Supplementary information

Electrochemically Promoted Diamidation of Alkenes to Dihydroimidazole Skeleton

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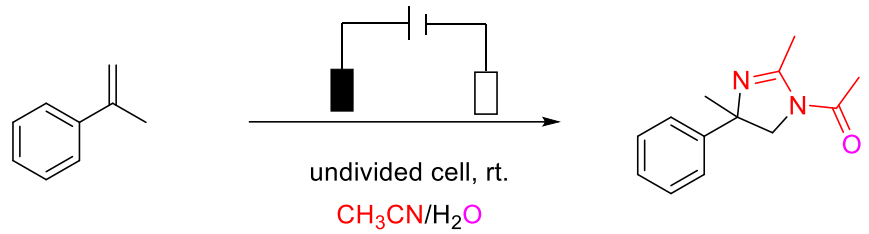
1. General Information

Without special instructions, all reagents and solvents were commercially available and were not further purified. All commercially available compounds are purchased from Bide Pharmaceuticals, Et_4NBF_4 purchased from Aladdin, Extra dry CH_3CN purchased from Energy chemical, alkenes were synthesized according to the published procedures.[1] Column chromatography on silica gel (300-400 mesh) was carried out using technical grade 60-90 °C petroleum ether (distillated prior to use) and analytical grade EtOAc (without further purification). NMR spectroscopy was performed on 400 MHz or 500 MHz instruments. Chemical shifts for ^1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from TMS (δ 0.00) and relative to the signal of chloroform-d (δ 7.26, singlet). The abbreviations used to explain the multiplicities were as follows: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from TMS (δ 0.00) and relative to the signal of chloroform-d (δ 77.16, triplet). The HRMS spectrum was measured by micromass QTOF2 Quadrupole/Time of Flight Tandem mass spectrometer with electron spray ionization. Cyclic voltammograms were recorded on a CHI 660E potentiostat. Single-crystal X-ray diffraction data were collected on a Rigaku XtaLAB Synergy, Dualflex, Rigaku XtaLAB Synergy-S diffractometer coupled to a RigakuHypix detector with Cu Kα radiation (λ = 1.54184 Å). The crystal was kept at a steady T = 100 K during the data collection. The structures were solved with the SHELXT solution program by using Olex 2 (Dolomanov et al., 2009) as the graphical interface. The model was refined using Least Squares minimisation with the 2018/3 version of the program SHELXL.

2. Additional Optimization of Reaction Conditions

Table S1 Optimization of reaction conditions [a]



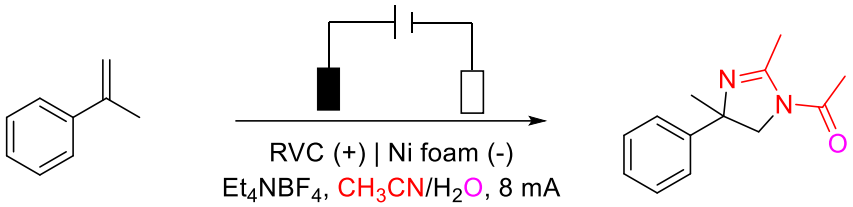
1a **2a**

Entry	Electrode	Electrolyte	Current (mA)	Extra dry [h] CH_3CN (mL)	Yield (%) [b]
1	GF (+) | GF (-)	Et_4NBr (2 eq.)	8	4	Trace
2	GF (+) | GF (-)	Et_4NCl (2 eq.)	8	4	Trace
3	GF (+) | GF (-)	Et_4NI (2 eq.)	8	4	Trace
4	GF (+) | GF (-)	Et_4NBF_4 (2 eq.)	8	4	25
5	GF (+) | GF (-)	Et_4NClO_4 (2 eq.)	8	4	21
6	GF (+) | GF (-)	Et_4NPF_6 (2 eq.)	8	4	20
7	GF (+) | GF (-)	Et_4NBF_4 (1 eq.)	8	4	23
8	GF (+) | GF (-)	Et_4NBF_4 (3 eq.)	8	4	34
9	GF (+) | GF (-)	Et_4NBF_4 (4 eq.)	8	4	43
10	GF (+) | GF (-)	Et_4NBF_4 (5 eq.)	8	4	36
11	GF (+) | GF (-)	Et_4NBF_4 (4 eq.)	8	2	34
12	GF (+) | GF (-)	Et_4NBF_4 (4 eq.)	8	6	51
13	GF (+) | GF (-)	Et_4NBF_4 (4 eq.)	8	8	43
14	RVC (+) | GF (-)	Et_4NBF_4 (4 eq.)	8	6	52
15	RVC (+) | Ni (-)	Et_4NBF_4 (4 eq.)	8	6	61
16	Pt (+) | Pt (-)	Et_4NBF_4 (4 eq.)	8	6	59
17	C (+) | C (-)	Et_4NBF_4 (4 eq.)	8	6	35
18	RVC (+) | Ni foam	Et_4NBF_4 (4 eq.)	8	6	70
19	RVC (+) | Pt (-)	Et_4NBF_4 (4 eq.)	8	6	68
20	GF (+) | RVC (-)	Et_4NBF_4 (4 eq.)	8	6	45
21	GF (+) | C Paper (-)	Et_4NBF_4 (4 eq.)	8	6	43
22	GF (+) | C Cloth (-)	Et_4NBF_4 (4 eq.)	8	6	38
23	RVC (+) | RVC (-)	Et_4NBF_4 (4 eq.)	8	6	50
24	Pt (-) | Ni foam (-)	Et_4NBF_4 (4 eq.)	8	6	58
25	RVC (+) | Ni foam	Et_4NBF_4 (4 eq.)	6	6	62
26	RVC (+) | Ni foam	Et_4NBF_4 (4 eq.)	10	6	64
27	RVC (+) | Ni foam	Et_4NBF_4 (4 eq.)	0	6	0
28[c]	RVC (+) | Ni foam	Et_4NBF_4 (4 eq.)	8	6:0.005	82
29[d]	RVC (+) | Ni foam	Et_4NBF_4 (4 eq.)	8	6:0.02	65
30[e]	RVC (+) | Ni foam	Et_4NBF_4 (4 eq.)	8	6:0.04	42

31[f]	RVC (+) | Ni foam	Et_4NBF_4 (4 eq.)	8	6:0.1	25
32[g]	RVC (+) | Ni foam	Et_4NBF_4 (4 eq.)	8	6:0.2	trace

[a] standard conditions: reticulated vitreous carbon (RVC (100 PPI, 1 cm × 1 cm × 1.2 cm)) anode, Ni foam (1 cm × 2 cm × 0.5 cm) cathode, undivided cell, constant current = 8 mA, **1a** (0.2 mmol, 1 equiv), Et_4NBF_4 (0.8 mmol, 4 equiv), extra dry CH_3CN and H_2O as solvent (extra dry CH_3CN = 6 mL, H_2O = 5 μL) , room temperature, [b] Isolated yields, [c] extra dry CH_3CN/H_2O (6:0.005) as solvent (extra dry CH_3CN = 6 mL, H_2O = 5 μL)， [d] extra dry CH_3CN/H_2O (6:0.02) as solvent (extra dry CH_3CN = 6 mL, H_2O = 20 μL), [e] extra dry CH_3CN/H_2O (6:0.04) as solvent (extra dry CH_3CN = 6 mL, H_2O = 40 μL), [f] extra dry CH_3CN/H_2O (extra dry 6:0.1) as solvent (extra dry CH_3CN = 6 mL, H_2O = 100 μL), [g] extra dry CH_3CN/H_2O (6:0.2) as solvent (extra dry CH_3CN = 6 mL, H_2O = 200 μL), [h] water ≤10 ppm.

3. General procedure for the preparation of products



1a **2a**

A 10 mL three-necked round-bottomed flask was charged with **1a** (0.2 mmol, 1 equiv), Et_4NBF_4 (0.8 mmol, 4.0 equiv), extra dry CH_3CN and H_2O as solvent (extra dry CH_3CN = 6 mL, H_2O = 5 μL). The flask was equipped with a reticulated vitreous carbon (RVC) anode (100 PPI, 1 cm × 1 cm × 1.2 cm) and a Ni foam (1 cm × 2 cm × 0.5 cm) cathode, the distance between the two electrodes was 2.8 cm. Electrolysis was carried out at room temperature under air atmosphere, which using a constant current of 8 mA until the substrate was completely consumed (monitored by TLC, about 3 ~ 6 hours). When the reaction was finished, the reaction mixture was washed with water and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel to afford the **2a**. (petroleum ether/ethyl acetate = 1: 1).

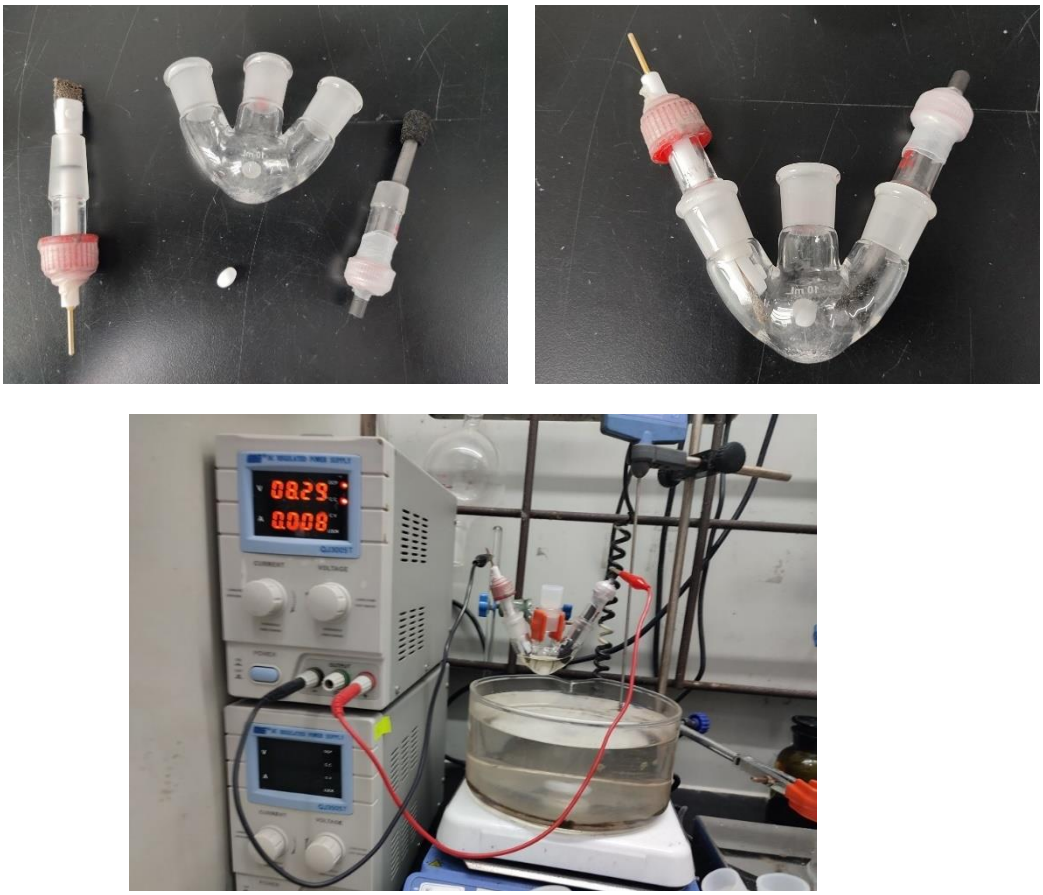
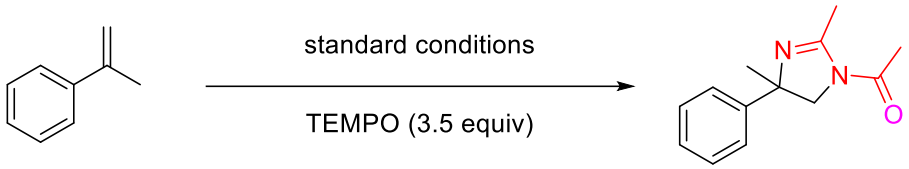


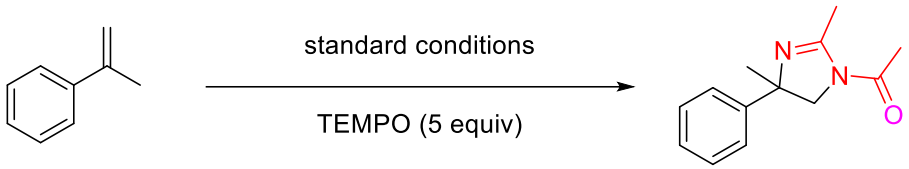
Figure S1 Electrolysis setup

4. Control experiments

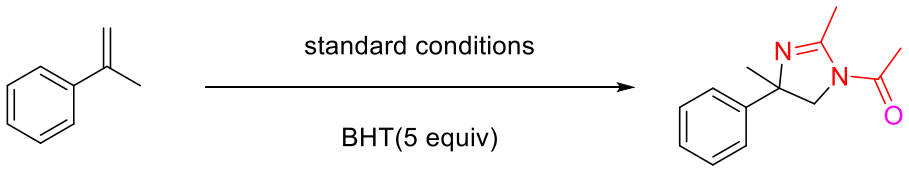
4.1 TEMPO and BHT trapped experiment



1a yield < 10%

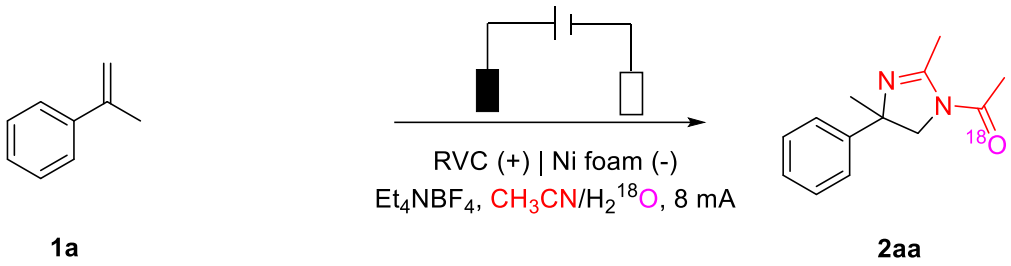


1a Trace



1a Trace

4.2 $H_2{}^{18}O$-labeling experiment



1a **2aa**

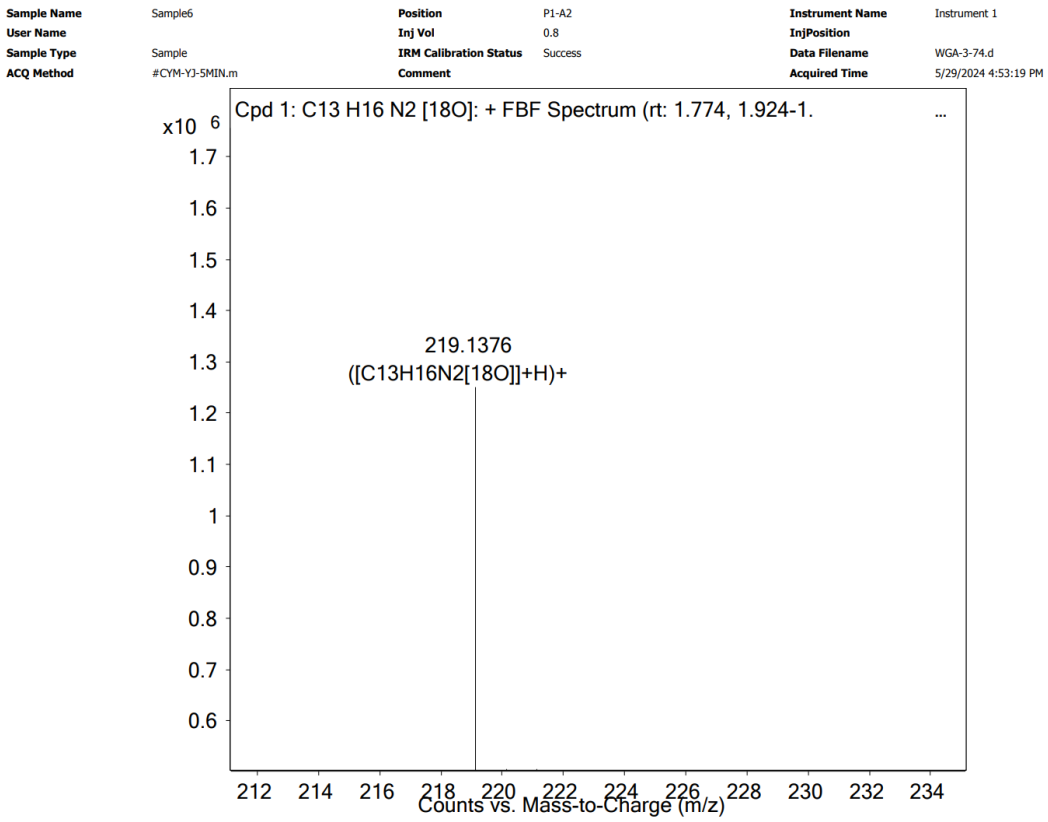
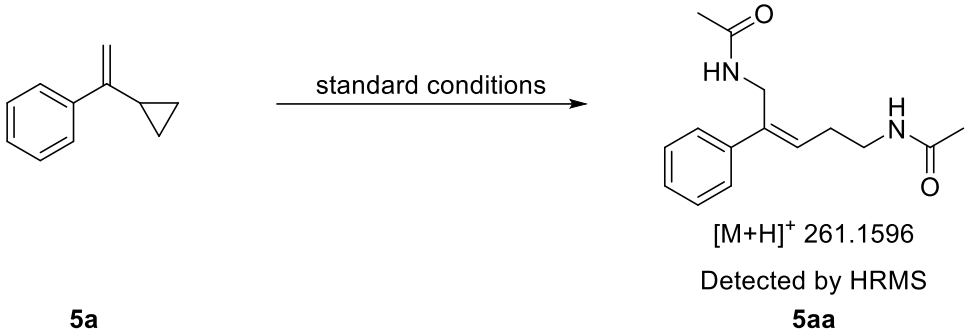


Figure S2 HRMS analysis compound **2aa**. **HRMS** (m/z) [ESI]: calculated for $C_{13}H_{17}N_2[18O]^+$ $[M+H]^+$: 219.1378, found 219.1376.

4.3 Radical clock experiments



5a **5aa**

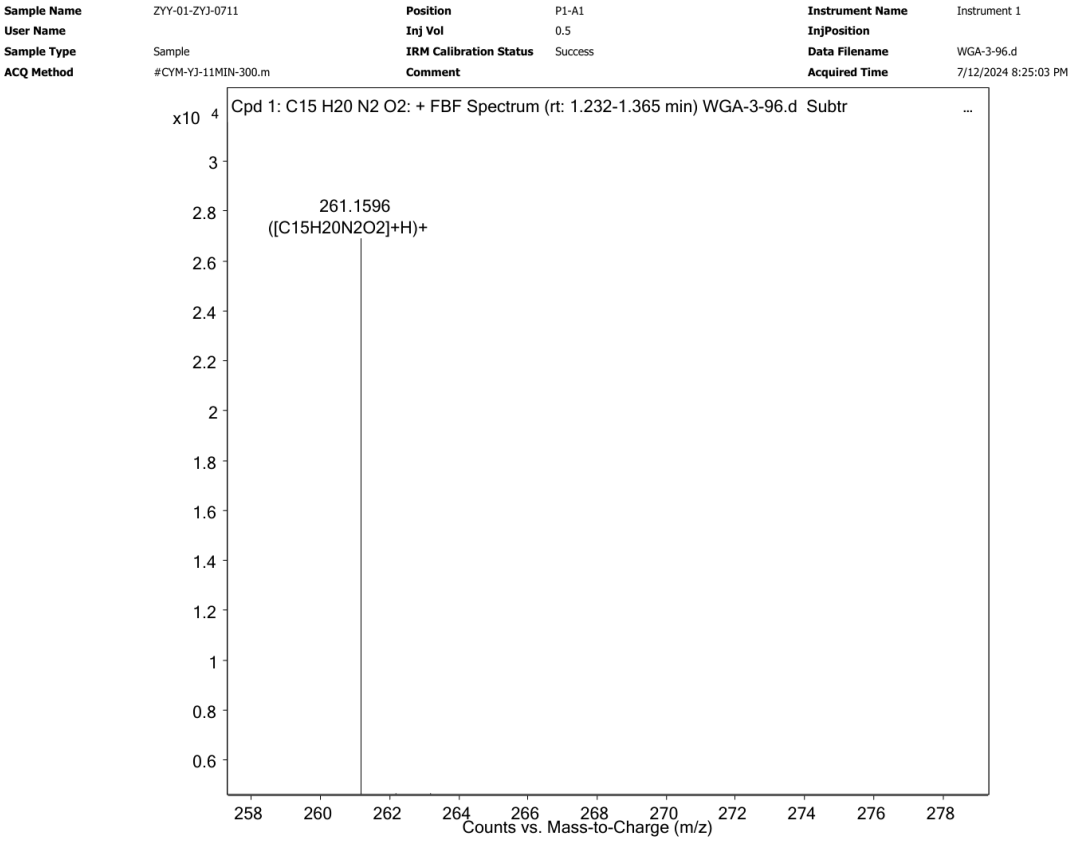


Figure S3 HRMS analysis compound **5aa**. **HRMS** (m/z) [ESI]: calculated for $C_{15}H_{21}N_2O_2^+$ [M+H]$^+$: 261.1598, found 261.1596.

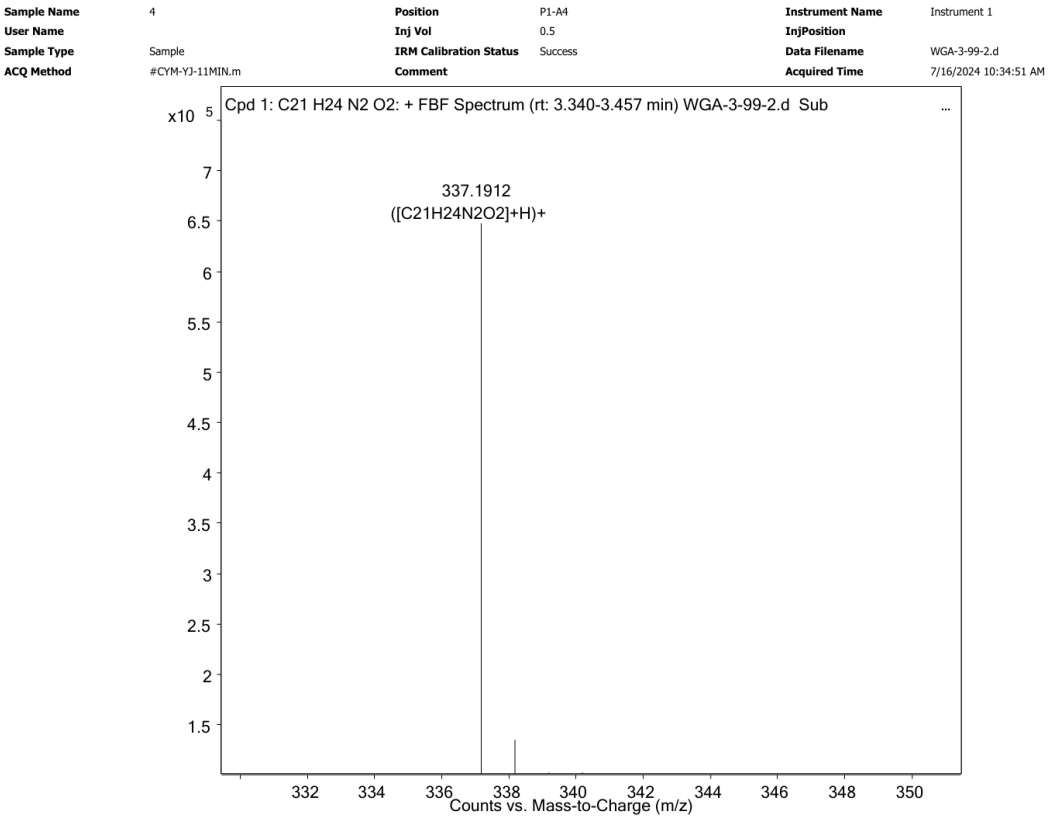
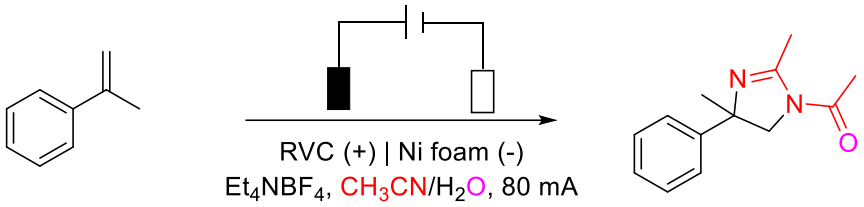


Figure S4 HRMS analysis compound **6aa**. **HRMS** (m/z) [ESI]: calculated for $C_{21}H_{25}N_2O_2^+$ [M+H]$^+$: 337.1911, found 337.1912.

5. Electrochemical applications

5.1 Preparation of gram - scale reactions



1a **2a**, 41%

A 400 mL round-bottom flask was charged with **1a** (8 mmol, 1 equiv), Et_4NBF_4 (32 mmol, 4.0 equiv), extra dry CH_3CN and H_2O as solvent (extra dry CH_3CN = 300 mL, H_2O = 250 μL). The flask was equipped with a reticulated vitreous carbon (RVC) anode (100 PPI, 3 cm × 2 cm × 2 cm) and a Ni foam (4 cm × 0.5 cm × 1 cm) cathode, Electrolysis was carried out at room temperature under air atmosphere, which using a constant current of 80 mA until the substrate was completely consumed (monitored by TLC, about 20 hours). When the reaction was finished, the reaction mixture was washed with water and extracted with ethyl acetate (3 × 100 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel to afford the **2a** in 41% yield (0.71 g) (petroleum ether/ethyl acetate = 3: 1 to 1: 1)

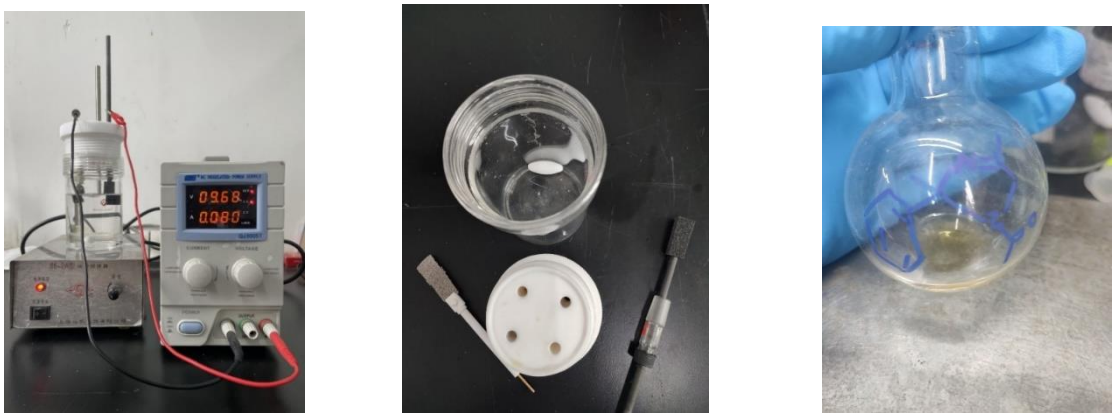
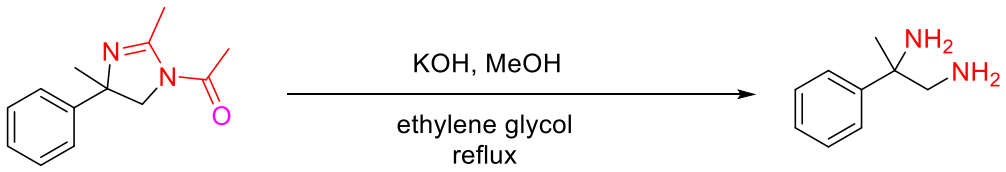


Figure S5 Electrolysis setup

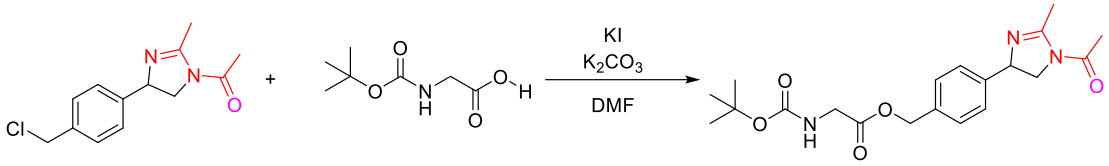
5.2 Dihydroimidazole hydrolysis



2a **2aaa**, 67%

2a (0.2 mmol) was added to a mixture of KOH (10 M in H_2O, 2.0 mL), MeOH (2.0 mL), and ethylene glycol (2.0 M), and the mixture was stirred while being heated to reflux (135 ℃) for 48 h. After the reaction is complete, the methanol solvent is first removed by vacuum distillation. The solution is then added dropwise to a separately prepared 1M HCl (10 mL) solution. The mixture is then poured into water and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers are washed with brine and dried over anhydrous Na_2SO_4. After vacuum concentration. Then dissolve it in $NaHCO_3$ (aqueous solution) (15 mL) and extract with CH_2Cl_2 (3 × 20 mL). Combine the organic layers and dry with Na_2SO_4, and concentrated under reduced pressure to obtain 20 mg (67% yield) of diamine product **2aaa**.

5.3 Dihydroimidazole-modified amino acids



4e **4ee**, 42%

In a dry round bottom flask, BOC-Glycine (0.08 mmol) was dissolved in DMF (3 mL). Then, K_2CO_3 (0.12 mmol), KI (0.12 mmol), and **4e** (0.08 mmol) were added, and the reaction was stirred at room temperature for 5 h. After completion of the reaction, 10 mL of ethyl acetate was added, followed by 10 mL of H_2O. The reaction mixture was then extracted with ethyl acetate (3 x 10 mL), and the combined products were washed with saturated saline. The combined organic phases were washed with saturated brine. The organic layer was then dried with Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (eluent: PE/EA = 1:1) to give the desired product **4ee** (42%).

6. Cyclic Voltammetry Studies

The cyclic voltammograms were recorded in an electrolyte solution of Et_4NBF_4 (0.1 M) in extra dry CH_3CN/H_2O using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and an Ag/AgCl reference electrode. The scan rate was 100 mV/s

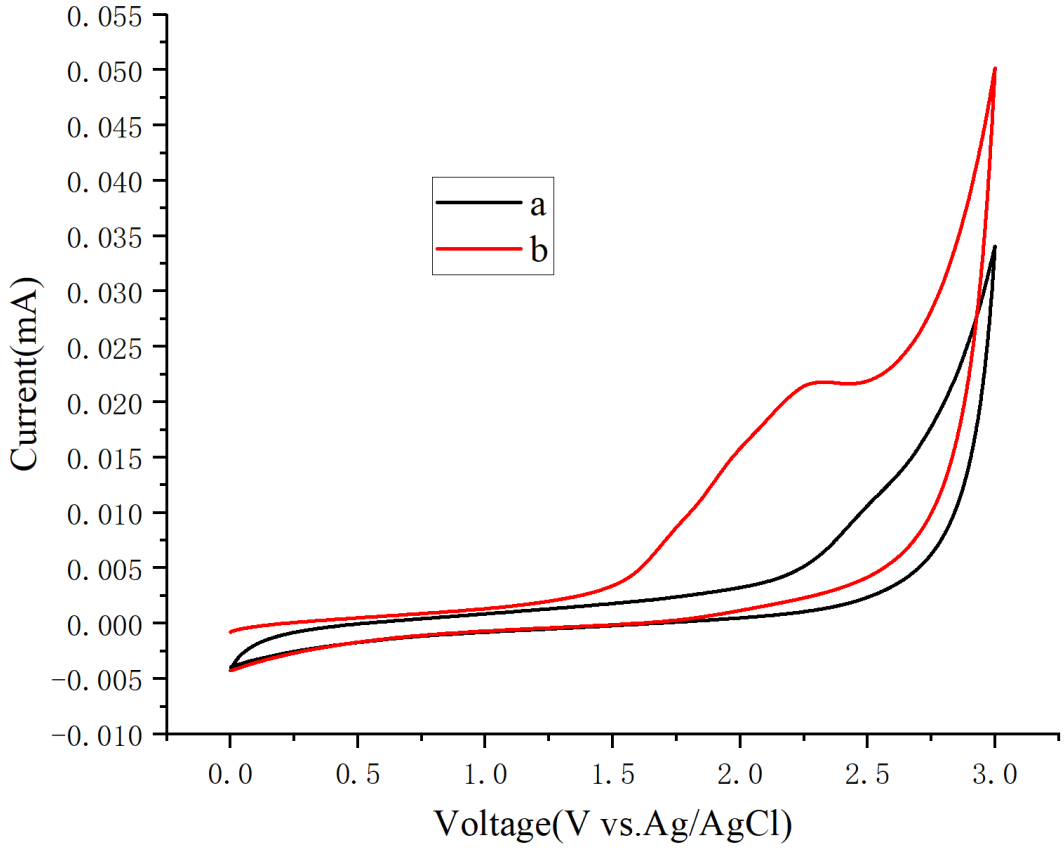
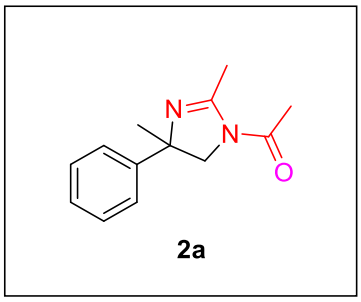


Figure S6 Cyclic voltammograms in CH_3CN/H_2O (6:0.005) + 0.1 M Et_4NBF_4. (a) Blank. (b)**1a** (0.2 mmol). working electrode, glassy carbon disk. Charting with IUPAC. Init E (V) = 0 V, Final E (V) = 0 V, High E (V) = 2 V.

