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Selective C-H Trifluoromethylation of Benzimidazoles Through Photoredox catalysis

Guo-Lin Gao, Chao Yang and Wujiong Xia*

MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, State Key Laboratory of Urban Water Resource and Environment，School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150080, China

Xiawj@hit.edu.cn

SUPPORTING INFORMATION

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1. General Information:

^{1}H and ^{13}C NMR spectra were obtained on Bruker AV-400 or AV-600 instrument in $CDCl_3$ or Acetone-d_6 with TMS ($SiMe_4$) as internal standard. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. HRMS (ESI) spectra were recorded on a 1200-6520 Q-TOF/Agilent mass spectrometer using electrospray ionization. The single crystal data was collected on an Agilent Technology Super Nova Eos Dual system with a (Mo-Kα, λ = 0.71073 Å) micro focus source and focusing multilayer mirror optics. GC-MS analysis was performed on a 7890A-5975C/Agilent. All materials were used as received from commercial sources without further purification. Flash column chromatography was performed using 200-300 mesh silica gel. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book".

2. Preparation and Characterization of Substrates

2.1 Preparation of substituted N-methyl-benzimidazole.[1]

To a 100 mL round flask, 5 mmol substituted 1*H*-benzimidazole, 1.0 equiv. sodium hydroxide, magnetic stir bar and 20 mL tetrahydrofuran (THF) were added in sequence. After the reaction mixture was stirred for 10 minutes, 1.1 equiv. of methyl iodide was added. The reaction mixture was allowed to stir in room temperature overnight to finish the reaction. After the reaction finished (monitored by TLC), the reaction mixture was concentrated in *vacuo*, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the substituted N-methyl-benzimidazole.

2.2 Preparation of substituted N-benzyl-benzimidazole.[2]

To a 100 mL round flask, 5 mmol substituted 1*H*-benzimidazole, 1.0 equiv. sodium hydroxide, magnetic stir bar and 20 mL tetrahydrofuran (THF) were added in sequence. After the reaction mixture was stirred for 10 minutes, 1.0 equiv. of benzyl bromide was added. The reaction mixture was allowed to stir in room temperature overnight to finish the reaction. After the reaction finished (monitored by TLC), the reaction mixture was concentrated in *vacuo*, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the substituted N-benzyl-benzimidazole.

2.3 Preparation of substituted N-phenyl-benzimidazole.[3]

To a 100 mL round flask, 10 mmol substituted 1*H*-benzimidazole, 10% mol CuI (1 mmol), 1.0 equiv. potassium carbonate, magnetic stir bar and 20 mL dimethylsulfoxide (DMSO) were added in sequence, sealed the reaction tube. Evacuated and backfilled the reaction tube with nitrogen (3 cycles). Then the mixture of 11 mmol iodobenzene (1.1equiv.) with 10 mL of dimethylsulfoxide (DMSO) were injected. The reaction mixture was placed in a 110 ^{o}C oil bath for 8 hours. After the reaction finished (monitored by TLC), the reaction mixture was allowed to

1. J. Rentner and R. Breinbauer, C*hem. Commun.,* 2012, **48**, 10343.
2. O. Kose and S.Saito, *Org. Biomol. Chem.,* 2010**, 8**, 896.
3. A. K. Verma, J. Singh, V. K. Sankar, R.Chaudhary and R. Chandra, *Tetrahedron Lett.,* 2007**, 48**, 4207.

cool to room temperature and 50 mL of water was added to quench the reaction. The reaction mixture was extracted with 20 mL of ethyl acetate for 3 times, combined organic layer and dry over Na_2SO_4. The organics were filtrated and concentrated in *vacuo*, and the crude products were further purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the substituted N-phenyl-benzimidazole.

2.4 Preparation of *tert*-butyl 1*H*-benzo[*d*]imidazole-1-carboxylate.[4]

To a 50 mL round flask, 5 mmol benzimidazole, 1.0 equiv. sodium hydroxide, magnetic stir bar and 20 mL tetrahydrofuran (THF) were added in sequence. After the reaction mixture was stirred for 10 minutes, 1.0 equiv. of di-*tert*-butyl pyrocarbonate (Boc_2O) was added. The reaction mixture was allowed to stir in room temperature overnight to finish the reaction. After the reaction finished (monitored by TLC), the reaction mixture was concentrated in *vacuo*, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the *tert*-butyl 1*H*-benzo[*d*]imidazole-1-carboxylate.

2.5 Preparation of 1-tosyl-1*H*-benzo[*d*]imidazole.[5]

To a 50 mL round flask, 5 mmol benzimidazole, 1.0 equiv. sodium hydroxide, magnetic stir bar and 20 mL tetrahydrofuran (THF) were added in sequence. After the reaction mixture was stirred for 10 minutes, 1.0 equiv. of 4-methylbenzene-1-sulfonyl chloride (TSCl) was added. The reaction mixture was allowed to stir in room temperature overnight to finish the reaction. After the reaction finished (monitored by TLC), the reaction mixture was concentrated in *vacuo*, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the 1-tosyl-1*H*-benzo[*d*]imidazole.

2.6 Preparation of (1-methyl-1*H*-benzo[*d*]imidazol-2-yl)methyl acetate.

To a 50 mL round flask, 5 mmol (1*H*-benzo[*d*]imidazol-2-yl)methanol, 1.0 equiv. sodium hydroxide, magnetic stir bar and 20 mL tetrahydrofuran (THF) were added in sequence. After the reaction mixture was stirred for 10 minutes, 1.1 equiv. of methyl iodide was added. The reaction mixture was allowed to stir in room temperature overnight to finish the reaction. After the reaction finished (monitored by TLC), the reaction mixture was concentrated in *vacuo*, the residue was added 20 mL tetrahydrofuran (THF) and 5 mL triethylamine in sequence. After the reaction mixture was stirred for 10 minutes, 1.0 equiv. of acetylchloride was added. The reaction mixture was allowed to stir in room temperature overnight to finish the reaction. After the reaction finished (monitored by TLC), the reaction mixture was concentrated in *vacuo*, the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give (1-methyl-1*H*-benzo[*d*]imidazol-2-yl)methyl acetate.

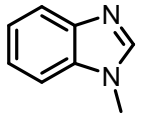
2.7 Preparation of 2-(methoxymethyl)-1-methyl-1*H*-benzo[*d*]imidazole.

To a 50 mL round flask, 5 mmol (1*H*-benzo[*d*]imidazol-2-yl)methanol, magnetic stir bar and 20 mL anhydrous tetrahydrofuran (THF) were added in sequence. After the reaction mixture was stirred for 10 minutes, 2.2 equiv. of sodium hydride was added. After the reaction mixture was

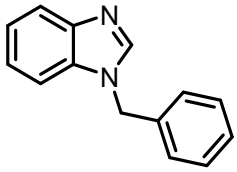
4. S.Sunitha, S. Kanjilal, P. S. Reddy and R. B. N. Prasad, *Tetrahedron Lett.,* 2008**, 49**, 2527.
5. Z. Peng, J. W. Wong, E. C. Hansen, A. L. A. Puchlopek-Dermenci and H. J. Clarke, *Org. Lett.,* 2014**, 16**, 860.

stirred for 10 minutes, 2.2 equiv. of methyl iodide was added. The reaction mixture was allowed to stir in room temperature overnight to finish the reaction. After the reaction finished (monitored by TLC), the reaction mixture was concentrated in *vacuo*, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give 2-(methoxymethyl)-1-methyl-1*H*-benzo[*d*]imidazole.

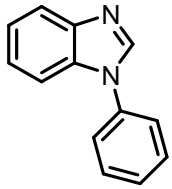
2.8 Characterization of substrates.



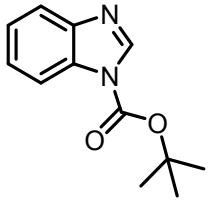
1-Methyl-1*H*-benzo[*d*]imidazole (**1a)**, brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 2H), 7.36 – 7.33 (m, 1H), 7.32 – 7.27 (m, 2H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.40, 143.37, 134.32, 122.77, 121.93, 120.00, 109.22, 30.82 (d, J = 5.1 Hz).



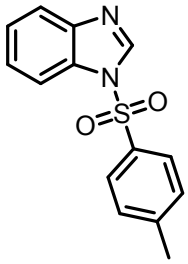
1-Benzyl-1*H*-benzo[*d*]imidazole (**1b)**, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.83 (dd, J = 6.7, 2.0 Hz, 1H), 7.35 – 7.22 (m, 6H), 7.18 – 7.16 (m, 2H), 5.33 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.91, 143.15, 135.40, 133.85, 128.95, 128.18, 127.00, 122.99, 122.18, 120.36, 109.95, 48.73.



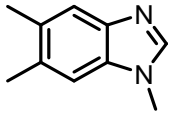
1-Phenyl-1*H*-benzo[*d*]imidazole (**1c**), brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.91 – 7.86 (m, 1H), 7.59 – 7.50 (m, 5H), 7.48 – 7.44 (m, 1H), 7.37 – 7.30 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.96, 142.22 (d, J = 2.9 Hz), 136.27, 133.61, 129.99, 127.97, 123.98, 123.63, 122.73, 120.54, 110.40.



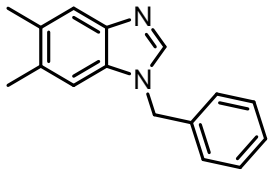
Tert-butyl 1*H*-benzo[*d*]imidazole-1-carboxylate (**1d**), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.99 (d, J = 7.4 Hz, 1H), 7.79 (d, J = 7.2 Hz, 1H), 7.41 – 7.33 (m, 2H), 1.70 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.03, 144.04, 141.99, 131.31, 125.14, 124.19, 120.57, 114.30, 85.53, 28.02.



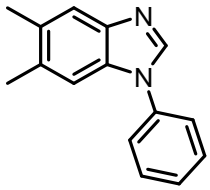
1-Tosyl-1*H*-benzo[*d*]imidazole (**1e**), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.87 (t, *J* = 7.9 Hz, 3H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.16, 143.97, 141.18, 134.46, 130.69, 130.29, 127.20, 125.50, 124.70, 121.02, 112.44, 21.62.



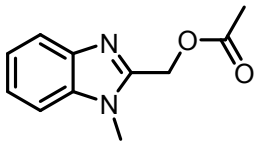
1,5,6-trimethyl-1*H*-benzo[*d*]imidazole(**1g**), brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.55 (s, 1H), 7.14 (s, 1H), 3.76 (s, 3H), 2.39 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.60, 141.96, 132.94, 132.08, 130.94, 119.98, 109.48, 30.92, 20.49, 20.19.



1-Benzyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole (**1h**), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.58 (s, 1H), 7.34 – 7.27 (m, 3H), 7.15 (d, *J* = 7.1 Hz, 2H), 7.04 (s, 1H), 5.29 (s, 2H), 2.36 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.53, 142.45, 135.79, 132.44, 132.19, 131.08, 128.92, 128.04, 126.85, 120.33, 110.03, 48.58, 20.53, 20.21.

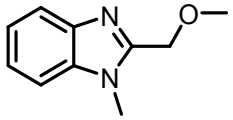


5,6-Dimethyl-1-phenyl-1*H*-benzo[*d*]imidazole (**1i**), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.63 (s, 1H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.31 (s, 1H), 2.40 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.62, 141.45, 136.62, 132.84, 132.11, 131.64, 129.93, 127.67, 123.81, 120.47, 110.51, 20.54, 20.22.

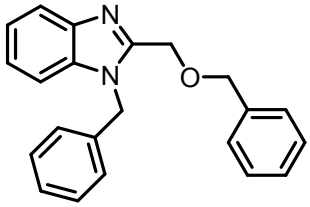


(1-Methyl-1*H*-benzo[*d*]imidazol-2-yl)methyl acetate (**1k**), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.2 Hz, 1H), 7.34 – 7.25 (m, 3H), 5.33 (s, 2H), 3.76 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.06, 148.26, 142.05, 135.67, 123.11, 122.21, 119.91, 109.30, 58.04

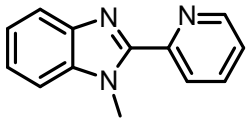
(t, J = 3.6 Hz), 29.86 (t, J = 3.9 Hz), 20.46 (d, J = 2.0 Hz).



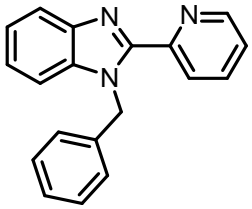
2-(Methoxymethyl)-1-methyl-1*H*-benzo[*d*]imidazole (**1l**), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.2 Hz, 1H), 7.35 – 7.24 (m, 3H), 4.74 (s, 2H), 3.81 (s, 3H), 3.39 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.36, 142.05, 136.13, 122.85, 122.00, 119.82, 109.18, 67.06, 58.14, 29.89 (d, J = 4.8 Hz).



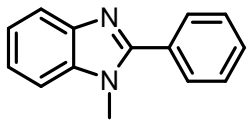
1-Benzyl-2-(benzyloxymethyl)-1*H*-benzo[*d*]imidazole (**1m**), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 1H), 7.30 – 7.24 (m, 11H), 7.07 – 7.06 (m, 2H), 5.47 (s, 2H), 4.80 (s, 2H), 4.55 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.54, 142.31, 137.16, 136.01, 135.84, 128.80, 128.39, 127.93, 127.85, 127.74, 126.45, 123.24, 122.28, 120.10, 110.01, 72.61, 65.10, 47.28.



1-Methyl-2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole (**1o**), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.6 Hz, 1H), 8.39 (d, J = 8.0 Hz, 1H), 7.83 (t, J = 7.4 Hz, 2H), 7.43 (d, J = 7.9 Hz, 1H), 7.36 – 7.29 (m, 3H), 4.27 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.57, 150.25, 148.50, 142.48, 137.22, 136.74, 124.64, 123.63, 123.23, 122.51, 119.95, 109.85, 32.62.

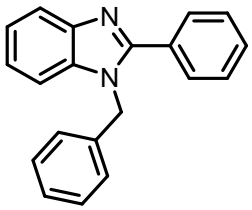


1-Benzyl-2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole (**1p**), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 4.3 Hz, 1H), 8.43 (d, J = 8.0 Hz, 1H), 7.88 – 7.80 (m, 2H), 7.34 – 7.15 (m, 9H), 6.19 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.49, 149.89, 148.56, 142.68, 137.39, 136.78, 136.75, 128.50, 127.26, 126.73, 124.61, 123.78, 123.49, 122.72, 120.06, 110.71, 48.83.

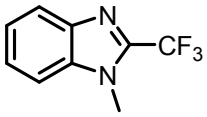


1-Methyl-2-phenyl-1*H*-benzo[*d*]imidazole (**1r**), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 1H), 7.76 – 7.73 (m, 2H), 7.53 – 7.46 (m, 3H), 7.39 – 7.34 (m, 1H), 7.33 – 7.28 (m, 2H),

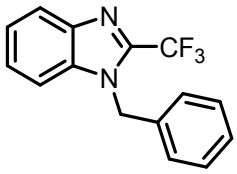
3.82 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.65, 142.84, 136.46, 130.09, 129.61, 129.32, 128.57, 122.65, 122.31, 119.71, 109.54, 31.56.



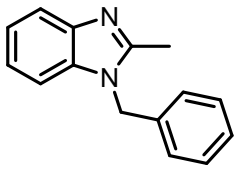
1-Benzyl-2-phenyl-1*H*-benzo[*d*]imidazole (**1s**), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.69 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.35 – 7.29 (m, 4H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.10 (d, *J* = 6.9 Hz, 2H), 5.45 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.14, 143.16, 136.36, 136.02, 130.04, 129.87, 129.22, 129.02, 128.71, 127.73, 125.92, 122.99, 122.63, 119.96, 110.49, 48.33.



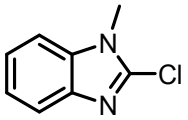
1-Methyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**1u**), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.41 – 7.36 (m, 1H), 3.94 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.93, 140.80 (q, *J* = 38.5 Hz), 135.98, 125.28, 123.59, 121.55, 119.08 (q, *J* = 271 Hz), 110.03, 30.72 (d, *J* = 2.0 Hz).



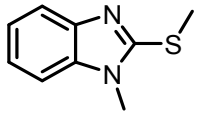
1-Benzyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**1v**), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 1H), 7.38 – 7.27 (m, 6H), 7.10 (d, *J* = 7.8 Hz, 2H), 5.54 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.17, 140.87 (q, *J* = 38.5 Hz), 135.57, 134.83, 128.99, 128.22, 126.26, 125.53, 123.78, 121.68, 119.12 (q, *J* = 272 Hz), 111.09, 48.41 (d, *J* = 1.7 Hz).



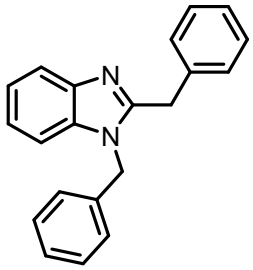
1-Benzyl-2-methyl-1*H*-benzo[*d*]imidazole (**1x**), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 1H), 7.30 – 7.15 (m, 6H), 7.02 (d, *J* = 7.6 Hz, 2H), 5.25 (s, 2H), 2.53 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.76, 142.57, 135.75, 135.36, 128.87, 127.77, 126.09, 122.14, 121.87, 119.02, 109.23, 46.91, 13.91.



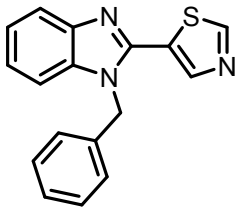
2-Chloro-1-methyl-1*H*-benzo[*d*]imidazole (**1z**), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 6.9 Hz, 1H), 7.32 – 7.25 (m, 3H), 3.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.60, 140.91, 135.58, 123.07, 122.63, 119.34, 109.20, 30.46.



1-Methyl-2-(methylthio)-1*H*-benzo[*d*]imidazole (**1ae**), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 1H), 7.23 – 7.17 (m, 3H), 3.63 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.08, 143.32, 136.80, 121.61, 121.59, 117.95, 108.19, 29.76, 14.51.



1,2-Dibenzyl-1*H*-benzo[*d*]imidazole (**1af**), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.1, 0.8 Hz, 1H), 7.28 – 7.17 (m, 11H), 6.92 (dd, *J* = 6.4, 2.8 Hz, 2H), 5.18 (s, 2H), 4.25 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.34, 142.64, 136.03, 135.74 (2C), 128.84, 128.76, 128.44, 127.76, 126.93, 126.12, 122.53, 122.05, 119.58, 109.57, 47.03, 34.51.



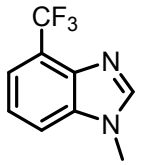
5-(1-Benzyl-1*H*-benzo[*d*]imidazol-2-yl)thiazole (**1ag**), White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 2.1 Hz, 1H), 8.31 (d, *J* = 2.1 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.18 (m, 6H), 7.14 (d, *J* = 6.6 Hz, 2H), 6.07 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.93, 147.72, 146.84, 142.96, 136.98, 135.89, 128.59, 127.41, 126.62, 123.19, 122.75, 121.25, 119.67, 110.57, 48.44.

3. Preparation and Characterization of Products

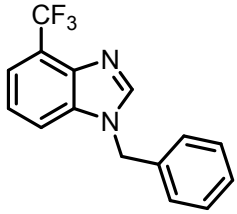
3.1 The preparation of products.

To a 10 mL bottom flask, magnetic stir bar, substrate **1** (0.1 mmol), Togni's reagent (0.15 mmol), Li_2CO_3 (0.15 mmol), *fac*-Ir(ppy)$_3$ (0.0025 mmol), anhydrous CH_3CN (1.0 mL) were added in sequence and sealed the flask. Evacuated and backfilled it with nitrogen (3 cycles) under -78 ^{o}C. Then the flask was irradiated by 5 W blue LEDs in room temperature for 3 days. After the substrate was consumed (monitored by TLC), the mixture was filtered and the filtrate concentrated in *vacuo*. The residue was purified by precipitation thin-layer chromatography (PTLC) using hexanes: ethyl acetate (10:1 to 1:1 depending on the substrates) as the eluant to afford the desired product **2**.

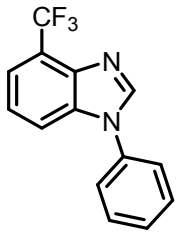
3.2 Characterization of products.



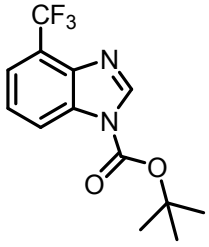
1-Methyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2a**), isolated yield 75%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.77, 140.15, 135.39, 123.94 (q, *J* = 273 Hz), 122.13, 121.19 (q, *J* = 32.5 Hz), 119.48 (q, *J* = 4.9 Hz), 113.32, 31.18. **HRMS** (ESI) *m/z* calcd for $C_9H_8F_3N_2^+$ $[M+H]^+$ 201.0640, found 201.0643.



1-Benzyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2b**), isolated yield 65%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.38 – 7.28 (m, 4H), 7.19 – 7.17 (m, 2H), 5.40 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.51, 140.49, 134.76, 134.76, 129.14, 128.51, 126.98, 123.91 (q, *J* = 273 Hz), 122.33, 121.42 (q, *J* = 32.5 Hz), 119.71 (q, *J* = 4.8 Hz), 114.03, 49.08. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{12}F_3N_2^+$ $[M+H]^+$ 277.0953, found 277.0953.

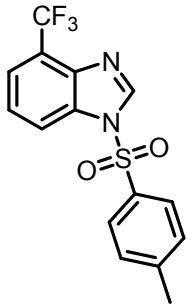


1-Phenyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2c**), isolated yield 82%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.59 (m, 3H), 7.54 – 7.49 (m, 3H), 7.39 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.60, 140.48, 135.54, 134.75, 130.21, 128.71, 124.36, 123.86 (q, *J* = 273 Hz), 122.96, 121.60 (q, *J* = 32.6 Hz), 120.18 (q, *J* = 4.8 Hz), 114.41. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{10}F_3N_2^+$ $[M+H]^+$ 263.0796, found 263.0793.

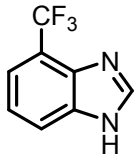


Tert-butyl 4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole-1-carboxylate (**2d**), isolated yield 55%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 7.6

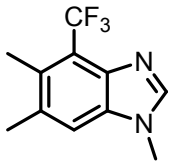
Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 1.72 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.52, 143.22, 140.73, 132.36, 124.64, 123.53 (q, *J* = 273 Hz), 121.85 (q, *J* = 33.1 Hz), 121.44 (q, *J* = 4.8 Hz), 118.23, 86.52, 28.00. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{14}F_3N_2O_2^+$ $[M+H]^+$ 287.1007, found 287.1002.



1-Tosyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2e**), isolated yield 60%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.79, 142.54, 140.61, 134.03, 131.64, 130.54, 127.33, 125.03, 123.23 (q, *J* = 273 Hz), 122.33 (q, *J* = 33.2 Hz), 121.98 (q, *J* = 4.8 Hz), 116.30, 21.70. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{12}F_3N_2O_2S^+$ $[M+H]^+$ 341.0572, found 341.0570.

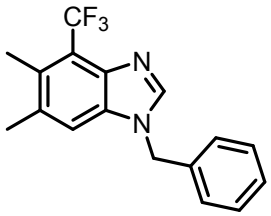


4-(Tifluoromethyl)-1*H*-benzo[*d*]imidazole (**2f**), isolated yield 90%, white solid.[6] ^{1}H NMR (400 MHz, Acetone) δ 12.12 (s, 1H), 8.35 (s, 1H), 7.90 (s, 1H), 7.57 (d, *J* = 7.1 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (151 MHz, Acetone) δ 144.05, 125.35 (q, *J* = 271 Hz), 122.74, 119.59, 116.79. **HRMS** (ESI) *m/z* calcd for $C_8H_6F_3N_2^+$ $[M+H]^+$ 187.0483, found 187.0486.

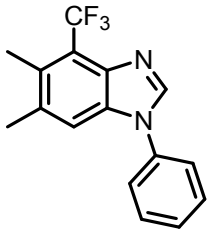


1,5,6-Trimethyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2g**), isolated yield 70%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.74 (s, 1H), 3.88 (q, *J* = 3.3 Hz, 3H), 2.50 (q, *J* = 3.2 Hz, 3H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.74, 144.07, 132.09, 132.02 (q, *J* = 2.1 Hz), 130.51, 124.97 (q, *J* = 273 Hz), 124.74, 112.99 (q, *J* = 31.6 Hz), 35.32 (q, *J* = 7.9 Hz), 21.35, 16.95 (q, *J* = 4.7 Hz). **HRMS** (ESI) *m/z* calcd for $C_{11}H_{12}F_3N_2^+$ $[M+H]^+$ 229.0953, found 229.0946.

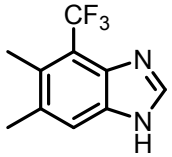
6. H. Kimoto, S. Fujii and L. A. Cohen, *J. Org. Chem.,* 1982, **47**, 2867.



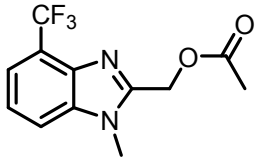
1-Benzyl-5,6-dimethyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2h**), isolated yield 63%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.36 – 7.31 (m, 3H), 7.23 (s, 1H), 7.15 – 7.11 (m, 2H), 5.34 (s, 2H), 2.45 (d, *J* = 1.9 Hz, 3H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.52 (d, *J* = 1.7 Hz), 139.68, 135.15, 133.48, 132.73, 130.93 (q, *J* = 2.1 Hz), 129.06, 128.31, 126.74, 125.17 (q, *J* = 276 Hz), 119.67 (q, *J* = 29.7 Hz), 113.92, 48.66, 21.53, 16.06 (q, *J* = 3.0 Hz). **HRMS** (ESI) *m/z* calcd for $C_{17}H_{16}F_3N_2^+$ $[M+H]^+$ 305.1266, found 305.1263.



5,6-Dimethyl-1-phenyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2i**), isolated yield 71%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.60 (t, *J* = 7.7 Hz, 2H), 7.52 – 7.46 (m, 4H), 2.50 (d, *J* = 1.8 Hz, 3H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.44 (d, *J* = 1.7 Hz), 139.83, 135.75, 134.10, 132.67, 131.38 (d, *J* = 2.1 Hz), 130.11, 128.38, 125.14 (q, *J* = 276 Hz), 124.30, 119.81 (q, *J* = 29.7 Hz), 114.27, 21.52, 16.11 (q, *J* = 3.2 Hz). **HRMS** (ESI) *m/z* calcd for $C_{16}H_{14}F_3N_2^+$ $[M+H]^+$ 291.1109, found 291.1112.

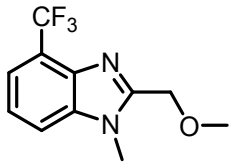


5,6-Dimethyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2j**), isolated yield 81%, white solid. ^{1}H NMR (400 MHz, Acetone) δ 11.55 (s, 1H), 8.14 (s, 1H), 7.74 (s, 1H), 2.46 (d, *J* = 1.7 Hz, 3H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, Acetone) δ 143.91, 143.26, 133.52, 132.70, 132.45, 131.65, 126.60 (q, *J* = 273 Hz), 125.05, 20.82, 16.07. **HRMS** (ESI) *m/z* calcd for $C_{10}H_{10}F_3N_2^+$ $[M+H]^+$ 215.0796, found 215.0799.

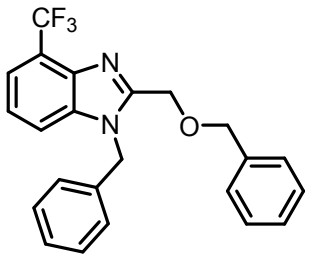


(1-Methyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-2-yl)methyl acetate (**2k**), isolated yield 67%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.39 (t, *J* = 7.9 Hz, 1H), 5.43 (s, 2H), 3.87 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.16, 150.01, 138.87, 136.89,

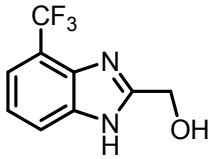
123.84 (q, J = 273 Hz), 122.58, 121.27 (q, J = 32.5 Hz), 119.92 (q, J = 5.0 Hz), 113.45, 58.21, 30.42, 20.59. **HRMS** (ESI) *m/z* calcd for $C_{12}H_{12}F_3N_2O_2^+$ $[M+H]^+$ 273.0851, found 273.0853.



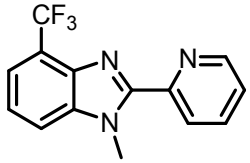
2-(Methoxymethyl)-1-methyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2l**), isolated yield 66%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.54 (m, 2H), 7.36 (t, J = 7.9 Hz, 1H), 4.83 (s, 2H), 3.90 (s, 3H), 3.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.14, 138.84, 137.21, 123.95 (q, J = 272 Hz), 122.11, 121.02 (q, J = 32.3 Hz), 119.50 (q, J = 4.8 Hz), 113.16, 67.13, 58.49, 30.37. **HRMS** (ESI) *m/z* calcd for $C_{11}H_{12}F_3N_2O^+$ $[M+H]^+$ 245.0902, found 245.0911.



1-Benzyl-2-(benzyloxymethyl)-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2m**), isolated yield 56%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.5 Hz, 1H), 7.41 (d, J = 8.2 Hz, 1H), 7.30 – 7.24 (m, 9H), 7.06 – 7.04 (m, 2H), 5.51 (s, 2H), 4.88 (s, 2H), 4.58 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.22, 139.00, 137.00, 136.78, 135.45, 128.93, 128.42, 128.03, 128.01, 127.96, 126.48, 123.95 (q, J = 273 Hz), 122.39, 121.18 (q, J = 32.5 Hz), 119.68 (q, J = 4.8 Hz), 113.94, 73.09, 65.21, 47.65. **HRMS** (ESI) *m/z* calcd for $C_{23}H_{20}F_3N_2O^+$ $[M+H]^+$ 397.1528, found 397.1536.



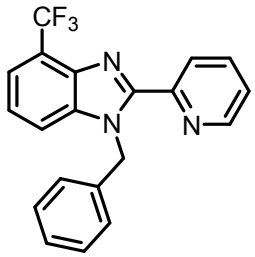
(4-(Trifluoromethyl)-1*H*-benzo[*d*]imidazol-2-yl)methanol (**2n**), isolated yield 69%, white solid.[7] ^{1}H NMR (400 MHz, Acetone) δ 11.91 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 5.01 (s, 1H), 4.92 (s, 2H). ^{13}C NMR (101 MHz, Acetone) δ 157.87, 125.38 (q, J = 272 Hz), 122.12, 119.61, 59.04. **HRMS** (ESI) *m/z* calcd for $C_9H_8F_3N_2O^+$ $[M+H]^+$ 217.0589, found 217.0588.



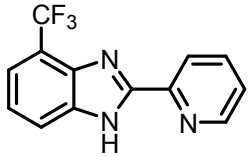
1-Methyl-2-(pyridin-2-yl)-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2o**), isolated yield 70%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, J = 4.8, 0.7 Hz, 1H), 8.48 (d, J = 8.0 Hz, 1H), 7.85 (td, J = 7.8, 1.8 Hz, 1H), 7.60 (t, J = 8.7 Hz, 2H), 7.39 – 7.34 (m, 2H), 4.30 (s, 3H). ^{13}C NMR

7. B. C. Bishop, A. S. Jones and J. Tatlow, *J. Chem. Soc.,* 1964, 3076.

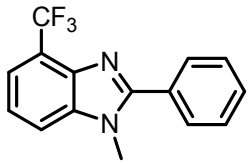
(151 MHz, $CDCl_3$) δ 151.66, 150.07, 148.54, 139.29, 138.24, 136.92, 125.60, 124.12, 124.08 (q, *J* = 273 Hz), 122.20, 120.68 (q, *J* = 32.3 Hz), 119.88 (q, *J* = 5.0 Hz), 113.73, 32.87. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{11}F_3N_3^+$ $[M+H]^+$ 278.0905, found 278.0906.



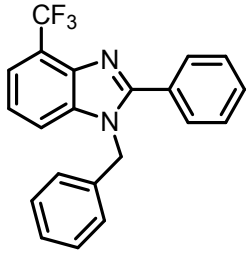
1-Benzyl-2-(pyridin-2-yl)-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2p**), isolated yield 65%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.8, 0.8 Hz, 1H), 8.54 (d, *J* = 8.0 Hz, 1H), 7.84 (td, *J* = 7.8, 1.8 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.33 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 7.30 – 7.21 (m, 4H), 7.16 – 7.14 (m, 2H), 6.22 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.25, 150.02, 148.59, 139.50, 137.71, 136.98, 136.87, 128.66, 127.54, 126.77, 125.60, 124.27, 124.06 (q, *J* = 273 Hz), 122.46, 121.12 (q, *J* = 32.3 Hz), 120.08 (q, *J* = 5.0 Hz), 114.58, 49.09. **HRMS** (ESI) *m/z* calcd for $C_{20}H_{15}F_3N_3^+$ $[M+H]^+$ 354.1218, found 354.1208.



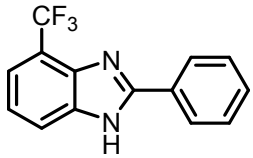
2-(Pyridin-2-yl)-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2q**), isolated yield 75%, white solid. ^{1}H NMR (400 MHz, Acetone) δ 12.53 (s, 1H), 8.70 (d, *J* = 4.7 Hz, 1H), 8.46 (d, *J* = 7.9 Hz, 1H), 8.01 (td, *J* = 7.8, 1.6 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, Acetone) δ 153.42, 150.43, 149.15, 141.87, 138.23, 136.92, 125.95, 125.37 (q, *J* = 270 Hz), 123.44, 122.75, 121.17 (q, *J* = 32.2 Hz), 120.20 (q, *J* = 5.1 Hz), 117.12. **HRMS** (ESI) *m/z* calcd for $C_{13}H_9F_3N_3^+$ $[M+H]^+$ 264.0749, found 264.0753.



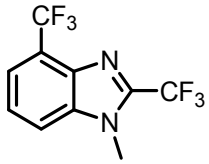
1-Methyl-2-phenyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2r**), isolated yield 53%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.75 (m, 2H), 7.58 (dd, *J* = 7.8, 4.8 Hz, 2H), 7.54 – 7.51 (m, 3H), 7.37 (t, *J* = 7.7 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.34, 139.75, 137.49, 130.12, 129.81, 129.58, 128.71, 124.06 (q, *J* = 273 Hz), 121.79, 120.88 (q, *J* = 32.4 Hz), 119.71 (q, *J* = 4.8 Hz), 113.42, 31.83. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{12}F_3N_2^+$ $[M+H]^+$ 277.0953, found 277.0950.



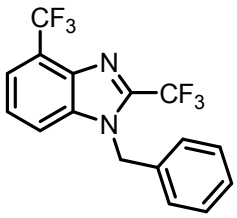
1-Benzyl-2-phenyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2s**), isolated yield 41%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.69 (m, 2H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.49 – 7.43 (m, 3H), 7.39 – 7.27 (m, 5H), 7.08 (d, *J* = 6.4 Hz, 2H), 5.47 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.68, 139.99, 136.91, 135.79, 130.28, 129.61, 129.46, 129.15, 128.78, 127.99, 125.91, 124.04 (q, *J* = 273 Hz), 122.05, 121.05 (q, *J* = 32.5 Hz), 119.94 (q, *J* = 4.8 Hz), 114.33, 48.51. **HRMS** (ESI) *m/z* calcd for $C_{21}H_{16}F_3N_2^+$ $[M+H]^+$ 353.1266, found 353.1266.



2-Phenyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2t**), isolated yield 61%, white solid.[8] ^{1}H NMR (400 MHz, Acetone) δ 12.32 (s, 1H), 8.28 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.84 (s, 1H), 7.58 – 7.52 (m, 4H), 7.38 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, Acetone) δ 131.30, 130.70, 129.80, 127.89, 125.37 (q, *J* = 273 Hz), 122.74, 120.03, 116.32. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{10}F_3N_2^+$ $[M+H]^+$ 263.0796, found 263.0793.



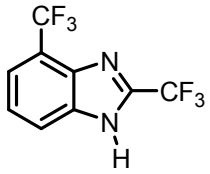
1-Methyl-2,4-bis(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2u**), isolated yield 51%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 2H), 7.52 (t, *J* = 7.9 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.16 (q, *J* = 39.4 Hz), 137.56, 136.92, 124.55, 123.40 (q, *J* = 273 Hz), 122.86 (q, *J* = 33.1 Hz), 121.13 (q, *J* = 5.0 Hz), 118.75 (q, *J* = 272 Hz), 114.12, 31.11 (d, *J* = 2.1 Hz). **HRMS** (ESI) *m/z* calcd for $C_{10}H_7F_6N_2^+$ $[M+H]^+$ 269.0513, found 269.0509.



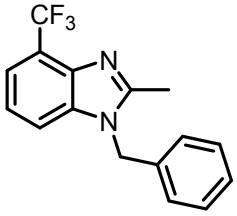
1-Benzyl-2,4-bis(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2v**), isolated yield 46%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.3 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.37 – 7.30 (m, 3H), 7.11 – 7.09 (m, 2H), 5.58 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.22 (q, *J* =

8. J. Kim, J. Kim, H. Lee, B. M. Lee and B. H. Kim, *Tetrahedron,* 2011**, 67**, 8027.

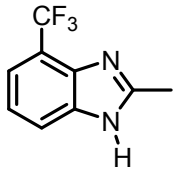
38.6 Hz), 137.81, 136.47, 134.24, 129.16, 128.52, 126.25, 124.76, 123.39 (q, *J* = 273 Hz), 122.95 (q, *J* = 33.1 Hz), 121.29 (q, *J* = 4.8 Hz), 118.79 (q, *J* = 272 Hz), 115.20, 48.78 (d, *J* = 1.8 Hz). **HRMS** (ESI) *m/z* calcd for $C_{16}H_{11}F_6N_2^+$ $[M+H]^+$ 345.0826, found 345.0830.



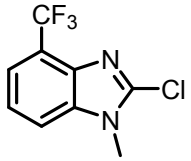
2,4-Bis(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2w**), isolated yield 60%, white solid.[9] ^{1}H NMR (400 MHz, Acetone) δ 13.19 (s, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (151 MHz, Acetone) δ 125.43, 124.75 (q, *J* = 272 Hz), 121.76, 119.82 (q, *J* = 271 Hz). **HRMS** (ESI) *m/z* calcd for $C_9H_5F_6N_2^+$ $[M+H]^+$ 255.0357, found 255.0360.



1-Benzyl-2-methyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2x**), isolated yield 62%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.29 (m, 3H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.05 – 7.03 (m, 2H), 5.35 (s, 2H), 2.64 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.77, 139.44, 136.40, 135.13, 129.10, 128.14, 126.13, 124.09 (q, *J* = 273 Hz), 121.44, 120.20 (q, *J* = 32.3 Hz), 119.32 (q, *J* = 5.0 Hz), 113.18, 47.30, 14.20. **HRMS** (ESI) *m/z* calcd for $C_{16}H_{14}F_3N_2^+$ $[M+H]^+$ 291.1109, found 291.1113.



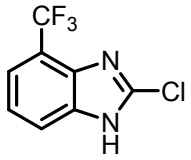
2-Methyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2y**), isolated yield 80%, white solid.[10] ^{1}H NMR (400 MHz, Acetone) δ 11.80 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (151 MHz, Acetone) δ 154.35, 125.43 (q, *J* = 271 Hz), 121.79, 119.28 (d, *J* = 5.1 Hz), 14.83. **HRMS** (ESI) *m/z* calcd for $C_9H_8F_3N_2^+$ $[M+H]^+$ 201.0640, found 201.0639.



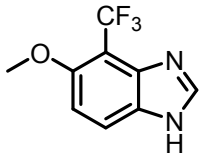
2-Chloro-1-methyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2z**), isolated yield 34%, white

9. J. Zhu, Z. Chen, H. Xie, S. Li and Y. Wu, *J. Fluorine Chem.,* 2012**, 133**, 134.
10. J. M. Travins, R. C. Bernotas, D. H. Kaufman, E. Quinet, P. Nambi, I. Feingold, C. Huselton, A. Wilhelmsson, A. Goos-Nilsson and J. Wrobel, *Bioorg. Med. Chem. Lett.,* 2010**, 20**, 526.

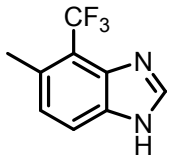
solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.86, 138.25, 136.47, 123.58 (q, *J* = 273 Hz), 122.43, 120.64 (q, *J* = 32.9 Hz), 120.09 (q, *J* = 32.9 Hz), 113.08, 30.82. **HRMS** (ESI) *m/z* calcd for $C_9H_7ClF_3N_2^+$ $[M+H]^+$ 235.0250, found 235.0253.



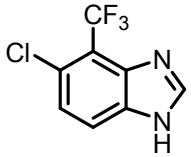
2-Chloro-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2aa**), isolated yield 56%, white solid.[11] ^{1}H NMR (400 MHz, Acetone) δ 12.53 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (151 MHz, Acetone) δ 141.81, 124.90 (q, *J* = 271 Hz), 123.32, 120.59. **HRMS** (ESI) *m/z* calcd for $C_8H_5ClF_3N_2^+$ $[M+H]^+$ 221.0093, found 221.0095.



5-Methoxy-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2ab**), isolated yield 85%, white solid. ^{1}H NMR (400 MHz, Acetone) δ 11.60 (s, 1H), 8.14 (s, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.18 (d, *J* = 8.9 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (151 MHz, Acetone) δ 143.48, 125.61 (q, *J* = 271 Hz), 125.08, 108.48, 57.48. **HRMS** (ESI) *m/z* calcd for $C_9H_8F_3N_2O^+$ $[M+H]^+$ 217.0589, found 217.0595.

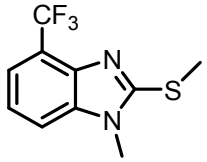


5-Methyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2ac**), isolated yield 79%, white solid. ^{1}H NMR (400 MHz, Acetone) δ 11.75 (s, 1H), 8.22 (s, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 2.59 (q, *J* = 2.2 Hz, 3H). ^{13}C NMR (101 MHz, Acetone) δ 143.75, 132.52, 126.44, 126.37 (q, *J* = 274 Hz), 124.05, 19.51. **HRMS** (ESI) *m/z* calcd for $C_9H_8F_3N_2^+$ $[M+H]^+$ 201.0640, found 201.0636.

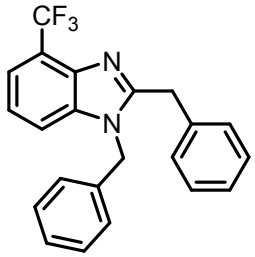


5-Chloro-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2ad**), isolated yield 59%, white solid. ^{1}H NMR (400 MHz, Acetone) δ 12.06 (s, 1H), 8.35 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (151 MHz, Acetone) δ 145.30, 125.38, 124.70 (q, *J* = 273 Hz). **HRMS** (ESI) *m/z* calcd for $C_8H_5ClF_3N_2^+$ $[M+H]^+$ 221.0093, found 221.0092.

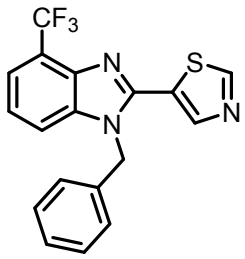
11. Y. Ogino, N. Ohtake, Y. Nagae, K. Matsuda, M. Moriya, T. Suga, M. Ishikawa, M. Kanesaka, Y. Mitobe, J. Ito, T. Kanno, A. Ishihara, H. Iwaasa, T. Ohe, A. Kanatani and T. Fukami, *Bioorg. Med. Chem. Lett.,* 2008**, 18**, 5010.



1-Methyl-2-(methylthio)-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2ae**), isolated yield 45%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 3.69 (s, 3H), 2.84 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.45, 140.25, 138.05, 124.09 (q, *J* = 273 Hz), 120.70, 119.14 (q, *J* = 32.3 Hz), 118.83 (q, *J* = 4.8 Hz), 111.80, 30.03, 14.71. **HRMS** (ESI) *m/z* calcd for $C_{10}H_{10}F_3N_2S^+$ $[M+H]^+$ 247.0517, found 247.0512.



1,2-Dibenzyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2af**), isolated yield 47%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.20 (m, 9H), 6.89 – 6.87 (m, 2H), 5.18 (s, 2H), 4.35 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.05, 139.43, 136.77, 135.59, 135.08, 128.97, 128.86, 128.42, 128.01, 127.09, 126.11, 124.08 (q, *J* = 273 Hz), 121.73, 120.66 (q, *J* = 32.2 Hz), 119.45 (q, *J* = 5.0 Hz), 113.48, 47.34, 34.63. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{18}F_3N_2^+$ $[M+H]^+$ 367.1422, found 367.1423.

