

Supporting Information

Visible-light-induced selective amination of enol ethers with N-alkoxyamides by using DDQ as photoredox catalyst

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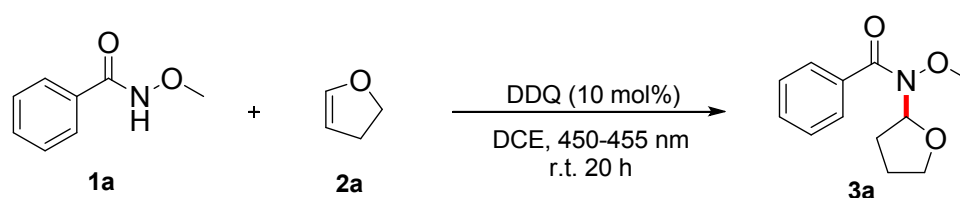
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1. General considerations

All ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer (400 MHz or 100 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J , are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI) or a Waters Micromass GCT Premier (oa-TOF) Mass Spectrometer (EI).

N-Alkoxyamides were prepared according to the reported method [Y. Fukui, P. Liu, Q. Liu, Z.-T. He, N.-Y. Wu, P. Tian, and G.-Q. Lin, *J. Am. Chem. Soc.*, 2014, **136**, 15607]. The chemicals and solvents were purchased from commercial suppliers either from Aldrich (USA) or Shanghai Chemical Company (China) without further purification. All the solvents were dried and freshly distilled prior to use. Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2 .

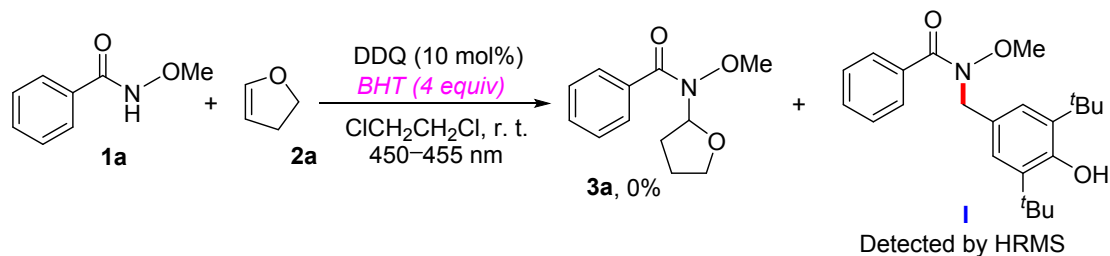
2. General procedure for the model reaction



N-Methoxybenzamide (**1a**, 0.20 mmol), 2,3-dihydrofuran (**2a**, 0.60 mmol), DDQ (0.020 mmol, 10 mol%) and DCE (3.0 mL) were sequence added to an oven-dried reaction vessel equipped with magnetic stirring bar. Then the reaction vessel was irradiated using blue LED (450–455 nm, 1.5 W) under air atmosphere at room temperature for 20 h. After the reaction was completed, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 7/1) to give the desired product **3a** in 86% yield as a colorless oil.

3. Free radical trapping experiments

3.1 Free radical trapping with BHT



N-Methoxybenzamide (**1a**, 0.20 mmol), 2,3-dihydrofuran (**2a**, 0.60 mmol), DDQ (0.020 mmol, 10 mol%), DCE (3.0 mL) and 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT, 0.80 mmol) were added to an oven-dried reaction vessel equipped with magnetic stirring bar. Then the reaction vessel was irradiated by using 1.5 W LED (450–455 nm) under air atmosphere at room temperature for 20 h. After the reaction was completed, no desired product **3a** was detected and an adduct **I** of *N*-radical from **1a** with BHT was detected by HPLC-HRMS analysis (Figure S1), indicating that the desired reaction was completely inhibited. It is suggested that a radical pathway might be involved in this transformation.

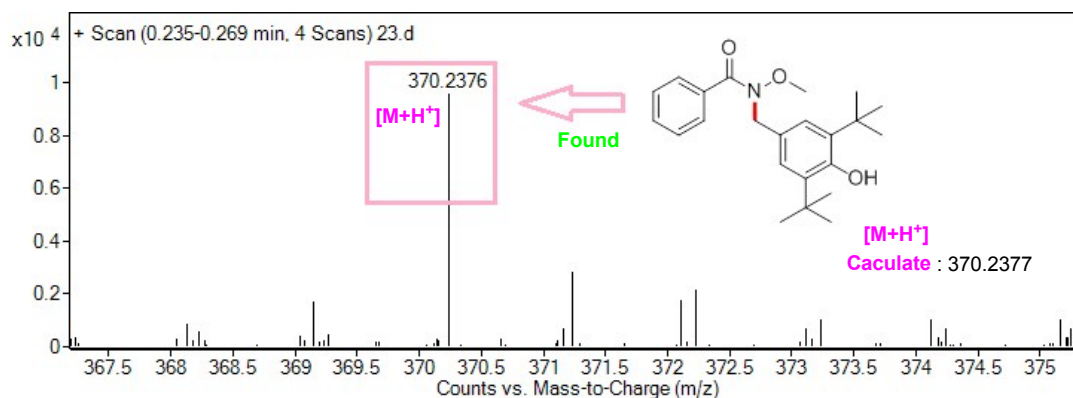
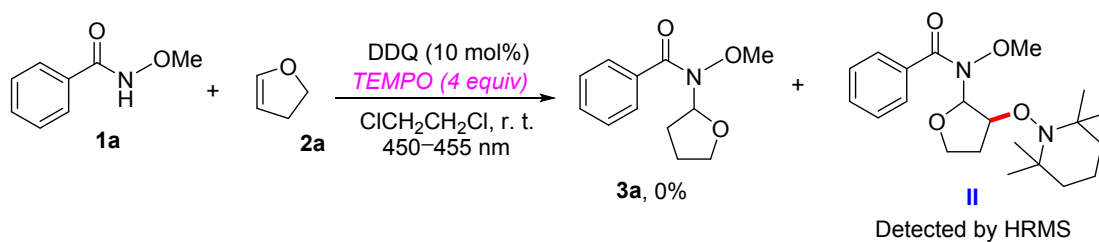


Figure S1. HRMS analysis of the adduct **I** of *N*-radical from **1a** with BHT

3.2 Free radical trapping with TEMPO



N-Methoxybenzamide (**1a**, 0.20 mmol), 2,3-dihydrofuran (**2a**, 0.60 mmol), DDQ (0.020 mmol, 10 mol%), DCE (3.0 mL) and 2,2,6,6-tetramethyl-1-oxylpiperidine (TEMPO, 0.80 mmol) were added to an oven-dried reaction vessel equipped with magnetic stirring bar. Then the reaction vessel was irradiated by using 1.5 W LED (450–455 nm) under air atmosphere at room temperature for 20 h. After the reaction was completed, no desired product **3a** was detected and the corresponding adduct **II** of *N*-radical from **1a** with **2a** and TEMPO was observed by HPLC-HRMS analysis (Figure S2), illustrating that the desired reaction was completely inhibited. It is suggested that the new carbon-centered radical might be a key intermediate in reaction and a radical pathway might be involved in this transformation.

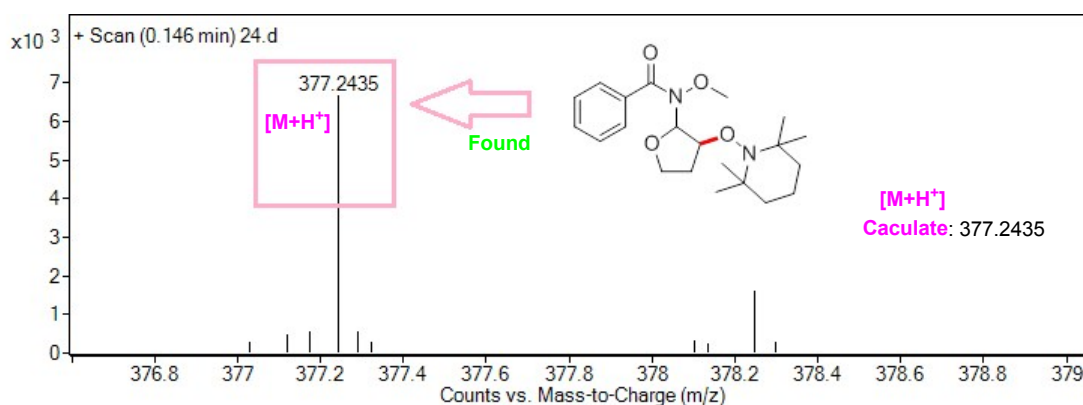


Figure S2. HRMS analysis of the adduct of **II** of *N*-radical from **1a** with **2a** and TEMPO

4. Absorption spectra of DDQ in DCE

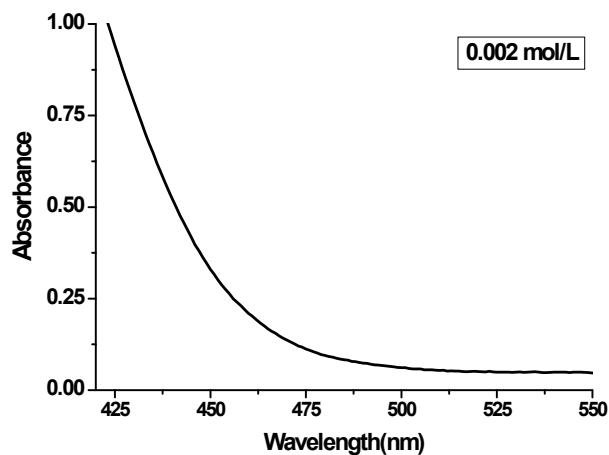


Figure S3 Absorption spectra of DDQ in DCE

5. Cyclic voltammetry (CV) measurements

The cyclic voltammetry (CV) measurements (using an Ag/AgCl reference electrode) were carried out using tetrabutylammonium tetrafluoroborate (0.1 M in DCE) as electrolyte and selected *N*-methoxybenzamide, DDQ and 2,3-dihydrofuran as 0.002 M in DCE and the results were summarized in the following Figure S4. The applied potential range is 1.5~-1.0 V vs. Ag/AgCl at a sweep rate of 140 mV/s using a CHI 760E electrochemical workstation at ambient temperature.