7. Characterization Data for the Products



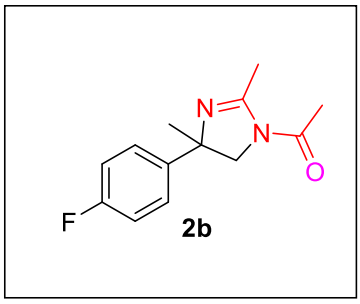
1-(2,4-dimethyl-4-phenyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (35.4 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 82% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.32 (m, 4H), 7.27 (m, 1H), 3.93 (s, 2H), 2.51 (s, 3H), 2.17 (s, 3H), 1.61 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 168.0, 157.0, 147.0, 128.7, 127.1, 125.2, 69.6, 61.2, 30.2, 25.1, 19.0.

HRMS (m/z) (ESI): calculated for $C_{13}H_{17}N_2O^+$ $[M+H]^+$: 217.1335, found: 217.1337.



1-(4-(4-fluorophenyl)-2,4-dimethyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

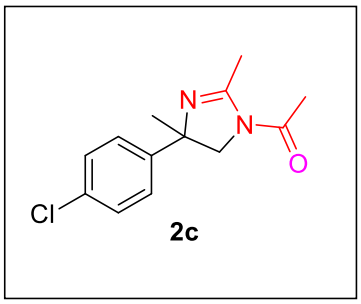
The title compound (35.6 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 76% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (qd, J = 5.2, 2.1 Hz, 2H), 7.07 – 6.96 (m, 2H), 3.88 (qd, J = 10.0, 4.5 Hz, 2H), 2.47 (d, J = 4.7 Hz, 3H), 2.16 (d, J = 4.4 Hz, 3H), 1.57 (d, J = 4.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 161.9 (d, J = 252.5 Hz), 157.1, 142.8 (d, J = 3.0 Hz), 126.9 (d, J = 8.08 Hz), 115.4 (d, J = 21.2 Hz), 69.1, 61.2, 30.3, 25.1, 19.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.92.

HRMS (m/z) (ESI): calculated for $C_{13}H_{16}FN_2O^+$ $[M+H]^+$: 235.1242, found: 235.1244.



2c

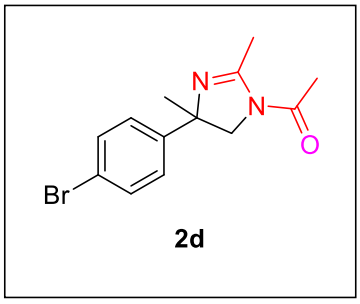
1-(4-(4-chlorophenyl)-2,4-dimethyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (35.5 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 71% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (s, 4H), 3.92 – 3.80 (m, 2H), 2.45 (s, 3H), 2.14 (s, 3H), 1.54 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.0, 157.2, 145.5, 132.9, 128.7, 126.7, 69.2, 61.0, 30.2, 25.0, 19.0.

HRMS (m/z) (ESI): calculated for $C_{13}H_{16}ClN_2O^+$ [M+H] $^+$: 251.0946, found: 251.0948.



2d

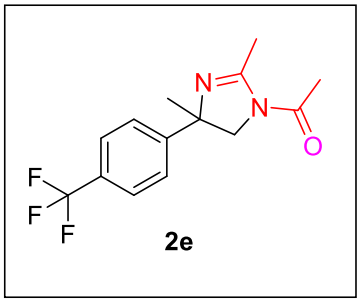
1-(4-(4-bromophenyl)-2,4-dimethyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (42.9 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 73% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.43 (m, 2H), 7.26 – 7.22 (m, 2H), 3.90 (d, J = 9.8 Hz, 1H), 3.84 (d, J = 9.8 Hz, 1H), 2.47 (s, 3H), 2.15 (s, 3H), 1.56 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.0, 157.2, 146.1, 131.7, 127.1, 121.0, 69.3, 61.0, 30.2, 25.0, 19.0.

HRMS (m/z) (ESI): calculated for $C_{13}H_{16}BrN_2O^+$ [M+H] $^+$: 295.0441, found: 295.0442.



2e

1-(2,4-dimethyl-4-(4-(trifluoromethyl) phenyl)-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (40.9 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 72% yield, yellow oil.

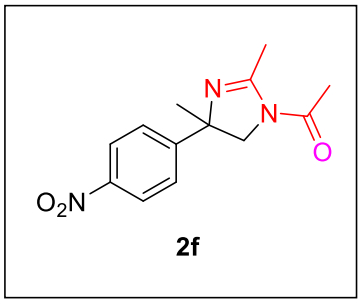
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 3.94 (d, J

= 9.8 Hz, 1H), 3.86 (d, *J* = 9.7 Hz, 1H), 2.46 (d, *J* = 1.9 Hz, 3H), 2.14 (s, 3H), 1.57 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 157.4, 150.9, 129.4 (q, *J* = 30.3 Hz), 125.7, 125.6 (q, *J* = 4.0 Hz), 122.8, 69.5, 60.8, 30.2, 25.0, 19.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.47.

HRMS (m/z) (ESI): calculated for $C_{14}H_{19}F_3N_3O^+$ $[M+NH_4]^+$: 302.1475, found: 302.1473.



2f

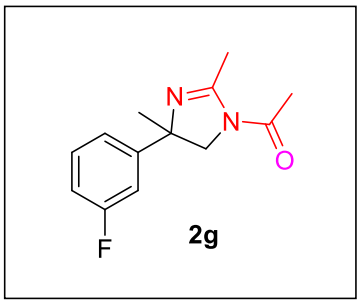
1-(2,4-dimethyl-4-(4-nitrophenyl)-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (31.9 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 61% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 8.17 (m, 2H), 7.58 – 7.54 (m, 2H), 3.99 (d, *J* = 9.9 Hz, 1H), 3.88 (d, *J* = 9.9 Hz, 1H), 2.48 (s, 3H), 2.18 (s, 3H), 1.60 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.0, 157.7, 154.2, 147.0, 126.4, 124.0, 69.6, 60.5, 30.4, 25.0, 19.0.

HRMS (m/z) (ESI): calculated for $C_{13}H_{16}N_3O_3^+$ $[M+H]^+$: 262.1187, found: 262.1189.



2g

1-(4-(3-fluorophenyl)-2,4-dimethyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

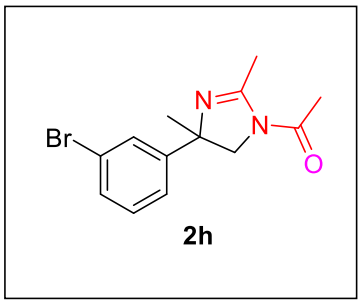
The title compound (38.9 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 83% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.26 (m, 1H), 7.13 – 7.06 (m, 2H), 6.94 – 6.88 (m, 1H), 3.91 – 3.83 (m, 2H), 2.49 – 2.44 (m, 3H), 2.14 (s, 3H), 1.56 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 163.0 (d, *J* = 252.5 Hz), 157.3, 149.7 (d, *J* = 10.1 Hz), 130.2 (d, *J* = 10.1 Hz), 120.8 (d, *J* = 10.1 Hz), 113.9 (d, *J* = 20.2 Hz), 112.5 (d, *J* = 20.2 Hz), 69.3, 60.9, 30.1, 25.0, 18.9.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.42.

HRMS (m/z) (ESI): calculated for $C_{13}H_{16}FN_2O^+$ $[M+H]^+$: 235.1242, found: 235.1244.



2h

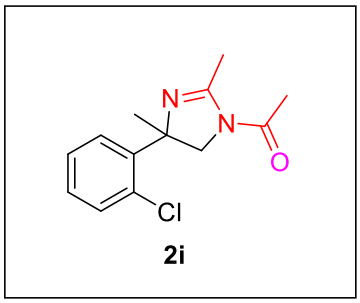
1-(4-(3-bromophenyl)-2,4-dimethyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (38.8 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 66% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.49 (m, 1H), 7.38 (dd, *J* = 6.9, 4.3 Hz, 1H), 7.29 (dt, *J* = 7.9, 4.8 Hz, 1H), 7.21 (td, *J* = 7.7, 4.4 Hz, 1H), 3.89 (qd, *J* = 10.0, 4.3 Hz, 2H), 2.48 (d, *J* = 4.6 Hz, 3H), 2.16 (d, *J* = 4.4 Hz, 3H), 1.57 (d, *J* = 4.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 157.3, 149.3, 130.2, 130.2, 128.5, 123.9, 122.8, 69.2, 60.9, 30.2, 25.0, 18.9.

HRMS (m/z) (ESI): calculated for $C_{13}H_{16}BrN_2O^+$ $[M+H]^+$: 295.0441, found: 295.0442.



2i

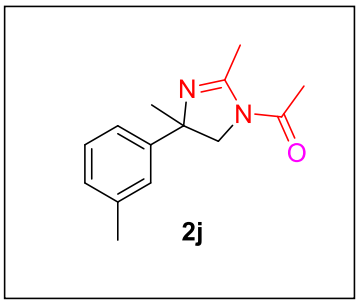
1-(4-(2-chlorophenyl)-2,4-dimethyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (32.5 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 65% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.37 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.27 – 7.19 (m, 2H), 4.20 (d, *J* = 10.5 Hz, 1H), 4.04 (d, *J* = 10.4 Hz, 1H), 2.49 (s, 3H), 2.19 (s, 3H), 1.65 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 156.3, 144.1, 131.0, 130.9, 128.6, 128.5, 127.1, 69.8, 59.6, 28.4, 25.1, 19.0.

HRMS (m/z) (ESI): calculated for $C_{13}H_{16}ClN_2O^+$ $[M+H]^+$: 251.0946, found: 251.0949.



2j

1-(2,4-dimethyl-4-(m-tolyl)-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

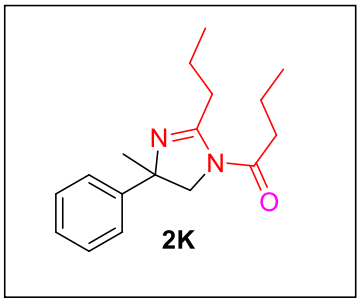
The title compound (25.3 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate

= 3: 1 to 1: 1) in 55% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (t, *J* = 7.6 Hz, 1H), 7.20 – 7.13 (m, 2H), 7.06 (d, *J* = 7.4 Hz, 1H), 3.90 (s, 2H), 2.48 (s, 3H), 2.35 (s, 3H), 2.15 (s, 3H), 1.58 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.0, 156.8, 147.0, 138.2, 128.5, 127.7, 125.8, 122.1, 69.5, 61.1, 30.2, 25.0, 21.6, 19.0.

HRMS (m/z) (ESI): calculated for $C_{14}H_{19}N_2O^+$ [M+H] $^+$: 231.1492, found: 231.1496.



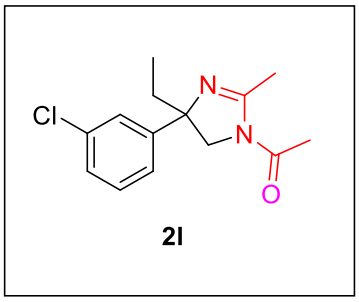
1-(4-methyl-4-phenyl-2-propyl-4,5-dihydro-1H-imidazol-1-yl) butan-1-one.

The title compound (33.3 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 10: 1) in 61% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.31 (m, 4H), 7.24 (td, *J* = 5.0, 2.3 Hz, 1H), 3.89 (d, *J* = 9.7 Hz, 1H), 3.85 (d, *J* = 9.7 Hz, 1H), 2.87 (td, *J* = 7.2, 2.5 Hz, 2H), 2.36 – 2.23 (m, 2H), 1.76 (q, *J* = 7.5 Hz, 2H), 1.69 – 1.63 (m, 2H), 1.59 (s, 3H), 1.03 (t, *J* = 7.4 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 170.4, 160.6, 147.3, 128.6, 127.0, 125.3, 69.6, 60.8, 39.0, 33.8, 30.2, 20.4, 17.7, 14.1, 13.8.

HRMS (m/z) (ESI): calculated for $C_{17}H_{25}N_2O^+$ [M+H] $^+$: 273.1962, found: 273.1959.



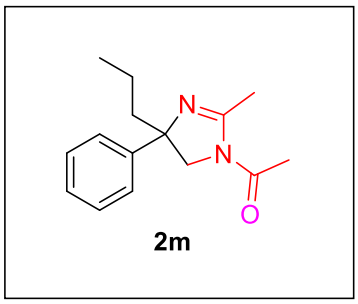
1-(4-(3-chlorophenyl)-4-ethyl-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (39.1 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 74% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (s, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.23 (dd, *J* = 6.5, 4.6 Hz, 2H), 3.96 (d, *J* = 10.0 Hz, 1H), 3.86 (d, *J* = 9.9 Hz, 1H), 2.49 (d, *J* = 1.5 Hz, 3H), 2.17 (s, 3H), 1.90 – 1.81 (m, 2H), 0.85 – 0.80 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 157.2, 148.5, 134.4, 129.8, 127.0, 126.0, 123.8, 72.8, 58.6, 36.1, 25.0, 18.8, 8.3.

HRMS (m/z) (ESI): calculated for $C_{14}H_{18}ClN_2O^+$ [M+H] $^+$: 265.1103, found: 265.1108.



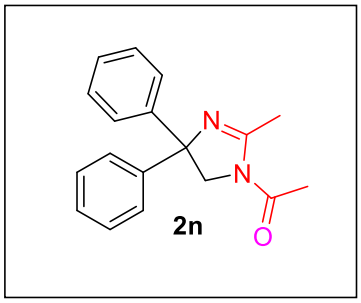
1-(2-methyl-4-phenyl-4-propyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (32.2 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 66% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.29 (m, 4H), 7.25 – 7.20 (m, 1H), 3.96 (d, *J* = 9.9 Hz, 1H), 3.89 (d, *J* = 9.8 Hz, 1H), 2.48 (s, 3H), 2.15 (s, 3H), 1.80 (qdd, *J* = 13.6, 11.5, 4.8 Hz, 2H), 1.33 (tdd, *J* = 12.1, 7.4, 5.0 Hz, 1H), 1.21 – 1.07 (m, 1H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 156.8, 146.7, 128.5, 126.9, 125.5, 72.8, 59.2, 46.0, 25.0, 18.9, 17.3, 14.3.

HRMS (m/z) (ESI): calculated for $C_{15}H_{21}N_2O^+$ [M+H] $^+$: 245.1649, found: 245.1650.



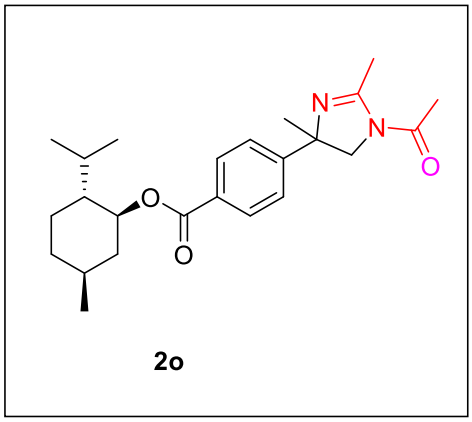
1-(2-methyl-4,4-diphenyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (33.9 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 61% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 3.9 Hz, 10H), 4.44 (s, 2H), 2.53 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.7, 158.7, 146.2, 128.7, 127.3, 126.5, 68.4, 60.6, 25.1, 19.0.

HRMS (m/z) (ESI): calculated for $C_{18}H_{19}N_2O^+$ [M+H] $^+$: 279.1492, found: 279.1496.



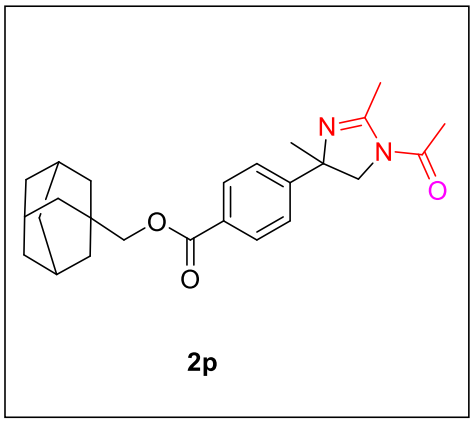
(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-(1-acetyl-2,4-dimethyl-4,5-dihydro-1H-imidazol-4-yl) benzoate.

The title compound (43.8 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 55% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.96 (m, 2H), 7.48 – 7.39 (m, 2H), 4.90 (td, *J* = 10.9, 4.4 Hz, 1H), 3.98 – 3.83 (m, 2H), 2.47 (s, 3H), 2.14 (s, 3H), 2.11 – 2.05 (m, 1H), 1.95 – 1.86 (m, 1H), 1.74 – 1.67 (m, 2H), 1.58 (s, 3H), 1.56 – 1.48 (m, 2H), 1.14 – 1.04 (m, 2H), 0.94 – 0.86 (m, 7H), 0.76 (dd, *J* = 7.0, 1.3 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 165.8, 157.1, 151.9, 151.8, 130.0, 129.7, 129.7, 125.2, 74.9, 69.6, 60.8, 47.3, 41.0, 34.4, 31.5, 30.3, 30.2, 26.6, 26.6, 25.0, 23.8, 22.1, 20.8, 19.0, 16.6.

HRMS (m/z) (ESI): calculated for $C_{24}H_{35}N_2O_3^+$ [M+H] $^+$: 399.2643, found: 399.2651.



2p

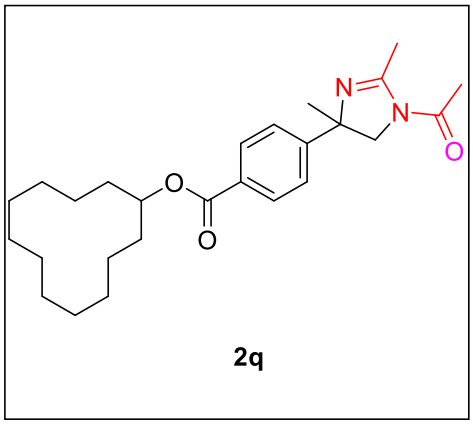
Adamantan-1-ylmethyl 4-(1-acetyl-2,4-dimethyl-4,5-dihydro-1H-imidazol-4-yl) benzoate.

The title compound (35.1 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 43% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 3.97 – 3.87 (m, 4H), 2.49 (s, 3H), 2.17 (s, 3H), 2.00 (s, 3H), 1.77 – 1.65 (m, 7H), 1.63 – 1.60 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 166.5, 157.6, 151.9, 130.0, 129.5, 125.3, 74.6, 69.6, 60.9, 39.5, 37.1, 33.7, 30.3, 28.2, 25.1, 19.0.

HRMS (m/z) (ESI): calculated for $C_{25}H_{33}N_2O_3^+$ [M+H] $^+$: 409.2486, found: 409.2496.

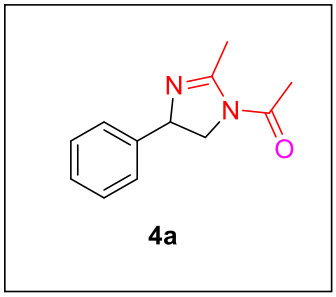


2q

Cyclododecyl 4-(1-acetyl-2,4-dimethyl-4,5-dihydro-1H-imidazol-4-yl) benzoate.

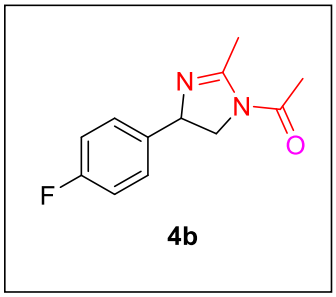
The title compound (34.1 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 40% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 5.24 (tt, *J* = 7.3, 4.6 Hz, 1H), 3.97 – 3.82 (m, 2H), 2.49 (s, 3H), 2.16 (s, 3H), 1.81 (dt, *J* = 13.3, 6.7 Hz, 2H), 1.63 (dd, *J* = 10.4, 4.4 Hz, 2H), 1.59 (s, 3H), 1.44 (p, *J* = 6.8, 4.9 Hz, 9H), 1.39 – 1.32 (m, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 166.1, 157.3, 151.7, 130.0, 129.8, 125.2, 73.1, 69.6, 60.9, 30.3, 29.2, 29.2, 25.1, 24.3, 24.1, 23.5, 23.3, 23.3, 21.0, 19.0.
HRMS (m/z) (ESI): calculated for $C_{26}H_{39}N_2O_3^+$ [M+H] $^+$: 427.2956, found: 427.2961.



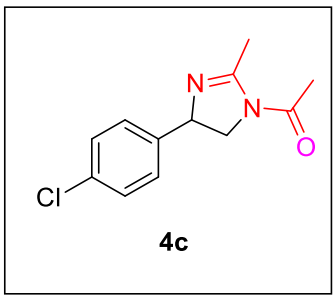
4a

1-(2-methyl-4-phenyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.
The title compound (30.3 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 1: 1 to 0: 1) in 75% yield, yellow oil.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (m, 2H), 7.34 – 7.26 (m, 3H), 5.13 (ddd, *J* = 10.2, 7.8, 1.8 Hz, 1H), 4.28 (t, *J* = 10.2 Hz, 1H), 3.73 (dd, *J* = 10.0, 7.5 Hz, 1H), 2.52 (d, *J* = 1.6 Hz, 3H), 2.20 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.0, 159.2, 142.3, 129.0, 127.8, 126.6, 66.9, 55.3, 25.1, 18.9.
HRMS (m/z) (ESI): calculated for $C_{12}H_{15}N_2O^+$ [M+H] $^+$: 203.1179, found: 203.1175.



4b

1-(4-(4-fluorophenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.
The title compound (26.9 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 2: 1 to 0: 1) in 61% yield, yellow oil.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.17 (m, 2H), 7.07 – 7.00 (m, 2H), 5.09 (ddd, *J* = 9.8, 7.7, 1.8 Hz, 1H), 4.25 (t, *J* = 10.2 Hz, 1H), 3.66 (dd, *J* = 10.1, 7.6 Hz, 1H), 2.49 (d, *J* = 1.7 Hz, 3H), 2.18 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 162.6 (d, *J* = 242.4 Hz), 159.5, 138.1 (d, *J* = 10.1 Hz), 128.3 (d, *J* = 10.1 Hz), 115.8 (d, *J* = 20.2 Hz), 66.3, 55.4, 25.1, 18.9.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.72.
HRMS (m/z) (ESI): calculated for $C_{12}H_{14}FN_2O^+$ [M+H] $^+$: 221.1085, found: 221.1077.



4c

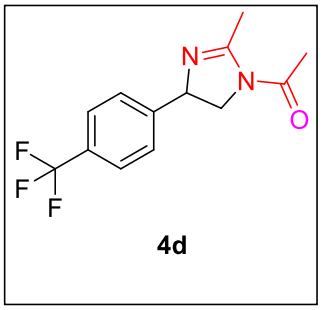
1-(4-(4-chlorophenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (27.4 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 58% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 2H), 7.21 – 7.15 (m, 2H), 5.08 (ddd, *J* = 10.0, 7.8, 1.9 Hz, 1H), 4.24 (t, *J* = 10.2 Hz, 1H), 3.64 (dd, *J* = 10.0, 7.6 Hz, 1H), 2.49 (d, *J* = 1.7 Hz, 3H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 159.7, 140.7, 133.7, 129.1, 128.0, 66.2, 55.2, 25.1, 19.0.

HRMS (m/z) (ESI): calculated for $C_{12}H_{14}ClN_2O^+$[M+H] $^+$: 237.0790, found: 237.0783.



4d

1-(2-methyl-4-(4-(trifluoromethyl) phenyl)-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

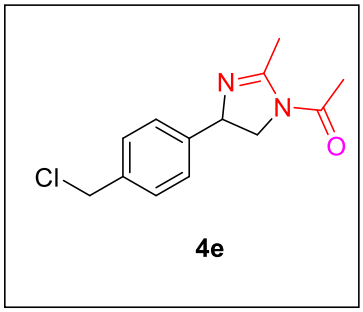
The title compound (33.5 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 62% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 5.18 (t, *J* = 9.2 Hz, 1H), 4.29 (t, *J* = 10.3 Hz, 1H), 3.67 (dd, *J* = 10.1, 7.6 Hz, 1H), 2.51 (d, *J* = 1.6 Hz, 3H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 159.9, 146.2, 130.1 (q, *J* = 32.3 Hz), 127.0, 125.9 (q, *J* = 4.0 Hz), 123.9 (q, *J* = 273.7 Hz), 66.5, 55.0, 25.1, 19.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.51.

HRMS (m/z) (ESI): calculated for $C_{13}H_{14}F_3N_2O^+$ [M+H] $^+$: 271.1053, found: 271.1057.



4e

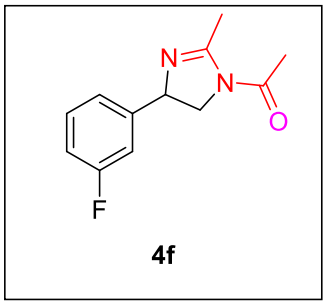
1-(4-(4-(chloromethyl) phenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl)ethan-1-one.

The title compound (33.5 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 67% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 5.17 – 5.09 (m, 1H), 4.58 (s, 2H), 4.26 (t, *J* = 10.2 Hz, 1H), 3.70 (dd, *J* = 10.0, 7.5 Hz, 1H), 2.51 (d, *J* = 1.6 Hz, 3H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 160.0, 142.5, 137.1, 129.3, 127.0, 66.5, 55.2, 46.0, 25.2, 19.0.

HRMS (m/z) (ESI): calculated for $C_{13}H_{16}ClN_2O^+$ [M+H] $^+$: 251.0946, found: 251.0947.



4f

1-(4-(3-fluorophenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

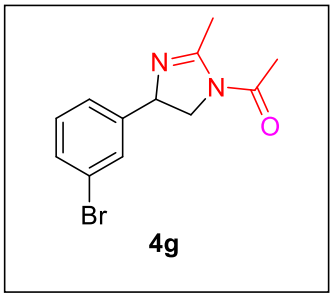
The title compound (35.2 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 80% yield, yellow oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 (m,1H), 7.02 (m, 1H), 7.00 – 6.94 (m, 2H), 5.10 (ddd, *J* = 9.9, 7.7, 1.9 Hz, 1H), 4.25 (t, *J* = 10.3 Hz, 1H), 3.67 (dd, *J* = 10.1, 7.6 Hz, 1H), 2.49 (d, *J* = 1.6 Hz, 3H), 2.17 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.0, 163.2 (d, *J* = 202.0 Hz), 159.6, 144.9 (d, *J* = 6.1 Hz), 130.5 (d, *J* = 10.1 Hz), 122.2 (d, *J* = 2.0 Hz), 114.7 (d, *J* = 20.2 Hz), 113.6 (d, *J* = 20.2 Hz), 66.5, 55.1, 25.1, 19.0.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -112.33.

HRMS (m/z) (ESI): calculated for $C_{12}H_{14}FN_2O^+$ [M+H] $^+$: 221.1085, found: 221.1080.



4g

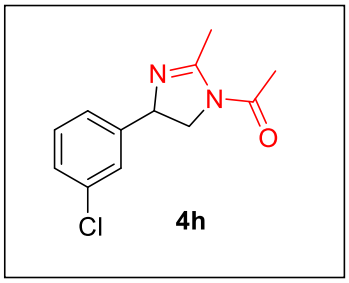
1-(4-(3-bromophenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (39.8 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 71% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.38 (m, 2H), 7.25 – 7.15 (m, 2H), 5.08 (ddd, *J* = 10.2, 7.8, 1.9 Hz, 1H), 4.24 (t, *J* = 10.3 Hz, 1H), 3.66 (dd, *J* = 10.1, 7.7 Hz, 1H), 2.49 (d, *J* = 1.7 Hz, 3H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 159.7, 144.6, 130.9, 130.5, 129.7, 125.3, 123.1, 66.4, 55.1, 25.1, 19.0.

HRMS (m/z) (ESI): calculated for $C_{12}H_{14}BrN_2O^+$ [M+H] $^+$: 281.0285, found: 281.0281.



4h

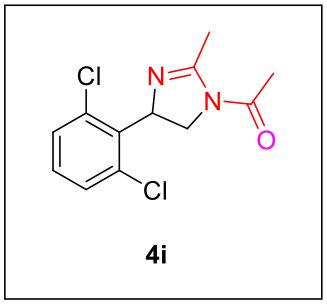
1-(4-(3-chlorophenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (28.8 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 61% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.25 (d, *J* = 1.9 Hz, 1H), 7.14 (dt, *J* = 7.0, 1.9 Hz, 1H), 5.10 (ddd, *J* = 10.0, 7.7, 1.9 Hz, 1H), 4.26 (t, *J* = 10.3 Hz, 1H), 3.68 (dd, *J* = 10.1, 7.6 Hz, 1H), 2.51 (d, *J* = 1.7 Hz, 3H), 2.19 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 159.7, 144.3, 134.8, 130.2, 128.0, 126.8, 124.8, 66.4, 55.1, 25.1, 19.0.

HRMS (m/z) (ESI): calculated for $C_{12}H_{14}ClN_2O^+$ [M+H] $^+$: 237.0790, found: 237.0795.



4i

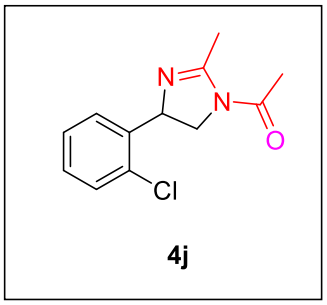
1-(4-(2,6-dichlorophenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (33.5 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 62% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.15 (dd, *J* = 8.5, 7.5 Hz, 1H), 5.98 – 5.89 (m, 1H), 4.15 (dd, *J* = 11.5, 10.1 Hz, 1H), 3.98 (dd, *J* = 10.0, 8.4 Hz, 1H), 2.44 (d, *J* = 1.9 Hz, 3H), 2.19 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 160.5, 135.9, 134.9, 129.5, 129.5, 63.5, 51.3, 25.1, 18.8.

HRMS (m/z) (ESI): calculated for $C_{12}H_{13}Cl_2N_2O^+$ [M+H] $^+$: 271.0400, found: 271.0400.



4j

1-(4-(2-chlorophenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (24.6 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate

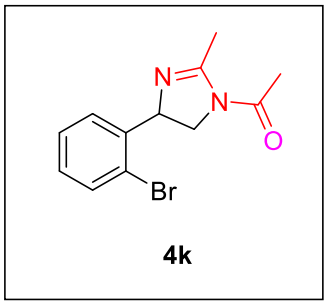
= 3: 1 to 1: 1) in 52% yield, white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 1H), 7.34 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.30 – 7.22 (m, 2H), 5.47 – 5.39 (m, 1H), 4.40 (t, *J* = 10.4 Hz, 1H), 3.54 (dd, *J* = 10.1, 7.5 Hz, 1H), 2.54 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 160.3, 140.3, 132.3, 129.5, 128.9, 127.7, 127.3, 64.5, 54.4, 25.2, 19.1.

HRMS (m/z) (ESI): calculated for $C_{12}H_{14}ClN_2O^+$ [M+H] $^+$: 237.0790, found: 237.0784.

MP: 102-106 ℃



4k

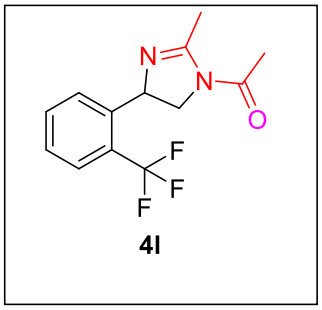
1-(4-(2-bromophenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (28.0 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 50% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.31 (qd, *J* = 7.8, 1.8 Hz, 2H), 7.16 (ddd, *J* = 7.8, 6.6, 2.5 Hz, 1H), 5.44 – 5.36 (m, 1H), 4.42 (t, *J* = 10.3 Hz, 1H), 3.52 (dd, *J* = 10.1, 7.4 Hz, 1H), 2.54 (d, *J* = 1.7 Hz, 3H), 2.15 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 160.4, 142.0, 132.8, 129.2, 128.0, 127.9, 122.6, 66.3, 54.5, 25.2, 19.1.

HRMS (m/z) (ESI): calculated for $C_{12}H_{14}BrN_2O^+$ [M+H] $^+$: 281.0285, found: 281.0286.



4l

1-(2-methyl-4-(2-(trifluoromethyl) phenyl)-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (35.1 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 65% yield, white solid.

