N-Bromoacetamide-mediated Domino Cyclization and Elimination of Homoallylic Trichloroacetimidates: A Novel Approach toward the Synthesis of 1-Bromo-2-Amino-3-Butene Derivatives

Supporting Information

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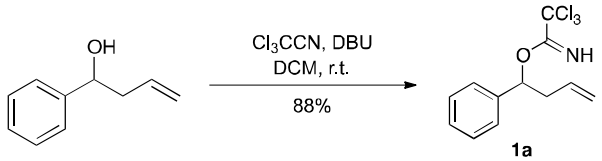
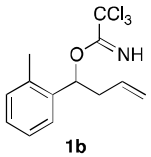
Typical Procedures for the preparation of 1:
Preparation of 1a:



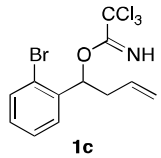
1a

To a solution of 1-phenylbut-3-en-1-ol (0.444 g, 3.0 mmol, 1.0 equiv) in dry dichloromethane (6.0 mL) was added Cl_3CCN (0.45 mL, 9.0 mmol, 3.0 equiv) followed by DBU (45 μL, 0.30 mmol, 10 mol %). The mixture was stirred at room temperature overnight before being concentrated in vacuo and purified by flash chromatography on neutral Al_2O_3 (20/1 hexane/ethyl acetate) to provide **1a** (0.768 g, 88%) (R_f 0.8, PE/EA = 10:1) as pale-yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.29 (s, 1 H), 7.57-7.23 (m, 5 H), 5.99-5.88 (dd, J = 8.0, 5.6 Hz, 1 H), 5.88-5.72 (m, 1 H), 5.22-5.04 (m, 2 H), 2.91-2.75 (m, 1 H), 2.75-2.56 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.6, 139.7, 133.1, 128.4, 128.0, 126.2, 118.2, 91.7, 80.1, 41.1; HRMS (ESI): calcd for $C_{12}H_{13}NOCl_3$ [M^++H] 292.0063, found 292.0093.



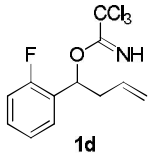
1b

1b (0.833 g, 91%) (R_f 0.8, PE/EA = 10:1) was prepared following the typical procedure in 3.0 mmol scale as pale-yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.25 (s, 1 H), 7.53-7.42 (m, 1 H), 7.30-7.10 (m, 3 H), 6.06 (dd, J = 8.4, 5.2 Hz, 1 H), 5.94-5.75 (m, 1 H), 5.12 (m, 2 H), 2.86-2.62 (m, 1 H), 2.62-2.52 (m, 1 H), 2.45 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.4, 138.2, 135.0, 133.3, 130.2, 127.8, 126.2, 125.5, 118.1, 91.7, 77.1, 40.3, 19.2; HRMS (ESI): calcd for $C_{13}H_{15}NOCl_3$ [M^++H] 306.0219, found 306.0264.



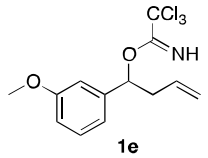
1c

1c (0.952 g, 86%) (R_f 0.8, PE/EA = 10:1) was prepared following the typical procedure in 3.0 mmol scale as pale-yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.35 (s, 1 H), 7.56 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.51 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.32 (dt, *J* = 7.6, 1.0 Hz, 1 H), 7.16 (dt, *J* = 7.6, 1.6 Hz, 1 H), 6.22 (dd, *J* = 8.0, 4.8 Hz, 1 H), 5.96-5.83 (m, 1 H), 5.21-5.06 (m, 2 H), 2.79-2.60 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.2, 139.3, 132.8, 129.2, 127.7, 126.9, 121.9, 118.4, 91.5, 79.0, 39.6; HRMS (ESI): calcd for $C_{12}H_{12}NOCl_3Br$ $[M^+ + H]$ 369.9168, found 369.9197.



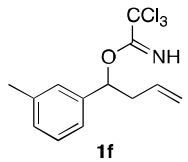
1d

1d (0.751 g, 81%) (R_f 0.8, PE/EA = 10:1) was prepared following the typical procedure in 3.0 mmol scale as pale-yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.34 (s, 1 H), 7.48 (dt, *J* = 7.6, 1.6 Hz, 1 H), 7.33-7.24 (m, 1 H), 7.15 (dt, *J* = 7.2, 1.1 Hz, 1 H), 7.10-7.01 (m, 1 H), 6.23 (dd, *J* = 7.6, 5.6 Hz, 1 H), 5.91-5.76 (m, 1 H), 5.19-5.04 (m, 2 H), 2.87-2.63 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.3, 160.9, 158.4, 132.6, 129.5, 129.4, 127.22, 127.18, 127.05, 126.9, 124.19, 124.16, 118.5, 115.5, 115.3, 91.5, 74.04, 74.02, 39.8; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -117.04; HRMS (ESI): calcd for $C_{12}H_{12}NOCl_3F$ $[M^+ + H]$ 309.9969, found 310.0009.



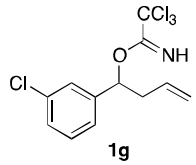
1e

1e (0.799 g, 83%) (R_f 0.8, PE/EA = 5:1) was prepared following the typical procedure in 3.0 mmol scale as colorless oil. *Two sets of signals were observed in the ^{13}C NMR spectrum of **1e**, which was also found in 1-(3' -methylphenyl)-but-3-en-1-ol in the literature[1]*. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.29 (s, 1 H), 7.28 (t, *J* = 8.0 Hz, 1 H), 7.06-6.80 (m, 3 H), 5.93-5.69 (m, 2 H), 5.22-5.04 (m, 2 H), 3.81 (s, 3 H), 2.87-2.73 (m, 1 H), 2.73-2.56 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.5, 159.7, 141.3, 133.1, 132.0, 129.8, 129.4, 119.2, 118.6, 118.5, 118.2, 114.0, 113.4, 112.0, 111.6, 91.7, 80.6, 79.9, 55.3, 55.2, 41.1, 40.6; HRMS (ESI): calcd for $C_{13}H_{15}NO_2Cl_3$ $[M^+ + H]$ 322.0168, found 322.0164.



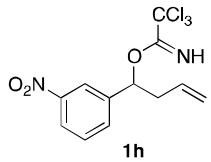
1f

1f (0.805 g, 88%) (R_f 0.8, PE/EA = 10:1) was prepared following the typical procedure in 3.0 mmol scale as pale-yellow oil. *Two sets of signals were observed in the ^{13}C NMR spectrum of **1f.*** . **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.28 (s, 1 H), 7.36-7.03 (m, 4 H), 5.94-5.67 (m, 2 H), 5.25-5.00 (m, 2 H), 2.89-2.72 (m, 1 H), 2.72-2.56 (m, 1 H), 2.36 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.6, 139.7, 138.0, 133.2, 132.2, 129.5, 128.8, 128.6, 128.3, 127.1, 126.9, 123.4, 123.2, 119.1, 118.1, 91.7, 80.9, 80.2, 41.2, 40.1, 21.5; HRMS (ESI): calcd for $C_{13}H_{15}NOCl_3$ $[M^+ + H]$ 306.0219, found 306.0236.



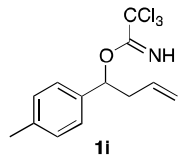
1g

1g (0.799 g, 82%) (R_f 0.8, PE/EA = 10:1) was prepared following the typical procedure in 3.0 mmol scale as pale-yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.32 (s, 1 H), 7.40 (s, 1 H), 7.34-7.22 (m, 3 H), 5.92-5.70 (m, 2 H), 5.22-5.02 (m, 2 H), 2.86-2.72 (m, 1 H), 2.72-2.53 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.4, 141.7, 134.4, 132.6, 129.7, 128.2, 126.4, 124.4, 118.7, 91.5, 79.3, 40.9; HRMS (ESI): calcd for $C_{12}H_{12}NOCl_4$ [M^++H] 325.9673, found 325.9682.



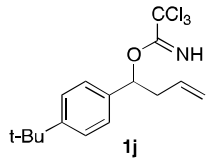
1h

1h (0.766 g, 76%) (R_f 0.5, PE/EA = 5:1) was prepared following the typical procedure in 3.0 mmol scale as brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.36 (s, 1 H), 8.29 (t, J = 2.0 Hz, 1 H), 8.21-8.13 (m, 1 H), 7.69-7.76 (m, 1 H), 7.54 (t, J = 8.0 Hz, 1 H), 5.97 (dd, J = 7.6, 5.6 Hz, 1 H), 5.87-5.72 (m, 1 H), 5.21-5.07 (m, 2 H), 2.91-2.75 (m, 1 H), 2.75-2.58 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.3, 148.4, 141.8, 132.4, 131.9, 129.4, 123.0, 121.4, 119.2, 91.2, 78.7, 40.7; HRMS (ESI): calcd for $C_{12}H_{12}N_2O_3Cl_3$ [M^++H] 336.9914, found 336.9909.



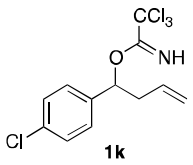
1i

1i (0.750 g, 82%) (R_f 0.8, PE/EA = 10:1) was prepared following the typical procedure in 3.0 mmol scale as pale-yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.27 (s, 1 H), 7.39-7.27 (m, 2 H), 7.23-7.14 (m, 2 H), 5.92-5.68 (m, 2 H), 5.22-5.02 (m, 2 H), 2.90-2.72 (m, 1 H), 2.72-2.56 (m, 1 H), 2.35 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.6, 137.7, 136.7, 133.2, 129.1, 126.2, 118.1, 91.8, 80.1, 41.1, 21.2; HRMS (ESI): calcd for $C_{13}H_{15}NOCl_3$ [M^++H] 306.0219, found 306.0246.



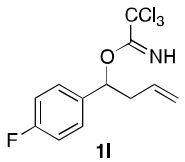
1j

1j (0.916 g, 88%) (R_f 0.8, PE/EA = 10:1) was prepared following the typical procedure in 3.0 mmol scale as pale-yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.28 (s, 1 H), 7.45-7.28 (m, 4 H), 5.95-5.71 (m, 2 H), 5.21-5.03 (m, 2 H), 2.89-2.72 (m, 1 H), 2.72-2.55 (m, 1 H), 1.32 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.6, 150.8, 136.6, 133.4, 125.8, 125.3, 118.0, 91.8, 80.0, 41.1, 34.6, 31.3; HRMS (ESI): calcd for $C_{16}H_{21}NOCl_3$ [M^++H] 348.0689, found 348.0663.



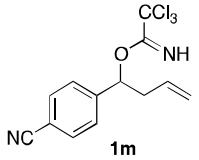
1k

1k (0.761 g, 78%) (R_f 0.8, PE/EA = 10:1) was prepared following the typical procedure in 3.0 mmol scale as pale-yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.31 (s, 1 H), 7.34 (s, 4 H), 5.85 (dd, *J* = 7.6, 5.6 Hz, 1 H), 5.83-5.71 (m, 1 H), 5.16-5.05 (m, 2 H), 2.83-2.72 (m, 1 H), 2.72-2.56 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.4, 138.1, 133.8, 132.6, 128.6, 127.7, 118.6, 91.5, 79.4, 40.8; HRMS (ESI): calcd for $C_{12}H_{12}NOCl_4$ [M^++H] 325.9673, found 325.9639.



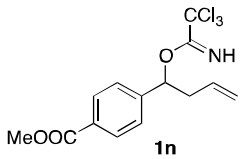
1l

1l (0.742 g, 80%) (R_f 0.8, PE/EA = 10:1) was prepared following the typical procedure in 3.0 mmol scale as pale-yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.30 (s, 1 H), 7.50-7.30 (m, 2 H), 7.16-6.95 (m, 2 H), 6.01-5.66 (m, 2 H), 5.24-4.99 (m, 2 H), 2.90-2.72 (m, 1 H), 2.72-2.52 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.7, 161.5, 161.2, 135.4, 135.3, 132.8, 128.2, 128.1, 118.5, 115.4, 115.2, 91.6, 79.4, 40.9; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -114.08; HRMS (ESI): calcd for $C_{12}H_{12}NOCl_3F$ [M^++H] 309.9969, found 309.9982.



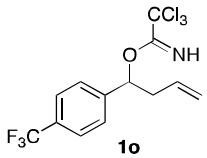
1m

1m (0.872 g, 92%) (R_f 0.7, PE/EA = 5:1) was prepared following the typical procedure in 3.0 mmol scale as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.34 (s, 1 H), 7.72-7.62 (m, 2 H), 7.54-7.46 (m, 2 H), 5.90 (dd, *J* = 7.2, 5.6 Hz, 1 H), 5.83-5.68 (m, 1 H), 5.19-5.05 (m, 2 H), 2.83-2.73 (m, 1 H), 2.73-2.57 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.3, 144.9, 132.3, 132.0, 126.9, 119.1, 118.6, 111.9, 91.3, 79.1, 40.6; HRMS (ESI): calcd for $C_{13}H_{12}N_2OCl_3$ [M^++H] 317.0015, found 317.0026.



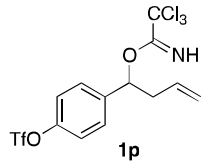
1n

1n (0.712 g, 68%) (R_f 0.6, PE/EA = 10:1) was prepared following the typical procedure in 3.0 mmol scale as pale-yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.31 (s, 1 H), 8.00-7.99 (m, 2 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 5.92 (dd, *J* = 7.6, 5.6 Hz, 1 H), 5.86-5.70 (m, 1 H), 5.19-5.03 (m, 2 H), 3.91 (s, 3 H), 2.86-2.72 (m, 1 H), 2.72-2.57 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.8, 161.4, 144.7, 132.5, 129.81, 129.77, 126.2, 118.7, 91.2, 79.5, 52.1, 40.8; HRMS (ESI): calcd for $C_{14}H_{15}NO_3Cl_3$ [M^++H] 350.0118, found 350.0107.



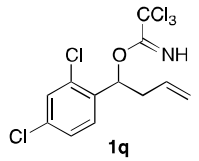
1o

1o (0.926 g, 86%) (R_f 0.8, PE/EA = 10:1) was prepared following the typical procedure in 3.0 mmol scale as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.33 (s, 1 H), 7.62 (d, *J* = 8.4 Hz, 2 H), 7.52 (d, *J* = 8.4 Hz, 2 H), 5.92 (dd, *J* = 7.6, 6.0 Hz, 1 H), 5.86-5.73 (m, 1 H), 5.23-5.05 (m, 2 H), 2.87-2.72 (m, 1 H), 2.72-2.57 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.4, 143.6, 132.3, 130.3, 126.5, 125.49, 125.46, 125.42, 125.38, 122.7, 118.8, 91.4, 79.3, 40.8; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -62.59; HRMS (ESI): calcd for $C_{13}H_{12}NOCl_3F_3$ [M^++H] 359.9937, found 359.9933.



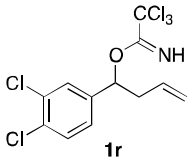
1p

1p (0.961 g, 73%) (R_f 0.8, PE/EA = 10:1) was prepared following the typical procedure in 3.0 mmol scale as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.34 (s, 1 H), 7.55-7.44 (m, 2 H), 7.33-7.23 (m, 2 H), 5.91 (dd, *J* = 7.6, 5.6 Hz, 1 H), 5.85-5.70 (m, 1 H), 5.19-5.06 (m, 2 H), 2.84-2.72 (m, 1 H), 2.72-2.57 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.3, 149.0, 140.2, 132.3, 128.1, 121.3, 120.3, 118.9, 117.1, 91.4, 78.9, 40.8; HRMS (ESI): calcd for $C_{13}H_{12}NO_4Cl_3F_3S$ [M^++H] 439.9505, found 439.9477.



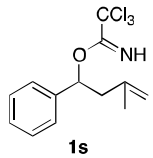
1q

1q (0.872 g, 81%) (R_f 0.8, PE/EA = 10:1) was prepared following the typical procedure in 3.0 mmol scale as pale-yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.35 (s, 1 H), 7.44 (d, *J* = 8.4 Hz, 1 H), 7.39 (d, *J* = 2.0 Hz, 1 H), 7.29-7.22 (m, 1 H), 6.22 (t, *J* = 6.4 Hz, 1 H), 5.92-5.77 (m, 1 H), 5.18-5.05 (m, 2 H), 2.73-2.62 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.1, 136.3, 134.1, 132.7, 132.3, 129.3, 127.7, 127.4, 118.8, 91.3, 76.3, 39.4; HRMS (ESI): calcd for $C_{12}H_{11}NOCl_5$ [M^++H] 359.9283, found 359.9292.



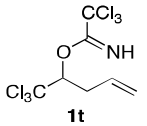
1r

1r (0.829 g, 77%) (R_f 0.8, PE/EA = 10:1) was prepared following the typical procedure in 3.0 mmol scale as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.34 (s, 1 H), 7.49 (d, *J* = 2.0 Hz, 1 H), 7.46-7.39 (m, 1 H), 7.26-7.21 (m, 1 H), 5.89-5.68 (m, 2 H), 5.22-5.05 (m, 2 H), 2.83-2.72 (m, 1 H), 2.72-2.53 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.3, 139.9, 132.6, 132.2, 132.0, 130.5, 128.4, 125.7, 119.0, 91.3, 78.7, 40.7; HRMS (ESI): calcd for $C_{12}H_{11}NOCl_5$ [M^++H] 359.9283, found 359.9249.



1s

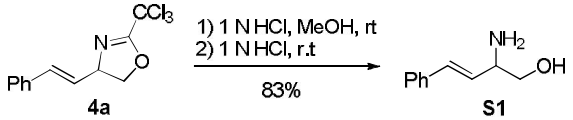
1s (0.695 g, 76%) (R_f 0.8, PE/EA = 10:1) was prepared following the typical procedure in 3.0 mmol scale as pale-red oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.26 (s, 1 H), 7.52-7.26 (m, 5 H), 6.01 (dd, *J* = 8.8, 4.8 Hz, 1 H), 4.85-4.80 (m, 1 H), 4.80-4.74 (m, 1 H), 2.79 (dd, *J* = 14.4, 8.8 Hz, 1 H), 2.51 (dd, *J* = 14.4, 5.2 Hz, 1 H), 1.79 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.6, 140.8, 140.1, 128.4, 128.0, 126.2, 113.8, 91.7, 79.3, 45.1, 22.8; HRMS (ESI): calcd for $C_{13}H_{15}NOCl_3$ [M^++H] 306.0219, found 306.0227.



1t

1t (0.775 g, 78%) (R_f 0.7, PE/EA = 10:1) was prepared following the typical procedure in 3.0 mmol scale as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.63 (s, 1 H), 5.88 (dd, *J* = 9.6, 2.4 Hz, 1 H), 5.86-5.77 (m, 1 H), 5.29-5.12 (m, 2 H), 3.11-2.90 (m, 1 H), 2.80-2.68 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.7, 131.3, 119.6, 99.1, 90.8, 83.7, 35.5; HRMS (ESI): calcd for $C_7H_8NOCl_6$ [M^++H] 331.8732, found 331.8726.

Hydrolysis of 4a to amino alcohol S1:

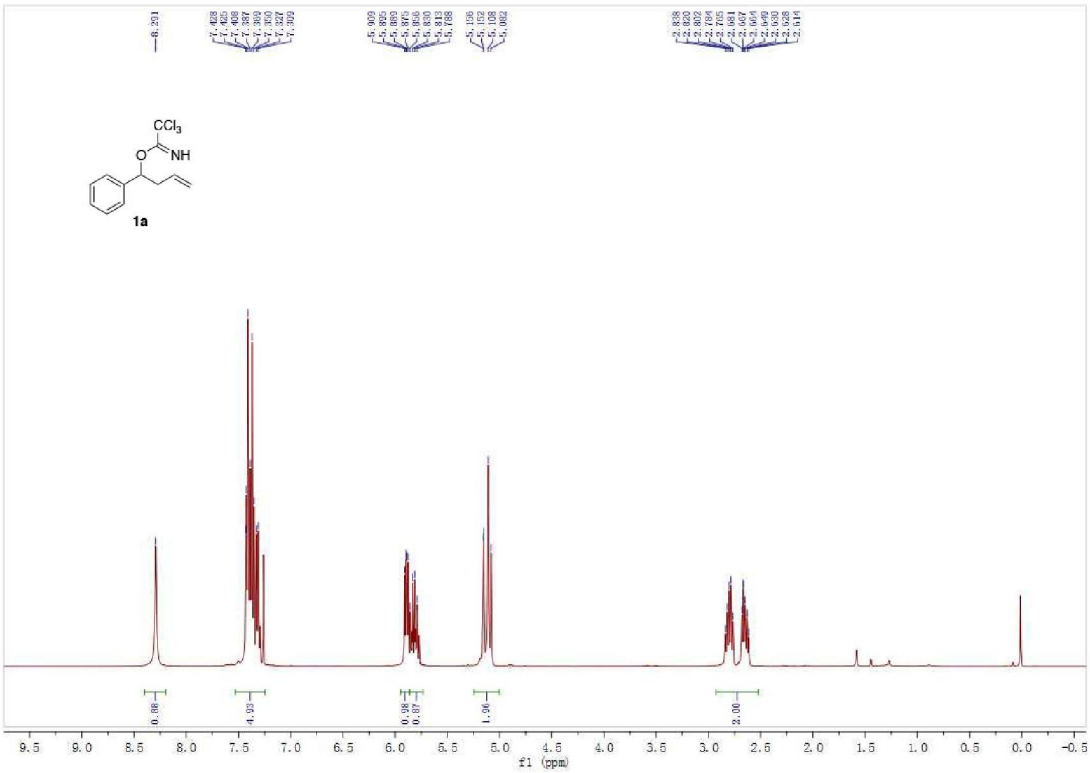


4a **S1**

To a solution of **4a** (58 mg, 0.20 mmol) in methanol (2.0 mL) was added 1 *N* hydrochloric acid (2.0 mL) and the mixture was stirred at 25 °C for 1.5 h until complete consumption of the starting material as monitored by TLC analysis. 1 *N* NaOH (3.0 ml) was added to the solution and stirred at room temperature overnight. Water (10 ml) was added and the mixture was extracted with dichloromethane (3×10 ml), washed with brine (15 ml), dried over sodium sulfate, filtrated and concentrated to afford **S1** (27 mg, 83%, 93% purity) as a white solid. The spectra were consist with the previously reported analysis data.[2] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45-7.18 (m, 5 H), 6.57 (d, *J* = 16.0 Hz, 1 H), 6.16 (dd, *J* = 16.0, 6.8 Hz, 1 H), 3.74-3.57 (m, 2 H), 3.46 (dd, *J* = 10.0, 7.2 Hz, 1 H), 1.99 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 136.7, 130.8, 130.7, 128.6, 127.7, 126.4, 66.6, 55.4.

References:

1. Huang, J.-M.; Dong Y. *Chem. Commun*., **2009**, 3943-3945.
2. (a) Felpin, F. X.; Boubekeur, K.; Lebreton, J. *Eur. J. Org. Chem*. **2003**, 4518-4527. (b) Felpin, F. X.; Boubekeur, K.; Lebreton, J. *J. Org. Chem*. **2004**, *69*, 1497-1503.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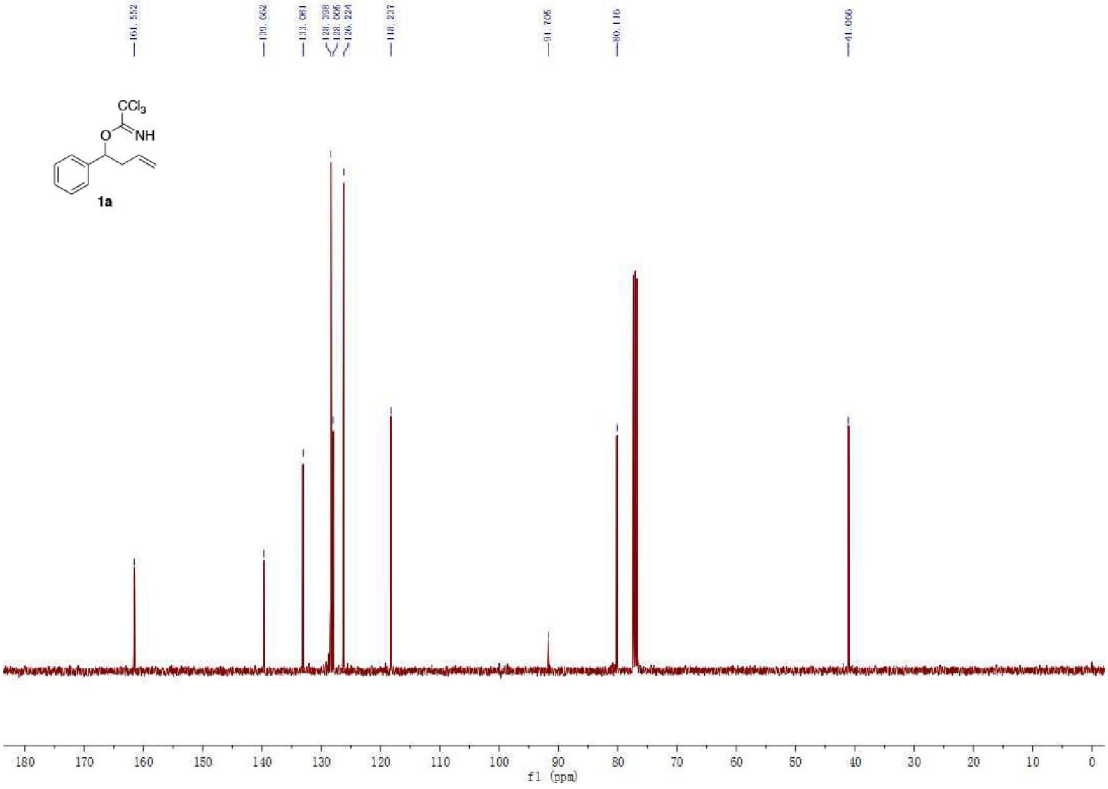
NH
1a
f1 (ppm)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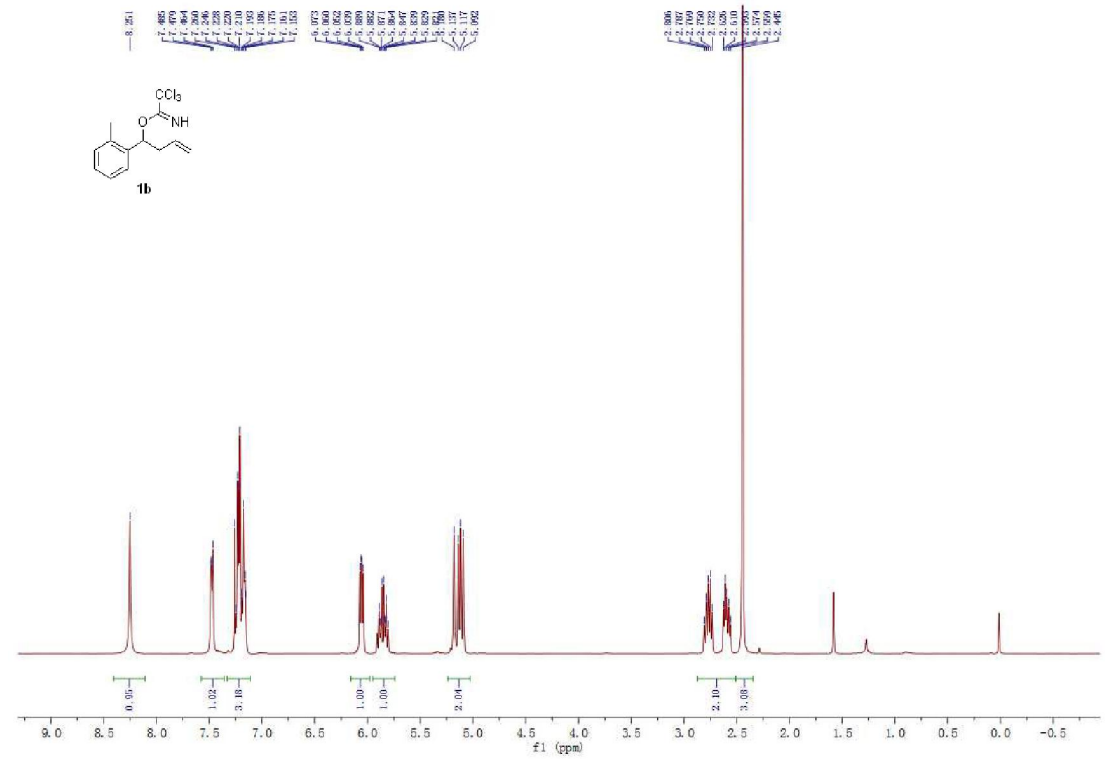
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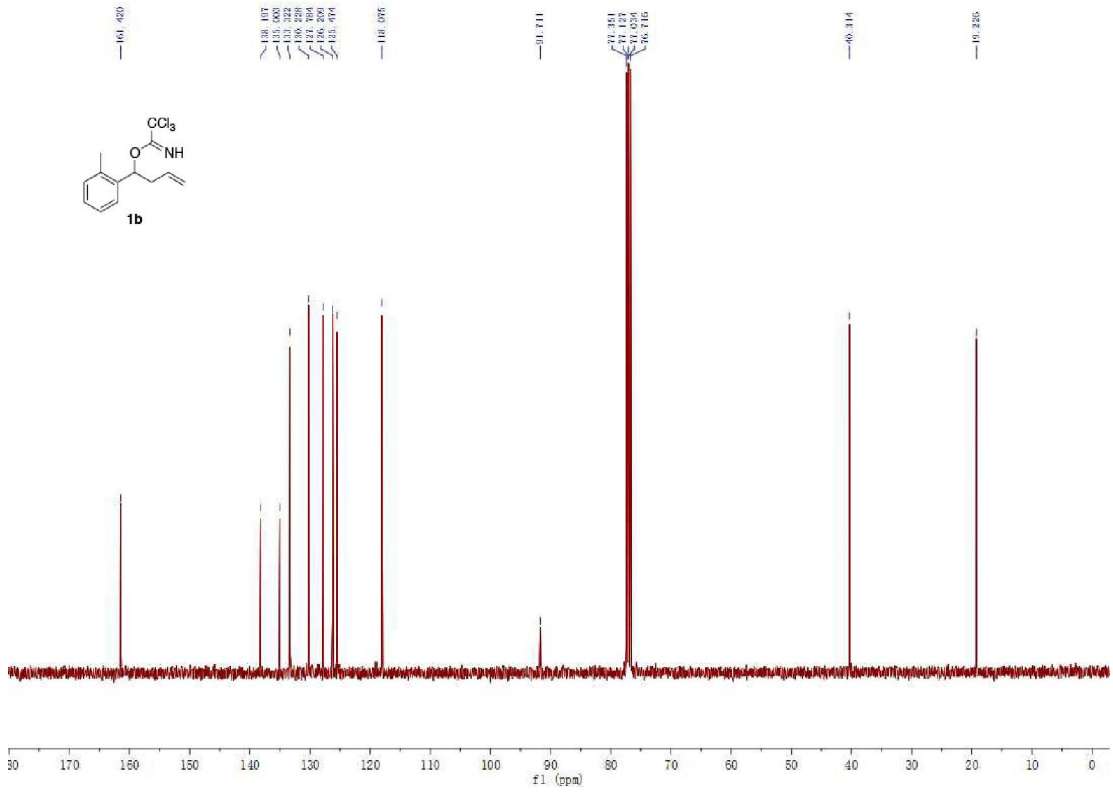
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1b
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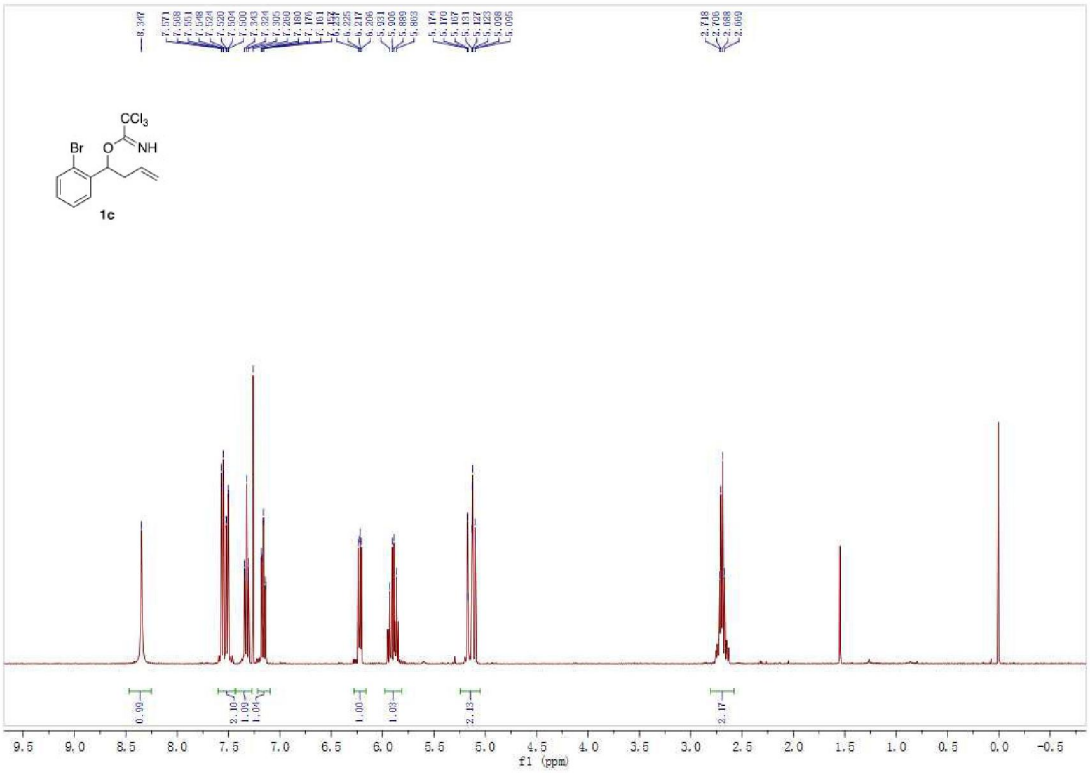
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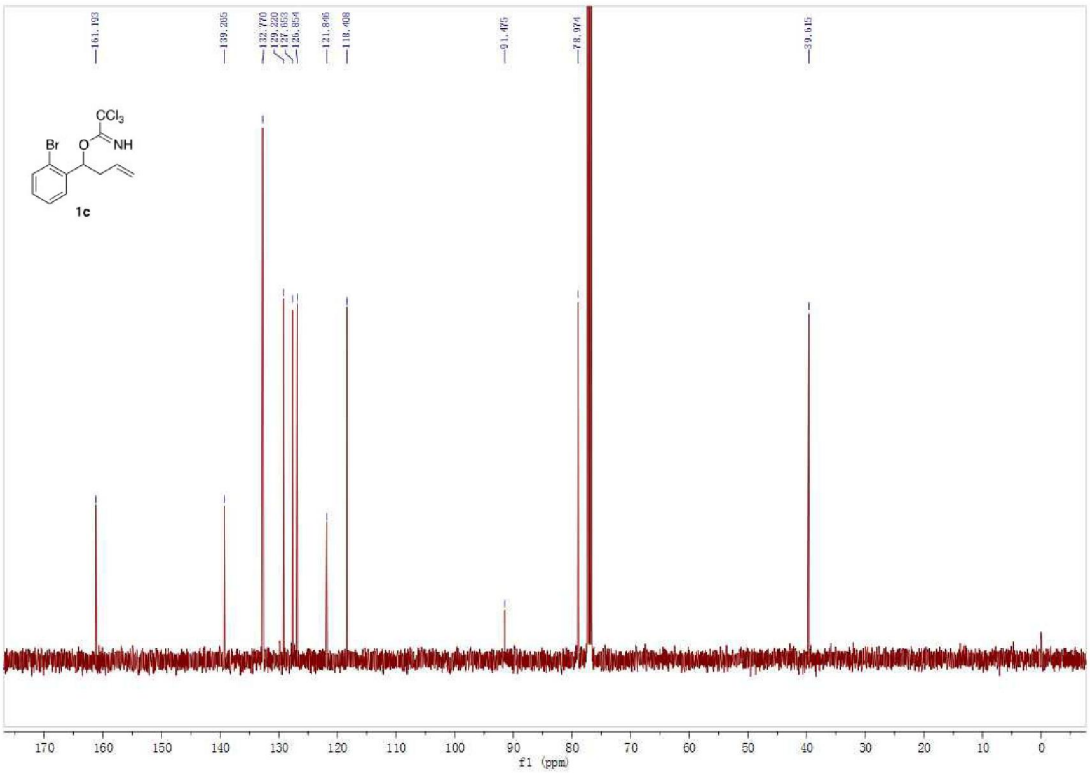
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Br
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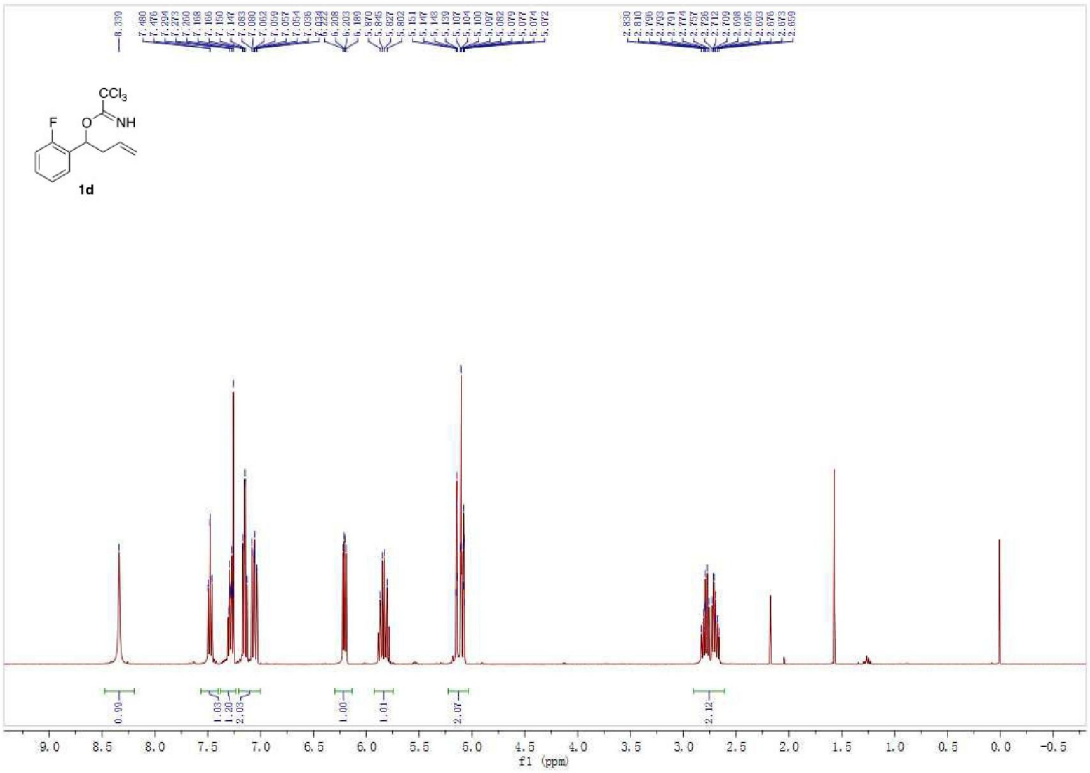
NH
1c
f1 (ppm)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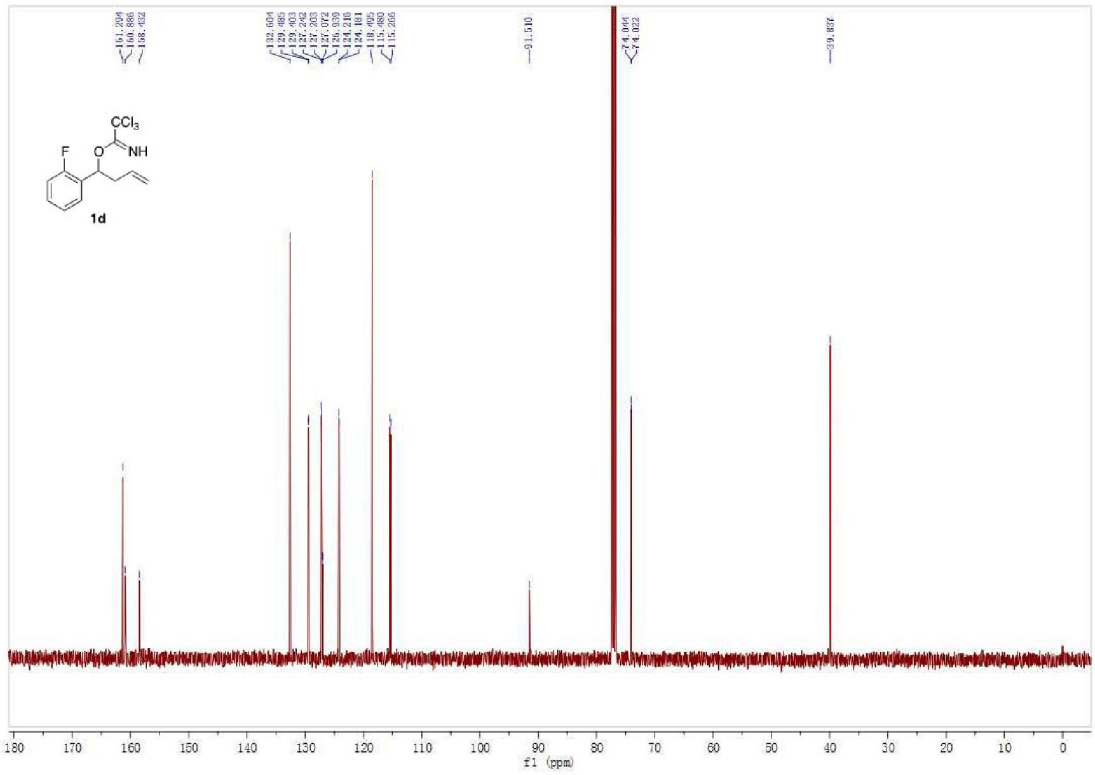
f1 (ppm)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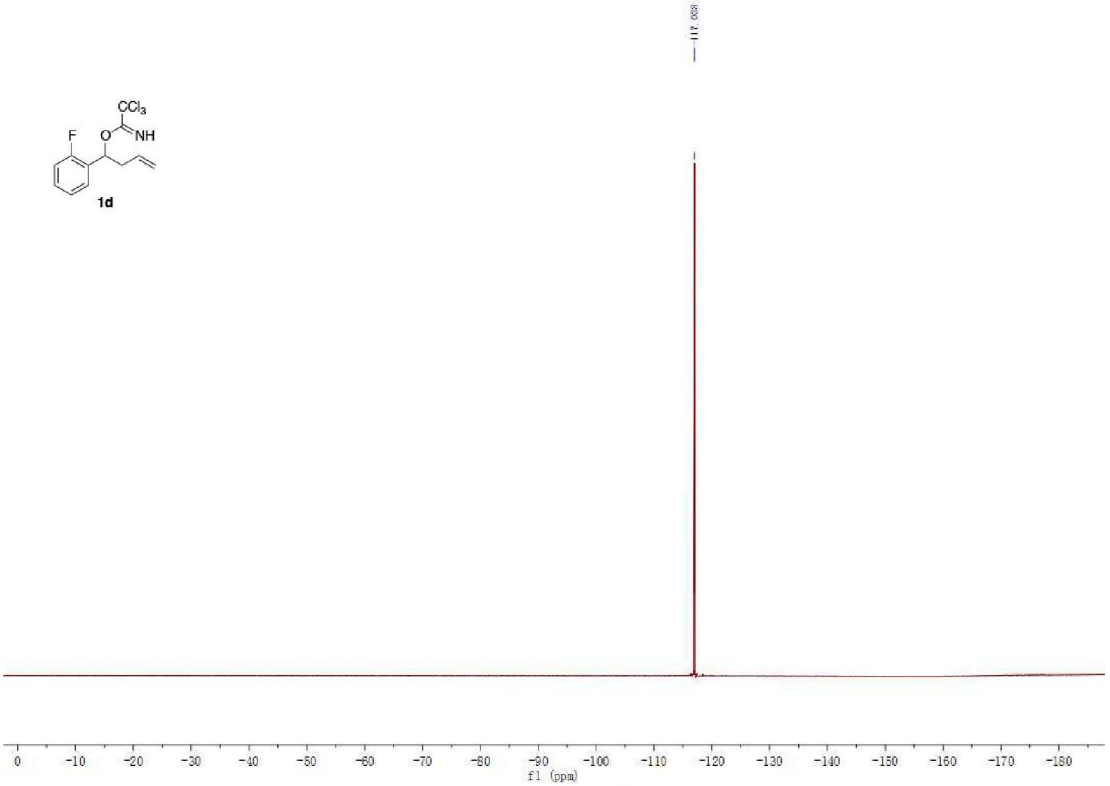
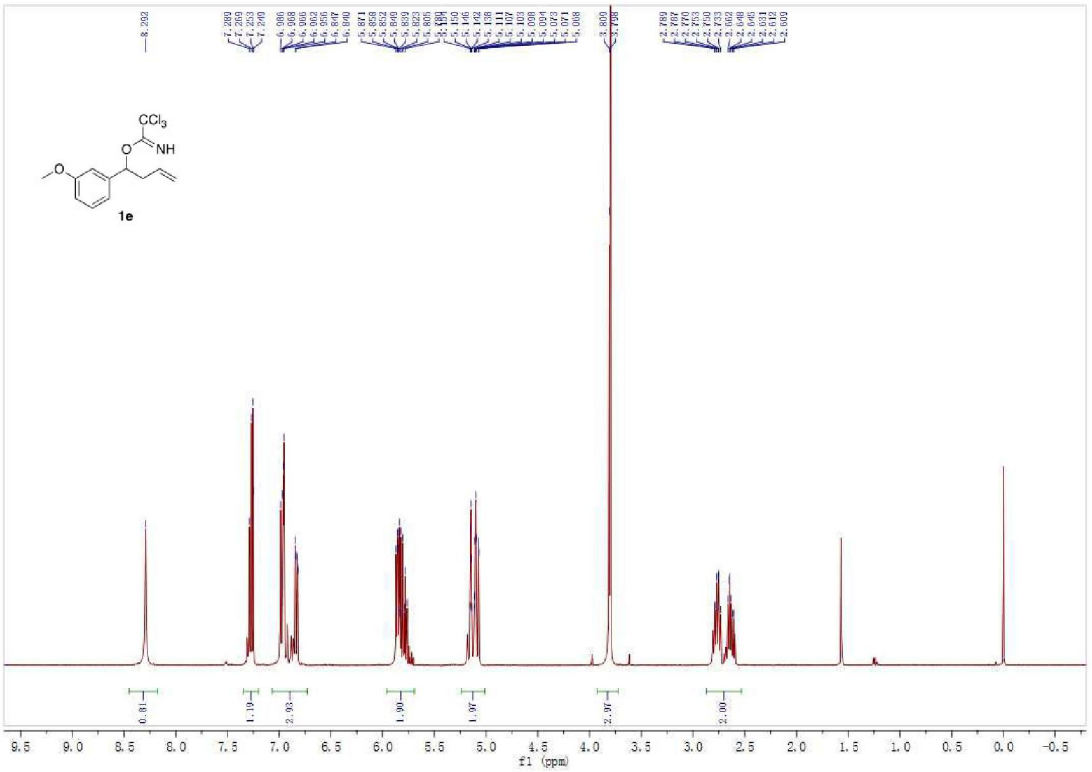
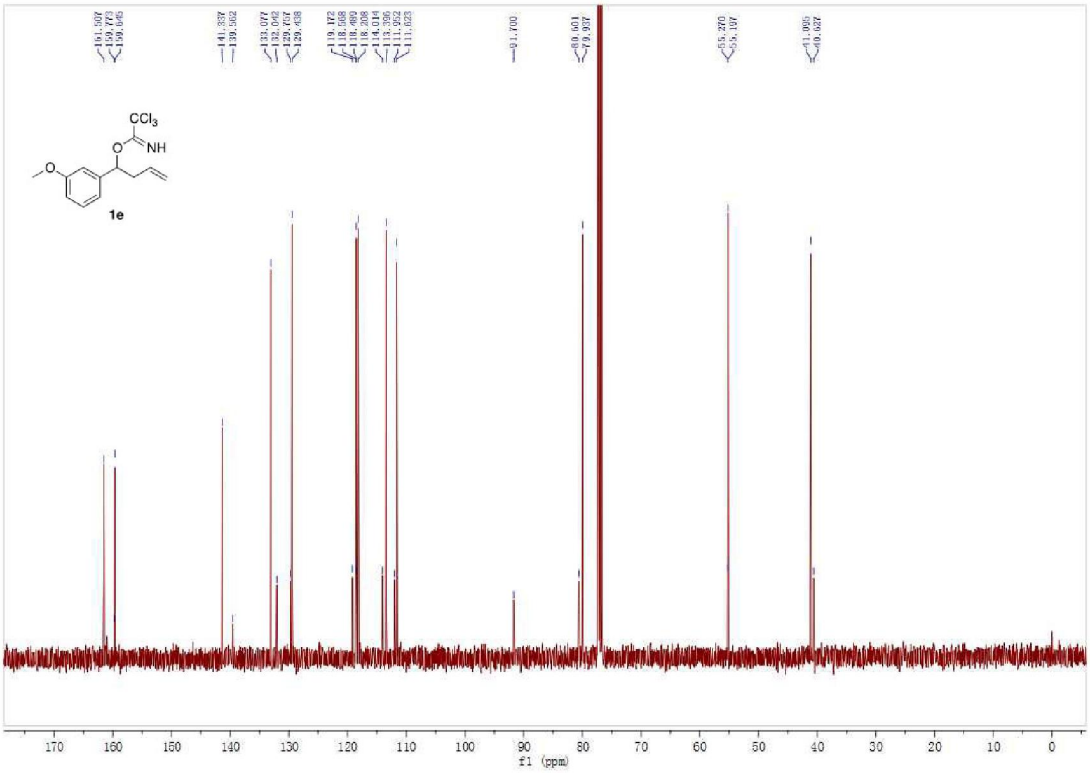
1d
f1 (ppm)

