

*Supporting Information*

## **Rhodium(I)-catalyzed *N*-arylation of arylazocarboxylates: facile access to unsymmetrical *N,N*-diarylhydrazides**

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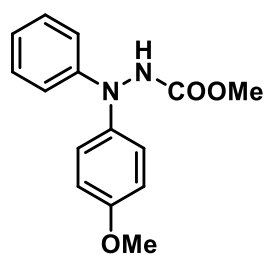
## I. General Information

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or argon. Solvents were dried and distilled by standard procedures. NMR spectra were recorded on Bruker Advance III 400 (400 MHz for  $^1\text{H}$ ; 100 MHz for  $^{13}\text{C}$ ; 376 MHz for  $^{19}\text{F}$ ) or Bruker Advance III 600 (600 MHz for  $^1\text{H}$ ; 150 MHz for  $^{13}\text{C}$ , 564 MHz for  $^{19}\text{F}$ ) in  $\text{CDCl}_3$  with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in ppm and coupling constants are given in Hz. Data for  $^1\text{H}$  NMR are recorded as follows: chemical shift ( $\delta$ , ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. Data for  $^{13}\text{C}$  NMR are reported in terms of chemical shift ( $\delta$ , ppm). High-resolution mass spectra (HRMS) were measured in ESI mode.

## II. General Procedure for the Synthesis of *N,N*-diarylhydrazides and Characterization Data

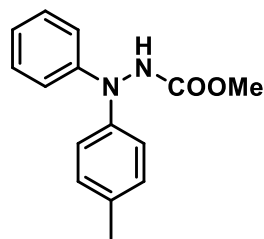
Under an argon atmosphere, a solution of  $[\text{Rh}(\text{cod})\text{Cl}]_2$  (0.5 mg, 0.001 mmol, 0.5 mol%), arylazocarboxylate (0.2 mmol), arylboronic acid (0.4 mmol),  $\text{K}_2\text{CO}_3$  (55.3 mg, 0.4 mmol) in 2 mL of toluene was stirred at room temperature for 12 h. The reaction was quenched with sat. aq. NaCl. Then the mixture was extracted with EtOAc (10 mL x 3). The combined organic layer was washed with brine (30 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was purified by flash chromatography to afford the corresponding *N,N*-diarylhydrazide.

### Methyl 2,2-diphenylhydrazine-1-carboxylate (3a)



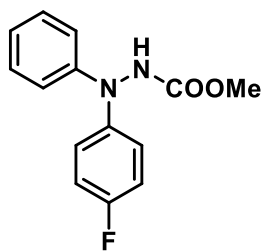
White solid, 64 mg, 99% yield.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.32–7.18 (m, 4H), 7.00 (s, 1H), 6.93–6.85 (m, 5H), 3.80 (s, 3H), 3.74 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  157.4, 156.5, 147.5, 139.0, 129.1, 125.6, 120.9, 115.5, 114.8, 55.6, 52.9. HRMS (ESI) for  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_3$   $[\text{M}+\text{H}]^+$ : calcd. 273.1234, found 273.1233.

### Methyl 2-phenyl-2-(*p*-tolyl)hydrazine-1-carboxylate (3b)



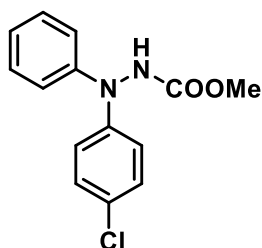
White solid, 48.0 mg, 94% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.31–7.21 (m, 2H), 7.16–7.07 (m, 4H), 7.07–7.03 (d,  $J = 8.0$  Hz, 2H), 7.00–6.93 (m, 1H), 6.67 (br, 1H), 3.75 (s, 3H), 2.32 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  156.5, 146.8, 143.6, 133.7, 130.0, 129.1, 122.0, 121.5, 117.8, 52.8, 20.8. HRMS (ESI) for  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$ : calcd. 257.1285, found 257.1279.

**Methyl 2-(4-fluorophenyl)-2-phenylhydrazine-1-carboxylate (3c)**



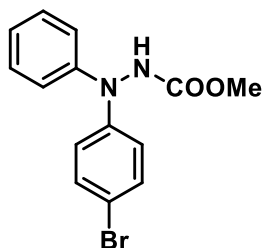
White solid, 52.0 mg, 99% yield.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.26–7.24 (m, 2H), 7.21–7.12 (m, 2H), 7.08 (s, 1H), 7.05–6.93 (m, 5H), 3.74 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  158.2 (d,  $J_{\text{C-F}} = 170.4$  Hz), 156.5, 146.7, 142.2, 129.3, 123.1, 122.4, 117.6, 116.1 (d,  $J_{\text{C-F}} = 22.7$  Hz), 53.0.  $^{19}\text{F}$  NMR (377 MHz, Chloroform-*d*),  $\delta$  -118.61. HRMS (ESI) for  $\text{C}_{14}\text{H}_{13}\text{FN}_2\text{O}_2$   $[\text{M}+\text{H}]^+$ : calcd. 261.1034, found 261.1030.

**Methyl 2-(4-chlorophenyl)-2-phenylhydrazine-1-carboxylate (3d)**



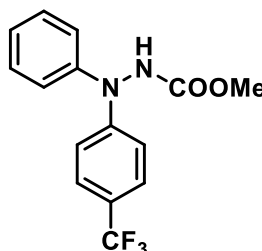
White solid, 52.5 mg, 94% yield.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.34–7.28 (m, 2H), 7.24 (d,  $J = 8.3$  Hz, 2H), 7.18–7.10 (m, 2H), 7.10–7.03 (m, 3H), 7.00 (s, 1H), 3.77 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  156.4, 145.7, 144.9, 129.5, 129.3, 127.9, 123.8, 120.4, 120.1, 53.1. HRMS (ESI) for  $\text{C}_{14}\text{H}_{13}\text{ClN}_2\text{O}_2$   $[\text{M}+\text{H}]^+$ : calcd. 277.0738, found 277.0735.

**Methyl 2-(4-bromophenyl)-2-phenylhydrazine-1-carboxylate (3e)**



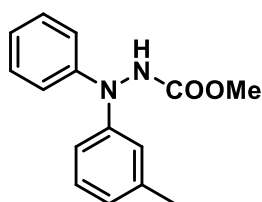
Yellow solid, 64.1 mg, 99% yield.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.37 (d,  $J = 8.4$  Hz, 2H), 7.34–7.29 (m, 2H), 7.19–7.12 (m, 2H), 7.11–7.06 (m, 1H), 7.04–6.93 (m, 3H), 3.77 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  156.3, 145.4, 132.1, 129.4, 123.9, 120.4, 120.3, 120.1, 115.0, 53.0. HRMS (ESI) for  $\text{C}_{14}\text{H}_{13}\text{BrN}_2\text{O}_2$   $[\text{M}+\text{H}]^+$ : calcd. 321.0233, found 321.0229.

**Methyl 2,2-diphenylhydrazine-1-carboxylate (3f)**



White solid, 52.1 mg, 86% yield.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.47 (d,  $J = 8.3$  Hz, 2H), 7.41–7.35 (m, 2H), 7.34–7.26 (m, 2H), 7.24–7.18 (m, 1H), 7.09 (br, 1H), 7.05 (d,  $J = 8.3$  Hz, 2H), 3.78 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  156.3, 149.5, 144.6, 129.8, 126.5 (q,  $J_{\text{C-F}} = 4.2$  Hz), 124.6 (q,  $J_{\text{C-F}} = 269.1$  Hz), 125.5, 123.5, 122.9, 115.5, 53.2.  $^{19}\text{F}$  NMR (377 MHz, Chloroform-*d*),  $\delta$  -61.65. HRMS (ESI) for  $\text{C}_{15}\text{H}_{13}\text{F}_3\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$ : calcd. 311.1002, found 311.0997.

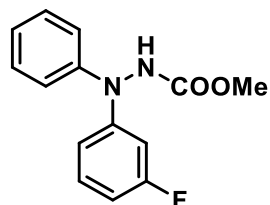
**Methyl 2-phenyl-2-(*m*-tolyl)hydrazine-1-carboxylate (3g)**



White solid, 44.4 mg, 87% yield.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.33–7.27 (m, 2H), 7.21–7.16 (m, 1H), 7.16–7.10 (m, 2H), 7.07–6.91 (m, 3H), 6.90–6.85 (m, 1H), 3.77 (s, 3H), 2.32 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,

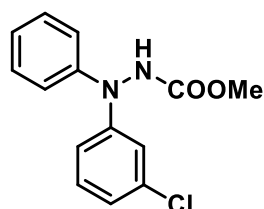
Chloroform-*d*)  $\delta$  156.5, 146.4, 139.2, 129.2, 129.1, 124.2, 122.9, 120.5, 119.4, 117.0, 52.9, 21.6.  
HRMS (ESI) for  $C_{15}H_{16}N_2O_2$   $[M+H]^+$ : calcd. 257.1285, found 257.1280.

#### Methyl 2-(3-fluorophenyl)-2-phenylhydrazine-1-carboxylate (3h)



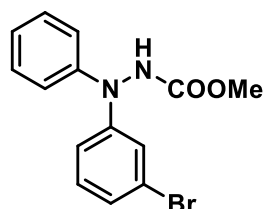
White solid, 48.0 mg, 94% yield.  $^1H$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.37–7.30 (m, 2H), 7.23 (s, 1H), 7.23–7.15 (m, 2H), 7.15–7.11 (m, 1H), 6.80–6.78 (m, 1H), 6.78–6.73 (m, 1H), 6.69–6.62 (m, 1H), 3.75 (s, 3H).  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  163.6( $J_{C-F}$  = 242.9 Hz), 156.4, 148.4, 145.2, 130.3(d,  $J_{C-F}$  = 9.6 Hz), 129.5, 124.9, 122.1, 112.7 (d,  $J_{C-F}$  = 3.2 Hz), 108.62(d,  $J_{C-F}$  = 21.3 Hz), 104.6( $J_{C-F}$  = 25.9 Hz), 53.1.  $^{19}F$  NMR (377 MHz, Chloroform-*d*),  $\delta$  -111.99. HRMS (ESI) for  $C_{14}H_{13}FN_2O_2$   $[M+H]^+$ : calcd. 261.1034, found 261.1031.

#### Methyl 2-(3-chlorophenyl)-2-phenylhydrazine-1-carboxylate (3i)



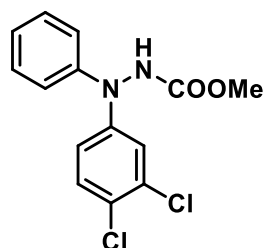
Yellow solid, 52.5 mg, 95% yield,  $^1H$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.38–7.31 (m, 2H), 7.23–7.15 (m, 3H), 7.15–7.11 (m, 1H), 7.06 (s, 1H), 7.02 (br, 1H), 6.98–6.89 (m, 2H), 3.77 (s, 3H).  $^{13}C$  NMR (150 MHz, Chloroform-*d*)  $\delta$  156.3, 147.8, 145.2, 135.0, 130.2, 129.6, 124.8, 122.1, 121.8, 117.6, 115.7, 53.1. HRMS (ESI) for  $C_{14}H_{13}ClN_2O_2$   $[M+H]^+$ : calcd. 277.0738, found 277.0735.

#### Methyl 2-(3-bromophenyl)-2-phenylhydrazine-1-carboxylate (3j)



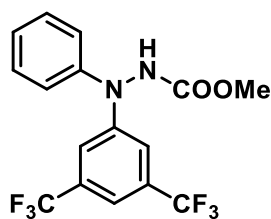
White solid, 64.3 mg, 99% yield.  $^1H$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.38–7.29 (m, 2H), 7.24–7.15 (m, 3H), 7.16–7.02 (m, 4H), 7.00–6.94 (m, 1H), 3.76 (s, 3H).  $^{13}C$  NMR (150 MHz, Chloroform-*d*)  $\delta$  147.8, 145.1, 130.4, 129.5, 125.0, 124.7, 123.0, 121.6, 121.1, 120.4, 116.2, 53.0. HRMS (ESI) for  $C_{14}H_{13}BrN_2O_2$   $[M+H]^+$ : calcd. 321.0233, found 321.0229.

#### Methyl 2-(3,4-dichlorophenyl)-2-phenylhydrazine-1-carboxylate (3k)



White solid, 58.0 mg, 94% yield.  $^1H$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.36–7.30 (m, 2H), 7.29–7.23 (m, 1H), 7.23–7.10 (m, 5H), 6.87 (dd,  $J$  = 8.8, 2.7 Hz, 1H), 3.75 (s, 3H).  $^{13}C$  NMR (150 MHz, Chloroform-*d*)  $\delta$  146.2, 144.9, 133.0, 130.7, 129.7, 125.1, 125.0, 121.9, 119.0, 116.9, 77.4, 53.2. HRMS (ESI) for  $C_{14}H_{12}Cl_2N_2O_2$   $[M+H]^+$ : calcd. 309.0203, found 309.0202.

**Methyl 2-(3,5-bis(trifluoromethyl)phenyl)-2-phenylhydrazine-1-carboxylate (3l)**

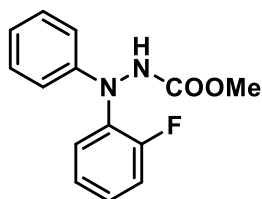


White solid, 68.3 mg, 90% yield.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$

7.33–7.45 (m, 5H), 7.33–7.24 (m, 3H), 7.16 (s, 1H), 3.78 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  156.1, 148.3, 144.0, 132.6 (q,  $J_{\text{C-F}} = 32.9$  Hz), 130.2, 126.9, 123.9, 123.4 (q,  $J_{\text{C-F}} = 271.4$  Hz), 115.2, 114.3, 53.4.  $^{19}\text{F}$  NMR (377 MHz, Chloroform-*d*)  $\delta$  -63.06. HRMS (ESI) for  $\text{C}_{16}\text{H}_{12}\text{F}_6\text{N}_2\text{O}_2$   $[\text{M-H}]^+$ :

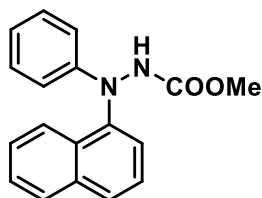
calcd. 377.0730, found 377.0726.

**Methyl 2-(2-fluorophenyl)-2-phenylhydrazine-1-carboxylate (3m)**



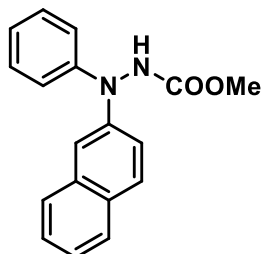
Yellowish white solid, 42mg, 81% yield,  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.55 (s, 1H), 7.26–7.21 (m, 3H), 7.19–7.13 (m, 2H), 7.09 (s, 1H), 6.93–6.88 (m, 1H), 6.85–6.9 (m, 2H), 3.75 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  158.3 (d,  $J_{\text{C-F}} = 248.1$  Hz), 156.5, 147.1, 132.4 (d,  $J_{\text{C-F}} = 10.4$  Hz), 129.2, 128.5, 128.2, 124.9, 121.0, 117.1, 114.1, 53.0.  $^{19}\text{F}$  NMR (377 MHz, Chloroform-*d*)  $\delta$  -121.25. HRMS (ESI) for  $\text{C}_{14}\text{H}_{13}\text{FN}_2\text{O}_2$   $[\text{M+H}]^+$ : calcd. 261.1034, found 261.1030.

**Methyl 2-(naphthalen-1-yl)-2-phenylhydrazine-1-carboxylate (3n)**



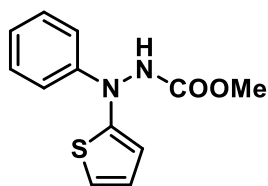
White solid, 52.6 mg, 90% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.06 (s, 1H), 7.91 (d,  $J = 8.0$  Hz, 1H), 7.85 (d,  $J = 8.2$  Hz, 1H), 7.64 (s, 1H), 7.55–7.45 (m, 3H), 7.23–7.14 (m, 2H), 7.07 (s, 1H), 6.91–6.84 (m, 1H), 6.72 (d,  $J = 8.0$  Hz, 2H), 3.75 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  156.6, 148.7, 141.8, 135.0, 130.6, 129.2, 128.5, 128.1, 126.9, 126.5, 126.3, 125.3, 123.8, 120.2, 113.8, 52.9. HRMS (ESI) for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$   $[\text{M+H}]^+$ : calcd. 293.1285, found 293.1280.

**Methyl 2-(naphthalen-2-yl)-2-phenylhydrazine-1-carboxylate (3o)**



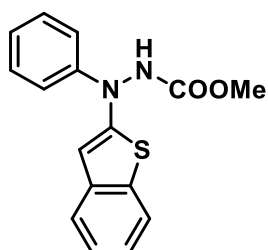
White solid, 54.0 mg, 93% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.80–7.73 (m, 2H), 7.71 (d,  $J = 8.2$  Hz, 1H), 7.52 (s, 1H), 7.47–7.40 (m, 1H), 7.40–7.29 (m, 4H), 7.22 (d,  $J = 8.0$  Hz, 2H), 7.12–7.04 (m, 2H), 3.79 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  156.5, 146.3, 143.9, 134.3, 129.4, 129.1, 127.7, 127.3, 126.6, 124.7, 123.5, 120.5, 119.9, 115.5, 114.8, 53.1. HRMS (ESI) for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$   $[\text{M+H}]^+$ : calcd. 293.1285, found 293.1287.

**Methyl 2-phenyl-2-(thiophen-2-yl)hydrazine-1-carboxylate (3p)**



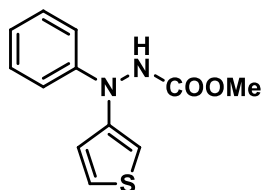
White solid, 46.1 mg, 93% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.25–7.20 (m, 2H), 7.15–7.11 (m, 1H), 7.05 (s, 1H), 7.00 – 6.90 (m, 5H), 3.78 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  156.1, 148.6, 147.7, 129.1, 125.7, 123.4, 123.2, 121.2, 114.2, 53.1. HRMS (ESI) for  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : calcd. 249.0692, found 249.0694.

**Methyl 2-(benzo[*b*]thiophen-2-yl)-2-phenylhydrazine-1-carboxylate (3q)**



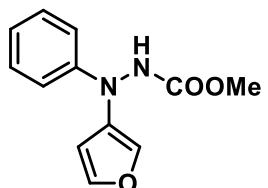
White solid, 61.3 mg, 80% yield.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.68 (d,  $J = 7.8$  Hz, 1H), 7.60 (d,  $J = 7.8$  Hz, 1H), 7.35–7.28 (m, 3H), 7.27–7.09 (m, 4H), 7.08–7.01 (m, 1H), 6.99–6.86 (m, 1H), 3.79 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  156.1, 150.1, 146.3, 138.9, 136.1, 129.4, 124.7, 123.9, 123.2, 123.0, 122.3, 117.3, 113.5, 53.3. HRMS (ESI) for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : calcd. 299.0849, found 299.0850.

**Methyl 2-phenyl-2-(thiophen-3-yl)hydrazine-1-carboxylate (3r)**



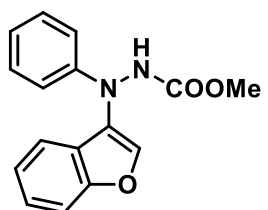
White solid, 47.1 mg, 95% yield,  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.29–7.23 (m, 3H), 7.06 (d,  $J = 8.4$  Hz, 2H), 7.03–6.76 (m, 4H), 3.76 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  156.4, 147.2, 145.2, 129.2, 125.6, 123.2, 122.1, 116.7, 112.2, 53.0. HRMS (ESI) for  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : calcd. 249.0692, found 249.0694.

**Methyl 2-(furan-3-yl)-2-phenylhydrazine-1-carboxylate (3s)**



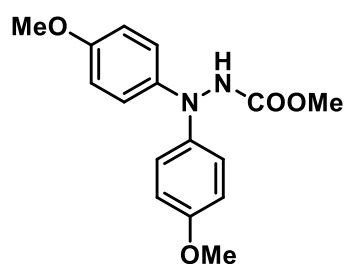
Brown solid, 43.2 mg, 93% yield,  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.50 (s, 1H), 7.37 (s, 1H), 7.29–7.21 (m, 2H), 6.99 (d,  $J = 8.4$  Hz, 2H), 6.89–6.96 (m, 2H), 6.43 (s, 1H), 3.76 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  156.3, 147.3, 143.0, 135.8, 133.3, 129.2, 121.2, 114.9, 108.0, 52.9. HRMS (ESI) for  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_3$   $[\text{M}+\text{H}]^+$ : calcd. 233.0921, found 233.0923.

**Methyl 2-(benzofuran-3-yl)-2-phenylhydrazine-1-carboxylate (3t)**



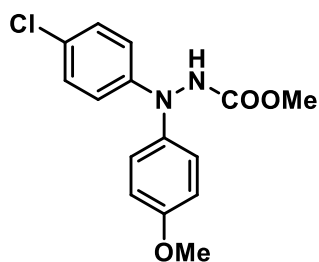
Yellow solid, 48.1 mg, 85% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.50–7.46 (m, 1H), 7.41–7.36 (m, 1H), 7.35–7.28 (m, 2H), 7.25–7.20 (m, 2H), 7.17–7.12 (m, 3H), 7.08–7.02 (m, 1H), 6.38 (s, 1H), 3.80 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  156.2, 153.9, 151.6, 144.9, 129.3, 128.9, 123.5, 123.2, 123.1, 120.4, 116.6, 111.0, 93.7, 53.2. HRMS (ESI) for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_3$   $[\text{M}+\text{H}]^+$ : calcd. 283.1077, found 283.1079.

**Methyl 2,2-bis(4-methoxyphenyl)hydrazine-1-carboxylate (4a)**



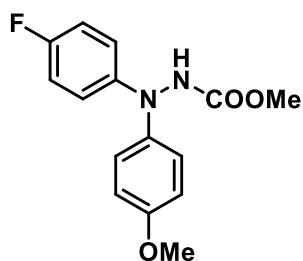
White solid, 61.0 mg, 99% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.03 (d,  $J$  = 8.0 Hz, 4H), 6.87–6.78 (m, 5H), 3.78 (s, 6H), 3.75 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  155.7, 140.7, 121.1, 120.9, 114.6, 55.7, 52.8. HRMS (ESI) for  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_4$   $[\text{M}+\text{H}]^+$ : calcd. 303.1339, found 303.1335.

**Methyl 2-(3-chlorophenyl)-2-(4-methoxyphenyl)hydrazine-1-carboxylate (4b)**



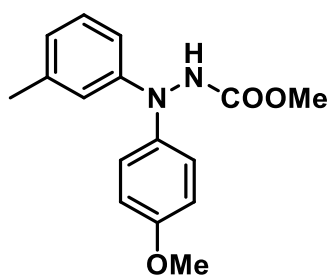
White solid, 57.4 mg, 94% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.25–7.18 (m, 2H), 7.15 (d,  $J$  = 8.8 Hz, 2H), 7.01 (s, 1H), 6.91–6.85 (m, 2H), 6.84–6.78 (m, 2H), 3.81 (s, 3H), 3.74 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  157.7, 146.3, 138.5, 129.0, 126.0, 125.6, 116.5, 114.9, 55.7, 53.0. HRMS (ESI) for  $\text{C}_{15}\text{H}_{15}\text{ClN}_2\text{O}_3$   $[\text{M}+\text{H}]^+$ : calcd. 307.0844, found 307.0841.

**Methyl 2-(4-fluorophenyl)-2-(4-methoxyphenyl)hydrazine-1-carboxylate (4c)**



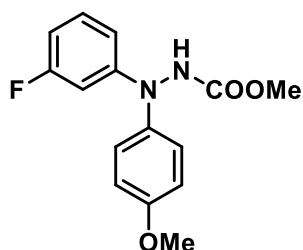
White solid, 58.5 mg, 99% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.20–7.09 (m, 2H), 6.94–6.85 (m, 7H), 3.80 (s, 3H), 3.75 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  158.2 (d,  $J_{\text{C-F}}$  = 238.7 Hz), 156.9, 156.5, 143.7, 139.5, 124.0, 118.4 (d,  $J_{\text{C-F}}$  = 7.9 Hz), 115.7 (d,  $J_{\text{C-F}}$  = 22.5 Hz), 114.8, 55.7, 52.9.  $^{19}\text{F}$  NMR (377 MHz, Chloroform-*d*)  $\delta$  -122.80. HRMS (ESI) for  $\text{C}_{15}\text{H}_{15}\text{FN}_2\text{O}_3$   $[\text{M}+\text{H}]^+$ : calcd. 291.1139, found 291.1136.

**Methyl 2-(4-methoxyphenyl)-2-(*m*-tolyl)hydrazine-1-carboxylate (4d)**



White solid, 57.0 mg, 99% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.25–7.15 (m, 2H), 7.14–7.01 (m, 1H), 6.93–6.85 (m, 3H), 6.76–6.67 (m, 3H), 3.81 (s, 3H), 3.76 (s, 3H), 2.28 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  157.2, 156.6, 147.5, 139.1, 139.0, 128.9, 125.4, 121.9, 116.3, 114.7, 112.9, 55.6, 52.8, 21.7. HRMS (ESI) for  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_3$   $[\text{M}+\text{H}]^+$ : calcd. 287.1390, found 287.1392.

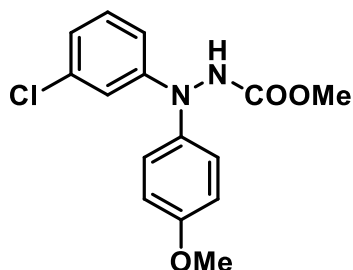
**Methyl 2-(3-fluorophenyl)-2-(4-methoxyphenyl)hydrazine-1-carboxylate (4e)**



White solid, 57.1 mg, 97% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.34–7.26 (m, 2H), 7.17–7.09 (m, 1H), 6.96–6.87 (m, 3H), 6.64–6.50 (m, 3H), 3.82 (s, 3H), 3.76 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  163.7 (d,  $J_{\text{C-F}}$  = 243.5 Hz), 158.1, 156.4, 149.7 (d,  $J_{\text{C-F}}$  = 8.0 Hz), 138.0,

130.2 (d,  $J_{C-F} = 10.2$  Hz), 127.0, 114.9, 109.9, 106.8 (d,  $J_{C-F} = 21.4$  Hz), 101.7 (d,  $J_{C-F} = 26.2$  Hz), 55.6, 53.0.  $^{19}\text{F}$  NMR (377 MHz, Chloroform-*d*),  $\delta$  -112.35. HRMS (ESI) for  $\text{C}_{15}\text{H}_{15}\text{FN}_2\text{O}_3$   $[\text{M}+\text{H}]^+$ : calcd. 291.1139, found 291.1142.

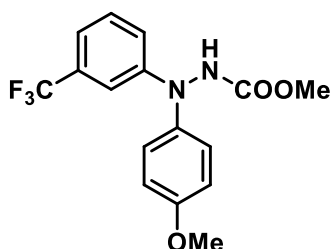
**Methyl 2-(3-fluorophenyl)-2-(4-methoxyphenyl)hydrazine-1-carboxylate (4f)**



found 307.0847.

White solid, 57.6 mg, 92% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.30–7.26 (m, 2H), 7.15–7.10 (m, 1H), 6.96–6.88 (m, 3H), 6.87–6.80 (m, 2H), 6.72 (d,  $J = 7.6$  Hz, 1H), 3.82 (s, 3H), 3.76 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  158.2, 156.3, 149.0, 138.0, 135.0, 130.1, 127.0, 120.4, 115.0, 114.6, 112.7, 55.7, 53.1. HRMS (ESI) for  $\text{C}_{15}\text{H}_{15}\text{ClN}_2\text{O}_3$   $[\text{M}+\text{H}]^+$ : calcd. 307.0844,

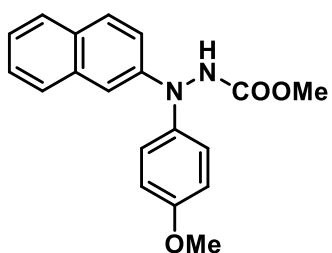
**Methyl 2-(4-methoxyphenyl)-2-(3-(trifluoromethyl)phenyl)hydrazine-1-carboxylate (4g)**



calcd. 341.1108, found 341.1112.

White solid, 64.6 mg, 95% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.34–7.26 (m, 3H), 7.14–7.06 (m, 2H), 7.02–6.90 (m, 4H), 3.83 (s, 3H), 3.77 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  158.3, 156.4, 148.3, 137.8, 131.5 (q,  $J_{C-F} = 32.2$  Hz), 129.6, 127.0, 124.3 (q,  $J_{C-F} = 272.1$  Hz), 117.5, 116.9, 115.1, 110.9, 55.6, 53.1.  $^{19}\text{F}$  NMR (377 MHz, Chloroform-*d*),  $\delta$  -65.57. HRMS (ESI) for  $\text{C}_{16}\text{H}_{15}\text{F}_3\text{N}_2\text{O}_3$   $[\text{M}+\text{H}]^+$ :

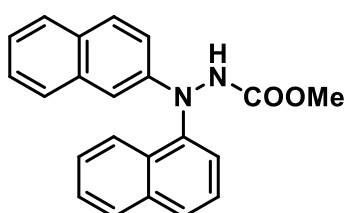
**Methyl 2-(4-methoxyphenyl)-2-(naphthalen-2-yl)hydrazine-1-carboxylate (4h)**



114.8, 110.6, 55.7 53.0. HRMS (ESI) for  $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_3$   $[\text{M}+\text{H}]^+$ : calcd. 323.1390, found 323.1385.

White solid, 64.0 mg, 99% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.72 (d,  $J = 8.2$  Hz, 1H), 7.68 (d,  $J = 9.0$  Hz, 1H), 7.65 (d,  $J = 8.2$  Hz, 1H), 7.44–7.35 (m, 1H), 7.34–7.27 (m, 3H), 7.26–7.21 (m, 1H), 7.18–7.12 (m, 1H), 7.04 (s, 1H), 6.95–6.85 (m, 2H), 3.83 (s, 3H), 3.78 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  157.5, 145.3, 139.2, 134.4, 129.2, 128.9, 127.7, 127.0, 126.6, 125.6, 125.0, 123.8, 117.9,

**Methyl 2-(naphthalen-1-yl)-2-(naphthalen-2-yl)hydrazine-1-carboxylate (4i)**

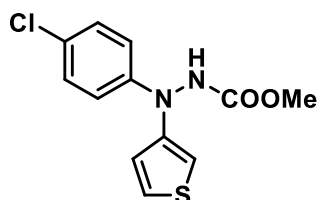


White solid, 64.4 mg, 94% yield.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  8.09 (s, 1H), 7.93 (d,  $J = 7.8$  Hz, 1H), 7.88 (d,  $J = 8.4$  Hz, 1H), 7.70 (d,  $J = 8.2$  Hz, 2H), 7.63 (d,  $J = 9.0$  Hz, 1H), 7.60 (d,  $J = 8.2$  Hz, 1H), 7.56–7.49 (m, 2H), 7.46–7.40 (m, 1H), 7.39–7.33 (m, 1H),



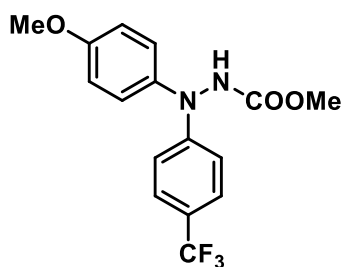
7.29–7.25 (m, 1H), 7.17 (s, 1H), 7.11 (s, 1H), 6.96 (s, 1H), 3.78 (s, 3H). <sup>13</sup>C NMR (150 MHz, Chloroform-*d*) δ 146.5, 141.9, 135.1, 134.5, 129.2, 128.9, 128.6, 128.3, 127.7, 127.0, 126.9, 126.6, 126.3, 125.4, 123.7, 123.6, 116.6, 108.5, 53.0. HRMS (ESI) for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: calcd. 343.1441, found 343.1444.

**Methyl 2-(4-chlorophenyl)-2-(thiophen-3-yl)hydrazine-1-carboxylate (4j)**



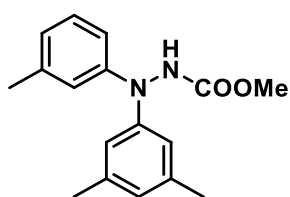
White solid, 57.9 mg, 99% yield. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.29–7.26 (m, 1H), 7.20 (d, *J* = 3.0 Hz, 2H), 7.05 (s, 1H), 6.99–6.92 (m, 3H), 6.91–6.80 (m, 1H), 3.76 (s, 3H). <sup>13</sup>C NMR (150 MHz, Chloroform-*d*) δ 156.2, 145.9, 144.6, 129.1, 126.8, 125.9, 123.3, 117.6, 113.3, 53.1. HRMS (ESI) for C<sub>12</sub>H<sub>11</sub>ClN<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup>: calcd. 283.0303, found 283.0305.

**Methyl 2-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)hydrazine-1-carboxylate (4k)**



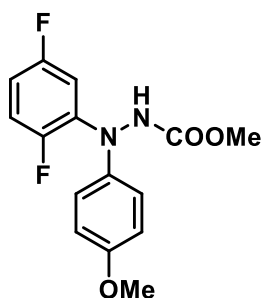
White solid, 76.2 mg, 99% yield. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.8 Hz, 2H), 7.37–7.27 (m, 2H), 7.03 (s, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3.76 (s, 3H). <sup>13</sup>C NMR (150 MHz, Chloroform-*d*) δ 158.6, 156.3, 150.5, 137.4, 127.7, 126.5 (q, *J*<sub>C-F</sub> = 3.5 Hz), 124.7 (q, *J*<sub>C-F</sub> = 271.2 Hz), 121.8 (q, *J*<sub>C-F</sub> = 30.7 Hz), 115.1, 113.4, 55.7, 53.1. <sup>19</sup>F NMR (377 MHz, Chloroform-*d*), δ -70.57. HRMS (ESI) for C<sub>16</sub>H<sub>15</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup>: calcd. 341.1108, found 341.1111.

**Methyl 2-(3,5-dimethylphenyl)-2-(m-tolyl)hydrazine-1-carboxylate (4l)**



White solid, 51.7 mg, 91% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.21–7.12 (m, 1H), 7.01–6.80 (m, 4H), 6.80–6.71 (m, 2H), 6.69 (s, 1H), 3.77 (s, 3H), 2.31 (s, 3H), 2.27 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.5, 146.5, 146.3, 139.1, 129.1, 125.1, 123.9, 120.1, 117.7, 117.2, 116.6, 52.9, 21.7, 21.5. HRMS (ESI) for C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: calcd. 258.1598, found 285.1599.

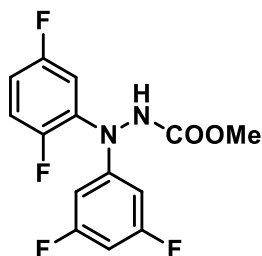
**Methyl 2-(2,5-difluorophenyl)-2-(4-methoxyphenyl)hydrazine-1-carboxylate (4m)**



White solid, 44.4 mg, 72% yield. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.14 (s, 1H), 7.03 (s, 2H), 6.97–6.87 (m, 2H), 6.85–6.81 (m, 2H), 6.78 (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H). <sup>13</sup>C NMR (150 MHz, Chloroform-*d*) δ 158.8 (d, *J*<sub>C-F</sub> = 243.5 Hz), 156.5, 155.8, 152.3 (d, *J*<sub>C-F</sub> = 245.1 Hz), 139.9, 135.0, 119.3, 118.2, 117.5, 114.6, 111.8 (d, *J*<sub>C-F</sub> = 25.8 Hz), 55.7, 53.1. <sup>19</sup>F NMR

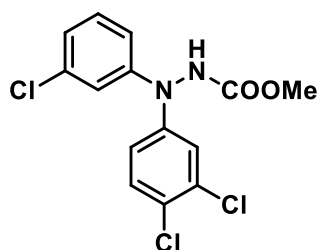
(377 MHz, Chloroform-*d*),  $\delta$  -117.07, -127.12. HRMS (ESI) for  $C_{15}H_{14}F_2N_2O_3$   $[M+H]^+$ : calcd. 309.1045, found 309.1048.

**Methyl 2-(2,5-difluorophenyl)-2-(3,5-difluorophenyl)hydrazine-1-carboxylate (4n)**



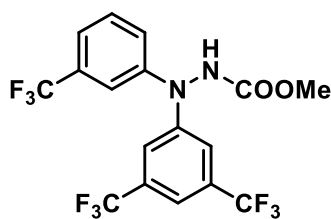
White solid, 52.8 mg, 84% yield.  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.31 (s, 1H), 7.19–1.08 (m, 2H), 7.06–6.98 (m, 1H), 6.41–6.36 (m, 1H), 6.36–6.30 (m, 2H), 3.78 (s, 3H).  $^{13}C$  NMR (100 MHz, Chloroform-*d*)  $\delta$  164.0 (dd,  $J_{C-F}$  = 244.7, 15.3 Hz), 158.6 (dd,  $J_{C-F}$  = 244.1, 2.0 Hz), 156.06, 154.35 (dd,  $J_{C-F}$  = 249.7, 3.2 Hz), 149.17 (t,  $J_{C-F}$  = 12.5 Hz), 131.8 (dd,  $J_{C-F}$  = 13.1, 10.1 Hz), 117.9 (dd,  $J_{C-F}$  = 20.1, 7.1 Hz), 116.1 (dd,  $J_{C-F}$  = 18.8, 7.0 Hz), 115.83 (dd,  $J_{C-F}$  = 24.0, 8.3 Hz), 97.2 (dd,  $J_{C-F}$  = 20.5, 8.3 Hz), 96.4 (t,  $J_{C-F}$  = 26.1 Hz), 53.4.  $^{19}F$  NMR (377 MHz, Chloroform-*d*),  $\delta$  -108.86, -115.68, -126.39. HRMS (ESI) for  $C_{14}H_{10}F_4N_2O_2$   $[M+H]^+$ : calcd. 315.0751, found 315.0755.

**Methyl 2-(3-chlorophenyl)-2-(3,4-dichlorophenyl)hydrazine-1-carboxylate (4o)**



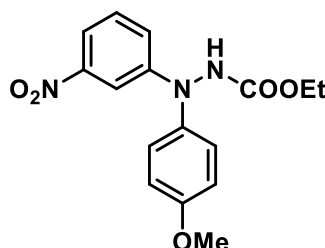
White solid, 66.1 mg, 96% yield.  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.34–7.28 (m, 3H), 7.17–7.10 (m, 3H), 7.02 (s, 1H), 6.92–6.85 (m, 1H), 3.77 (s, 3H).  $^{13}C$  NMR (150 MHz, Chloroform-*d*)  $\delta$  156.2, 145.7, 143.5, 133.2, 130.8, 130.1, 129.7, 125.7, 122.8, 122.3, 119.5, 117.4, 53.3. HRMS (ESI) for  $C_{14}H_{10}Cl_3N_2O_2$   $[M-H]^+$ : calcd. 342.9813, found 342.9808.

