

Electronic Supplementary Information

Solvent-promoted Catalyst-free *N*-Formylation of Amines Using Carbon Dioxide under Ambient Conditions

Hui Lv,^{ab} Qi Xing,^b Chengtao Yue,^b Ziqiang Lei^{*a} and Fuwei Li^{*b}

^a Key Laboratory of Eco-Environment-Related Polymer Materials of Ministry of Education, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China.

^b Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou, 730000, China.

Email: Leizq@nwnu.edu.cn
fuweili@licp.cas.cn

Electronic Supplementary Information Contents:

1) General information.....	S2
2) Experimental procedure for <i>N</i> -formylation of amine.....	S2
3) Different chemical shifts of morpholine in different deuterated solvents.....	S3
4) <i>In-situ</i> ²⁹ Si spectra for the formylation of morpholine.....	S4
5) <i>In-situ</i> ¹ H NMR spectra for the reaction of morpholine with PhSiH ₃ in d ⁶ -DMSO.....	S5
6) <i>In-situ</i> ¹³ C NMR spectra for the reaction of morpholine with PhSiH ₃ in d ⁶ -DMSO.....	S6
7) The formylation of various amines and NMR analysis.....	S7-S11
8) ¹ H NMR and ¹³ C NMR copies of products.....	S11-S32
9) References.....	S33

1) General Information

All substrates were purchased and used as received without further purification. All solvents were purchased from commercial suppliers. Among these solvents, THF and dioxane were distilled by Na, DMSO and DMF were distilled by CaH₂, others were dried over 4 Å molecular sieves prior to use, and all solvents were kept in glove box. 4 Å molecular sieves were dried under dynamic vacuum at 400°C for 24 h prior to use. NMR spectra of the products were recorded using a Bruker Advance TM spectrometer operating at 400 MHz for ¹H and 100 MHz for ¹³C in CDCl₃ unless otherwise noted. Isolated yield was obtained by preparative thin-layer chromatography, and ethyl acetate/petroleum ether was used as the eluent.

2) Experimental Procedure for *N*-formylation of amine.

Table S1. Optimization of the formylation of morpholine.^a

Entry	Solvent	Hydrosilane	Yield (%) ^b
1	n-Hexane	PhSiH ₃	n.r.
2	Benzene	PhSiH ₃	n.r.
3	Toluene	PhSiH ₃	trace
4	THF	PhSiH ₃	trace
5	1,4-dioxane	PhSiH ₃	trace
6	CHCl ₃	PhSiH ₃	n.r.
7	CH ₃ CN	PhSiH ₃	12
8	DMF	PhSiH ₃	>99
9	DMSO	PhSiH ₃	>99
10	2 equiv. DMSO in THF	PhSiH ₃	19
11	4 equiv. DMSO in THF	PhSiH ₃	32
12	6 equiv. DMSO in THF	PhSiH ₃	35
13	8 equiv. DMSO in THF	PhSiH ₃	62
14	10 equiv. DMSO in THF	PhSiH ₃	90
15 ^c	DMSO	Et ₃ SiH	>99
16 ^d	DMSO	(EtO) ₃ SiH	>99

^a Reaction conditions: morpholine (0.5 mmol), R₃SiH (0.75 mmol), CO₂ (1 atm), solvent (2 mL), room temperature, 24 h. ^b The yield was determined by GC, calibrated using n-hexadecane as the internal standard. ^c Et₃SiH (2.25 mmol). ^d (EtO)₃SiH (2.25 mmol).

Experimental procedure of Table S1, entry 9: A 50 mL Schlenk tube with a magnetic bar was charged with morpholine (0.5 mmol), PhSiH_3 (0.75 mmol), and DMSO (2 mL). Then the tube was sealed and pressurized with 1.0 atm CO_2 after it was vacuumed and flushed with CO_2 three times. After that, it was stirred at room temperature for 24 h. After the reaction was completed, the yield was determined by GC, calibrated using n-hexadecane as the internal standard.

3) Different chemical shifts of morpholine in different deuterated solvents.

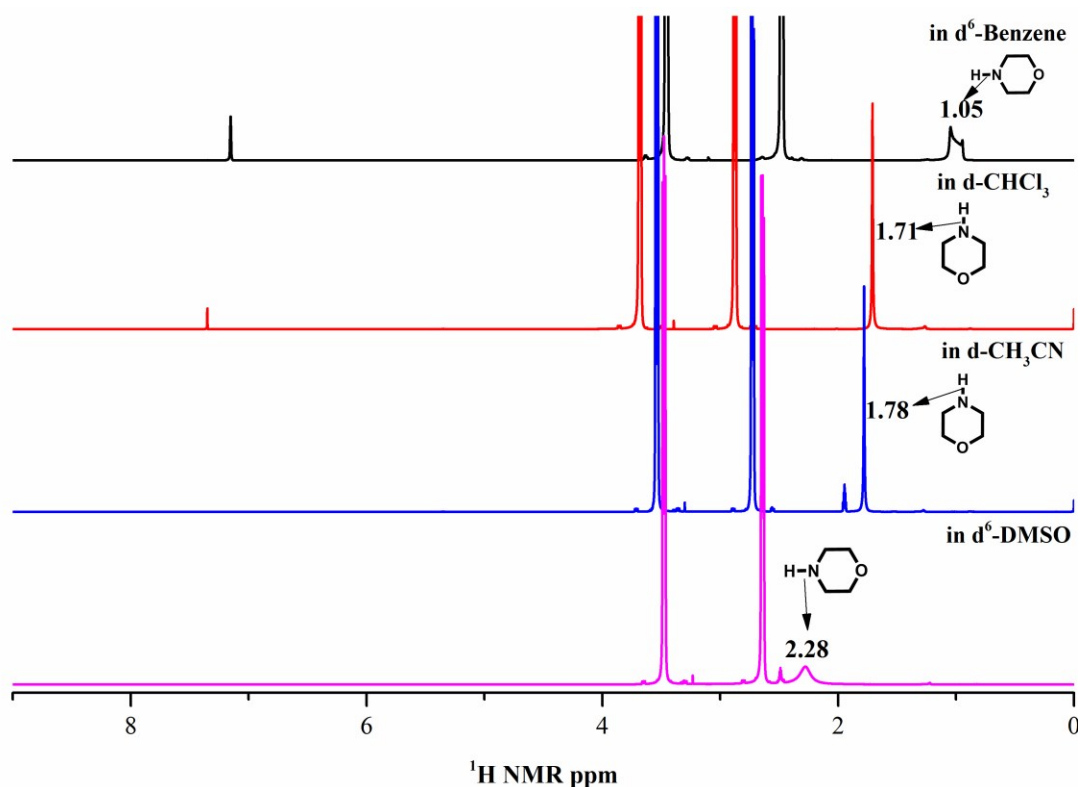


Figure S1. ^1H NMR spectra of morpholine in different deuterated solvents. Solvents (0.5 mL), morpholine (0.5 mmol). It's found that the ^1H signals for N-H proton of morpholine in different solvents followed the order: d^6 -DMSO (2.28 ppm) > CD_3CN (1.78 ppm) > CDCl_3 (1.71 ppm) > d^6 -benzene (1.05 ppm), which is in agreement with the polarity order of these solvents. This result confirmed the influence of solvents polarity on the property of amine.

4) In-situ ^{29}Si spectra for the formylation of morpholine.

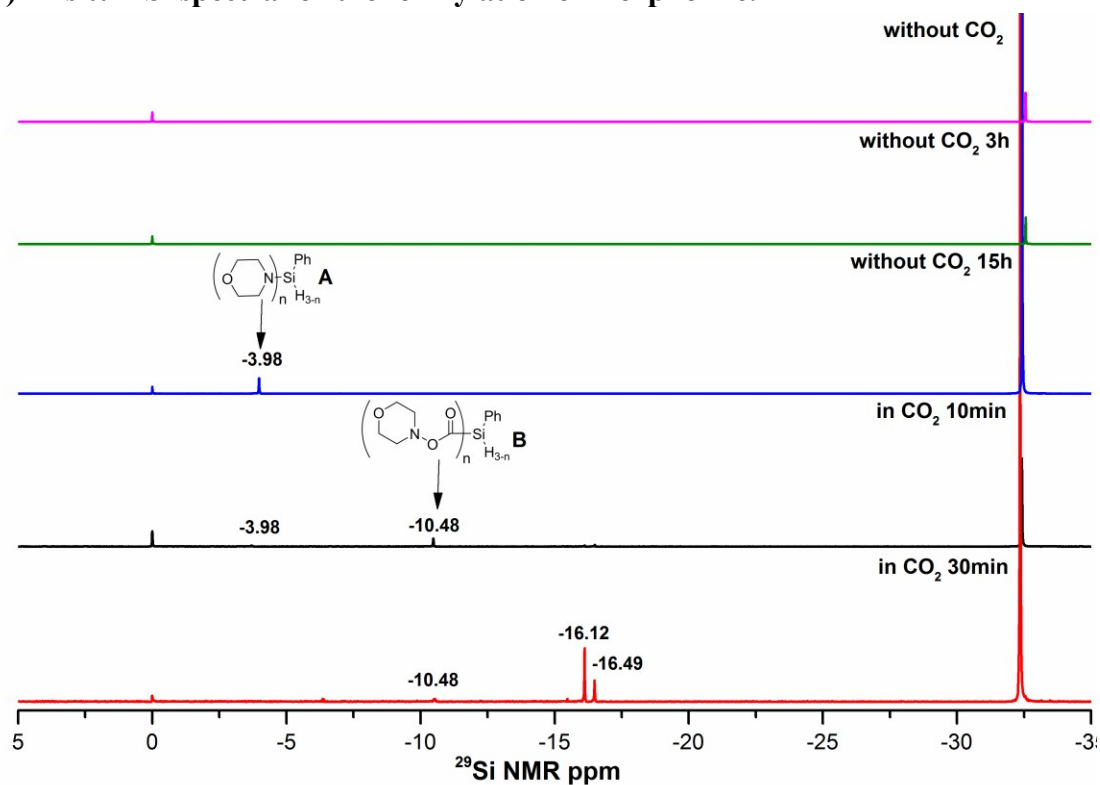


Figure S2. *In-situ* ^{29}Si spectra of morpholine (0.25 mmol) and PhSiH_3 (0.375 mmol) exposed to CO_2 (1 atm) at room temperature (0.5 mL $\text{d}^6\text{-DMSO}$, with TMSA as internal standard). The mixture was stirred throughout the whole course. (TMSA: Trimethyl silyl acetylene)

5) In-situ ^1H NMR spectra for the reaction of morpholine with PhSiH_3 in d^6 -DMSO.

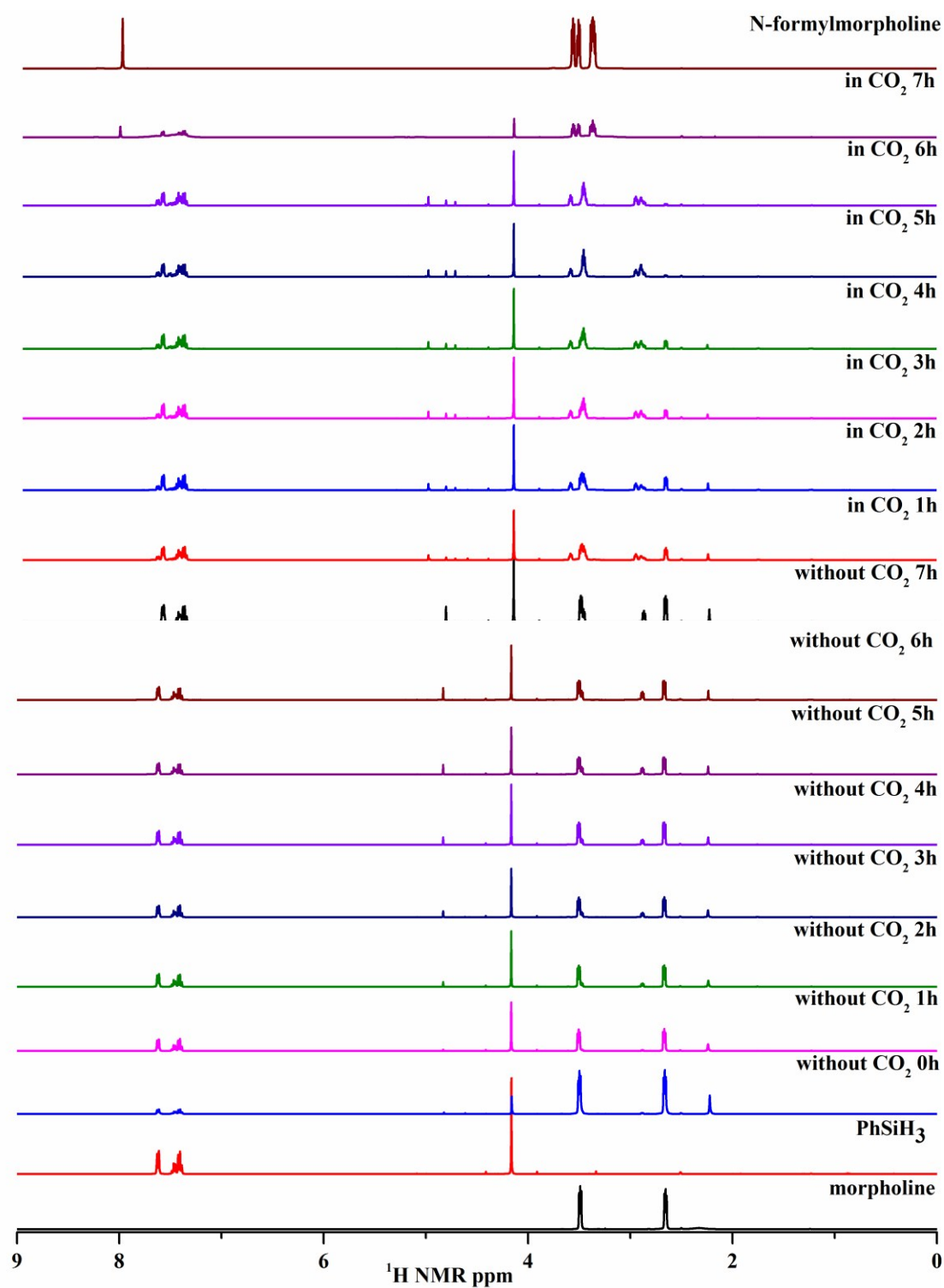


Figure S3. *In-situ* ^1H NMR spectra of morpholine (0.25 mmol) and PhSiH_3 (0.375 mmol) in d^6 -DMSO. CO_2 (1 atm), room temperature. The mixture was shaken from 1 to 6 hours and stirred from 6 to 7 hour. (TMS as internal standard).

6) In-situ ^{13}C NMR spectra for the reaction of morpholine with PhSiH_3 in $\text{d}^6\text{-DMSO}$.¹

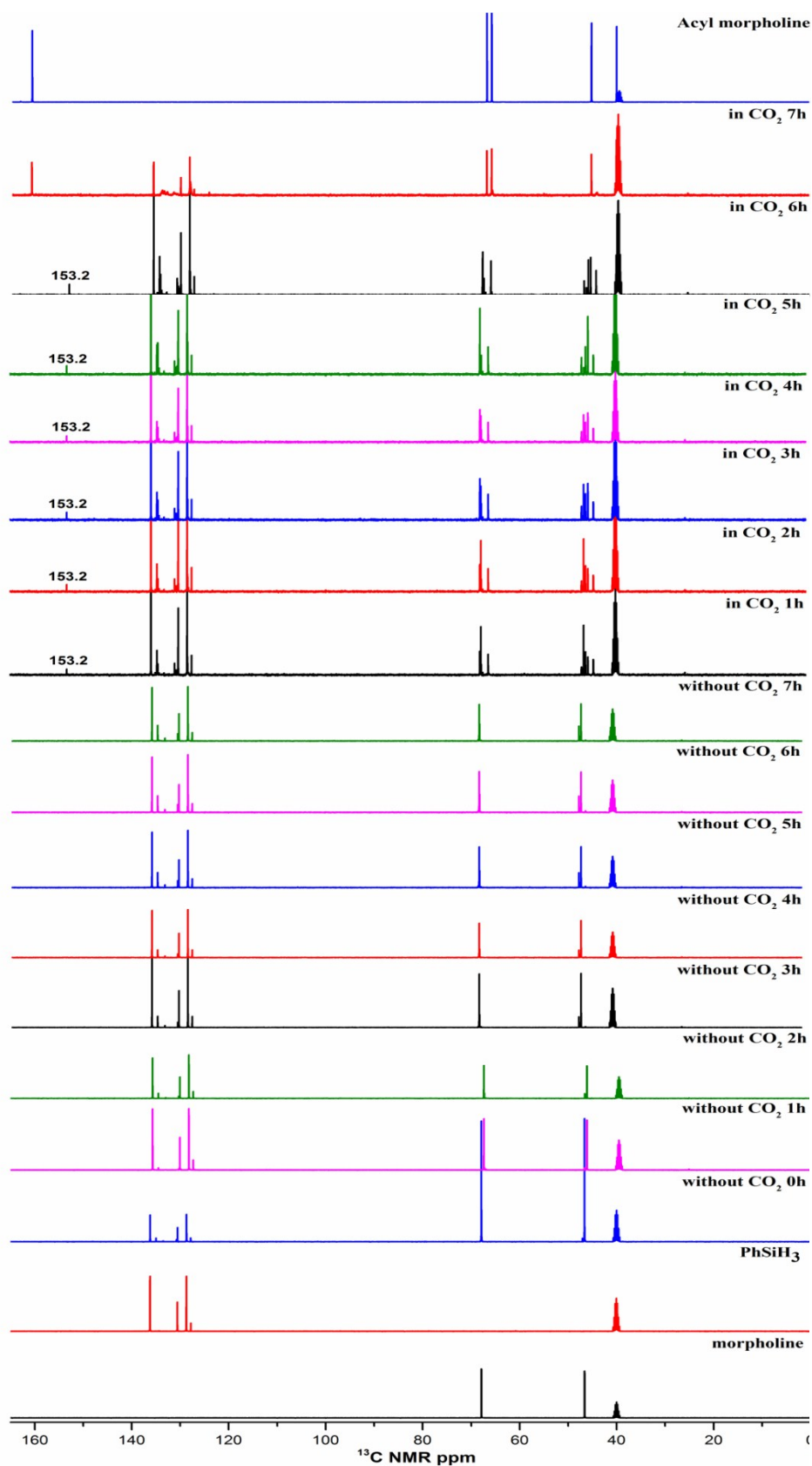


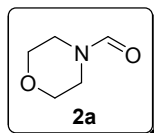
Figure S4. In-situ ^{13}C NMR spectra of morpholine (0.25mmol) and PhSiH_3

(0.375mmol) in d⁶-DMSO. CO₂ (1 atm), room temperature. The mixture was shaken from 1 to 6 hours and stirred from 6 to 7 hour. (TMS as internal standard).

