

Supporting information

Benzothiadiazoles Incorporated in a Metal-Organic Framework for improved photocatalysis in Azacycles Synthesis

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1. Materials and Methods

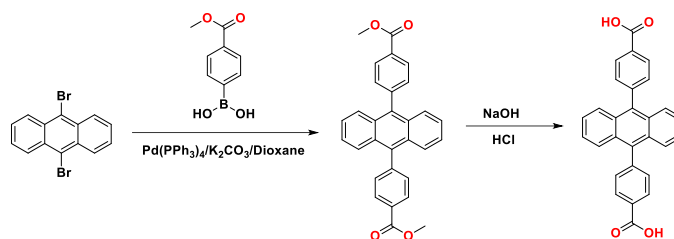
Unless otherwise noted, all materials were used as received from commercial sources without further purification. The products phase purity was examined by powder XRD in the angular range of $2\theta = 5-50^\circ$, using a Bruker D8 ADVANCE X-ray powder diffractometer (Cu $K\alpha$, 1.5418 Å). UV-visible diffuse reflectance spectra were conducted with BaSO₄ pellets on a Lambda750 spectrometer. Ultraviolet-visible spectra were recorded on a Lambda750 spectrophotometer equipped with a xenon discharge lamp. The Fluorescent spectra were recorded on FluoroMax-4 fluorescence spectrometer equipped with a xenon discharge lamp. The electrochemical measurements were performed in a conventional three-electrode cell on a CHI-760E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd, China). Photocatalytic measurements were conducted on a RLH-18-22 photoreactor instrument (the distance between the lamp and the reaction vessel was 4mm). Electron paramagnetic resonance (EPR) signals were recorded on a Bruker E500-9.5/12 at room temperature under visible-light irradiation using a blue LED (400-470 nm). ¹H NMR and ¹³C NMR experiments were performed with a JEOL ECZ400S/L1 spectrometer. Mass spectra were carried out on a Maxis Ultimate 300HPLC·Maxis Ultimate 300hplc.

2. Density functional theory calculations

Structures of compounds ATDB, BTDB, IBTDB and TBTDB were optimized and characterized by frequency calculations to be energy minima (zero imaginary frequencies) at the B3LYP³/6-31g(d,p) level of density functional theory (DFT). The HOMO-LUMO energies were then obtained from the output files. All calculations were performed with Gaussian 09.^[1]

3. Synthesis and Characterization of organic linker

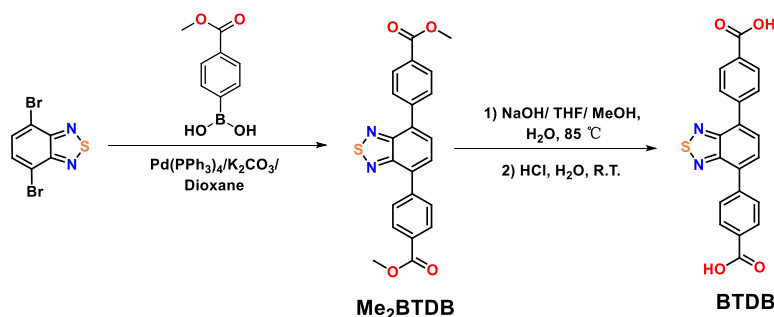
3.1 The synthesis of ATDB



Scheme S1. Synthesis of ATDB molecule

9,10-Dibromoanthracene (2.85 g, 8.5 mmol), 4-(methoxycarbonyl)phenylboronic acid (3.8 g, 21.2 mmol), K_2CO_3 (4.2 g, 30 mmol), and catalyst $[Pd(PPh_3)_4]$ (1.0 g, 0.86 mmol) were dissolved in dioxane (150 mL) under Ar in 250 ml three necked flask. The mixture was stirred at 120 °C for 24 h. Dichloromethane (100 mL) and water (50 mL) were added, the organic layer was separated, and the aqueous layer was extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine (200 mL), dried over anhydrous Na_2SO_4 , and filtered. The solvent was removed under reduced pressure and the residue was purified by passing through a silica plug with dichloromethane/petroleum ether (1:1) as the eluent to give a light-yellow solid (yield: 87%). 1H NMR (400 MHz, Chloroform- d) δ 8.29 (d, $J = 8.1$ Hz, 4H), 7.61 (dd, $J = 6.7$, 3.1 Hz, 4H), 7.57 (d, $J = 8.0$ Hz, 4H), 7.34 (dd, $J = 7.0$, 3.3 Hz, 4H), 4.02 (s, 6H). The solid was mixed with NaOH solution (0.1 M, 150 ml) and refluxed at 100 °C for 12 h. The resulting solution was cooled to room temperature and tuned to pH 5 by HCl. The light yellow precipitate was filtered and dried. 1H NMR (400 MHz, DMSO- d_6) δ 13.16 (s, 2H), 8.22 (d, $J = 8.1$ Hz, 4H), 7.62 (d, $J = 8.1$ Hz, 4H), 7.58 -7.52 (m, 4H), 7.46 (q, $J = 3.6$, 3.2 Hz, 4H).^[2]

3.2 The synthesis of BTDB



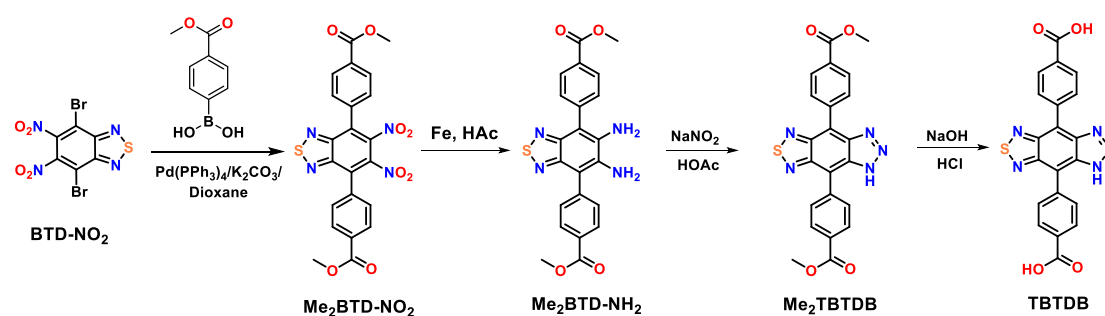
Scheme S2. Synthesis of BTDB molecule

4,7-dibromo-2,1,3-benzothiadiazole (1.0 g, 3.4 mmol), methyl 4-boronobenzoate (1.5 g, 8.5 mmol), potassium carbonate (2.6 g, 20.4 mmol) and $Pd(PPh_3)_4$ (78.6 mg, 0.068

mmol) were added into one 250 mL round-bottle flask containing 80 mL dioxane. The reaction solution was degassed four times. Then the mixture was heated to reflux at 110 °C for 72 h under argon atmosphere. After cooling down to room temperature, the mixture was extracted five times with ethyl acetate, then the organic layers were combined and dried over anhydrous Na₂SO₄ and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography to give the target product (yield 83%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 7.9 Hz, 4H), 8.07 (d, *J* = 7.7 Hz, 4H), 7.87 (s, 2H), 3.98 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 166.90, 153.90, 141.6, 133.0, 130.0, 129.4, 128.6, 52.4.^[3]

2.5 mmol compound Me₂BTDB was added to a solution containing 30 mL CH₃OH, 30 mL THF and 30 mL water with 1.0 g NaOH. The mixture was heated to reflux at 80 °C overnight. After cooling down to room temperature, the organic solvent was removed under reduced pressure and the resulted aqueous was filtered. Then the filtrate was neutralized using 2M HCl to obtain the precipitate, which was filtered to offer the final product BTDB.^[3]

3.3 The synthesis of TBTDB



Scheme S3. Synthesis of TBTDB molecule

The synthesis of Me₂BTD-NO₂. BTD-NO₂ (0.65 g, 1.7 mmol), methyl 4-boronobenzoate (0.75 g, 4.25 mmol), potassium carbonate (1.3 g, 10.2 mmol) and Pd(PPh₃)₄ (39.3 mg, 0.034 mmol) were added into one 100 mL round-bottle flask containing 40 mL dioxane. The reaction solution was degassed four times. Then the mixture was heated to reflux at 110 °C for 72 h under argon atmosphere. After cooling down to room temperature, the mixture was extracted five times with ethyl acetate, then

the organic layers were combined and dried over anhydrous Na₂SO₄ and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography to give the target product (yield 89%). ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, J = 2.0 Hz, 4H), 7.65 (d, J = 1.9 Hz, 4H), 3.97 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 166.20, 152.70, 142.56, 134.66, 132.11, 130.29, 129.36, 128.77, 52.62.^[4]

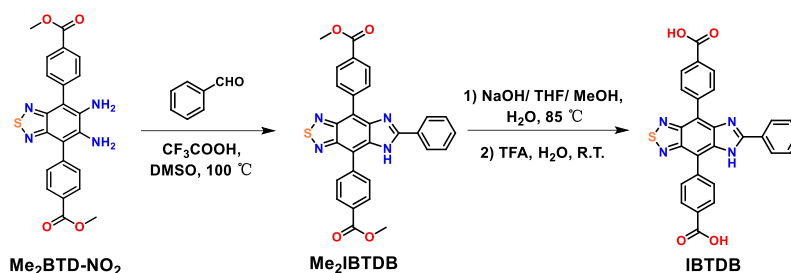
The synthesis of Me₂BTD-NH₂. A 100 mL round bottom flask was charged with Me₂BTD-NO₂ (0.5 g, 1.0 mmol), iron powder (0.68 g, 12.1 mmol), and acetic acid (30 mL). The reaction was heated to 100 °C for 2 h, then cooled to room temperature and diluted with water (50 mL). The product was extracted with CH₃COOC₂H₅ (3 × 40 mL). The combined organic layers were washed with water and dried over anhydrous Na₂SO₄, filtered, and solvent removed under reduced pressure to give the crude product, which was further purified using column chromatograph to give orange solid (yield: 76%). ¹H NMR (400 MHz, DMSO-d₆) δ 8.11 (d, J = 7.8 Hz, 4H), 7.67 (d, J = 7.8 Hz, 4H), 5.62 (s, 4H), 3.91 (s, 6H).^[4]

The synthesis of Me₂TBTDB. To a solution of compound 4 (738 mg, 1.7 mmol) in 80 mL acetic acid was added NaNO₂ (300 mg, 4 mmol) at room temperature. The resulting mixture was then stirred at room temperature for 3 h. The reaction mixture was diluted with H₂O, and extracted with ethyl acetate. The combined organic layers were washed saturated NaHCO₃ aqueous solution, dried over Na₂SO₄, and concentrated in vacuo to give a red residue. The residue was purified by chromatography on silica gel column (CH₂Cl₂/MeOH =60:1 v/v) to furnish the desired product (yield: 86%).^[5] ¹H NMR (400 MHz, Trifluoroacetic Acid-d) δ 8.37 (d, J = 7.9 Hz, 4H), 8.06 (d, J = 7.9 Hz, 4H), 4.09 (s, 6H). HRMS Calcd (ESI) m/z for C₂₂H₁₄N₅O₄S: [M-H]⁻ 444.0771, Found: 444.0772.

The synthesis of TBTDB. The resultant solid was added to a solution containing 10 mL CH₃OH, 10 mL THF and 10 mL water with 0.3 g NaOH. The mixture was heated to reflux at 90 °C overnight. After cooling down to room temperature, the organic solvent was removed under reduced pressure and the resulted aqueous was filtered. Then the filtrate was neutralized using 2M HCl to obtain the precipitate, which was filtered to offer the final product TBTDB (yield 88%). ¹H NMR (400 MHz,

Trifluoroacetic Acid-*d*) δ 8.48 (s, 4H), 8.14 (s, 4H). HRMS Calcd (ESI) *m/z* for $C_{20}H_{10}N_5O_4S$: $[M-H]^-$ 416.0458, Found: 416.0519.

3.4 The synthesis of IBTDB



Scheme S4. Synthesis of IBTDB molecule

The synthesis of Me-IBTDB. Benzaldehyde, and Me₂BTD-NH₂ (0.087 g, 0.2 mmol) were dissolved in DMSO (5 mL). Then, trifluoroacetic acid (100 μ L) was added dropwise into the mixture with rapid stirring. Then the mixture was heated to reflux at 110 °C for 12 h under nitrogen atmosphere. After cooling down to room temperature, the mixture was diluted with distilled water (100 mL), the mixture was extracted five times with ethyl acetate, then the organic layers were combined and dried over anhydrous Na₂SO₄ and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography to give the target product (yield 81%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.90 (s, 1H), 8.49 (d, *J* = 8.3 Hz, 2H), 8.39 – 8.22 (m, 2H), 8.19 (t, *J* = 7.9 Hz, 4H), 8.08 (d, *J* = 7.9 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 3H), 3.94 (s, 6H).^[6]

The synthesis of IBTDB. 2.5 mmol compound Me-IBTDB was added to a solution containing 30 mL CH₃OH, 30 mL THF and 30 mL water with 1.0 g NaOH. The mixture was heated to reflux at 80 °C overnight. After cooling down to room temperature, the organic solvent was removed under reduced pressure and the resulted aqueous was filtered. Then the filtrate was neutralized using 2M HCl to obtain the precipitate, which was filtered to offer the final product IBTDB (yield 90%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.07 (s, 2H), 12.88 (s, 1H), 8.45 (d, *J* = 8.1 Hz, 2H), 8.39 (d, *J* = 7.3 Hz, 2H), 8.23 – 8.14 (m, 4H), 8.05 (d, *J* = 7.9 Hz, 2H), 7.59 (d, *J* = 7.1 Hz, 3H).^[6]

4. Synthesis of UiO-66 and UiO-66-L

4.1 Synthesis of UiO-66

A mixture of $ZrCl_4$ (47 mg, 0.2 mmol), H_2BDC (16 mg, 0.1 mmol) and acetic acid (1.2 g) in 6 mL DMF was sonicated for 5 minutes and then transferred into a Teflon liner at room temperature. The vessel was sealed and placed in an oven at 120 °C for 72 h under static conditions before cooling slowly to room temperature in 12 hours. The precipitates were isolated by centrifugation, washed with DMF three times and followed by washing with methanol two times. After drying under vacuum for 6 h, the obtained product was washed thoroughly with acetone. Finally, the solids were dried at 150 °C under vacuum.

4.2 Synthesis of UiO-66-L

UiO-66-L (50 mg) was added to the solution (3 mmol/L) of the ligand (L = ATDB, BTDB, IBTDB, TBTDB) in DMF (5 mL) and stirred at room temperature for 24 h. The resulting powder product was centrifuged and washed with DMF and methanol thoroughly until the physisorbed ligands removed thoroughly. Finally, the material was dried overnight at 100 °C.

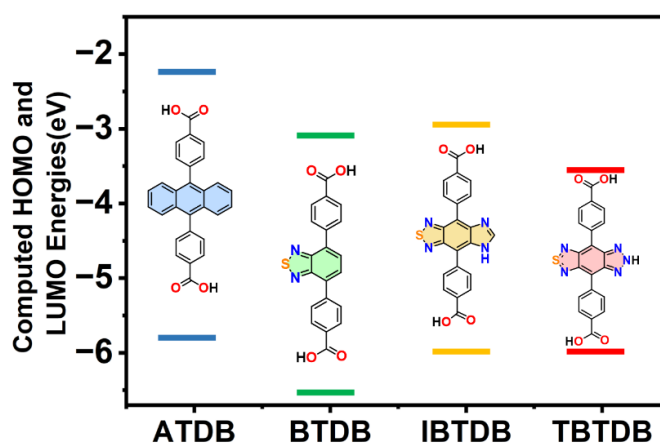


Figure S1. Molecular structures and calculated HOMO–LUMO energy levels of ATDB, BTDB, IBTDB, and TBTDB.

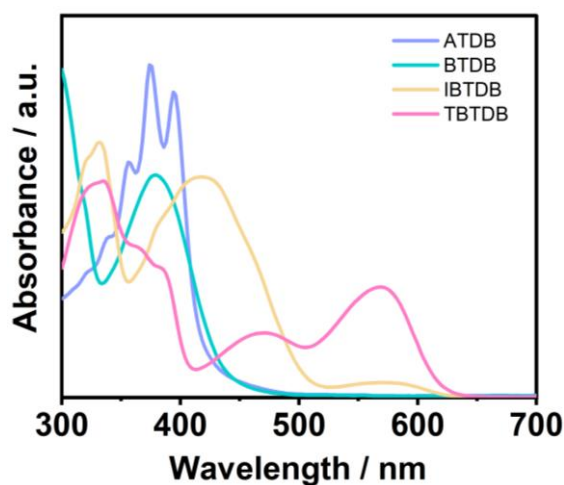


Figure S2. UV-vis adsorption spectra of ATDB, BTDB, IBTDB, and TBTDB in DMF solution.

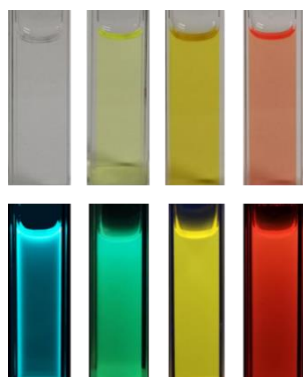


Figure S3. Photographs of the ATDB, BTDB, IBTDB and TBTDB in DMF solution under daylight and 365 nm excitation.

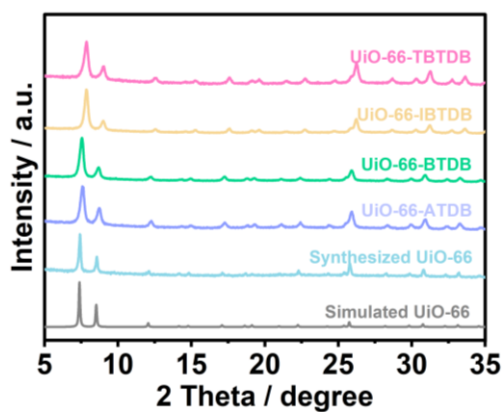


Figure S4. PXRD patterns of the four UiO-66-L MOFs.

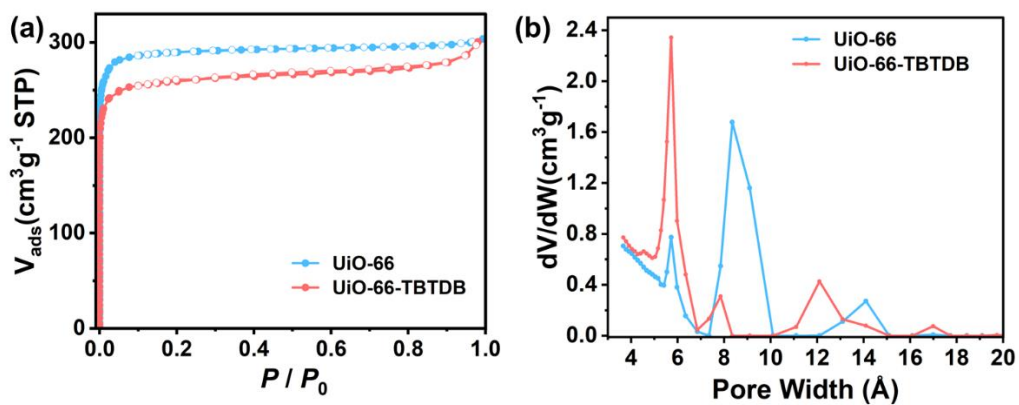


Figure S5. N_2 adsorption-desorption isotherm (a), and pore size distribution (b) for UiO-66 and UiO-66-TBTDB.

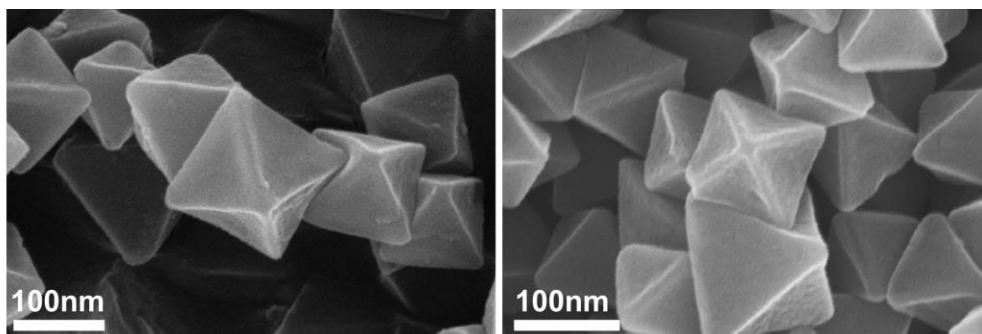


Figure S6. SEM images of UiO-66 (a) and UiO-66-TBTDB (b).

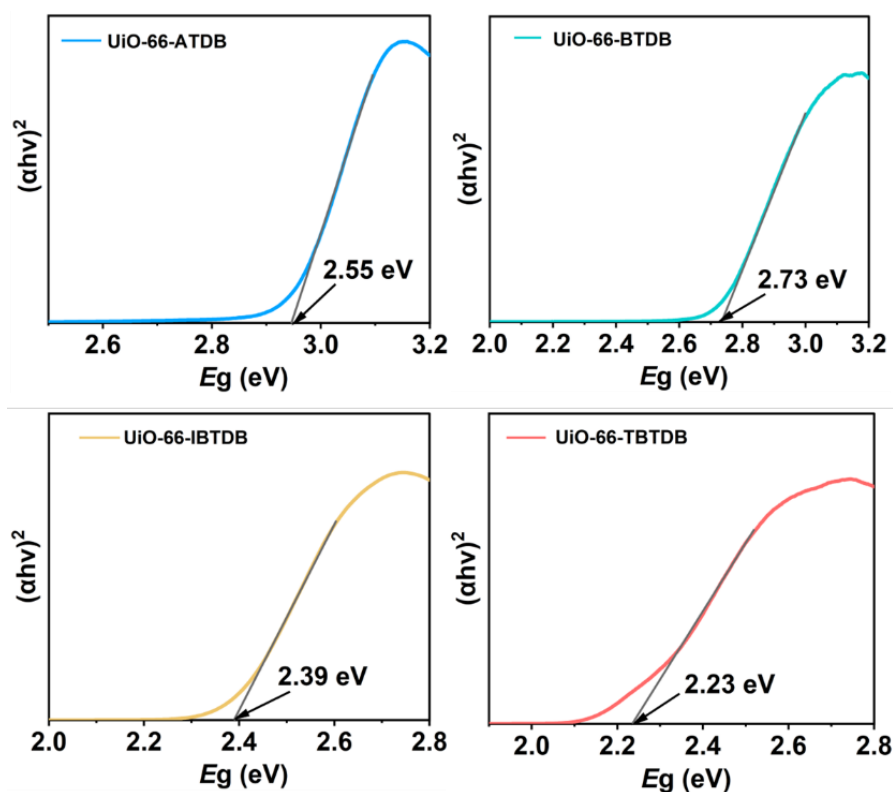


Figure S7. The tauc plot for UiO-66-ATDB, UiO-66-BTDB, UiO-66-IBTDB, UiO-66-TBTDB.

