Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Radical-mediated Intramolecular *β*-C(sp^3)−H Amidation of Alkylimidates: Facile Synthesis of 1,2-Amino Alcohols

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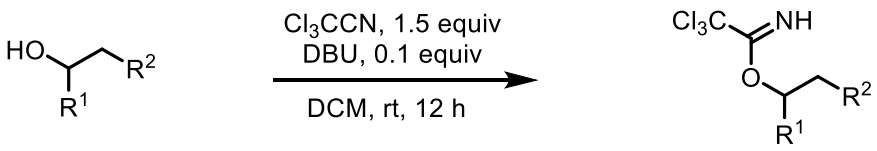
1. Reagents: All commercial materials were used as received unless otherwise noted. DCM were dried by distillation over CaH_2. THF and toluene were dried by distillation over sodium/benzophenone. TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λ_{max} = 254 nm). Flash chromatography was performed using Silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co., China. $PhI(OAc)_2$ (99%, Energy Chemical), NIS (99%, J&K Chemical), DCE (99.5%, TCI chemical) were used in the radical-mediated β-C(sp^3)-H amination reactions.

2. Instruments: NMR spectra were recorded on Bruker AVANCE AV 400 instruments and all NMR experiments were reported in units, parts per million (ppm), using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, br s = broad singlet, m = multiplet. High resolution ESI mass experiments were operated on Waters Xevo G2-Xs QT or Thermo-Fisher Scientific Q instrument. X-ray crystallography was recorded on SuperNova diffractometer.

Note: For most of the trichloroacetimidates, we were unable to detect the molecular ion peaks for HRMS analysis, only the trichloroacetimidate cleavaged fragments were observed.

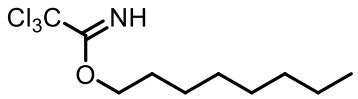
3. Preparation of imidate substrates

3.1 General procedure for preparation of trichloroacetimidate substrates



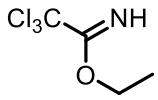
Scheme S1

To a stirred mixture of alcohol (10 mmol, 1 equiv) in 20 mL of dichloromethane, was added trichloroacetonitrile (1.5 mL, 15 mmol, 1.5 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.15 mL, 1 mmol, 0.1 equiv). The resulting reaction mixture was continuously stirred at room temperature. After 12 h, the reaction mixture was diluted with water, the aqueous phase was separated and extracted with dichloromethane. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by column chromatography with triethylamine-treated silica gel using 3% of triethylamine in hexane as eluent to give the desired product.



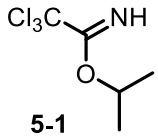
1

Compound **1** was prepared following the general procedure in 94% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 40:1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (br s, 1H), 4.27 (t, *J* = 6.6 Hz, 2H), 1.82–1.72 (m, 2H), 1.48–1.38 (m, 2H), 1.35–1.25 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H);**^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1, 91.8, 69.7, 31.9, 29.3, 28.3, 25.9, 22.7, 14.2.



4-1

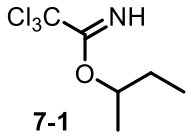
Compound **4-1** was prepared following the general procedure in 93% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (br s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.6, 91. 6, 65.3, 13.7.



5-1

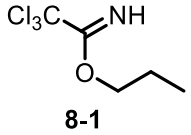
Compound **5-1**[1] was prepared followingthe general procedure in 77% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (br s, 1H), 5.15–4.97 (m, 1H), 1.28 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ

162.0, 92.0, 72.7, 21.1. The spectra data are consistent with those reported in literature.



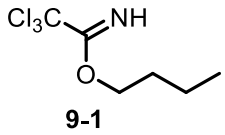
7-1

Compound **7-1** was prepared following the general procedure in 82% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 40:1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (br s, 1H), 5.02–4.89 (m, 1H), 1.83–1.60 (m, 2H), 1.33 (d, *J* = 6.2 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5, 92.2, 77.6, 28.7, 18.6, 9.7.



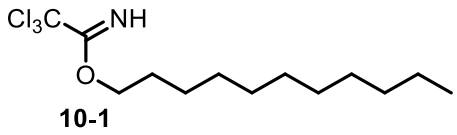
8-1

Compound **8-1** was prepared following the general procedure in 90% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (br s, 1H), 4.15 (t, *J* = 6.5 Hz, 2H), 1.77–1.61 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.8, 91.6, 70.9, 21.6, 10.3.



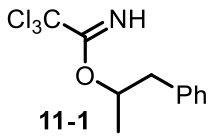
9-1

Compound **9-1** was prepared following the general procedure in 91% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (br s, 1H), 4.28 (t, *J* = 6.5 Hz, 2H), 1.81–1.70 (m, 2H), 1.54–1.40 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2, 91.8, 69.5, 30.4, 19.2, 13.8.



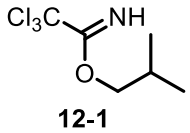
10-1

Compound **10-1**was prepared following the general procedure in 96% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (br s, 1H), 4.25 (t, *J* = 6.6 Hz, 2H), 1.78–1.69 (m, 2H), 1.46–1.35 (m, 2H), 1.35–1.18 (m, 14H), 0.85 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0, 91.8, 69.7, 32.0, 29.69, 29.66, 29.61, 29.4, 29.3, 28.3, 25.9, 22.8, 14.2; **HRMS** (ESI) calcd for $C_{11}H_{22}$ [M-$C_2H_2Cl_3NO$]$^+$: 154.1722, found: 154.1720.



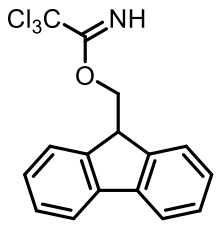
11-1

Compound **11-1** was prepared following the general procedure in 84% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (br s, 1H), 7.32–7.18 (m, 5H), 5.30–5.19 (m, 1H), 3.10 (dd, *J* = 13.8, 6.7 Hz, 1H), 2.88 (dd, *J* = 13.8, 6.2 Hz, 1H), 1.34 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.9, 137.4, 129.6, 128.3, 126.5, 91.9, 76.7, 41.7, 18.5; **HRMS** (ESI) calcd for C_9H_{10} [M-$C_2H_2Cl_3NO$]$^+$: 118.0783, found: 118.0781.



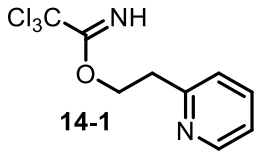
12-1

Compound **12-1** was prepared following the general procedure in 89% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (br s, 1H), 4.05 (d, *J* = 6.6 Hz, 2H), 2.17–2.05 (m, 1H), 1.00 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2, 91.8, 75.6, 27.8, 19.1.



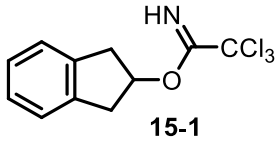
13-1

Compound **13-1** was prepared following the general procedure in 56% yield as white solid (R_f = 0.3, Hexanes:EtOAc = 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (br s, 1H), 7.81 (d, *J* = 7.5 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 4.55 (d, *J* = 7.6 Hz, 2H), 4.43 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9, 143.7, 141.4, 128.0, 127.3, 125.6, 120.1, 91.5, 71.8, 46.7; **HRMS** (ESI) calcd for $C_{14}H_{10}$ [M-$C_2H_2Cl_3NO$]$^+$: 178.0783, found: 178.0780.



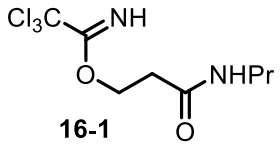
14-1

Compound **14-1** was prepared following the general procedure in 79% yield as colorless oil (R_f = 0.3, Hexanes:EtOAc = 10:1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.7 Hz, 1H), 8.30 (br s, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 1H), 7.17–7.11 (m, 1H), 4.68 (t, *J* = 6.6 Hz, 2H), 3.27 (t, *J* = 6.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5, 157.7, 149.4, 136.2, 123.6, 121.6, 91.3, 68.4, 36.9; **HRMS** (ESI) calcd for C_7H_7N $[M\text{-}C_2H_2Cl_3NO]^+$: 105.0578, found: 105.0577.



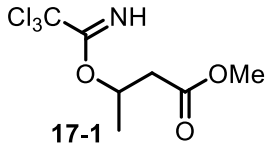
15-1

Compound **15-1** was prepared following the general procedure in 87% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (br s, 1H), 7.27–7.22 (m, 2H), 7.21–7.16 (m, 2H), 5.72–5.65 (m, 1H), 3.42 (dd, *J* = 17.1, 6.7 Hz, 2H), 3.18 (dd, *J* = 17.1, 3.3 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5, 140.3, 126.9, 124.7, 91.7, 80.0, 39.2; **HRMS** (ESI) calcd for C_9H_8 $[M\text{-}C_2H_2Cl_3NO]^+$: 116.0626, found: 116.0621.



16-1

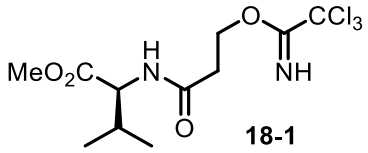
Compound **16-1** was prepared following the general procedure in 84% yield as colorless oil (R_f = 0.5, Hexanes:EtOAc = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (br s, 1H), 6.10 (brs, 1H), 4.54 (t, *J* = 6.1 Hz, 2H), 3.18 (dd, *J* = 13.3, 6.9 Hz, 2H), 2.62 (t, *J* = 6.1 Hz, 2H), 1.56–1.42 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 162.2, 91.1, 65.6, 41.2, 35.4, 22.6, 11.3; **HRMS** (ESI) calcd for $C_6H_{11}NO$ $[M\text{-}C_2H_2Cl_3NO]^+$: 113.0841, found: 113.0840.



17-1

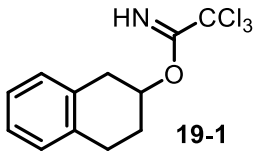
Compound **17-1** was prepared following the general procedure in 65% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (br s, 1H), 5.48–5.37 (m, 1H), 3.68 (s, 3H), 2.83 (dd, *J* = 15.7, 7.6 Hz, 1H), 2.61 (dd, *J* = 15.7, 5.7 Hz, 1H), 1.42 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.5,

161.6, 91.5, 72.4, 51.8, 40.2, 18.8; **HRMS** (ESI) calcd for $C_5H_8O_2$ [M-$C_2H_2Cl_3NO$]$^+$: 100.0524, found: 100.0522.



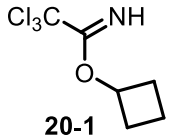
18-1

Compound **18-1** was prepared following the general procedure in 71% yield as colorless oil (R_f = 0.5, Hexanes:EtOAc = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (br s, 1H), 6.33 (d, *J* = 8.3 Hz, 1H), 4.65-4.55 (m, 3H), 3.71 (s, 3H), 2.70 (t, *J* = 5.7 Hz, 2H), 2.18–2.08 (m, 1H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.5, 169.7, 162.5, 91.2, 65.5, 57.2, 52.3, 35.8, 31.5, 19.0, 18.0.



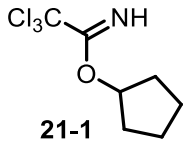
19-1

Compound **19-1** was prepared following the general procedure in 74% yield as colorless oil (R_f = 0.3, Hexanes:EtOAc = 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (br s, 1H), 7.15–7.02 (m, 4H), 5.39–5.27 (m, 1H), 3.20 (dd, *J* = 16.7, 5.1 Hz, 1H), 3.05–2.92 (m, 2H), 2.87–2.77 (m, 1H), 2.17–2.02 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0, 135.5, 133.4, 129.3, 128.5, 126.04, 125.96, 91.8, 74.7, 33.8, 27.1, 26.4; **HRMS** (ESI) calcd for $C_{10}H_{10}$ [M-$C_2H_2Cl_3NO$]$^+$: 130.0783, found: 130.0782.



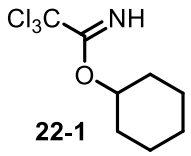
20-1

Compound **20-1**[2] was prepared following the general procedure in 76% yield as colorless oil (R_f = 0.3, Hexanes:EtOAc = 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (br s, 1H), 5.16–5.01 (m, 1H), 2.47–2.38 (m, 2H), 2.23–2.11 (m, 2H), 1.90–1.80 (m, 1H), 1.71–1.59 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.9, 91.6, 73.4, 30.0, 13.5. The spectra data are consistent with those reported in literature.



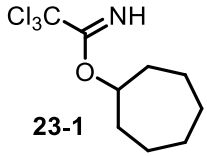
21-1

Compound **21-1** was prepared following the general procedure in 84% yield as colorless oil (= 0.4, Hexanes:EtOAc = 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (br s, 1H), 5.32–5.26 (m, 1H), 1.93–1.83 (m, 4H), 1.81–1.74 (m, 2H), 1.67–1.59 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5, 92.1, 82.3, 32.3, 23.9; **HRMS** (ESI) calcd for C_5H_8 $[M\text{-}C_2H_2Cl_3NO]^+$: 68.0626, found: 68.0623.



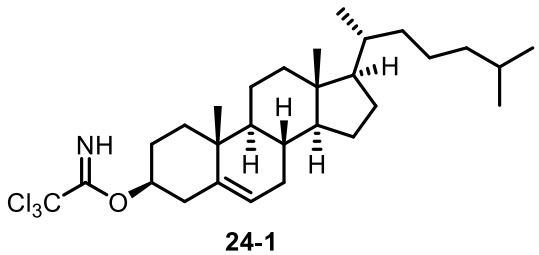
22-1

Compound **22-1** was prepared following the general procedure in 81% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 40:1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (br s, 1H), 4.97–4.89 (m, 1H), 1.96–1.88 (m, 2H), 1.81–1.73 (m, 2H), 1.69–1.60 (m, 2H), 1.57–1.48 (m, 1H), 1.47–1.35 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2, 92.2, 77.4, 30.7, 25.6, 23.4; **HRMS** (ESI) calcd for C_6H_{10} $[M\text{-}C_2H_2Cl_3NO]^+$: 82.0783, found: 82.0783.



23-1

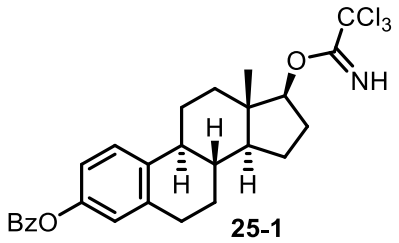
Compound **23-1** was prepared following the general procedure in 81% yield as colorless oil (R_f = 0.5, Hexanes:EtOAc = 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (br s, 1H), 5.11–4.99 (m, 1H), 2.01–1.92 (m, 2H), 1.86–1.76 (m, 2H), 1.73–1.65 (m, 2H), 1.61–1.53 (m, 4H), 1.51–1.42 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0, 92.2, 80.0, 32.9, 28.3, 22.8; **HRMS** (ESI) calcd for C_7H_{12} $[M\text{-}C_2H_2Cl_3NO]^+$: 96.0939, found: 96.0939.



24-1

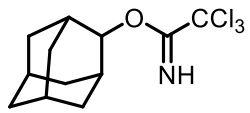
Compound **24-1** was prepared following the general procedure in 65% yield as white solid (R_f = 0.5, Hexanes:EtOAc = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (br s, 1H), 5.41 (d, *J* = 4.4 Hz, 1H), 4.81–4.71 (m, 1H), 2.52 (dd, *J* = 12.7, 3.2 Hz, 1H), 2.43 (t, *J*

= 11.6 Hz, 1H), 2.07–1.94 (m, 3H), 1.93–1.87 (m, 1H), 1.87–1.77 (m, 1H), 1.76–1.65 (m, 1H), 1.61–1.44 (m, 7H), 1.38–1.09 (m, 11H), 1.05 (s, 3H), 1.01–0.95 (m, 2H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 5.4 Hz, 6H), 0.68 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1, 139.6, 123.0, 92.1, 79.0, 56.8, 56.3, 50.2, 42.4, 39.9, 39.7, 37.5, 37.1, 36.8, 36.3, 35.9, 32.1, 32.0, 28.4, 28.2, 27.2, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0; **HRMS** (ESI) calcd for $C_{27}H_{44}$ [M-$C_2H_2Cl_3NO$]$^+$: 368.3443, found: 368.3456.



25-1

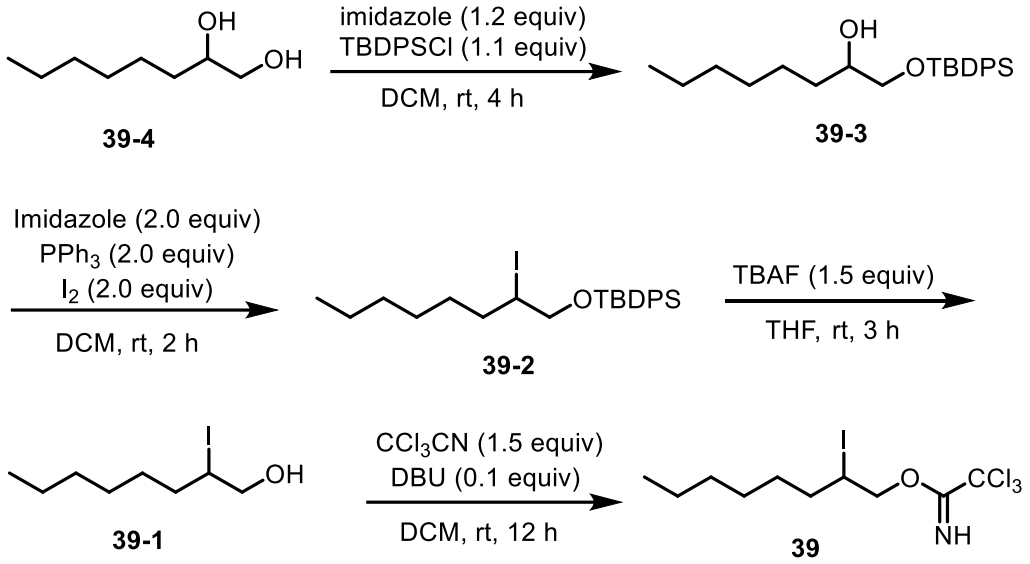
Compound **25-1** was prepared following the general procedure in 81% yield as white solid (R_f = 0.4, Hexanes:EtOAc = 8:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 3.4 Hz, 2H), 8.20 (s, 1H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.95 (s, 1H), 4.85 (t, *J* = 8.2 Hz, 1H), 2.98–2.84 (m, 2H), 2.42–2.28 (m, 3H), 2.04 (d, *J* = 12.0 Hz, 1H), 1.97–1.89 (m, 1H), 1.85–1.77 (m, 1H), 1.72–1.65 (m, 1H), 1.64–1.30 (m, 6H), 0.97 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 163.1, 148.8, 138.3, 138.0, 133.6, 130.3, 129.8, 128.6, 126.6, 121.8, 118.8, 92.1, 87.5, 49.8, 44.2, 43.6, 38.3, 37.1, 29.7, 27.2, 27.1, 26.2, 23.4, 12.2; **HRMS** (ESI) calcd for $C_{25}H_{26}O_2$ [M-$C_2H_2Cl_3NO$]$^+$: 358.1933, found: 358.1934.



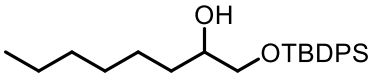
37

Compound **37** was prepared following the general procedure in 83% yield as white solid (R_f = 0.4, Hexanes:EtOAc = 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (br s, 1H), 5.05 (t, *J* = 3.1 Hz, 1H), 2.23–2.10 (m, 4H), 1.91–1.75 (m, 8H), 1.62–1.57 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2, 92.3, 82.1, 37.5, 36.4, 31.9, 31.3, 27.3, 27.2; **HRMS** (ESI) calcd for $C_{10}H_{14}$ [M-$C_2H_2Cl_3NO$]$^+$: 134.1096, found: 134.1093.

3.2 Preparation of compound **39**

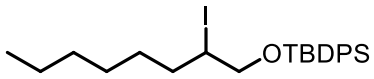


Scheme S2



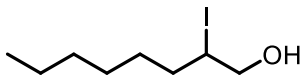
39-3

To a suspension of 1,2-octanediol **39-4** (1.6 mL, 10 mmol, 1 equiv) and imidazole (0.82 g, 12 mmol, 1.2 equiv) in CH_2Cl_2 (50 mL) was added TBDPSCl (2.60 mL, 10 mmol, 1.0 equiv) dropwise over 10 min. The reaction mixture was stirred at room temperature for 4 hours and then half of the CH_2Cl_2 was removed at reduced pressure. The remaining suspension was diluted with 250 mL of hexanes and the resulting precipitate was removed by filtration. The filtrate was concentrated and the crude product was purified by chromatography (5% to 30% EtOAc-hexanes) to give 3.26 g (85% yield) of compound **39-3** as colorless oil (R_f = 0.6, Hexanes:EtOAc = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76–7.60 (m, 4H), 7.50–7.39 (m, 6H), 3.80–3.74 (m, 1H), 3.70 (dd, *J* = 10.1, 3.1 Hz, 1H), 3.54 (dd, *J* = 9.7, 7.7 Hz, 1H), 2.60 (br s, 1H), 1.54–1.39 (m, 3H), 1.35–1.23 (m, 7H), 1.12 (s, 9H), 0.91 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.6, 133.3, 129.9, 127.9, 72.1, 68.2, 32.9, 31.9, 29.4, 27.0, 25.6, 22.7, 19.4, 14.2.



39-2

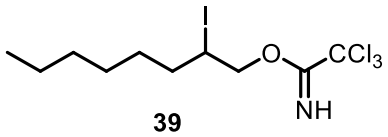
Triphenylphosphine (4.46 g, 17 mmol, 2 equiv), imidazole (1.16 g, 17 mmol, 2 equiv) and iodine (4.31 g, 17 mmol, 2 equiv) were dissolved in dichloromethane (40 mL), the resulting mixture was stirred at room temperature for 1 hour. Then a solution of compound **39-3** (3.26 g, 8.5 mmol, 1.0 equiv) in dichloromethane (10 mL) was added dropwise over 10 minutes. The resulting solution was continuously stirred at room temperature for 1 hour and then washed with 40 mL H_2O and 40 mL of a sodium hydrogen sulfite ($NaHSO_3$) solution. The organic phase was dried over $MgSO_4$, filtered and evaporated on a rotary evaporator. During this evaporation triphenylphosphine oxide crystallized as a white mass. The crude product was transferred into a 25 mL beaker, homogenized with 3 mL diethyl ether, and filtered. The filter cake was washed with diethyl ether (2 x 5 mL), leaving pure white triphenylphosphine oxide. The combined filtrate was concentrated *in vacuo*, the resulting residue was purified by column chromatography (1% to 5% EtOAc-hexanes) to give 3.68 g (87%) of compound **39-2** as colorless oil (R_f = 0.7, Hexanes:EtOAc = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68–7.61 (m, 4H), 7.40–7.30 (m, 6H), 4.11–4.01 (m, 1H), 3.86 (dd, *J* = 10.8, 5.4 Hz, 1H), 3.75 (dd, *J* = 10.7, 7.2 Hz, 1H), 1.90–1.79 (m, 1H), 1.79–1.68 (m, 1H), 1.52–1.41 (m, 1H), 1.34–1.19 (m, 7H), 1.05 (s, 9H), 0.85 (t, *J* = 6.6 Hz, 3H).



39-1

A solution of compound **39-2** (3.68 g, 7.4 mmol, 1 equiv) in tetrahydrofuran (20 mL) was added to a mixture of tetrabutylammonium fluoride (TBAF) (2.88 g, 11 mmol, 1.5 equiv) and acetic acid in tetrahydrofuran (The pH value was adjusted to 5 by controlling the amount of acetic acid). The resulting reaction mixture was continuously stirred at room temperature. After 3 hours, the reaction mixture was diluted with water, the aqueous phase was separated and extracted with dichloromethane. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated *in*

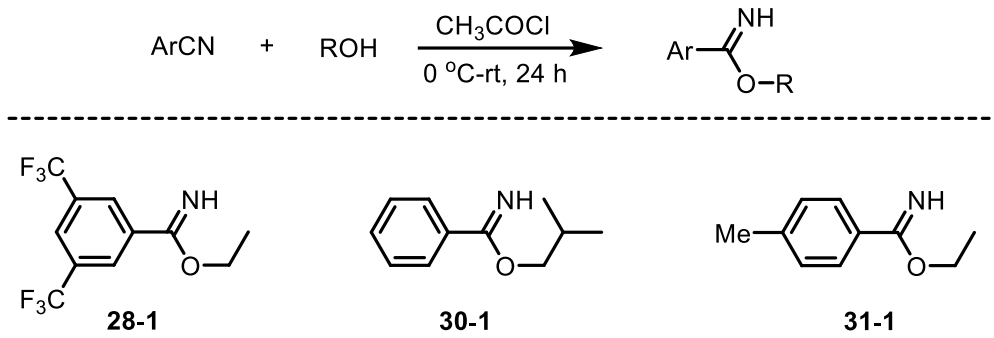
vacuo. The residue was purified by column chromatography (5% to 30% EtOAc-hexanes) to give compound **39-1** (1.72 g) in 91% yield as colorless oil (R_f = 0.5, Hexanes:EtOAc = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.28–4.18 (m, 1H), 3.80–3.65 (m, 2H), 2.01 (t, *J* = 6.8 Hz, 1H), 1.93–1.81 (m, 1H), 1.81–1.71 (m, 1H), 1.58–1.47 (m, 1H), 1.42–1.26 (m, 7H), 0.88 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 68.7, 42.3, 36.4, 31.7, 29.5, 28.6, 22.7, 14.2.



39

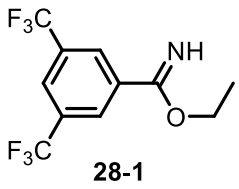
To a stirred mixture of compound **39-1** (1.72 g, 6.7 mmol, 1 equiv) in 20 mL of dichloromethane, was added trichloroacetonitrile (1.0 mL, 10 mmol, 1.5 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.1 mL, 0.67 mmol, 0.1 equiv). The resulting reaction mixture was continuously stirred at room temperature. After 12 hours, the reaction mixture was diluted with water, the aqueous phase was separated and extracted with dichloromethane. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by column chromatography with triethylamine-treated silica gel using 3% of triethylamine in hexane as eluent to give compound **39** (2.35 g) in 88% yield as colorless oil (R_f = 0.2, Hexanes:EtOAc = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (br s, 1H), 4.59 (dd, *J* = 11.3, 5.7 Hz, 1H), 4.43 (dd, *J* = 11.3, 7.6 Hz, 1H), 4.36–4.28 (m, 1H), 1.90–1.79 (m, 2H), 1.60–1.47 (m, 1H), 1.43–1.36 (m, 1H), 1.34–1.24 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0, 91.2, 73.6, 36.3, 31.6, 29.7, 29.0, 28.5, 22.6, 14.2.

3.3 Experimental procedure for preparation of benzimidates 28-1, 30-1, 31-1



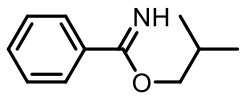
Scheme S3

Acetyl chloride (7.1 mL, 100 mmol, 10 equiv) was added dropwise to a stirred mixture of aromatic cyanide (10 mmol, 1 equiv) in the corresponding alcohol (20 mL) at 0 °C. The resulting solution was allowed to warm up to room temperature and continuously stirred for 24 hours. The reaction mixture was then concentrated *in vacuo*. The residue was dissolved in dichloromethane and washed with Sat. $NaHCO_3$ and brine. The organic layer was separated, dried with Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by chromatography on silica gel (10-30% EtOAc in hexanes) to give the desired product.



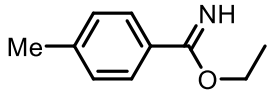
28-1

Compound **28-1** (3.5:1 mixture of inseparable isomers) was prepared in 45% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 20:1).**^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.58 (br s, 1H), 8.52–8.32 (m, 2H), 7.99 (s, 1H), 4.24 (q, J = 6.9 Hz, 1.51H), 4.11 (q, J = 6.6 Hz, 0.44H), 1.28 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 161.4, 157.8, 136.4, 134.3, 130.7 (q, $J_{C\text{-}F}$ = 33 Hz), 127.4, 123.6, 123.0 (q, $J_{C\text{-}F}$ = 270 Hz), 61.4, 61.0, 13.6, 13.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.00 (s, 6F)； **HRMS** (ESI) calcd for $C_{11}H_{10}F_6NO$ [M+H$^+$]: 286.0661, found: 286.0660.



30-1

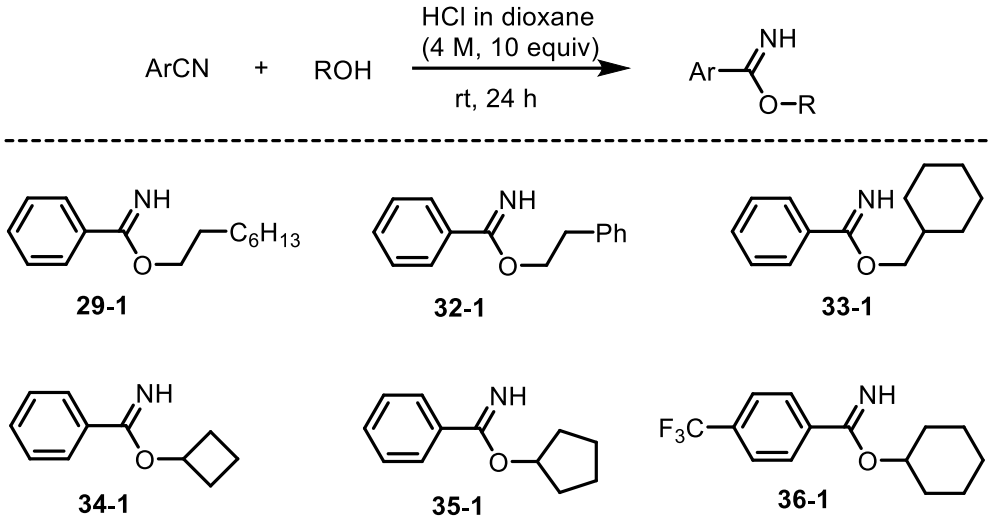
Compound **30-1** was prepared in 58% yield as colorless oil (R_f = 0.3, Hexanes:EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 6.5 Hz, 2H), 7.46–7.39 (m, 3H), 4.03 (d, *J* = 5.9 Hz, 2H), 2.19–2.06 (m, 1H), 1.05 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 133.0, 130.8, 128.5, 126.7, 72.3, 27.9, 19.4.



31-1

Compound **31-1** was prepared in 61% yield as colorless oil (R_f = 0.6, Hexanes:EtOAc = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.37 (q, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H)； **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.6, 140.8, 130.0, 129.0, 126.5, 61.5, 21.2, 14.1.

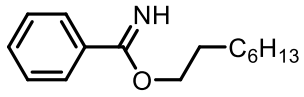
3.4 Experimental procedure for preparation of benzimidates 29-1, 32-1, 33-1, 34-1, 35-1, 36-1



Scheme S4

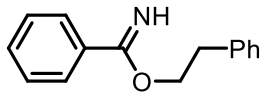
A mixture of corresponding alcohol (5 mmol, 1 equiv) and aromatic cyanide (5 mmol, 1 equiv) in 4 M HCl in dioxane (12.5 mL, 50 mmol, 10 equiv) were stirred at room temperature for 24 hours. The reaction mixture was then concentrated *in vacuo*. The residue was dissolved in dichloromethane, washed with Sat. $NaHCO_3$ and brine. The organic layer was separated, dried with Na_2SO_4, filtered and concentrated *in vacuo*. The

resulting residue was purified by chromatography on silica gel (10-30% EtOAc in hexanes) to give the desired product.



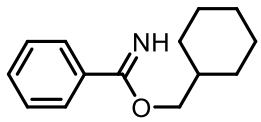
29-1

Compound **29-1** was prepared in 65% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.0 Hz, 2H), 7.47–7.36 (m, 3H), 4.24 (t, *J* = 6.6 Hz, 2H), 1.84–1.75 (m, 2H), 1.52–1.42 (m, 2H), 1.39–1.24 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.9, 133.0, 130.8, 128.5, 126.7, 77.5, 77.2, 76.8, 66.2, 31.9, 29.4, 29.3, 28.7, 26.3, 22.7, 14.1; **HRMS** (ESI) calcd for $C_{15}H_{24}NO$ [M+H$^+$]: 234.1852, found: 234.1855.



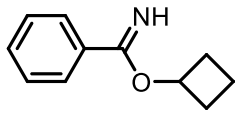
32-1

Compound **32-1** was prepared in 72% yield as colorless oil (R_f = 0.3, Hexanes:EtOAc = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (s, 2H), 7.47–7.37 (m, 3H), 7.34–7.30 (m, 4H), 7.27–7.21 (m, 1H), 4.51 (br s, 2H), 3.13 (t, *J* = 6.9 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.2, 138.6, 132.7, 130.9, 129.1, 128.5, 126.6, 126.4, 66.7, 35.2; **HRMS** (ESI) calcd for $C_{15}H_{16}NO$ [M+H$^+$]: 226.1226, found: 226.1226.



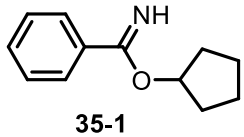
33-1

Compound **33-1** was prepared in 67% yield as colorless oil (R_f = 0.3, Hexanes:EtOAc = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.0 Hz, 2H), 7.42–7.32 (m, 3H), 4.03 (d, *J* = 5.8 Hz, 2H), 1.89–1.78 (m, 3H), 1.77–1.70 (m, 2H), 1.70–1.62 (m, 1H), 1.32–1.15 (m, 3H), 1.12–1.01 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.7, 132.9, 130.7, 128.3, 126.6, 71.2, 37.2, 29.9, 26.4, 25.8; **HRMS** (ESI) calcd for $C_{14}H_{20}NO$ [M+H$^+$]: 218.1539, found: 218.1544.



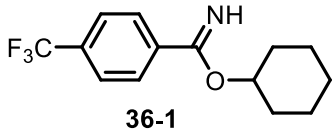
34-1

Compound **34-1** was prepared in 41%yield as colorless oil (R_f = 0.3, Hexanes:EtOAc = 20:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.85 (br s, 1H), 7.82 (d, *J* = 7.0 Hz, 2H), 7.53–7.38 (m, 3H), 5.17–5.06 (m, 1H), 2.42–2.31 (m, 2H), 2.13–2.00 (m, 2H), 1.77 (q, *J* = 10.1 Hz, 1H), 1.69–1.55 (m, 1H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 163.9, 132.3, 130.5, 128.2, 126.8, 68.8, 30.2, 13.3; **HRMS** (ESI) calcd for $C_{11}H_{14}NO$ [M+H$^+$]: 176.1070, found: 176.1074.



35-1

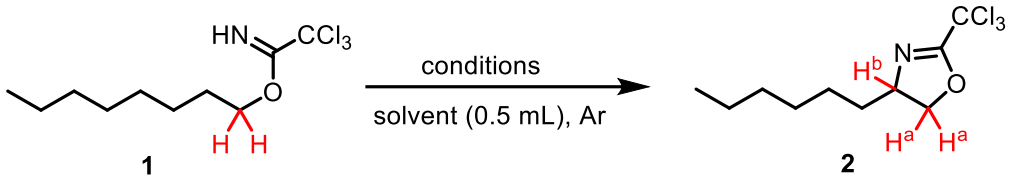
Compound **35-1** was prepared in 36% yield as colorless oil (R_f = 0.3, Hexanes:EtOAc = 20:1).**^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.82 (br s, 1H), 7.83–7.77 (m, 2H), 7.53–7.40 (m, 3H), 5.36–5.30 (m, 1H), 1.99–1.83 (m, 2H), 1.82–1.68 (m, 4H), 1.65–1.54 (m, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.5, 132.8, 130.6, 128.4, 126.8, 76.6, 32.3, 23.6; **HRMS** (ESI) calcd for $C_{12}H_{16}NO$ [M+H$^+$]: 190.1226, found: 190.1226.



36-1

Compound **36-1** (4.8:1 mixture of inseparable isomers) was prepared in 30% yield as colorless oil (R_f = 0.3, Hexanes:EtOAc = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.12 (d, *J* = 7.8 Hz, 0.34H), 8.02 (d, *J* = 8.2 Hz, 1.58H), 7.80 (d, *J* = 8.3 Hz, 2H), 5.04–4.93 (m, 0.81H), 4.70–4.61 (m, 0.17H), 1.98–1.81 (m, 2H), 1.71–1.65 (m, 2H), 1.57–1.45 (m, 3H), 1.42–1.24 (m, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 162.9, 136.2, 130.6 (q, $J_{C\text{-}F}$ = 32.0 Hz), 129.9,127.6, 125.4, 72.1, 30.8, 25.2, 23.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.86 (s, 3F); **HRMS** (ESI) calcd for $C_{14}H_{17}F_3NO$ [M+H$^+$]: 272.1257, found: 272.1260.

4. Optimization of reaction conditions



1

δ 4.27 (t, *J* = 6.6 Hz, 2H)

2

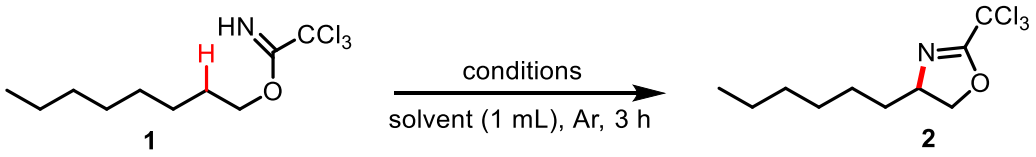
H^a: δ 4.62 (t, *J* = 8.0 Hz, 1H)
δ 4.19 (t, *J* = 8.0 Hz, 1H)
H^b: δ 4.34-4.24 (m, 1H)

Scheme S5

Reactions were carried out in a 12 mL sealed vial at a 0.2 mmol scale on bench top. The vials were purged with Ar for 1 min if necessary. After 3 hours, the reactions mixture were cooled to room temperature and concentrated *in vacuo*, the crude residue was dissolved in 1 mL of deuterated chloroform for ^{1}H-NMR analysis. 1,1,2,2-tetrachloroethane (33.6 mg, 0.2 mmol, 1 equiv, a singlet peak around 5.97 ppm was set as 2.00) was added as internal standard. Yields of compounds **2** were determined based on the following method:

Yield of **2** = integration of peak (δ 4.62) × 100%

Table S1. Evaluation of different oxidants and solvents[a]



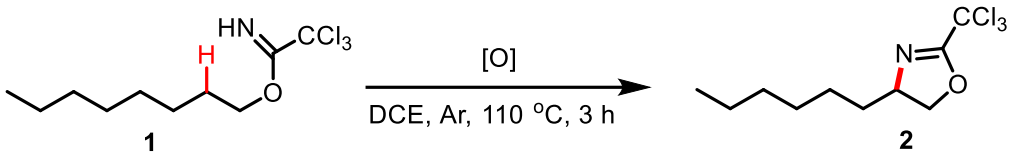
1 **2**

entry	reagents (equiv)	solvent	temperature (°C)	yield (%)[b]
1	$Pd(OAc)_2$ (0.1), $PhI(OAc)_2$ (2)	toluene	100	ND[c]
2	$Pd(OAc)_2$ (0.1), NIS (2)	toluene	100	37
3	NIS (2)	toluene	100	56
4	$PhI(OAc)_2$ (2), I_2 (0.2)	toluene	100	46

5	$PhI(OAc)_2$ (2)	toluene	100	ND
6	I_2 (2)	toluene	100	ND
7	NIS (2)	toluene	110	54
8	NIS (2)	DCE	110	70
9	NIS (3)	toluene	110	68
10	NIS (3)	CH_3CN	110	41
11	NIS (3)	DCE	110	86
12	NIS (3), in darkness	DCE	110	81
13	NIS (3), in air	DCE	110	65
14	NIS (3), Ag_2O (1.5)	DCE	110	85
15	NIS (3), Cs_2CO_3 (2)	DCE	110	85

(a) All the reactions were run on a 0.2 mmol scale. (b) ^{1}H-NMR yield using 1,1,2,2-tetrachloroethane as internal standard. (c) ND: not detected.

Table S2. Evaluation of more oxidants and reaction concentration[a]



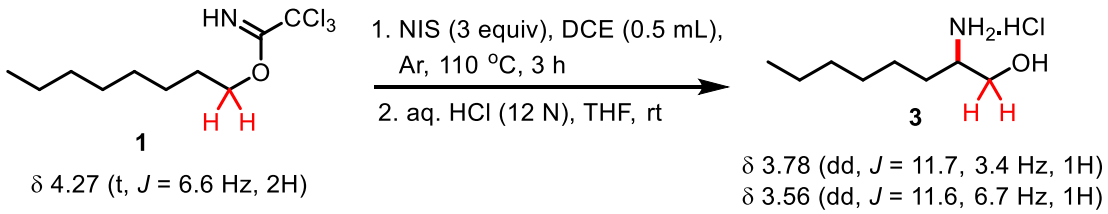
1 2

entry	oxidant (equiv)	DCE (mL)	yield (%)[b]
1	BPO (3)	1	ND[c]
2	CAN (3)	1	ND
3	*t*-BuOOH (3)	1	ND
4	NFSI (3)	1	ND
5	NCS (3)	1	ND
6	NBS (3)	1	<5
7	NIS (3)	1	86
8	NIS (1)	1	30

9	NIS (2)	1	68
10	NIS (5)	1	83
11	NIS (3)	0.2	84
12	NIS (3)	0.5	86
13	NIS (3)	2.0	82
14	NIS (3)	5.0	83

(a) All the reactions were run on a 0.2 mmol scale. (b) ^{1}H-NMR yield using 1,1,2,2-tetrachloroethane as internal standard. (c) ND: not detected.

Table S3. Evaluation of different hydrolization conditions

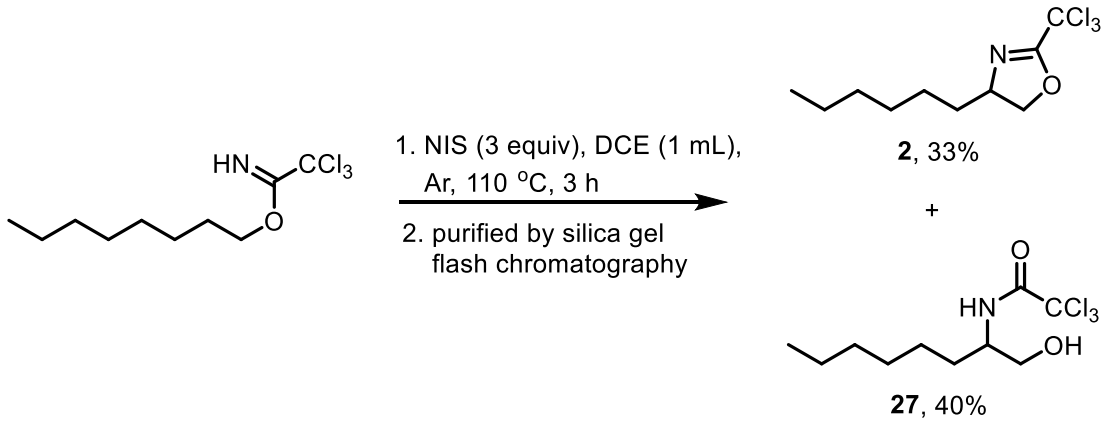


entry	THF (mL)	aq. HCl (equiv)	time (h)	yield (%)
1	0	10	5	39
2	0.5	10	5	75
3	1	10	5	83
4	2	10	5	84
5	3	10	5	80
6	5	10	5	85
7	2	1	5	8
8	2	2	5	26
9	2	3	5	53
10	2	5	5	79
11	2	10	0.5	78
12	2	10	1	84
13	2	10	2	82

A mixture of octyl trichloroacetimidate **1** (55 mg, 0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 ^{o}C for 3 hours. The mixture was then cooled to room temperature and diluted with THF (if necessary). Specific amount of aq. HCl (12 M) was added according to the Table S2, and the resulting mixture was continuously stirred at room temperature. Then the mixture was concentrated *in vacuo*, the crude residue was dissolved in 1 mL of deuterated chloroform for ^{1}H-NMR analysis. 1,1,2,2-tetrachloroethane (33.6 mg, 0.2 mmol, 1 equiv, a singlet peak around 5.97 ppm was set as 2.00) was added as internal standard. Yields of compounds **3** were determined based on the following method:

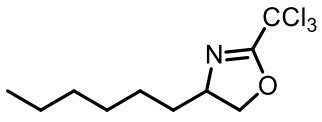
Yield of **3** = integration of peak (δ 3.78) × 100%

5. Hydrolization of oxazoline 2 under different conditions



Scheme S6

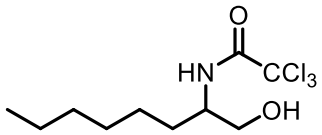
A mixture of octyl trichloroacetimidate **1** (55 mg, 0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 ^{o}C for 3 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*, the residue was purified by silica gel flash chromatography to give oxazoline **2** in 33% yield as colorless oil and **27** in 40% yield as white solid.



2

R_f = 0.4, Hexanes:EtOAc = 10:1

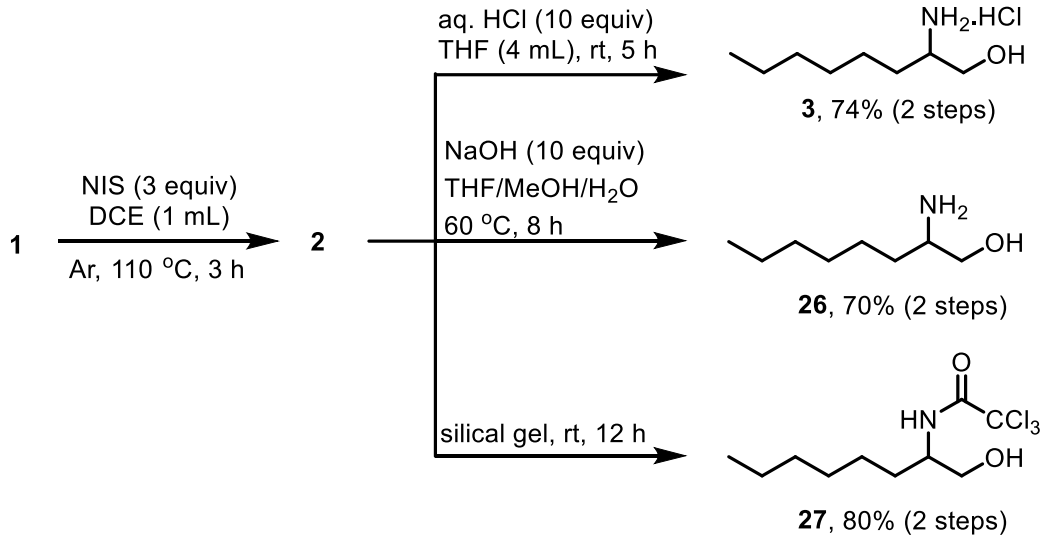
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.62 (t, *J* = 8.0 Hz, 1H), 4.34–4.24 (m, 1H), 4.19 (t, *J* = 8.0 Hz, 1H), 1.77–1.66 (m, 1H), 1.59–1.48 (m, 1H), 1.42–1.34 (m, 1H), 1.32–1.21 (m, 7H), 0.83 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1, 86.7, 75.9, 67.1, 34.9, 31.7, 29.1, 25.4, 22.6, 14.1; **HRMS** (ESI) calcd for $C_{10}H_{17}Cl_3NO$ [M+H$^+$]: 272.0370, found: 272.0376.



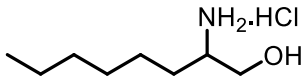
27

R_f = 0.5, Hexanes:EtOAc = 4:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (d, *J* = 7.7 Hz, 1H), 4.01–3.91 (m, 1H), 3.79 (dd, *J* = 11.1, 3.6 Hz, 1H), 3.72 (dd, *J* = 11.0, 4.3 Hz, 1H), 1.78 (br s, 1H), 1.67–1.58 (m, 3H), 1.39–1.32 (m, 3H), 1.32–1.26 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.3, 92.8, 63.9, 53.5, 31.7, 30.9, 29.1, 25.9, 22.6, 14.1; **HRMS** (ESI) calcd for $C_{10}H_{19}Cl_3NO_2$ [M+H$^+$]: 290.0476, found: 290.0467.

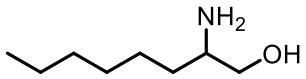


Scheme S8



3

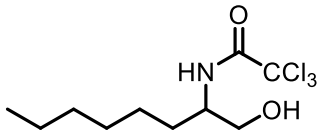
A mixture of octyl trichloroacetimidate **1** (55 mg, 0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. The mixture was then cooled to room temperature and diluted with THF (4 mL). aq. HCl (166 µL, 12 M, 10 equiv) was added, and the resulting mixture was continuously stirred for 5 h at room temperature. Then the mixture was concentrated *in vacuo,* the crude residue was purified by chromatography on silica gel (5%-10% methanol in dichloromethane) to give compound **3**[3] in 74% yield as pale yellow oil (R_f = 0.4, CH_2Cl_2:MeOH = 8:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 3.78 (dd, *J* = 11.7, 3.4 Hz, 1H), 3.56 (dd, *J* = 11.6, 6.7 Hz, 1H), 3.24–3.16 (m, 1H), 1.73–1.56 (m, 2H), 1.36 (m, 8H), 0.94 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR** (101 MHz, MeOD-*d*$_4$) δ 63.0, 55.4, 33.3, 31.1, 30.8, 27.1, 24.2, 15.1.



26

A mixture of octyl trichloroacetimidate **1** (55 mg, 0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. The mixture was then cooled to room temperature and concentrated *in vacuo*. The residue was dissolved in a mixture of THF/MeOH/H_2O (4/1/1, 1.5 mL) at room temperature. The reaction mixture was heated at 60 °C for 8 hours. After been cooled to room temperature, the mixture was diluted with water (5 mL) and extracted with DCM (10 mL × 3). The combined organic layer was washed with water and brine, dried with Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (5%-10% methanol in dichloromethane) to give compound **26** in 70% yield as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.65 (s, 3H), 4.00 (d, *J* = 11.0 Hz, 1H), 3.89-3.81 (m, 1H), 3.73

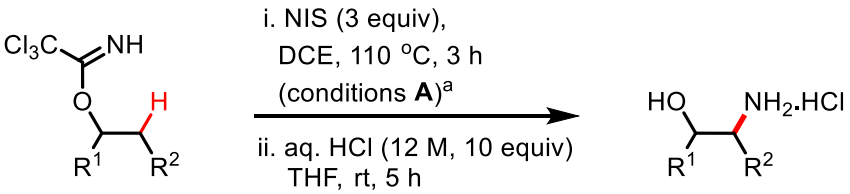
(s, 1H), 1.92-1.81 (m, 1H), 1.78-1.65 (m, 1H), 1.44-1.21 (m, 8H), 0.88 (t, *J* = 5.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 61.4, 54. 7, 31. 7, 29.7, 29.2, 25.8, 22.7, 14.2.



27

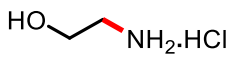
A mixture of octyl trichloroacetimidate **1** (55 mg, 0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. The mixture was then cooled to room temperature and mixed with silica gel (500 mg) and concentrated. The resulting mixture was placed at room temperature overnight then purified by silica gel flash chromatography to give compound **27** in 80% yield.

6. Substrate scope of *β*-C(sp^3)-H amination of trichloroacetimidates



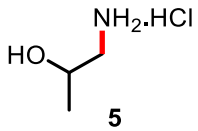
Scheme S8

6.1 General experimental procedure A for preparation of 1,2-aminol alcohol hydrochlorides: A mixture of trichloroacetimidate (0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. The mixture was then cooled to room temperature and diluted with THF (4 mL). aq. HCl (166 µL, 12 M, 10 equiv) was added, and the resulting mixture was continuously stirred for 5 h at room temperature. Then the mixture was concentrated *in vacuo,* the crude residue was purified by chromatography on silica gel (5%-10% methanol in dichloromethane) to give the desired product.



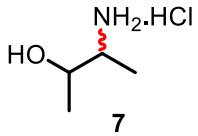
4

Compound **4**[4] was prepared following the general procedure A in 63% yield as pale yellow oil (R_f = 0.3, CH_2Cl_2:MeOH = 2:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 3.80 (t, *J* = 5.1 Hz, 2H), 3. 08 (t, *J* = 5.1 Hz, 2H); **^{13}C NMR** (101 MHz, MeOD-*d*$_4$) δ 59.7, 43.7.



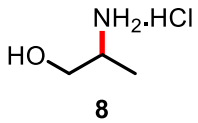
5

Compound **5**[5] was prepared following the general procedure A in 69% yield as pale yellow oil (R_f = 0.3, CH_2Cl_2:MeOH = 4:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 4.04–3.94 (m, 1H), 3.03 (dd, *J* = 12.7, 2.9 Hz, 1H), 2.79 (dd, *J* = 12.6, 9.3 Hz, 1H), 1.26 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (101 MHz, MeOD-*d*$_4$) δ 65.7, 48.0, 21.9.



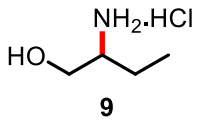
7

Compound **7**[6] (1.8:1 mixture of inseparable isomers) was prepared following the general procedure A in 39% yield as pale yellow oil (R_f = 0.3, CH_2Cl_2:MeOH = 4:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 3.99–3.92 (m, 0.37H), 3.71–3.61 (m, 0.69H), 3.31–3.22 (m, 0.48H), 3.10–3.01 (m, 0.66H), 1.31–1.20 (m, 6H); **^{13}C NMR** (101 MHz, MeOD-*d*$_4$) δ 70.3, 68.4, 55.7, 54.2, 21.2, 19.5, 16.6, 13.3.



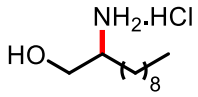
8

Compound **8**[7] was prepared following the general procedure A in 74% yield as pale yellow oil (R_f = 0.3, CH_2Cl_2:MeOH = 4:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 3.75 (dd, *J* = 11.6, 3.9 Hz, 1H), 3.53 (dd, *J* = 11.6, 7.1 Hz, 1H), 3.42–3.34 (m, 1H), 1.30 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (101 MHz, MeOD-*d*$_4$) δ 64.8, 51.4, 16.0.



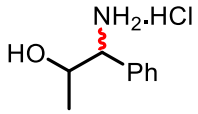
9

Compound **9**[8] was prepared following the general procedure A in 76% yield as pale yellow oil (R_f = 0.4, CH_2Cl_2:MeOH = 4:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 3.80 (dd, *J* = 11.7, 3.7 Hz, 1H), 3.60 (dd, *J* = 11.8, 6.7 Hz, 1H), 3.21–3.13 (m, 1H), 1.78–1.65 (m, 2H), 1.06 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (101 MHz, MeOD-*d*$_4$) δ 62.4, 56.6, 24.0, 11.0.



