

Electronic Supplementary Information

Cobalt(III)-Catalyzed weakly coordinating arylurea-directed regio-selective mono-olefination

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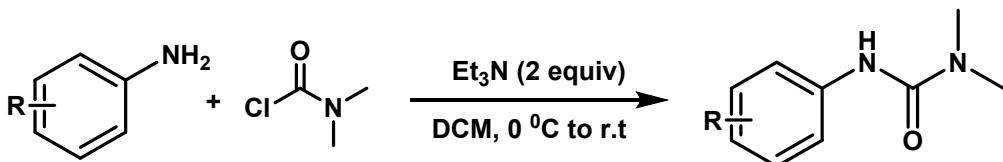
1. General Information

Anhydrous solvents were prepared according to standard methods. Commercially available chemicals were used as received without further purification. NMR spectra were recorded on 400 MHz spectrometers. Chemical shifts are quoted in ppm relative to CDCl_3 or DMSO-d_6 . High-resolution mass spectra (HR-MS) were obtained with a Q-TOF (ESI).

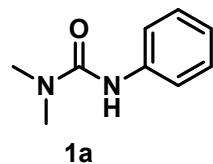
2. Experimental Section

2.1 Preparation and characterization of substrates

2.1.1 General procedure for the preparation of substrates (**1a-1o**).^[1-5]

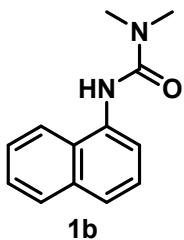


In 50 mL three neck round bottom flask aniline derivatives (10 mmol) and triethylamine (20 mmol) were dissolved in anhydrous CH_2Cl_2 (10 mL), then chloroformic acid dimethyl amide (20 mmol) was added dropwise. The reaction mixture was stirred overnight at r. t. After completion, the reaction was diluted with CH_2Cl_2 (30 mL), washed by sat. NaHCO_3 (30 mL), 2N HCl (30 mL), brine (20 mL) and dried over MgSO_4 . The organic solvent was removed by evaporation. the crude products were purified by recrystallization in diethylehter afforded the corresponding N-arylurea. The NMR datas for these substrates match the corresponding literatures.^[1-5]

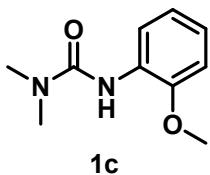


1,1-dimethyl-3-phenylurea (1a)^[1]: ^1H NMR (400 MHz, CDCl_3) δ : 7.39-7.35 (m, 2H), 7.31-7.26 (m, 2H), 7.05-6.99 (m, 1H), 6.31 (br, 1H), 3.03 (s, 6H); ^{13}C NMR (100 S2

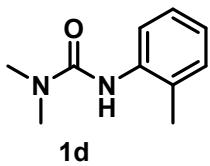
MHz, CDCl₃) δ: 155.72, 139.13, 128.77, 122.87, 120.49, 36.39.



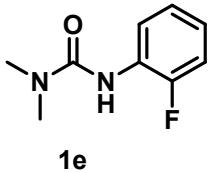
1,1-dimethyl-3-(naphthalen-1-yl)urea (1b) ^[1]: ¹H NMR (400 MHz, CDCl₃) 1H δ 7.85-7.87 (m, 2H), 7.76-7.78 (m, 1H), 7.68-7.62 (m, 1H), 7.55-7.42 (m, 3H), 6.64 (br, 1H), 3.13 (s, 6H); ¹³C NMR(100 MHz, CDCl₃) δ 155.92, 134.17, 133.88, 128.71, 127.75, 126.01, 125.86, 125.77, 124.79, 120.84, 120.52, 36.65.



3-(2-methoxyphenyl)-1,1-dimethylurea (1c)^[2]: ¹H NMR (400 MHz, CDCl₃) δ 8.18-8.16 (m, 1H), 7.07 (br, 1H), 6.95-6.91 (m, 2H), 6.85-6.83 (m, 1H), 3.86 (s, 3H), 3.03 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 155.49, 147.48, 128.98, 121.77, 121.13, 118.80, 109.60, 55.69, 36.28.

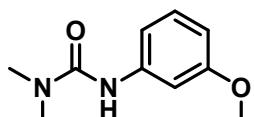


1,1-dimethyl-3-(o-tolyl)urea (1d) ^[1]: ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 8.0 Hz, 1 H), 7.19-7.13 (m, 2H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.15 (br, 1H), 3.01 (s, 6H), 2.23 (s, 3H); ¹³C NMR(100 MHz, CDCl₃) δ 155.86, 137.09, 130.09, 128.56, 126.50, 123.67, 122.60, 36.27, 17.64.



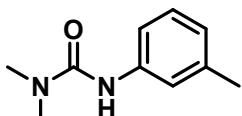
3-(2-fluorophenyl)-1,1-dimethylurea (1e) ^[2]: ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 8.0 Hz, 1 H), 7.19-7.13 (m, 2H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.15 (br, 1H), 3.01 (s,

6H), 2.23 (s, 3H); ^{13}C NMR(100 MHz, CDCl_3) δ 155.86, 137.09, 130.09, 128.56, 126.50, 123.67, 122.60, 36.27, 17.64.



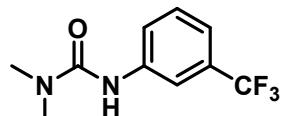
1f

3-(3-methoxyphenyl)-1,1-dimethylurea (1f) ^[3]: ^1H NMR (400 MHz, CDCl_3) δ 7.20-7.13 (m, 2H), 6.84-6.81 (m, 1H), 6.60-6.57 (m, 1H), 6.32 (br, 1H), 3.80 (s, 3H), 3.03 (s, 6H); ^{13}C NMR(100 MHz, CDCl_3) δ 160.17, 155.56, 140.43, 129.44, 111.67, 109.03, 105.10, 55.25, 36.45



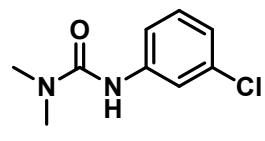
1g

1,1-dimethyl-3-(m-tolyl)urea (1g) ^[1]: ^1H NMR (400 MHz, DMSO-d_6) δ 8.15 (br, 1H), 7.28-7.23 (m, 2 H), 7.08 (t, $J = 8.0$ Hz, 1H), 6.74-6.71 (m, 1H), 2.90 (s, 6H), 2.23 (s, 3 H); ^{13}C NMR(100 MHz, CDCl_3) δ 155.70, 139.02, 138.70, 128.63, 123.73, 120.48, 116.77, 36.41, 21.47.



1h

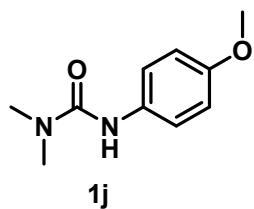
1,1-dimethyl-3-(3-(trifluoromethyl)phenyl)urea (1h) ^[4]: ^1H NMR (400 MHz, CDCl_3) δ 7.67 (s, 1H), 7.59 (d, $J = 8.0$ Hz, 1H), 7.39 (t, $J = 8.0$ Hz, 1H), 7.30-7.27 (m, 1H), 6.45 (br, 1H), 3.05 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 155.31, 139.72, 131.09 (q, $J_{\text{C-F}} = 32.0$ Hz), 129.27, 123.96 (q, $J_{\text{C-F}} = 271.0$ Hz), 122.78, 119.39 (q, $J_{\text{C-F}} = 40.0$ Hz), 116.35 (q, $J_{\text{C-F}} = 40.0$ Hz), 36.43.



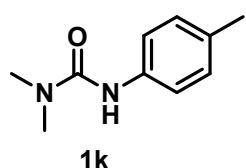
1i

3-(3-chlorophenyl)-1,1-dimethylurea (1i) ^[1]: ^1H NMR (400 MHz, CDCl_3) δ 7.50 (t, $J = 8.0$ Hz, 1H), 7.25-7.22 (m, 1H), 7.19 (t, $J = 8.0$ Hz, 1H), 7.01-6.98 (m, 1H), 6.32 S4

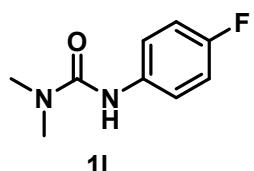
(br, 1H), 3.03 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.22, 140.33, 134.47, 129.77, 122.91, 119.70, 117.58, 36.45.



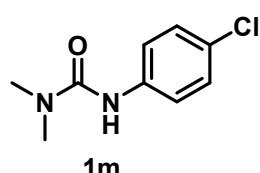
3-(4-methoxyphenyl)-1,1-dimethylurea (1j) ^[1]: ^1H NMR (400 MHz, CDCl_3) δ 7.25-7.22 (m, 2H), 6.84-6.79 (m, 2H), 6.17 (br, 1H), 3.76 (s, 3H), 2.99 (s, 6H); ^{13}C NMR(100 MHz, CDCl_3) δ 156.18, 155.71, 132.14, 122.24, 114.01, 55.46, 36.39.



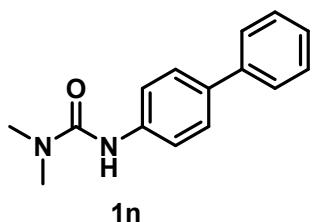
1,1-dimethyl-3-(p-tolyl)urea (1k) ^[1]: ^1H NMR (400 MHz, CDCl_3) δ 7.26-7.23 (m, 2H), 7.09-7.06 (m, 2H), 6.30 (br, 1H), 3.00 (s, 6H), 2.29 (s, 3H); ^{13}C NMR(100 MHz, CDCl_3) δ 155.91, 136.54, 132.32, 129.20, 120.09, 36.33, 20.64.



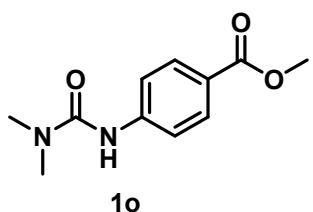
3-(4-fluorophenyl)-1,1-dimethylurea (1l) ^[1]: ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.30 (m, 2H), 7.00-6.95 (m, 2H), 6.26 (br, 1H), 3.03 (s, 6H); ^{13}C NMR(100 MHz, CDCl_3) δ 158.84 (d, $J_{\text{C-F}} = 241.0$ Hz), 156.09, 134.79, 121.83 (d, $J_{\text{C-F}} = 7.0$ Hz), 115.41 (d, $J_{\text{C-F}} = 23.0$ Hz), 36.43.



3-(4-chlorophenyl)-1,1-dimethylurea (1m) ^[1]: ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.32 (m, 2H), 7.25-7.22 (m, 2H), 6.30 (br, 1H), 3.03 (s, 6H); ^{13}C NMR(100 MHz, CDCl_3) δ 160.44, 155.69, 128.81, 127.89, 120.96, 36.45.



3-([1,1'-biphenyl]-4-yl)-1,1-dimethylurea (1n)^[5]: ¹H NMR (400 MHz, CDCl₃) δ 7.59-7.51 (m, 4H), 7.48-7.39 (m, 4H), 7.33-7.28 (m, 1H), 6.38 (br, 1H), 3.05 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 155.61, 140.70, 138.48, 135.77, 128.70, 127.49,



126.83, 126.74, 120.01, 36.49.

Methyl-4-(3,3-dimethylureido) benzoate (1o)^[1]: ¹H NMR (400 MHz, CDCl₃) δ 7.95-7.92 (m, 2H), 7.47-7.45 (m, 2H), 6.68 (br, 1H), 3.87 (s, 3H), 3.03 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 166.84, 155.13, 143.73, 130.61, 123.89, 118.41, 51.83, 36.44.

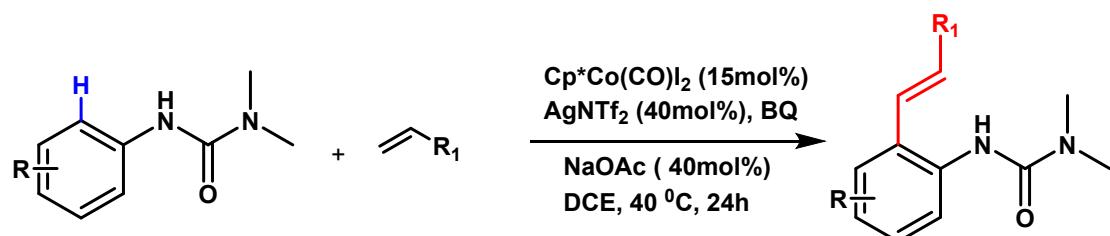
2.2 References

- 1 Lv, H.; Shi, J.; Wu, B.; Guo, Y.; Huang, J.; Yi, W. One-Pot Synthesis of 2,3-Difunctionalized Indoles via Rh(III)-Catalyzed Carbenoid Insertion C-H Activation/Cyclization. *Org. Biomol. Chem.*, 2017, **15**, 8054-8058.
- 2 Kathiravana, S.; Nicholls, I. A. Rhodium(III)-Catalysed Aerobic Synthesis of Highly Functionalized Indoles from N-arylurea under Mild Conditions through C-H Activation. *Chem. Commun.*, 2014, **50**, 14964-14967.
- 3 Nishikata, T.; Abela, A. R.; Lipshutz, B. H. Room Temperature C-H Activation and Cross-Coupling of Aryl Ureas in Water. *Angew. Chem., Int. Ed.*, 2010, **49**, 781-784.

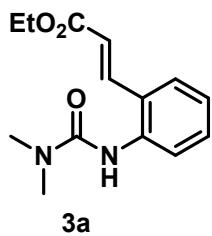
4 Houlden, C. E.; Bailey, C. D.; Ford, J. G.; Gagne, M. R.; Lloyd-Jones, G. C.; Booker-Milburn, K. I. Distinct Reactivity of Pd(OTs)₂: the Intermolecular Pd(II)-catalyzed 1,2-Carboamination of Dienes. *J. Am. Chem. Soc.*, 2008, **130**, 10066-10067.

5 Manna, M. K.; Hossian, A.; Jana, R. Merging C-H Activation and Alkene Difunctionalization at Room Temperature: A Palladium-Catalyzed Divergent Synthesis of Indoles and Indolines. *Org. Lett.*, 2015, **17**, 672-675.

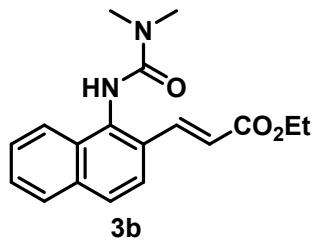
2.3 General procedure for Co(III)-catalyzed C-H olefination



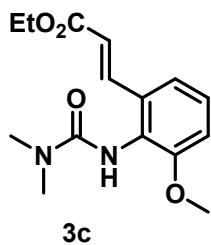
To a 25 mL Schlenk-type sealed tube equipped with a magnetic stirring bar was added the substrate (0.1 mmol), $\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$ (7.4 mg, 0.015 mmol), BQ (21.6 mg, 0.2 mmol), AgNTf_2 (0.04 mmol), NaOAc (3.2 mg, 0.04 mmol), olefin (0.25 mmol) and DCE (2.0 mL). The tube was heated to 40°C for 24 hours. After cooled to room temperature, the reaction mixture was filtered through a pad of silica gel. The silica gel was washed with an additional 10 mL of DCM . The filtrate was concentrated *in vacuo* to afford crude products, which was purified by flash column chromatography on silica gel using hexanes/ EtOAc (1/1) as the eluent to give the pure product.



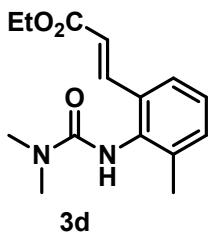
Ethyl-(E)-3-(2-(3,3-dimethylureido)phenyl)acrylate (3a): ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 16.0$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.51 (d, $J = 8.0$ Hz, 1H), 7.34 (t, $J = 8.0$ Hz, 1H), 7.12 (t, $J = 8.0$ Hz, 1H), 6.38 (d, $J = 16.0$ Hz, 1H), 6.35 (br, 1H), 4.27 (q, $J = 8.0$ Hz, 2H), 3.04 (s, 6H), 1.32 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR(100 MHz, CDCl_3) δ 166.87, 155.91, 139.78, 137.51, 130.66, 127.54, 126.98, 124.99, 124.70, 119.97, 60.56, 36.51, 14.24; HRMS (EI-TOF): m/zCalcd. for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 263.1396, found 263.1398.



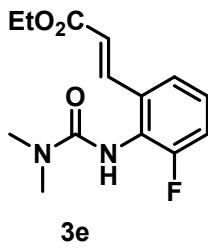
Ethyl-(E)-3-(1-(3,3-dimethylureido)naphthalen-2-yl)acrylate (3b): ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, $J = 16.0$ Hz, 1H), 7.94 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.82 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.78-7.66 (m, 2H), 7.56-7.46 (m, 2H), 6.51 (d, $J = 16.0$ Hz, 1H), 6.35 (br, 1H), 4.26 (q, $J = 8.0$ Hz, 2H), 3.15 (s, 6H), 1.34 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR(100 MHz, CDCl_3) 167.13, 156.22, 140.41, 135.27, 133.98, 131.54, 129.27, 128.24, 127.55, 127.14, 127.08, 123.56, 123.00, 119.72, 60.52, 36.74, 14.30; HRMS (EI-TOF): m/zCalcd. for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 313.1552, found 313.1554.



Ethyl-(E)-3-(2-(3,3-dimethylureido)-3-methoxyphenyl)acrylate (3c): ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 16.0 Hz, 1 H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.23 (br, 1H), 4.22 (q, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 3.06 (s, 6H), 1.31 (t, *J* = 8.0 Hz, 3H); ¹³C NMR(100 MHz, CDCl₃) δ 167.29, 156.84, 152.83, 141.46, 131.87, 127.44, 125.77, 118.72, 118.19, 111.43, 60.28, 55.80, 36.62, 14.29; HRMS (EI-TOF): m/zCalcd. for C₁₅H₂₀N₂O₄[M+H]⁺: 293.1501, found 293.1504.

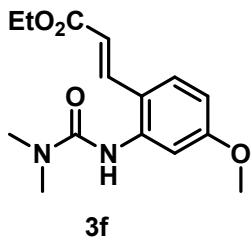


Ethyl-(E)-3-(2-(3,3-dimethylureido)-3-methylphenyl)acrylate (3d): ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 16.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 8.0 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 5.94 (br, 1H), 4.23 (q, *J* = 8.0 Hz, 2H), 3.06 (s, 6H), 2.26 (s, 3H), 1.32 (t, *J* = 8.0 Hz, 3H); ¹³C NMR(100 MHz, CDCl₃) δ 167.09, 156.30, 140.99, 136.42, 135.98, 132.35, 126.76, 124.49, 119.35, 60.41, 36.60, 18.31, 14.27; HRMS (EI-TOF): m/zCalcd. for C₁₅H₂₀N₂O₃[M+Na]⁺: 299.1372, found 299.1374.

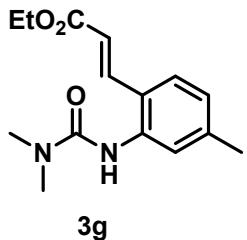


Ethyl-(E)-3-(2-(3,3-dimethylureido)-3-fluorophenyl)acrylate (3e): ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 16.0 Hz, 1H), 7.45-7.38 (m, 1H), 7.21-7.16 (m, 1H), 7.13-7.08 (m, 1H), 6.41 (dd, *J* = 16.0, 4.0 Hz, 1H), 6.08 (br, 1H), 4.23 (q, *J* = 8.0, Hz, 2H), 3.06 (s, 6H), 1.31 (t, *J* = 8.0 Hz, 3H); ¹³C NMR(100 MHz, CDCl₃) δ 166.86, 157.47 (d, *J*_{C-F} = 244.0 Hz), 156.06, 139.74 (d, *J*_{C-F} = 4.0 Hz), 133.72, 126.76 (d, *J*_{C-F} = 9.0 Hz), 125.87 (d, *J*_{C-F} = 13.0 Hz), 122.14 (d, *J*_{C-F} = 3.0 Hz), 119.76, 116.66 (d, *J*_{C-F} = 20.0 Hz), 60.52, 36.61, 14.24 ; HRMS (EI-TOF): m/zCalcd. for

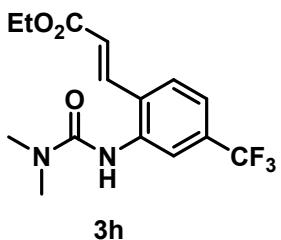
$C_{14}H_{17}FN_2O_3[M+H]^+$: 281.1302, found 281.1304.



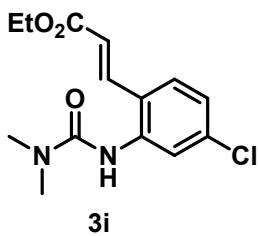
Ethyl-(E)-3-(2-(3,3-dimethylureido)-4-methoxyphenyl)acrylate (3f): 1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, $J = 16.0$ Hz, 1H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.37 (d, $J = 4.0$ Hz, 1H), 6.67 (dd, $J = 8.0, 4.0$ Hz, 1H), 6.45 (br, 1H), 6.28 (d, $J = 16.0$ Hz, 1H), 4.23 (q, $J = 8.0$ Hz, 2H), 3.82 (s, 3H), 3.06 (s, 6H), 1.31 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 167.21, 161.75, 155.54, 139.18, 139.10, 128.32, 118.82, 117.48, 111.69, 108.04, 60.44, 55.44, 36.55, 14.30; HRMS (EI-TOF): m/zCalcd. for $C_{15}H_{20}N_2O_4$ $[M+H]^+$: 293.1501, found 293.1500.



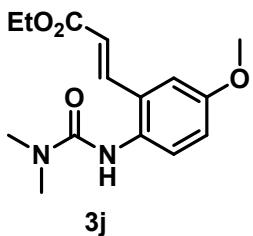
Ethyl-(E)-3-(2-(3,3-dimethylureido)-4-methylphenyl)acrylate (3g): 1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, $J = 16.0$ Hz, 1H), 7.47 (s, 1H), 7.42 (d, $J = 8.0$ Hz, 1H), 6.94 (d, $J = 8.0$ Hz, 1H), 6.35 (d, $J = 16.0$ Hz, 1H), 6.30 (br, 1H), 4.24 (q, $J = 8.0$ Hz, 2H), 3.05 (s, 6H), 2.34 (s, 3H), 1.32 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 167.18, 156.02, 141.47, 139.78, 137.52, 127.00, 125.81, 125.51, 124.69, 119.03, 60.61, 36.65, 21.62, 14.40; HRMS (EI-TOF): m/zCalcd. for $C_{15}H_{20}N_2O_3$ $[M+H]^+$: 277.1552, found 277.1553.



Ethyl-(E)-3-(2-(3,3-dimethylureido)-4-(trifluoromethyl)phenyl)acrylate (3h): ¹H NMR (400 MHz, CDCl₃) δ 8.09-7.99 (m, 1H), 7.77 (d, *J* = 16.0 Hz, 1 H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.38-7.32 (m, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.45 (br, 1H), 4.23(q, *J* = 8.0 Hz, 2H), 3.07(s, 6H), 1.34 (t, *J* = 8.0 Hz, 3H); ¹³C NMR(100 MHz, CDCl₃) δ 166.29, 155.25, 138.29, 137.82, 132.22 (*q*, *J*_{C-F} = 33.0 Hz), 129.97, 127.62, 123.59(*q*, *J*_{C-F} = 267.0 Hz), 122.61, 121.18 (*q*, *J*_{C-F} = 1.0 Hz), 121.81 (*q*, *J*_{C-F} = 4.0 Hz), 60.90, 36.54, 14.23; HRMS (EI-TOF): m/zCalcd. for C₁₅H₁₇F₃N₂O₃[M+H]⁺: 331.1270, found 331.1271.

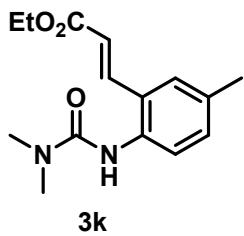


Ethyl-(E)-3-(4-chloro-2-(3,3-dimethylureido)phenyl)acrylate (3i): ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 16.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.08 (dd, *J* = 4.0, 2.0 Hz, 1H), 6.40 (br, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 8.0 Hz, 2H), 3.05 (s, 6H), 1.32 (t, *J* = 8.0 Hz, 3H). ¹³C NMR(100 MHz, CDCl₃) δ 166.60, 155.30, 138.56, 138.47, 136.28, 127.95, 125.26, 124.60, 124.32, 120.45, 60.68, 36.50, 14.23; HRMS (EI-TOF): m/zCalcd. for C₁₄H₁₇N₂O₃ [M+H]⁺: 297.1006, found 297.1007.

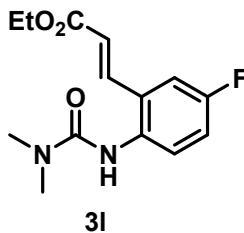


Ethyl-(E)-3-(2-(3,3-dimethylureido)-5-methoxyphenyl)acrylate (3j): ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 16.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 4.0 Hz, 1H), 6.93 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.12 (br, 1H), 4.25 (q, *J* = 8.0 Hz, 2H), 3.81 (s, 3H), 3.04 (s, 6H), 1.33 (t, *J* = 8.0 Hz, 3H); ¹³C NMR(100 MHz, CDCl₃) δ 166.83, 157.08, 156.53, 139.86, 130.62, 130.11, 127.93, S11

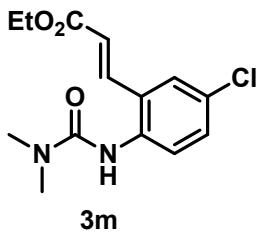
119.98, 116.95, 110.94, 60.59, 55.52, 36.55, 14.27; HRMS (EI-TOF): m/zCalcd. for C₁₅H₂₀N₂O₃[M+H]⁺: 293.1501, found 293.1503.



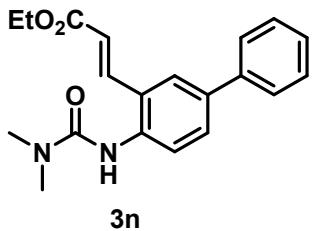
Ethyl-(E)-3-(2-(3,3-dimethylureido)-5-methylphenyl)acrylate (3k): ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 16.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.37-7.32 (m, 1H), 7.16 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1 H), 6.24 (br, 1 H), 4.24 (q, *J* = 8.0 Hz, 2 H), 3.04 (s, 6 H), 2.32 (s, 3H), 1.32 (t, *J* = 8.0 Hz, 3 H); ¹³C NMR(100 MHz, CDCl₃) δ 166.95, 156.12, 139.92, 135.01, 134.49, 131.57, 127.70, 127.28, 125.35, 119.66, 60.52, 36.54, 20.84, 14.27; HRMS (EI-TOF): m/zCalcd. for C₁₅H₂₀N₂O₃[M+H]⁺: 277.1552, found 277.1553.



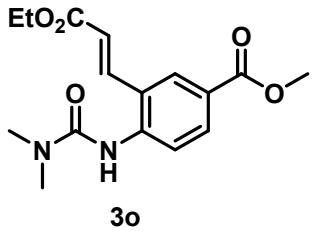
Ethyl-(E)-3-(2-(3,3-dimethylureido)-5-fluorophenyl)acrylate (3l): ¹H NMR (400 MHz, CDCl₃) δ 7.76 (dd, *J* = 16.0, 2.0 Hz, 1H), 7.51 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.22 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.06 (ddd, *J* = 8.0, 8.0, 2.0 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.23 (br, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.04 (s, 6H), 1.32 (t, *J* = 8.0 Hz, 3H); ¹³C NMR(100 MHz, CDCl₃) δ 166.55 , 159.82 (d, *J*_{C-F} = 243.0 Hz), 156.04 , 138.76 , 133.52 , 130.09 (d, *J*_{C-F} = 1.0 Hz), 127.78 (d, *J*_{C-F} = 8.0 Hz), 120.96 , 117.54 (d, *J*_{C-F} = 23.0 Hz), 112.82 (d, *J*_{C-F} = 23.0 Hz), 60.71, 36.51, 14.22; HRMS (EI-TOF): m/zCalcd. for C₁₄H₁₇FN₂O₃[M+H]⁺: 281.1302, found 281.1303.



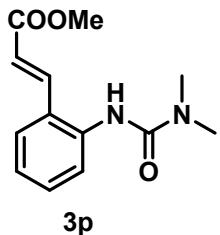
Ethyl-(E)-3-(5-chloro-2-(3,3-dimethylureido)phenyl)acrylate (3m): ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 16.0$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.46 (d, $J = 2.0$ Hz, 1H), 7.29 (dd, $J = 8.0, 2.0$ Hz, 1H), 6.37 (d, $J = 16.0$ Hz, 1H), 6.36 (br, 1H), 4.24 (q, $J = 8.0$ Hz, 2H), 3.04 (s, 6H), 1.32 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR(100 MHz, CDCl_3) δ 166.47, 155.58, 138.36, 136.04, 130.38, 129.95, 128.85, 126.58, 126.23, 121.25, 60.74, 36.52, 14.22; HRMS (EI-TOF): m/zCalcd. for $\text{C}_{14}\text{H}_{17}\text{ClN}_2\text{O}_3[\text{M}+\text{Na}]^+$: 319.0825, found 319.0827.



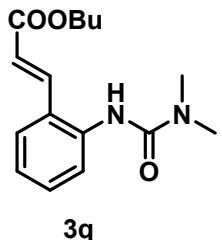
Ethyl-(E)-3-(4-(3,3-dimethylureido)-[1,1'-biphenyl]-3-yl)acrylate (3n): ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 16.0$ Hz, 1H), 7.72-7.71 (m, 2H), 7.59-7.55 (m, 3H), 7.43 (t, $J = 8.0$ Hz, 2H), 7.38-7.32 (m, 1H), 6.47 (d, $J = 16.0$ Hz, 1H), 6.41 (br, 1H), 4.26 (q, $J = 8.0$ Hz, 2H), 3.07 (s, 6H), 1.33 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR(100 MHz, CDCl_3) δ 166.78, 155.76, 140.09, 139.71, 137.49, 136.76, 129.43, 128.81, 127.42, 127.36, 126.88, 125.62, 125.00, 120.49, 60.64, 36.58, 14.27; HRMS (EI-TOF): m/zCalcd. for $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_3[\text{M}+\text{H}]^+$: 339.1709, found 339.1706.



Methyl-(E)-4-(3,3-dimethylureido)-3-(3-ethoxy-3-oxoprop-1-en-1-yl)benzoate (3o): ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 2.0$ Hz, 1H), 7.99 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.77 (d, $J = 16.0$ Hz, 1H), 6.58 (br, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 4.27 (q, $J = 8.0$ Hz, 2H), 3.90 (s, 3H), 3.07 (s, 6H), 1.34 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR(100 MHz, CDCl_3) δ 166.46, 166.32, 154.85, 141.54, 138.41, 131.73, 129.07, 125.15, 122.23, 122.00, 60.80, 52.12, 36.60, 14.25; HRMS (EI-TOF): m/zCalcd. for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_4[\text{M}+\text{H}]^+$: 321.1451, found 321.1453.

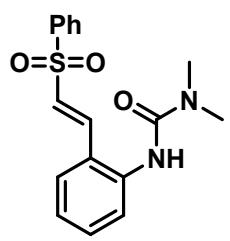


Methyl-(E)-3-(2-(3,3-dimethylureido)phenyl)acrylate (3p): ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 16.0$ Hz, 1H), 7.59 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.51 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.34 (td, $J = 8.0, 2.0$ Hz, 1H), 7.13 (t, $J = 8.0$ Hz, 1H), 6.39 (d, $J = 16.0$ Hz, 1H), 6.36 (br, 1H), 3.70 (s, 3H), 3.04 (s, 6H); ^{13}C NMR(100 MHz, CDCl_3) δ 167.31, 155.91, 140.12, 137.54, 130.72, 127.58, 127.02, 125.07, 124.75, 119.47, 51.74, 36.52; HRMS (EI-TOF): m/zCalcd. for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_3[\text{M}+\text{Na}]^+$: 271.1059, found 271.1062.