5. Electrochemical Measurements

MOF powder was ground with poly(vinylidene fluoride) and then ultrasonically dispersed in acetone. The resultant slurry was then drop-casted onto indium tin oxide (ITO) glass with an area of 0.5×0.5 cm². A Pt wire (counter electrode), a Ag/AgCl electrode (reference electrode), and a coated ITO conductive glass (working electrode) were assembled into a three-electrode system with 0.5 M Na₂SO₄ aqueous solution used as the electrolyte. The photocurrent measurements were conducted under the irradiation of a 300 W xenon lamp (100 mW cm^{-1}) with a 420 nm cut-off filter. The Mott-Schottky plots were collected at 1000 Hz.

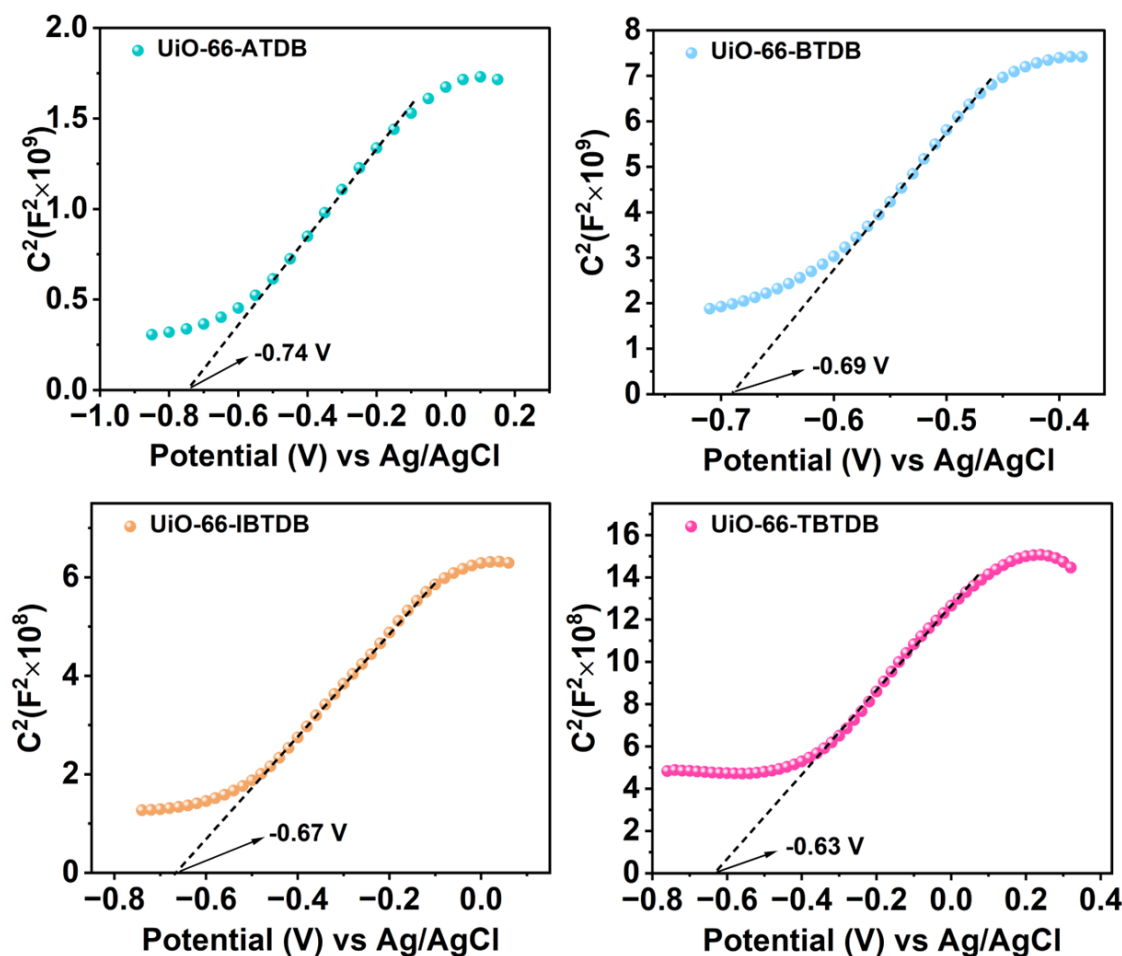


Figure S8. Mott-Schottky plots for UiO-66-ATDB, UiO-66-BTDB, UiO-66-IBTDB, UiO-66-TBTDB

6. Catalysis Details

6.1 Photocatalytic synthesis of azacycles.

In a typical reaction system, aniline derivatives (0.2 mmol), aldehydes (0.25 mmol), catalyst UiO-66-L (10 mg) and MeOH (3 mL) were added to a flat quartz glass jar with a magnetic stirrer. A 20 W blue LED (450-455 nm) was used as the light source by bottom irradiation. The temperature of the reaction was in the range of 25 ± 5 °C. After 4 h of reaction, the mixture was centrifuged to remove UiO-66-L samples and extracted three times with ethyl acetate, then the organic layers were combined and dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography to give the target product.

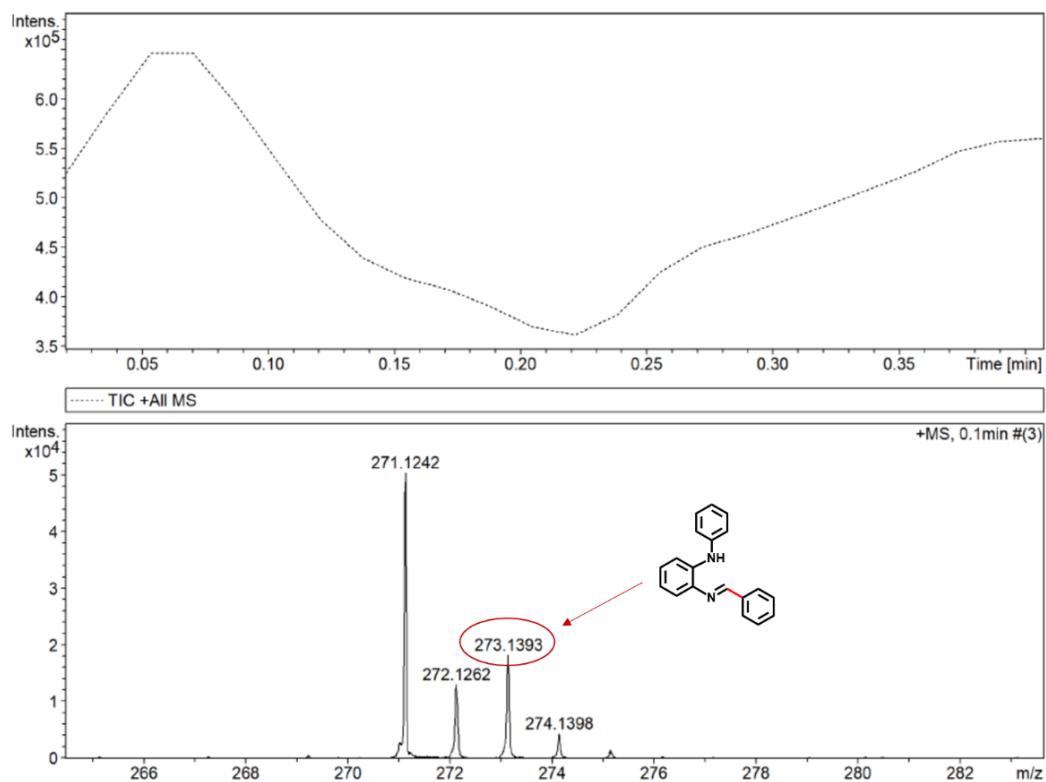


Figure S9. HRMS of the intermediate I in the photocatalytic synthesis of 1,2-diphenyl-1H-benzo[d]imidazole (**c1**).

6.2. Heterogeneous Catalysis Nature

Filtration experiment. In a flat quartz glass jar with a magnetic stirrer, benzaldehyde (0.25 mmol), 2-aminodiphenylamine (0.2 mmol), MeOH (3 mL) and UiO-68-TBTDB (10 mg) were added. The open-air reaction container was placed under a 10 W blue LED lamp and stirred for 4 h. After reacting for 40 min, the catalyst was removed through gravity filtration. The yields were then monitored at different periods.

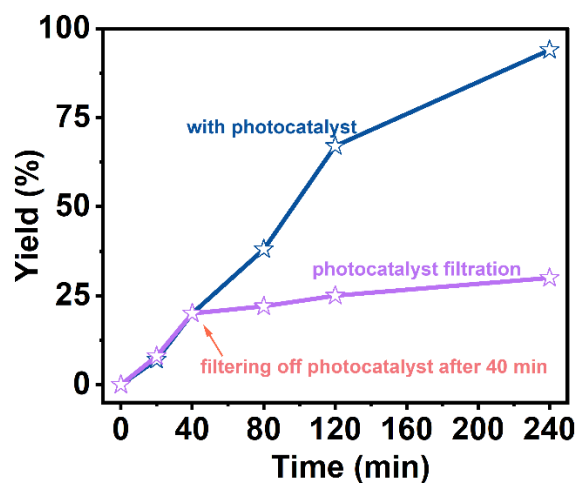


Figure S10. Leaching test experiment of UiO-66-TBTDB.

Recycling experiments. The recycling experiments were carried out with 2-aminodiphenylamine and benzaldehyde under the optimized reaction condition. After the reaction, UiO-68-TBTDB was separated via filtration, then washed thoroughly with ethyl acetate. The recycled UiO-68-TBTDB was dried and then subject to the next cycle.

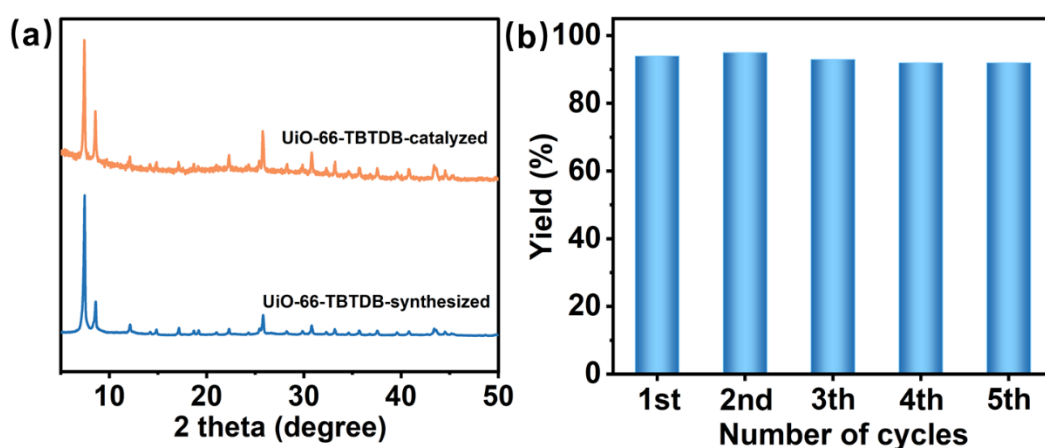


Figure S11. (a) PXRD patterns of the as-synthesized UiO-68-TBTDB and catalysts after 5 cycles.

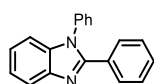
(b) Recycling of UiO-68-TBTDB for photocatalytic synthesis of **c1**.

Table S1. Quenching experiments of reaction conditions ^a

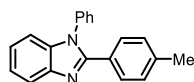
Entry	Deviation from standard condition	Yield ^b (%)
1	no variation	94
2	TEMPO	18
3	IPA	90
4	NaN ₃	26
5	BQ	22
6	AgNO ₃	25
7	C ₂ O ₄ (NH ₄) ₂	32

^a Standard conditions: **a1** (0.2 mmol), **b2** (0.25 mmol), catalyst (10 mg), MeOH (3 mL), 10 W blue LED lamps, room temperature, air, 4 h. ^b Isolated yields.

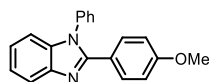
7. ¹H NMR and ¹³C NMR of products



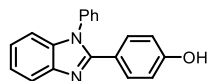
1,2-diphenyl-1*H*-benzo[*d*]imidazole (c1); 94% yield; white solid; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.48 (td, *J* = 8.4, 5.4 Hz, 3H), 7.35 – 7.29 (m, 6H), 7.26 – 7.24 (m, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 152.5, 143.1, 137.3, 137.1, 130.0, 130.0, 129.6 (2C), 128.6, 128.4, 127.5, 123.4, 123.1, 119.9, 110.6. HRMS Calcd (ESI) *m/z* for C₁₉H₁₅N₂: [M+H]⁺ 271.1230, Found: 271.1236.



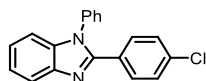
1-phenyl-2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole (c2); 97% yield; white solid; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.9 Hz, 1H), 7.48 (dt, *J* = 11.4, 6.9 Hz, 5H), 7.31 (td, *J* = 8.0, 7.0, 4.5 Hz, 3H), 7.24 (dd, *J* = 6.7, 2.5 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 2.32 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 152.6, 143.0, 139.7, 137.3, 137.2, 130.0, 129.4, 129.2, 128.6, 127.5, 127.1, 123.3, 123.0, 119.8, 110.5, 21.5. HRMS Calcd (ESI) *m/z* for C₂₀H₁₇N₂: [M+H]⁺ 285.1386, Found: 285.1375.



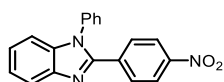
2-(4-methoxyphenyl)-1-phenyl-1*H*-benzo[*d*]imidazole (c3); 96% yield; white solid; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.58 – 7.40 (m, 5H), 7.32 (ddd, *J* = 7.9, 6.1, 1.9 Hz, 3H), 7.26 – 7.18 (m, 2H), 6.97 – 6.62 (m, 2H), 3.78 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 160.6, 152.4, 143.0, 137.3, 137.2, 131.0, 130.0, 128.6, 127.6, 123.1, 123.0, 122.3, 119.6, 113.9, 110.4, 55.4. HRMS Calcd (ESI) *m/z* for C₂₀H₁₇N₂O: [M+H]⁺ 301.1335, Found: 301.1342.



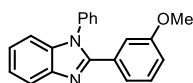
4-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenol (c4); 92% yield; white solid; ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.92 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.52 (m, 3H), 7.41 (dd, *J* = 7.0, 1.9 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 6.73 (d, *J* = 8.7 Hz, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 159.2, 152.8, 143.1, 137.6, 137.3, 131.2, 130.6, 129.2, 128.1, 123.3, 123.0, 120.9, 119.5, 115.7, 110.7. HRMS Calcd (ESI) *m/z* for C₁₉H₁₅N₂O: [M+H]⁺ 287.1179, Found: 287.1170.



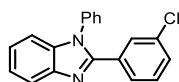
2-(4-chlorophenyl)-1-phenyl-1H-benzo[d]imidazole (c5); 93% yield; white solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, $J = 8.0$ Hz, 1H), 7.50 (d, $J = 7.4$ Hz, 4H), 7.36 – 7.23 (m, 8H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.3, 142.9, 137.3, 136.8, 135.8, 130.8, 130.1, 128.9, 128.7, 128.5, 127.5, 123.7, 123.3, 120.0, 110.6. HRMS Calcd (ESI) m/z for $\text{C}_{19}\text{H}_{14}\text{ClN}_2$: $[\text{M}+\text{H}]^+$ 305.0840, Found: 305.0833.



2-(4-nitrophenyl)-1-phenyl-1H-benzo[d]imidazole (c6); 91% yield; white solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.18 – 8.12 (m, 2H), 7.92 (d, $J = 7.7$ Hz, 1H), 7.79 – 7.74 (m, 2H), 7.60 – 7.53 (m, 3H), 7.42 – 7.36 (m, 1H), 7.36 – 7.31 (m, 3H), 7.27 (dd, $J = 7.9, 1.5$ Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.7, 148.1, 142.9, 137.5, 136.4, 136.1, 130.4, 130.2, 129.4, 127.4, 124.6, 123.8, 123.6, 120.4, 110.9. HRMS Calcd (ESI) m/z for $\text{C}_{19}\text{H}_{14}\text{N}_3\text{O}_2$: $[\text{M}+\text{H}]^+$ 316.1081, Found: 316.1088.

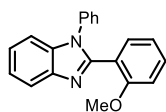


2-(3-methoxyphenyl)-1-phenyl-1H-benzo[d]imidazole (c7); 93% yield; white solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, $J = 8.4$ Hz, 1H), 7.51 – 7.45 (m, 3H), 7.34 – 7.30 (m, 3H), 7.25 (dd, $J = 6.5, 1.3$ Hz, 2H), 7.20 – 7.14 (m, 2H), 7.12 – 7.08 (m, 1H), 6.91 – 6.87 (m, 1H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.4, 152.3, 142.9, 137.3, 137.1, 131.1, 130.0, 129.4, 128.7, 127.5, 123.5, 123.2, 122.0, 119.9, 116.4, 114.1, 110.6, 55.3. HRMS Calcd (ESI) m/z for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}$: $[\text{M}+\text{H}]^+$ 301.1335, Found: 301.1329.

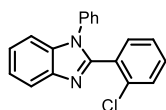


2-(3-chlorophenyl)-1-phenyl-1H-benzo[d]imidazole (c8); 88% yield; white solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, $J = 7.9$ Hz, 1H), 7.67 (t, $J = 2.0$ Hz, 1H), 7.55 – 7.48 (m, 3H), 7.37 – 7.34 (m, 1H), 7.33 – 7.29 (m, 4H), 7.28 – 7.23 (m, 2H), 7.19 (t, $J = 7.8$ Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.9, 142.8, 137.3, 136.7, 134.5, 131.7, 130.1, 129.7, 129.62, 129.60, 129.0, 127.5, 127.4, 123.9, 123.4,

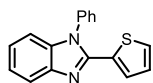
120.1, 110.7. HRMS Calcd (ESI) m/z for $C_{19}H_{14}ClN_2$: $[M+H]^+$ 305.0840, Found: 305.0847.



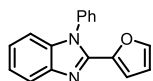
2-(2-methoxyphenyl)-1-phenyl-1H-benzo[d]imidazole (c9); 84% yield; white solid; 1H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, $J = 7.8$ Hz, 1H), 7.68 – 7.64 (m, 1H), 7.42 – 7.34 (m, 5H), 7.30 (dd, $J = 15.5, 7.5$ Hz, 2H), 7.24 (t, $J = 7.1$ Hz, 2H), 7.03 (t, $J = 7.5$ Hz, 1H), 6.72 (d, $J = 8.4$ Hz, 1H), 3.30 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.0, 151.4, 143.2, 137.3, 136.1, 132.3, 131.6, 129.1, 127.7, 126.0, 123.2, 122.7, 120.8, 120.0, 119.9, 110.9, 110.4, 54.8. HRMS Calcd (ESI) m/z for $C_{20}H_{17}N_2O$: $[M+H]^+$ 301.1335, Found: 301.1344.



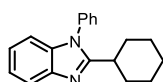
2-(2-chlorophenyl)-1-phenyl-1H-benzo[d]imidazole (c10); 86% yield; white solid; 1H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, $J = 7.8$ Hz, 1H), 7.51 (d, $J = 7.2$ Hz, 1H), 7.41 – 7.35 (m, 5H), 7.35 – 7.31 (m, 3H), 7.31 – 7.27 (m, 1H), 7.27 – 7.24 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.6, 143.0, 136.1, 135.9, 134.2, 132.6, 131.1, 130.3, 129.8, 129.5, 128.3, 126.72, 126.68, 123.8, 123.1, 120.4, 110.7. HRMS Calcd (ESI) m/z for $C_{19}H_{14}ClN_2$: $[M+H]^+$ 305.0840, Found: 305.0839.



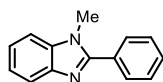
1-phenyl-2-(thiophen-2-yl)-1H-benzo[d]imidazole (c11); 89% yield; white solid; 1H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, $J = 8.0$ Hz, 1H), 7.65 – 7.55 (m, 3H), 7.41 (dd, $J = 6.5, 3.2$ Hz, 2H), 7.36 – 7.28 (m, 2H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.06 (d, $J = 8.0$ Hz, 1H), 6.92 – 6.87 (m, 1H), 6.84 (d, $J = 3.9$ Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.5, 142.8, 137.8, 136.5, 132.7, 130.3, 129.8, 128.5, 128.4, 128.3, 127.7, 123.5, 123.2, 119.6, 110.3. HRMS Calcd (ESI) m/z for $C_{17}H_{13}N_2S$: $[M+H]^+$ 277.0794, Found: 277.0789.



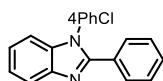
2-(furan-2-yl)-1-phenyl-1H-benzo[d]imidazole (c12); 90% yield; white solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, $J = 7.9$ Hz, 1H), 7.61 – 7.54 (m, 3H), 7.49 – 7.36 (m, 3H), 7.30 (t, $J = 7.6$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.07 (d, $J = 8.0$ Hz, 1H), 6.37 – 6.31 (m, 1H), 6.14 (d, $J = 3.7$ Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.5, 144.3, 142.9, 137.2, 136.4, 130.09, 130.08, 129.6, 128.1, 123.7, 123.2, 120.0, 112.3, 111.6, 110.3. HRMS Calcd (ESI) m/z for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}$: $[\text{M}+\text{H}]^+$ 261.1022, Found: 261.1031.



