Me
N
O
1625.28
1554.41
1486.60
1444.37
1412.64
1344.50
1238.22
1074.21
1060.50
1038.00
1020.36
964.74
924.13
864.91
775.90
757.40
729.85
698.55
686.58
480.77
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

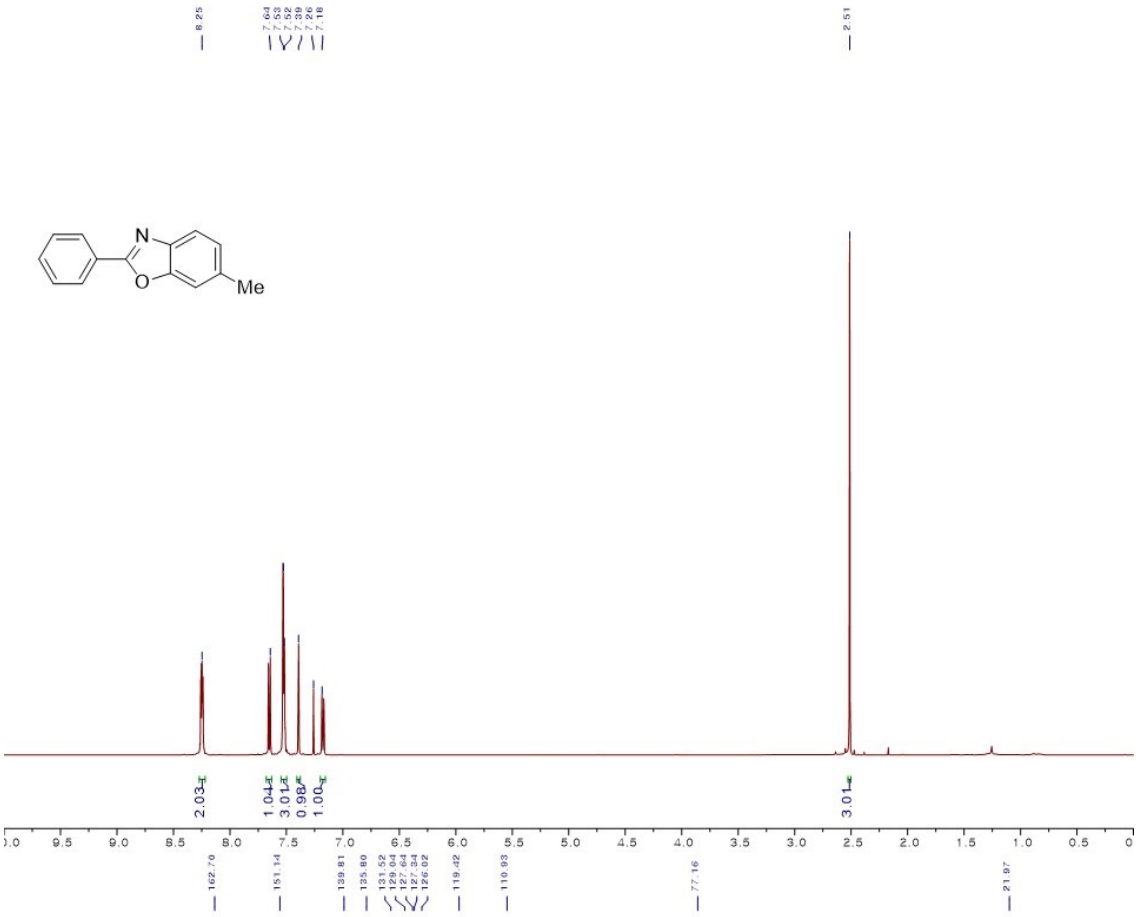
5-Methyl-2-phenylbenzoxazole (**3ac**)

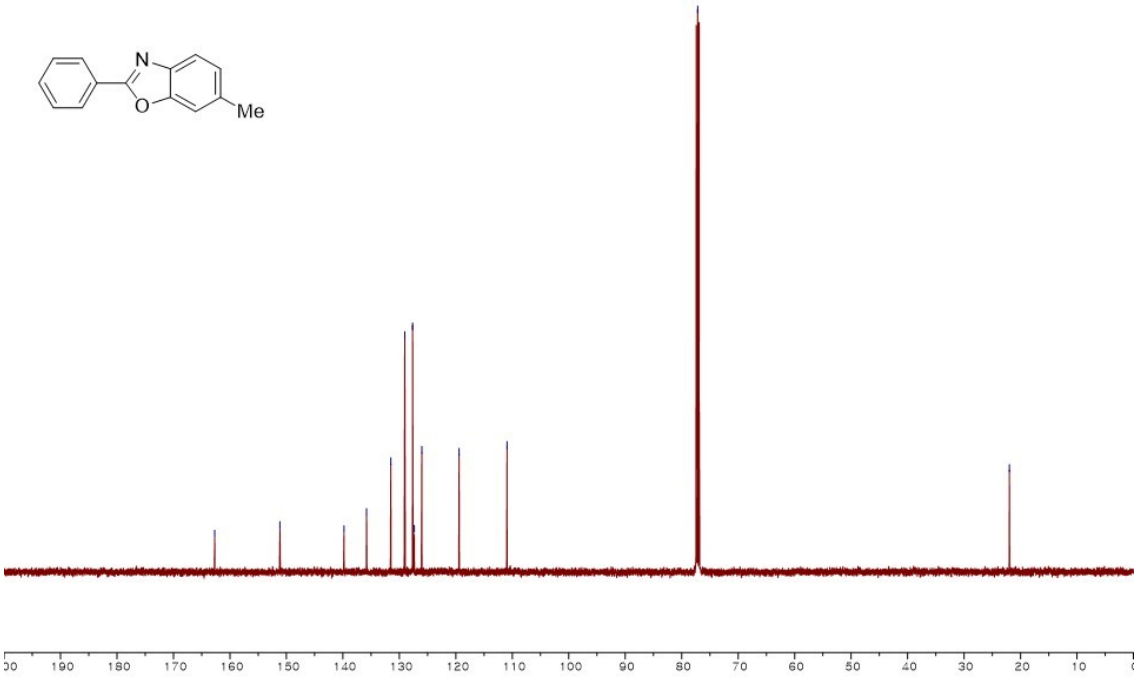


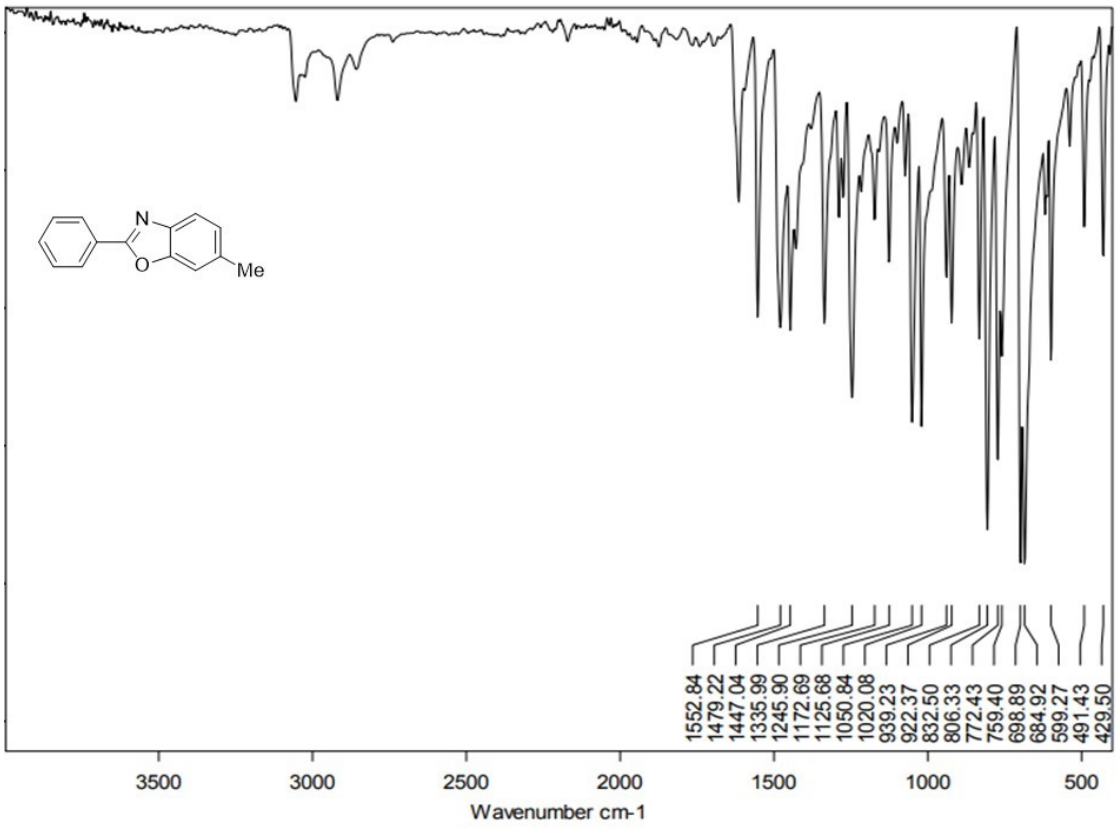



N
O
Me
2918.42
1551.37
1474.62
1446.08
1334.42
1285.00
1263.58
1198.05
1053.31
1020.60
925.24
825.80
794.64
774.23
754.54
699.58
685.12
596.39
490.57
427.97
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