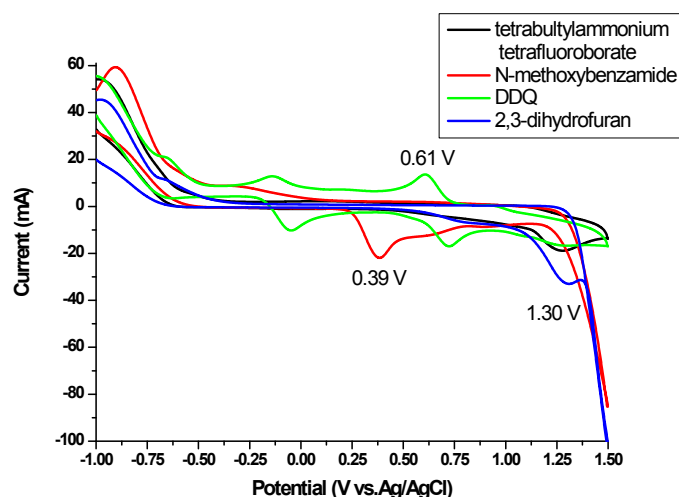
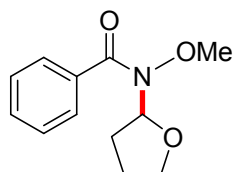
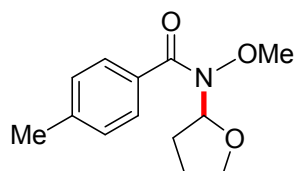


Figure S4 Cyclic voltammetry (CV) curves of DDQ, *N*-methoxybenzamide, 2,3-dihydrofuran and tetrabutylammonium tetrafluoroborate

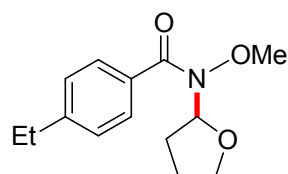
6. Characterization data for all products



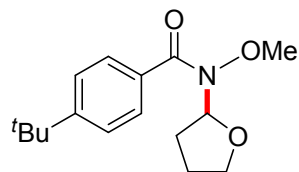
***N*-Methoxy-*N*-(tetrahydrofuran-2-yl)benzamide (3a):**^{8a} Colorless liquid; 86% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.66–7.64 (m, 2H), 7.48–7.38 (m, 3H), 5.85 (q, *J* = 3.8 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 1H), 3.83–3.77 (m, 4H), 2.30–2.24 (m, 1H), 2.17–2.08 (m, 1H), 2.04–1.97 (m, 1H), 1.93–1.87 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 168.73, 134.17, 130.51, 127.97, 127.73, 88.90, 68.60, 64.13, 28.00, 25.30.



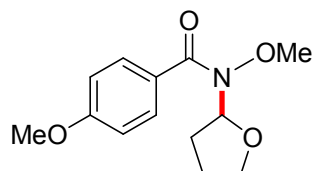
***N*-Methoxy-4-methyl-*N*-(tetrahydrofuran-2-yl)benzamide (3b):** Colorless liquid; 78% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 5.87 (q, *J* = 7.1 Hz, 1H), 4.13–4.08 (m, 1H), 3.84–3.80 (m, 1H), 3.79 (s, 3H), 2.38 (s, 3H), 2.32–2.24 (m, 1H), 2.19–2.09 (m, 1H), 2.06–1.97 (m, 1H), 1.94–1.87 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 169.07, 141.14, 131.47, 128.84, 128.16, 89.29, 68.81, 64.31, 28.22, 25.56, 21.37. HRMS (EI): Calcd. for C₁₃H₁₇NO₃: 235.1208, found: 235.1218.



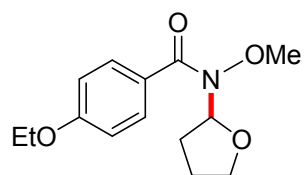
4-Ethyl-*N*-methoxy-*N*-(tetrahydrofuran-2-yl)benzamide (3c): Colorless liquid; 72% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 5.86 (q, *J* = 3.9 Hz, 1H), 4.11 (q, *J* = 7.0 Hz, 1H), 3.84–3.78 (m, 4H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.32–2.24 (m, 1H), 2.17–2.11 (m, 1H), 2.06–1.97 (m, 1H), 1.94–1.87 (m, 1H), 1.24 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 169.02, 147.31, 131.64, 128.16, 127.62, 89.28, 68.75, 64.23, 28.65, 28.16, 25.50, 15.11. HRMS (EI): Calcd. for C₁₃H₁₇NO₃: 249.1365, found: 249.1367.



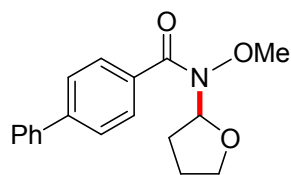
4-(tert-Butyl)-N-methoxy-N-(tetrahydrofuran-2-yl)benzamide (3d):^{8a} Colorless liquid; 80% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 5.88–5.85 (m, 1H), 4.11 (q, *J* = 6.9 Hz, 1H), 3.84–3.79 (m, 4H), 2.32–2.25 (m, 1H), 2.18–2.11 (m, 1H), 2.06–1.99 (m, 1H), 1.94–1.89 (m, 1H), 1.33 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 168.88, 154.11, 131.36, 127.86, 125.07, 89.33, 68.75, 64.20, 34.71, 31.00, 28.14, 25.50.



N,4-Dimethoxy-N-(tetrahydrofuran-2-yl)benzamide (3e): Colorless liquid; 85% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.91 (q, *J* = 4.0 Hz, 1H), 4.14–4.08 (m, 1H), 3.84–3.81 (m, 4H), 3.78 (s, 3H), 2.32–2.25 (m, 1H), 2.20–2.10 (m, 1H), 2.07–2.00 (m, 1H), 1.97–1.89 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 168.69, 161.69, 130.28, 126.32, 113.45, 88.30, 68.78, 64.27, 55.25, 28.18, 25.56. HRMS (EI): Calcd. for C₁₃H₁₇NO₄: 251.1158, found: 251.1161.

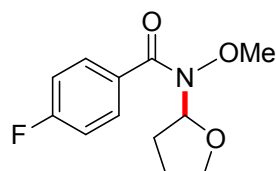


4-Ethoxy-N-methoxy-N-(tetrahydrofuran-2-yl)benzamide (3f): Colorless liquid; 80% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 5.91 (q, *J* = 4.0 Hz, 1H), 4.13–4.04 (m, 3H), 3.82 (q, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 2.32–2.25 (m, 1H), 2.19–2.11 (m, 1H), 2.05–1.98 (m, 1H), 1.95–1.88 (m, 1H), 1.42 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 168.72, 161.08, 130.23, 126.11, 113.90, 89.29, 68.72, 64.20, 63.46, 28.14, 25.51, 14.54. HRMS (EI): Calcd. for C₁₃H₁₇NO₃: 265.1314, found: 265.1318.

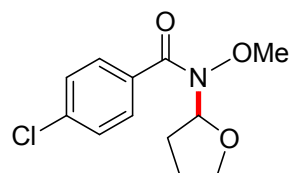


***N*-Methoxy-*N*-(tetrahydrofuran-2-yl)-[1,1'-biphenyl]-4-carboxamide (3g):**

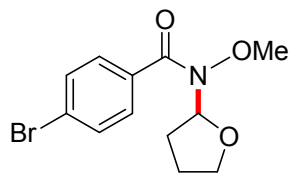
Colorless liquid; 70% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, $J = 8.2$ Hz, 2H), 7.64–7.59 (m, 4H), 7.45 (t, $J = 7.5$ Hz, 2H), 7.39–7.35 (m, 1H), 5.92 (q, $J = 3.9$ Hz, 1H), 4.12 (q, $J = 7.4$ Hz, 1H), 3.86–3.80 (m, 4H), 2.35–2.27 (m, 1H), 2.21–2.12 (m, 1H), 2.09–2.02 (m, 1H), 1.96–1.90 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 168.81, 143.65, 140.04, 133.10, 128.81, 128.66, 127.85, 127.09, 126.88, 89.24, 68.87, 64.47, 28.28, 25.57. HRMS (EI): Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_3$: 297.1365, found: 297.1375.



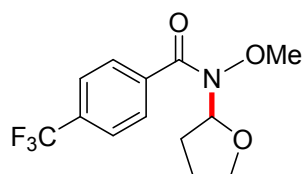
4-Fluoro-*N*-methoxy-*N*-(tetrahydrofuran-2-yl)benzamide (3h): Colorless liquid; 77% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.74–7.70 (m, 2H), 7.12–7.08 (m, 2H), 5.89 (q, $J = 4.0$ Hz, 1H), 4.11 (q, $J = 7.4$ Hz, 1H), 3.83 (q, $J = 7.1$ Hz, 1H), 3.77 (s, 3H), 2.33–2.25 (m, 1H), 2.20–2.12 (m, 1H), 2.10–2.01 (m, 1H), 1.95–1.89 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.98, 164.13 (d, $J = 249.9$ Hz), 130.62 (d, $J = 8.7$ Hz), 130.33 (d, $J = 3.1$ Hz), 115.30 (d, $J = 21.6$ Hz), 88.95, 68.86, 64.51, 28.26, 25.54. HRMS (EI): Calcd. for $\text{C}_{12}\text{H}_{14}\text{FNO}_3$: 239.0958, found: 239.0956.



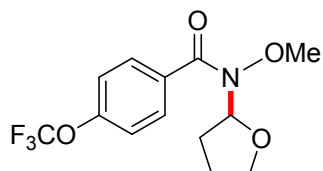
4-Chloro-*N*-methoxy-*N*-(tetrahydrofuran-2-yl)benzamide (3i): Colorless liquid; 75% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.64 (d, $J = 8.3$ Hz, 2H), 7.39 (d, $J = 8.2$ Hz, 2H), 5.89–5.87 (m, 1H), 4.11 (q, $J = 7.2$ Hz, 1H), 3.83 (q, $J = 7.2$ Hz, 1H), 3.76 (s, 3H), 2.32–2.24 (m, 1H), 2.20–2.11 (m, 1H), 2.07–2.01 (m, 1H), 1.97–1.90 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.97, 136.98, 132.68, 129.65, 128.48, 88.86, 68.87, 64.60, 28.27, 25.52. HRMS (EI): Calcd. for $\text{C}_{12}\text{H}_{14}\text{ClNO}_3$: 255.0662, found: 255.0667.



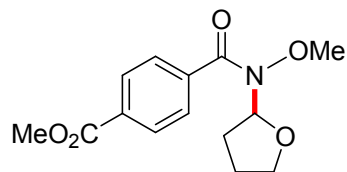
4-Bromo-*N*-methoxy-*N*-(tetrahydrofuran-2-yl)benzamide (3j):^{8a} Colorless liquid; 77% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.56 (s, 4H), 5.89–5.86 (m, 1H), 4.13–4.08 (m, 1H), 3.85–3.80 (m, 1H), 3.76 (s, 3H), 2.32–2.24 (m, 1H), 2.19–2.11 (m, 1H), 2.07–2.01 (m, 1H), 1.97–1.90 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 168.07, 133.20, 131.49, 129.84, 125.41, 88.89, 68.91, 64.66, 28.31, 25.56.