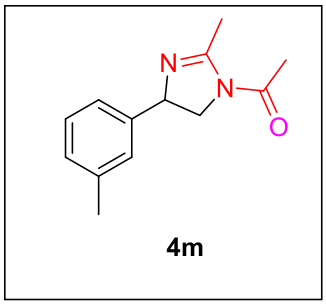
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 5.50 (t, *J* = 9.2 Hz, 1H), 4.26 (t, *J* = 10.4 Hz, 1H), 3.52 (dd, *J* = 10.2, 7.6 Hz, 1H), 2.54 (d, *J* = 1.6 Hz, 3H), 2.14 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 160.5, 140.9, 132.8, 127.8 (q, *J* = 12.1 Hz), 127.4 (q, *J* = 30.3 Hz), 125.9 (q, *J* = 10.1 Hz), 123.1, 63.0, 55.7 (q, *J* = 2.02 Hz), 25.1, 19.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -58.91.

HRMS (m/z) (ESI): calculated for $C_{13}H_{14}F_3N_2O^+$ [M+H] $^+$: 271.1053, found: 271.1054.

MP: 110~114 ℃



4m

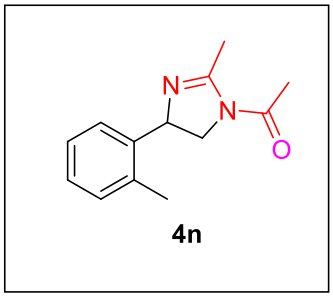
1-(2-methyl-4-(m-tolyl)-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (19.5 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 45% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.06 – 6.98 (m, 2H), 5.07 (ddd, *J* = 9.9, 7.7, 1.9 Hz, 1H), 4.22 (t, *J* = 10.2 Hz, 1H), 3.69 (dd, *J* = 10.0, 7.6 Hz, 1H), 2.50 (d, *J* = 1.7 Hz, 3H), 2.35 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 159.0, 142.2, 138.7, 128.8, 128.5, 127.1, 123.6, 70.0, 55.3, 25.1, 21.6, 19.0.

HRMS (m/z) (ESI): calculated for $C_{13}H_{17}N_2O^+$ $[M+H]^+$: 217.1336, found: 217.1329.



4n

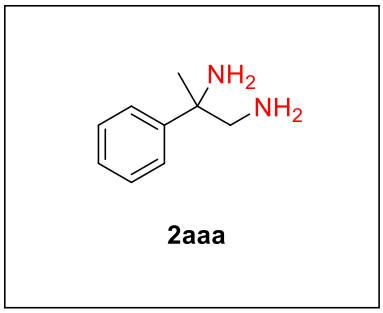
1-(2-methyl-4-(o-tolyl)-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one.

The title compound (17.7 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 3: 1 to 1: 1) in 41% yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.14 (m, 4H), 5.29 (ddd, *J* = 10.7, 7.5, 1.8 Hz, 1H), 4.28 (t, *J* = 10.1 Hz, 1H), 3.56 (dd, *J* = 9.8, 7.5 Hz, 1H), 2.53 (d, *J* = 1.7 Hz, 3H), 2.33 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 159.4, 140.8, 134.6, 130.5, 127.6, 126.7, 125.8, 63.8, 54.6, 25.2, 19.6, 19.0.

HRMS (m/z) (ESI): calculated for $C_{13}H_{17}N_2O^+$ $[M+H]^+$: 217.1336, found: 217.1336.



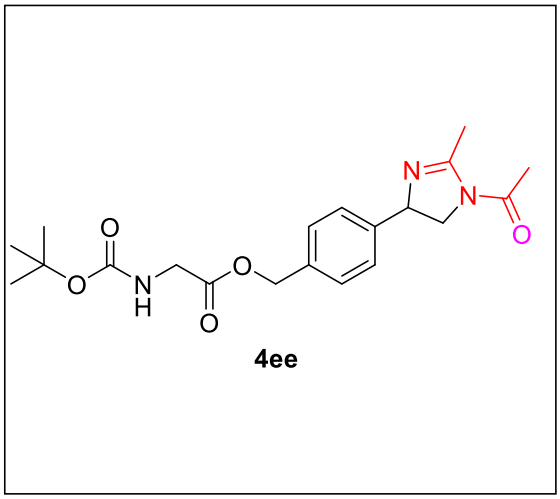
2aaa

2-phenylpropane-1,2-diamine.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.40 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 2.91 (d, *J* = 13.0 Hz, 1H), 2.74 (d, *J* = 12.9 Hz, 1H), 1.80 (s, 4H), 1.42 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.9, 128.4, 126.6, 125.5, 56.2, 54.5, 28.8.

HRMS (m/z) (ESI): calculated for $C_9H_{15}N_2^+$ [M+H] $^+$: 151.1230, found: 151.1228.



4ee

4-(1-acetyl-2-methyl-4,5-dihydro-1H-imidazol-4-yl) benzyl (tert-butoxycarbonyl) glycinate.

The title compound (13.1 mg) was isolated by flash chromatography (petroleum ether/ethyl acetate = 1: 1 to 0: 1) in 42 % yield, yellow oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.35 (d, *J* = 7.9 Hz, 2H), 7.26 (s, 2H), 5.17 (s, 2H), 5.14 (d, *J* = 6.7 Hz, 1H), 5.00 (s, 1H), 4.29 (t, *J* = 10.2 Hz, 1H), 3.94 (d, *J* = 5.7 Hz, 2H), 3.72 (dd, *J* = 10.0, 7.5 Hz, 1H), 2.54 (s, 3H), 2.19 (s, 3H), 1.44 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-d) δ 170.2, 162.7, 167.9, 155.7, 134.9, 129.0, 126.7, 66.7, 66.1, 55.1, 42.5, 29.2, 25.0, 18.7.

HRMS (m/z) (ESI): calculated for $C_{20}H_{28}N_3O_5^+$ [M+H] $^+$: 390.2024, found: 390.2022.

8. Single-Crystal X-Ray Diffraction

Single-crystal X-ray diffraction data were collected on a Rigaku XtaLAB Synergy, Dualflex, Rigaku XtaLAB Synergy-S diffractometer coupled to a RigakuHypix detector with Cu Kα radiation (λ = 1.54184 Å). Single crystals suitable for X-ray diffraction were obtained by recrystallization from a solution of $CHCl_3$ layered the crystal was kept at a steady T = 100 K during the data collection. The structures were solved with the SHELXT solution program by using Olex 2 (Dolomanov et al., 2009) as the graphical interface. The model was refined using Least Squares minimisation with the 2018/3 version of the program SHELXL.[2]

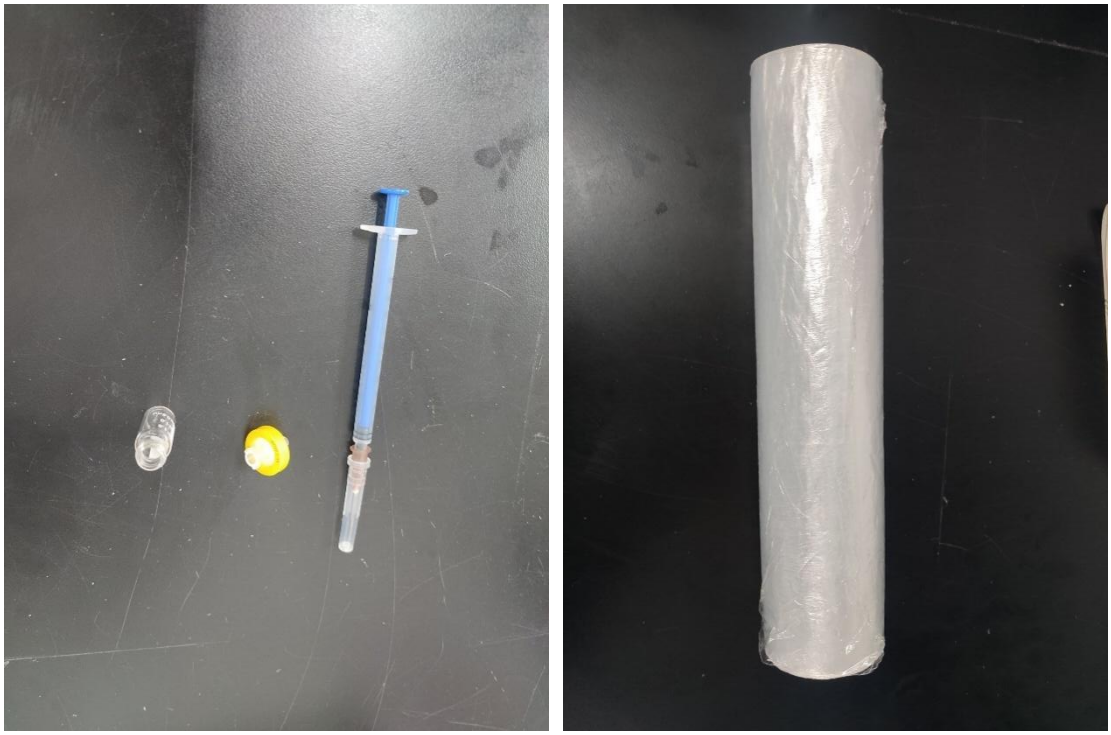


Figure S7 Preparation of crystals: The solvent used was $CHCl_3$, and after the solid was fully dissolved, it was drawn up in a 1 mL syringe, punched through the filter membrane into a small-mouthed glass vial, sealed with a cling film, and then several holes were pierced with a needle, and left to evaporate until crystals were produced.

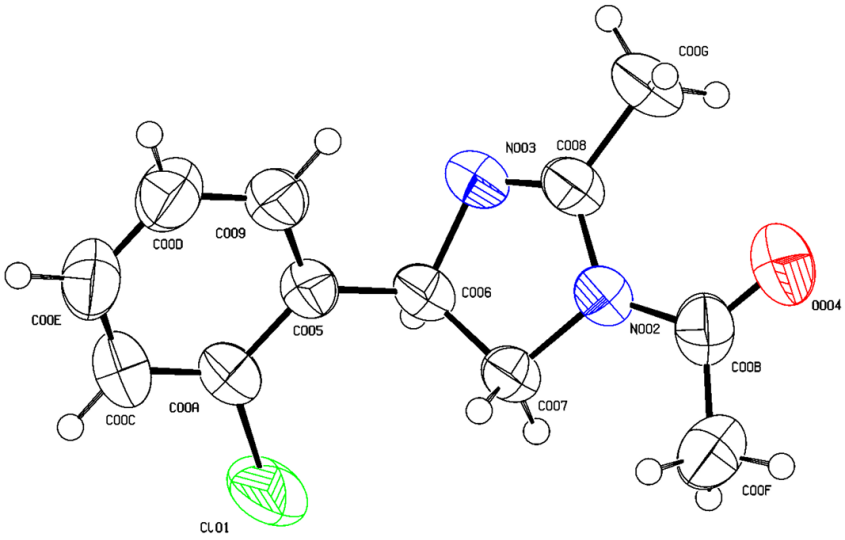


Figure S8 X-ray molecular structure of **4j** (ellipsoids set at 50% probability).

Table S2 Crystal data and structure refinement for **4j**

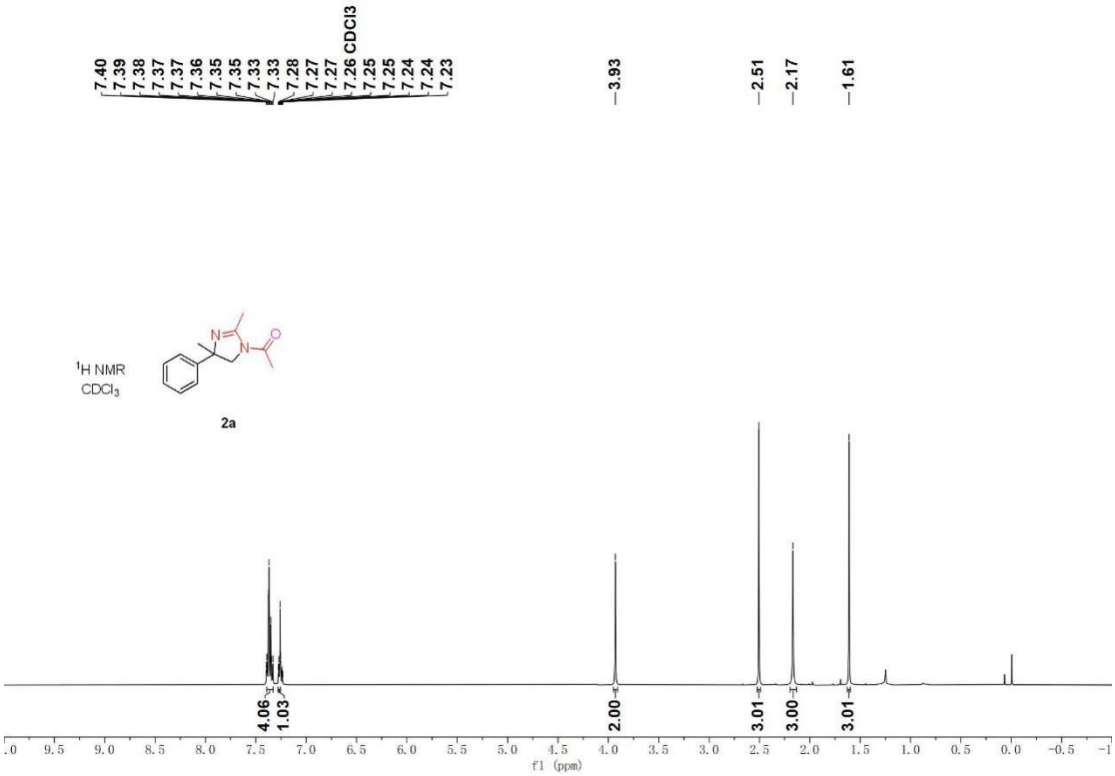
Identification code	**4j**
Empirical formula	$C_{12}H_{13}ClN_2O$
Formula weight	236.69
Temperature/K	295.89(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.3724(5)
b/Å	10.2633(5)
c/Å	13.8066(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1186.38(11)
Z	4
ρ_{calc}g/cm^3	1.325
μ/mm^{-1}	2.690
F(000)	496.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.74 to 153.67
Index ranges	$-6 \le h \le 10$, $-12 \le k \le 12$, $-16 \le l \le 16$
Reflections collected	5283
Independent reflections	2177 [R_{int} = 0.0201, R_{sigma} = 0.0255]
Data/restraints/parameters	2177/0/147
Goodness-of-fit on F^2	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0455, wR_2 = 0.1326
Final R indexes [all data]	R_1 = 0.0500, wR_2 = 0.1366
Largest diff. peak/hole / e Å^{-3}	0.12/-0.25

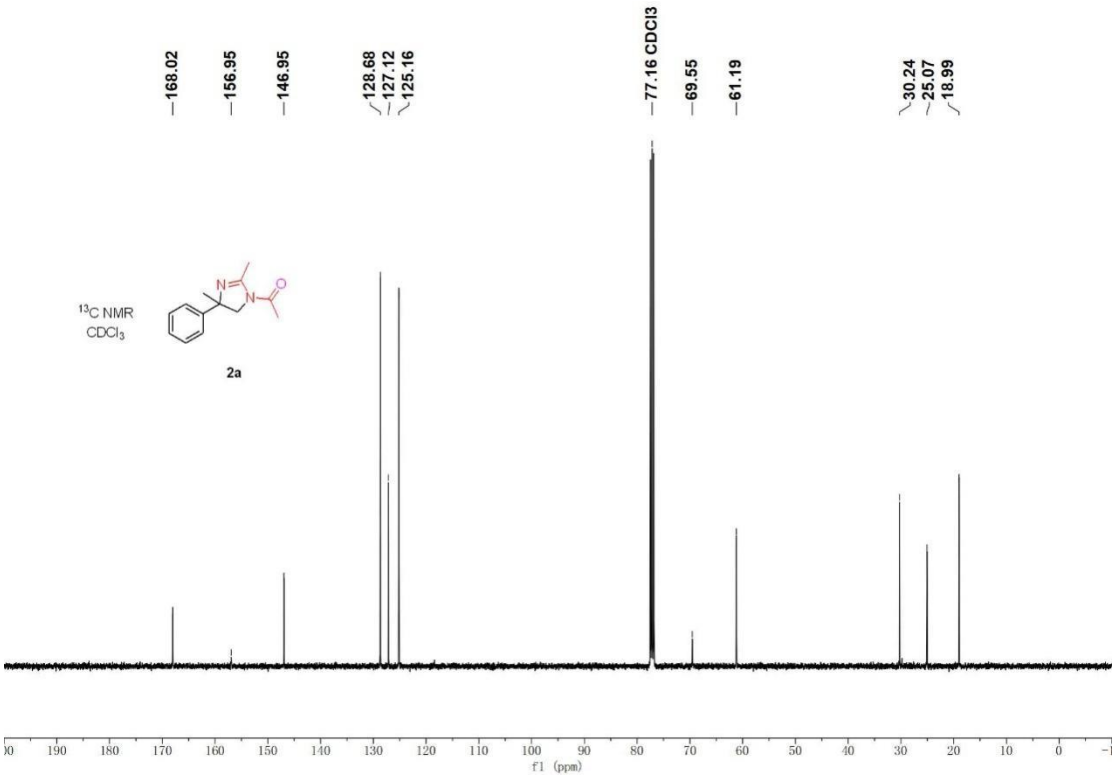
Table S3 Selected bond distances and angles for **4j**.

Bond Distances(Å)	
Cl01- C00A	1.743(3)
N002 - C007	1.475(4)
N002 - C008	1.411(4)
N002 - C00B	1.369(4)
N003 - C006	1.468(4)
N003 - C008	1.264(4)
O004 - C00B	1.214(4)
C005 - C006	1.510(4)
C005 - C009	1.383(4)
Cl01 - C00A	1.743(3)
N002 - C007	1.475(4)
N002 - C008	1.411(4)
N002 - C00B	1.369(4)
N003 - C006	1.468(4)
N003 - C008	1.264(4)
O004 - C00B	1.214(4)
C005 - C006	1.510(4)
C005 - C009	1.383(4)

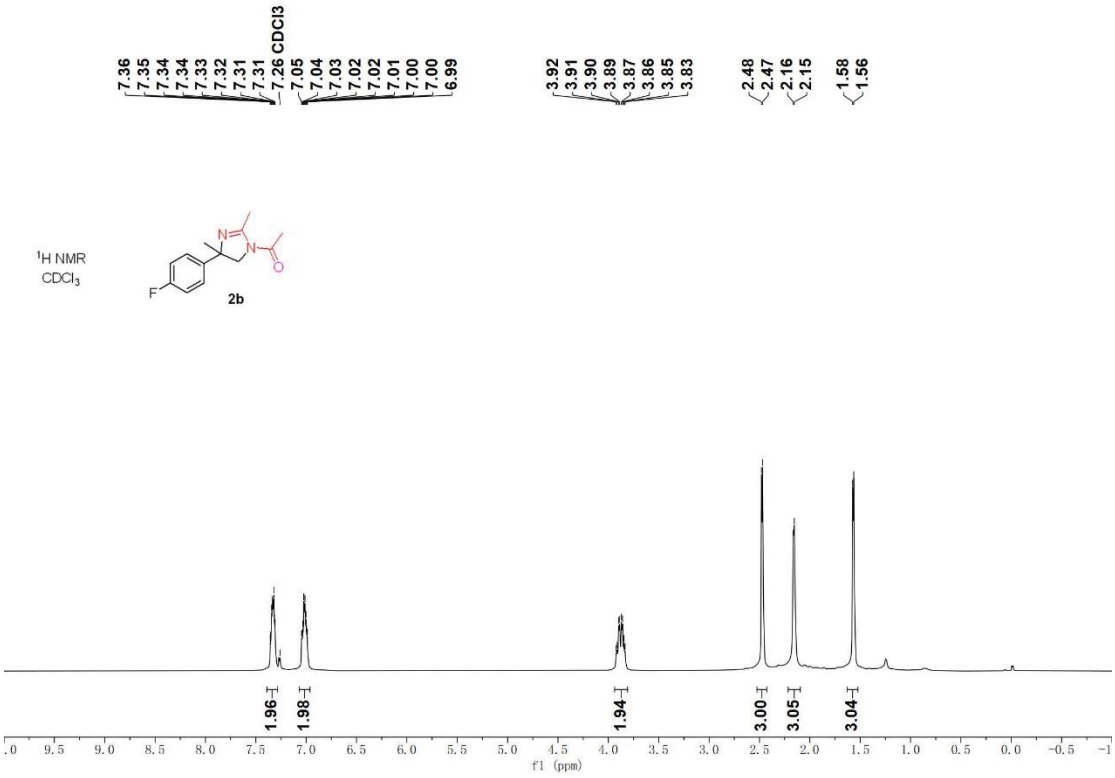
9. Copies of ^{1}H NMR and ^{13}C NMR for the Products

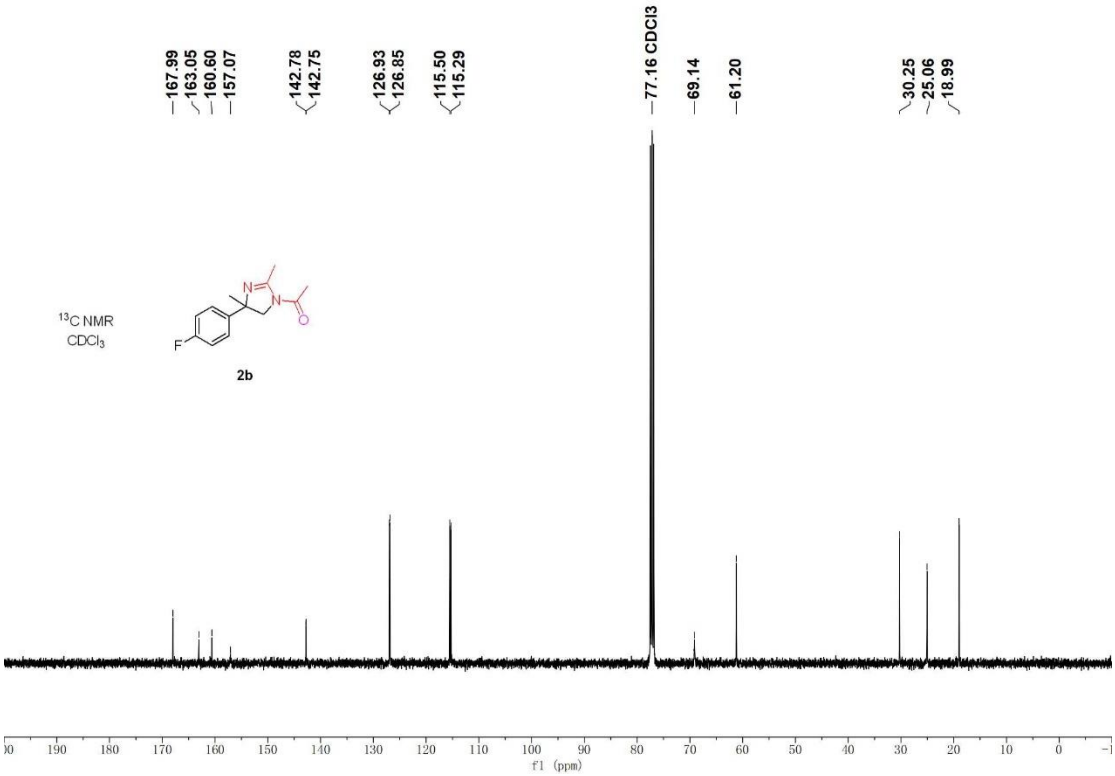
1-(2,4-dimethyl-4-phenyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**2a**)

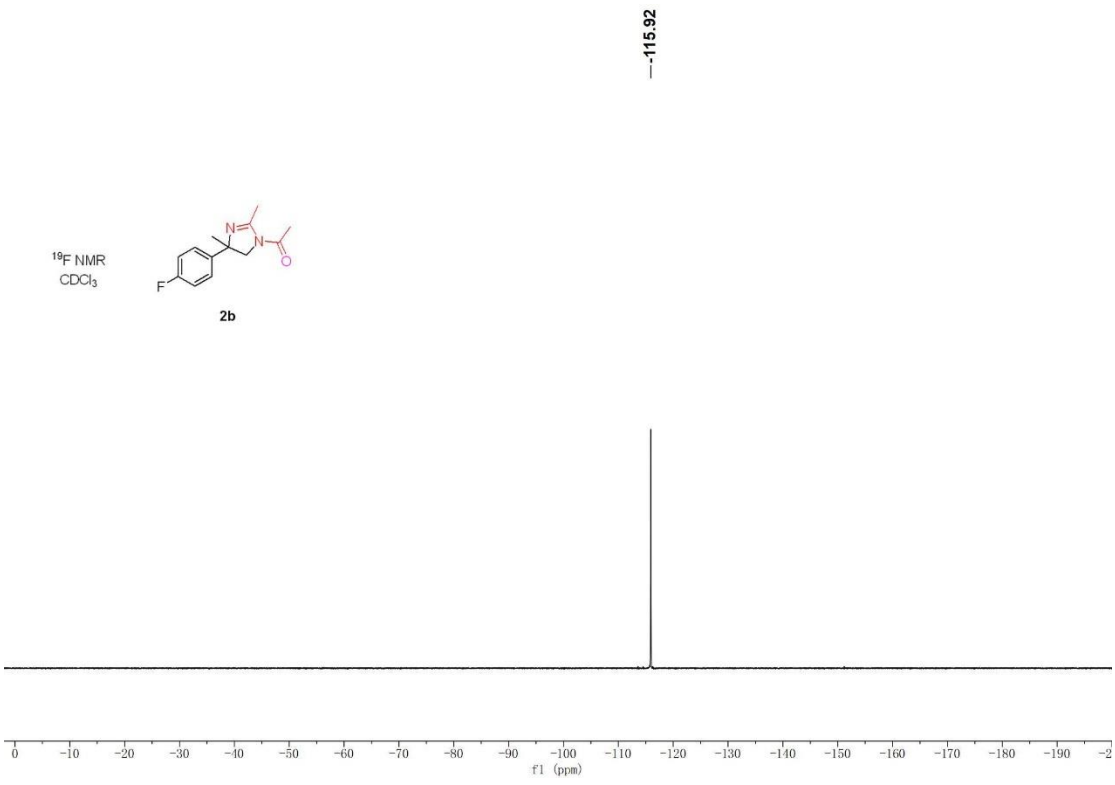




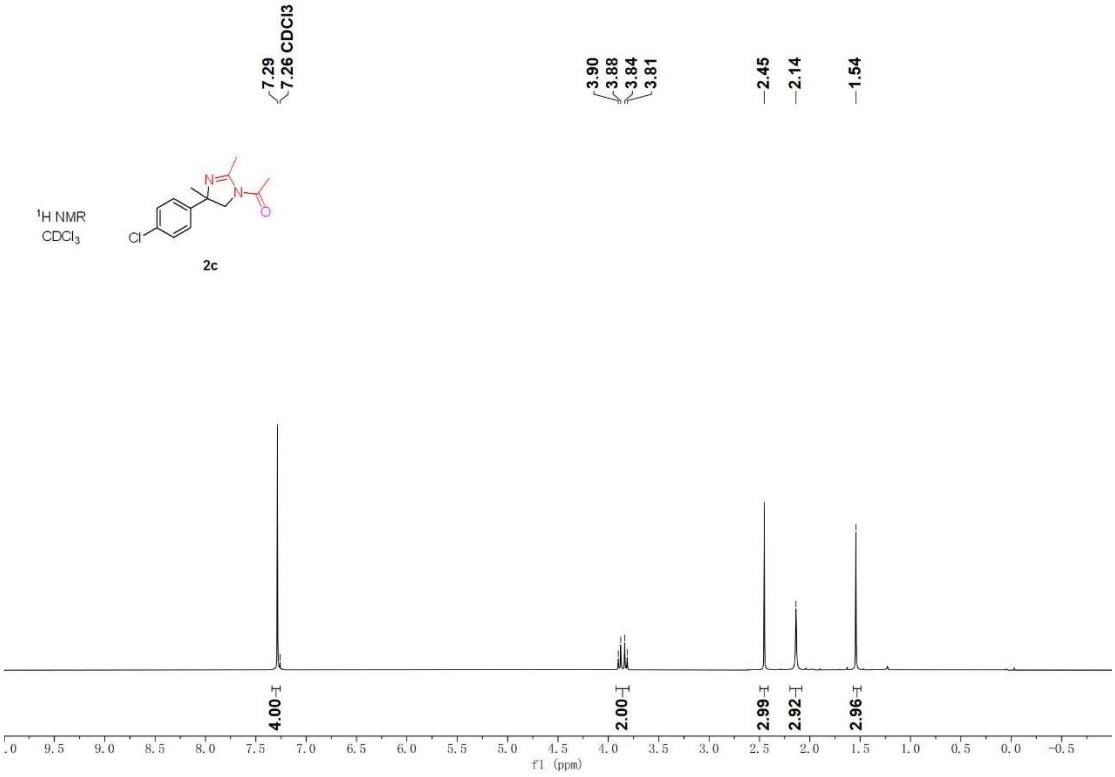
1-(4-(4-fluorophenyl)-2,4-dimethyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**2b**)

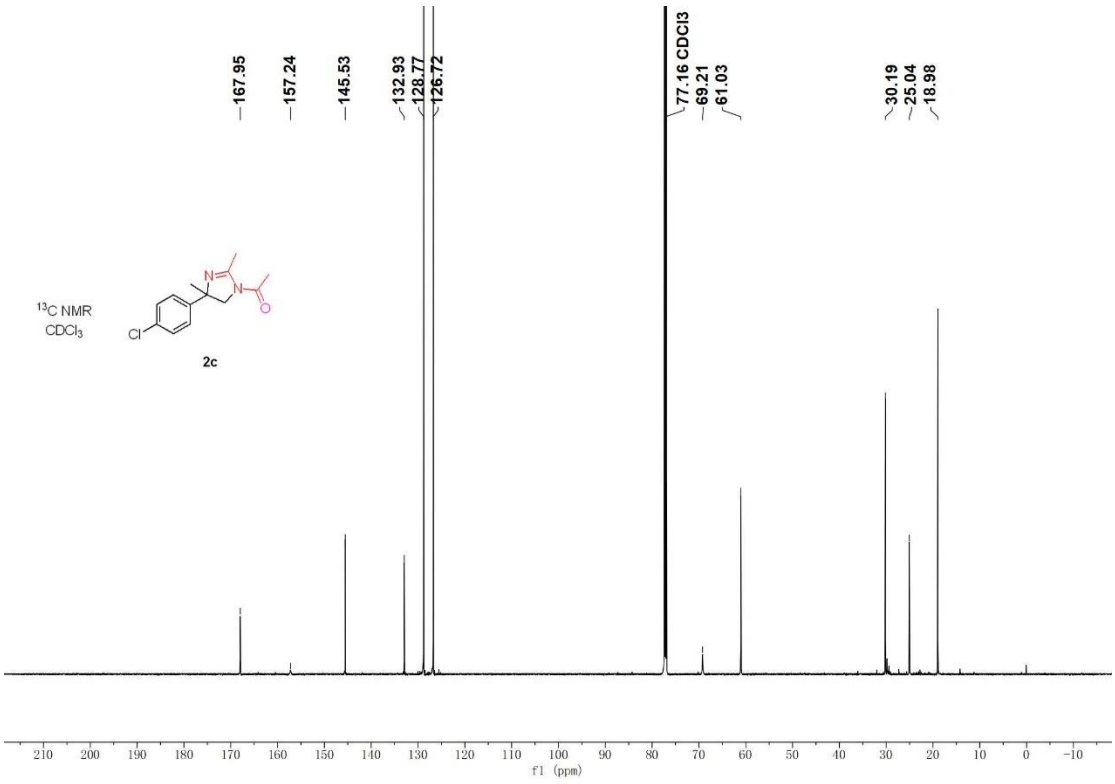




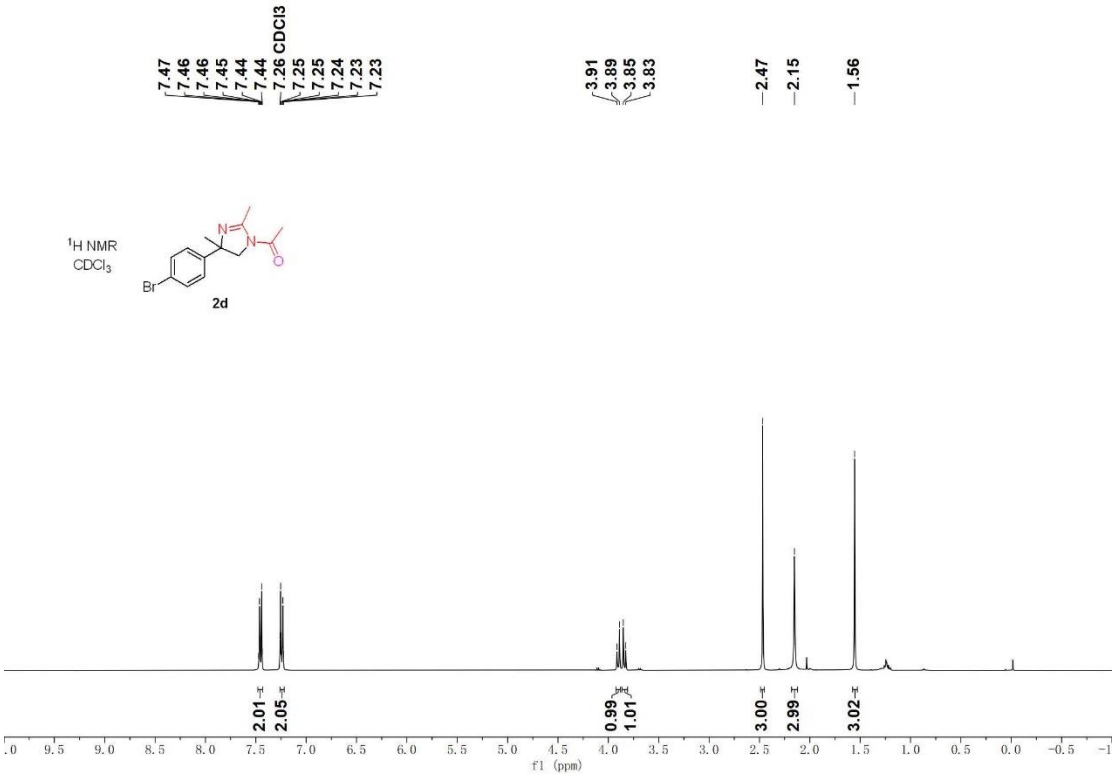

-115.92
19F NMR
CDCl3
N
N
O
F
2b
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−2
f1 (ppm)