**Methyl 2-(3,5-bis(trifluoromethyl)phenyl)-2-(3-(trifluoromethyl)phenyl)hydrazine-1-carboxylate (4p)**



White solid, 82.1 mg, 92% yield.  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.56–7.47 (m, 4H), 7.47–7.30 (m, 3H), 7.19 (s, 1H), 3.82 (s, 3H).  $^{13}C$  NMR (100 MHz, Chloroform-*d*)  $\delta$  155.9, 147.3, 144.8, 133.2, 132.8, 130.6, 125.3, 123.7 (q,  $J_{C-F}$  = 270.9 Hz), 123.2 (q,  $J_{C-F}$  = 271.5 Hz), 122.5, 118.9, 117.0, 115.9 (h,  $J_{C-F}$  = 3.9 Hz), 53.7.  $^{19}F$  NMR (377 MHz, Chloroform-*d*),  $\delta$  -62.88, -63.11. HRMS (ESI) for  $C_{17}H_{10}F_9N_2O_2$   $[M-H]^+$ : calcd. 445.0604, found 445.0596.

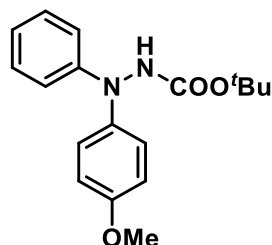
**Ethyl 2-(4-methoxyphenyl)-2-(3-nitrophenyl)hydrazine-1-carboxylate (4q)**



White solid, 52.4 mg, 82% yield.  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.72–7.63 (m, 2H), 7.38–7.28 (m, 3H), 7.16–7.06 (m, 1H), 7.01–6.88 (m, 3H), 4.22 (q,  $J$  = 7.2 Hz, 2H), 3.84 (s, 3H), 1.29 (s, 3H).  $^{13}C$  NMR (100 MHz, Chloroform-*d*)  $\delta$  158.7, 155.9, 149.3, 137.2,

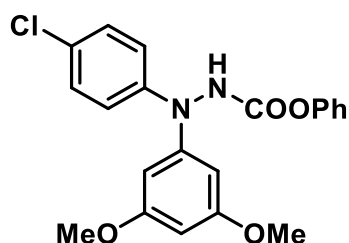
134.4, 129.8, 127.5, 119.6, 115.3 114.6, 108.4, 62.4, 55.7, 14.6. HRMS (ESI) for  $C_{16}H_{17}N_3O_5$   $[M+H]^+$ : calcd. 332.1241, found 332.1241.

***tert*-Butyl 2-(4-methoxyphenyl)-2-phenylhydrazine-1-carboxylate (4r)**



White solid, 58.6 mg, 93% yield.  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.25–7.16 (m, 4H), 6.94–6.83 (m, 5H), 6.80 (s, 1H), 3.80 (s, 3H), 1.48 (s, 9H).  $^{13}C$  NMR (100 MHz, Chloroform-*d*)  $\delta$  157.1, 155.1, 147.7, 139.3, 129.1, 125.2, 120.7, 115.5, 114.7, 81.2, 55.6, 28.4. HRMS (ESI) for  $C_{18}H_{22}N_2NaO_3$   $[M+Na]^+$ : calcd. 337.1523, found 337.1519.

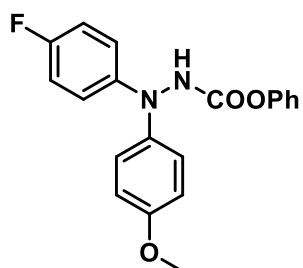
**Phenyl 2-(4-chlorophenyl)-2-(3,5-dimethoxyphenyl)hydrazine-1-carboxylate (4s)**



White solid, 64.6 mg, 81% yield.  $^1H$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.40–7.32 (m, 3H), 7.31–7.25 (m, 2H), 7.23–7.12 (m, 4H), 7.07–6.93 (m, 1H), 6.35–6.25 (m, 2H), 6.19 (s, 1H), 3.74 (s, 6H).  $^{13}C$  NMR (150 MHz, Chloroform-*d*)  $\delta$  161.6, 154.0, 150.7, 144.4, 129.6, 129.5, 125.9, 122.4, 121.9, 121.4, 97.8, 95.3, 55.5.

HRMS (ESI) for  $C_{21}H_{19}ClN_2O_4$   $[M+H]^+$ : calcd. 399.1106, found 399.1109.

**Phenyl 2-(4-fluorophenyl)-2-(4-methoxyphenyl)hydrazine-1-carboxylate (4t)**



White solid, 49.3 mg, 70% yield.  $^1H$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.38–7.31 (m, 2H), 7.28–7.24 (m, 1H), 7.24–7.18 (m, 3H), 7.18–7.13 (m, 1H), 7.04–6.93 (m, 5H), 6.92–6.86 (m, 2H), 3.81 (s, 3H).  $^{13}C$  NMR (150 MHz, Chloroform-*d*)  $\delta$  158.2 (d,  $J_{C-F}$  = 284.9 Hz), 157.6, 154.1, 150.7, 143.6, 139.4, 129.5, 125.8, 124.4, 121.4, 118.6 (d,  $J_{C-F}$  = 7.8 Hz), 115.9 (d,  $J_{C-F}$  = 22.3 Hz), 114.9, 55.7.  $^{19}F$  NMR (377 MHz, Chloroform-*d*),  $\delta$  -122.46.

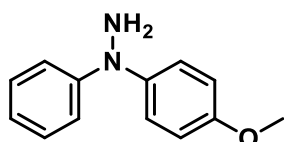
HRMS (ESI) for  $C_{20}H_{17}FN_2O_3$   $[M+H]^+$ : calcd. 353.1296, found 353.1300.

### III. The Gram-scale Synthesis of **3a**

A solution of catalyst  $[Rh(cod)Cl]_2$  (15.0 mg, 0.03 mmol), arylazocarboxylate **1a** (1.0 g, 6.1 mmol), 4-methoxyphenylboronic acid (1.85 g, 12.2 mmol) and  $K_2CO_3$  (3.37 g, 24.4 mmol) in 30 mL of toluene was stirred at ambient temperature under argon. After being stirred at ambient temperature for 24 h, the reaction was quenched with sat. aq. NaCl. Then the mixture was extracted with EtOAc (50 mL x 3). The combined organic layer was washed with brine (100 mL), dried over  $Na_2SO_4$  and concentrated. Finally, the desired product **3a** (1.57 g, 95% isolated yield) was afforded after purification of the residue by column chromatography.

#### IV. General Procedure and Characterization Data of 5a

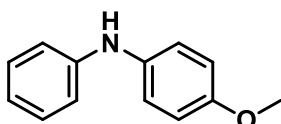
To a solution of *tert*-butyl-2-(4-methoxyphenyl)-2-phenylhydrazine-1-carboxylate **4r** (62.8 mg, 0.2 mmol) in 2.0 mL Dioxane was added HCl (2 mmol). Then the reaction was stirred for 12 h at room temperature. The reaction was quenched with sat. aq. NaHCO<sub>3</sub>. Then the mixture was extracted with EtOAc (10 mL x 3). The combined organic layer was washed with brine (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash column chromatography on silica gels using PE/EA as an eluent to obtain 1-(4-methoxyphenyl)-1-phenylhydrazine **5a**.



Colorless oil, 33.8 mg, 79% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.24–7.17 (m, 2H), 7.10–7.05 (m, 2H), 6.92–6.88 (m, 2H), 6.88–6.80 (m, 3H), 5.49 (s, 1H), 3.80 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 156.6, 150.6, 142.9, 128.9, 124.8, 119.9, 116.1, 114.8, 55.7. HRMS (ESI) for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>O [M+H-NH<sub>3</sub>]<sup>+</sup>: calcd. 198.0914, found 198.0913.

#### V. General Procedure and Characterization Data of 5b

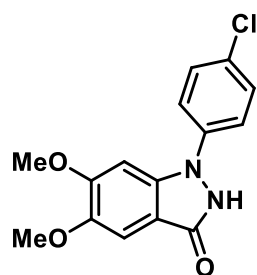
To a solution of *tert*-butyl-2-(4-methoxyphenyl)-2-phenylhydrazine-1-carboxylate **4r** (62.8 mg, 0.2 mmol) in 1.0 mL DCM were added TFA (228.0 mg, 2 mmol) at 0 °C. The reaction was slowly warmed up to room temperature and stirred for 3 h. The reaction was quenched with sat. aq. NaHCO<sub>3</sub>. Then the mixture was extracted with EtOAc (10 mL x 3). The combined organic layer was washed with brine (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash column chromatography on silica gels using PE/EA as an eluent to obtain 4-methoxy-*N*-phenylaniline **5b**.



White solid, 36.2 mg, 91% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.24–7.16 (m, 2H), 7.13 – 7.05 (m, 2H), 6.93–6.89 (m, 2H), 6.88 – 6.78 (m, 3H), 5.49 (s, 1H), 3.80 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.4, 145.3, 135.9, 129.4, 122.4, 119.7, 115.8, 114.8, 55.7. HRMS (ESI) for C<sub>13</sub>H<sub>14</sub>NO [M+H]<sup>+</sup>: calcd. 200.1070, found 200.1069.

#### VI. General Procedure and Characterization Data of 6a

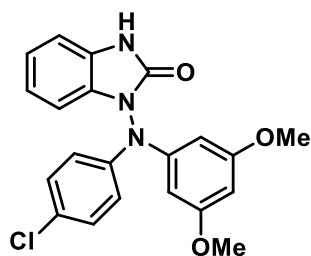
To a solution of phenyl-2-(4-chlorophenyl)-2-(3,5-dimethoxyphenyl)-hydrazine-1-carboxylate **4s** (0.1 mmol, 39.8 mg) and PhCF<sub>3</sub> (1.0 mL) was added to a microwave vial. The microwave vial was capped and heated in a microwave reactor for 3 h at 200 °C. Then the reaction was cooled to room temperature and the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford 1-(4-chlorophenyl)-4,6-dimethoxy-1,2-dihydro-3H-indazol-3-one **6a**.



Yellow solid, 25.2 mg, 83% yield.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.53 (d,  $J = 8.4$  Hz, 2H), 7.45 (d,  $J = 8.4$  Hz, 2H), 6.46 (s, 1H), 6.14 (s, 1H), 3.95 (s, 3H), 3.83 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  163.4, 157.1, 155.6, 143.3, 138.7, 131.4, 129.8, 123.7, 99.9, 93.0, 84.4, 56.0, 55.9. HRMS (ESI) for  $\text{C}_{15}\text{H}_{13}\text{ClN}_2\text{O}_3$   $[\text{M}+\text{H}]^+$ : calcd. 305.0687, found 305.0688.

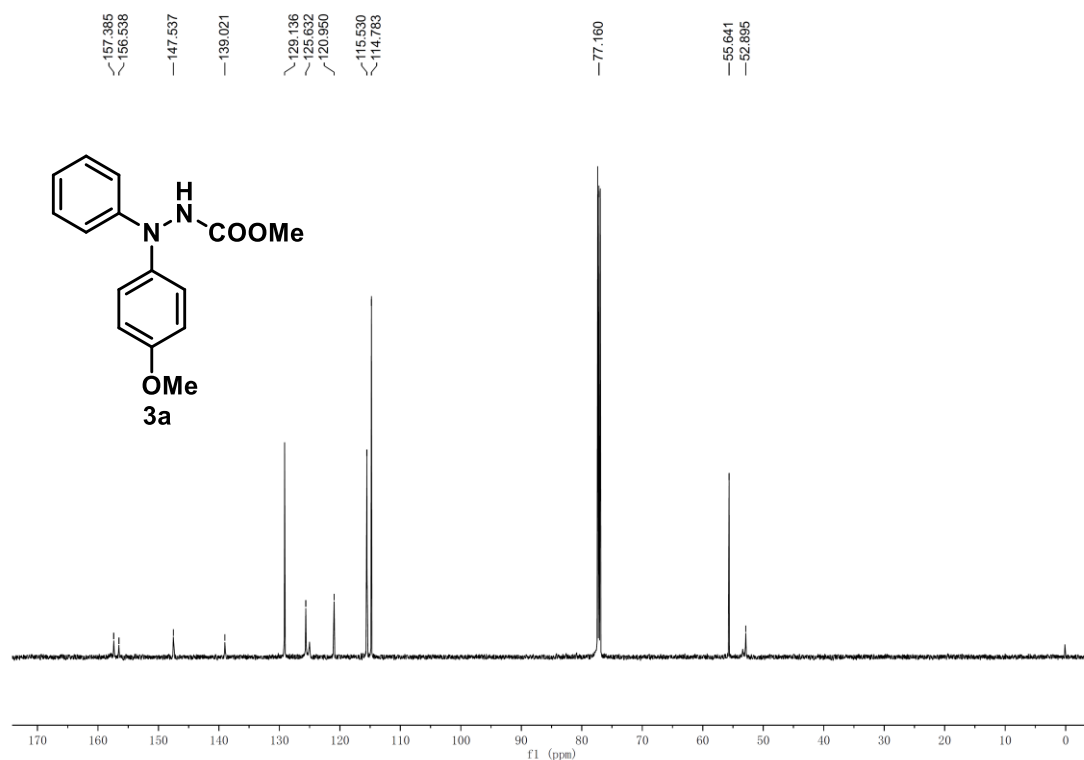
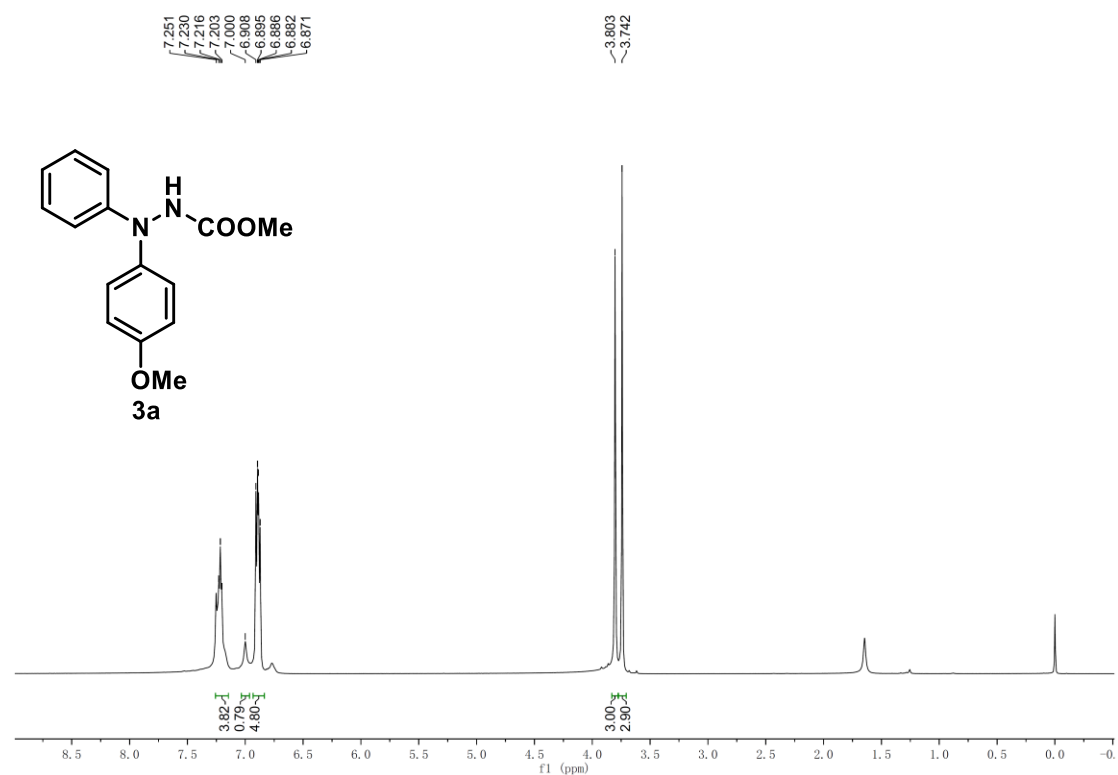
## VII. General Procedure and Characterization Data of 6b

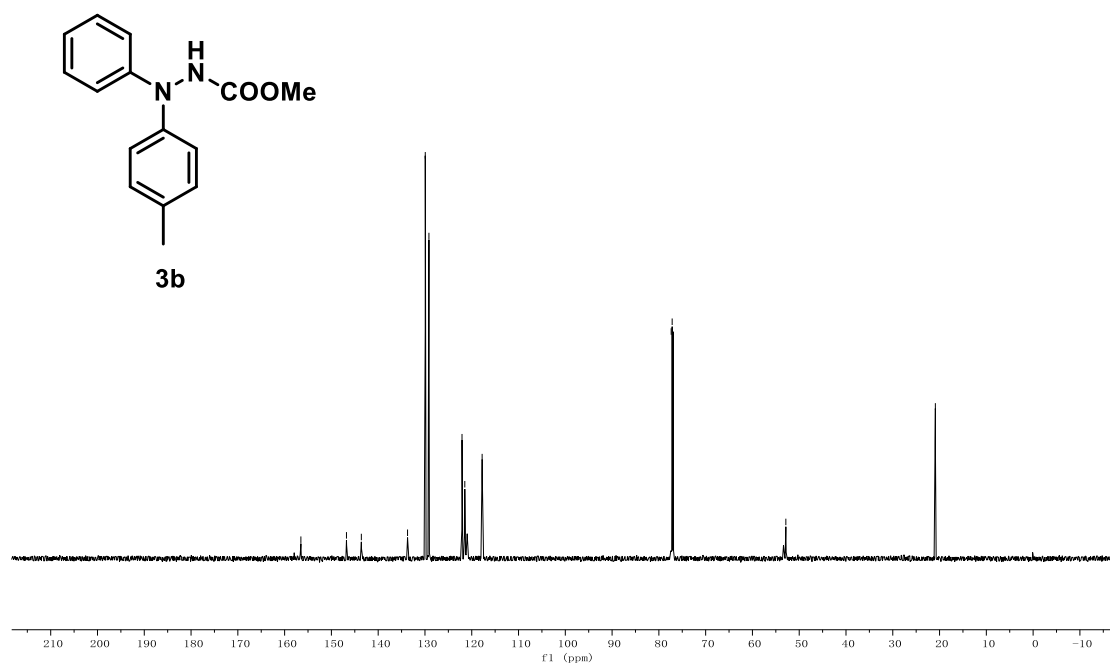
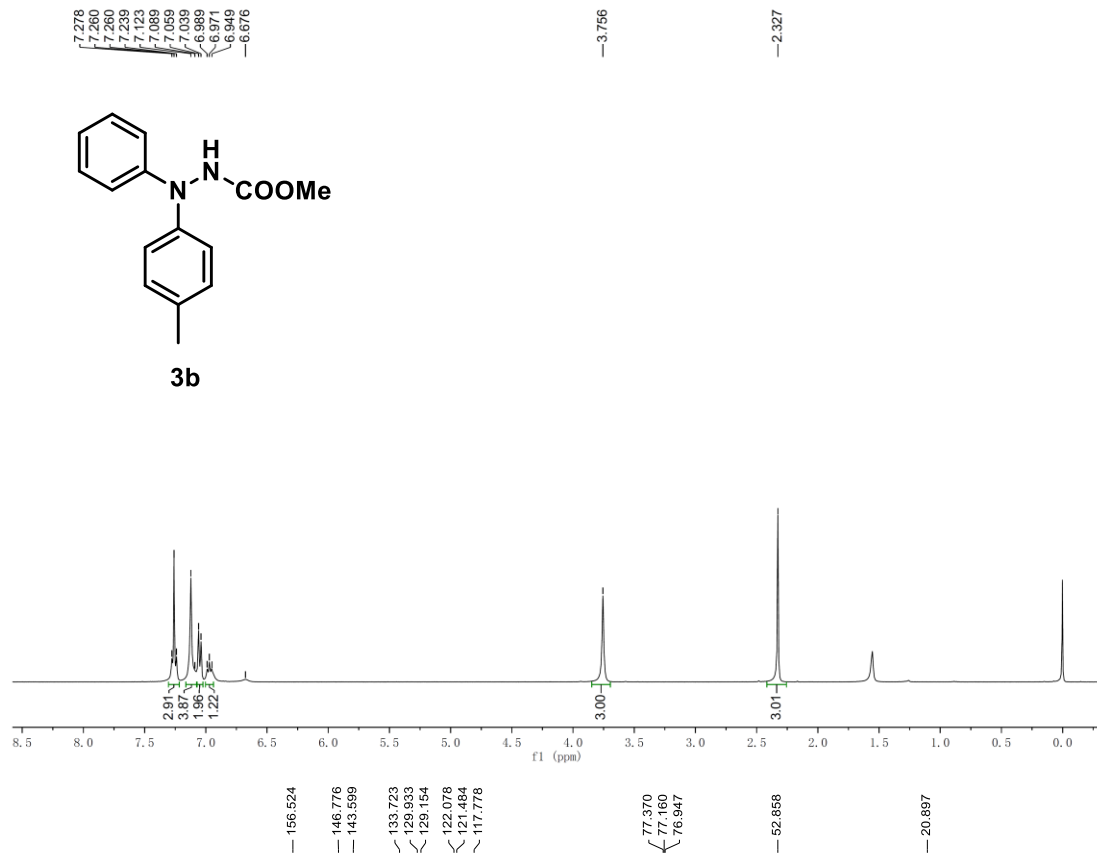
Under an argon atmosphere, a mixture of phenyl-2-(4-chlorophenyl)-2-(3,5-dimethoxyphenyl)-hydrazine-1-carboxylate **4s** (0.20 mmol, 79.8 mg), 2-iodoaniline (0.30 mmol, 65.7 mg), DABCO (0.60 mmol, 67.3 mg) in  $\text{PhCF}_3$  (2.0 mL) was stirred at 100 °C for 12 h. Then the solvent was removed under reduced pressure. To the residue was added CuI (0.020 mmol, 3.8 mg, 10 mol%), 1,10-phenanthroline (0.040 mmol, 7.2 mg, 20 mol%), and DMSO (2.0 mL). Then the reaction was stirred at 100 °C for 5 h under argon. The reaction was cooled to room temperature and quenched with sat. aq. NaCl. Then the mixture was extracted with EtOAc (10 mL x 3). The combined organic layer was dried over  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was purified by flash chromatography on silica gel to afford 1-((4-Chlorophenyl)(3,5-dimethoxyphenyl)amino)-1,3-dihydro-2H-benzo[d]imidazol-2-one **6b**.

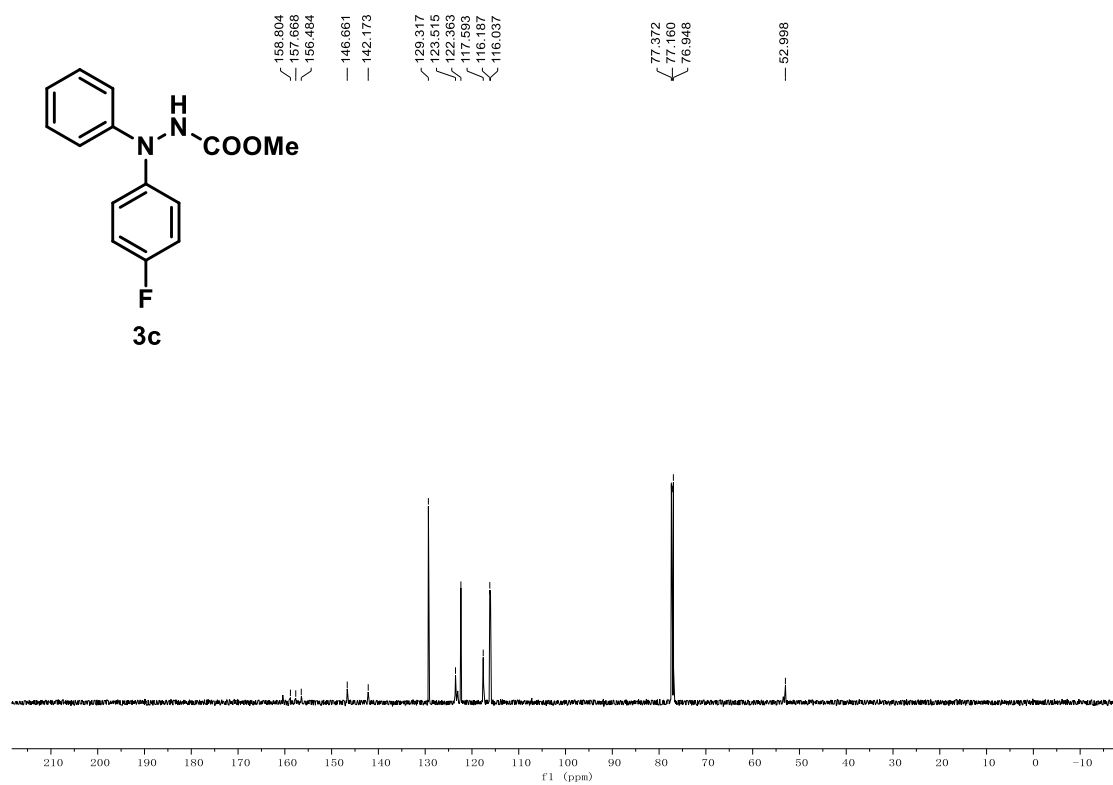
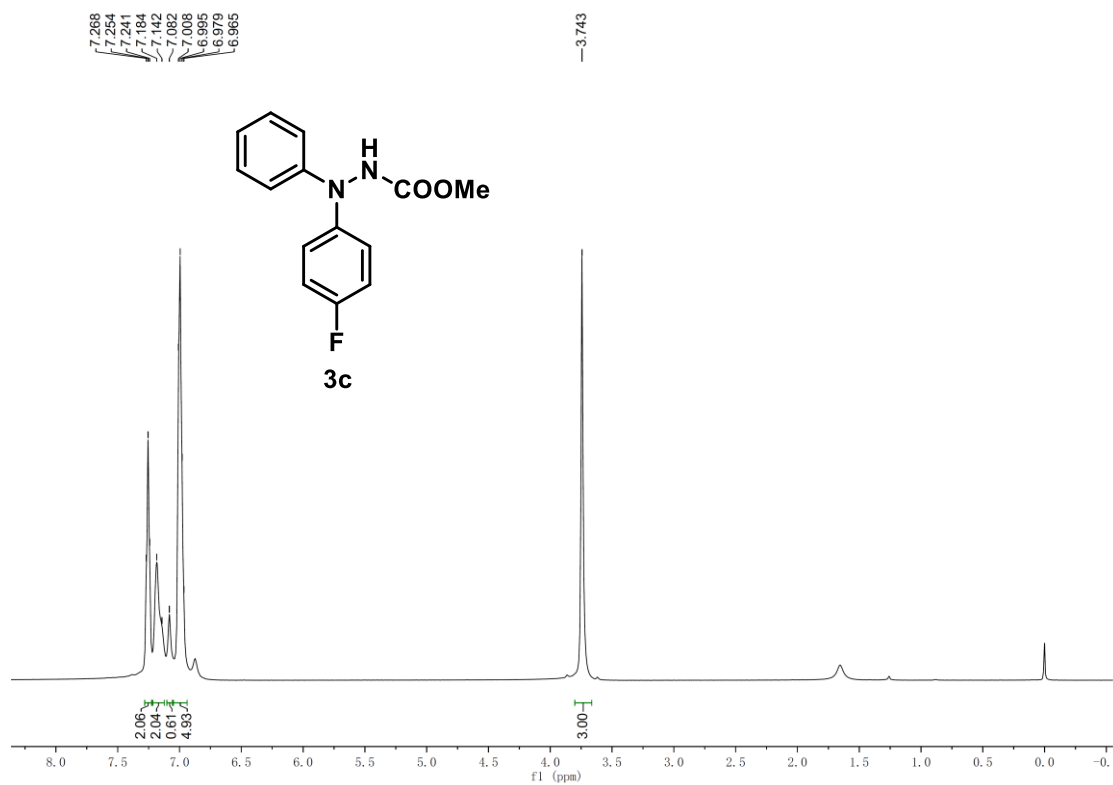


White solid, 71.1 mg, 90% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  10.30 (s, 1H), 7.27–7.22 (m, 2H), 7.21–7.17 (m, 2H), 7.09–7.02 (m, 4H), 6.27 (d,  $J = 2.1$  Hz, 2H), 6.19–6.17 (m, 1H), 3.69 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  161.7, 154.1, 146.1, 142.8, 129.6, 129.1, 126.1, 123.0, 122.2, 122.1, 110.7, 108.5, 97.9, 95.5, 55.5. HRMS (ESI) for  $\text{C}_{21}\text{H}_{18}\text{ClN}_2\text{O}_3$   $[\text{M}+\text{H}]^+$ : calcd. 396.1109, found 396.1110.

### VIII. Copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra

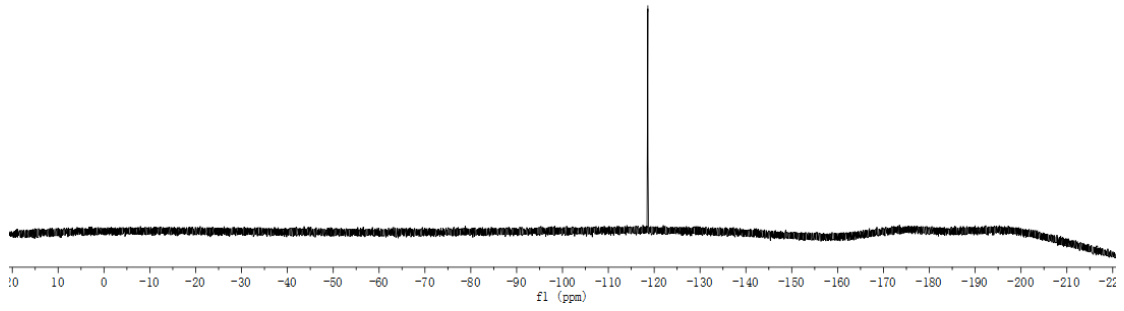
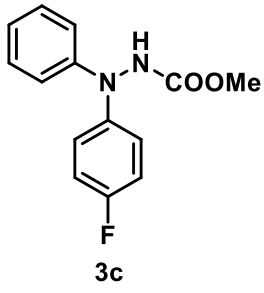






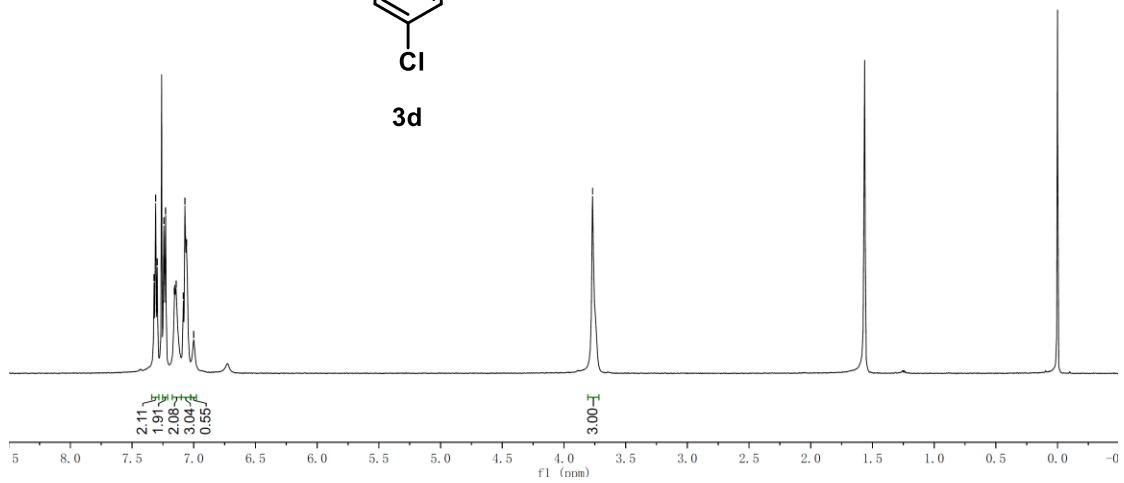
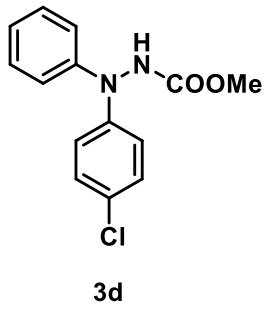


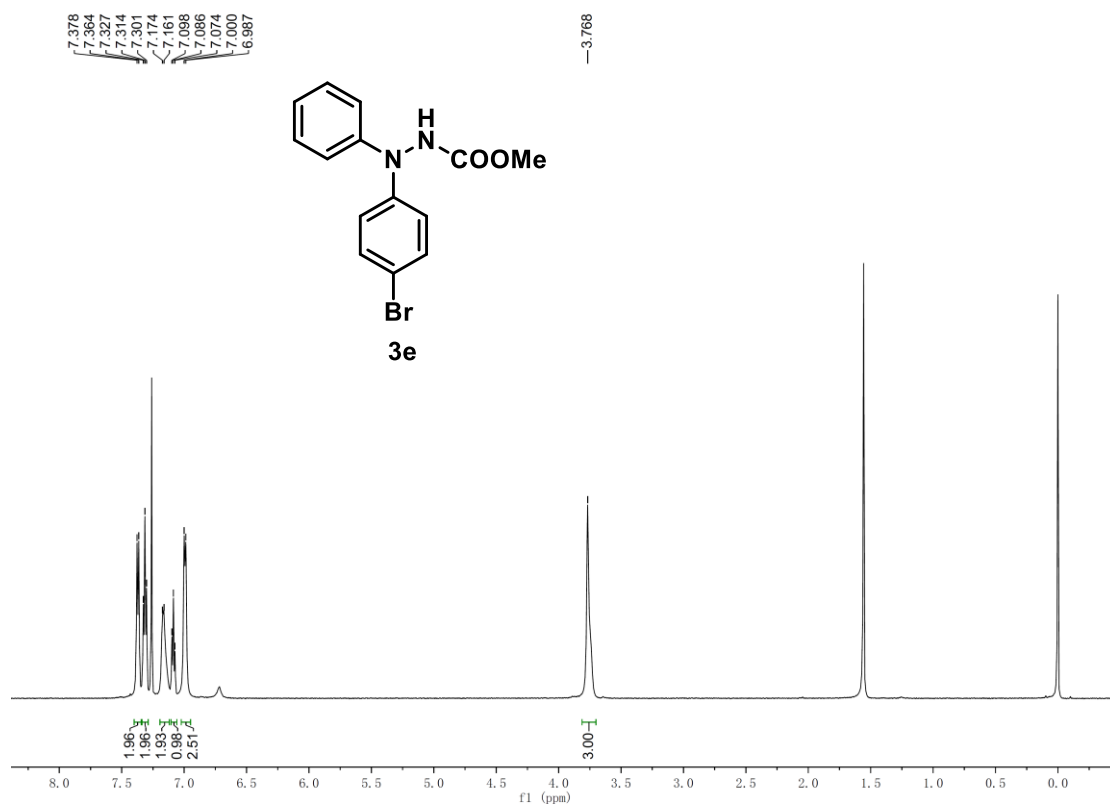
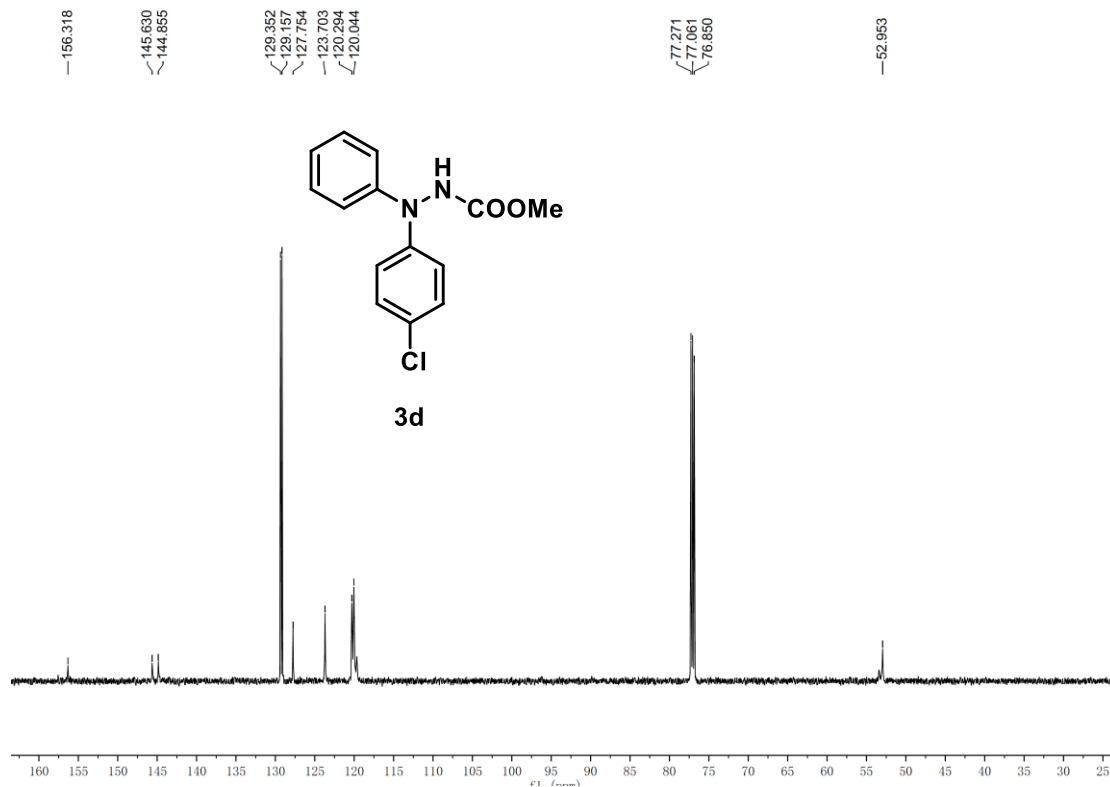
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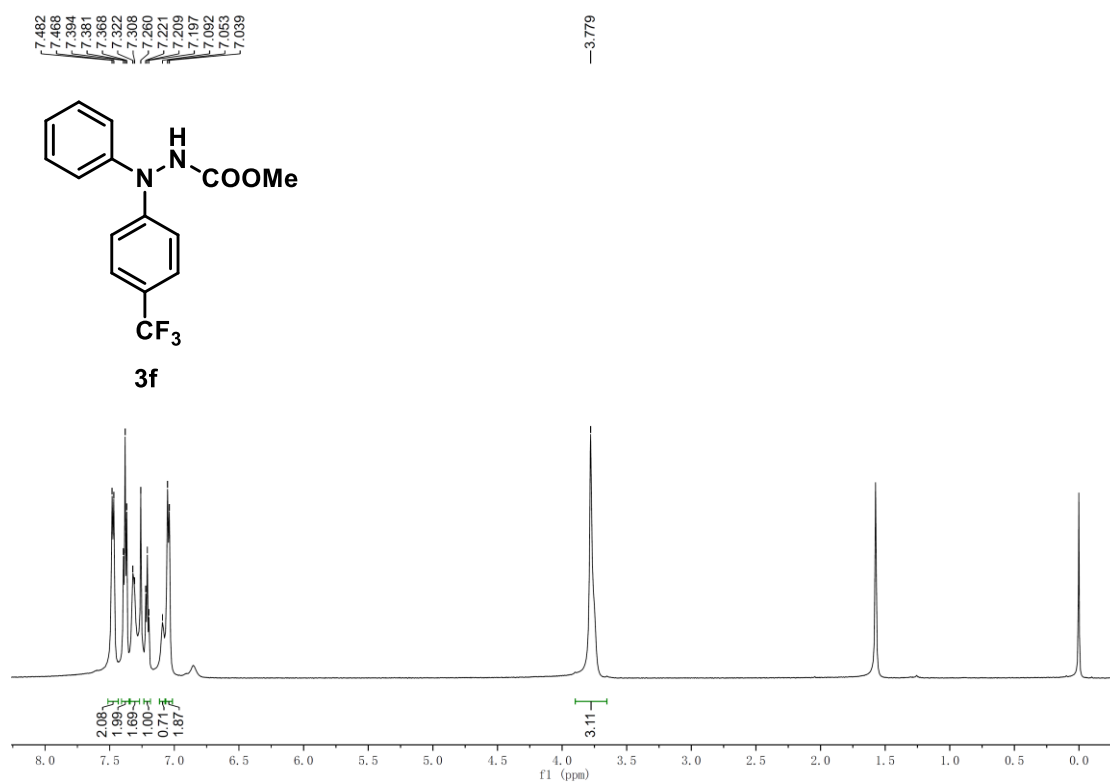
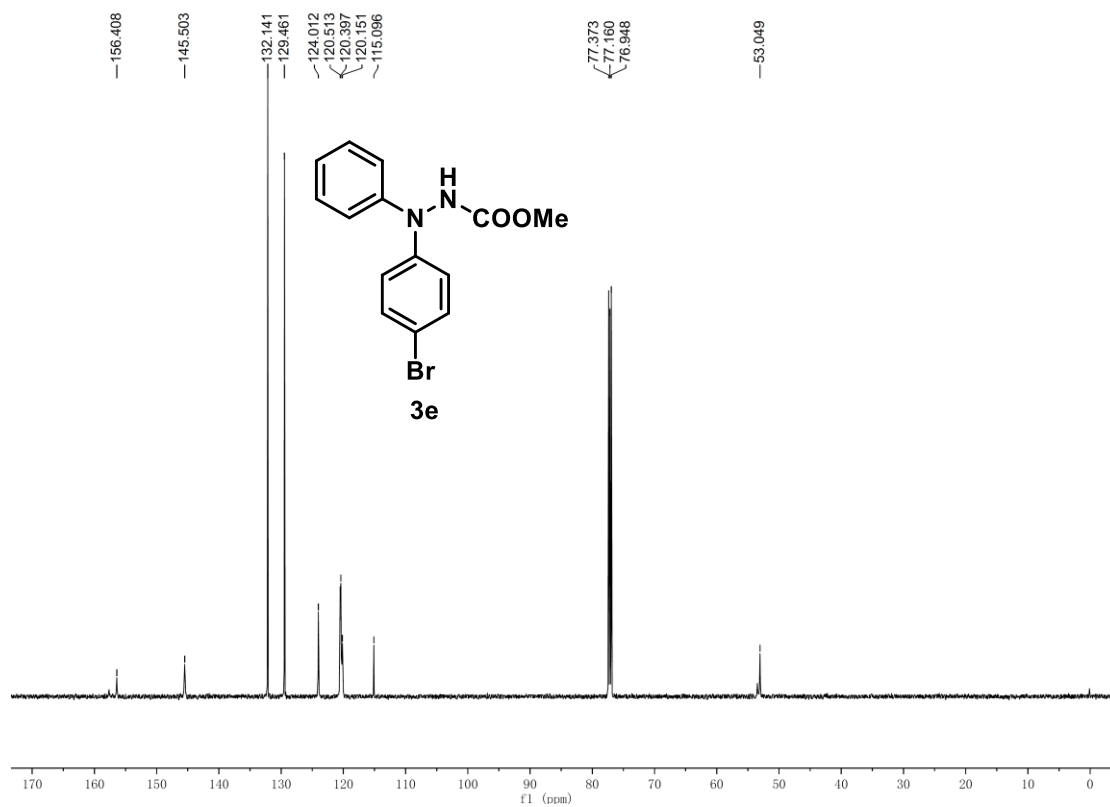