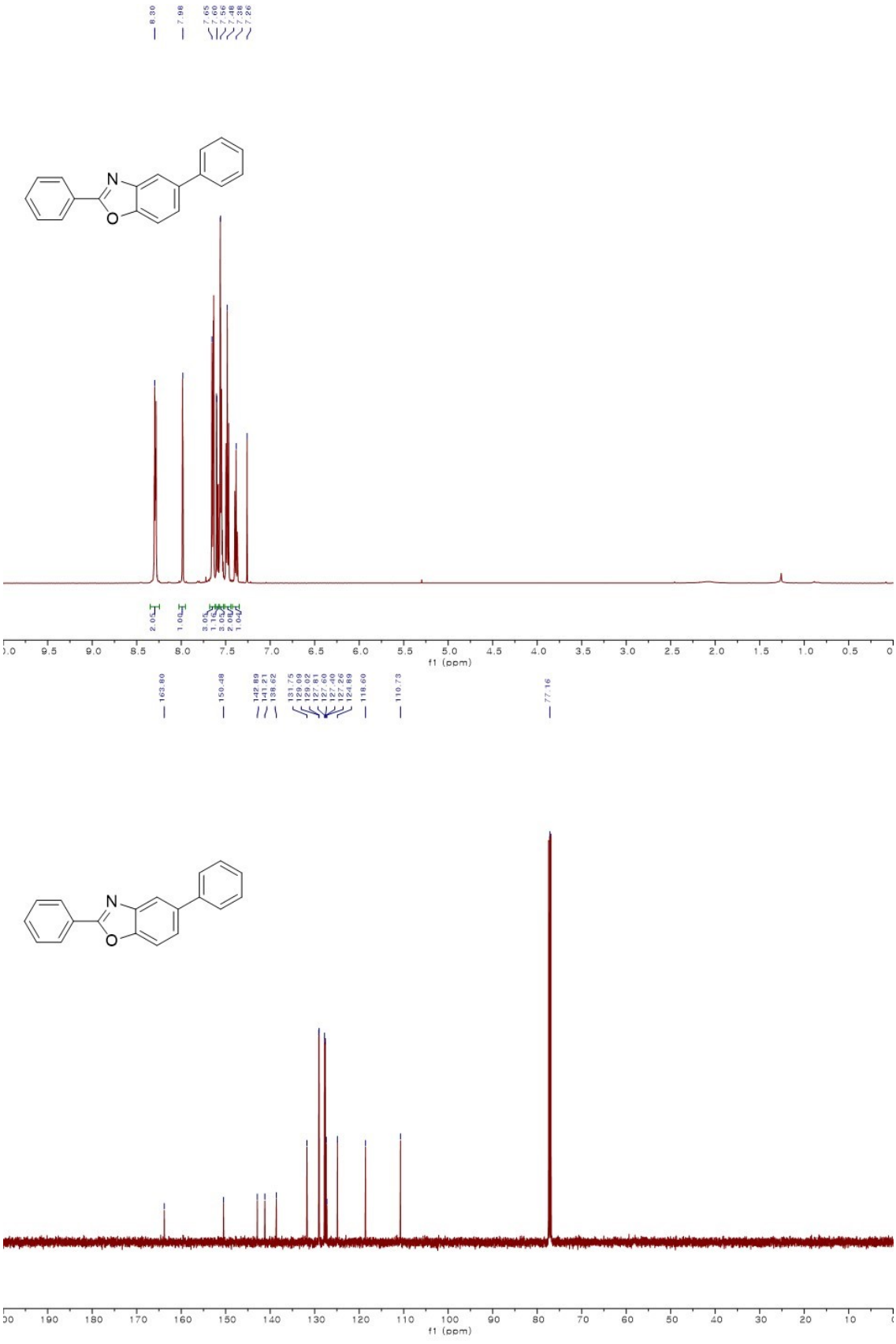
6-Methyl-2-phenylbenzoxazole (**3ad**)