271.1062.

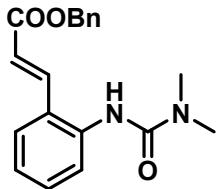
Butyl-(E)-3-(2-(3,3-dimethylureido)phenyl)acrylate (3q): ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 16.0$ Hz, 1H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.52 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.39-7.31 (m, 1H), 7.13 (t, $J = 8.0$ Hz, 1H), 6.39 (d, $J = 16.0$ Hz, 1H), 6.34 (br, 1H), 4.19 (t, $J = 8.0$ Hz, 2H), 3.09 (s, 6 H), 1.71-1.63 (m, 2H), 1.47-1.38 (m, 2H), 0.96 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR(100 MHz, CDCl_3) δ 166.94, 155.86, 139.75, 137.53, 130.65, 127.50, 126.96, 124.95, 124.65, 119.97, 64.46, 36.50, 30.66, 19.14,



13.70; HRMS (EI-TOF): m/zCalcd. for $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_3[\text{M}+\text{Na}]^+$: 313.1528, found 313.1300.

(E)-1,1-dimethyl-3-(2-(phenylsulfonyl)vinyl)phenyl)urea (3r): ^1H NMR (400

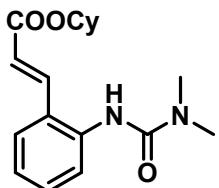
MHz, CDCl₃) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 16.0 Hz, 1H), 7.64-7.49 (m, 4H), 7.44-7.33 (m, 2H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.34 (br, 1H), 3.07 (s, 6H); ¹³C NMR(100 MHz, CDCl₃) δ 155.85, 140.40, 138.57, 137.99, 133.42,



3s

131.56, 129.33, 128.20, 127.73, 127.39, 126.29, 125.59, 125.14, 36.59; HRMS (EI-TOF): m/zCalcd. for C₁₇H₁₈N₂O₃[M+H]⁺: 331.1116, found 331.1117.

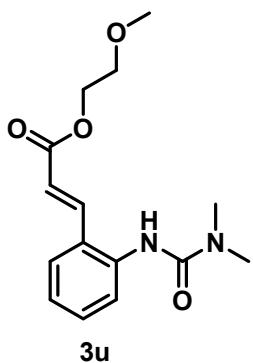
Benzyl-(E)-3-(2-(3,3-dimethylureido)phenyl)acrylate (3s): ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 16.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.51 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.42-7.31 (m, 6H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.37 (br, 1H), 5.22 (s, 2H), 3.01 (s, 6H); ¹³C NMR(100 MHz, CDCl₃) δ 166.63, 155.88, 140.42, 137.63, 135.87, 130.75, 128.53, 128.22, 128.18, 127.56, 126.90, 125.13, 124.74,



3t

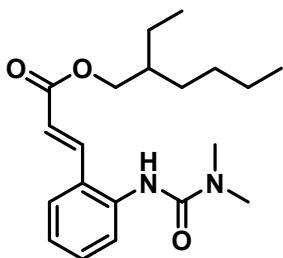
119.30, 66.36, 36.45; HRMS (EI-TOF): m/zCalcd. for C₁₉H₂₀N₂O₃[M+H]⁺: 325.1552, found 325.1554.

Cyclohexyl-(E)-3-(2-(3,3-dimethylureido)phenyl)acrylate (3t): ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 16.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.52 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.38-7.32 (m, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.35 (br, 1H), 4.87 (tt, *J* = 8.0, 4.0 Hz, 1H), 3.06 (s, 6H), 1.93-1.86 (m, 2H), 1.78-1.72 (m, 2H), 1.59-1.35 (m, 6H); ¹³C NMR(100 MHz, CDCl₃) δ 166.28, 155.83, 139.39, 137.49, 130.60, 127.39, 126.95, 124.83, 124.59, 120.65, 72.83, 36.51, 31.64, 25.35, 23.69; HRMS (EI-TOF): m/zCalcd. for C₁₈H₂₄N₂O₃[M+H]⁺: 317.1865, found 317.1867.



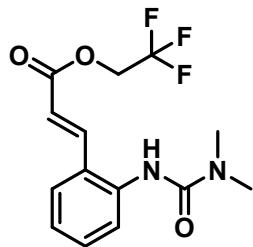
3u

2-methoxyethyl-(E)-3-(2-(3,3-dimethylureido)phenyl)acrylate (3u): ^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J = 16.0$ Hz, 1H), 7.60 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.52 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.35 (td, $J = 8.0, 2.0$ Hz, 1H), 7.13 (t, $J = 8.0$ Hz, 1H), 6.45 (d, $J = 16.0$ Hz, 1H), 6.35 (br, 1H), 4.38-4.30 (m, 2H), 3.70-3.63 (m, 2H), 3.41 (s, 3H), 3.04 (s, 6H); ^{13}C NMR(100 MHz, CDCl_3) δ 166.85, 155.96, 140.34, 137.59, 130.77, 127.58, 126.94, 125.13, 124.79, 119.37, 70.45, 63.58, 58.98, 36.50; HRMS (EI-TOF): m/zCalcd. for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_4[\text{M}+\text{Na}]^+$: 315.1321, found 315.1322.



3v

2-ethylhexyl-(E)-3-(2-(3,3-dimethylureido)phenyl)acrylate (3v): ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 16.0$ Hz, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.35 (t, $J = 8.0$ Hz, 1H), 7.13 (t, $J = 8.0$ Hz, 1H), 6.40 (d, $J = 16.0$ Hz, 1H), 6.33 (br, 1H), 4.15-4.06 (m, 2H), 3.05 (s, 6H), 1.60-1.66 (m, 1H), 1.43-1.29 (m, 8H), 0.94-0.88 (m, 6H); ^{13}C NMR(100 MHz, CDCl_3) δ 167.02, 155.79, 139.61, 137.48, 130.68, 127.40, 127.04, 124.82, 124.63, 120.18, 66.98, 38.79, 36.51, 30.42, 28.92, 23.81, 22.95, 14.04, 11.01; HRMS (EI-TOF): m/zCalcd. for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_3[\text{M}+\text{H}]^+$: 347.2335, found 347.2338.

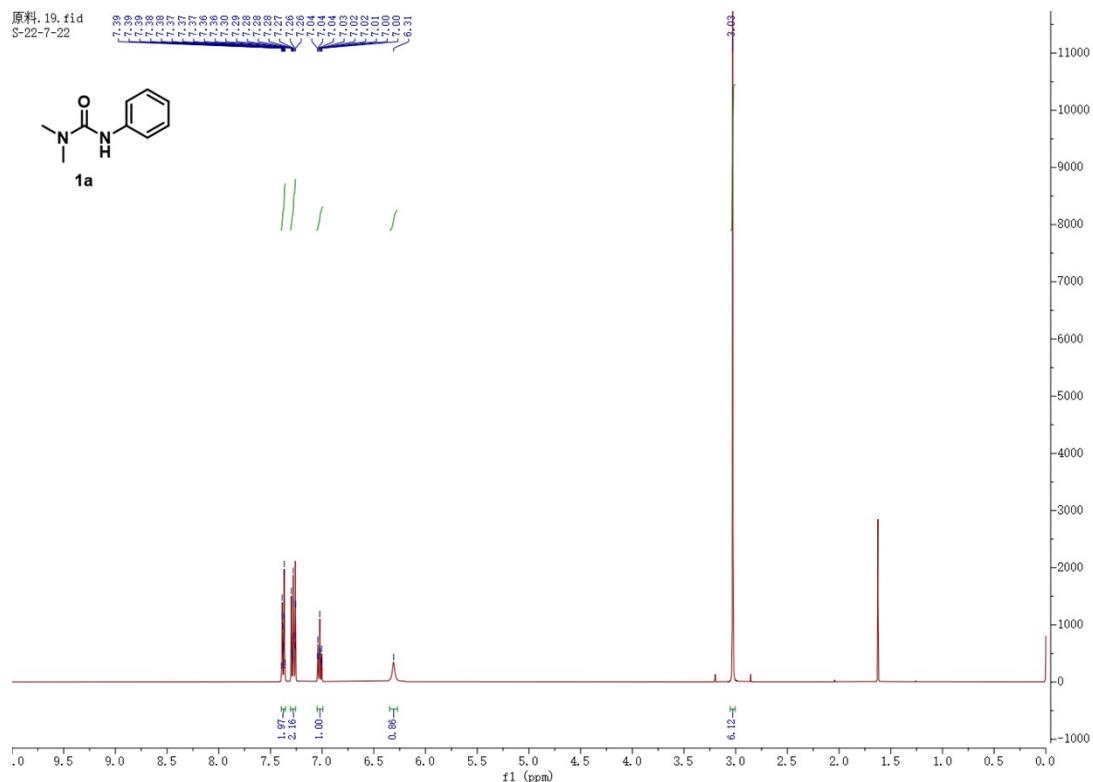


3w

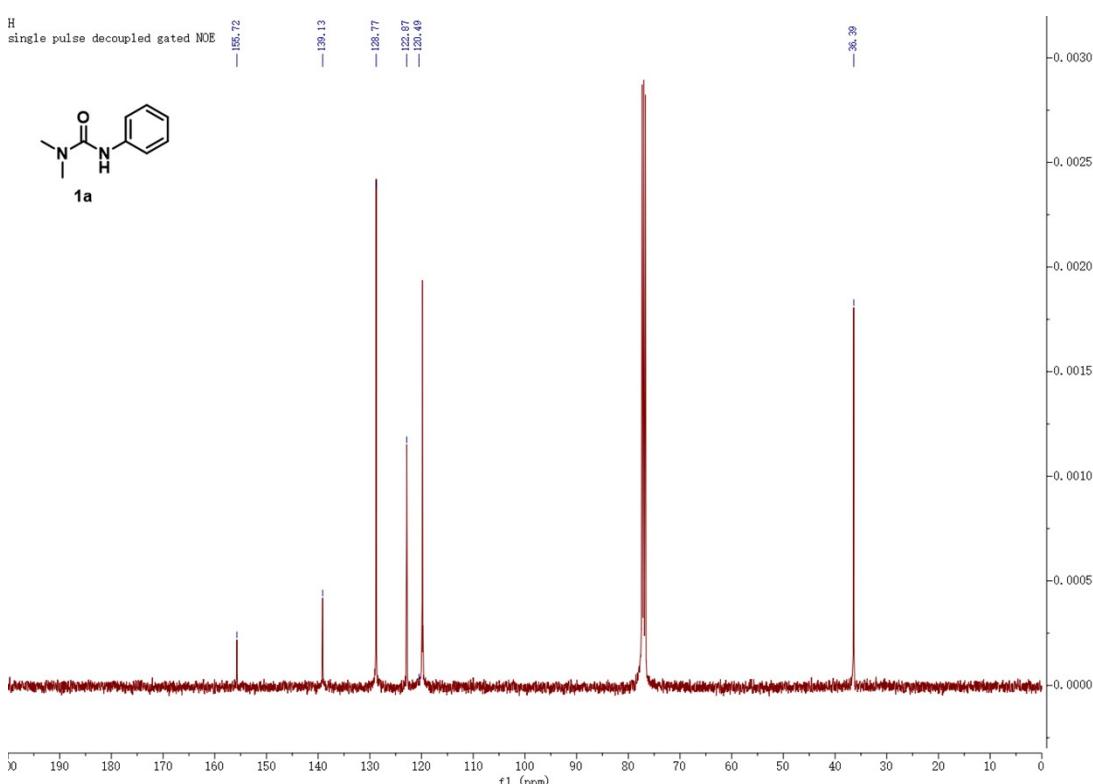
2,2,2-trifluoroethyl-(E)-3-(2-(3,3-dimethylureido)phenyl)acrylate (3w): ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 16.0$ Hz, 1H), 7.56 (dd, $J = 8.0, 2.0$ Hz, 2H), 7.39 (ddd, $J = 8.0, 8.0, 2.0$ Hz, 1H), 7.20-7.13 (m, 1H), 6.45 (d, $J = 16.0$ Hz, 1H), 6.31 (br, 1H), 4.58 (q, $J = 8.0$ Hz, 2H), 3.05 (s, 6H); ^{13}C NMR(100 MHz, CDCl_3) δ 165.01, 155.82, 142.36, 137.01, 131.38, 127.34, 127.10, 125.24, 125.01, 123.07 (q, $J_{\text{C}-\text{F}} = 275.0$ Hz), 117.37, 60.44 (q, $J_{\text{C}-\text{F}} = 36.0$ Hz), 36.53; HRMS (EI-TOF): m/z Calcd. for $\text{C}_{14}\text{H}_{15}\text{F}_3\text{N}_2\text{O}_3$ [$\text{M}+\text{H}]^+$: 317.1113, found 317.1112.

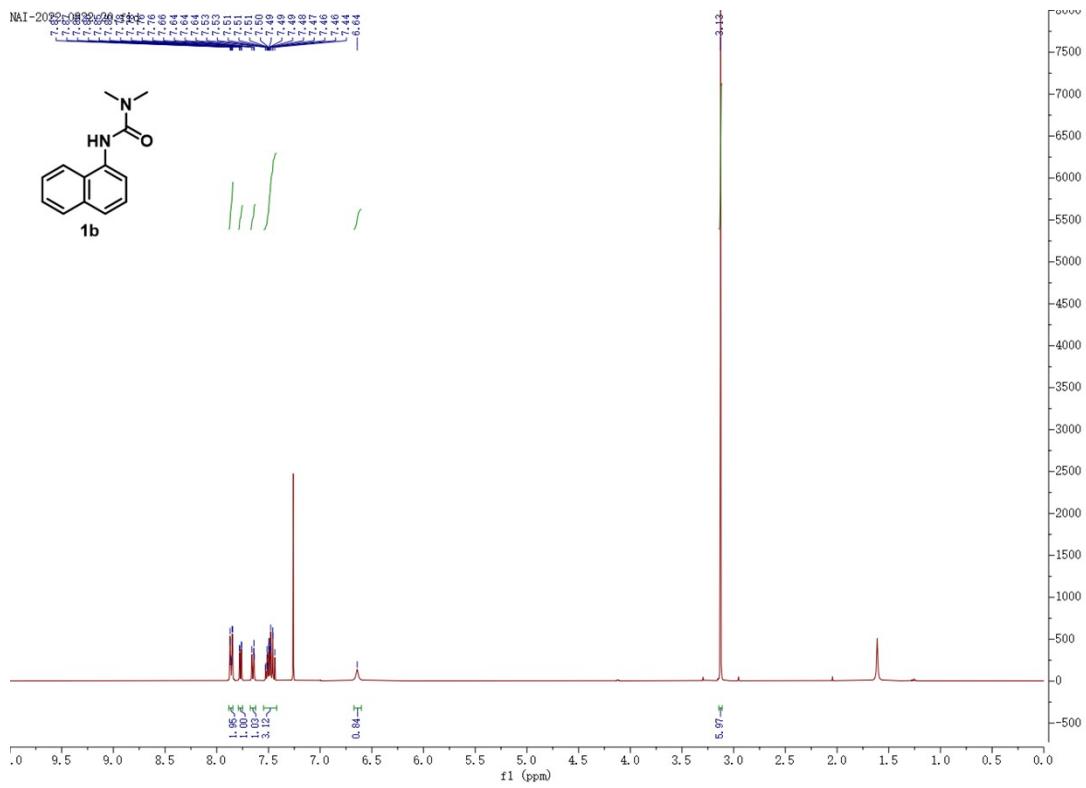
3.NMR Spectra for New Compounds

^1H NMR spectrum (400 MHz, CDCl_3) of **1a**



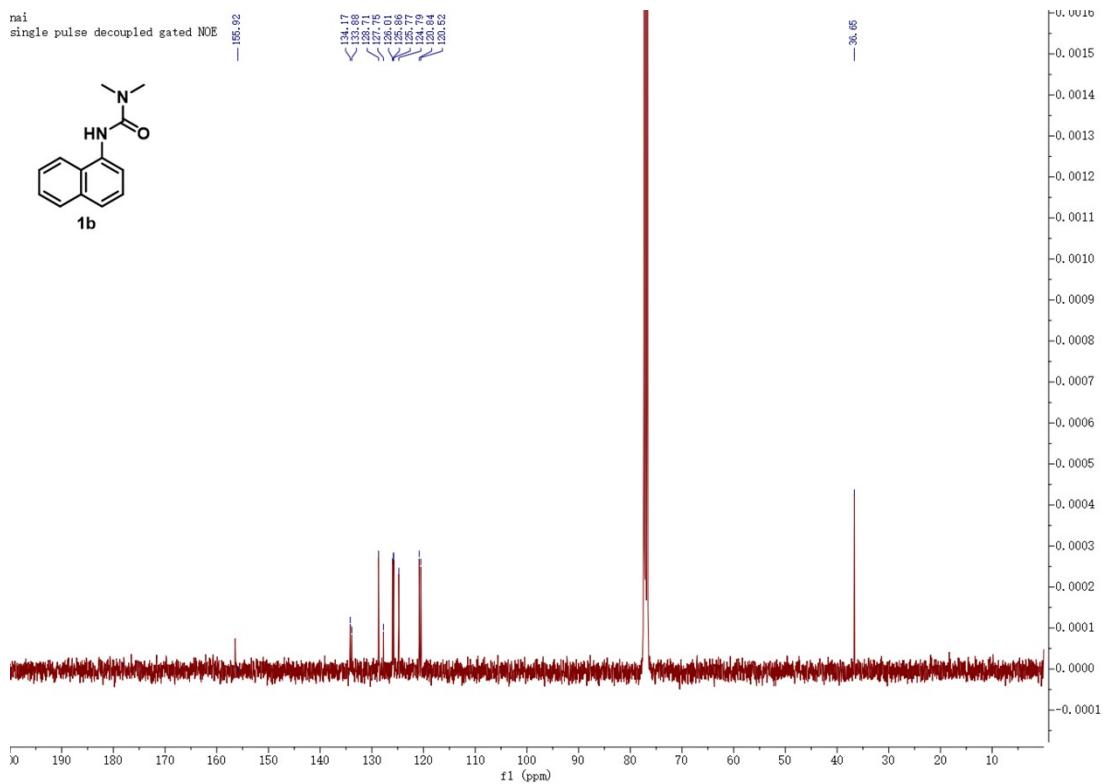
^{13}C spectrum (100 MHz, CDCl_3) of **1a**

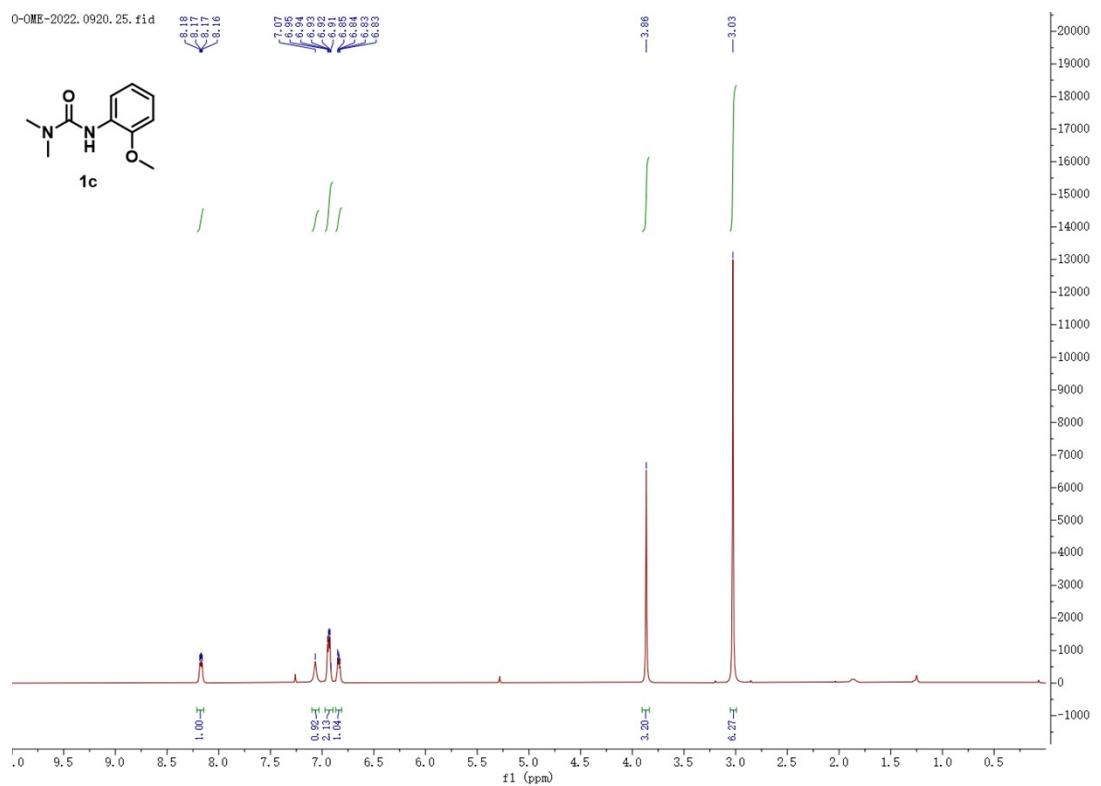




¹H NMR spectrum (400 MHz, CDCl₃) of **1b**

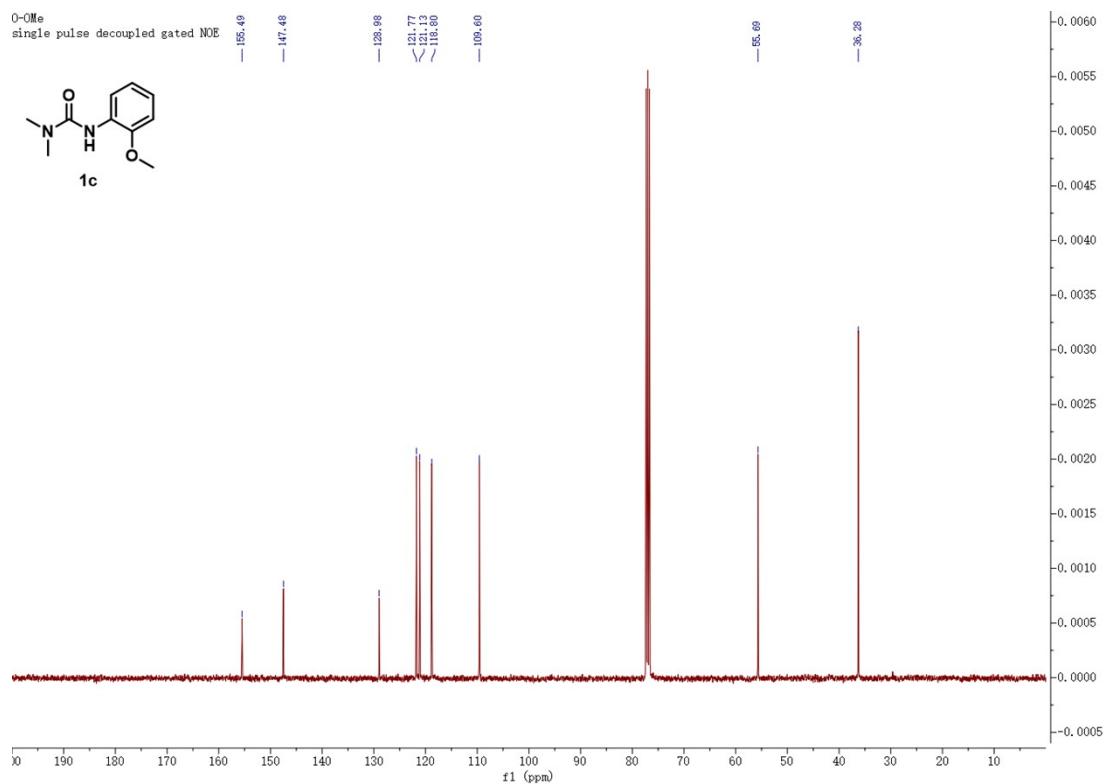
¹³C NMR spectrum (100 MHz, CDCl₃) of **1b**



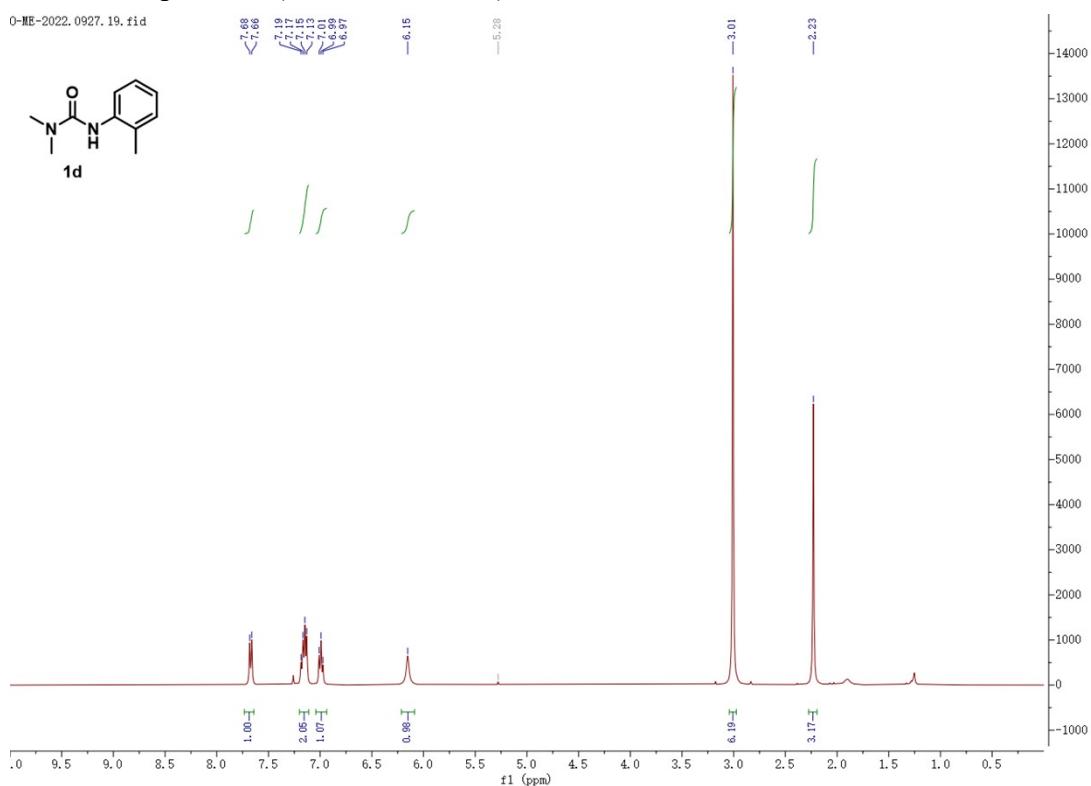


^1H NMR spectrum (400 MHz, CDCl_3) of **1c**

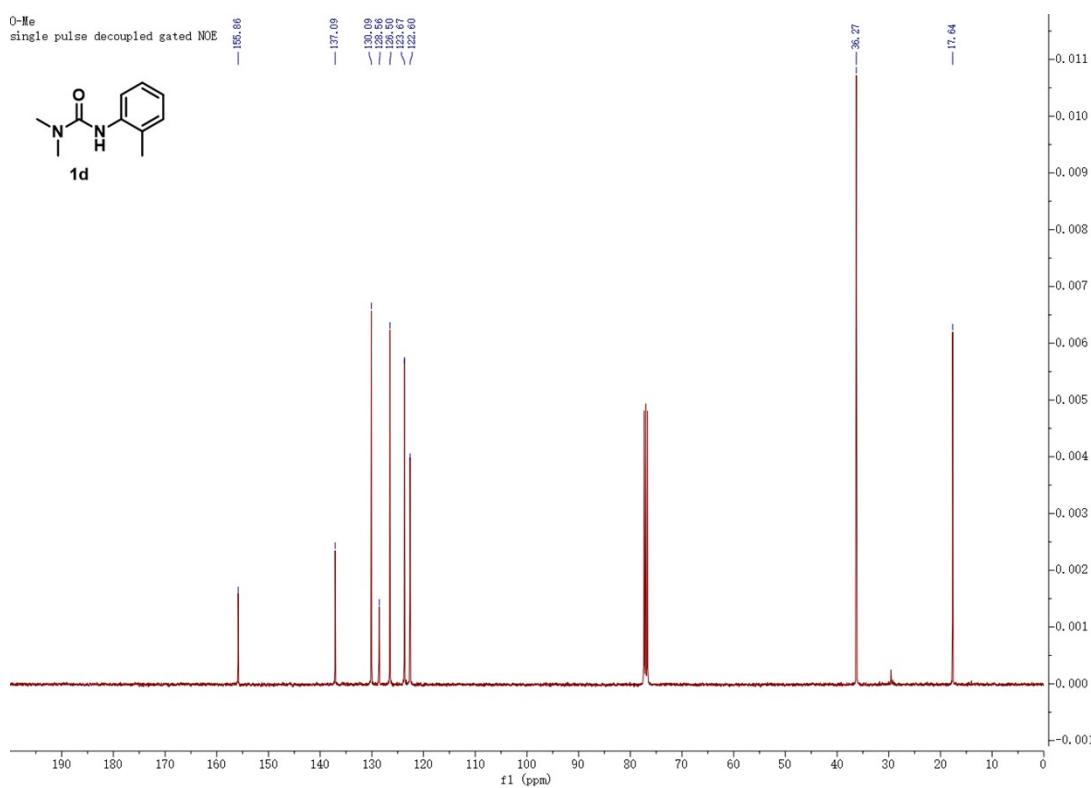
^{13}C NMR spectrum (100 MHz, CDCl_3) of **1c**



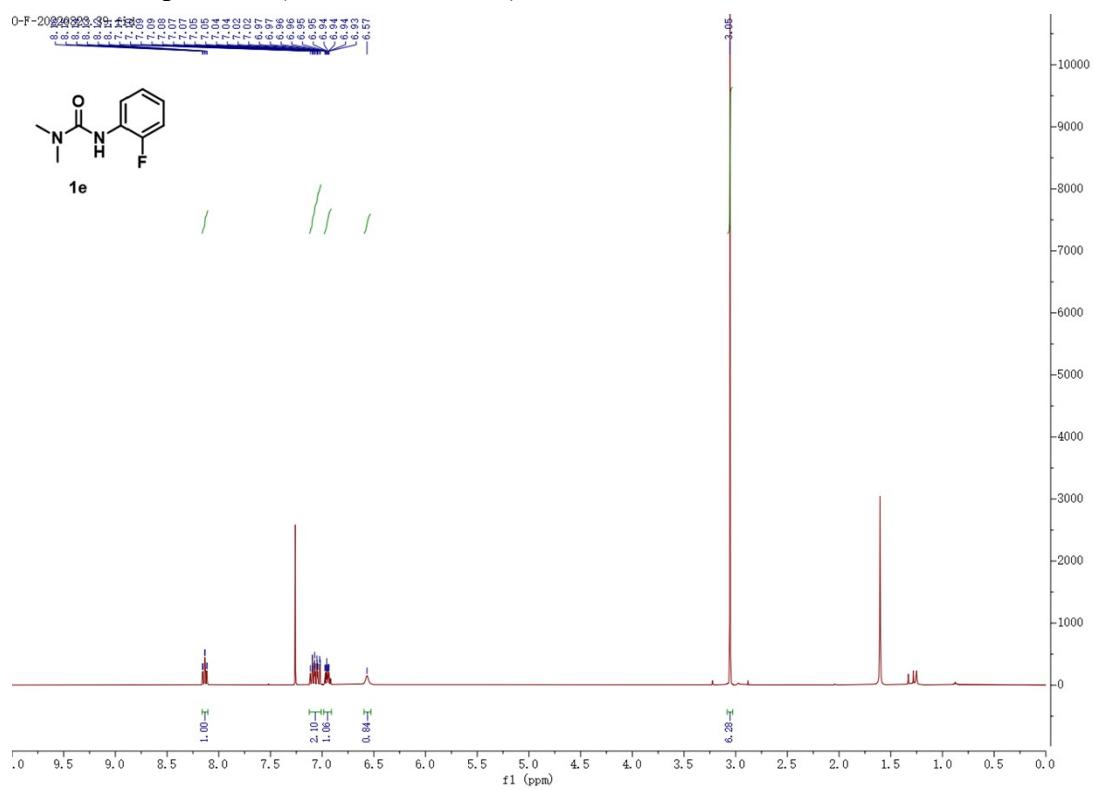
¹H NMR spectrum (400 MHz, CDCl₃) of **1d**