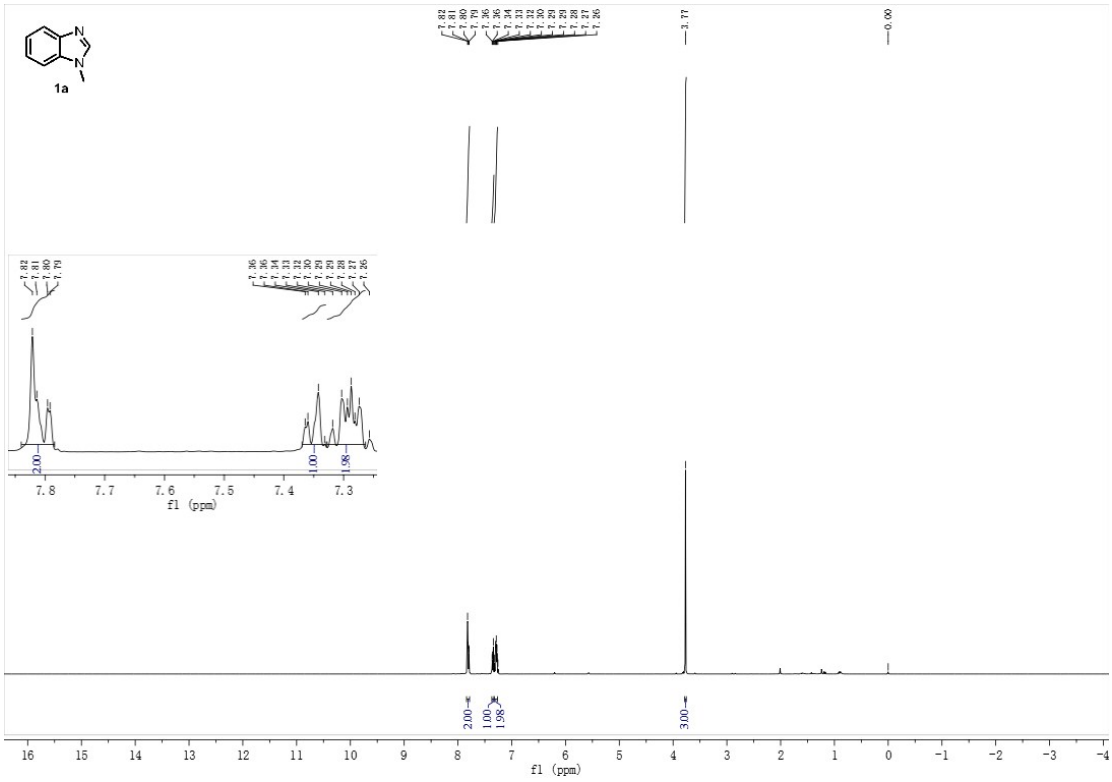


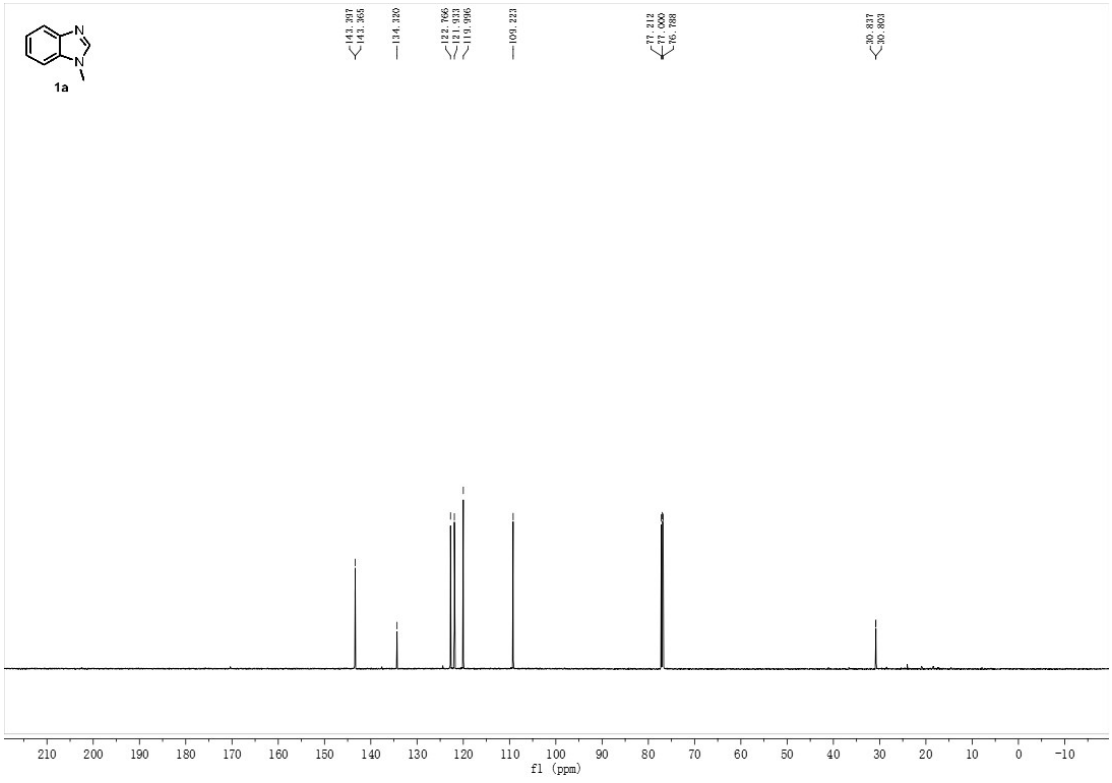
5-(1-Benzyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-2-yl)thiazole (**2ag**), isolated yield 43%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.90 (d, *J* = 7.1 Hz, 1H), 7.34 – 7.29 (m, 3H), 7.25 – 7.21 (m, 3H), 7.05 – 7.03 (m, 2H), 5.62 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.80, 146.56 (q, *J* = 2.3 Hz), 144.40, 143.11, 136.10, 135.42, 128.69, 128.00 (q, *J* = 38.7 Hz), 127.72, 126.51, 124.00, 122.81, 121.43 (q, *J* = 271 Hz), 120.85, 110.57, 48.24. **HRMS** (ESI) *m/z* calcd for $C_{18}H_{13}F_3N_3S^+$ $[M+H]^+$ 360.0782, found 360.0784.

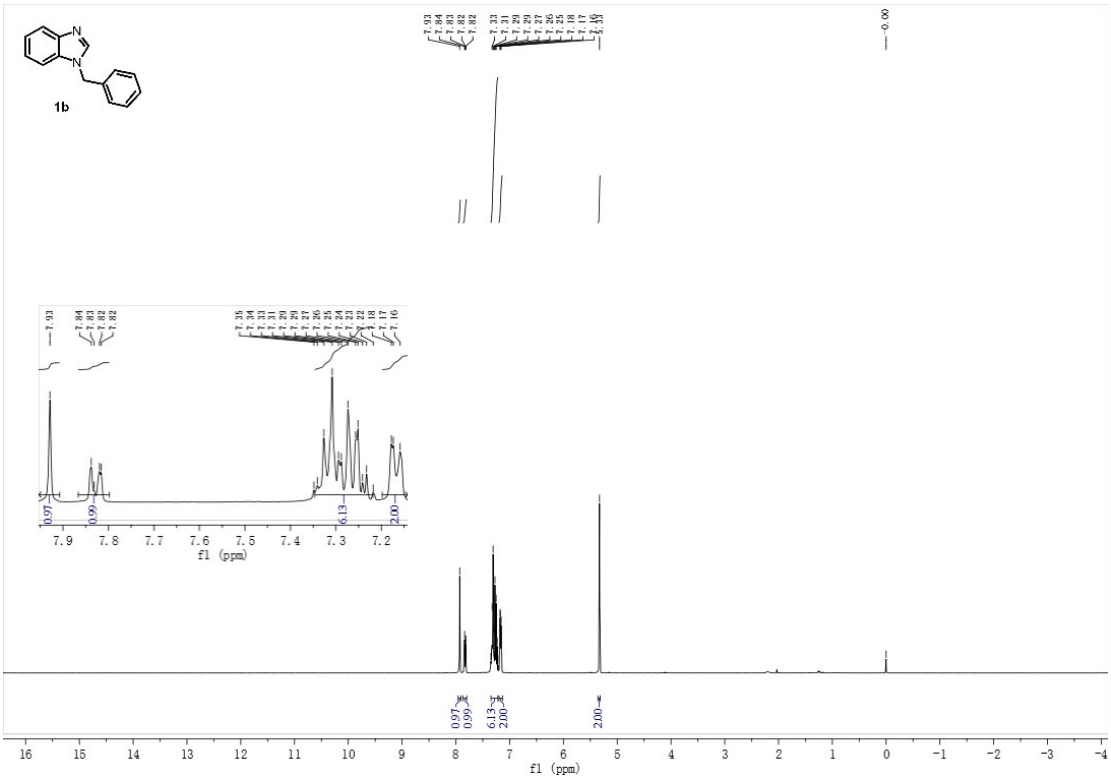
1-Methyl-7-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**3a**), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.91 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 3.98 (q,

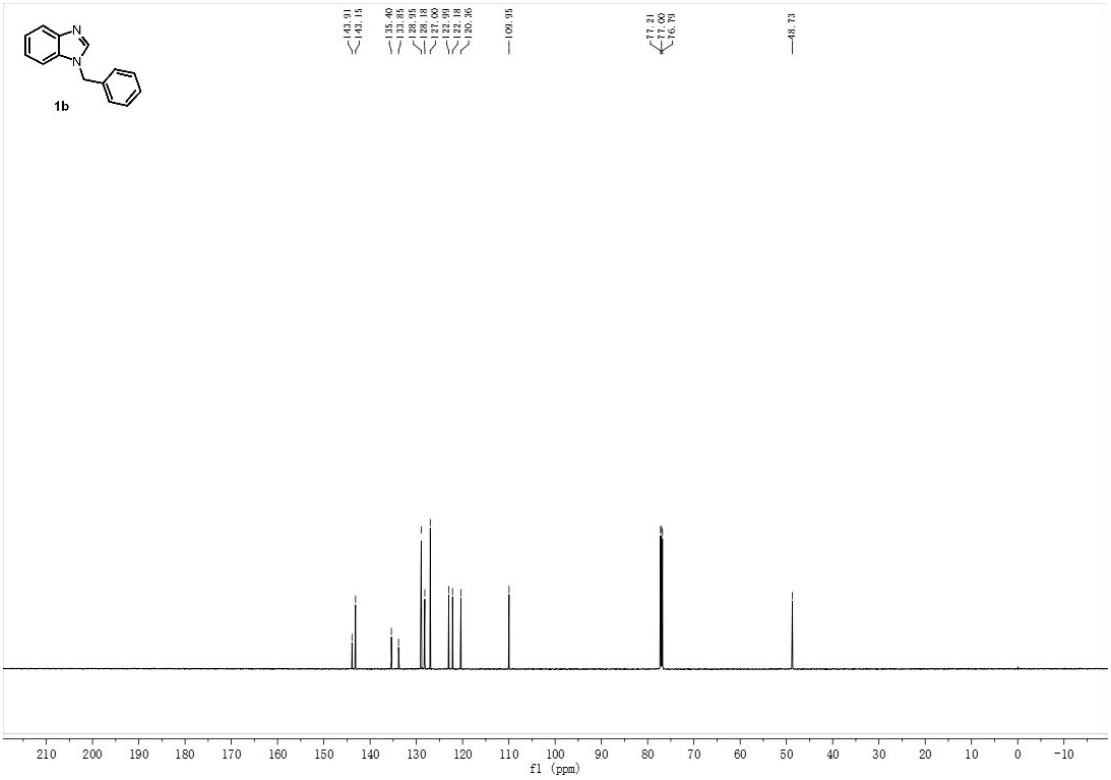
J = 0.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.24, 146.10, 130.27, 124.81, 123.80 (q, *J* = 271 Hz), 121.23, 121.21 (q, *J* = 6.0 Hz), 113.88 (q, *J* = 33.4 Hz), 33.92 (q, *J* = 5.4 Hz). **HRMS** (ESI) *m/z* calcd for $C_9H_8F_3N_2^+$ $[M+H]^+$ 201.0640, found 201.0647.

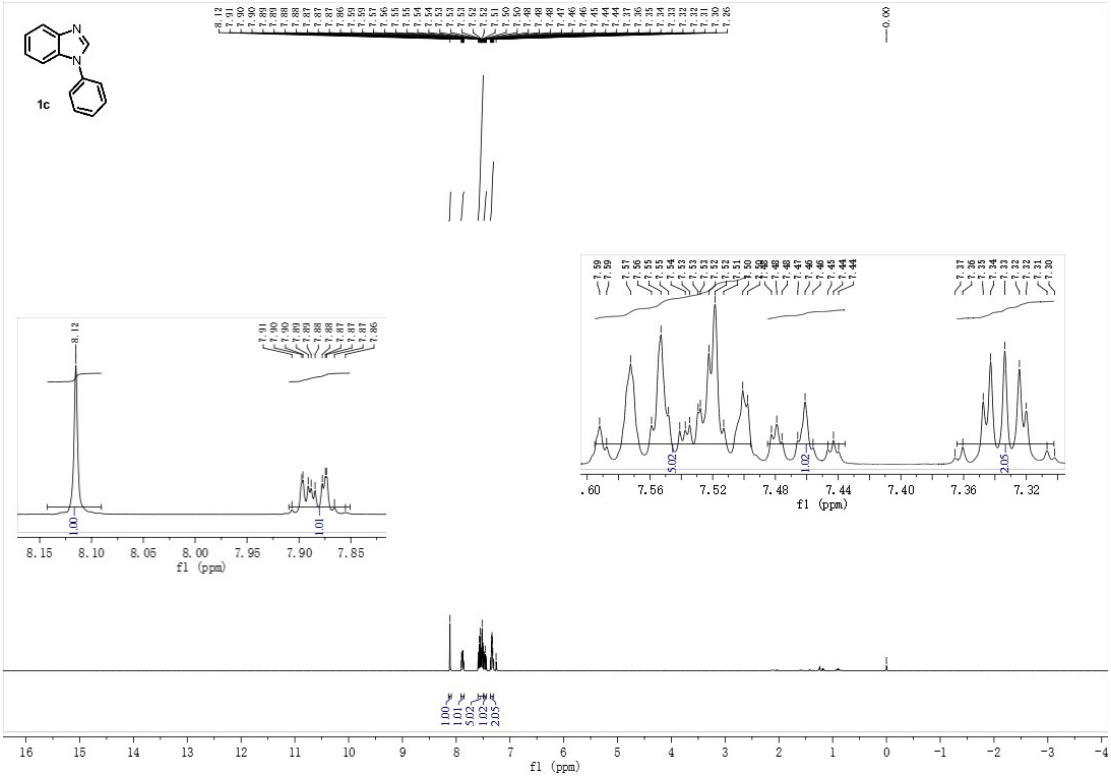
NMR spectrals:

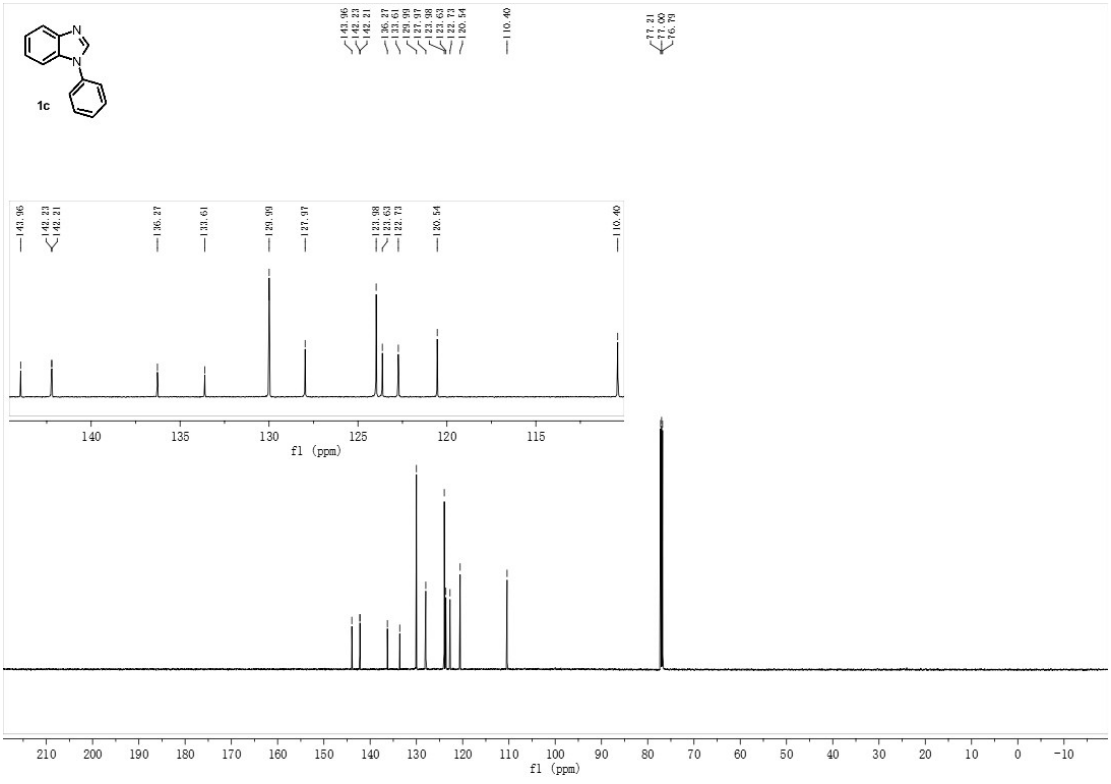


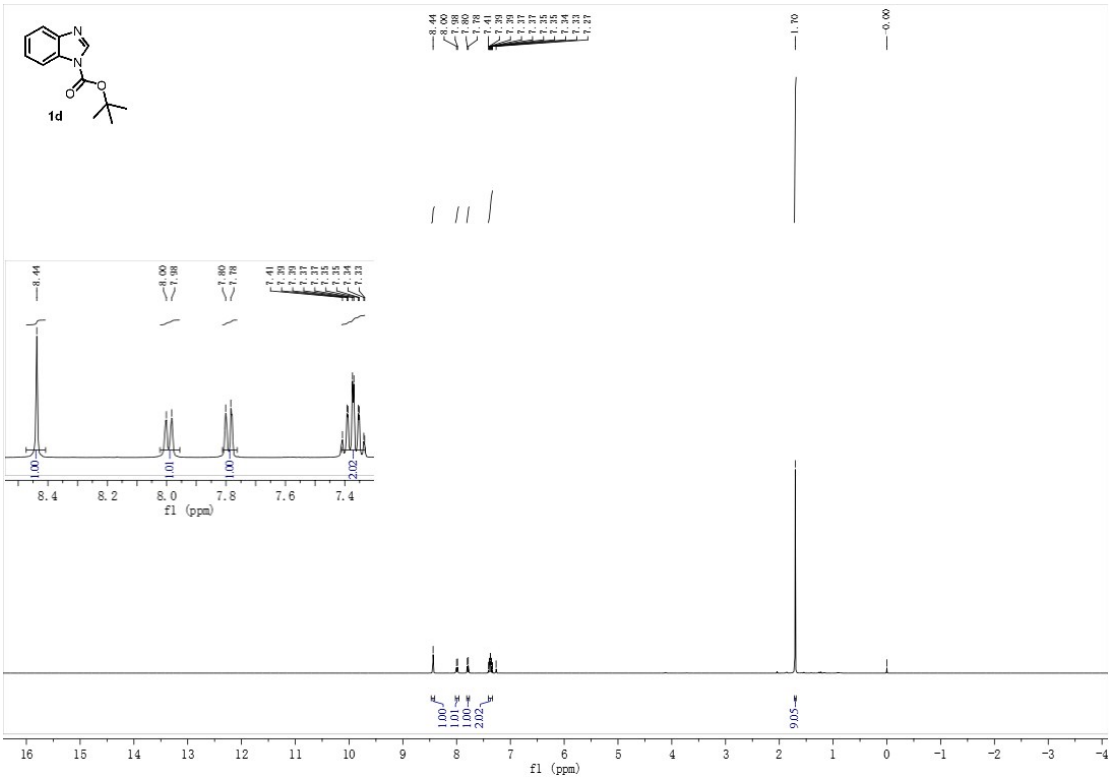


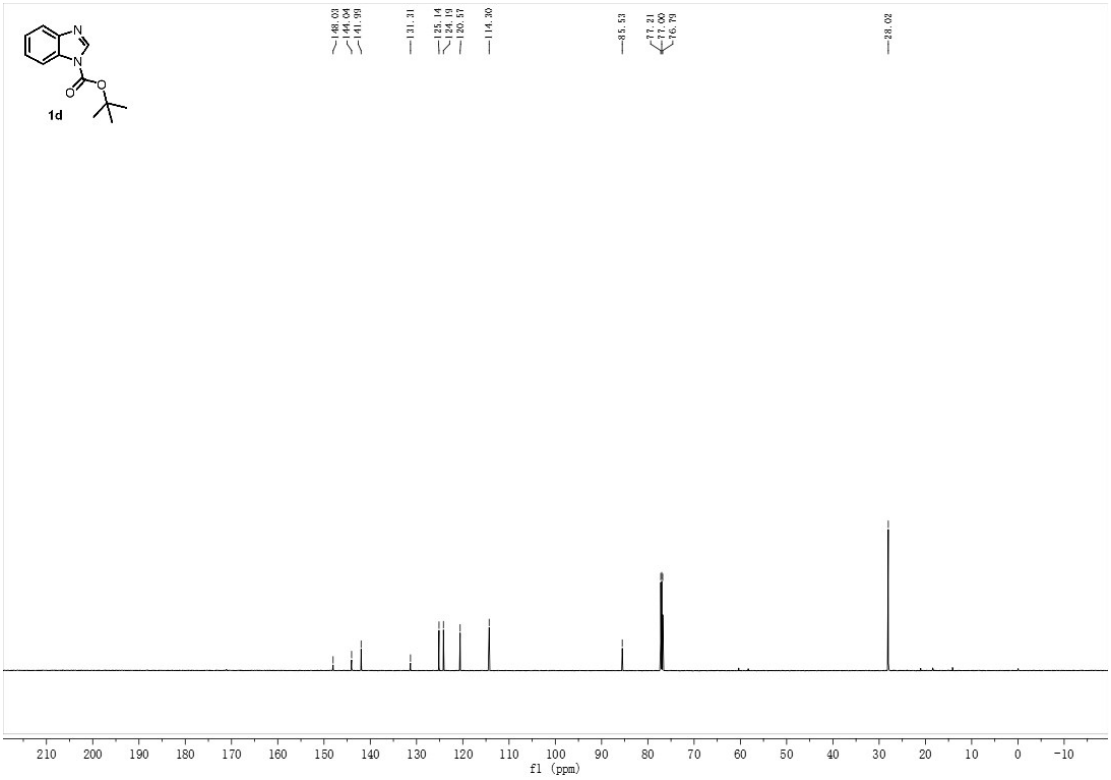

1b
7.93
7.84
7.83
7.82
7.82
7.33
7.31
7.29
7.29
7.27
7.26
7.25
7.18
7.17
7.16
0.00
0.97
0.99
6.13
2.00
2.00
f1 (ppm)

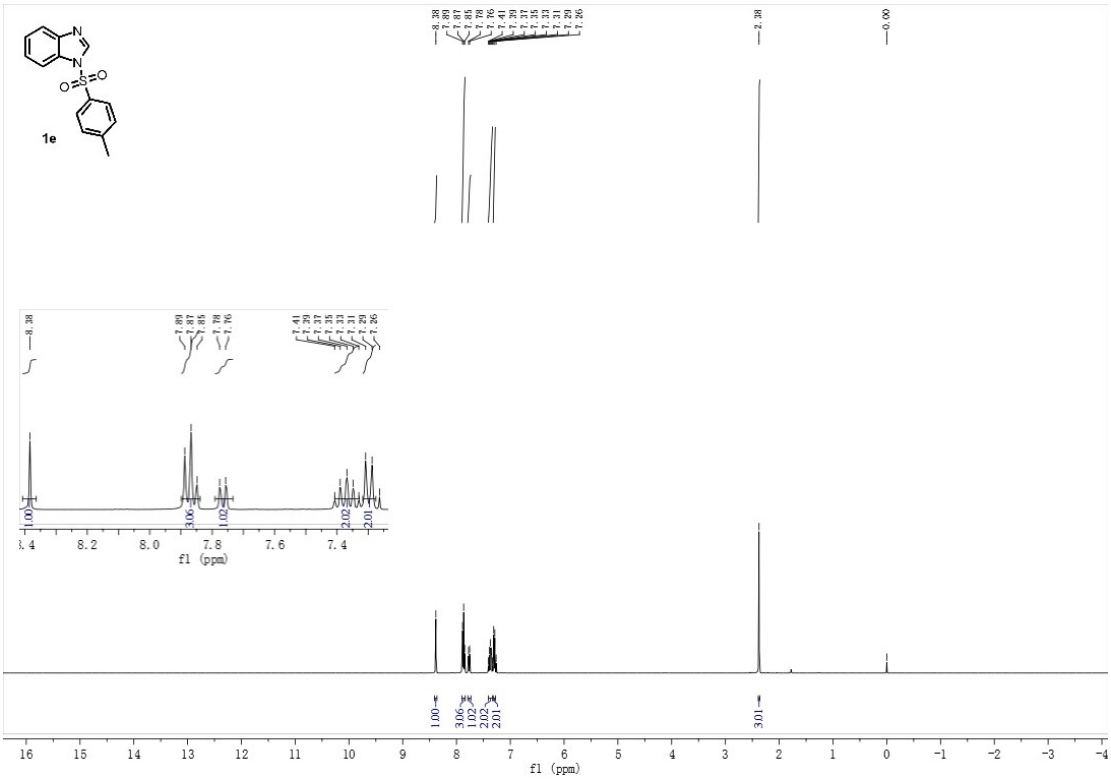

1b
143.91
143.15
135.40
133.85
128.95
128.18
127.06
122.99
122.18
120.36
109.95
77.21
77.00
76.79
48.73
f1 (ppm)

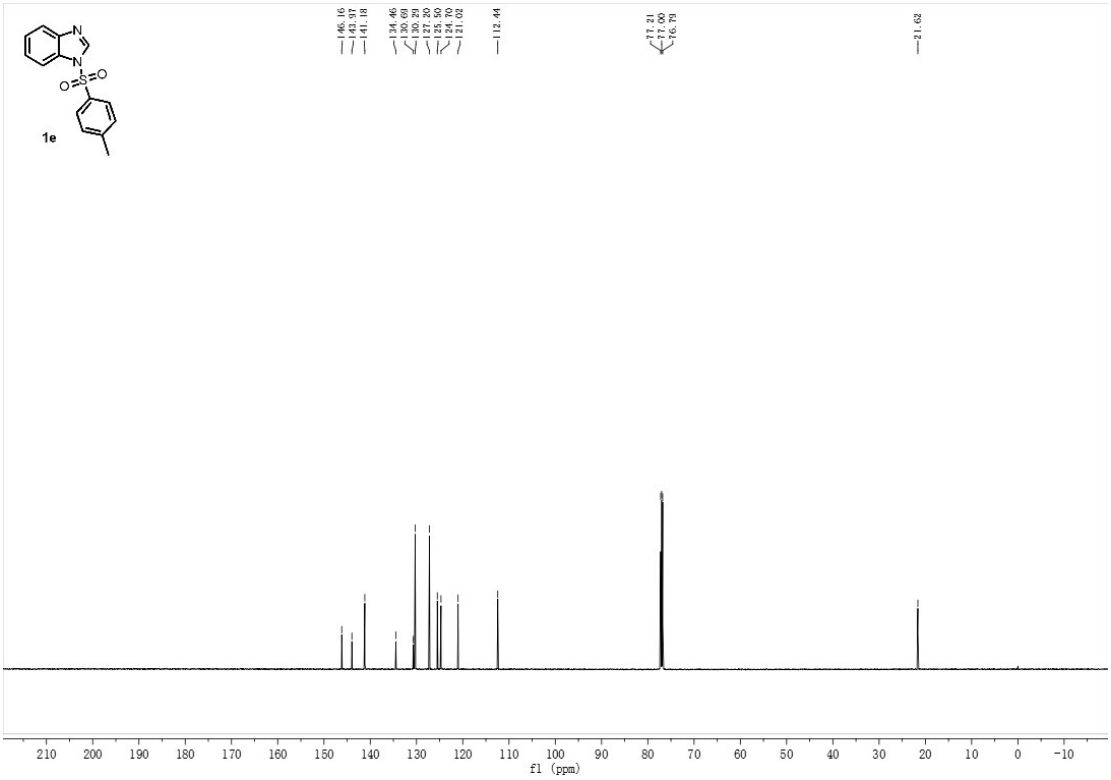

1c
f1 (ppm)

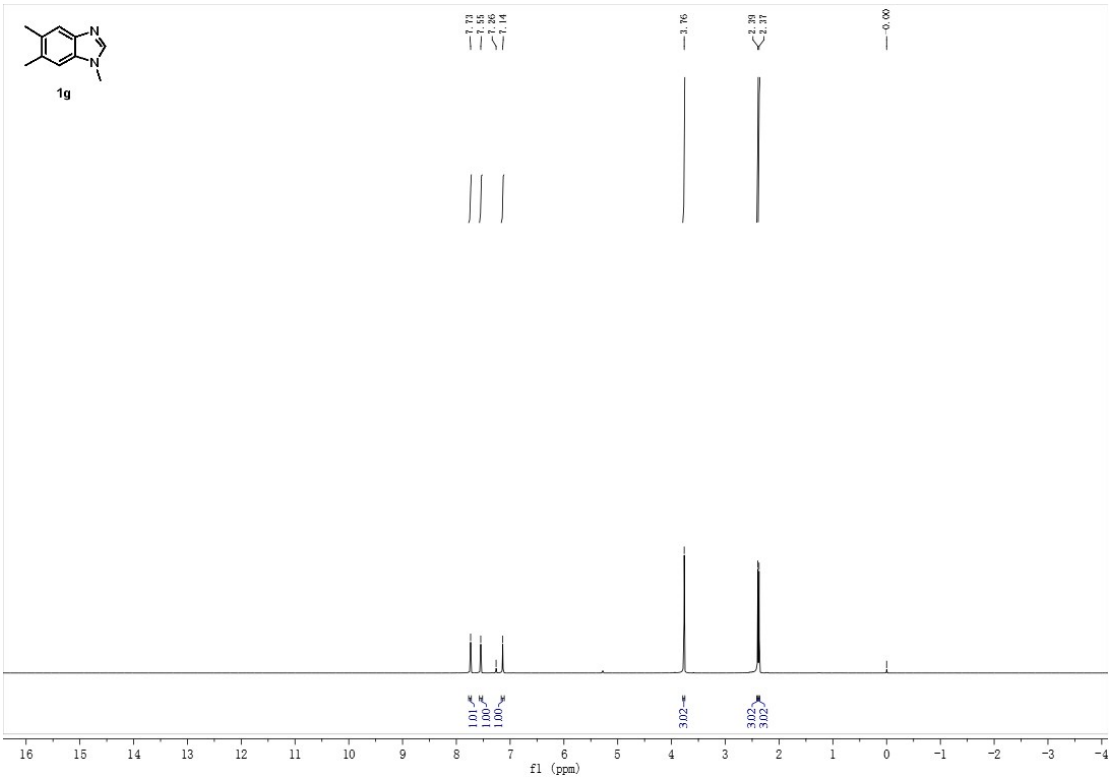

1c
f1 (ppm)

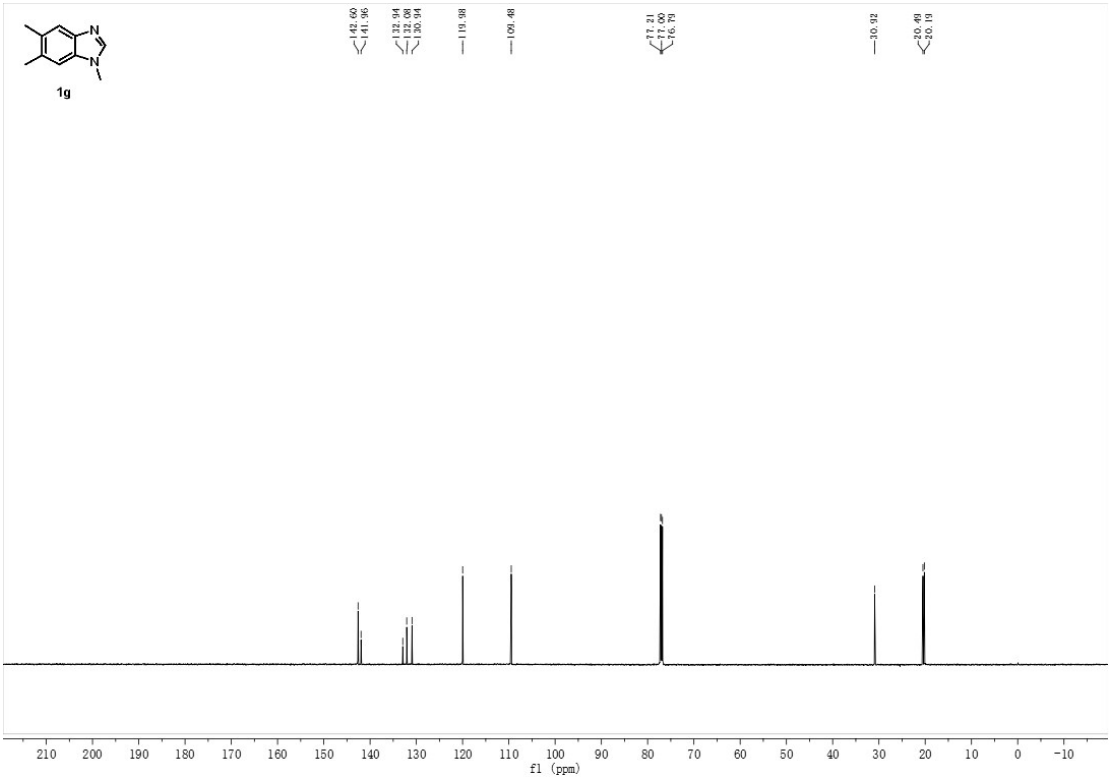

1d
8.44
8.00
7.98
7.80
7.78
7.41
7.39
7.37
7.35
7.34
7.33
7.27
1.70
0.00
1.00
1.01
1.00
2.02
9.05
f1 (ppm)

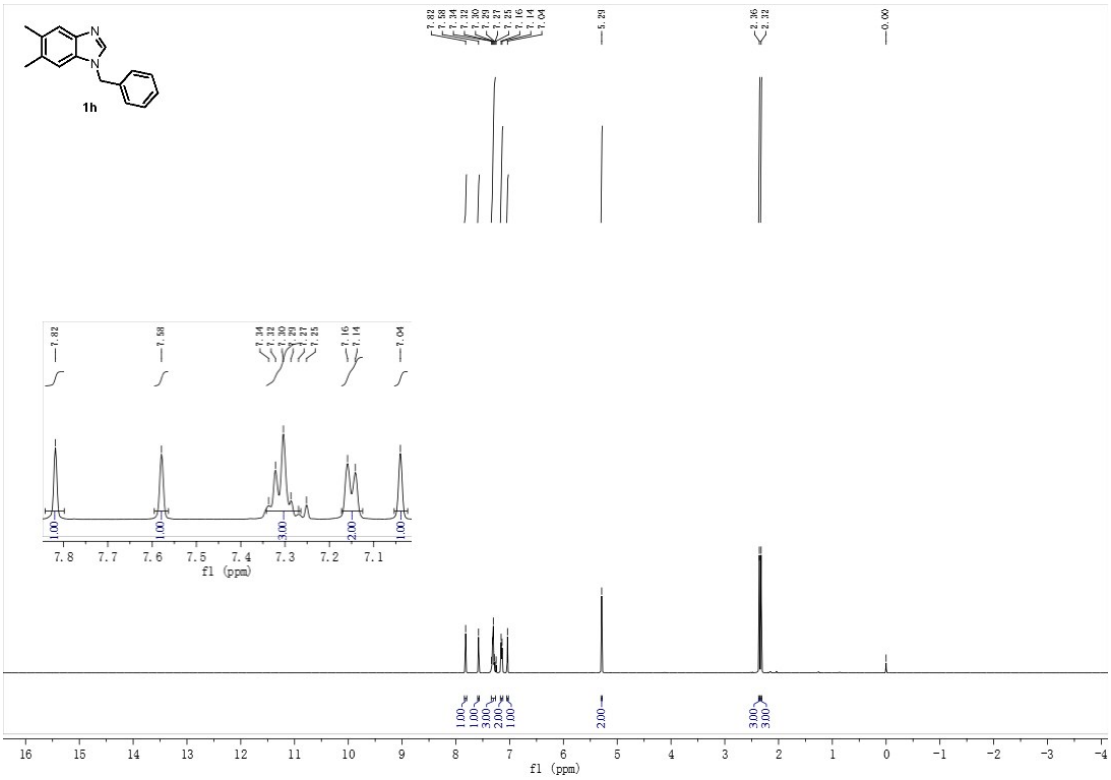

1d
148.03
144.04
141.99
131.31
125.14
124.10
120.57
114.30
85.53
77.21
77.00
76.79
28.02
f1 (ppm)

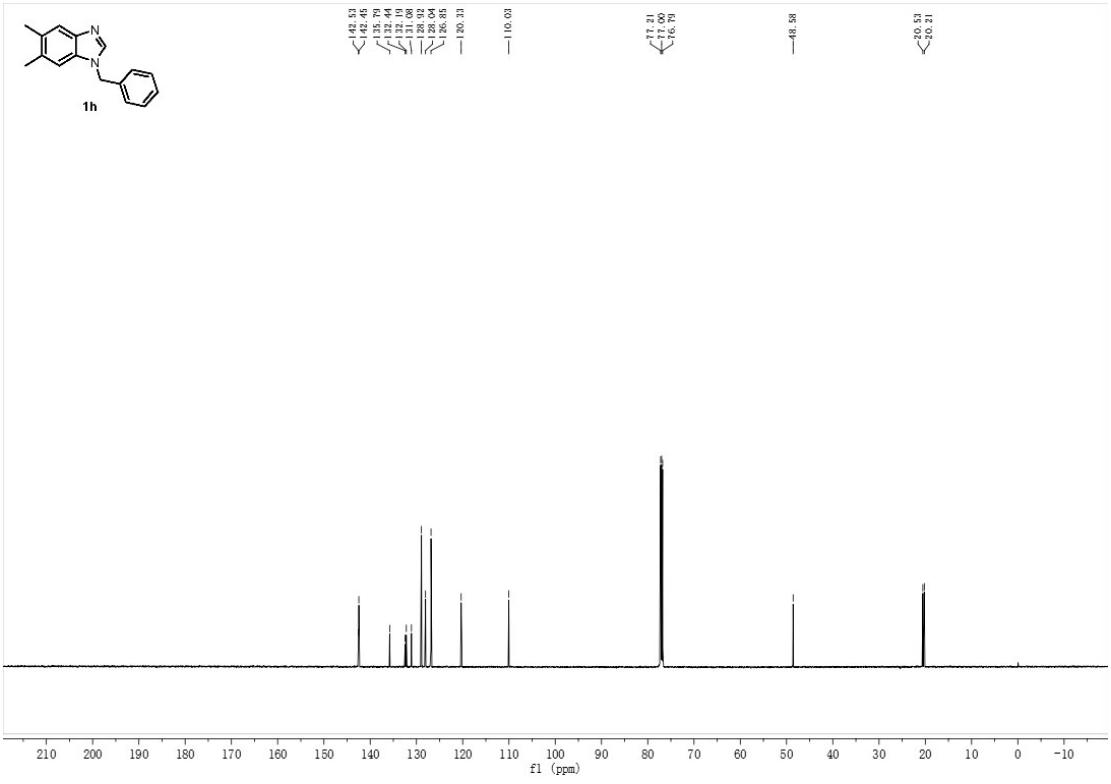

1e
8.38
7.89
7.87
7.85
7.78
7.76
7.41
7.39
7.37
7.35
7.33
7.31
7.29
7.26
2.38
0.00
1.00
3.06
1.02
2.02
2.01
3.01
f1 (ppm)

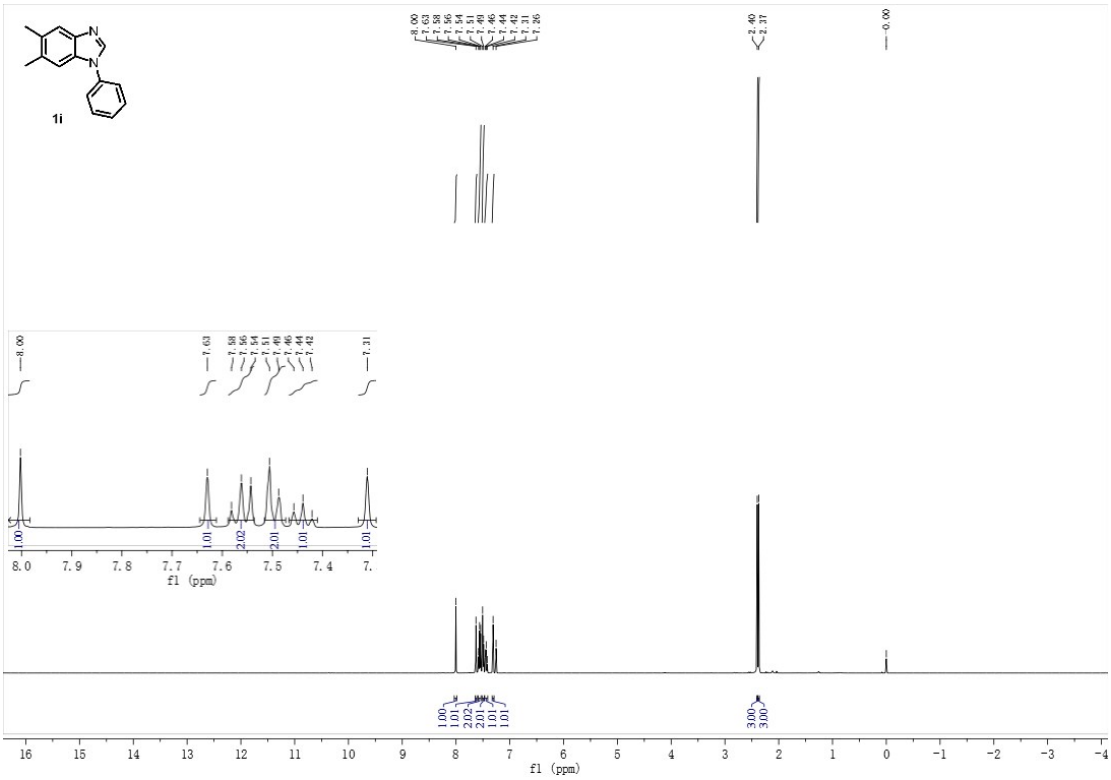

1e
146.16
143.97
141.18
134.46
130.69
130.29
127.30
125.90
124.70
121.02
112.44
77.21
77.00
76.79
21.62
f1 (ppm)

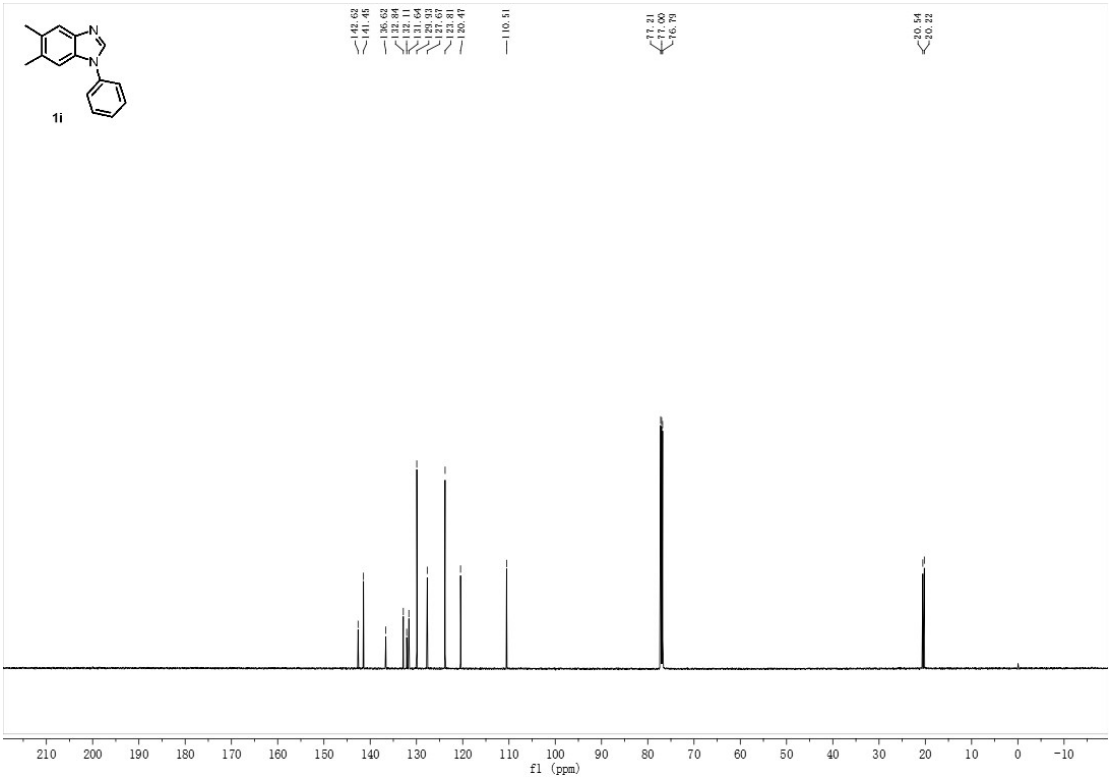

1g
7.73
7.55
7.36
7.14
3.76
2.39
2.37
0.00
1.01
1.00
1.00
3.02
3.02
3.02
f1 (ppm)