7) The formylation of various amines (1a to 1t) (Table 2)

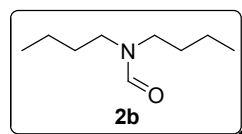
A mixture of amines **1** (0.5 mmol), PhSiH₃ (0.75 mmol), and DMSO (2 mL) was added into a 50 mL Schlenk tube with a magnetic bar in the glove box. Then the tube was sealed and pressurized with 1.0 atm CO₂ after it was vacuumed and flushed with CO₂ three times. After that, it was stirred at room temperature for 24 h. After the reaction was completed, the yield was determined by GC, calibrated using n-hexadecane as the internal standard. The spectroscopic data of all the products are presented below.

N-formylmorpholine(2a)²



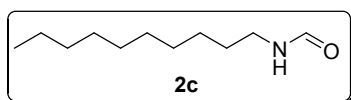
99% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.68 (s, 1H), 3.35 – 3.29 (m, 2H), 3.29 – 3.23 (m, 2H), 3.20 – 3.13 (m, 2H), 3.09 – 3.02 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 160.7, 66.9, 66.0, 45.4, 40.2.

N,N-dibutylformamide (2b)



99% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (s, 1H), 3.25 (dt, *J* = 14.3, 7.4 Hz, 4H), 1.57 – 1.45 (m, 4H), 1.37 – 1.25 (m, 4H), 0.94 (td, *J* = 7.3, 2.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 162.7, 47.2, 41.9, 30.7, 29.4, 20.1, 19.6, 13.8, 13.7.

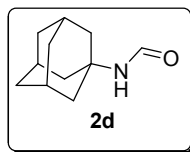
N-decylformamide (2c)



99% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (s, 1H), 6.21 (s, 1H), 3.16 (ddd, *J* = 27.7, 13.5, 6.8 Hz, 2H), 1.51 – 1.39 (m, 2H), 1.20 (d, *J* = 14.3 Hz, 14H), 0.81 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.4, 41.8, 38.2, 31.8, 31.2, 29.6 – 29.0, 26.8, 26.4, 22.6, 14.1.

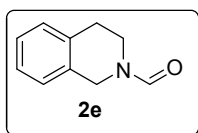
A mixture of amines **1** (0.5 mmol), PhSiH₃ (0.75 mmol), and DMSO (2 mL) was added into a 50 mL Schlenk tube with a magnetic bar in the glove box. Then the tube was sealed and pressurized with 1.0 atm CO₂ after it was vacuumed and flushed with CO₂ three times. After that, it was stirred at room temperature for 24 h. After the reaction was completed, the reaction mixture was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10:1 then 2:1) as the eluent to give products.

N-(1-Adamantyl)formamide (2d)⁵



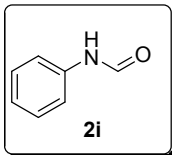
99% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 12.3 Hz, 0.67H), 7.96 (d, *J* = 1.7 Hz, 0.33H), 6.25 (s, 0.65H), 5.25 (s, 0.35H), 2.04 (d, *J* = 18.6 Hz, 3H), 1.96 (d, *J* = 2.4 Hz, 2H), 1.77 (d, *J* = 2.2 Hz, 4H), 1.68 – 1.56 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 162.3, 160.3, 52.1, 50.7, 44.1, 41.8, 36.2, 35.9, 29.4, 29.3.

3,4-dihydroisoquinoline-2(1H)-carbaldehyde (2e)²



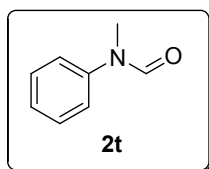
89% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 16.1 Hz, 1H), 7.20 – 6.93 (m, 4H), 4.47 (d, *J* = 66.5 Hz, 2H), 3.57 (dt, *J* = 59.3, 6.0 Hz, 2H), 2.81 – 2.64 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 161.5, 161, 134.2, 133.6, 132.4, 131.7, 128.9, 126.8, 126.4, 125.8, 46.9, 42.9, 42, 37.7, 29.5, 27.7.

N-phenylformamide (2i)



97% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.87 (s, 0.5H), 8.50 (dd, *J* = 146.1, 6.5 Hz, 1H), 8.00 (s, 0.43H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.32 (dt, *J* = 13.4, 8.0 Hz, 2H), 7.20 – 7.07 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 163, 159.5, 136.9, 129.8, 129.1, 125.3, 124.8, 120.1, 118.8.

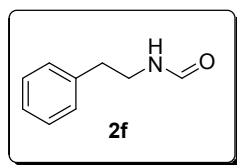
N-methyl-N-phenylformamide (2t)³



95% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.39 (s, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 2H), 3.24 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.4, 142.2, 129.6, 126.4, 122.4, 32.1.

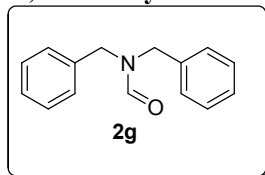
A mixture of amines **1** (0.5 mmol), PhSiH₃ (0.75 mmol), and DMSO (2 mL) was added into a 50 mL Schlenk tube with a magnetic bar in the glove box. Then the tube was sealed and pressurized with 1.0 atm CO₂ after it was vacuumed and flushed with CO₂ three times. After that, it was stirred at room temperature for 24 h. After the reaction was completed, the reaction mixture was purified by preparative thin-layer chromatography silica gel using n-hexane/ethyl acetate (2:1 or 1:1) as the eluent to give products.

N-phenethylformamide (2f)



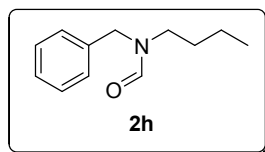
80% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.97 (s, 1H), 7.22 (dd, J = 9.9, 4.6 Hz, 2H), 7.13 (dd, J = 15.8, 7.2 Hz, 3H), 6.04 (s, 1H), 3.45 (dd, J = 13.3, 6.8 Hz, 2H), 2.73 (dd, J = 12.7, 5.7 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.6, 161.4, 138.6, 137.7, 128.8, 126.9, 126.6, 43.2, 39.2, 37.7, 35.5.

N,N-dibenzylformamide (2g)⁴



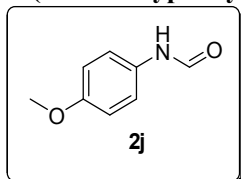
82% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.41 (s, 1H), 7.40 – 7.27 (m, 6H), 7.21 – 7.15 (m, 4H), 4.41 (s, 2H), 4.25 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.9, 136.0, 135.7, 129, 128.7, 128.6, 128.2, 127.7, 50.3, 44.7.

N-benzyl-N-butylformamide (2h)



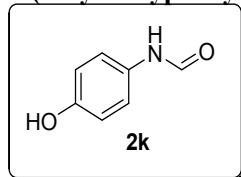
82% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, J = 33.0 Hz, 1H), 7.21 (ddt, J = 24.8, 17.0, 6.9 Hz, 5H), 4.38 (d, J = 60.6 Hz, 2H), 3.09 (dt, J = 14.2, 7.3 Hz, 2H), 1.47 – 1.32 (m, 2H), 1.19 (ddd, J = 9.3, 8.0, 2.5 Hz, 2H), 0.81 (td, J = 7.3, 3.7 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.8, 136.6, 136.3, 128.8, 128.6, 128.1, 127.5, 51.2, 46.5, 45.2, 41.7, 30.2, 29, 20.1, 19.6, 13.7, 13.6.

N-(4-methoxyphenyl)formamide (2j)³

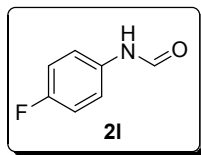


95% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.52 (d, J = 11.4 Hz, 0.49H), 8.34 (t, J = 26.0 Hz, 1H), 7.69 (s, 0.49H), 7.45 (d, J = 8.9 Hz, 1H), 7.04 (d, J = 8.8 Hz, 1H), 6.87 (dd, J = 13.0, 8.9 Hz, 2H), 3.79 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.3, 159.1, 157.6, 156.7, 130.0, 129.6, 121.9, 121.6, 114.9, 114.2, 55.5.

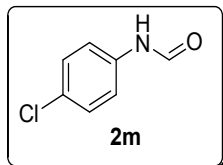
N-(4-hydroxyphenyl)formamide (2k)



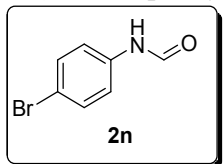
70% yield. ^1H NMR (400 MHz, DMSO) δ 9.92 (s, 1H), 9.28 (s, 1H), 8.53 (d, J = 11.2 Hz, 0.23H), 8.20 (d, J = 1.7 Hz, 0.78H), 7.42 (d, J = 8.8 Hz, 2H), 6.75 (dd, J = 9.0, 2.4 Hz, 2H). ^{13}C NMR (100 MHz, DMSO) δ 162.6, 158.9, 154.2, 153.5, 129.9, 129.6, 120.8, 120.2, 115.8, 115.2.

N-(4-fluorophenyl)formamide (2l)

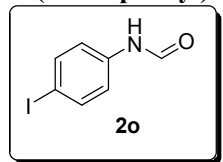
82% yield. ^1H NMR (400 MHz, DMSO) δ 10.30 – 10.12 (m, 1H), 8.27 (d, J = 1.8 Hz, 1H), 7.69 – 7.55 (m, 2H), 7.18 – 7.12 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ 162.6, 159.4, 156.9, 134.6, 120.9, 119.5, 116.0, 115.8, 115.5, 115.3.

N-(4-chlorophenyl)formamide (2m)

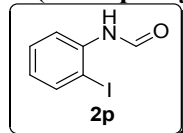
79% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.85 (d, J = 9.8 Hz, 0.47H), 8.66 (d, J = 11.3 Hz, 0.5H), 8.35 (d, J = 1.5 Hz, 0.58H), 7.92 (s, 0.55H), 7.50 (d, J = 8.8 Hz, 1H), 7.34 – 7.26 (m, 2H), 7.04 (d, J = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.8, 159.3, 135.4, 130.7, 129.8, 129.1, 121.3, 120.1.

N-(4-bromophenyl)formamide (2n)

96% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.67 (d, J = 11.2 Hz, 0.41H), 8.38 (d, J = 1.2 Hz, 0.68H), 7.50 – 7.44 (m, 4H), 6.99 (d, J = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.3, 158.9, 135.9, 132.8, 132.1, 121.5, 120.4, 118.3, 117.5.

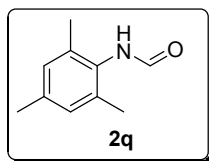
N-(4-iodophenyl)formamide (2o)

96% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.66 (d, J = 11.3 Hz, 0.51H), 8.49 (d, J = 9.9 Hz, 0.46H), 8.37 (d, J = 1.3 Hz, 1H), 7.64 (dd, J = 11.8, 8.7 Hz, 2H), 7.32 (d, J = 8.7 Hz, 1H), 6.86 (d, J = 8.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.3, 159.0, 138.7, 138.1, 136.6, 121.8, 120.5, 88.7, 88.2.

N-(2-iodophenyl)formamide (2p)

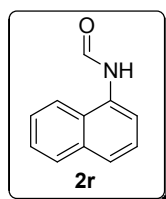
57% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.66 (t, J = 17.2 Hz, 1H), 8.36 (d, J = 1.4 Hz, 0.49H), 7.96 (s, 0.49H), 7.53 – 7.46 (m, 2H), 7.12 – 7.01 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.4, 159.1, 138, 134.3, 133.9, 131.2, 130.6, 128.7, 127.5, 119.2, 117.9, 94.8, 94.2.

N-mesitylformamide (2q)



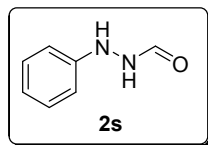
84% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, $J = 1.2$ Hz, 0.5H), 8.04 (d, $J = 11.9$ Hz, 0.5H), 7.17 (d, $J = 9.7$ Hz, 1H), 6.93 (s, 1H), 6.89 (s, 1H), 2.27 (d, $J = 14.2$ Hz, 6H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.2, 159.7, 137.6, 135.2, 135, 130.5, 129.8, 129.3, 129, 21.0, 20.9, 18.6, 18.4.

N-(naphthalen-1-yl)formamide (2r)



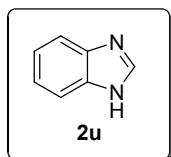
94% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.63 (d, $J = 10.8$ Hz, 1H), 8.47 – 8.21 (m, 1H), 8.01 (dd, $J = 13.0, 7.9$ Hz, 1H), 7.89 (dd, $J = 16.0, 8.0$ Hz, 1H), 7.77 (dd, $J = 26.4, 8.2$ Hz, 1H), 7.63 – 7.45 (m, 3H), 7.33 (d, $J = 7.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.9, 134.3, 128.9, 128.6, 127.8, 127.3 – 127.1, 127.1, 126.7, 126.2, 125.6, 121.2, 120.9, 120.3, 119.2, 100.0.

N'-phenylformohydrazide (2s)



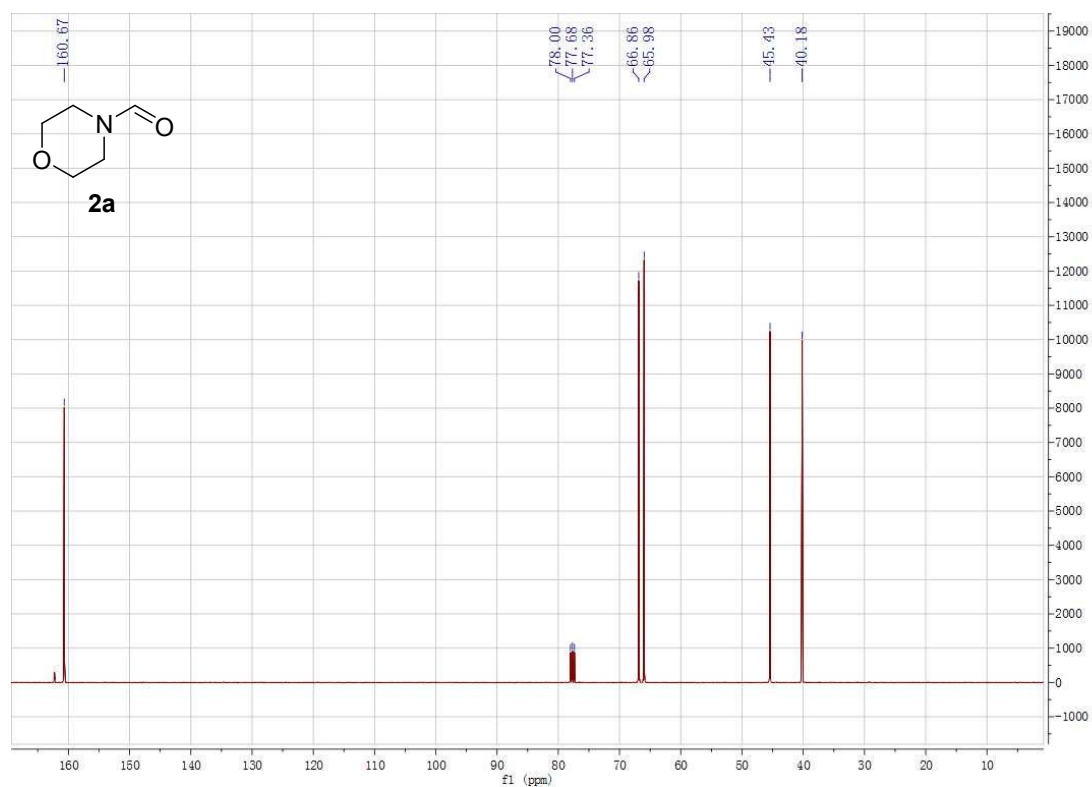
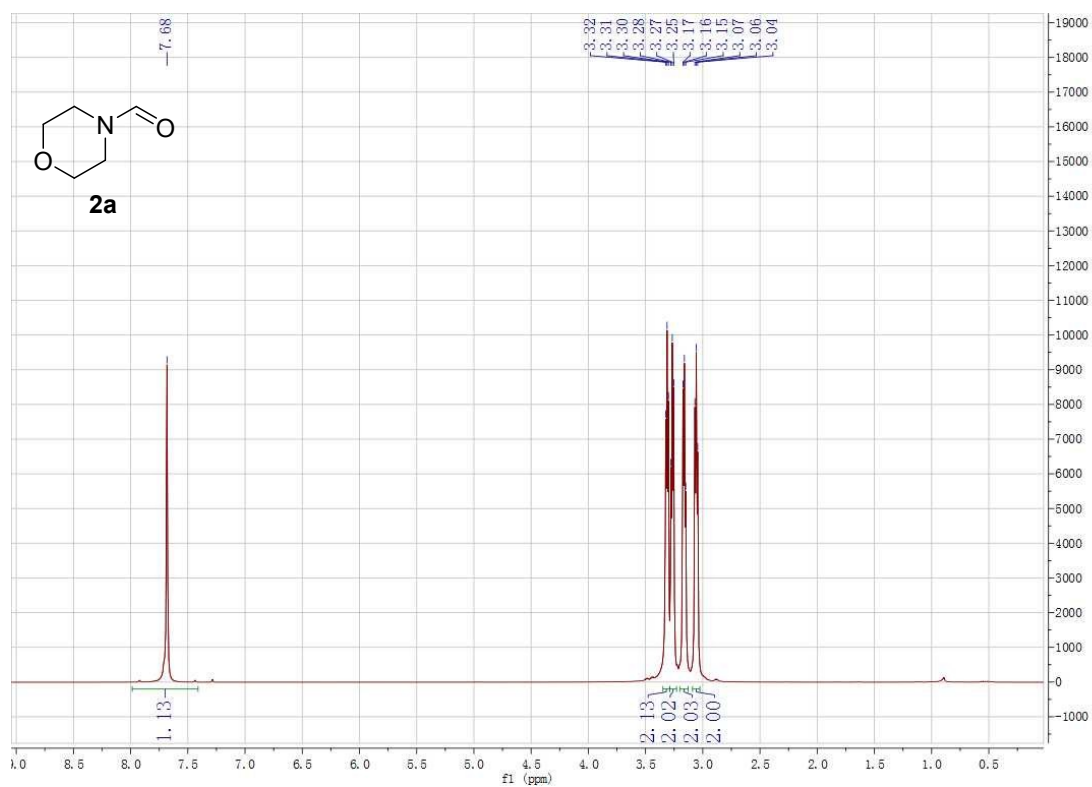
59% yield. ^1H NMR (400 MHz, DMSO) δ 9.86 – 9.33 (m, 1H), 8.16 – 7.98 (m, 1H), 7.79 (s, 1H), 7.17 (dd, $J = 13.2, 7.7$ Hz, 2H), 6.74 (dd, $J = 18.8, 10.0$ Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ 167.7, 160.5, 149.4, 148.7, 128.9, 128.7, 119.4, 118.6, 112.3, 112.1.