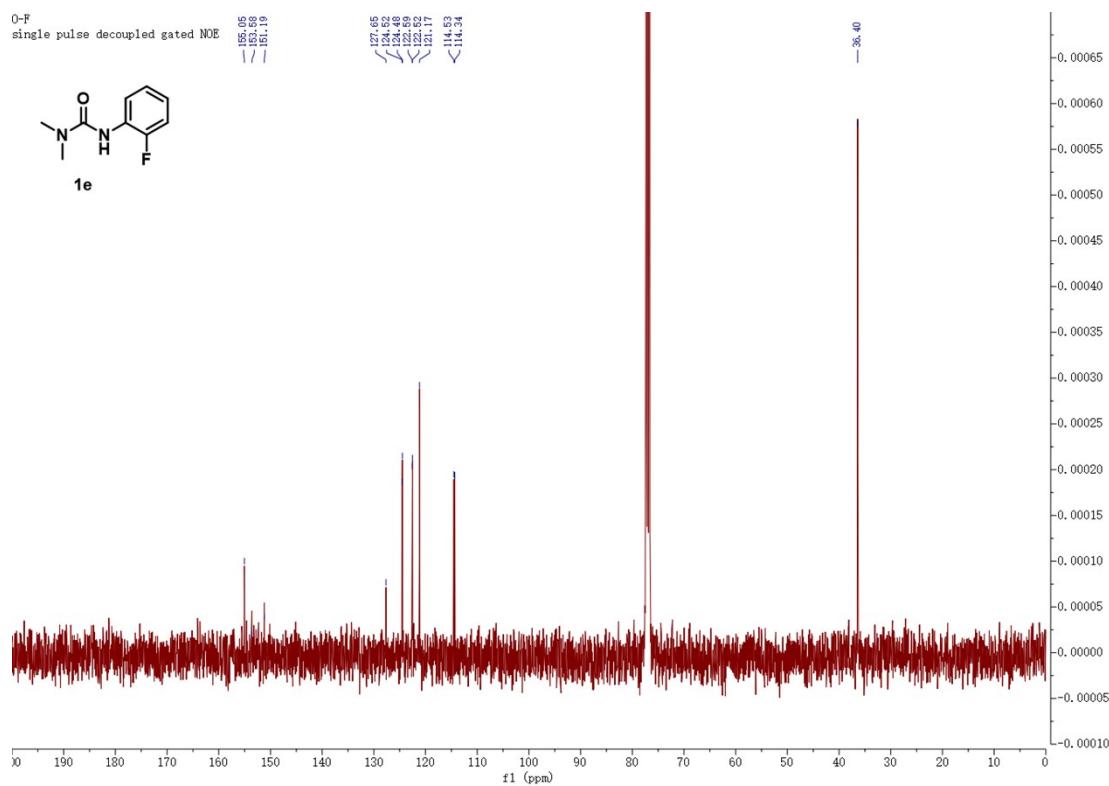
¹³C NMR spectrum (100 MHz, CDCl₃) of **1d**



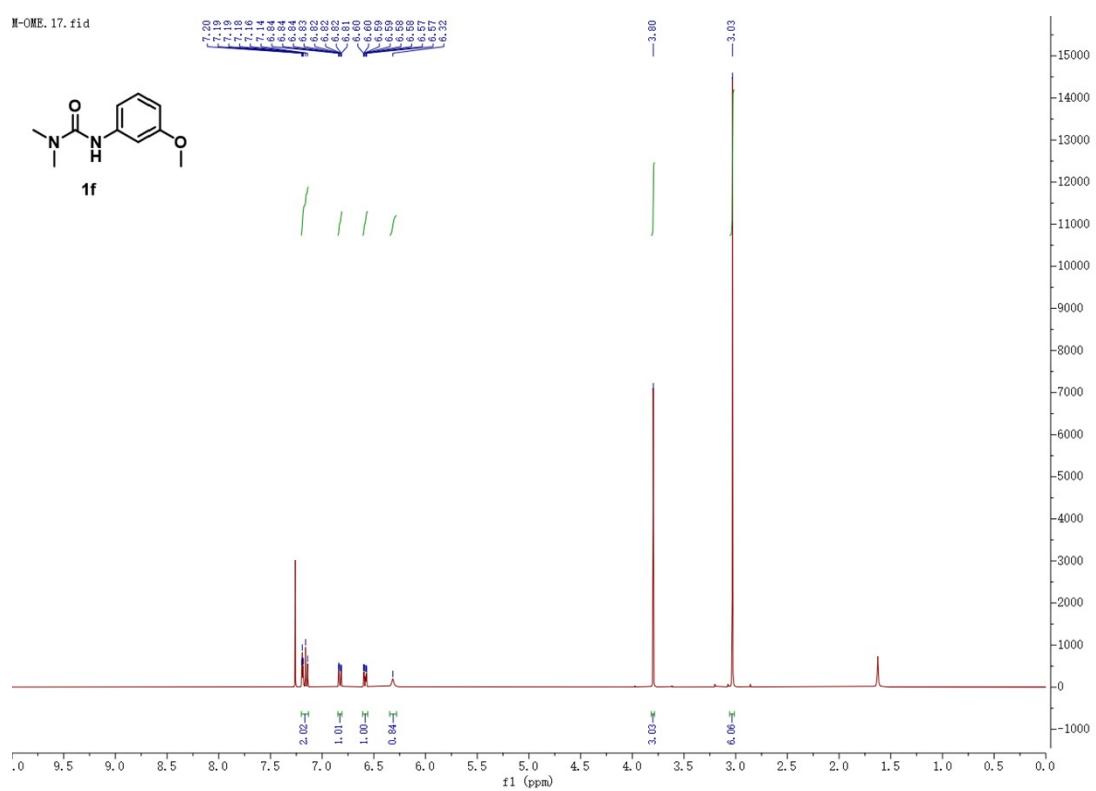
¹H NMR spectrum (400 MHz, CDCl₃) of **1e**



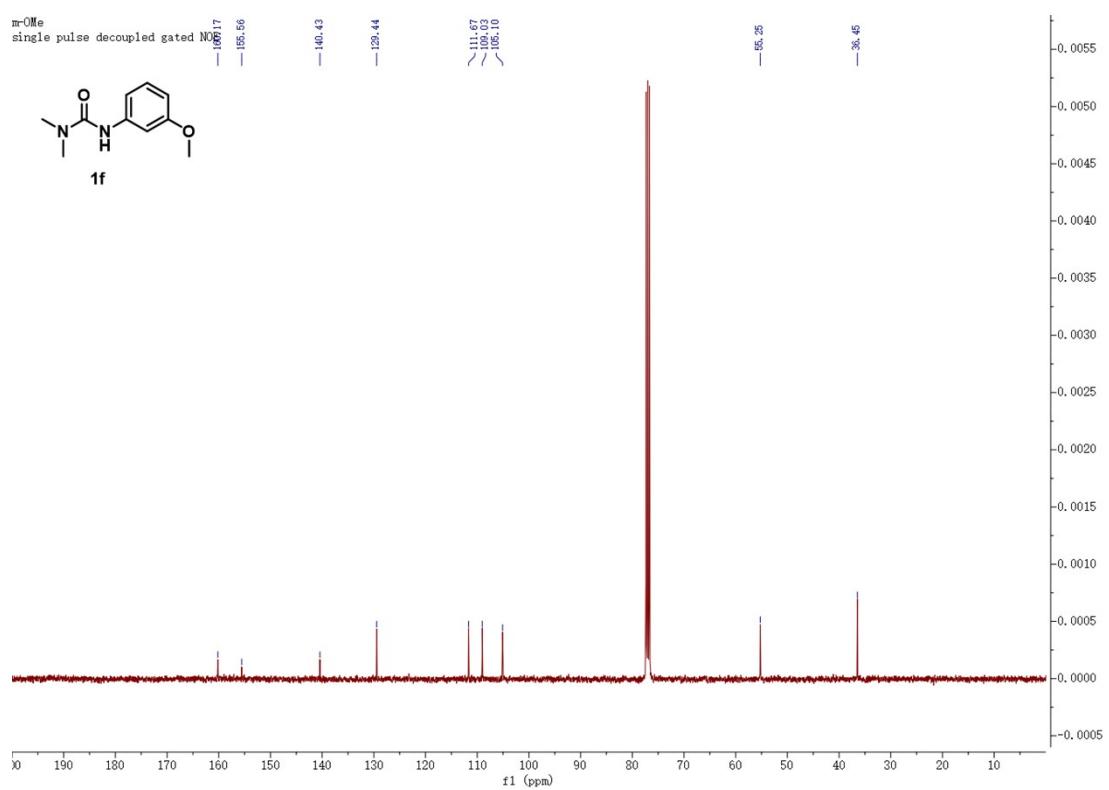
¹³C NMR spectrum (100 MHz, CDCl₃) of **1e**



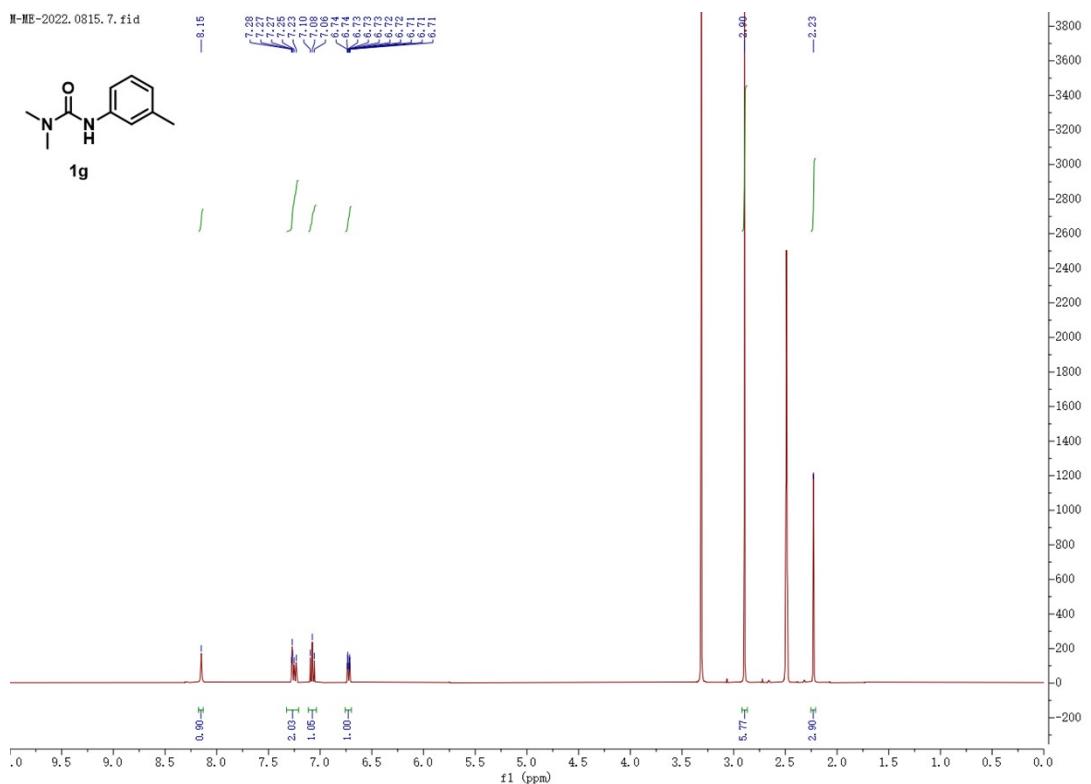
¹H NMR spectrum (400 MHz, CDCl₃) of **1f**



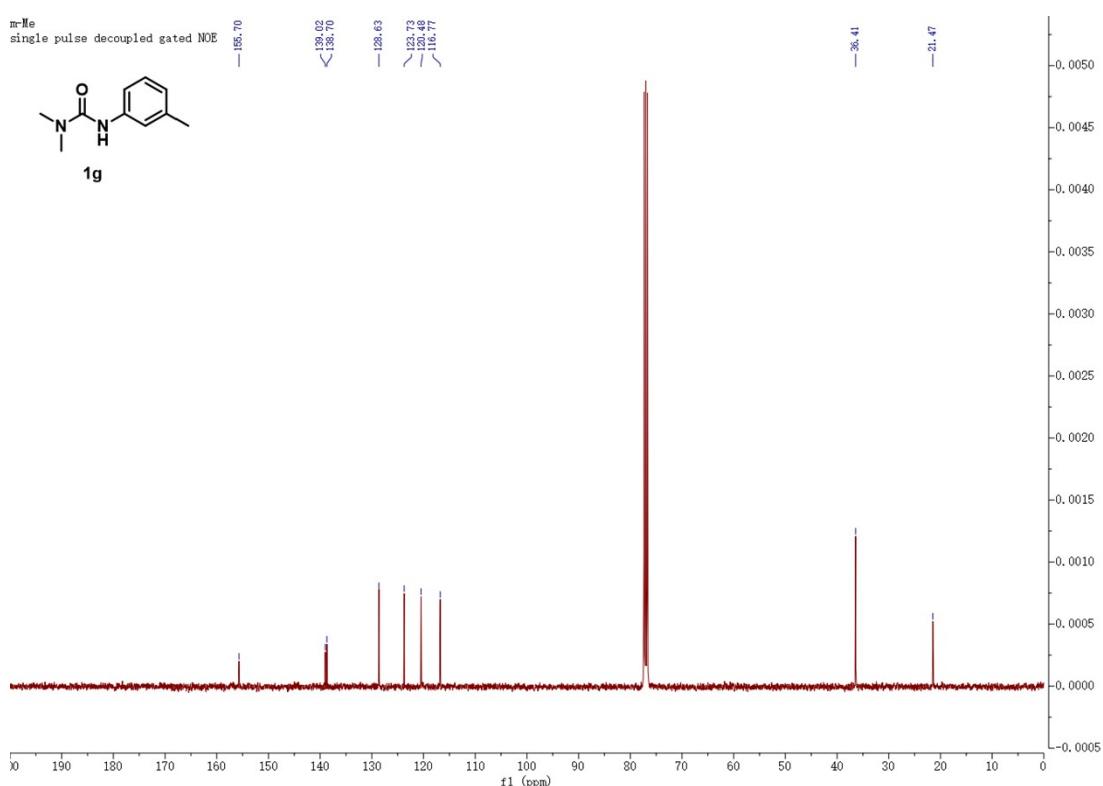
¹³C NMR spectrum (100 MHz, CDCl₃) of **1f**



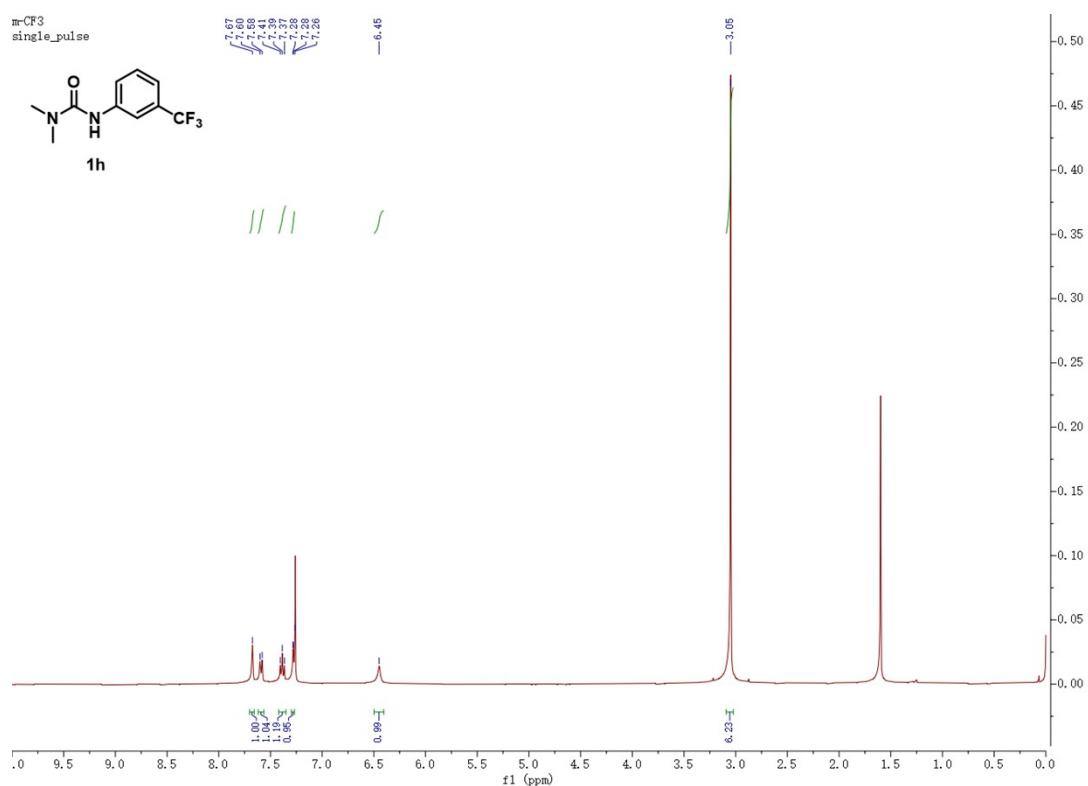
¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **1g**



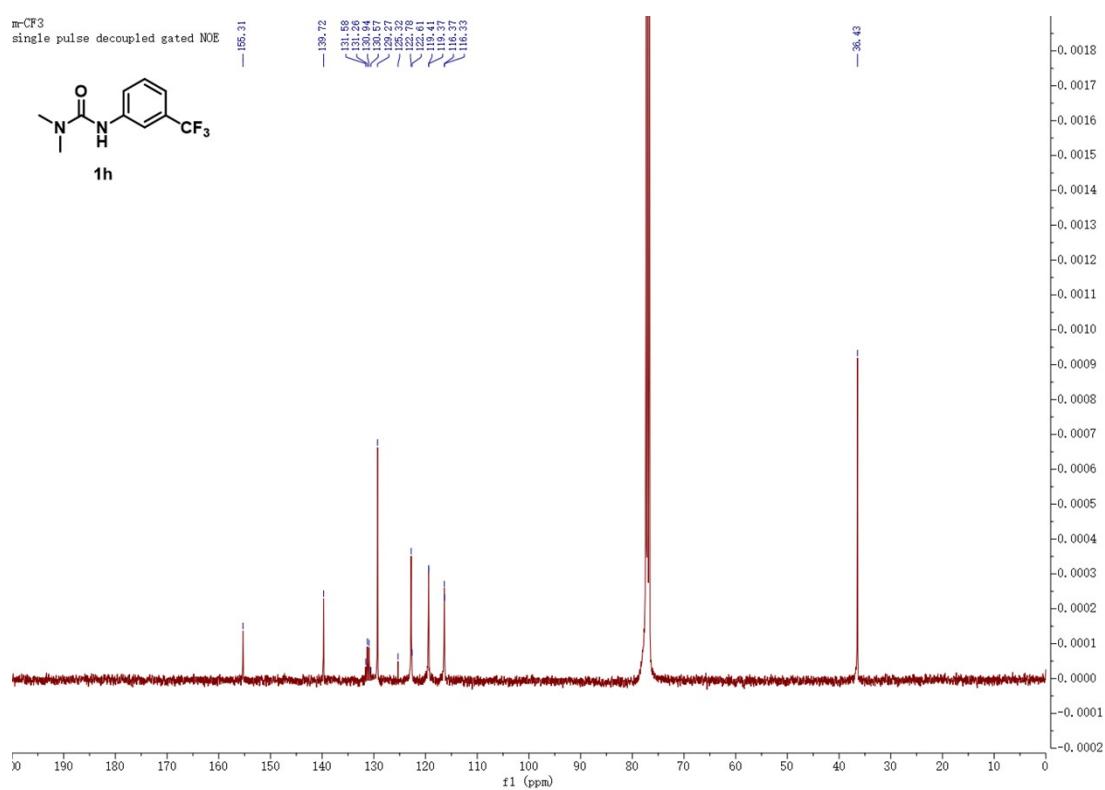
¹³C NMR spectrum (100 MHz, CDCl₃) of **1g**



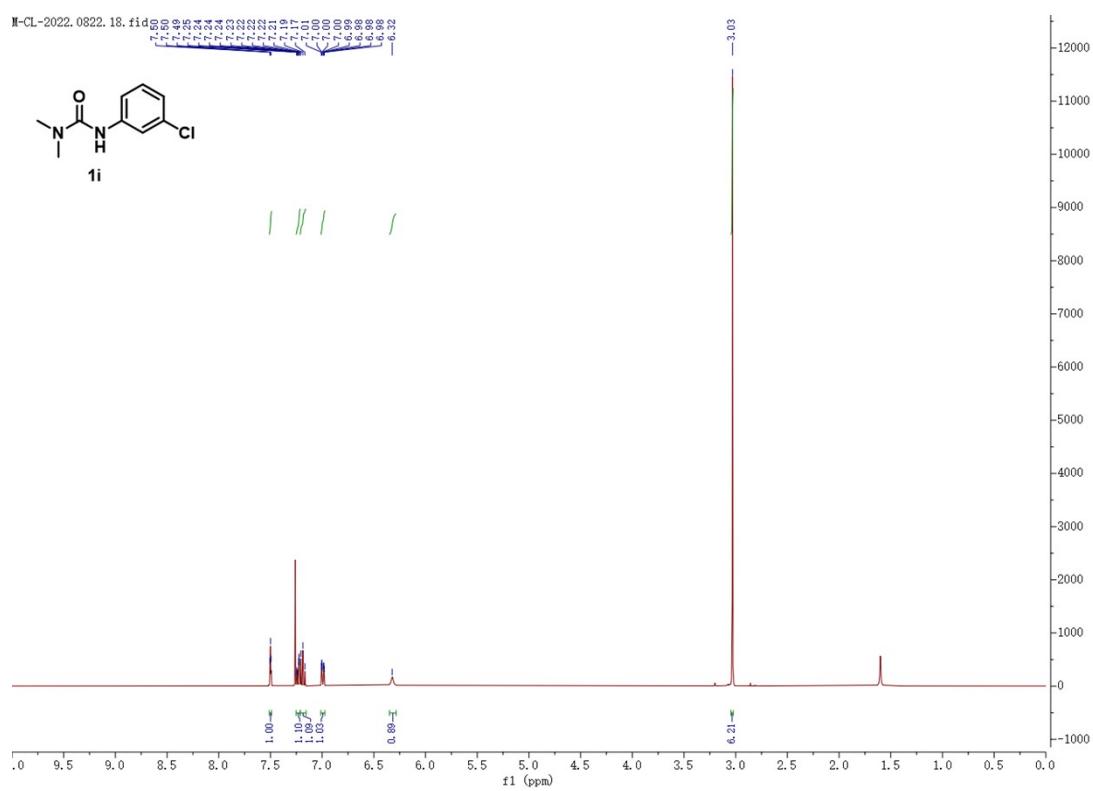
¹H NMR spectrum (400 MHz, CDCl₃) of **1h**



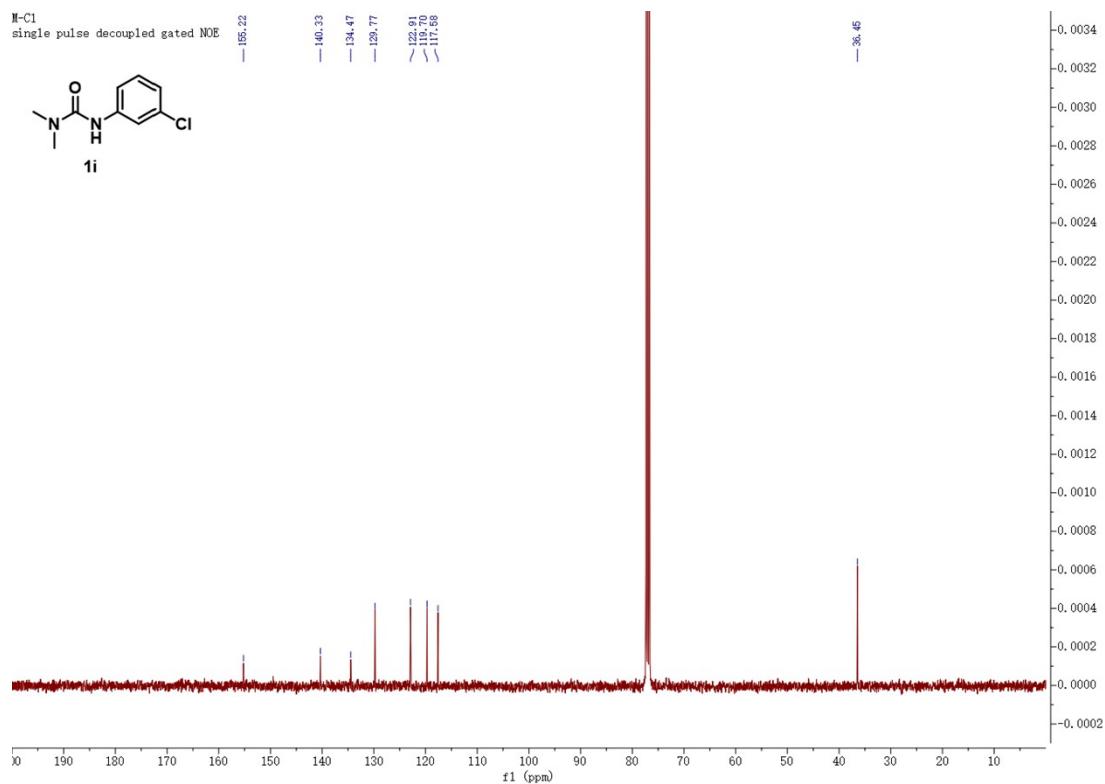
¹³C NMR spectrum (100 MHz, CDCl₃) of **1h**



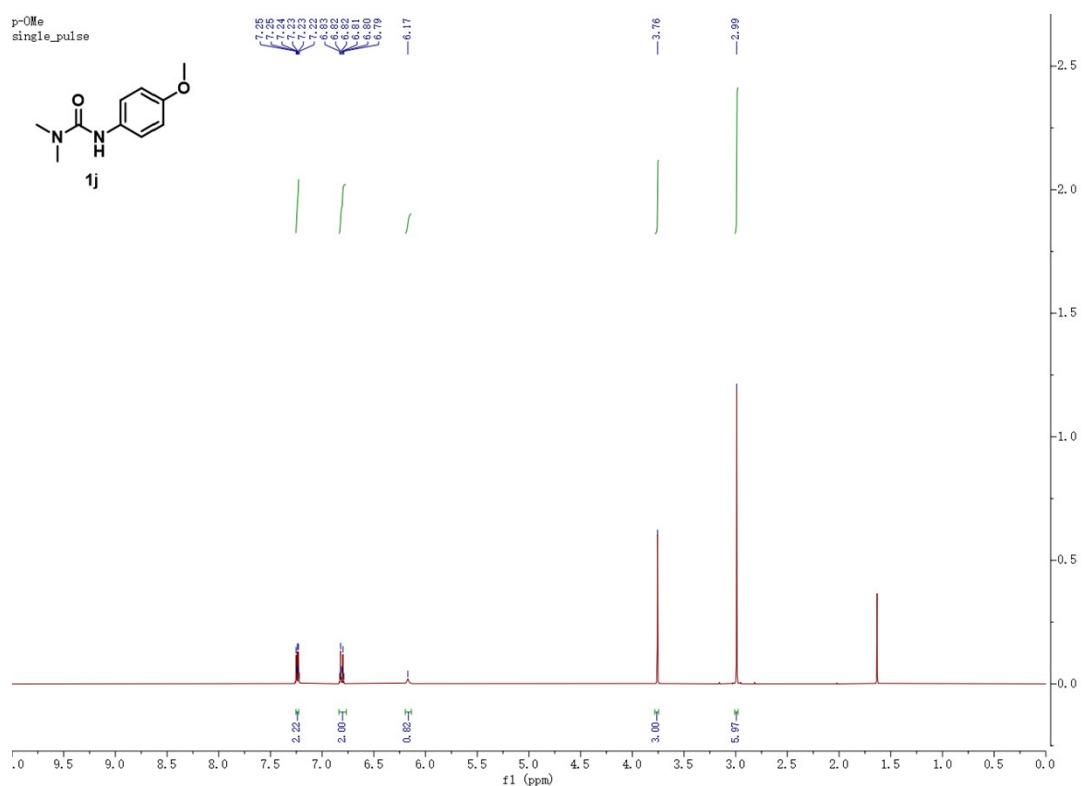
¹H NMR spectrum (400 MHz, CDCl₃) of **1i**



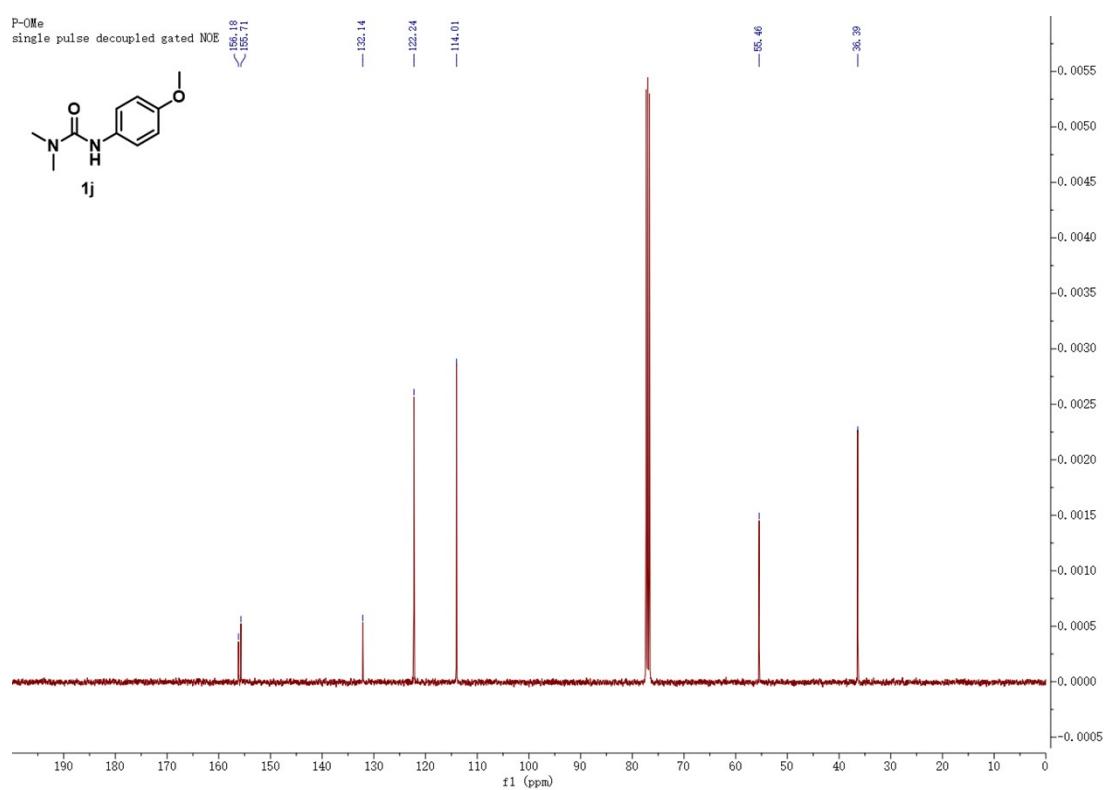
¹³C NMR spectrum (100 MHz, CDCl₃) of **1i**