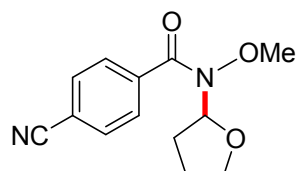
***N*-Methoxy-*N*-(tetrahydrofuran-2-yl)-4-(trifluoromethyl)benzamide (3k):**^{8a} White solid; 73% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 1H), 5.87 (s, 1H), 4.12 (q, *J* = 7.0 Hz, 1H), 3.84 (q, *J* = 7.3 Hz, 1H), 3.77 (s, 3H), 2.34–2.26 (m, 1H), 2.19–2.05 (m, 2H), 1.99–1.92 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 167.69, 137.86, 132.38 (q, *J* = 32.6 Hz), 128.38, 125.16 (q, *J* = 3.6 Hz), 123.56 (q, *J* = 270.8 Hz), 88.66, 68.88, 64.69, 28.25, 25.44.



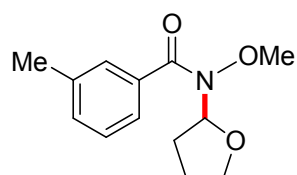
***N*-Methoxy-*N*-(tetrahydrofuran-2-yl)-4-(trifluoromethoxy)benzamide (3l):** Colorless liquid; 62% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 5.90–5.88 (m, 1H), 4.14–4.09 (m, 1H), 3.84 (q, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 2.33–2.26 (m, 1H), 2.21–2.13 (m, 1H), 2.11–2.04 (m, 1H), 1.98–1.92 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 167.74, 150.88, 132.84, 120.37, 120.30 (q, *J* = 256.6 Hz), 88.90, 68.92, 64.65, 28.31, 25.54. HRMS (EI): Calcd. for C₁₃H₁₇NO₃: 305.0875, found: 305.0869.



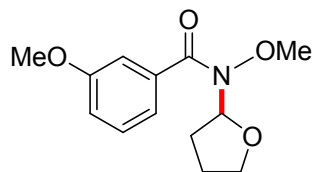
Methyl 4-(methoxy(tetrahydrofuran-2-yl)carbamoyl)benzoate (3m): Colorless liquid; 61% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.09 (d, $J = 8.1$ Hz, 2H), 7.72 (d, $J = 8.2$ Hz, 2H), 5.86 (s, 1H), 4.11 (q, $J = 6.6$ Hz, 1H), 3.94 (s, 3H), 3.83 (q, $J = 7.1$ Hz, 1H), 3.77 (s, 3H), 2.33–2.25 (m, 1H), 2.20–2.12 (m, 1H), 2.10–2.02 (m, 1H), 1.98–1.92 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 168.21, 166.21, 138.57, 132.00, 129.43, 127.96, 88.78, 68.91, 64.68, 52.25, 28.32, 25.50. HRMS (EI): Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_3$: 279.1107, found: 279.1115.



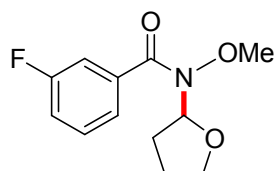
4-Cyano-N-methoxy-N-(tetrahydrofuran-2-yl)benzamide (3n): Colorless liquid; 56% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.79–7.77 (m, 2H), 7.73–7.71 (m, 2H), 5.88–5.87 (m, 1H), 4.14–4.09 (m, 1H), 3.87–3.82 (m, 1H), 3.75 (s, 3H), 2.32–2.26 (m, 1H), 2.19–2.06 (m, 2H), 1.99–1.94 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.32, 138.62, 132.05, 128.74, 117.96, 114.45, 88.60, 69.01, 64.96, 28.39, 25.51. HRMS (EI): Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_3$: 246.1004, found: 246.1007.



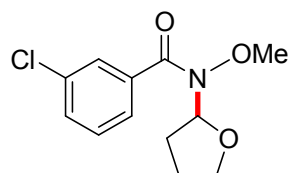
N-Methoxy-3-methyl-N-(tetrahydrofuran-2-yl)benzamide (3o): Colorless liquid; 82% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.45–7.42 (m, 2H), 7.31–7.26 (m, 2H), 5.85–5.82 (m, 1H), 4.11 (q, $J = 7.2$ Hz, 1H), 3.84–3.79 (m, 4H), 2.38 (s, 3H), 2.32–2.24 (m, 1H), 2.19–2.09 (m, 1H), 2.04–1.99 (m, 1H), 1.95–1.87 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.14, 138.06, 134.35, 131.42, 128.46, 128.02, 124.91, 89.26, 68.82, 64.27, 28.20, 25.51, 21.19. HRMS (EI): Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_3$: 235.1208, found: 235.1209.



***N*-Methoxy-3-methoxy-*N*-(tetrahydrofuran-2-yl)benzamide (3p):** Colorless liquid; 79% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.34–7.29 (m, 1H), 7.23–7.18 (m, 2H), 7.00 (dd, $J_1 = 8.2$ Hz, $J_2 = 2.5$ Hz, 1H), 5.84 (q, $J = 3.8$ Hz, 1H), 4.11 (q, $J = 7.4$ Hz, 1H), 3.83 (s, 3H), 3.82–3.81 (m, 4H), 2.32–2.24 (m, 1H), 2.20–2.11 (m, 1H), 2.07–2.00 (m, 1H), 1.96–1.90 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 168.67, 159.32, 135.61, 129.30, 120.15, 116.85, 113.04, 89.26, 68.85, 64.34, 55.29, 28.22, 25.53. HRMS (EI): Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_4$: 251.1158, found: 251.1166.



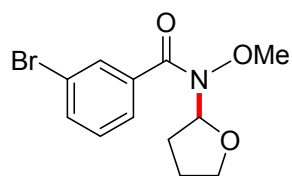
3-Fluoro-*N*-methoxy-*N*-(tetrahydrofuran-2-yl)benzamide (3q): Colorless liquid; 71% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.46 (d, $J = 7.6$ Hz, 1H), 7.43–7.37 (m, 1H), 7.20–7.15 (m, 1H), 5.87 (s, 1H), 4.14–4.09 (m, 1H), 3.83 (q, $J = 7.0$ Hz, 1H), 3.78 (s, 3H), 2.32–2.25 (m, 1H), 2.20–2.12 (m, 1H), 2.11–2.04 (m, 1H), 1.97–1.91 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.58, 162.18 (d, $J = 246.1$ Hz), 136.33 (d, $J = 7.1$ Hz), 129.95 (d, $J = 7.9$ Hz), 123.79 (d, $J = 3.2$ Hz), 117.77 (d, $J = 21.1$ Hz), 115.25 (d, $J = 23.2$ Hz), 88.87, 68.90, 64.59, 28.28, 25.50. HRMS (EI): Calcd. for $\text{C}_{12}\text{H}_{14}\text{FNO}_3$: 239.0958, found: 239.0955.



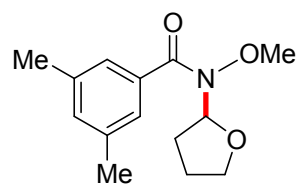
3-Chloro-*N*-methoxy-*N*-(tetrahydrofuran-2-yl)benzamide (3r): Colorless liquid; 72% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.66 (t, $J = 1.7$ Hz, 1H), 7.55 (d, $J = 7.6$ Hz, 1H), 7.46–7.43 (m, 1H), 7.38–7.34 (m, 1H), 5.87 (s, 1H), 4.14–4.09 (m, 1H), 3.84 (q, $J = 6.8$ Hz, 1H), 3.78 (s, 3H), 2.32–2.25 (m, 1H), 2.20–2.12 (m, 1H), 2.11–2.04 (m, 1H), 1.97–1.91 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.62,

136.11, 134.29, 130.87, 129.59, 128.21, 126.22, 88.89, 68.96, 64.68, 28.36, 25.54.

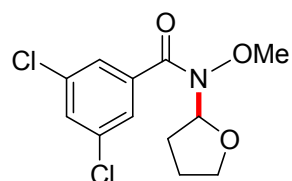
HRMS (EI): Calcd. for C₁₂H₁₄ClNO₃: 255.0662, found: 255.0659.



3-Bromo-*N*-methoxy-*N*-(tetrahydrofuran-2-yl)benzamide (3s): Colorless liquid; 78% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.81 (t, *J* = 1.7 Hz, 1H), 7.60 (dd, *J*₁ = 7.9 Hz, *J*₂ = 1.8 Hz, 2H), 7.32–7.28 (m, 1H), 5.87 (s, 1H), 4.14–4.08 (m, 1H), 3.86–3.81 (m, 1H), 3.77 (s, 3H), 2.32–2.24 (m, 1H), 2.20–2.12 (m, 1H), 2.11–2.04 (m, 1H), 1.97–1.92 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 167.39, 136.23, 133.72, 130.97, 129.77, 126.58, 122.19, 88.79, 68.89, 64.62, 28.29, 25.47. HRMS (EI): Calcd. for C₁₂H₁₄BrNO₃: 299.0157, found: 299.0153.

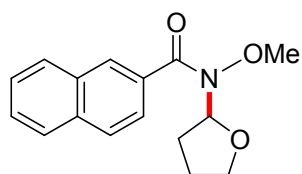


***N*-Methoxy-3,5-dimethyl-*N*-(tetrahydrofuran-2-yl)benzamide (3t):** Colorless liquid; 82% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.23 (s, 2H), 7.08 (s, 1H), 5.82 (q, *J* = 3.8 Hz, 1H), 4.10 (q, *J* = 6.8 Hz, 1H), 3.84–3.80 (m, 4H), 2.34 (s, 6H), 2.29–2.23 (m, 1H), 2.17–2.11 (m, 1H), 2.03–1.98 (m, 1H), 1.93–1.85 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 169.37, 137.87, 134.40, 132.28, 125.48, 89.39, 68.83, 64.22, 28.22, 25.52, 21.08. HRMS (EI): Calcd. for C₁₄H₁₉NO₃: 249.1365, found: 249.1370.

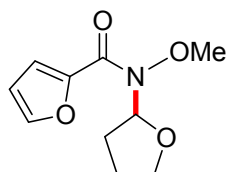


3,5-Dichloro-*N*-methoxy-*N*-(tetrahydrofuran-2-yl)benzamide (3u): Colorless liquid; 73% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.56 (s, 2H), 7.46–7.45 (m, 1H), 5.89 (s, 1H), 4.12–4.08 (m, 1H), 3.85–3.82 (m, 1H), 3.76 (s, 3H), 2.29–2.24 (m, 1H), 2.18–2.07 (m, 2H), 1.98–1.94 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 166.20, 137.03, 134.91, 130.63, 126.49, 88.52, 68.92, 64.84, 28.34, 25.40. HRMS (EI): Calcd.

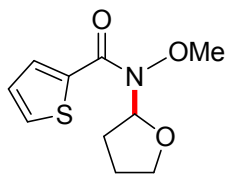
for C₁₂H₁₃Cl₂NO₃: 289.0272, found: 289.0279.