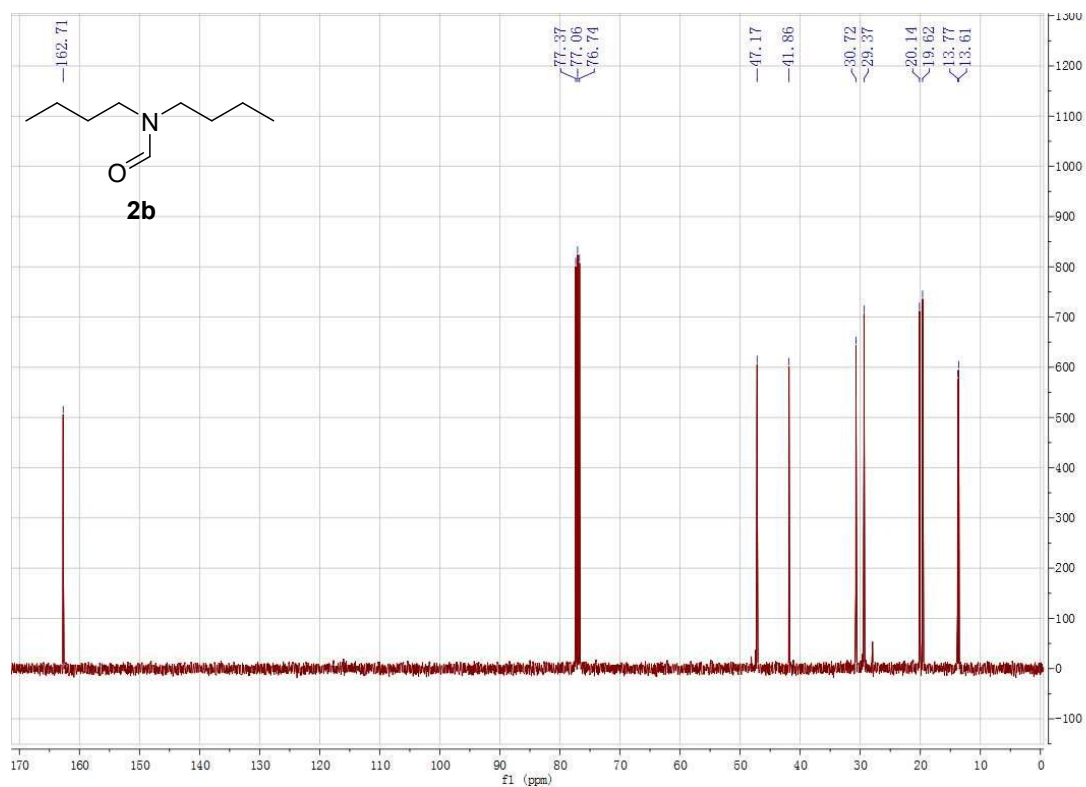
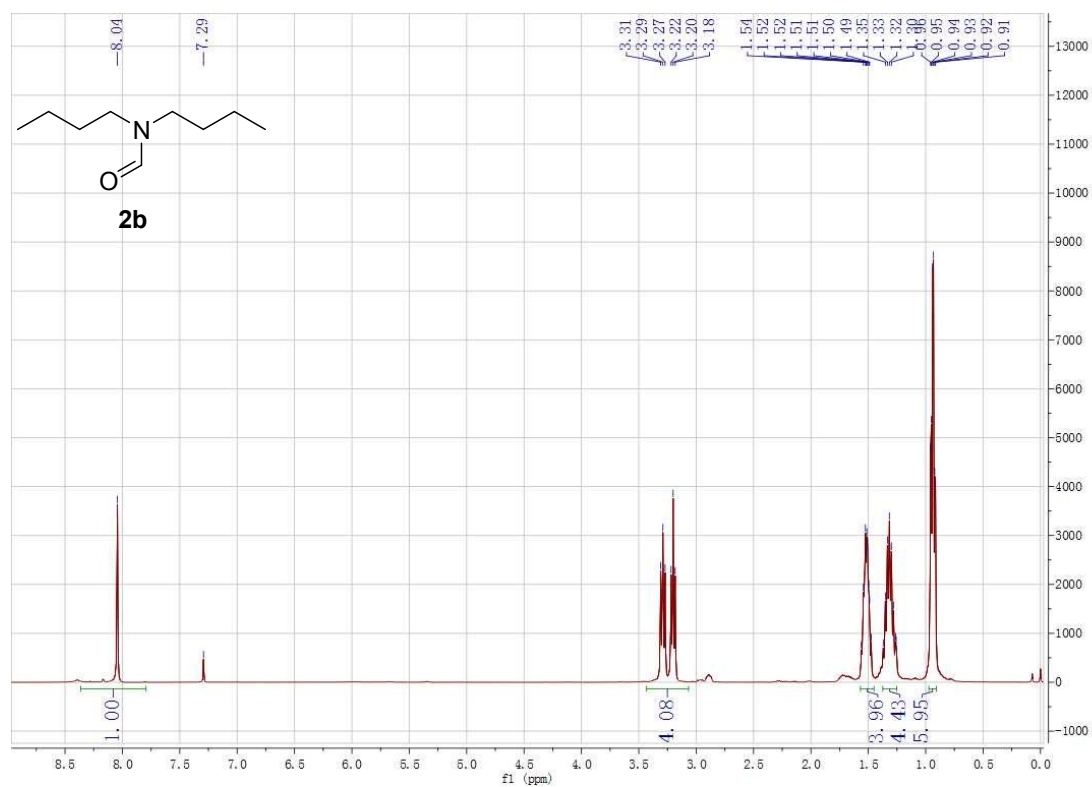
Benzimidazole (2u)

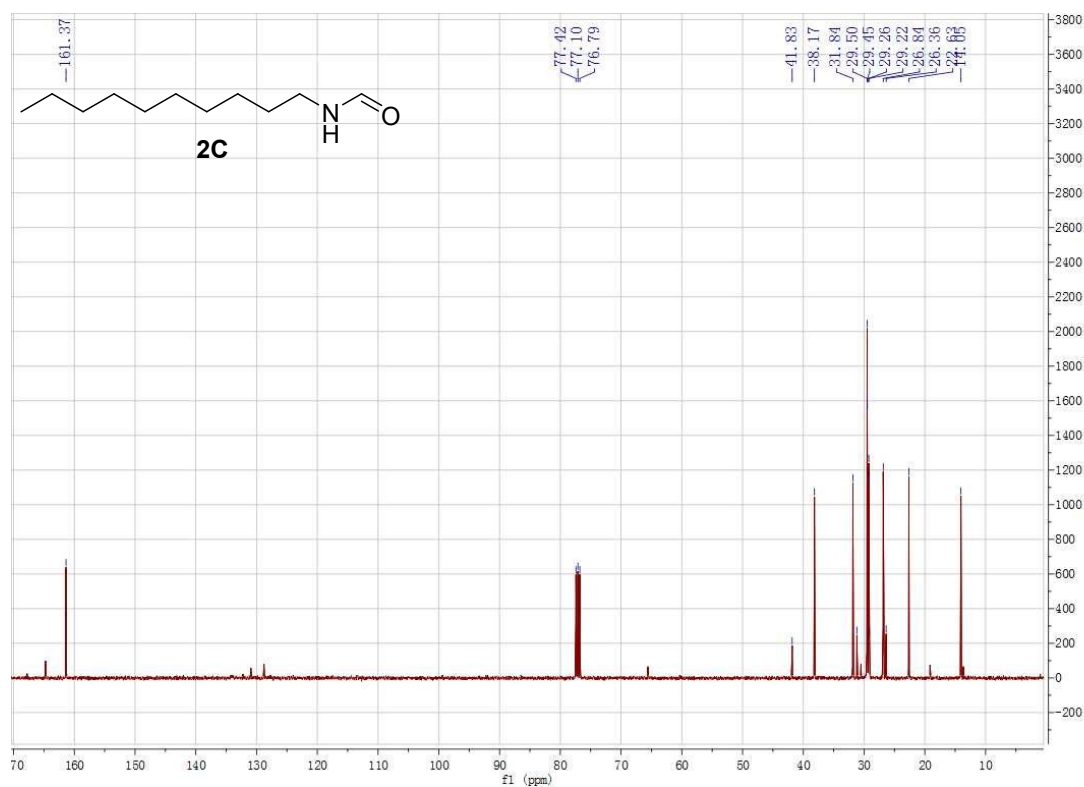
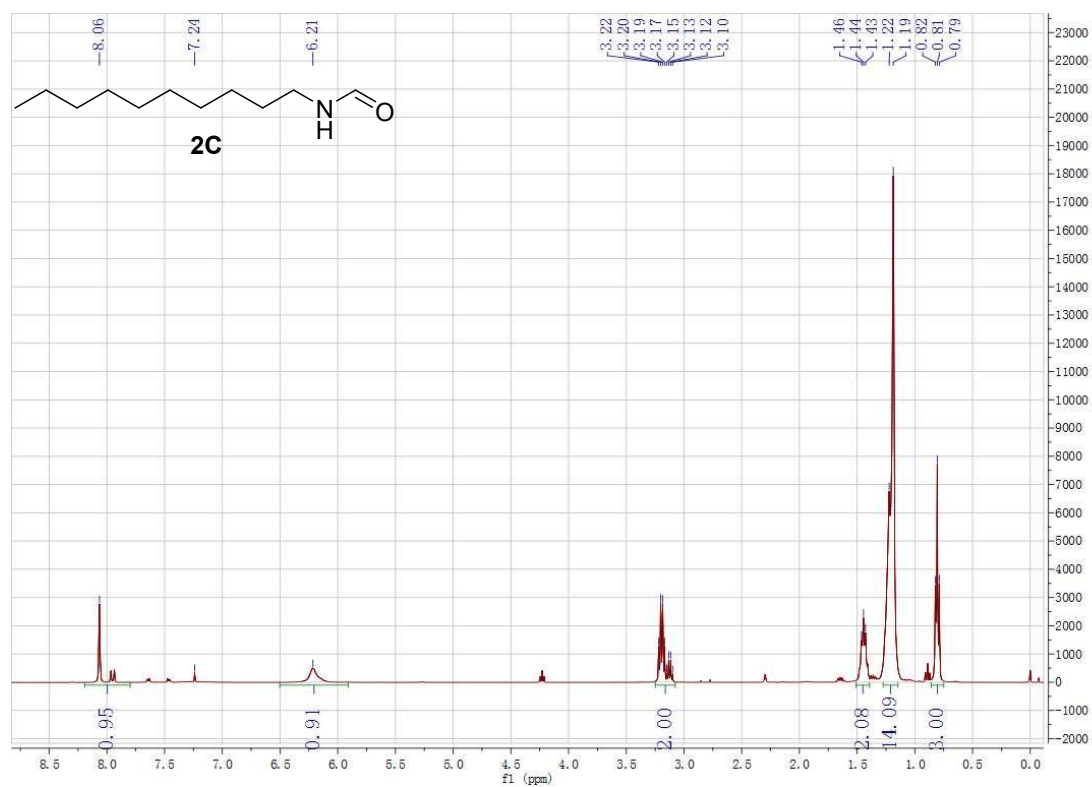


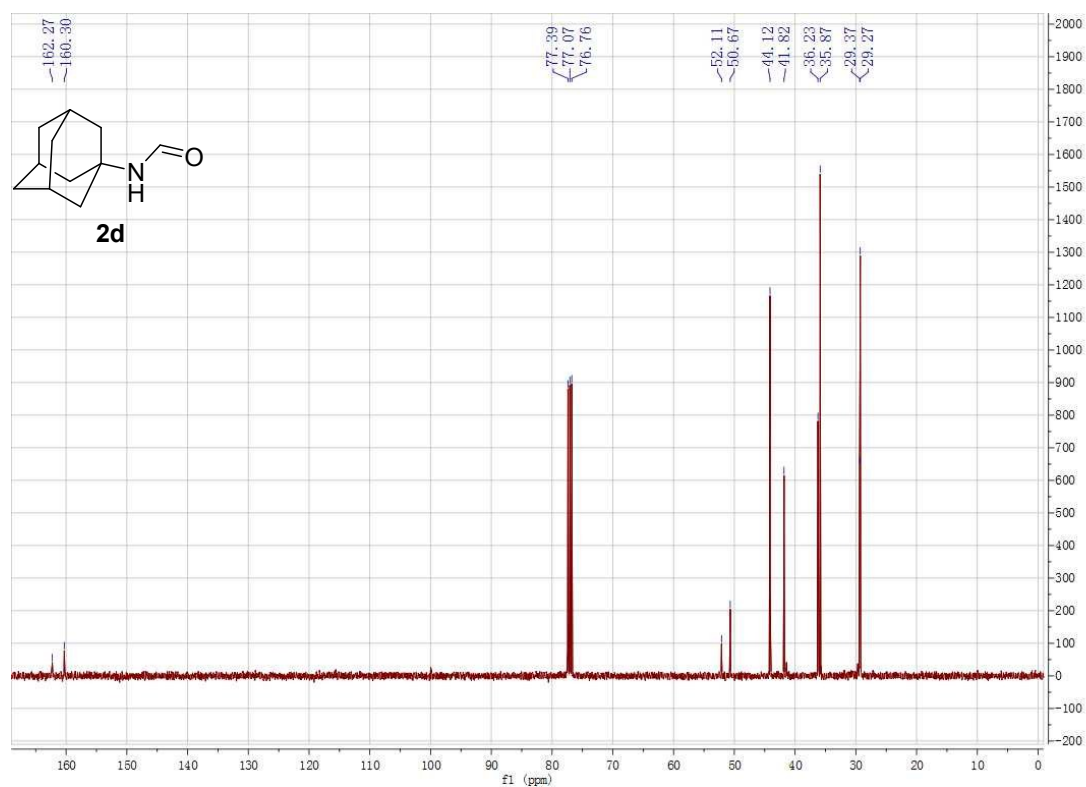
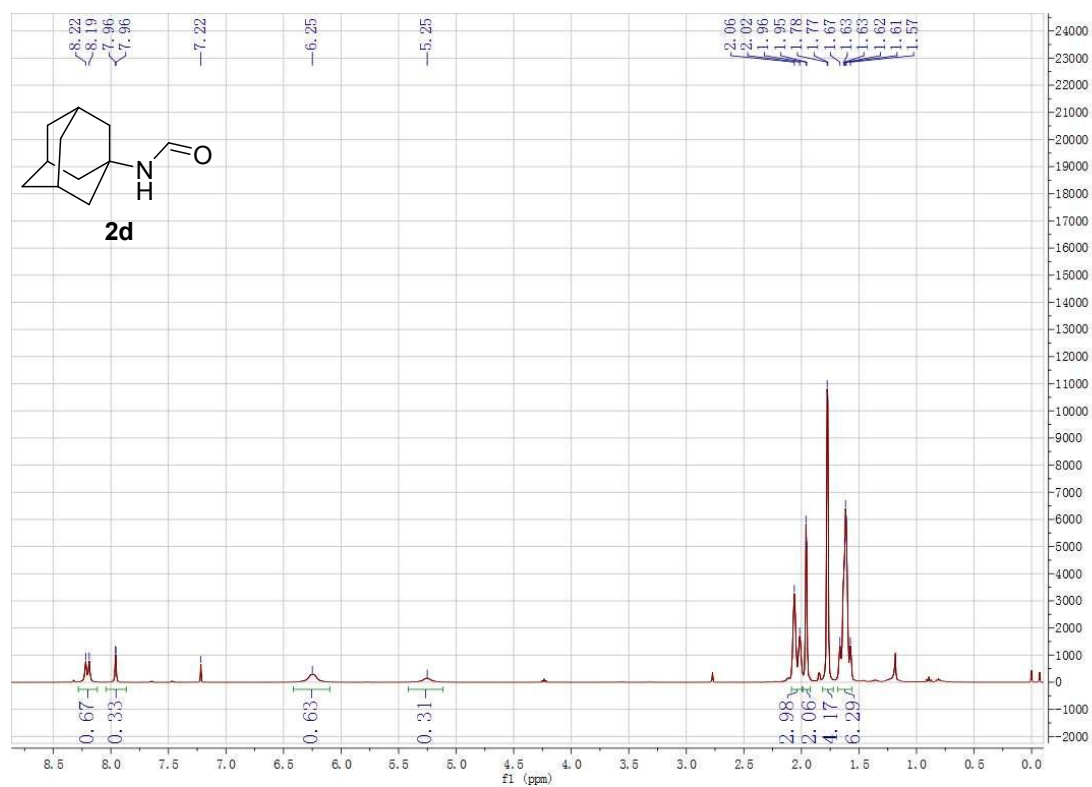
51% yield, separation by preparative HPLC using $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (3:2) as the eluent. ^1H NMR (400 MHz, DMSO) δ 12.51 (s, 1H), 8.25 (s, 1H), 7.62 (s, 2H), 7.29 – 7.15 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ 141.9, 121.7.