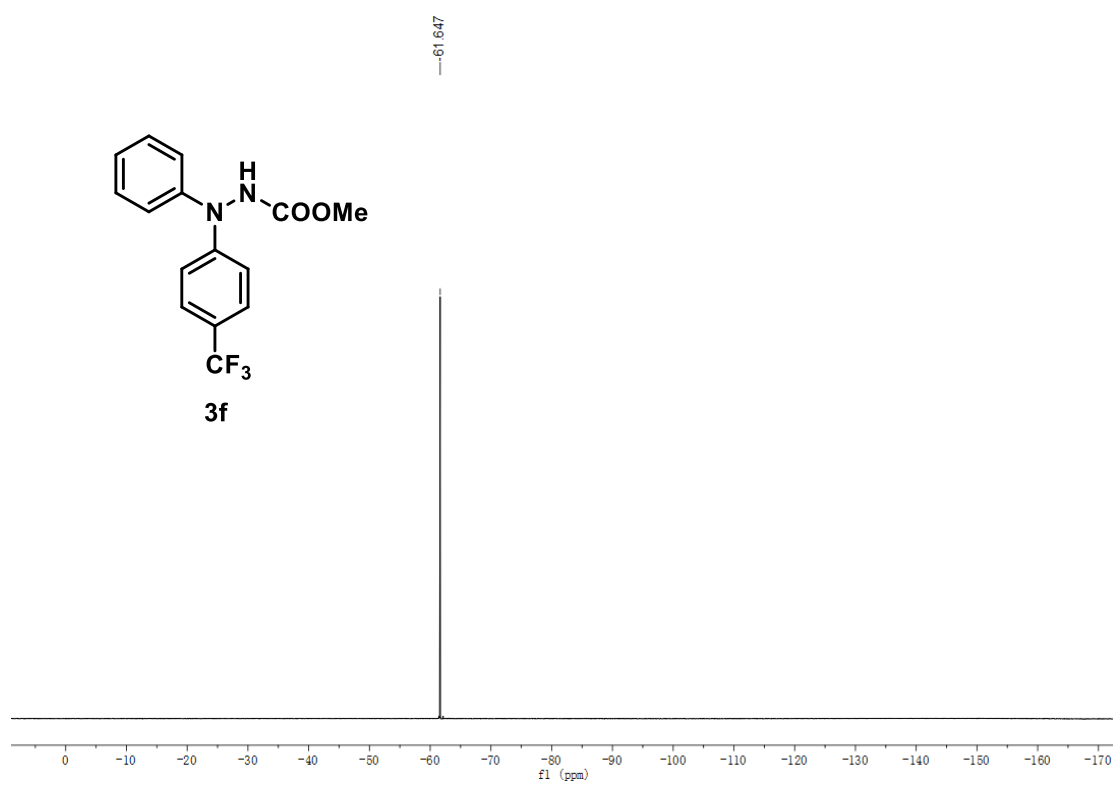
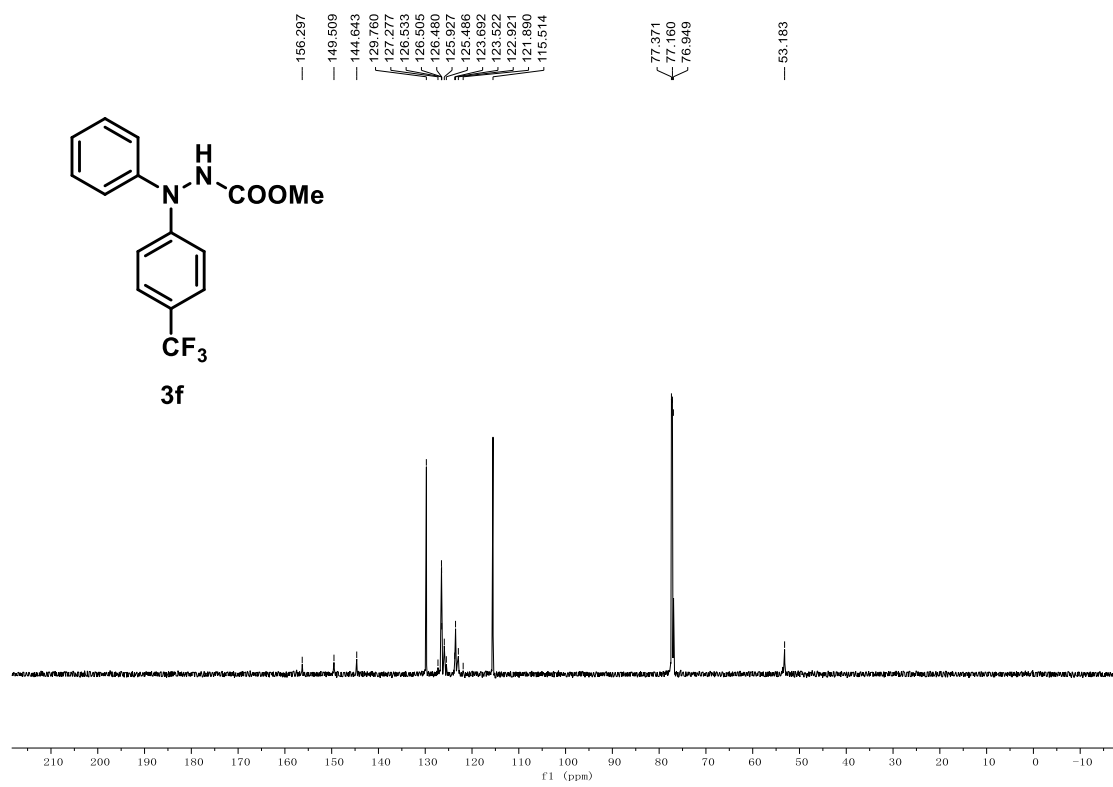
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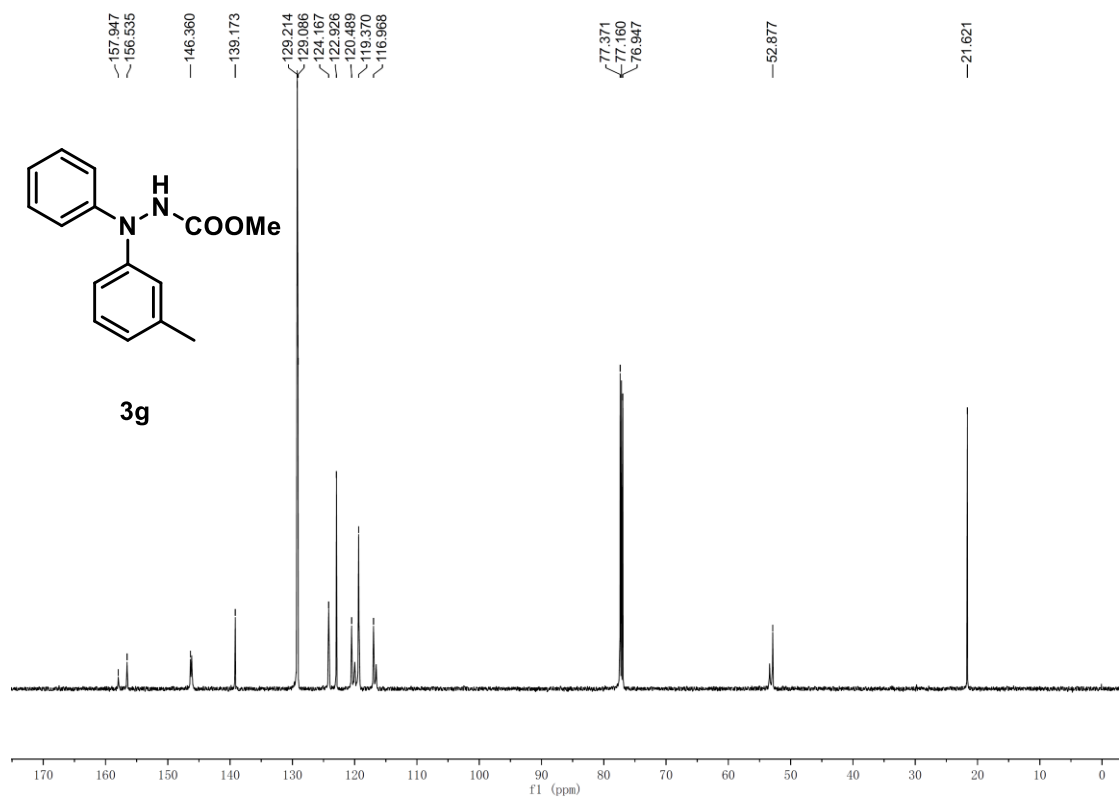
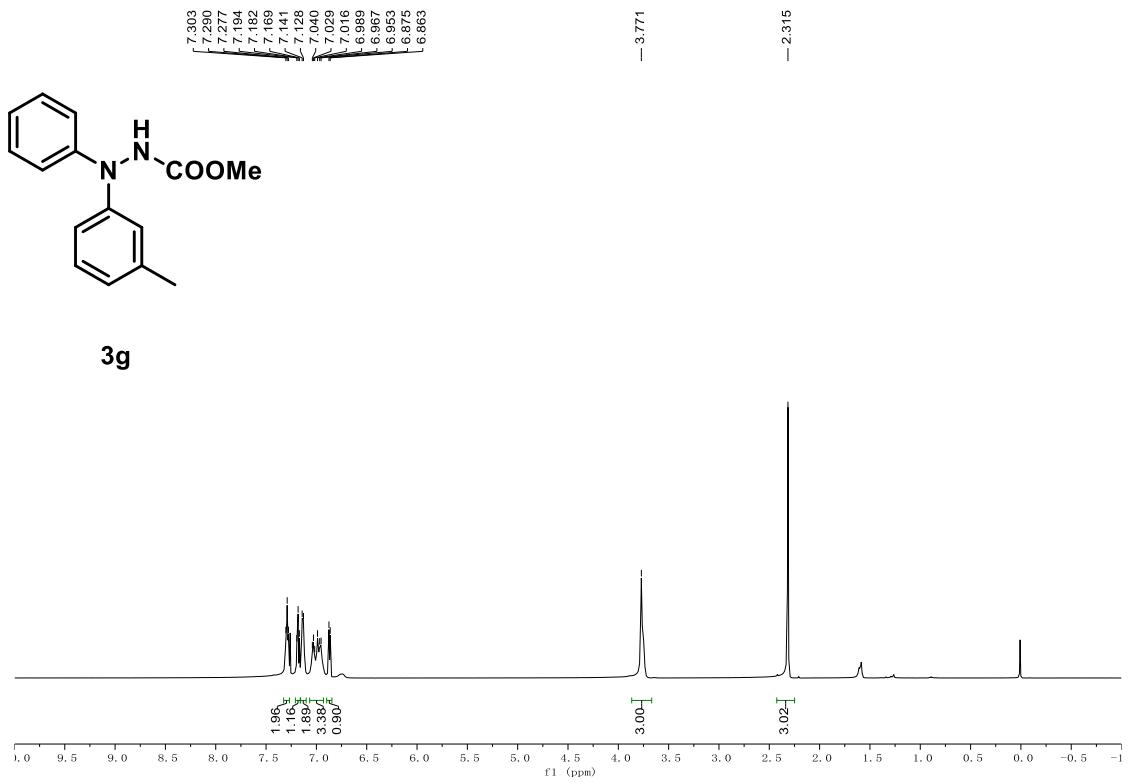
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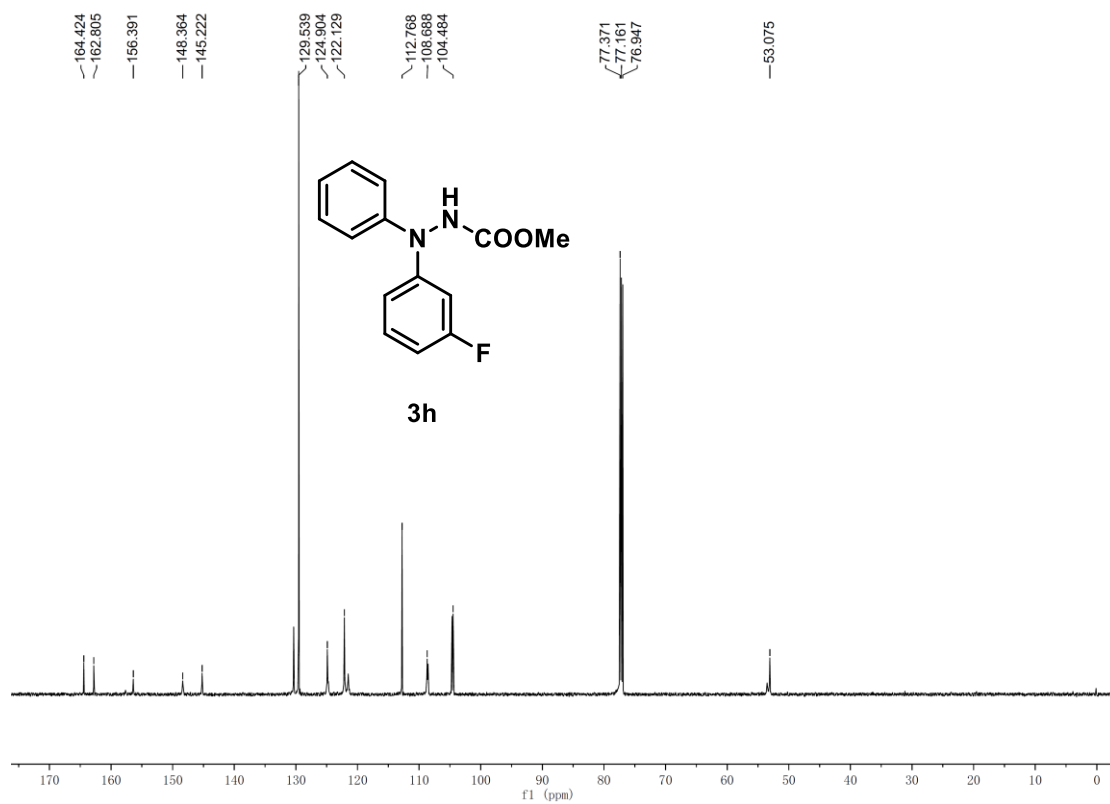
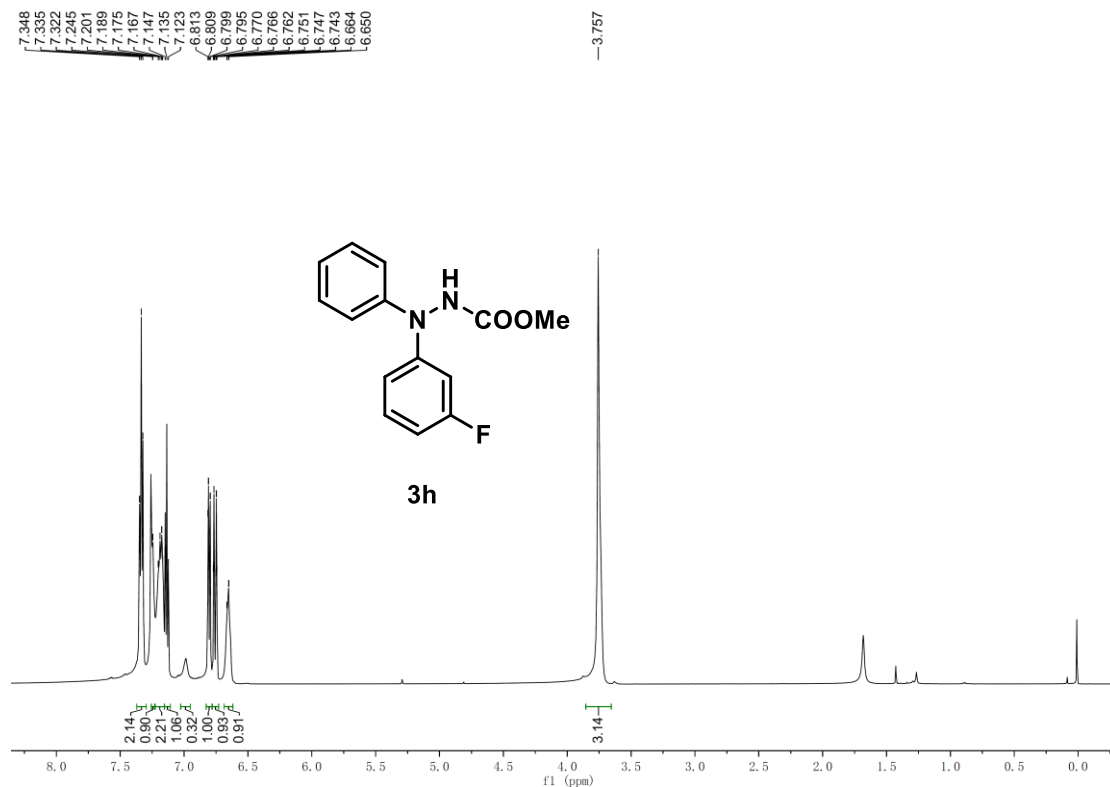


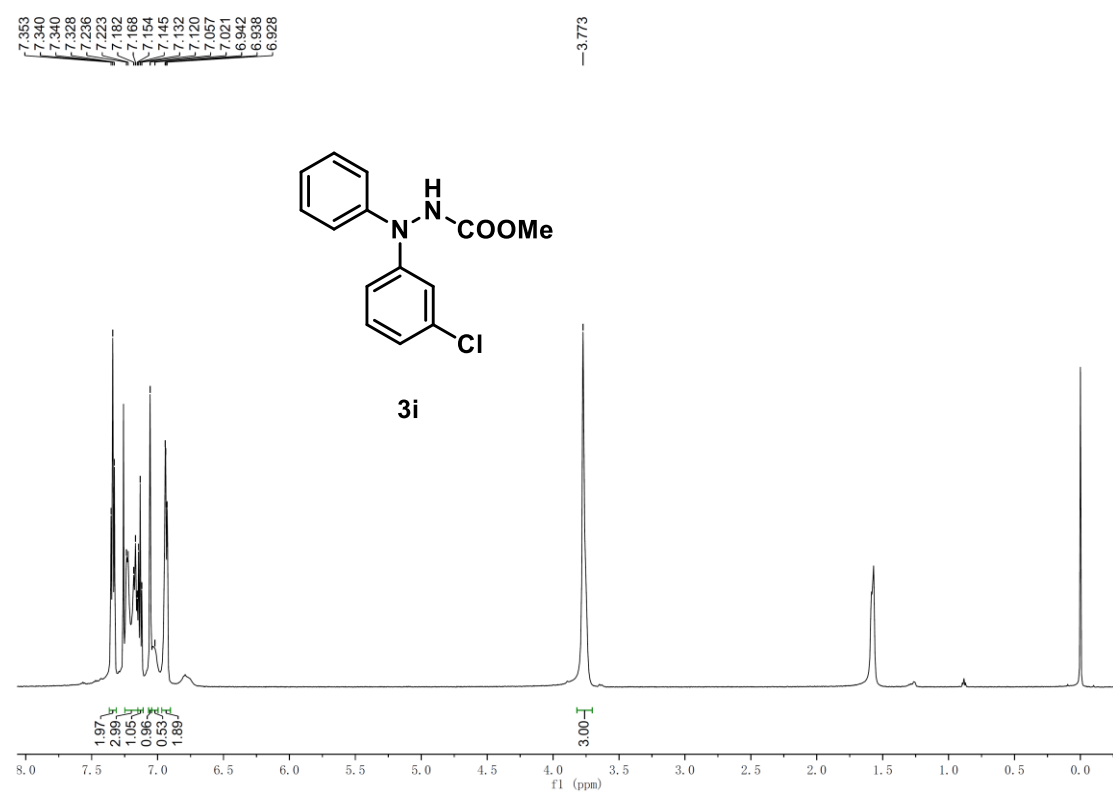
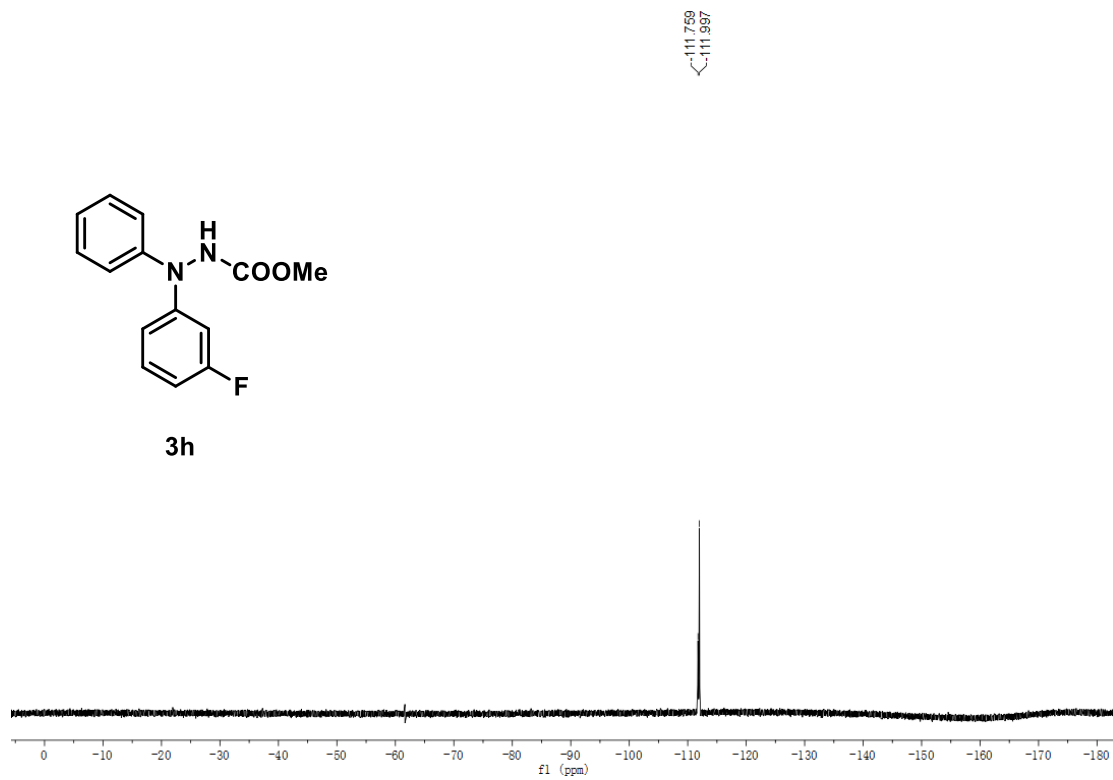


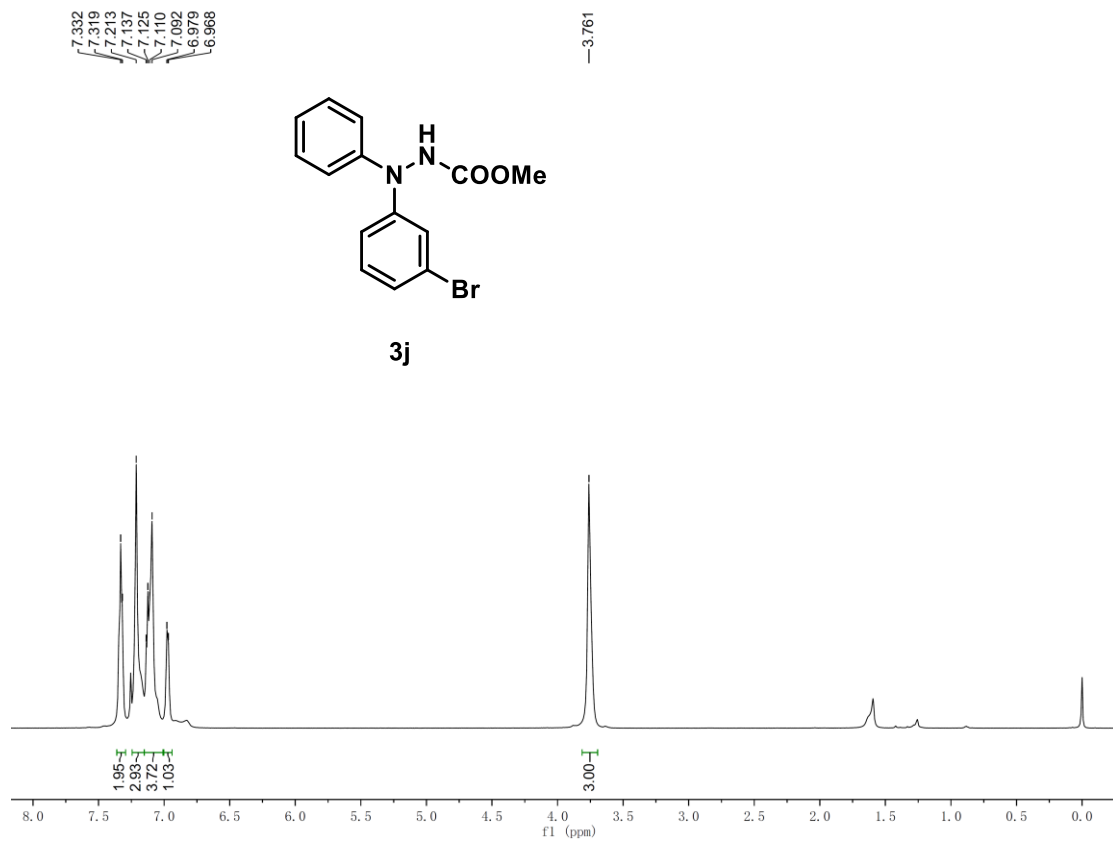
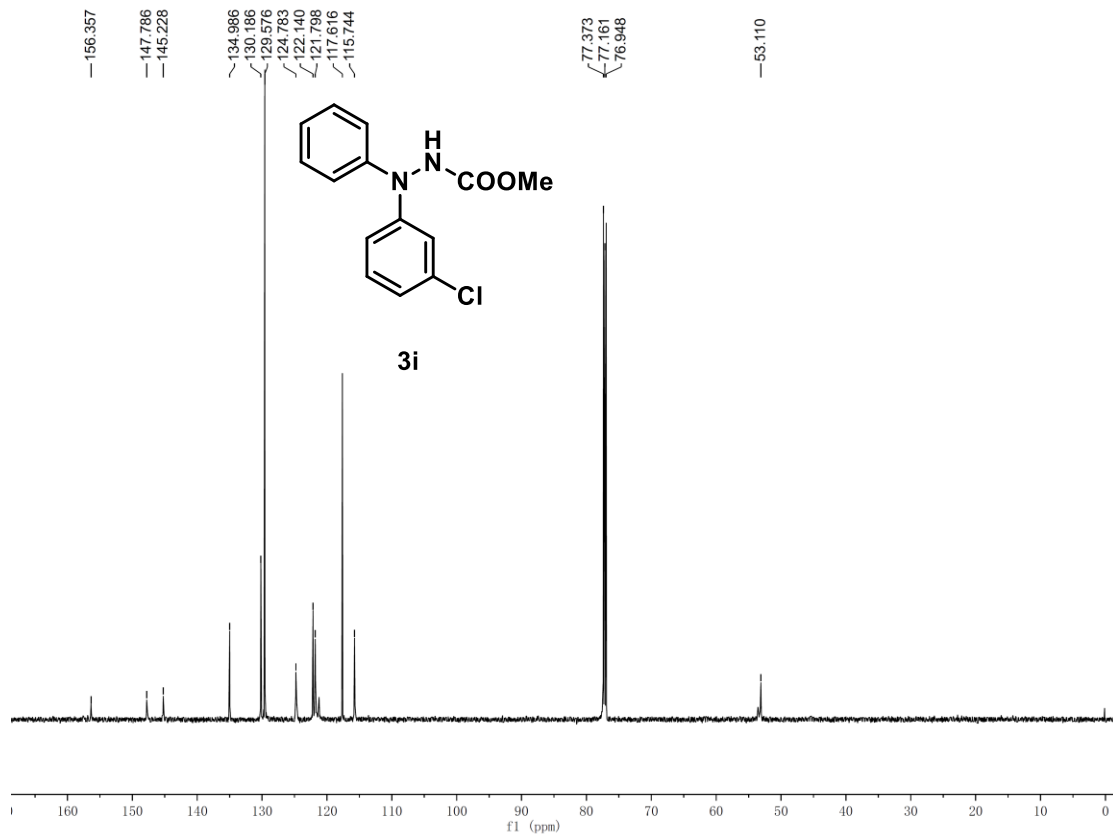




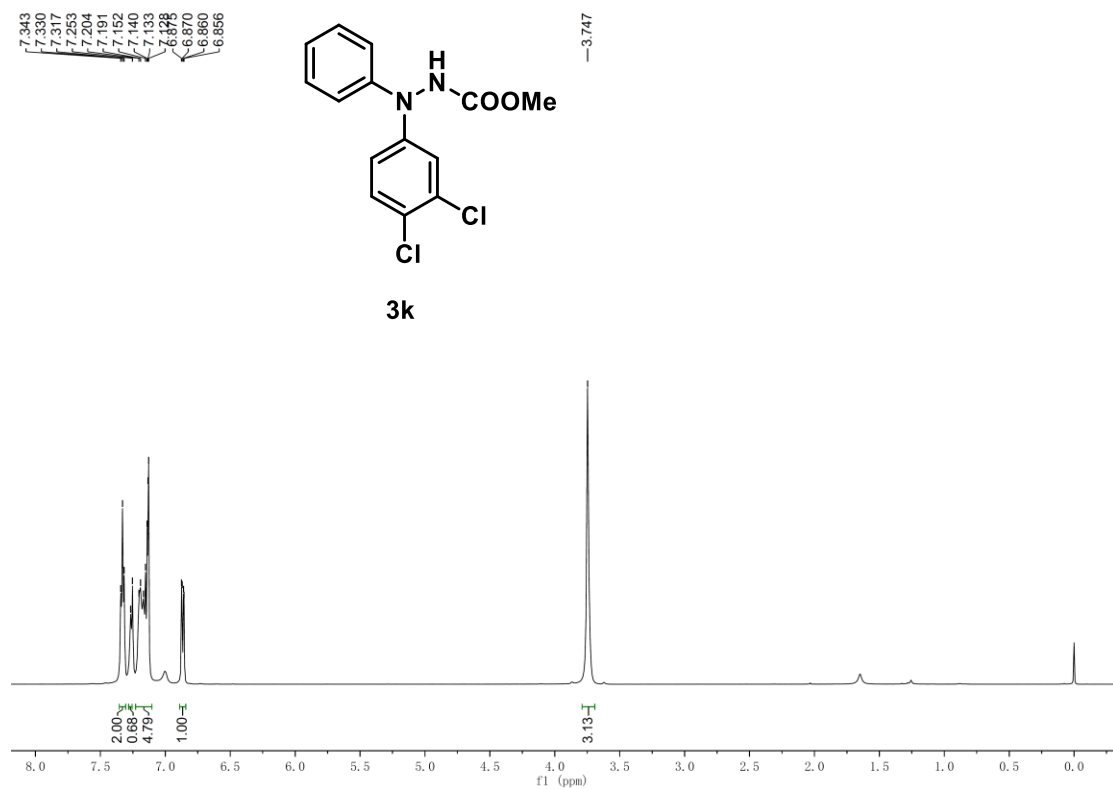
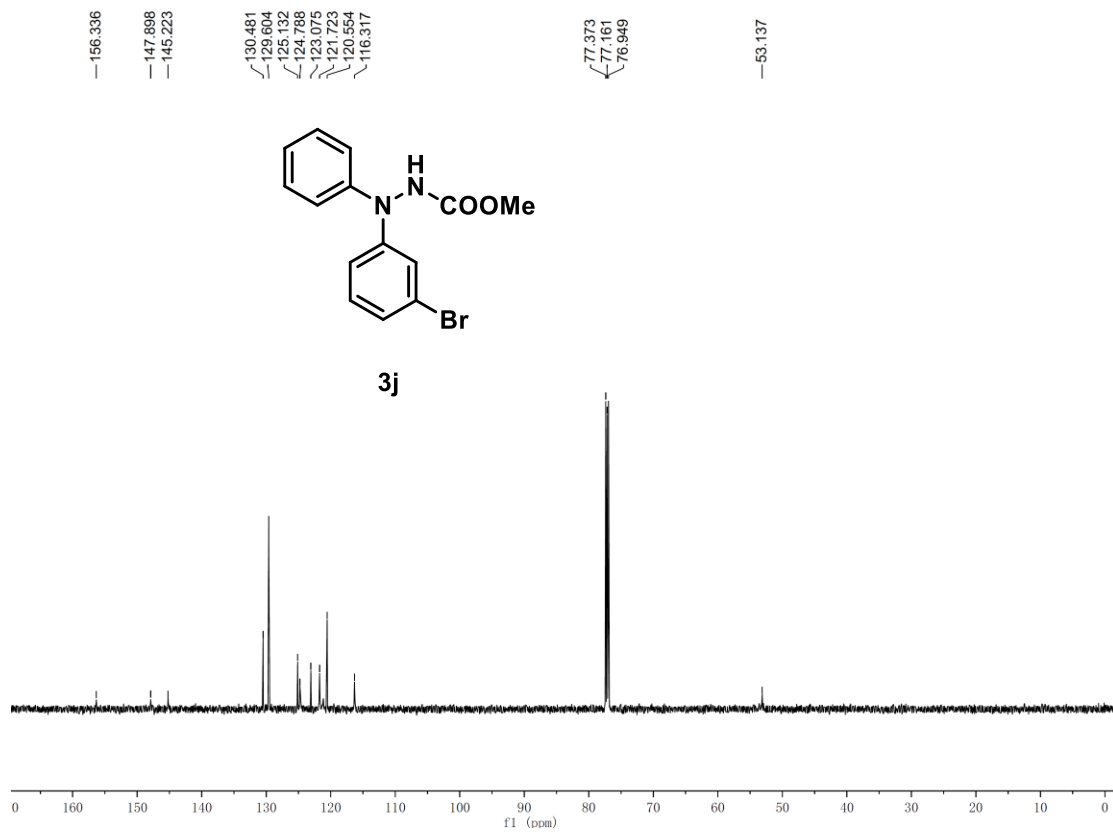