^{19}F NMR (376 MHz, $CDCl_3$)



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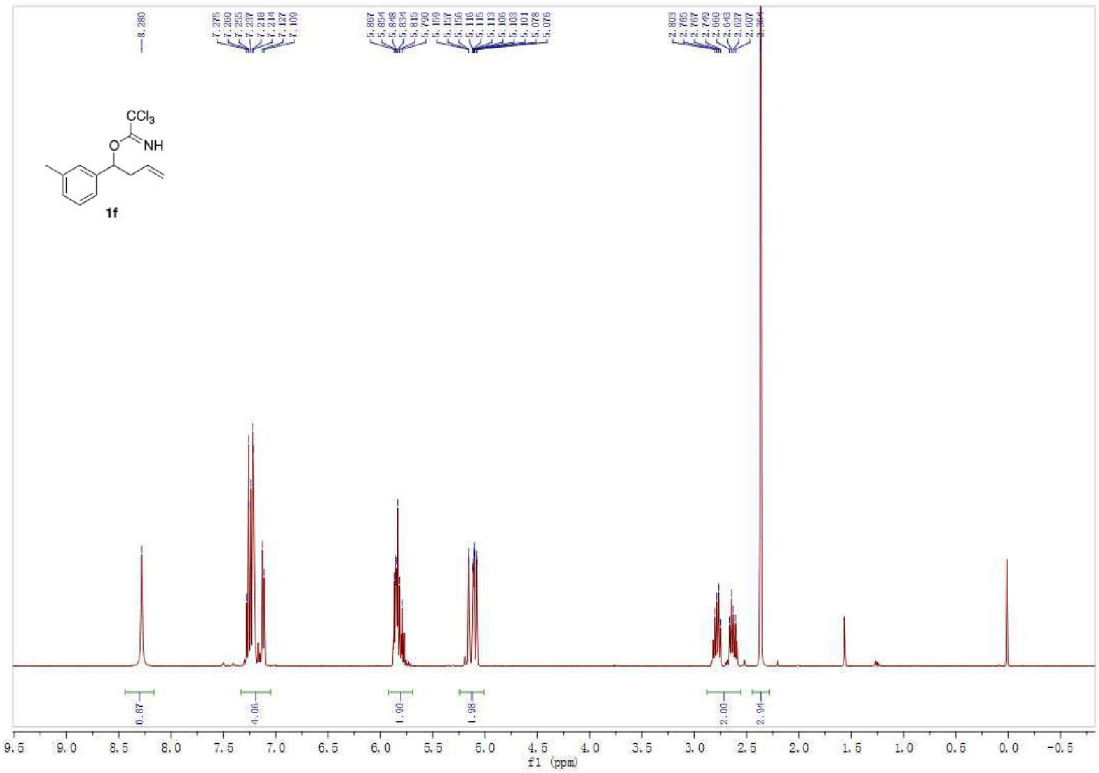
1e
f1 (ppm)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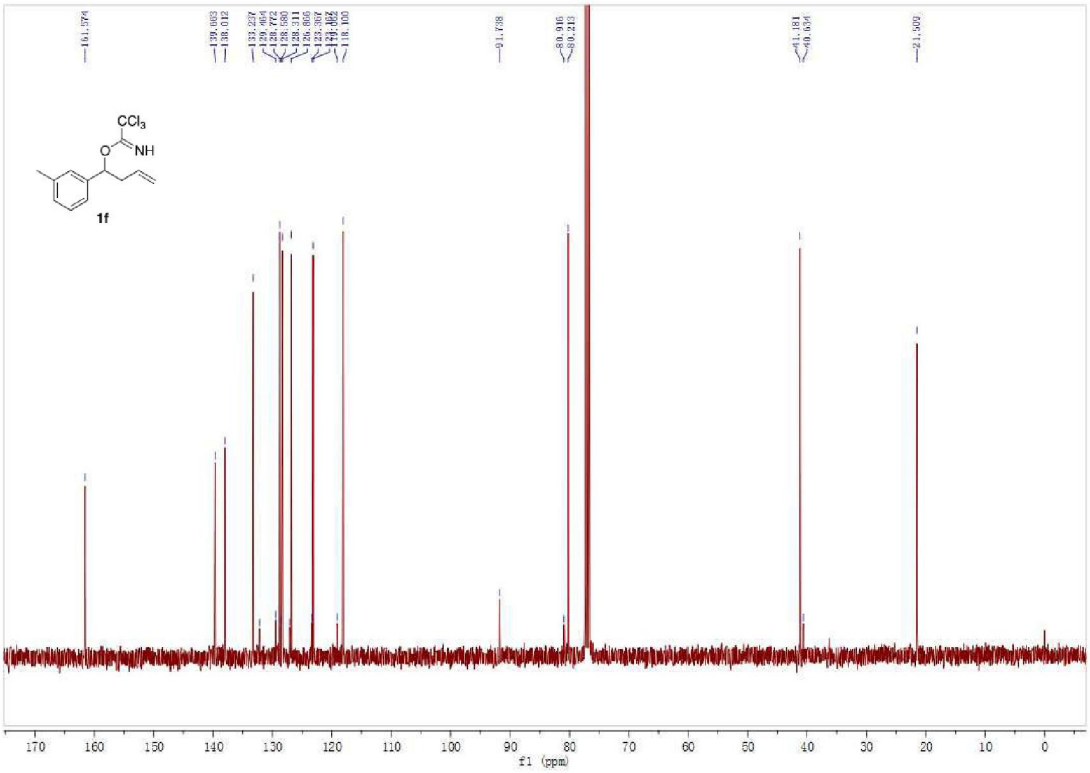
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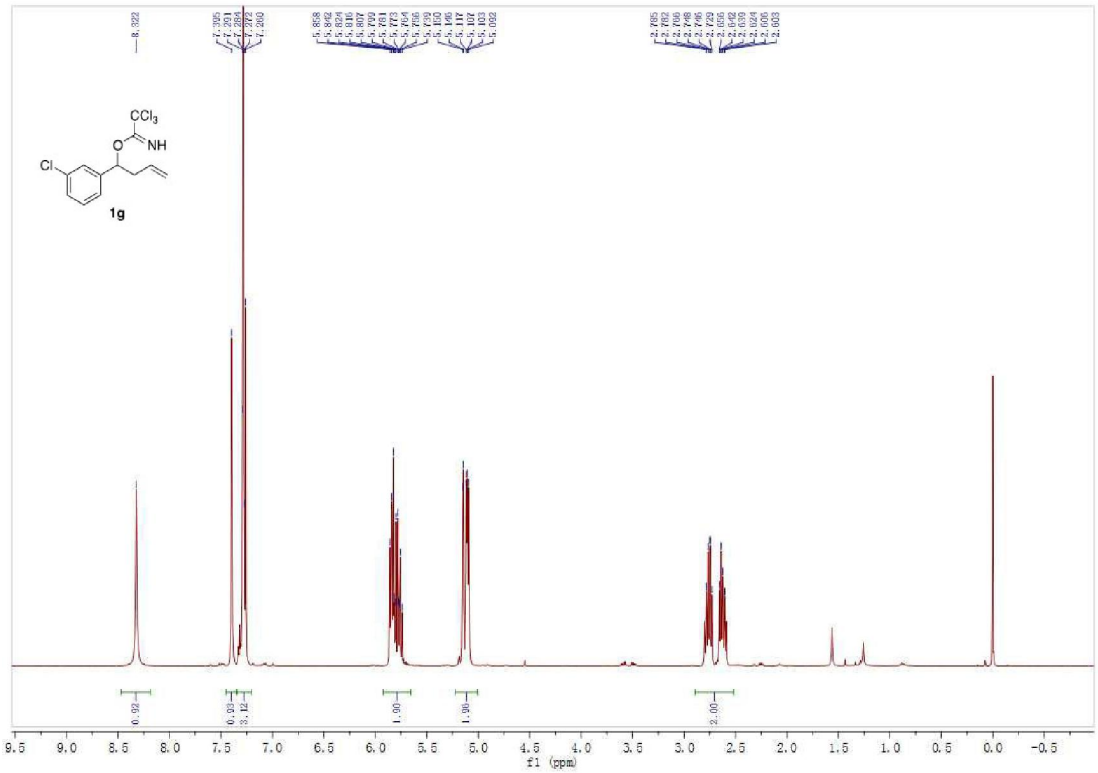
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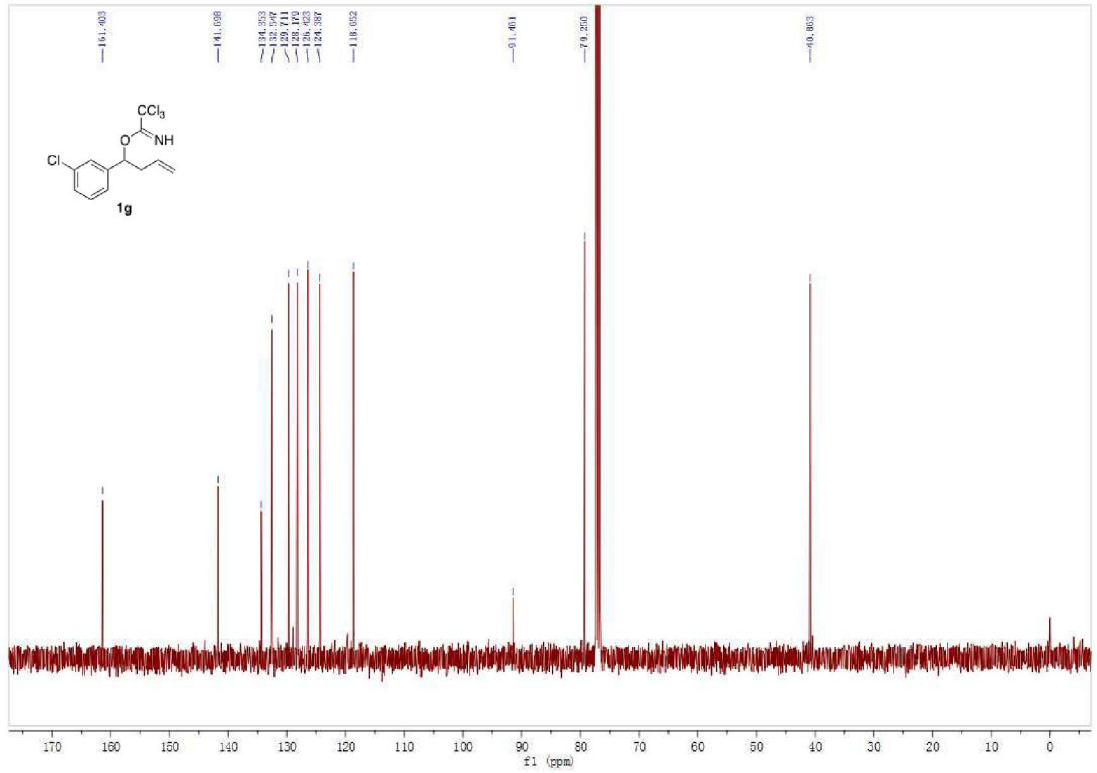
Cl
1g
f1 (ppm)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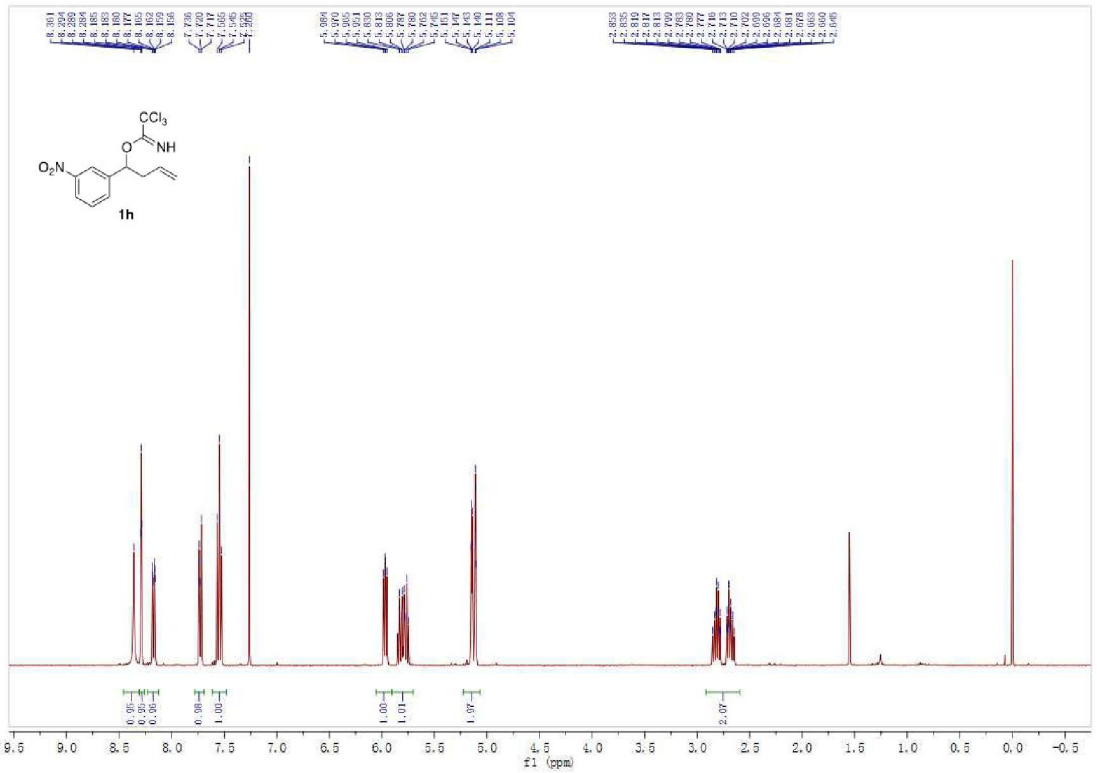
CCl3
O
NH
Cl
1g
f1 (ppm)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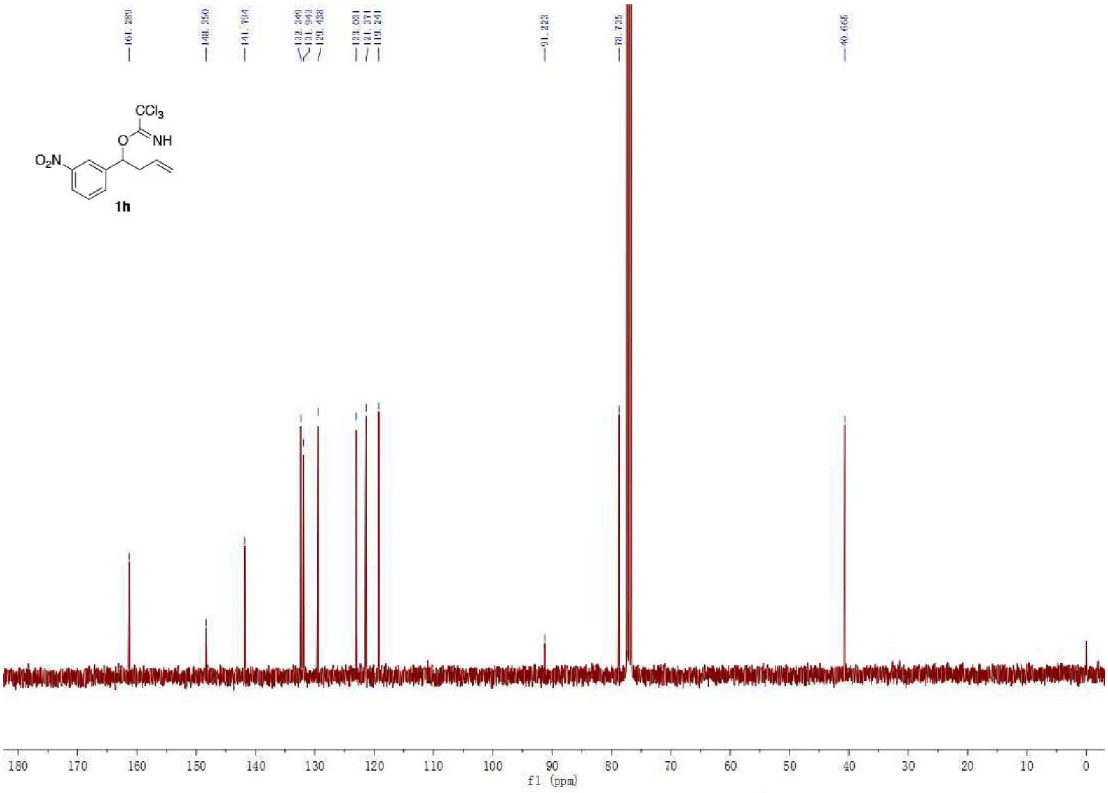
NH
O2N
1h
f1 (ppm)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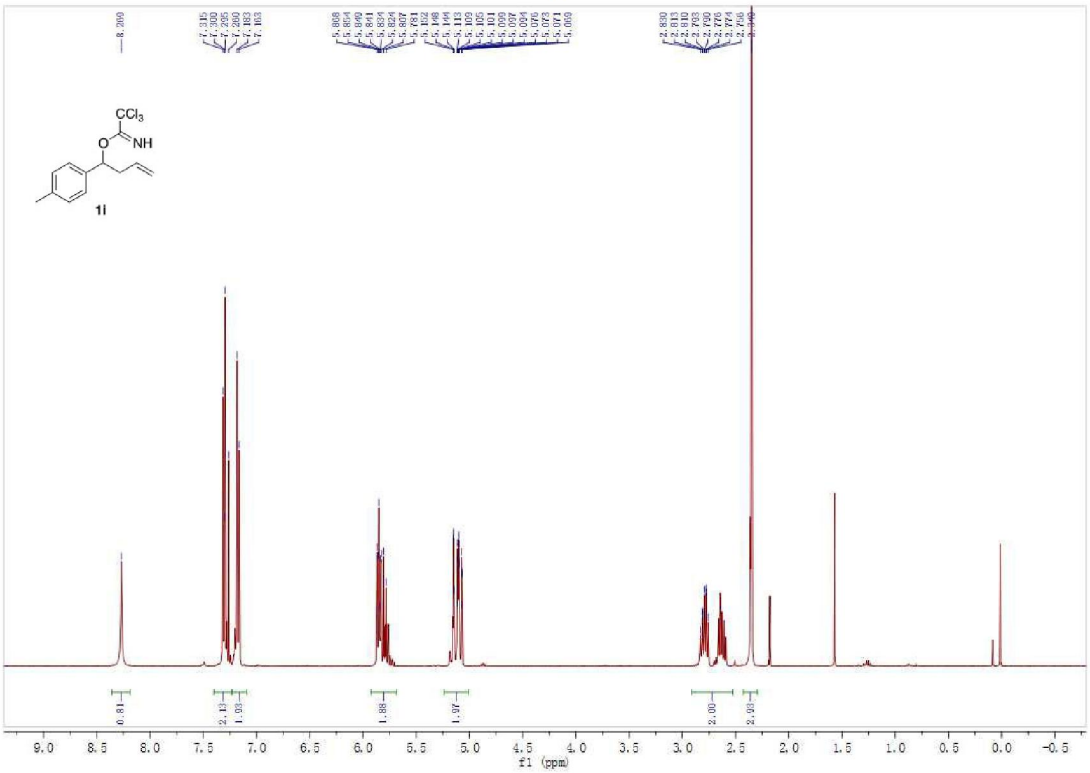
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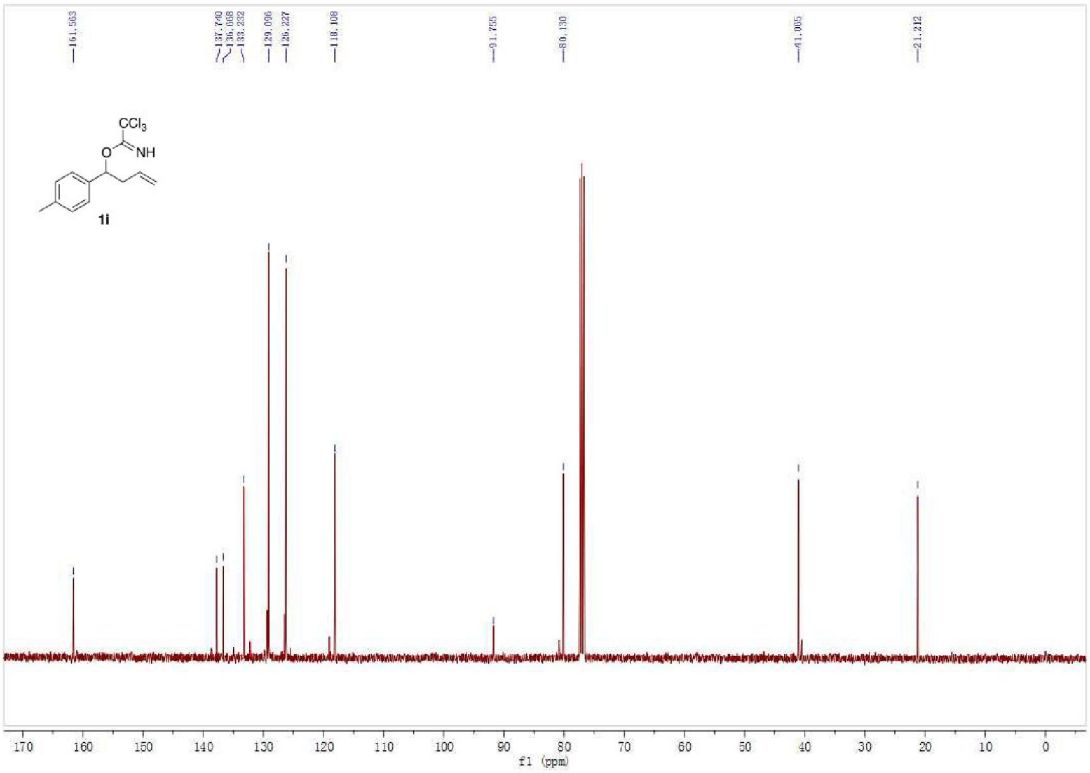
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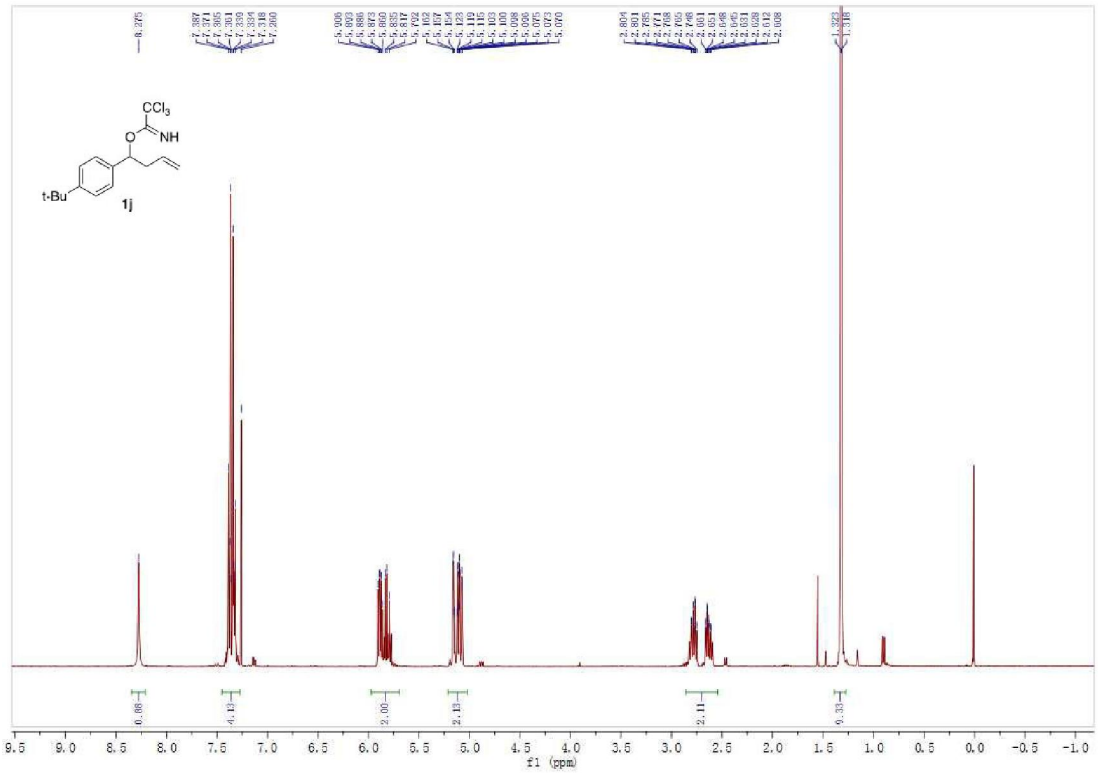
f1 (ppm)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2.038
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2.008
1.323
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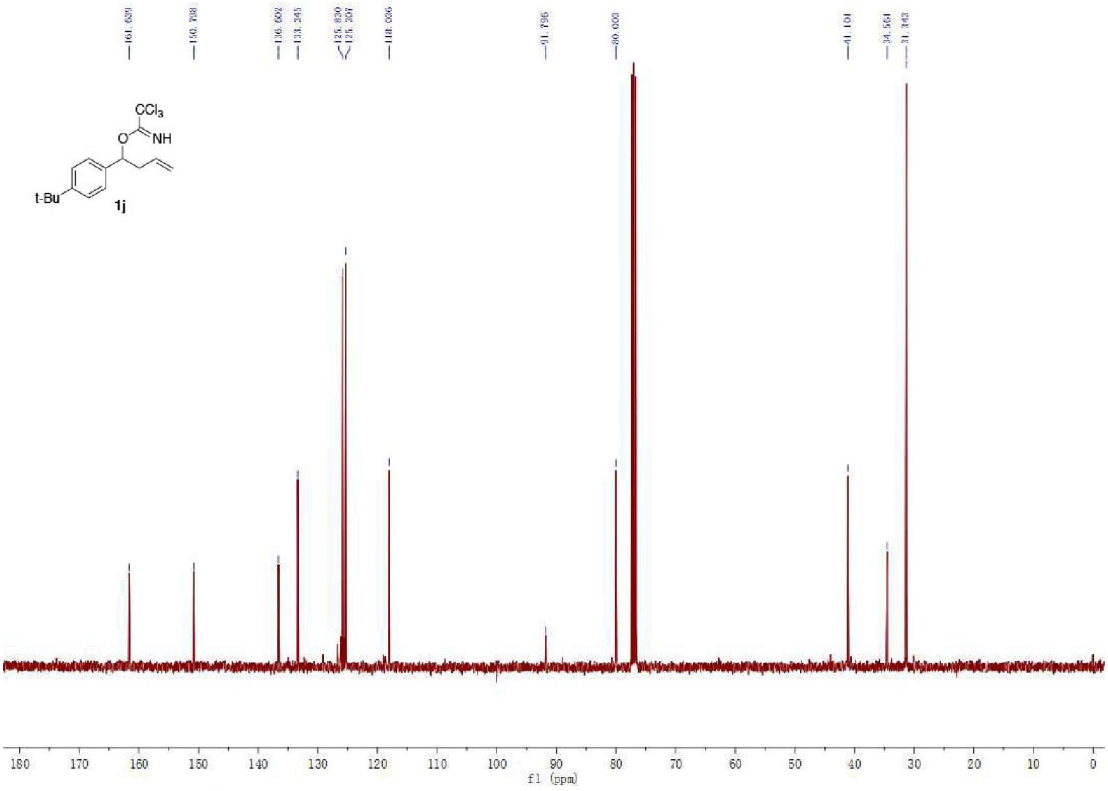
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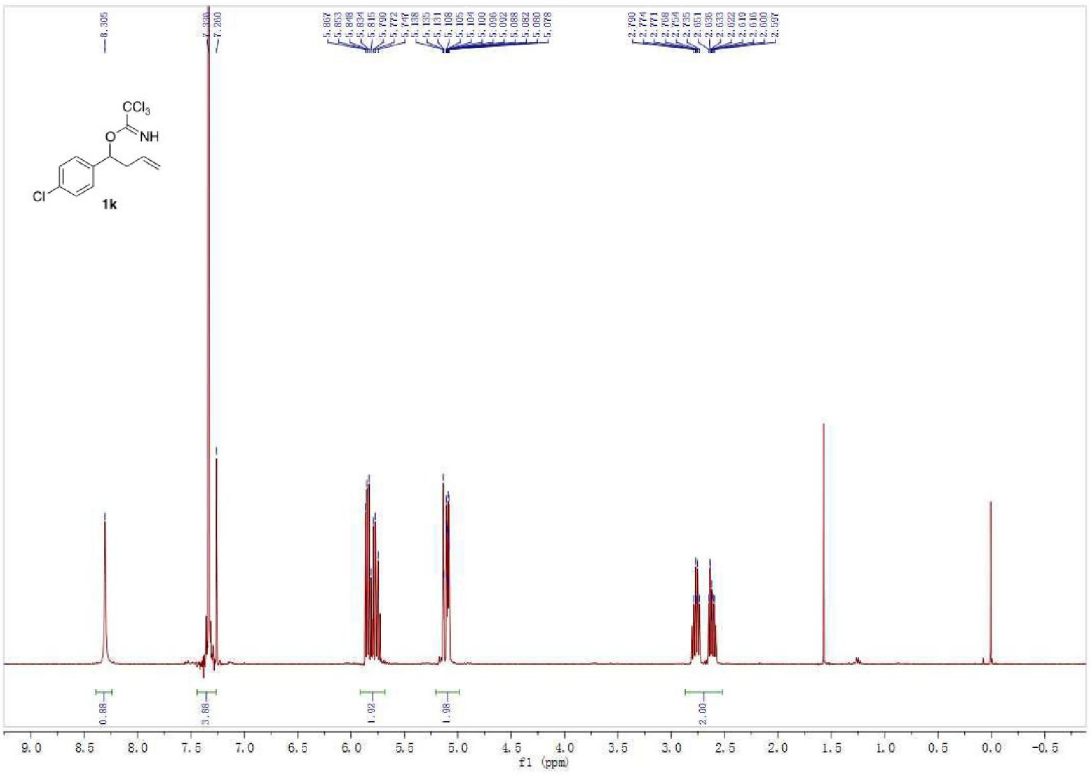
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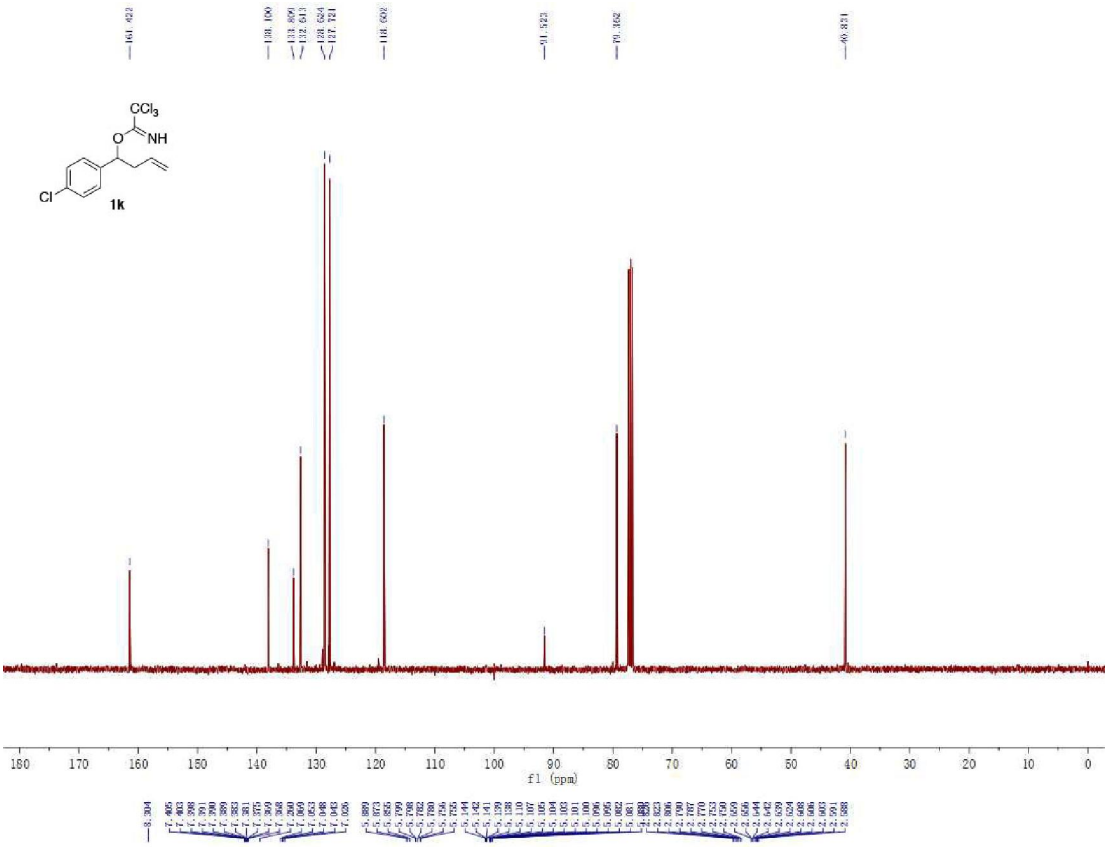
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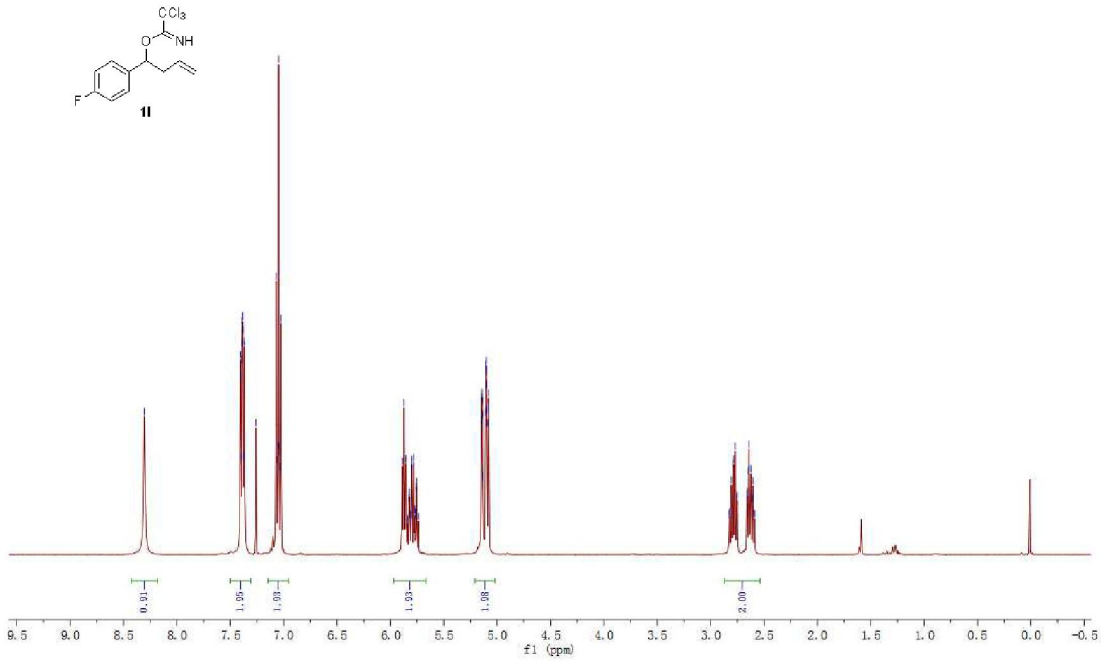
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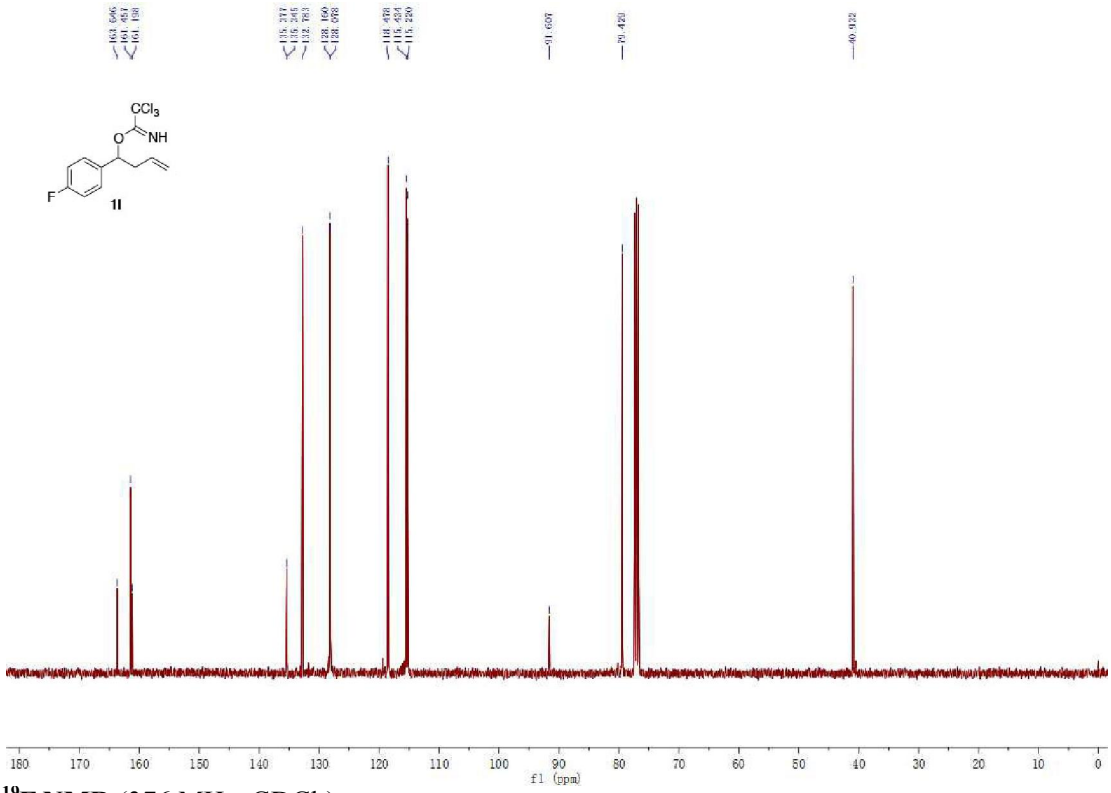
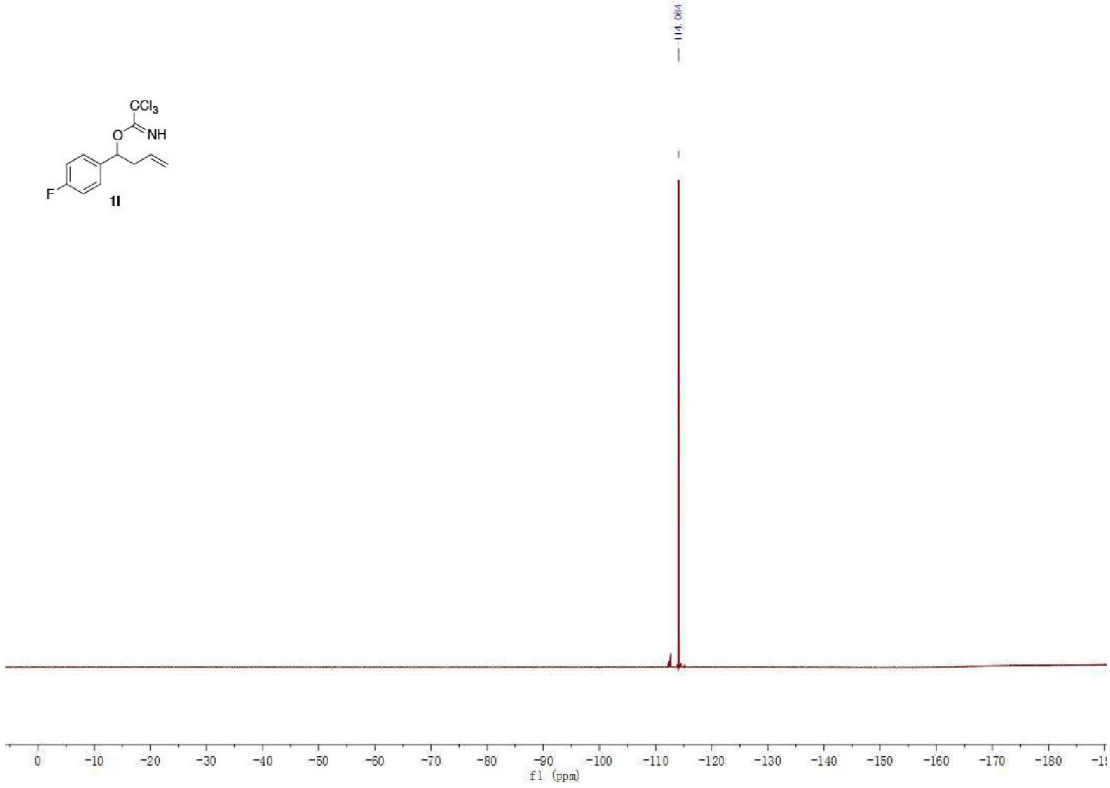
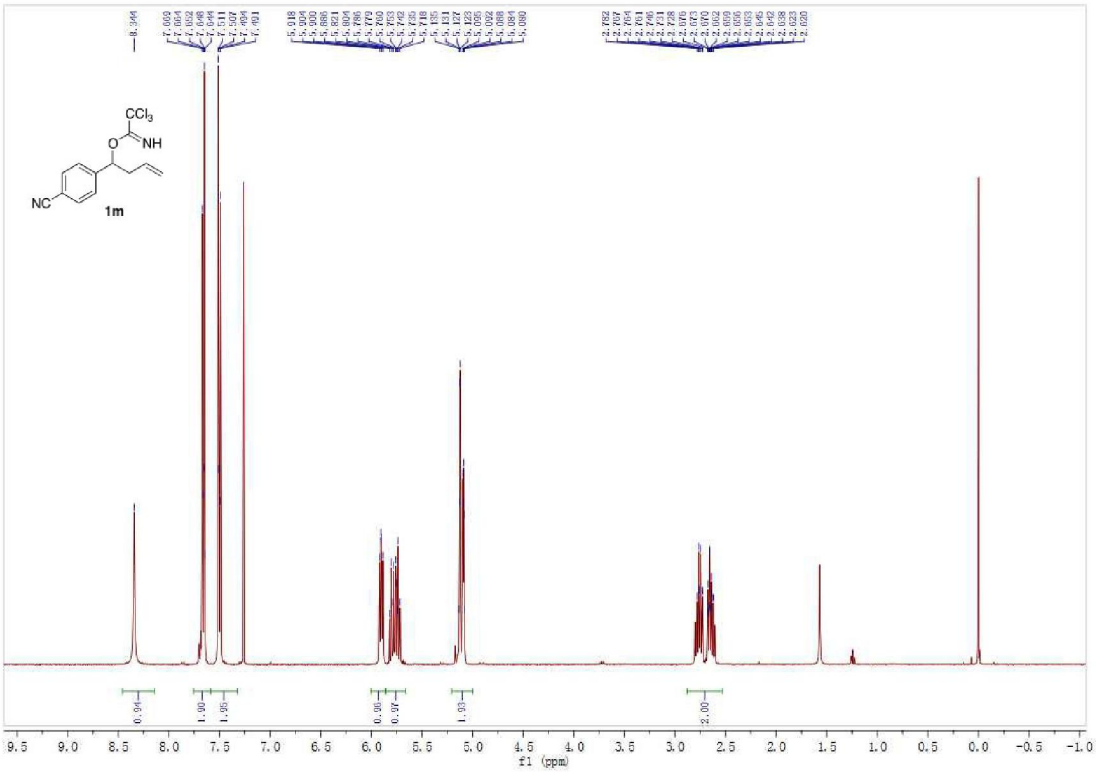


