# *Supporting Information*

# Palladium-Catalyzed Cross-Coupling Reaction of Isocyanides with Azides: A General Route to Unsymmetric Carbodiimide

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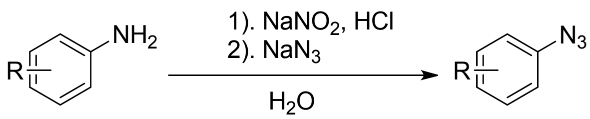
**General** All reactions were performed in a glass vial. Anhydrous solvents were distilled in small scale with $CaH_2$ or sodium and stored under $N_2$. The boiling point of petroleum ether is between 60 and 90$^o$C. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. $^1$H and $^{13}$C NMR spectra were recorded at 400 MHz and 100 MHz with Varian Mercury 400 spectrometer at ambient temperature. Chemical shifts are reported in ppm relative to chloroform ($^1$H, 7.26; $^{13}$C, 77.00) or DMSO ($^1$H, 2.50; $^{13}$C, 39.52). IR spectra were recorded with a Nicolet AVATAR 330 FT-IR spectrometer. Mass spectra were obtained on a Waters Auto Purification LC/MS system. HMRS were obtained on a Bruker Apex IV FTMS spectrometer, or Waters GCT Premier. All palladium catalysts were purchased from Sigma-Aldrich. All alkyl isocyanides and benzyl isocyanides are commercially available, unless stated otherwise.

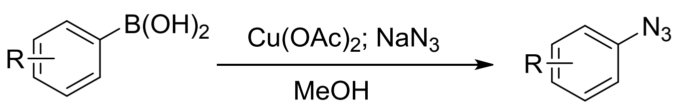
## General Procedures for the Preparation of Starting Materials

### General Procedure for the Preparation of Azides

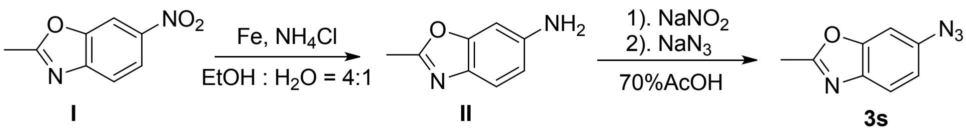
The aryl or heteroaryl azides **3a-c**[1], **3d**[3], **3e-f**[1], **3g**[4], **3h**[1],**3i**[6], **3j**[7], **3k**[1], **3l**[5], **3m**[1], **3n**[8], **3o**[2], **3q**, **3r**[9], **3t**[43], **3v**[44] were synthesized according to a standard procedure.[1]

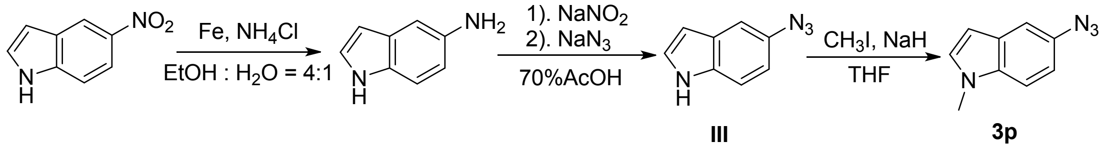



The aryl **3u**[45], **3w**[46] were synthesized according to a standard procedure.[47]



The heteroaryl azides **3p**, **3s** were synthesized according to the literature.[10]




A mixture of **I** (10 mmol), Fe (50 mmol), $NH_4Cl$ (100 mmol), EtOH (32 ml) and water (8 ml) was refluxed under $N_2$ protection for 4hours. The mixture was cooled to rt and filtered. The filtrate was concentrated and dissolved in water. The mixture was basified with $Na_2CO_3$ and extracted with EtOAc (20 ml x 2). The organic phases were combined, dried over $Na_2SO_4$ and concentrated in vacuum. The colorless crude products were directly used for next step without further purification.

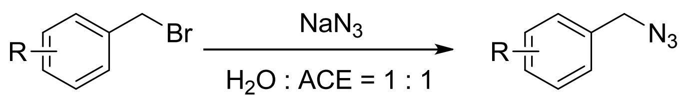
In a dried, 100 mL round-bottom flask, crude products **II** (740 mg, about 5 mmol) was dissolved in 70% AcOH (20 mL) and placed at 0 °C. After 10 min, $NaNO_2$ (448 mg, 6.5 mmol) dissolved in $H_2O$ (1 mL) was added dropwise, and the mixture was stirred for 10 min. $NaN_3$ (420 mg, 6.48 mmol) was added in portions. After 45 min, the mixture was slowly poured into $H_2O$ (25 mL) and saturated $K_2CO_3$ (19 mL) to form a neutral pH. This was extracted with ethyl acetate (4 × 50 mL), washed with brine, dried with $Na_2SO_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel, yields **3s** (611 mg, 65%).

**III** was prepared using the same procedure described for **3s**.

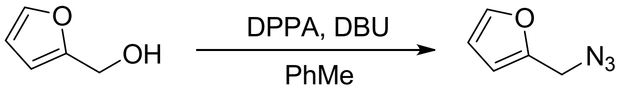
To a suspended solution of NaH (6.00 g, 60% dispersion in mineral oil, 9 mmol) in THF (20 mL), **III** (474 mg, 3 mmol) dissolved in THF (3 mL) was added dropwise at 0 °C. The heterogeneous mixture was stirred at 0 °C for 30 min and 2 h at rt. The mixture was then cooled to 0 °C, treated with iodomethane (640 ml, 4.5 mmol), and allowed to warm to rt. After 30 min, the reaction mixture was cooled to 0 °C, quenched with saturated $NH_4Cl$ (10 mL), and extracted with ethyl acetate (2×10 mL). The organic layers were combined, washed with brine, dried over anhydrous $Na_2SO_4$ and concentrated in vacuum. The resulting oil was purified by column chromatography on silica gel to provide **3p** (443mg, 86%).

Benzyl azides **4a-b**[11], **4c**[16], **4d**[12], **4e**[13], **4f**[11], **4h**[12], **4g**[15], **4k**[12] were synthesized with method A. **4i**[14], **4j**[17]were synthesized with method B.

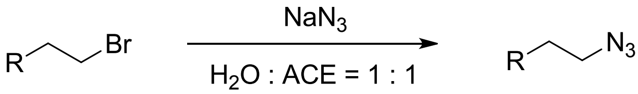
**Method A**[18]




**Method B**[17]

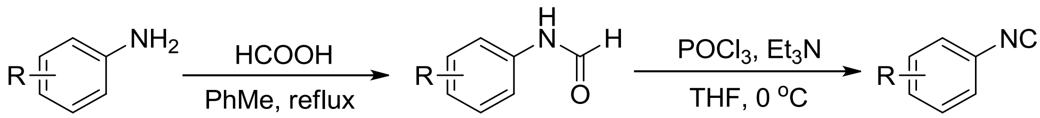



Alkyl azides **7a**[19], **7b**[19], **7c**[21], **7d**[20], **7e**[19], **7f**[22] were synthesized according to the literature.[19]




**General Procedure for the Preparation of Aryl isocyanides**

Aryl isocyanide **2e-g**[2] were synthesized according to the literature.[23]



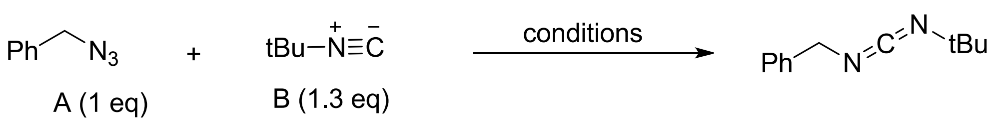

**Typical procedure for $Pd(PPh_3)_4$-catalyzed reactions of Isocyanide with Aryl azides**

To a 10ml glass vial was added $Pd(PPh_3)_4$ (6 mg, 0.005 mmol), THF (2ml), azide (**1a**, 24 mg, 0.2 mmol). Then the vessel was sealed, evacuated and purged with $N_2$. After 5min, isocyanide (**2a**, 20 mg, 0.24 mmol) was added by syringe. The mixture was stirred for 5 h at room temperature. Then volatiles were evaporated under reduced pressure, the resulting residue was purified by flash column chromatography to give colorless oil **3aa,** isolated yield 90%.

**Typical procedure for $Pd(PPh_3)_4$-catalyzed reactions of Isocyanide with Benzyl azides and Alkyl azides**

To a 10ml glass vial was added $Pd(PPh_3)_4$ (12 mg, 0.01 mmol), THF (2 ml), azide (**4a**, 27 mg, 0.2 mmol). Then the vessel was sealed, evacuated and purged with $N_2$. After 5 min, isocyanide (**2a**, 20 mg, 0.24 mmol) was added by syringe. The mixture was stirred for 10 h at 50 °C. Then volatiles were evaporated under reduced pressure, the resulting residue was purified by flash column chromatography to give colorless oil **5aa,** isolated yield 79%.

**Table *S1*. Additional Experiments on the Conditions of Pd-Catalyzed Reaction of Isocyanide with Benzyl azide.**[a]

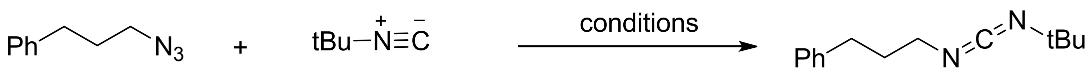



| Entry | Cat. / L (mol%) | Solvent | T [°C] | *t* [h] | Yield (%) [a] |
|---|---|---|---|---|---|
| 1 | $Pd(PPh_3)_4$(5) | PhMe | 60 | 18 | 63 |

| | | | | | |
|---|---|---|---|---|---|
| **2** | **$Pd(PPh_3)_4$(5)** | **THF** | **50** | **18** | **88(79)[b]** |
| 3 | $Pd(PPh_3)_4$(5) | DME | 50 | 24 | 30 |
| 4 | $Pd(PPh_3)_4$(5) | Dioxane | 50 | 18 | 76 |
| 5 | $Pd(PPh_3)_4$(5) | DCE | 50 | 28 | 46 |
| 6 | $Pd(OAc)_2$ | THF | 50 | 18 | <5 |
| 7 | $Pd(PPh_3)_2Cl_2$ | THF | 50 | 18 | <5 |
| 8 | $Pd_2(dba)_3$(2.5) | THF | 50 | 18 | 37 |
| 9 | $Pd_2(dba)_3$(2.5)/$PPh_3$(5) | THF | 50 | 18 | 40 |
| 10 | $Pd_2(dba)_3$(2.5)/$PPh_3$(10) | THF | 50 | 18 | 43 |
| 11 | $Pd_2(dba)_3$(2.5)/$PPh_3$(20) | THF | 50 | 18 | 65 |
| 12 | $Pd_2(dba)_3$(2.5)/$PPh_3$(25) | THF | 50 | 18 | 71 |
| 13[c] | $Pd(PPh_3)_4$(5) | THF | 50 | 18 | 73 |
| 14[d] | $Pd(PPh_3)_4$(10) | THF | 50 | 15 | 72 |

[a] Determined by $^1$HNMR using mesitylene as internal standard. [b] Isolated yield. [c] $Na_2SO_4$ (20 mg) was added. [d] **B** (1.5 eq).

**Table *S2.* Additional Experiments on the Conditions of Pd-Catalyzed Reaction of Isocyanide with Alkyl Azide.[a]**

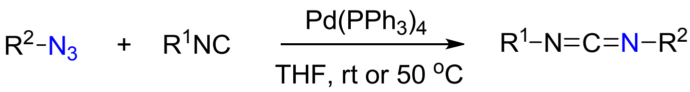



A (1 eq) B (1.3 eq)

| Entry | Cat. / L (mol%) | Solvent | T [°C] | *t* [h] | Yield% [a] |
|---|---|---|---|---|---|
| 1 | **$Pd(PPh_3)_4$(5)** | **THF** | **50** | **23** | **78 (65)[b]** |
| 2 | $Pd(PPh_3)_4$(5) | THF | 70 | 18 | 67 |
| 3[c] | $Pd(PPh_3)_4$(10) | THF | 50 | 15 | 74 |
| 4[d] | $Pd(PPh_3)_4$(5) | THF | 50 | 23 | 70 |

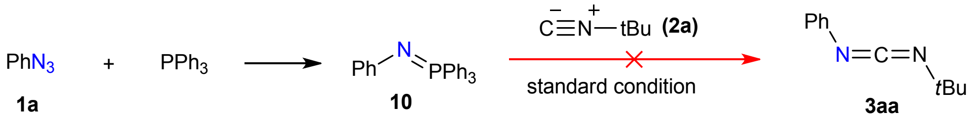
[a] Determined by $^1$HNMR using mesitylene as internal standard. [b] Isolated yield. [c] 4A MS (20 mg) was added. [d] Styrene (0.5 eq) was added as additive.

## Mechanistic Discussion

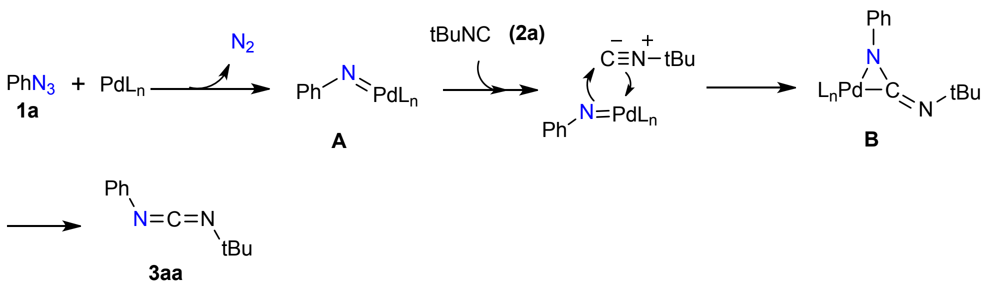



Based on the literature reports [25], there are three possible pathways that may be considered. (Mechanism ***a***, ***b***, ***c***)

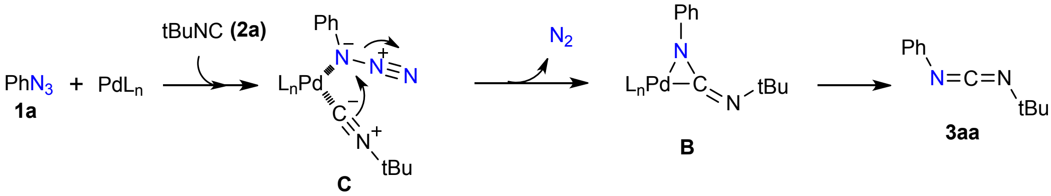
Mechanism ***a***




Mechanism ***b***




Mechanism ***c***

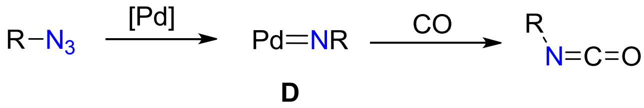



In mechanism ***a*,** the given intermediate *N*-(triphenylphosphoranylidene)-aniline (**10**) was speculated to be generated with triphenylphosphine and azide *via* aza-Wittig reaction. To elucidate this mechanism, 10 was prepared and isolated. When **10** was treated with **2a** under the standard reaction conditions, desired product could not be detected. Moreover, no intermediate **10** can be detected in the model reaction of **1a** with **2a** in TLC or $^{31}$P NMR (Figure *S1*). These results indicated that **10** are not a key intermediate in this transformation and no free $PPh_3$ are involved in the reaction of azides.

In mechanism ***b*,** firstly, palladium nitrene species **A** is formed from **1a** simultaneously with the release of $N_2$. Subsequently, the insertion of isocyanide (**2a**) into palladium nitrene species **A** occured to give intermediate **B**. The species **B** subsequently undergoes reductive elimination to give final products **3aa.**

In mechanism ***c*,** the first step of the reaction sequences involved a labile coordination of the organic azide and isocyanide to the metal, followed by the direct reaction of isocyanide with azide group to give species B without palladium nitrene intermediate formation.

Compared with mechanism ***b*** and mechanism ***c***, though mechanism ***c*** may also provide a plausible explanation for the course of reaction, Besenyei**[26]** group have successfully accomplished the preparation of stable palladium-nitrene intermediate **D** with azides and stoichiometric palladium complexes; subsequently, the species **D** can also react with CO (as a σ-donor/π-acceptor ligand as isocyanide) affording isocyanate. Thus, we consider the mechanism ***b*** is more plausible with the information currently available, although vigorous experiments are needed to unambiguously establish this mechanism.



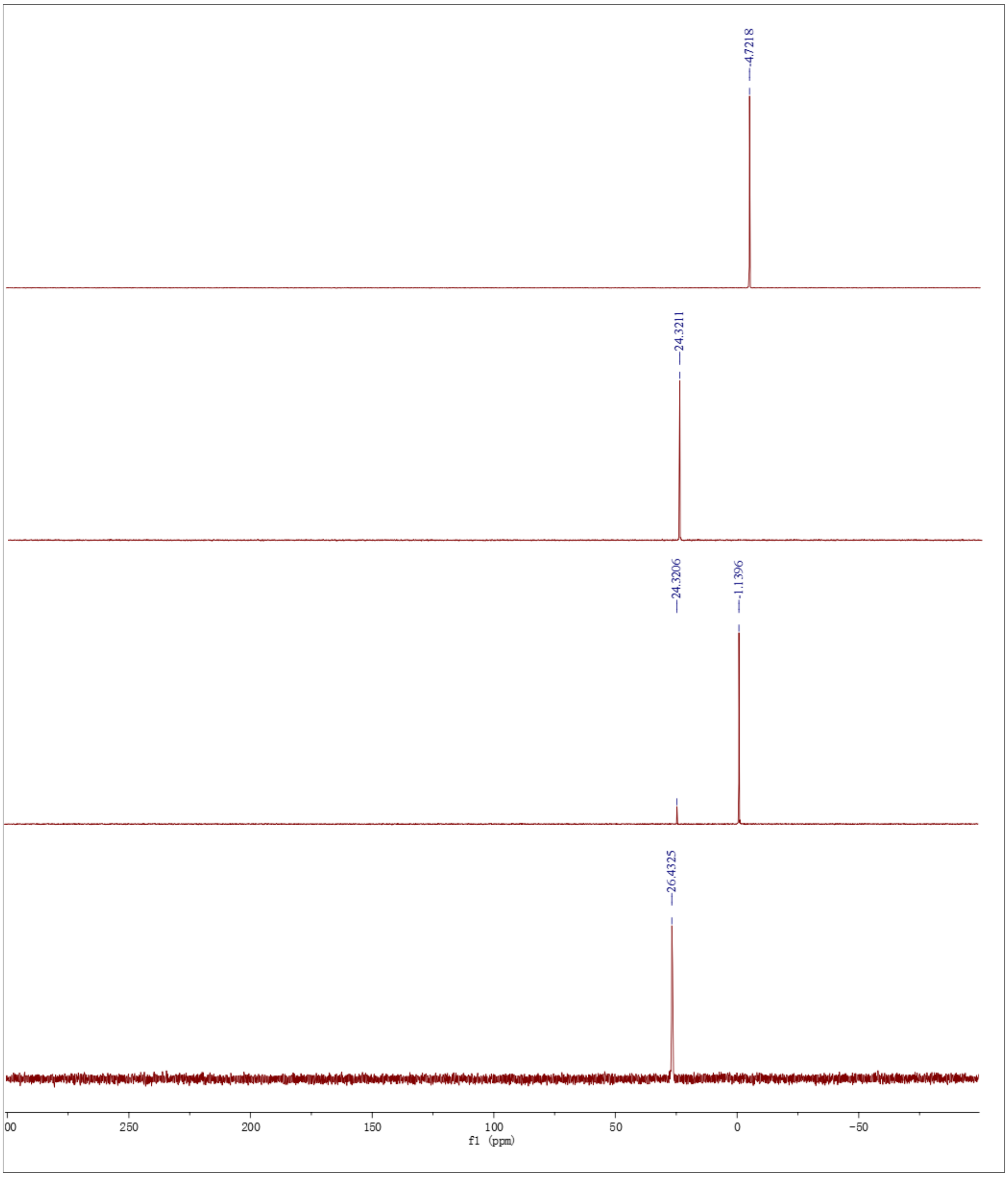
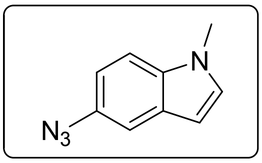



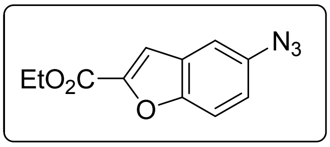

**Figure *S1*. $^{31}$P NMR of different products or mixture**

## Spectra Data



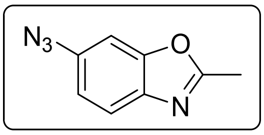

**5-azido-1-methyl-1*H*-indole (3p)**

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.06 (d, *J* = 3.1 Hz, 1H), 6.89 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.42 (dd, *J* = 3.1, 0.8 Hz, 1H), 3.77 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 134.47, 131.63, 130.19, 129.14, 113.52, 110.25, 100.54, 32.96. IR (neat, cm$^{-1}$): 2117, 1488, 1277, 720. HRMS *m/z* (EI) calcd for $C_9H_8N_4$ (M+) 172.0749, found 172.0751.



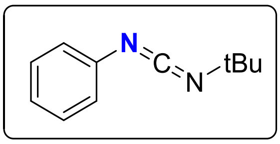

**Ethyl 5-azidobenzofuran-2-carboxylate (3q)**

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 1H), 7.45 (s, 1H), 7.30 (d, *J* = 2.3 Hz, 1H), 7.09 (dd, *J* = 8.9, 2.3 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.15, 152.96, 146.96, 136.11, 127.95, 119.33, 113.43, 113.06, 111.82, 61.64, 14.24. IR (neat, cm$^{-1}$): 2116, 1723, 1180. HRMS *m/z* (ES+) calcd for $C_{11}H_9N_3NaO_3$ ($[M+Na]^+$) 254.0536, found 254.0532.



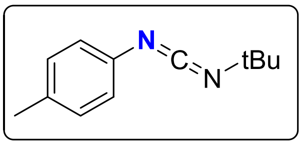

**6-azido-2-methylbenzo[*d*]oxazole (3s)**

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.5 Hz, 1H), 7.14 (d, *J* = 2.1 Hz, 1H), 6.99 (dd, *J* = 8.5, 2.1 Hz, 1H), 2.63 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 164.16, 151.55, 138.92, 137.01, 120.02, 115.53, 101.25, 14.49. IR (neat, cm$^{-1}$): 2113, 1478, 1305, 1228. HRMS *m/z* (EI) calcd for $C_8H_6N_4O$ (M+) 174.0542, found 174.0542.



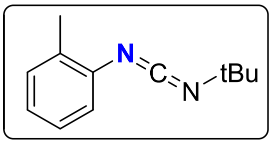

***N*-((*tert*-butylimino)methylene)aniline (3aa)**[27]

98% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.19 (m, 2H), 7.17 – 7.04 (m, 3H), 1.40 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.87, 136.28, 129.32, 124.56, 123.22, 57.39, 31.56.



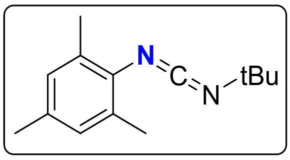
***N*-((*tert*-butylimino)methylene)-4-methylaniline(3ba)**[28]

93% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.05 (m, 2H), 7.02 – 6.95 (m, 2H), 2.31 (s, 3H), 1.39 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 137.94, 136.88, 134.25, 129.90, 122.98, 57.25, 31.54, 20.87.



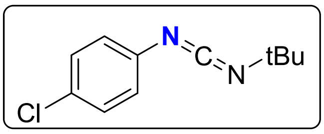
***N*-((*tert*-butylimino)methylene)-2-methylaniline (3ca)**

92% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.09 (m, 3H), 7.04 – 6.97 (m, 1H), 2.29 (s, 3H), 1.40 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.22, 135.60, 132.04, 130.65, 126.65, 124.43, 123.36, 56.97, 31.55, 18.13. IR (neat, $cm^{-1}$): 2114, 1498, 1186, 757. HRMS *m/z* (EI) calcd for $C_{12}H_{16}N_2$ (M+) 188.1313, found 188.1319.



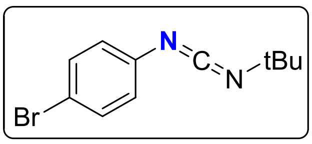
***N*-((*tert*-butylimino)methylene)-2,4,6-trimethylaniline (3da)**[27]

81% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, $J$ = 0.5 Hz, 2H), 2.31 (s, 6H), 2.24 (s, 3H), 1.35 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 134.13, 133.51, 132.75, 132.16, 128.72, 55.93, 31.29, 20.68, 18.98.



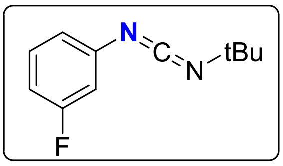
***N*-((*tert*-butylimino)methylene)-4-chloroaniline (3ea)**[29]

99% $^{1}$HNMR yield, colourless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 2H), 7.03 – 6.98 (m, 2H), 1.40 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.65, 135.62, 129.68, 129.35, 124.38, 57.65, 31.55.



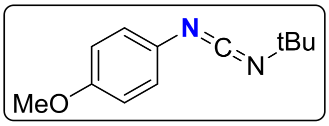
**4-bromo-*N*-((*tert*-butylimino)methylene)aniline (3fa)**[30]

93% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 6.97 – 6.92 (m, 2H), 1.40 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.21, 135.47, 132.31, 124.81, 117.33, 57.68, 31.56.



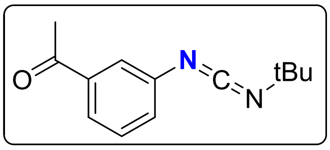
**N-((tert-butylimino)methylene)-3-fluoroaniline (3ga)**

92% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 1H), 6.89 – 6.85 (m, 1H), 6.84 – 6.76 (m, 2H), 1.41 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.21 (d, $J_{CF}$= 246.1 Hz), 142.92 (d, $J$ = 10.1 Hz), 135.23, 130.27 (d, $J$ = 9.4 Hz), 118.99 (d, $J$ = 2.9 Hz), 111.45 (d, $J$ = 21.3 Hz), 110.46 (d, $J$ = 23.2 Hz), 57.77, 31.56. IR (neat, cm$^{-1}$): 2118, 1609, 1180, 934. HRMS *m/z* (EI) calcd for $C_{11}H_{13}FN_2$ (M+) 192.1063, found 192.1068.



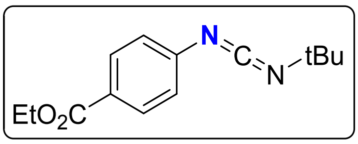
**N-((tert-butylimino)methylene)-4-methoxyaniline (3ha)**[29]

96% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.05 – 6.99 (m, 2H), 6.84 – 6.80 (m, 2H), 3.78 (s, 3H), 1.39 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 156.73, 137.25, 133.28, 124.04, 114.58, 57.17, 55.46 (d, $J$ = 2.3 Hz), 31.55.



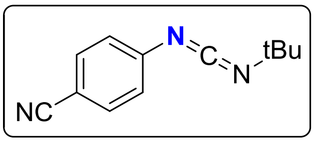
**1-(3-(((tert-butylimino)methylene)amino)phenyl)ethanone (3ia)**

95% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 2H), 7.38 (t, $J$ = 7.8 Hz, 1H), 7.30 – 7.25 (m, 1H), 2.59 (s, 3H), 1.43 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.48, 141.73, 138.26, 135.25, 129.51, 127.68, 124.35, 122.82, 57.73, 31.54, 26.66. IR (neat, cm$^{-1}$): 2123, 1687, 1256, 686. HRMS *m/z* (ES+) calcd for $C_{13}H_{16}N_2NaO$ ($[M+Na]^+$) 239.1155, found 239.1153.



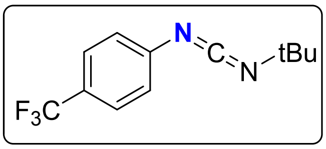
**Ethyl 4-(((tert-butylimino)methylene)amino)benzoate (3ja)**[29]

91% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, $J$ = 8.4, 1.0 Hz, 2H), 7.11 (dd, $J$ = 8.4, 1.0 Hz, 2H), 4.36 (q, $J$ = 7.1 Hz, 2H), 1.42 (s, 9H), 1.38 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.07, 145.98, 134.41, 130.94, 126.41, 122.96, 60.80, 57.98, 31.56, 14.30.



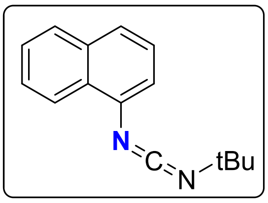
**4-(((*tert*-butylimino)methylene)amino)benzonitrile (3ka)**

91% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.15 – 7.10 (m, 2H), 1.43 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 146.45, 133.41, 132.94, 123.85, 118.87, 107.39, 58.35, 31.54. IR (neat, $cm^{-1}$): 2130, 1601, 1190, 841. HRMS *m/z* (ES+) calcd for $C_{12}H_{13}N_3Na$ ($[M+Na]^+$) 222.1002, found 222.1001.



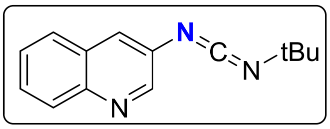
***N*-((*tert*-butylimino)methylene)-4-(trifluoromethyl)aniline (3la)**

92% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, $J$ = 8.4 Hz, 2H), 7.15 (d, $J$ = 8.3 Hz, 2H), 1.42 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 144.95, 134.42, 126.51 (q, $J$ = 3.7 Hz), 126.22, 124.14 (q, $J_{CF}$ = 271.5 Hz), 123.32, 57.99, 31.54. IR (neat, $cm^{-1}$): 2128, 1322, 1123, 1065, 843. HRMS *m/z* (EI+) calcd for $C_{12}H_{13}F_3N_2$ (M+) 242.1031, found 242.1038.



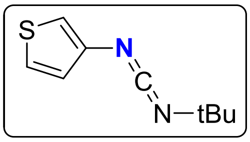
***N*-((*tert*-butylimino)methylene)naphthalen-1-amine(3ma)**[31]

90% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.27 (m, 1H), 7.82 – 7.77 (m, 1H), 7.60 (d, $J$ = 8.2 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.41 – 7.36 (m, 1H), 7.30 (dd, $J$ = 7.3, 1.1 Hz, 1H), 1.44 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.60, 137.48, 135.82, 134.31, 128.76, 127.65, 126.35, 125.78, 124.43, 123.56, 119.08, 57.44, 31.66.



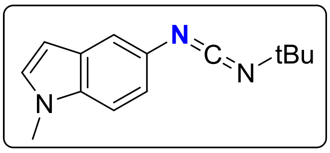
***N*-((*tert*-butylimino)methylene)quinolin-3-amine (3na)**

93% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, $J$ = 2.5 Hz, 1H), 8.05 (d, $J$ = 8.5 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.62 (ddd, $J$ = 8.4, 6.9, 1.5 Hz, 1H), 7.52 (ddd, $J$ = 8.1, 6.9, 1.2 Hz, 1H), 1.46 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 147.54, 145.42, 134.91, 134.66, 129.24, 128.43, 128.24, 127.16, 127.00, 126.65, 58.05, 31.57. IR (neat, $cm^{-1}$): 2119, 1182, 752. HRMS *m/z* (ES+) calcd for $C_{14}H_{16}N_3$ ($[M+H]^+$) 226.1339, found 226.1336.



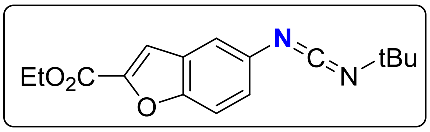
***N*-((*tert*-butylimino)methylene)thiophen-3-amine (3oa)**

95% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 5.1, 3.2 Hz, 1H), 6.88 (dd, *J* = 5.1, 1.4 Hz, 1H), 6.80 (dd, *J* = 3.2, 1.4 Hz, 1H), 1.39 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 138.38, 137.62, 125.37, 123.68, 113.22, 57.33, 31.48. IR (neat, $cm^{-1}$): 2114, 1184, 772. HRMS *m/z* (ES+) calcd for $C_9H_{13}N_2S$ ($[M+H]^+$) 181.0794, found 181.0800.



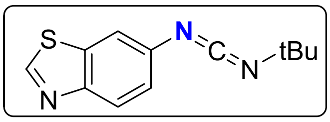
***N*-((*tert*-butylimino)methylene)-1-methyl-1*H*-indol-5-amine (3pa)**

75% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 2.1 Hz, 1H), 7.21 (d, *J* = 8.6 Hz, 1H), 7.04 – 6.98 (m, 2H), 6.40 (dd, *J* = 3.1, 0.8 Hz, 1H), 3.74 (s, 3H), 1.41 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 137.91, 134.40, 132.24, 129.75, 128.95, 117.69, 114.56, 109.72, 100.56, 56.97, 32.91, 31.58. IR (neat, $cm^{-1}$): 2923, 2124, 1240, 720. HRMS *m/z* (ES+) calcd for $C_{14}H_{18}N_3$ ($[M+H]^+$) 228.1495, found 228.1492.



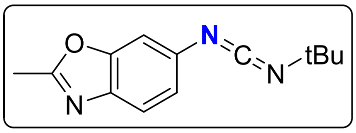
**Ethyl 5-(((*tert*-butylimino)methylene)amino)benzofuran-2-carboxylate (3qa)**

90% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 1H), 7.46 (d, *J* = 0.9 Hz, 1H), 7.36 – 7.33 (m, 1H), 7.20 (dd, *J* = 8.8, 2.2 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.49 – 1.36 (m, 12H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.32, 153.28 – 152.14 (m), 146.50, 136.97, 136.12, 127.71, 123.50, 115.98, 113.38, 112.89, 61.51, 57.44, 31.54, 14.25. IR (neat, $cm^{-1}$): 2115, 1731, 1181, 764. HRMS *m/z* (ES+) calcd for $C_{16}H_{18}N_2NaO_3$ ($[M+Na]^+$) 309.1210, found 309.1209.