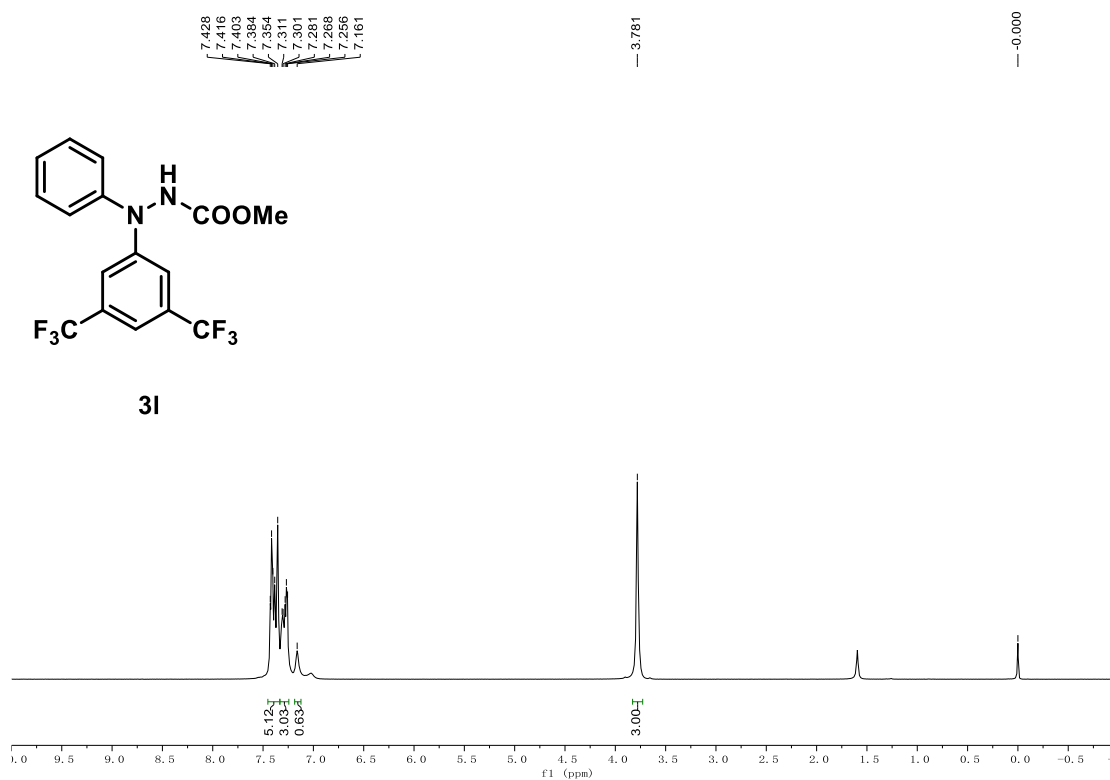
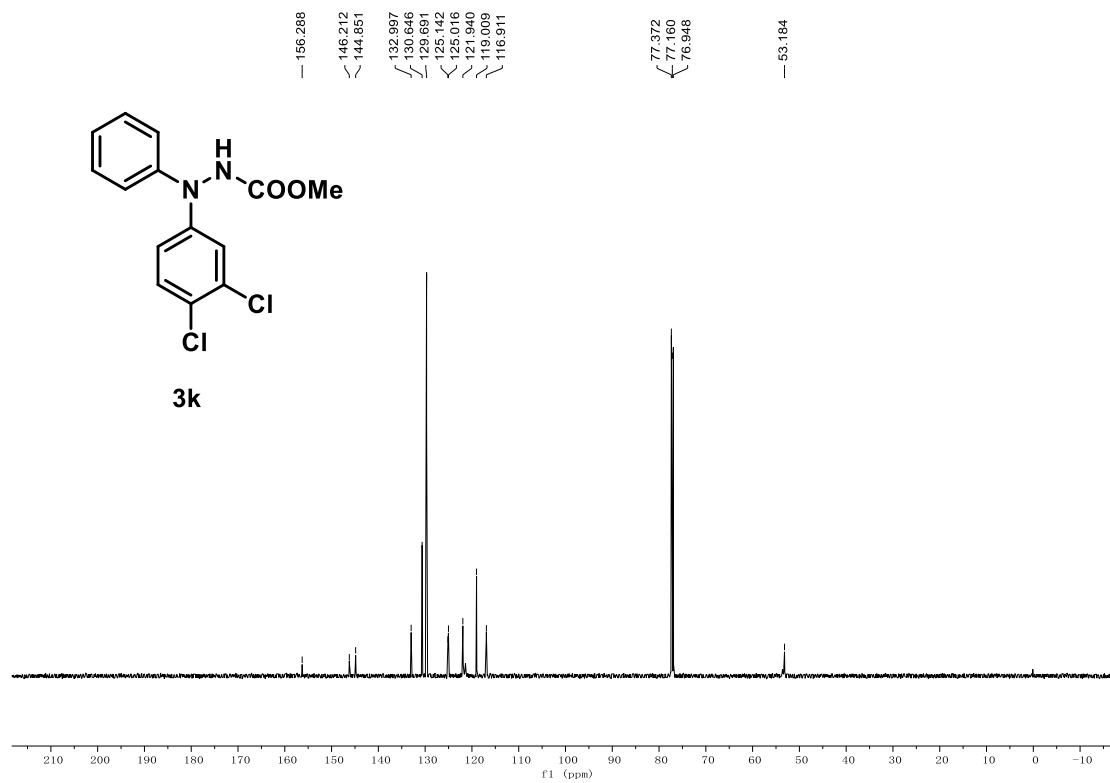


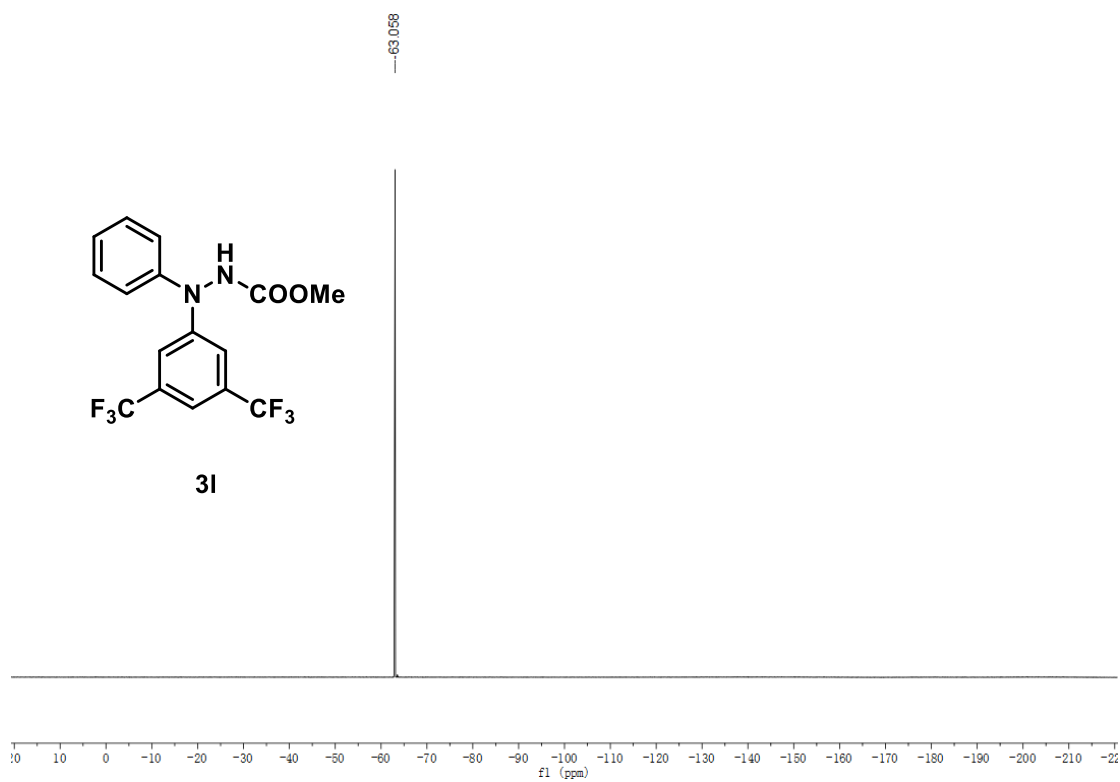
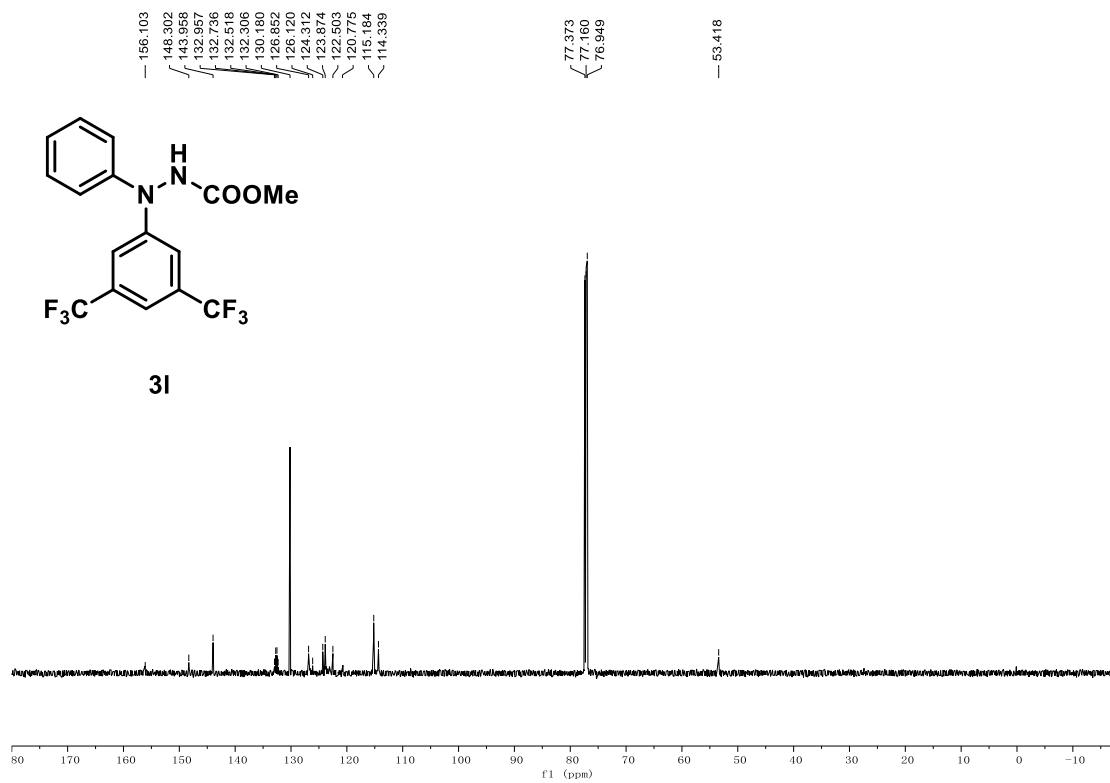


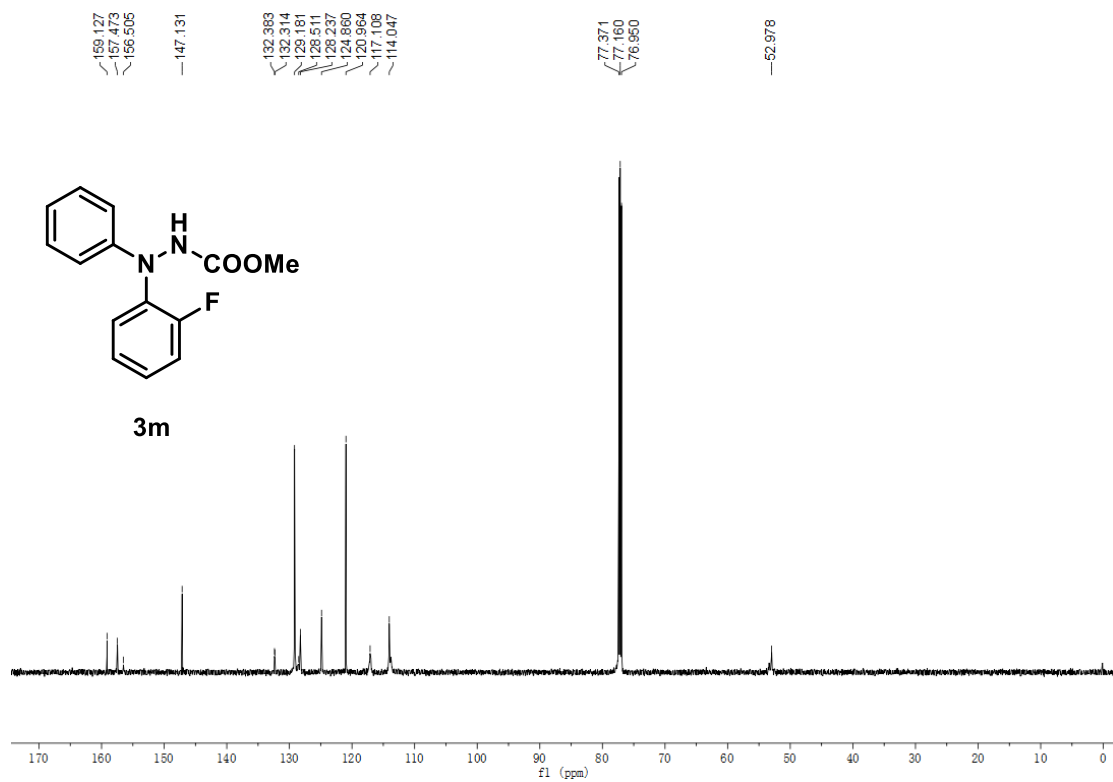
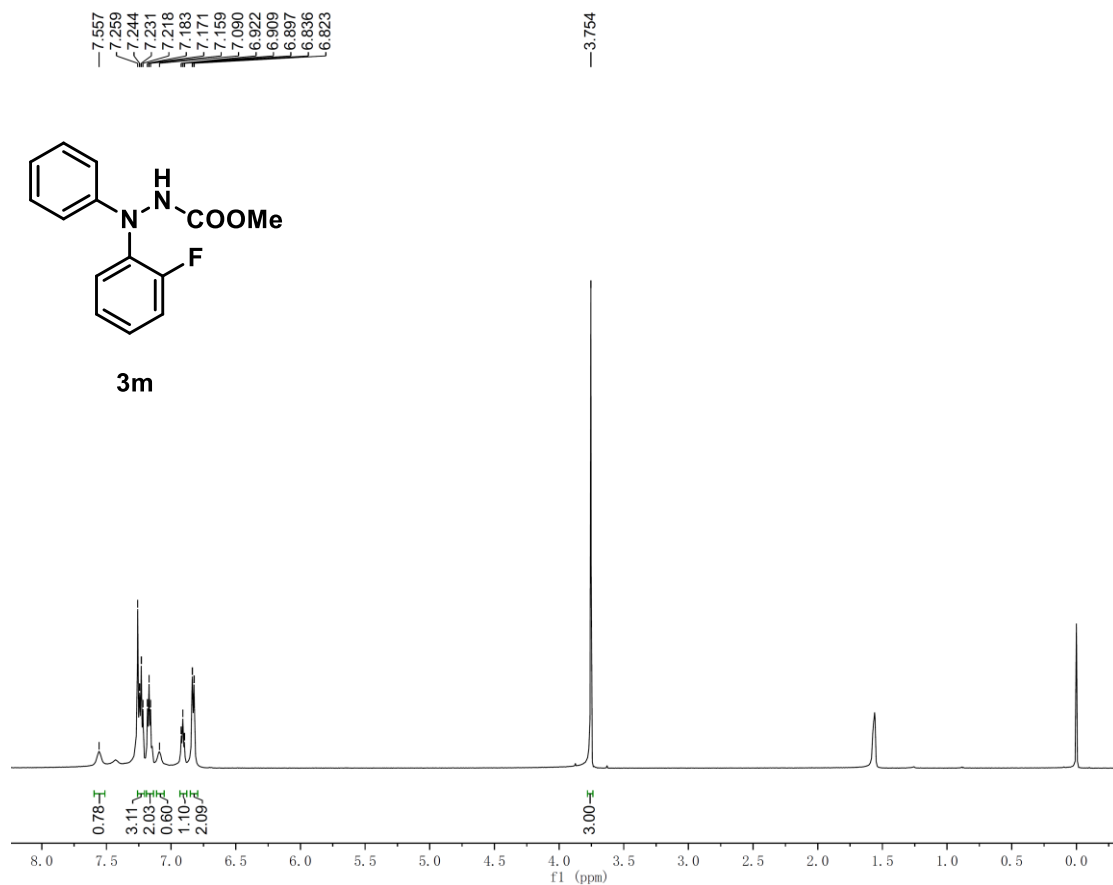


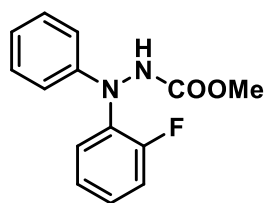




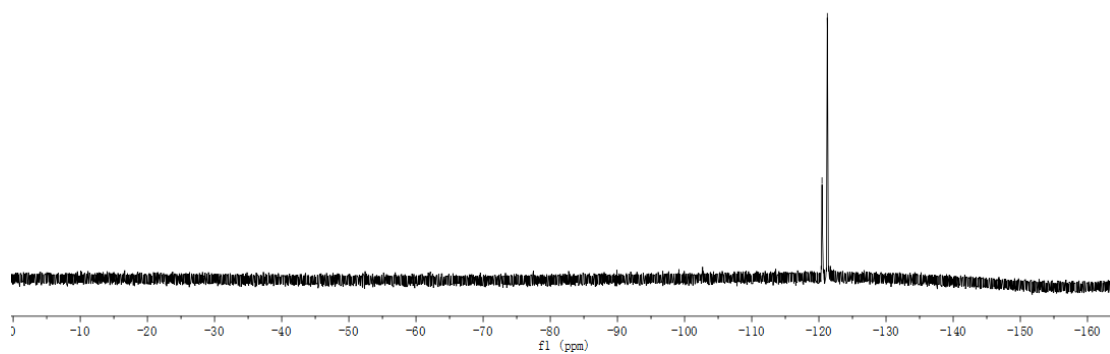






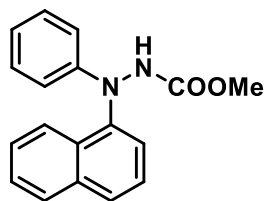


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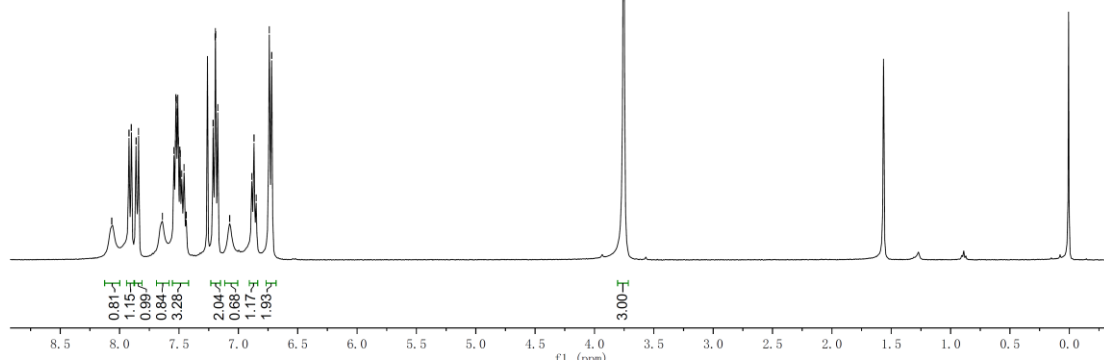


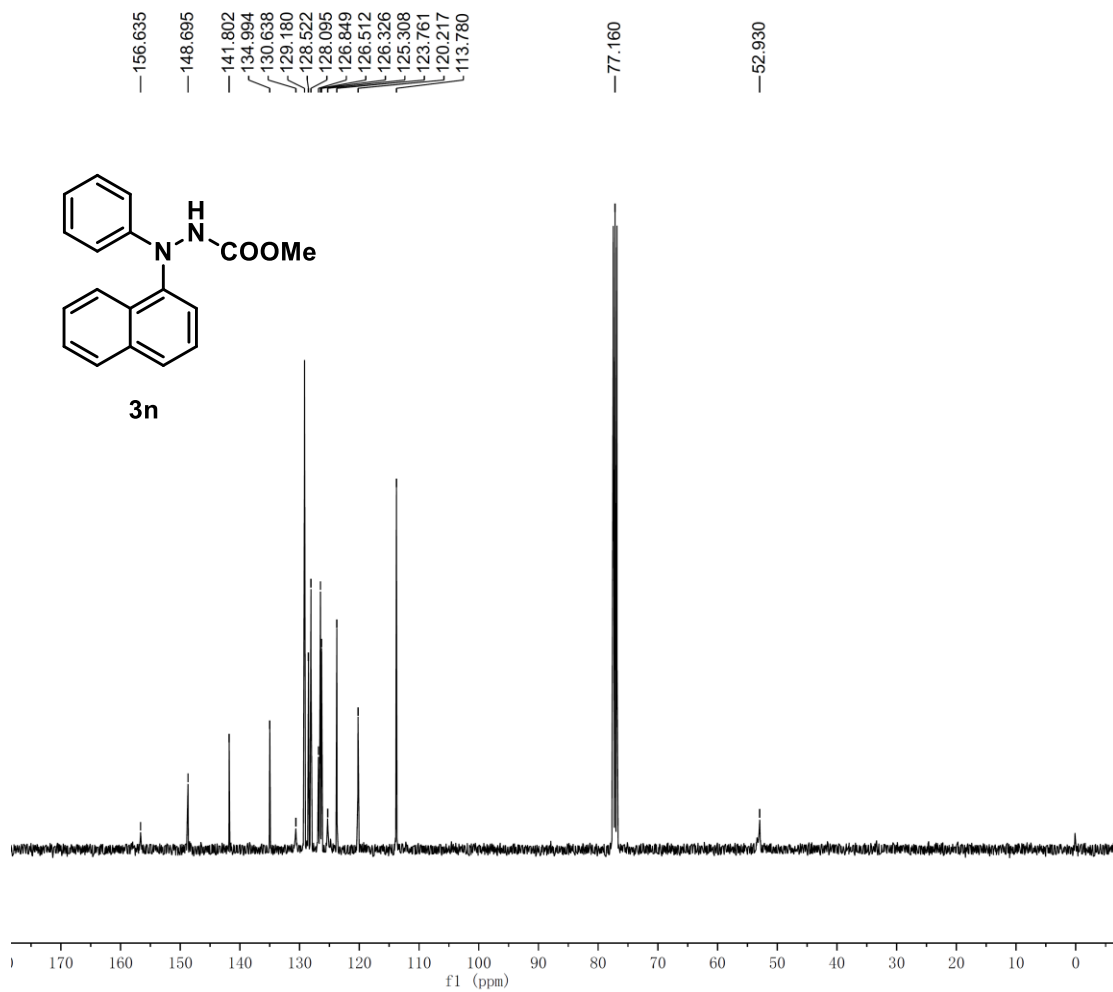
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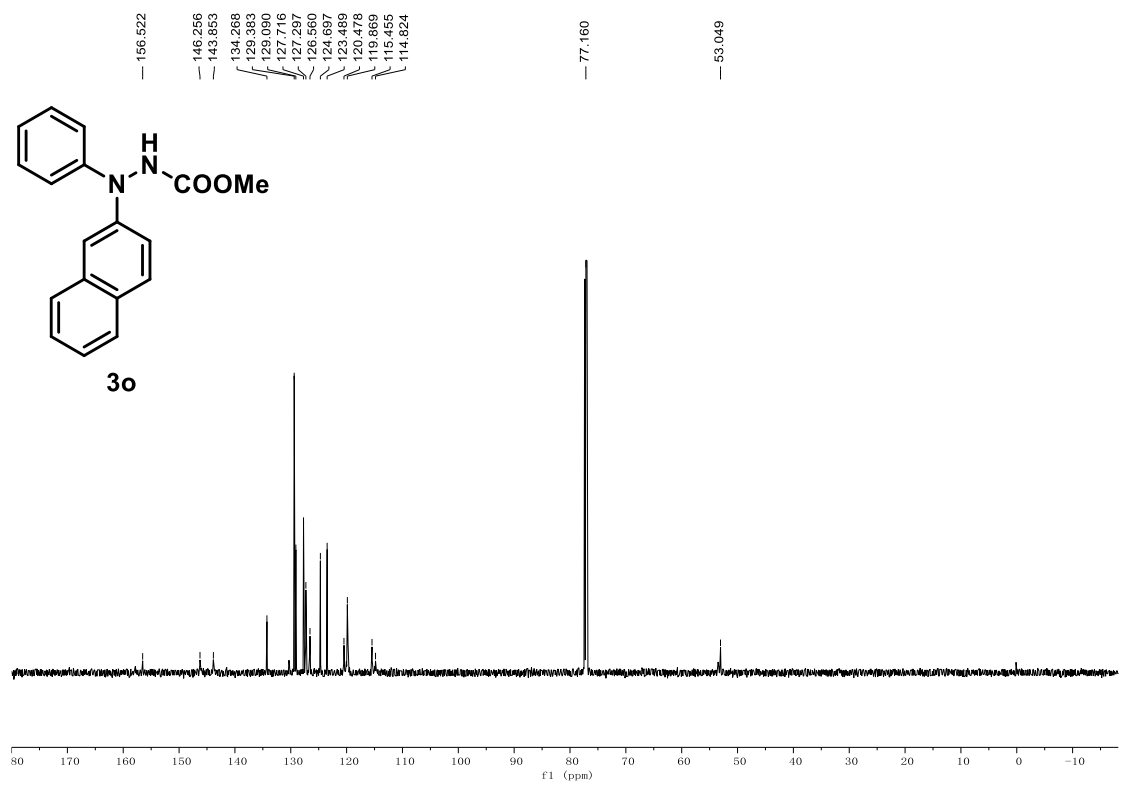
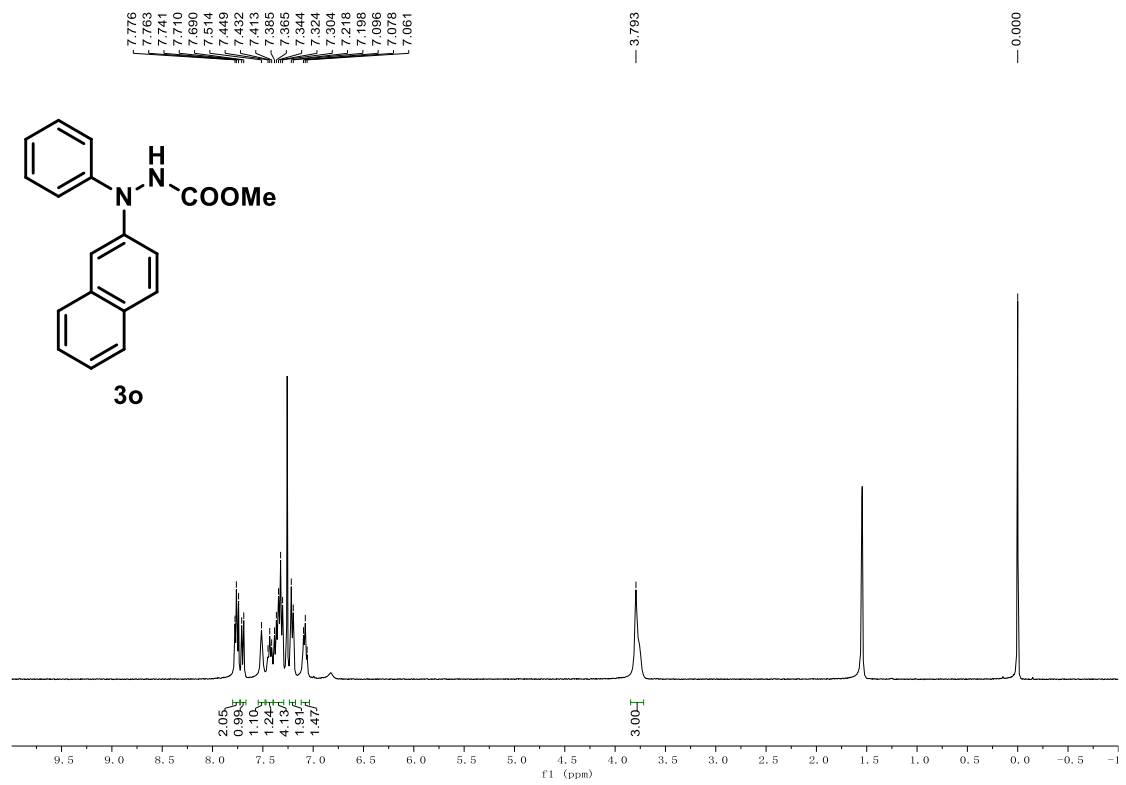
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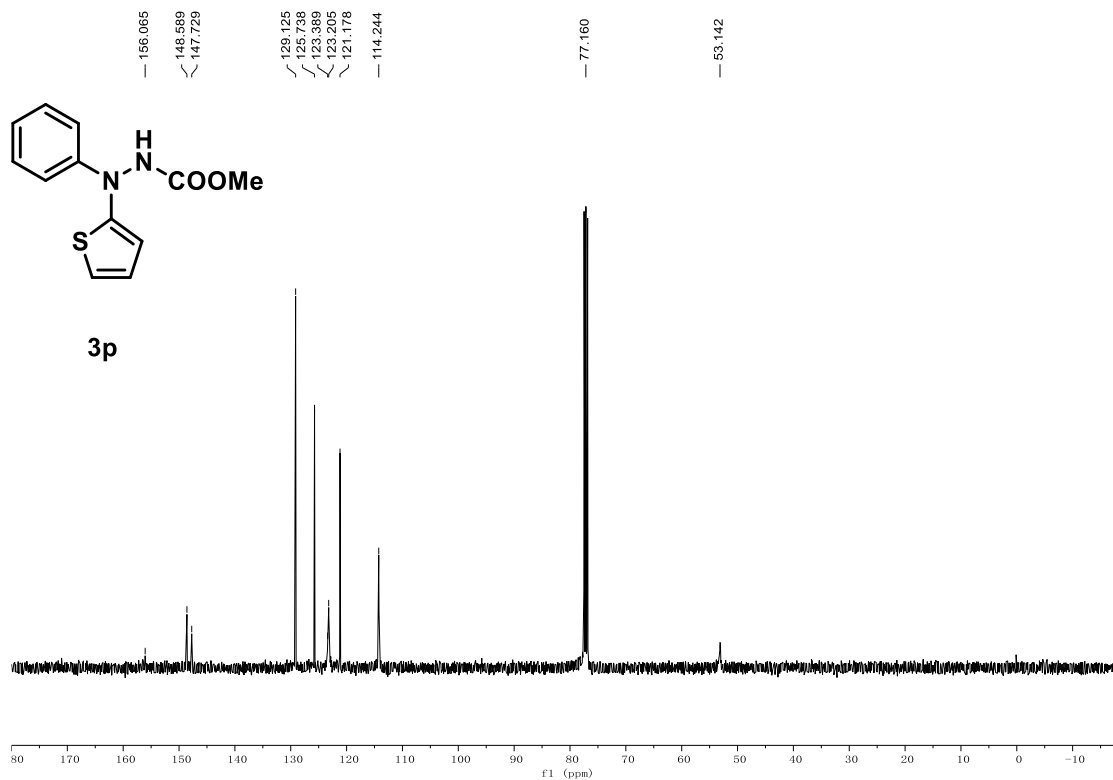
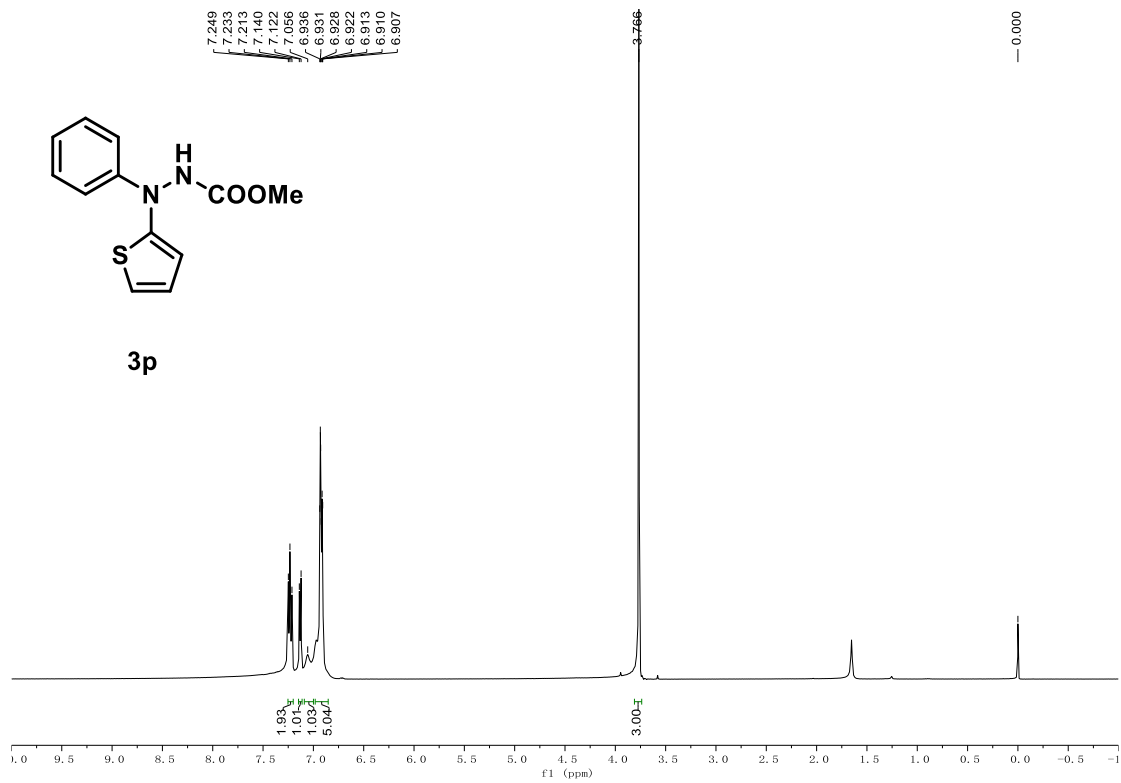


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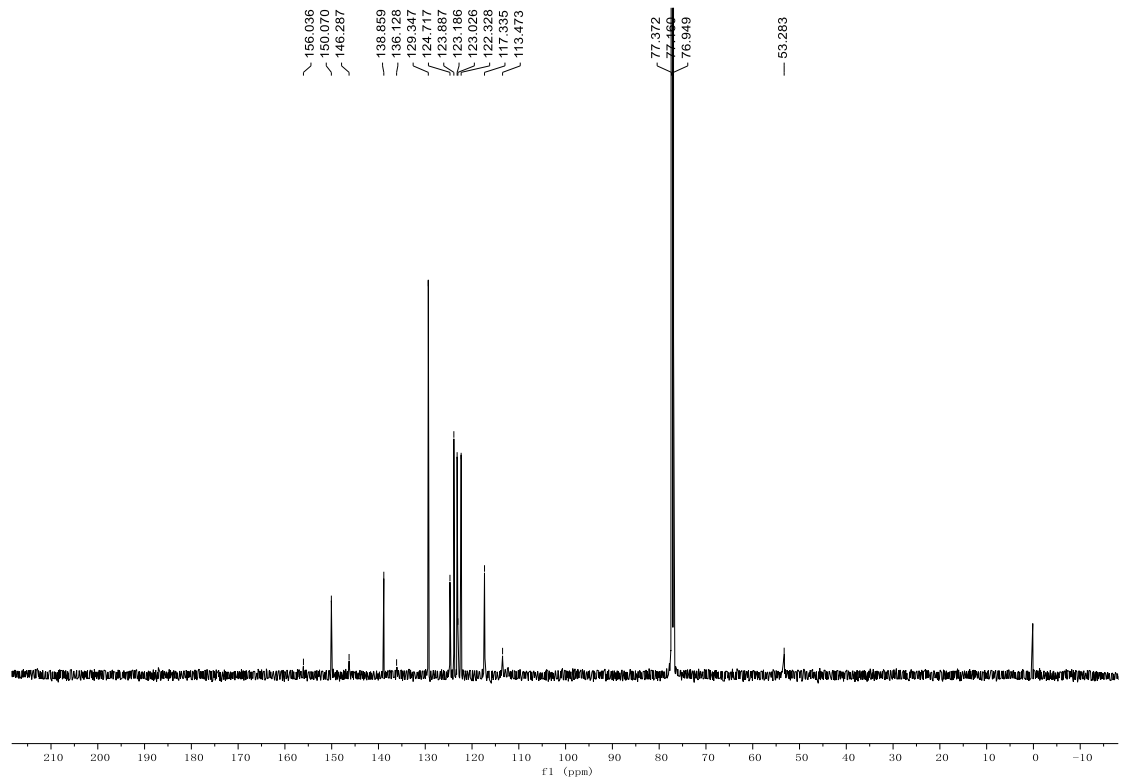
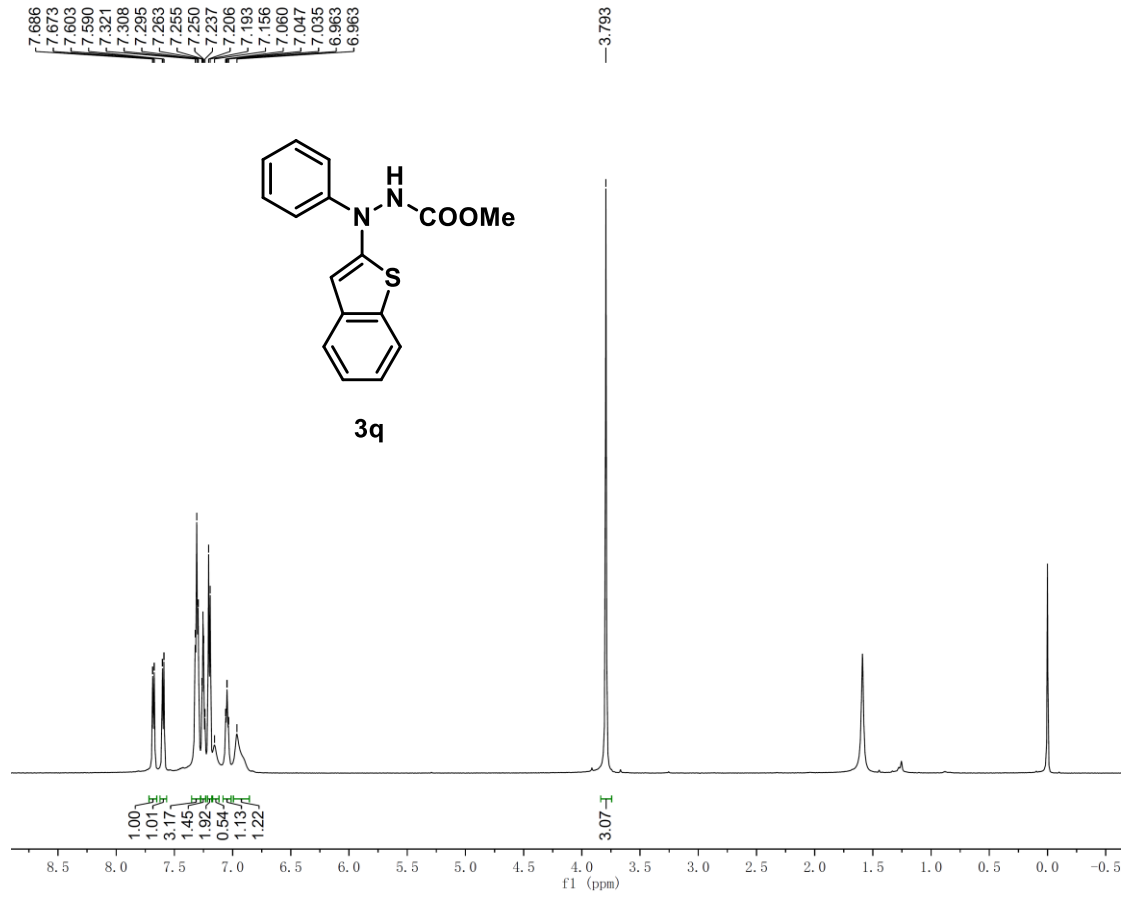