2-cyclohexyl-1-phenyl-1H-benzo[d]imidazole (c13); 83% yield; white solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, $J = 7.8$ Hz, 1H), 7.61 – 7.52 (m, 3H), 7.34 (dd, $J = 7.0, 1.9$ Hz, 2H), 7.25 (t, $J = 7.6$ Hz, 1H), 7.19 – 7.14 (m, 1H), 7.05 (d, $J = 8.0$ Hz, 1H), 2.75 – 2.64 (m, 1H), 1.92 – 1.76 (m, 6H), 1.70 – 1.62 (m, 1H), 1.34 – 1.15 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.4, 142.5, 136.5, 136.1, 130.0, 129.0, 127.7, 122.6, 122.4, 119.2, 110.1, 36.3, 32.1, 26.2, 25.8. HRMS Calcd (ESI) m/z for $\text{C}_{19}\text{H}_{21}\text{N}_2$: $[\text{M}+\text{H}]^+$ 277.1699, Found: 277.1692.

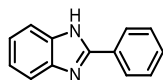


1-methyl-2-phenyl-1H-benzo[d]imidazole (c14); 97% yield; white solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.80 (m, 1H), 7.75 (dd, $J = 6.1, 2.1$ Hz, 2H), 7.54 – 7.47 (m, 3H), 7.38 – 7.35 (m, 1H), 7.33 – 7.28 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.9, 143.0, 136.7, 130.3, 129.8, 129.5, 128.8, 122.9, 122.5, 119.9, 109.8, 31.8. HRMS Calcd (ESI) m/z for $\text{C}_{14}\text{H}_{13}\text{N}_2$: $[\text{M}+\text{H}]^+$ 209.1073, Found: 209.1076.

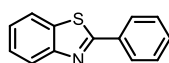


1-(4-chlorophenyl)-2-phenyl-1H-benzo[d]imidazole (c15); 92% yield; white solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, $J = 7.9$ Hz, 1H), 7.55 (d, $J = 7.1$ Hz, 2H), 7.47 (d, $J = 8.3$ Hz, 2H), 7.39 – 7.29 (m, 5H), 7.24 (d, $J = 8.6$ Hz, 3H). ^{13}C NMR (100

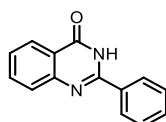
MHz, Chloroform-*d*) δ 152.4, 143.1, 137.0, 135.6, 134.5, 130.3, 129.8, 129.7, 129.6, 128.7, 128.6, 123.7, 123.3, 120.1, 110.3. HRMS Calcd (ESI) *m/z* for C₁₉H₁₄ClN₂: [M+H]⁺ 305.0840, Found: 305.0833.



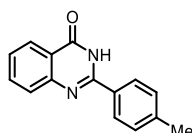
2-phenyl-1H-benzo[d]imidazole (c16); 95% yield; white solid; ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.92 (s, 1H), 8.18 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 3H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.18 (q, *J* = 4.8 Hz, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 151.8, 144.4, 135.6, 130.7, 130.4, 129.5, 127.0, 123.1, 122.2, 119.4, 111.9. HRMS Calcd (ESI) *m/z* for C₁₃H₁₁N₂: [M+H]⁺ 195.0917, Found: 195.0909.



2-phenylbenzo[d]thiazole (c17); 97% yield; white solid; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 8.06 (m, 3H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.52 – 7.46 (m, 4H), 7.40 – 7.35 (m, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 168.2, 154.2, 135.1, 133.7, 131.1, 129.1, 127.7, 126.5, 125.3, 123.3, 121.7. HRMS Calcd (ESI) *m/z* for C₁₃H₁₀NS: [M+H]⁺ 212.0528, Found: 212.0531.



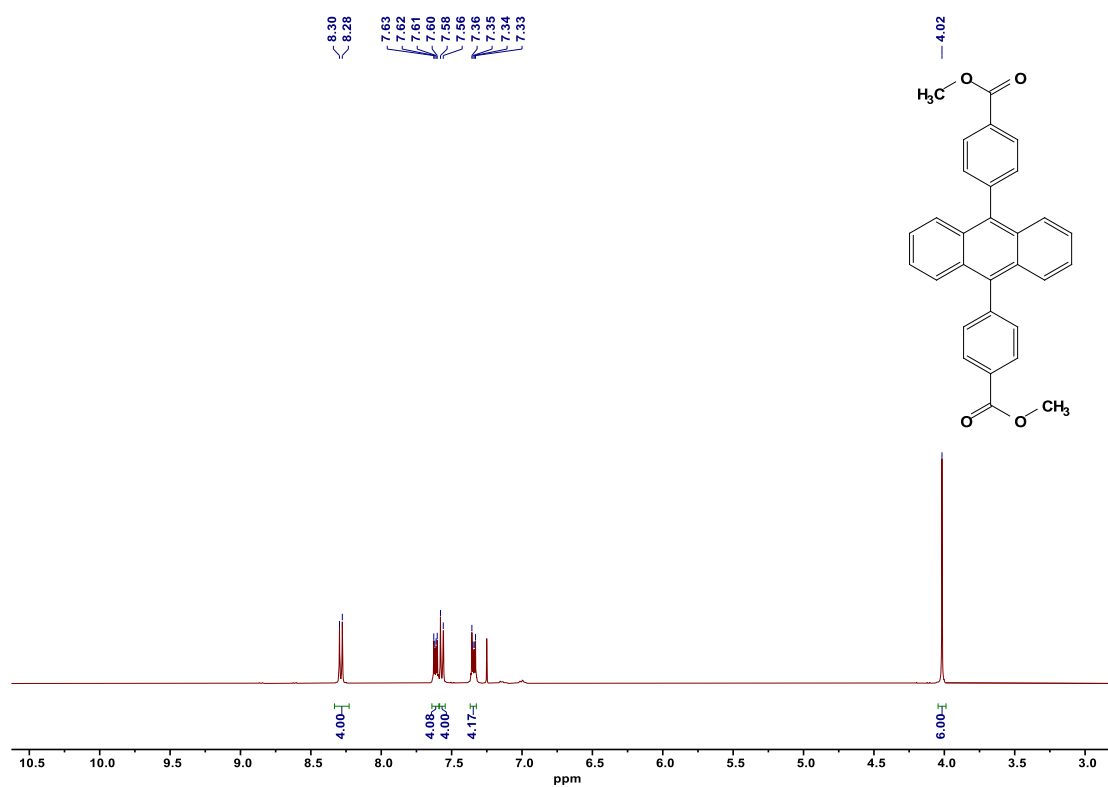
2-phenylquinazolin-4(3H)-one (c18); 92% yield; white solid; ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.14 (dd, *J* = 9.8, 7.8 Hz, 3H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.46 (m, 4H). HRMS Calcd (ESI) *m/z* for C₁₄H₁₁N₂O: [M+H]⁺ 223.0866, Found: 223.0872.

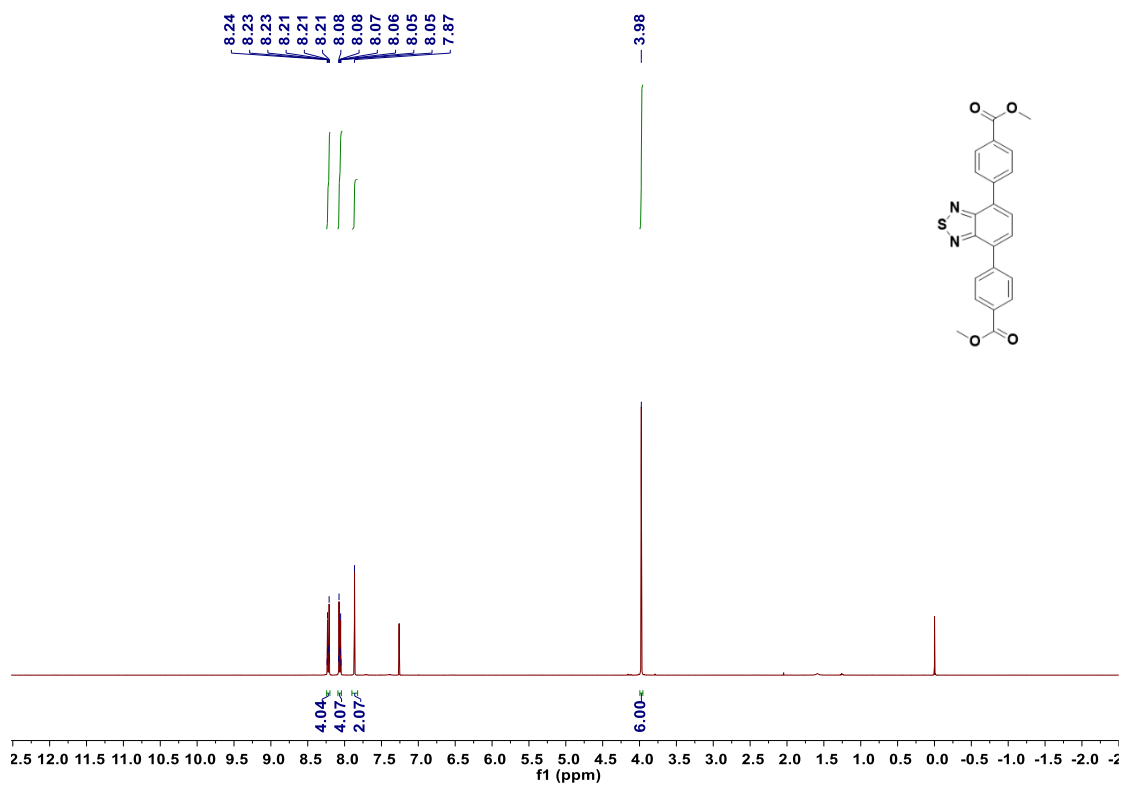
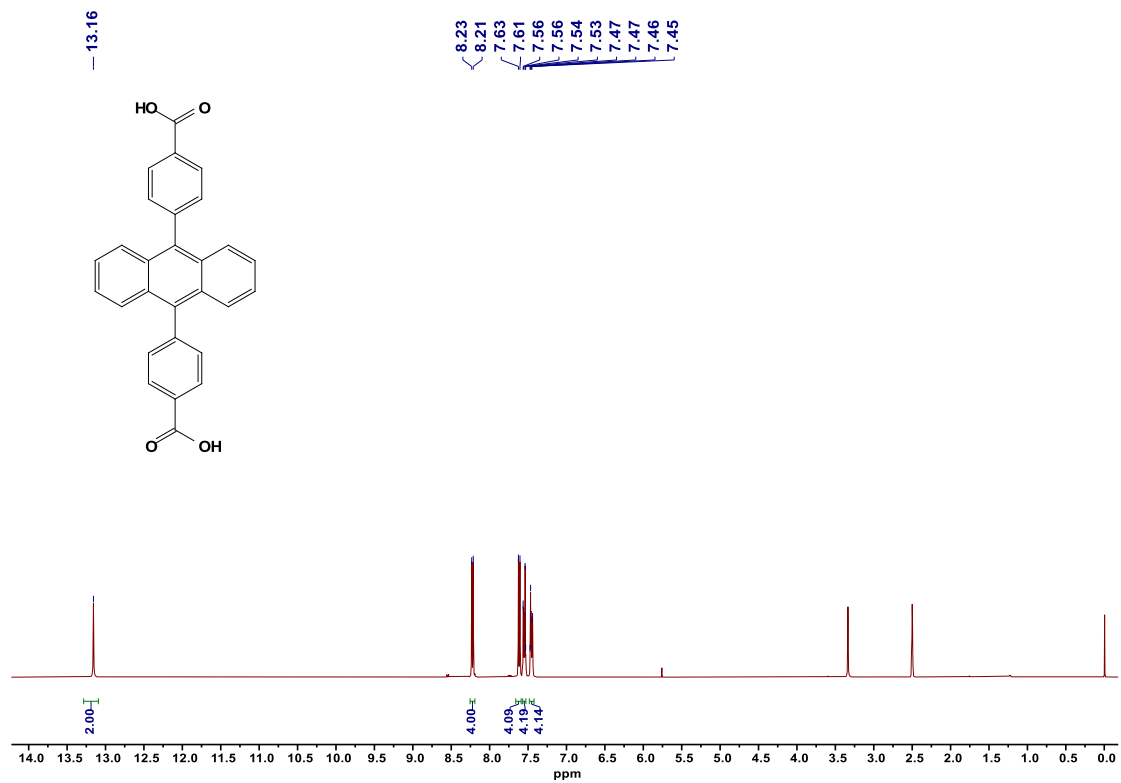


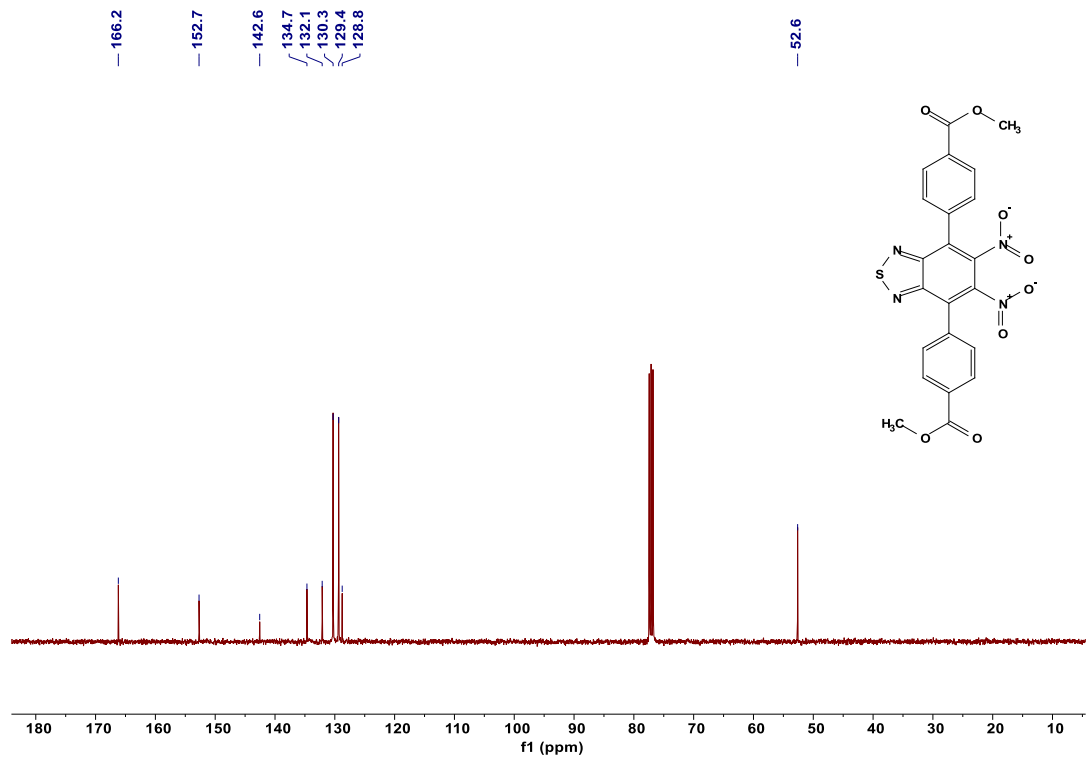
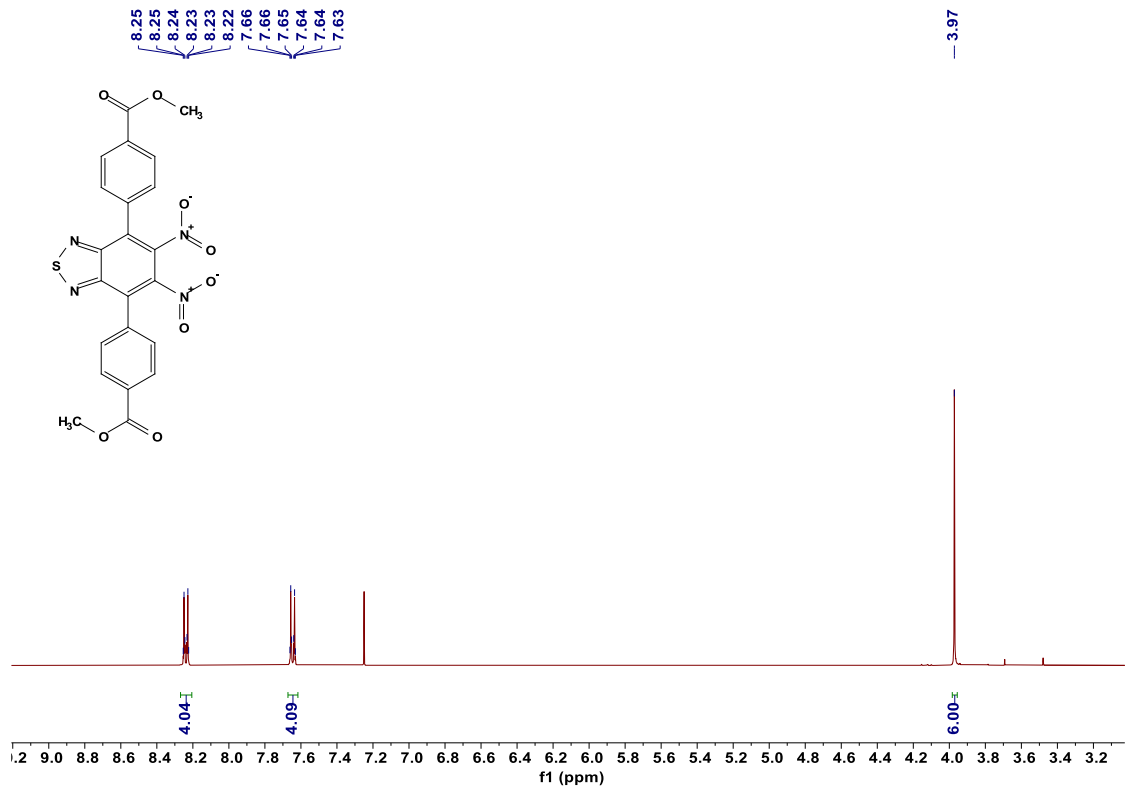
2-(*p*-tolyl)quinazolin-4(3H)-one (c19); 95% yield; white solid; ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.46 (s, 1H), 8.16 – 8.03 (m, 3H), 7.83 – 7.75 (m, 1H), 7.69 (d, *J* = 8.0

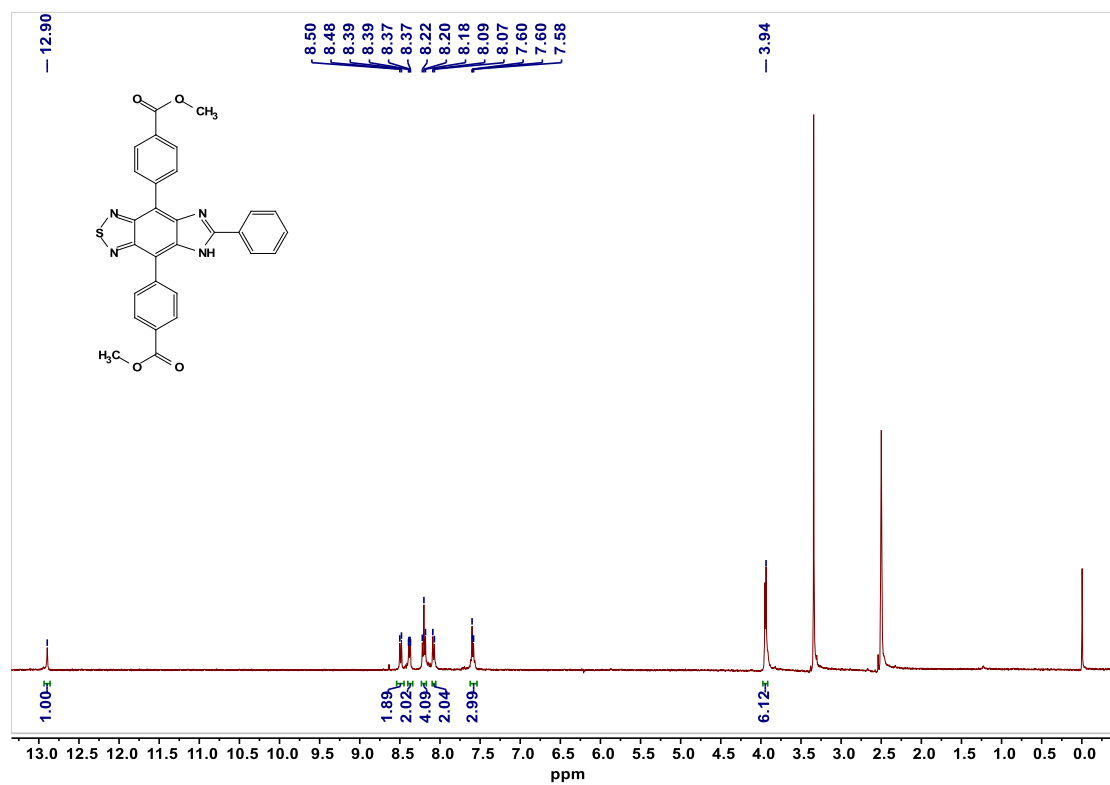
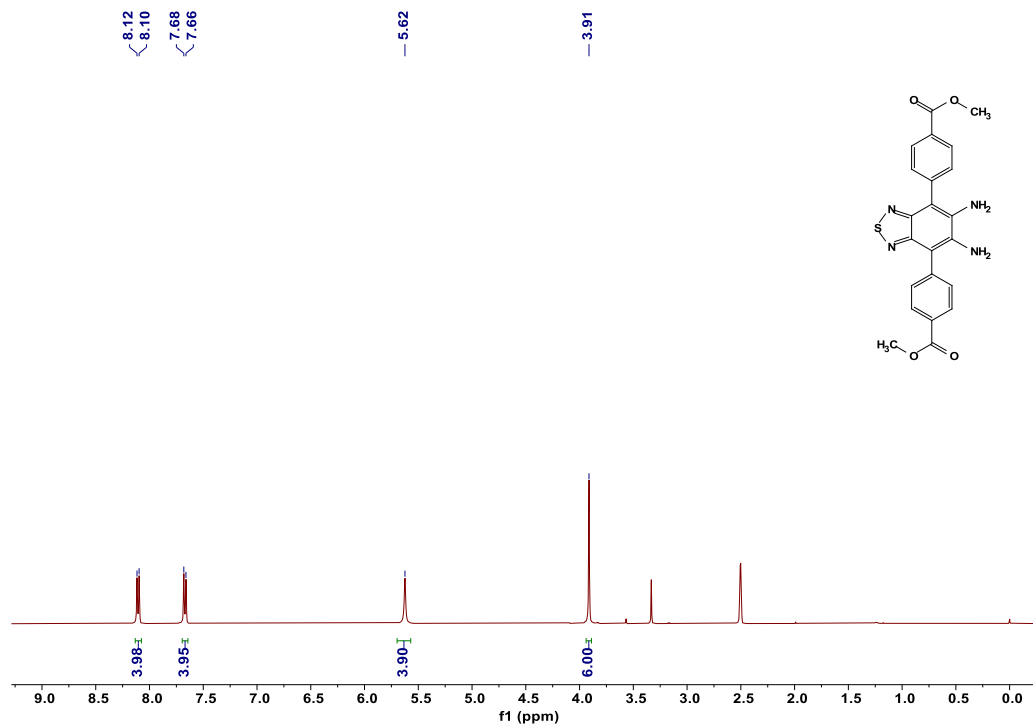
Hz, 1H), 7.47 (t, $J = 7.4$ Hz, 1H), 7.32 (d, $J = 8.1$ Hz, 2H), 2.36 (s, 3H). HRMS Calcd (ESI) m/z for $C_{15}H_{13}N_2O$: $[M+H]^+$ 237.1022, Found: 237.1017.