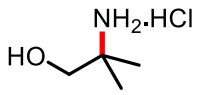
10

Compound **10** was prepared following the general procedure A in 77% yield as pale yellow oil (R_f = 0.5, CH_2Cl_2:MeOH = 8:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 3.78 (dd, *J* = 11.7, 3.6 Hz, 1H), 3.56 (dd, *J* = 11.7, 6.8 Hz, 1H), 3.25–3.14 (m, 1H), 1.73–1.55 (m, 2H), 1.49–1.28 (m, 14H), 0.93 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, MeOD-*d*$_4$) δ 63.0, 55.5, 33.7, 31.3, 31.24, 31.21, 31.17, 31.1, 27.2, 24.4, 15.2; **HRMS** (ESI) calcd for $C_{11}H_{26}NO$ [M+H$^+$]: 188.2009, found: 188.2013.



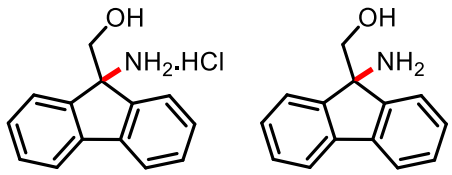
11

Compound **11**[9] (1.1:1 mixture of inseparable isomers) was prepared following the general procedure A in 63% yield as pale yellow oil (R_f = 0.4, CH_2Cl_2:MeOH = 8:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 7.57–7.42 (m, 5H), 4.29–4.21 (m, 1H), 4.14–4.04 (m, 0.58H), 4.00 (d, *J* = 9.2 Hz, 0.52H), 1.08 (d, *J* = 6.2 Hz, 1.6H), 1.08 (d, *J* = 6.3 Hz, 1.4H); **^{13}C NMR** (101 MHz, MeOD-*d*$_4$) δ 137.2, 135.7, 131.4, 131.2, 130.9, 130.6, 130.5, 129.8, 70.4, 68.8, 64.3, 61.9, 21.5, 20.5.



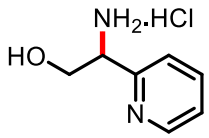
12

Compound **12**[10] was prepared following the general procedure A in 38% yield as pale yellow oil (R_f = 0.5, CH_2Cl_2:MeOH = 4:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 3.51 (s, 2H), 1.32 (s, 6H); **^{13}C NMR** (101 MHz, MeOD-*d*$_4$) δ 68.8, 57.0, 23.5.



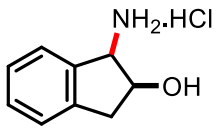
13 & **13'**

Compound **13-1** was aminated following the general procedure A to give compound **13** in 83% yield as white solid (R_f = 0.5, CH_2Cl_2:MeOH = 4:1). For easy characterization analysis by NMR, compound **13** was dissolved in dichloromethane, washed with Sat. $NaHCO_3$ and brine. The organic phase was dried with Na_2SO_4, filtered and concentrated *in vacuo* to afford compound **13'**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 3.71 (s, 2H), 2.75 (br s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.3, 139.7, 128.8, 127.9, 124.0, 120.2, 69.1, 65.9; **HRMS** (ESI) calcd for $C_{14}H_{14}NO$ [$M+H^+$]: 212.1070, found: 212.1068.



14

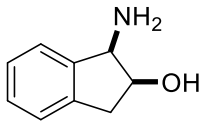
Compound **14**[11] was prepared following the general procedure A in 63% yield as pale yellow oil (R_f = 0.5, CH_2Cl_2:MeOH = 4:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 8.83 (d, *J* = 4.8 Hz, 1H), 8.33 (t, *J* = 7.7 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.80 (t, *J* = 6.3 Hz, 1H), 4.78–4.73 (m, 1H), 4.08 (dd, *J* = 11.6, 4.2 Hz, 1H), 3.96 (dd, *J* = 11.6, 6.2 Hz, 1H); **^{13}C NMR** (101 MHz, MeOD-*d*$_4$) δ 153.2, 147.7, 145.2, 128.1, 126.6, 63.9, 57.0.



15

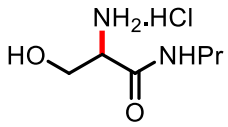
Compound **15** was prepared following the general procedure A in 77% yield as pale yellow oil (R_f = 0.3, CH_2Cl_2:MeOH = 4:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 7.53 (d, *J* = 7.3 Hz, 1H), 7.45–7.29 (m, 3H), 4.76 (dd, *J* = 11.0, 5.5 Hz, 1H), 4.63 (d, *J* = 5.2 Hz,

1H), 3.27 (dd, *J* = 16.3, 6.2 Hz, 1H), 3.06 (dd, *J* = 16.3, 4.9 Hz, 1H); **^{13}C NMR** (101 MHz, MeOD-d_4) δ 143.4, 138.3, 131.6, 129.1, 127.4, 127.1, 72.4, 59.2, 40.9; **HRMS** (ESI) calcd for $C_9H_{12}NO$ [M+H$^+$]: 150.0913, found: 150.0912.



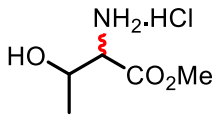
15'

Compound **15** was dissolved in ethyl acetate and washed with Sat. $NaHCO_3$ and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give compound **15'**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 5.1 Hz, 1H), 7.25 (m, 3H), 4.42–4.36 (m, 1H), 4.32 (d, *J* = 5.2 Hz, 1H), 3.10 (dd, *J* = 16.4, 5.5 Hz, 1H), 2.95 (dd, *J* = 16.4, 2.4 Hz, 1H), 2.38 (br s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 141.0, 128.1, 127.1, 125.6, 124.0, 72.9, 58.6, 39.5. The spectra data are consistent with those of *cis*-1-amino-2-indanol reported in literature.[12]



16

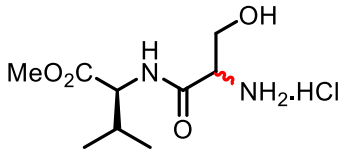
Compound **16** was prepared following the general procedure A in 76% yield as pale yellow oil (R_f = 0.3, CH_2Cl_2:MeOH = 4:1). **^{1}H NMR** (400 MHz, MeOD-d_4) δ 4.13–4.07 (m, 1H), 4.02 (dd, *J* = 11.7, 4.0 Hz, 1H), 3.91 (dd, *J* = 11.6, 6.2 Hz, 1H), 3.24 (t, *J* = 7.0 Hz, 2H), 1.66–1.52 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, MeOD-d_4) δ 169.0, 62.6, 57.0, 43.2, 24.2, 12.6; **HRMS** (ESI) calcd for $C_6H_{15}N_2O_2$ [M+H$^+$]: 147.1128, found: 147.1129.



17

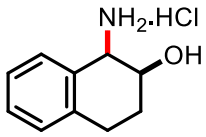
Compound **17**[13] (mixture of 1.6:1 inseparable isomers) was prepared following the general procedure A in 62% yield as pale yellow oil (R_f = 0.3, CH_2Cl_2:MeOH = 4:1).**^{1}H NMR** (400 MHz, MeOD-d_4) δ 4.35–4.23 (m, 1H), 4.11 (d, *J* = 2.5 Hz, 0.57H), 3.96 (d, *J* = 3.4 Hz, 0.40H), 3.88 (s, 3H), 1.35 (d, *J* = 6.5 Hz, 1.23H), 1.29 (d, *J* = 6.5 Hz, 1.72H);

^{13}C NMR (101 MHz, MeOD-*d*$_4$) δ 170.2, 169.4, 67.2, 67.1, 60.6, 60.2, 54.9, 54.7, 21.4, 19.6.



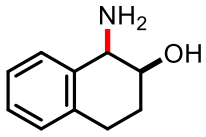
18

Compound **18**[14] (mixture of 1:1 inseparable isomers) was prepared following the general procedure A in 70% yield as pale yellow oil (R_f = 0.2, CH_2Cl_2:MeOH = 4:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 4.43 (t, *J* = 5.9 Hz, 1H), 4.09 (s, 1H), 4.05–3.96 (m, 1H), 3.91–3.80 (m, 1H), 3.75 (s, 3H), 2.30–2.16 (m, 1H), 0.99 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (101 MHz, MeOD-*d*$_4$) δ 173.1, 173.0, 168.52, 168.45, 62.5, 62.3, 59.5, 59.4, 56.5, 56.4, 54.5, 54.3, 31.9, 20.1, 19.2, 19.1.



19

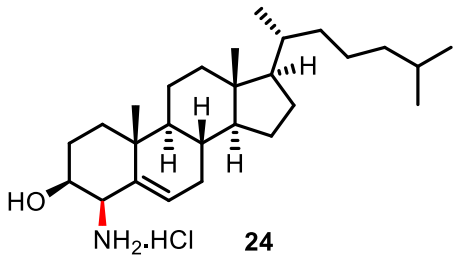
Compound **19** was prepared following the general procedure A in 68% yield as pale yellow oil (R_f = 0.4, CH_2Cl_2:MeOH = 4:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 7.43 (d, *J* = 7.3 Hz, 1H), 7.38–7.23 (m, 3H), 4.43 (d, *J* = 3.8 Hz, 1H), 4.28–4.17 (m, 1H), 3.11–3.01 (m, 1H), 2.97–2.85 (m, 1H), 2.11–2.00 (m, 1H), 1.99–1.86 (m, 1H); **^{13}C NMR** (101 MHz, MeOD-*d*$_4$) δ 138.8, 132.0, 131.5, 131.0, 130.9, 128.4, 67.4, 54.8, 28.6, 27.6; **HRMS** (ESI) calcd for $C_{10}H_{14}NO$ [M+H$^+$]: 164.1070, found: 164.1069.



19'

Compound **19** was dissolved in ethyl acetate and washed with Sat. $NaHCO_3$ and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give compound **19'**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.26 (m, 1H), 7.24–7.15 (m, 2H), 7.11 (d, *J* = 6.4 Hz, 1H), 3.97–3.86 (m, 2H), 2.97–2.86 (m, 1H), 2.85–2.72 (m, 1H), 2.28 (br s, 3H), 1.98–1.88 (m, 1H), 1.87–1.74 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.6, 135.8, 129.6, 128.9, 127.3, 126.4, 68.6, 52.5, 27.6, 26.8. The spectra

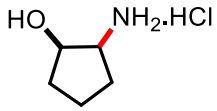
data are consistent with those of *cis*-1-amino-2-hydroxy-1,2,3,4-tetrahydronaphthalene reported in literature.[15]



24

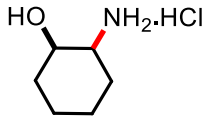
Compound **24** was prepared following the general procedure A in 62% yield on 0.2 mmol scale (84% yield was obtained on 2 mmol scale) as white solid (R_f = 0.6, CH_2Cl_2:MeOH = 8:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 5.90 (d, *J* = 2.0 Hz, 1H), 3.79 (t, *J* = 4.5 Hz, 1H), 3.74 (dd, *J* = 10.0, 4.5 Hz, 1H), 2.23–2.14 (m, 1H), 2.11–2.04 (m, 1H), 1.93–1.85 (m, 2H), 1.82–1.75 (m, 2H), 1.72–1.58 (m, 3H), 1.57–1.48 (m, 3H), 1.46–1.29 (m, 5H), 1.26–1.12 (m, 7H), 1.09 (s, 3H), 1.07–0.99 (m, 3H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.89 (dd, *J* = 6.6, 1.3 Hz, 6H), 0.74 (s, 3H); **^{13}C NMR** (101 MHz, MeOD-*d*$_4$) δ 139.4, 135.3, 70.2, 63.6, 61.4, 58.9, 58.1, 52.1, 44.2, 41.6, 41.4, 38.1, 37.8, 37.5, 34.0, 33.5, 30.9, 29.8, 26.7, 25.9, 25.7, 24.0, 23.7, 22.3, 21.6, 20.1, 13.1; **HRMS** (ESI) calcd for $C_{27}H_{48}NO$ [M+H$^+$]: 402.3730, found: 402.3732.

6.2 General experimental procedure B for preparation of 1,2-aminol alcohol hydrochlorides: A mixture of trichloroacetimidate (0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) and Ag_2O (69 mg, 0.3 mmol, 1.5 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 ^{o}C for 3 hours. The mixture was then cooled to room temperature, diluted with THF (4 mL) and filtered through a pad of Celite. aq. HCl (166 µL, 12 M, 10 equiv) was added, and the resulting mixture was continuously stirred for 5 h at 80 ^{o}C. Then the mixture was concentrated *in vacuo*, the residue was purified by chromatography on silica gel (5%-10% methanol in dichloromethane) to give the desired product.



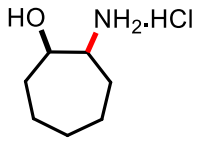
21

Compound **21** was prepared following the general procedure B in 68% yield (45% yield was obtained when the general procedure A was applied) as pale yellow oil (R_f = 0.4, CH_2Cl_2:MeOH = 4:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 4.25 (d, *J* = 3.6 Hz, 1H), 3.44 (dd, *J* = 12.8, 7.6 Hz, 1H), 2.15–2.03 (m, 1H), 2.01–1.89 (m, 2H), 1.84–1.72 (m, 2H), 1.71–1.61 (m, 1H); **^{13}C NMR** (101 MHz, MeOD-*d*$_4$) δ 72.7, 56.5, 34.6, 29.4, 22.2. The spectra data are consistent with those reported in literature.[16]



22

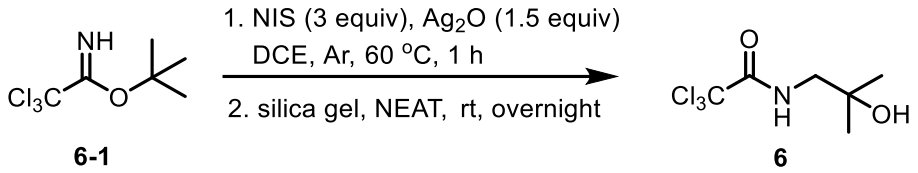
Compound **22** was prepared following the general procedure B in 48% yield as pale yellow oil (R_f = 0.4, CH_2Cl_2:MeOH = 8:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 4.02 (d, *J* = 2.3 Hz, 1H), 3.25–3.18 (m, 1H), 1.88–1.82 (m, 1H), 1.81–1.71 (m, 3H), 1.70–1.56 (m, 2H), 1.50–1.39 (m, 2H); **^{13}C NMR** (101 MHz, MeOD-*d*$_4$) δ 67.3, 54.8, 33.1, 26.9, 25.0, 20.9. The spectra data are consistent with those reported in literature.[17]



23

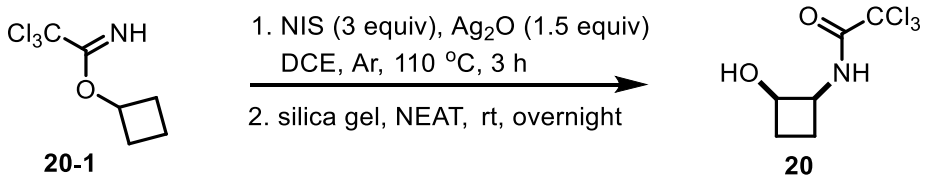
Compound **23** (3:1 mixture of inseparable isomers) was prepared following the general procedure B in 61% yield as pale yellow oil (R_f = 0.4, CH_2Cl_2:MeOH = 8:1). **^{1}H NMR** (400 MHz, MeOD-*d*$_4$) δ 4.07 (s, 1H), 3.60–3.51 (m, 0.32H), 3.30 (m, 1H), 2.98 (t, *J* = 8.7 Hz, 0.31H), 1.98–1.66 (m, 8H), 1.66–1.38 (m, 5H); **^{13}C NMR** (101 MHz, MeOD-*d*$_4$) δ 75.4, 70.6, 60.8, 57.9, 36.2, 34.7, 30.0, 29.7, 28.4, 28.3, 25.7, 25.0, 23.6, 22.8. The spectra data are consistent with those reported in literature.[18]

6.3 Experimental procedure for preparation of compound 6 and 20



Scheme S9

A mixture of commercial available tert-butyl trichloroacetimidate **6-1** (43.4 mg, 0.2 mmol, 1.0 equiv), NIS (135.0 mg, 0.6 mmol, 3 equiv) and Ag_2O (69 mg, 0.3 mmol, 1.5 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 60 °C for 1 h. After been cooled to room temperature, the reaction mixture was filtered through a pad of Celite and the filtrate was mixed with silica gel (500 mg) and concentrated. The resulting mixture was placed at room temperature overnight then purified by silica gel flash chromatography to give compound **6** in 40% yield as white solid (R_f = 0.4, Hexanes:EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (br s, 1H), 3.37 (d, *J* = 5.9 Hz, 2H), 1.78 (br s, 1H), 1.29 (s, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.6, 92.9, 70.9, 51.5, 27.5; **HRMS** (ESI) calcd for $C_6H_{11}Cl_3NO_2$ [M+H$^+$]: 233.9850, found: 233.9846.

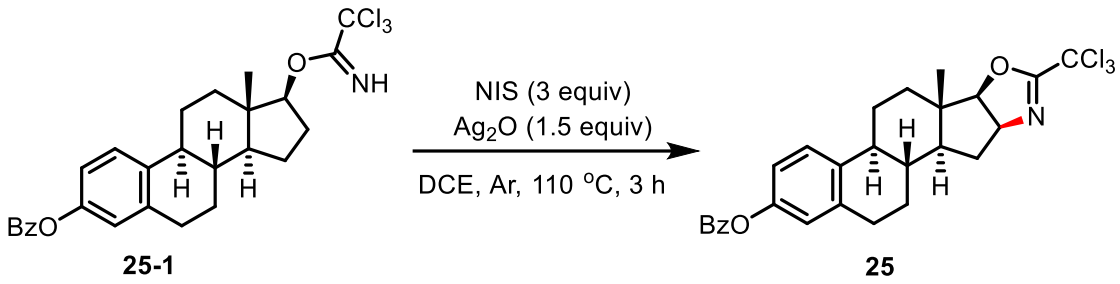


Scheme S10

A mixture of cyclobutyl trichloroacetimidate **20-1** (43 mg, 0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) and Ag_2O (69 mg, 0.3 mmol, 1.5 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 h. After been cooled to room temperature, the reaction mixture was filtered through a pad of Celite and the filtrate was mixed with silica gel (500 mg) and concentrated. The resulting mixture was placed at room temperature overnight then purified by silica gel flash chromatography to give compound **20** in 38% yield as colorless oil that solidifies at low temperature (R_f = 0.3, Hexanes:EtOAc = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (br s, 1H), 4.69–4.55 (m, 1H), 4.39–4.25 (m, 1H), 2.47 (br s, 1H), 2.32–2.21 (m, 2H), 2.14–2.04 (m, 1H), 2.04–1.93 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.8, 92.6, 68.6, 50.5, 28.0, 25.0; **HRMS** (ESI) calcd for $C_6H_9Cl_3NO_2$ [M+H$^+$]: 231.9693, found: 231.9688.

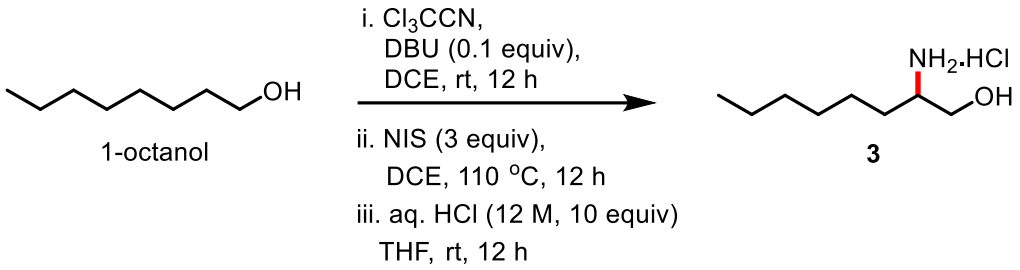
6.4 Experimental procedure for preparation of compound 25



Scheme S11

A mixture of compound **25-1** (104 mg, 0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) and Ag_2O (69 mg, 0.3 mmol, 1.5 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. After been cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of Celite. The filtrate was washed with Sat. Na_2SO_3 and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography to give compound **25** in 52% yield as white solid (R_f = 0.4, Hexanes:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 1H), 6.99 (d, *J* = 10.3 Hz, 1H), 6.94 (s, 1H), 4.77 (d, *J* = 9.9 Hz, 1H), 4.66 (dd, *J* = 17.3, 8.6 Hz, 1H), 2.95–2.88 (m, 2H), 2.49–2.36 (m, 2H), 2.35–2.27 (m, 1H), 2.19 (d, *J* = 11.8 Hz, 1H), 2.02–1.92 (m, 1H), 1.67–1.50 (m, 5H), 1.49–1.42 (m, 1H), 0.88 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 161.8, 148.9, 138.1, 137.3, 133.6, 130.2, 129.6, 128.6, 126.5, 121.8, 118.9, 94.5, 87.0, 71.0, 49.2, 45.5, 43.9, 37.7, 37.4, 32.2, 29.5, 27.7, 26.1, 12.2; **HRMS** (ESI) calcd for $C_{27}H_{27}Cl_3NO_3$ [M+H$^+$]: 518.1051, found: 518.1044.

6.5 Experimental procedure for gram scale reaction

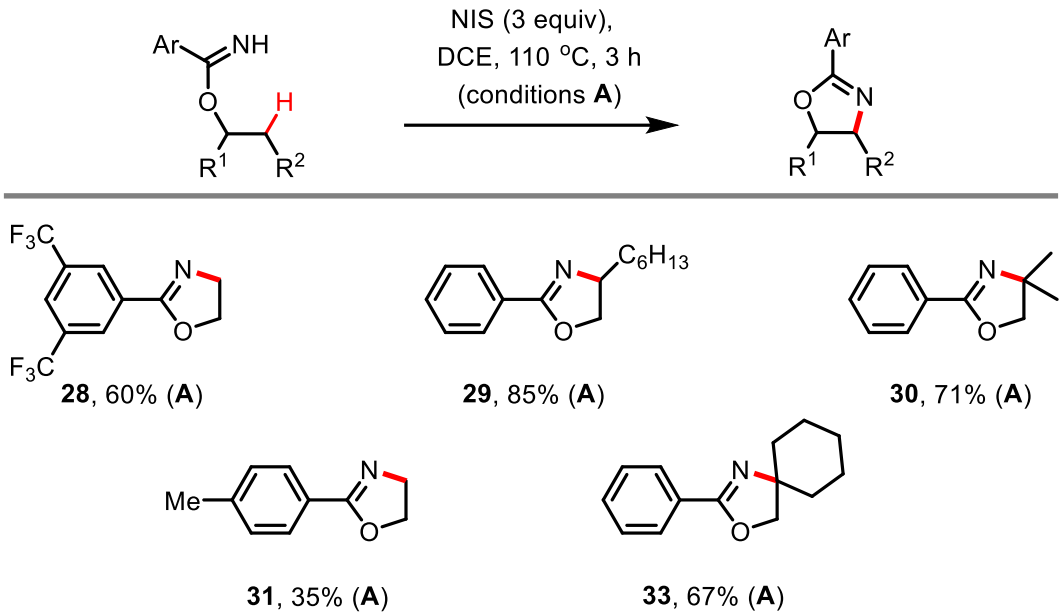


Scheme S12

A mixture of 1-octanol (1.04 g, 8 mmol, 1.0 equiv), trichloroacetonitrile (1.2 mL, 12 mmol, 1.5 equiv) and DBU (119 µL, 0.8 mmol, 0.1equiv) in 1,2-dichloroethane (30 mL) in a 100 mL sealed tube was stirred at room temperature. After 12 hours, NIS (5.4 g, 24 mmol, 3 equiv) was added to the above reaction mixture, the resulting suspension was heated to 110^{o}C and continuously stirred under an atmosphere of Argon. After 12 hours, the reaction mixture was cooled to room temperature and concentrated *in vacuo*. The resulting residue was dissolve in tetrahydrofuran (20 mL) and aq. HCl (6.7 mL, 12 M, 10 equiv) were added. The mixture was continuously stirred for 12 hours before concentrated *in vacuo* and the resulting residue was purified by silica gel flash chromatography to give compound **3** in 70% yield (1.01 g).

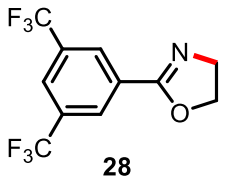
7. Substrate scope of *β*-C(sp^3)-H amination of benzimidates

7.1 General experimental C procedure H for *β* C-H amination of benzimidates.



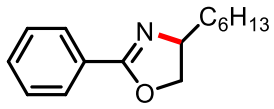
Scheme S13

A mixture of benzimidates (0.2 mmol, 1.0 equiv) and NIS (135 mg, 0.6 mmol, 3 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. After been cooled to room temperature, the reaction mixture was diluted with ethyl acetate and washed with Sat. Na_2SO_3 and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography to give the desired product.



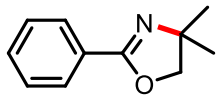
28

Compound **28** was prepared following the general procedure C in 60% yield as colorless oil. (R_f = 0.4, Hexanes:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (s, 2H), 7.96 (s, 1H), 4.51 (t, *J* = 9.6 Hz, 2H), 4.12 (t, *J* = 9.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4, 132.1 (q, J_{C-F} = 34 Hz), 130.0, 128.5, 124.8, 123.1 (q, J_{C-F} = 271 Hz), 68.4, 55.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.94 (s, 6F); **HRMS** (ESI) calcd for $C_{11}H_8F_6NO$ [M+H$^+$]: 284.0505, found: 284.0506.



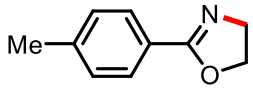
29

Compound **29**[19] was prepared following the general procedure C in 85% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02–7.92 (m, 2H), 7.51–7.45 (m, 1H), 7.44–7.37 (m, 2H), 4.49 (dd, *J* = 9.3, 8.2 Hz, 1H), 4.34–4.24 (m, 1H), 4.04 (t, *J* = 7.9 Hz, 1H), 1.85–1.71 (m, 1H), 1.61–1.52 (m, 1H), 1.51–1.43 (m, 1H), 1.43–1.26 (m, 7H), 0.90 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.4, 131.3, 128.4, 128.3, 128.0, 72.7, 66.9, 36.1, 31.8, 29.4, 26.0, 22.7, 14.2.



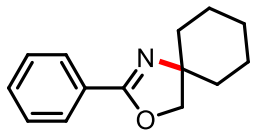
30

Compound **30**[20] was prepared following the general procedure C in 71% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96–7.91 (m, 2H), 7.48–7.43 (m, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 4.10 (s, 2H), 1.38 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2, 131.3, 128.4, 128.3, 128.2, 79.2, 67.7, 28.5.



31

Compound **31** was prepared following the general procedure C in 35% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.42 (t, *J* = 9.5 Hz, 2H), 4.05 (t, *J* = 9.5 Hz, 2H), 2.39 (s, 3H); **^{13}C NMR** (101 MHz, CDCl3) δ 164.8, 141.7, 129.1, 128.1, 124.9, 67.6, 54.8, 21.6. The spectra data are consistent with those reported in literature.[21]

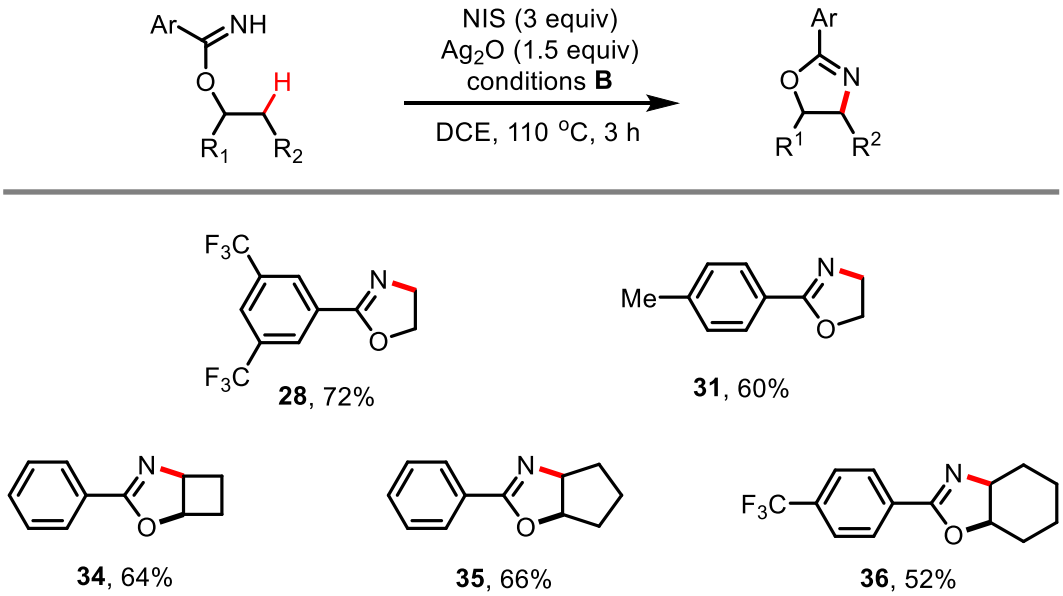


33

Compound **33** was prepared following the general procedure C in 67% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97–7.90 (m, 2H), 7.48–7.43 (m, 1H), 7.42–7.35 (m, 2H), 4.15 (s, 2H), 1.87–1.73 (m, 4H), 1.66–1.58

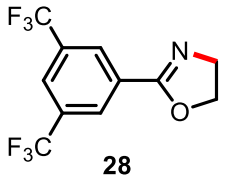
(m, 3H), 1.38–1.26 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.6, 131.0, 128.2, 128.1, 77.0, 71.2, 37.5, 25.2, 23.0; **HRMS** (ESI) calcd for $C_{14}H_{18}NO$ $[M+H^+]$: 216.1383, found: 216.1383.

7.2 General experimental D procedure H for *β* C-H amination of benzimidates.



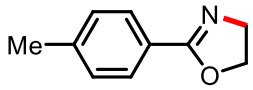
Scheme S14

A mixture of benzimidates (0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) and Ag_2O (69 mg, 0.3 mmol, 1.5 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. After been cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of Celite. The filtrate was washed with Sat. Na_2SO_3 and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography to give the desired product.



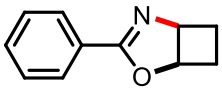
28

Compound **28** was prepared following the general procedure D in 72% yield as colorless oil.



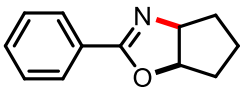
31

Compound **31** was prepared following the general procedure D in 60% yield.



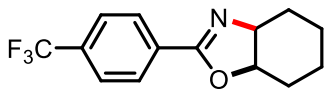
34

Compound **34** was prepared following the general procedure D in 64% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02–7.96 (m, 2H), 7.51–7.45 (m, 1H), 7.41 (dd, *J* = 11.4, 4.4 Hz, 2H), 5.06 (dd, *J* = 6.7, 3.9 Hz, 1H), 4.67 (dd, *J* = 5.6, 2.7 Hz, 1H), 2.58–2.48 (m, 2H), 2.35–2.25 (m, 1H), 2.22–2.12 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 131.5, 128.48, 128.45, 128.2, 79.0, 68.1, 30.2, 28.8; **HRMS** (ESI) calcd for $C_{11}H_{12}NO$ [M+H^+]: 174.0913, found: 174.0916.



35

Compound **35**[19] was prepared following the general procedure D in 66%yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 2H), 7.46 (t, *J* = 7.0 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 5.11 (t, *J* = 6.4 Hz,, 1H), 4.73 (t, *J* = 7.3 Hz, 1H), 2.08 (dd, *J* = 13.1, 6.0 Hz, 1H), 1.99 (dd, *J* = 13.0, 6.0 Hz, 1H), 1.80–1.71 (m, 1H), 1.70–1.62 (m, 2H), 1.56–1.42 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.9, 131.3, 128.4, 128.3, 127.9, 84.9, 71.9, 34.9, 34.1, 22.4.

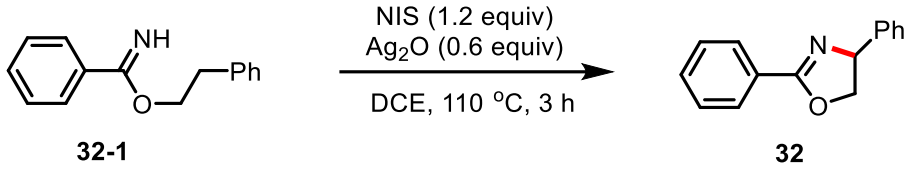


36

Compound **36**[22] was prepared following the general procedure D in 52% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 4.75–4.69 (m, 1H), 4.20–4.12 (m, 1H), 1.96–1.85 (m, 3H), 1.68–1.60 (m, 1H), 1.59–1.50 (m, 2H), 1.48–1.37 (m, 2H); **^{13}C NMR**

(101 MHz, $CDCl_3$) δ 163.2, 132.9 (q, J_{C-F} = 33 Hz), 131.8, 128.6, 125.4 (q, J_{C-F} = 4 Hz), 122.6, 79.4, 63.9, 27.7, 26.3, 19.9, 19.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.86 (s, 3F).

7.3 Experimental procedure for preparation of compound 32

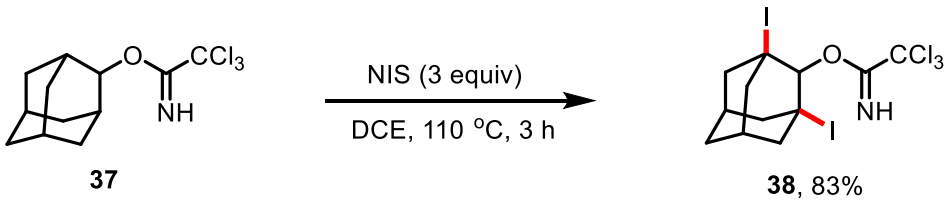


Scheme S15

A mixture of benzimidates **32-1** (45 mg, 0.2 mmol, 1.0 equiv), NIS (54 mg, 0.24 mmol, 1.2 equiv) and Ag_2O (28 mg, 0.12 mmol, 0.6 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. After been cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of Celite. The filtrate was washed with Sat. Na_2SO_3 and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo.* The residue was purified by silica gel flash chromatography to give compound **32**[23] in 82% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 10:1) .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11–8.05 (m, 2H), 7.56–7.49 (m, 1H), 7.48–7.43 (m, 2H), 7.41–7.28 (m, 5H), 5.40 (dd, *J* = 10.0, 8.2 Hz, 1H), 4.80 (dd, *J* = 10.1, 8.4 Hz, 1H), 4.29 (t, *J* = 8.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.8, 142.5, 131.6, 128.8, 128.55, 128.47, 127.71, 127.65, 126.9, 75.0, 70.2.

8. Mechanistic studies

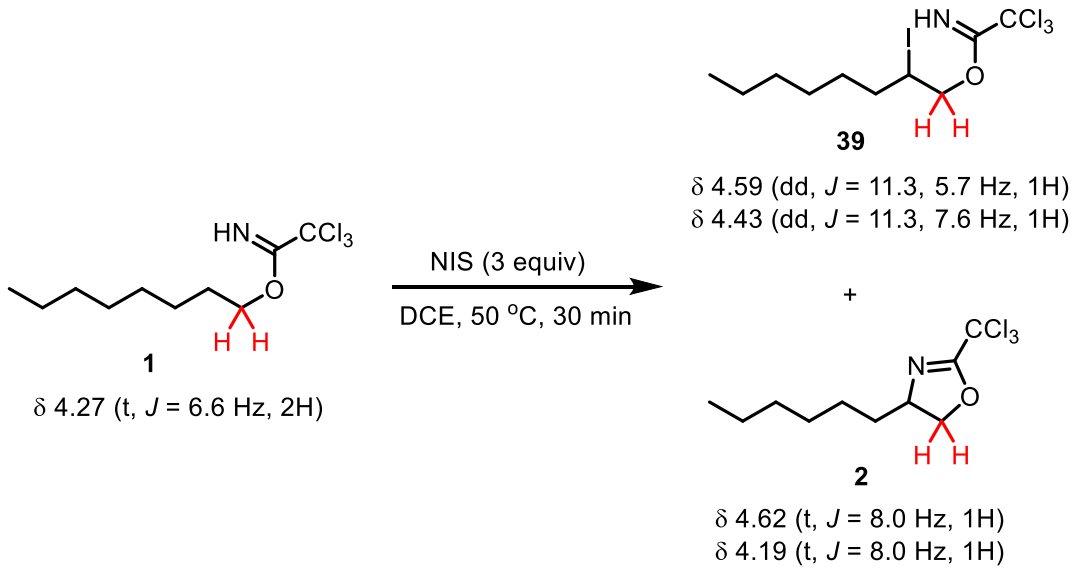
8.1 Reaction of 2-adamantanol substrate 37



Scheme S16

A mixture of compound **37** (59.3 mg, 0.2 mmol, 1.0 equiv), NIS (135.0 mg, 0.6 mmol, 0.1 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. After been cooled to room temperature, the mixture was washed with Sat. Na_2SO_3 and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography to give compound **38** in 83% yield as white solid (R_f = 0.2, Hexanes:EtOAc = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 5.94 (s, 1H), 2.97 (d, *J* = 12.6 Hz, 2H), 2.77 (s, 4H), 2.43 (d, *J* = 11.6 Hz, 2H), 1.87 (t, *J* = 19.0 Hz, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.0, 92.0, 87.4, 51.7, 44.8, 43.4, 36.1, 35.7, 33.9; **HRMS** (ESI) calcd for $C_{12}H_{15}Cl_3I_2NO$ [M+H$^+$]: 547.8303, found: 547.8292.

8.2 Observation of the iodinated intermediate 39



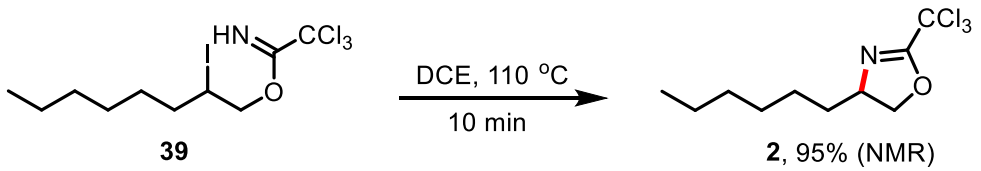
Scheme S17

A mixture of octyl trichloroacetimidate **1** (55 mg, 0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 50 °C for 30 minutes. The mixture was then cooled

to room temperature and concentrated *in vacuo,* the crude residue was dissolved in 1 mL of deuterated chloroform for ^{1}H-NMR analysis. 1,1,2,2-tetrachloroethane (33.6 mg, 0.2 mmol, 1 equiv, a singlet peak around 5.97 ppm was set as 2.00) was added as internal standard. Yields of compounds **2 and 39** were determined based on the following method:

Yield of **2** = integration of peak (δ 4.62) × 100%

Yield of **39** = integration of peak (δ 4.59) × 100%



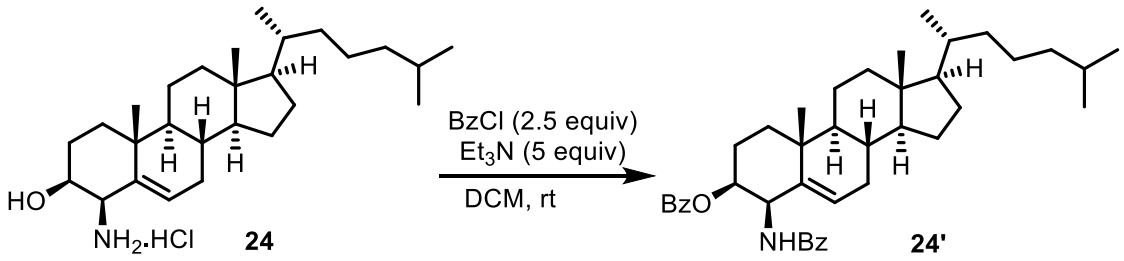
Scheme S18

A mixture of compound **39** (80 mg, 0.2 mmol, 1.0 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 10 minutes. The mixture was then cooled to room temperature and concentrated *in vacuo,* the crude residue was dissolved in 1 mL of deuterated chloroform for ^{1}H-NMR analysis. 1,1,2,2-tetrachloroethane (33.6 mg, 0.2 mmol, 1 equiv, a singlet peak around 5.97 ppm was set as 2.00) was added as internal standard. Yields of compounds **2**were determined based on the following method:

Yield of **2** = integration of peak (δ 4.62) × 100%

9. X-ray crystallographic data

9.1 X-ray crystallographic data for compound 24'



Scheme S19

Compound **24** (219 mg, 0.5 mmol, 1 equiv) was dissolved in dichloromethane (5 mL) and cooled to 0 ^{o}C. To this solution was added triethylamine (346 µL, 2.5 mmol, 5 equiv) followed by dropwise addition of benzoyl chloride (144 µL, 1.25 mmol, 2.5 equiv). The resulting mixture was continuously stirred for 5 h at room temperature, then diluted with dichloromethane and sat. NH_4Cl. The organic layer was washed with sat. $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography to give compound **24'** in 65% yield (198.3 mg) as white solid (R_f = 0.6, Hexanes:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.1 Hz, 2H), 7.73 (d, *J* = 6.8 Hz, 2H), 7.53–7.42 (m, 4H), 7.38-7.31 (m, 2H), 6.48 (d, *J* = 5.5 Hz, 1H), 5.97 (s, 1H), 5.15–5.05 (m, 2H), 2.21–2.12 (m, 1H), 2.08–1.90 (m, 5H), 1.88–1.80 (m, 1H), 1.55–1.45 (m, 4H), 1.39–1.27 (m, 7H), 1.20 (s, 3H), 1.15–1.07 (m, 4H), 1.06–0.96 (m, 4H), 0.91 (d, *J* = 3.8 Hz, 3H), 0.87 (d, *J* = 1.1 Hz, 3H), 0.86 (d, *J* = 2.0 Hz, 3H), 0.67 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 165.8, 139.0, 135.5, 133.0, 131.5, 130.6, 130.5, 129.8, 128.8, 128.4, 126.9, 73.4, 57.0, 56.2, 55.8, 50.4, 42.3, 39.7, 36.5, 36.3, 35.9, 32.3, 31.9, 29.9, 28.3, 28.2, 27.4, 24.4, 24.0, 23.4, 23.0, 22.7, 21.6, 20.6, 18.9, 12.0. **HRMS** (ESI) calcd for $C_{41}H_{56}NO_3$ [M+H^{+}]: 610.4255, found: 610.4255.

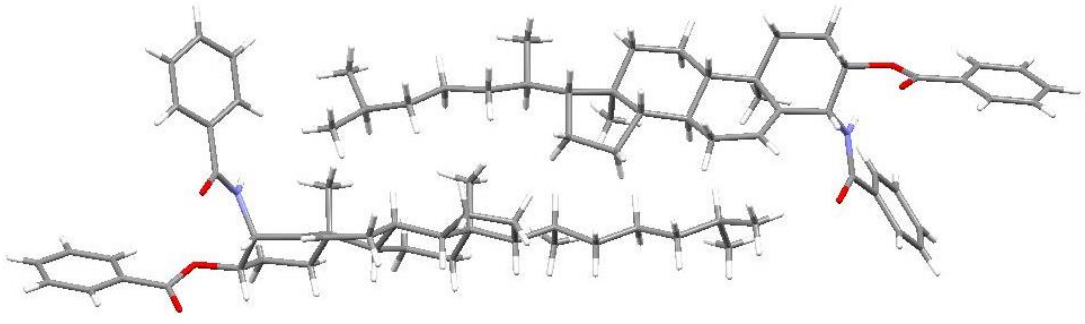


Figure S1.

Single crystals for X-ray studies were grown by slow evaporation of a solution of compound **24'** in a mixture of dichloromethane and hexane at room temperature. The X-ray crystal structure is deposited in the Cambridge Crystallographic Data Centre with a number of CCDC 1561816.

9.2 X-ray crystallographic data for compound 38

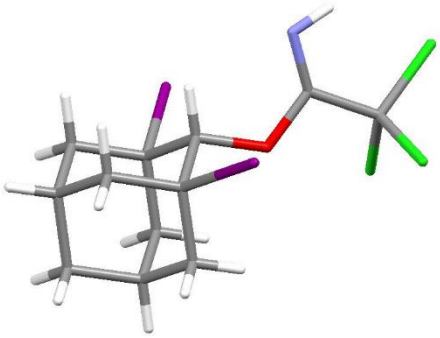


Figure S2.X-ray crystallographic data for compound **38**

Single crystals for X-ray studies were grown by slow evaporation of a solution of compound **38** in a mixture of dichloromethane and hexane at room temperature. The X-ray crystal structure is deposited in the Cambridge Crystallographic Data Centre with a number of CCDC 1561818.

Table S4. Parameters of crystallography structures

Compounds	**24'**	**38**
Formula	$C_{41}H_{55}NO_3$	$C_{12}H_{14}Cl_3I_2NO$
Mol. wt.	609.86	548.39
Crystal system	monoclinic	monoclinic
Space group	P 1 21 1	P 1 21/c 1
a (Å)	14.4864 (8)	12.7496 (5)
b (Å)	11.3225 (6)	10.1118 (3)
c (Å)	22.7080 (11)	12.9485 (4)
α (deg)	90	90
β (deg)	106.085 (6)	96.469 (3)

γ (deg)	90	90
V (Å^3)	3578.8 (3)	1658.71 (9)
Z	4	4
T (K)	120 (10)	298 (10)
$\rho_{calcd.}$(Mg/m^3)	1.132	2.196
μ (mm^{-1})	0.070	4.267
Final R indices [$I > 2\sigma(I)$]	R = 0.0641 wR2 = 0.1492	R = 0.0363 wR2 = 0.0870
S	1.027	1.054

10. References

[1] L.-D. Nie, F.-F. Wang, W. Ding, X.-X. Shi, X. Lu, *Tetrahedron: Asymmetry* **2013**, *24*, 638.

[2] I. A. I. AIi, X.-M. Zhu, E. S. H. E. Ashry, R. R. Schmidt, *ARKIVOC (Gainesville, FL, U.S)*. **2012**, *6*, 35.

[3] S. Andrew, A. Stobie, Pfizer Inc. Patent: *US2003/105097 A1*, **2003**

[4] J. Laduranty, C. Lion, D. Mesnard, L. Miginiac, *Bull. Soc. Chim. Belg.* **1984**, *93*, 903.

[5] J.-M. Huang, J.-F. Zhang, Y. Dong, W. Gong, *J. Org. Chem.* **2011,** *76*, 3511.

[6] F. Yuste, B. Ortiz, A. Carrasco, M. Peralta, L. Quintero, R. Sánchez-Obregón, F. Walls, J. L. García Ruano, *Tetrahedron: Asymmetry* **2000**, *11*, 3079.

[7] K. Olaf, D, Klaus, B, Michael, BASF SE Patent: *US2010/240928 A1*, **2010**.

[8] Gruppo Lepetit S.P.A. Patent: *US3953513 A1*, **1976**.

[9] M. G. N. Russell, V. G. Matassa, R. R. Pengilley, M. B. van Niel, B. Sohal, A. P. Watt, L. Hitzel, M. S. Beer, J. A. Stanton, H. B. Broughton, J. L. Castro, *J. Med. Chem.* **1999**, *42*, 4981.

[10] M. Dickmeis, H. Cinar, H. Ritter, *Macromol. Rapid. Commun.* **2013**, *34*, 263.

[11] C. Sandra, C. Sergio, G. Giampaolo, F. Massimo, *Tetrahedron* **1994**. *50*, 13493.

[12] W. J. Thompson, P. M. D. Fitzgerald, M. K. Holloway, E. A. Emini, P. L. Darke, B. M. McKeever, W. A. Schleif, J. C. Quintero, J. A. Zugay, *J. Med. Chem.* **1992**, *35*, 1685.

[13] X. Liang, C.-J. Lee, X. Chen, H. S. Chung, D. Zeng, C. R. H. Raetz, Y. Li, P. Zhou, E. J. Toone, *Bioorg. Med. Chem.* **2011**, *19*, 852.

[14] M. Falorni, S. Conti, G. Giacomelli, S. Cossu, F. Soccolini, *Tetrahedron: Asymmetry* **1995**, *6*, 287.

[15] K. Bhandari, S. Srivastava, G. Shankar, *Bioorg. Med. Chem*. **2004**, *12*, 4189.

[16] S. E. Schaus, J. F. Larrow, E. N. Jacobsen, *J. Org. Chem*. **1997**, *62*, 4197.

[17] P. G. Sammes, D. Thetford, *J. Chem. Soc., Perkin Trans. I* **1988**, 111.

[18] E. R. Jarvo, M. M. Vasbinder, S. J. Miller, *Tetrahedron* **2000**, *56*, 9773.

[19] V. R. Ward, M. A. Cooper, A. D. Ward, *J. Chem. Soc., Perkin Trans. I* **2001**, 944.

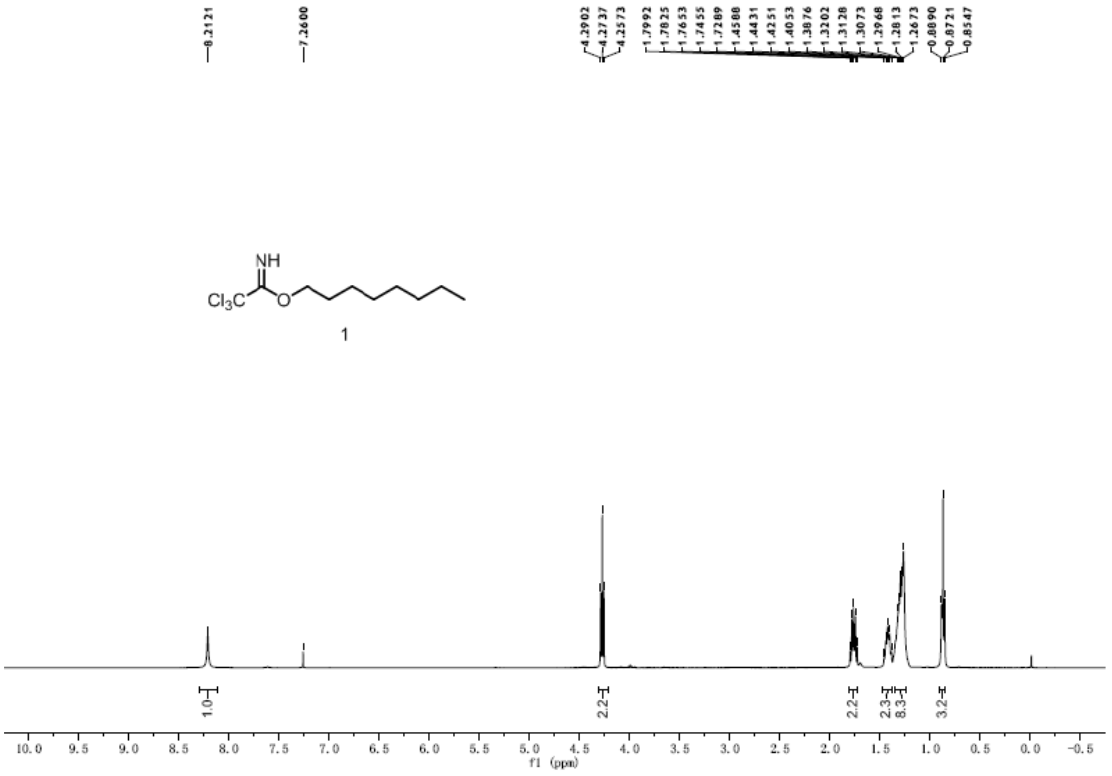
[20] N. Chatani, Y. Ie, F. Kakiuchi, S. Murai, *J. Am. Chem. Soc.* **1999**, *121*, 8645.

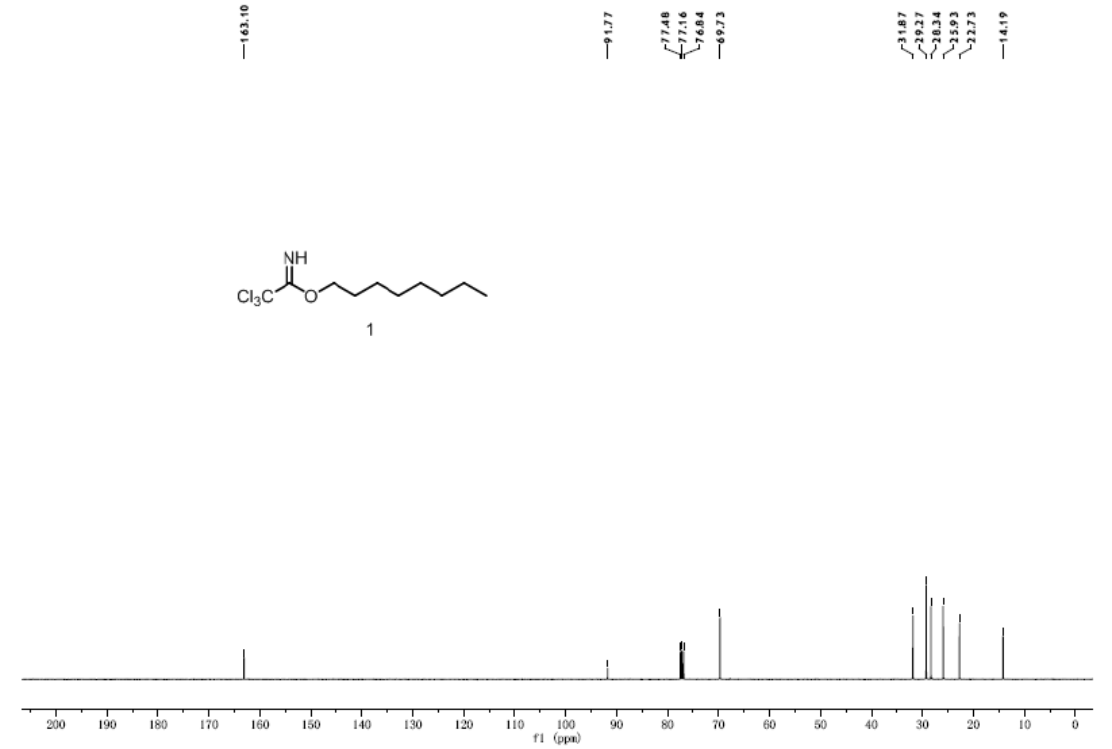
[21] M. C. Mollo, L. R. Orelli, *Org. Lett.* **2016**, *18*, 6116.

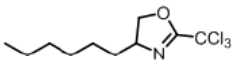
[22] D. Ferraris, W. J. Drury, C. Cox, T. Lectka, *J. Org. Chem.* **1998**, *63*, 4568.

[23] S. Hajra, S. Bar, D. Sinha, B. Maji, *J. Org. Chem.* **2008**, *73*, 4320.