^{19}F NMR (376 MHz, $CDCl_3$)

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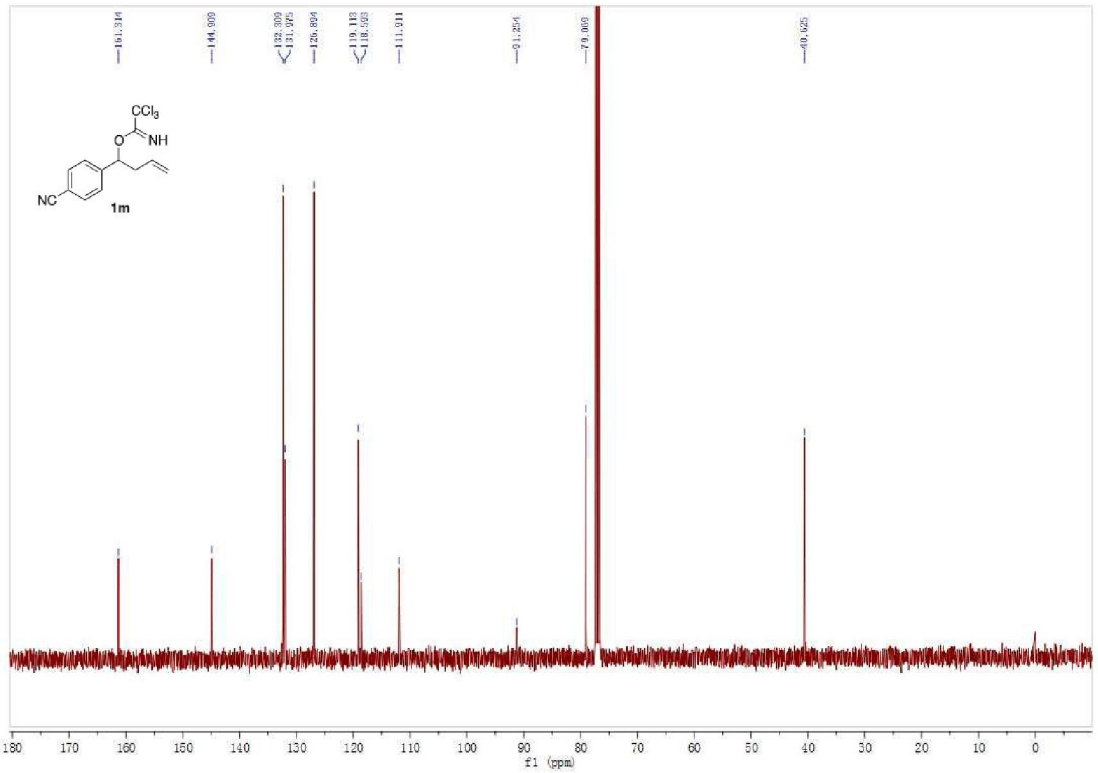
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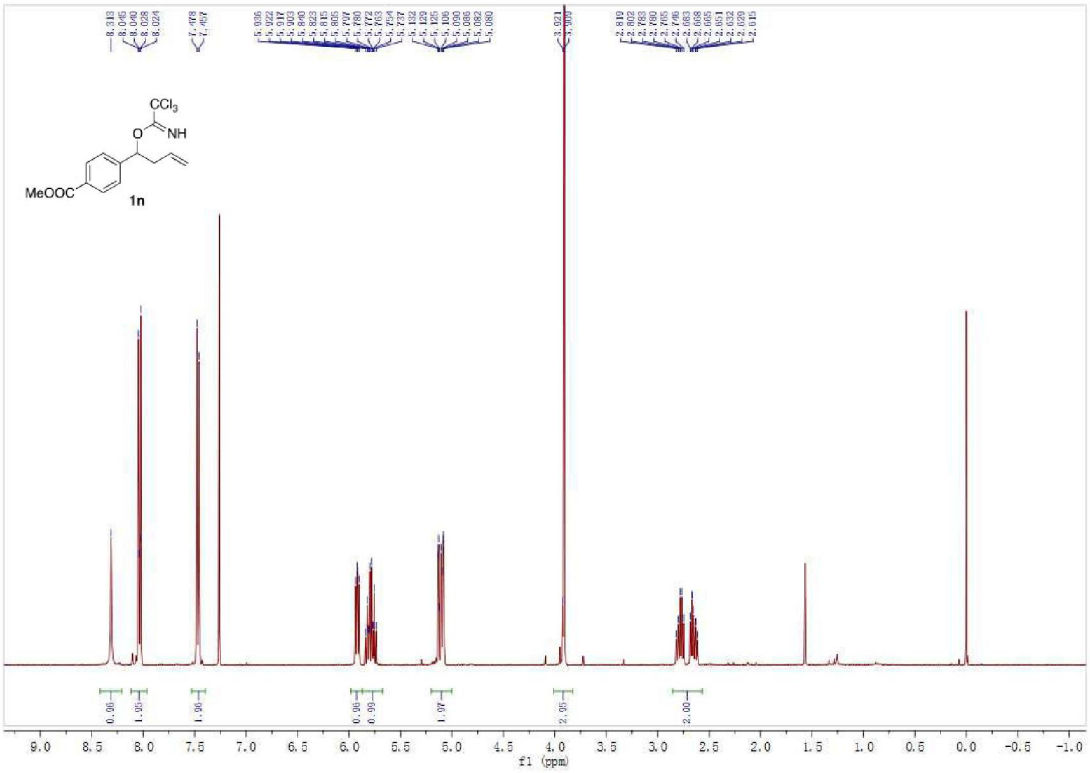
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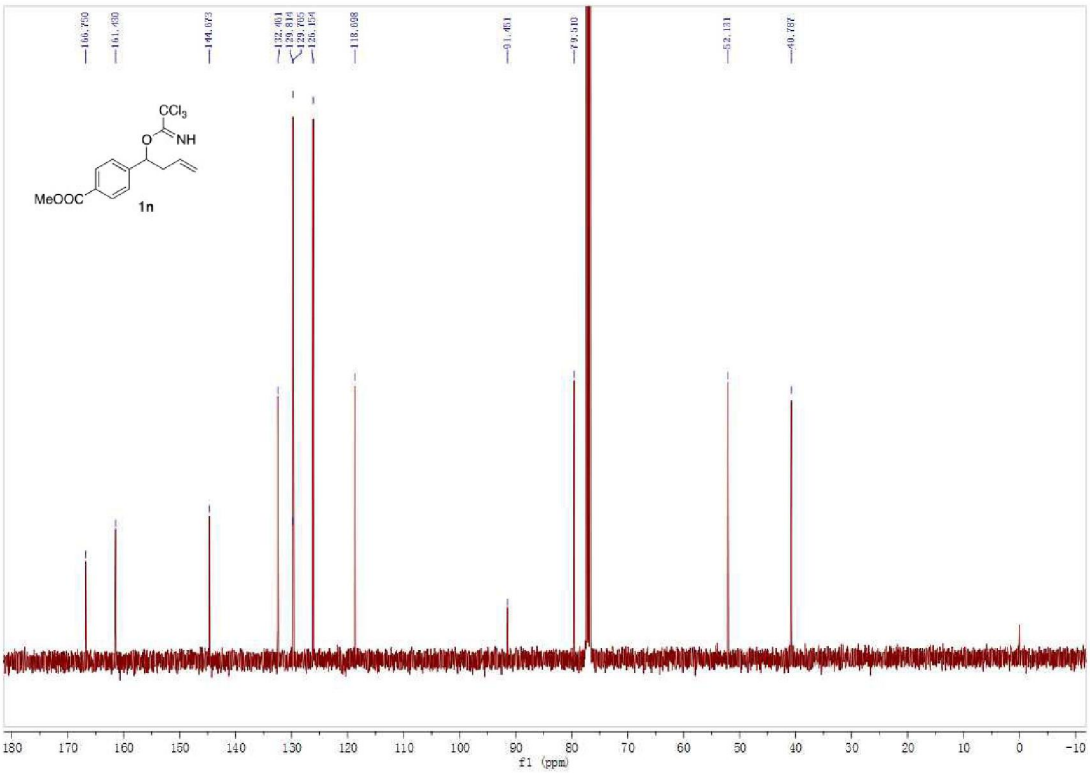
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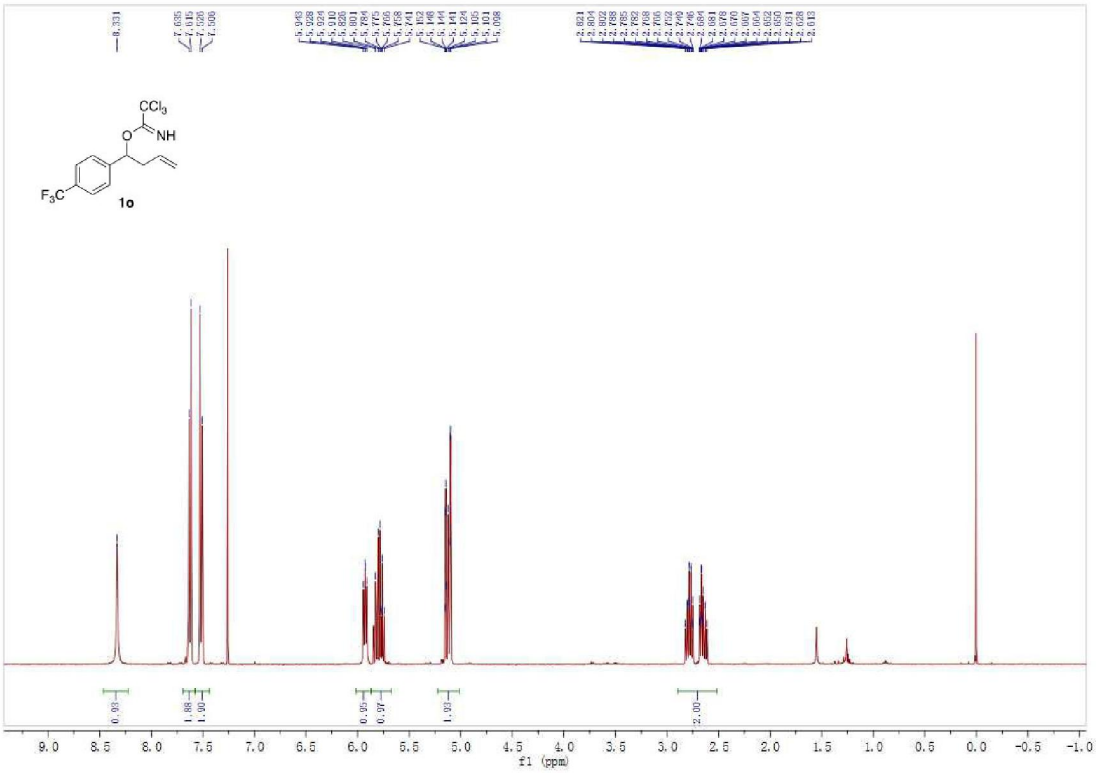
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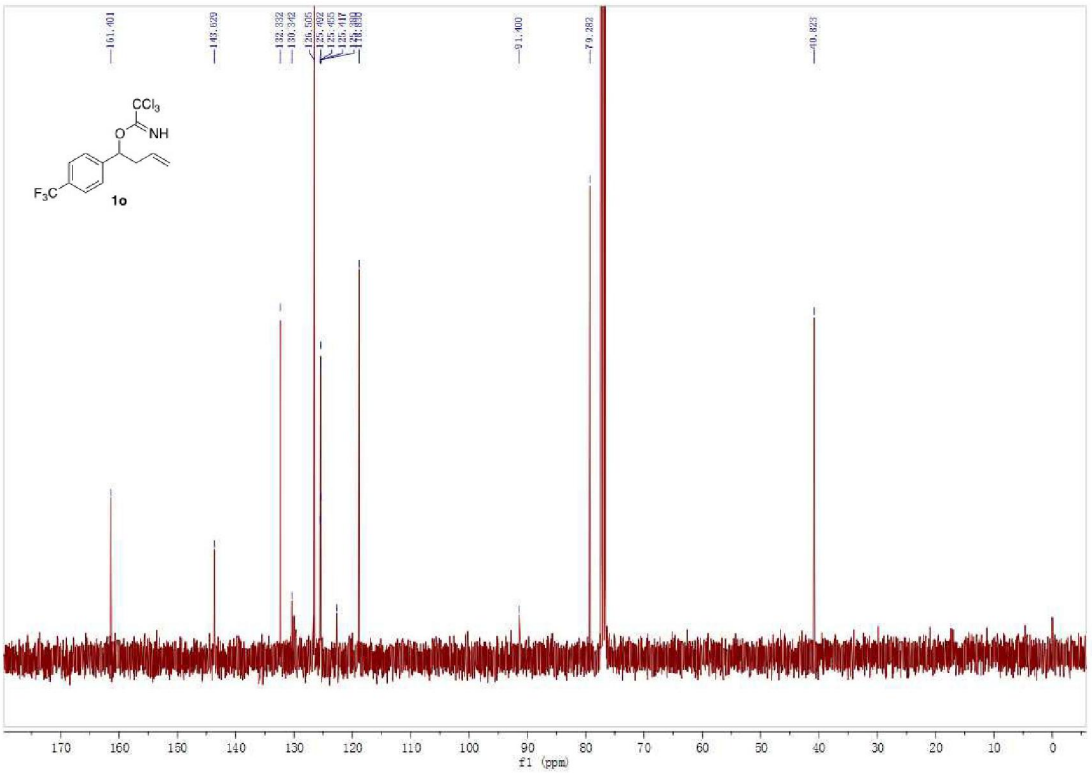
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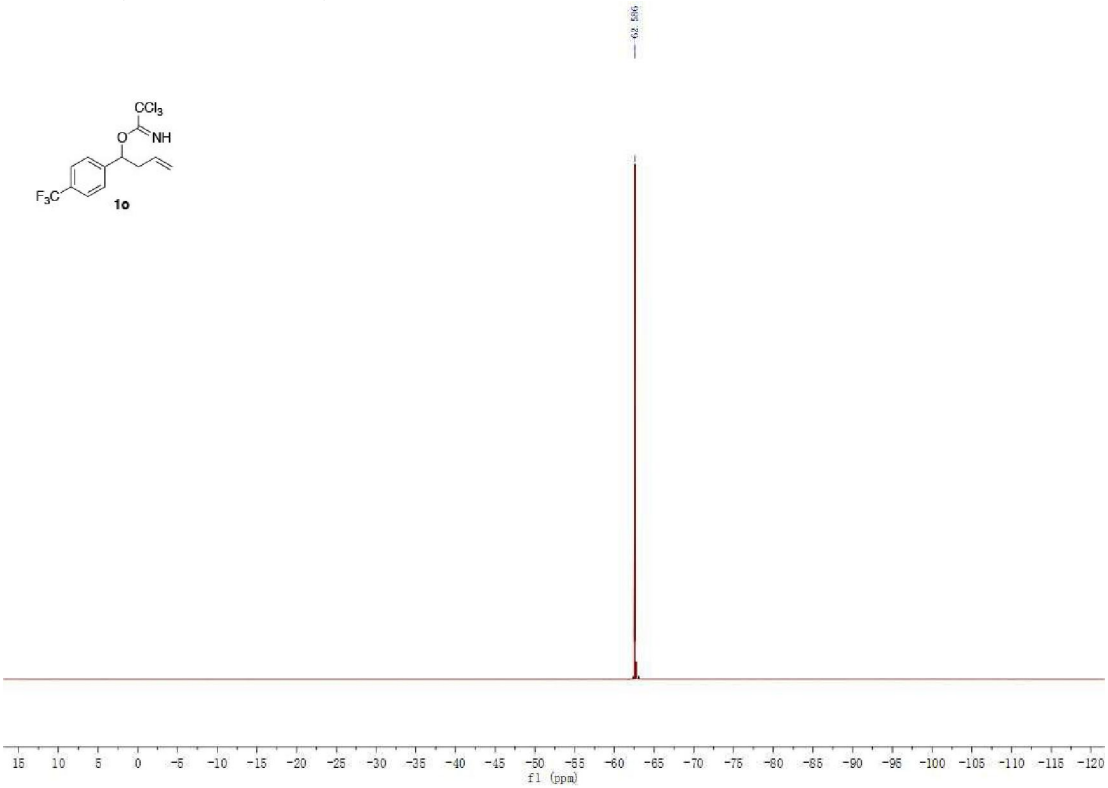
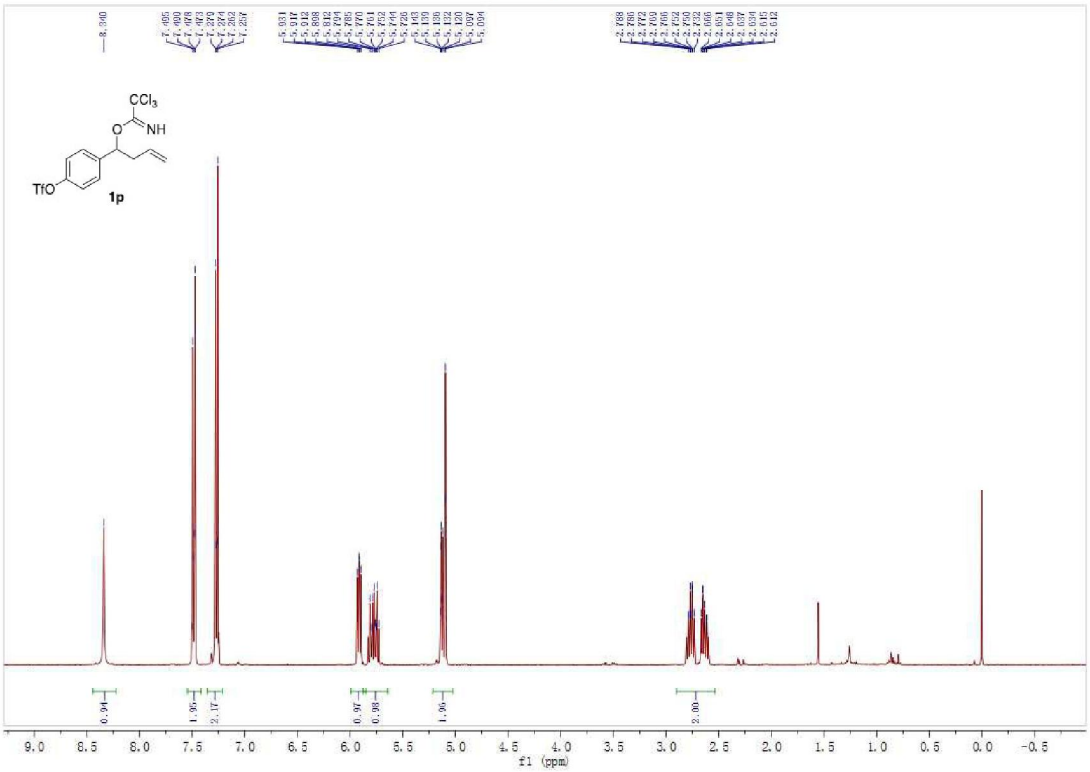
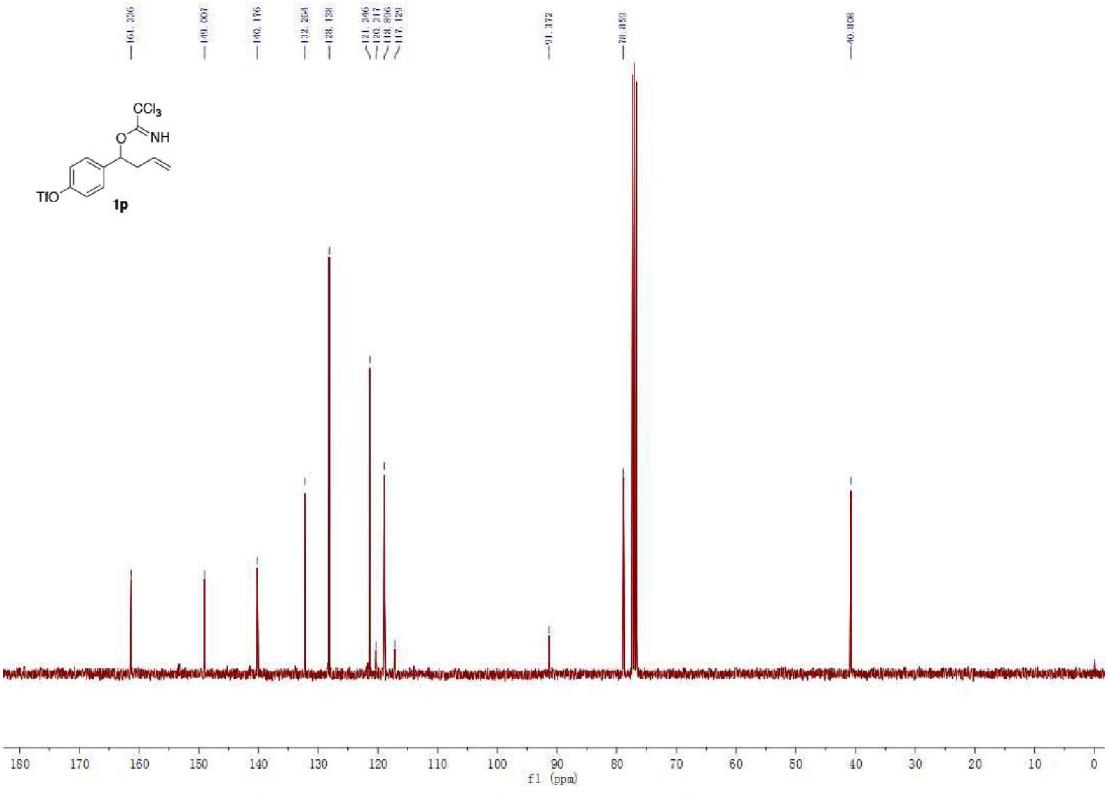
^{19}F NMR (376 MHz, $CDCl_3$)