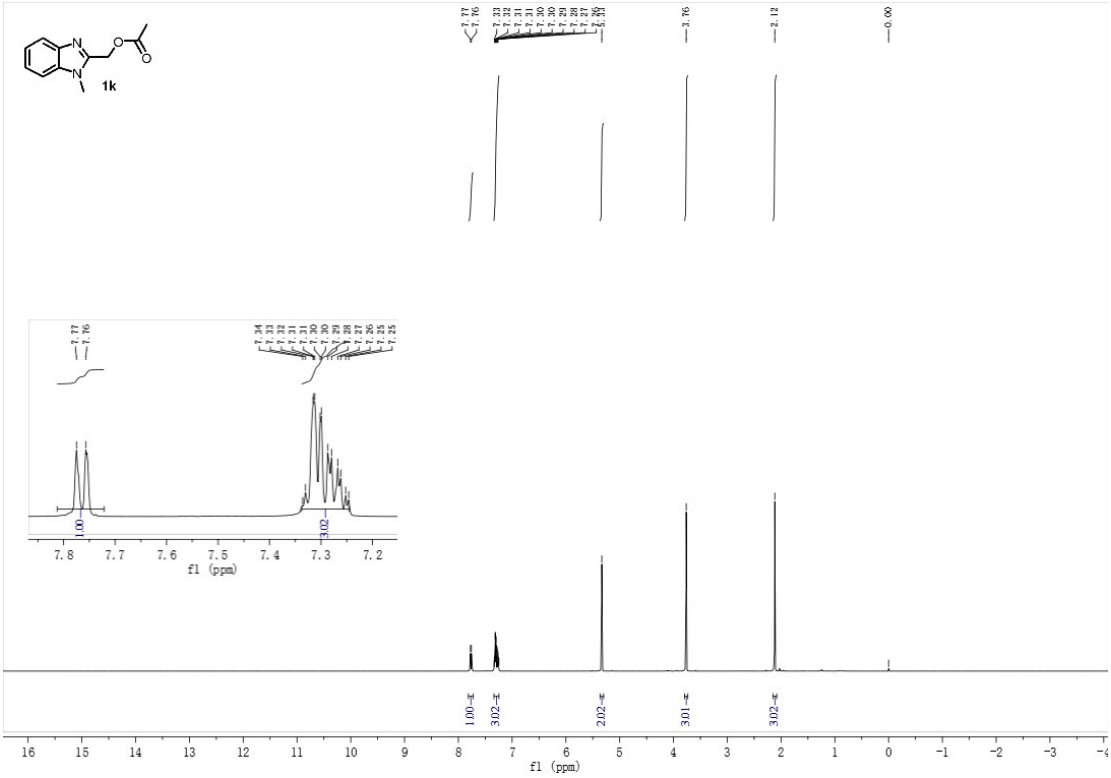

1g
142.69
141.96
132.94
131.08
130.94
119.98
109.48
77.21
77.00
76.79
30.92
20.49
20.19
f1 (ppm)

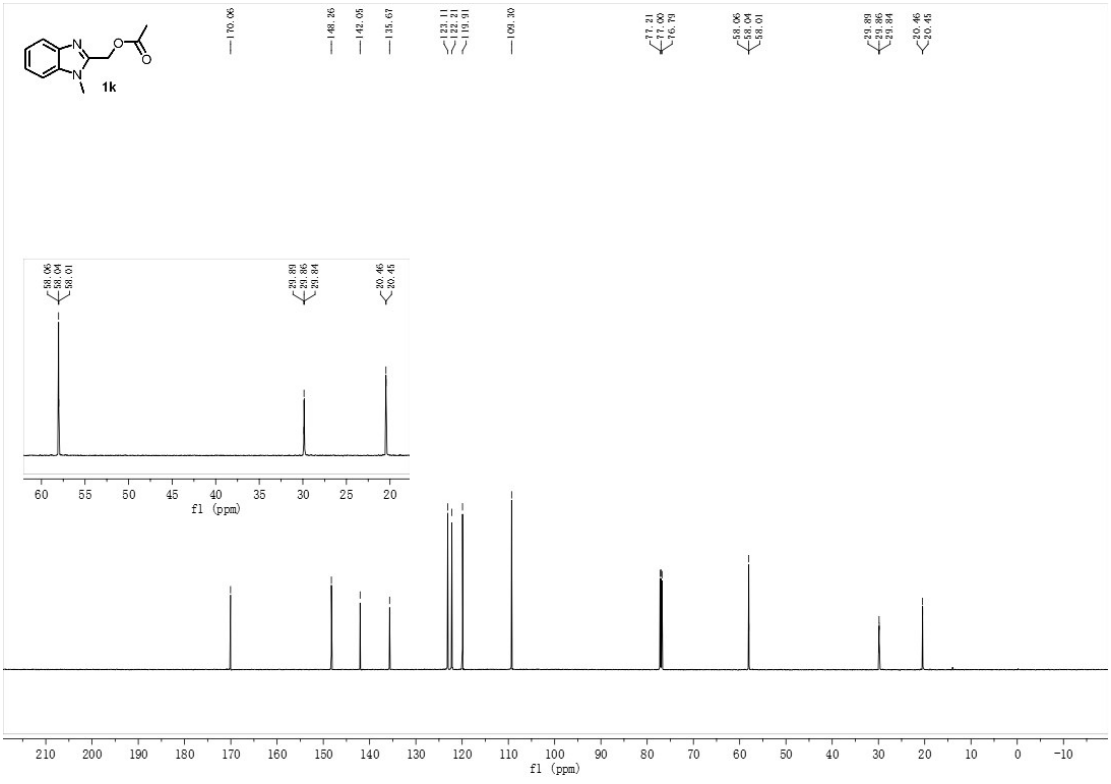

1h
f1 (ppm)

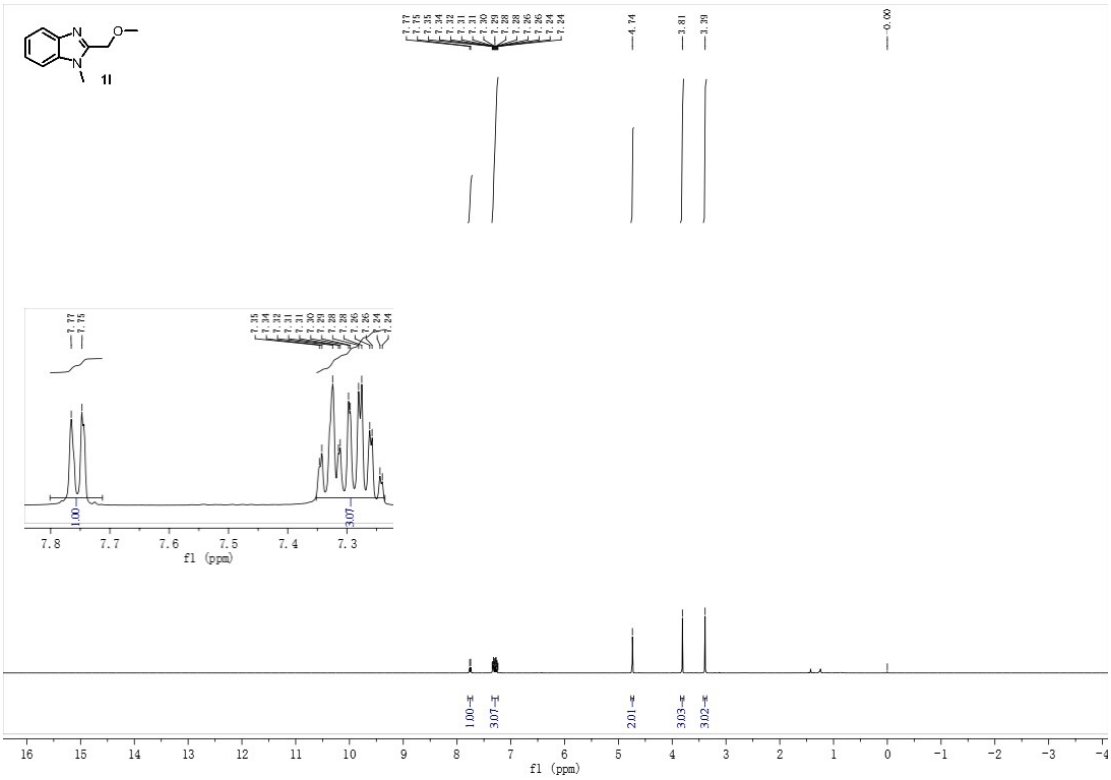

1h
f1 (ppm)

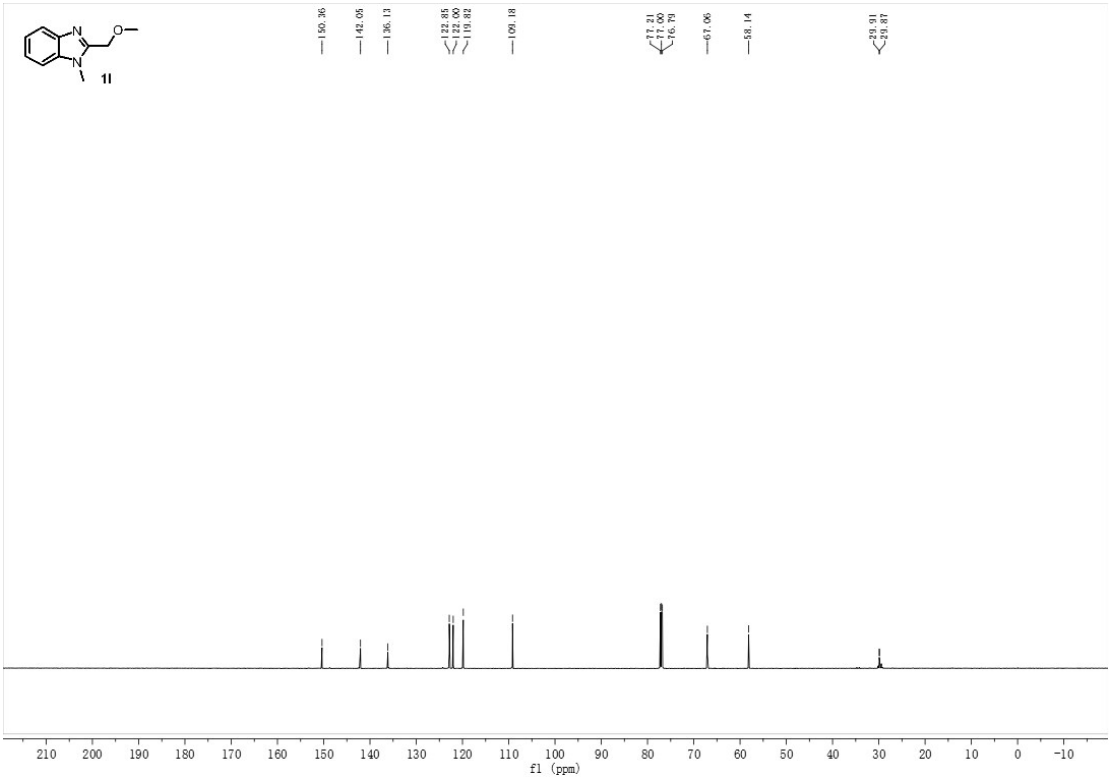

1i
8.00
7.63
7.58
7.56
7.54
7.51
7.49
7.46
7.44
7.42
7.31
7.26
2.40
2.37
0.00
f1 (ppm)

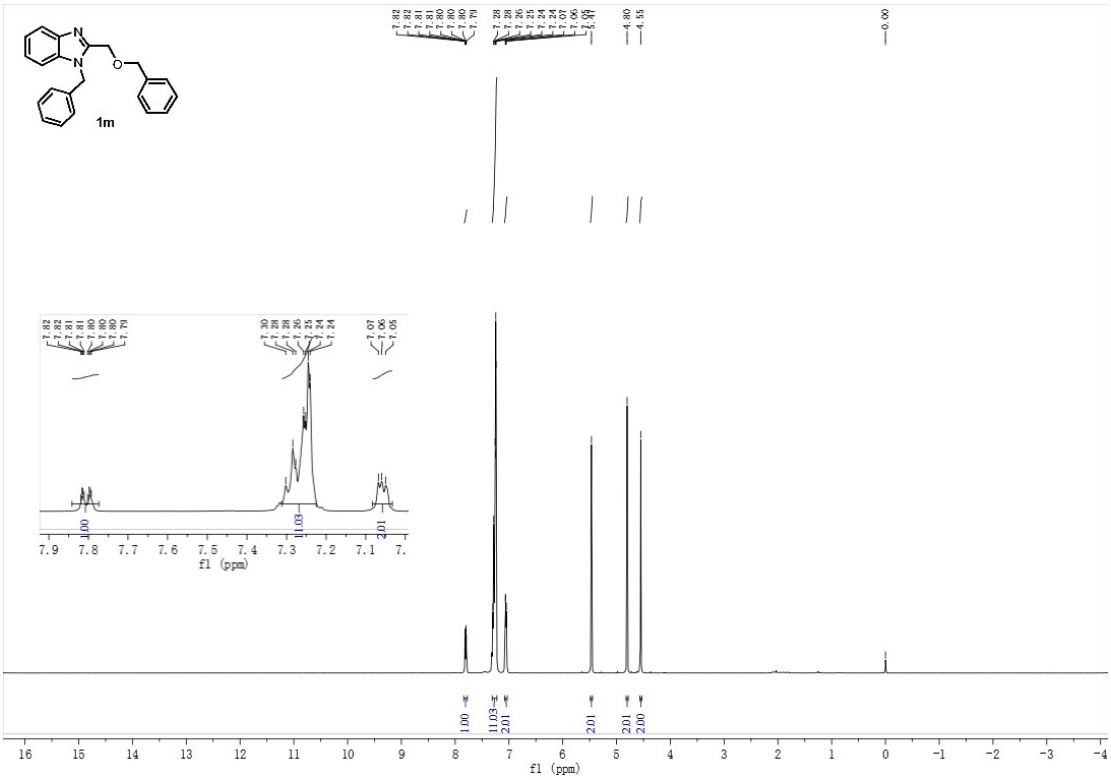

1i
142.62
141.46
136.62
132.84
131.11
131.64
129.93
127.67
123.61
120.47
110.51
77.21
77.00
76.79
20.54
20.22
f1 (ppm)

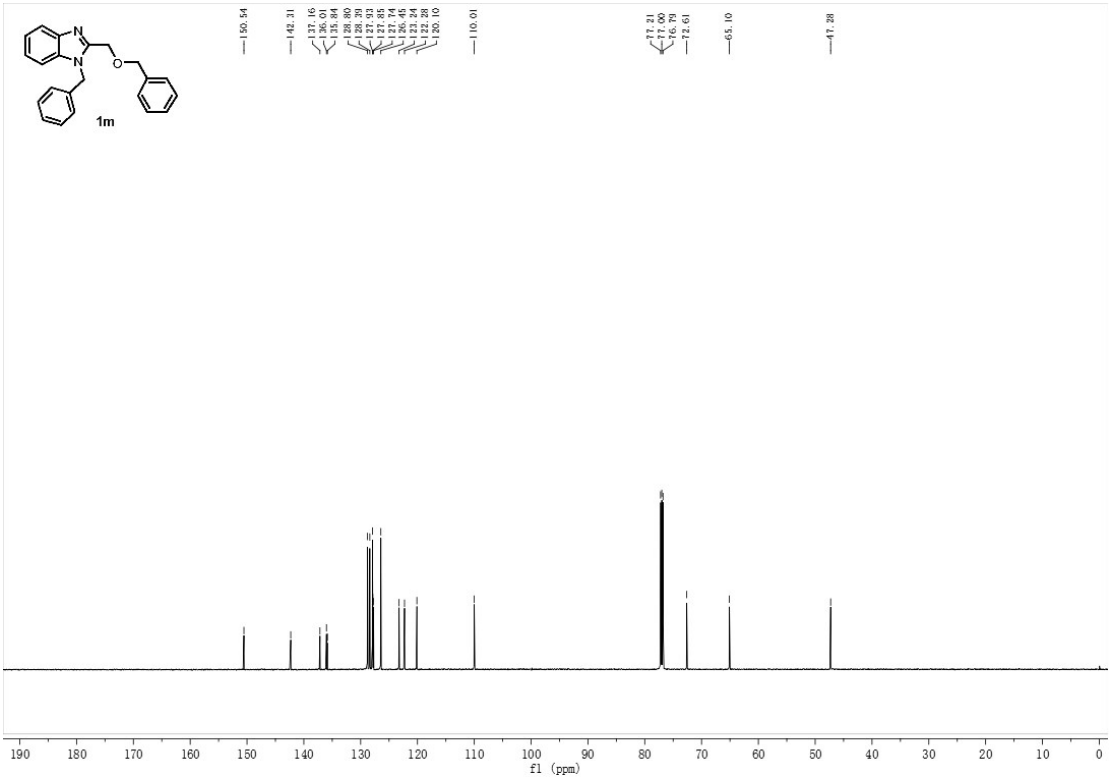

1k
7.77
7.76
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.27
7.26
7.25
3.76
2.12
0.00
1.00
3.02
f1 (ppm)
1.00
3.02
2.02
3.01
3.02

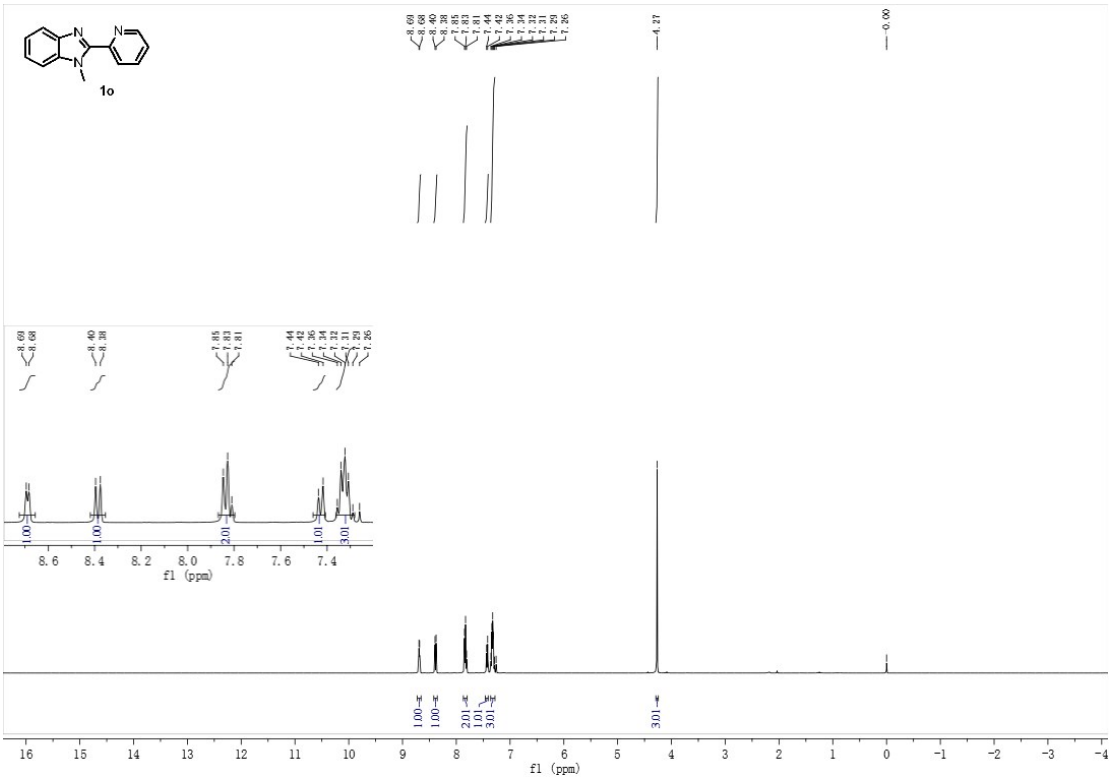

1k
170.06
148.26
142.05
135.67
123.11
122.21
119.91
109.30
77.21
77.00
76.79
58.06
58.04
58.01
29.89
29.86
29.84
20.46
20.45
f1 (ppm)

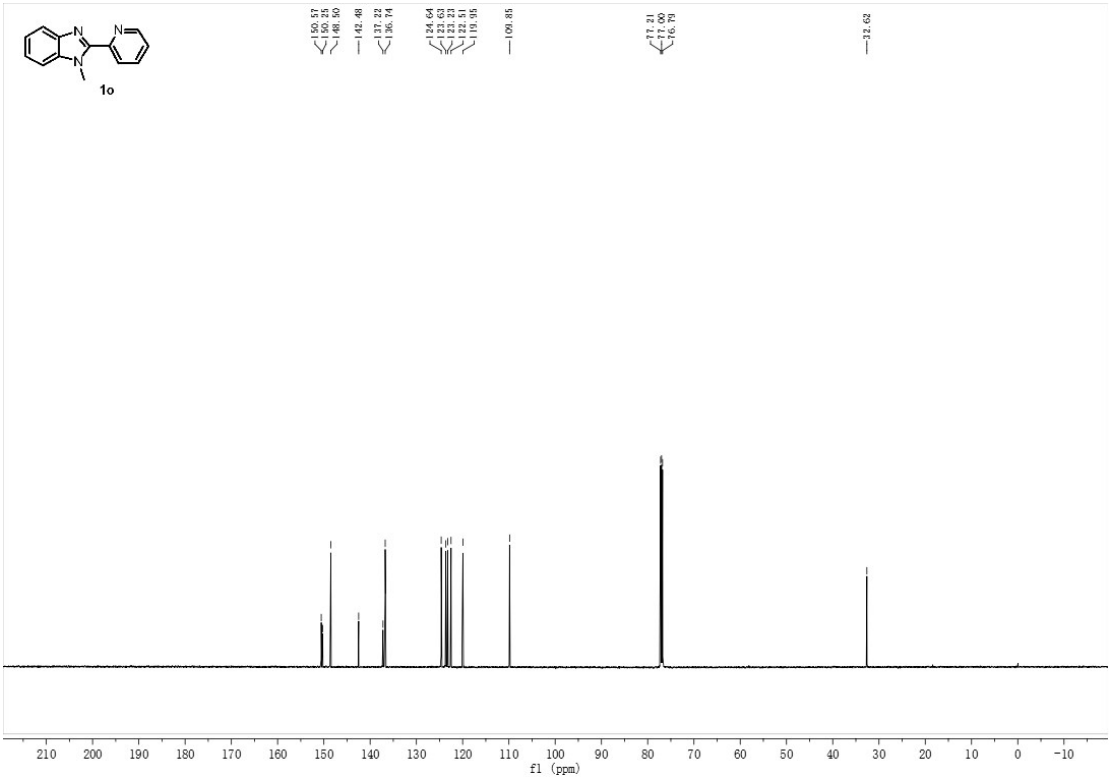

1l
7.77
7.75
7.35
7.34
7.32
7.31
7.31
7.30
7.29
7.28
7.28
7.26
7.26
7.24
7.24
4.74
3.81
3.39
0.00
1.00
3.07
7.8
7.7
7.6
7.5
7.4
7.3
f1 (ppm)
1.00
3.07
2.01
3.03
3.02
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

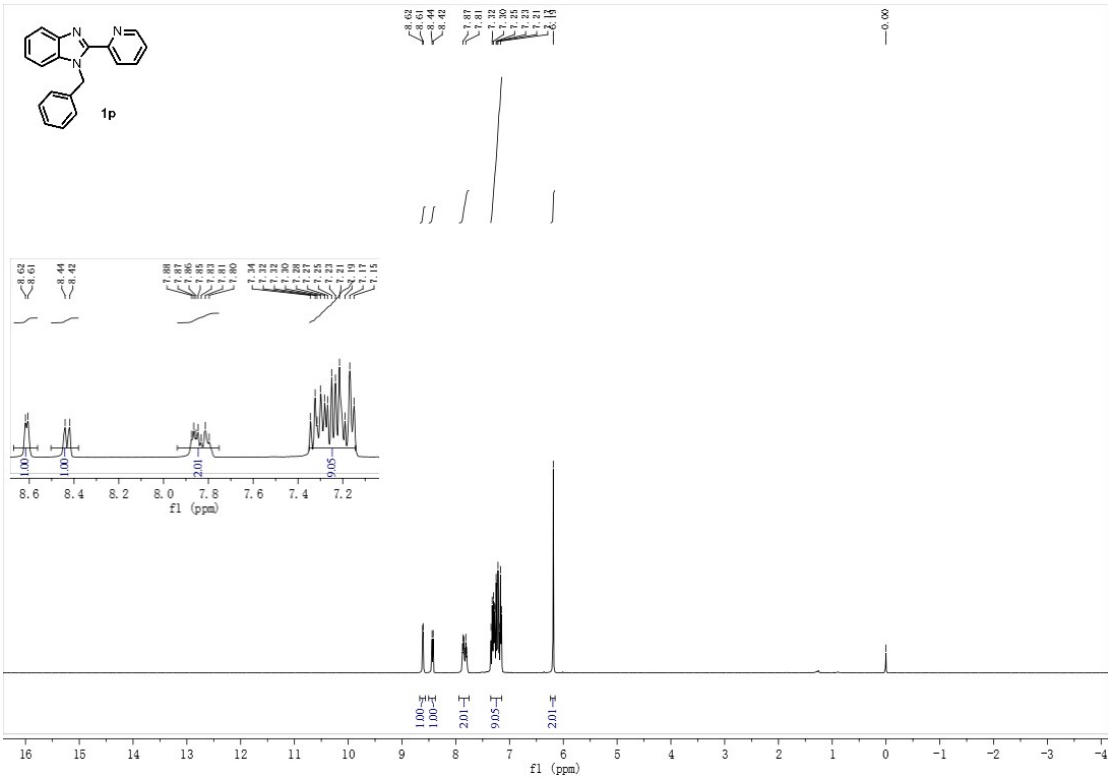

1l
150.36
142.05
136.13
122.85
122.00
119.82
109.18
77.21
77.00
76.79
67.06
58.14
29.91
29.87
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

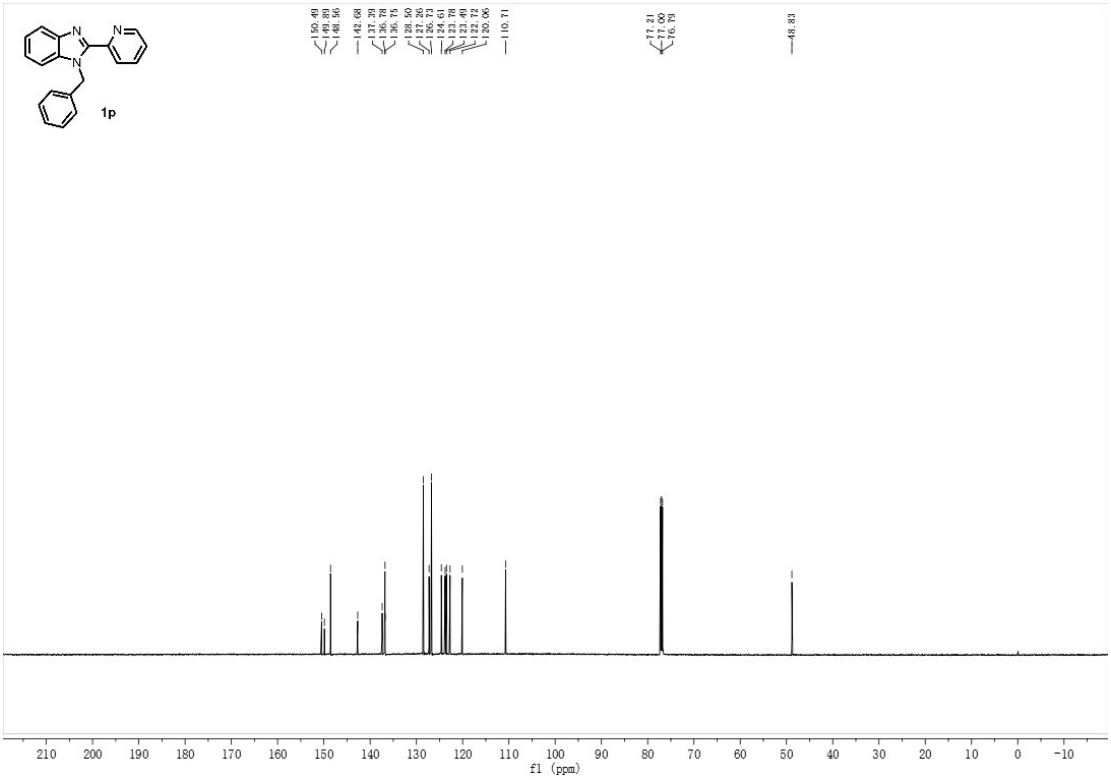

1m
f1 (ppm)

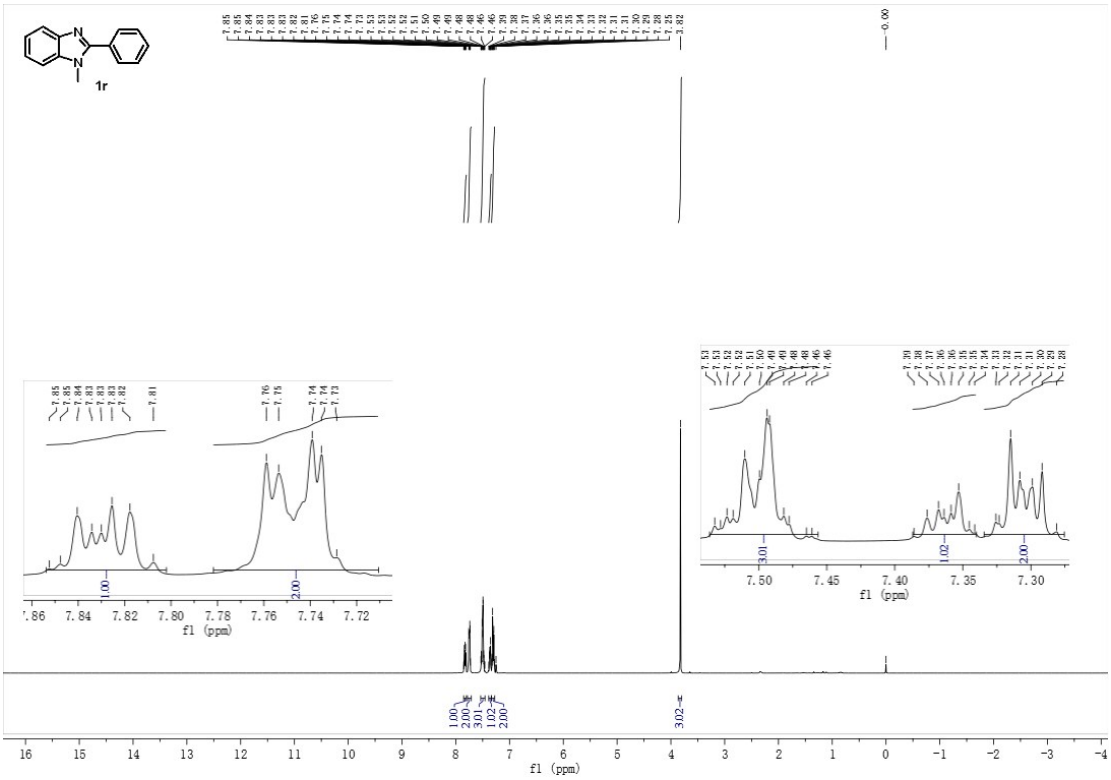

1m
f1 (ppm)

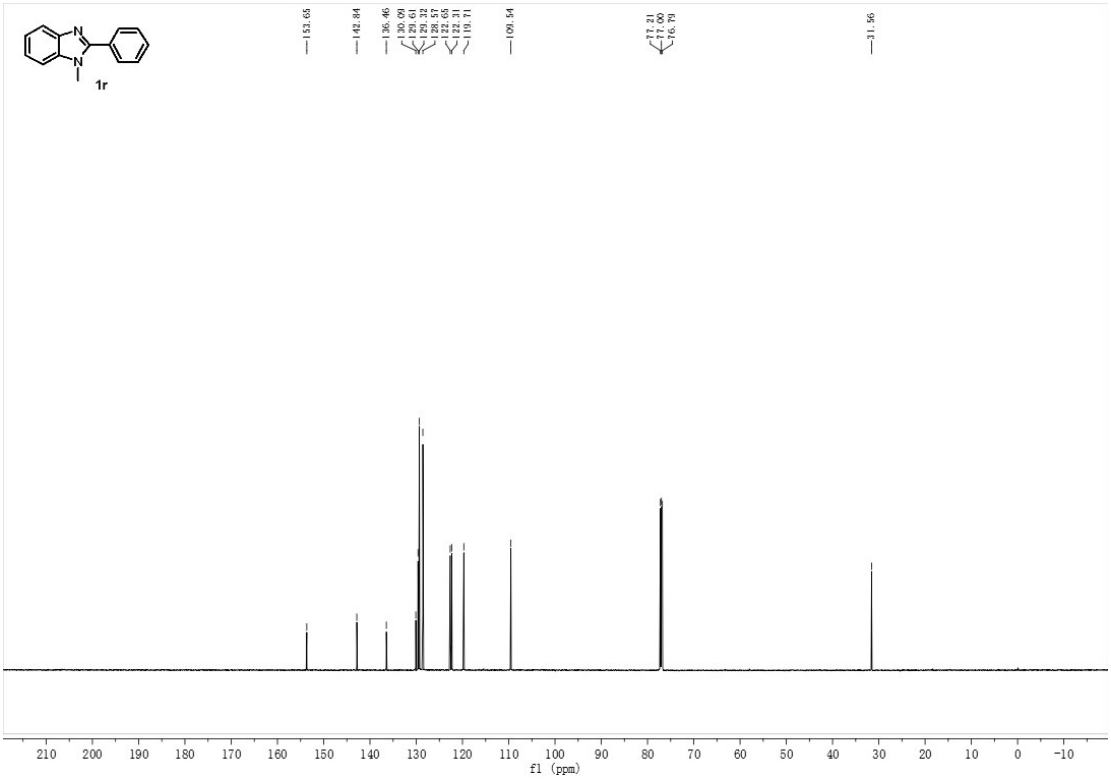

1o
8.69
8.68
8.40
8.38
7.85
7.83
7.81
7.44
7.42
7.36
7.34
7.32
7.31
7.29
7.26
4.27
0.00
1.00
1.00
2.01
1.01
3.01
3.01
f1 (ppm)

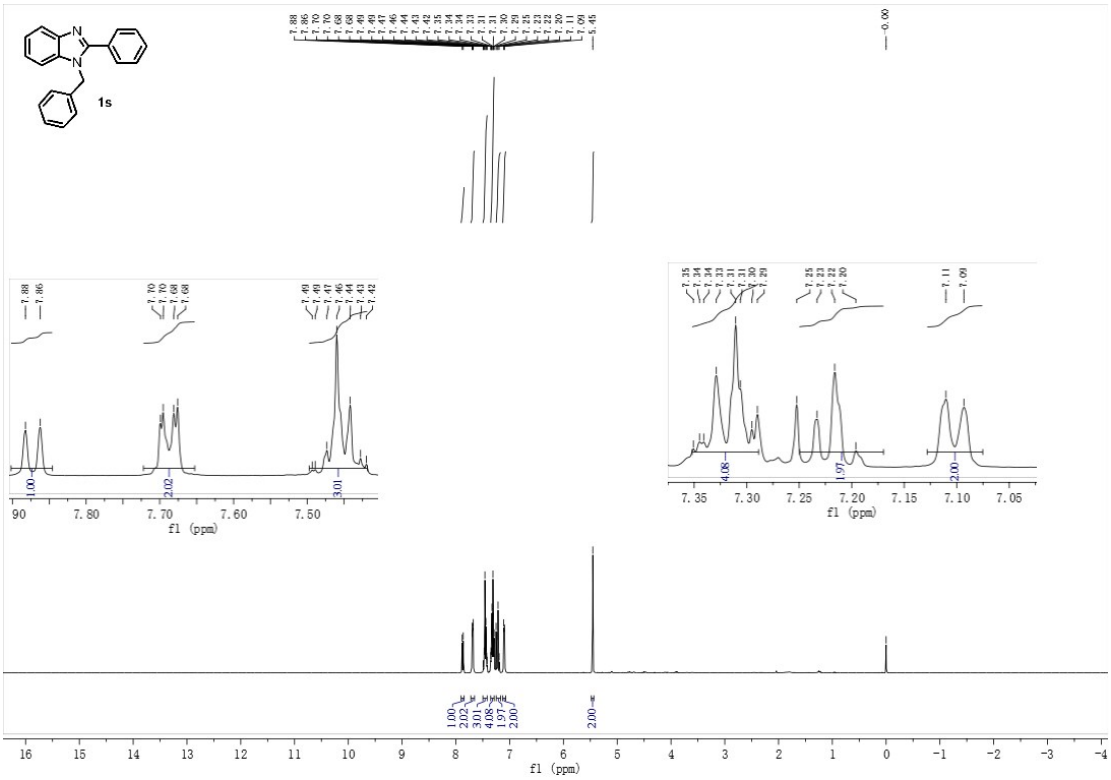

1o
150.57
150.25
148.90
142.48
137.32
136.74
124.64
123.63
123.23
122.51
119.95
109.85
77.21
77.00
76.79
32.62
f1 (ppm)

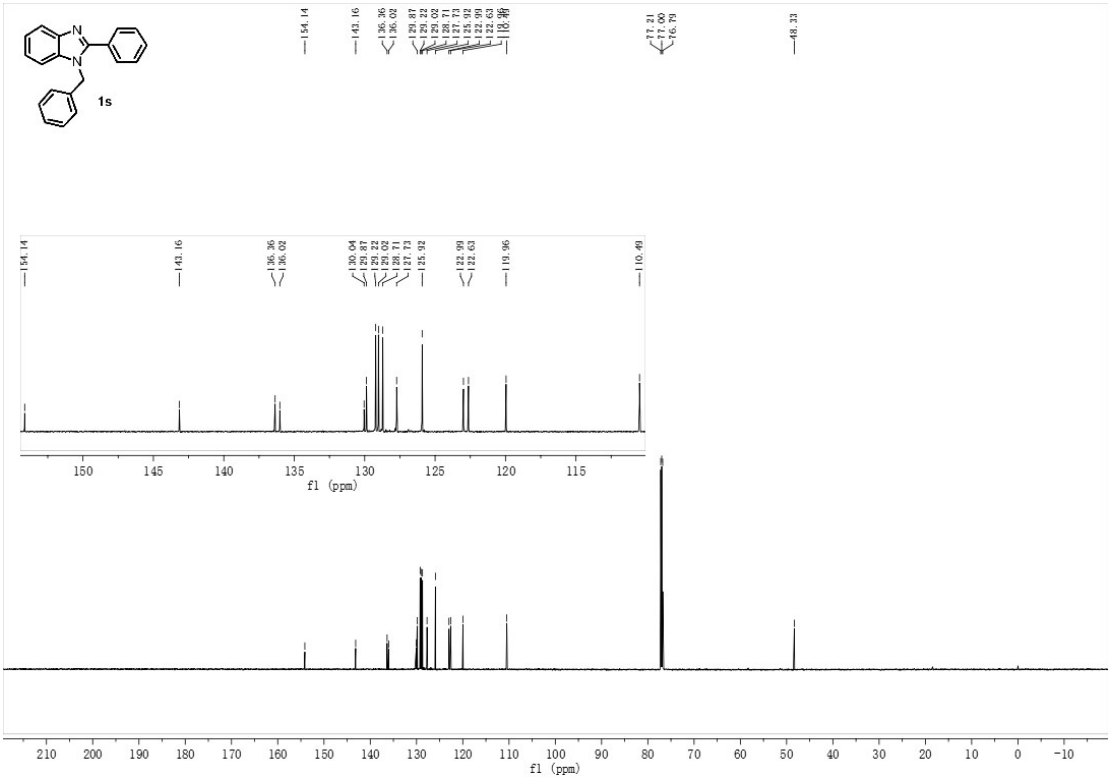

1p
8.62
8.61
8.44
8.42
7.87
7.81
7.32
7.30
7.25
7.23
7.21
6.18
0.00
1.00
1.00
2.01
9.05
2.01
f1 (ppm)

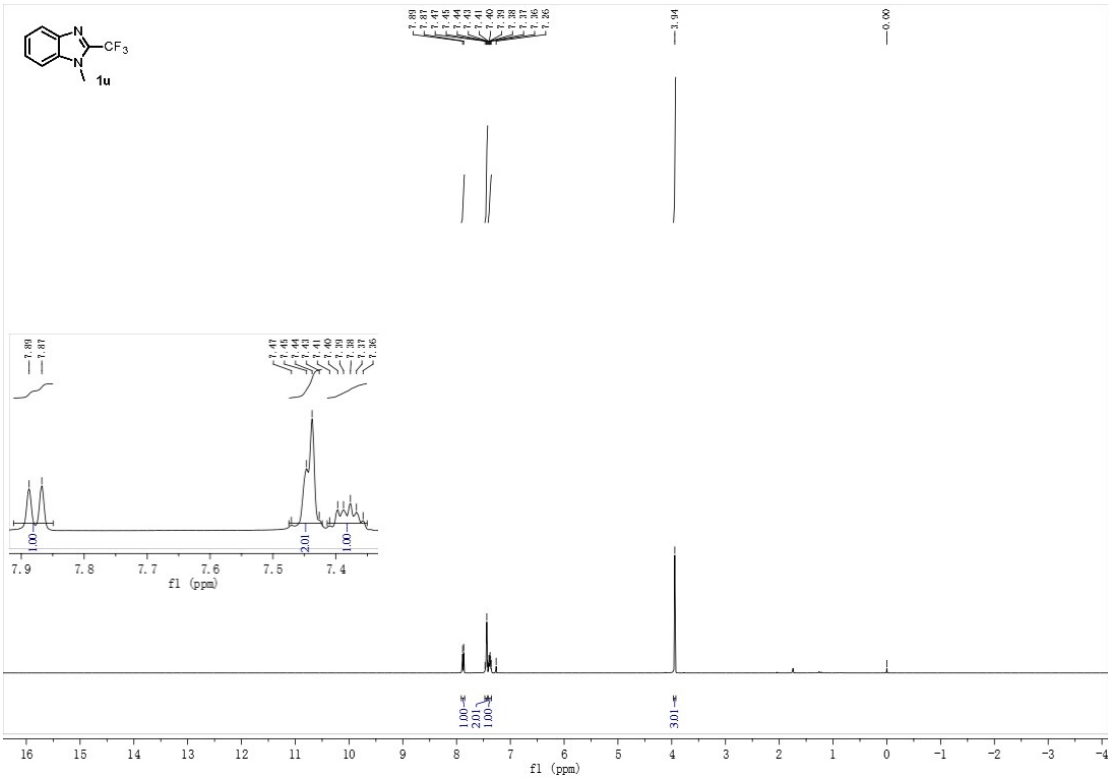

1p
150.49
149.89
148.96
142.68
137.39
136.78
136.75
128.90
127.36
126.73
124.61
123.78
123.46
122.72
120.06
110.71
77.21
77.00
76.79
48.83
f1 (ppm)

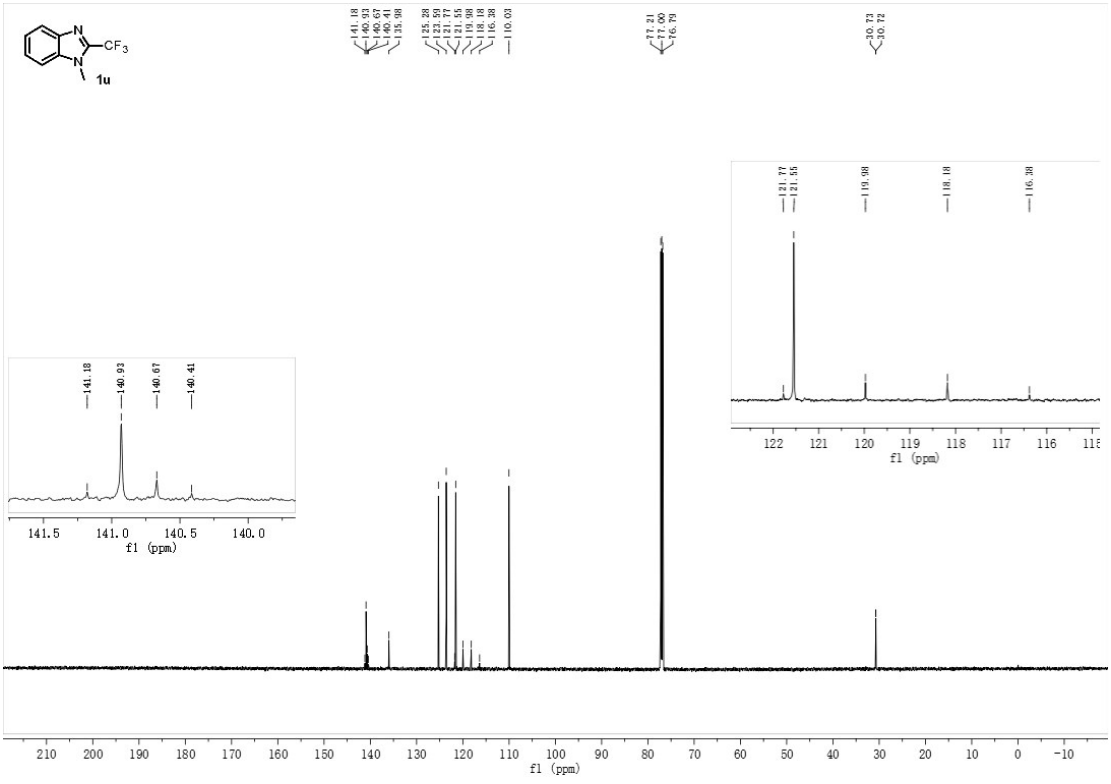

1r
f1 (ppm)