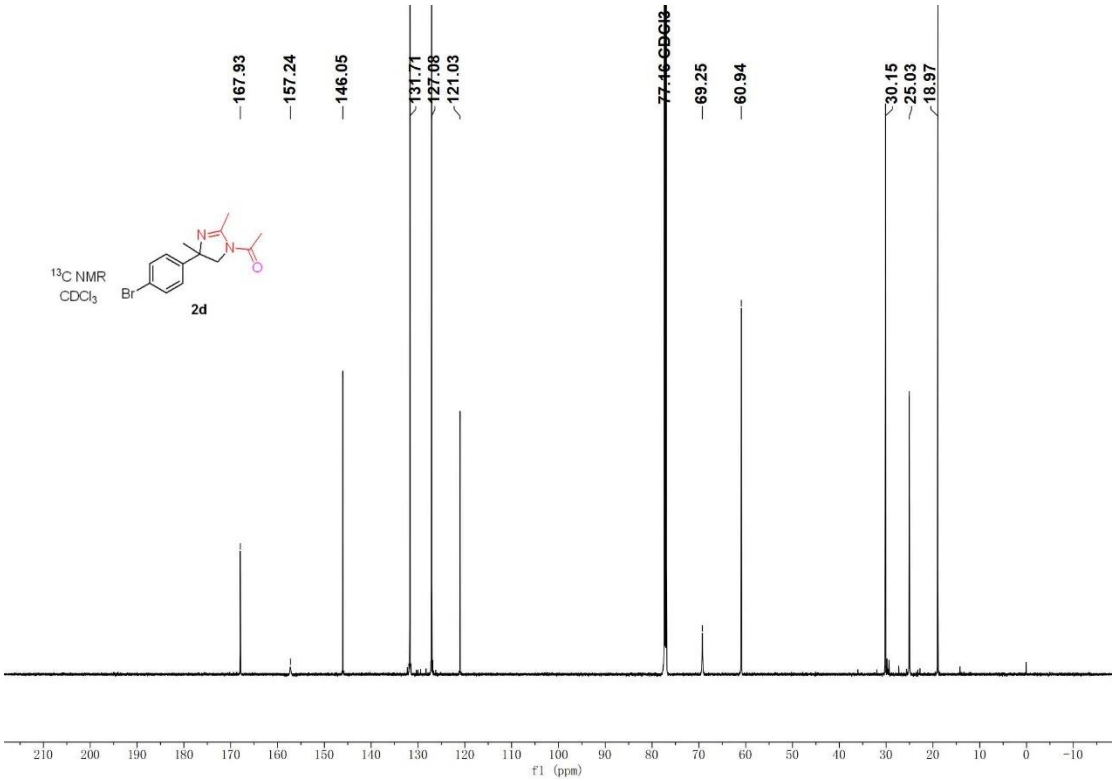
1-(4-(4-chlorophenyl)-2,4-dimethyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**2c**)



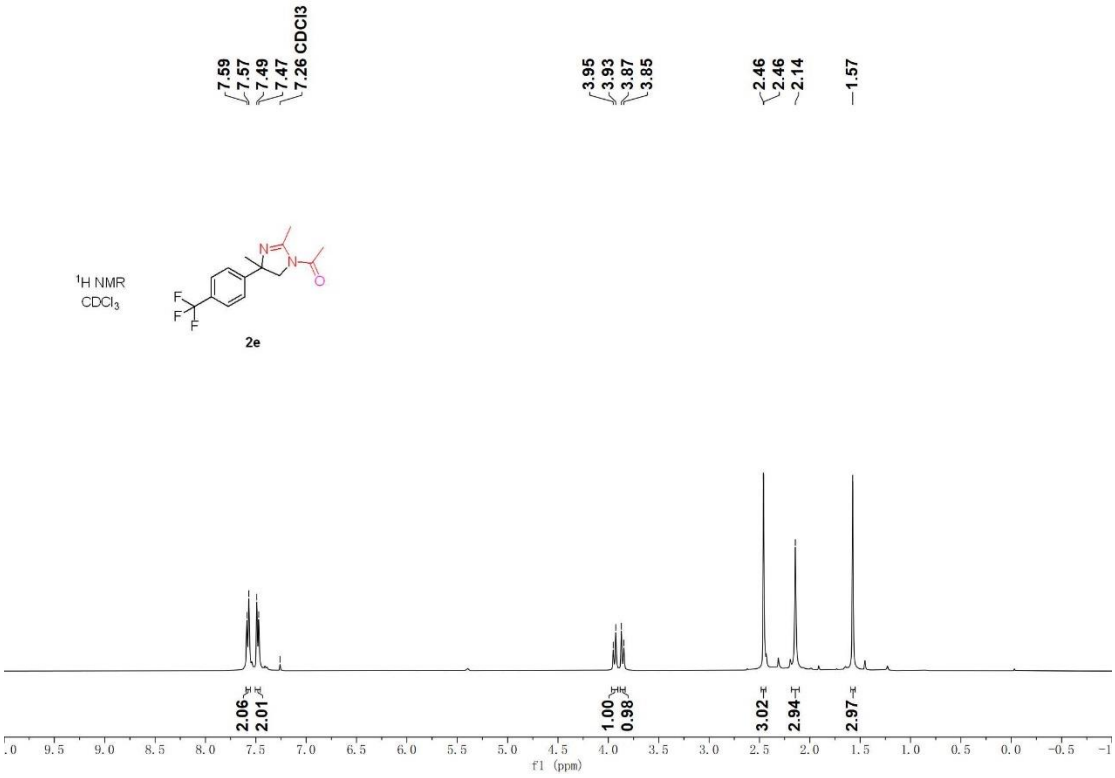


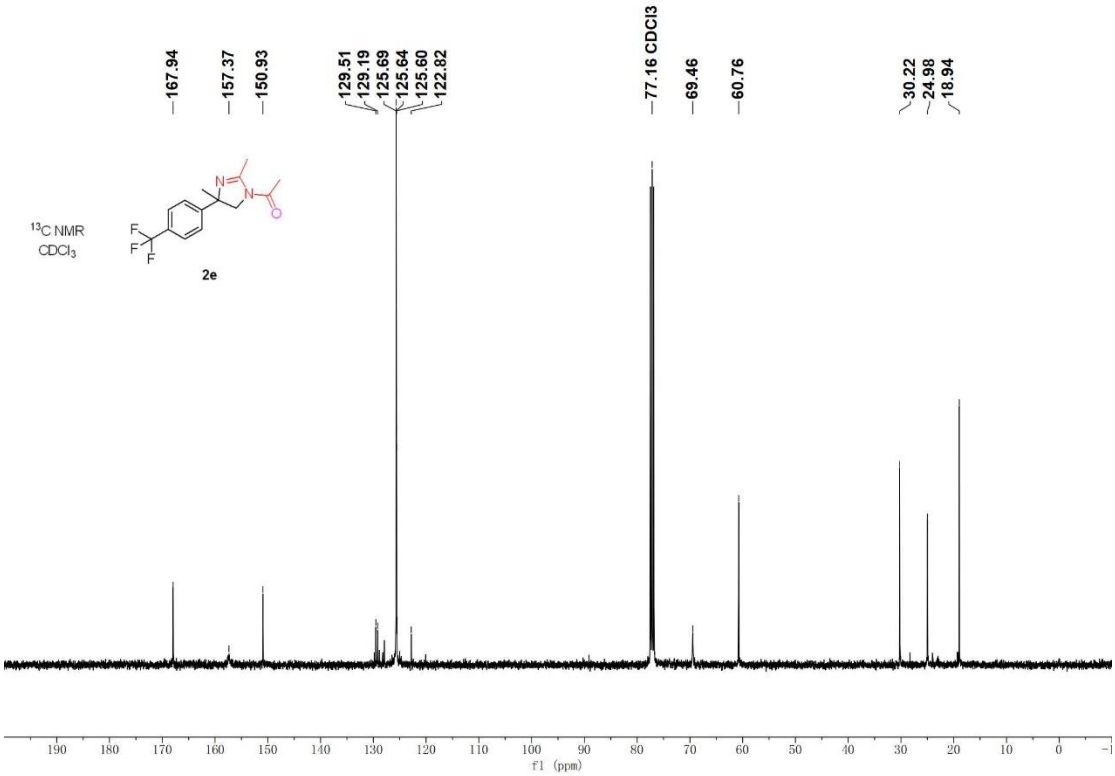
1-(4-(4-bromophenyl)-2,4-dimethyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**2d**)

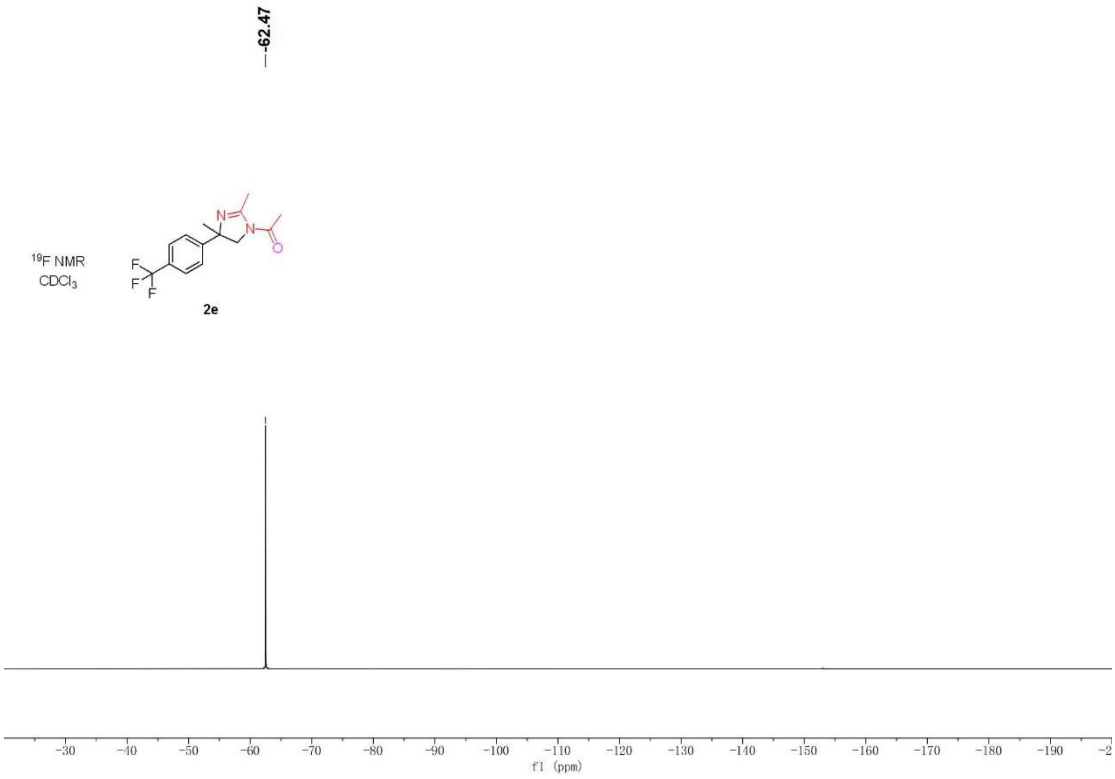




1-(2,4-dimethyl-4-(4-(trifluoromethyl) phenyl)-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**2e**)



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CDCl3
2e
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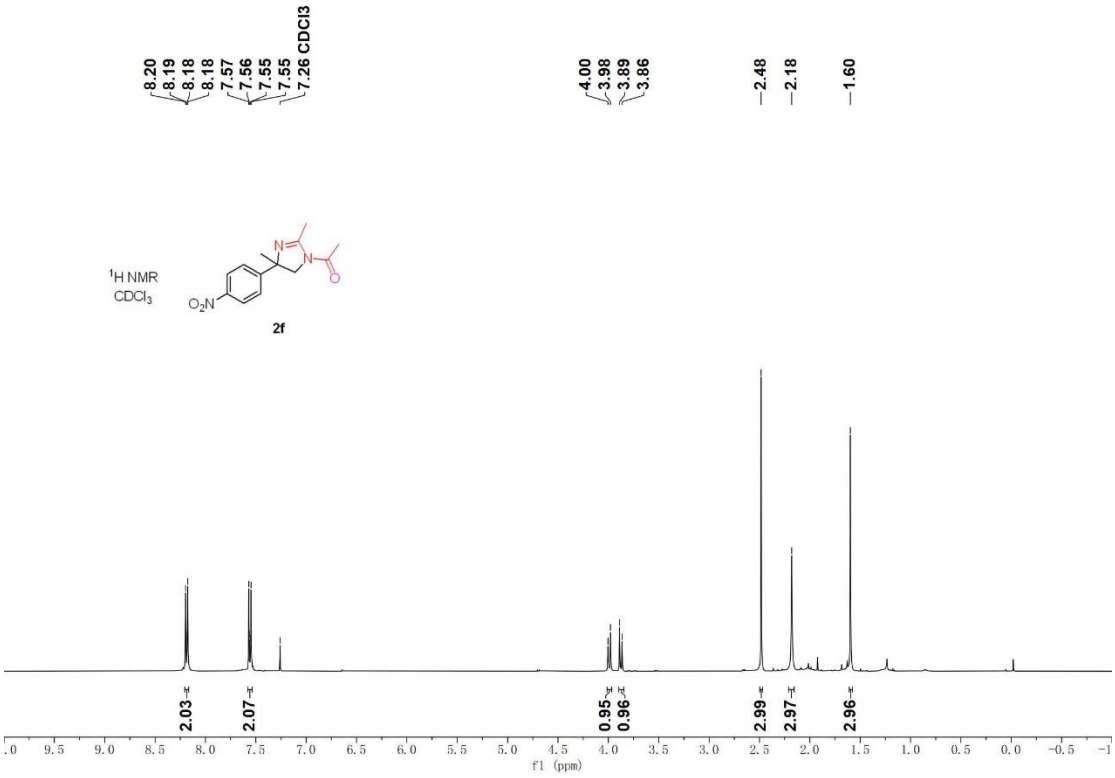
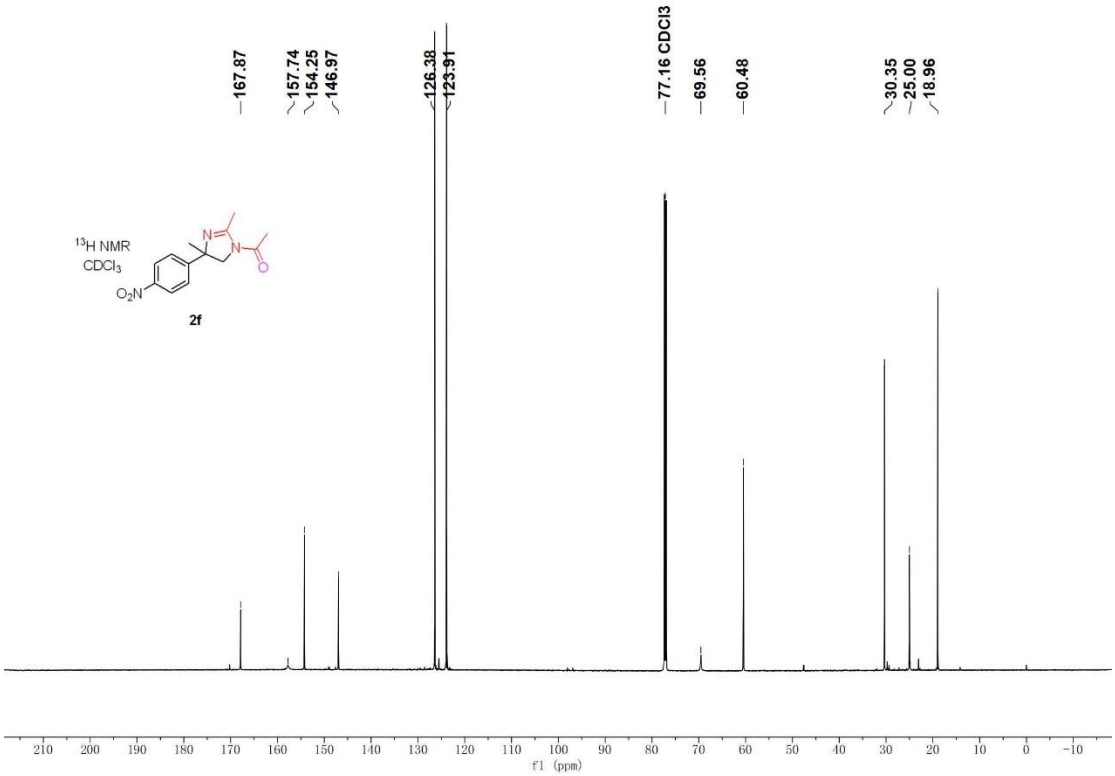
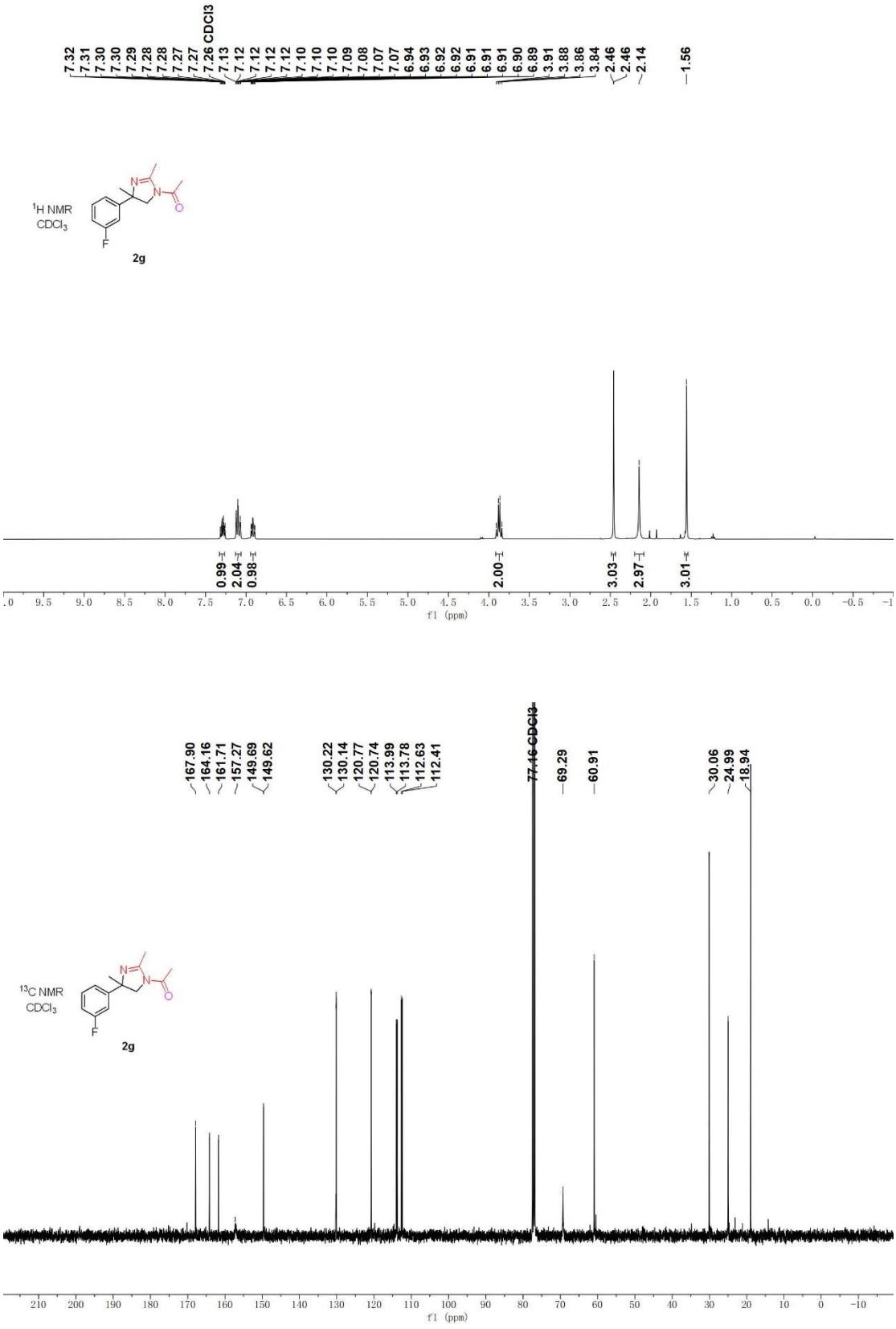
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

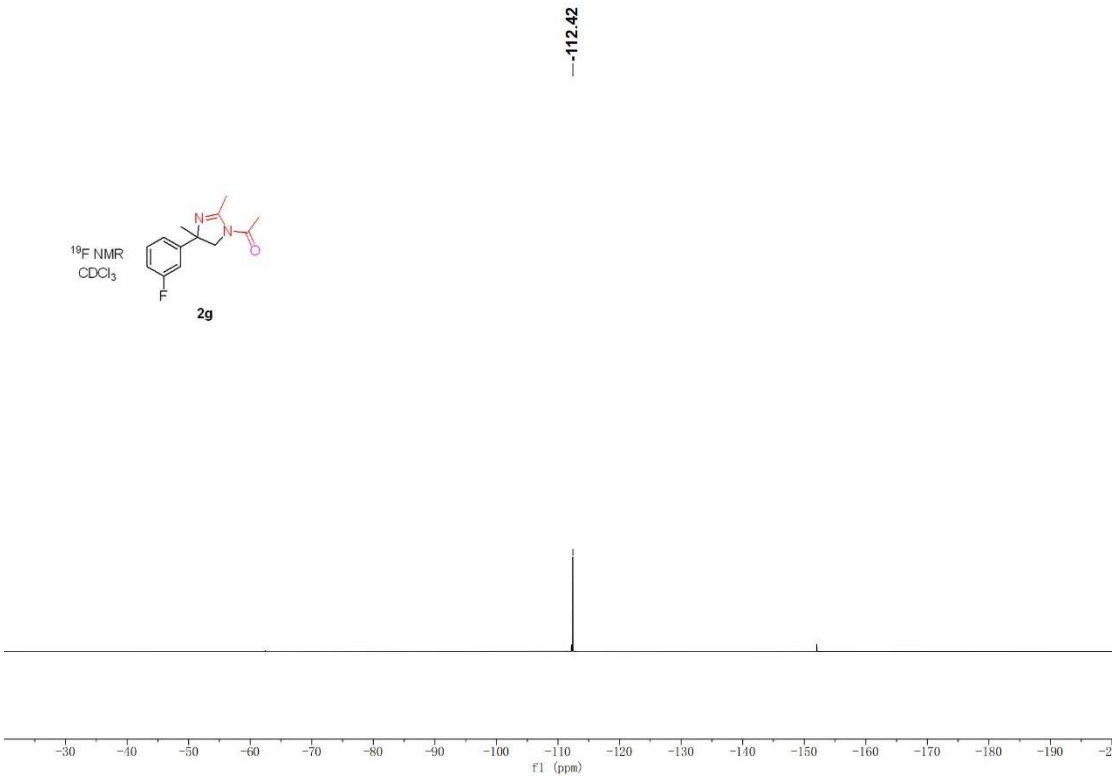
1-(2,4-dimethyl-4-(4-nitrophenyl)-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**2f**)





1-(4-(3-fluorophenyl)-2,4-dimethyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**2g**)

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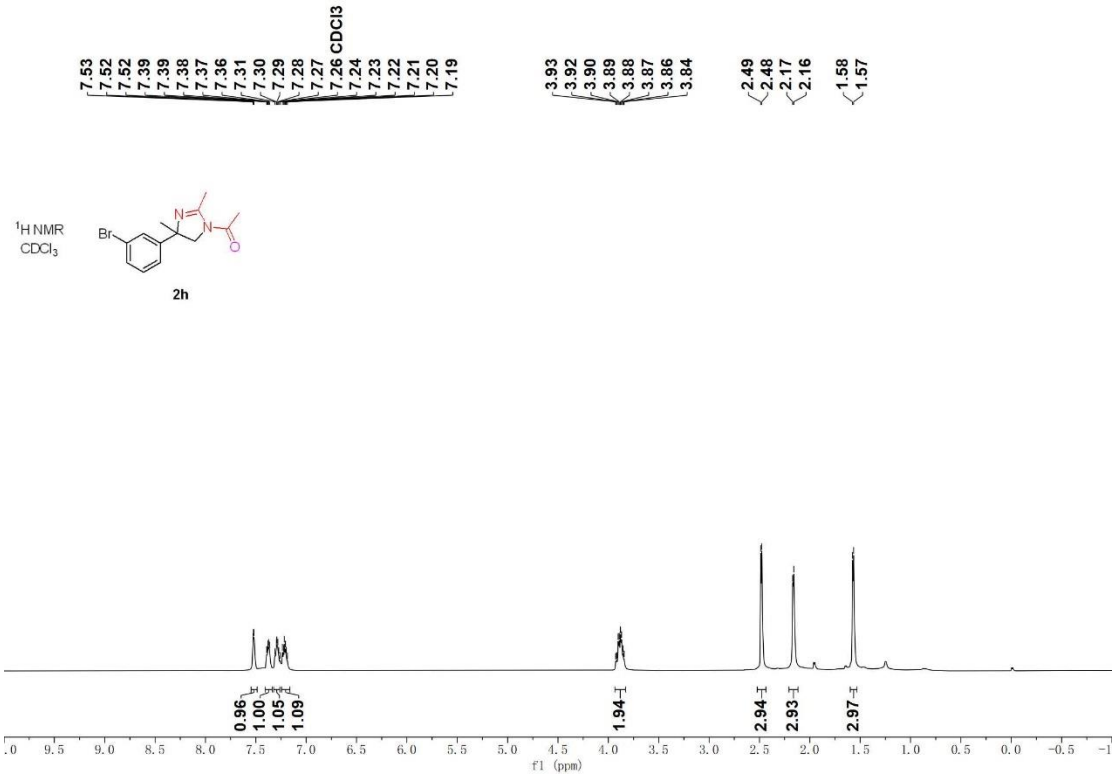
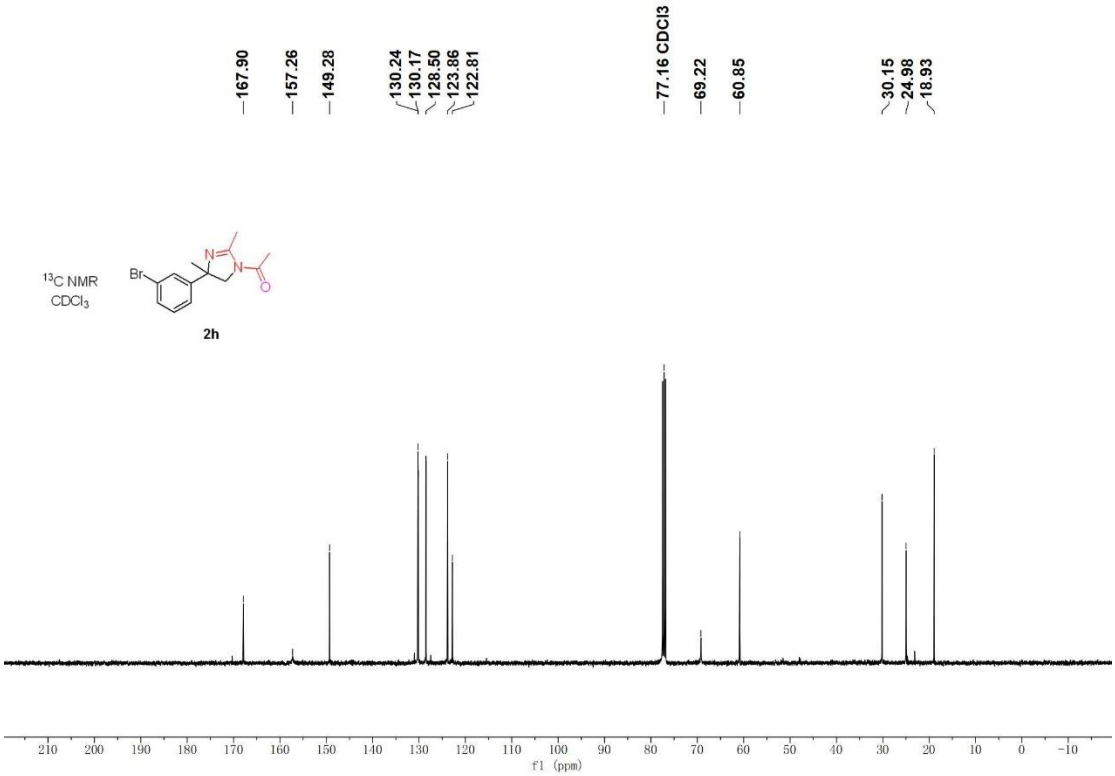
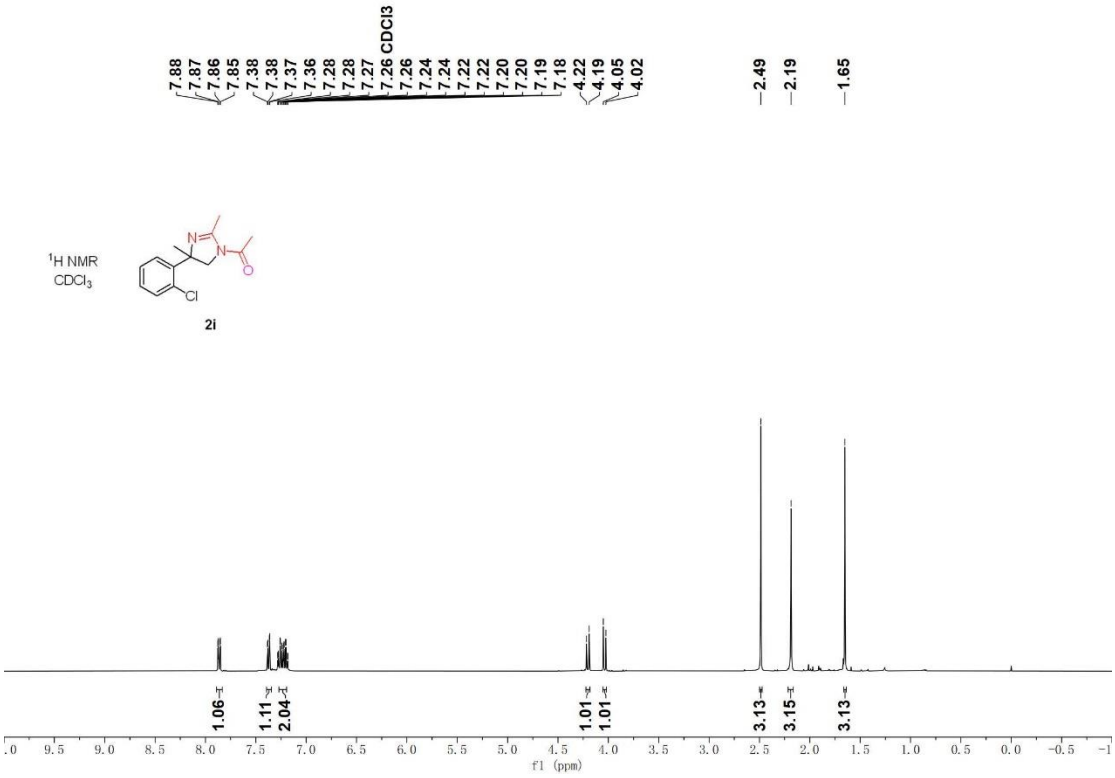
CDCl3
2g
F
N
N
O
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−2
f1 (ppm)