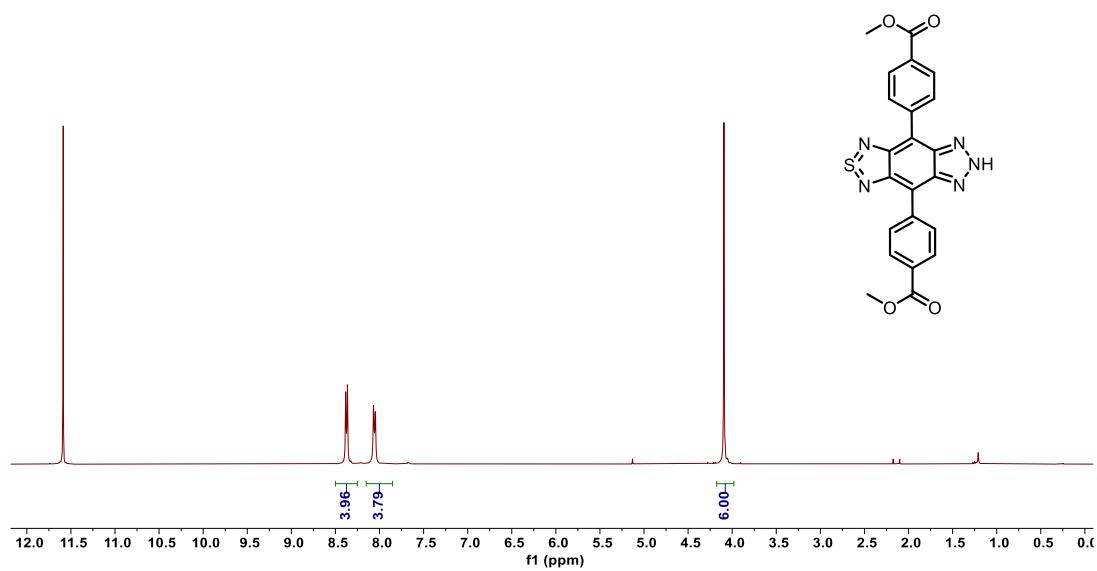
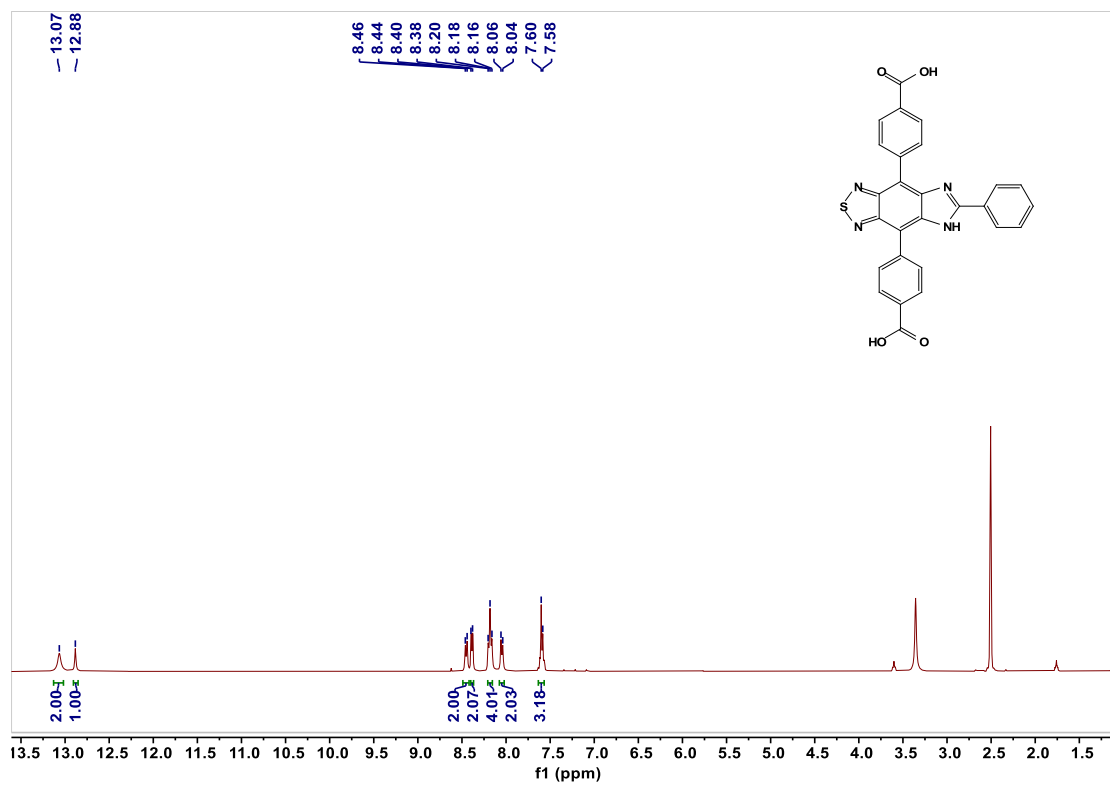
8. NMR spectra

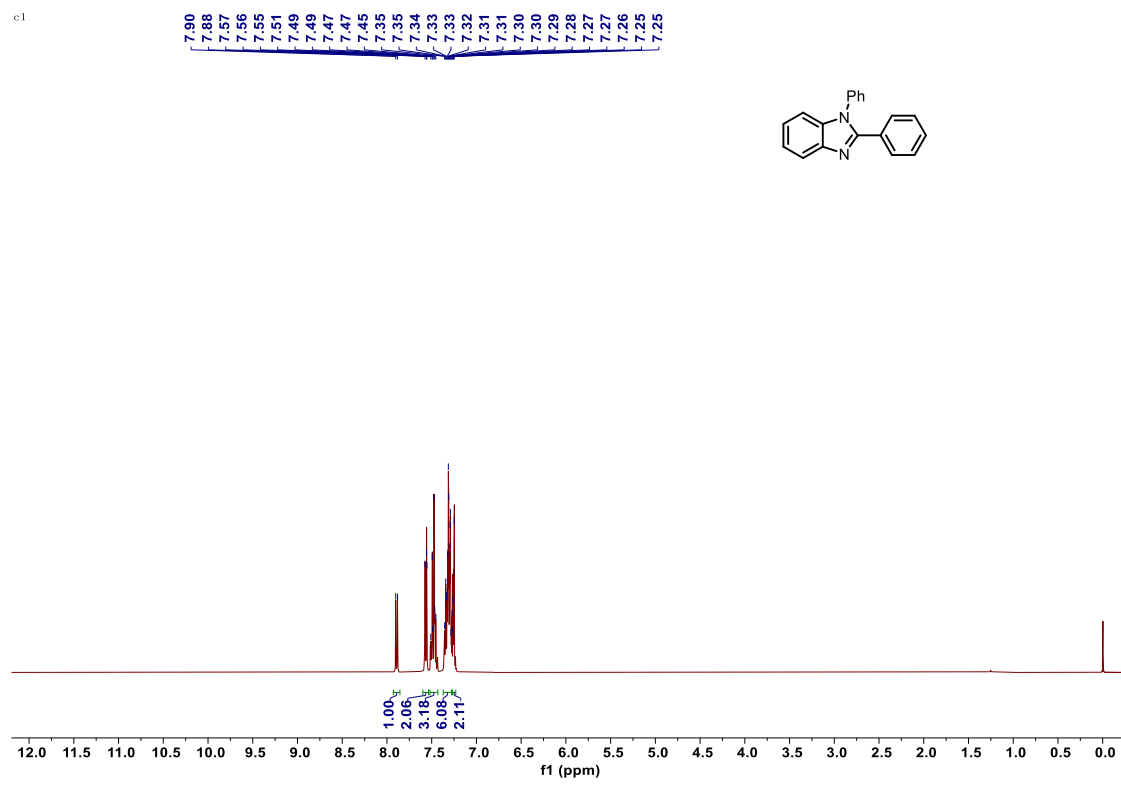
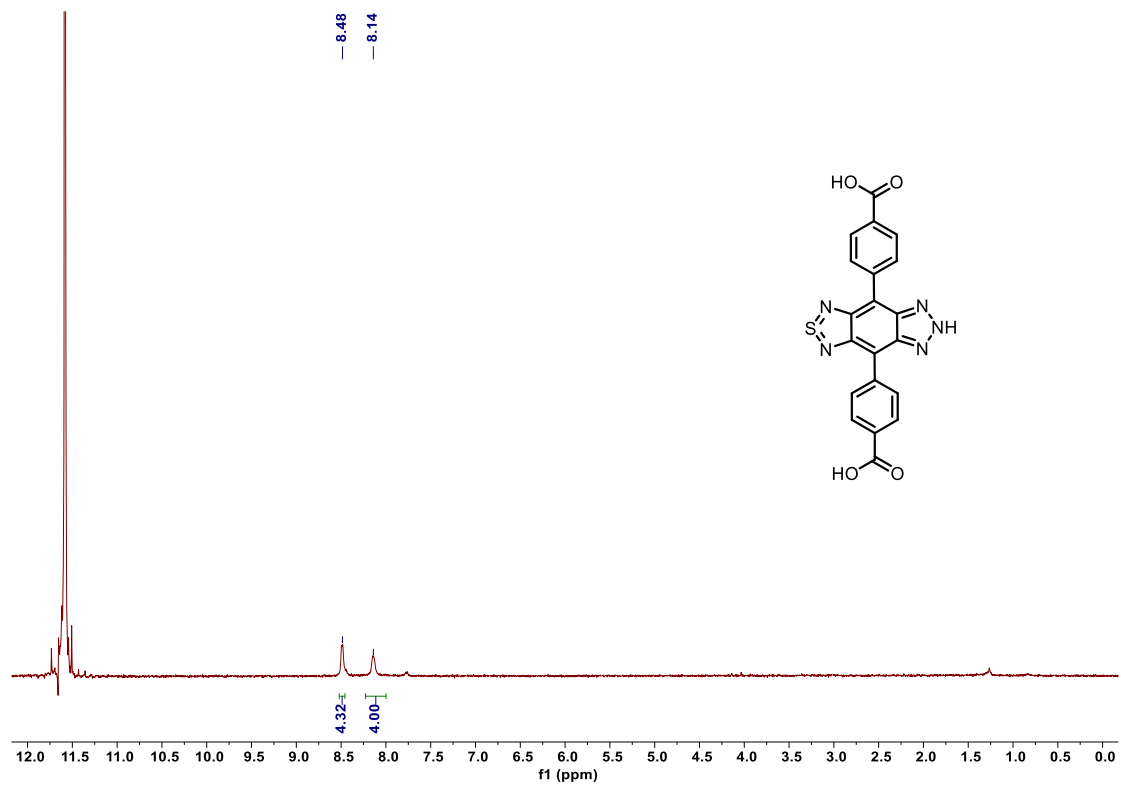






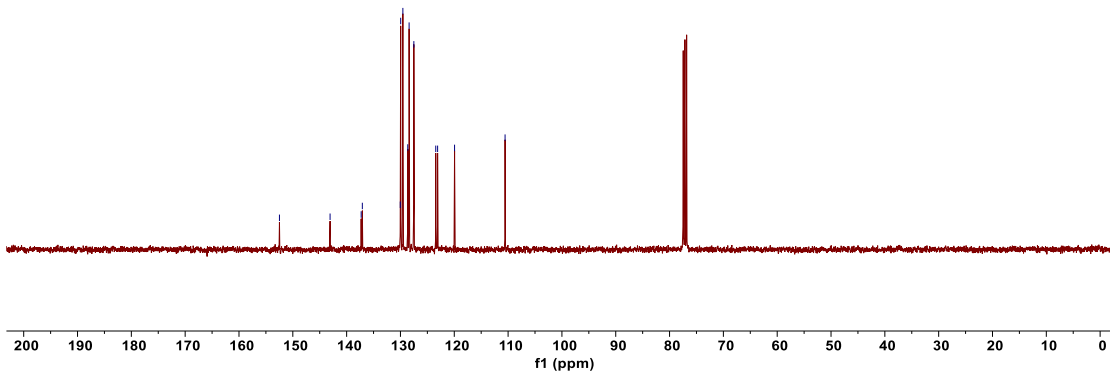
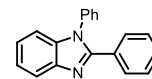


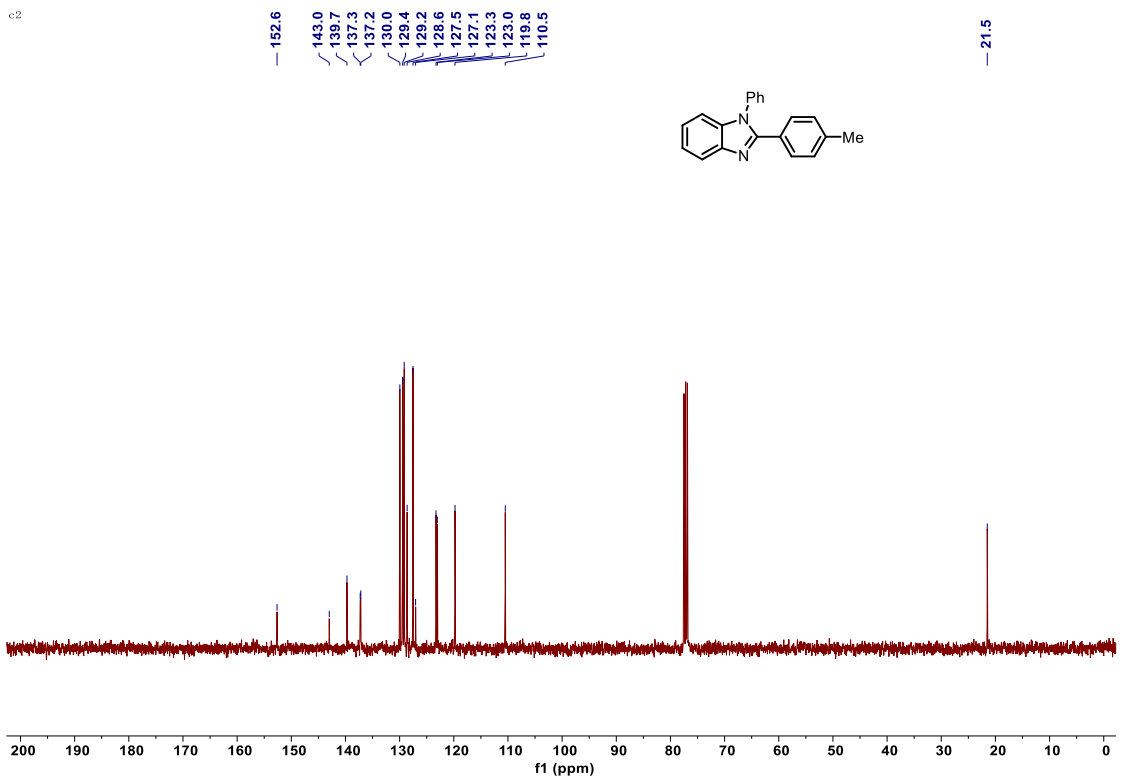
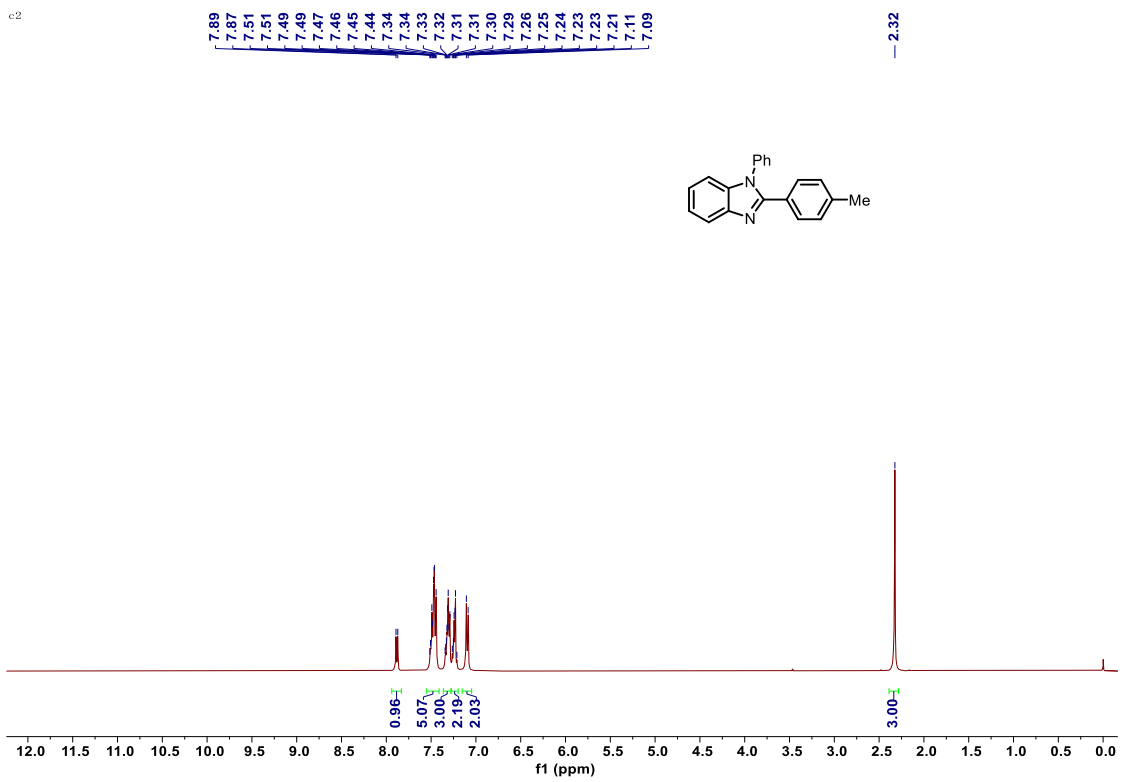