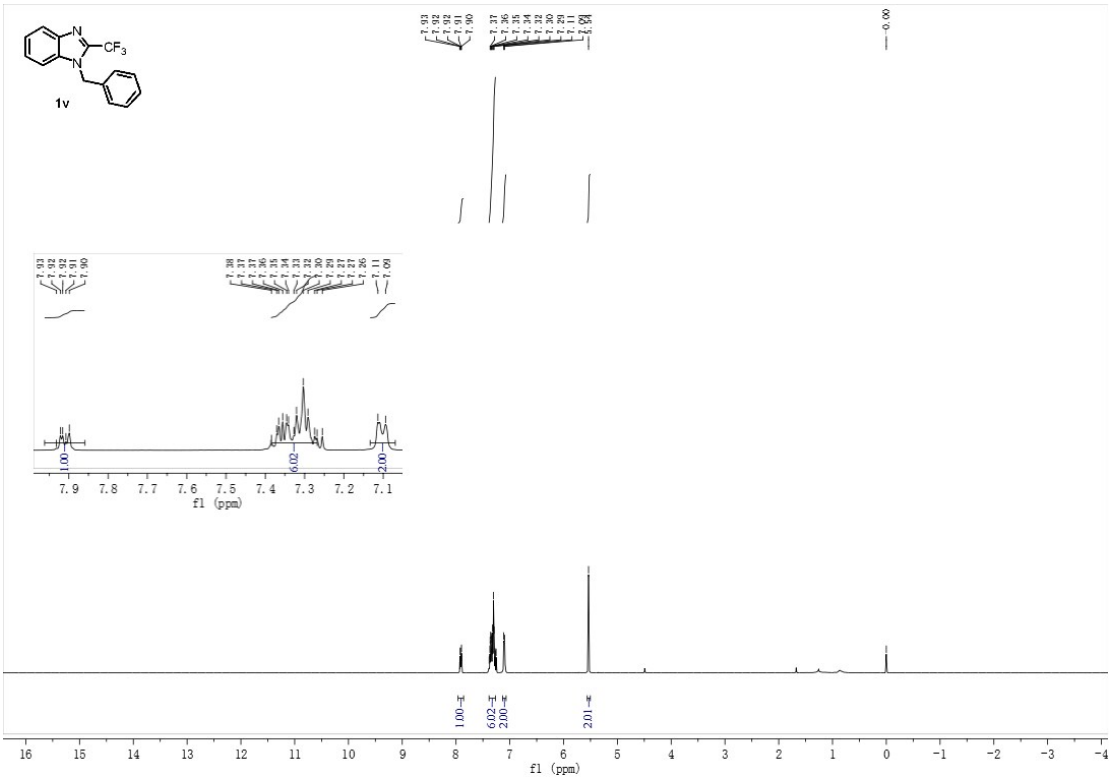

1r
f1 (ppm)

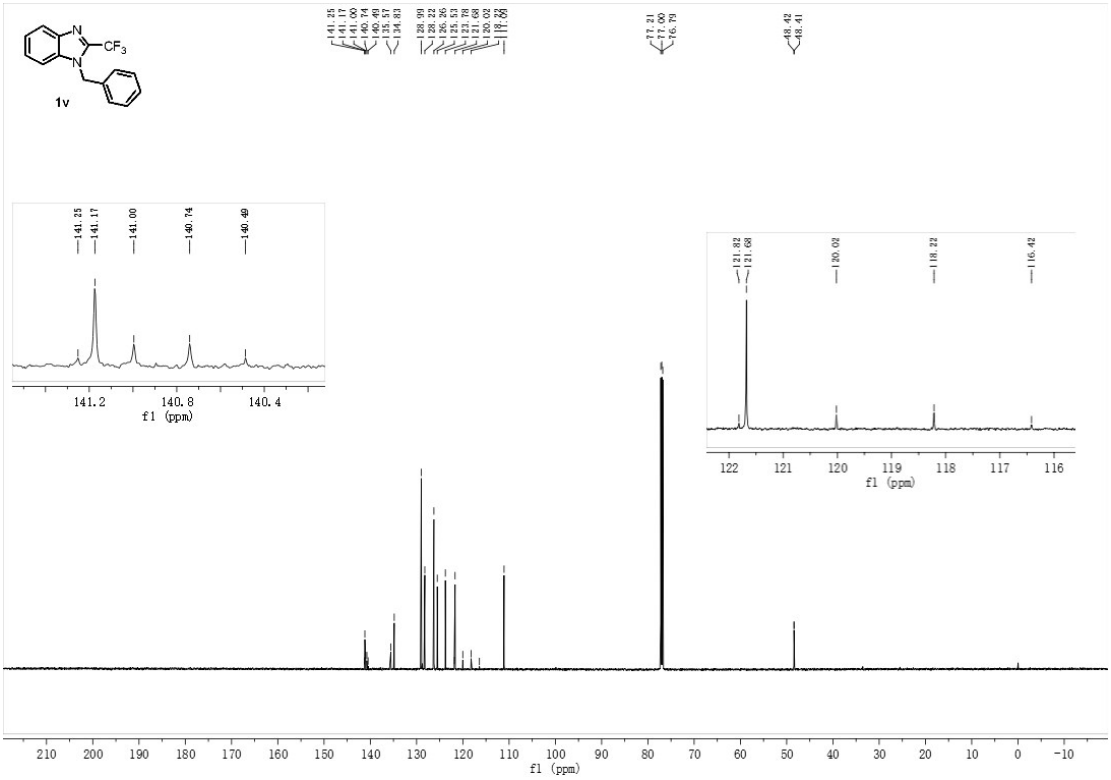

1s
f1 (ppm)

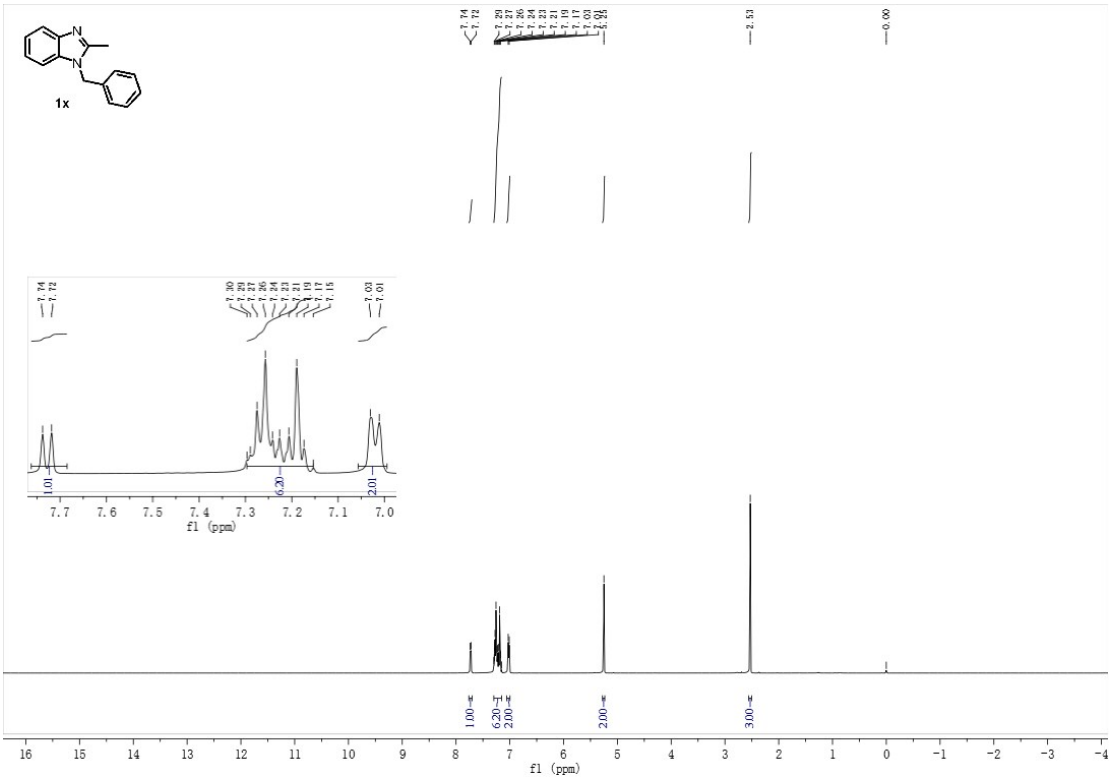

1s
f1 (ppm)

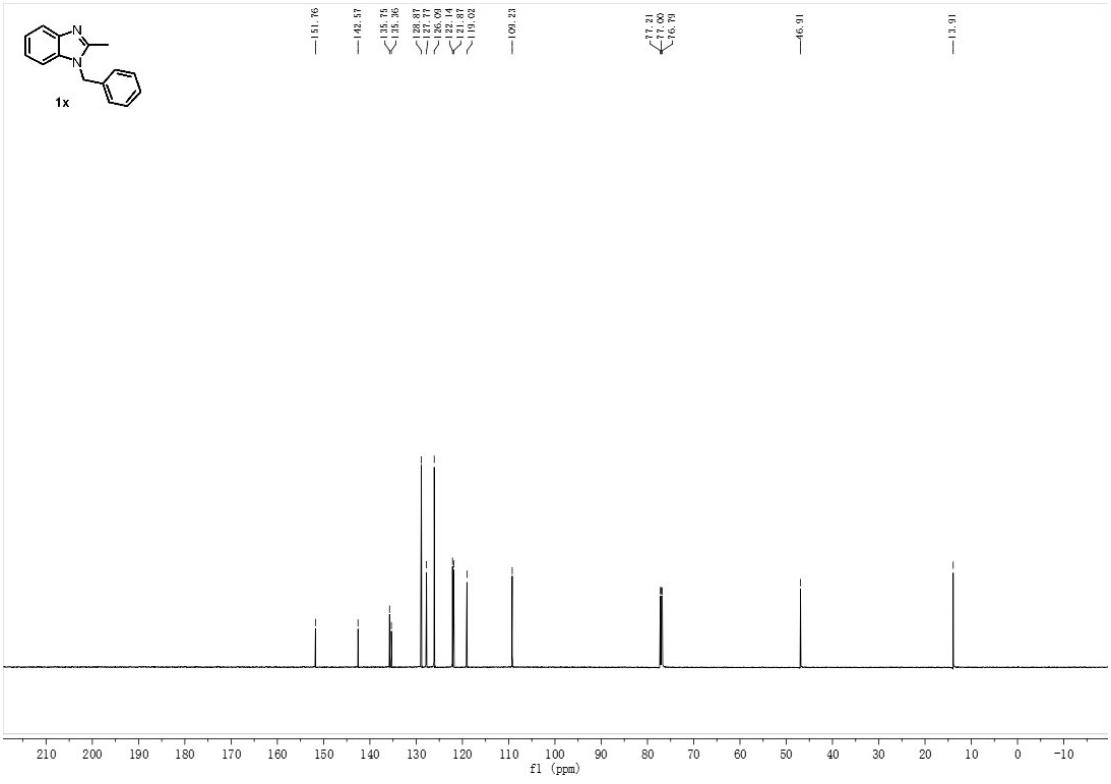

1u
f1 (ppm)

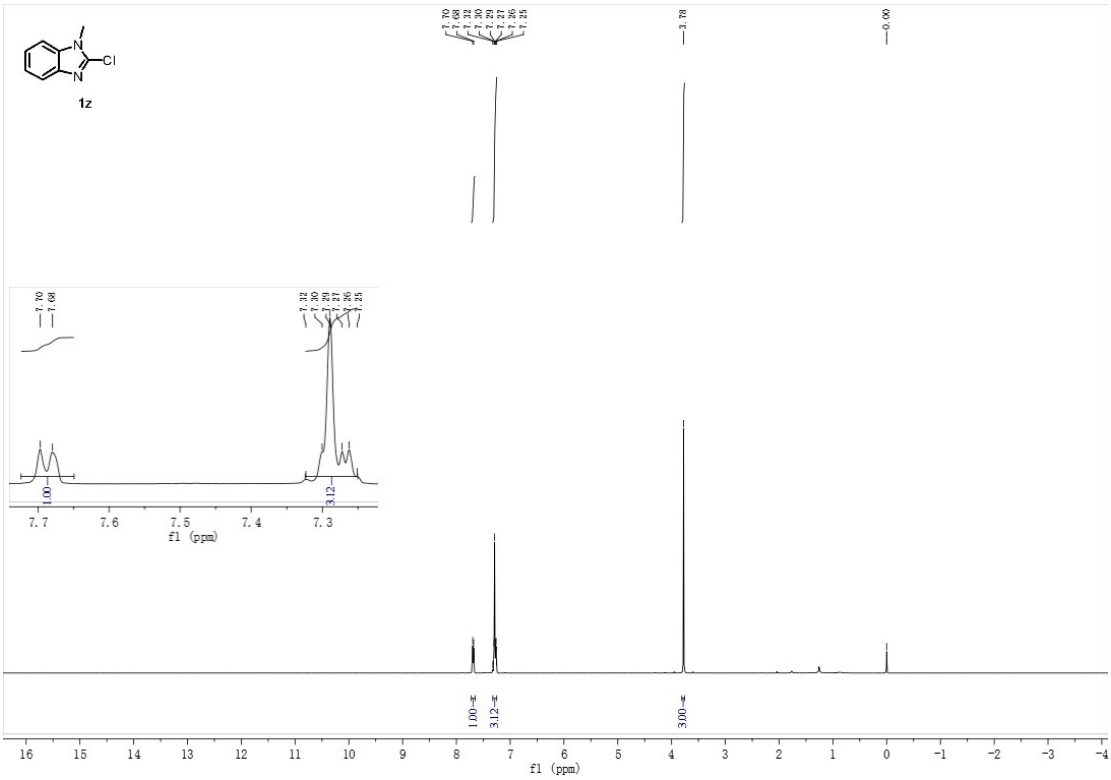

1u
f1 (ppm)

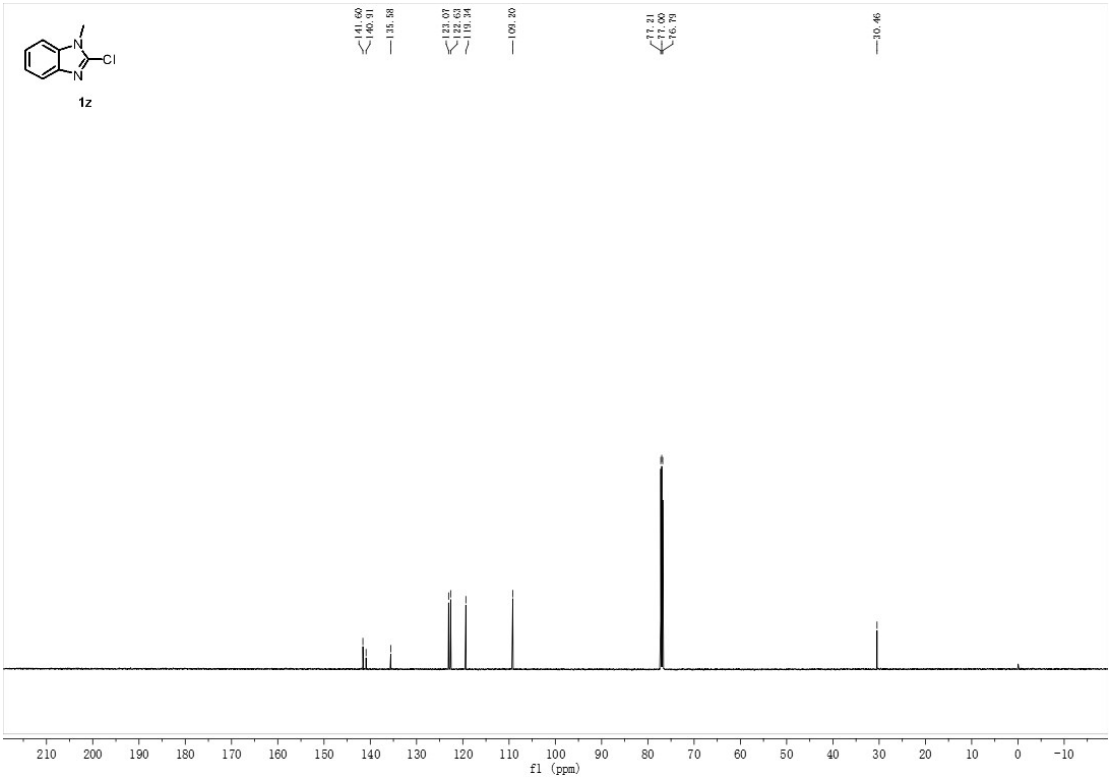

1v
1.00
6.02
2.00
2.01
f1 (ppm)

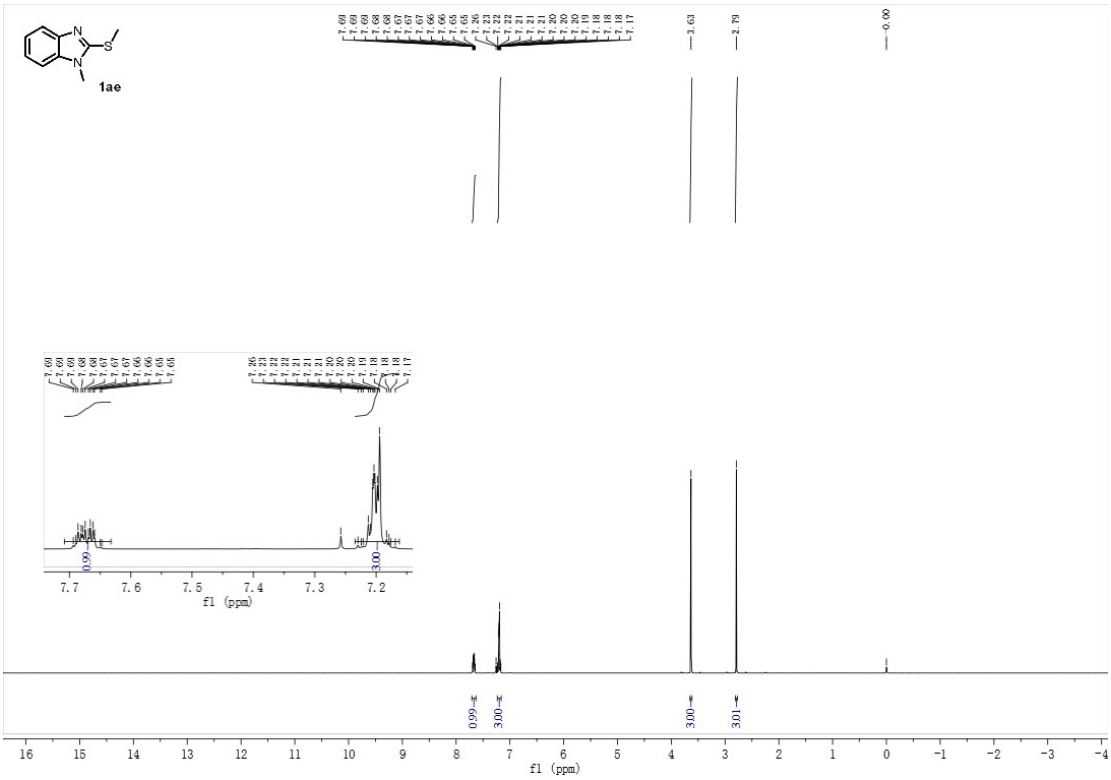

1v
f1 (ppm)

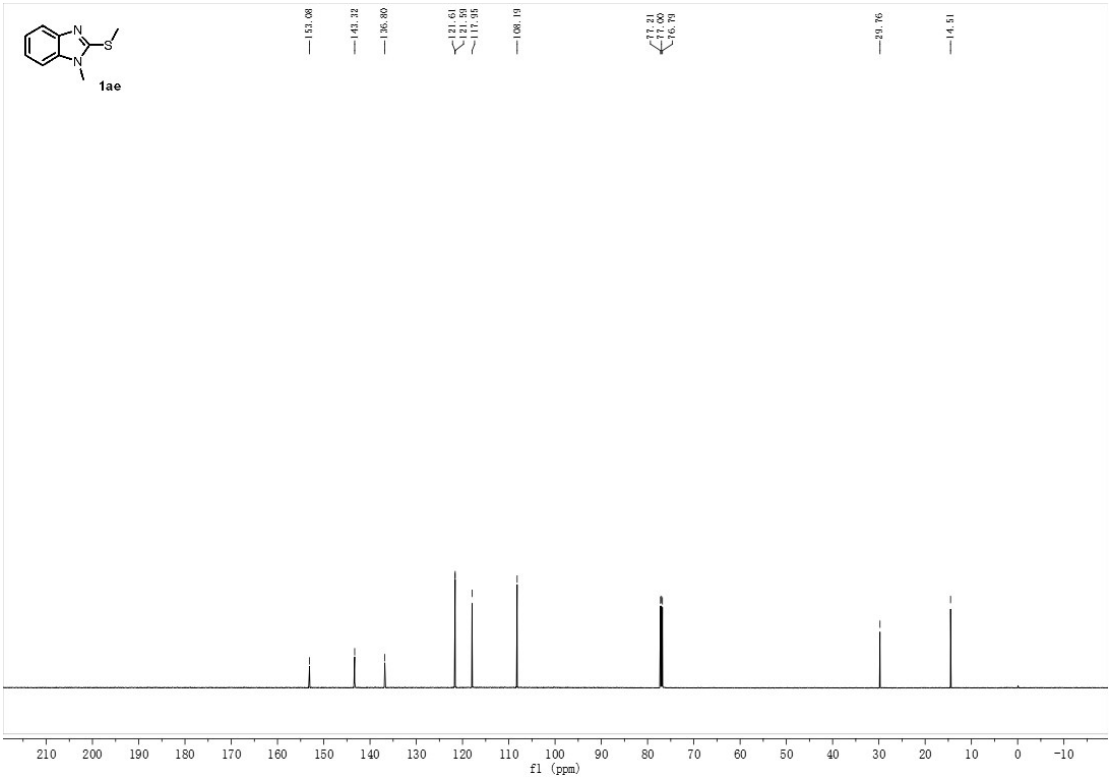

1x
7.74
7.72
7.29
7.27
7.26
7.24
7.23
7.21
7.19
7.17
7.03
7.01
5.25
2.53
0.00
1.00
6.20
2.00
2.00
3.00
f1 (ppm)

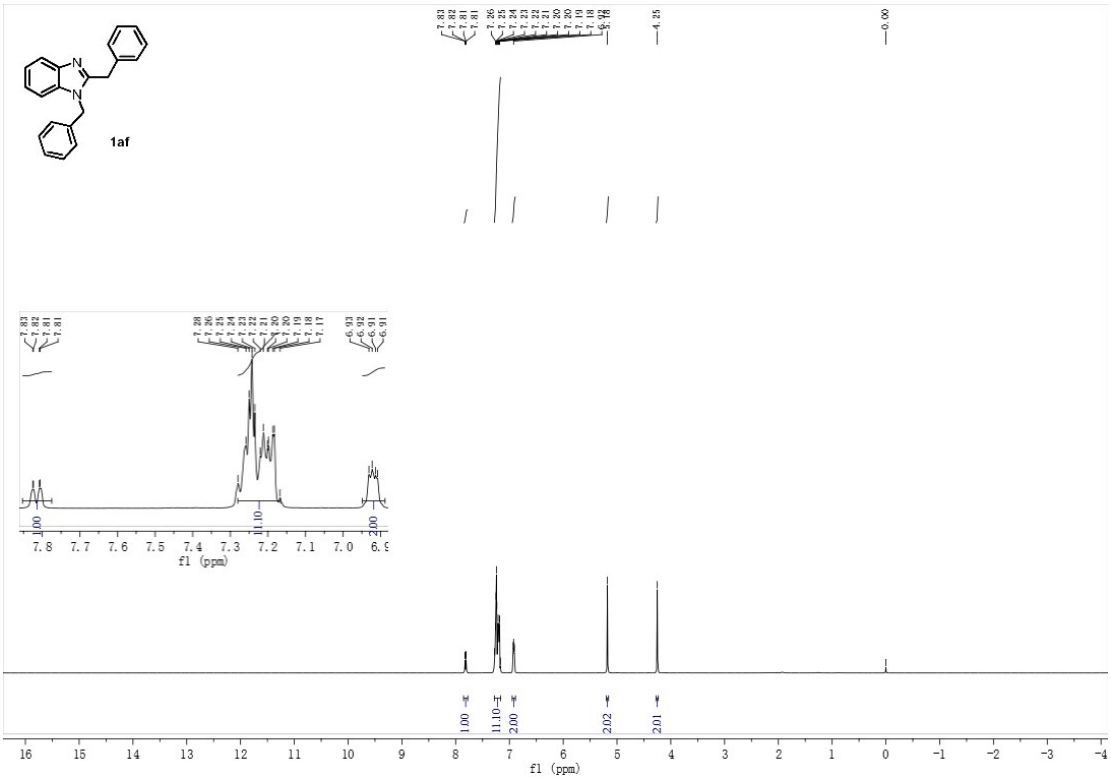

1x
151.76
142.57
135.75
135.36
128.87
127.77
126.09
123.14
121.87
119.02
109.23
77.21
77.00
76.79
46.91
13.91
f1 (ppm)

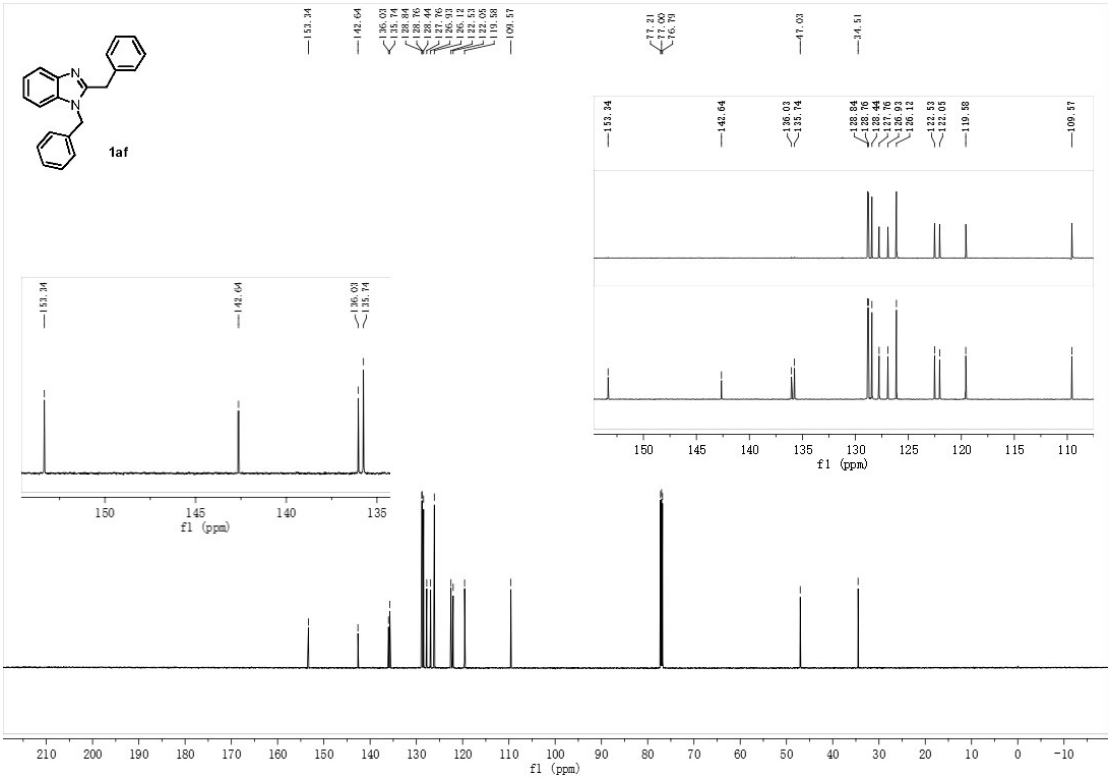

1z
7.70
7.68
7.32
7.30
7.29
7.27
7.26
7.25
3.78
0.00
1.00
3.12
3.00
f1 (ppm)

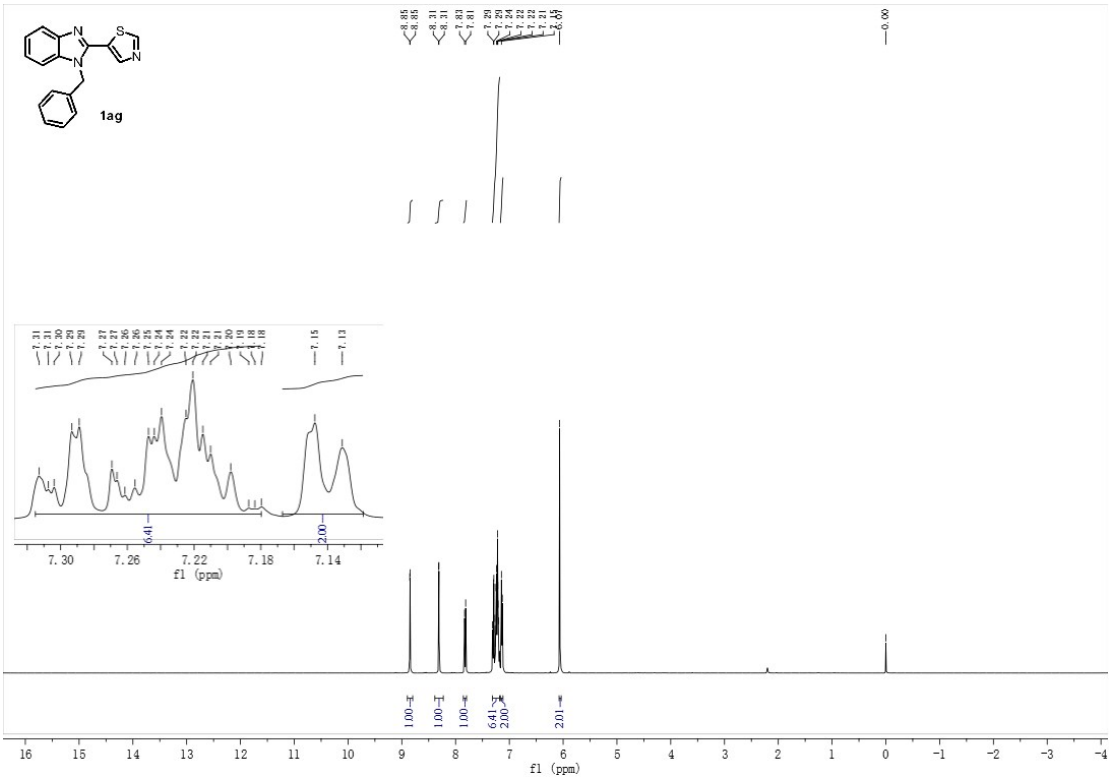

1z
141.69
140.91
135.58
123.07
122.63
119.34
109.20
77.21
77.00
76.79
30.46
f1 (ppm)

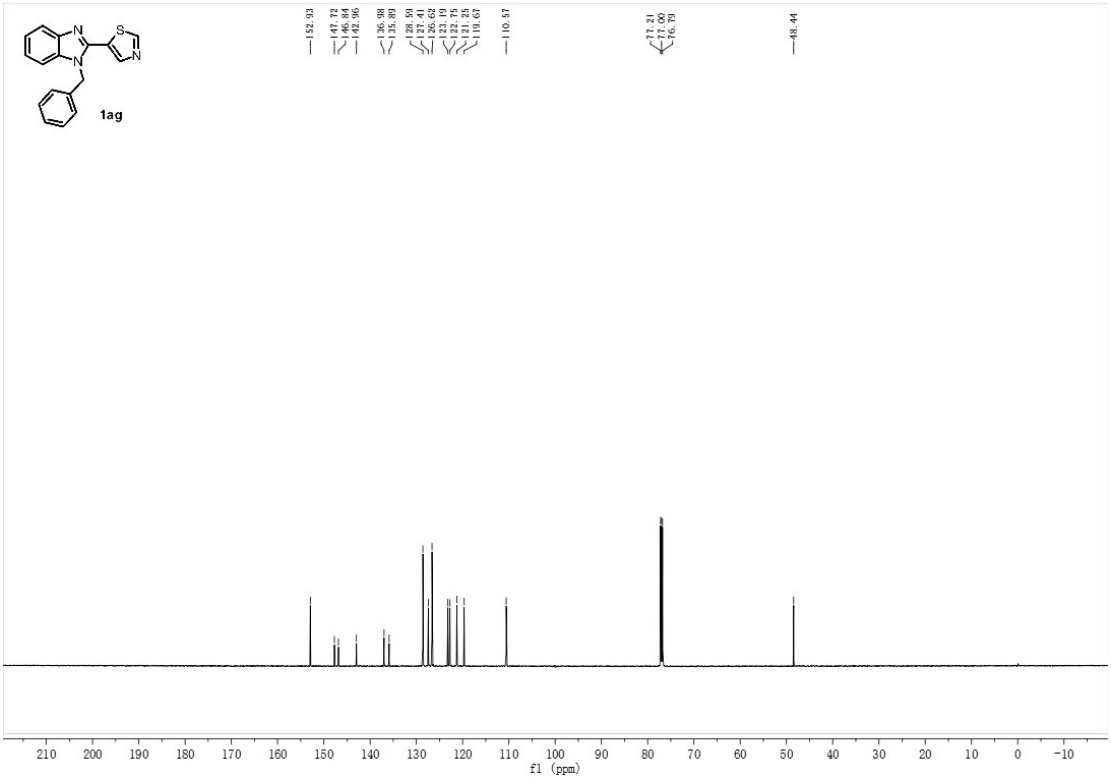

1ae
7.69
7.68
7.67
7.66
7.65
7.36
7.23
7.22
7.21
7.20
7.19
7.18
7.17
3.63
2.79
0.00
0.99
3.00
3.00
3.01
f1 (ppm)

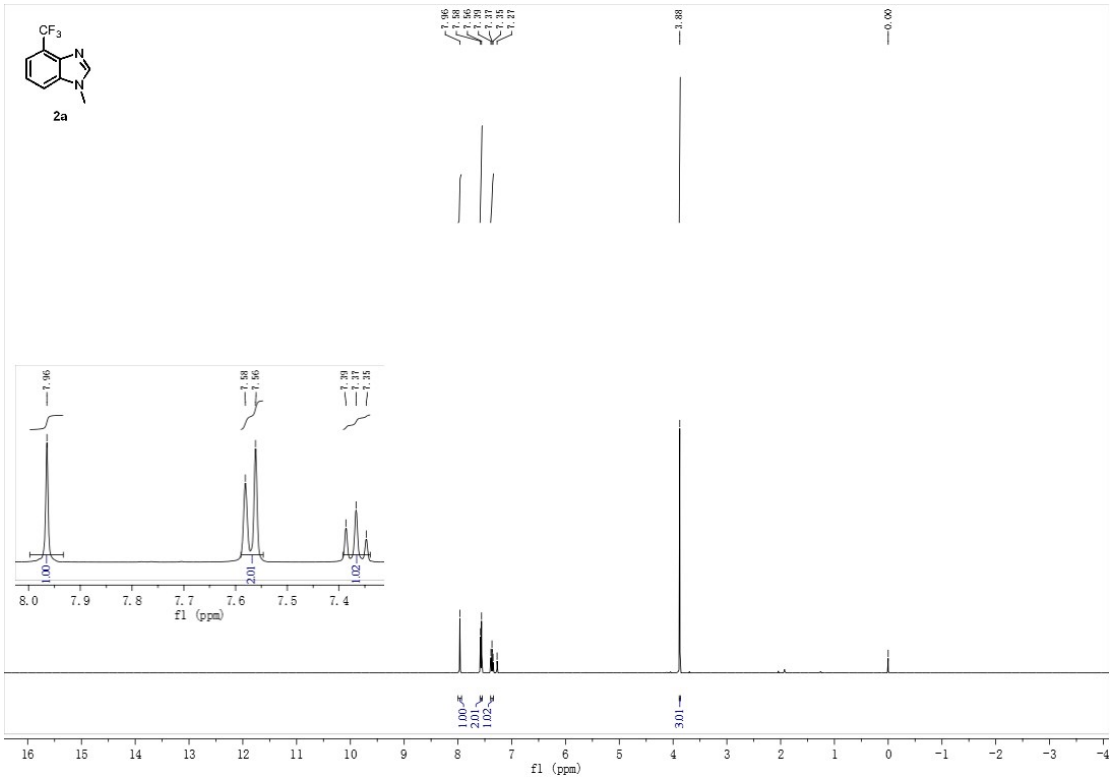

1ae
153.08
143.32
136.80
121.61
121.08
117.95
108.19
77.21
77.00
76.79
29.76
14.51
f1 (ppm)


1af
f1 (ppm)


1af
f1 (ppm)


1ag
f1 (ppm)


1ag
f1 (ppm)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7.96
7.58
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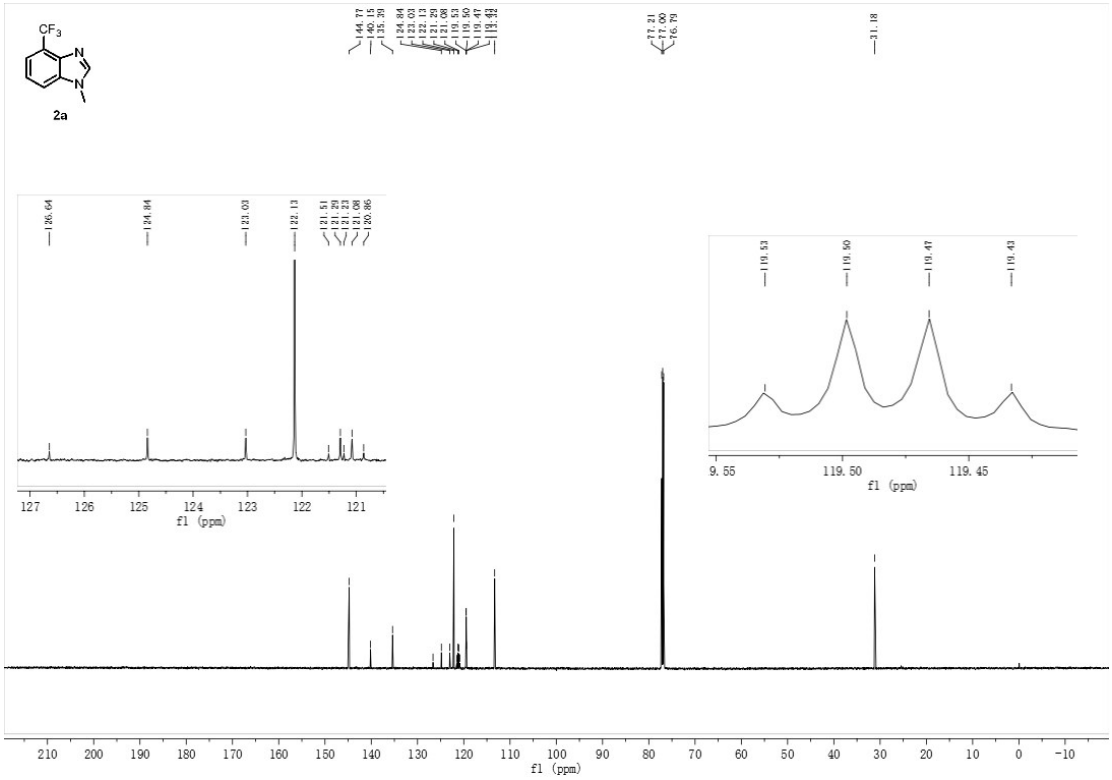
7.35
7.27
3.88
0.00
1.00
2.01
1.02
3.01
f1 (ppm)


2a
144.77
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135.39
124.84
123.03
122.13
121.51
121.29
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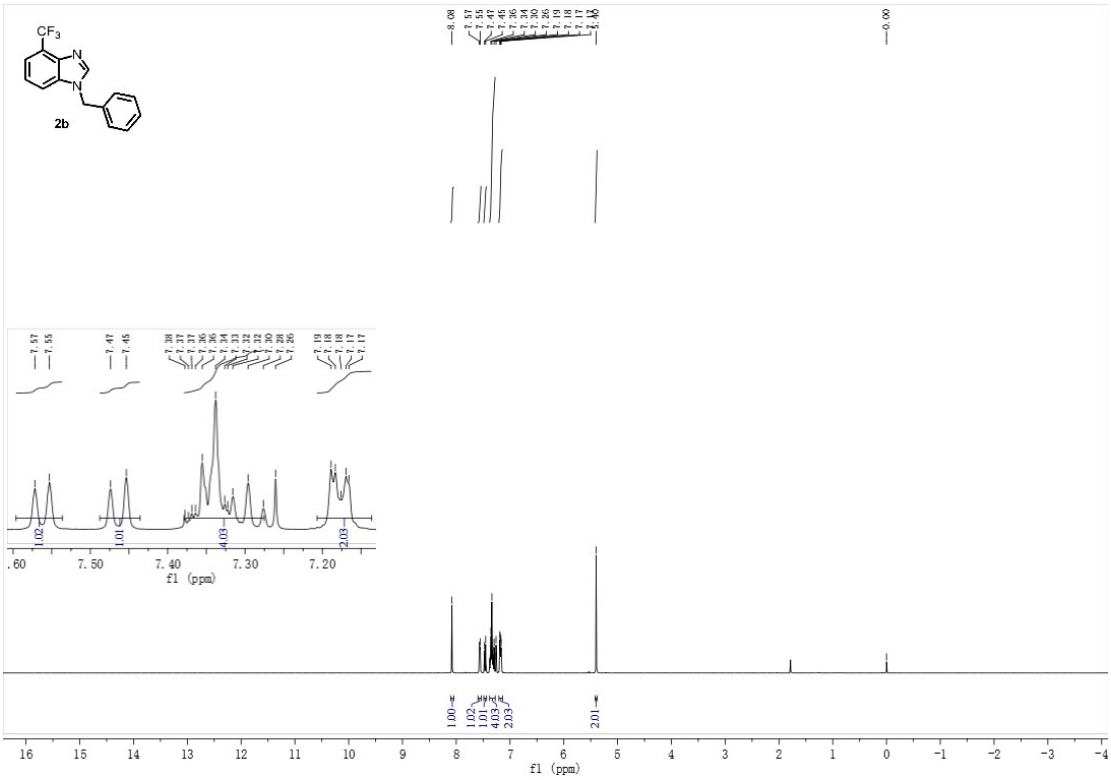
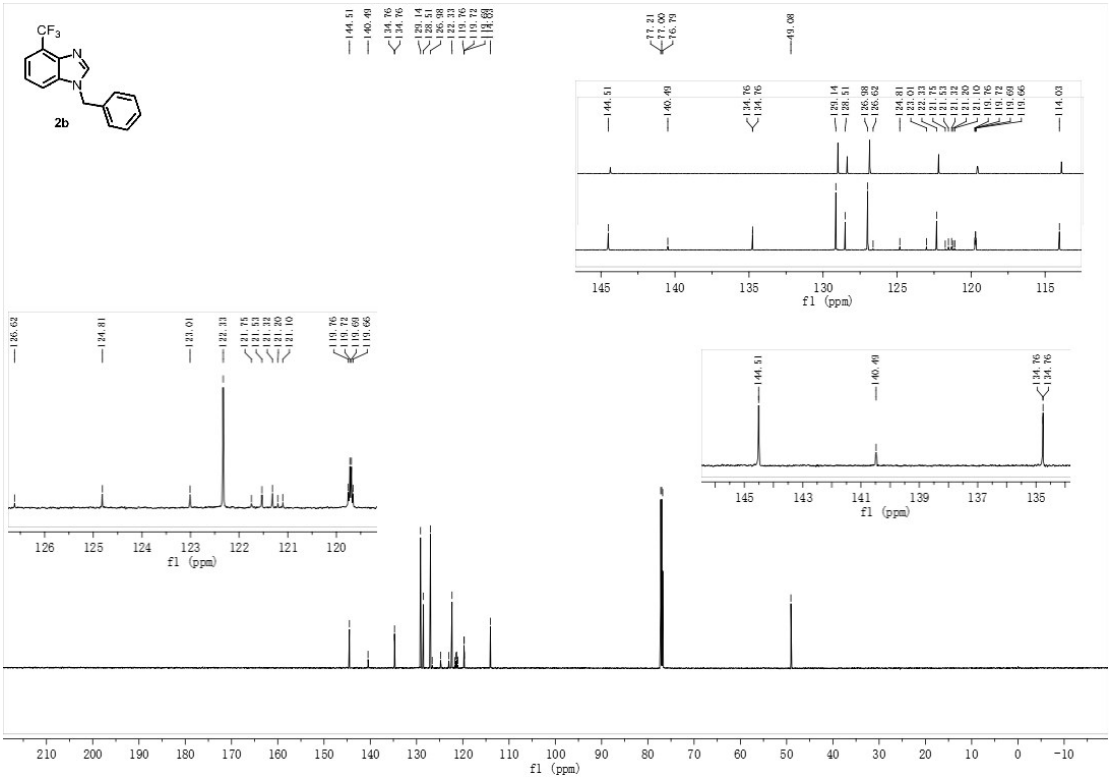
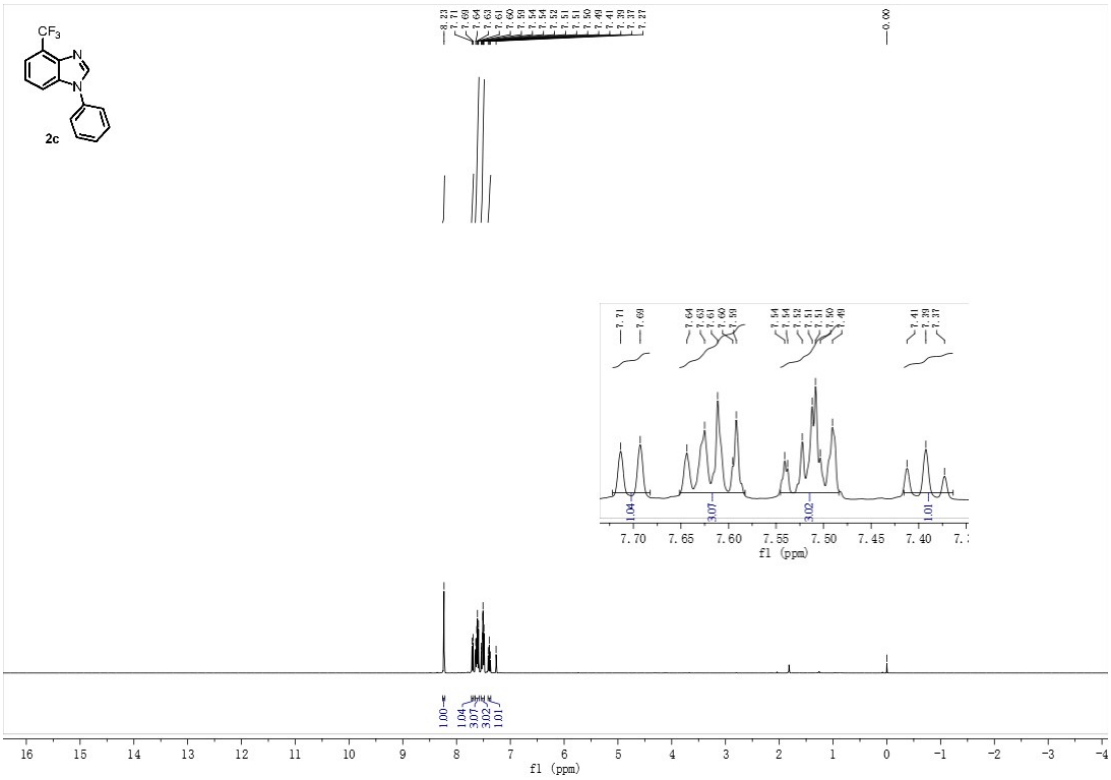
119.53
119.50
119.47
119.43
77.21
77.00
76.79
31.18
f1 (ppm)


