Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Divergent Synthesis of Carbamates and *N*-Methyl Carbamates from Dimethyl Carbonate and Nitroarenes with $Mo(CO)_6$ as a Multiple Promoter

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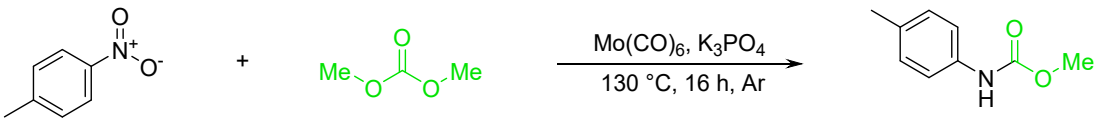
1. General Comments

Chemicals were purchased from Adamas, Bidepharm., TCI, Aladdin and used as such unless stated otherwise. All solvents like dimethyl carbonate were purchased from Adamas (Water ≤ 30 ppm (by K.F.), 99.9%, SafeDry, with molecular sieves, Safeseal). NMR spectra were recorded on Bruker AV 400 or Bruker Fourier 300 spectrometer. Chemical shifts (ppm) are given relative to TMS (0.00 ppm) for ^{1}H and $CDCl_3$ (77.0 ppm) for ^{13}C solvent. Multiplets were assigned as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), dd (doublet of doublet), m (multiplet) and br.s (broad singlet). High-resolution mass spectra HRMS spectra were recorded on a Thermo Scientific Exactive Orbitrap Mass Spectrometer under Electron Spray Ionization conditions preparing sample solution in methanol. The data are given as mass units per charge (m/z). GC yields were calculated using hexadecane as an internal standard. Gas chromatography analysis was performed on an Agilent 6820 instrument with an FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d. 0.25 μm film thickness) using nitrogen as carrier gas. The products were isolated from the reaction mixture by column chromatography on silica gel., 54-74 μm, 200-300 mesh (Yucheng Chemical CO., LTD, Shanghai).

NOTE: a) As carbon monoxide will be released from $Mo(CO)_6$, the reactions should only be handled in a well-ventilated fume hood and the laboratory should be well-equipped with a CO detector and alarm system; b) The reaction was conducted under reflux conditions (temperature is higher than the boiling point of DMC).

2. Experimental Setup

2.1 Screening of DMC solvent amount [a]

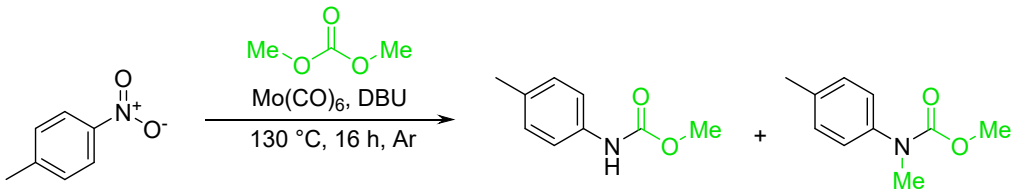


1a **2a** **3a**

entry	Volume (mL)	yield (%)
1	0.625	82
2	0.7	88
3	0.75	94
4	0.8	90
5	0.875	79

6	0.75	38

(Reaction conditions: **1a** (0.30 mmol, 1 equiv.), **2a** (x ml), K_3PO_4 (0.75 mmol, 2.5 equiv.), $Mo(CO)_6$ (0.3 mmol, 1 equiv), 130 °C, 16 h, under Ar, GC yields were determined by using hexadecane as the internal standard; [b] 1.5 equiv. K_3PO_4)

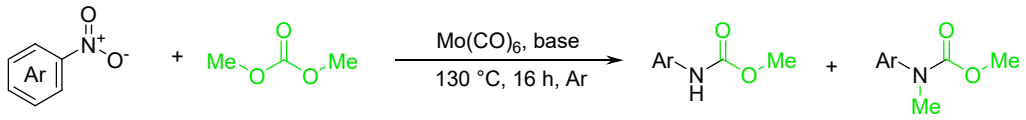


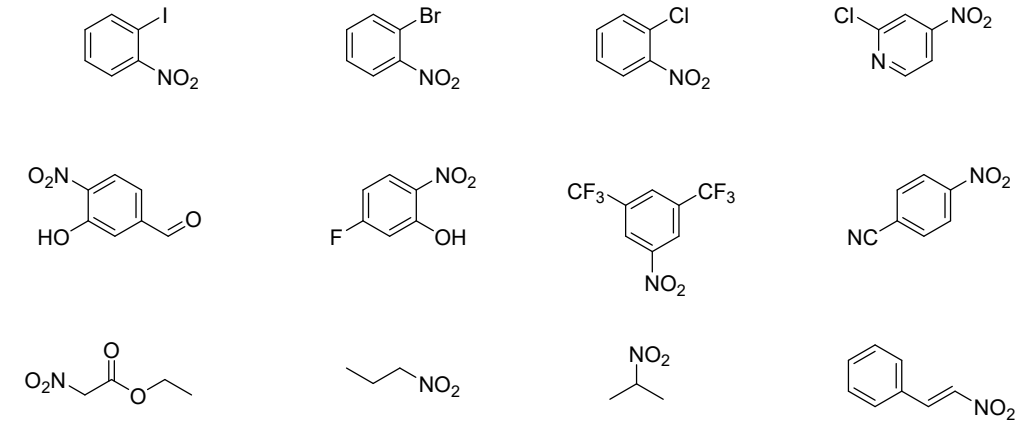
1a **3a** **4a**

entry	Volume **2a** (mL)	Yield **3a** (%)	Yield **4a** (%)
1	0.25	0	83
2	0.5	0	90
3	0.75	0	85
4	1	19	76
5	0.5	0	84

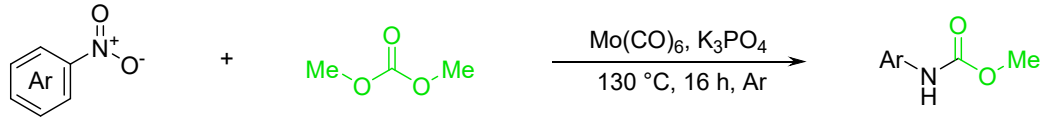
(Reaction conditions: **1a** (0.30 mmol, 1 equiv.), **2a** (x mL), DBU (0.75 mmol, 2.5 equiv.), $Mo(CO)_6$ (0.3 mmol, 1 equiv), 130 °C, 16 h, under Ar, GC yields; [b] 1.5 equiv. DBU)

2.2 Failed examples



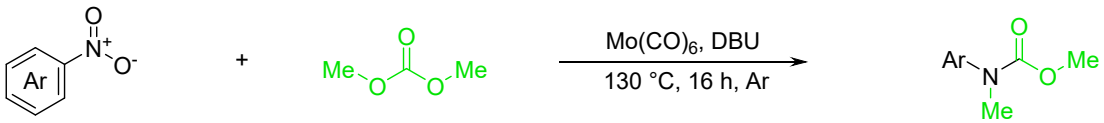


2.3 General process of nitrobenzene reaction with DMC



1a-1t **2a** **3a-3t**

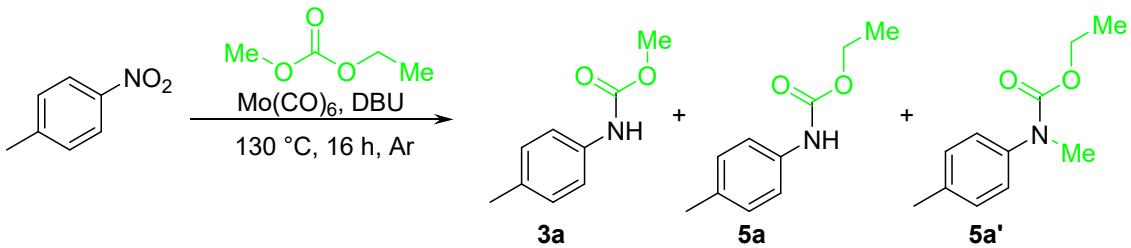
A flame-dried resealable Schlenk tube (10 mL) was added with aromatic nitro compounds **1a-1t** (0.3 mmol), $Mo(CO)_6$ (79.2 mg, 1 equivalent, 0.3 mmol) and K_3PO_4 (0.75 mmol, 2.5 equiv.). The Schlenk tube was capped with a rubber septum, evacuated, and backfilled with argon three times. The liquid **2a** (0.75 mL) were added through the septum, then the septum was replaced with a Teflon screwcap quickly. The Schlenk tube was put into an aluminum heating block and stirred at 130 °C for 16 hours. After the reaction was completed, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and concentrated in vacuo. The crude material was purified by column chromatography on silica gel (eluent: PE and EA) to give the target product **3a-3t**.



1a-1r **2a** **4a-4r**

A flame-dried resealable Schlenk tube (10 mL) was added with aromatic nitro compounds **1a-1r** (0.3 mmol), $Mo(CO)_6$ (79.2 mg, 1 equivalent, 0.3 mmol) and DBU (0.75 mmol, 2.5 equiv.). The Schlenk tube was capped with a rubber septum, evacuated, and backfilled with argon three times. The liquid **2a** (0.5 mL) were added through the septum, then the septum was replaced with a Teflon screwcap quickly. The Schlenk tube was put into an aluminum heating block and stirred at 130 °C for 16 hours. After the reaction was completed, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and concentrated in vacuo. The crude material was purified by column chromatography on silica gel (eluent: PE and EA) to give the target product **4a-4r**.

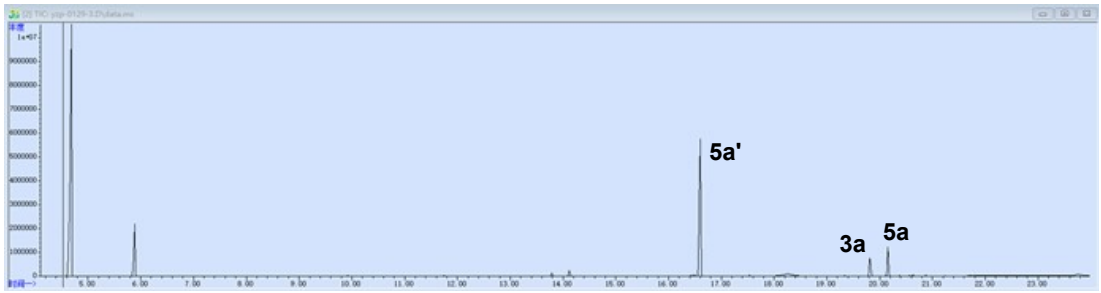
2.4 Investigation of ethyl methyl carbonate

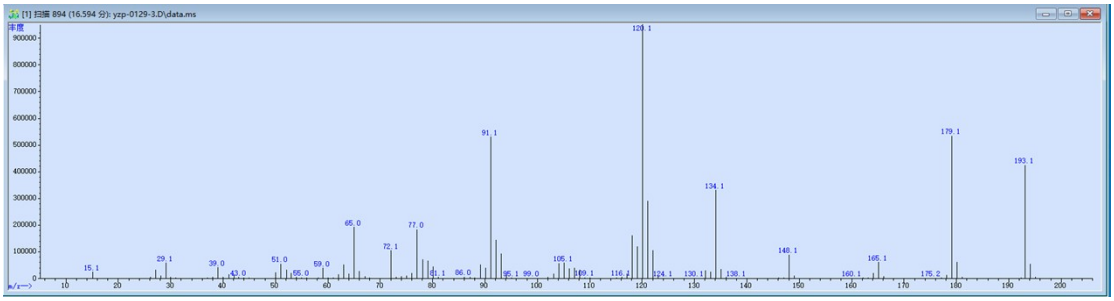


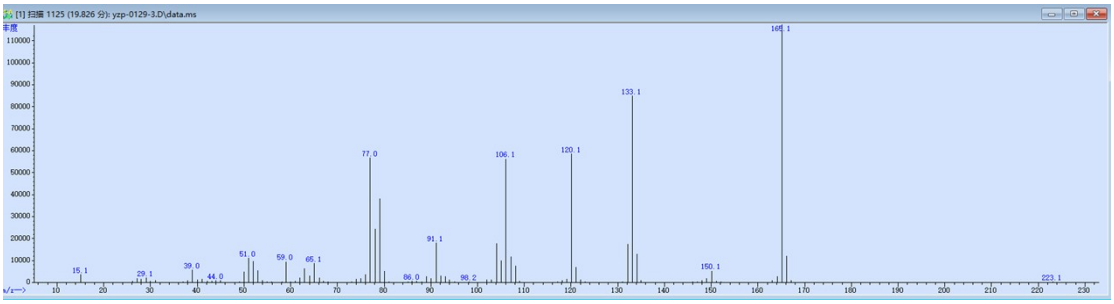
3a **5a** **5a'**

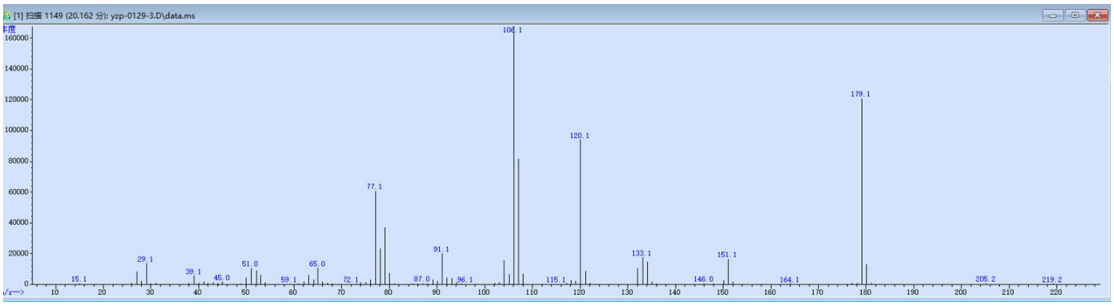
A flame-dried resealable Schlenk tube (10 mL) was added with aromatic nitro compounds **1a** (0.3 mmol), $Mo(CO)_6$ (79.2 mg, 1 equivalent, 0.3 mmol) and DBU (0.75 mmol, 2.5 equiv.). The Schlenk tube was capped with a rubber septum, evacuated, and backfilled with argon three times. The liquid ethyl methyl carbonate (0.5 mL) were added through the septum, then the septum was replaced with a Teflon screwcap

quickly. The Schlenk tube was put into an aluminum heating block and stirred at 130 °C for 16 hours. After the reaction was completed, the reaction mixture was analyzed by GC-MS.



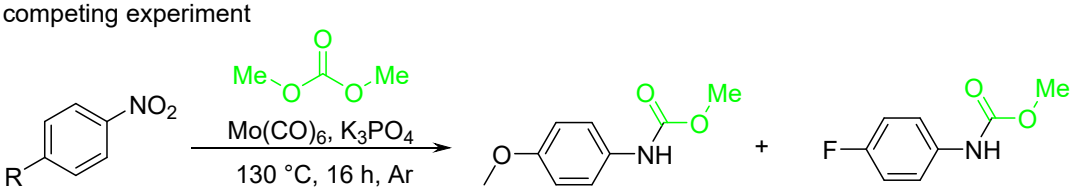






2.5 Competing experiment

g) competing experiment



R = MeO, **1e**
R = F, **1h**

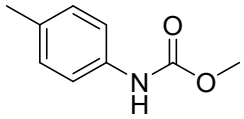
3e, 40%

3h, 29%

A flame-dried resealable Schlenk tube (10 mL) was added with aromatic nitro compounds **1e** (0.3 mmol)

and **1h** (0.3 mmol), $Mo(CO)_6$ (79.2 mg, 1 equivalent, 0.3 mmol) and K_3PO_4 (0.75 mmol, 2.5 equiv.). The Schlenk tube was capped with a rubber septum, evacuated, and backfilled with argon three times. The liquid **2a** (0.5 mL) were added through the septum, then the septum was replaced with a Teflon screwcap quickly. The Schlenk tube was put into an aluminum heating block and stirred at 130 °C for 16 hours. After the reaction was completed, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and concentrated in vacuo. The crude material was purified by column chromatography on silica gel (eluent: PE and EA) to give the target product **3e (**26 mg, 40%) and **3h** (15 mg, 29% yield).

3. Analytical Data

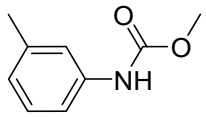


Methyl p-tolyl carbamate (3a): (47 mg, white solid, melting point: 90-91, yield: 94%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.68 (s, 1H), 3.76 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 154.34, 135.35, 133.13, 129.62, 118.92, 52.37, 20.84.

The analytical data are consistent with those reported in the literature.[1]

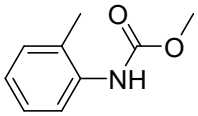


Methyl m-tolyl carbamate (3b): (45 mg, white solid, melting point: 61-62, yield: 91%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (td, *J* = 12.2, 10.9, 6.9 Hz, 3H), 6.94 – 6.78 (m, 1H), 6.57 (s, 1H), 3.77 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.21, 139.13, 137.88, 129.00, 124.45, 119.53, 115.98, 52.42, 21.60.

The analytical data are consistent with those reported in the literature.[2]

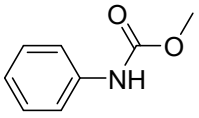


Methyl o-tolyl carbamate (3c): (46 mg, white solid, melting point: 57-58, yield:93%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.29 – 7.19 (m, 1H), 7.22 – 7.13 (m, 1H), 7.08 – 7.00 (m, 1H), 6.45 (s, 1H), 3.78 (s, 1H), 2.25 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.52, 135.90, 130.51, 126.98, 124.35, 121.28, 52.52, 17.75.

The analytical data are consistent with those reported in the literature.[2]

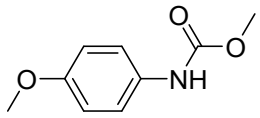


Methyl phenyl carbamate (3d): (39 mg, brown liquid, yield: 87%)

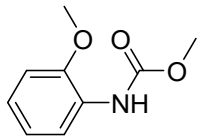
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.27 (m, 4H), 7.18 – 7.03 (m, 1H), 6.87 – 6.67 (m, 1H), 3.77 (d, *J* = 1.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.20, 137.98, 129.17, 123.60, 118.87, 52.45.

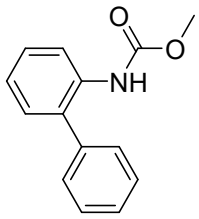
The analytical data are consistent with those reported in the literature.[1]



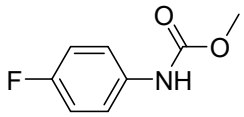
Methyl (4-methoxyphenyl) carbamate (3e): (50 mg, white solid, melting point: 71-72, yield: 93%)
(3t): (50 mg, white solid, yield: 93%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 – 6.81 (m, 2H), 6.68 (s, 1H), 3.76 (d, J = 10.0 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.13, 154.61, 131.03, 120.86, 114.35, 55.60, 52.38.
The analytical data are consistent with those reported in the literature.[1]



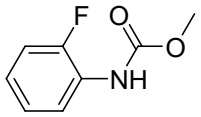
Methyl (2-methoxyphenyl) carbamate (3f): (51 mg, brown liquid, yield: 94%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.01 (m, 1H), 7.07 – 6.92 (m, 2H), 6.85 (dd, J = 7.6, 1.9 Hz, 1H), 3.85 (s, 3H), 3.78 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.10, 147.69, 127.72, 122.88, 121.24, 118.28, 110.09, 55.77, 52.38.
The analytical data are consistent with those reported in the literature.[1]



Methyl [1,1'-biphenyl]-2-ylcarbamate (3g): (61 mg, white solid, melting point: 180-182, yield: 90%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, J = 21.7, 7.8 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.44 – 7.40 (m, 1H), 7.40 – 7.34 (m, 3H), 7.22 (dd, J = 7.6, 1.7 Hz, 1H), 7.13 (td, J = 7.5, 1.2 Hz, 1H), 6.66 (s, 1H), 3.72 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.12, 138.22, 134.96, 131.62, 130.27, 129.40, 129.26, 128.63, 128.07, 123.49, 119.70, 52.40.
The analytical data are consistent with those reported in the literature.[2]



Methyl (4-fluorophenyl) carbamate (3h): (47 mg, brown solid, melting point: 78-79, yield: 93%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 9.1, 4.7 Hz, 2H), 6.99 (t, J = 8.7 Hz, 2H), 6.70 (s, 1H), 3.76 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.15 (d, $J_{C\text{-}F}$ = 243.41 Hz), 154.38, 133.94, 120.63, 115.79 (d, $J_{C\text{-}F}$ = 23.23 Hz), 52.54.
The analytical data are consistent with those reported in the literature.[1]

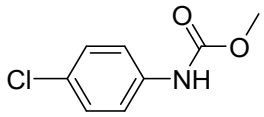


Methyl (2-fluorophenyl) carbamate (3i): (45 mg, colorless liquid, yield: 89%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.20 – 6.93 (m, 3H), 6.87 (s, 1H), 3.80 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.87, 152.30 (d, $J_{C\text{-}F}$ = 243.41 Hz), 126.53 (d, $J_{C\text{-}F}$ = 9.09 Hz), 124.75, 123.55 (d, $J_{C\text{-}F}$ = 8.08 Hz), 120.36, 114.96 (d, $J_{C\text{-}F}$ = 19.19 Hz), 52.69.

The analytical data are consistent with those reported in the literature.[2]

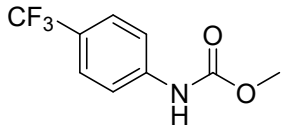


Methyl (4-chlorophenyl) carbamate (3j): (72 mg, white solid, melting point: 107-108, yield: 97%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.21 (m, 4H), 6.76 (s, 1H), 3.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.09, 136.59, 129.15, 128.58, 120.06, 52.60.

The analytical data are consistent with those reported in the literature.[1]

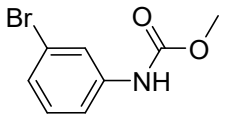


Methyl (4-(trifluoromethyl) phenyl) carbamate (3k): (52.5 mg, white solid, melting point: 118-120, yield: 80%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.6 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 6.77 (s, 1H), 3.80 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.83, 141.12, 126.50, 125.58 (d, $J_{C\text{-}F}$ =8.08 Hz), 124.08 (q, $J_{C\text{-}F}$ = 231.29 Hz), 118.20, 52.76.

The analytical data are consistent with those reported in the literature.[2]

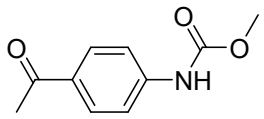


Methyl (3-bromophenyl) carbamate (3l): (65 mg, white solid, melting point: 82-83, yield: 95%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.28 (dt, J = 7.6, 1.8 Hz, 1H), 7.19 – 7.08 (m, 2H), 6.80 (s, 1H), 3.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.95, 139.32, 130.42, 126.54, 122.84, 121.72, 117.27, 52.65.

The analytical data are consistent with those reported in the literature.[5]



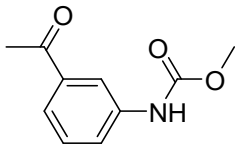
Methyl (4-acetylphenyl) carbamate (3m): (33 mg, yellow solid, melting point: 155-156, yield: 57%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 6.89 (s, 1H), 3.80 (s,

3H), 2.57 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.01, 153.66, 142.46, 132.42, 130.04, 117.75, 52.78, 26.53.

The analytical data are consistent with those reported in the literature.[5]

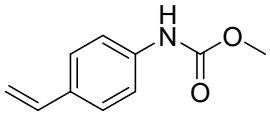


Methyl (3-acetylphenyl) carbamate (3n): (19 mg, yellow solid, melting point: 93-94, yield: 32%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.67 (dd, *J* = 17.3, 7.9 Hz, 2H), 7.41 (dt, *J* = 7.7, 4.0 Hz, 1H), 6.98 – 6.64 (m, 1H), 3.80 (s, 3H), 2.60 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.95, 154.10, 138.52, 138.06, 129.53, 123.51, 118.32, 52.66, 26.82.

The analytical data are consistent with those reported in the literature.[4]

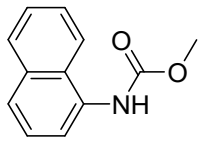


Methyl (4-vinylphenyl) carbamate (3o): (34 mg, white solid, melting point: 96-97, yield: 64%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 4H), 6.78 (s, 1H), 6.66 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.67 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.18 (dd, *J* = 10.9, 0.9 Hz, 1H), 3.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.11, 137.54, 136.23, 133.10, 127.02, 118.79, 112.81, 52.48.

The analytical data are consistent with those reported in the literature.[6]

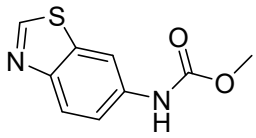


Methyl naphthalen-1-yl carbamate (3p): (52 mg, white solid, melting point: 115-116, yield: 87%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.77 (m, 3H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.43 (m, 3H), 6.96 (s, 1H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.08, 134.18, 132.56, 128.85, 126.88, 126.39, 126.14, 125.92, 125.27, 120.59, 119.40, 52.74.

The analytical data are consistent with those reported in the literature.[11]

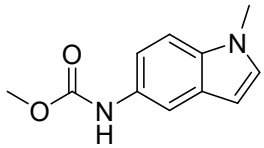


Methyl benzo[d]thiazol-6-yl carbamate (3q): (51 mg, yellow solid, melting point: 77-78, yield: 81%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.30 (s, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.28 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.92 (s, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.18, 153.11, 149.66, 135.91, 135.13, 123.78, 118.40, 111.18, 52.69.

HRMS (ESI-TOF) Calc. for $C_9H_9N_2O_2S^+$ $[M+H]^+$:209.0379; found: 209.0379.

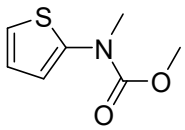


Methyl (1-methyl-1H-indol-5-yl) carbamate (3r): (28 mg, yellow solid, melting point: 148-149, yield: 46%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 1H), 7.73 (s, 1H), 7.57 (d, *J* = 3.7 Hz, 1H), 7.18 (dd, *J* = 8.9, 2.2 Hz, 1H), 6.79 (s, 1H), 6.53 (d, *J* = 3.7 Hz, 1H), 4.02 (s, 3H), 3.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.52, 151.49, 133.43, 131.06, 126.36, 116.59, 115.37, 111.11, 108.27, 53.92, 52.43.

HRMS (ESI-TOF) Calc. for $C_{11}H_{12}NaN_2O_2^+$ [M+Na] $^+$: 227.0791; found: 227.0795.



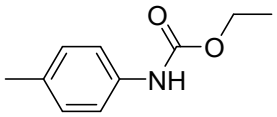
Methyl methyl(thiophen-2-yl) carbamate (3s): (21 mg, brown liquid, yield: 84%)

(4n): (19 mg, brown solid, yield: 27%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 – 6.82 (m, 2H), 6.59 (s, 1H), 3.82 (s, 3H), 3.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.44, 127.10, 124.31, 121.35, 112.03, 53.57, 14.22.

HRMS (ESI-TOF) Calc. for $C_7H_{10}NO_2S^+$ [M+H] $^+$: 172.0427; found: 172.0427.

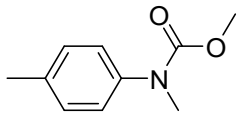


Ethyl p-tolyl carbamate (5a): (K_3PO_4, 29 mg, yellow solid, melting point: 48-49, yield: 54%); (DBU, 15 mg, yellow solid, yield: 27%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.55 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.89, 135.50, 133.08, 129.66, 118.98, 61.26, 20.86, 14.71.

The analytical data are consistent with those reported in the literature.[3]



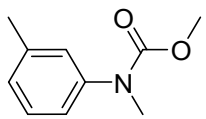
Methyl methyl(p-tolyl) carbamate (4a): (48 mg, yellow liquid, yield: 90%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.02 (m, 4H), 3.69 (s, 3H), 3.27 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.42, 140.82, 136.15, 129.66, 125.82, 53.00, 38.06, 21.09.

GC-MS (EI, 70ev): m/z (%) = 179 ([M]$^+$, 100), 143 (10), 134 (28), 120(66), 91 (55), 72 (40), 39 (5).

HRMS (ESI-TOF) Calc. for $C_{10}H_{14}NO_2^+$ [M+H] $^+$: 180.1019; found: 180.1026.

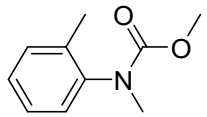


Methyl methyl(m-tolyl) carbamate (4b): (52 mg, white liquid, yield: 99%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.04 (d, *J* = 6.6 Hz, 3H), 3.70 (s, 3H), 3.28 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.35, 143.29, 138.93, 128.81, 127.16, 126.63, 122.99, 53.00, 37.99, 21.45.

HRMS (ESI-TOF) Calc. for $C_{10}H_{14}NO_2^+$ [M+H] $^+$: 180.1019; found: 180.1026.

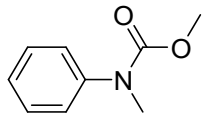


Methyl methyl(o-tolyl) carbamate (4c): (47 mg, white liquid, yield: 88%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 3H), 7.10 (dd, *J* = 5.4, 3.6 Hz, 1H), 3.63 (s, 3H), 3.20 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.47, 141.76, 135.65, 130.98, 127.67, 127.42, 126.98, 53.02, 37.51, 17.45.

HRMS (ESI-TOF) Calc. for $C_{10}H_{14}NO_2^+$ [M+H] $^+$: 180.1019; found: 180.1026.

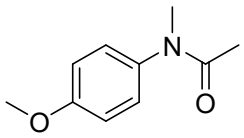


Methyl methyl(phenyl) carbamate (4d): (42 mg, yellow liquid, yield: 85%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 2H), 7.24 – 7.13 (m, 3H), 3.63 (s, 3H), 3.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.27, 143.36, 128.99, 126.25, 125.88, 53.01, 37.90.

The analytical data are consistent with those reported in the literature.[8]



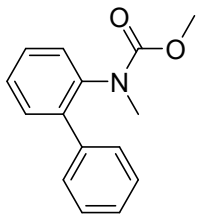
Methyl (4-(N-methyl acetamido) phenyl) carbonate (4e): (23 mg, white liquid, yield: 53%)

(4o): (31 mg, white liquid, yield: 72%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.3 Hz, 2H), 6.95 – 6.79 (m, 2H), 3.79 (s, 3H), 3.68 (s, 3H), 3.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.94, 156.56, 136.30, 127.30, 114.26, 55.52, 52.99, 38.28.

The analytical data are consistent with those reported in the literature.[9]



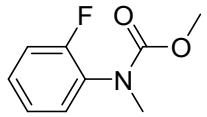
Methyl [1,1'-biphenyl]-2-yl(methyl) carbamate (4f): (46 mg, white liquid, yield: 64%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.40 – 7.38 (m, 2H), 7.36 (d, *J* = 3.1 Hz, 2H), 7.31

– 7.27 (m, 2H), 7.25 (dd, *J* = 3.9, 2.6 Hz, 1H), 3.50 (s, 3H), 2.98 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.32, 140.70, 139.82, 139.45, 130.96, 128.59, 128.42, 128.37, 128.19, 127.69, 127.51, 52.84, 37.91.

The analytical data are consistent with those reported in the literature.[8]



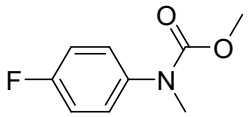
Methyl (2-fluorophenyl) (methyl) carbamate (4g): (29 mg, yellow liquid, yield: 52%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.14 (m, 2H), 7.13 – 6.98 (m, 2H), 3.62 (s, 3H), 3.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.29, 156.52 (d, J = 56.56 Hz), 130.78, 129.11, 128.72 (d, J = 8.08 Hz), 124.54, 116.61(d, J = 20.20 Hz), 53.24, 37.68.

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.57.

HRMS (ESI-TOF) Calc. for $C_9H_{11}FNO_2^+$ [M+H] $^+$: 184.0768; found: 184.0776



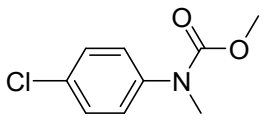
Methyl (4-fluorophenyl) (methyl) carbamate (4h): (34 mg, white liquid, yield: 62%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.8, 4.8 Hz, 2H), 7.03 (dd, *J* = 9.1, 8.1 Hz, 2H), 3.69 (s, 3H), 3.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.82 (d, J = 245.43 Hz), 156.30, 139.35, 127.71,115.85 (d, J = 23.23 Hz), 53.13, 38.11.

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.55.

HRMS (ESI-TOF) Calc. for $C_9H_{11}FNO_2^+$ [M+H] $^+$: 184.0768; found: 184.0776

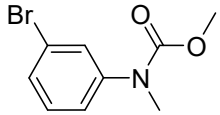


Methyl (4-chlorophenyl) (methyl) carbamate (4i): (47 mg, white liquid, yield: 78%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.30 (d, *J* = 2.1 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 2H), 3.71 (s, 3H), 3.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.08, 141.93, 131.69, 129.11, 127.11, 53.16, 37.81.

The analytical data are consistent with those reported in the literature.[10]



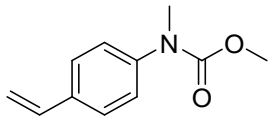
Methyl (3-bromophenyl) (methyl) carbamate (4j): (53 mg, white liquid, yield: 73%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 2.0 Hz, 1H), 7.34 (dt, *J* = 7.3, 1.9 Hz, 1H), 7.24 – 7.16 (m, 2H), 3.72 (s, 3H), 3.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.94, 144.64, 130.18, 129.22, 128.94, 124.41, 122.26, 53.22, 37.74.

HRMS (ESI-TOF) Calc. for $C_9H_{10}Br^{79}NaNO_2^+$ [M+Na] $^+$: 265.9787; found: 265.9800

HRMS (ESI-TOF) Calc. for $C_9H_{10}Br^{81}NaNO_2^+$ [M+Na] $^+$: 267.9787; found: 267.9781

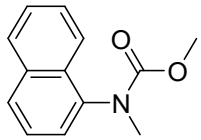


Methyl methyl(4-vinylphenyl) carbamate (4k): (28 mg, white liquid, yield: 49%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.25 (dd, *J* = 10.9, 0.9 Hz, 1H), 3.71 (s, 3H), 3.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.21, 142.74, 136.09, 135.54, 126.74, 125.80, 114.19, 53.10, 37.83.

HRMS (ESI-TOF) Calc. for $C_{11}H_{14}NO_2^+$ [M+H] $^+$: 192.1019; found: 192.1019

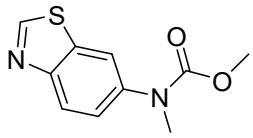


Methyl methyl(naphthalen-1-yl) carbamate (4l): (63 mg, yellow liquid, yield: 98%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 1H), 7.81 (t, *J* = 7.6 Hz, 2H), 7.58 – 7.44 (m, 3H), 7.35 (d, *J* = 7.4 Hz, 1H), 3.58 (s, 3H), 3.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.13, 139.62, 134.68, 130.32, 128.61, 128.11, 126.95, 126.41, 125.85, 124.97, 122.67, 53.14, 38.56.

HRMS (ESI-TOF) Calc. for $C_{13}H_{15}NO_2^+$ [M+H] $^+$: 216.1019 ; found: 216.1022

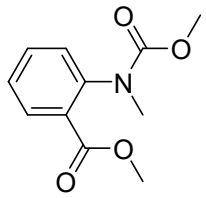


Methyl benzo[d]thiazol-6-yl(methyl) carbamate (4m): (21 mg, brown liquid, yield: 31%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 1.6 Hz, 1H), 8.10 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.84 (s, 1H), 7.40 (d, *J* = 8.7 Hz, 1H), 3.72 (s, 3H), 3.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.29, 154.56, 151.47, 141.07, 134.24, 124.86, 123.79, 119.24, 53.26, 38.32.