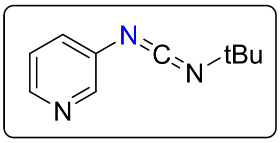
***N*-((*tert*-butylimino)methylene)benzo[*d*]thiazol-6-amine (3ra)**

94% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.27 (dd, *J* = 8.6, 2.2 Hz, 1H), 1.44 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 153.04, 150.44, 139.04, 135.46, 134.81, 123.95, 122.35, 115.52, 57.72, 31.56. IR (neat, $cm^{-1}$): 2125, 1185, 828. HRMS *m/z* (ES+) calcd for $C_{12}H_{14}N_3S$ ($[M+H]^+$) 232.0903, found 232.0899.



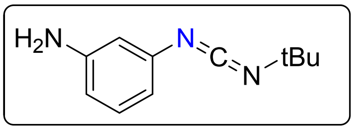
**N-((tert-butylimino)methylene)-2-methylbenzo[d]oxazol-6-amine (3sa)**

81% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 1H), 7.18 (dd, *J* = 2.0, 0.5 Hz, 1H), 7.06 (ddd, *J* = 8.4, 2.0, 0.6 Hz, 1H), 2.61 (s, 3H), 1.42 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.78, 151.38, 138.54, 137.99, 135.93, 119.79, 119.38, 105.00, 57.61, 31.55, 14.46. IR (neat, $cm^{-1}$): 2116, 1619, 1184, 856. HRMS *m/z* (ES+) calcd for $C_{13}H_{16}N_3O$ ($[M+H]^+$) 230.1288, found 230.1284.



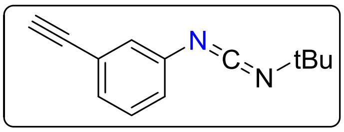
**N-((tert-butylimino)methylene)pyridin-3-amine(3ta)**[48]

86% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 2.6 Hz, 1H), 8.33 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.36 (ddd, *J* = 8.1, 2.6, 1.5 Hz, 1H), 7.22 (ddd, *J* = 8.1, 4.7, 0.7 Hz, 1H), 1.42 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 145.37, 144.98, 138.17, 134.58, 129.88, 123.79, 57.87, 31.54.



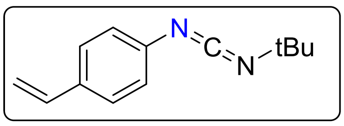
**$N^1$-((tert-butylimino)methylene)benzene-1,3-diamine(3ua)**

87% $^{1}$HNMR yield, white solid, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.05 (t, *J* = 7.8 Hz, 1H), 6.56 – 6.47 (m, 1H), 6.46 – 6.35 (m, 1H), 3.67 (s, 2H), 1.39 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 147.41, 141.74, 136.43, 129.99, 113.45, 111.52, 109.79, 57.29, 31.55. IR (neat, $cm^{-1}$): 2114, 1600, 1181, 686. HRMS *m/z* (EI+) calcd for $C_{11}H_{15}N_3$ (M+) 189.1266, found 189.1268.



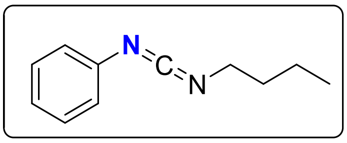
**N-((tert-butylimino)methylene)-3-ethynylaniline(3va)**

92% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.17 (m, 3H), 7.12 – 7.02 (m, 1H), 3.08 (s, 1H), 1.41 (s, 9H).$^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.20, 135.35, 129.29, 128.25, 126.63, 123.87, 123.12, 82.99, 77.49, 57.60, 31.54. IR (neat, $cm^{-1}$): 2135, 2116, 1598, 1179, 685. HRMS *m/z* (EI+) calcd for $C_{13}H_{14}N_2$ (M+) 198.1157, found 198.1157.



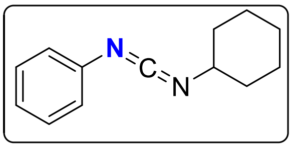
**N-((tert-butylimino)methylene)-4-vinylaniline(3wa)**

96% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.09 – 6.97 (m, 2H), 6.66 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.67 (dd, *J* = 17.6, 0.7 Hz, 1H), 5.19 (dd, *J* = 10.9, 0.7 Hz, 1H), 1.40 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.40, 136.15, 136.06, 134.11, 127.19, 123.26, 112.96, 57.51, 31.57. IR (neat, $cm^{-1}$): 2107, 1512, 1191, 841. HRMS *m/z* (EI+) calcd for $C_{13}H_{16}N_2$ (M+) 200.1313, found 200.1314.



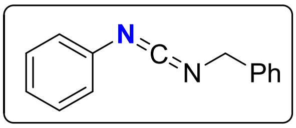
**N-((butylimino)methylene)aniline (3ab)**[32]

95% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.13 – 7.05 (m, 3H), 3.41 (t, *J* = 6.8 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.51 – 1.40 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.71, 135.97, 129.30, 124.50, 123.41, 46.50, 33.37, 19.93, 13.56.



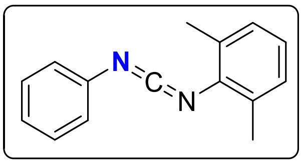
**N-((cyclohexylimino)methylene)aniline (3ac)**[32]

90% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.15 – 7.04 (m, 3H), 3.47 (ddd, *J* = 13.5, 9.6, 3.8 Hz, 1H), 2.07 – 1.96 (m, 2H), 1.82 – 1.71 (m, 2H), 1.61 – 1.43 (m, 3H), 1.41 – 1.21 (m, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.86, 136.16, 129.29, 124.46, 123.29, 56.60, 34.90, 25.29, 24.34.



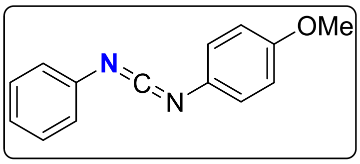
**N-((benzylimino)methylene)aniline (3ad)**[32]

93% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 7.27 – 7.21 (m, 2H), 7.11 – 7.05 (m, 1H), 7.02 – 6.95 (m, 2H), 4.55 (s, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.90, 137.76, 137.24, 129.27, 128.75, 127.76, 127.34, 124.81, 123.59, 50.45.



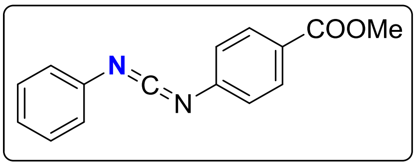
**2,6-dimethyl-N-((phenylimino)methylene)aniline (3ae)**[27]

82% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.20 – 7.10 (m, 3H), 7.07 – 6.96 (m, 3H), 2.39 (s, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.83, 134.91, 132.84, 131.54, 129.46, 128.19, 125.15, 124.74, 123.67, 19.01.



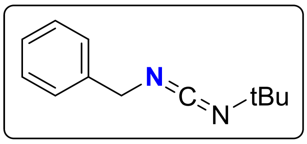
**4-methoxy-N-((phenylimino)methylene)aniline (3af)**[33]

73% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.20 – 7.14 (m, 3H), 7.13 – 7.08 (m, 2H), 6.88 – 6.82 (m, 2H), 3.79 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.44, 138.90, 135.80, 130.65, 129.44, 125.39, 125.14, 124.05, 114.69, 55.47.



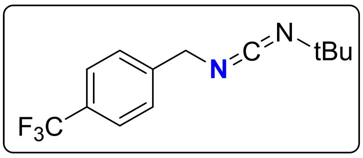

**Methyl 4-(((phenylimino)methylene)amino)benzoate (3ag)**

52% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 2H), 7.37 – 7.31 (m, 2H), 7.23 – 7.15 (m, 5H), 3.90 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.39, 143.39, 137.30, 134.07, 131.09, 129.58, 127.07, 126.02, 124.40, 124.01, 52.13. IR (neat, cm$^{-1}$): 2118, 1608, 1180, 934. HRMS *m/z* (ES+) calcd for $C_{15}H_{13}N_2O_2$ ($[M+H]^+$) 253.0971, found 253.0968.



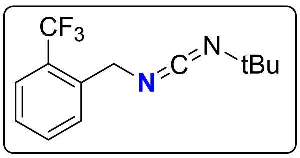

***N*-((benzylimino)methylene)-2-methylpropan-2-amine (5aa)**[29]

88% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 5H), 4.32 (s, 2H), 1.13 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.71, 138.71, 128.49, 127.82, 127.44, 55.24, 50.80, 31.10.



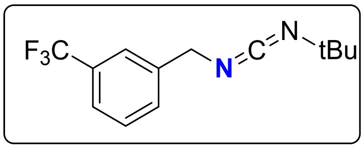

**2-methyl-*N*-(((4-(trifluoromethyl)benzyl)imino)methylene)propan-2-amine (5ba)**

82% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, $J$ = 8.2 Hz, 2H), 7.44 (d, $J$ = 8.1 Hz, 2H), 4.42 (s, 2H), 1.19 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 142.63, 140.10, 129.80, 129.48, 127.85, 125.45 (dd, $J$ = 7.5, 3.7 Hz), 122.71, 55.51, 50.19, 31.15. IR (neat, cm$^{-1}$): 2126, 1326, 1127, 1067. HRMS *m/z* (ES+) calcd for $C_{13}H_{16}F_3N_2$ ($[M+H]^+$) 257.1260, found 257.1257.



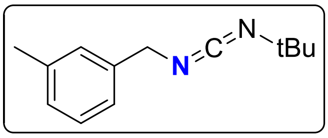

**2-methyl-*N*-(((2-(trifluoromethyl)benzyl)imino)methylene)propan-2-amine (5ca)**

90% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.59 (m, 2H), 7.57 (t, $J$ = 7.5 Hz, 1H), 7.38 (t, $J$ = 7.6 Hz, 1H), 4.56 (s, 2H), 1.17 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.07, 137.02, 132.10, 130.19, 127.81, 127.44, 125.76 (q, $J$ = 5.6 Hz), 124.20 (q, $J_{CF}$ = 274.0 Hz), 55.46, 47.09, 31.14. IR (neat, cm$^{-1}$): 2123, 1314, 1164, 1117, 768. HRMS *m/z* (EI) calcd for $C_{13}H_{15}F_3N_2$ (M+) 256.1187, found 256.1187.



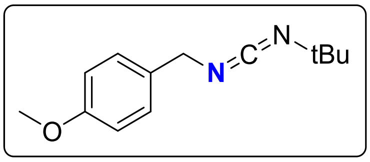

**2-methyl-*N*-(((3-(trifluoromethyl)benzyl)imino)methylene)propan-2-amine (5da)**

89% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.51 (m, 3H), 4.41 (s, 2H), 1.17 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.10, 139.68, 131.04, 130.72, 129.02, 124.45 (dd, $J$ = 7.6, 3.8 Hz), 124.26 (dd, $J$ = 7.6, 3.7 Hz), 123.99 (q, $J_{CF}$= 272.1 Hz), 55.54, 50.26, 31.15. IR (neat, cm$^{-1}$): 2124, 1328, 1128, 1074. HRMS *m/z* (EI) calcd for $C_{13}H_{15}F_3N_2$ (M+) 256.1187, found 256.1192.



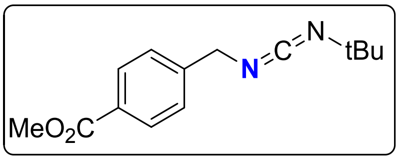

**2-methyl-*N*-(((3-methylbenzyl)imino)methylene)propan-2-amine (5ea)**[34]

80% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, $J$ = 7.6 Hz, 1H), 7.11 (dd, $J$ = 14.8, 7.2 Hz, 3H), 4.29 (s, 2H), 2.35 (s, 3H), 1.14 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.72, 138.62, 138.10, 128.53, 128.38, 128.13, 124.83, 55.21, 50.76, 31.11, 21.32.



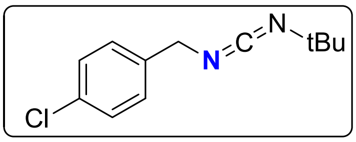

***N*-(((4-methoxybenzyl)imino)methylene)-2-methylpropan-2-amine (5fa)**[35]

72% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 6.90 – 6.86 (m, 2H), 4.25 (s, 2H), 3.80 (s, 3H), 1.13 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 158.90, 140.94, 131.04, 129.14, 113.81, 55.22 (d, $J$ = 2.1 Hz), 55.17, 50.25, 31.10.



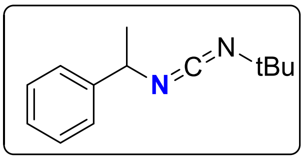

**Methyl 4-((((*tert*-butylimino)methylene)amino)methyl)benzoate (5ga)**

84% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 7.42 – 7.37 (m, 2H), 4.41 (s, 2H), 3.92 (s, 3H), 1.17 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.75, 143.72, 140.15, 129.82, 129.19, 127.54, 55.46, 52.04, 50.36, 31.18. IR (neat, cm$^{-1}$): 2118, 1724, 1278, 1106, 755. HRMS *m/z* (EI) calcd for $C_{14}H_{18}N_2O_2$ (M+) 246.1368, found 246.1372.



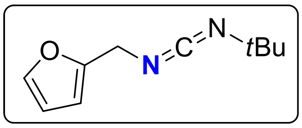

***N*-(((4-chlorobenzyl)imino)methylene)-2-methylpropan-2-amine (5ha)**

70% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.27 – 7.23 (m, 2H), 4.31 (s, 2H), 1.17 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.39, 137.19, 133.20, 129.10, 128.64, 55.44, 50.07, 31.19. IR (neat, cm$^{-1}$): 2122, 1492, 798. HRMS *m/z* (EI) calcd for $C_{12}H_{15}ClN_2$ (M+) 222.0924, found 222.0926.



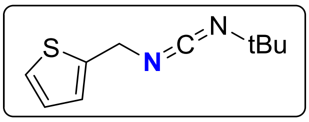

**2-methyl-*N*-(((1-phenylethyl)imino)methylene)propan-2-amine (5ia)**[36]

56% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 4.4 Hz, 4H), 7.29 – 7.23 (m, 1H), 4.58 (q, *J* = 6.8 Hz, 1H), 1.55 (d, *J* = 6.8 Hz, 3H), 1.18 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.89, 139.91, 128.40, 127.26, 126.02, 56.65 (d, *J* = 1.6 Hz), 55.21, 31.18, 24.44.



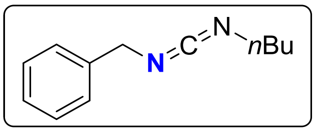

***N*-(((furan-2-ylmethyl)imino)methylene)-2-methylpropan-2-amine (5ja)**

72% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.33 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.26 (dd, *J* = 3.2, 0.6 Hz, 1H), 4.28 (s, 2H), 1.20 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 152.22, 142.21, 141.23, 110.31, 107.56, 55.46, 43.27, 31.04. IR (neat, cm$^{-1}$): 2925, 2129, 662. HRMS *m/z* (EI) calcd for $C_{10}H_{14}N_2O$ (M+) 178.1106, found 178.1108.



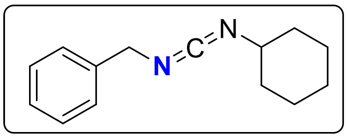

**2-methyl-*N*-(((thiophen-2-ylmethyl)imino)methylene)propan-2-amine (5ka)**

88% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.01 – 6.95 (m, 2H), 4.48 (s, 2H), 1.16 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.35, 140.83, 126.81, 125.84, 124.97, 55.53, 45.12, 31.10. IR (neat, cm$^{-1}$): 2120, 1186, 703. HRMS *m/z* (EI) calcd for $C_{10}H_{14}N_2S$ (M+) 194.0878, found 194.0880.



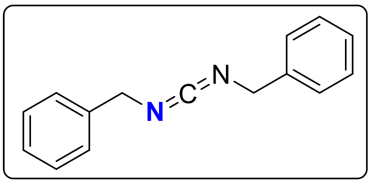

***N*-((benzylimino)methylene)butan-1-amine (5ab)**[37]

73% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 5H), 4.35 (s, 2H), 3.14 (t, *J* = 6.8 Hz, 2H), 1.47 – 1.39 (m, 2H), 1.33 – 1.23 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.74, 138.62, 128.50, 127.44, 127.36, 50.47, 46.18, 33.19, 19.77, 13.53.



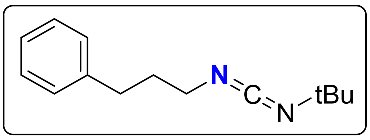

***N*-((benzylimino)methylene)cyclohexanamine (5ac)**[37]

74% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 5H), 4.34 (s, 2H), 3.20 – 3.09 (m, 1H), 1.82 – 1.73 (m, 2H), 1.70 – 1.62 (m, 2H), 1.55 – 1.47 (m, 1H), 1.28 – 1.12 (m, 5H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.66, 138.65, 128.49, 127.62, 127.37, 55.62, 50.67, 34.63, 25.31, 24.42.



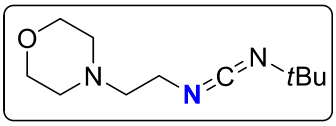

***N,N'*-methanediylidenebis(1-phenylmethanamine) (5ad)**[32]

40% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 6H), 7.22 – 7.14 (m, 4H), 4.30 (s, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.27, 138.24, 128.57, 127.48, 127.45, 50.32.



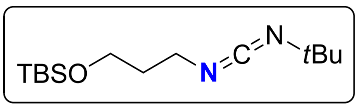

***N*-((*tert*-butylimino)methylene)-3-phenylpropan-1-amine (7aa)**

78% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.22 – 7.16 (m, 3H), 3.24 (t, $J$ = 6.8 Hz, 2H), 2.73 – 2.67 (m, 2H), 1.95 – 1.83 (m, 2H), 1.29 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.34, 139.75, 128.40, 128.32, 125.85, 55.01, 46.15, 32.96, 31.31. IR (neat, cm$^{-1}$): 2122, 1188, 699. HRMS *m/z* (EI) calcd for $C_{14}H_{20}N_2$ (M+) 216.1626, found 216.1626.




**2-methyl-*N*-(((2-morpholinoethyl)imino)methylene)propan-2-amine (7ba)**[38]

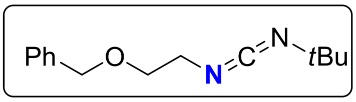
66% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 3.75 – 3.71 (m, 4H), 3.33 (t, $J$ = 6.3 Hz, 2H), 2.54 (t, $J$ = 6.3 Hz, 2H), 2.51 – 2.46 (m, 4H), 1.30 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.72, 66.82, 59.48, 55.12, 53.63, 43.67, 31.29.




**3-((*tert*-butyldimethylsilyl)oxy)-*N*-((*tert*-butylimino)methylene)propan-1-amine (7ca)**

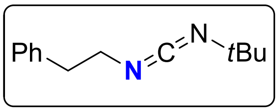
55% $^{1}$HNMR yield, colorless oil, $^{1}$H NMR (400 MHz, $CDCl_3$) δ 3.70 (t, $J$ = 6.0 Hz, 2H), 3.32 (t, $J$ = 6.8 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.28 (s, 9H), 0.89 (s, 9H), 0.05 (s, 6H). $^{13}$C NMR (101 MHz,

$CDCl_3$) δ 139.96, 60.05, 55.00, 43.54, 34.37, 31.32, 25.89, 18.27, -5.37. IR (neat, $cm^{-1}$): 2126, 1101, 837, 776. HRMS *m/z* (ES+) calcd for $C_{14}H_{31}N_2OSi$ ($[M+H]^+$) 271.2220, found 271.2197.



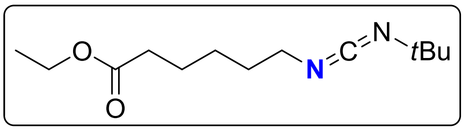
***N*-(((2-(benzyloxy)ethyl)imino)methylene)-2-methylpropan-2-amine (7da)**

74% $^1$HNMR yield, colorless oil, $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 5H), 4.56 (s, 2H), 3.59 (t, *J* = 5.4 Hz, 2H), 3.40 (t, *J* = 5.4 Hz, 2H), 1.26 (s, 9H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 140.14, 137.95, 128.30, 127.69, 127.59, 73.01, 69.94, 55.12, 46.70, 31.17. IR (neat, $cm^{-1}$): 2125, 1189, 698. HRMS *m/z* (ES+) calcd for $C_{14}H_{20}N_2NaO$ ($[M+Na]^+$) 255.1468, found 255.1468.



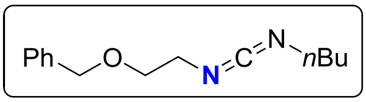
**2-methyl-*N*-((phenethylimino)methylene)propan-2-amine (7ea)**[27]

54% $^1$HNMR yield, colorless oil, $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.24 – 7.18 (m, 3H), 3.48 – 3.44 (m, 2H), 2.87 (t, *J* = 7.3 Hz, 2H), 1.19 (s, 9H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 139.75, 138.82, 128.73, 128.43, 126.39, 55.02, 48.14, 37.76, 31.14.



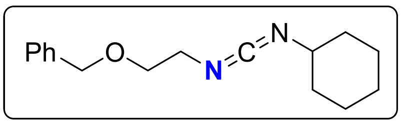
**Ethyl 6-(((*tert*-butylimino)methylene)amino)hexanoate (7fa)**

48% $^1$HNMR yield, colorless oil, $^1H$ NMR (400 MHz, $CDCl_3$) δ 4.09 (q, *J* = 7.1 Hz, 2H), 3.18 (t, *J* = 6.9 Hz, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 1.66 – 1.51 (m, 4H), 1.42 – 1.32 (m, 2H), 1.24 (s, 9H), 1.23 – 1.19 (m, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 173.48, 139.80, 60.15, 54.93, 46.64, 34.12, 31.26, 31.02, 26.35, 24.46, 14.16. IR (neat, $cm^{-1}$): 2122, 1736, 1186. HRMS *m/z* (ES+) calcd for $C_{13}H_{24}N_2NaO_2$ ($[M+Na]^+$) 263.1730, found 263.1731.



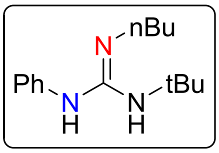
***N*-(((2-(benzyloxy)ethyl)imino)methylene)butan-1-amine (7db)**

50% $^1$HNMR yield, colorless oil, $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 4H), 7.31 – 7.26 (m, 1H), 4.57 (s, 2H), 3.60 (t, *J* = 5.3 Hz, 2H), 3.39 (t, *J* = 5.3 Hz, 2H), 3.17 (t, *J* = 6.9 Hz, 2H), 1.57 – 1.48 (m, 2H), 1.40 – 1.29 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 140.82, 137.95, 128.31, 127.62, 73.07, 69.88, 46.52, 46.28, 33.14, 19.88, 13.59. IR (neat, $cm^{-1}$): 2127, 697. HRMS *m/z* (ES+) calcd for $C_{14}H_{20}N_2NaO$ ($[M+Na]^+$) 255.1468, found 255.1468.



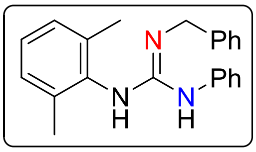
***N*-(((2-(benzyloxy)ethyl)imino)methylene)cyclohexanamine (7dc)**

67% $^1$HNMR yield, colorless oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 4H), 7.30 – 7.26 (m, 1H), 4.56 (s, 2H), 3.60 (t, $J$ = 5.3 Hz, 2H), 3.39 (t, $J$ = 5.3 Hz, 2H), 3.25 – 3.14 (m, 1H), 1.92 – 1.83 (m, 2H), 1.73 – 1.65 (m, 2H), 1.56 – 1.47 (m, 1H), 1.35 – 1.12 (m, 5H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.43, 137.94, 128.27, 127.61, 127.56, 73.02, 69.94, 55.59, 46.60, 34.57, 25.31, 24.49. IR (neat, $cm^{-1}$): 2122, 1116, 697. HRMS *m/z* (ES+) calcd for $C_{16}H_{23}N_2O$ ($[M+H]^+$) 259.1805, found 259.1804.



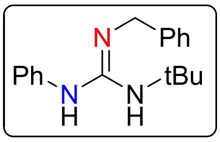

**1-(*tert*-butyl)-2-butyl-3-phenylguanidine (8a)**

67% yield, yellow oil, $^1$H NMR (300 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 2H), 6.95 – 6.87 (m, 1H), 6.86 – 6.80 (m, 2H), 3.75 (br, 1H), 3.68 (br, 1H), 3.17 (t, $J$ = 6.8 Hz, 2H), 1.60 – 1.45 (m, 2H), 1.43 – 1.29 (m, 11H), 0.93 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.04, 150.38, 129.13, 123.29, 121.17, 50.60, 41.66, 31.86, 30.13, 20.19, 13.82. IR (neat, $cm^{-1}$): 1633, 1589, 1487, 699. HRMS *m/z* (ES+) calcd for $C_{15}H_{26}N_3$ ($[M+H]^+$) 248.2121, found 248.2121.



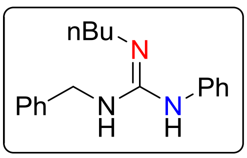

**2-benzyl-1-(2, 6-dimethylphenyl)-3-phenylguanidine (8b)**

60% yield, yellow oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.16 (m, 7H), 7.12 – 6.83 (m, 6H), 5.34 (br, 1H), 4.55 (s, 2H), 3.85 (br, 1H), 2.20 (s, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 156.14, 147.48, 147.11, 139.47, 129.88, 129.36, 128.63, 128.41, 128.26, 127.56, 127.39, 127.02, 45.40, 18.18. IR (neat, $cm^{-1}$): 1642, 1586, 1497, 752, 698. HRMS *m/z* (ES+) calcd for $C_{22}H_{24}N_3$ ($[M+H]^+$) 330.1965, found 330.1967.



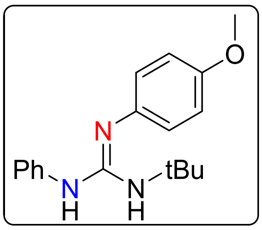

**2-benzyl-1-(*tert*-butyl)-3-phenylguanidine (8c)**

73% yield, yellow oil,$^1$H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 4H), 7.29 – 7.22 (m, 3H), 6.97 – 6.85 (m, 3H), 4.38 (s, 2H), 4.17 (br, 1H), 3.70 (br, 1H), 1.27 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 150.97, 149.62, 139.10, 129.26, 128.64, 127.42, 127.32, 123.23, 121.59, 50.90, 46.33, 30.08. IR (neat, $cm^{-1}$): 1635, 1588, 1486, 698. HRMS *m/z* (ES+) calcd for $C_{18}H_{24}N_3$ ($[M+H]^+$) 282.1965, found 282.1963.



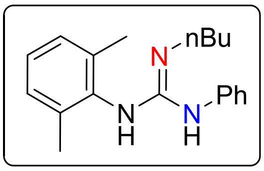

**1-benzyl-2-butyl-3-phenylguanidine (8d)**[39]

70% yield, yellow oil, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 7H), 7.00 – 6.93 (m, 1H), 6.93 – 6.89 (m, 2H), 4.38 (s, 2H), 4.21 (br, 1H), 3.76 (br, 1H), 3.11 (t, $J$ = 7.1 Hz, 2H), 1.49 – 1.37 (m, 2H), 1.25 (dq, $J$ = 14.3, 7.3 Hz, 2H), 0.87 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.18, 150.05, 139.04, 129.26, 128.69, 127.39, 127.32, 123.54, 121.52, 45.99, 41.62, 31.76, 19.94, 13.74.



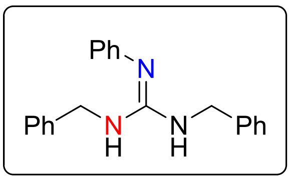

**1-(*tert*-butyl)-2-(4-methoxyphenyl)-3-phenylguanidine (8e)**[40]

51% yield, white solid, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.25 (dd, $J$ = 10.0, 5.4 Hz, 2H), 7.03 – 6.90 (m, 4H), 6.87 – 6.73 (m, 3H), 5.70 (br, 1H), 3.96 (br, 1H), 3.76 (s, 3H), 1.41 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 150.05, 147.30, 129.30, 125.46, 123.74, 123.15, 121.90, 121.36, 114.62, 55.45, 51.06, 29.46.



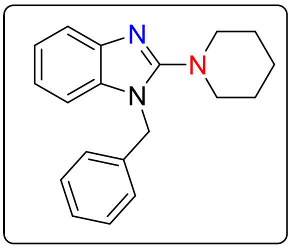

**2-butyl-1-(2, 6-dimethylphenyl)-3-phenylguanidine (8f)**

68% yield, yellow oil, $^1$H NMR (400 MHz, DMSO) δ 7.48 – 7.10 (m, 4H), 7.00 – 6.66 (m, 4H), 5.01 (br, 1H), 3.13 – 2.98 (m, 2H), 2.08 (s, 6H), 1.43 (dt, $J$ = 14.6, 7.1 Hz, 2H), 1.25 (dq, $J$ = 14.5, 7.2 Hz, 2H), 0.85 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 152.79, 147.29, 146.36, 141.60, 128.98, 128.35, 127.49, 120.49, 119.30, 41.17, 31.80, 19.50, 18.33, 13.69. IR (neat, $cm^{-1}$): 1647, 1588, 1497, 653. HRMS *m/z* (ES+) calcd for $C_{19}H_{26}N_3$ ($[M+H]^+$) 296.2121, found 296.2113.




**1, 3-dibenzyl-2-phenylguanidine(8g)**[41]

65% yield, white solid, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.16 (m, 12H), 7.01 – 6.88 (m, 3H), 4.33 (br, $4H_{PhCH2}$, $2H_{NH}$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.00, 149.40, 138.69, 129.32, 128.61, 127.30, 127.11, 123.46, 121.83, 45.87.



**1-benzyl-2-(piperidin-1-yl)-1H-benzo[*d*]imidazole (9)**[42]

72% isolated yield, white solid. $^1$H NMR (400 MHz,$CDCl_3$) δ 7.65 – 7.61 (m, 1H), 7.33 – 7.24 (m, 3H), 7.20 – 7.14 (m, 3H), 7.05 (td, *J* = 7.7, 0.8 Hz, 1H), 7.00 – 6.95 (m, 1H), 5.19 (s, 2H), 3.23 – 3.16 (m, 4H), 1.70 – 1.56 (m, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.03, 141.66, 136.44, 135.35, 128.81, 127.44, 126.06, 121.69, 121.10, 117.89, 109.24, 51.86, 47.64, 25.67, 24.12.