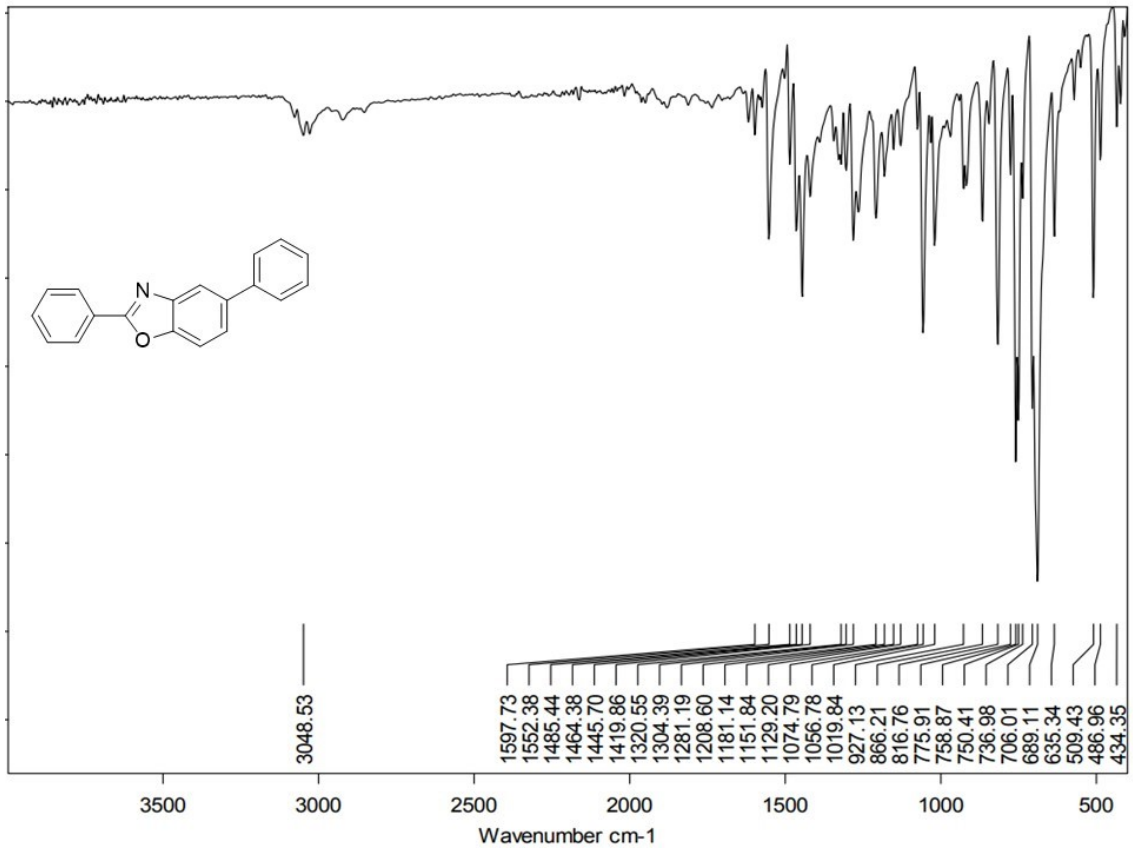




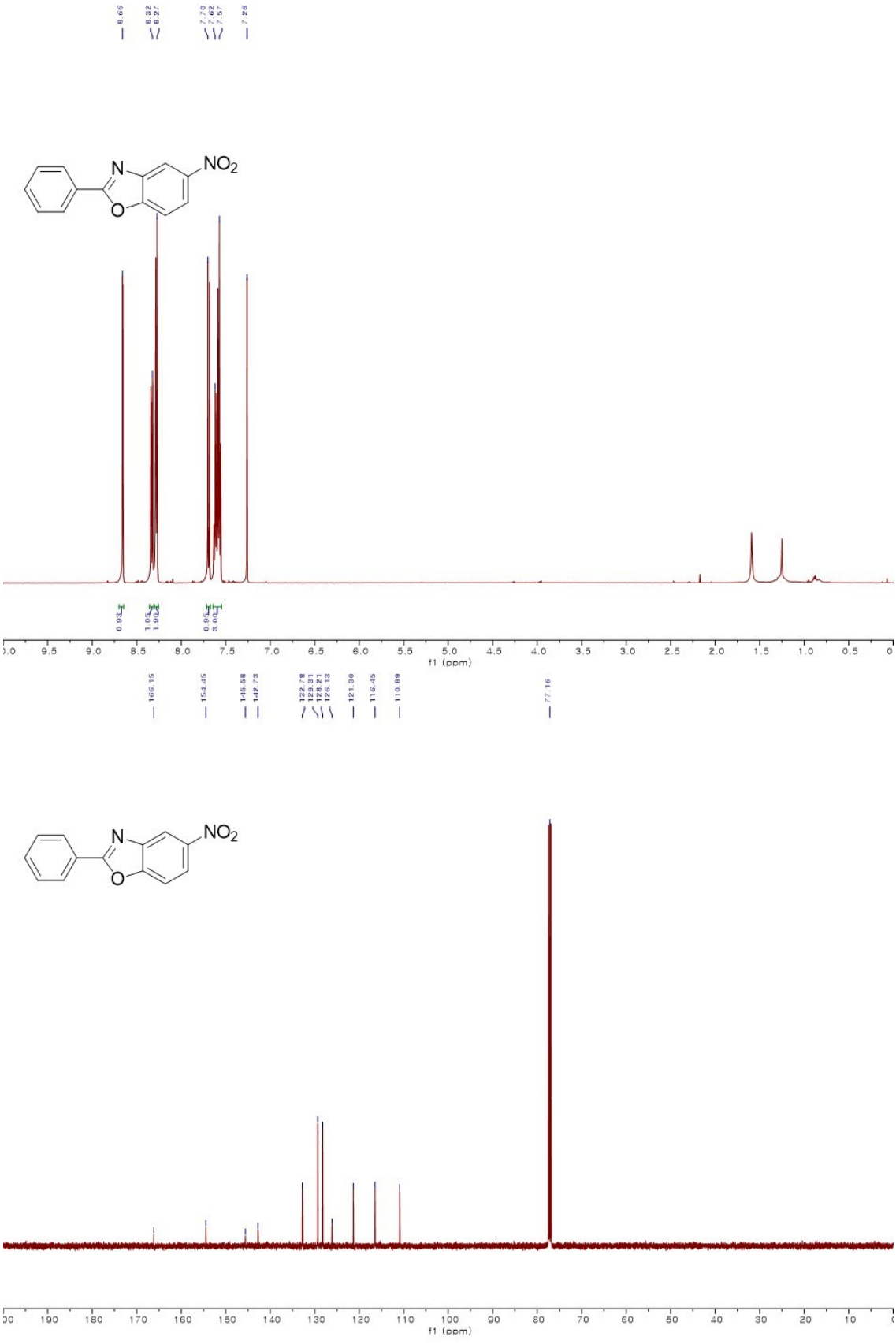

N
O
Me
1552.84
1479.22
1447.04
1335.99
1245.90
1172.69
1125.68
1050.84
1020.08
939.23
922.37
832.50
806.33
772.43
759.40
698.89
684.92
599.27
491.43
429.50
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

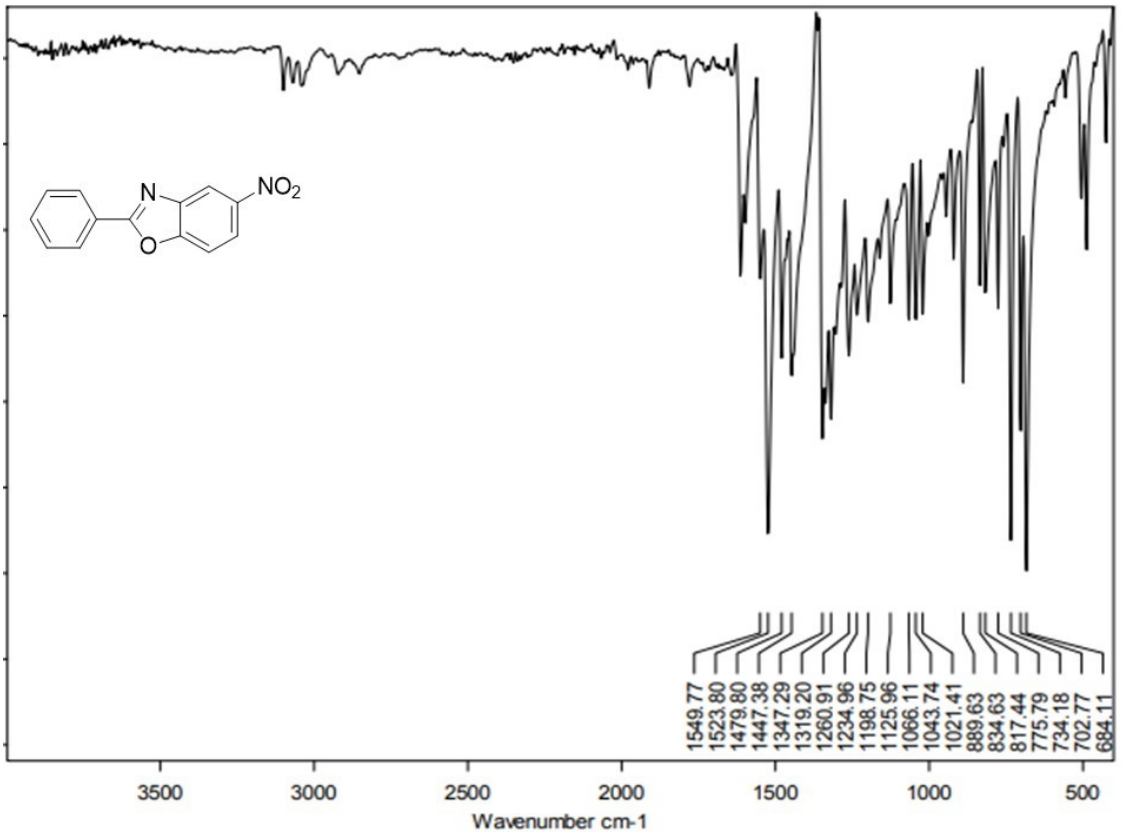
2,5-Diphenylbenzoxazole (**3ae**)