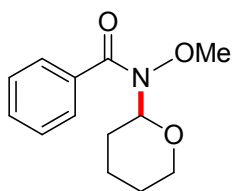
***N*-Methoxy-*N*-(tetrahydrofuran-2-yl)-2-naphthamide (3v):**^{8a} Colorless liquid; 59% yield; ¹H NMR (400 MHz, CDCl₃): δ 8.20 (s, 1H), 7.92–7.85 (m, 3H), 7.74–7.72 (m, 1H), 7.57–7.50 (m, 2H), 5.94 (q, *J* = 4.0 Hz, 1H), 4.16–4.10 (m, 1H), 3.85–3.80 (m, 4H), 2.36–2.28 (m, 1H), 2.21–2.11 (m, 1H), 2.08–1.99 (m, 1H), 1.94–1.88 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 169.07, 134.25, 132.43, 131.65, 128.74, 128.51, 127.99, 127.67, 127.46, 126.59, 124.74, 89.25, 68.89, 64.52, 28.30, 25.58.



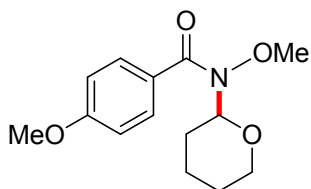
***N*-Methoxy-*N*-(tetrahydrofuran-2-yl)furan-2-carboxamide (3w):**^{8a} Colorless liquid; 67% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.60 (s, 1H), 7.19 (q, *J* = 3.5 Hz, 1H), 6.52 (t, *J* = 1.7 Hz, 1H), 6.28–6.25 (m, 1H), 4.11 (q, *J* = 6.6 Hz, 1H), 3.89 (s, 3H), 3.87–3.85 (m, 1H), 2.27–2.20 (m, 1H), 2.18–2.11 (m, 2H), 2.01–1.95 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 159.10, 145.78, 145.43, 117.87, 111.59, 88.09, 68.84, 65.33, 28.41, 25.42.



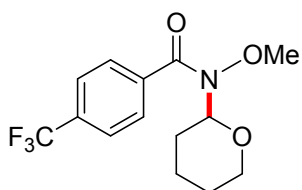
***N*-Methoxy-*N*-(tetrahydrofuran-2-yl)thiophene-2-carboxamide (3x):**^{8a} Colorless liquid; 84% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, *J* = 3.8 Hz, 1H), 7.57 (d, *J* = 5.0 Hz, 1H), 7.10 (t, *J* = 4.5 Hz, 1H), 6.30 (q, *J* = 4.5 Hz, 1H), 4.11 (q, *J* = 6.4 Hz, 1H), 3.90 (s, 3H), 3.87–3.85 (m, 1H), 2.27–2.19 (m, 1H), 2.17–2.09 (m, 2H), 2.00–1.94 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 162.59, 134.43, 133.80, 132.48, 126.81, 88.17, 68.73, 65.88, 28.46, 25.42.



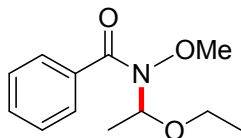
***N*-Methoxy-*N*-(tetrahydro-2*H*-pyran-2-yl)benzamide (4a):**^{8a} Colorless liquid; 62% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.70–7.68 (m, 2H), 7.49–7.45 (m, 1H), 7.42–7.38 (m, 2H), 5.25–5.23 (m, 1H), 4.07 (d, *J* = 11.2 Hz, 1H), 3.71 (s, 3H), 3.48 (t, *J* = 11.3 Hz, 1H), 2.11–2.01 (m, 1H), 1.98–1.95 (m, 1H), 1.77–1.74 (m, 1H), 1.59–1.47 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 169.41, 134.21, 130.65, 127.97, 85.89, 68.11, 64.80, 27.66, 24.91, 22.99.



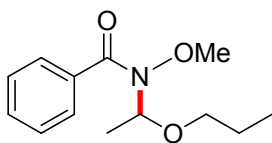
***N*-Methoxy-4-methoxy-*N*-(tetrahydro-2*H*-pyran-2-yl)benzamide (4b):**^{8a} Colorless liquid; 61% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.75–7.73 (m, 2H), 6.91–6.89 (m, 2H), 5.29 (d, *J* = 10.5 Hz, 1H), 4.09–4.06 (m, 1H), 3.85 (s, 3H), 3.70 (s, 3H), 3.54–3.49 (m, 1H), 2.07–1.95 (m, 2H), 1.77–1.74 (m, 1H), 1.60–1.47 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 168.91, 161.69, 130.43, 126.19, 113.29, 86.02, 68.16, 64.77, 55.25, 27.76, 25.02, 23.11.



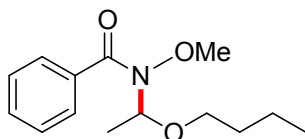
***N*-Methoxy-*N*-(tetrahydro-2*H*-pyran-2-yl)-4-(trifluoromethyl)benzamide (4c):**^{8a} White solid; 59% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 5.29 (s, 1H), 4.11–4.07 (m, 1H), 3.69 (s, 3H), 3.52 (t, *J* = 11 Hz, 1H), 2.08–1.98 (m, 2H), 1.79–1.76 (m, 1H), 1.62–1.52 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 168.20, 137.70, 132.40 (q, *J* = 32.5 Hz), 128.44, 125.02 (q, *J* = 3.7 Hz), 122.29, 85.53, 68.23, 65.14, 27.61, 24.90, 22.96.



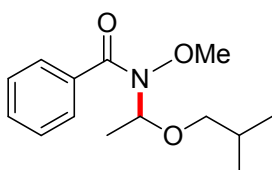
***N*-(1-Ethoxyethyl)-*N*-methoxybenzamide (4d)**: Colorless liquid; 41% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.68–7.65 (m, 2H), 7.50–7.39 (m, 3H), 5.70 (s, 1H), 3.74–3.68 (m, 1H), 3.67 (s, 3H), 1.61 (d, $J = 1.8$ Hz, 1H), 1.53 (d, $J = 6.0$ Hz, 3H), 1.21 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.33, 134.40, 130.71, 128.11, 83.52, 64.80, 63.61, 18.32, 14.99. HRMS (EI): Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_3$: 223.1208, found: 223.1202.



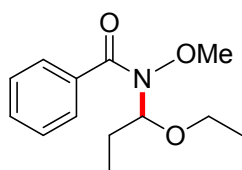
***N*-Methoxy-*N*-(1-propoxyethyl)benzamide (4e)**: Colorless liquid; 45% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, $J = 7.8$ Hz, 2H), 7.48–7.39 (m, 3H), 5.69 (s, 1H), 3.66 (s, 3H), 3.65–3.59 (m, 1H), 3.42 (q, $J = 6.8$ Hz, 1H), 1.62–1.57 (m, 2H), 1.53 (d, $J = 6.0$ Hz, 3H), 0.93 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.21, 134.31, 130.60, 128.00, 83.70, 69.87, 64.68, 22.68, 18.14, 10.47. HRMS (EI): Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_3$: 237.1365, found: 237.1368.



***N*-(1-Butoxyethyl)-*N*-methoxybenzamide (4f)**: Colorless liquid; 47% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.66 (d, $J = 7.8$ Hz, 2H), 7.48–7.39 (m, 3H), 5.68 (s, 1H), 3.69–3.63 (m, 4H), 3.46 (q, $J = 6.7$ Hz, 1H), 1.59–1.54 (m, 2H), 1.52 (d, $J = 6.0$ Hz, 3H), 1.40–1.35 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.24, 134.39, 130.60, 128.02, 83.74, 68.06, 64.69, 31.58, 19.23, 18.17, 13.74. HRMS (EI): Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_3$: 251.1521, found: 251.1522.

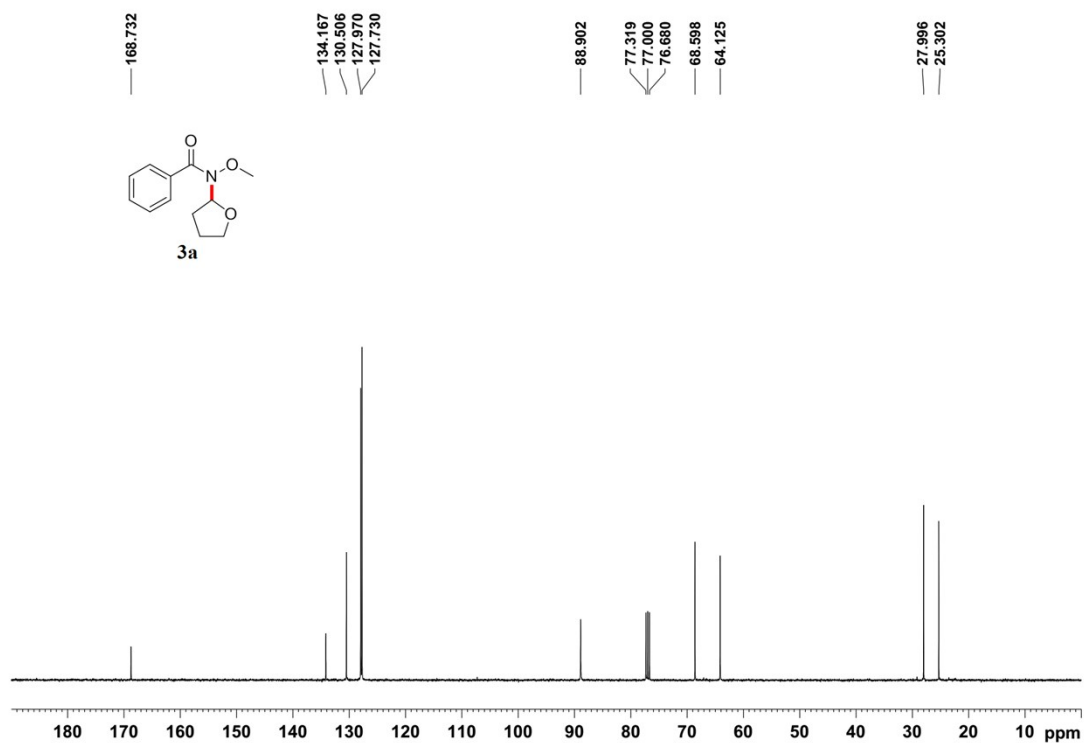
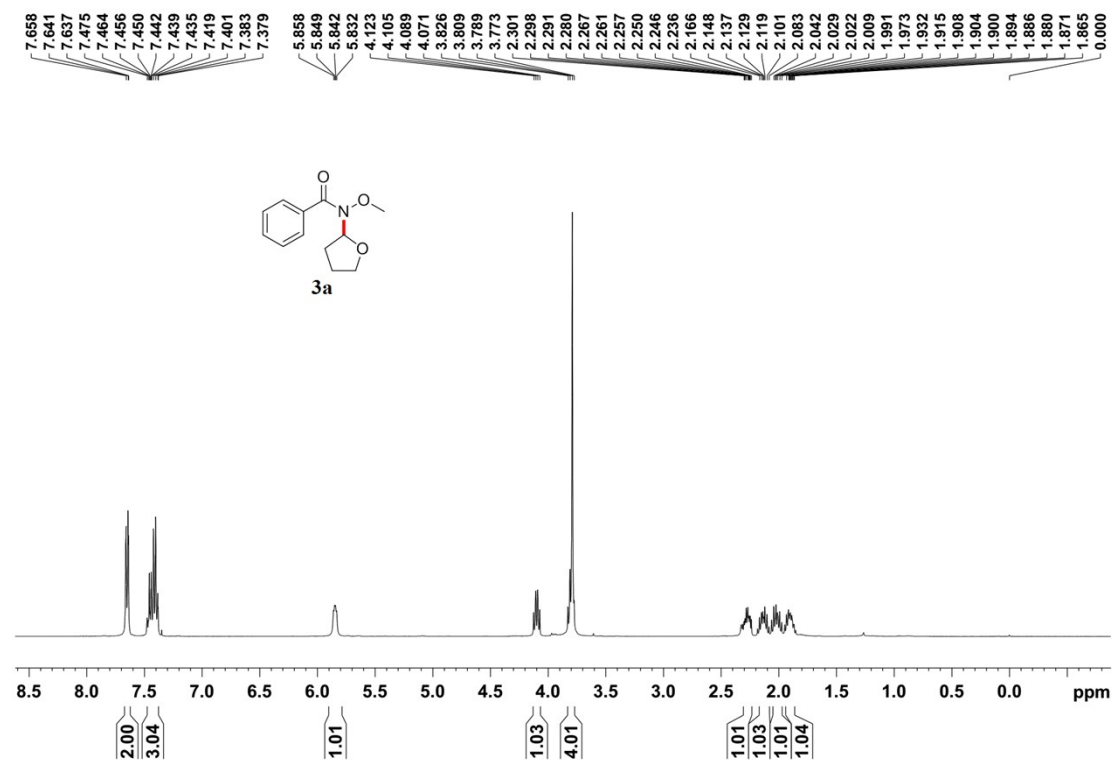