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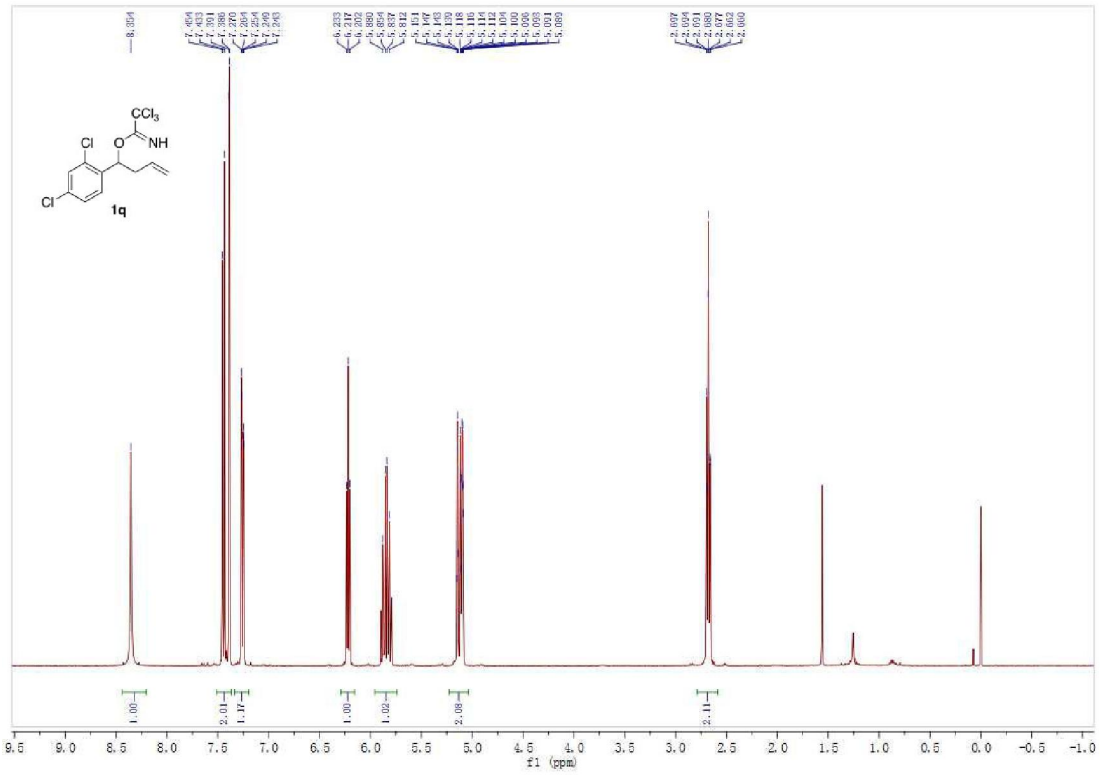
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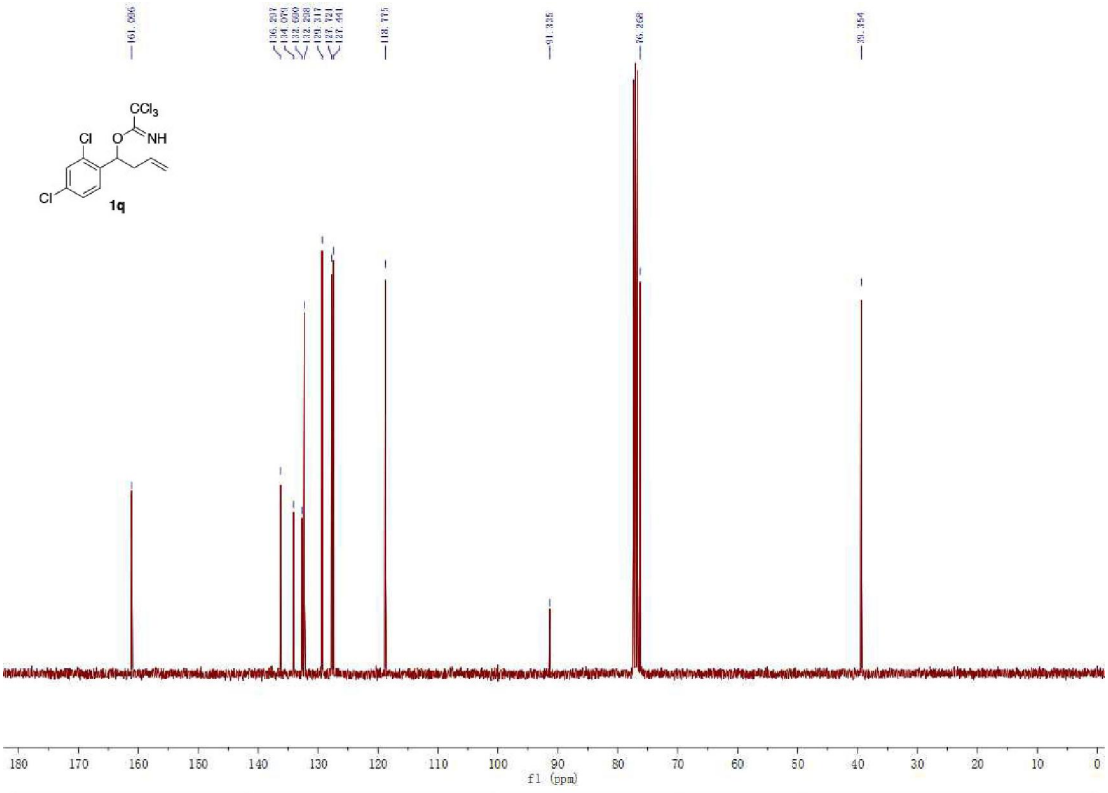
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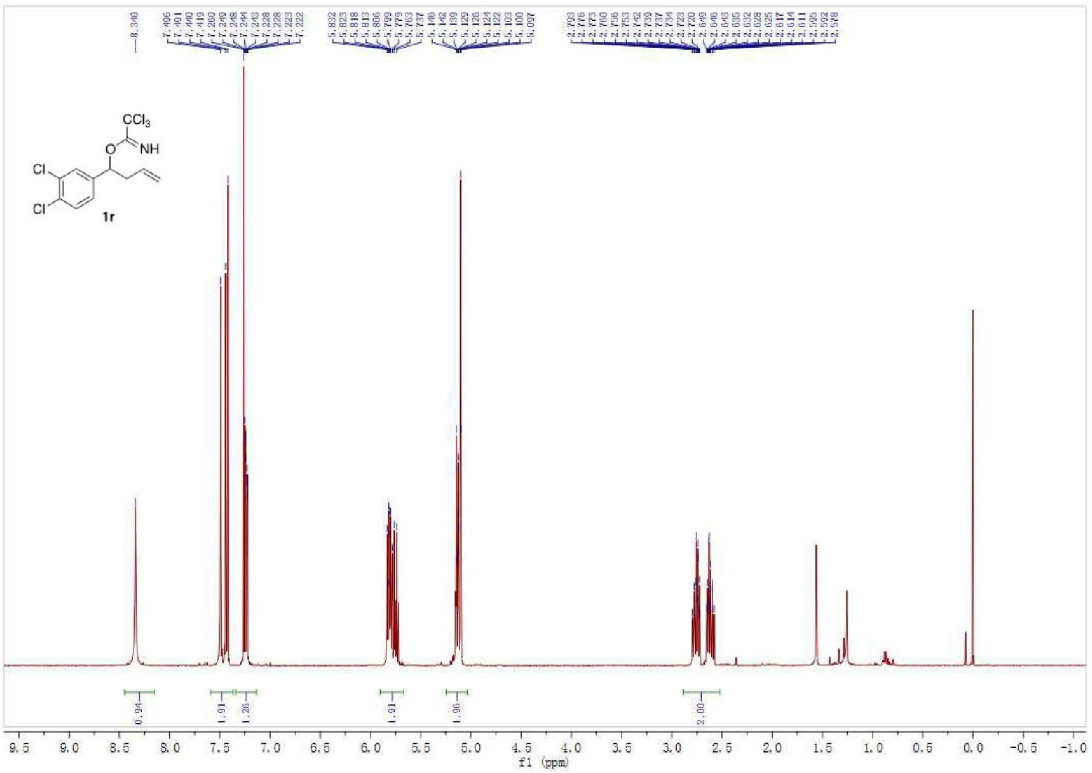
Cl
1q
f1 (ppm)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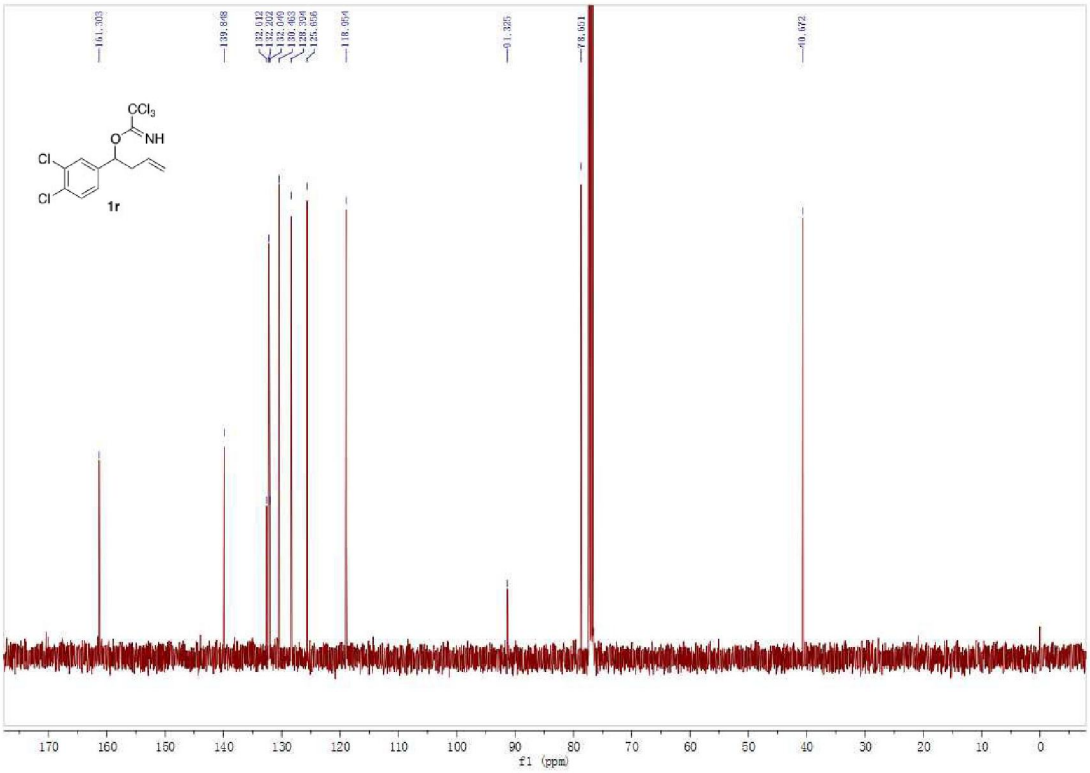
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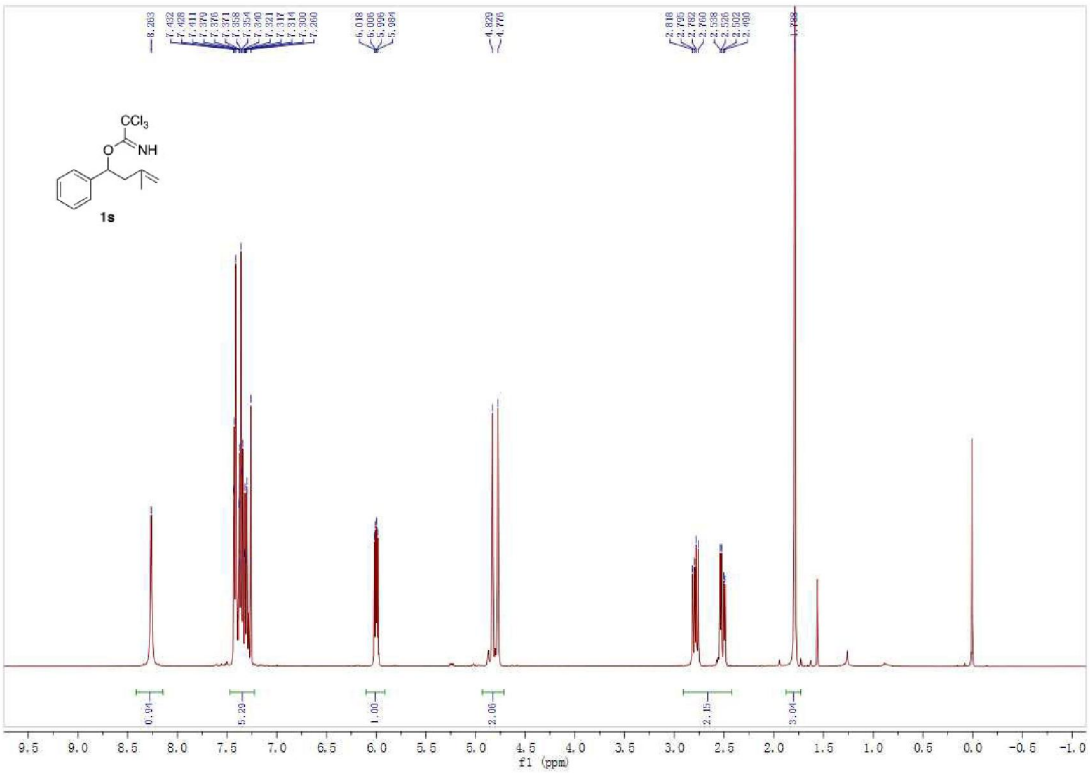
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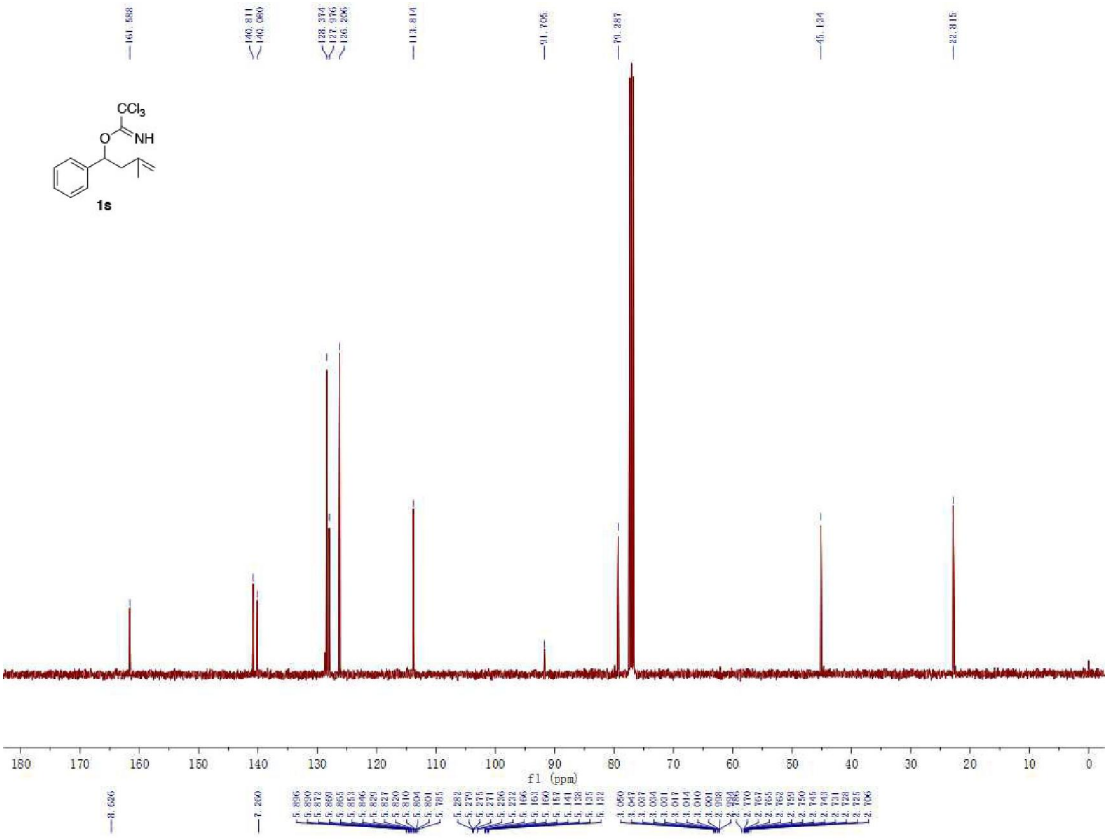
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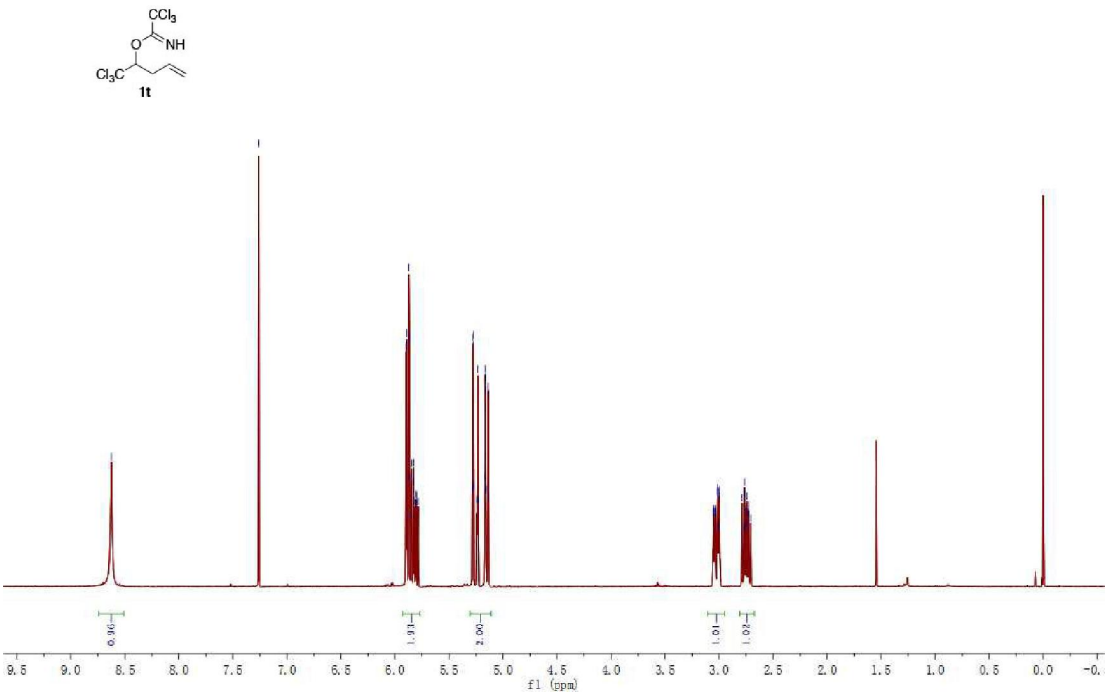
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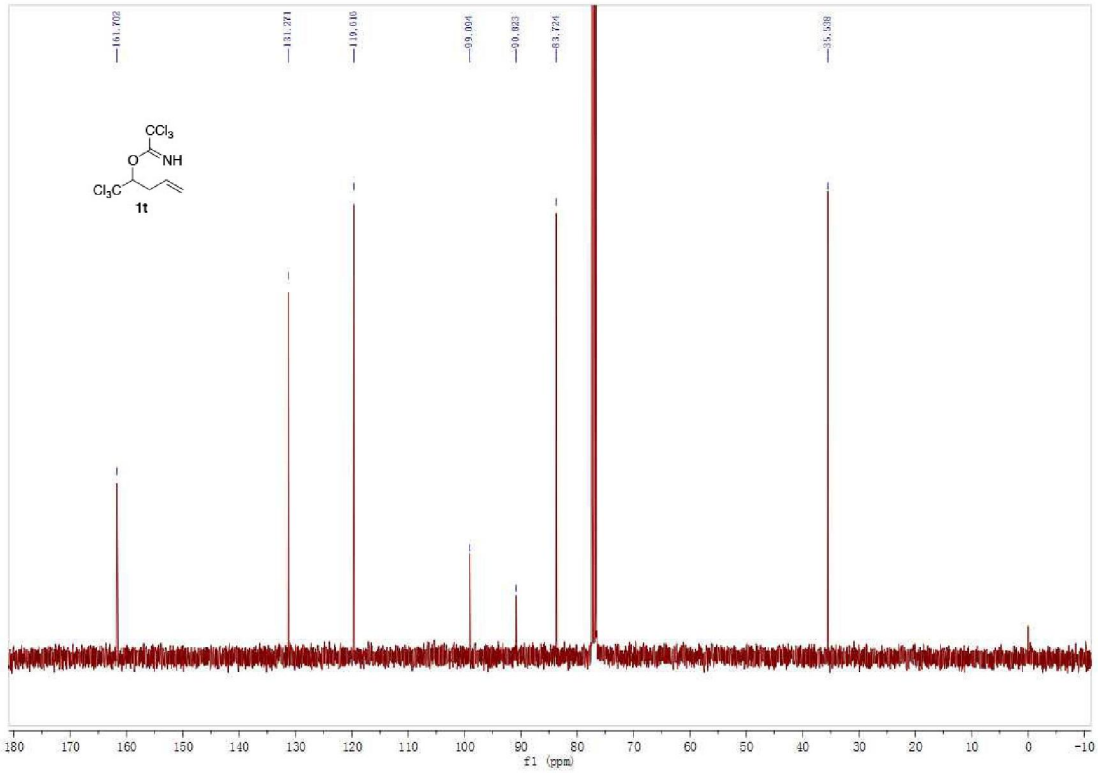
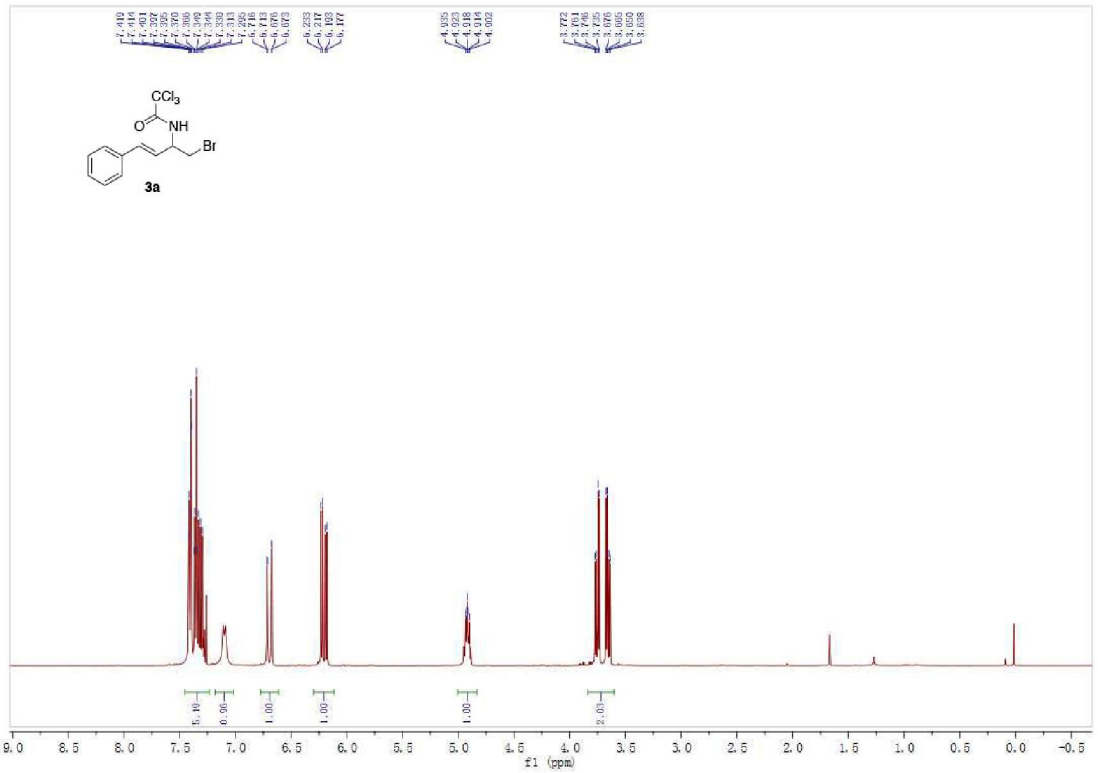
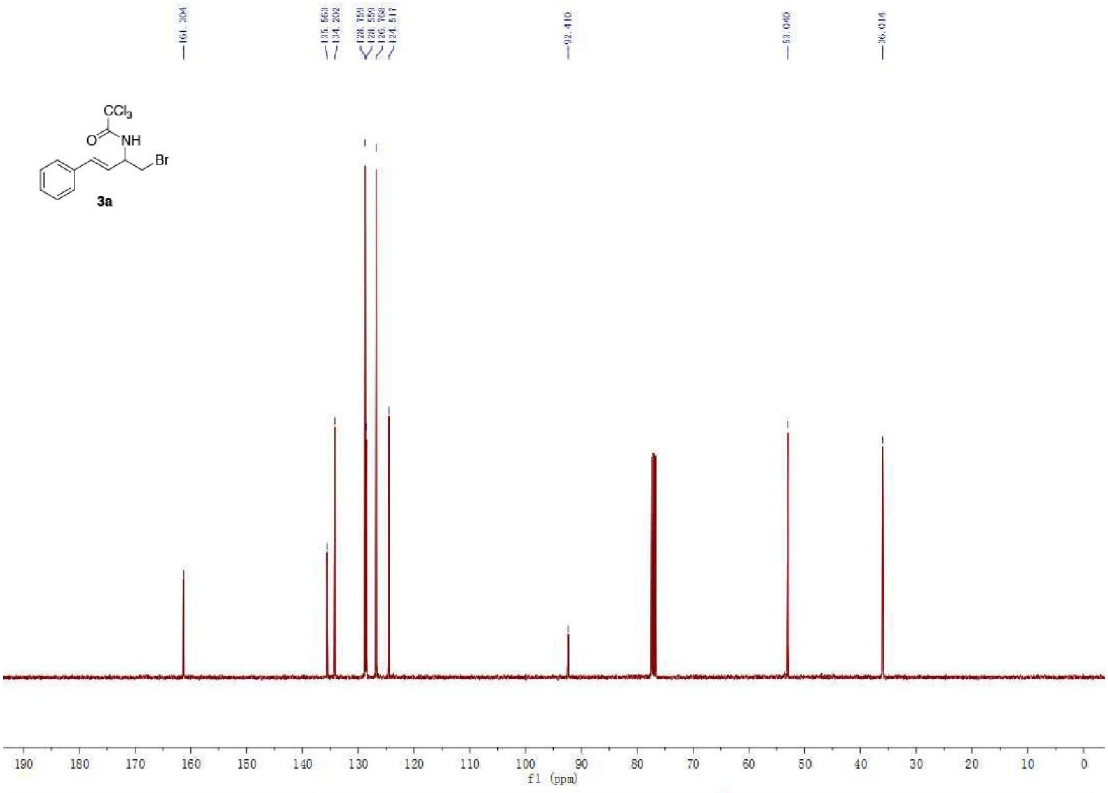
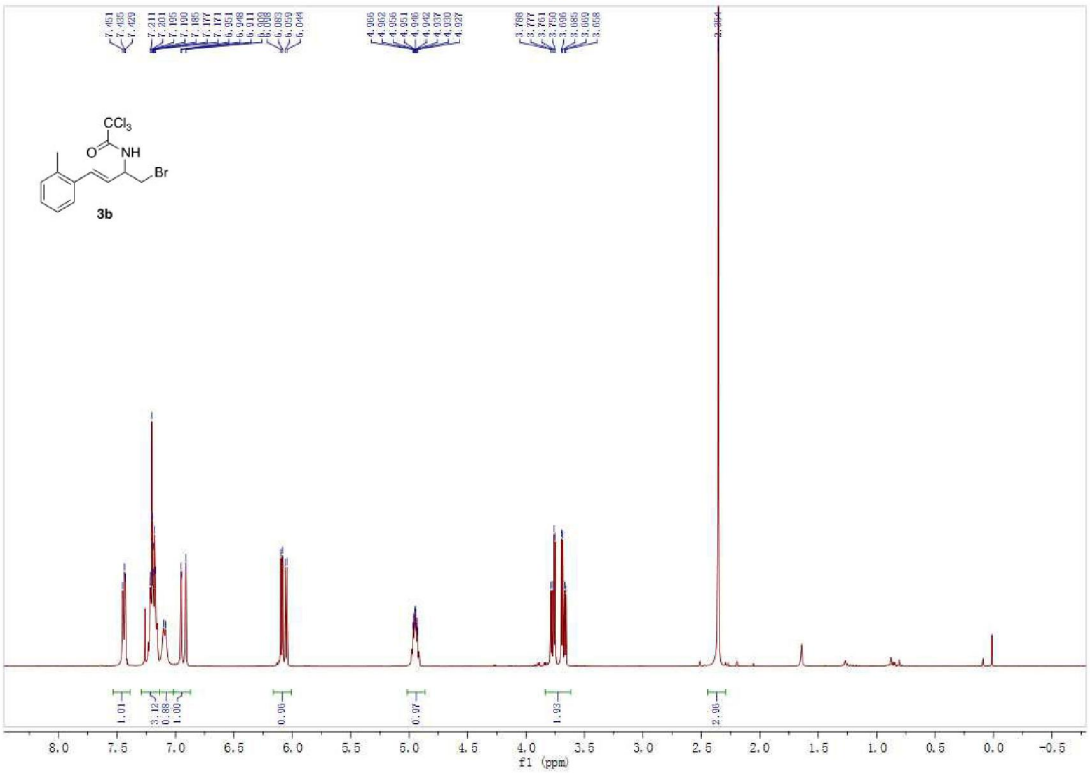
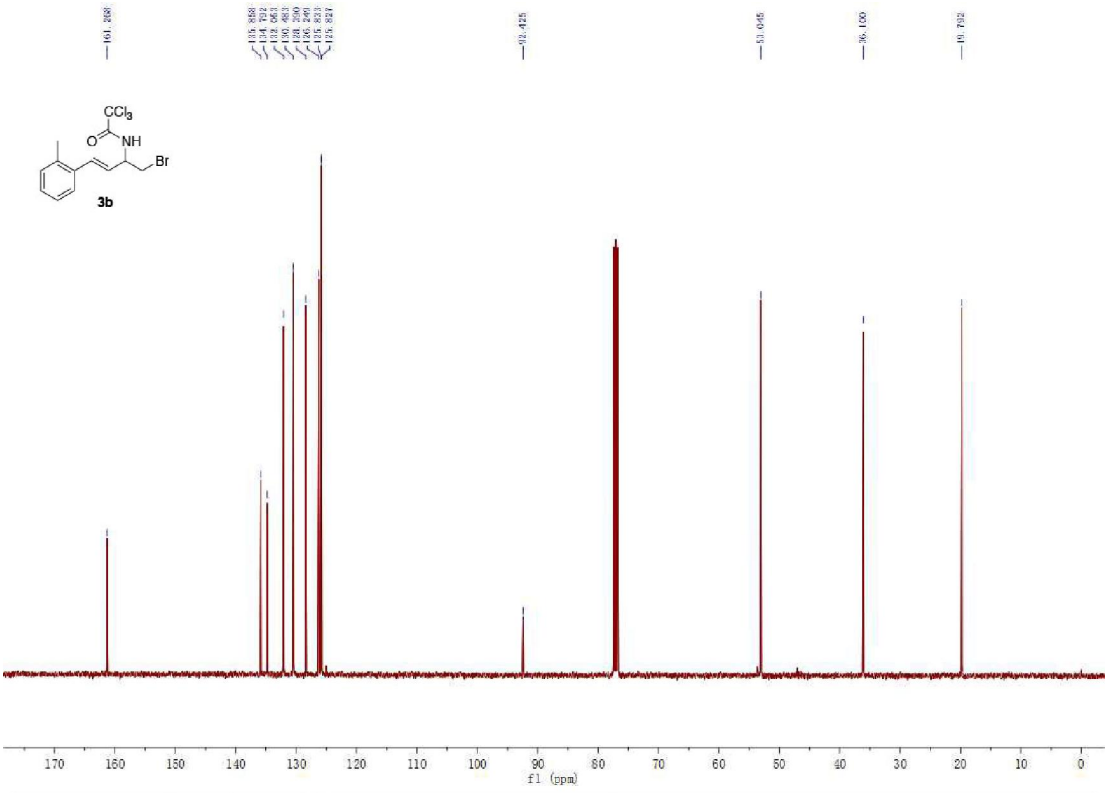
1t
f1 (ppm)

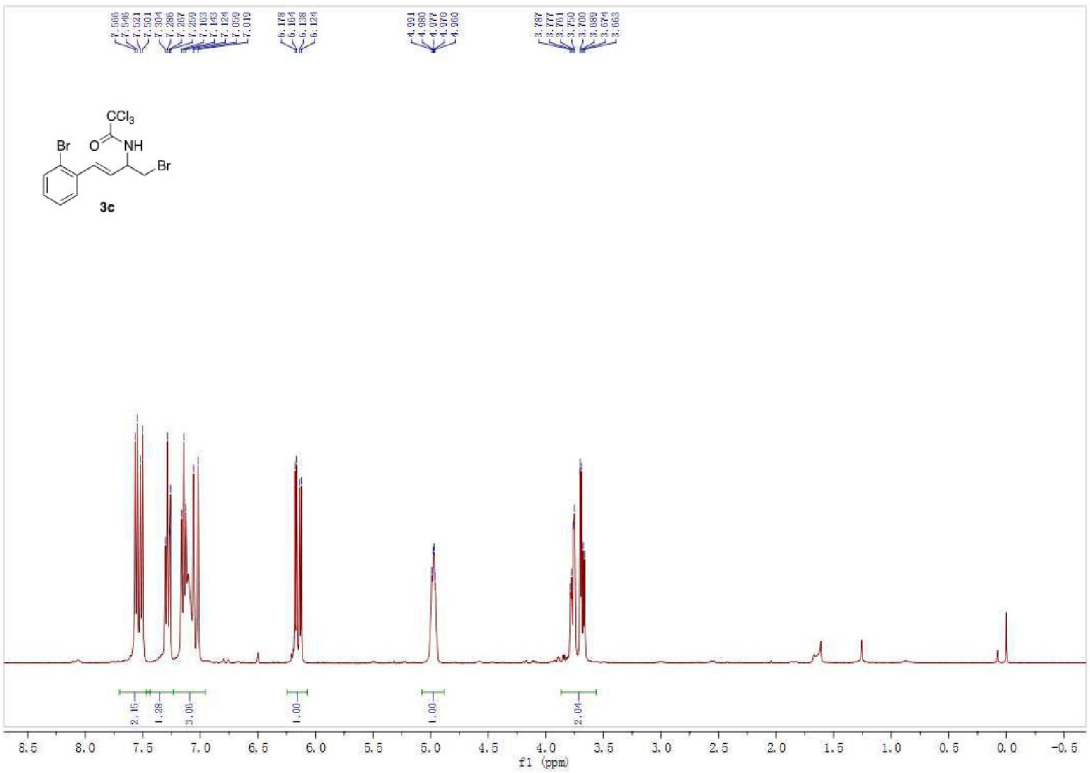

161.702
131.271
119.016
99.094
90.823
83.724
35.538
CCl3
O
NH
Cl3C
1t
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

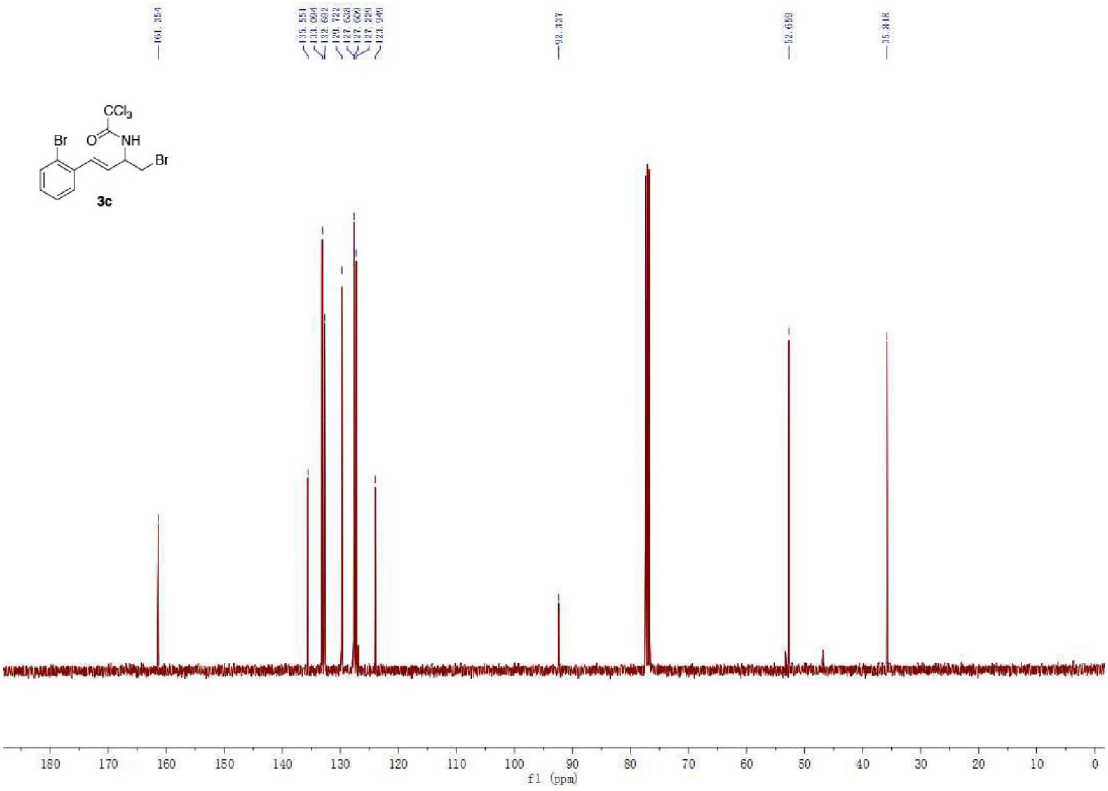

CCl3
O
NH
Br
3a
5.10
0.96
1.00
1.00
1.00
2.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

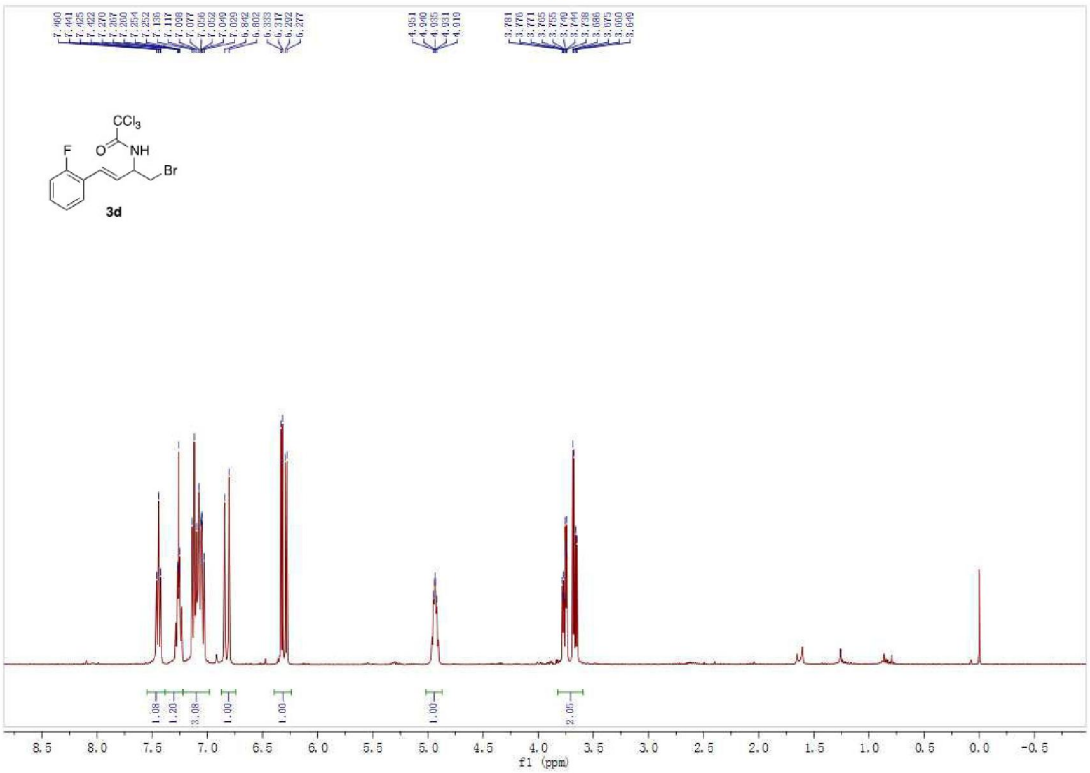

CCl3
O
NH
Br
3a
161.204
135.563
134.202
128.750
128.555
126.958
124.517
92.410
53.049
36.014
f1 (ppm)

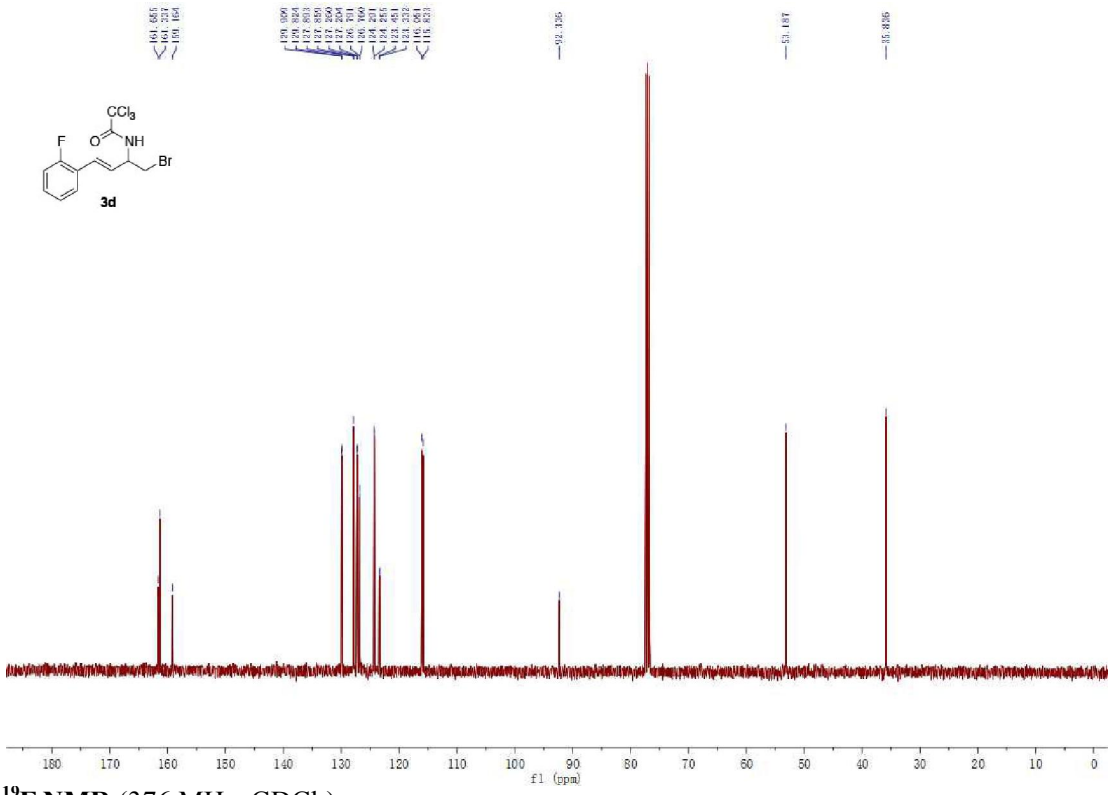

CCl3
O
NH
Br
3b
1.01
3.12
0.88
1.00
0.98
0.97
1.93
2.00
f1 (ppm)


CCl3
O
NH
Br
3b
f1 (ppm)