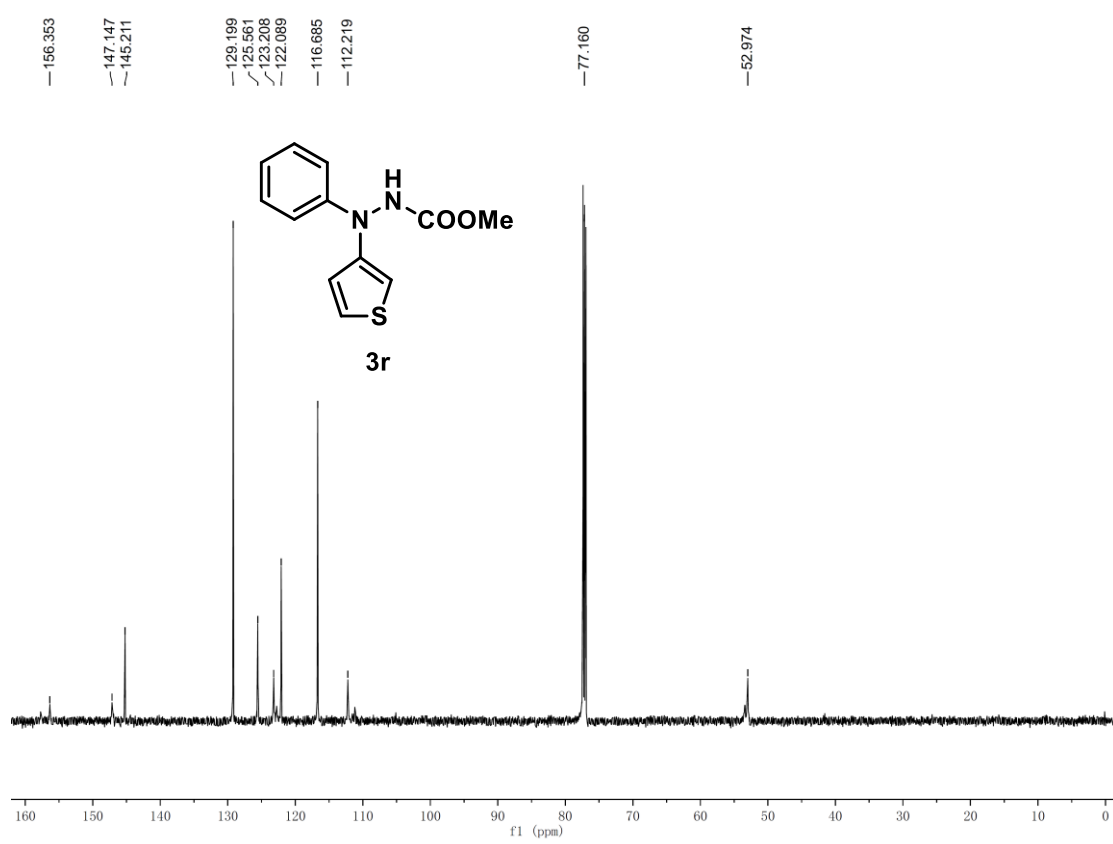
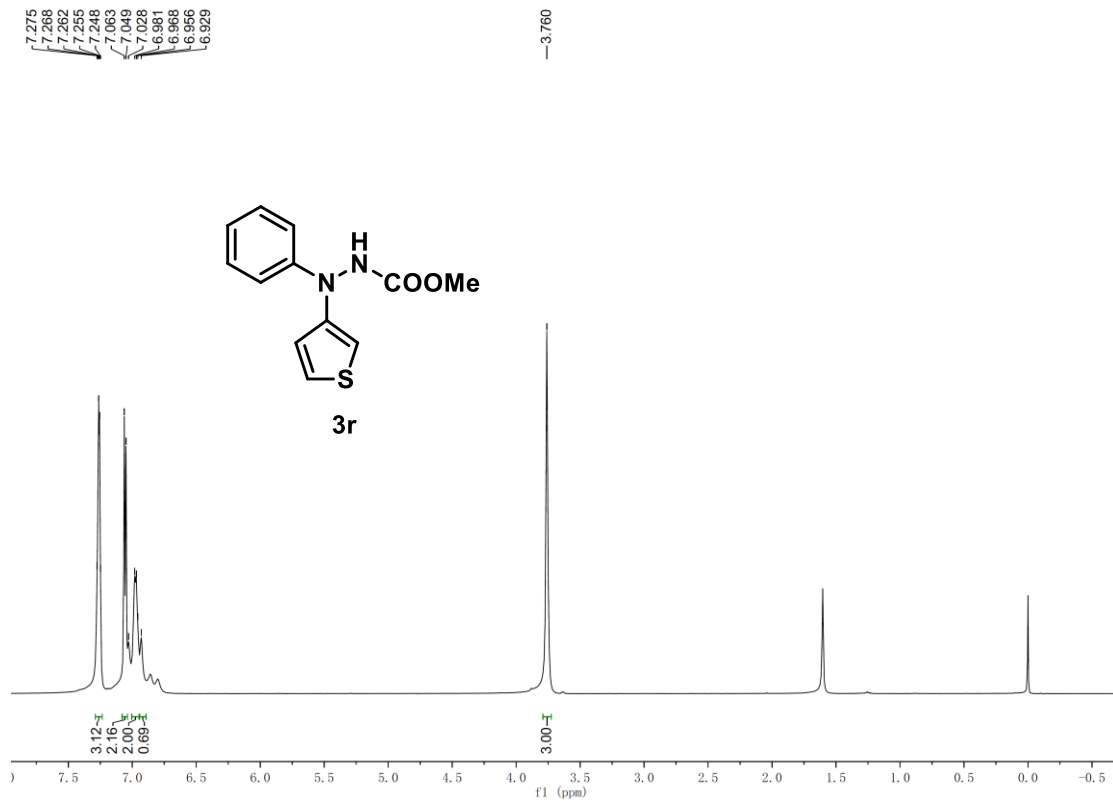


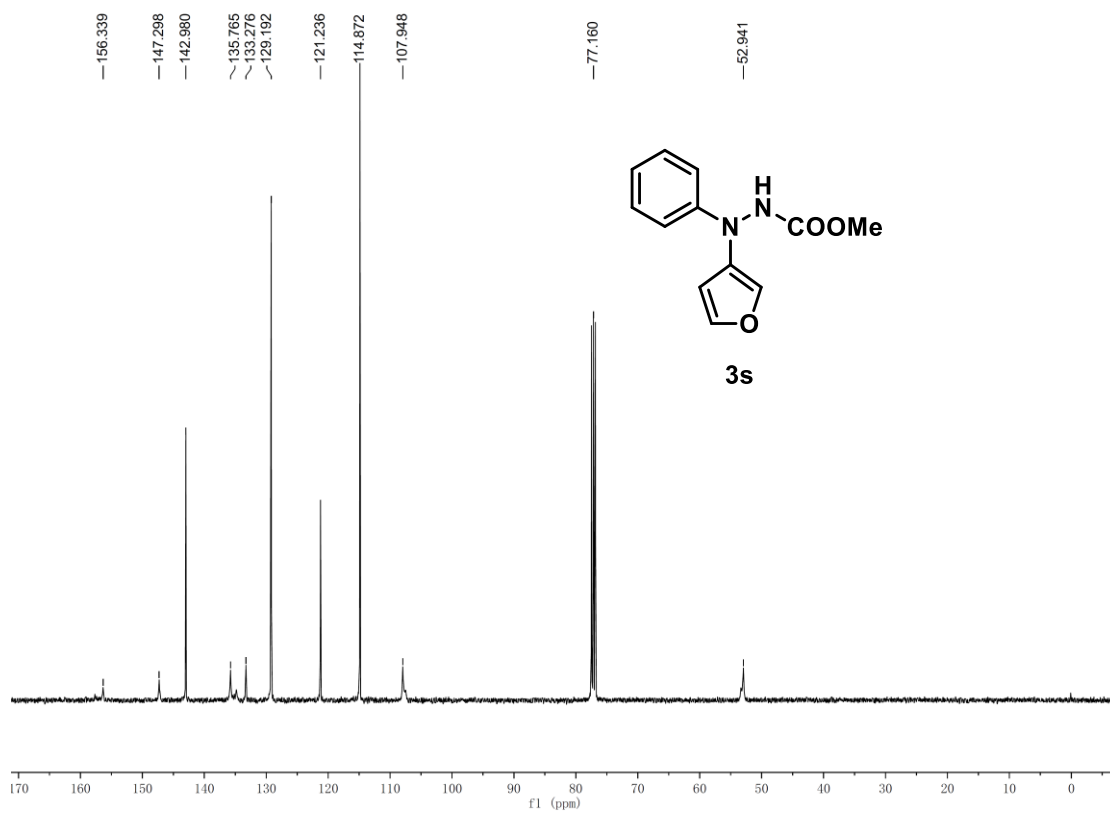
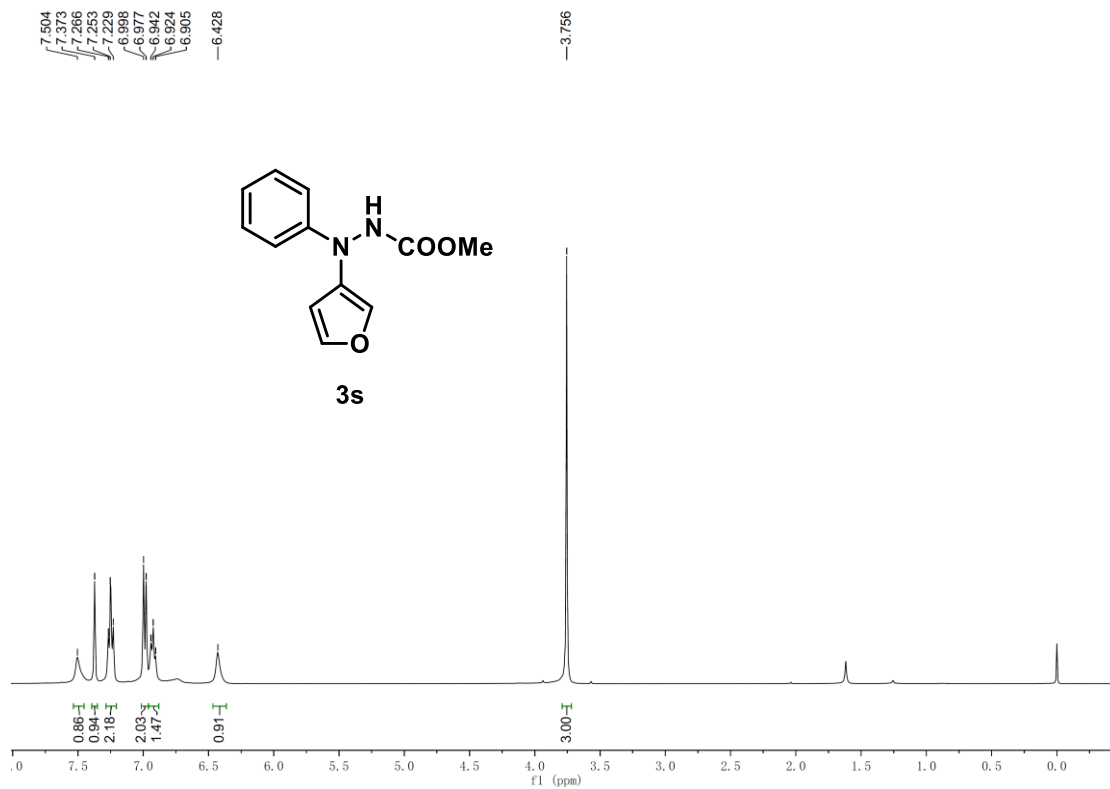


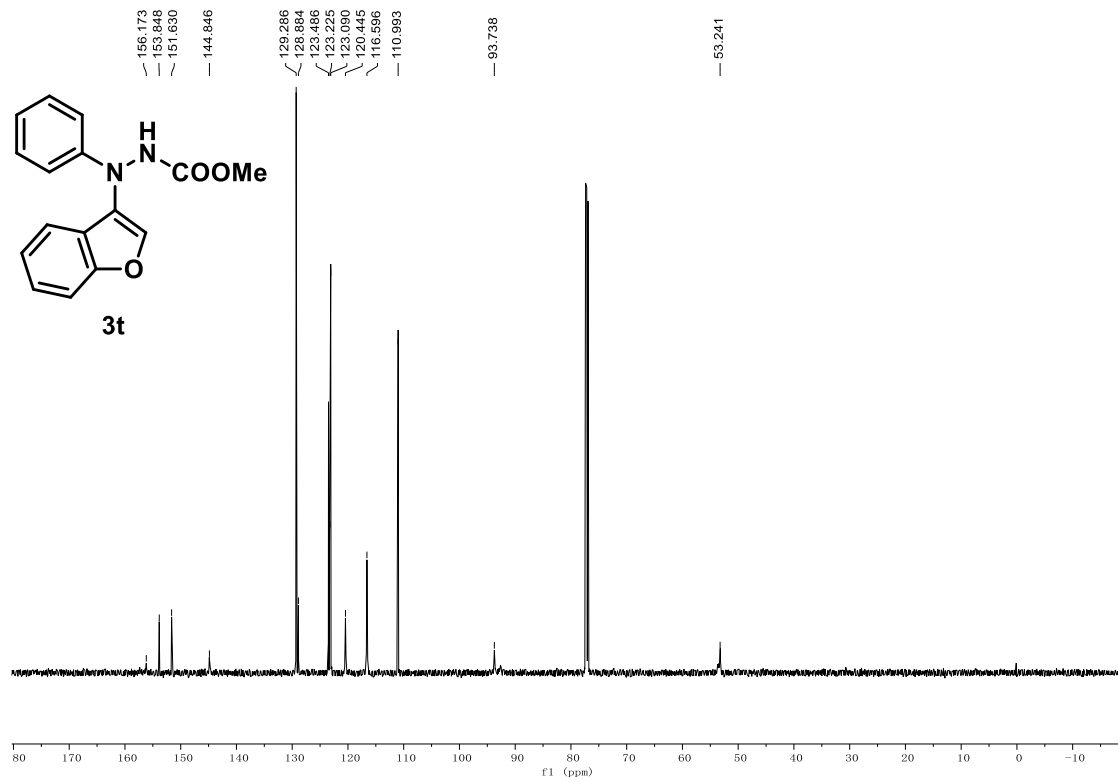
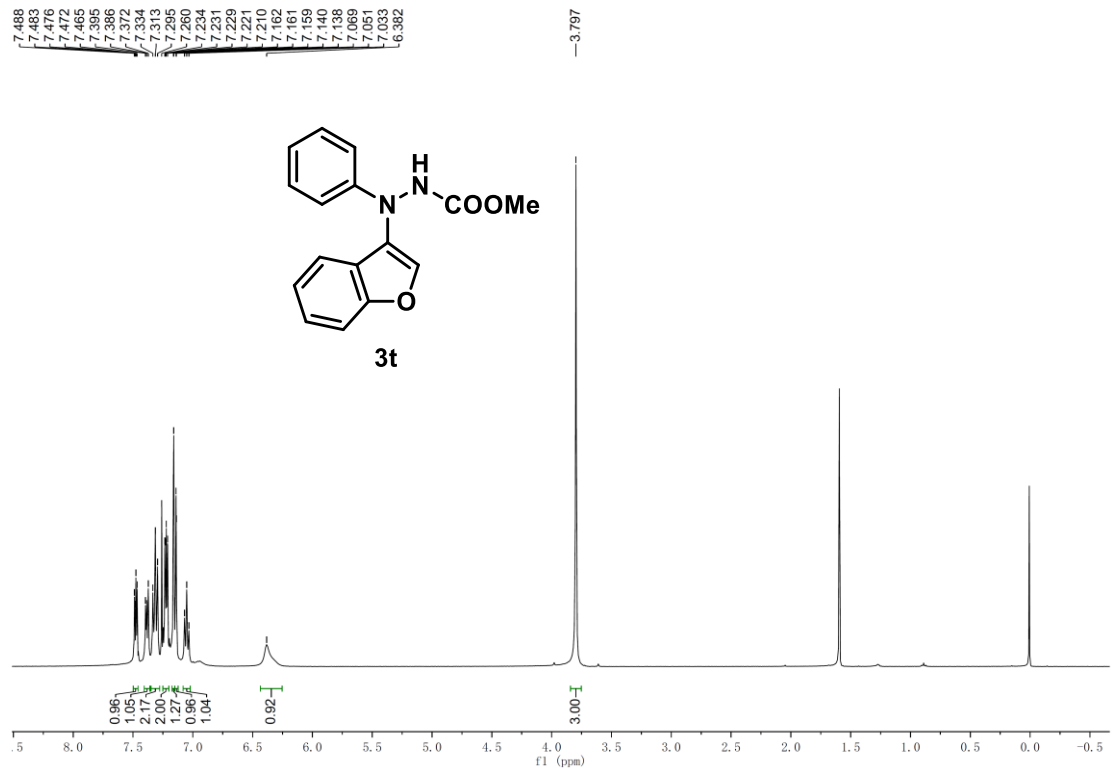


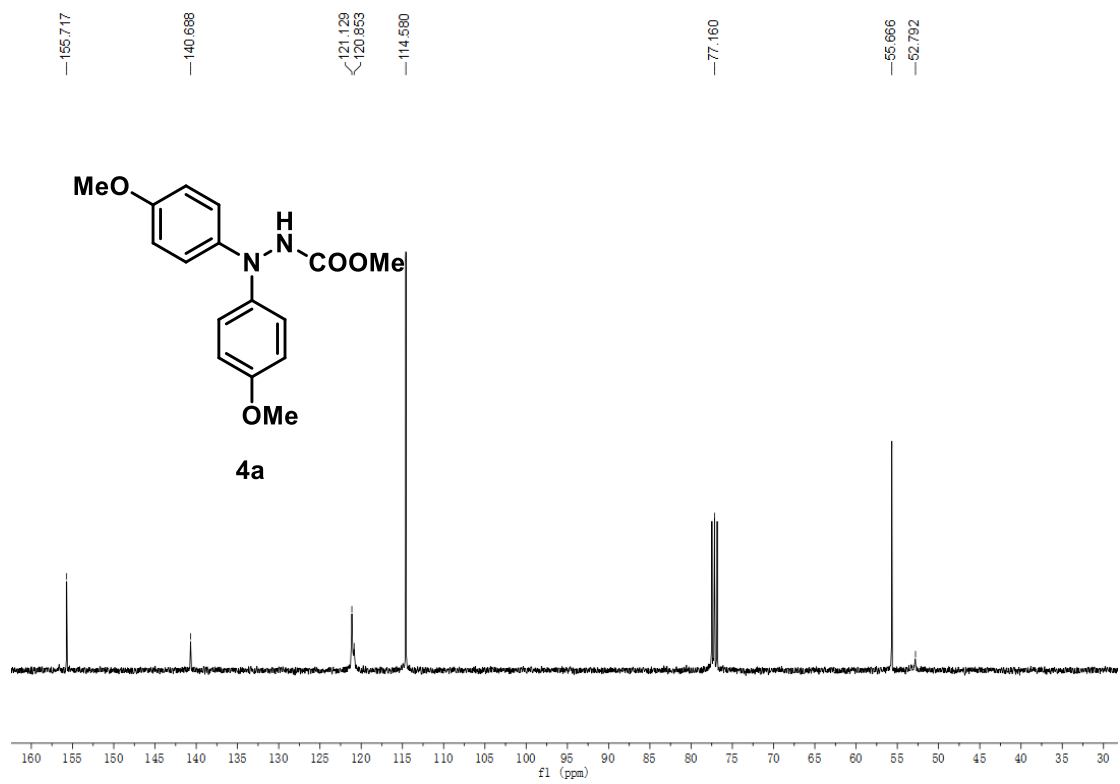
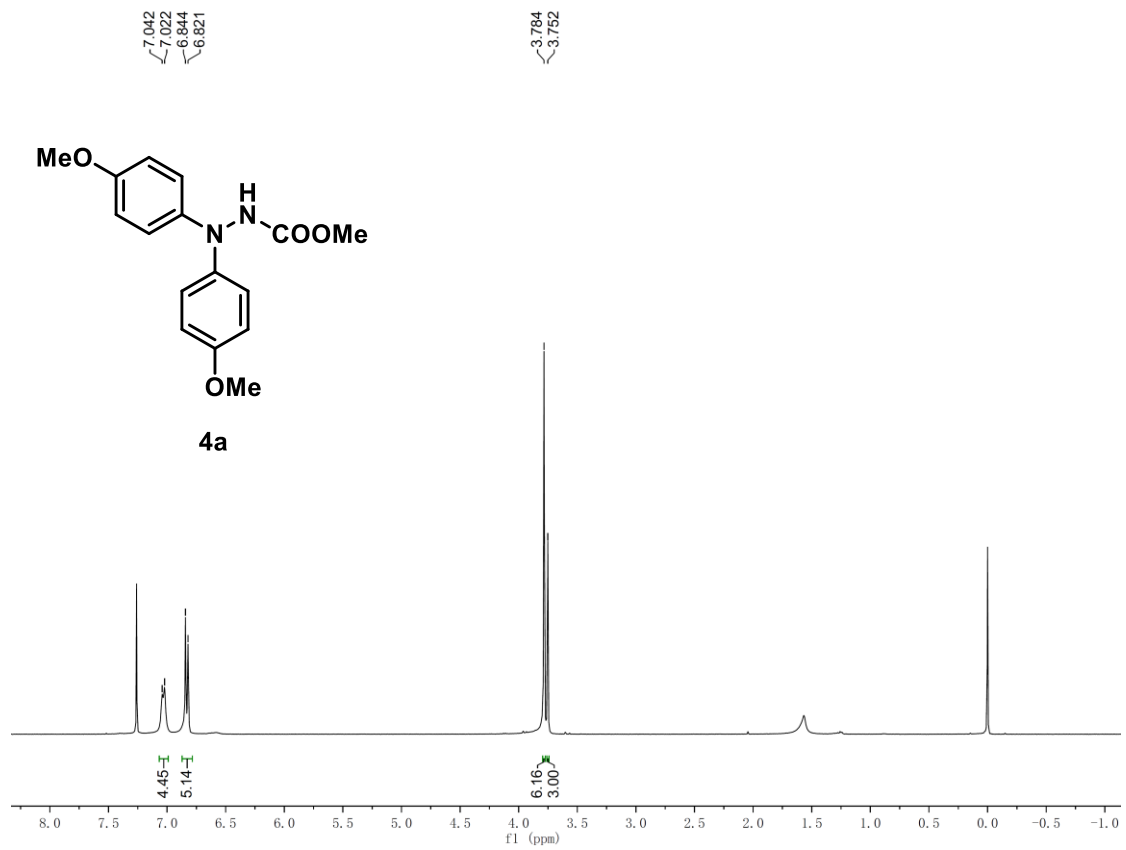


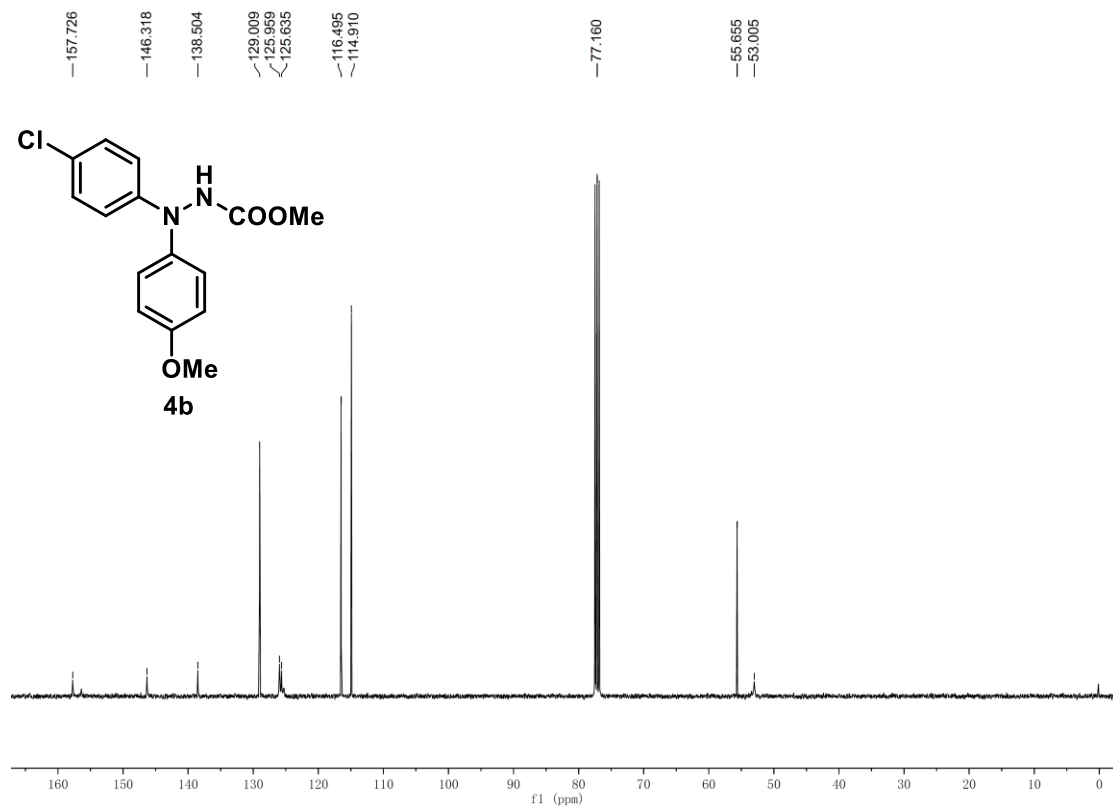
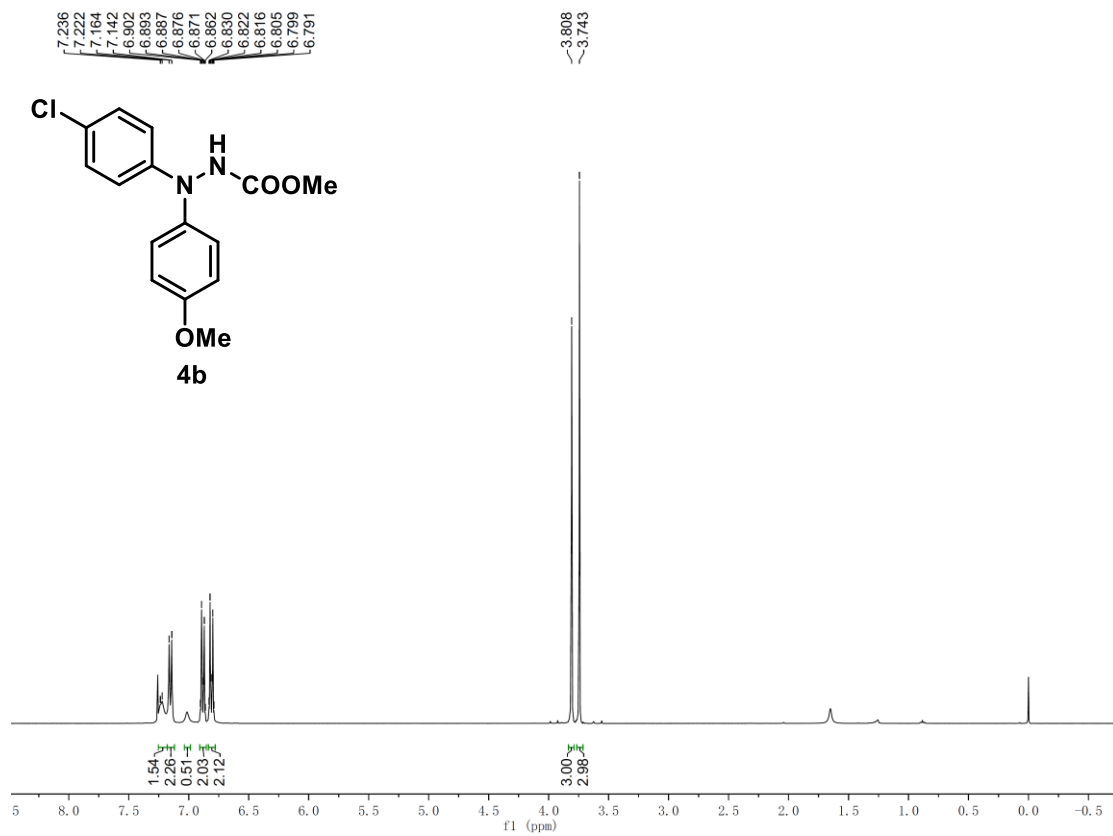


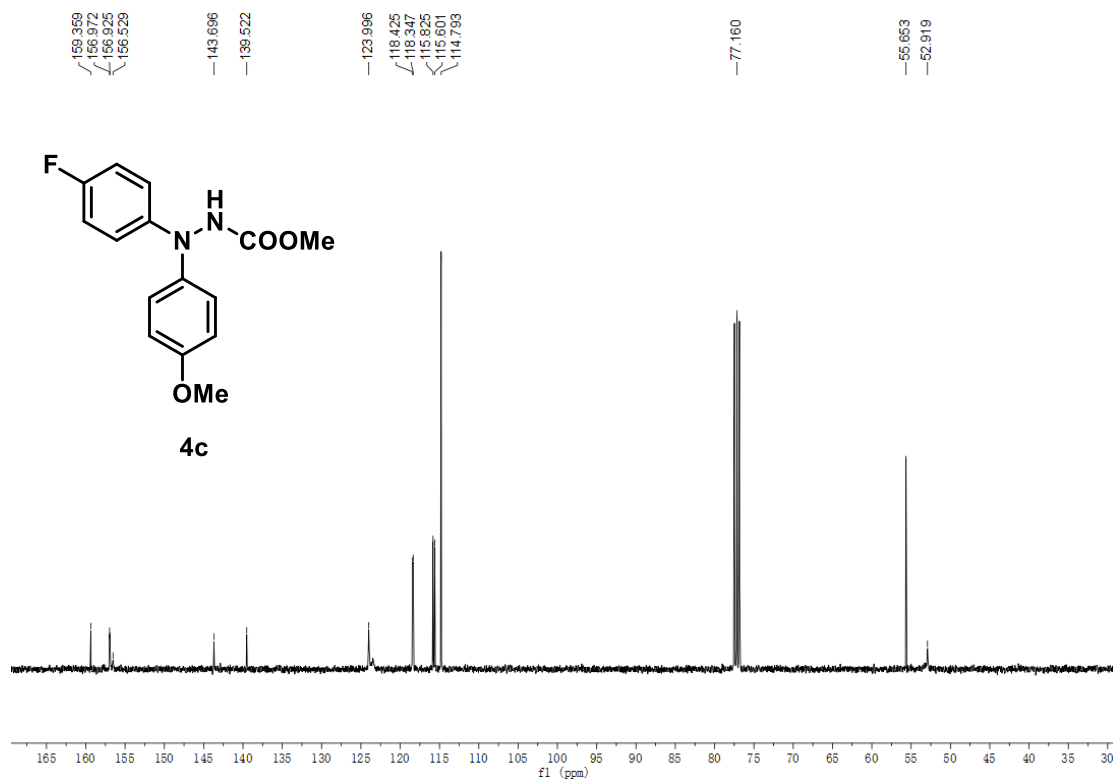
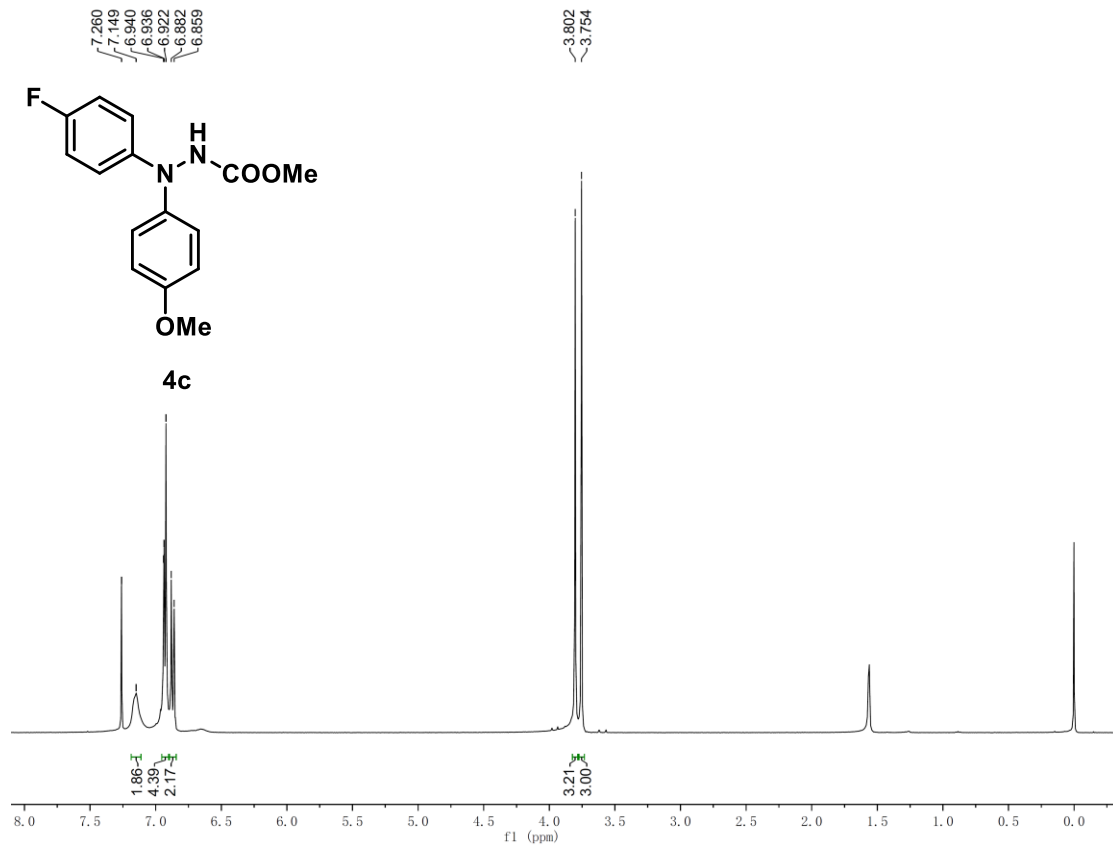


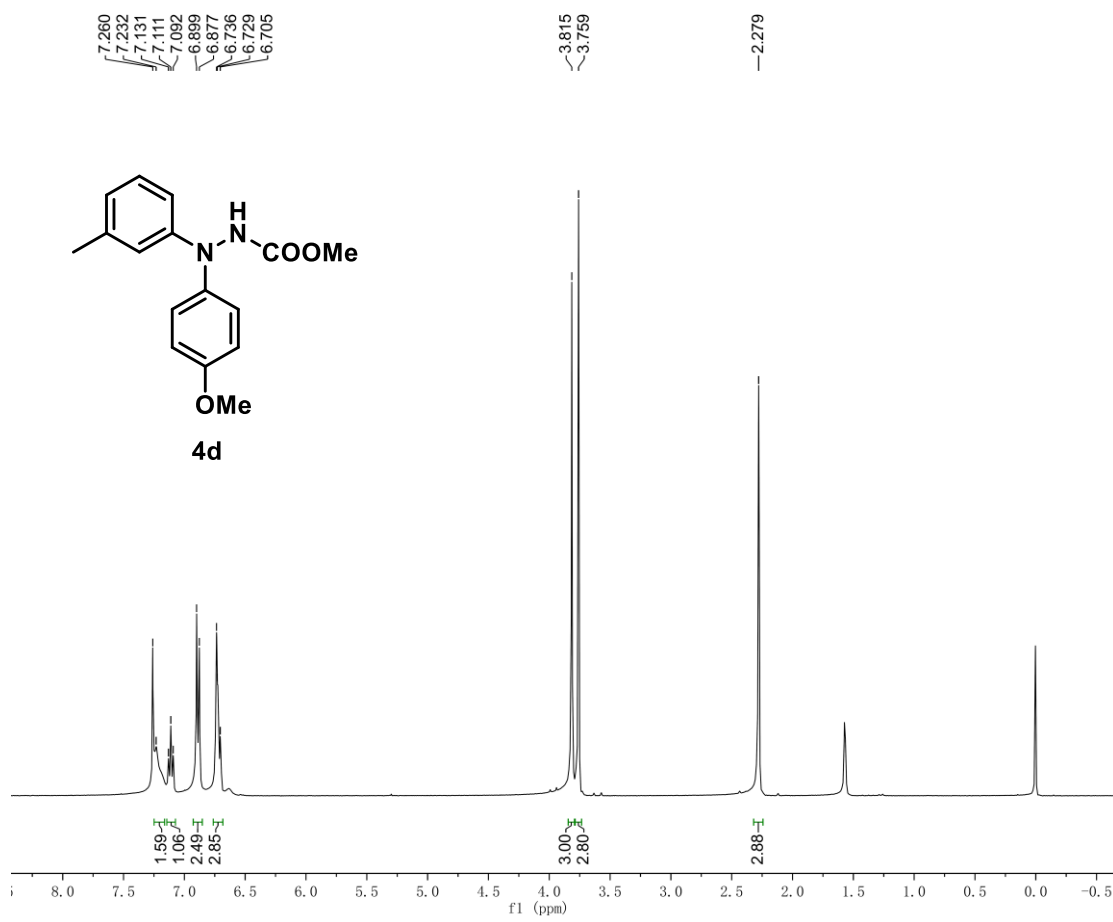
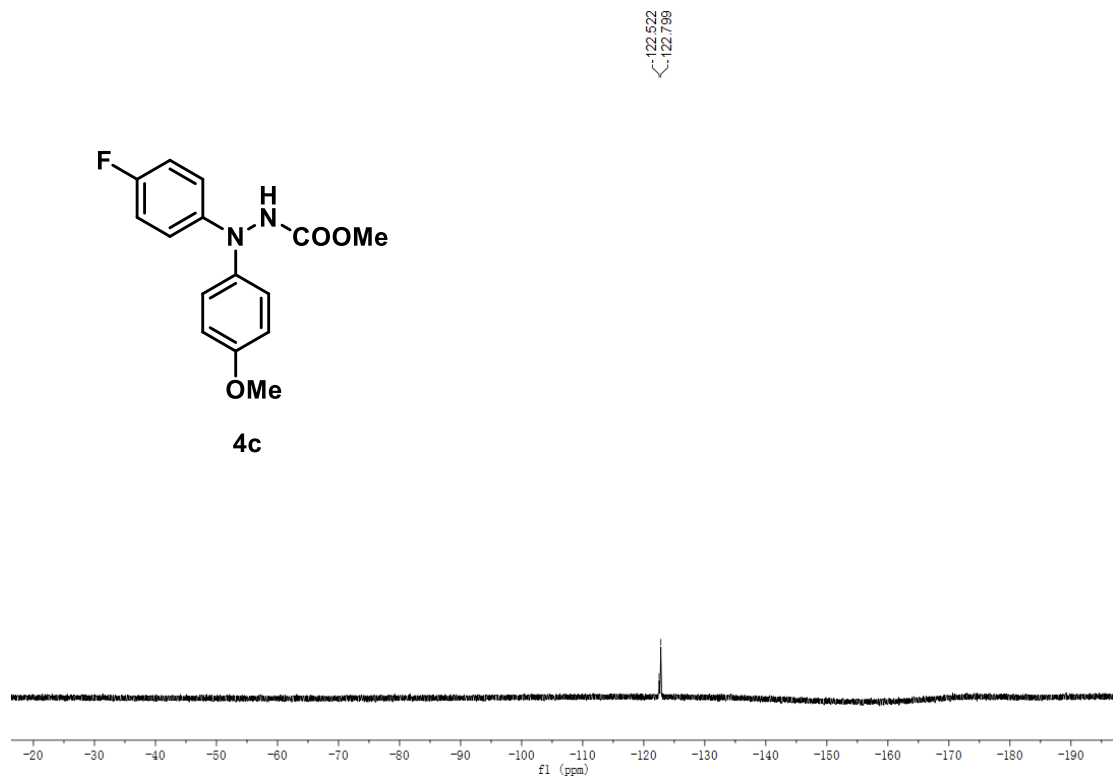