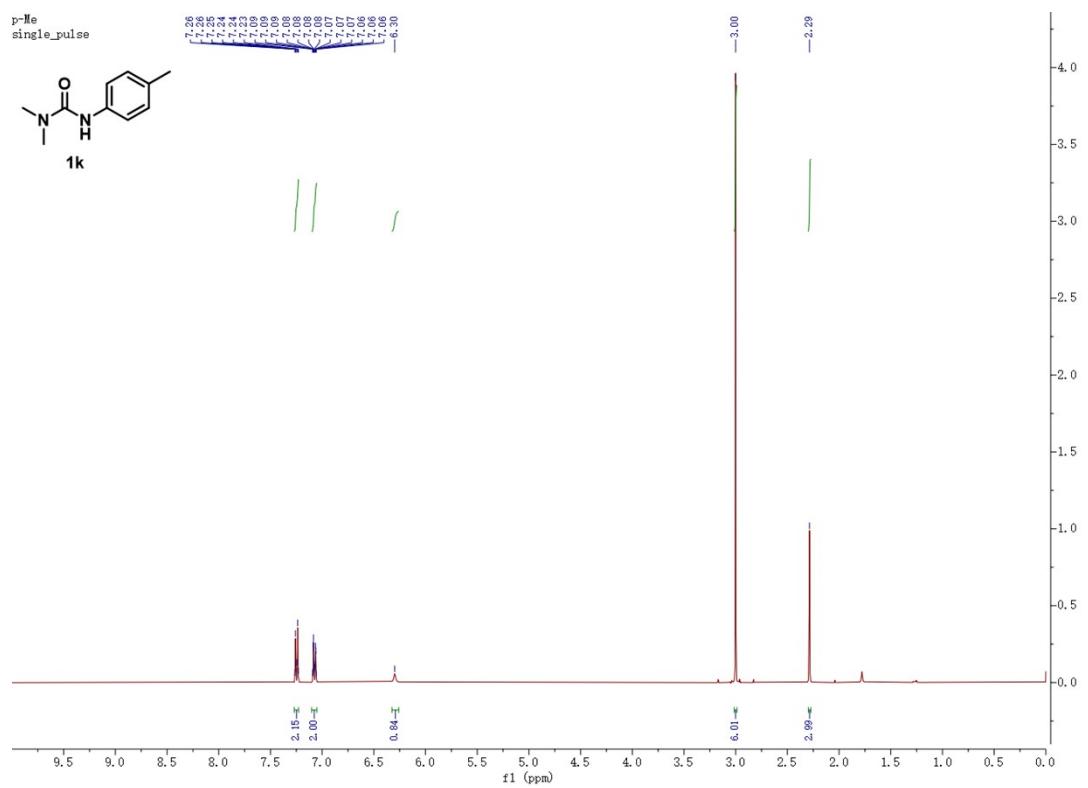
¹H NMR spectrum (400 MHz, CDCl₃) of **1j**



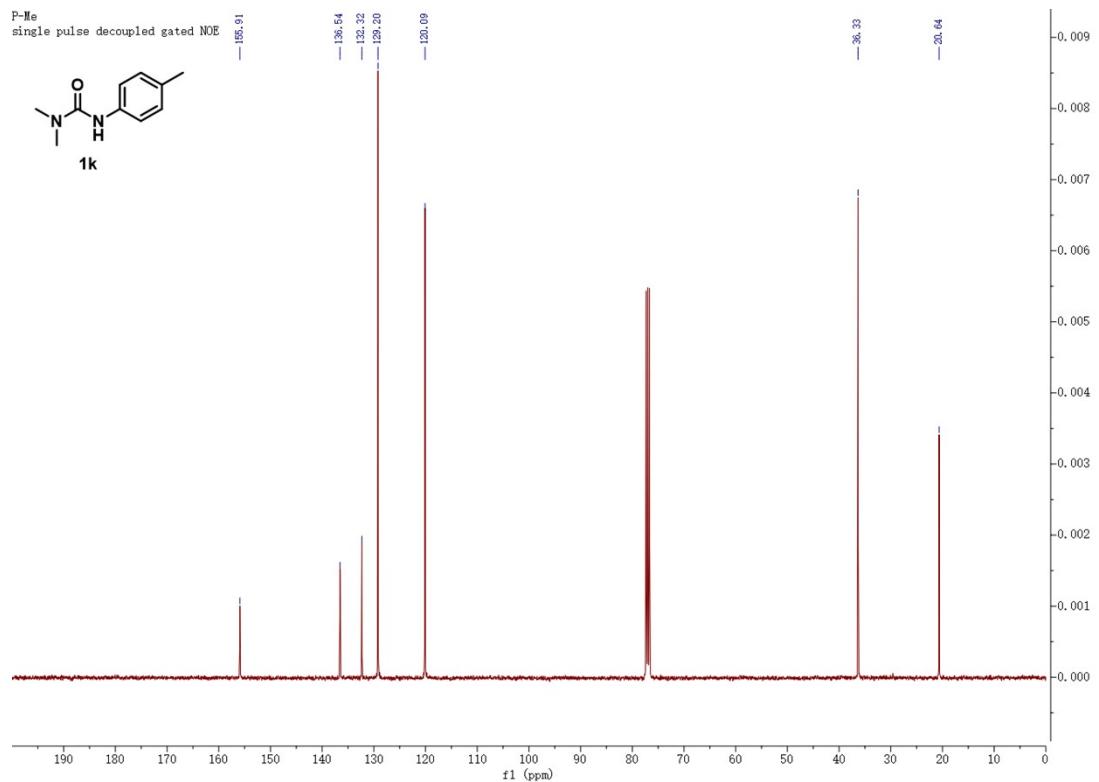
¹³C NMR spectrum (100 MHz, CDCl₃) of **1j**



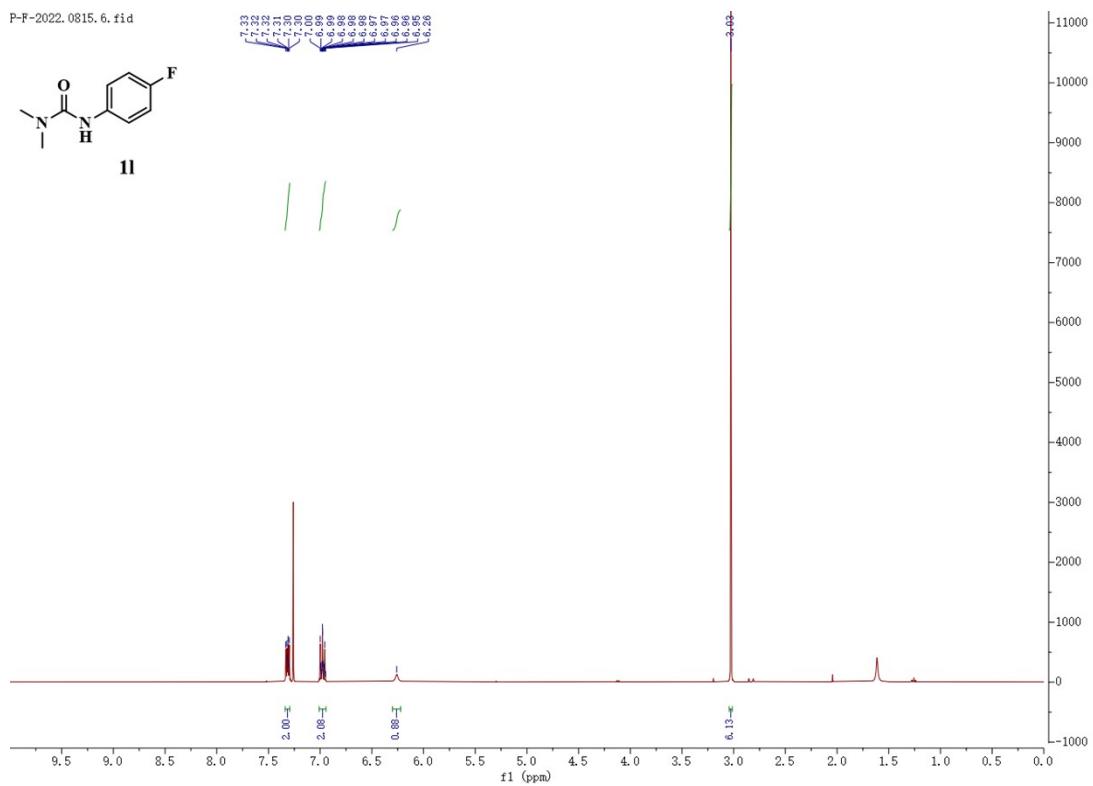
¹H NMR spectrum (400 MHz, CDCl₃) of **1k**



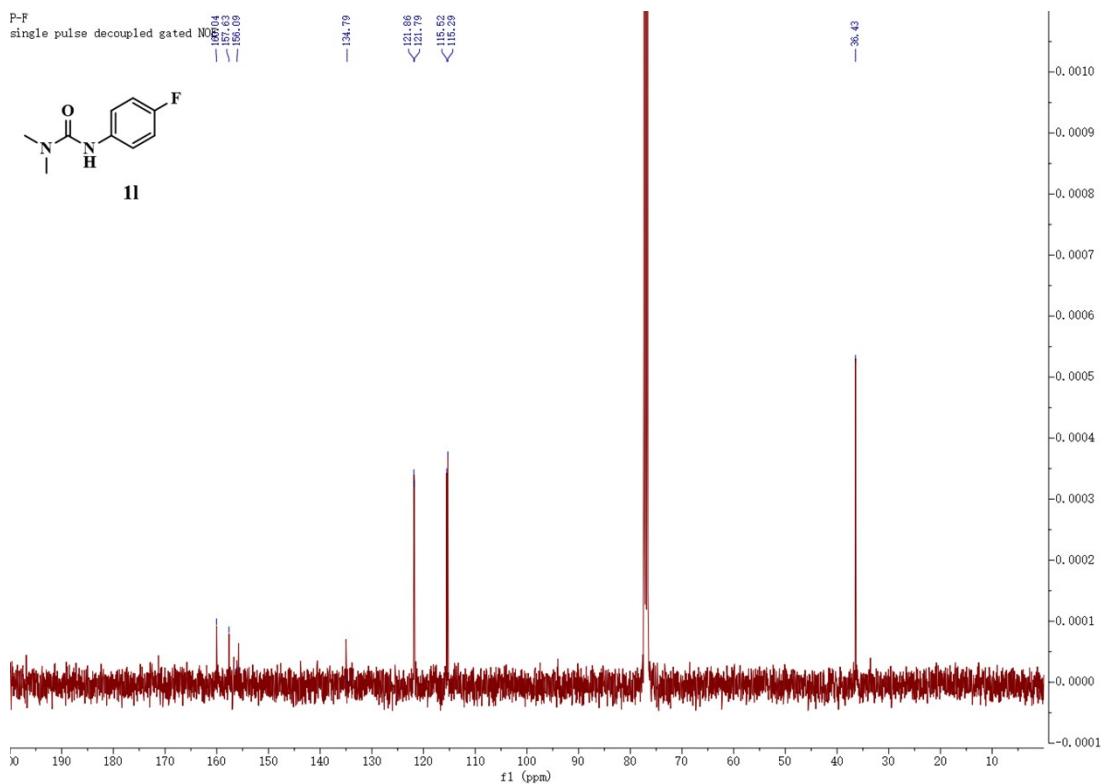
¹³C spectrum (100 MHz, CDCl₃) of **1k**



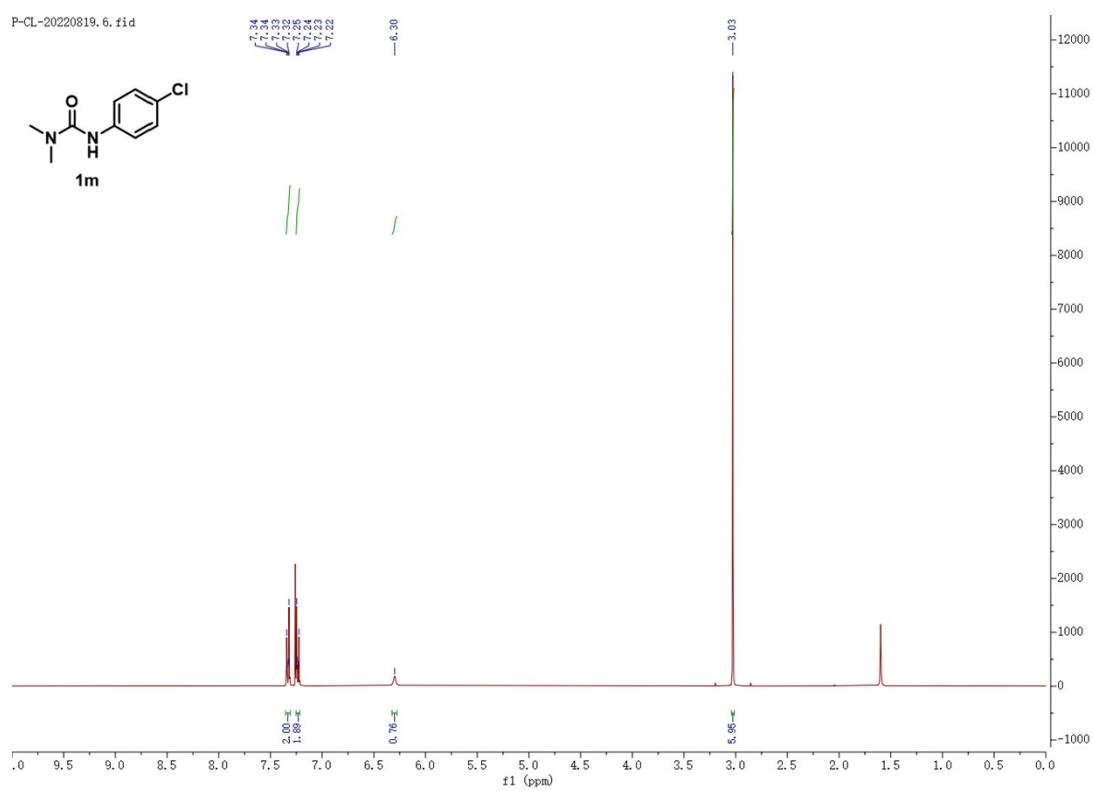
¹H NMR spectrum (400 MHz, CDCl₃) of **1l**



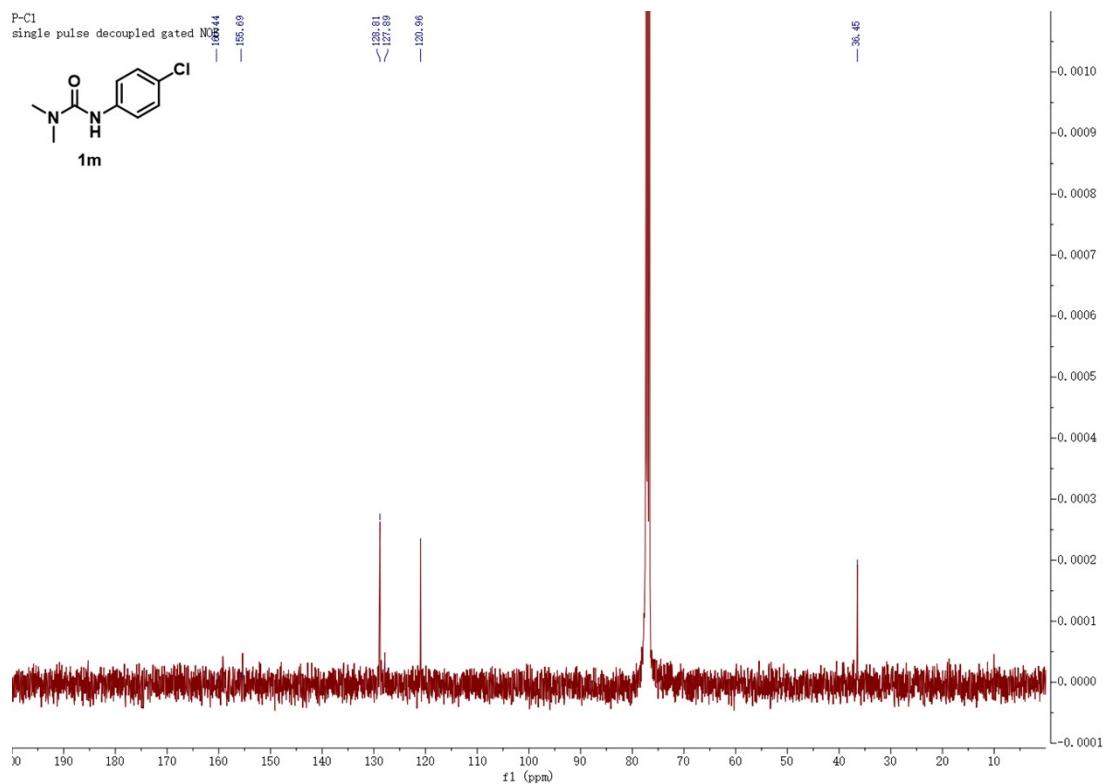
¹³C NMR spectrum (100 MHz, CDCl₃) of **1l**



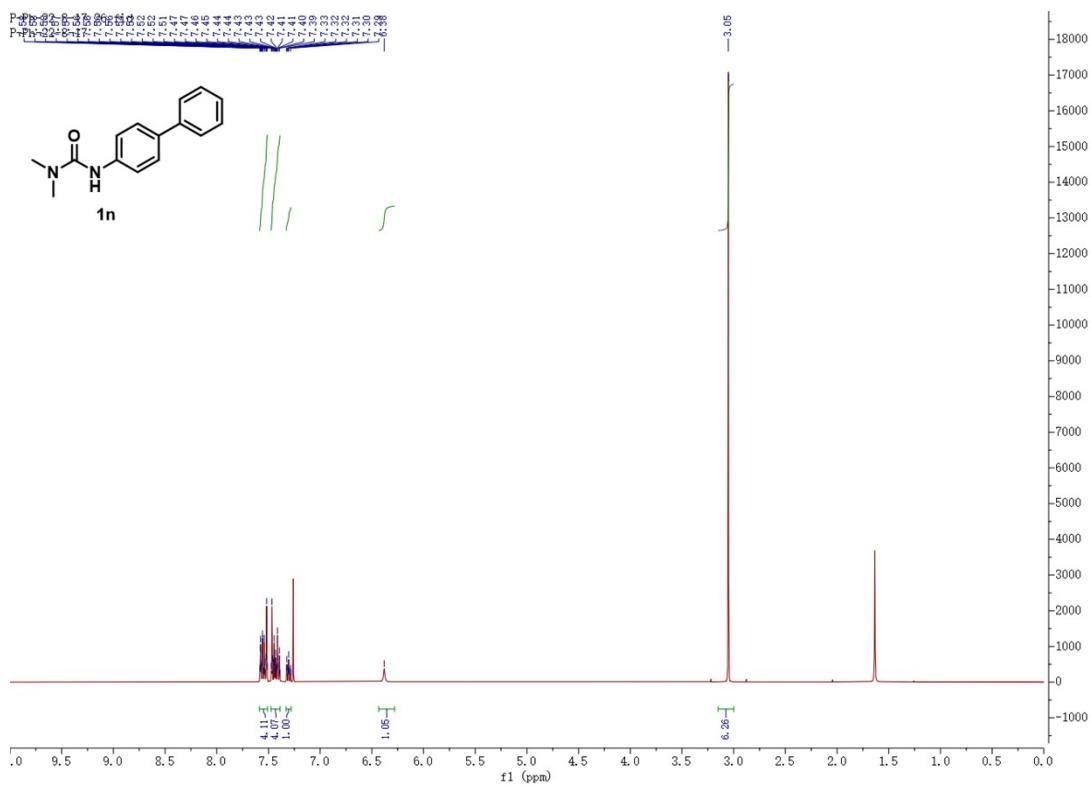
¹H NMR spectrum (400 MHz, CDCl₃) of **1m**



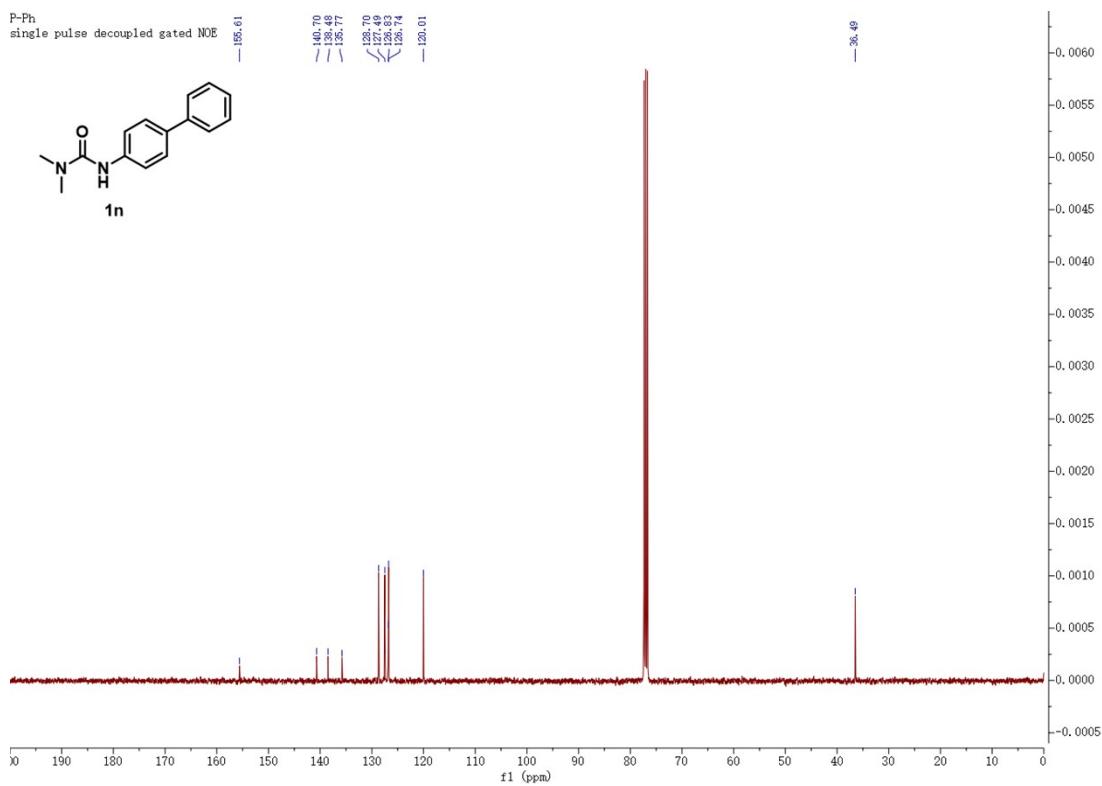
¹³C NMR spectrum (100 MHz, CDCl₃) of **1m**



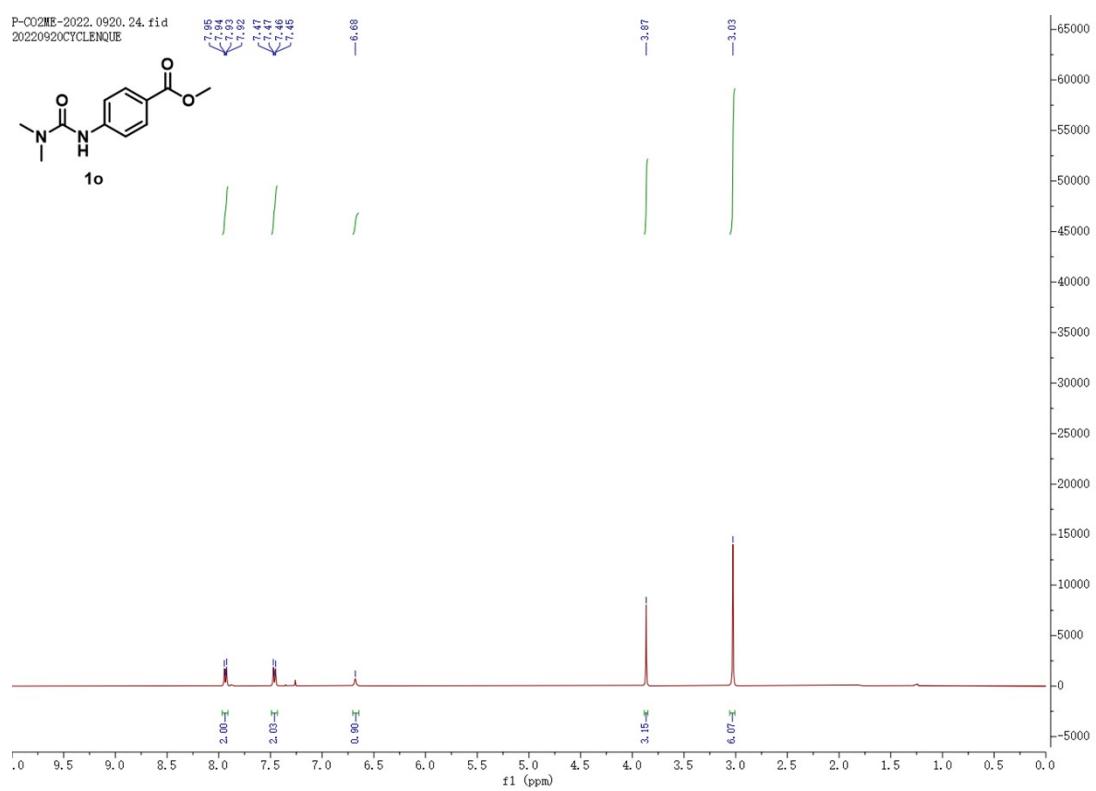
¹H NMR spectrum (400 MHz, CDCl₃) of **1n**



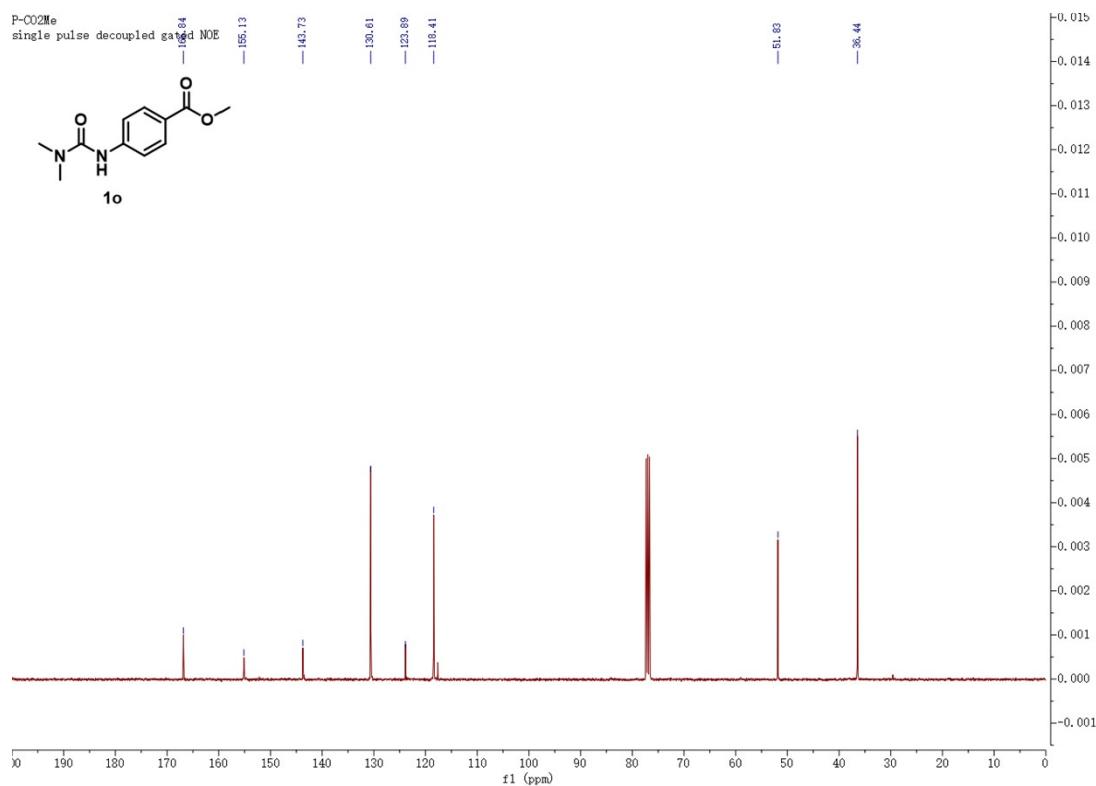
¹³C NMR spectrum (100 MHz, CDCl₃) of **1n**



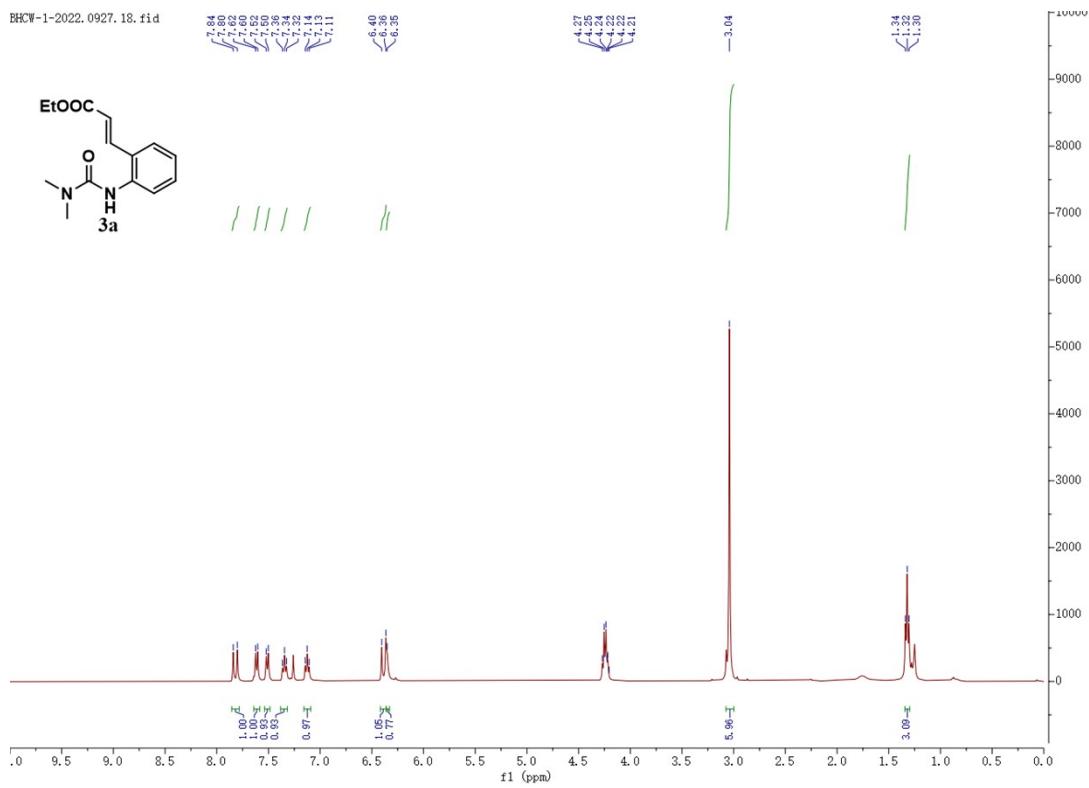
¹H NMR spectrum (400 MHz, CDCl₃) of **1o**