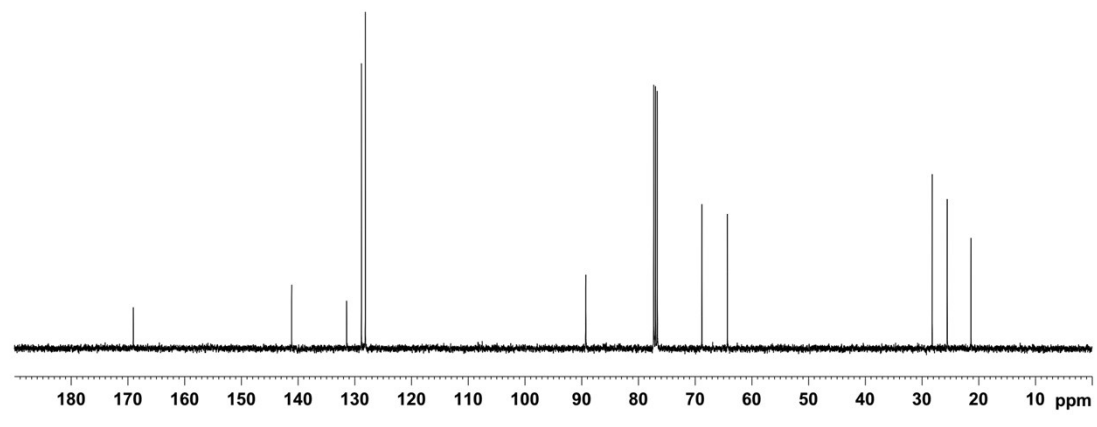
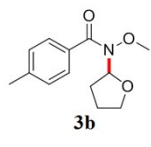
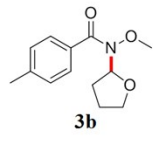
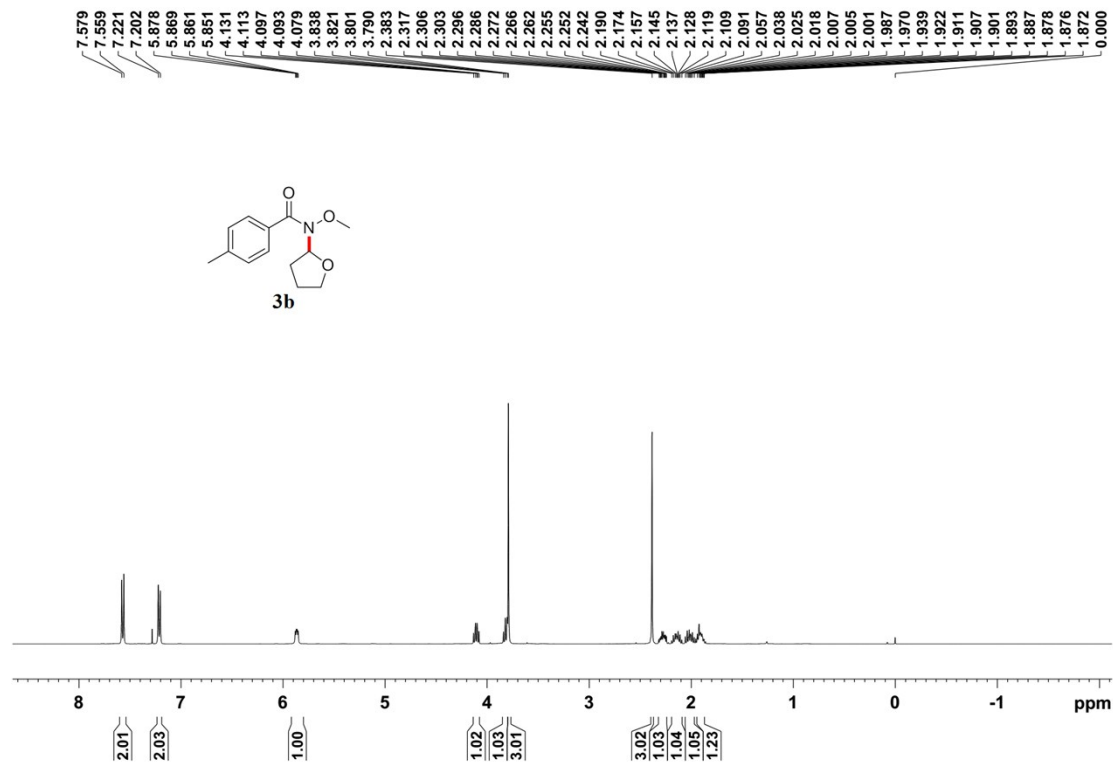
***N*-(1-*iso*-Butoxyethyl)-*N*-methoxybenzamide (4g)**: Colorless liquid; 43% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.67–7.65 (m, 2H), 7.49–7.45 (m, 1H), 7.43–7.39 (m, 2H), 5.67 (s, 1H), 3.67 (s, 3H), 3.42 (q, $J = 6.8$ Hz, 1H), 3.26–3.22 (m, 1H), 1.90–1.80 (m, 1H), 1.52 (d, $J = 6.0$ Hz, 3H), 0.91 (dd, $J_1 = 6.7$ Hz, $J_2 = 0.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.29, 134.43, 130.66, 128.08, 84.05, 75.17, 64.75, 28.40, 19.33, 19.31, 18.15. HRMS (EI): Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_3$: 251.1521, found: 251.1526.

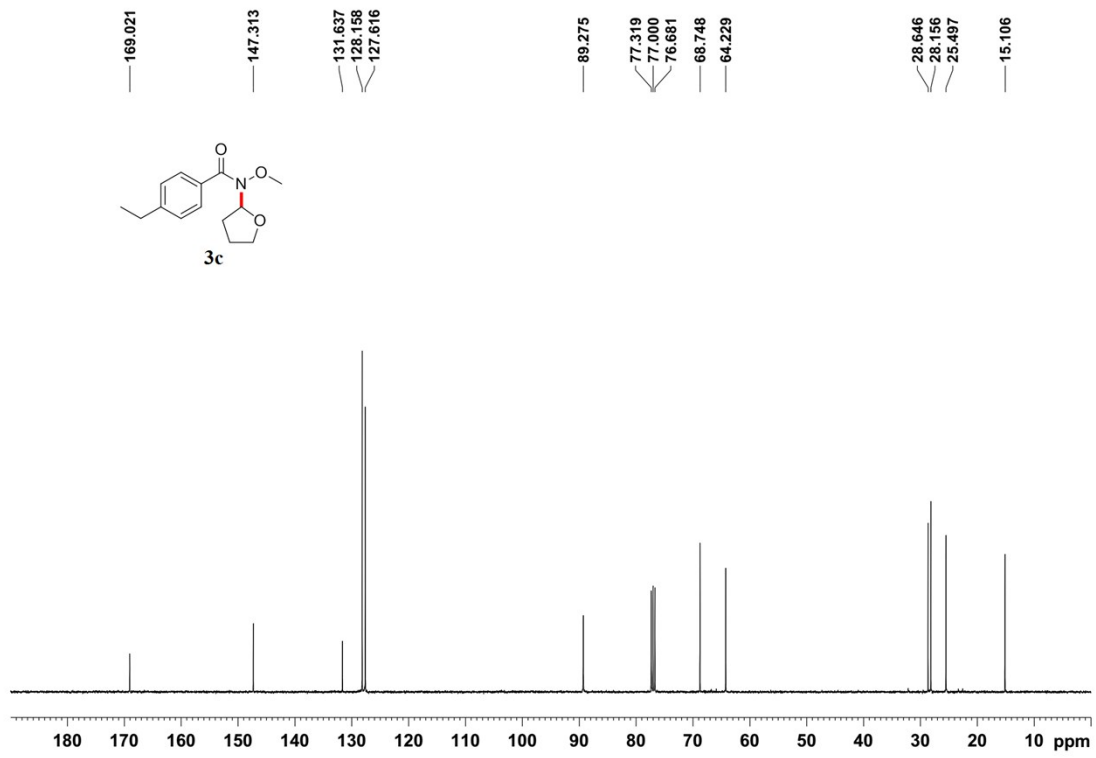
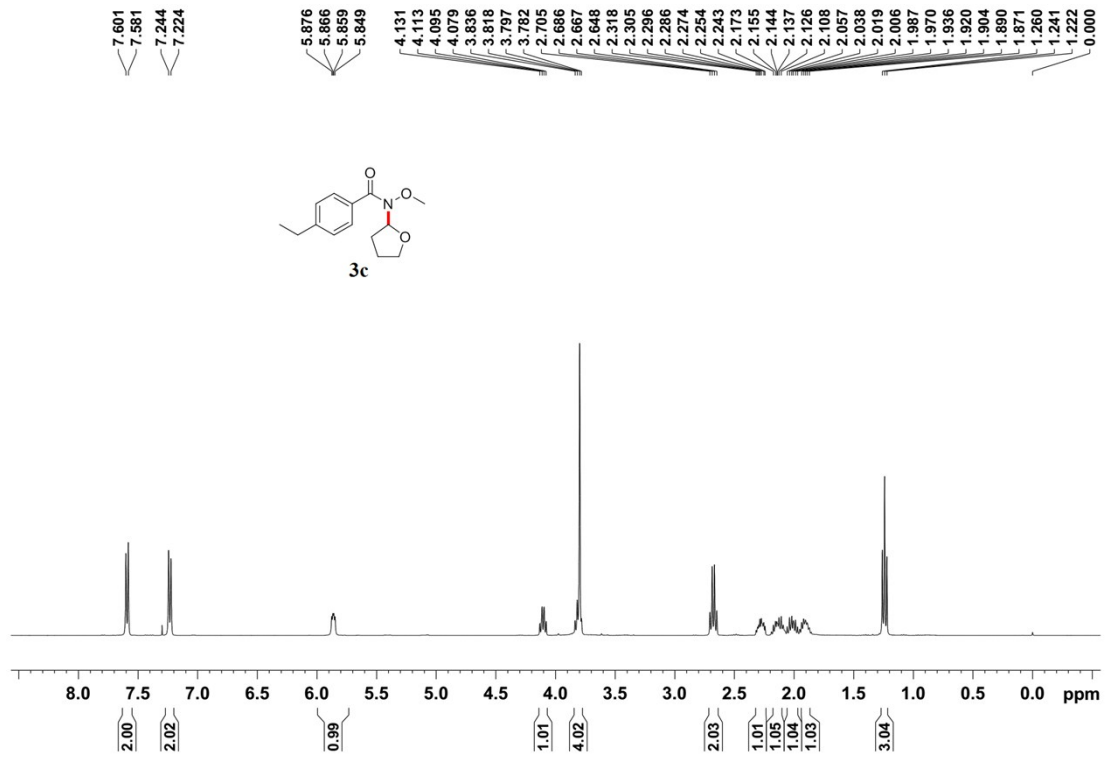


