Supporting information for:

NBS-Mediated C(sp³)-H Amidation of *N,N*-Dimethylamides with *N*-Acyloxyamides

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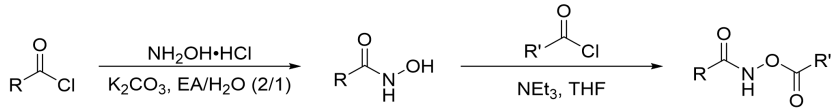
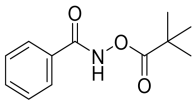
I. General Information

Unless otherwise stated, all anhydrous solvents, reagents and starting materials were commercially available and used as received. The following reagents were purchased and used as received: *N*-Chlorosuccinimide (Energy Chemical), *N*-Bromosuccinimide (Energy Chemical), *N*-Iodosuccinimide (Energy Chemical), *N,N*-Dimethylacetamide (TCI), *N,N*-Dimethylformamide (TCI), Dichloromethane (Sigma-Aldrich), Ethyl acetate (Sigma-Aldrich), Acetonitrile (Sigma-Aldrich). Flash column chromatography was performed using 300−400 mesh silica with the proper solvent system according to thin layer chromatography (TLC) analysis using UV light to visualize the reaction components. NMR spectra were recorded on a Bruker-400 instrument or Bruker-500 instrument. ^{1}H NMR chemical shifts were referenced to tetramethylsilane (TMS) signal (0 ppm), ^{13}C NMR chemical shifts were referenced to the solvent resonance [77.00 ppm, $CDCl_3$]. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, q = quadruplet. High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF-Q II instrument (ESI).

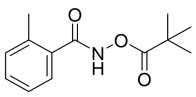
II. Procedures for the Synthesis of Starting Materials



General procedure for the synthesis of *N*-acyloxyamides:[1] A 250 mL round-bottom flask was charged with K_2CO_3 (20 mmol, 2 equiv), ethyl acetate (EA) (40 mL), and water (20 mL). Hydroxylamine hydrochloride (20 mmol, 2 equiv) was added, and the mixture was cooled to 0 °C. Acid chloride (10 mmol) was then added dropwise. The resulting solution was stirred at room temperature for 6 hours. The organic phase was separated, and the aqueous phase was extracted with EA (40 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude hydroxamic acid was added with THF (40 mL) and Et_3N (13 mmol, 1.3 equiv), then stirred for a while before the dropwise addition of acid chloride (10 mmol, 1 equiv). After stirring for 16 hours, the reaction mixture was added with EA (40 mL), water (20 mL), and HCl (1 M, 1 mL). The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (PE/EA) as the eluent to give the desired product, *N*-acyloxyamides **1**.

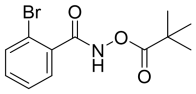


***N*-(pivaloyloxy)benzamide (1a):**[1] White solid (1.81 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.55-7.51 (m, 1H), 7.44-7.39 (m, 2H), 1.34 (s, 9H).

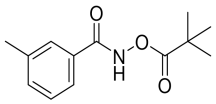


2-methyl-*N*-(pivaloyloxy)benzamide (1b):[1] White solid (1.41 g, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.48 (d, J = 7.0 Hz, 1H), 7.38-7.34 (m, 1H), 7.28-7.08 (m, 2H), 2.47 (s, 3H), 1.33 (s, 9H).

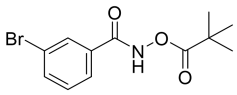
[1] Zhang, X. Y.; Lin, B.; Chen, J. J.; Chen, J. H.; Luo, Y. S.; Xia, Y. Z. *Org. Lett*. **2021**, *23*, 819.



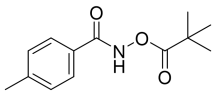
2-bromo-*N*-(pivaloyloxy)benzamide (1c):[2] White solid (1.92 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.44 – 7.31 (m, 2H), 1.36 (s, 9H).



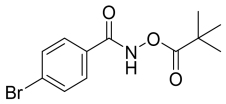
3-methyl-*N*-(pivaloyloxy)benzamide (1d):[1] White solid (1.64 g, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.36 (s, 1H), 7.62 (s, 1H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.37-7.32 (m, 2H), 2.39 (s, 3H), 1.36 (s, 9H).



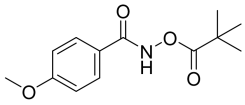
3-bromo-*N*-(pivaloyloxy)benzamide (1e):[3] White solid (2.43 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.96 (s, 1H), 7.71 (dd, *J* = 14.4, 8.0 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 1.36 (s, 9H).



4-methyl-*N*-(pivaloyloxy)benzamide (1f):[1] White solid (1.57 g, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.33 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 1.36 (s, 9H).



4-bromo-*N*-(pivaloyloxy)benzamide (1g):[1] White solid (2.13 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 1.36 (s, 9H).

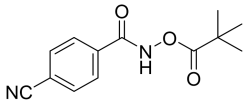


4-methoxy-*N*-(pivaloyloxy)benzamide (1h):[1] White solid (1.90 g, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 3.85 (s, 3H), 1.36 (s,

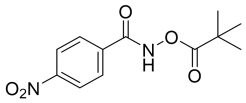
[2] Lin, S.; Lin, B.; Zhang, Z. T.; Chen, J. H.; Luo, Y. S.; Xia, Y. Z. *Org. Lett.* **2022**, *24*, 3302.

[3] Huang, W. M.; Yan, H. B.; Wang, Q. Q.; Chen, J. H.; Luo, Y. S.; Xia, Y. Z. *Org. Chem. Front.* **2024**, *11*, 2561.

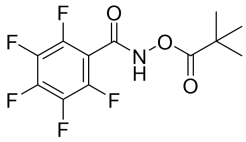
9H).



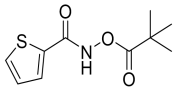
4-cyano-*N*-(pivaloyloxy)benzamide (1i):[1] White solid (1.60 g, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 1.36 (s, 9H).



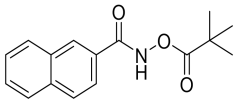
4-nitro-*N*-(pivaloyloxy)benzamide (1j):[1] White solid (1.91 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.31 (d, J = 8.0 Hz, 2H), 7.98 (d, J = 8.5 Hz, 2H), 1.37 (s, 9H).



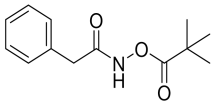
2,3,4,5,6-pentafluoro-*N*-(pivaloyloxy)benzamide (1k): White solid (1.43 g, 46%). m.p. 72.9-82.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 1.36 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.4, 175.9, 154.9, 145.7, 144.2, 143.7, 142.2, 138.7, 136.7, 38.4, 26.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -138.31 (d, *J* = 17.9 Hz, 2F), -147.93 (t, *J* = 19.8 Hz, 1F), -159.16 (t, *J* = 17.3 Hz, 2F). HRMS (ESI) calculated for $[M+H]^+$: 312.0654, found 312.0661.



***N*-(pivaloyloxy)thiophene-2-carboxamide (1l):**[1] White solid (1.65 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 7.67 (d, *J* = 3.2 Hz, 1H), 7.58 (d, *J* = 4.8 Hz, 1H), 7.13 (t, *J* = 4.4 Hz, 1H), 1.36 (s, 9H).

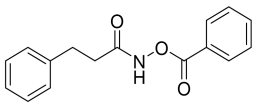


***N*-(pivaloyloxy)-2-naphthamide (1m):**[1] White solid (2.22 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.36 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.0 Hz, 1H), 7.60-7.52 (m, 2H), 7.48-7.44 (m, 1H), 1.37 (s, 9H).

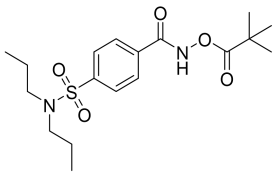


2-phenyl-*N*-(pivaloyloxy)acetamide (1n):[1] White solid (1.24 g, 53%). ^{1}H NMR (400 MHz,

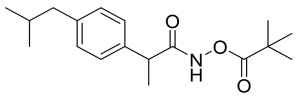
$CDCl_3$) δ 8.77 (s, 1H), 7.40 – 7.28 (m, 5H), 3.64 (s, 2H), 1.29 (s, 9H).



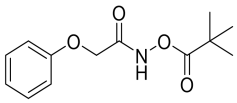
***N*-(benzoyloxy)-3-phenylpropanamide (1o):**[4] White solid (1.91 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.09 (d, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.35 – 7.18 (m, 5H), 3.05 (t, *J* = 7.6 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H).



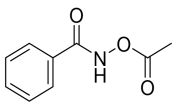
4-(*N*,*N*-dipropylsulfamoyl)-*N*-(pivaloyloxy)benzamide (1p):[3] White solid (2.03 g, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.89 (dd, *J* = 19.6, 8.0 Hz, 4H), 3.09 (t, *J* = 7.6 Hz, 4H), 1.60-1.48 (m, 4H), 1.37 (s, 9H), 0.87 (t, *J* = 7.2 Hz, 6H).



2-(4-isobutylphenyl)-*N*-(pivaloyloxy)propanamide (1q): White solid (1.92 g, 63%). m.p. 124.0-124.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.25 (d, *J* = 12.0 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 3.65 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.95 – 1.76 (m, 1H), 1.56 (d, *J* = 7.2 Hz, 3H), 1.28 (s, 9H), 0.90 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.5, 172.9, 141.2, 136.7, 129.7, 127.4, 45.0, 44.1, 38.3, 30.1, 26.9, 22.4, 18.3. HRMS (ESI) calculated for $[M+H]^+$: 306.2064, found 306.2062.



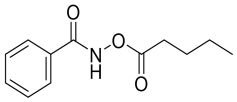
2-phenoxy-*N*-(pivaloyloxy)acetamide (1r):[5] White solid (1.55 g, 62%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 4.67 (s, 2H), 1.34 (s, 9H).



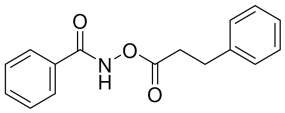
[4] Keum, H.; Jung, H.; Jeong, J.; Kim, D.; Chang, S. *Angew. Chem. Int. Ed.* **2021**, *60*, 25235.

[5] Hou, M.; Zhang, Zhang, Z. D.; Lai, X. J.; Zong, Q. S.; Ren, M. F.; Bai, T. W.; Qiu, G. Y. *Synthesis* **2024**, *56*, 496.

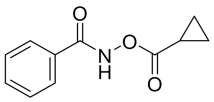
***N*-acetoxybenzamide (1s):**[1] White solid (1.48 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 2.30 (s, 3H).



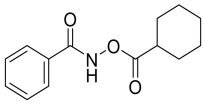
***N*-(pentanoyloxy)benzamide (1t):**[6] White solid (1.68 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.79 – 1.67 (m, 2H), 1.50 – 1.36 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H).



***N*-((3-phenylpropanoyl)oxy)benzamide (1u):** White solid (1.77 g, 66%). m.p. 97.2-97.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.84 – 7.73 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.26 (m, 2H), 7.22 (d, *J* = 7.6 Hz, 3H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.86 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3, 166.4, 139.5, 132.8, 130.7, 128.8, 128.6, 128.3, 127.5, 126.6, 33.3, 30.5. HRMS (ESI) calculated for $[M+H]^+$: 270.1125, found 270.1131.

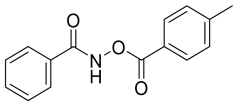


***N*-((cyclopropanecarbonyl)oxy)benzamide (1v):** White solid (1.29 g, 63%). m.p. 87.0-88.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 1.95-1.84 (m, 1H), 1.23-1.16 (m, 2H), 1.12-1.04 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 166.4, 132.7, 130.8, 128.8, 127.5, 10.9, 9.7. HRMS (ESI) calculated for $[M+H]^+$: 206.0812, found 206.0818.

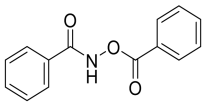


***N*-((cyclohexanecarbonyl)oxy)benzamide (1w):**[6] White solid (1.75 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 2.70-2.56 (m, 1H), 2.03 (d, *J* = 13.2 Hz, 2H), 1.81 (d, *J* = 12.4 Hz, 2H), 1.73-1.50 (m, 3H), 1.41-1.23 (m, 3H).

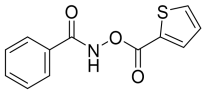
[6] Bian, M. Y.; Mawjuda, H.; Gao, H.; Xu, H. Y.; Zhou, Z.; Yi, W. *Org. Lett.* **2020**, *22*, 9677.



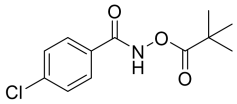
***N*-((4-methylbenzoyl)oxy)benzamide (1x):**[7] White solid (1.32 g, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H).



***N*-(benzoyloxy)benzamide (1y):**[1] White solid (1.80 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.16 (d, *J* = 7.2 Hz, 2H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.50 (dd, *J* = 16.8, 8.0 Hz, 4H).

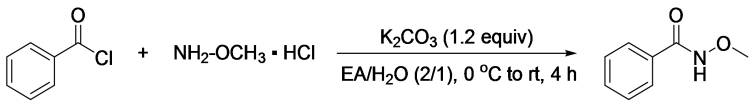


***N*-((thiophene-2-carbonyl)oxy)benzamide (1z):**[7] White solid (1.11 g, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.01 (s, 1H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.72 (d, *J* = 3.6 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.18 (s, 1H).



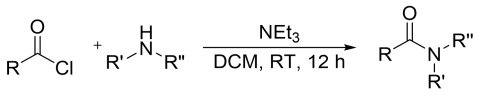
4-chloro-*N*-(pivaloyloxy)benzamide (1c'):[1] White solid (1.66 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.79 – 7.71 (m, 2H), 7.45 – 7.39 (m, 2H), 1.35 (s, 9H).

[7] Wang, K. K.; Li, Y. L.; Zhao, Y. C.; Zhang, S. S.; Chen, R. X.; Sun, A. L. *RSC Adv.* **2021**, *11*, 40193.

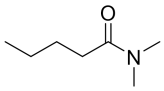


General procedure for the synthesis of *N*-acyloxyamides:[8] To a solution of K_2CO_3 (1.66 g, 12.0 mmol) in a mixture of EtOAc/ H_2O (2:1, 30 mL), methoxyammonium chloride (1.00 g, 12.0 mmol) was added. The resulting solution was cooled to 0 °C, followed by the dropwise addition of benzoyl chloride (1.2 mL, 10 mmol). The reaction mixture was warmed to room temperature and stirred for 4 hours. The organic phase was separated, and the aqueous phase was extracted with EtOAc (15 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether: ethyl acetate = 3:1) to give the desired product, *N*-acyloxyamides **1c'** [White solid, 1.22 g, 81%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 2.29 (s, 3H).].

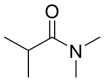
[8] Zou, C.; Jiang, J. J.; Wang, J. *Org. Lett.* **2019**, *21*, 4971.



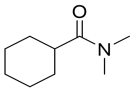
General procedure for the synthesis of tertiary amides:[9] To a solution of the amine (10 mmol, 1.0 equiv) and triethylamine (2.0 equiv) in CH_2Cl_2 (0.1 M) at 0 °C, the corresponding acyl chloride (1.2 equiv) was added dropwise. The resulting reaction mixture was allowed to warm to 25 °C while stirring overnight (12 hours). After this time, a saturated aqueous solution of sodium bicarbonate was added, and the biphasic system was separated. The aqueous phase was extracted with CH_2Cl_2 (three times), and the organic phases were combined and dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated under reduced pressure. The resulting crude material was purified by flash column chromatography on silica gel with a solvent system of petroleum ether and ethyl acetate to afford the desired compound.



***N,N*-dimethylpentanamide (2c):**[9] Colorless liquid (1.00 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.01 (s, 3H), 2.94 (s, 3H), 2.37 – 2.26 (m, 2H), 1.68 – 1.55 (m, 2H), 1.42 – 1.30 (m, 2H), 0.96 – 0.87 (m, 3H).



***N,N*-dimethylisobutyramide (2d):**[10] Colorless liquid (0.95 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.04 (s, 3H), 2.94 (s, 3H), 2.87 – 2.75 (m, 1H), 1.11 (d, J = 6.8 Hz, 6H).

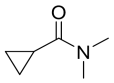


***N,N*-dimethylcyclohexanecarboxamide (2e):**[11] Colorless liquid (1.07 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.04 (s, 3H), 2.93 (s, 3H), 2.56-2.43 (m, 1H), 1.86 -1.63 (m, 5H), 1.58-1.43 (m, 2H), 1.34-1.18 (m, 3H).

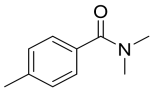
[9] Feng, M. H.; Mosiagin, I.; Kaiser, D.; Spinozzi, E.; Maryasin, B.; Maulide, N. *J. Am. Chem. Soc.* **2022**, *144*, 13044.

[10] Xue, Y.; Park, H. S.; Jiang, C.; Yu, J. Q. *ACS Catal.* **2021**, *11*, 14188.

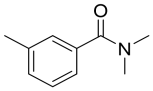
[11] Huang, Y. J.; Zhang, J. *Synthesis* **2022**, *54*, 3595.



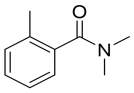
***N,N*-dimethylcyclopropanecarboxamide (2f):**[12] Colorless liquid (0.67 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.18 (s, 3H), 2.97 (s, 3H), 1.81-1.70 (m, 1H), 1.00-0.92 (m, 2H), 0.78-0.72 (m, 2H).



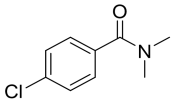
***N,N*,4-trimethylbenzamide (2h):**[11] Colorless oil (1.10 g, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.36 (m, 1H), 7.35-7.23 (m, 3H), 3.14 (s, 3H), 2.86 (s, 3H).



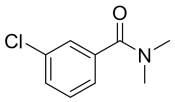
***N,N*,3-trimethylbenzamide (2i):**[13] Colorless oil (1.22 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.12 (m, 4H), 3.10 (s, 3H), 2.97 (s, 3H), 2.36 (s, 3H).



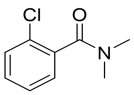
***N,N*,2-trimethylbenzamide (2j):**[13] Colorless oil (0.91 g, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.11 (m, 4H), 3.13 (s, 3H), 2.83 (s, 3H), 2.29 (s, 3H).



4-chloro-*N,N*-dimethylbenzamide (2k):[11] Colorless oil (1.45 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 4H), 3.10 (s, 3H), 2.98 (s, 3H).



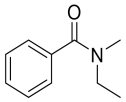
3-chloro-*N,N*-dimethylbenzamide (2l):[11] Colorless oil (1.30 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.22 (m, 4H), 3.11 (s, 3H), 2.98 (s, 3H).



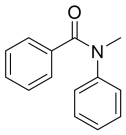
[12] Park, H.; Chekshin, N.; Shen, P. X.; Yu, J. Q. *ACS Catal*. **2018**, *8*, 9292.

[13] Bai, C. H.; Yao, X. F.; Li, Y. W. *ACS Catal.* **2015**, *5*, 884.

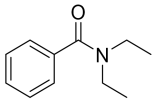
2-chloro-*N,N*-dimethylbenzamide (2m):[14] Colorless oil (1.39 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.24 (m, 4H), 3.14 (s, 3H), 2.86 (s, 3H).



***N*-ethyl-*N*-methylbenzamide(2p):**[15] Colorless oil (0.91 g, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.33 (m, 5H), 3.73 – 3.17 (m, 2H), 3.14 – 2.82 (m, 3H), 1.31 – 1.02 (m, 3H).



***N*-methyl-*N*-phenylbenzamide (2q):**[16] Colorless oil (1.16 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.24 – 7.10 (m, 6H), 7.02 (d, J = 7.6 Hz, 2H), 3.49 (s, 3H).



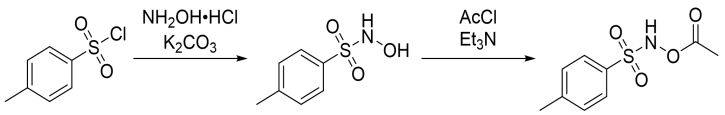
***N,N*-diethylbenzamide(2r):**[17] Colorless oil (1.18 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 5H), 3.54 (s, 2H), 3.25 (s, 2H), 1.24 (s, 3H), 1.11 (s, 3H).

[14] Jaiswal, V.; Mondal, B.; Singh, K.; Das, D.; Saha, J. *Org. Lett.* **2019**, *21*, 5848.

[15] Zhou, L.; Qiu, J.; Wang, C. C.; Zhang, F.; Yang, K.; Song, Q. L. *Org. Lett.* **2022**, *24*, 3249.

[16] Li, G. C.; Ji, C. L.; Hong, X.; Szostak, M. *J. Am. Chem. Soc.* **2019**, *141*, 11161.

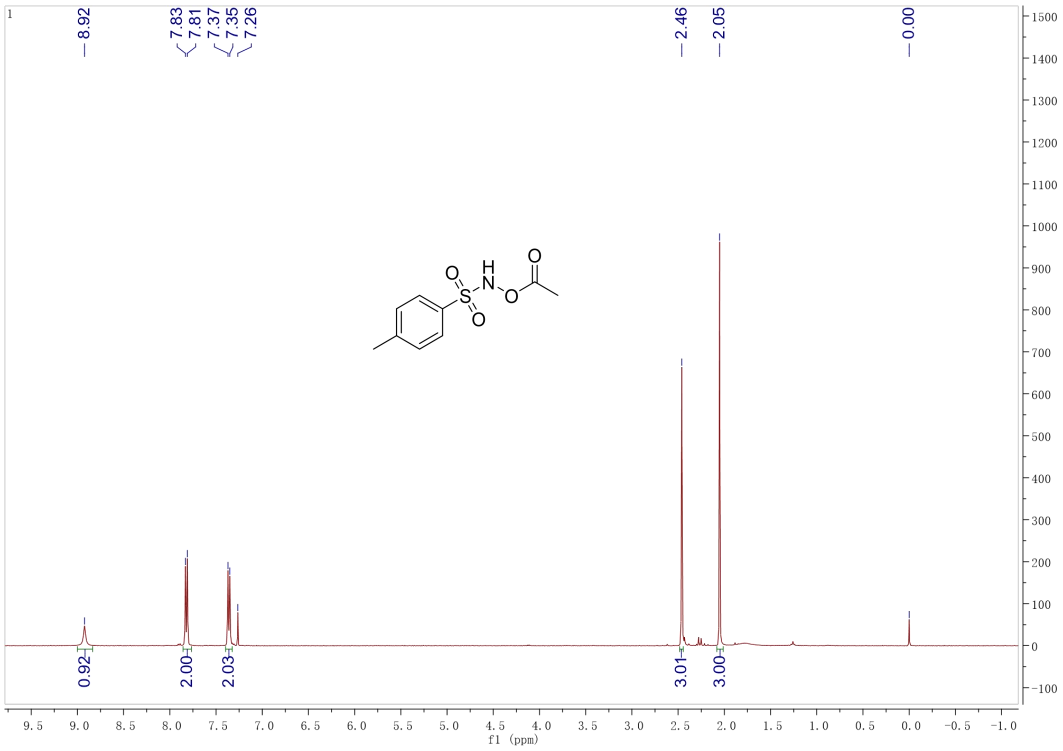
[17] Rauser, M.; Warzecha, D. P.; Niggemann, M. *Angew. Chem. Int. Ed.* **2018**, *57*, 5903.



Procedure for the synthesis of *N*-hydroxy-4-methylbenzenesulfonamide:[18] 1.29 g (20 mmol, 2.0 equiv) of hydroxylamine hydrochloride was dissolved in 3 mL of water at 0 °C. A solution of 2.76 g (20 mmol, 2.0 equiv) of K_2CO_3 dissolved in 3 mL of water was added to the hydroxylamine hydrochloride solution dropwise while maintaining the internal reaction temperature between 5 and 15 °C. After stirring the solution for 15 minutes, 12 mL of tetrahydrofuran (THF) and 3 mL of methanol were added; subsequently, 1.91 g (10 mmol, 1.0 equiv) of 4-methylbenzenesulfonyl chloride was added portionwise while maintaining the internal reaction temperature between 5 and 15 °C. Upon complete addition, the reaction was allowed to rise to room temperature. After stirring for 4 hours at room temperature, the organic solvents were removed under reduced pressure using a rotary evaporator. The resulting aqueous suspension was extracted with 2 × 20 mL of diethyl ether. The combined organic layers were dried over $MgSO_4$. The solvent from the mixture was then removed under reduced pressure and the residue was dried under high vacuum to afford 1.32 g (70% yield) of *N*-hydroxy-4-methylbenzenesulfonamide, which was used for the next synthetic step without further purification. *N*-hydroxy-4-methylbenzenesulfonamide was dissolved in 20 mL of tetrahydrofuran at -78 °C. 0.86 g (8.5 mmol, 1.2 equiv) of triethylamine was added dropwise. After stirring the mixture for 15 minutes at this temperature, 0.67 g (8.5 mmol, 1.2 equiv) of acetyl chloride was added dropwise. The reaction mixture was stirred for 4 hours at -78 °C. The reaction mixture was allowed to warm to room temperature; the white solid formed during the reaction was filtered off. The filtrate was evaporated to afford a white solid. The resulting solid was dissolved in 50 mL of dichloromethane and washed with 2 × 20 mL of 1M HCl. The organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product obtained was dissolved in 10 mL of boiling ethyl acetate and then cooled to room temperature

[18] Wang, A.; Venditto, N. J.; Darcy, J. W.; Emmert, M. H. *Organometallics* **2017**, 36, 1259.

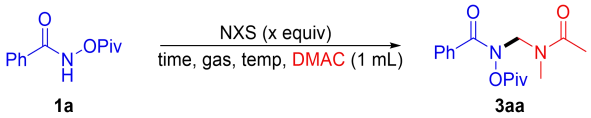
overnight to afford 1.13 g of a clean white solid as product **5a** (yield: 70%). This product was isolated by filtration and dried under vacuum. [^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H), 2.05 (s, 3H).]



^{1}H NMR (400 MHz, $CDCl_3$)

III. Optimization studies:

Table S1: Screening of NXS, Time, Temperature, etc.[a]

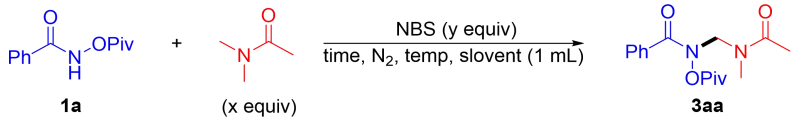


1a **3aa**

Entry	NXS (equiv)	Time (h)	Temp (°C)	Gas	Yield (%)[b]
1	NCS (3)	24	40	N_2	99
2	NBS (3)	24	40	N_2	99
3	NIS (3)	24	40	N_2	nr
4	NBS (3)	2	40	N_2	95
5	NBS (3)	4	40	N_2	99
6	**NBS (2)**	**4**	**40**	**N_2**	**99**
7	NCS (2)	4	40	N_2	48
8	NBS (1)	4	40	N_2	47
9	NBS (0.5)	4	40	N_2	16
10	NBS (2)	4	rt	N_2	45
11	NBS (2)	4	rt	air	trace

[a]Reaction conditions: **1a** (0.20 mmol). [b]Isolated yields.

Table S2: Screening of Time, Temperature, Slovent, etc.[a]

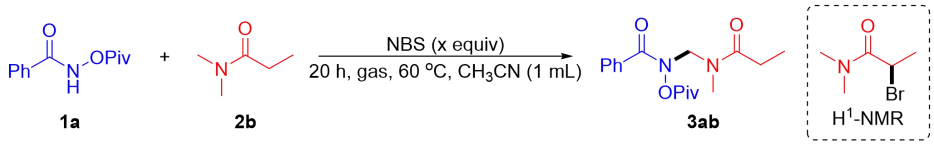


1a (x equiv) **3aa**

Entry	DMAC (x equiv)	NBS (y equiv)	Time (h)	Temp (°C)	Slovent (1 mL)	Yield (%)[b]
1	10	2	4	40	DCM	44
2	10	2	4	40	CH_3CN	49
3	10	2	4	40	EA	30
4	10	2	4	80	CH_3CN	67
5	10	2	12	80	CH_3CN	80
6	**10**	**2**	**20**	**60**	**CH_3CN**	**96**
7	5	2	20	60	CH_3CN	67
8	2.5	2	20	60	CH_3CN	45
9	1.25	2	20	60	CH_3CN	31
10	5	2.2	20	60	CH_3CN	78
11	5	2.5	20	60	CH_3CN	83
12	5	3	20	60	CH_3CN	88

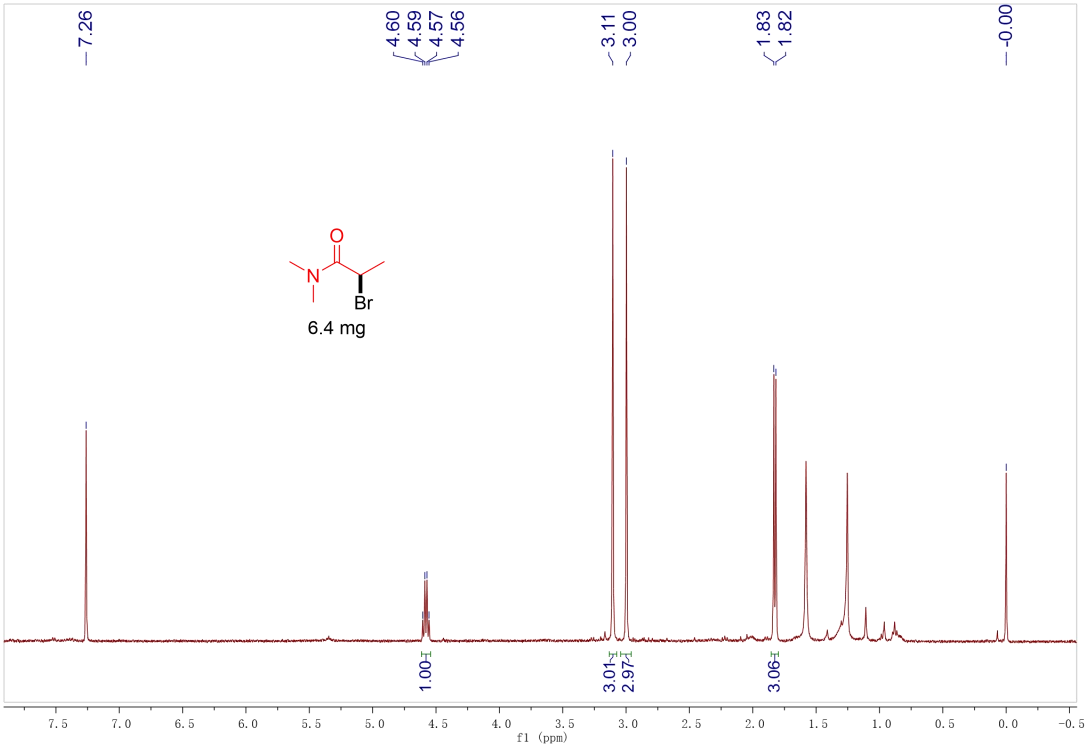
[a]Reaction conditions: **1a** (0.20 mmol). [b]Isolated yields.

Table S3: Screening of operating environment.[a]



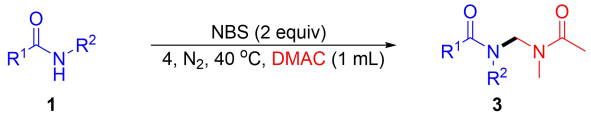
Entry	NBS (x equiv)	Gas	Yield (%)[b]
1	2	Operate under N_2 protection	52
2	2	Operate in a glove box	75
3	3	Operate in a glove box	83

[a]Reaction Conditions: **1a** (0.2 mmol), **2b** (2 mmol). [b]Isolated yields.



^{1}H NMR (400 MHz, $CDCl_3$)

IV. General procedure for the synthesis of methylenebisamides:



1 3

General procedure A: A flame-dried 10 mL Schlenk tube was cooled to room temperature and filled with N_2. To this tube, *N*-acyloxyamide **1** (0.20 mmol) and NBS (2.0 equiv) were added. DMAC (1.0 mL) was added by syringe under a flow of nitrogen. The resulting mixture was stirred at 40 °C for 4 hours. After completion, the reaction mixture was cooled to room temperature, and the residue was diluted with ethyl acetate (10 mL). The resulting solution was washed with saturated sodium carbonate solution (5 mL × 3). The organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography [300-400 mesh silica, ethyl acetate/petroleum ether = 2:1 to 1:3] to afford the desired methylenebisamide product.

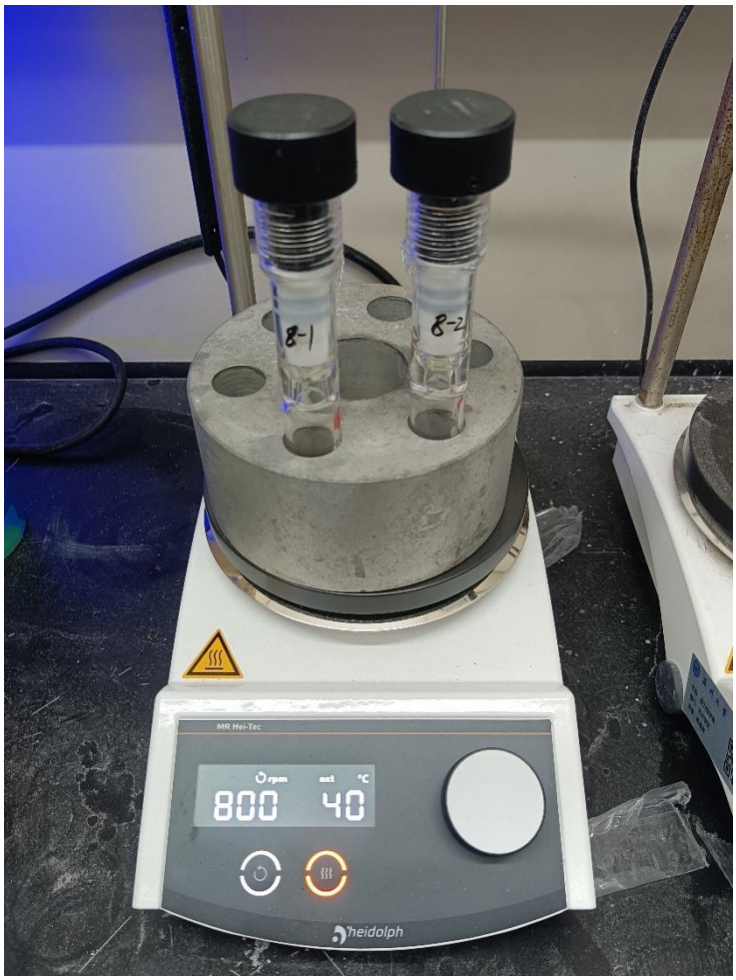
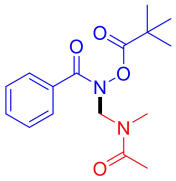
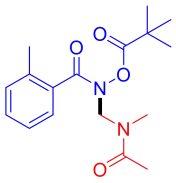


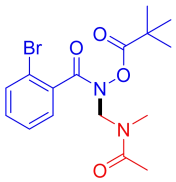
Figure S1. reaction unit



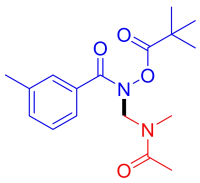
***N*-((*N*-methylacetamido)methyl)-*N*-(pivaloyloxy)benzamide (3aa):** light yellow oil (61.4 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55-7.50 (m, 2H), 7.47-7.34 (m, 3H), 5.44 (s, 2H), 3.17 (s, 2.28H), 3.04 (s, 0.74H), 2.20 (s, 0.74H), 2.07 (s, 2.27H), 0.97 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 175.8, 175.6, 172.0, 171.3, 171.1, 170.8, 133.0, 132.6, 131.1, 130.7, 128.0, 127.8, 127.7, 127.5, 62.7, 57.7, 38.0, 37.8, 35.4, 33.0, 26.3, 26.3, 21.4, 21.1. HRMS (ESI) calculated for $[M+H]^+$: 307.1652, found 307.1643.



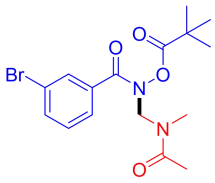
2-methyl-*N*-((*N*-methylacetamido)methyl)-*N*-(pivaloyloxy)benzamide (3ba): light yellow oil (63.4 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.10 (m, 4H), 5.46 (s, 2H), 3.19 (s, 2.2H), 3.04 (s, 0.8H), 2.37 (s, 3H), 2.18 (s, 0.8H), 2.06 (s, 2.2H), 0.86 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 175.7, 172.0, 170.8, 135.6, 135.3, 133.4, 133.0, 130.4, 130.1, 130.0, 129.7, 126.9, 126.7, 125.3, 125.1, 61.7, 56.8, 38.1, 37.9, 35.4, 33.2, 29.6, 26.2, 21.5, 21.1, 18.9. HRMS (ESI) calculated for $[M+H]^+$: 321.1809, found 321.1801.



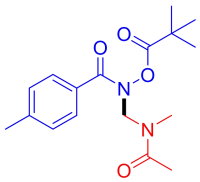
2-bromo-*N*-((*N*-methylacetamido)methyl)-*N*-(pivaloyloxy)benzamide (3ca): light yellow oil (75.8 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.53 (m, 1H), 7.37-7.22 (m, 3H), 5.49 (s, 2H), 3.22 (s, 2.3H), 3.08 (s, 0.7H), 2.22 (s, 0.7H), 2.08 (s, 2.3H), 0.86 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 175.6, 172.1, 168.9, 135.8, 135.4, 132.5, 132.3, 131.2, 130.9, 128.3, 128.1, 127.1, 127.0, 119.3, 119.2, 61.5, 56.7, 38.1, 37.8, 35.6, 33.5, 29.59, 26.2, 21.5, 21.2. HRMS (ESI) calculated for $[M+H]^+$: 385.0757, found 385.0758.



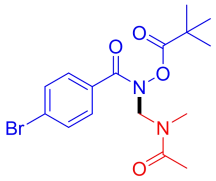
3-methyl-*N*-((*N*-methylacetamido)methyl)-*N*-(pivaloyloxy)benzamide (3da): light yellow oil (64.1 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.20 (m, 4H), 5.44 (s, 2H), 3.17 (s, 2.2H), 3.04 (s, 0.8H), 2.35 (s, 3H), 2.19 (s, 0.8H), 2.07 (s, 2.2H), 0.99 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 175.7, 172.0, 171.5, 171.3, 170.9, 137.9, 137.7, 133.0, 132.5, 131.9, 131.5, 128.3, 128.2, 128.0, 127.8, 124.9, 124.8, 62.7, 57.8, 38.1, 38.0, 35.5, 33.1, 29.6, 26.4, 21.6, 21.2. HRMS (ESI) calculated for $[M+H]^+$: 321.1809 found 321.1803.



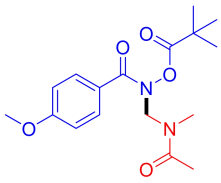
3-bromo-*N*-((*N*-methylacetamido)methyl)-*N*-(pivaloyloxy)benzamide (3ea): light yellow solid (74.3 mg, 99% yield). m.p. 66.8-94.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.44 (m, 3H), 7.32-7.26 (m, 1H), 5.43 (s, 2H), 3.18 (s, 2.4H), 3.04 (s, 0.6H), 2.21 (s, 0.6H), 2.08 (s, 2.4H), 1.01 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 175.9, 175.7, 172.2, 170.9, 169.8, 169.5, 134.9, 134.4, 134.2, 133.9, 130.8, 130.7, 129.9, 129.7, 126.6, 126.5, 121.9, 121.8, 62.7, 57.9, 38.2, 38.0, 35.7, 33.2, 26.5, 26.5, 21.6, 21.3. HRMS (ESI) calculated for $[M+H]^+$: 385.0757, found 385.0750.



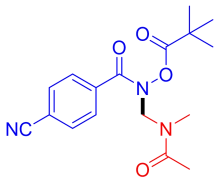
4-methyl-*N*-((*N*-methylacetamido)methyl)-*N*-(pivaloyloxy)benzamide (3fa): light yellow solid (63.6 mg, 99% yield). m.p. 39.7-40.4 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.0 Hz, 2H), 7.18 (t, J = 9.5 Hz, 2H), 5.43 (s, 2H), 3.16 (s, 2.2H), 3.03 (s, 0.8H), 2.36 (s, 3H), 2.19 (s, 0.8H), 2.06 (s, 2.2H), 1.01 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 175.9, 175.8, 172.0, 171.4, 171.3, 170.9, 141.8, 141.3, 130.1, 129.7, 128.7, 128.5, 128.0, 127.9, 62.9, 57.9, 38.1, 38.0, 35.5, 33.1, 29.6, 26.5, 21.6, 21.4, 21.2. HRMS (ESI) calculated for $[M+H]^+$: 321.1809, found 321.1817.



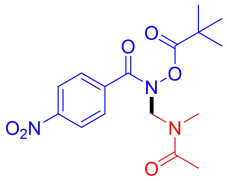
4-bromo-*N*-((*N*-methylacetamido)methyl)-*N*-(pivaloyloxy)benzamide (3ga): light yellow solid (75.2 mg, 99% yield). m.p. 62.9-67.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.39 (m, 4H), 5.42 (s, 2H), 3.17 (s, 2.4H), 3.03 (s, 0.6H), 2.20 (s, 0.6H), 2.07 (s, 2.4H), 1.01 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 175.9, 175.7, 172.1, 170.8, 170.4, 170.3, 131.9, 131.4, 131.4, 131.2, 129.5, 129.5, 125.9, 125.4, 62.8, 57.9, 38.1, 38.0, 35.7, 33.2, 29.60, 26.5, 21.6, 21.3. HRMS (ESI) calculated for $[M+H]^+$: 385.0757, found 385.0749.



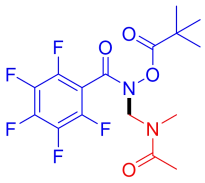
4-methoxy-*N*-((*N*-methylacetamido)methyl)-*N*-(pivaloyloxy)benzamide (3ha): light yellow oil (67.3 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8.5 Hz, 2H), 6.88 (t, J = 9.0 Hz, 2H), 5.43 (s, 2H), 3.92 (s, 0.6H), 3.82 (s, 2.4H), 3.16 (s, 2.2H), 3.04 (s, 0.8H), 2.20 (s, 0.8H), 2.07 (s, 2.2H), 1.04 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.0, 175.9, 172.1, 171.1, 162.1, 161.8, 133.3, 130.3, 130.1, 129.4, 126.1, 125.1, 124.5, 113.4, 113.2, 111.0, 110.8, 63.1, 58.1, 56.3, 55.4, 55.3, 38.2, 38.1, 35.6, 33.1, 29.6, 26.6, 21.6, 21.3. HRMS (ESI) calculated for $[M+H]^+$: 337.1758, found 337.1752.



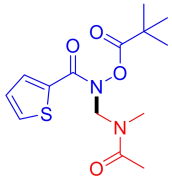
4-cyano-*N*-((*N*-methylacetamido)methyl)-*N*-(pivaloyloxy)benzamide (3ia): light yellow solid (6 mg, 90% yield). m.p. 106.4-107.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, J = 8.5 Hz, 2H), 7.72 (d, J = 8.5 Hz, 2H), 5.45 (s, 2H), 3.20 (s, 2.5H), 3.06 (s, 0.5H), 2.23 (s, 0.5H), 2.09 (s, 2.5H), 0.98 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 175.9, 175.7, 172.2, 170.8, 169.4, 169.2, 149.2, 149.0, 139.2, 138.7, 129.0, 128.9, 123.3, 123.4, 62.8, 58.1, 38.1, 38.0, 35.8, 33.3, 29.6, 26.5, 26.4, 21.6, 21.3. HRMS (ESI) calculated for $[M+H]^+$: 332.1605, found 332.1601.