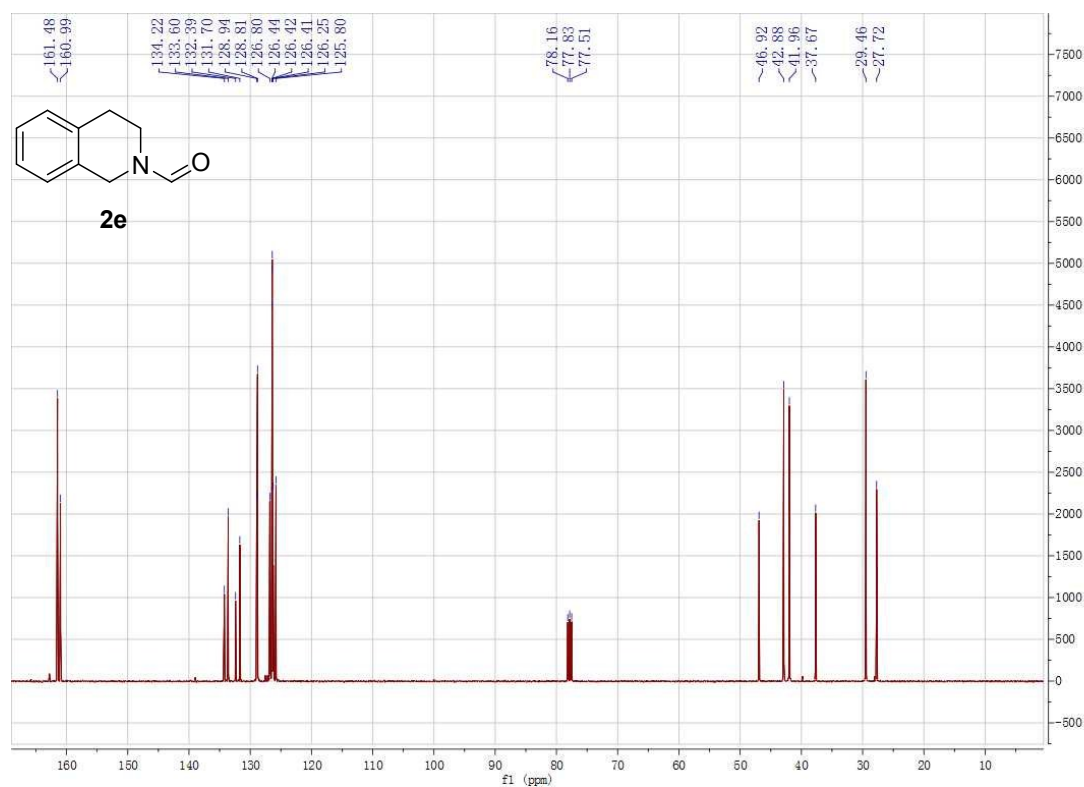
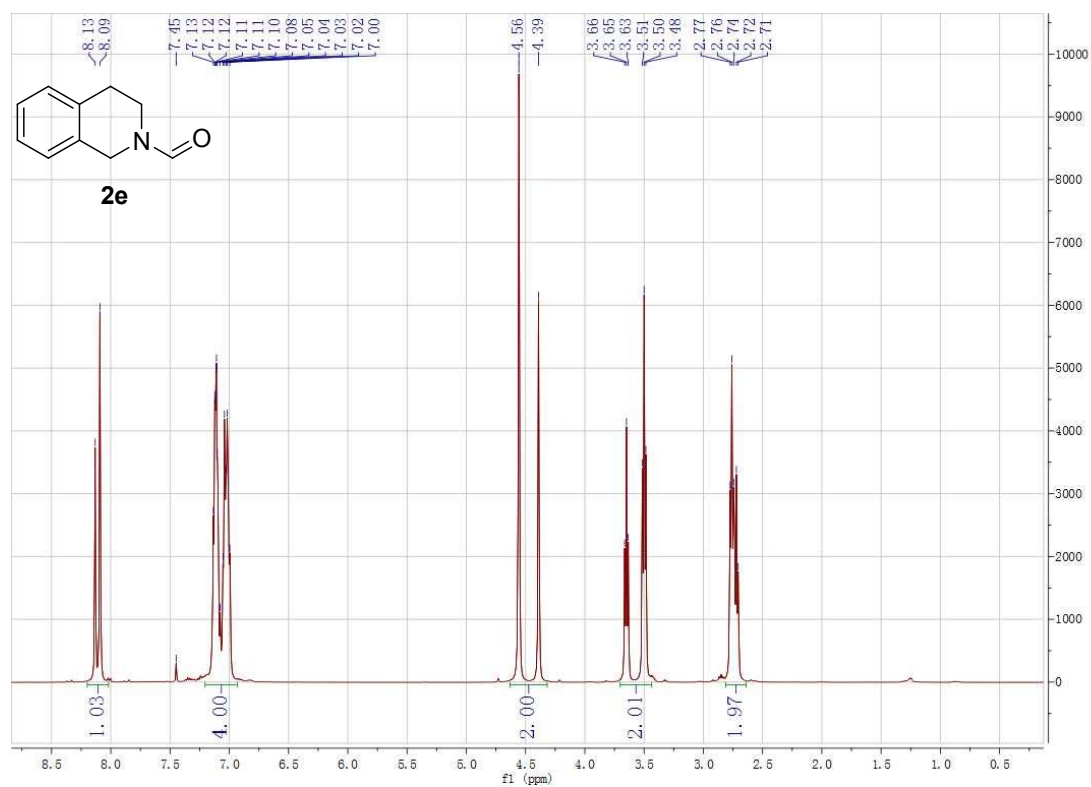
8) ^1H NMR and ^{13}C NMR Copies of Products

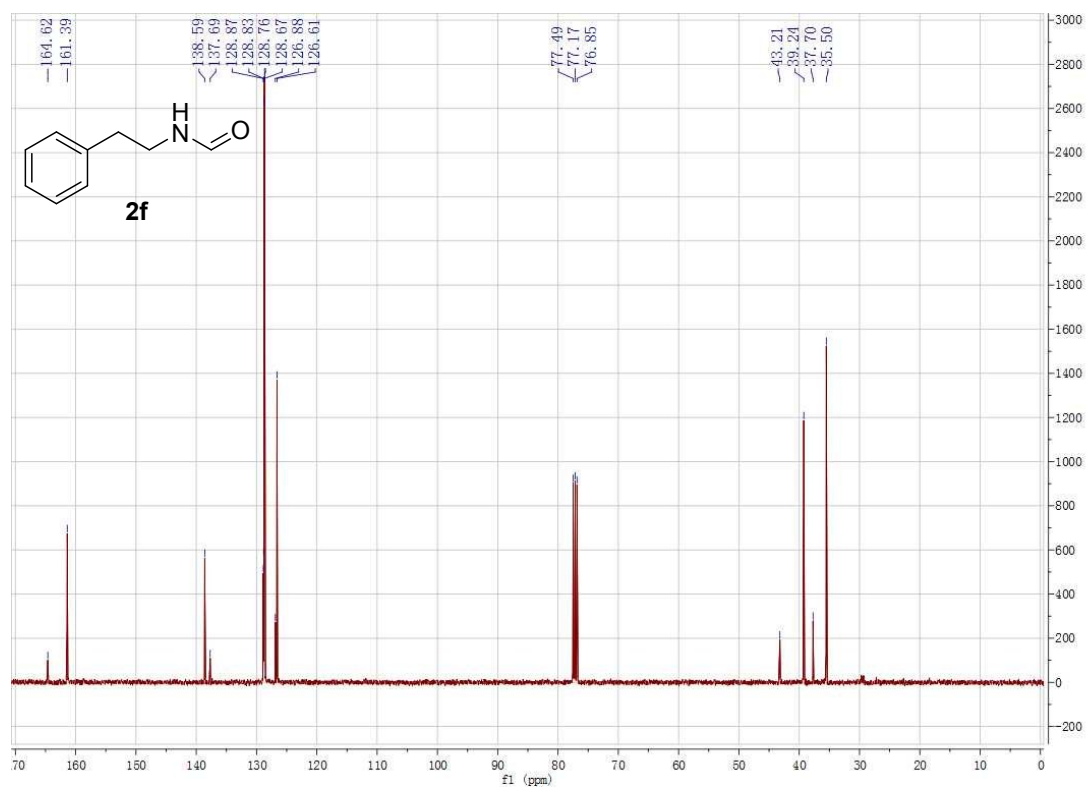
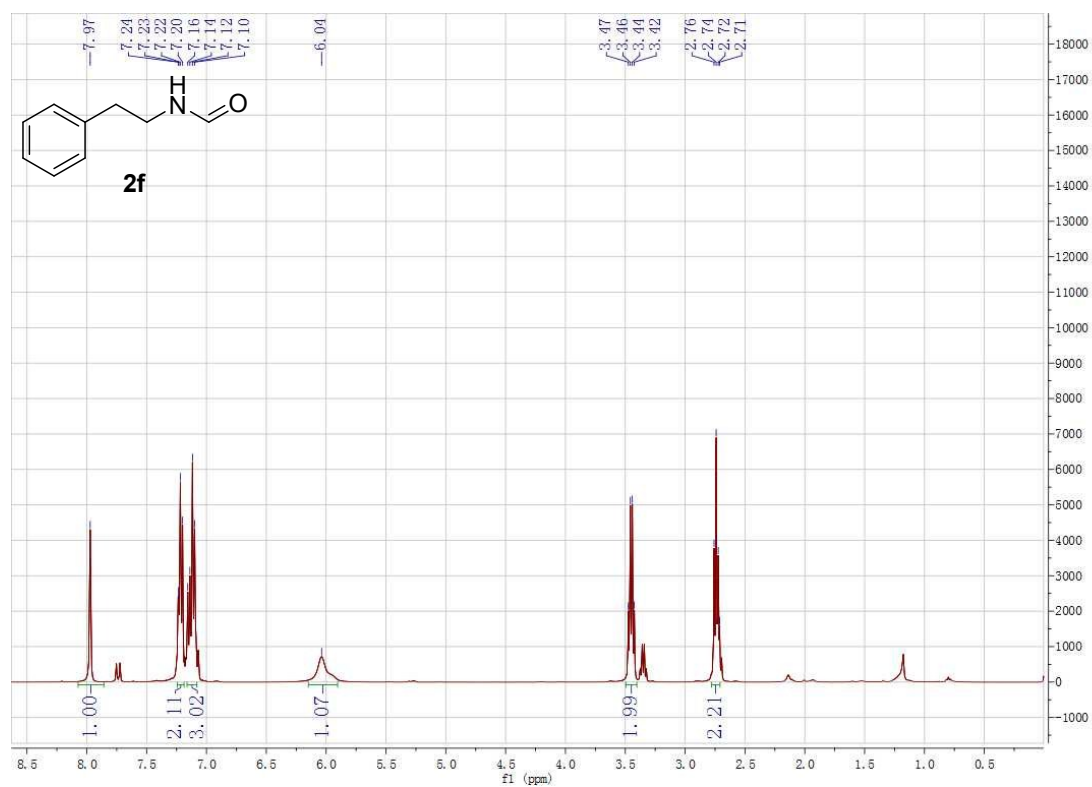


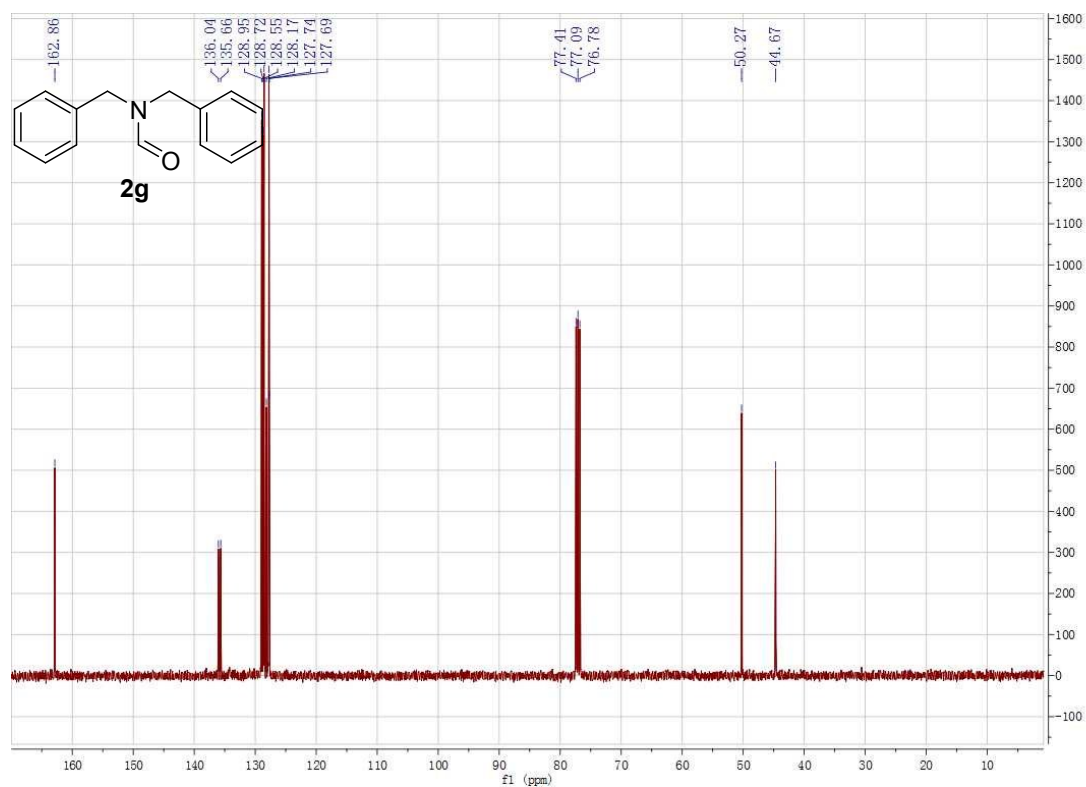
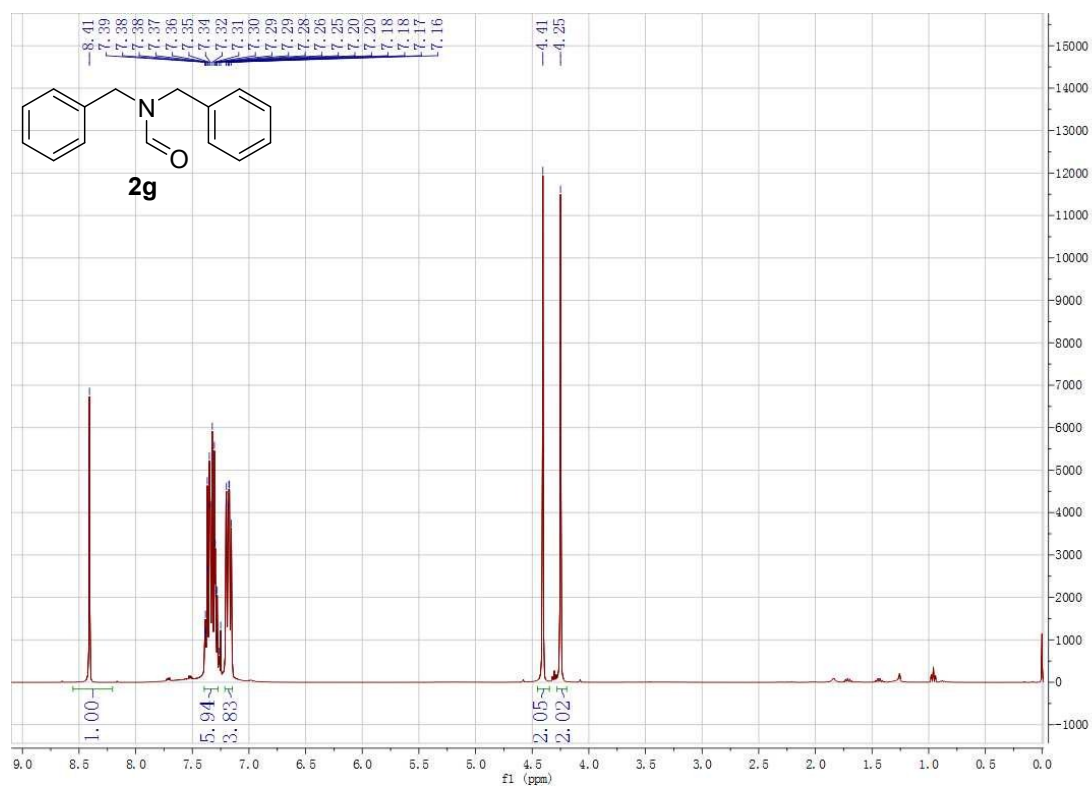


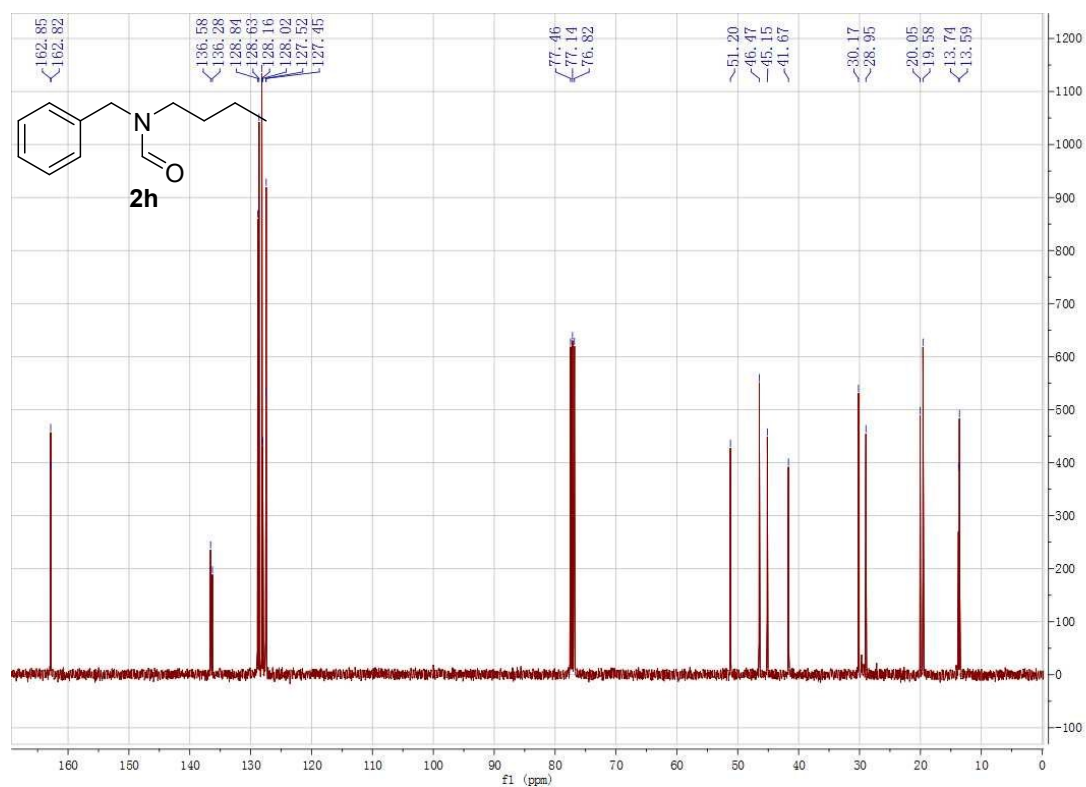
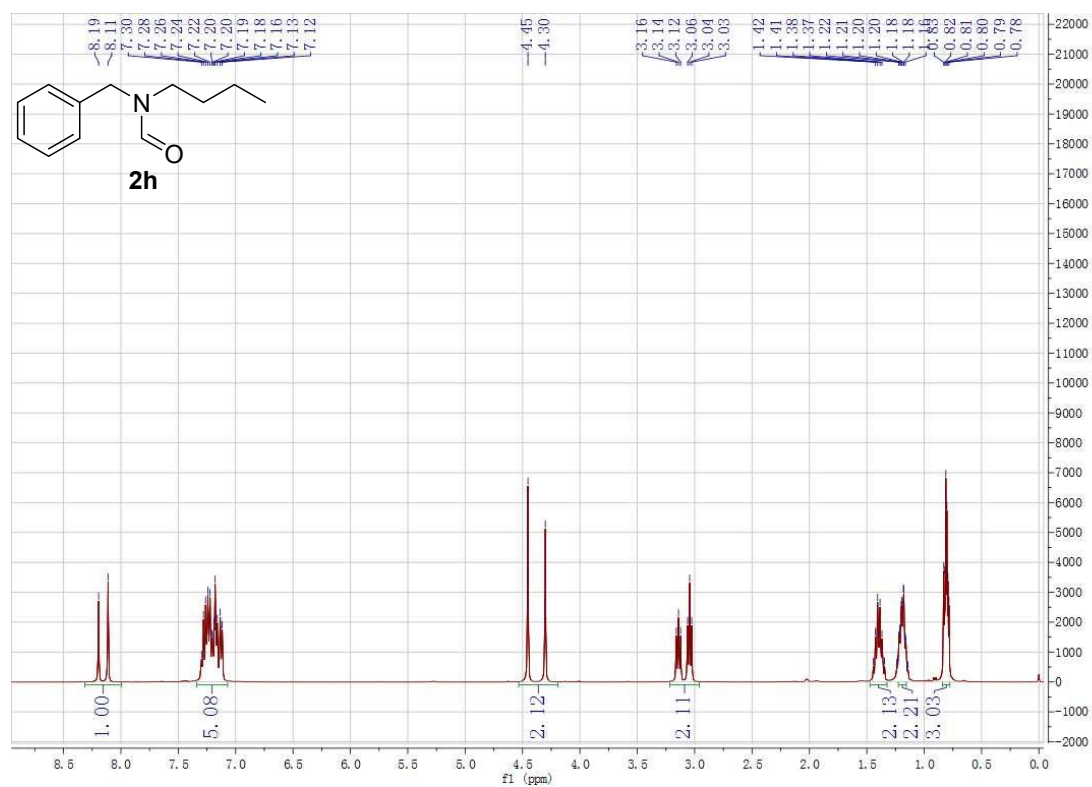