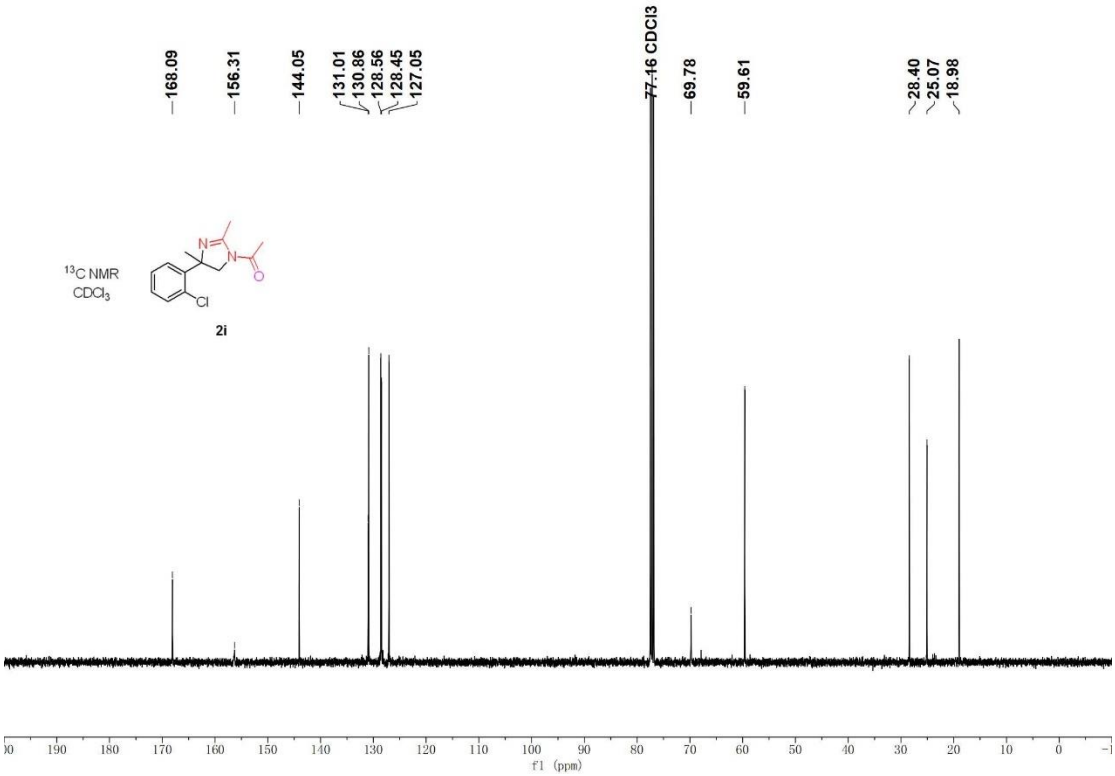
1-(4-(3-bromophenyl)-2,4-dimethyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**2h**)



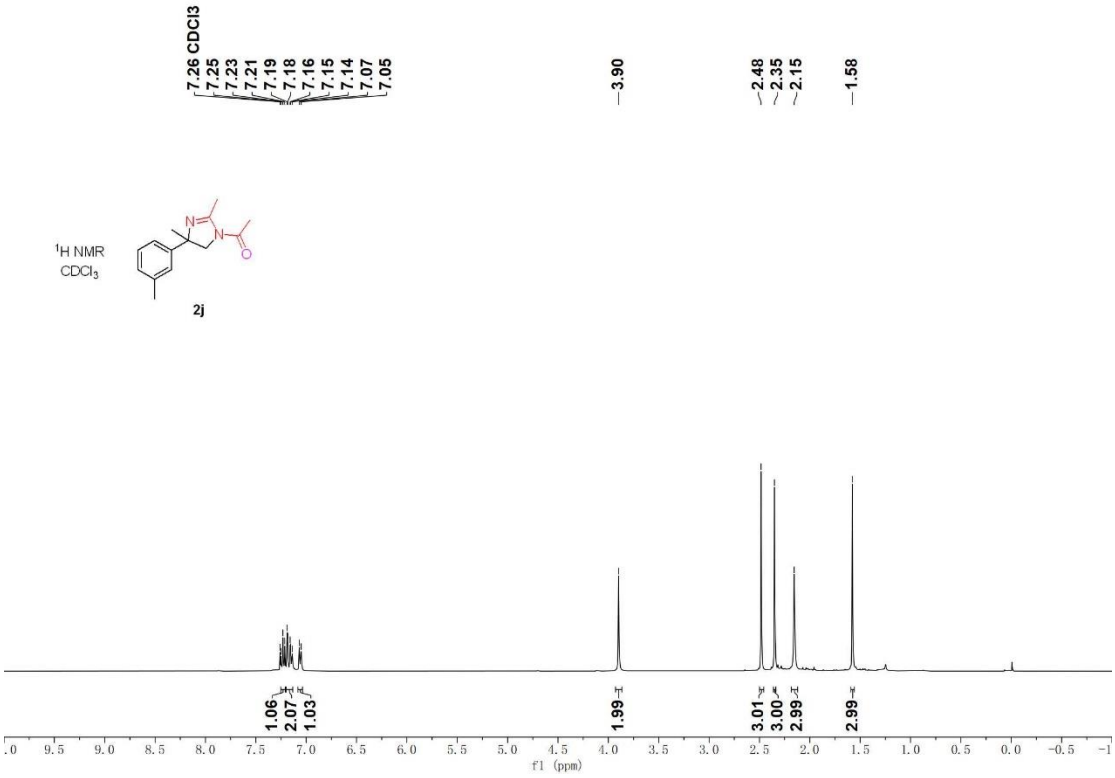


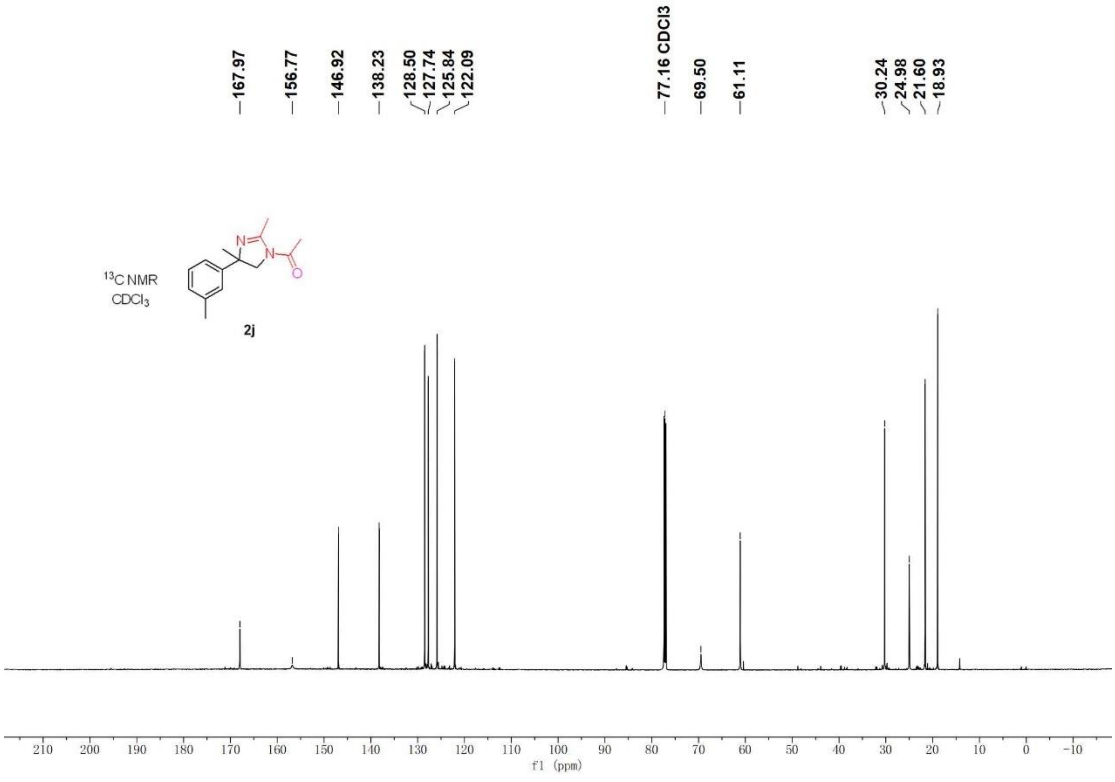
1-(4-(2-chlorophenyl)-2,4-dimethyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**2i**)



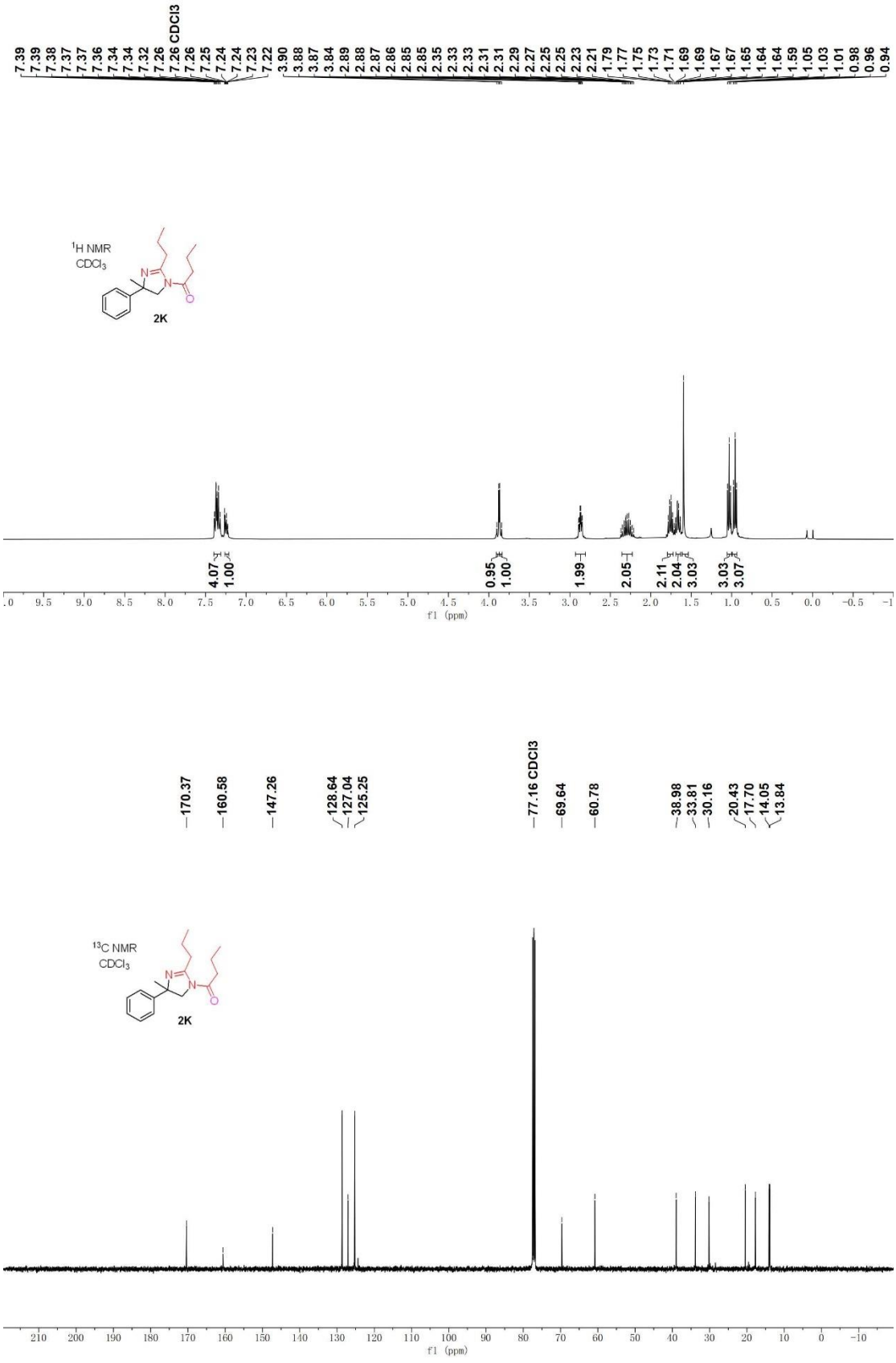


1-(2,4-dimethyl-4-(m-tolyl)-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**2j**)

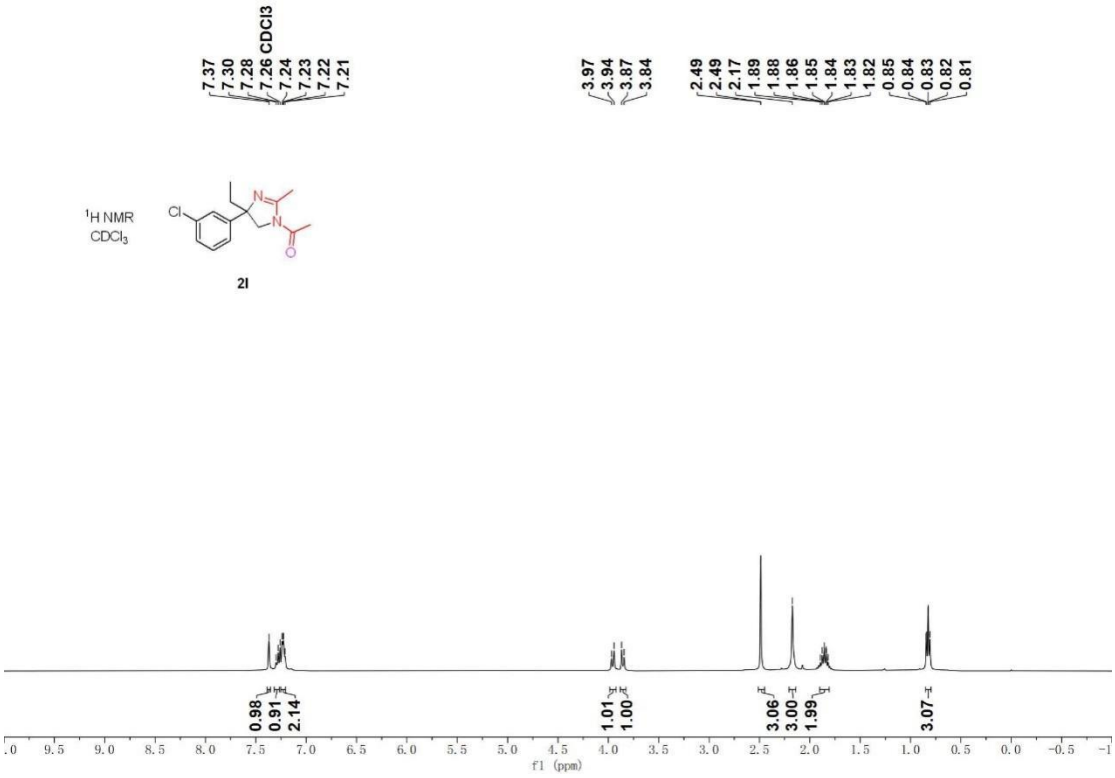


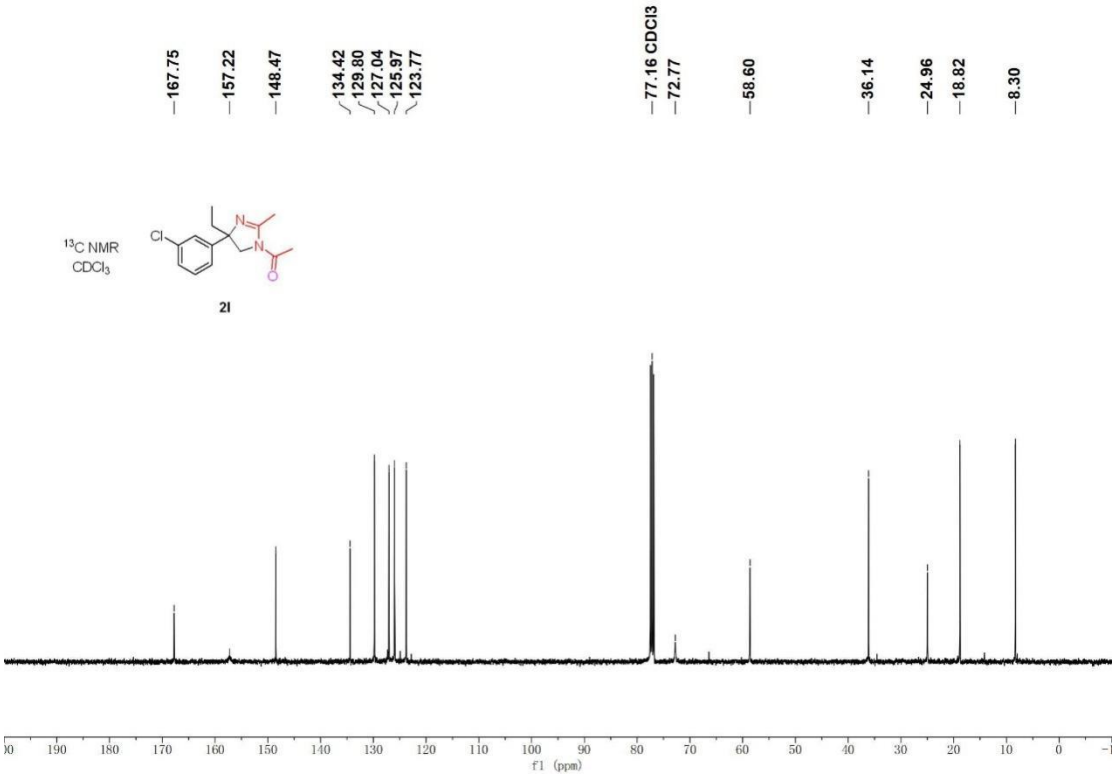


1-(4-methyl-4-phenyl-2-propyl-4,5-dihydro-1H-imidazol-1-yl) butan-1-one (**2k**)

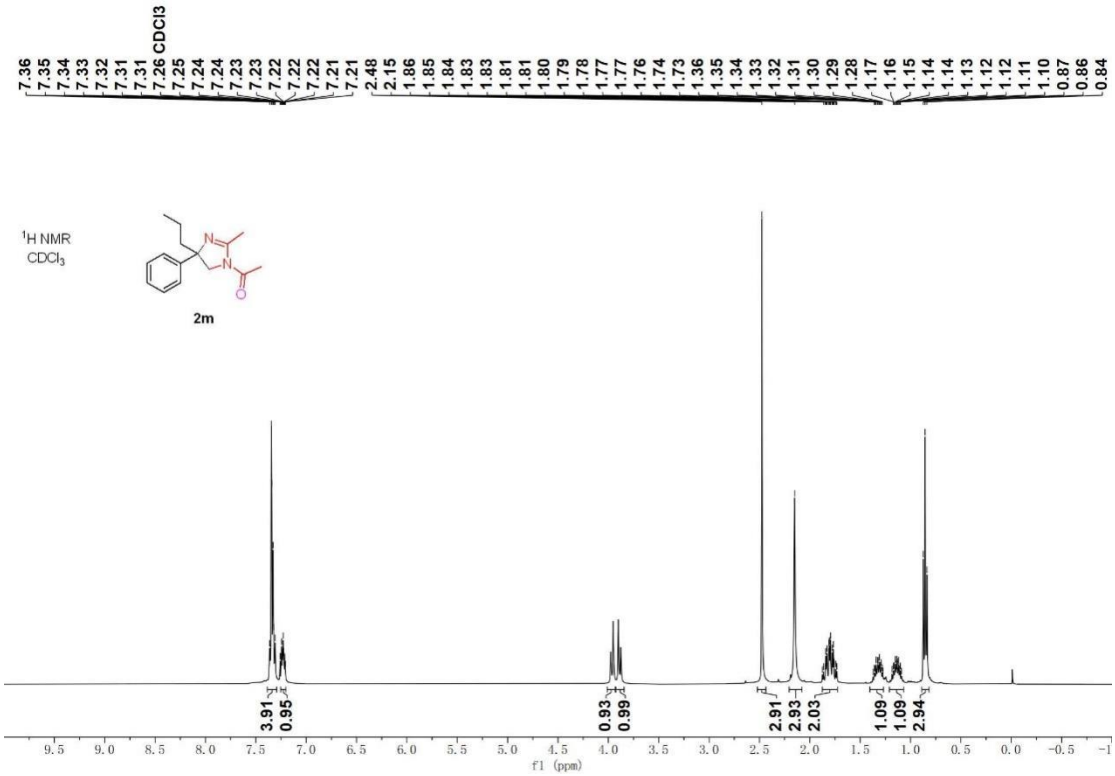


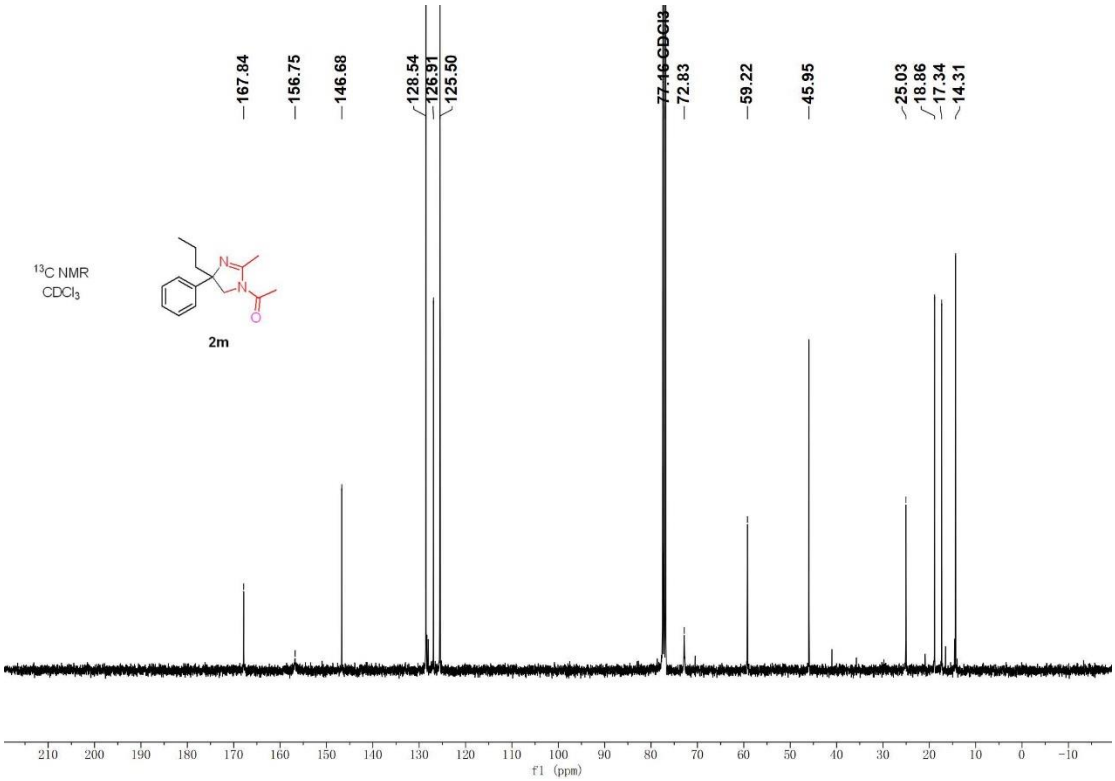
1-(4-(3-chlorophenyl)-4-ethyl-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**2l)**



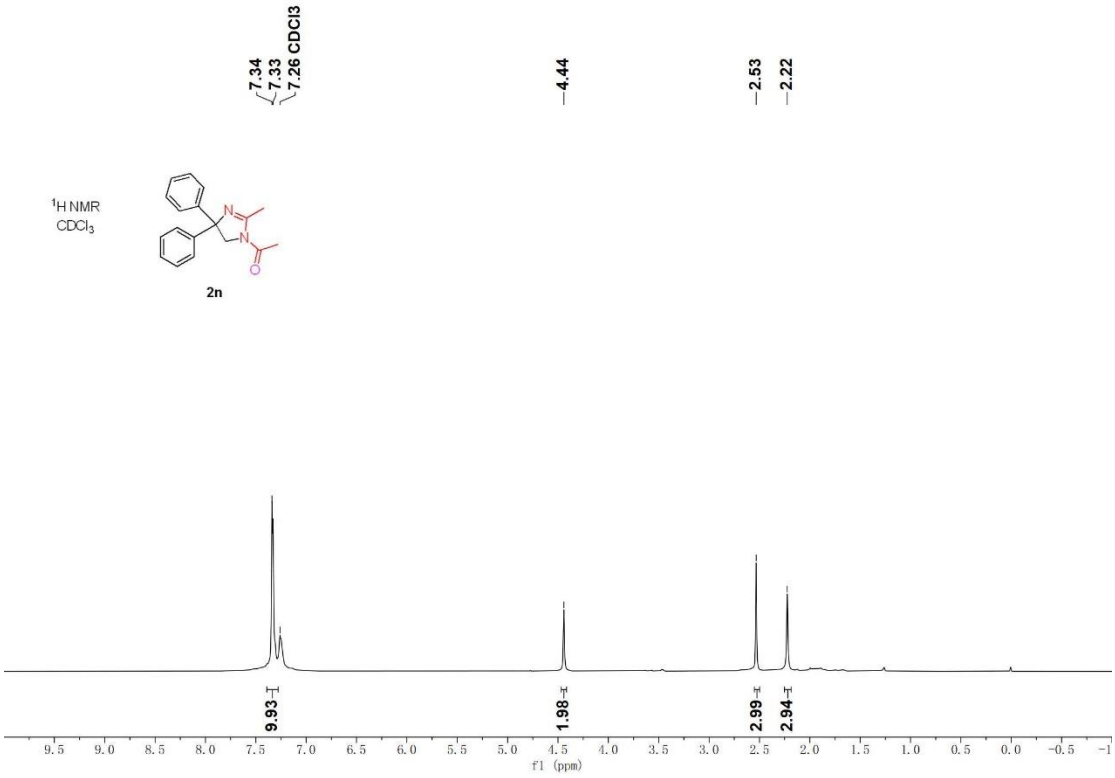


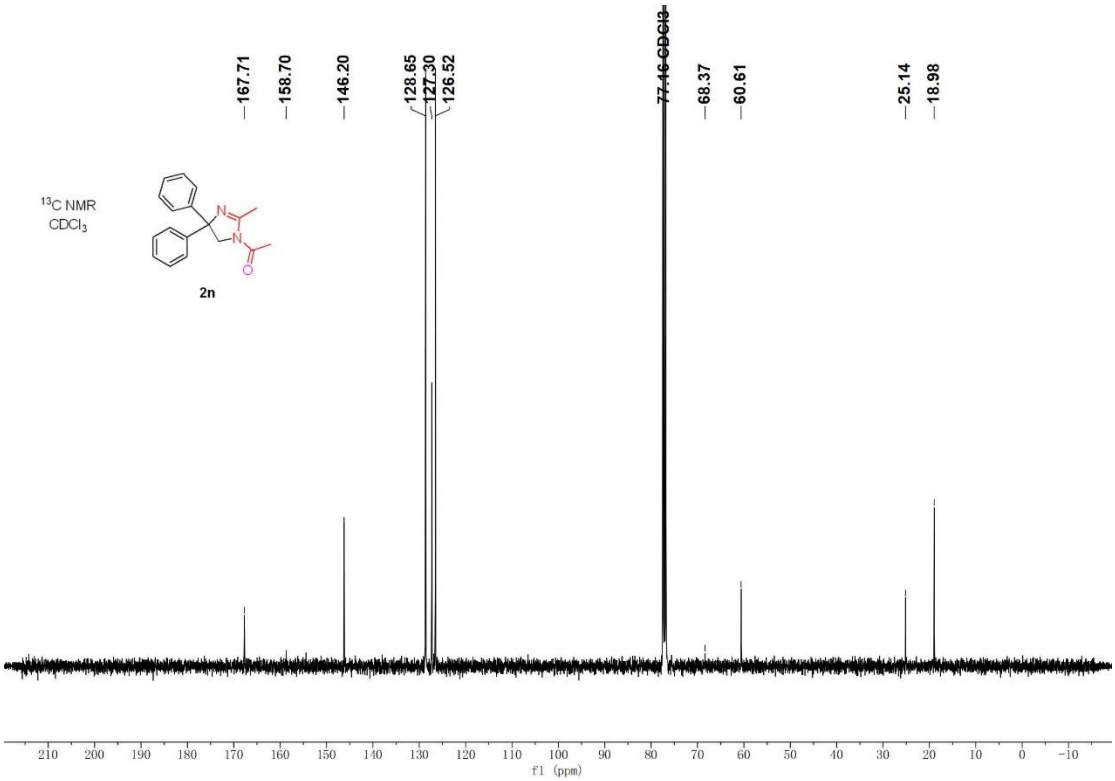
1-(2-methyl-4-phenyl-4-propyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one **(2m)**



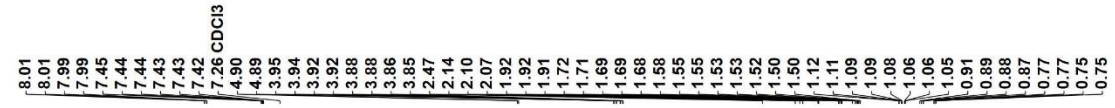


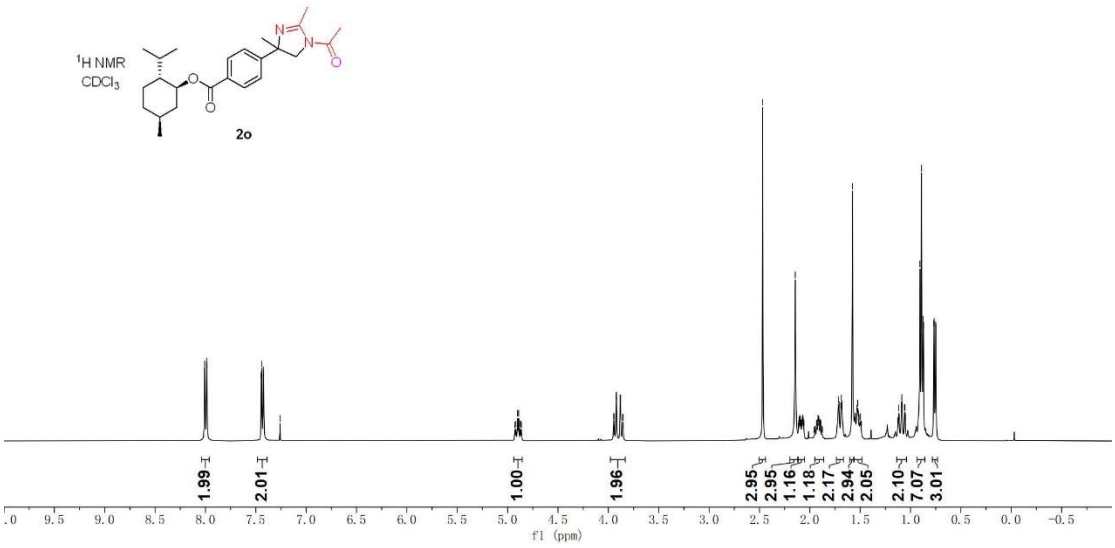
1-(2-methyl-4,4-diphenyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**2n**)

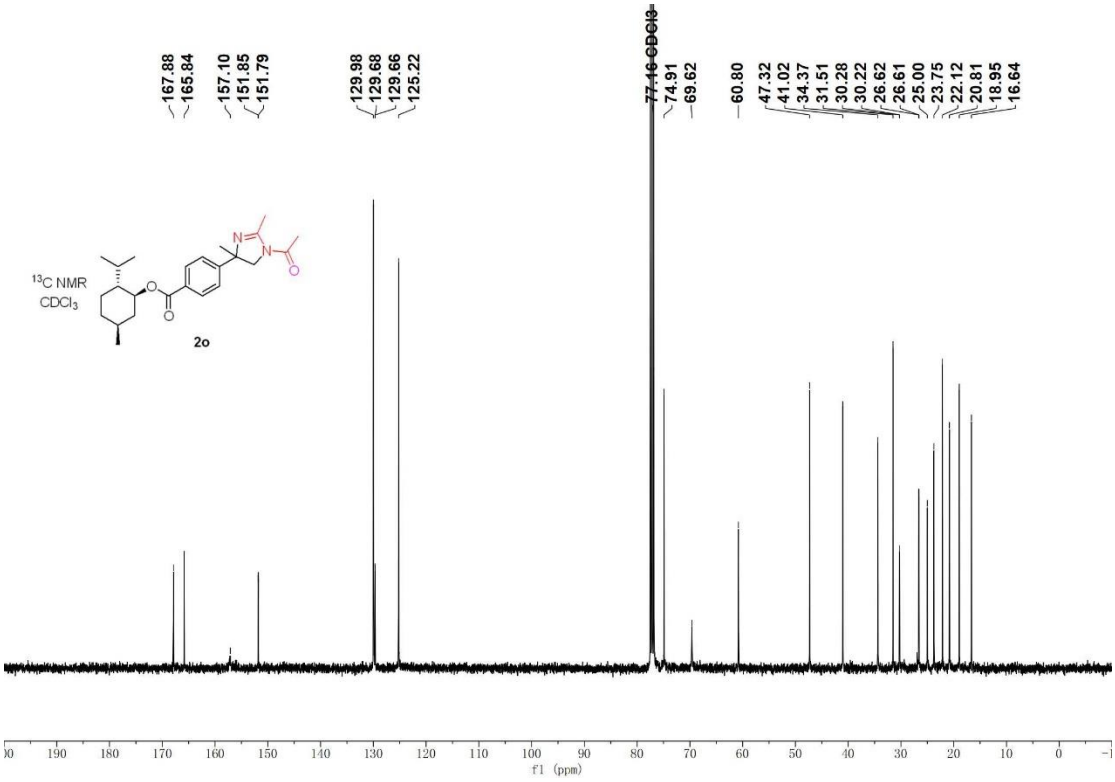




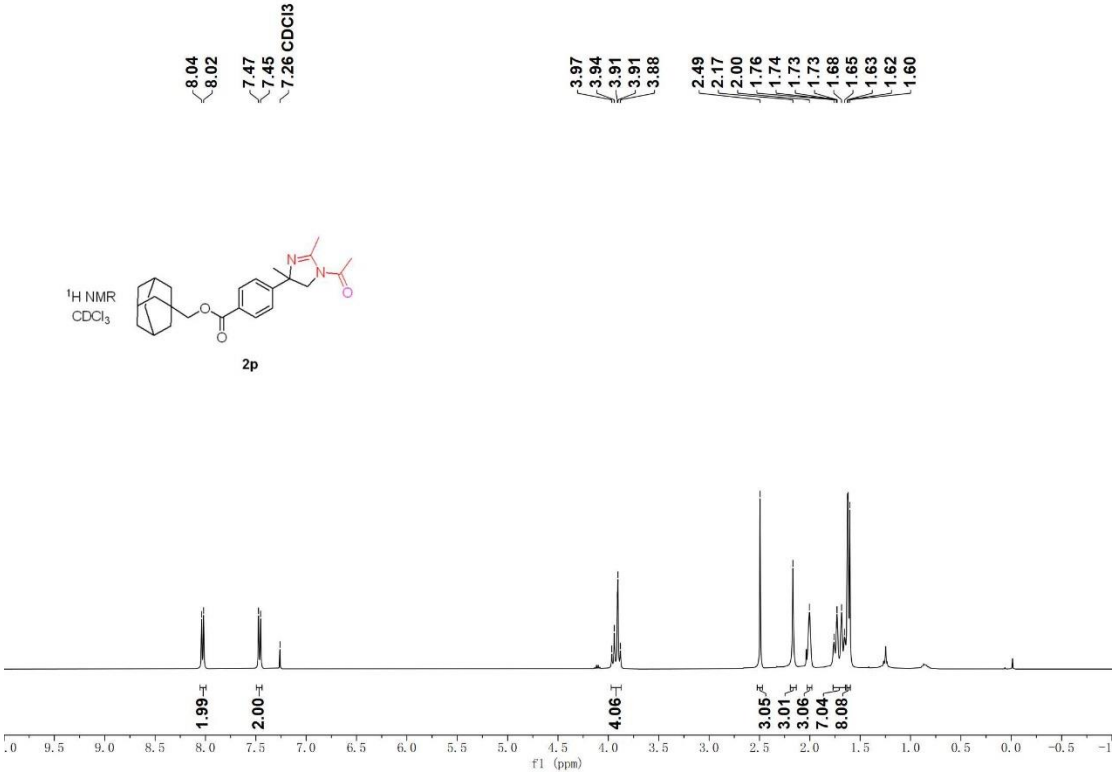
(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-(1-acetyl-2,4-dimethyl-4,5-dihydro-1H-imidazol-4-yl) benzoate (**2o**)