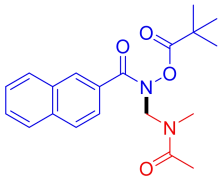
***N*-((*N*-methylacetamido)methyl)-4-nitro-*N*-(pivaloyloxy)benzamide (3ja):** light yellow solid (27.6 mg, 40% yield). m.p. 96.5-100.2 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (t, *J* = 10.0 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 5.44 (s, 2H), 3.20 (s, 2.5H), 3.06 (s, 0.5H), 2.22 (s, 0.5H), 2.08 (s, 2.5H), 0.98 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 175.7, 172.2, 170.7, 169.4, 169.2, 149.0, 139.2, 129.00, 128.9, 123.3, 123.2, 62.8, 58.1, 38.1, 38.0, 35.8, 33.3, 26.9, 26.4, 21.6, 21.3. HRMS (ESI) calculated for $[M+Na]^+$: 374.1323, found 374.1332.



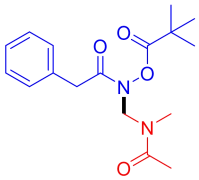
2,3,4,5,6-pentafluoro-*N*-((*N*-methylacetamido)methyl)-*N*-(pivaloyloxy)benzamide (3ka): white solid (71.1 mg, 91% yield). m.p. 117.1-117.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 (s, 2H), 3.17 (s, 2.6H), 3.01 (s, 0.4H), 2.19 (s, 0.4H), 2.08 (s, 2.6H), 1.04 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.5, 172.2, 159.1, 144.4, 143.3, 142.4, 141.3, 138.3, 136.3, 109.1, 57.1, 38.0, 35.3, 26.4, 21.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -137.79 – -139.05 (m, *J* = 52.5 Hz, 3F), -150.19 (t, *J* = 20.3 Hz, 1F), -160.41 (s, 1F).



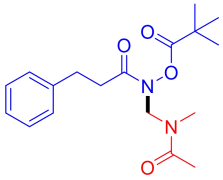
***N*-((*N*-methylacetamido)methyl)-*N*-(pivaloyloxy)thiophene-2-carboxamide (3la):** light yellow oil (62.4 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77-7.41 (m, 2H), 7.12-7.03 (m, 1H), 5.46 (s, 2H), 3.15 (s, 2.5H), 3.03 (s, 0.5H), 2.22 (s, 0.5H), 2.08 (s, 2.5H), 1.26 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2, 176.1, 175.9, 172.1, 170.9, 163.8, 163.6, 162.3, 134.4, 133.4, 133.4, 133.3, 132.9, 132.7, 131.7, 131.5, 130.0, 127.0, 126.9, 119.9, 63.2, 58.2, 58.1, 38.5, 38.4, 35.4, 33.1, 29.6, 26.9, 21.6, 21.3. HRMS (ESI) calculated for $[M+H]^+$: 313.1217, found 313.1224.



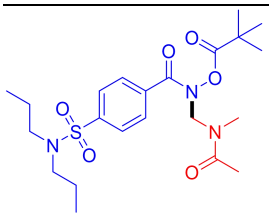
***N*-((*N*-methylacetamido)methyl)-*N*-(pivaloyloxy)-2-naphthamide (3ma):** light yellow oil (70.3 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.92-7.80 (m, 3H), 7.65-7.48 (m, 3H), 5.50 (s, 2H), 3.21 (s, 2.3H), 3.08 (s, 0.7H), 2.22 (s, 0.7H), 2.08 (s, 2.3H), 0.93 (s, 9H). 13C NMR (126 MHz, CDCl3) δ 176.0, 175.8, 172.1, 171.4, 171.2, 170.9, 134.3, 134.2, 132.1, 130.2, 129.7, 128.6, 128.5, 128.3, 128.0, 127.8, 127.7, 127.7, 127.6, 126.9, 126.7, 124.5, 124.4, 63.0, 58.0, 38.1, 38.0, 35.6, 33.2, 29.6, 26.5, 21.6, 21.3. HRMS (ESI) calculated for $[M+H]^+$: 357.1809, found 357.1802.



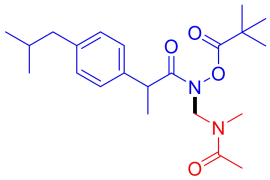
***N*-((*N*-methylacetamido)methyl)-2-phenyl-*N*-(pivaloyloxy)acetamide (3na):** light yellow oil (63.3 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.16 (m, 5H), 5.34 (s, 2H), 3.57 (s, 2H), 3.04 (s, 2.5H), 2.92 (s, 0.5H), 2.15 (s, 0.5H), 2.04 (s, 2.5H), 1.30 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 172.0, 170.7, 133.4, 132.9, 129.3, 128.6, 128.5, 127.3, 127.1, 57.1, 38.6, 38.4, 38.3, 35.3, 32.9, 29.6, 26.9, 21.5, 21.2. HRMS (ESI) calculated for $[M+H]^+$: 321.1809, found 321.1804.



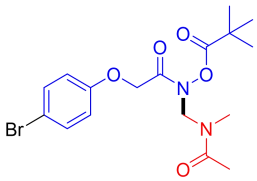
***N*-(benzoyloxy)-*N*-((*N*-methylacetamido)methyl)-3-phenylpropanamide (3oa):** light yellow oil (47.8 mg, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07-7.98 (m, 2H), 7.72-7.61 (m, 1H), 7.56-7.44 (m, 2H), 7.30 -7.10 (m, 5H), 5.43 (s, 2H), 3.11 (s, 2H), 3.02-2.91 (m, 3H), 2.70-2.56 (m, 2H), 2.07 (s, 1H), 2.00 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 170.9, 164.3, 140.5, 140.3, 135.1, 134.3, 130.1, 129.2, 128.8, 128.5, 128.4, 128.3, 126.6, 126.3, 126.2, 125.7, 61.5, 57.5, 35.4, 33.8, 33.7, 33.2, 30.1, 21.5, 21.0. HRMS (ESI) calculated for $[M+H]^+$: 355.1652, found 355.1661.



4-(*N*,*N*-dipropylsulfamoyl)-*N*-((*N*-methylacetamido)methyl)-*N*-(pivaloyloxy)benzamide (3pa): colorless oil (90.6 mg, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 5.44 (s, 2H), 3.19 (s, 2.4H), 3.05 (t, *J* = 7.5 Hz, 4.6H), 2.22 (s, 0.6H), 2.08 (s, 2.4H), 1.59-1.49 (m, 4H), 0.97 (s, 9H), 0.87 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 172.1, 170.0, 142.8, 142.4, 136.8, 136.3, 128.5, 128.4, 126.8, 126.6, 62.7, 57.9, 50.0, 38.1, 38.0, 35.7, 33.3, 26.5, 26.4, 21.9, 21.6, 21.3, 11.1. HRMS (ESI) calculated for $[M+H]^+$: 470.2319, found 470.2328.

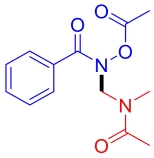


2-(4-isobutylphenyl)-*N*-((*N*-methylacetamido)methyl)-*N*-(pivaloyloxy)propanamide (3qa): light yellow oil (60.4 mg, 77% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.04 (m, 4H), 5.33 (s, 2H), 3.83 – 3.57 (m, 1H), 2.98 (s, 2.4H), 2.81 (s, 0.6H), 2.44 (d, *J* = 7.0 Hz, 2H), 2.12 (s, 0.6H), 2.01 (s, 2.4H), 1.90 – 1.77 (m, 1H), 1.44 (d, *J* = 7.0 Hz, 3H), 1.24 (s, 9H), 0.88 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 171.8, 170.6, 140.7, 140.4, 137.4, 137.0, 129.5, 129.3, 128.1, 127.4, 127.0, 126.9, 63.8, 57.0, 44.9, 44.9, 41.6, 38.3, 38.2, 36.4, 35.0, 30.1, 26.9, 26.8, 22.3, 22.2, 21.5, 21.2, 20.4, 19.5. HRMS (ESI) calculated for $[M+Na]^+$: 413.2411, found 413.2403.

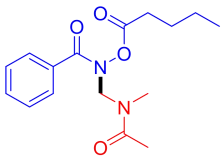


2-(4-chlorophenoxy)-*N*-((*N*-methylacetamido)methyl)-*N*-(pivaloyloxy)acetamide (3ra): light yellow oil (41.0 mg, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.37 (m, 2H), 6.85-6.75 (m, 2H), 5.35 (s, 2H), 4.59 (s, 2H), 3.09 (s, 2.6H), 2.97 (s, 0.4H), 2.18 (s, 0.4H), 2.08 (s, 2.6H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 175.7, 175.0, 172.2, 170.7, 168.4, 157.0, 156.8, 132.5,

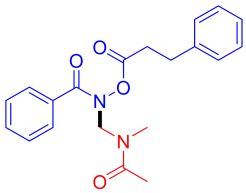
132.4, 116.4, 114.3, 114.0, 65.0, 60.3, 57.5, 38.6, 38.4, 35.4, 33.1, 27.0, 26.9, 21.5, 21.2, 14.1. HRMS (ESI) calculated for $[M+H]^+$: 415.0863, found 415.0866.



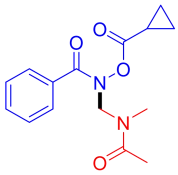
***N*-acetoxy-*N*-((*N*-methylacetamido)methyl)benzamide (3sa):** light yellow oil (52.9 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.56 (m, 2H), 7.52-7.36 (m, 3H), 5.41 (s, 2H), 3.16 (s, 2.4H), 3.03 (s, 0.6H), 2.18 (s, 0.6H), 2.08 (s, 2.4H), 1.96 (s, 0.6H), 1.93 (s, 2.4H). 13C NMR (126 MHz, CDCl3) δ 172.4, 170.8, 170.4, 168.7, 168.2, 132.8, 132.4, 131.5, 131.2, 128.3, 128.1, 127.8, 63.0, 58.4, 35.8, 33.0, 29.6, 21.6, 21.0, 18.2, 18.1. HRMS (ESI) calculated for $[M+H]^+$: 265.1183, found 265.1191.



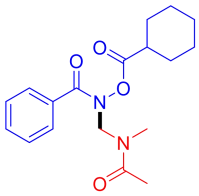
***N*-((*N*-methylacetamido)methyl)-*N*-(pentanoyloxy)benzamide (3ta):** light yellow oil (60.4 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 7.5 Hz, 2H), 7.51-7.35 (m, 3H), 5.42 (s, 2H), 3.17 (s, 2.3H), 3.03 (s, 0.7H), 2.18 (s, 2.7H), 2.07 (s, 2.3H), 1.43-1.32 (m, 2H), 1.13 -1.01 (m, 2H), 0.77 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 171.6, 171.2, 171.0, 170.8, 170.7, 132.9, 132.5, 131.3, 131.0, 128.2, 128.0, 127.9, 127.8, 62.8, 58.2, 35.7, 33.0, 31.1, 29.6, 26.1, 26.0, 21.7, 21.6, 21.1, 13.4. HRMS (ESI) calculated for $[M+H]^+$: 307.1652, found 307.1662.



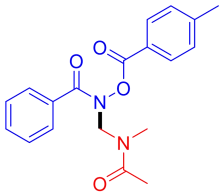
***N*-((*N*-methylacetamido)methyl)-*N*-((3-phenylpropanoyl)oxy)benzamide (3ua):** light yellow oil (70.3 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 7.5 Hz, 2H), 7.46-7.32 (m, 3H), 7.26-7.14 (m, 3H), 7.04 (d, J = 7.0 Hz, 2H), 5.42 (s, 2H), 3.14 (s, 2.3H), 2.94 (s, 0.7H), 2.77 -2.69 (m, 2H), 2.60-2.42 (m, 2H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4, 170.9, 170.9, 170.5, 139.5, 139.0, 132.8, 132.4, 131.5, 131.1, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 126.7, 126.3, 63.0, 58.4, 35.8, 33.1, 32.9, 29.9, 29.8, 29.5, 21.6, 20.9. HRMS (ESI) calculated for $[M+H]^+$: 355.1652, found 355.1643.



***N*-((cyclopropanecarbonyl)oxy)-*N*-((*N*-methylacetamido)methyl)benzamide (3va):** light yellow oil (57.7 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.5 Hz, 2H), 7.52-7.36 (m, 3H), 5.43 (s, 2H), 3.15 (s, 2H), 3.04 (s, 1H), 2.19 (s, 1H), 2.08 (s, 2H), 1.58-1.48 (m, 1H), 0.92-0.79 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 172.6, 172.2, 171.0, 170.7, 132.9, 132.5, 131.3, 131.0, 128.1, 128.0, 127.9, 127.8, 62.8, 58.4, 35.7, 33.1, 21.6, 21.0, 10.7, 10.5, 9.3, 9.0. HRMS (ESI) calculated for $[M+H]^+$: 291.1339, found 291.1337.

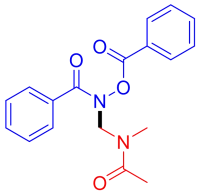


***N*-((cyclohexanecarbonyl)oxy)-*N*-((*N*-methylacetamido)methyl)benzamide (3wa):** light yellow oil (61.9 mg, 94% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.5 Hz, 2H), 7.48-7.34 (m, 3H), 5.43 (s, 2H), 3.17 (s, 2.3H), 3.03 (s, 0.7H), 2.18 (s, 1.7H), 2.06 (s, 2.3H), 1.74-1.43 (m, 5H), 1.14 (s, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 173.4, 172.2, 171.2, 170.9, 170.8, 133.0, 132.6, 131.2, 130.9, 128.5, 128.1, 127.9, 127.8, 127.7, 127.5, 62.7, 60.3, 57.9, 40.9, 40.7, 35.6, 33.0, 29.6, 28.1, 28.0, 25.2, 25.1, 24.8, 24.8, 21.5, 21.1, 14.1. HRMS (ESI) calculated for $[M+H]^+$: 375.2278, found 375.2281.

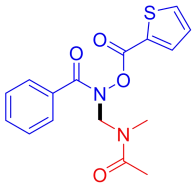


***N*-((*N*-methylacetamido)methyl)-*N*-((4-methylbenzoyl)oxy)benzamide (3xa):** light yellow oil (67.7 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.73 (m, 2H), 7.67-7.60 (m, 2H), 7.58-7.29 (m, 4H), 7.24 -7.16 (m, 2H), 5.65-5.35 (m, 2H), 3.21 (s, 2H), 3.07 (s, 1H), 2.39 (s, 1H), 2.36 (s, 2H), 2.11 (s, 1H), 2.02 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 171.0, 170.8, 164.8, 164.3, 145.9, 145.0, 134.0, 132.8, 132.4, 131.4, 131.1, 129.8, 129.6, 129.3, 128.9, 128.5, 128.2, 128.1, 128.0, 127.9, 123.8, 123.0, 62.9, 60.3, 58.8, 35.8, 33.2, 29.6, 21.7, 21.5, 21.0, 14.1. HRMS

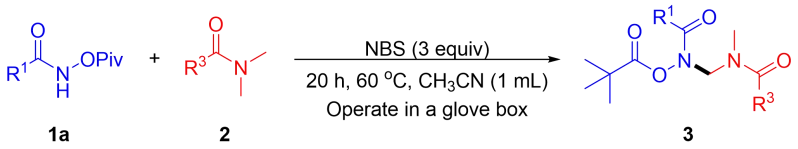
(ESI) calculated for $[M+H]^+$: 341.1496, found 341.1486.



***N*-(benzoyloxy)-*N*-((*N*-methylacetamido)methyl)benzamide (3ya):** light yellow oil (58.5 mg, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91-7.83 (m, 2H), 7.68-7.52 (m, 3H), 7.46-7.29 (m, 5H), 5.56 (s, 2H), 3.22 (s, 2H), 3.08 (s, 1H), 2.12 (s, 1H), 2.03 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.2, 171.1, 171.1, 170.8, 164.8, 164.4, 134.7, 134.0, 132.8, 132.3, 131.5, 131.2, 129.8, 128.9, 128.6, 128.2, 128.1, 127.9, 126.7, 125.9, 63.1, 58.9, 35.8, 33.2, 21.5, 21.0. HRMS (ESI) calculated for $[M+H]^+$: 327.1339, found 327.1347.



***N*-((*N*-methylacetamido)methyl)-*N*-((thiophene-2-carbonyl)oxy)benzamide (3za):** light yellow oil (64.9 mg, 97% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81-7.75 (m, 1H), 7.69-7.58 (m, 3H), 7.45-7.30 (m, 3H), 7.14-7.04 (m, 1H), 5.54 (s, 2H), 3.20 (s, 2H), 3.07 (s, 1H), 2.15 (s, 1H), 2.04 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 171.0, 170.9, 170.6, 160.1, 159.8, 135.9, 135.4, 135.2, 134.4, 132.6, 132.1, 131.5, 131.2, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.6, 63.1, 58.9, 35.8, 33.2, 21.5, 21.1. HRMS (ESI) calculated for $[M+H]^+$: 333.0904, found 333.0901.



General Procedure B: A flame-dried 10 mL Schlenk tube was cooled to room temperature and filled with N_2. To this tube were added *N*-acyloxyamide **1** (0.20 mmol) and NBS (2.0 equiv). Then, *N,N*-dimethylamide **2** (10.0 equiv) and CH_3CN (1.0 mL) were added to this tube in the glove box. The tube was then removed and the mixture was stirred at 60 °C for 20 to 30 hours. After completion, the reaction mixture was cooled to room temperature, and the residue was diluted with ethyl acetate (10 mL). The resulting solution was washed with saturated sodium carbonate solution (5 mL × 3). The organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography [300-400 mesh silica, ethyl acetate/petroleum ether = 2:1 to 1:3] to afford the desired methylenebisamide product.

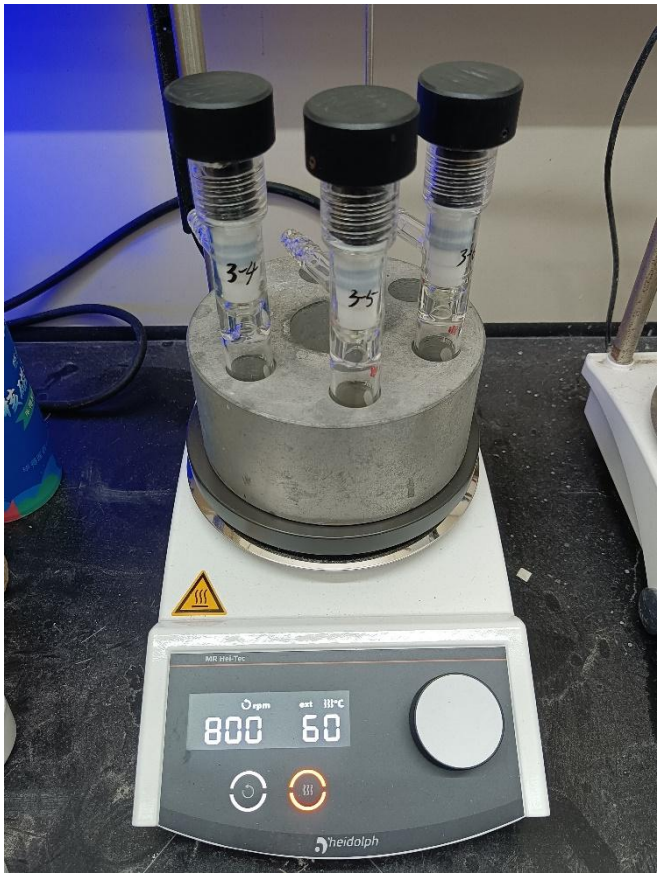
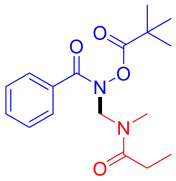
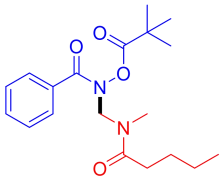


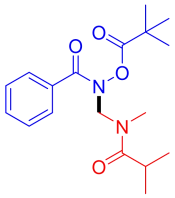
Figure S2. reaction unit



***N*-((*N*-methylpropionamido)methyl)-*N*-(pivaloyloxy)benzamide (3ab):** light yellow oil (53.1 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.49 (m, 2H), 7.48-7.34 (m, 3H), 5.46 (s, 2H), 3.16 (s, 2.4H), 3.05 (s, 0.6H), 2.49-2.43 (m, 0.4H), 2.34-2.28 (m, 1.6H), 1.10 (t, *J* = 7.5 Hz, 3H), 0.96 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 175.7, 175.0, 174.1, 171.4, 133.2, 132.7, 131.1, 130.7, 128.0, 127.9, 127.8, 127.6, 61.7, 58.1, 38.1, 37.9, 37.1, 34.7, 33.3, 32.6, 31.8, 29.9, 29.6, 29.3, 27.0, 26.5, 26.4, 26.1, 22.6, 19.6, 14.0, 9.2, 8.8. HRMS (ESI) calculated for $[M+H]^+$: 321.1809, found 321.1799.

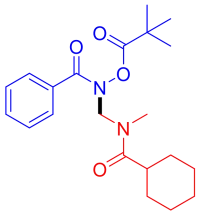


***N*-((*N*-methylpentanamido)methyl)-*N*-(pivaloyloxy)benzamide (3ac):** light yellow oil (70.3 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.46-7.34 (m, 3H), 5.46 (s, 2H), 3.17 (s, 2.4H), 3.04 (s, 0.6H), 2.42 (t, *J* = 7.5 Hz, 0.4H), 2.29 (t, *J* = 7.5 Hz, 1.6H), 1.68-1.53 (m, 2H), 1.41-1.30 (m, 2H), 0.96 (s, 9H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 175.8, 174.5, 173.6, 171.4, 171.2, 133.2, 132.8, 131.2, 130.8, 128.1, 127.9, 127.8, 127.7, 61.9, 58.1, 38.1, 37.9, 34.8, 33.3, 33.0, 32.7, 27.3, 26.8, 26.5, 22.4, 13.8. HRMS (ESI) calculated for $[M+H]^+$: 349.2122, found 349.2131.

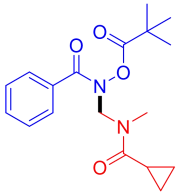


***N*-((*N*-methylisobutyramido)methyl)-*N*-(pivaloyloxy)benzamide (3ad):** white solid (52.8 mg, 79% yield). m.p. 58.8-60.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.0 Hz, 2H), 7.45-7.34 (m, 3H), 5.47 (s, 2H), 3.23 (s, 2.5H), 3.05 (s, 0.5H), 2.95-2.72 (m, 1H), 1.15 (d, *J* = 6.5 Hz, 1H), 1.10 (d, *J* = 6.5 Hz, 5H), 0.96 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.2, 175.9, 171.4, 133.3,

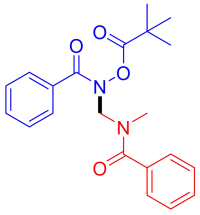
131.2, 130.7, 128.1, 127.9, 127.9, 127.6, 61.7, 58.3, 37.9, 34.6, 30.2, 26.5, 19.7, 19.0. HRMS (ESI) calculated for $[M+H]^+$: 335.1965, found 335.1971.



***N*-((*N*-methylcyclohexanecarboxamido)methyl)-*N*-(pivaloyloxy)benzamide (3ae):** light yellow solid (58.1 mg, 76% yield). m.p. 57.7-59.9 ℃. 1H NMR (500 MHz, CDCl3) δ 7.51 (d, J = 7.0 Hz, 2H), 7.47-7.34 (m, 3H), 5.45 (s, 2H), 3.22 (s, 2.5H), 3.03 (s, 0.5H), 2.62-2.44 (m, 1H), 1.83-1.67 (m, 5H), 1.48-1.22 (m, 5H), 0.95 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.2, 175.8, 171.3, 133.3, 132.7, 131.1, 130.6, 128.1, 127.9, 127.8, 127.6, 61.7, 58.2, 40.5, 40.3, 38.1, 37.9, 34.6, 33.5, 29.6, 28.9, 26.5, 25.7, 25.6. HRMS (ESI) calculated for $[M+H]^+$: 375.2278, found 375.2281.

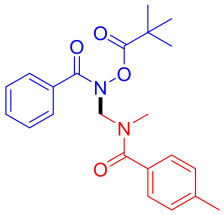


***N*-((*N*-methylcyclopropanecarboxamido)methyl)-*N*-(pivaloyloxy)benzamide (3af):** light yellow solid (47.1 mg, 72% yield). m.p. 77.1-81.8 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.0 Hz, 2H), 7.48-7.34 (m, 3H), 5.47 (s, 2H), 3.34 (s, 2.2H), 3.07 (s, 0.8H), 1.91-1.72 (m, 1H), 1.01-0.88 (m, 11H), 0.84-0.76 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 175.8, 174.9, 174.0, 171.4, 171.1, 133.3, 132.8, 131.1, 130.7, 128.1, 127.9, 127.8, 127.7, 61.6, 58.3, 38.1, 37.9, 34.8, 34.0, 26.4, 10.9, 8.4, 7.8. HRMS (ESI) calculated for $[M+H]^+$: 333.1809, found 333.1807.

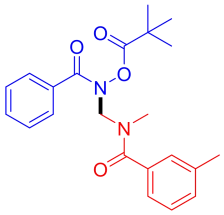


***N*-methyl-*N*-((*N*-(pivaloyloxy)benzamido)methyl)benzamide (3ag):** light yellow oil (63.9 mg, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.33 (m, 10H), 5.64 (s, 2H), 3.14 (s, 3H), 1.01 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2, 172.5, 171.4, 135.4, 133.1, 130.9, 129.9, 128.4, 128.0,

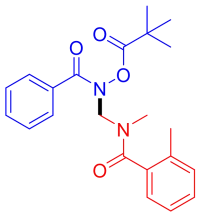
127.7, 126.8, 58.2, 38.0, 37.2, 26.5. HRMS (ESI) calculated for $[M+H]^+$: 369.1809, found 369.1813.



N,4-dimethyl-*N*-((*N*-(pivaloyloxy)benzamido)methyl)benzamide (3ah): white solid (47.9 mg, 63% yield). m.p. 83.2-86.8 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.14 (m, 9H), 5.63 (s, 2H), 3.16 (s, 3H), 2.37 (s, 3H), 1.00 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2, 172.6, 171.4, 140.1, 133.1, 132.4, 130.9, 129.0, 128.0, 127.7, 127.0, 58.2, 38.0, 37.3, 26.5, 21.3. HRMS (ESI) calculated for $[M+H]^+$: 383.1965, found 383.1975.

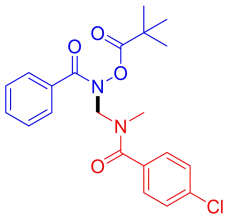


N,3-dimethyl-*N*-((*N*-(pivaloyloxy)benzamido)methyl)benzamide (3ai): colorless oil (36.4 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.34 (m, 5H), 7.32 – 7.11 (m, 4H), 5.63 (s, 2H), 3.14 (s, 3H), 2.36 (s, 3H), 1.01 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2, 172.7, 171.4, 138.3, 135.5, 133.2, 130.9, 130.6, 128.2, 128.0, 127.8, 127.4, 123.8, 58.2, 53.4, 38.1, 37.3, 26.5, 21.3. HRMS (ESI) calculated for $[M+H]^+$: 383.1965, found 383.1974.

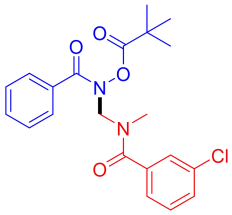


N,2-dimethyl-*N*-((*N*-(pivaloyloxy)benzamido)methyl)benzamide (3aj)： light yellow oil (42.6 mg, 56% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.06 (m, 9H), 5.64 (s, 1.6H), 5.32 (s, 0.2H), 3.27 (s, 0.5H), 2.99 (s, 2.5H), 2.32 (s, 3H), 1.03 (s, 7.5H), 0.83 (s, 1.5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.0, 172.6, 171.4, 135.7, 134.6, 133.9, 133.8, 133.0, 131.2, 130.9, 130.6, 130.4, 129.3, 129.0, 128.0, 127.9, 127.7, 126.3, 125.9, 125.7, 125.5, 122.0, 69.6, 63.3, 57.8, 46.0, 38.0, 37.9,

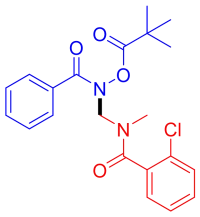
36.1, 32.2, 27.0, 26.5, 26.3, 19.1, 18.8, 8.5. HRMS (ESI) calculated for $[M+H]^+$: 383.1965, found 383.1964.



4-chloro-*N*-methyl-*N*-((*N*-(pivaloyloxy)benzamido)methyl)benzamide (3ak): light yellow solid (69.2 mg, 86% yield). m.p. 107.5-108.2 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.31 (m, 9H), 5.63 (s, 2H), 3.15 (s, 3H), 0.99 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 171.3, 135.9, 133.7, 132.9, 130.9, 128.6, 128.3, 127.9, 127.7, 58.2, 38.0, 37.3, 26.4. HRMS (ESI) calculated for $[M+Na]^+$: 425.1239, found 425.1244.

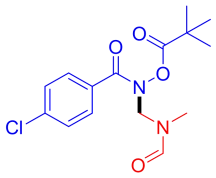


3-chloro-*N*-methyl-*N*-((*N*-(pivaloyloxy)benzamido)methyl)benzamide (3al): light yellow oil (75.0 mg, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.22 (m, 9H), 5.63 (s, 2H), 3.14 (s, 3H), 1.00 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 171.4, 170.9, 137.1, 134.5, 132.9, 130.9, 123.0, 129.8, 128.0, 127.7, 126.9, 124.8, 58.1, 38.0, 37.2, 26.5. HRMS (ESI) calculated for $[M+Na]^+$: 425.1239, found 425.1248.



2-chloro-*N*-methyl-*N*-((*N*-(pivaloyloxy)benzamido)methyl)benzamide (3am): light yellow oil (35.4 mg, 45% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.31 (m, 9H), 5.63 (s, 2H), 3.27 (s, 0.5H), 3.03 (s, 2.5H), 1.03 (s, 7.5H), 0.87 (s, 1.5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 171.2, 169.7, 168.7, 135.5, 134.9, 133.0, 132.5, 131.2, 130.9, 130.7, 130.6, 130.4, 130.0, 129.7, 128.6,

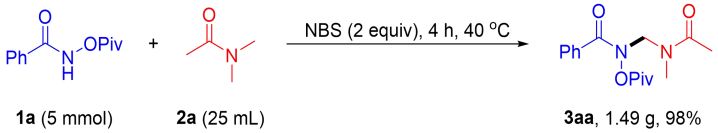
128.1, 128.0, 127.9, 127.7, 127.5, 127.2, 127.1, 63.3, 57.8, 38.1, 38.0, 35.9, 32.5, 26.6, 26.4. HRMS (ESI) calculated for $[M+H]^+$: 425.1239, found 425.1229.



4-chloro-*N*-((*N*-methylformamido)methyl)-*N*-(pivaloyloxy)benzamide (3a'n): light yellow oil (19.2 mg, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 5.27 (s, 2H), 3.11 (s, 1.1H), 3.01 (s, 1.9H), 1.03 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 175.6, 170.6, 170.4, 163.7, 162.8, 137.7, 137.4, 131.2, 130.9, 129.4, 128.6, 128.5, 128.3, 61.9, 55.2, 38.2, 38.0, 34.1, 29.8, 27.3, 26.6.

V. Applications of the methodology:

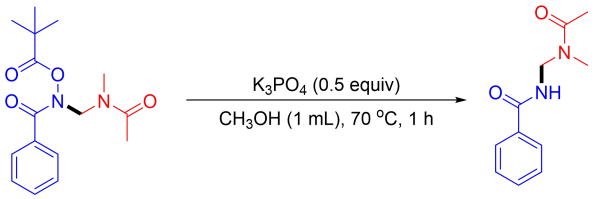
Gram-scale reaction：



1a (5 mmol) **2a** (25 mL) **3aa**, 1.49 g, 98%

A flame-dried 100 mL Schlenk tube was cooled to room temperature and filled with N_2. To this flask, *N*-(pivaloyloxy)benzamide **1a** (5 mmol) and NBS (2.0 equiv) were added. DMAC (25 mL) was added by syringe under a flow of nitrogen. The resulting mixture was stirred at 40 °C for 4 hours. After completion, the reaction mixture was cooled to room temperature, and the residue was diluted with ethyl acetate (50 mL). The resulting solution was washed with a saturated sodium carbonate solution (10 mL, three times). The organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel 300-400 mesh, ethyl acetate/petroleum ether = 2:1 to 1:3) to afford the desired methylenebisamide product (1.49 g, 98% yield).

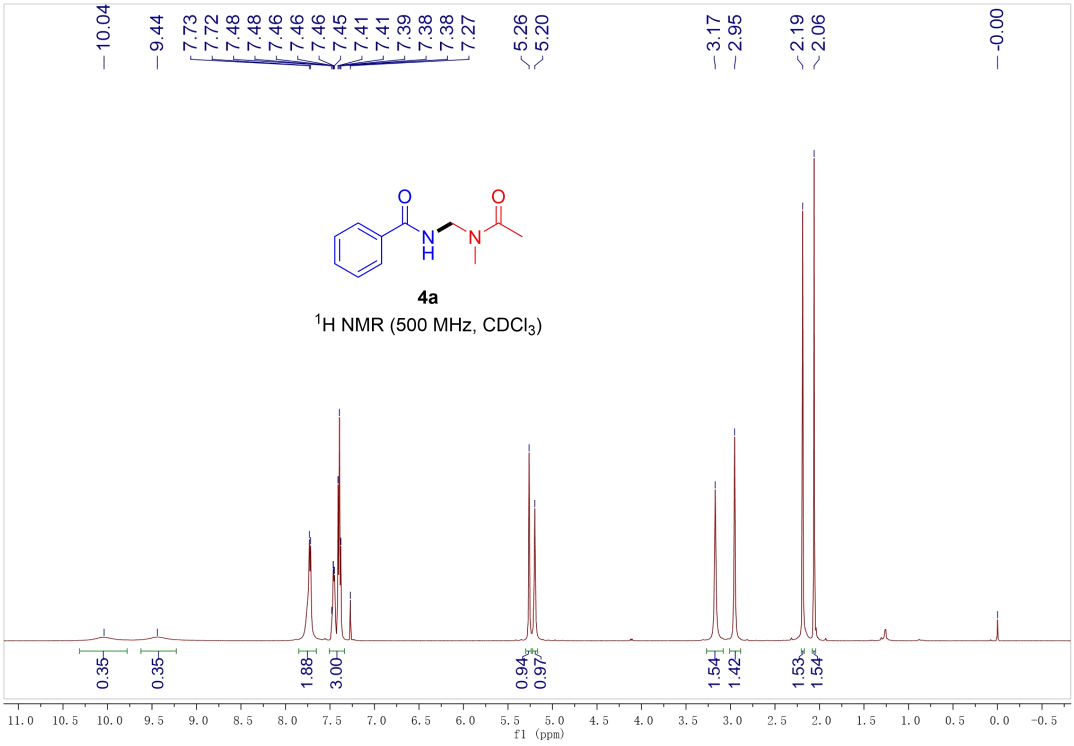
***Removal of acyloxy*:**

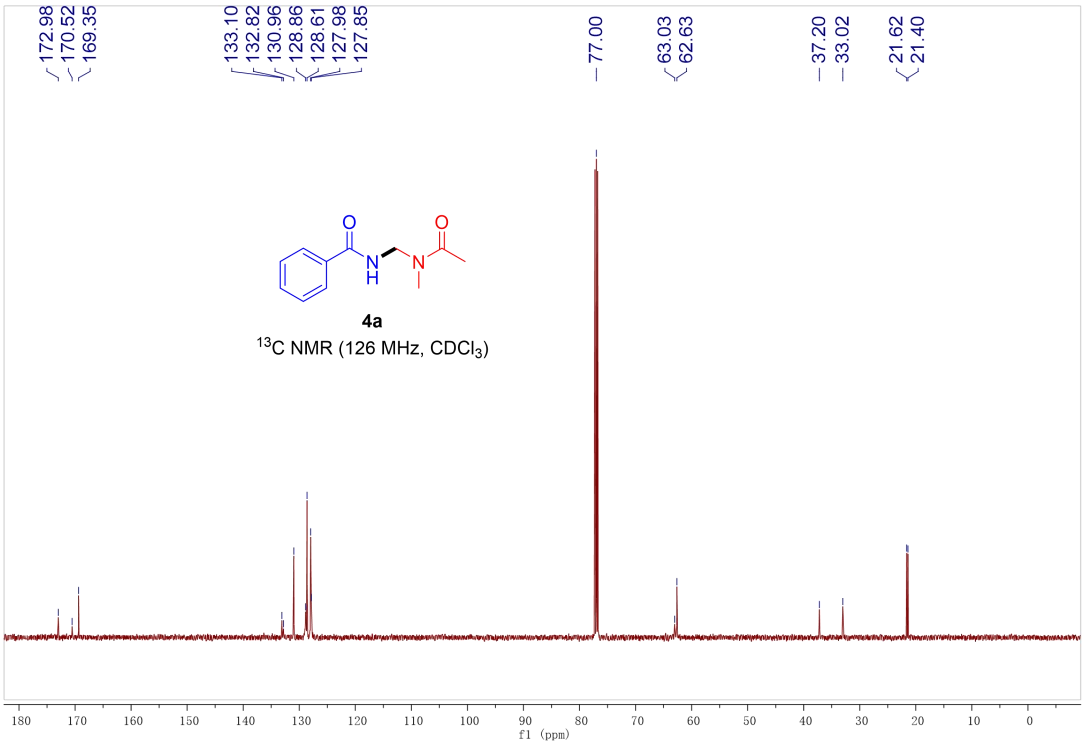


(0.3 mmol) 53.7 mg, 86%

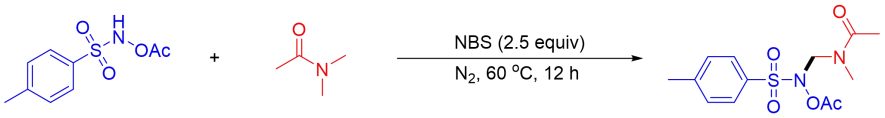
A flame-dried 10 mL Schlenk tube was cooled to room temperature. To this Schlenk tube were added **3aa** (0.3 mmol), K_3PO_4 (0.5 equiv), and CH_3OH (1.0 mL). The resulting mixture was stirred at 70 °C for 1 hour. The reaction mixture was cooled to room temperature, and the residue was concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel 300-400 mesh, ethyl acetate) to afford the desired product (53.7 mg, 86% yield).

***N*-((*N*-methylacetamido)methyl)benzamide (4a):** light yellow oil (53.7 mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (s, 0.35H), 9.44 (s, 0.35H), 7.72 (d, J = 7.5 Hz, 2H), 7.51-7.34 (m, 3H), 5.26 (s, 1H), 5.20 (s, 1H), 3.17 (s, 1.5H), 2.95 (s, 1.5H), 2.19 (s, 1.5H), 2.06 (s, 1.5H). 13C NMR (126 MHz, CDCl3) δ 173.0, 170.5, 169.4, 133.1, 132.8, 131.0, 128.9, 128.6, 128.0, 127.9, 63.0, 62.6, 37.2, 33.0, 21.6, 21.4. HRMS (ESI) calculated for $[M+H]^+$: 207.1128, found 207.1136.




172.98
170.52
169.35
133.10
132.82
130.96
128.86
128.61
127.98
127.85
77.00
63.03
62.63
37.20
33.02
21.62
21.40
O
N
H
N
O
4a
13C NMR (126 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

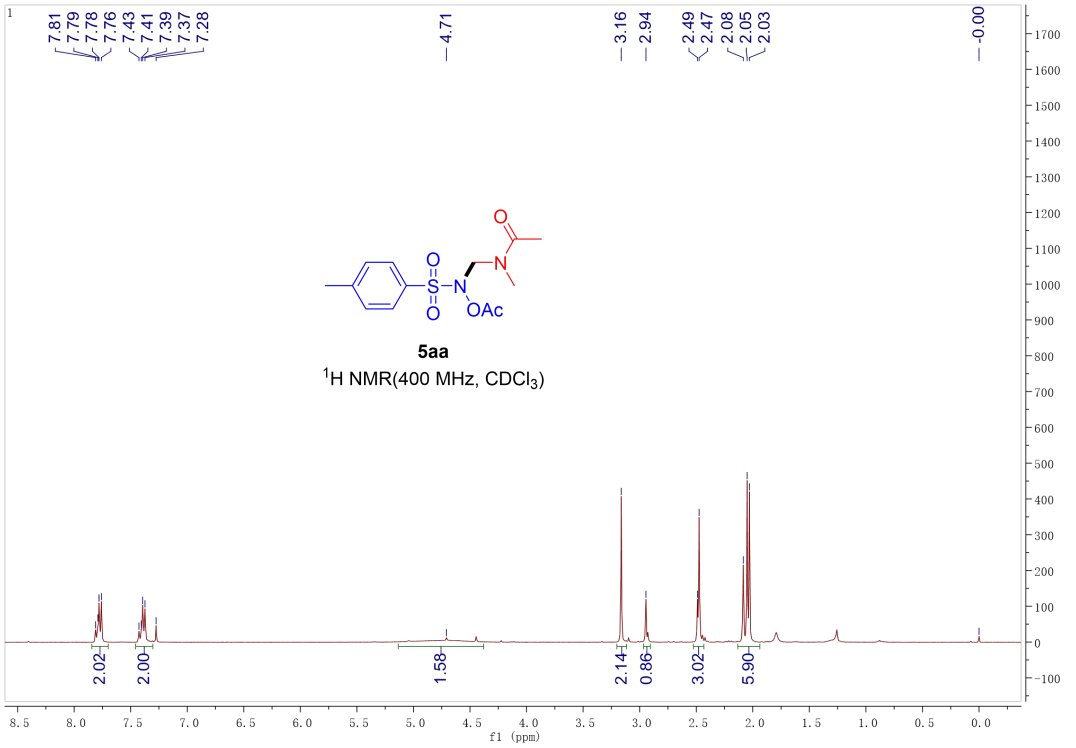
***Sulfonamidation*：**



5a (0.3 mmol) (1 mL) **5aa**, 57%

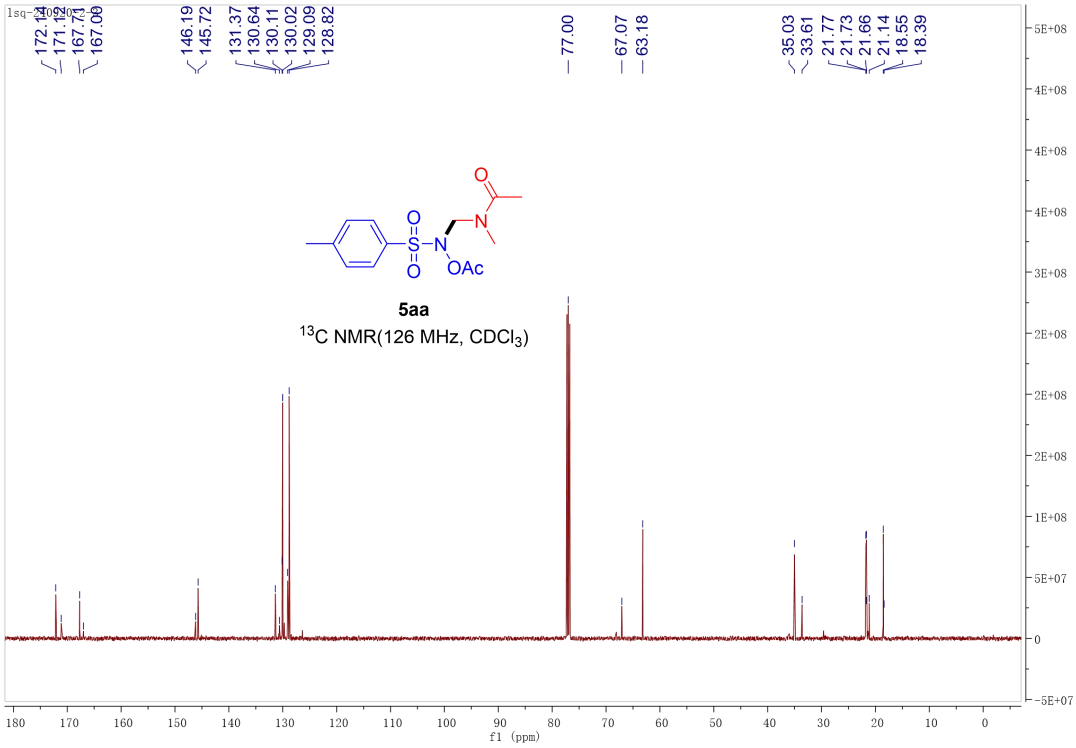
A flame-dried 10 mL Schlenk tube was cooled to room temperature and filled with N_2. To this Schlenk tube were added *N*-hydroxy-4-methylbenzenesulfonamide **5a** (0.3 mmol), and NBS (2.5 equiv). DMAc (1.0 mL) was added by syringe under a flow of nitrogen. The resulting mixture was stirred at 60 °C for 12 hours. After completion, the reaction mixture was cooled to room temperature, and the residue was diluted with ethyl acetate (10 mL). The resulting solution was washed with a saturated sodium carbonate solution (5 mL, three times). The organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel 300-400 mesh, ethyl acetate/petroleum ether = 2:1 to 1:3) to afford the desired methylenebisamide product **5aa** (52.4 mg, 57% yield).