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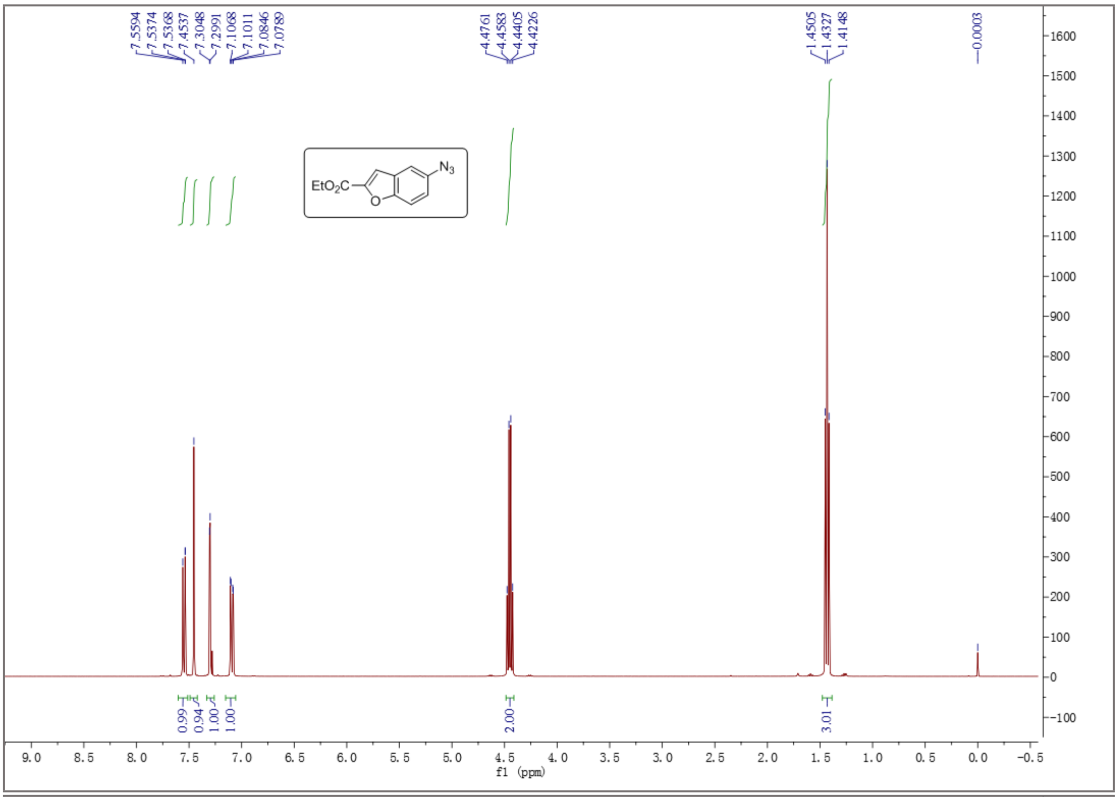
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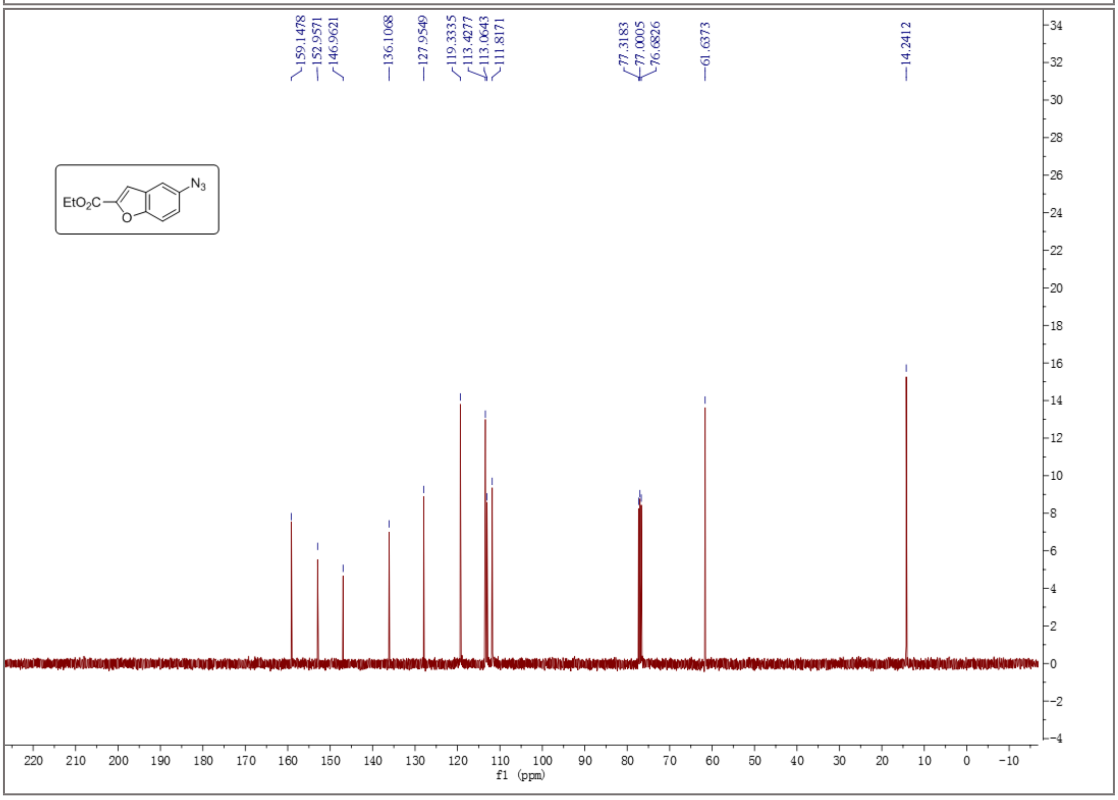
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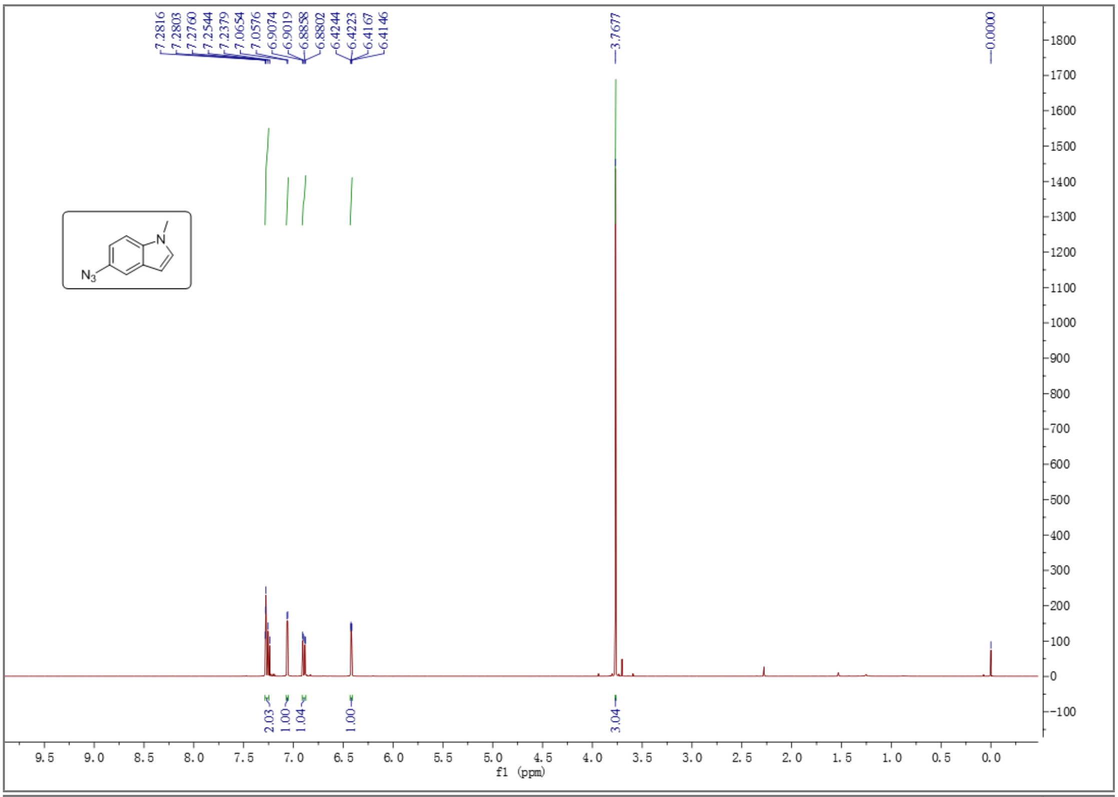
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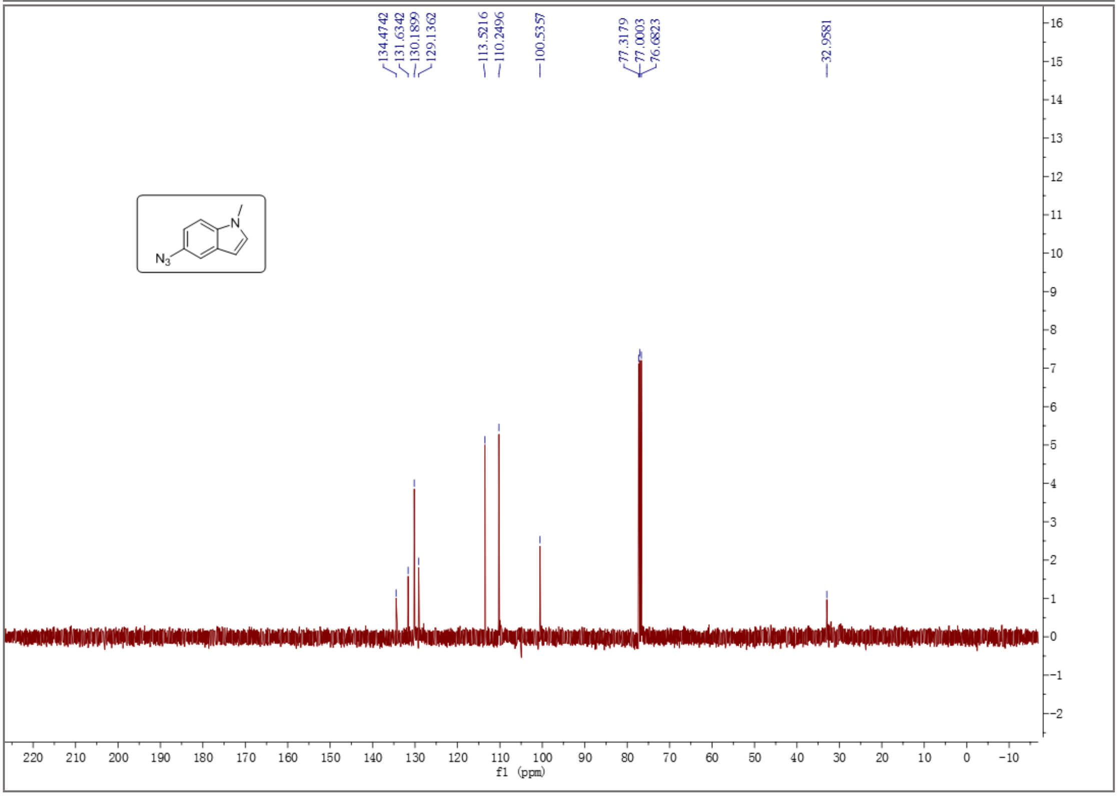
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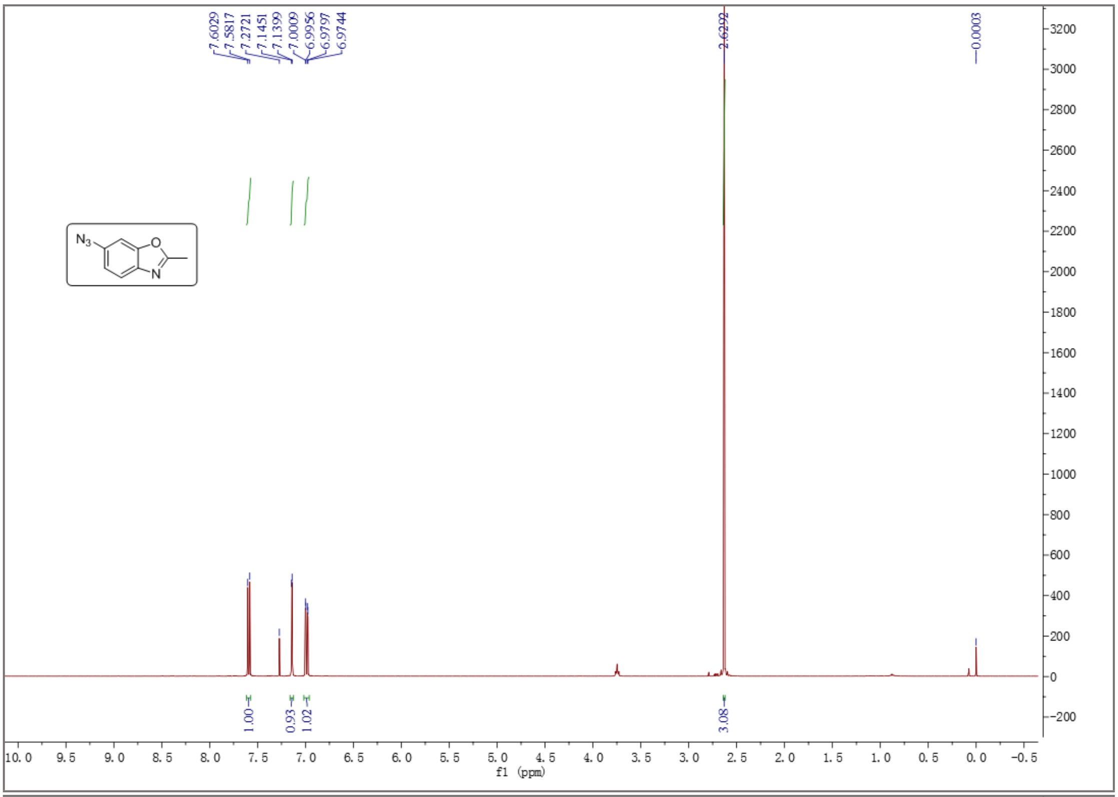
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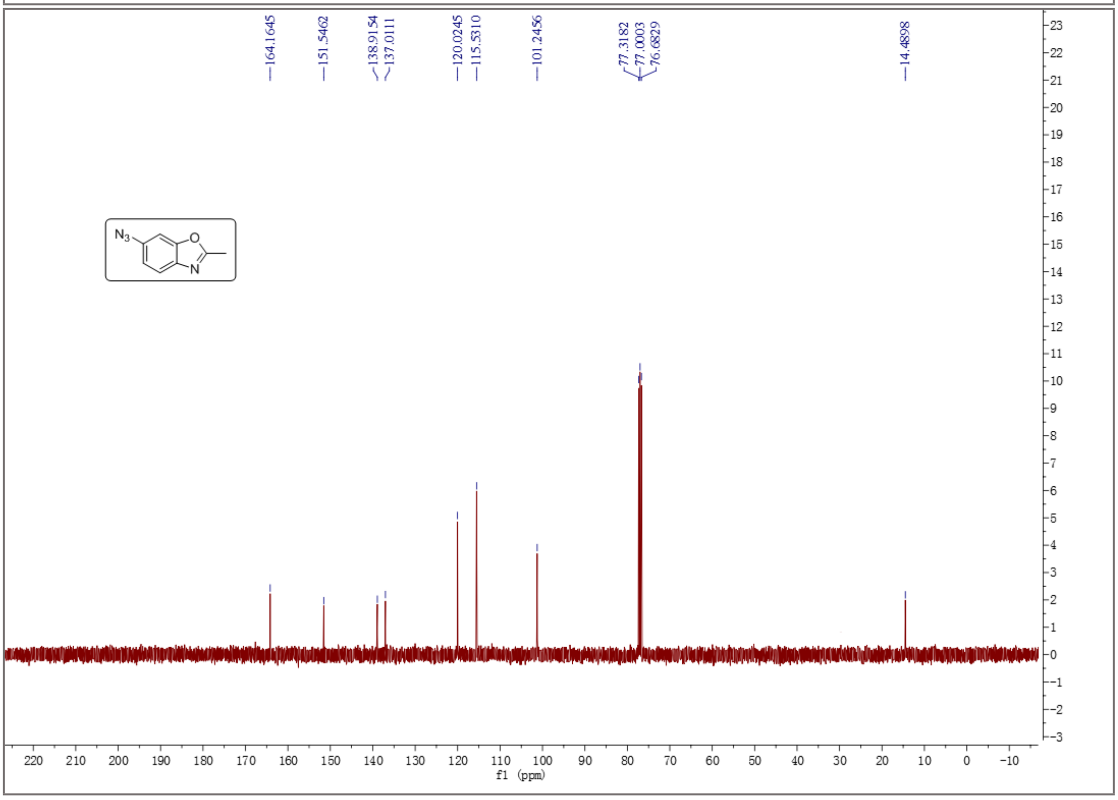
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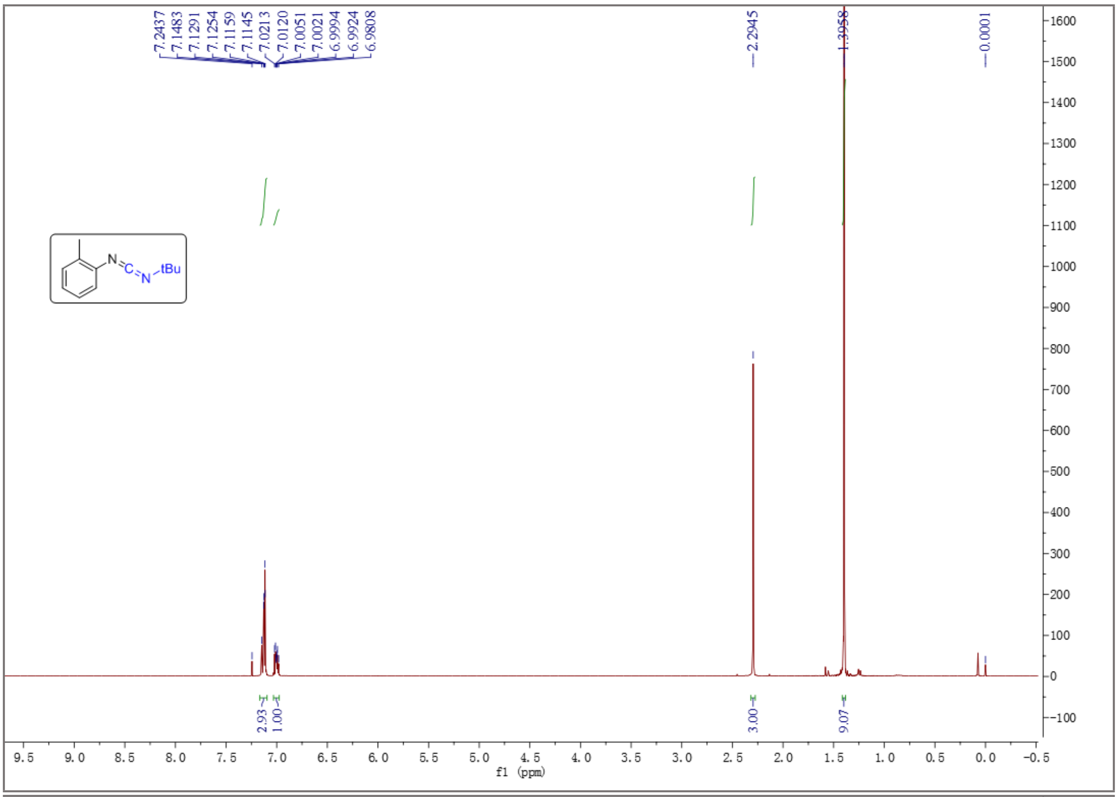

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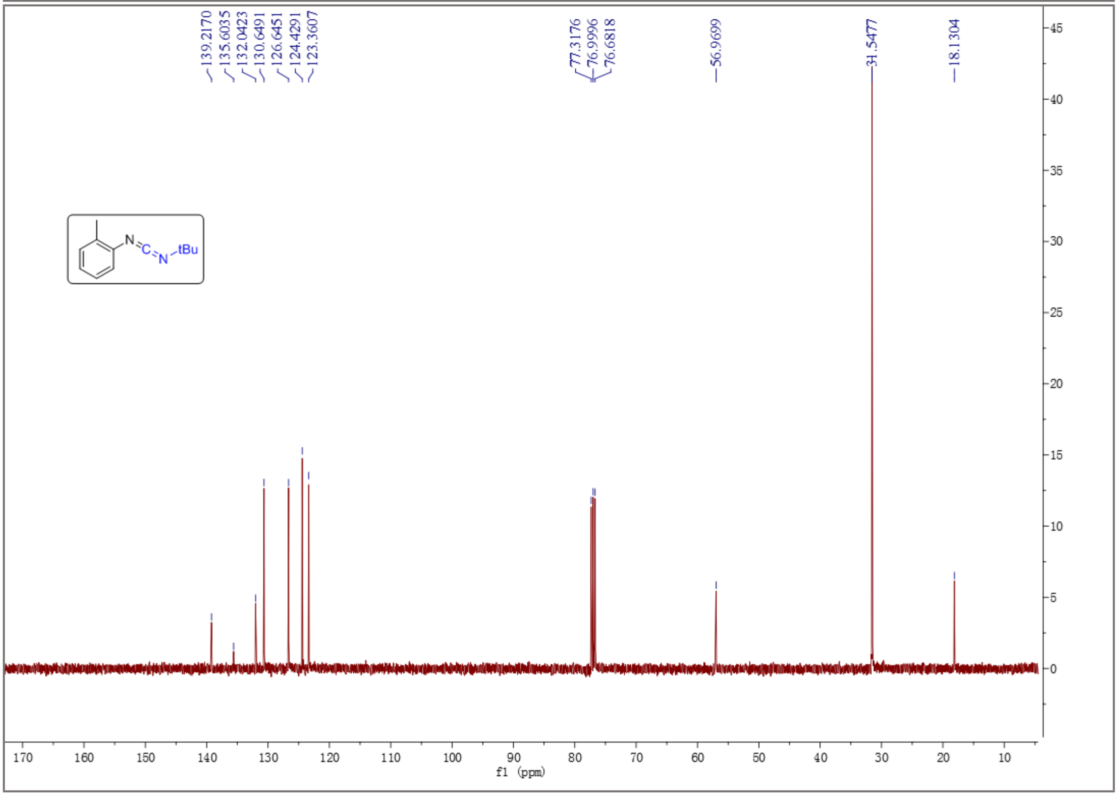

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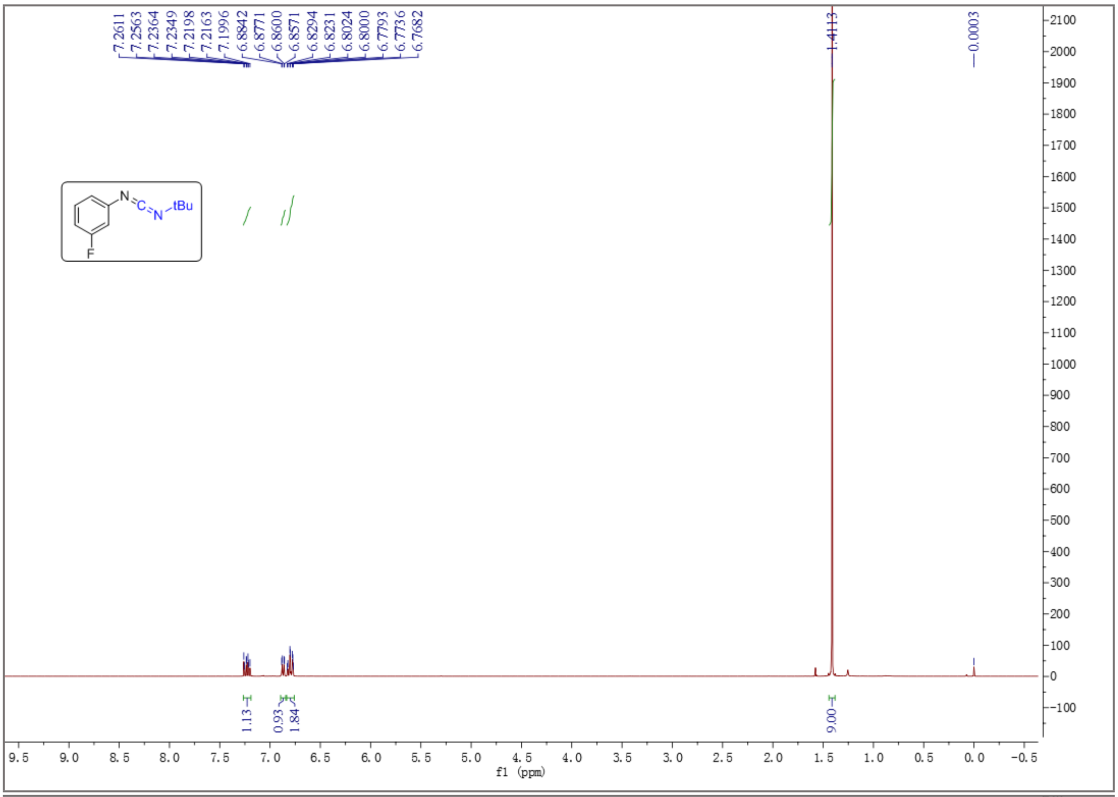
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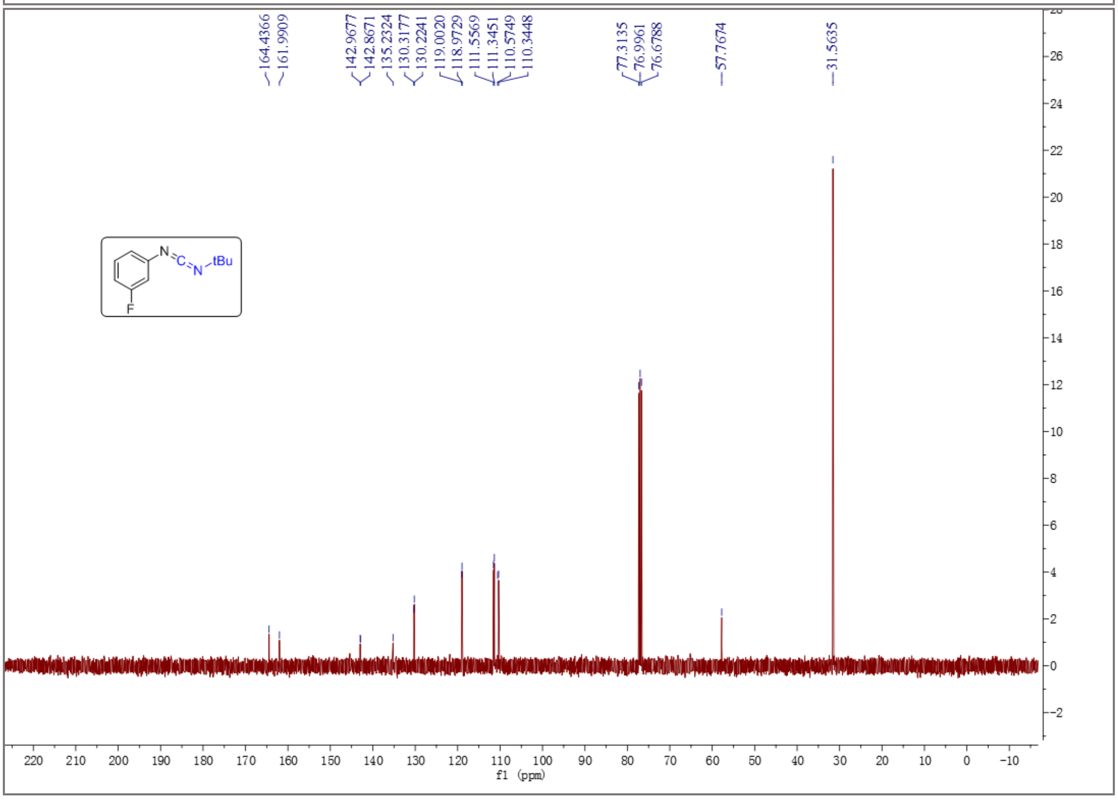
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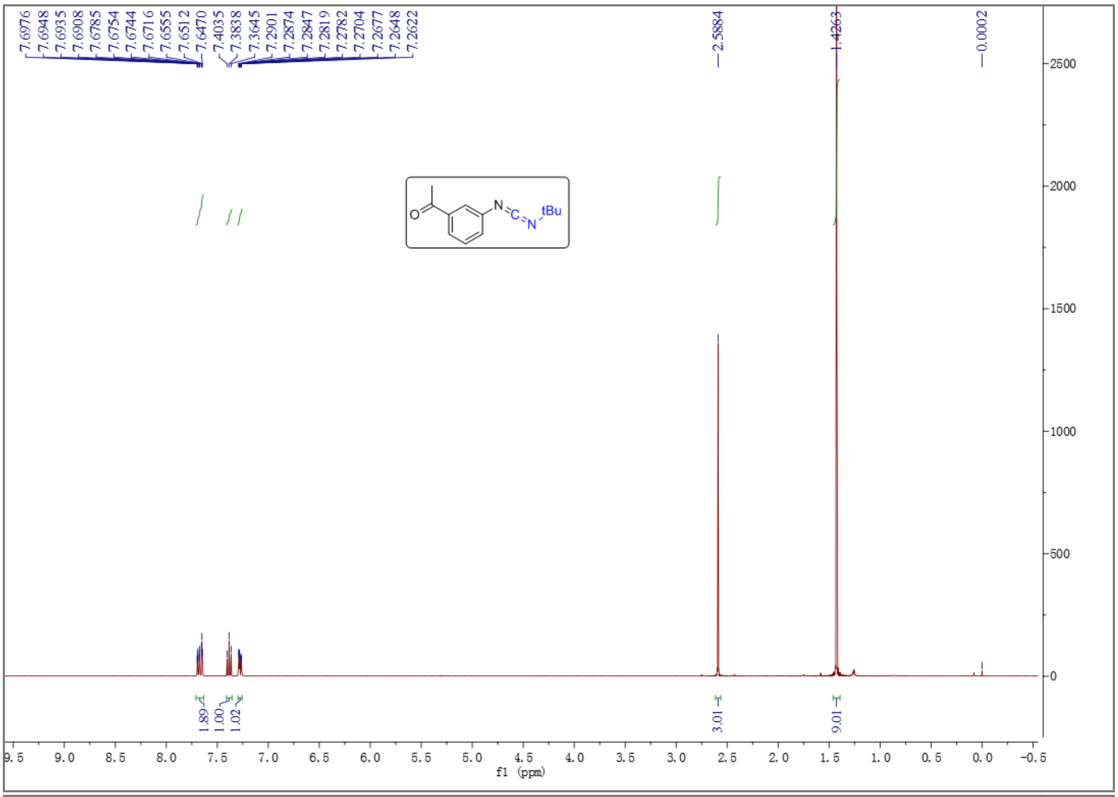
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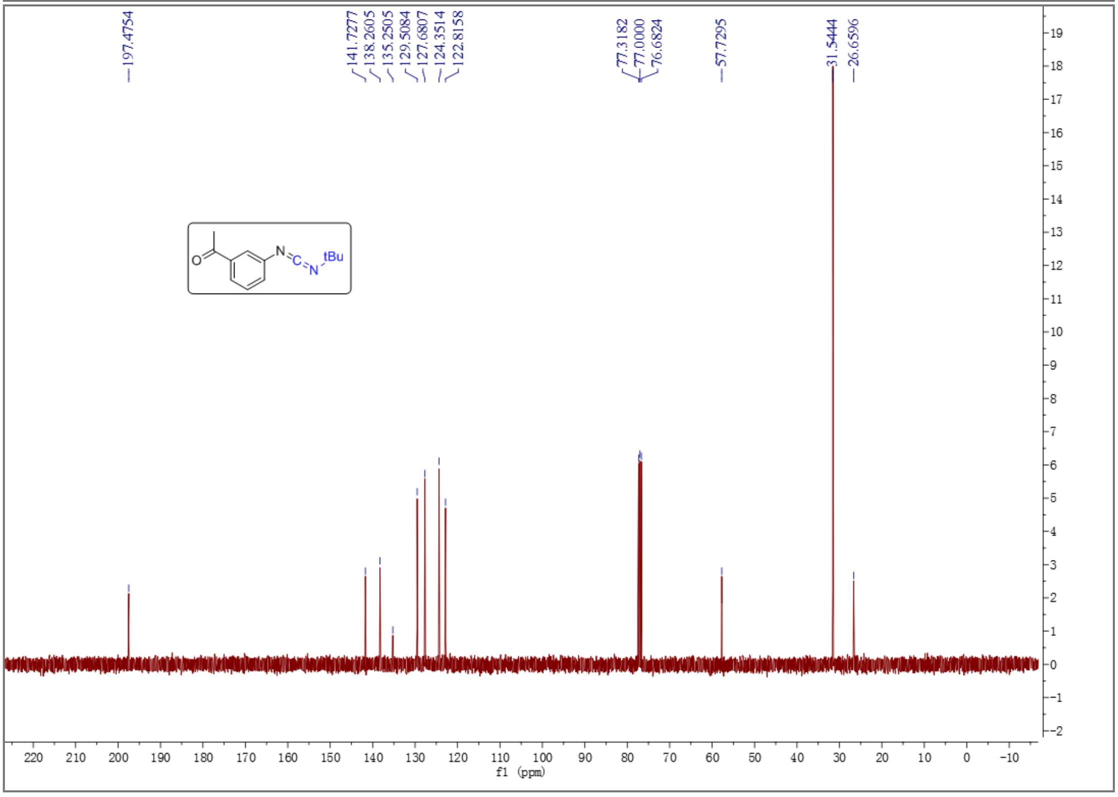
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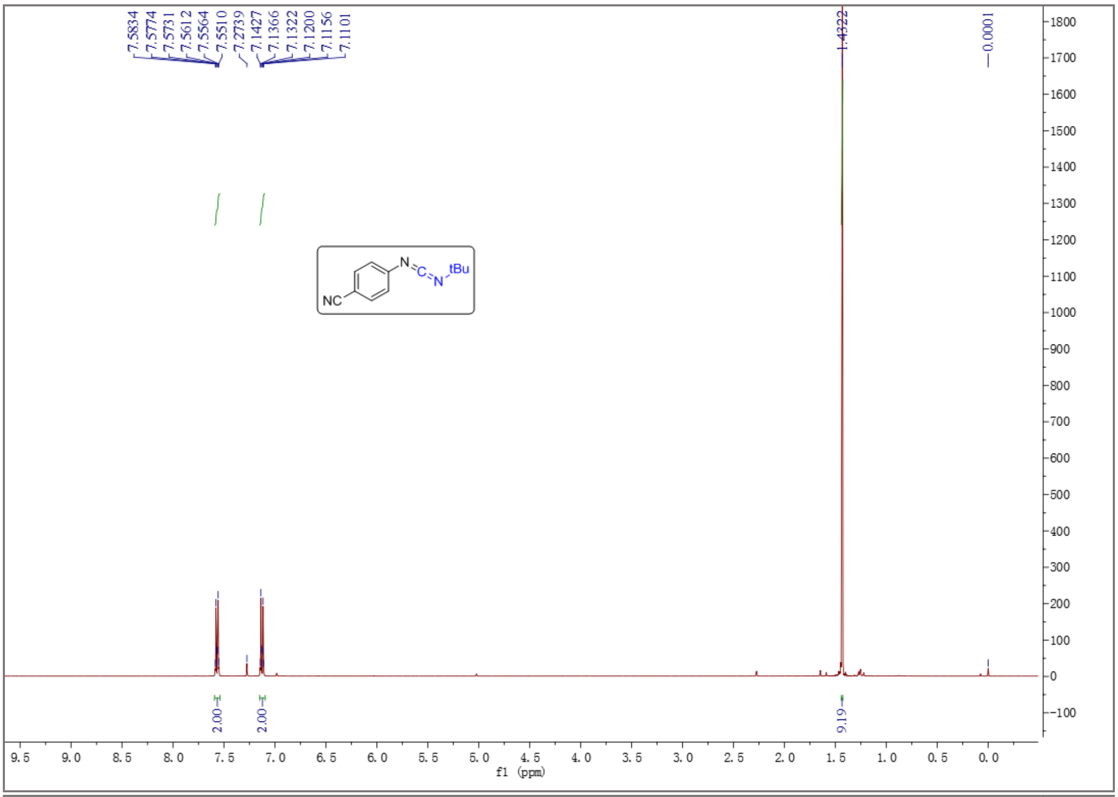
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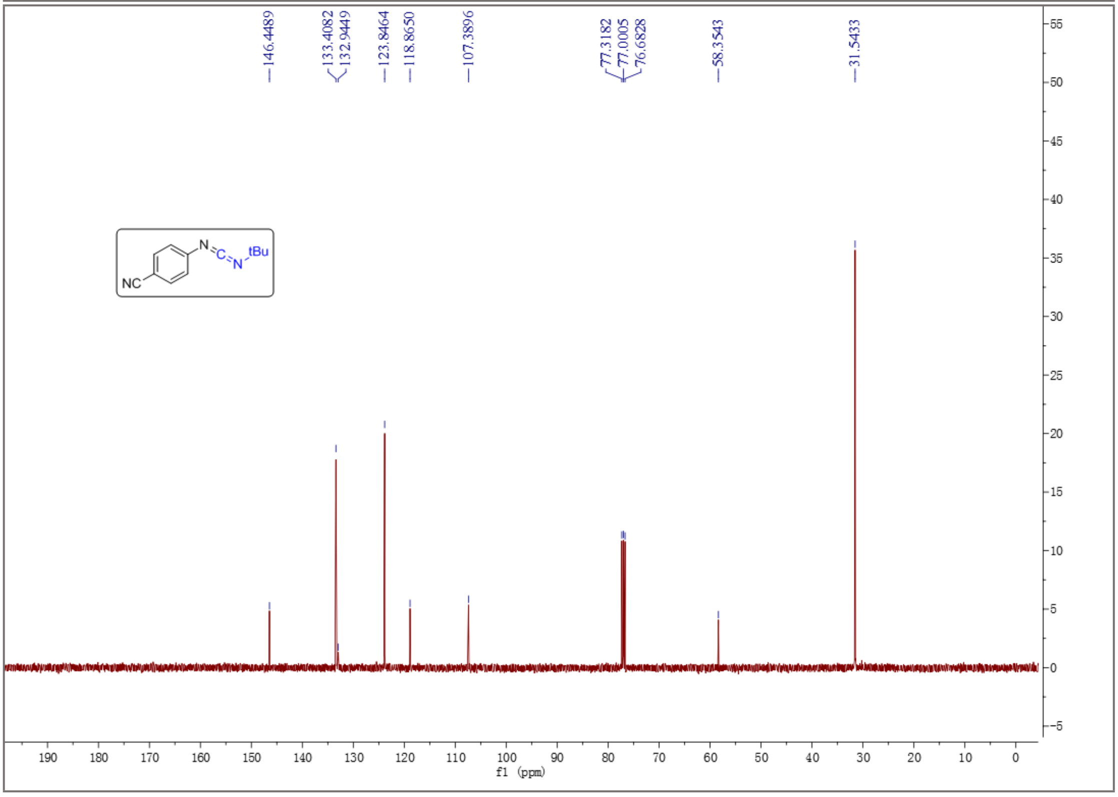
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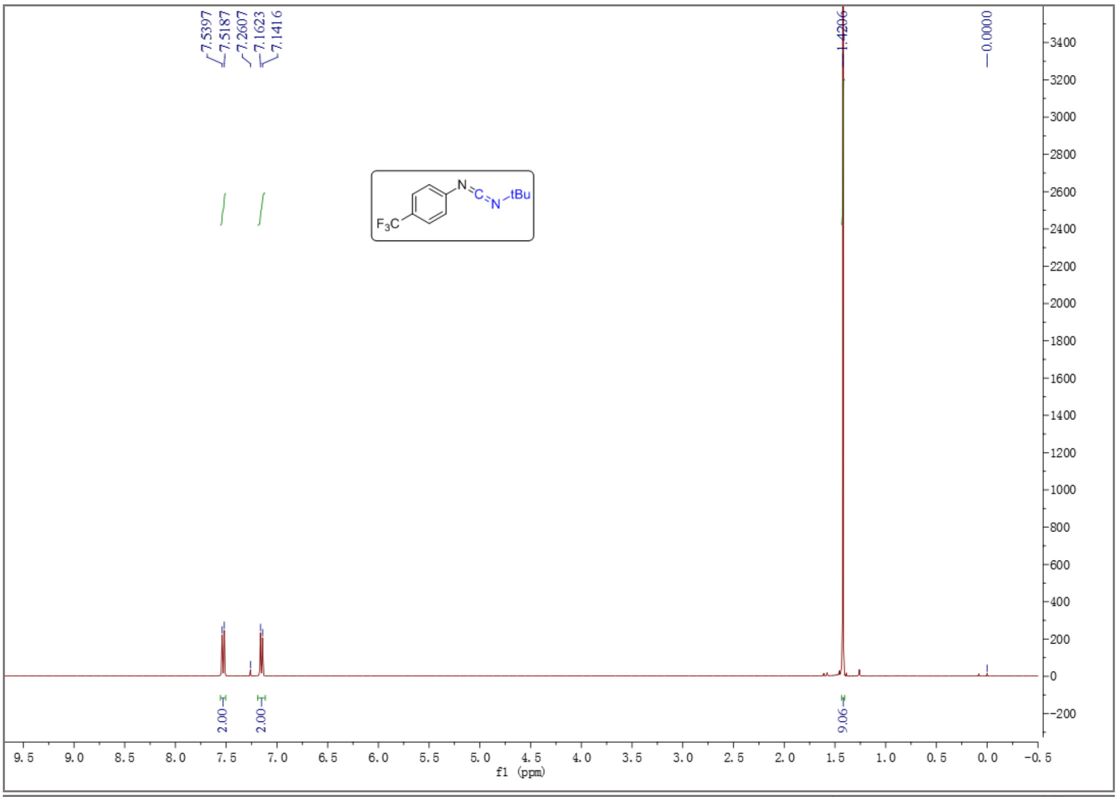
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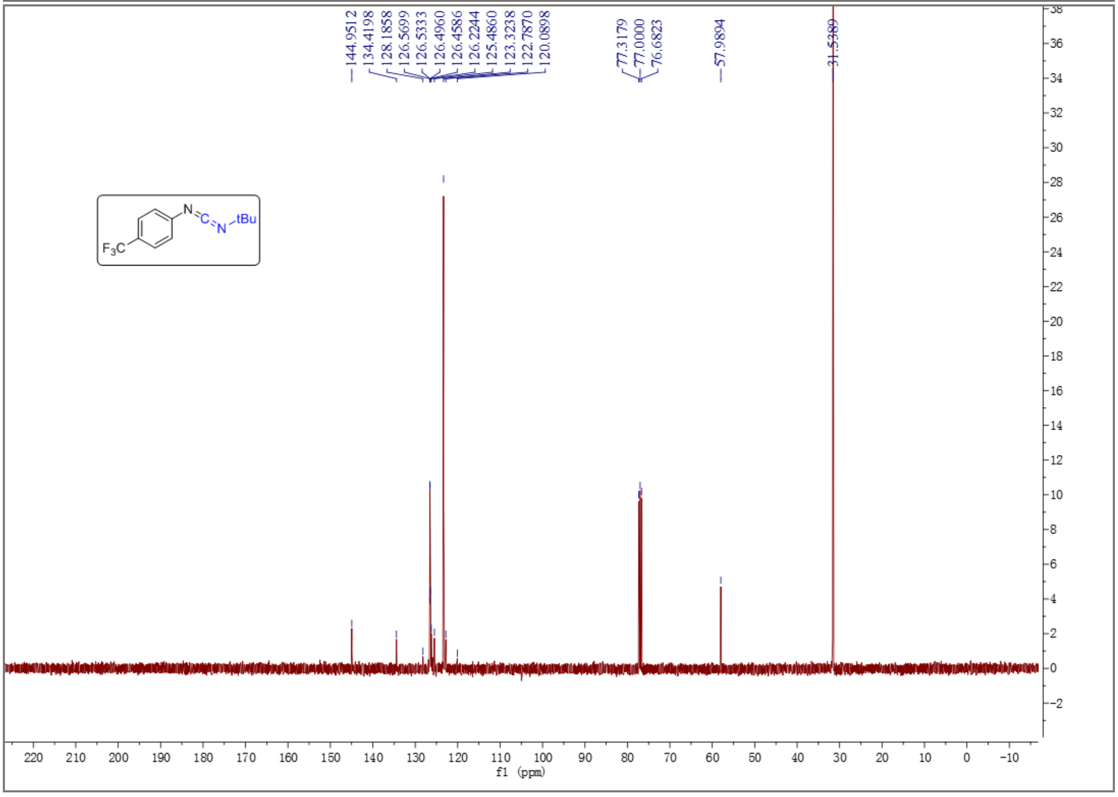
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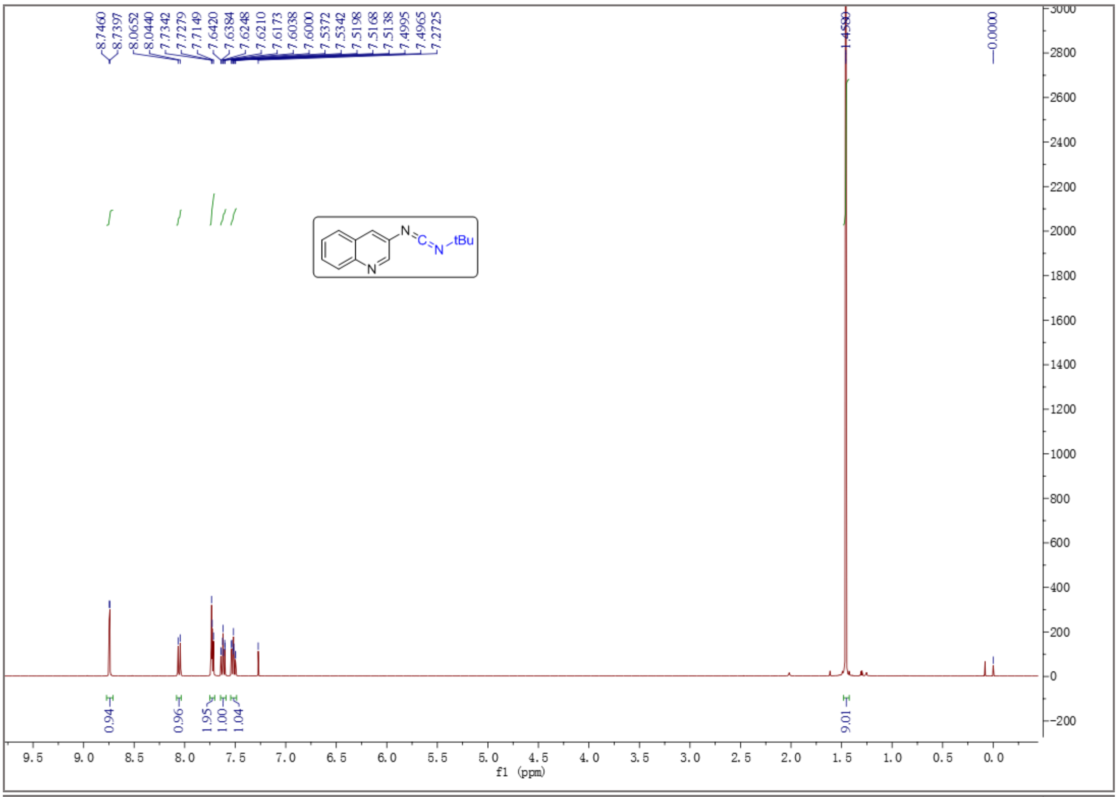