2b
f1 (ppm)


2b
f1 (ppm)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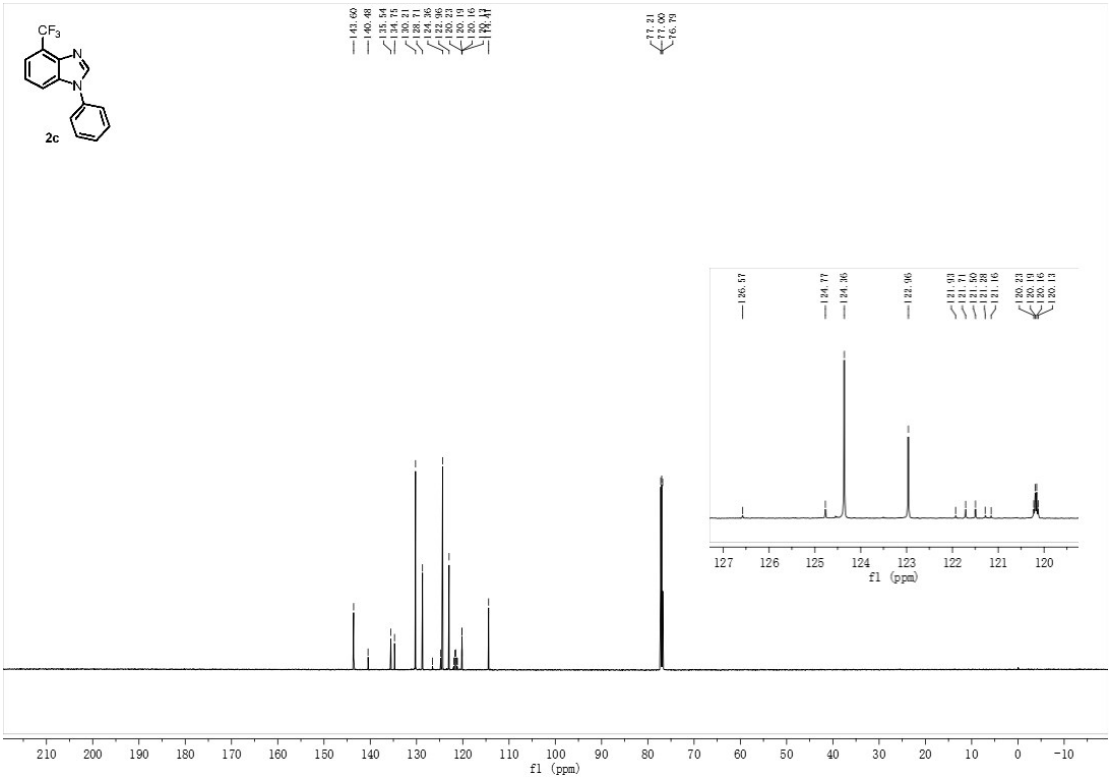
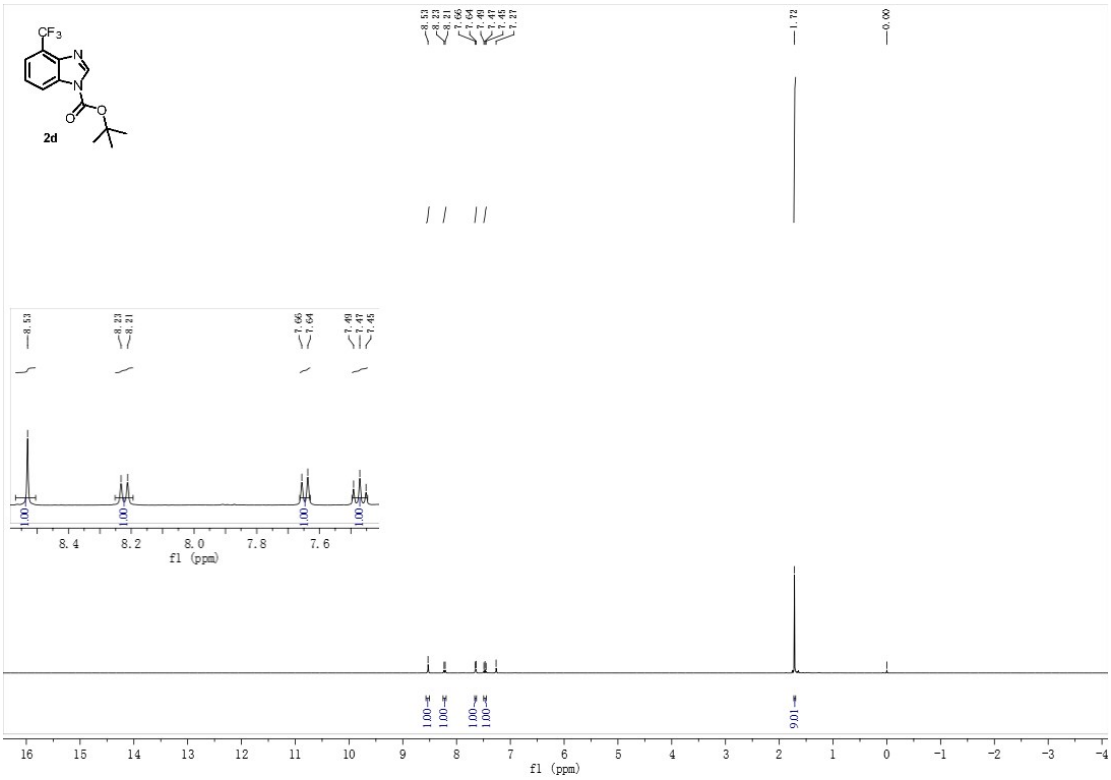
f1 (ppm)


2c
f1 (ppm)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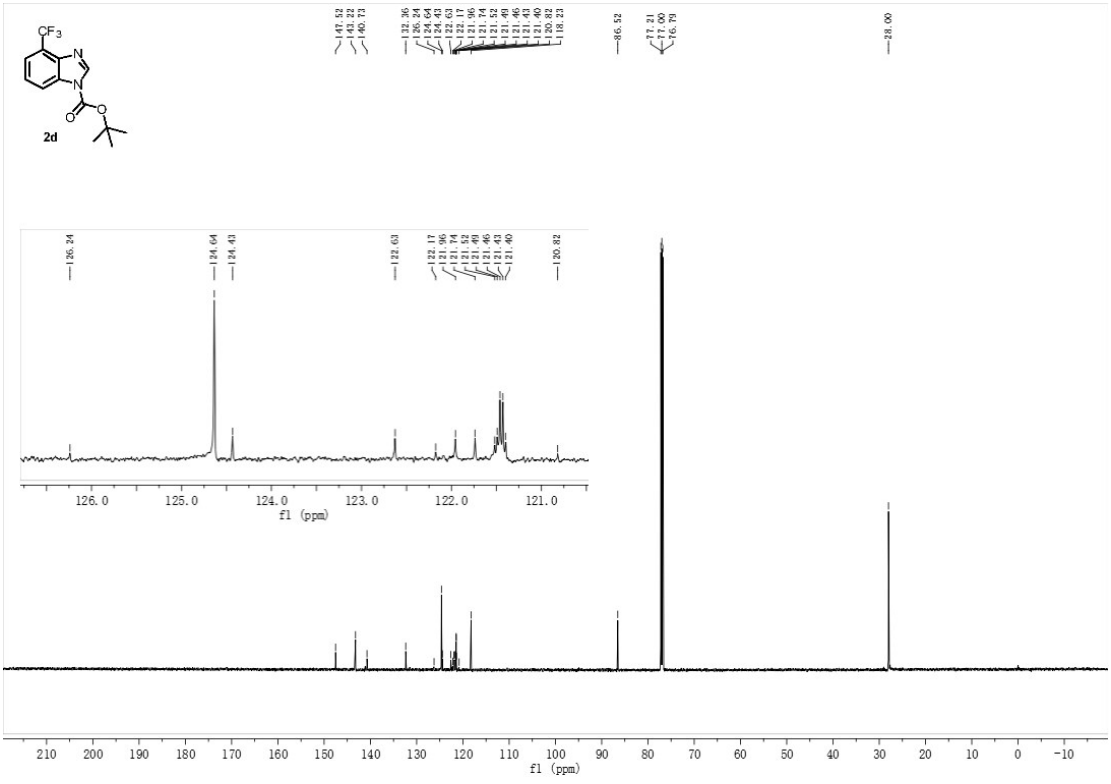
f1 (ppm)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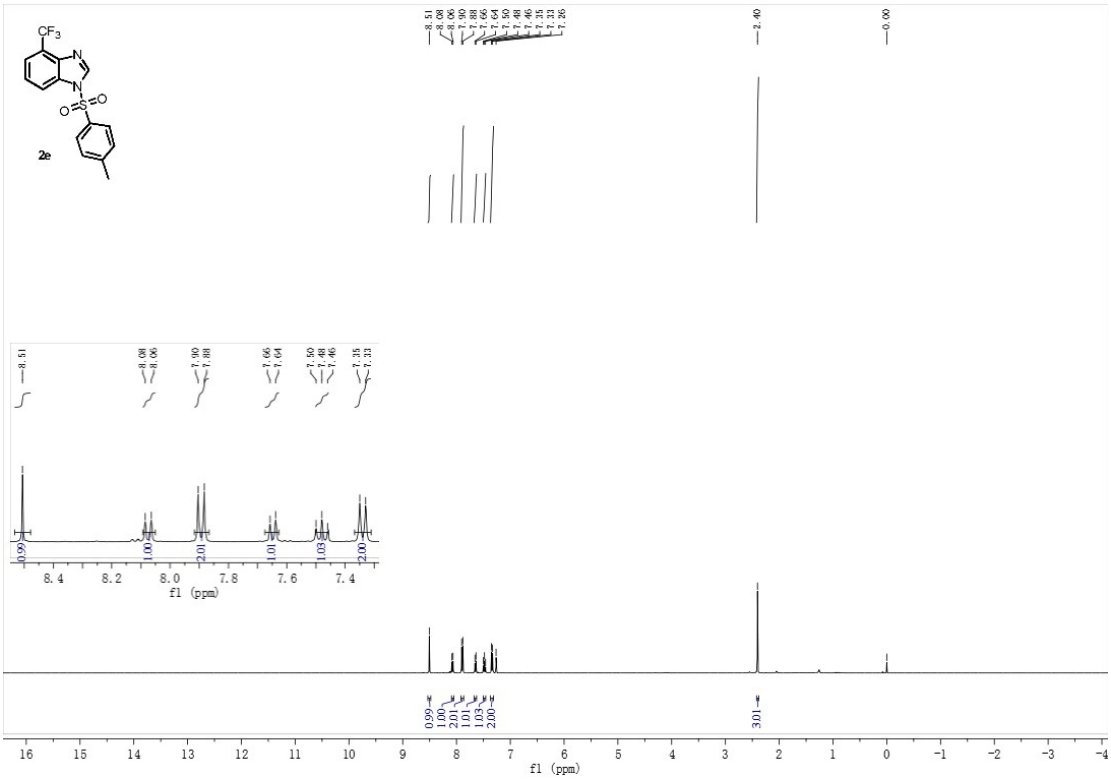
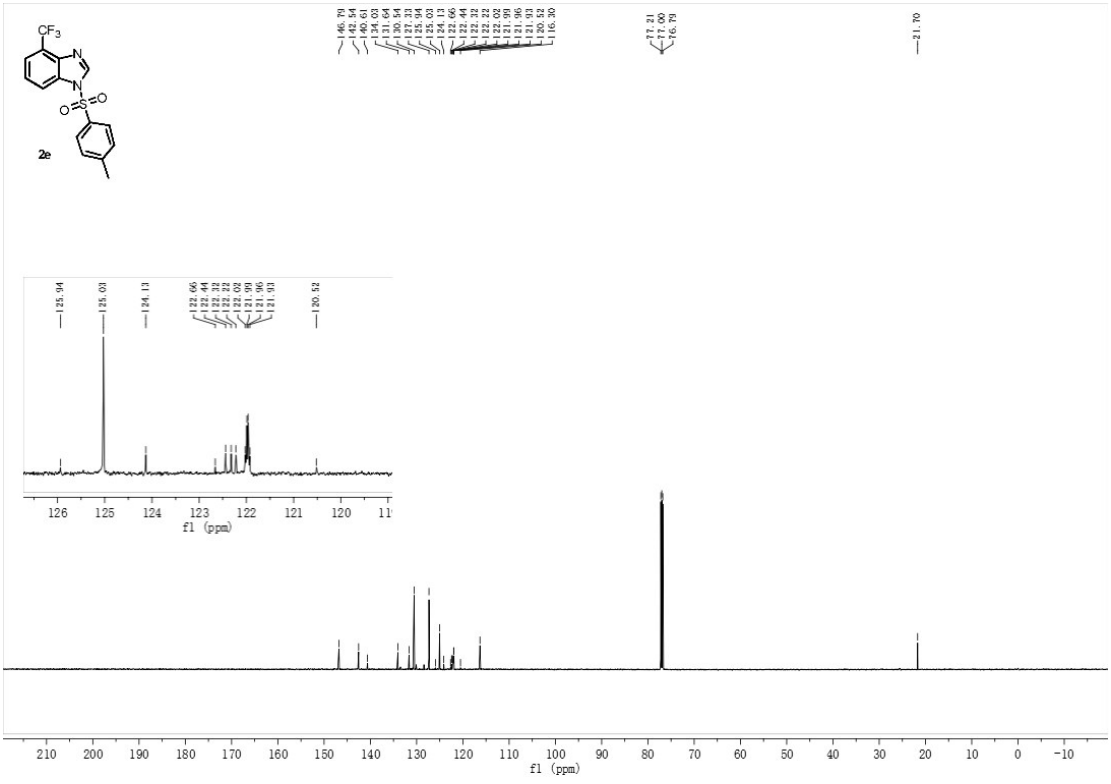
f1 (ppm)


2e
f1 (ppm)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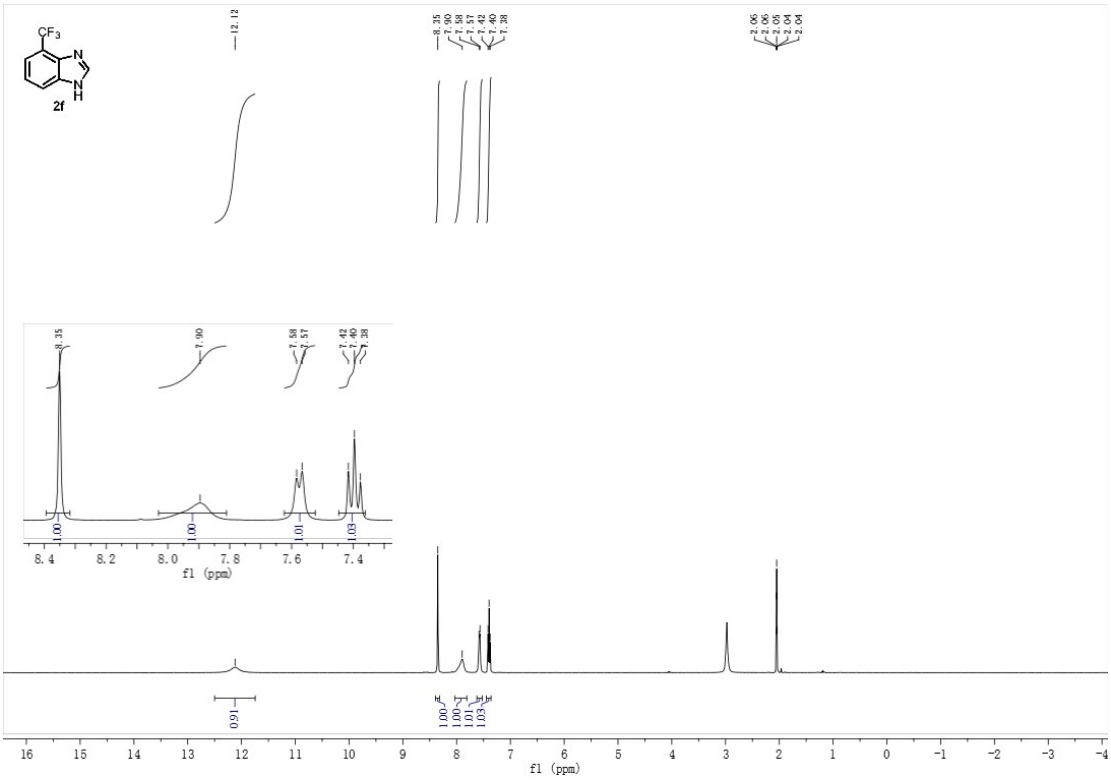
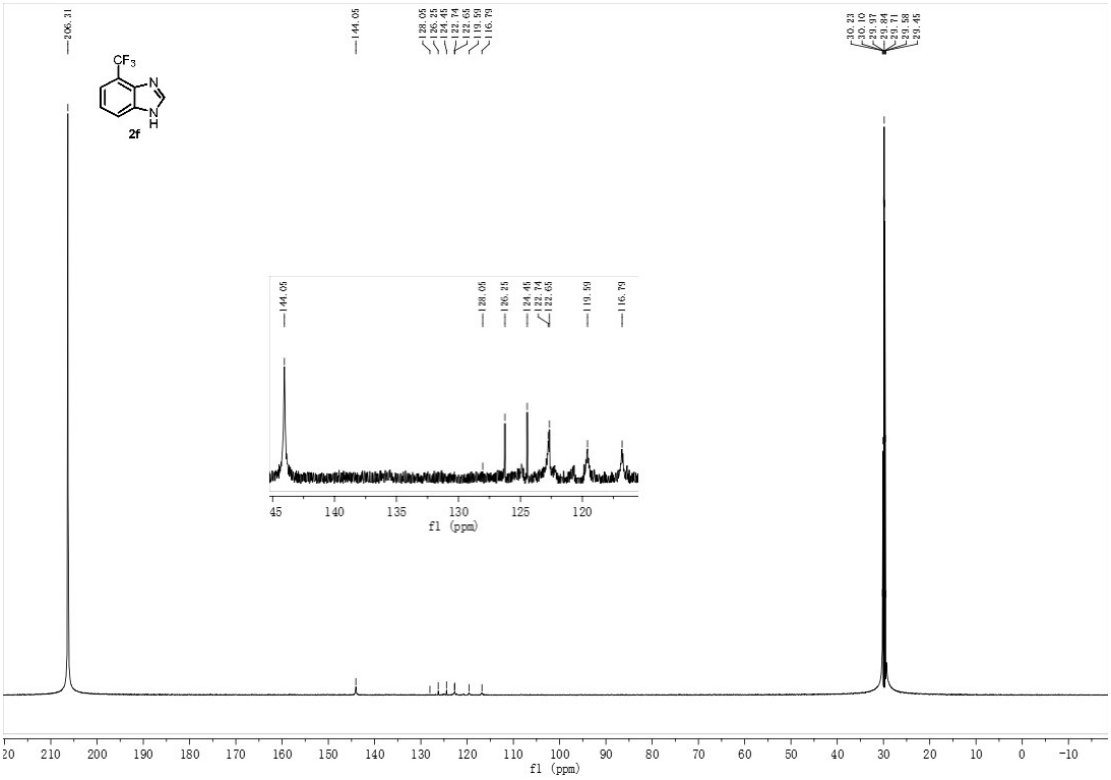
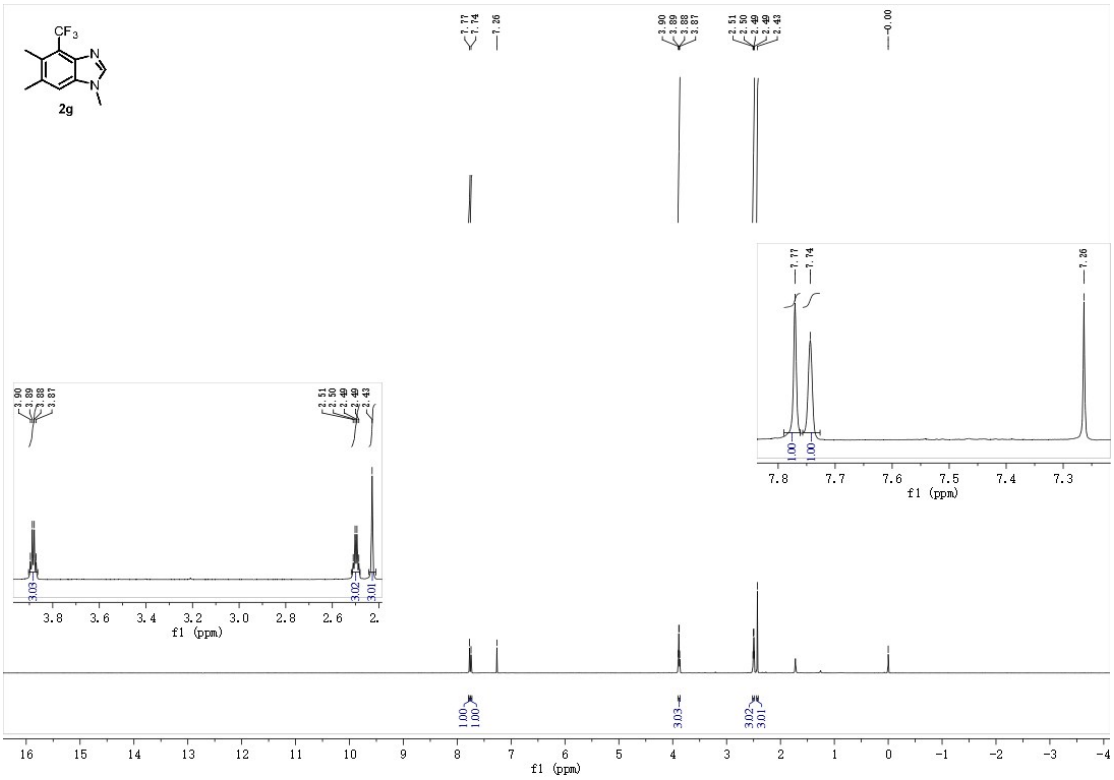
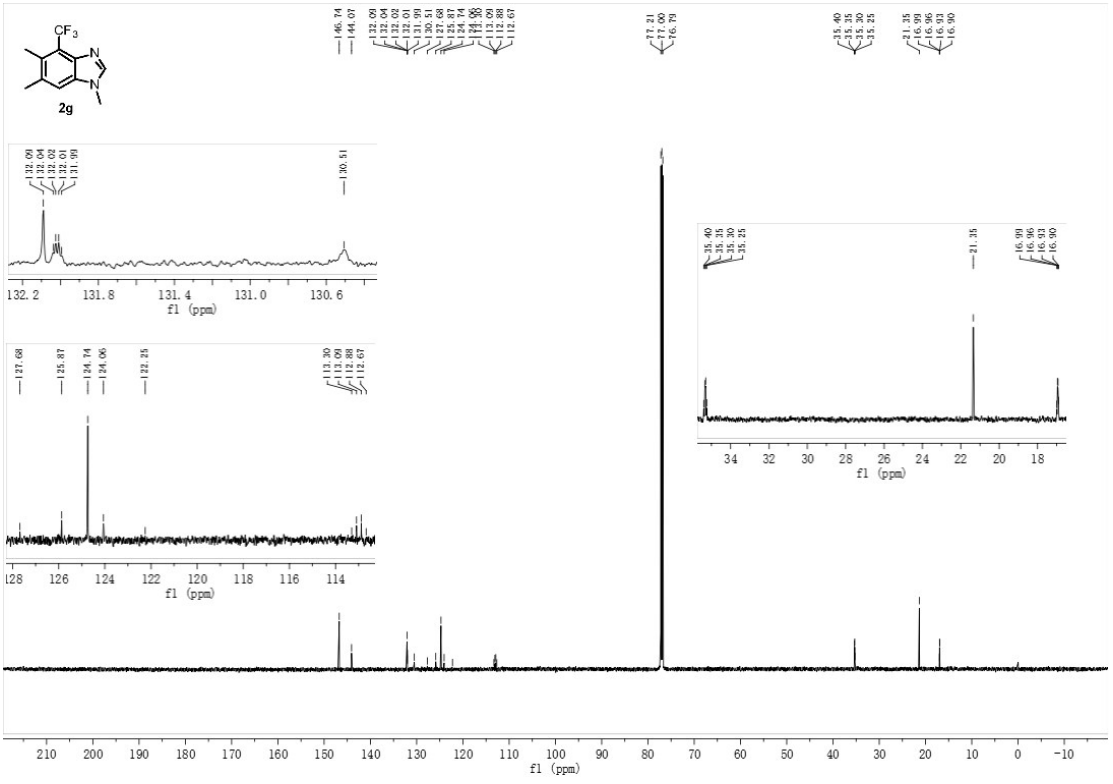
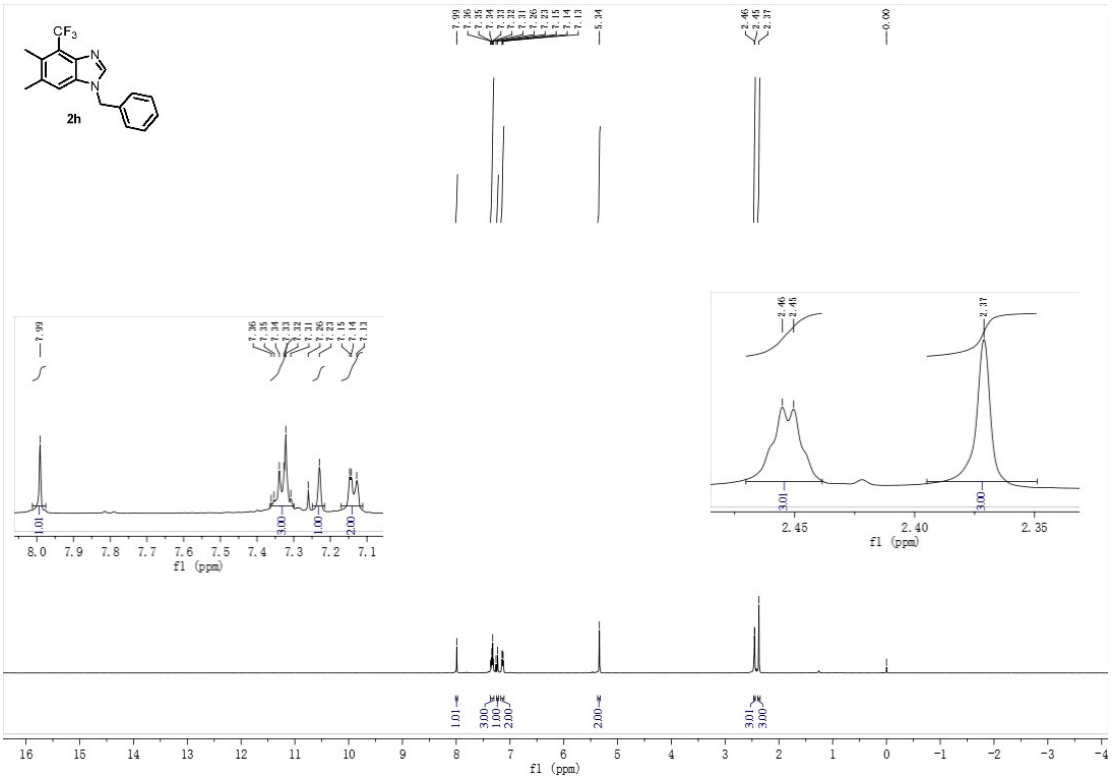
f1 (ppm)

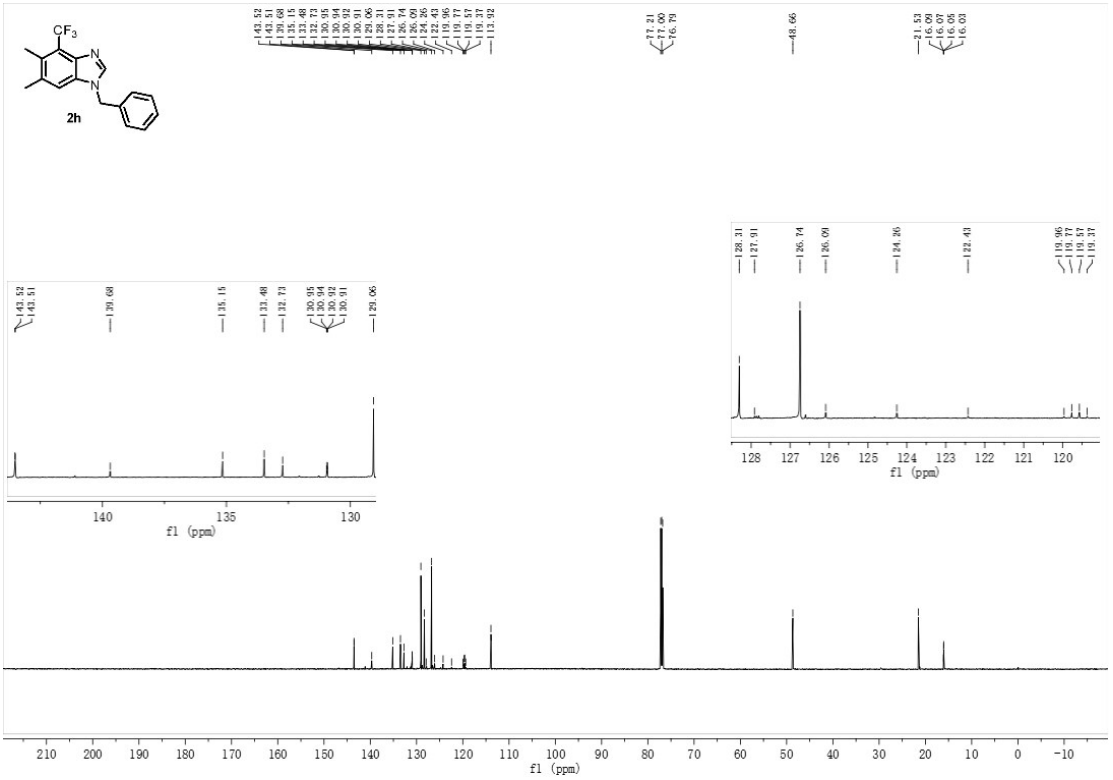

2f
f1 (ppm)


2f
f1 (ppm)


2g
f1 (ppm)


2g
f1 (ppm)


2h
f1 (ppm)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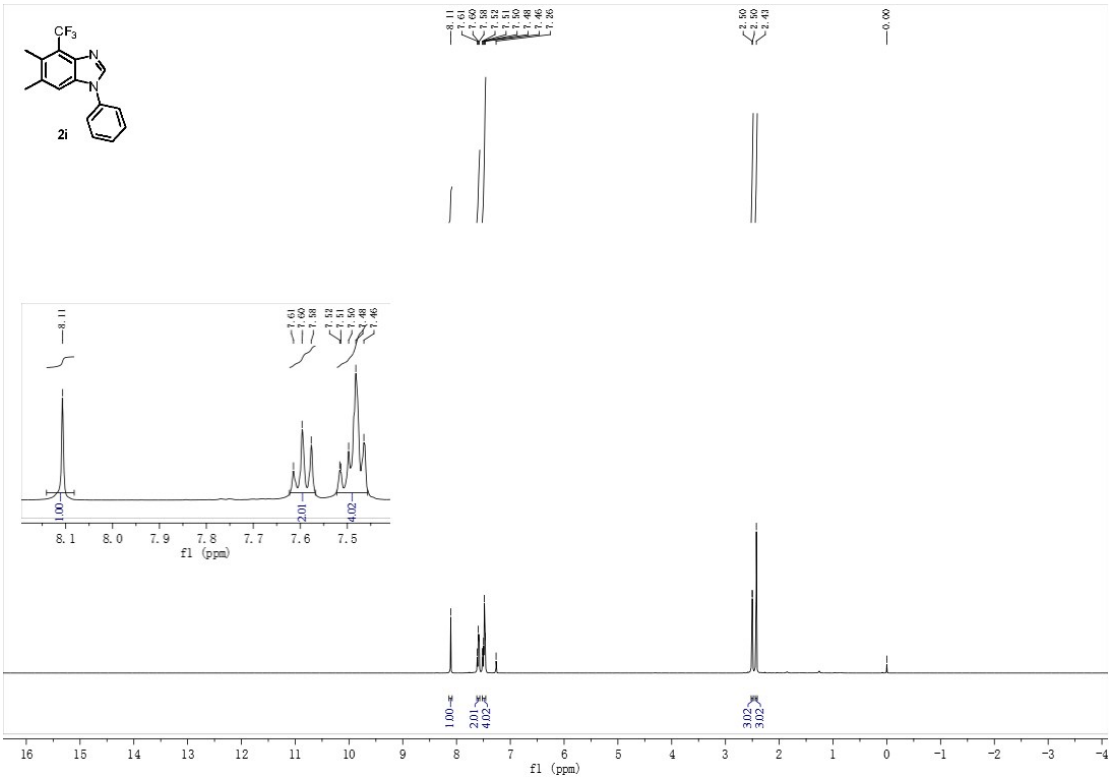
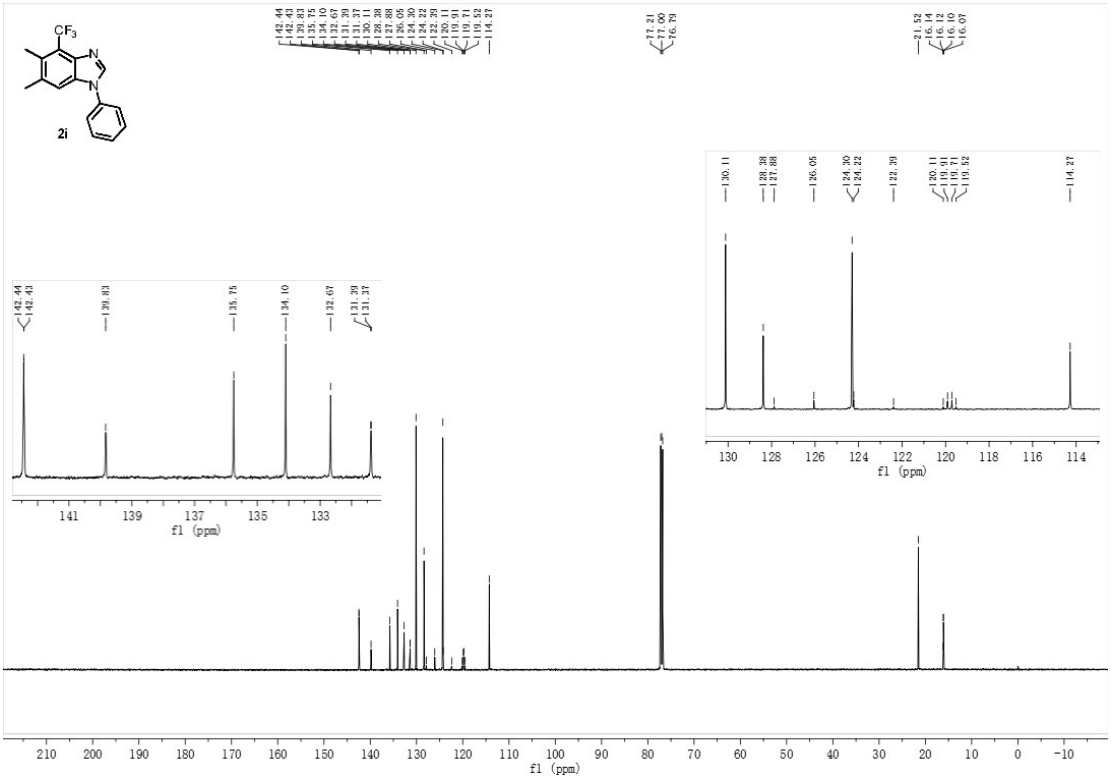
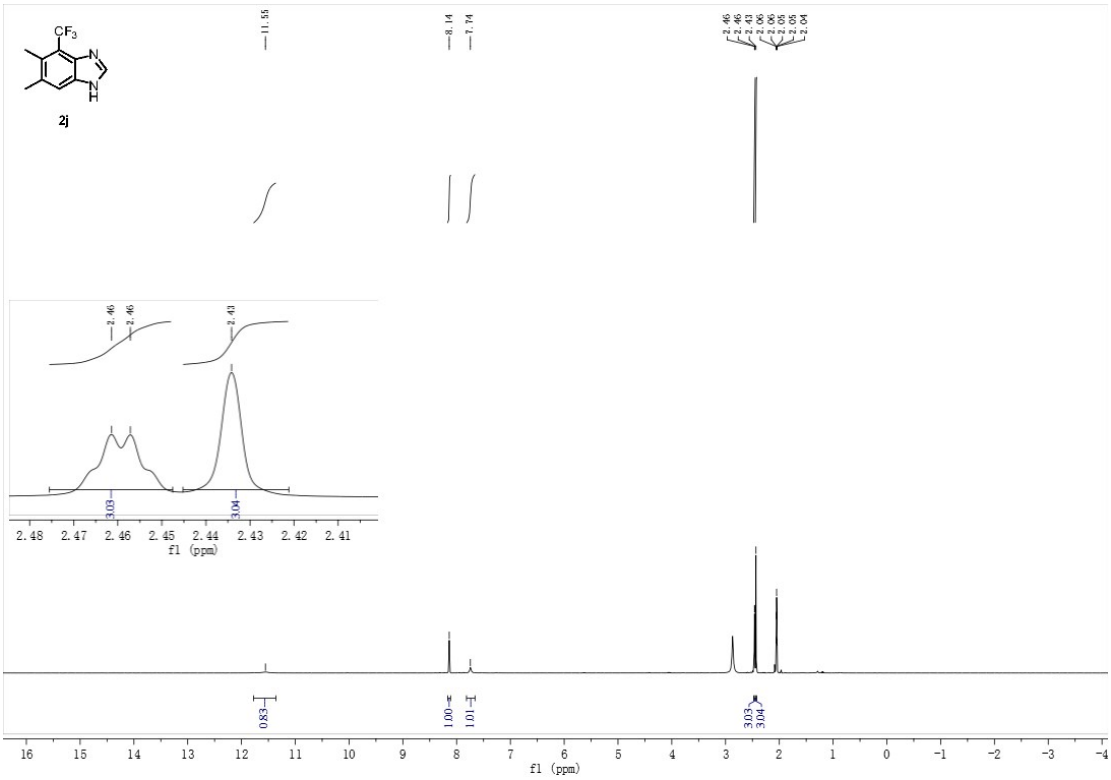
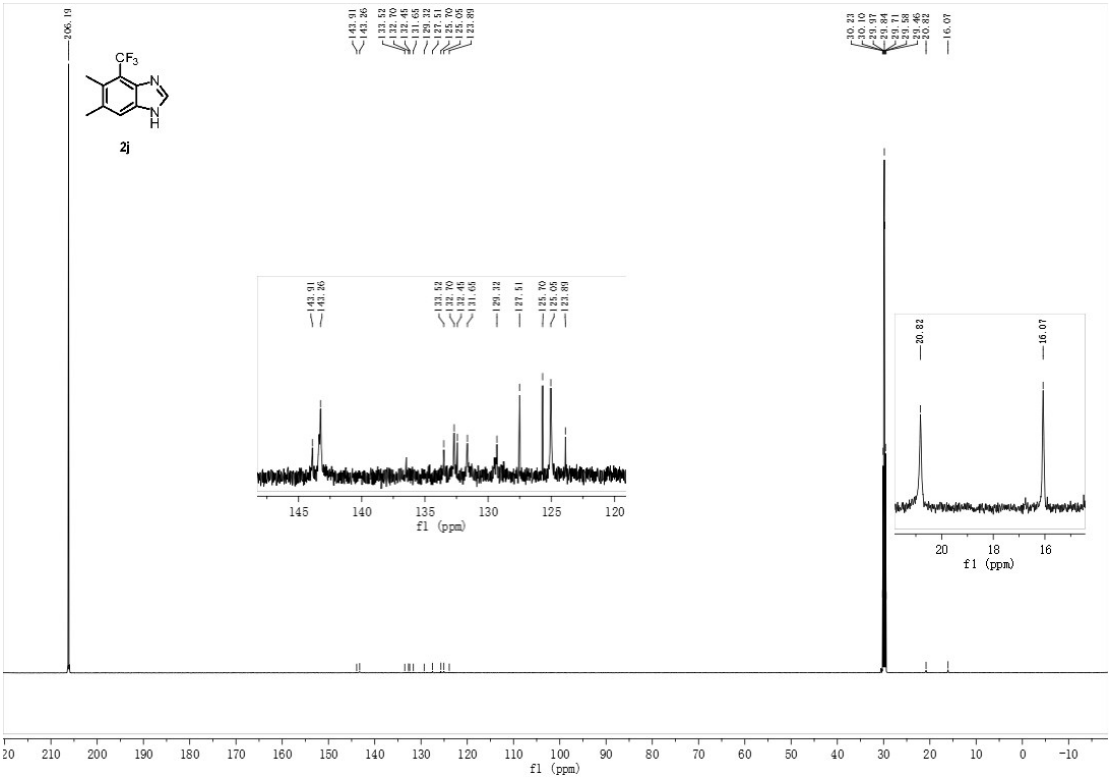
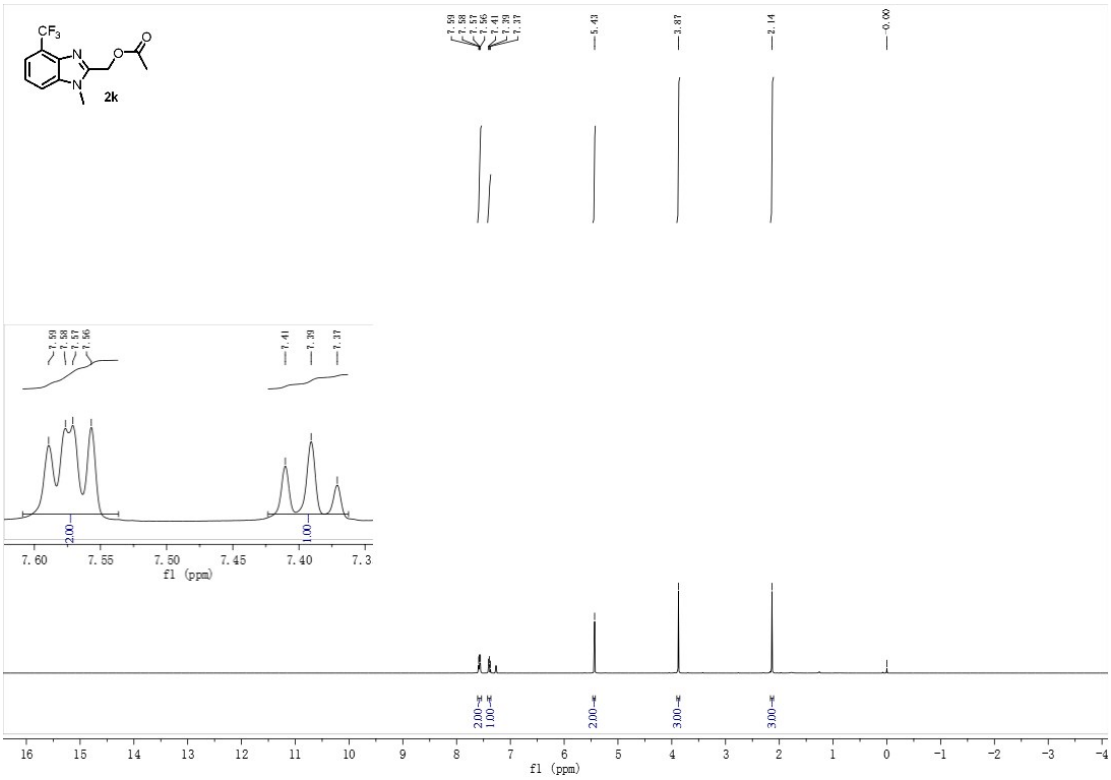
f1 (ppm)


2i
f1 (ppm)


2i
f1 (ppm)


2j
11.55
8.14
7.74
2.46
2.46
2.43
2.06
2.06
2.05
2.04
0.83
1.00
1.01
3.03
3.04
f1 (ppm)


2j
206.19
143.91
143.36
133.52
132.70
132.46
131.65
129.32
127.51
125.70
125.05
123.89
30.23
30.10
29.97
29.84
29.71
29.58
29.46
20.82
16.07
f1 (ppm)