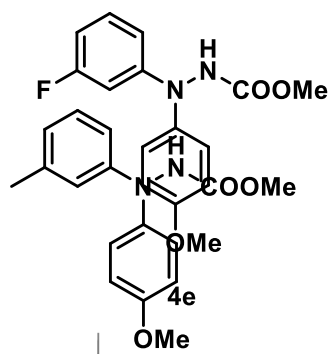
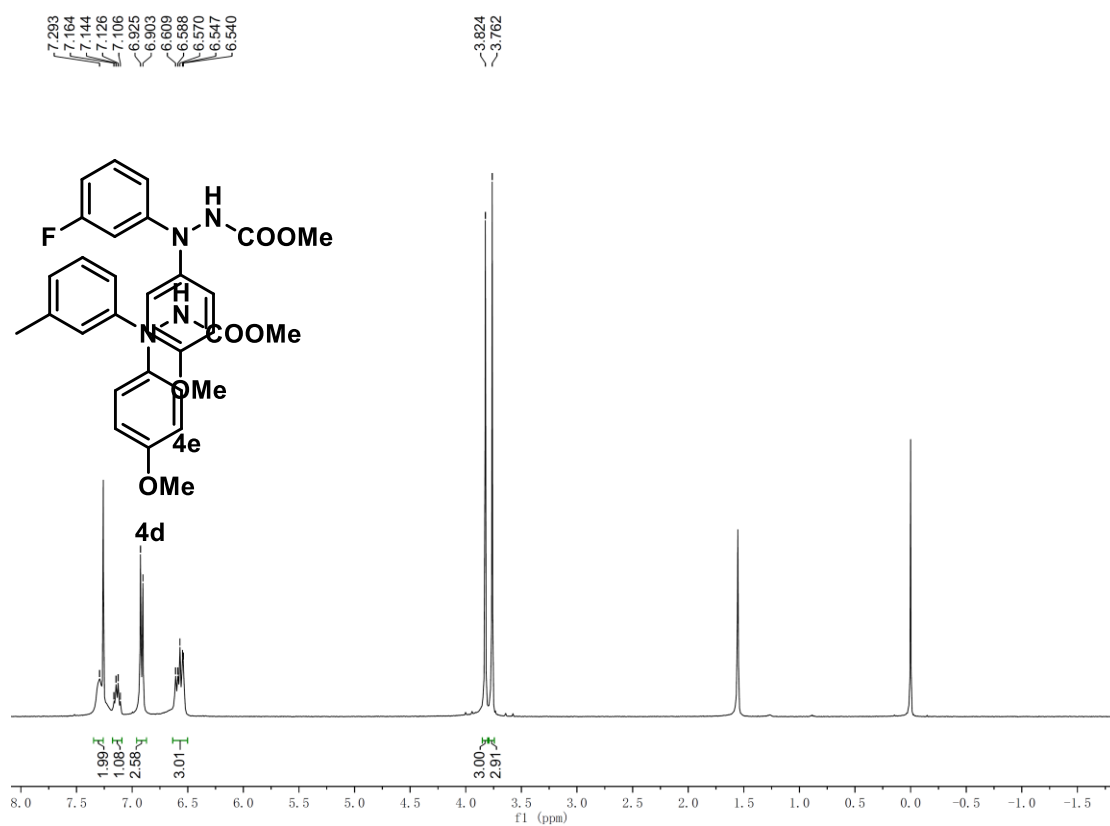
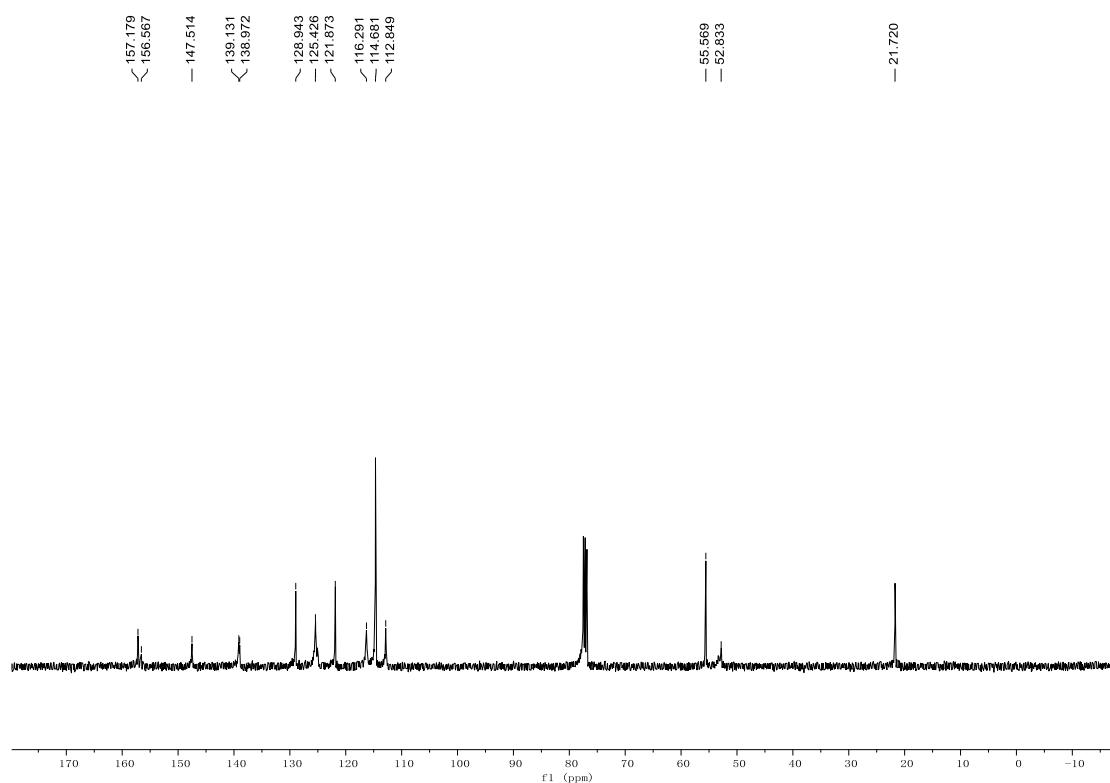


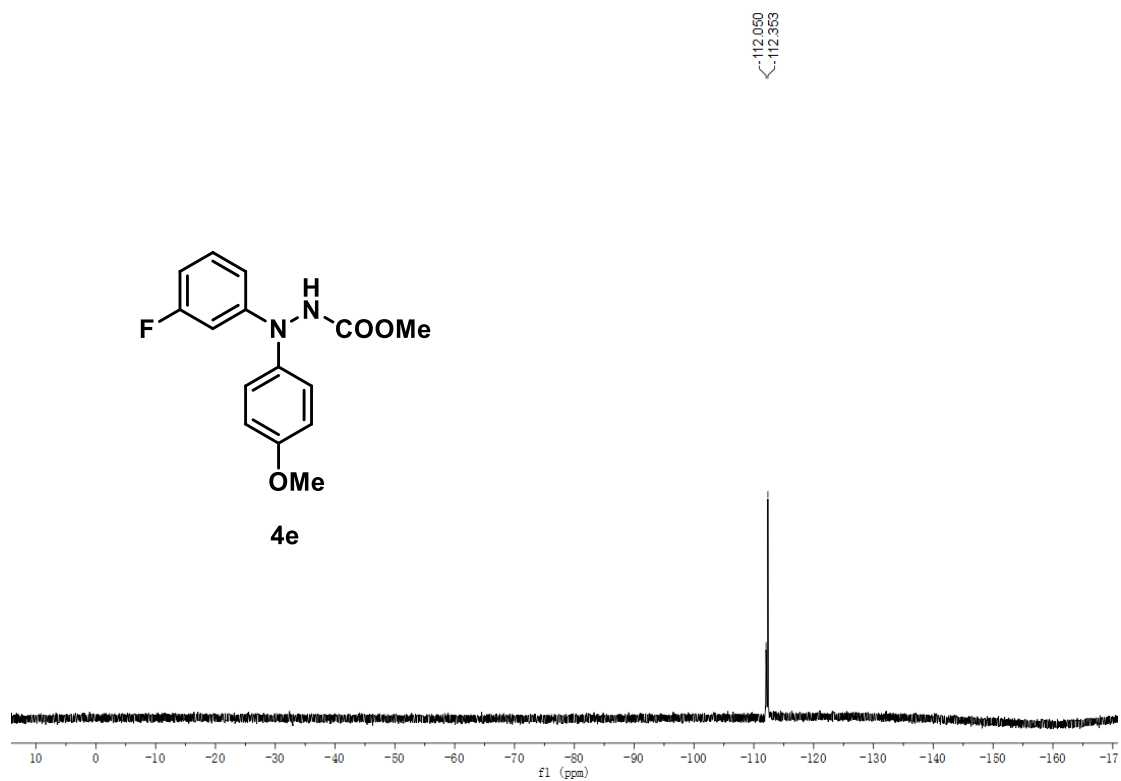
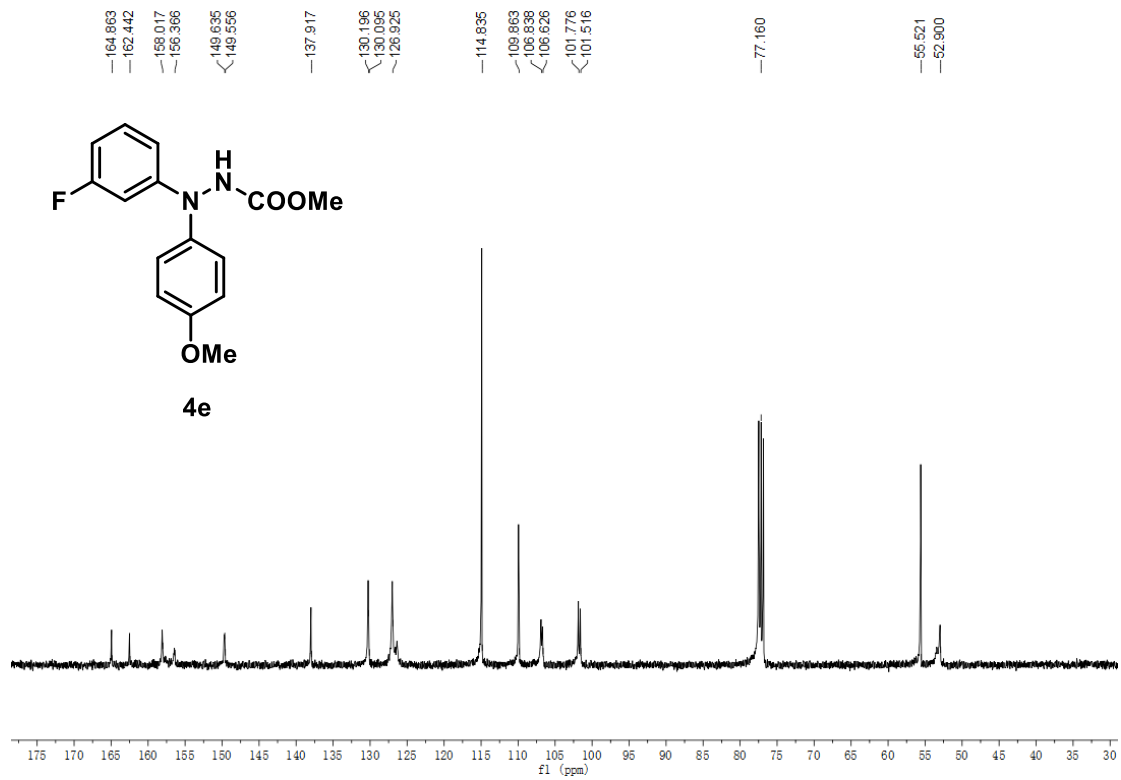


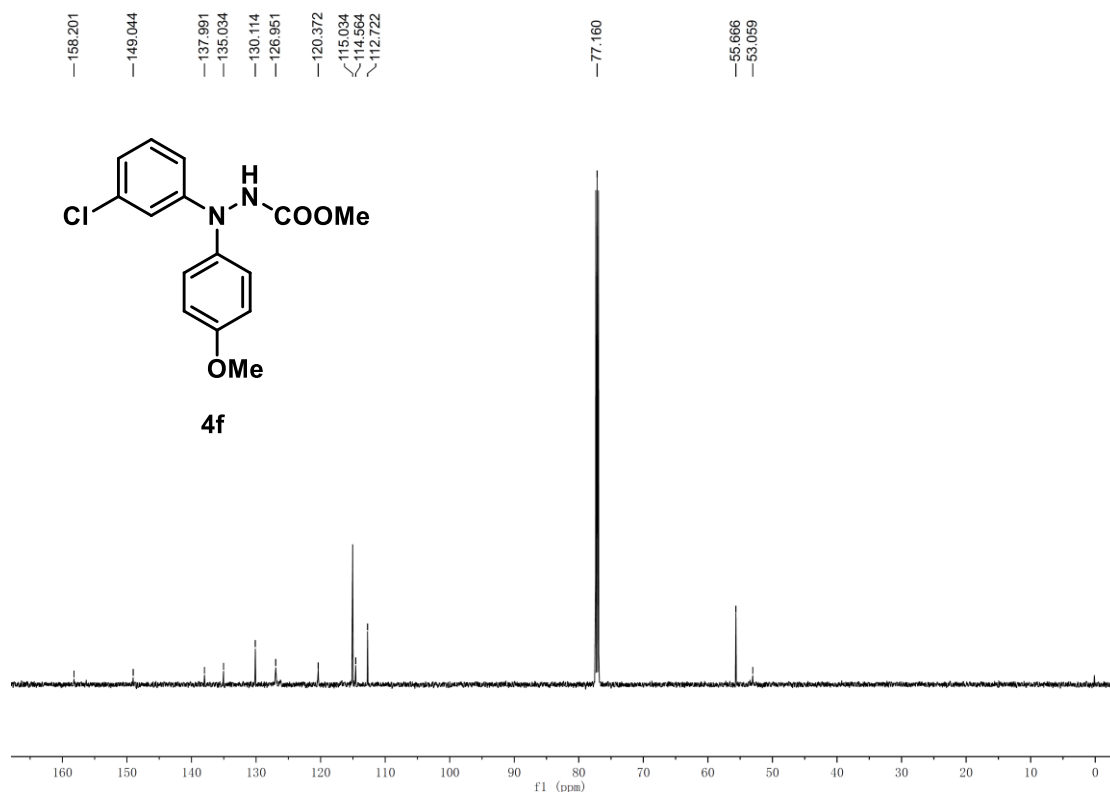
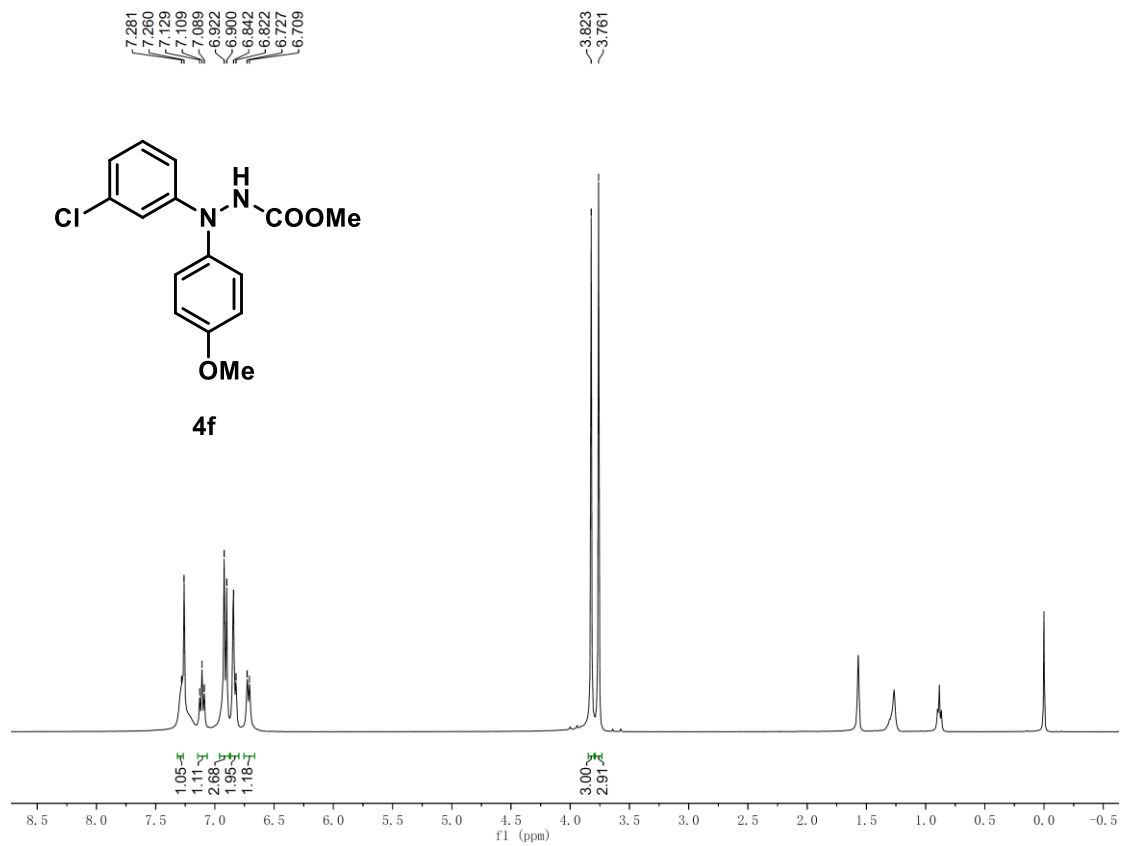


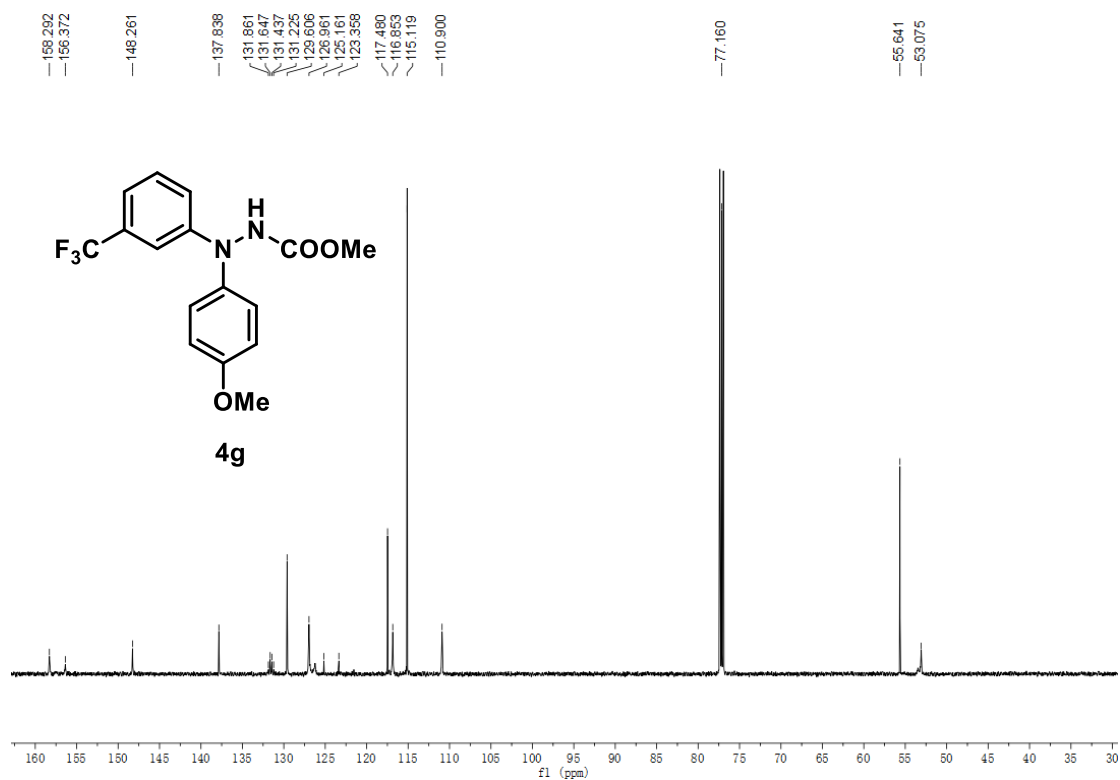
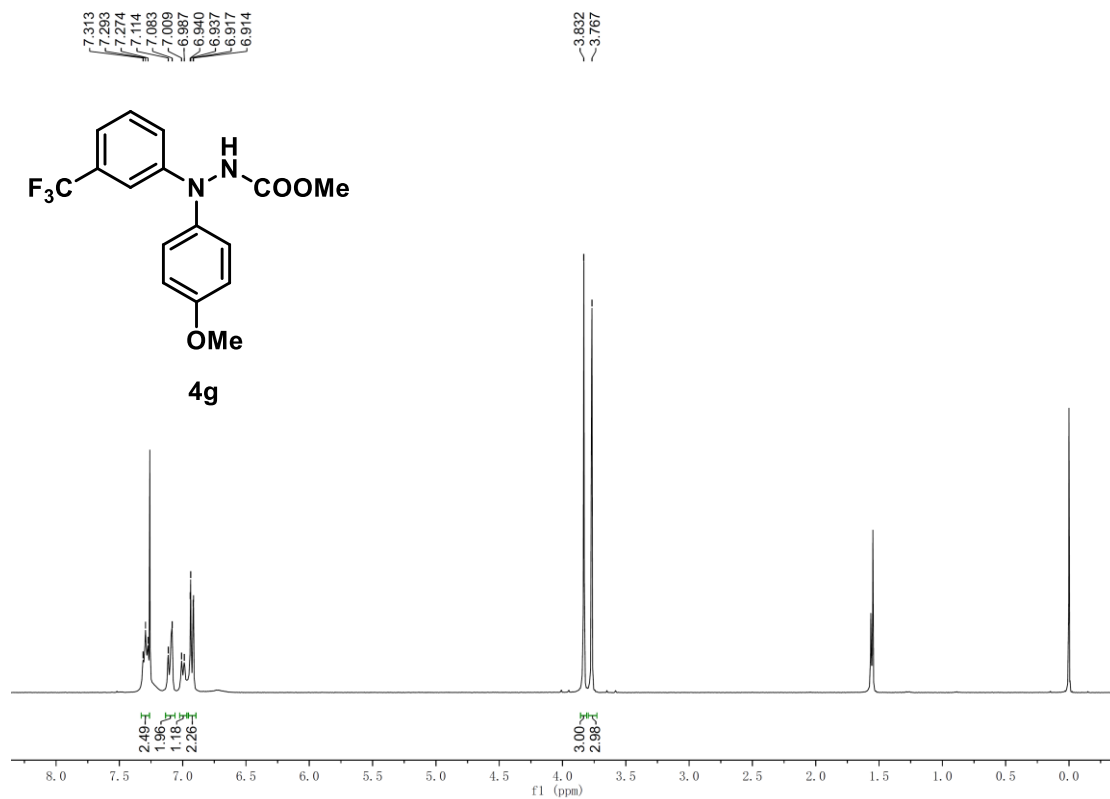


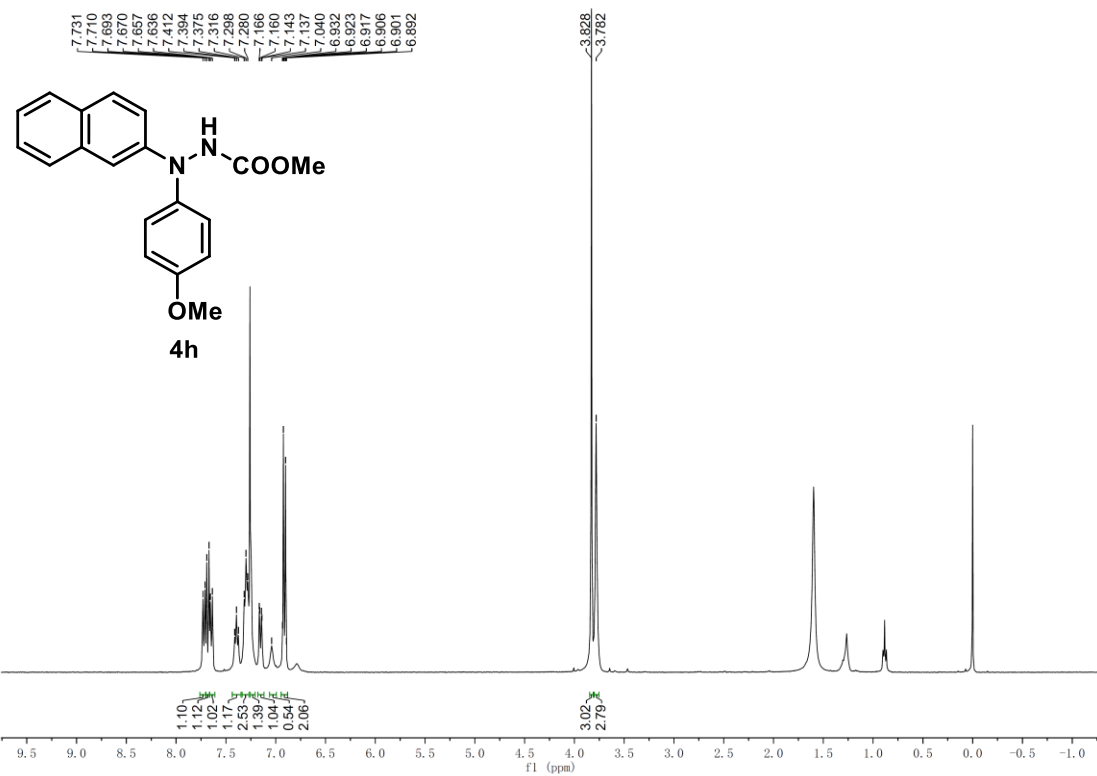
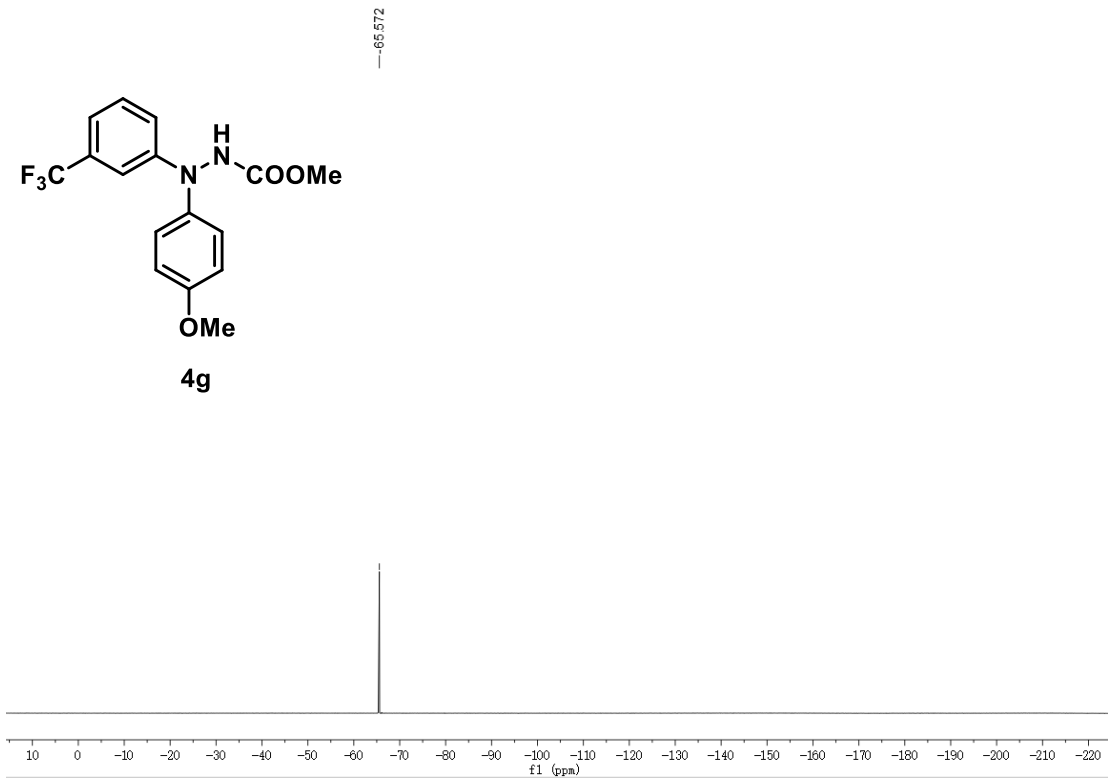
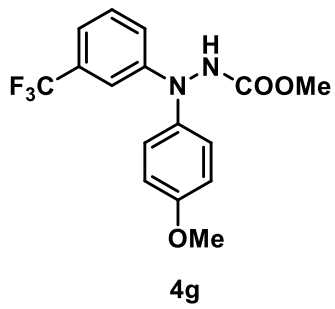


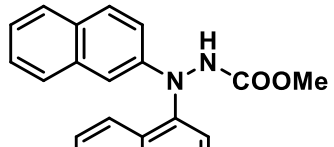
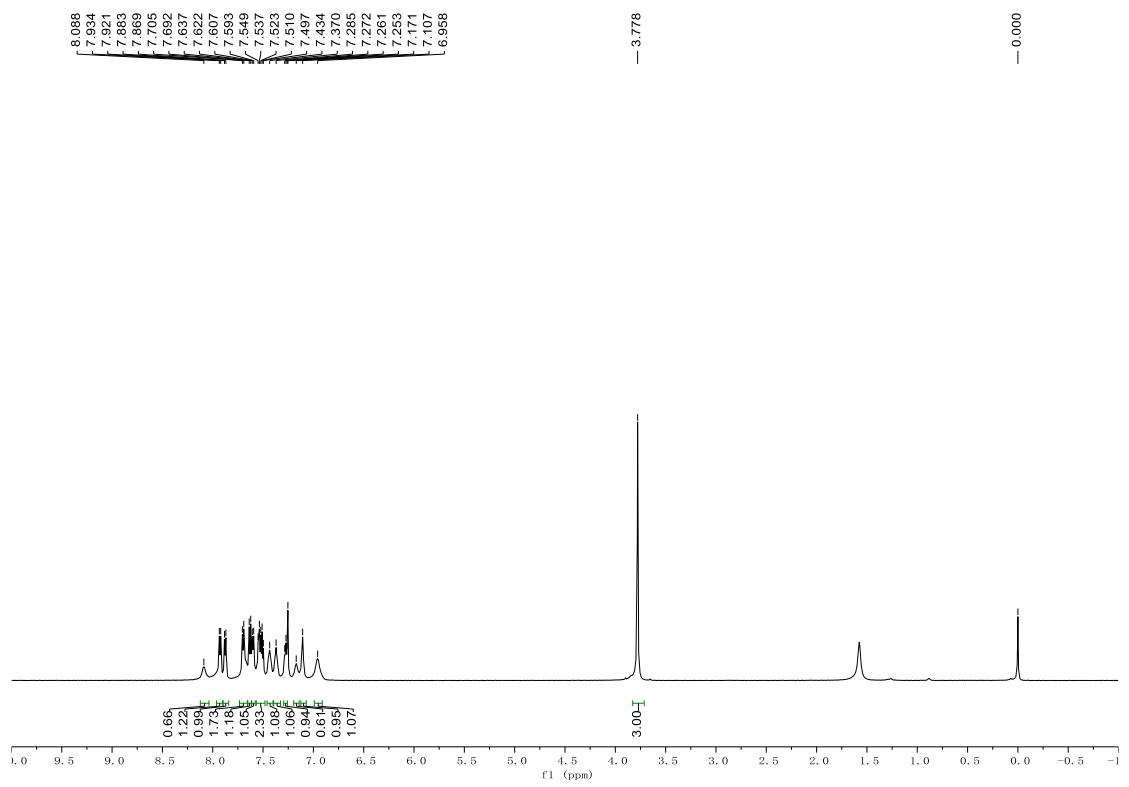
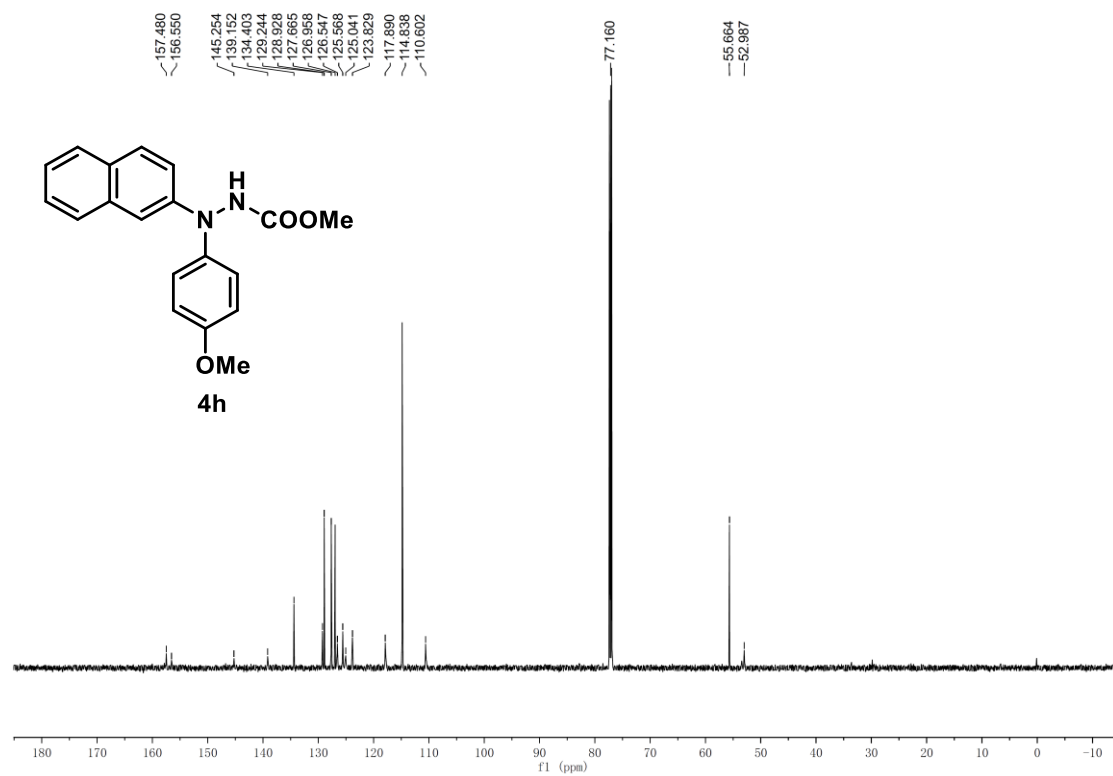