HRMS (ESI-TOF) Calc. for $C_{10}H_{10}NaN_2O_2S^+$ [M+Na] $^+$: 245.0355; found: 245.0357

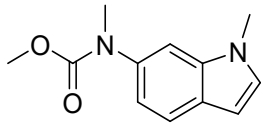


Methyl 2-((methoxycarbonyl)(methyl)amino) benzoate (4p): (30 mg, white liquid, yield: 45%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.90 (m, 1H), 7.65 – 7.50 (m, 1H), 7.35 (q, *J* = 7.2, 6.6 Hz, 1H), 7.26 (q, *J* = 7.9, 6.7 Hz, 1H), 3.87 (s, 3H), 3.58 (s, 3H), 3.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.51, 156.13, 143.07, 133.26, 131.42, 128.75, 128.27, 127.28, 52.93, 52.46, 38.29.

HRMS (ESI-TOF) Calc. for $C_{11}H_{14}NO_4^+$ [M+H] $^+$: 246.0737; found: 246.0748

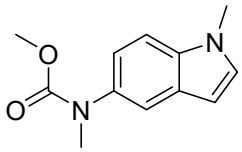


Methyl methyl(1-methyl-1H-indol-6-yl) carbamate (4q): (38 mg, yellow liquid, yield: 59%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.3 Hz, 1H), 7.22 – 7.12 (m, 1H), 7.07 (d, *J* = 3.1 Hz, 1H), 6.96 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.48 (dd, *J* = 3.0, 0.9 Hz, 1H), 3.77 (s, 3H), 3.73 – 3.61 (m, 3H), 3.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.89, 137.76, 136.71, 129.89, 127.21, 121.18, 118.29, 107.35, 101.18, 52.99, 38.95, 32.99.

HRMS (ESI-TOF) Calc. for $C_{12}H_{14}NaN_2O_2^+$ $[M+Na]^+$: 241.0947; found: 241.0954.

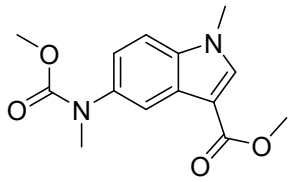


Methyl methyl(1-methyl-1H-indol-5-yl) carbamate (4r): (25 mg, brown liquid, yield: 38%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.08 (d, *J* = 3.2 Hz, 2H), 6.52 – 6.44 (m, 1H), 3.79 (s, 3H), 3.67 (s, 3H), 3.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.01, 135.61, 135.31, 129.98, 128.67, 120.54, 118.55, 109.57, 101.28, 52.95, 39.00, 33.06.

HRMS (ESI-TOF) Calc. for $C_{12}H_{14}NaN_2O_2^+$ $[M+Na]^+$: 241.0947; found: 241.0954.



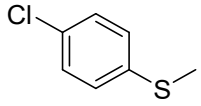
Methyl 5-((methoxycarbonyl)(methyl)amino)-1-methyl-1H-indole-3-carboxylate (4r'):

(33 mg, brown liquid, yield: 42%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.1 Hz, 1H), 7.79 (s, 1H), 7.32 (d, *J* = 8.7 Hz, 1H), 7.16 (d, *J* = 8.7 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 3.68 (s, 3H), 3.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.35, 156.82, 138.10, 136.15, 135.71, 127.01, 122.14, 119.22, 110.34, 107.22, 53.09, 51.21, 38.92, 33.76.

HRMS (ESI-TOF) Calc. for $C_{14}H_{17}N_2O_4^+$ $[M+H]^+$: 277.1183; found: 277.1187



(4-Chlorophenyl) (methyl) sulfane : (40 mg, white liquid, yield: 84%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.23 – 7.16 (m, 2H), 2.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.14, 131.06, 129.05, 128.08, 77.48, 77.16, 76.85, 16.26.

The analytical data are consistent with those reported in the literature.[7]

4. References

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5. NMR Spectroscopic Data for Products