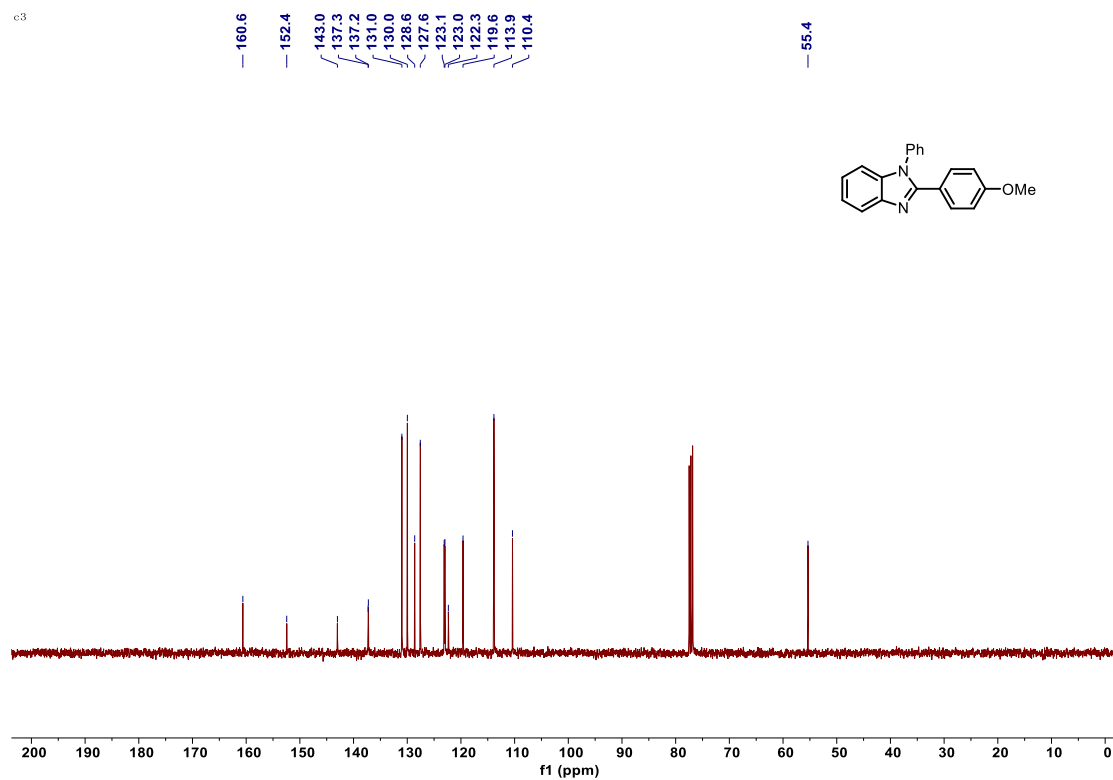
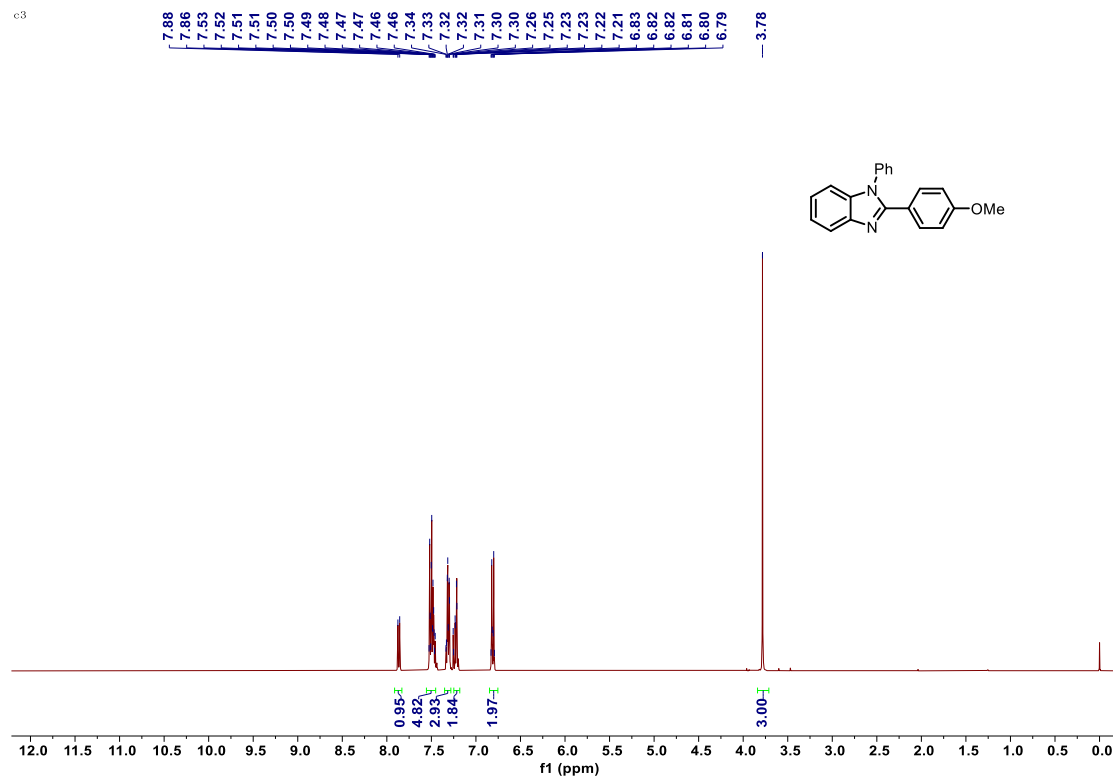


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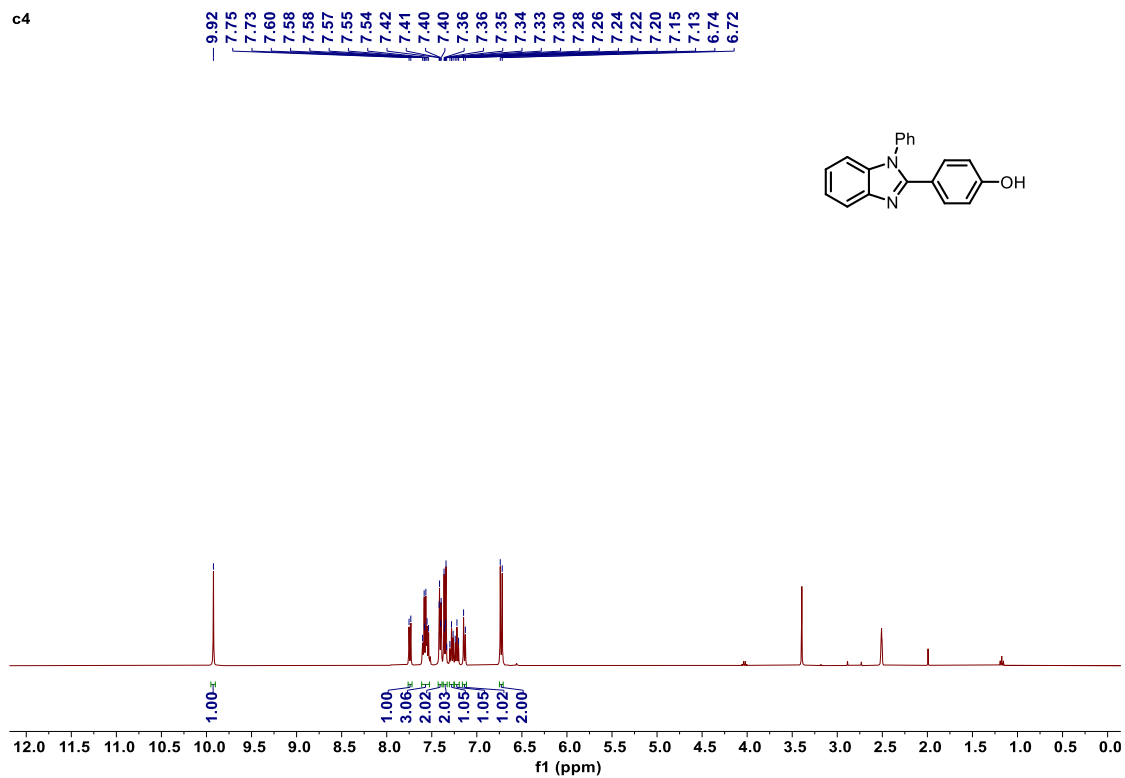
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110.6



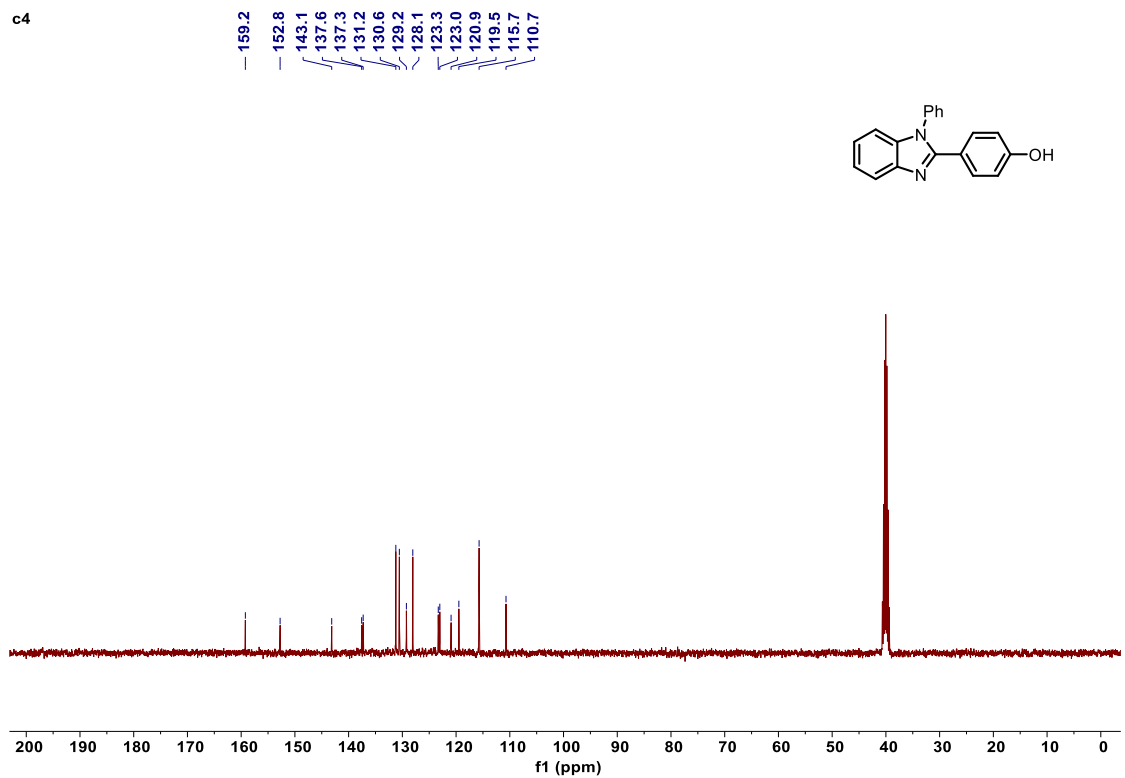




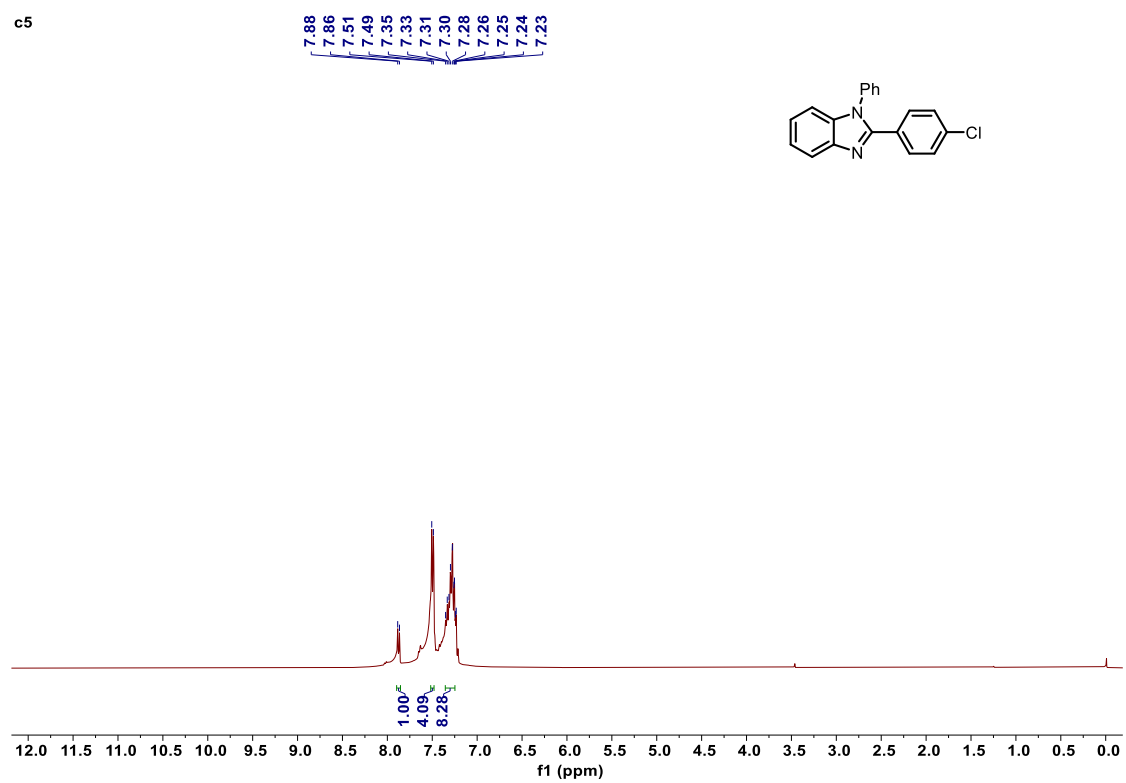
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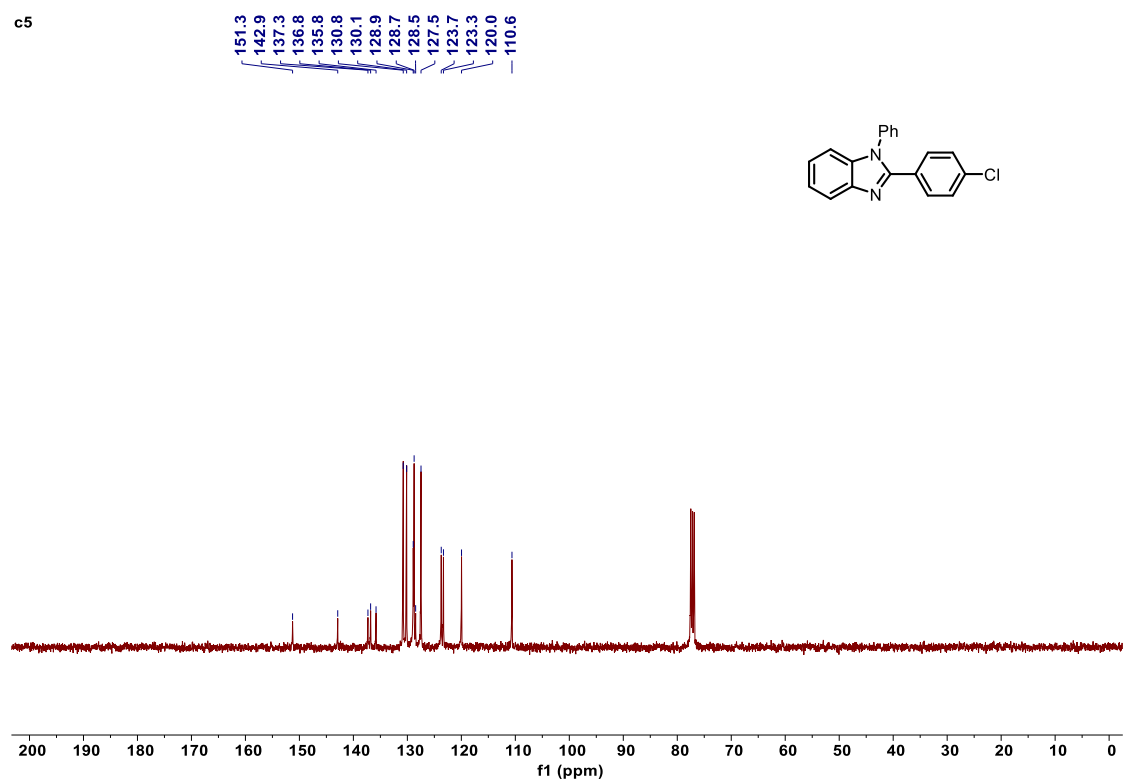
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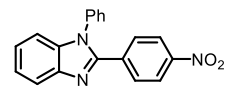
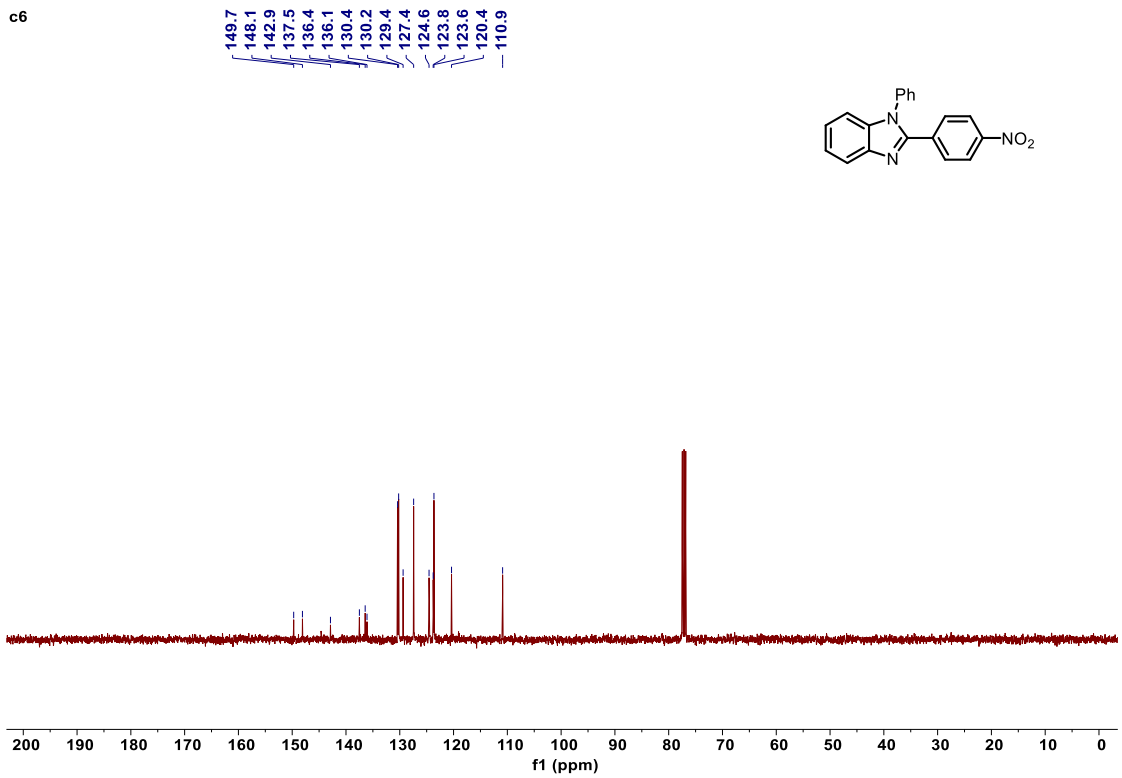
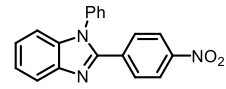
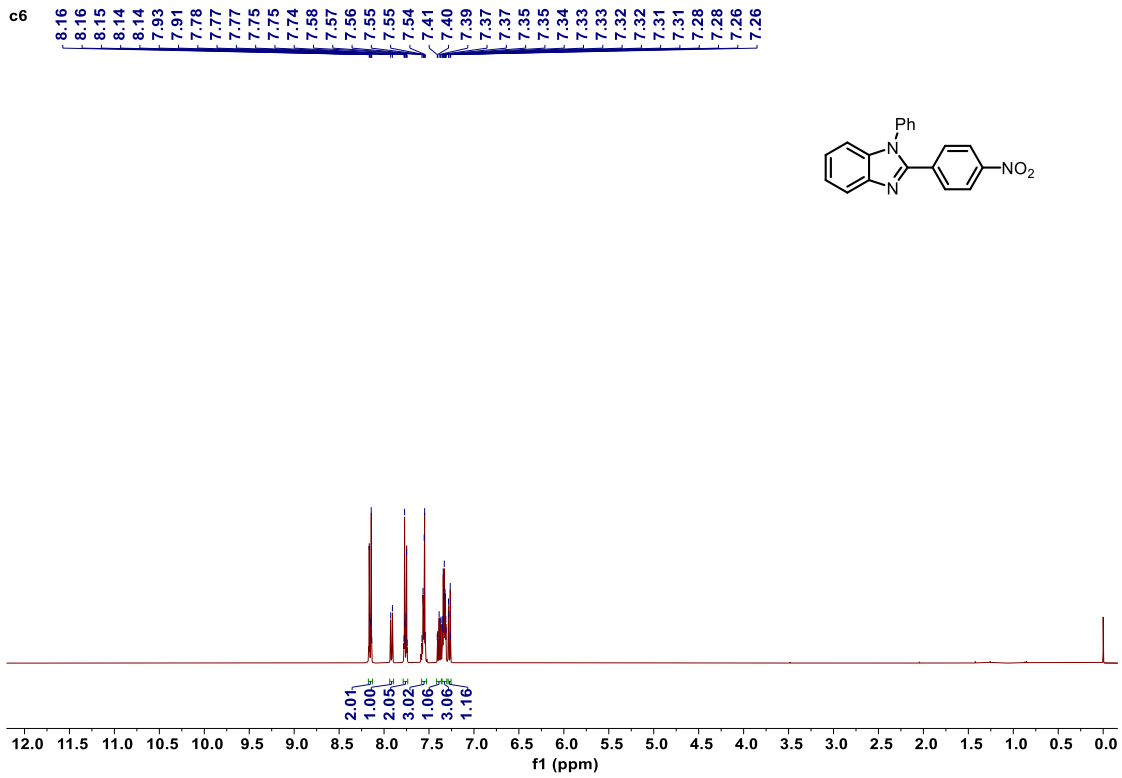