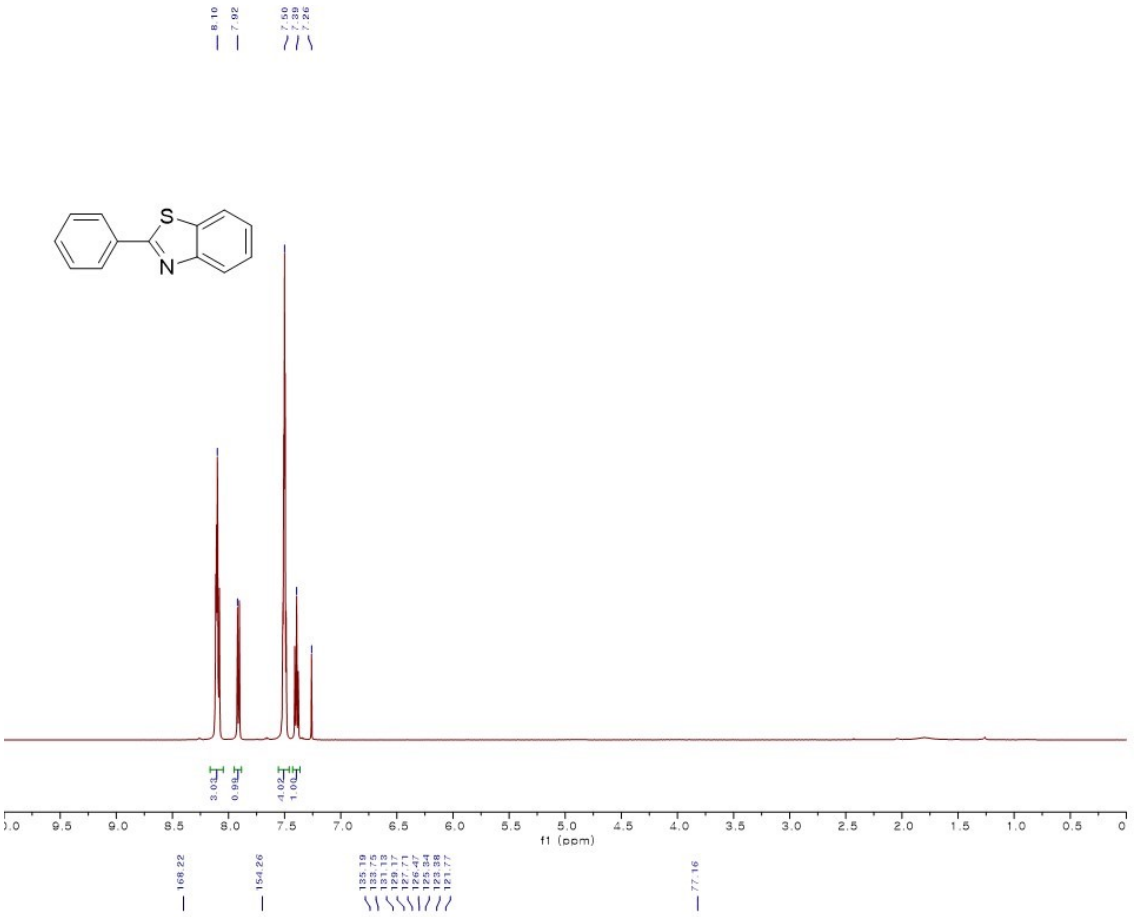

N
O
3048.53
1597.73
1552.38
1485.44
1464.38
1445.70
1419.86
1320.55
1304.39
1281.19
1208.60
1181.14
1151.84
1129.20
1074.79
1056.78
1019.84
927.13
866.21
816.76
775.91
758.87
750.41
736.98
706.01
689.11
635.34
509.43
486.96
434.35
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

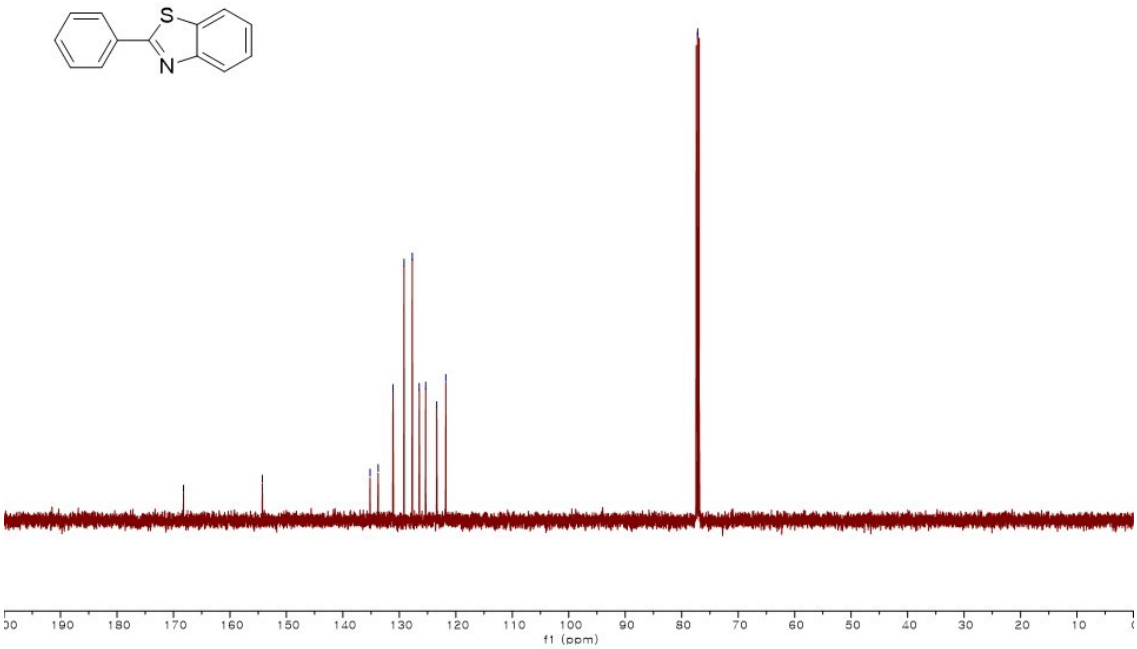
5-Nitro-2-phenylbenzoxazole (**3af**)

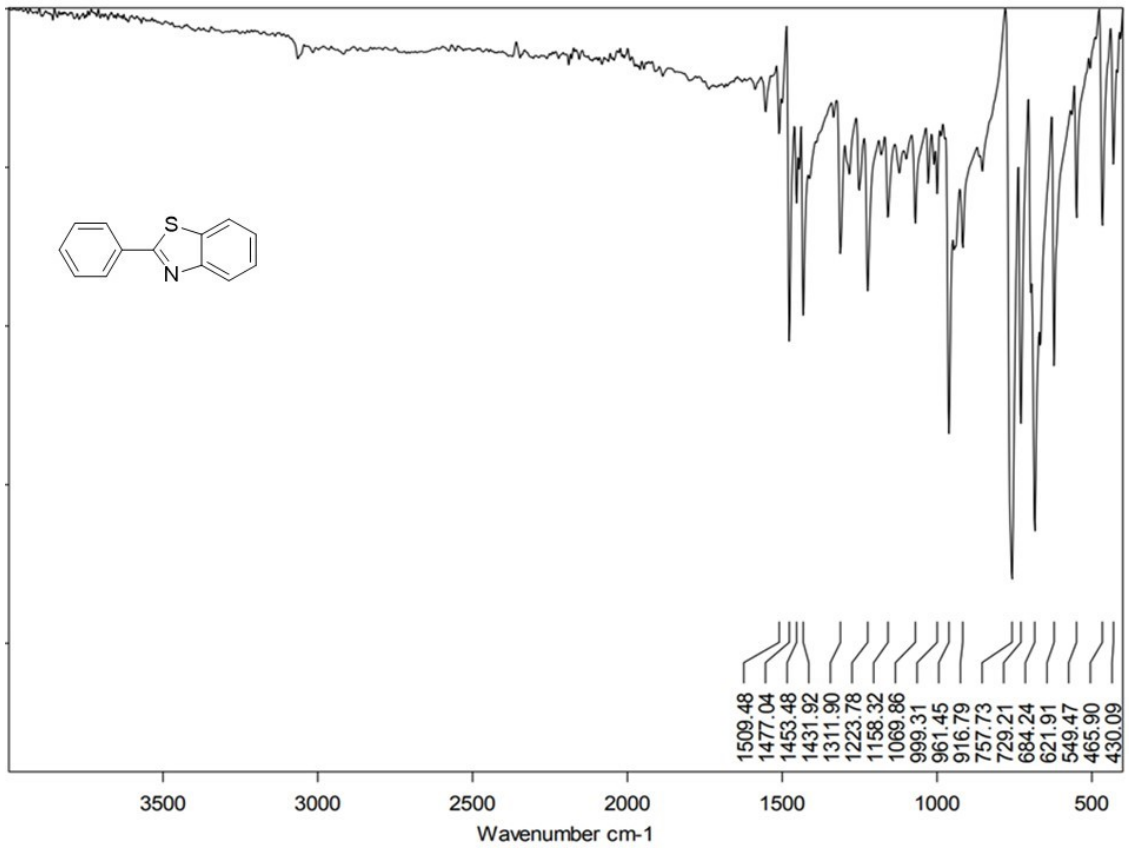



N
O
NO2
1549.77
1523.80
1479.80
1447.38
1347.29
1319.20
1260.91
1234.96
1198.75
1125.96
1066.11
1043.74
1021.41
889.63
834.63
817.44
775.79
734.18
702.77
684.11
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