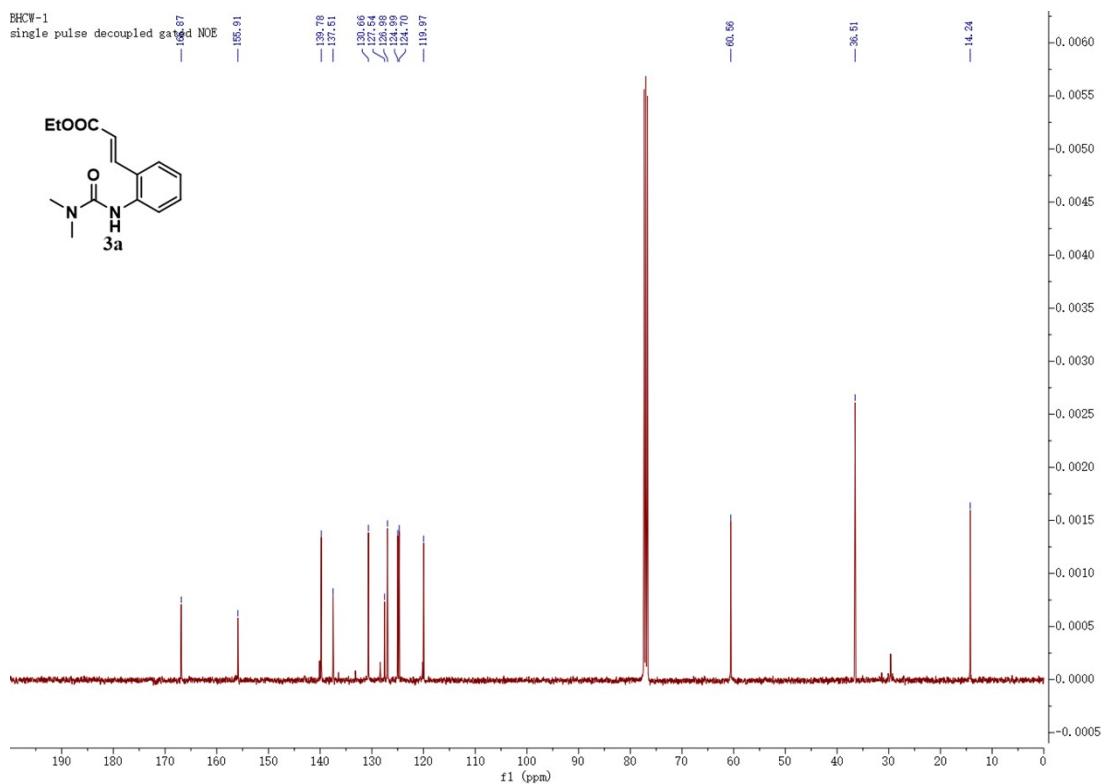
¹³C NMR spectrum (100 MHz, CDCl₃) of **1o**



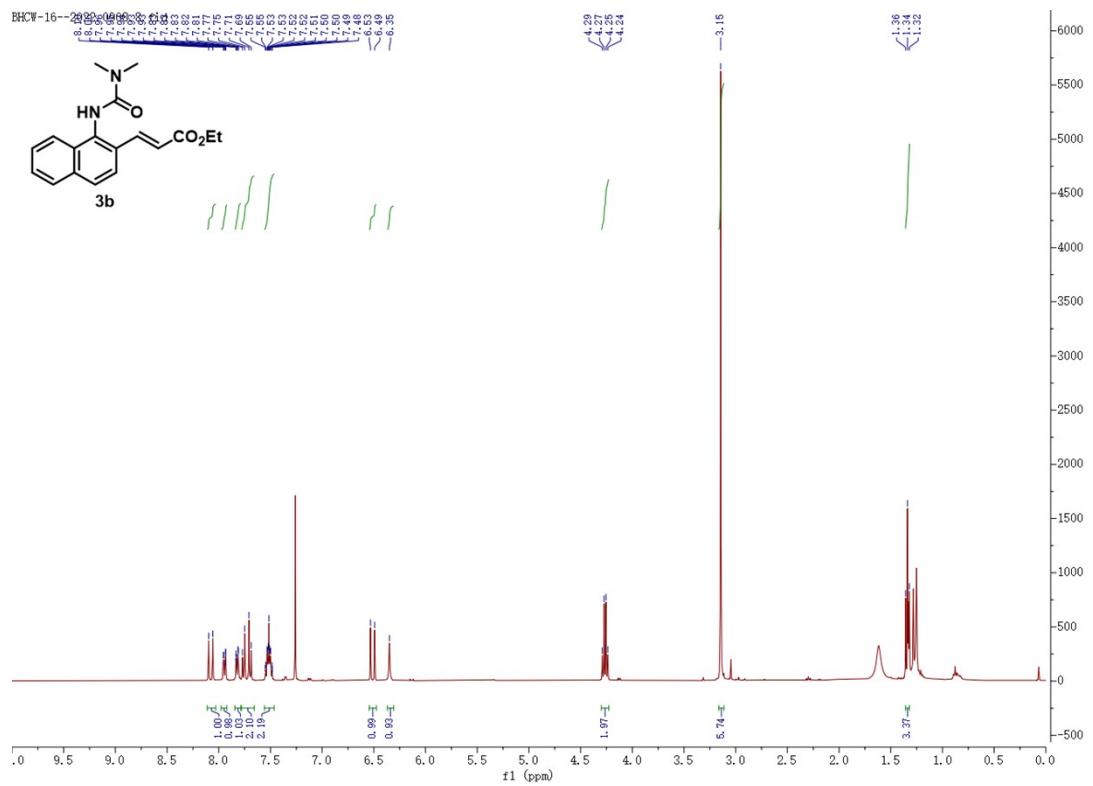
¹H NMR spectrum (400 MHz, CDCl₃) of 3a



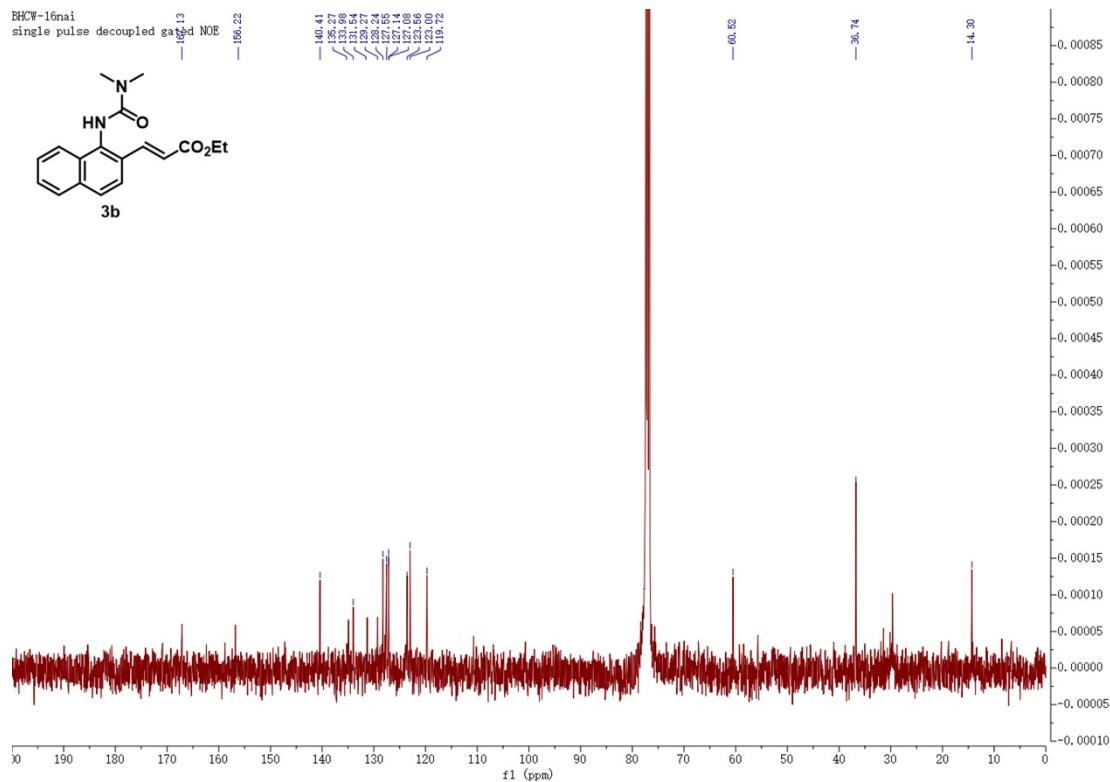
¹³C NMR spectrum (100 MHz, CDCl₃) of 3a



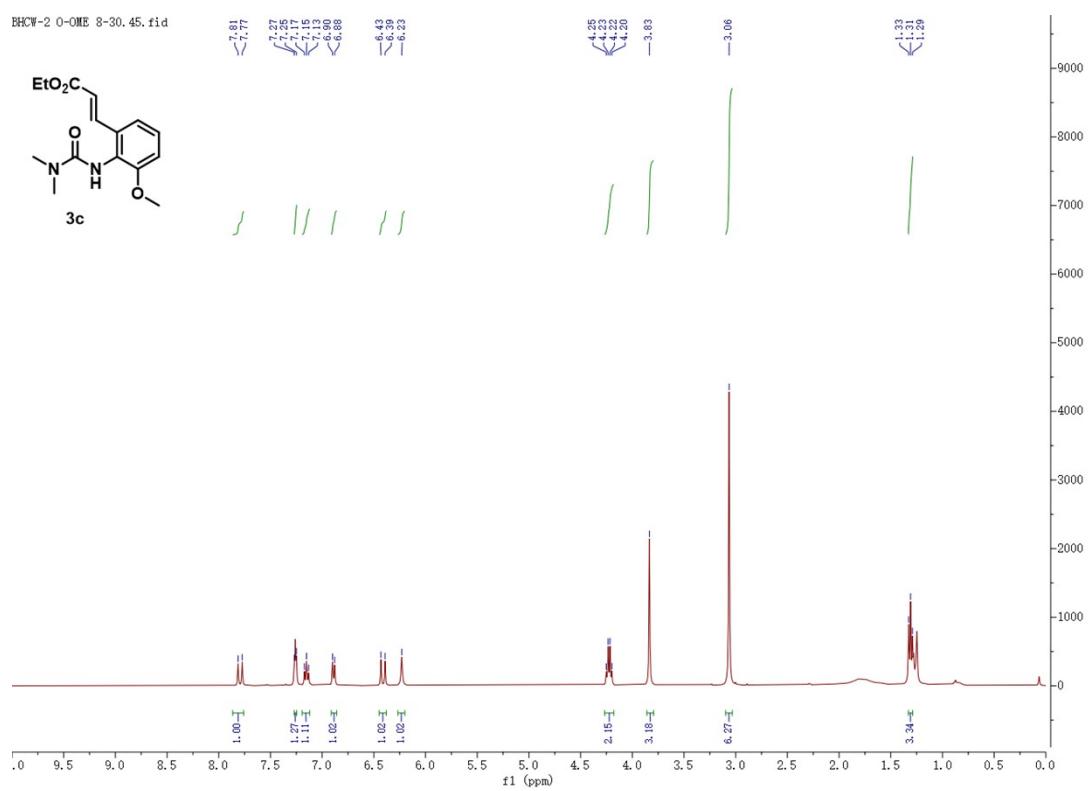
¹H NMR spectrum (400 MHz, CDCl₃) of **3b**



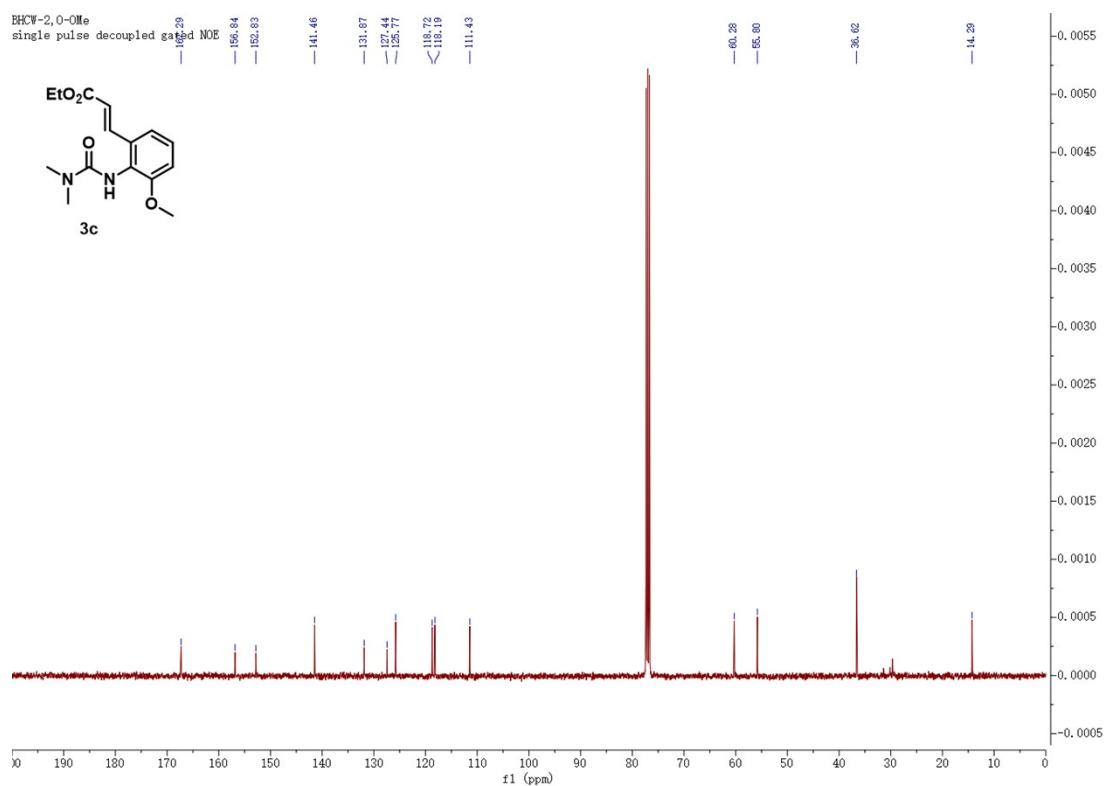
¹³C NMR spectrum (100 MHz, CDCl₃) of **3b**



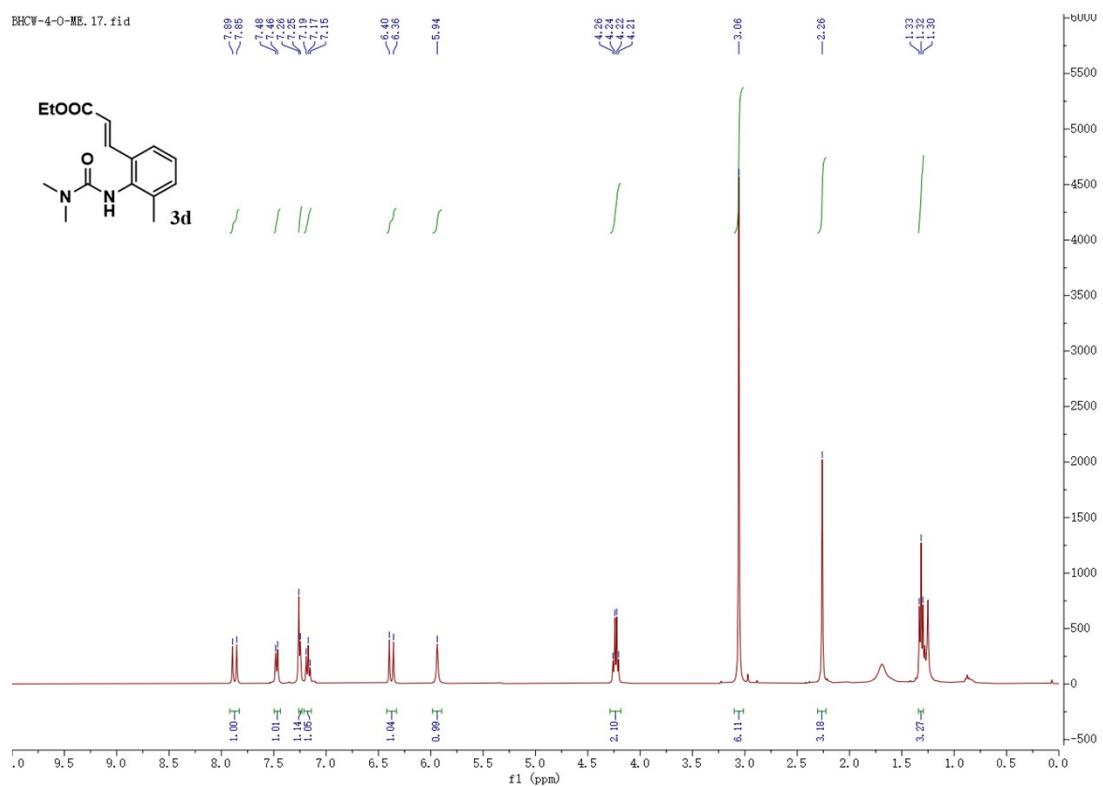
¹H NMR spectrum (400 MHz, CDCl₃) of 3c



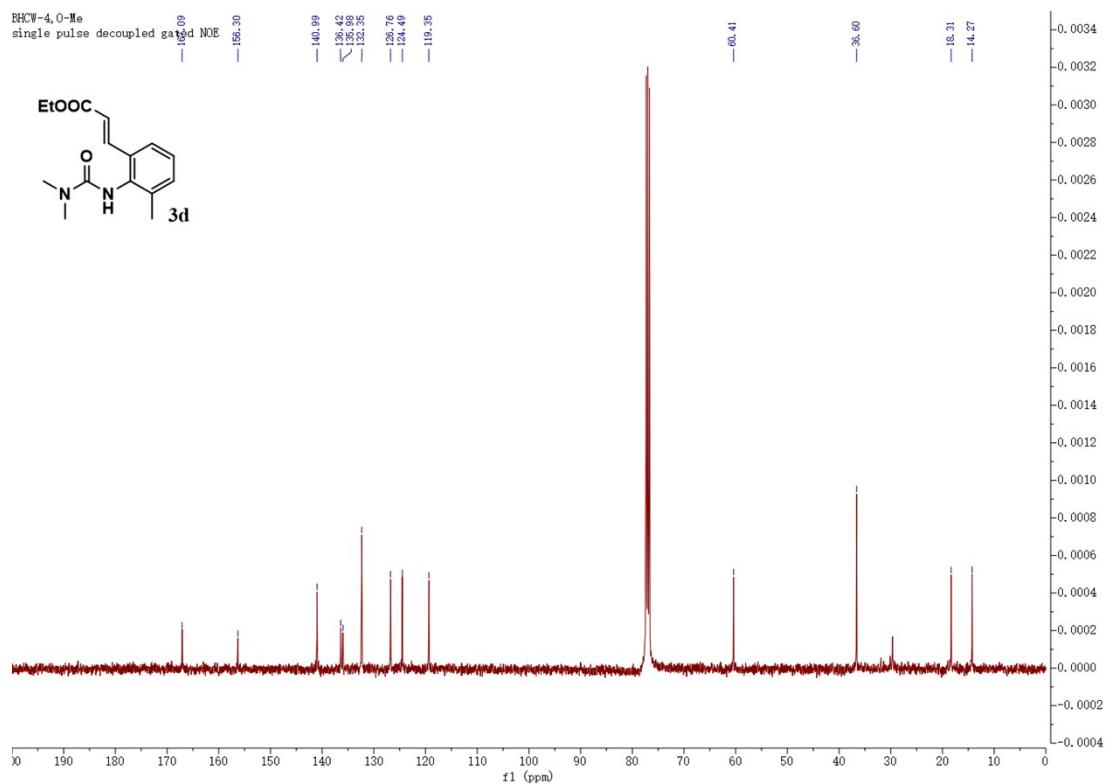
¹³C NMR spectrum (100 MHz, CDCl₃) of 3c



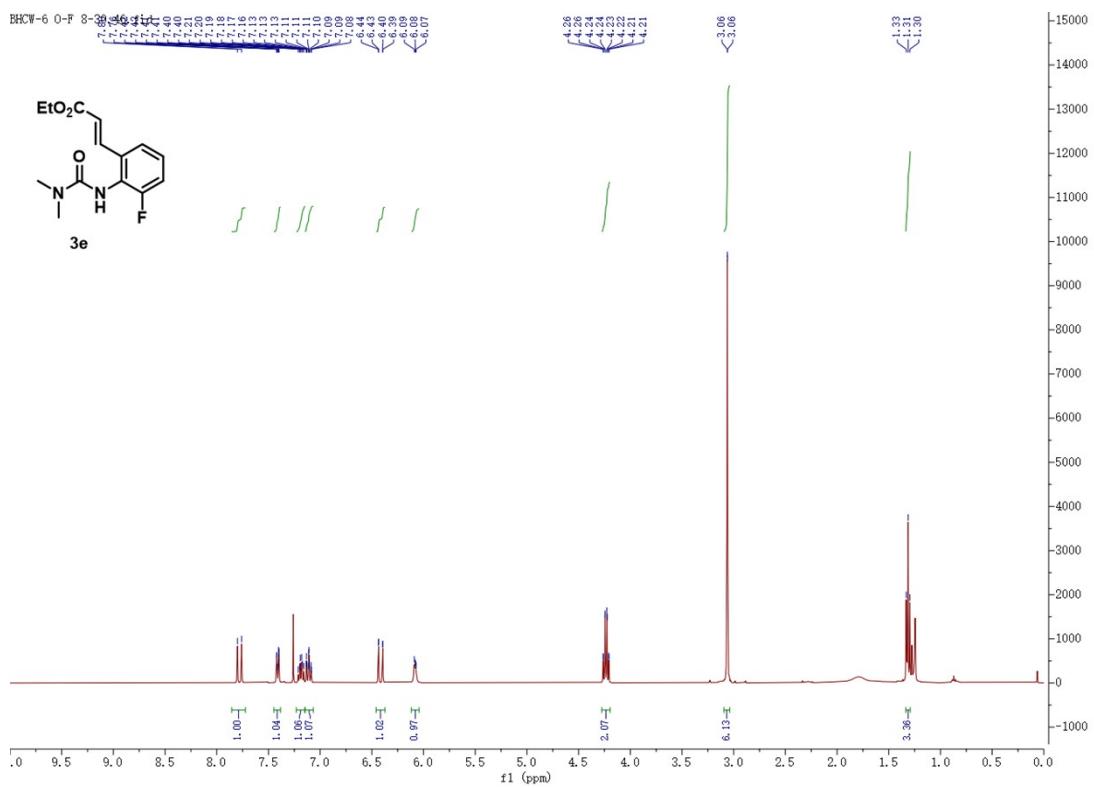
¹H NMR spectrum (400 MHz, CDCl₃) of 3d



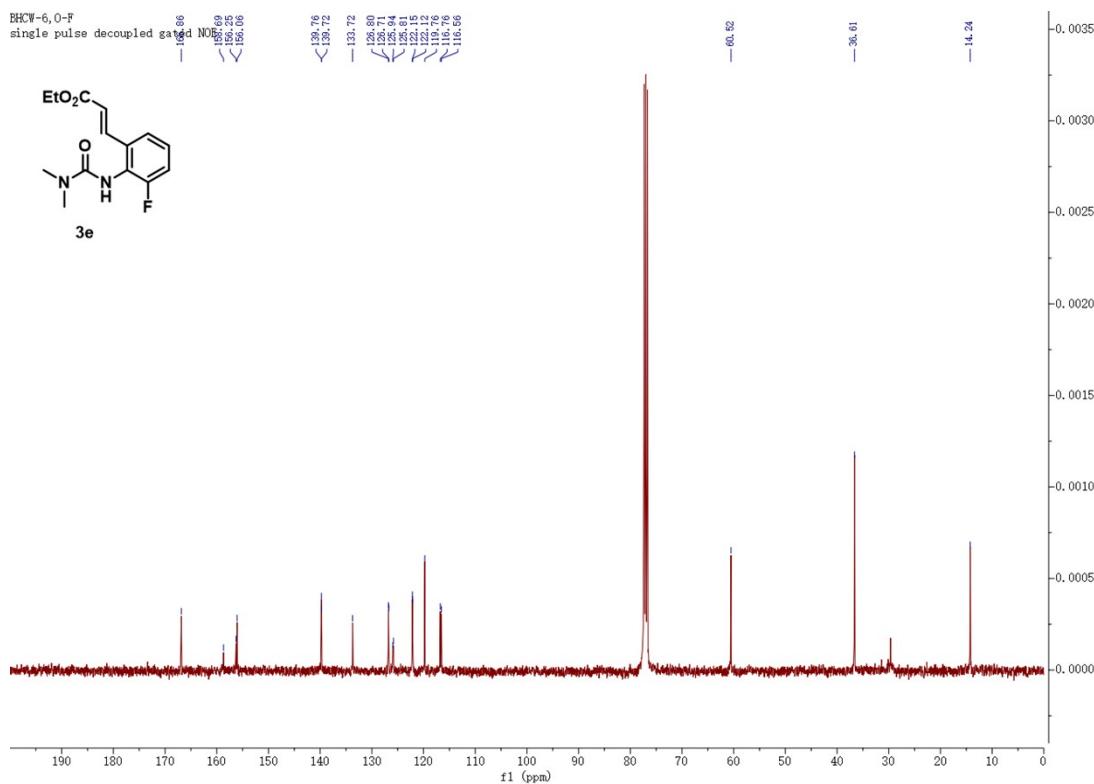
¹³C NMR spectrum (100 MHz, CDCl₃) of 3d



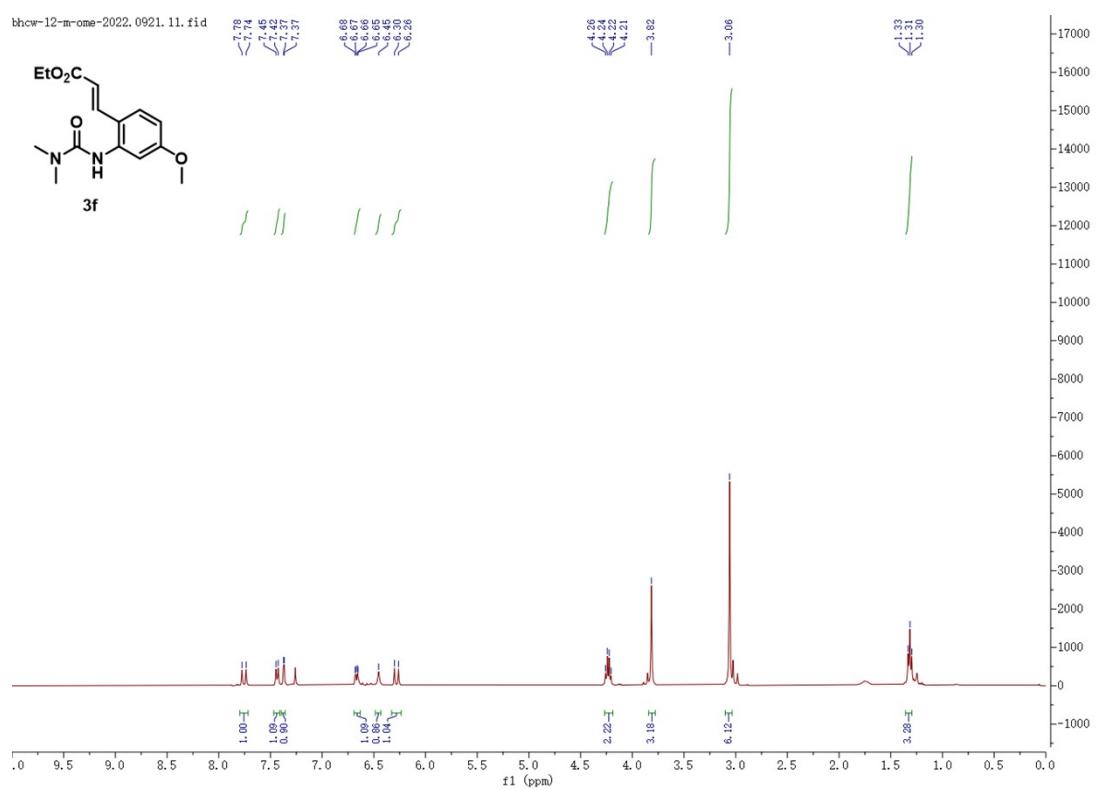
¹H NMR spectrum (400 MHz, CDCl₃) of **3e**