11. NMR Spectra







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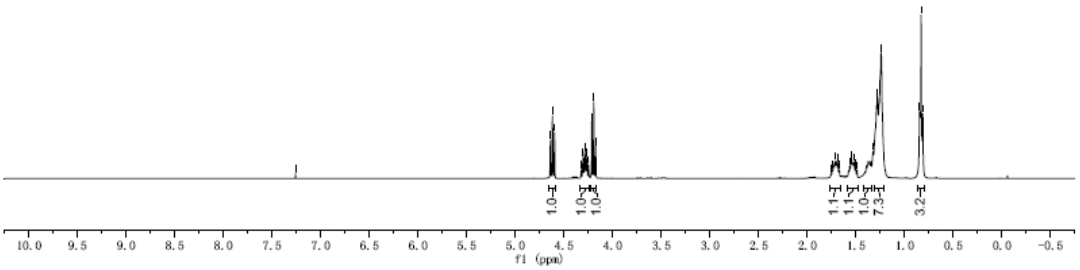

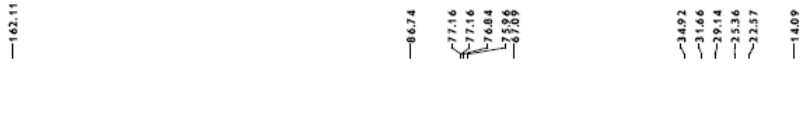

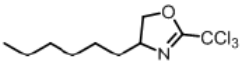

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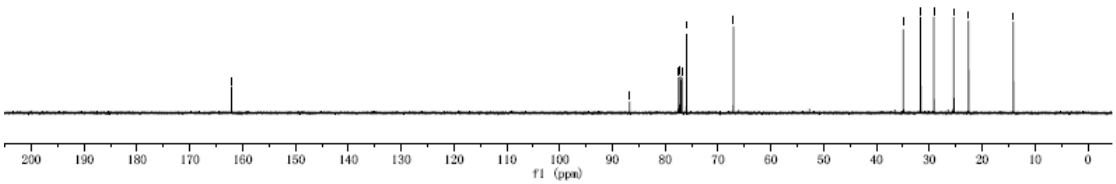

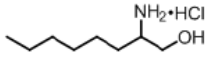

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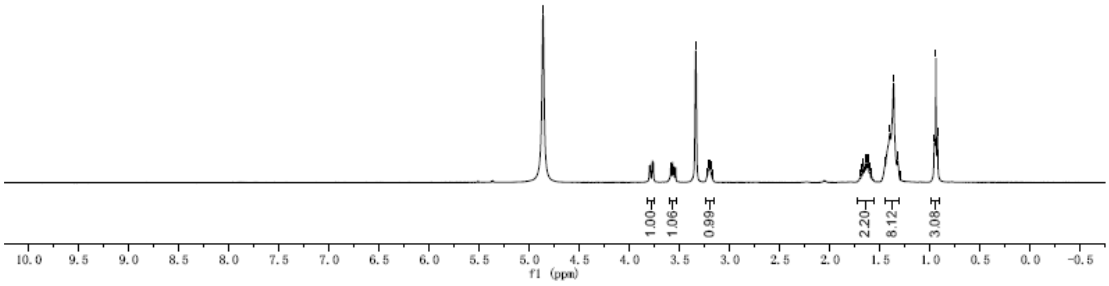

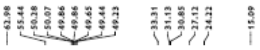

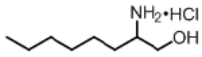

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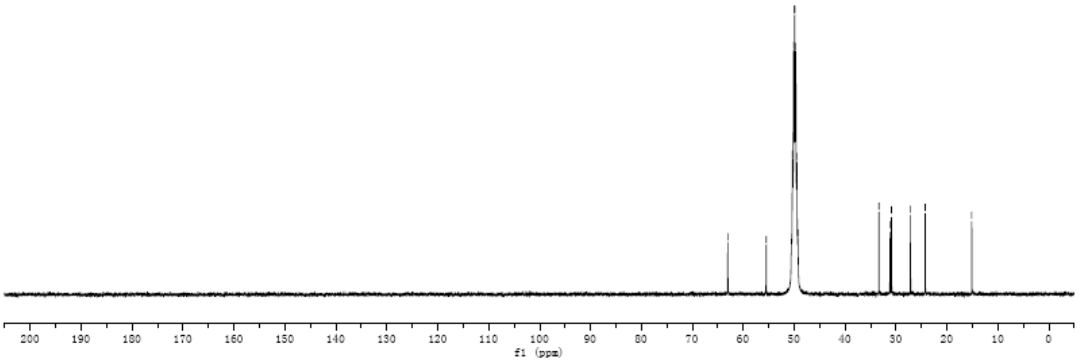

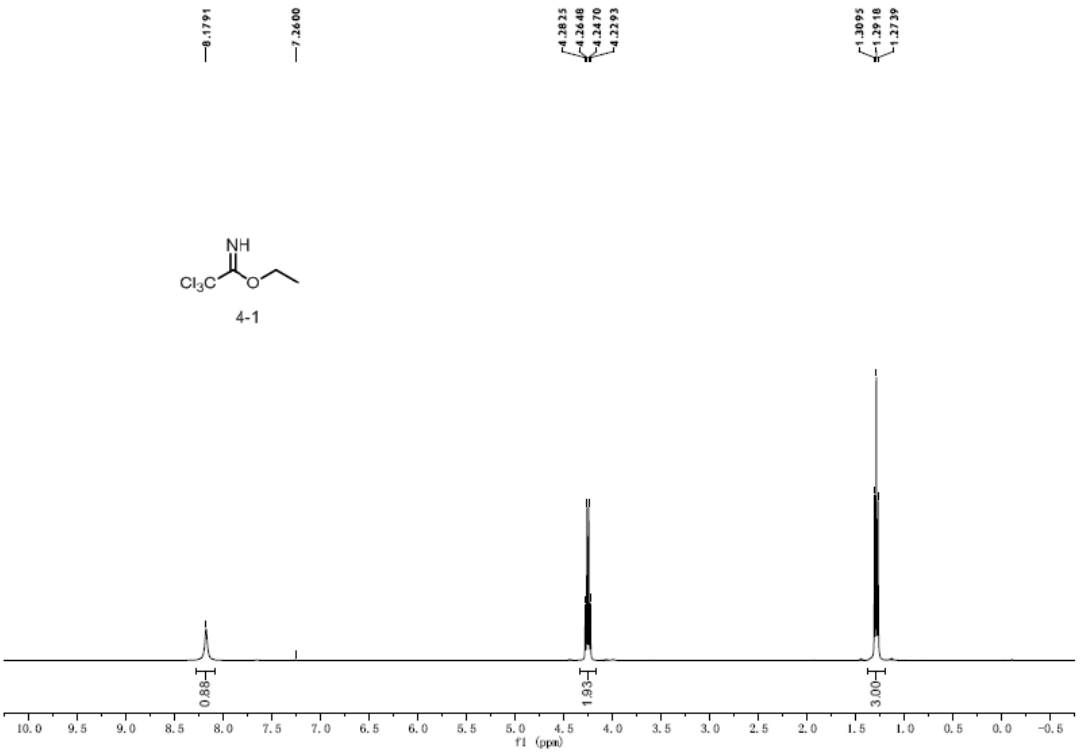
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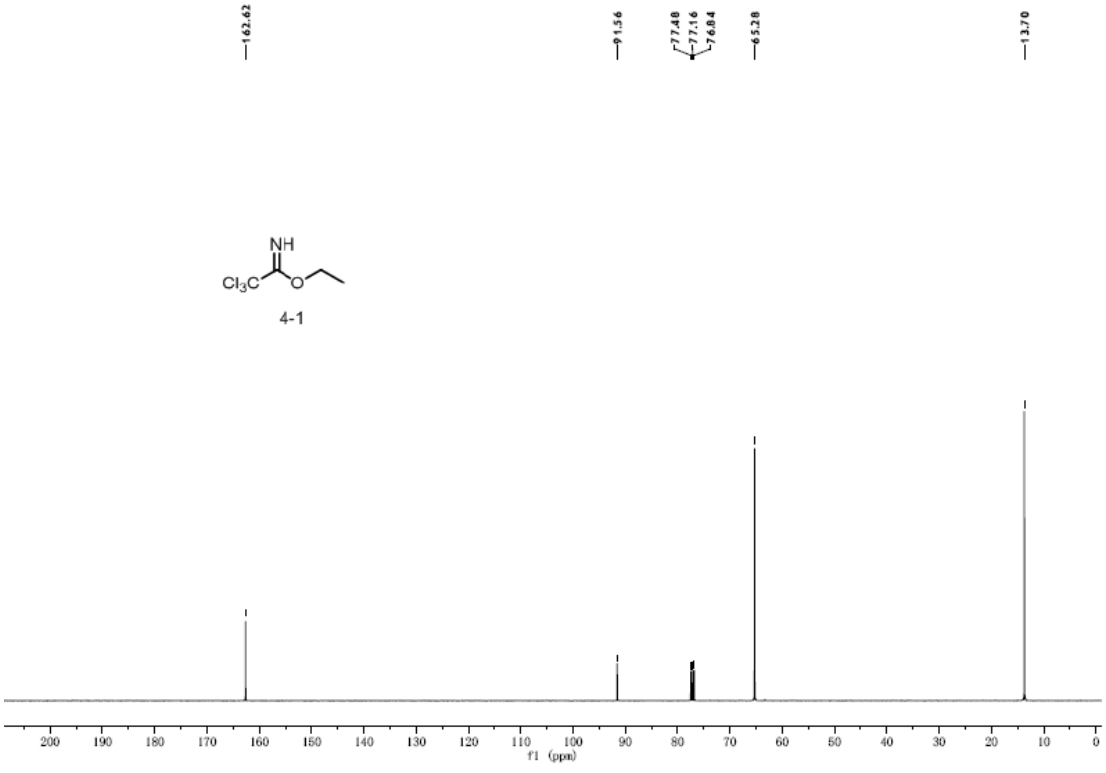
4.2825
4.2648
4.2470
4.2293
1.3095
1.2918
1.2739
NH
Cl3C
O
4-1
0.88
1.93
3.00
f1 (ppm)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77.48
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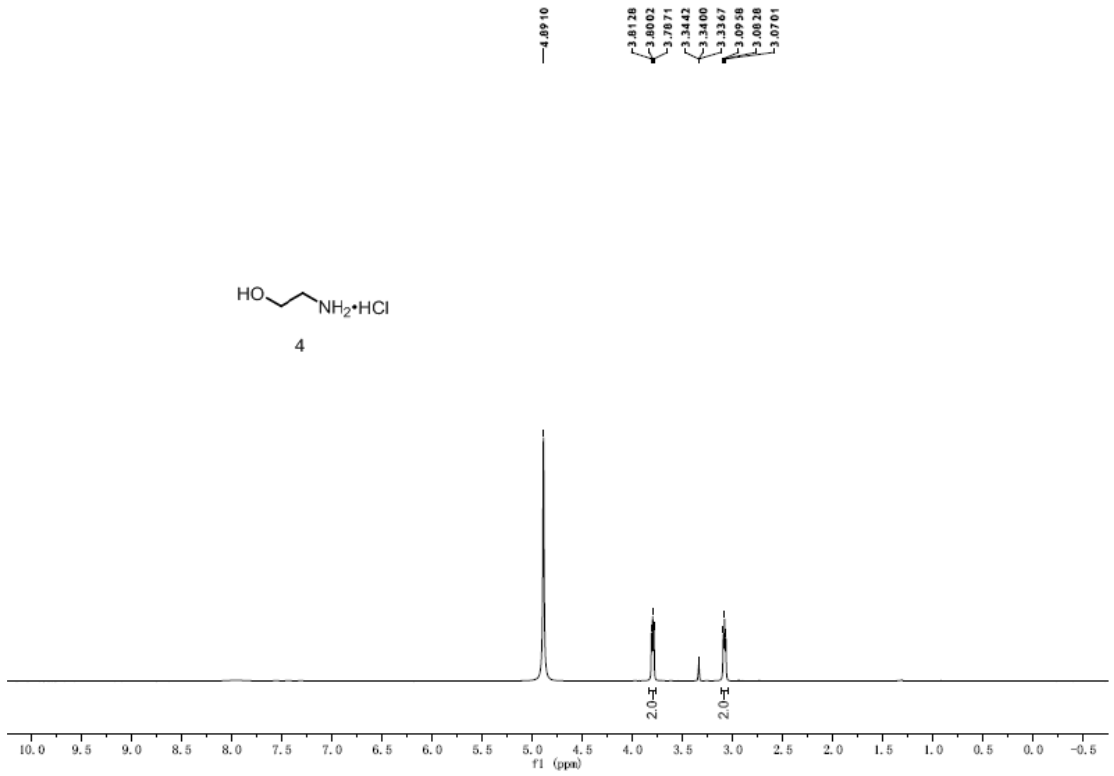
76.84
65.28
13.70
NH
Cl3C
O
4-1
f1 (ppm)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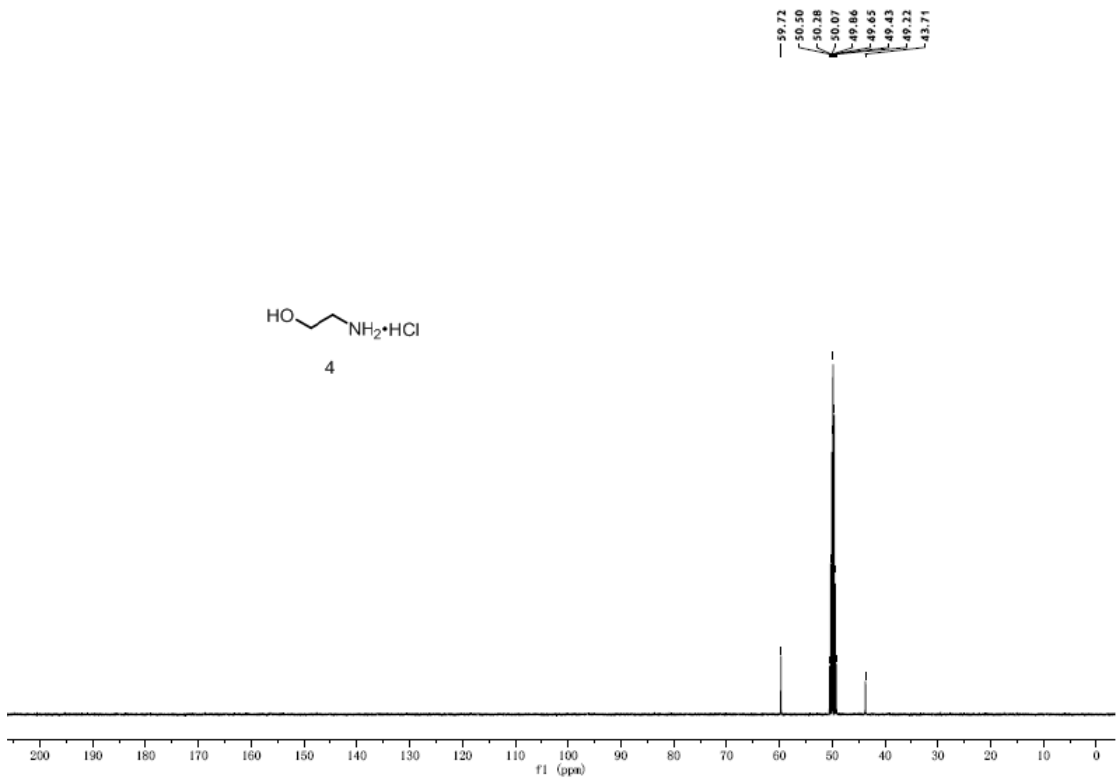
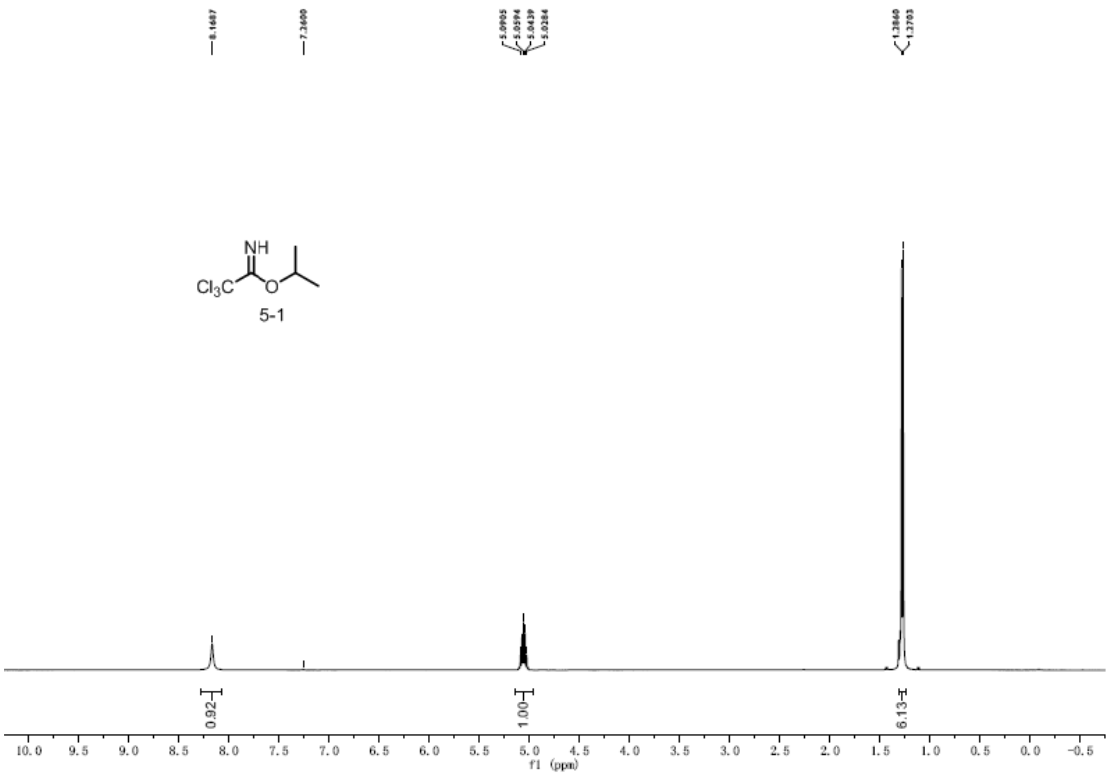
3.8128
3.8002
3.7071
3.3442
3.3400
3.3367
3.0958
3.0028
3.0701
HO
NH2•HCl
4
2.0
2.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


59.72
50.50
50.28
50.07
49.86
49.65
49.43
49.22
43.71
HO
NH2•HCl
4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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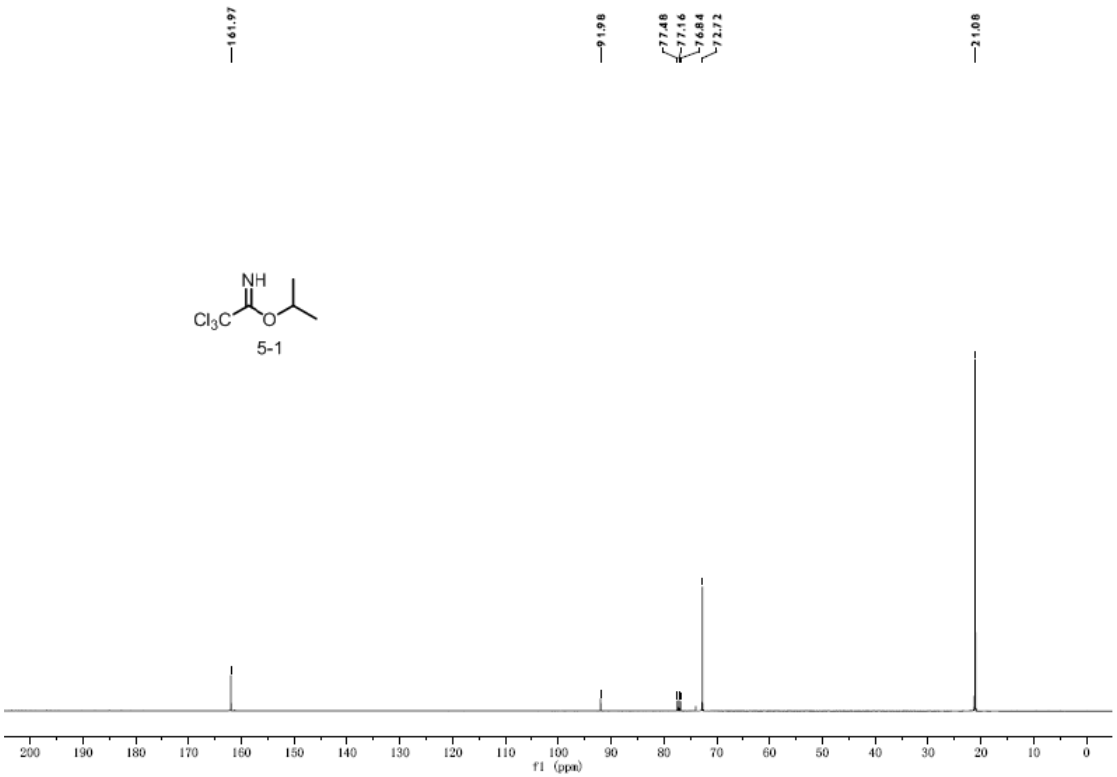
5.0905
5.0594
5.0439
5.0284
1.3840
1.3703
NH
Cl3C
O
5-1
0.92
1.00
6.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.16
76.84
72.72
21.08
NH
Cl3C
O
5-1
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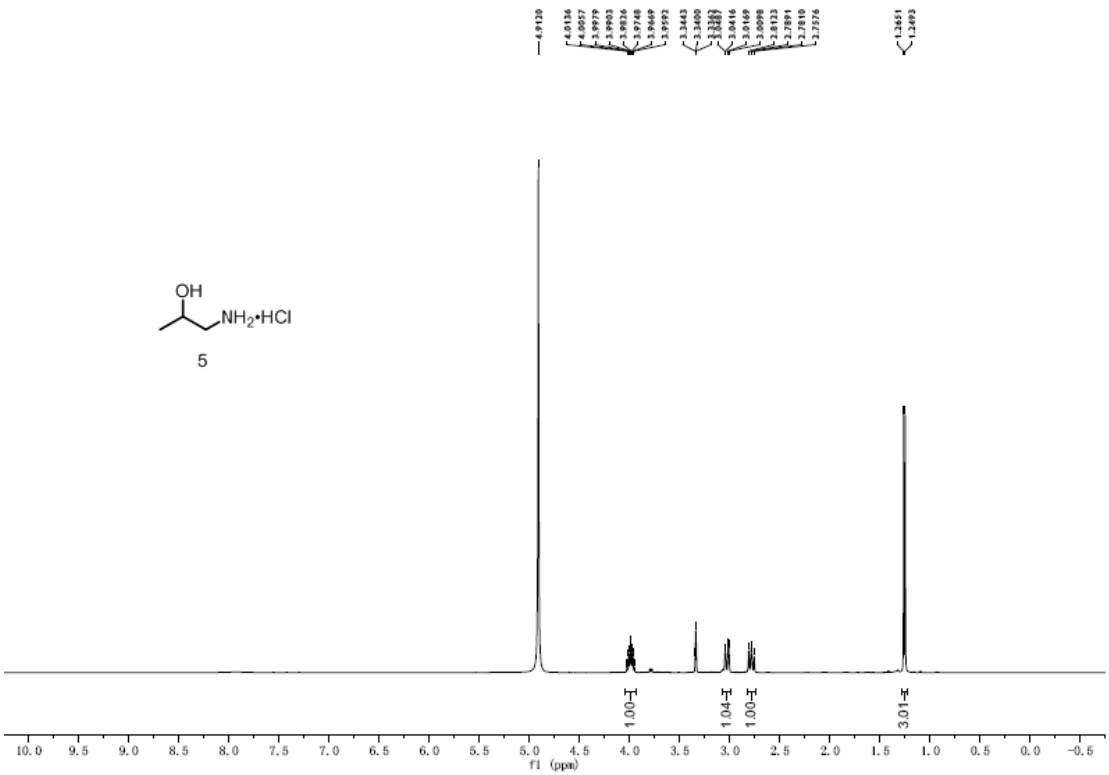
f1 (ppm)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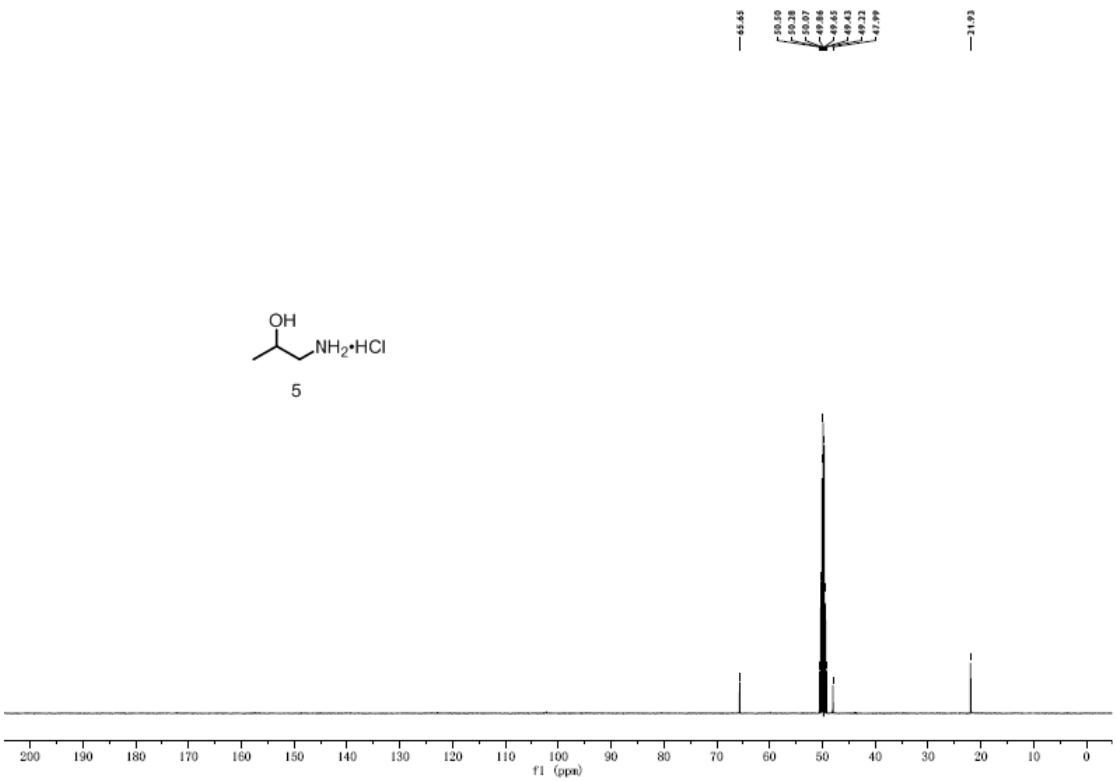
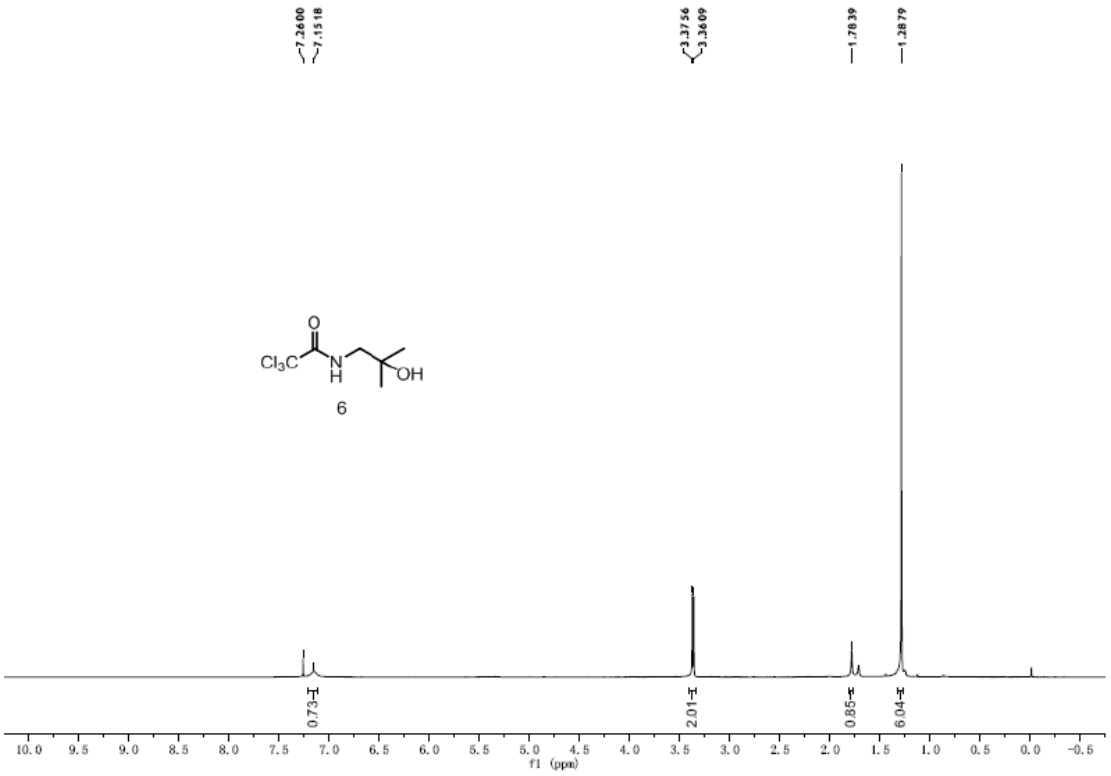
NH2•HCl
5
1.00
1.04
1.00
3.01
f1 (ppm)


OH
NH2•HCl
5
f1 (ppm)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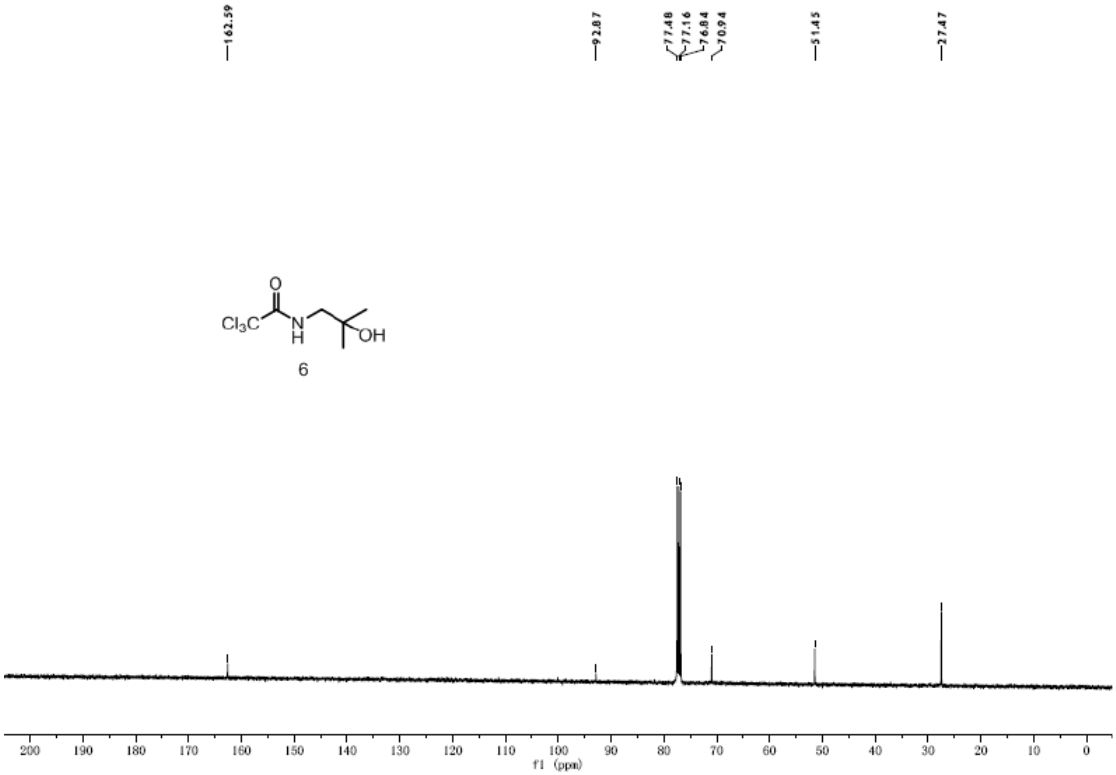
3.3756
3.3609
1.7039
1.2879
O
Cl3C
N
H
OH
6
0.73
2.01
0.85
6.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.16
76.84
70.94
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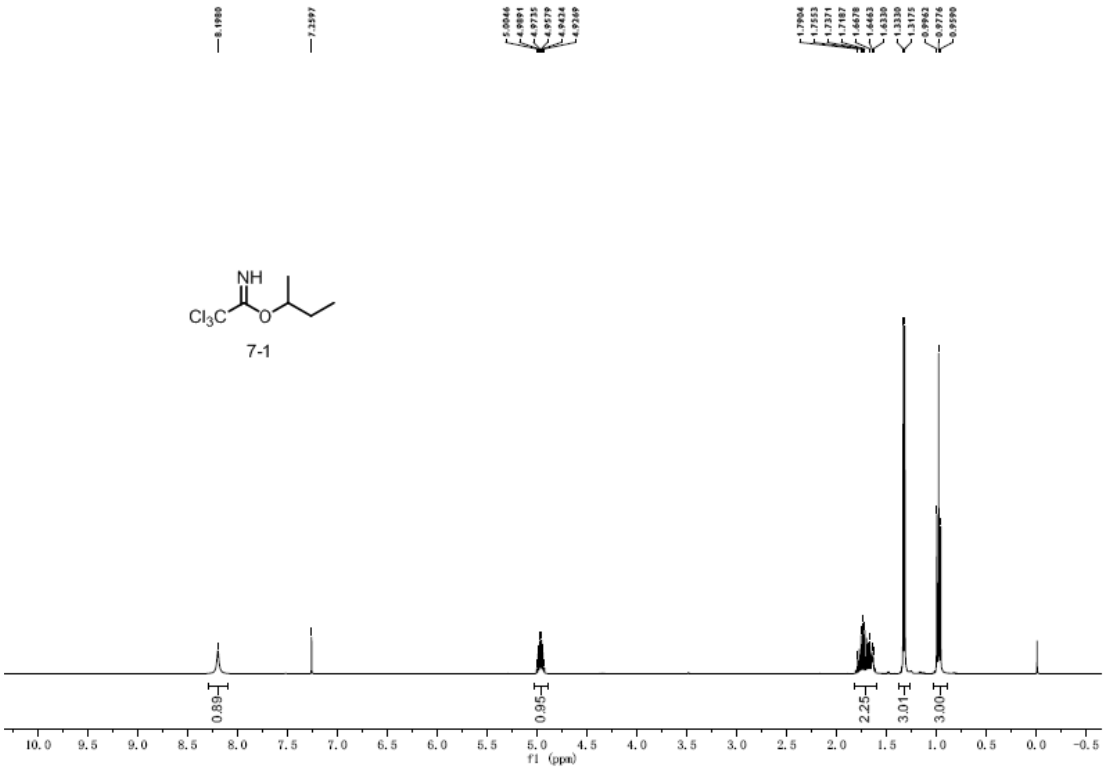
27.47
O
Cl3C
N
H
OH
6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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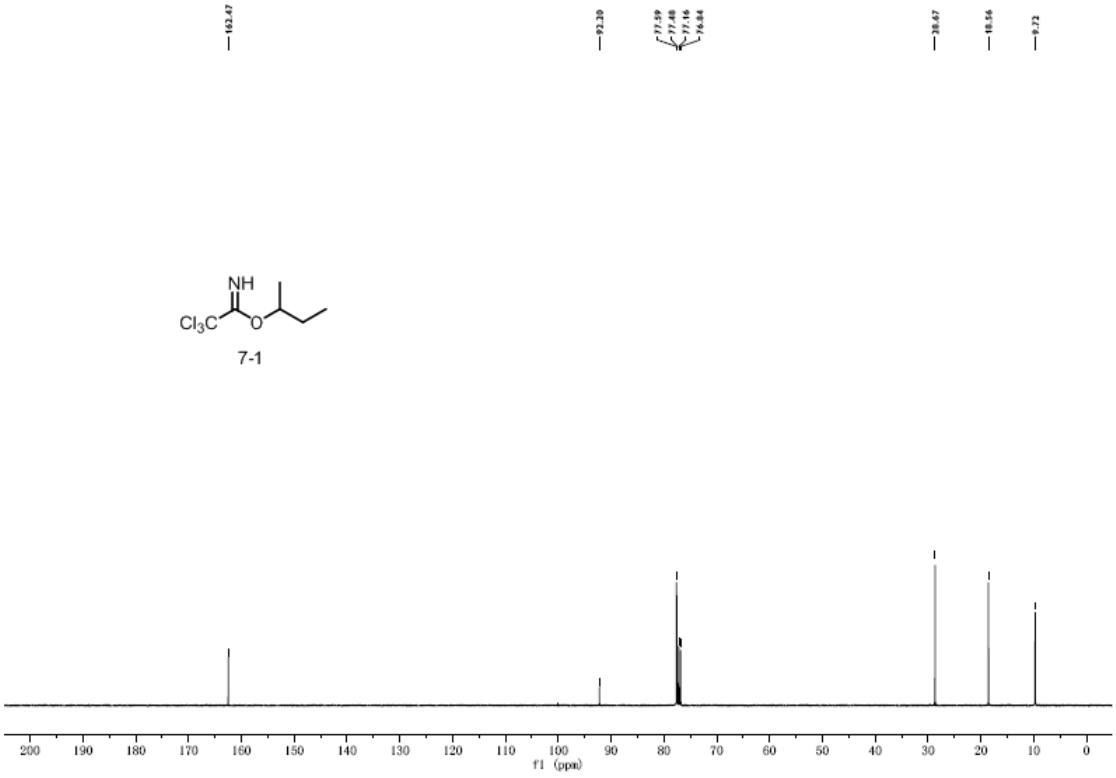
1.7301
1.7167
1.6678
1.6463
1.6330
1.3330
1.3175
0.9963
0.9774
0.9590
NH
Cl3C
O
7-1
0.89
0.95
2.25
3.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.59
77.48
77.16
76.84
28.67
18.56
9.72
NH
Cl3C
O
7-1
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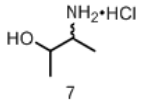
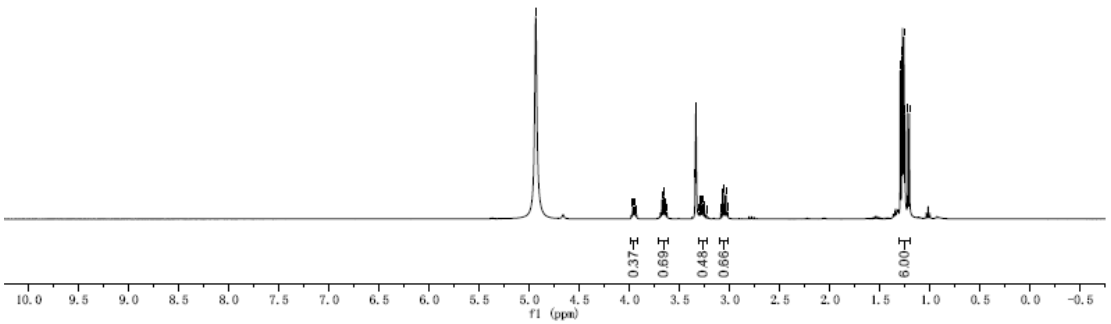
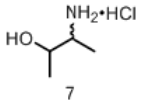
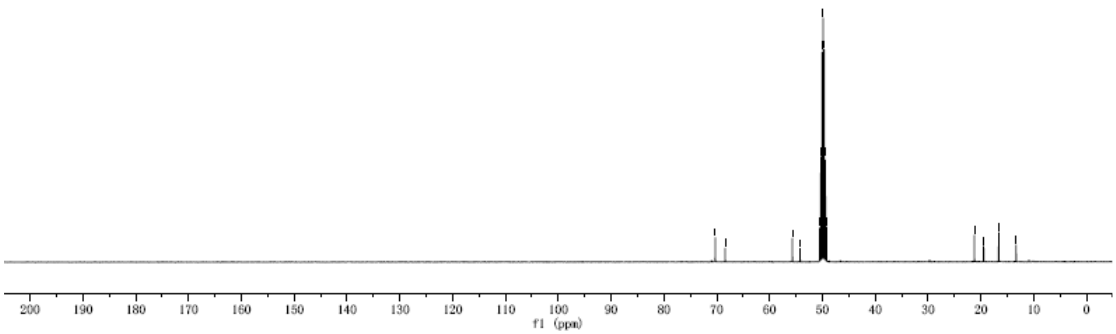
f1 (ppm)


NH2•HCl
HO
7


0.37 H
0.69 H
0.48 H
0.66 H
6.00 H
f1 (ppm)


NH2•HCl
HO
7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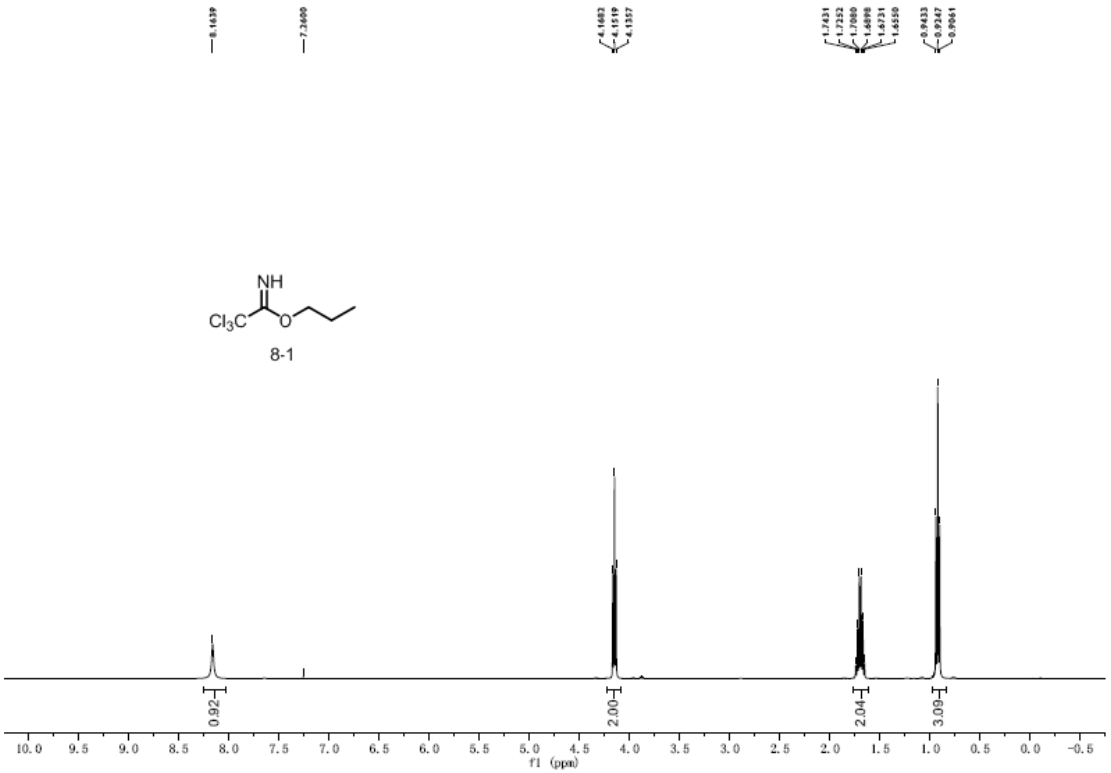
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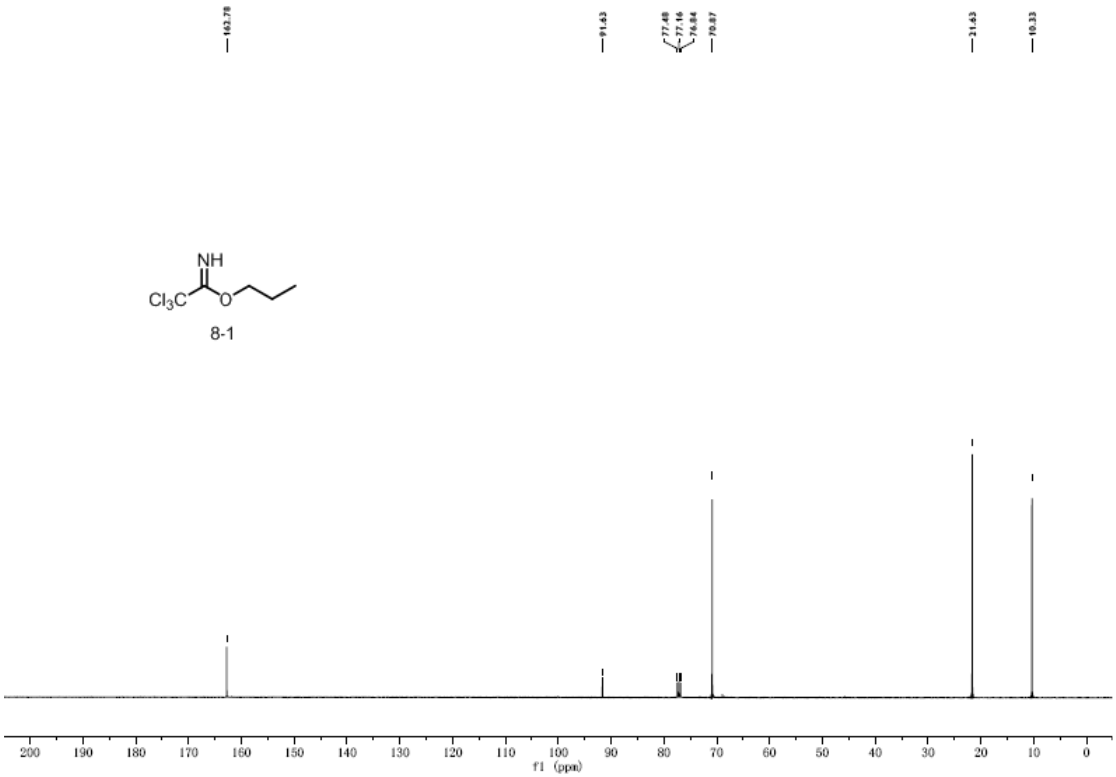
1.7080
1.6898
1.6731
1.6550
0.9433
0.9247
0.9061
NH
Cl3C
O
8-1
0.92
2.00
2.04
3.09
f1 (ppm)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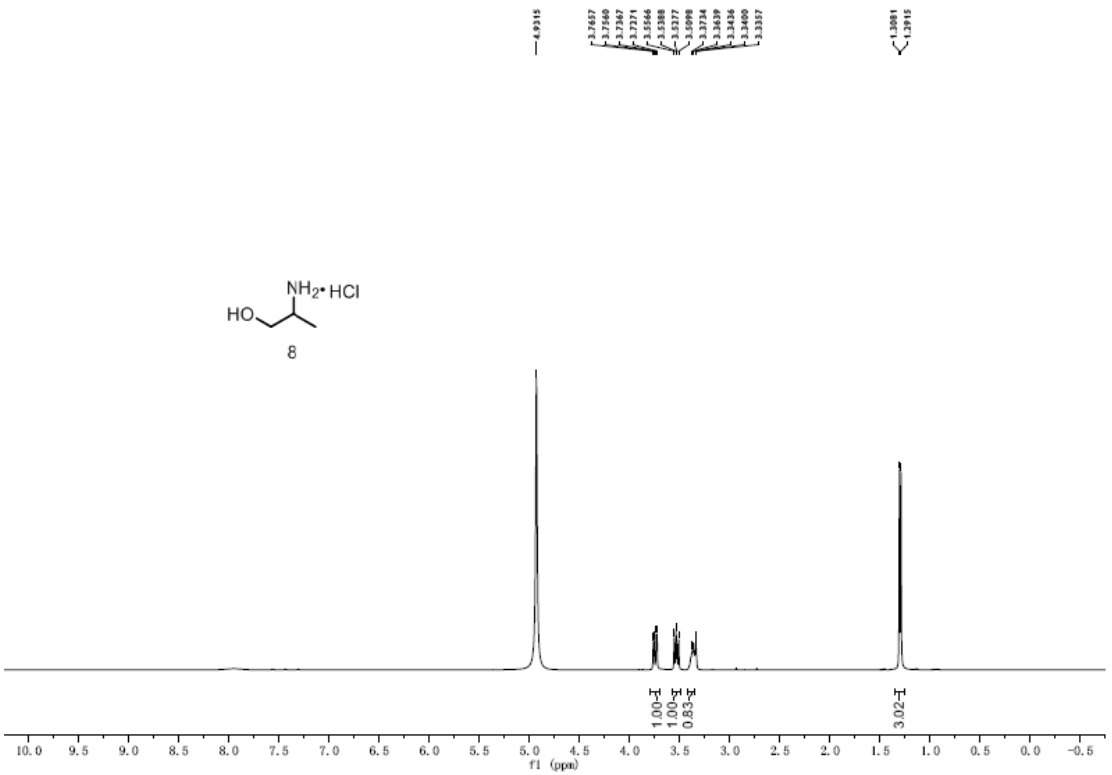
21.63
10.33
NH
Cl3C
O
8-1
f1 (ppm)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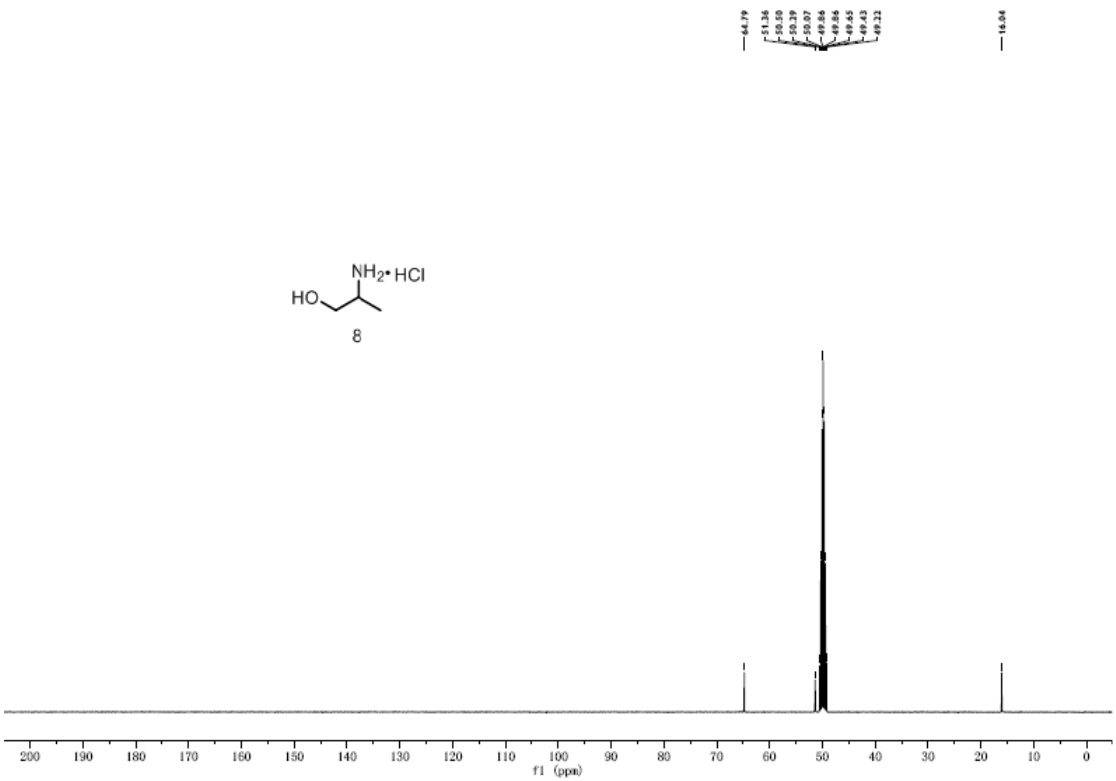
3.7560
3.7367
3.7271
3.5566
3.5388
3.5277
3.5098
3.3734
3.3639
3.3436
3.3400
3.3357
1.3081
1.2915
NH2• HCl
HO
8
1.00-I
1.00-I
0.83-I
3.02-I
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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50.07
49.86
49.65
49.43
49.22
16.04
NH2• HCl
HO
8
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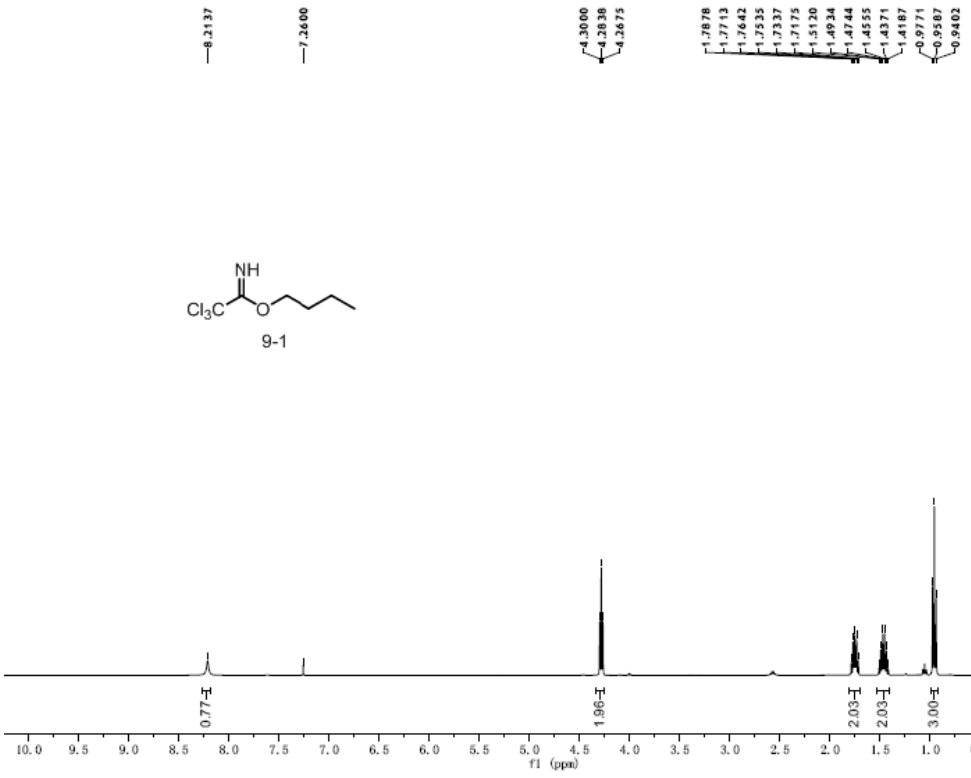
f1 (ppm)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4.2675
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1.7642
1.7535
1.7337
1.7175
1.5120
1.4934
1.4744
1.4555
1.4371
1.4187
0.9771
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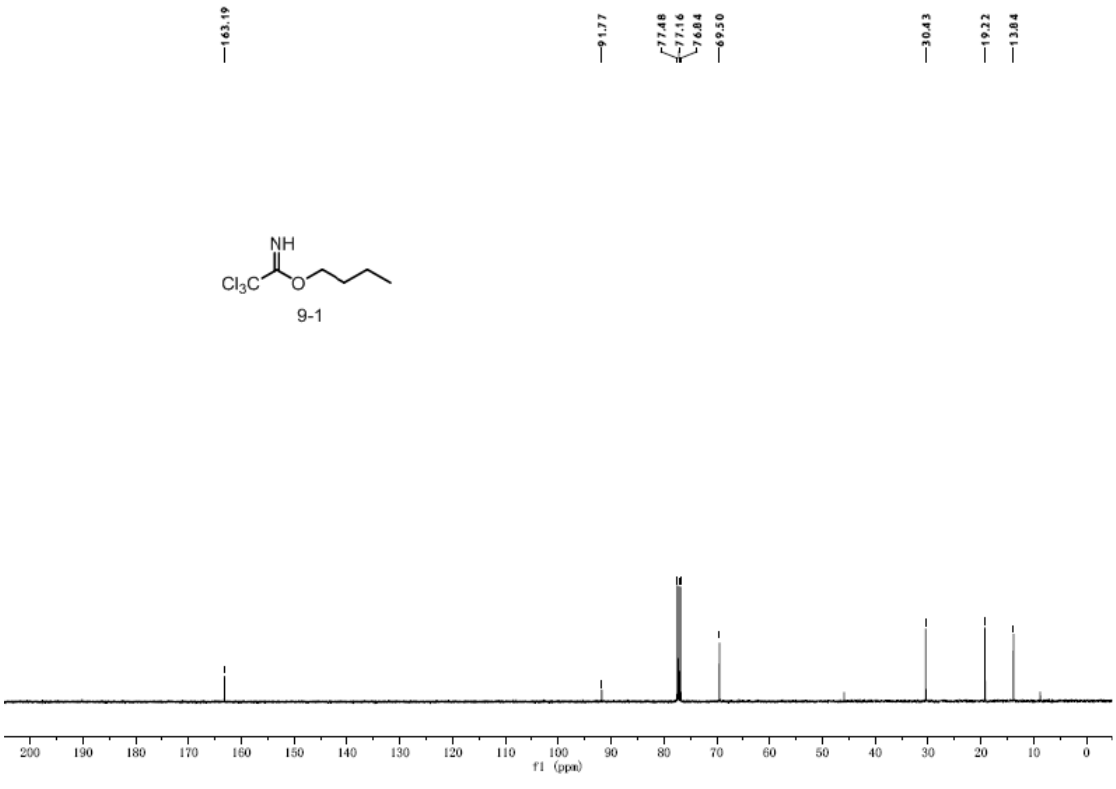
Cl3C
O
9-1
0.77
1.96
2.03
2.03
3.00
f1 (ppm)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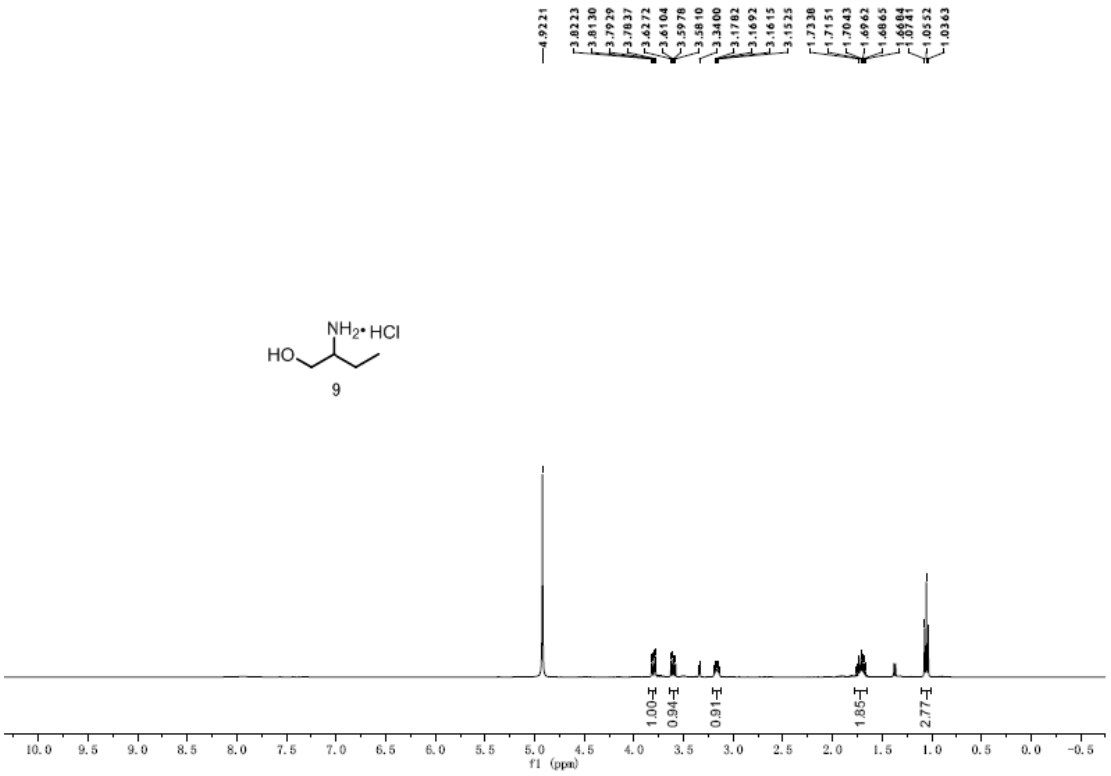
30.43
19.22
13.84
NH
Cl3C
O
9-1
f1 (ppm)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3.8130
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3.6272
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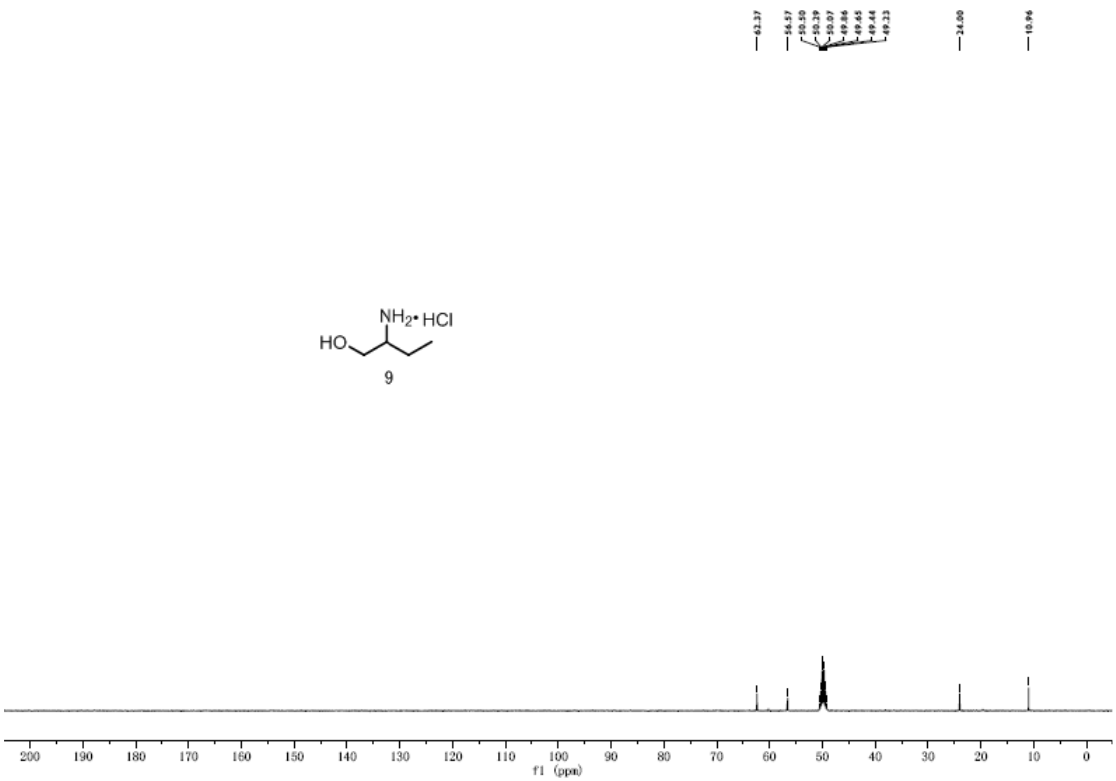
3.5978
3.5810
3.3400
3.1782
3.1692
3.1615
3.1525
1.7338
1.7151
1.7043
1.6962
1.6865
1.6684
1.6541
1.0552
1.0363
NH2• HCl
HO
9
1.00
0.94
0.91
1.85
2.77
f1 (ppm)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49.65
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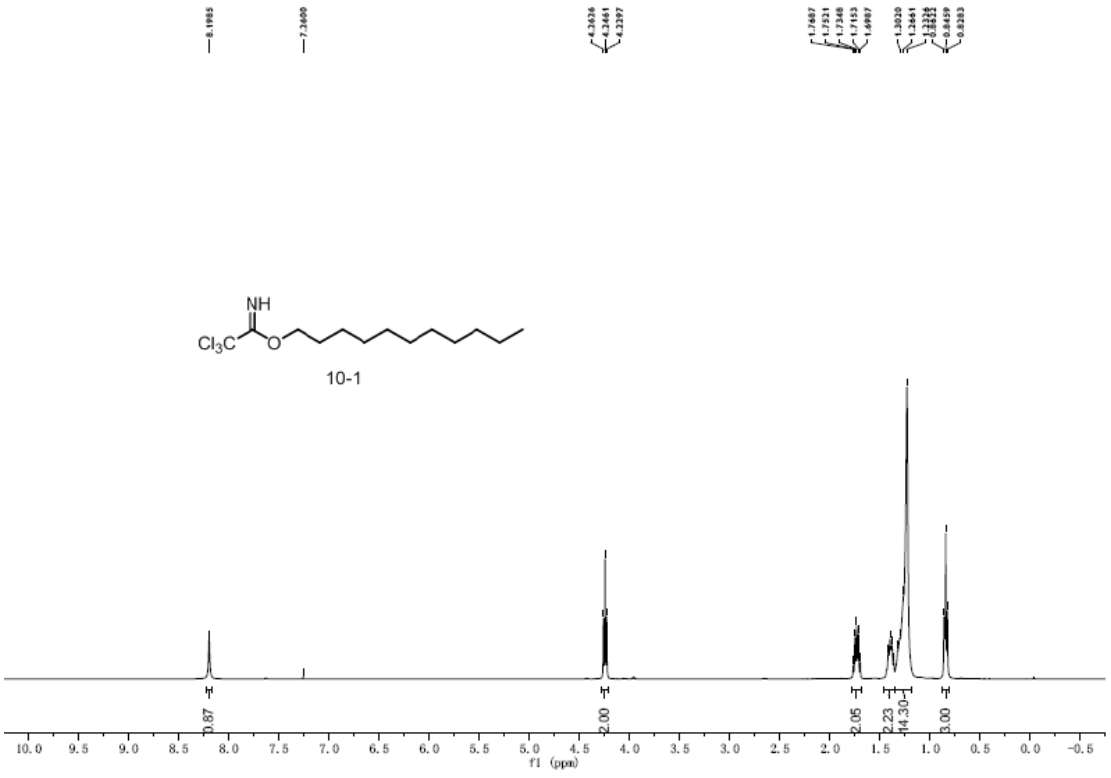
49.23
24.00
10.96
NH2• HCl
HO
9
f1 (ppm)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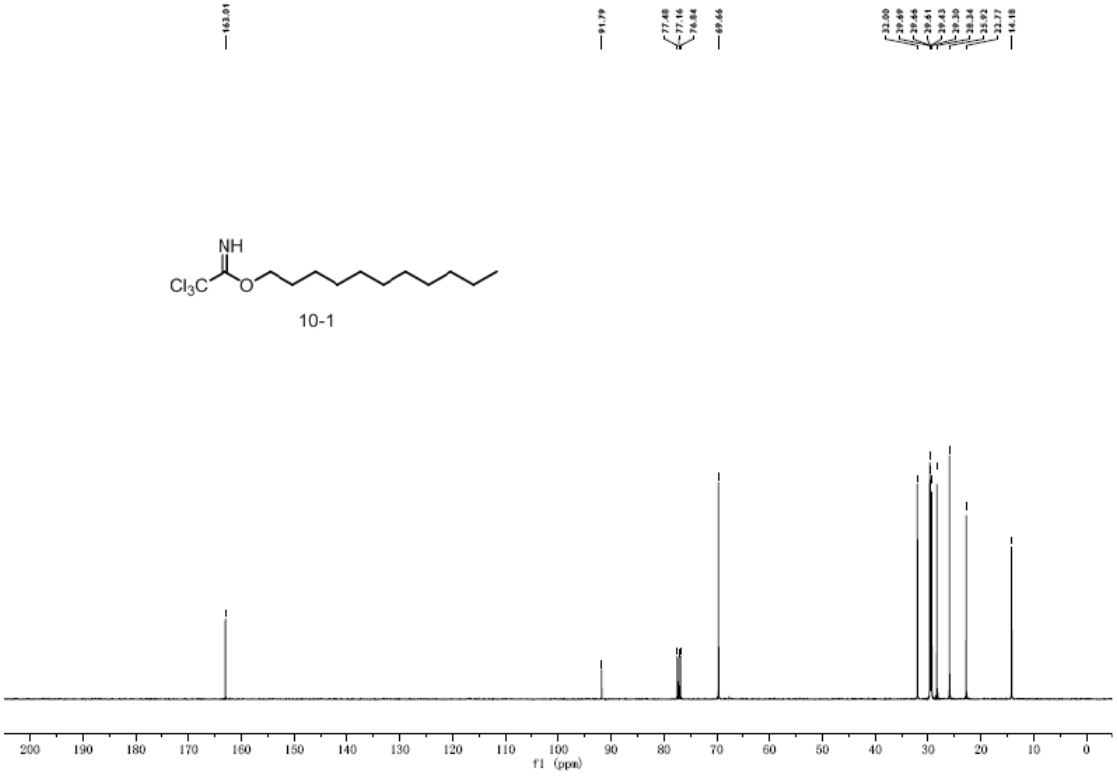
4.2297
1.7487
1.7531
1.7348
1.7153
1.6987
1.3020
1.2641
0.8459
0.8283
NH
Cl3C
O
10-1
0.87
2.00
2.05
2.23
14.30
3.00
f1 (ppm)