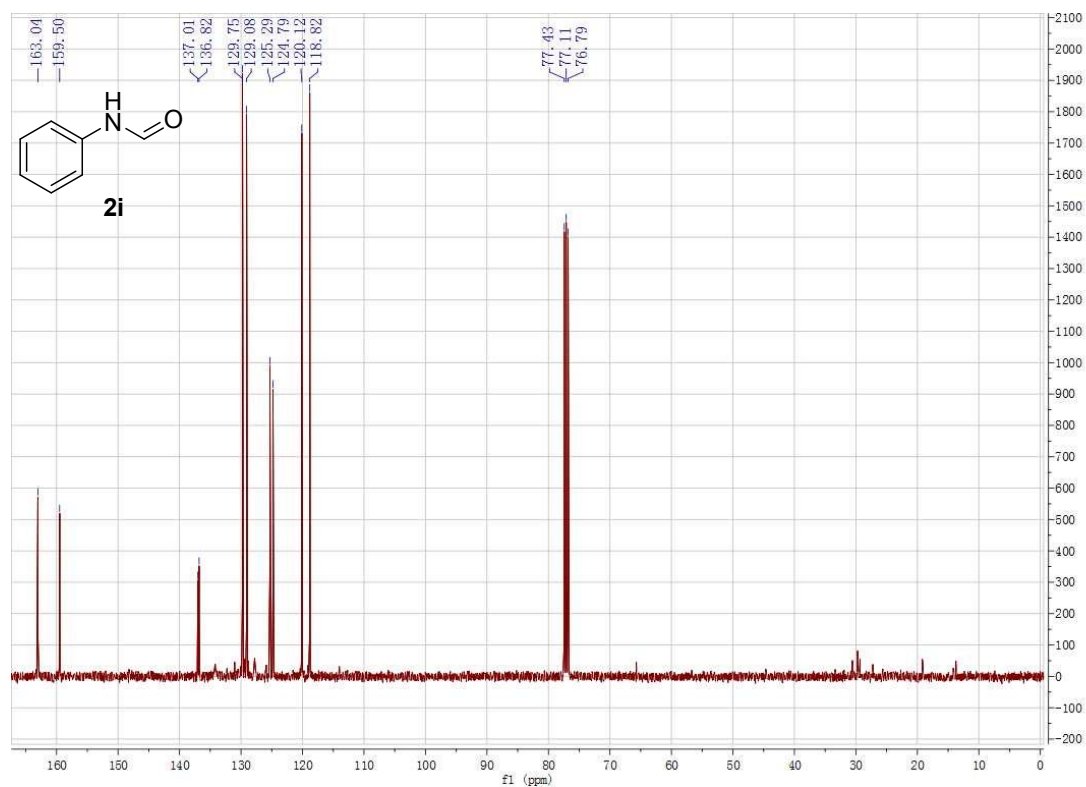
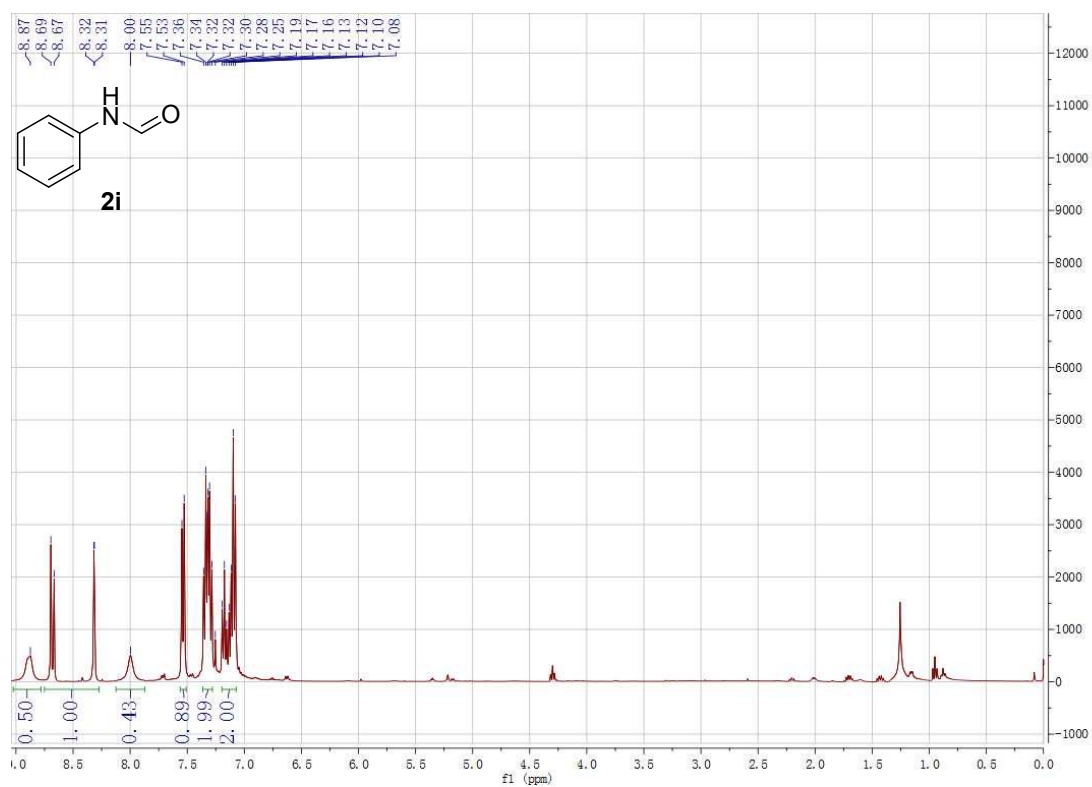


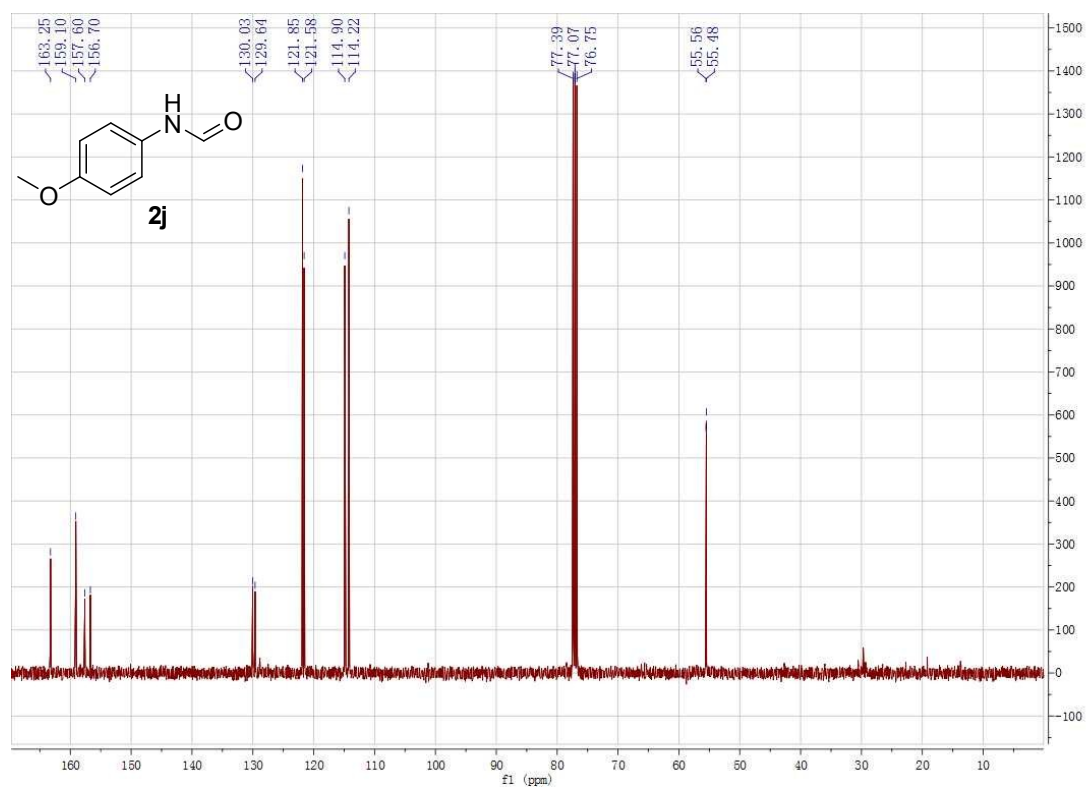
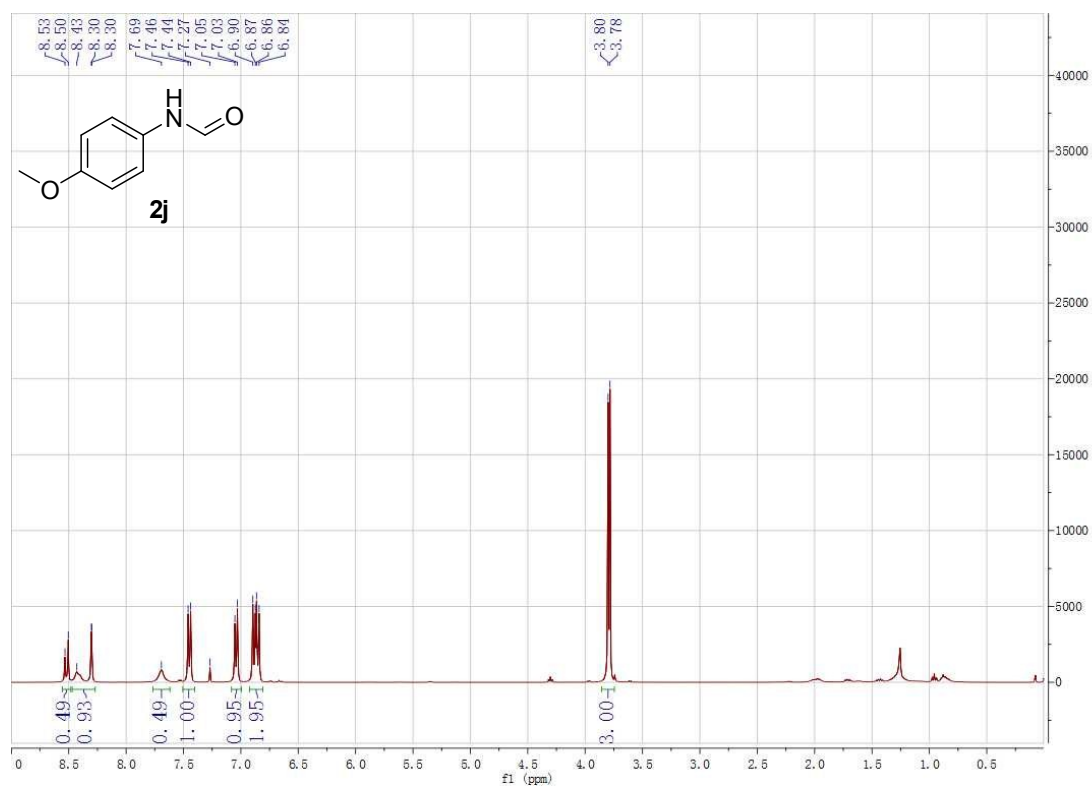


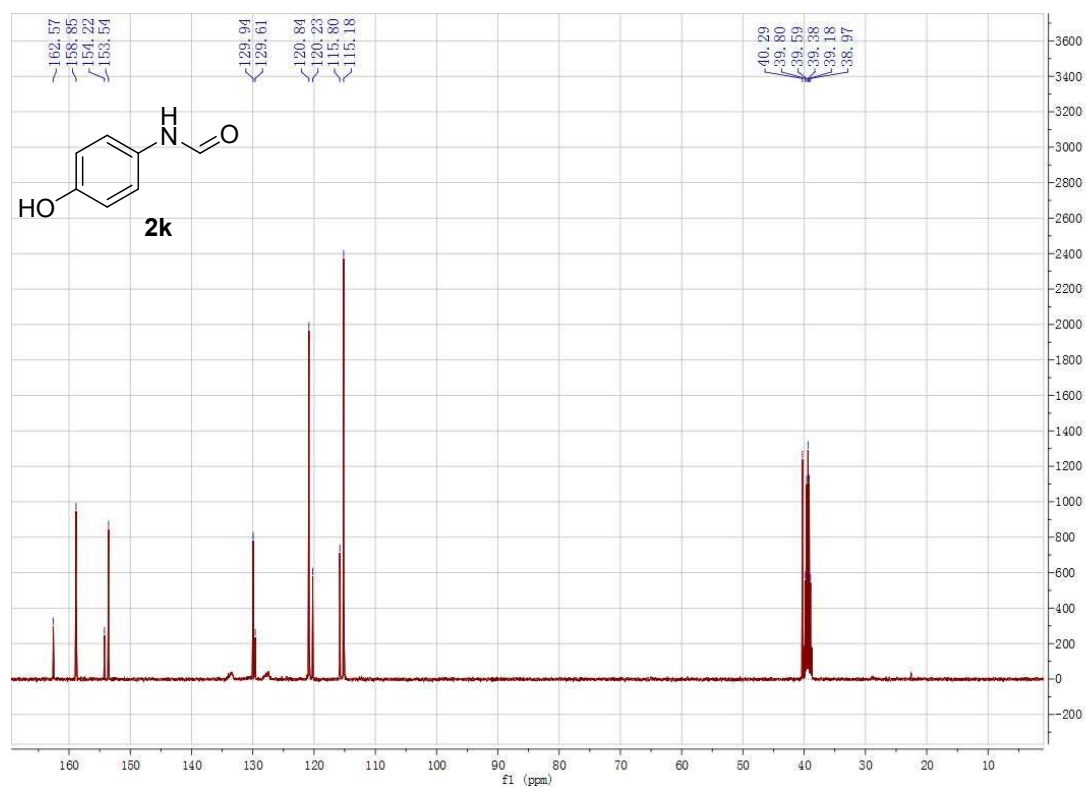
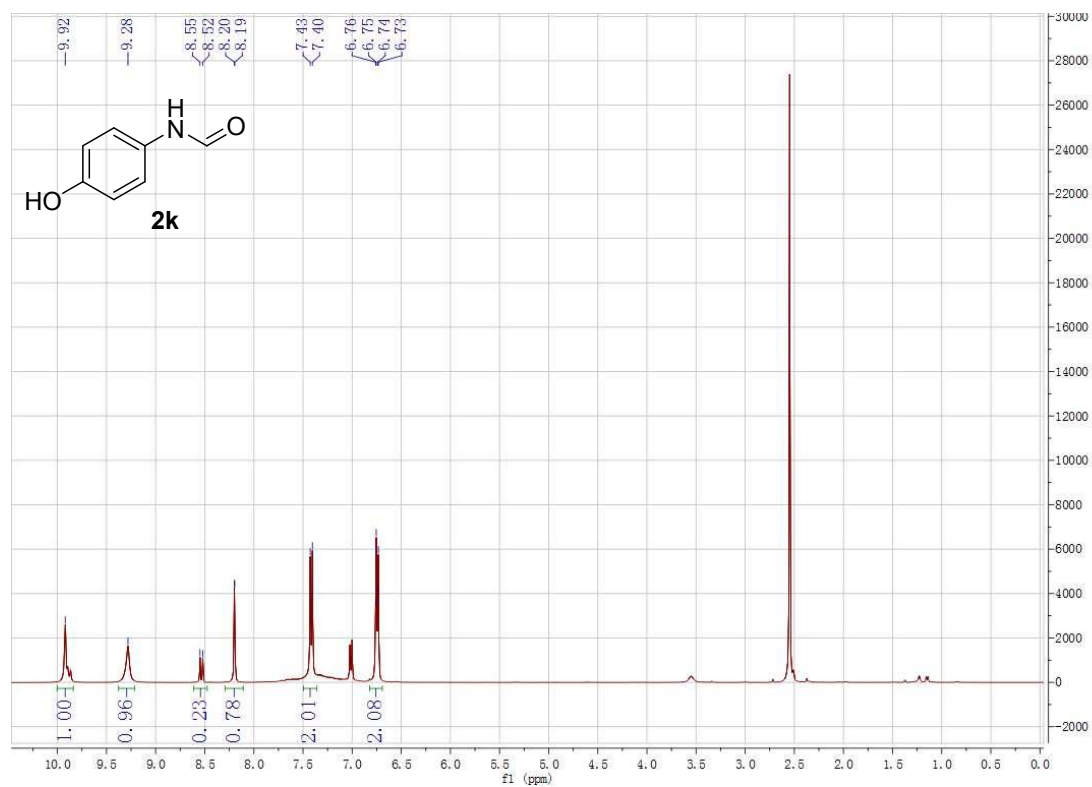