Figure S1 ^{1}H NMR spectrum for compound 3a

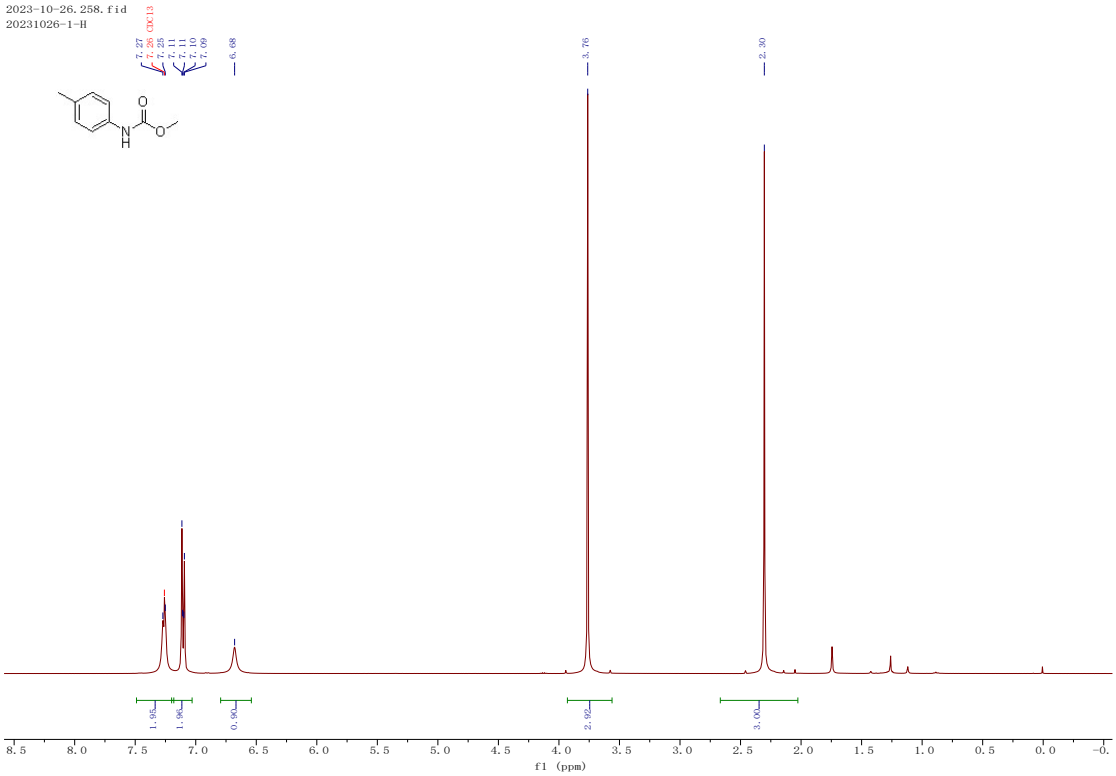

Figure S2 ^{13}C NMR spectrum for compound 3a

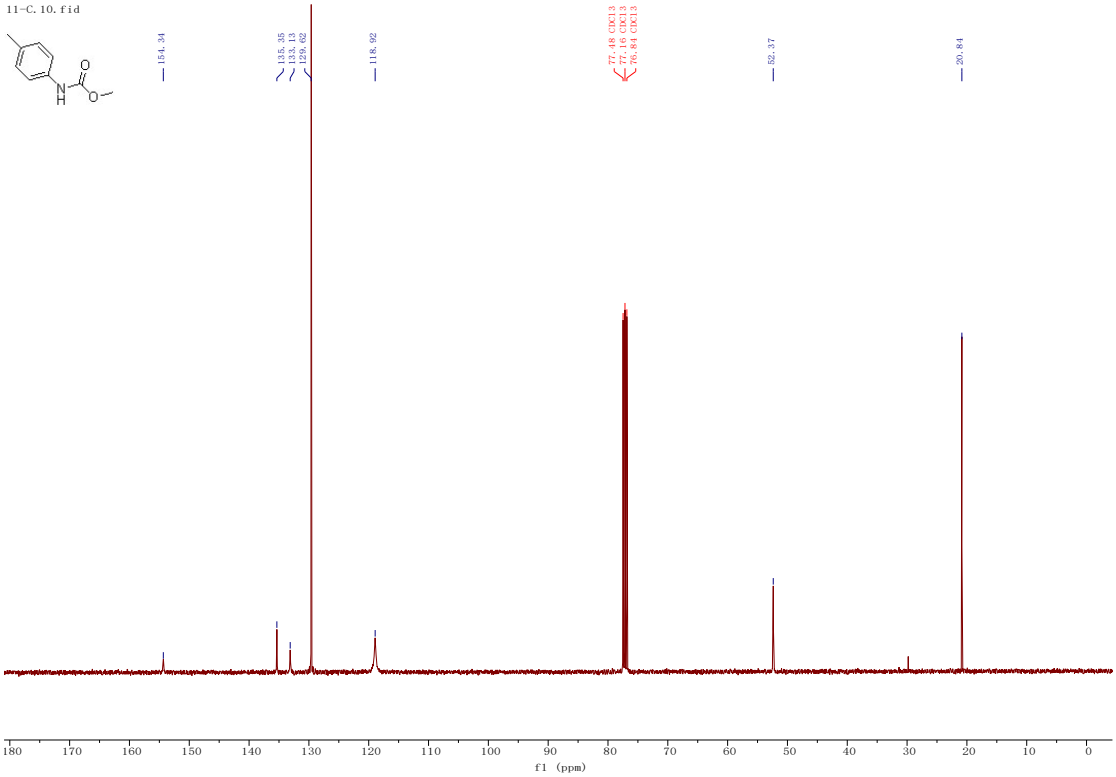

Figure S3 ^{1}H NMR spectrum for compound 3b

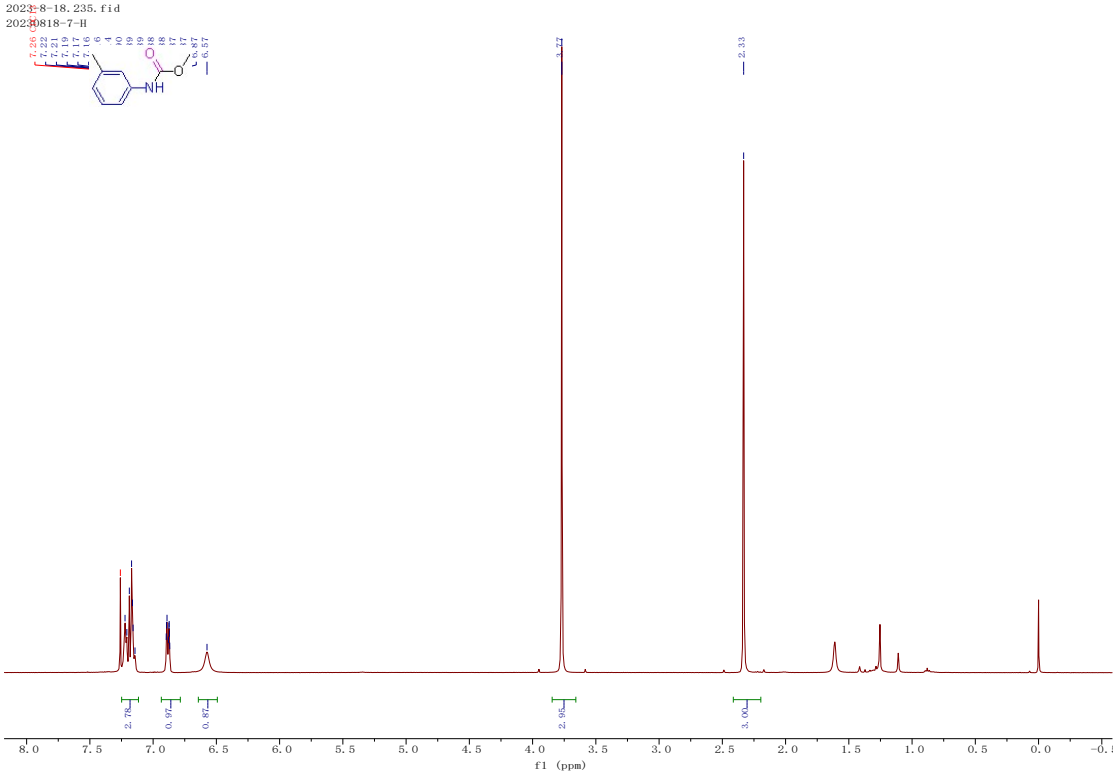

Figure S4 ^{13}C NMR spectrum for compound 3b

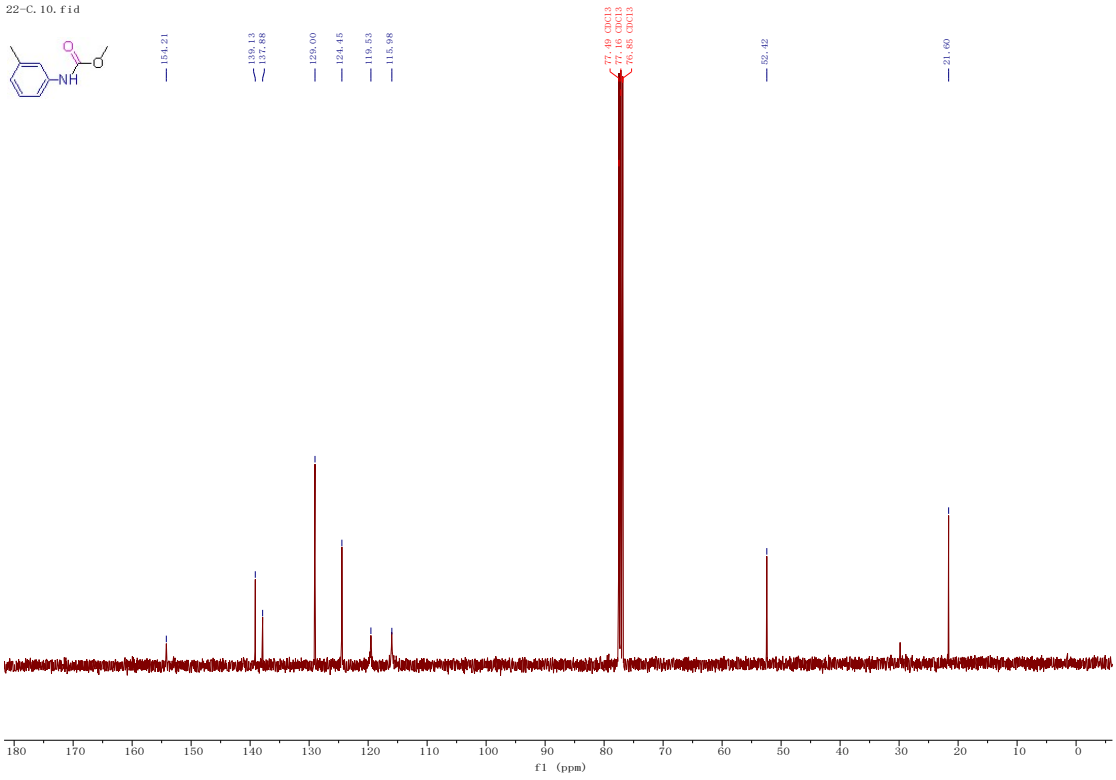

Figure S5 ^{1}H NMR spectrum for compound 3c

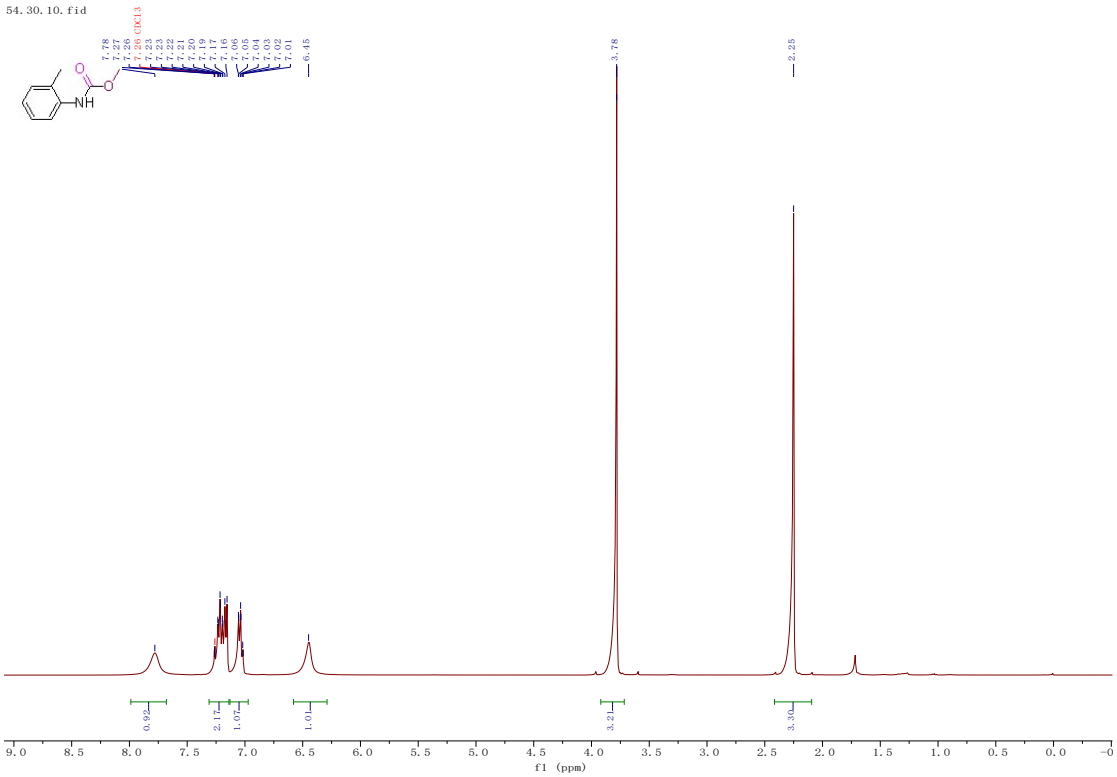

Figure S6 ^{13}C NMR spectrum for compound 3c

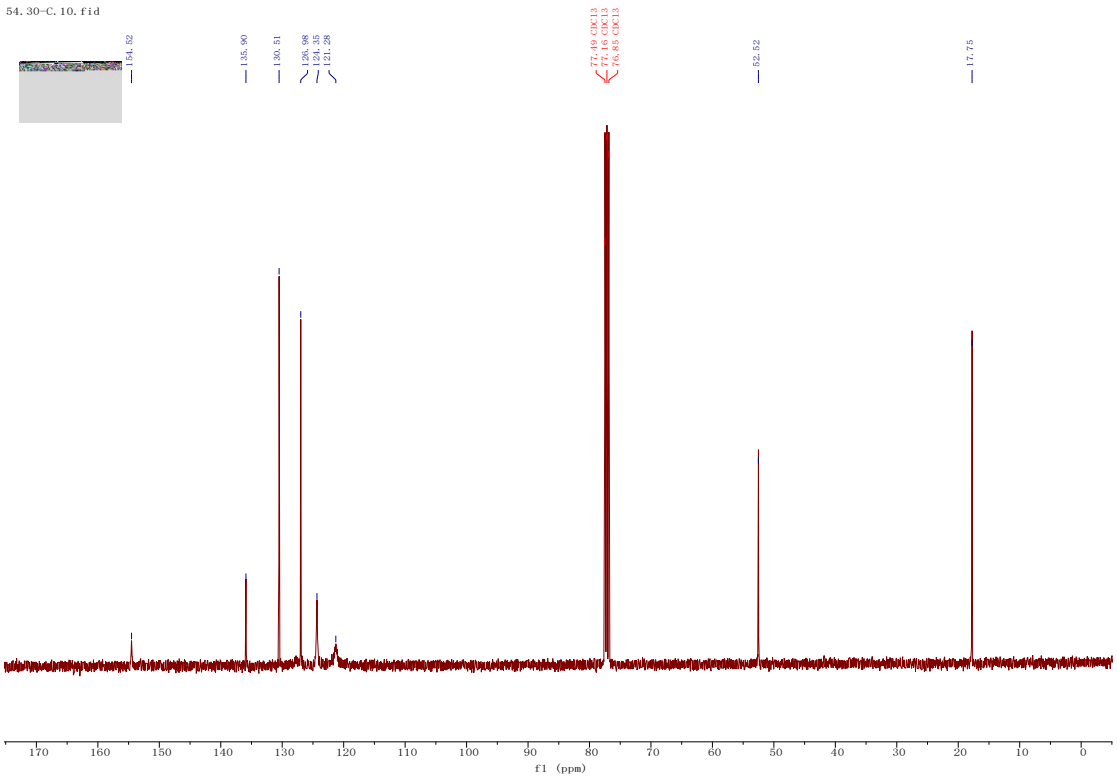

Figure S7 ^{1}H NMR spectrum for compound 3d

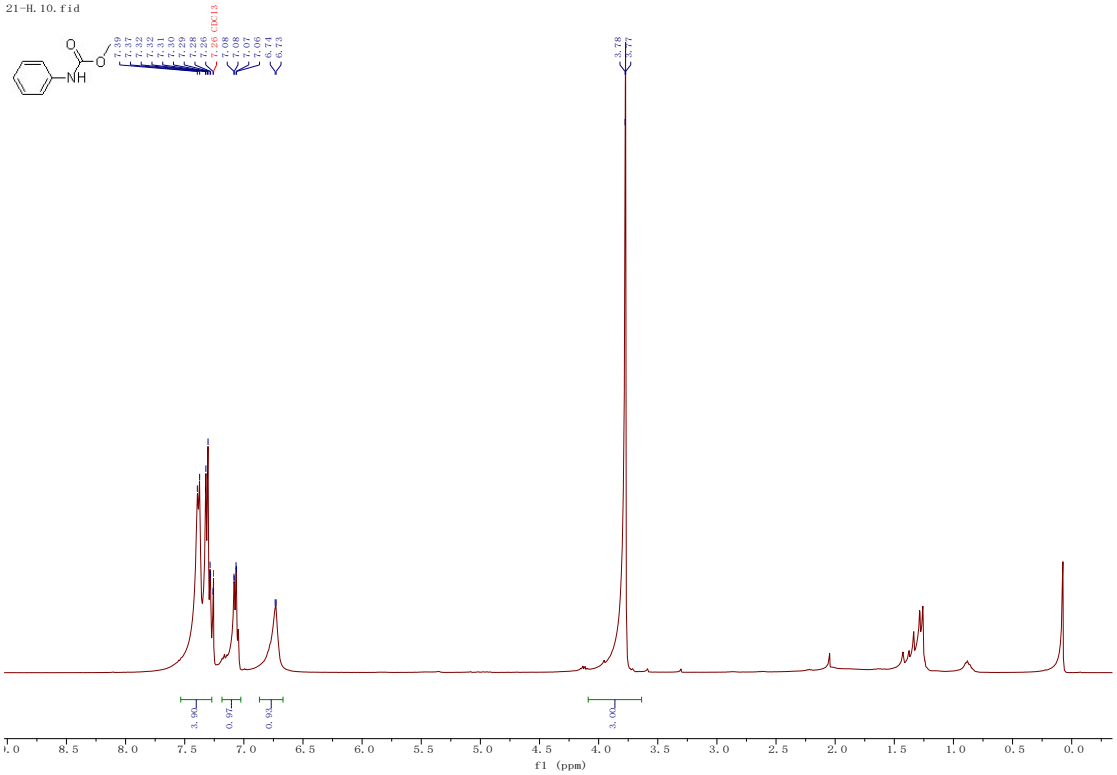

Figure S8 ^{13}C NMR spectrum for compound 3d

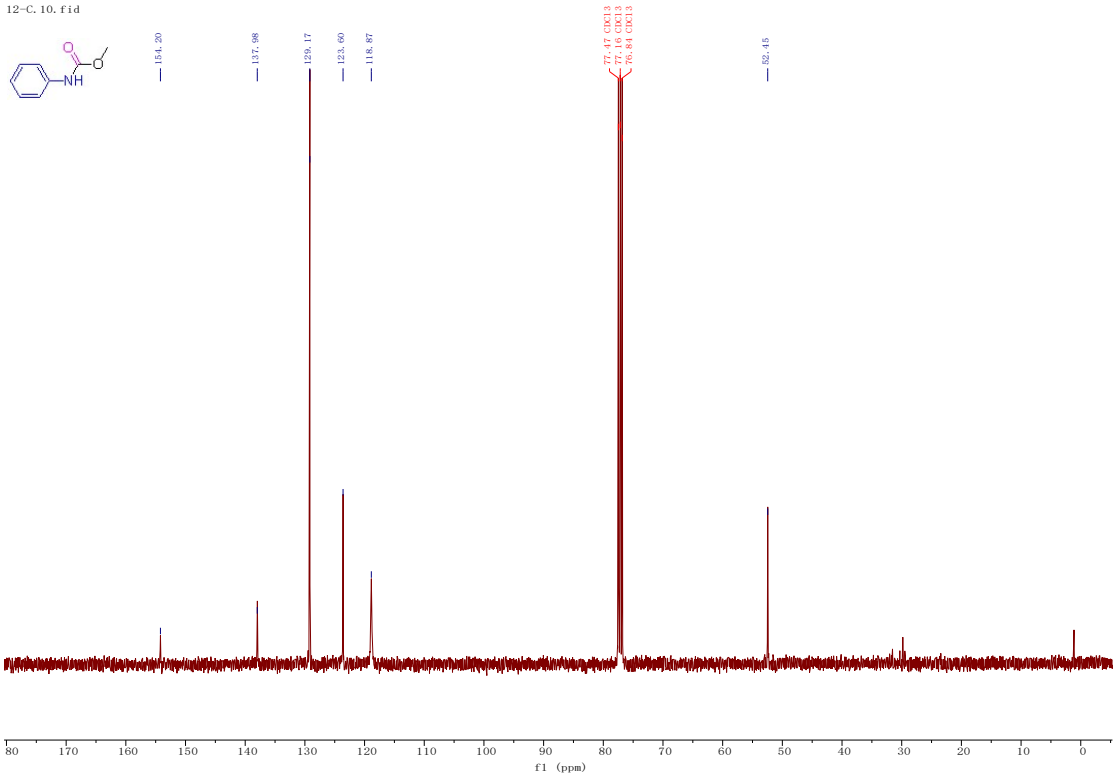

Figure S9 ^{1}H NMR spectrum for compound 3e and 3t

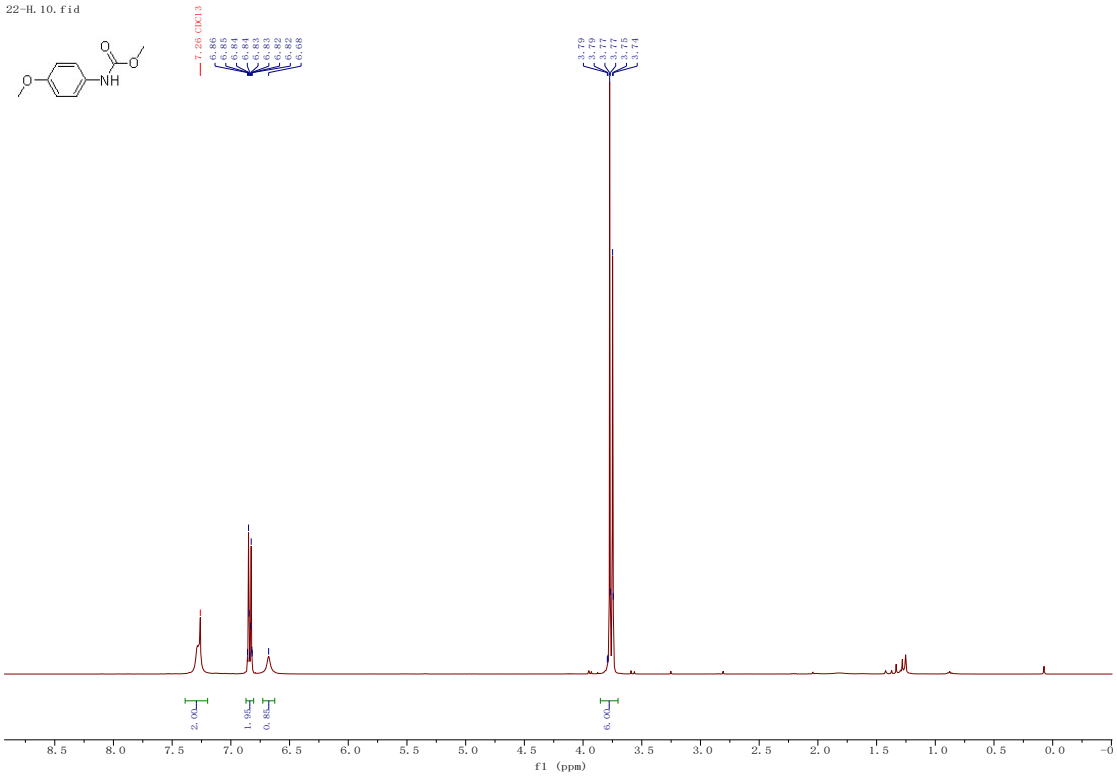

Figure S10 ^{13}C NMR spectrum for compound 3e and 3t

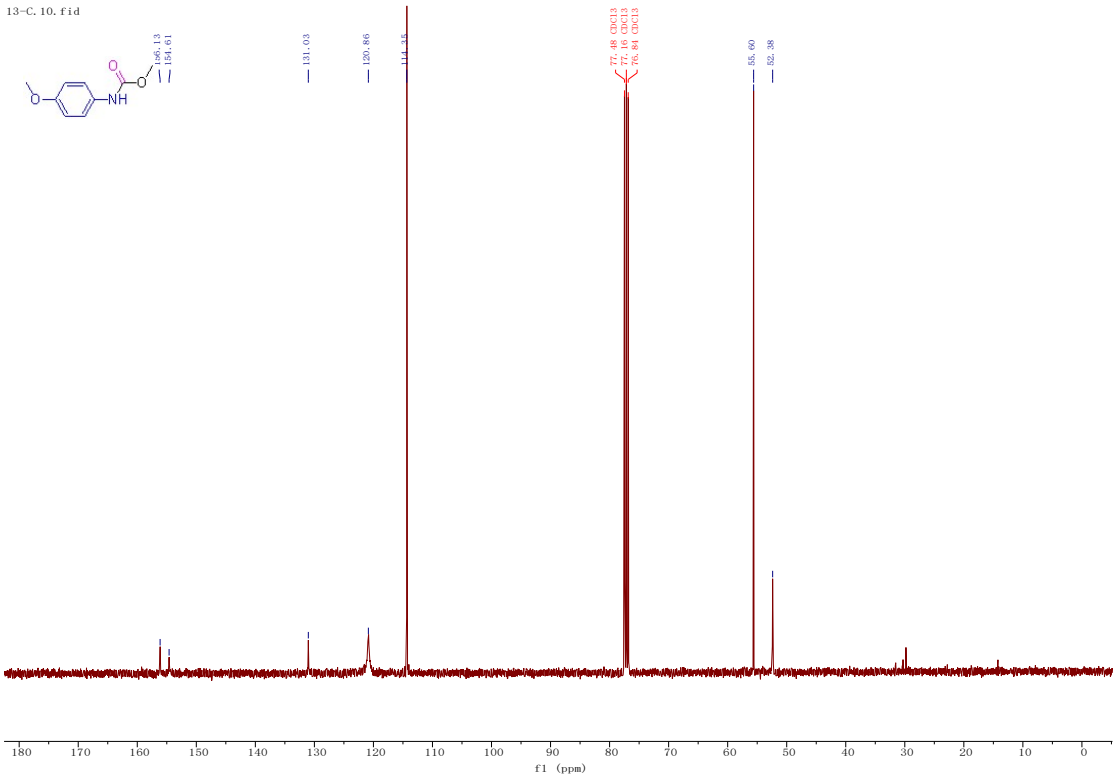

Figure S11 ^{1}H NMR spectrum for compound 3f

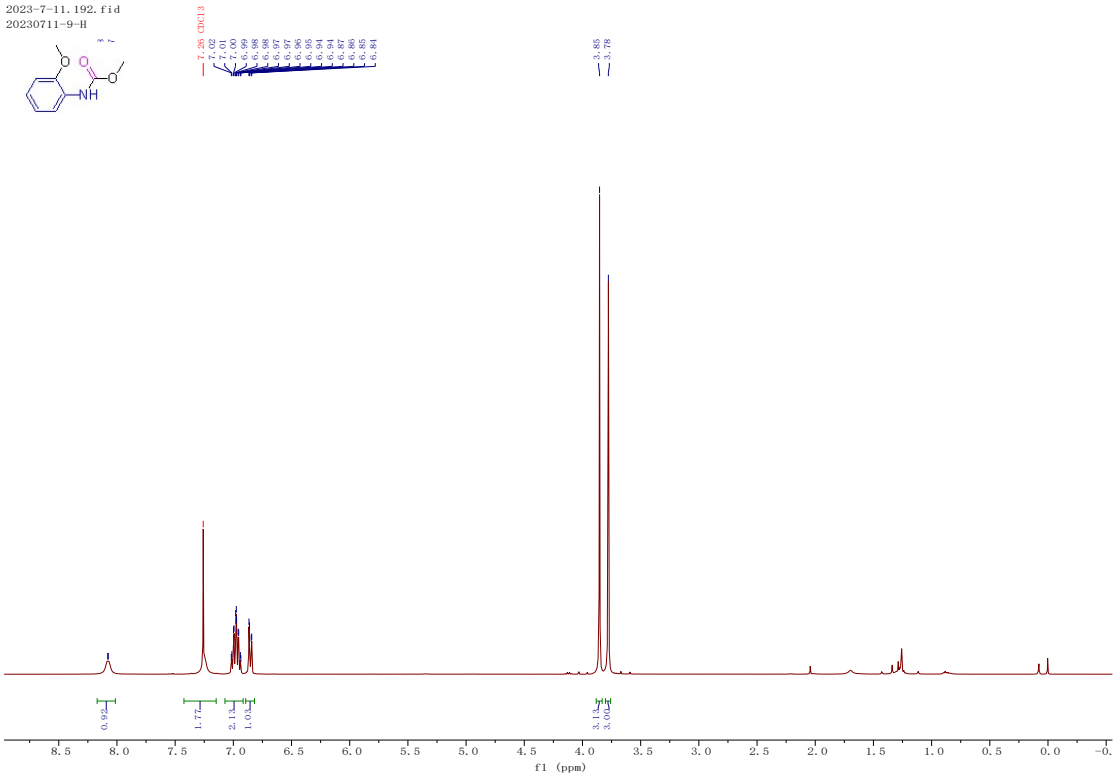

Figure S12 ^{13}C NMR spectrum for compound 3f

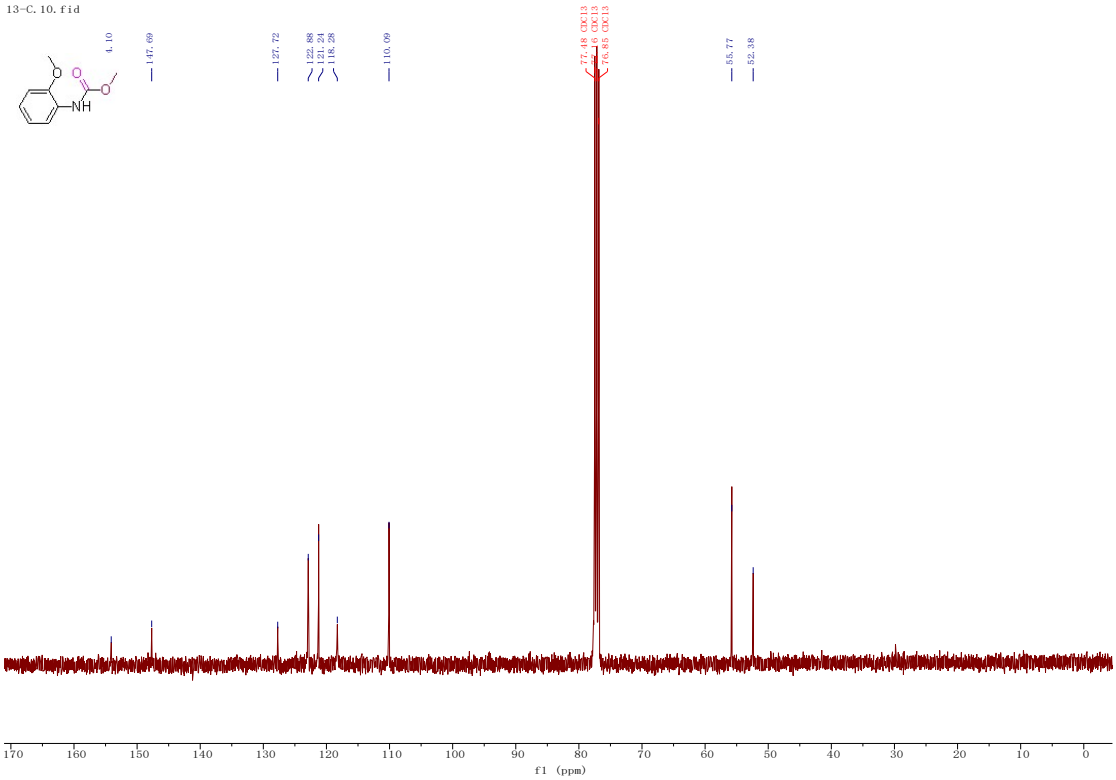

Figure S13 ^{1}H NMR spectrum for compound 3g

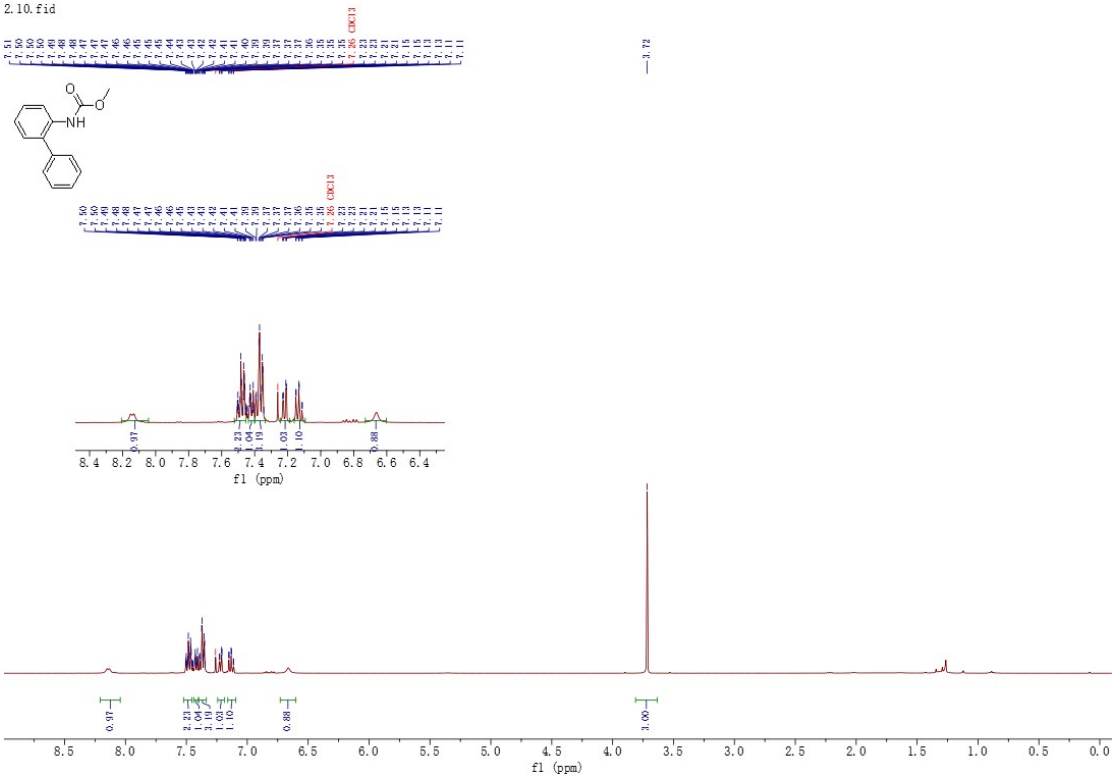

Figure S14 ^{13}C NMR spectrum for compound 3g

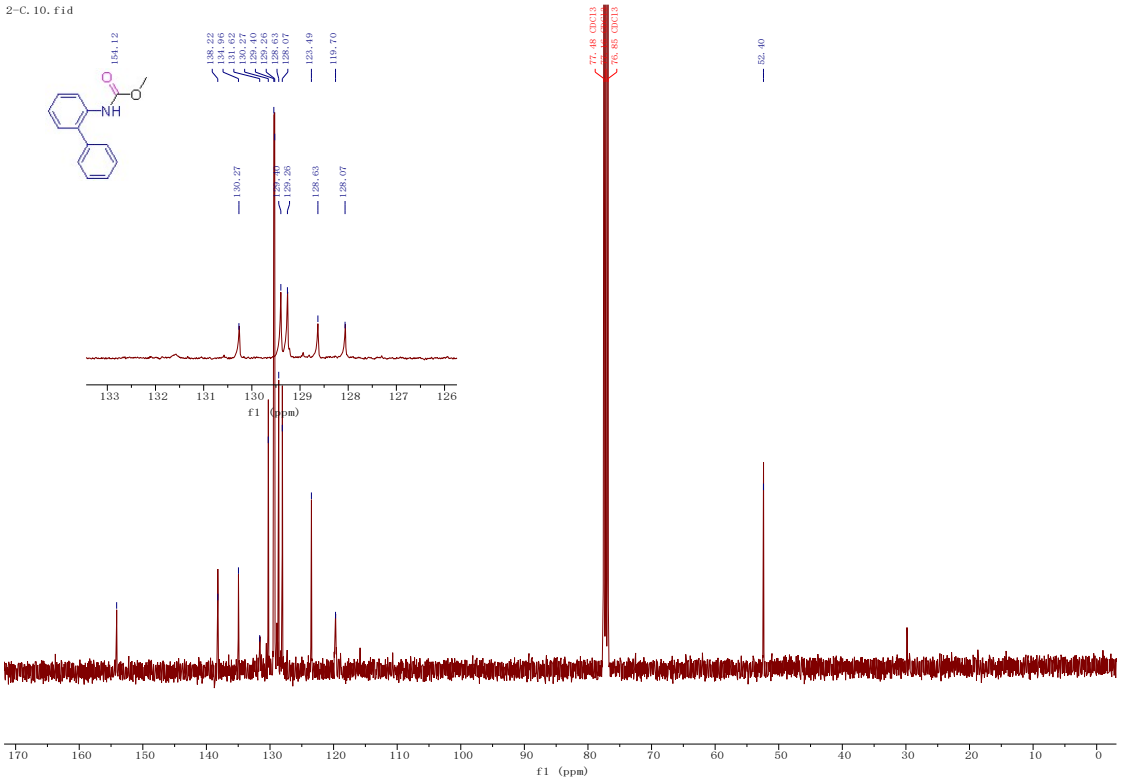

Figure S15 ^{1}H NMR spectrum for compound 3h

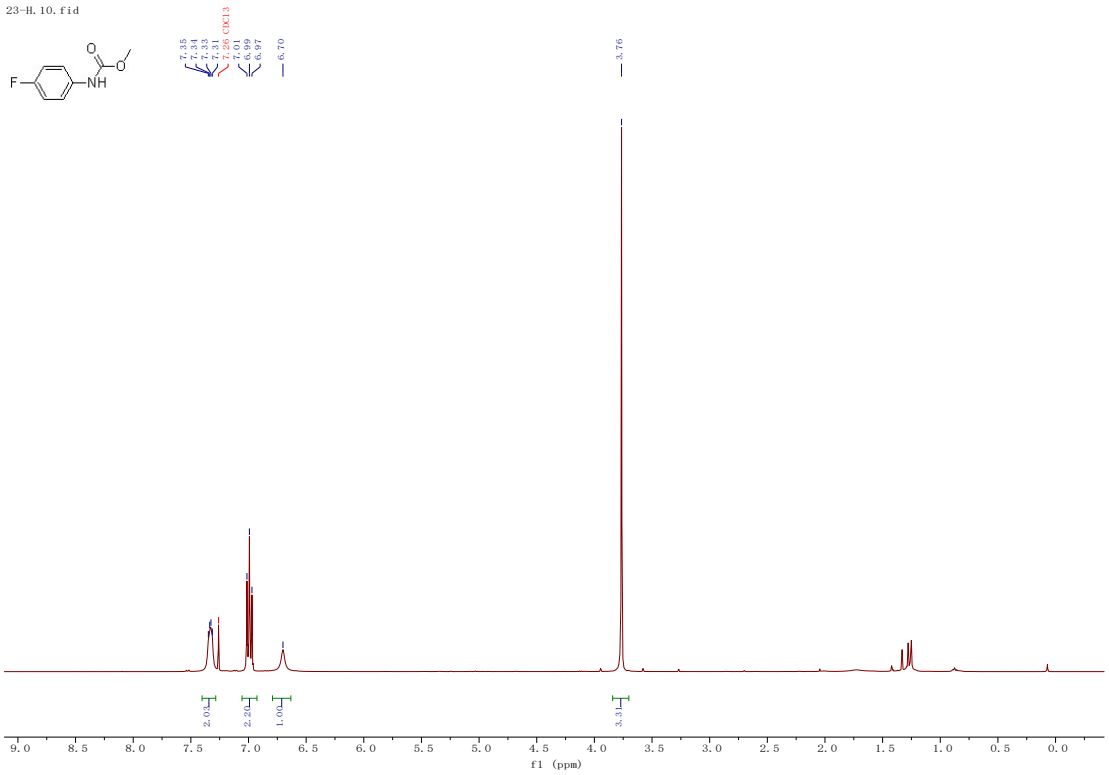

