

Electronic Supplementary Information (ESI)

An efficient and facile synthesis of benzimidazo[1,2-*a*]benzimidazoles via copper-catalyzed domino addition/double cyclization

Guodong Yuan,[§] Haiquan Liu,[§] Jilong Gao, Hongjuan Xu, Liu Jiang, Xiaoxia Wang, and Xin Lv*

^a Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, People's Republic of China.
e-Mail: lvxin@zjnu.cn

Table of Contents

General Information.....	P2
General Procedure for the Synthesis of Product 3	P2
Spectral Data for the Products.....	P3-P9
References.....	P9
Copies of ¹ H and ¹³ C NMR Spectra for the Products.....	P10-P30

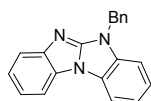
General Information.

All domino reactions were performed in an oven-dried Schlenk tube equipped with a magnetic stir bar under nitrogen atmosphere. 1,4-Dioxane, DMF, toluene, and CH₃CN were distilled from CaH₂. Bis-(*o*-haloaryl)carbodiimides were prepared according to the known literature.¹ All other reagents were commercially available and used as received, if not stated otherwise. All melting points are uncorrected. The NMR spectra were recorded in CDCl₃ or *d*⁶-DMSO on a 400 MHz or 600 MHz instrument with TMS as internal standard. Chemical shifts (δ) were reported in ppm with respect to TMS. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad), coupling constant (J, Hz) and integration. TLC was carried out with 0.2 mm thick silica gel plates (GF254). Visualization was accomplished by UV light. The columns were hand packed with silica gel 60 (160-200 mesh). Key products were confirmed by high-resolution mass spectra (HRMS), which were carried out using a TOF-MS instrument with an ESI source.

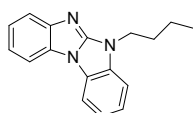
General Procedure for the Synthesis of Product 3.

An oven-dried Schlenk tube was charged with CuCl (0.05 mmol, 10 mol%), 1,10-phen·H₂O (0.1 mmol, 20 mol%), and K₃PO₄ (2.0 mmol, 4 equiv). The Schlenk tube was capped, and then evacuated and backfilled with N₂ (3 times). Under a positive pressure of nitrogen, a solution of active primary amine **2** (0.55 mmol, 1.1 equiv) in dioxane (1.5 mL) was added *via* syringe. The mixture was stirred at 60 °C for about 10 min. Then a solution of bis-(*o*-haloaryl)carbodiimide **1** (0.5 mmol, 1.0 equiv) in dioxane (1.5 mL) was added dropwise *via* syringe (for about 20 min). The Schlenk tube was sealed and allowed to prestir at 60 °C for 1 h. Then the mixture was stirred at 100 °C for 12 - 24 h. After being cooled to rt, the mixture was passed through a pad of silica gel and rinsed with EtOAc (30 mL). The combined filtrate was concentrated, and the residue was purified by column chromatography on silica gel using petrol/EtOAc (4:1, v:v) as eluent to afford product **3**.

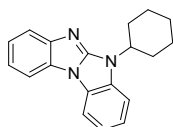
Spectral Data for the Products.



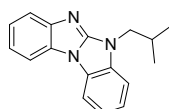
5-Benzyl-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3a**). White solid. Mp: 156 – 158 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.80 – 7.83 (m, 2H), 7.76 – 7.78 (m, 1H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.41 (m, 1H), 7.33 – 7.36 (m, 2H), 7.27 – 7.32 (m, 4H), 7.23 – 7.24 (m, 1H), 5.50 (s, 2H). ¹³C NMR (150 MHz, CDCl₃): δ 153.8, 147.3, 135.6, 135.4, 128.9, 128.4, 128.1, 127.4, 125.4, 123.1, 123.0, 121.3, 119.9, 118.5, 110.6, 110.21, 110.20, 47.0. HRMS (ESI): calcd for C₂₀H₁₆N₃ [M + H]⁺ 298.1339, found 298.1330.



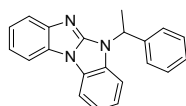
5-Butyl-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3b**). White solid. Mp: 71 – 73 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.74 – 7.79 (m, 3H), 7.23 – 7.37 (m, 5H), 4.26 (t, *J* = 7.4 Hz, 2H), 1.93 – 2.00 (m, 2H), 1.43 – 1.52 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 147.4, 135.6, 128.3, 125.2, 123.0, 122.9, 120.9, 119.7, 118.4, 110.6, 110.1, 110.0, 109.5, 43.2, 30.6, 20.2, 13.8. HRMS (ESI): calcd for C₁₇H₁₈N₃ [M + H]⁺ 264.1495, found 264.1507.



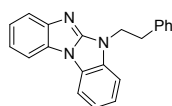
5-Cyclohexyl-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3c**). White solid. Mp: 169 – 171 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.33 – 7.38 (m, 2H), 7.25 – 7.31 (m, 2H), 4.43 – 4.48 (m, 1H), 2.42 – 2.49 (m, 2H), 2.10 – 2.12 (m, 2H), 2.02 – 2.04 (m, 2H), 1.82 – 1.84 (m, 1H), 1.43 – 1.59 (m, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 153.1, 147.4, 134.9, 127.9, 125.3, 122.9, 122.8, 120.7, 119.6, 118.3, 110.6, 110.5, 110.0, 55.5, 30.6, 25.9, 25.2. HRMS (ESI): calcd for C₁₉H₂₀N₃ [M + H]⁺ 290.1652, found 290.1647.



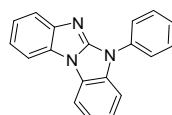
5-Isobutyl-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3d**). Yellow solid. Mp: 128 – 130 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.74 – 7.80 (m, 3H), 7.25 – 7.35 (m, 5H), 4.06 (d, *J* = 7.6 Hz, 2H), 2.47 – 2.54 (m, 1H), 1.05 (d, *J* = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 153.8, 147.3, 136.0, 128.2, 125.1, 123.0, 122.9, 120.9, 119.7, 118.4, 110.6, 110.1, 109.8, 50.8, 28.2, 20.2. HRMS (ESI): calcd for C₁₇H₁₈N₃ [M + H]⁺ 264.1495, found 264.1503.



5-(1-Phenylethyl)-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3e**). White solid. Mp: 84 – 86 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.82 (t, *J* = 7.9 Hz, 2H), 7.73 – 7.75 (m, 1H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.33 – 7.39 (m, 3H), 7.15 – 7.31 (m, 4H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.02 (q, *J* = 7.2 Hz, 1H), 2.19 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 153.6, 147.4, 140.0, 134.5, 128.8, 128.1, 127.9, 126.6, 125.5, 123.0, 122.9, 121.0, 119.8, 118.5, 111.3, 110.6, 110.1, 54.2, 18.7. HRMS (ESI): calcd for C₂₁H₁₈N₃ [M + H]⁺ 312.1495, found 312.1516.

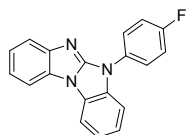


5-Phenethyl-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3f**). Yellow solid. Mp: 126 – 128 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.71 – 7.73 (m, 1H), 7.35 – 7.40 (m, 1H), 7.20 – 7.30 (m, 8H), 7.08 – 7.10 (m, 1H), 4.48 (t, *J* = 7.6 Hz, 2H), 3.28 (t, *J* = 7.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 153.3, 147.4, 137.9, 135.5, 128.9, 128.7, 128.3, 126.8, 125.1, 123.0, 122.9, 121.0, 119.8, 118.4, 110.6, 110.2, 109.5, 45.0, 34.8. HRMS (ESI): calcd for C₂₁H₁₈N₃ [M + H]⁺ 312.1495, found 312.1489.

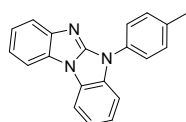


5-Phenyl-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3g**). White solid. Mp: 144 – 146 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.78 – 7.85 (m, 5H), 7.62 (t, *J* = 7.8 Hz, 2H), 7.52 – 7.54 (m, 1H), 7.43 – 7.47 (m, 1H), 7.27 – 7.38 (m, 4H). ¹³C NMR (100 MHz,

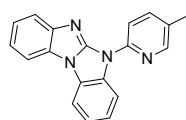
CDCl₃): δ 152.5, 147.1, 135.2, 135.0, 130.1, 128.0, 127.5, 125.5, 124.4 (d, J = 17.6 Hz), 123.3, 123.1, 122.1, 120.3, 119.0, 110.8, 110.7, 110.2. HRMS (ESI): calcd for C₁₉H₁₄N₃ [M + H]⁺ 284.1182, found 284.1171.



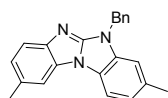
5-(4-Fluorophenyl)-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3h**). White solid. Mp: 190 – 192 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.79 – 7.87 (m, 5H), 7.50 (d, J = 7.9 Hz, 1H), 7.33 – 7.42 (m, 6H). ¹³C NMR (150 MHz, CDCl₃): δ 162.4, 160.8, 152.6, 147.0, 135.2, 126.7 (d, J = 8.4 Hz), 125.6, 123.4, 123.2, 122.3, 120.4, 119.0, 117.1, 116.9, 110.9, 110.5, 110.2. HRMS (ESI): calcd for C₁₉H₁₃FN₃ [M + H]⁺ 302.1088, found 302.1094.



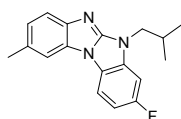
5-(*p*-Tolyl)-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3i**). White solid. Mp: 162 – 164 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.83 – 7.87 (m, 2H), 7.80 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 8.2 Hz, 2H), 7.30 – 7.40 (m, 4H), 2.49 (s, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 152.8, 147.2, 137.7, 135.3, 132.5, 130.6, 128.1, 125.5, 124.6, 123.3, 123.1, 121.9, 120.2, 118.9, 110.8, 110.7, 110.2, 21.27. HRMS (ESI): calcd for C₂₀H₁₆N₃ [M + H]⁺ 298.1339, found 298.1346.



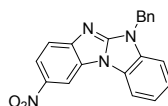
5-(5-Methylpyridin-2-yl)-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3j**). White solid. Mp: 156 – 158 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.76 – 8.78 (m, 1H), 8.68 (d, J = 8.4 Hz, 1H), 8.42 (s, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.77 – 7.80 (m, 2H), 7.39 – 7.42 (m, 3H), 7.34 – 7.36 (m, 1H), 2.43 (s, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 151.4, 148.8, 148.0, 146.8, 139.3, 133.9, 129.9, 127.6, 125.7, 123.7, 123.2, 120.8, 119.1, 116.4, 114.6, 110.3, 110.1, 18.0. HRMS (ESI): calcd for C₁₉H₁₅N₄ [M + H]⁺ 299.1291, found 299.1287.



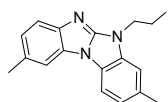
5-Benzyl-3,9-dimethyl-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3k**). White solid. Mp: 195 – 197 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.60 – 7.63 (m, 3H), 7.34 – 7.40 (m, 5H), 7.07 – 7.19 (m, 2H), 7.01 (s, 1H), 5.44 (s, 2H), 2.58 (s, 3H), 2.46 (s, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 153.8, 145.1, 135.8, 135.7, 133.1, 129.6, 128.9, 128.6, 128.0, 127.3, 123.9, 123.4, 121.9, 118.0, 110.5, 110.4, 110.2, 46.8, 21.8, 21.7. HRMS (ESI): calcd for C₂₂H₂₀N₃ [M + H]⁺ 326.1652, found 326.1645.



3-Fluoro-5-isobutyl-9-methyl-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3l**). Yellow solid. Mp: 140 – 142 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.63 – 7.65 (m, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.46 (m, 1H), 7.05 – 7.11 (m, 3H), 4.00 (d, *J* = 7.8 Hz, 2H), 2.51 (s, 3H), 2.46 – 2.50 (m, 1H), 1.05 (d, *J* = 6.6 Hz, 6H). ¹³C NMR (150 MHz, CDCl₃): δ 158.1, 156.5, 154.4, 143.4, 136.2, 133.5, 127.6, 122.7, 121.6, 118.4 (d, *J* = 9.6 Hz), 110.1 (q, *J* = 20.8 Hz), 100.0, 97.5 (d, *J* = 28.2 Hz), 50.8, 28.1, 21.9, 20.2. HRMS (ESI): calcd for C₁₈H₁₉FN₃ [M + H]⁺ 296.1558, found 296.1575.

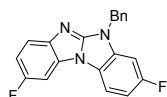


5-Benzyl-9-nitro-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3m**). White solid. Mp: 160 – 162 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.78 – 7.81 (m, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.33 – 7.36 (m, 2H), 7.30 – 7.32 (m, 3H), 7.25 (d, *J* = 7.6 Hz, 1H), 5.52 (s, 2H). ¹³C NMR (150MHz, CDCl₃): δ 153.7, 135.5, 135.4, 128.9, 128.4, 128.1, 127.4, 125.5, 123.2, 123.1, 121.4, 120.0, 118.5, 110.6, 110.25, 110.20, 47.1. HRMS (ESI): calcd for C₂₀H₁₅N₄O₂ [M + H]⁺ 343.1190, found 343.1213.

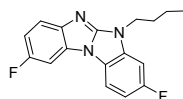


3,9-Dimethyl-5-propyl-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3n**). Yellow

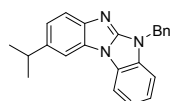
solid. Mp: 133 – 135 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.56 – 7.64 (m, 3H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.06 – 7.10 (m, 2H), 4.18 (t, *J* = 7.4 Hz, 2H), 2.57 (s, 3H), 2.52 (s, 3H), 1.98 – 2.04 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 153.6, 145.2, 135.9, 132.9, 129.3, 128.4, 123.8, 123.2, 121.4, 117.8, 110.3, 110.1, 109.9, 44.9, 21.8, 21.7, 21.6, 11.4. HRMS (ESI): calcd for C₁₈H₂₀N₃ [M + H]⁺ 278.1652, found 278.1648.



5-Benzyl-3,9-difluoro-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3o**). White solid. Mp: 217-219 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.67 – 7.70 (m, 1H), 7.60 – 7.63 (m, 1H), 7.48 – 7.49 (m, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.36 – 7.38 (m, 2H), 7.32 – 7.34 (m, 1H), 7.11 – 7.14 (m, 1H), 7.00 – 7.03 (m, 1H), 6.95 – 6.97 (m, 1H), 5.44 (s, 2H). ¹³C NMR (150 MHz, CDCl₃): δ 160.4, 158.8, 156.9, 134.8, 129.1, 128.4, 127.5, 119.0, 118.9, 110.9, 111.0, 110.6, 110.5, 108.2, 108.1, 98.6 (d, *J* = 28.4 Hz), 97.5 (d, *J* = 28.4 Hz), 47.3. HRMS (ESI): calcd for C₂₀H₁₄F₂N₃ [M + H]⁺ 334.1150, found 334.1165.