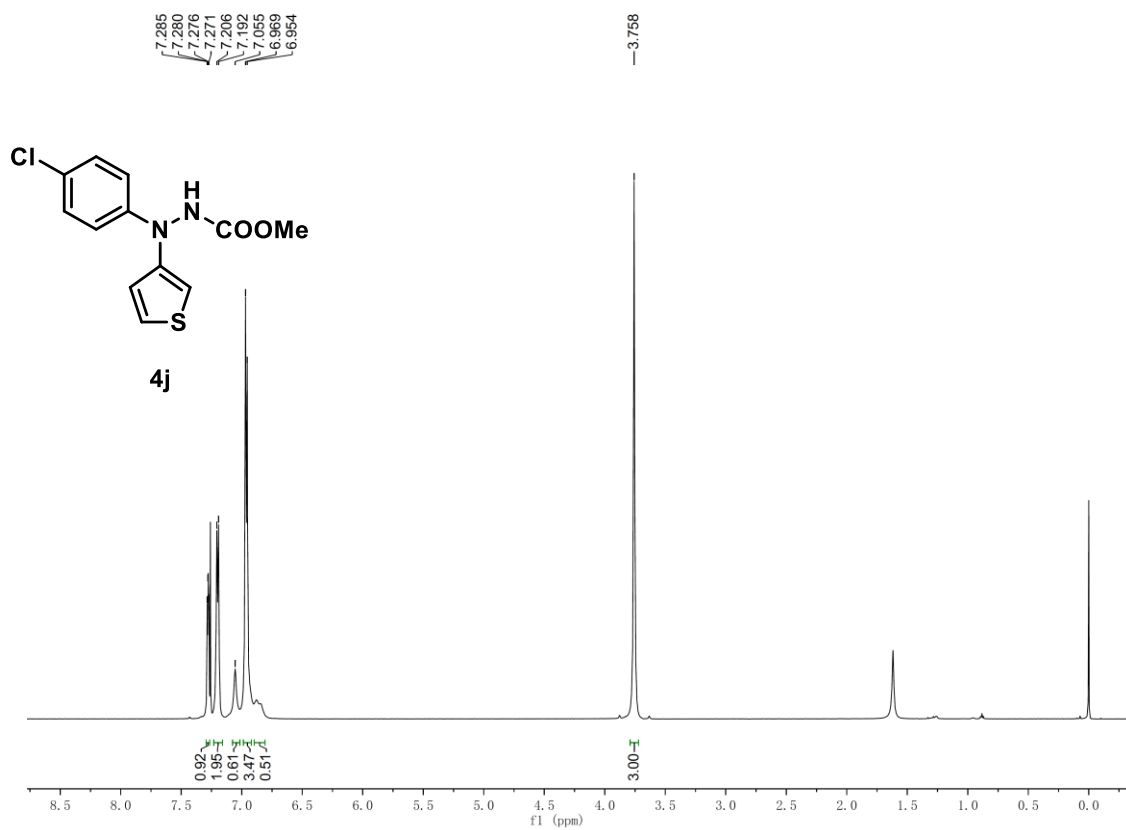
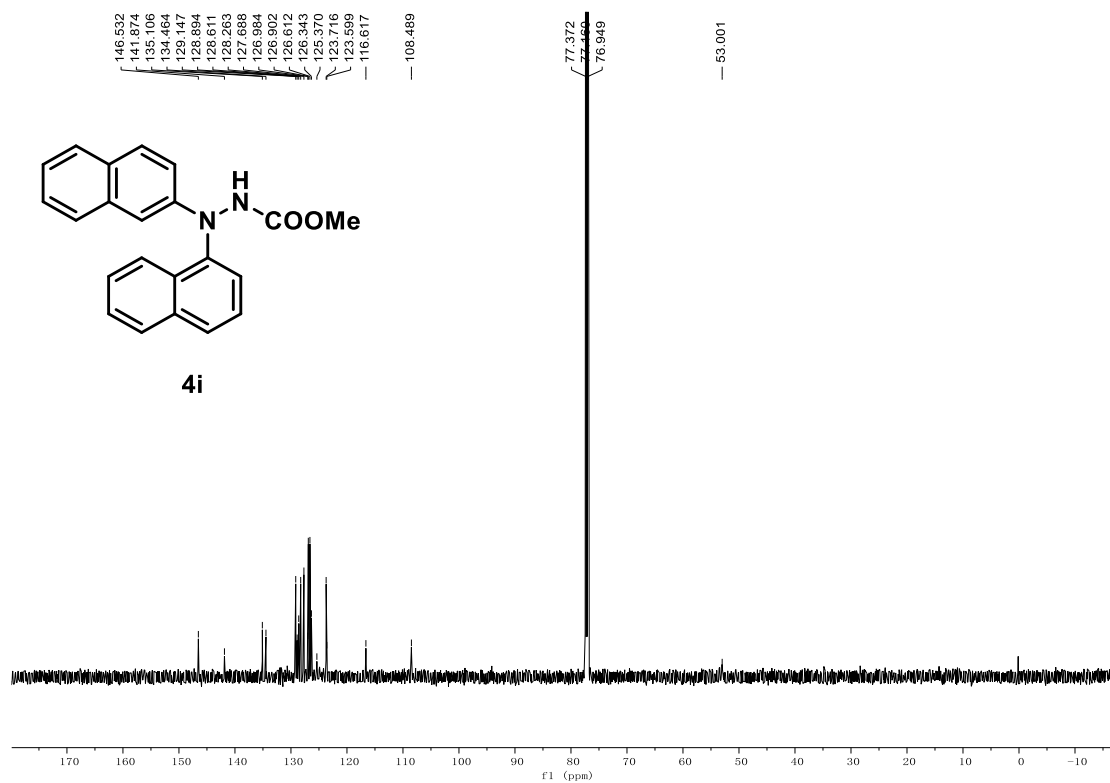


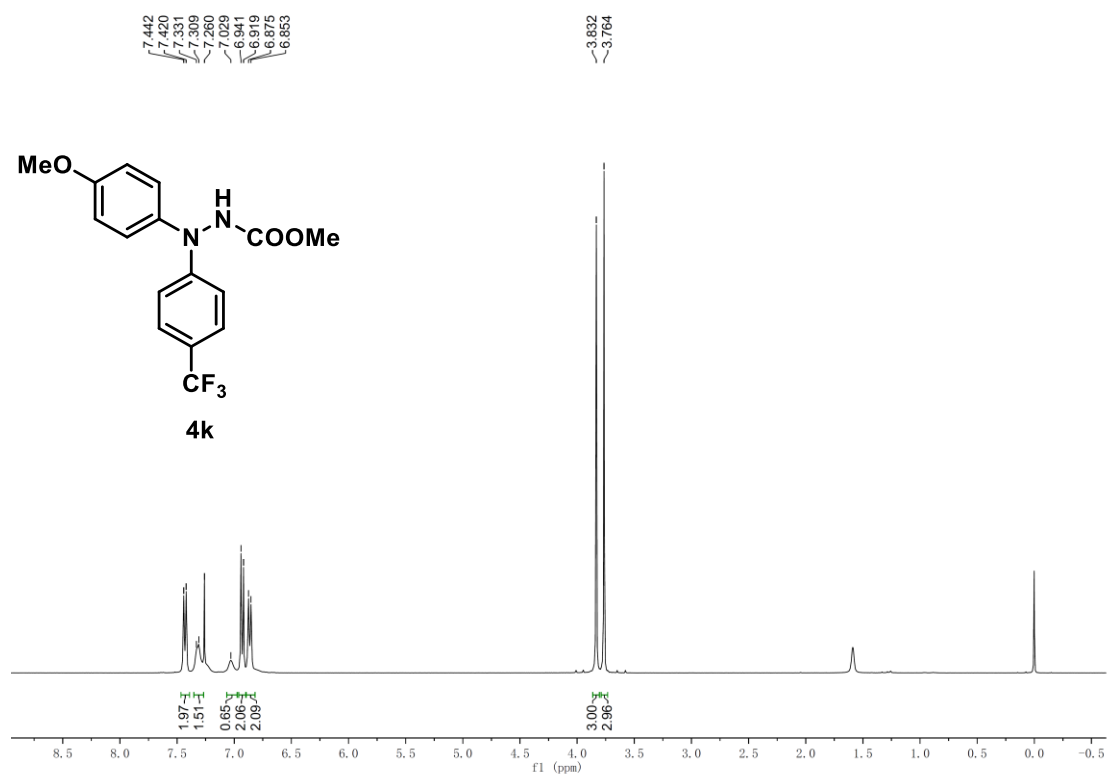
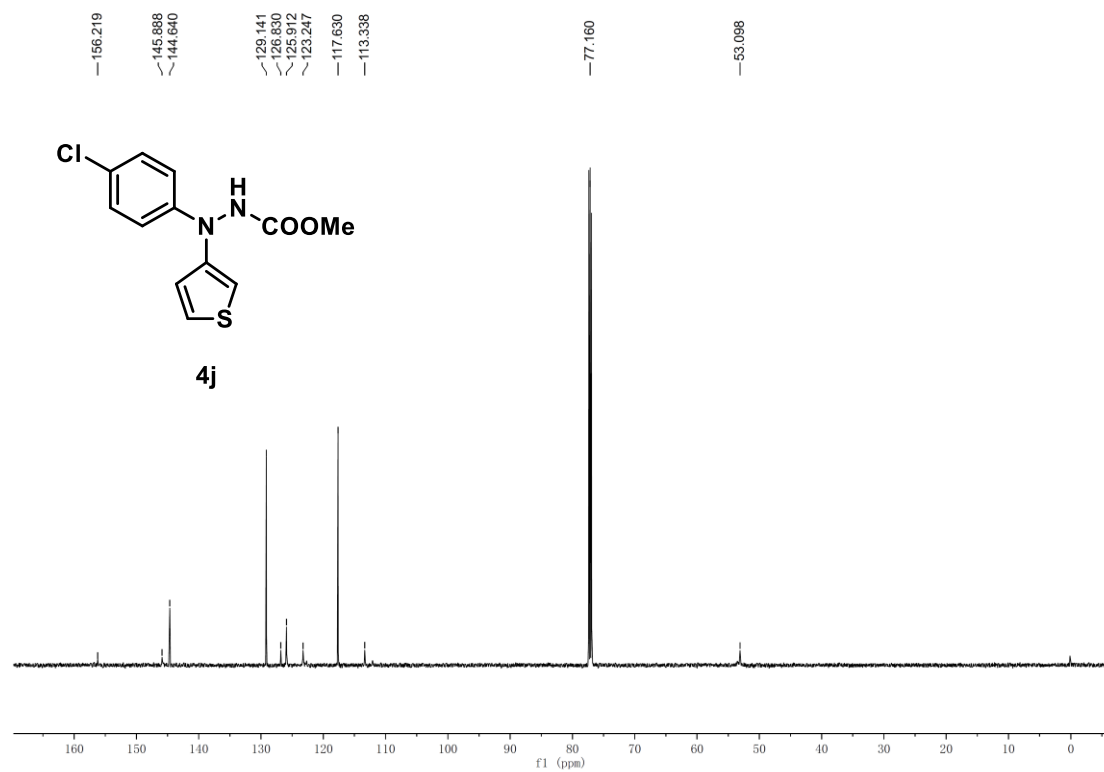




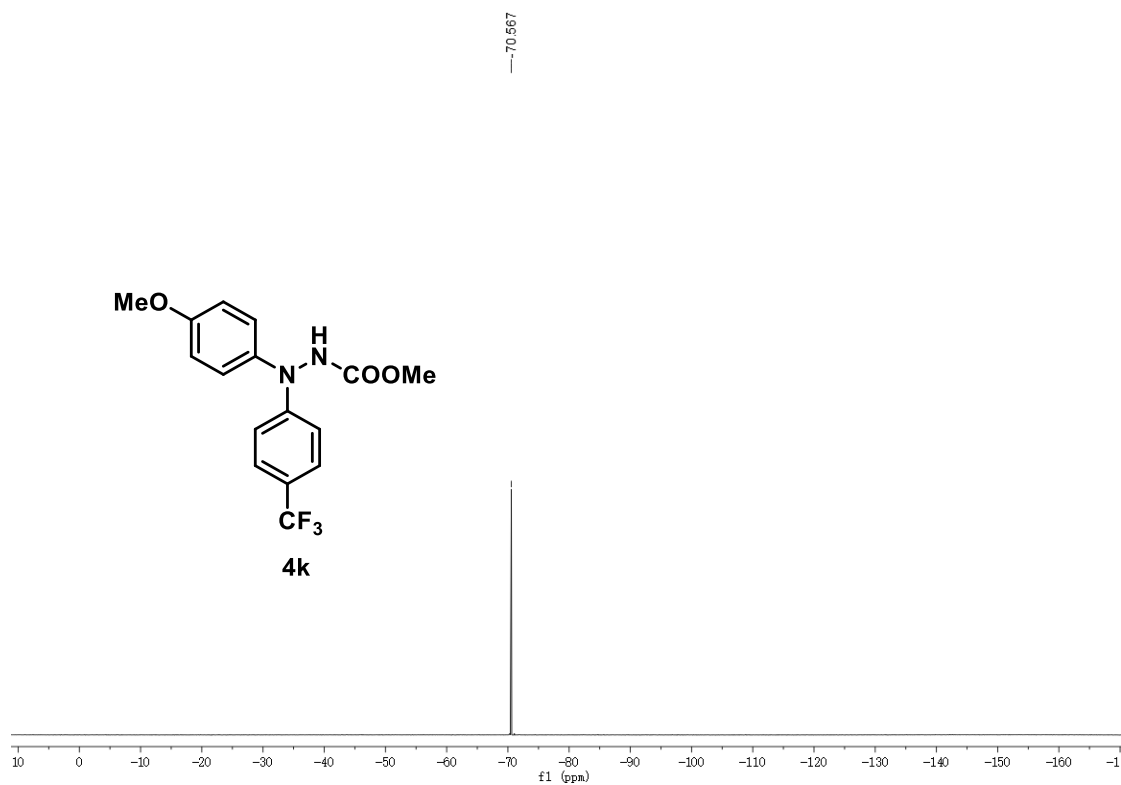
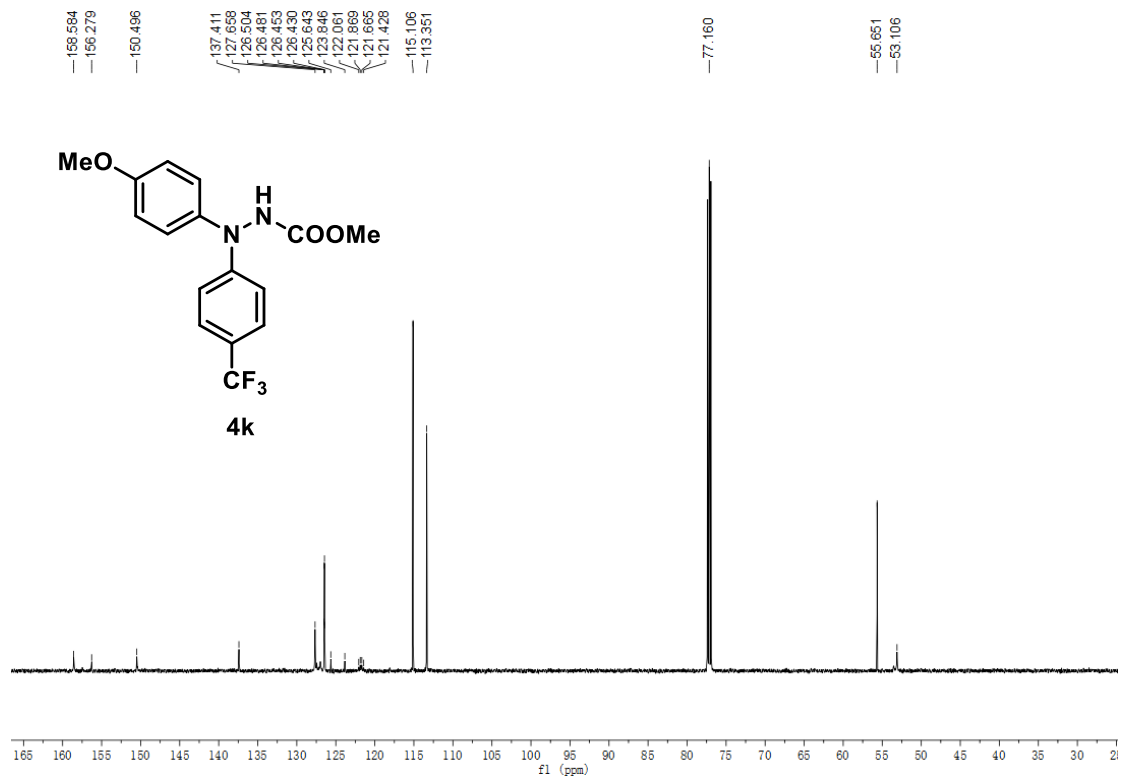


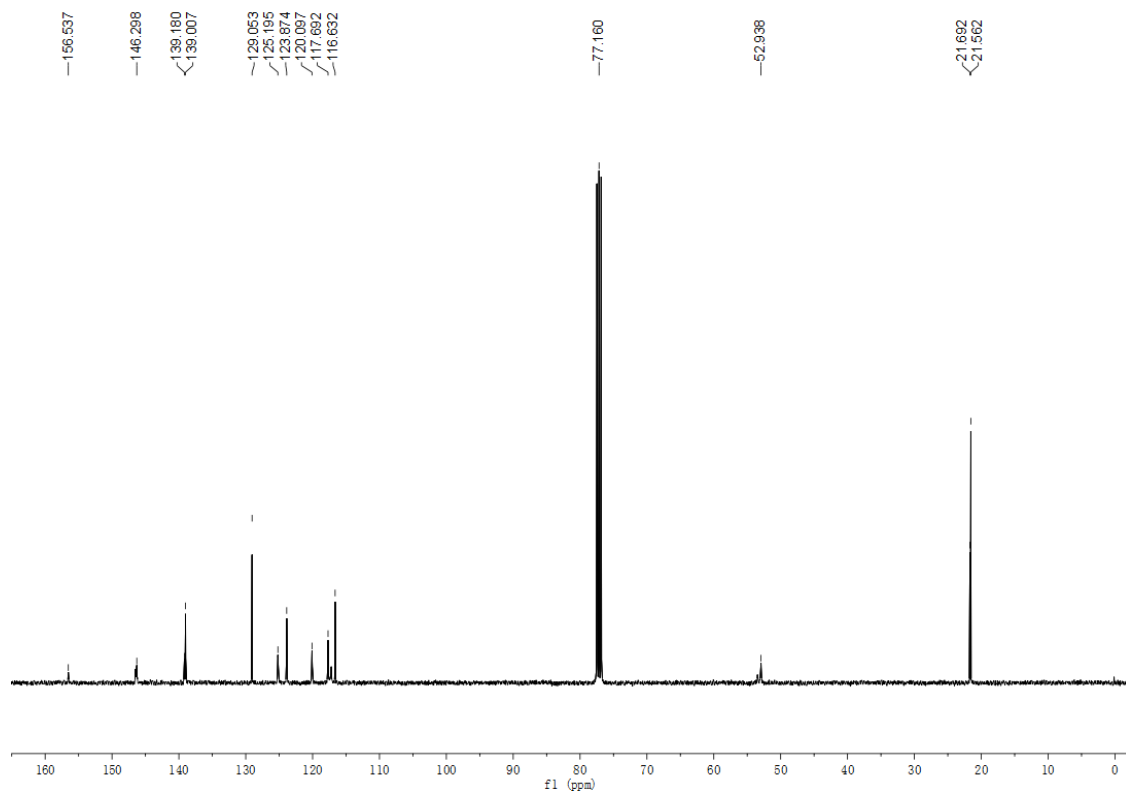
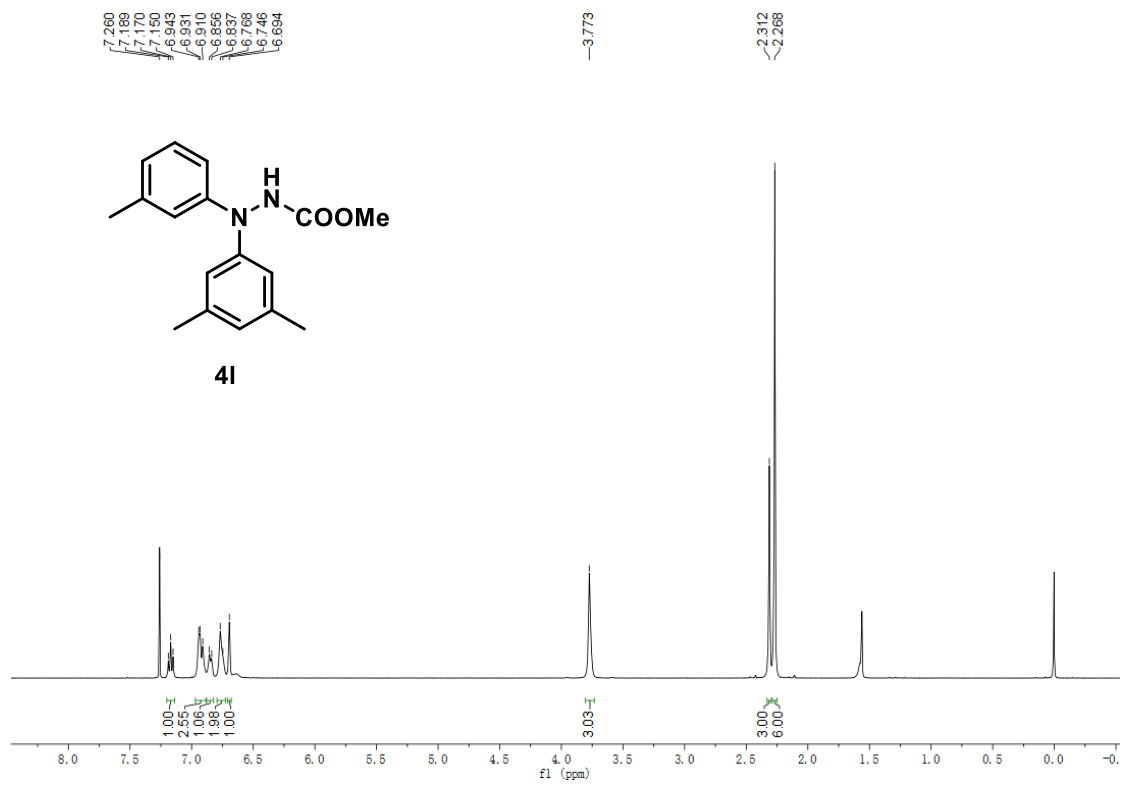


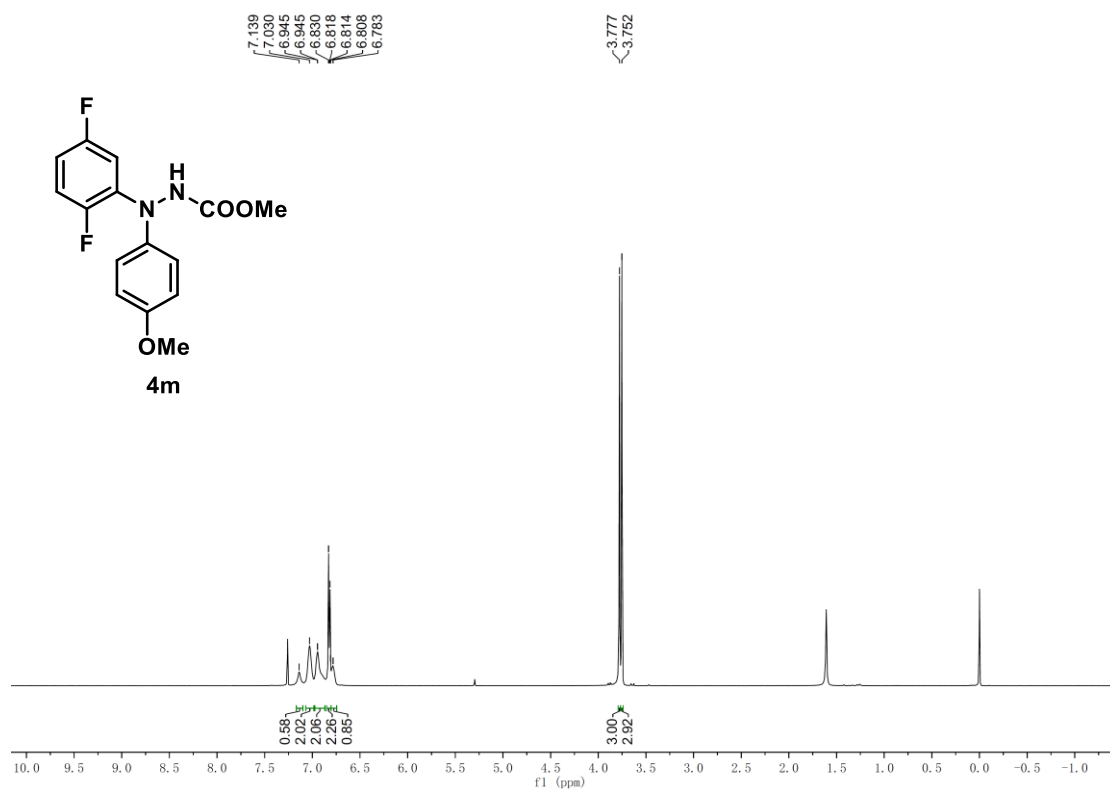
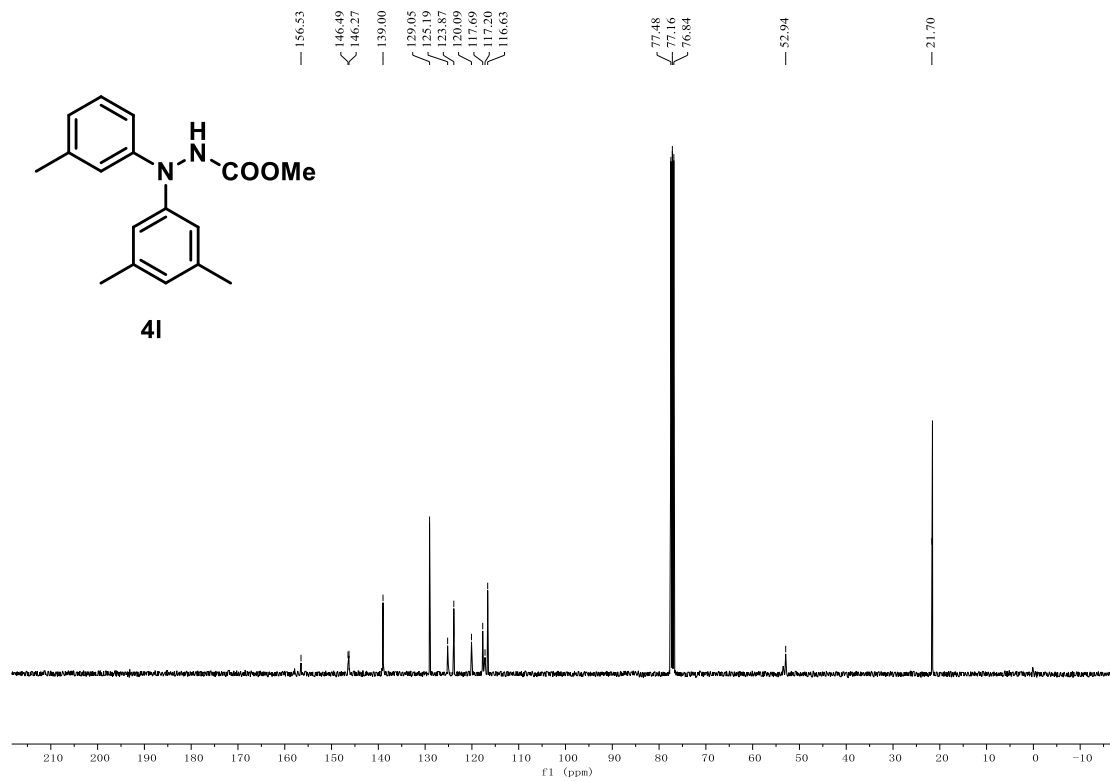


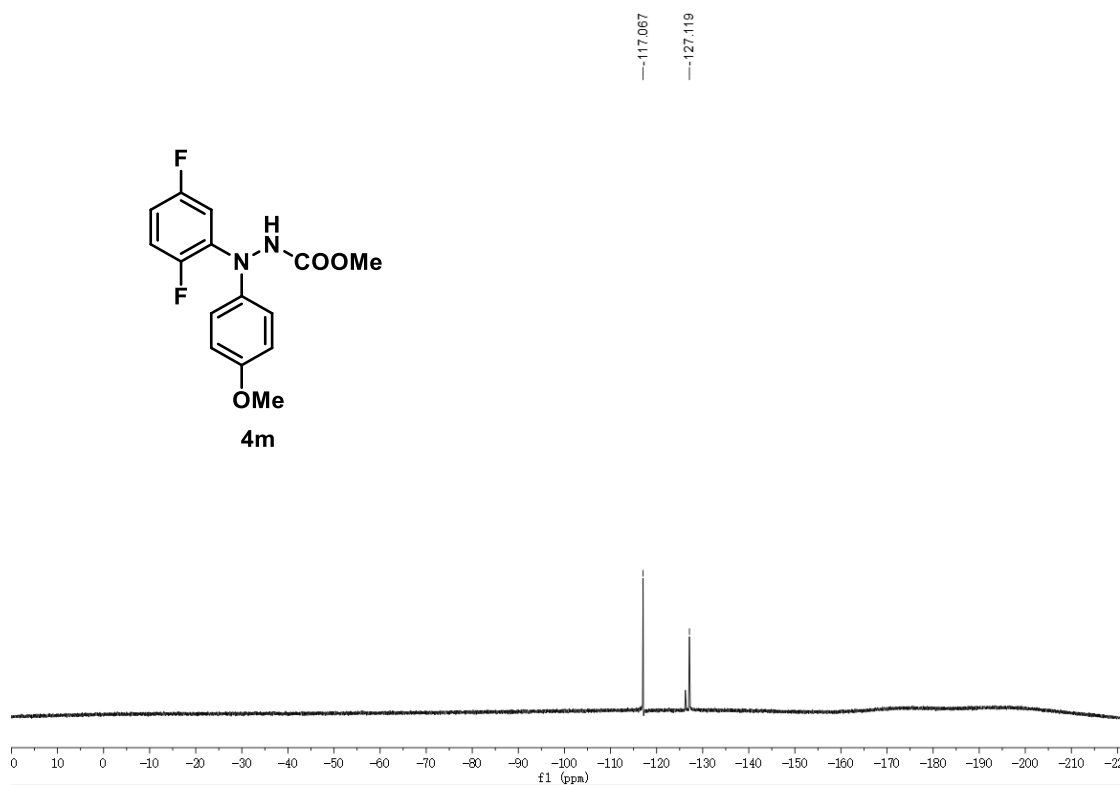
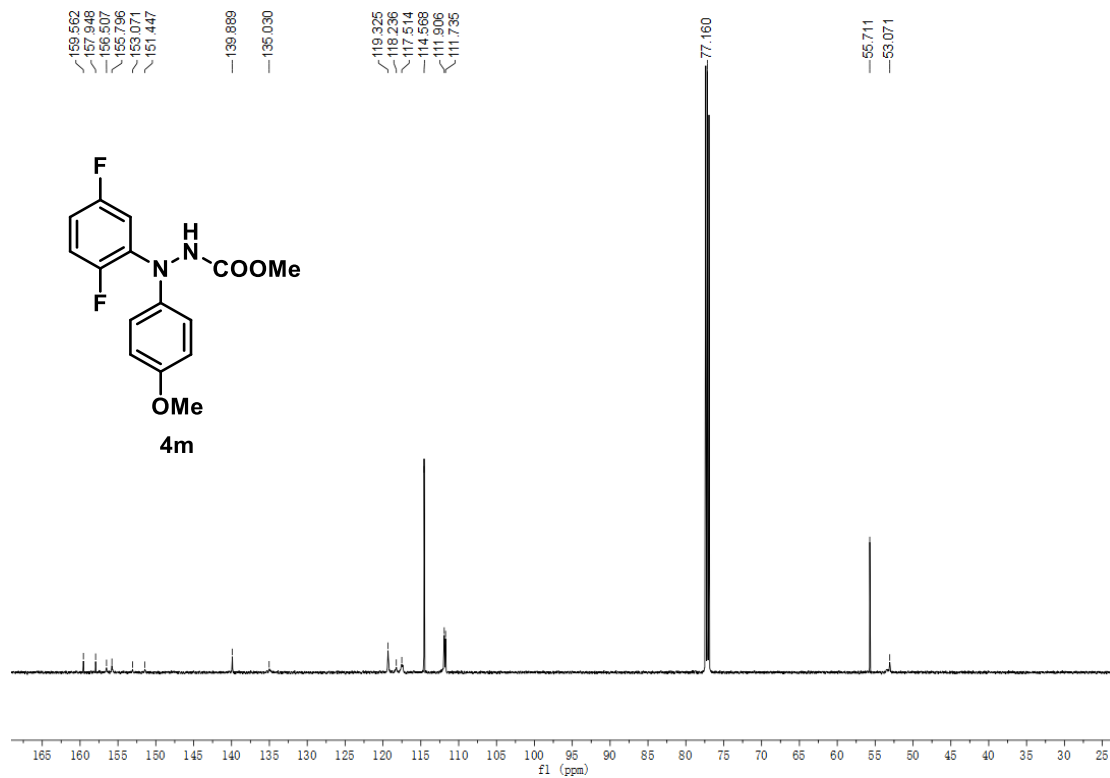


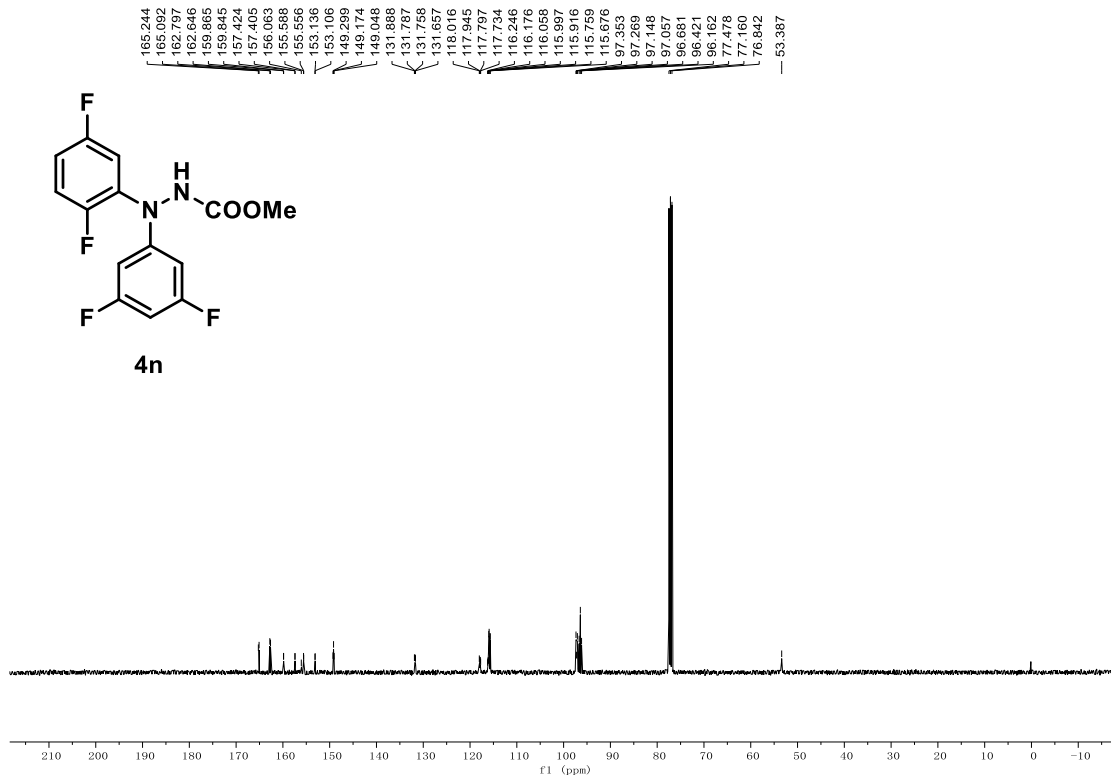
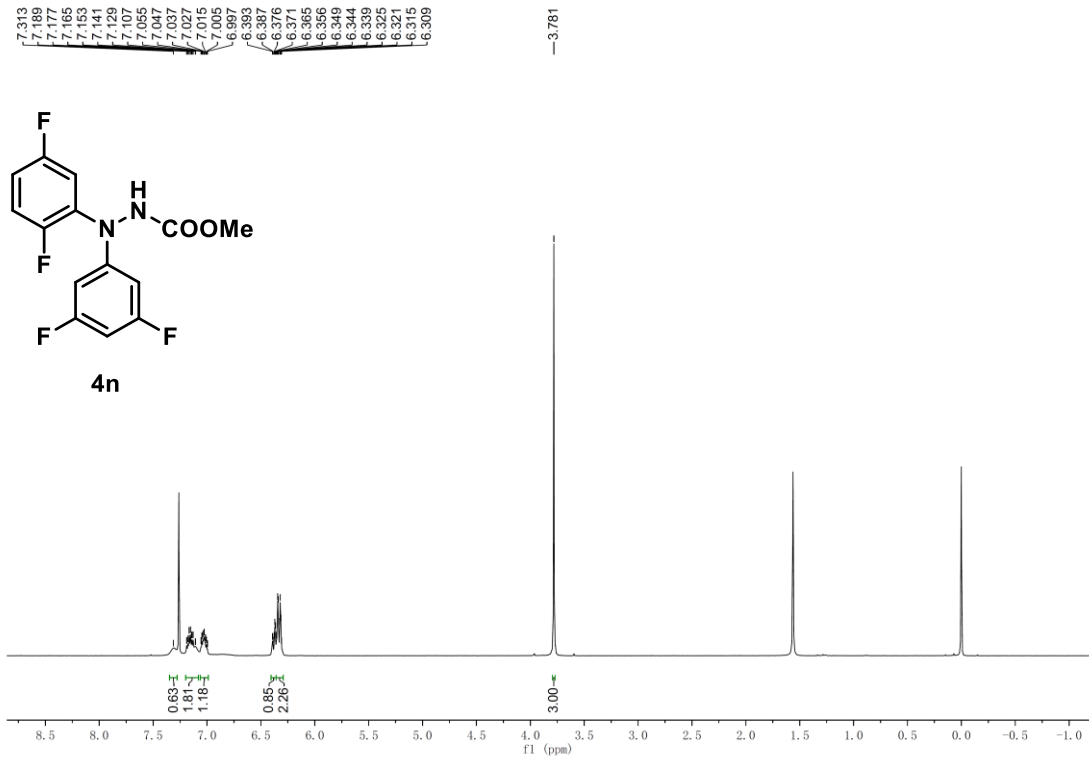