Figure S16 ^{13}C NMR spectrum for compound 3h

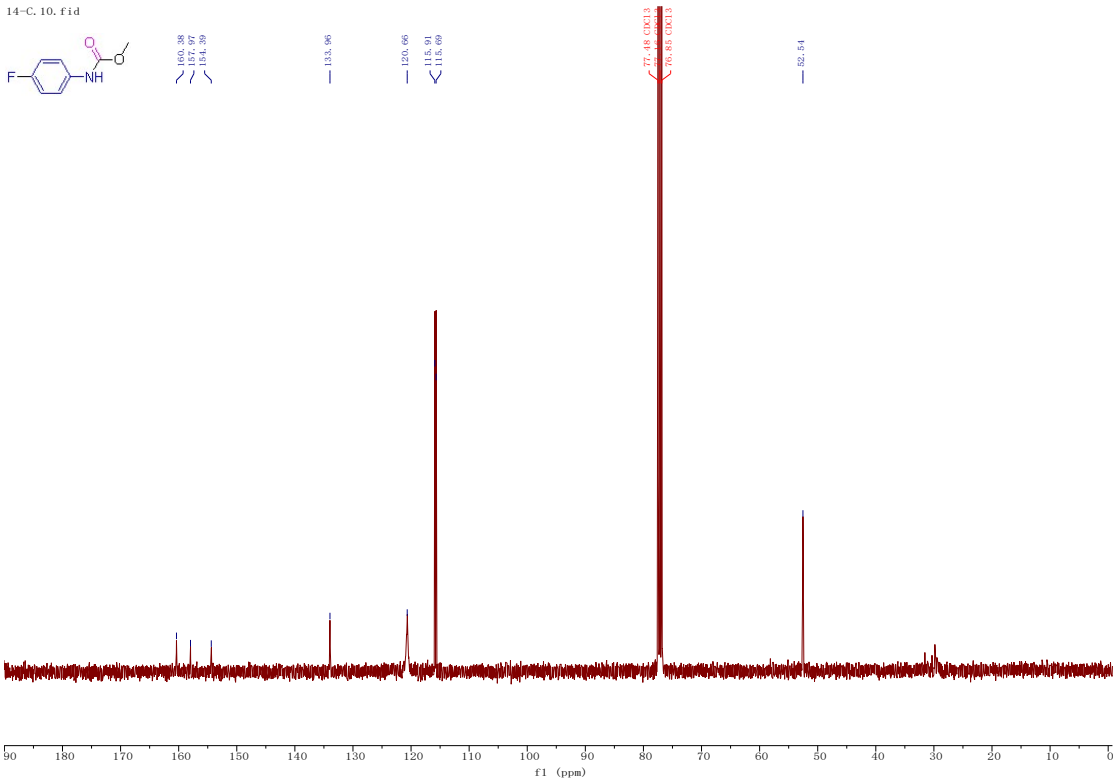

Figure S17 ^{1}H NMR spectrum for compound 3i

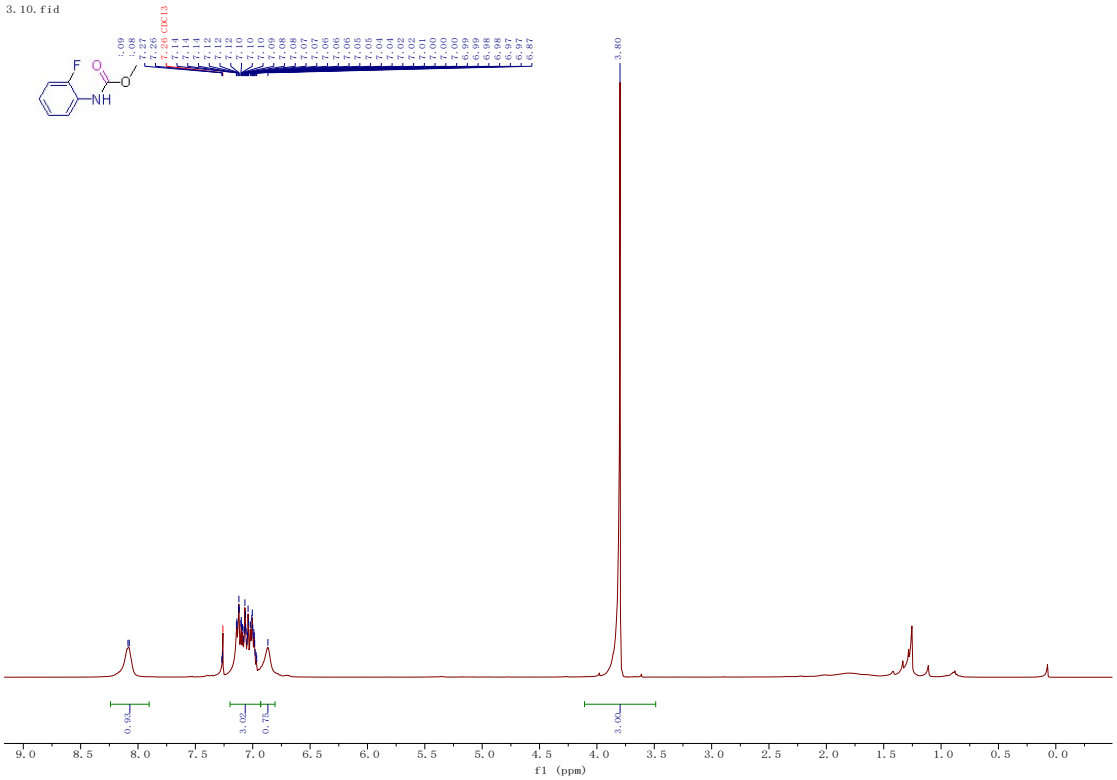

Figure S18 ^{13}C NMR spectrum for compound 3i

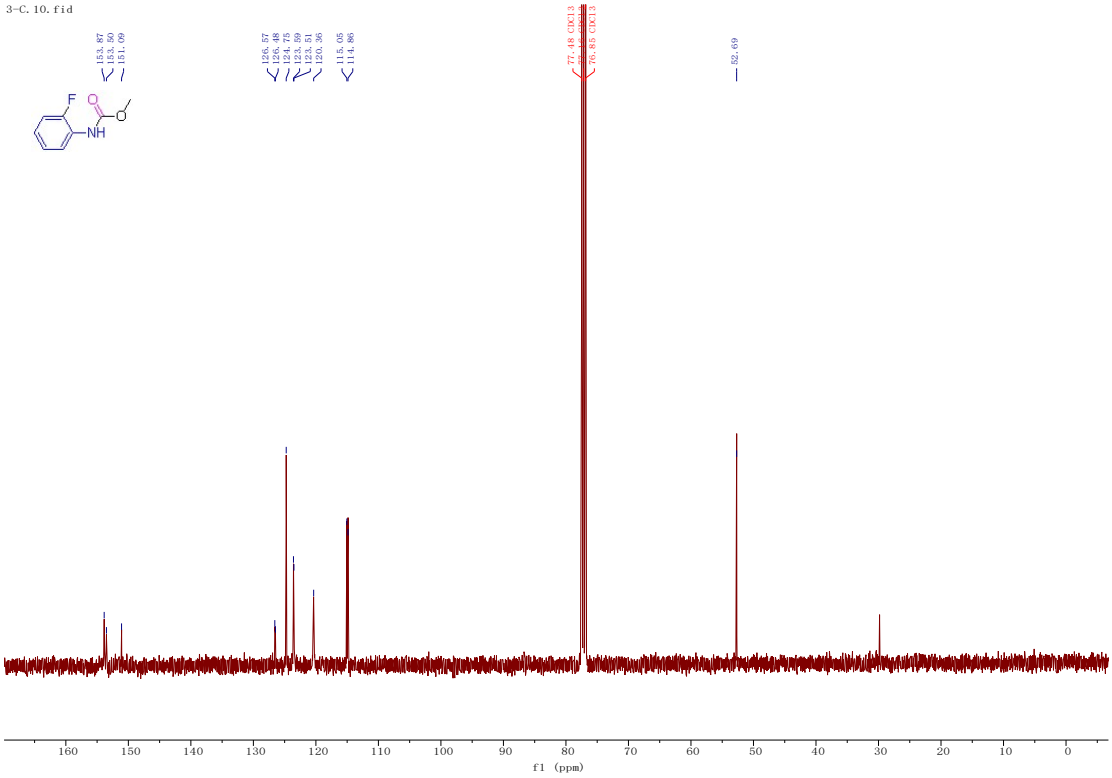

Figure S19 ^{1}H NMR spectrum for compound 3j

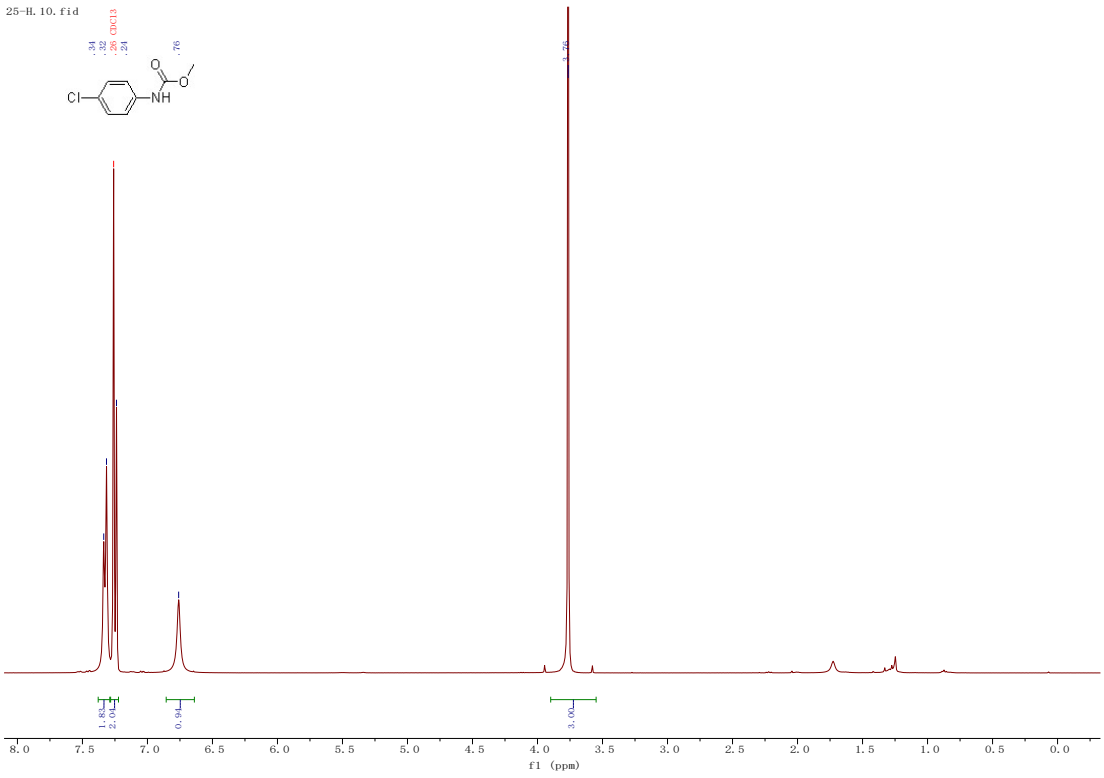

Figure S20 ^{13}C NMR spectrum for compound 3j

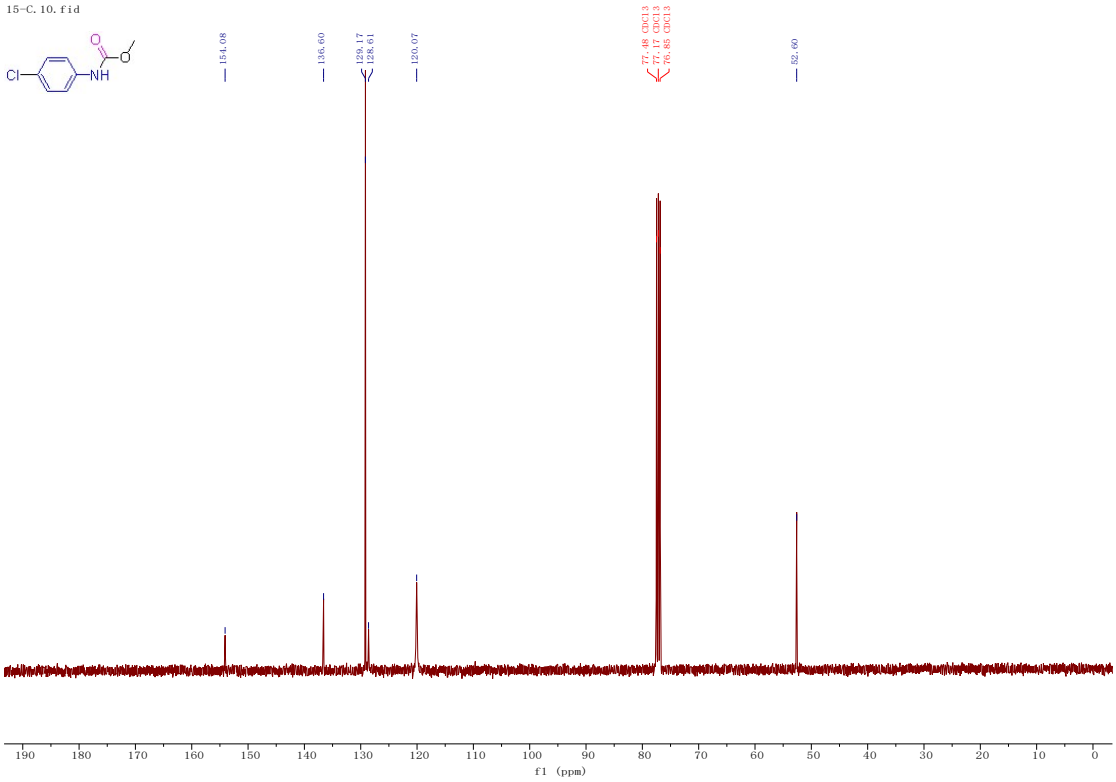

Figure S21 ^{1}H NMR spectrum for compound 3k

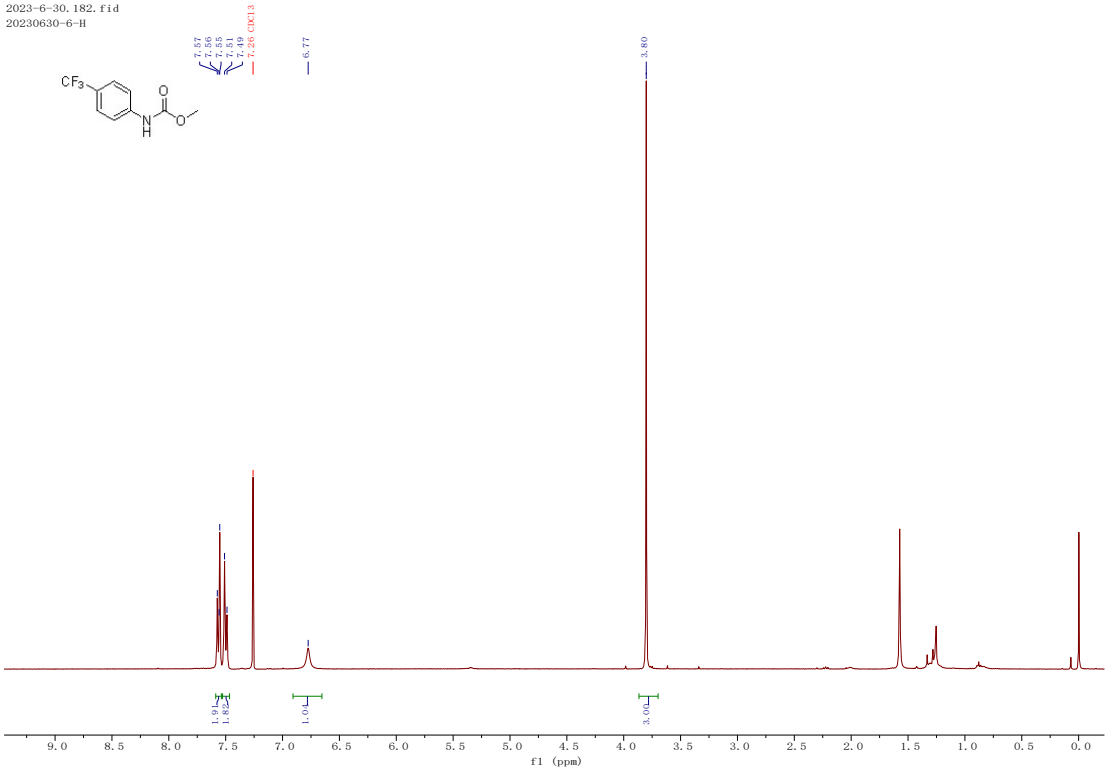

Figure S22 ^{13}C NMR spectrum for compound 3k

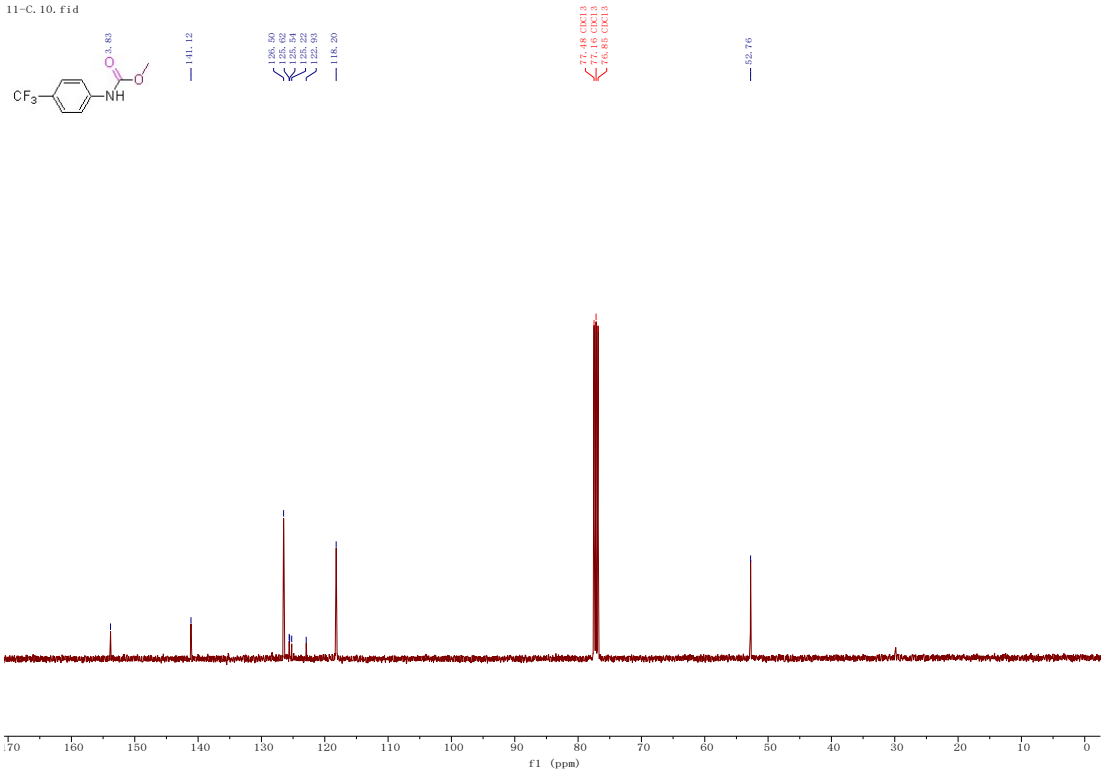

Figure S23 ^{1}H NMR spectrum for compound 3l

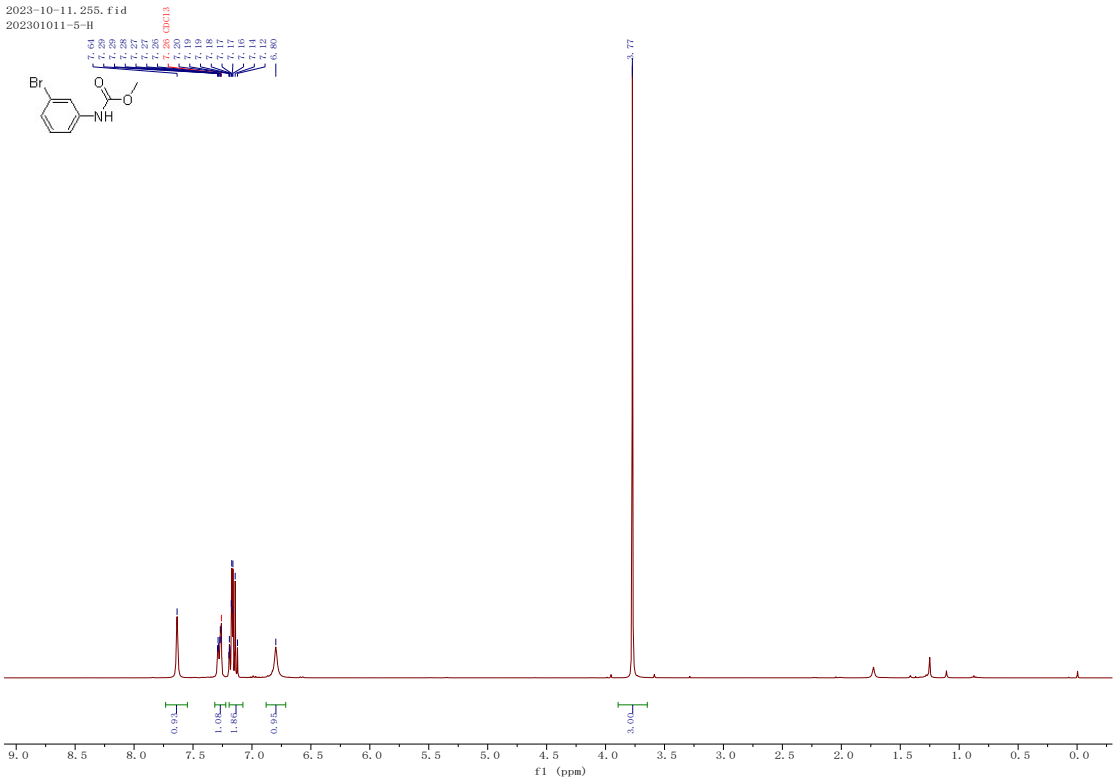

Figure S24 ^{13}C NMR spectrum for compound 3l

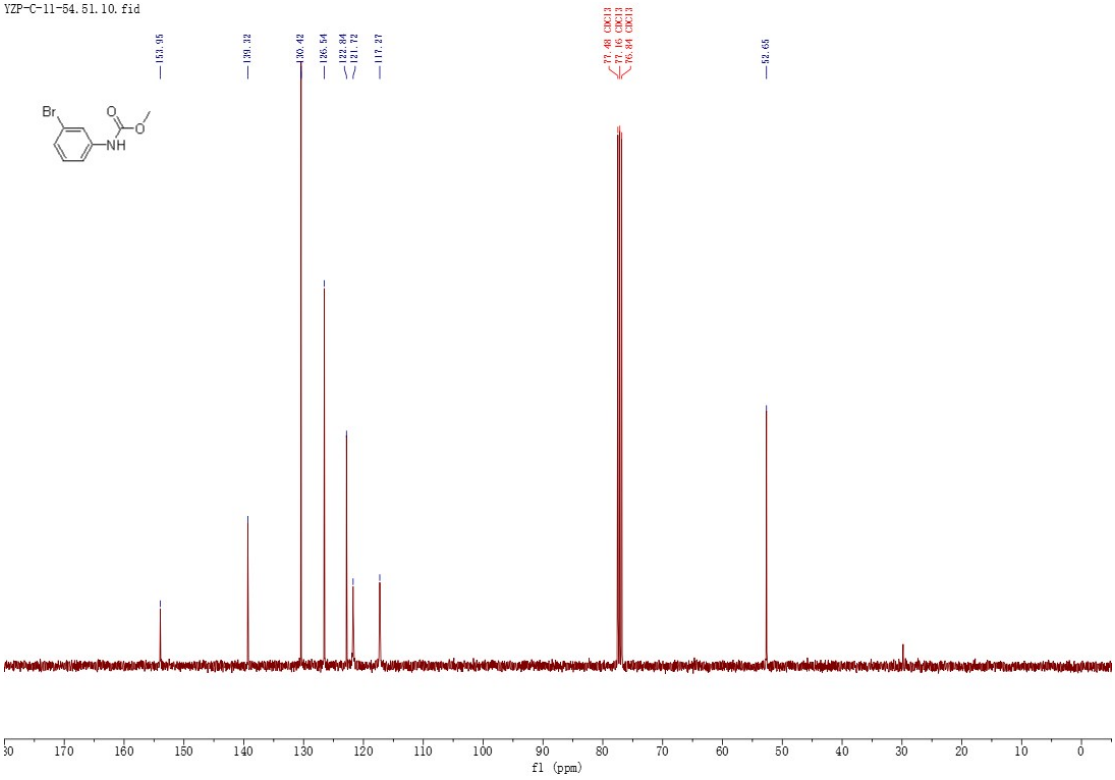

Figure S25 ^{1}H NMR spectrum for compound 3m

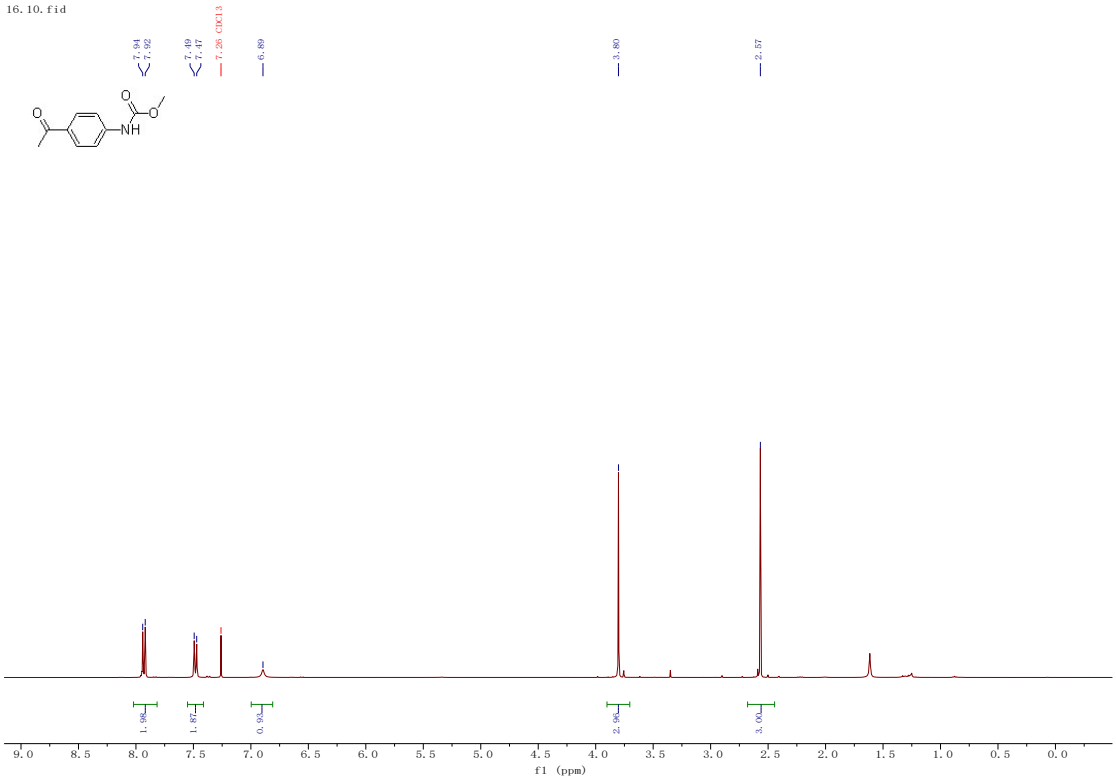

Figure S26 ^{13}C NMR spectrum for compound 3m

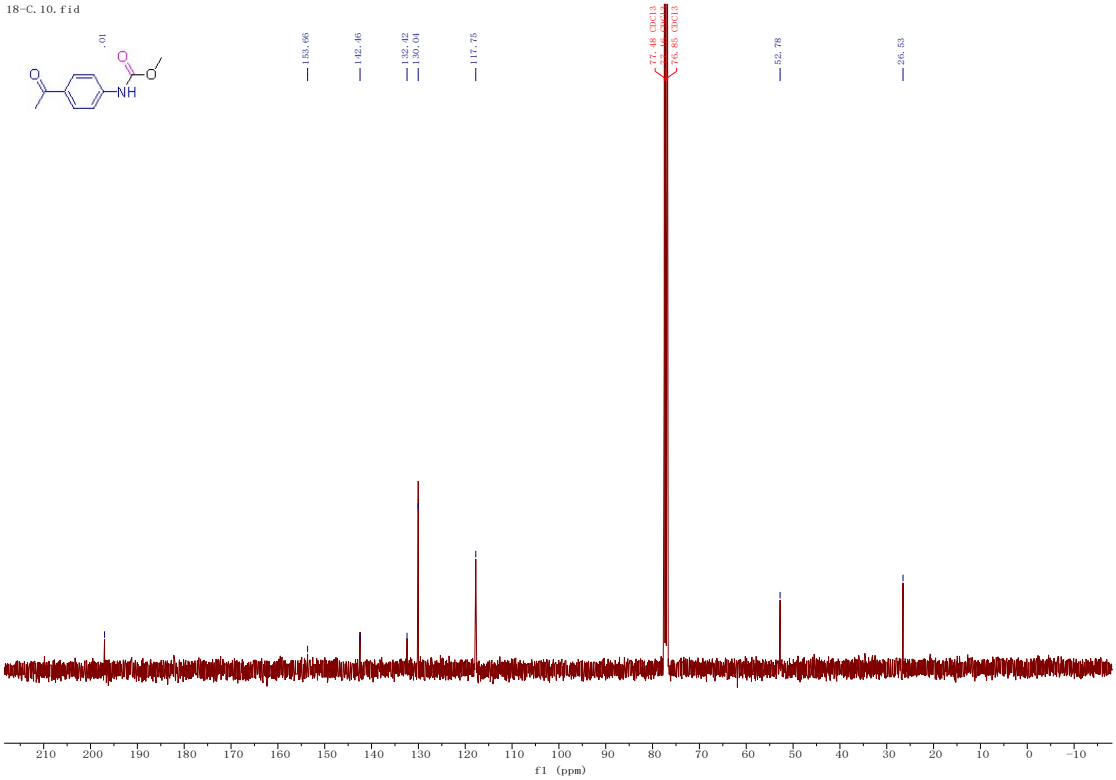

Figure S27 ^{1}H NMR spectrum for compound 3n

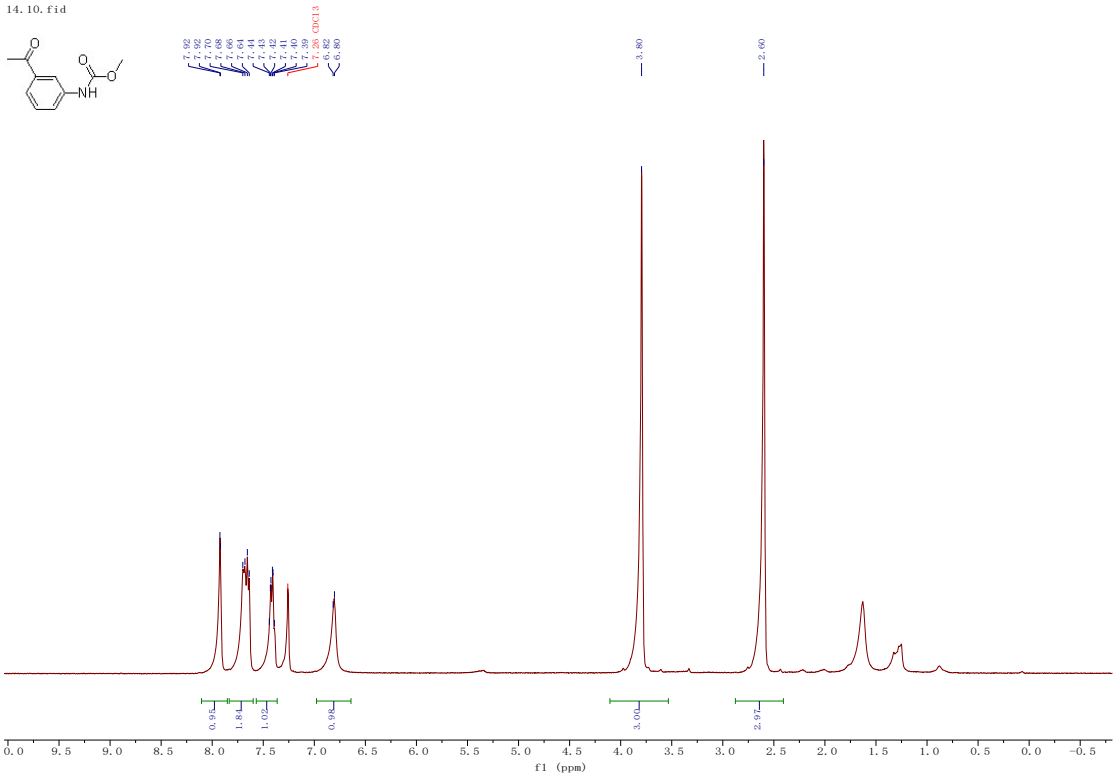

Figure S28 ^{13}C NMR spectrum for compound 3n

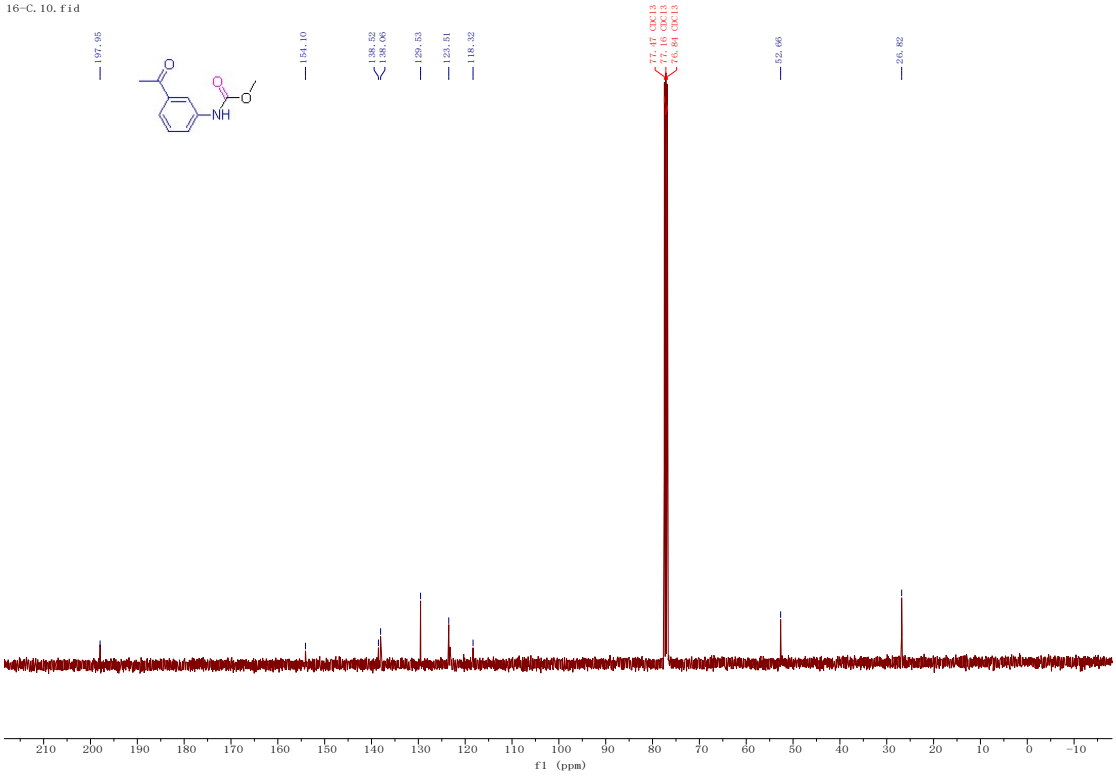

Figure S29 ^{1}H NMR spectrum for compound 3o

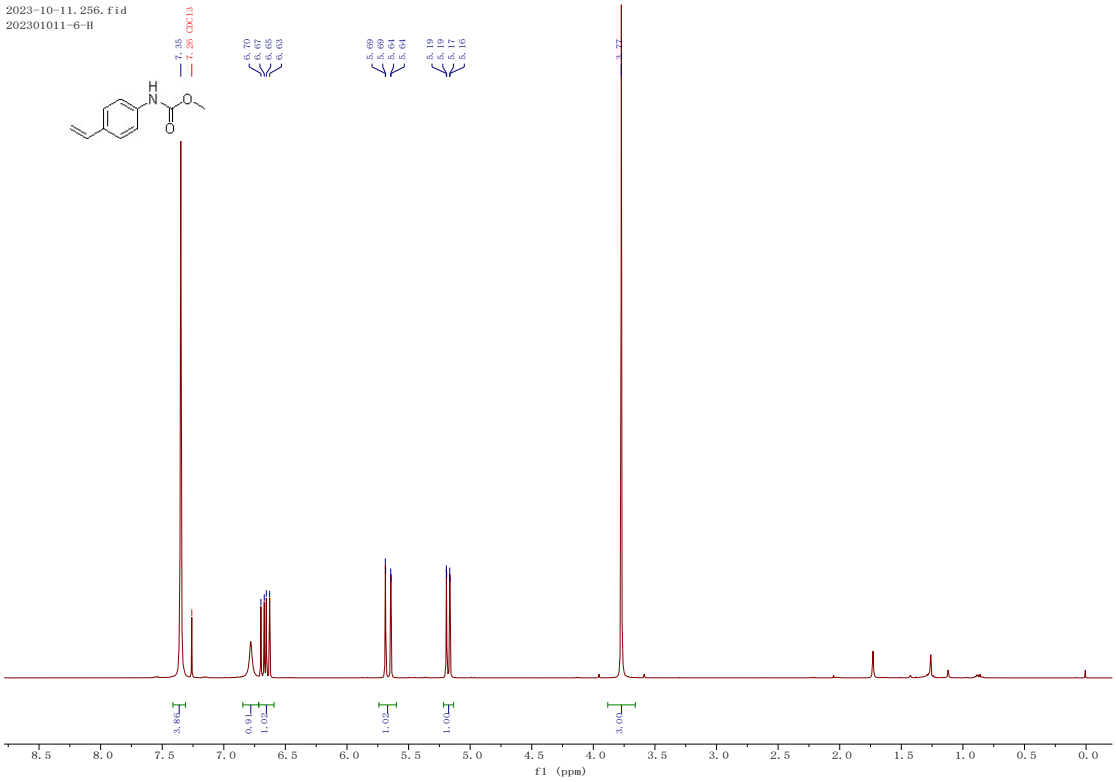

Figure S30 ^{13}C NMR spectrum for compound 3o