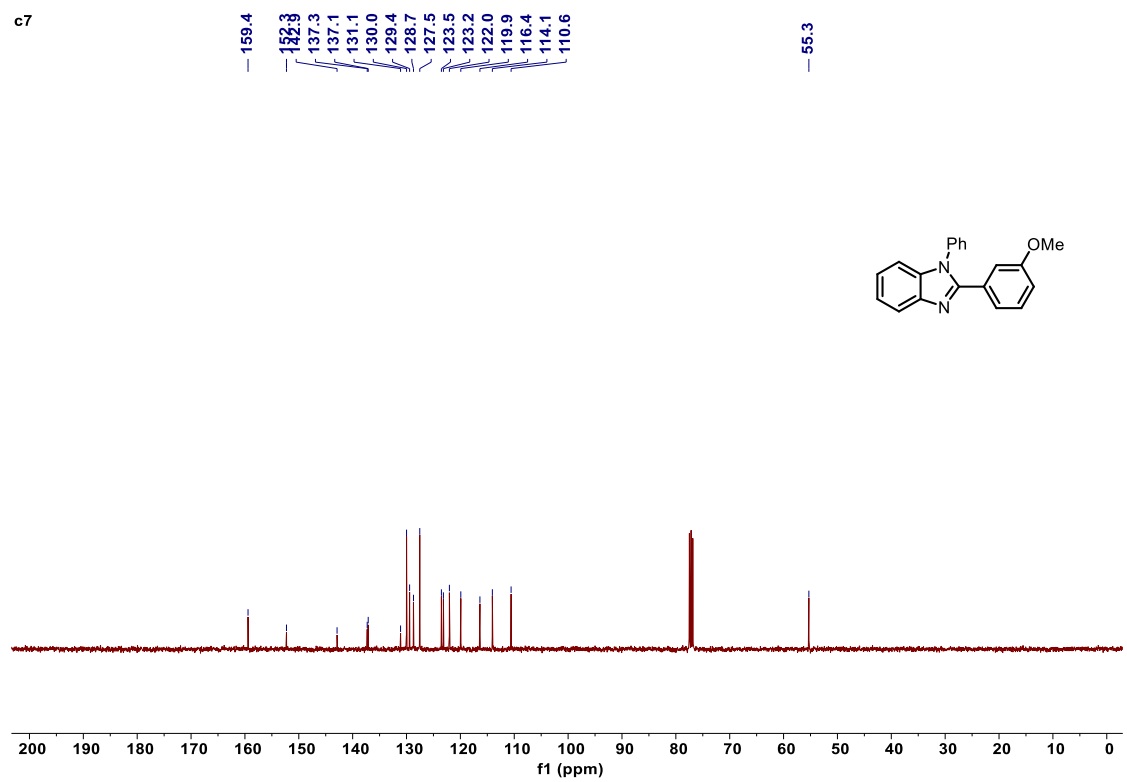
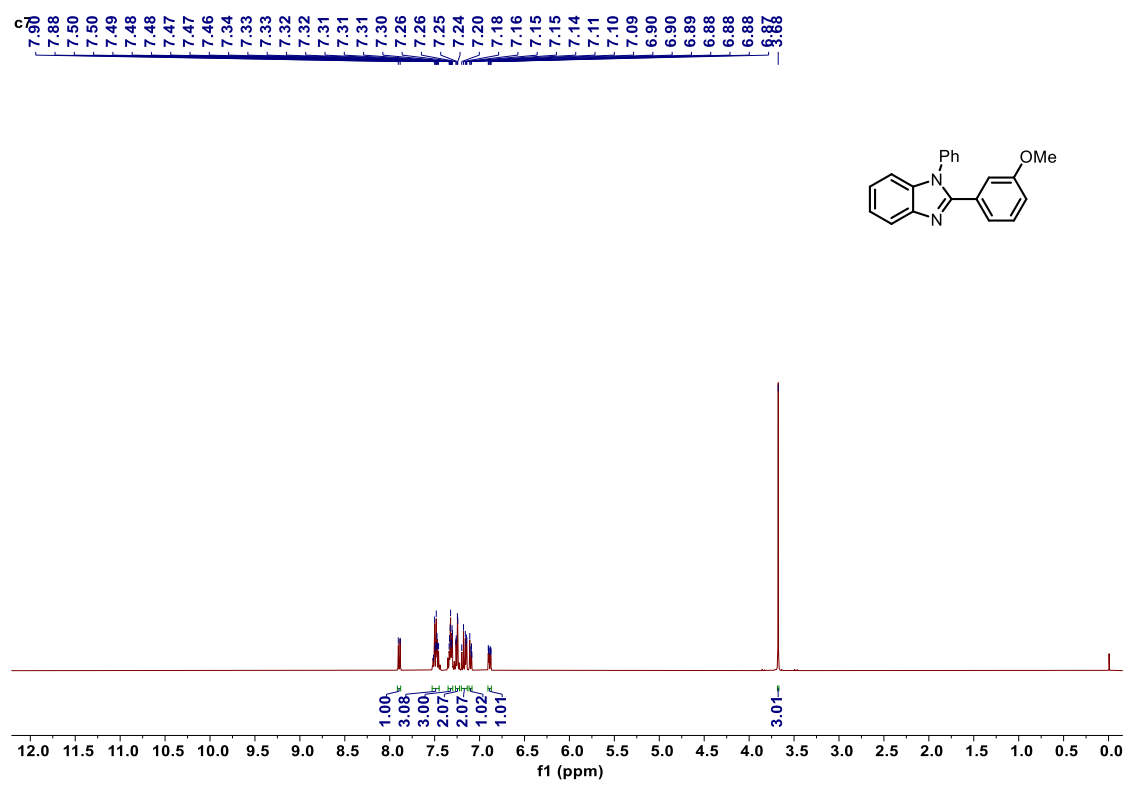
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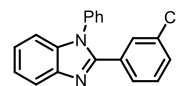
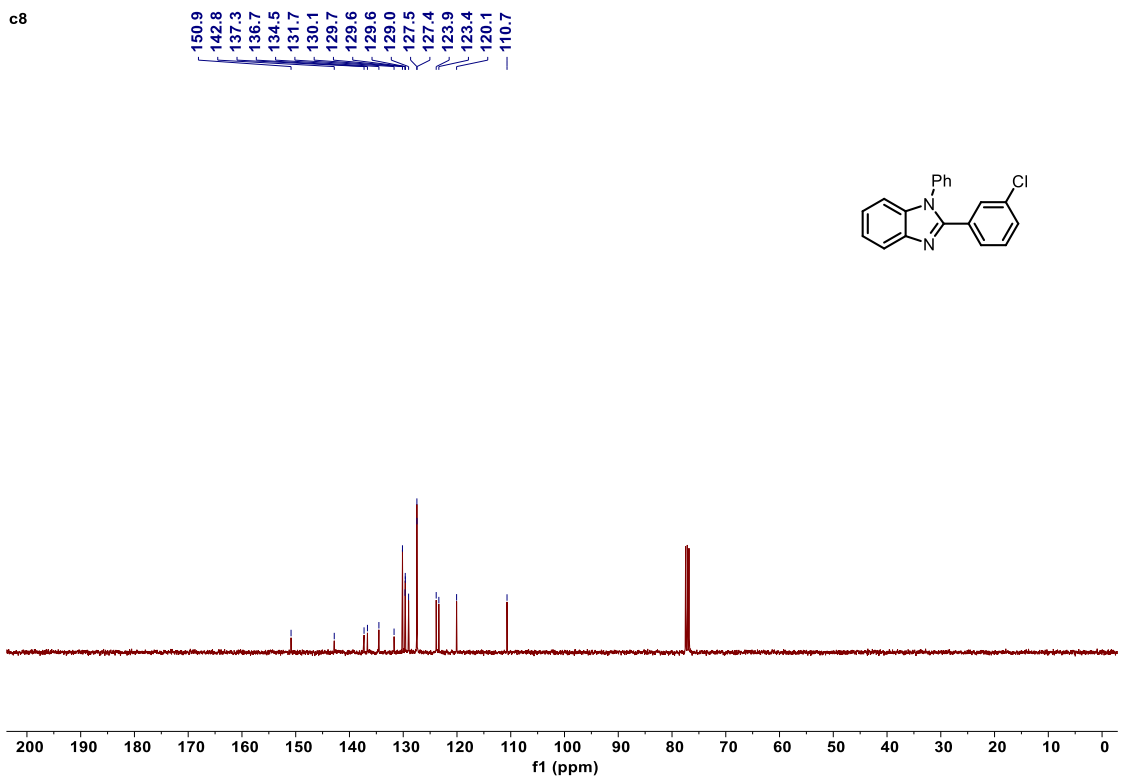
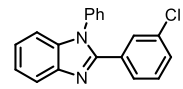
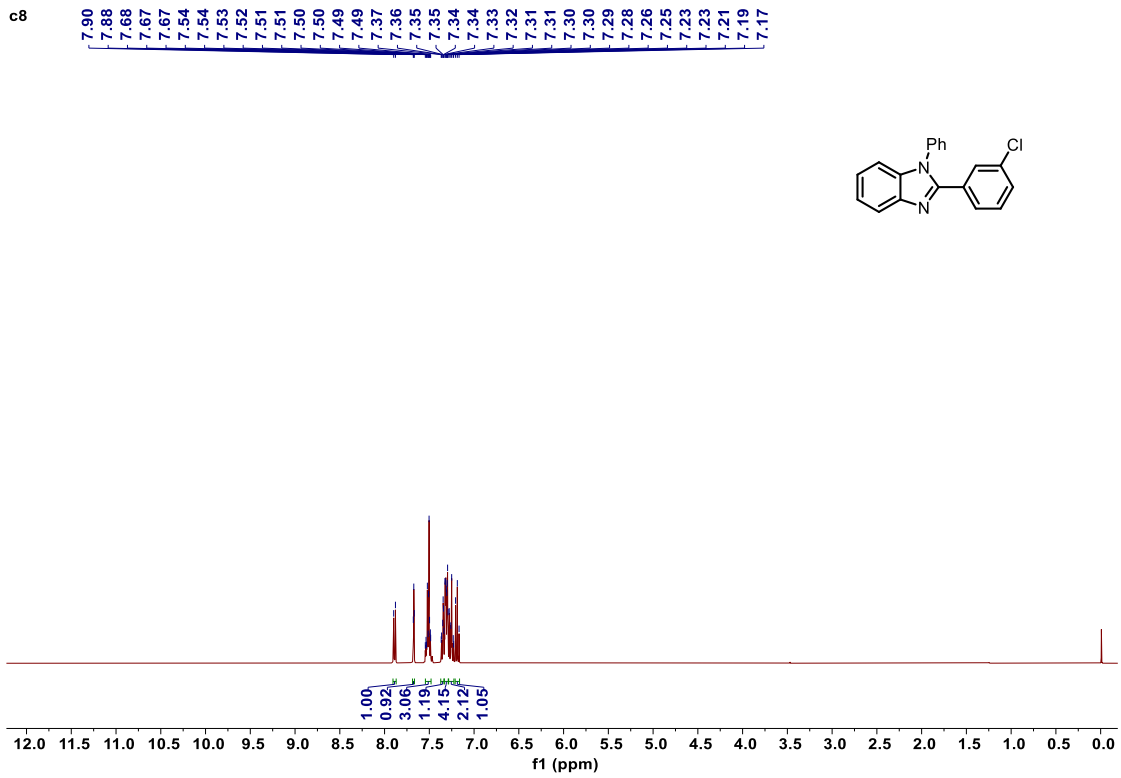


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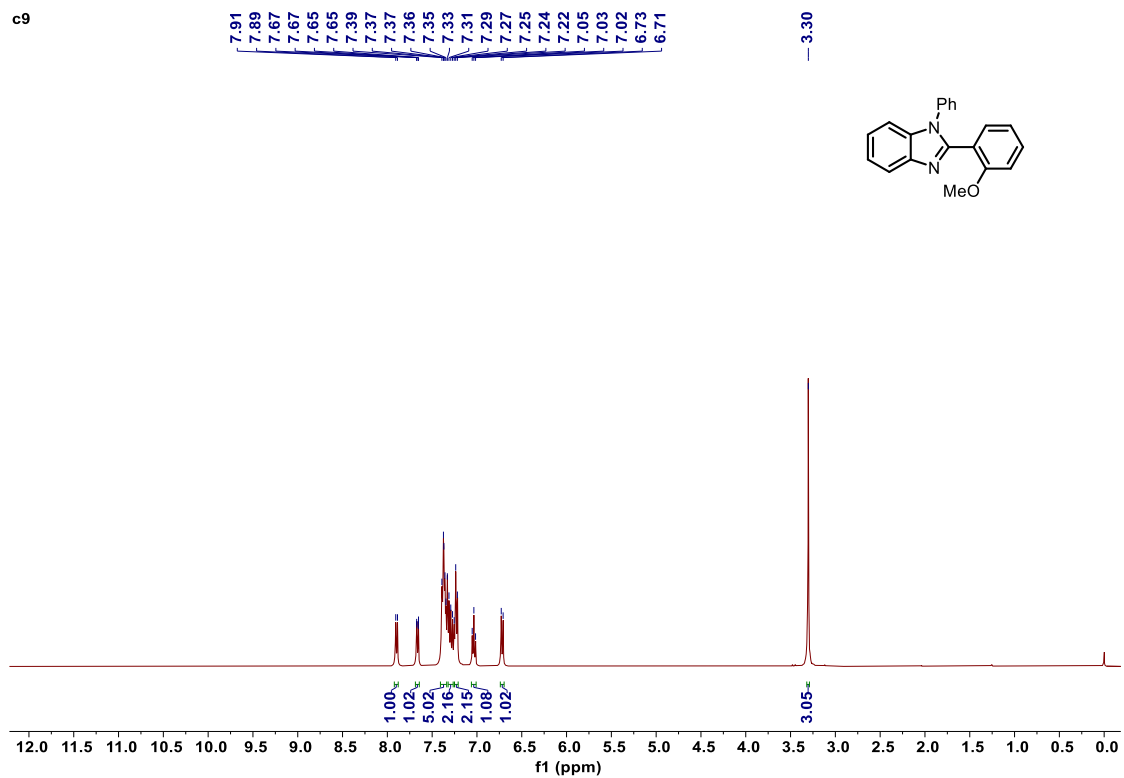




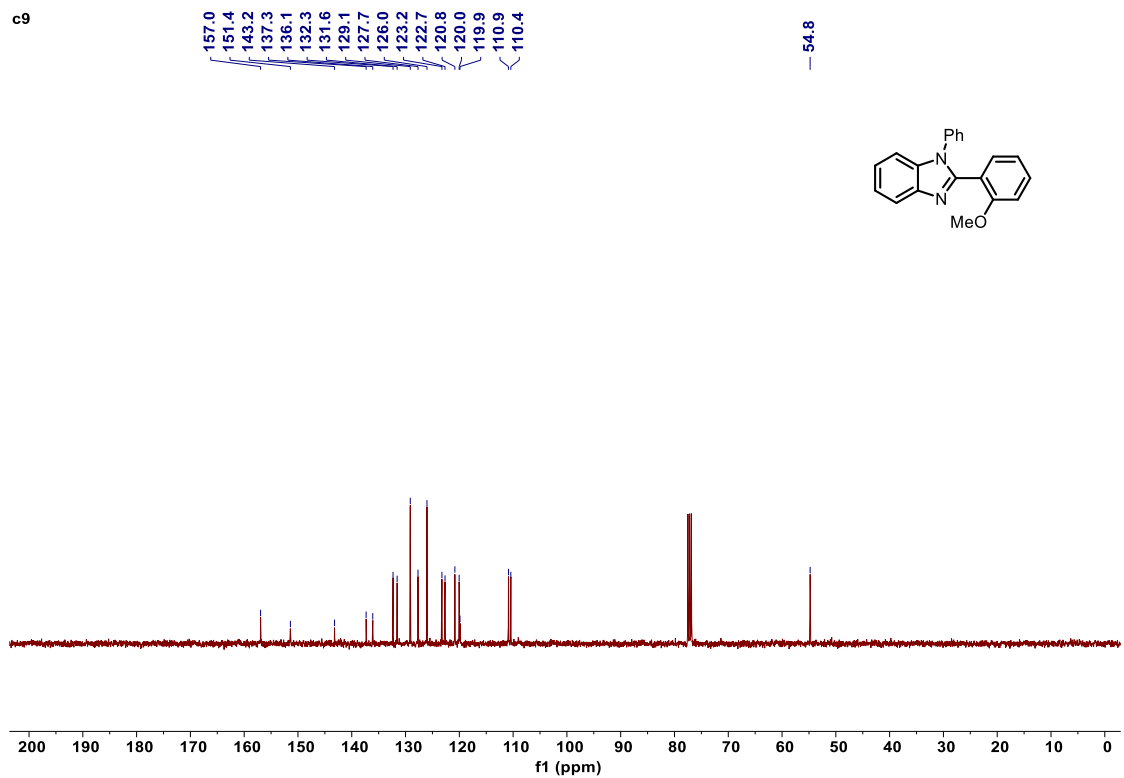




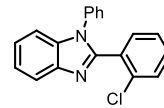
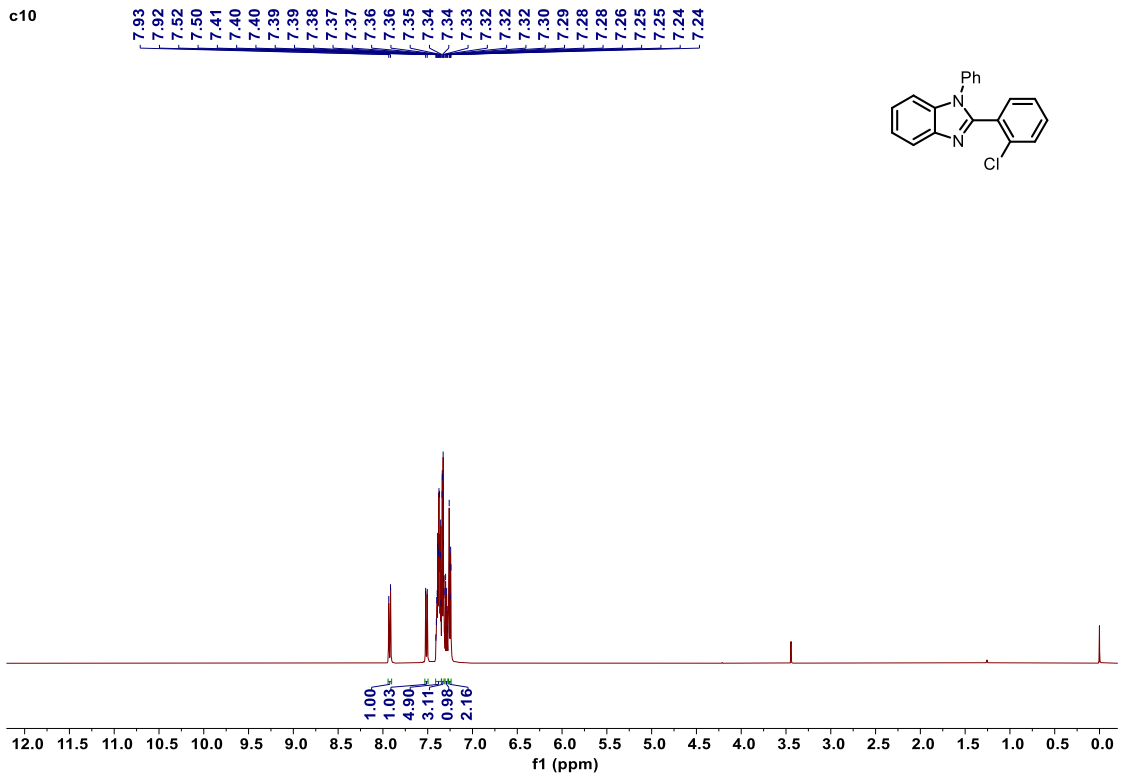
c9