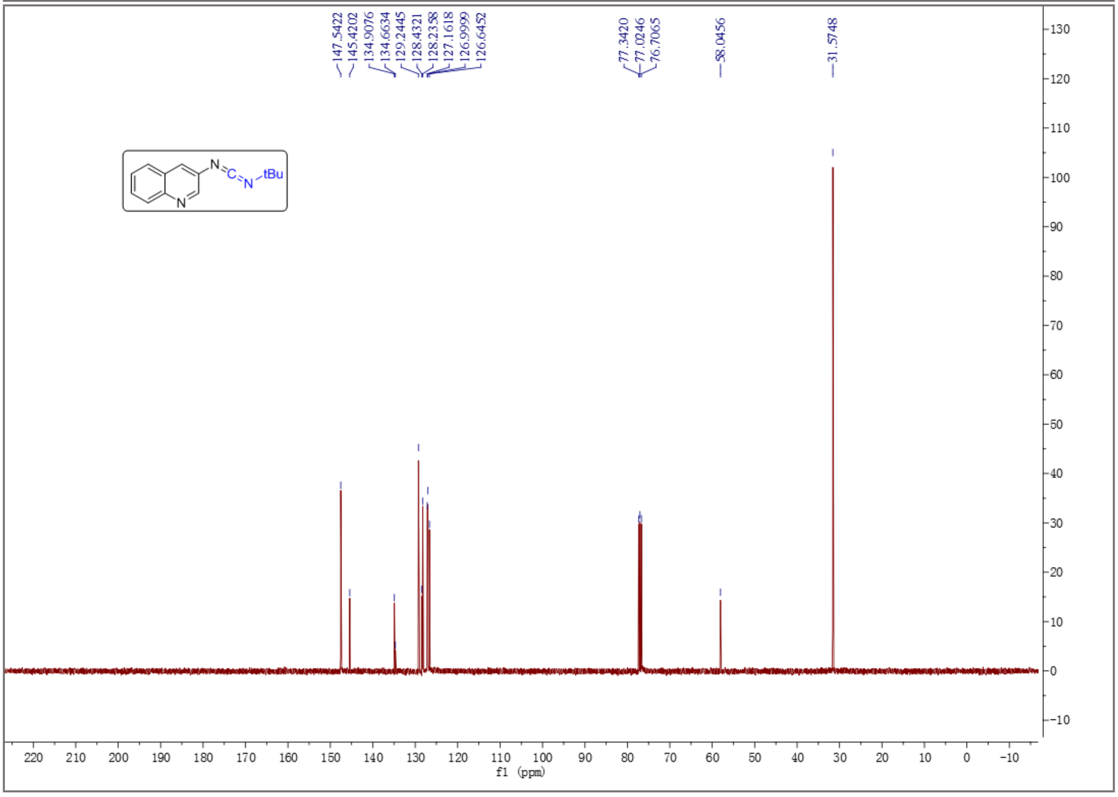

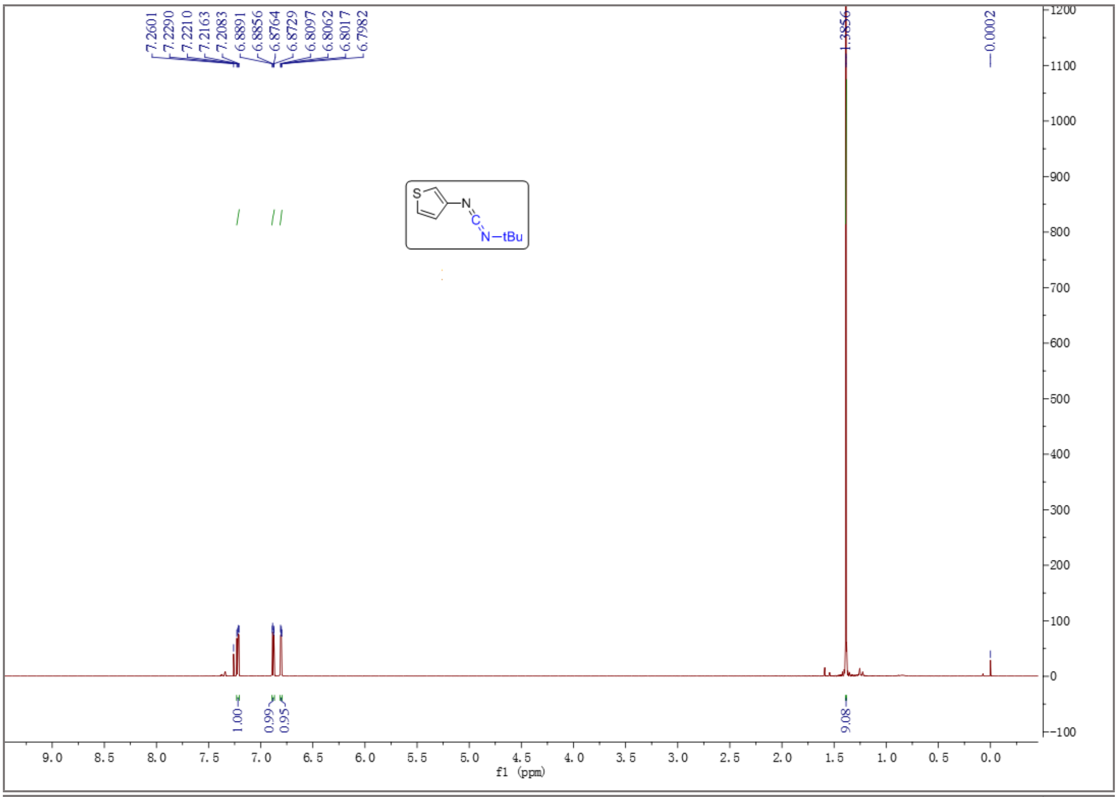

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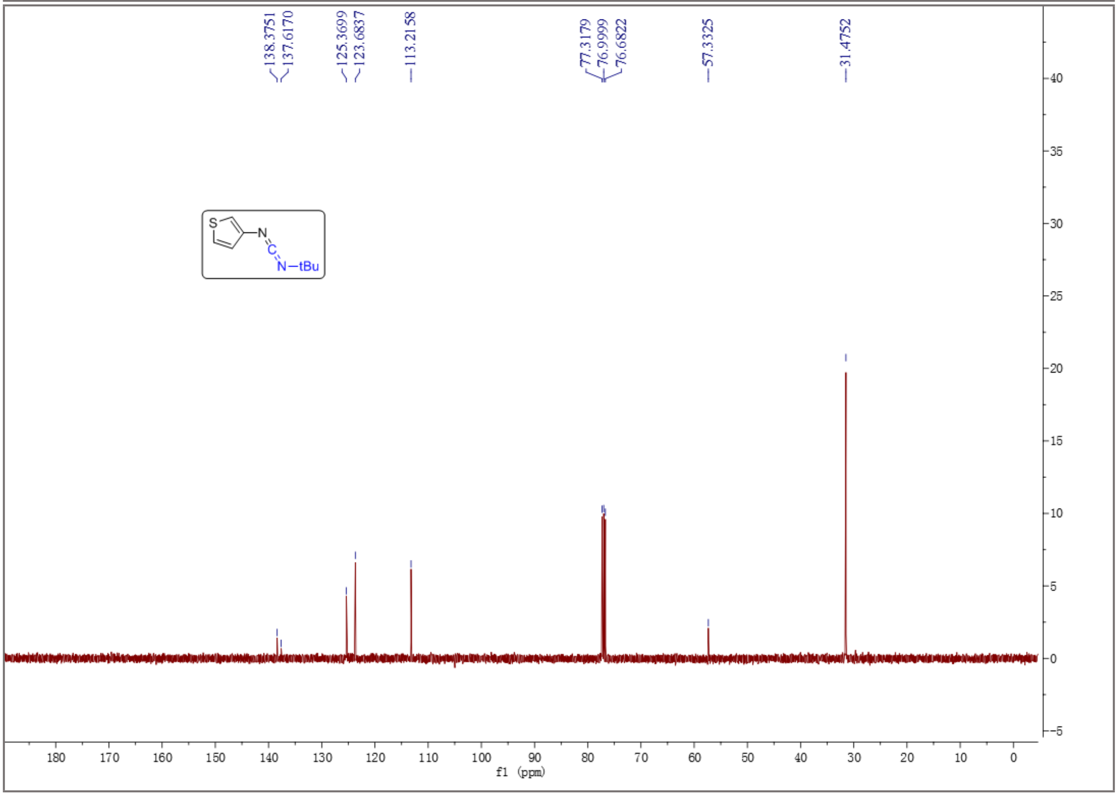

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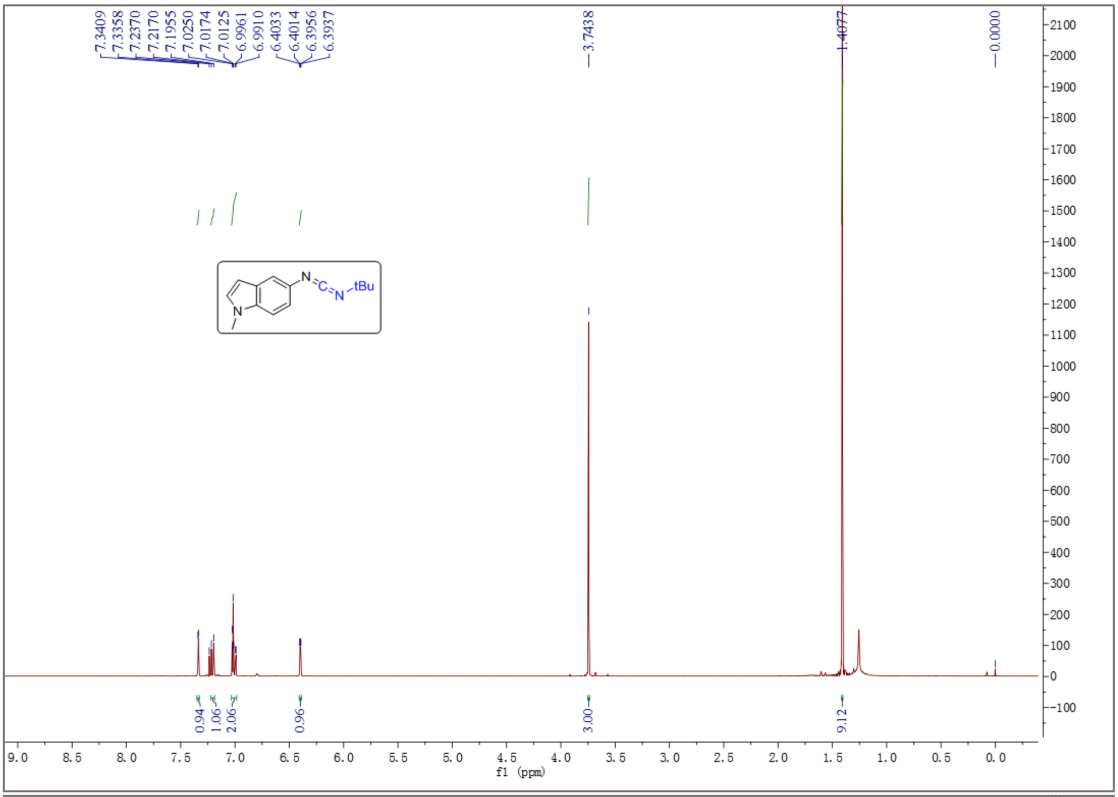

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6.3956
6.3937
3.7438
1.4077
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N=C=N-tBu
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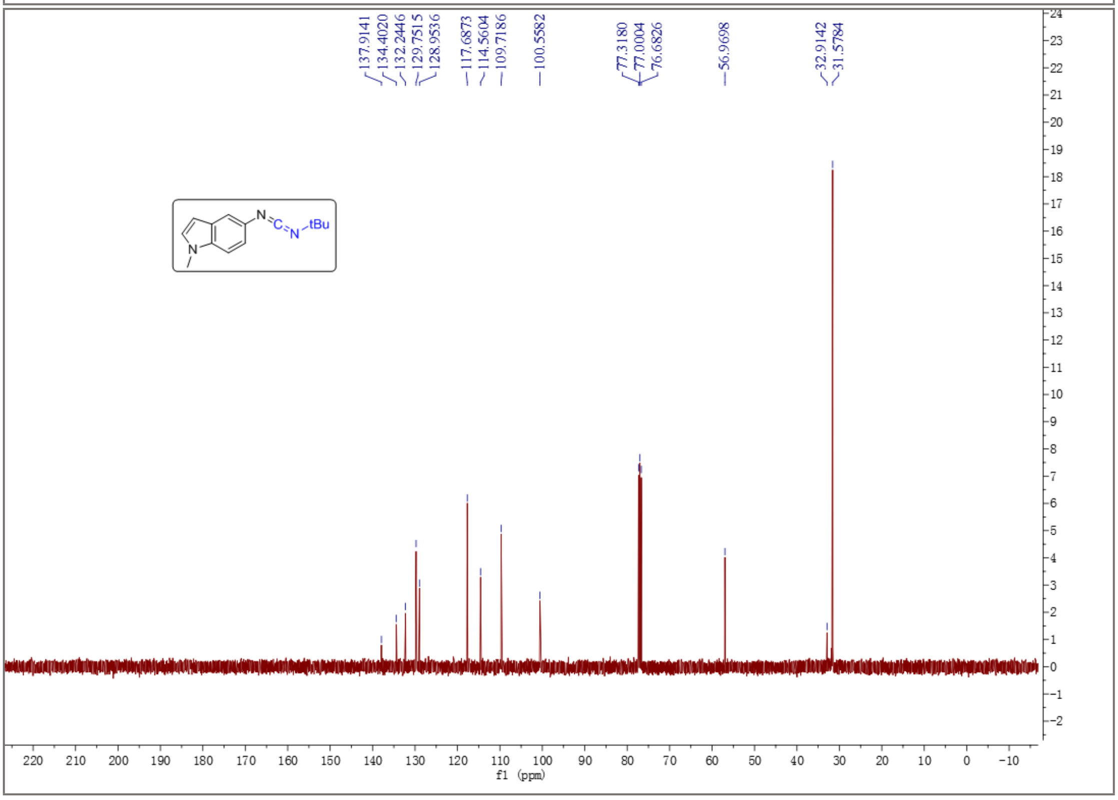
1.06
2.06
0.96
3.00
9.12
f1 (ppm)

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132.2446
129.7515
128.9536
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114.5604
109.7186
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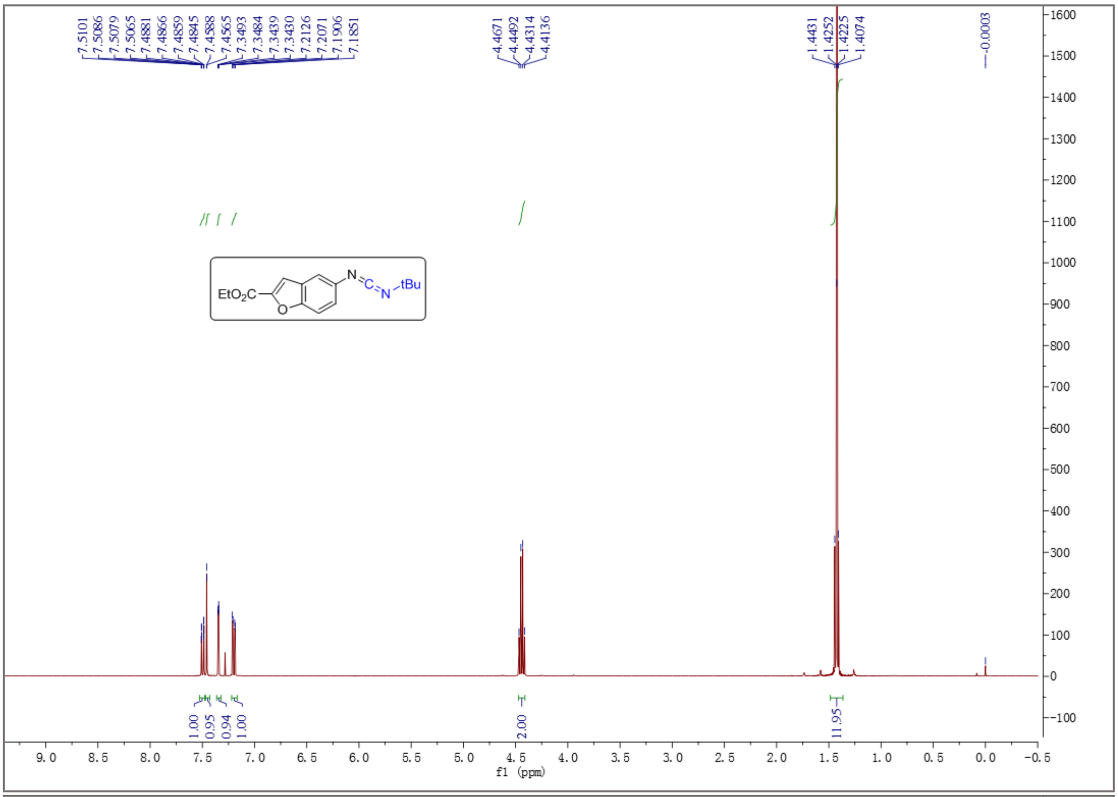
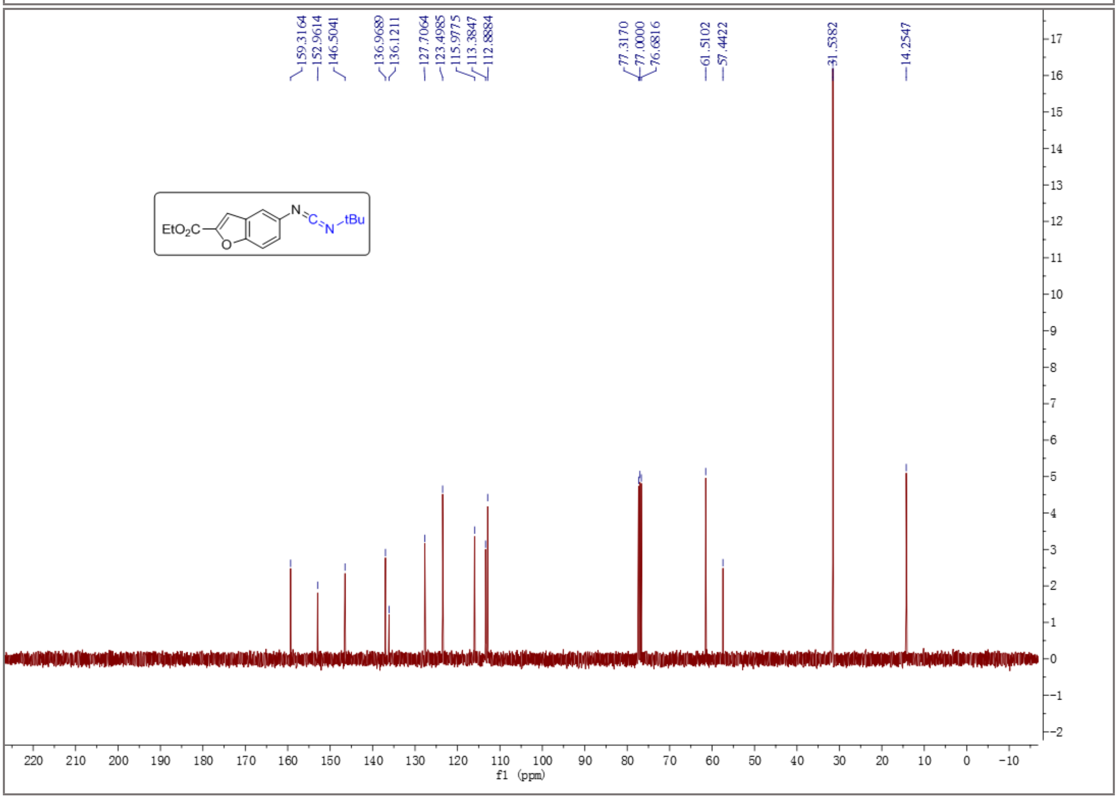
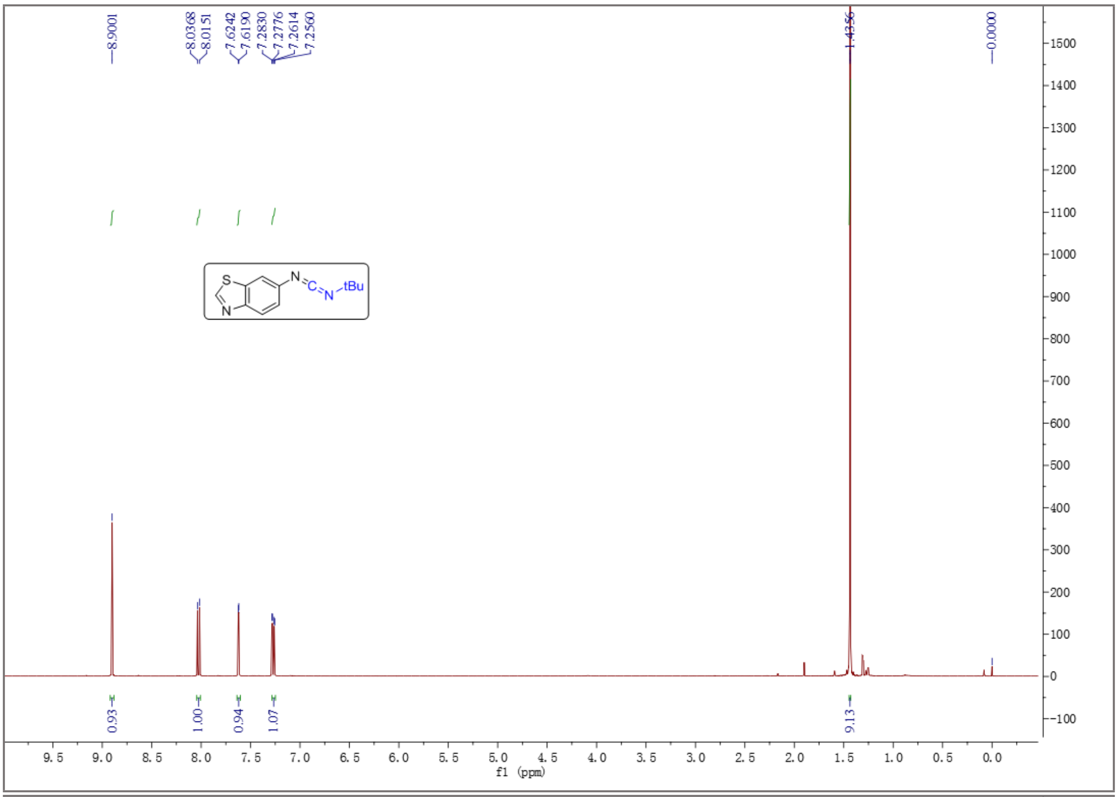
77.0004
76.6826
56.9698
32.9142
31.5784
N=C=N-tBu
f1 (ppm)