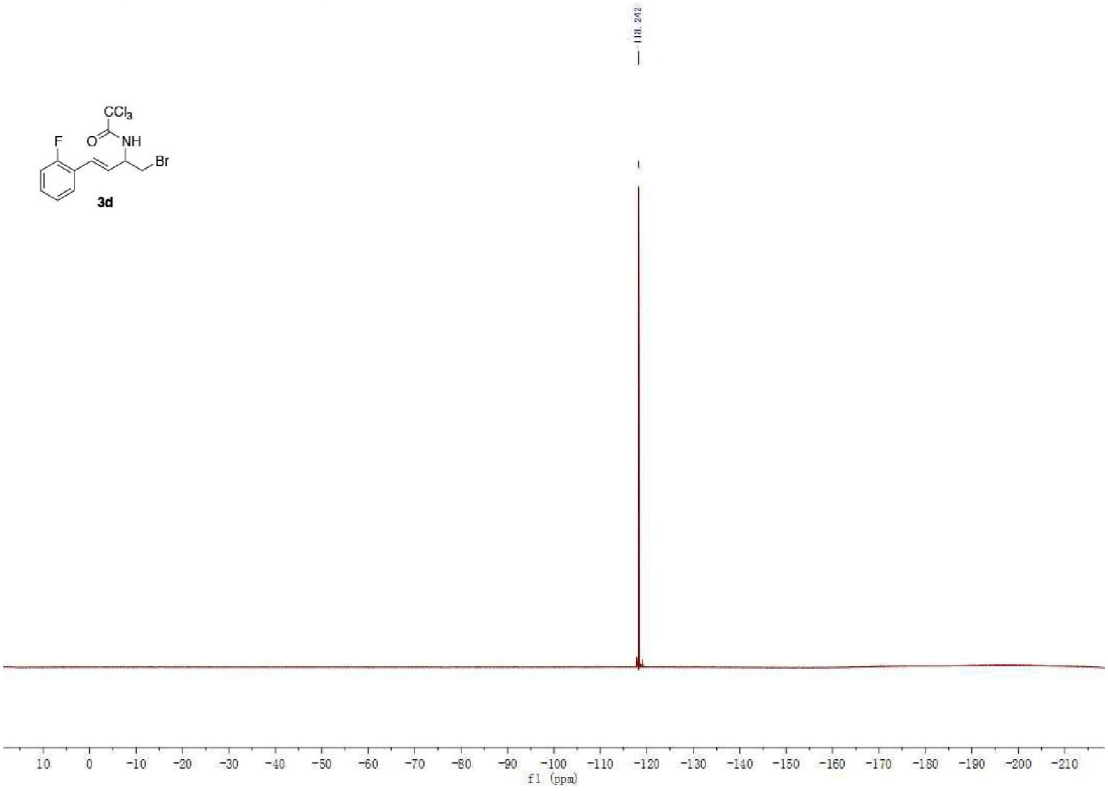

CCl3
Br
O
NH
Br
3c
f1 (ppm)

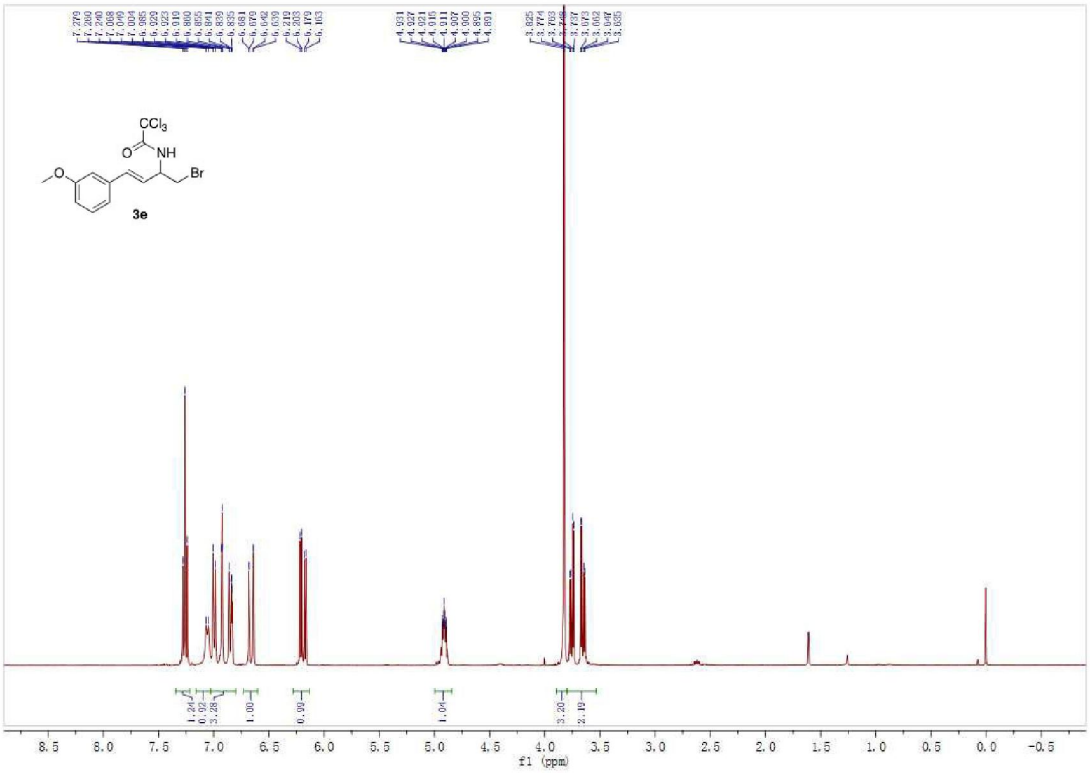

CCl3
O
NH
Br
Br
3c
f1 (ppm)

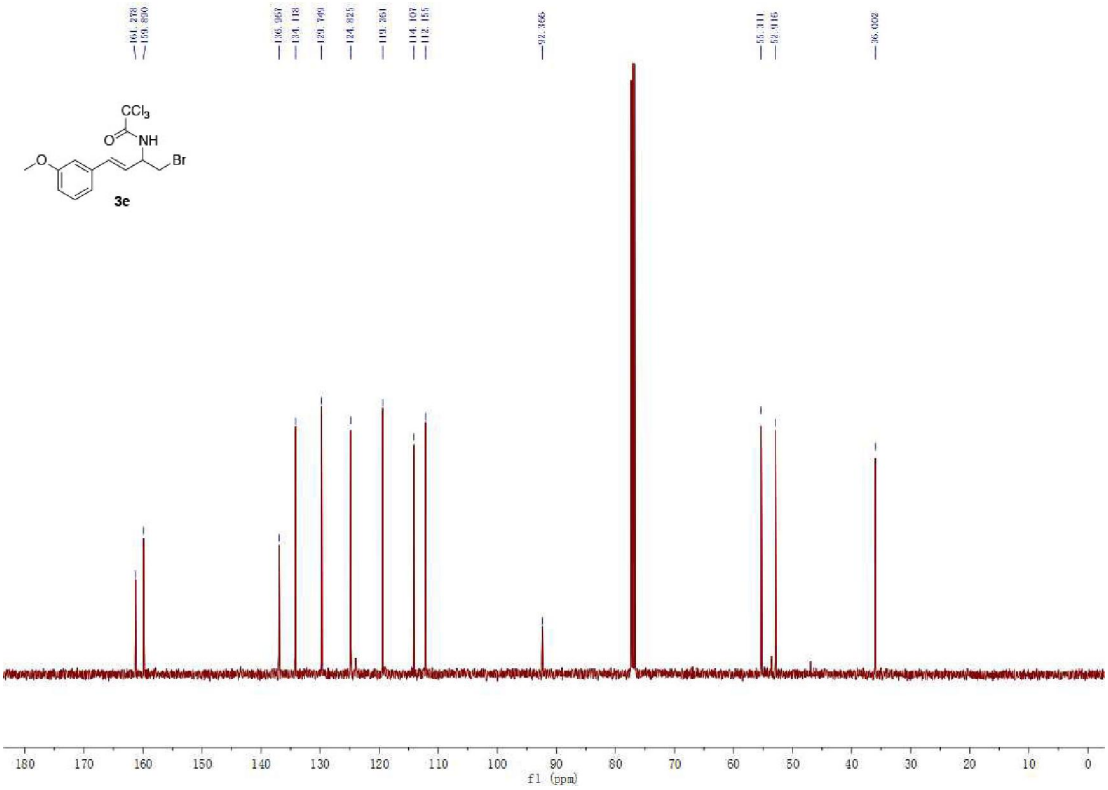

CCl3
O
NH
F
Br
3d
f1 (ppm)

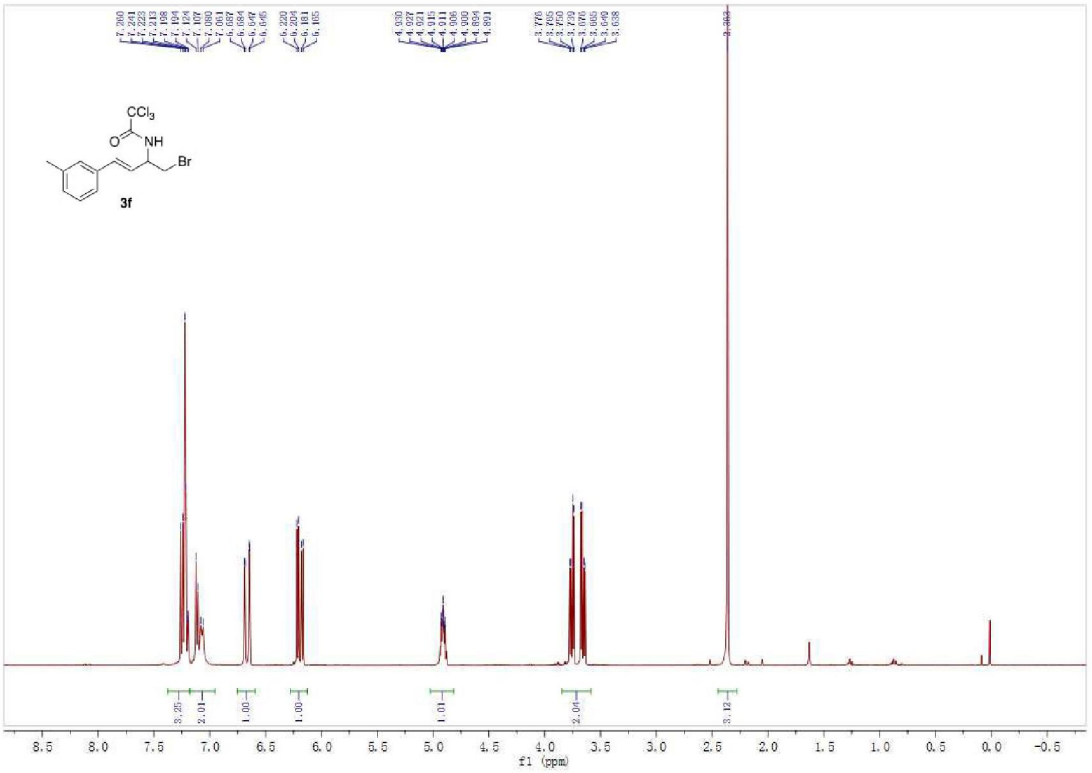


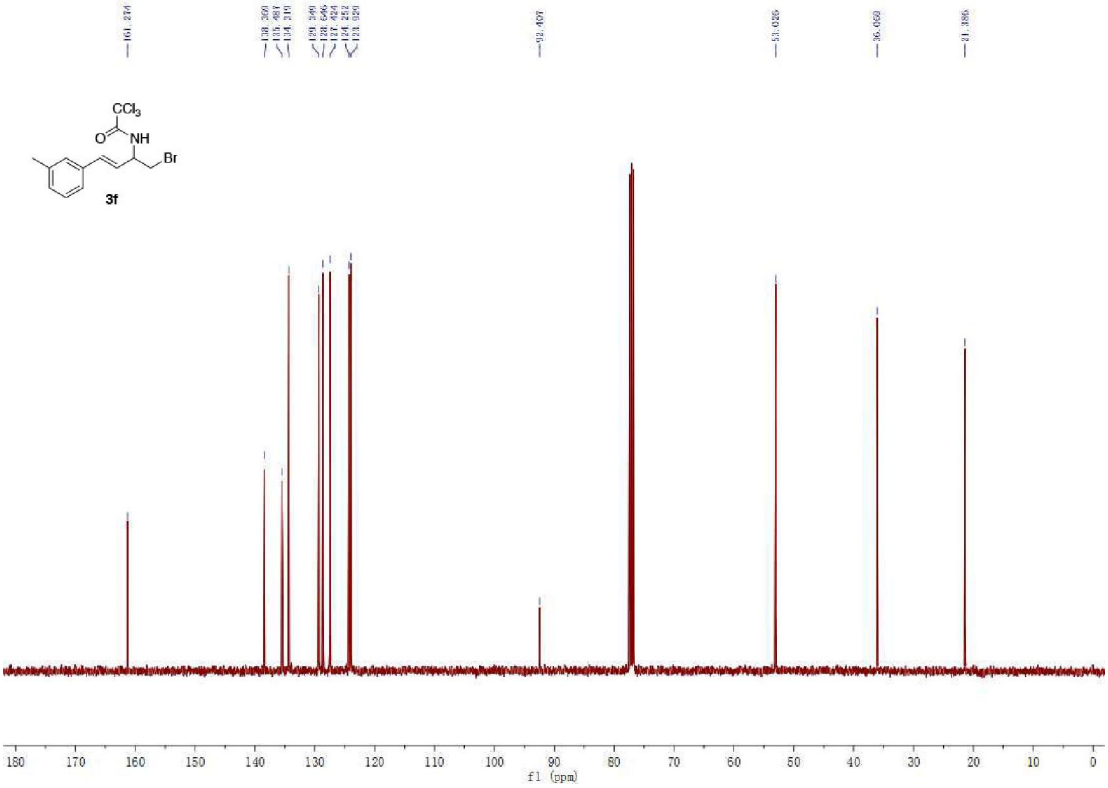
^{19}F NMR (376 MHz, $CDCl_3$)

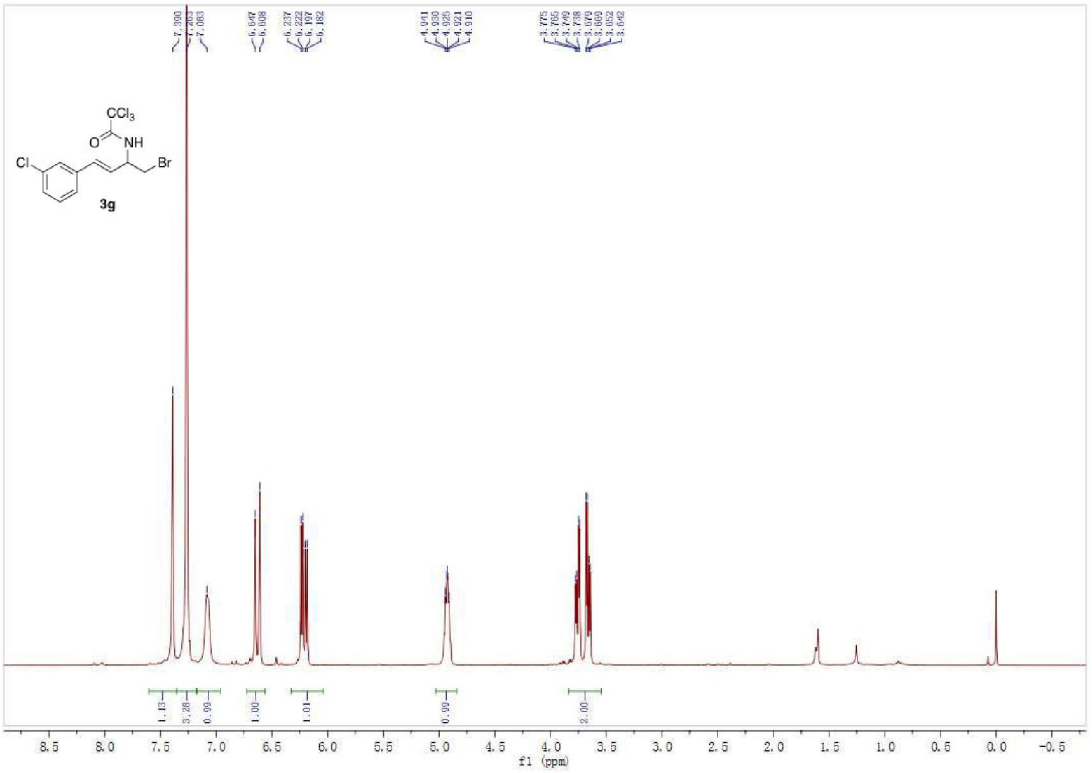


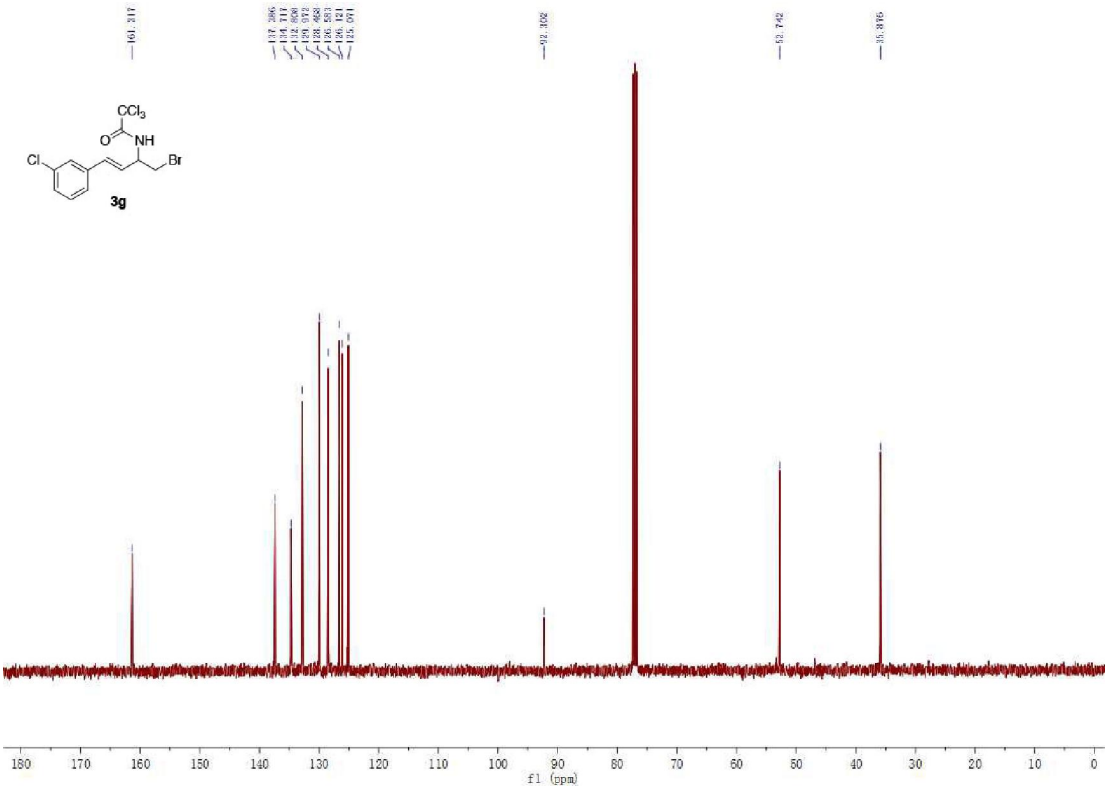

CCl3
NH
O
Br
3e
f1 (ppm)

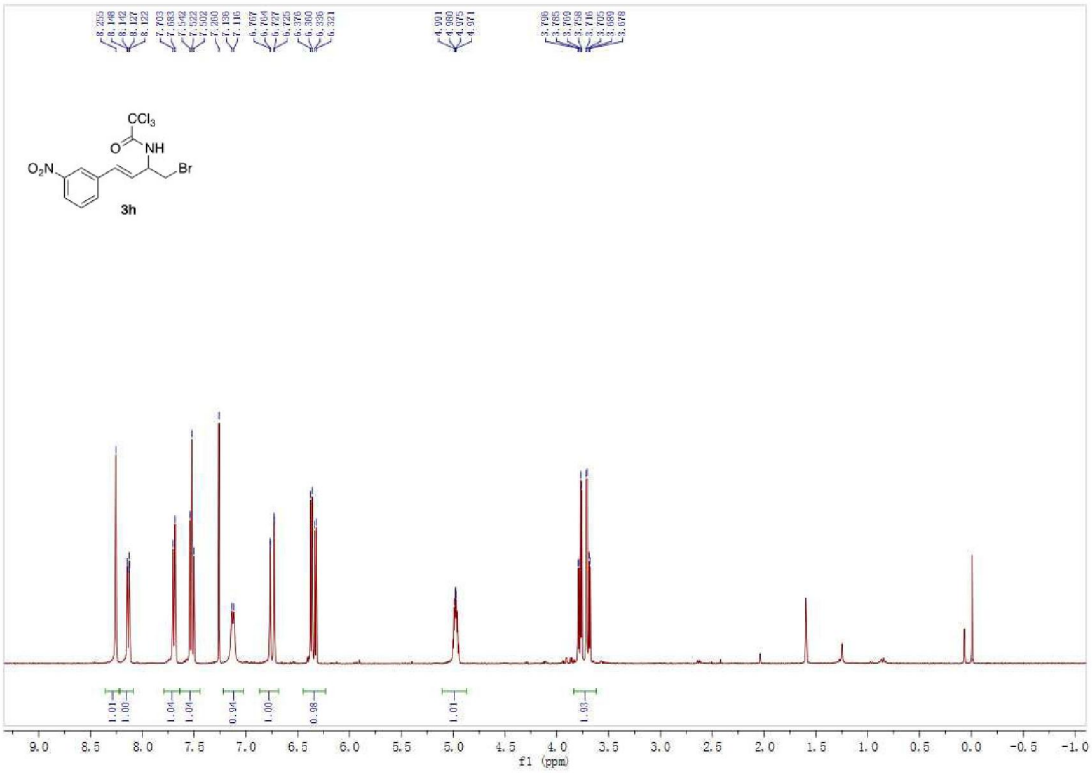

CCl3
NH
O
Br
3e
f1 (ppm)

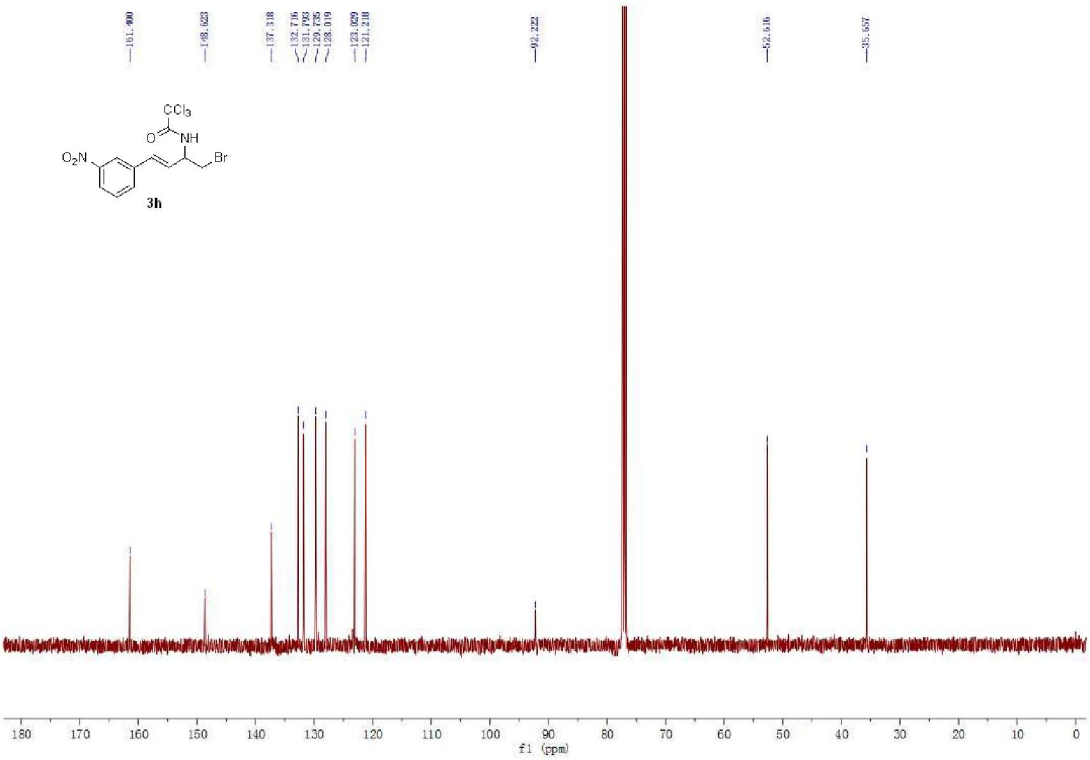

CCl3
O
NH
Br
3f
f1 (ppm)

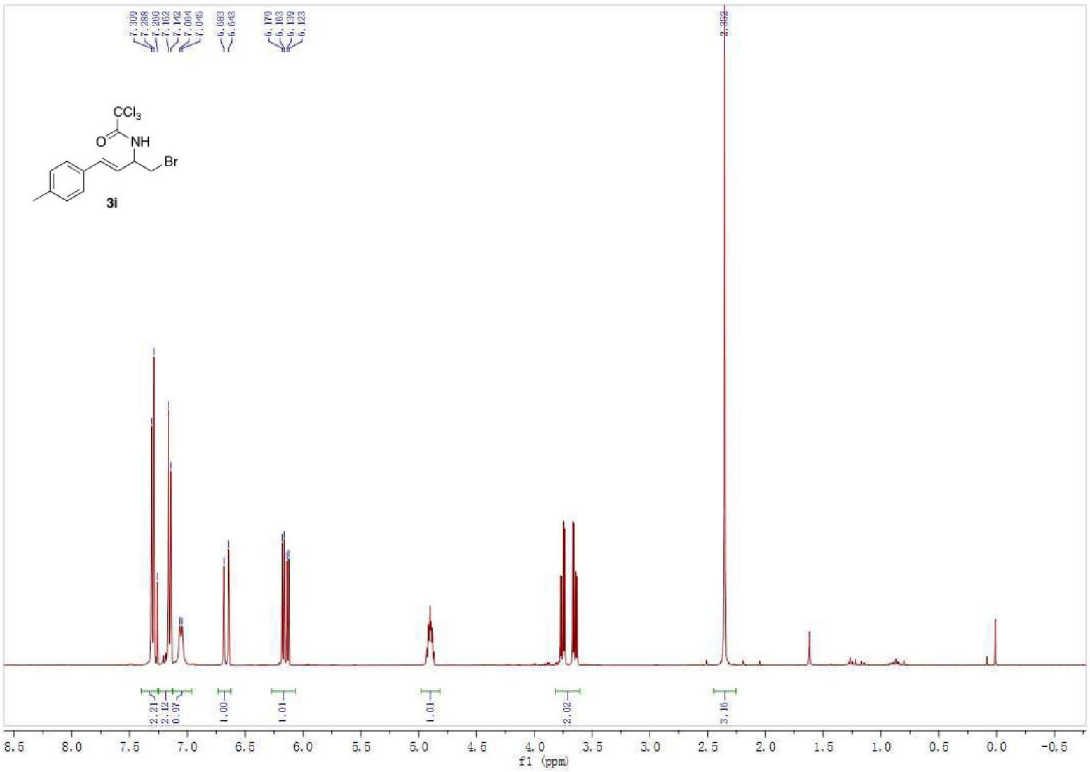

CCl3
O
NH
Br
3f
f1 (ppm)

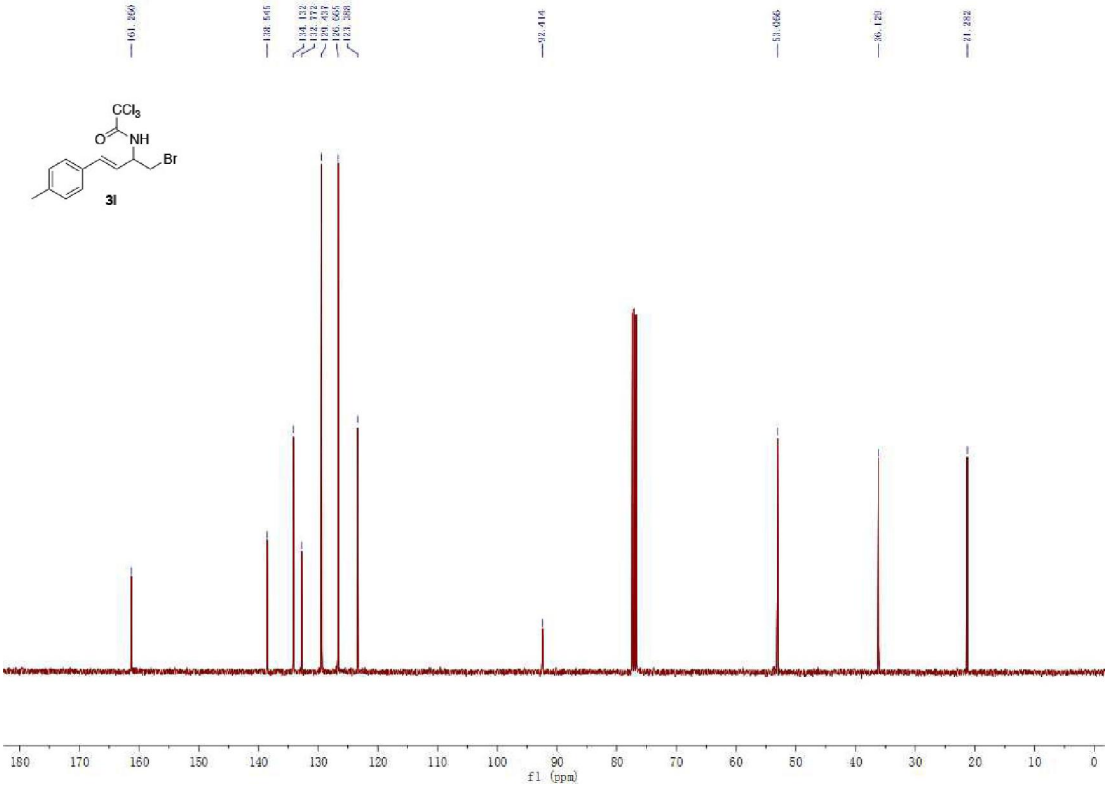

CCl3
O
NH
Cl
Br
3g
f1 (ppm)

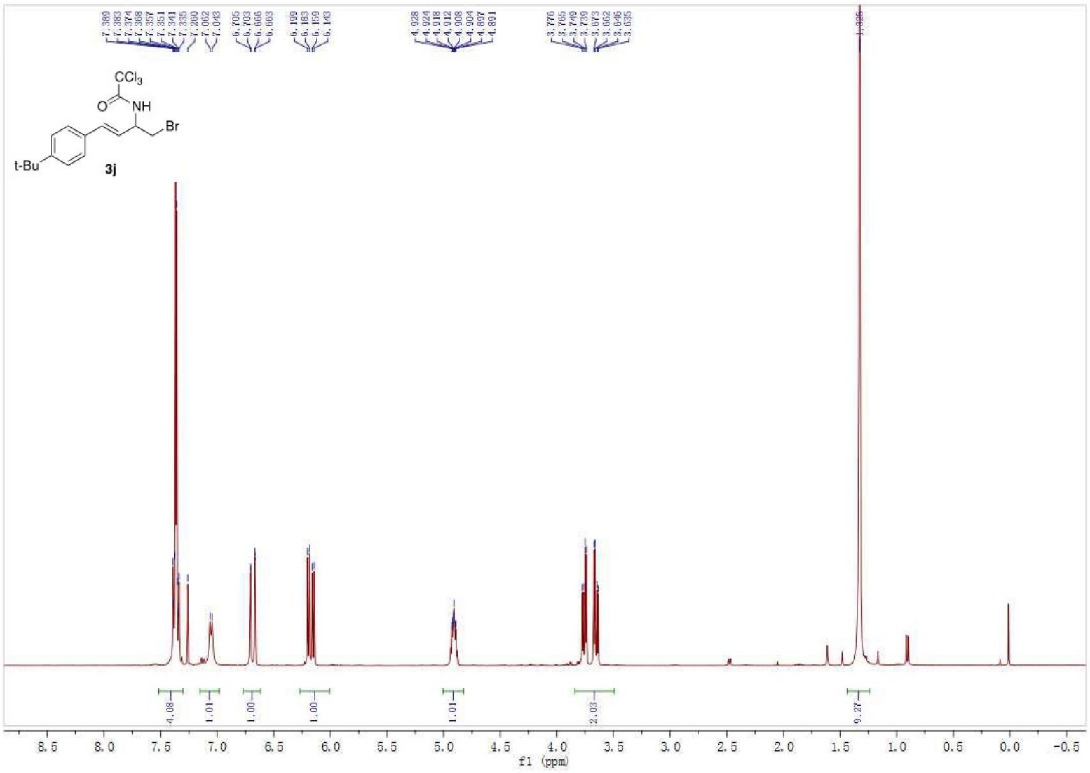

CCl3
O
NH
Cl
Br
3g
f1 (ppm)

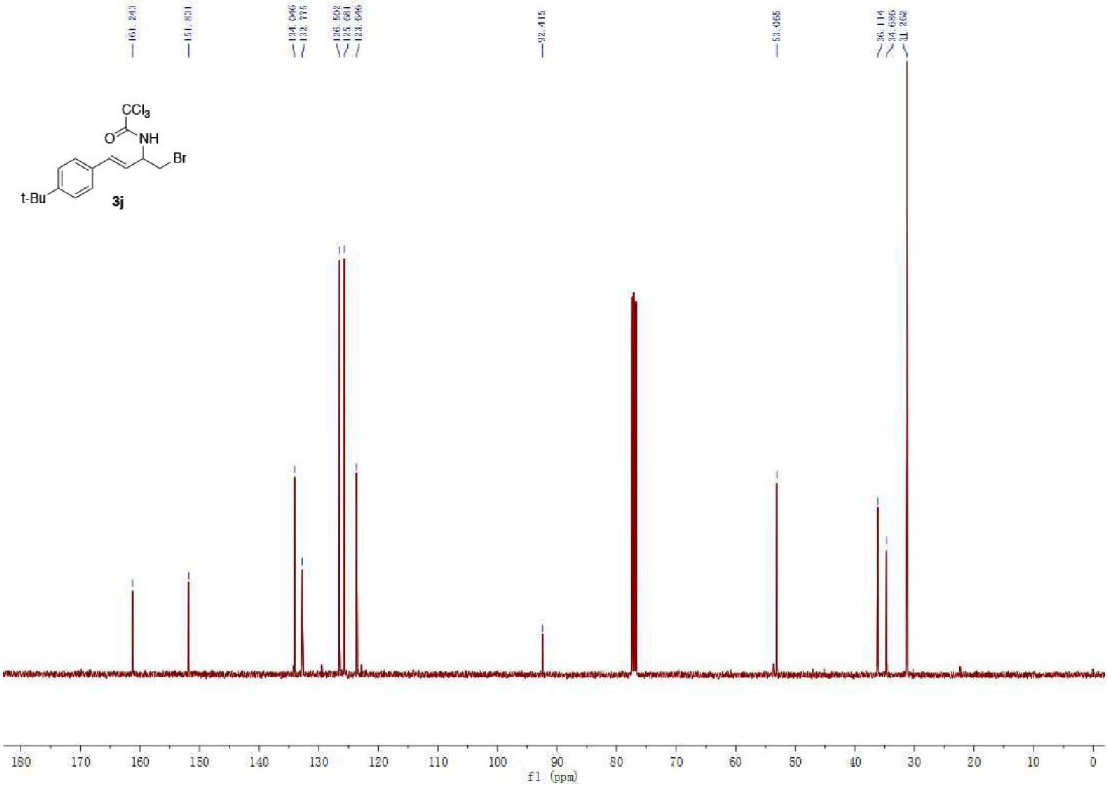

CCl3
O
NH
O2N
Br
3h
f1 (ppm)

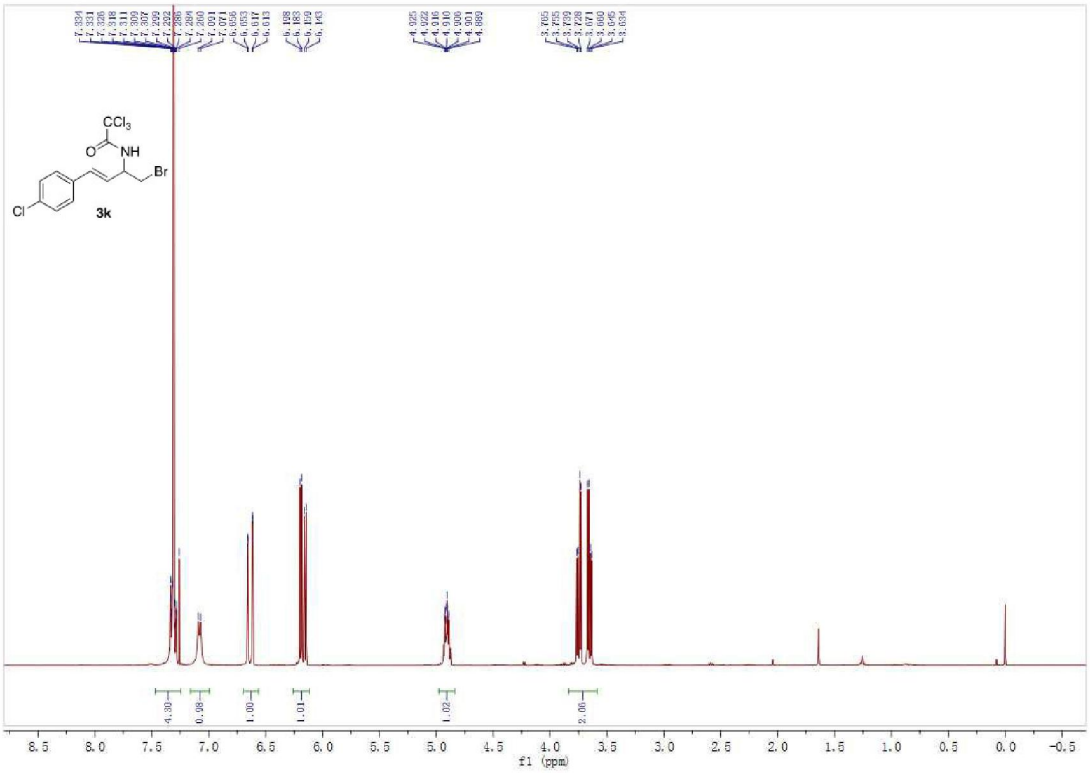

CCl3
O
NH
O2N
Br
3h
f1 (ppm)

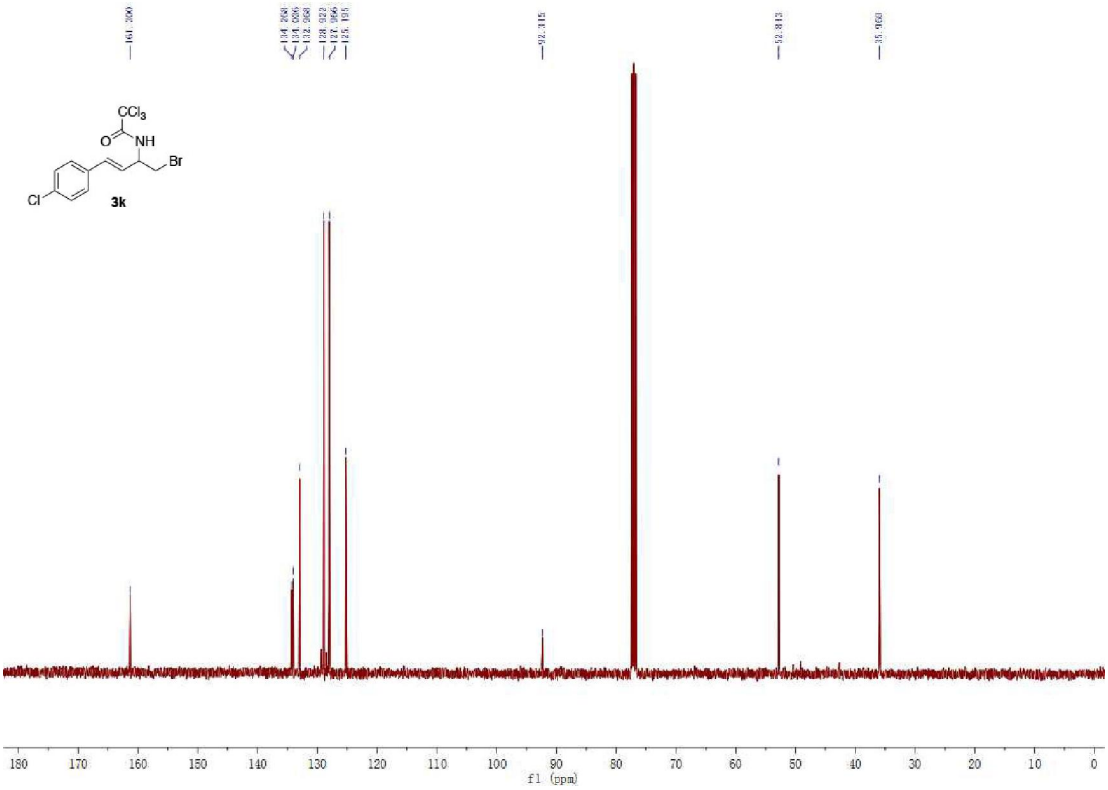

CCl3
O
NH
Br
3i
f1 (ppm)