***N*-(((*N*-acetoxy-4-methylphenyl)sulfonamido)methyl)-*N*-methylacetamide (5aa):** Colorless oil (52.4 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.70 (m, 2H), 7.46 – 7.30 (m, 2H), 4.71 (s, 2H), 3.16 (s, 2.14H), 2.94 (s, 0.86H), 2.48 (s, 3H), 2.13 – 1.94 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 171.1, 167.7, 167.0, 146.2, 145.7, 131.4, 130.6, 130.1, 130.0, 129.1, 128.8, 67.1, 63.2, 35.0, 33.6, 21.8, 21.7, 21.7, 21.1, 18.6, 18.4. HRMS (ESI) calculated for $[M+H]^+$: 315.1009, found 315.1012.



5aa

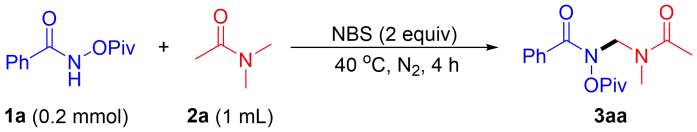
^{1}H NMR(400 MHz, $CDCl_3$)



5aa

^{13}C NMR(126 MHz, $CDCl_3$)

VI. Mechanistic studies:



Condition	Standard Condition	no NBS	no **1a**	no **1a** and no NBS
Code	A	B	C	D

Solution	HBr/DMAC (0.4 mmol/mL)	Br_2/DMAC (0.2 mmol/mL)	Succinimide/DMAC (0.4 mmol/mL)
Code	E	F	G

Figure S3. The states of the different solutions

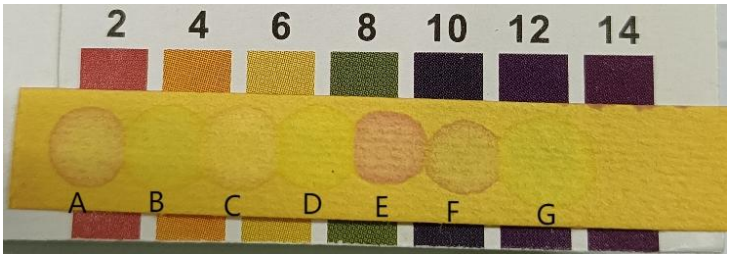


Figure S4. Acid detection with pH test paper

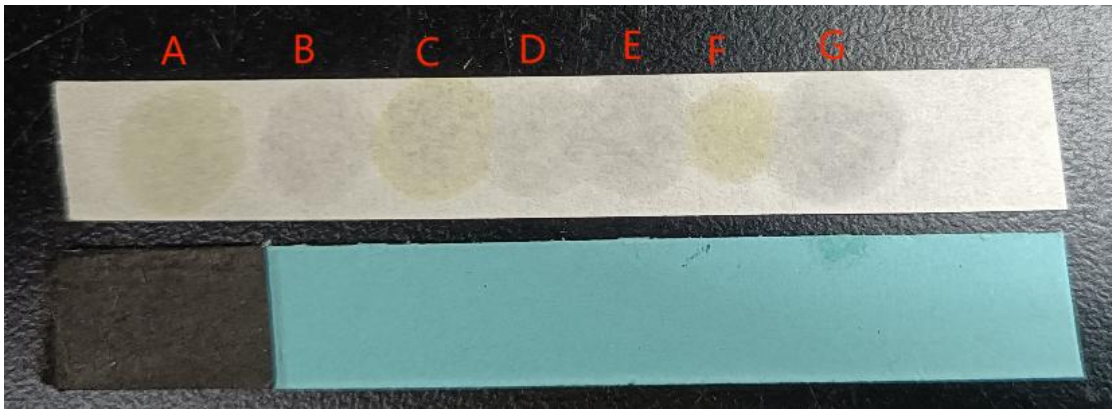
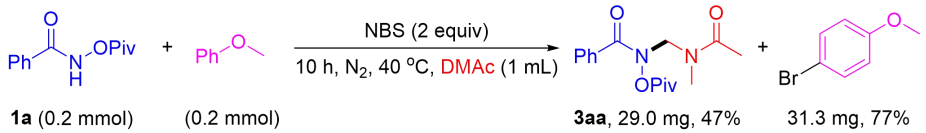


Figure S5. Bromine detected with starch potassium iodide test paper

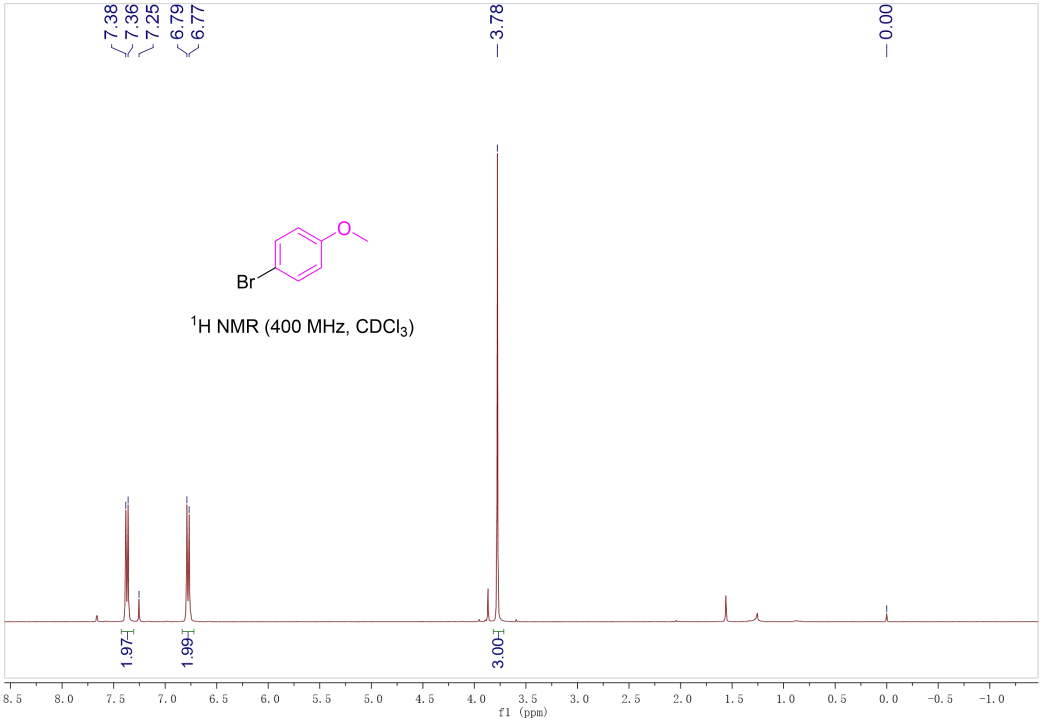
The states of A, C, and F were similar, and bromine was produced during the reaction.

***Bromination reaction*:**



A flame-dried 10 mL Schlenk tube was cooled to room temperature and filled with N_2. To this Schlenk tube were added *N*-(pivaloyloxy)benzamide **1a** (0.2 mmol), anisole (0.2 mmol), and NBS (2.0 equiv). DMAc (1.0 mL) was added by syringe under a flow of nitrogen. The resulting mixture was stirred at 40 °C for 10 hours. After completion, the reaction mixture was cooled to room temperature, and the residue was diluted with ethyl acetate (10 mL). The resulting solution was washed with a saturated sodium carbonate solution (5 mL, three times). The organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel 300-400 mesh, ethyl acetate/petroleum ether = 2:1 to 1:3) to afford the desired products **3aa** (29.0 mg, 47% yield) and 4-bromoanisole [31.3 mg; 77%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H)].

The above experiments indicated the bromination of electron-rich phenyl ring occurs rapidly, explaining the formation of **3ra** from **1ra** in Scheme 2.



[1]H-NMR analysis：

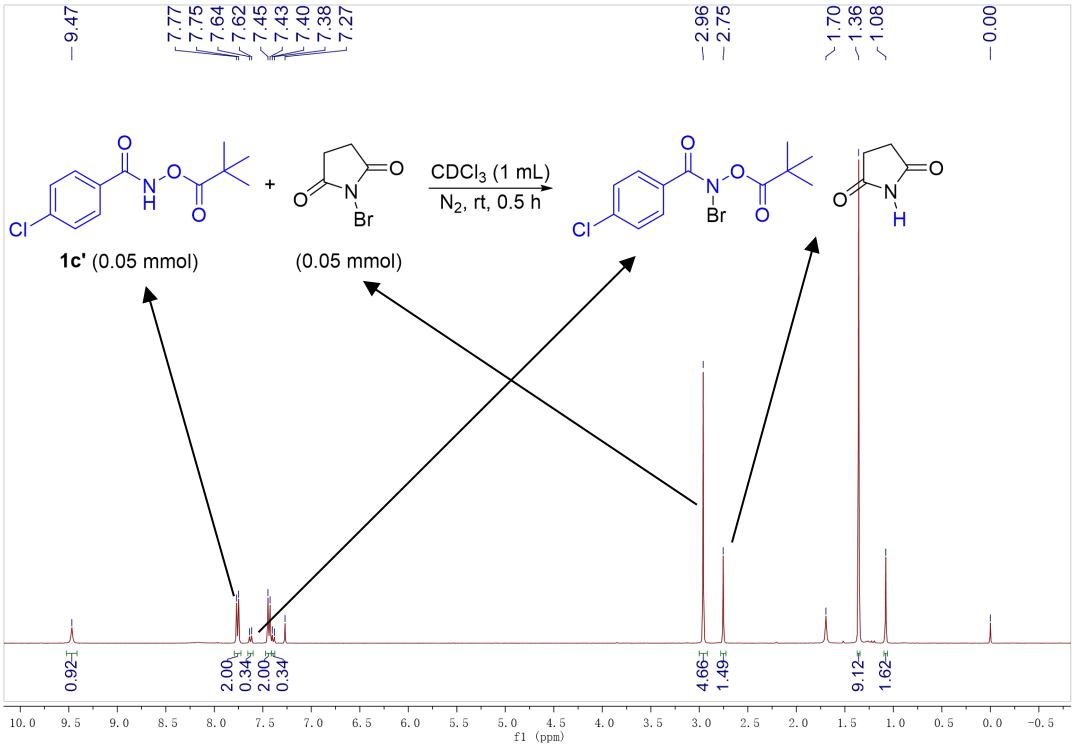


Figure S6. [1]H-NMR spectra for reaction of compound **1c'** with NBS in $CDCl_3$ (1 mL) showing the involvement of *N*-bromination

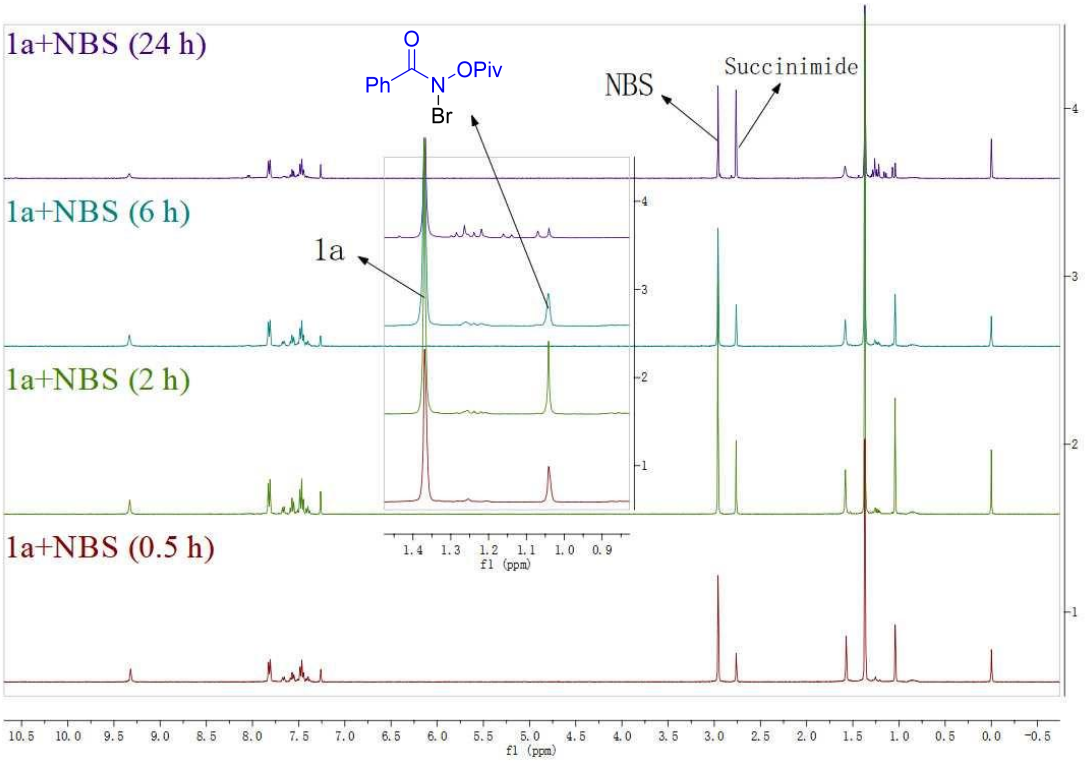


Figure S7. [1]H-NMR spectra for the reaction of compound **1a** with NBS (1:1) in $CDCl_3$ (1 mL) showing the involvement of *N*-bromination

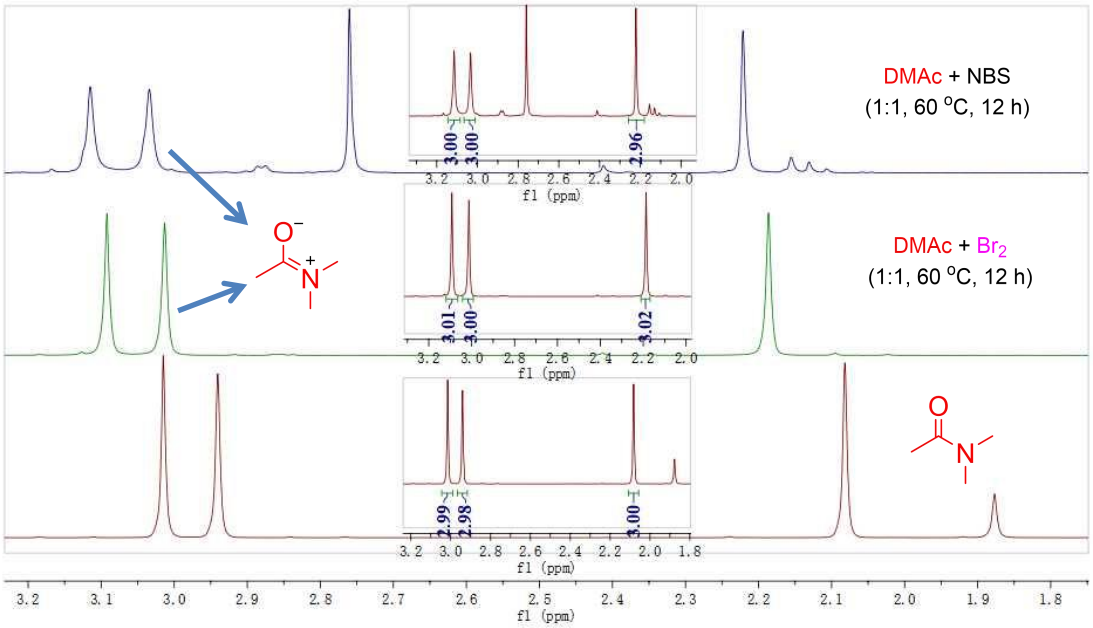


Figure S8. ^{1}H-NMR spectra of **DMAc** and NBS (Br_2) showing the interaction between the two species in $CDCl_3$ (1 mL) and no brominated product could be detected

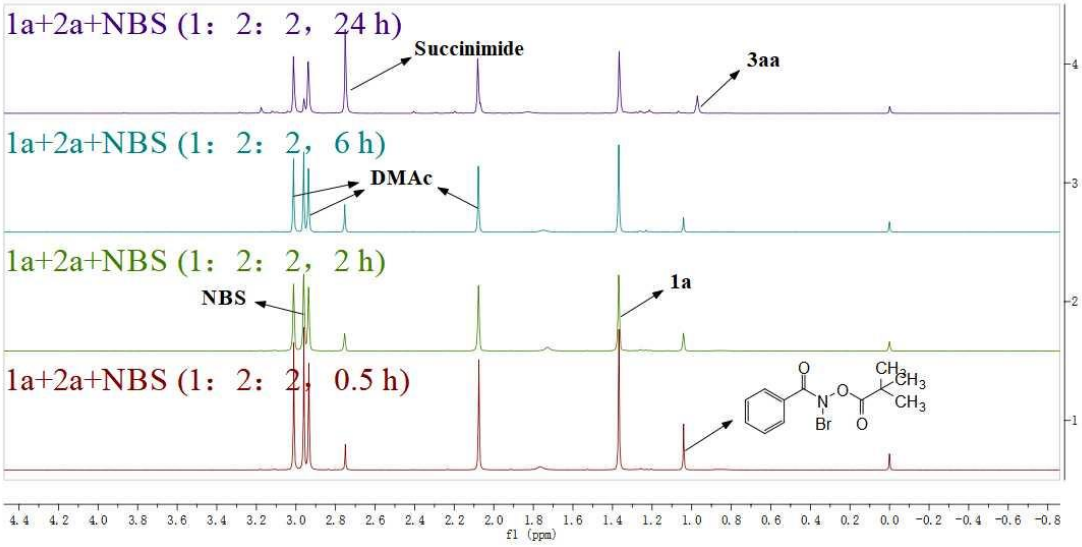
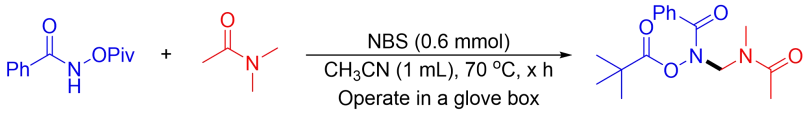


Figure S9. Monitoring the reaction progress by 1H NMR showing the C-C homo-coupling product of DMAc could not be detected when DMAc was not used in large excess

Dependence of the reaction rate on concentration of 1a:



1a **2a** **3aa**

A flame-dried 10 mL Schlenk tube was cooled to room temperature. To this tube were added **1a** (x mmol) and NBS (0.6 mmol). Then, *N,N*-dimethylamide **2a** (2 mmol) and CH_3CN (1.0 mL) were added to this tube in the glove box. The mixture was then stirred at 70 °C for x hours (Yields were determined by ^1H NMR using dibromomethane as the internal standard).

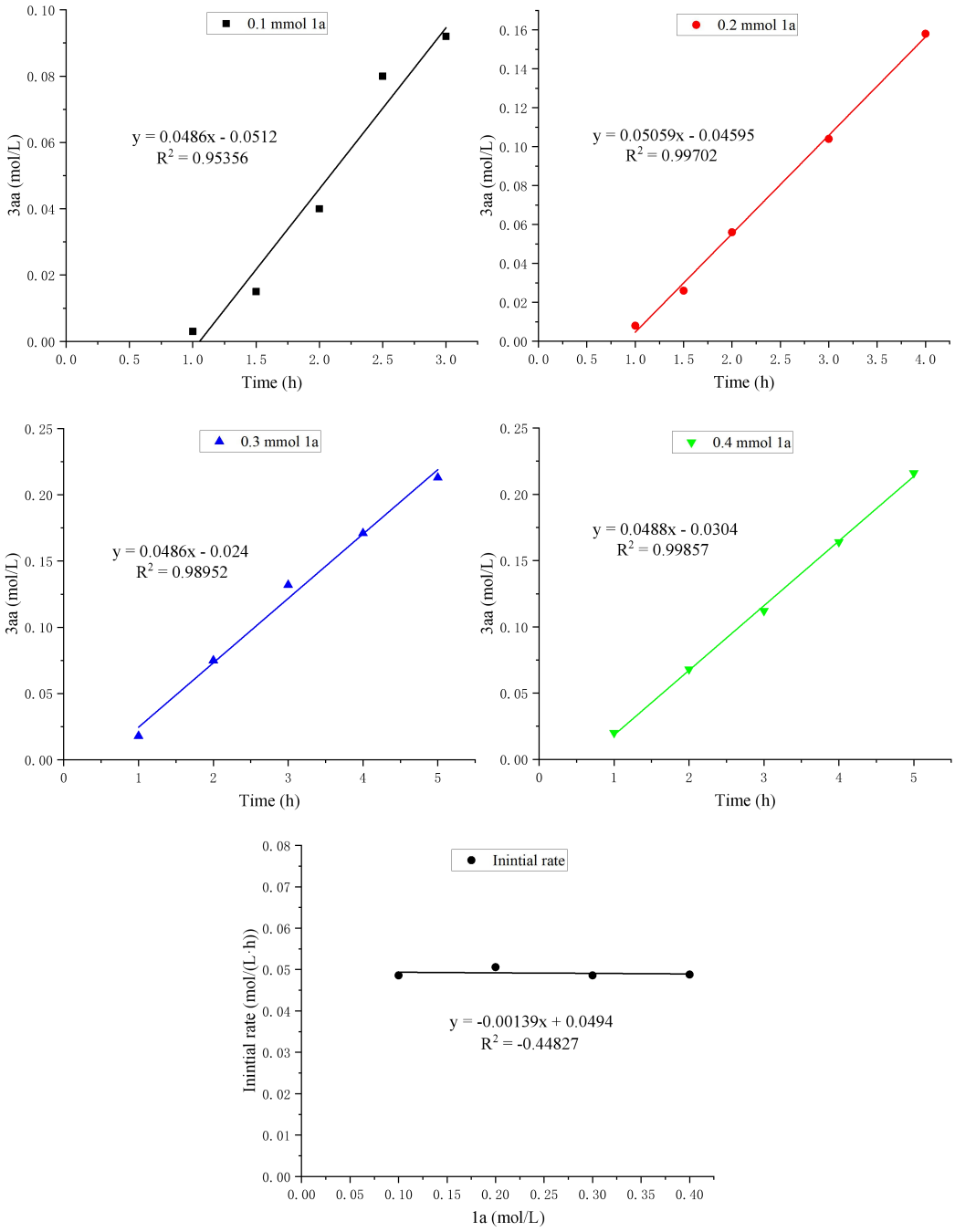
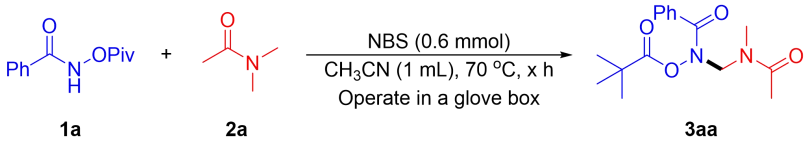


Figure S10. Dependence of the reaction rate on concentration of 1a

Dependence of the reaction rate on concentration of 2a:



1a **2a** **3aa**

A flame-dried 10 mL Schlenk tube was cooled to room temperature. To this tube were added **1a** (0.2 mmol) and NBS (0.6 mmol). Then, *N,N*-dimethylamide **2a** (x mmol) and CH_3CN (1.0 mL) were added to this tube in the glove box. The mixture was then stirred at 70 °C for x hours (Yields were determined by ^1H NMR using dibromomethane as the internal standard).

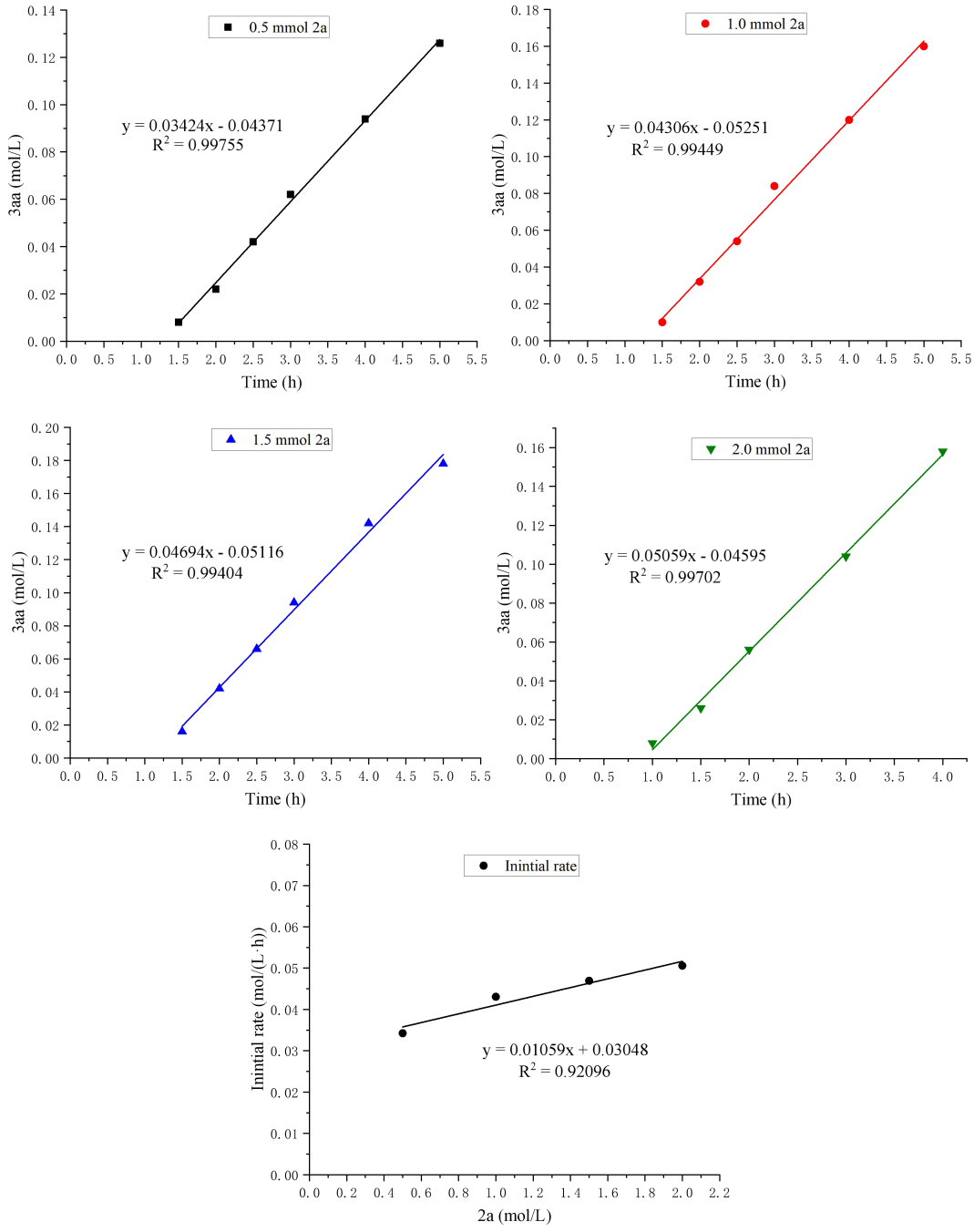
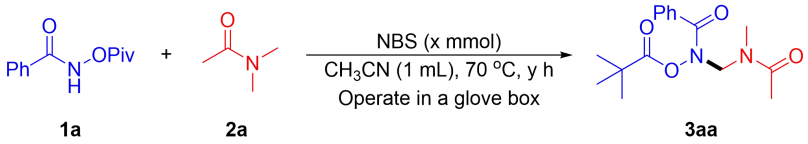


Figure S11. Dependence of the reaction rate on concentration of 2a

Dependence of the reaction rate on concentration of NBS:



1a **2a** **3aa**

A flame-dried 10 mL Schlenk tube was cooled to room temperature. To this tube were added **1a** (0.2 mmol) and NBS (x mmol). Then, *N,N*-dimethylamide **2a** (2 mmol) and CH_3CN (1.0 mL) were added to this tube in the glove box. The mixture was stirred at 70 °C for x hours (Yields were determined by ^1H NMR using dibromomethane as the internal standard).

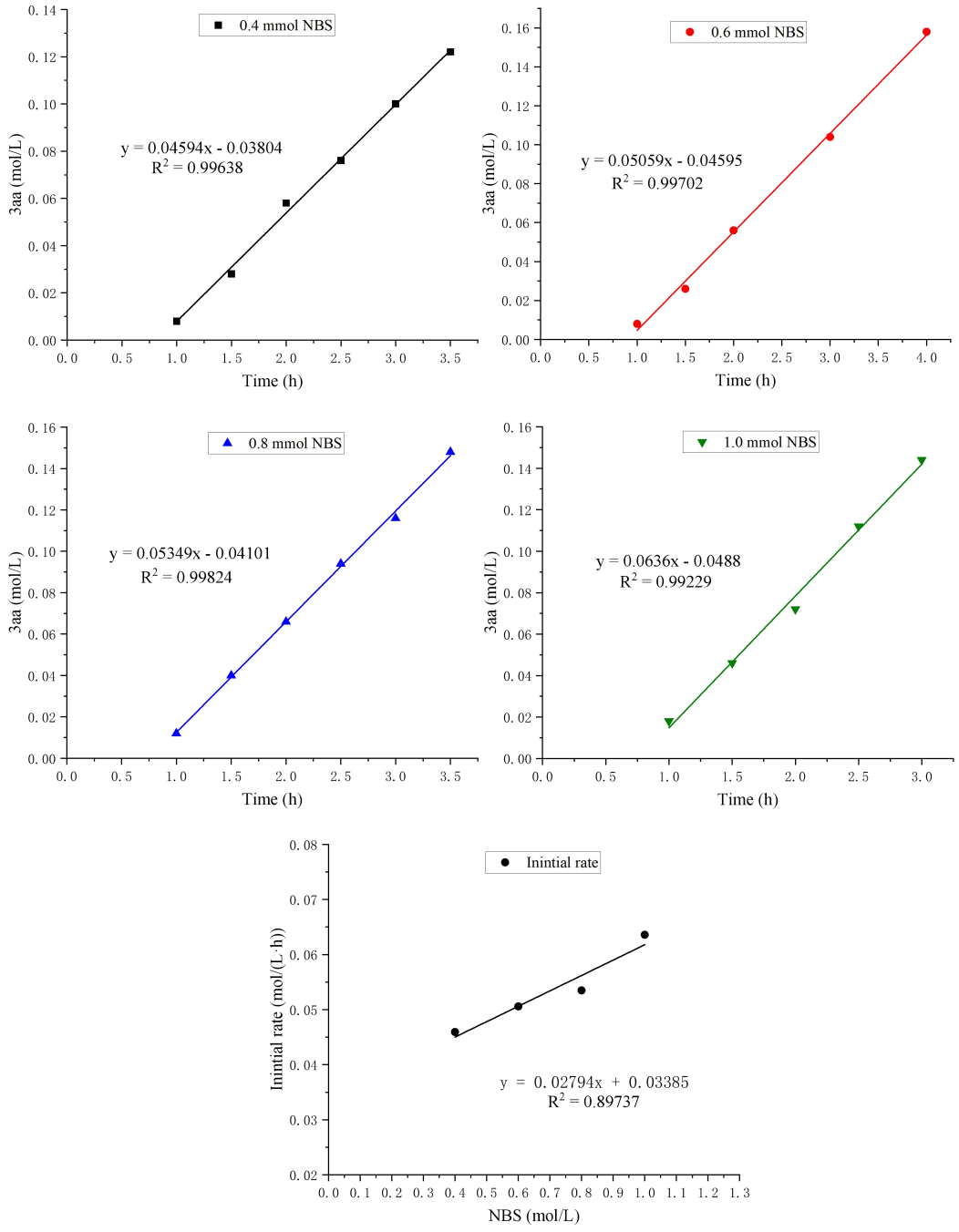
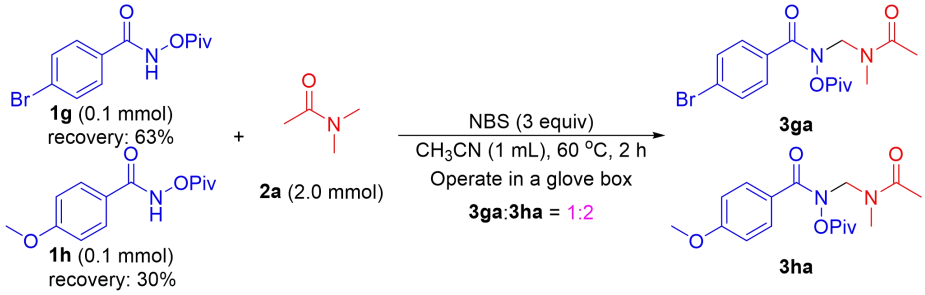
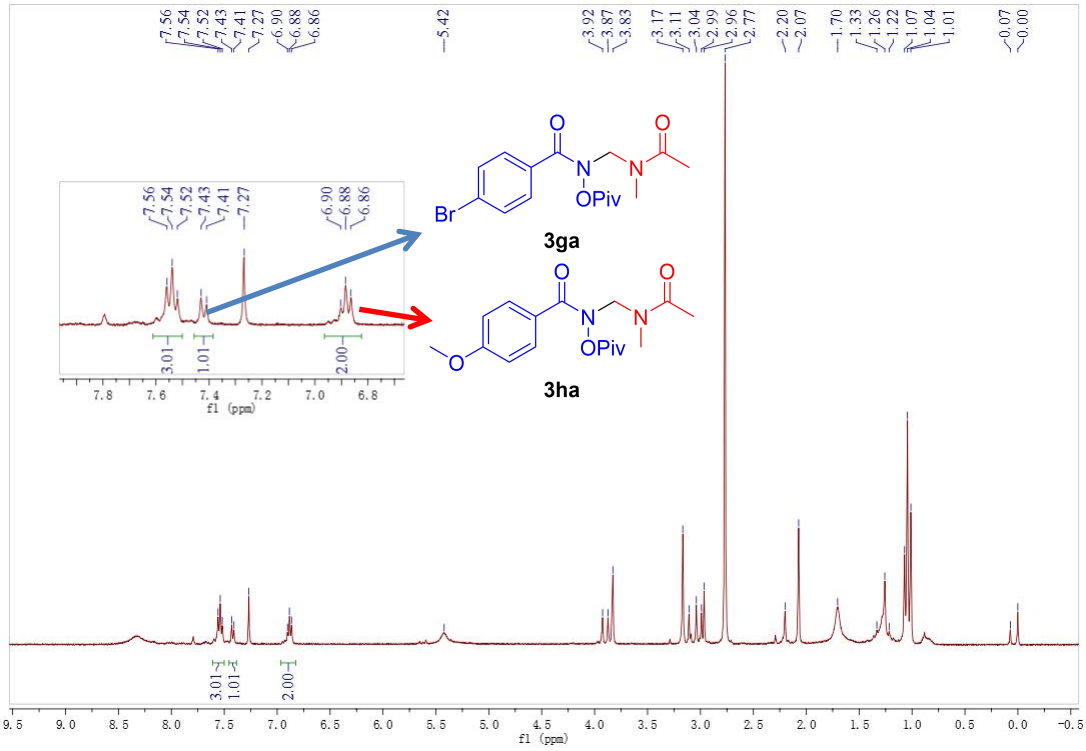


Figure S12. Dependence of the reaction rate on concentration of NBS

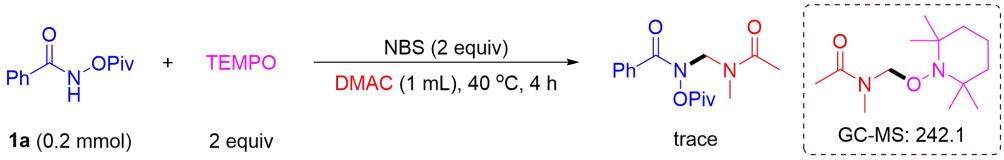
Competitive experiment:



A flame-dried 10 mL Schlenk tube was cooled to room temperature. To this tube were added **1g** (0.10 mmol), **1h** (0.10 mmol) and NBS (0.6 mmol). Then, **2a** (2.0 mmol) and CH_3CN (1.0 mL) were added to this tube in the glove box. The tube was then removed and the mixture was stirred at 60 °C for 2 hours. After completion, the reaction mixture was cooled to room temperature (Recovery yields were determined by ^1H NMR using dibromomethane as the internal standard), and the residue was diluted with ethyl acetate (10 mL). The resulting solution was washed with saturated sodium carbonate solution (5 mL × 3). The organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography, resulting in a mixture of products (9.9 mg, **3ga**:**3ha** = 1:2, Ratios were determined by ^1H NMR).

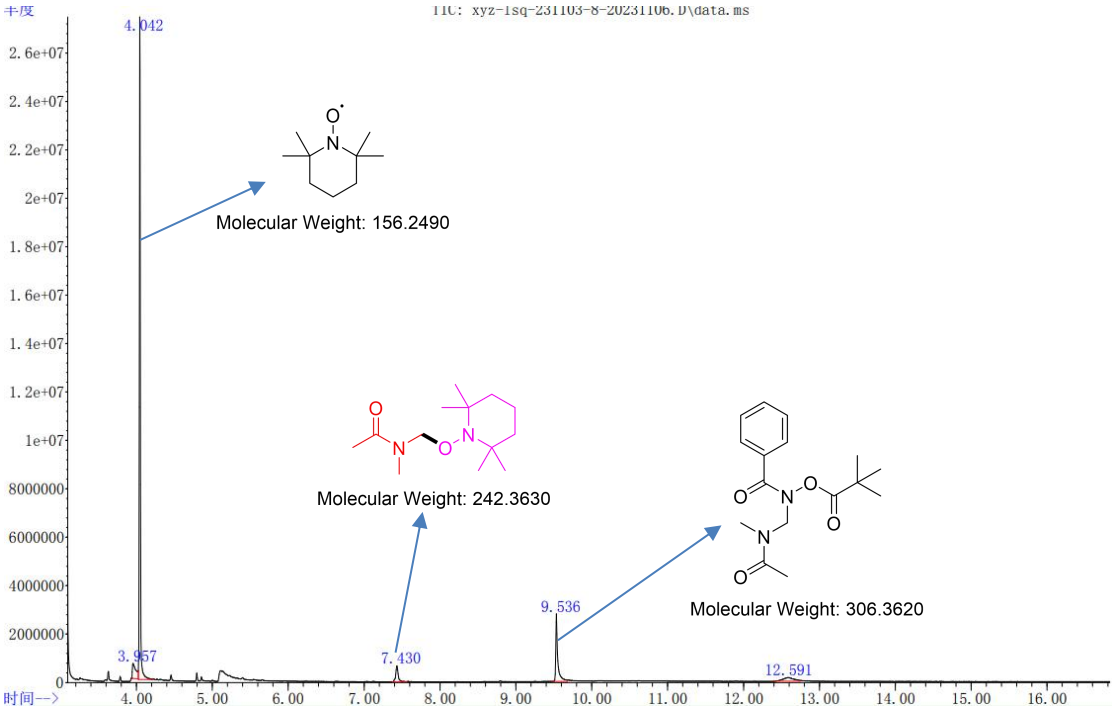


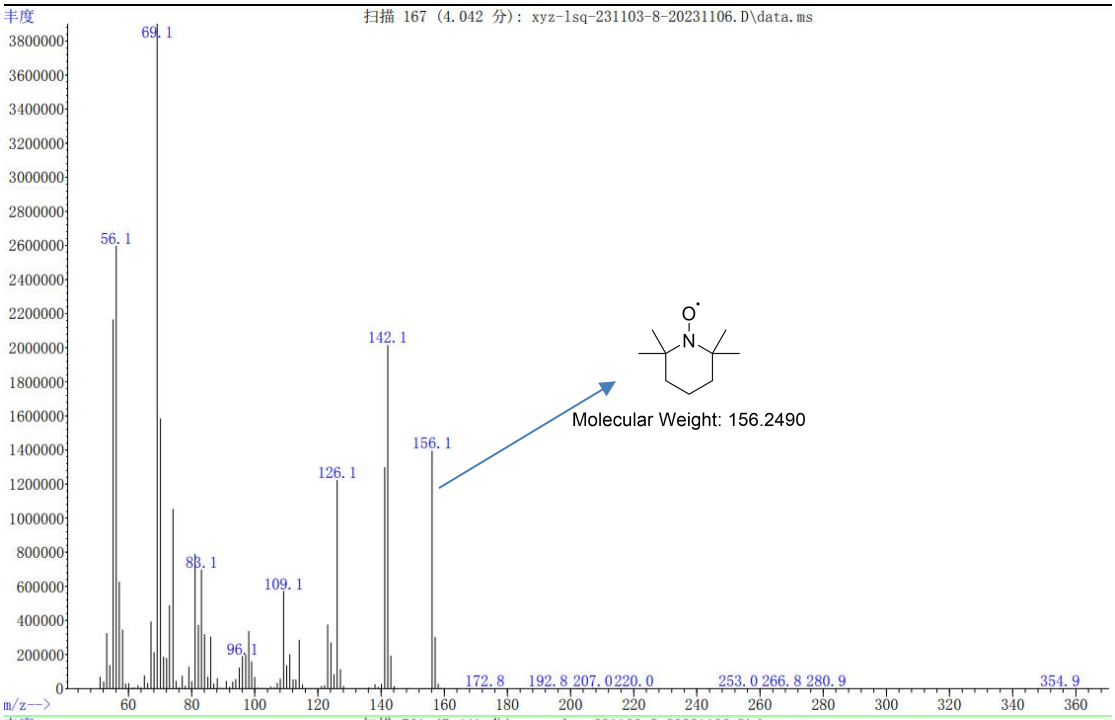
GC-MS spectra from radical trapping experiment:



1a (0.2 mmol) 2 equiv trace

A flame-dried 10 mL Schlenk tube was cooled to room temperature and filled with N_2. To this Schlenk tube were added *N*-(pivaloyloxy)benzamide **1a** (0.2 mmol), TEMPO (2.0 equiv), and NBS (2.0 equiv). DMAc (1.0 mL) was added by syringe under a flow of nitrogen. The resulting mixture was stirred at 40 °C for 4 hours. After completion, the reaction mixture was cooled to room temperature, and the residue was diluted with ethyl acetate (10 mL).