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8.0151
7.6242
7.6190
7.2830
7.2776
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7.2560
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0.0000
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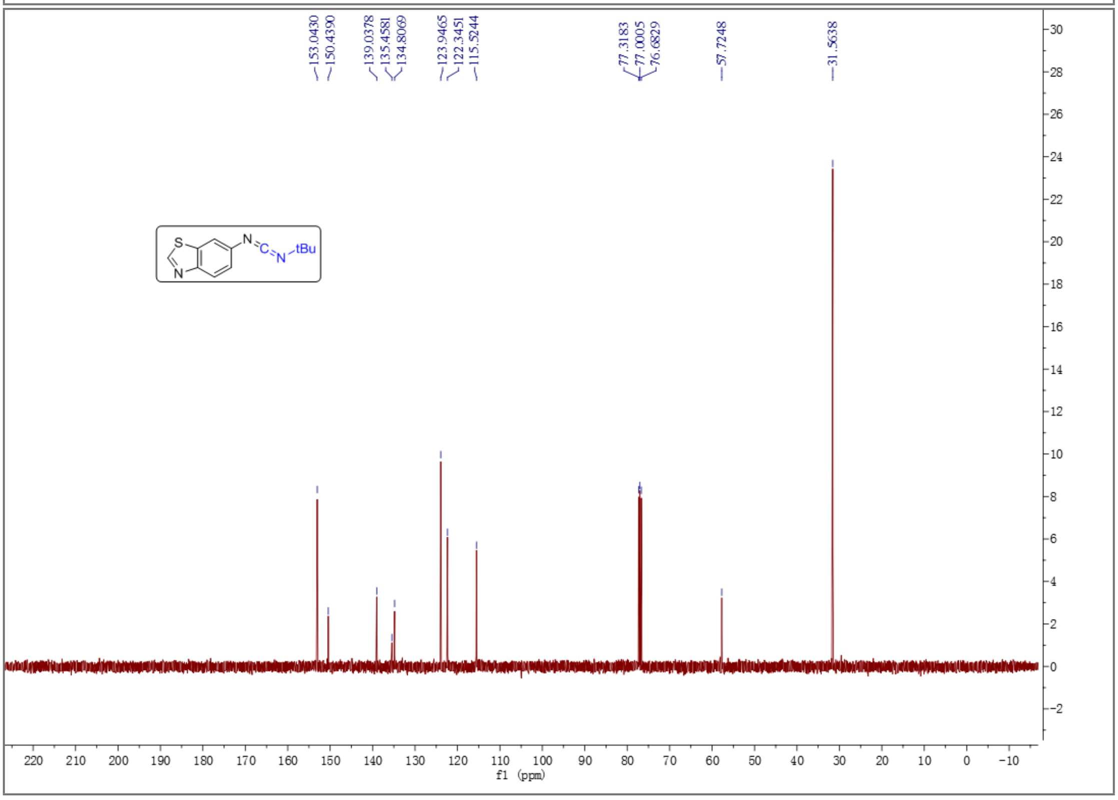
1.00
0.94
1.07
9.13
N
C
N
tBu
S
N
f1 (ppm)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150.4390
139.0378
135.4581
134.8069
123.9465
122.3451
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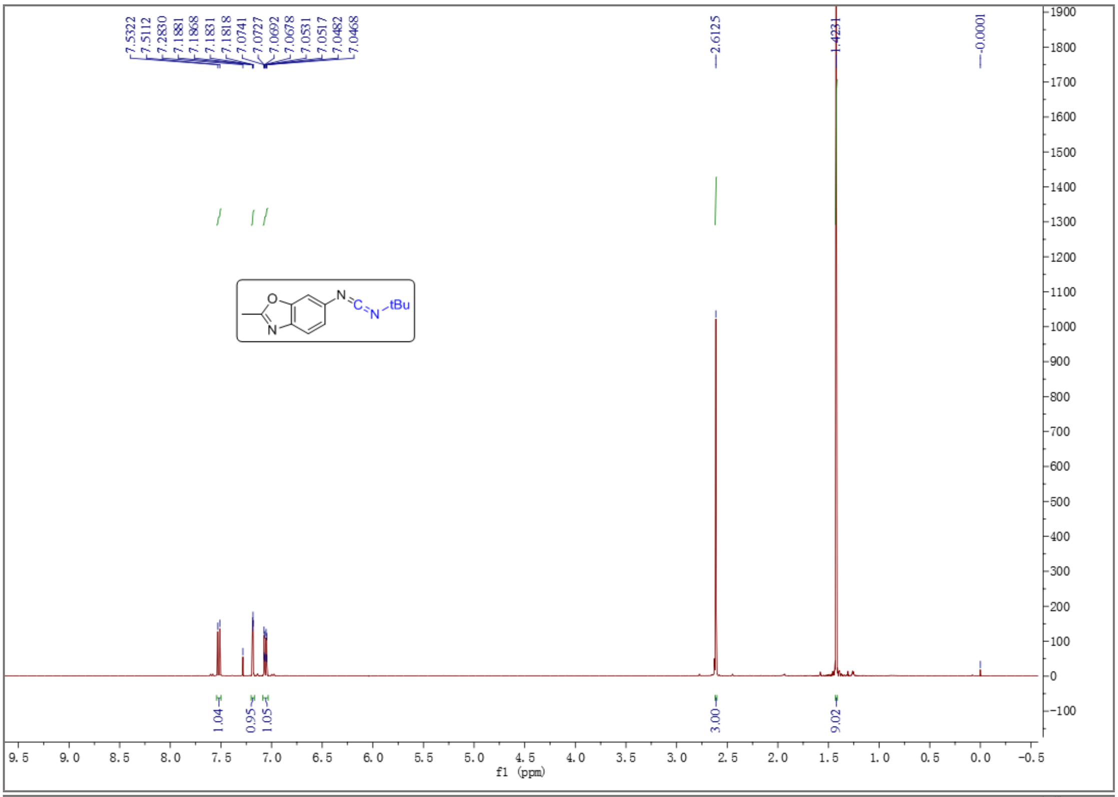
77.0005
76.6829
57.7248
31.5638
N
C
N
tBu
S
N
f1 (ppm)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7.2830
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7.1868
7.1831
7.1818
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7.0727
7.0692
7.0678
7.0531
7.0517
7.0482
7.0468
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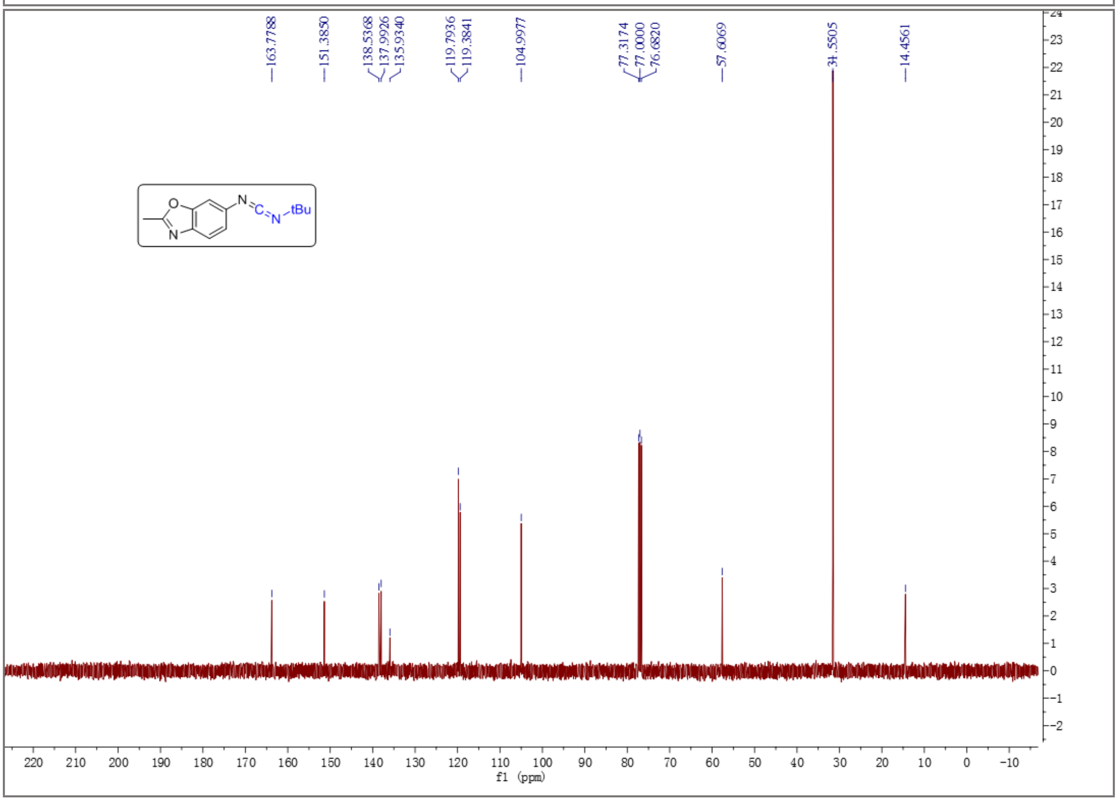
1.4231
-0.0001
tBu
1.04
0.95
1.05
3.00
9.02
f1 (ppm)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138.5368
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135.9340
119.7936
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77.0000
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31.5505
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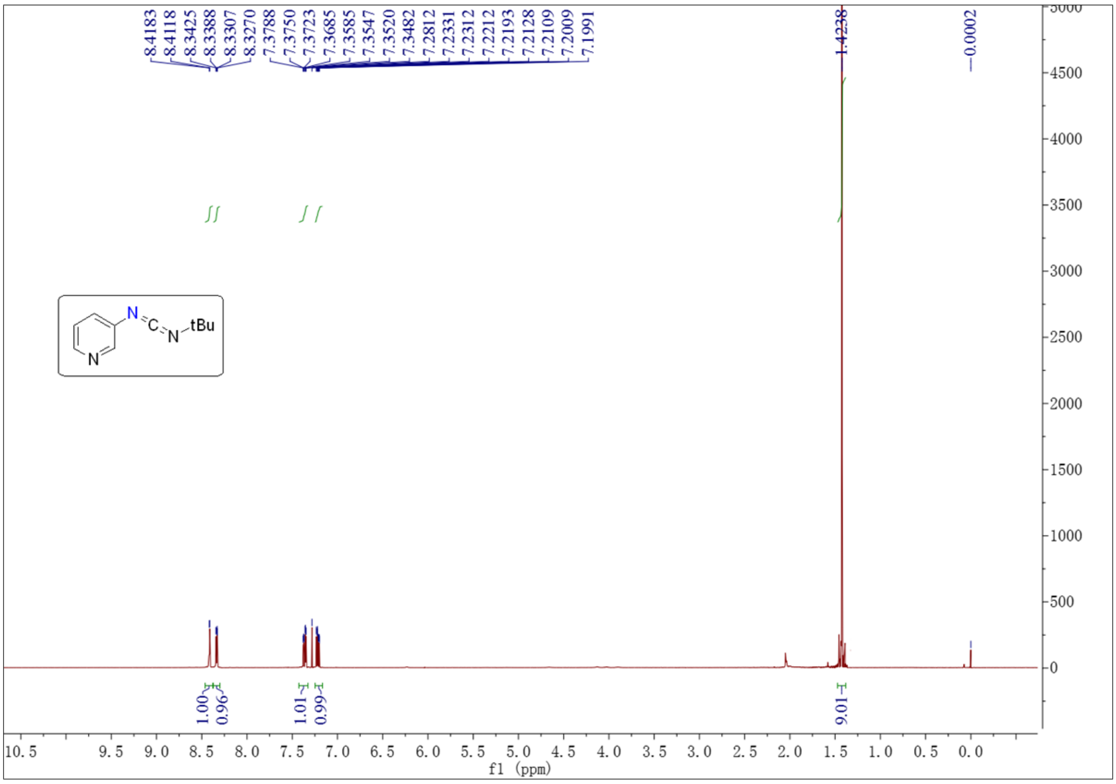
tBu
f1 (ppm)



8.4183
8.4118
8.3425
8.3388
8.3307
8.3270
7.3788
7.3750
7.3723
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7.3585
7.3547
7.3520
7.3482
7.2812
7.2331
7.2312
7.2212
7.2193
7.2128
7.2109
7.2009
7.1991
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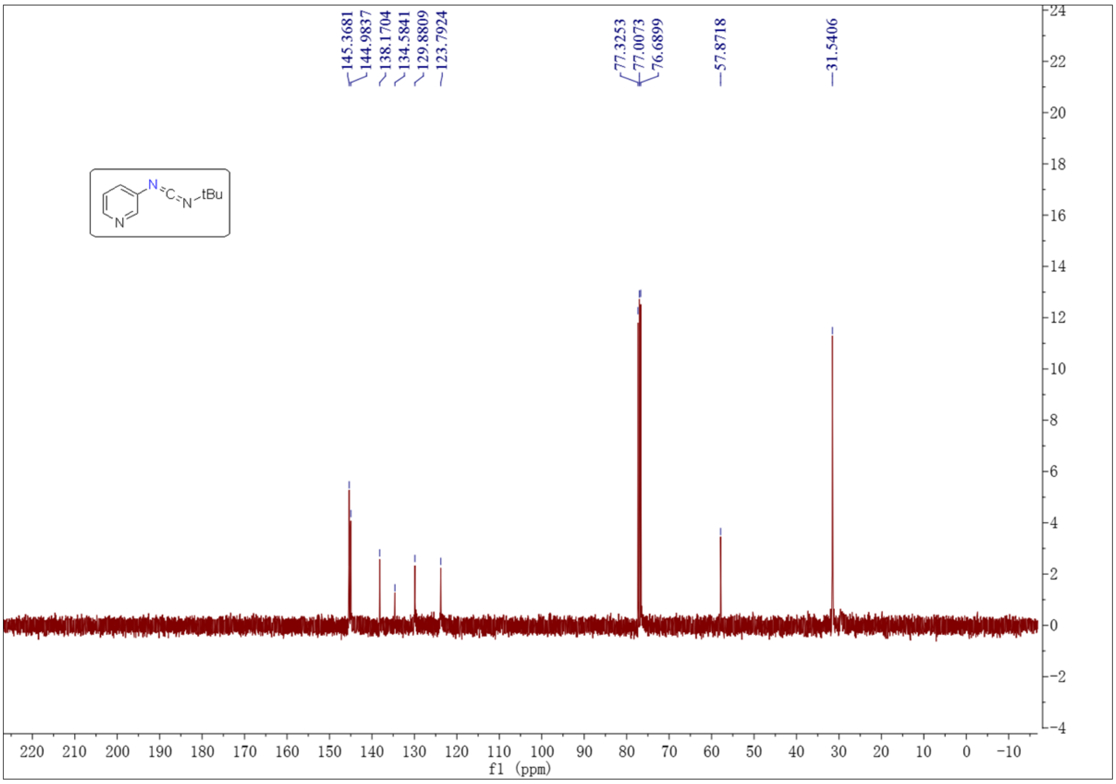
0.0002
N
C
N
tBu
N
1.00
0.96
1.01
0.99
9.01
f1 (ppm)

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144.9837
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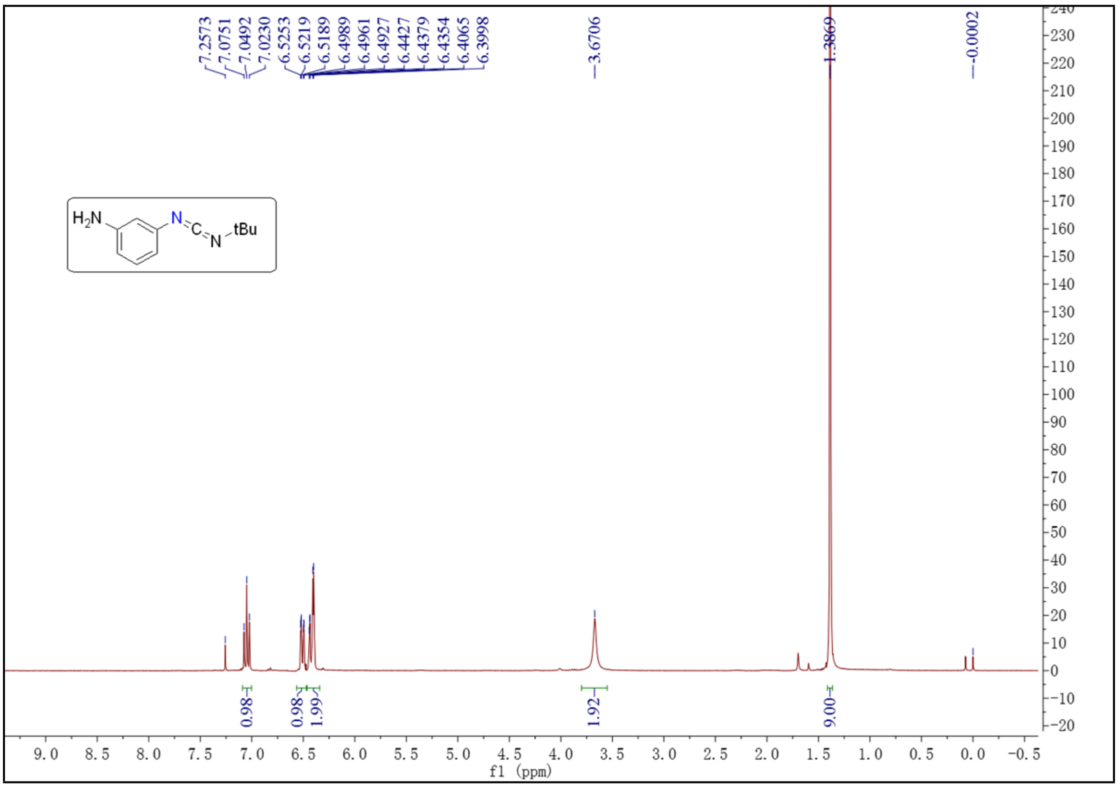
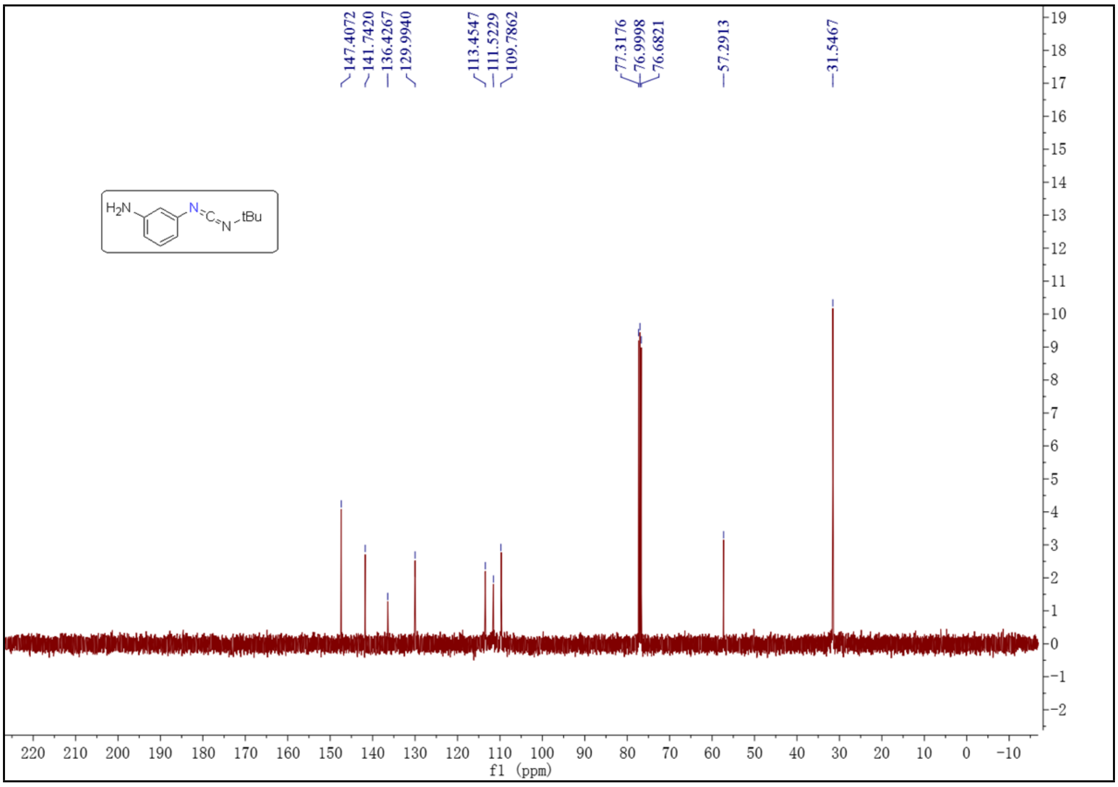
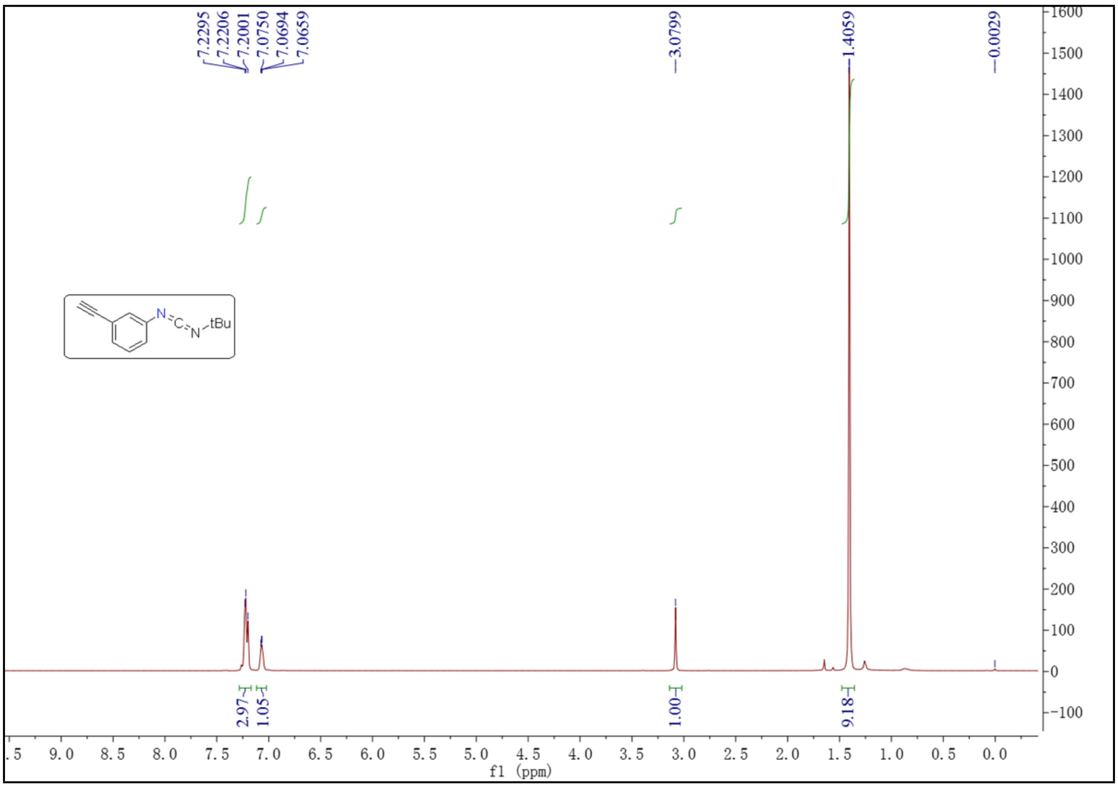
C
N
tBu
N
f1 (ppm)



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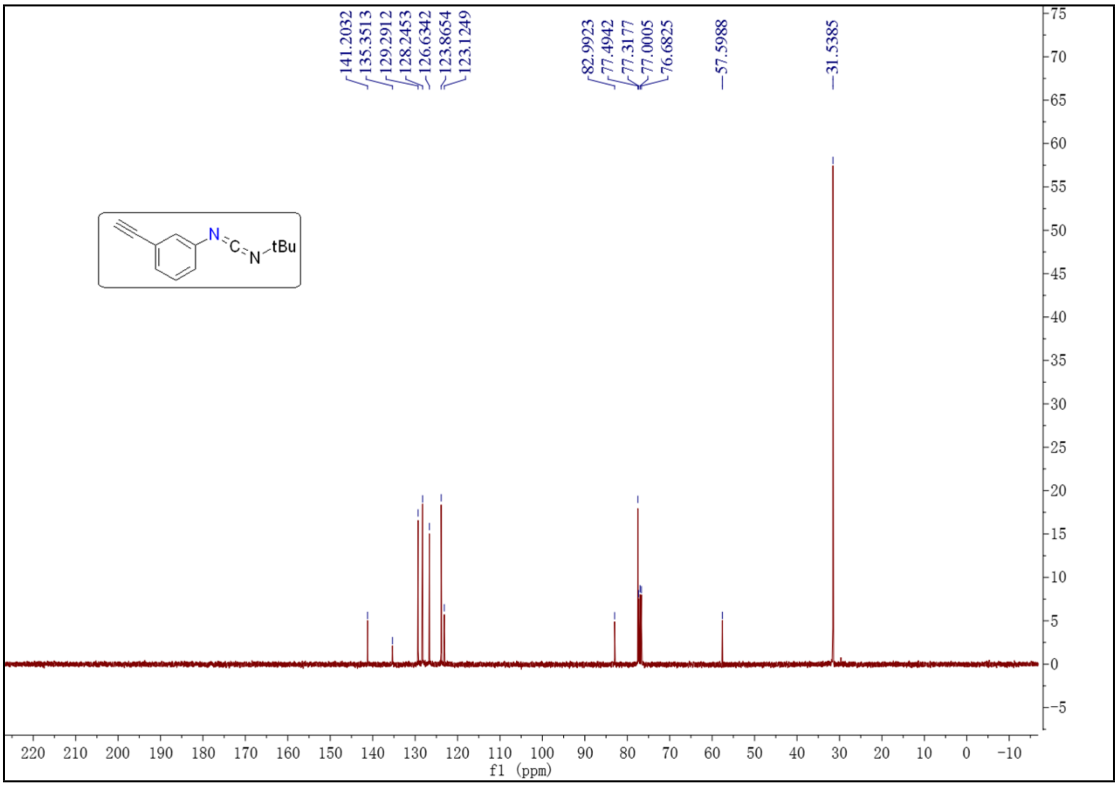
7.2206
7.2001
7.0750
7.0694
7.0659
3.0799
1.4059
0.0029
2.97
1.05
1.00
9.18
tBu
f1 (ppm)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135.3513
129.2912
128.2453
126.6342
123.8654
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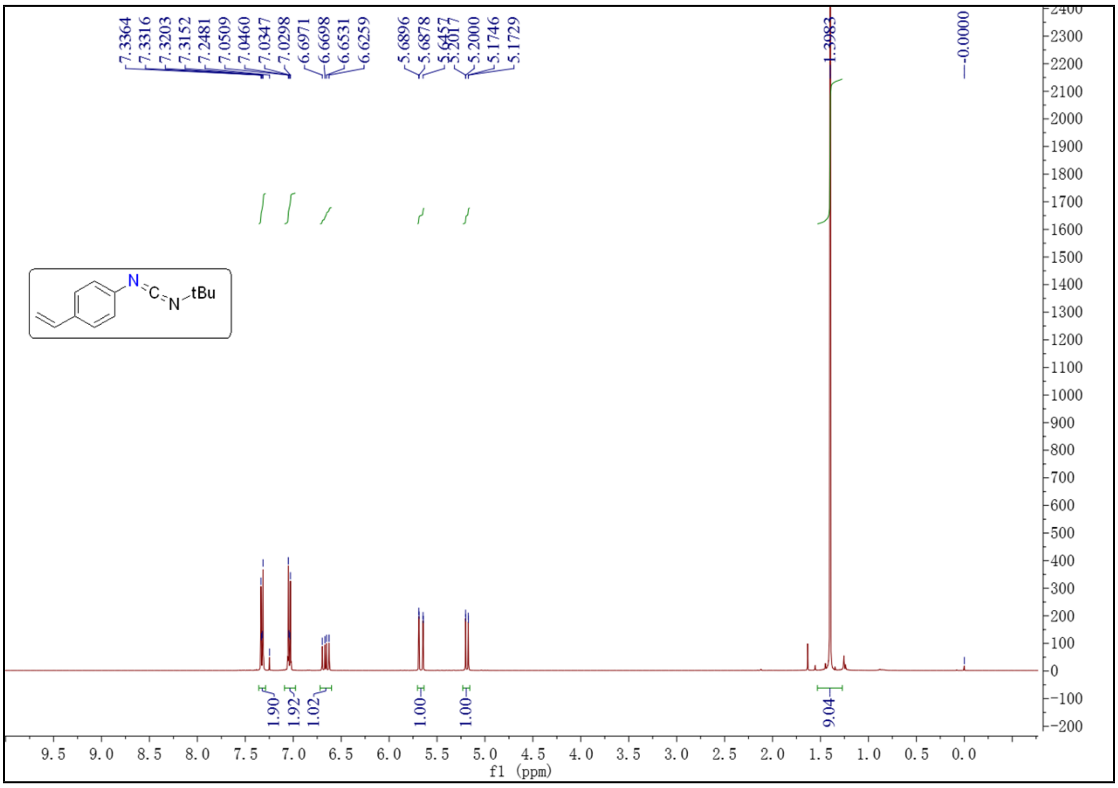
31.5385
tBu
f1 (ppm)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7.3203
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7.2481
7.0509
7.0460
7.0347
7.0298
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6.6698
6.6531
6.6259
5.6896
5.6878
5.6457
5.2017
5.2000
5.1746
5.1729
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-0.0000
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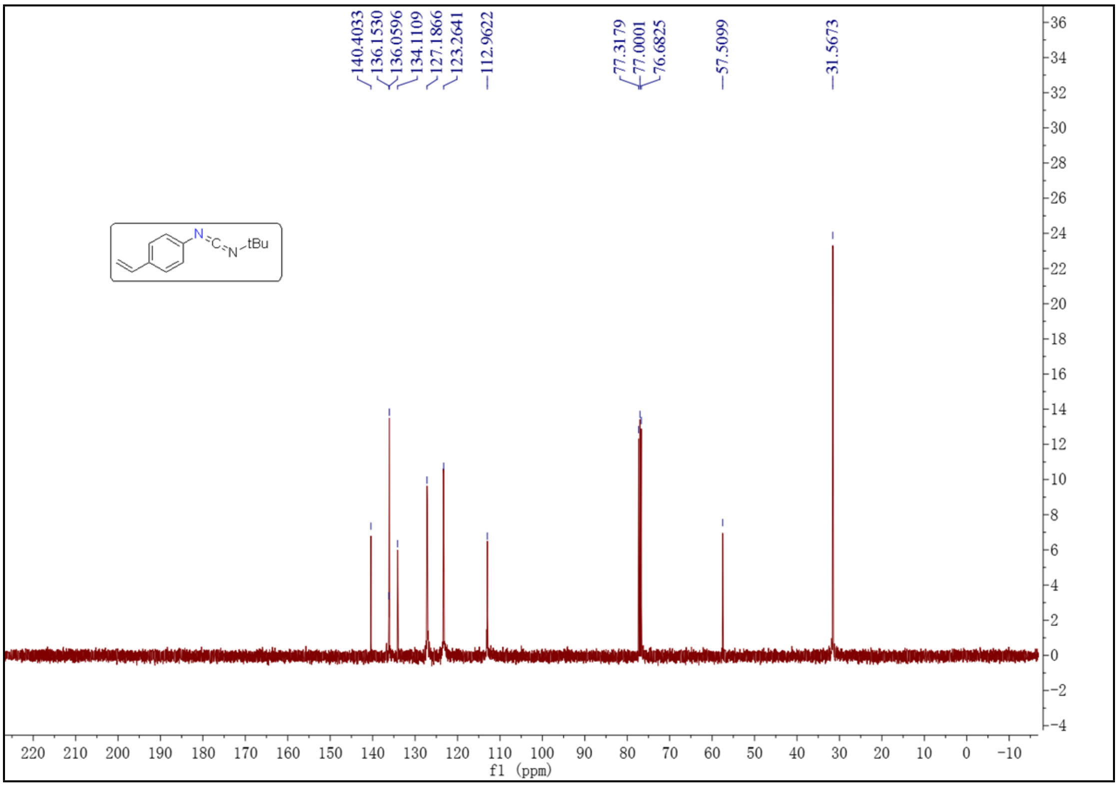
C
N
tBu
1.90
1.92
1.02
1.00
1.00
9.04
f1 (ppm)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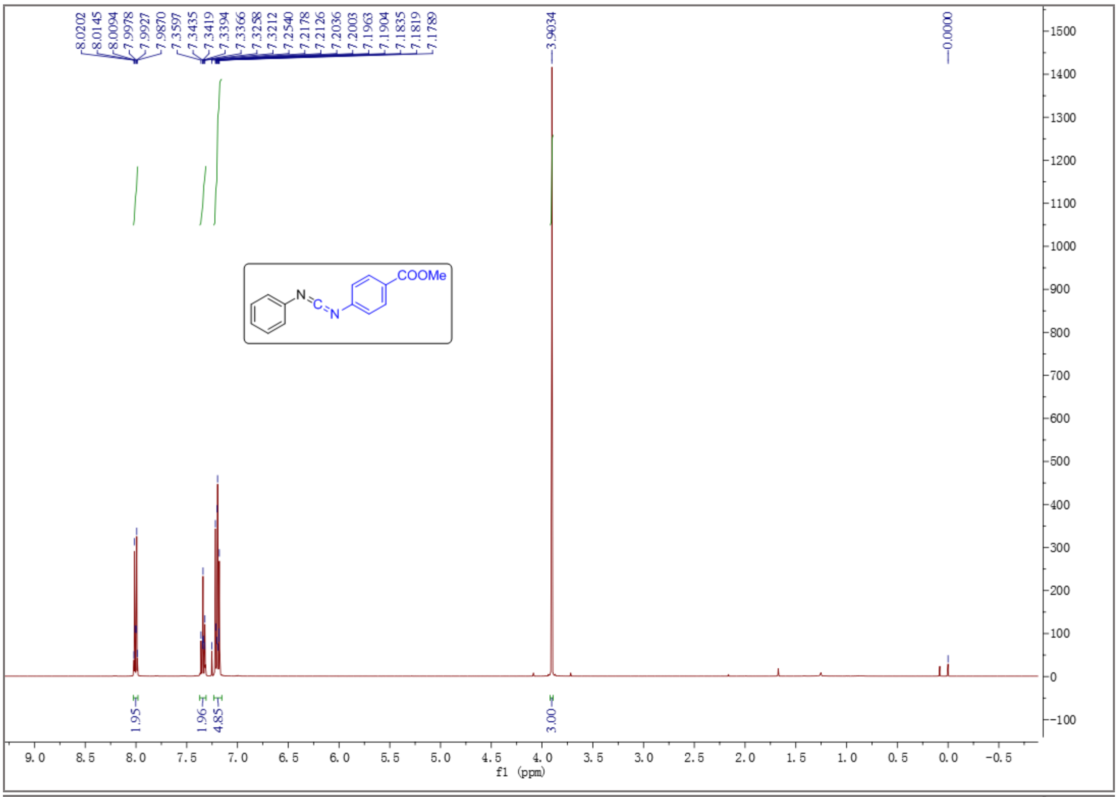
31.5673
N
C
N
tBu
f1 (ppm)