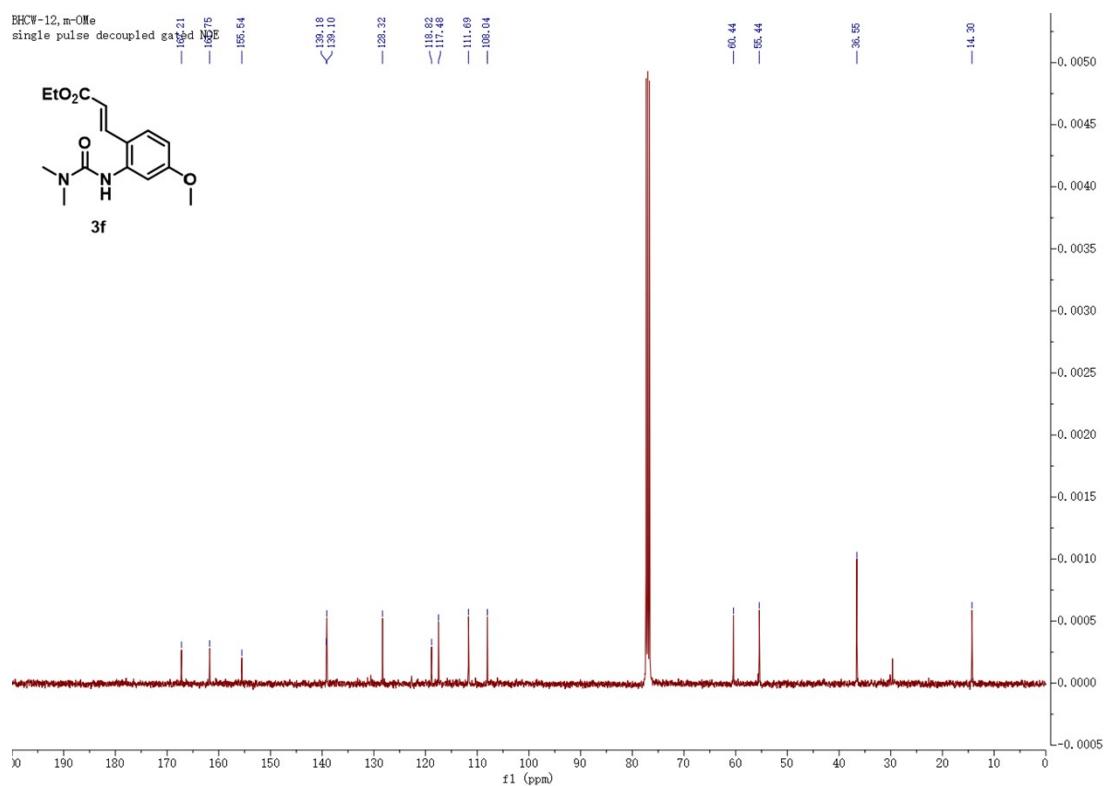
¹³C NMR spectrum (100 MHz, CDCl₃) of 3e



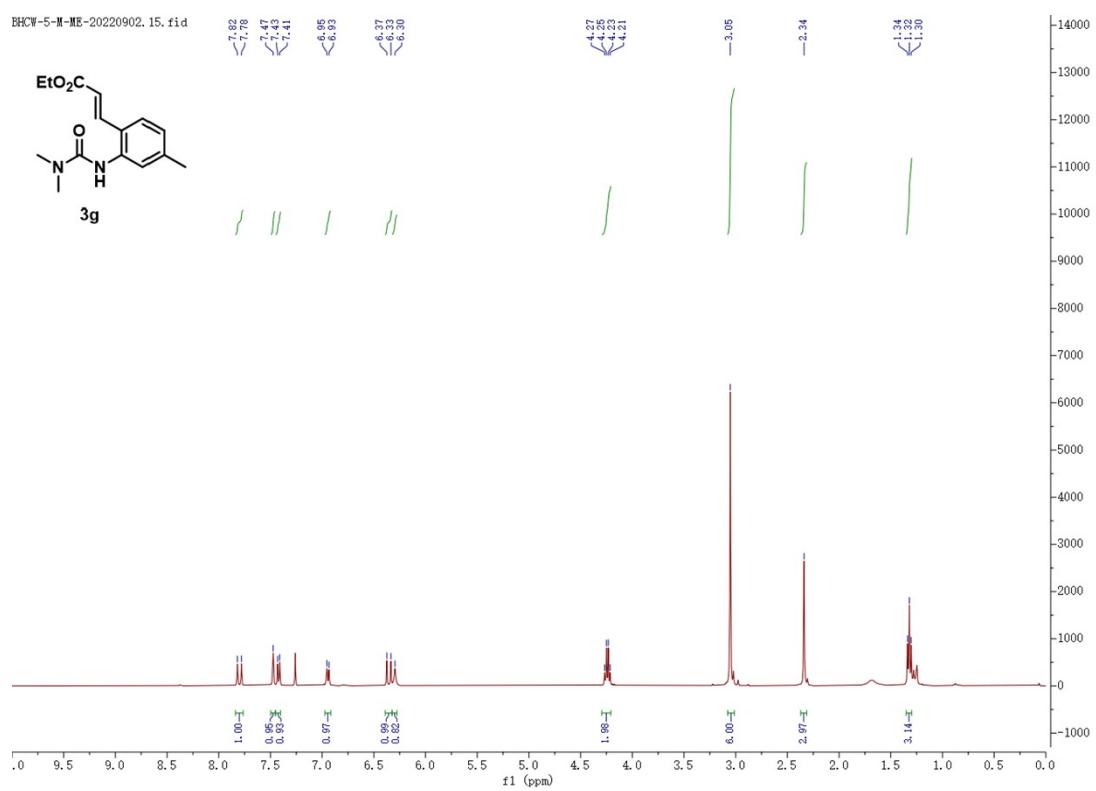
¹H NMR spectrum (400 MHz, CDCl₃) of **3f**



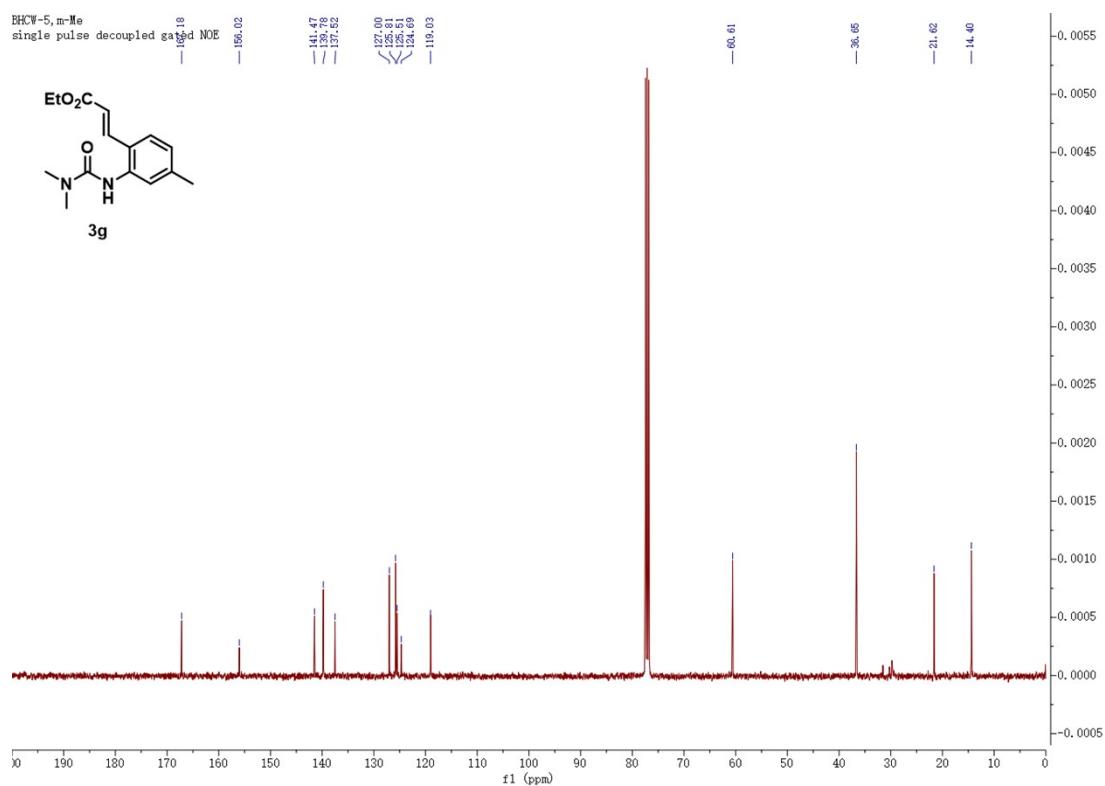
¹³C NMR spectrum (100 MHz, CDCl₃) of **3f**



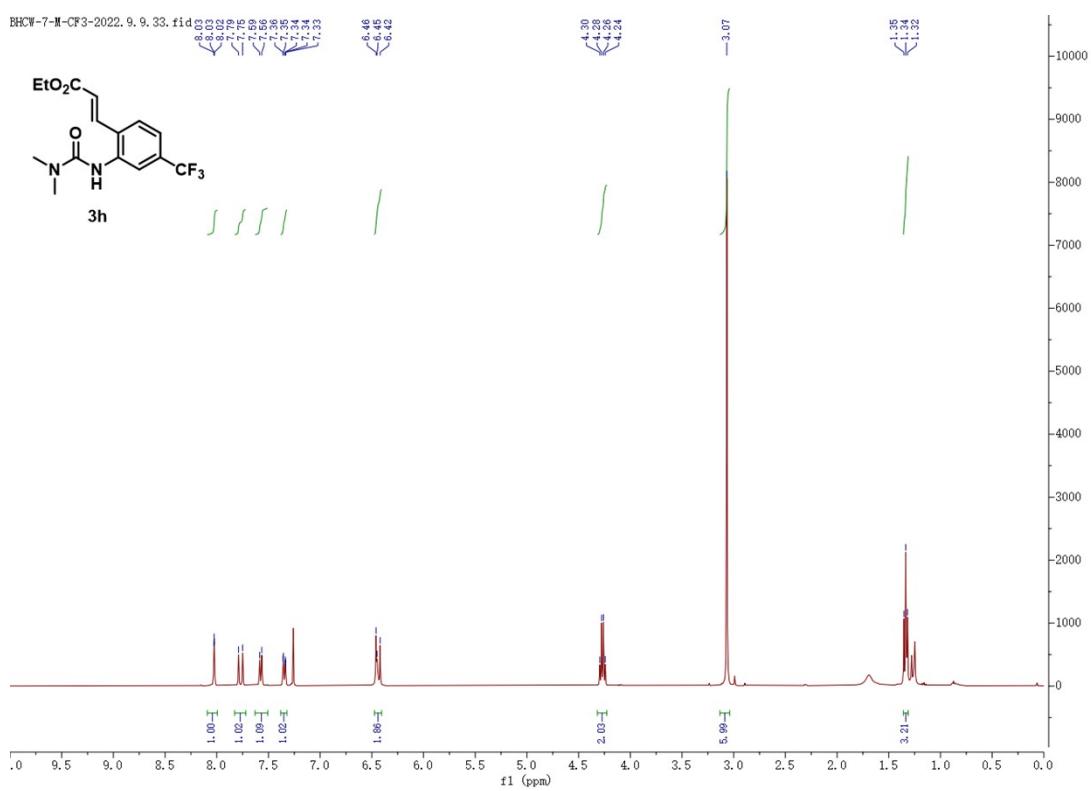
¹H NMR spectrum (400 MHz, CDCl₃) of 3g



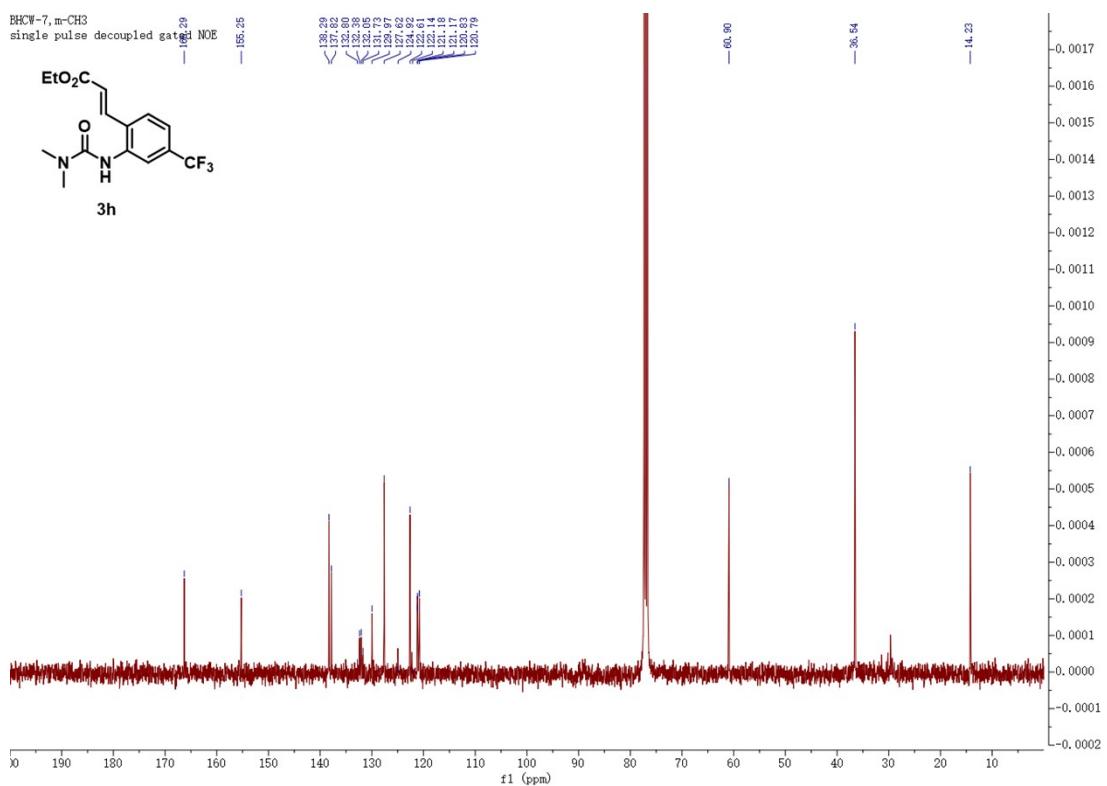
¹³C NMR spectrum (100 MHz, CDCl₃) of 3g



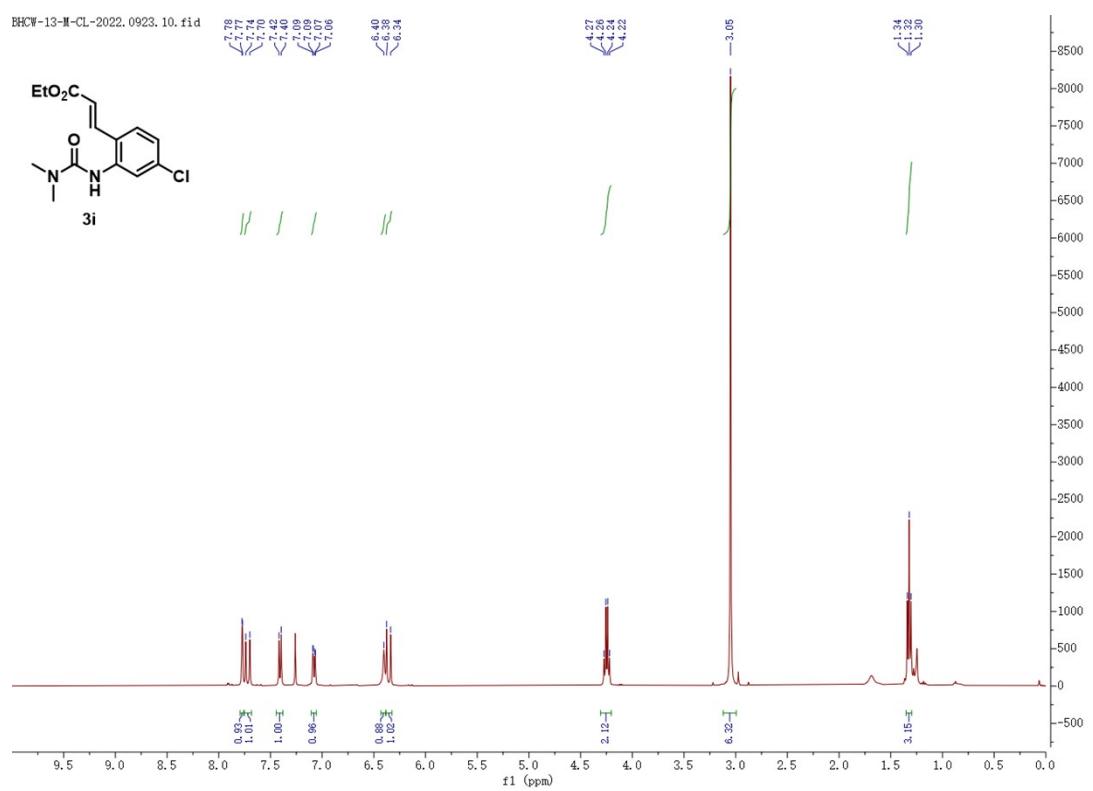
¹H NMR spectrum (400 MHz, CDCl₃) of **3h**



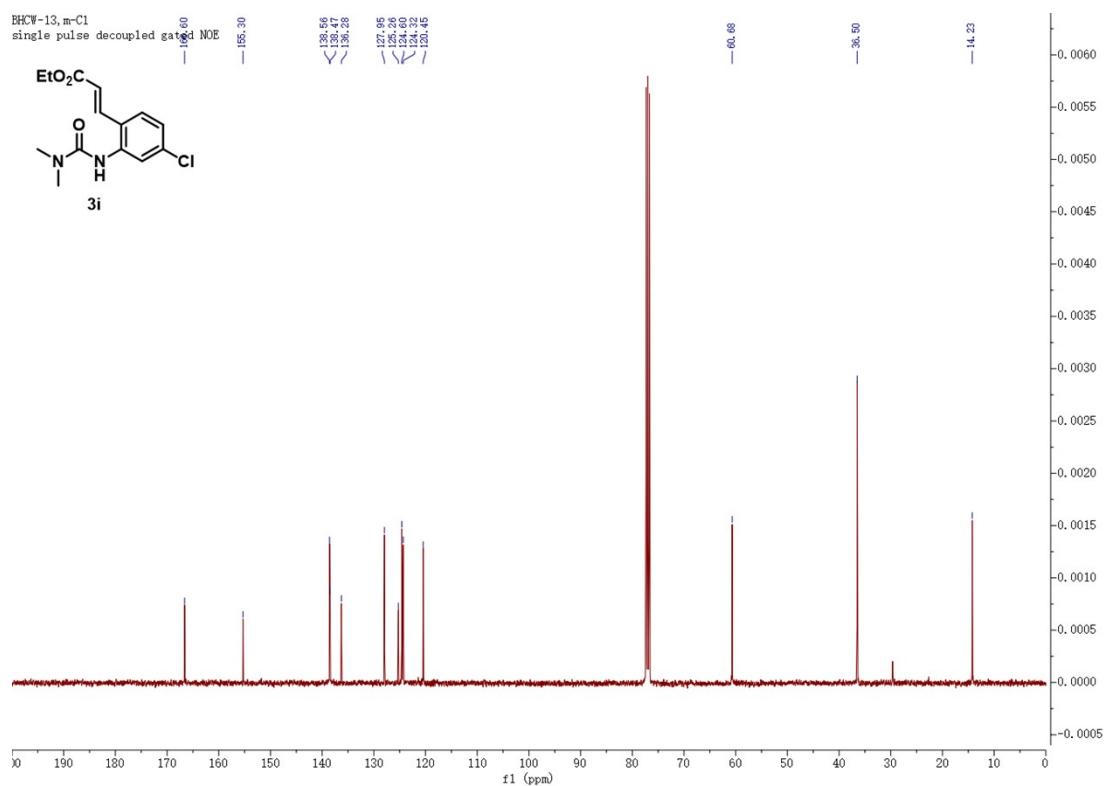
¹³C NMR spectrum (100 MHz, CDCl₃) of **3h**



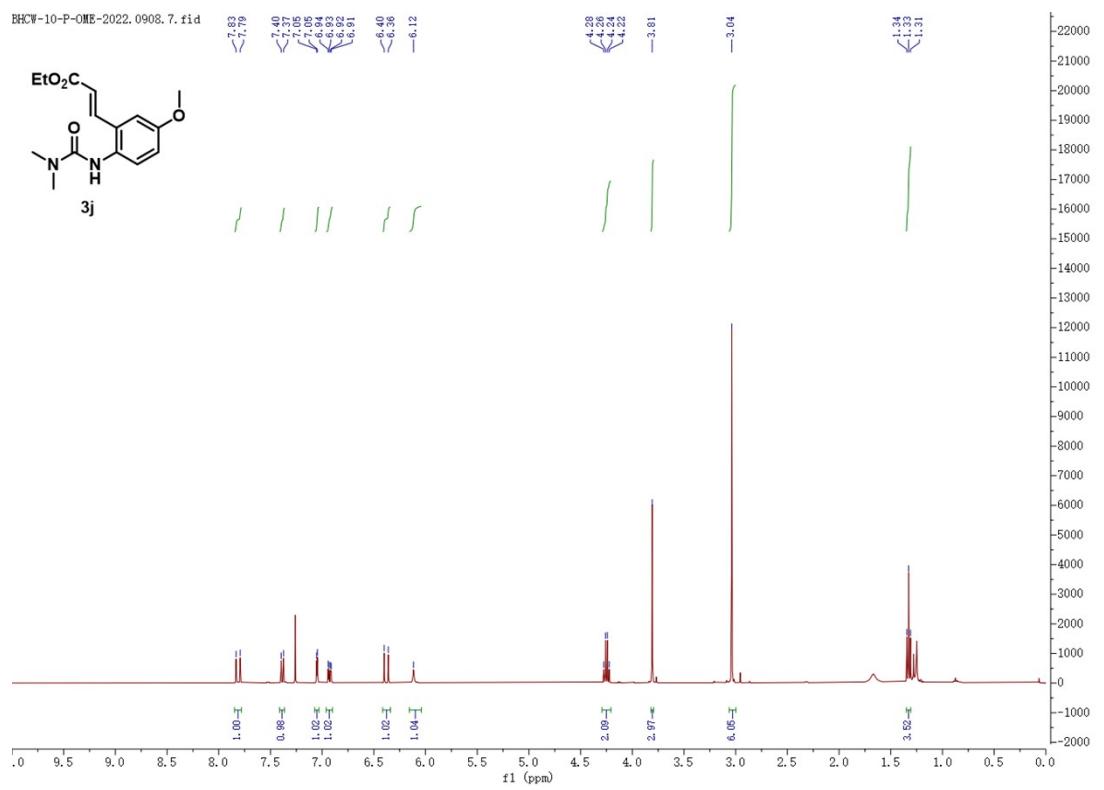
¹H NMR spectrum (400 MHz, CDCl₃) of **3i**



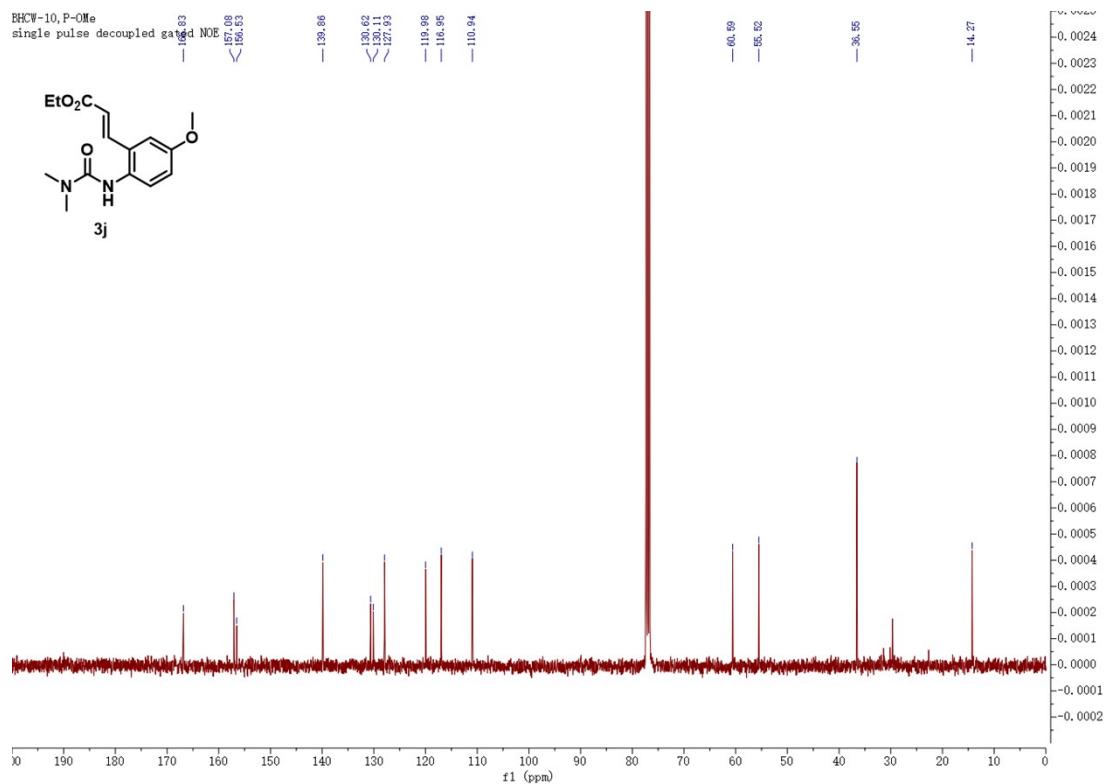
¹³C NMR spectrum (100 MHz, CDCl₃) of **3i**



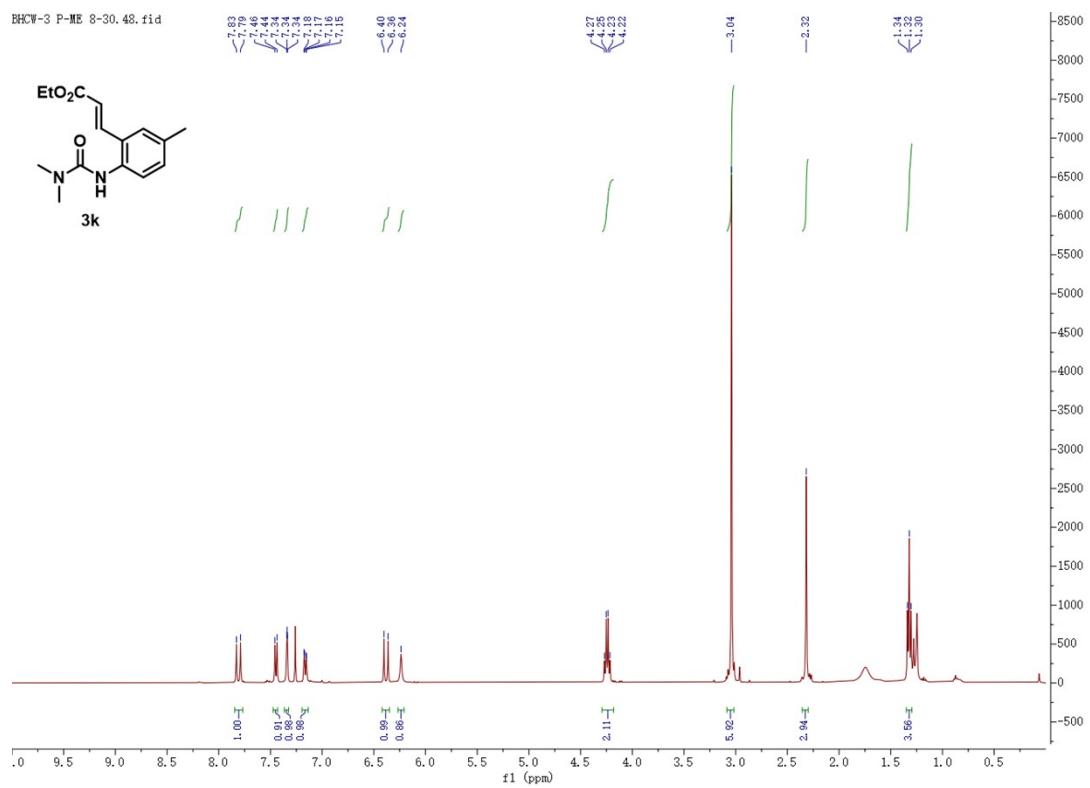
¹H NMR spectrum (400 MHz, CDCl₃) of 3j



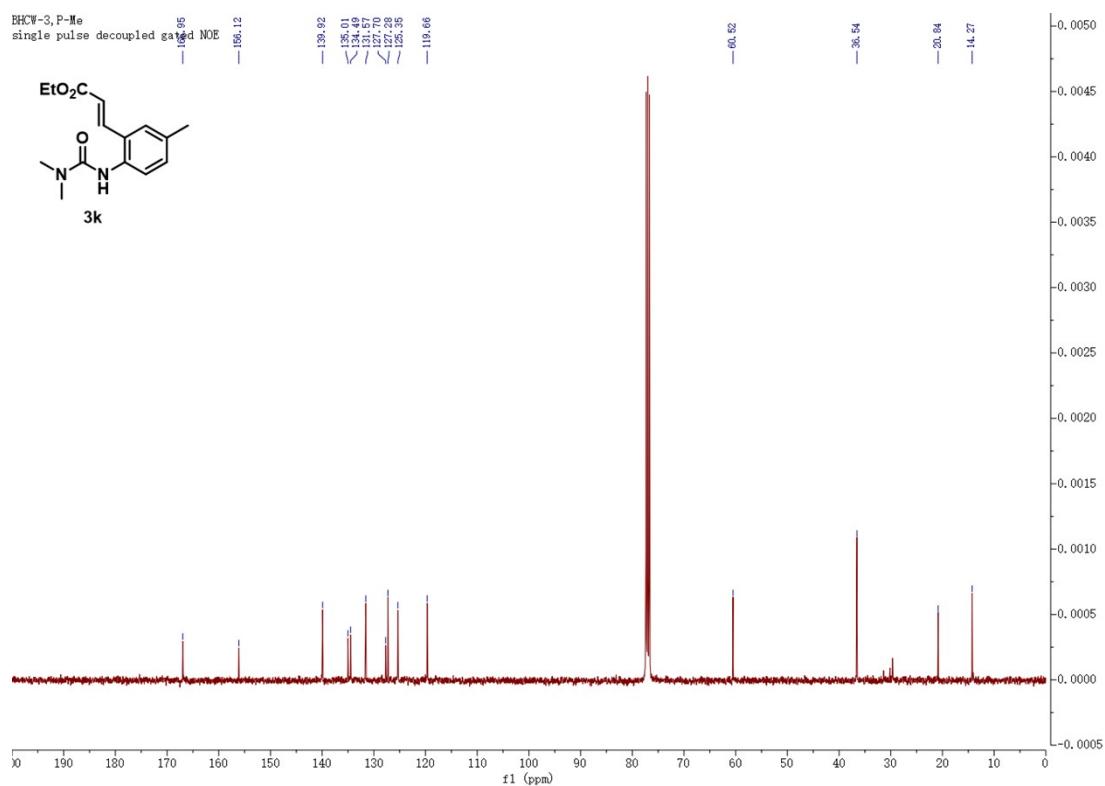
¹³C NMR spectrum (100 MHz, CDCl₃) of 3j



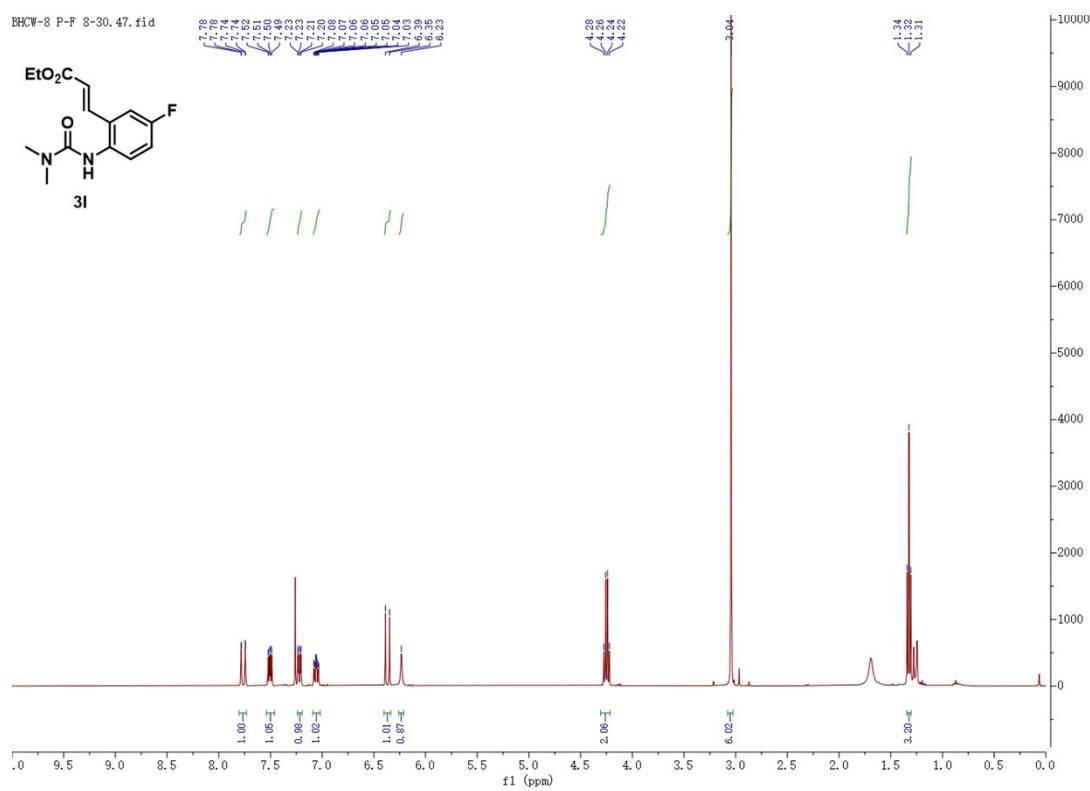
¹H NMR spectrum (400 MHz, CDCl₃) of **3k**