2k
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7.57
7.56
7.41
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7.37
5.43
3.87
2.14
0.00
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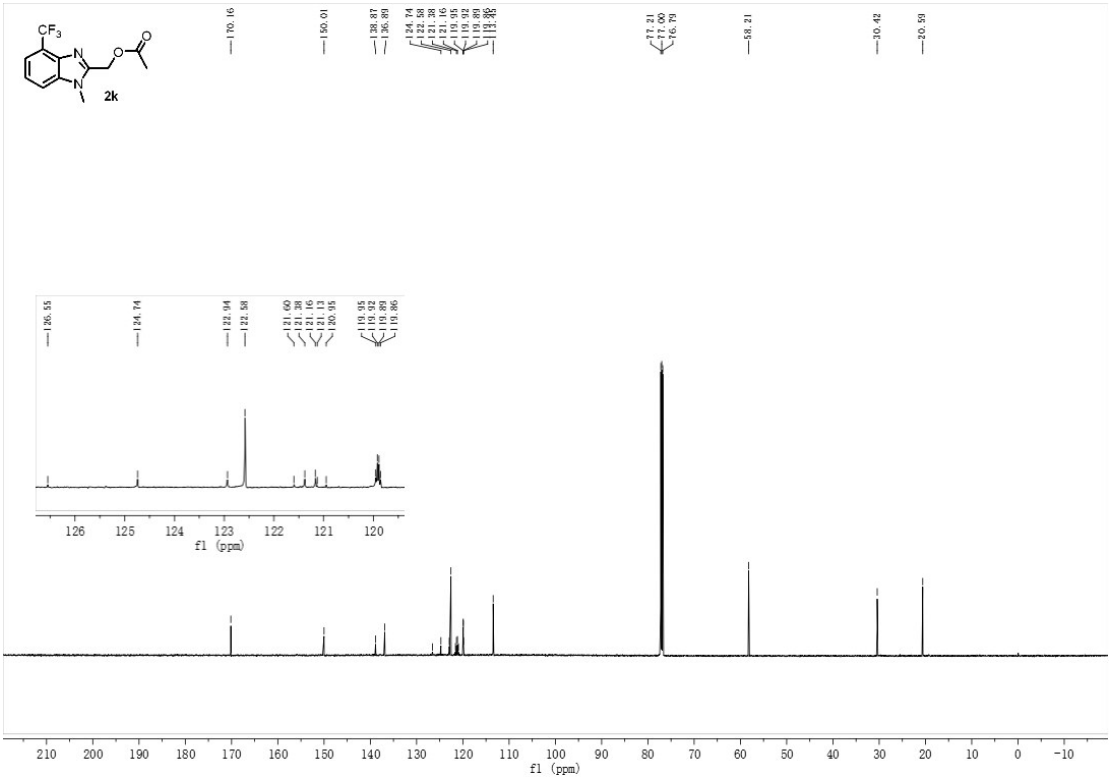
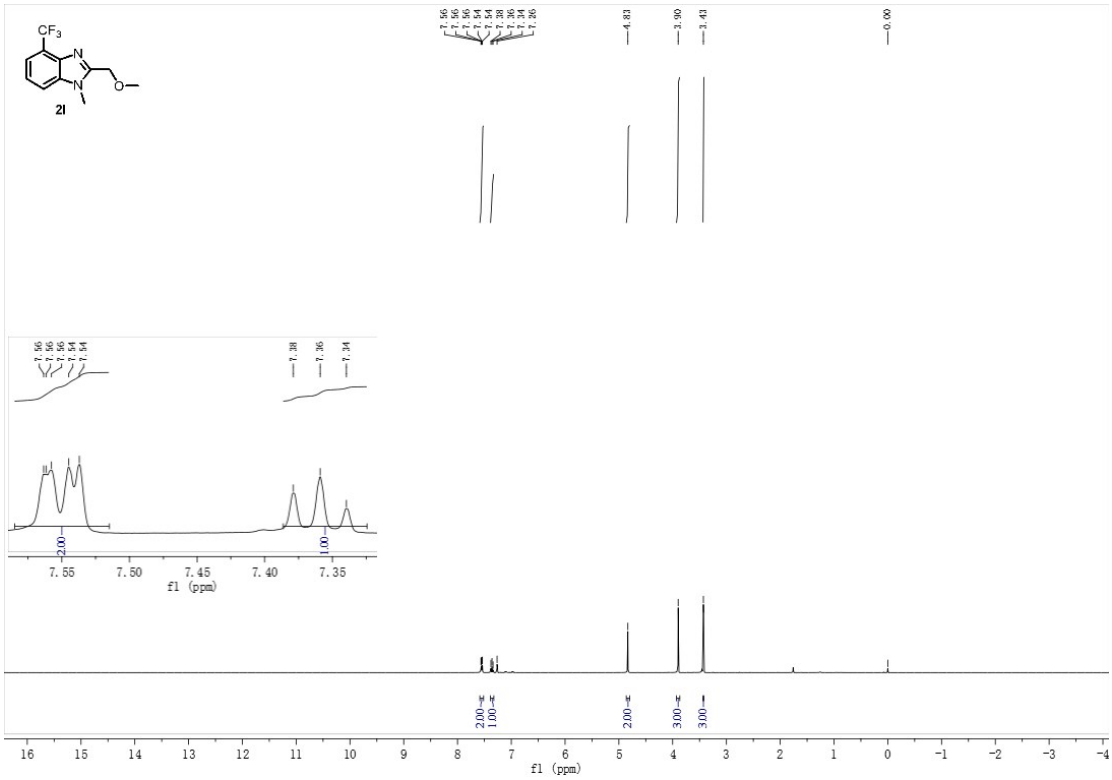
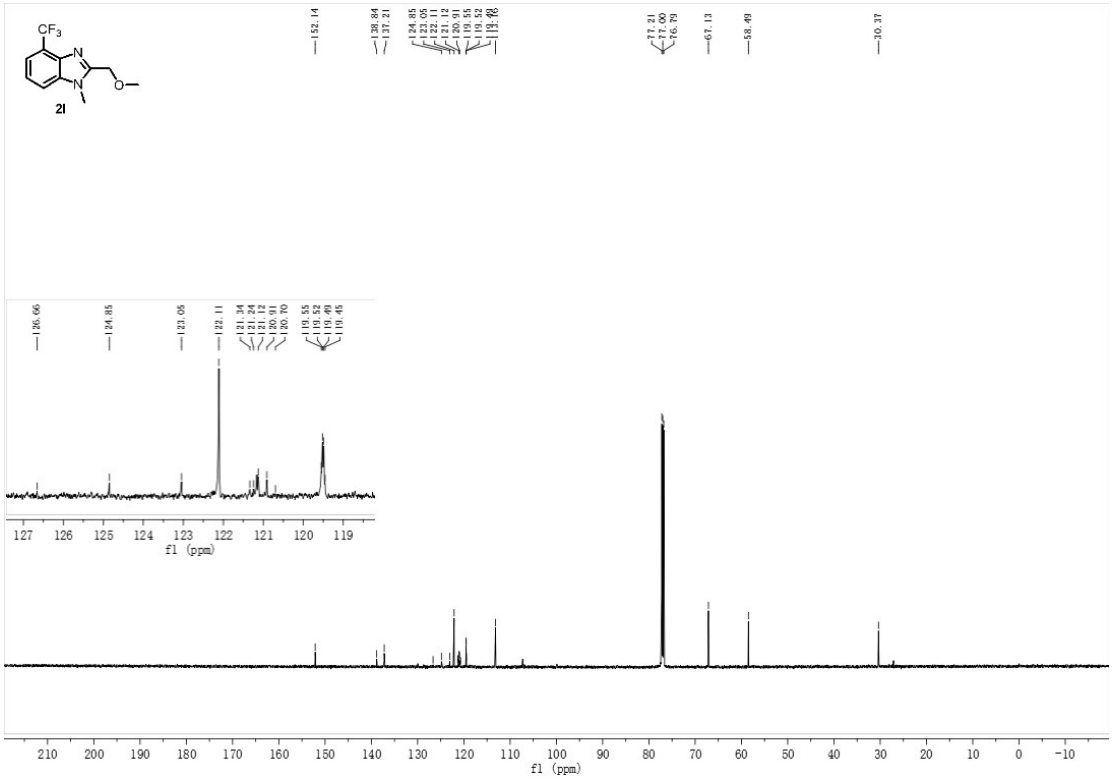
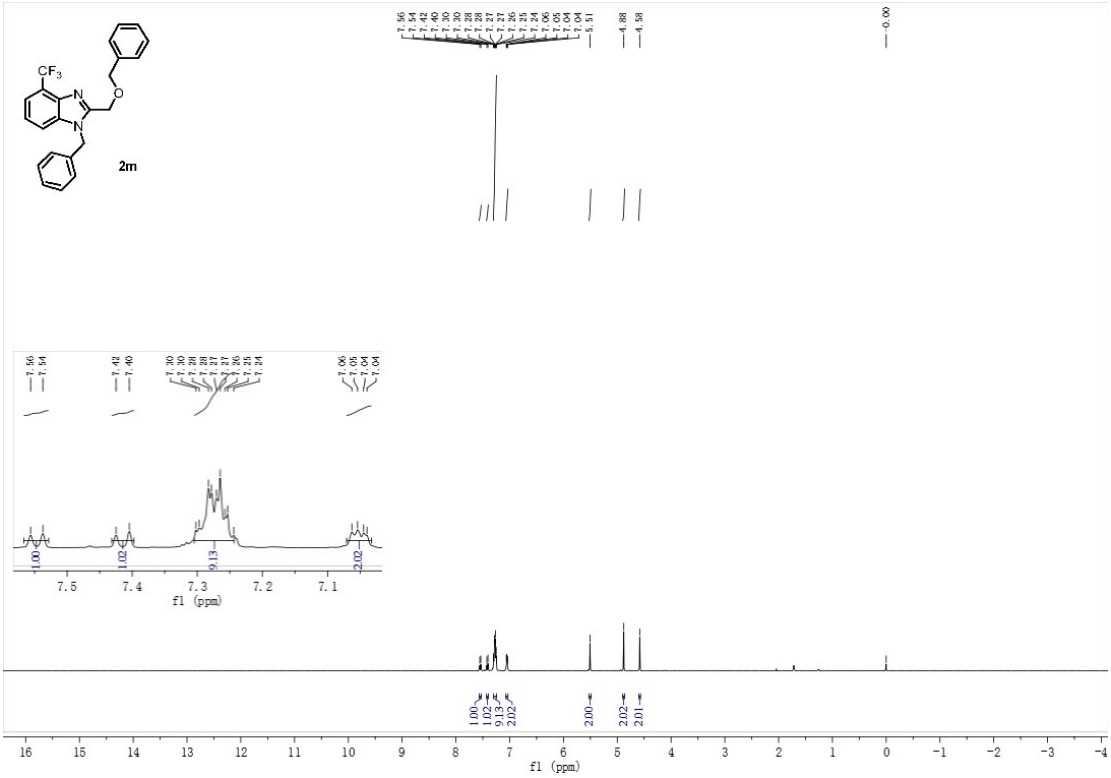
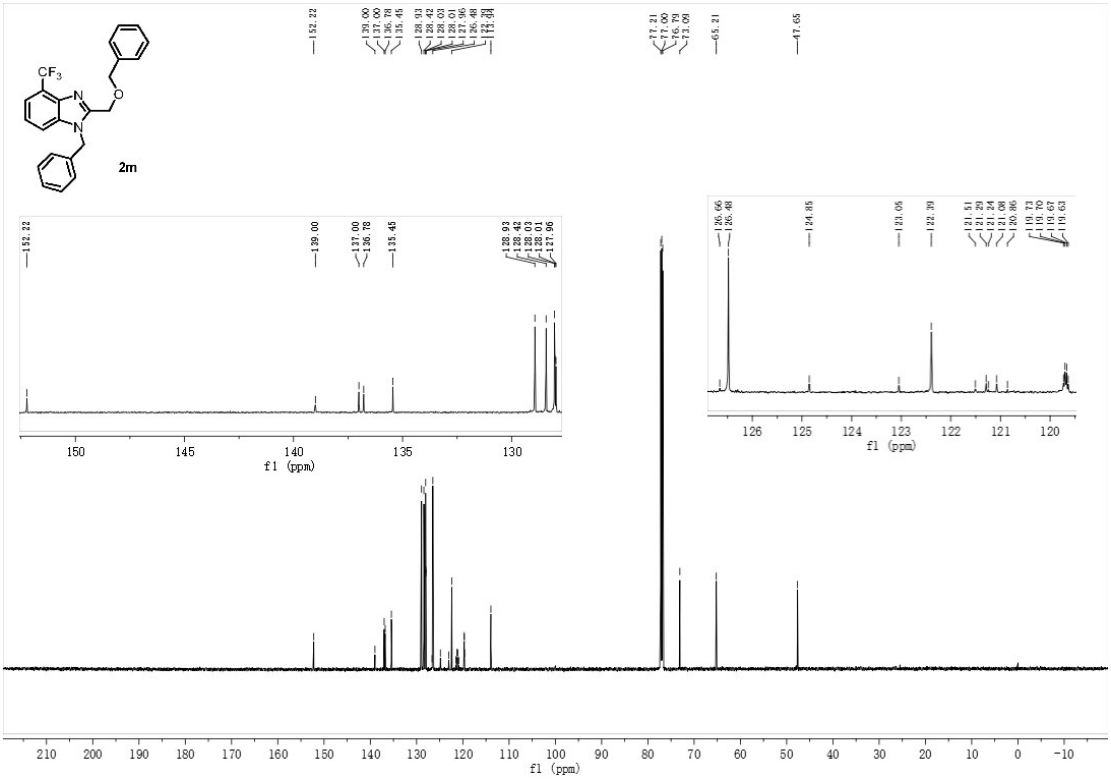
1.00
2.00
3.00
3.00
f1 (ppm)

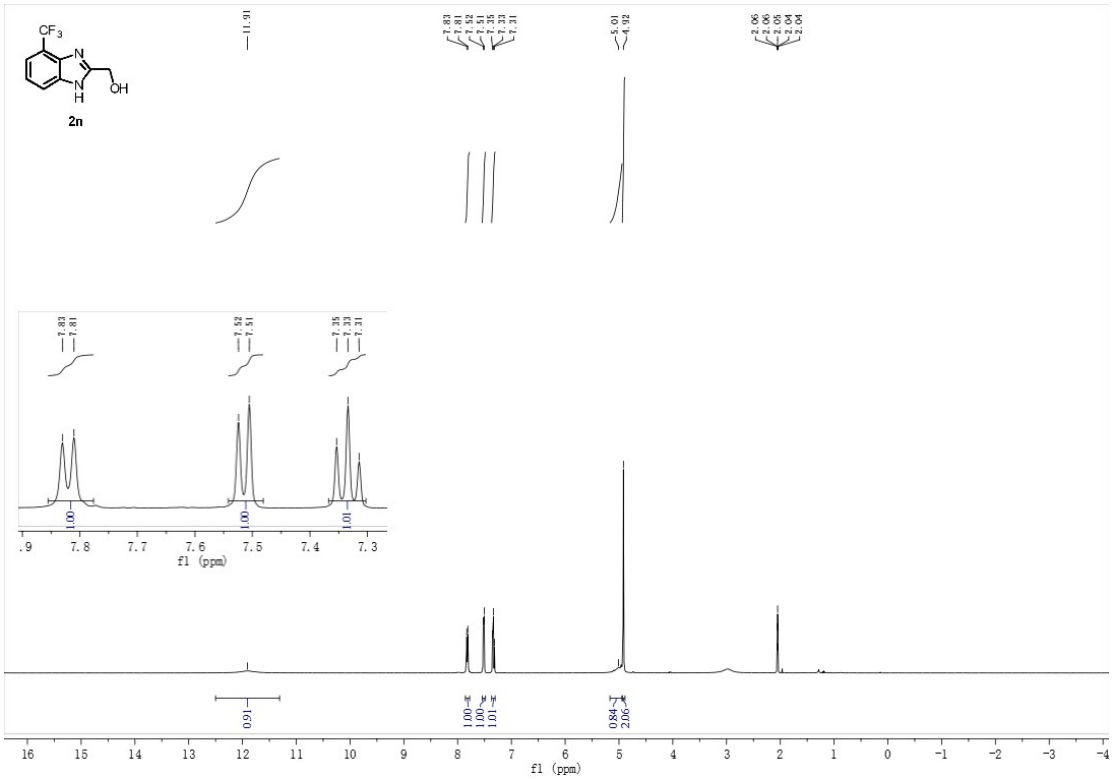

2k
170.16
150.01
138.87
136.89
124.74
122.58
121.38
121.16
119.95
119.92
119.89
119.86
113.48
77.21
77.00
76.79
58.21
30.42
20.59
126.55
124.74
122.94
122.58
121.60
121.38
121.16
121.13
120.95
119.95
119.92
119.89
119.86
f1 (ppm)

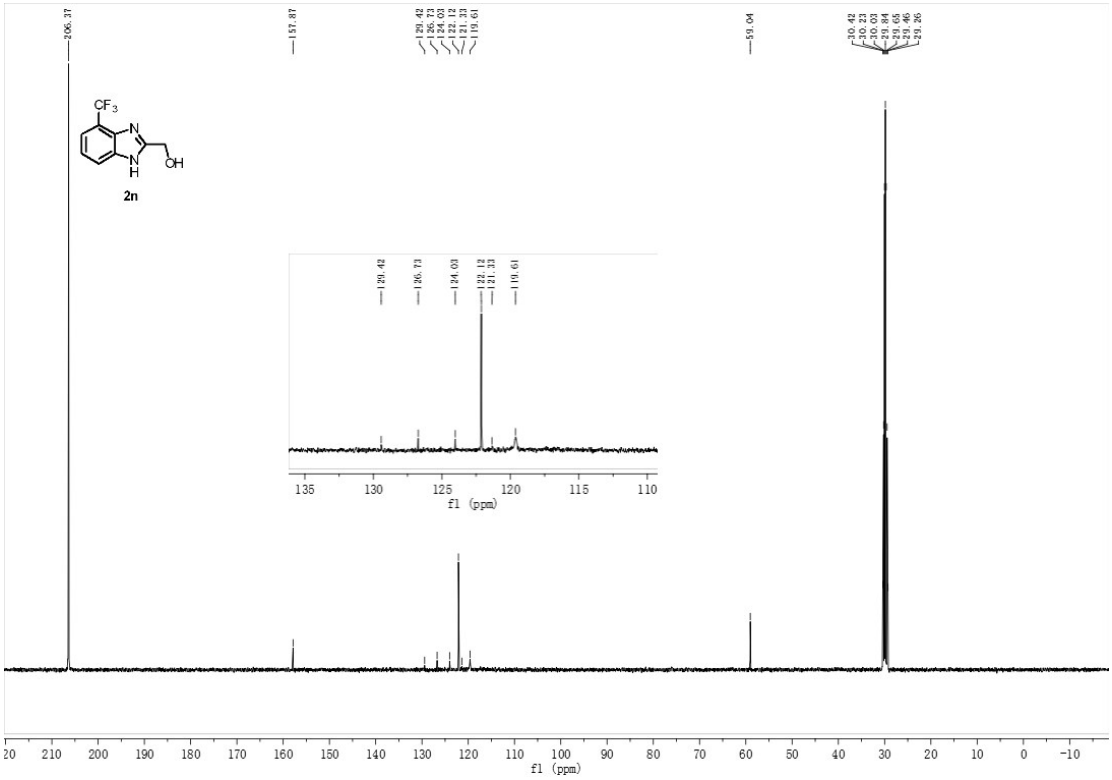

CF3
N
N
O
2l
7.56
7.56
7.55
7.54
7.54
7.38
7.36
7.34
7.34
7.26
4.83
3.90
3.43
0.00
7.38
7.36
7.34
2.00
1.00
7.55
7.50
7.45
7.40
7.35
f1 (ppm)
2.00
1.00
2.00
3.00
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
−4
f1 (ppm)

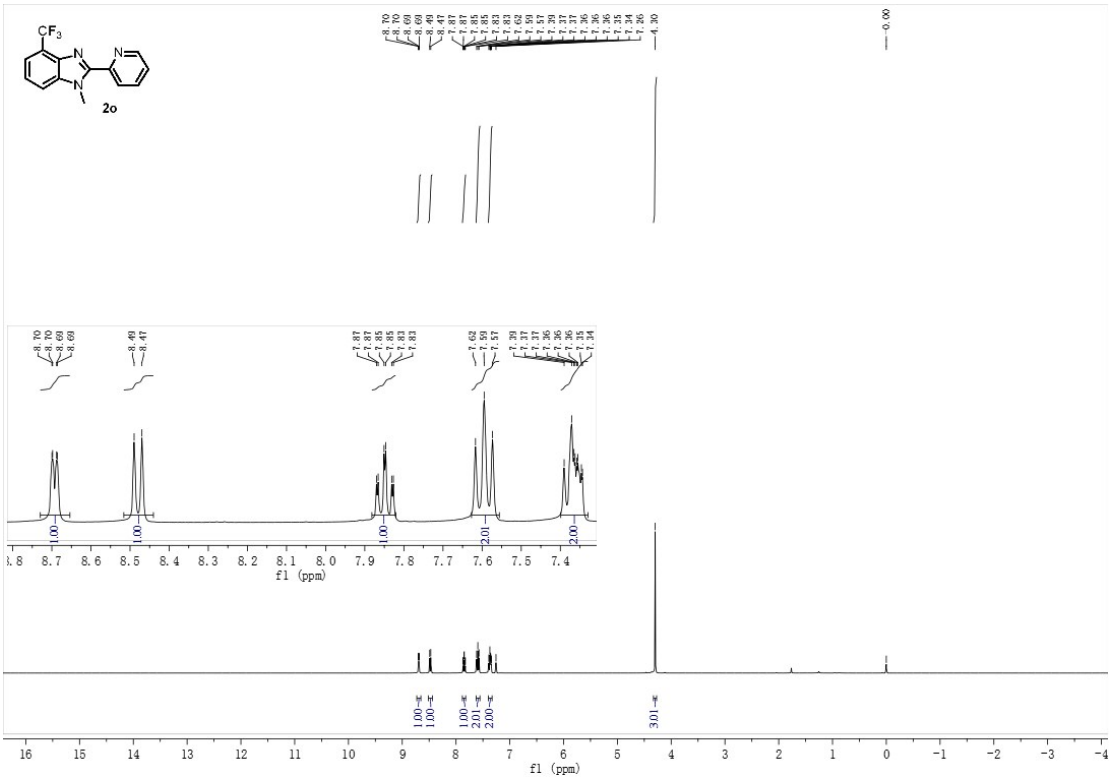

CF3
N
N
O
2l
152.14
138.84
137.21
124.85
123.05
122.11
121.34
121.24
121.12
120.91
120.70
119.55
119.52
119.49
119.45
113.78
77.21
77.00
76.79
67.13
58.49
30.37
125.66
124.85
123.05
122.11
121.34
121.24
121.12
120.91
120.70
119.55
119.52
119.49
119.45
127
126
125
124
123
122
121
120
119
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

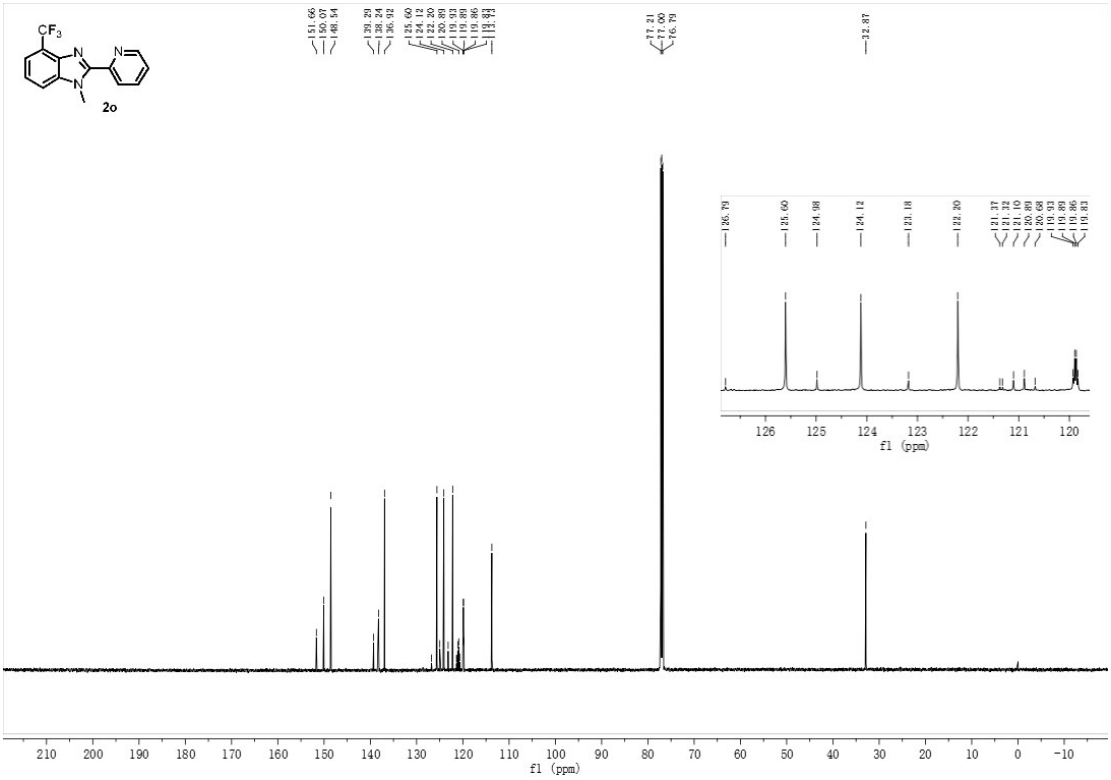

2m
f1 (ppm)

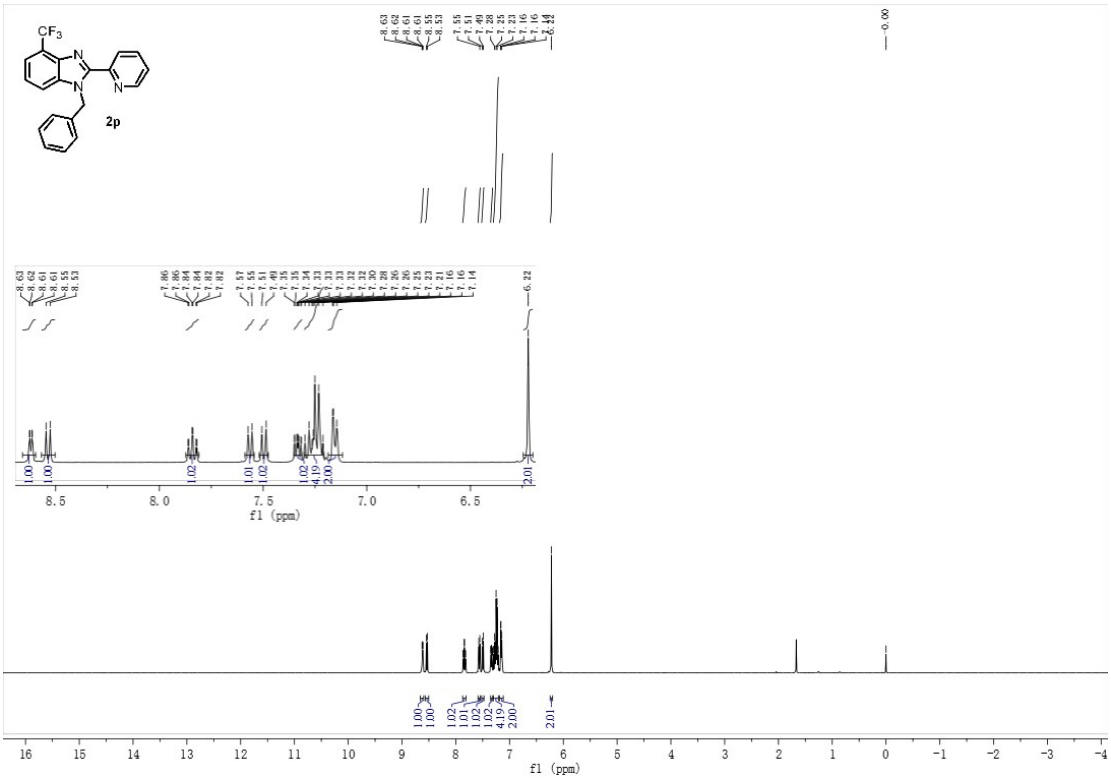

2m
f1 (ppm)

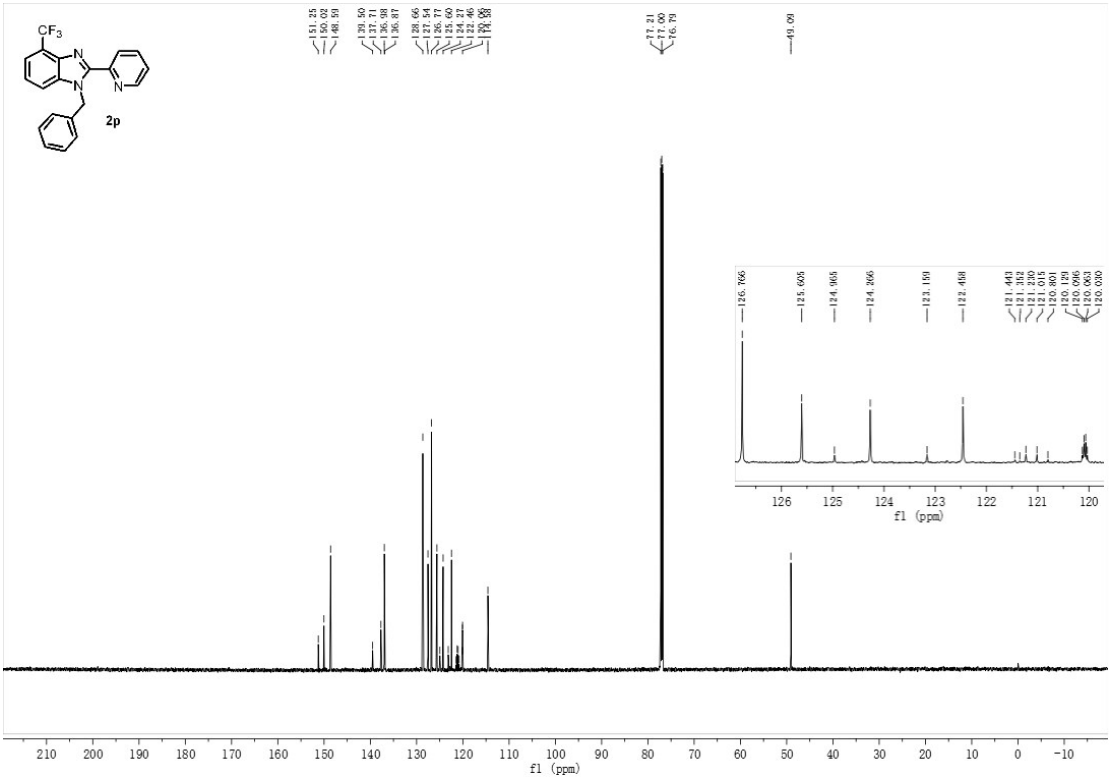

2n
f1 (ppm)

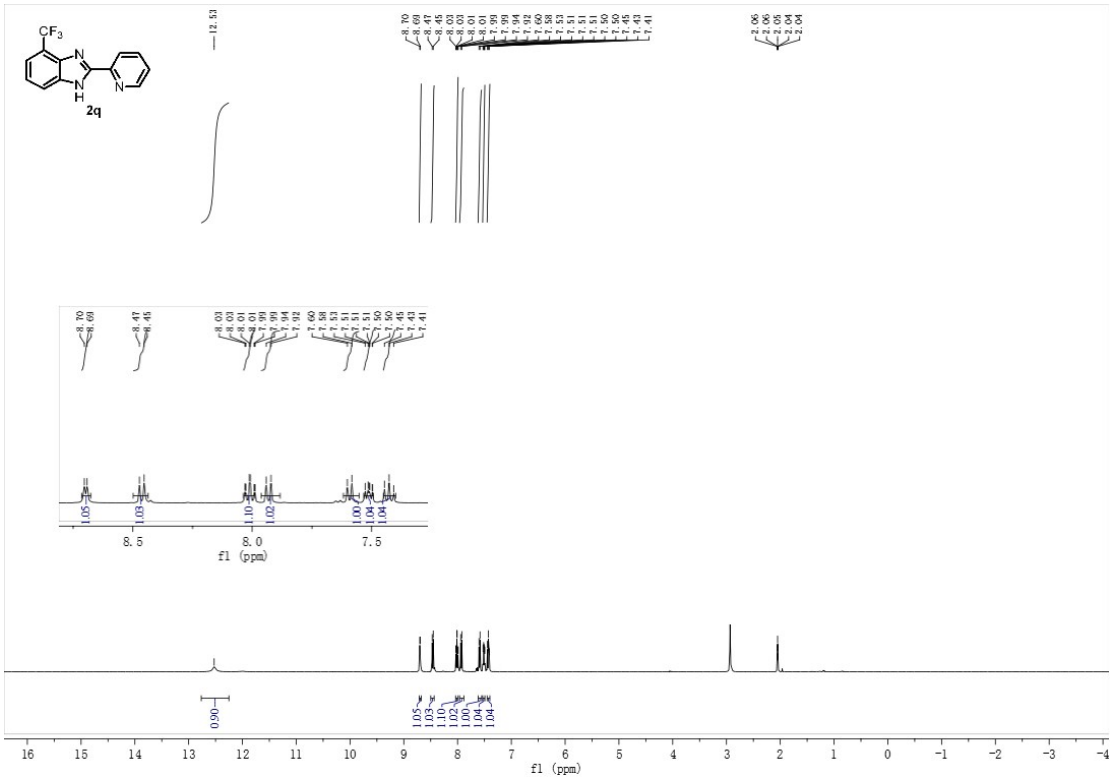

2n
f1 (ppm)


2o
f1 (ppm)


2o
f1 (ppm)


2p
f1 (ppm)


2p
f1 (ppm)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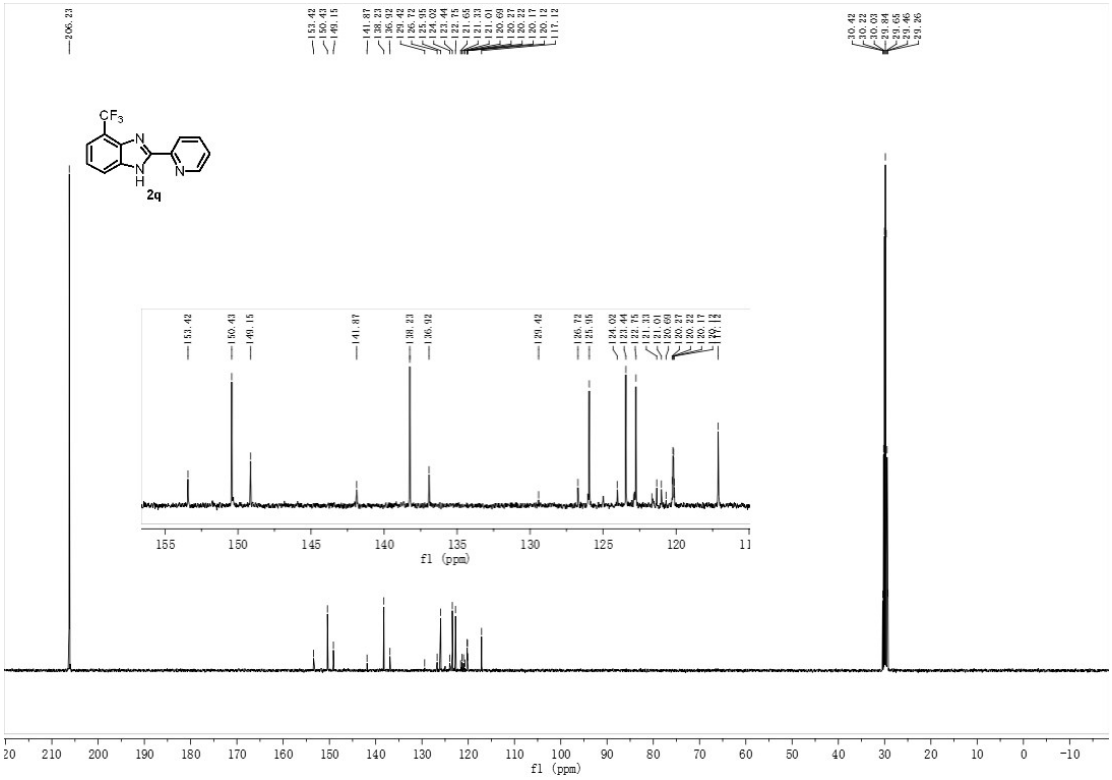
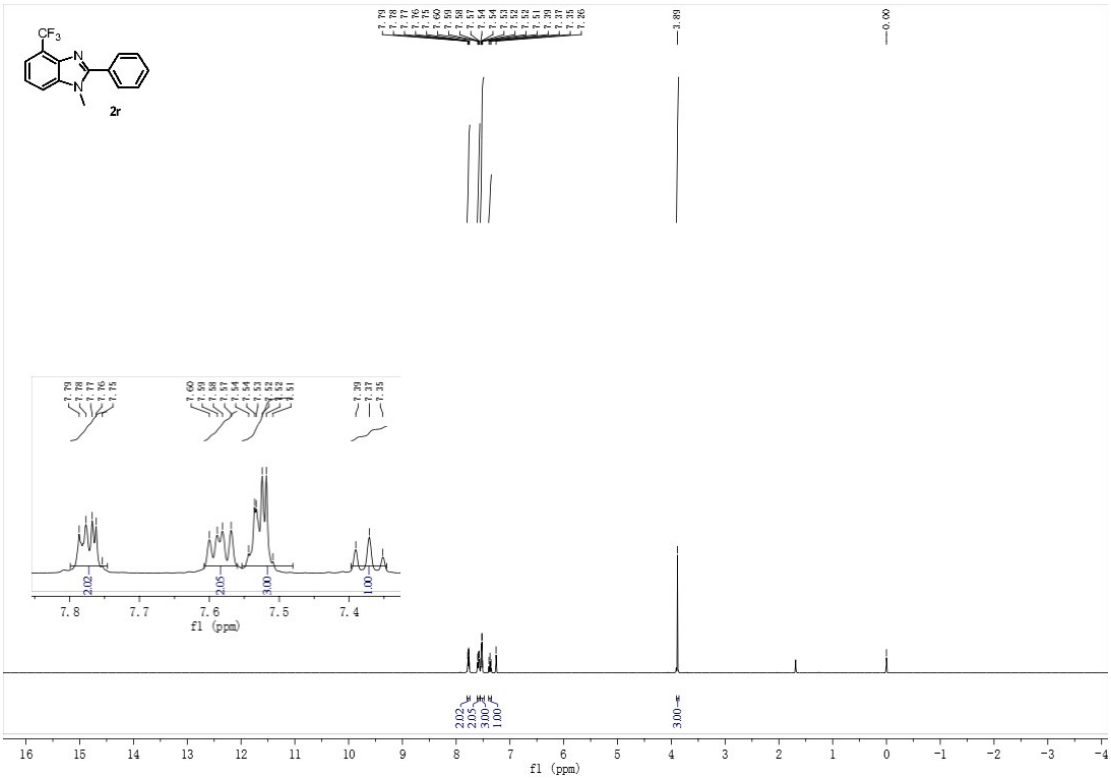
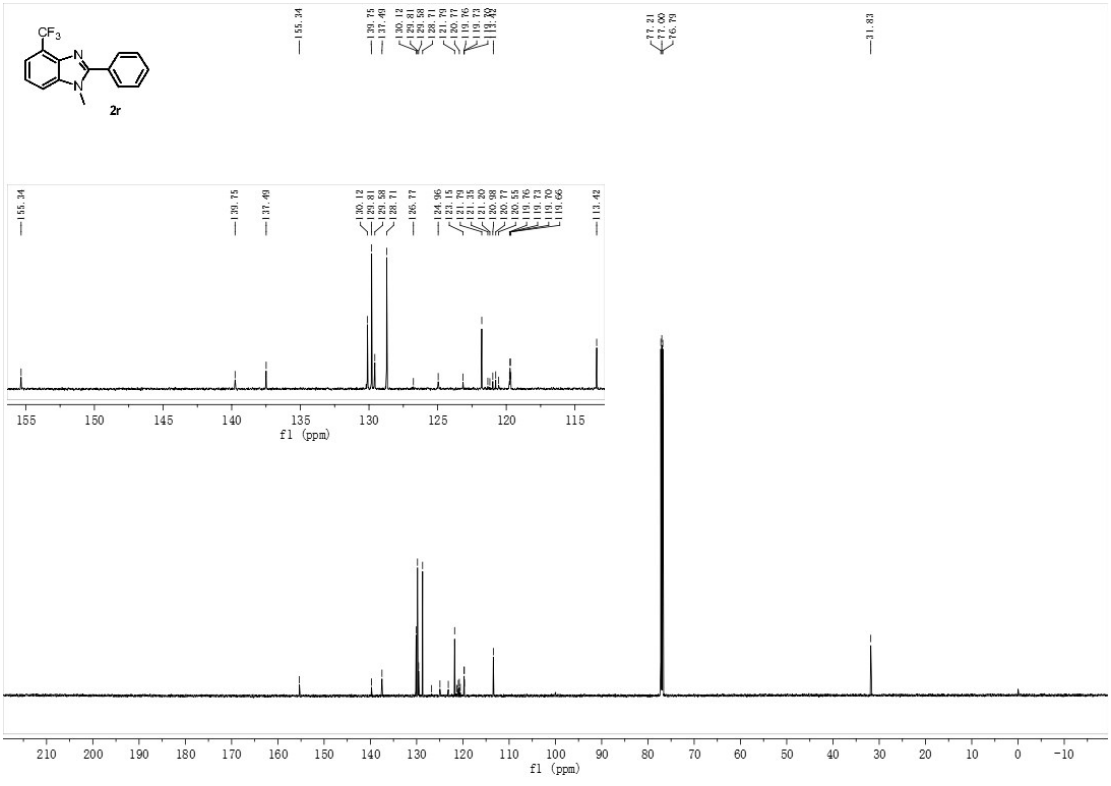
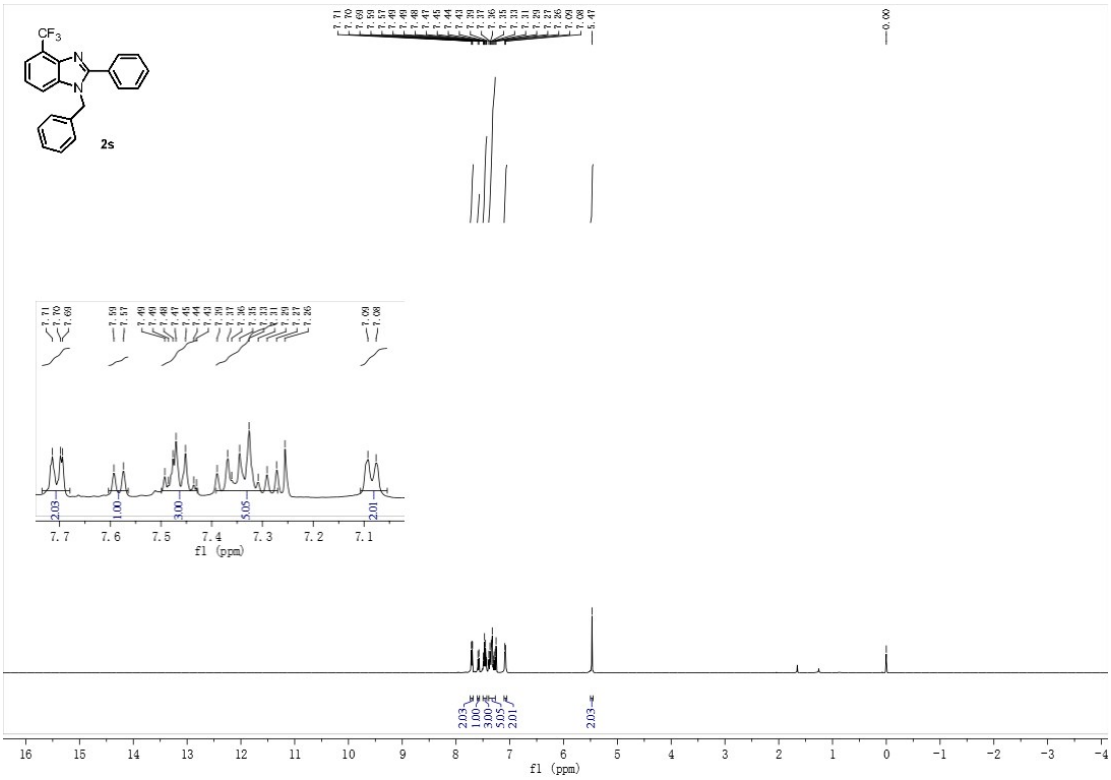
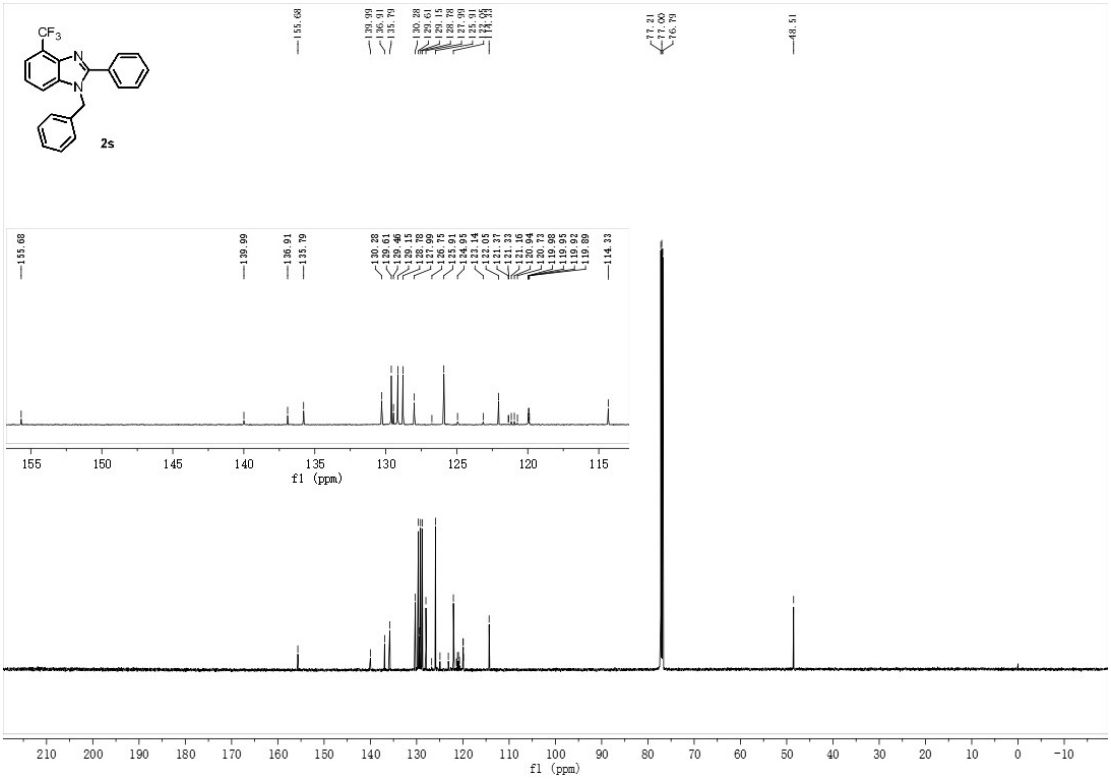
f1 (ppm)