8.0202
8.0145
8.0094
7.9978
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7.3435
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7.3258
7.3212
7.2540
7.2178
7.2126
7.2036
7.2003
7.1963
7.1904
7.1835
7.1819
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N
C
N
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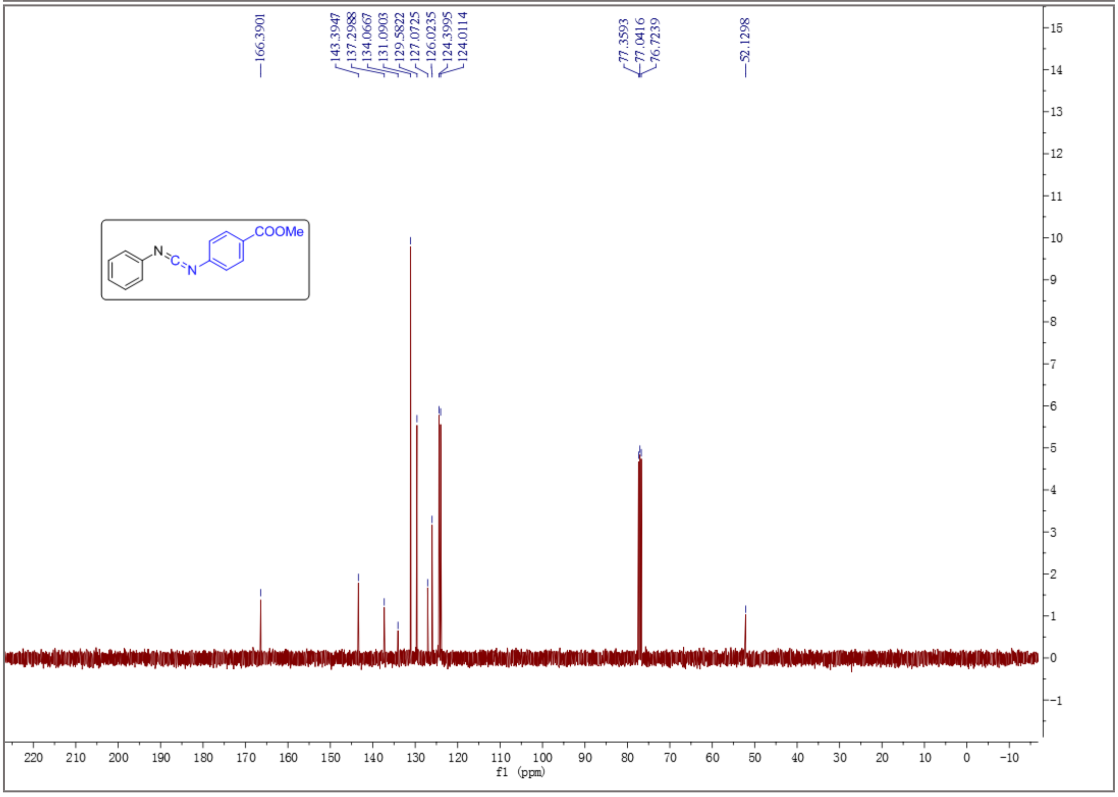
1.96
4.85
3.00
f1 (ppm)



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143.3947
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131.0903
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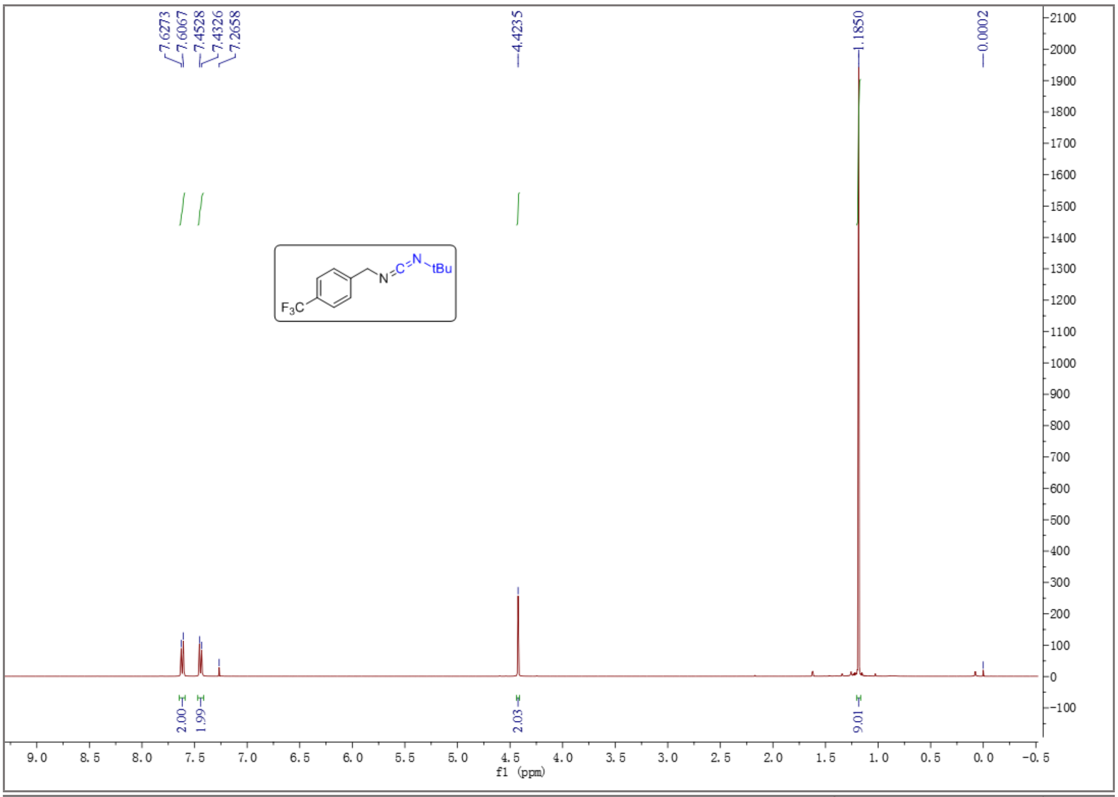
COOMe
N
C
N
f1 (ppm)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7.2658
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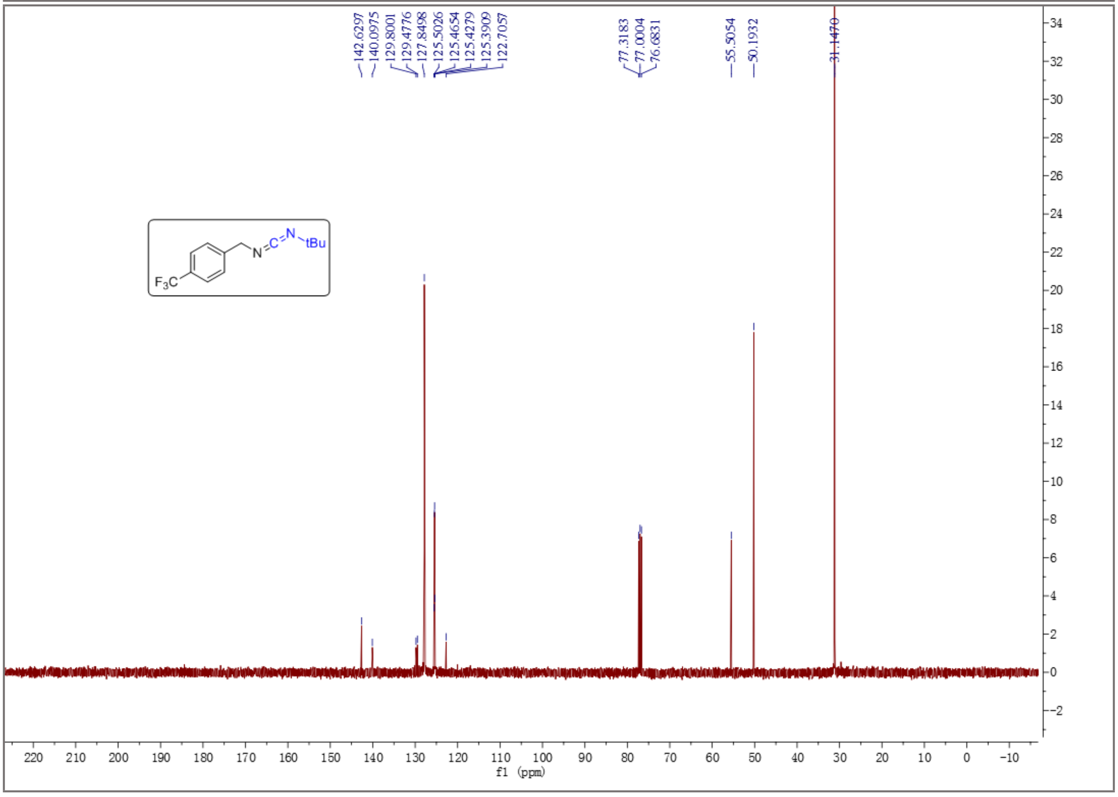
tBu
F3C
2.00
1.99
2.03
9.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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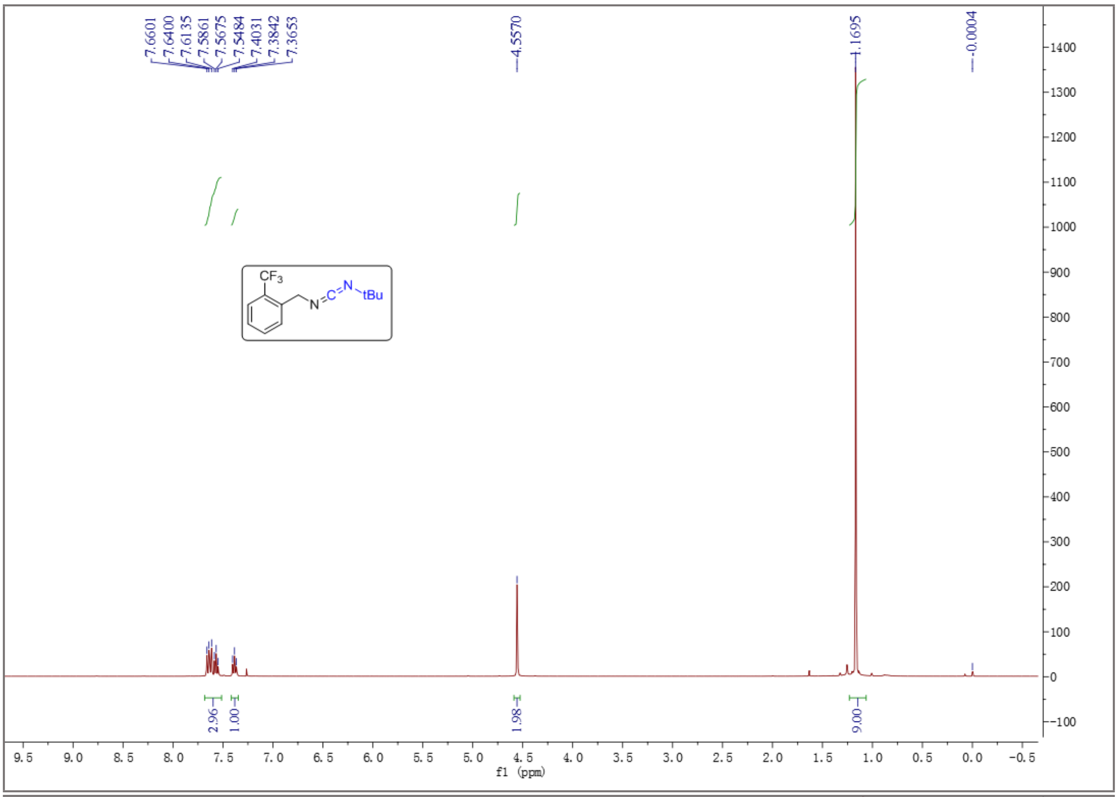
77.0004
76.6831
55.5054
50.1932
31.1470
N=C=N
tBu
F3C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.5675
7.5484
7.4031
7.3842
7.3653
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-0.0004
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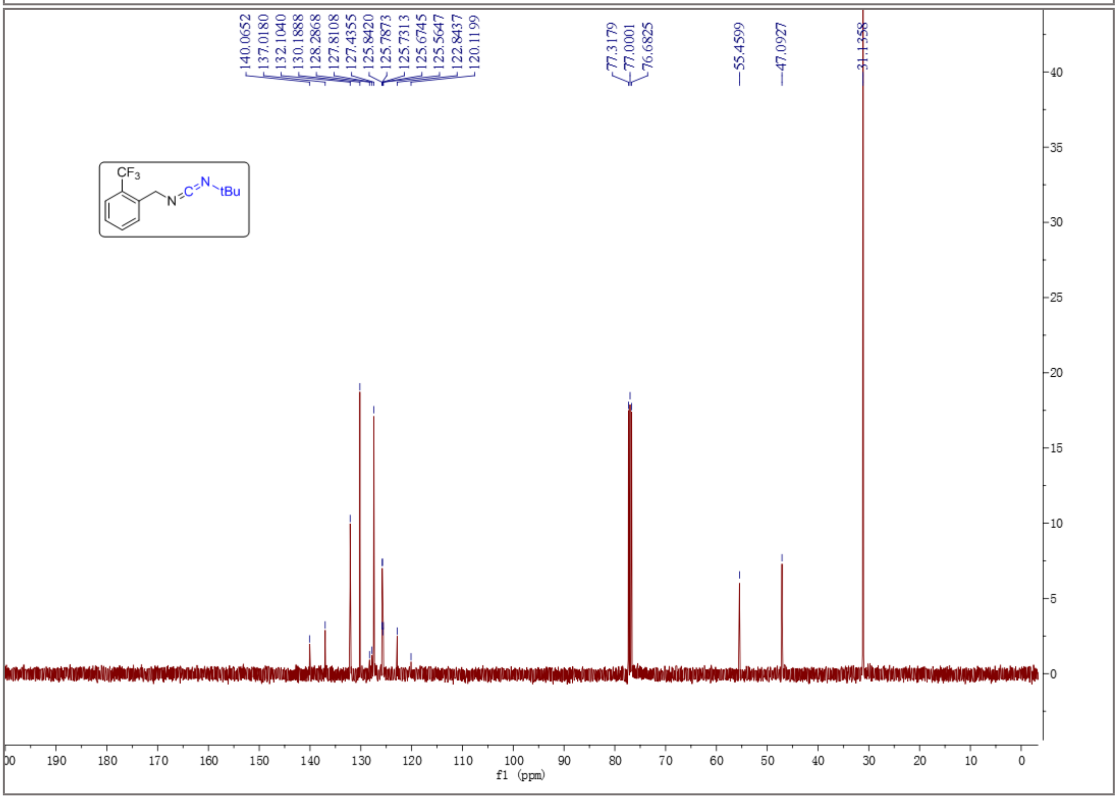
N=C=N
tBu
2.96
1.00
1.98
9.00
f1 (ppm)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125.5647
122.8437
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47.0927
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CF3
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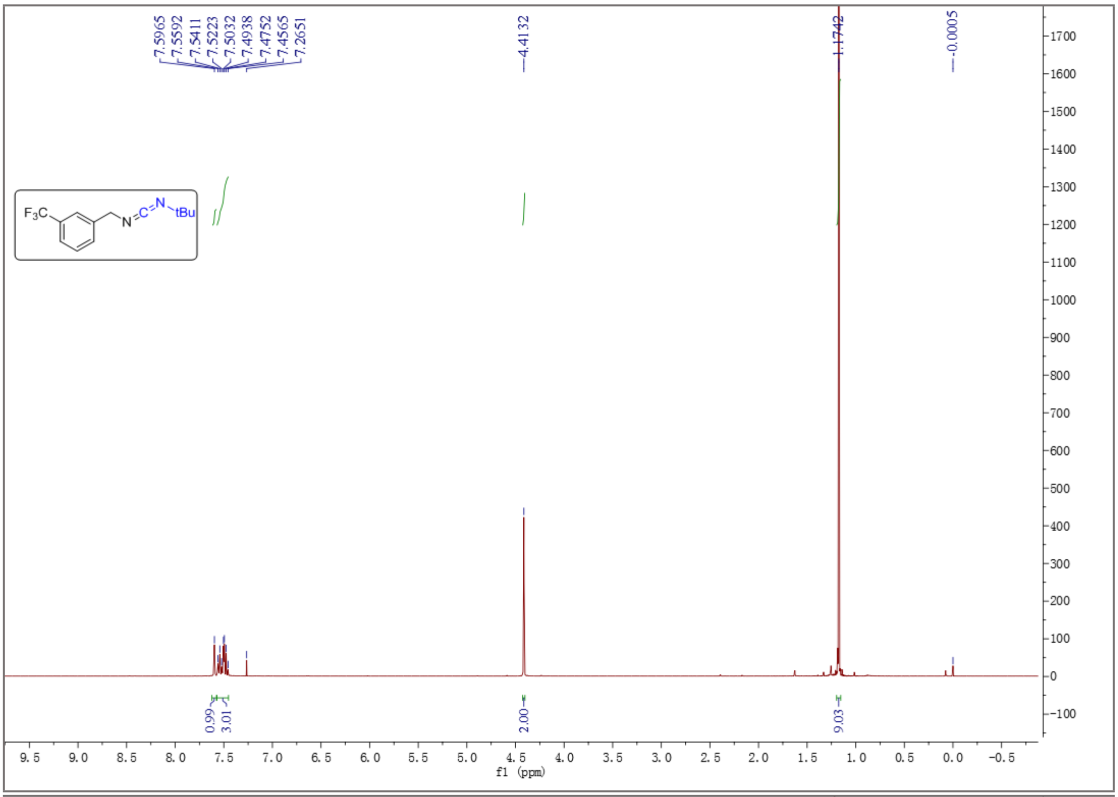
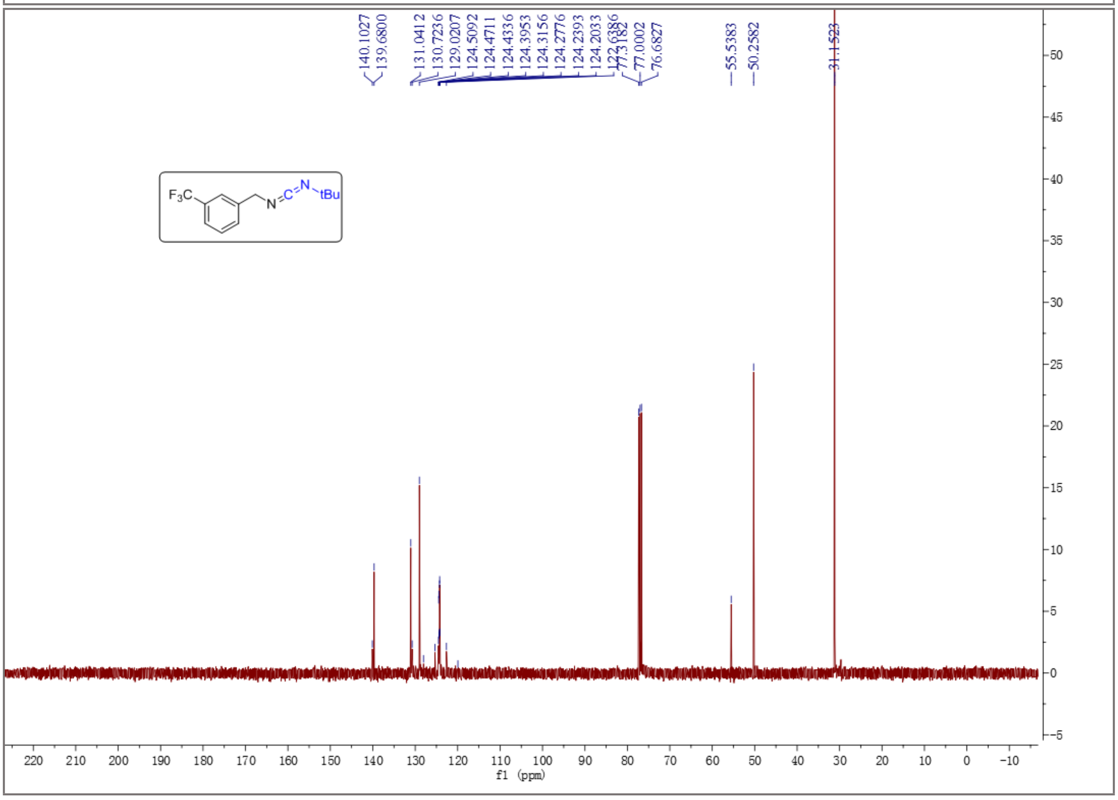
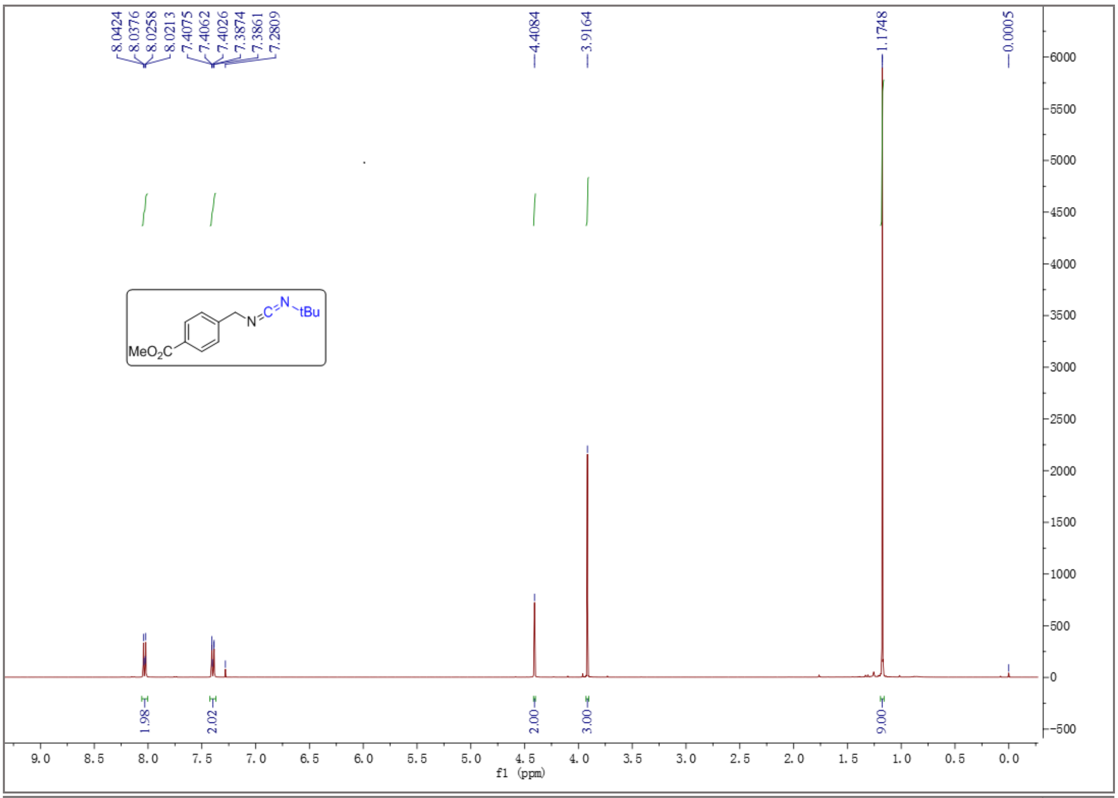
tBu
f1 (ppm)



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8.0213
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7.4062
7.4026
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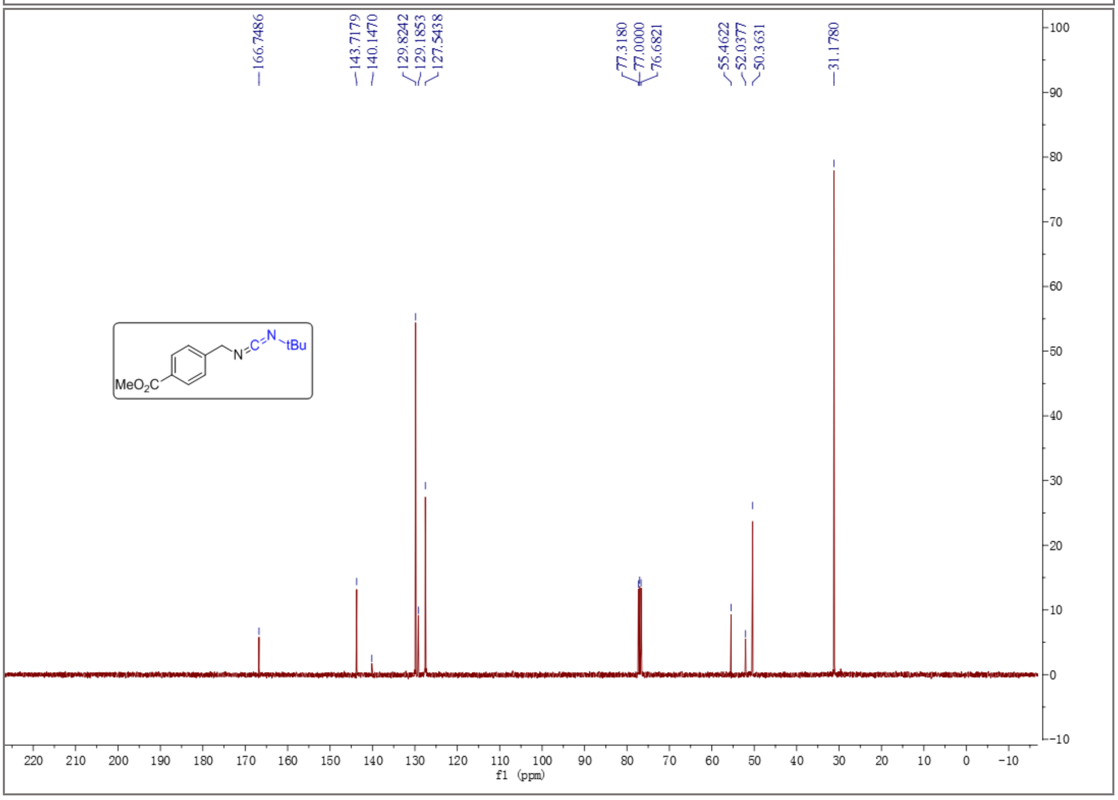
7.3861
7.2809
4.4084
3.9164
1.1748
-0.0005
MeO2C
N
C
N
tBu
1.98
2.02
2.00
3.00
9.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500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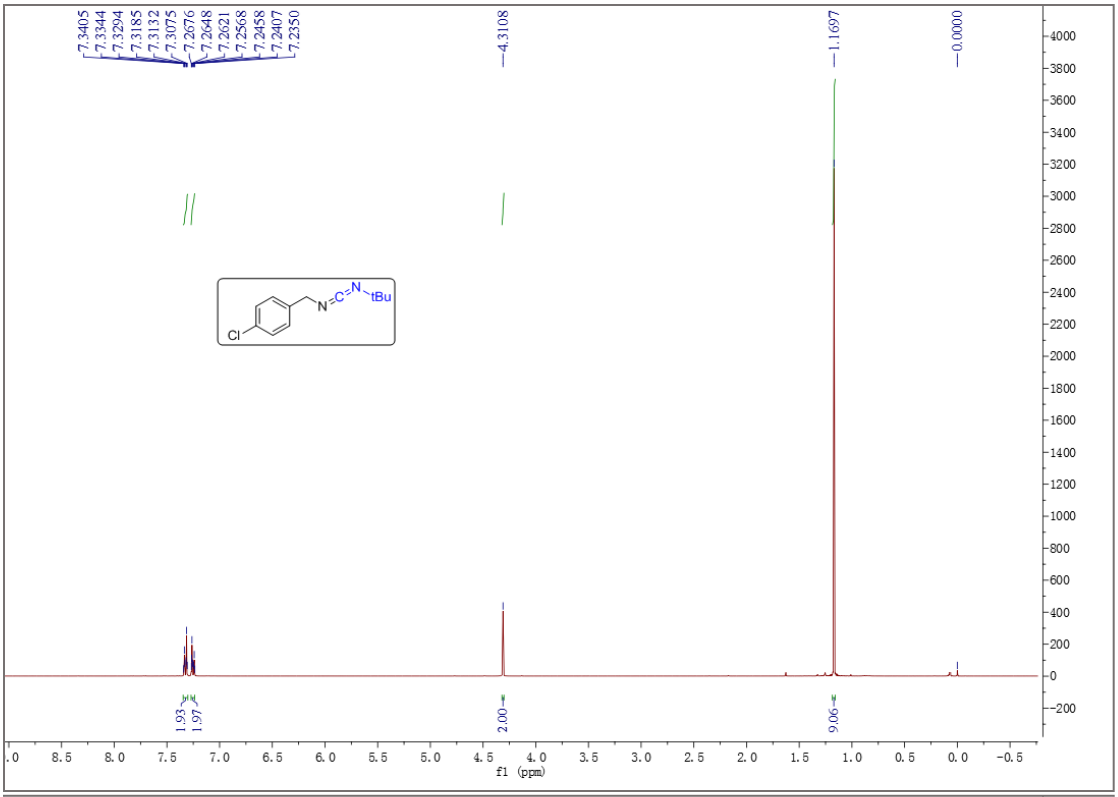
52.0377
50.3631
31.1780
MeO2C
N
C
N
tBu
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
100 90 80 70 60 50 40 30 20 10 0 -10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7.2676
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7.2621
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7.2458
7.2407
7.2350
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Cl
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tBu
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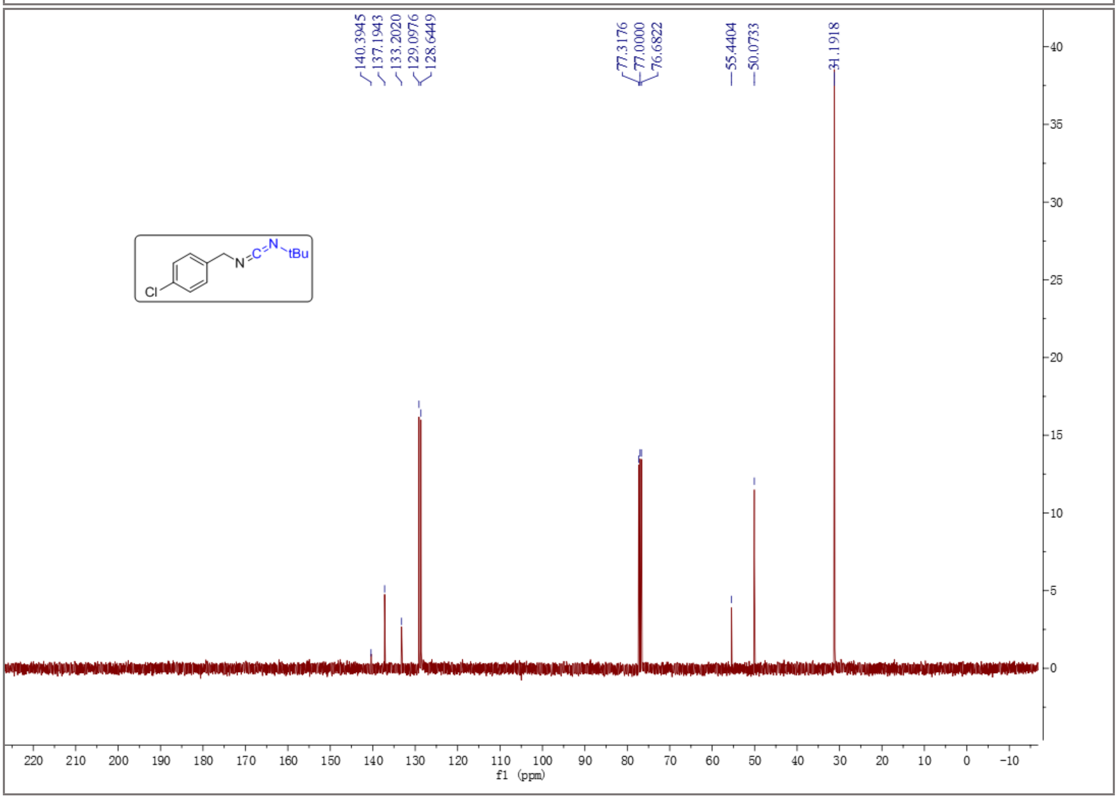
9.06
f1 (ppm)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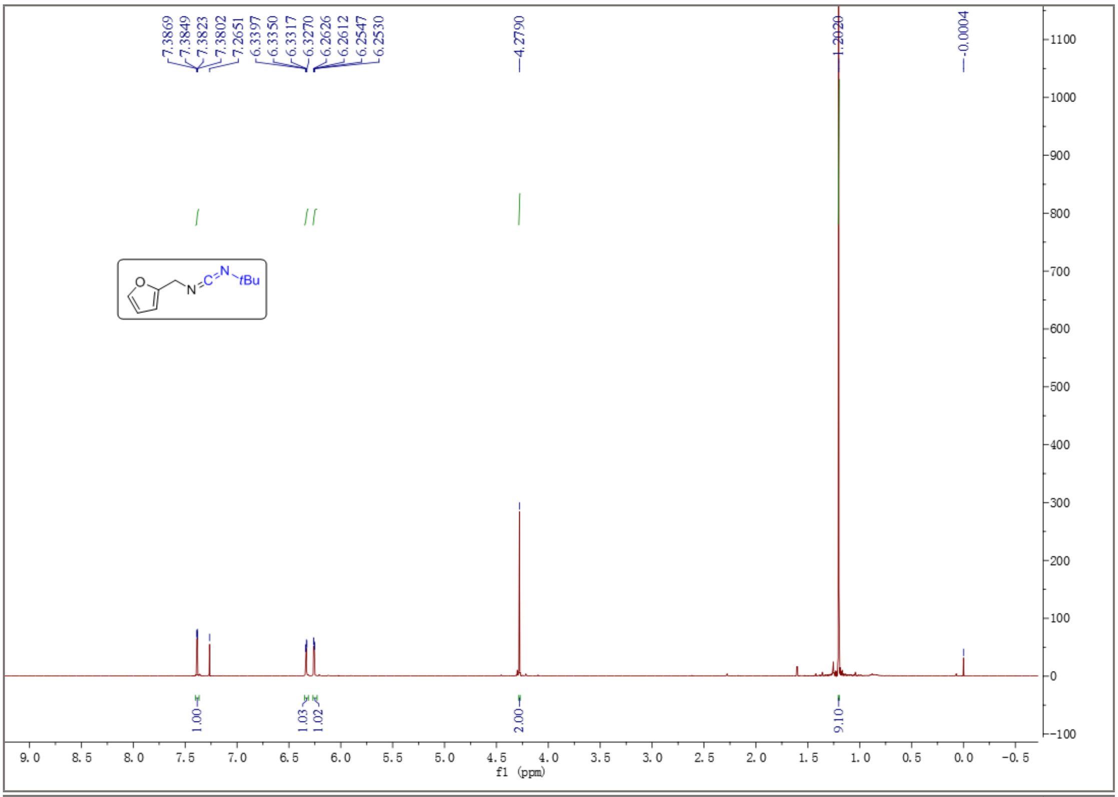
tBu
f1 (ppm)