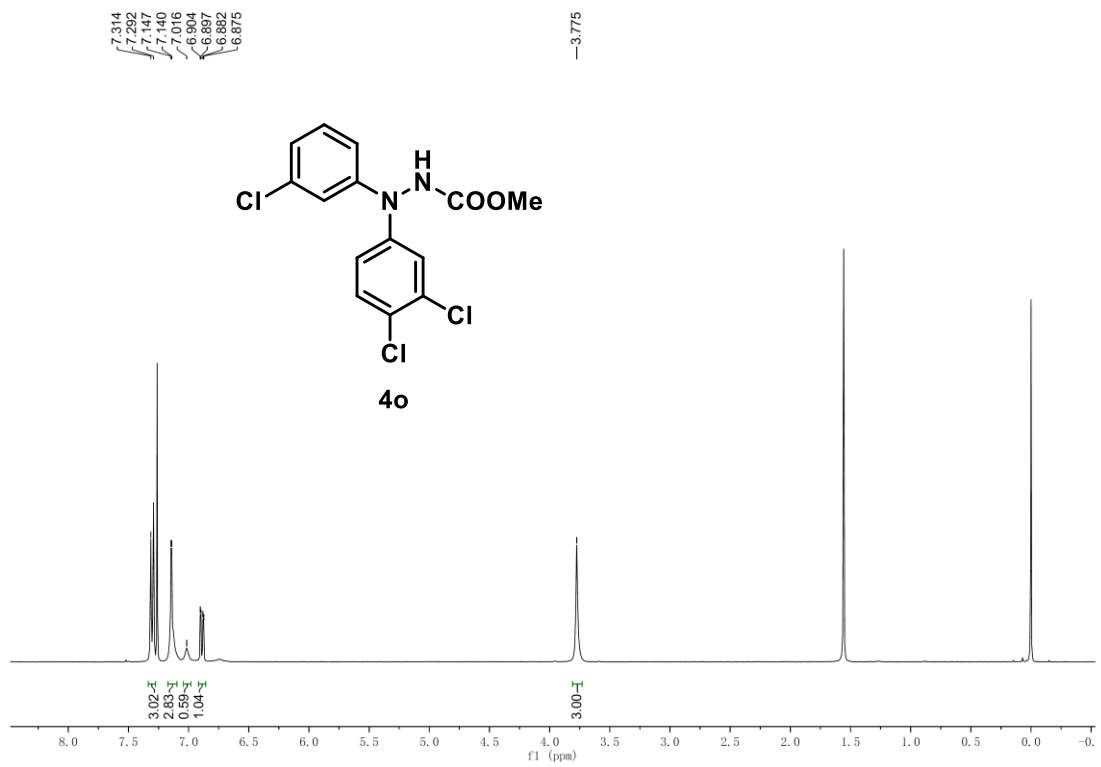
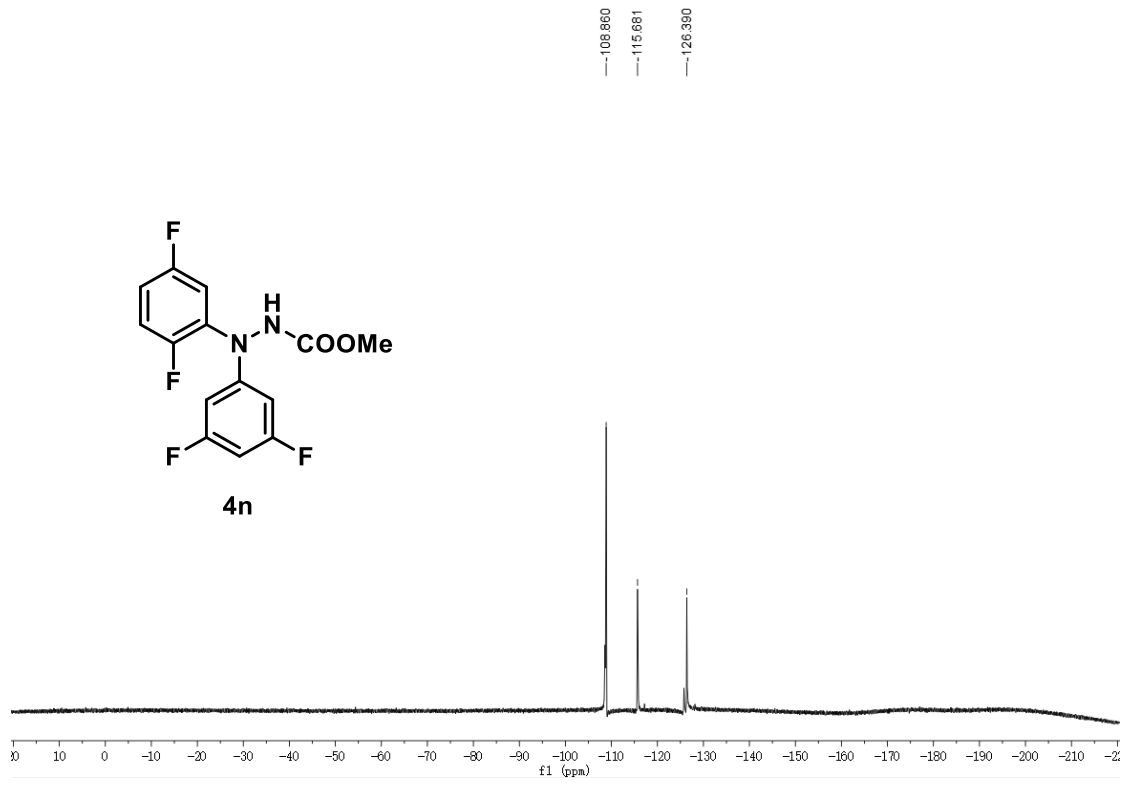


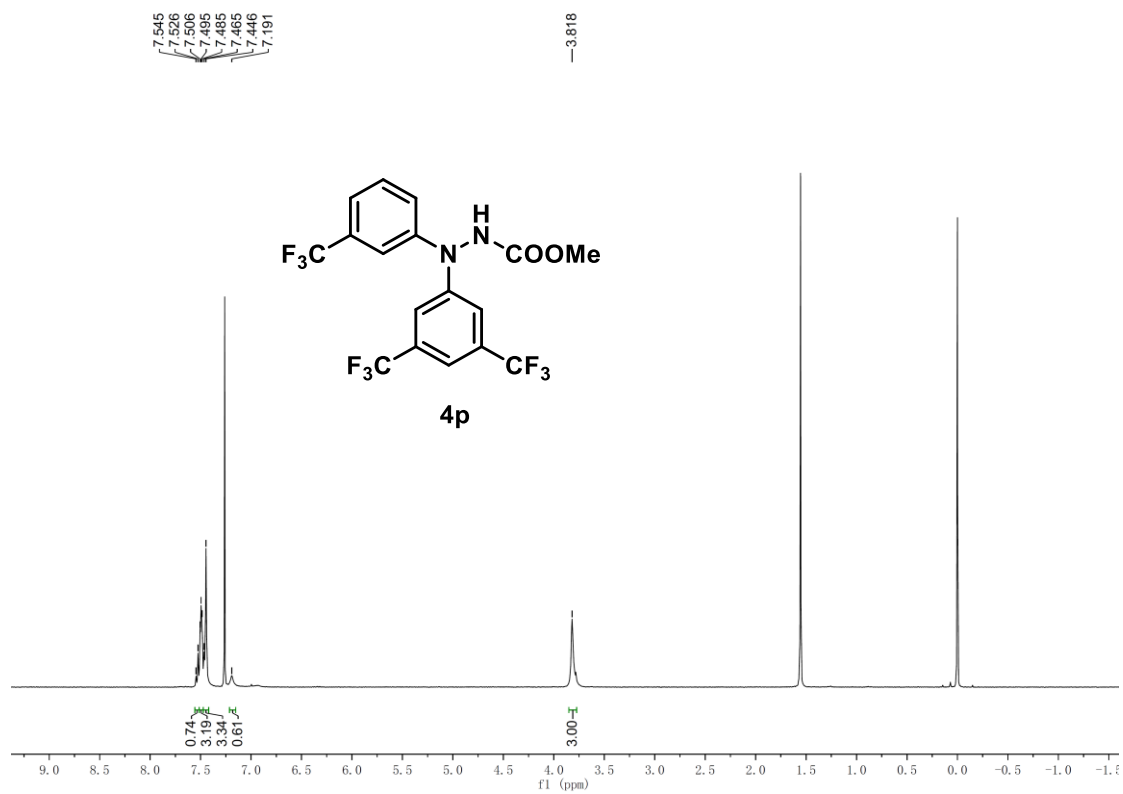
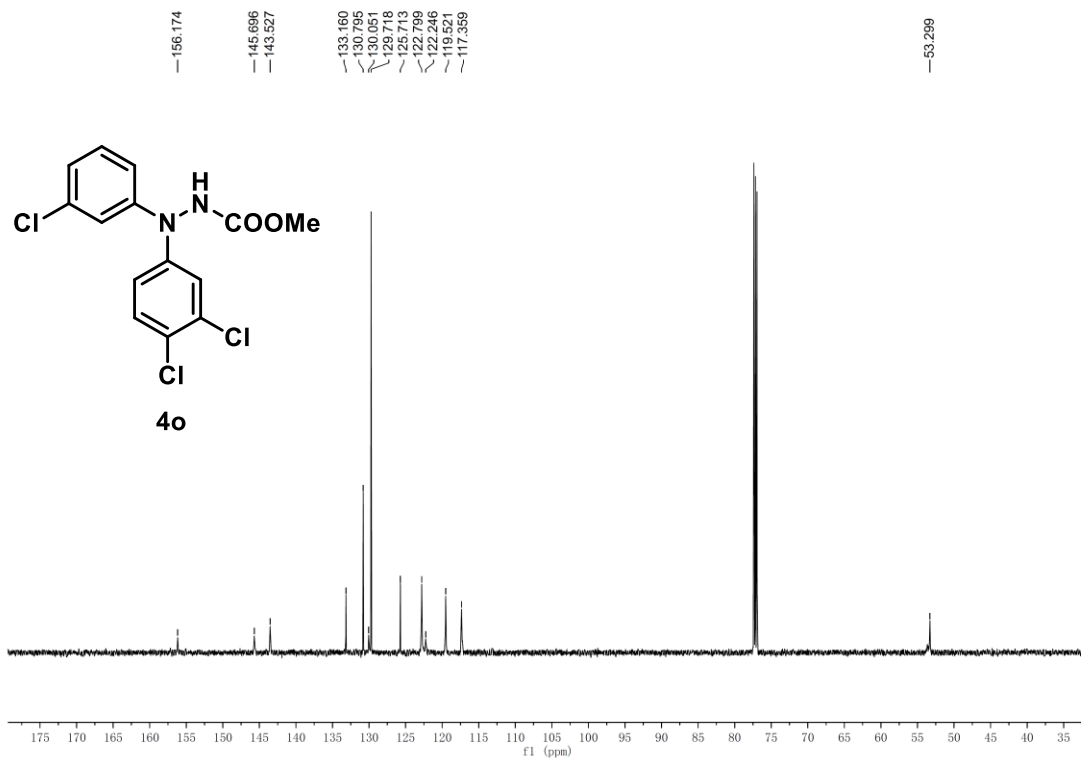


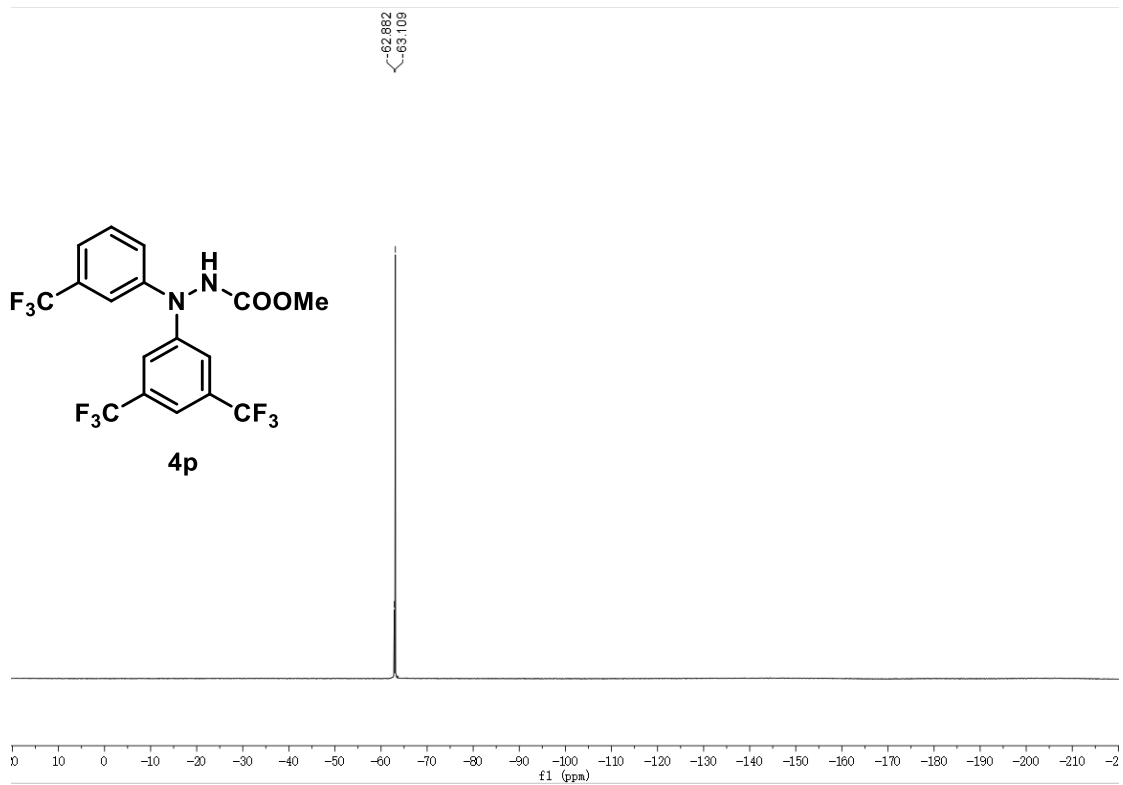
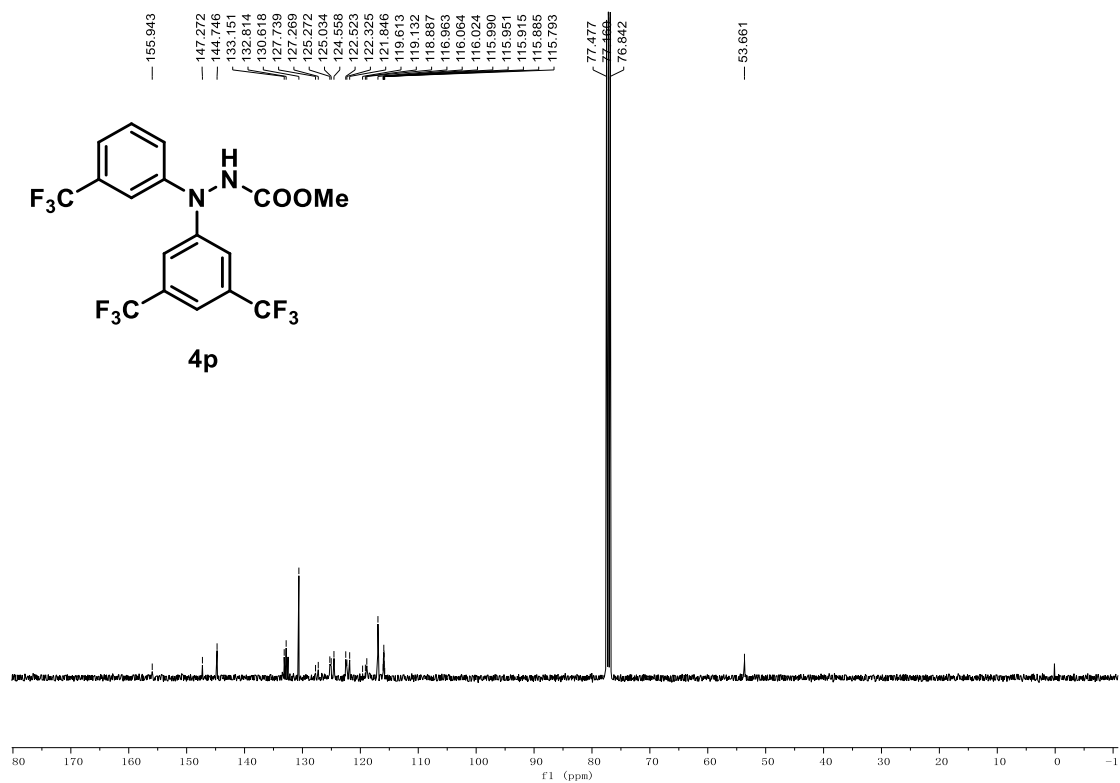




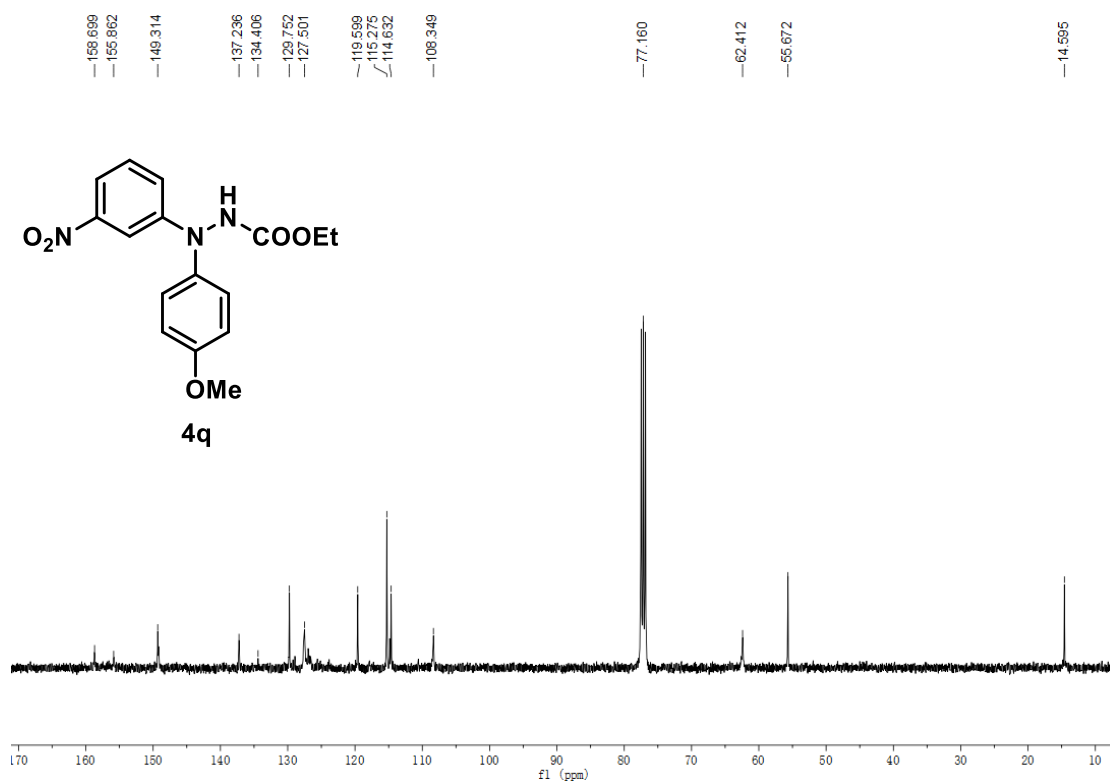
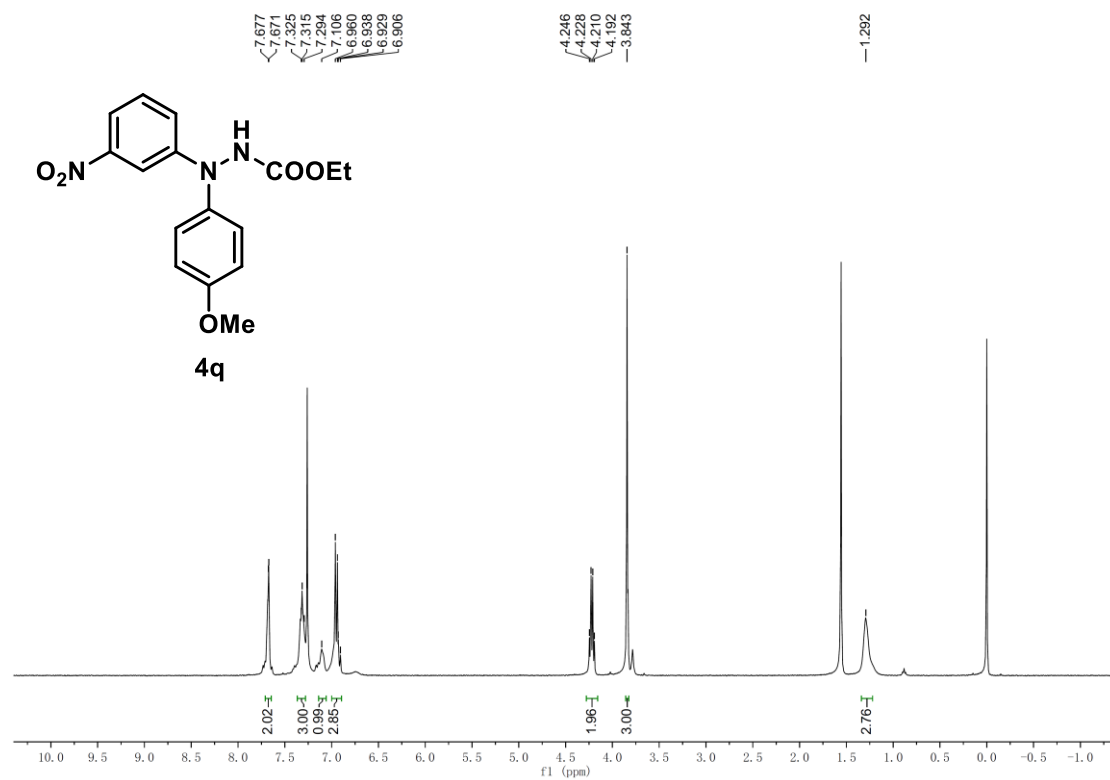


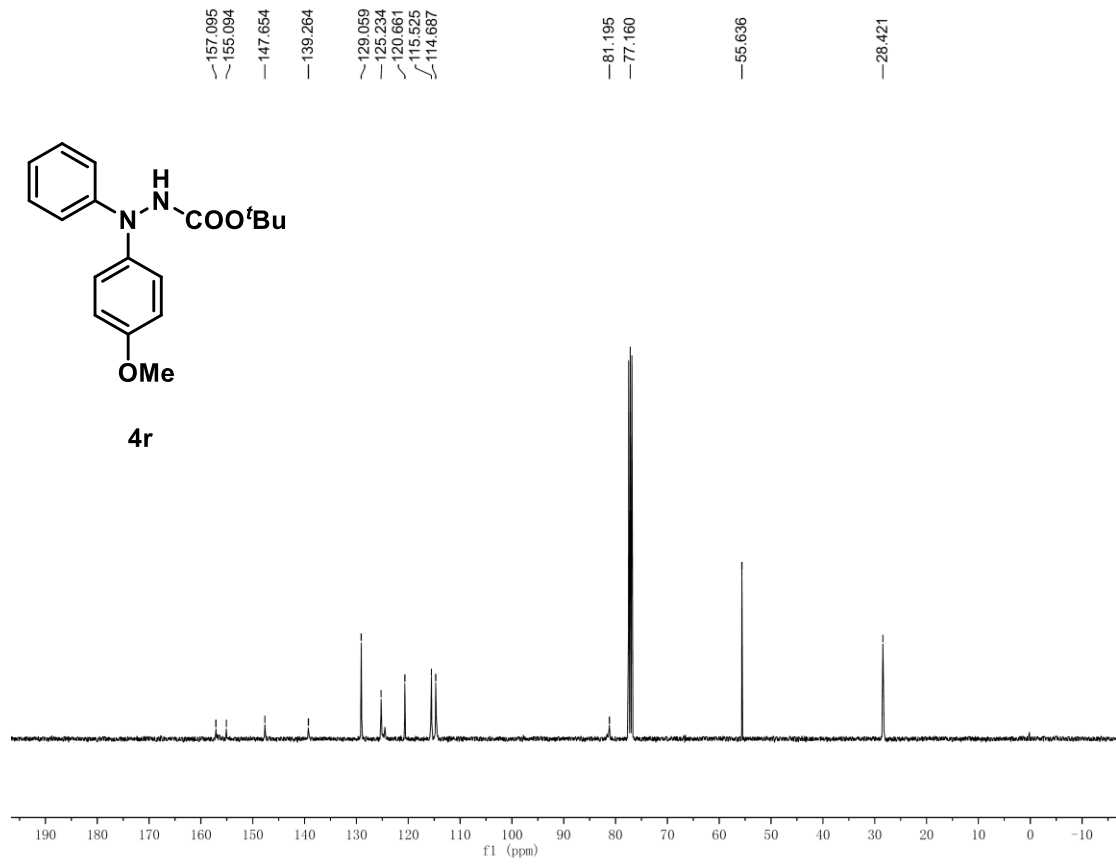
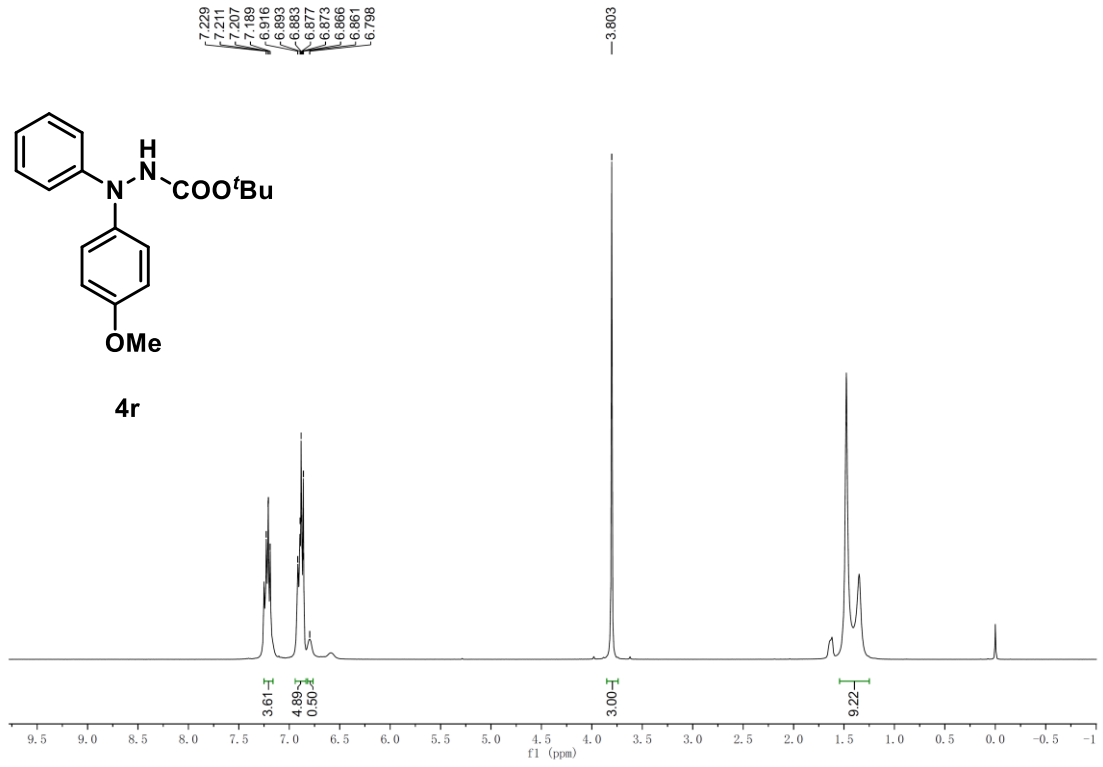


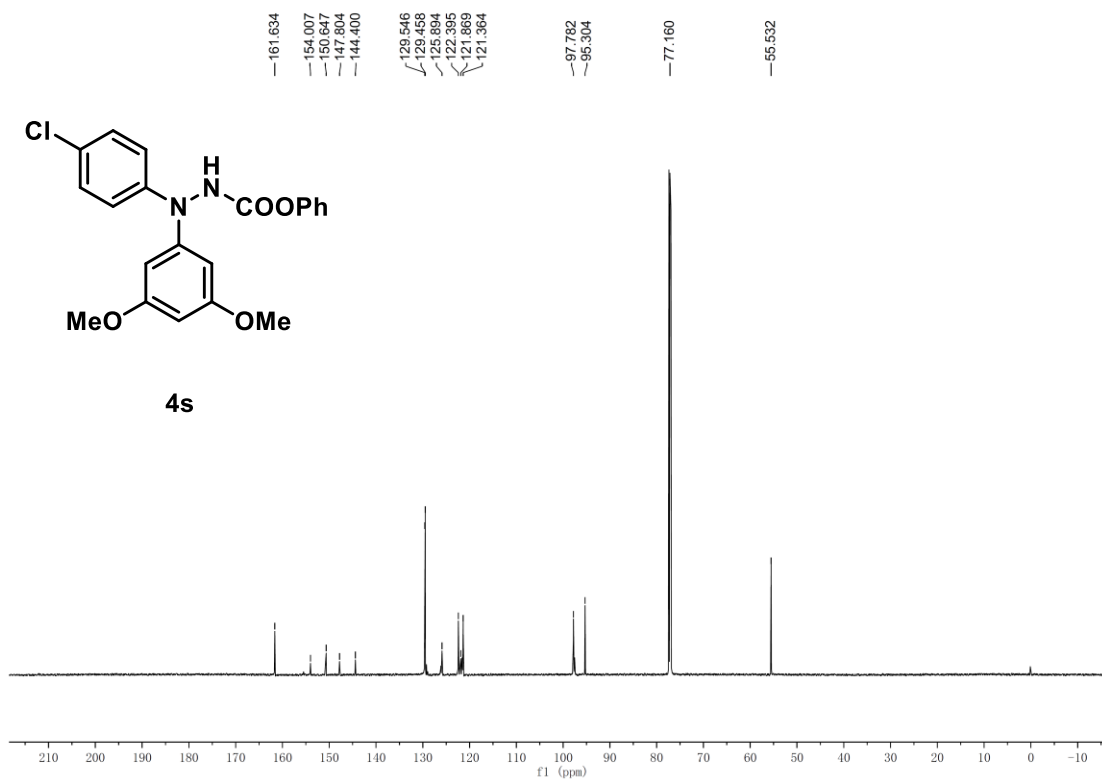
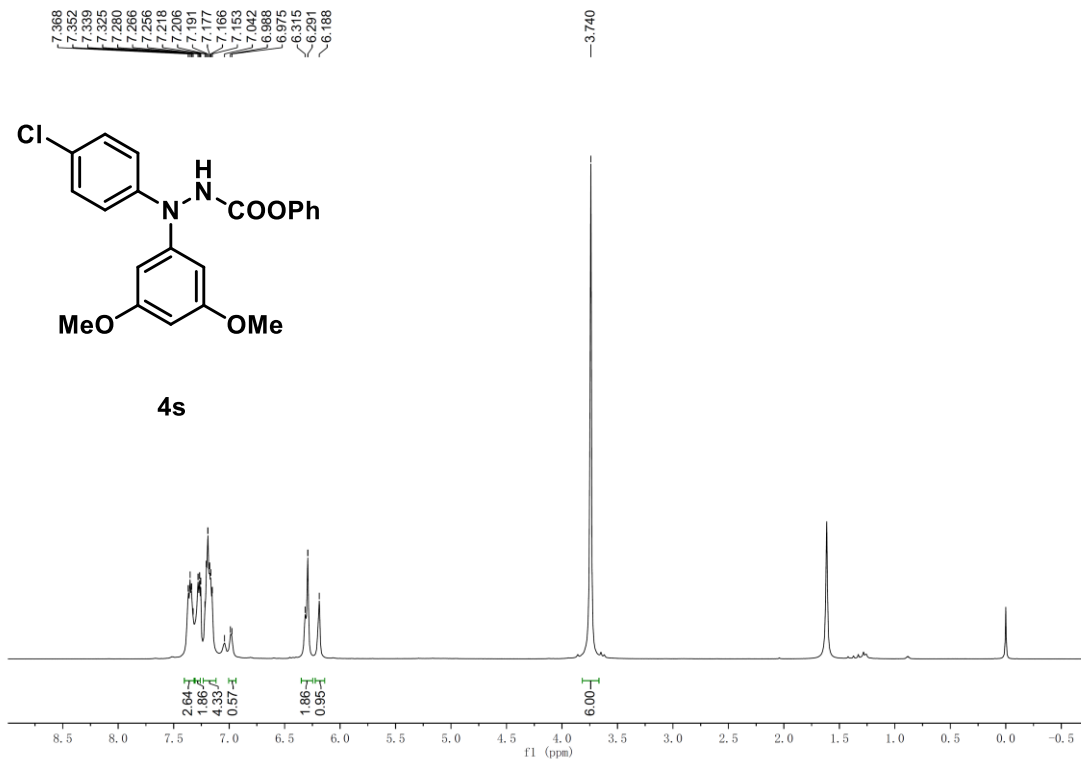


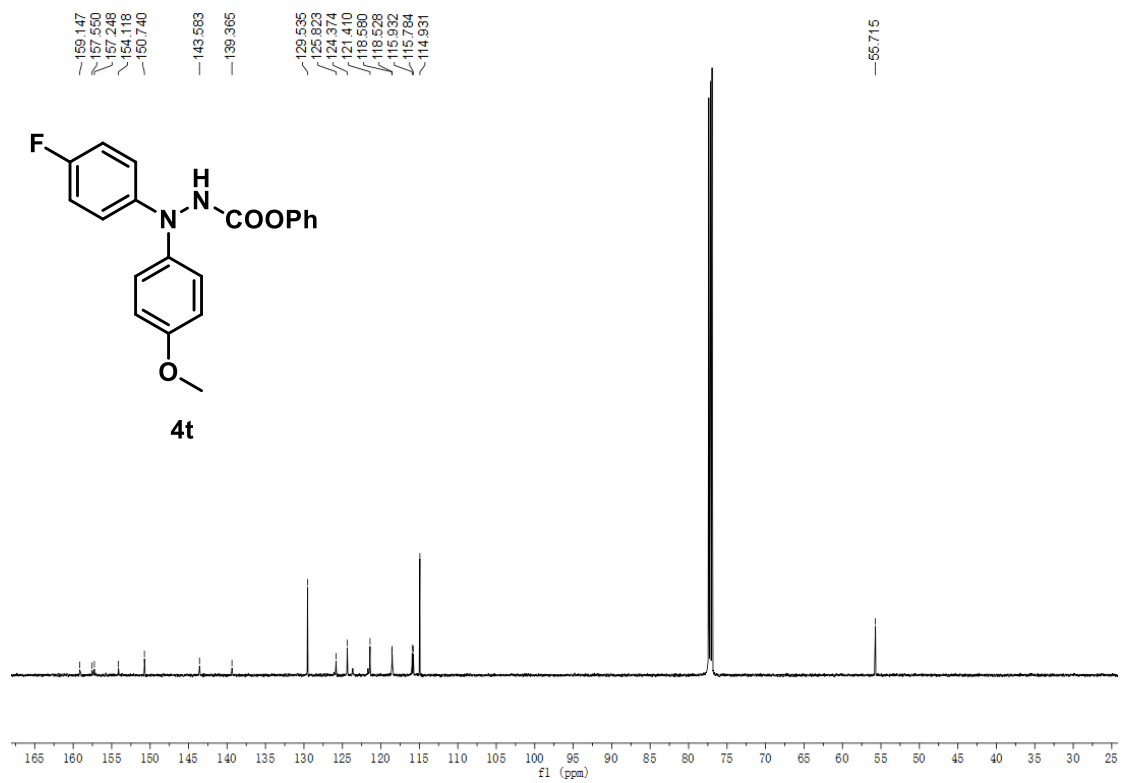
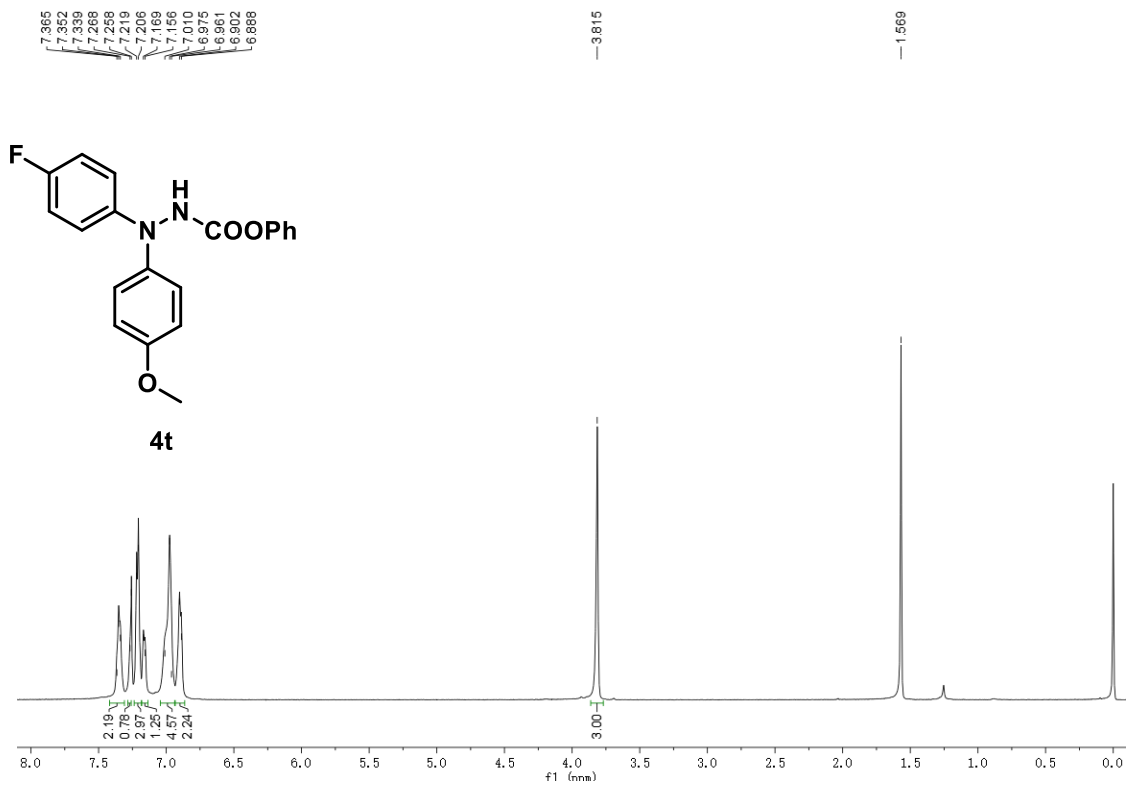


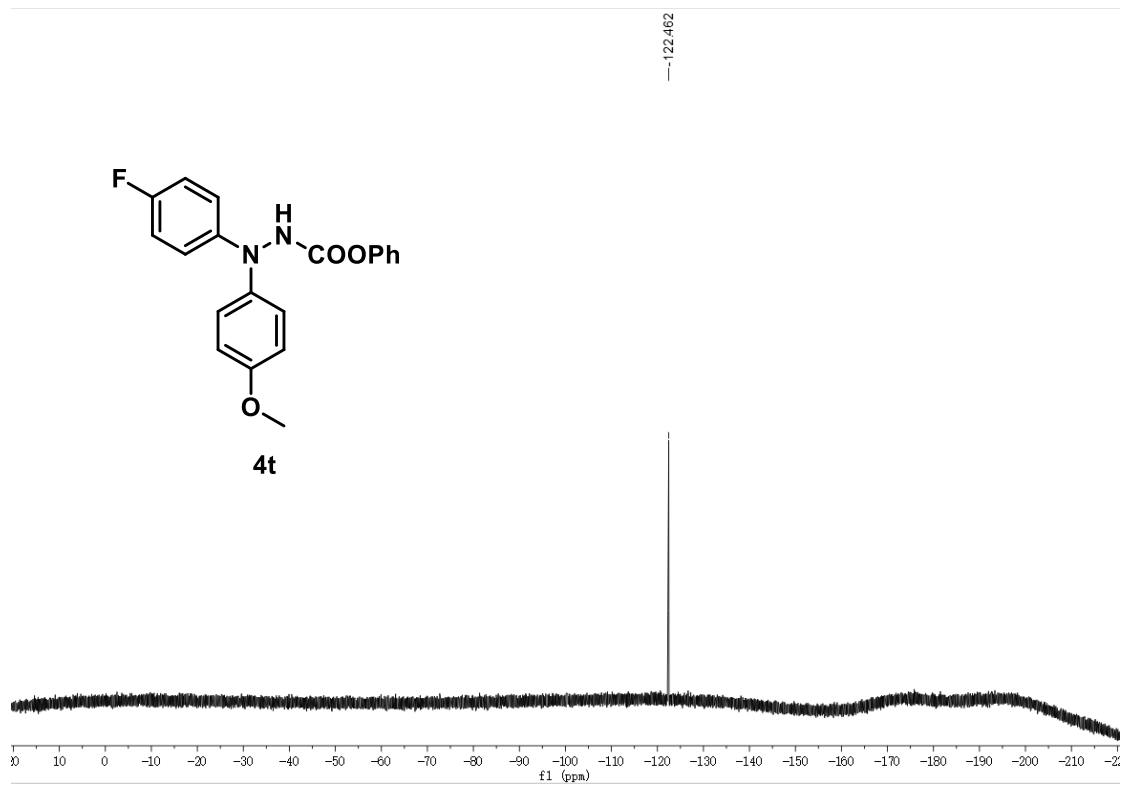












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