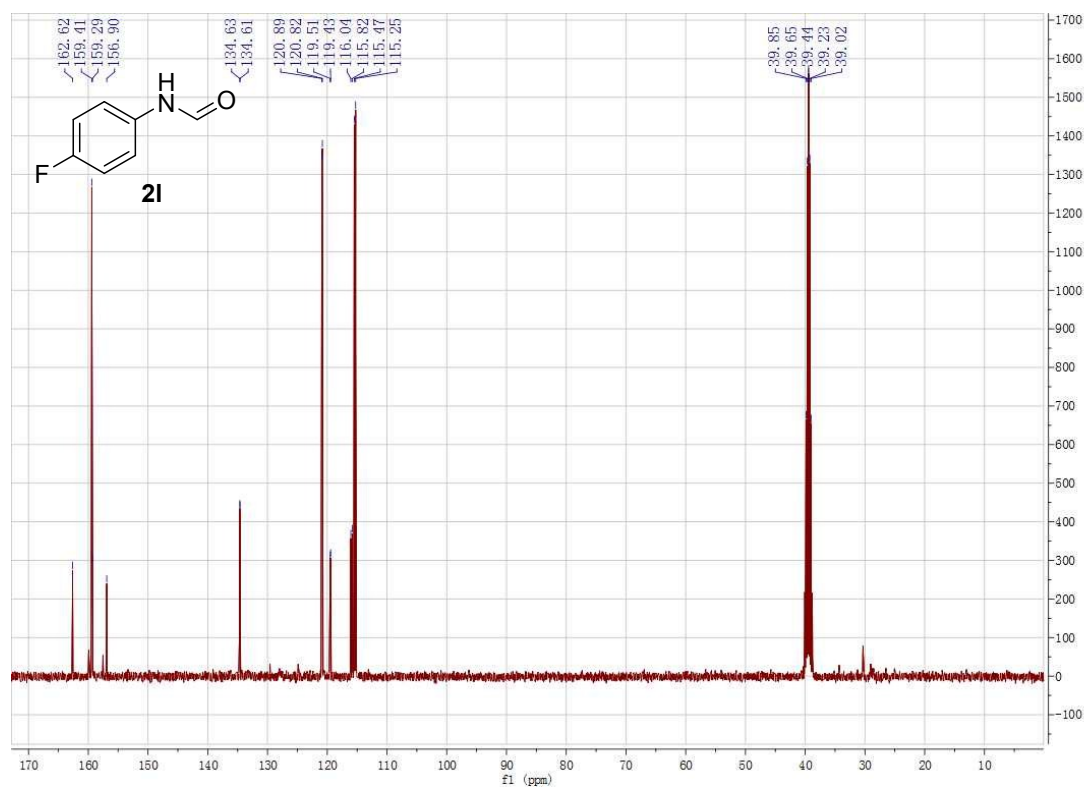
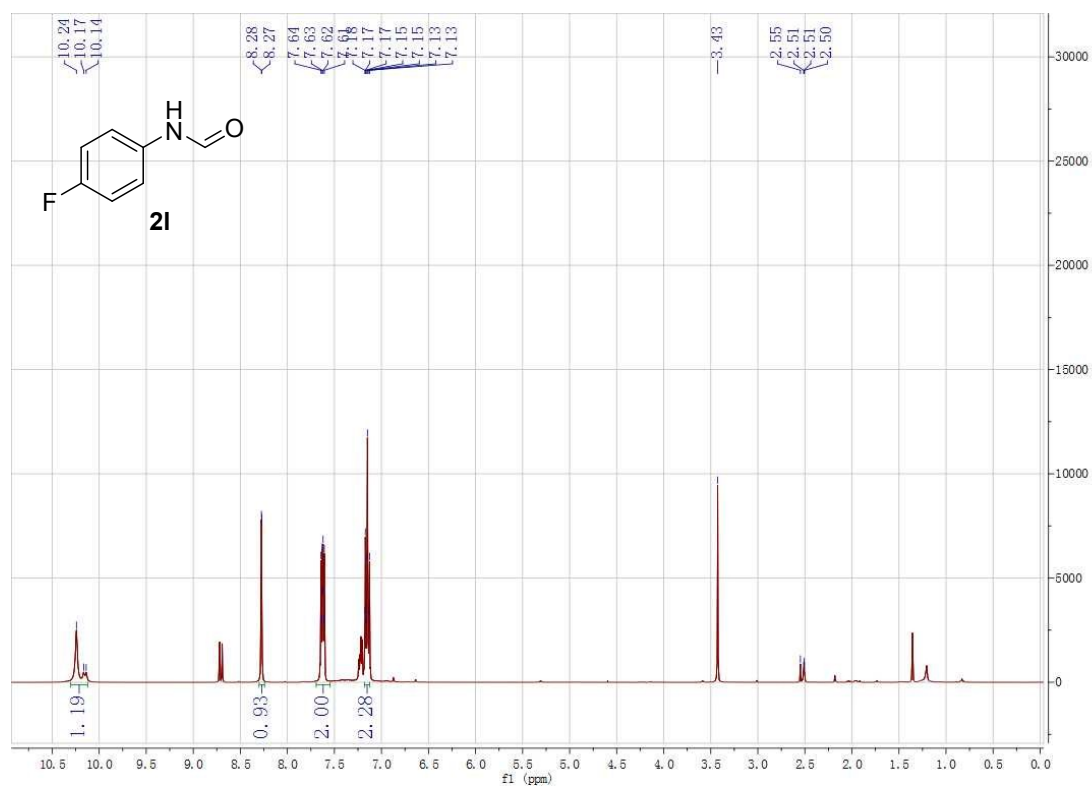


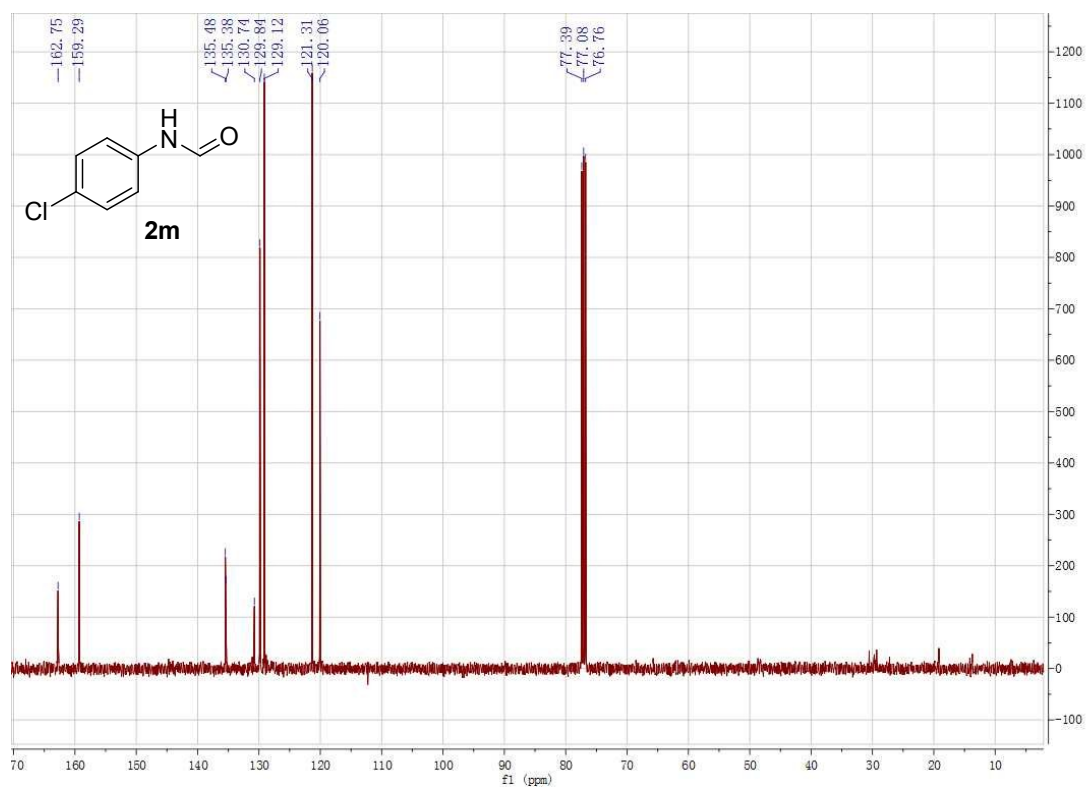
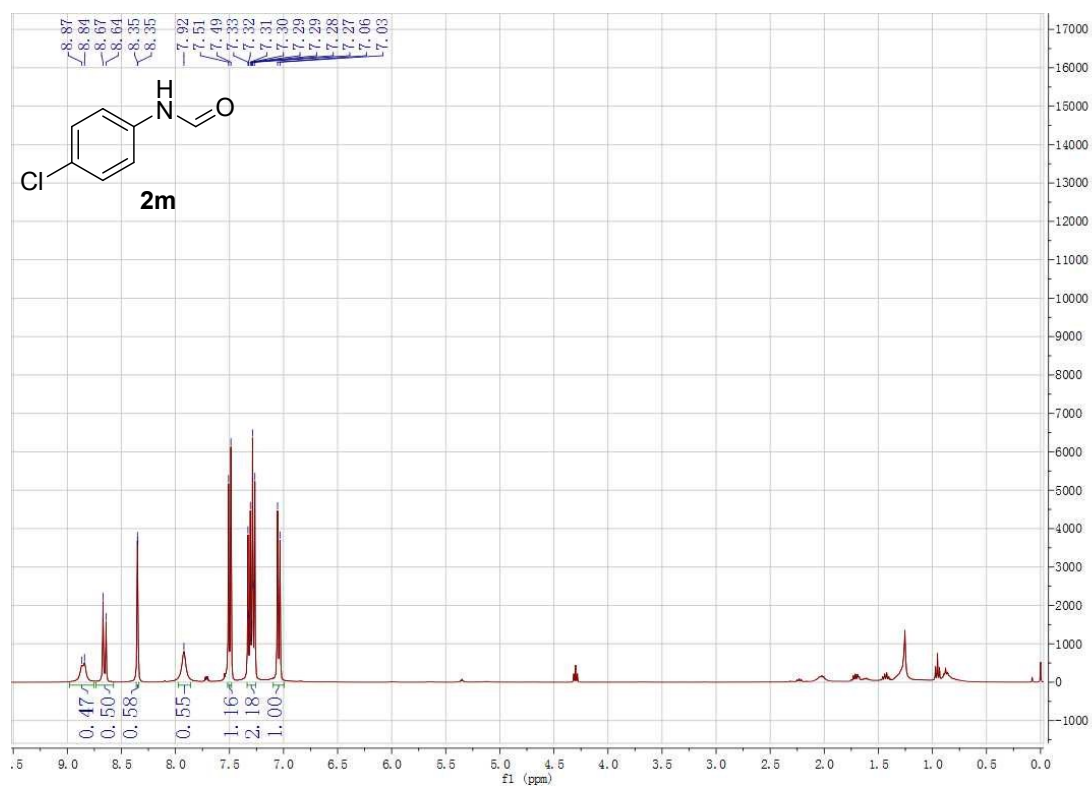


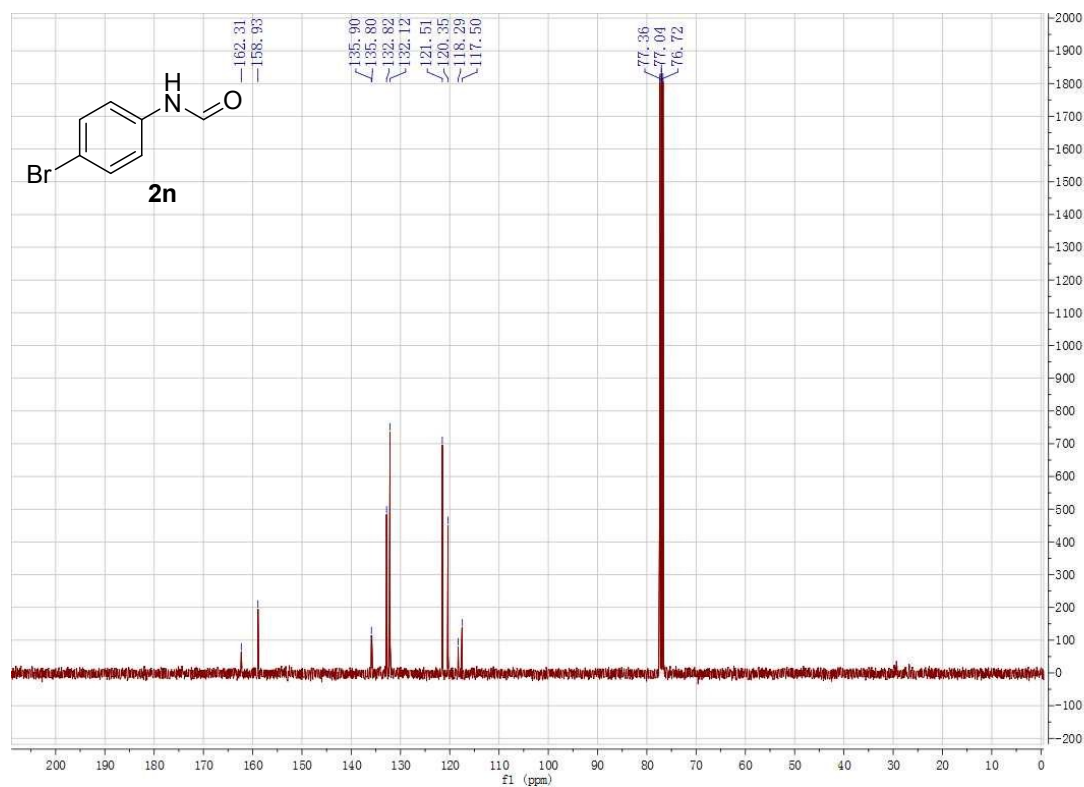
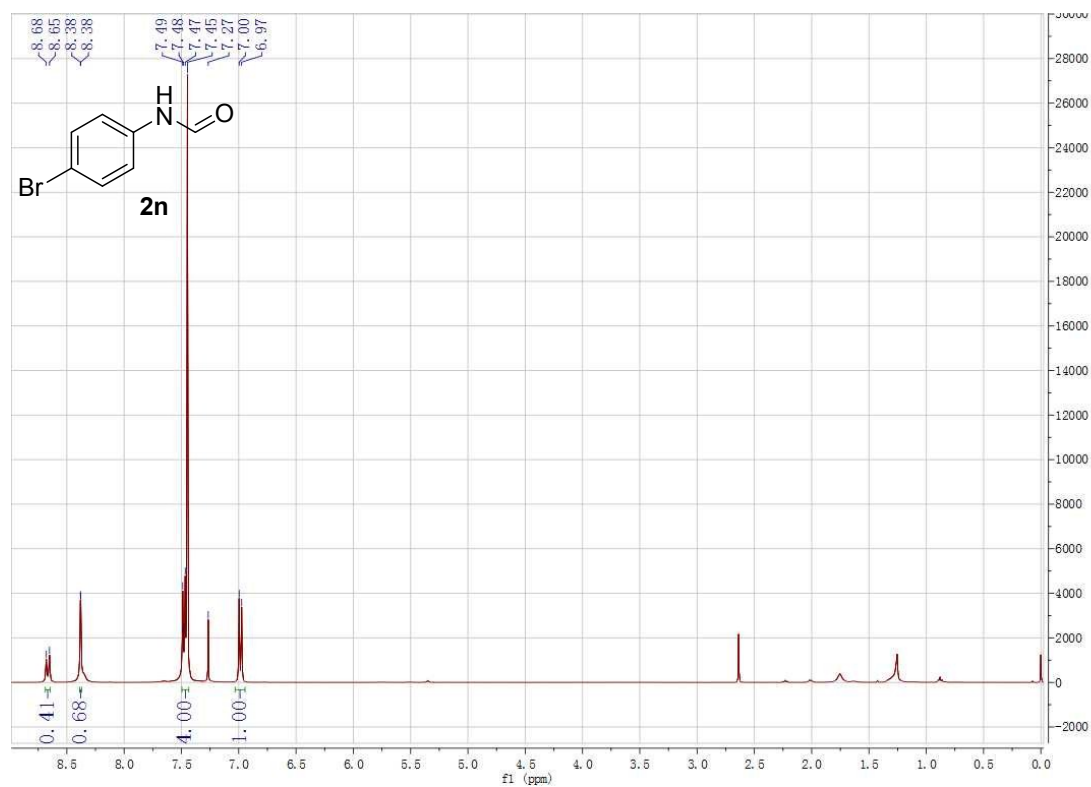