163.01
91.79
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77.16
76.84
69.66
32.00
29.69
29.66
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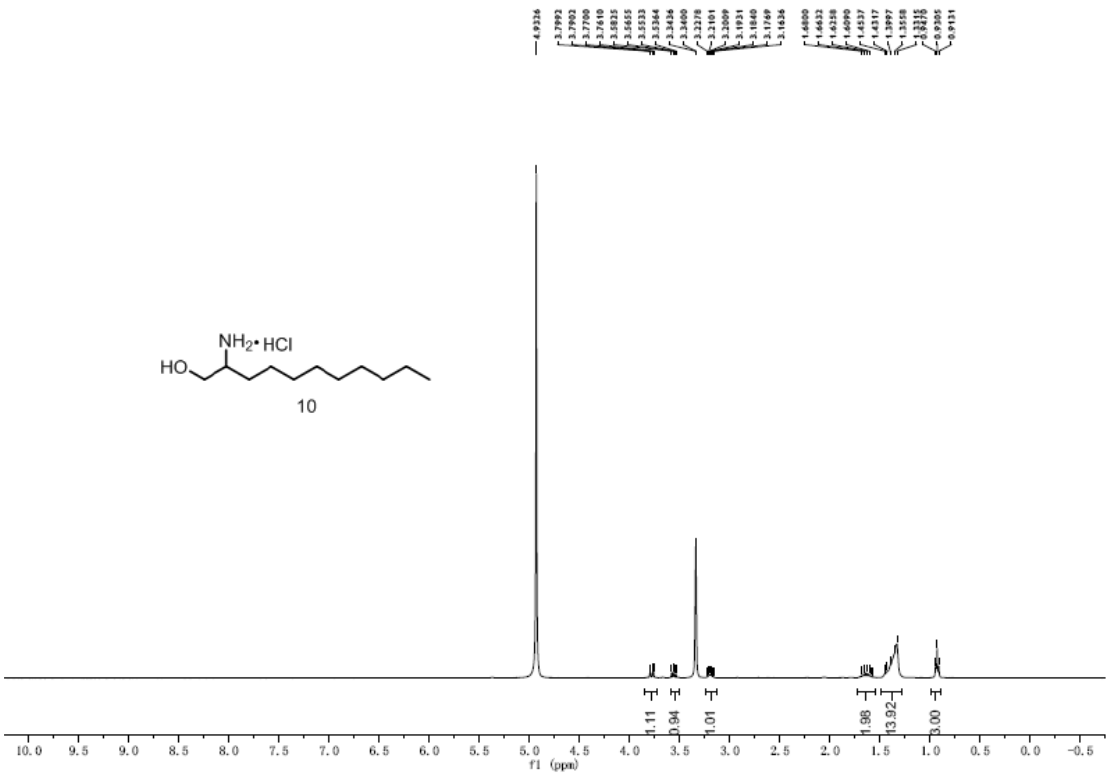
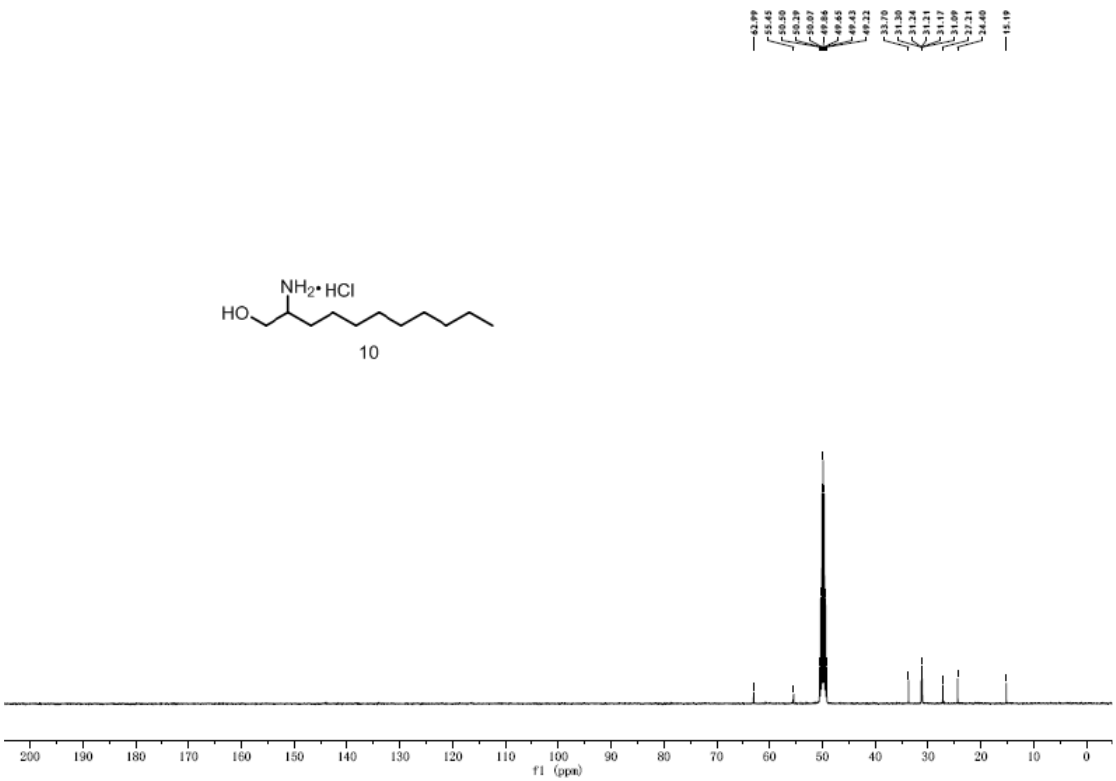
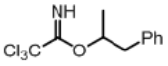
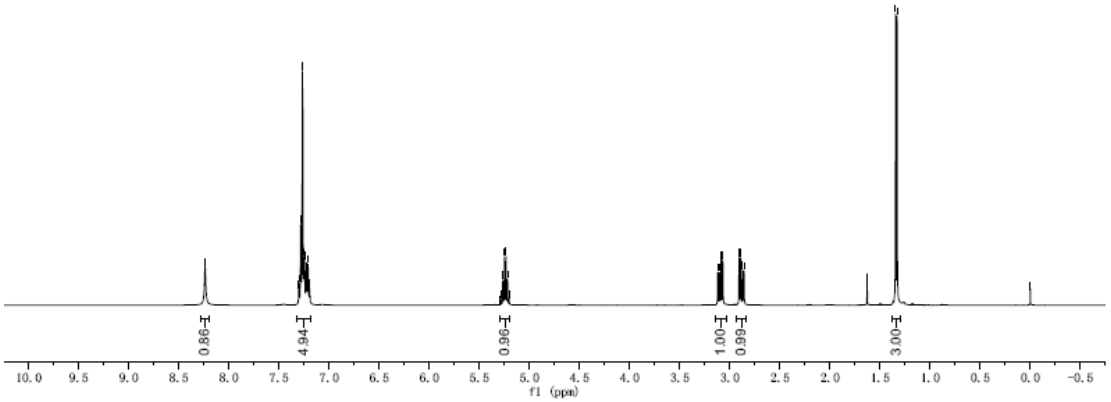
29.30
28.34
25.92
22.77
14.18
NH
Cl3C
O
10-1
f1 (ppm)

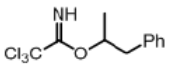

NH2• HCl
HO
10
1.11
0.94
1.01
1.98
13.92
3.00
f1 (ppm)


NH2• HCl
HO
10
f1 (ppm)

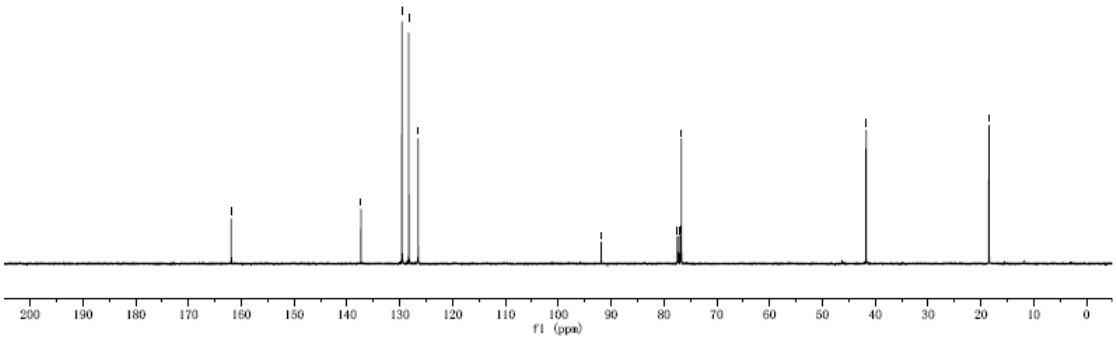


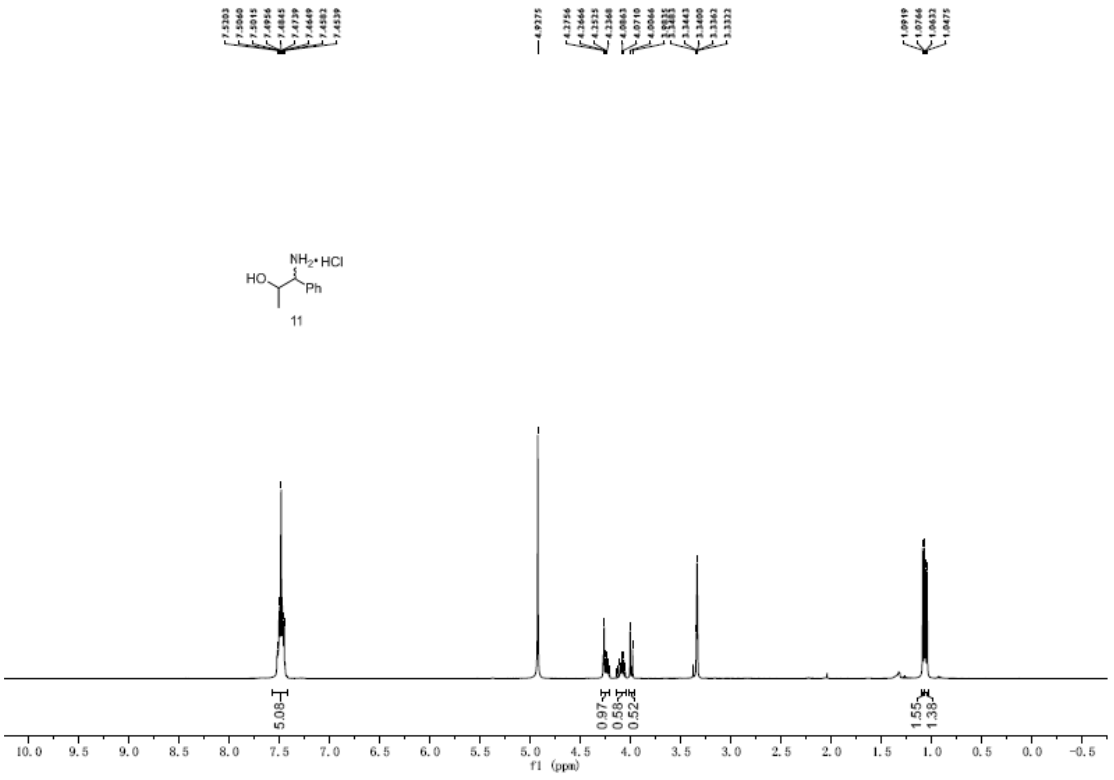
11-1

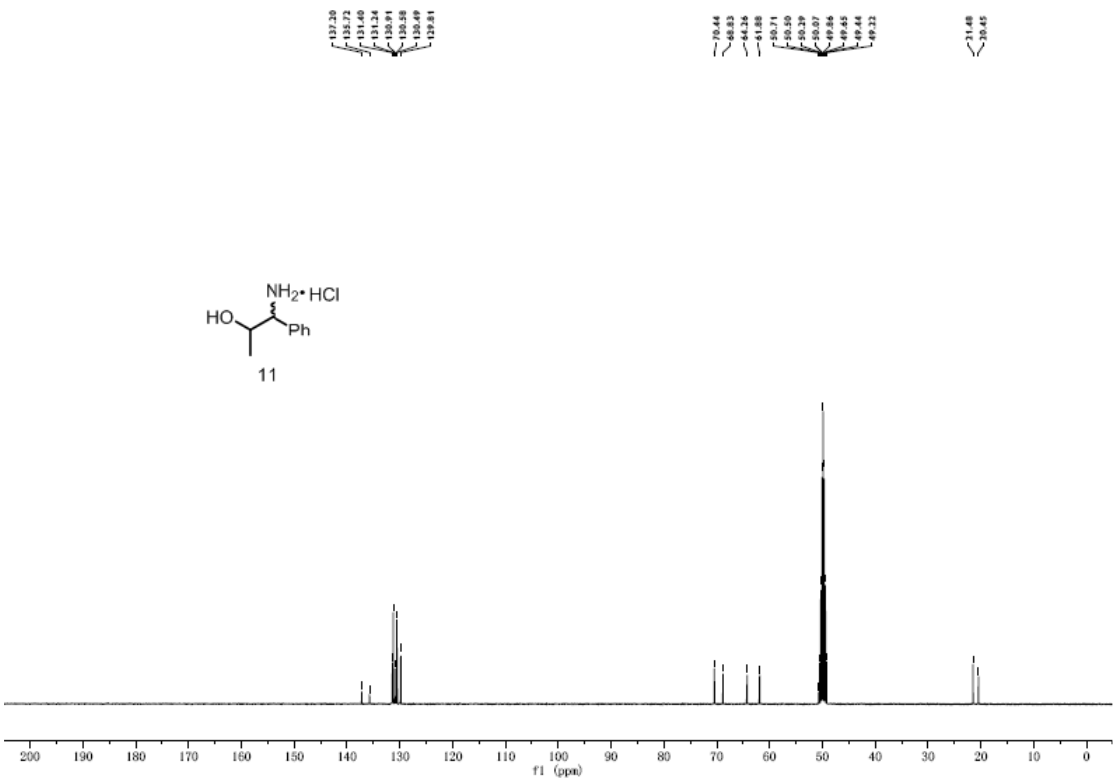


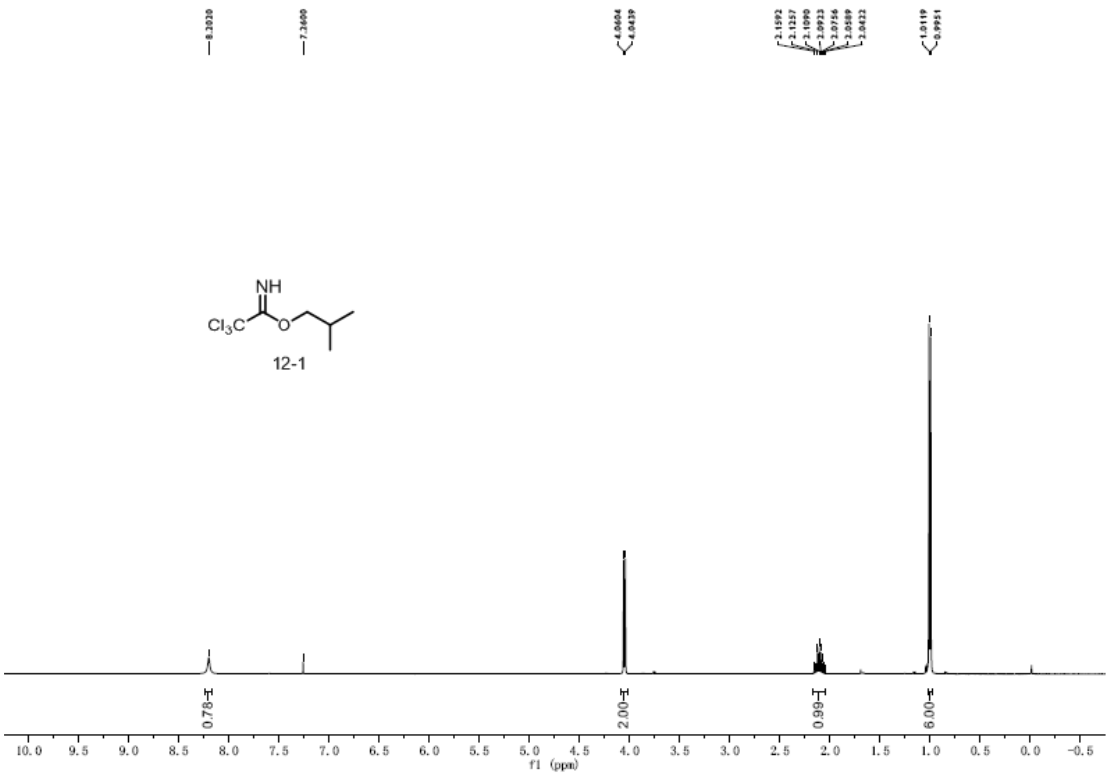


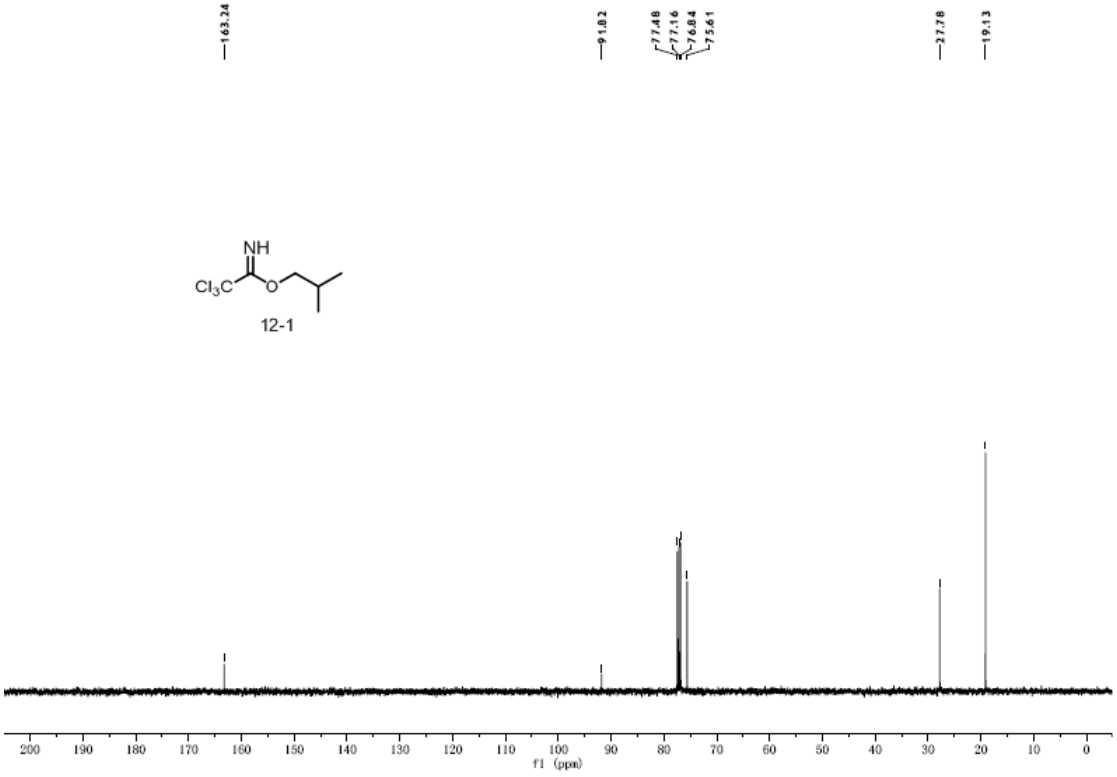
11-1

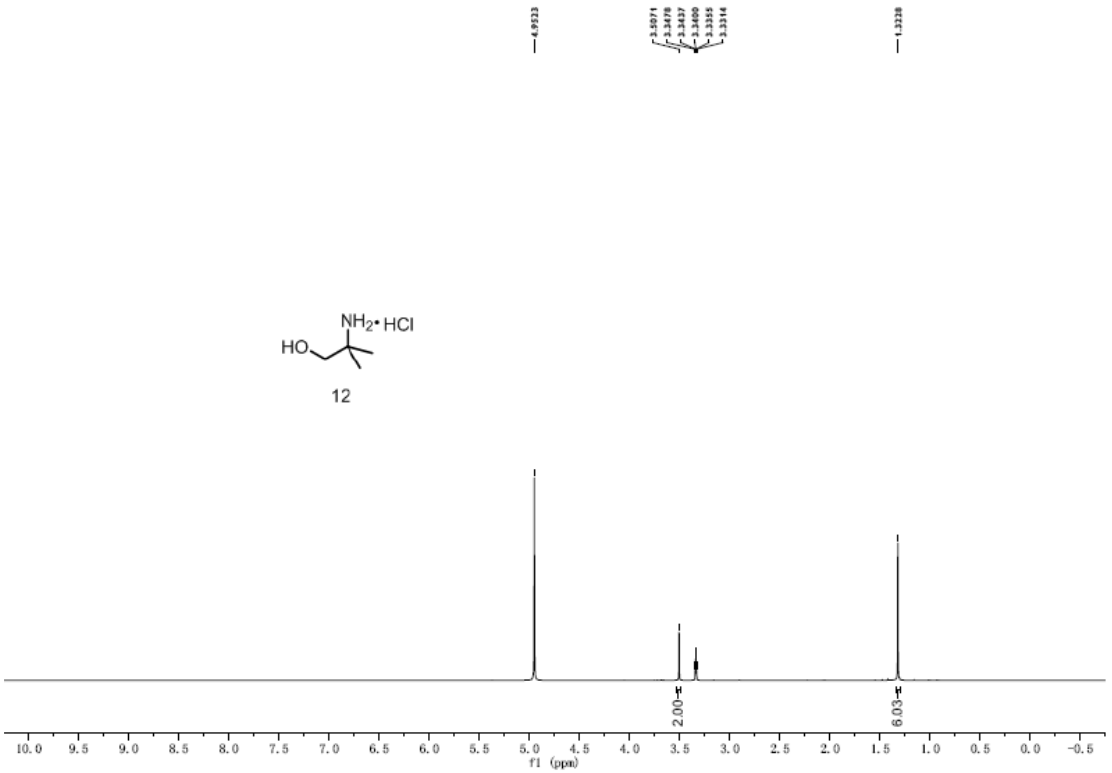


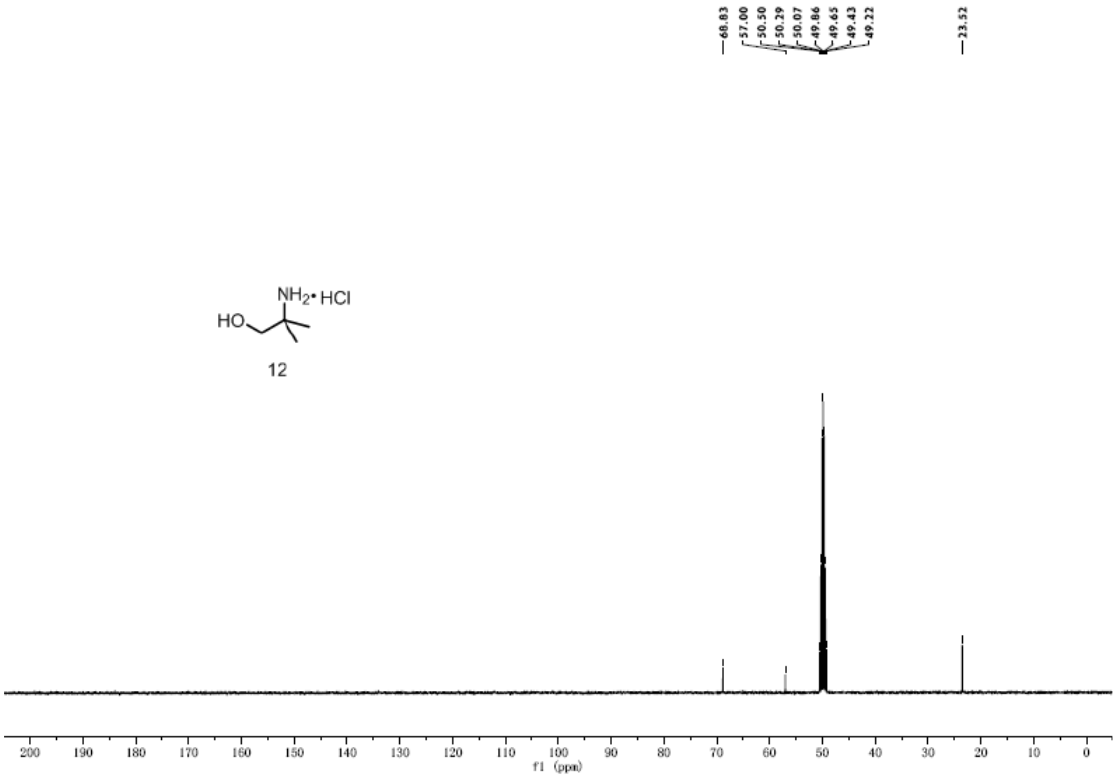

NH2• HCl
HO
Ph
11
5.08
0.97
0.58
0.52
1.55
1.38
f1 (ppm)

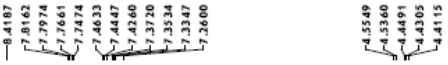

NH2• HCl
HO
Ph
11
f1 (ppm)

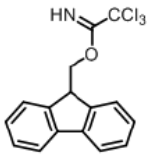

8.2030
7.2600
4.0604
4.0439
2.1592
2.1257
2.1090
2.0923
2.0756
2.0589
2.0422
1.0119
0.9951
NH
Cl3C
O
12-1
0.78
2.00
0.99
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


163.24
91.82
77.48
77.16
76.84
75.61
27.78
19.13
NH
Cl3C
O
12-1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

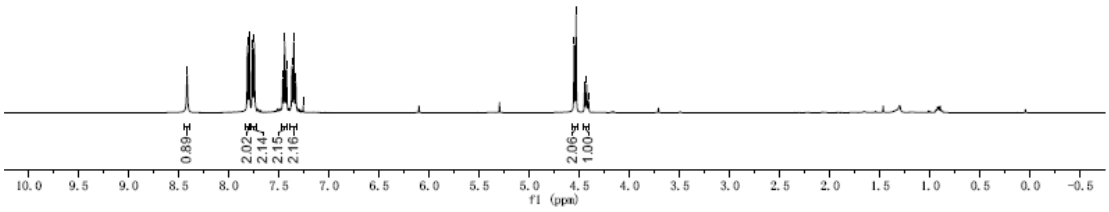

4.9533
3.5071
3.3478
3.3437
3.3400
3.3355
3.3314
1.3238
NH2• HCl
HO
12
2.00
6.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


68.83
57.00
50.50
50.29
50.07
49.86
49.65
49.43
49.22
23.52
NH2• HCl
HO
12
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

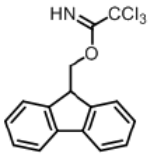

8.4187
7.8162
7.7974
7.7661
7.7474
7.4633
7.4447
7.4260
7.3720
7.3534
7.3347
7.2600
4.5549
4.5360
4.4491
4.4305
4.4115


HN
CCl3
O

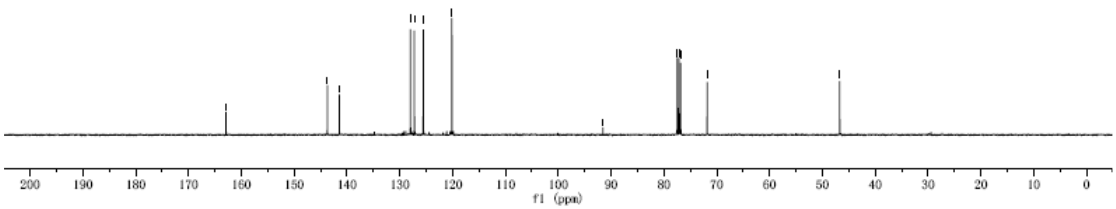
13-1


0.89
2.02
2.14
2.15
2.16
2.06
1.00
10.0 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)

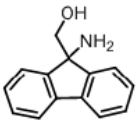

162.90
143.71
141.44
127.99
127.25
125.55
120.14
91.53
77.48
77.16
76.84
71.81
46.72


HN
CCl3
O

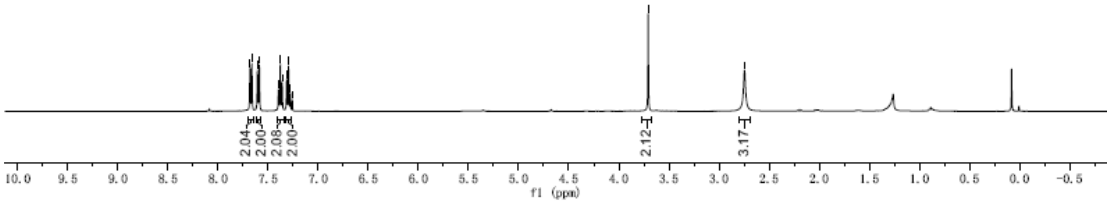
13-1


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

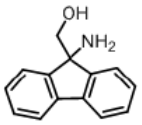

7.6018
7.6632
7.6074
7.5889
7.3972
7.3786
7.3600
7.3157
7.2971
7.2786
7.2600
3.7068
3.7450


OH
NH2

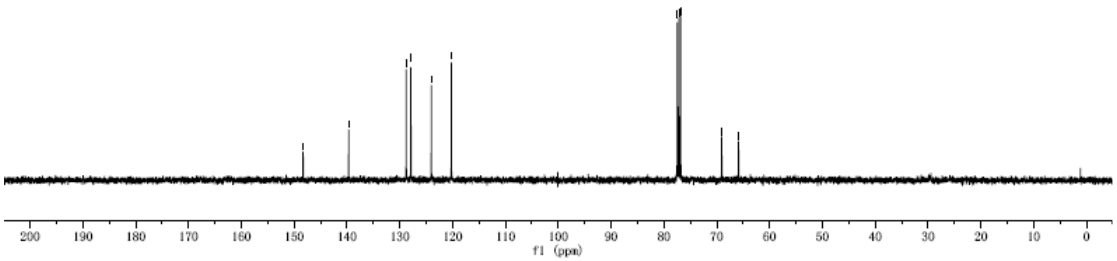
13

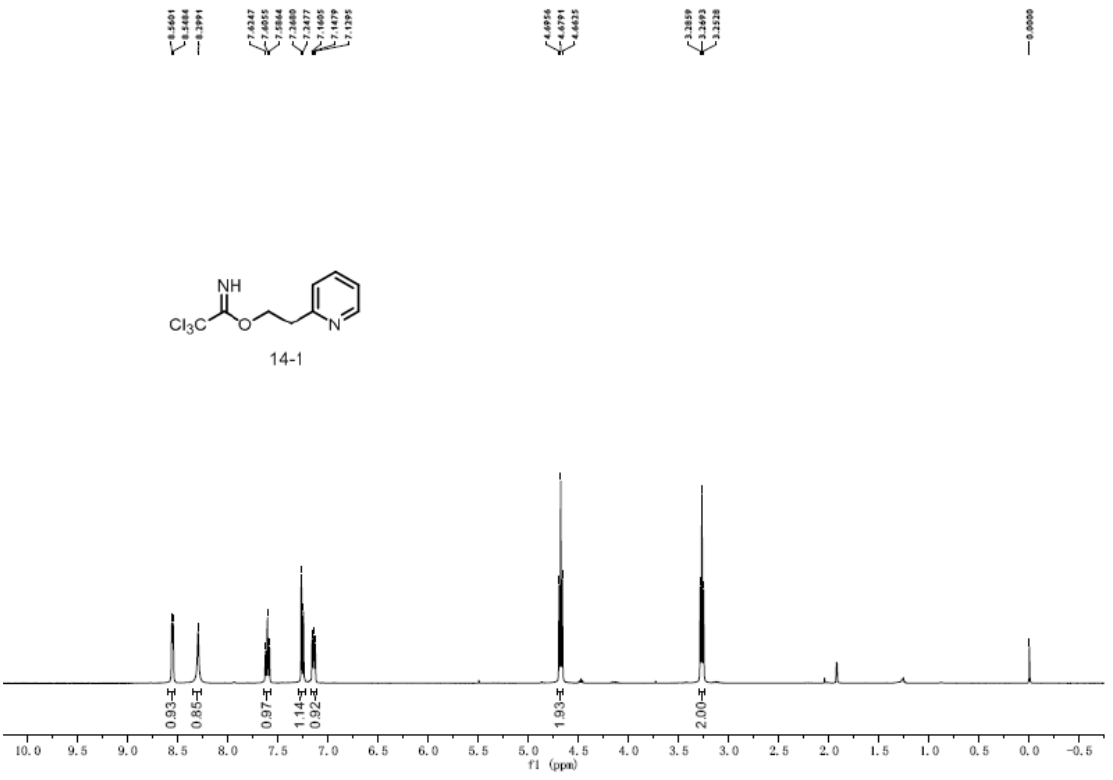

2.04
2.00
2.08
2.00
2.12
3.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

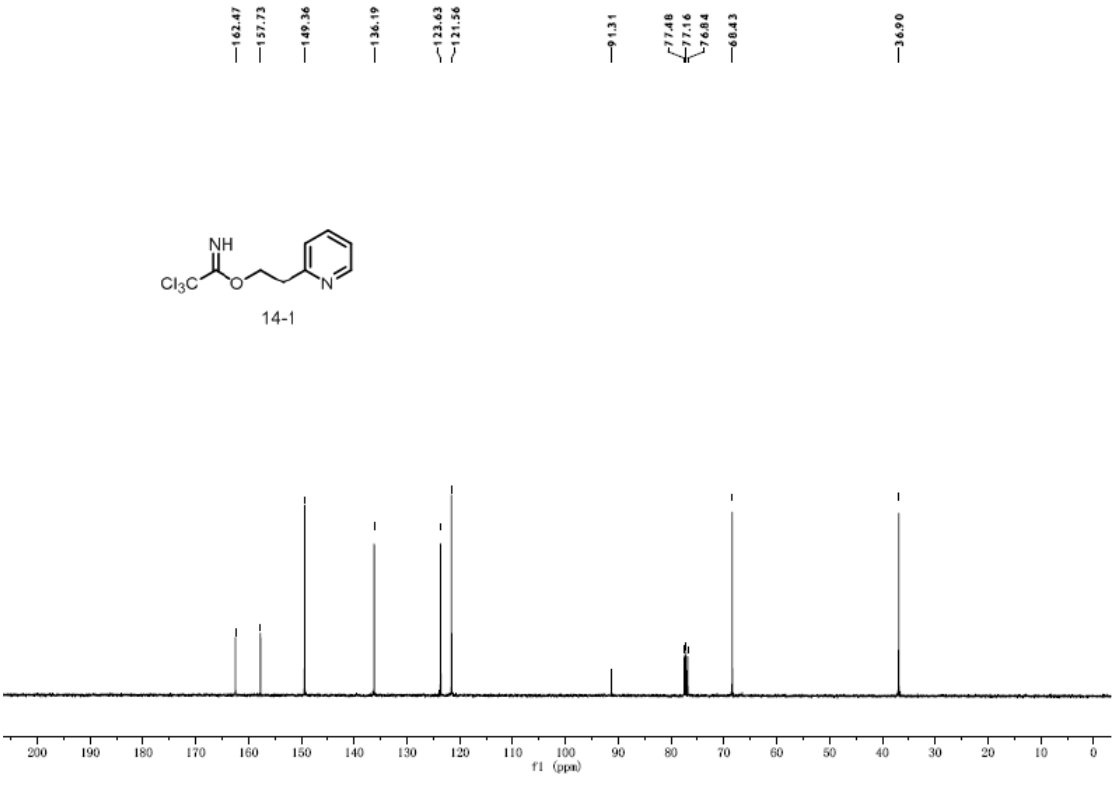

148.32
139.68
128.79
127.90
124.02
120.24
77.48
77.16
76.84
69.06
65.87

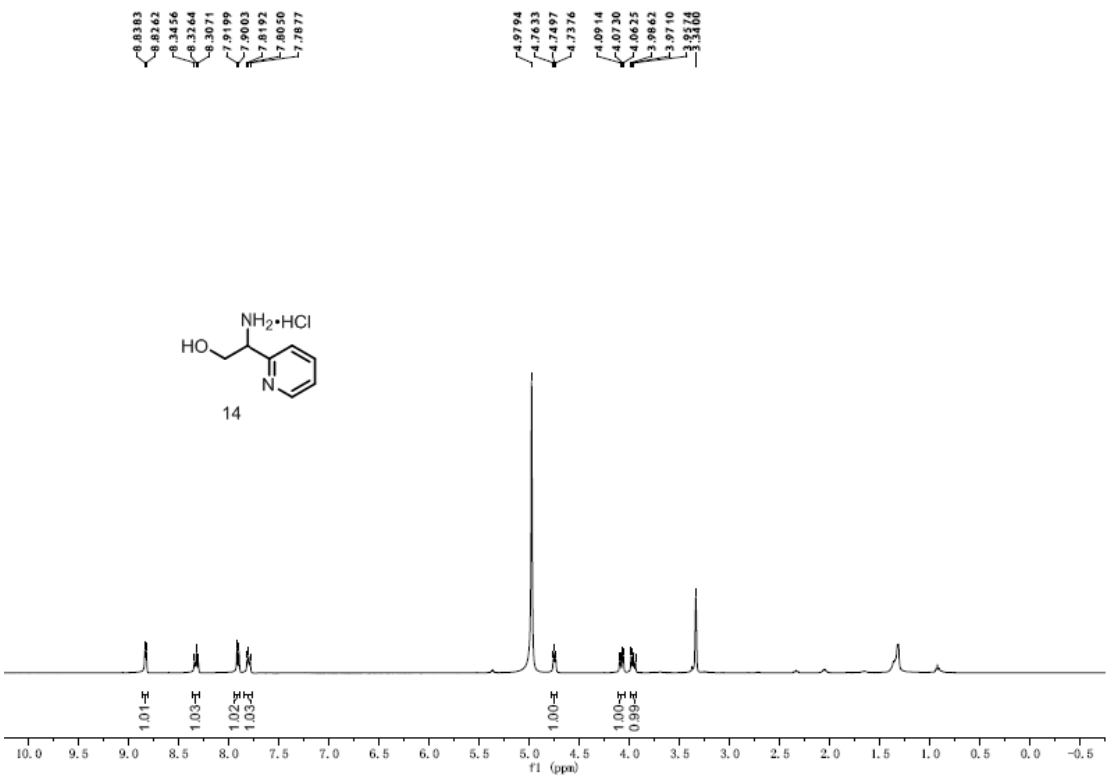

OH
NH2

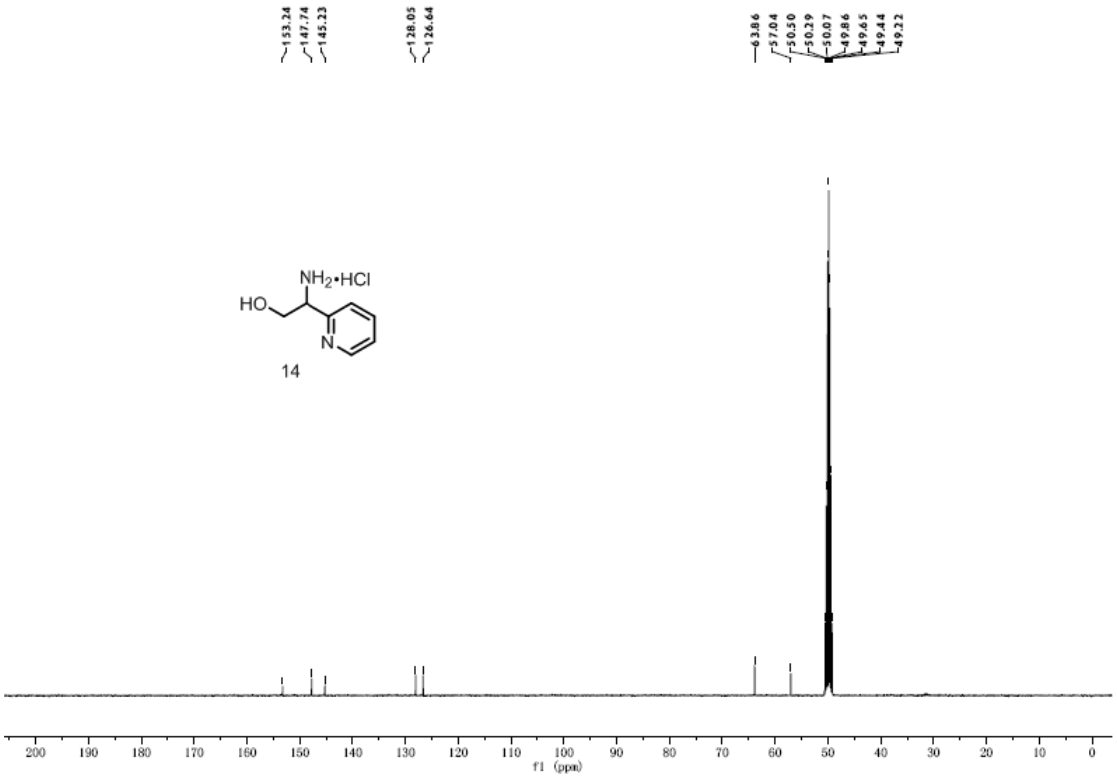
13

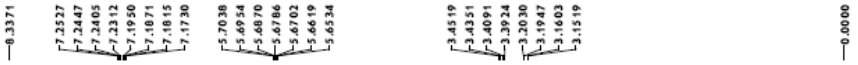

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

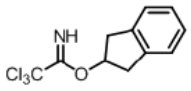

8.5601
8.5484
8.3991
7.6347
7.6055
7.5864
7.3480
7.3477
7.1605
7.1479
7.1295
4.4956
4.4791
4.4635
3.3859
3.3693
3.2528
0.0000
NH
Cl3C
O
N
14-1
0.93
0.85
0.97
1.14
0.92
1.93
2.00
f1 (ppm)