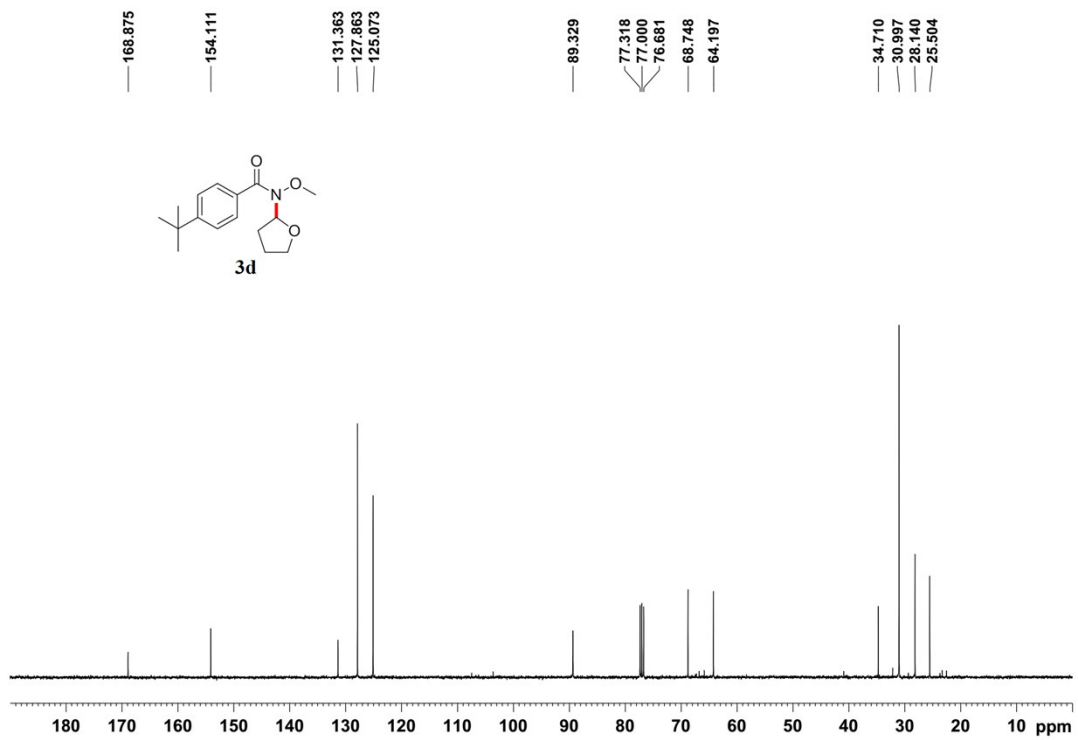
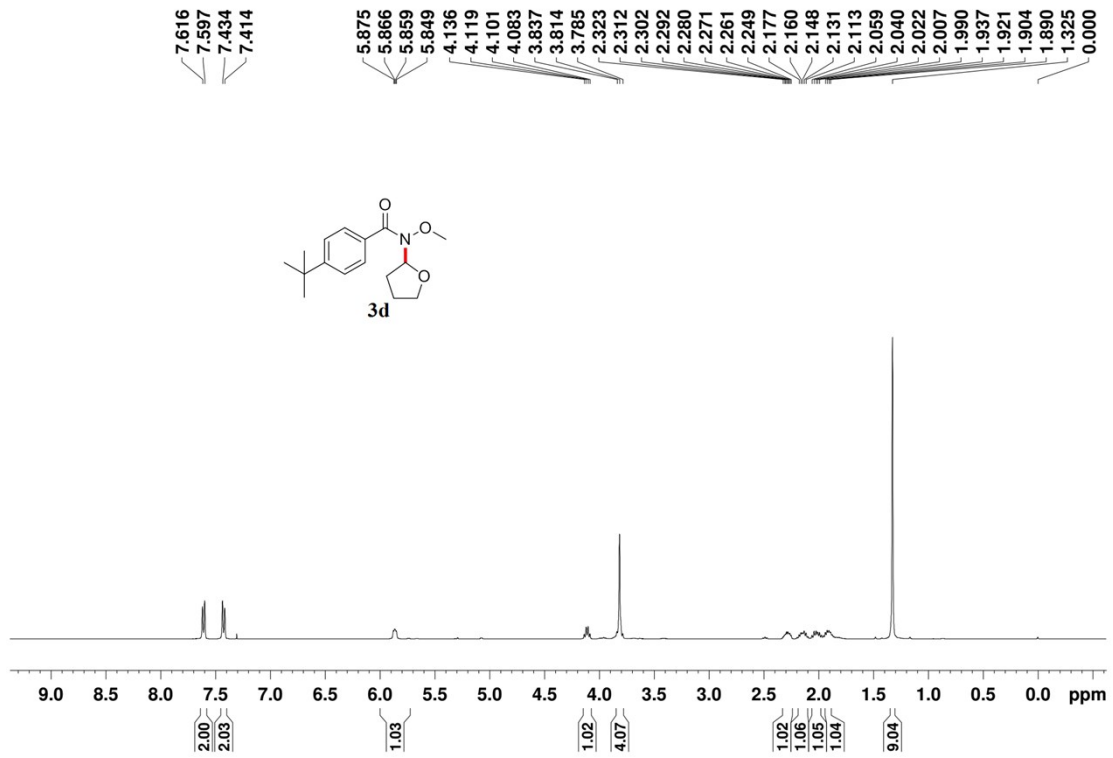
***N*-(1-Ethoxypropyl)-*N*-methoxybenzamide (4h)**: Colorless liquid; 43% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, $J = 7.4$ Hz, 2H), 7.49–7.39 (m, 3H), 5.47–5.44 (m, 1H), 3.81–3.73 (m, 1H), 3.65 (s, 3H), 3.56 (s, 1H), 1.97–1.88 (m, 2H), 1.22 (t, $J = 7.0$ Hz, 3H), 0.98 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.67, 134.40, 130.61, 128.10, 128.04, 88.35, 64.74, 63.80, 25.31, 14.96, 9.48. HRMS (EI): Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_3$: 237.1365, found: 237.1370.