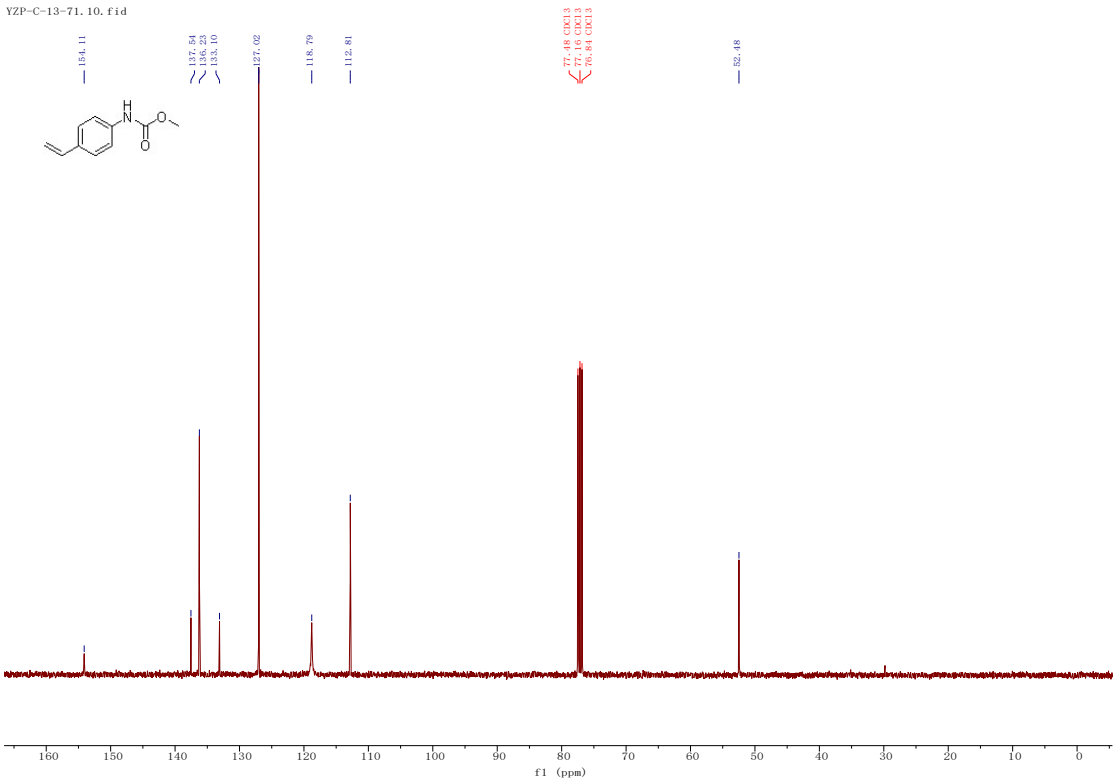

Figure S31 ^{1}H NMR spectrum for compound 3p

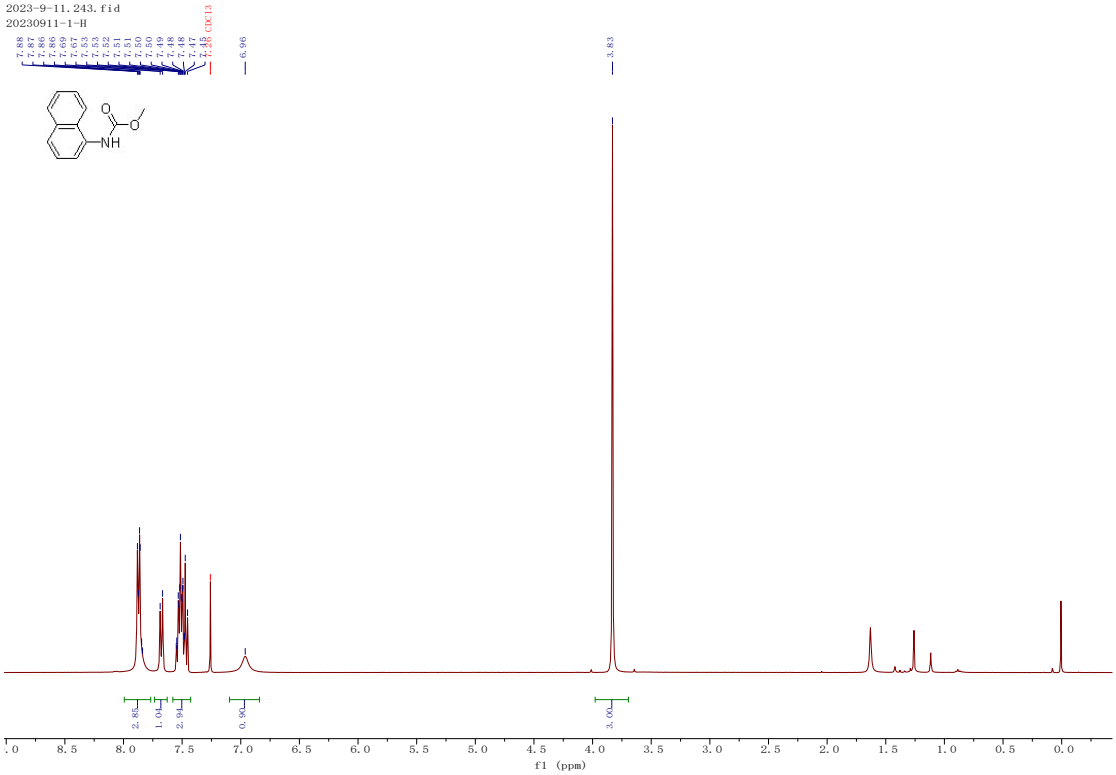

Figure S32 ^{13}C NMR spectrum for compound 3p

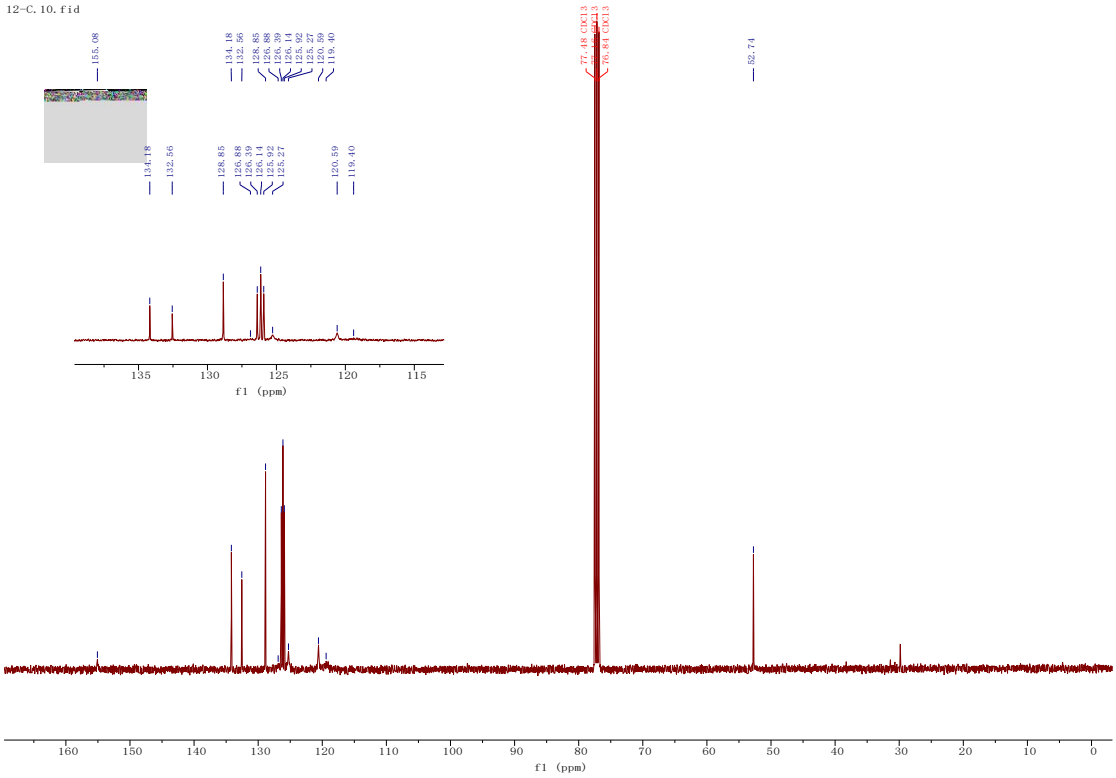

Figure S33 ^{1}H NMR spectrum for compound 3q

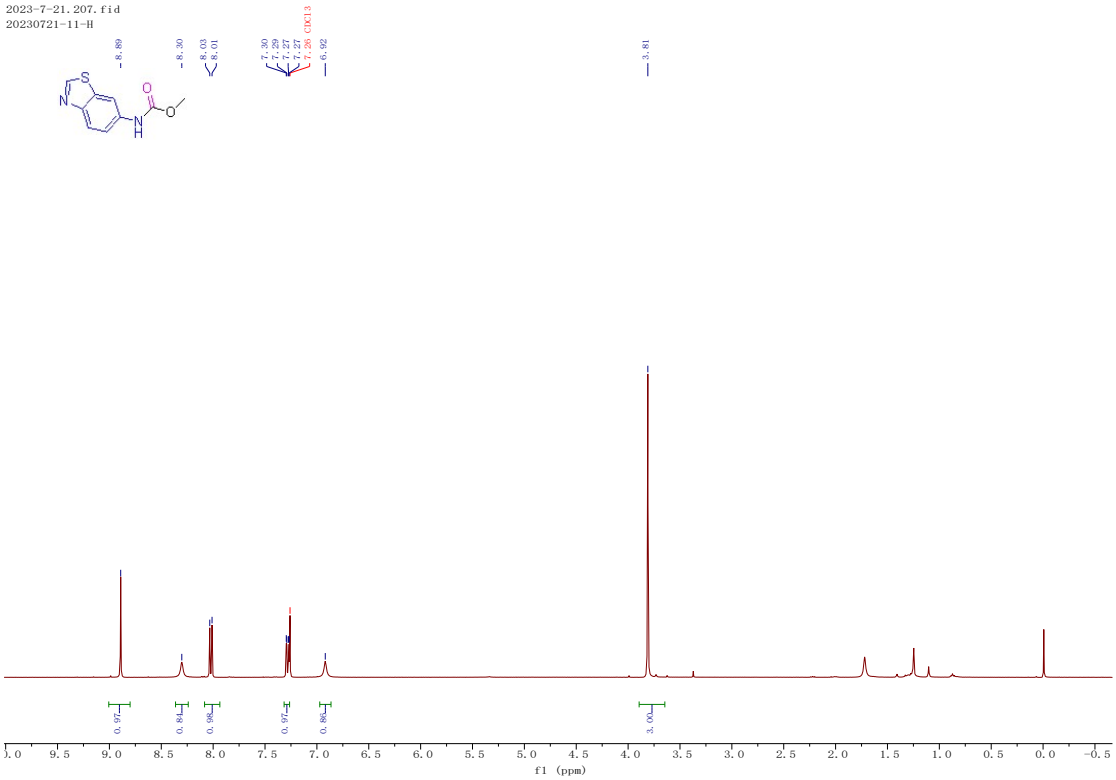

Figure S34 ^{13}C NMR spectrum for compound 3q

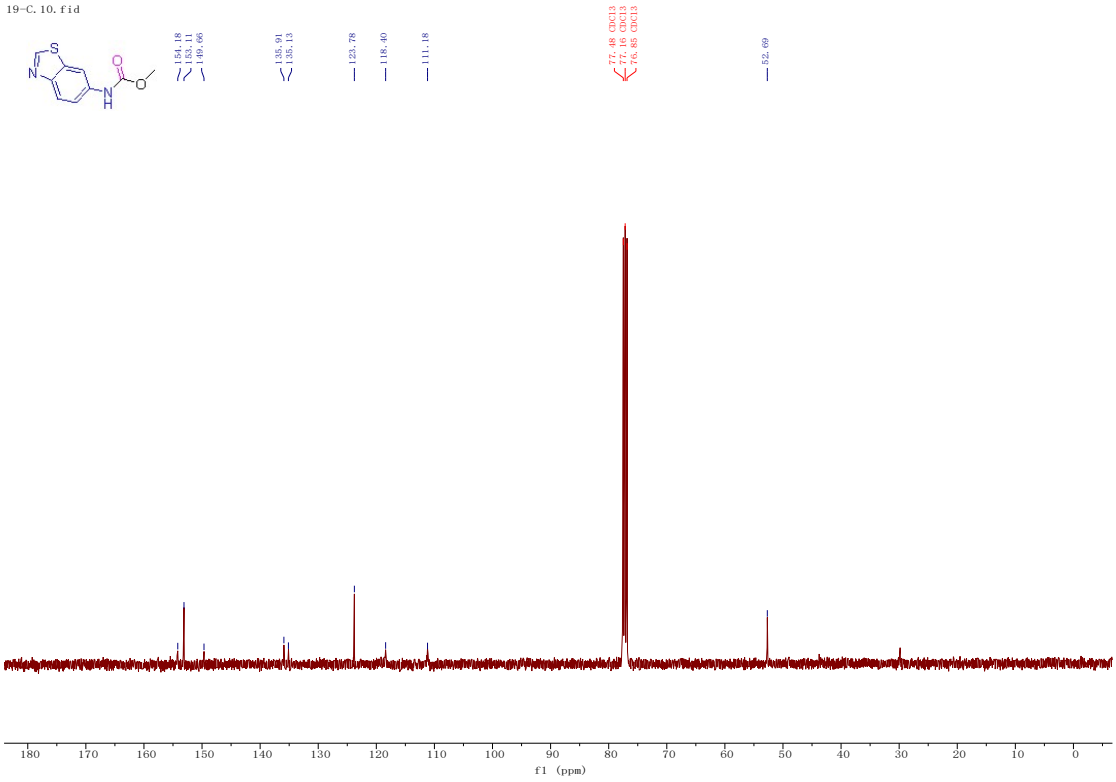

Figure S35 HRMS spectrum for compound 3q

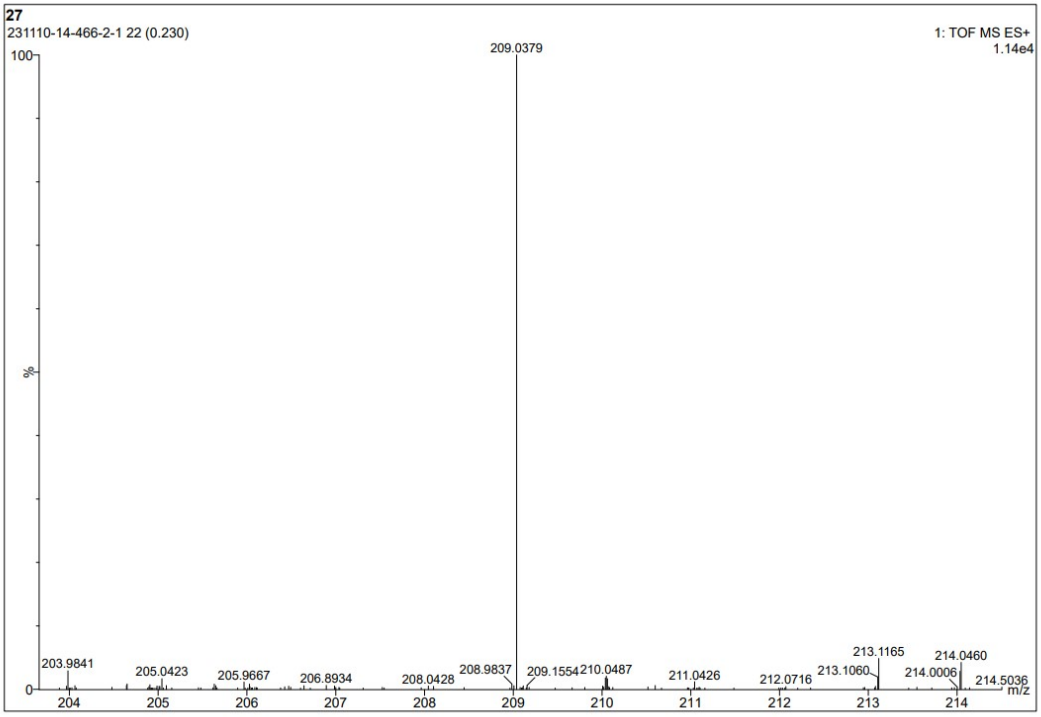

Figure S36 ^{1}H NMR spectrum for compound 3r

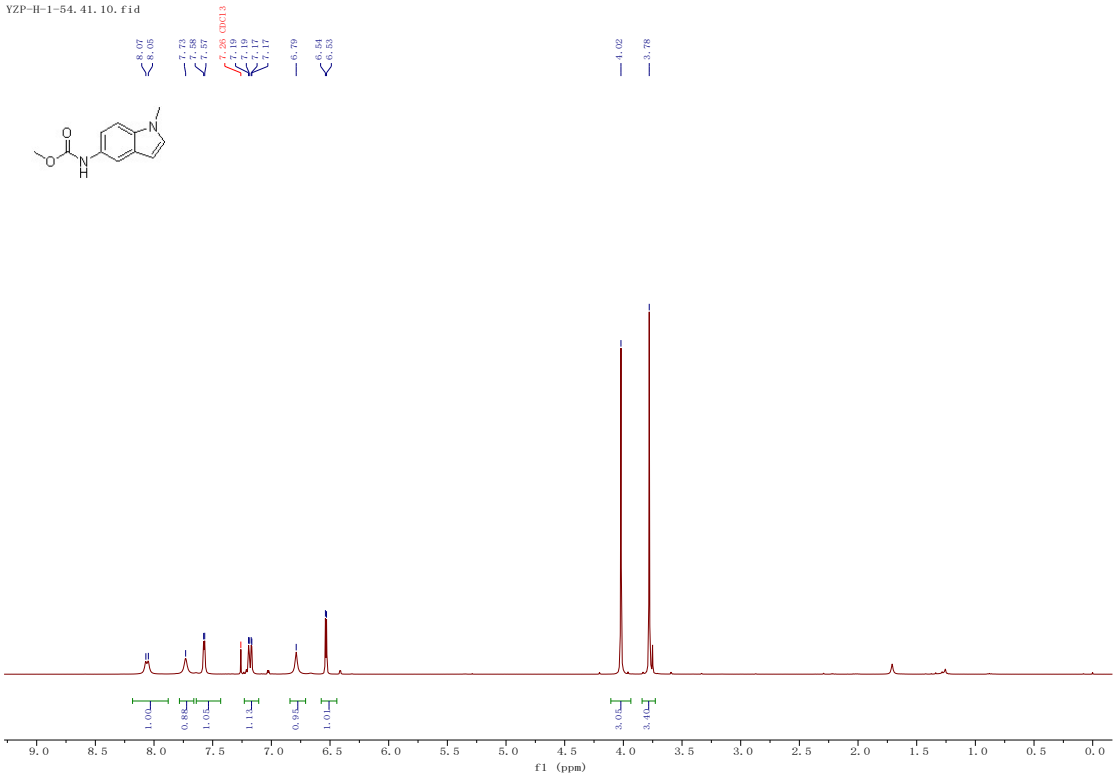

Figure S37 ^{13}C NMR spectrum for compound 3r

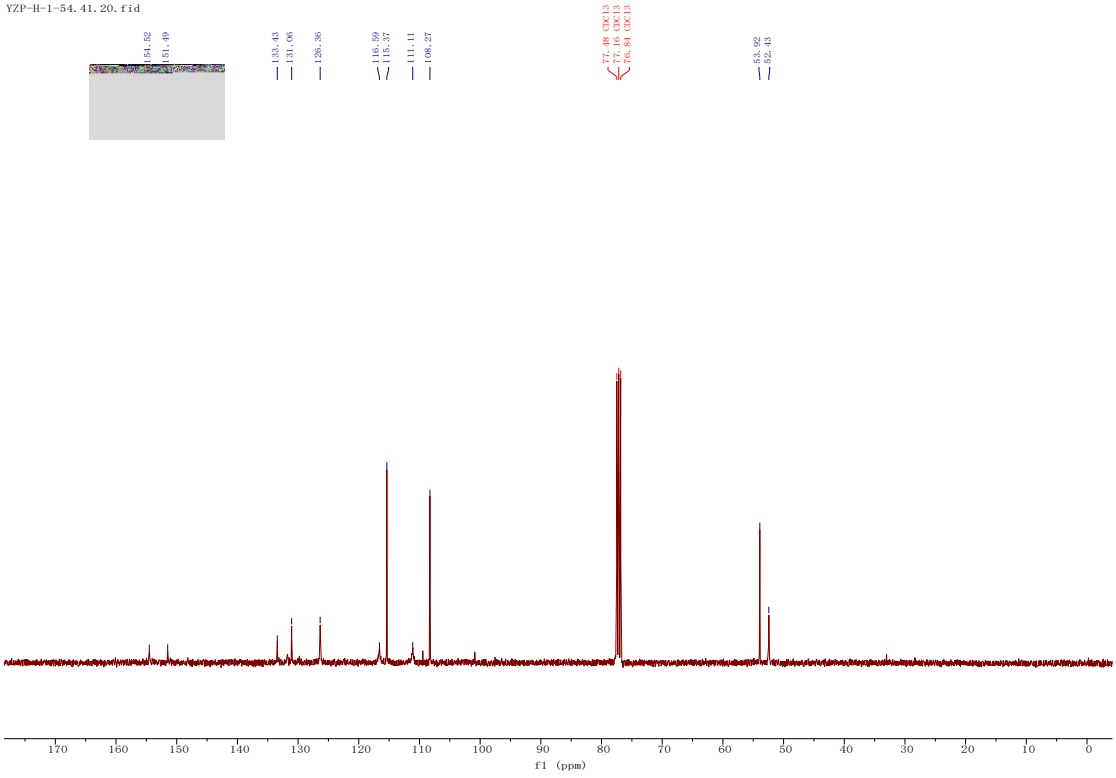

Figure S38 HRMS spectrum for compound 3r

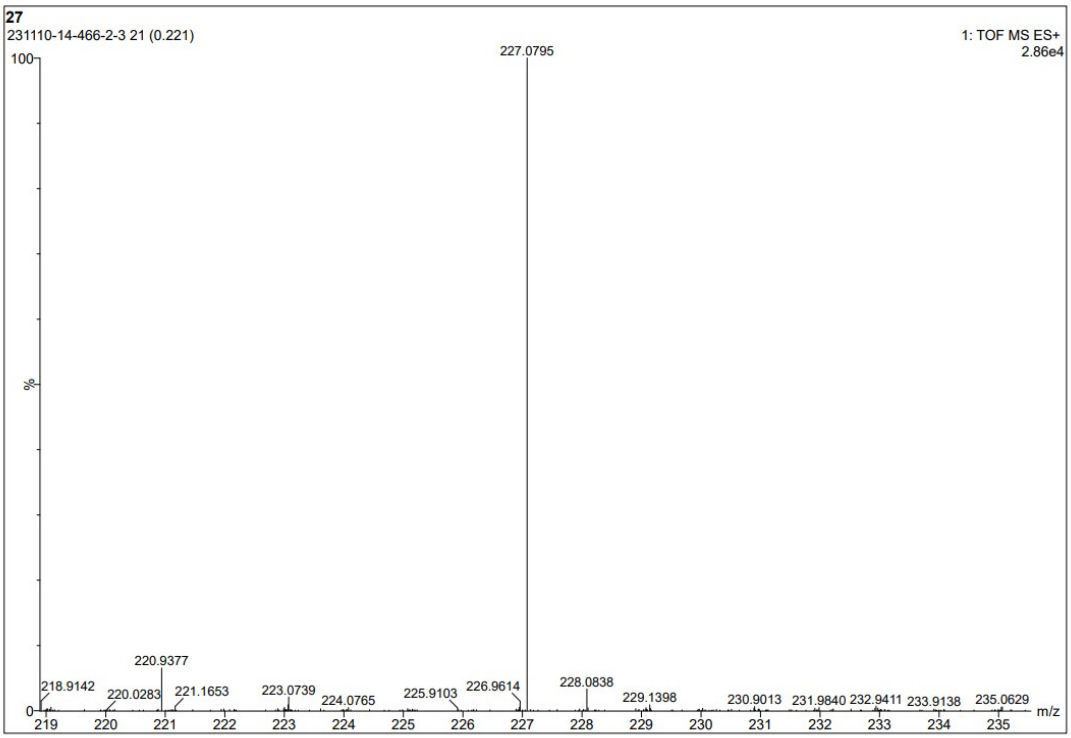

Figure S39 ^{1}H NMR spectrum for compound 3s and 4n

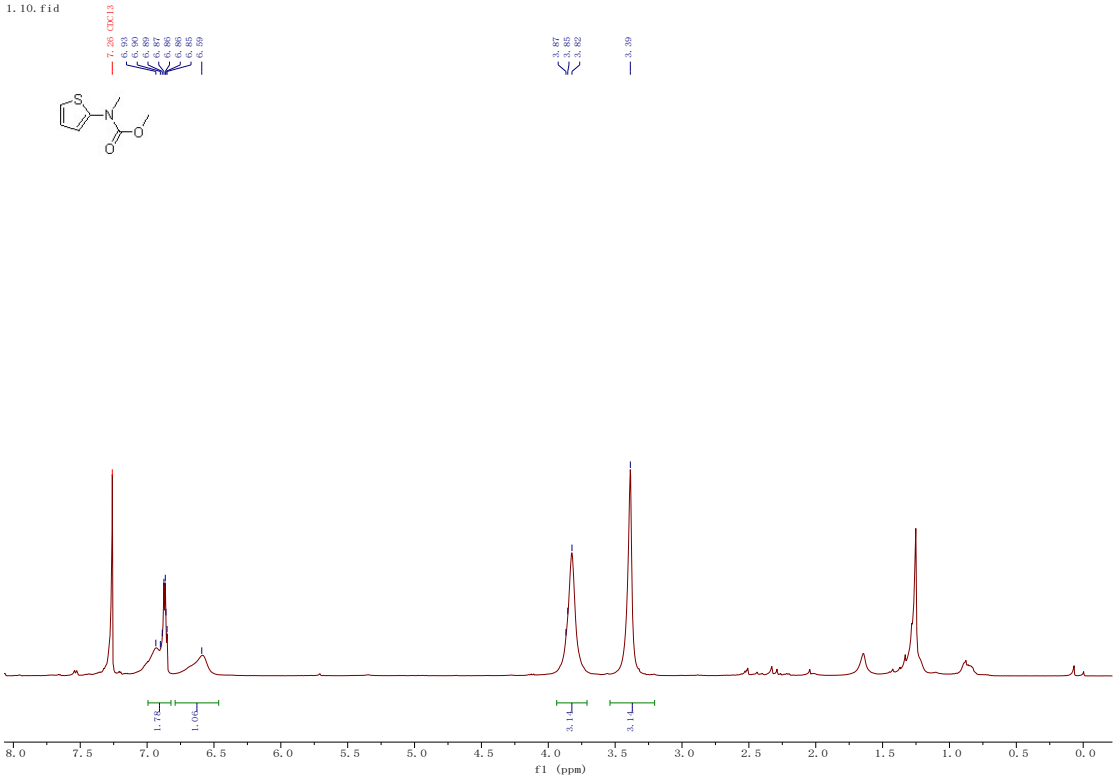

Figure S40 ^{13}C NMR spectrum for compound 3s and 4n

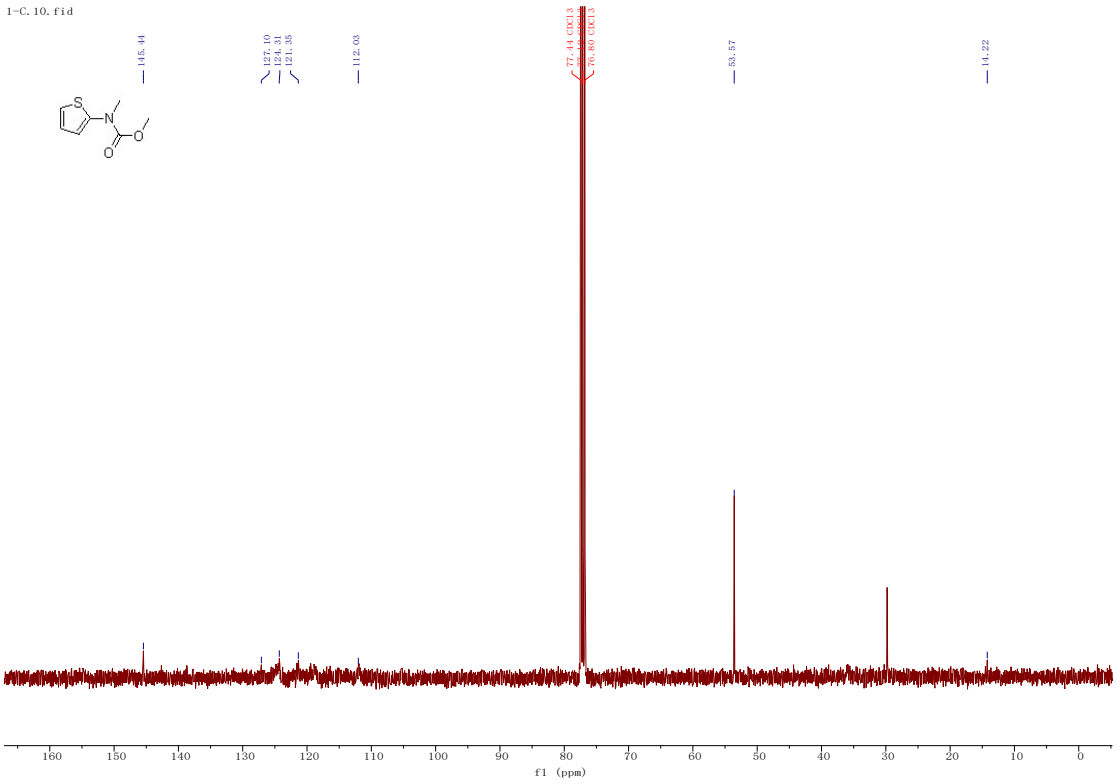

Figure S41 HRMS spectrum for compound 3s and 4n

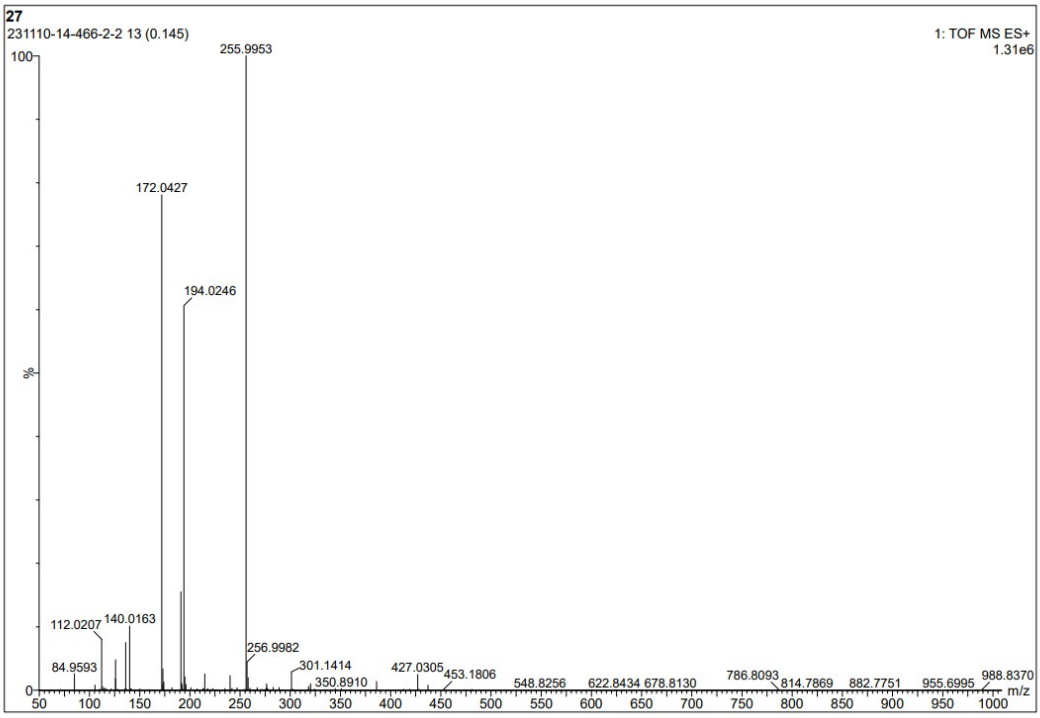

Figure S42 ^{1}H NMR spectrum for compound 5a

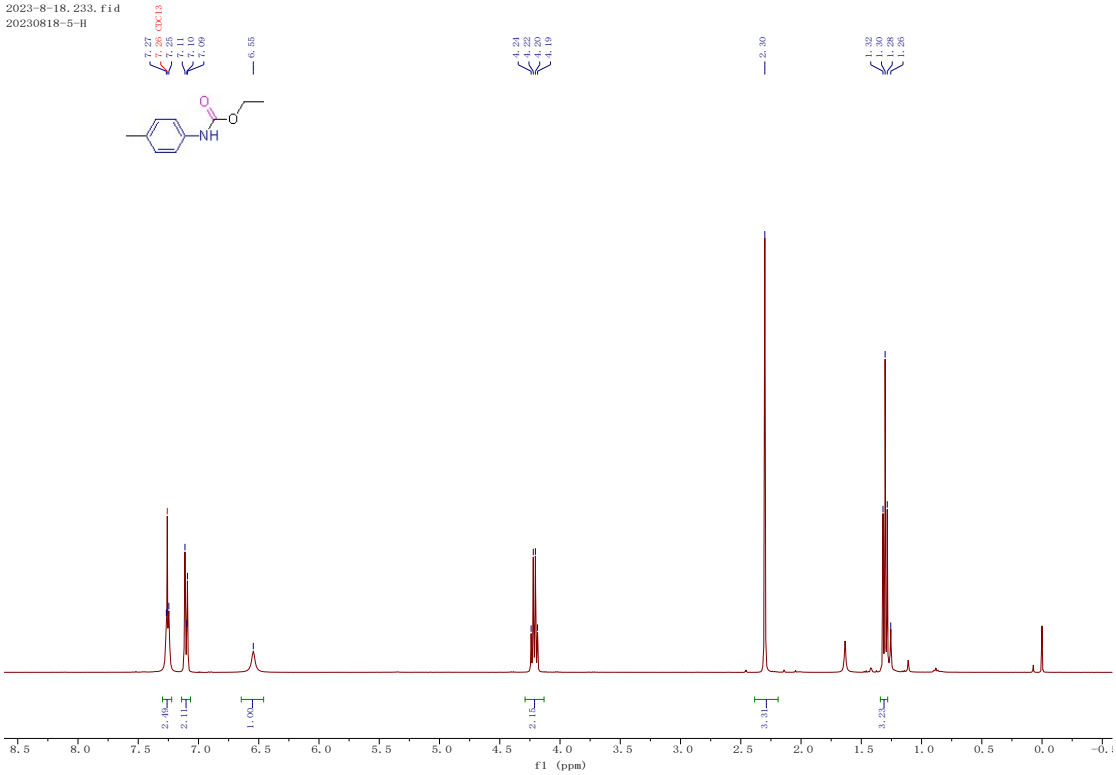

Figure S43 ^{13}C NMR spectrum for compound 5a

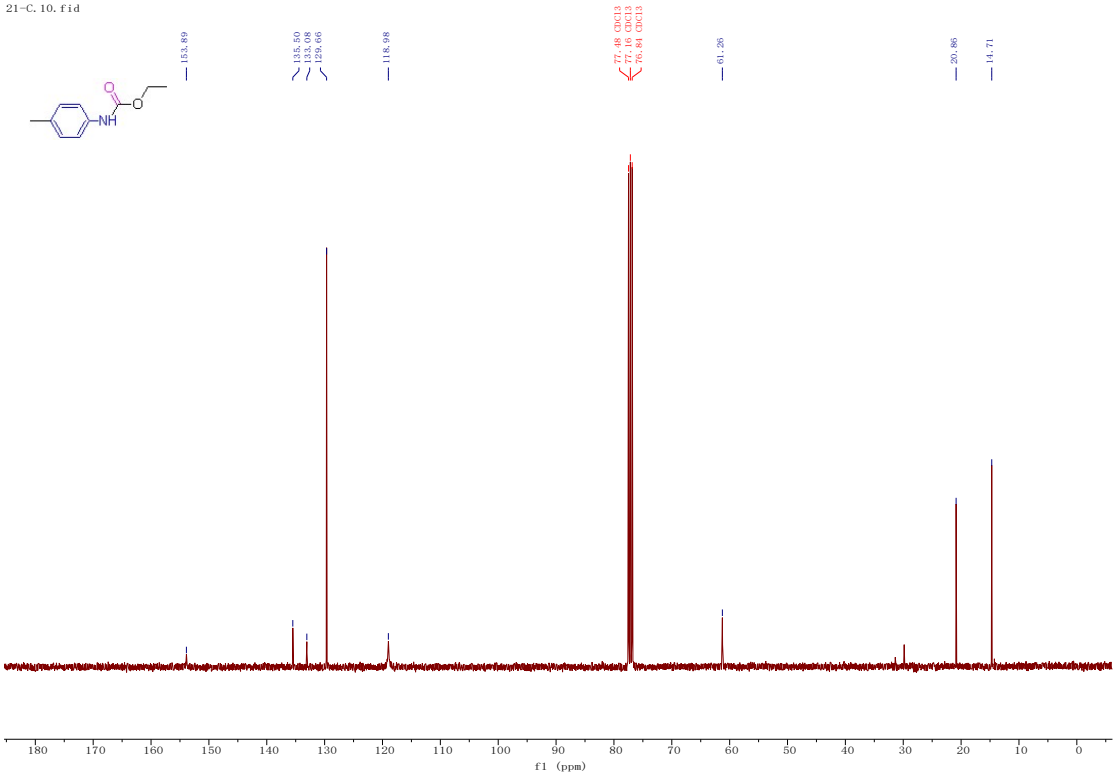

Figure S44 ^{1}H NMR spectrum for compound 4a

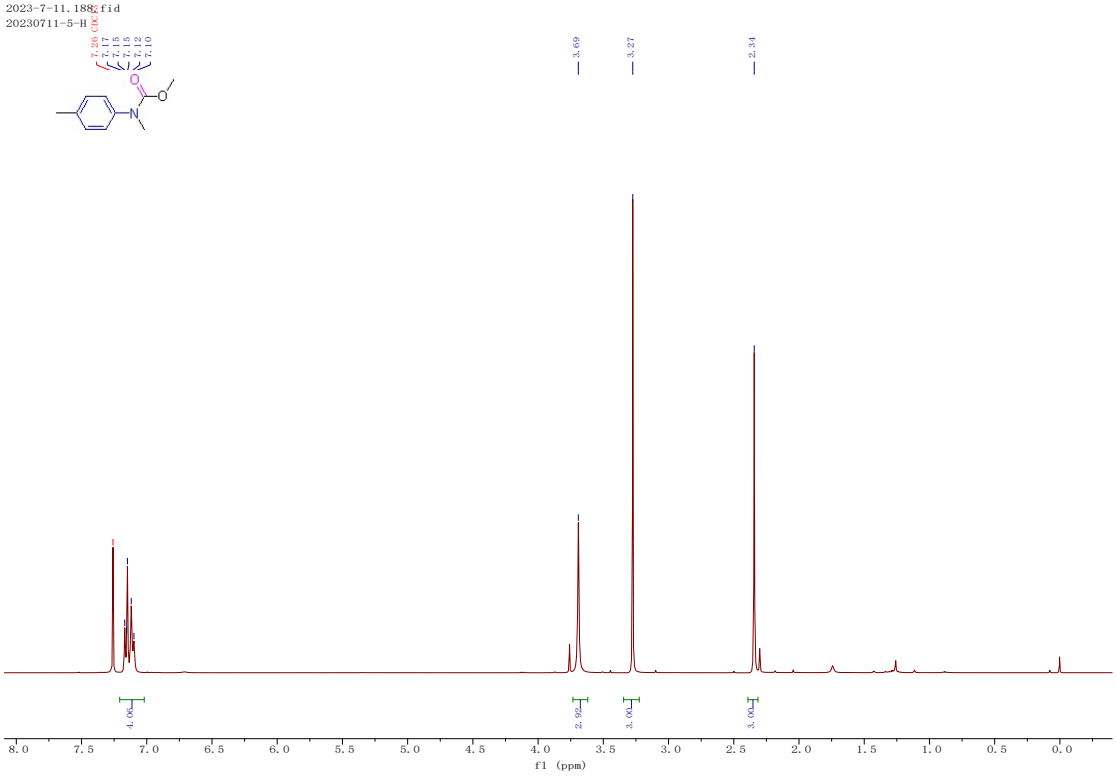

Figure S45 ^{13}C NMR spectrum for compound 4a