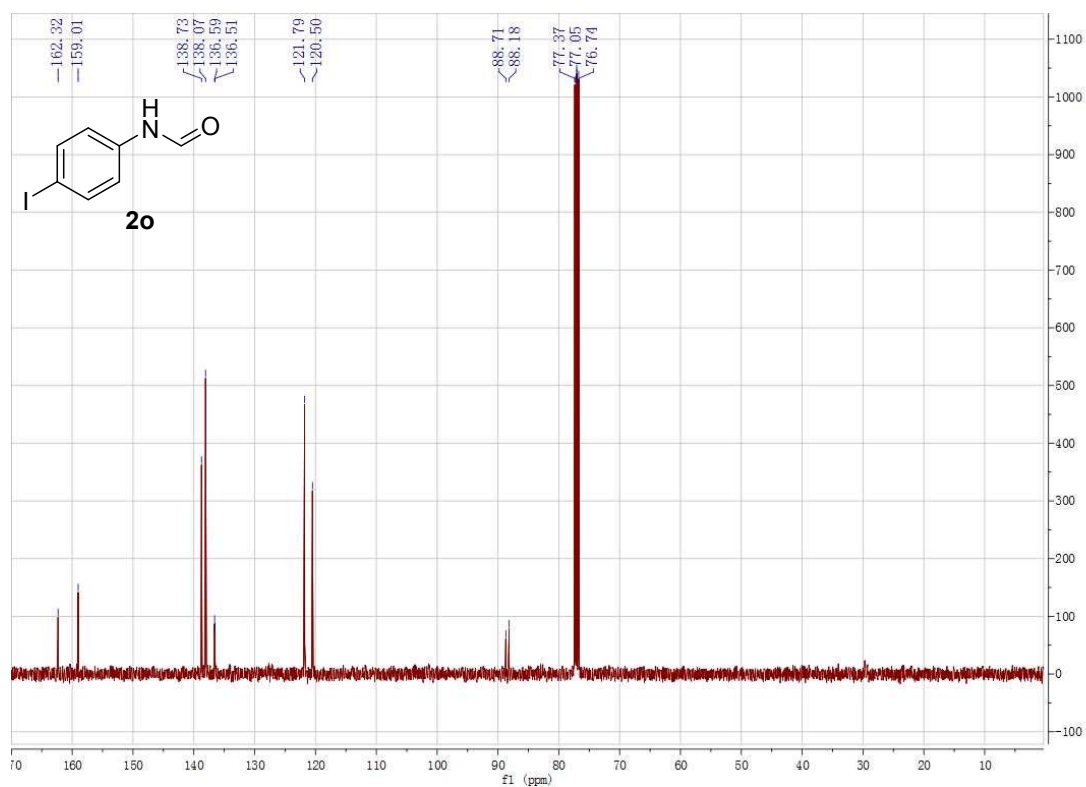
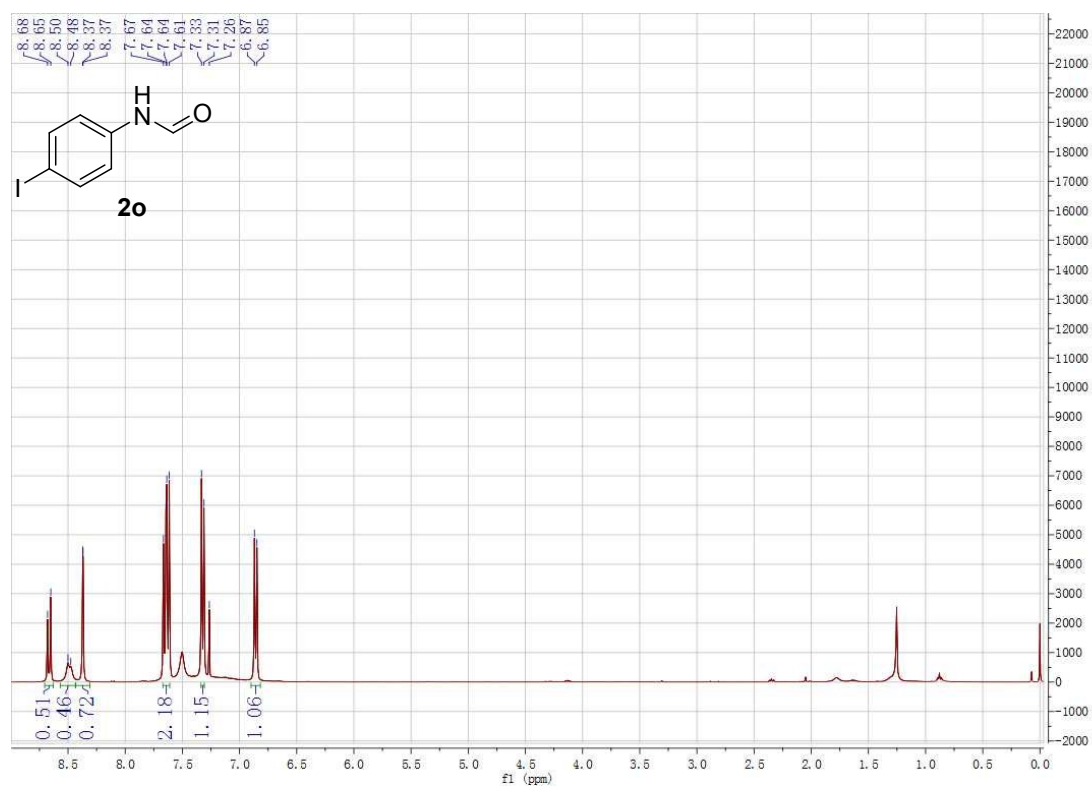


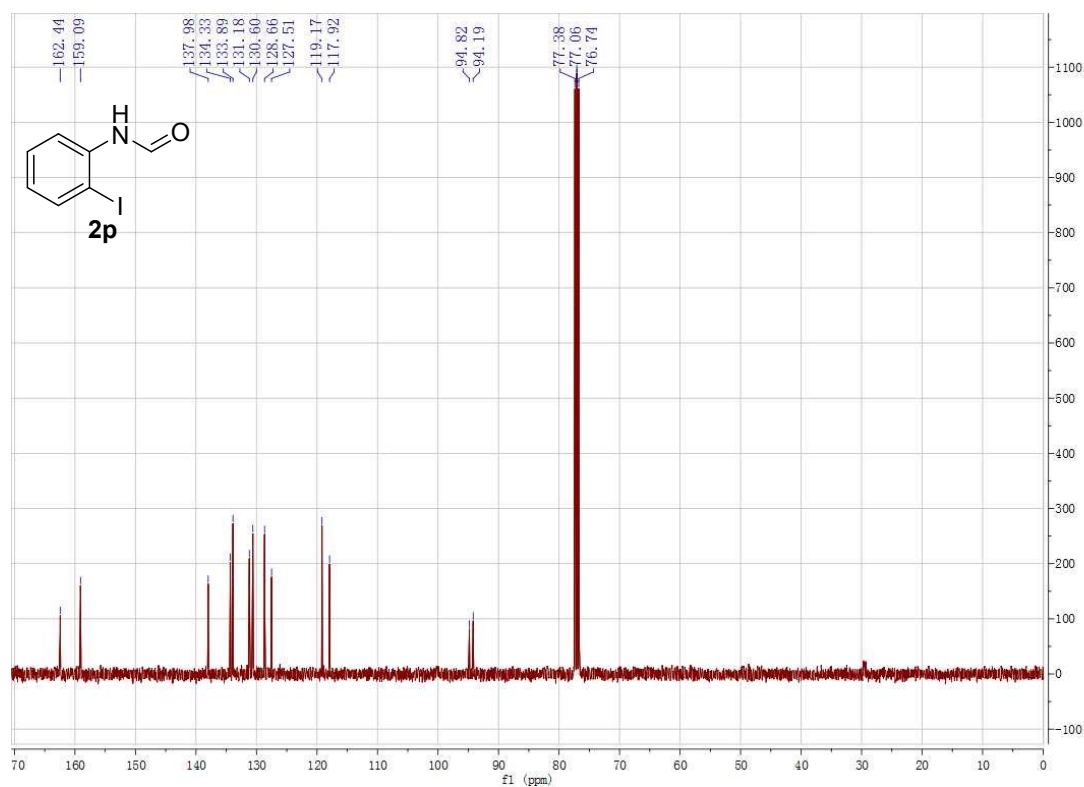
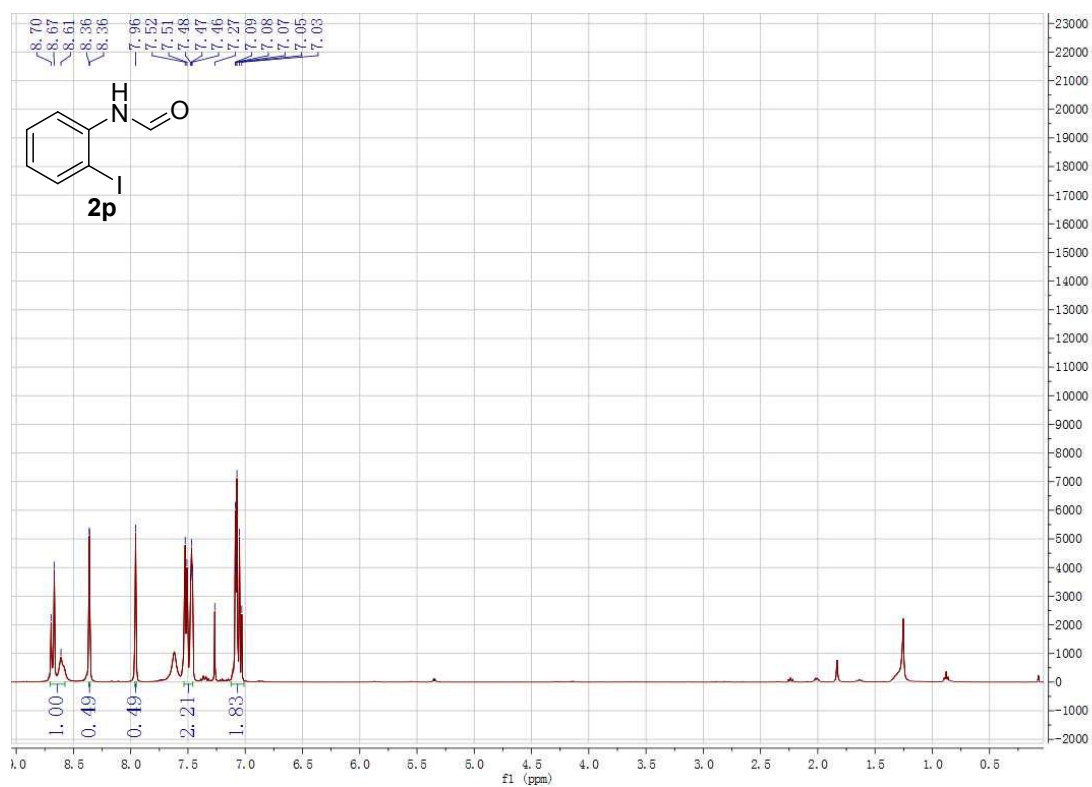


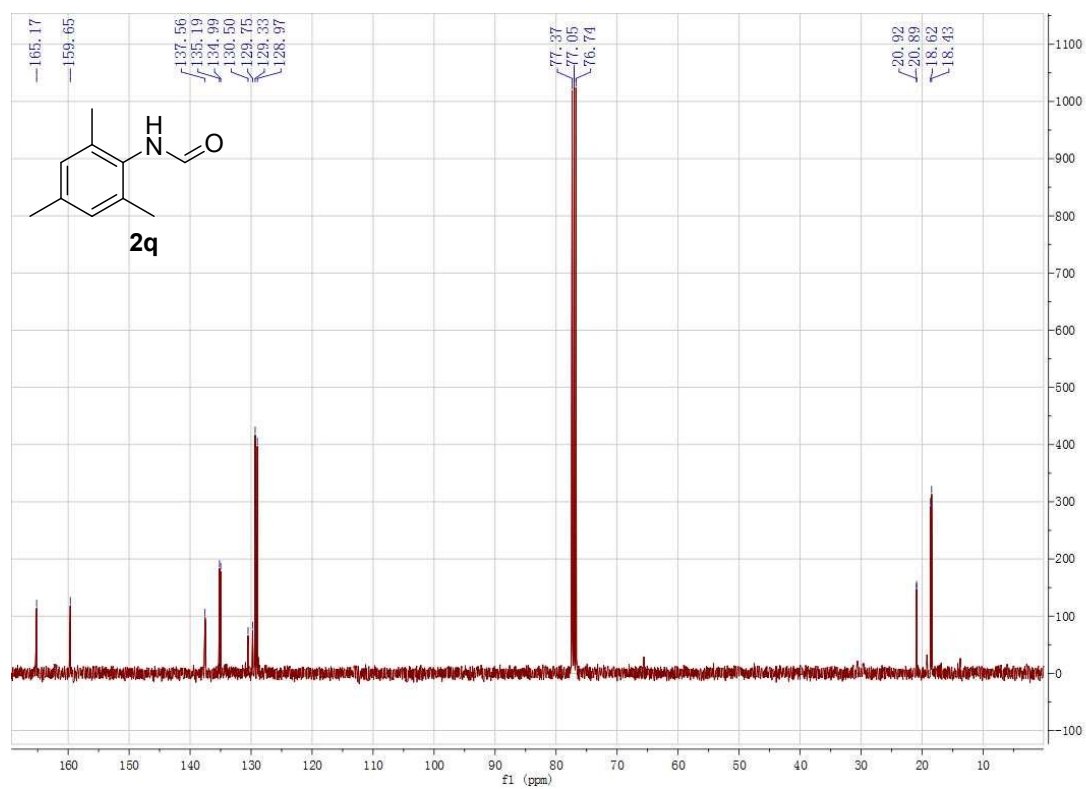
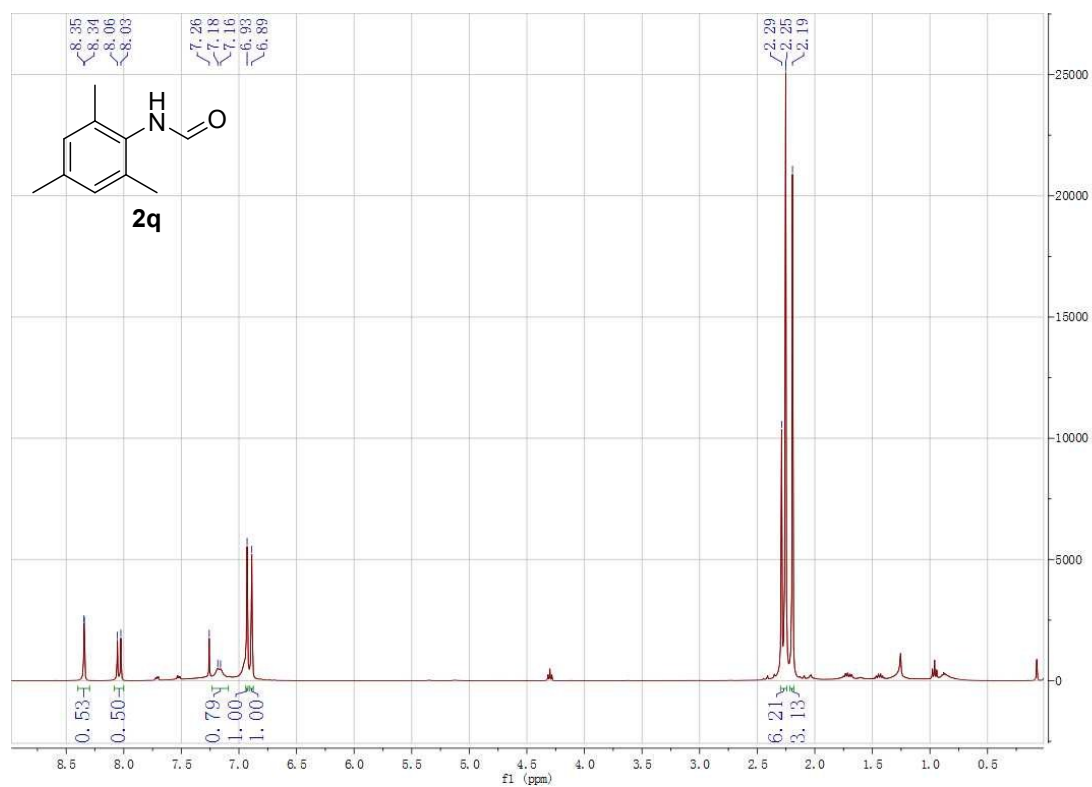


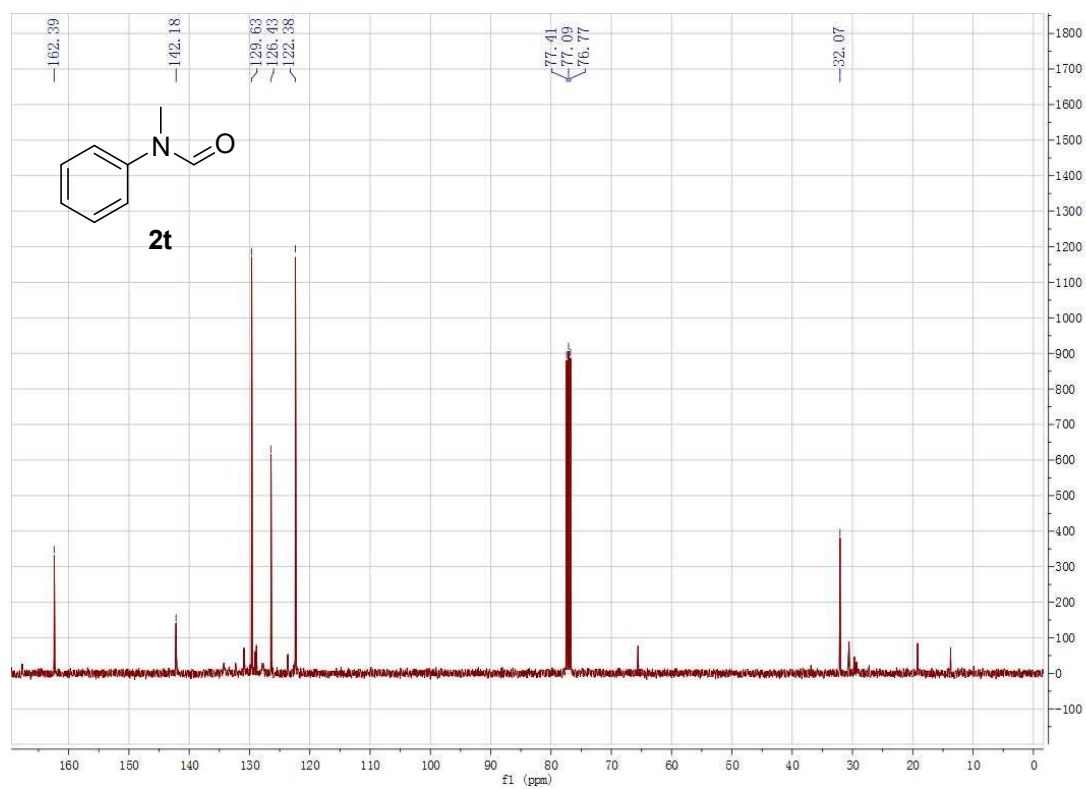
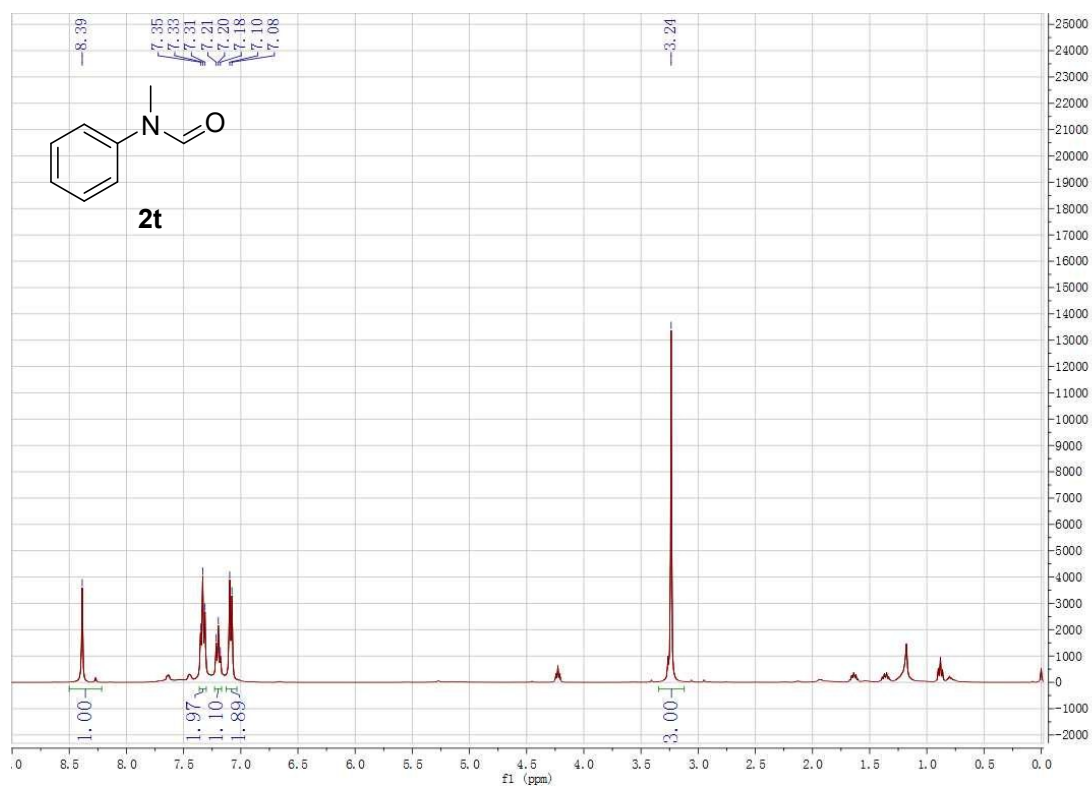