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6.3317
6.3270
6.2626
6.2612
6.2547
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1.02
2.00
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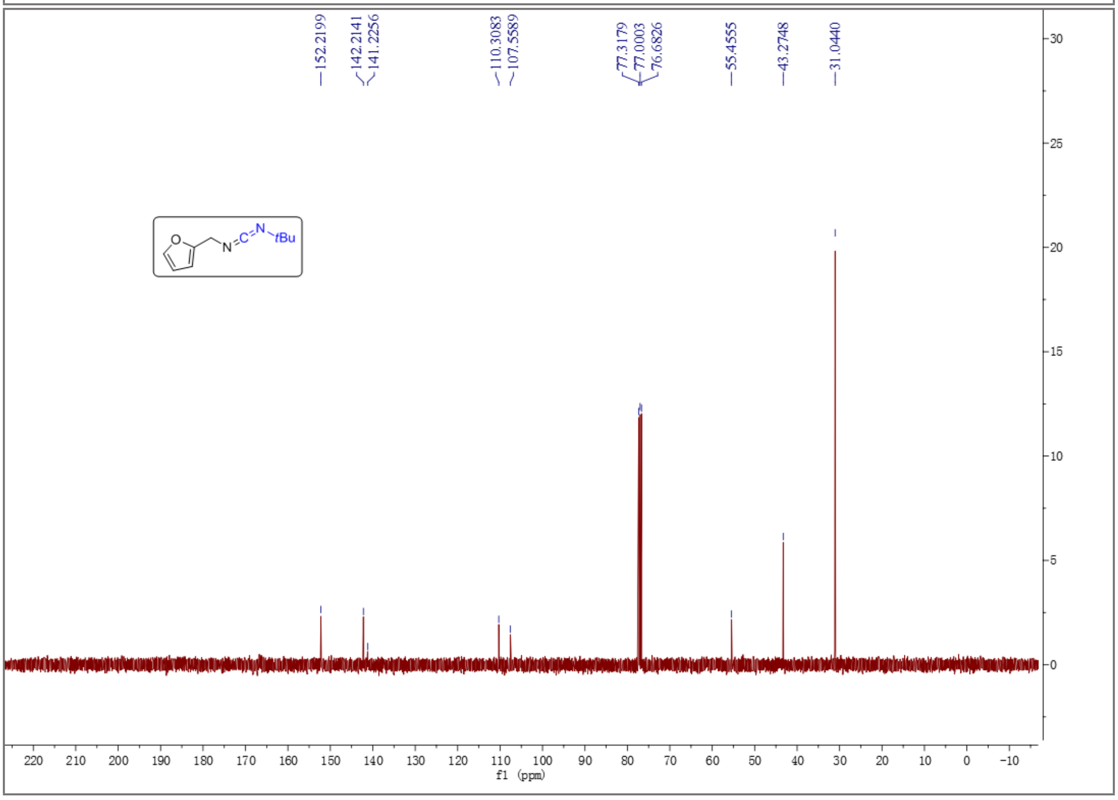
tBu
f1 (ppm)

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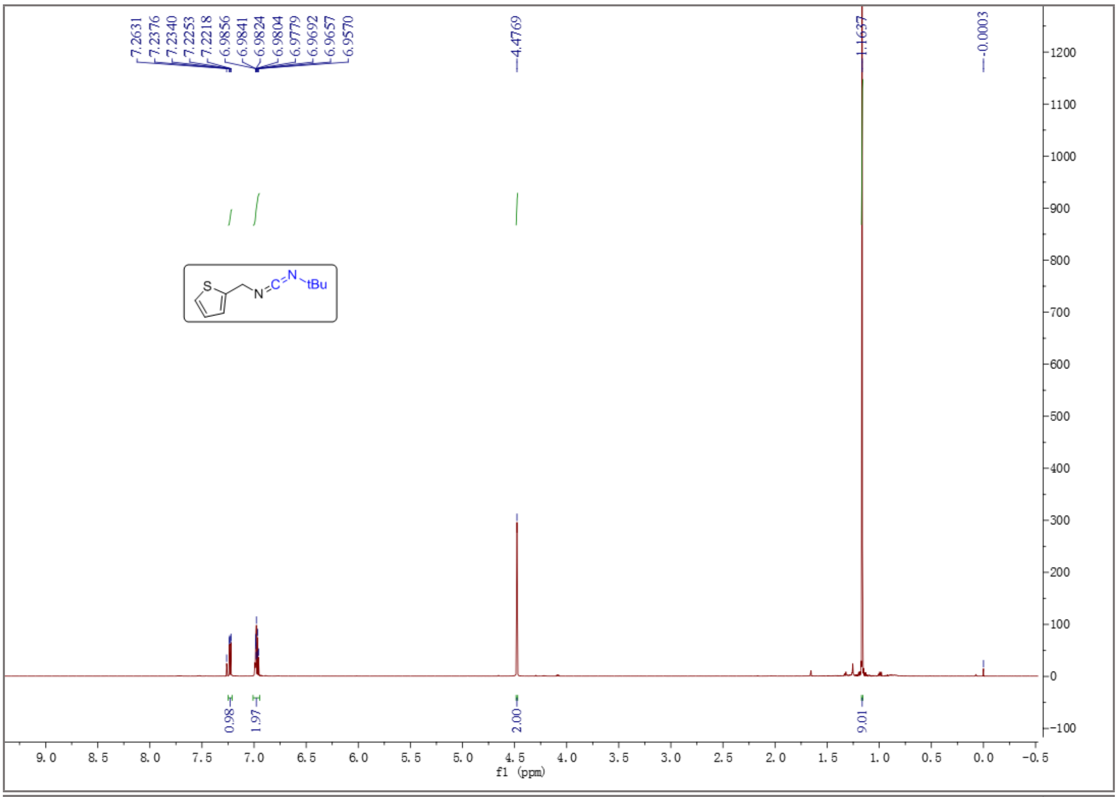
f1 (ppm)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6.9841
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6.9692
6.9657
6.9570
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C
N
tBu
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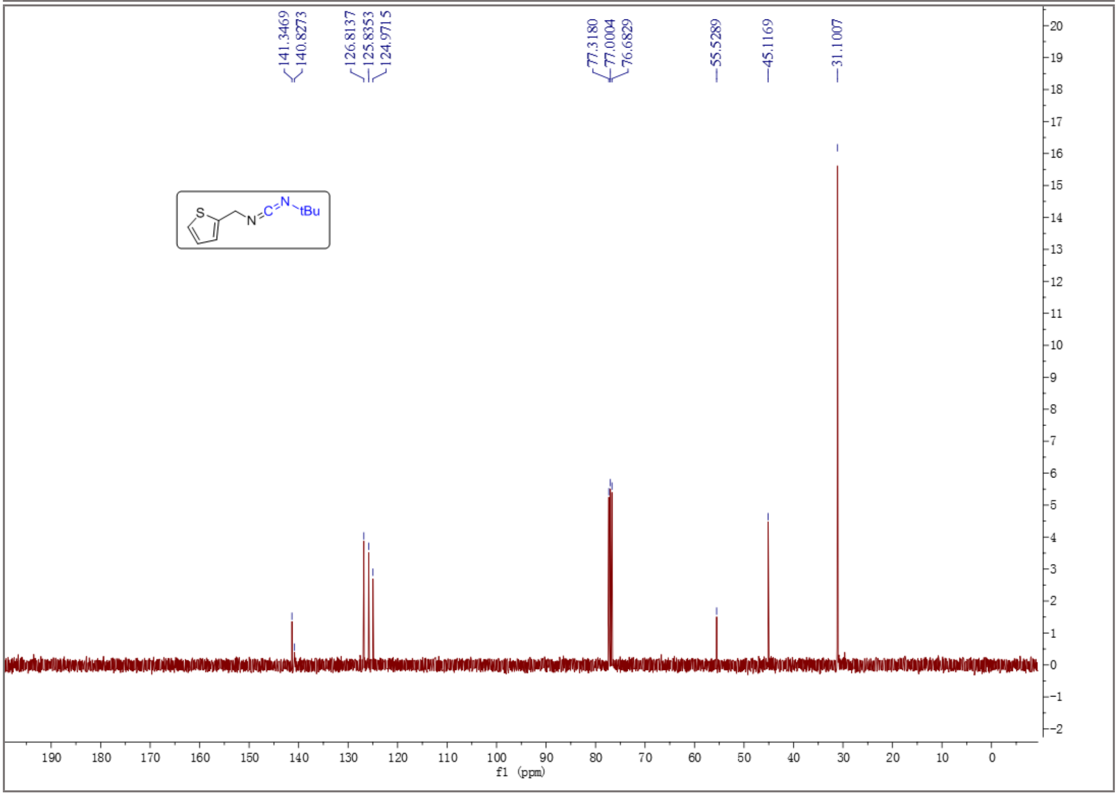
9.01
f1 (ppm)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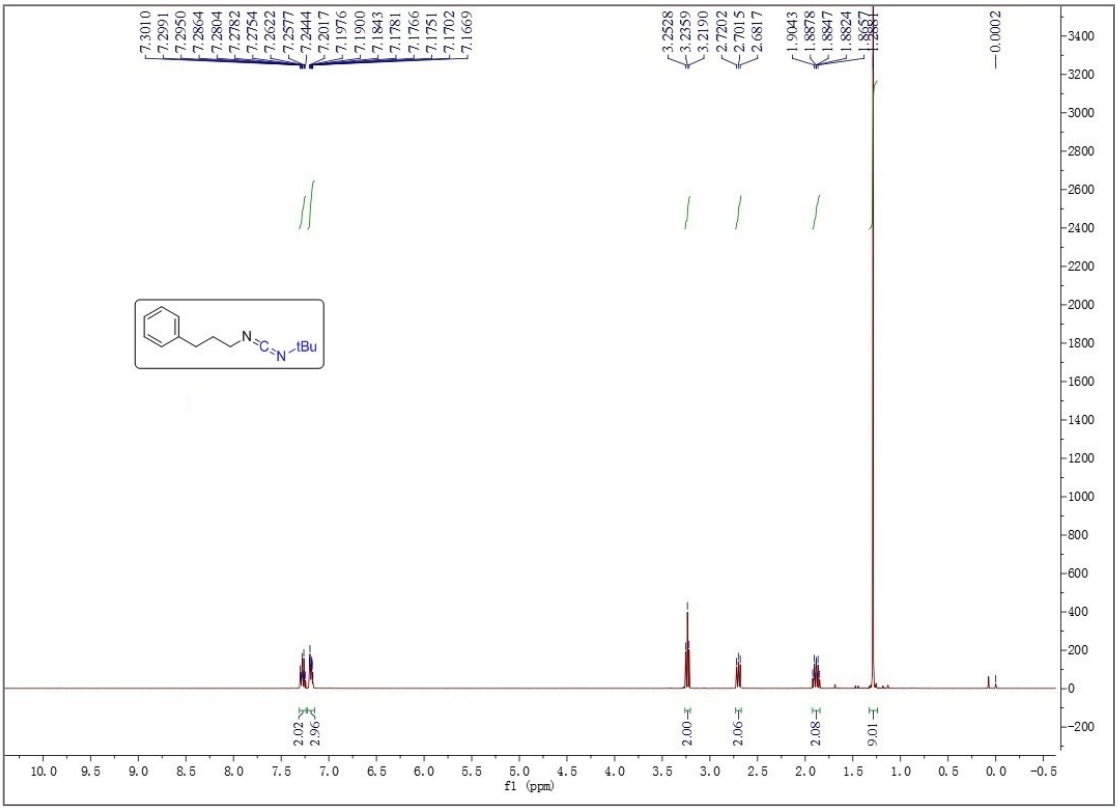
C
N
tBu
f1 (ppm)



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7.1976
7.1900
7.1843
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7.1766
7.1751
7.1702
7.1669
3.2528
3.2359
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2.7202
2.7015
2.6817
1.9043
1.8878
1.8847
1.8824
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N
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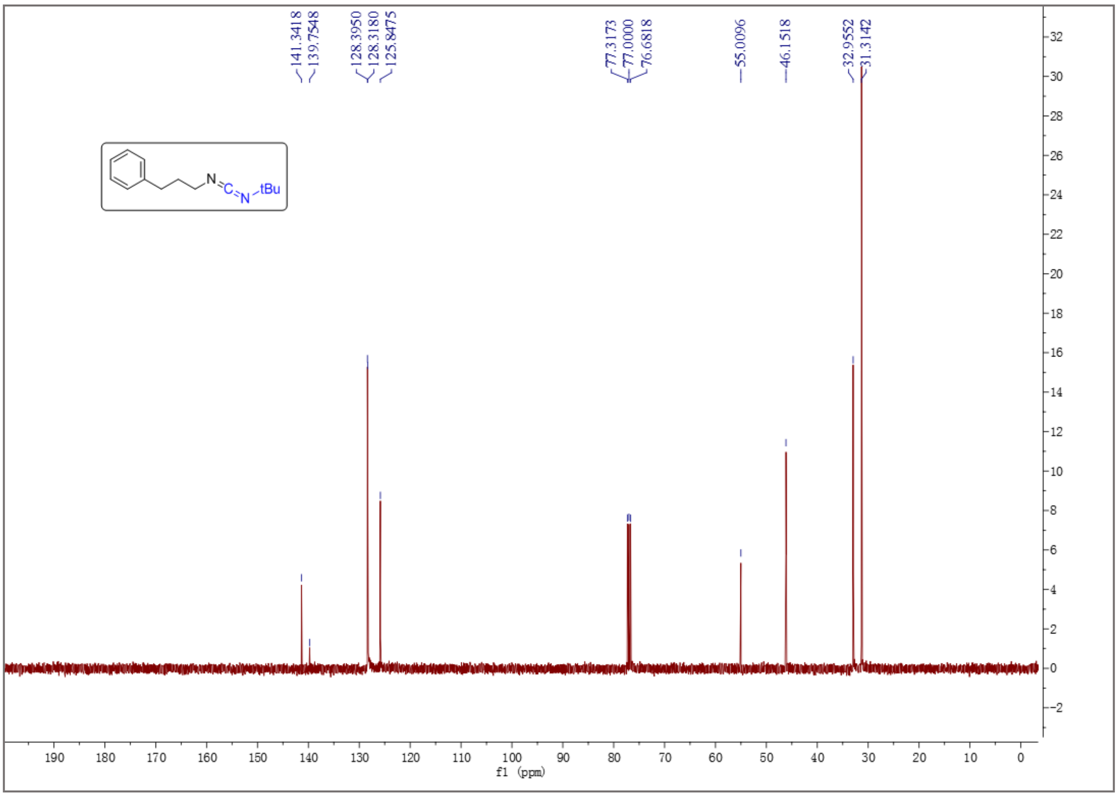
2.00
2.06
2.08
9.01
f1 (ppm)

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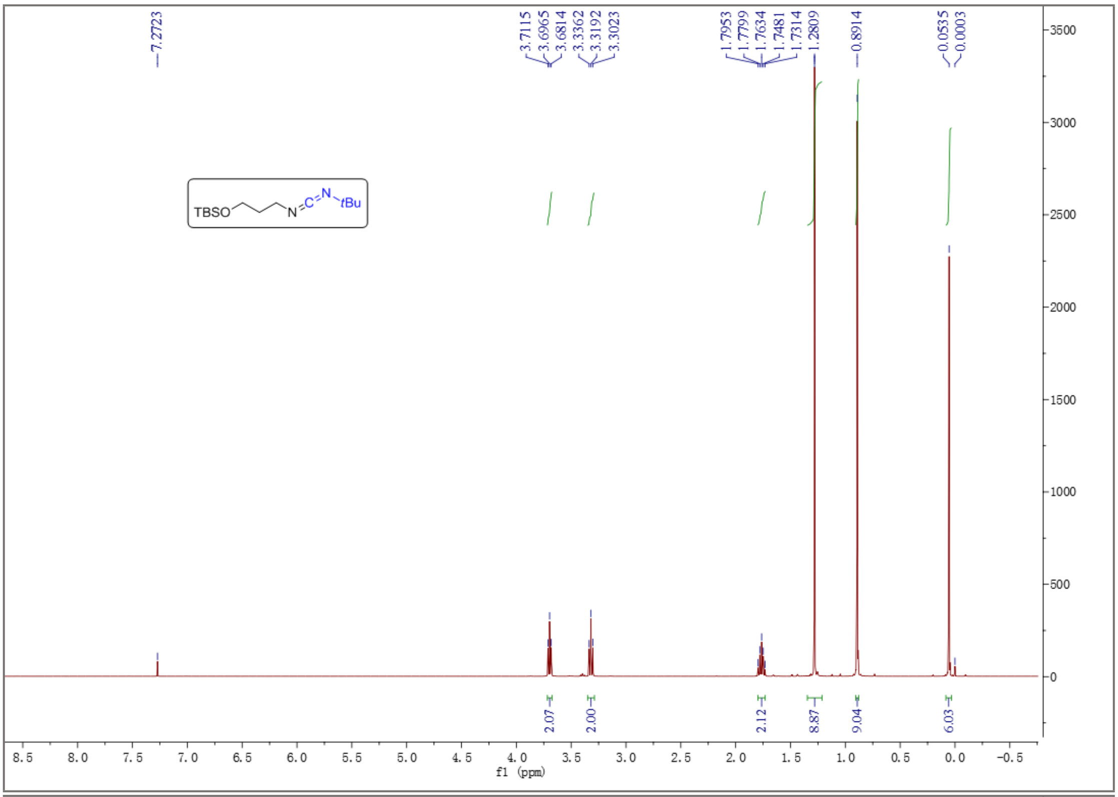
tBu
f1 (ppm)



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1.7799
1.7634
1.7481
1.7314
1.2809
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0.0535
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C
N
tBu
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2.00
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8.87
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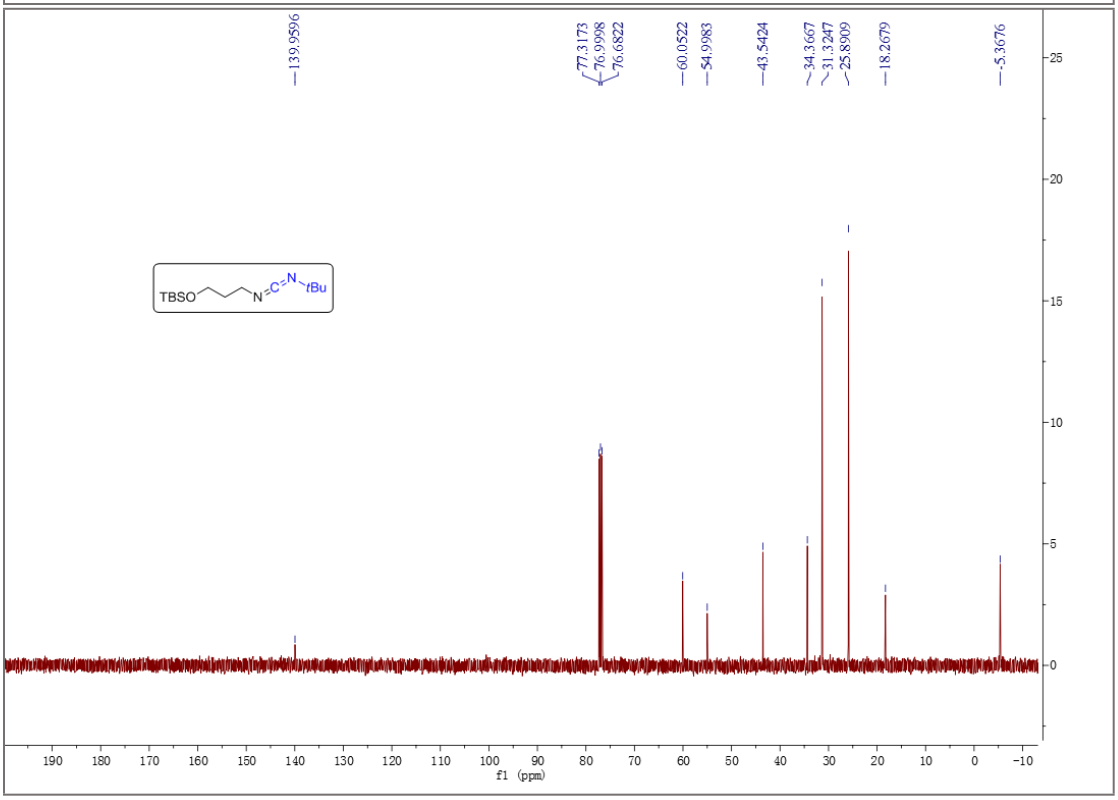
6.03
f1 (ppm)

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TBSO
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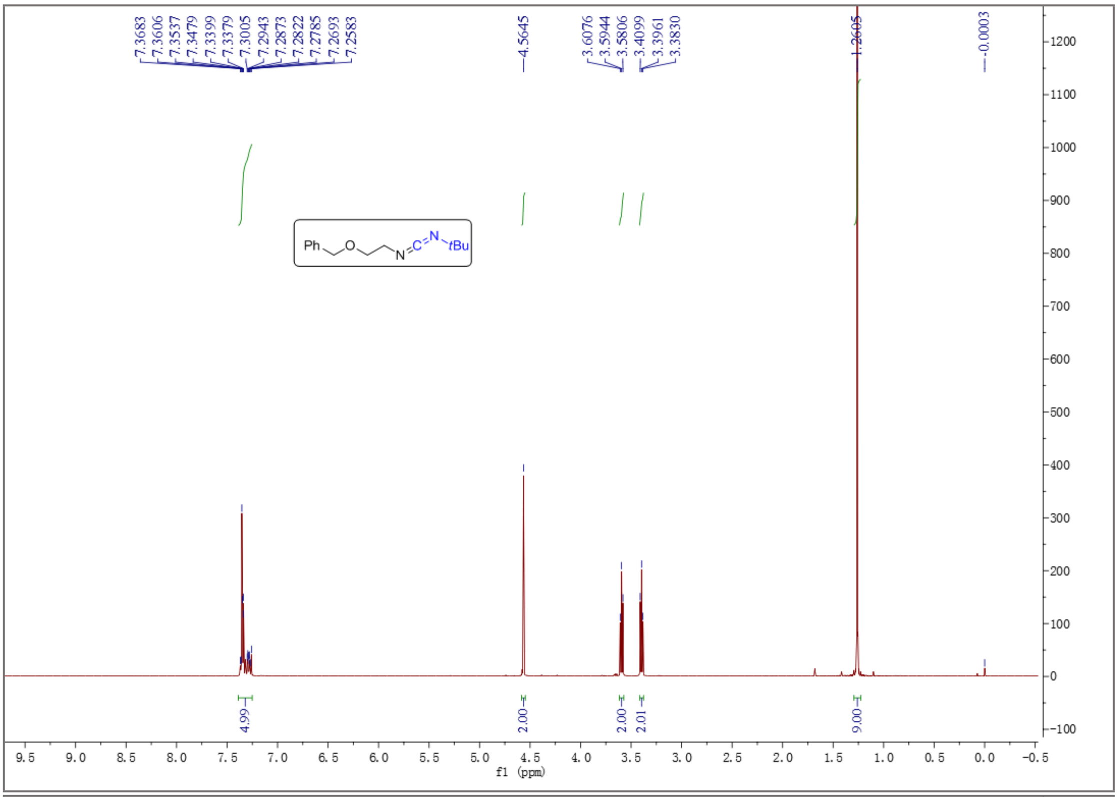
C
N
tBu
f1 (ppm)



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7.2693
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3.5944
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3.3830
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C
N
tBu
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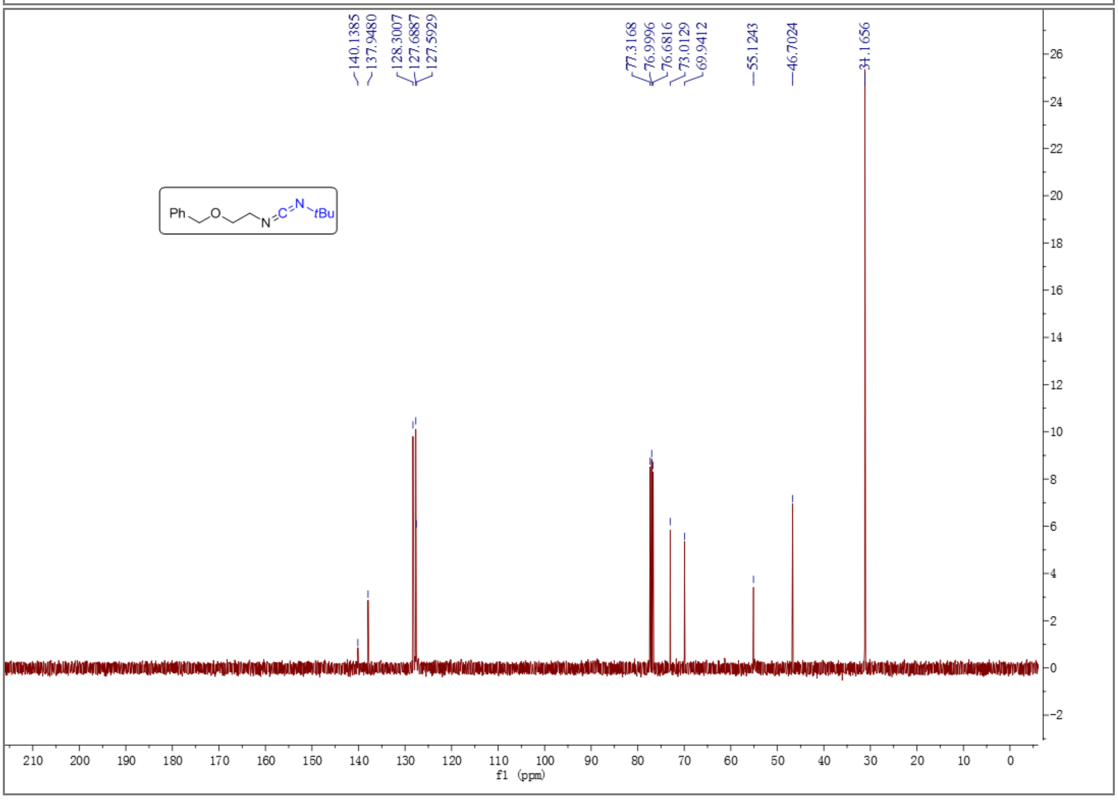
2.00
2.00
2.01
9.00
f1 (ppm)

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Ph
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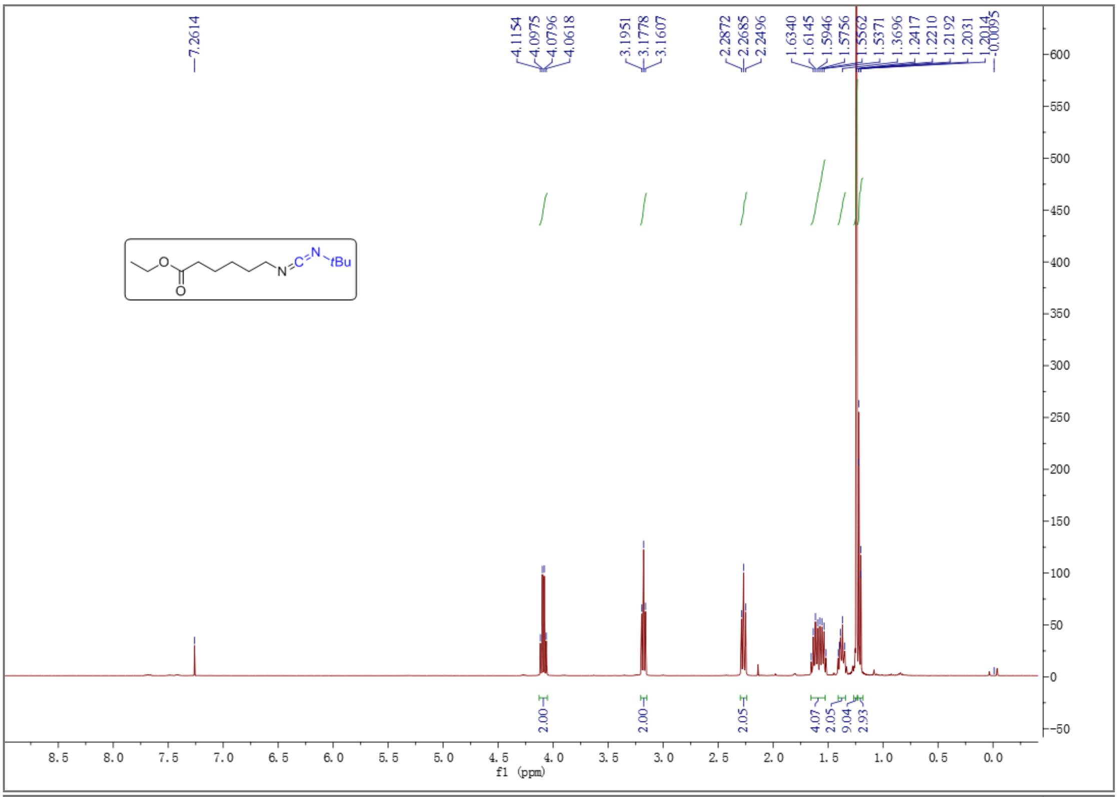
C
N
tBu
f1 (ppm)



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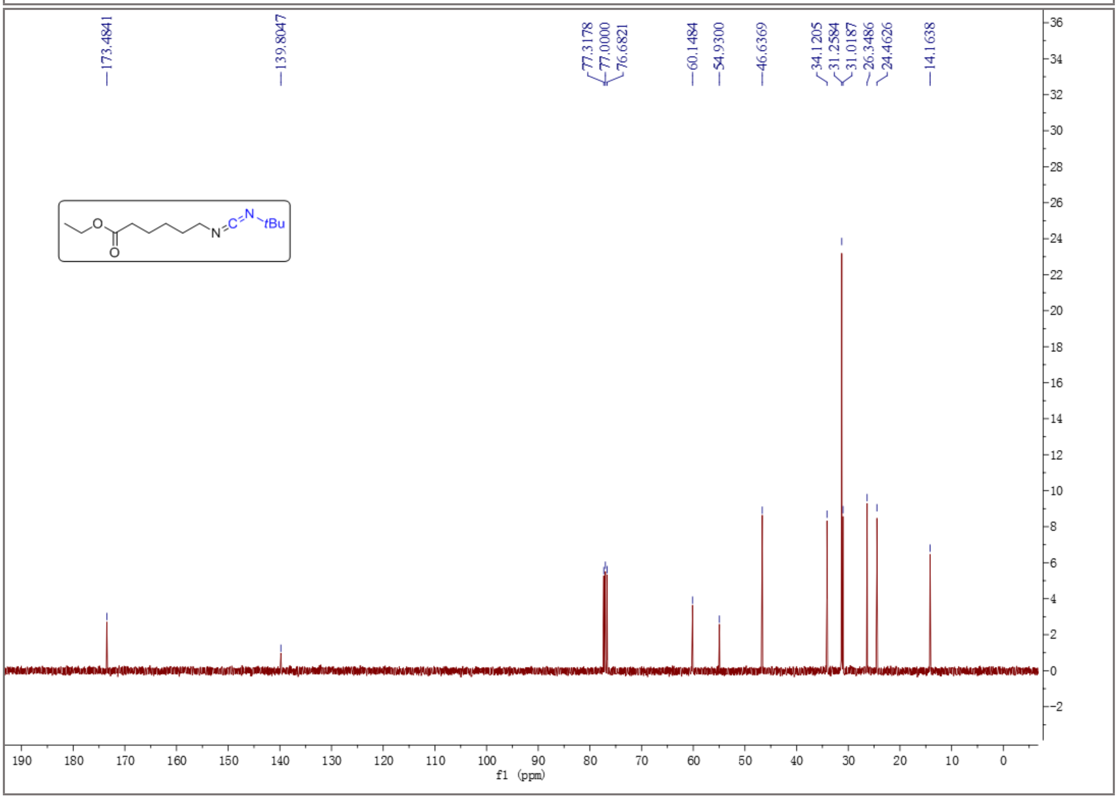
2.00
2.00
2.05
4.07
2.05
9.04
2.93
f1 (ppm)

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77.0000
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26.3486
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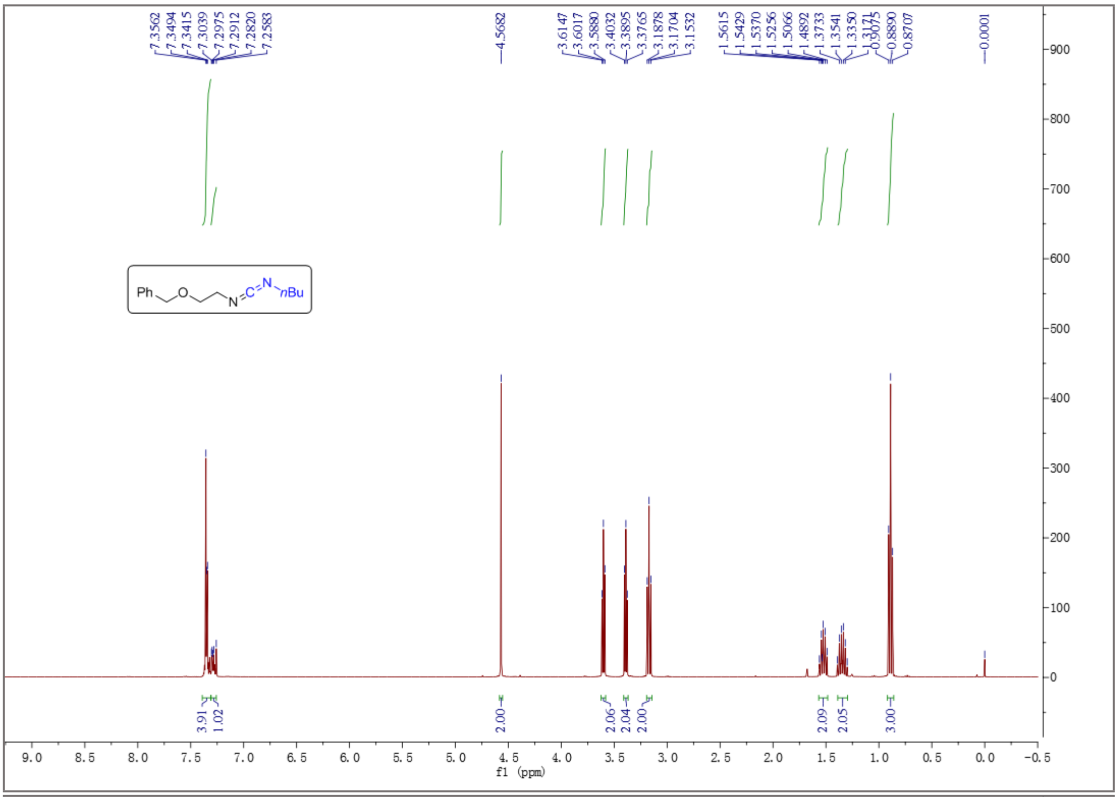
f1 (ppm)