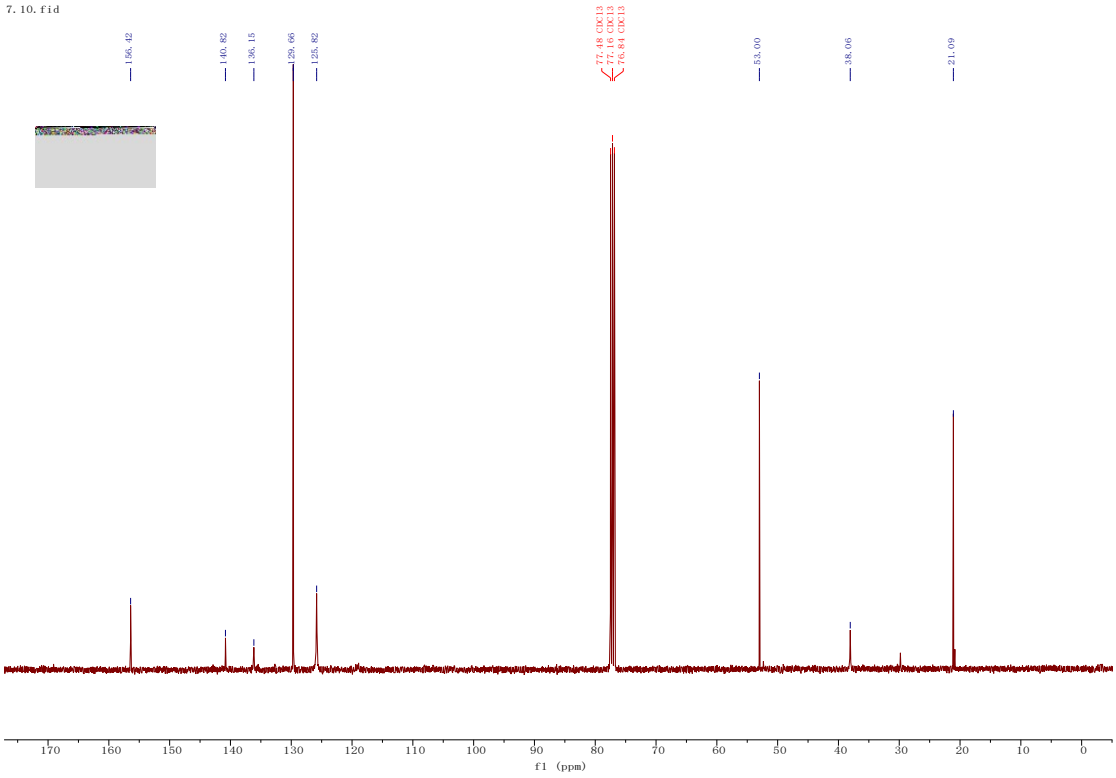

Figure S46 HRMS spectrum for compound 4a

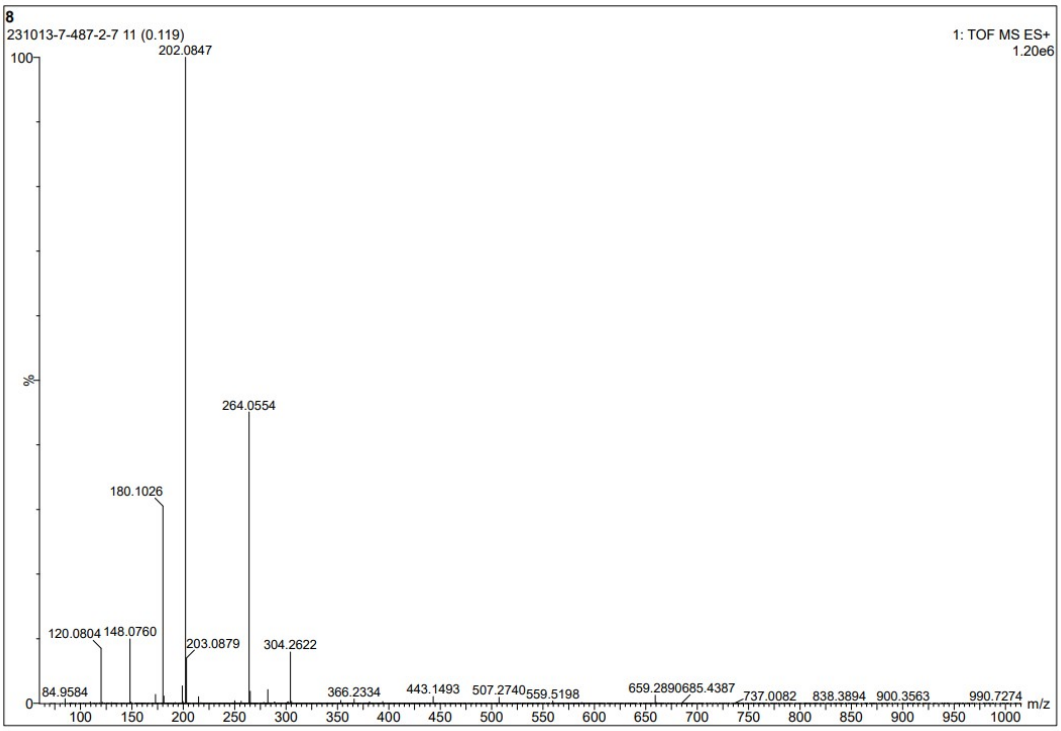

Figure S47 ^{1}H NMR spectrum for compound 4b

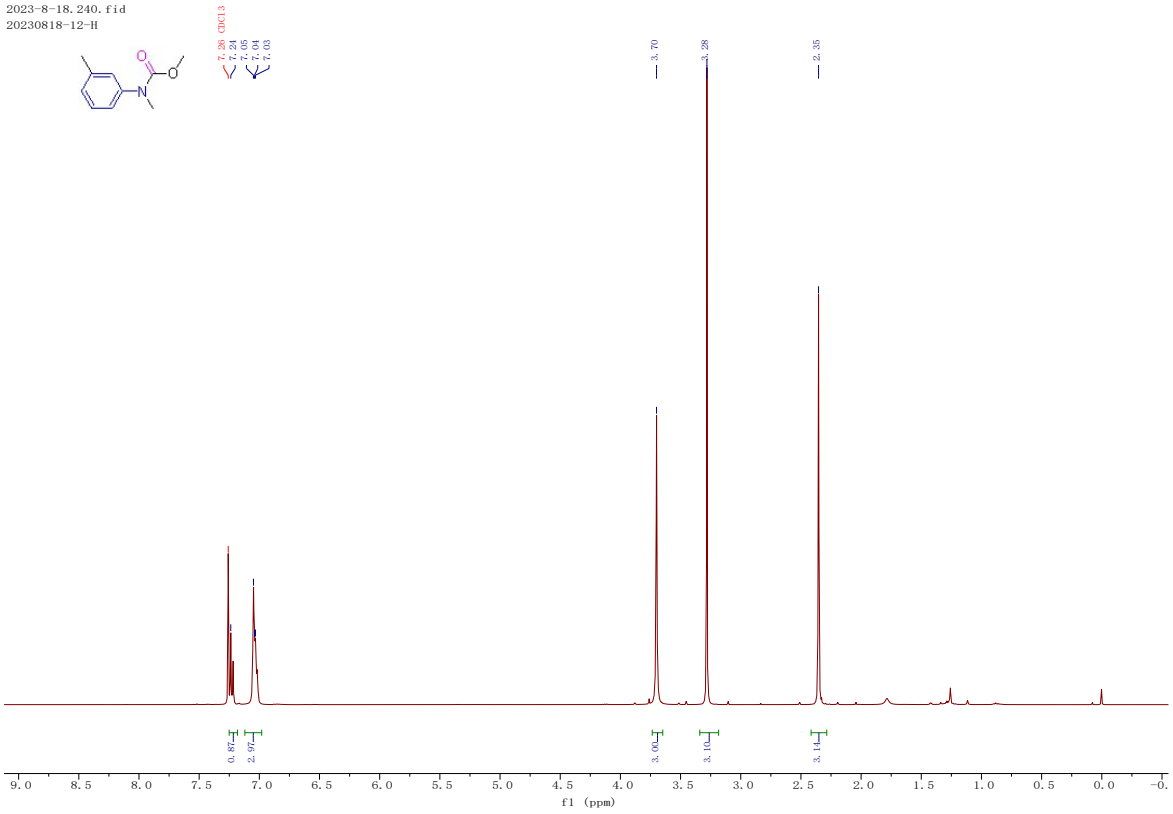

Figure S48 ^{13}C NMR spectrum for compound 4b

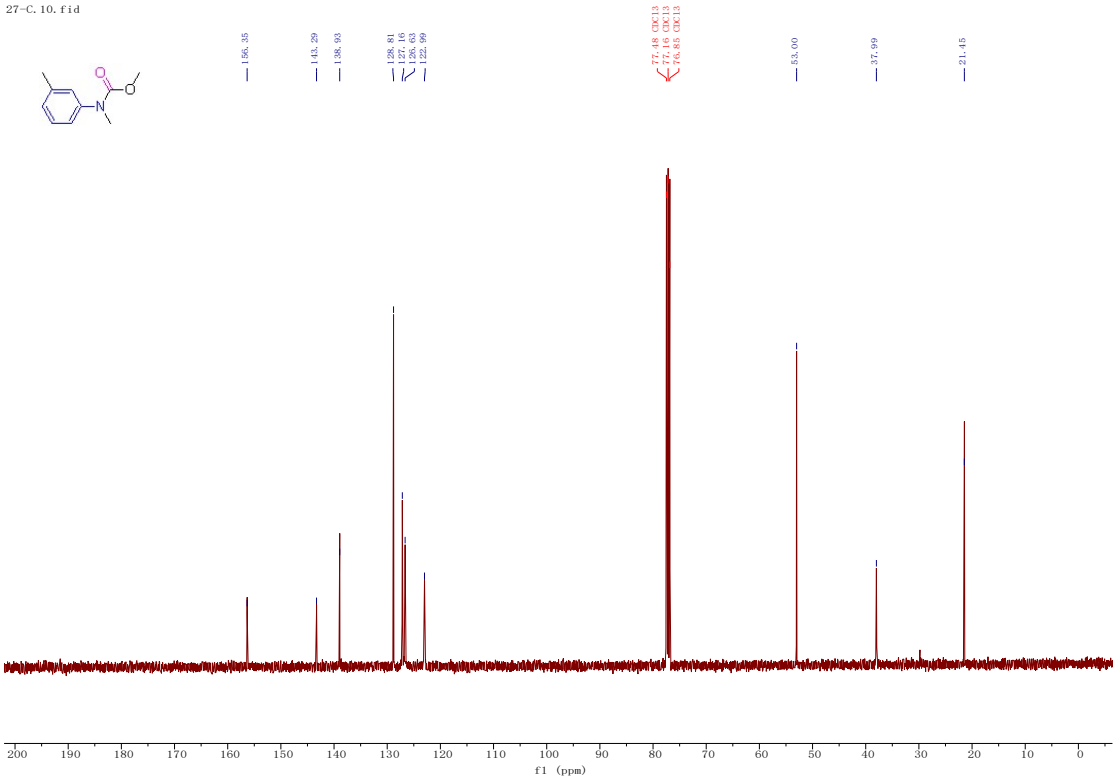

Figure S49 ^{1}H NMR spectrum for compound 4c

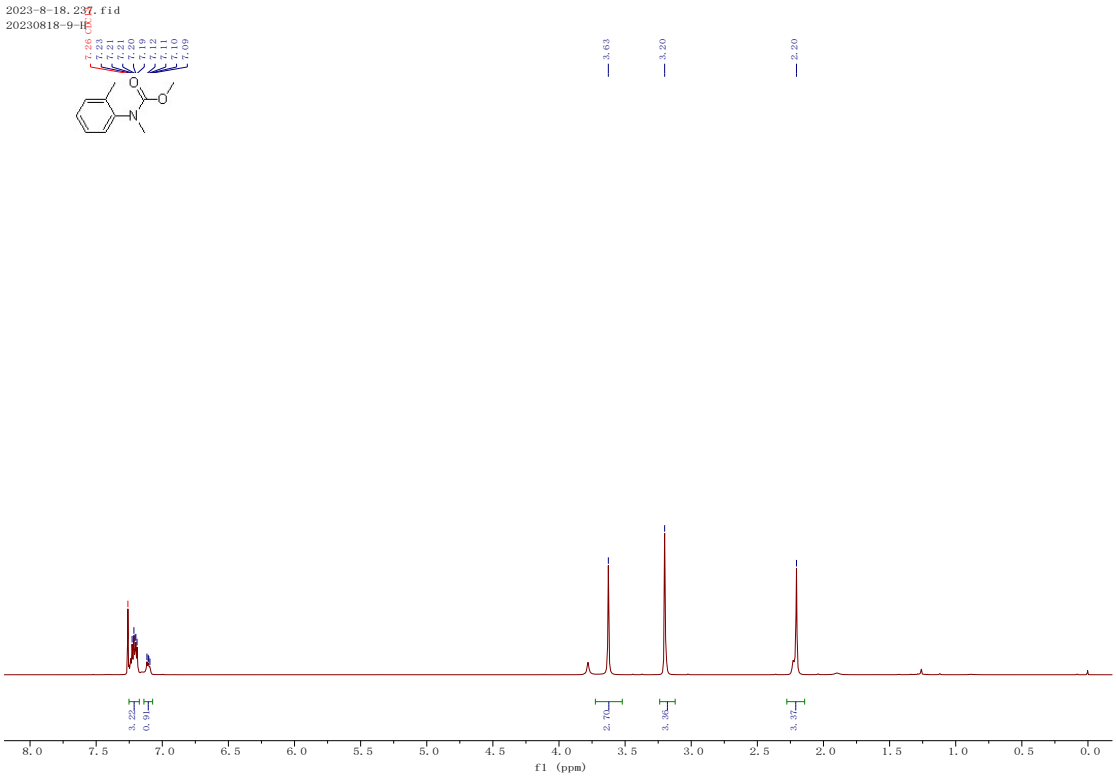

Figure S50 ^{13}C NMR spectrum for compound 4c

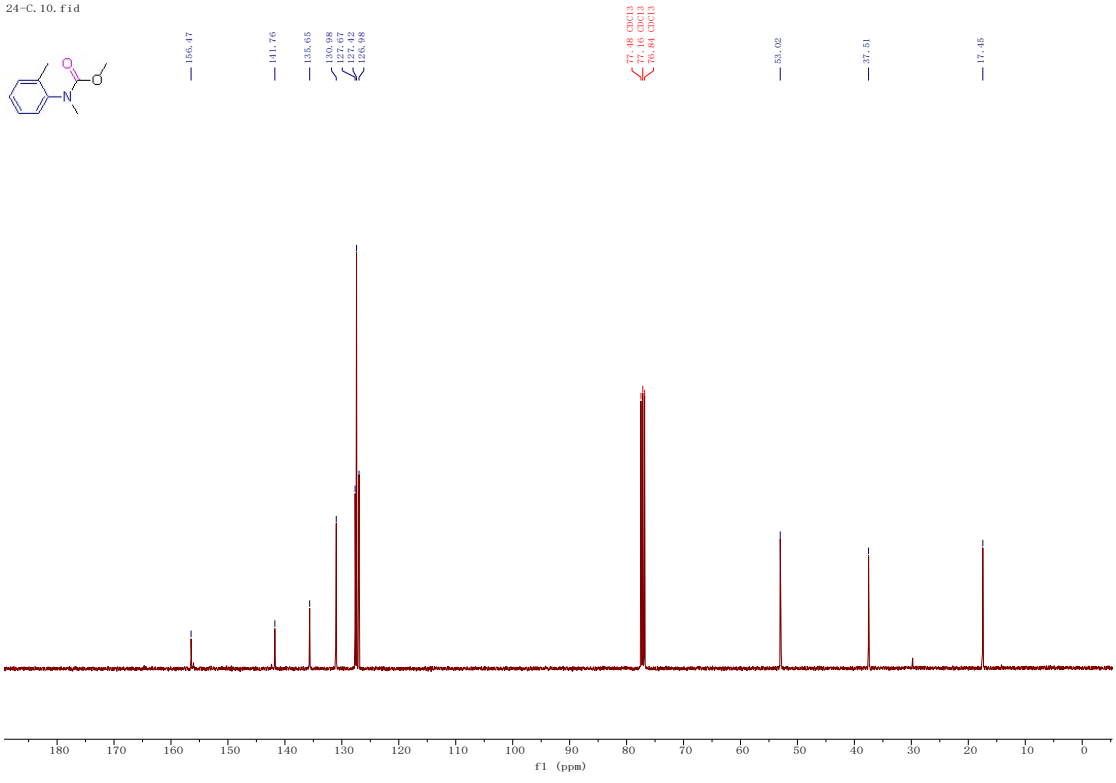

Figure S51 ^{1}H NMR spectrum for compound 4d

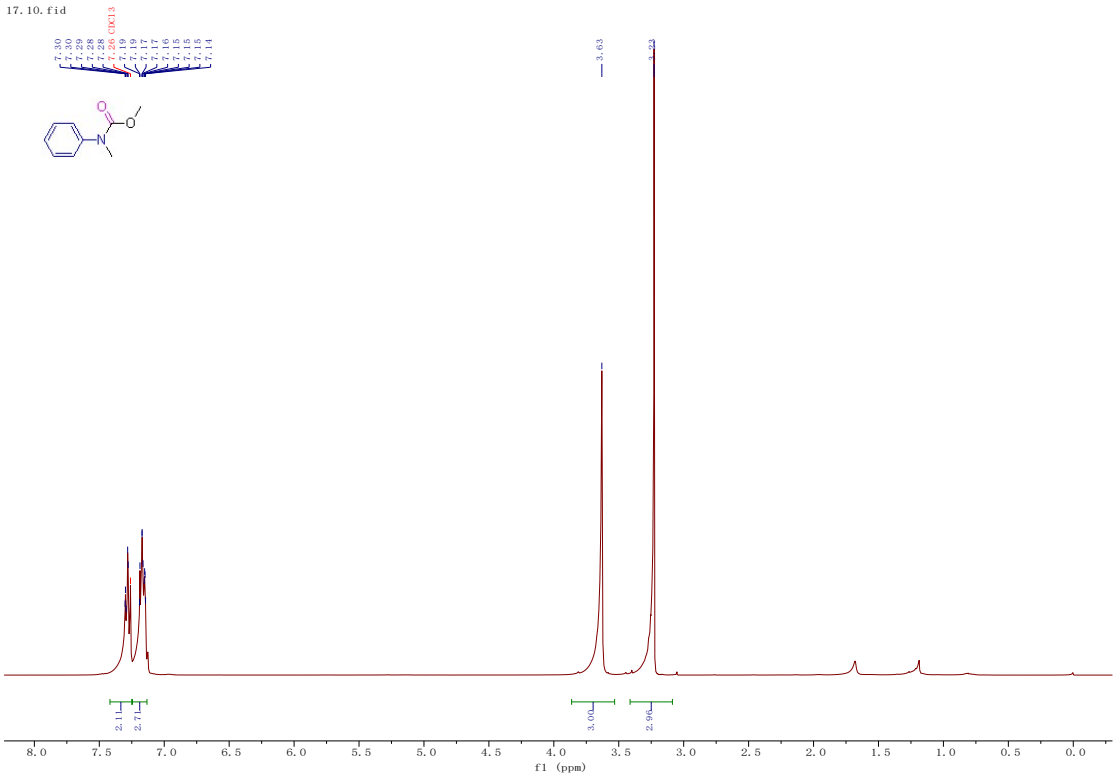

Figure S52 ^{13}C NMR spectrum for compound 4d

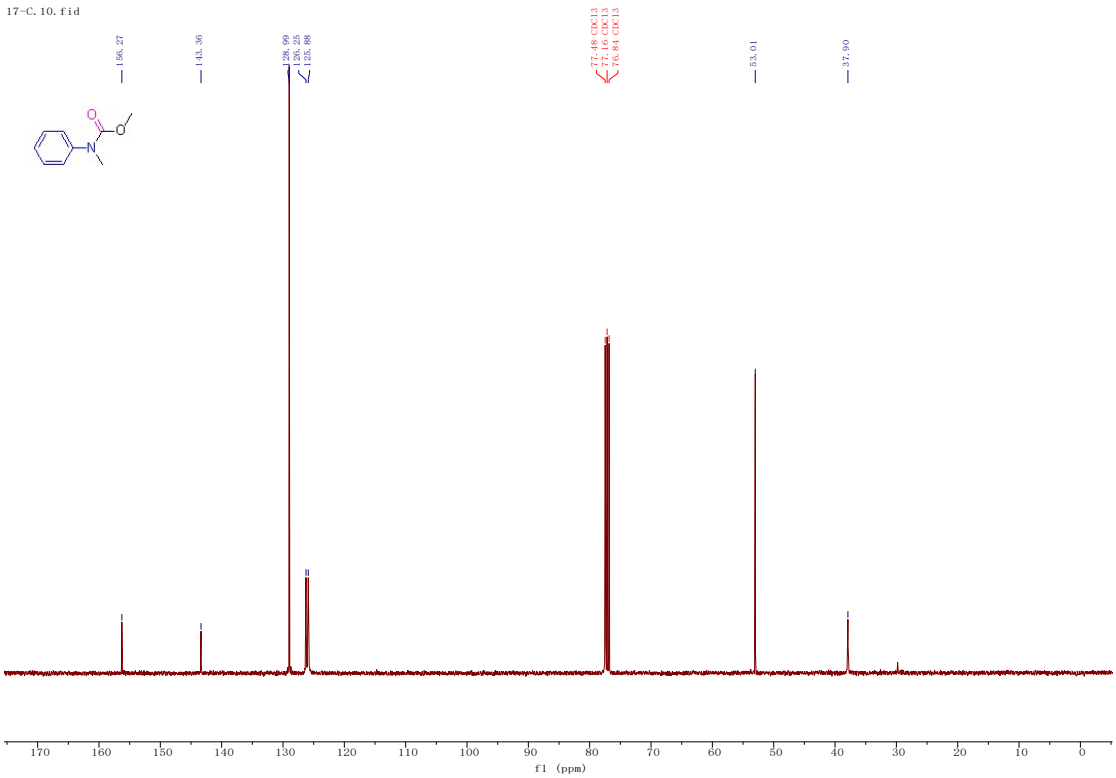

Figure S53 ^{1}H NMR spectrum for compound 4e and 4o

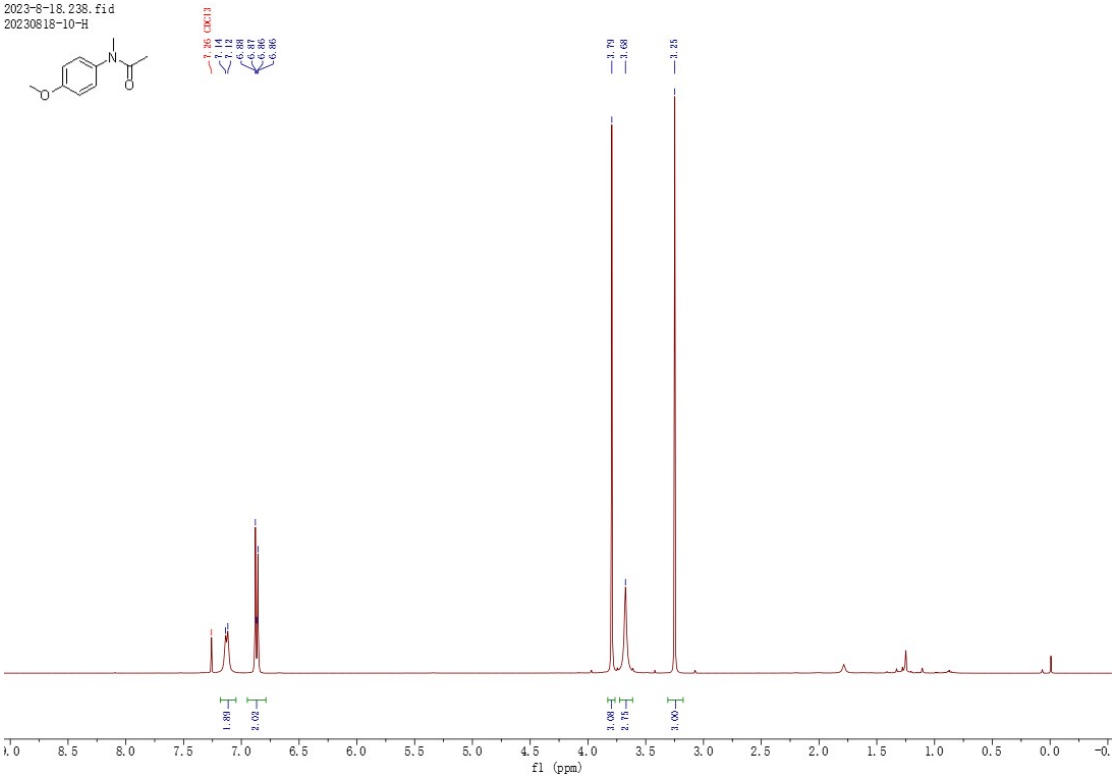

Figure S54 ^{13}C NMR spectrum for compound 4e and 4o

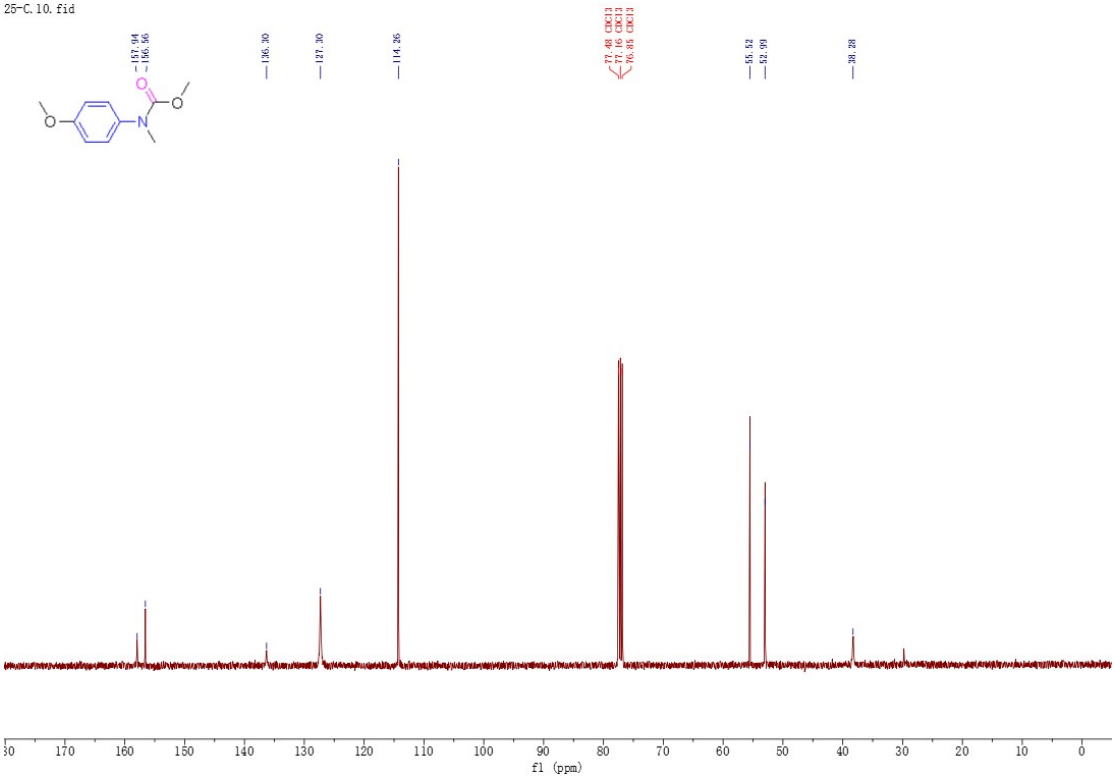

Figure S55 ^{1}H NMR spectrum for compound 4f

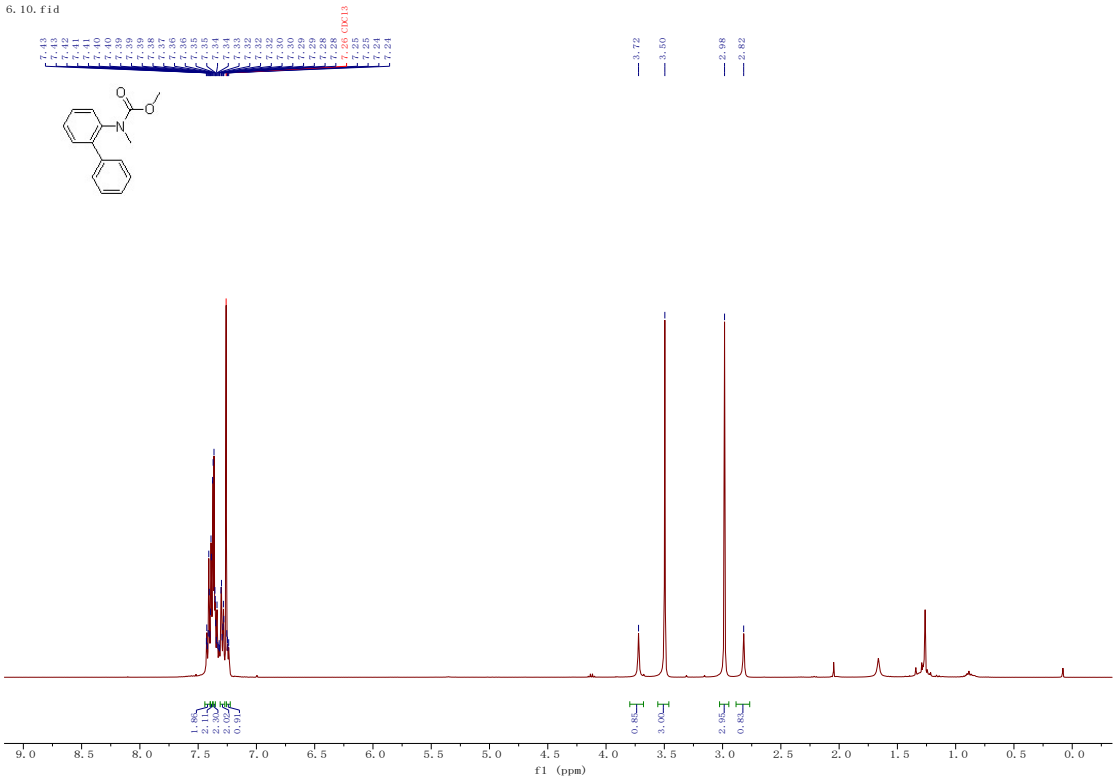

Figure S56 ^{13}C NMR spectrum for compound 4f

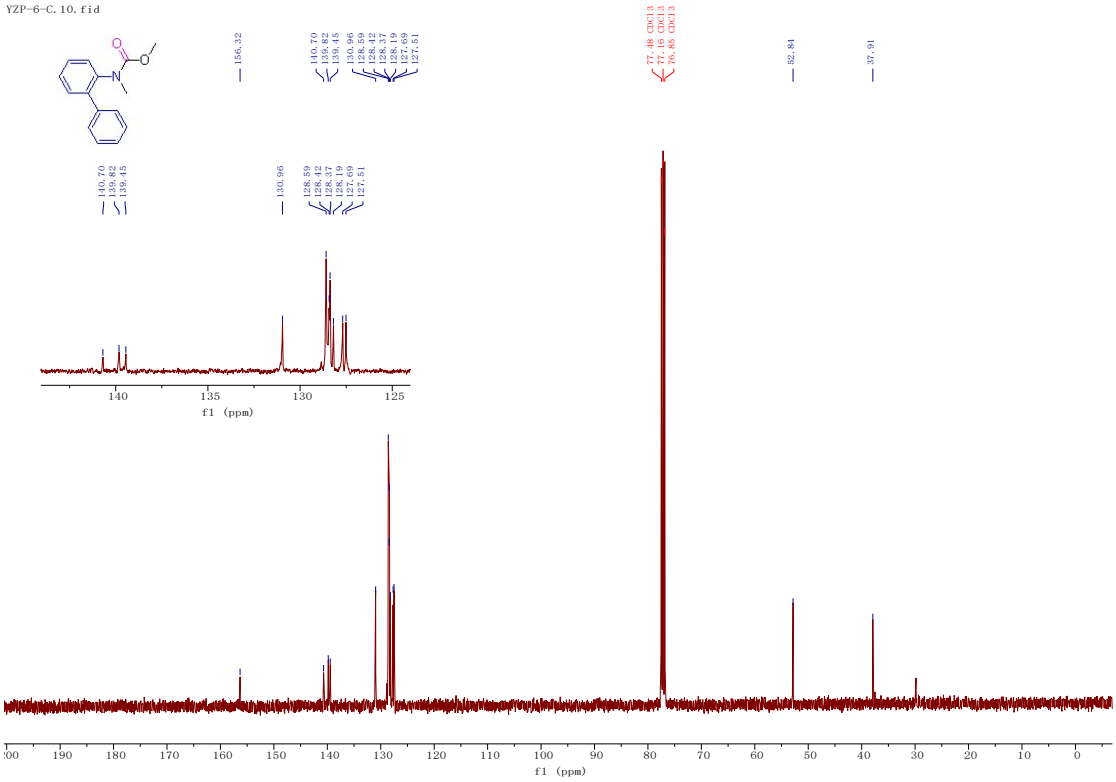

Figure S57 ^{1}H NMR spectrum for compound 4g

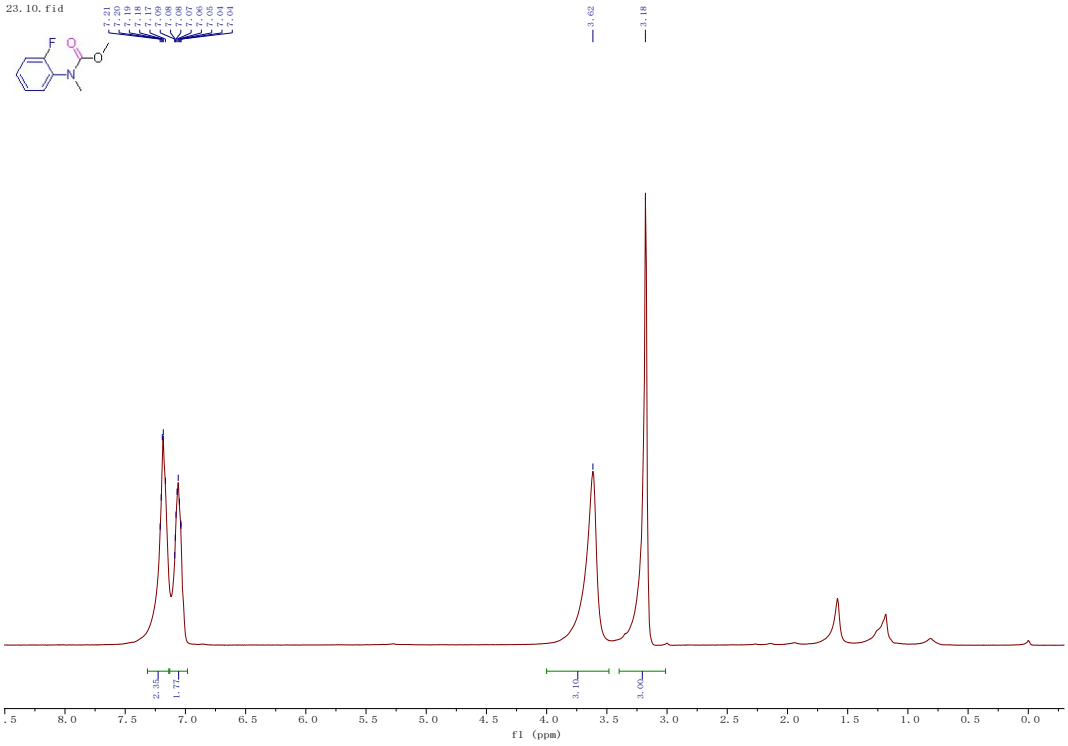

Figure S58 ^{13}C NMR spectrum for compound 4g

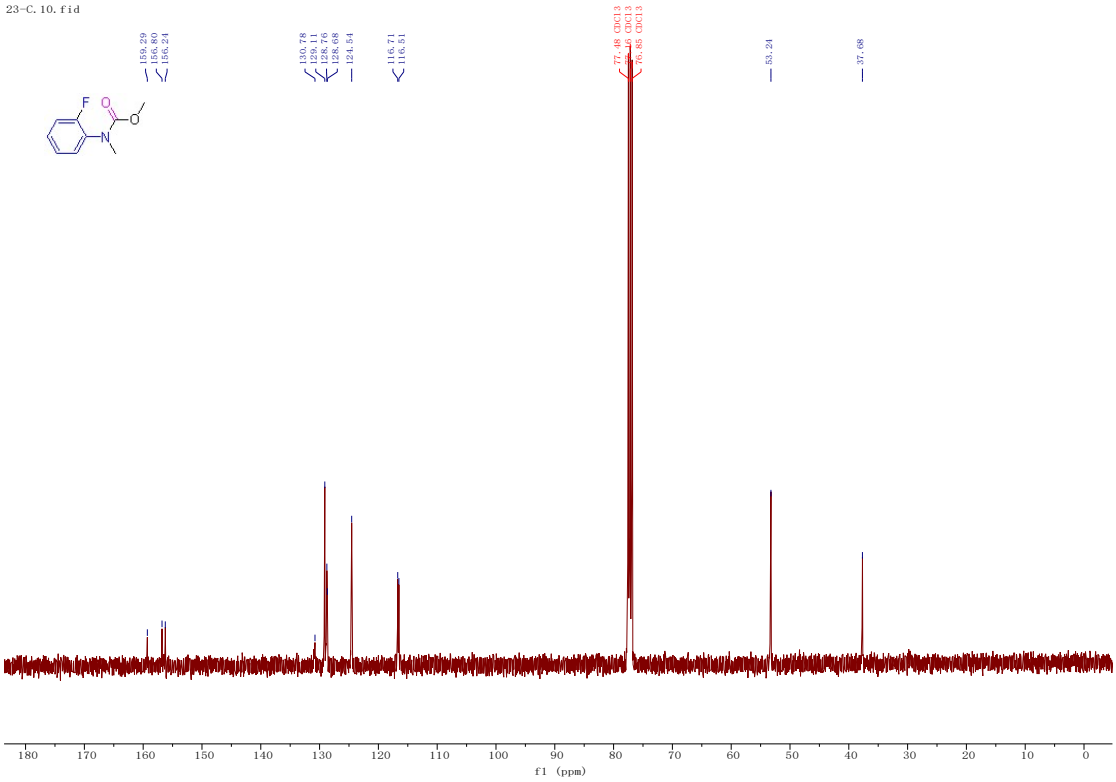

Figure S59 ^{19}F NMR spectrum for compound 4g

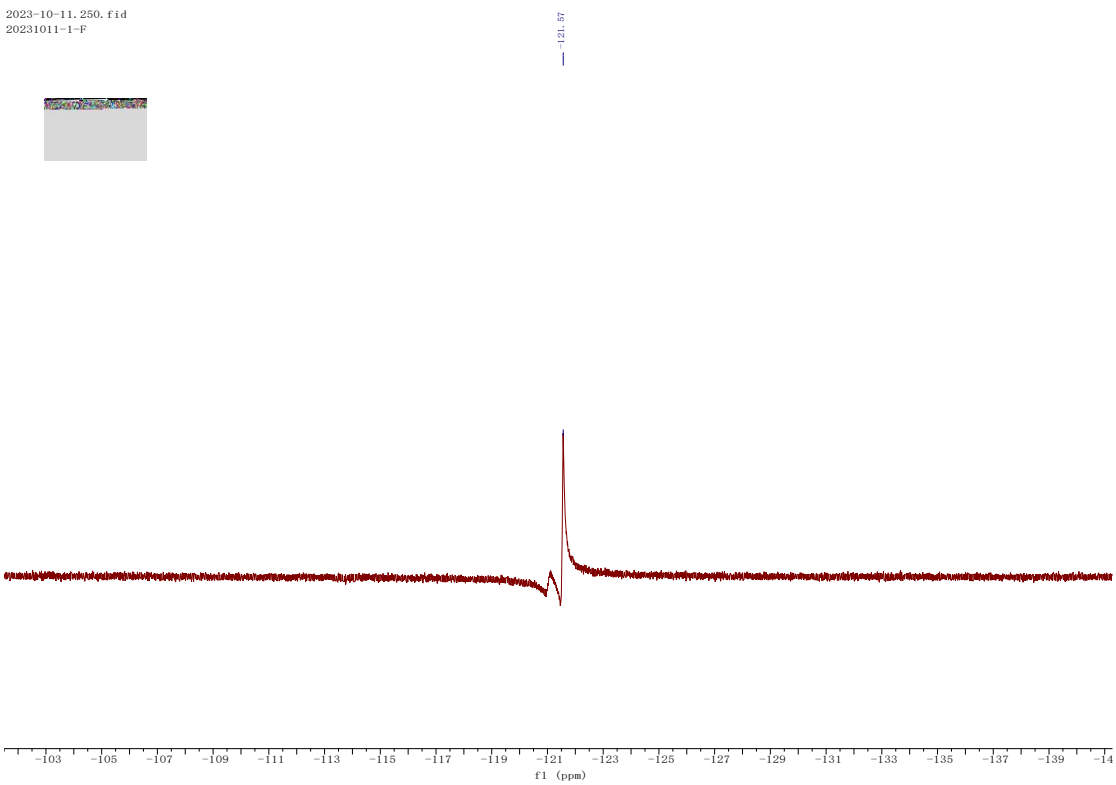

Figure S60 HRMS spectrum for compound 4g and 4h