丰度
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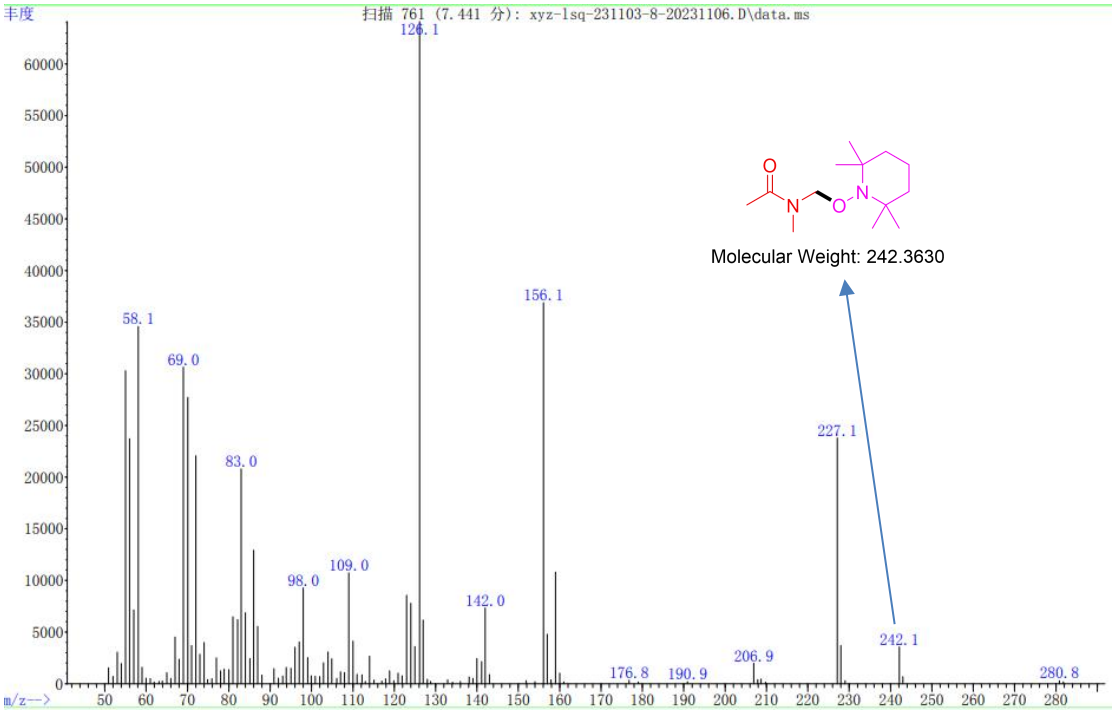
69.1
56.1
142.1
156.1
126.1
83.1
109.1
96.1
Molecular Weight: 156.2490
m/z-->


丰度
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227.1
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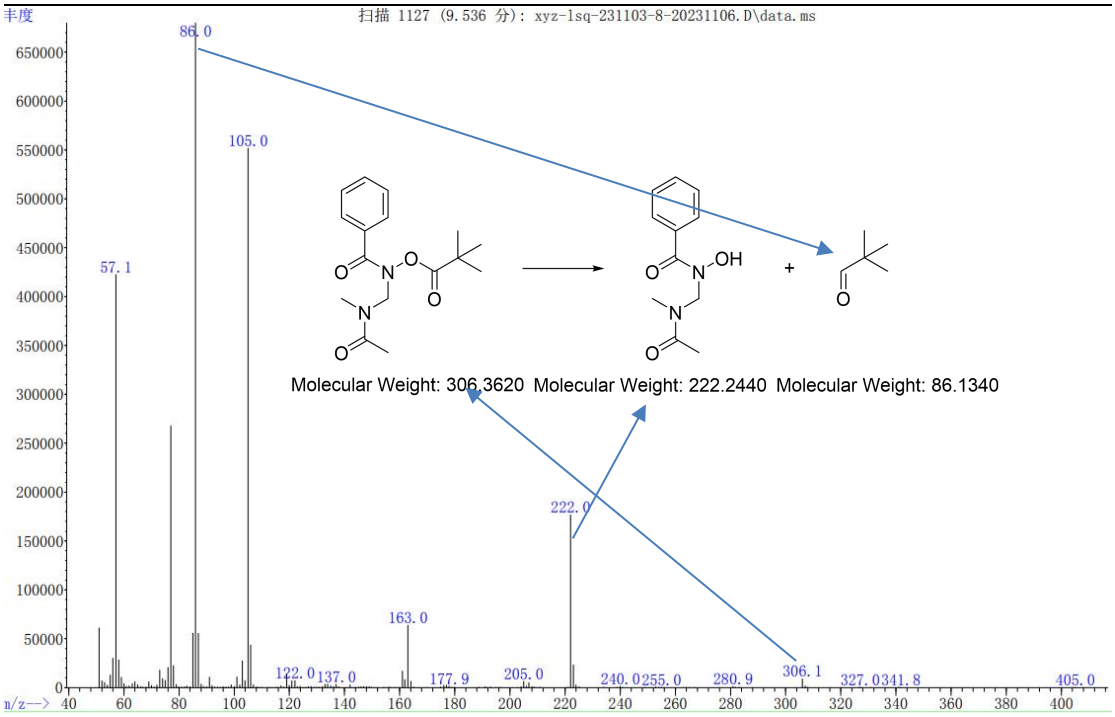
98.0
142.0
242.1
206.9
Molecular Weight: 242.3630
m/z-->


丰度
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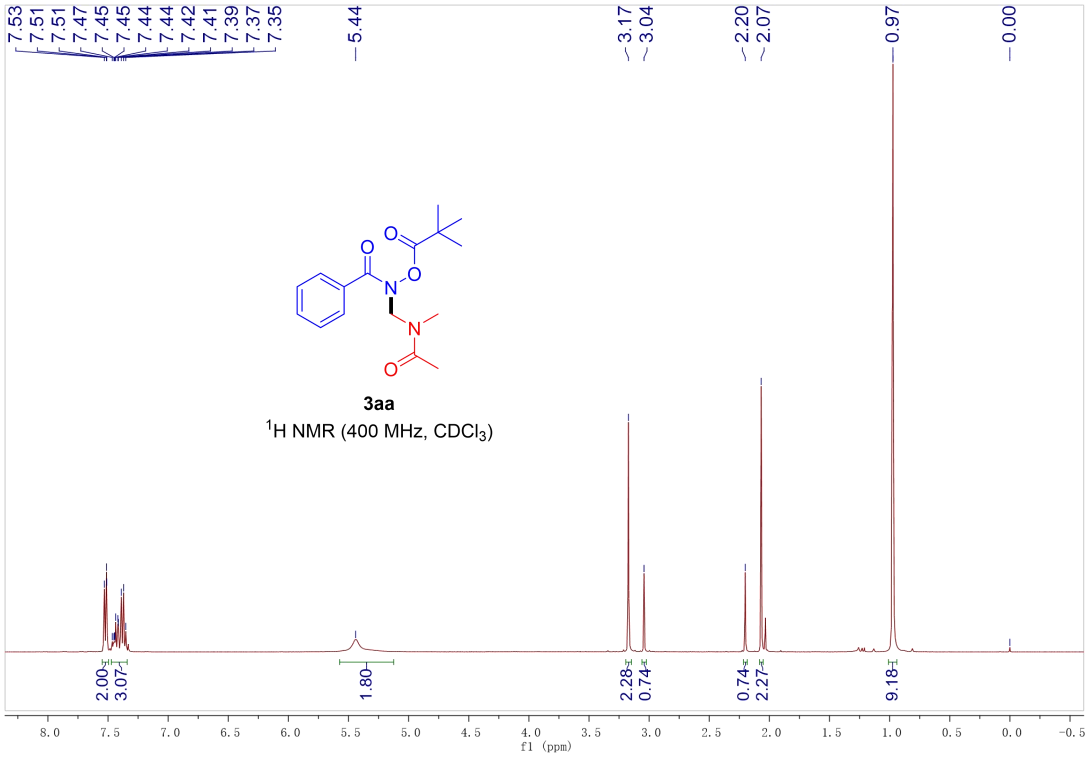
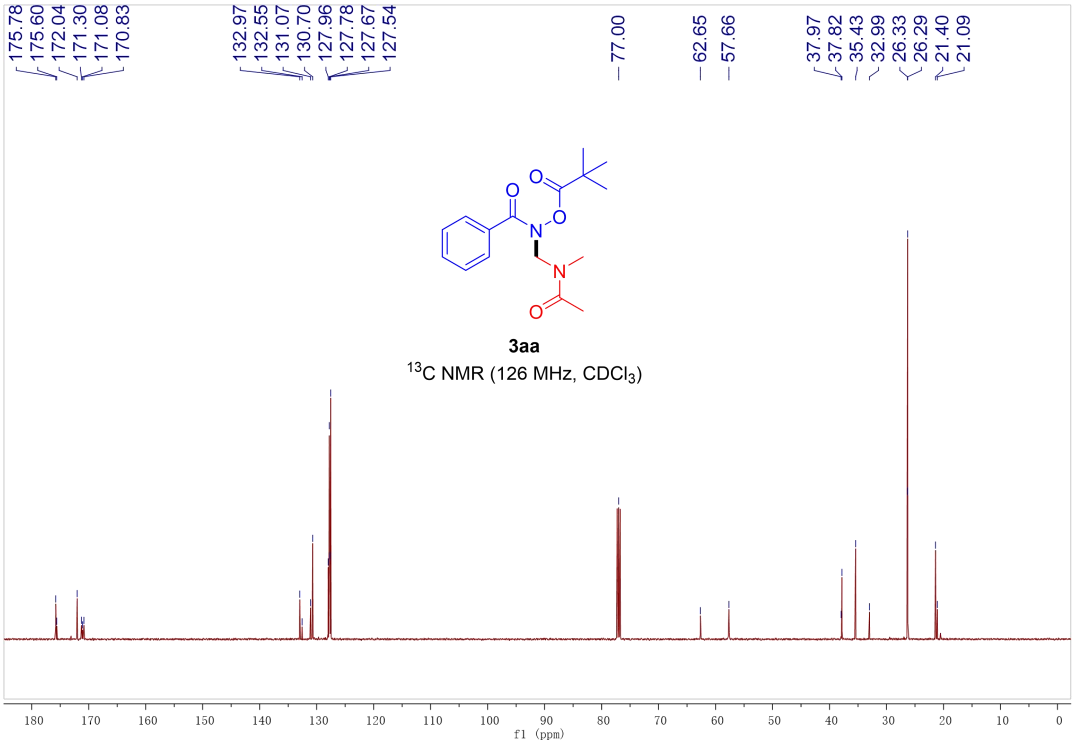
57.1
222.0
163.0
122.0
137.0
177.9
205.0
240.0
255.0
280.9
306.1
327.0
341.8
405.0
m/z-->
Molecular Weight: 306.3620
Molecular Weight: 222.2440
Molecular Weight: 86.1340

VII. NMR spectra:



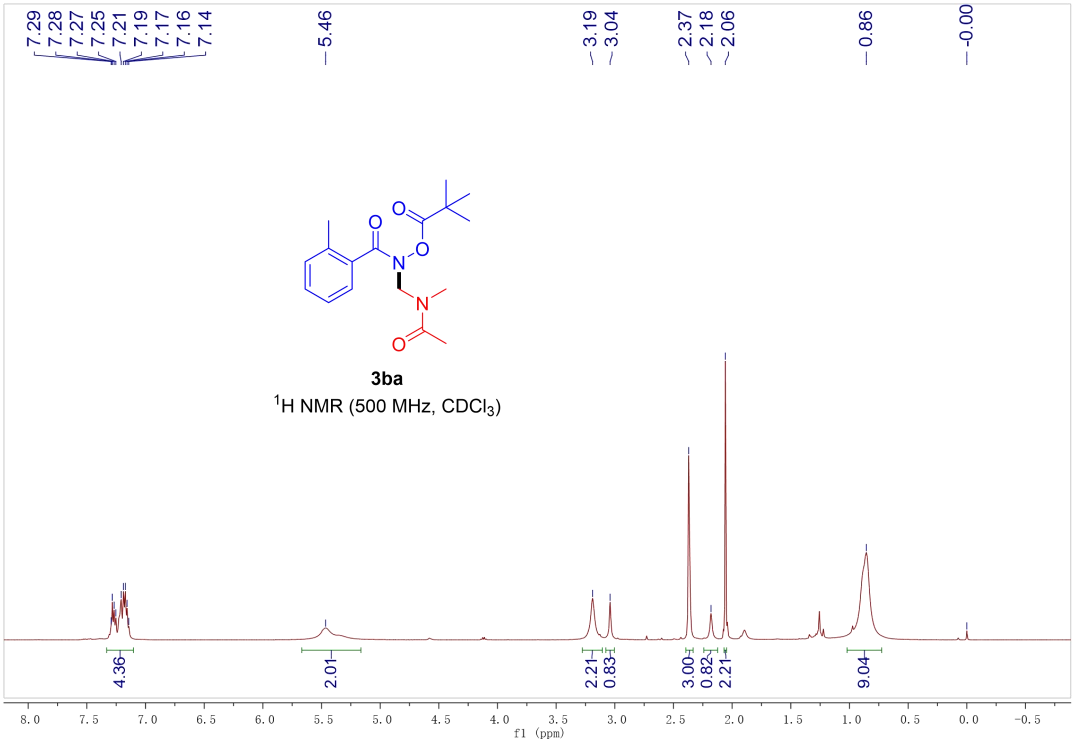
3aa

^{1}H NMR (400 MHz, $CDCl_3$)



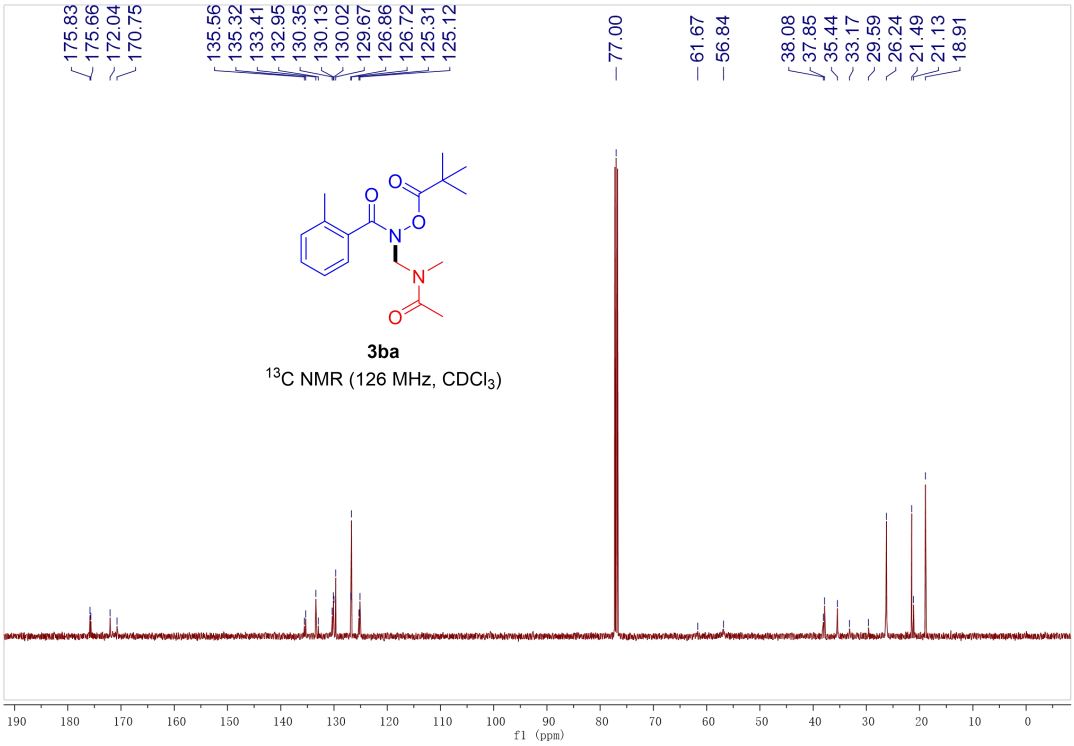
3aa

^{13}C NMR (126 MHz, $CDCl_3$)



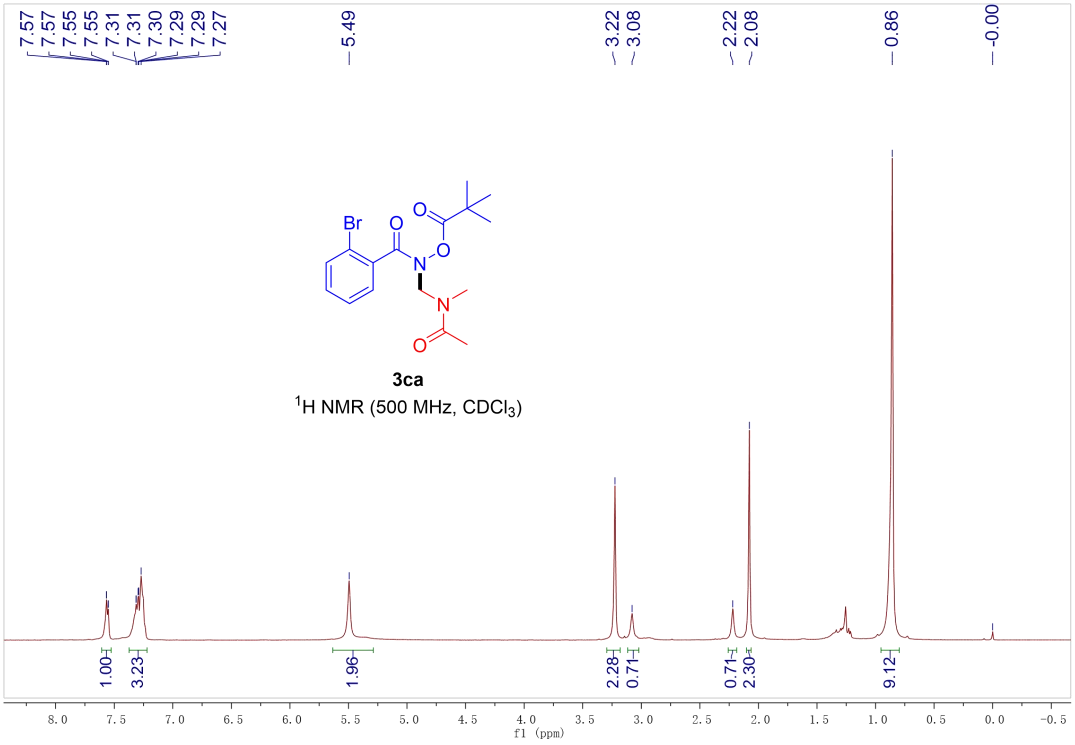
3ba

^{1}H NMR (500 MHz, $CDCl_3$)



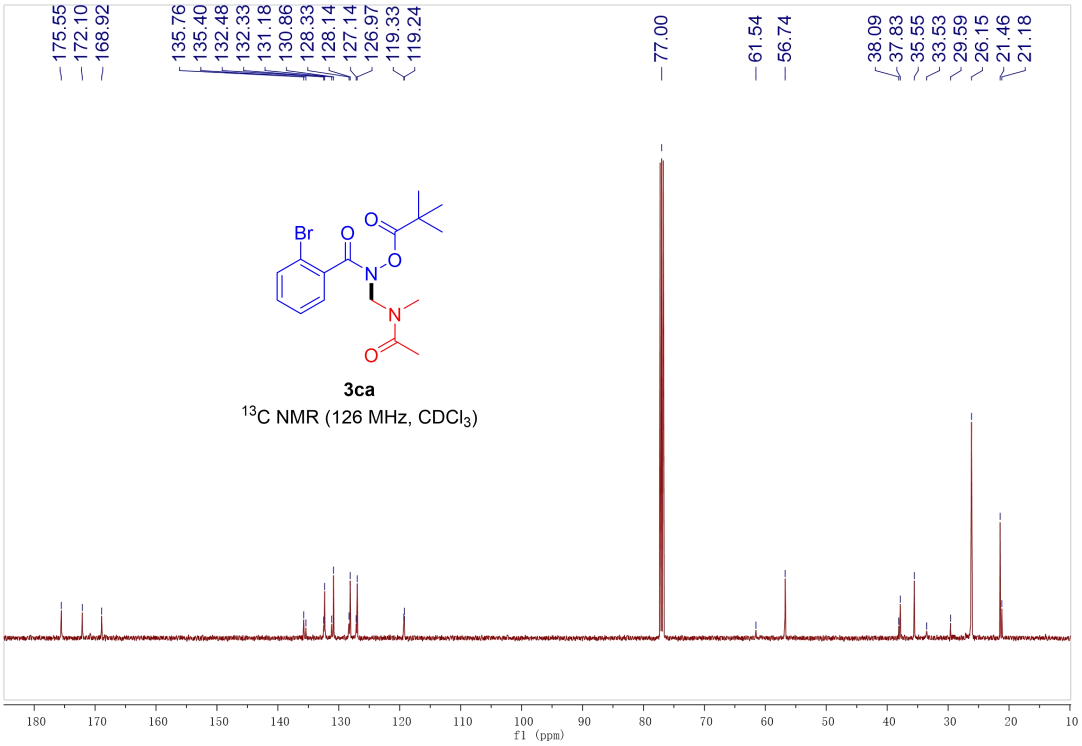
3ba

^{13}C NMR (126 MHz, $CDCl_3$)



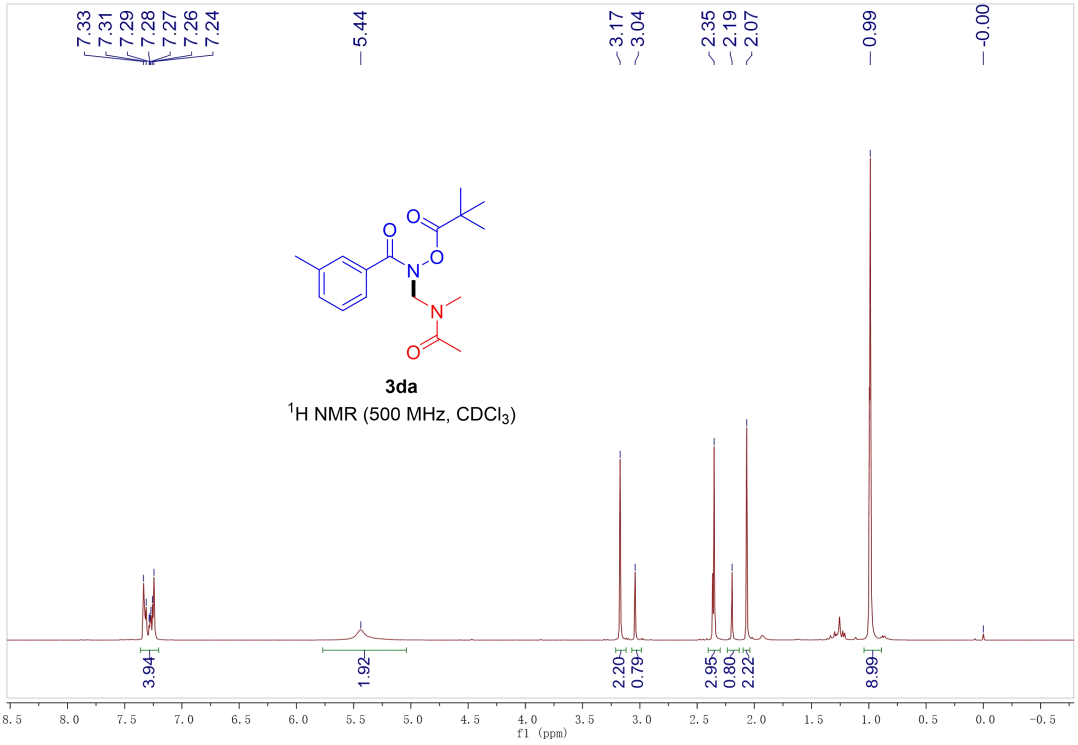
3ca

^{1}H NMR (500 MHz, $CDCl_3$)



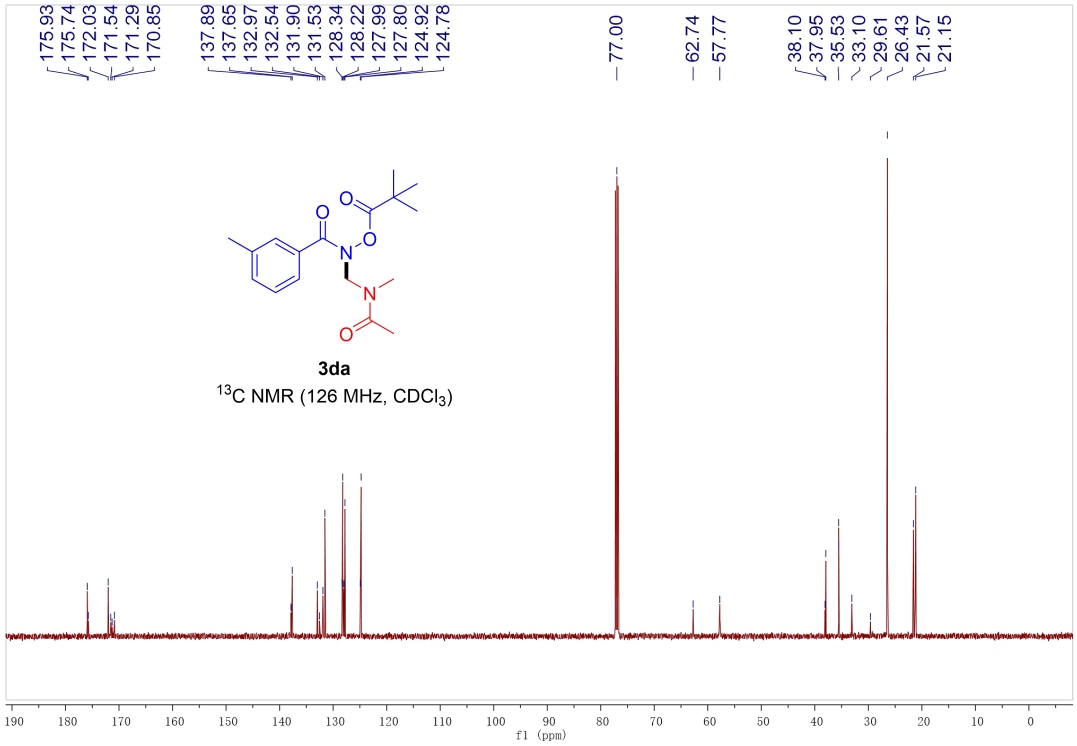
3ca

^{13}C NMR (126 MHz, $CDCl_3$)



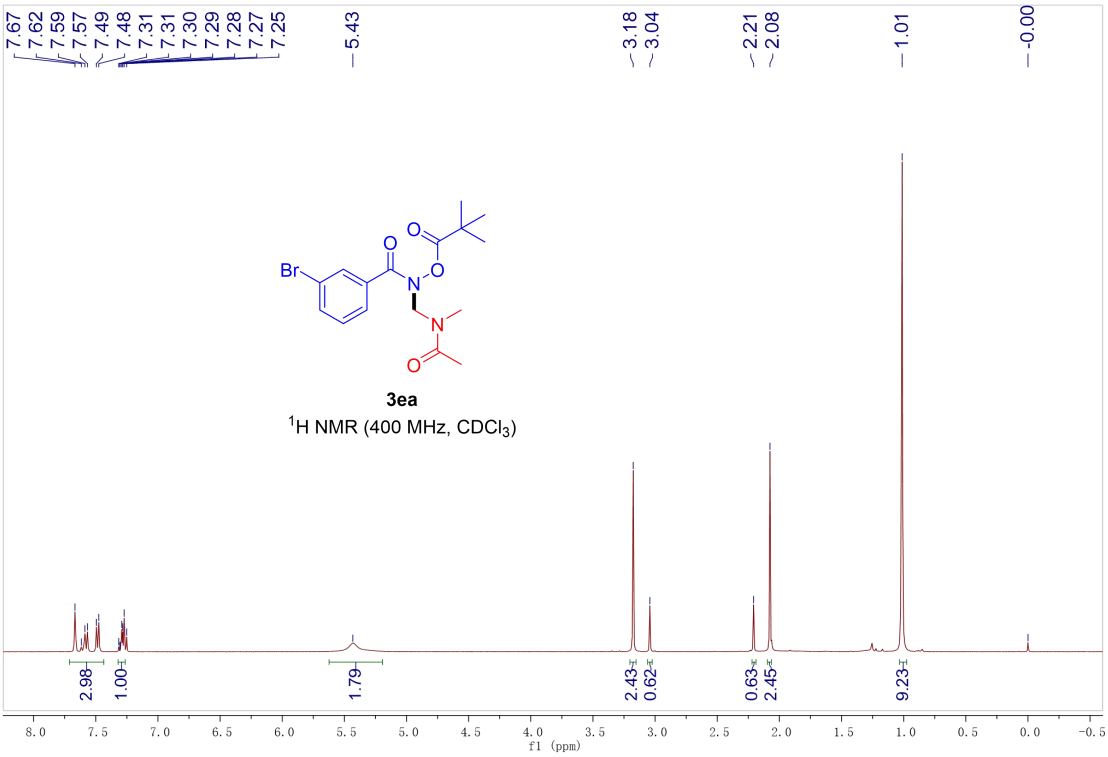
3da

^{1}H NMR (500 MHz, $CDCl_3$)



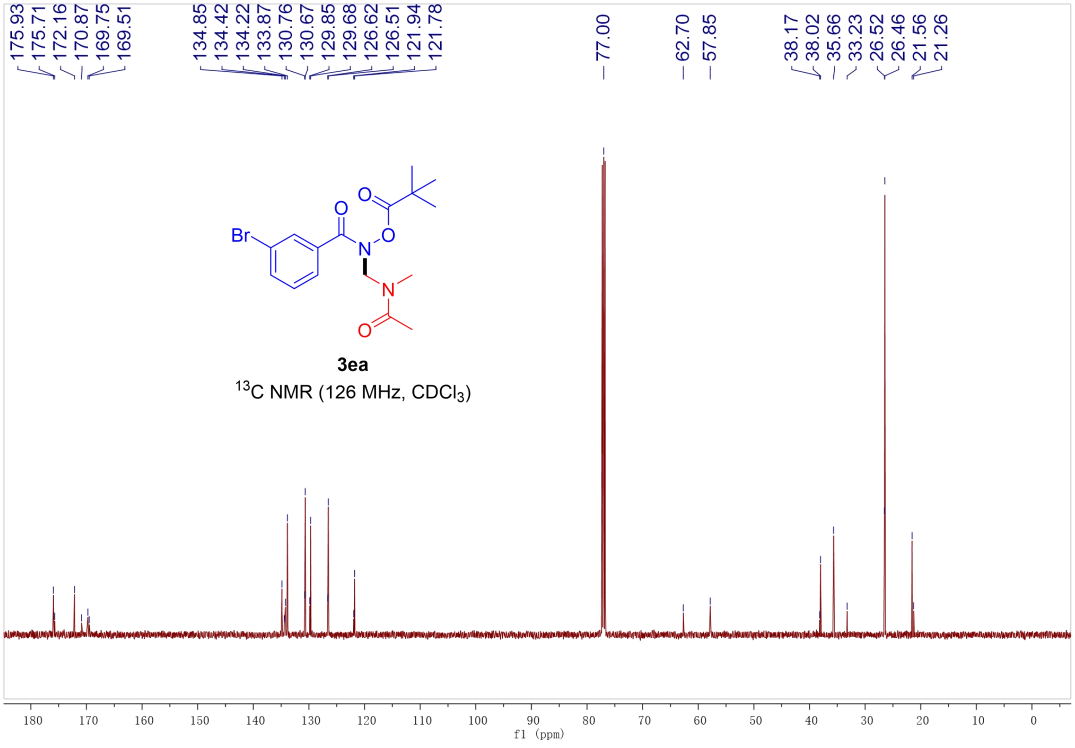
3da

^{13}C NMR (126 MHz, $CDCl_3$)



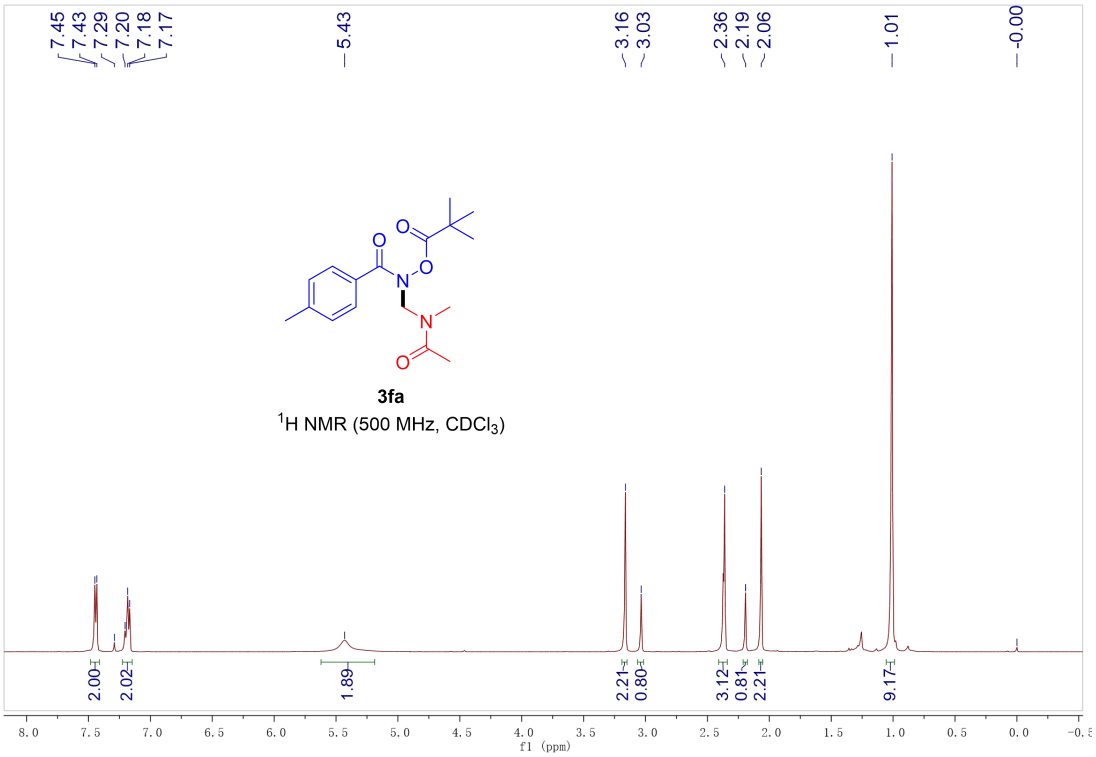
3ea

^{1}H NMR (400 MHz, $CDCl_3$)



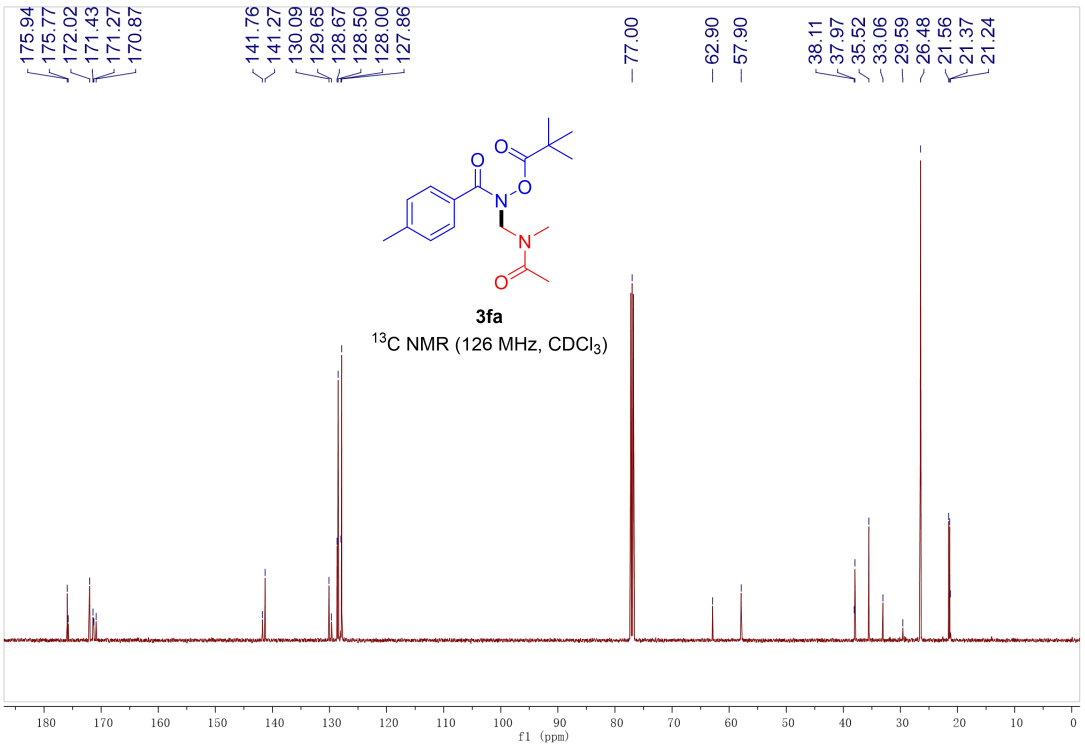
3ea

^{13}C NMR (126 MHz, $CDCl_3$)



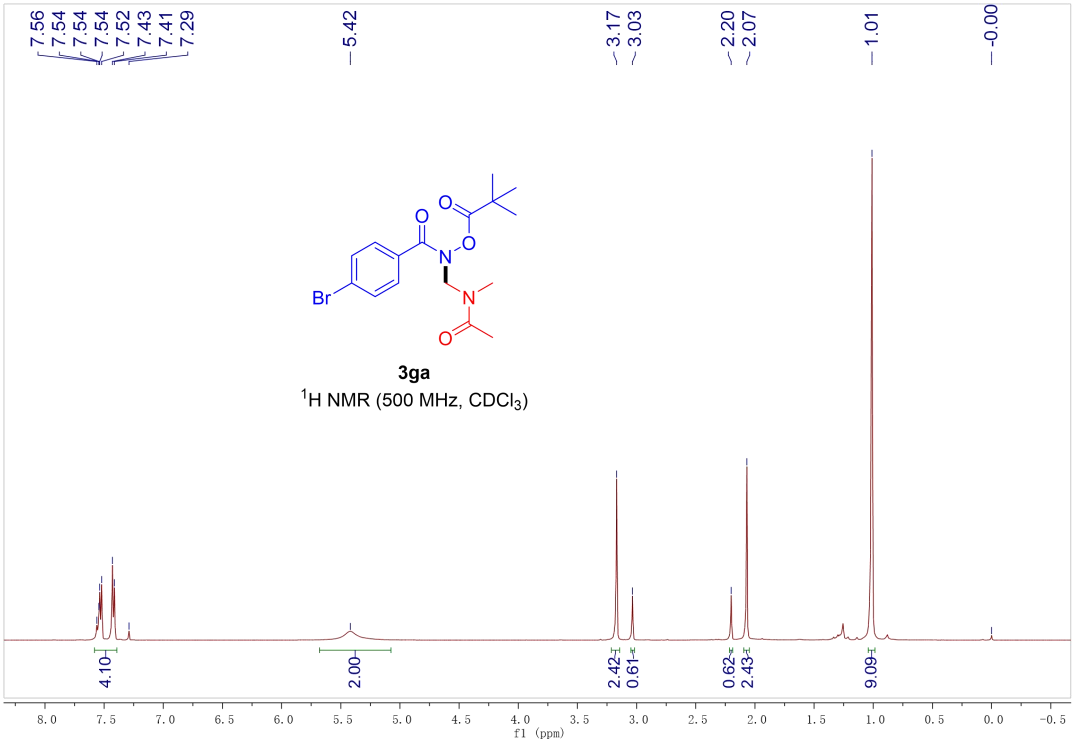
3fa

^{1}H NMR (500 MHz, $CDCl_3$)



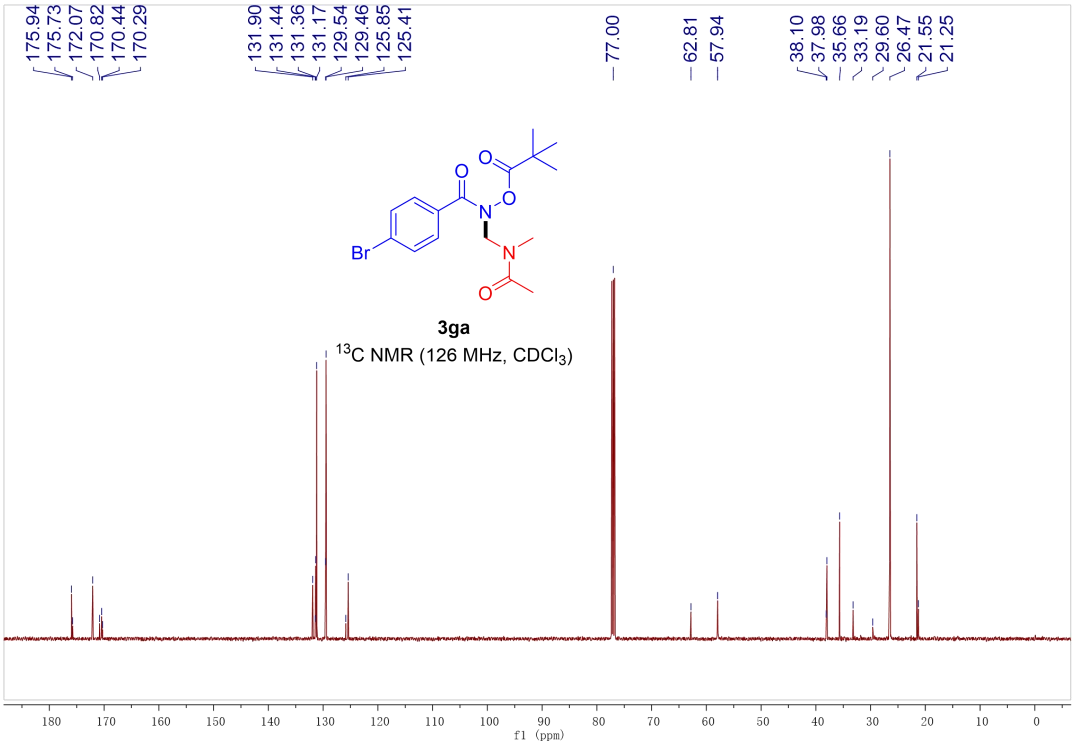
3fa

^{13}C NMR (126 MHz, $CDCl_3$)