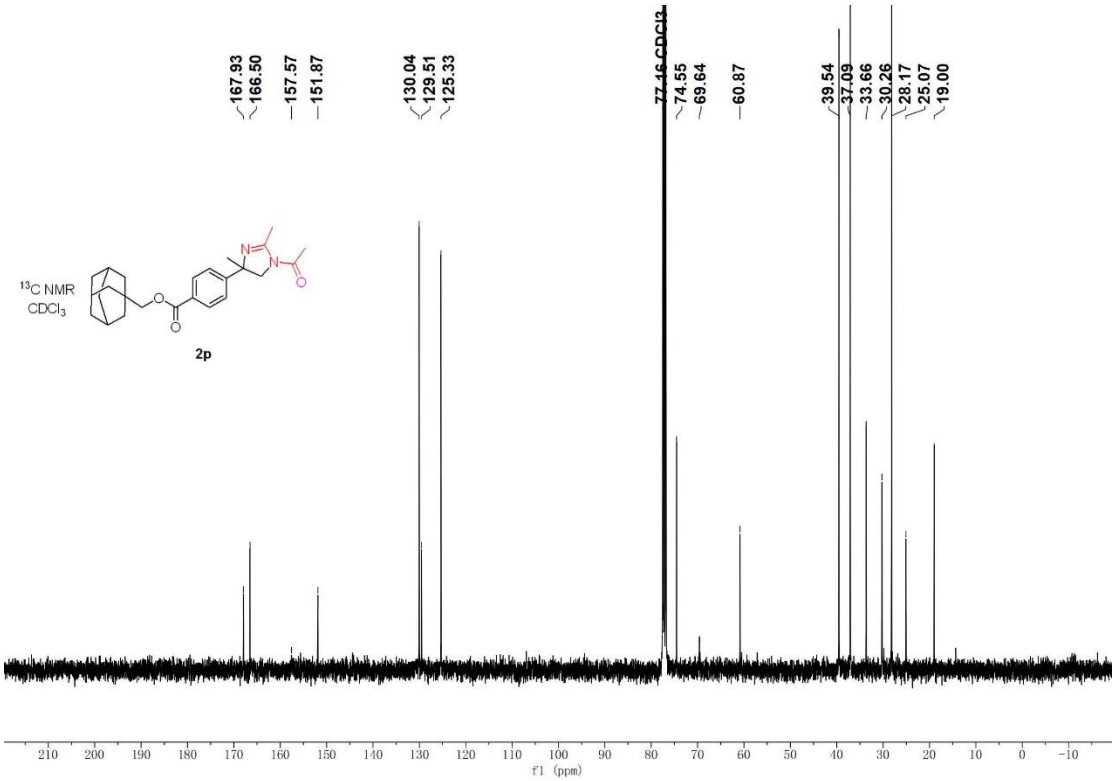




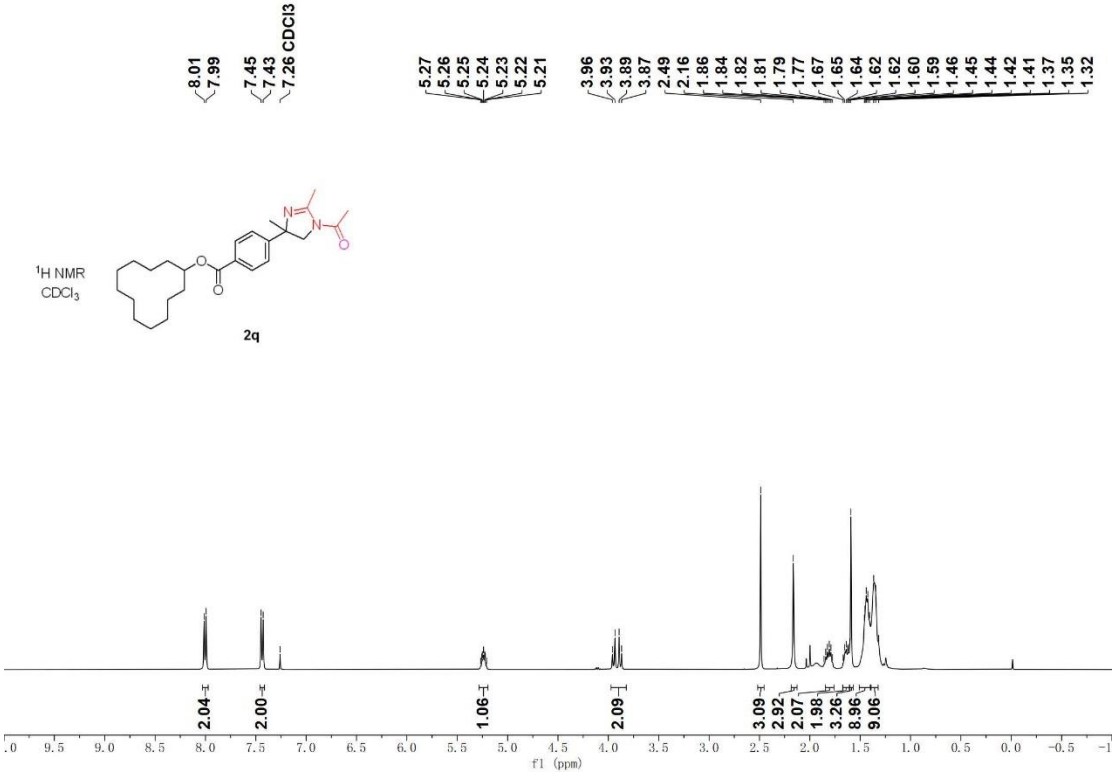


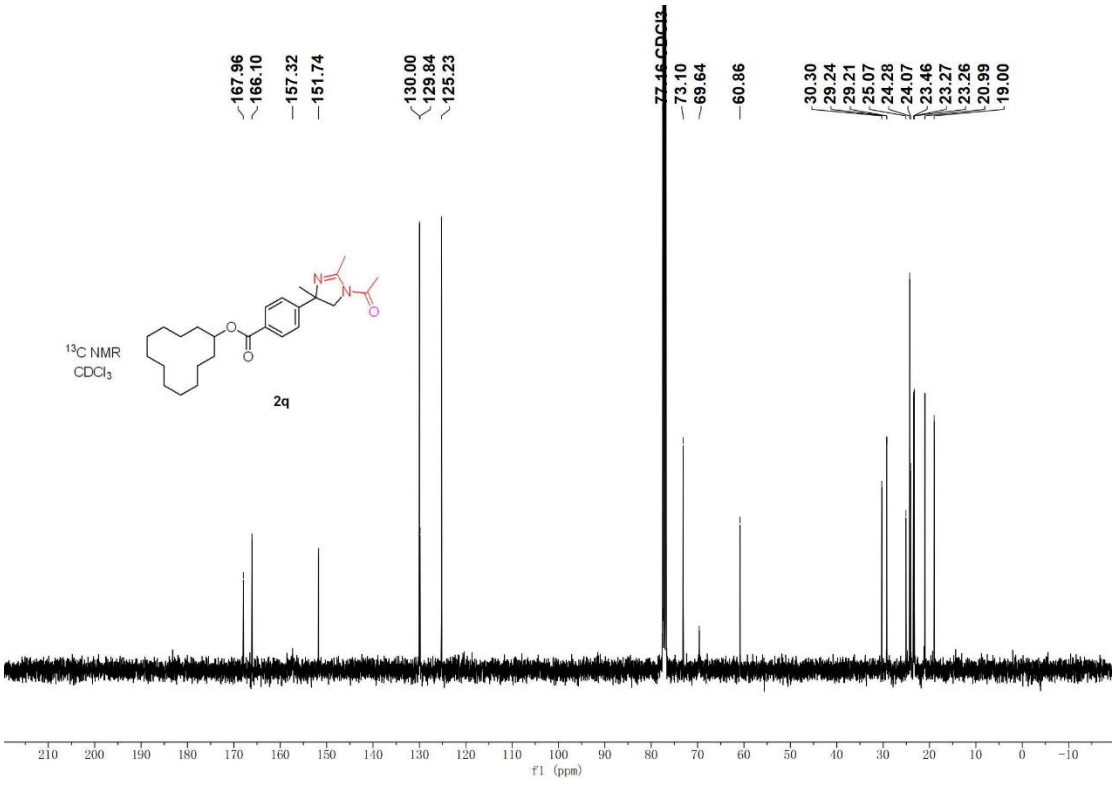
Adamantan-1-ylmethyl 4-(1-acetyl-2,4-dimethyl-4,5-dihydro-1H-imidazol-4-yl) benzoate (**2p**)



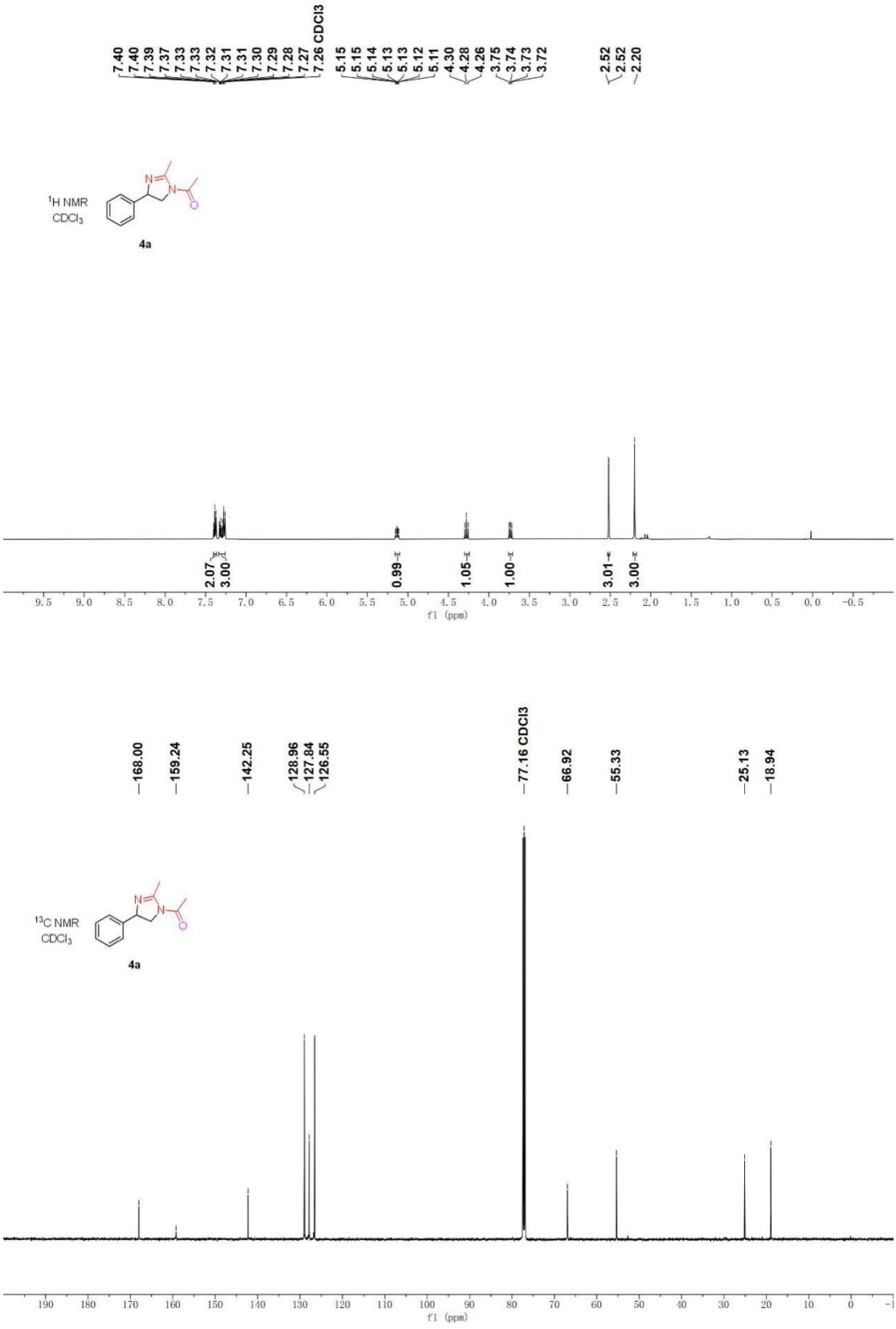


Cyclododecyl 4-(1-acetyl-2,4-dimethyl-4,5-dihydro-1H-imidazol-4-yl) benzoate (**2q**)

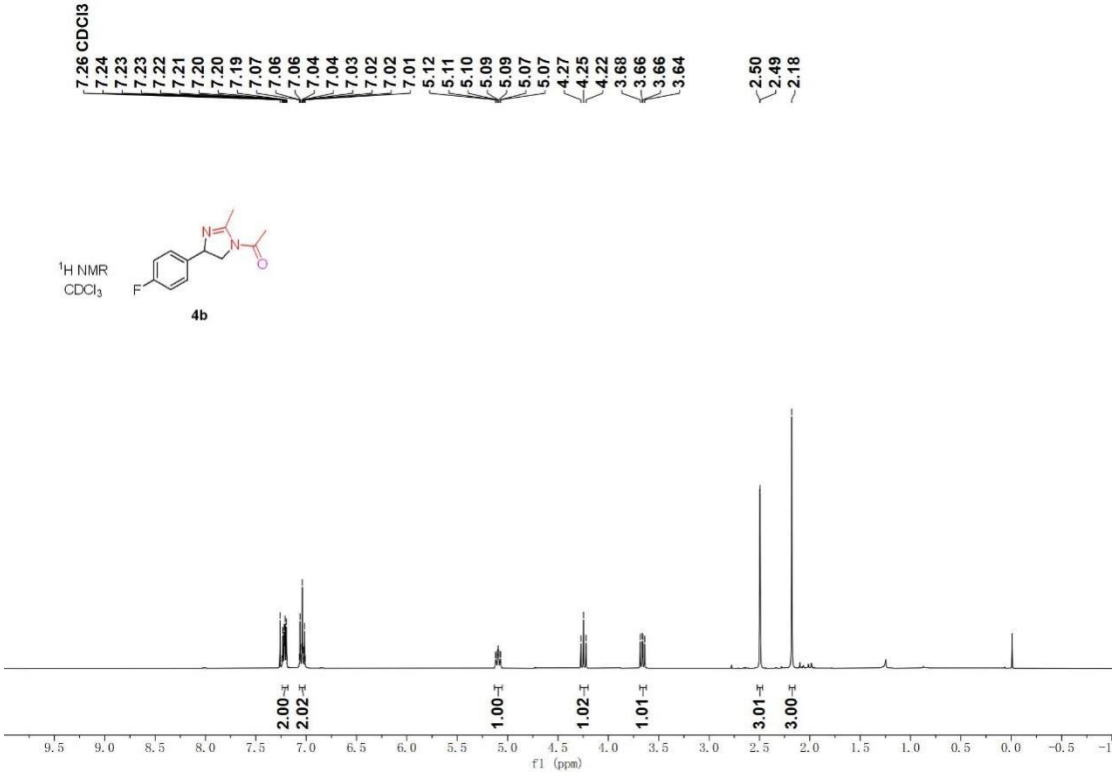


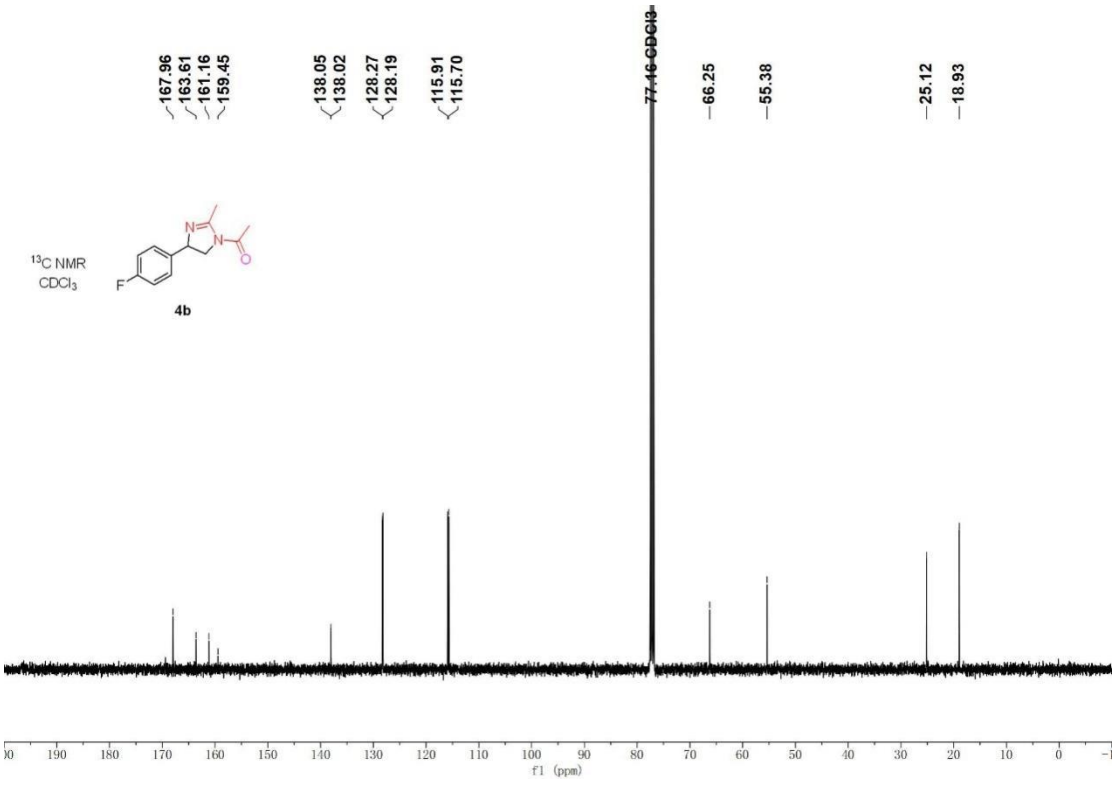


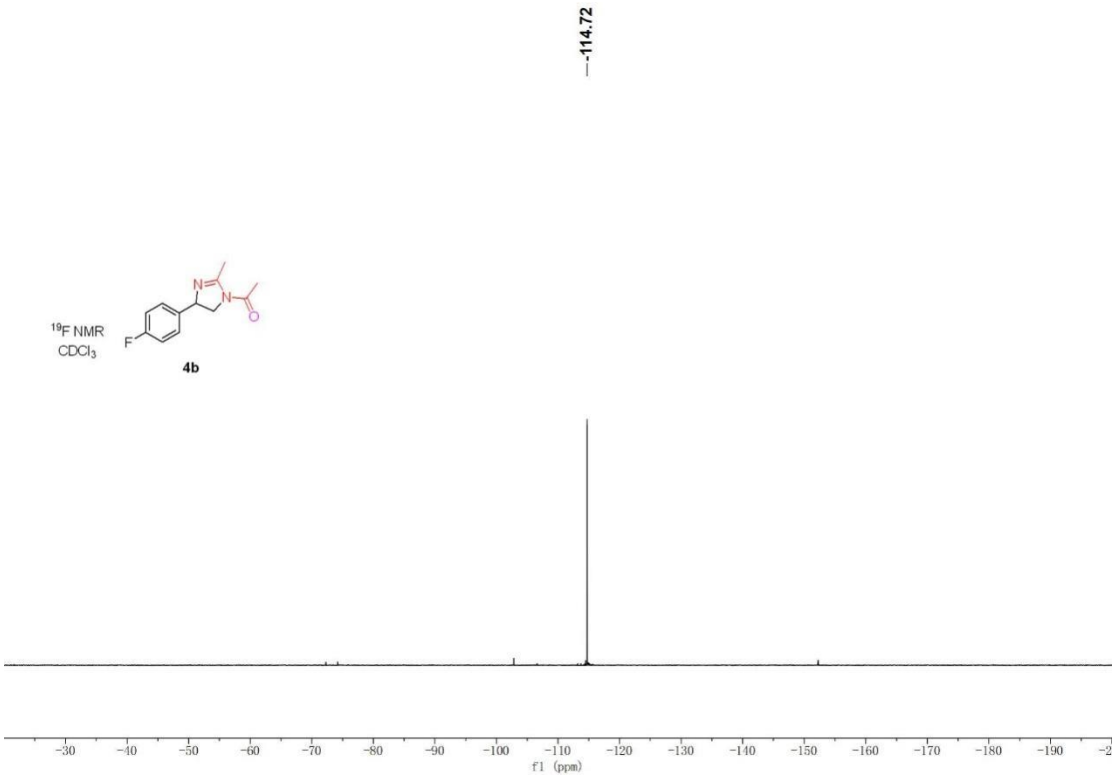
1-(2-methyl-4-phenyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**4a**)



1-(4-(4-fluorophenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**4b**)



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CDCl3
F
N
N
O
4b
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-40
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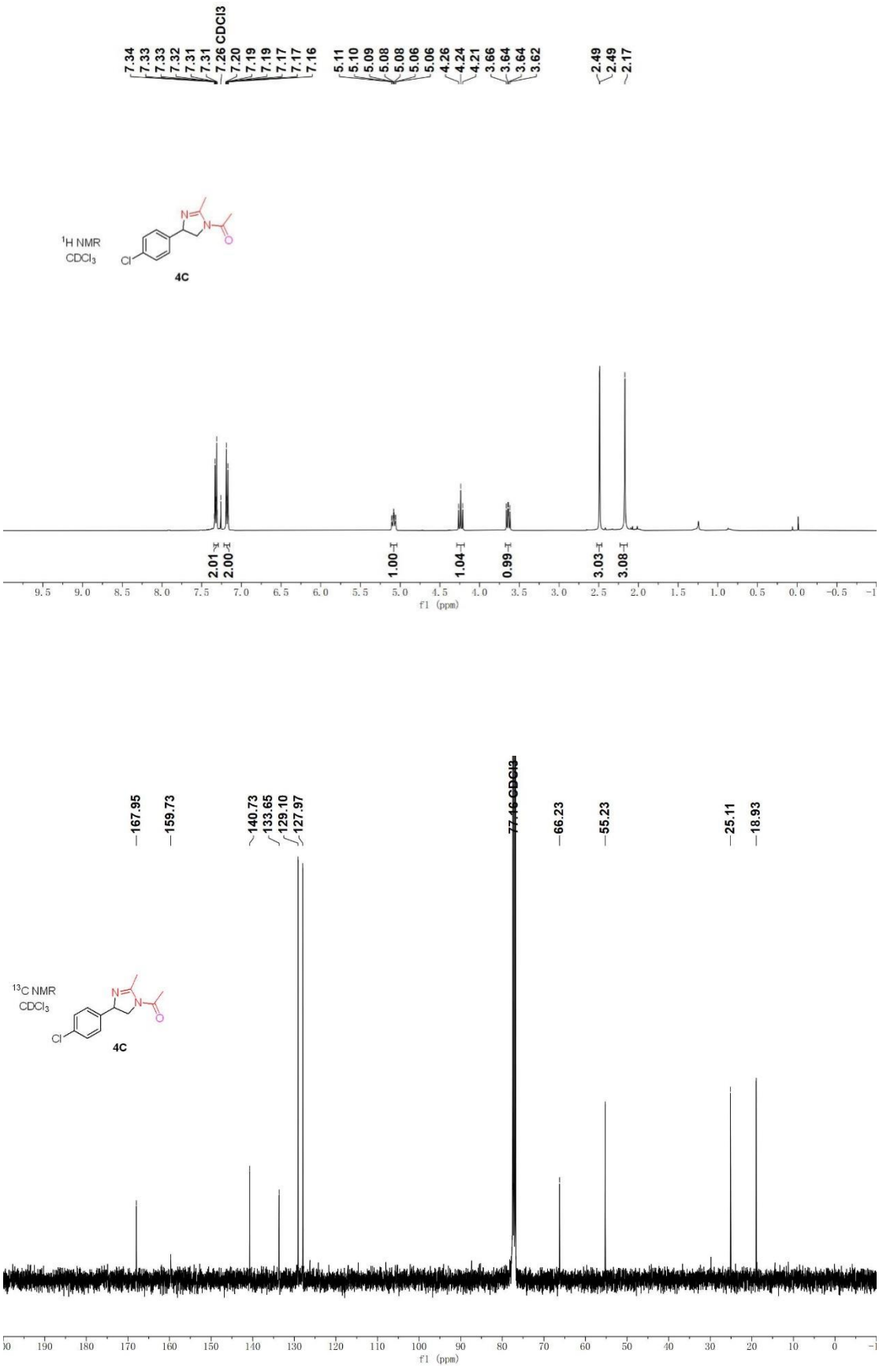
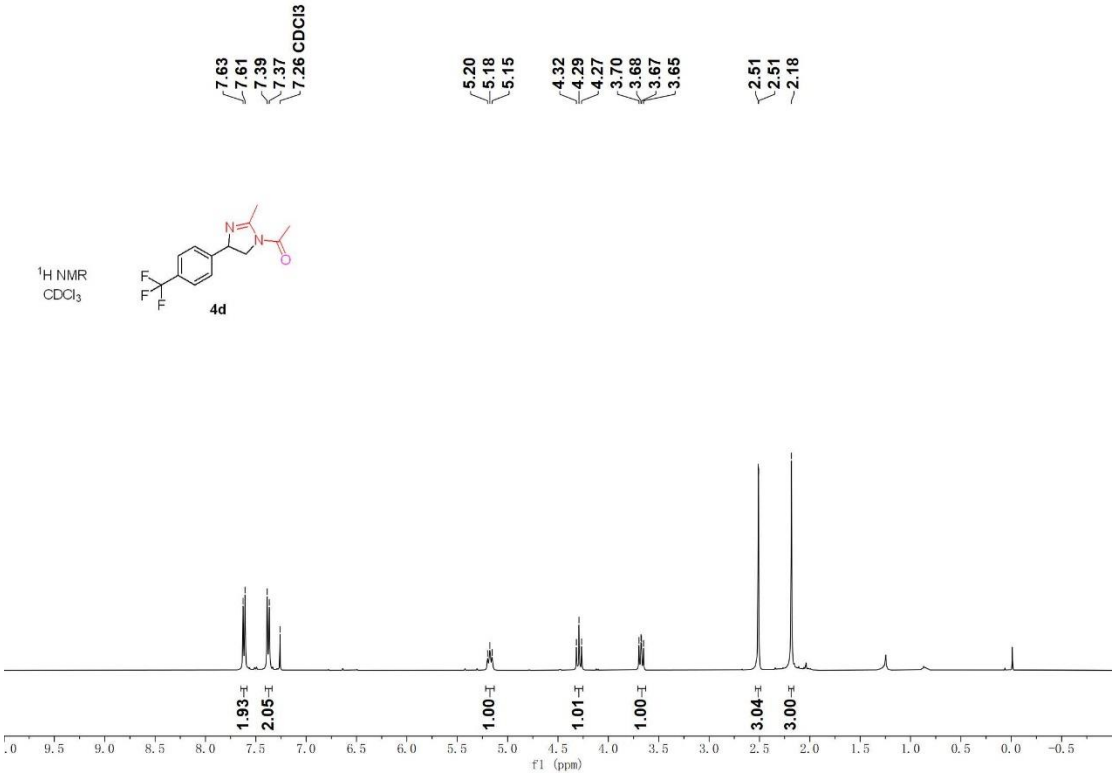
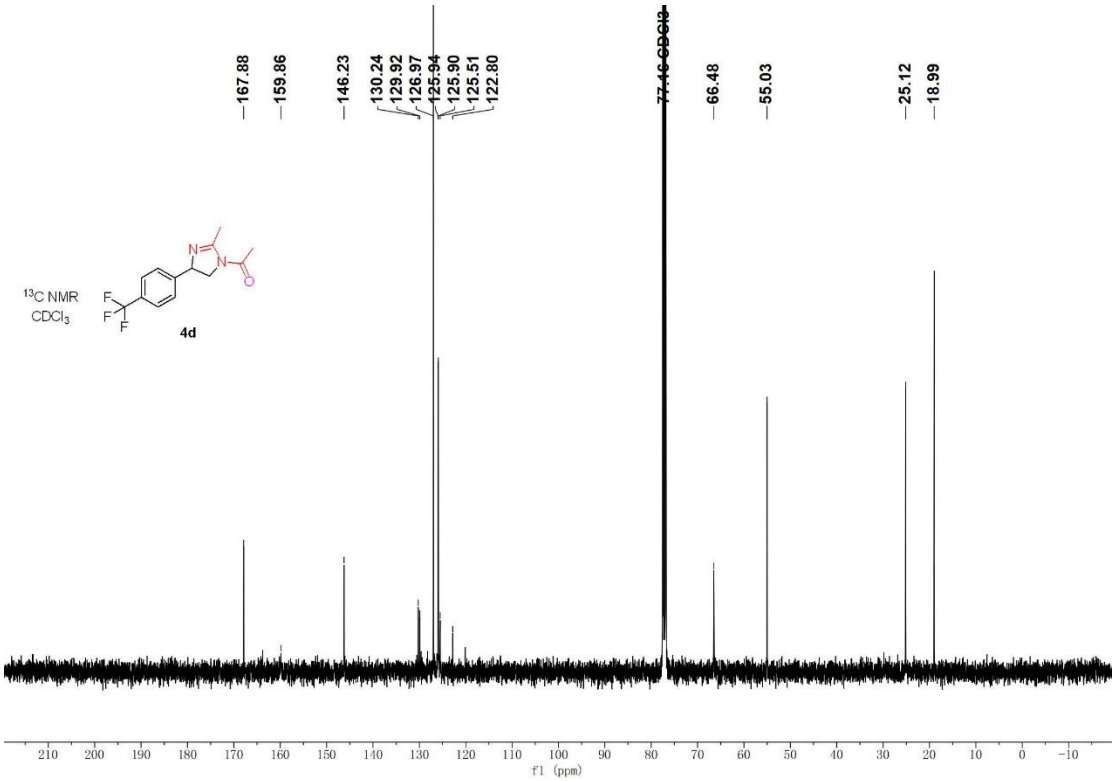
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