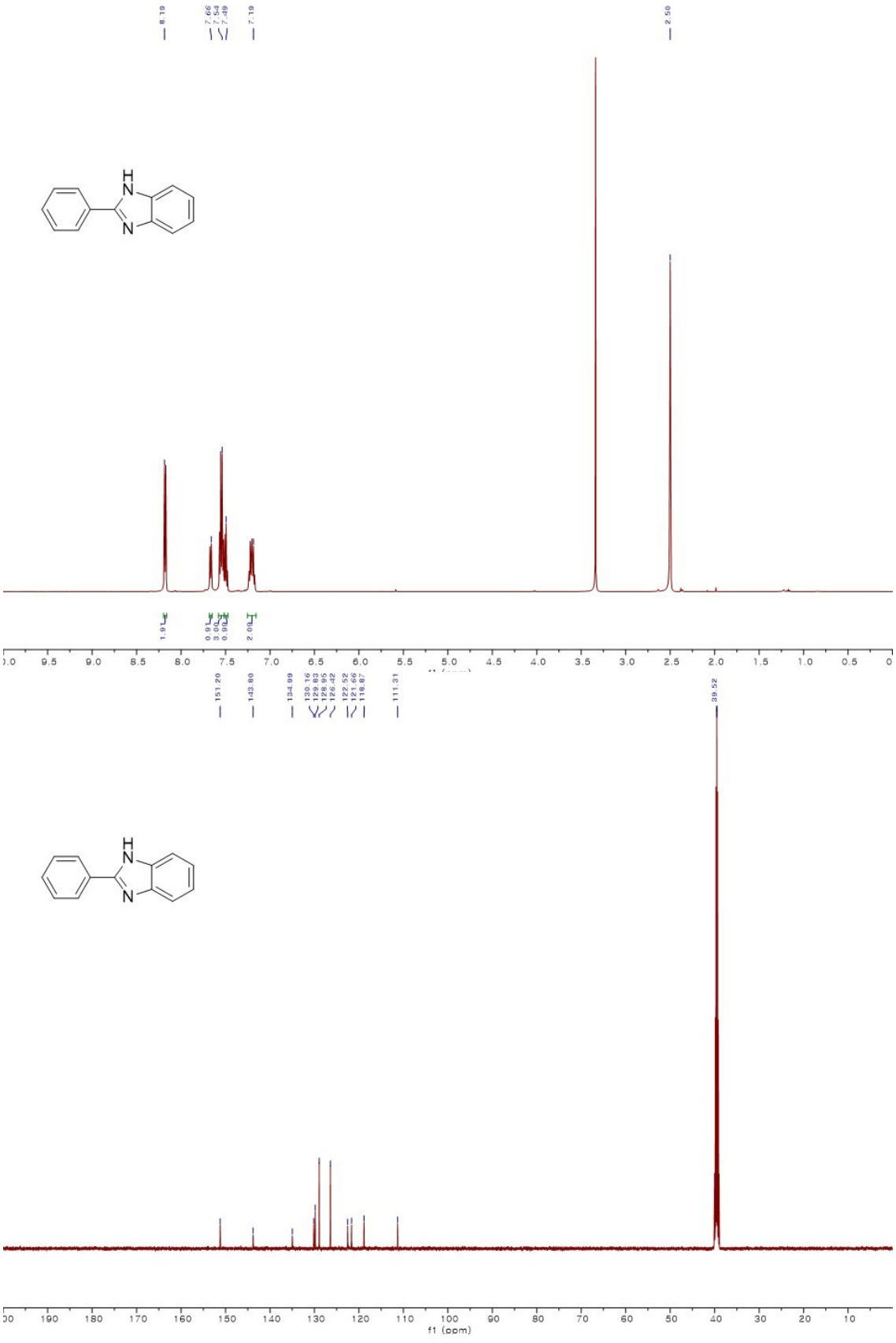
2-Phenylbenzothiazole (**3ag**)

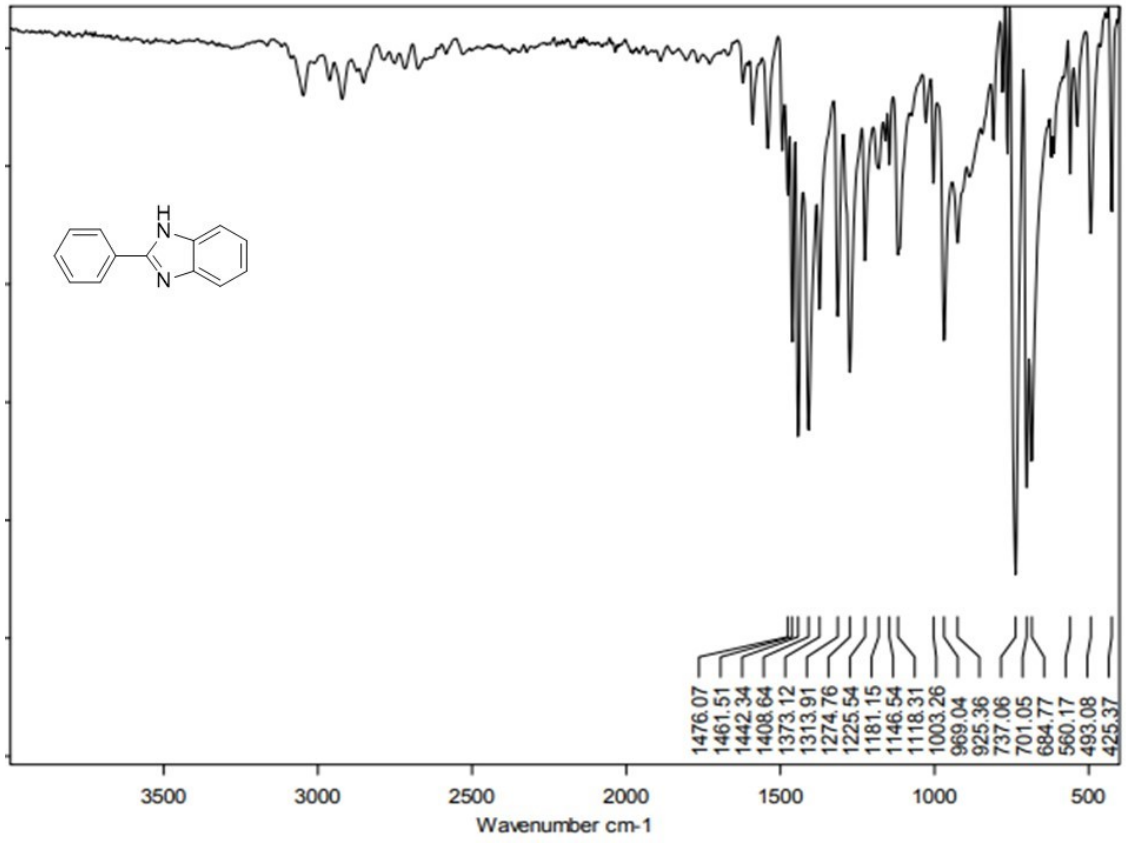




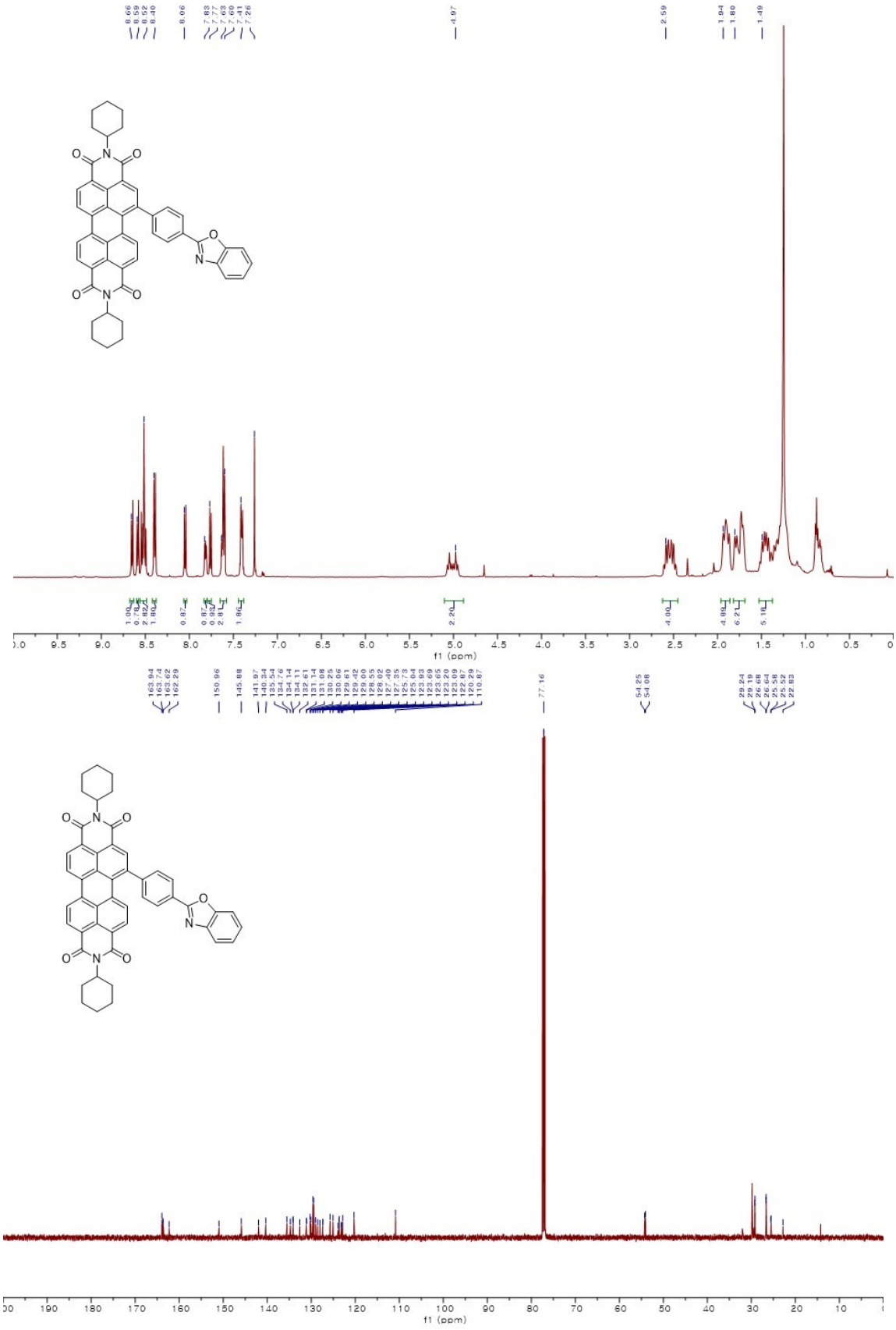

S
N
1509.48
1477.04
1453.48
1431.92
1311.90
1223.78
1158.32
1069.86
999.31
961.45
916.79
757.73
729.21
684.24
621.91
549.47
465.90
430.09
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