162.47
157.73
149.36
136.19
123.63
121.56
91.31
77.48
77.16
76.84
68.43
36.90
NH
Cl3C
O
N
14-1
f1 (ppm)

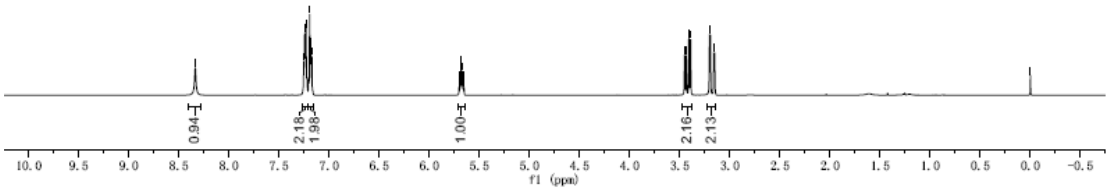

8.8383
8.8262
8.3456
8.3264
8.3071
7.9199
7.9003
7.8192
7.8050
7.7877
4.9794
4.7633
4.7497
4.7376
4.0914
4.0730
4.0625
3.9862
3.9710
3.8574
3.5100
NH2•HCl
HO
N
14
1.01
1.03
1.02
1.03
1.00
1.00
0.99
f1 (ppm)

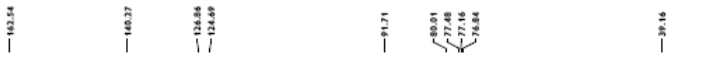

153.24
147.74
145.23
128.05
126.64
63.86
57.04
50.50
50.29
50.07
49.86
49.65
49.44
49.22
NH2•HCl
HO
N
14
f1 (ppm)

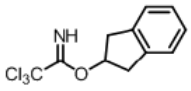

0.3371
7.2527
7.2447
7.2405
7.2312
7.1950
7.1071
7.1015
7.1730
5.7038
5.6954
5.6870
5.6786
5.6702
5.6619
5.6534
3.4519
3.4351
3.4091
3.3924
3.2030
3.1947
3.1603
3.1519
0.0000


NH
Cl3C
O

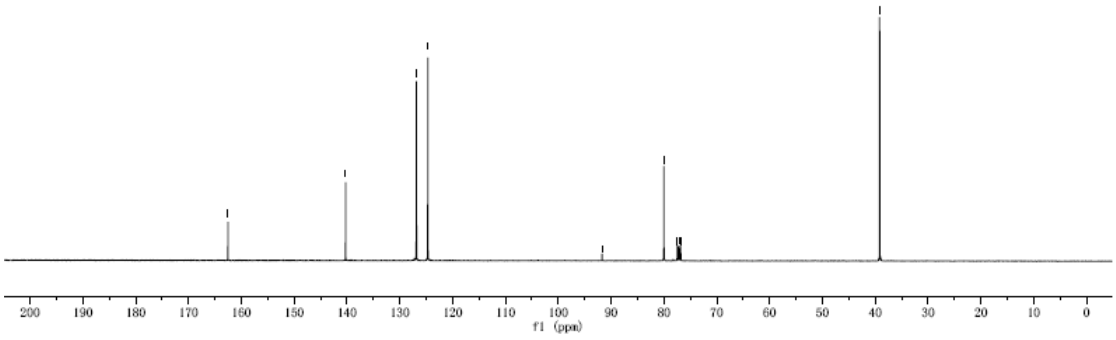
15-1

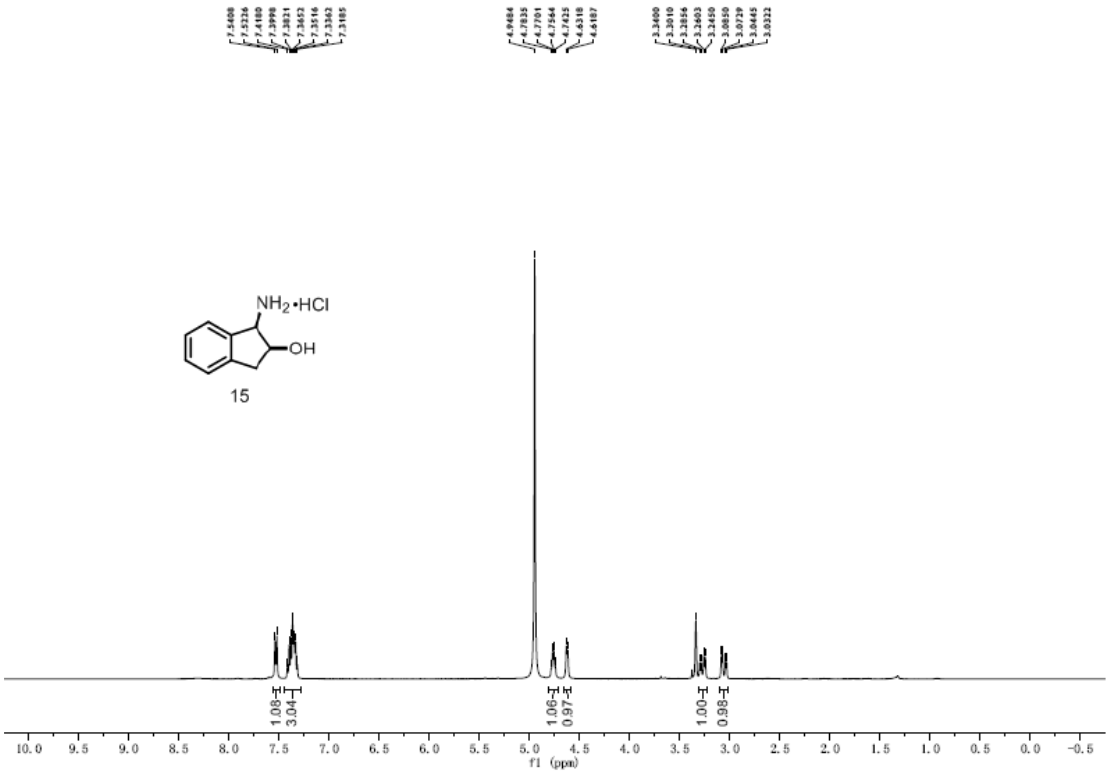

0.94
2.18
1.98
1.00
2.16
2.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

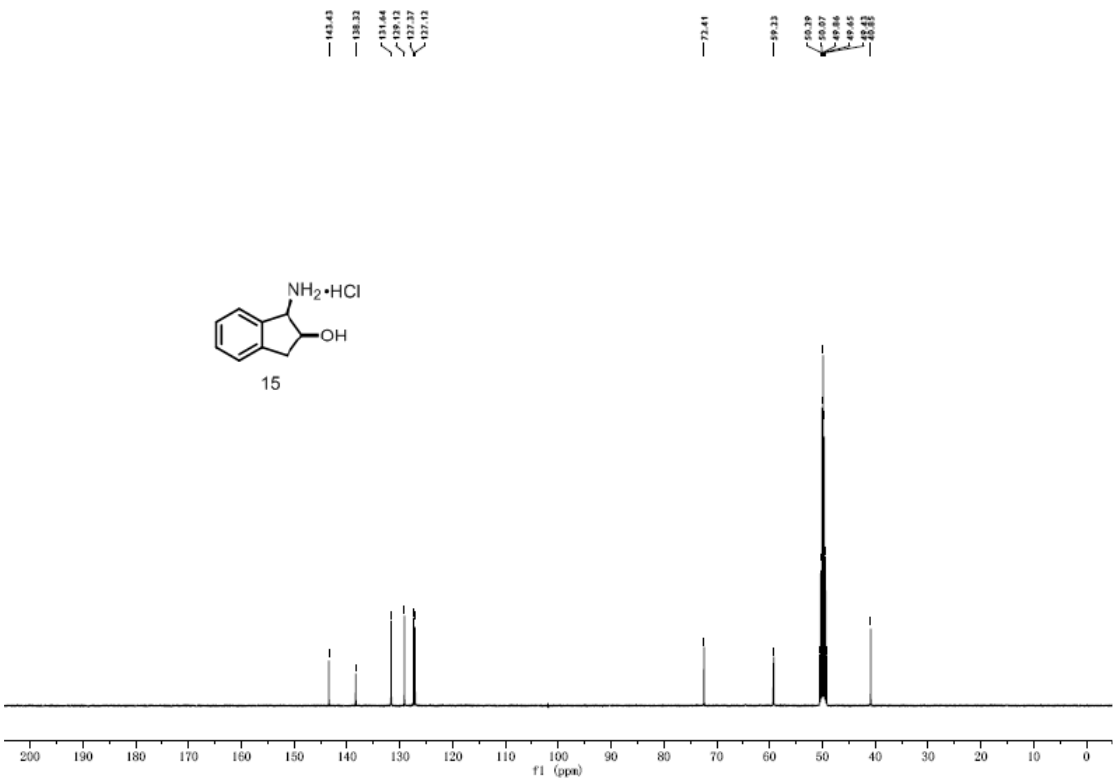

163.54
140.37
135.86
134.69
91.71
80.01
77.48
77.16
76.84
39.16

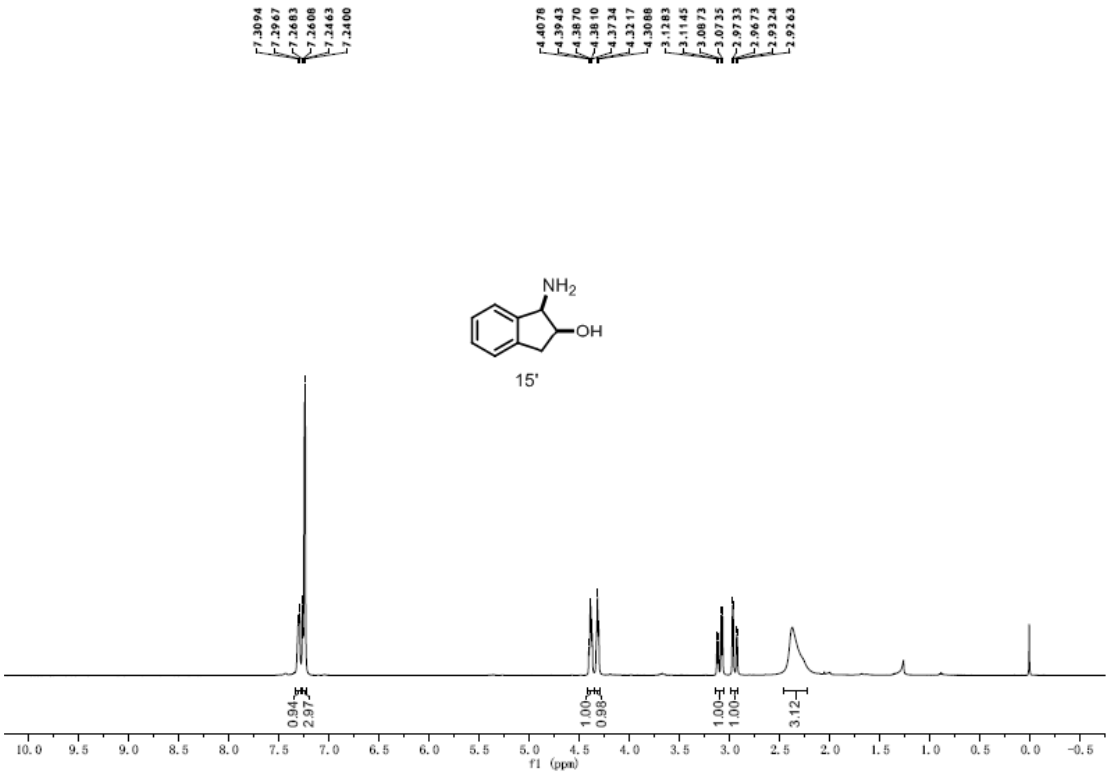

NH
Cl3C
O

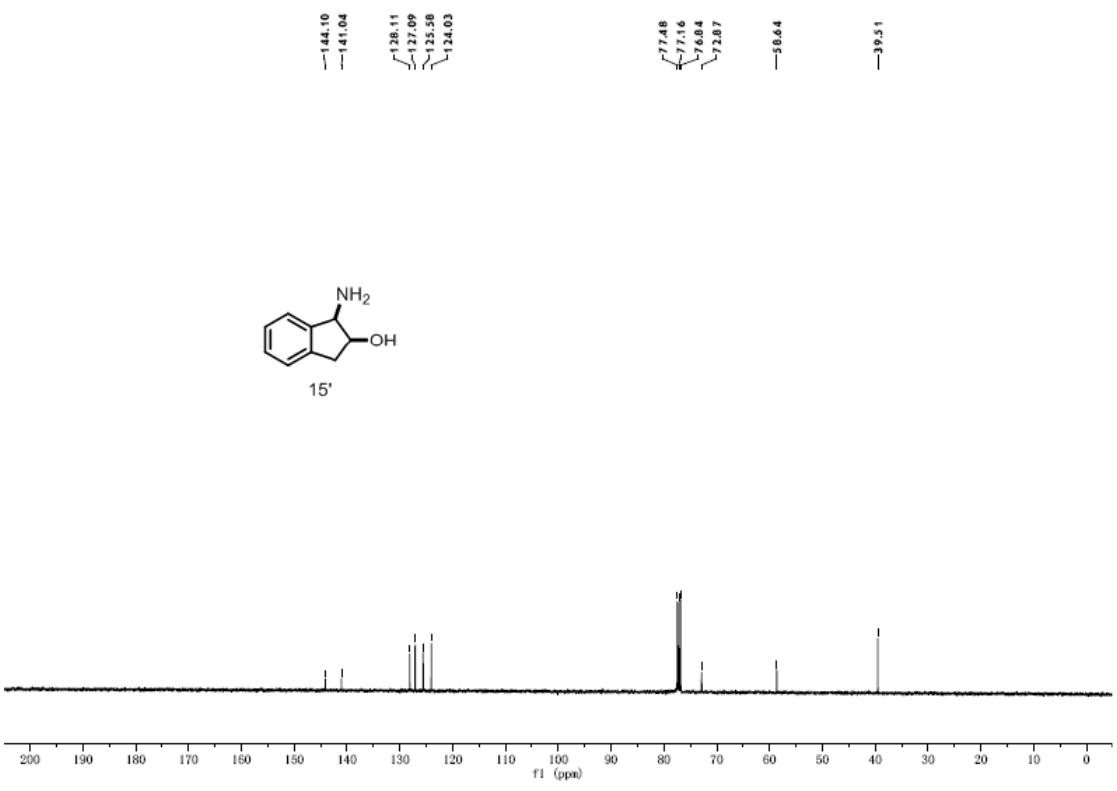
15-1

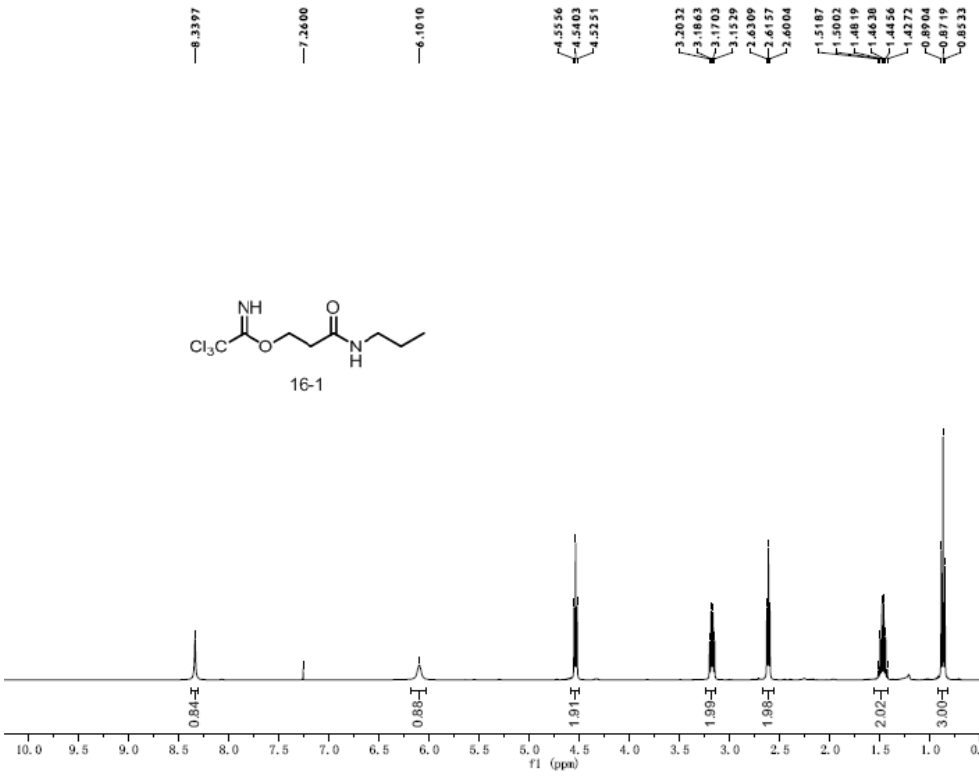

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

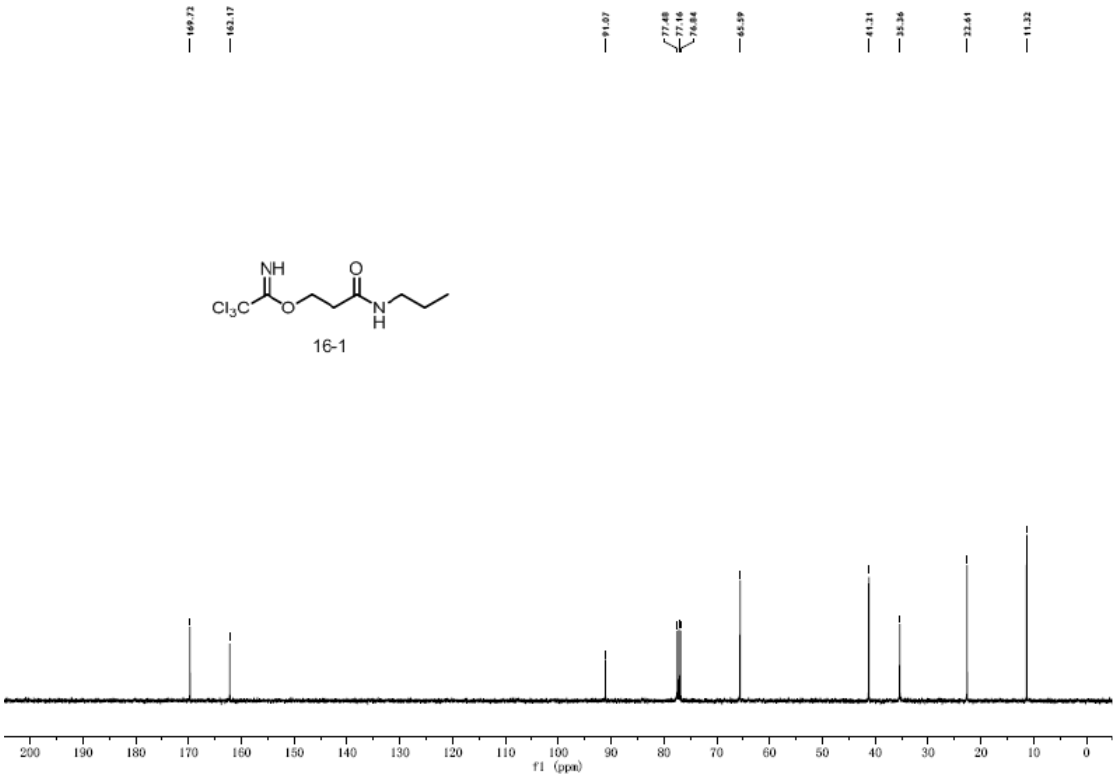

NH2•HCl
OH
15
1.08
3.04
1.06
0.97
1.00
0.98
f1 (ppm)

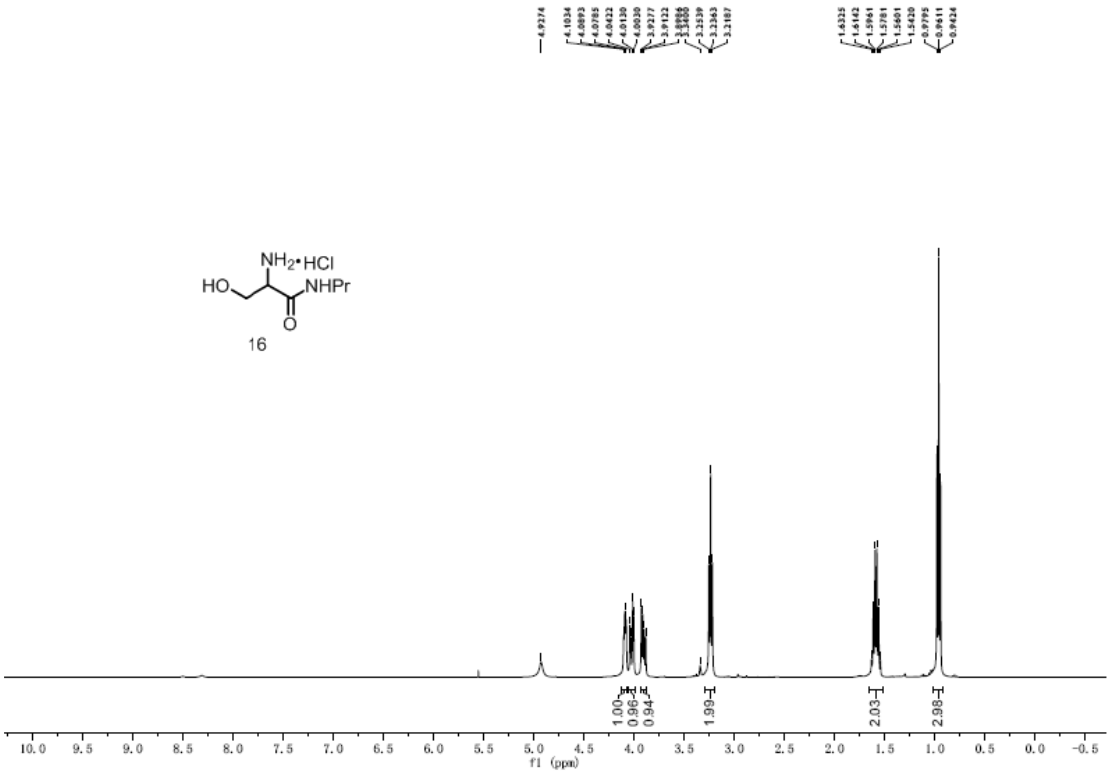

NH2•HCl
OH
15
f1 (ppm)

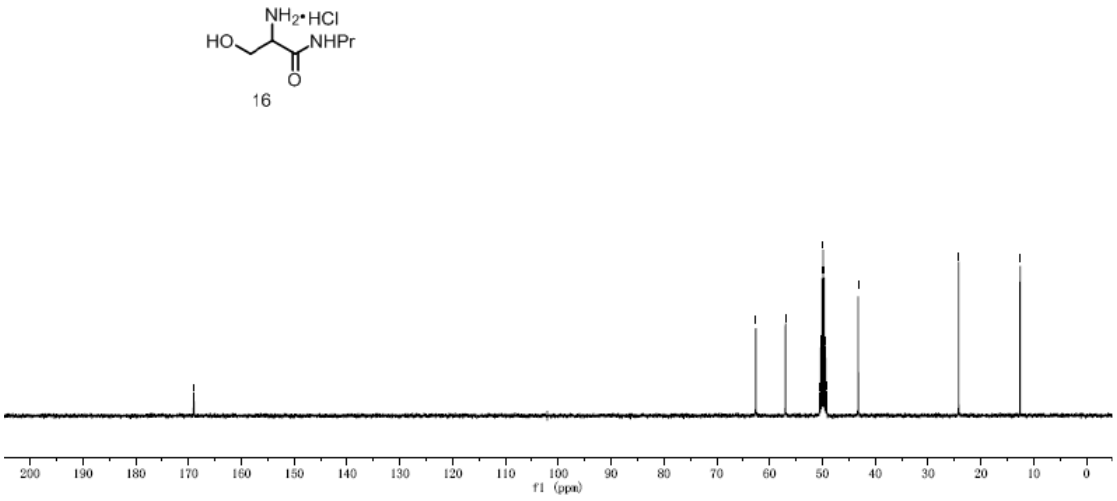

7.3094
7.2967
7.2683
7.2608
7.2463
7.2400
4.4078
4.3943
4.3870
4.3810
4.3734
4.3317
4.3088
3.1283
3.1145
3.0873
3.0735
2.9733
2.9673
2.9324
2.9263
NH2
OH
15'
0.94
2.97
1.00
0.98
1.00
1.00
3.12
f1 (ppm)

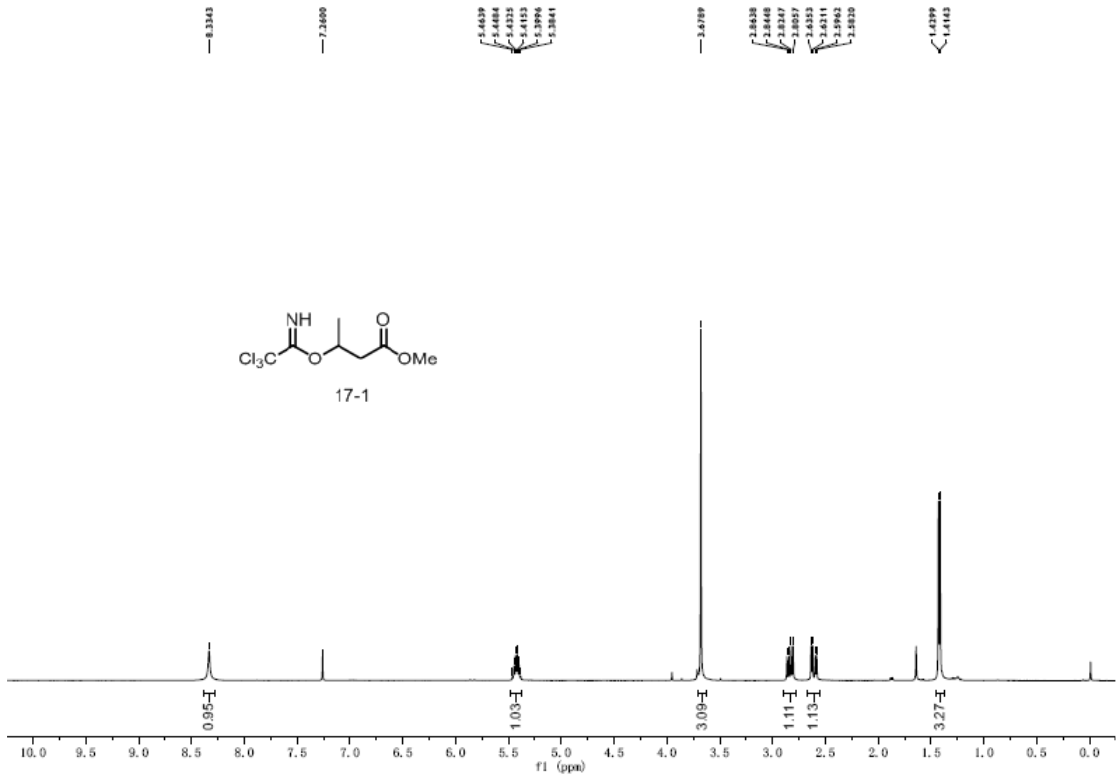

144.10
141.04
128.11
127.09
125.50
124.03
77.48
77.16
76.84
72.87
58.64
39.51
NH2
OH
15'
f1 (ppm)

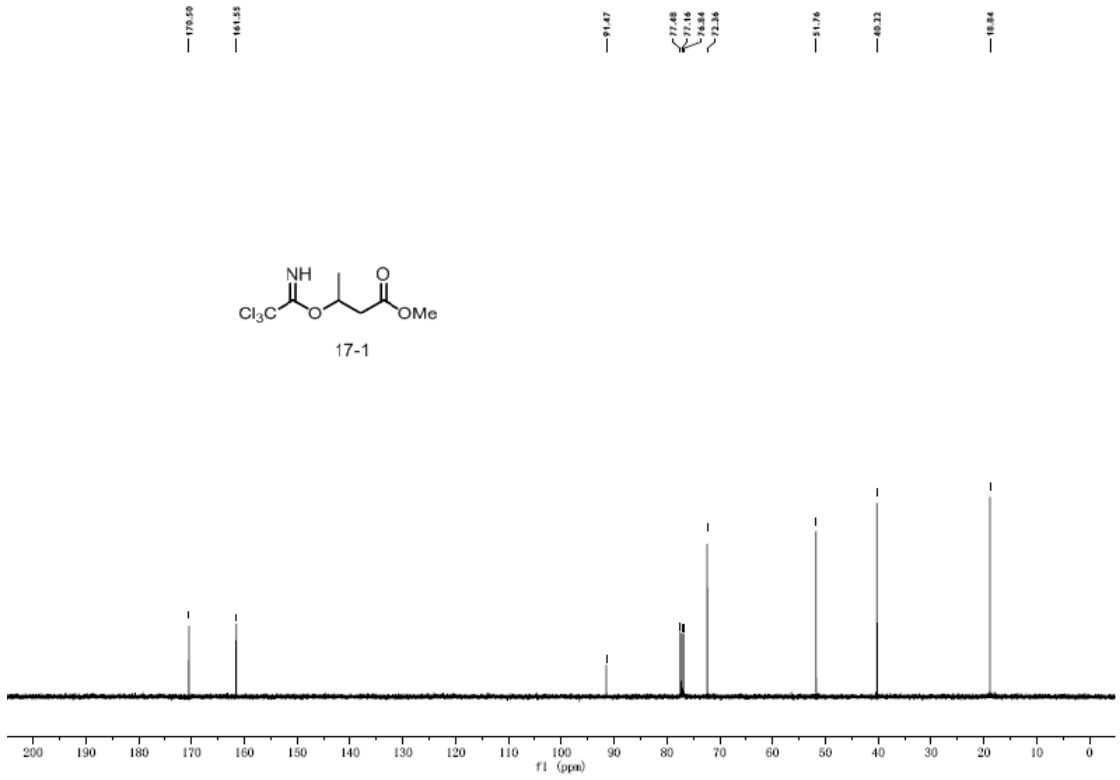

8.3397
7.2600
6.1010
4.5556
4.5403
4.5251
3.2032
3.1863
3.1703
3.1529
2.6309
2.6157
2.6004
1.5187
1.5002
1.4819
1.4638
1.4456
1.4272
0.8904
0.8719
0.8533
NH
O
Cl3C
O
N
H
16-1
0.84
0.88
1.91
1.99
1.98
2.02
3.00
f1 (ppm)

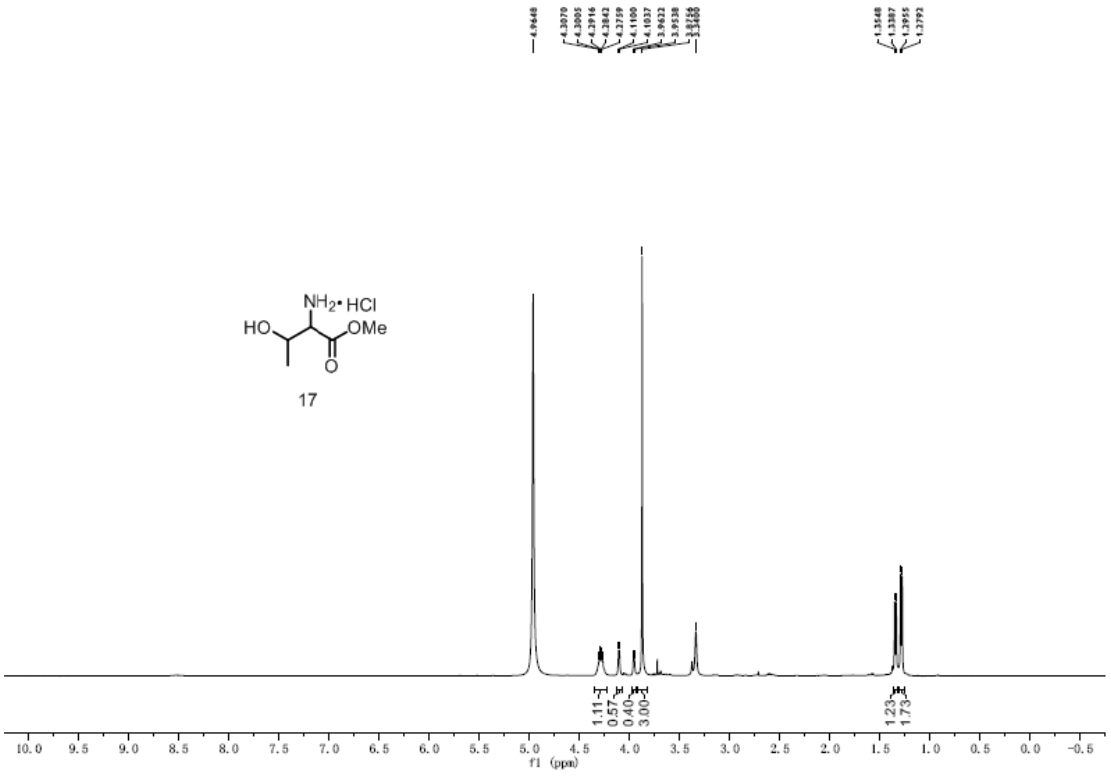

169.72
162.17
91.07
77.48
77.16
76.84
65.59
41.21
35.36
22.61
11.32
NH
O
Cl3C
O
N
H
16-1
f1 (ppm)

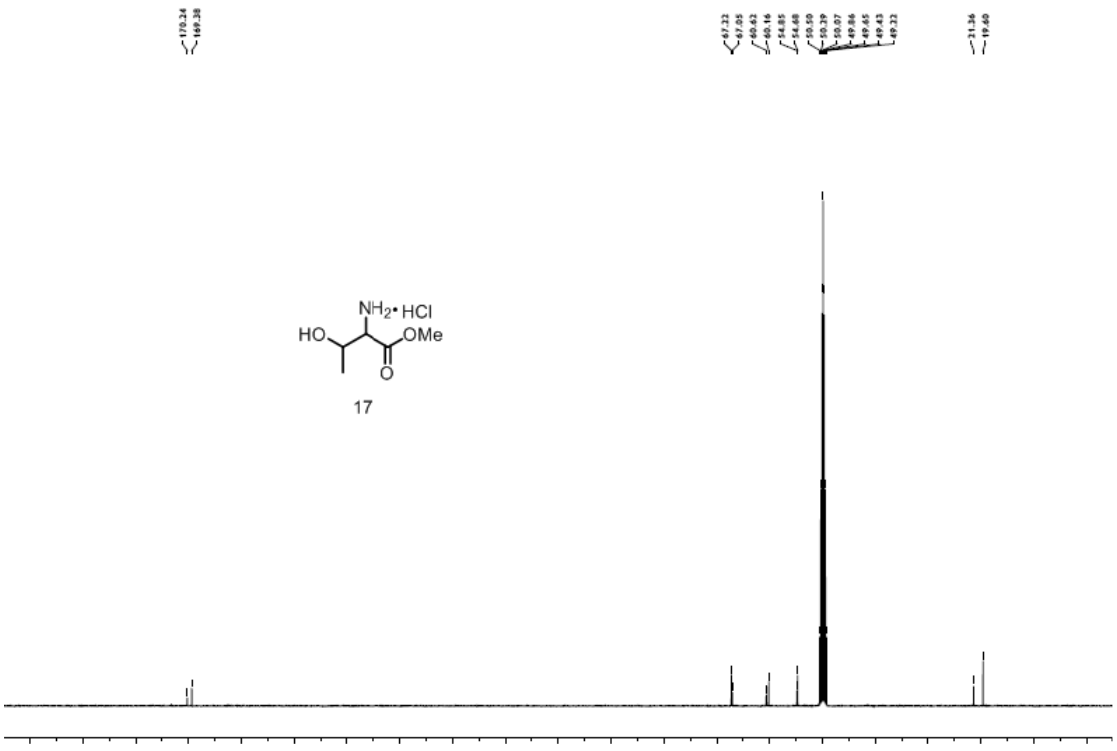

NH2•HCl
HO
NHPr
O
16
1.00
0.96
0.94
1.99
2.03
2.98
f1 (ppm)

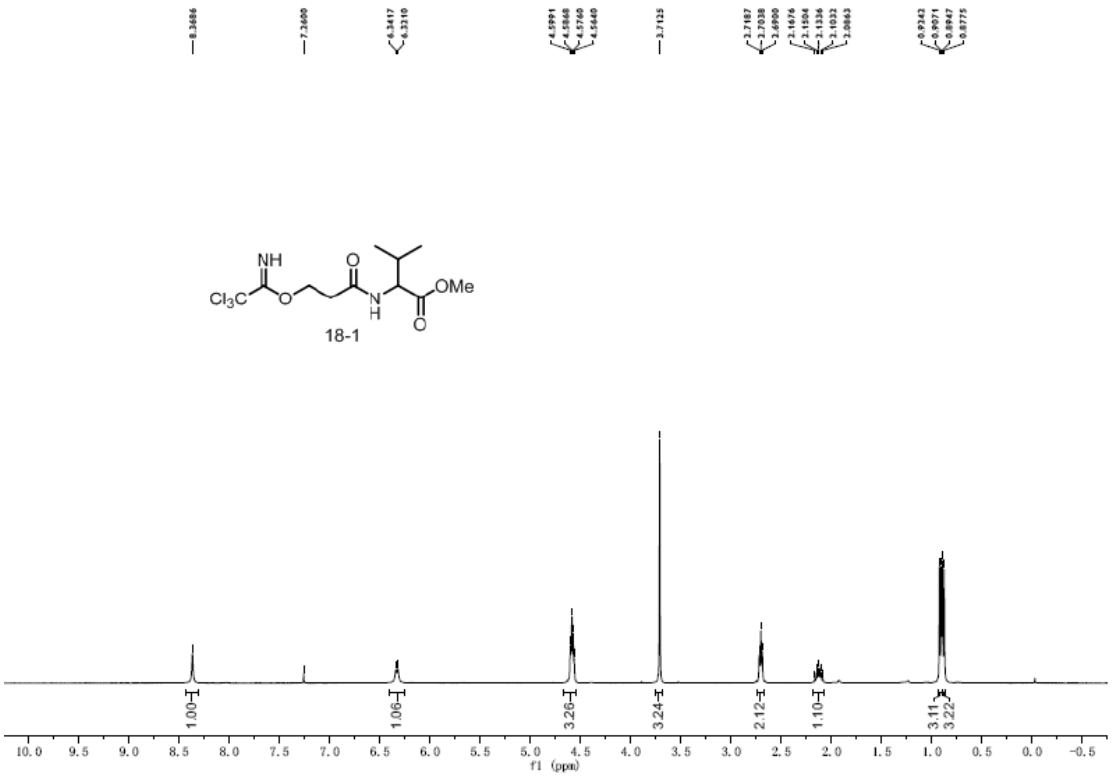

NH2•HCl
HO
NHPr
O
16
f1 (ppm)

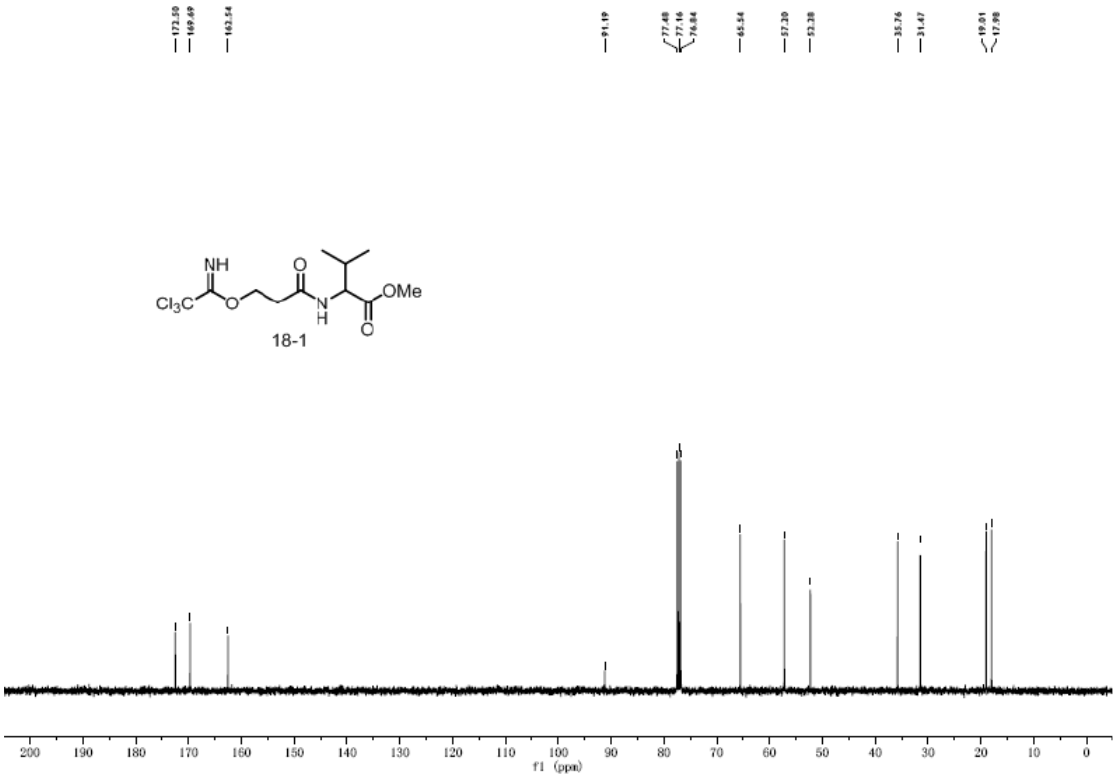

8.3343
7.2600
5.4639
5.4484
5.4335
5.4153
5.3996
5.3841
3.6789
2.8638
2.8448
2.8347
2.8057
2.6353
2.6211
2.5962
2.5820
1.4399
1.4143
NH
O
Cl3C
O
OMe
17-1
0.95
1.03
3.09
1.11
1.13
3.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

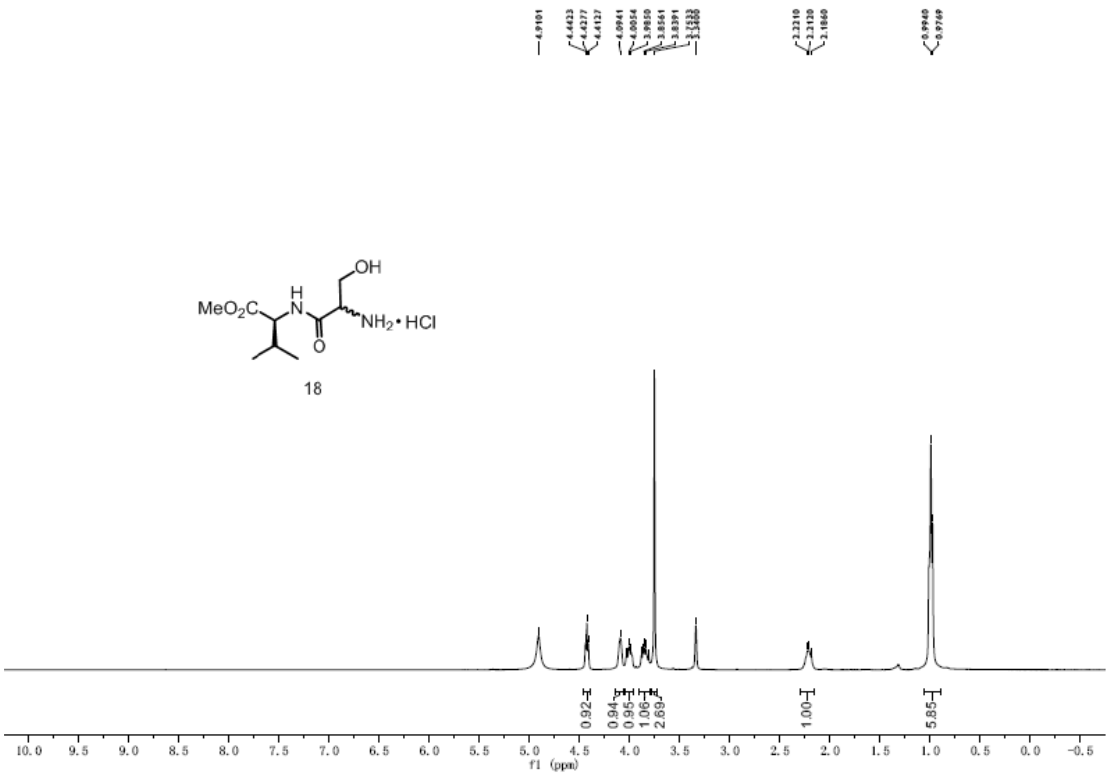

170.59
161.55
91.47
77.48
77.16
76.84
72.26
51.76
40.22
18.84
NH
O
Cl3C
O
OMe
17-1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

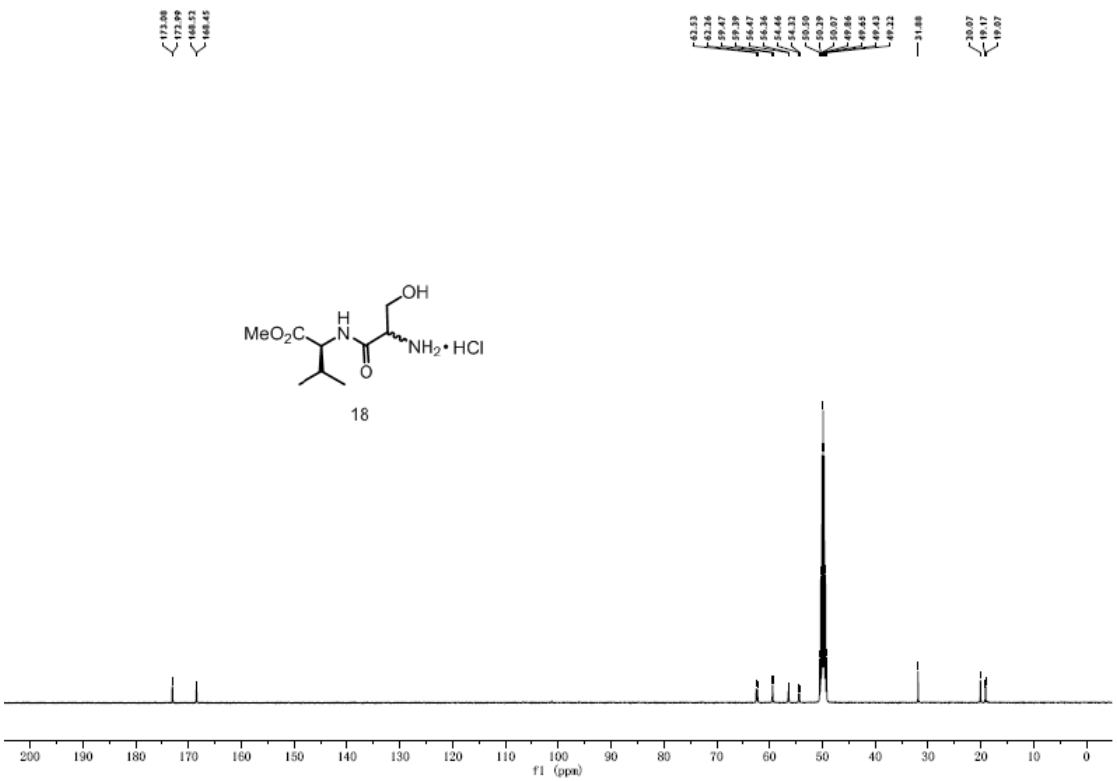

NH2• HCl
HO
OMe
O
17
1.11
0.57
0.40
3.00
1.23
1.73
f1 (ppm)

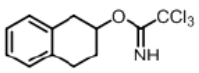

NH2• HCl
HO
OMe
O
17


8.3686
7.2600
6.3417
6.3310
4.5991
4.5868
4.5760
4.5440
3.7135
3.7187
3.7038
3.6900
2.1676
2.1504
2.1336
2.1032
2.0063
0.9342
0.9071
0.8947
0.8775
NH
O
Cl3C
O
N
H
OMe
O
18-1
1.00
1.06
3.26
3.24
2.12
1.10
3.11
3.22
10.0 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)

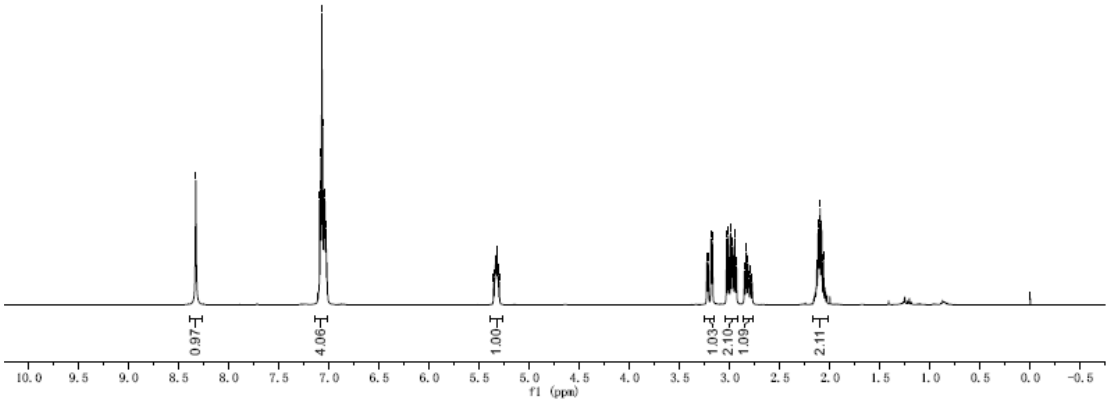

172.50
169.69
163.54
91.19
77.48
77.16
76.84
65.54
57.20
53.28
35.76
31.47
19.01
17.98
NH
O
Cl3C
O
N
H
OMe
O
18-1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

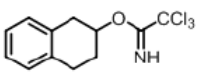

OH
MeO2C
H
N
O
NH2 • HCl
18
0.92
0.94
0.95
1.06
2.69
1.00
5.85
f1 (ppm)


OH
MeO2C
H
N
O
NH2 • HCl
18
f1 (ppm)

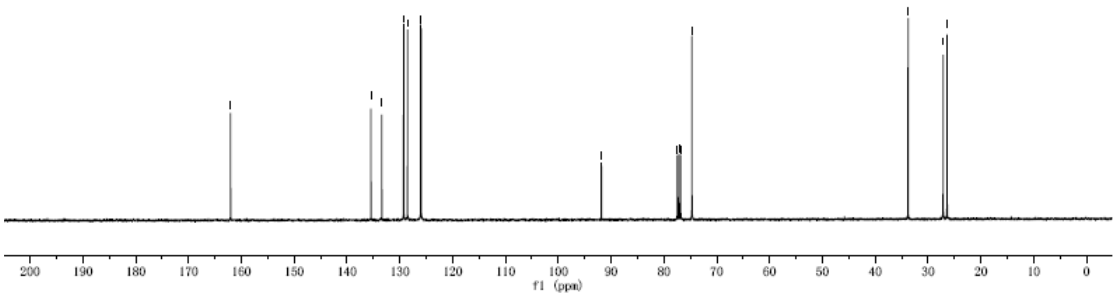


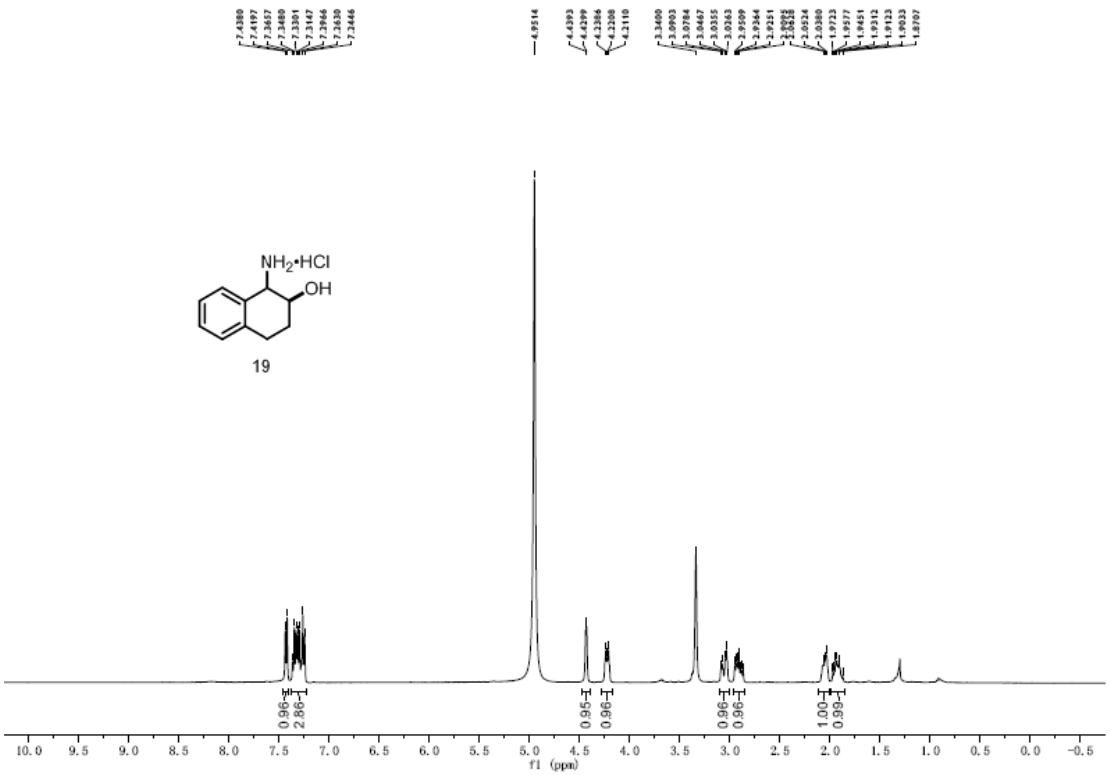
19-1

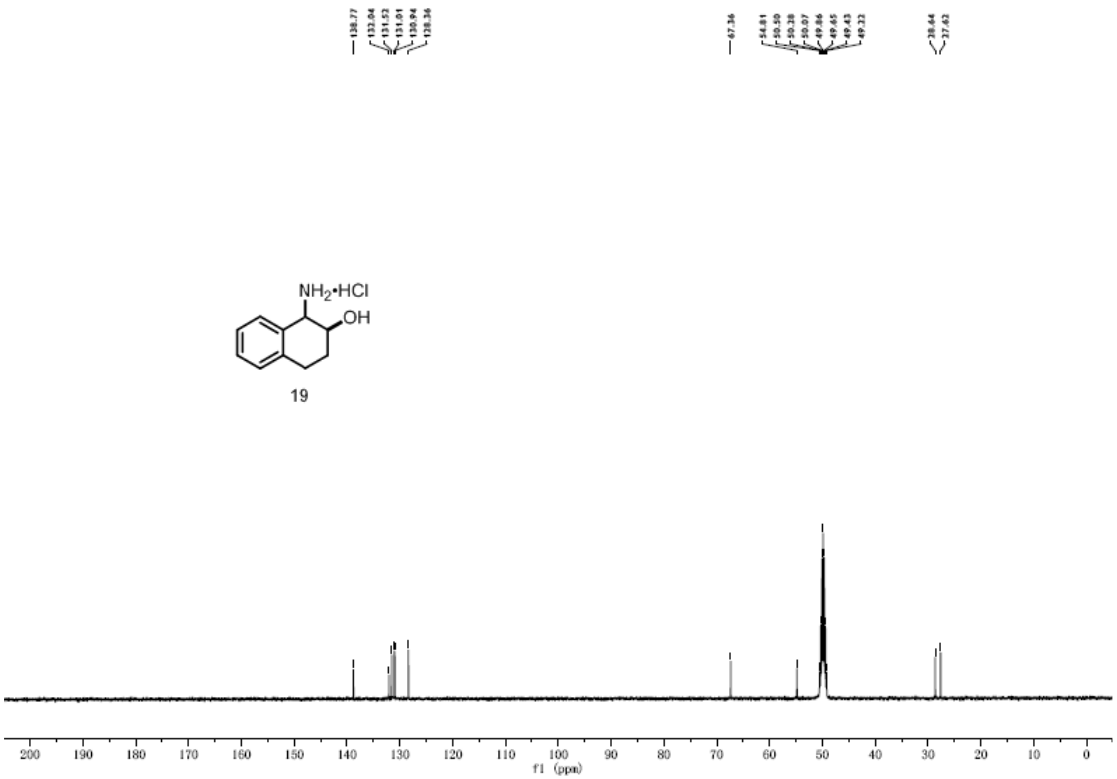


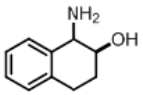


19-1

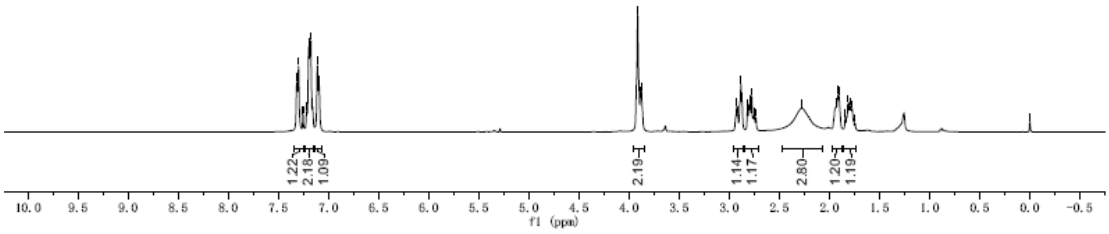


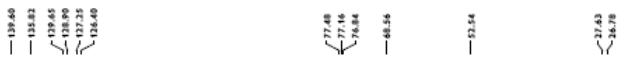

NH2•HCl
OH
19
0.96
2.88
0.95
0.96
0.96
0.96
1.00
0.99
f1 (ppm)