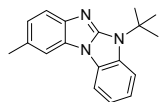


5-Butyl-3,9-difluoro-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3p**). White solid. Mp: 235 – 237 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.63 – 7.65 (m, 1H), 7.57 – 7.59 (m, 1H), 7.42 – 7.44 (m, 1H), 7.00 – 7.10 (m, 3H), 4.21 (t, *J* = 7.2 Hz, 2H), 1.94 – 1.98 (m, 2H), 1.46 – 1.50 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 160.4, 158.3, 156.7, 143.2, 136.5 (d, *J* = 12.4 Hz), 127.5 (d, *J* = 12.4 Hz), 121.3, 118.7 (d, *J* = 9.6 Hz), 110.8 (d, *J* = 10.6 Hz), 110.3 (d, *J* = 24.0 Hz), 107.6 (d, *J* = 24.0 Hz), 97.8 (d, *J* = 28.4 Hz), 97.4 (d, *J* = 28.4 Hz), 43.5, 30.4, 20.2, 13.7. HRMS (ESI): calcd for C₁₇H₁₆F₂N₃ [M + H]⁺ 300.1307, found 300.1331.

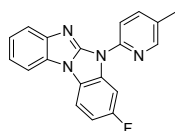


5-Benzyl-9-isopropyl-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3q**). White solid. Mp 146 – 148 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.80 (t, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.42 (m, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.33 (m, 2H), 7.17 – 7.18 (m, 1H), 7.10 (s, 1H), 5.49 (s, 2H), 3.00 – 3.07 (m, 1H), 1.31 (d, *J* = 6.9 Hz, 6H). ¹³C NMR (150 MHz, CDCl₃): δ 154.0, 147.2, 144.6,

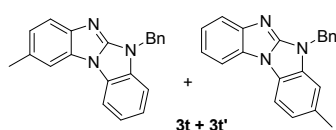
135.7, 135.6, 128.9, 128.4, 128.0, 127.5, 123.6, 122.8, 119.8, 119.5, 118.4, 110.4, 110.1, 108.2, 46.9, 34.4, 24.4. HRMS (ESI): calcd for C₂₃H₂₂N₃ [M + H]⁺ 340.1808, found 340.1800.



5-(*tert*-Butyl)-9-methyl-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3r**). Yellow viscous liquid. ¹H NMR (600 MHz, CDCl₃): δ 7.68 (s, 1H), 7.58 – 7.61 (m, 1H), 7.29 – 7.35 (m, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.98 – 7.00 (m, 1H), 6.68 – 6.73 (m, 1H), 2.49 (s, 3H), 1.53 (s, 9H). ¹³C NMR (150 MHz, CDCl₃): δ 151.9, 143.2, 141.9, 140.9, 135.0, 130.5, 130.2, 123.2, 121.6, 119.6, 116.5, 107.8, 52.2, 29.4, 21.1. HRMS (ESI): calcd for C₁₈H₂₀N₃ [M + H]⁺ 278.1652, found 278.1643.



3-Fluoro-5-(5-methylpyridin-2-yl)-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3s**). White solid. Mp 165 – 167 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.75 – 8.78 (m, 1H), 8.60 – 8.69 (m, 1H), 8.42 (s, 1H), 7.70 – 7.85 (m, 3H), 7.46 – 7.54 (m, 1H), 7.34 – 7.41 (m, 2H), 7.09 – 7.15 (m, 1H), 2.43 (s, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 147.9, 139.2, 133.9, 129.9, 125.3, 124.0, 123.7, 123.1, 122.8, 119.4 (d, *J* = 10.0 Hz), 116.5, 114.5, 110.8, 110.6, 110.3, 110.1, 97.8, 97.6, 18.0. HRMS (ESI): calcd for C₁₉H₁₄FN₄ [M + H]⁺ 317.1197, found 317.1175.

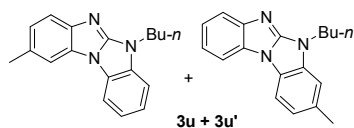


5-Benzyl-9-methyl-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole + 5-benzyl-3-methyl-5*H*-benzo[*d*]benzo[4,5]imidazo[1,2-*a*]imidazole (**3t** + **3t'**). White solid.

Major (approximate attribution): ¹H NMR (600 MHz, CDCl₃): δ 7.78 – 7.81 (m, 2H), 7.65 – 7.66 (m, 1H), 7.29 – 7.44 (m, 7H), 7.09 – 7.12 (m, 1H), 7.05 (s, 1H), 5.48 (s, 2H), 2.48 (s, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 142.0, 135.7, 133.3, 128.9, 128.4, 128.0, 127.3, 123.0, 122.8, 122.1, 119.8, 118.5, 110.6, 110.3, 110.1, 46.9, 21.8.

Minor (approximate attribution): ¹H NMR (600 MHz, CDCl₃): δ 7.83 – 7.84 (m, 2H), 7.61 (m, 1H), 7.29 – 7.44 (m, 7H), 7.18 – 7.21 (m, 1H), 7.03 (s, 1H), 5.51 (s, 2H),

2.59 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ 141.5, 135.6, 133.2, 129.0, 128.4, 128.0, 127.4, 123.0, 122.8, 122.1, 119.8, 118.5, 110.6, 110.3, 110.1, 47.0, 22.1.



5-Butyl-9-methyl-5H-benzo[d]benzo[4,5]imidazo[1,2-a]imidazole + 5-butyl-3-methyl-5H-benzo[d]benzo[4,5]imidazo[1,2-a]imidazole (**3u** + **3u'**). White solid.

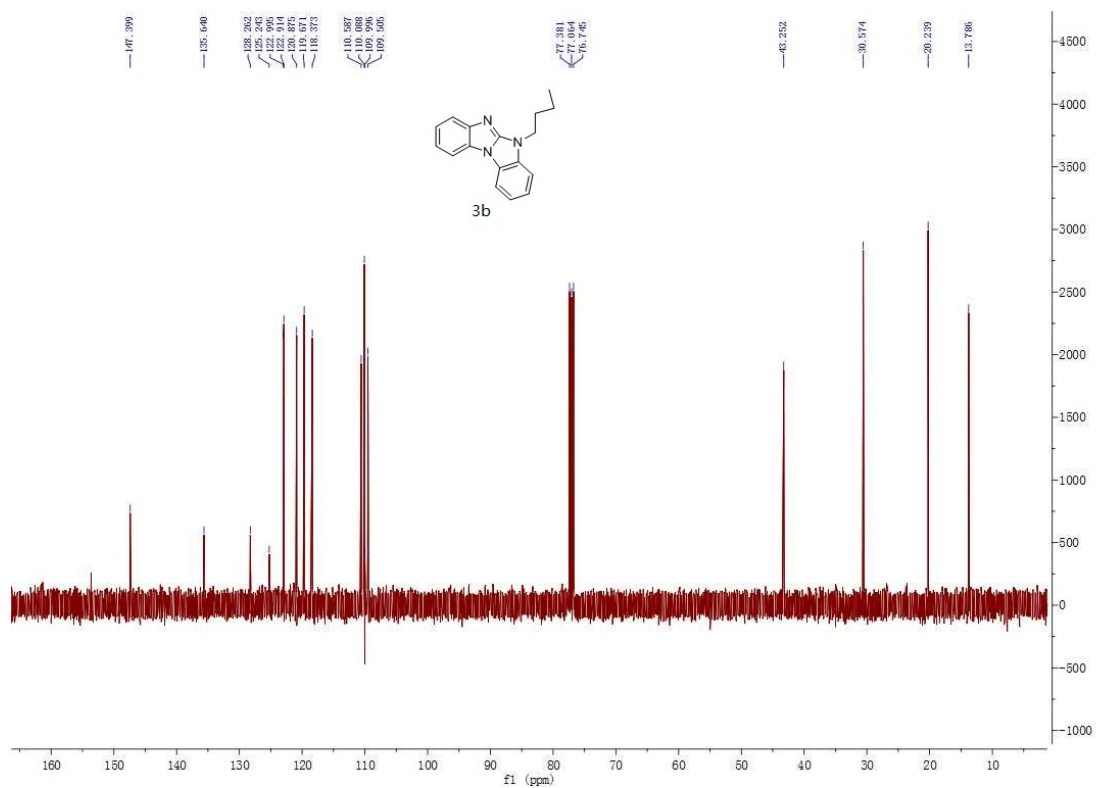
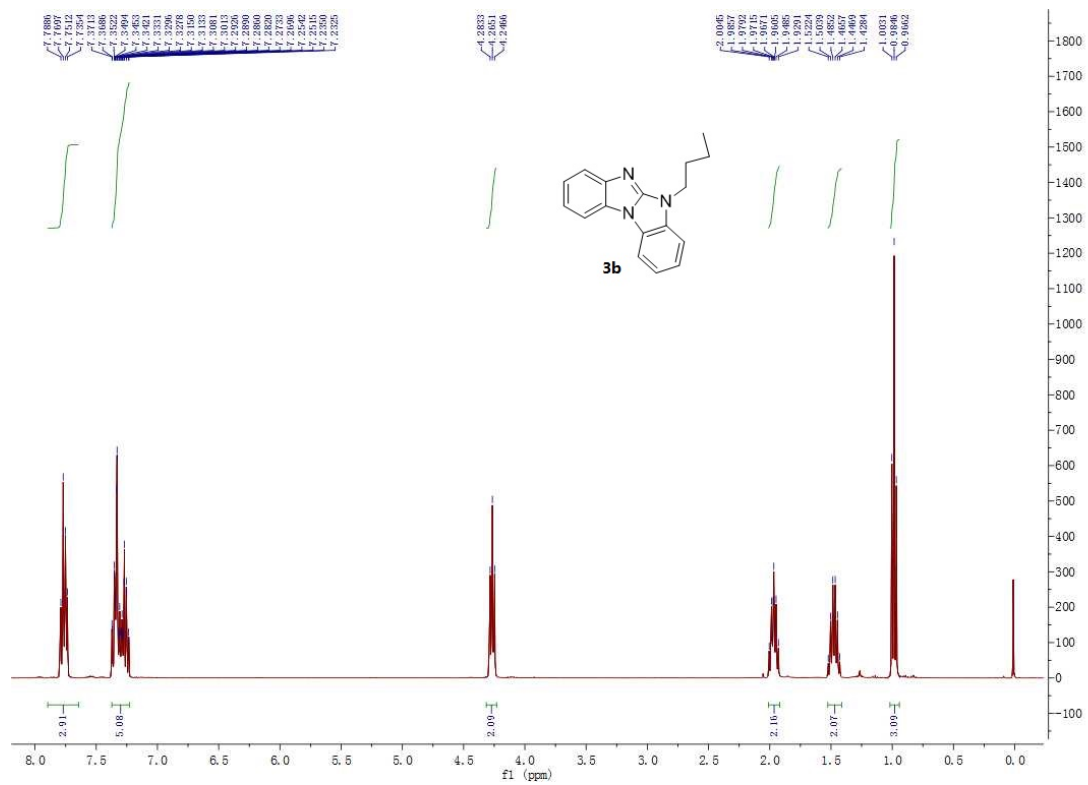
Major (approximate attribution): ^1H NMR (600 MHz, CDCl_3): δ 7.75 (d, $J = 7.9$ Hz, 1H), 7.62 – 7.66 (m, 1H), 7.42 (d, $J = 7.9$ Hz, 1H), 7.30 – 7.33 (m, 1H), 7.16 – 7.25 (m, 2H), 6.94 – 6.98 (m, 1H), 4.12 – 4.16 (m, 2H), 2.44 (s, 3H), 1.89 – 1.91 (m, 2H), 1.43 – 1.46 (m, 2H), 0.95 – 0.98 (m, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ 153.5, 147.2, 135.6, 132.9, 128.1, 123.0, 122.8, 122.6, 121.5, 119.2, 118.2, 110.4, 109.9, 43.1, 30.6, 21.8, 20.2, 13.8.

Minor (approximate attribution): ^1H NMR (600 MHz, CDCl_3): δ 7.75 (d, $J = 7.9$ Hz, 1H), 7.57 – 7.58 (m, 1H), 7.42 (d, $J = 7.9$ Hz, 1H), 7.30 – 7.33 (m, 1H), 7.11 – 7.12 (m, 2H), 6.94 – 6.98 (m, 1H), 4.12 – 4.16 (m, 2H), 2.50 (s, 3H), 1.89 – 1.91 (m, 2H), 1.43 – 1.46 (m, 2H), 0.95 – 0.98 (m, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ 153.5, 147.3, 135.1, 132.8, 129.2, 125.0, 123.7, 122.9, 120.7, 119.6, 118.3, 110.3, 109.3, 43.1, 30.6, 21.7, 20.2, 13.8.