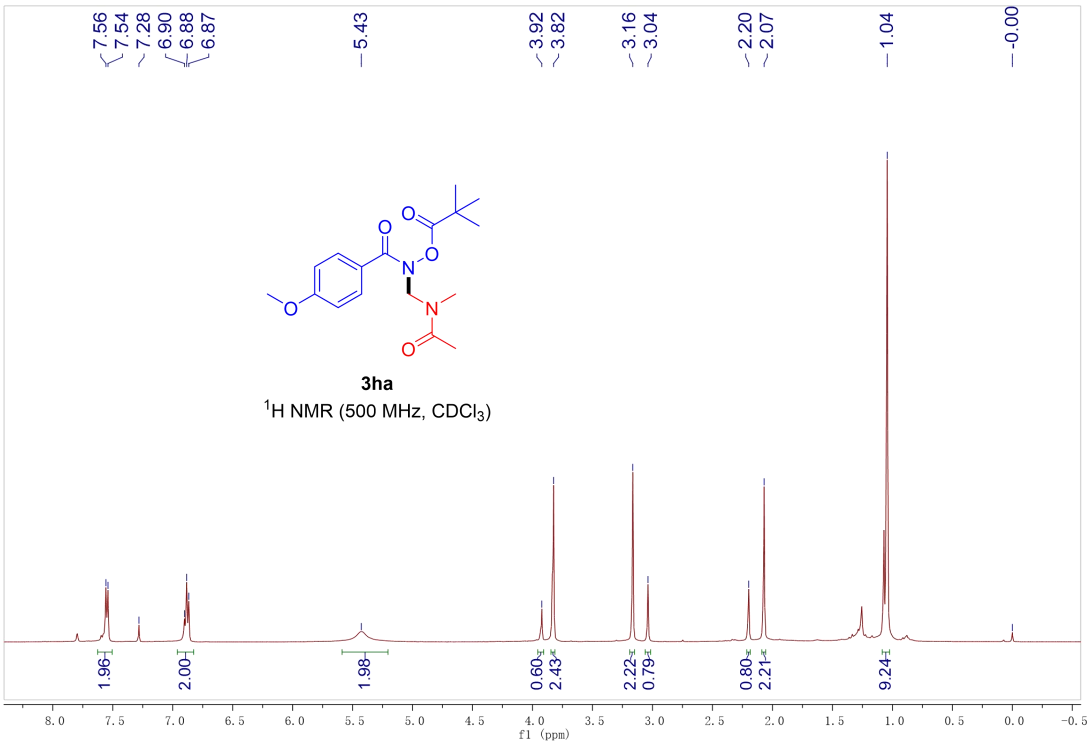
3ga

^{1}H NMR (500 MHz, $CDCl_3$)



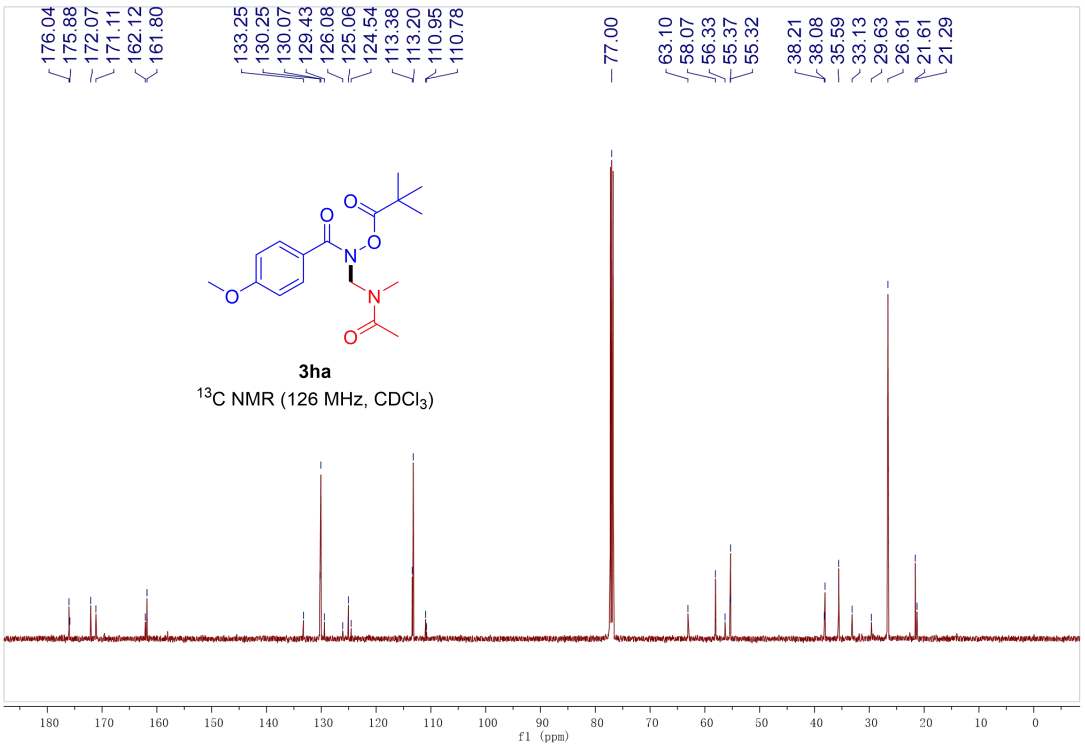
3ga

^{13}C NMR (126 MHz, $CDCl_3$)



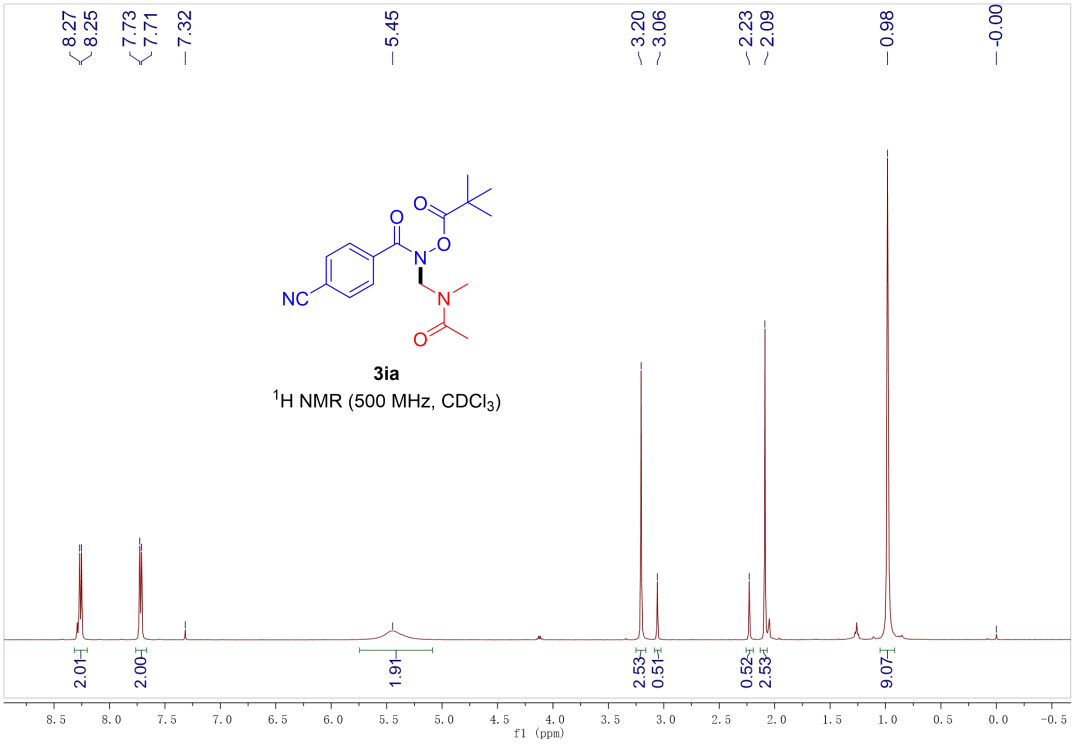
3ha

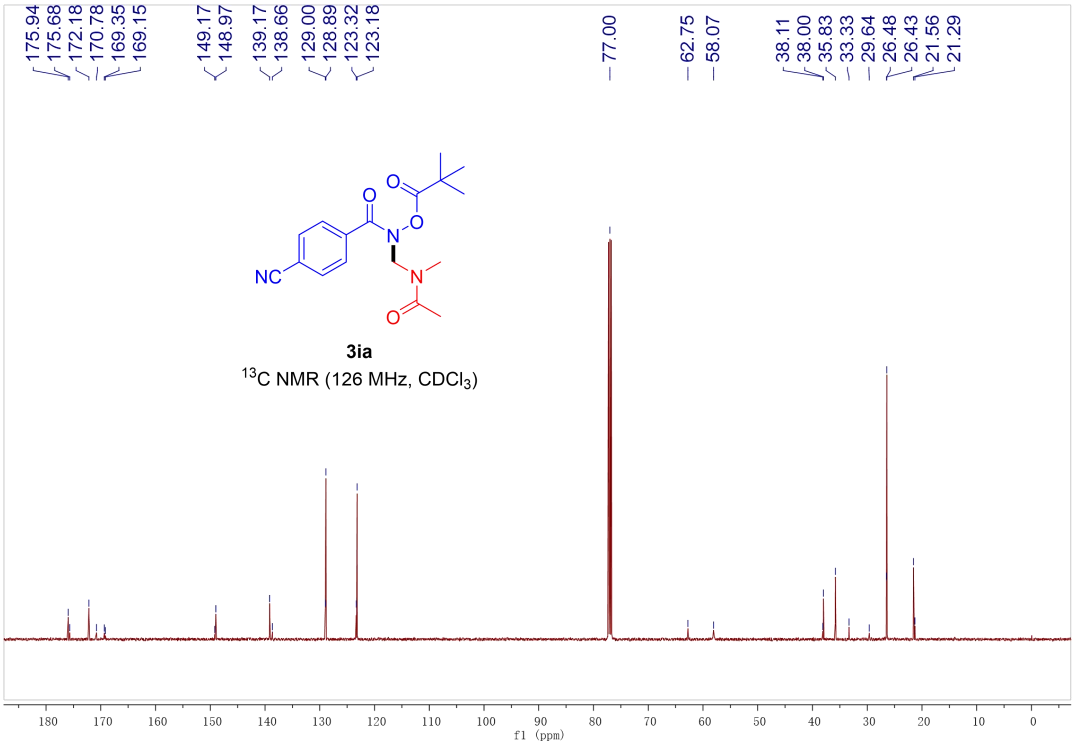
^{1}H NMR (500 MHz, $CDCl_3$)

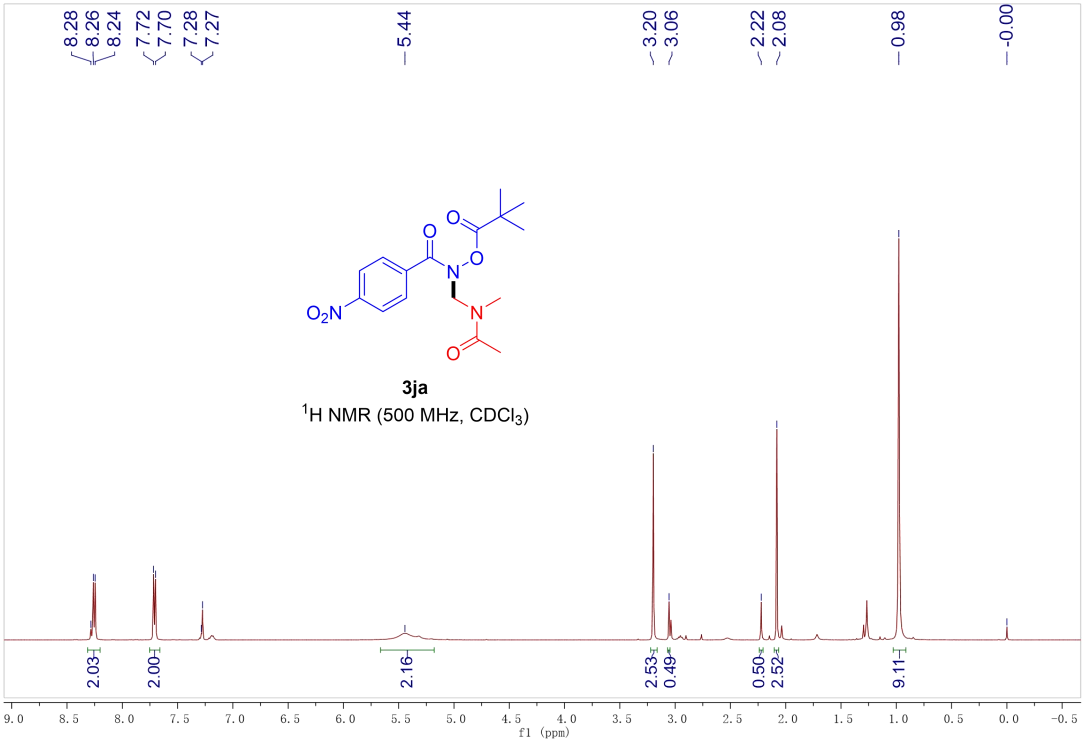


3ha

^{13}C NMR (126 MHz, $CDCl_3$)

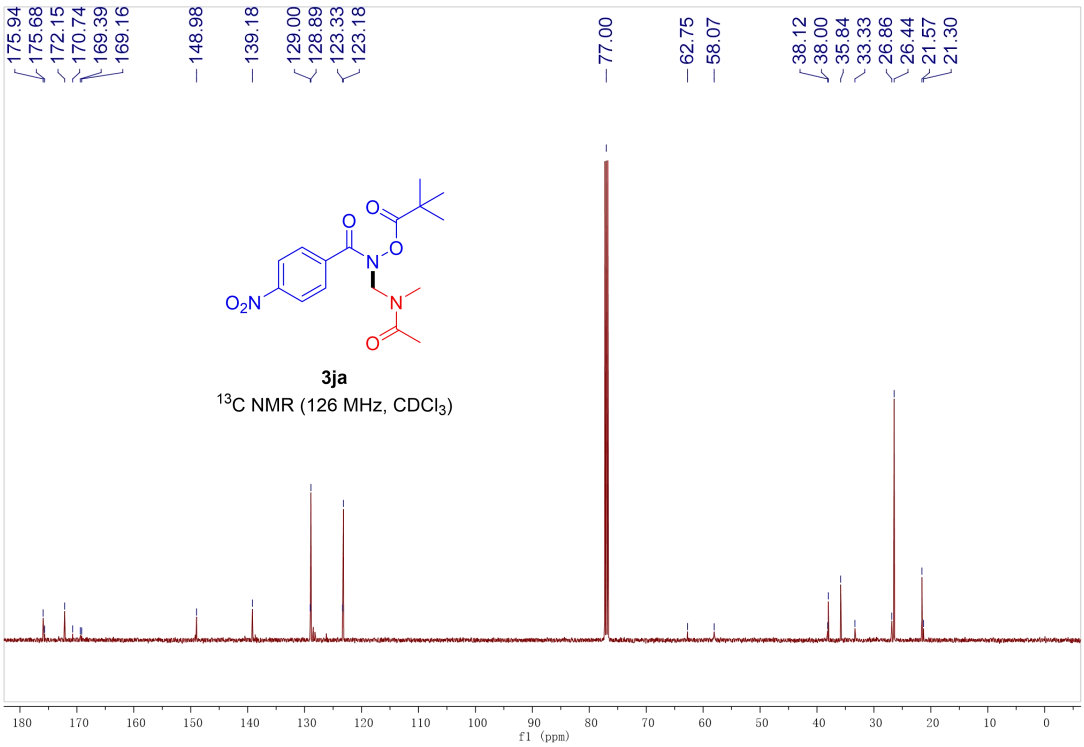

8.27
8.25
7.73
7.71
7.32
5.45
3.20
3.06
2.23
2.09
0.98
-0.00
NC
O
O
O
N
O
N
O
3ia
1H NMR (500 MHz, CDCl3)
2.01
2.00
1.91
2.53
0.51
0.52
2.53
9.07
f1 (ppm)


175.94
175.68
172.18
170.78
169.35
169.15
149.17
148.97
139.17
138.66
129.00
128.89
123.32
123.18
77.00
62.75
58.07
38.11
38.00
35.83
33.33
29.64
26.48
26.43
21.56
21.29
NC
O
O
O
N
O
N
O
3ia
13C NMR (126 MHz, CDCl3)
f1 (ppm)



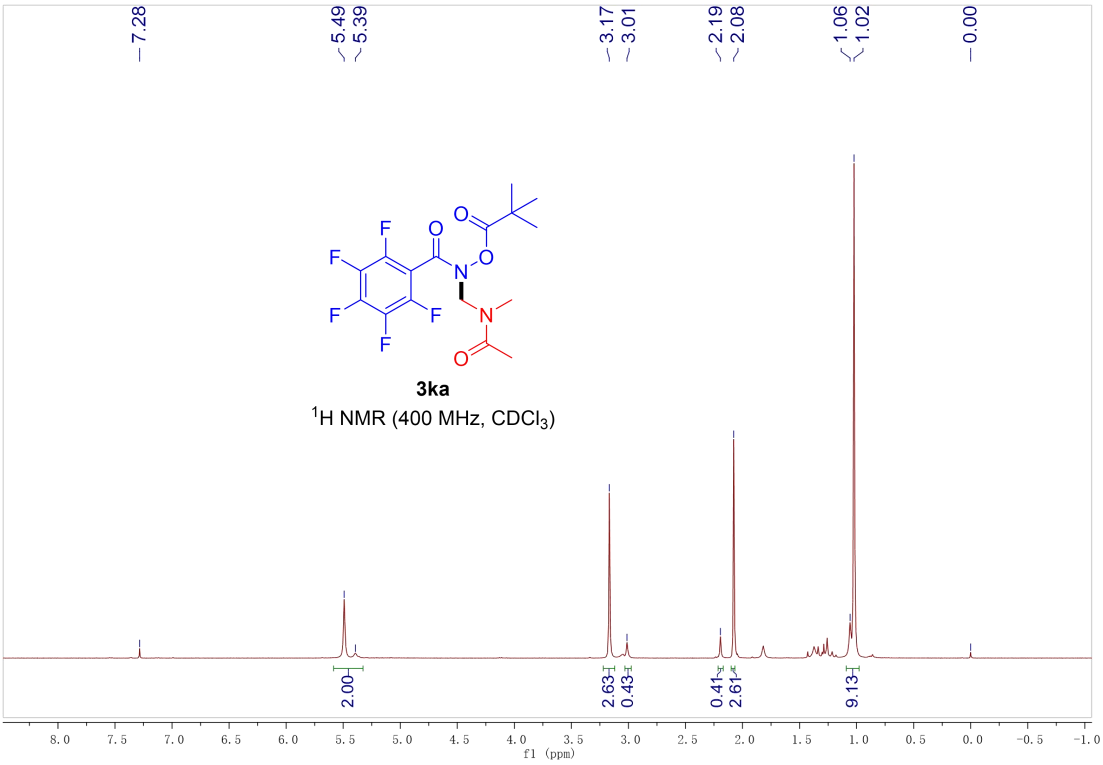
3ja

^{1}H NMR (500 MHz, $CDCl_3$)



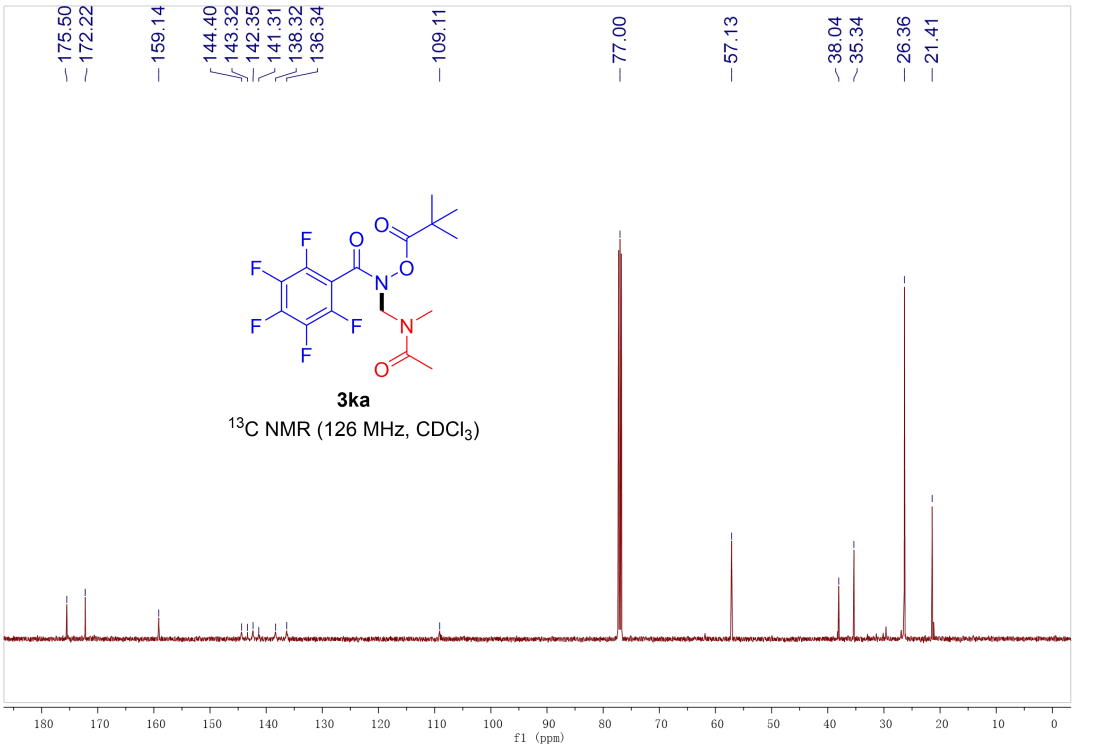
3ja

^{13}C NMR (126 MHz, $CDCl_3$)



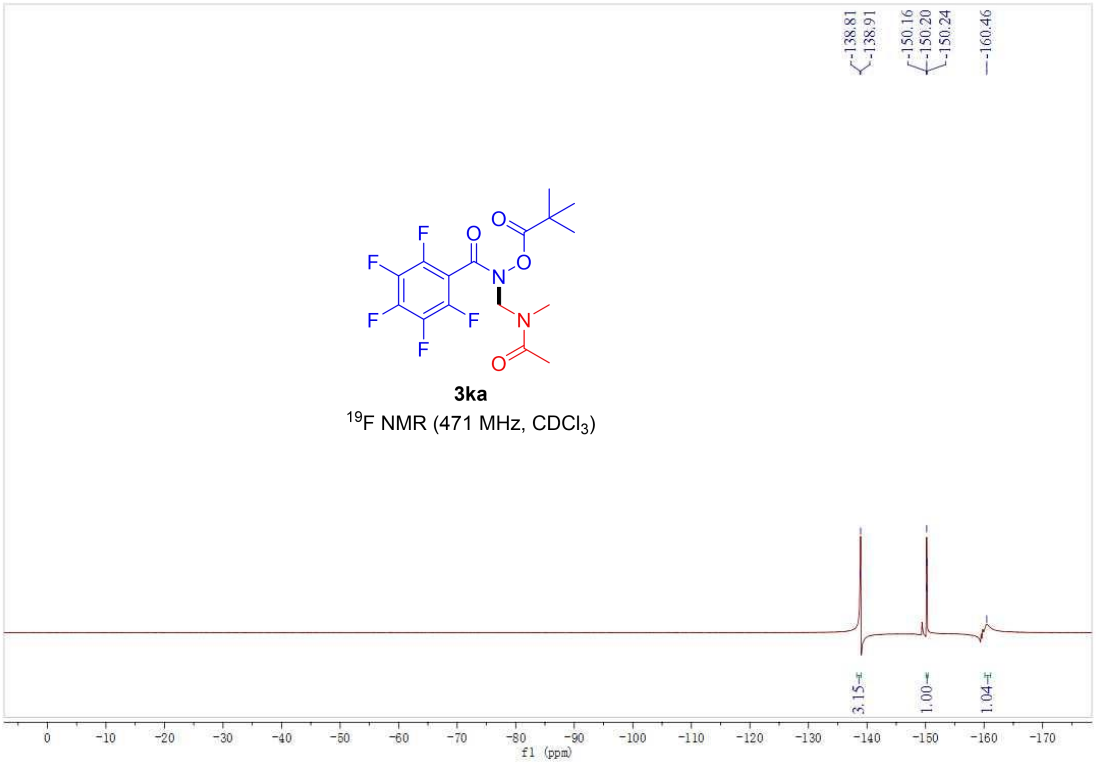
3ka

^{1}H NMR (400 MHz, $CDCl_3$)



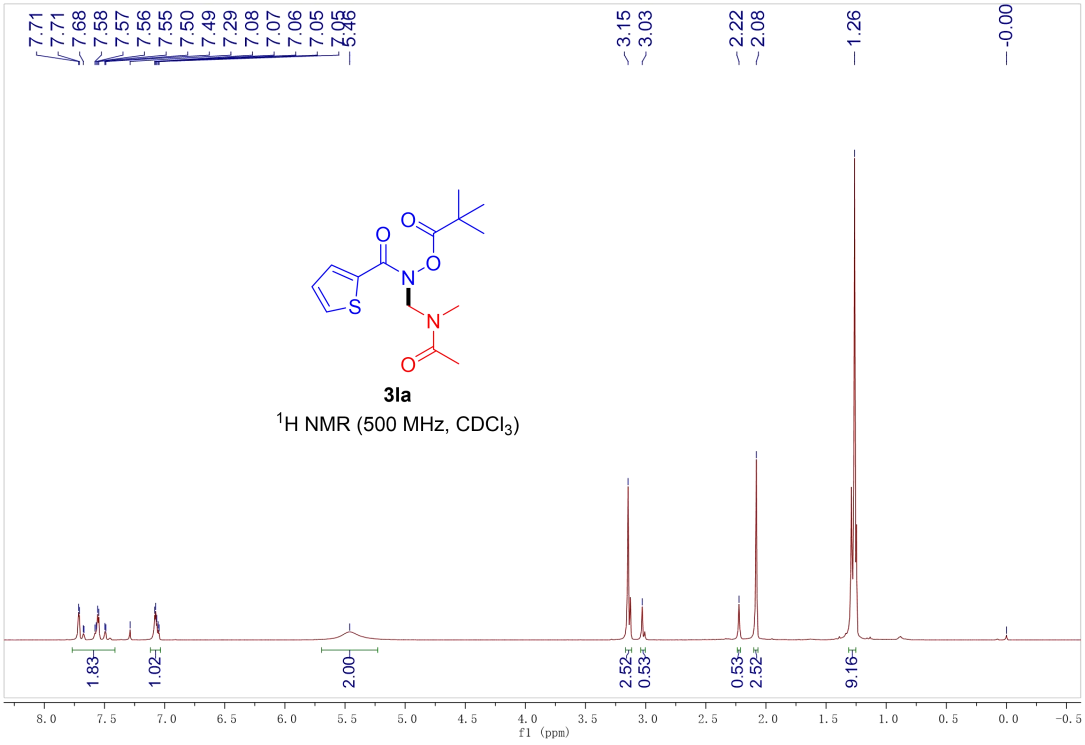
3ka

^{13}C NMR (126 MHz, $CDCl_3$)



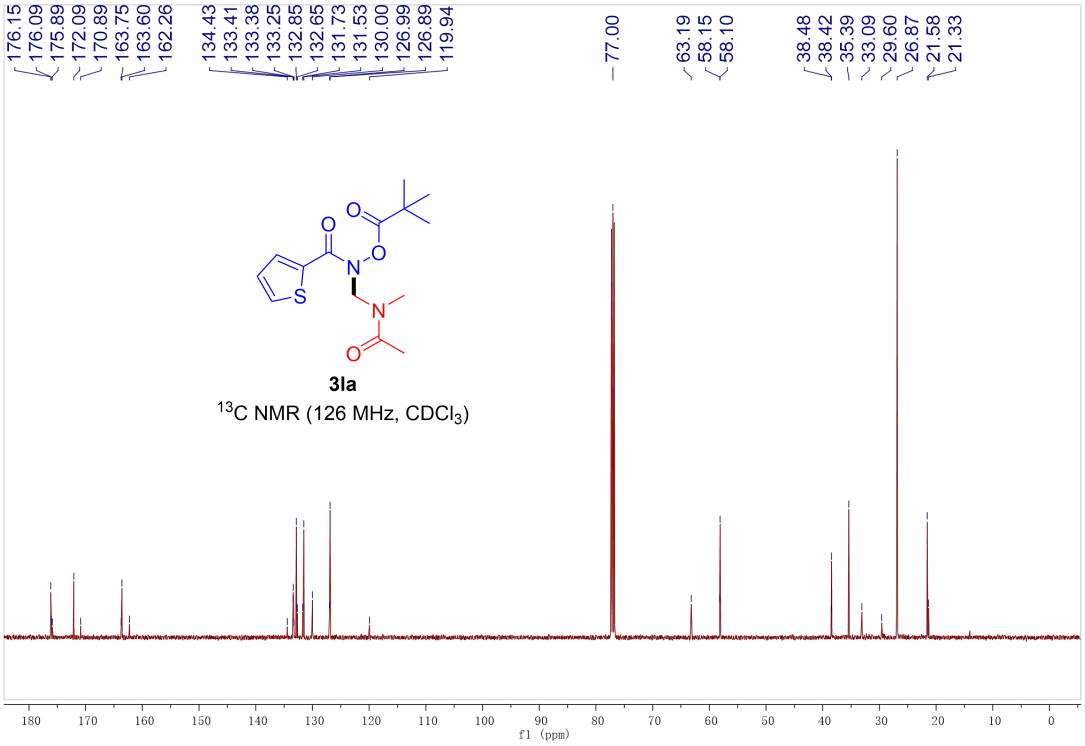
3ka

^{19}F NMR (471 MHz, $CDCl_3$)



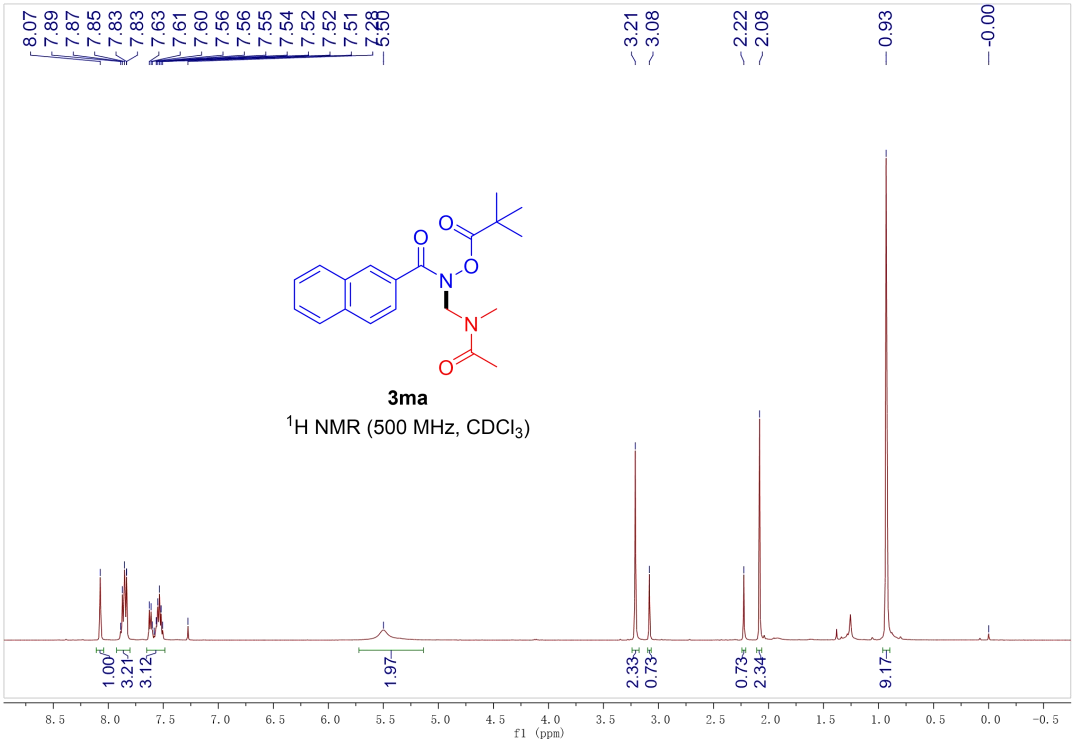
3la

^{1}H NMR (500 MHz, $CDCl_3$)



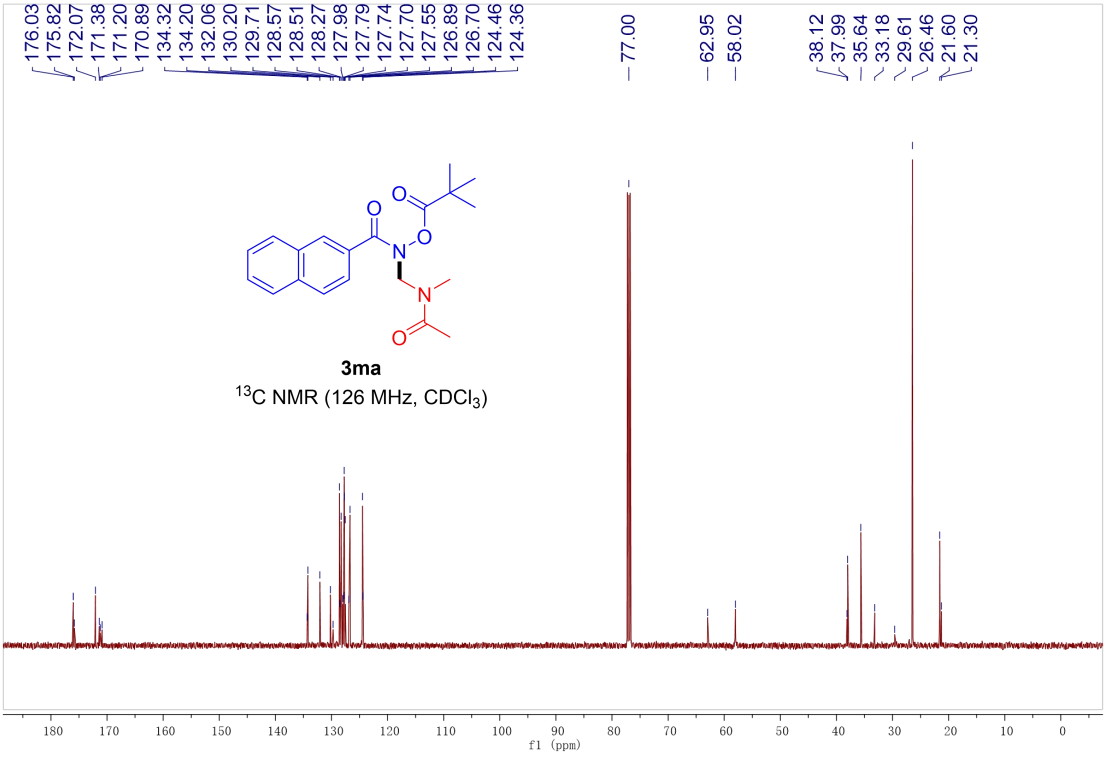
3la

^{13}C NMR (126 MHz, $CDCl_3$)



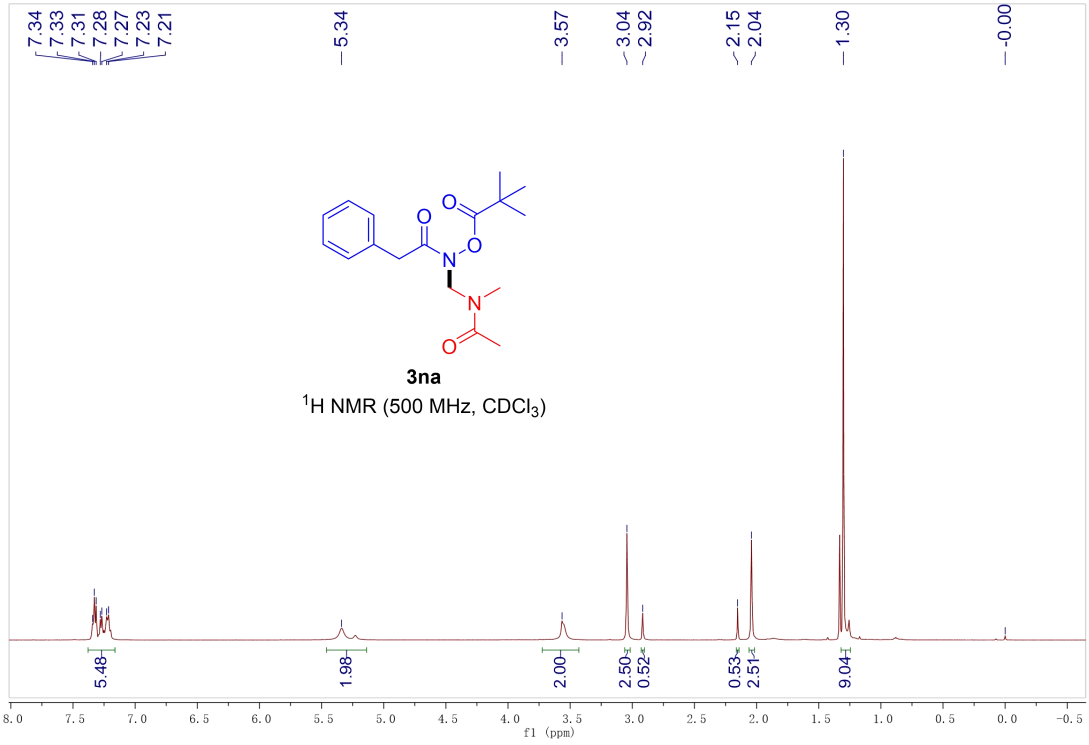
3ma

^{1}H NMR (500 MHz, $CDCl_3$)



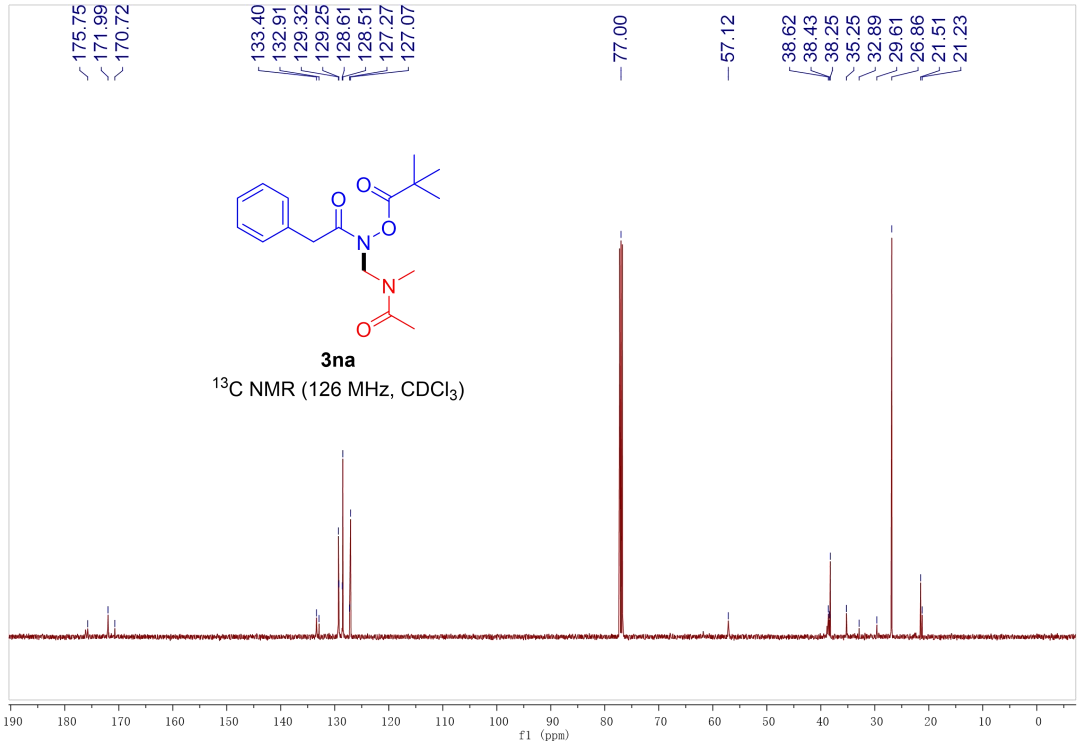
3ma

^{13}C NMR (126 MHz, $CDCl_3$)



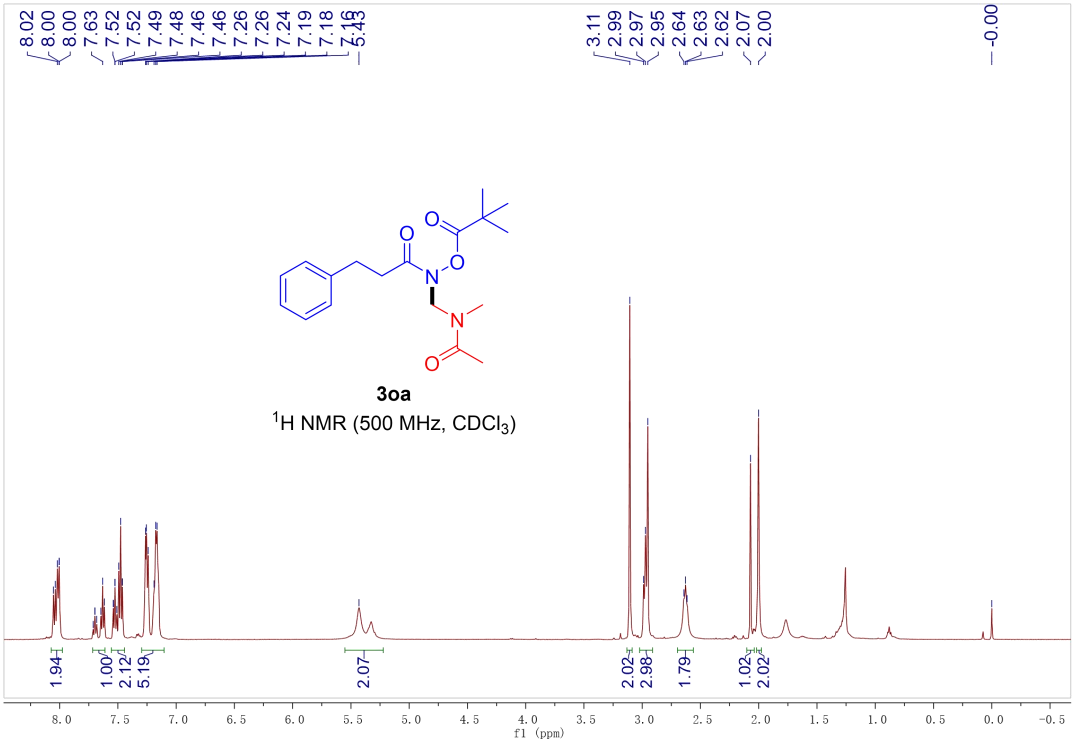
3na

^{1}H NMR (500 MHz, $CDCl_3$)



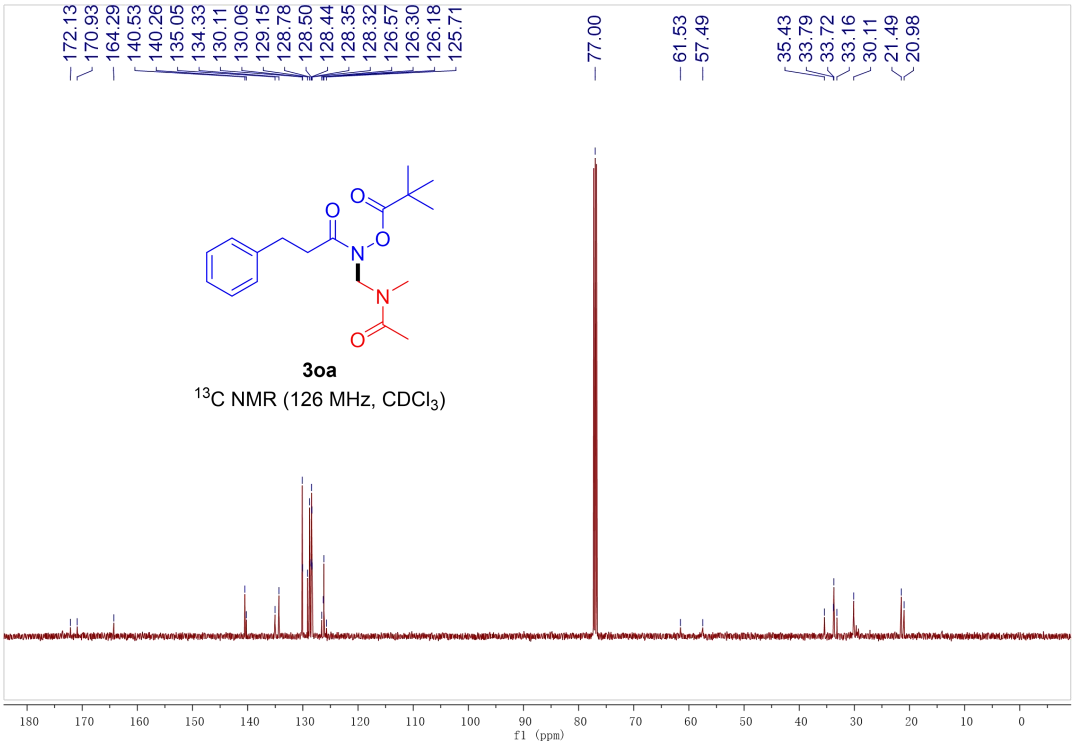
3na

^{13}C NMR (126 MHz, $CDCl_3$)