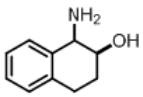

NH2•HCl
OH
19
f1 (ppm)


NH2
OH

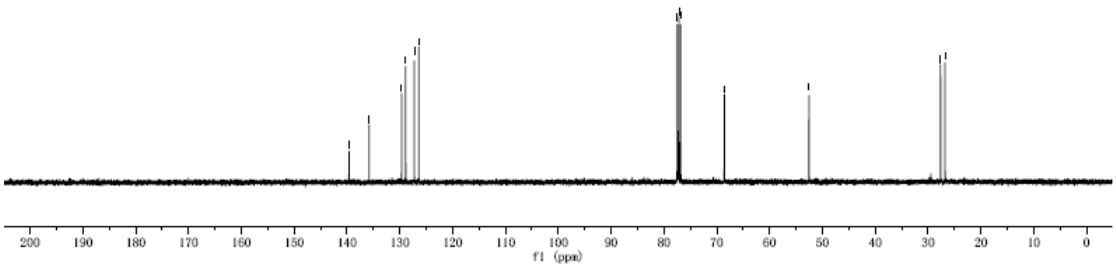
19'

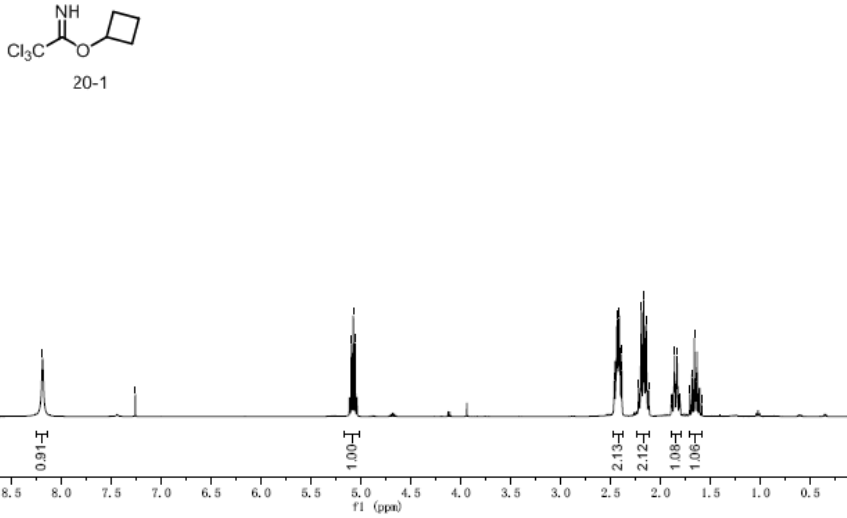

1.22
2.18
1.09
2.19
1.14
1.17
2.80
1.20
1.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

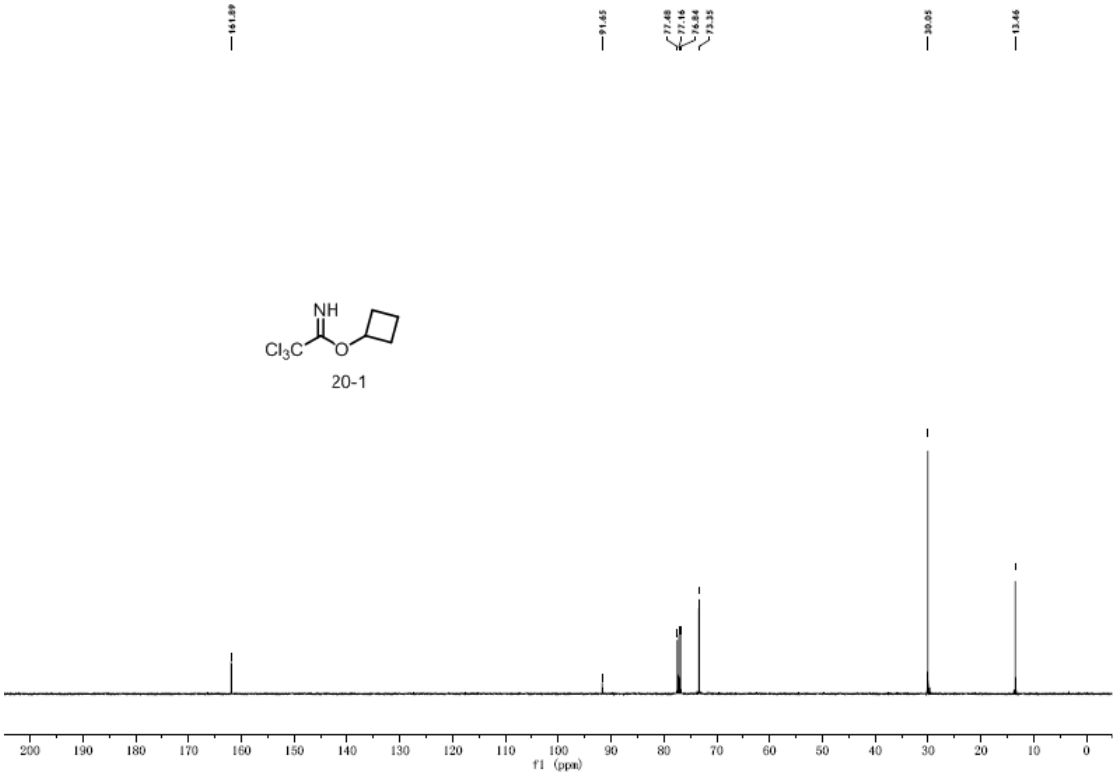



NH2
OH

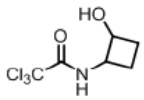
19'


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

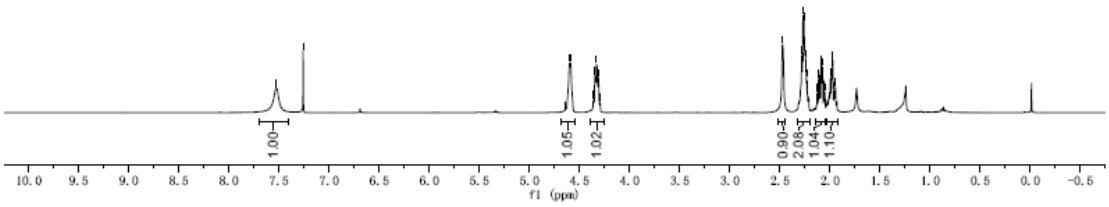

NH
Cl3C
O
20-1
0.91
1.00
2.13
2.12
1.08
1.06
f1 (ppm)


NH
Cl3C
O
20-1
f1 (ppm)

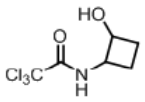

7.5295
7.2600
4.6466
4.5960
4.5960
4.5914
4.3616
4.3475
4.3318
4.3114
4.2965
2.4743
2.2812
2.2752
2.2702
2.2589
2.2440
2.2339
2.2279
2.1287
2.1141
2.0889
2.0753
2.0612
2.0511
1.9959
1.9814
1.9737
1.9588
1.9451


HO
O
Cl3C
N
H

20

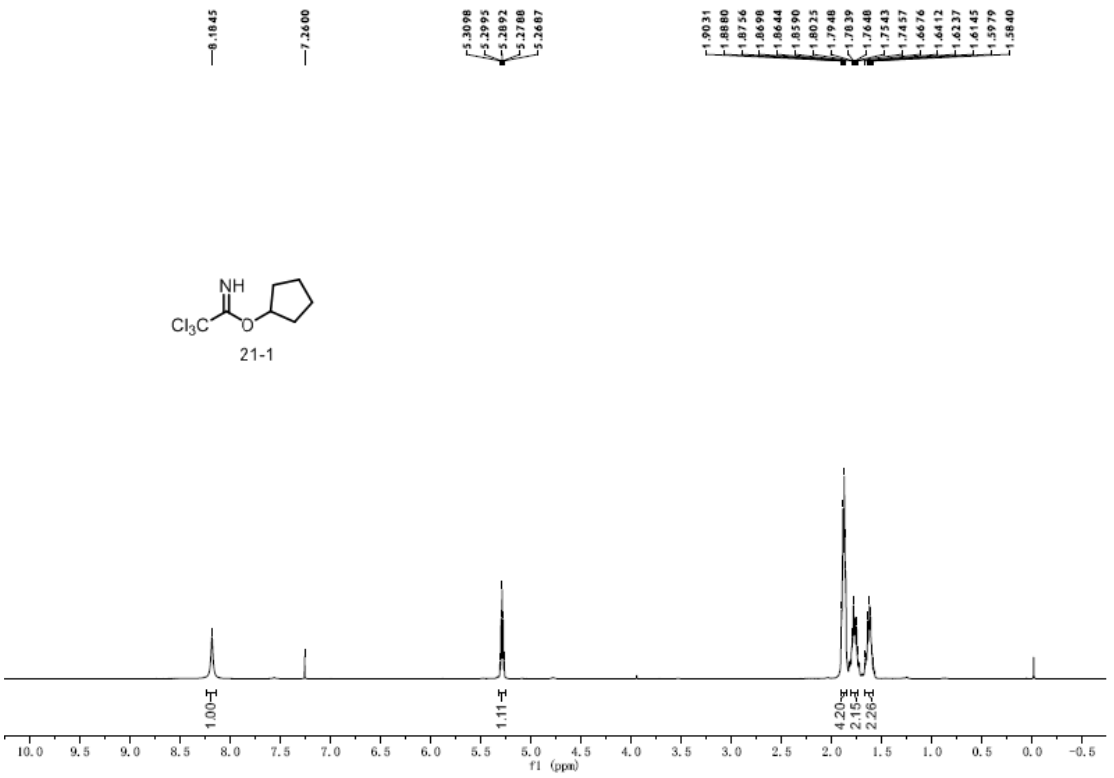

1.00
1.05
1.02
0.90
2.08
1.04
1.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

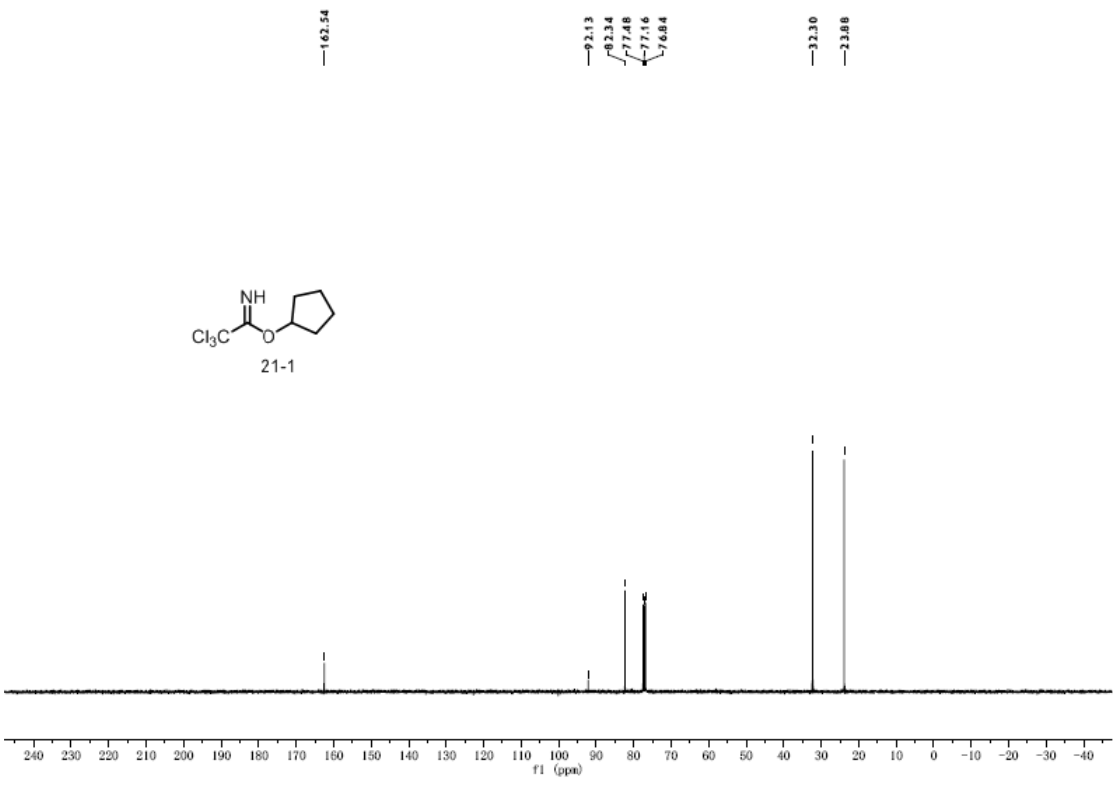

161.84
92.63
77.48
77.16
76.84
68.57
50.46
22.97
14.99

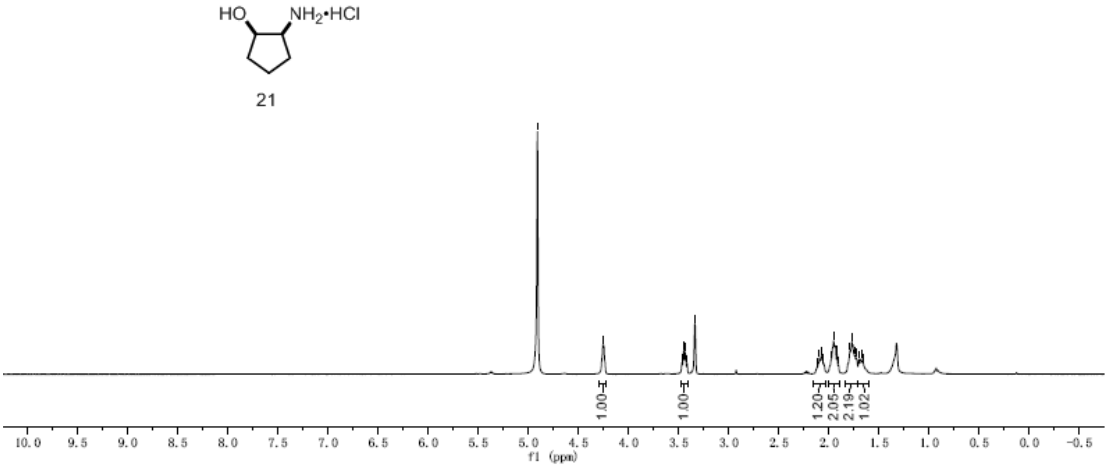

HO
O
Cl3C
N
H

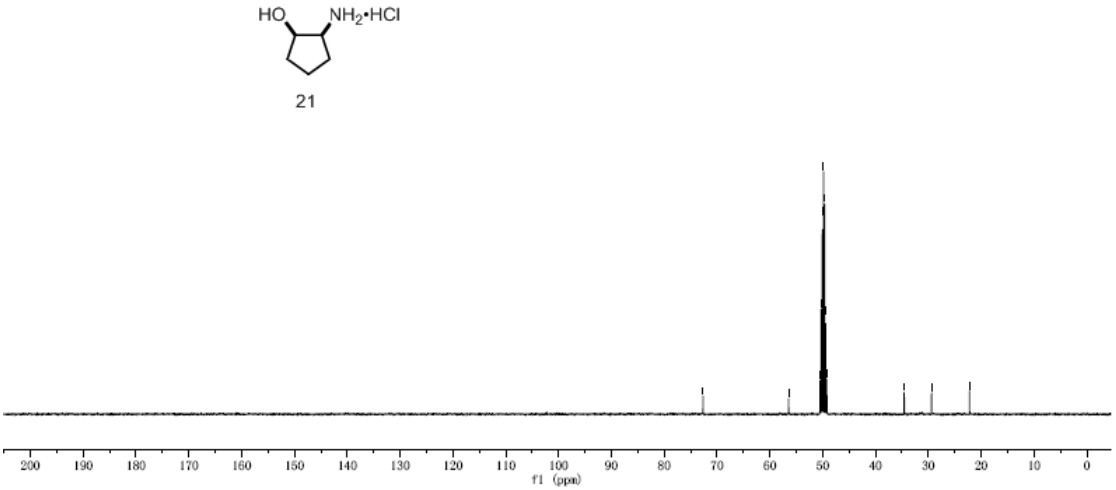
20

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

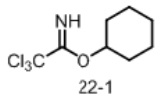

8.1845
7.2600
5.3098
5.2995
5.2892
5.2788
5.2687
1.9031
1.8880
1.8756
1.8698
1.8644
1.8590
1.8035
1.7948
1.7039
1.7648
1.7543
1.7457
1.6676
1.6412
1.6237
1.6145
1.5979
1.5840
NH
Cl3C
O
21-1
1.00
1.11
4.20
2.15
2.26
f1 (ppm)


162.54
92.13
82.34
77.48
77.16
76.84
32.30
23.88
NH
Cl3C
O
21-1
f1 (ppm)

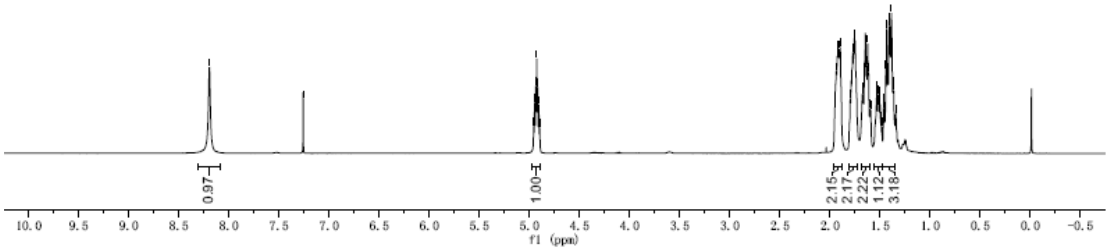

HO
NH2•HCl
21
1.00
1.00
1.20
2.05
2.19
1.02
f1 (ppm)


HO
NH2•HCl
21
f1 (ppm)

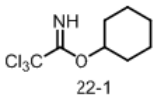

0.1957
7.2600
4.9582
4.9491
4.9381
4.9283
4.9186
4.9076
4.8985
1.9373
1.9270
1.9171
1.9067
1.8978
1.7892
1.7732
1.7652
1.7579
1.7498
1.6783
1.6687
1.6361
1.6248
1.6160
1.5359
1.5298
1.5147
1.5095
1.4437
1.4349
1.4254
1.4215
1.4115
1.4032
1.3877
1.3728


NH
Cl3C
O

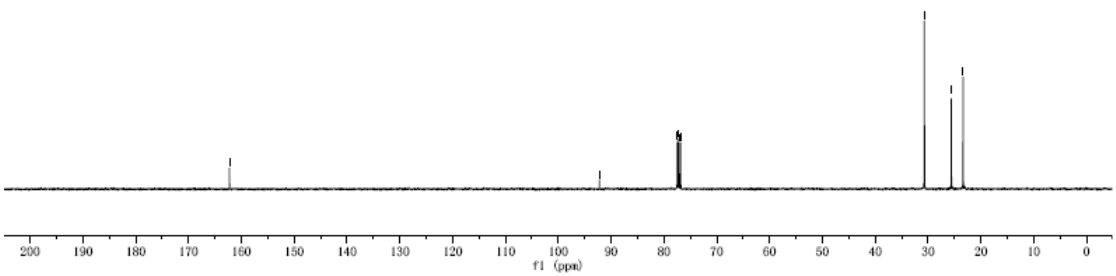
22-1

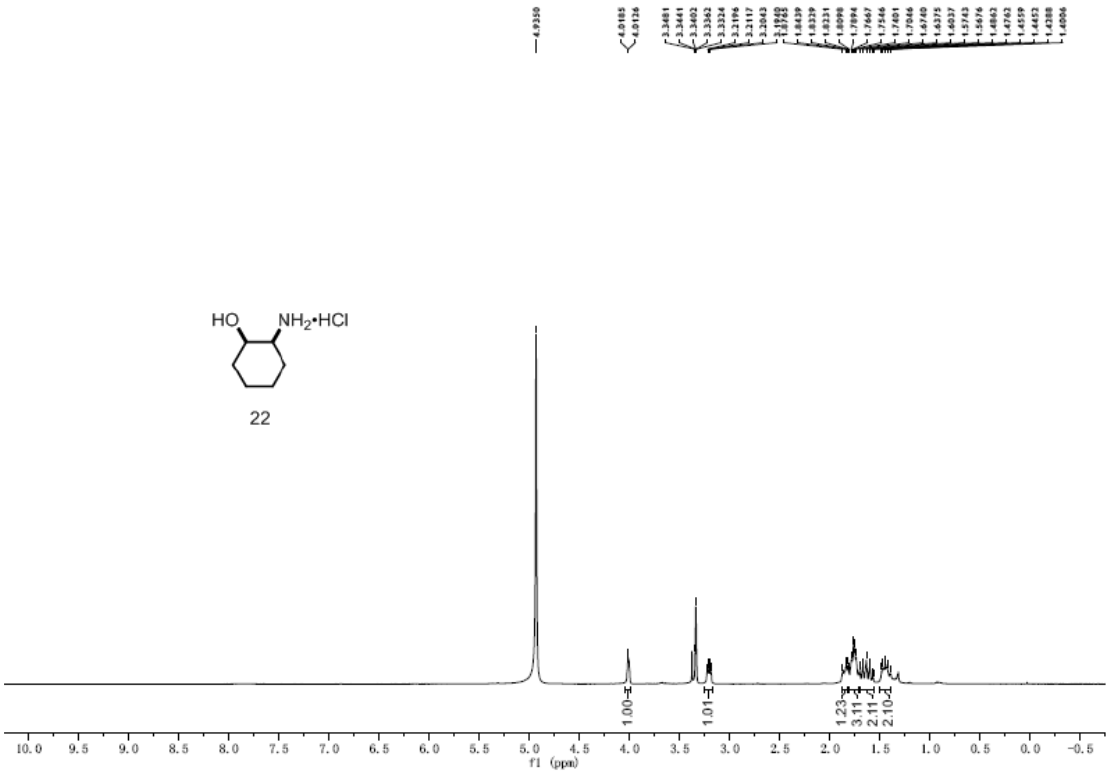

0.97
1.00
2.15
2.17
2.22
1.12
3.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

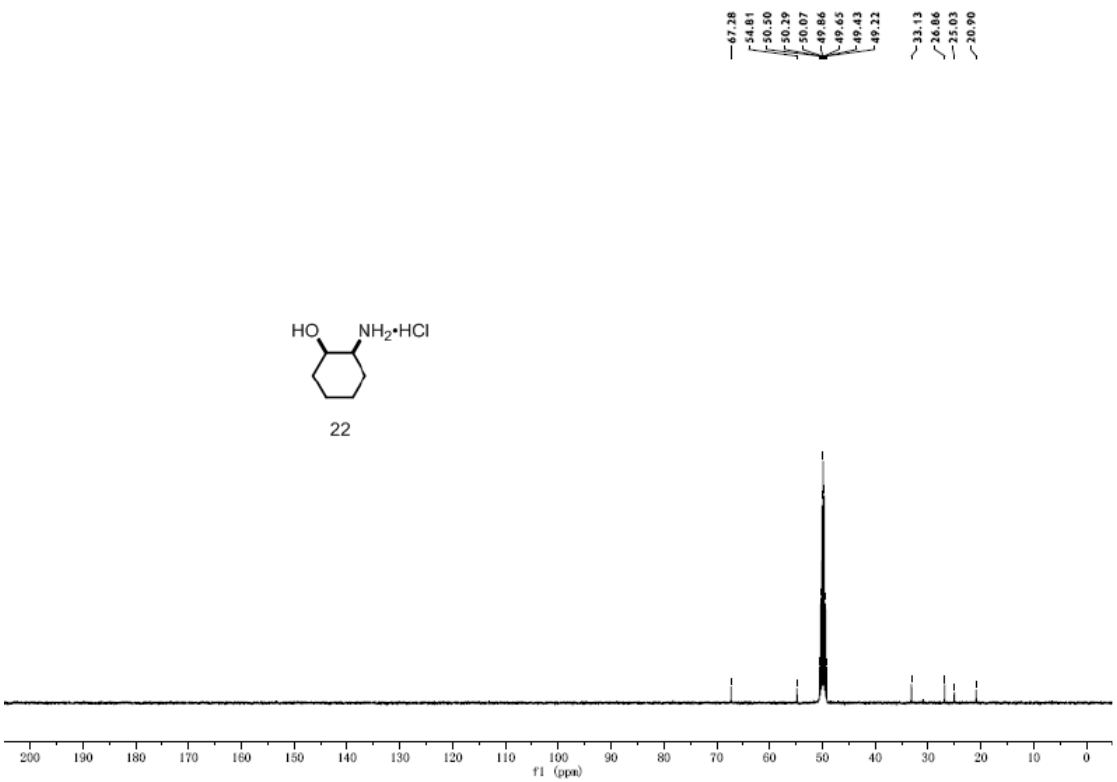

162.24
92.21
77.48
77.38
77.16
76.84
30.69
25.59
23.37

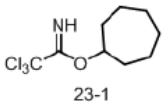

NH
Cl3C
O

22-1

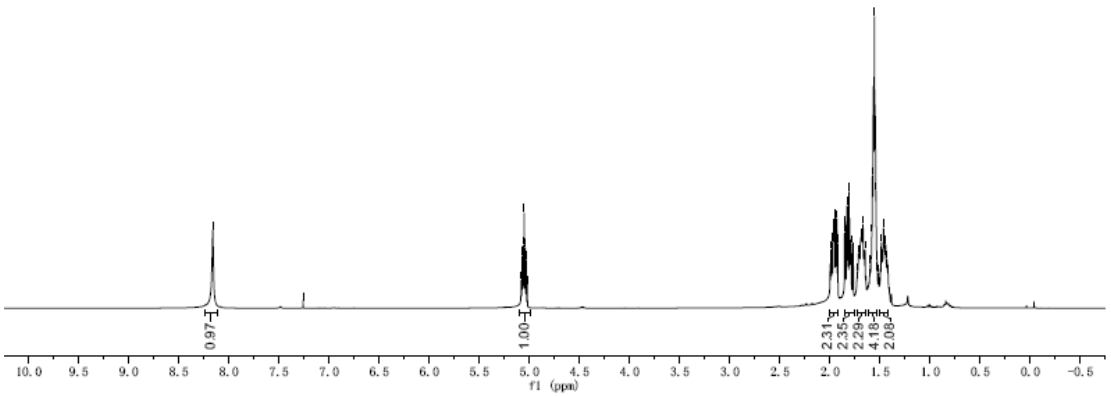

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

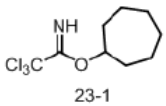

HO
NH2•HCl
22
1.00
1.01
1.23
3.11
2.11
2.10
f1 (ppm)


HO
NH2•HCl
22
f1 (ppm)

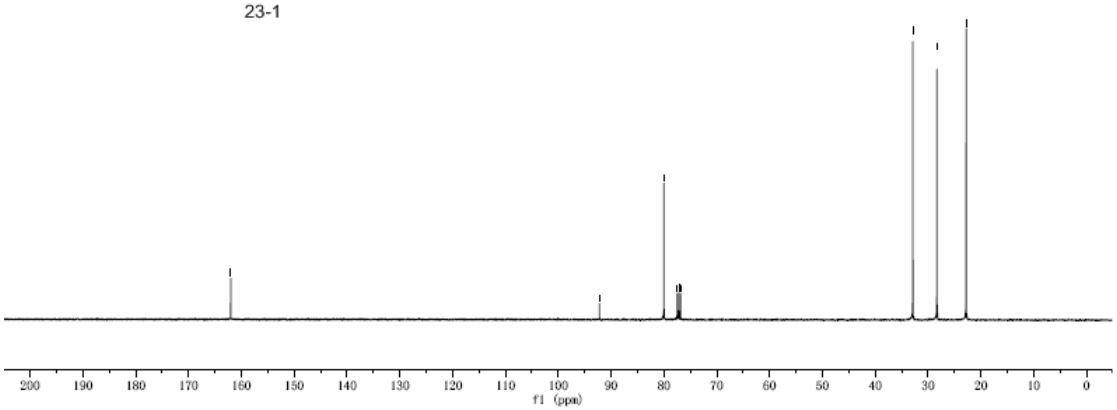


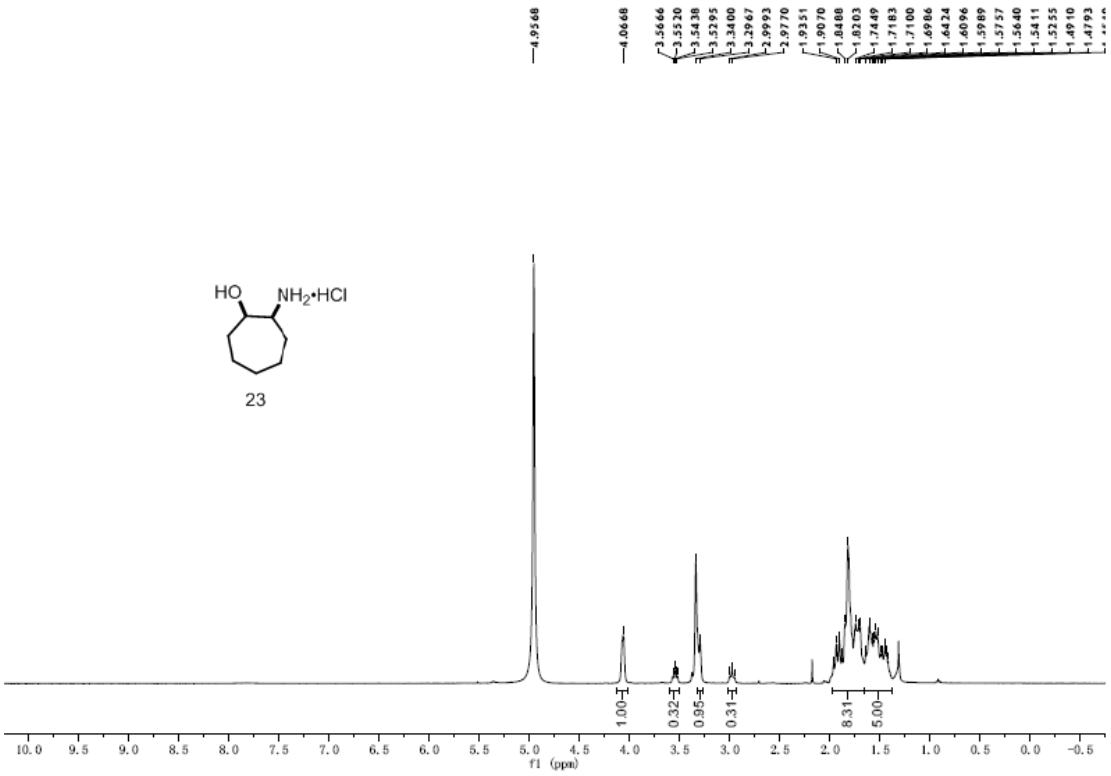
23-1

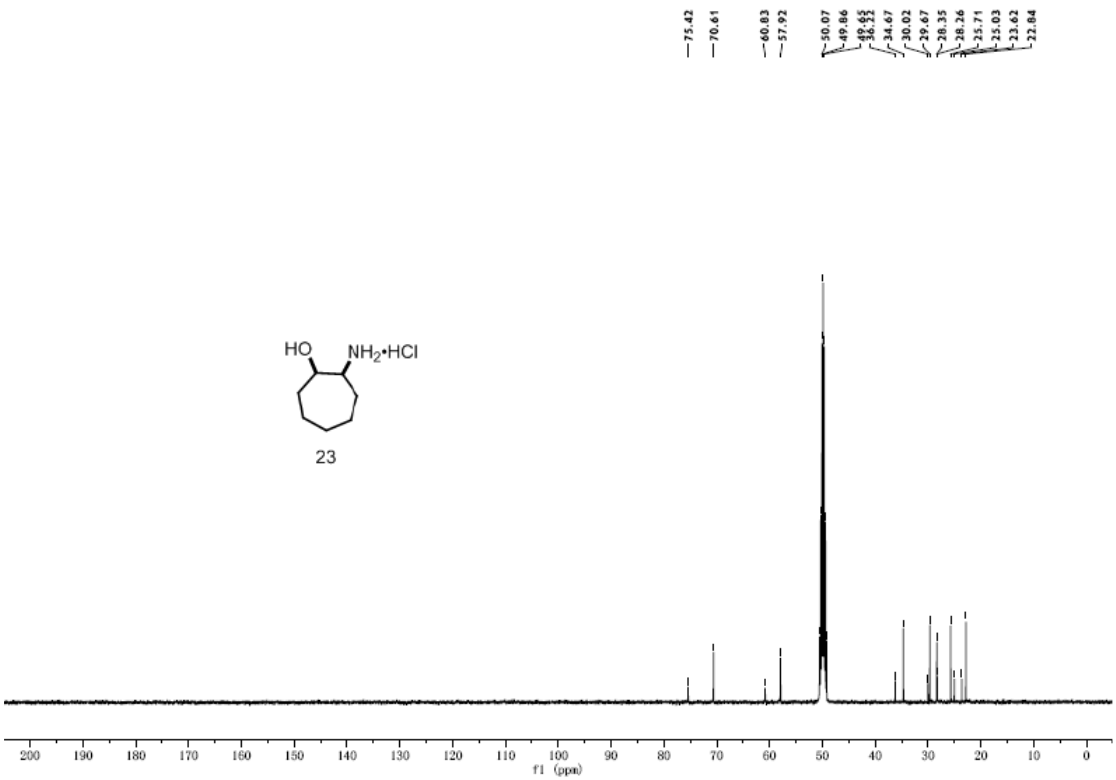


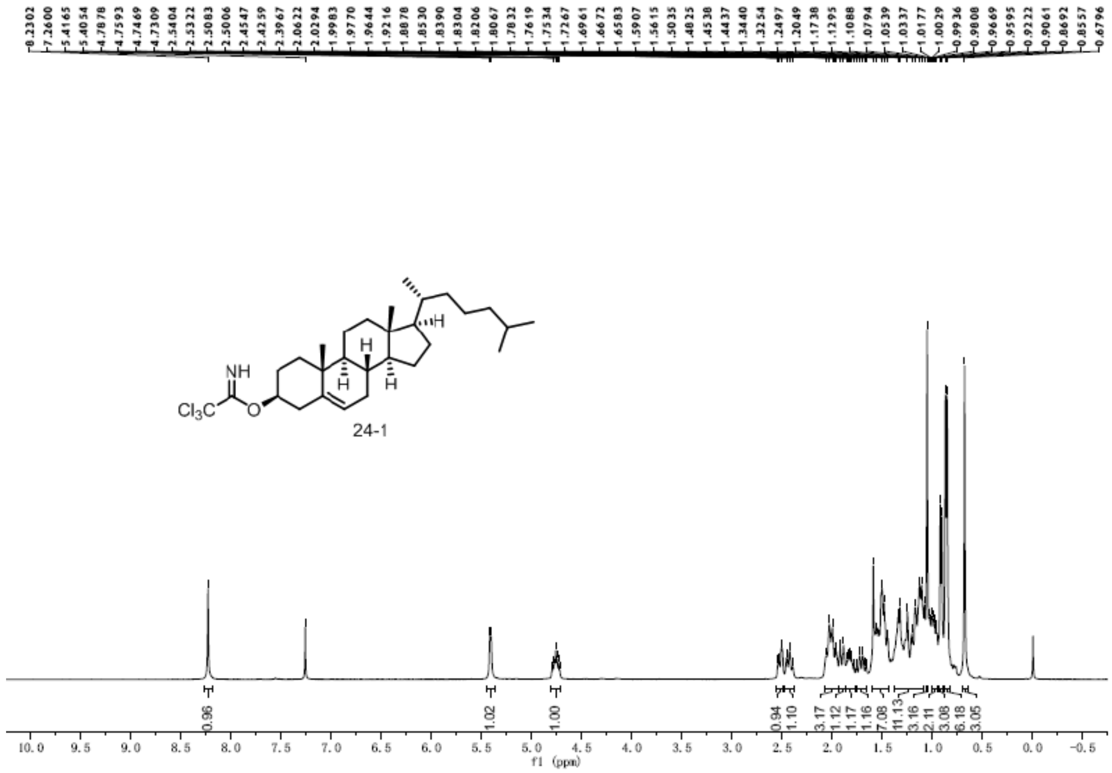


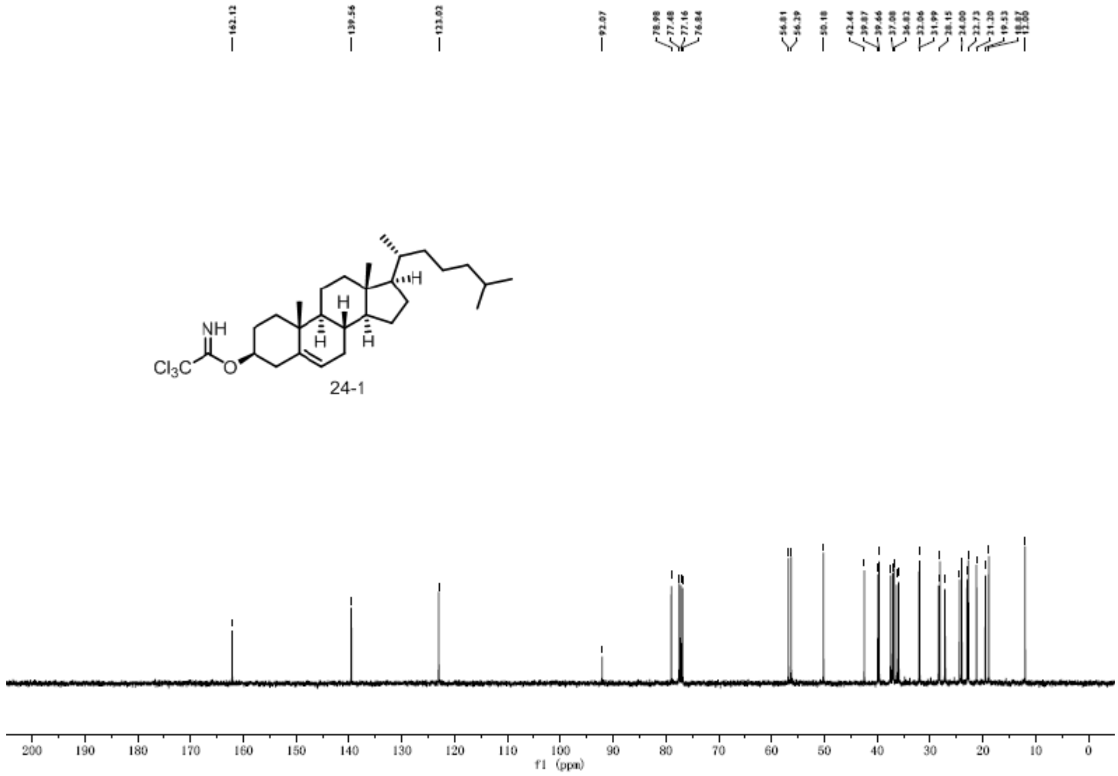
23-1

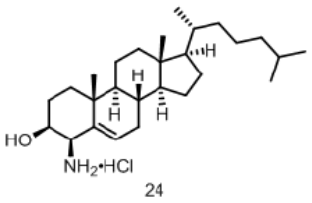



HO
NH2•HCl
23
4.9568
4.0668
3.5666
3.5520
3.5438
3.5295
3.3400
3.2967
2.9993
2.9770
1.9351
1.9070
1.8488
1.8203
1.7449
1.7183
1.7100
1.6986
1.6424
1.6096
1.5989
1.5757
1.5640
1.5411
1.5255
1.4910
1.4793
1.00
0.32
0.95
0.31
8.31
5.00
f1 (ppm)

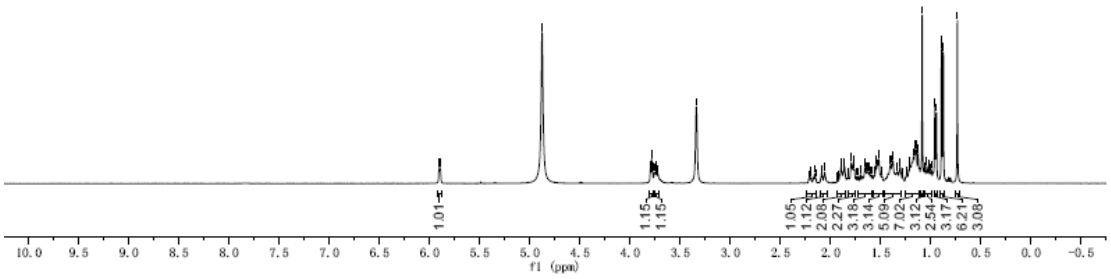

HO
NH2•HCl
23
75.42
70.61
60.83
57.92
50.07
49.86
49.65
36.22
34.67
30.02
29.67
28.35
28.26
25.71
25.03
23.62
22.84
f1 (ppm)

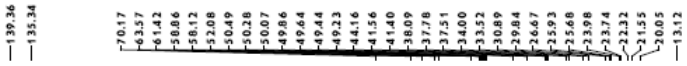

8.2302 7.2600 5.4165 5.4054 4.7878 4.7593 4.7469 4.7309 2.5404 2.5322 2.5083 2.5006 2.4547 2.4259 2.3967 2.0622 2.0294 1.9983 1.9770 1.9644 1.9216 1.8878 1.8530 1.8390 1.8304 1.8206 1.8067 1.7832 1.7619 1.7534 1.7267 1.6961 1.6672 1.6583 1.5907 1.5615 1.5035 1.4825 1.4538 1.4437 1.3440 1.3254 1.2497 1.2049 1.1738 1.1295 1.1088 1.0794 1.0539 1.0337 1.0177 1.0029 0.9936 0.9808 0.9669 0.9595 0.9222 0.9061 0.8692 0.8557 0.6796
NH
Cl3C
O
H
24-1
0.96 1.02 1.00 0.94 1.10 3.17 1.12 1.17 1.16 7.08 11.13 3.16 2.11 3.08 6.18 3.05
f1 (ppm)

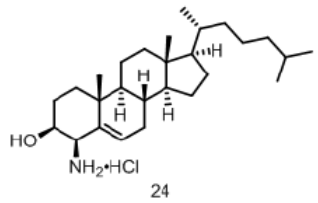

162.12 139.56 123.02 92.07 78.98 77.48 77.16 76.84 56.81 56.29 50.18 42.44 39.87 39.66 37.08 36.82 32.06 31.99 28.15 24.00 22.73 21.30 19.53 12.00
NH
Cl3C
O
H
24-1
f1 (ppm)


HO
NH2•HCl

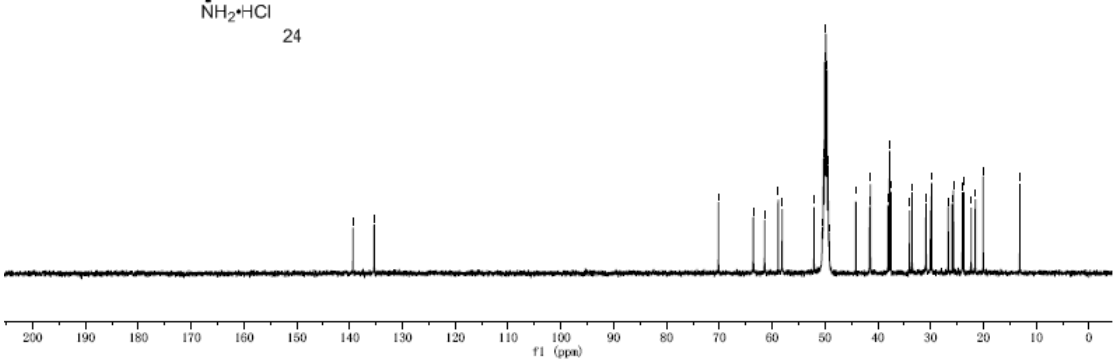
24

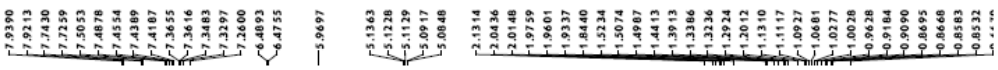

1.01
1.15
1.15
1.05
1.12
2.08
2.27
3.18
3.14
5.09
7.02
3.12
2.54
3.17
6.21
3.08
f1 (ppm)

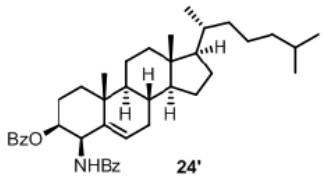



HO
NH2•HCl

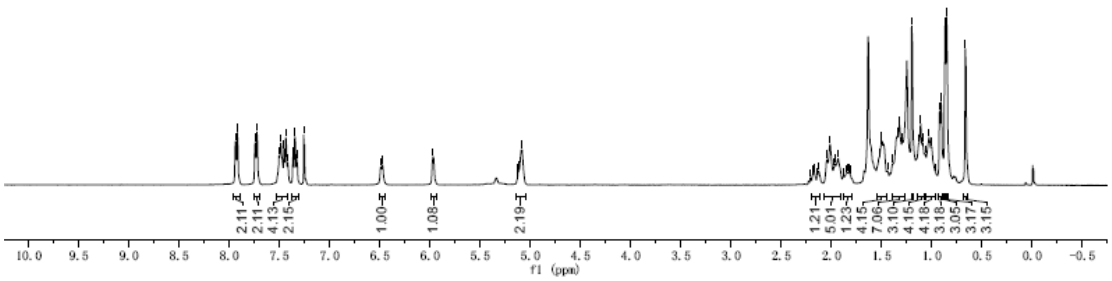
24

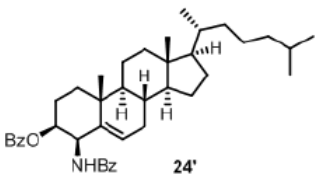

f1 (ppm)



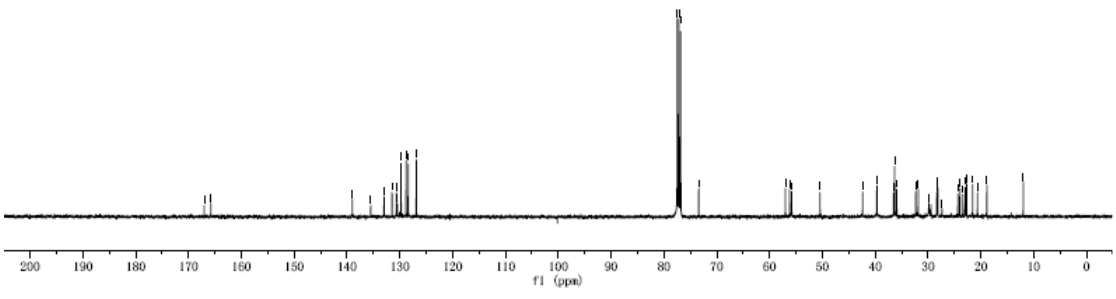

BzO
NHBz

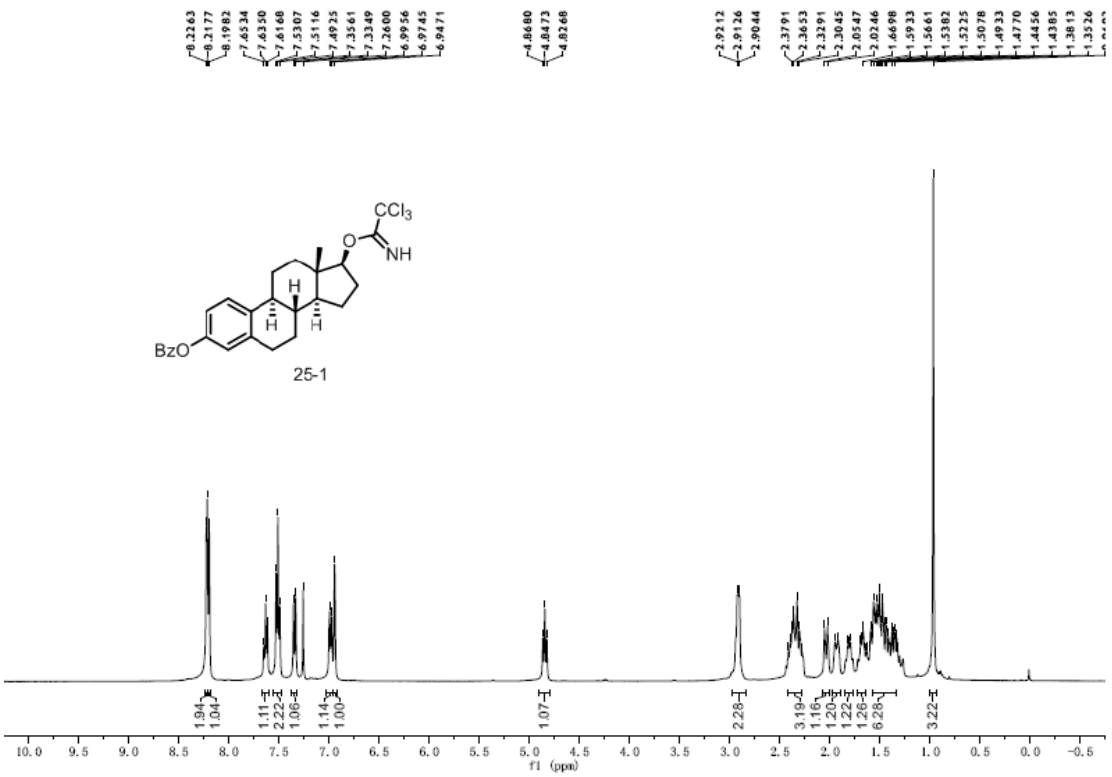
24'

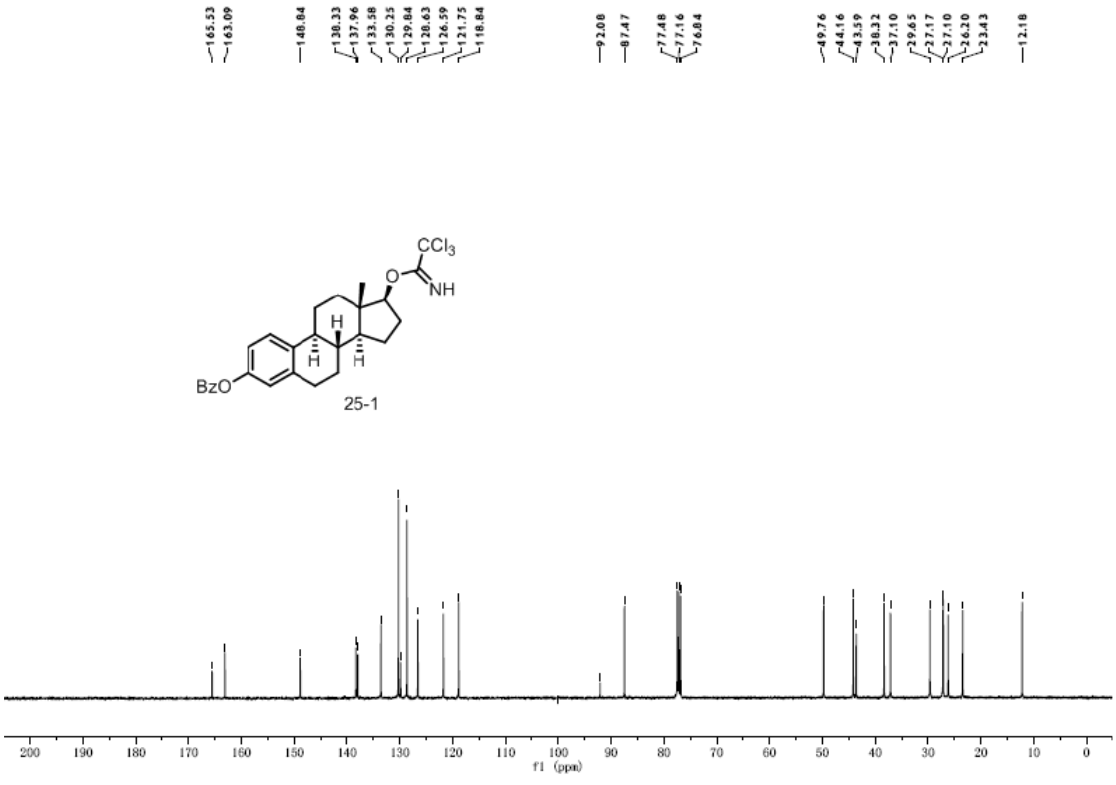

2.11
2.11
4.13
2.15
1.00
1.08
2.19
1.21
5.01
1.23
4.15
7.06
3.10
4.15
4.18
3.18
3.05
3.17
3.15
f1 (ppm)