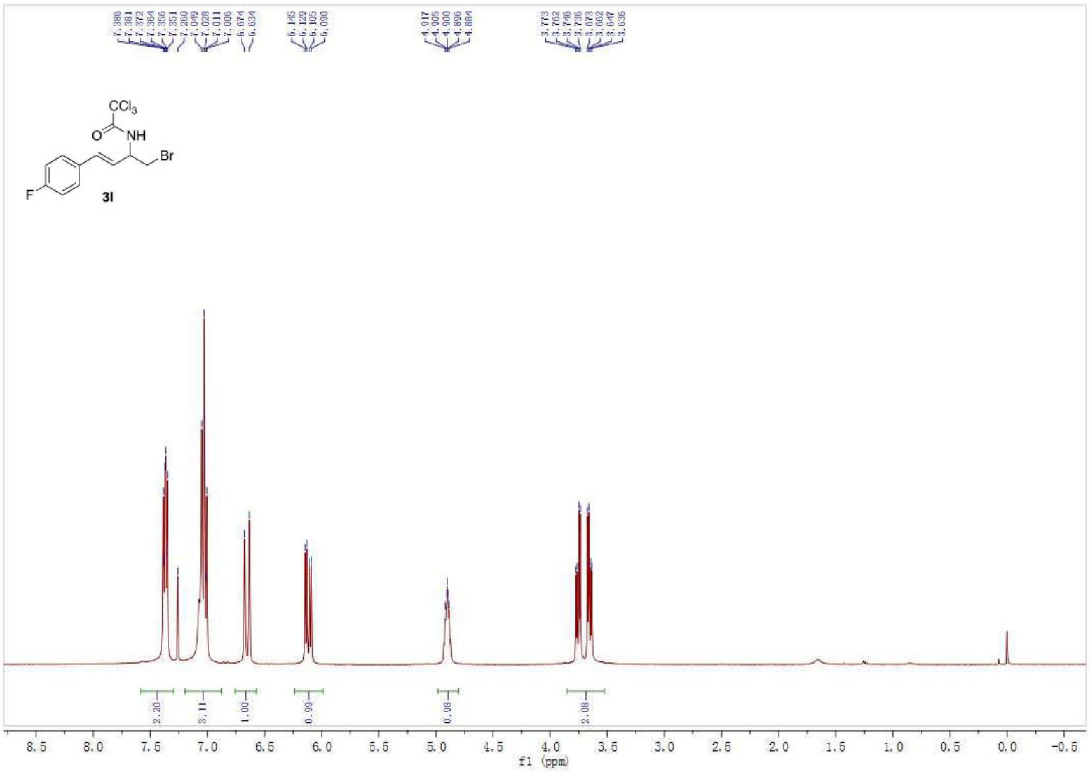

CCl3
O
NH
Br
3i
f1 (ppm)

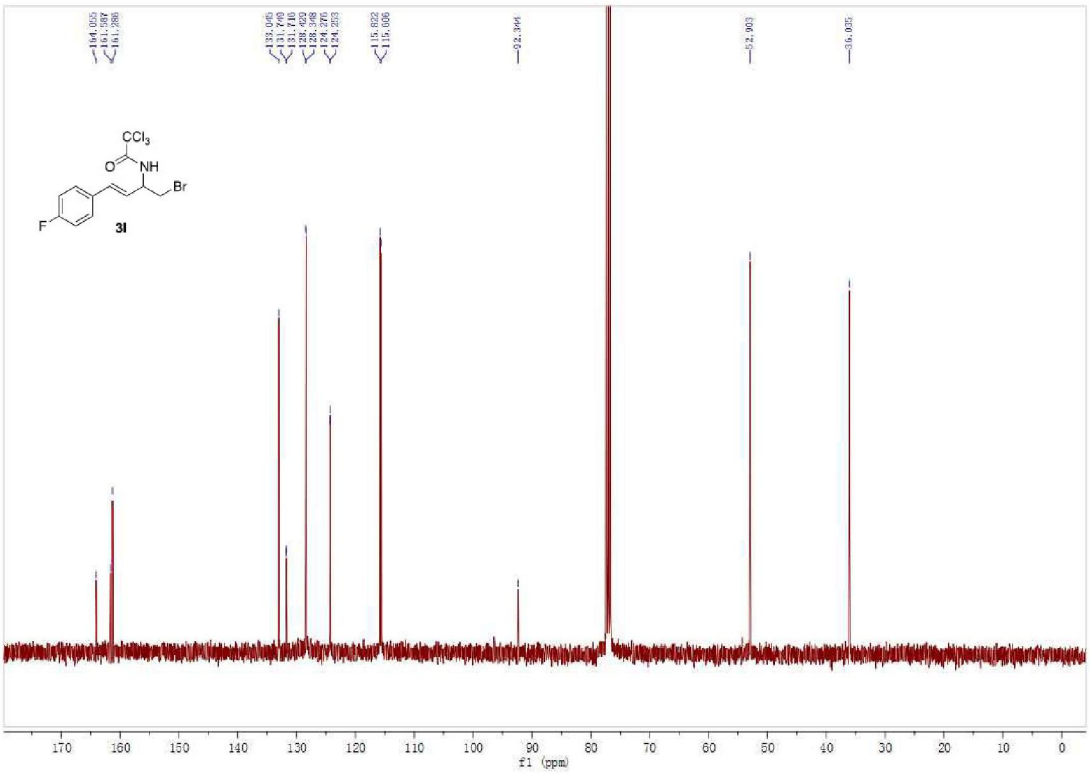

CCl3
O
NH
Br
t-Bu
3j
f1 (ppm)


CCl3
O
NH
Br
t-Bu
3j
f1 (ppm)

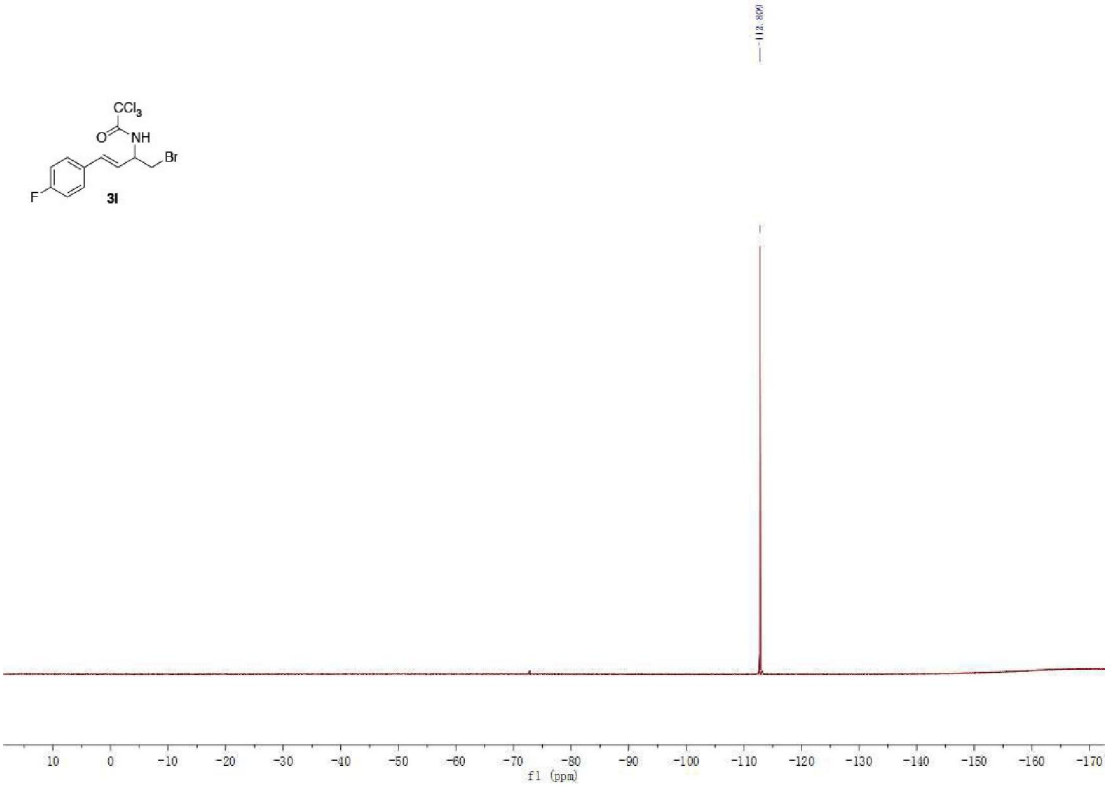

CCl3
O
NH
Br
Cl
3k
f1 (ppm)

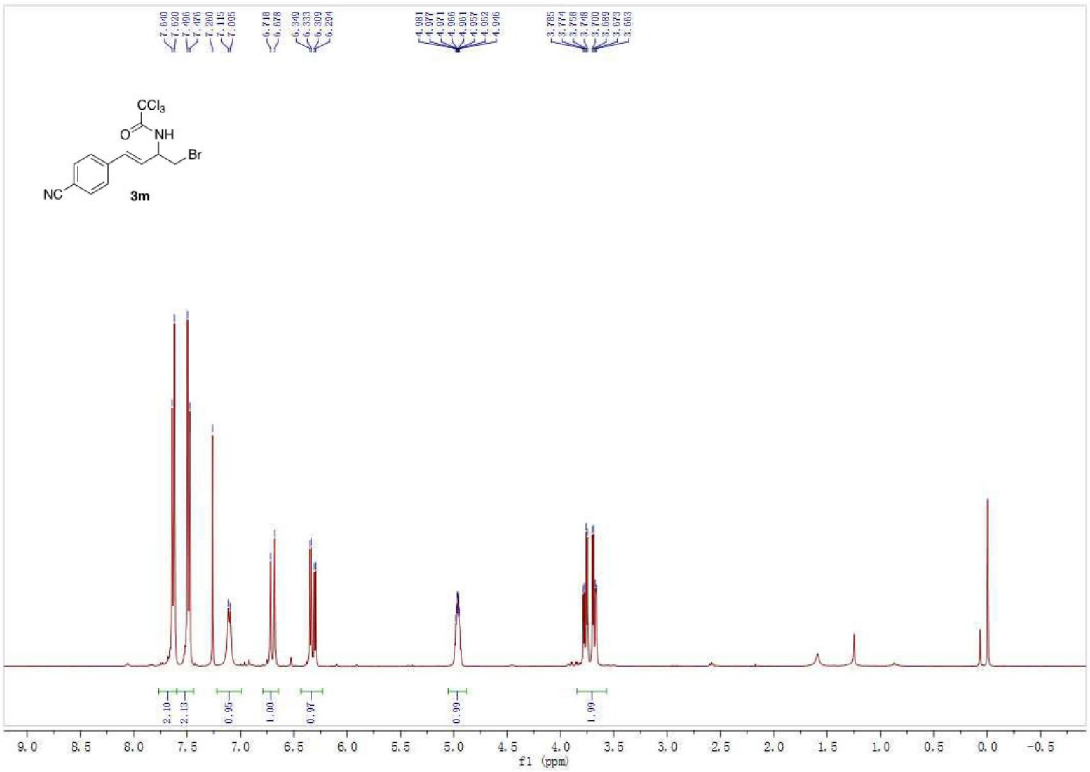

CCl3
O
NH
Br
Cl
3k
f1 (ppm)

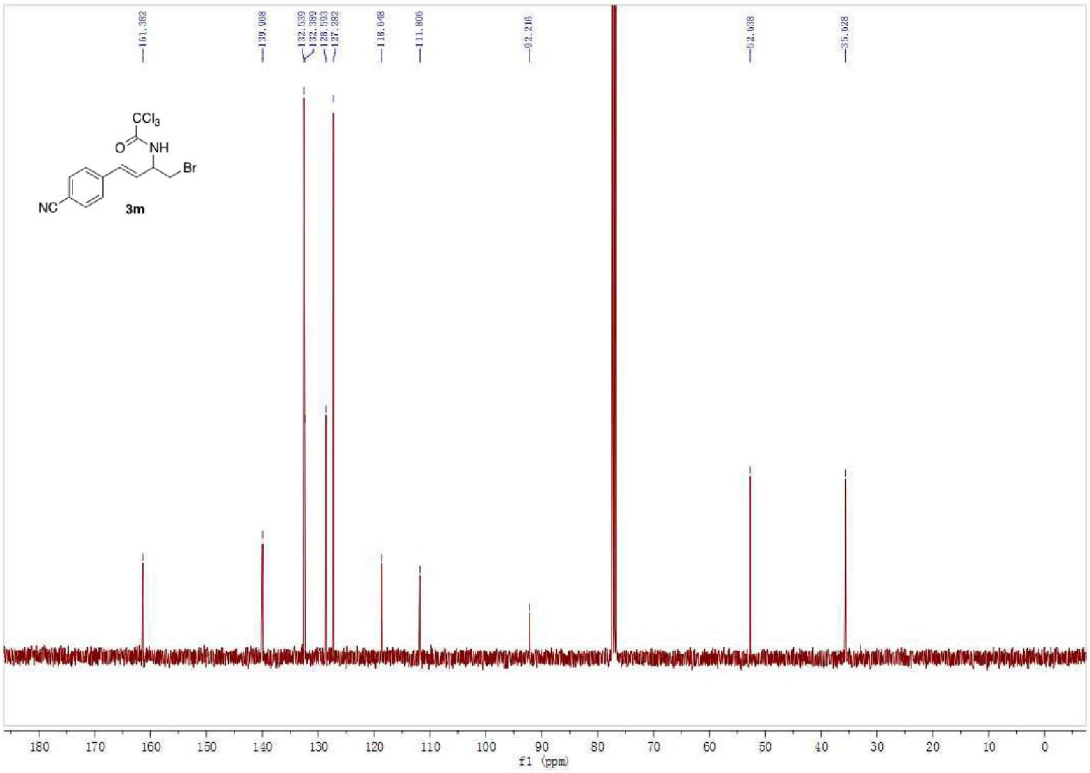

CCl3
O
NH
Br
F
3l
f1 (ppm)

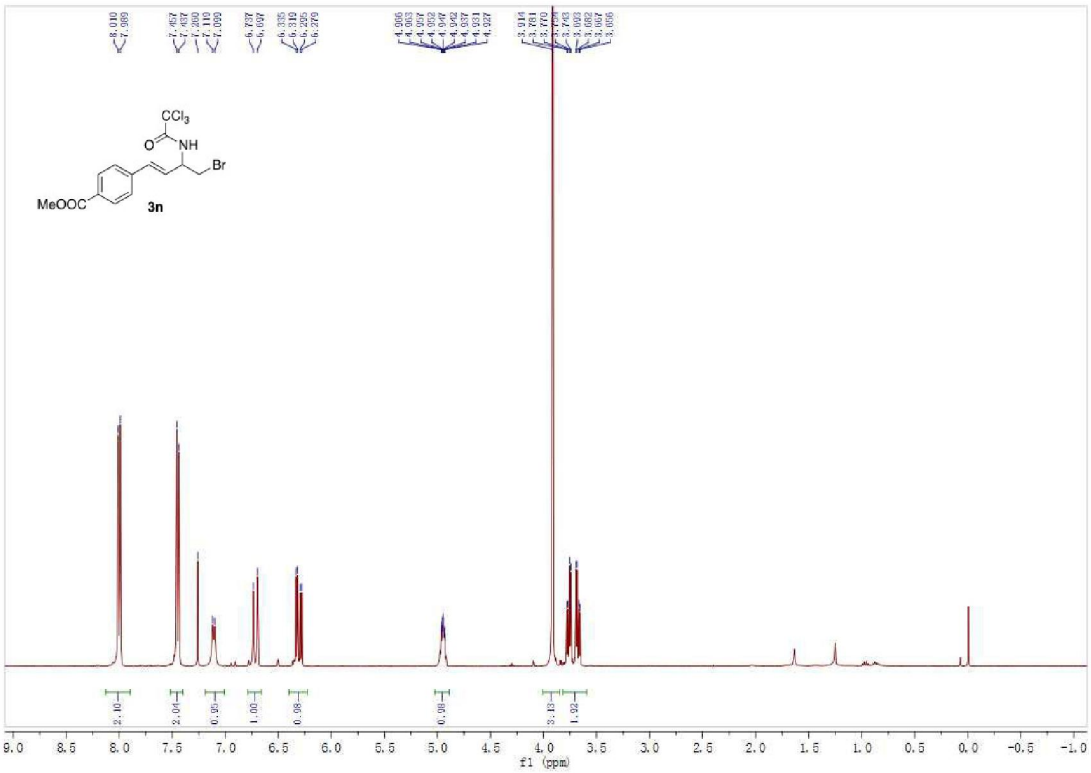

CCl3
O
NH
Br
F
3l
f1 (ppm)

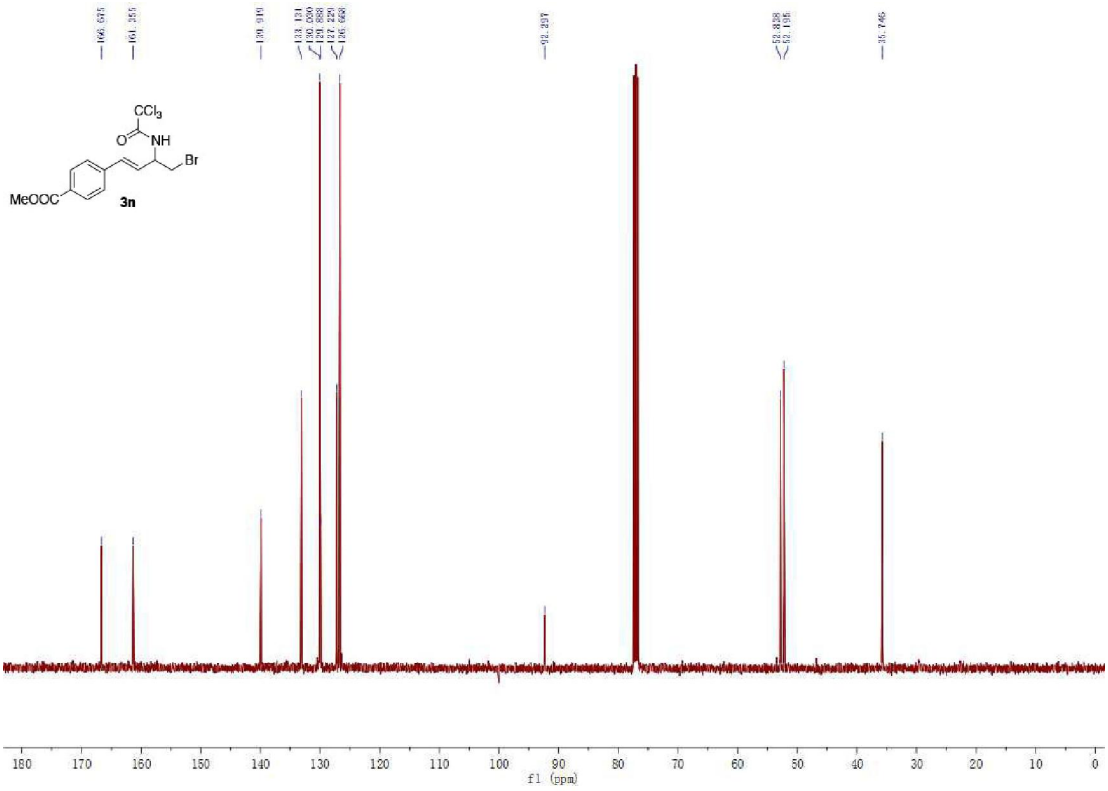
^{19}F NMR (376 MHz, $CDCl_3$)

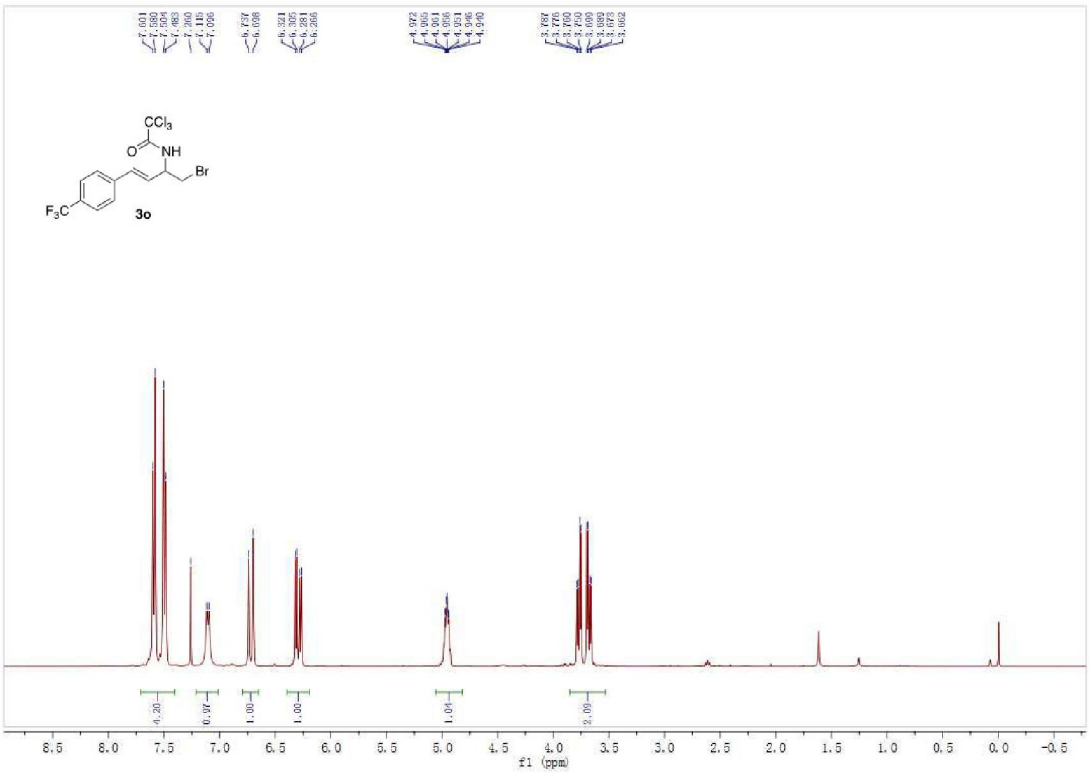


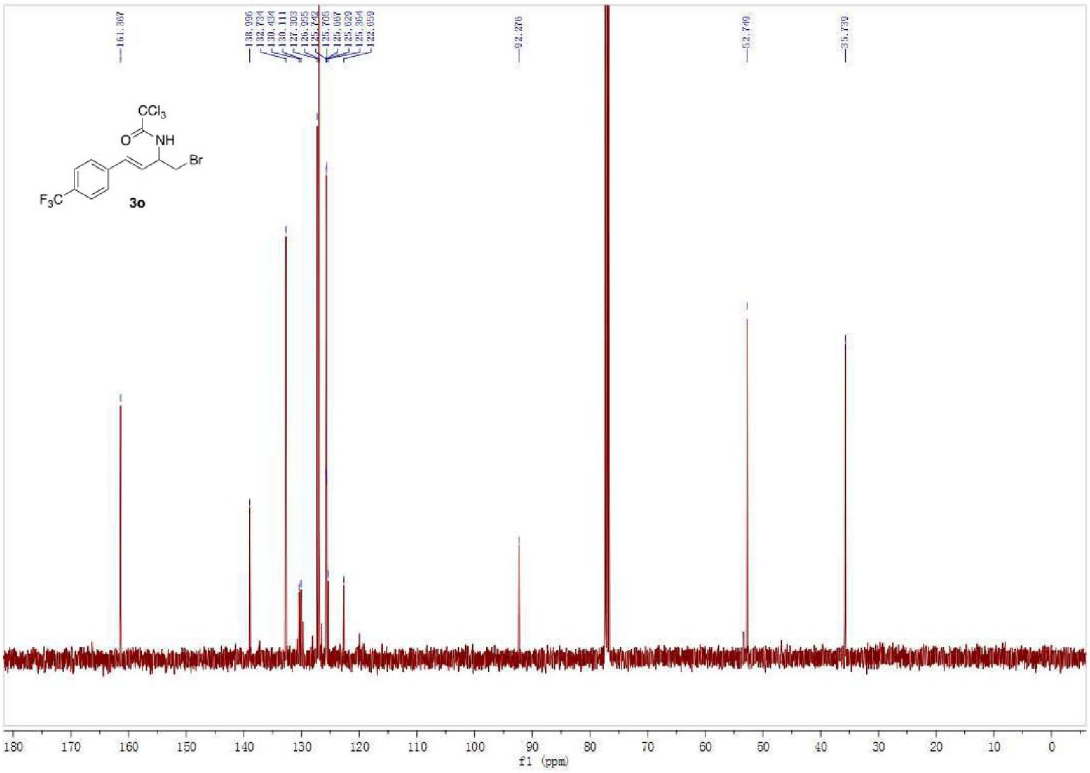



161.382
139.008
132.539
132.389
128.593
127.282
118.098
111.806
62.216
52.638
35.628
CCl3
O
NH
Br
NC
3m
f1 (ppm)

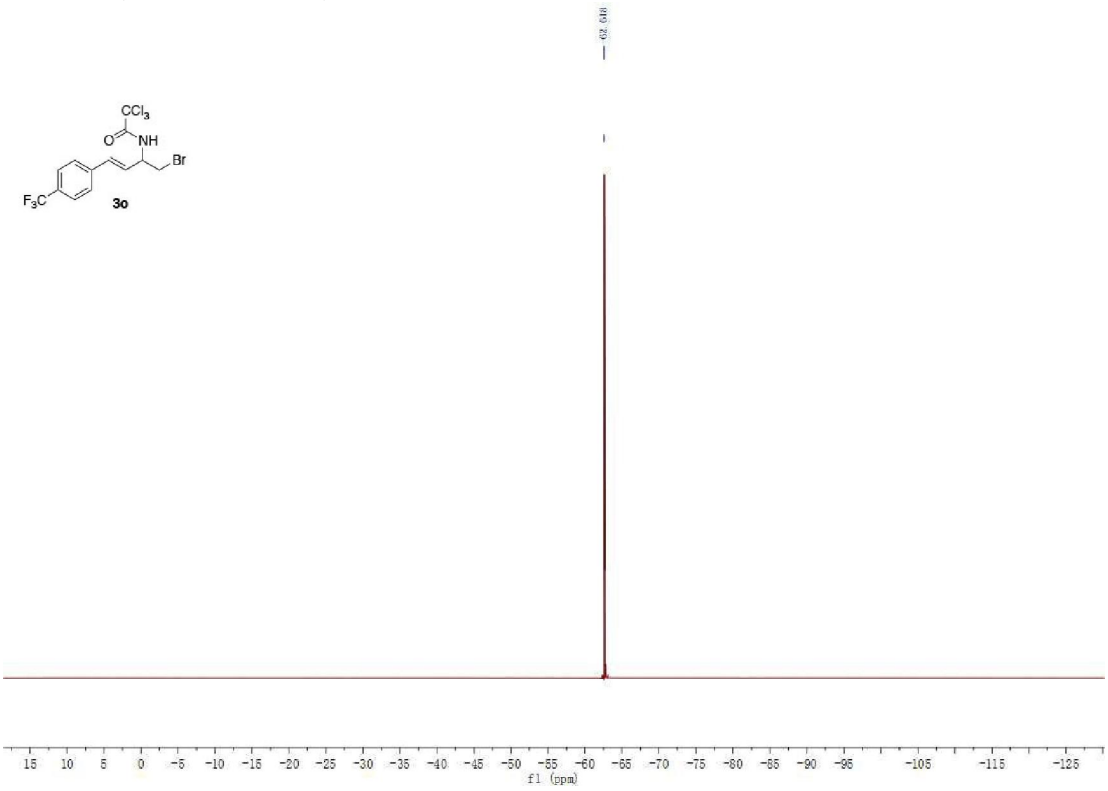

8.010
7.989
7.467
7.457
7.200
7.110
7.099
6.727
6.697
6.335
6.318
6.295
6.270
4.966
4.963
4.957
4.952
4.947
4.942
4.937
4.931
4.927
3.914
3.781
3.779
3.743
3.693
3.682
3.667
3.656
2.10
2.04
0.90
1.00
0.98
0.98
3.13
1.92
CCl3
O
NH
Br
MeOOC
3n
f1 (ppm)

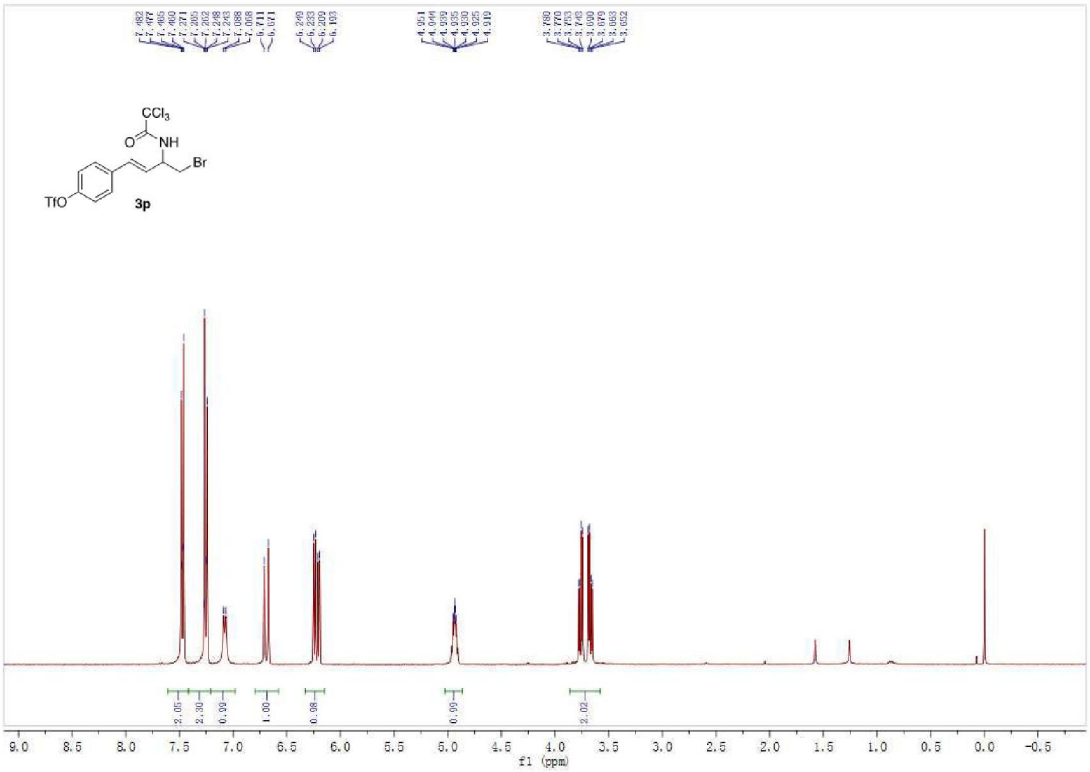

166.635
161.355
139.910
133.191
129.098
129.888
127.229
126.660
92.297
62.838
62.195
35.746
CCl3
O
NH
Br
MeOOC
3n
f1 (ppm)

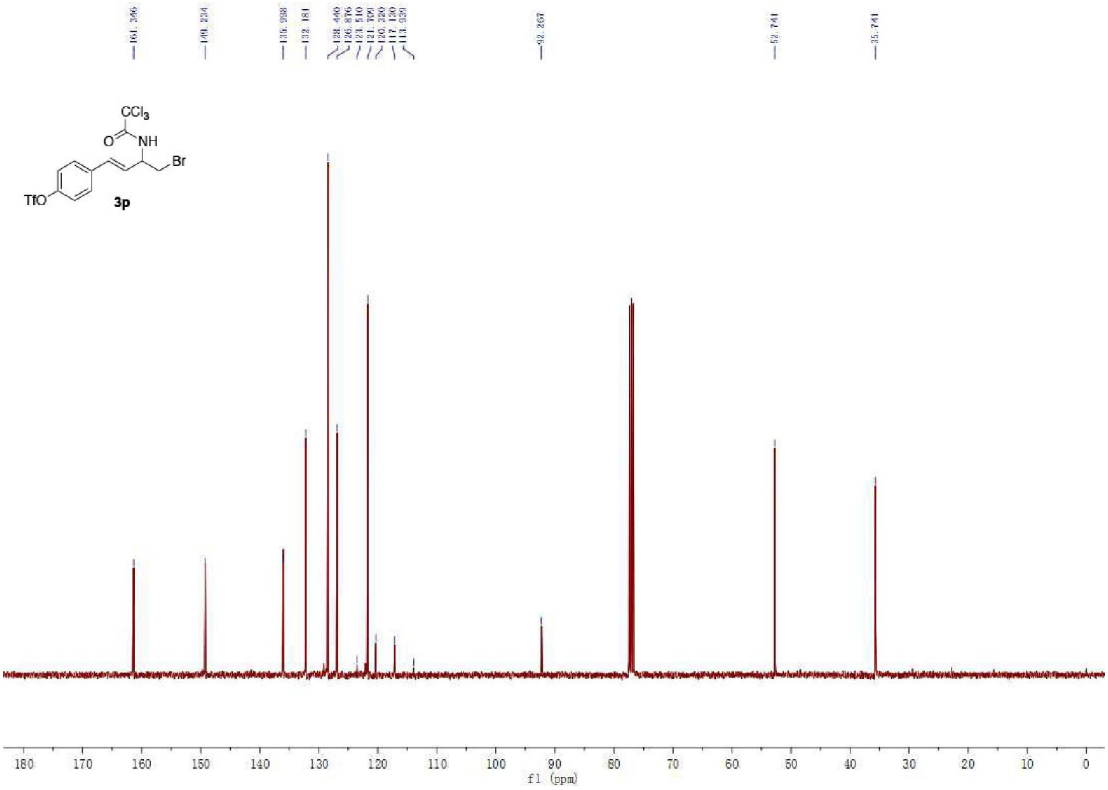

7.601
7.580
7.564
7.498
7.360
7.118
7.096
6.737
6.098
6.321
6.305
6.281
6.265
4.972
4.965
4.961
4.956
4.951
4.946
4.940
3.787
3.776
3.760
3.750
3.699
3.689
3.673
3.662
CCl3
O
NH
Br
F3C
3o
0.20
0.97
1.00
1.00
1.04
2.09
f1 (ppm)

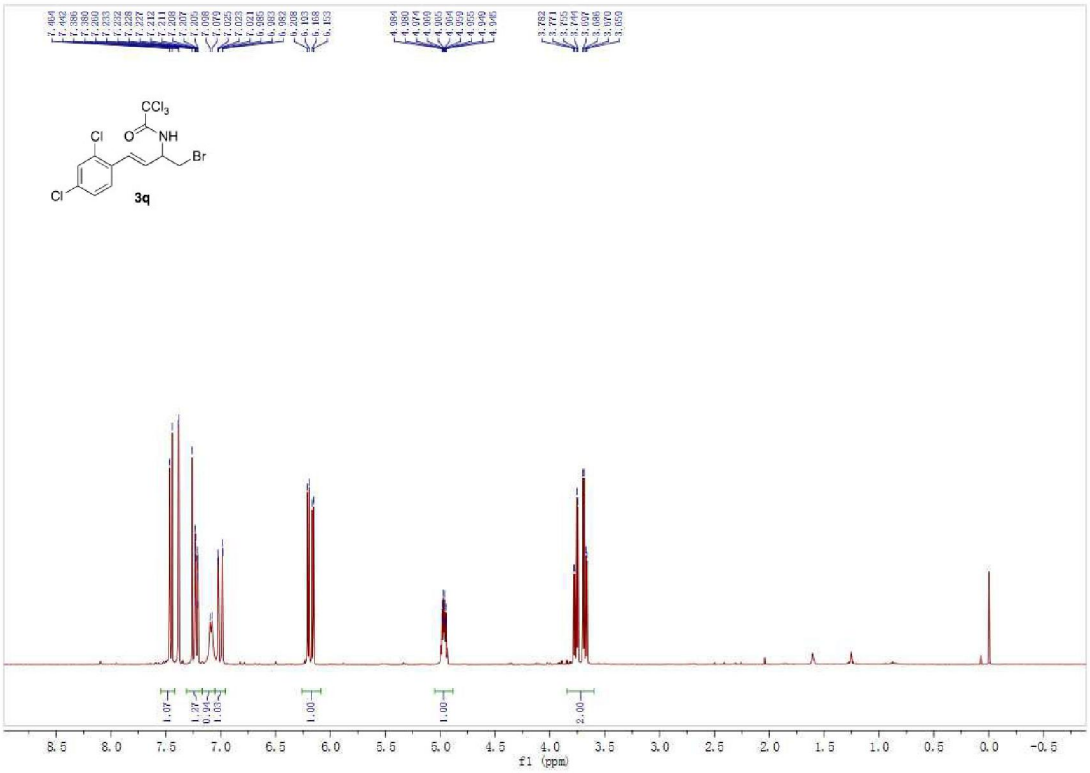


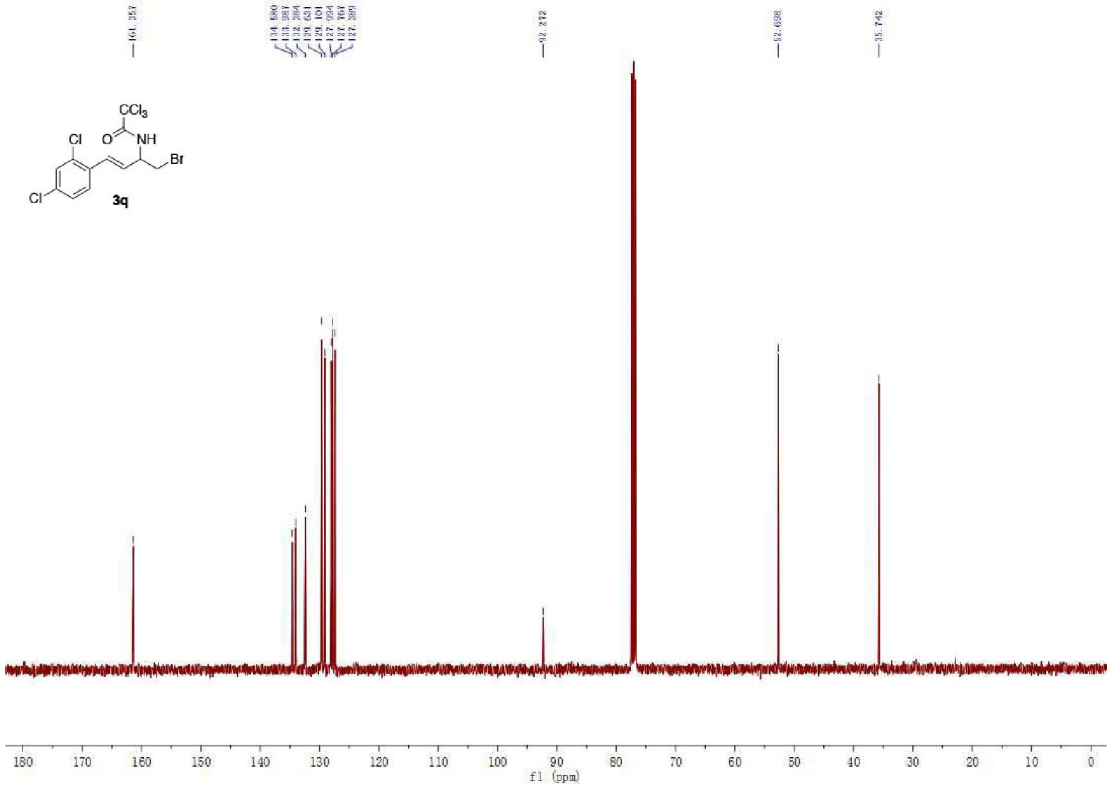
^{19}F NMR (376 MHz, $CDCl_3$)