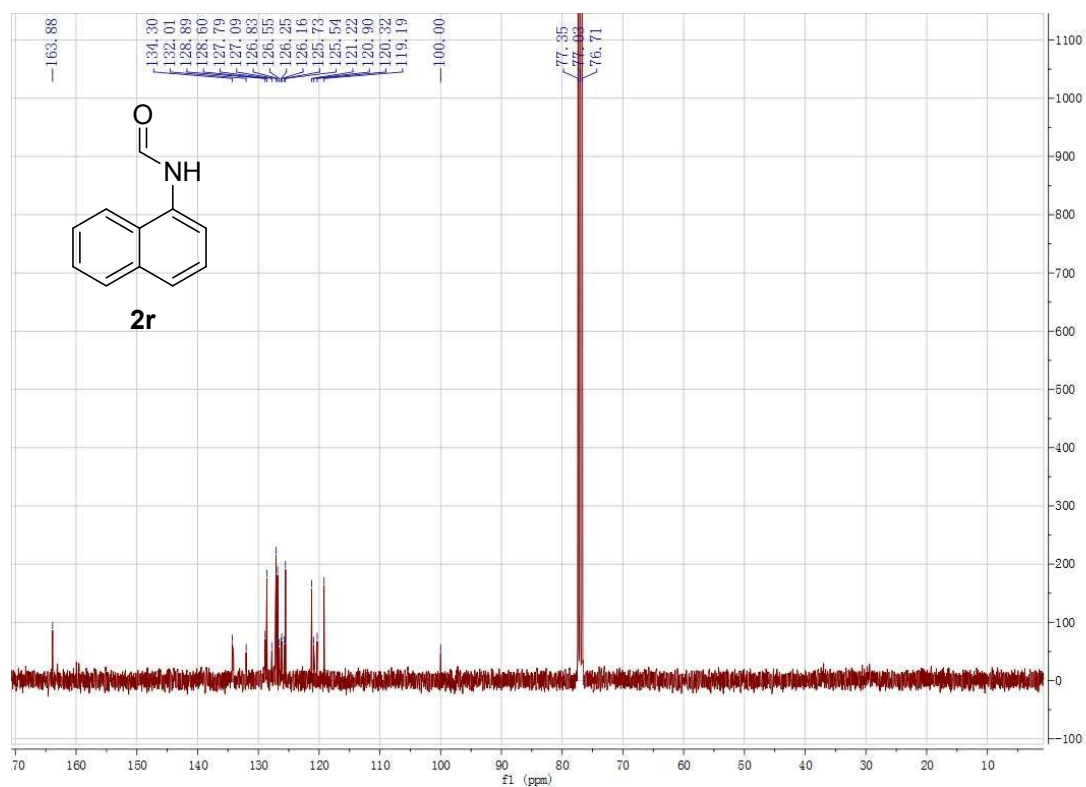
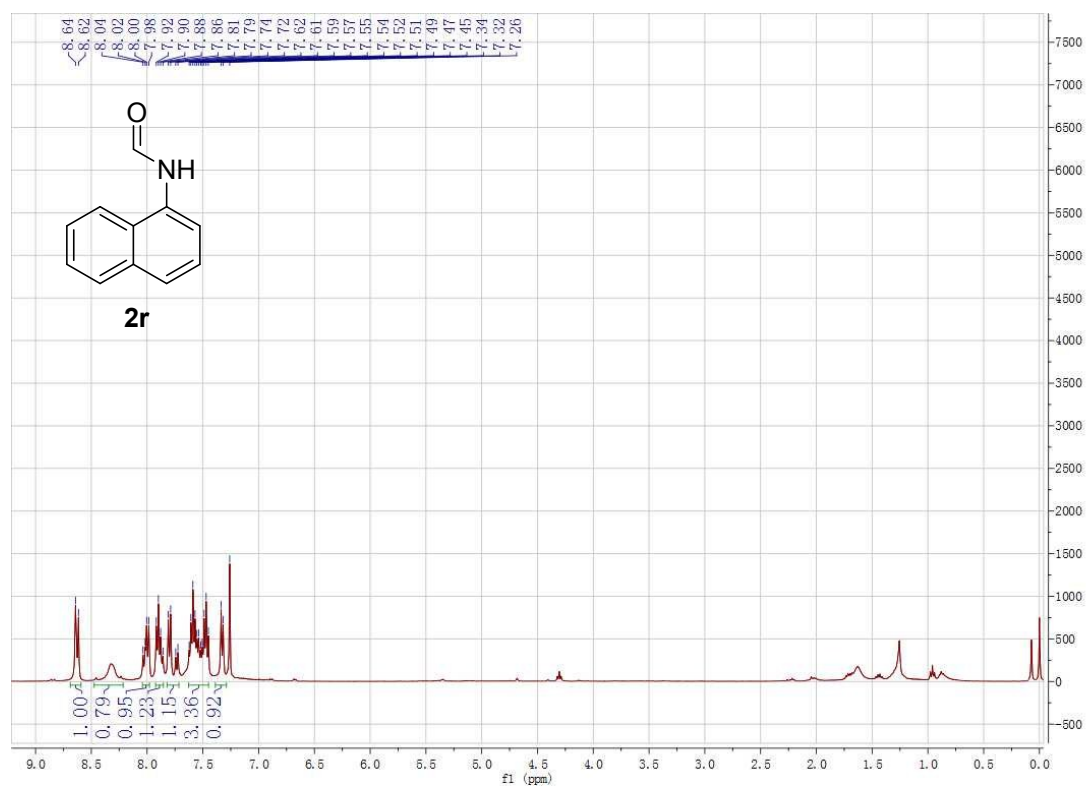


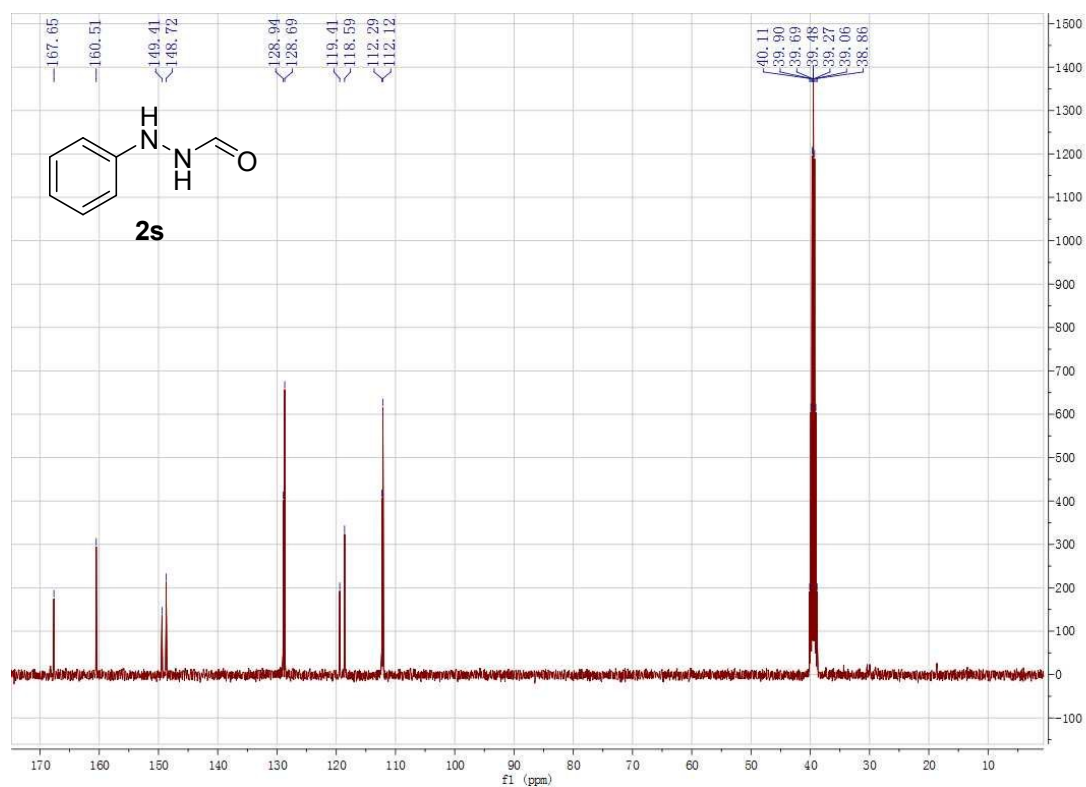
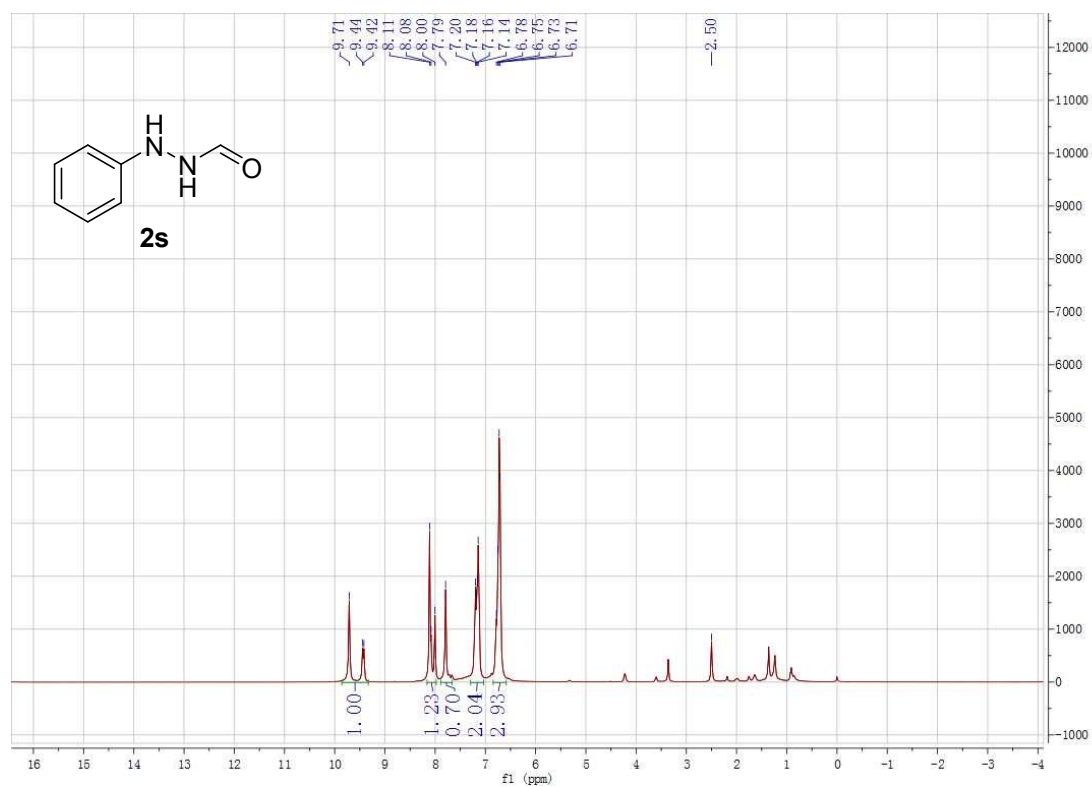


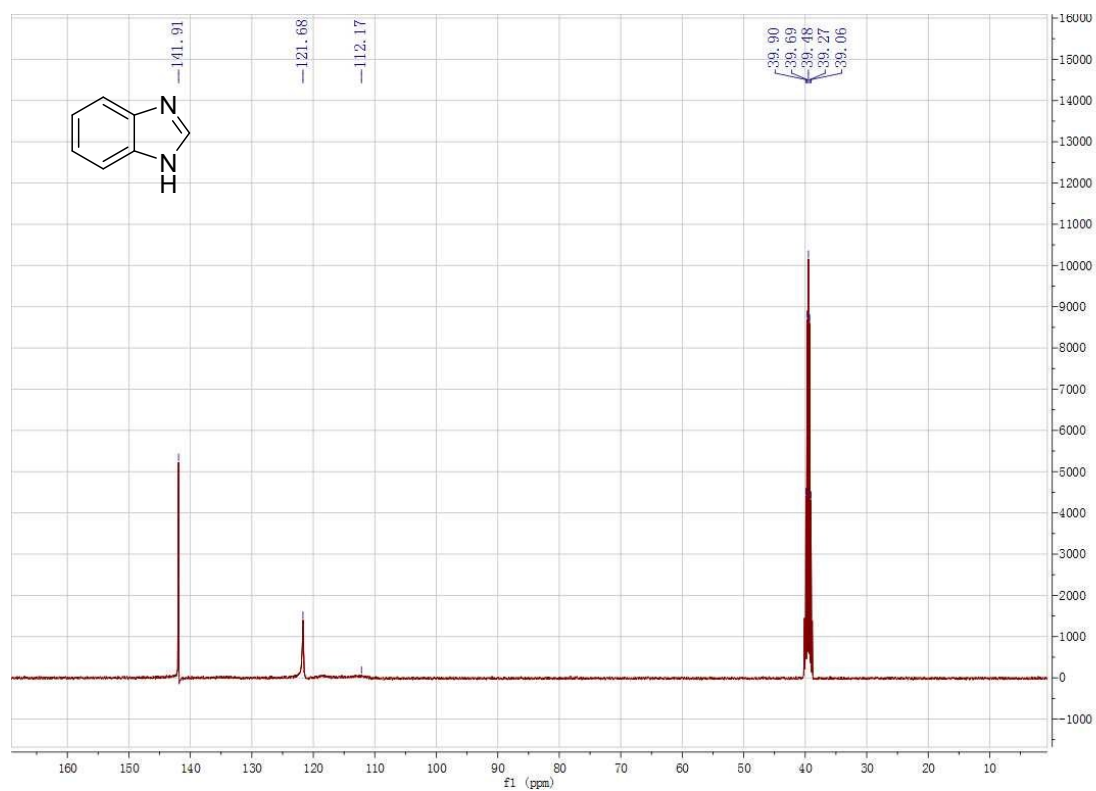
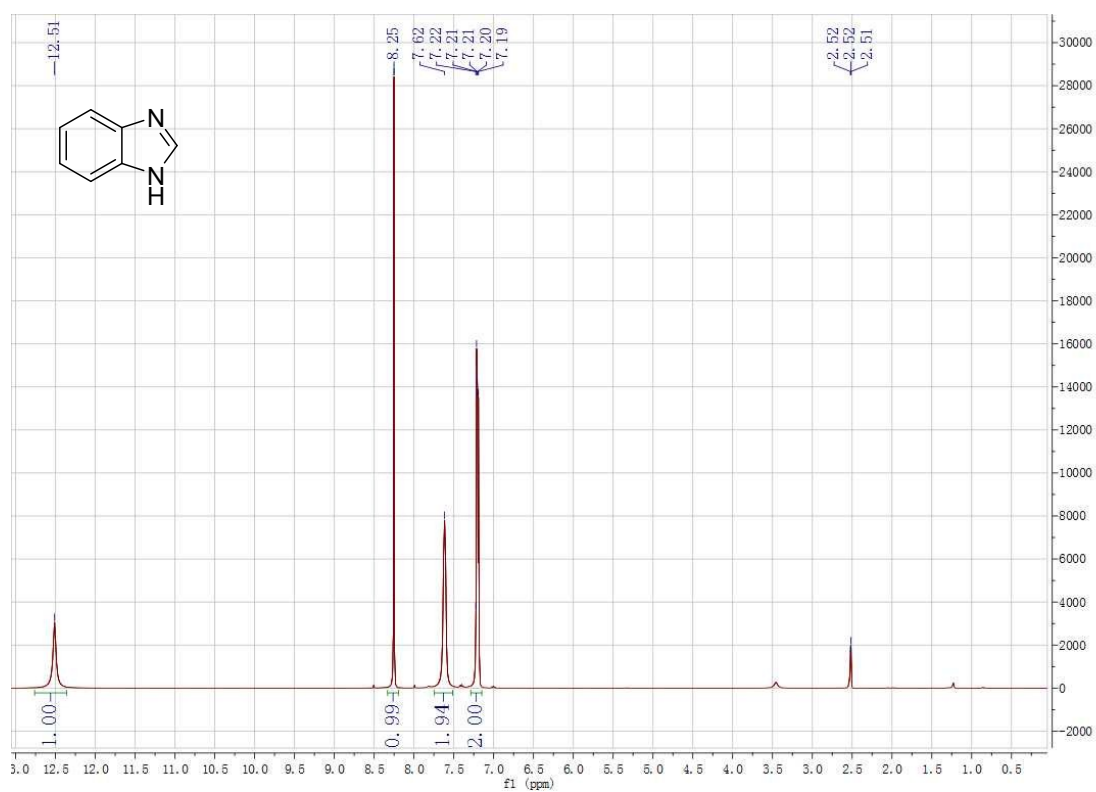












9) References

1. Lucero Gonzalez-Sebastian, Marcos Flores-Alamo, and Juventino J. Garcia. *Organometallics* **2013**, 32, 7186–7194
2. Thanh V. Q. Nguyen, Woo-Jin Yoo, and Shu Kobayashi. *Angew. Chem. Int. Ed.* **2015**, 54, 9209–9212.
3. Che Chang Chong and Rei Kinjo. *Angew. Chem. Int. Ed.* **2015**, 54, 12116–12120.
4. Leiduan Hao, Yanfei Zhao, Bo Yu, Zhenzhen Yang, Hongye Zhang, Buxing Han, Xiang Gao, and Zhimin Liu. *ACS Catal.* **2015**, 5, 4989–4993.
5. Ryo Shintani and Kyoko Nozaki. *Organometallics* **2013**, 32, 2459–2462.