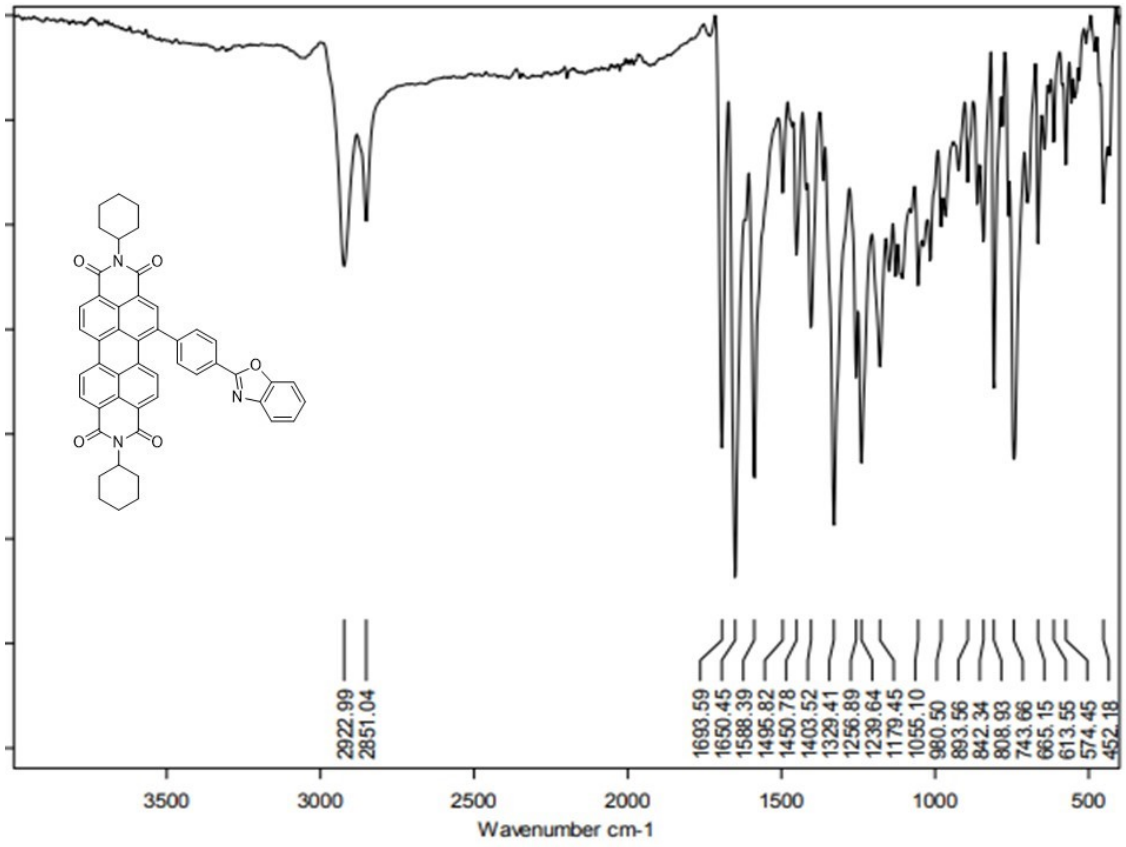
2-Pheny-1H-lbenzoimidazole (**3ah**)



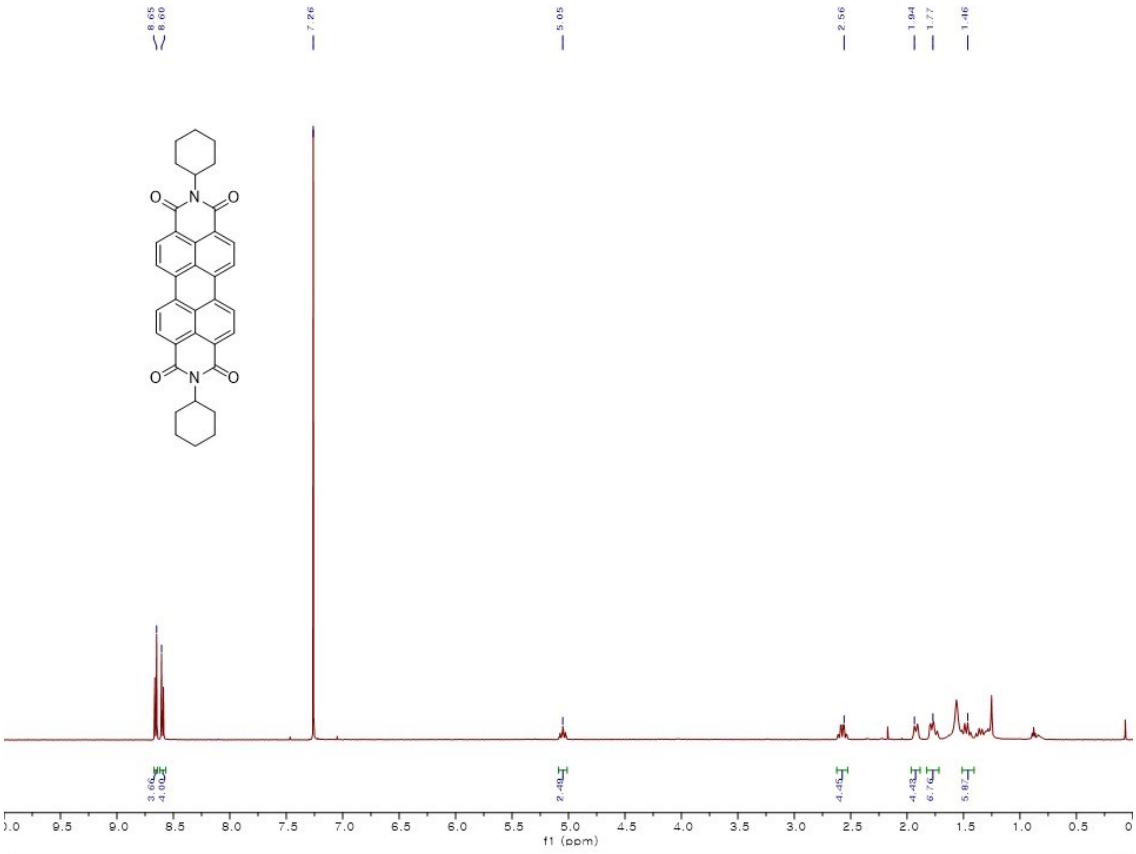

1476.07
1461.51
1442.34
1408.64
1373.12
1313.91
1274.76
1225.54
1181.15
1146.54
1118.31
1003.26
969.04
925.36
737.06
701.05
684.77
560.17
493.08
425.37
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