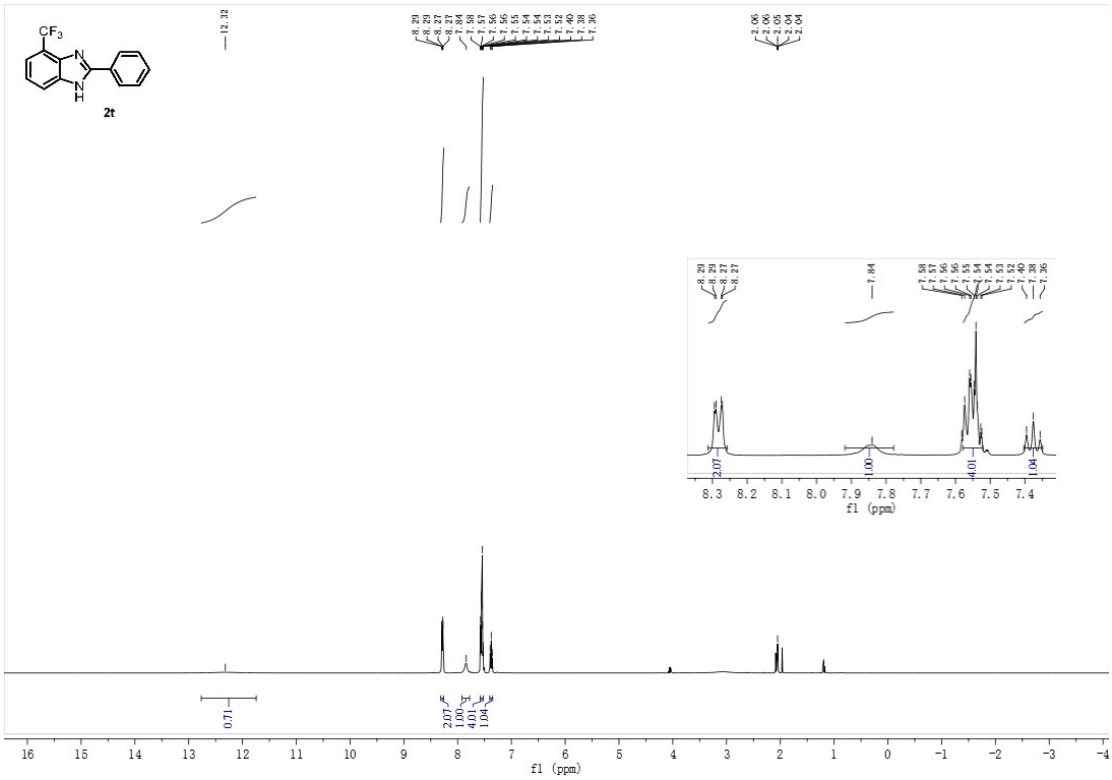

2q
f1 (ppm)


2r
f1 (ppm)


2r
f1 (ppm)


2s
f1 (ppm)


2s
f1 (ppm)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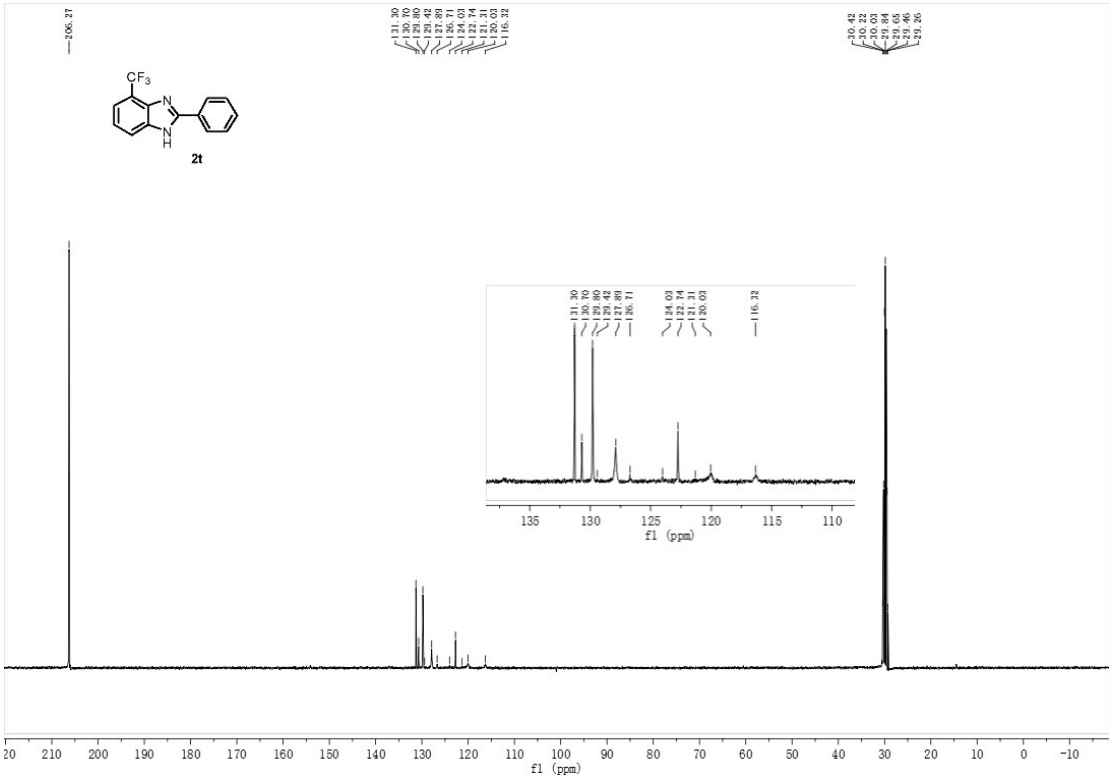
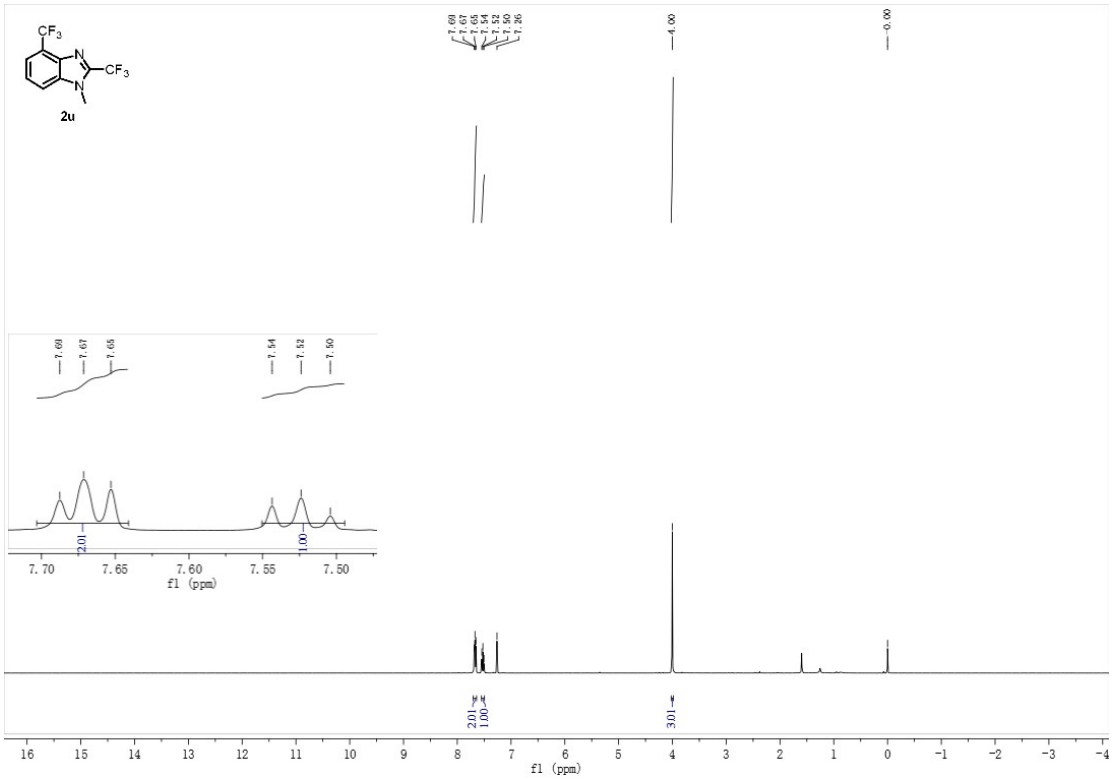
f1 (ppm)


2t
f1 (ppm)


2u
7.69
7.67
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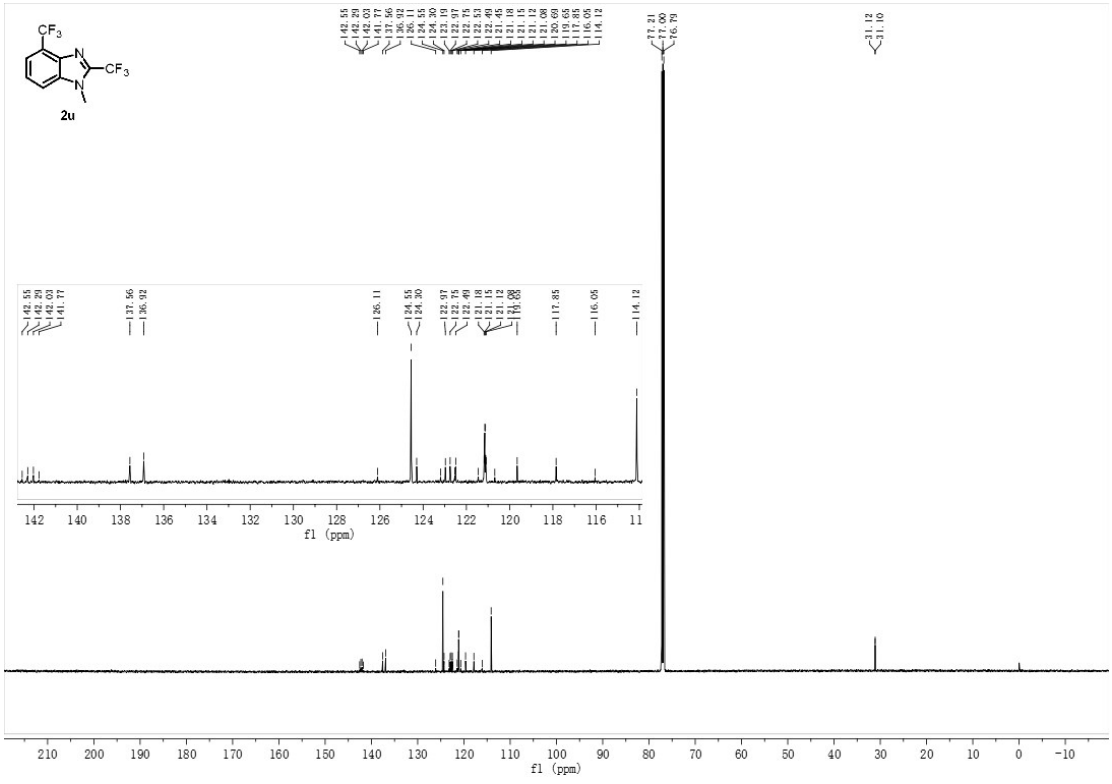
7.52
7.50
7.26
4.00
0.00
2.01
1.00
3.01
f1 (ppm)


2u
142.55
142.29
142.03
141.77
137.56
136.92
126.11
124.55
124.30
122.97
122.75
122.49
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77.21
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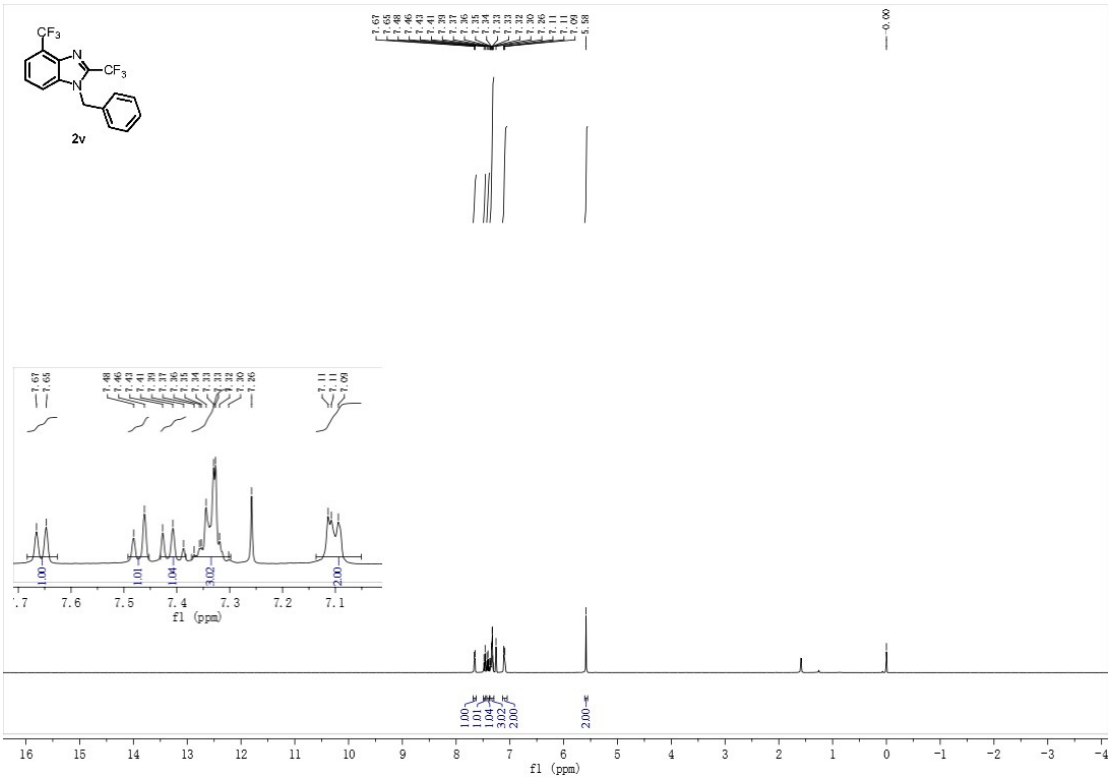
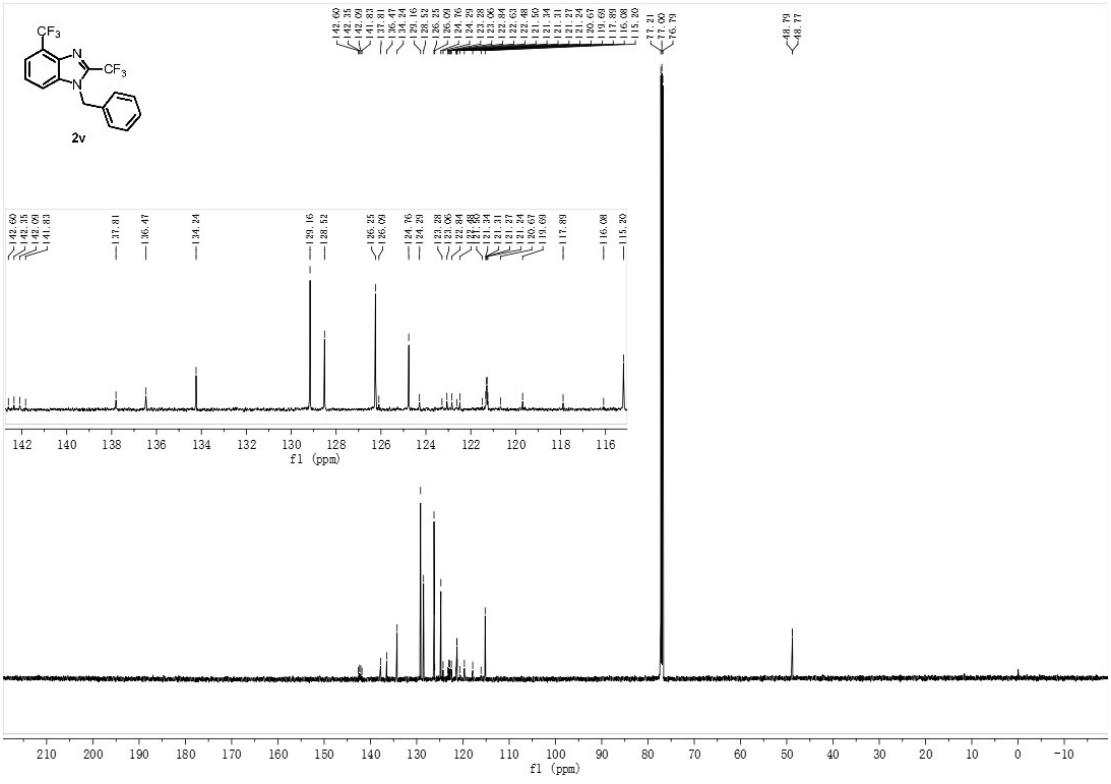
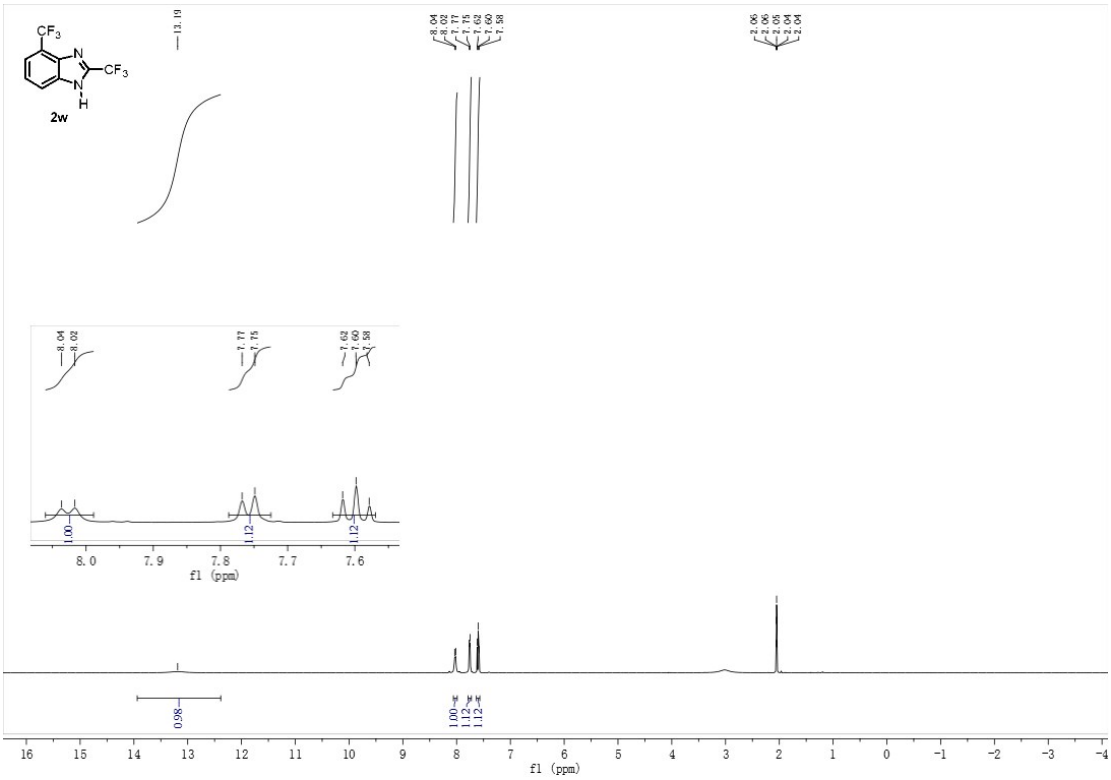
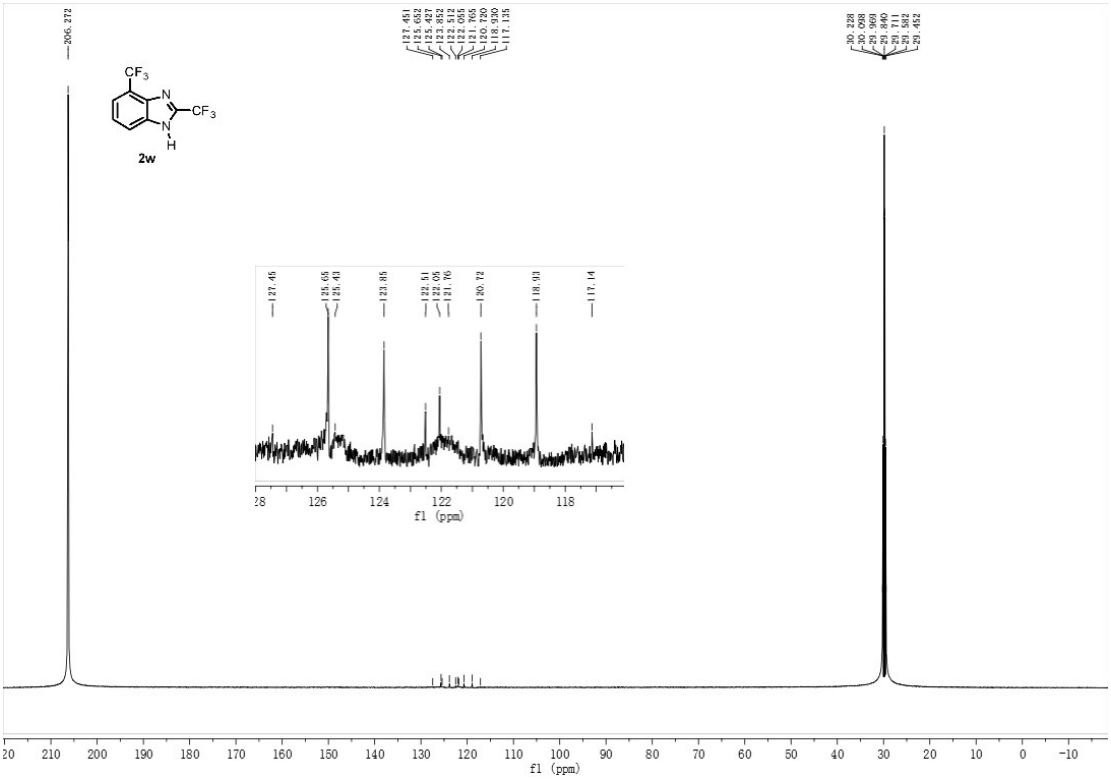
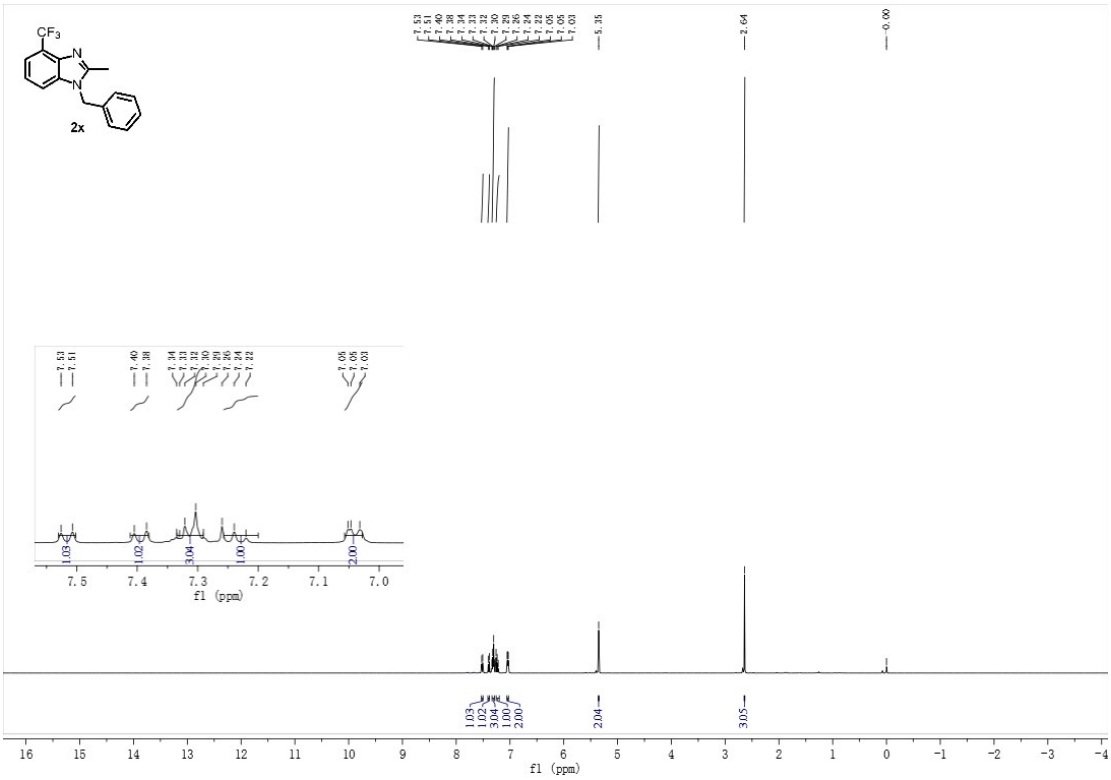
76.79
31.12
31.10
f1 (ppm)


2v
f1 (ppm)


2v
f1 (ppm)


2w
f1 (ppm)


2w
f1 (ppm)


2x
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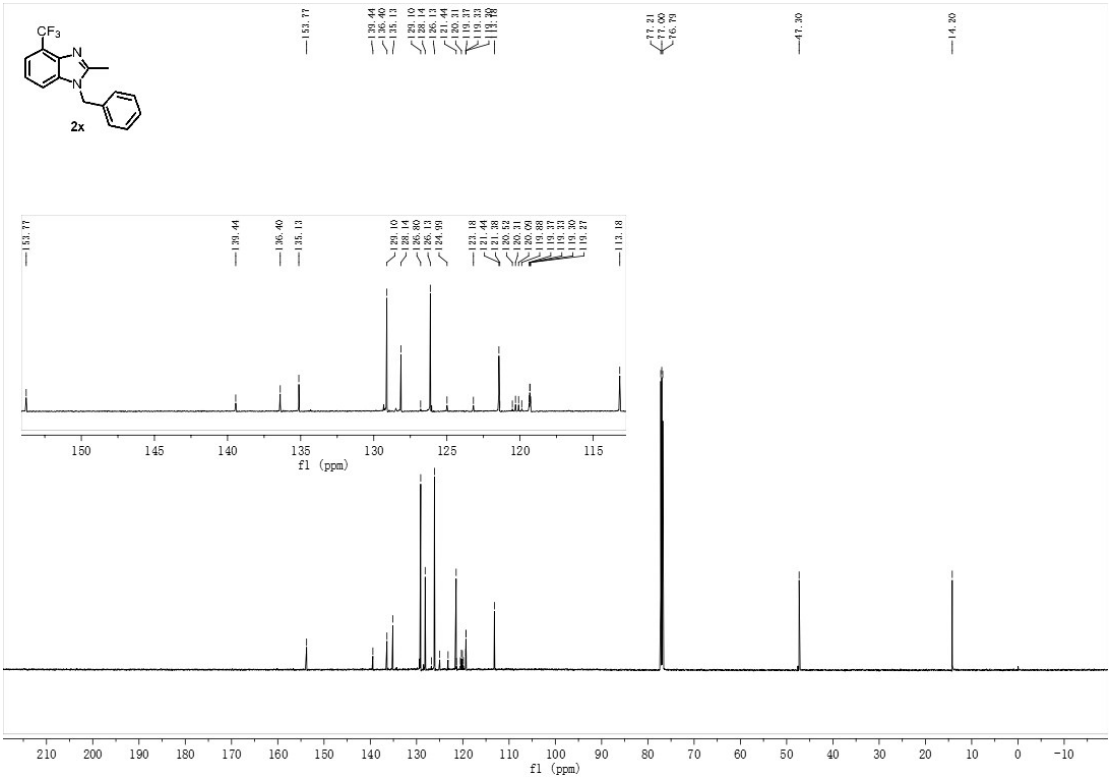
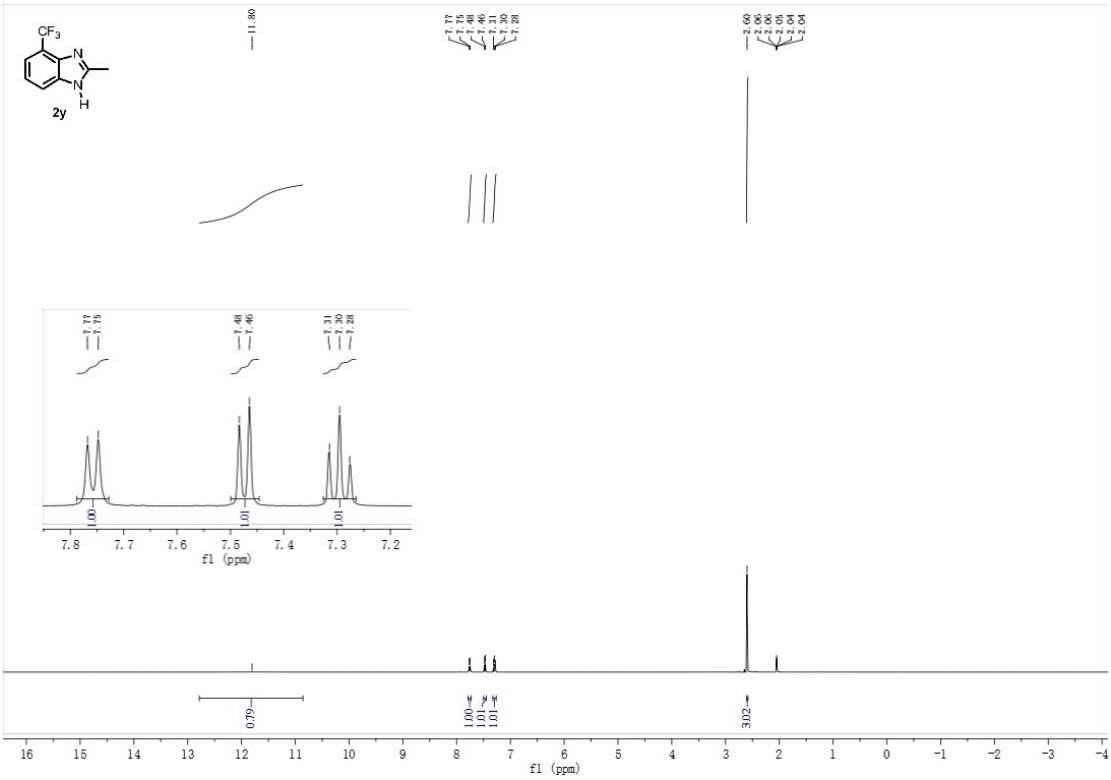
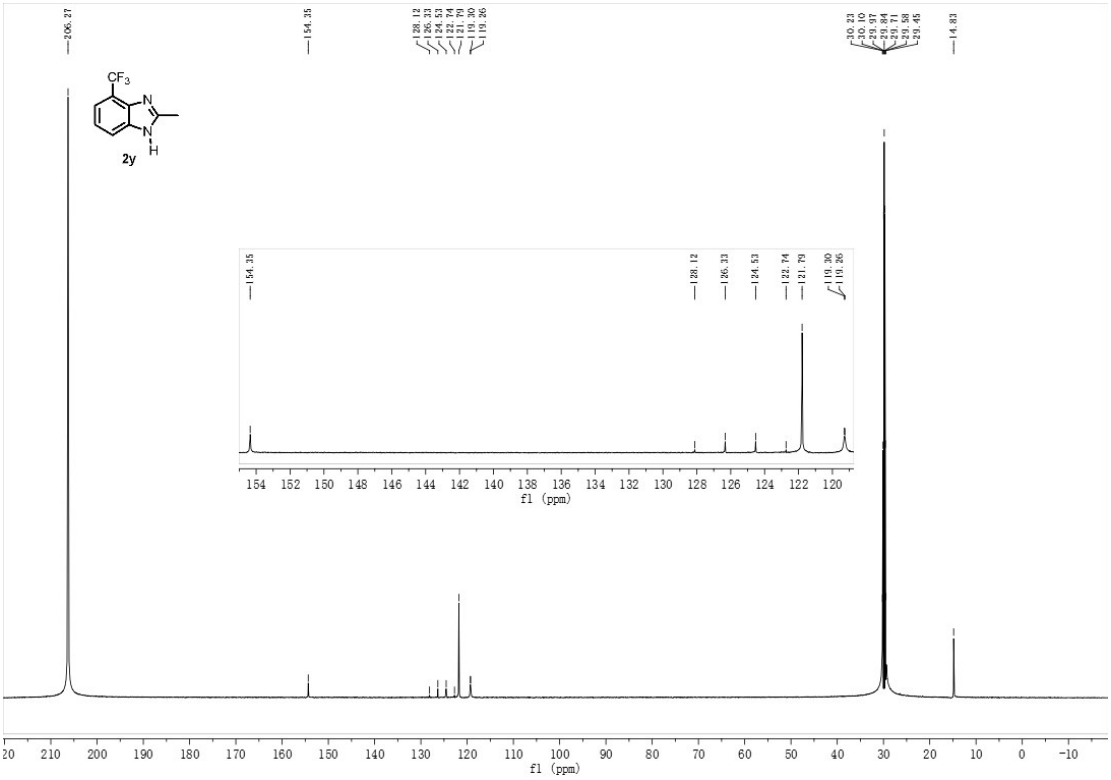

2x
f1 (ppm)


2y
11.80
7.77
7.75
7.48
7.46
7.31
7.30
7.28
2.60
2.06
2.06
2.05
2.04
2.04
1.00
1.01
1.01
f1 (ppm)
0.79
1.00
1.01
1.01
3.02
f1 (ppm)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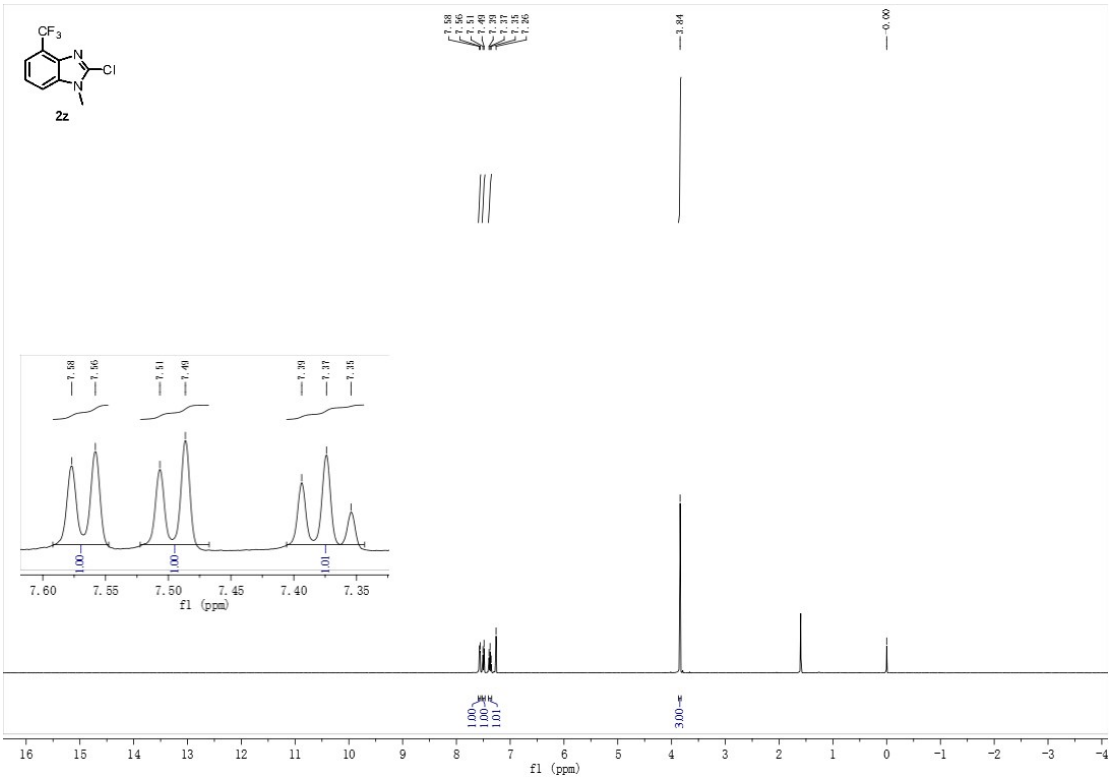
128.12
126.33
124.53
122.74
121.79
119.30
119.26
30.23
30.10
29.97
29.84
29.71
29.58
29.45
14.83
154.35
128.12
126.33
124.53
122.74
121.79
119.30
119.26
f1 (ppm)
f1 (ppm)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7.49
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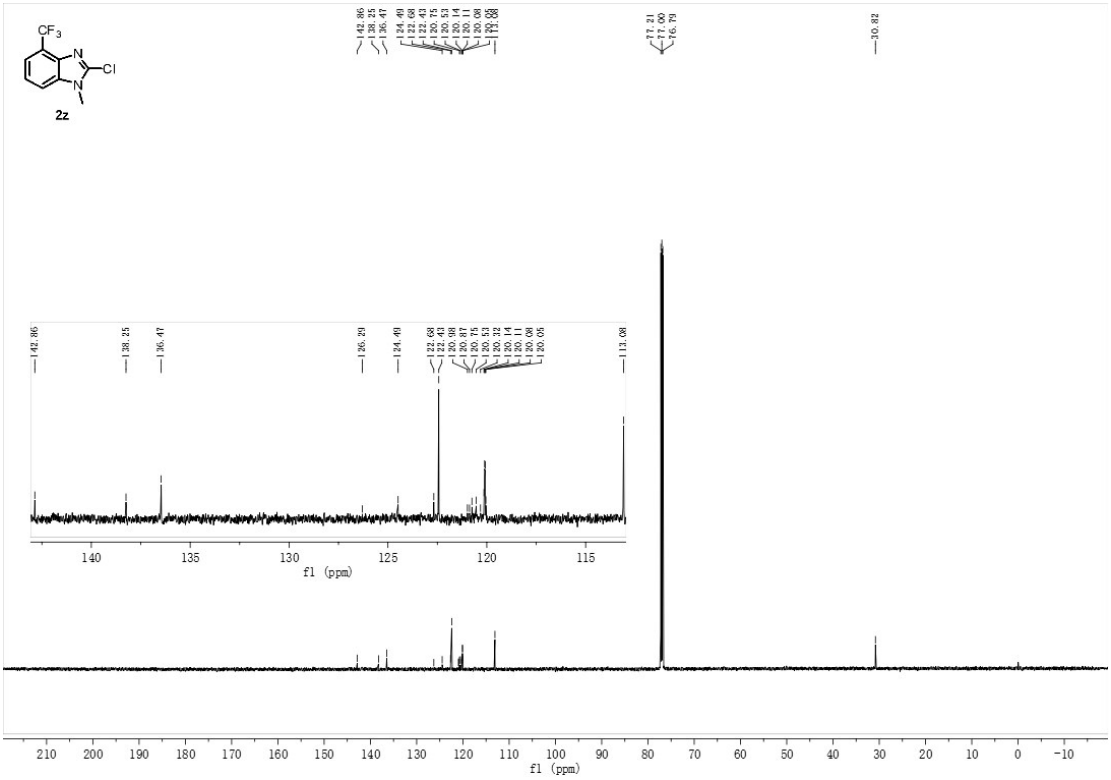
3.84
0.00
1.00
1.00
1.01
3.00
f1 (ppm)