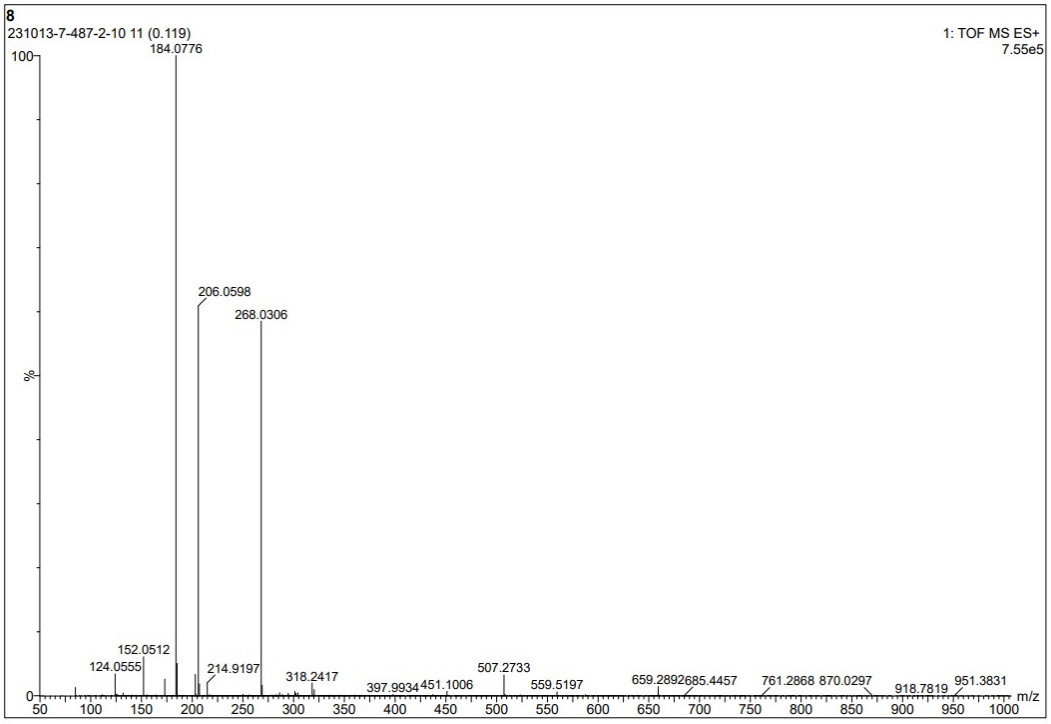

Figure S61 ^{1}H NMR spectrum for compound 4h

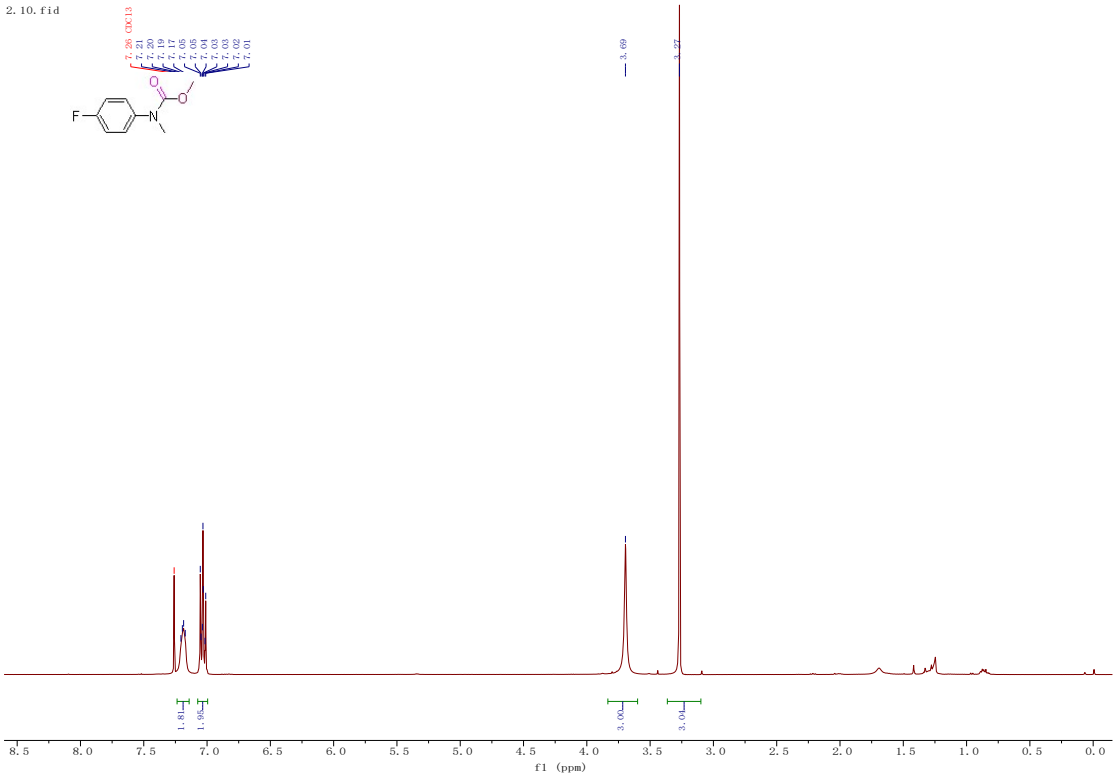

Figure S62 ^{13}C NMR spectrum for compound 4h

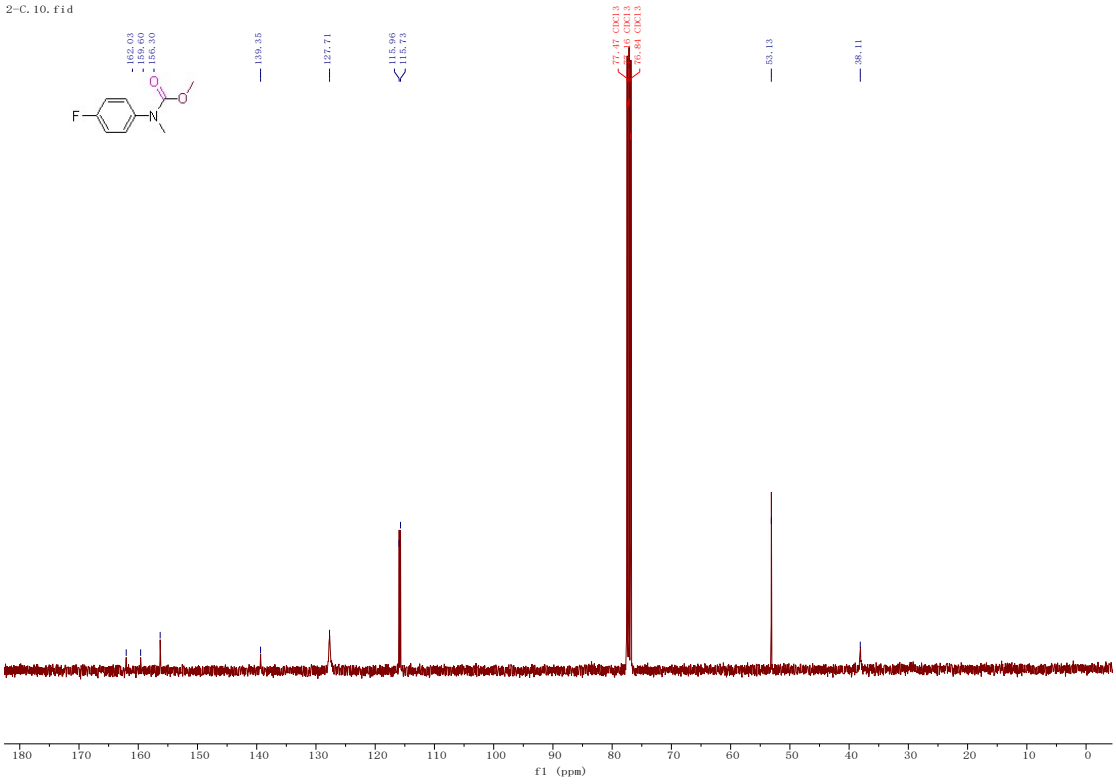

Figure S63 ^{19}F NMR spectrum for compound 4h

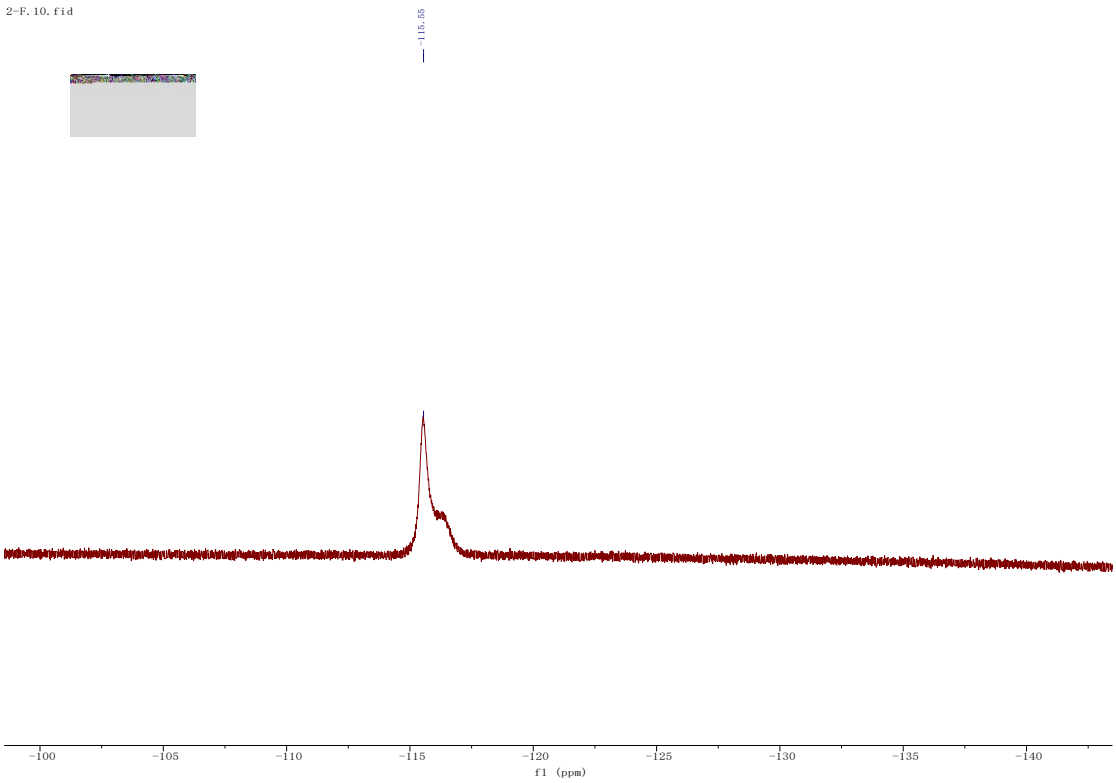

Figure S64 ^{1}H NMR spectrum for compound 4i

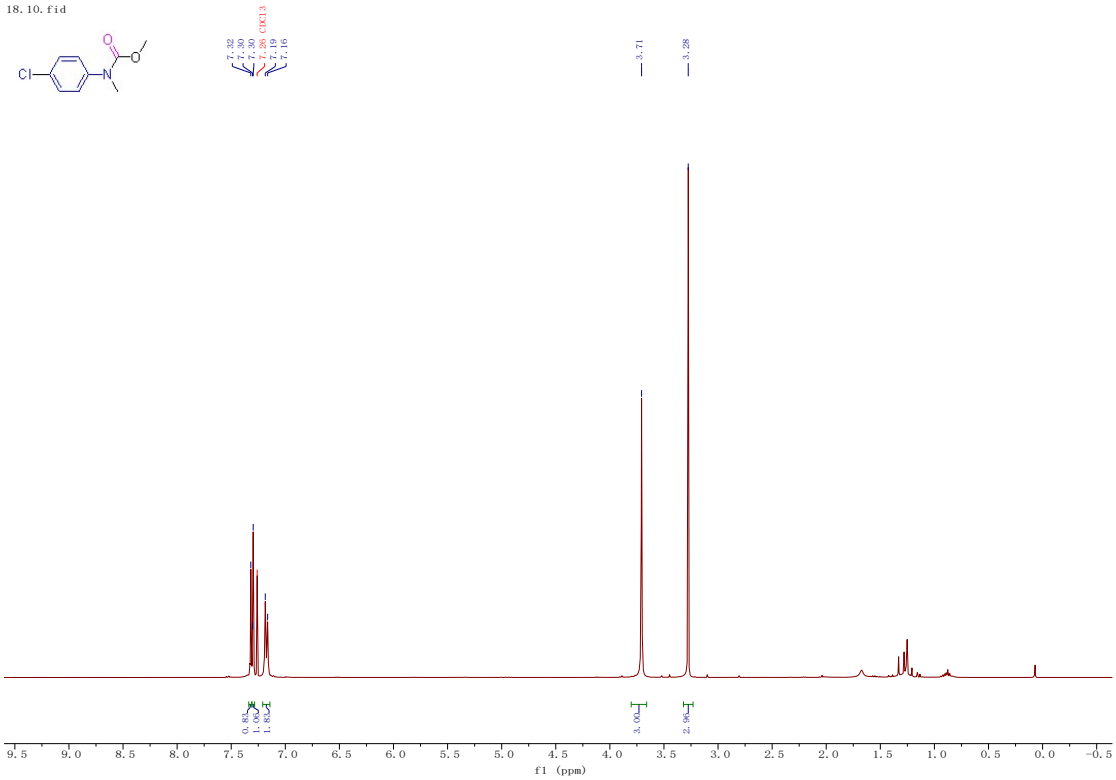

Figure S65 ^{13}C NMR spectrum for compound 4i

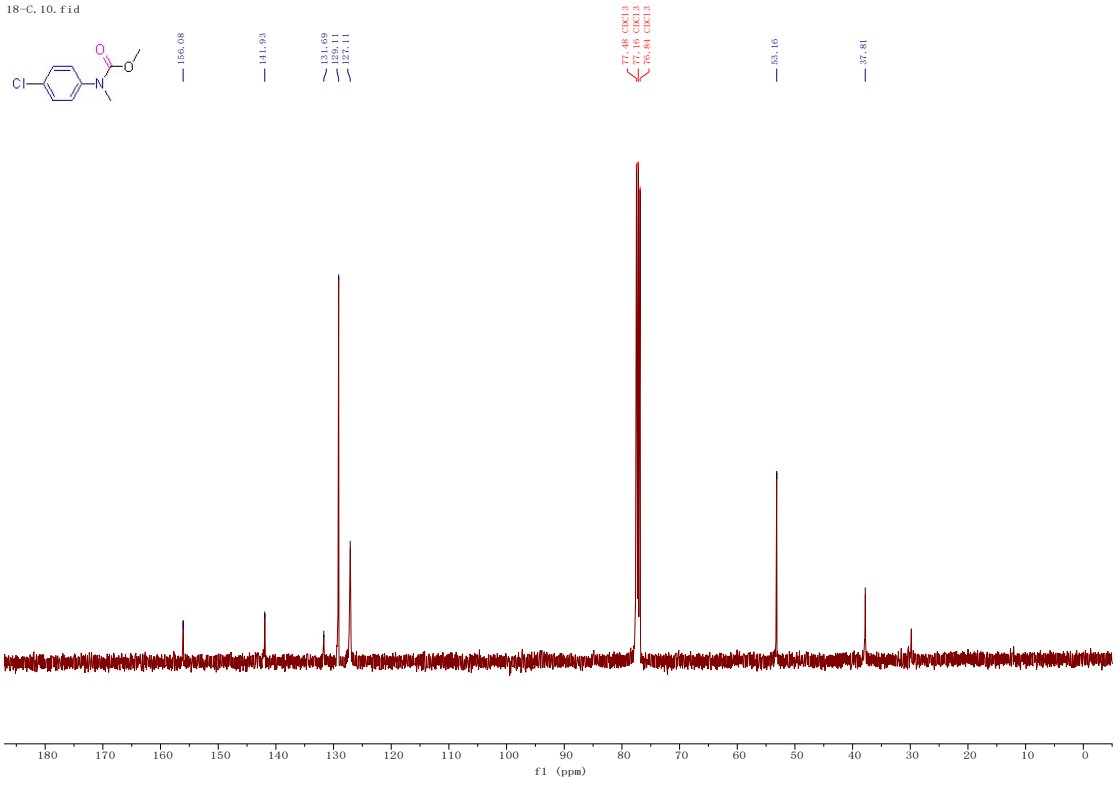

Figure S66 ^{1}H NMR spectrum for compound 4j

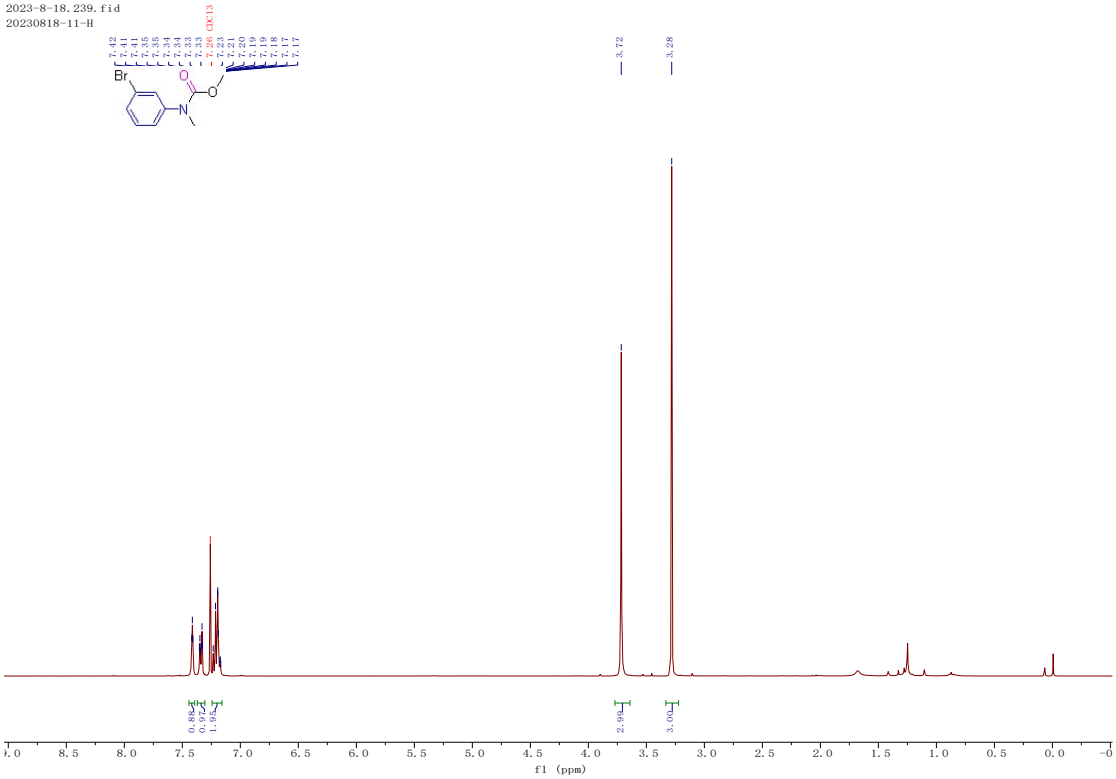

Figure S67 ^{13}C NMR spectrum for compound 4j

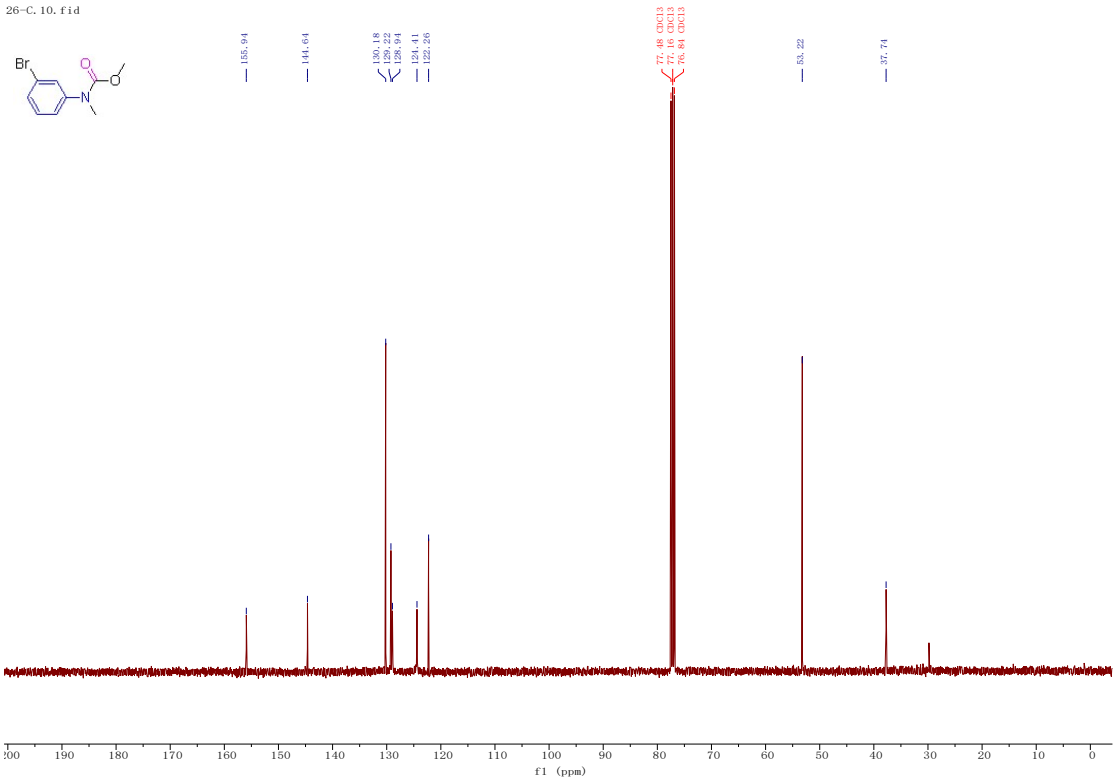

Figure S68 HRMS spectrum for compound 4j

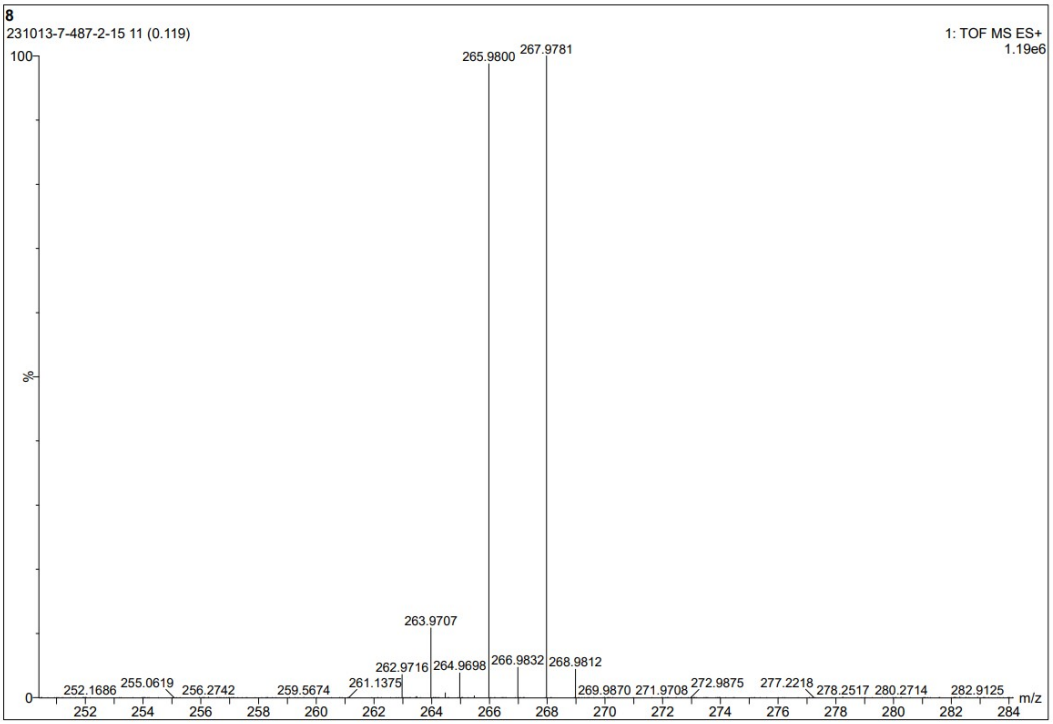

Figure S69 ^{1}H NMR spectrum for compound 4k

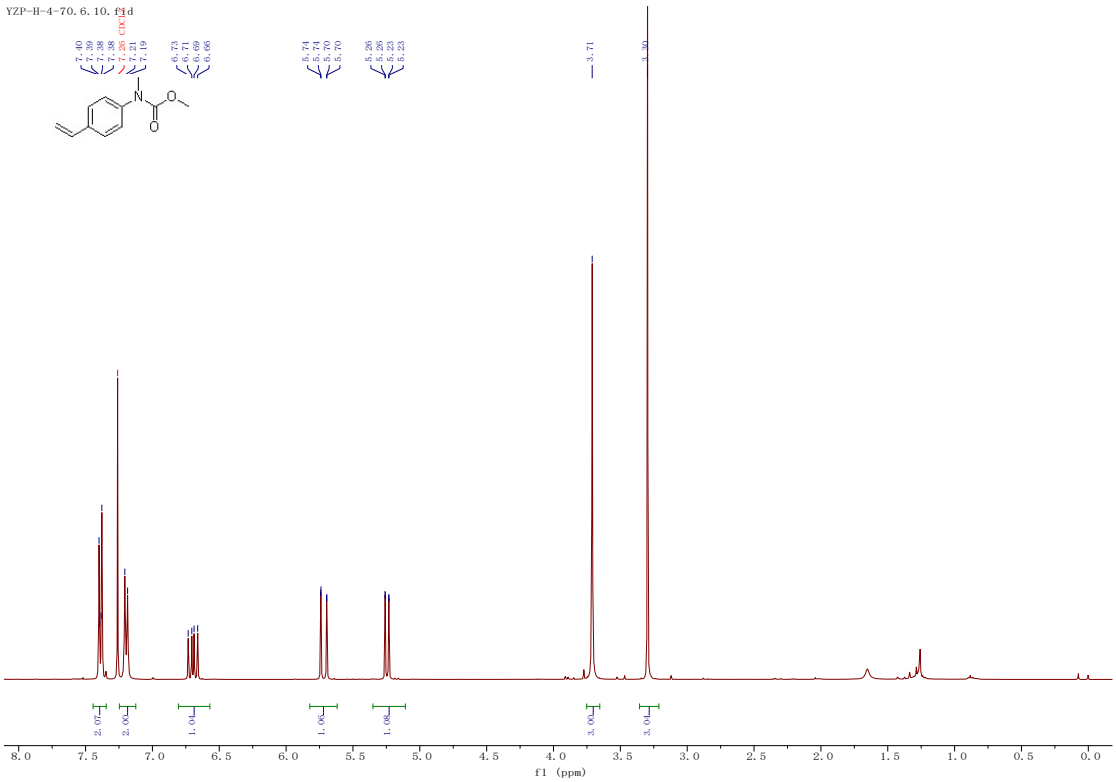

Figure S70 ^{13}C NMR spectrum for compound 4k

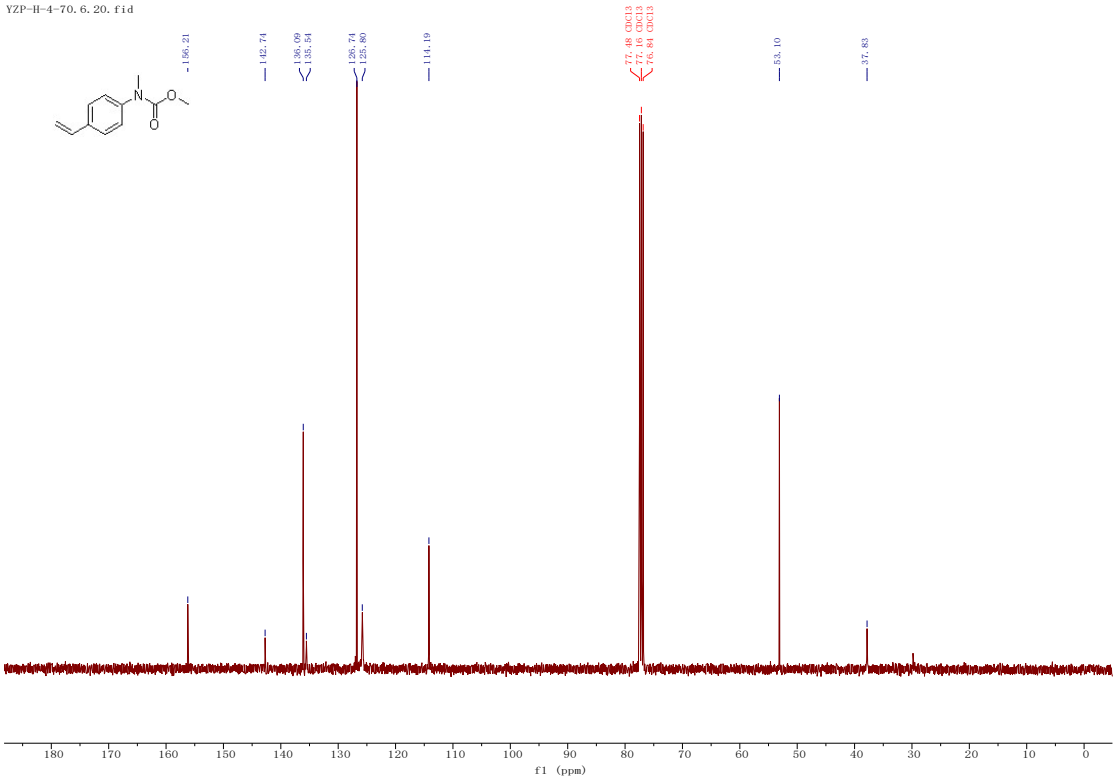

Figure S71 HRMS spectrum for compound 4k

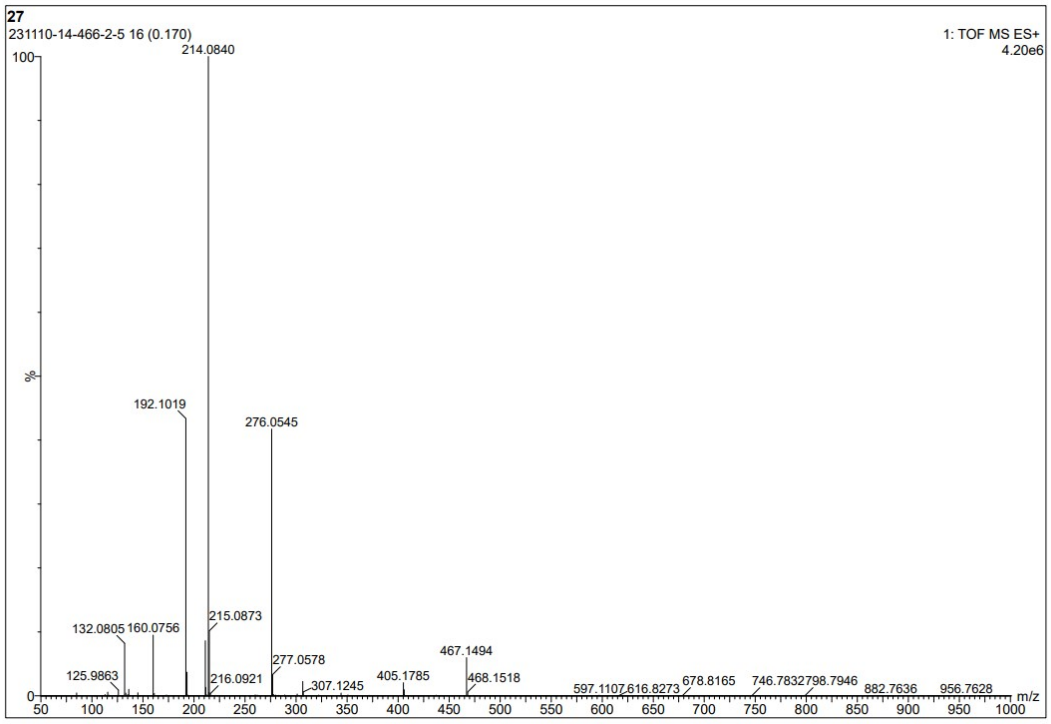

Figure S72 ^{1}H NMR spectrum for compound 4l

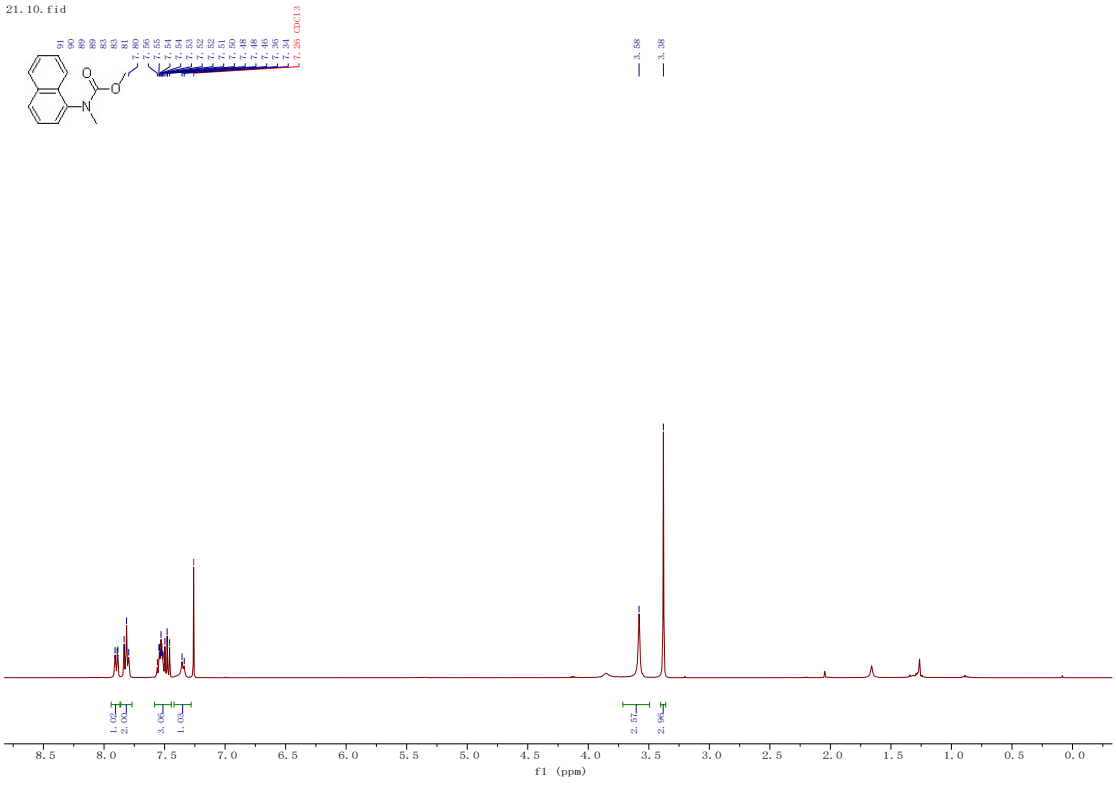

Figure S73 ^{13}C NMR spectrum for compound 4l

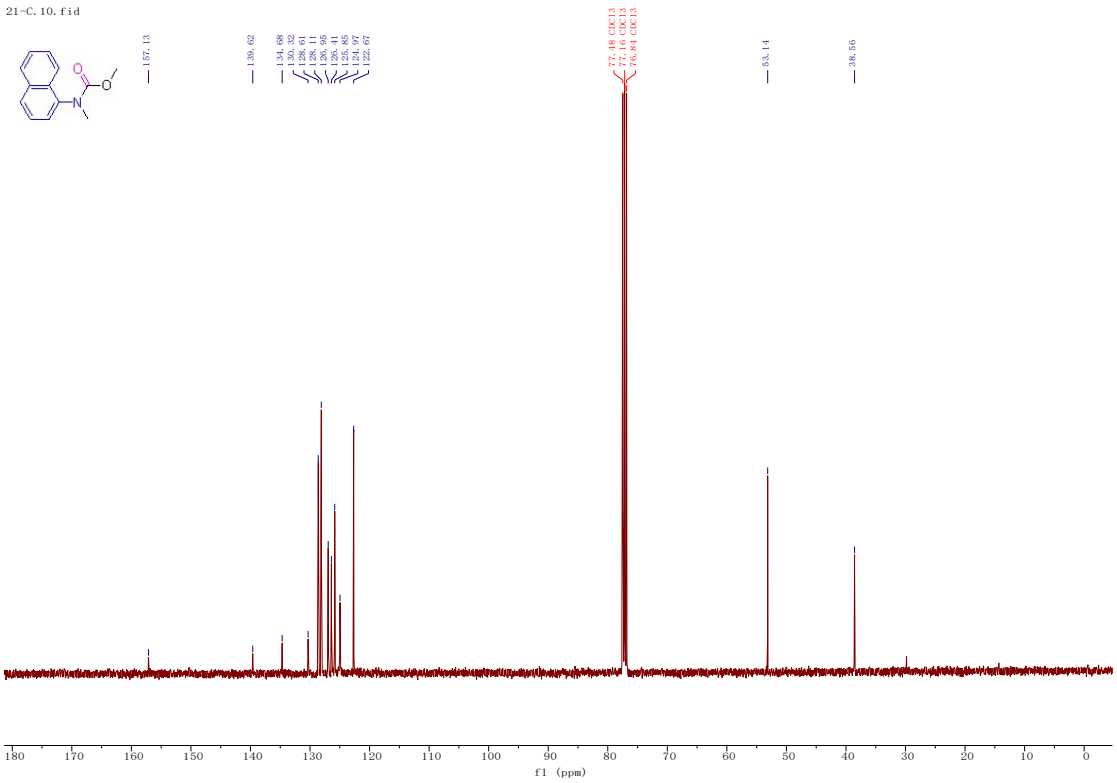

Figure S74 HRMS spectrum for compound 4l

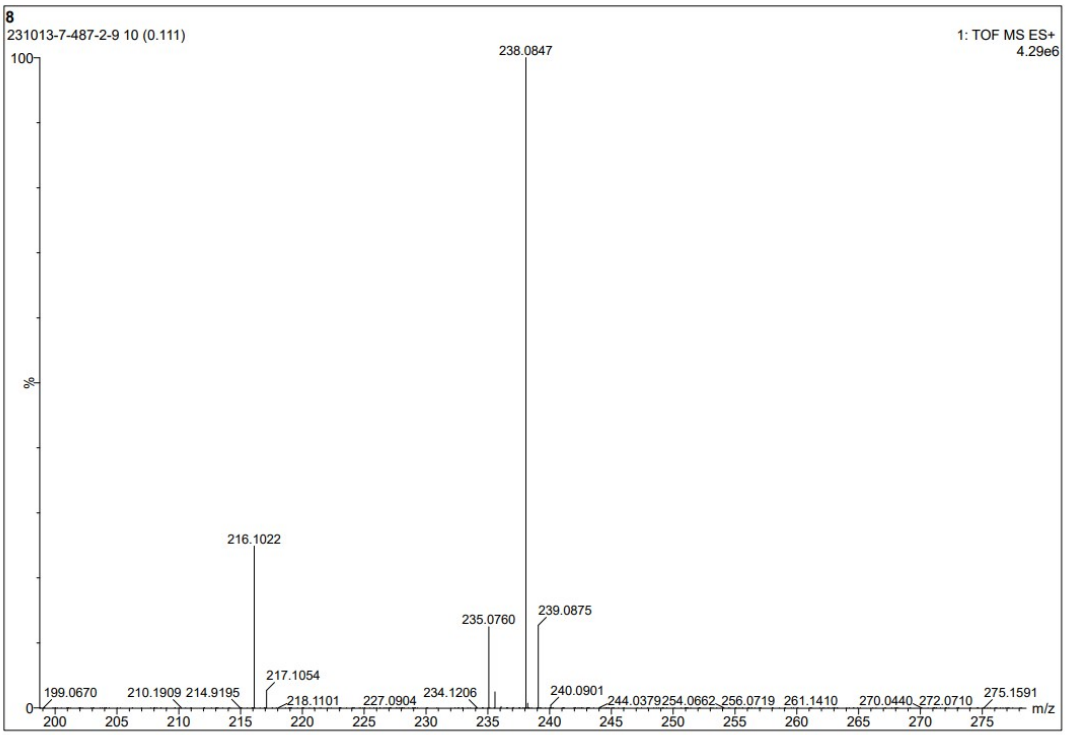

Figure S75 ^{1}H NMR spectrum for compound 4m