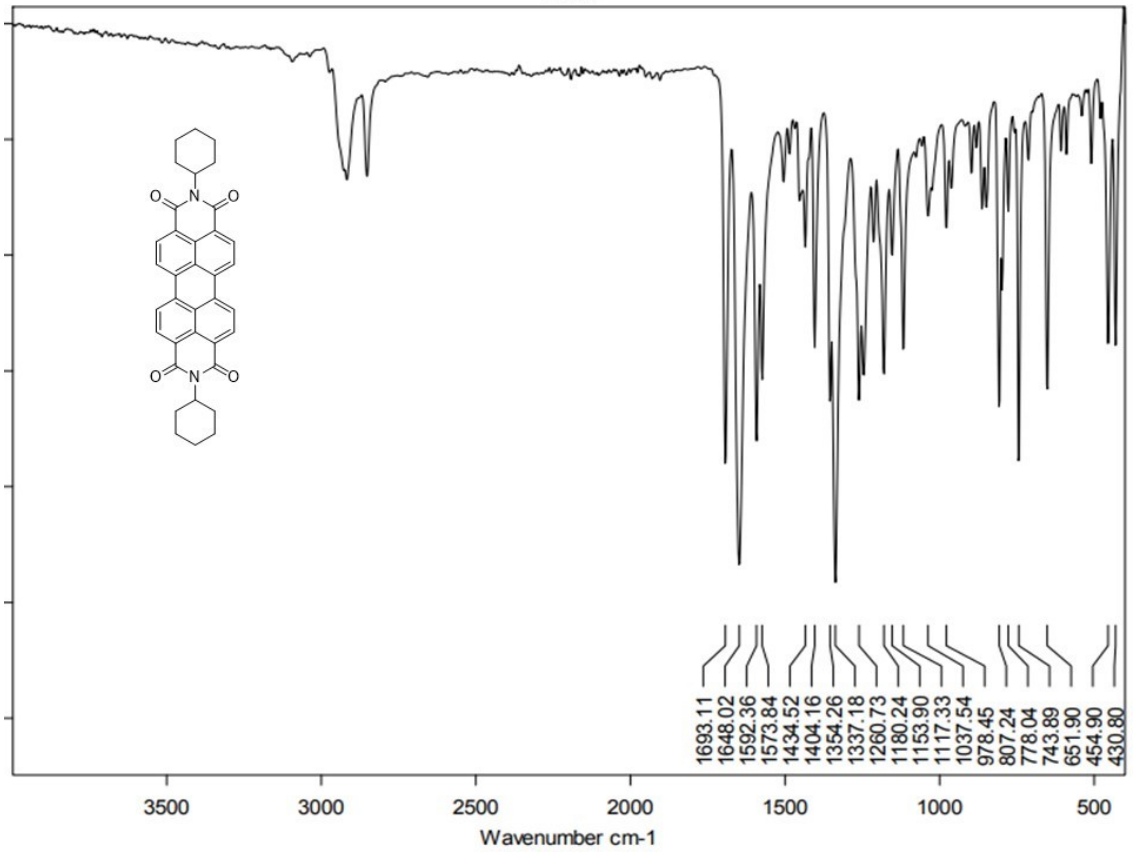
PDI-Ph-Benzox (Perylenediimide-phenylbenzoxazole, **3ja**)



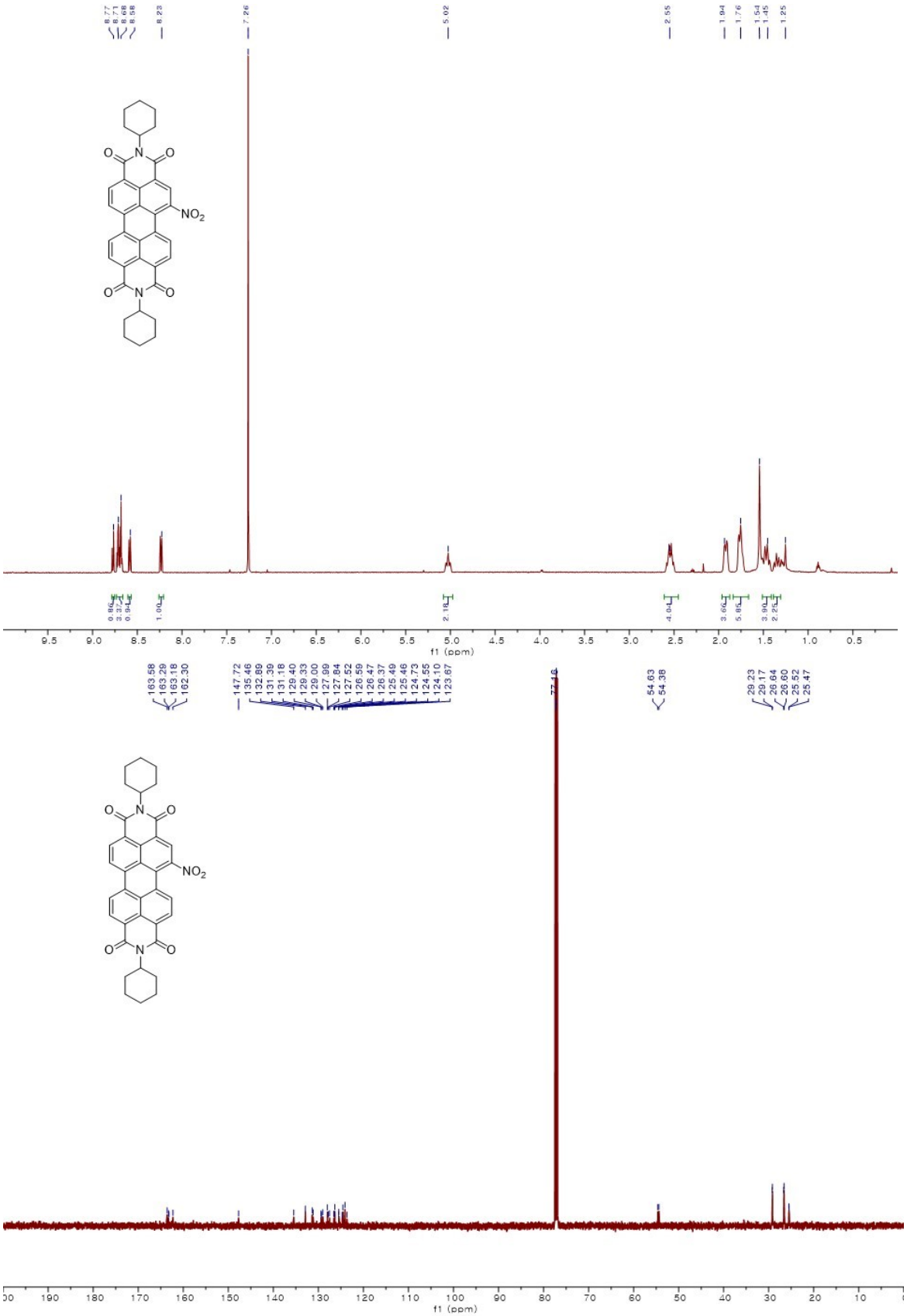

2922.99
2851.04
1693.59
1650.45
1588.39
1495.82
1450.78
1403.52
1329.41
1256.89
1239.64
1179.45
1055.10
980.50
893.56
842.34
808.93
743.66
665.15
613.55
574.45
452.18
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

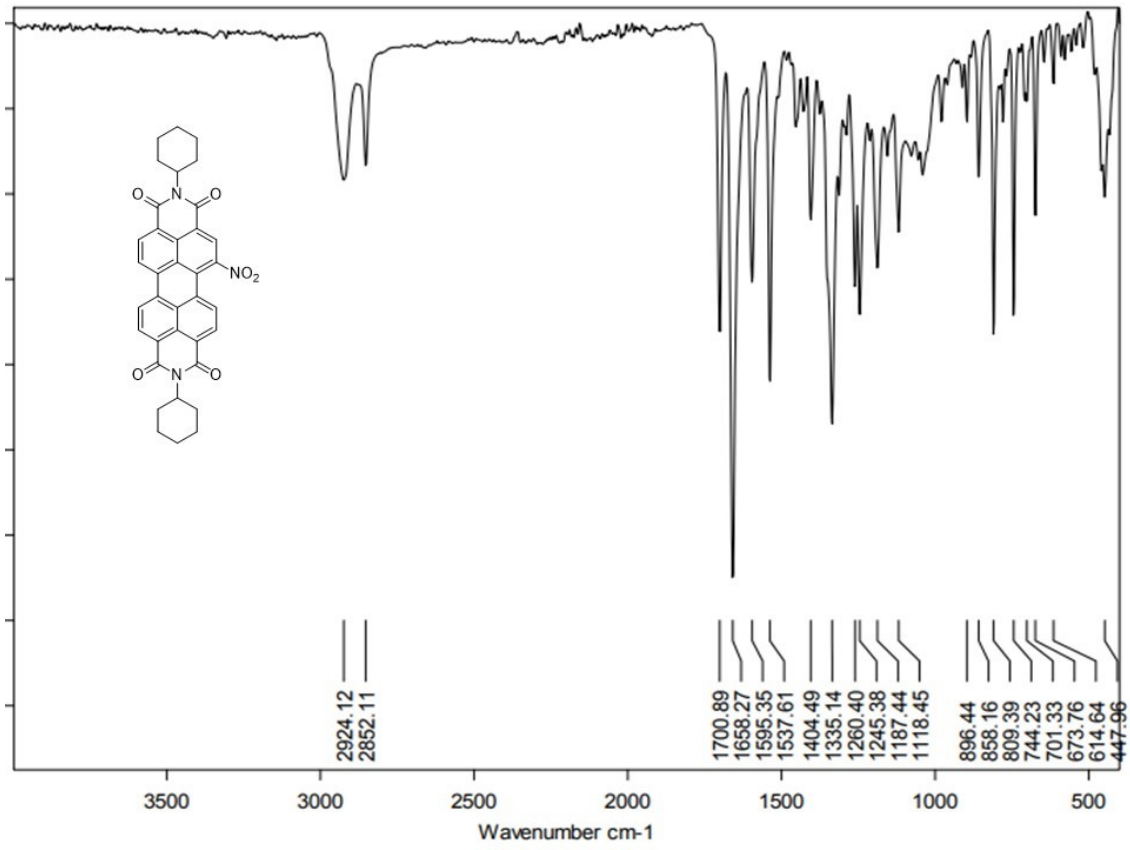
PDI (Perylenediimide)