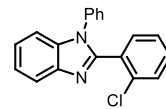
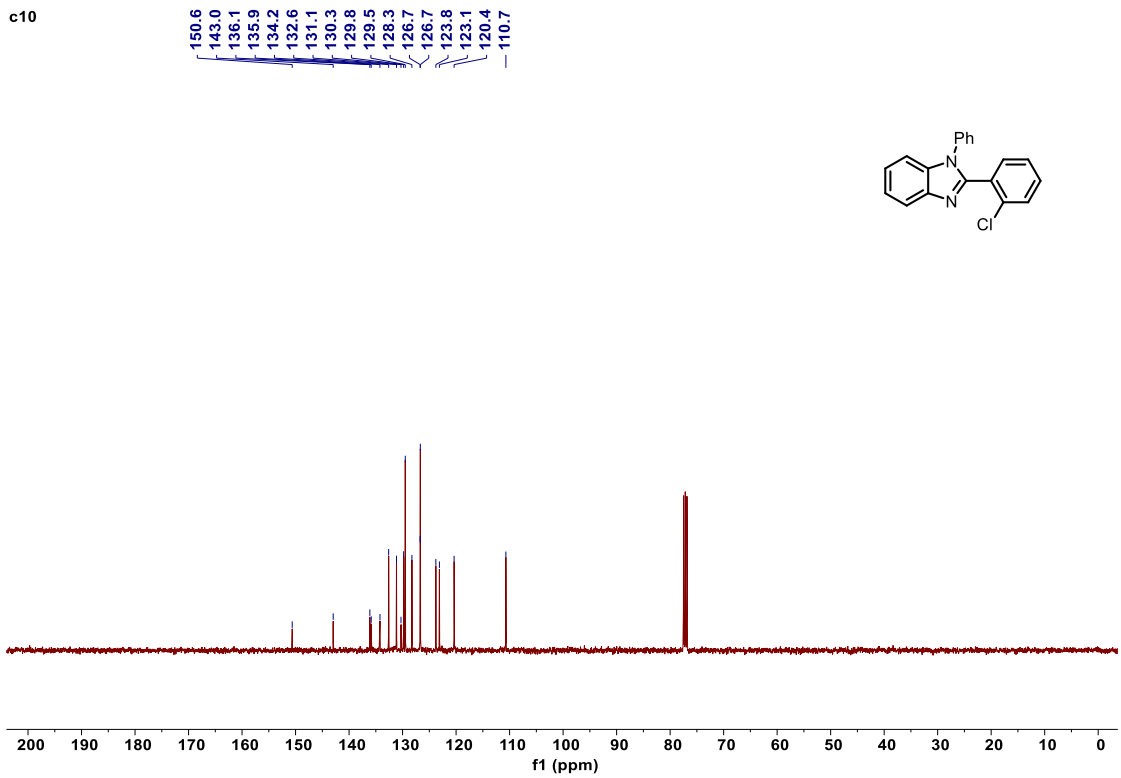
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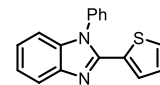
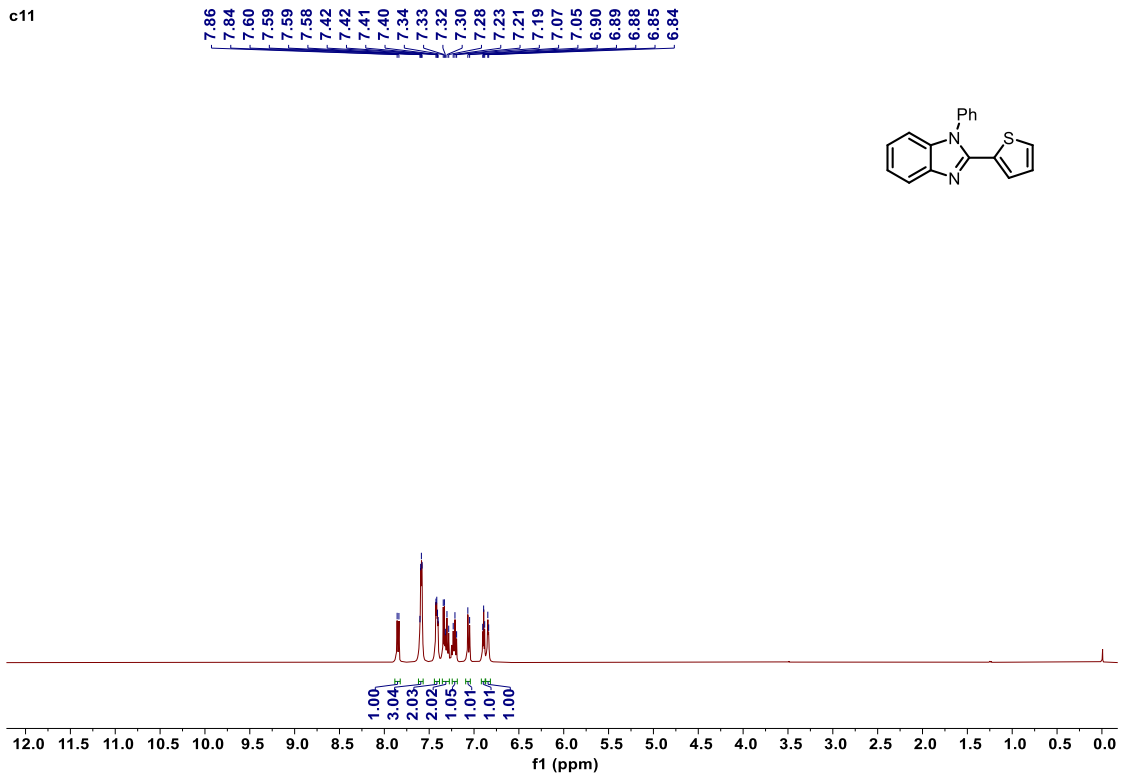
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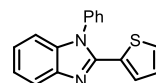
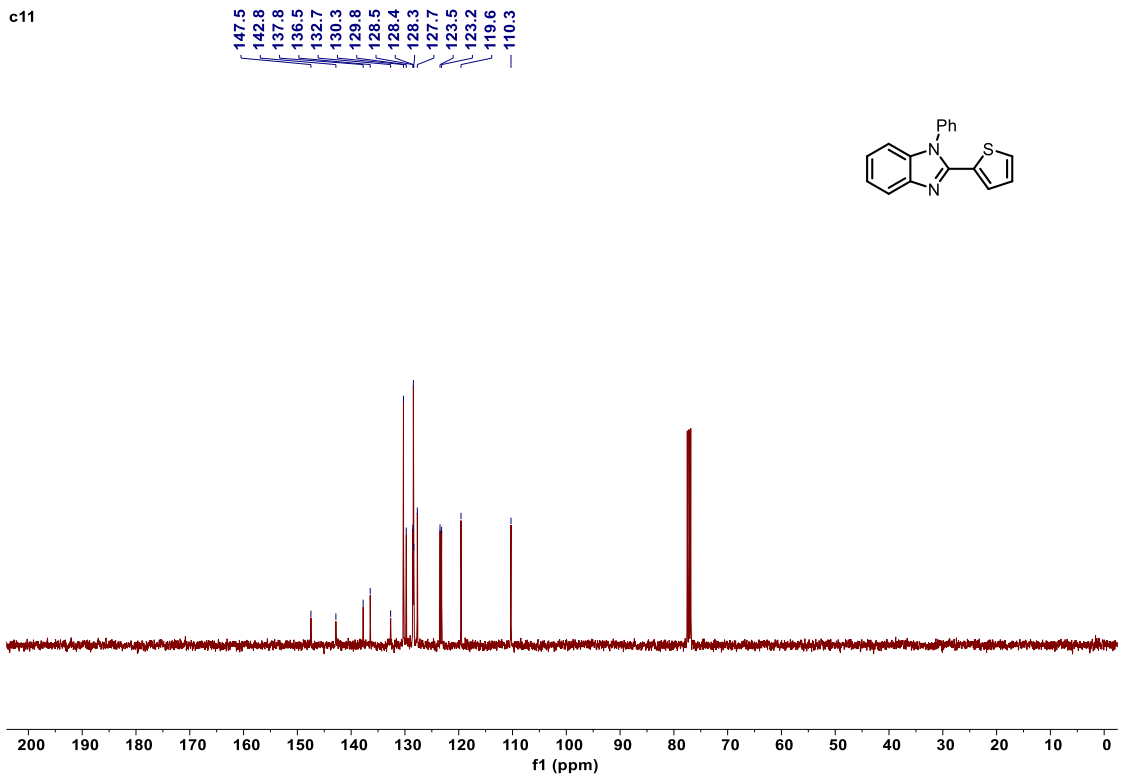
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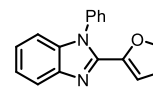
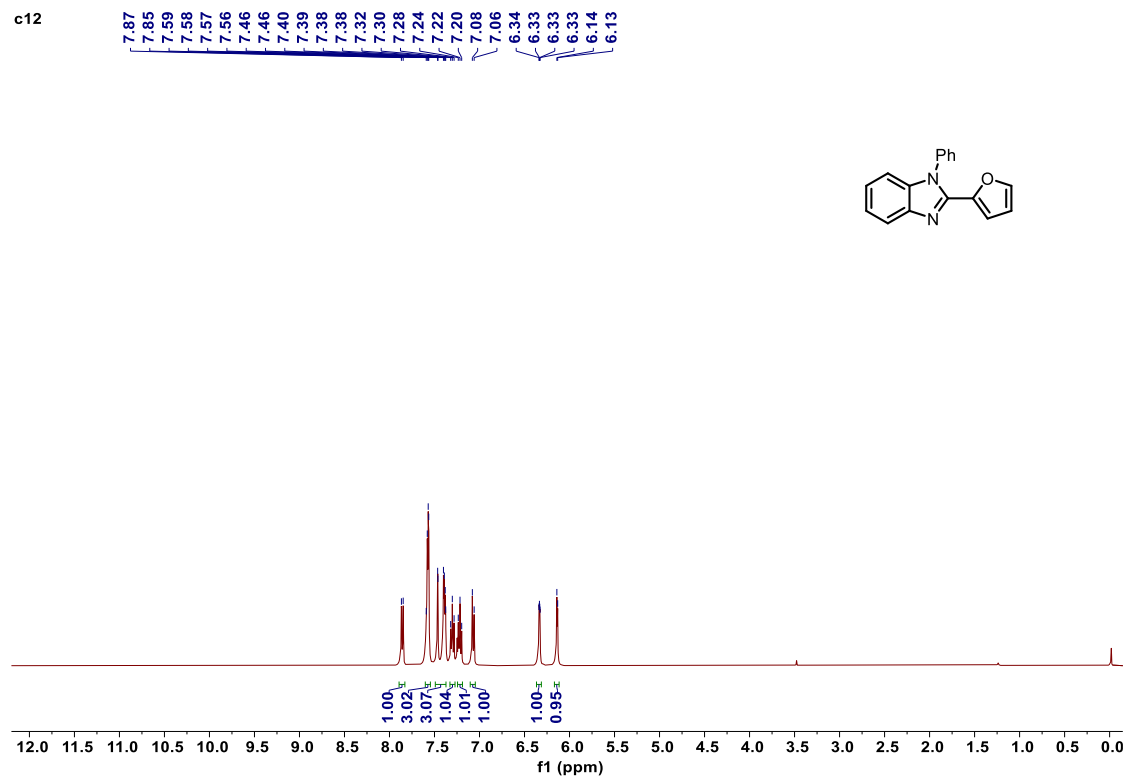
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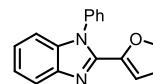
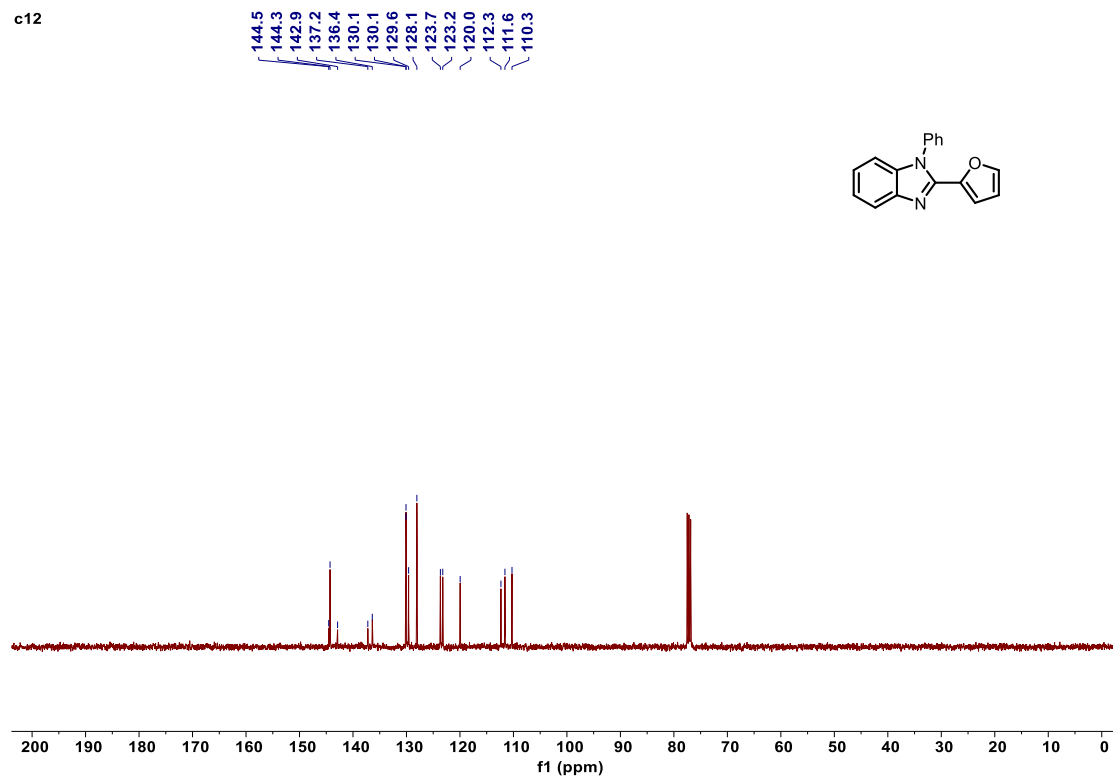
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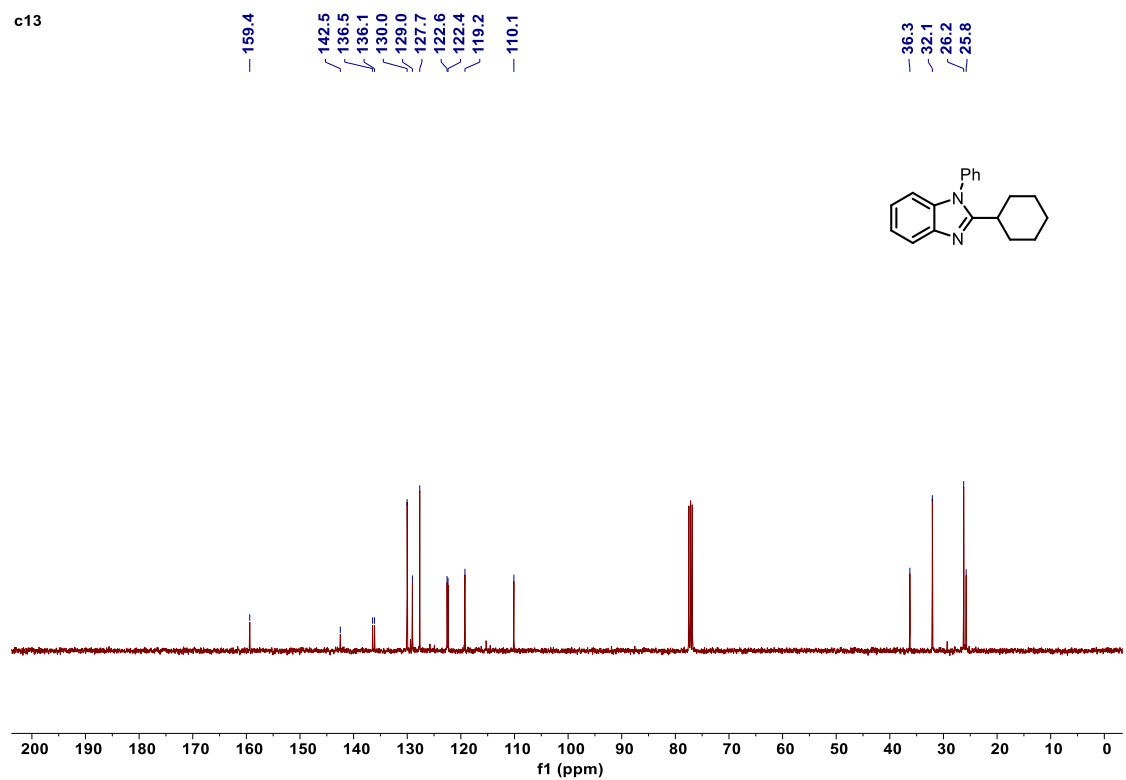
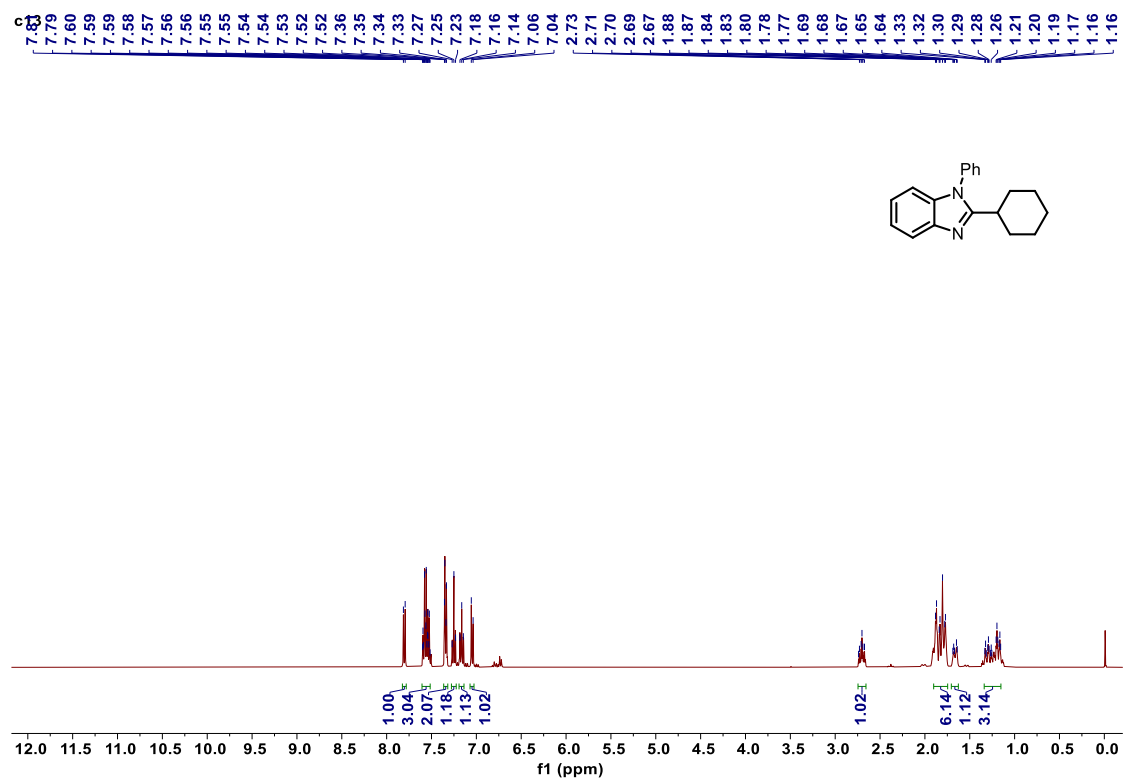


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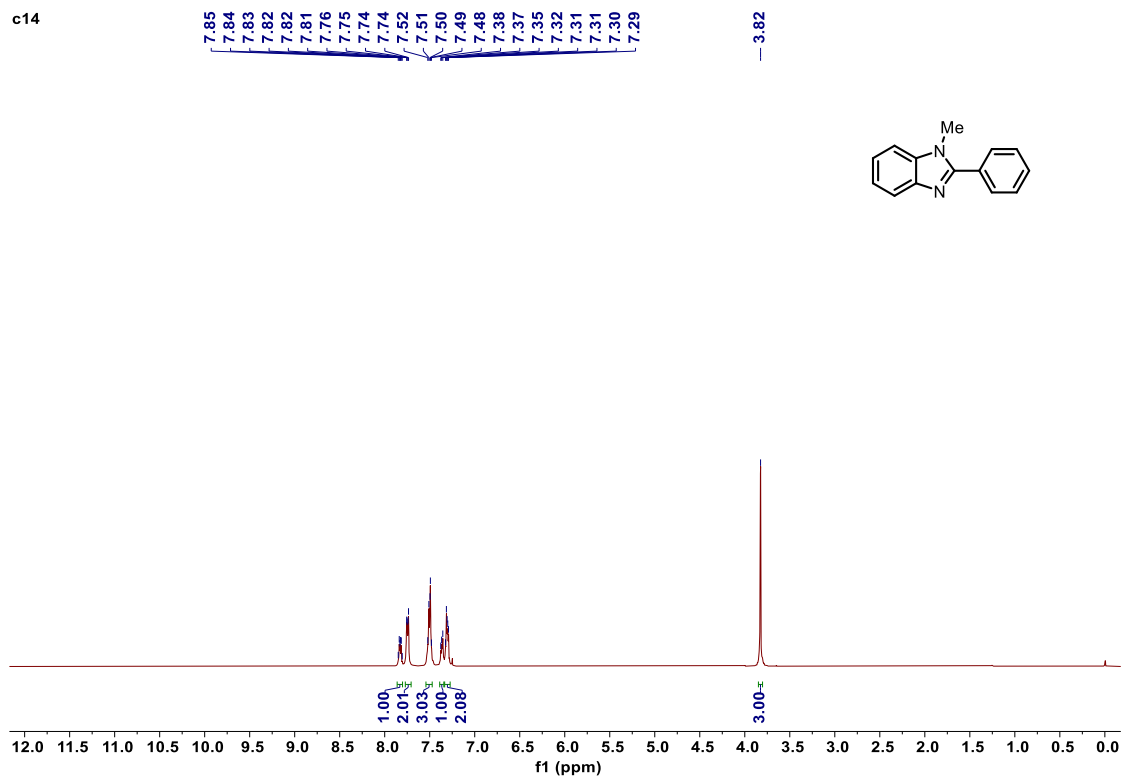


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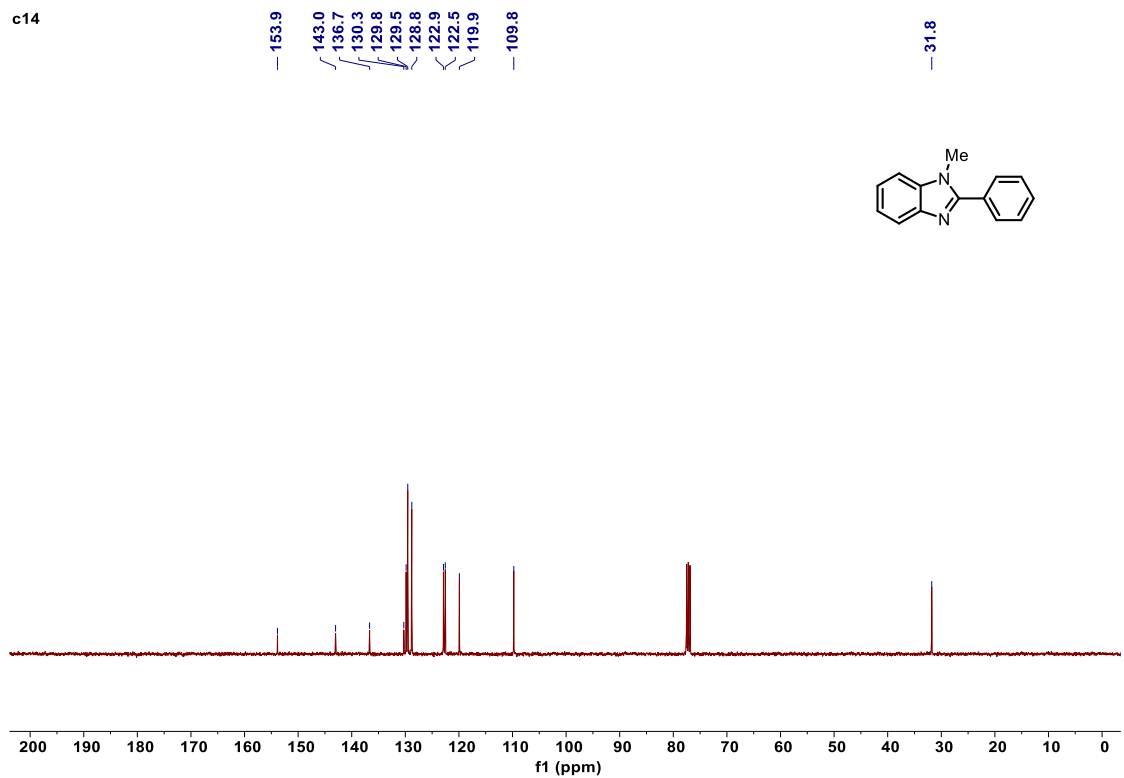