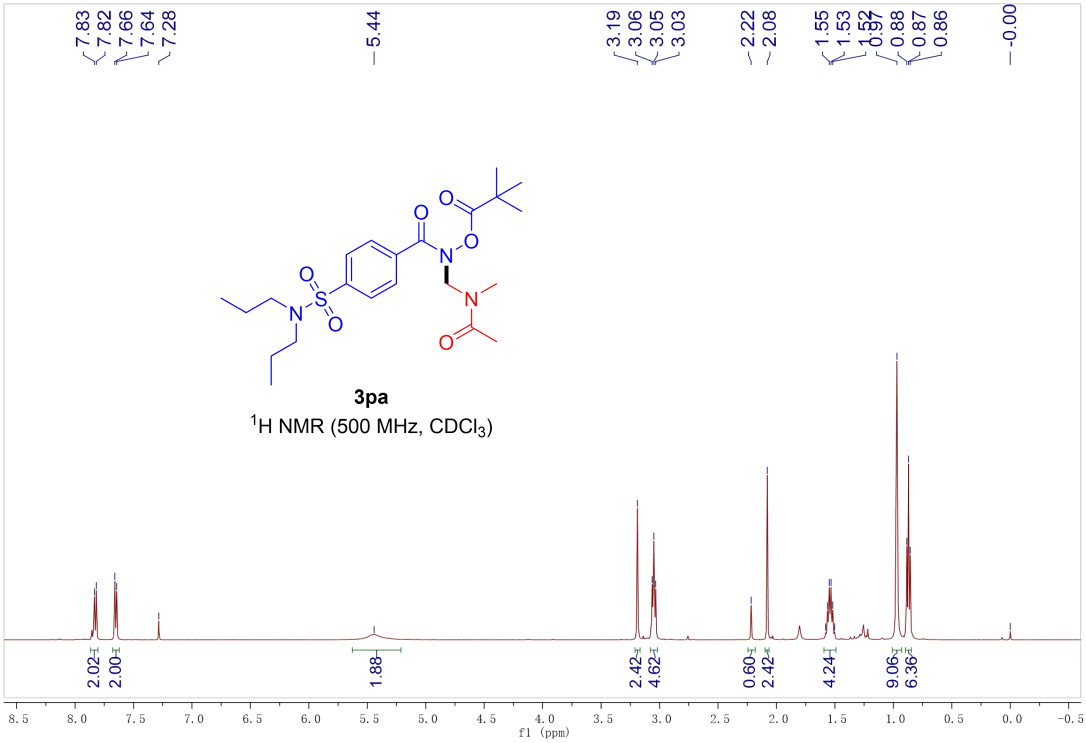
3oa

^{1}H NMR (500 MHz, $CDCl_3$)



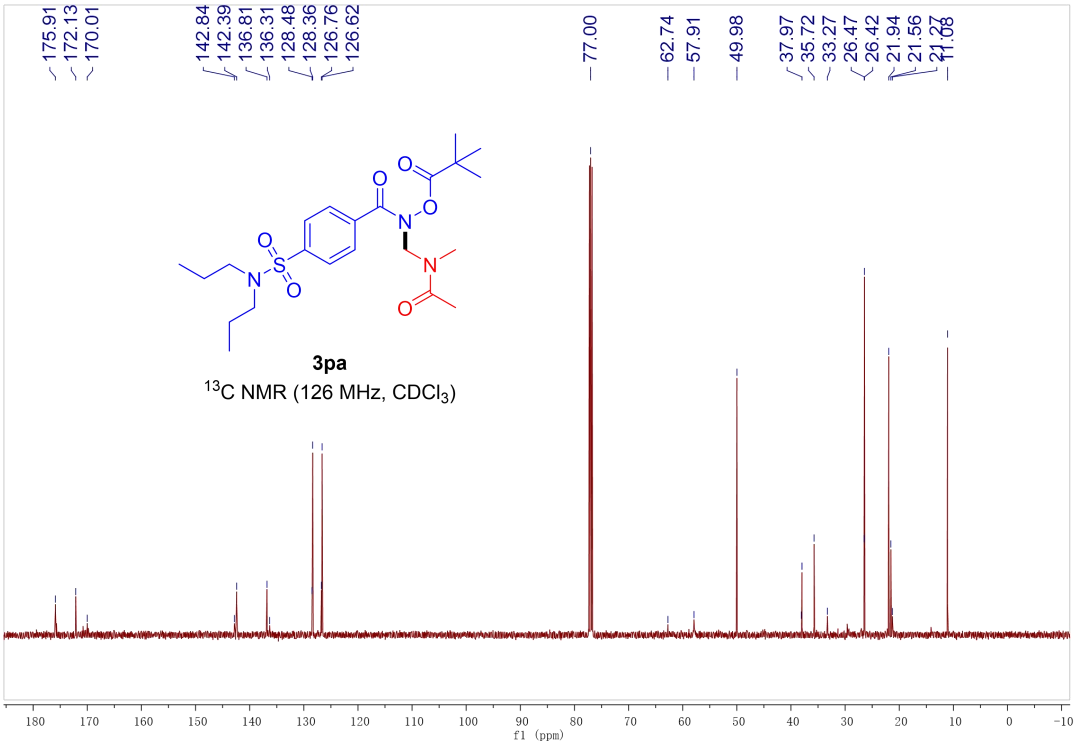
3oa

^{13}C NMR (126 MHz, $CDCl_3$)



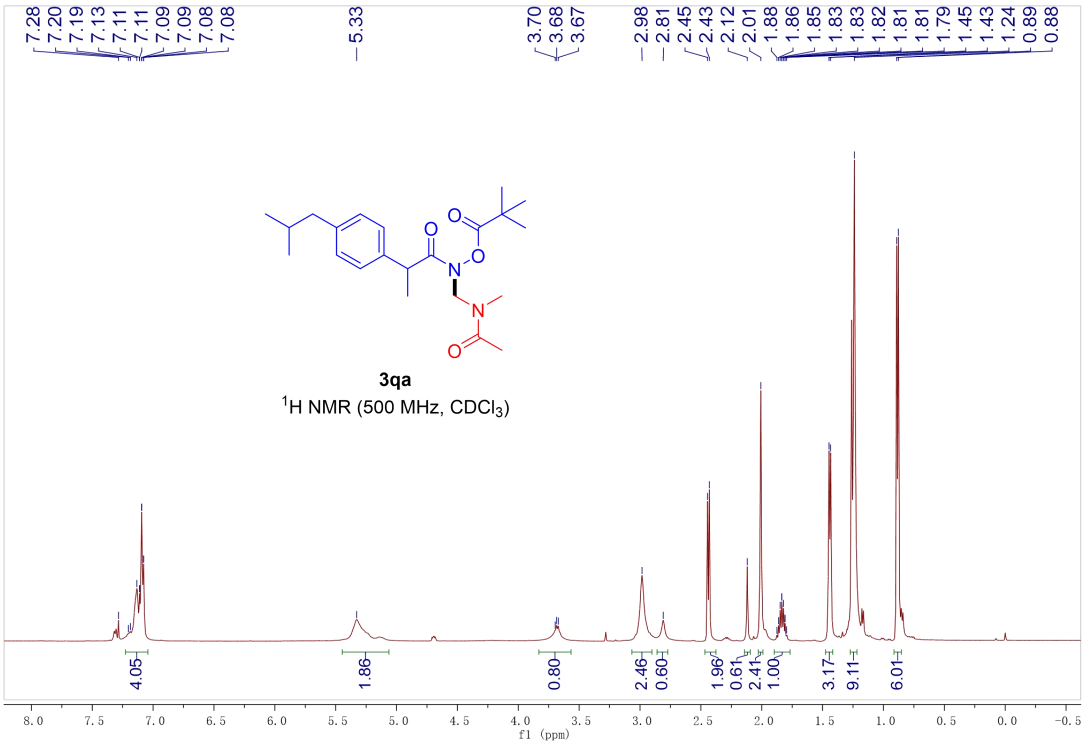
3pa

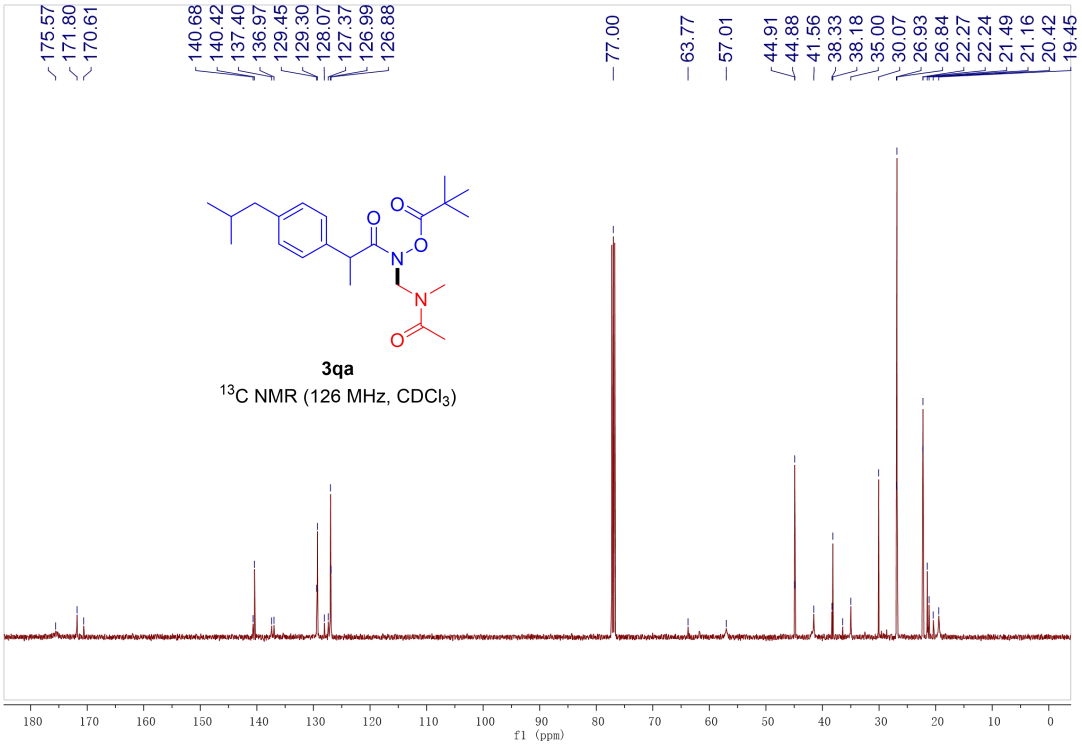
^{1}H NMR (500 MHz, $CDCl_3$)

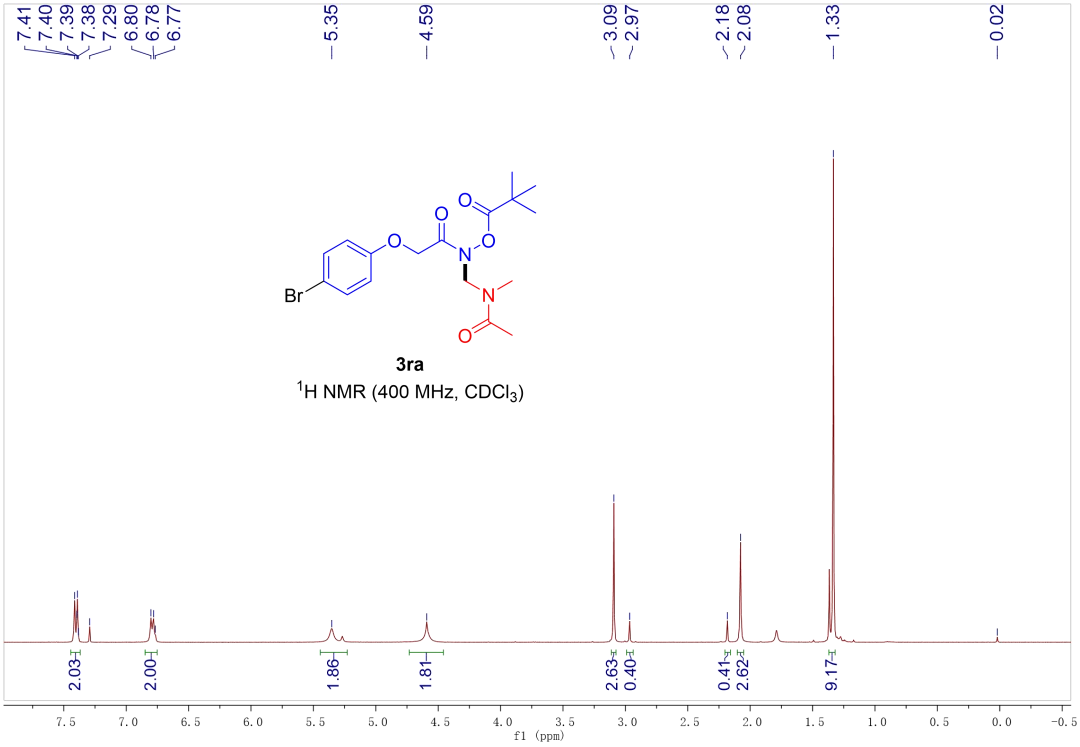


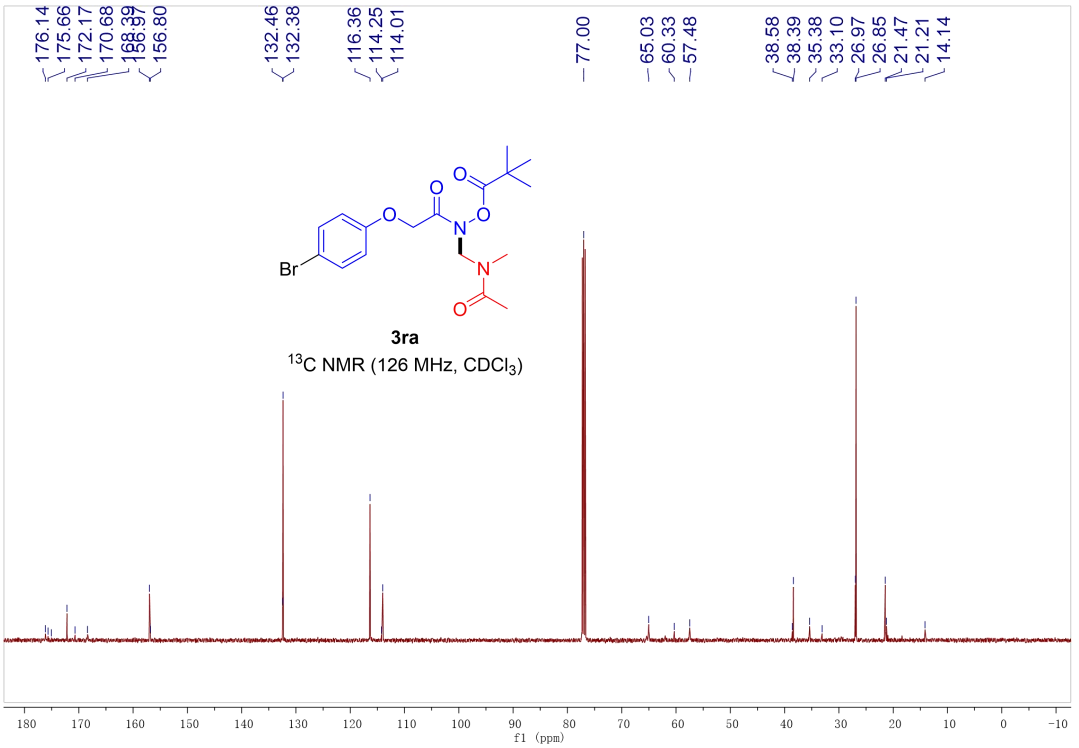
3pa

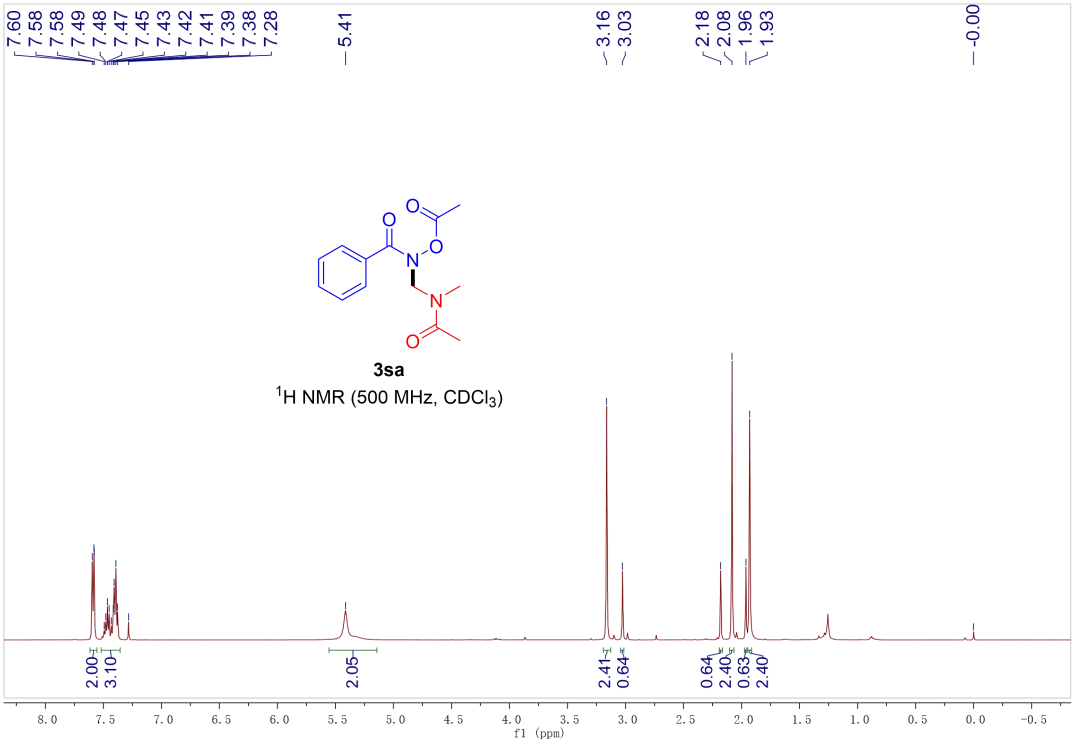
^{13}C NMR (126 MHz, $CDCl_3$)


7.28
7.20
7.19
7.13
7.11
7.11
7.09
7.09
7.08
7.08
5.33
3.70
3.68
3.67
2.98
2.81
2.45
2.43
2.12
2.01
1.88
1.86
1.85
1.83
1.83
1.82
1.81
1.81
1.79
1.45
1.43
1.24
0.89
0.88
3qa
1H NMR (500 MHz, CDCl3)
4.05
1.86
0.80
2.46
0.60
1.96
0.61
2.41
1.00
3.17
9.11
6.01
f1 (ppm)


175.57
171.80
170.61
140.68
140.42
137.40
136.97
129.45
129.30
128.07
127.37
126.99
126.88
77.00
63.77
57.01
44.91
44.88
41.56
38.33
38.18
35.00
30.07
26.93
26.84
22.27
22.24
21.49
21.16
20.42
19.45
3qa
13C NMR (126 MHz, CDCl3)
f1 (ppm)

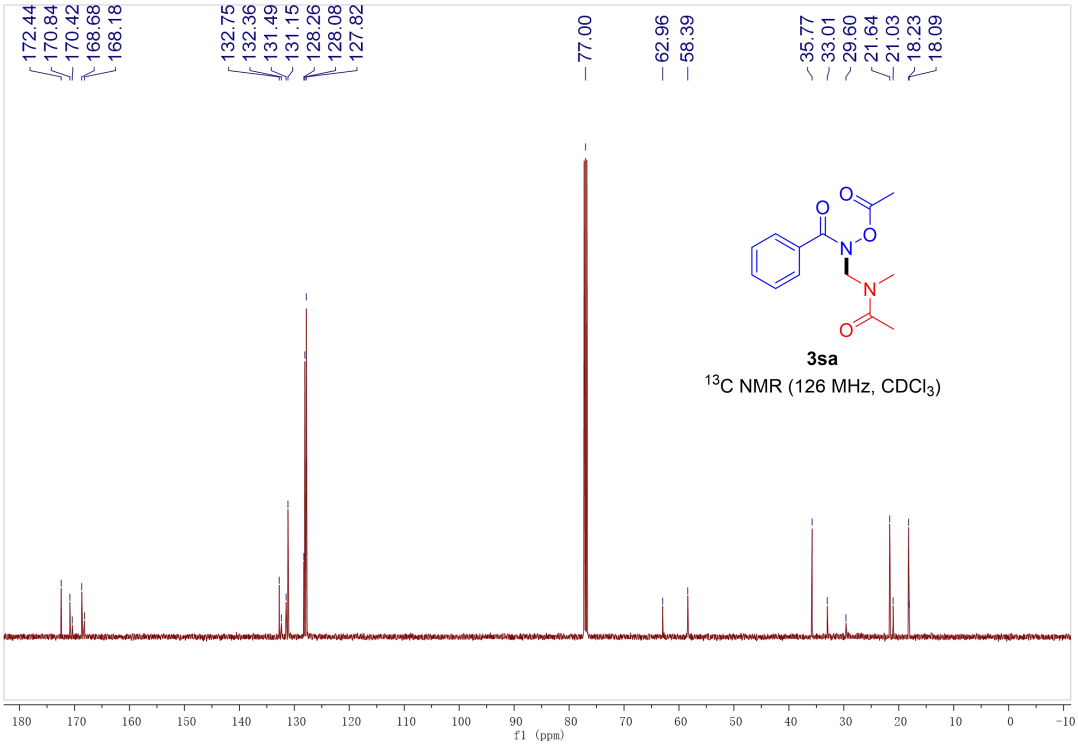

7.41
7.40
7.39
7.38
7.29
6.80
6.78
6.77
5.35
4.59
3.09
2.97
2.18
2.08
1.33
0.02
Br
O
N
3ra
1H NMR (400 MHz, CDCl3)
2.03
2.00
1.86
1.81
2.63
0.40
0.41
2.62
9.17
f1 (ppm)


176.14
175.66
172.17
170.68
156.97
156.80
132.46
132.38
116.36
114.25
114.01
77.00
65.03
60.33
57.48
38.58
38.39
35.38
33.10
26.97
26.85
21.47
21.21
14.14
Br
O
N
3ra
13C NMR (126 MHz, CDCl3)
f1 (ppm)



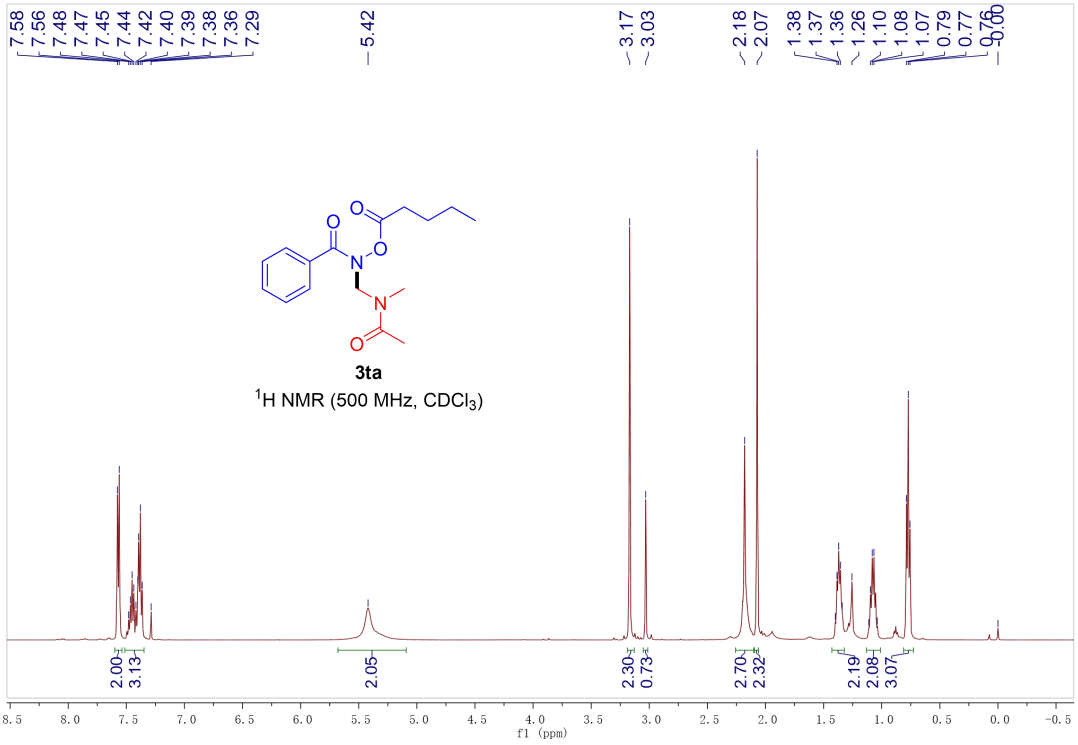
3sa

^{1}H NMR (500 MHz, $CDCl_3$)



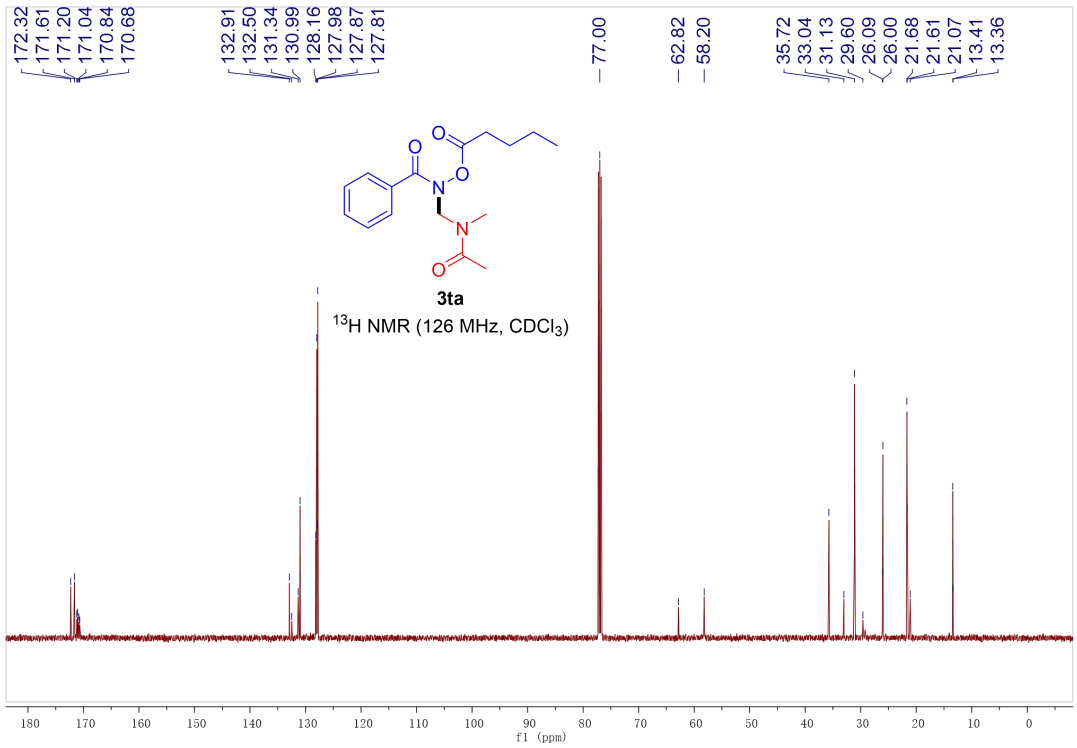
3sa

^{13}C NMR (126 MHz, $CDCl_3$)



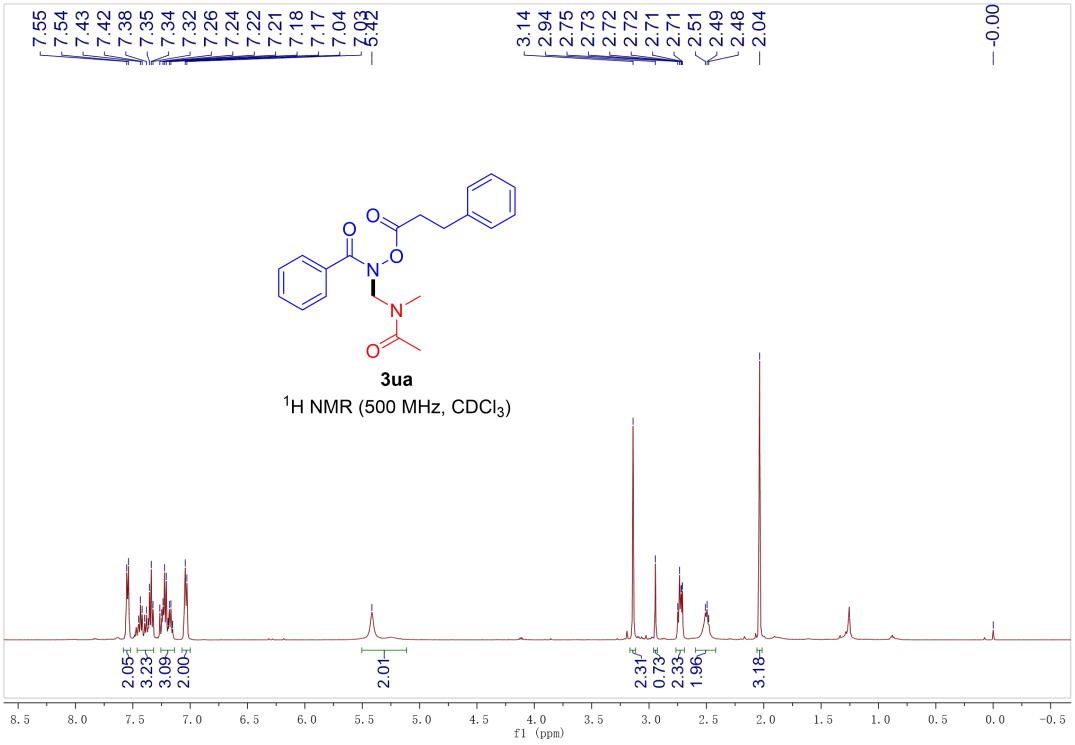
3ta

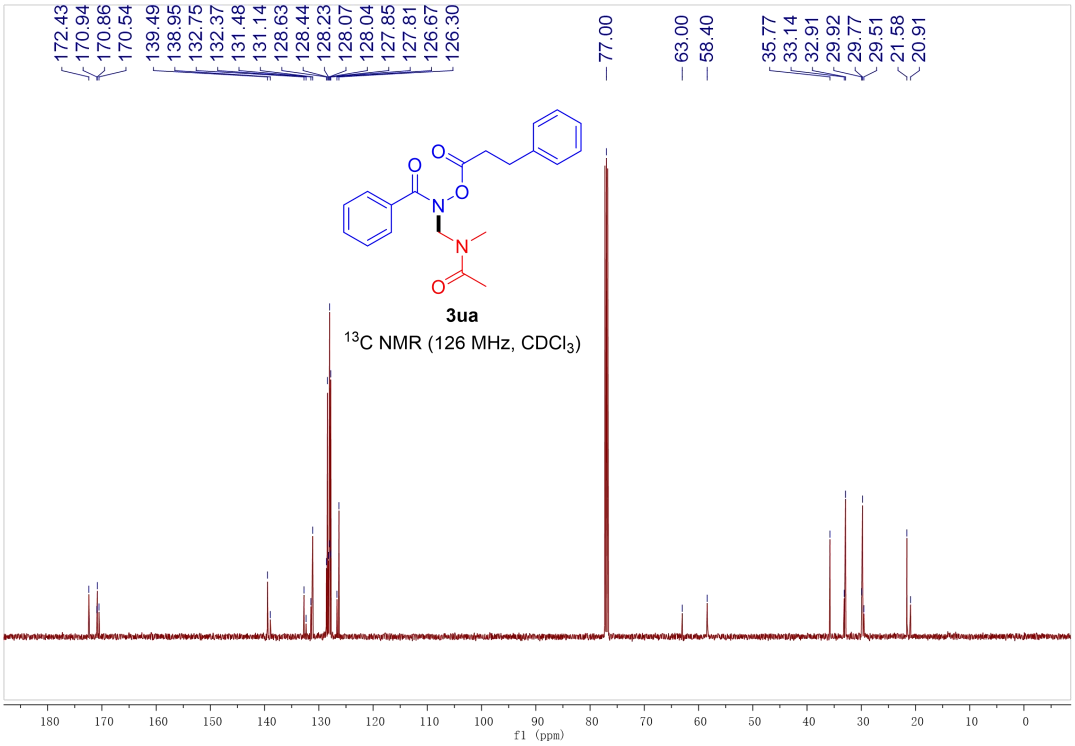
^{1}H NMR (500 MHz, $CDCl_3$)

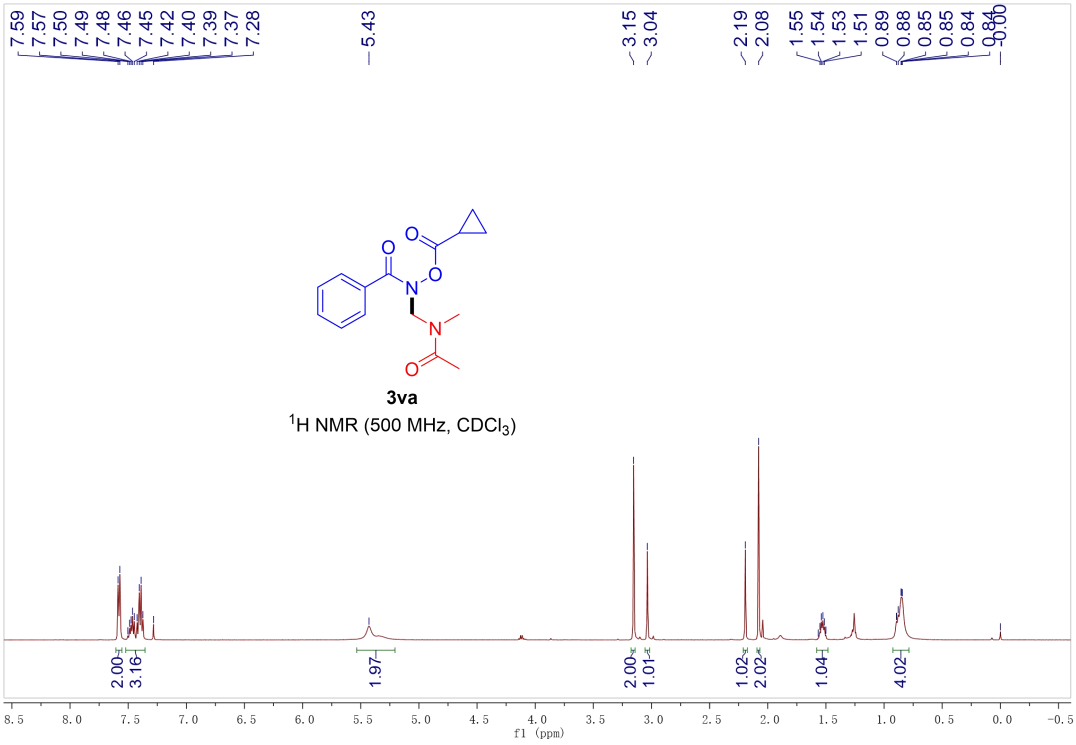


3ta

^{13}H NMR (126 MHz, $CDCl_3$)

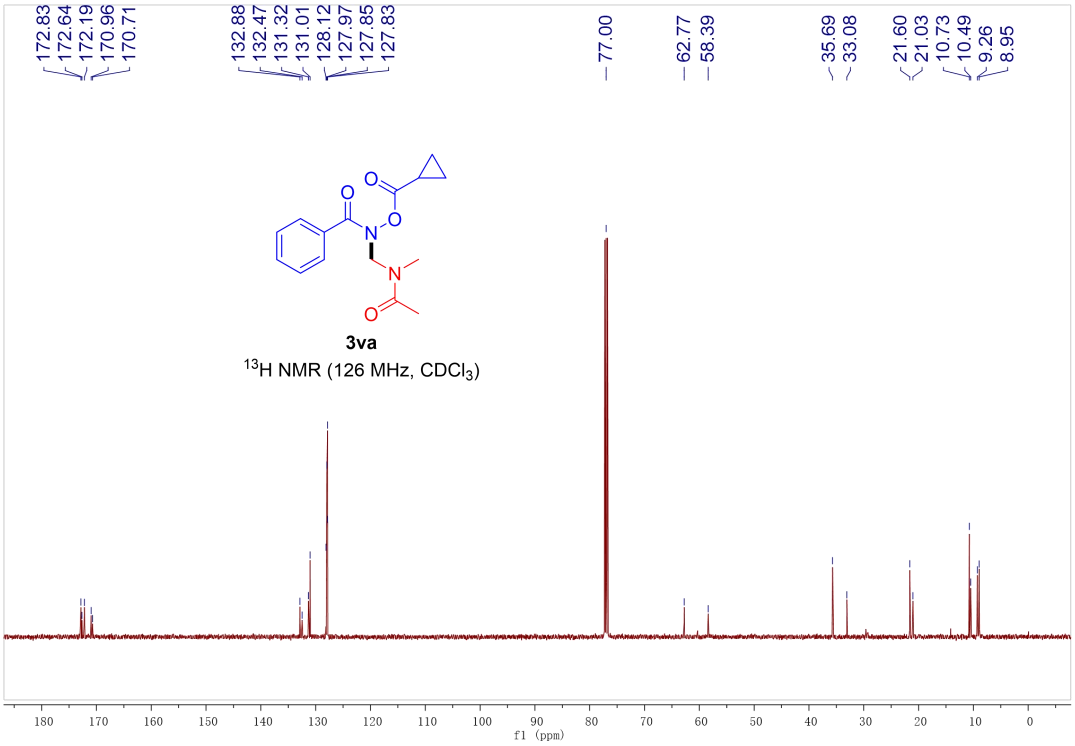

7.55
7.54
7.43
7.42
7.38
7.35
7.34
7.32
7.26
7.24
7.22
7.21
7.18
7.17
7.04
7.03
5.42
3.14
2.94
2.75
2.73
2.72
2.72
2.71
2.71
2.51
2.49
2.48
2.04
-0.00
O
O
N
O
N
O
3ua
1H NMR (500 MHz, CDCl3)
2.05
3.23
3.09
2.00
2.01
2.31
0.73
2.33
1.96
3.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


172.43
170.94
170.86
170.54
139.49
138.95
132.75
132.37
131.48
131.14
128.63
128.44
128.23
128.07
128.04
127.85
127.81
126.67
126.30
77.00
63.00
58.40
35.77
33.14
32.91
29.92
29.77
29.51
21.58
20.91
O
O
N
O
N
O
3ua
13C NMR (126 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



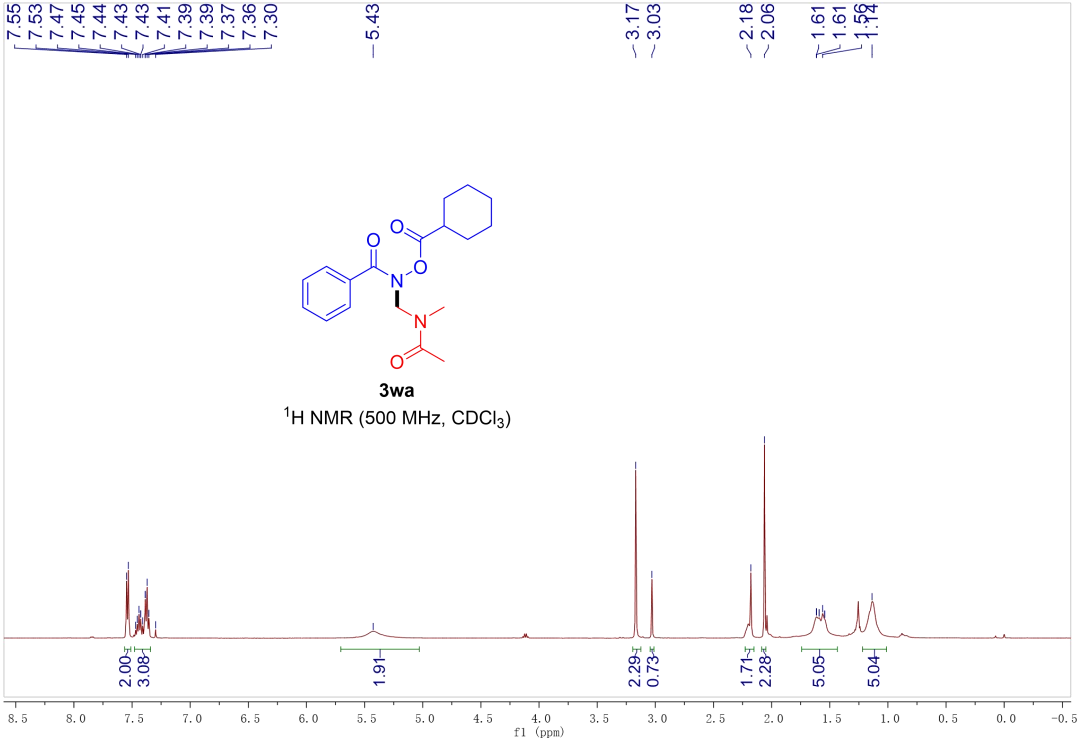
3va

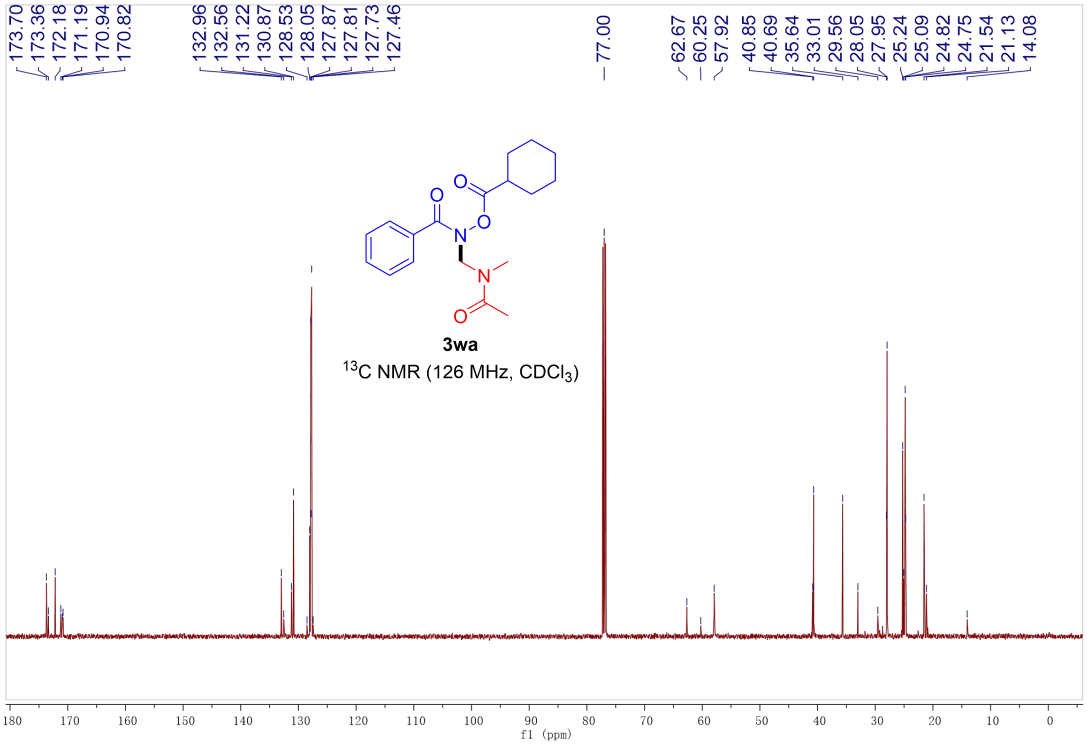
^{1}H NMR (500 MHz, $CDCl_3$)