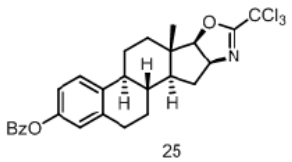

BzO
NHBz

24'

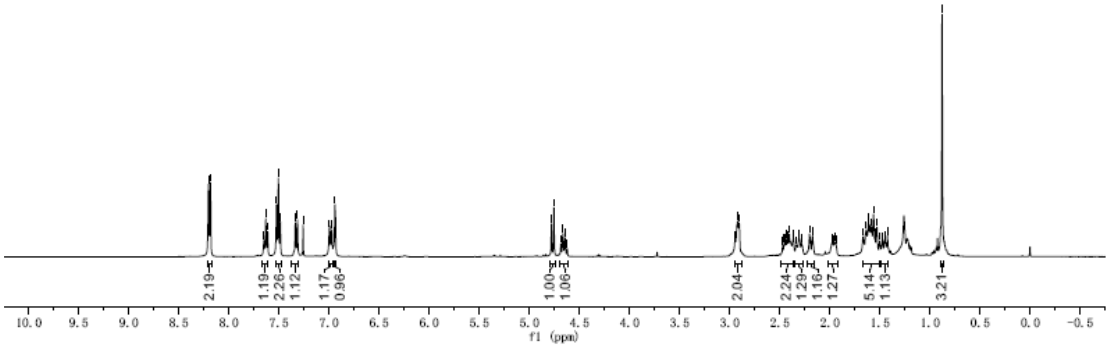

f1 (ppm)

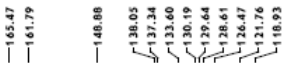

CCl3
O
NH
H
H
H
BzO
25-1
f1 (ppm)

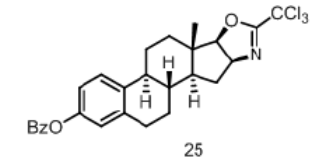

CCl3
O
NH
H
H
H
BzO
25-1
f1 (ppm)


CCl3
O
N
H
H
H
BzO

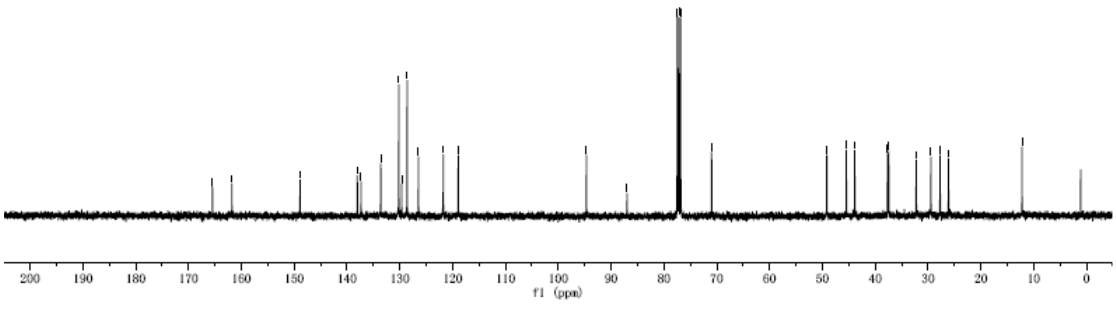
25


2.19
1.19
2.26
1.12
1.17
0.96
1.00
1.06
2.04
2.24
1.29
1.16
1.27
5.14
1.13
3.21
f1 (ppm)

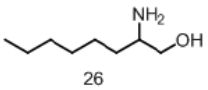



CCl3
O
N
H
H
H
BzO

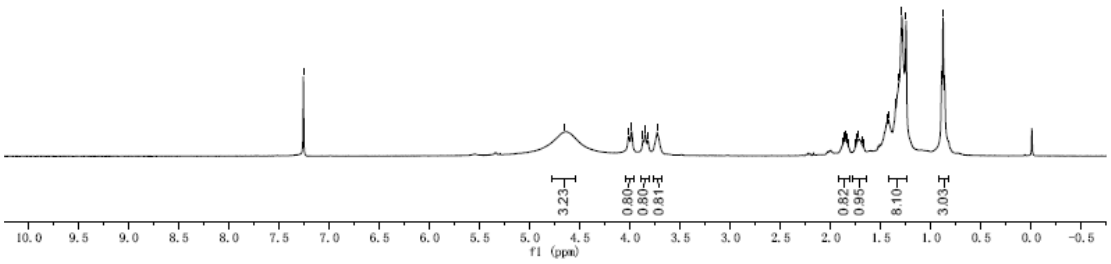
25


f1 (ppm)

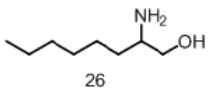

7.2600
4.6514
4.0144
3.9070
3.8733
3.8507
3.8233
3.7320
1.8865
1.8665
1.8525
1.8358
1.8194
1.7587
1.7403
1.7214
1.6855
1.6686
1.4426
1.4246
1.3505
1.3203
1.2909
1.2490
0.8933
0.8806
0.8643


NH2
OH

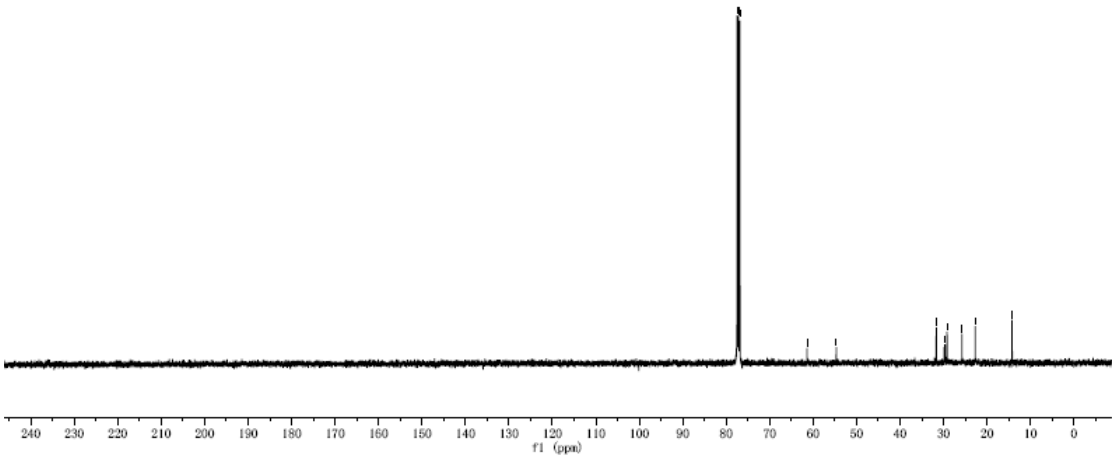
26


3.23
0.80
0.80
0.81
0.82
0.95
8.10
3.03
10.0 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)

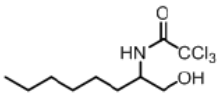

77.48
77.16
76.84
61.39
54.67
31.67
29.66
29.18
25.76
22.71
14.23


NH2
OH

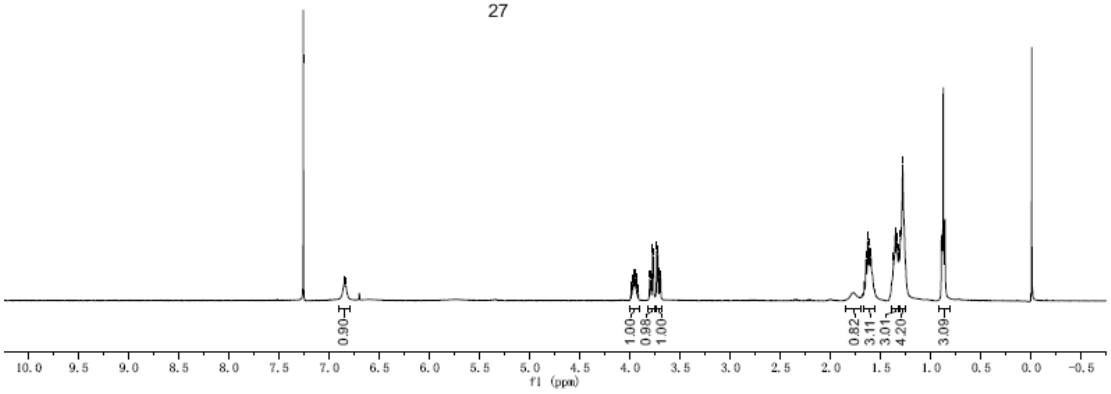
26


240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

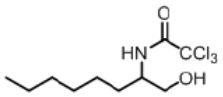

7.2600
6.8561
6.8369
3.9973
3.9872
3.9770
3.9668
3.9606
3.9567
3.9505
3.9404
3.9300
3.9201
3.8062
3.7972
3.7786
3.7696
3.7358
3.7251
3.7083
3.6975
1.6493
1.6324
1.6187
1.6125
1.5986
1.3759
1.3589
1.3472
1.3409
1.3220
1.3063
1.2894
1.2835


O
HN
CCl3
OH

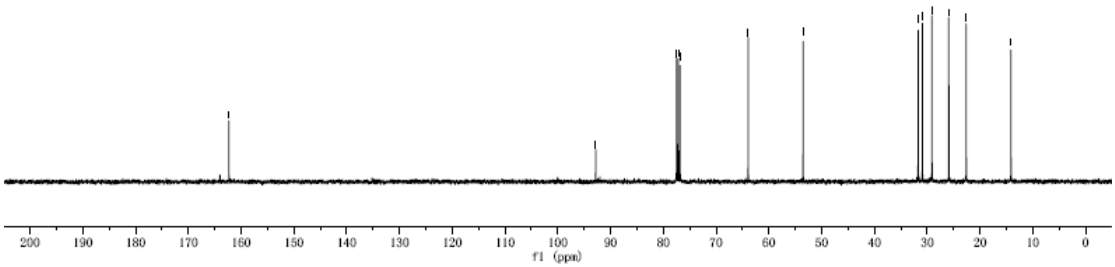
27


0.90
1.00
0.98
1.00
0.82
3.11
3.01
4.20
3.09
10.0 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)

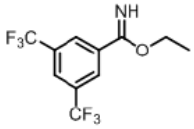

162.30
92.82
77.48
77.16
76.84
63.91
53.52
31.71
30.91
29.10
25.91
22.60
14.12


O
HN
CCl3
OH

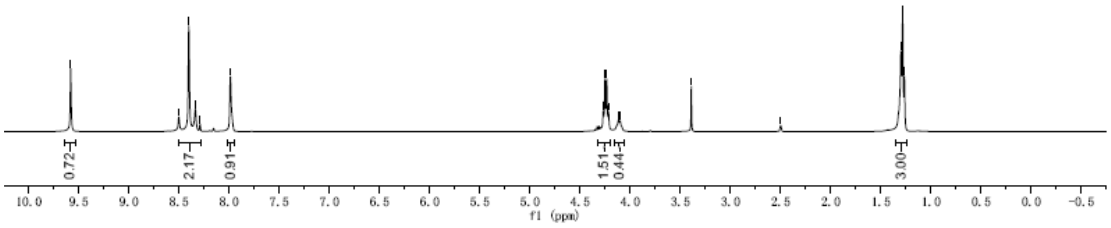
27


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

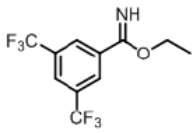

9.5012
8.5023
8.4029
8.3378
8.2909
7.9881
4.2694
4.2522
4.2346
4.2172
4.1177
4.1012
3.3915
2.5000
1.3009
1.2835
1.2658


NH
F3C
O
CF3

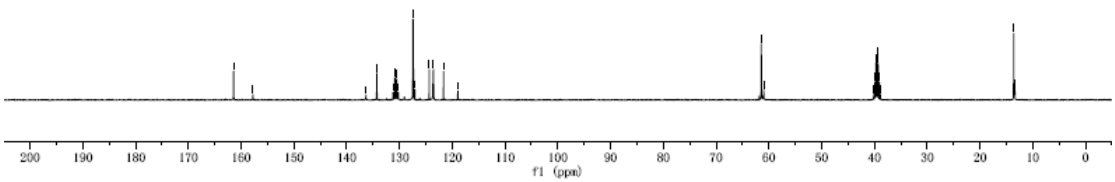
28-1

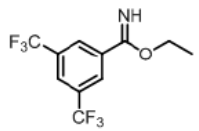

0.72
2.17
0.91
1.51
0.44
3.00
f1 (ppm)


161.42
157.76
136.35
134.29
131.20
130.87
130.54
130.21
127.43
127.06
124.35
123.57
121.65
116.94
61.43
60.98
40.13
39.92
39.71
39.50
39.29
39.08
38.88
13.61
13.40


NH
F3C
O
CF3

28-1

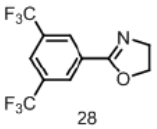

f1 (ppm)


NH
F3C
O
CF3

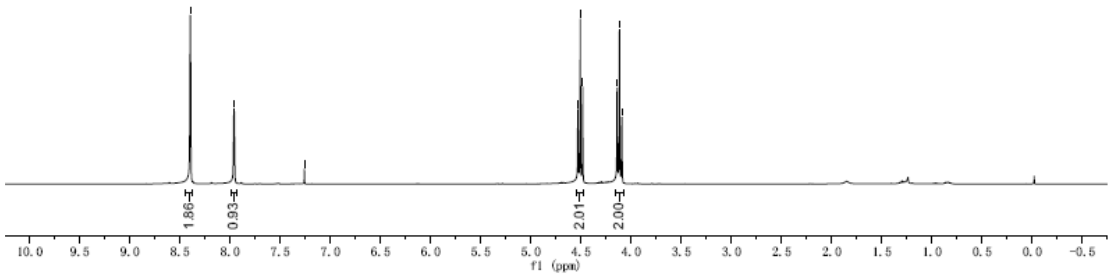
28-1

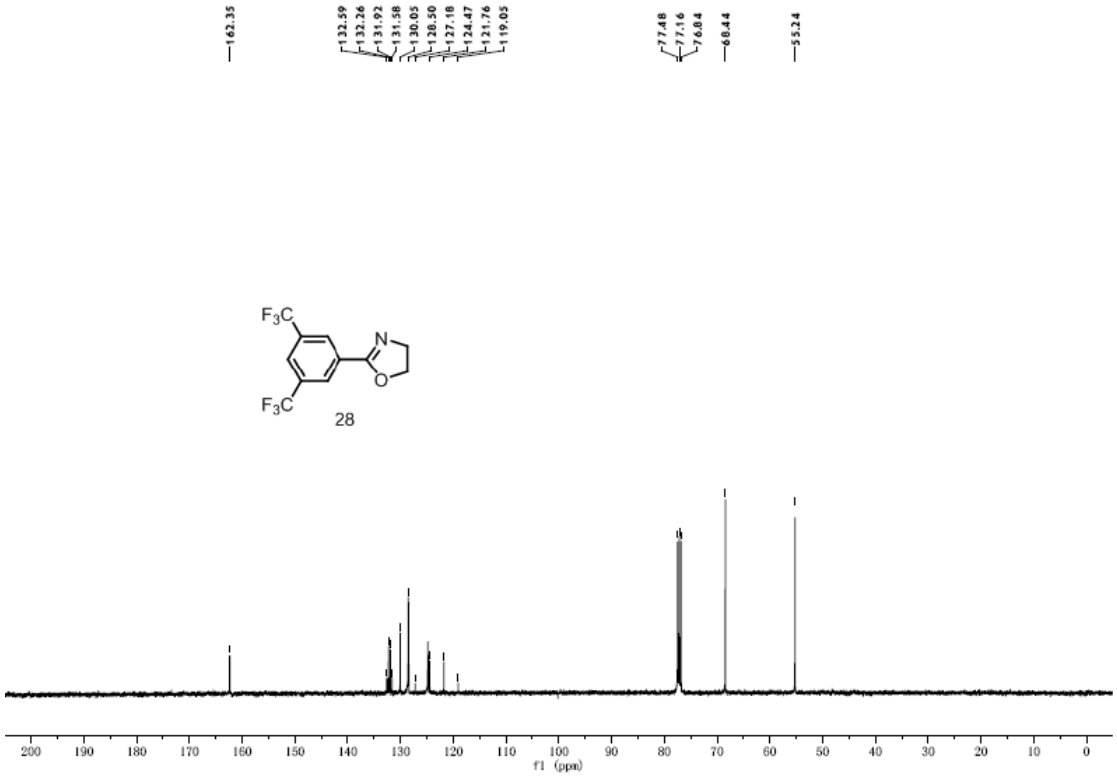
-63.00
f1 (ppm)

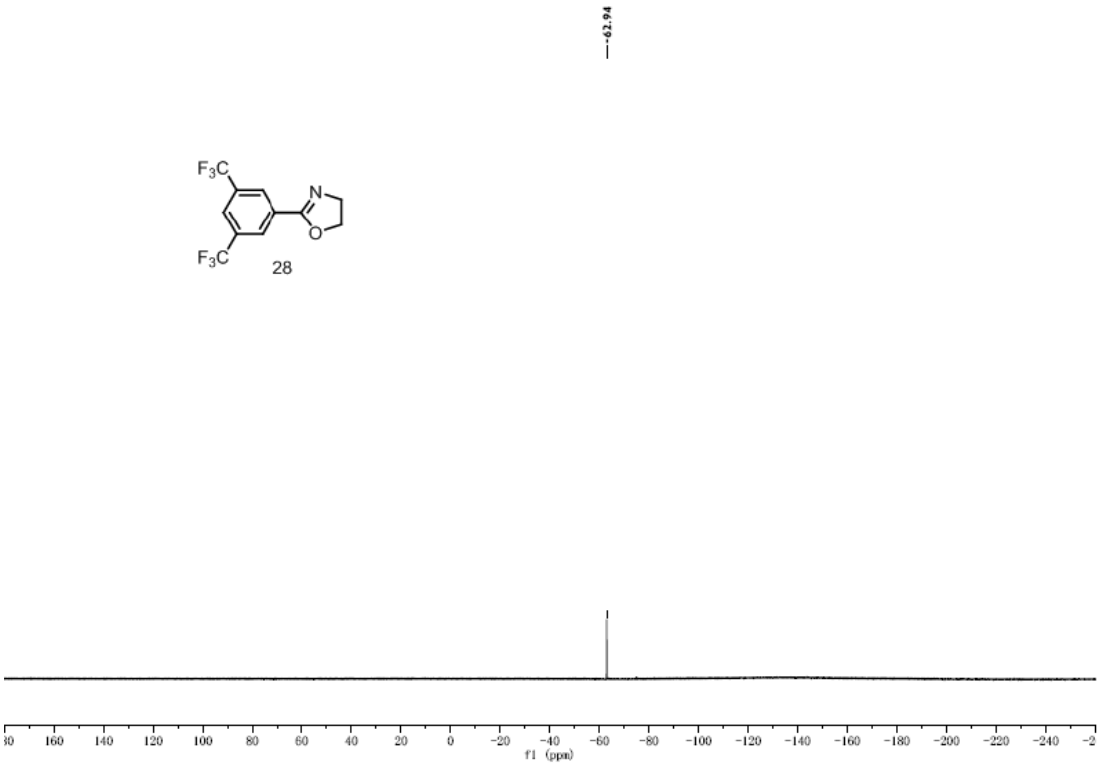

8.3981
7.9618
7.2600
4.5327
4.5085
4.4846
4.1415
4.1176
4.0935


F3C
N
O
F3C

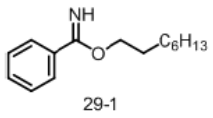
28


1.86
0.93
2.01
2.00
f1 (ppm)

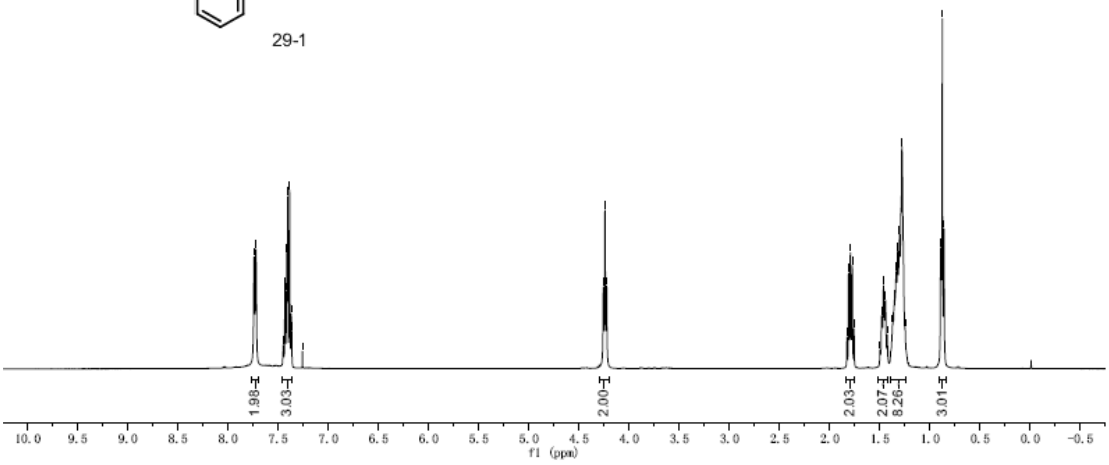

162.35
132.59
132.26
131.92
131.58
130.05
128.50
127.18
124.47
121.76
119.05
77.48
77.16
76.84
60.44
55.24
F3C
CF3
N
O
28
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-62.94
F3C
CF3
N
O
28
30 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -2
f1 (ppm)

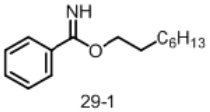

7.7416
7.7240
7.4522
7.4340
7.4271
7.4204
7.4167
7.4124
7.4062
7.3878
7.3751
7.3709
7.3660
7.2600
4.2589
4.2424
4.2259
1.8291
1.8123
1.7948
1.7750
1.7583
1.4989
1.4826
1.4641
1.4442
1.4266
1.3738
1.3683
1.3586
1.3532
1.3379
1.3230
1.3046
1.2894
1.2803
1.2486
0.8947
0.8780
0.8665


NH
O
C6H13

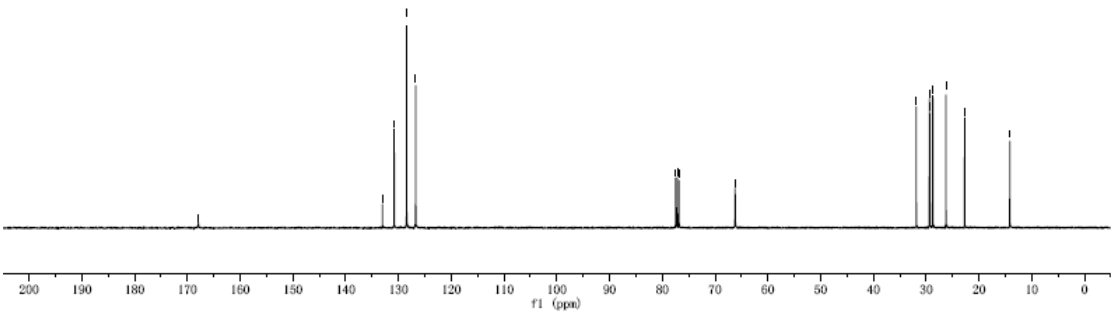
29-1

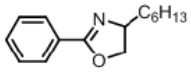

1.98
3.03
2.00
2.03
2.07
8.26
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


167.91
133.03
130.81
128.45
126.73
77.48
77.16
76.84
66.21
31.88
29.40
29.30
28.75
26.26
22.71
14.15

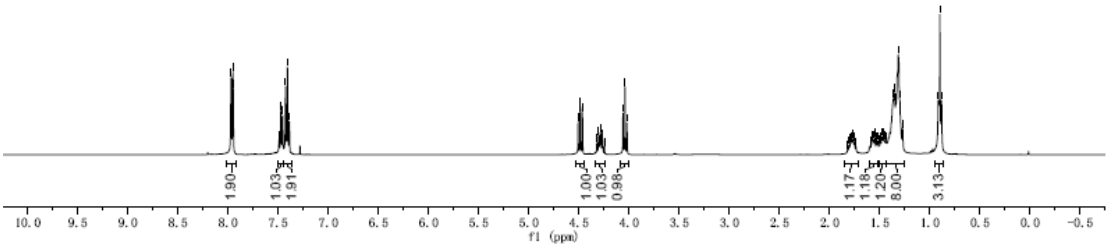

NH
O
C6H13

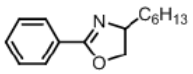
29-1


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

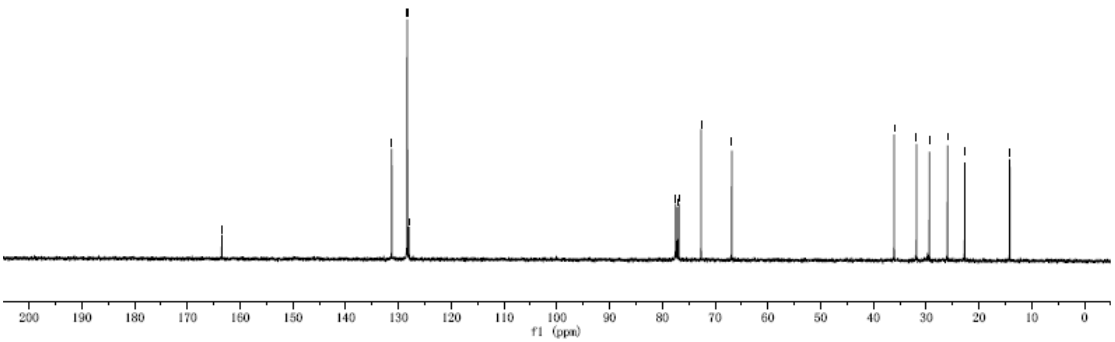


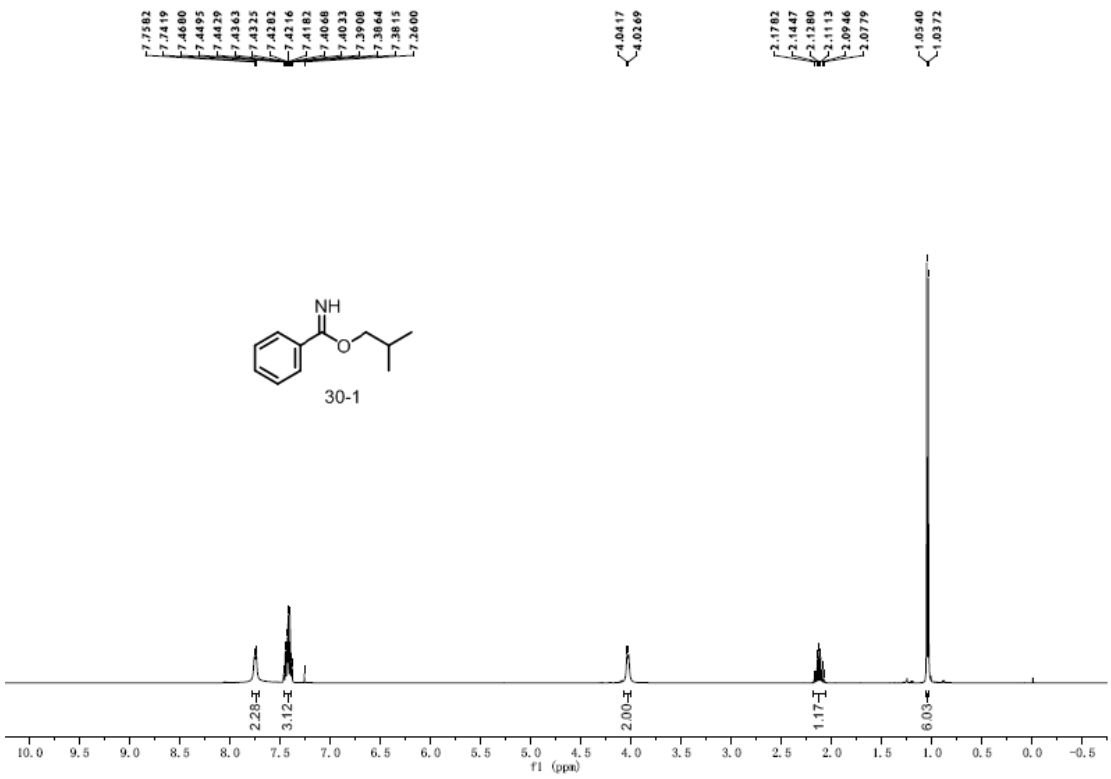
29





29

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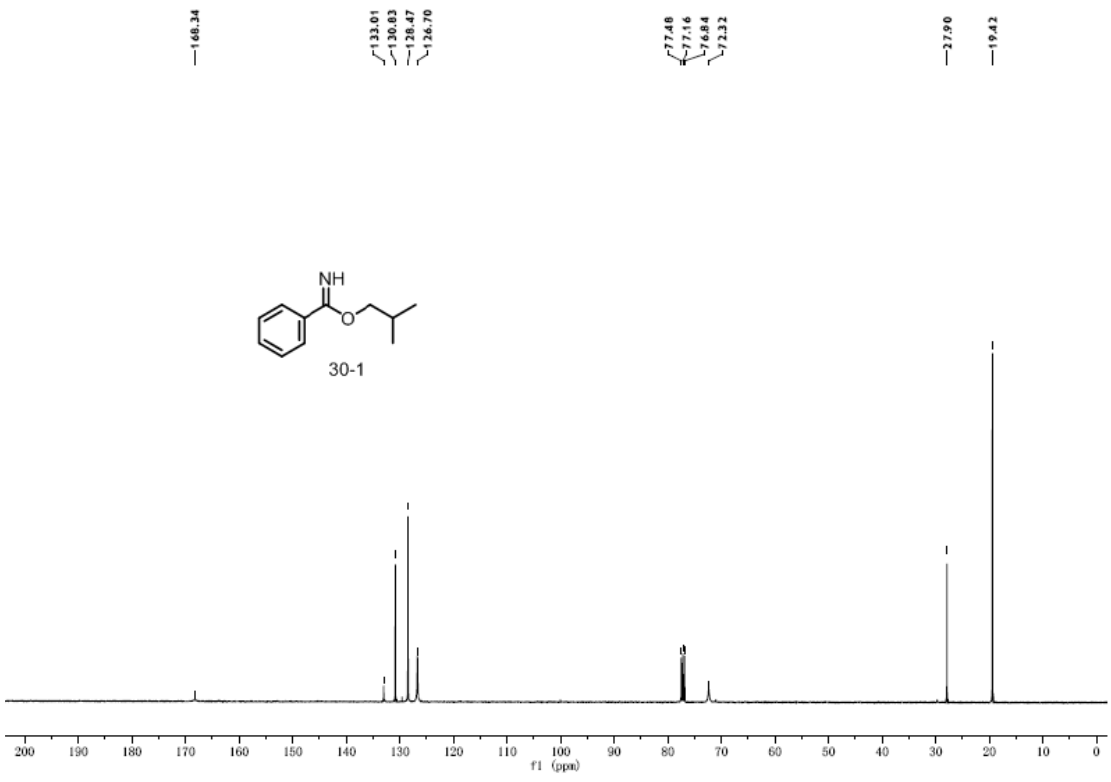
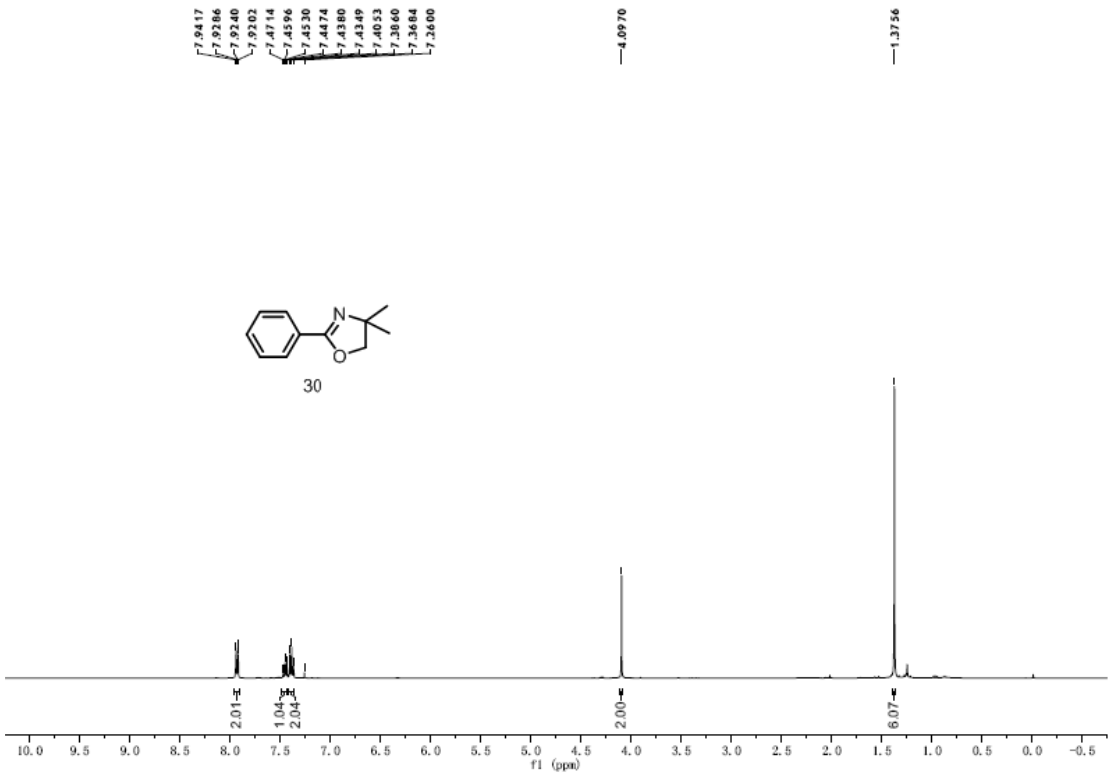
7.4660
7.4495
7.4429
7.4363
7.4325
7.4282
7.4216
7.4182
7.4068
7.4033
7.3908
7.3864
7.3815
7.2600
4.0417
4.0269
2.1782
2.1447
2.1280
2.1113
2.0946
2.0779
1.0540
1.0372
NH
O
30-1
2.28
3.12
2.00
1.17
6.03
f1 (ppm)


168.34
133.01
130.03
128.47
126.70
77.48
77.16
76.84
72.32
27.90
19.42
NH
O
30-1
f1 (ppm)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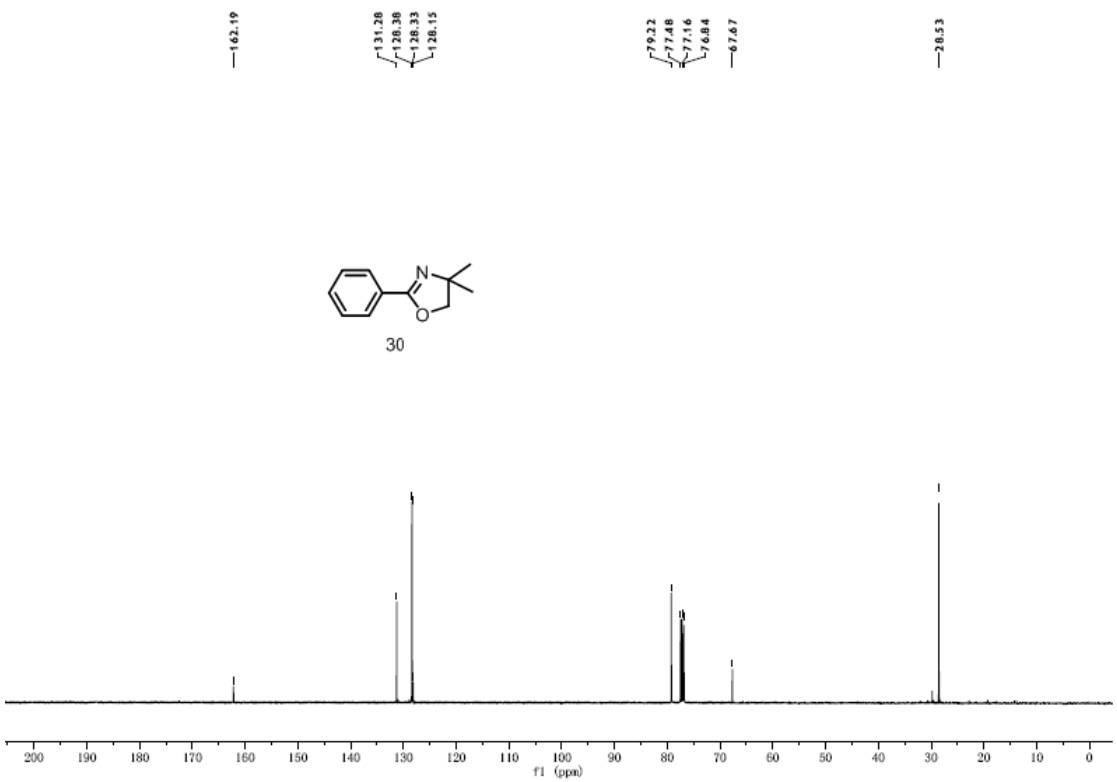
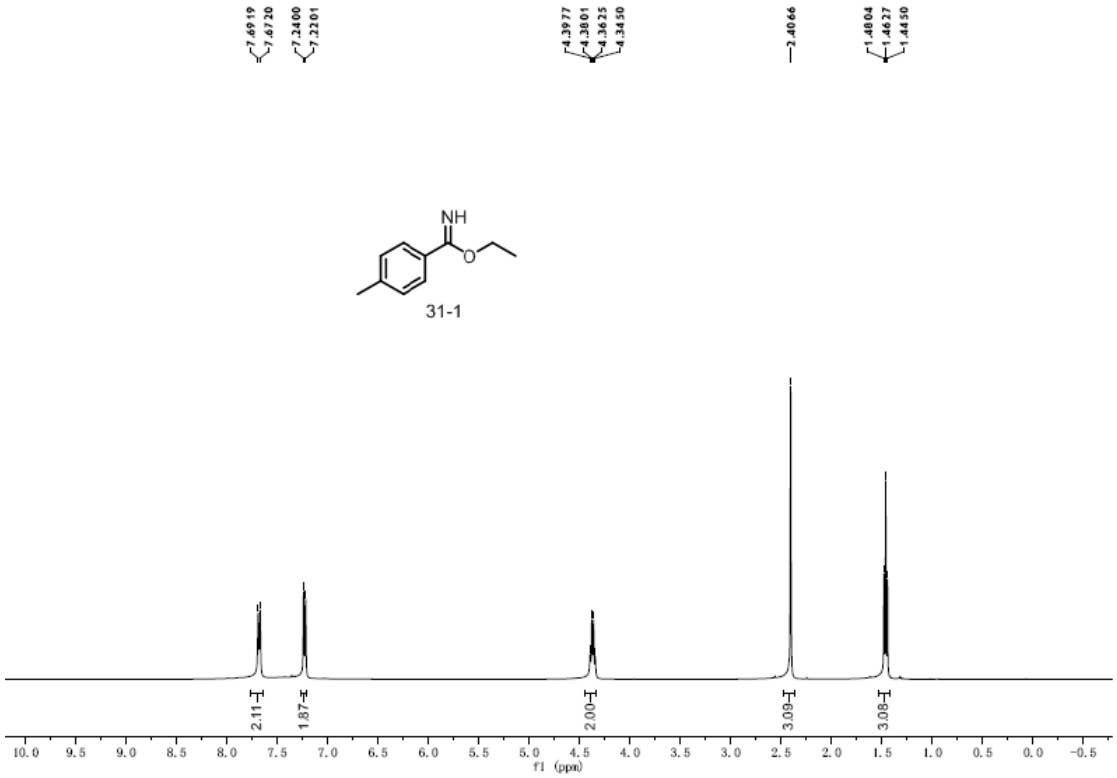
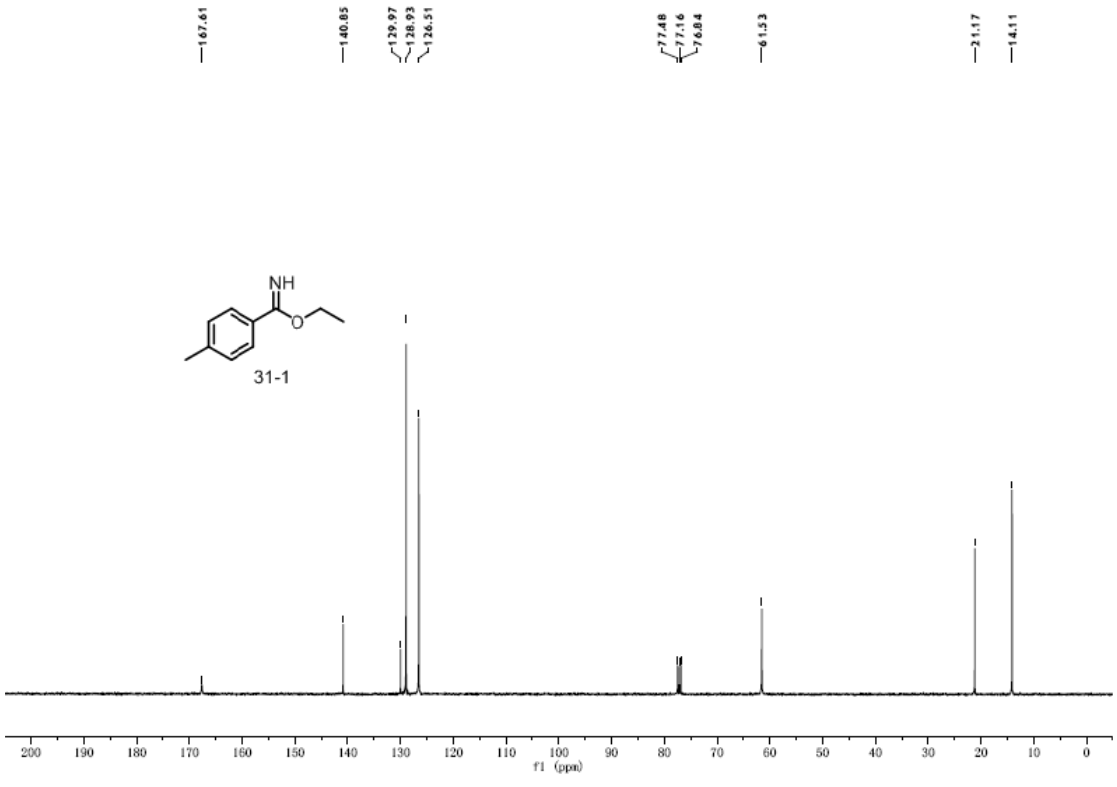
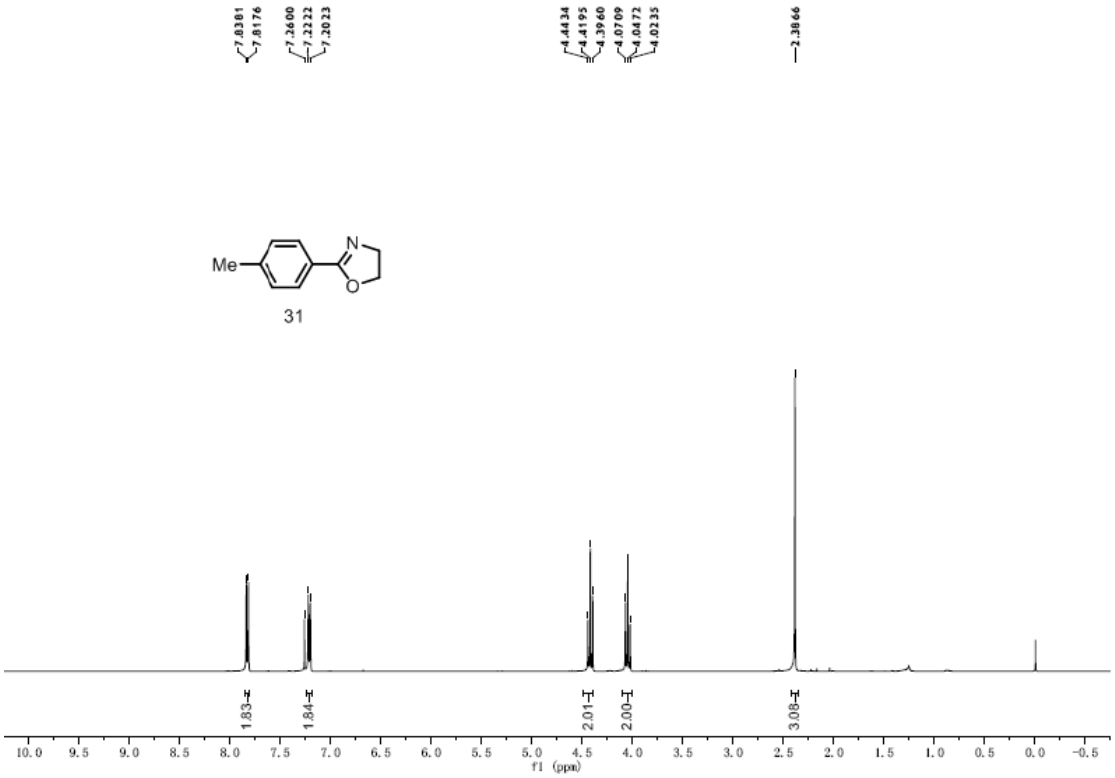
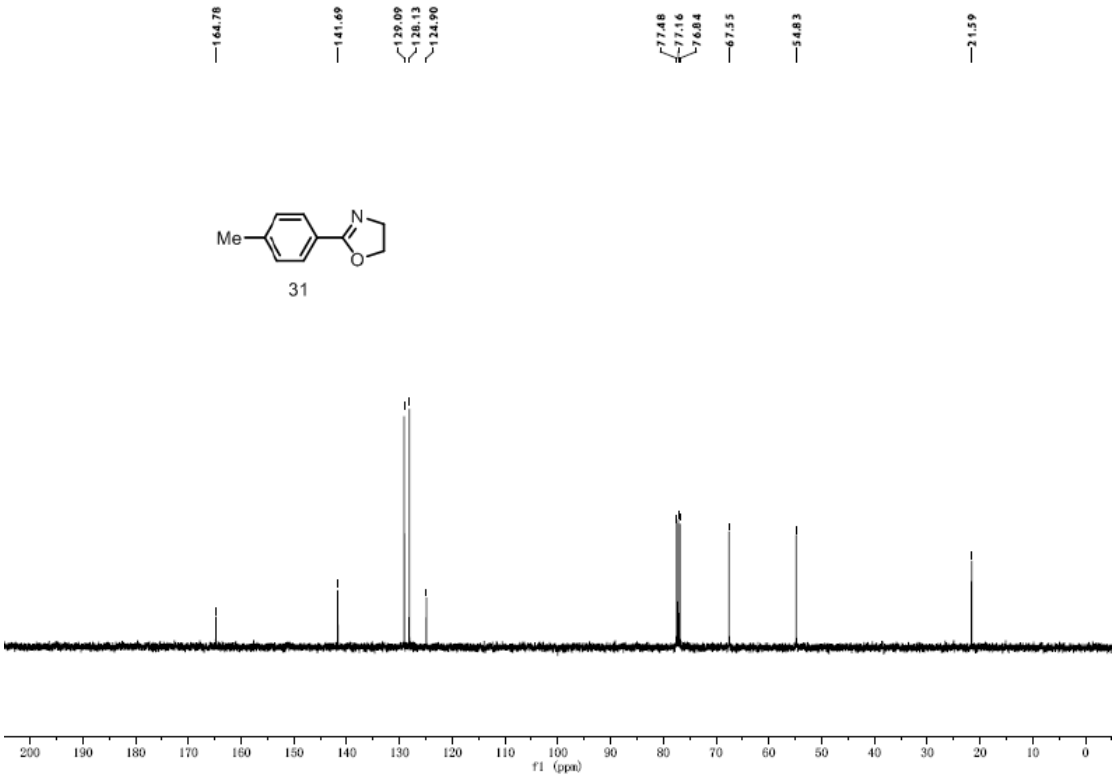
7.9240
7.9202
7.4714
7.4596
7.4530
7.4474
7.4380
7.4349
7.4053
7.3860
7.3684
7.2600
4.0970
1.3756
30
2.01
1.04
2.04
2.00
6.07
f1 (ppm)


162.19
131.20
128.38
128.33
128.15
79.22
77.48
77.16
76.84
67.67
28.53
30
f1 (ppm)


7.6919
7.6720
7.2400
7.2201
4.3977
4.3801
4.3625
4.3450
2.4066
1.4004
1.4627
1.4450
NH
O
31-1
2.11
1.87
2.00
3.09
3.08
f1 (ppm)


167.61
140.85
129.97
128.93
126.51
77.48
77.16
76.84
61.53
21.17
14.11
NH
O
31-1
f1 (ppm)


7.8381
7.8176
7.2600
7.2222
7.2023
4.4434
4.4195
4.3960
4.0709
4.0472
4.0235
2.3866
Me
N
O
31
1.83
1.84
2.01
2.00
3.08
f1 (ppm)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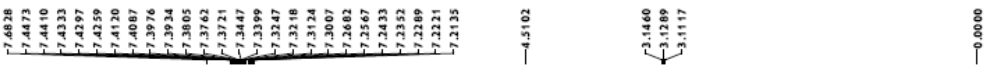
141.69
129.09
128.13
124.90
77.48
77.16
76.84
67.55
54.83
21.59
Me
N
O
31
f1 (ppm)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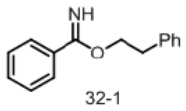
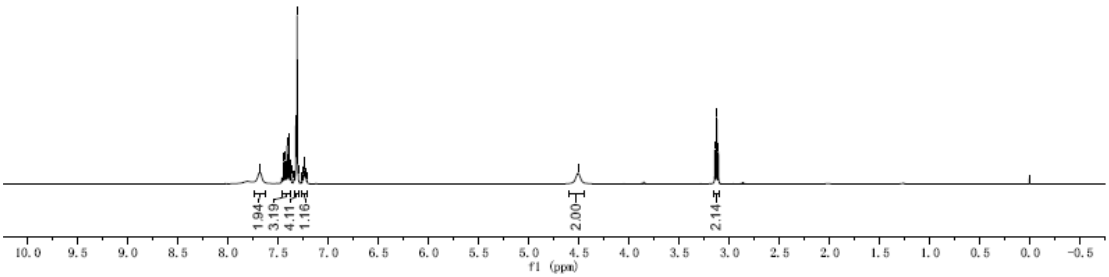
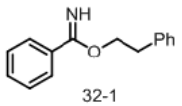
7.4410
7.4333
7.4297
7.4259
7.4130
7.4067
7.3976
7.3934
7.3805
7.3762
7.3721
7.3447
7.3399
7.3247
7.3218
7.3124
7.3007
7.2602
7.2567
7.2433
7.2352
7.2269
7.2221
7.2135
4.5102
3.1460
3.1289
3.1117
0.0000


NH
O
Ph

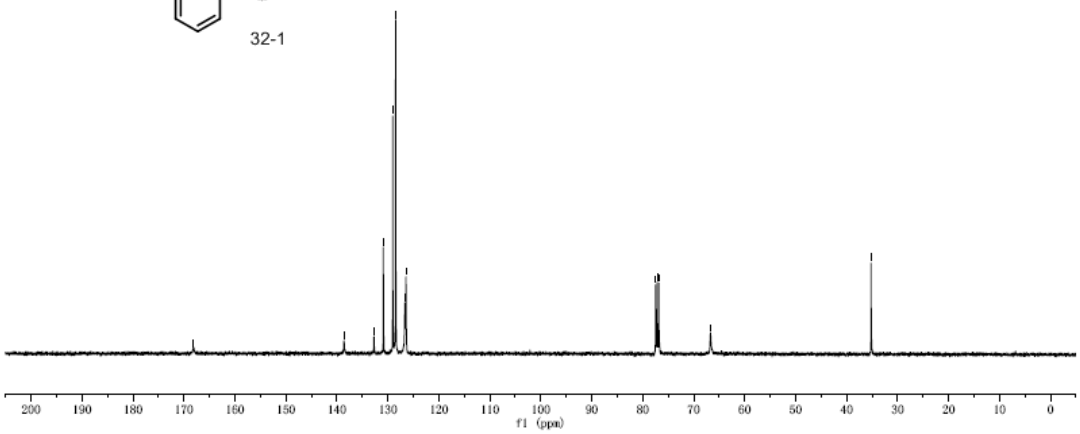
32-1

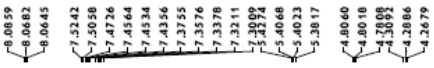

1.94
3.19
4.11
1.16
2.00
2.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

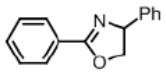

168.20
130.62
132.72
130.88
129.05
128.48
126.64
126.44
77.48
77.16
76.84
66.70
35.21