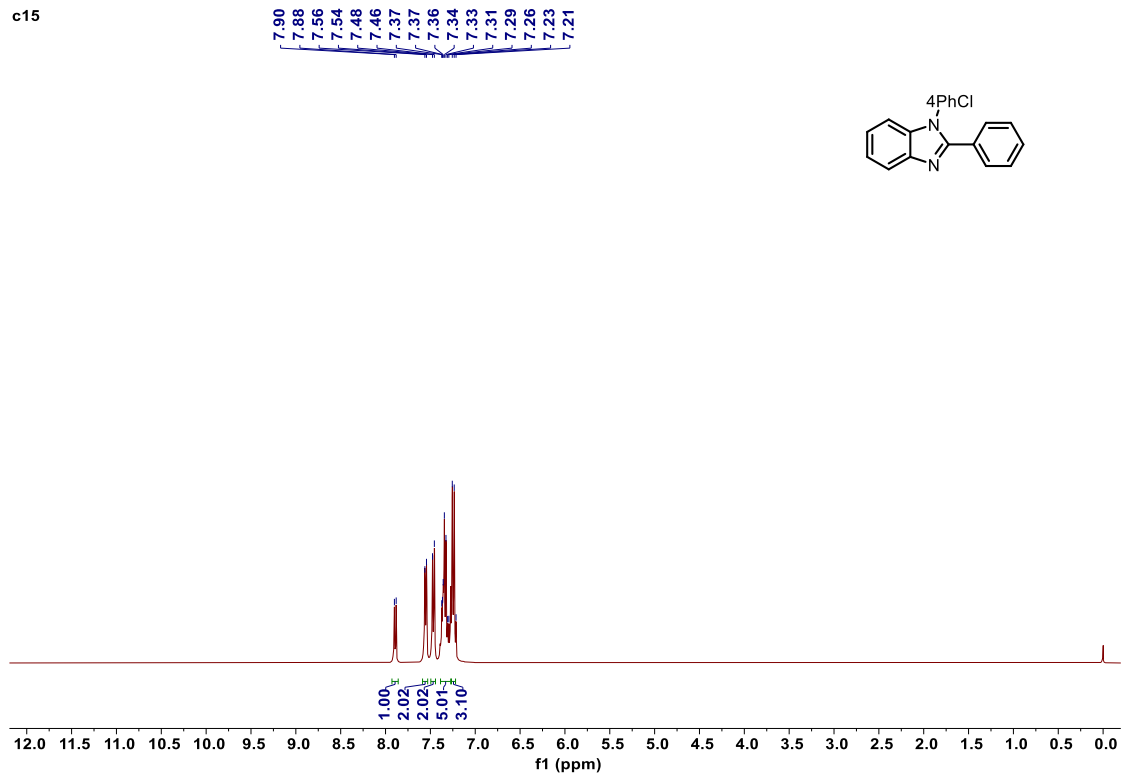
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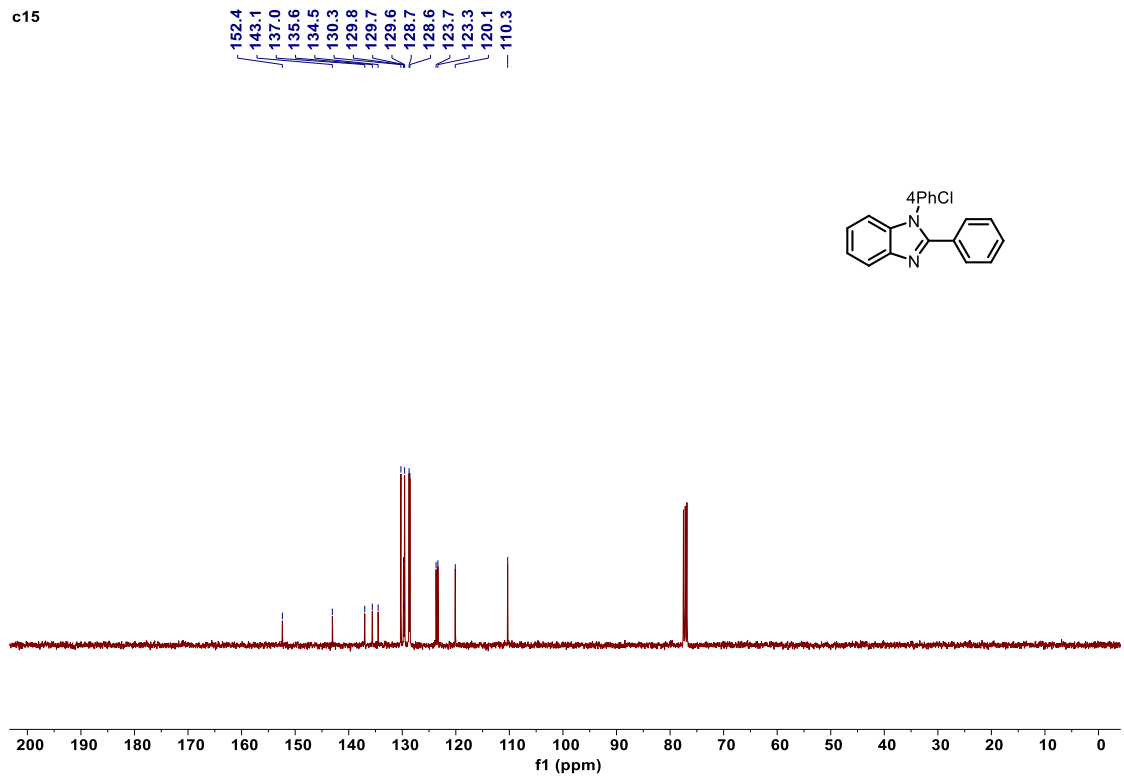
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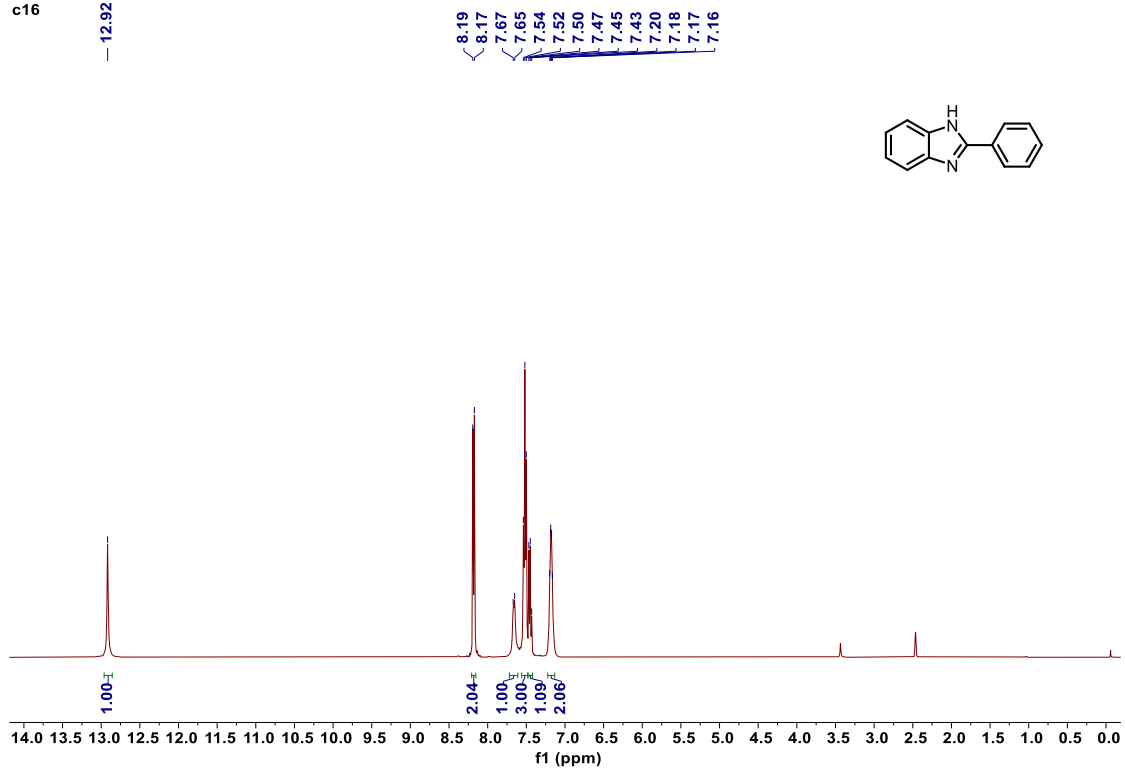


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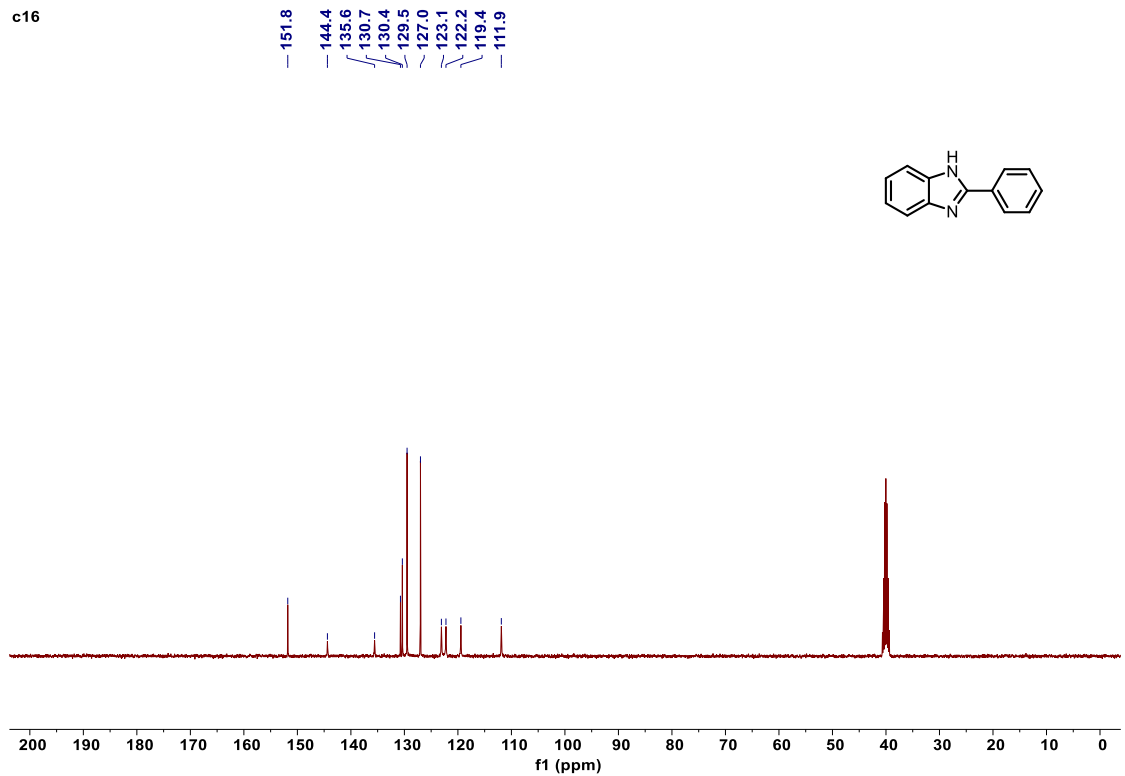
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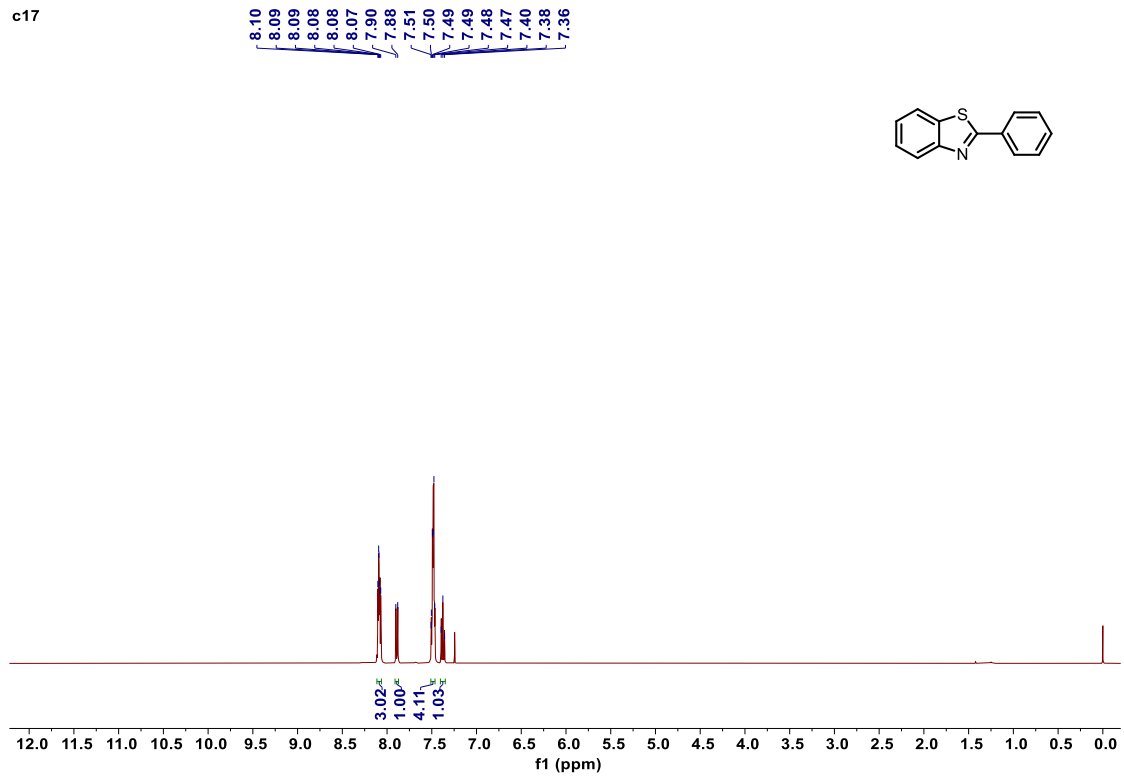


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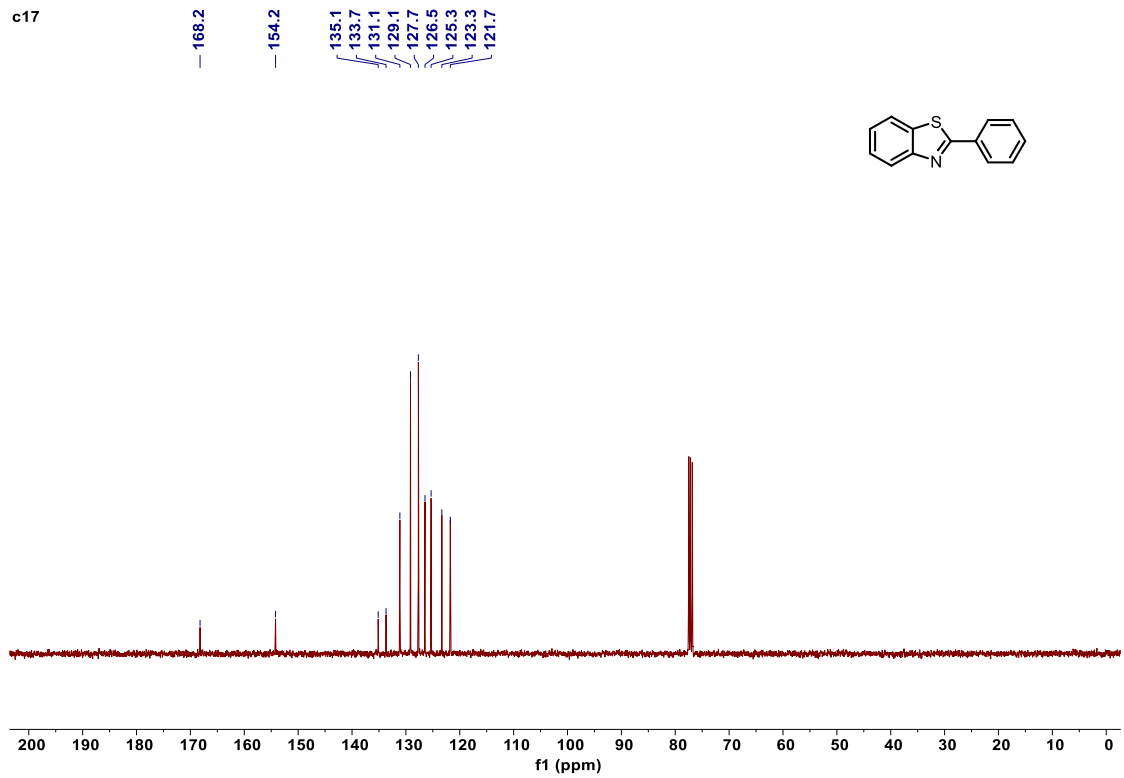
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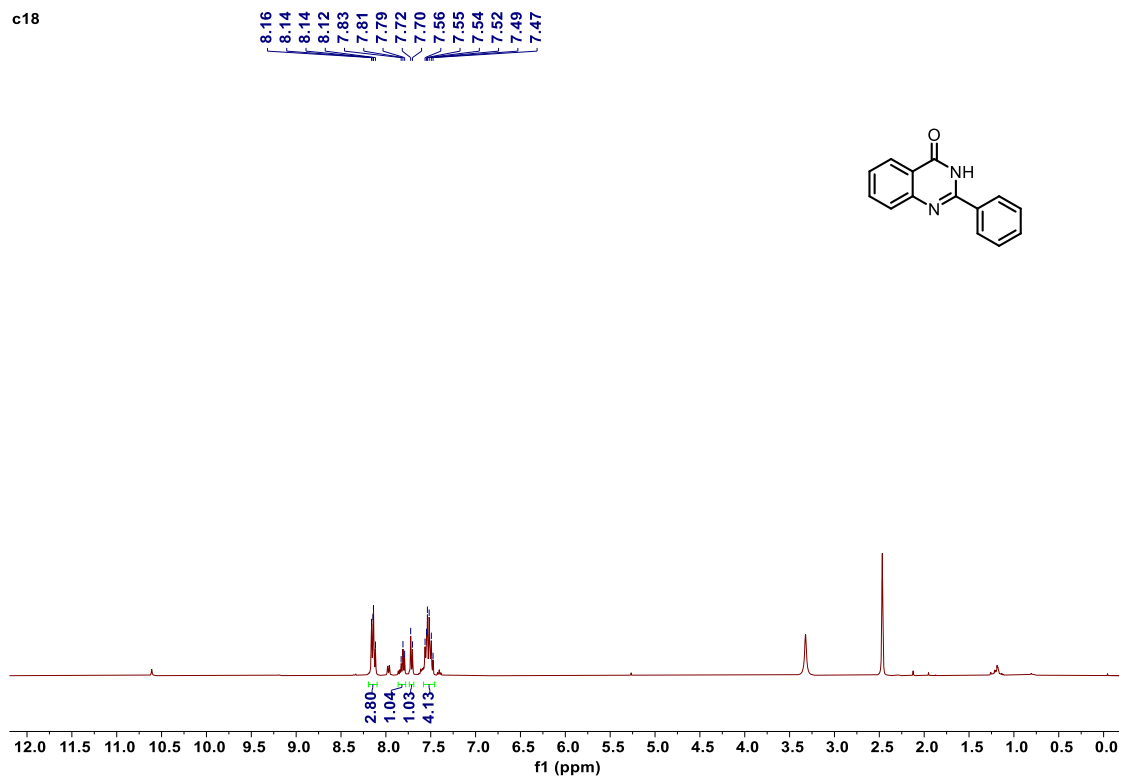
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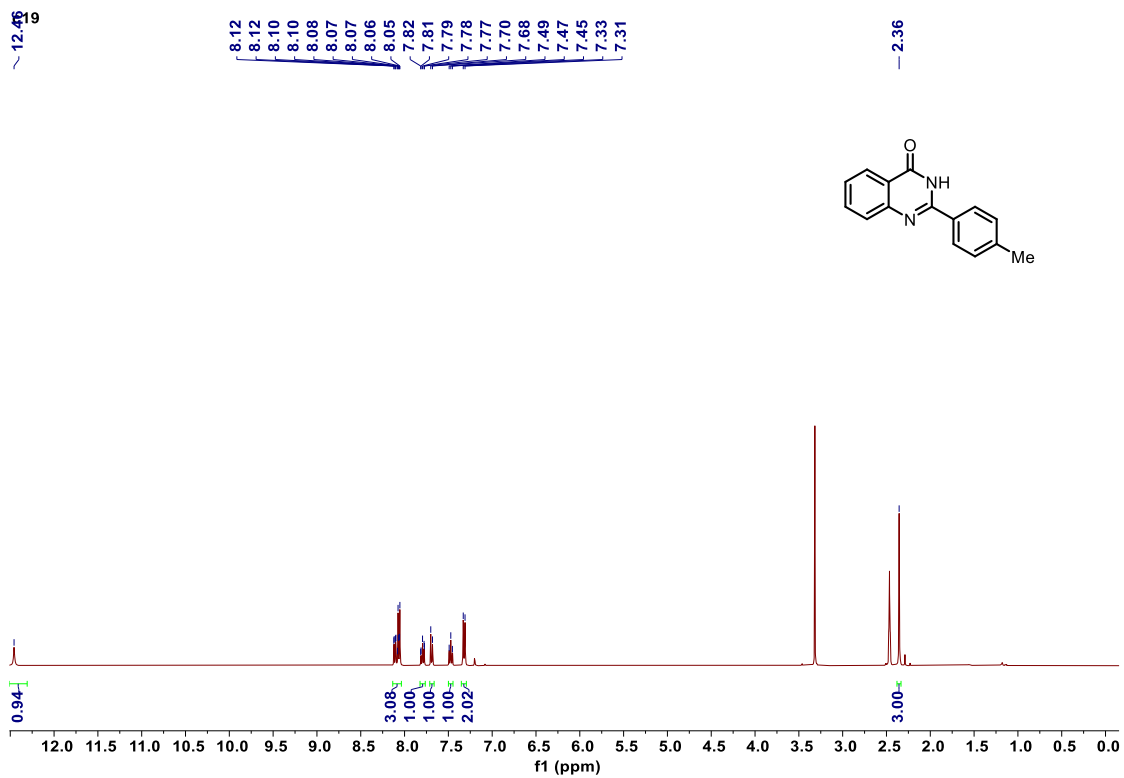
c17



c18



c19



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