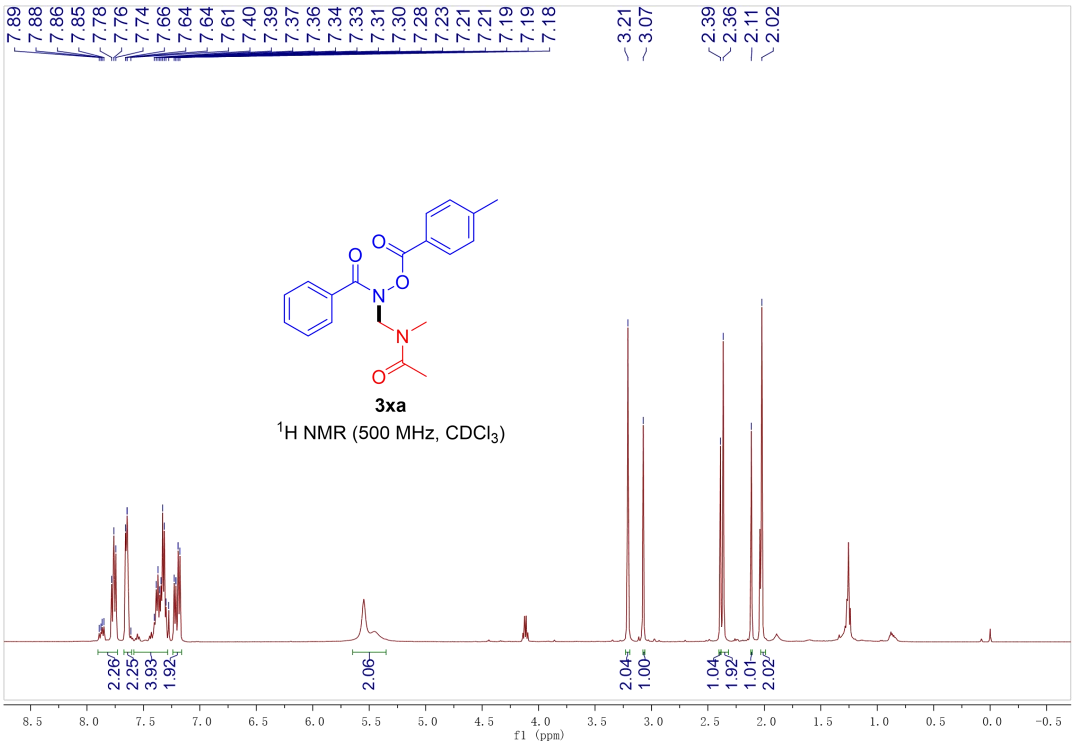


3va

^{13}H NMR (126 MHz, $CDCl_3$)

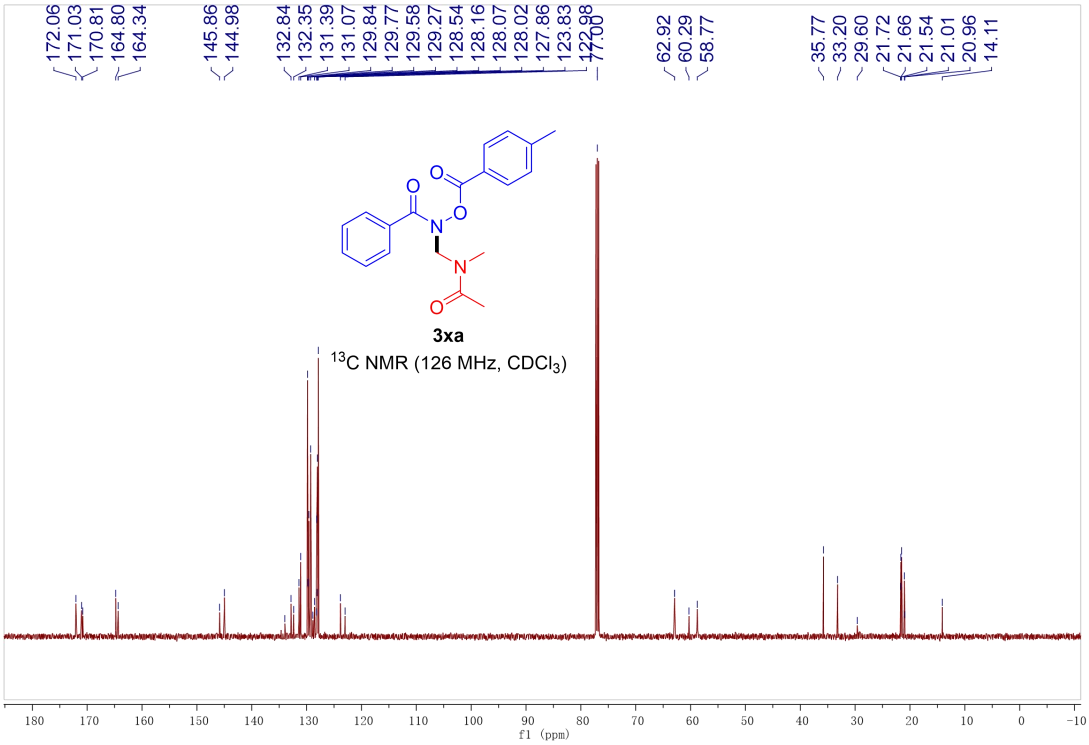

7.55
7.53
7.47
7.45
7.44
7.43
7.43
7.41
7.39
7.39
7.37
7.36
7.30
5.43
3.17
3.03
2.18
2.06
1.61
1.61
1.56
1.14
O
O
N
O
N
O
3wa
1H NMR (500 MHz, CDCl3)
2.00
3.08
1.91
2.29
0.73
1.71
2.28
5.05
5.04
f1 (ppm)


173.70
173.36
172.18
171.19
170.94
170.82
132.96
132.56
131.22
130.87
128.53
128.05
127.87
127.81
127.73
127.46
77.00
62.67
60.25
57.92
40.85
40.69
35.64
33.01
29.56
28.05
27.95
25.24
25.09
24.82
24.75
21.54
21.13
14.08
O
O
N
O
N
O
3wa
13C NMR (126 MHz, CDCl3)
f1 (ppm)



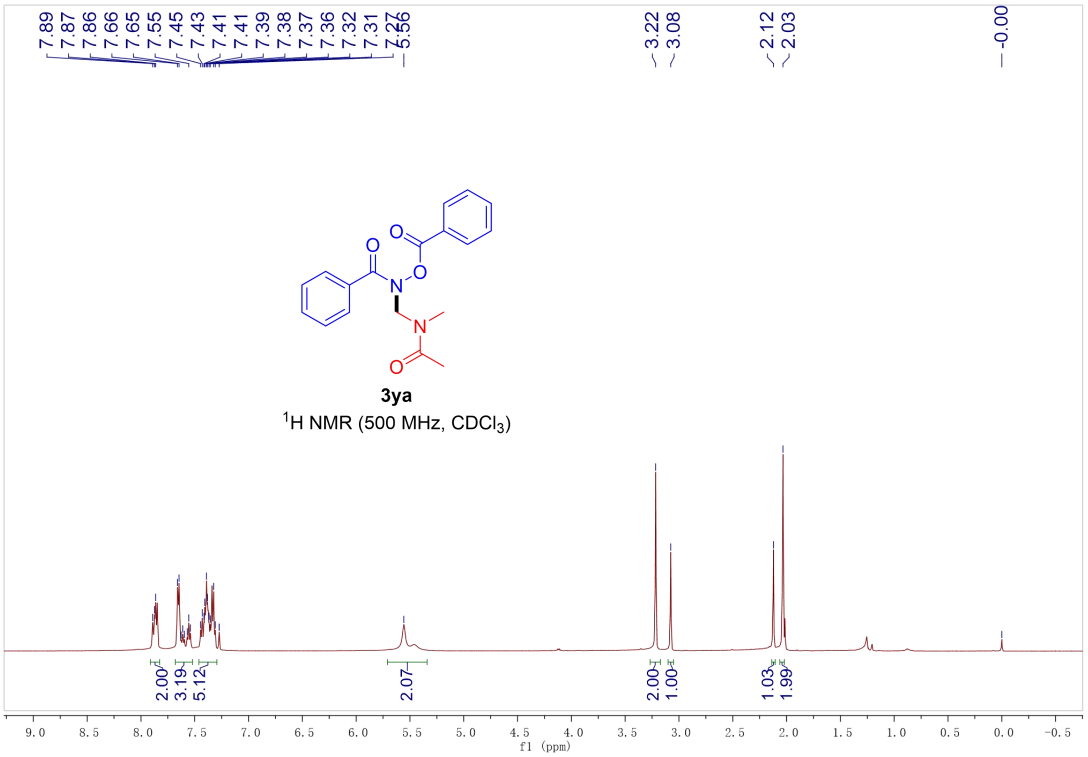
3xa

^{1}H NMR (500 MHz, $CDCl_3$)



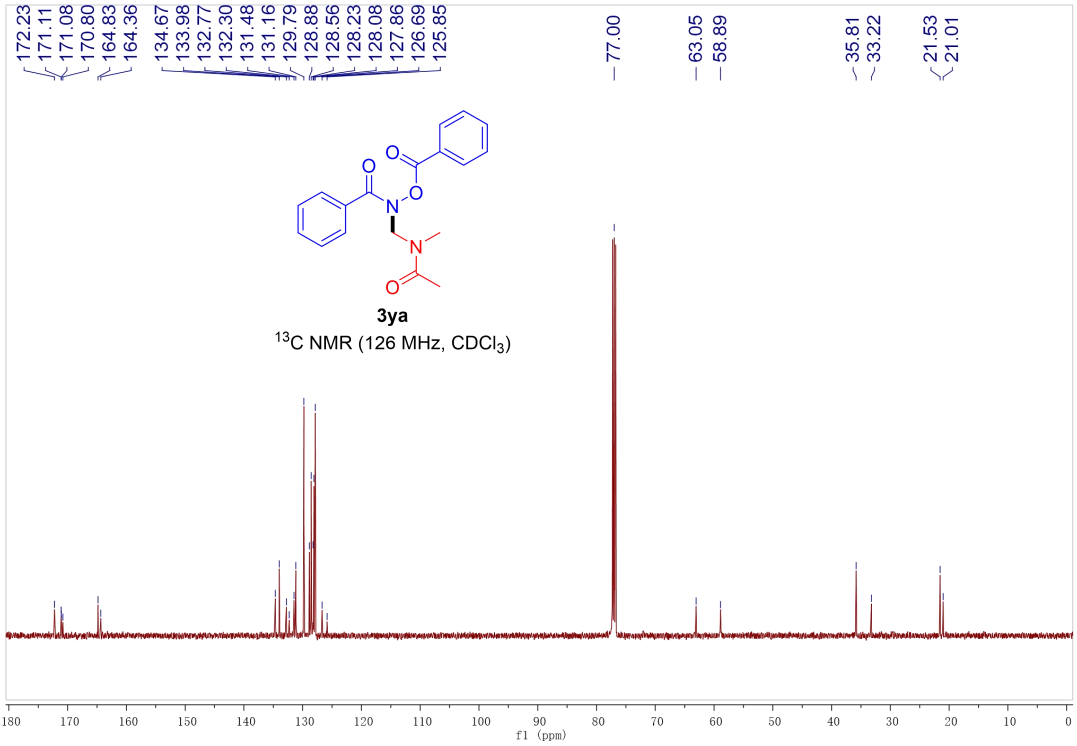
3xa

^{13}C NMR (126 MHz, $CDCl_3$)



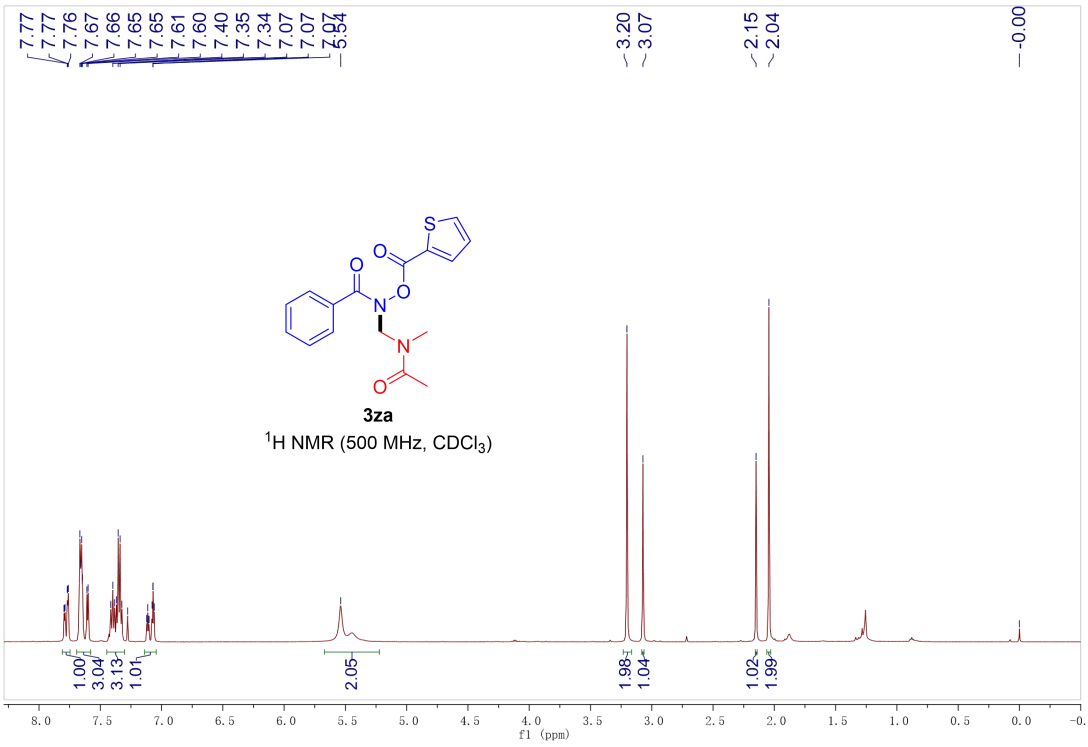
3ya

^{1}H NMR (500 MHz, $CDCl_3$)



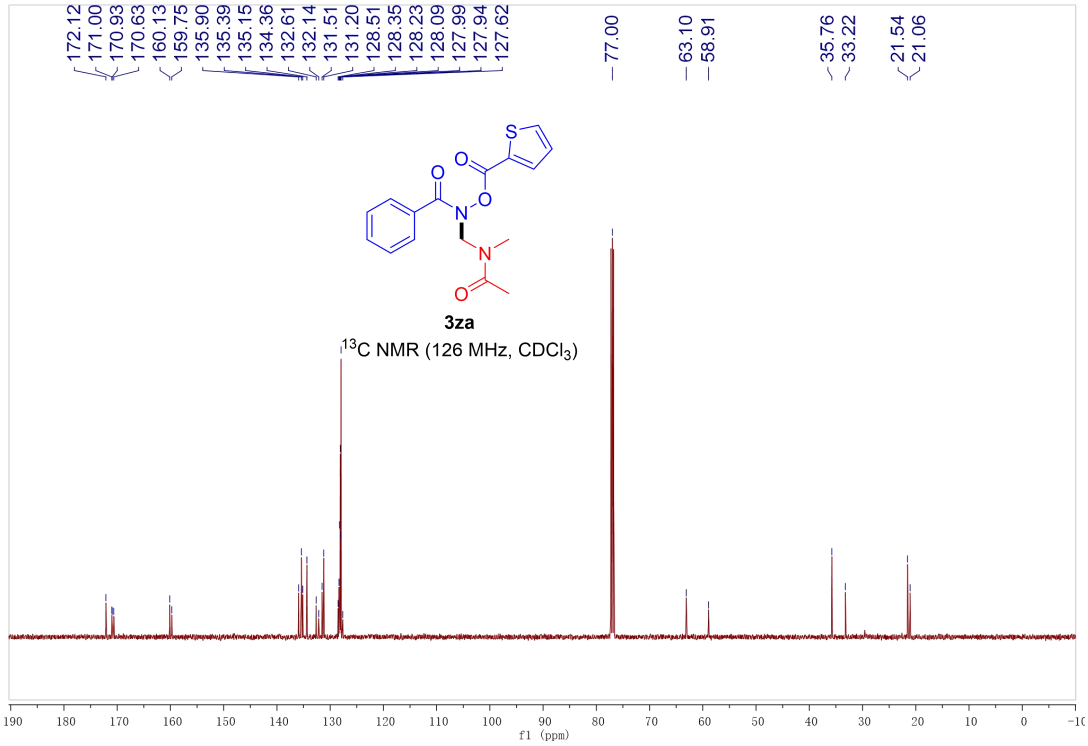
3ya

^{13}C NMR (126 MHz, $CDCl_3$)



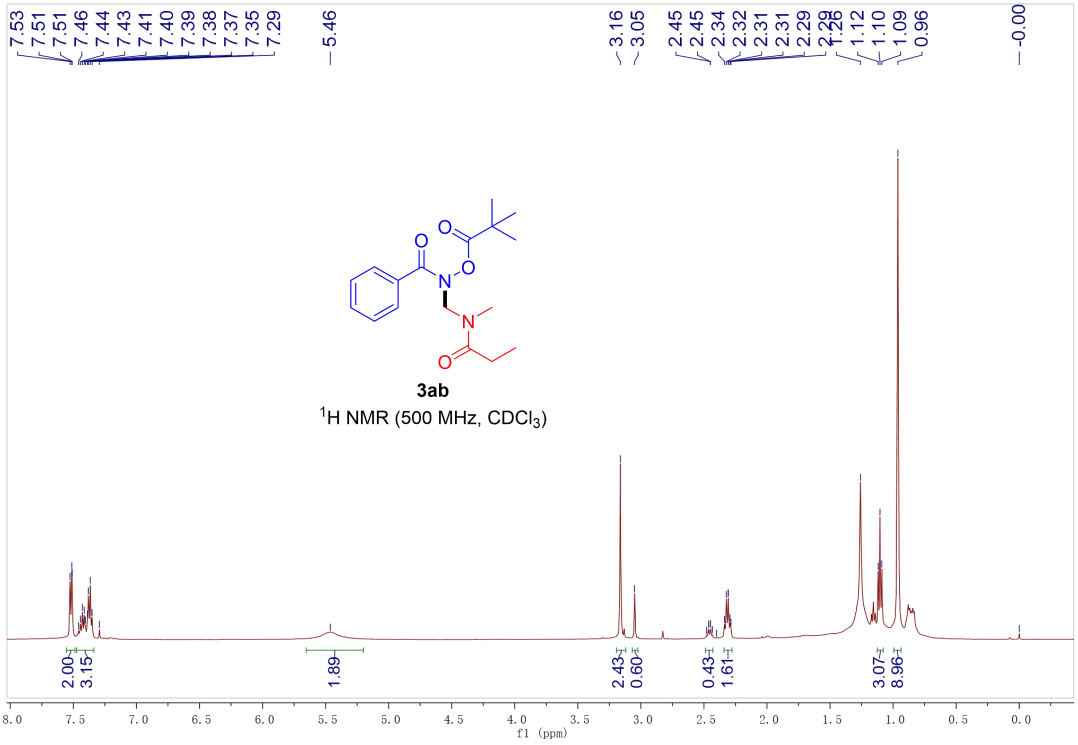
3za

^{1}H NMR (500 MHz, $CDCl_3$)



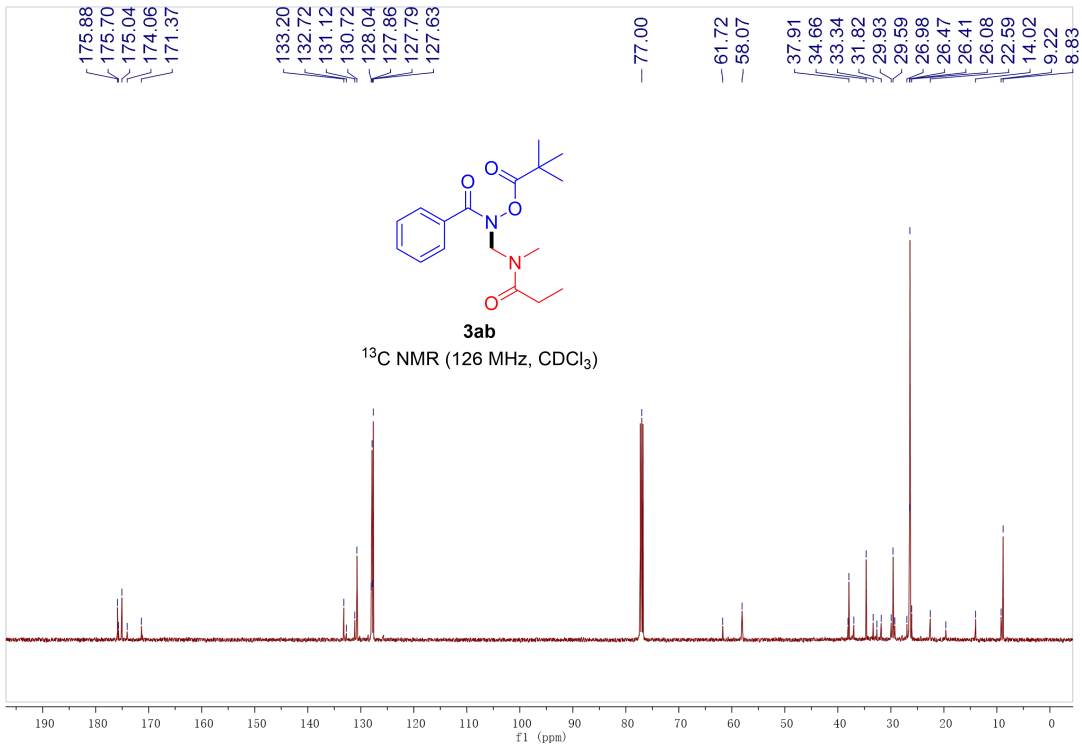
3za

^{13}C NMR (126 MHz, $CDCl_3$)



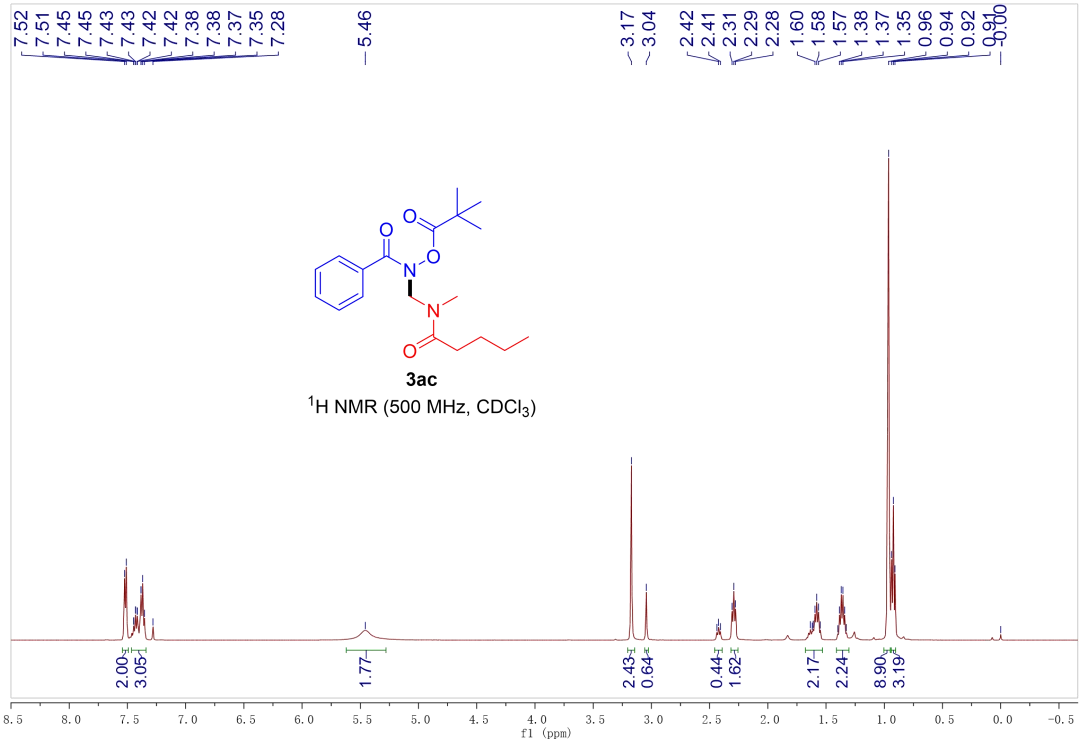
3ab

^{1}H NMR (500 MHz, $CDCl_3$)



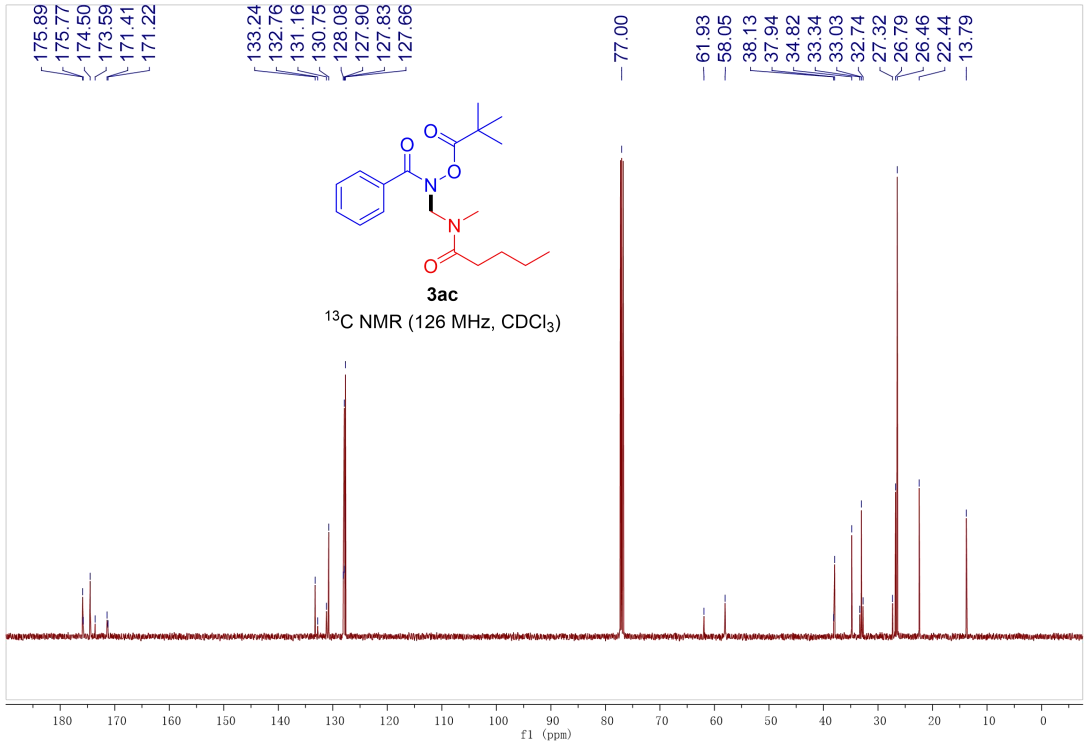
3ab

^{13}C NMR (126 MHz, $CDCl_3$)



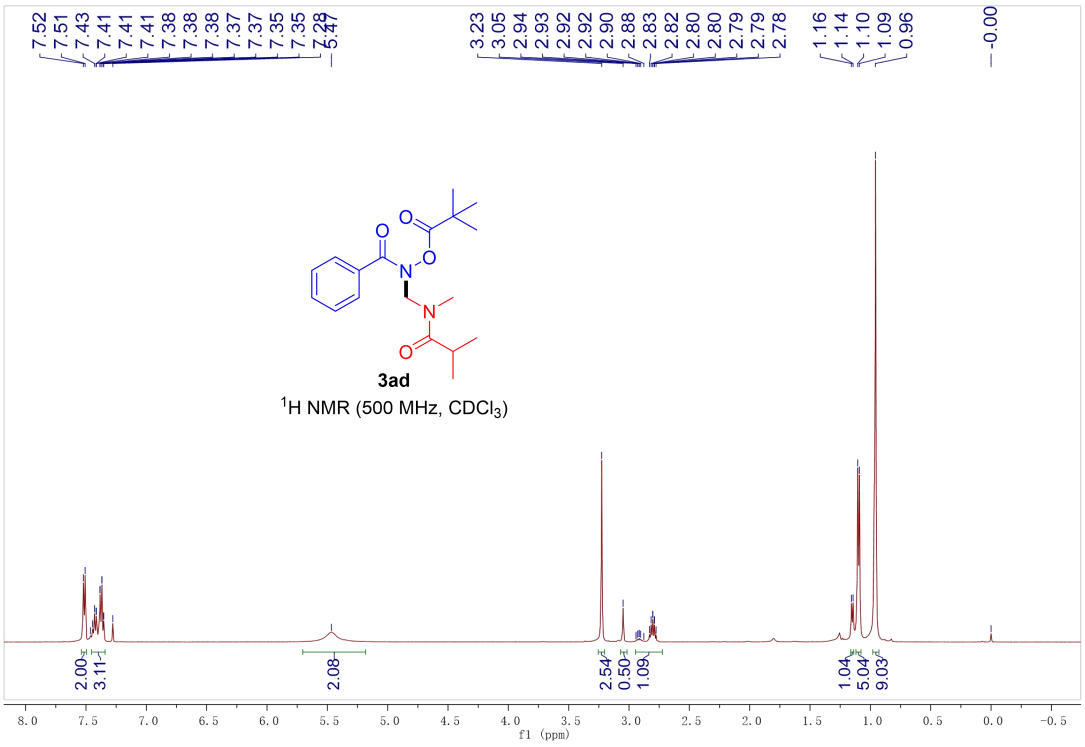
3ac

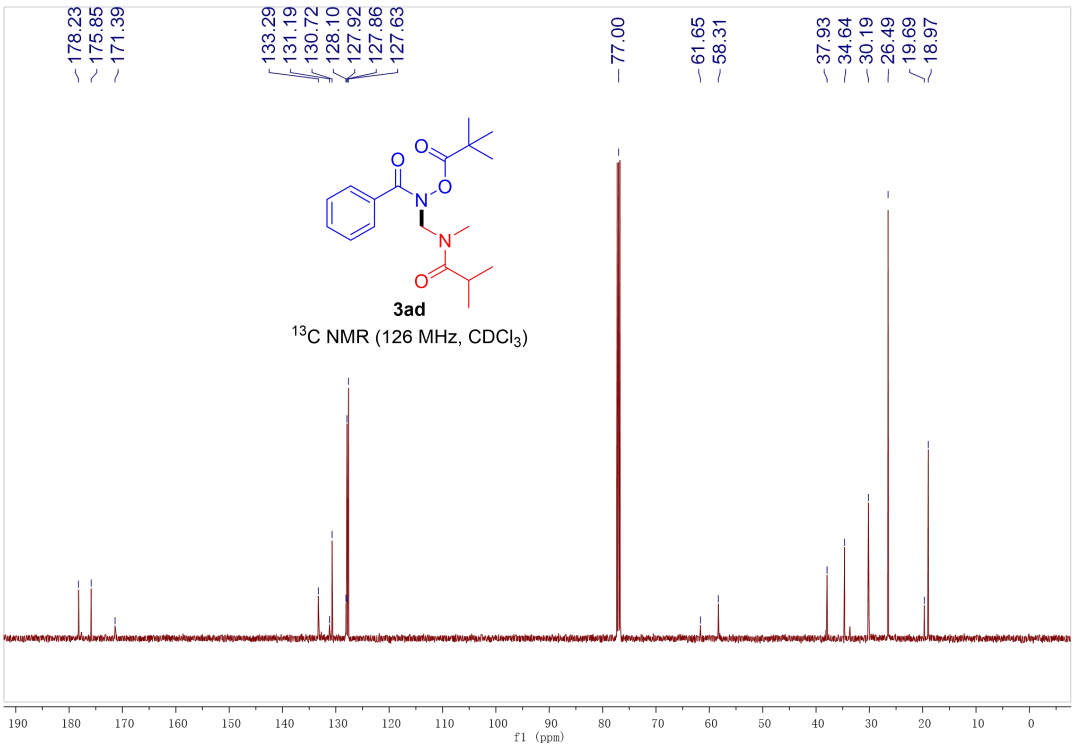
^{1}H NMR (500 MHz, $CDCl_3$)

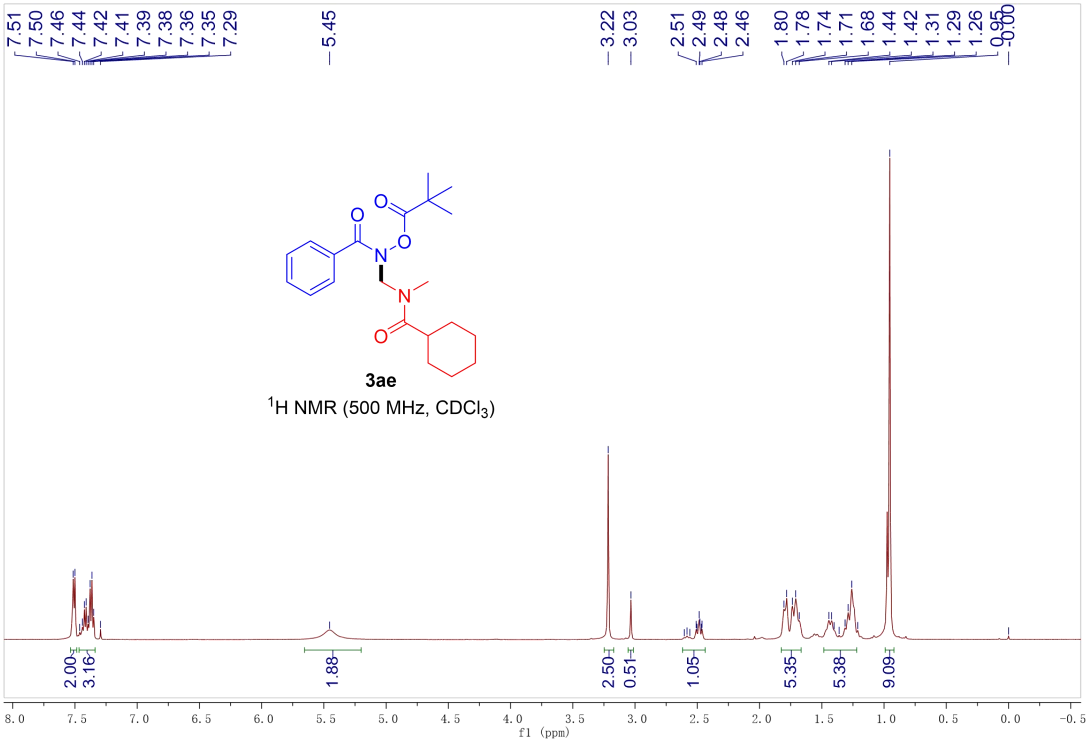


3ac

^{13}C NMR (126 MHz, $CDCl_3$)

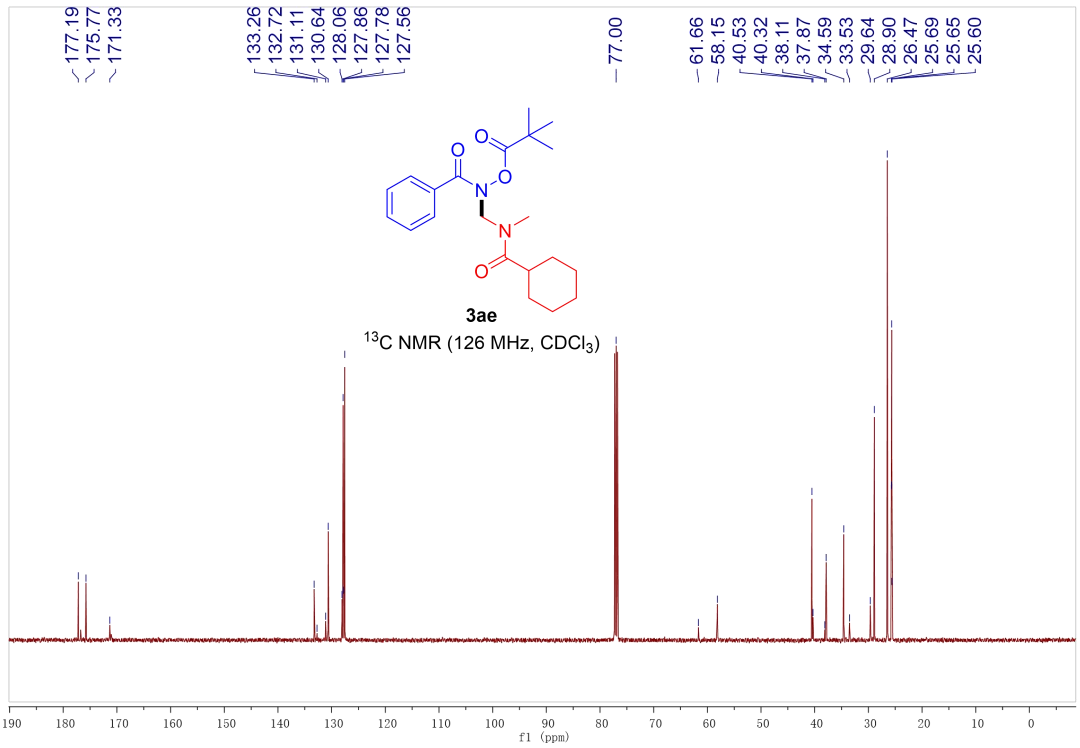

7.52
7.51
7.43
7.41
7.41
7.41
7.38
7.38
7.38
7.37
7.37
7.35
7.35
7.28
5.47
3.23
3.05
2.94
2.93
2.92
2.92
2.90
2.88
2.83
2.82
2.80
2.80
2.79
2.79
2.78
1.16
1.14
1.10
1.09
0.96
-0.00
3ad
1H NMR (500 MHz, CDCl3)
2.00
3.11
2.08
2.54
0.50
1.09
1.04
5.04
9.03
f1 (ppm)


178.23
175.85
171.39
133.29
131.19
130.72
128.10
127.92
127.86
127.63
77.00
61.65
58.31
37.93
34.64
30.19
26.49
19.69
18.97
3ad
13C NMR (126 MHz, CDCl3)
f1 (ppm)



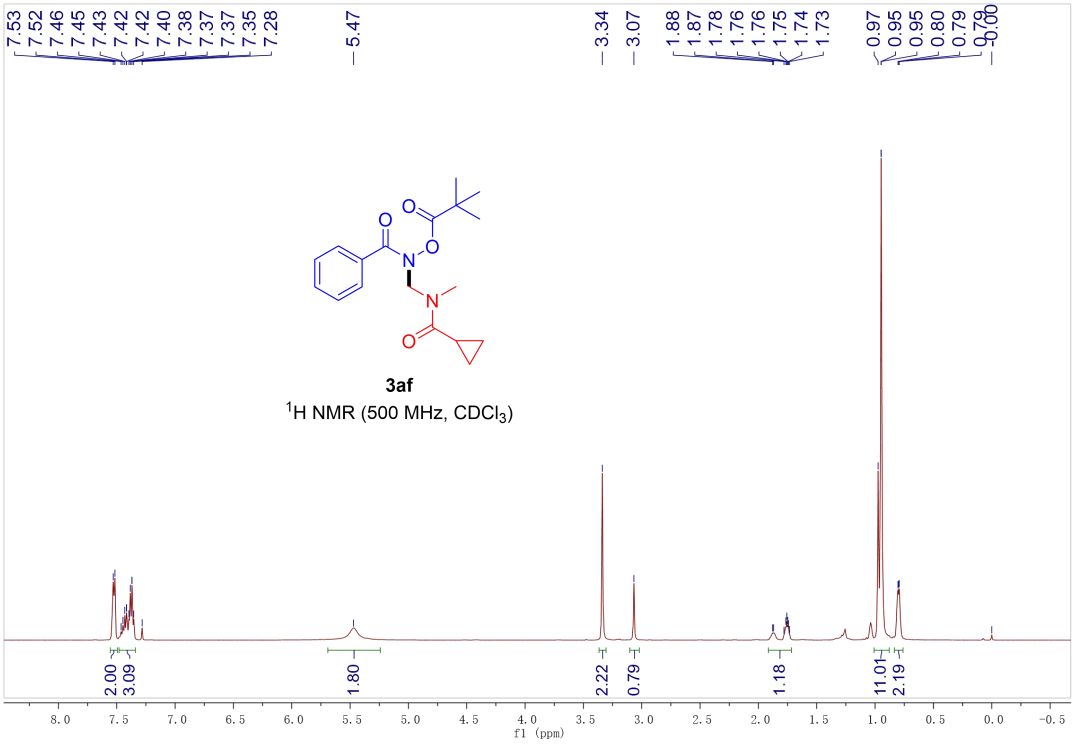
3ae

^{1}H NMR (500 MHz, $CDCl_3$)



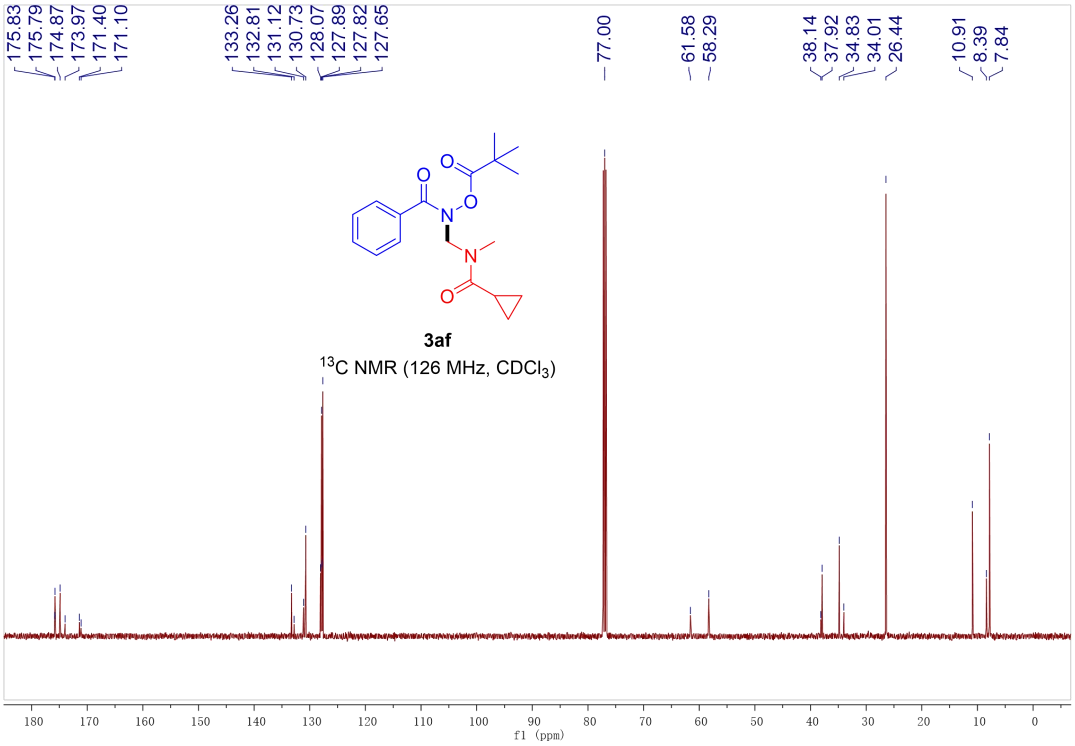
3ae

^{13}C NMR (126 MHz, $CDCl_3$)