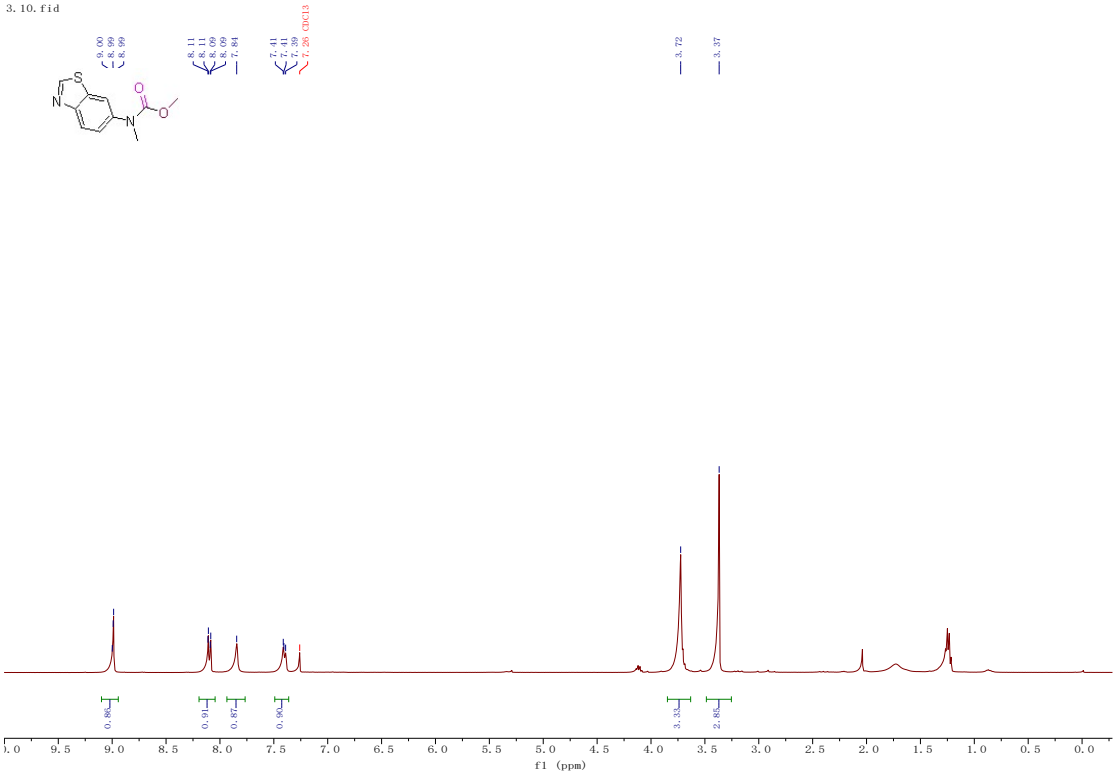

Figure S76 ^{13}C NMR spectrum for compound 4m

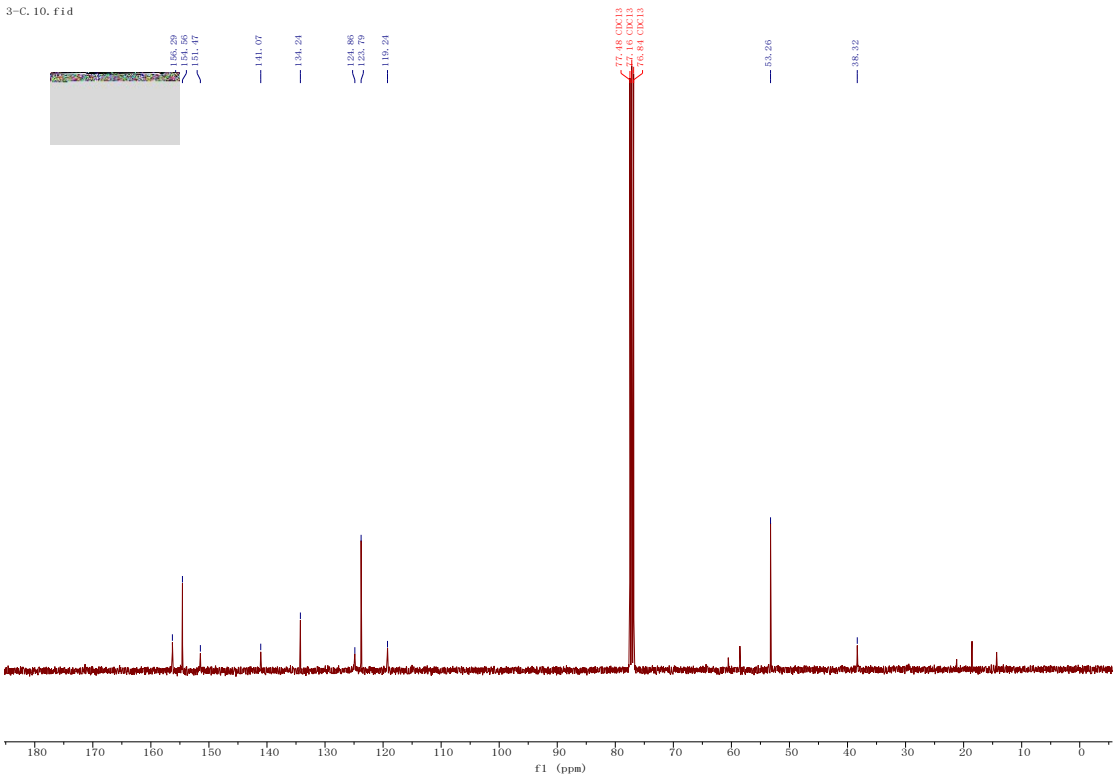

Figure S77 HRMS spectrum for compound 4m

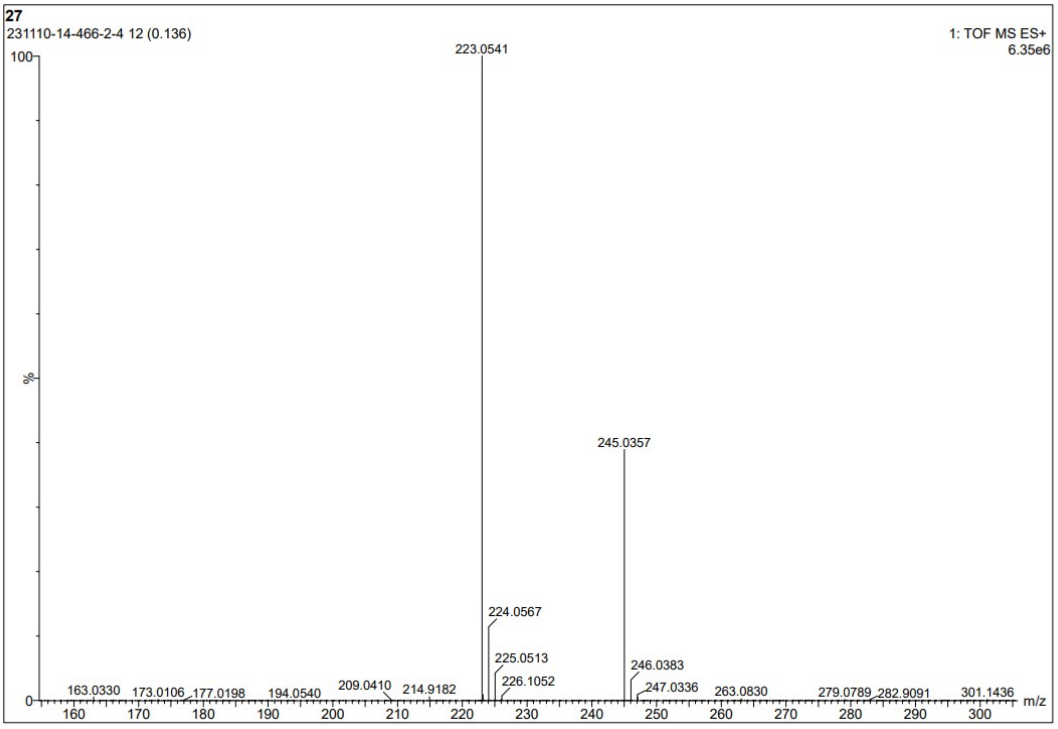

Figure S78 ^{1}H NMR spectrum for compound 4p

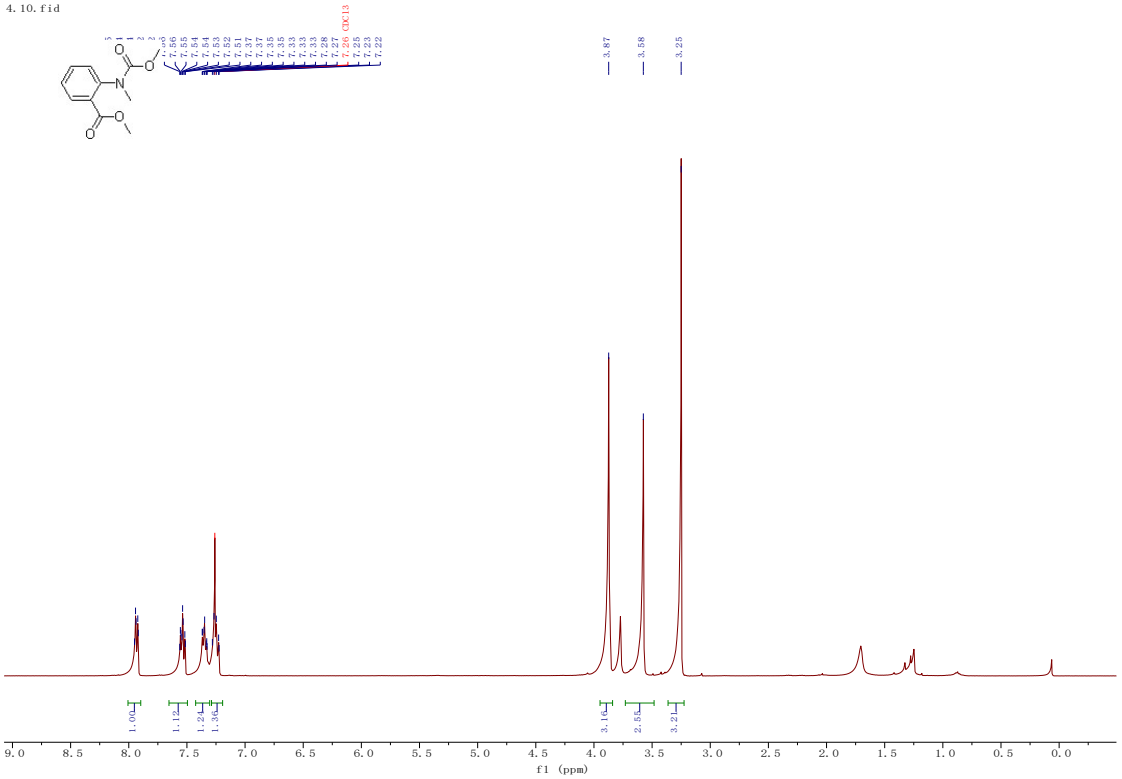

Figure S79 ^{13}C NMR spectrum for compound 4p

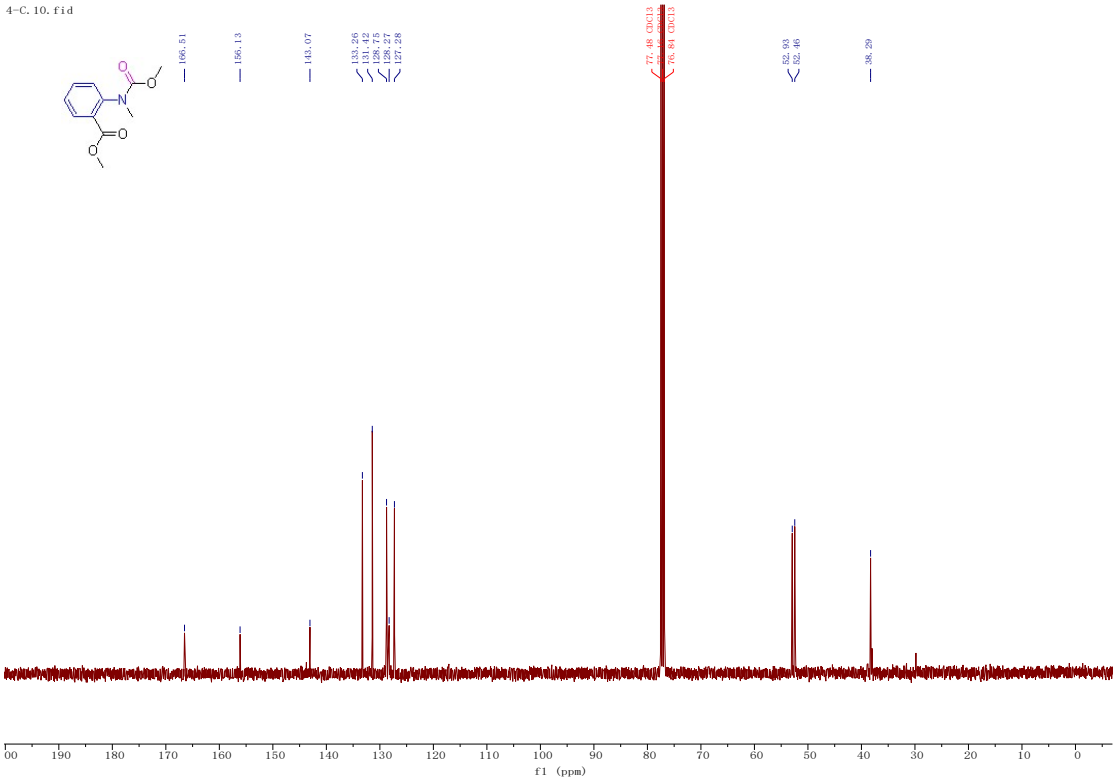

Figure S80 HRMS spectrum for compound 4p

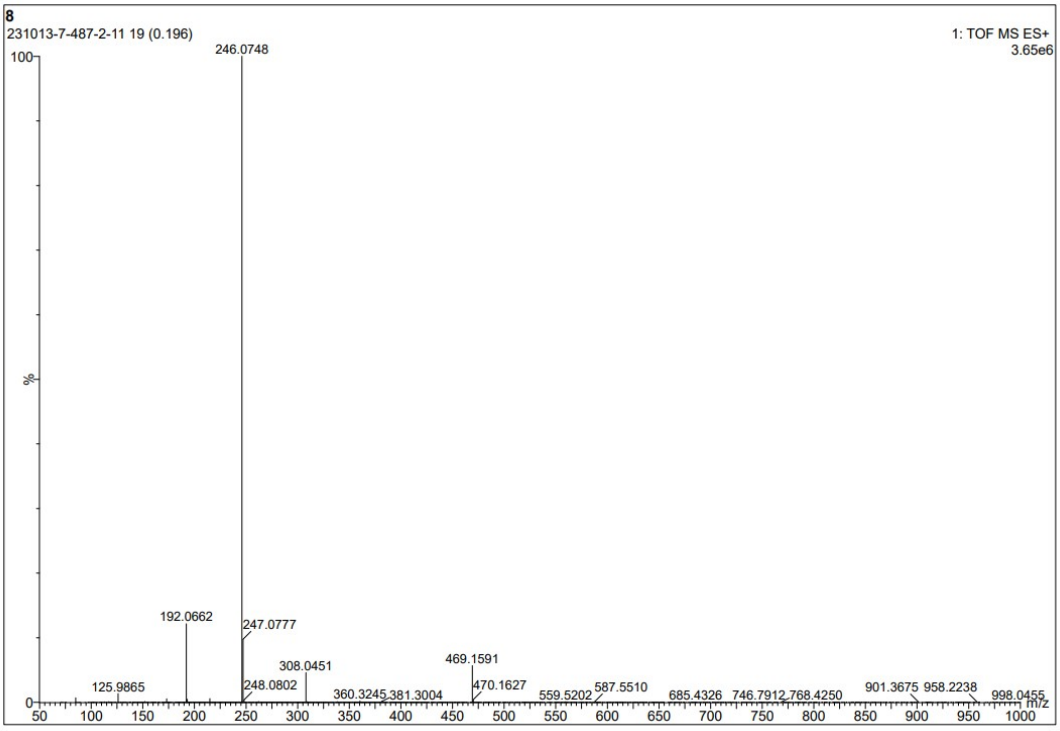

Figure S81 ^{1}H NMR spectrum for compound 4q

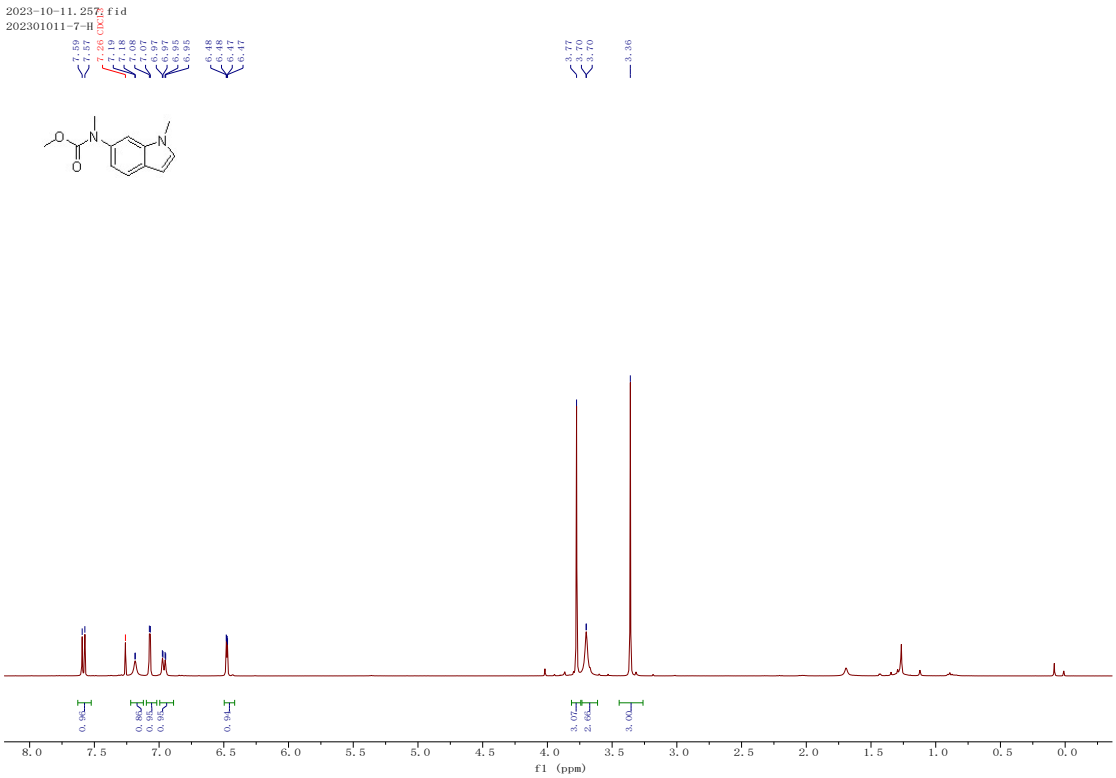

Figure S82 ^{13}C NMR spectrum for compound 4q

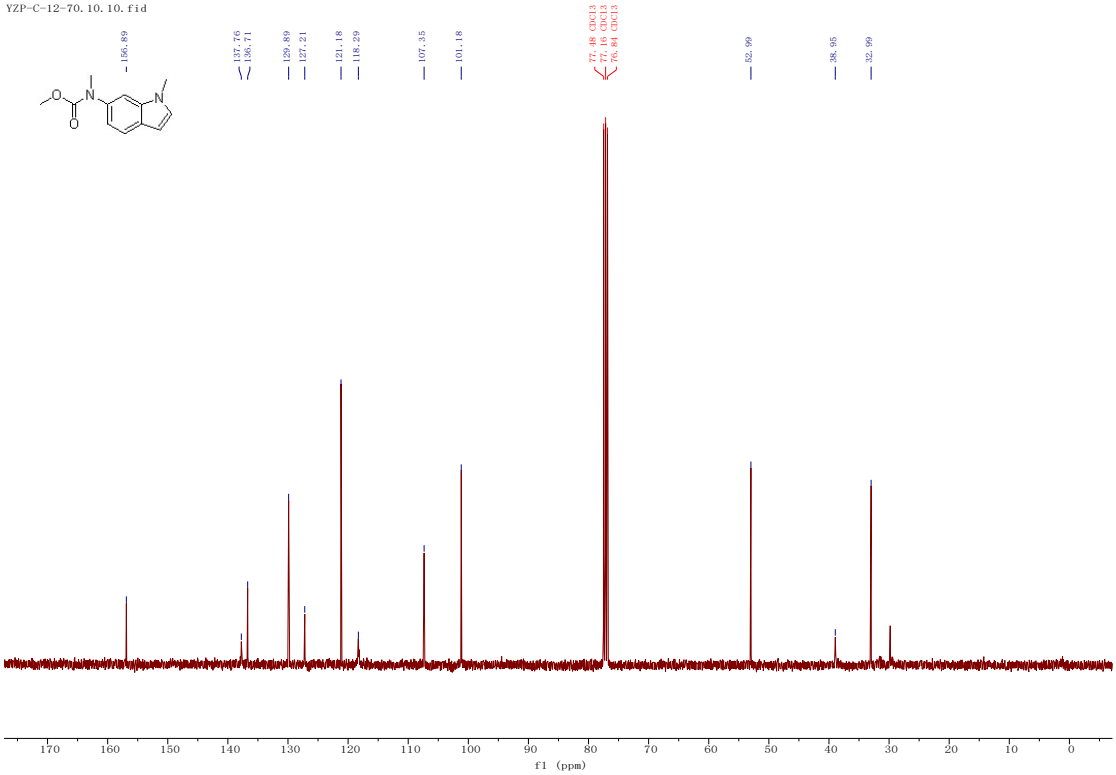

Figure S83 HRMS spectrum for compound 4q and 4r

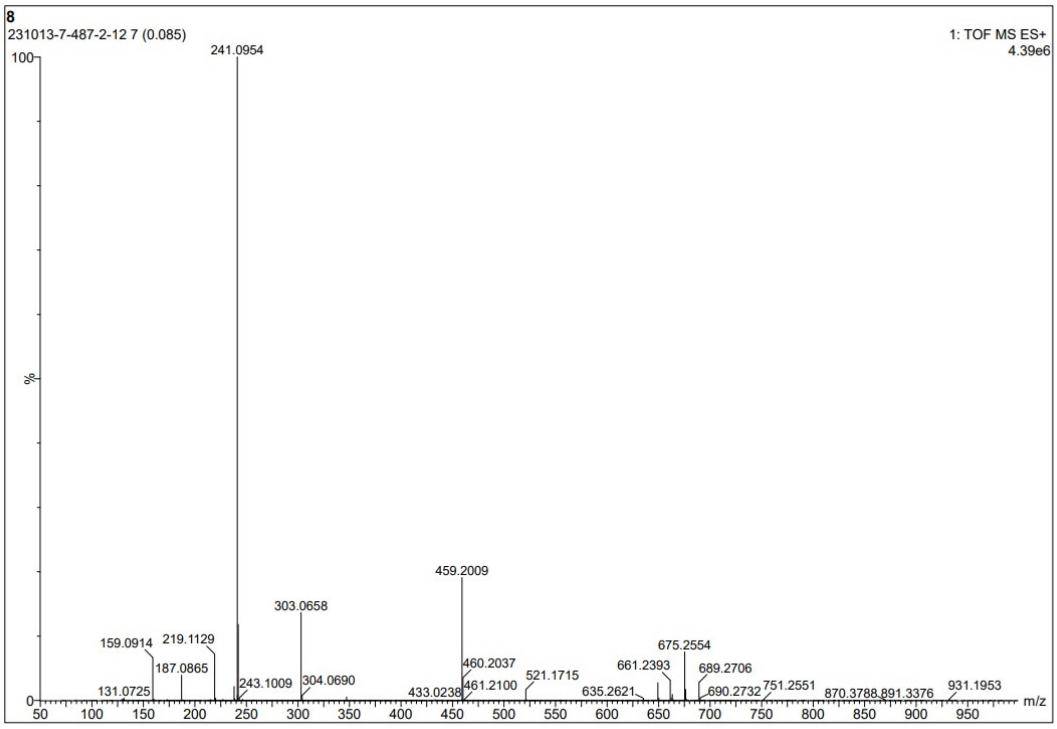

Figure S84 ^{1}H NMR spectrum for compound 4r

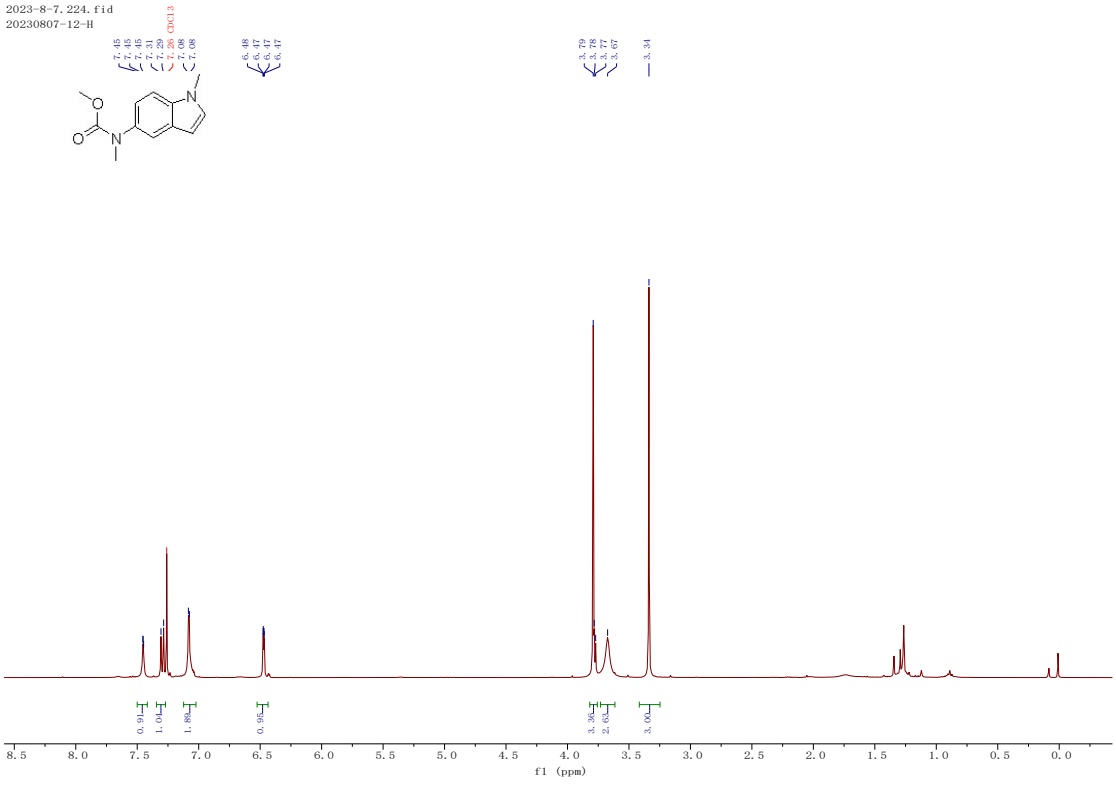

Figure S85 ^{13}C NMR spectrum for compound 4r

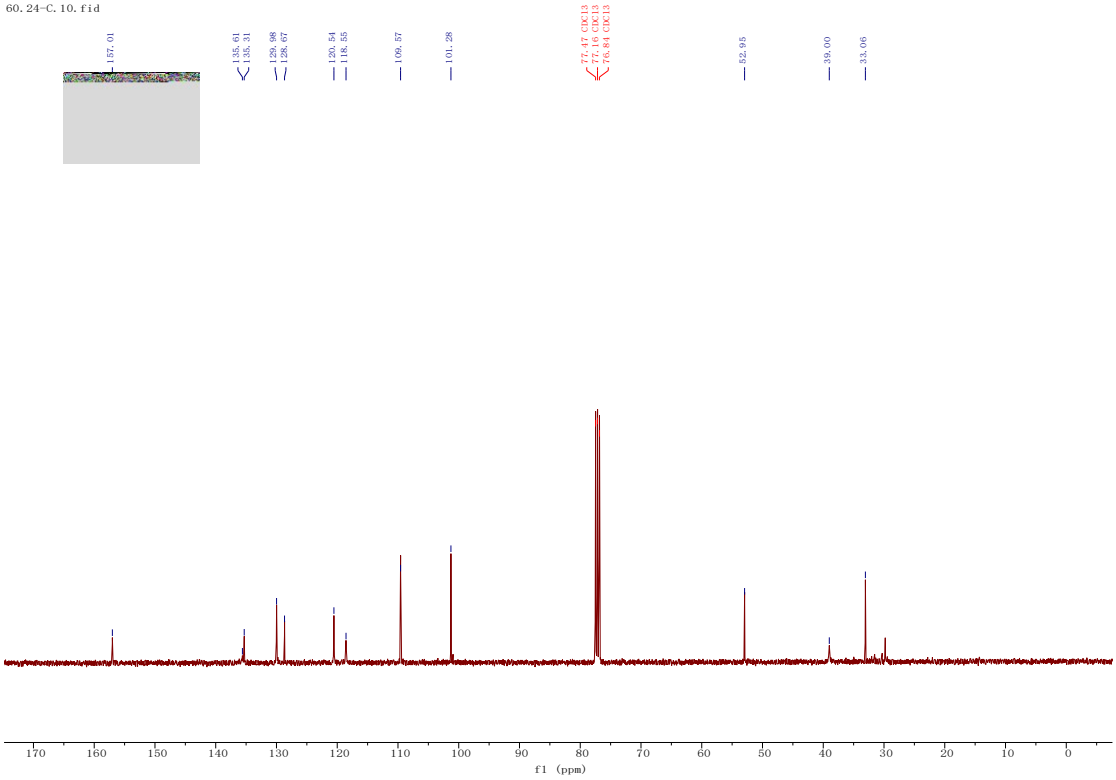

Figure S86 ^{1}H NMR spectrum for compound 4 r'

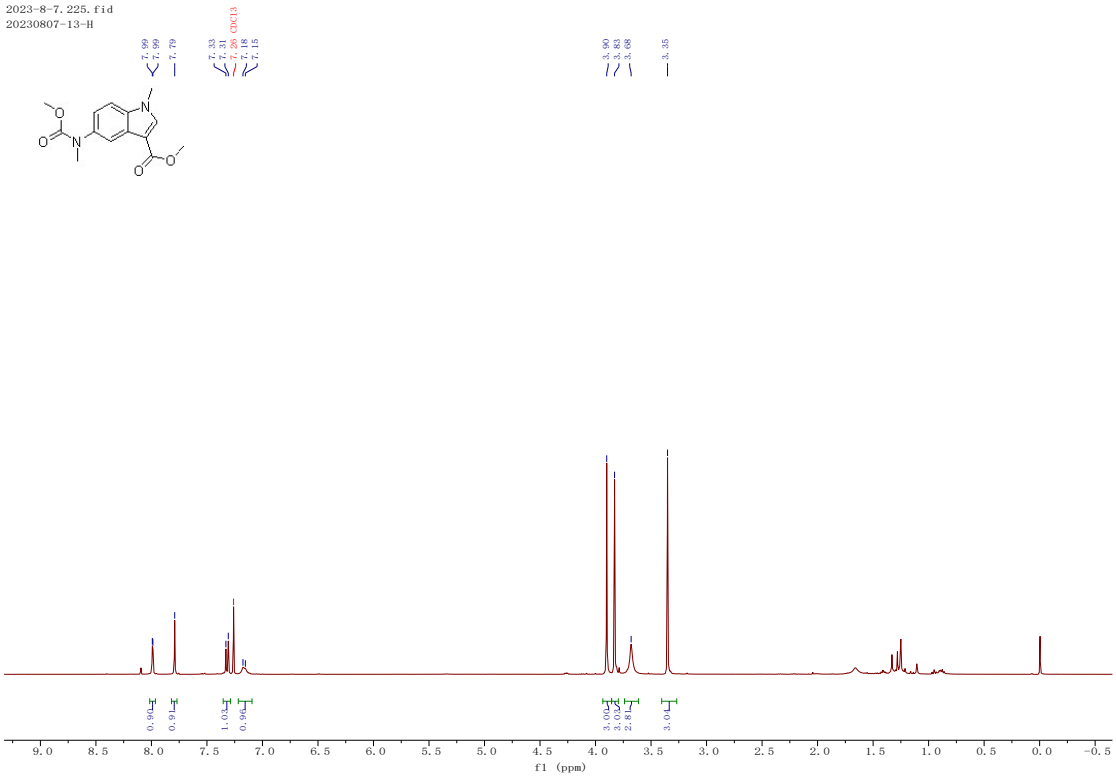

Figure S87 ^{13}C NMR spectrum for compound 4 r'

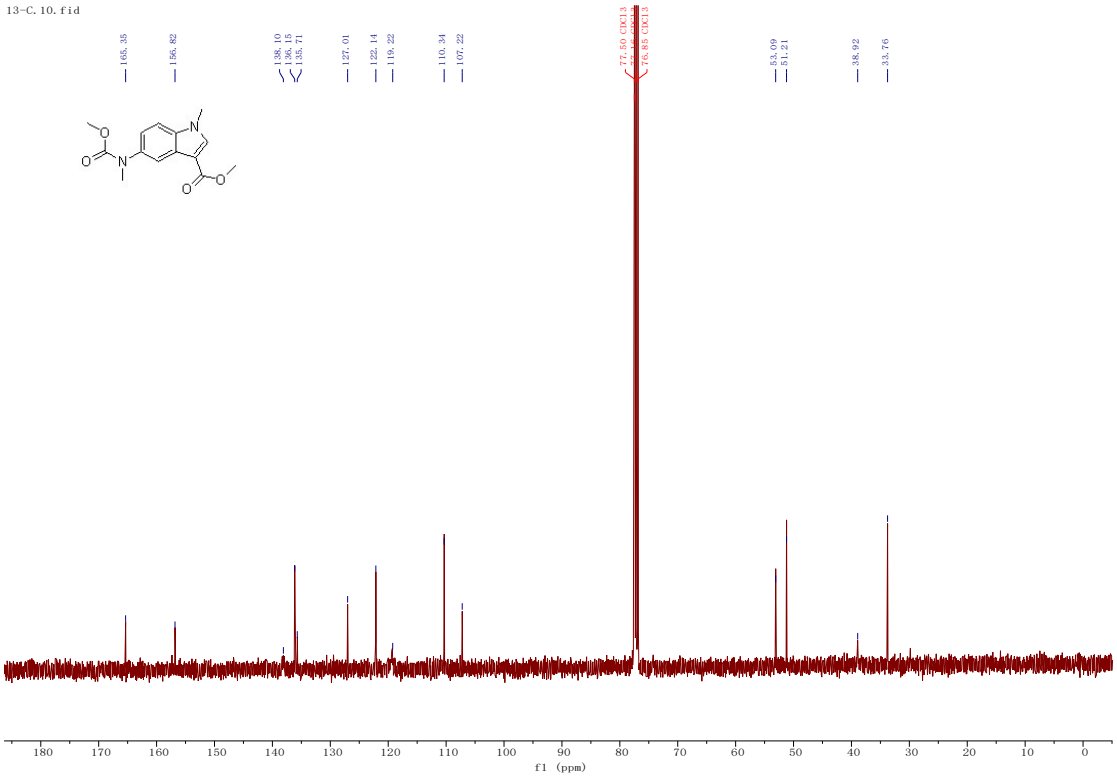

Figure S88 HRMS spectrum for compound 4 r'

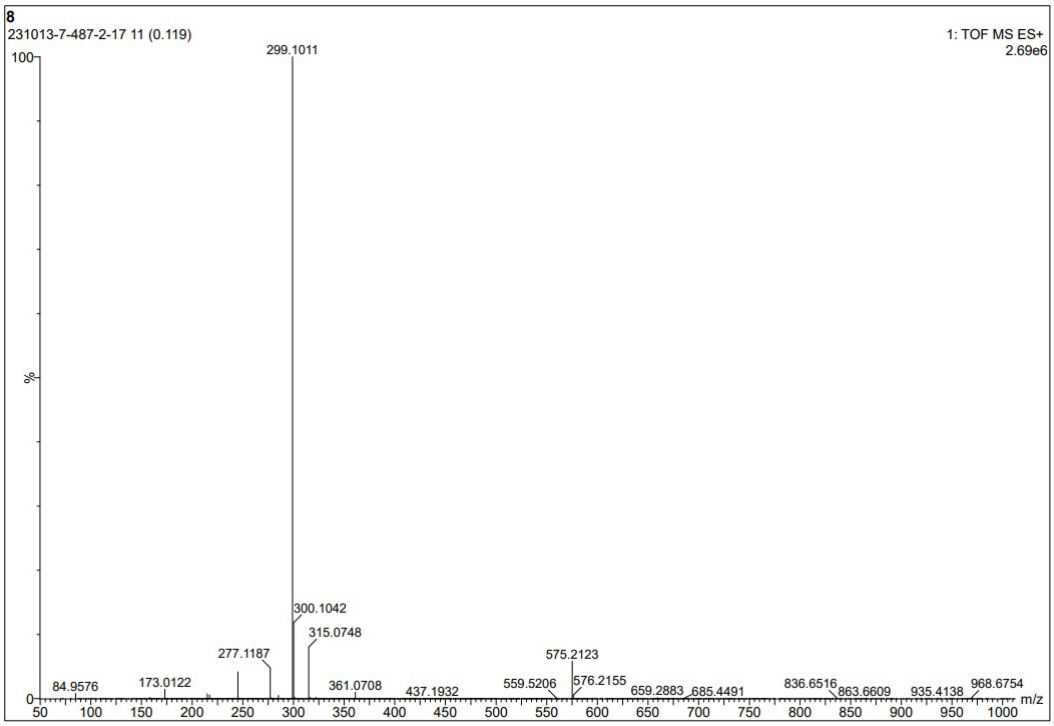

Figure S89 ^{1}H NMR spectrum for compound 6a

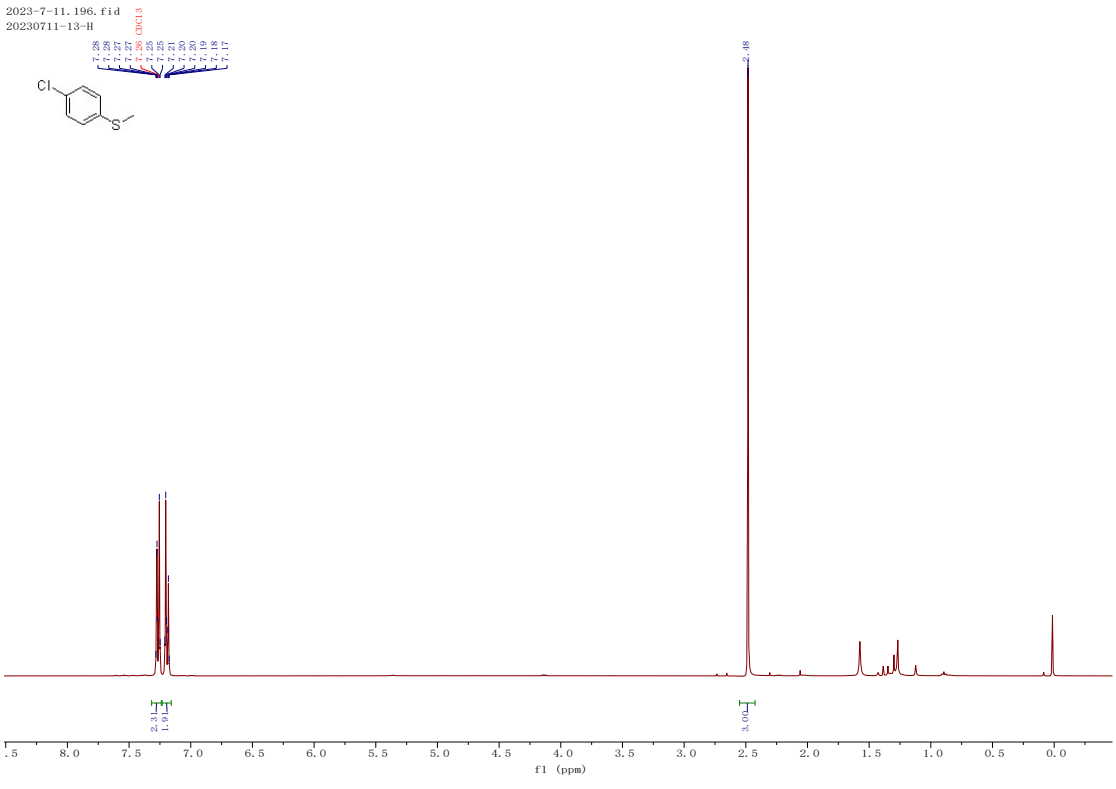

Figure S90 ^{13}C NMR spectrum for compound 6a