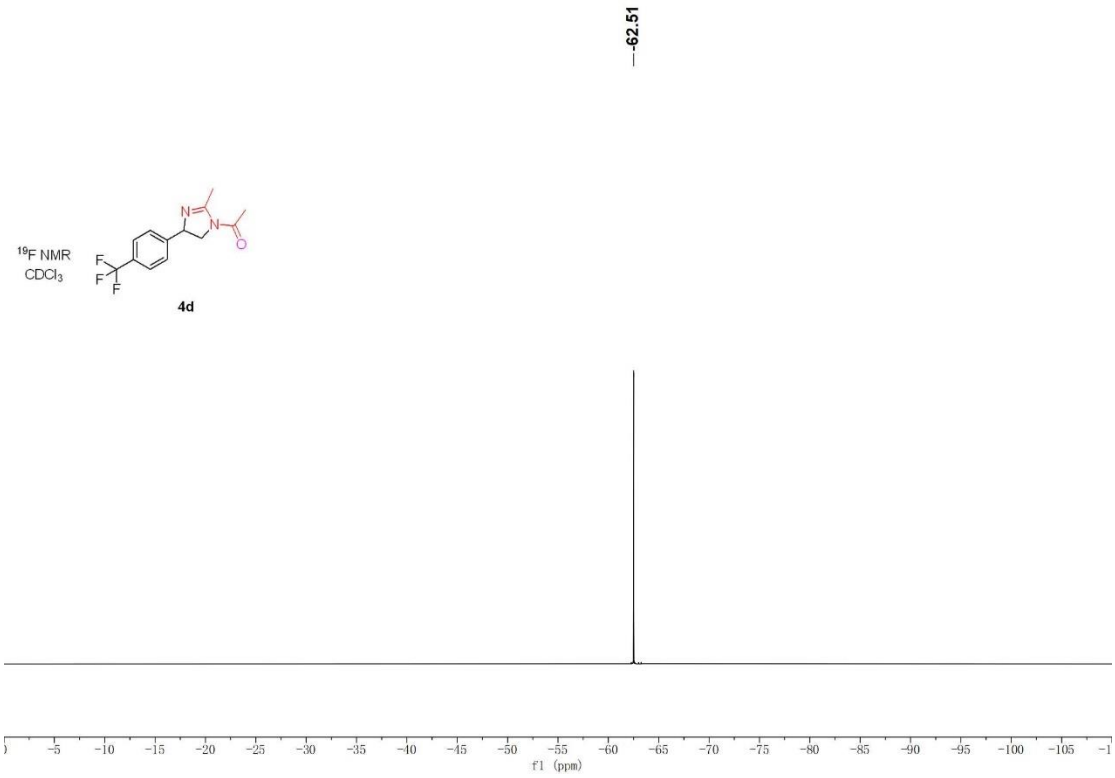
1-(4-(4-chlorophenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**4c**)



1-(2-methyl-4-(4-(trifluoromethyl) phenyl)-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**4d**)



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CDCl3
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-60
-65
-70
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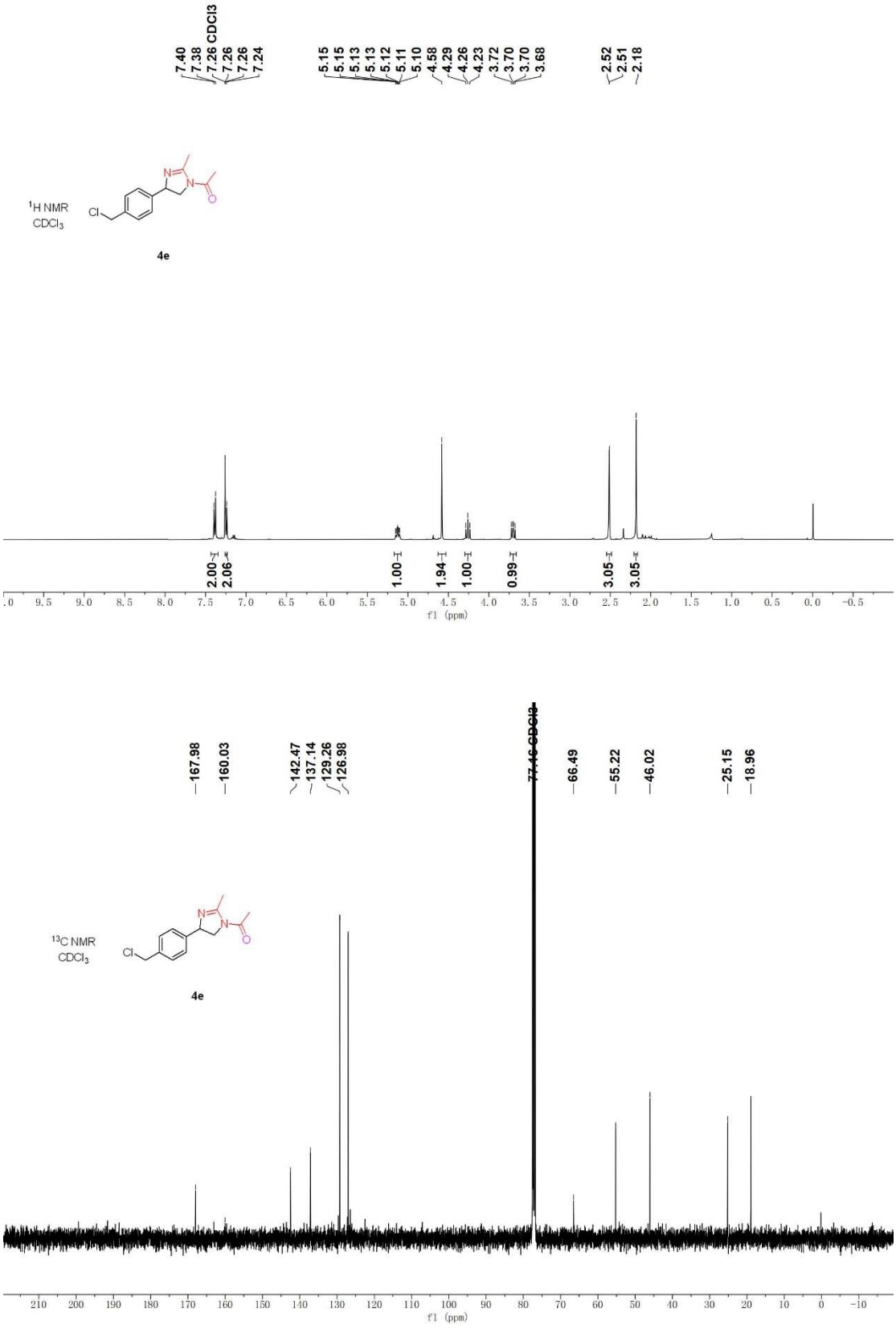
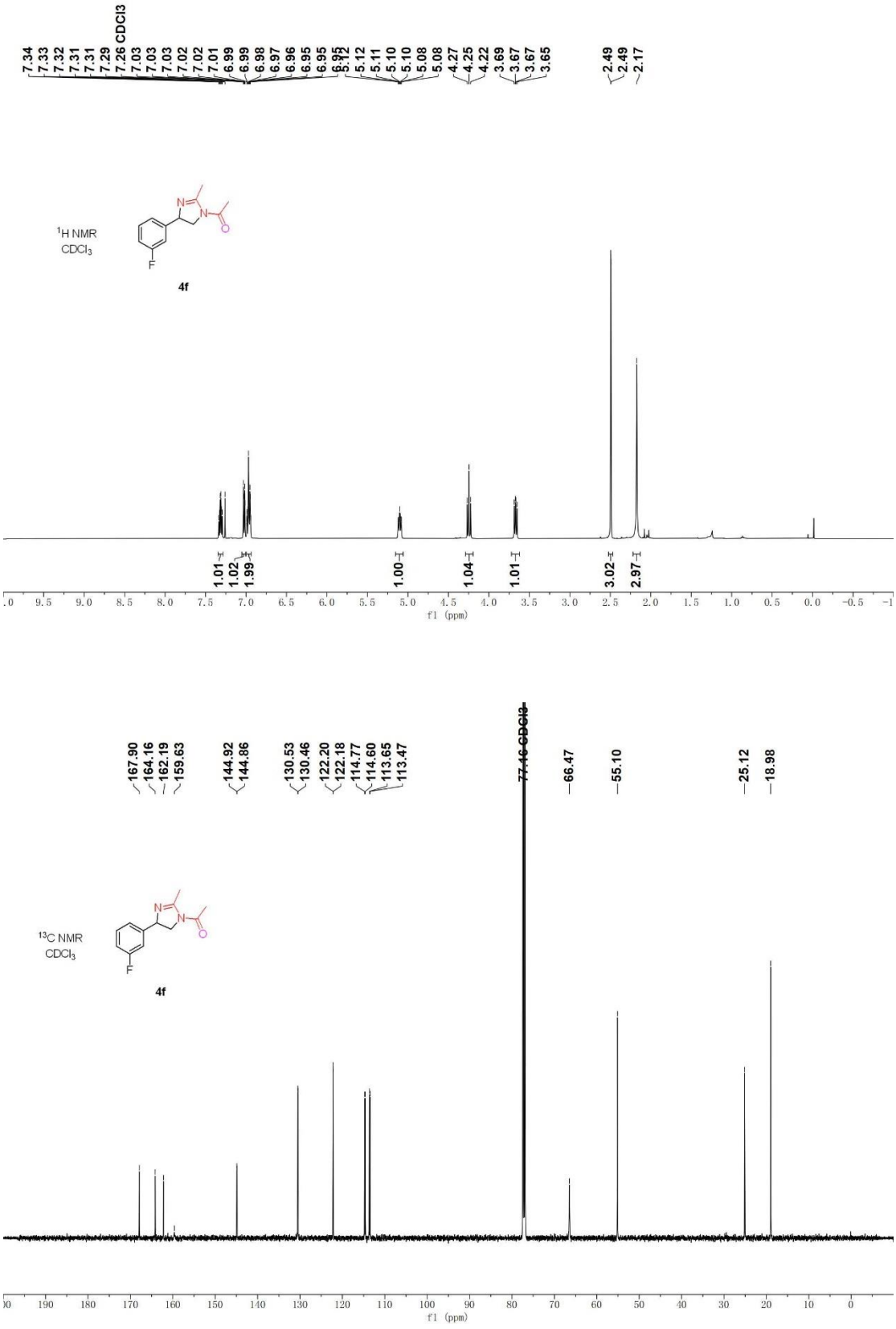
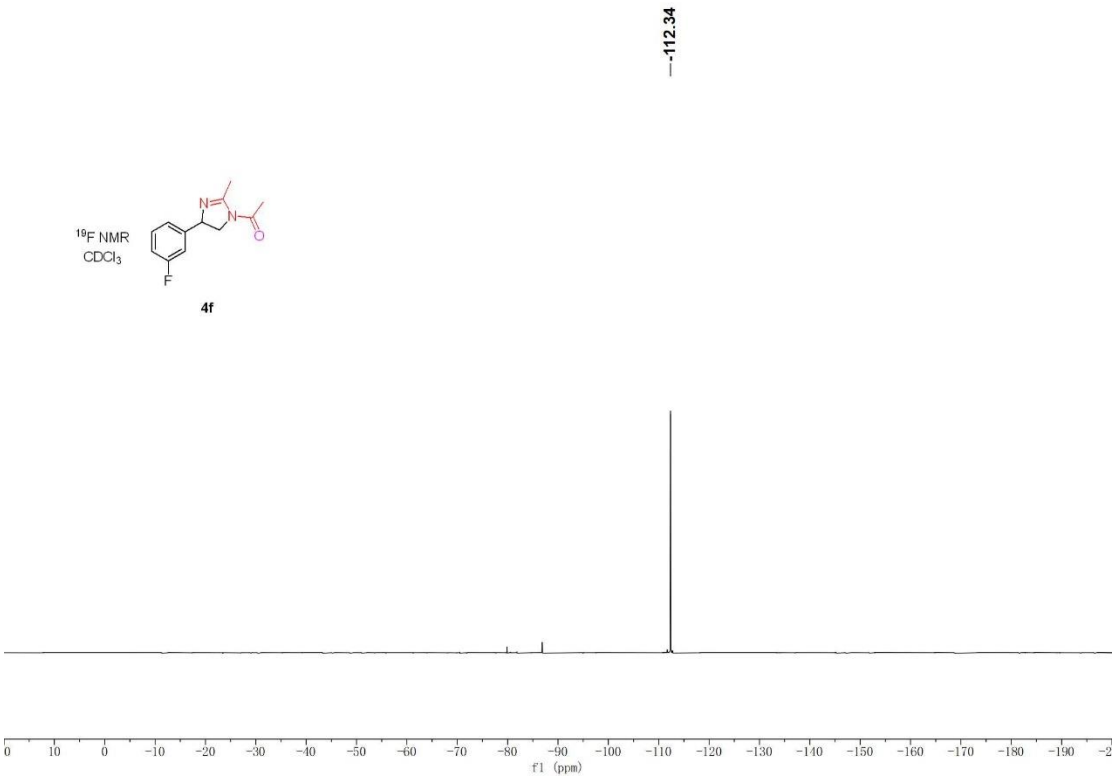
-80
-85
-90
-95
-100
-105
f1 (ppm)

1-(4-(4-(chloromethyl) phenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**4e**)



1-(4-(3-fluorophenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**4f**)

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$CDCl_3$
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4f
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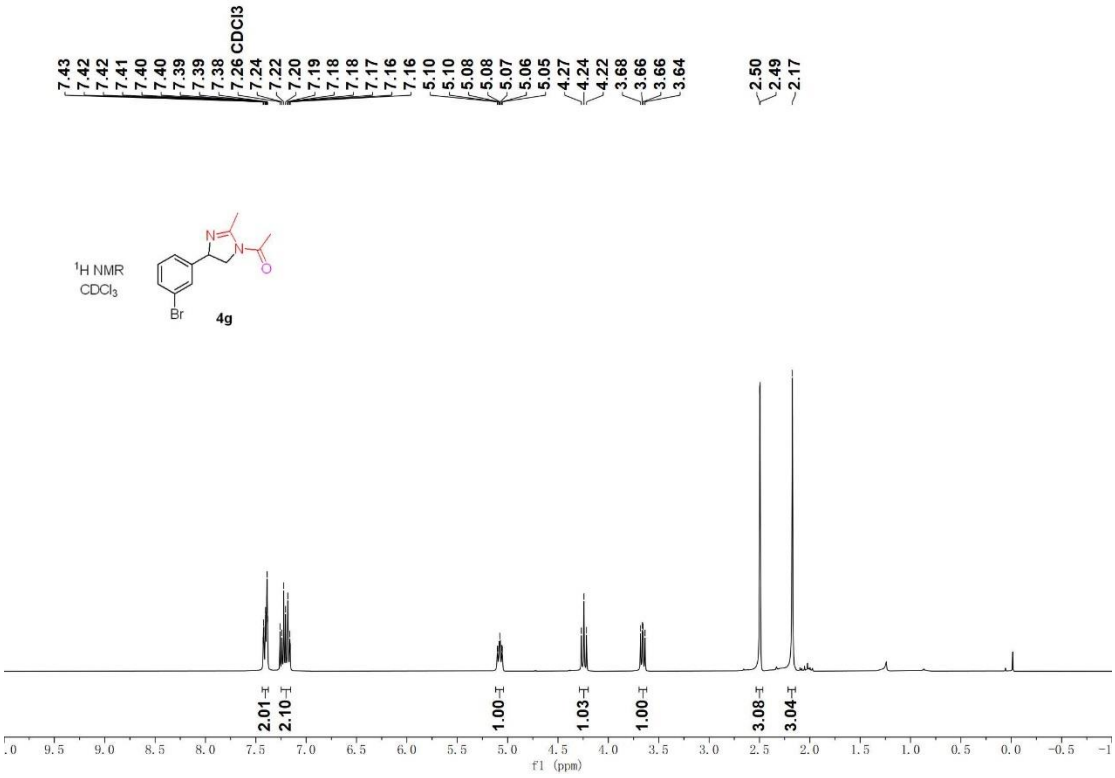
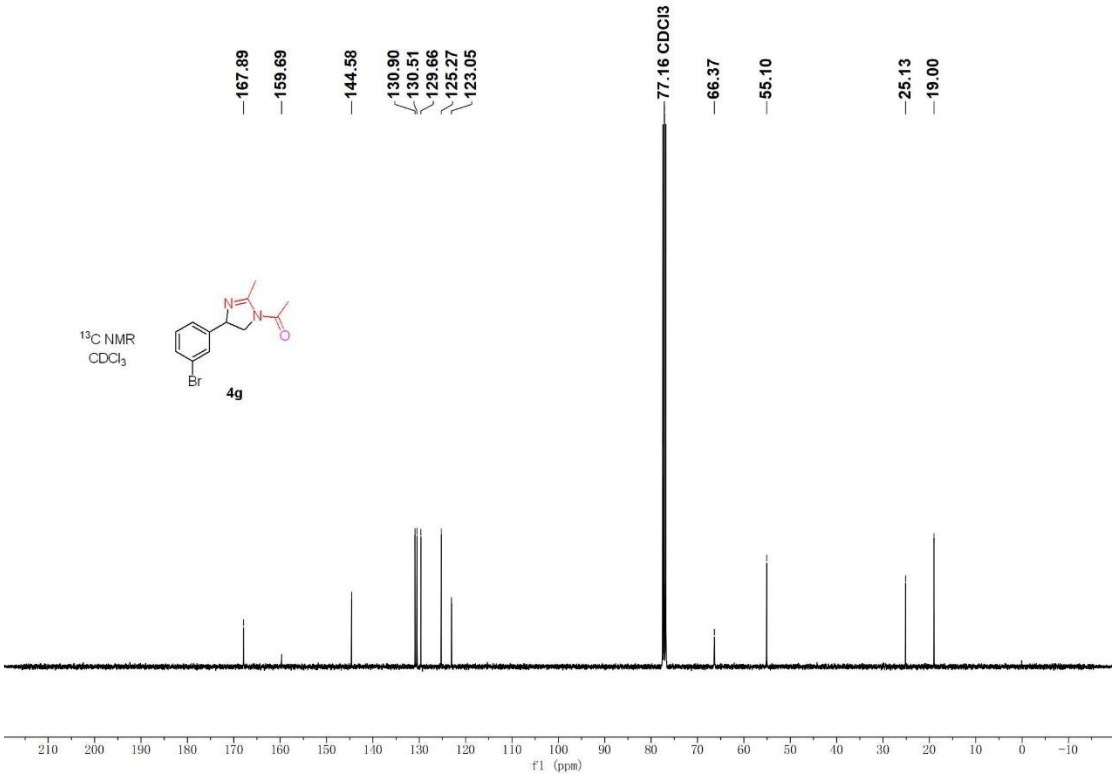
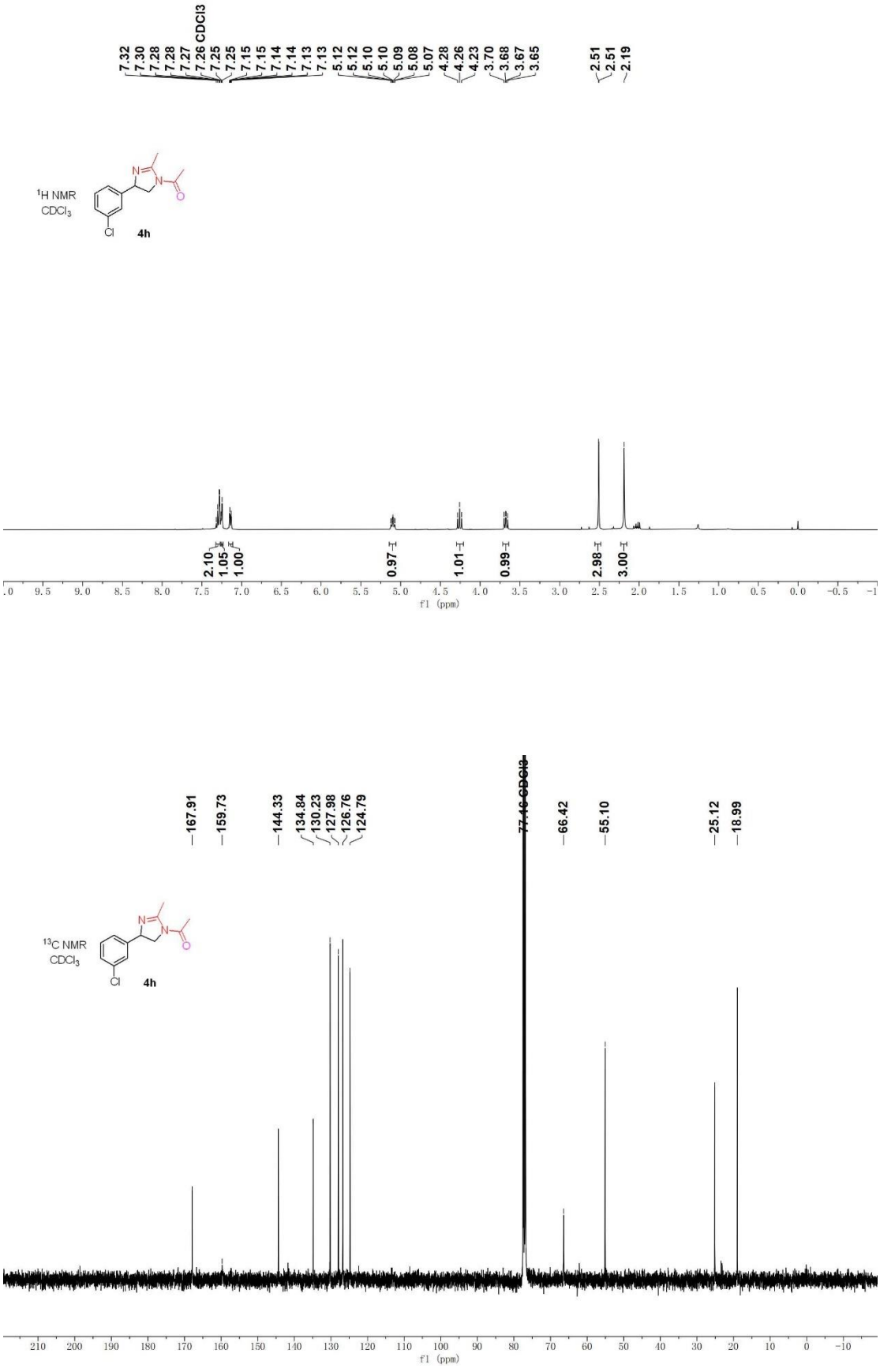
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−2
f1 (ppm)

1-(4-(3-bromophenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**4g**)

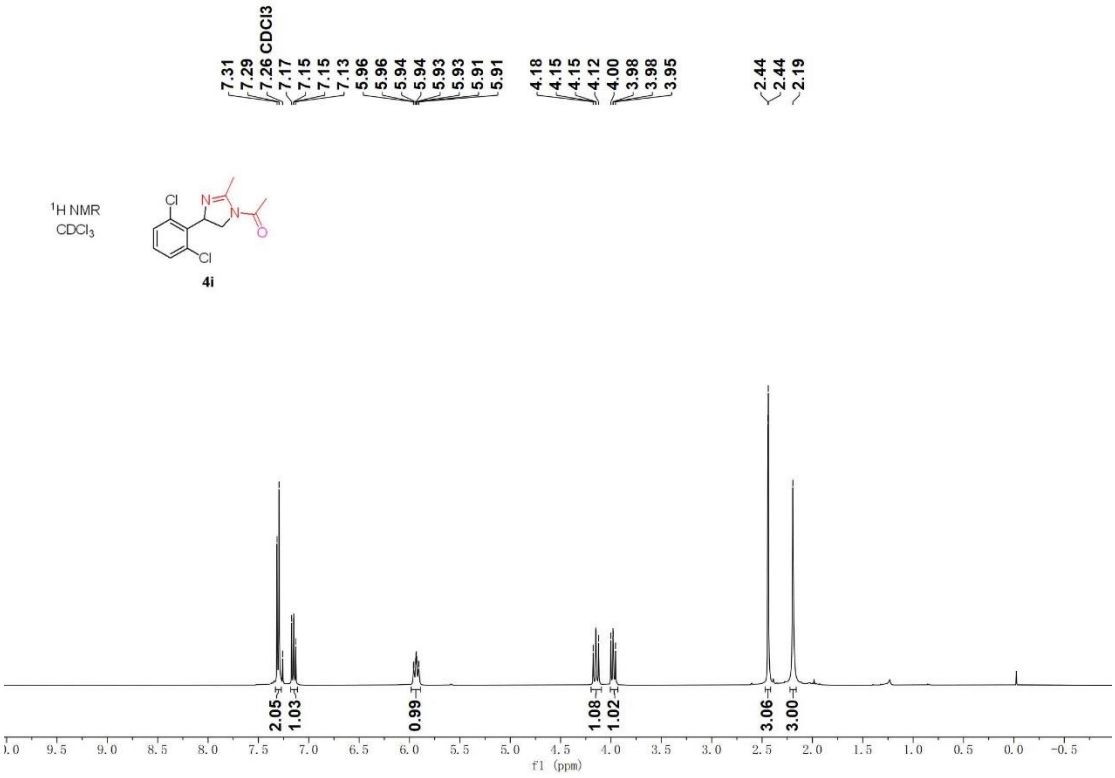


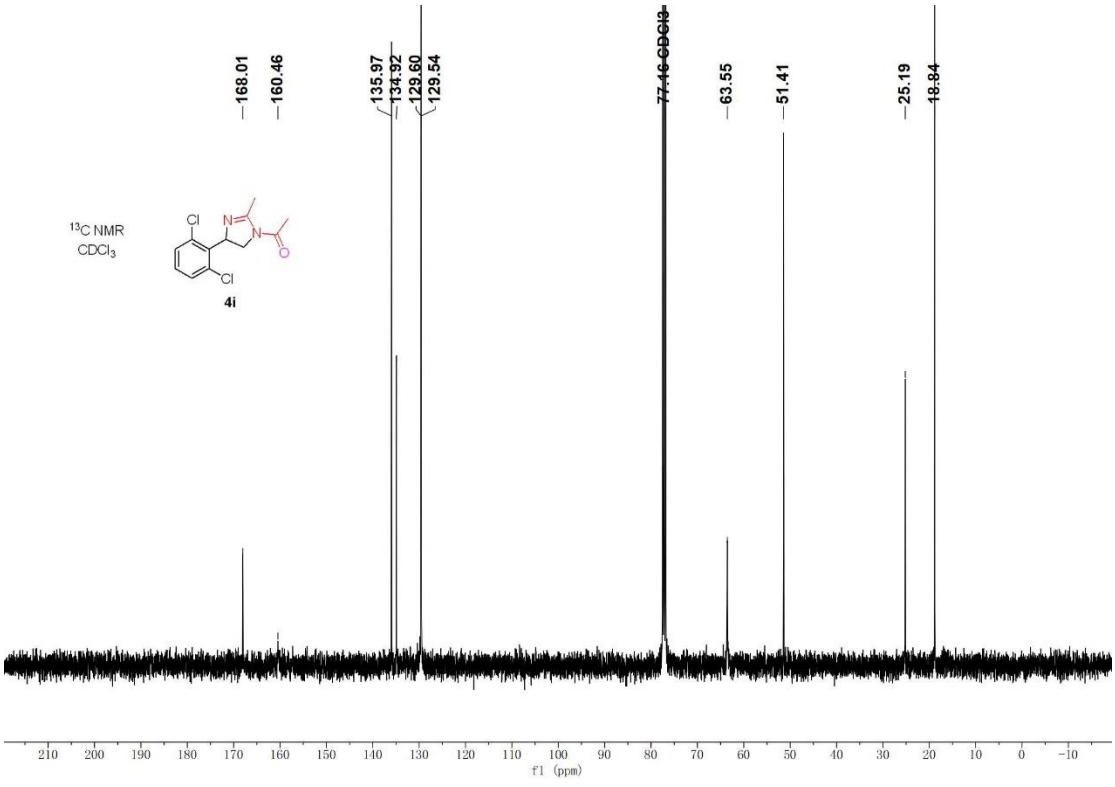


1-(4-(3-chlorophenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one(**4h**)

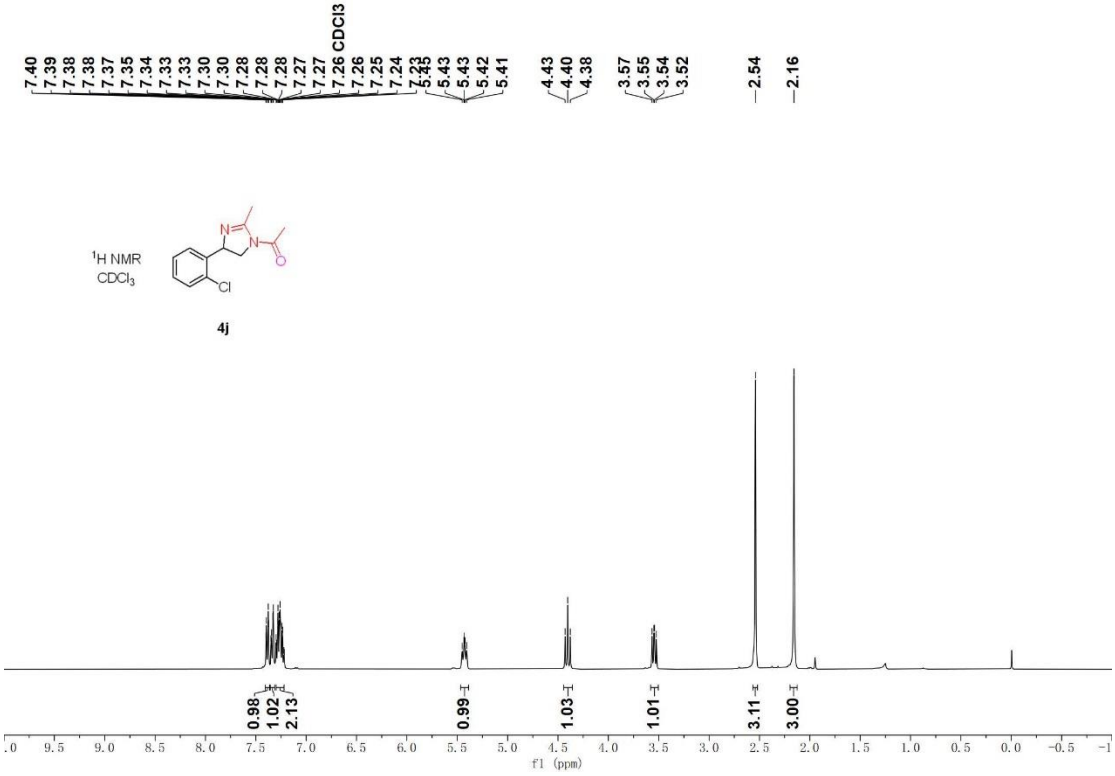


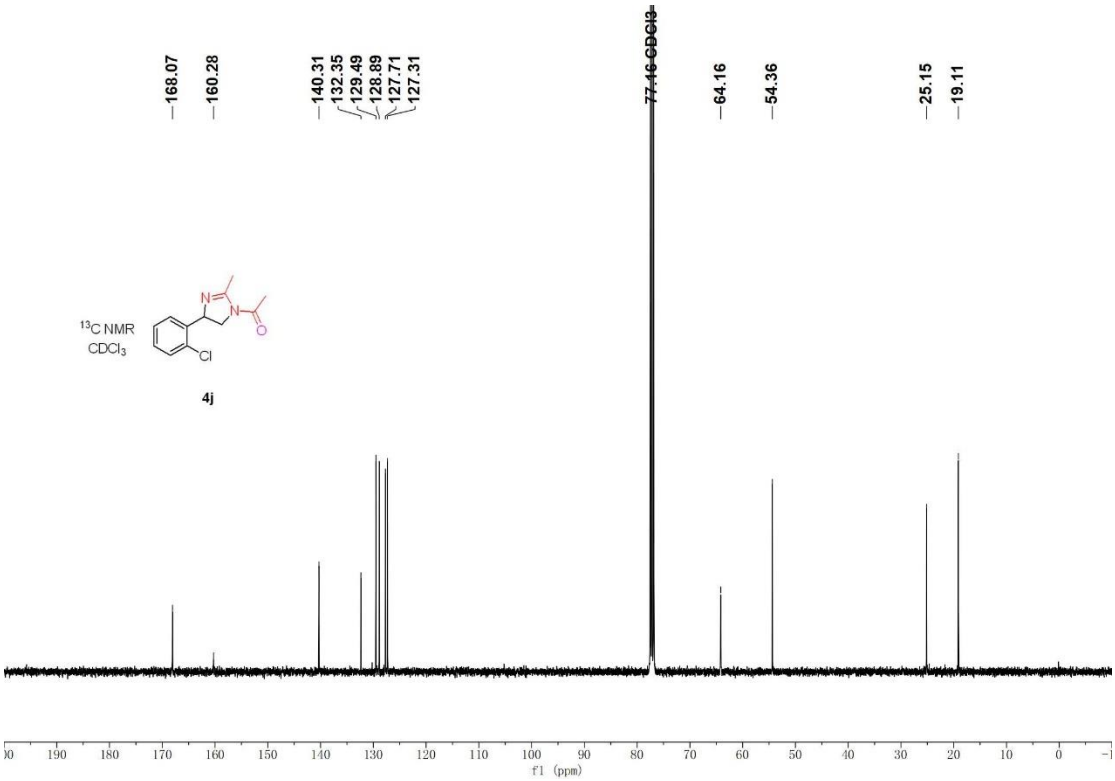
1-(4-(2,6-dichlorophenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**4i**)