2z
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124.49
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120.97
120.75
120.53
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120.11
120.08
120.05
113.08
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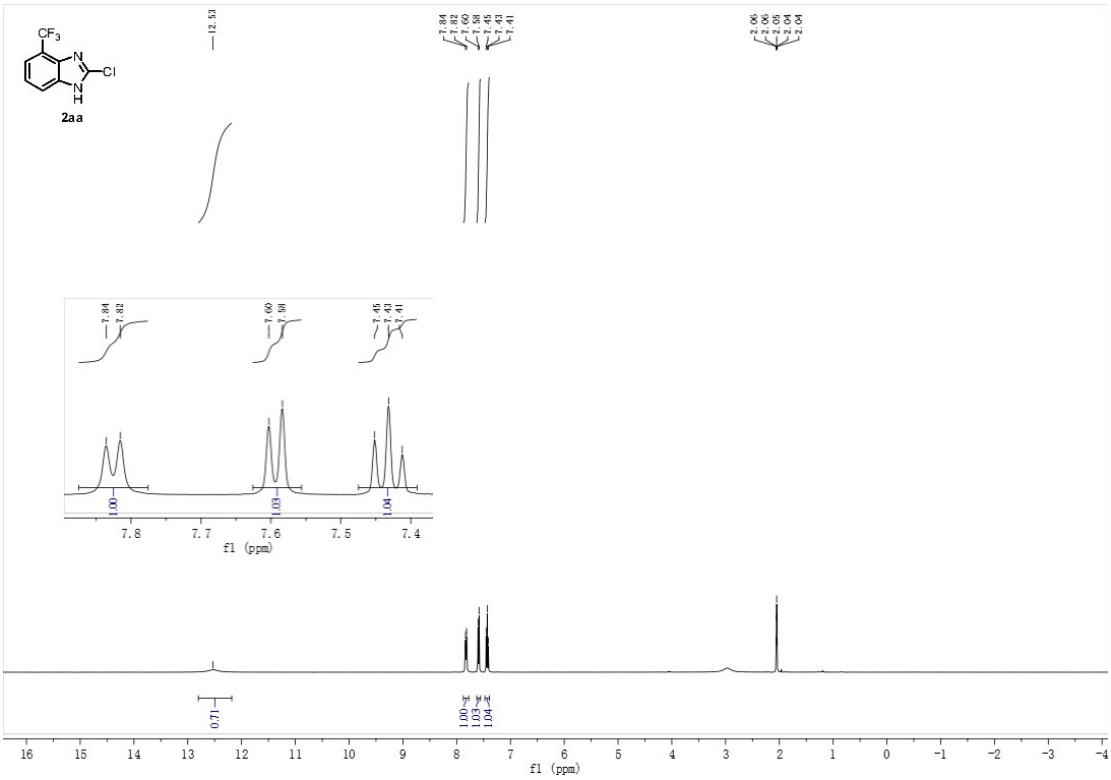
77.00
76.79
30.82
f1 (ppm)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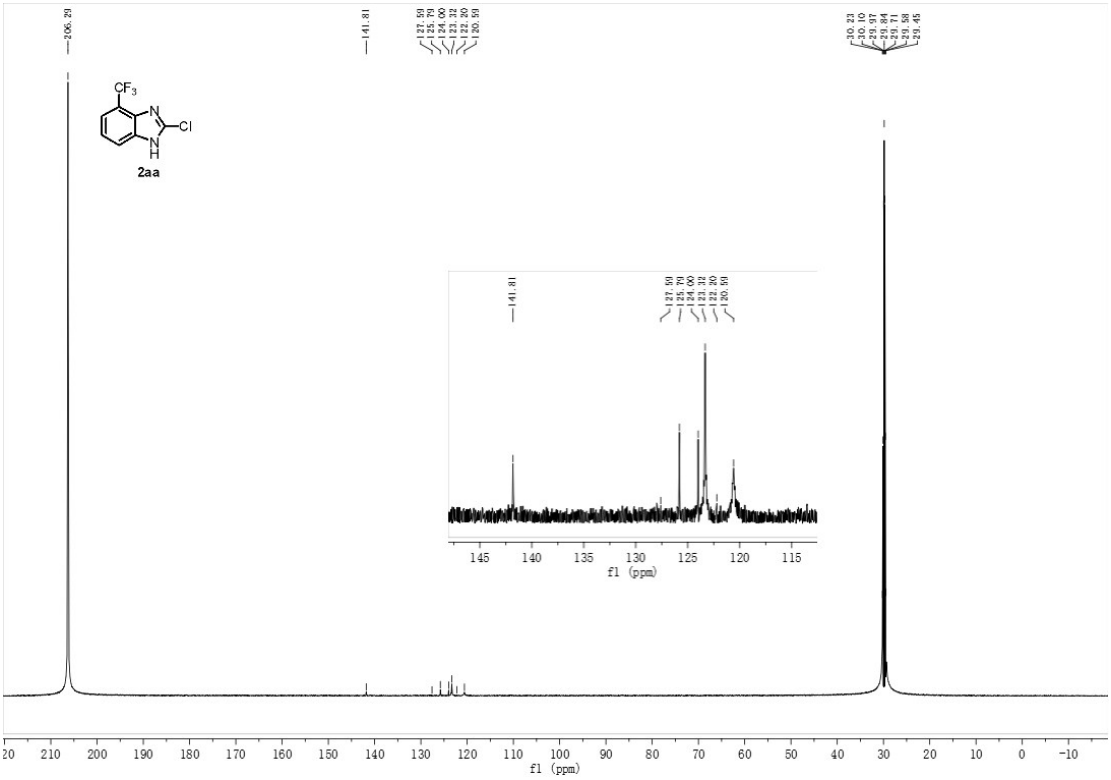
f1 (ppm)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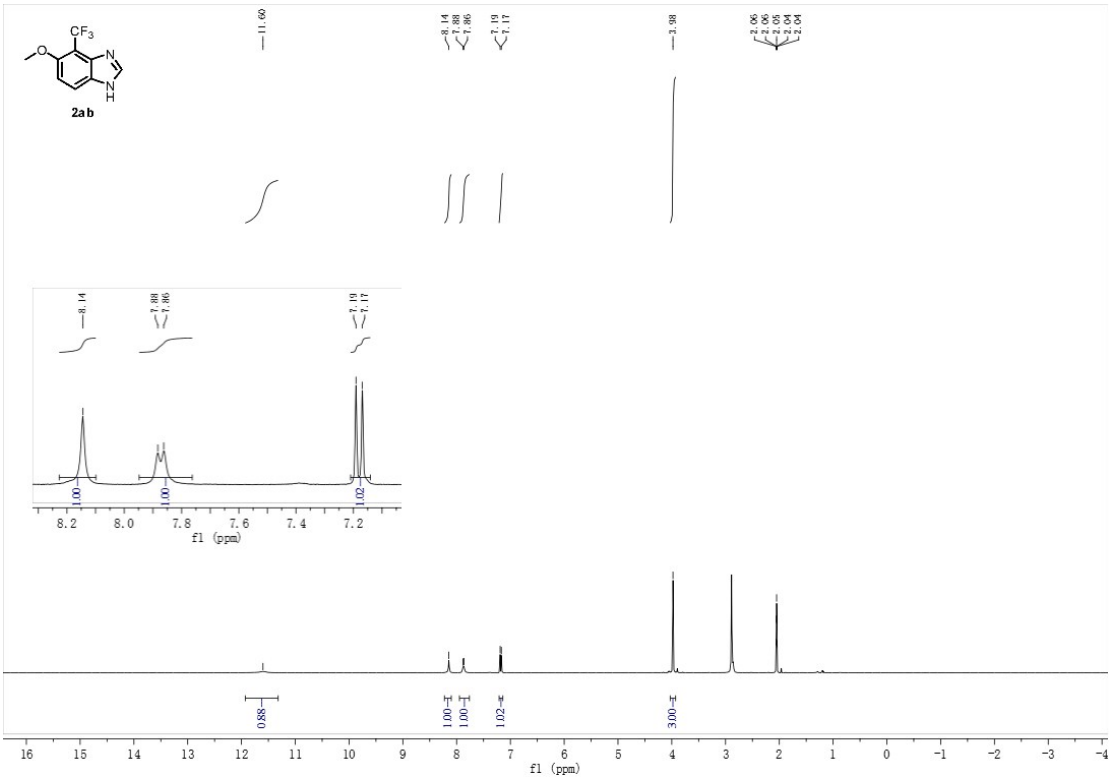
f1 (ppm)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7.19
7.17
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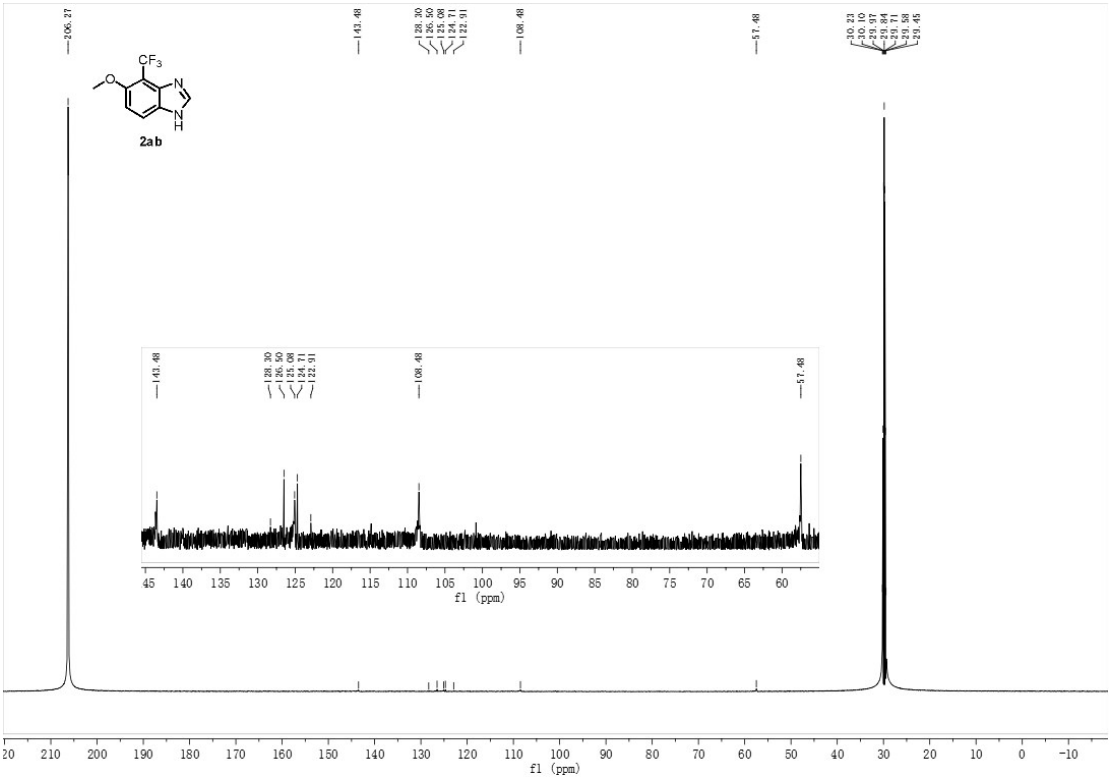
2.04
0.88
1.00
1.00
1.02
3.00
f1 (ppm)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126.50
125.08
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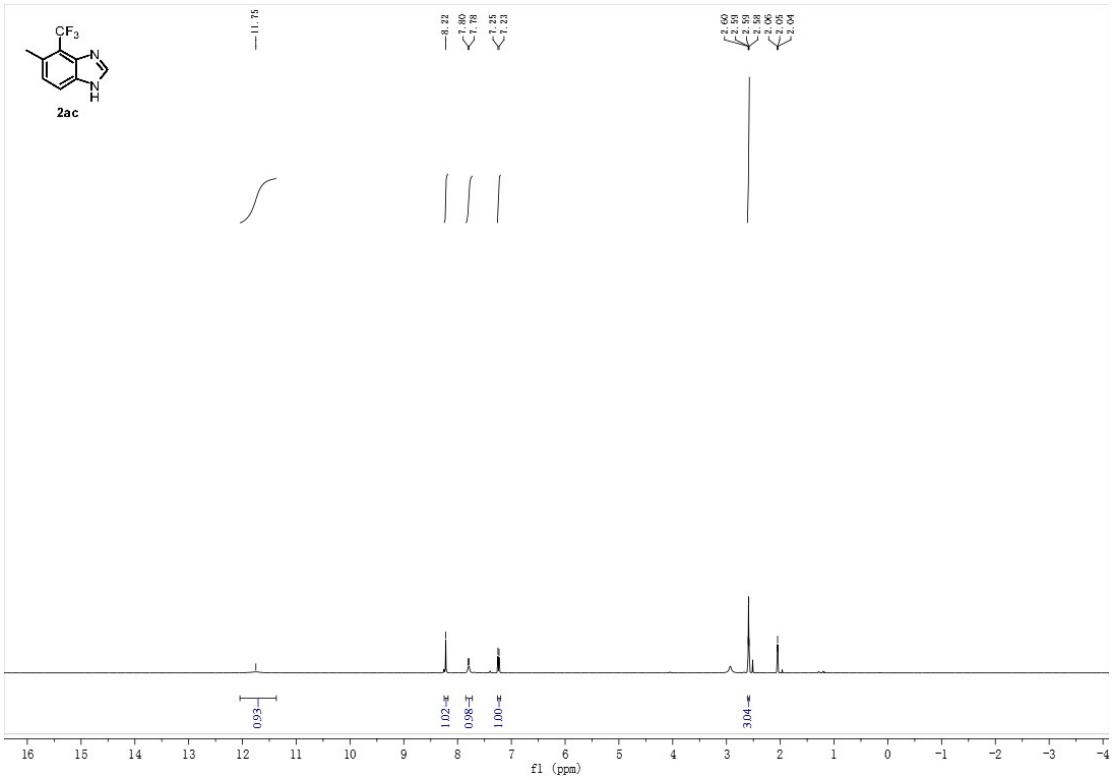
29.84
29.71
29.58
29.45
f1 (ppm)


2ac
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7.80
7.78
7.25
7.23
2.60
2.59
2.59
2.58
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2.05
2.04
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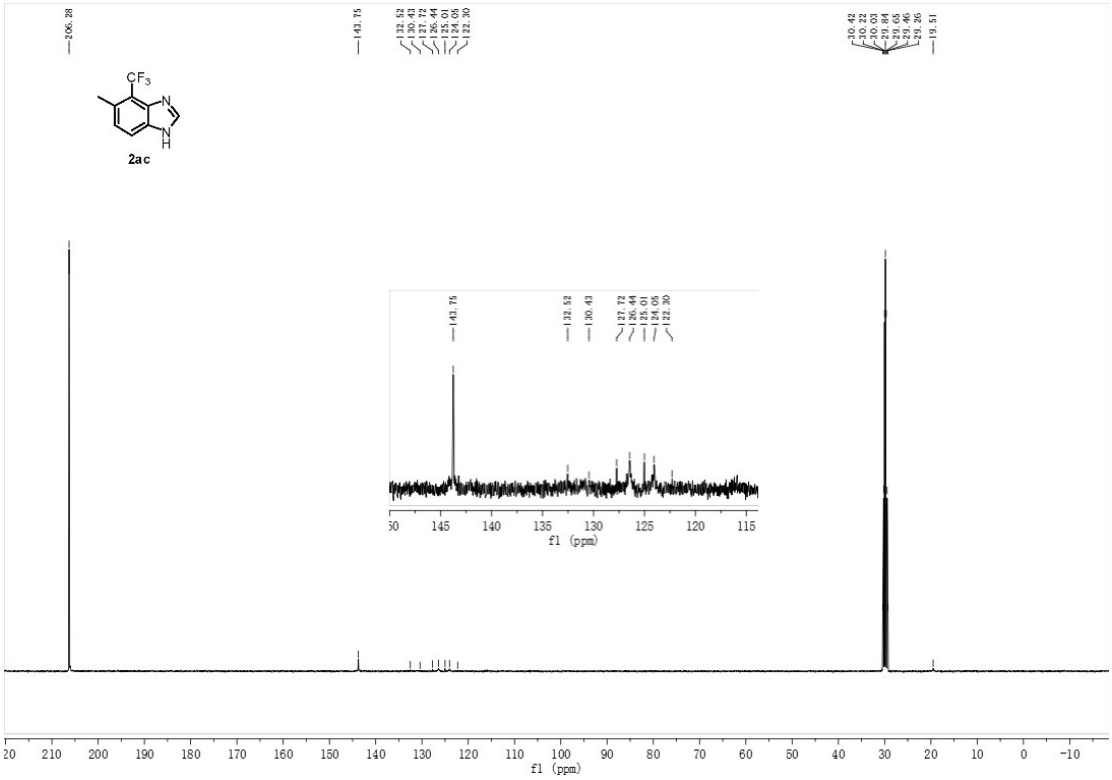
1.02
0.98
1.00
3.04
f1 (ppm)


206.28
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132.52
130.43
127.72
126.44
125.01
124.05
122.30
30.42
30.22
30.03
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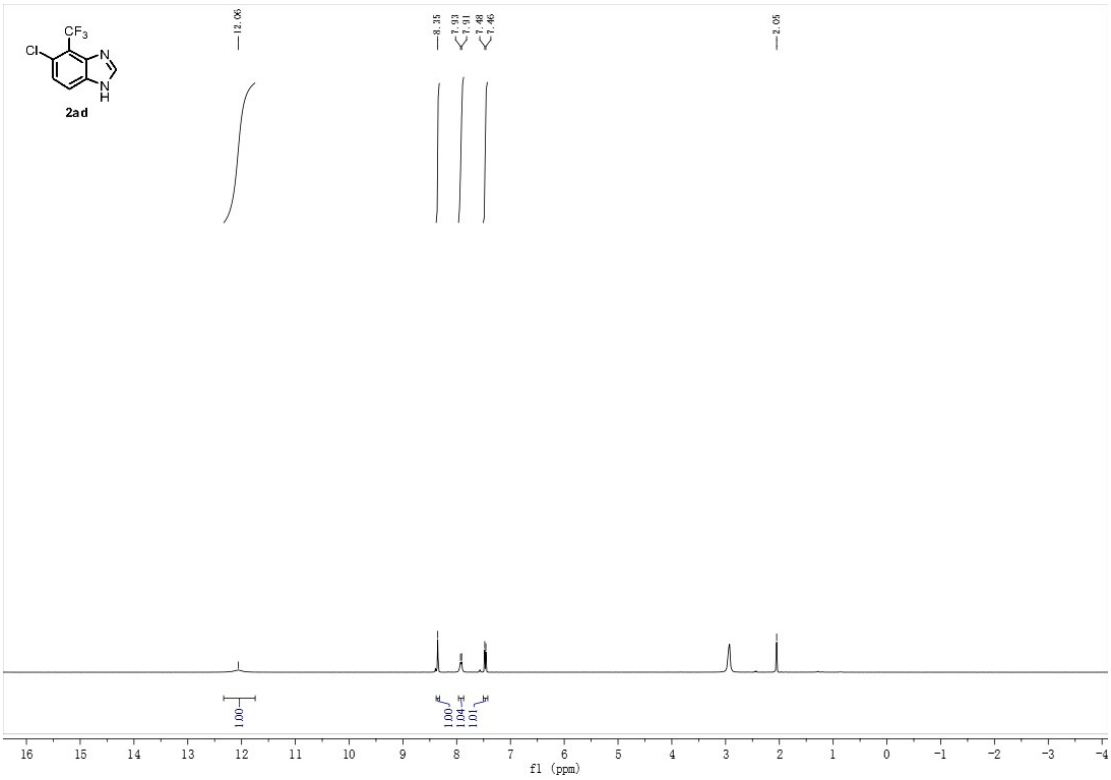
29.46
29.26
19.51
2ac
f1 (ppm)


2ad
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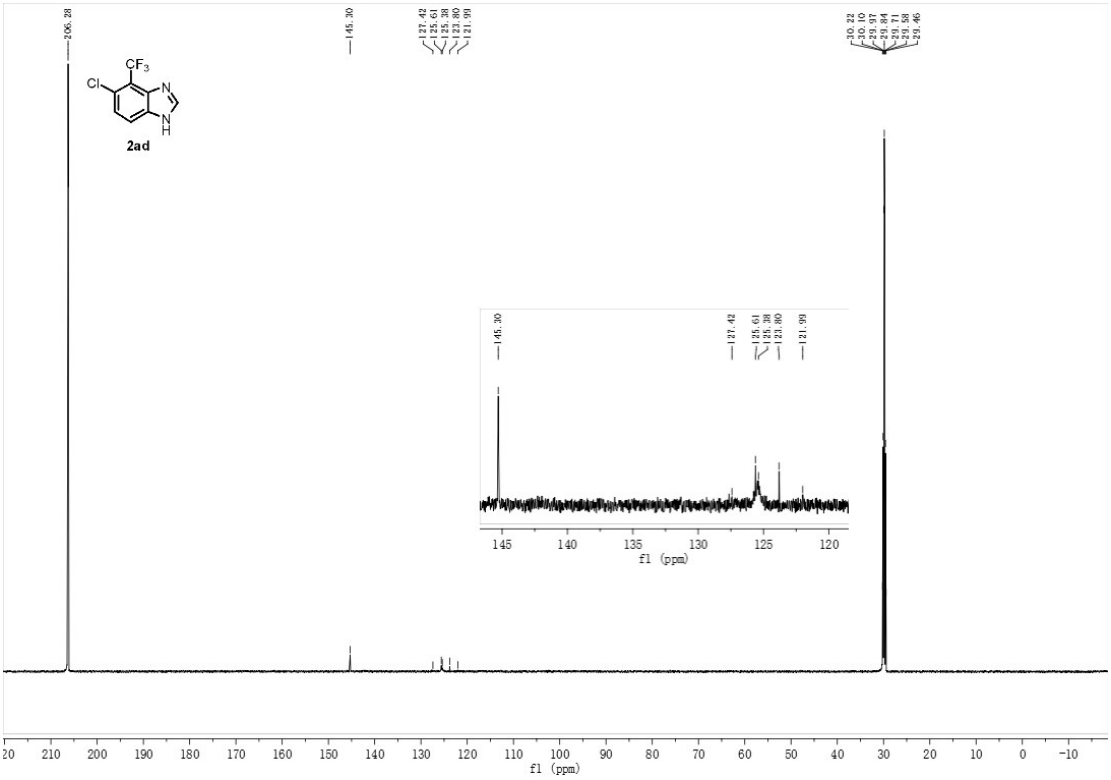
7.93
7.91
7.48
7.46
2.05
1.00
1.00
1.04
1.01
f1 (ppm)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125.38
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121.99
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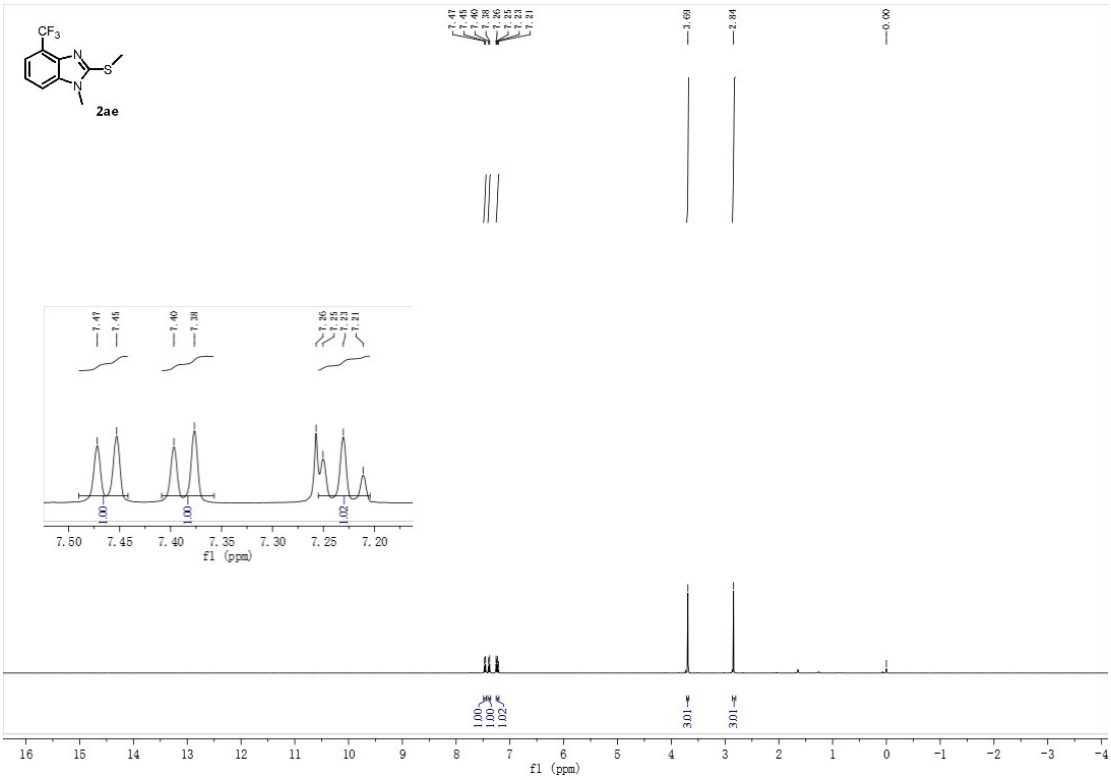
30.10
29.97
29.84
29.71
29.58
29.46
f1 (ppm)


2ae
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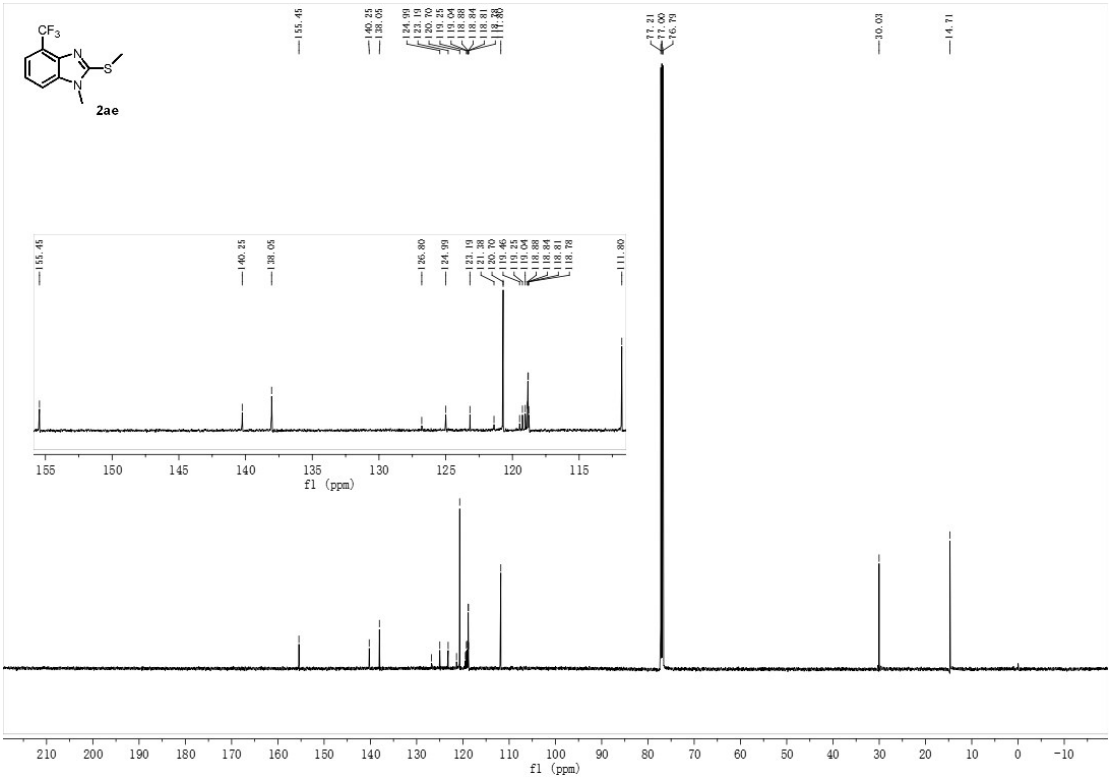
7.38
7.26
7.25
7.23
7.21
3.68
2.84
0.00
1.00
1.00
1.02
3.01
3.01
f1 (ppm)


2ae
155.45
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138.05
124.99
123.19
120.70
119.25
119.04
118.88
118.84
118.81
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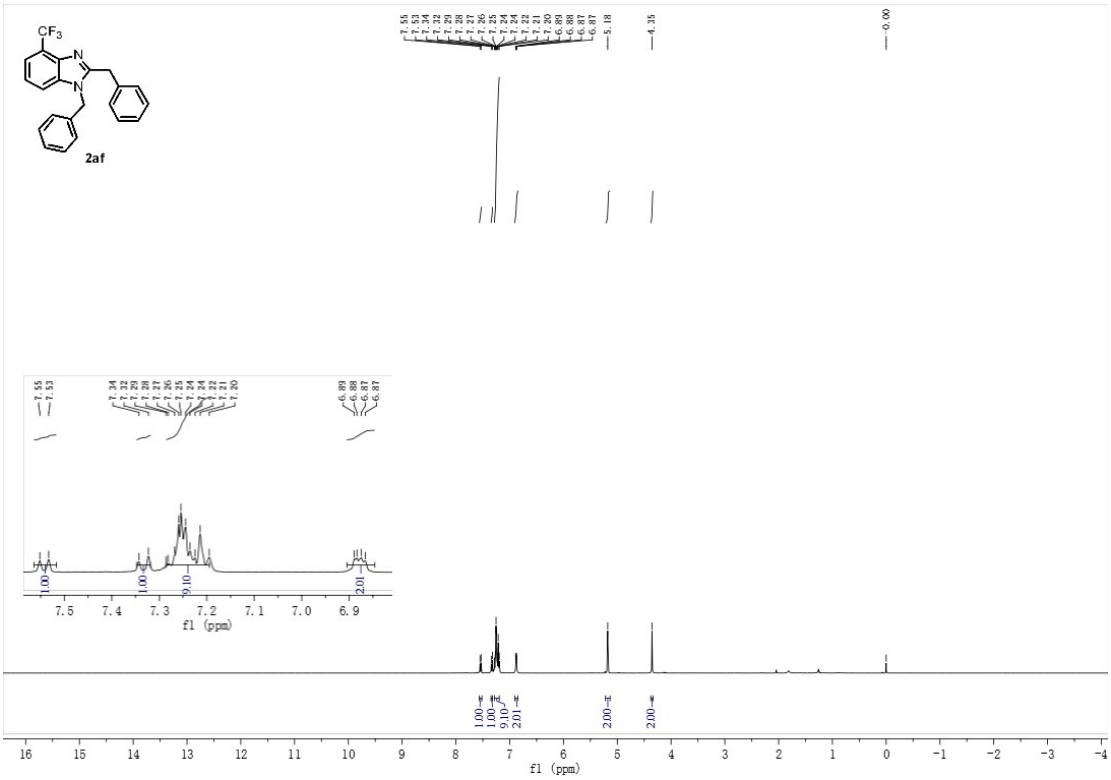
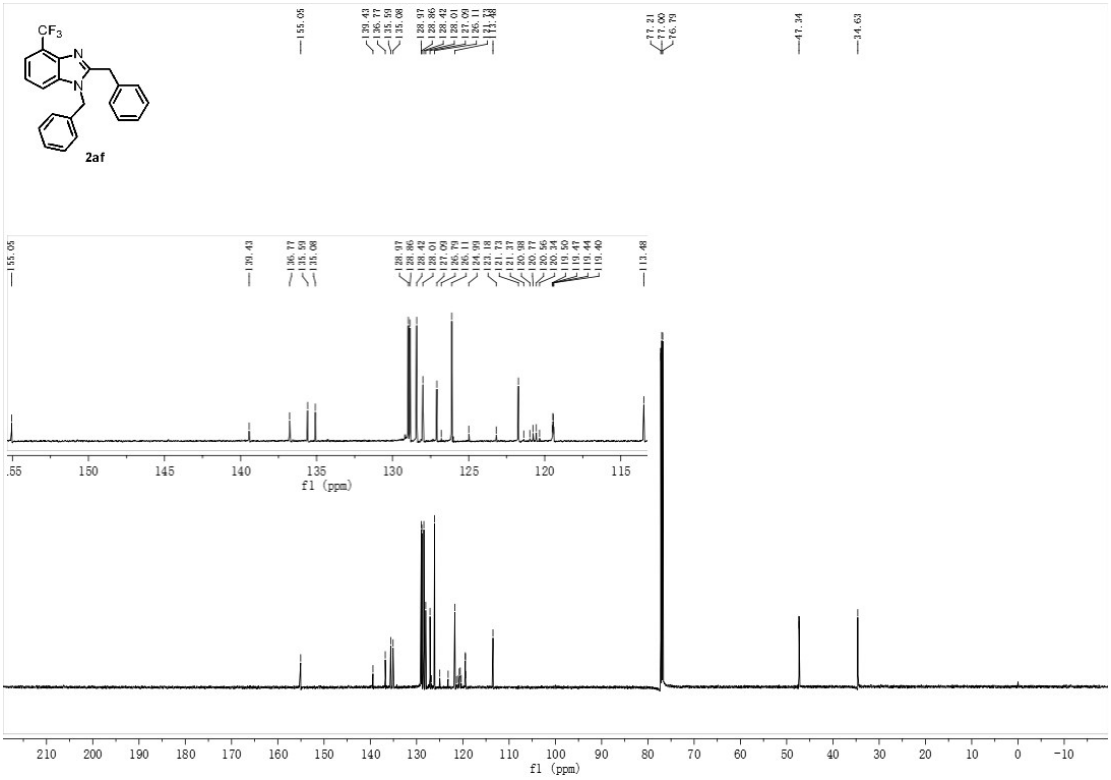
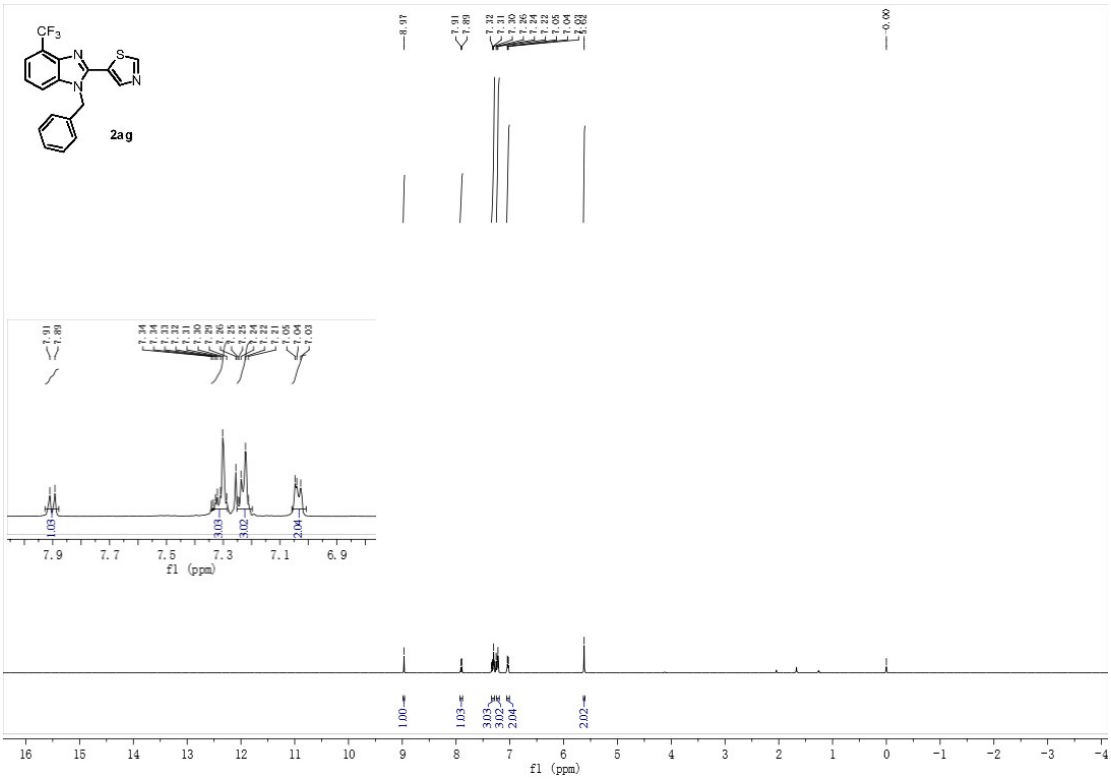
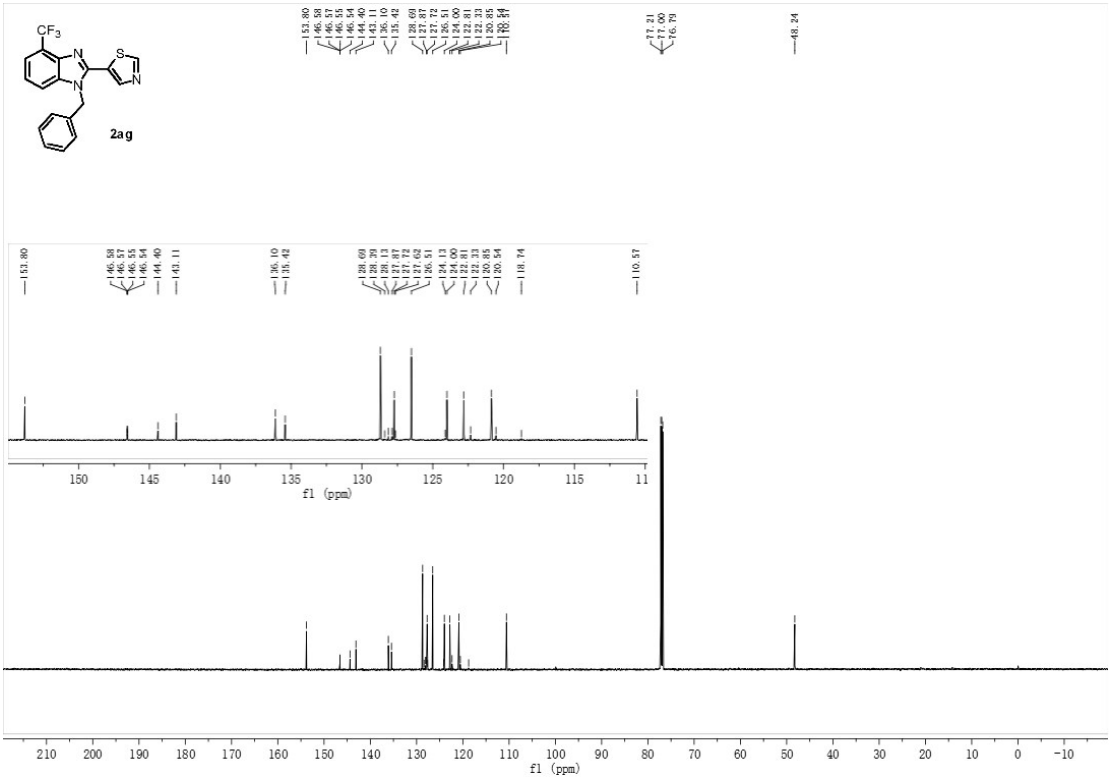
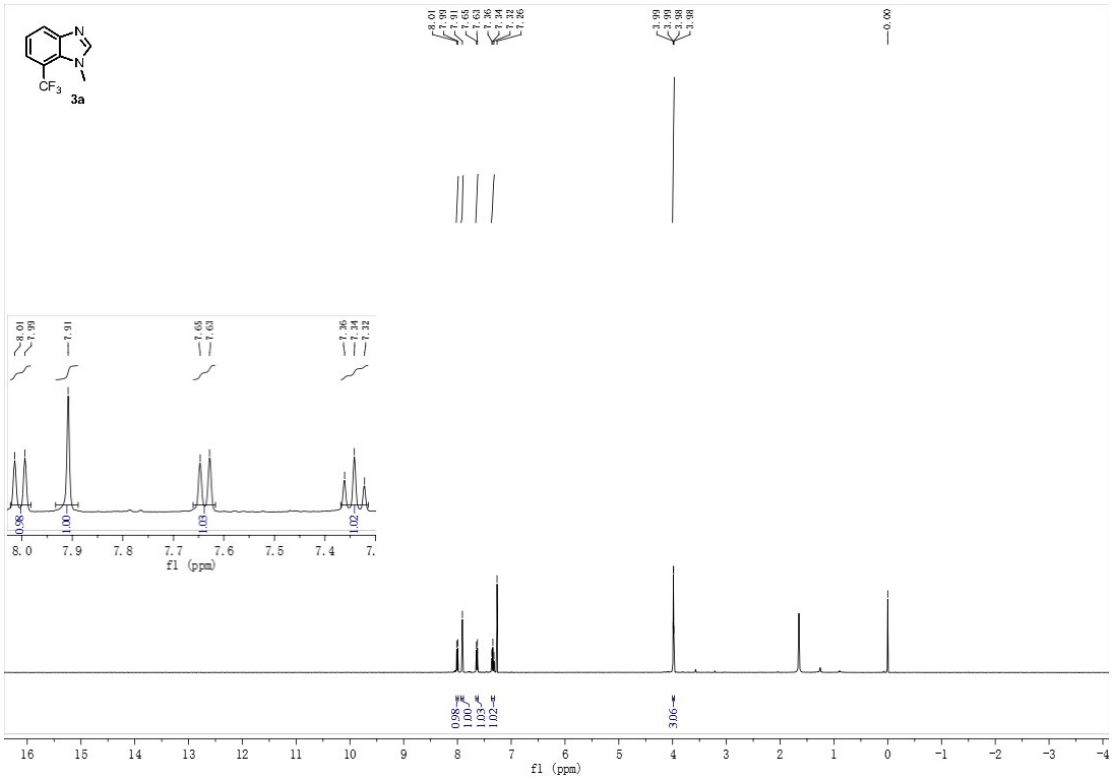
77.00
76.79
30.03
14.71
f1 (ppm)


2af
f1 (ppm)


2af
f1 (ppm)


2ag
f1 (ppm)


2ag
f1 (ppm)


3a
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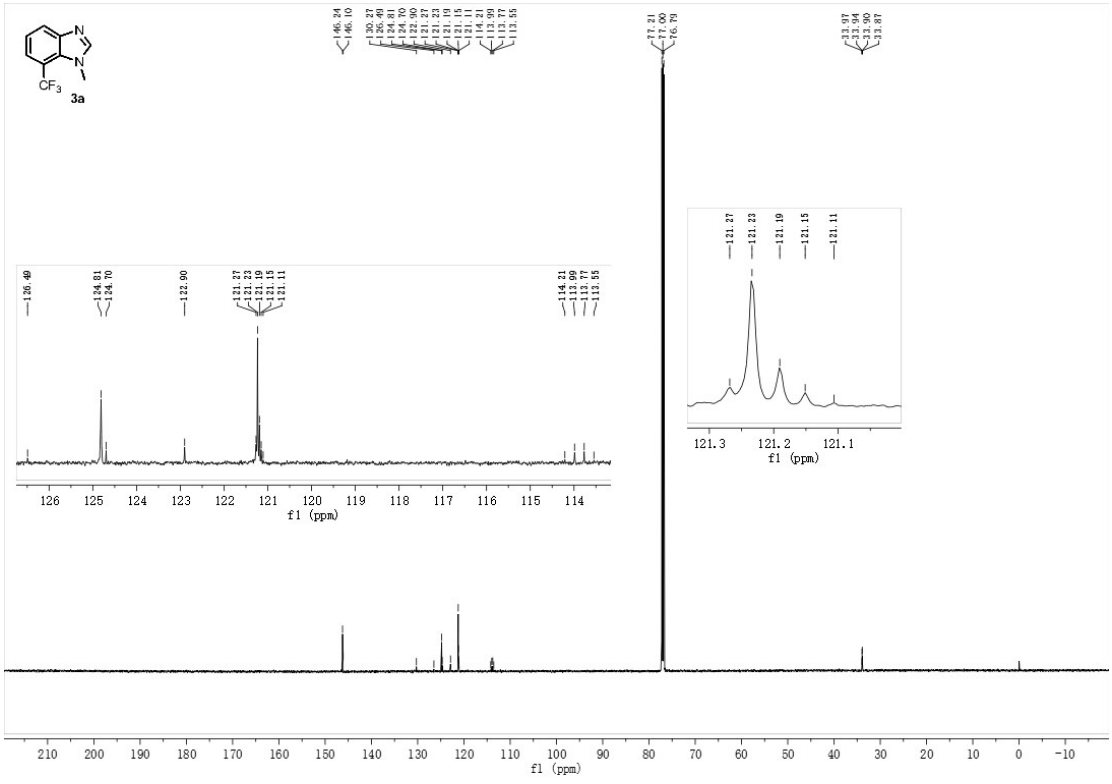
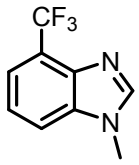

3a
f1 (ppm)

X-ray data:



1-Methyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2a**).

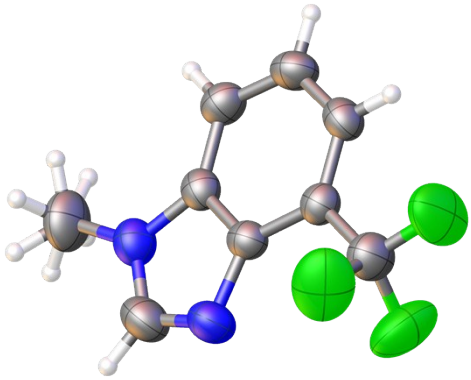
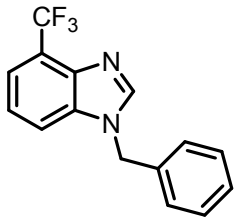


Table S1. Crystal data and structure refinement for 2a.

Identification code	**2a**
Empirical formula	$C_9H_7F_3N_2$
Formula weight	200.17
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pnma
a/Å	12.8186(10)
b/Å	6.8399(6)
c/Å	9.8413(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	862.87(12)
Z	4
ρ_{calc}g/cm^3	1.541
μ/mm^{-1}	0.140
F(000)	408.0
Crystal size/mm^3	0.12 × 0.1 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.356 to 50.688
Index ranges	-15 ≤ h ≤ 14, -8 ≤ k ≤ 5, -10 ≤ l ≤ 11
Reflections collected	2301
Independent reflections	864 [R_{int} = 0.0304, R_{sigma} = 0.0356]
Data/restraints/parameters	864/0/83

Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0471, wR_2 = 0.1138
Final R indexes [all data]	R_1 = 0.0728, wR_2 = 0.1361
Largest diff. peak/hole / e $Å^{-3}$	0.17/-0.21



1-Benzyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2b**).

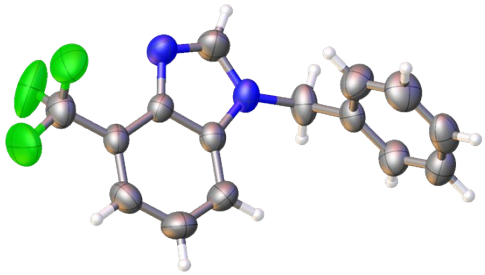
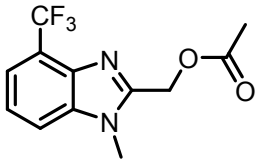


Table S2. Crystal data and structure refinement for 2b.

Identification code	**2b**
Empirical formula	$C_{15}H_{11}F_3N_2$
Formula weight	276.26
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.7224(7)
b/Å	11.5982(5)
c/Å	11.6209(8)
α/°	90
β/°	92.780(6)
γ/°	90
Volume/$Å^3$	1308.87(14)
Z	4
$\rho_{calc}g/cm^3$	1.402
μ/mm^{-1}	0.114
F(000)	568.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.39 to 50.69
Index ranges	$-8 \le h \le 11$, $-13 \le k \le 11$, $-13 \le l \le 12$
Reflections collected	5040

Independent reflections	2380 [R_{int} = 0.0334, R_{sigma} = 0.0542]
Data/restraints/parameters	2380/0/181
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0558, wR_2 = 0.1167
Final R indexes [all data]	R_1 = 0.1083, wR_2 = 0.1442
Largest diff. peak/hole / e $Å^{-3}$	0.14/-0.16



(1-Methyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-2-yl)methyl acetate (**2k**)

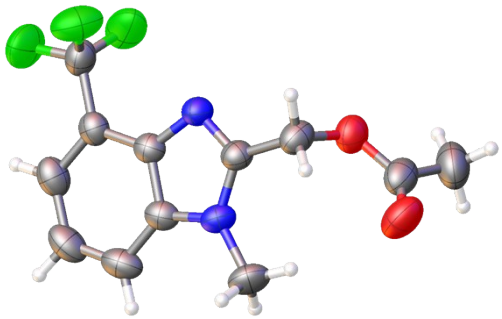
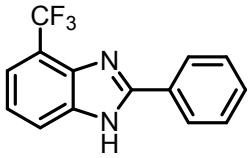


Table S3. Crystal data and structure refinement for 2k.

Identification code	2k
Empirical formula	$C_{12}H_{11}F_3N_2O_2$
Formula weight	272.23
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.2208(7)
b/Å	9.3833(13)
c/Å	9.5826(11)
α/°	102.706(11)
β/°	105.918(10)
γ/°	97.358(10)
Volume/$Å^3$	596.67(13)
Z	2
$\rho_{calc}g/cm^3$	1.515
μ/mm^{-1}	0.135
F(000)	280.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data	5.99 to 50.696

collection/°	
Index ranges	$-7 \leqslant h \leqslant 8$, $-11 \leqslant k \leqslant 7$, $-10 \leqslant l \leqslant 11$
Reflections collected	3924
Independent reflections	2172 [R_{int} = 0.0261, R_{sigma} = 0.0418]
Data/restraints/parameters	2172/0/175
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ(I)]	R_1 = 0.0553, wR_2 = 0.1419
Final R indexes [all data]	R_1 = 0.0723, wR_2 = 0.1590
Largest diff. peak/hole / e Å^{-3}	0.34/-0.22



2-Phenyl-4-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2t**)

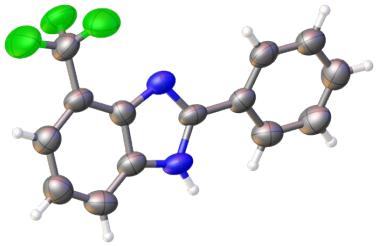


Table S4. Crystal data and structure refinement for 2t.

Identification code	2s
Empirical formula	$C_{14}H_9F_3N_2$
Formula weight	262.23
Temperature/K	293(2)
Crystal system	tetragonal
Space group	$P4_12_12$
a/Å	11.5964(5)
b/Å	11.5964(5)
c/Å	17.7913(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2392.5(2)

Z	8
ρ_{calc}g/cm^3	1.456
μ/mm^{-1}	0.120
F(000)	1072.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.772 to 50.664
Index ranges	-8 ≤ h ≤ 13, -9 ≤ k ≤ 12, -21 ≤ l ≤ 20
Reflections collected	5592
Independent reflections	2178 [R_{int} = 0.0449, R_{sigma} = 0.0498]
Data/restraints/parameters	2178/0/172
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0618, wR_2 = 0.1667
Final R indexes [all data]	R_1 = 0.0832, wR_2 = 0.1864
Largest diff. peak/hole / e Å^{-3}	0.32/-0.22
Flack parameter	-0.6(10)