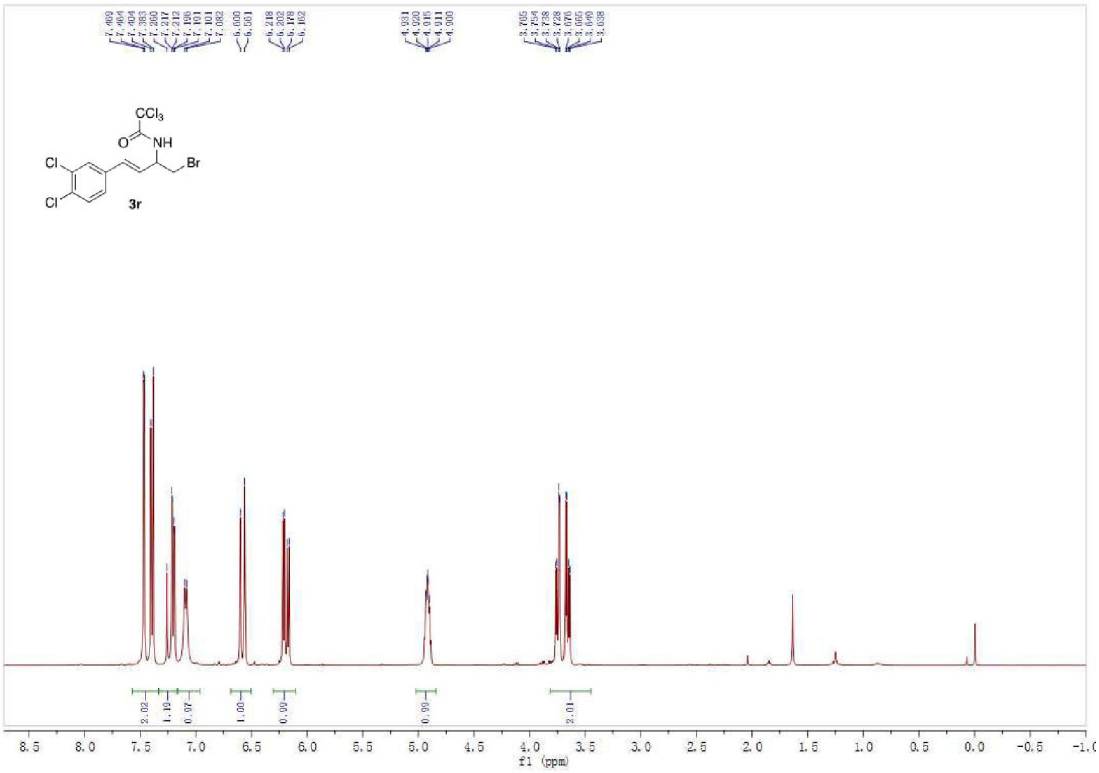


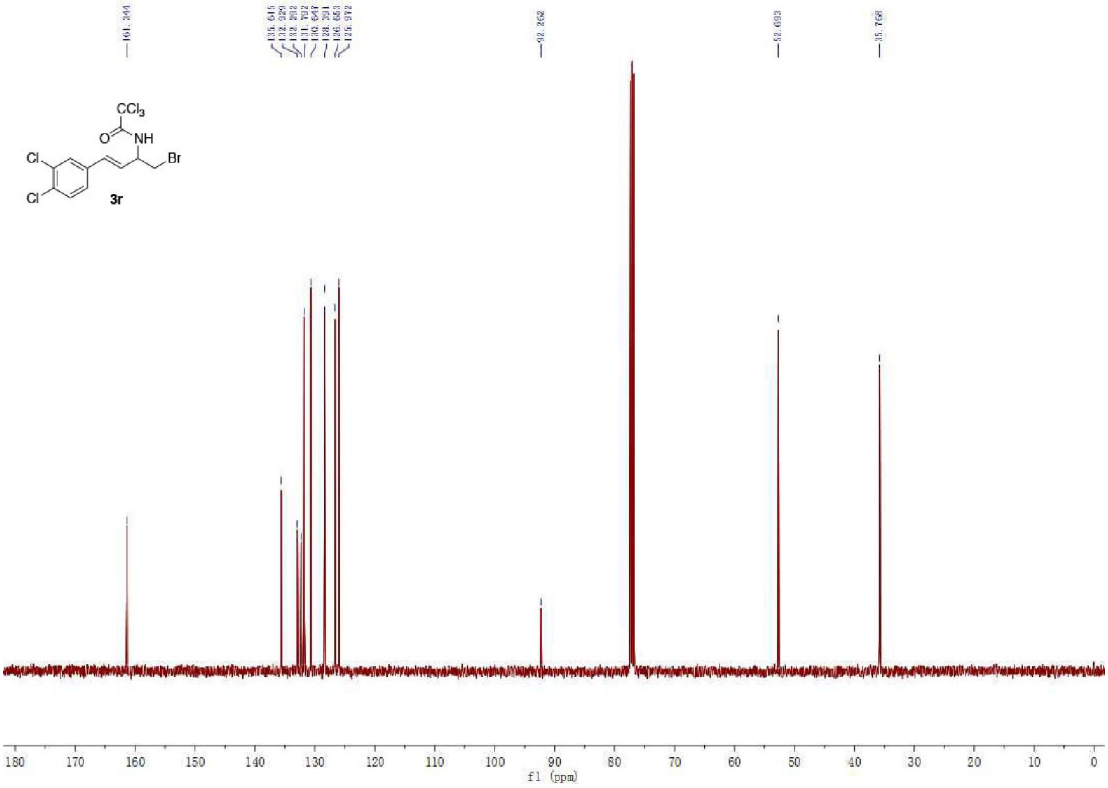

CCl3
O
NH
Br
TfO
3p
f1 (ppm)

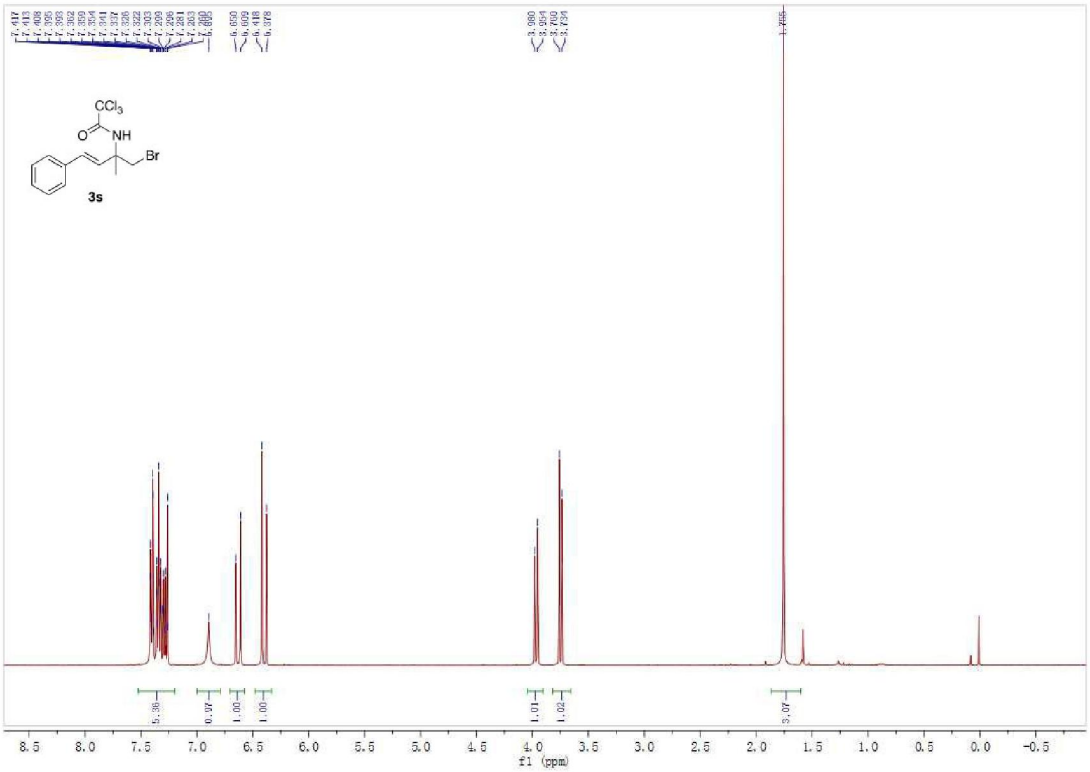

CCl3
O
NH
Br
TfO
3p
f1 (ppm)

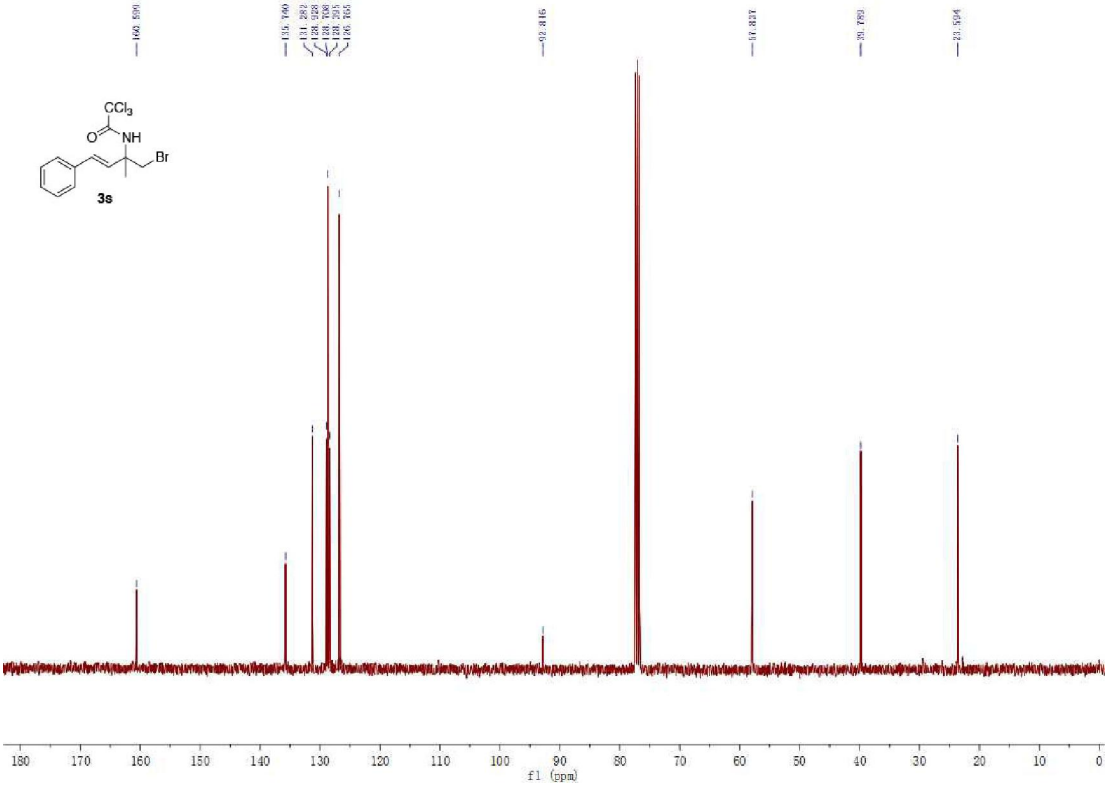

CCl3
O
NH
Cl
Br
Cl
3q
1.07
1.27
0.94
1.03
1.00
1.00
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

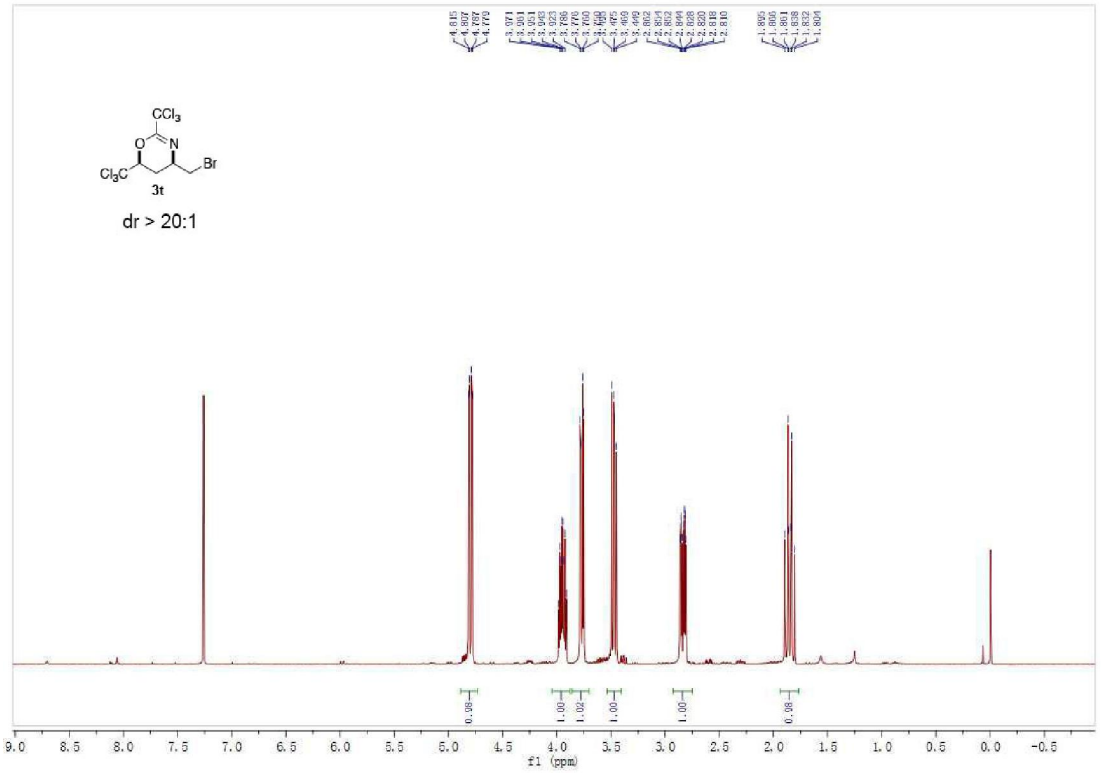

164.357
92.272
52.698
35.742
CCl3
O
NH
Cl
Br
Cl
3q
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

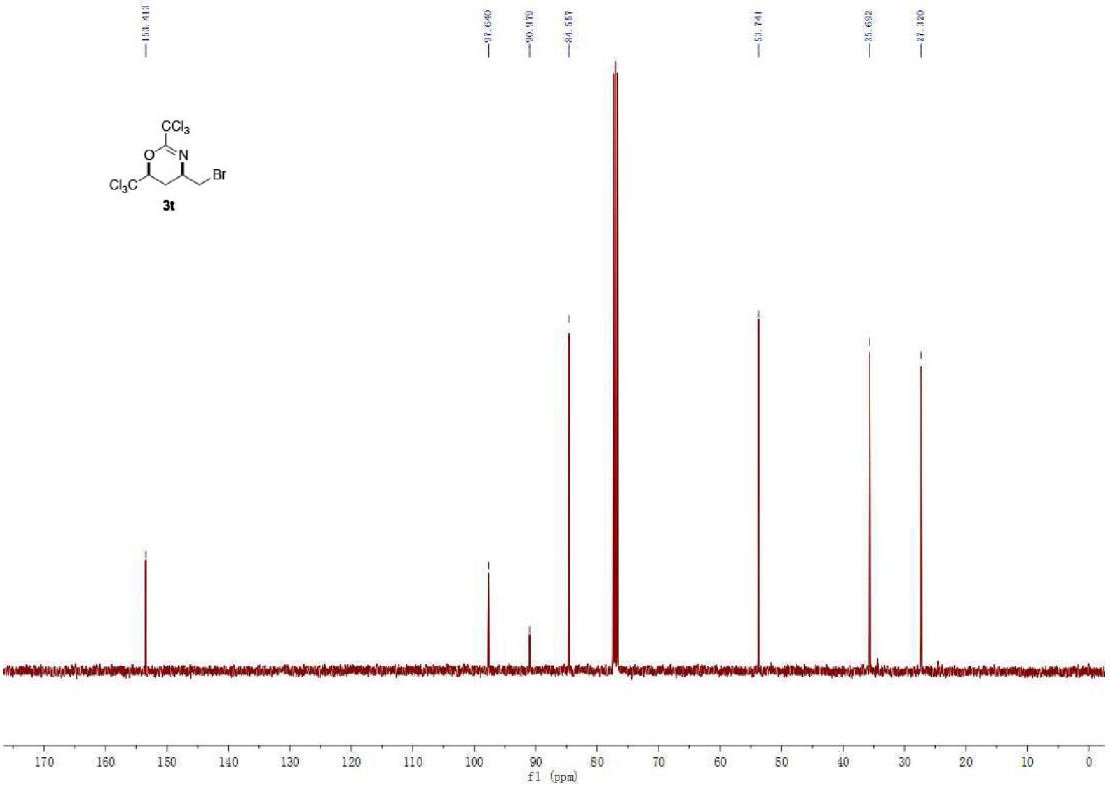

CCl3
O
NH
Br
Cl
Cl
3r
f1 (ppm)

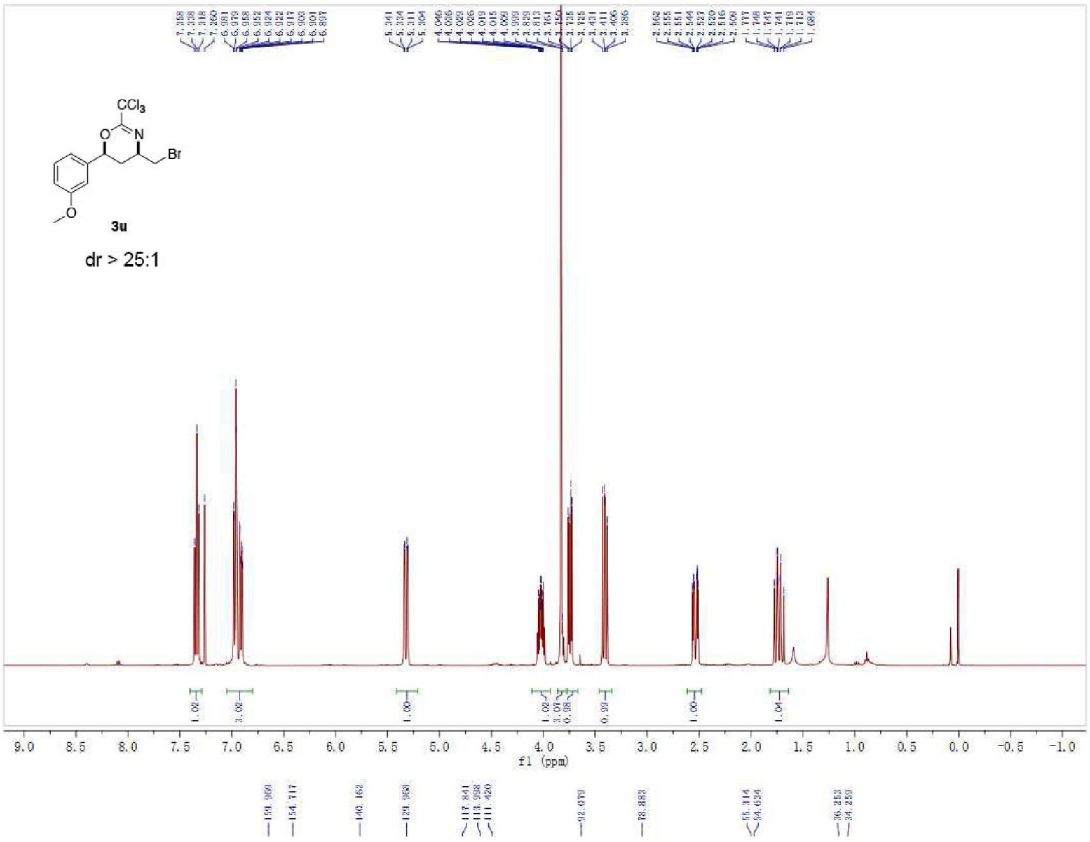

CCl3
O
NH
Br
Cl
Cl
3r
f1 (ppm)

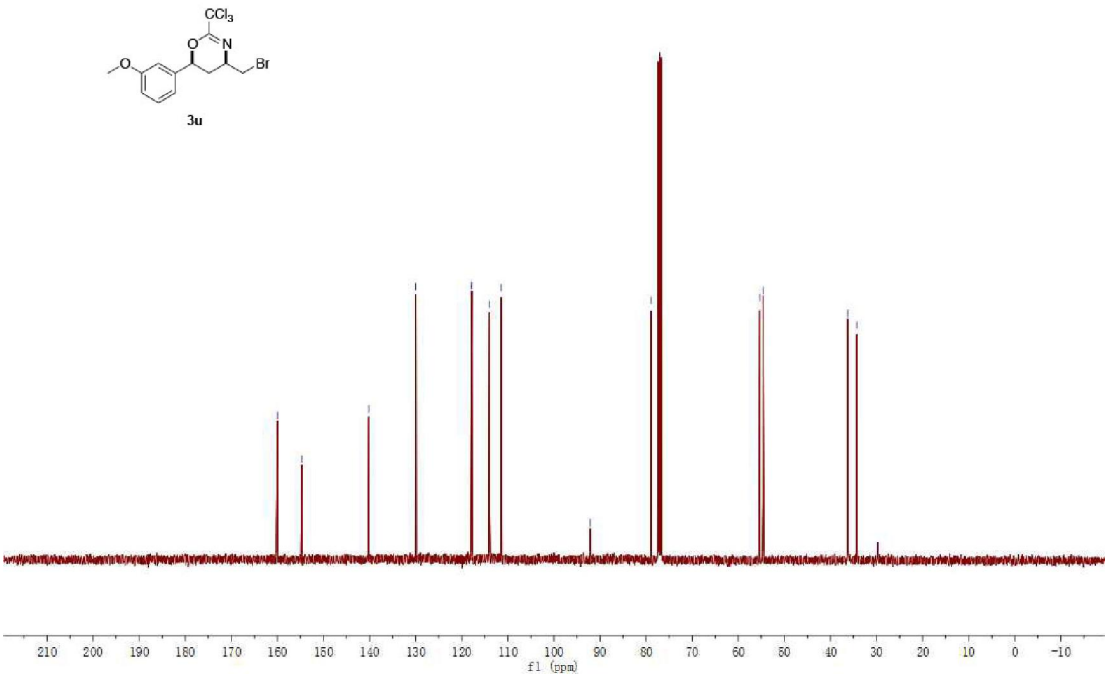

CCl3
O
NH
Br
3s
f1 (ppm)


CCl3
O
NH
Br
3s
f1 (ppm)

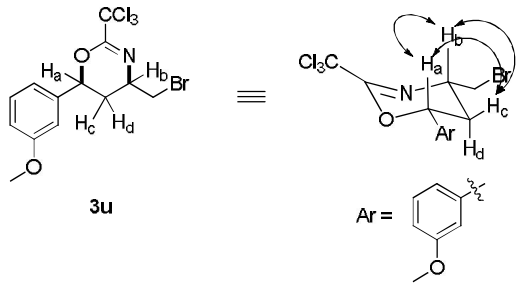

CCl3
O
N
Cl3C
Br
3t
dr > 20:1
f1 (ppm)

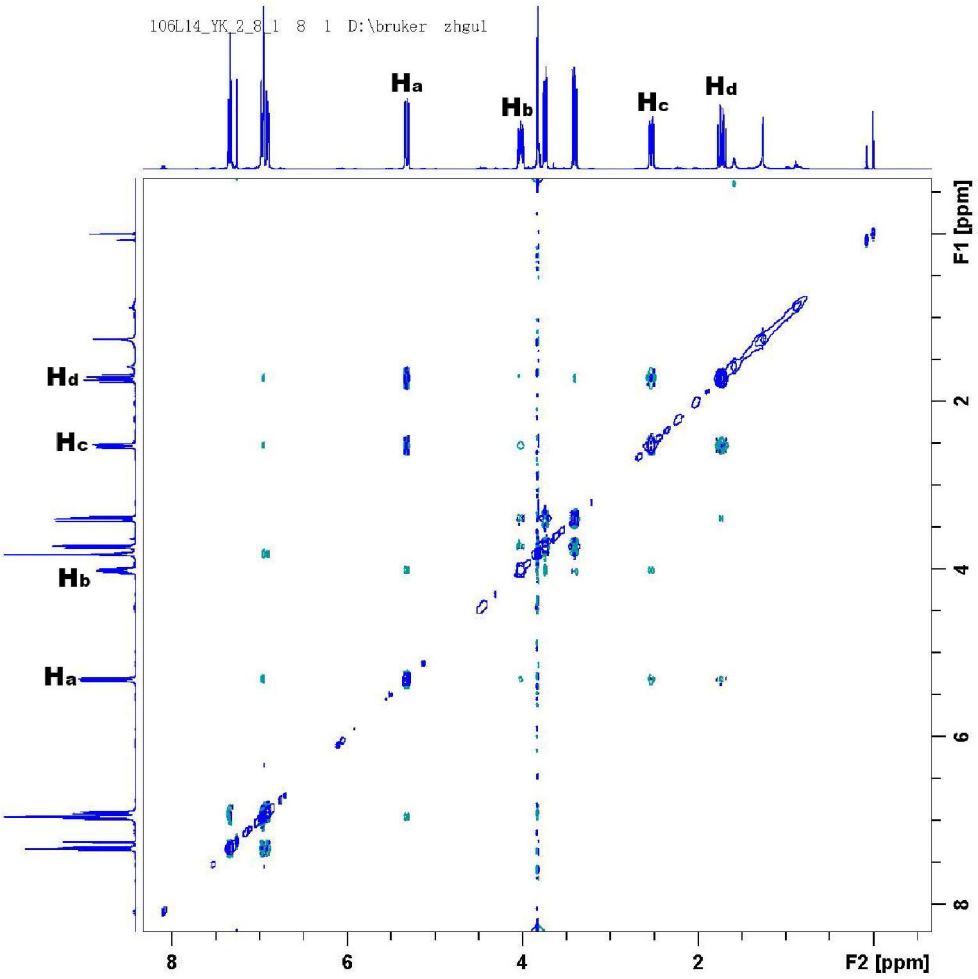

CCl3
O
N
Cl3C
Br
3t
f1 (ppm)


CCl3
O
N
Br
O
3u
dr > 25:1
f1 (ppm)

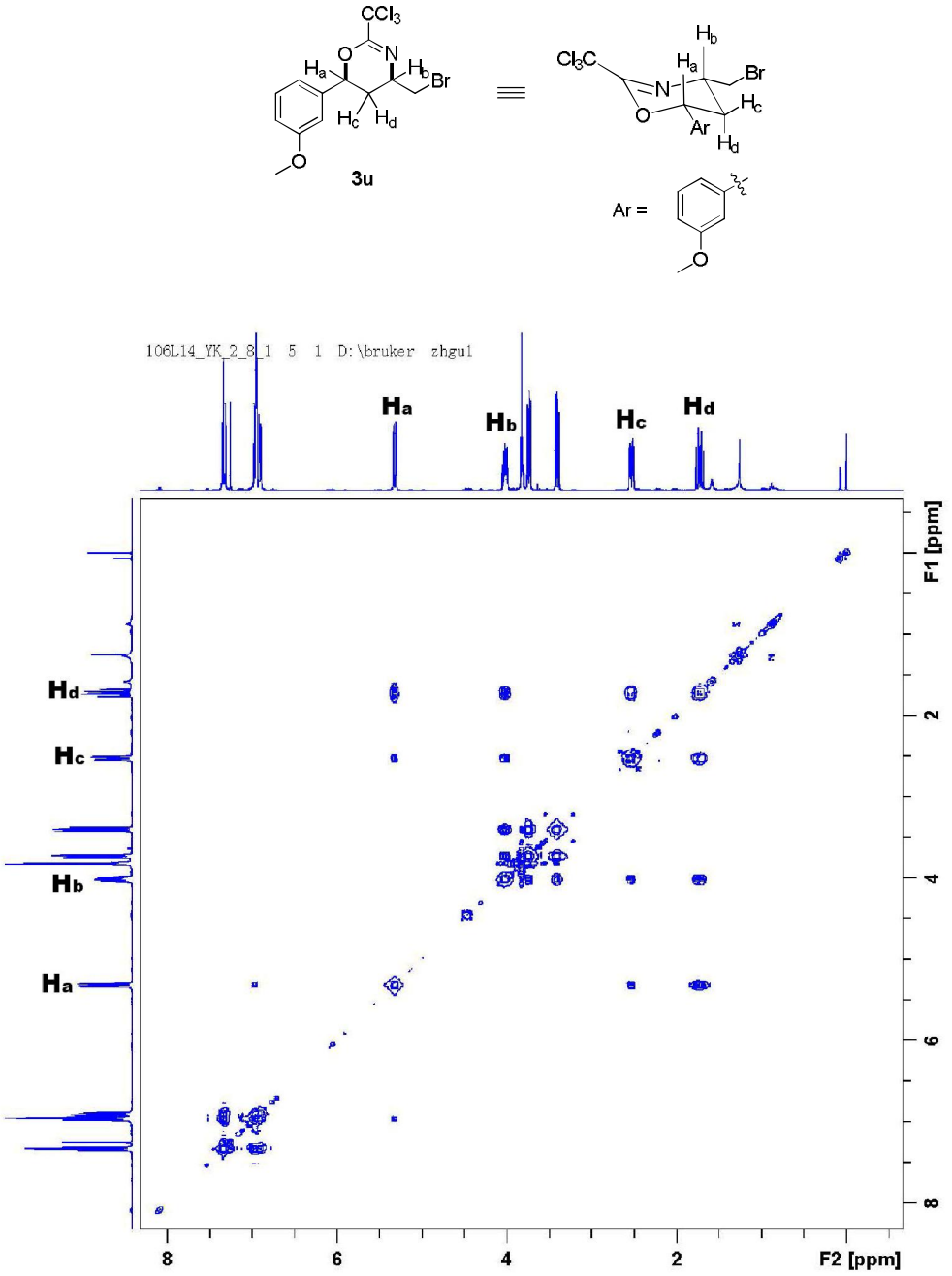

CCl3
O
N
Br
O
3u
f1 (ppm)

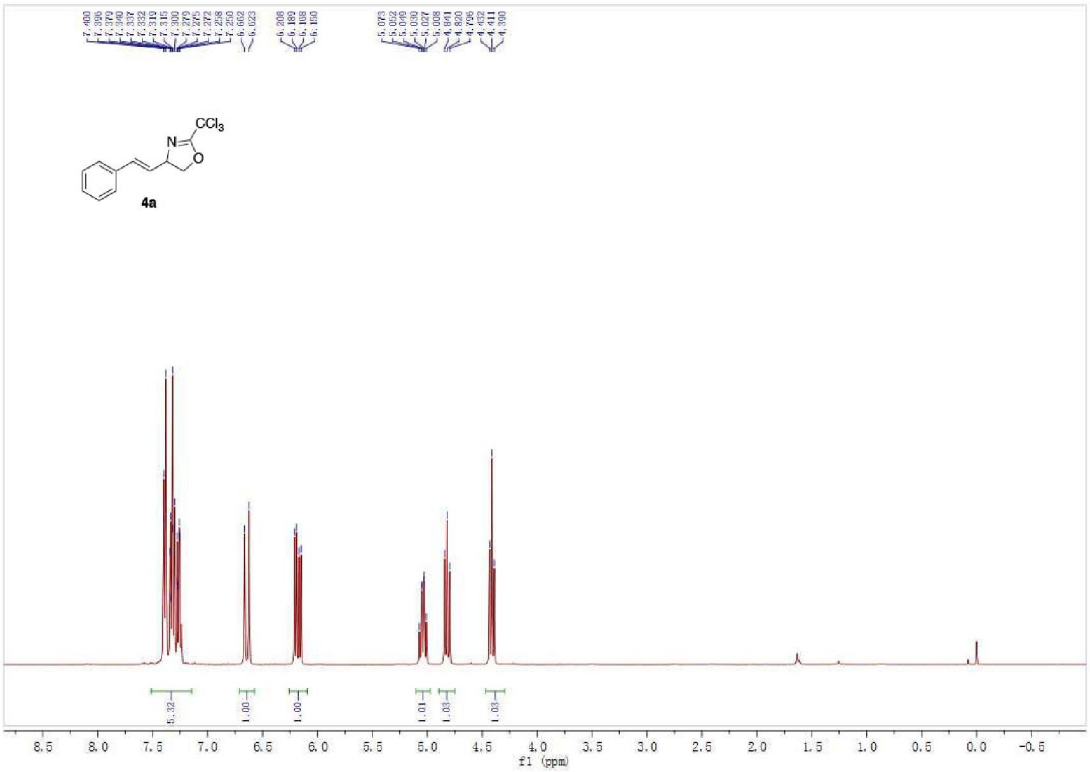
The NOE correlation of **3u**

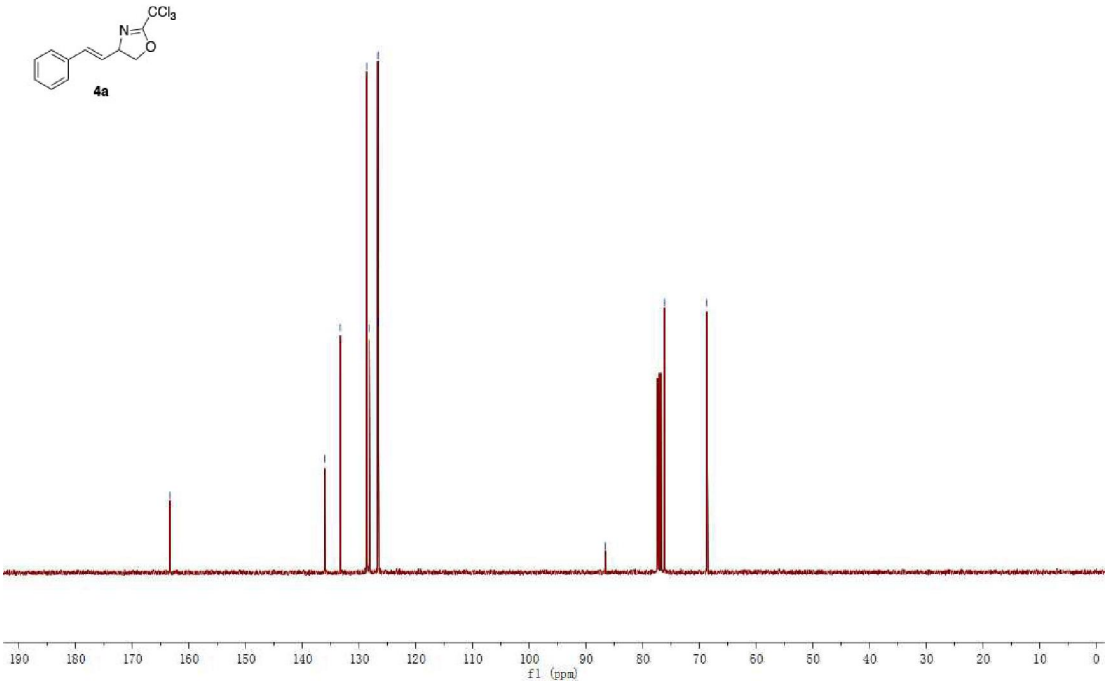


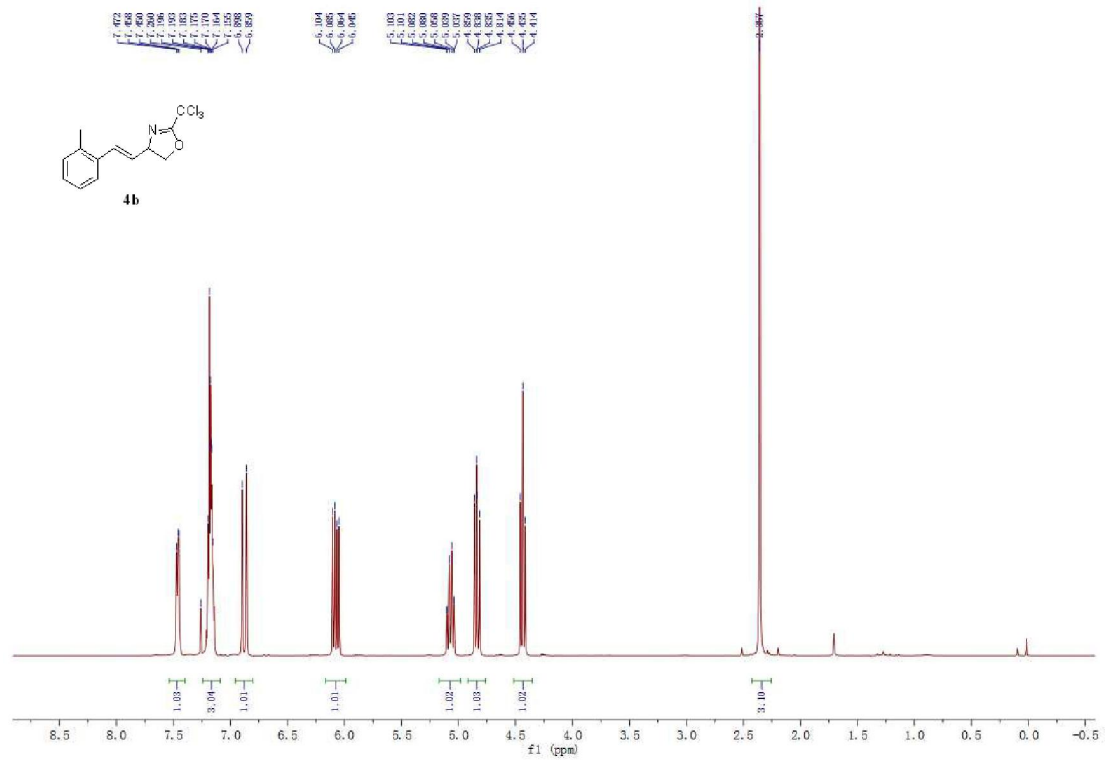


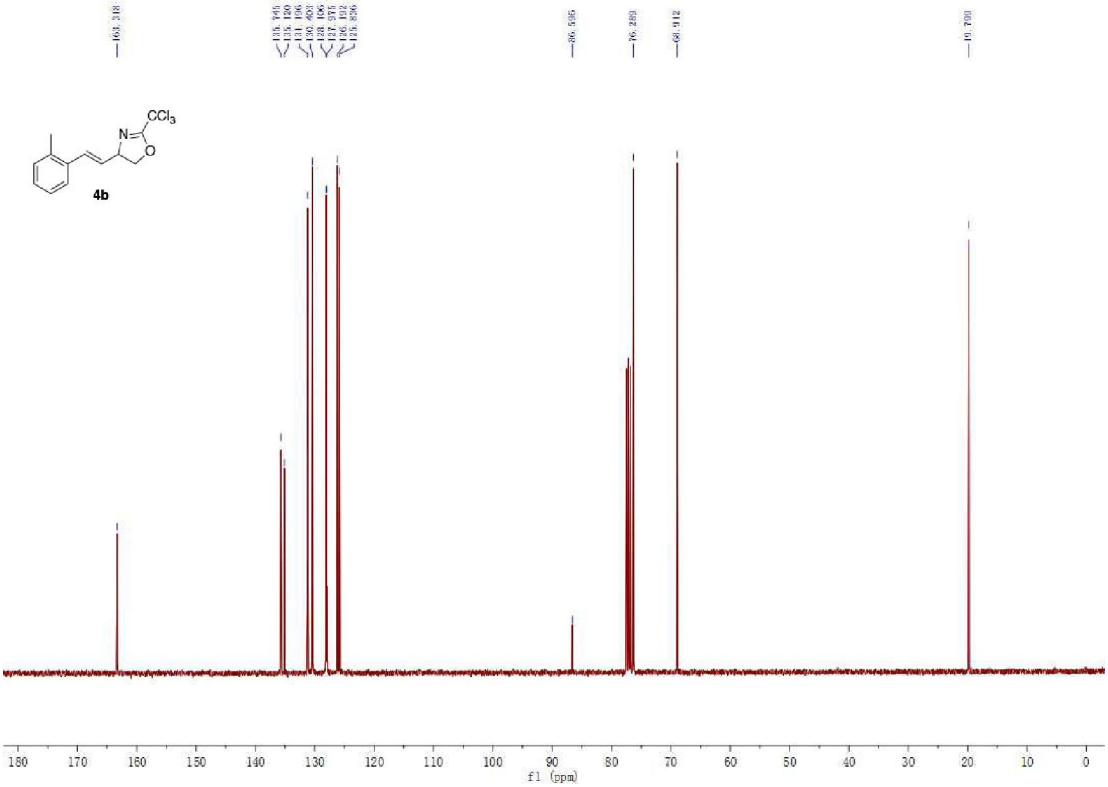
The H,H-COSY of **3u**

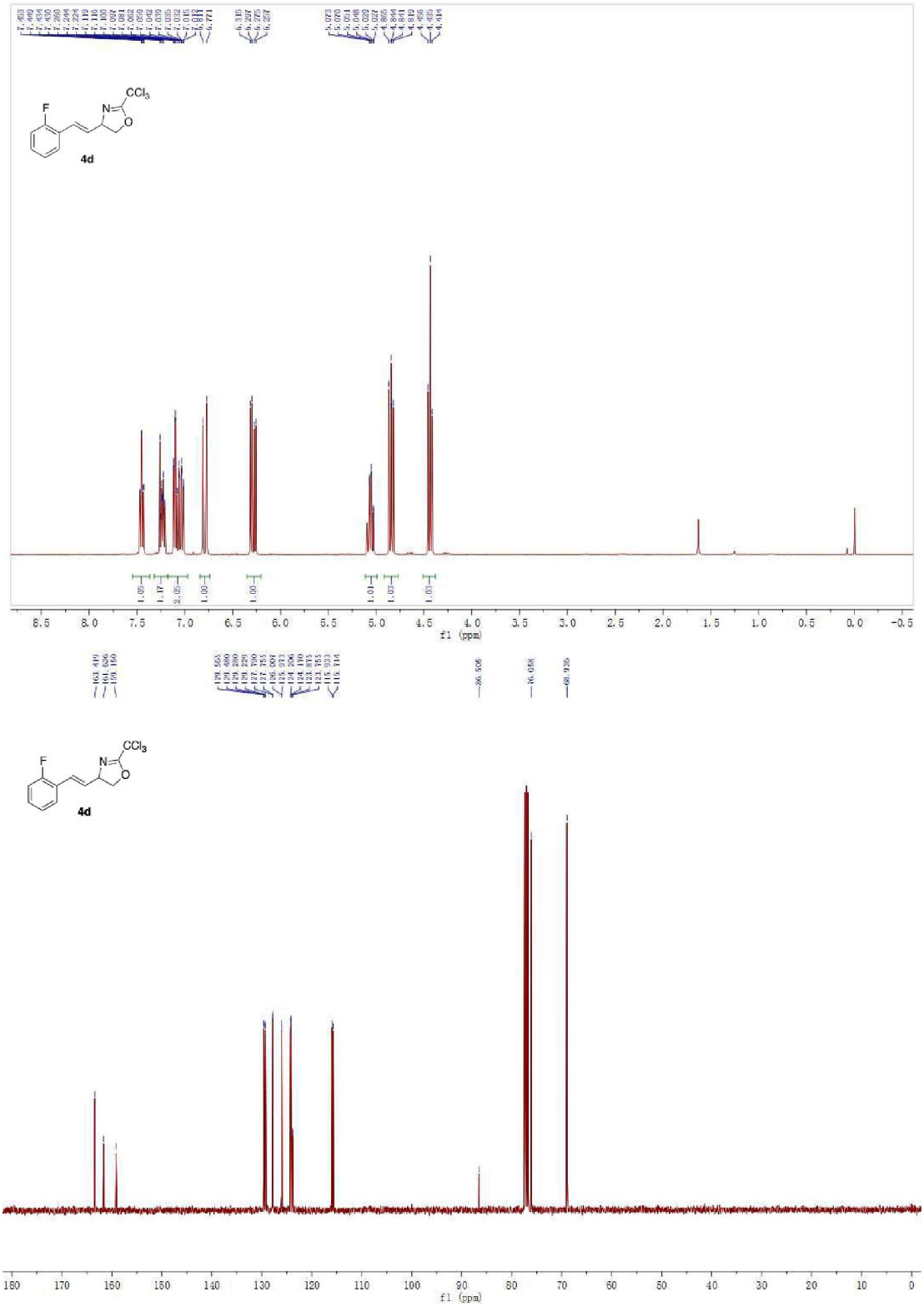

CCl3
O
N
Ha
Hb
Br
Hc
Hd
O
3u
Cl3C
Hb
Ha
Br
N
Hc
O
Ar
Hd
Ar =
O
106L14_YK_2_8_1 5 1 D:\bruker zhgu1
Ha
Hb
Hc
Hd
Hd
Hc
Hb
Ha
F1 [ppm]
2
4
6
8
8
6
4
2
F2 [ppm]