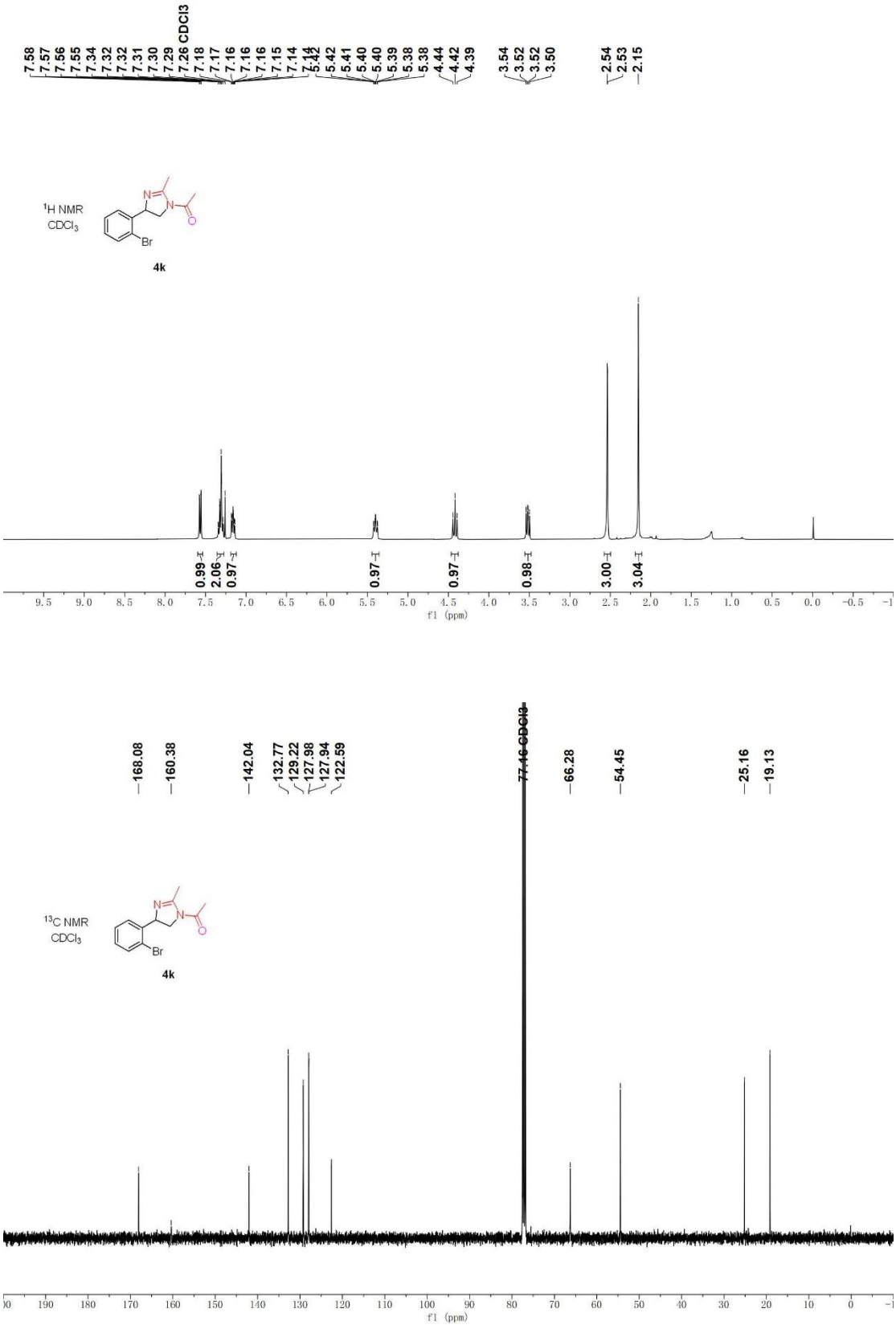


1-(4-(2-chlorophenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one(**4j**)

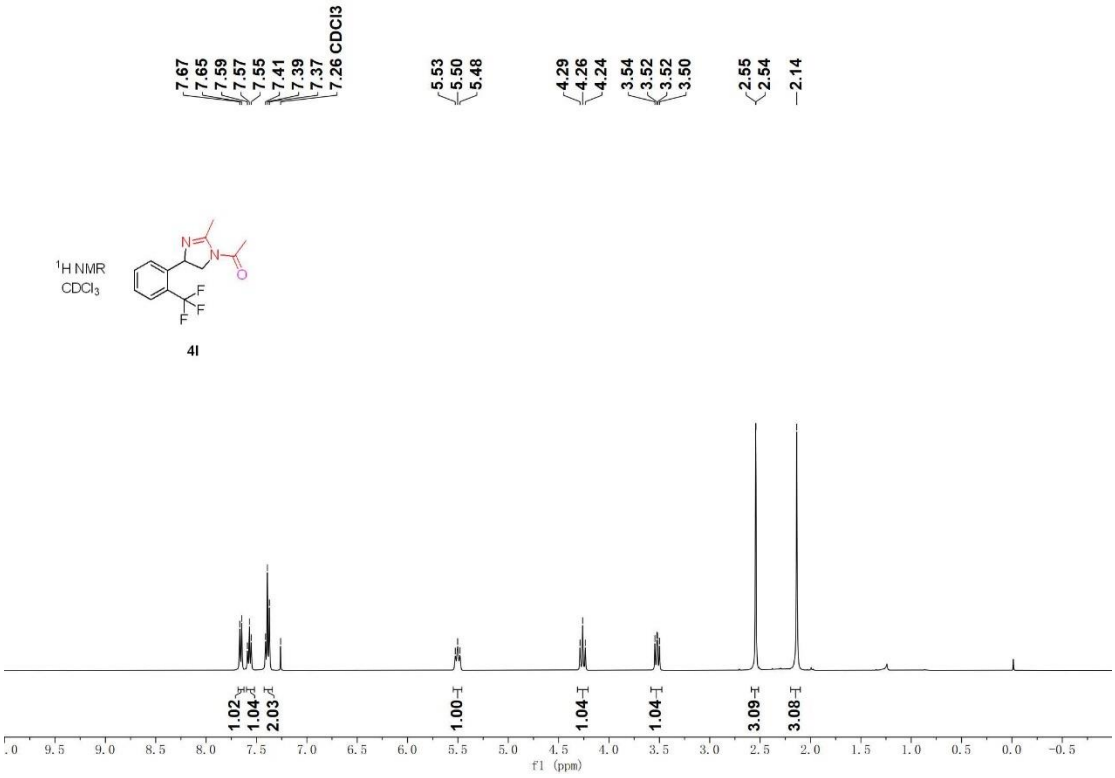


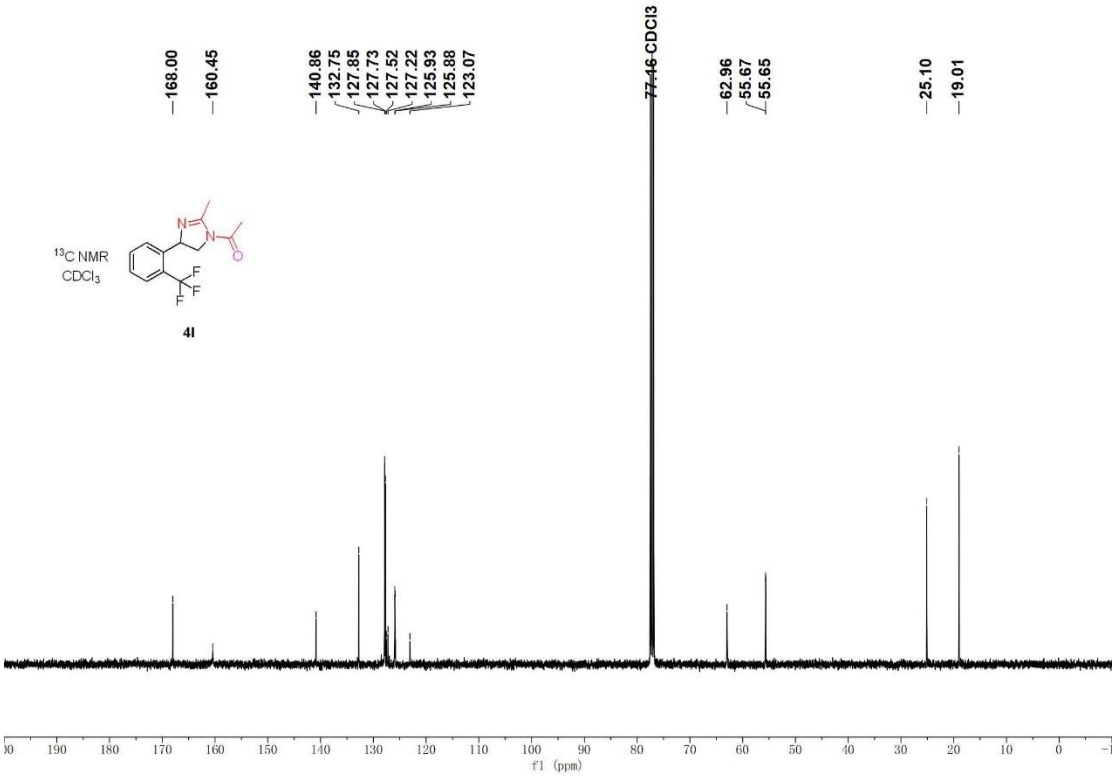


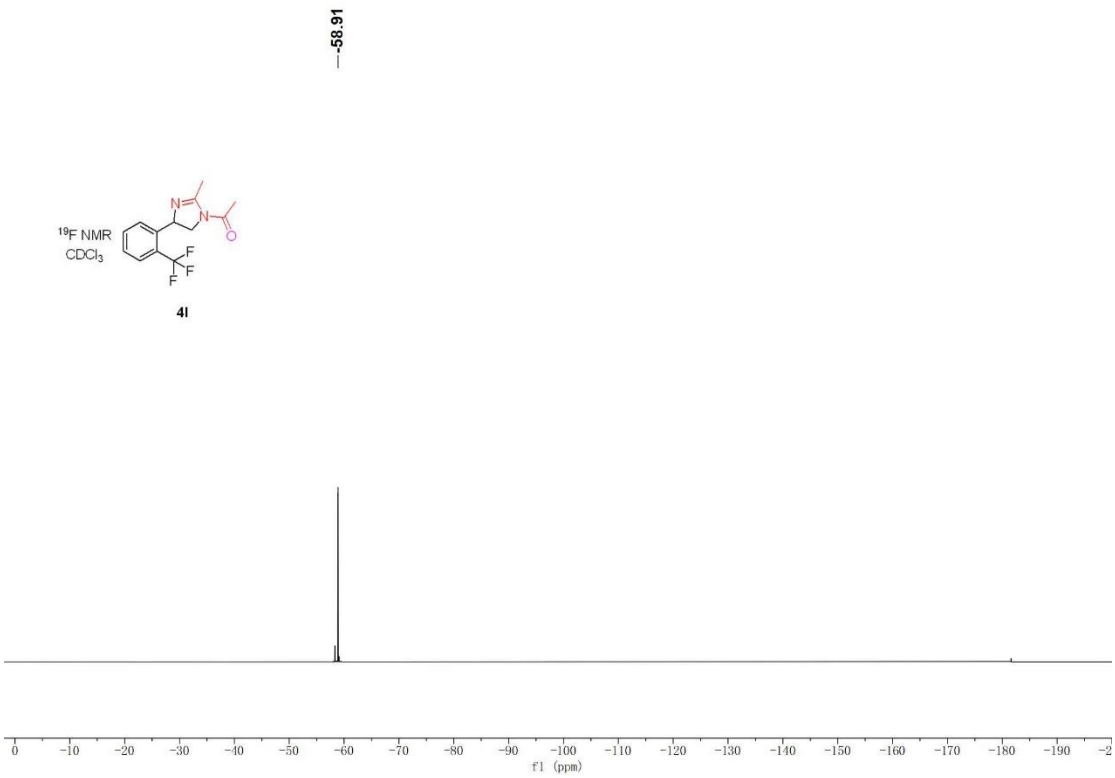
1-(4-(2-bromophenyl)-2-methyl-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**4k**)



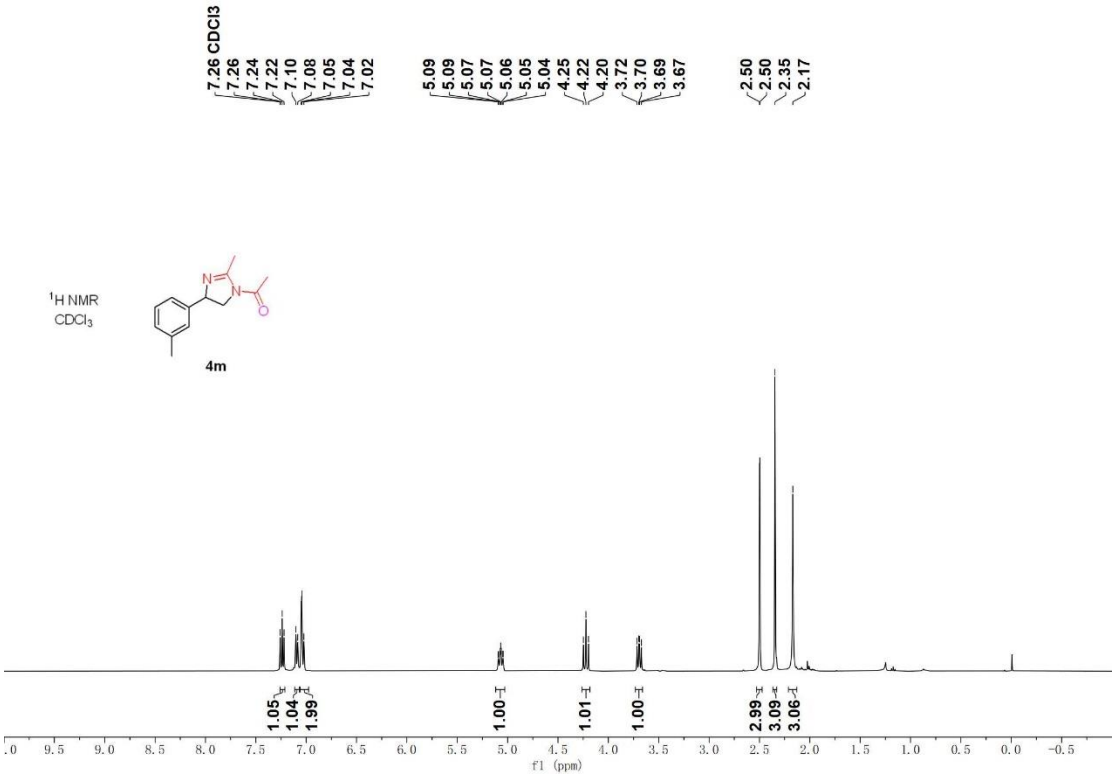
1-(2-methyl-4-(2-(trifluoromethyl) phenyl)-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**4l**)

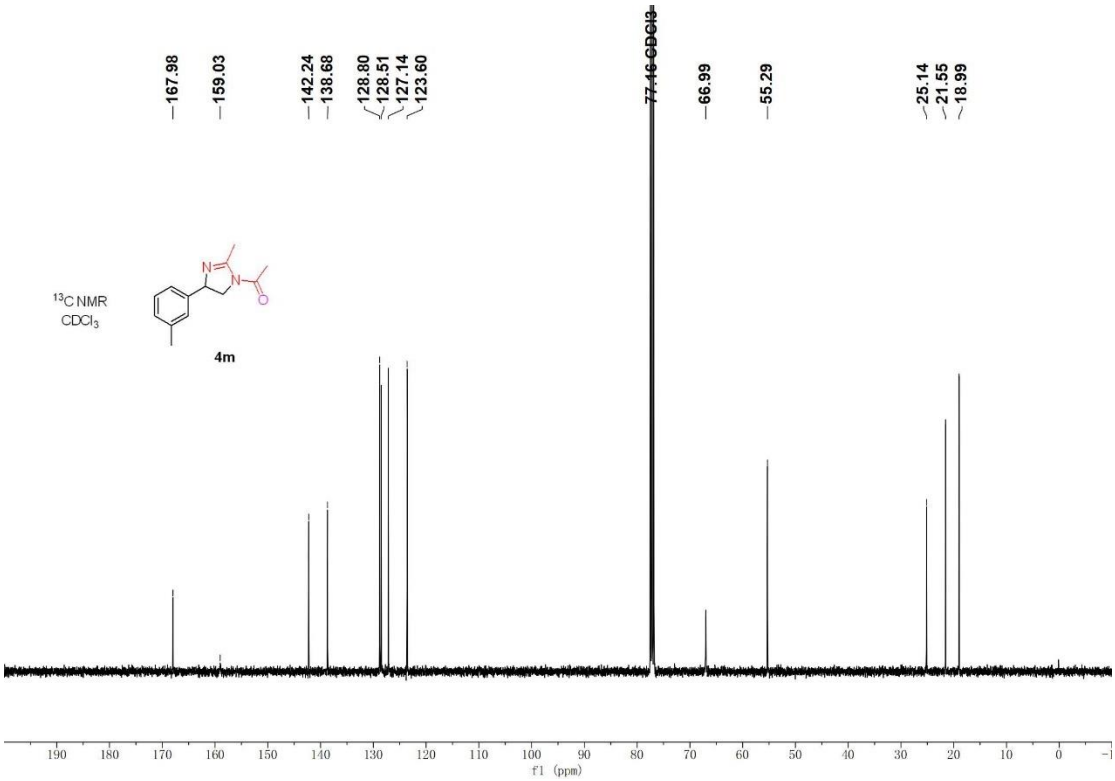




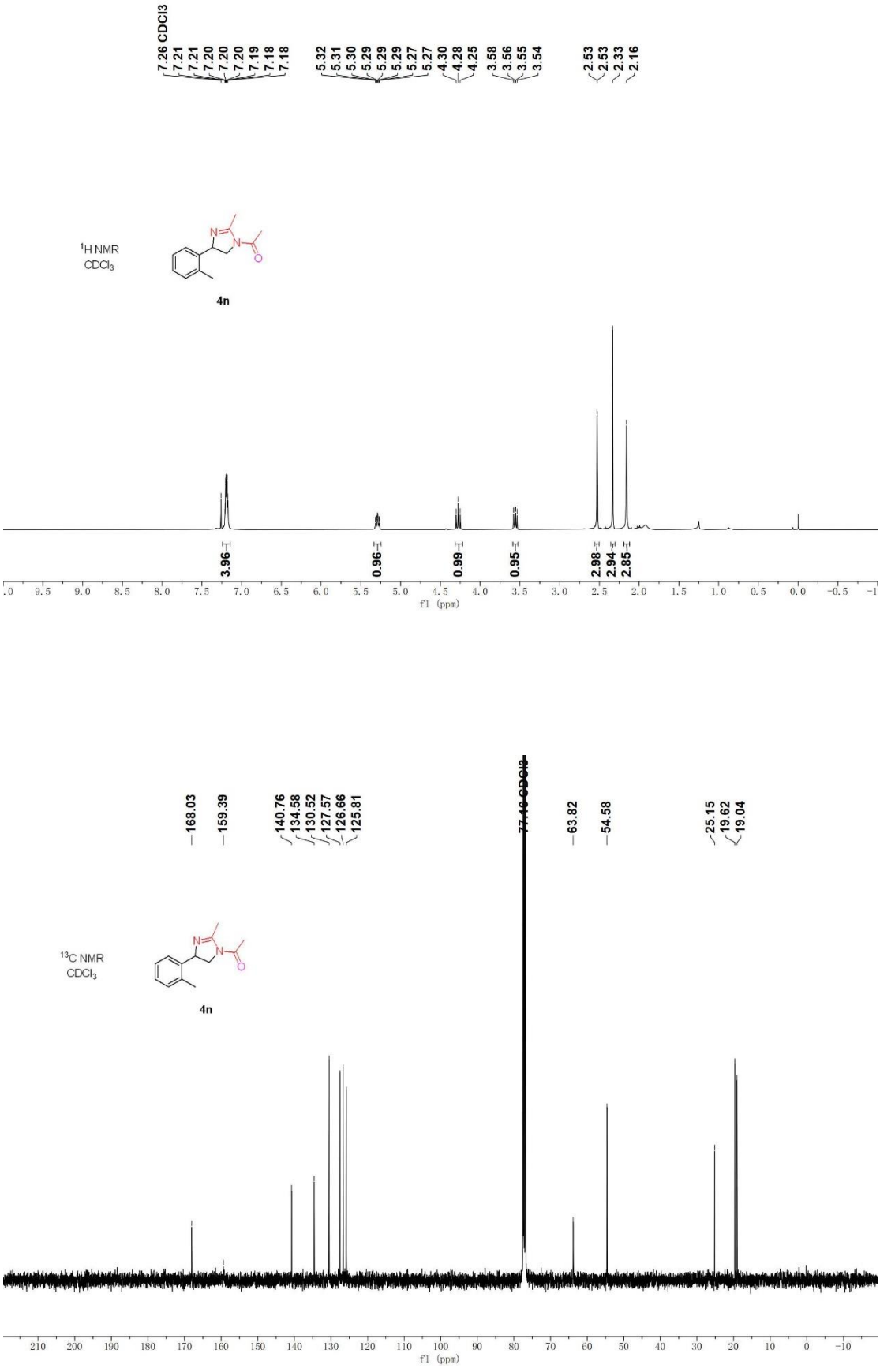

-58.91
^{19}F NMR
$CDCl_3$
4l
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−2
f1 (ppm)

1-(2-methyl-4-(m-tolyl)-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**4m**)

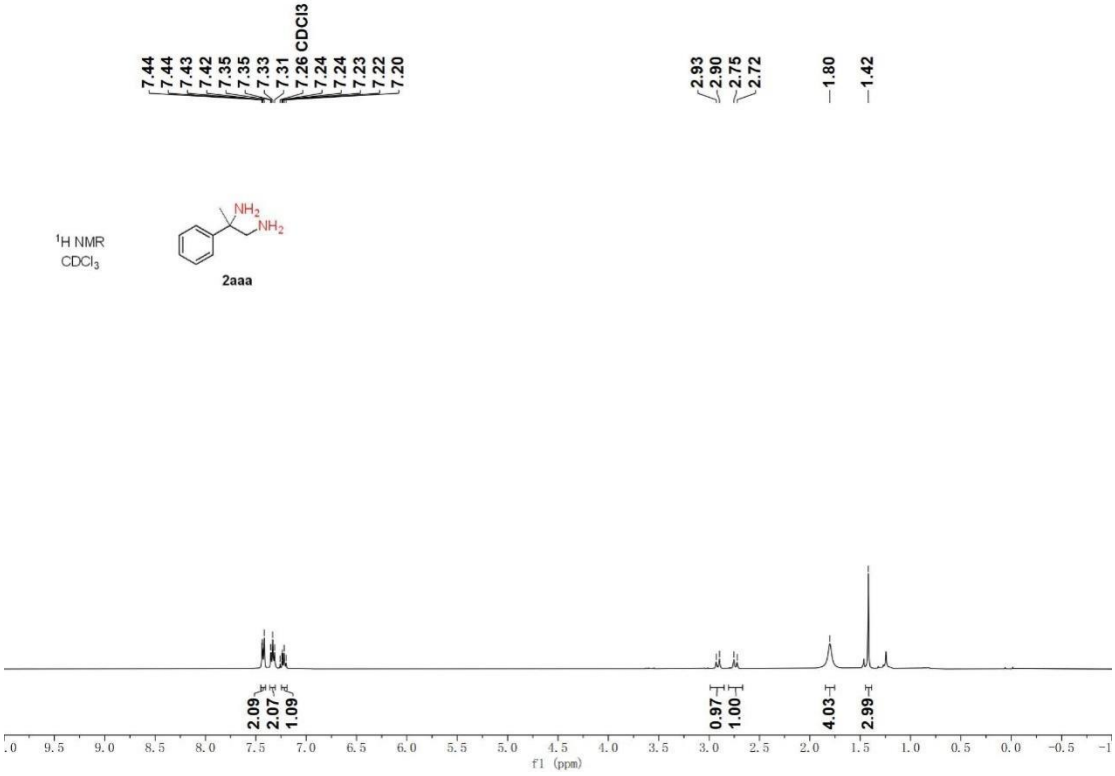


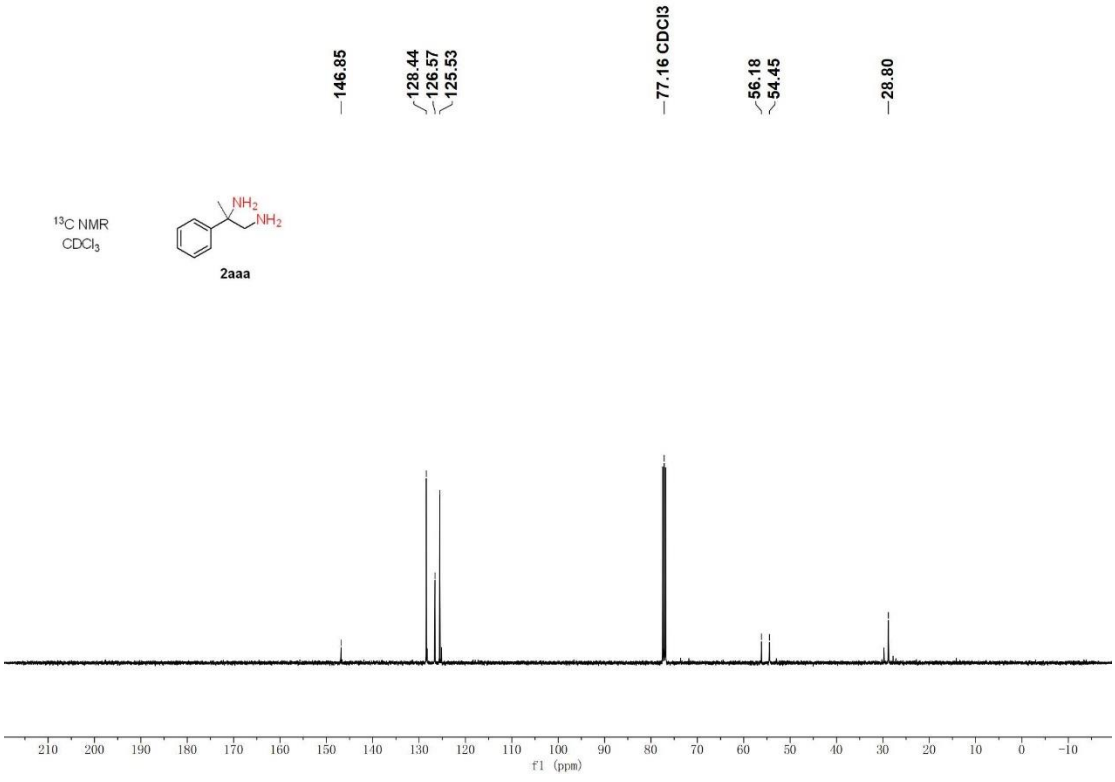


1-(2-methyl-4-(o-tolyl)-4,5-dihydro-1H-imidazol-1-yl) ethan-1-one (**4n**)

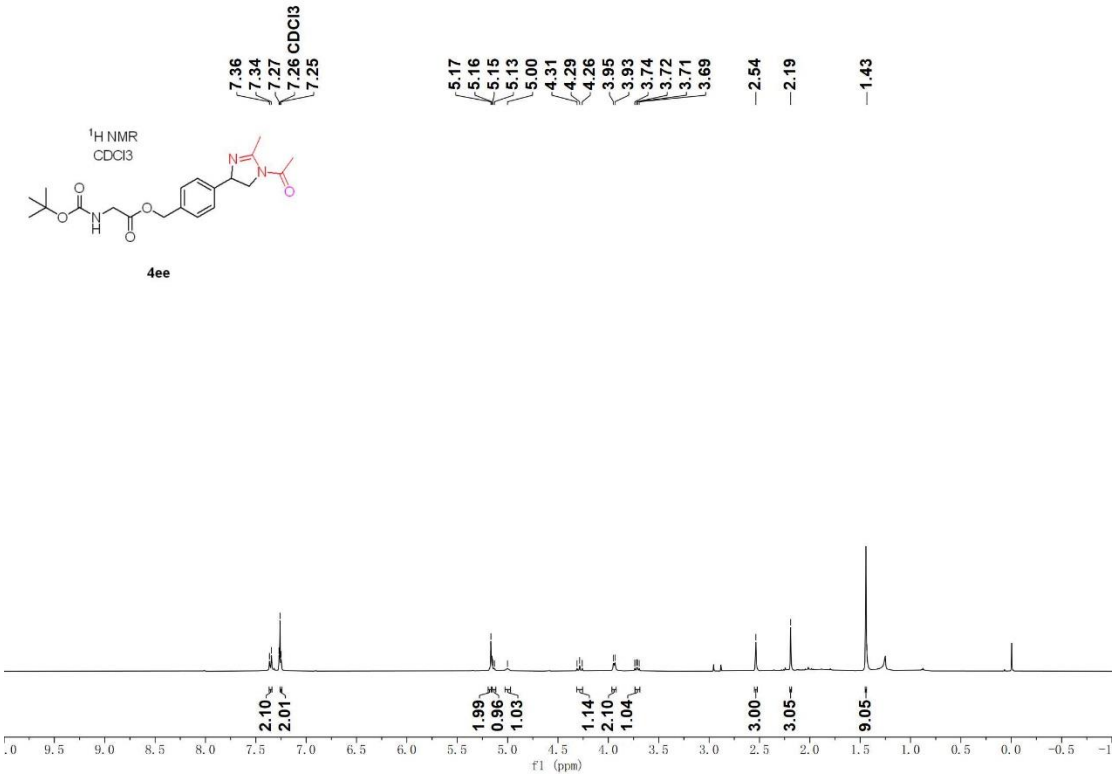


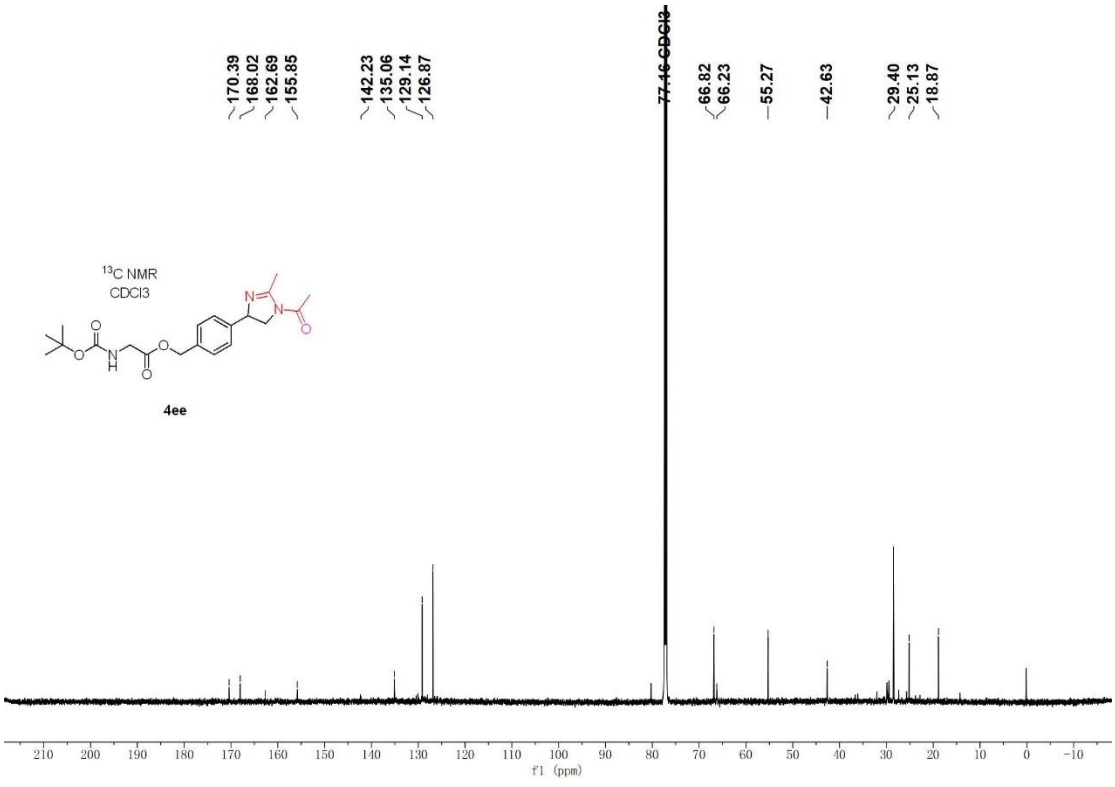
2-phenylpropane-1,2-diamine (**2aaa**)





4-(1-acetyl-2-methyl-4,5-dihydro-1H-imidazol-4-yl) benzyl (tert-butoxycarbonyl) glycinate (**4ee**)





10. Reference

(1) (a) M. T. Chin, T. Yang, K. P. Quirion, C. Lian, P. Liu, J. He and T. Diao. Implementing a Doping Approach for Poly (methyl methacrylate) Recycling in a Circular Economy. *J. Am. Chem. Soc*., 2024, **146**, 5786–5792; (b) X. Mao, M.-M. Li, P. Wang, Q. Cao, W. Zhou and W. Ding. Transition-Metal-Free Anti-Markovnikov Hydroarylation of Alkenes with Aryl Chlorides through Consecutive Photoinduced Electron Transfer. *Org. Lett*., 2024, **26**, 1265–1270.
(2) Sheldrick, G. M. Wisconsin, USA. SHELXTL; Siemens analytical X-ray systems: madison.