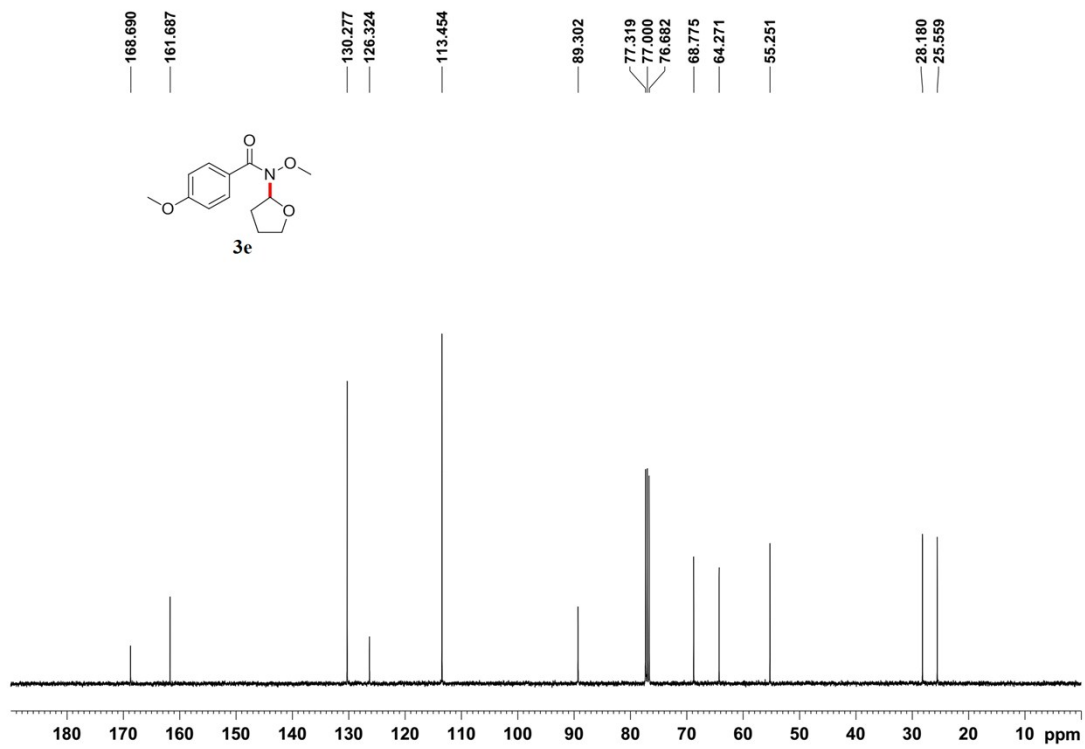
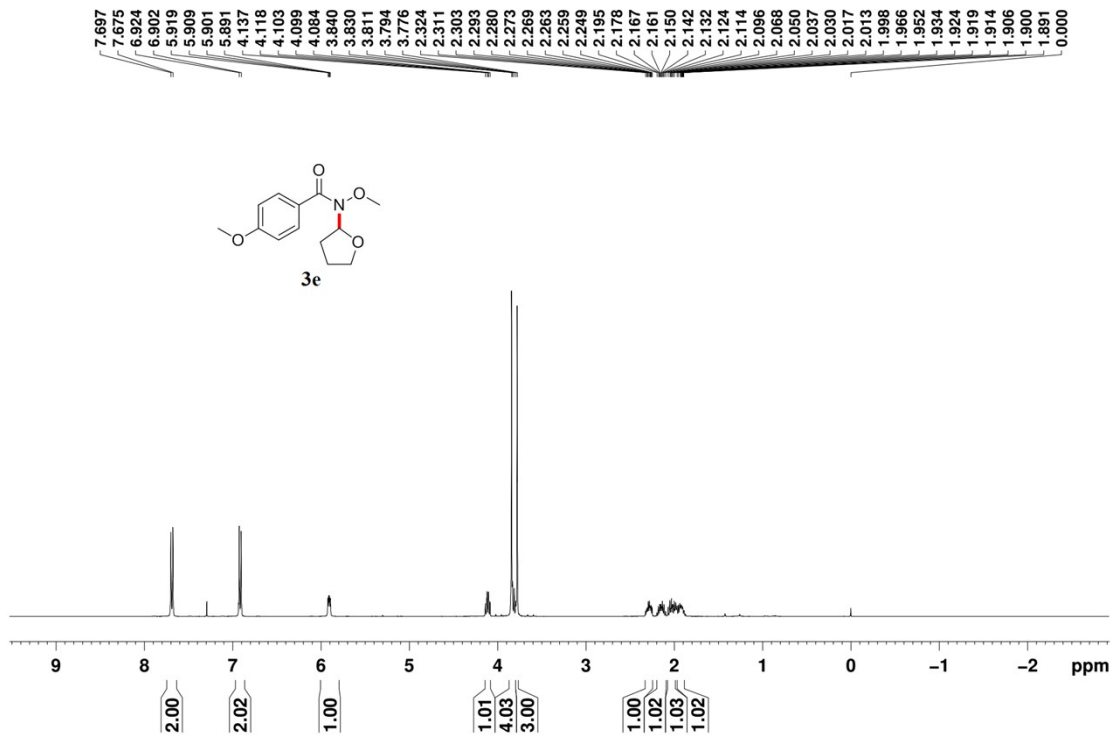
7. ¹H and ¹³C NMR spectra of the products

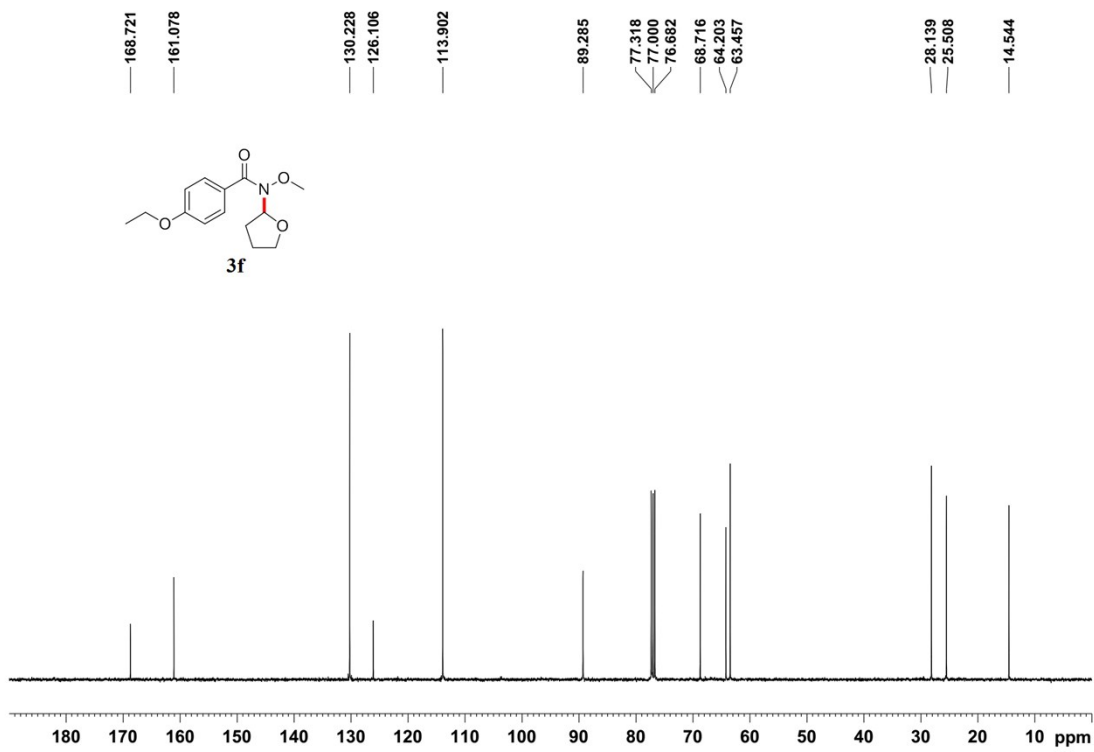
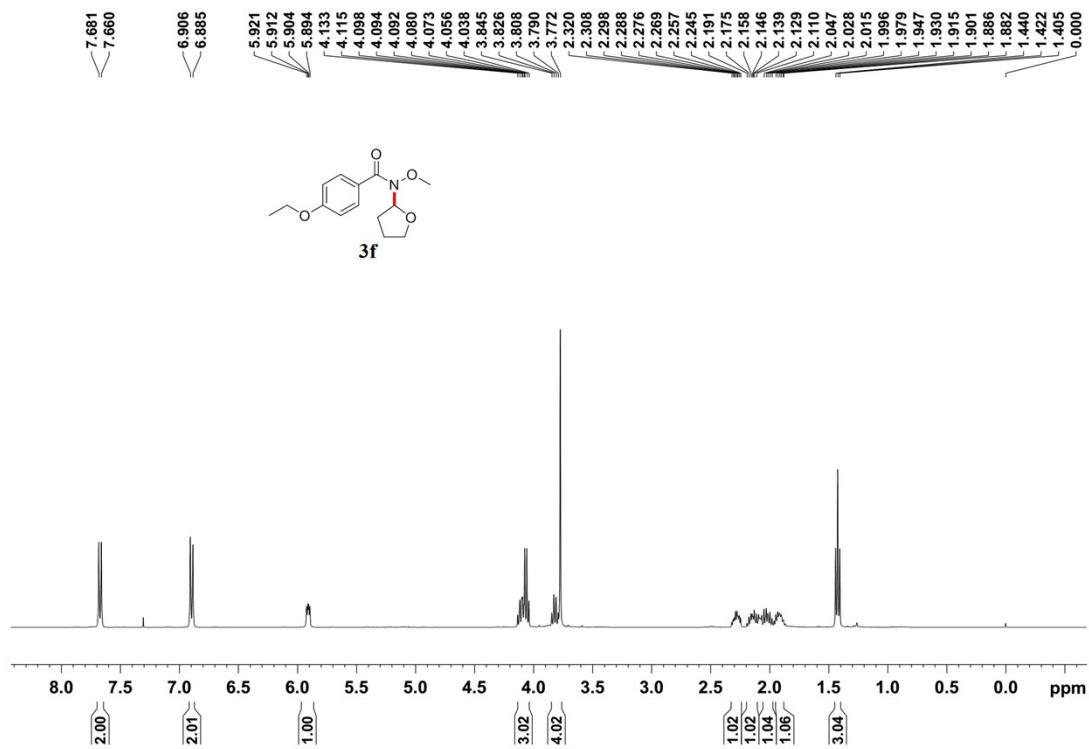


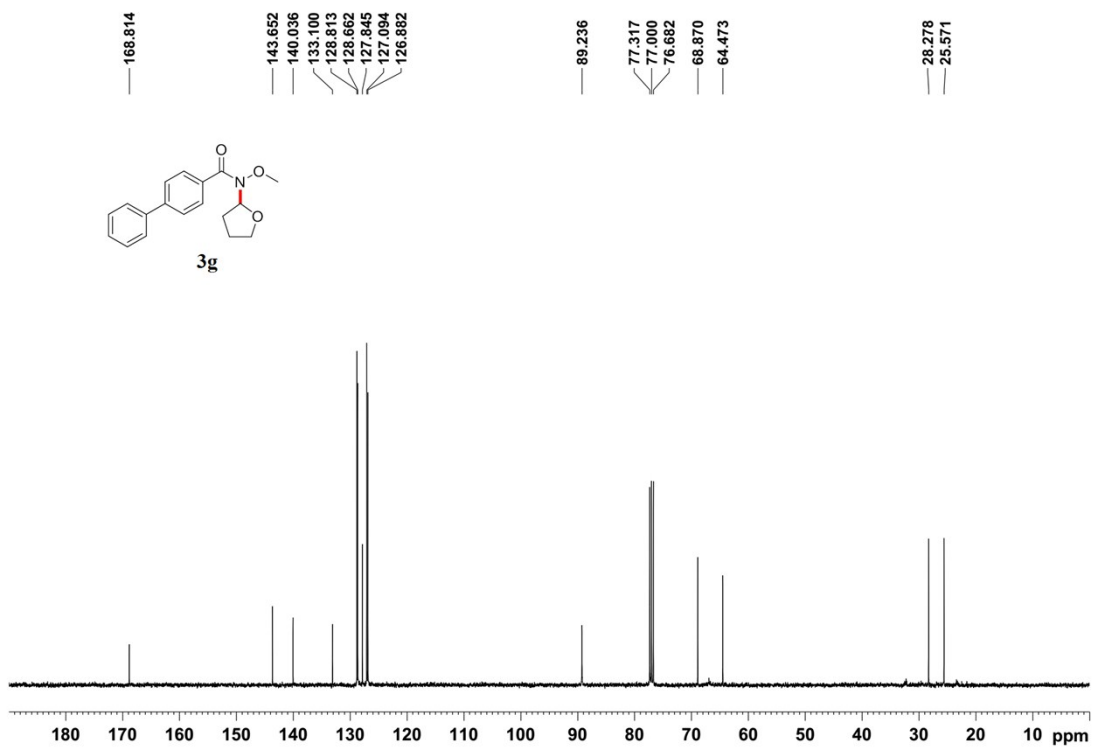
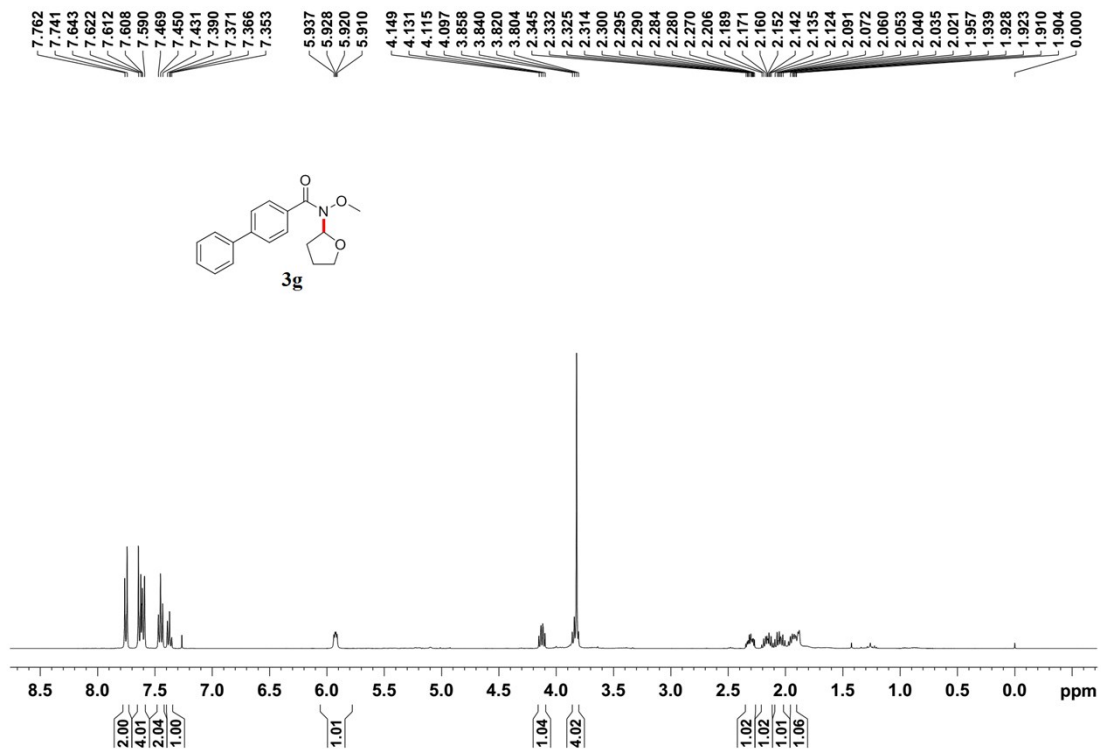