CCl3
N
O
4a
f1 (ppm)

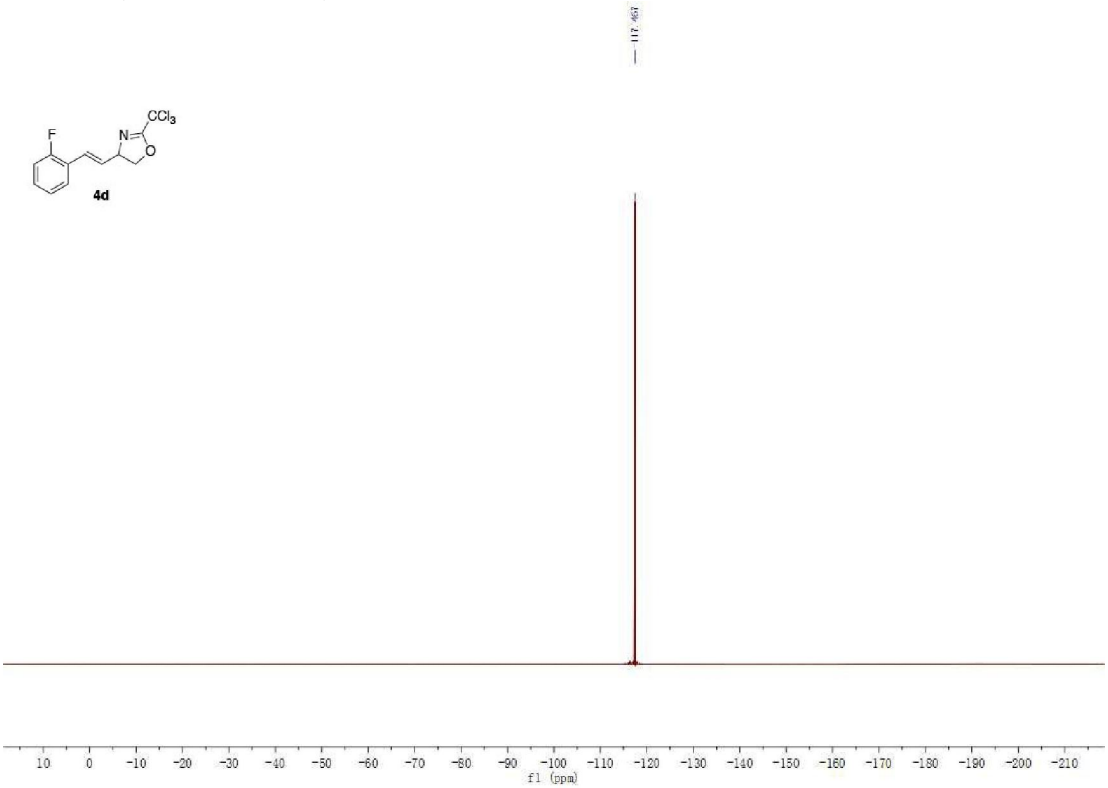

CCl3
N
O
4a
f1 (ppm)

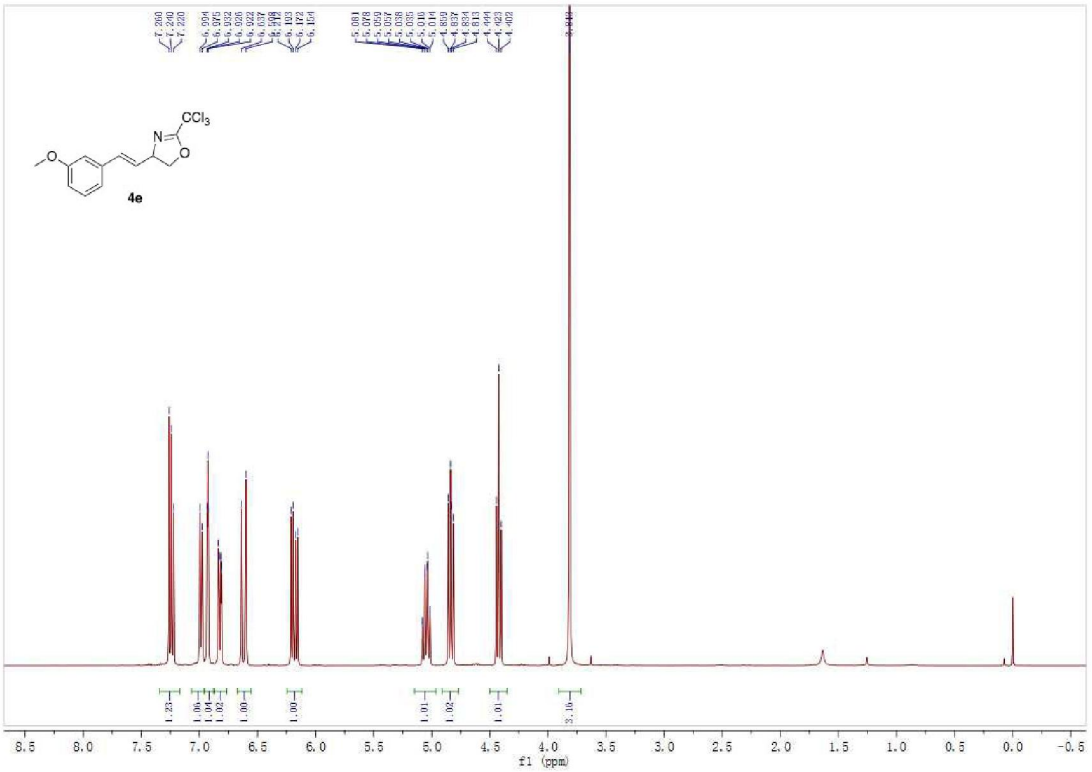

CCl3
N
O
4b
f1 (ppm)

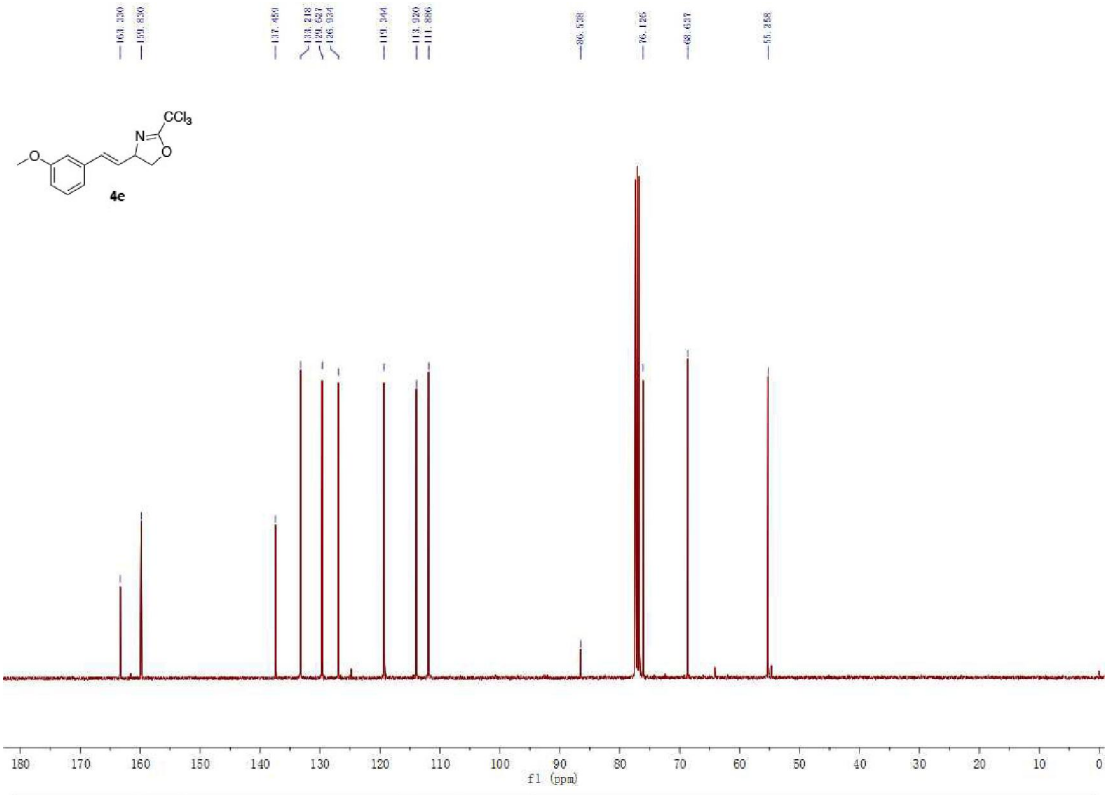

CCl3
N
O
4b
f1 (ppm)

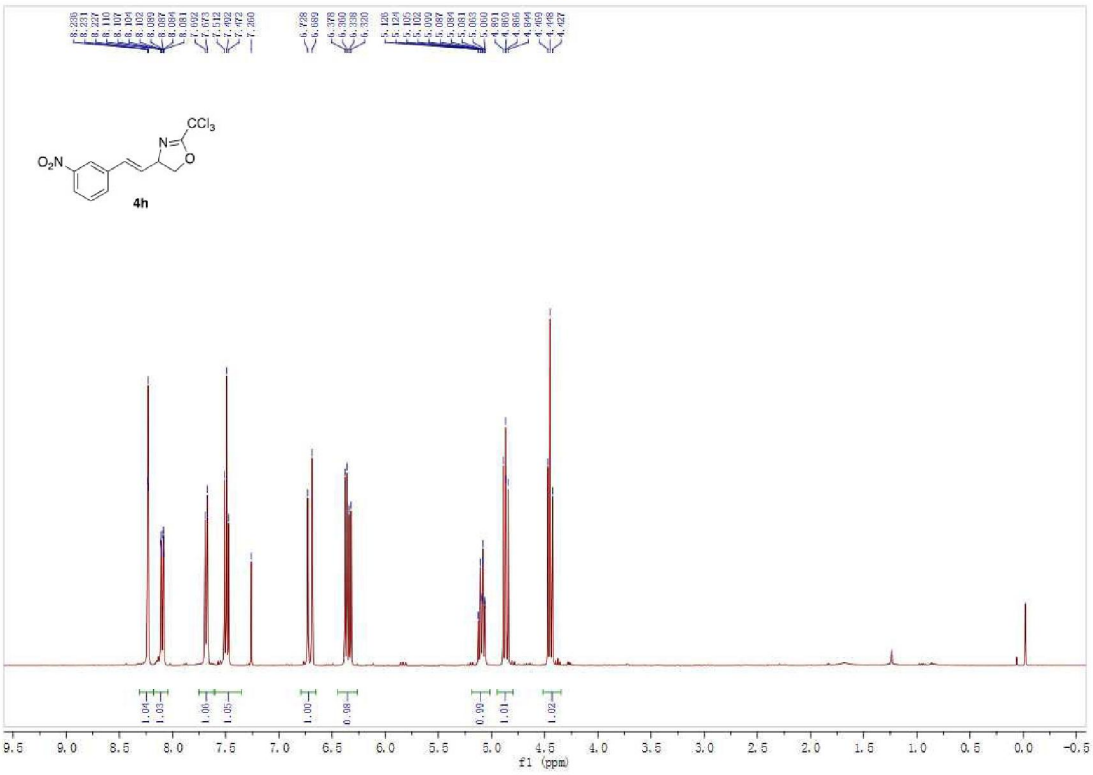

4d
f1 (ppm)
4d
f1 (ppm)

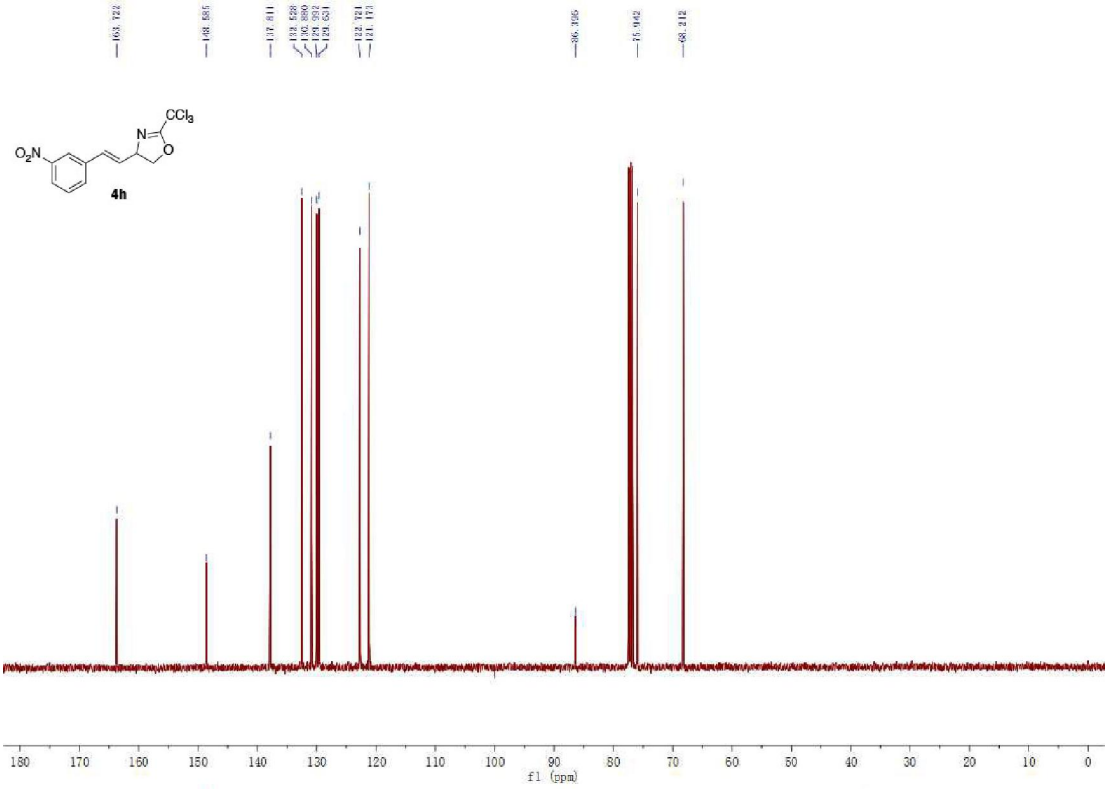
^{19}F NMR (376 MHz, $CDCl_3$)

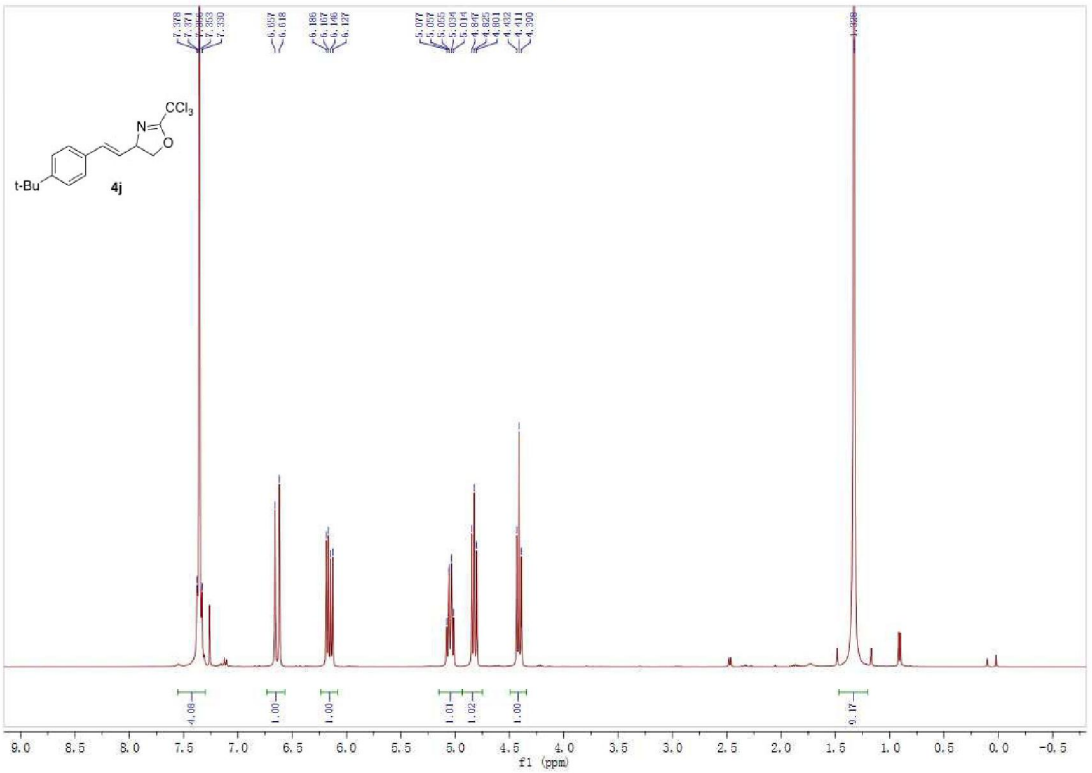


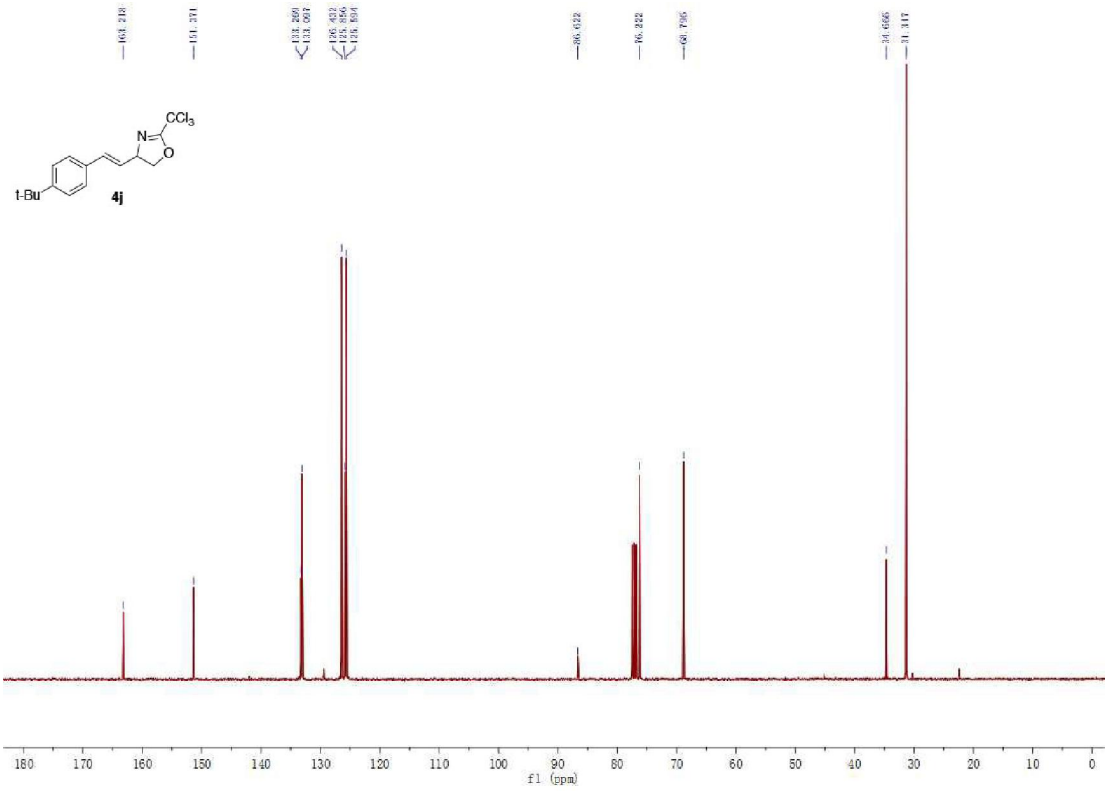


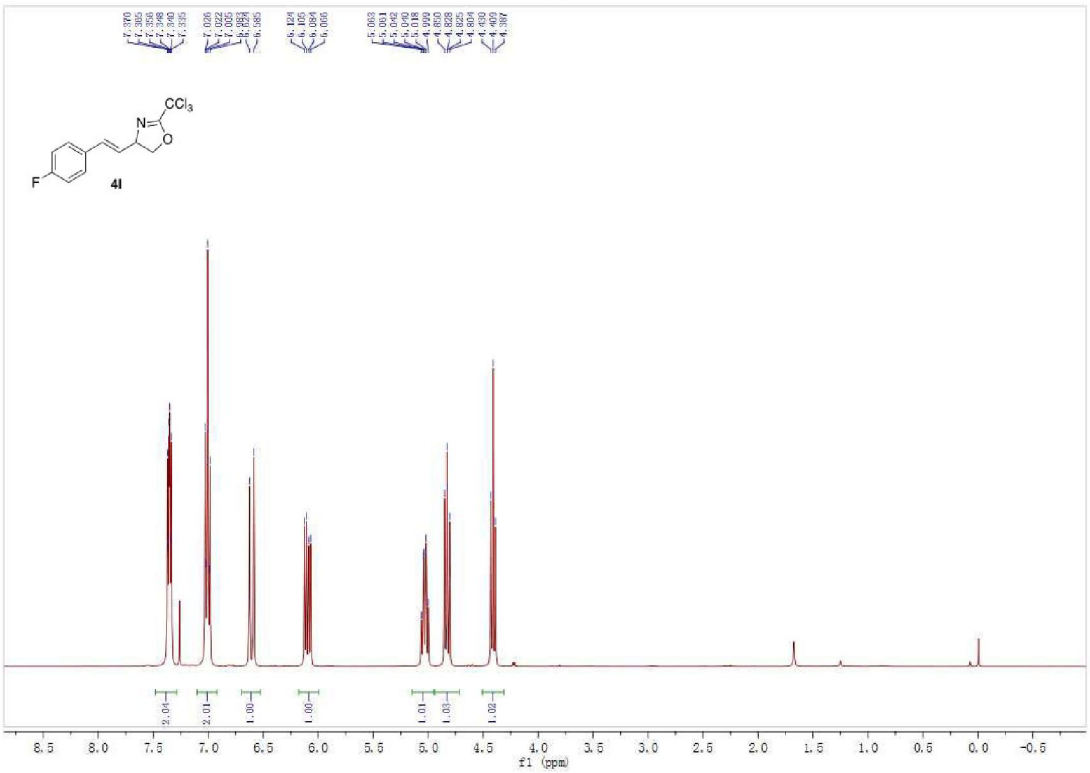

163.330
159.830
137.459
133.218
129.627
126.024
119.344
113.920
111.896
86.528
76.125
68.697
55.358
CCl3
N
O
O
4e
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

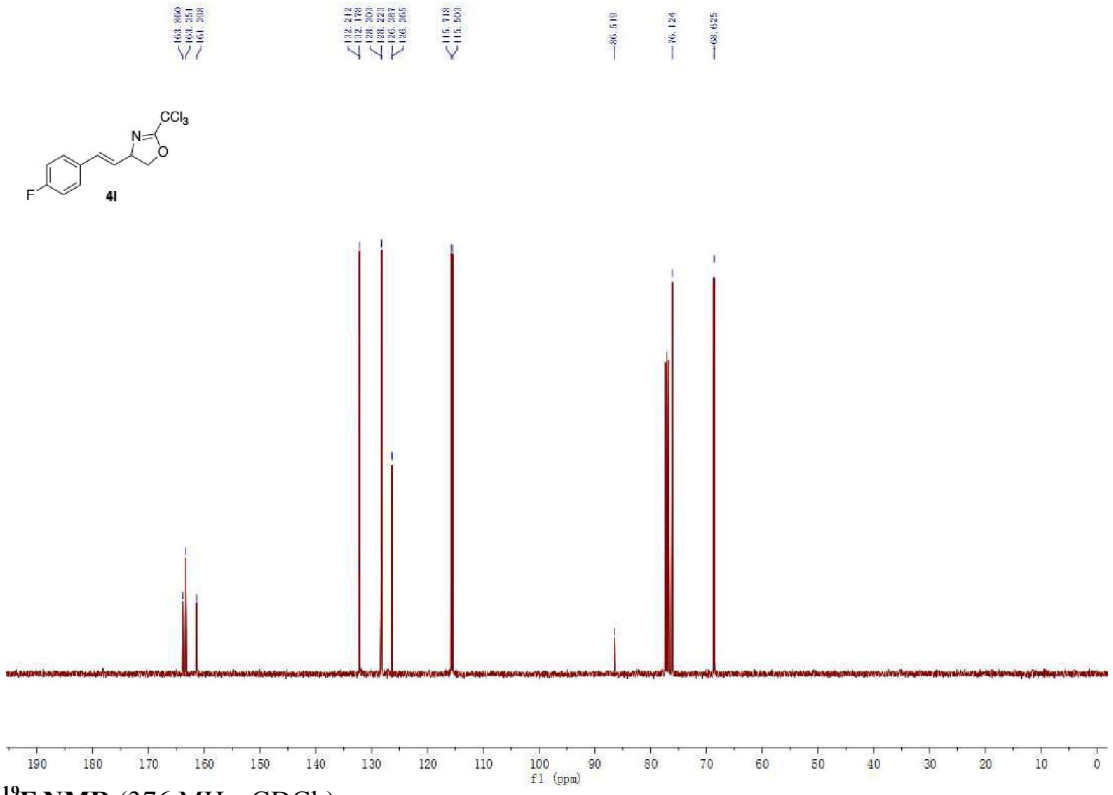

8.238
8.231
8.227
8.110
8.104
8.102
8.089
8.087
8.084
8.081
7.692
7.675
7.513
7.492
7.472
7.260
6.728
6.699
6.375
6.369
6.338
6.330
5.126
5.123
5.105
5.102
5.089
5.087
5.084
5.081
5.063
5.059
4.893
4.880
4.866
4.864
4.448
4.427
CCl3
N
O
O2N
4h
1.04
1.03
1.00
1.05
1.00
0.98
0.99
1.01
1.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


163.722
148.585
137.611
132.528
130.880
129.992
129.554
122.724
121.173
86.396
75.492
68.212
CCl3
N
O
O2N
4h
f1 (ppm)

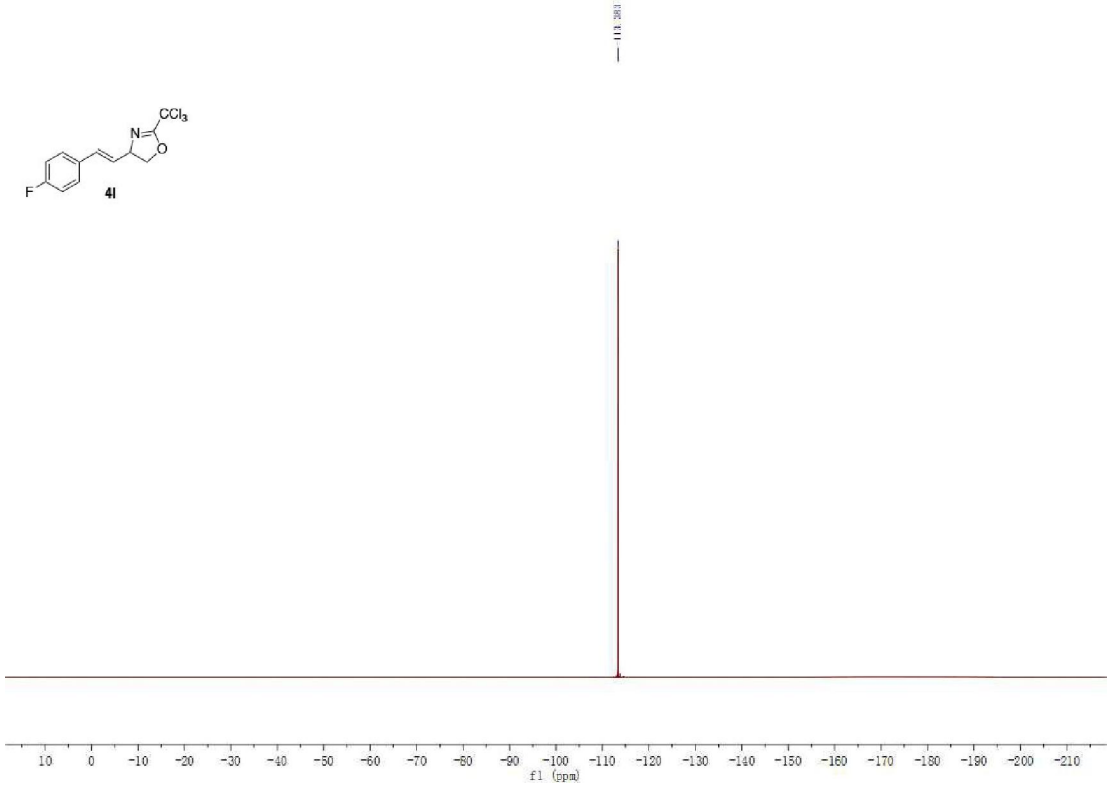

7.378
7.371
7.366
7.353
7.330
6.057
6.018
6.186
6.167
6.146
6.127
5.077
5.057
5.055
5.034
5.014
4.847
4.825
4.811
4.432
4.411
4.390
1.308
CCl3
N
O
t-Bu
4j
4.08
1.00
1.00
1.01
1.02
1.08
9.17
f1 (ppm)

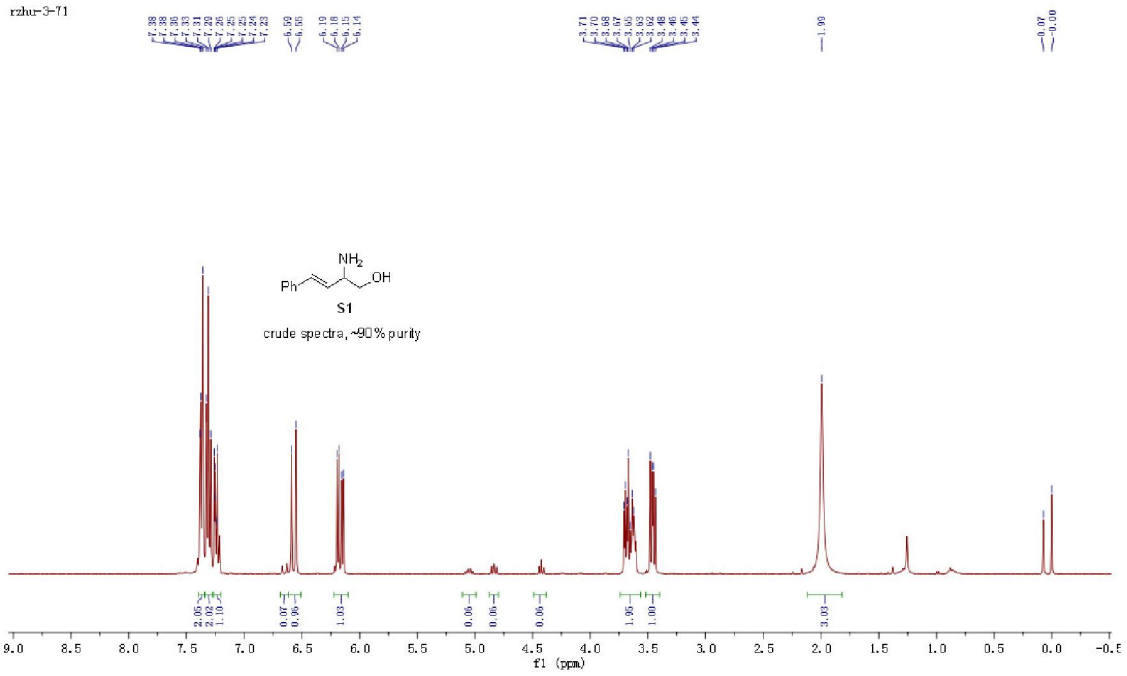

CCl3
N
O
t-Bu
4j
f1 (ppm)

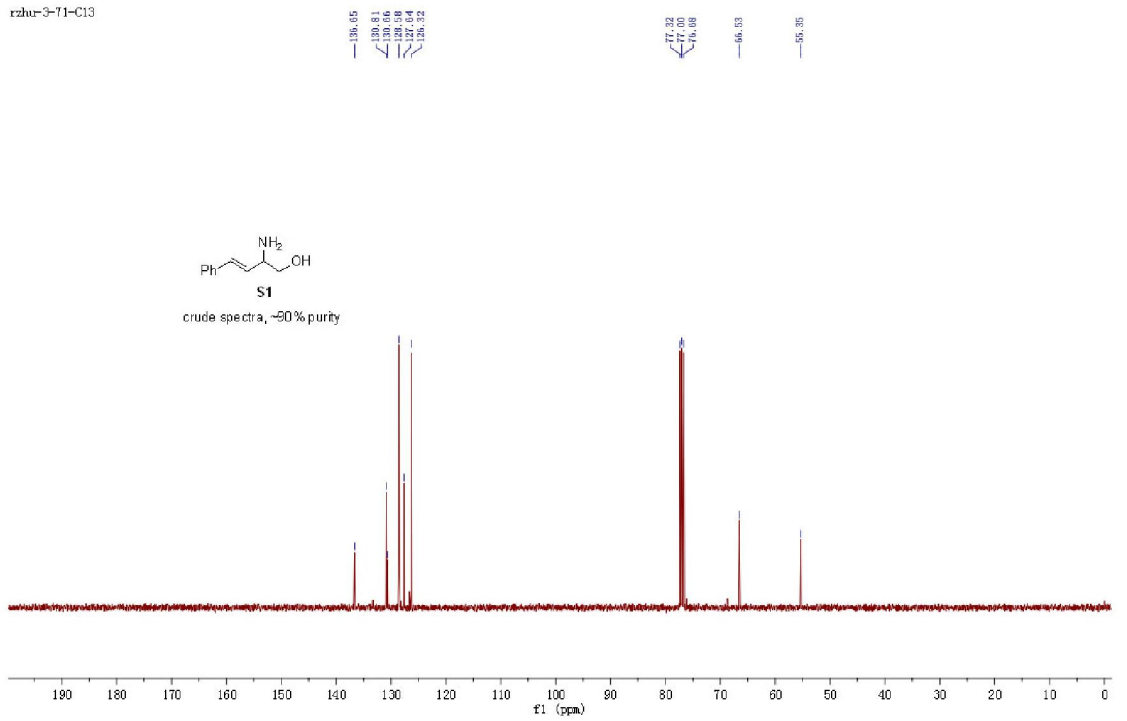

CCl3
N
O
F
4l
f1 (ppm)



^{19}F NMR (376 MHz, $CDCl_3$)




rzhu-3-71
NH2
Ph
OH
S1
crude spectra, ~90% purity
f1 (ppm)


rzhu-3-71-C13
NH2
Ph
OH
S1
crude spectra, ~90% purity
f1 (ppm)