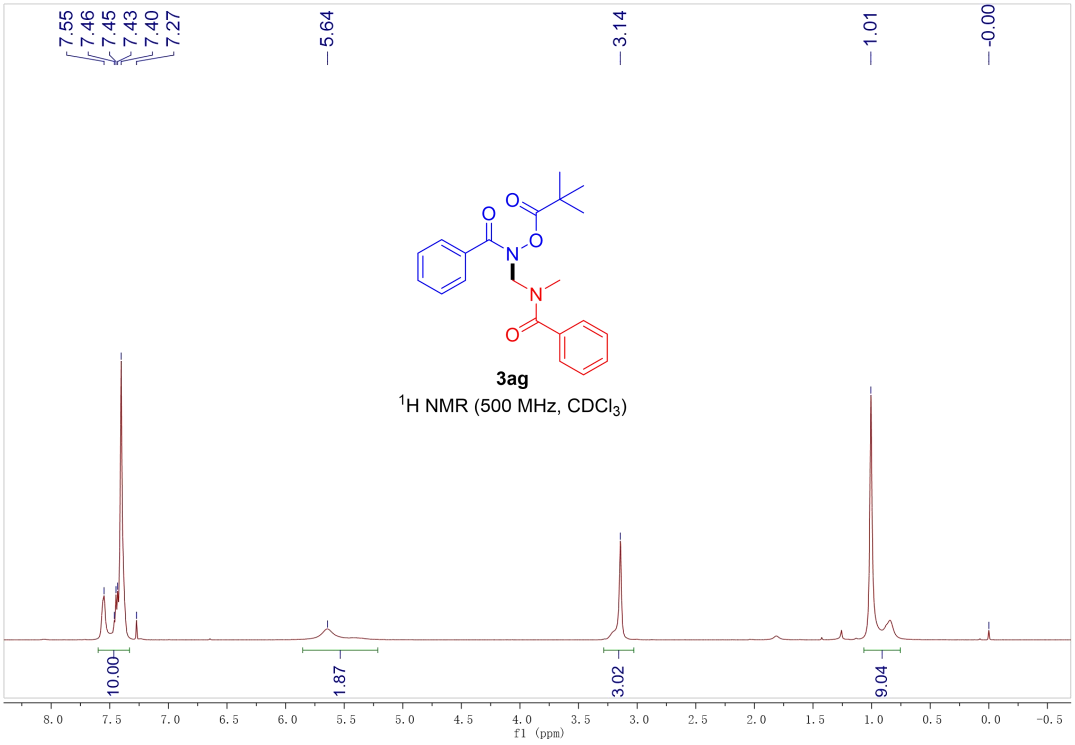
3af

^{1}H NMR (500 MHz, $CDCl_3$)



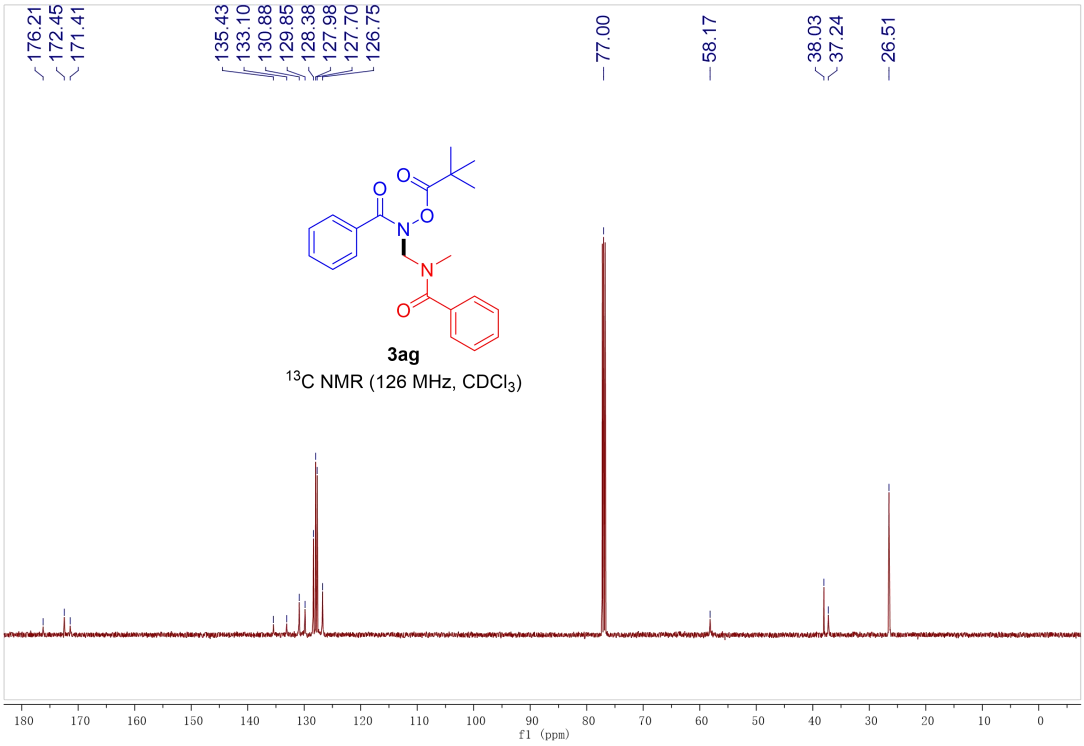
3af

^{13}C NMR (126 MHz, $CDCl_3$)



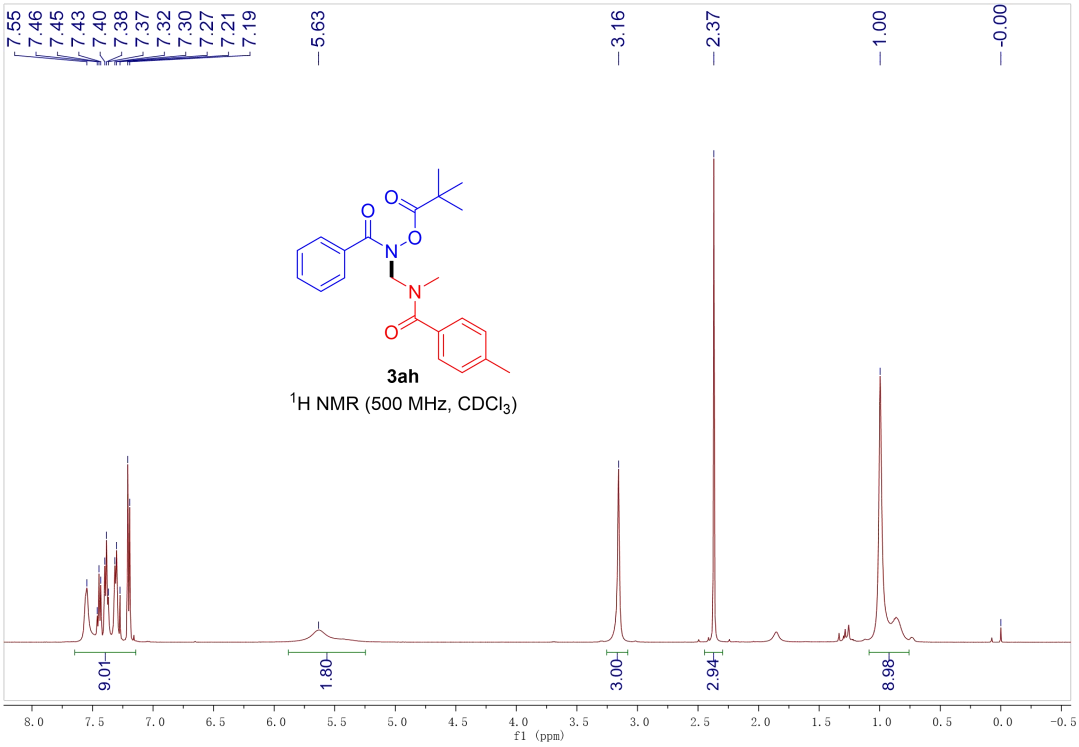
3ag

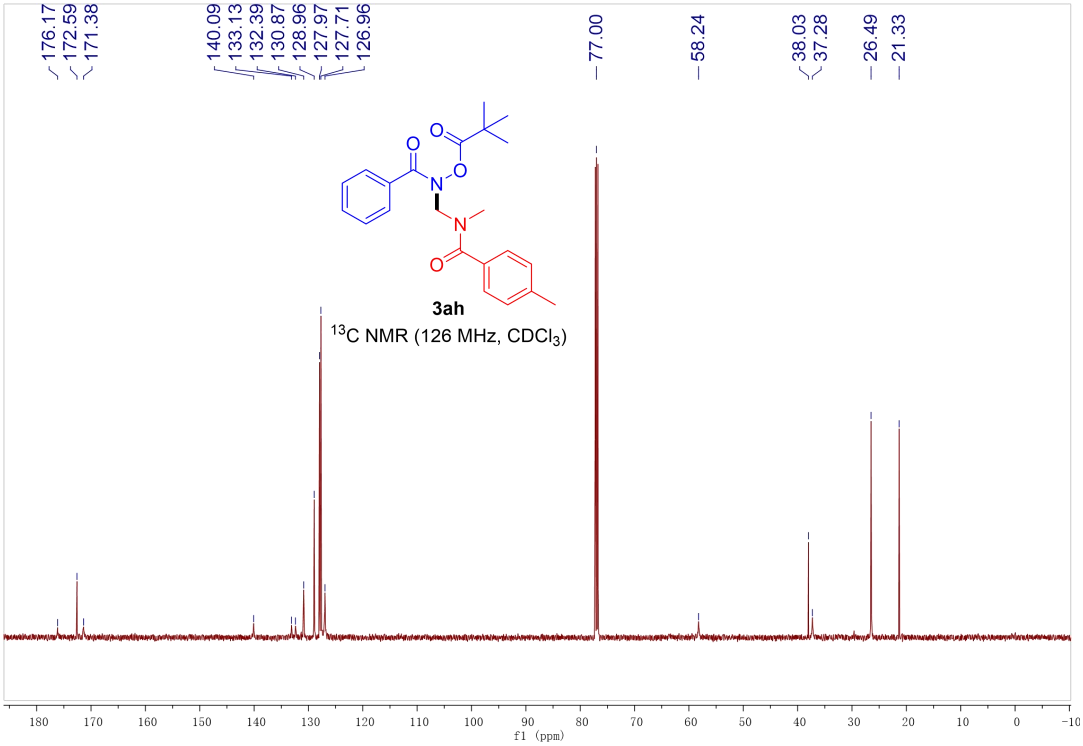
^{1}H NMR (500 MHz, $CDCl_3$)

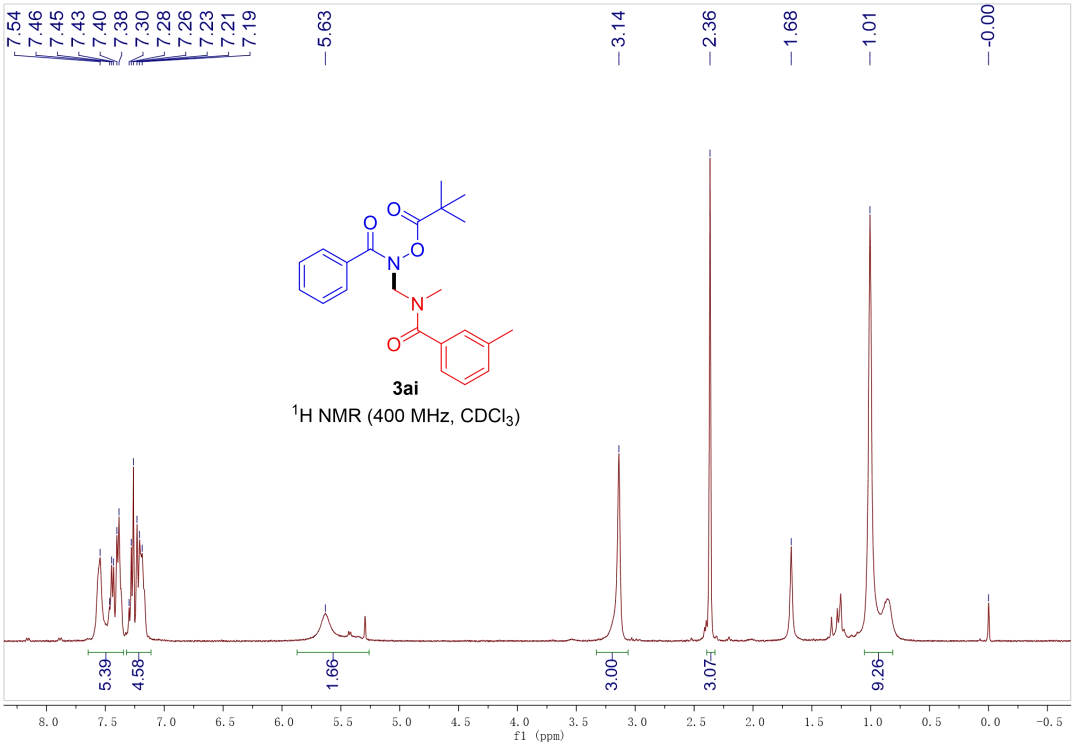


3ag

^{13}C NMR (126 MHz, $CDCl_3$)

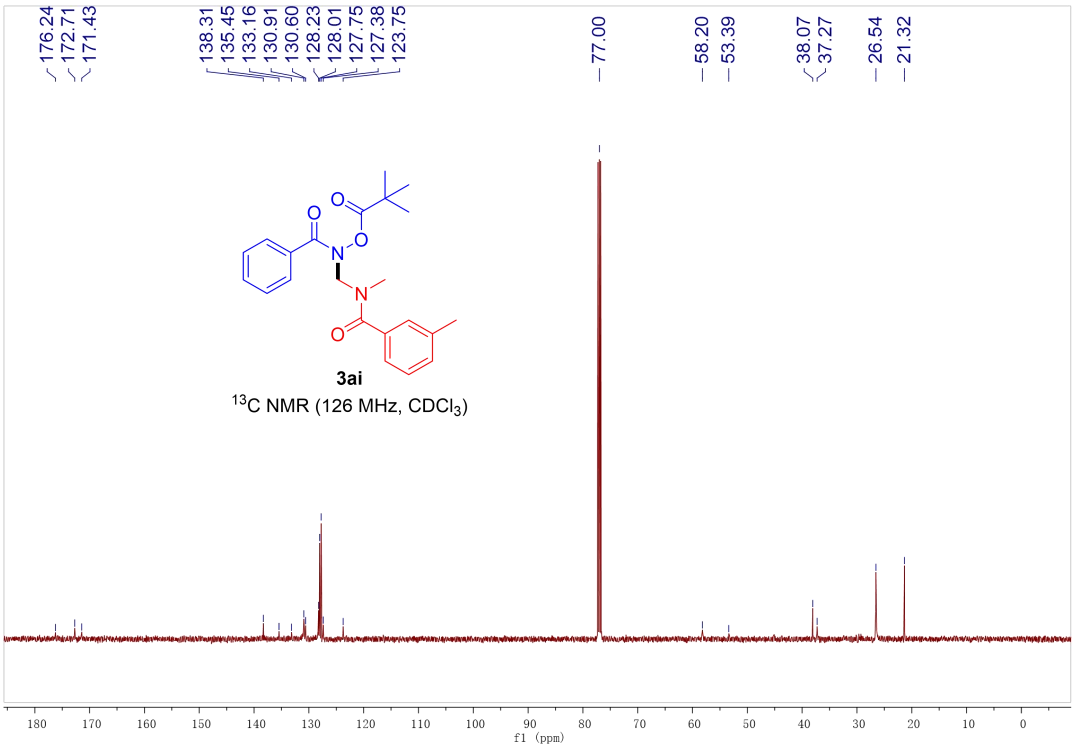

7.55
7.46
7.45
7.43
7.40
7.38
7.37
7.32
7.30
7.27
7.21
7.19
5.63
3.16
2.37
1.00
-0.00
3ah
1H NMR (500 MHz, CDCl3)
9.01
1.80
3.00
2.94
8.98
f1 (ppm)


176.17
172.59
171.38
140.09
133.13
132.39
130.87
128.96
127.97
127.71
126.96
77.00
58.24
38.03
37.28
26.49
21.33
3ah
13C NMR (126 MHz, CDCl3)
f1 (ppm)



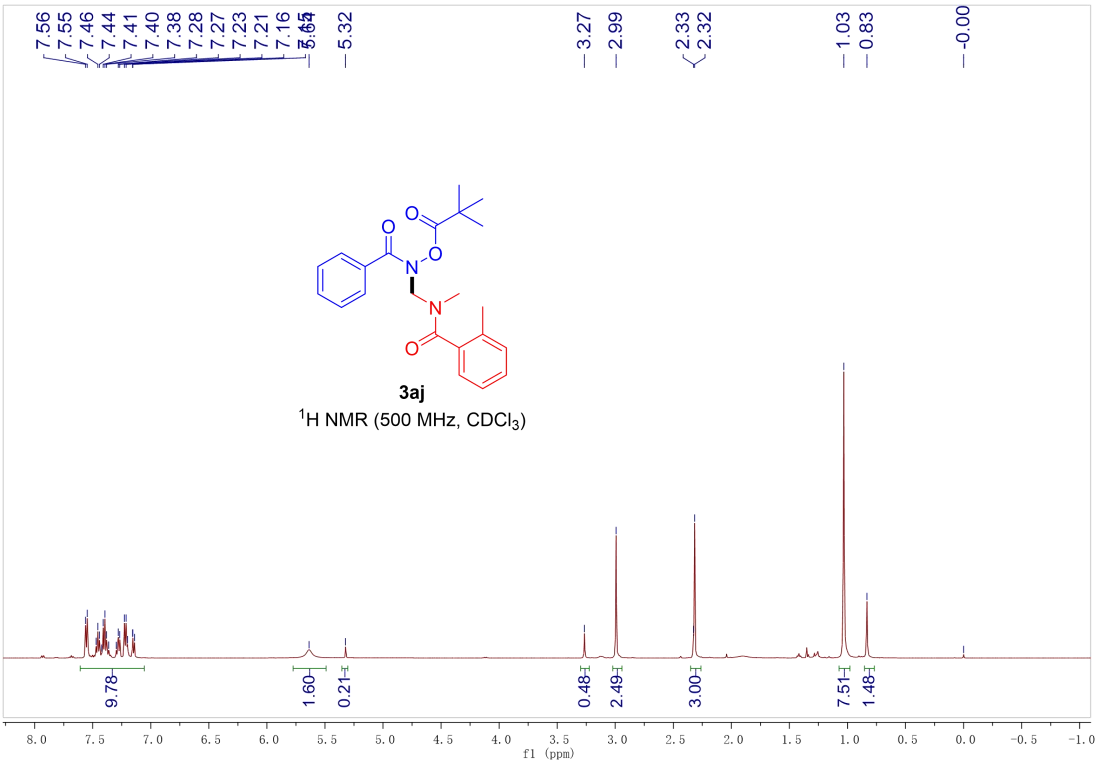
3ai

^{1}H NMR (400 MHz, $CDCl_3$)



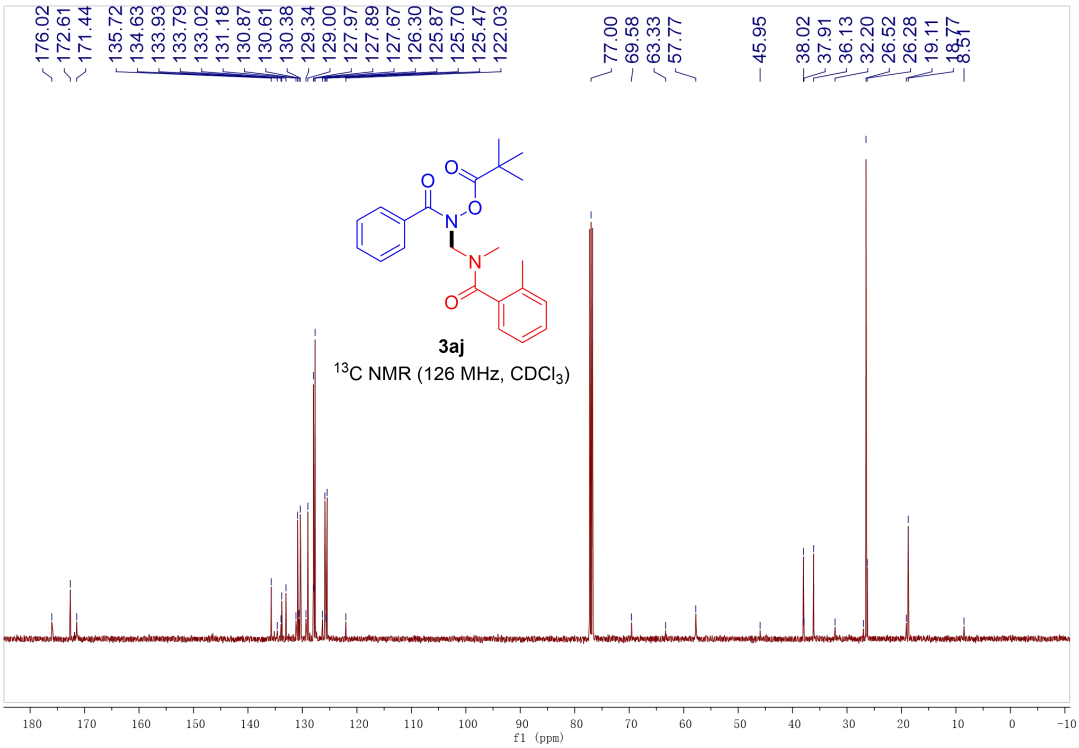
3ai

^{13}C NMR (126 MHz, $CDCl_3$)



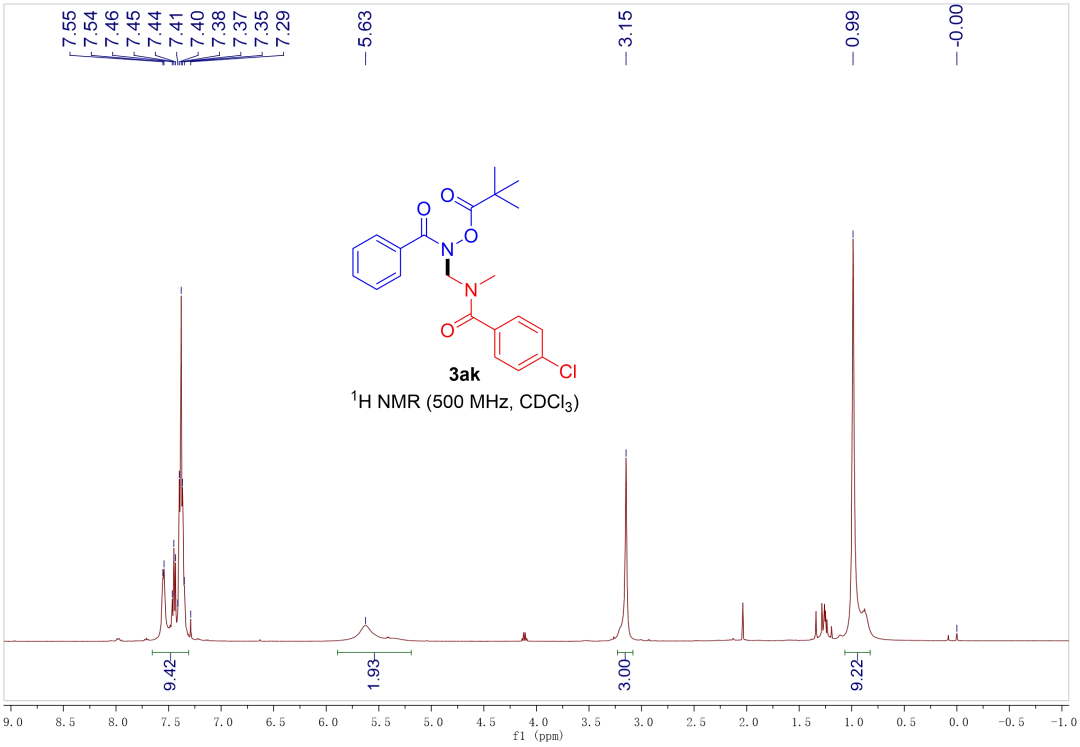
3aj

^{1}H NMR (500 MHz, $CDCl_3$)



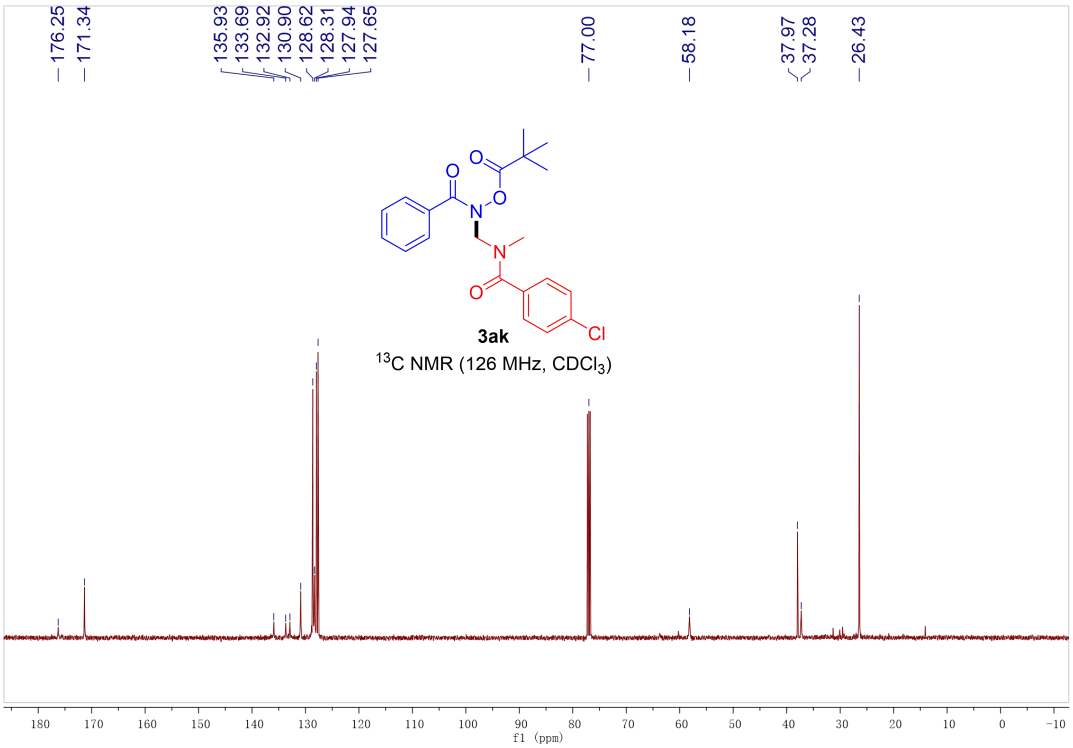
3aj

^{13}C NMR (126 MHz, $CDCl_3$)



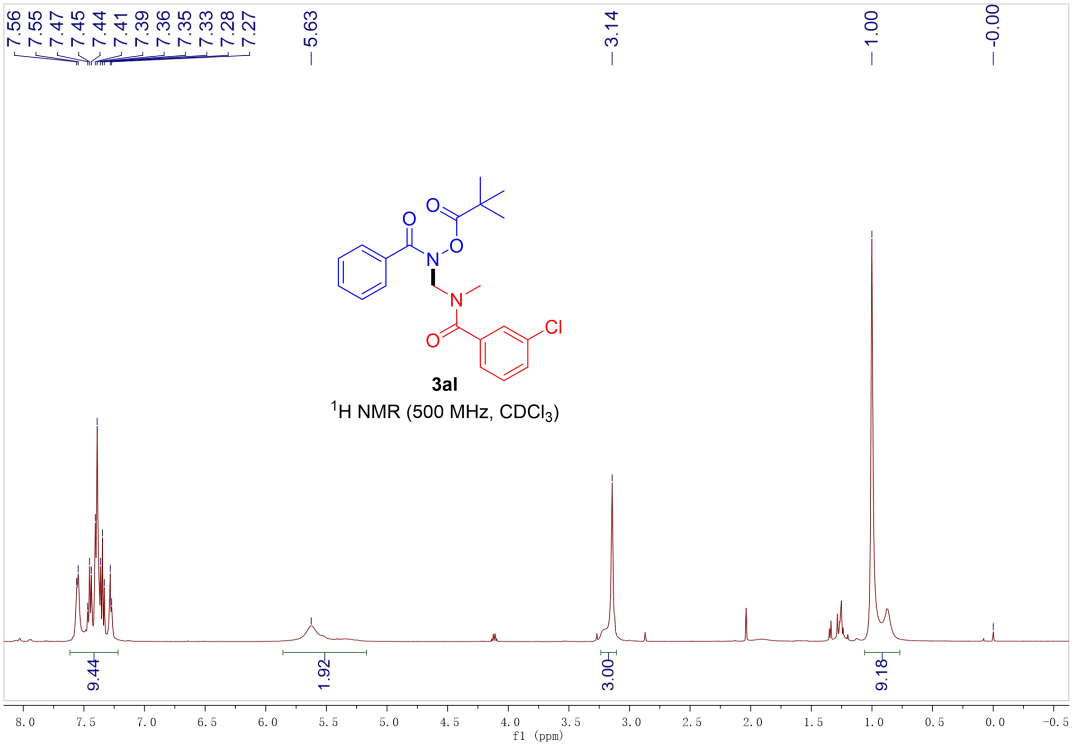
3ak

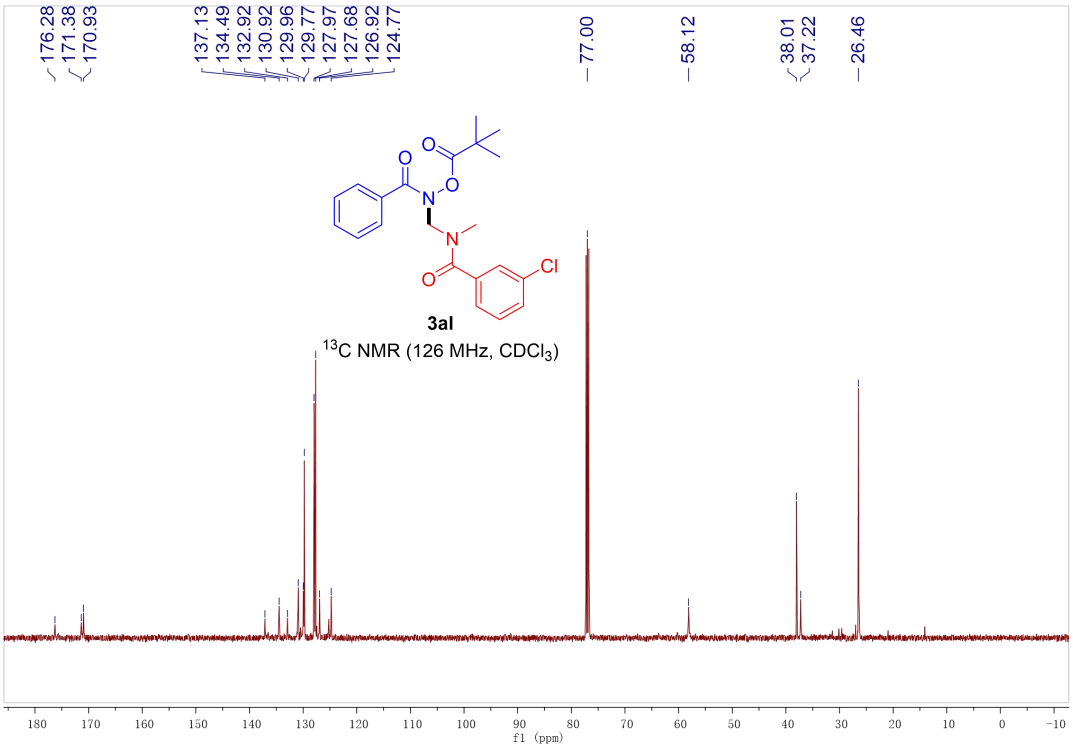
^{1}H NMR (500 MHz, $CDCl_3$)

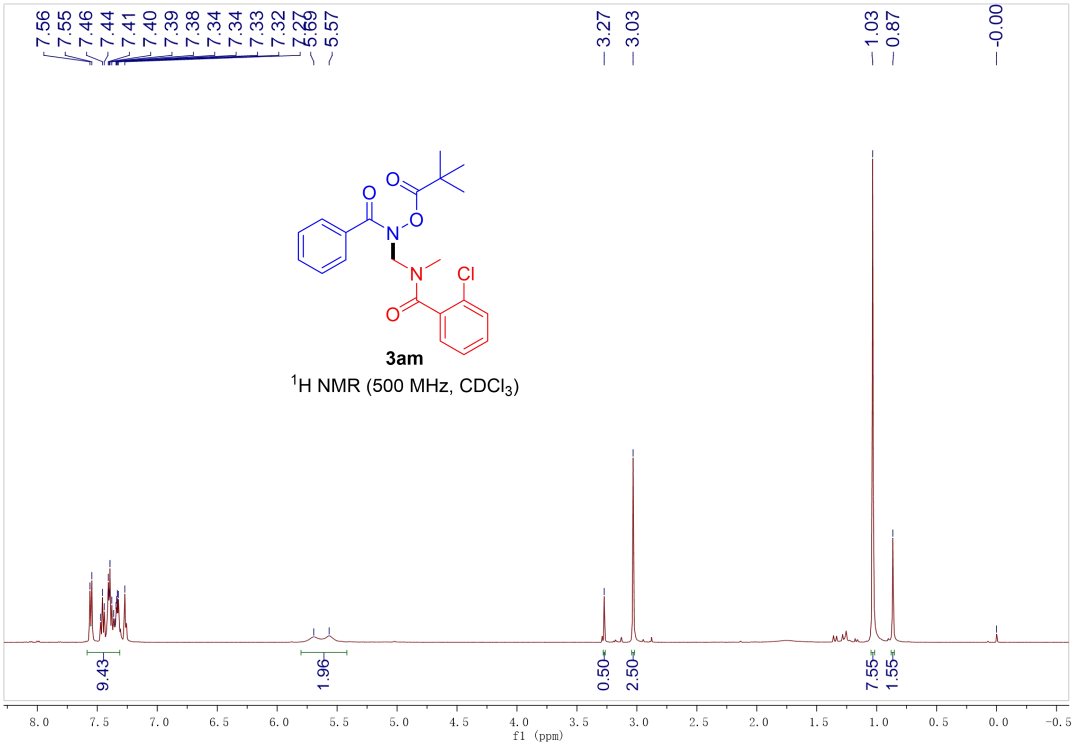


3ak

^{13}C NMR (126 MHz, $CDCl_3$)

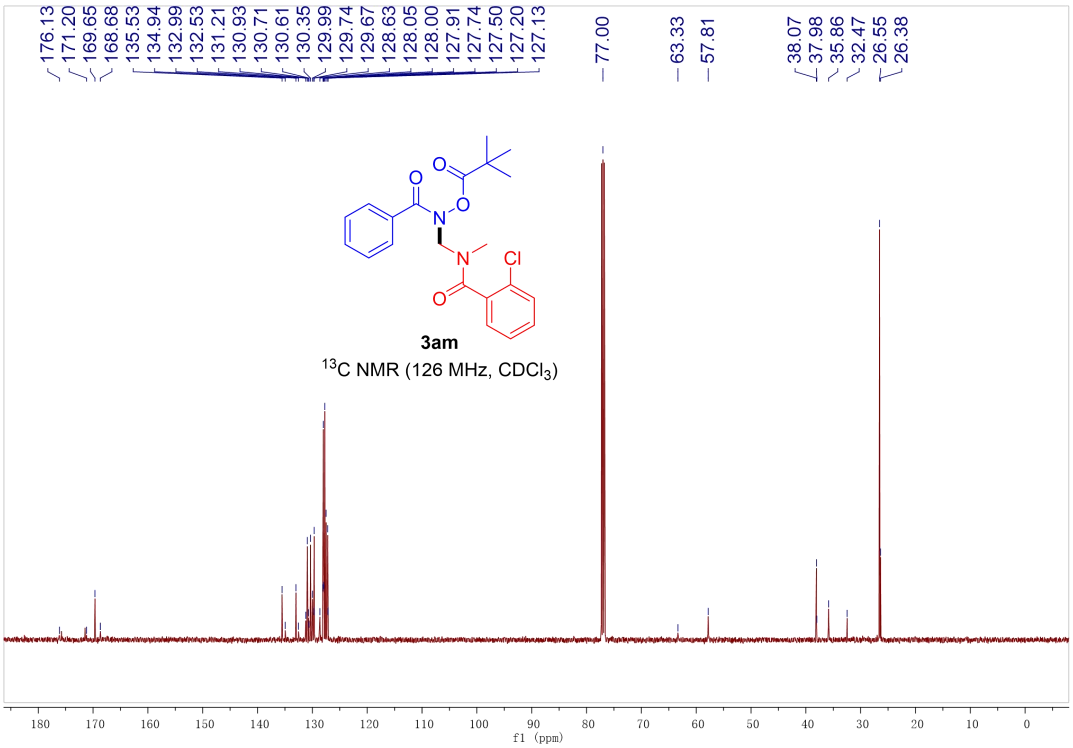

7.56
7.55
7.47
7.45
7.44
7.41
7.39
7.36
7.35
7.33
7.28
7.27
5.63
3.14
1.00
-0.00
O
O
N
O
N
O
Cl
3al
1H NMR (500 MHz, CDCl3)
9.44
1.92
3.00
9.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


176.28
171.38
170.93
137.13
134.49
132.92
130.92
129.96
129.77
127.97
127.68
126.92
124.77
77.00
58.12
38.01
37.22
26.46
O
O
N
O
N
O
Cl
3al
13C NMR (126 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



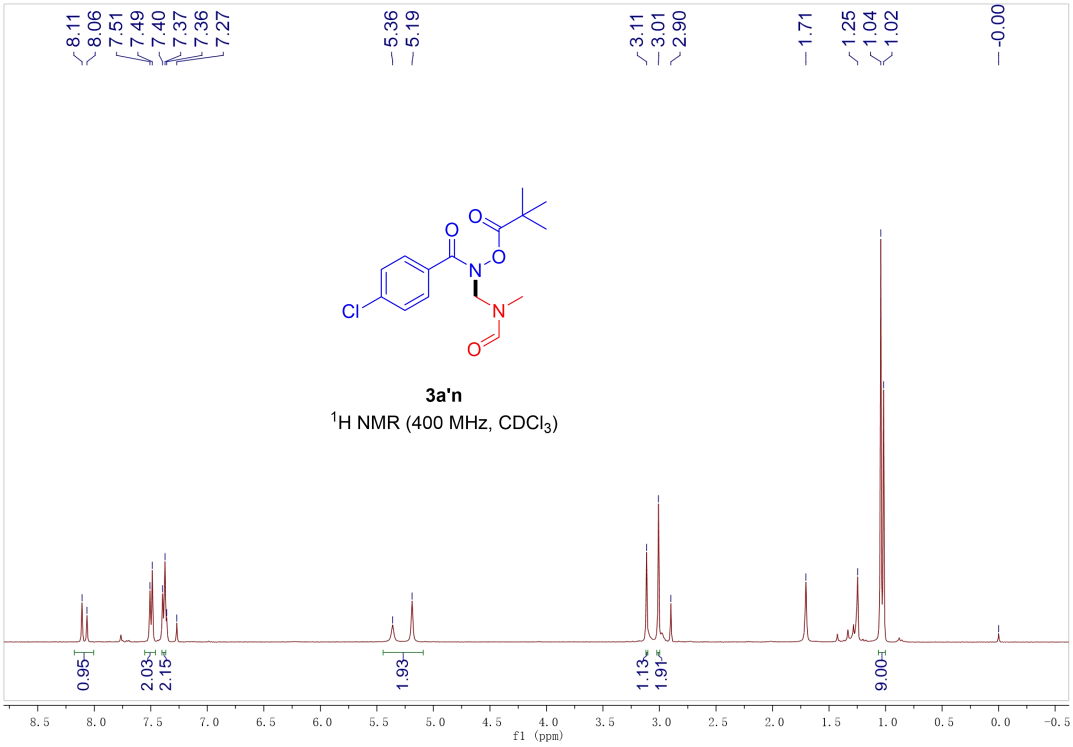
3am

^{1}H NMR (500 MHz, $CDCl_3$)



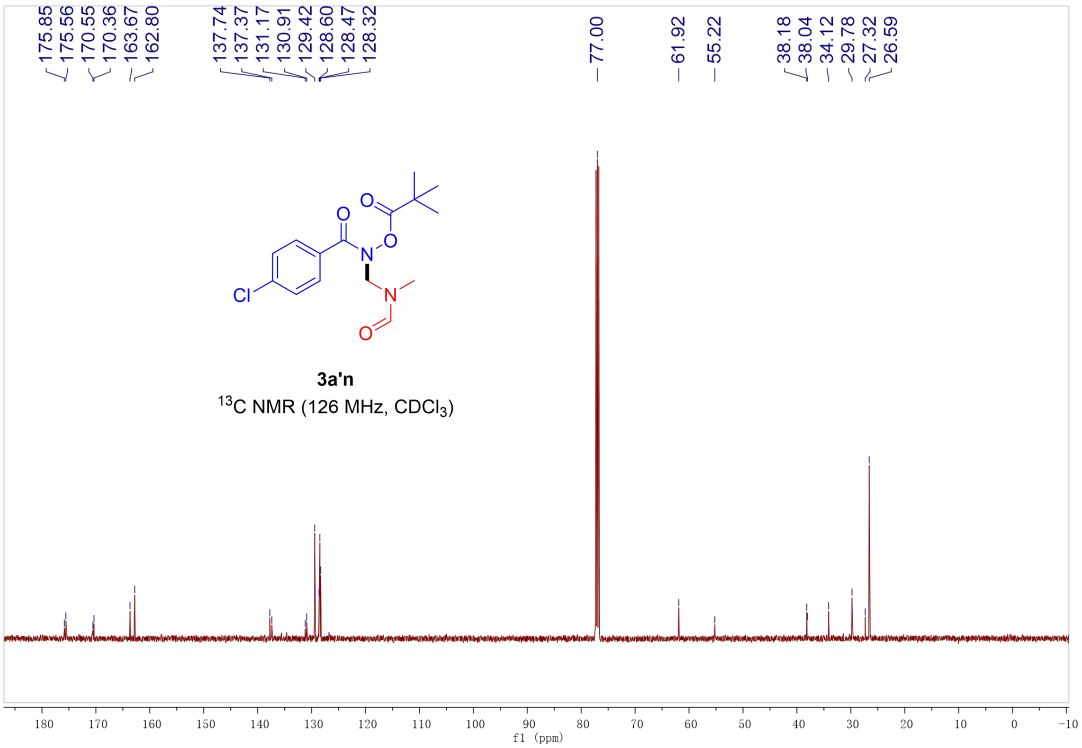
3am

^{13}C NMR (126 MHz, $CDCl_3$)



3a'n

^{1}H NMR (400 MHz, $CDCl_3$)



3a'n

^{13}C NMR (126 MHz, $CDCl_3$)