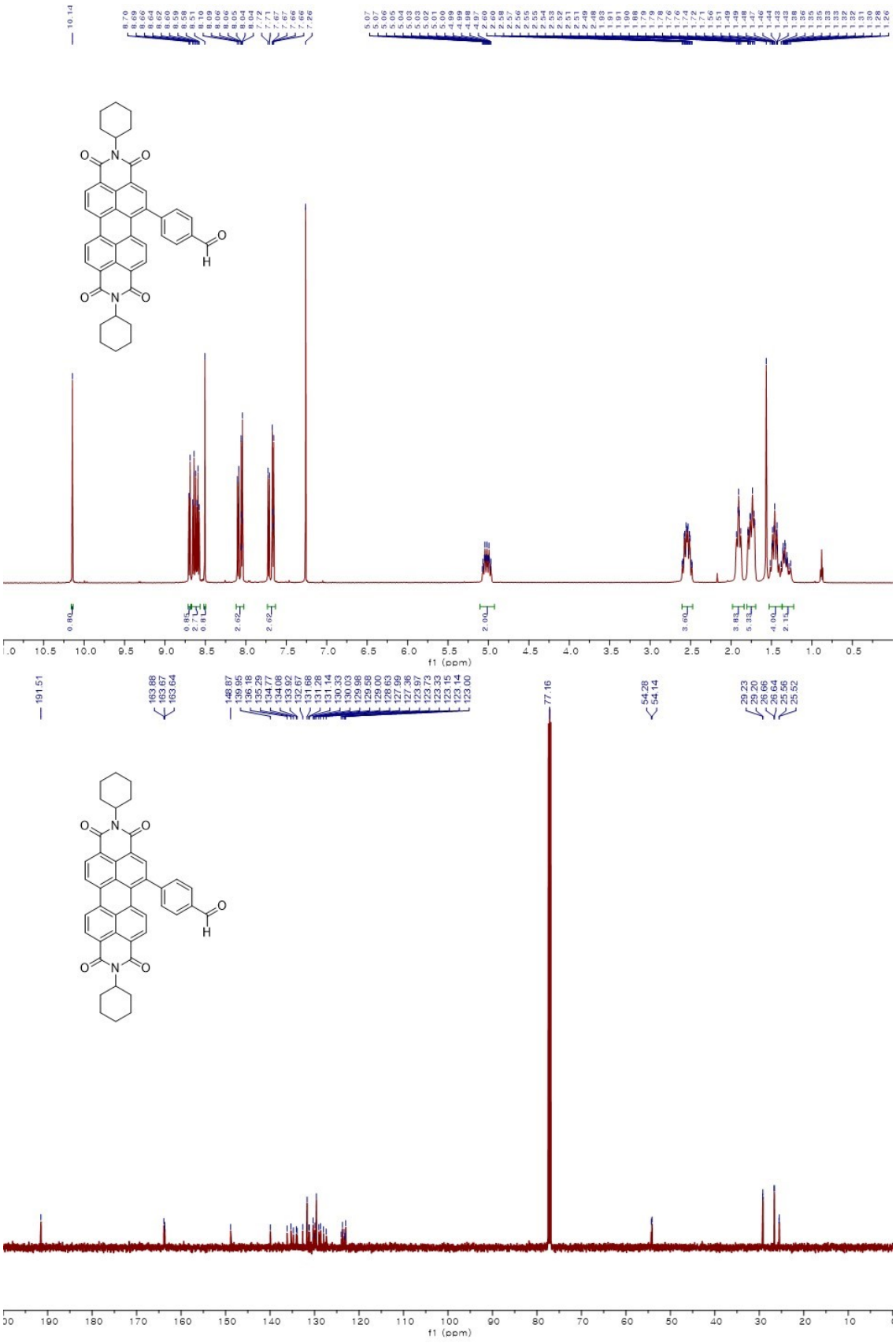


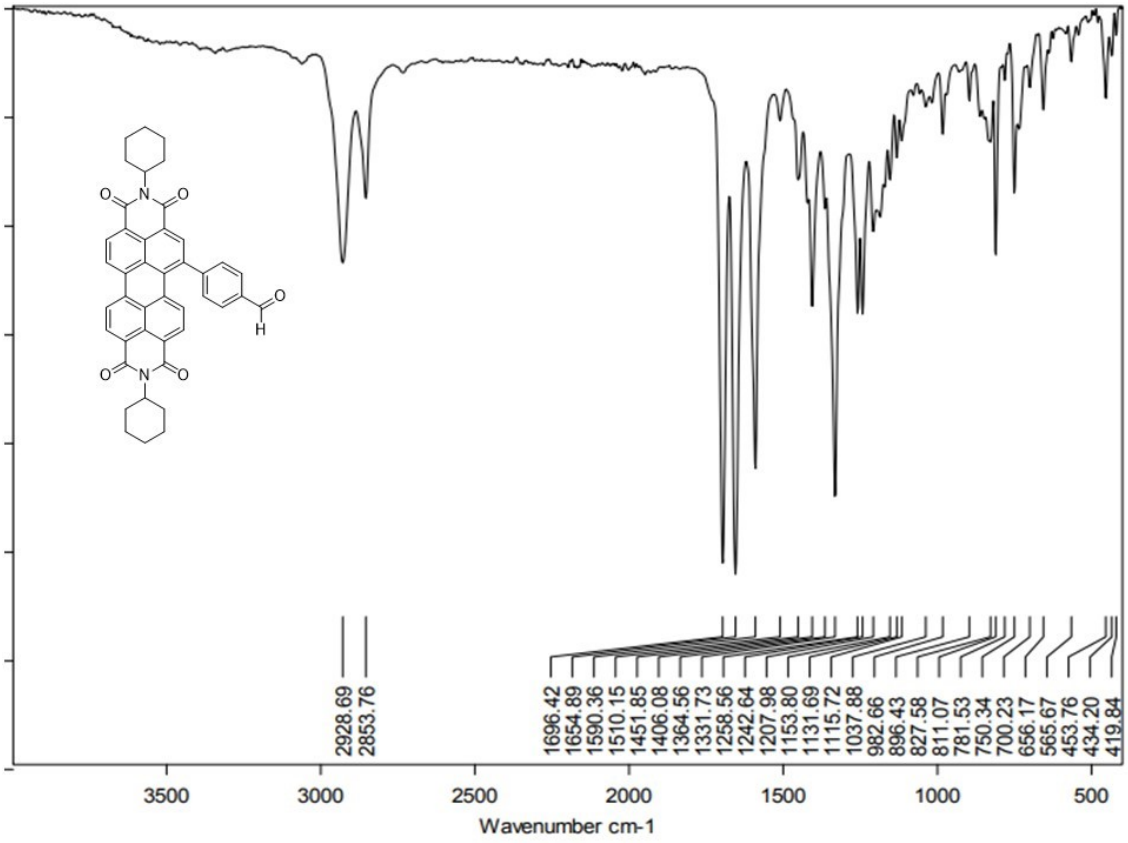
PDI-NO_2 (Perylenediimide-NO_2)




2924.12
2852.11
1700.89
1658.27
1595.35
1537.61
1404.49
1335.14
1260.40
1245.38
1187.44
1118.45
896.44
858.16
809.39
744.23
701.33
673.76
614.64
447.96
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

PDI-Ph-CHO (Perylenediimide-phenylaldehyde)




2928.69
2853.76
1696.42
1654.89
1590.36
1510.15
1451.85
1406.08
1364.56
1331.73
1258.56
1242.64
1207.98
1153.80
1131.69
1115.72
1037.88
982.66
896.43
827.58
811.07
781.53
750.34
700.23
656.17
565.67
453.76
434.20
419.84
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1