NH
O
Ph

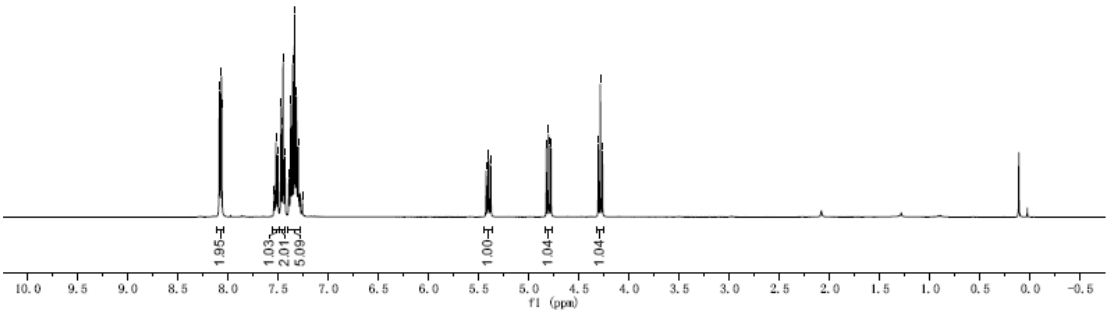
32-1

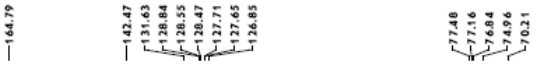

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

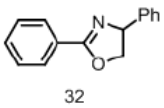




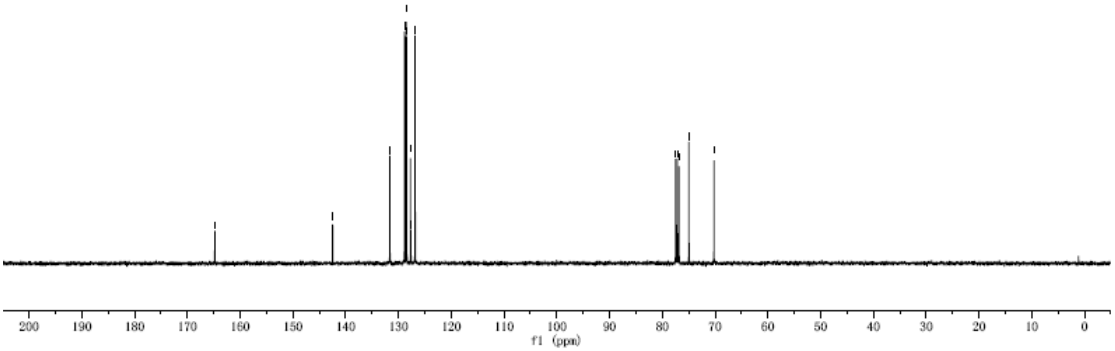
32

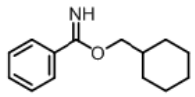




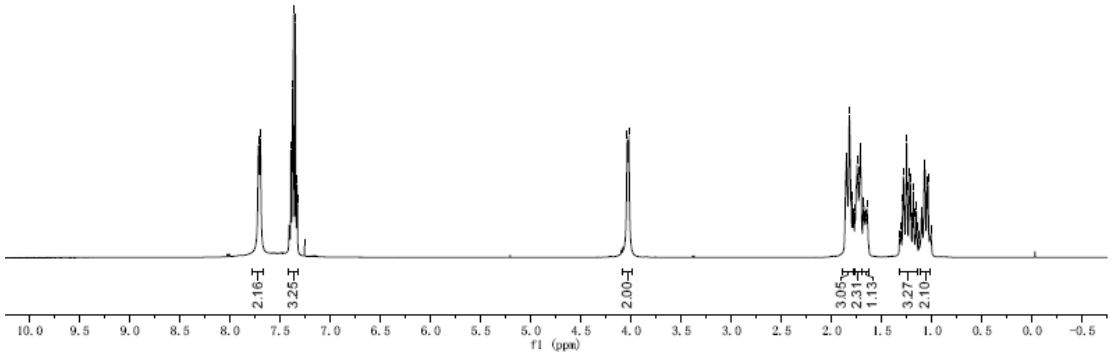


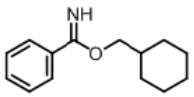
32



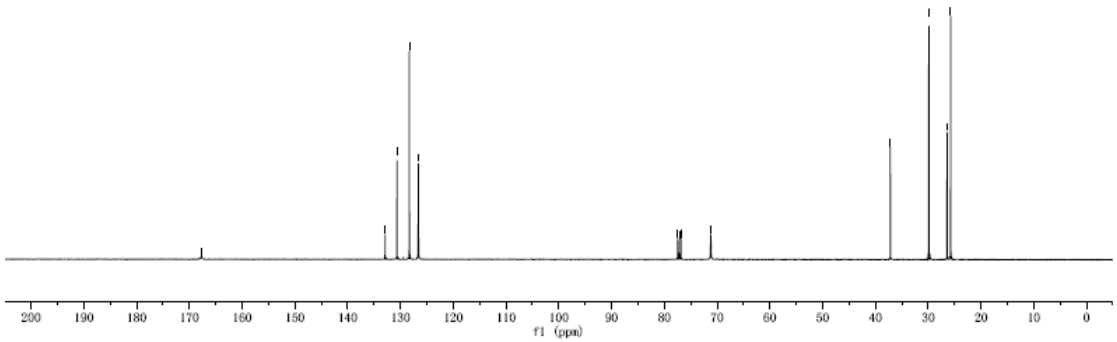


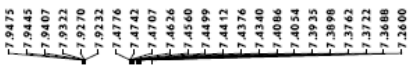
33-1





33-1

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7.4776
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7.4707
7.4626
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7.4499
7.4412
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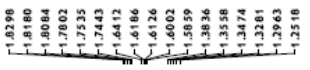
7.3898
7.3762
7.3722
7.3688
7.2600


1.8298
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1.7802
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1.7443
1.6412
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1.6002
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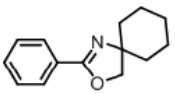
1.3836
1.3558
1.3474
1.3281
1.2963
1.2518



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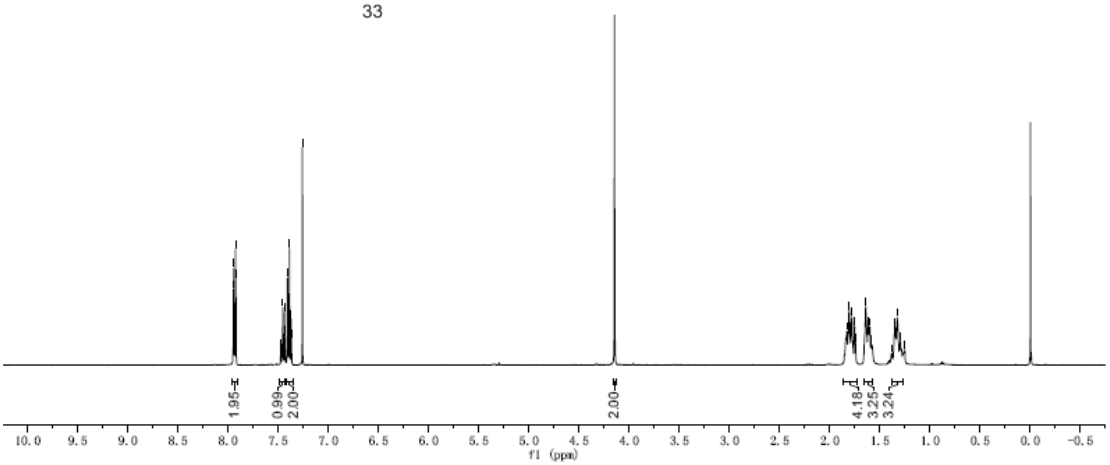
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0.99
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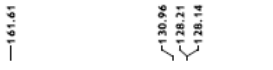
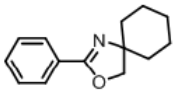
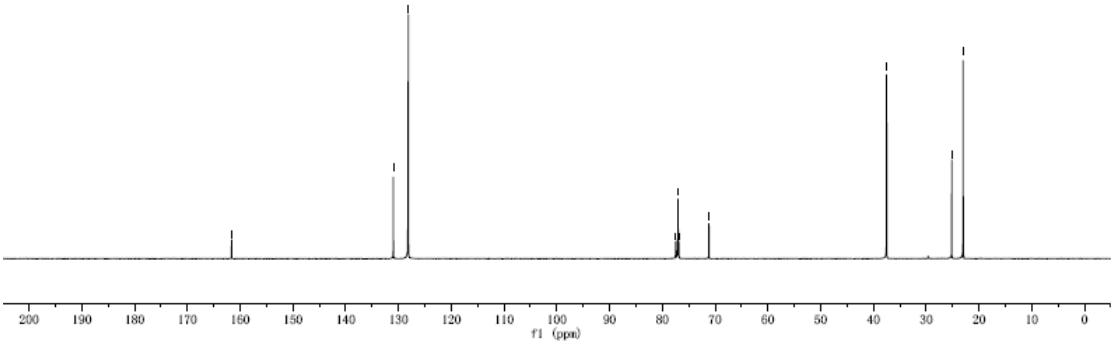
2.00
4.18
3.25
3.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


161.61
130.96
128.21
128.14
77.48
77.16
77.02
76.84
71.17
37.51
25.16
23.00



33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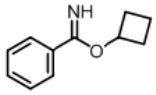
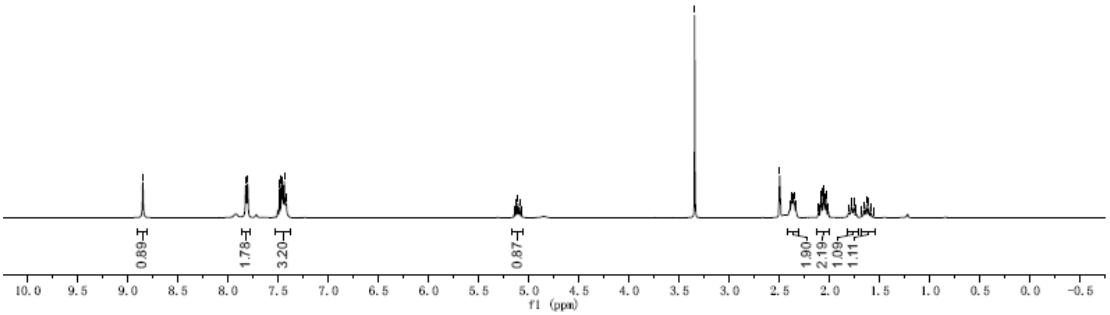
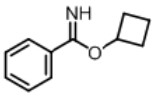
f1 (ppm)

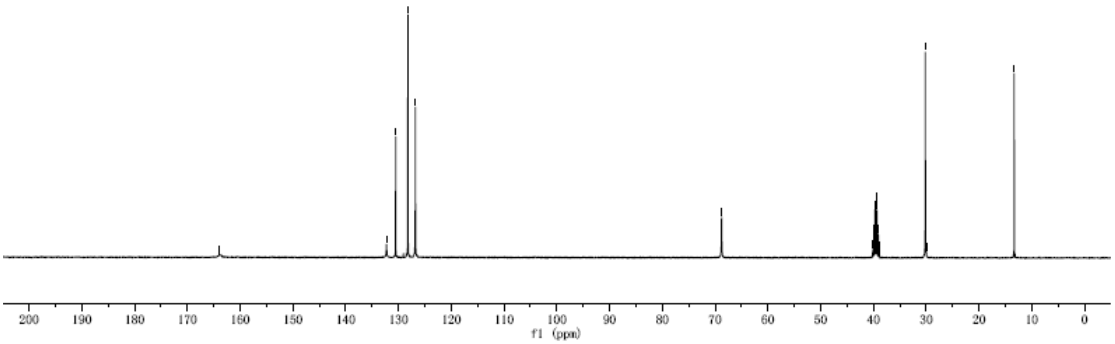


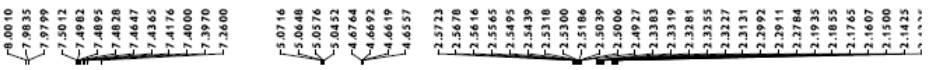
34-1

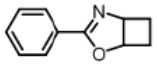




34-1







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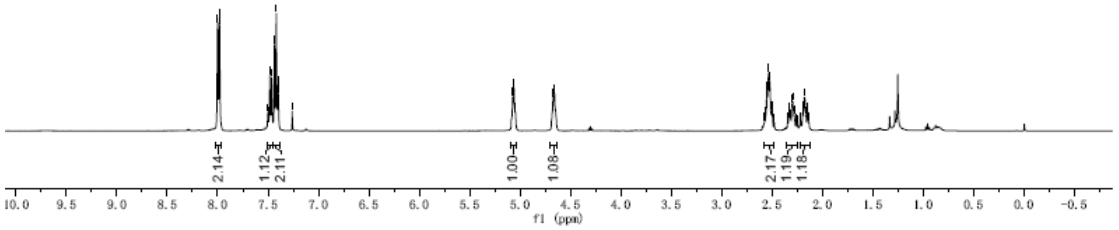
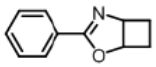
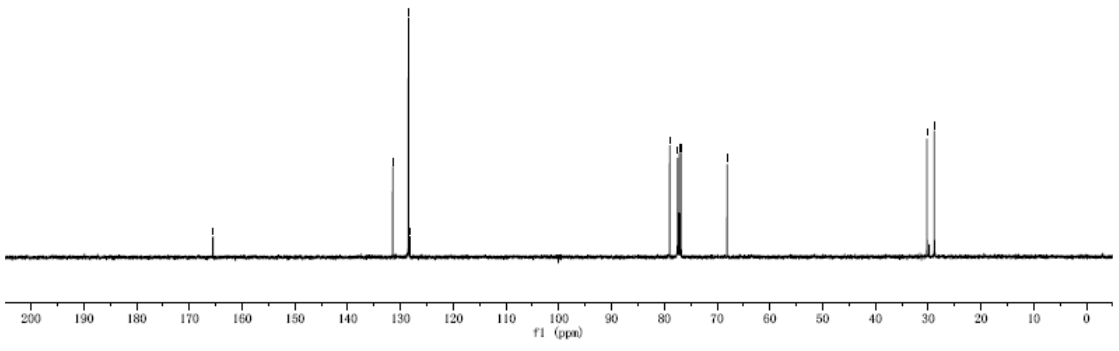
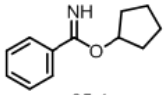


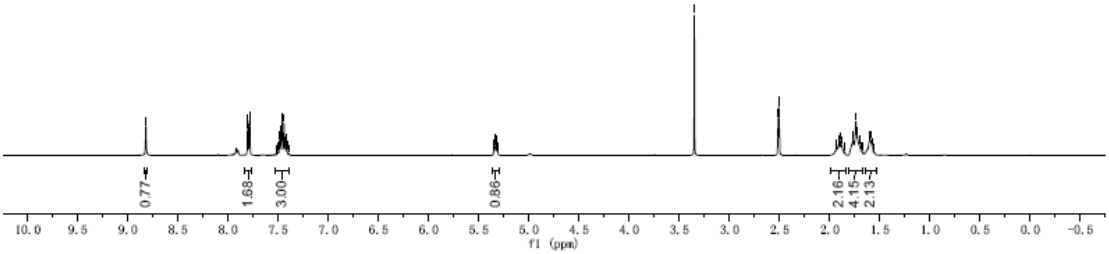


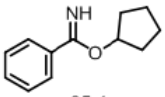
34



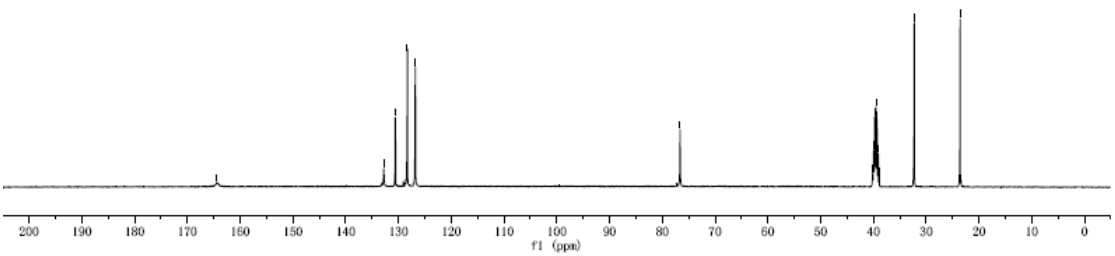


35-1





35-1

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4.7250
4.7067
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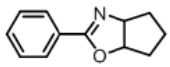
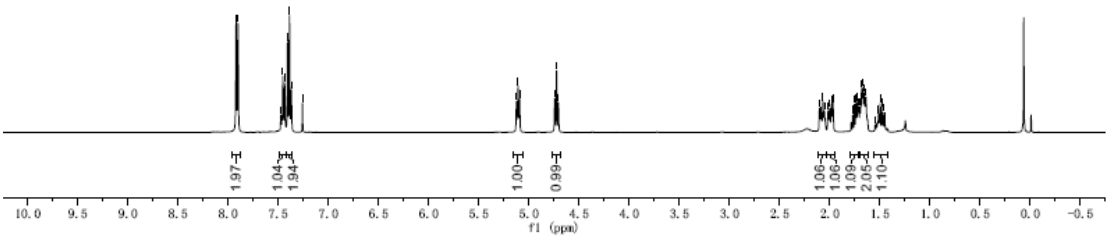
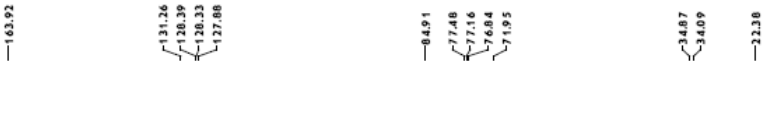
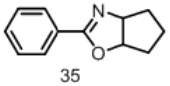


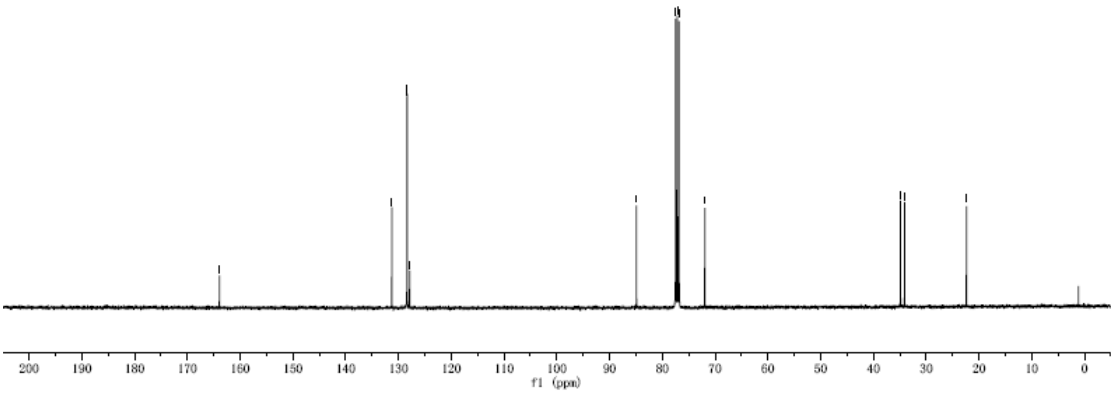
35

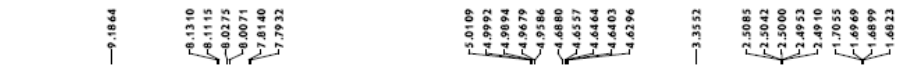

1.97
1.04
1.94
1.00
0.99
1.06
1.06
1.09
2.05
1.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

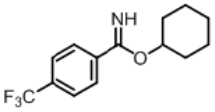

163.92
131.26
128.39
128.33
127.68
84.91
77.48
77.16
76.84
71.95
34.87
34.09
22.30



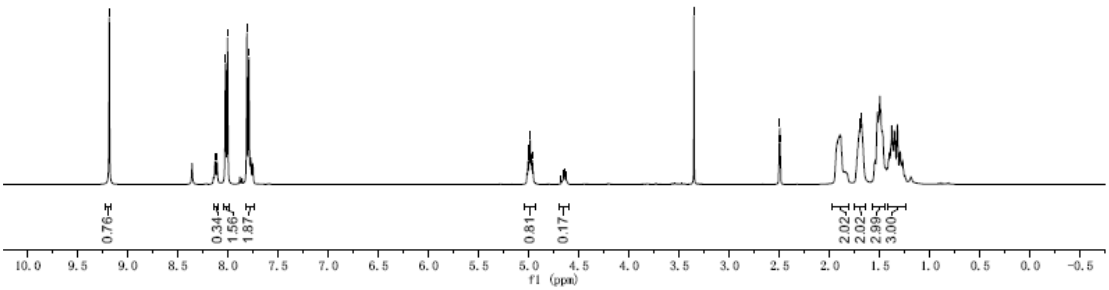
35


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

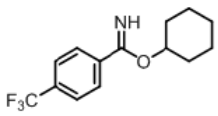

9.1864
8.1310
8.1115
8.0275
8.0071
7.8140
7.7932
5.0109
4.9992
4.9894
4.9679
4.9586
4.6880
4.6557
4.6464
4.6403
4.6296
3.3552
2.5085
2.5042
2.5000
2.4953
2.4910
1.7055
1.6969
1.6899
1.6823


NH
O
F3C

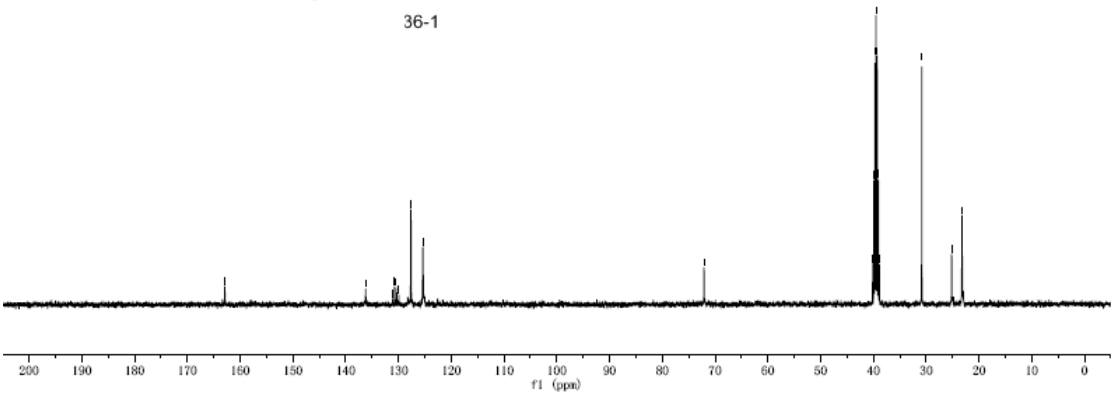
36-1

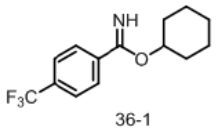

0.76
0.34
1.56
1.87
0.81
0.17
2.02
2.02
2.99
3.00
f1 (ppm)


162.90
136.22
131.09
130.77
130.45
130.30
129.92
127.63
125.37
72.10
40.13
39.92
39.71
39.50
39.29
39.08
38.88
30.84
25.18
23.22


NH
O
F3C

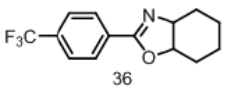
36-1


f1 (ppm)

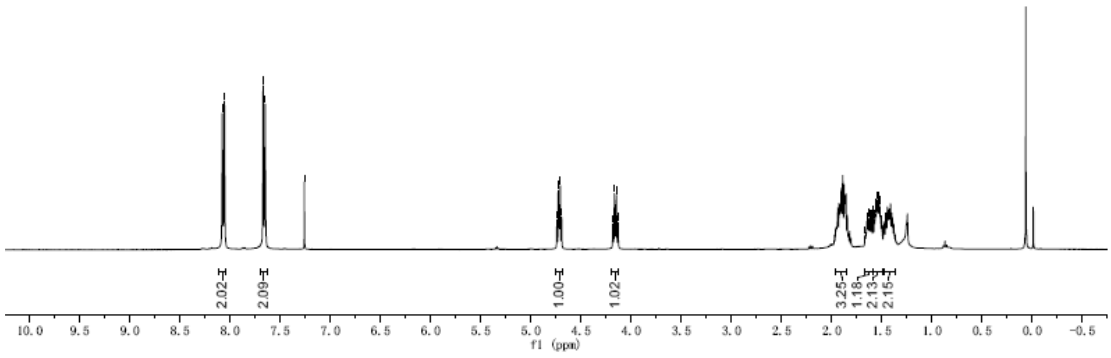

NH
O
F3C

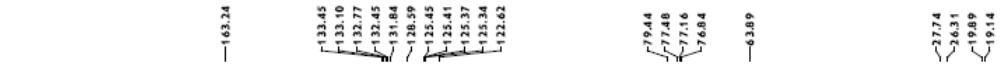
36-1

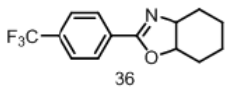
-62.86
f1 (ppm)
8.0786
8.0584
7.6719
7.6515
7.2600
4.7413
4.7282
4.7208
4.7152
4.7077
4.6946
4.1835
4.1681
4.1479
4.1319
1.6693
1.6495
1.6393
1.6333
1.6225
1.6162
1.6055
1.5984
1.5756
1.5649
1.5556
1.5471
1.5354
1.5317
1.5227
1.5135
1.5071
1.5013


F3C
N
O

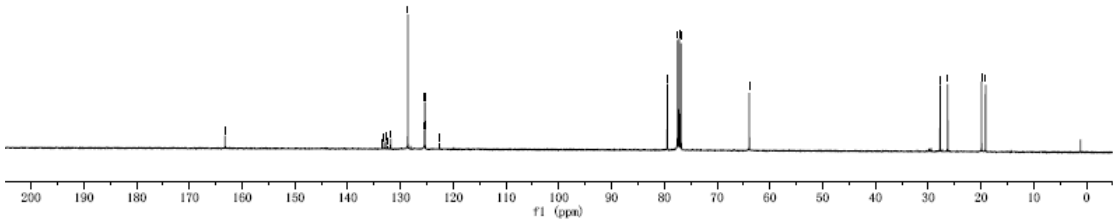
36


2.02
2.09
1.00
1.02
3.25
1.18
2.13
2.15
f1 (ppm)

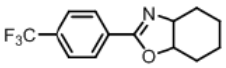

163.24
133.45
133.10
132.77
132.45
131.84
128.59
125.45
125.41
125.37
125.34
122.62
79.44
77.48
77.16
76.84
63.89
27.74
26.31
19.89
19.14


F3C
N
O

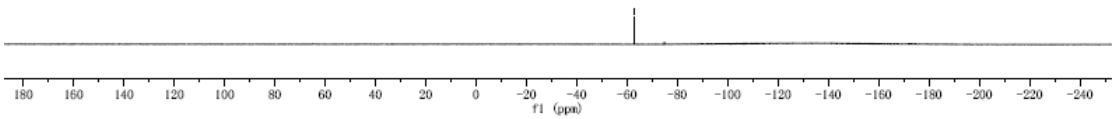
36

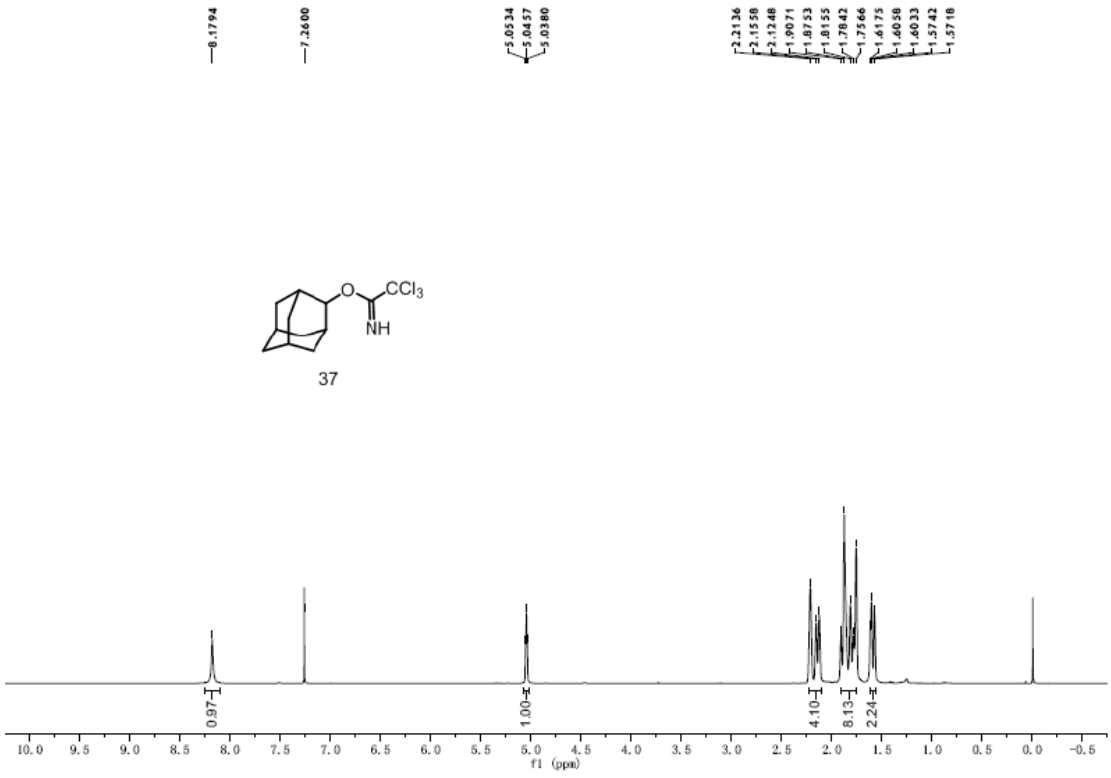

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

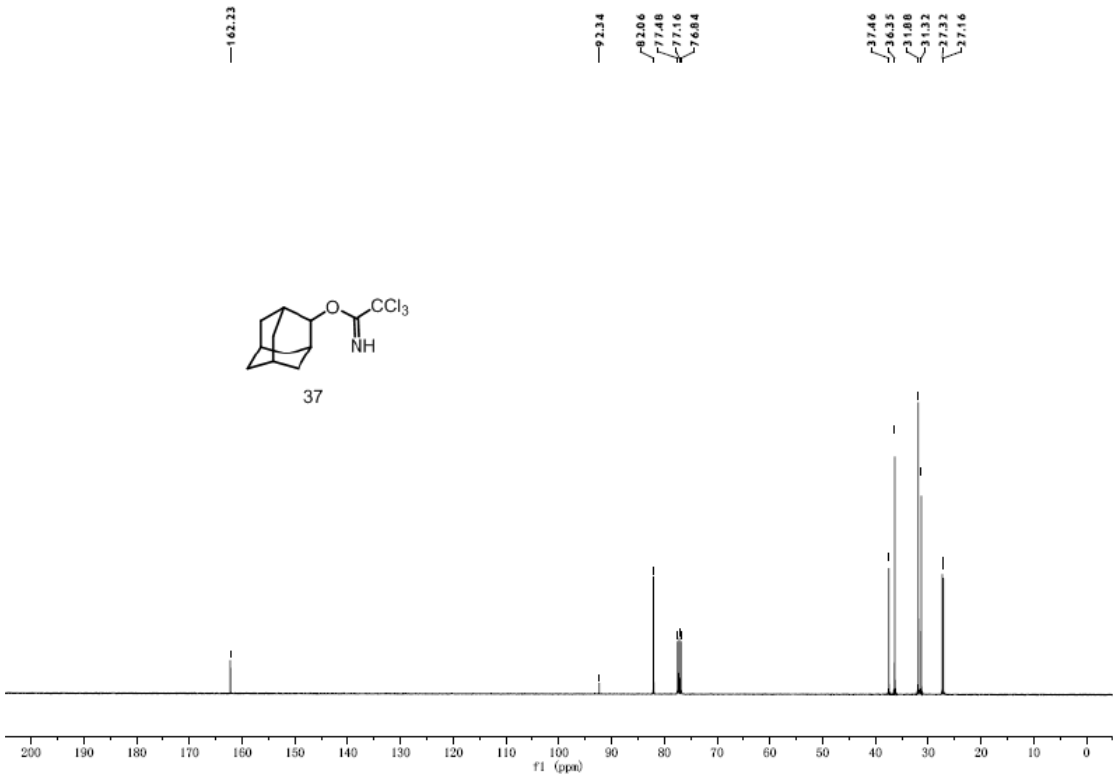
-62.86

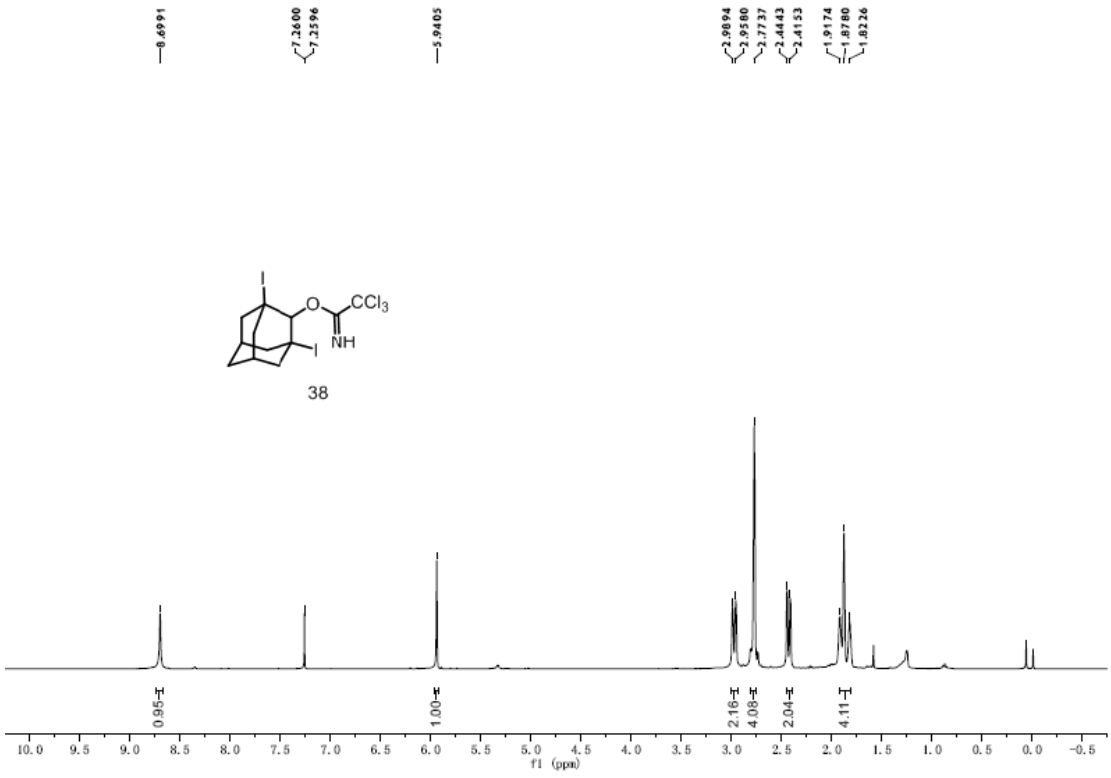

F3C
N
O

36

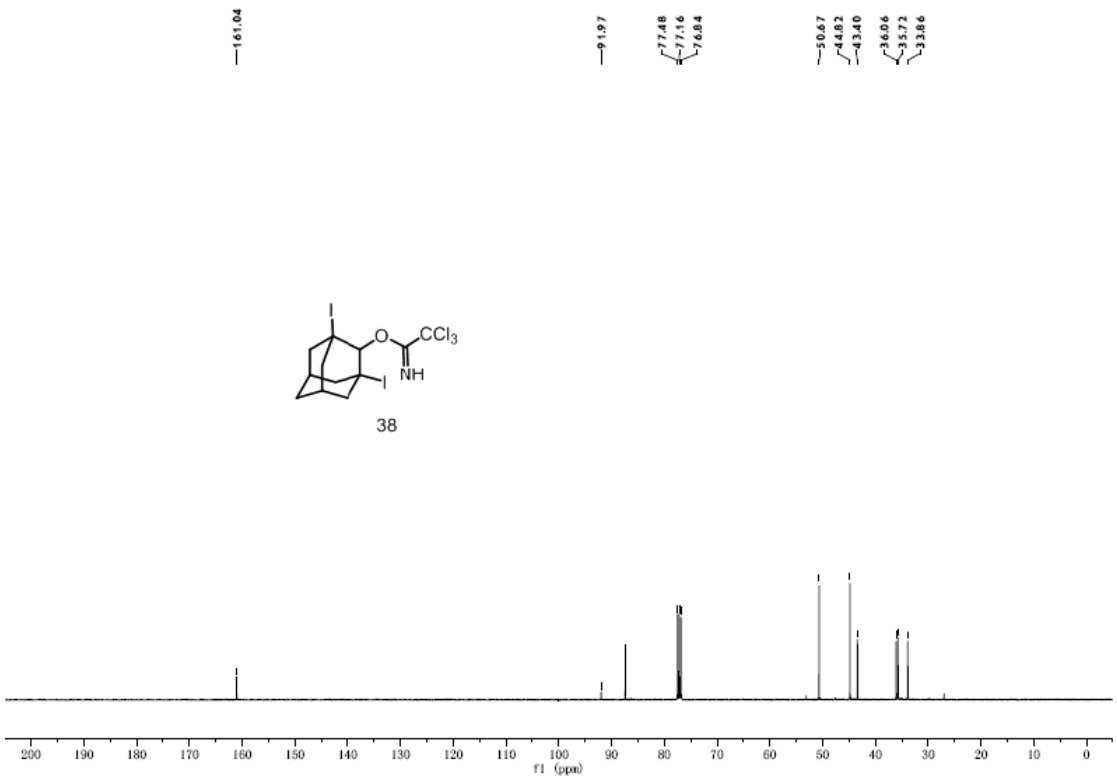

180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)


8.1794
7.2600
5.0534
5.0457
5.0380
2.2136
2.1558
2.1248
1.9071
1.8753
1.8155
1.7842
1.7566
1.6175
1.6058
1.6033
1.5742
1.5718
O
CCl3
NH
37
0.97
1.00
4.10
8.13
2.24
f1 (ppm)

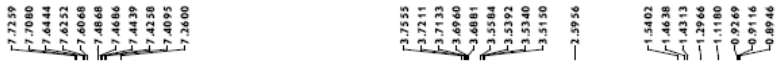

162.23
92.34
82.06
77.48
77.16
76.84
37.46
36.35
31.88
31.32
27.32
27.16
O
CCl3
NH
37
f1 (ppm)

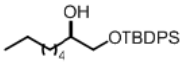

8.6991
7.2600
7.2596
5.9405
2.9694
2.9580
2.7737
2.4443
2.4153
1.9174
1.8780
1.8226
I
O
CCl3
NH
I
0.95
1.00
2.16
4.08
2.04
4.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

38

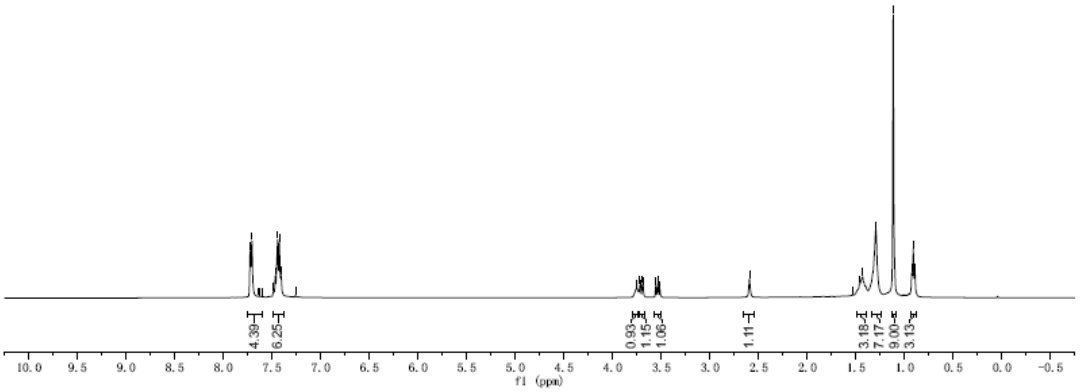

161.04
91.97
77.48
77.16
76.84
50.67
44.82
43.40
36.06
35.72
33.86
I
O
CCl3
NH
I
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

38

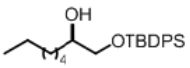

7.7259
7.7080
7.6444
7.6252
7.6068
7.4868
7.4686
7.4439
7.4258
7.4095
7.2600
3.7555
3.7211
3.7133
3.6960
3.6881
3.5584
3.5392
3.5340
3.5150
2.5956
1.5402
1.4638
1.4313
1.2966
1.1180
0.9269
0.9116
0.8946


OH
OTBDPS
4

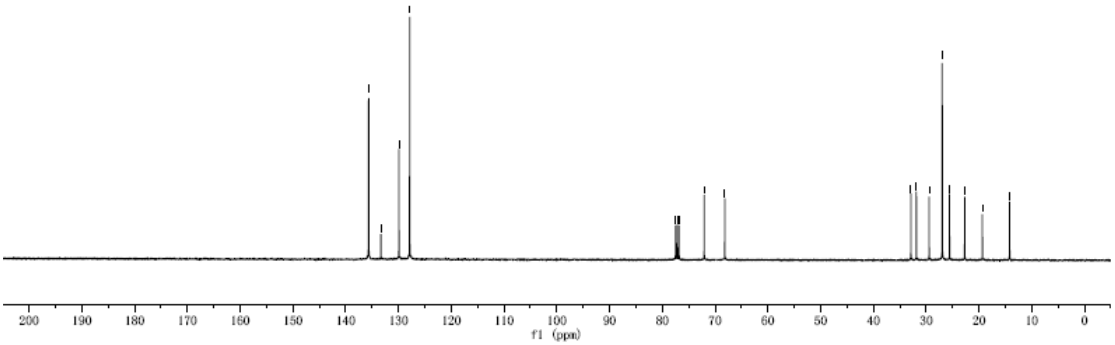
39-3

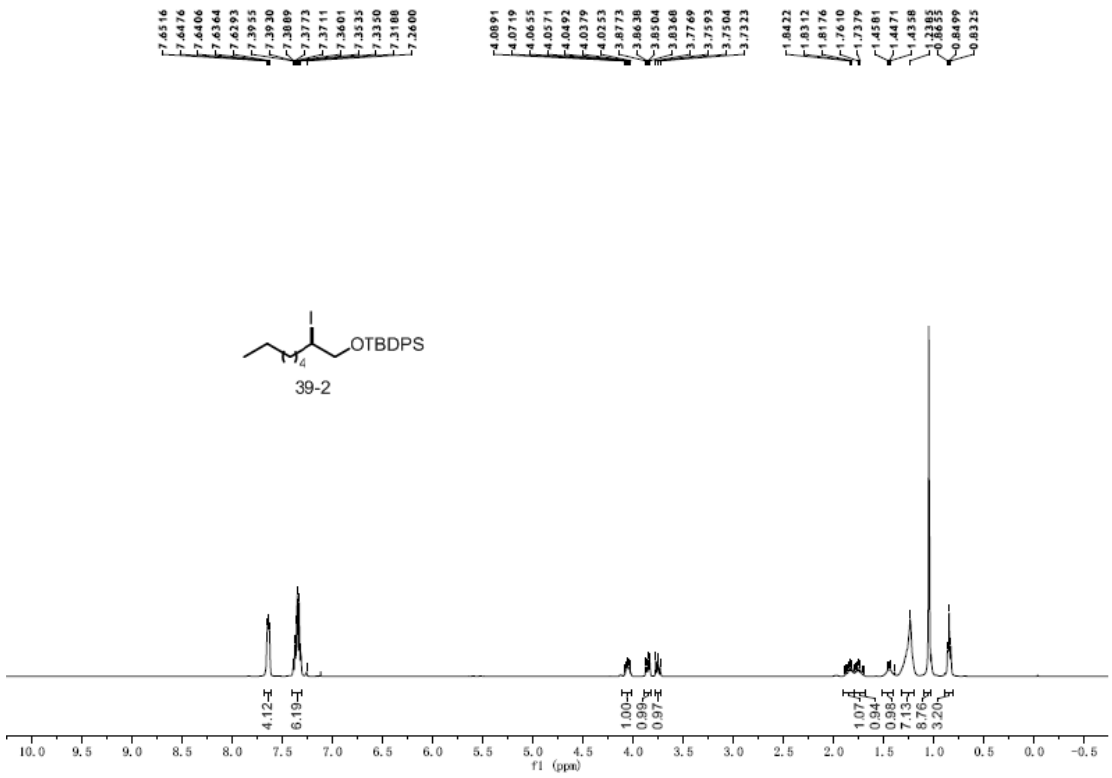

4.39
6.25
0.93
1.15
1.06
1.11
3.18
7.17
9.00
3.13
f1 (ppm)

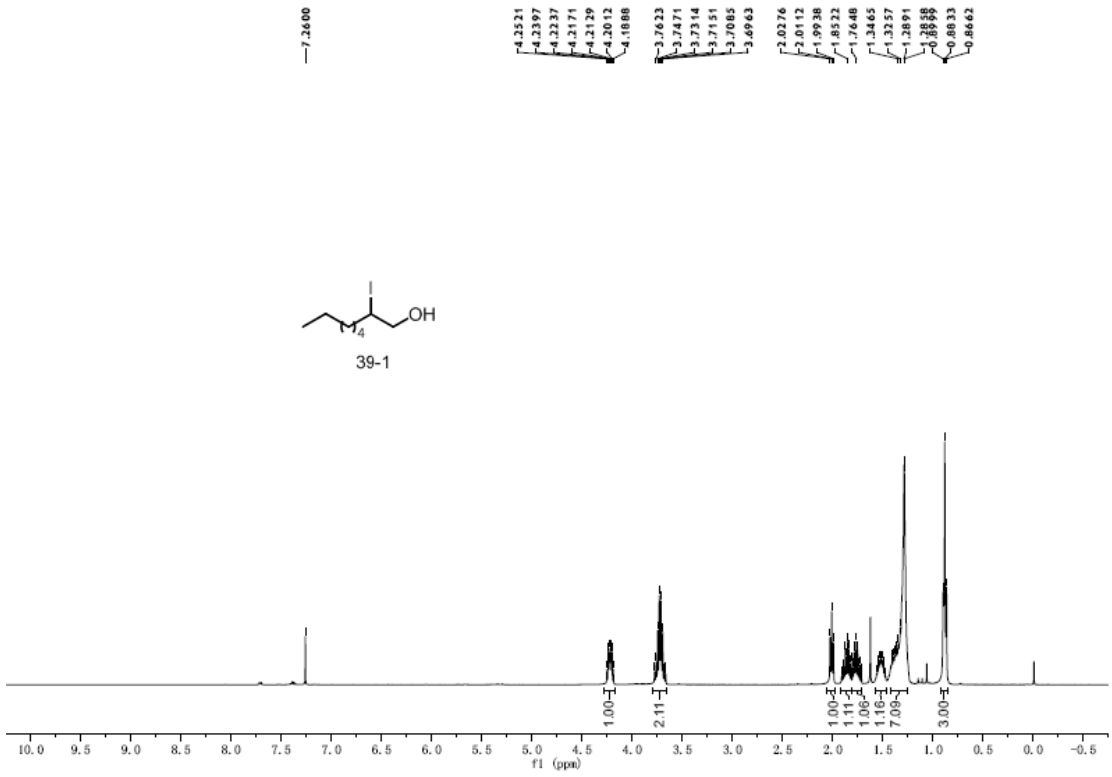

135.64
133.30
129.90
127.88
77.48
77.16
76.84
72.07
68.17
32.90
31.87
29.44
26.97
25.59
22.70
19.35
14.20

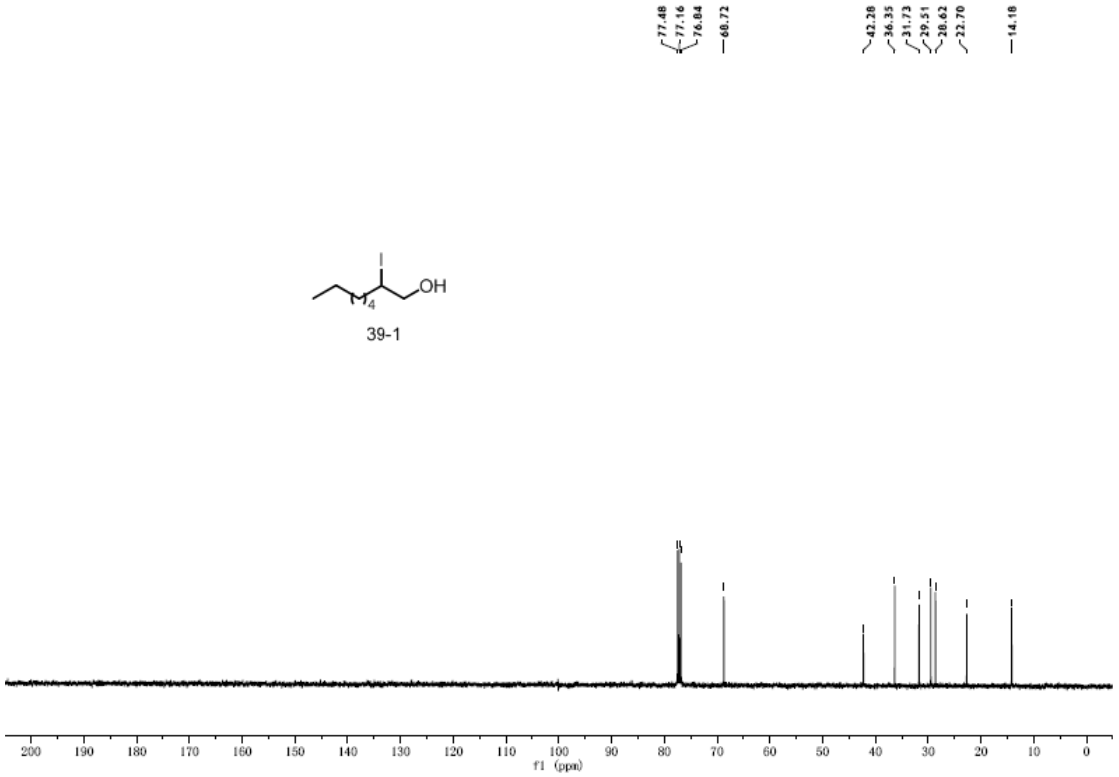

OH
OTBDPS
4

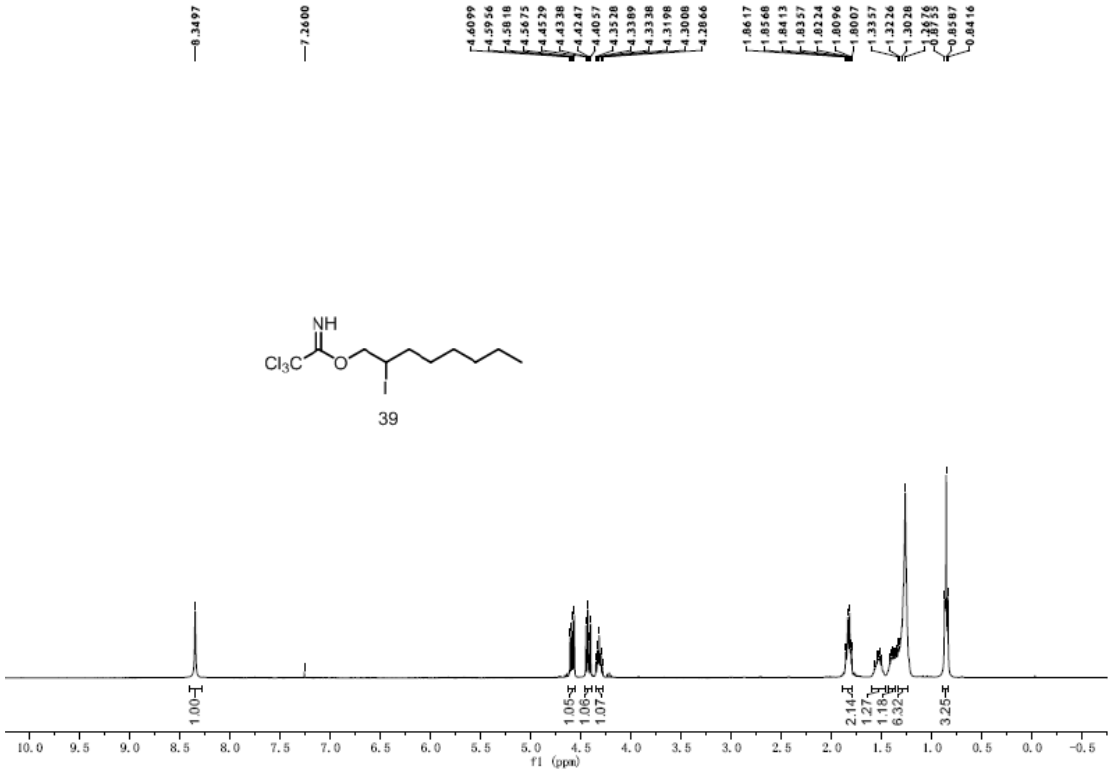
39-3

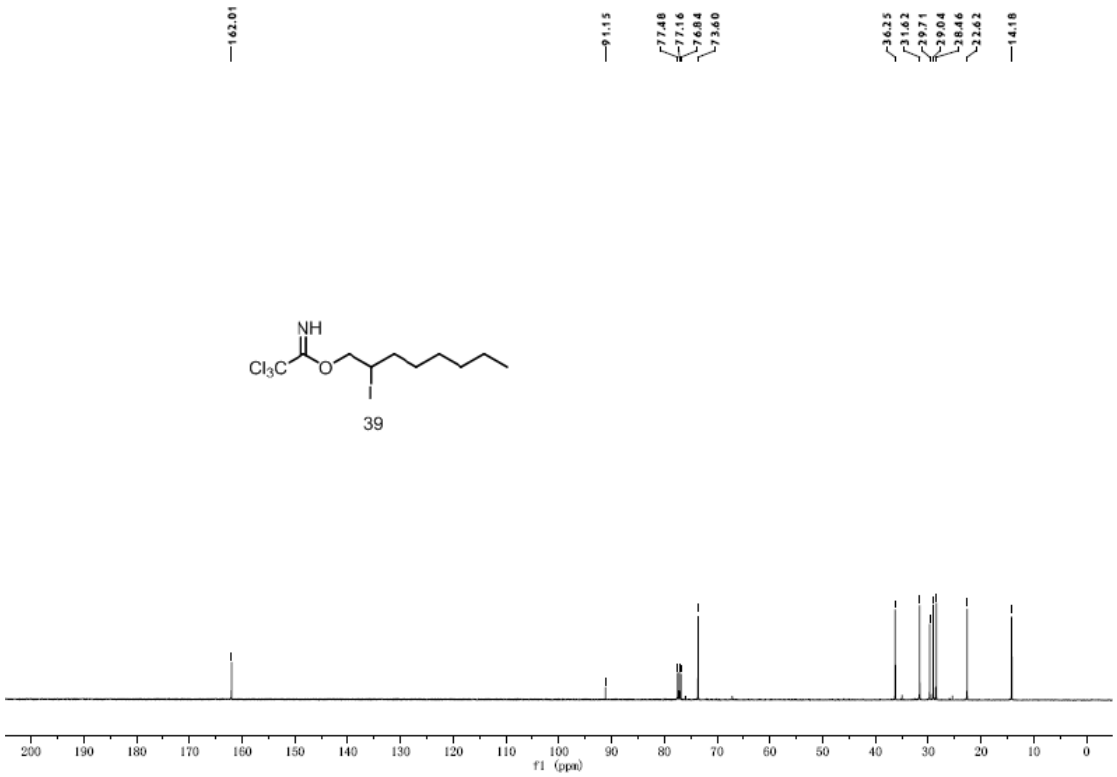

f1 (ppm)


OTBDPS
39-2
f1 (ppm)


OH
39-1
f1 (ppm)


77.48
77.16
76.84
60.72
42.28
36.35
31.73
29.51
28.62
22.70
14.18
I
OH
4
39-1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


0.3497
7.2600
4.6099
4.5956
4.5818
4.5675
4.4529
4.4338
4.4247
4.4057
4.3528
4.3389
4.3338
4.3198
4.3008
4.2066
1.8617
1.8568
1.8413
1.8357
1.8224
1.8096
1.8007
1.3357
1.3226
1.3028
0.8587
0.8416
NH
Cl3C
O
I
39
1.00
1.05
1.06
1.07
2.14
1.27
1.18
6.32
3.25
10.0 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)


162.01
91.15
77.48
77.16
76.84
73.60
36.25
31.62
29.71
29.04
28.46
22.62
14.18
NH
Cl3C
O
I
39
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)