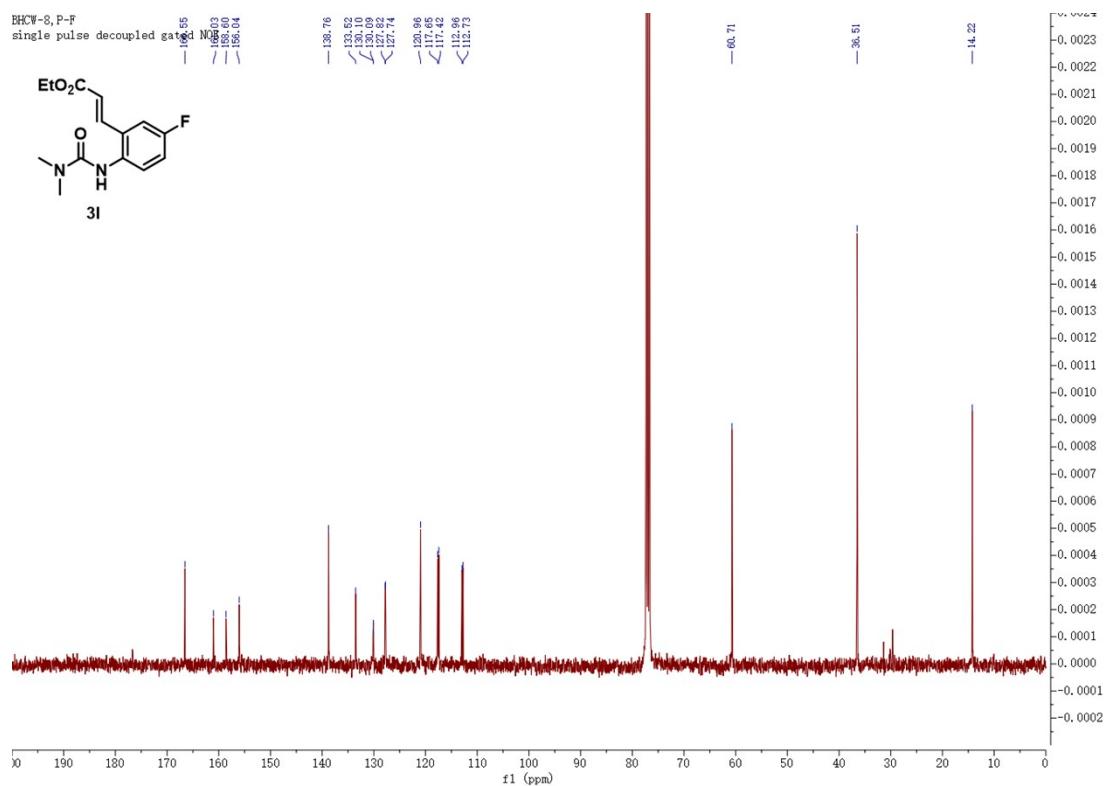
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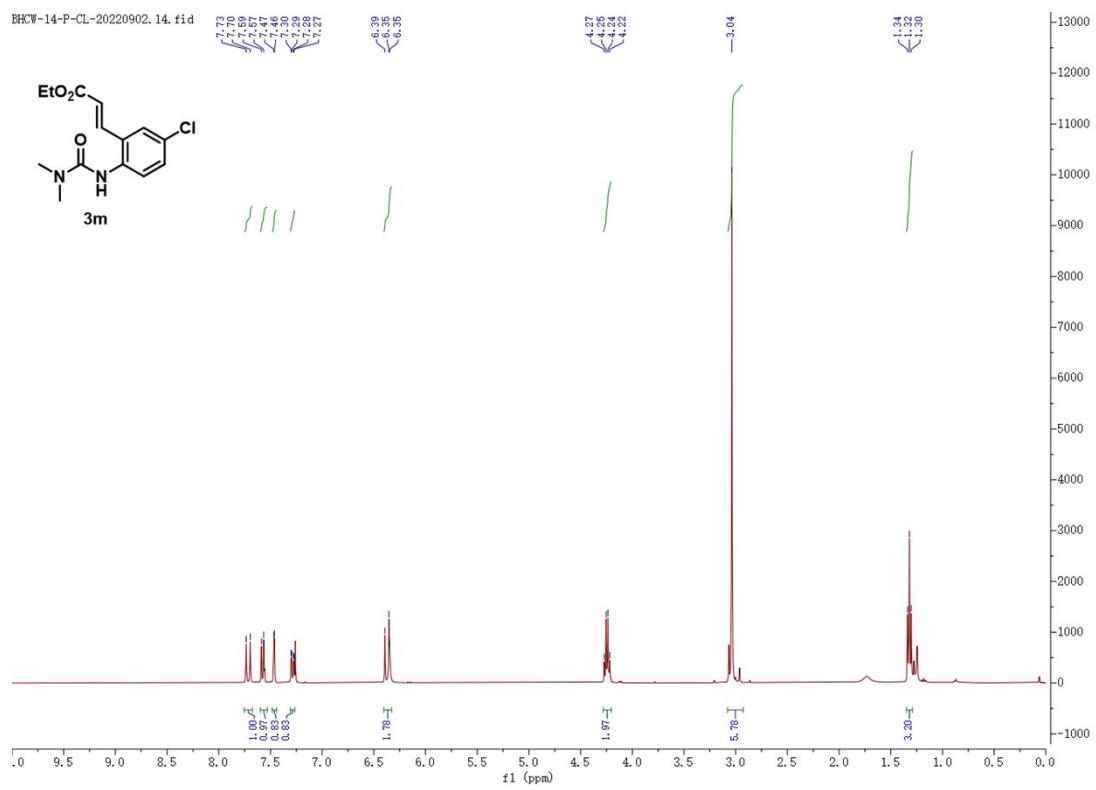
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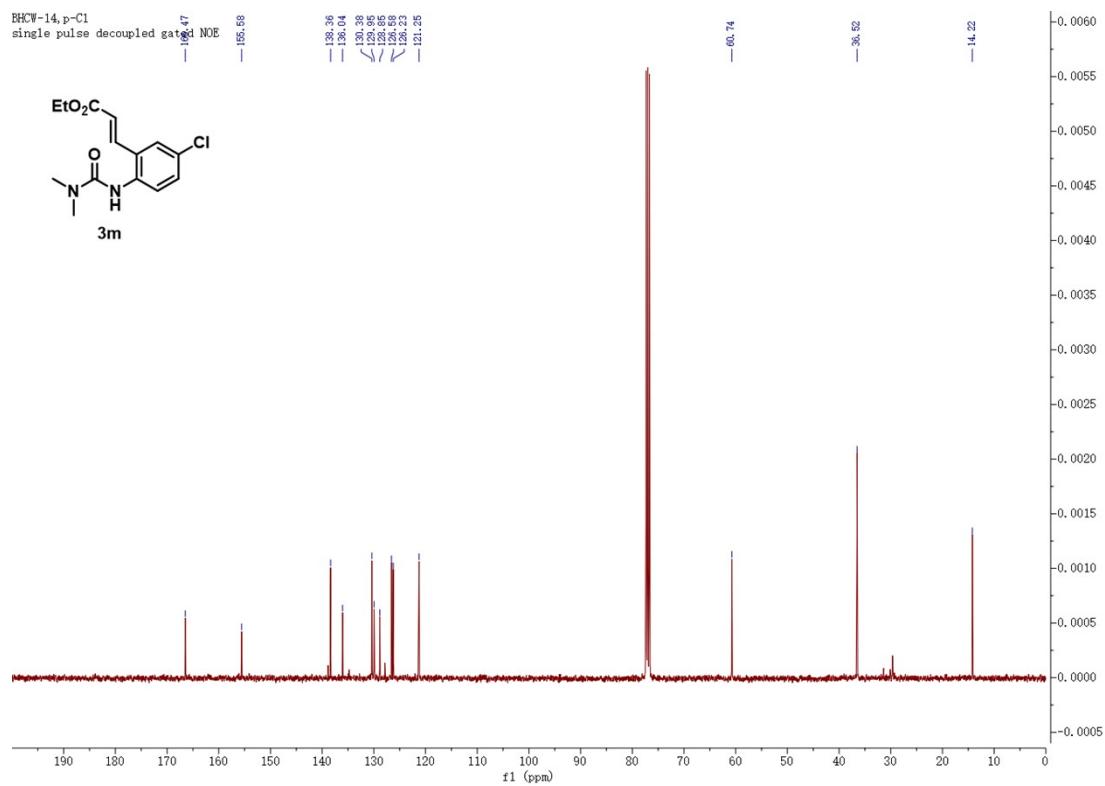
¹³C NMR spectrum (100 MHz, CDCl₃) of **3l**



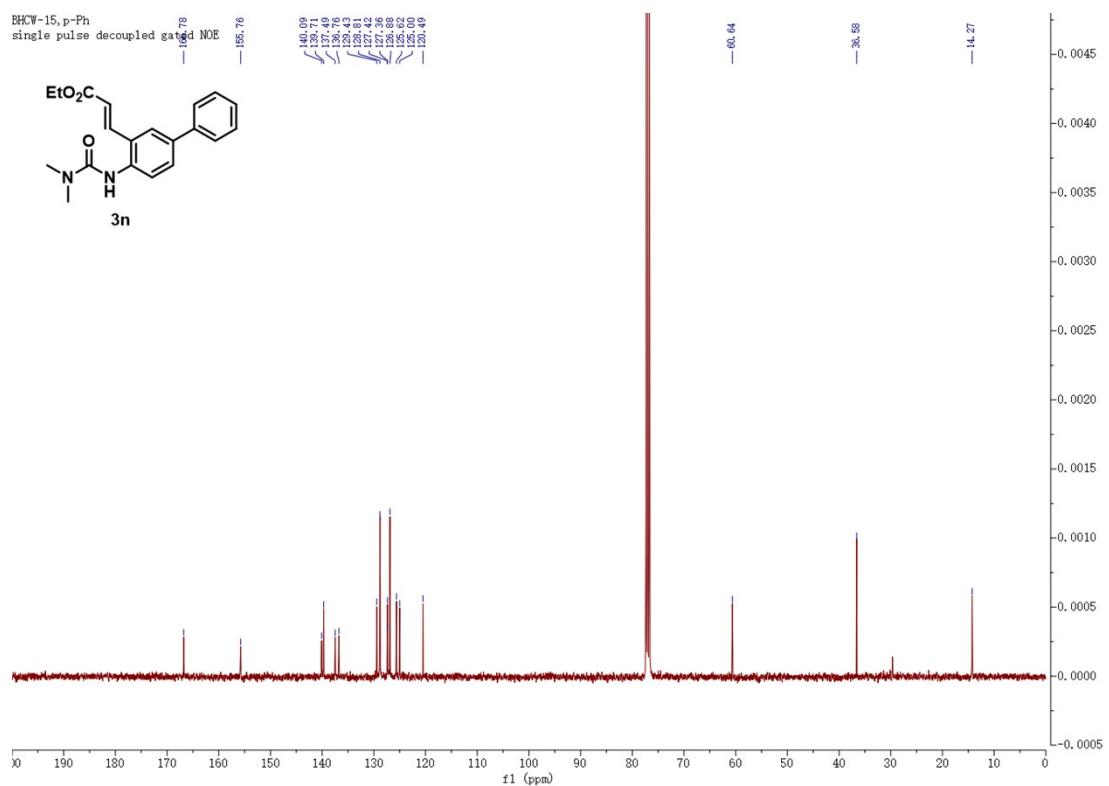
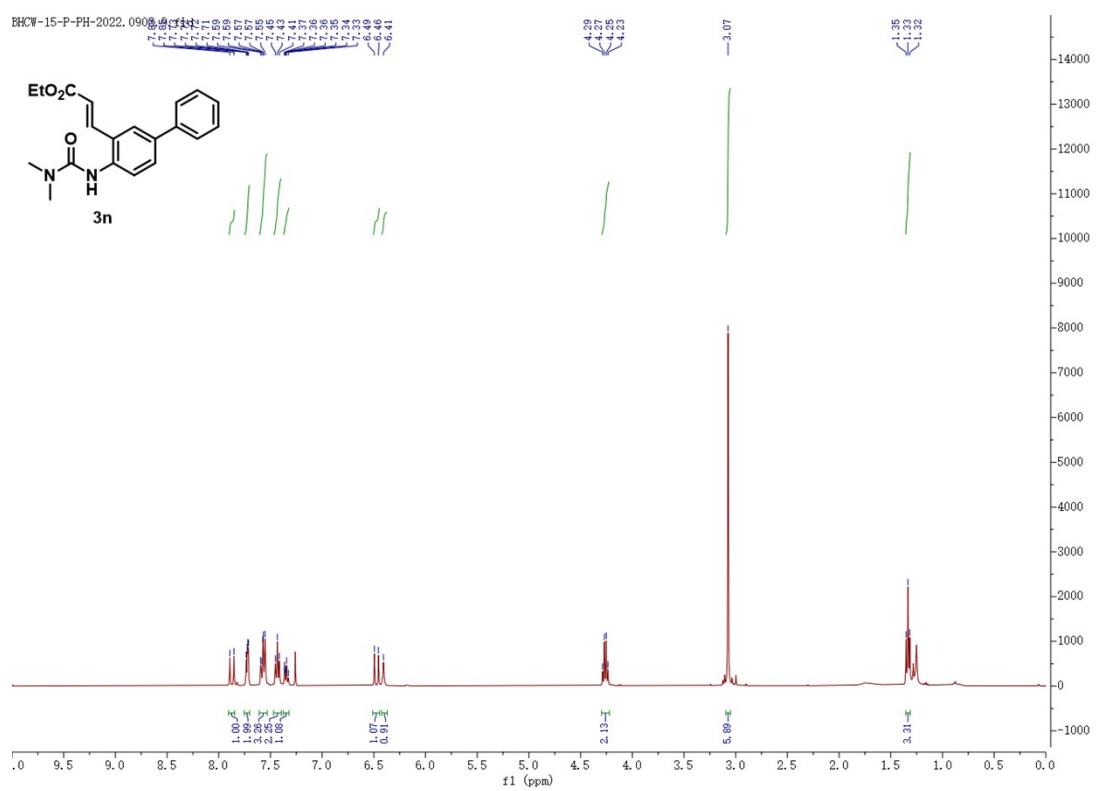
¹H NMR spectrum (400 MHz, CDCl₃) of **3m**



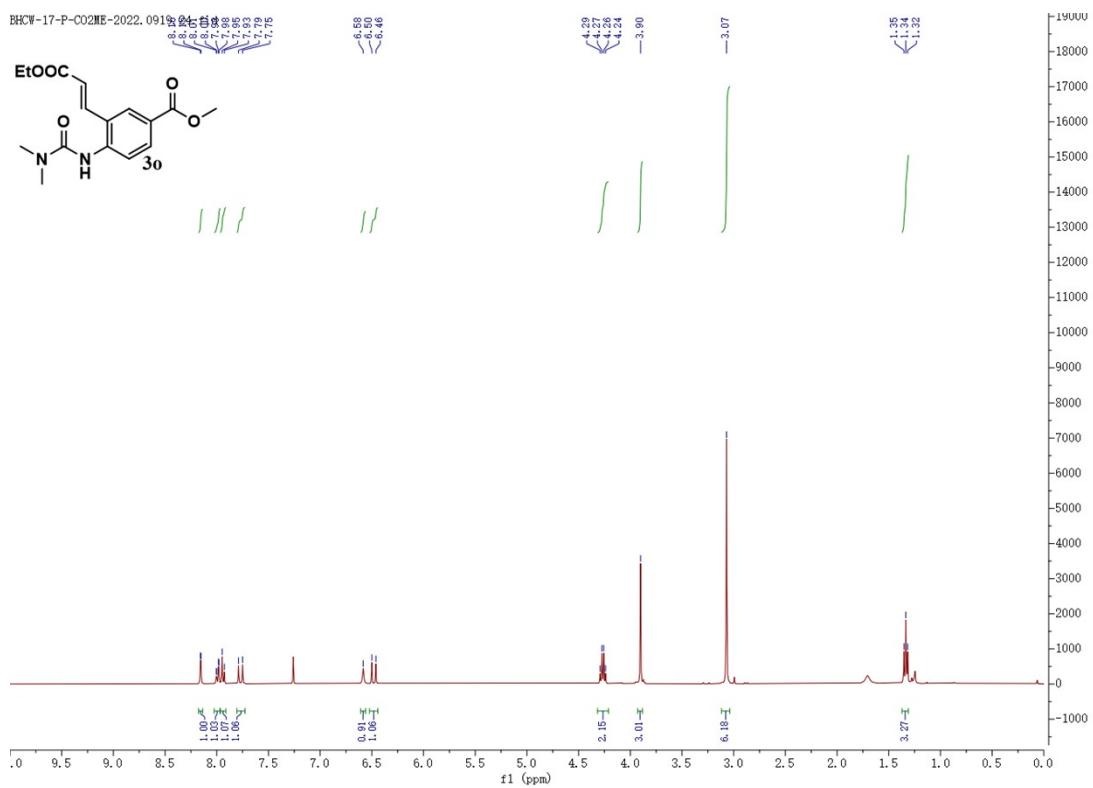
¹³C NMR spectrum (100 MHz, CDCl₃) of **3m**



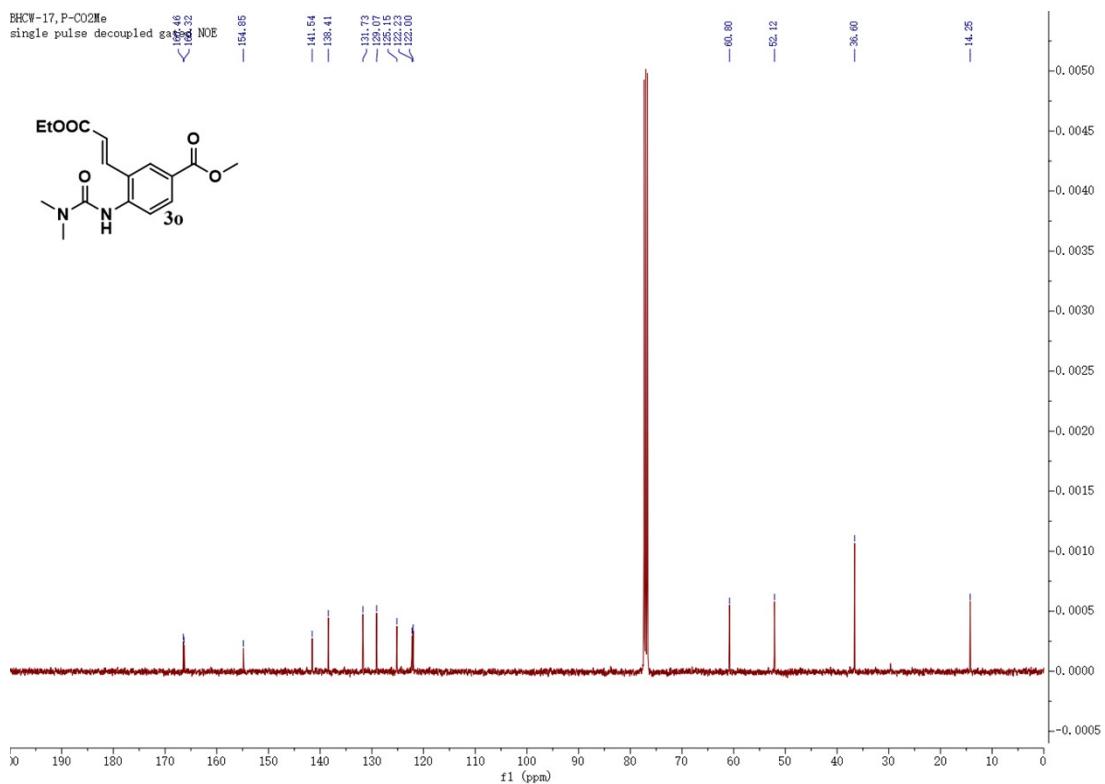
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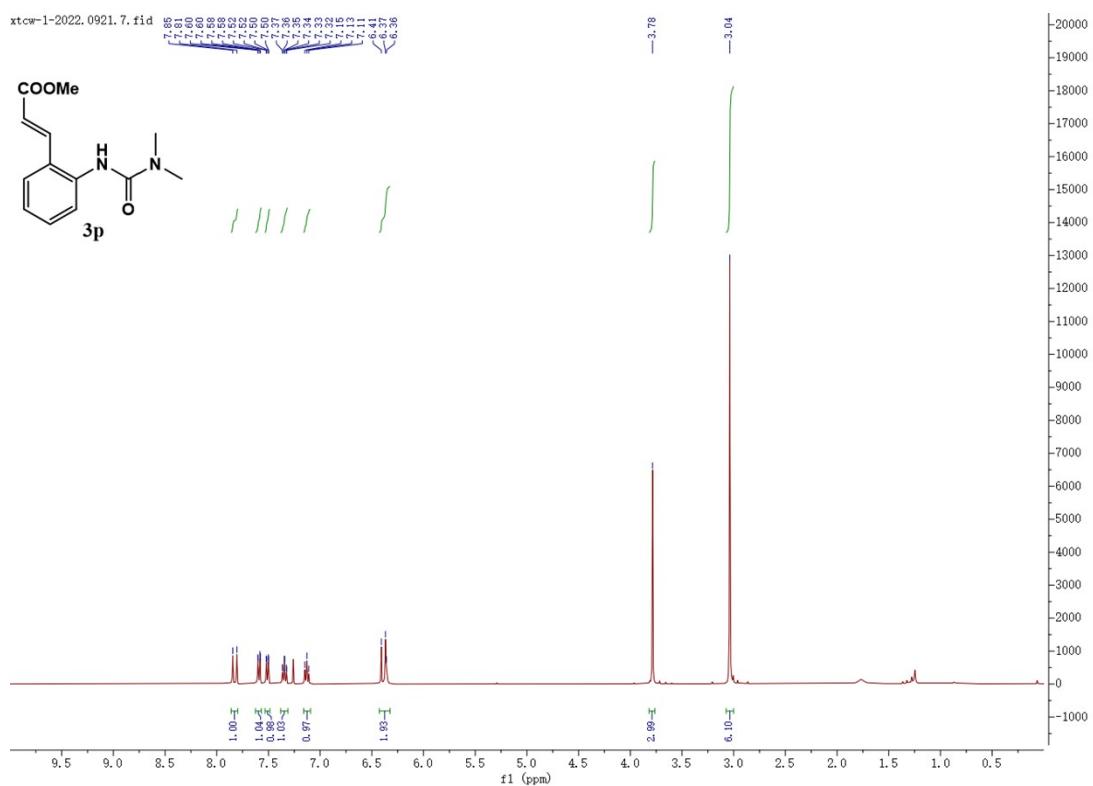
¹H NMR spectrum (400 MHz, CDCl₃) of **3o**



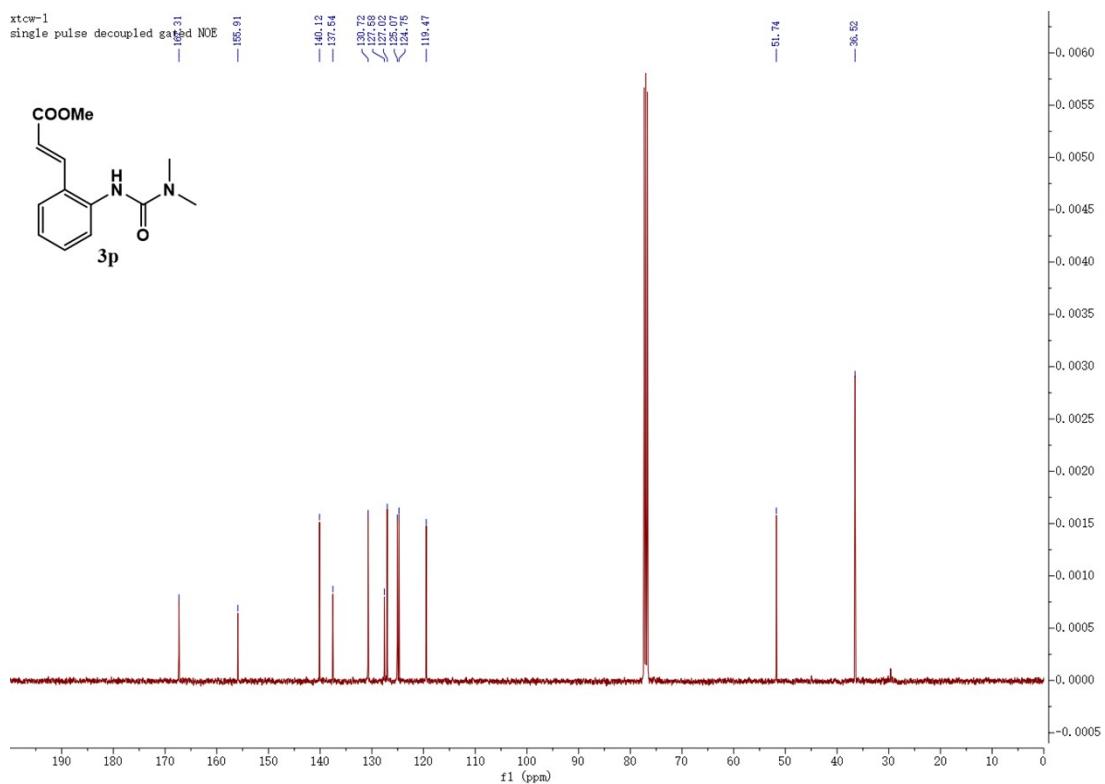
¹³C NMR spectrum (100 MHz, CDCl₃) of **3o**