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7.3415
7.3039
7.2975
7.2912
7.2820
7.2583
4.5682
3.6147
3.6017
3.5880
3.4032
3.3895
3.3765
3.1878
3.1704
3.1532
1.5615
1.5429
1.5370
1.5256
1.5066
1.4892
1.3733
1.3541
1.3350
1.3171
0.9075
0.8890
0.8707
0.0001
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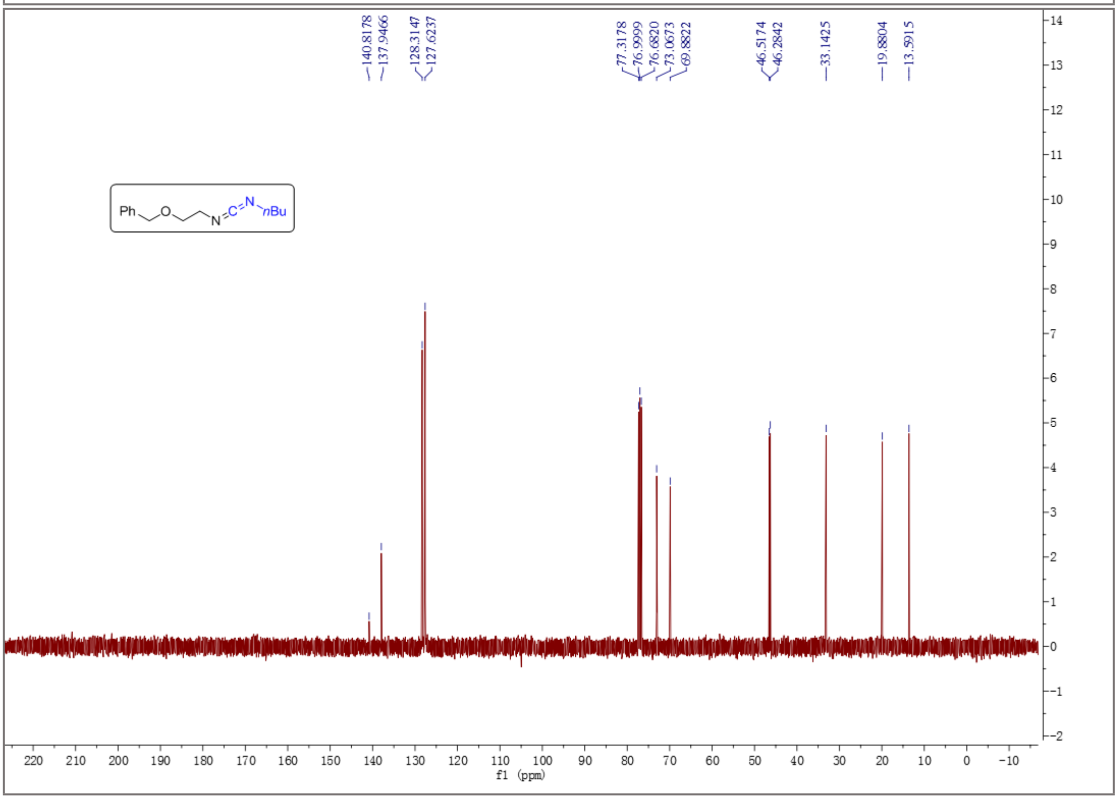
1.02
2.00
2.06
2.04
2.00
2.09
2.05
3.00
f1 (ppm)

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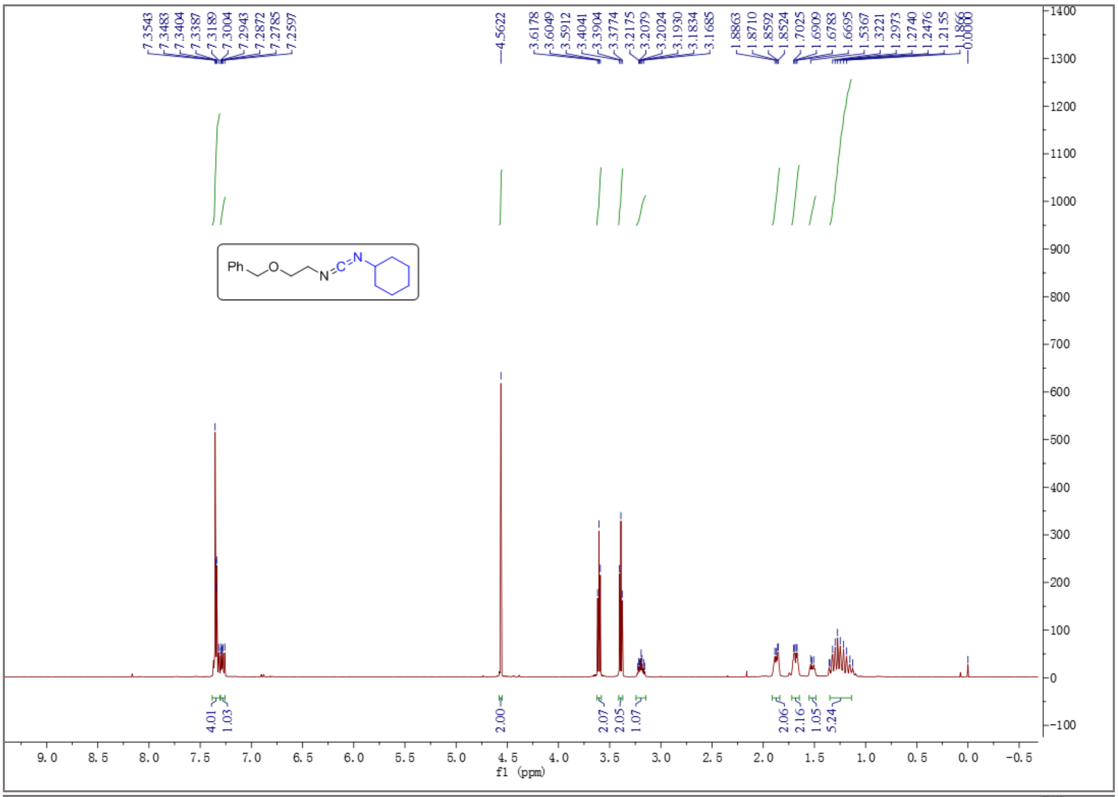
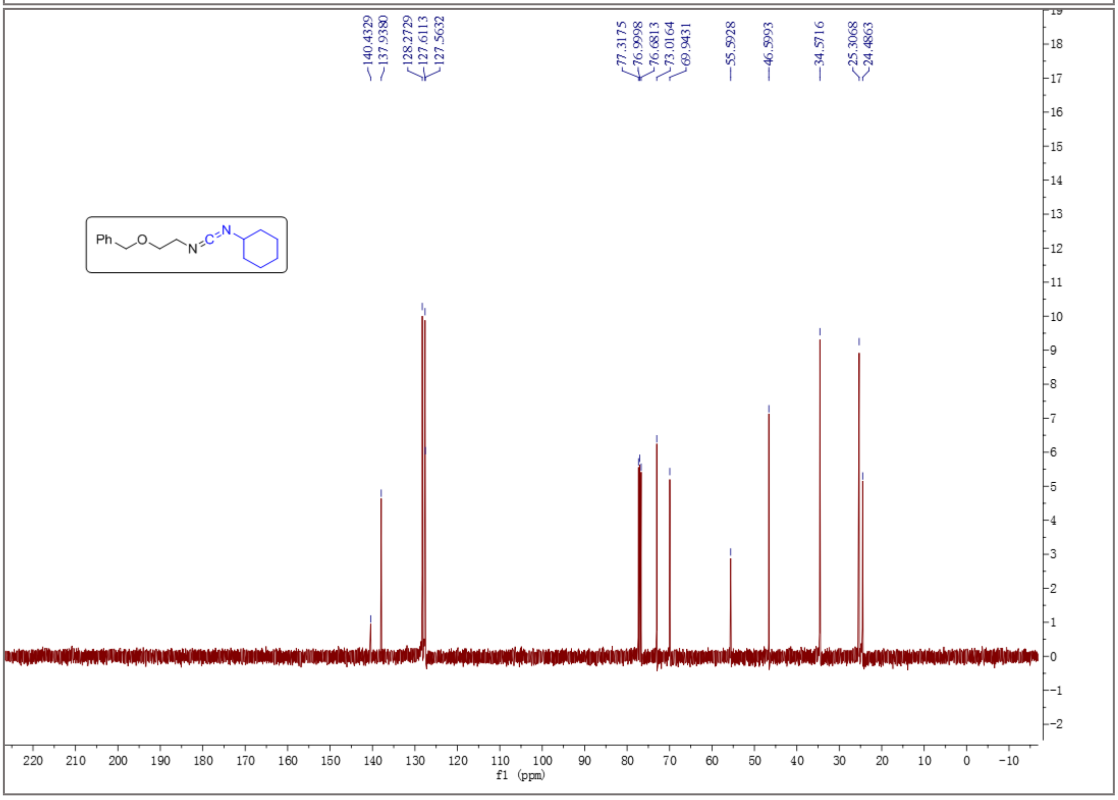
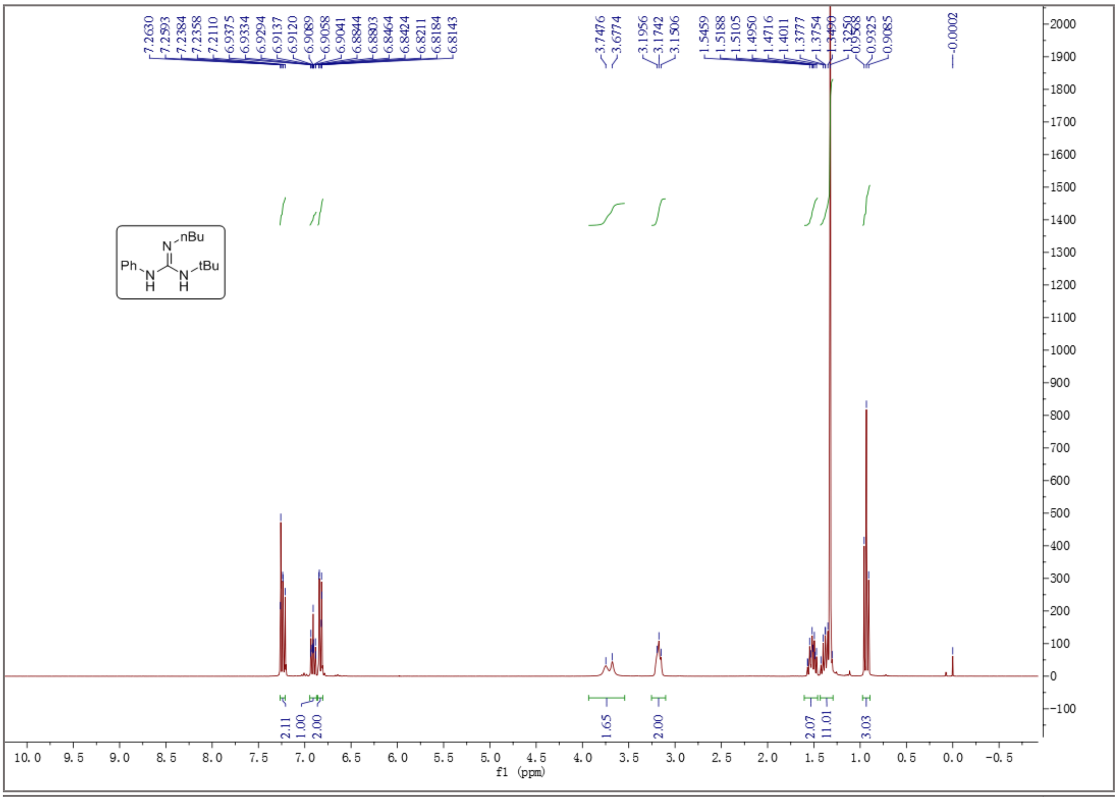
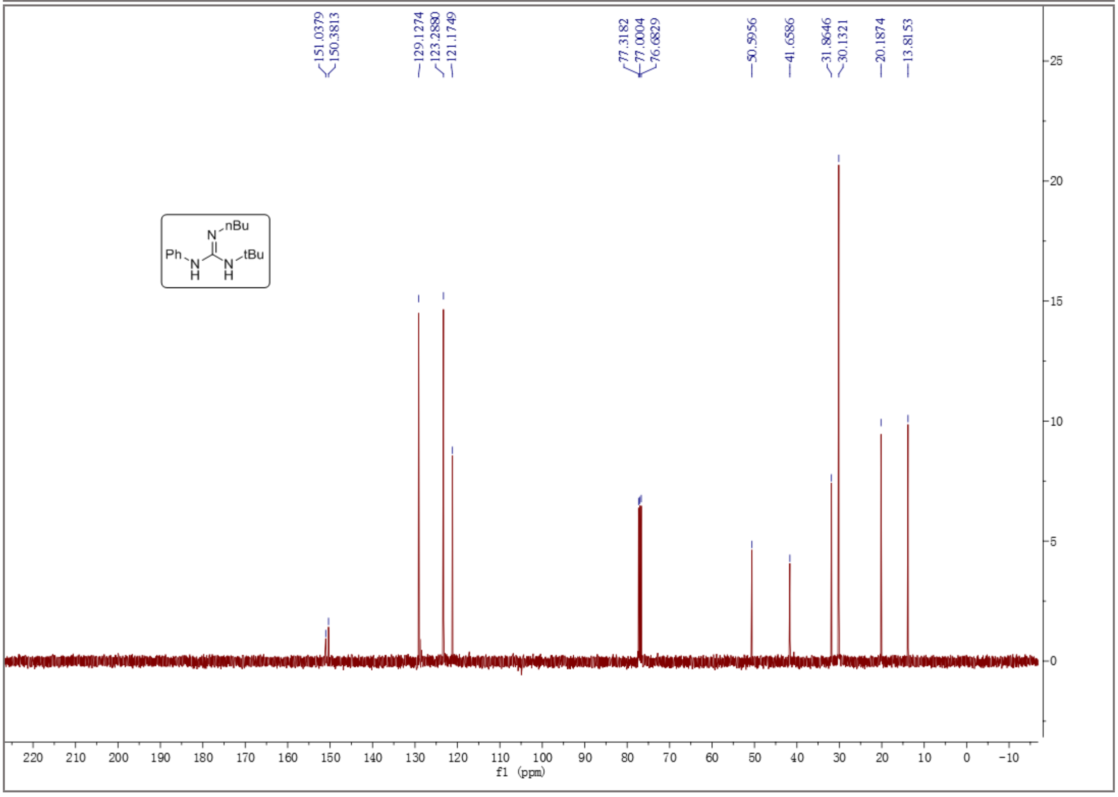
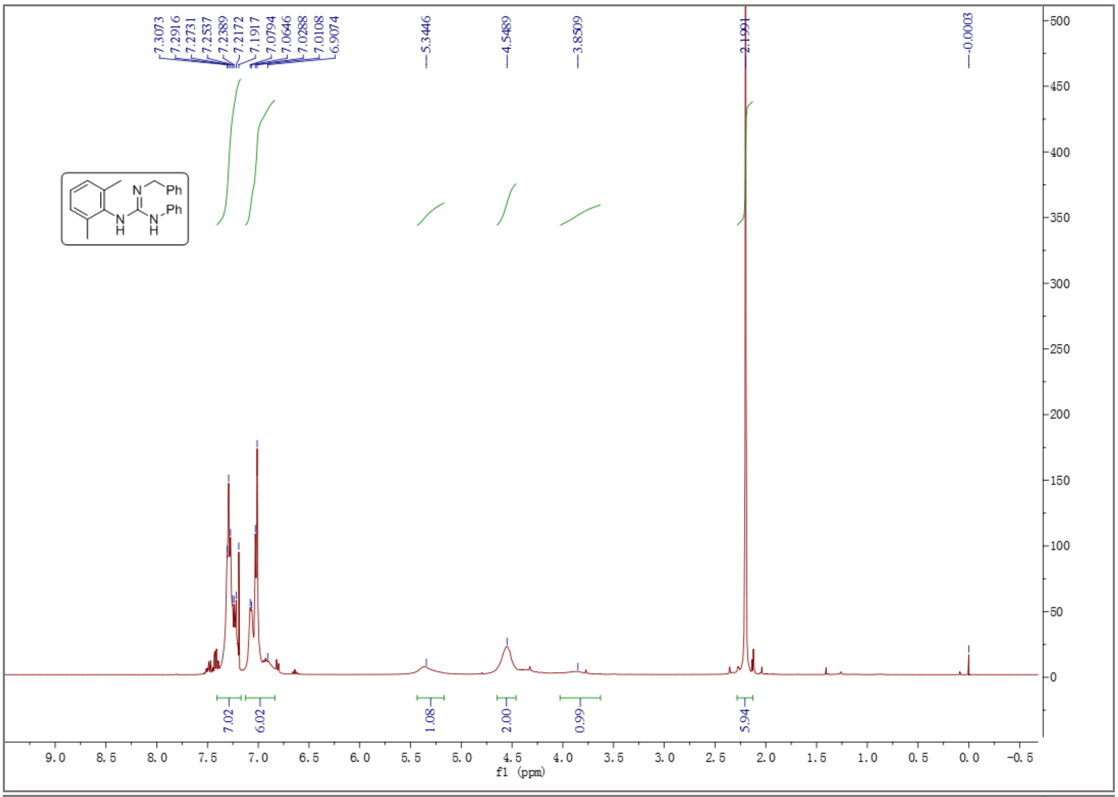
f1 (ppm)











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7.2389
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7.1917
7.0794
7.0646
7.0288
7.0108
6.9074
5.3446
4.5489
3.8509
2.1991
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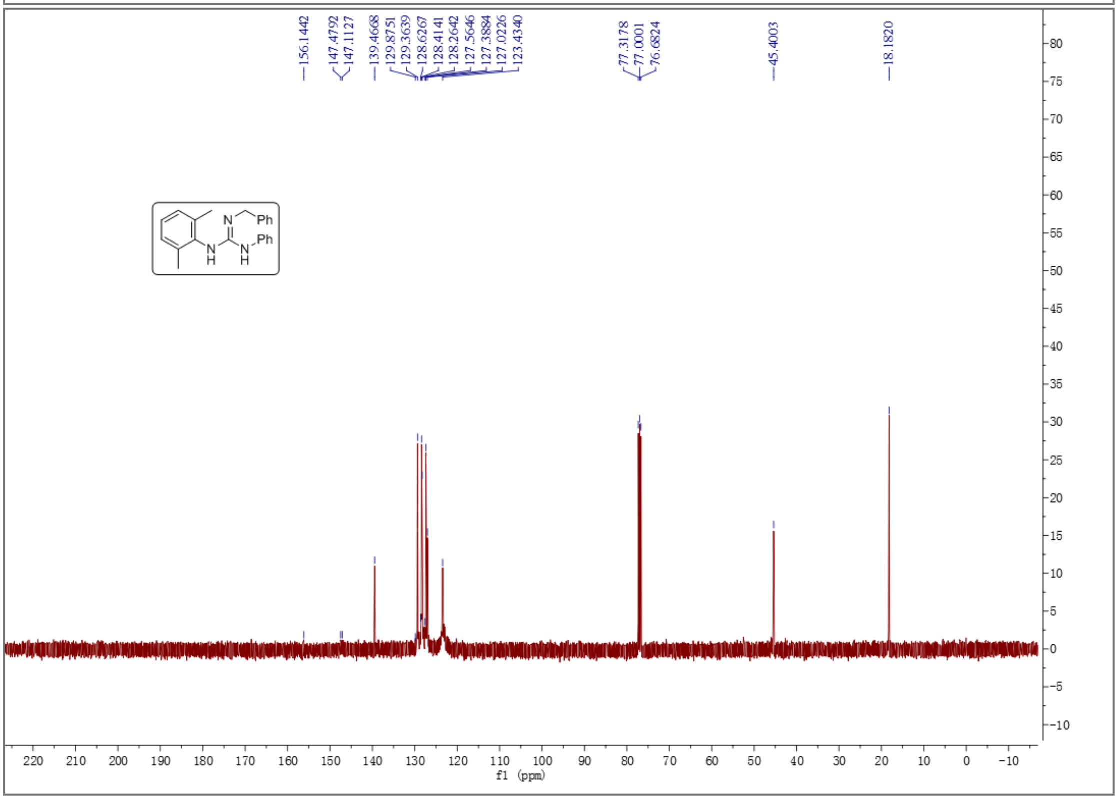
Ph
NH
N
H
Ph
7.02
6.02
1.08
2.00
0.99
5.94
f1 (ppm)

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127.5646
127.3884
127.0226
123.4340
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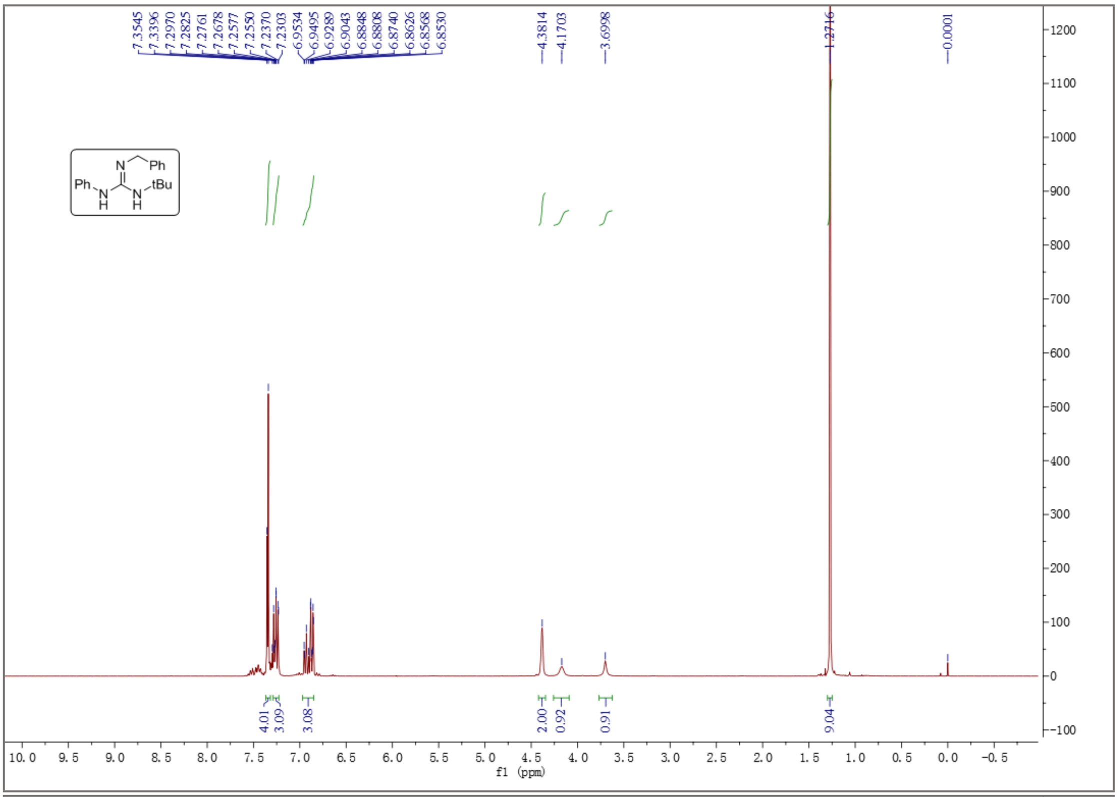
77.0001
76.6824
45.4003
18.1820
N
Ph
NH
N
H
Ph
f1 (ppm)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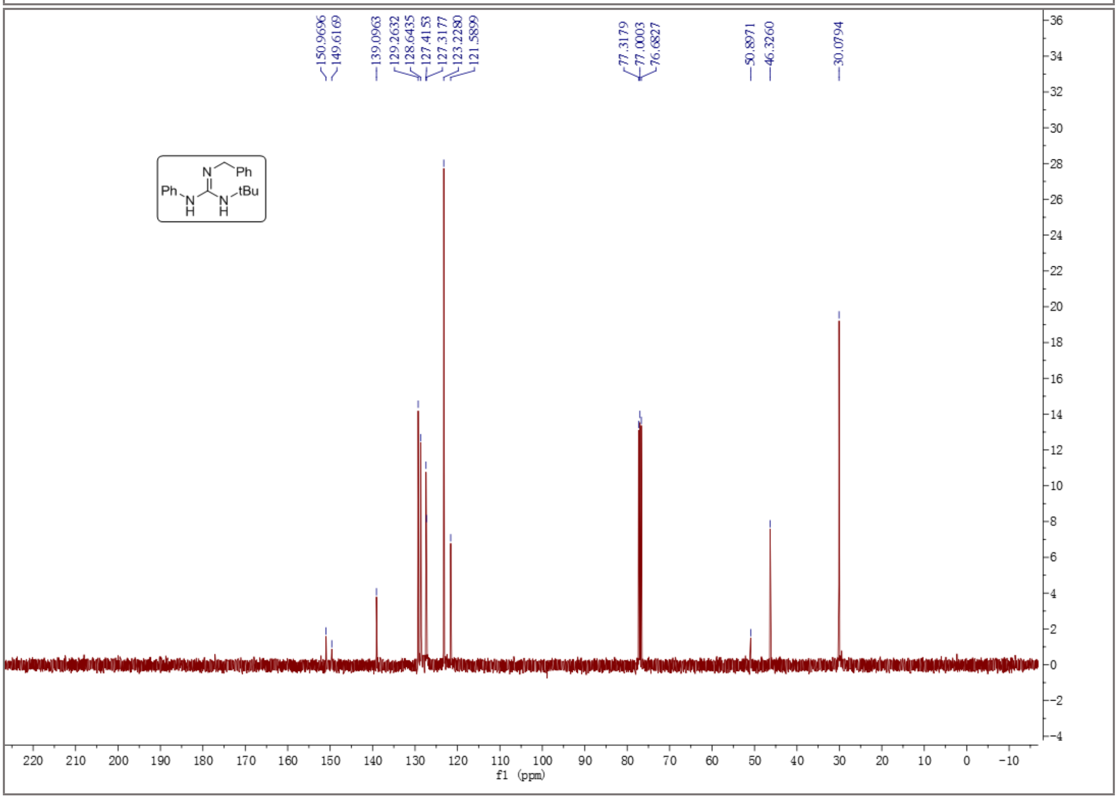
6.9495
6.9289
6.9043
6.8848
6.8808
6.8740
6.8626
6.8568
6.8530
4.3814
4.1703
3.6998
1.2716
0.0001
Ph
N
H
N
Ph
N
H
tBu
4.01
3.09
3.08
2.00
0.92
0.91
9.04
f1 (ppm)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139.0963
129.2632
128.6435
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121.5899
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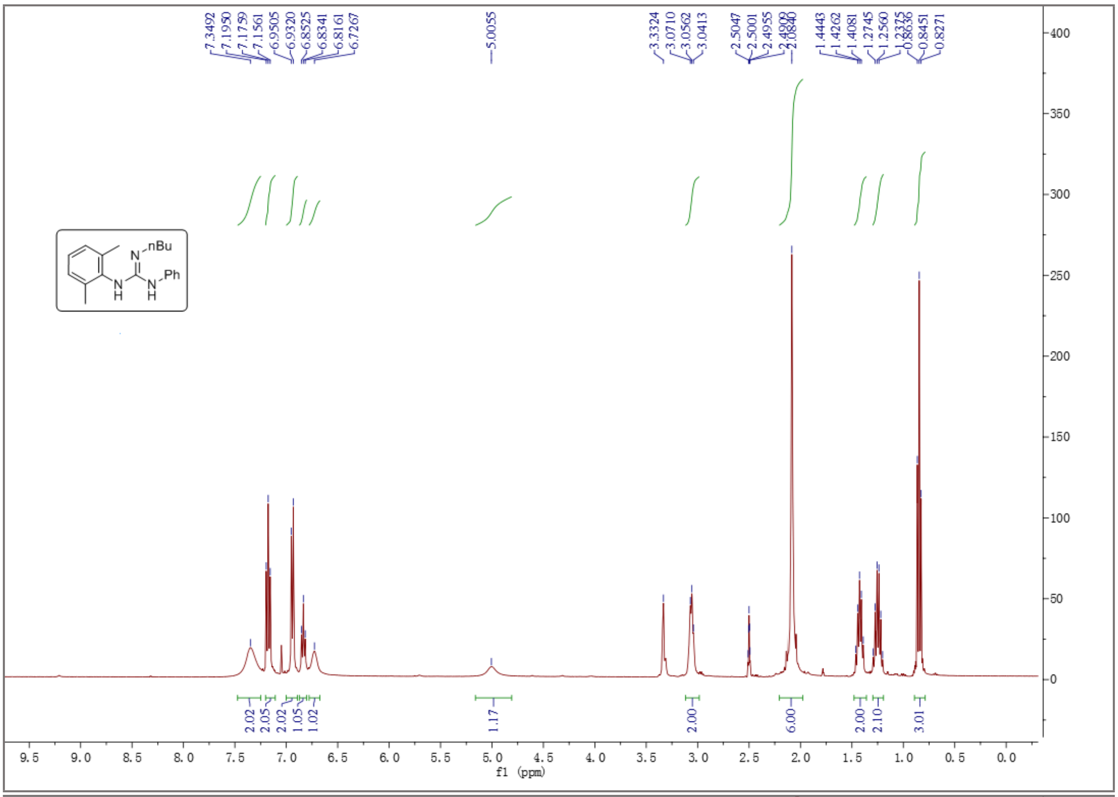
77.0003
76.6827
50.8971
46.3260
30.0794
f1 (ppm)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7.1950
7.1759
7.1561
6.9505
6.9320
6.8525
6.8341
6.8161
6.7267
5.0055
3.3324
3.0710
3.0562
3.0413
2.5047
2.5001
2.4955
2.0840
1.4443
1.4262
1.4081
1.2745
1.2560
0.8451
0.8271
nBu
N
N
H
N
H
Ph
2.02
2.05
2.02
1.05
1.02
1.17
2.00
6.00
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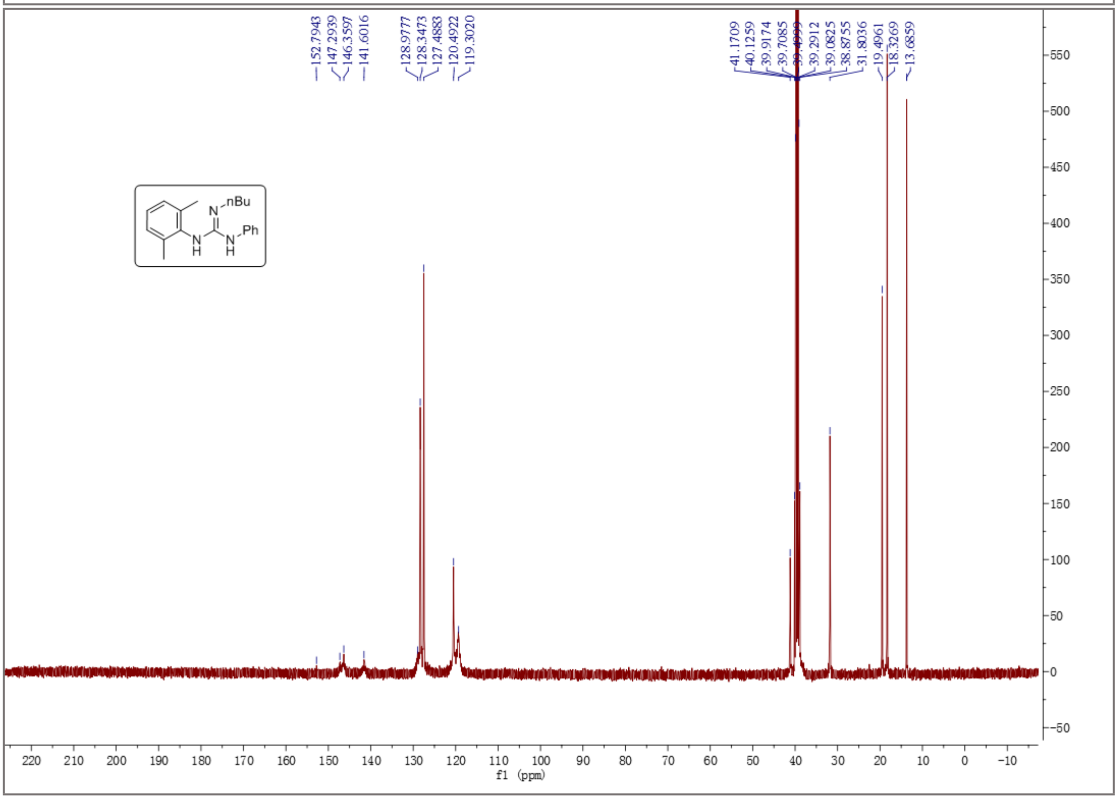
2.10
3.01
f1 (ppm)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119.3020
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40.1259
39.9174
39.7085
39.2912
39.0825
38.8755
31.8036
19.4961
18.3269
13.6859
nBu
N
N
H
N
H
Ph
f1 (ppm)