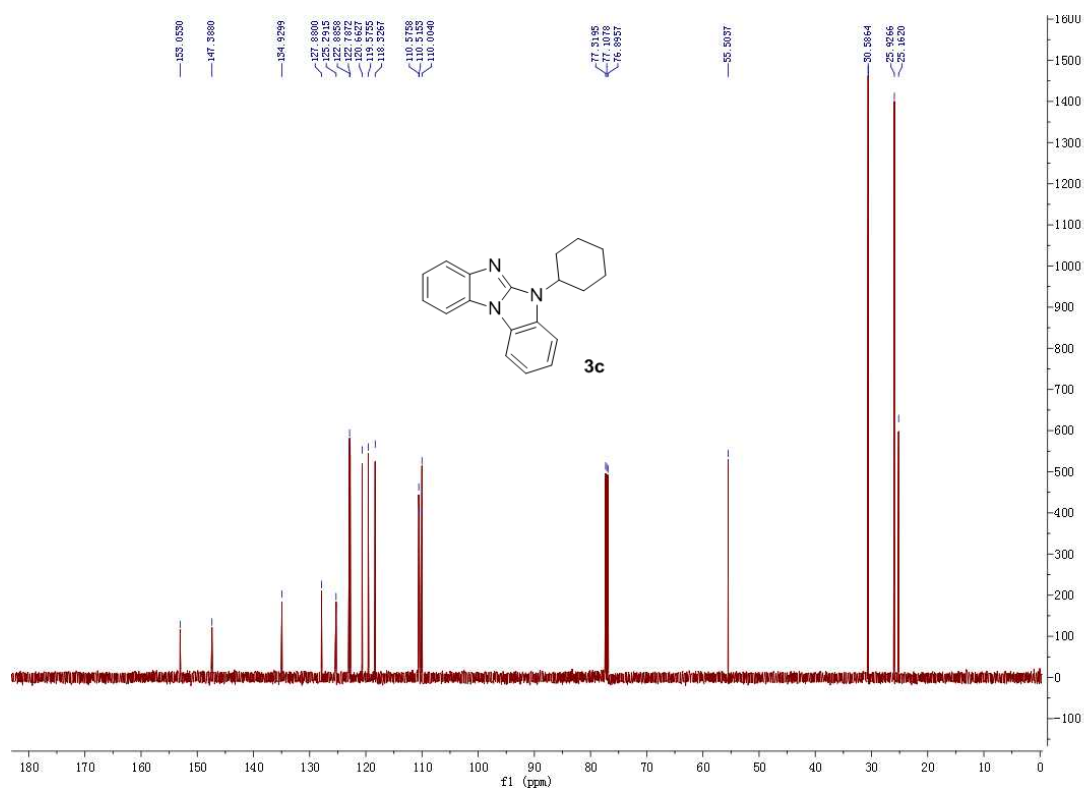
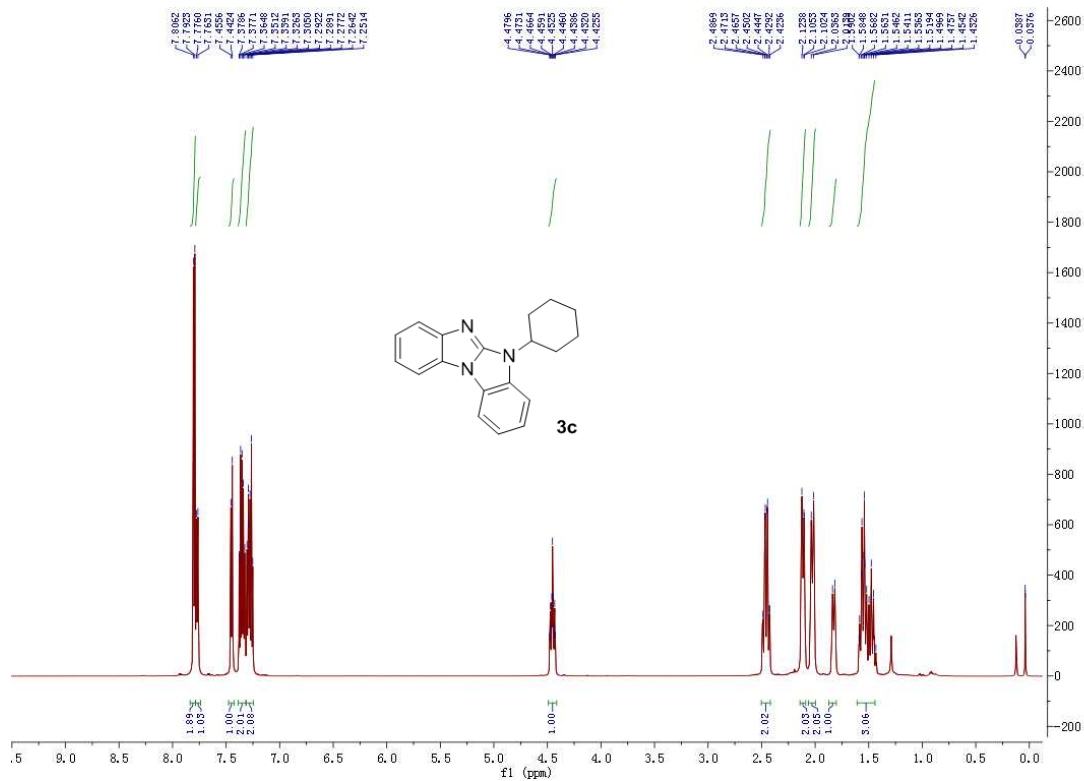
References:

1. F. L. Zeng and H. Alper, *Org. Lett.* 2010, **12**, 3642-3644.

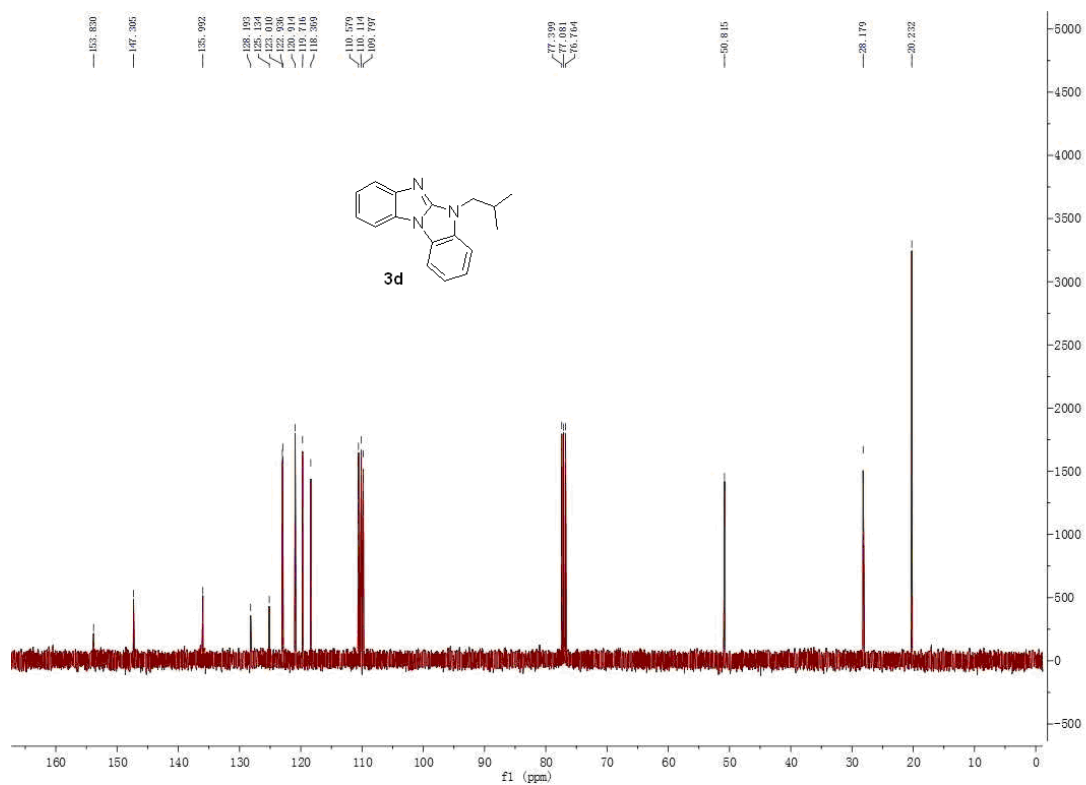
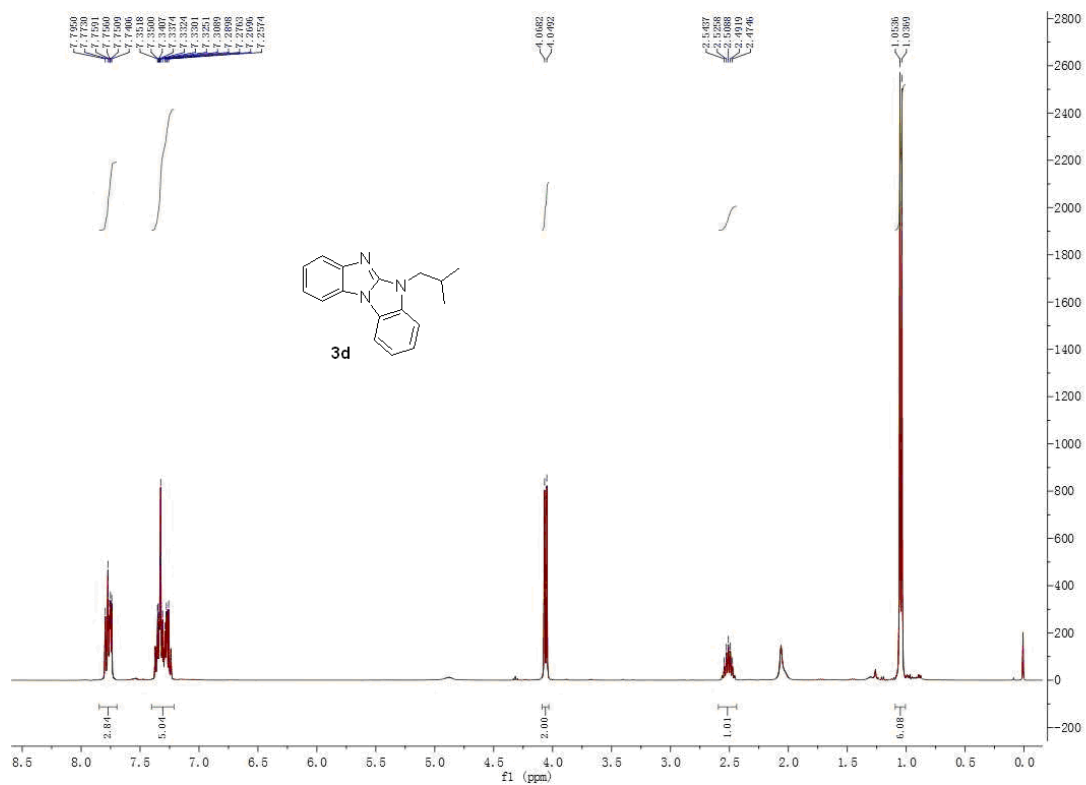
3b:



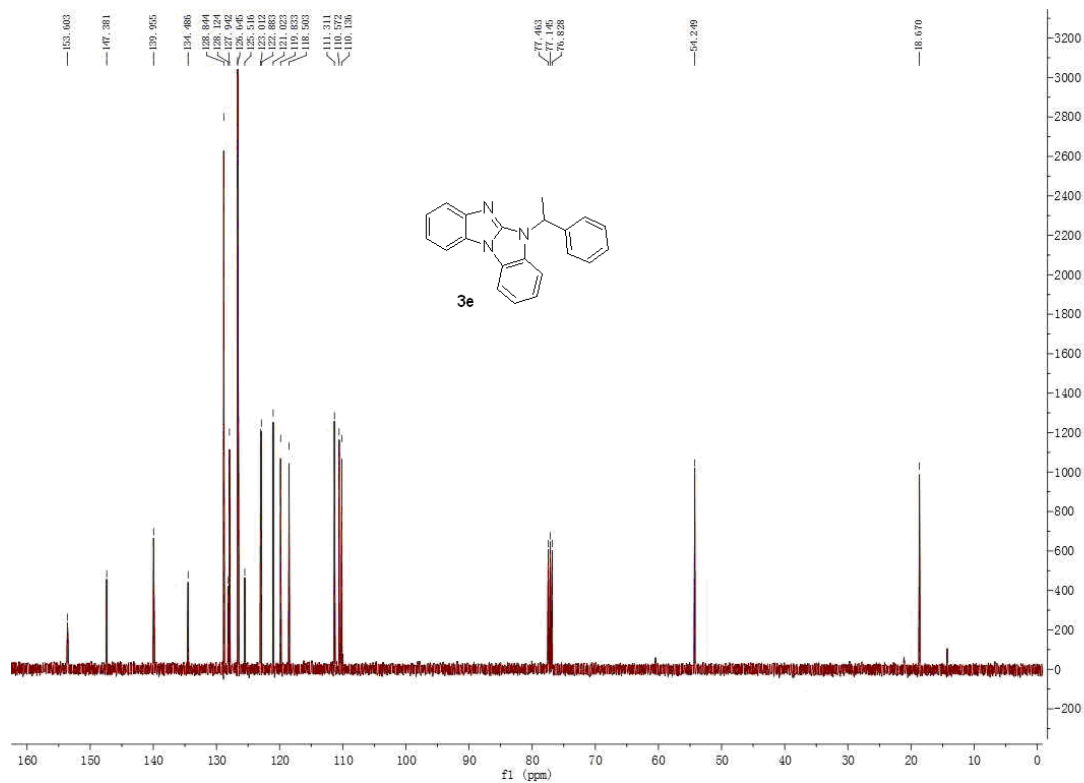
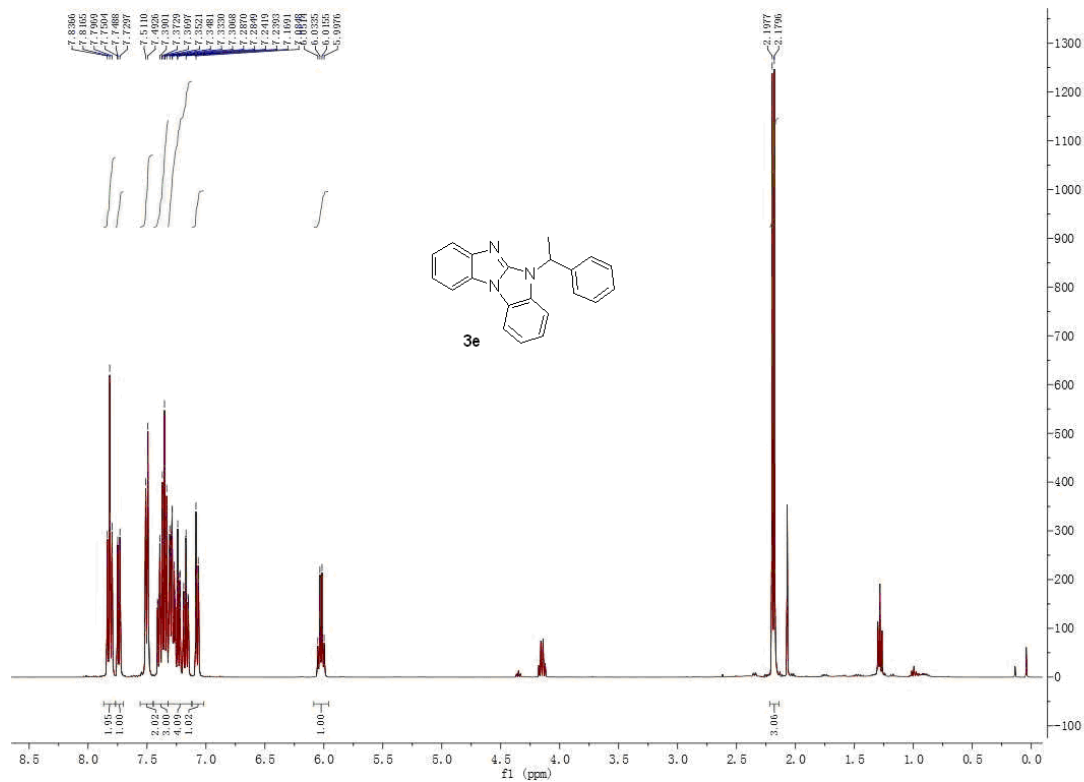
3c:



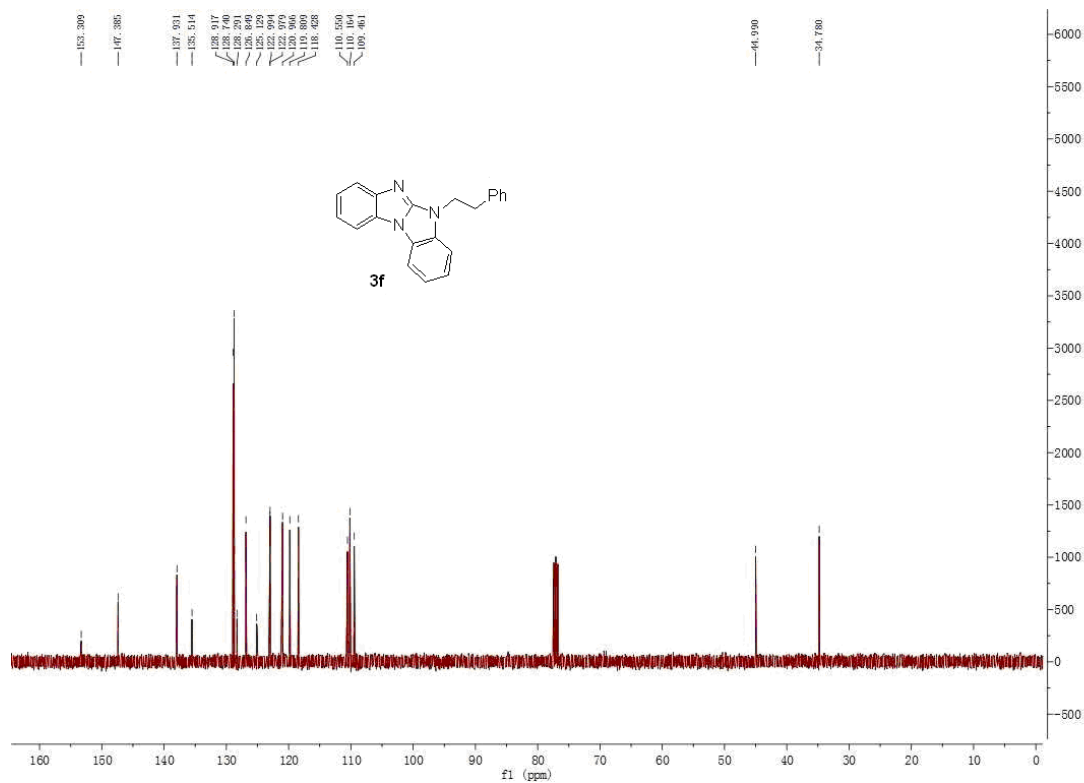
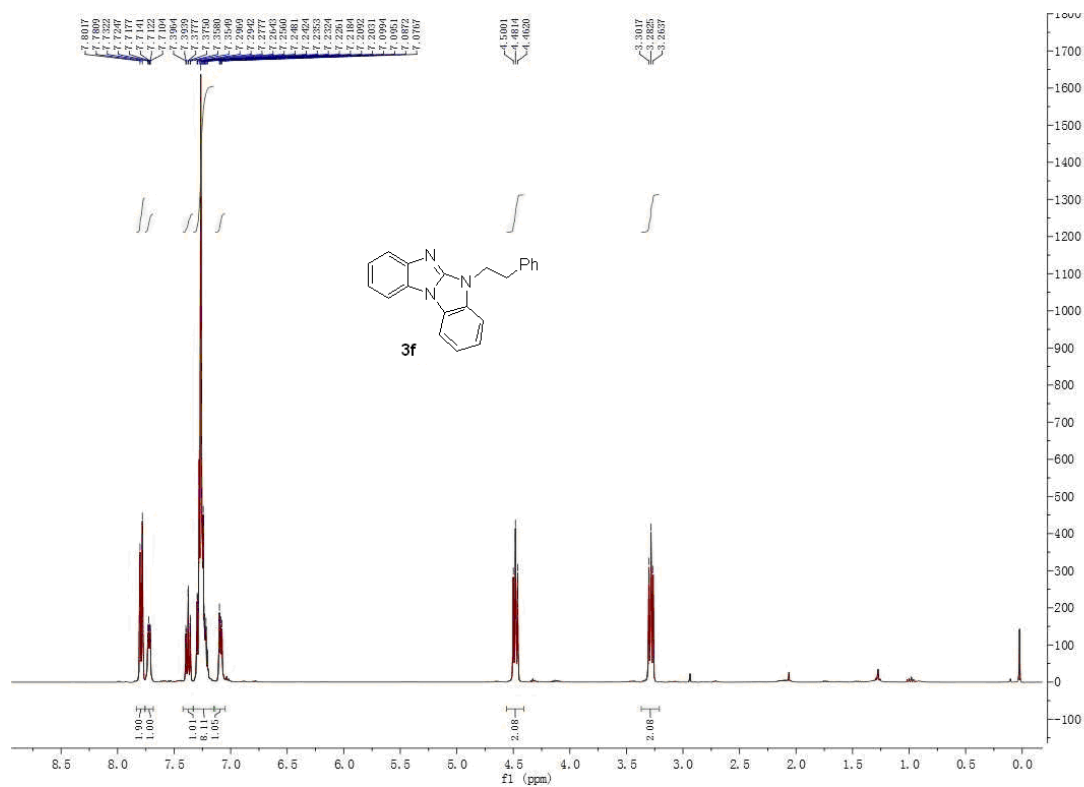
3d:



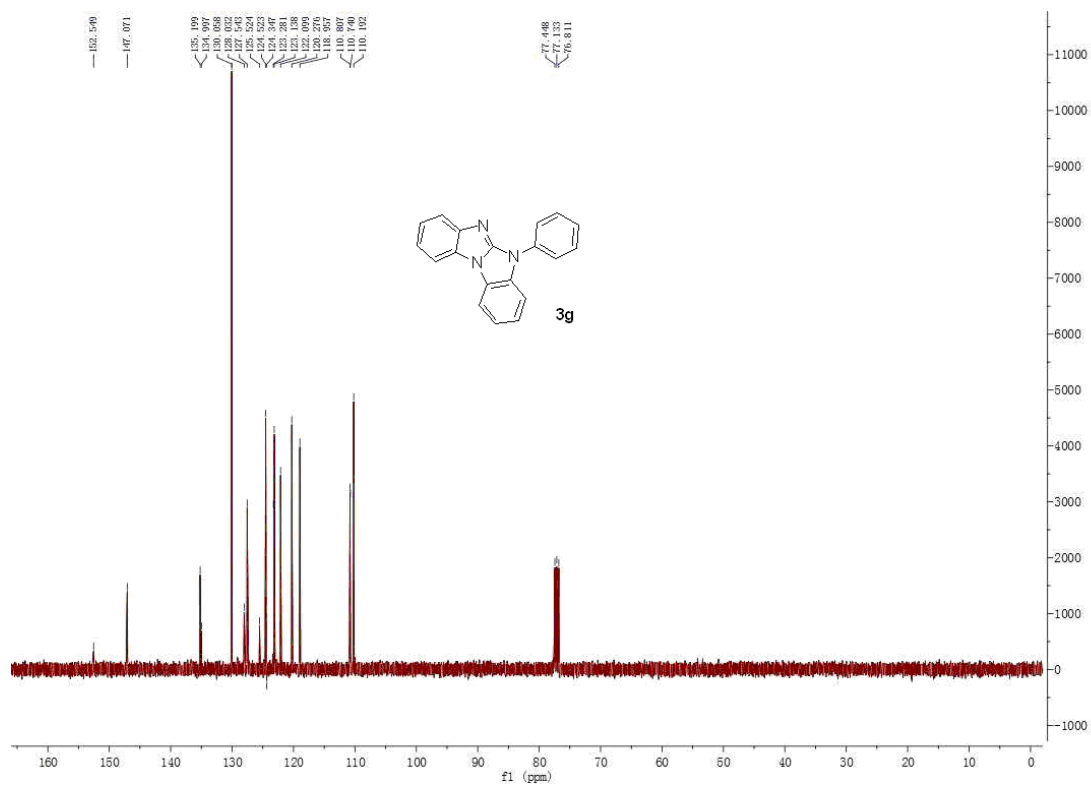
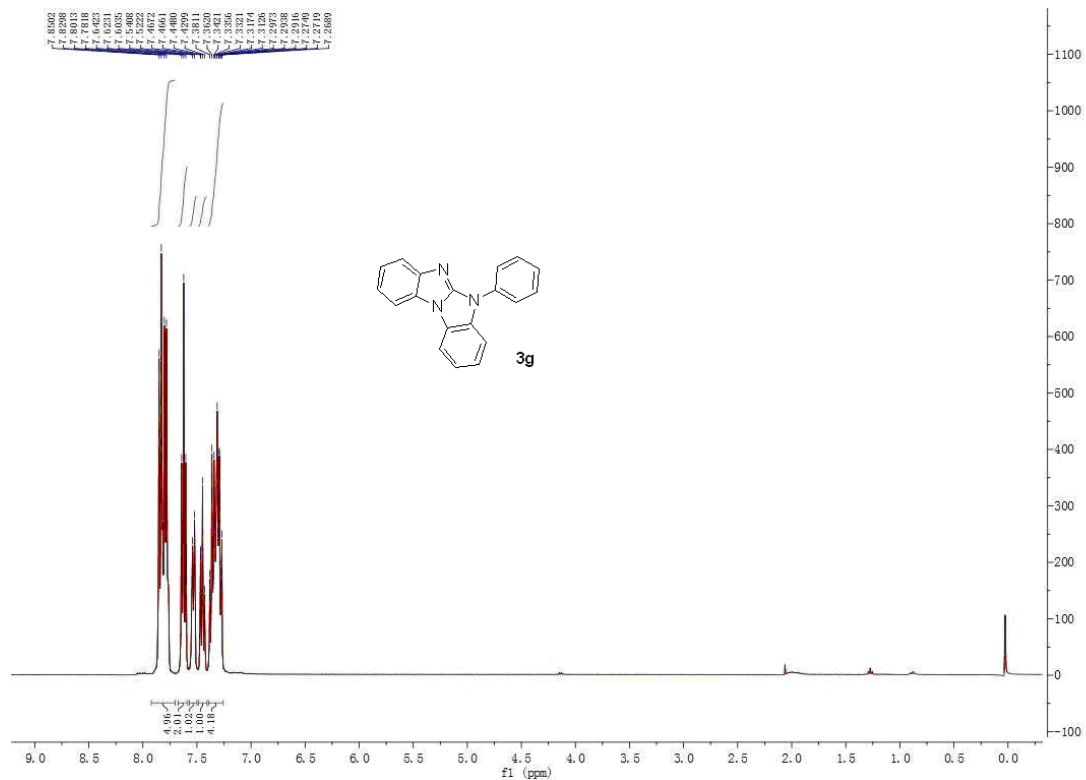
3e:



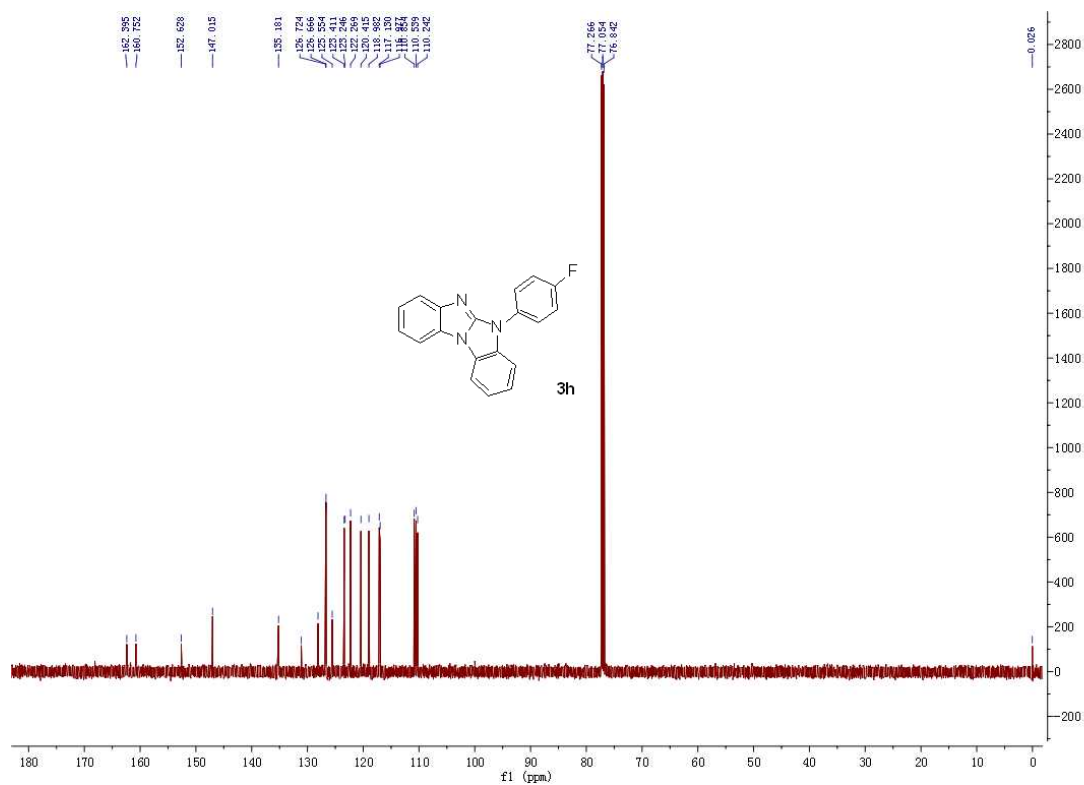
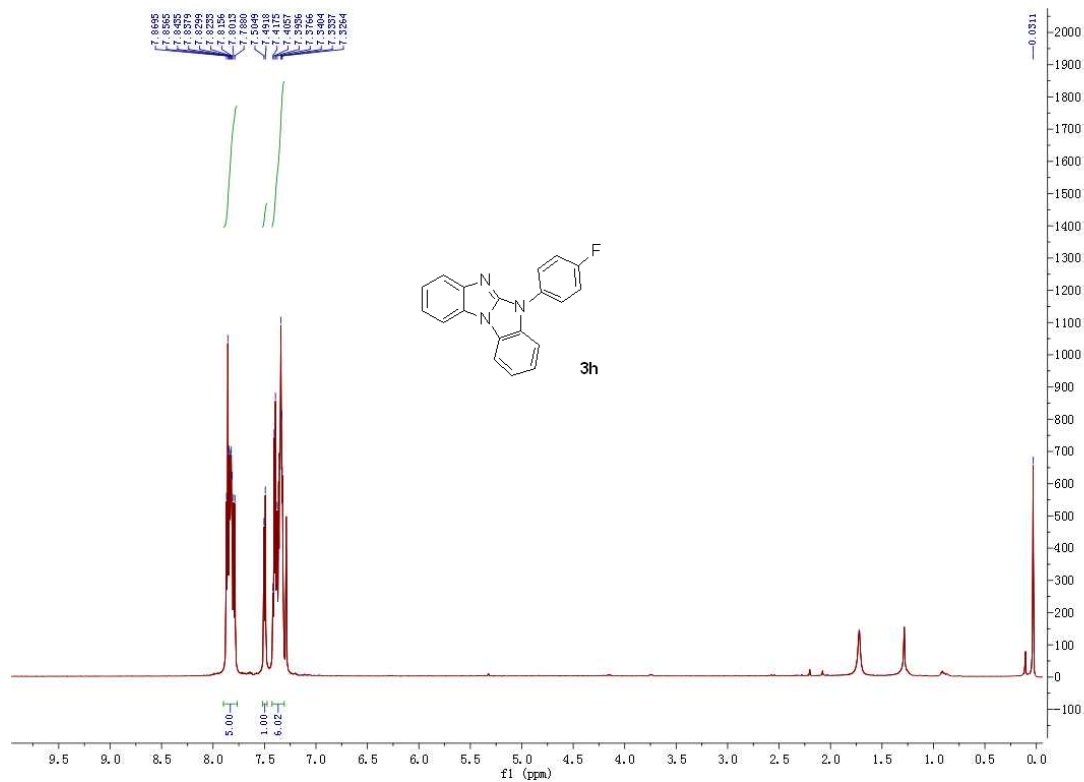
3f:



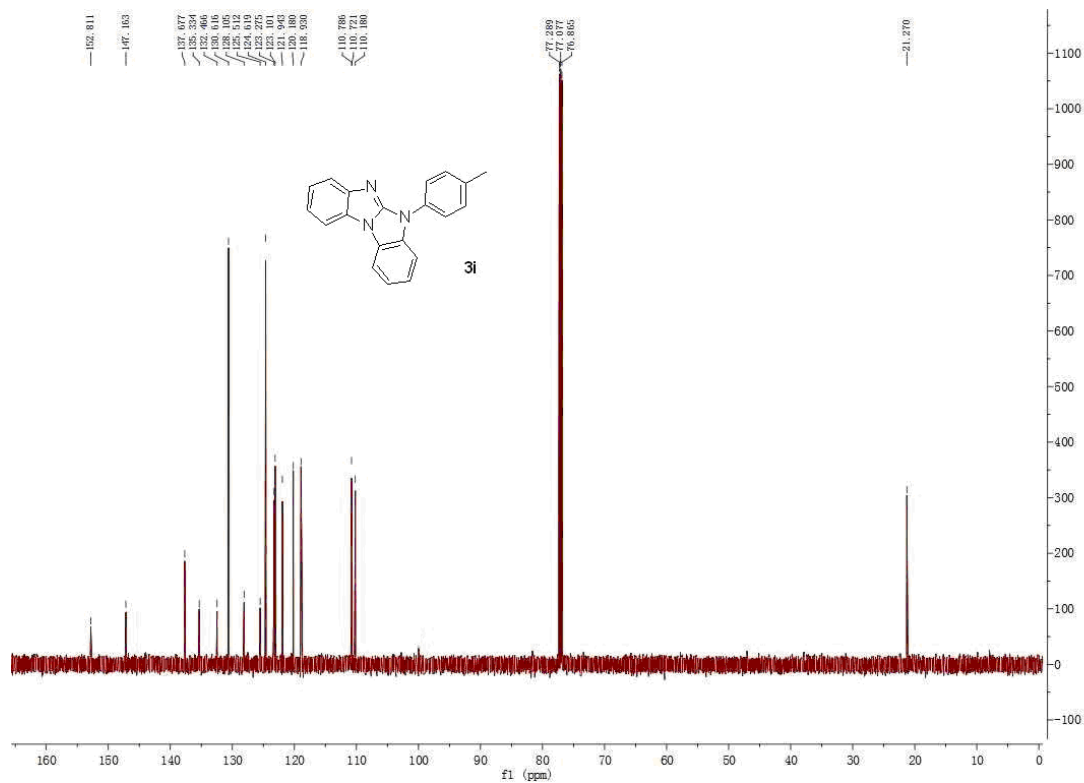
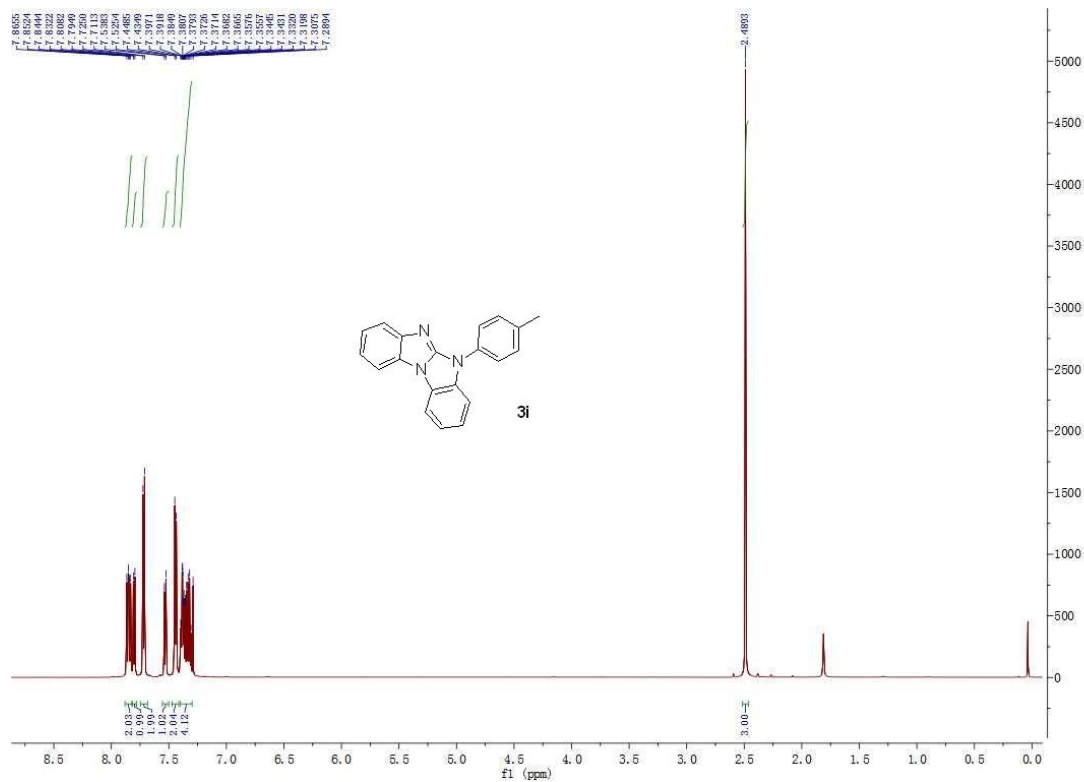
3g:



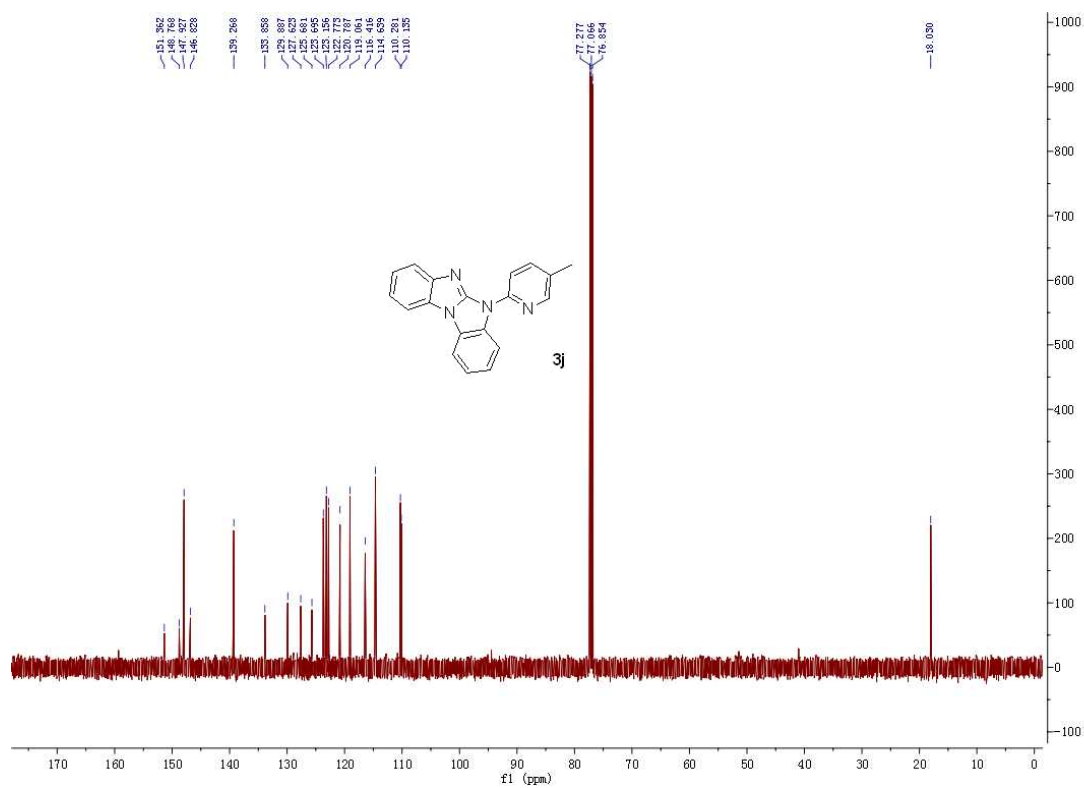
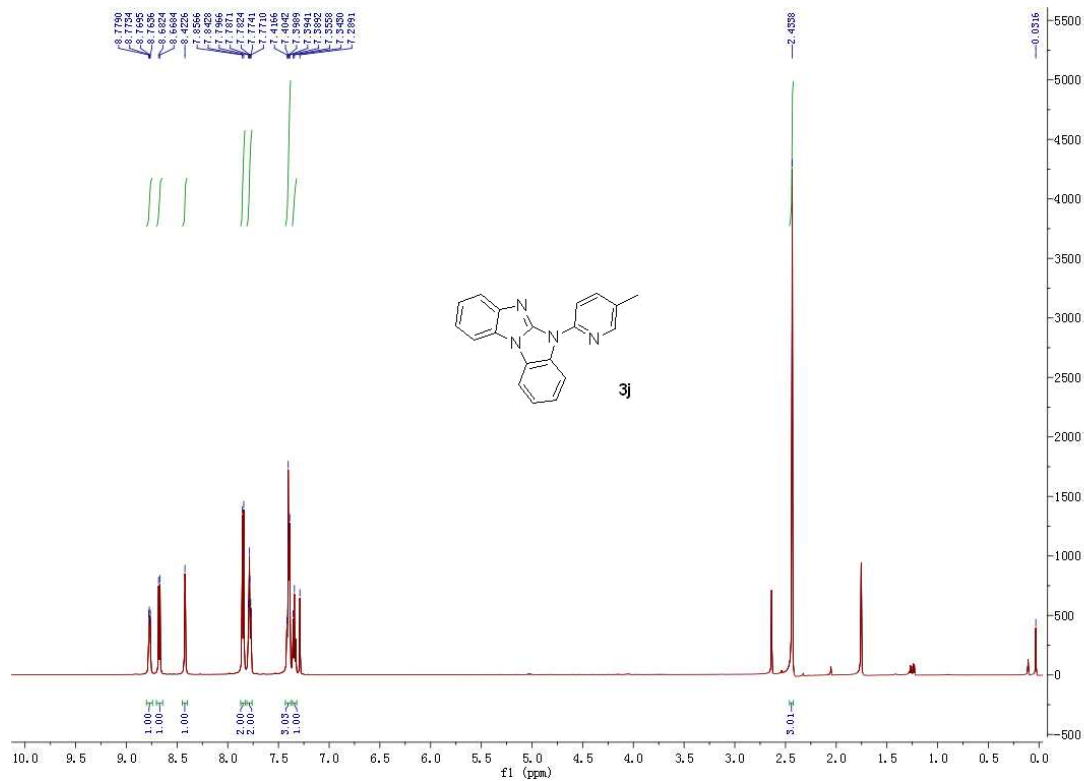
3h:



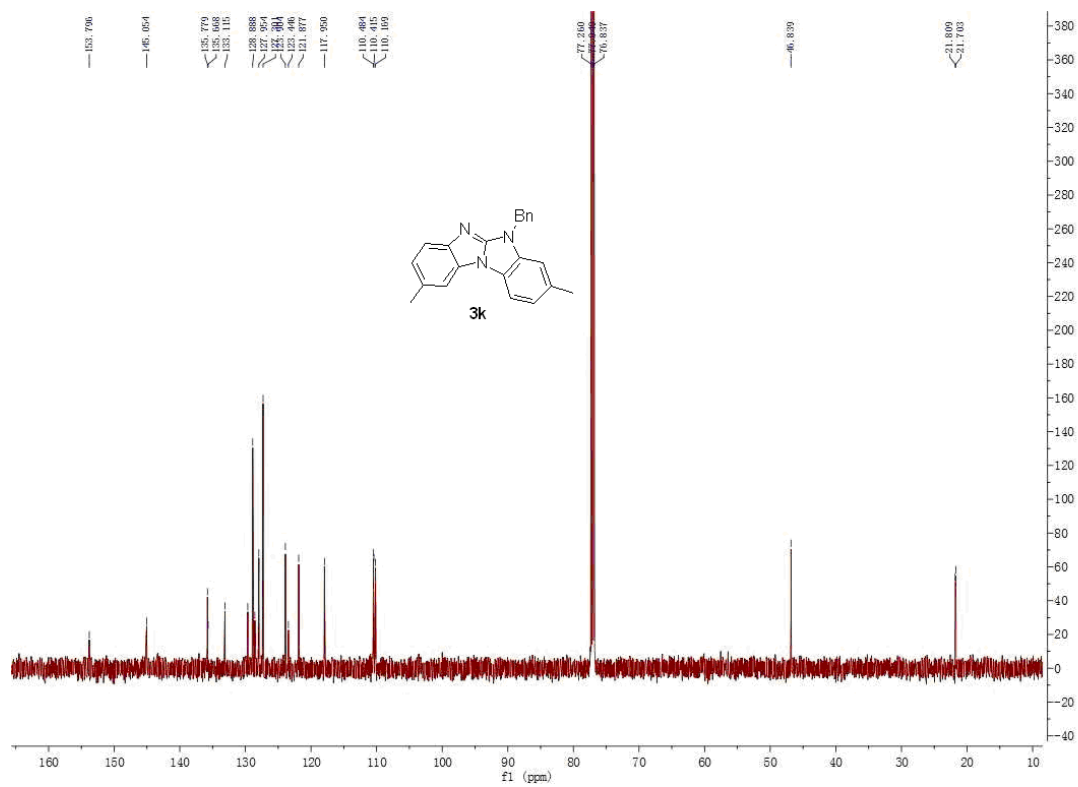
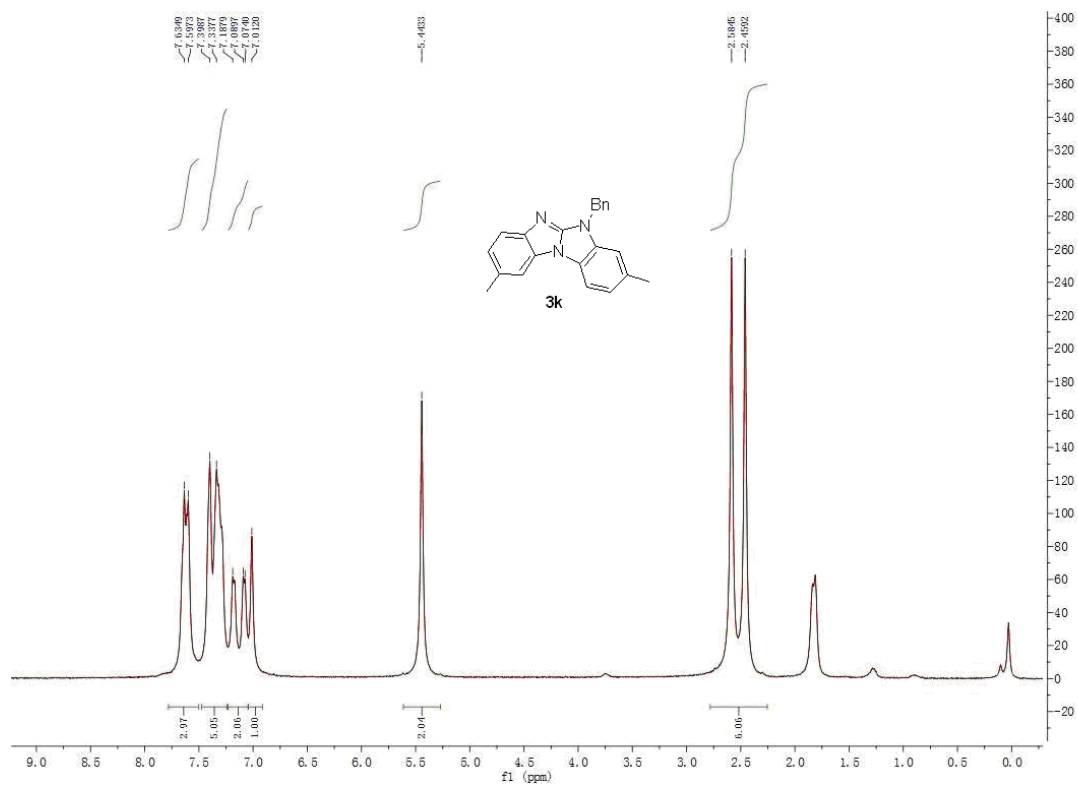
3i:



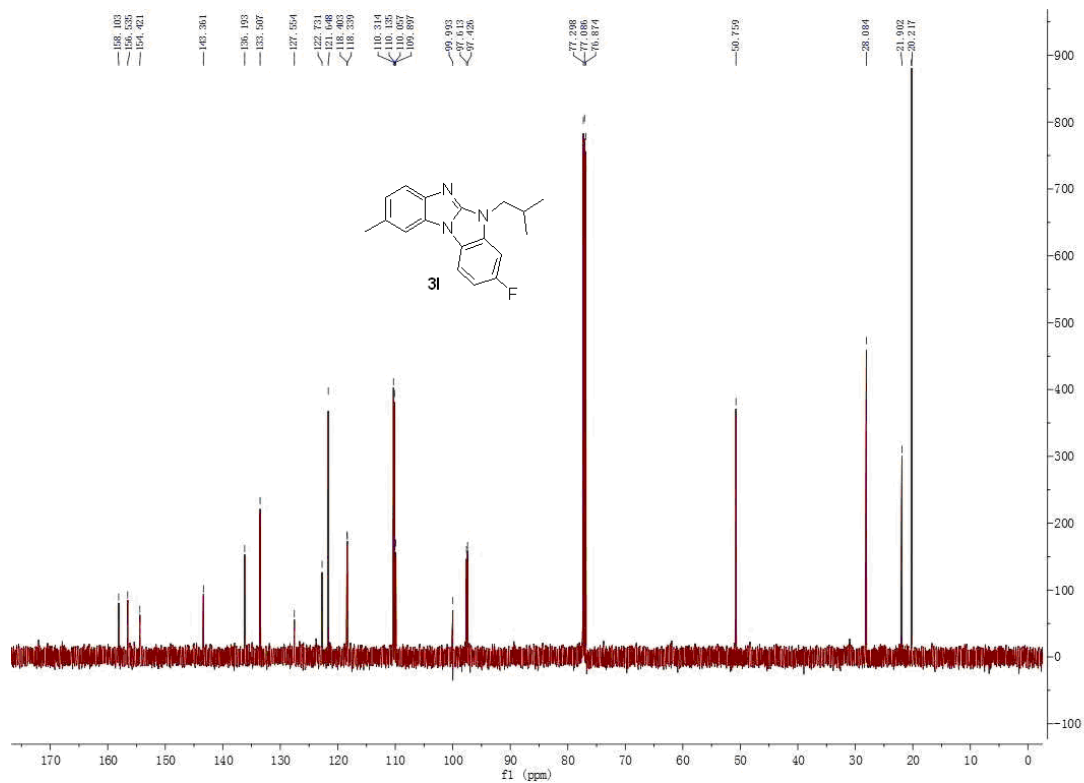
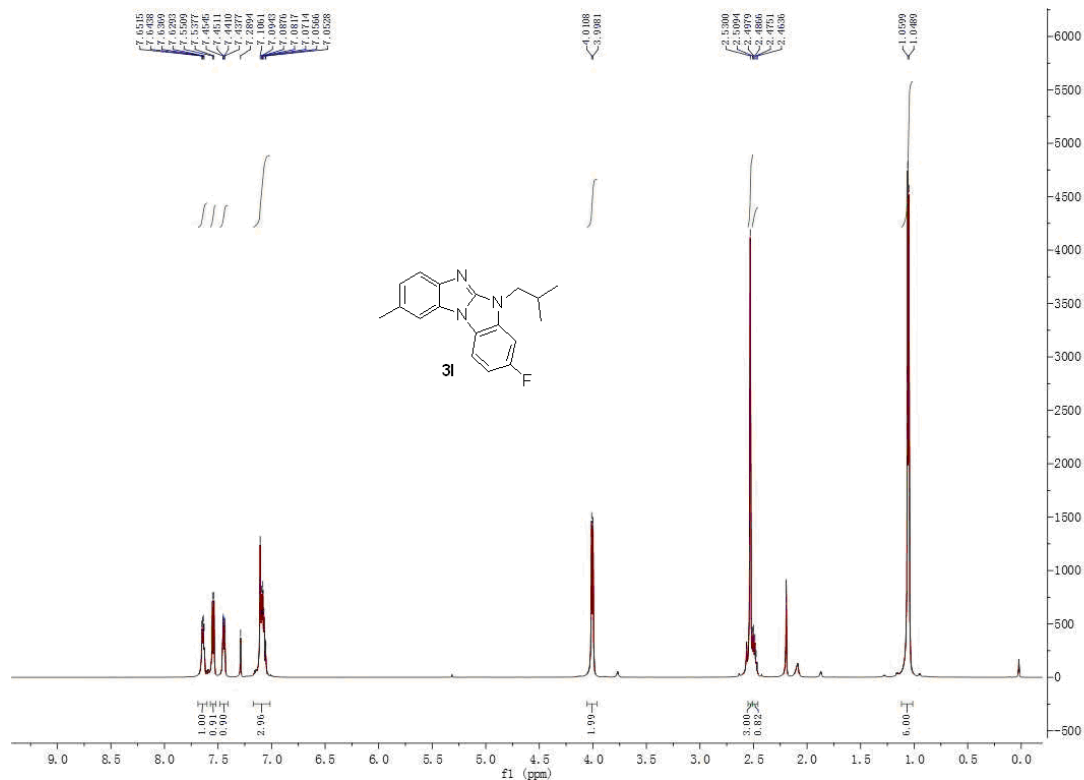
3j:



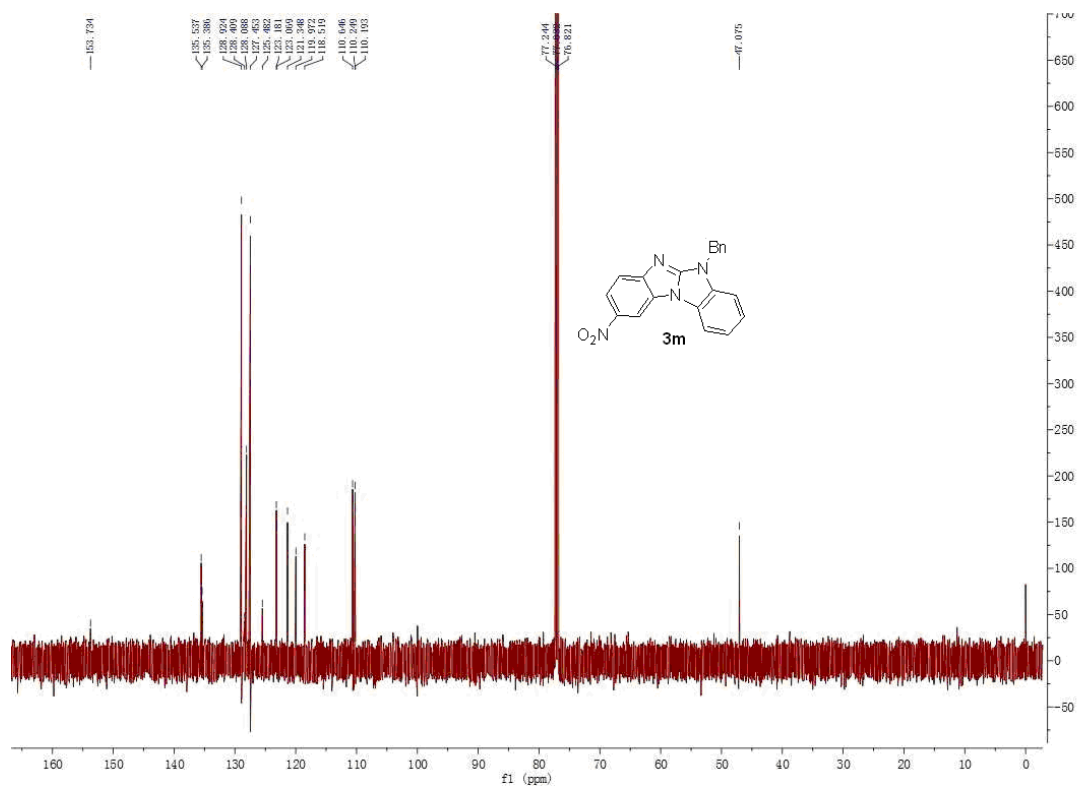
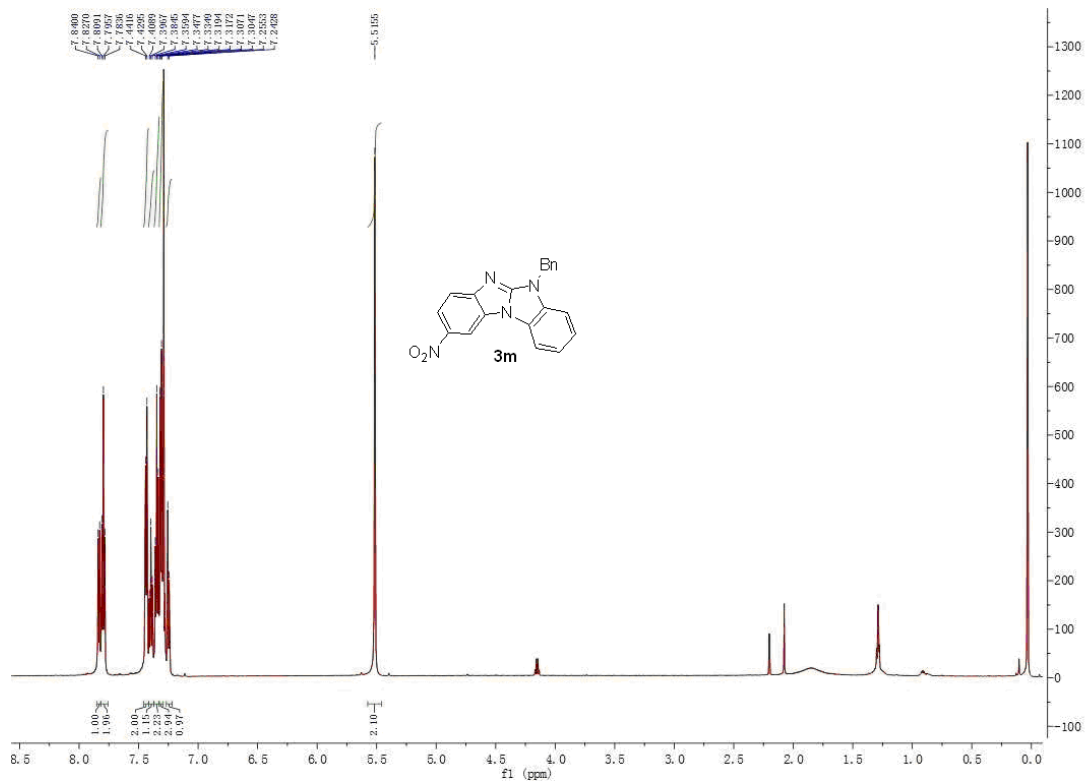
3k:



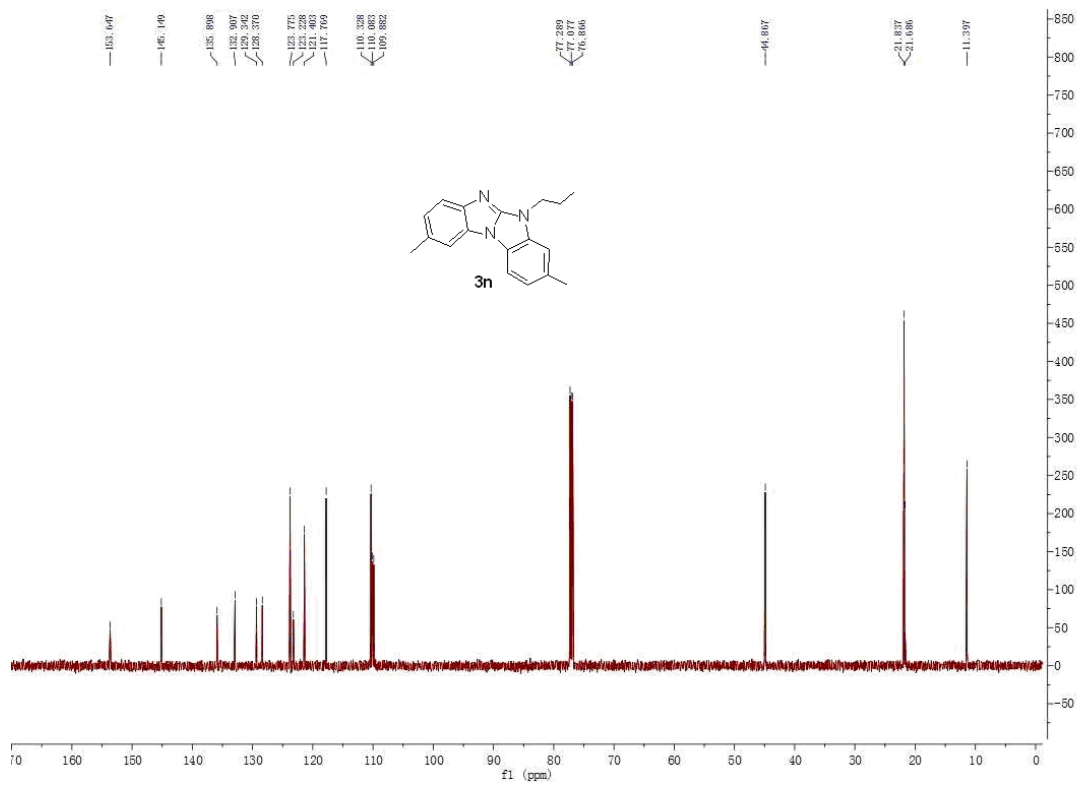
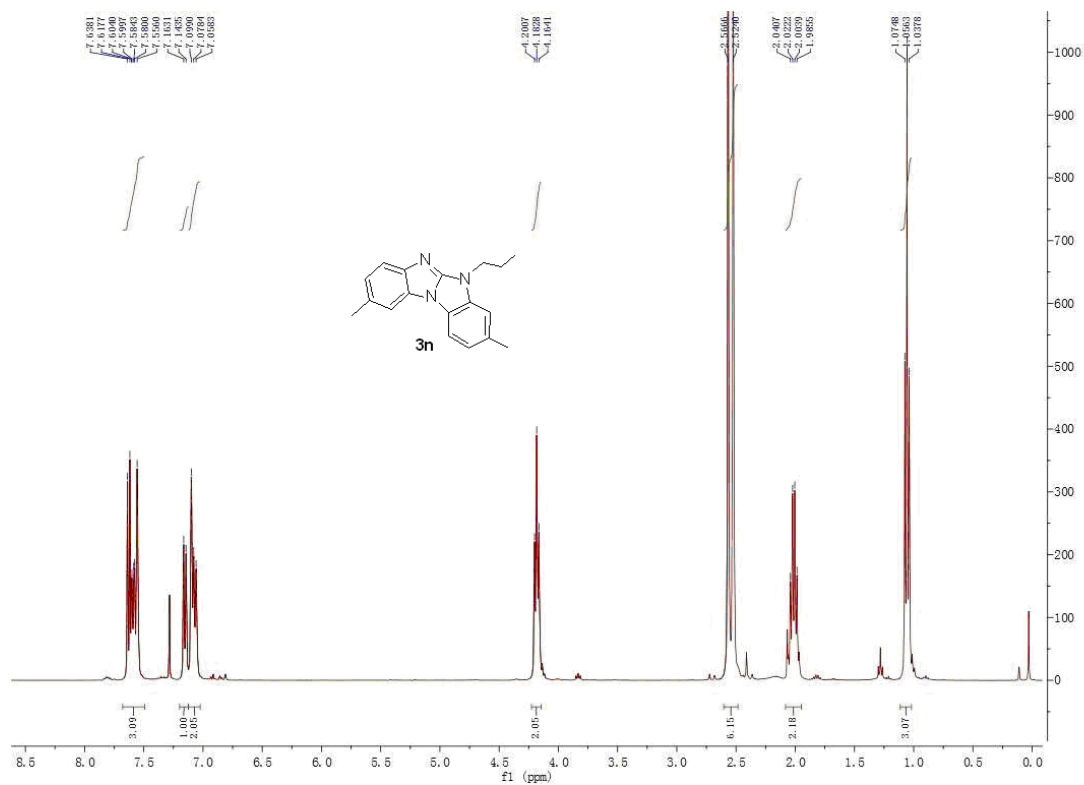
3l:



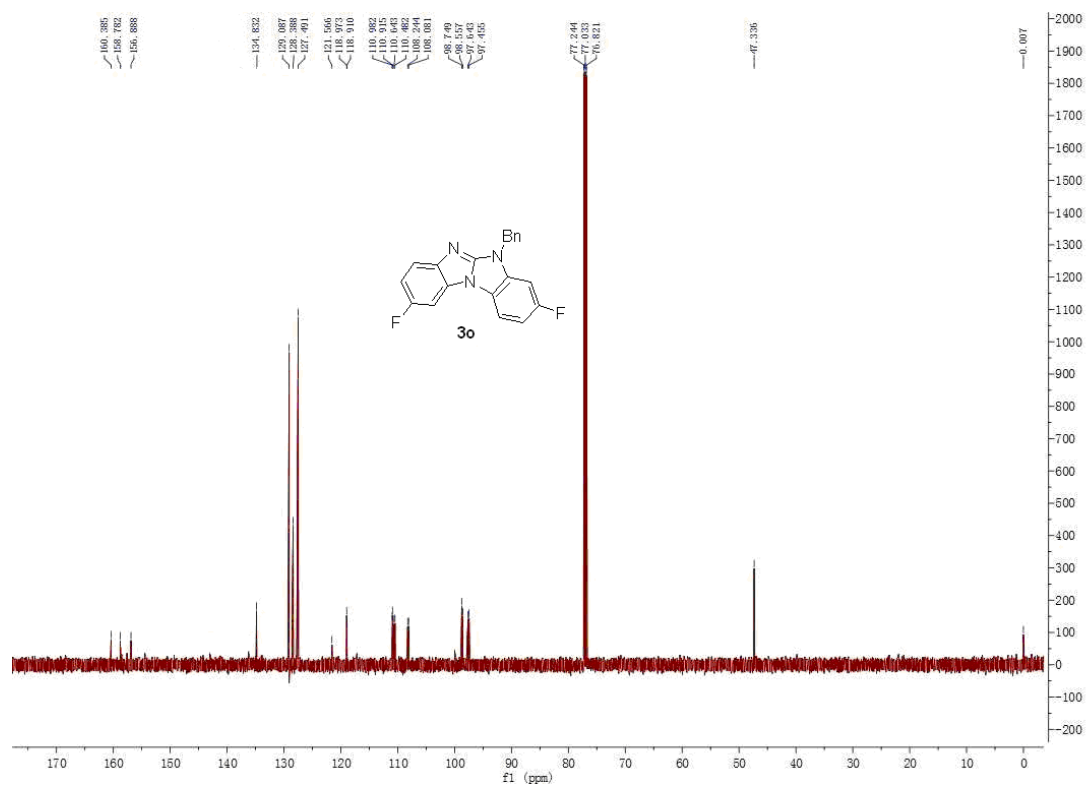
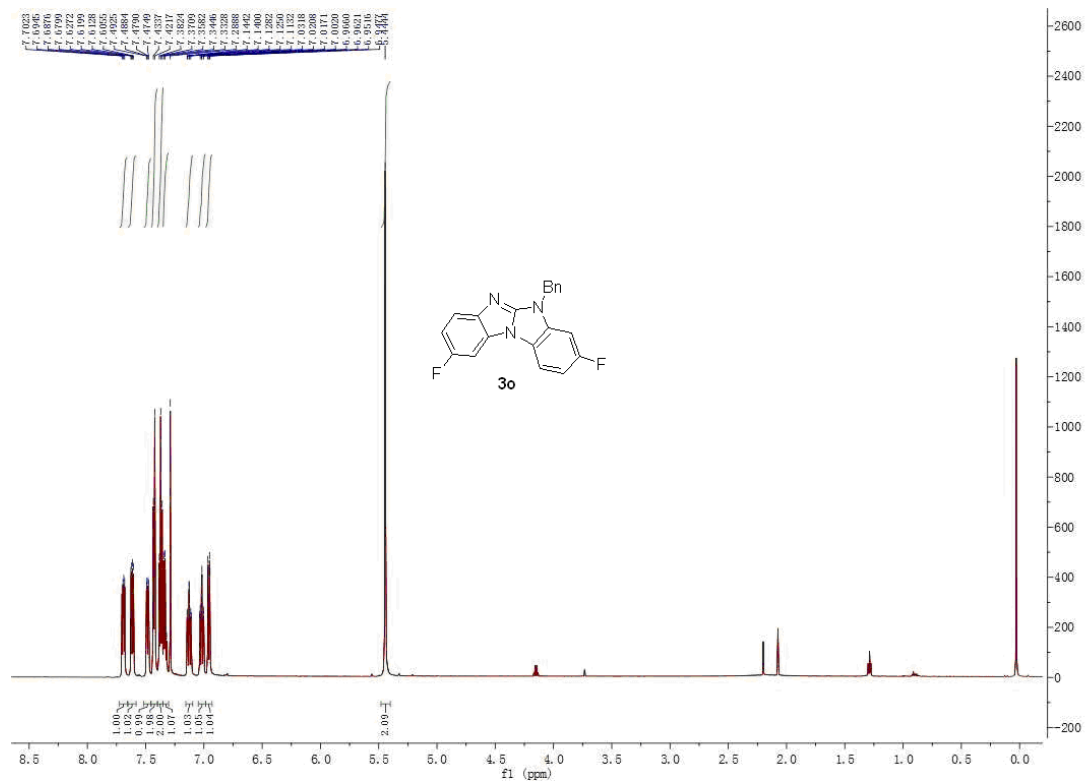
3m:



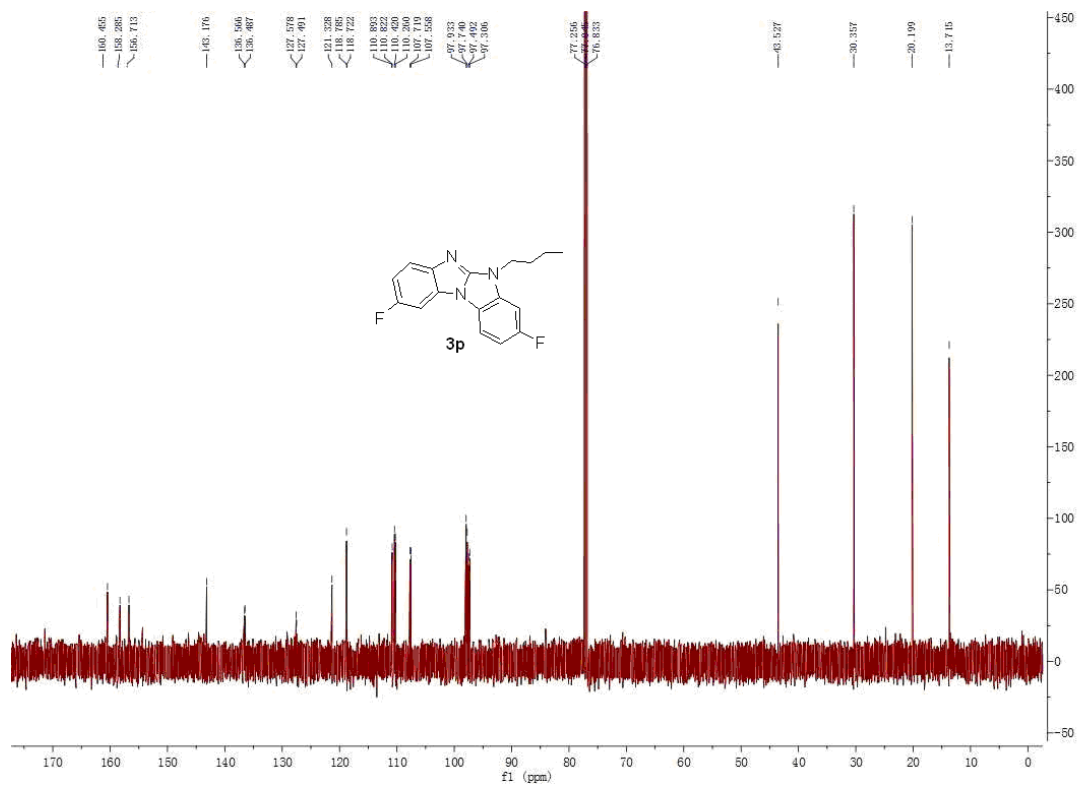
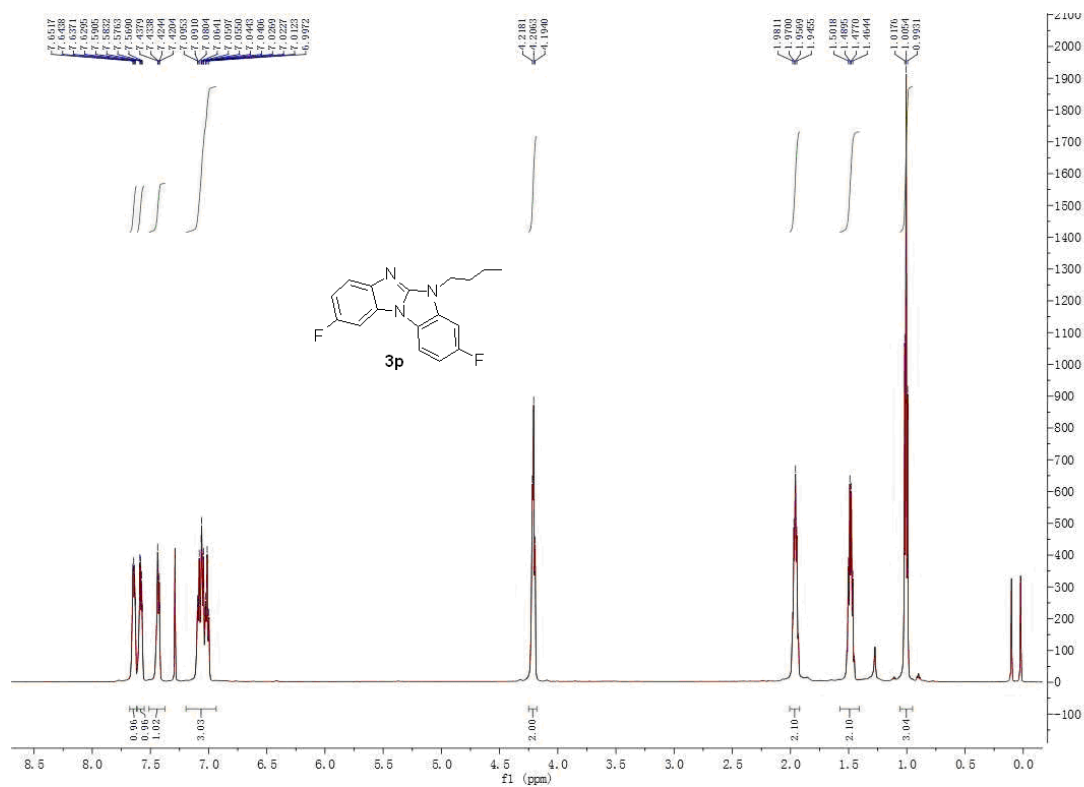
3n:



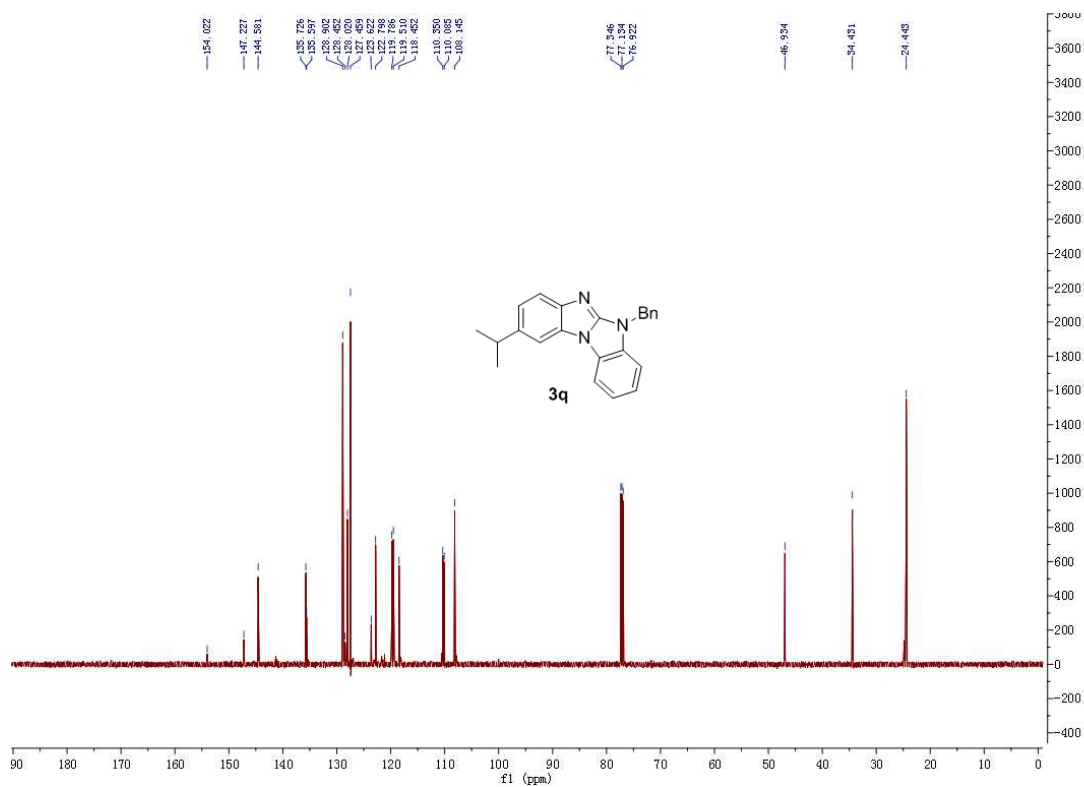
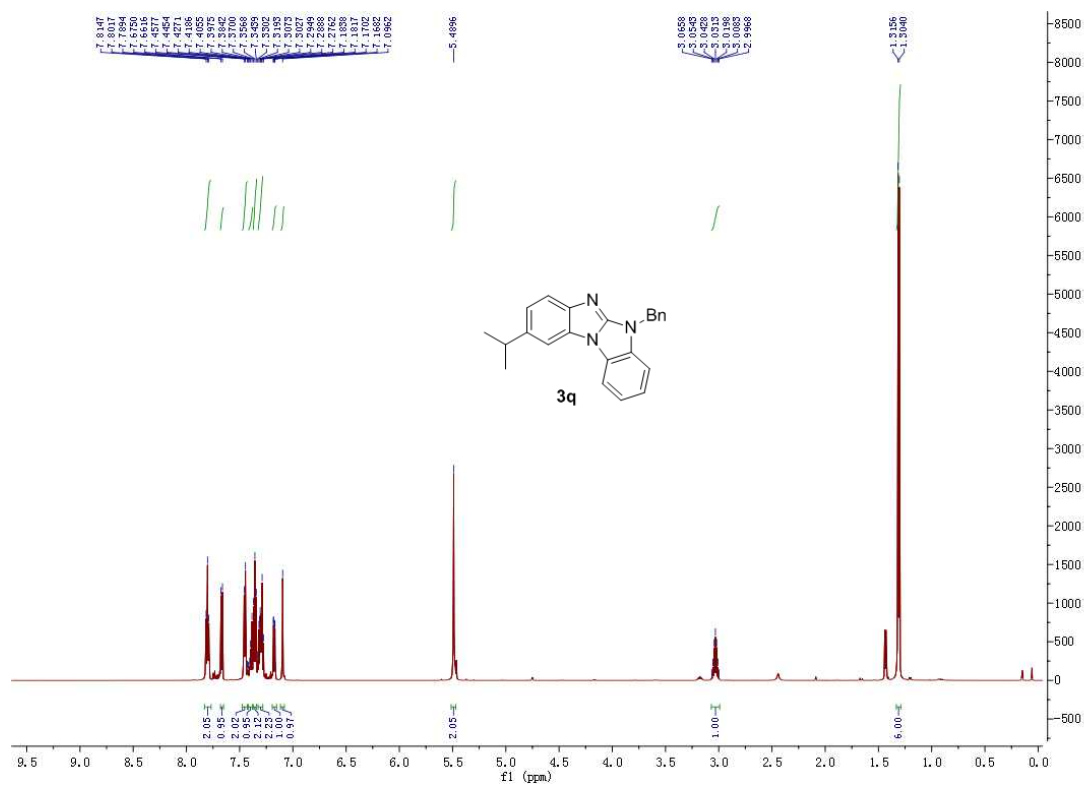
3o:



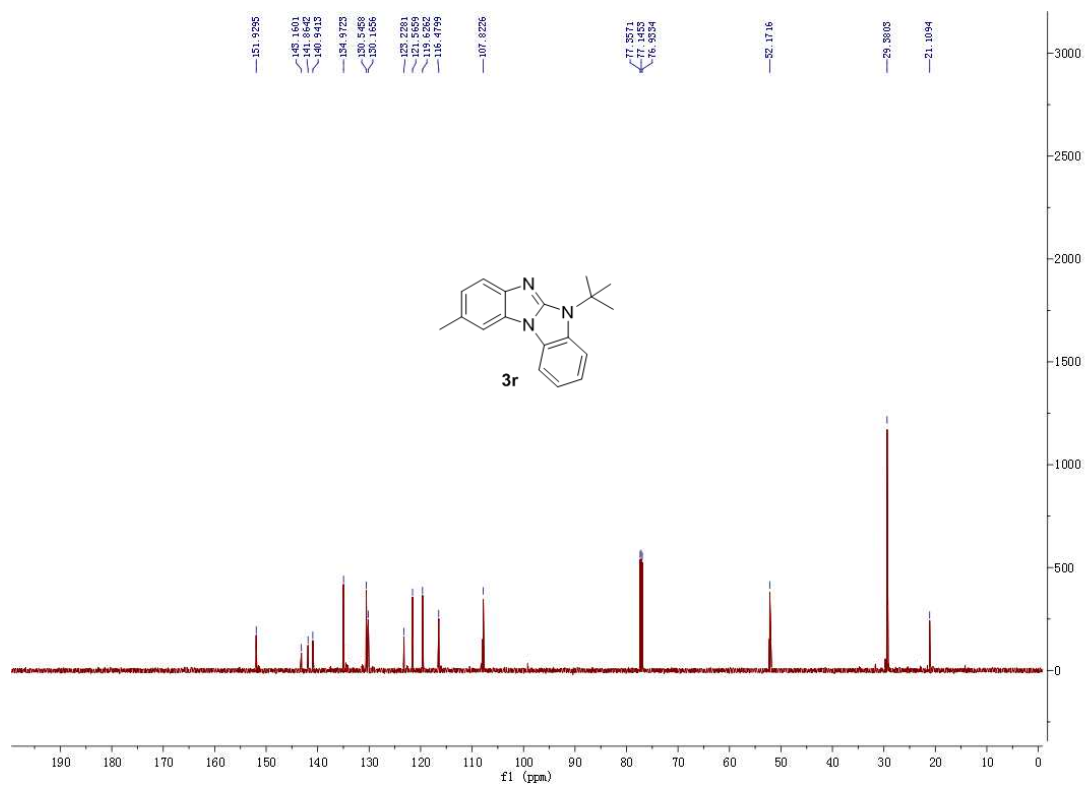
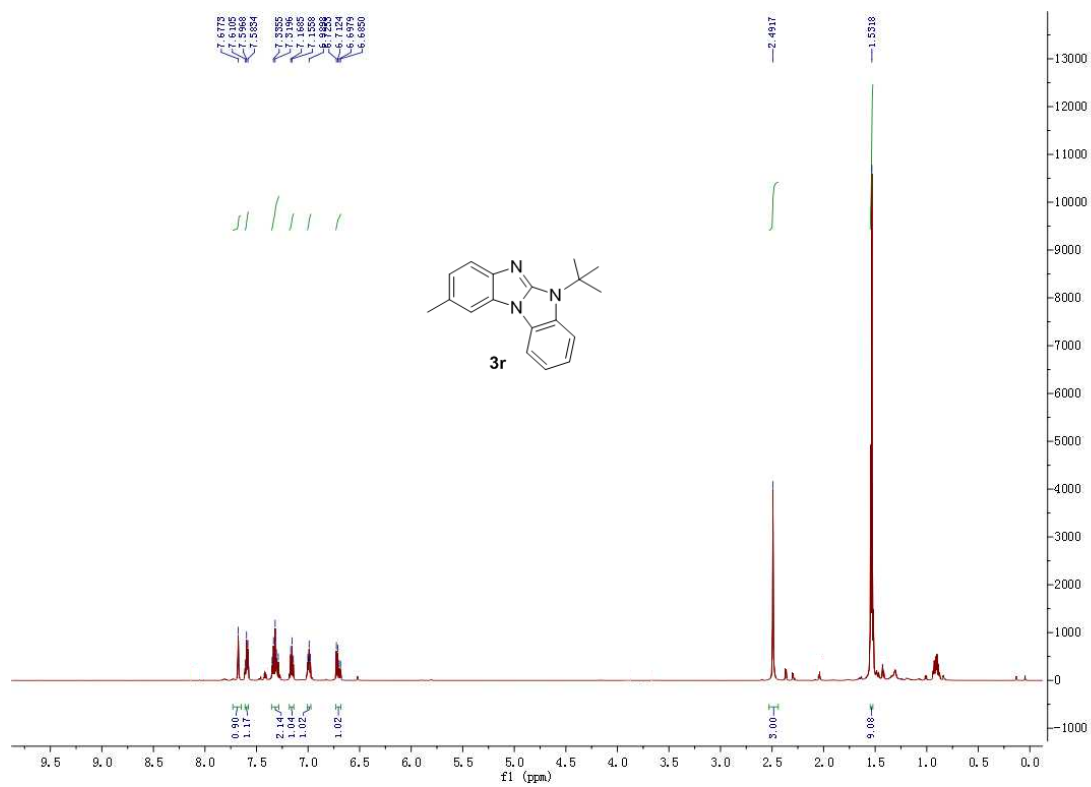
3p:



3q:



3r:



3u + 3u':