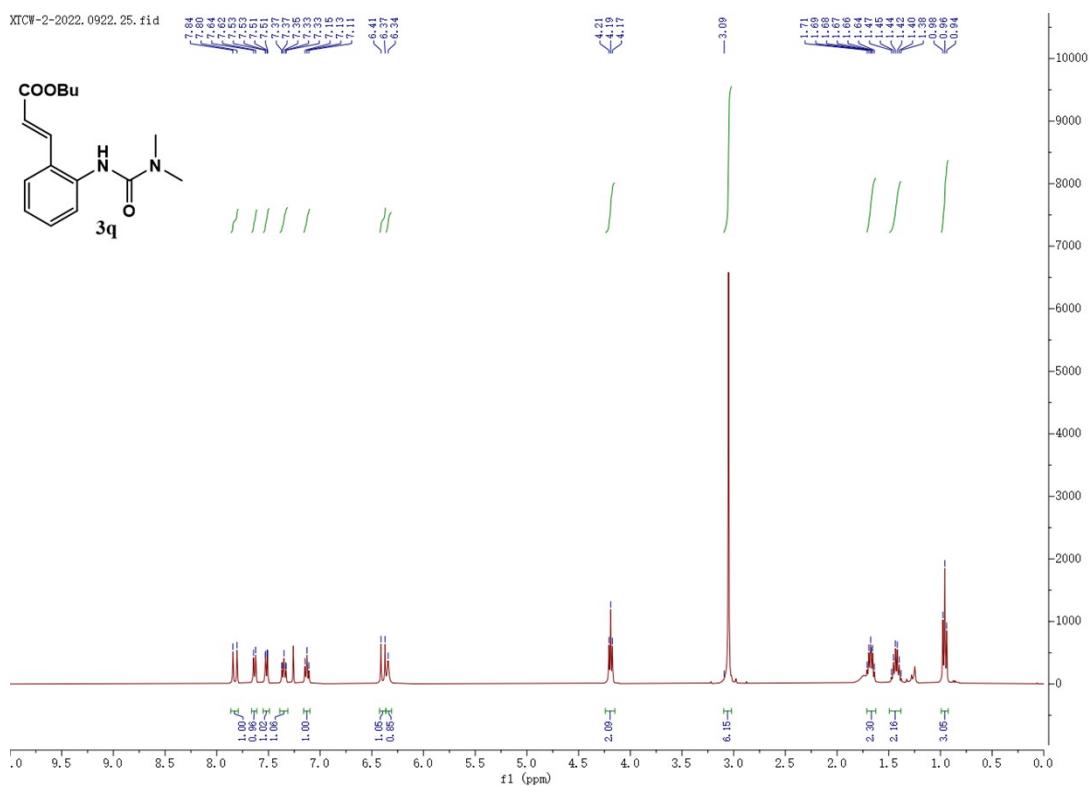
¹H NMR spectrum (400 MHz, CDCl₃) of 3p



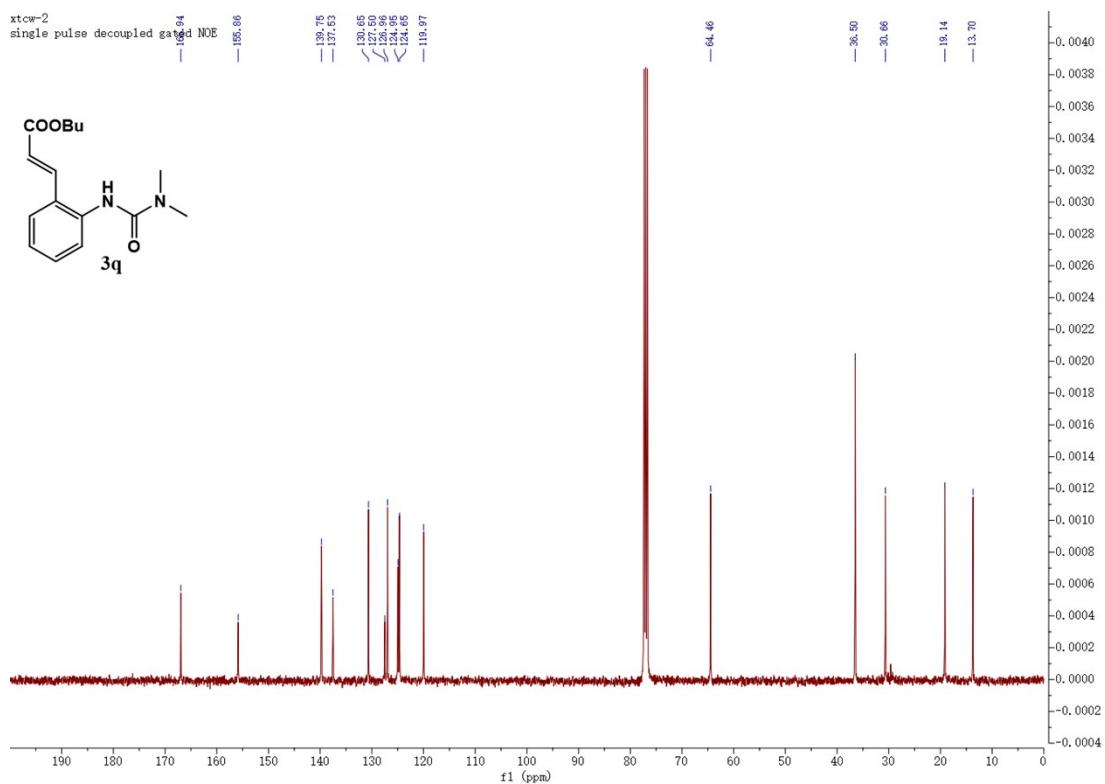
¹³C NMR spectrum (100 MHz, CDCl₃) of 3p



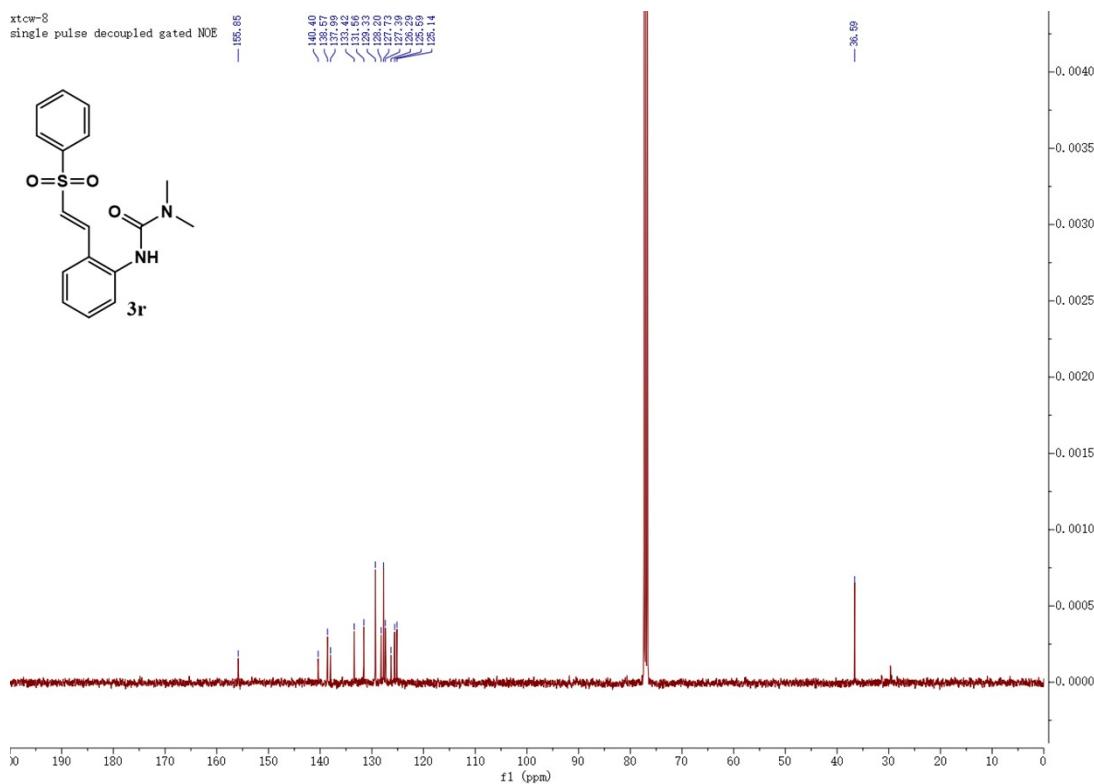
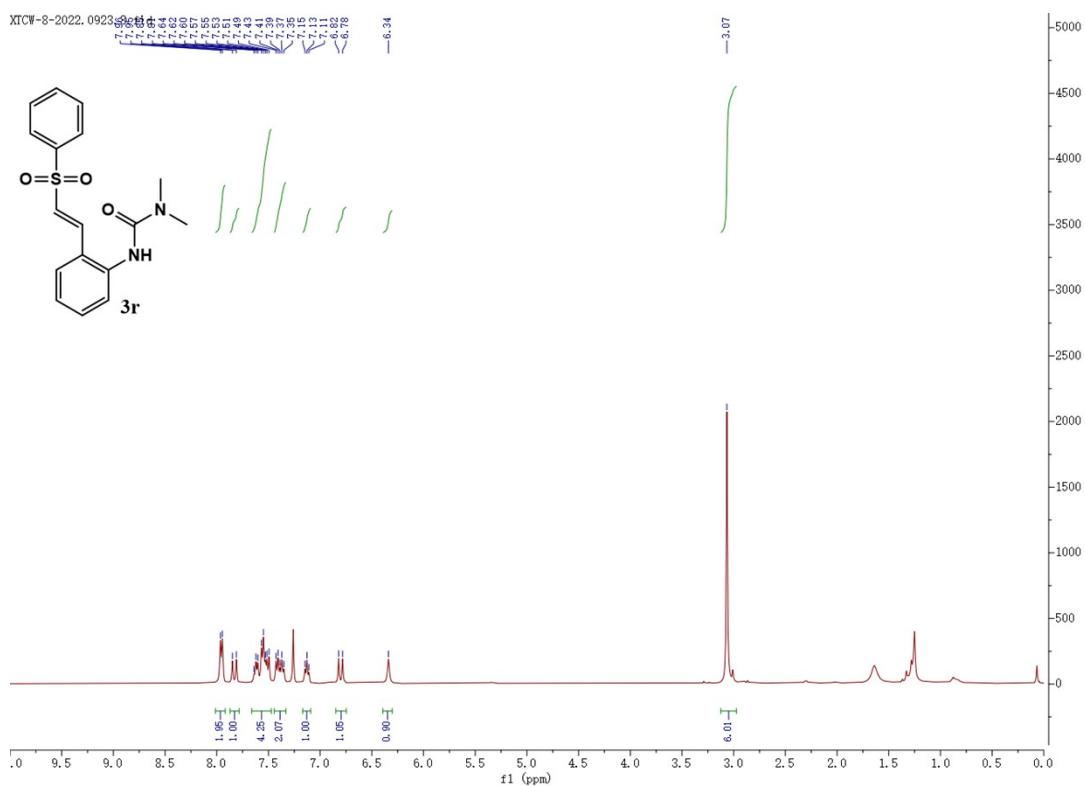
¹H NMR spectrum (400 MHz, CDCl₃) of 3q



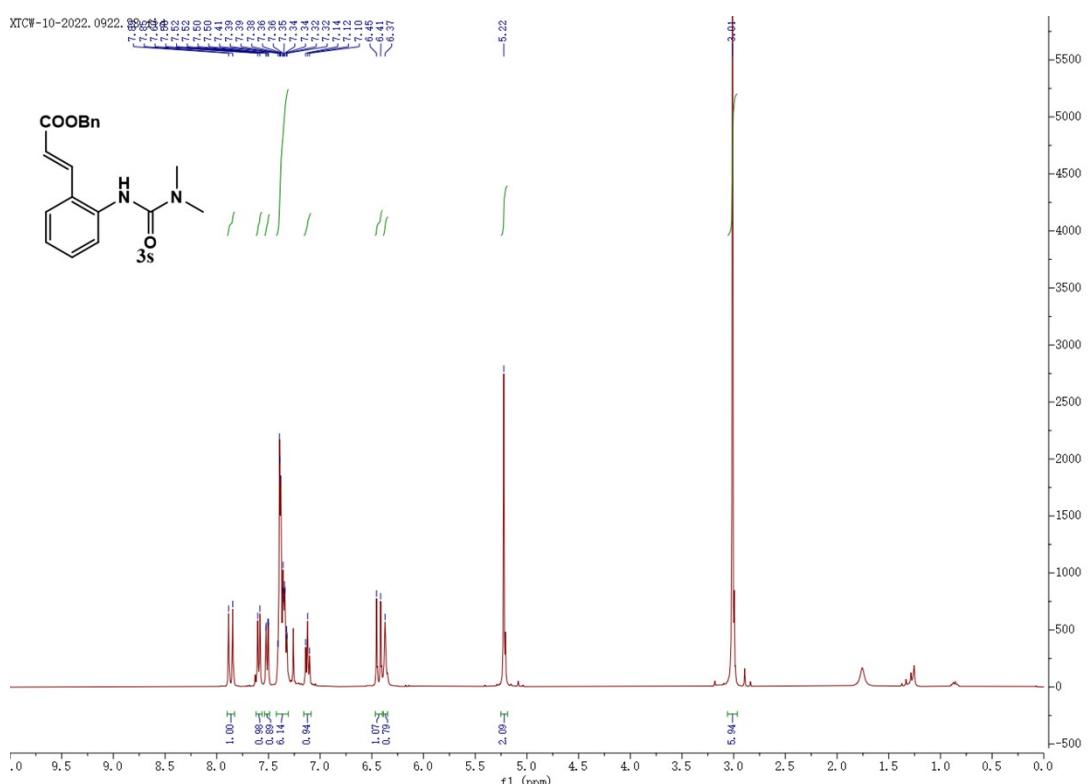
¹³C NMR spectrum (100 MHz, CDCl₃) of 3q



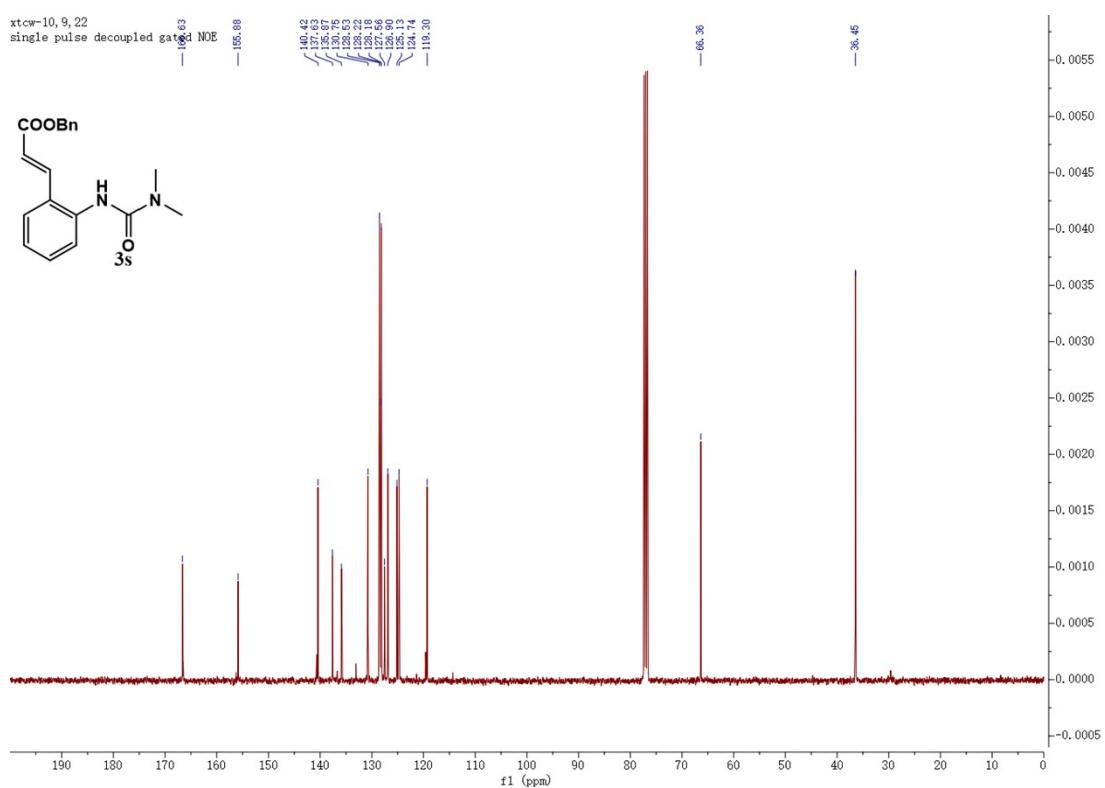
¹H NMR spectrum (400 MHz, CDCl₃) of **3r**



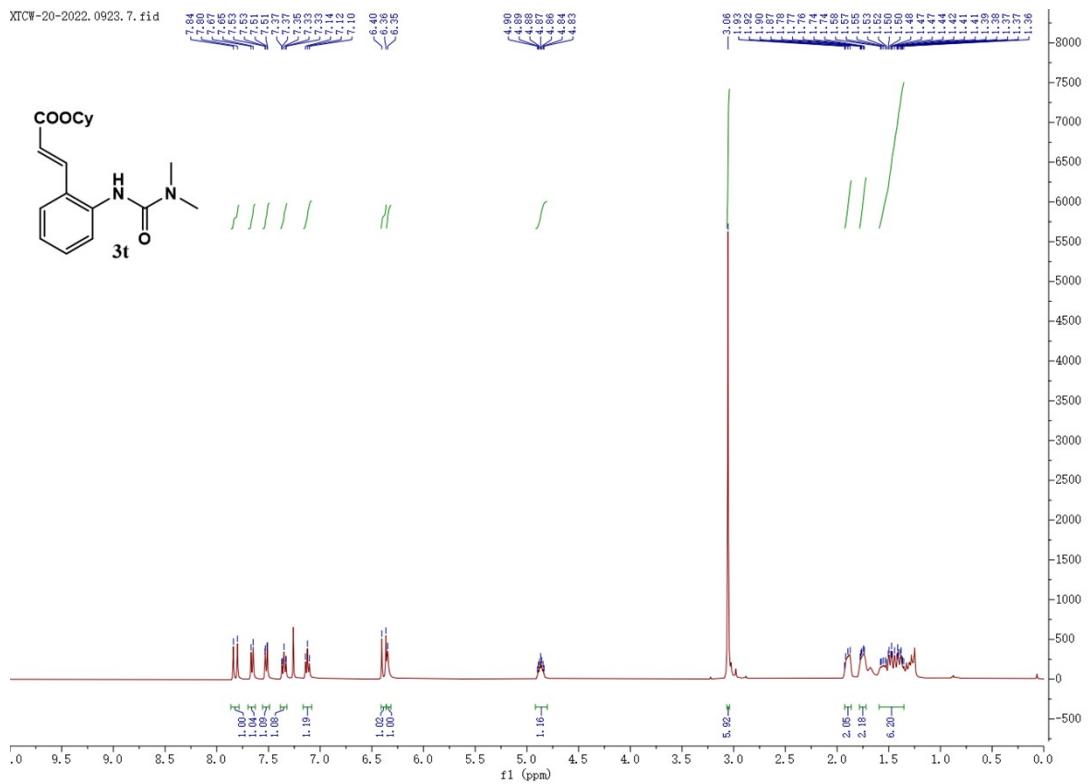
¹H NMR spectrum (400 MHz, CDCl₃) of **3s**



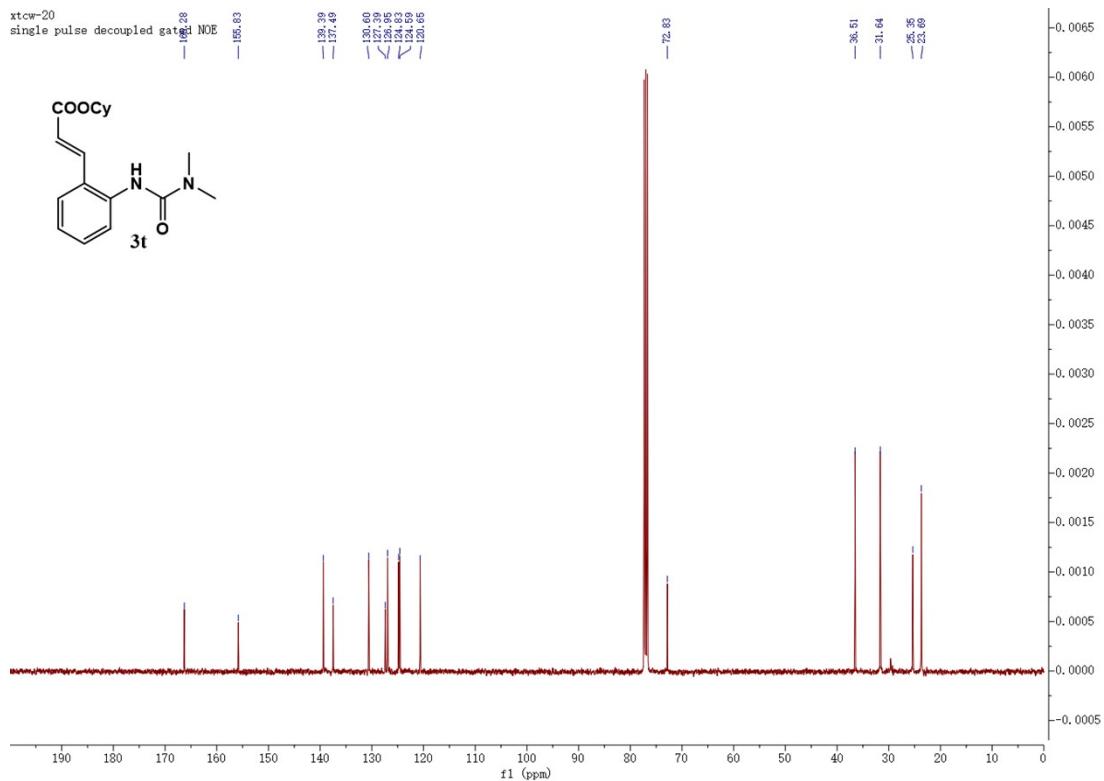
¹³C NMR spectrum (100 MHz, CDCl₃) of 3s



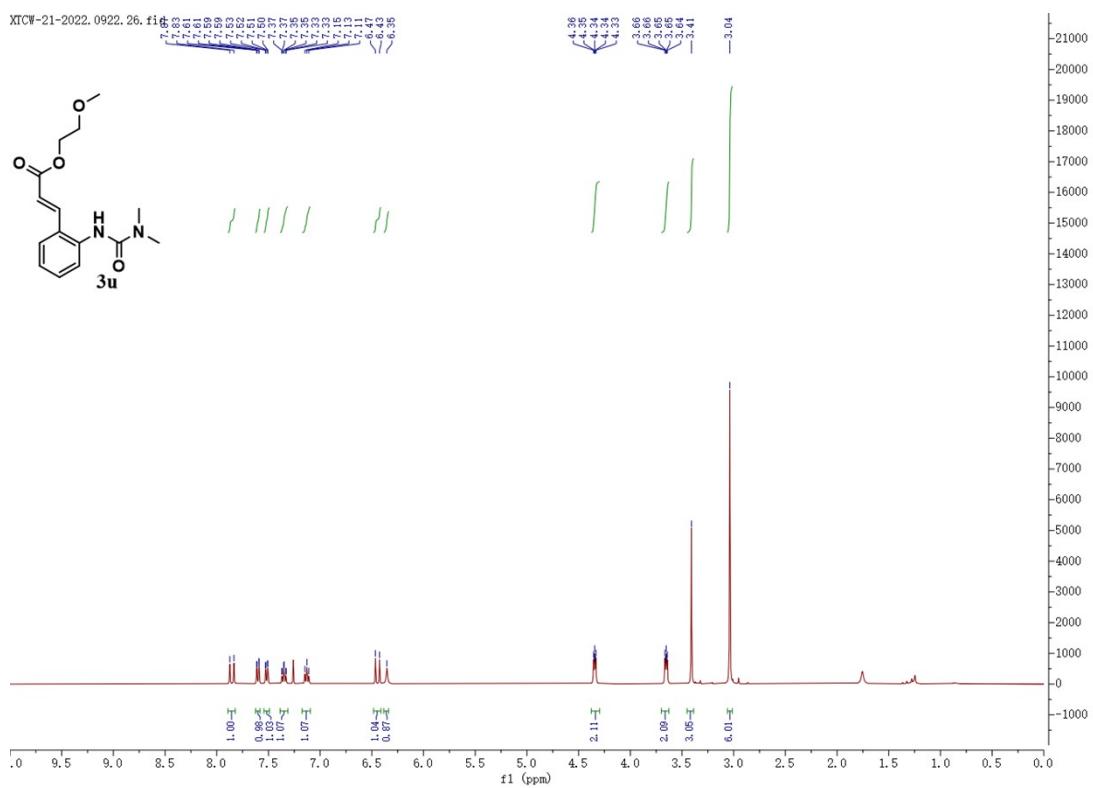
¹H NMR spectrum (400 MHz, CDCl₃) of **3t**



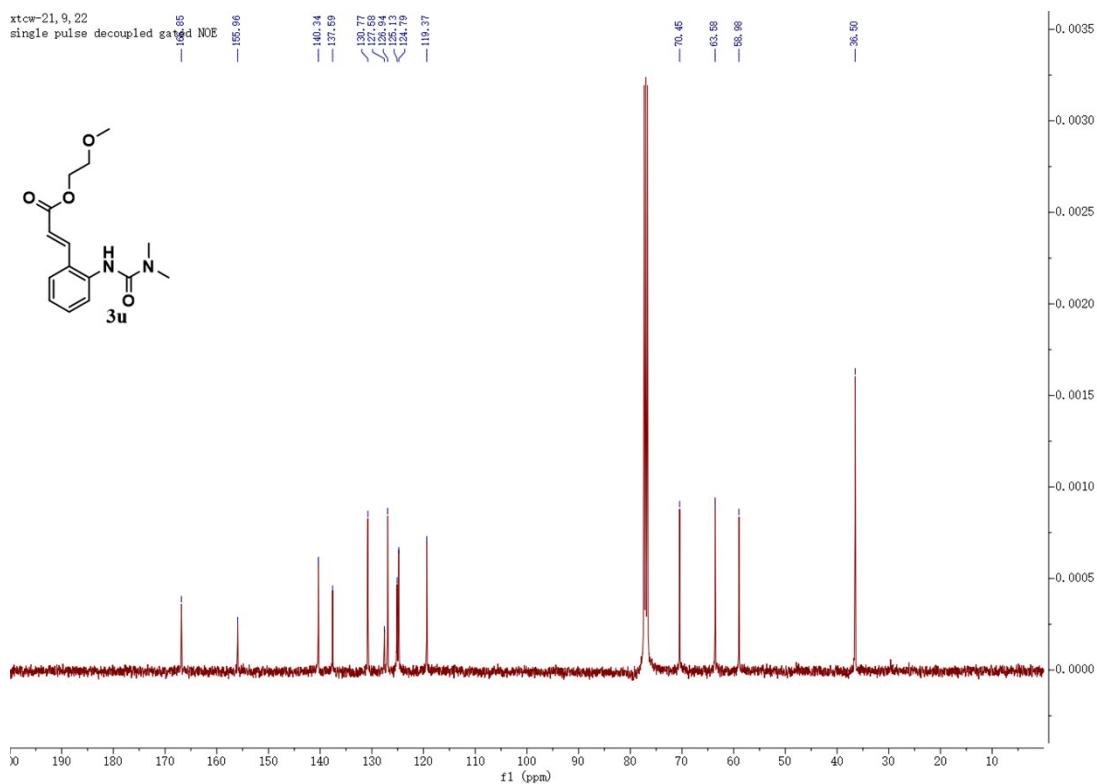
¹³C NMR spectrum (100 MHz, CDCl₃) of **3t**



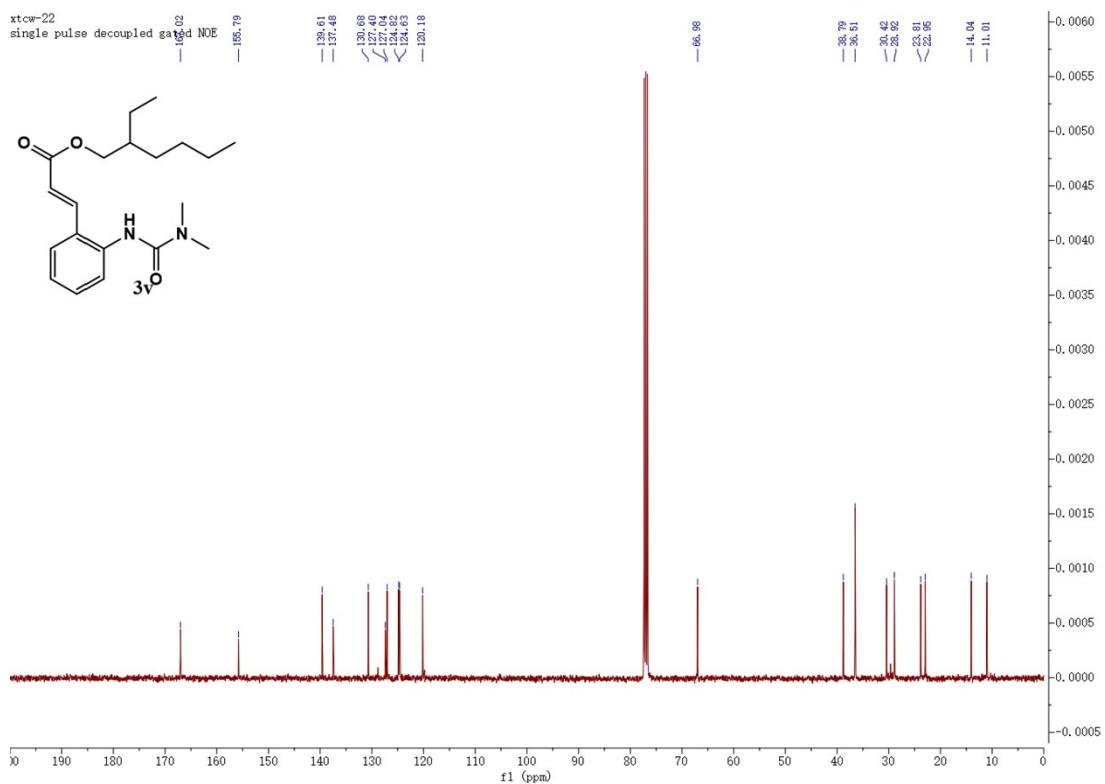
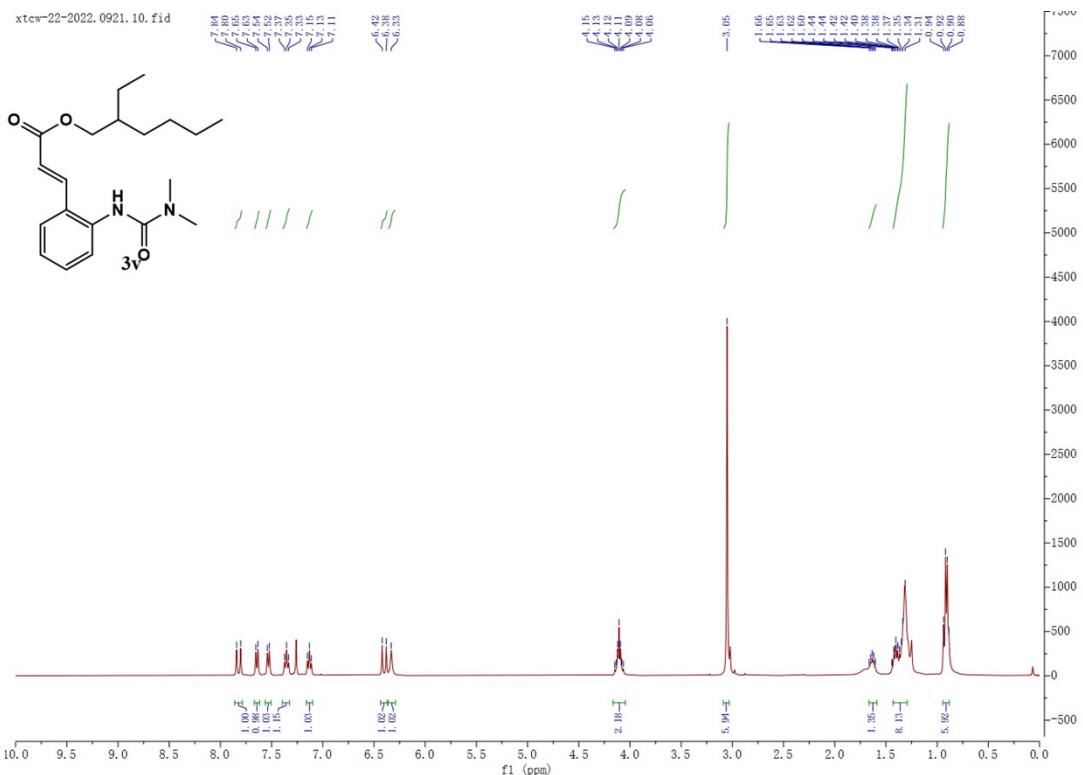
¹H NMR spectrum (400 MHz, CDCl₃) of **3u**



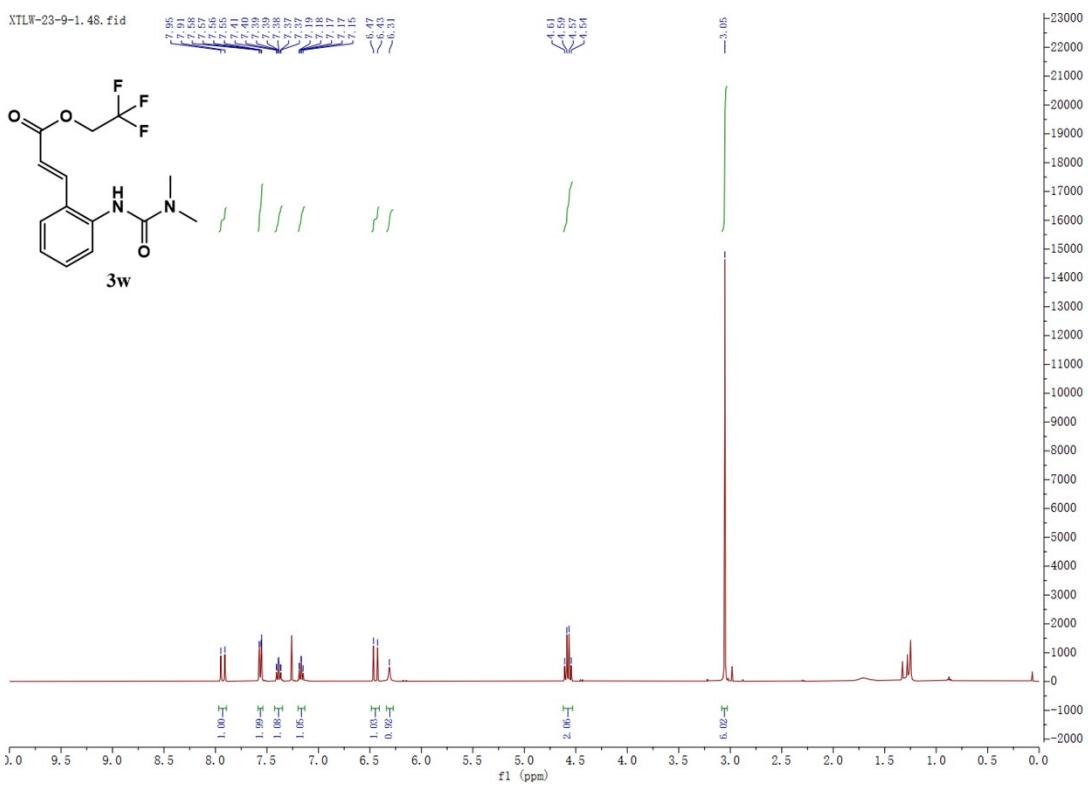
¹³C NMR spectrum (100 MHz, CDCl₃) of **3u**



¹H NMR spectrum (400 MHz, CDCl₃) of 3v



¹H NMR spectrum (400 MHz, CDCl₃) of 3w



¹³C NMR spectrum (100 MHz, CDCl₃) of **3w**