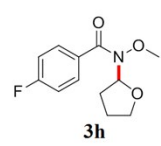
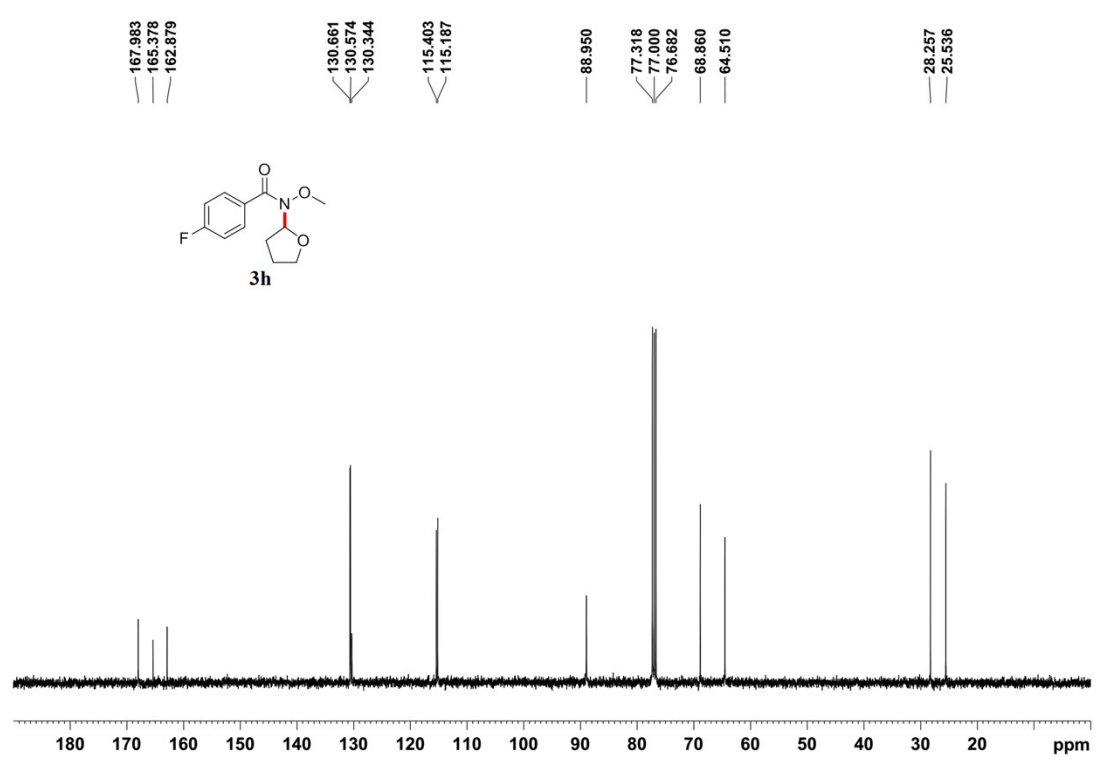
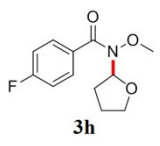
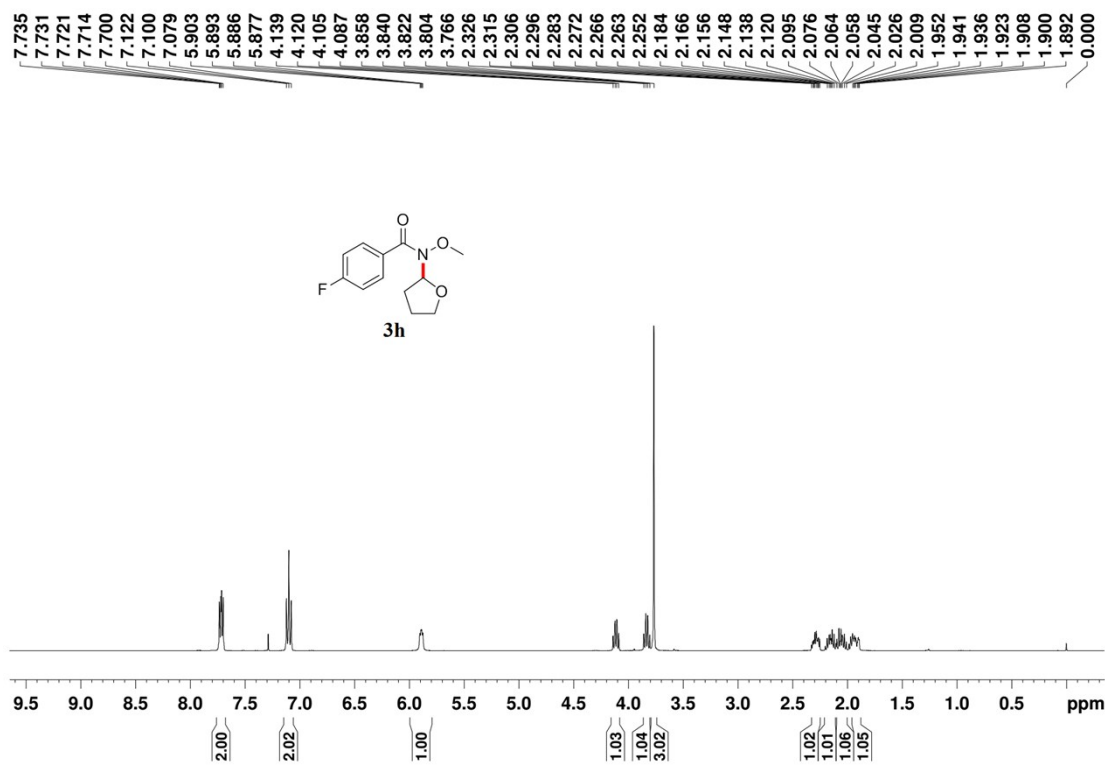


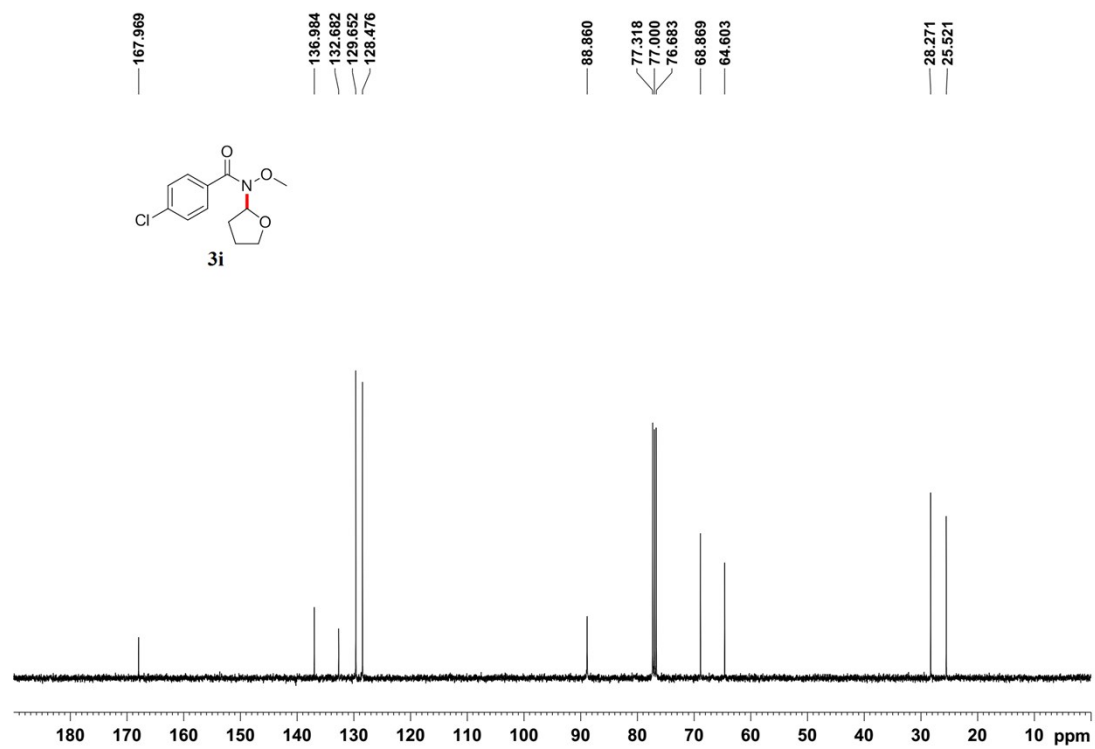
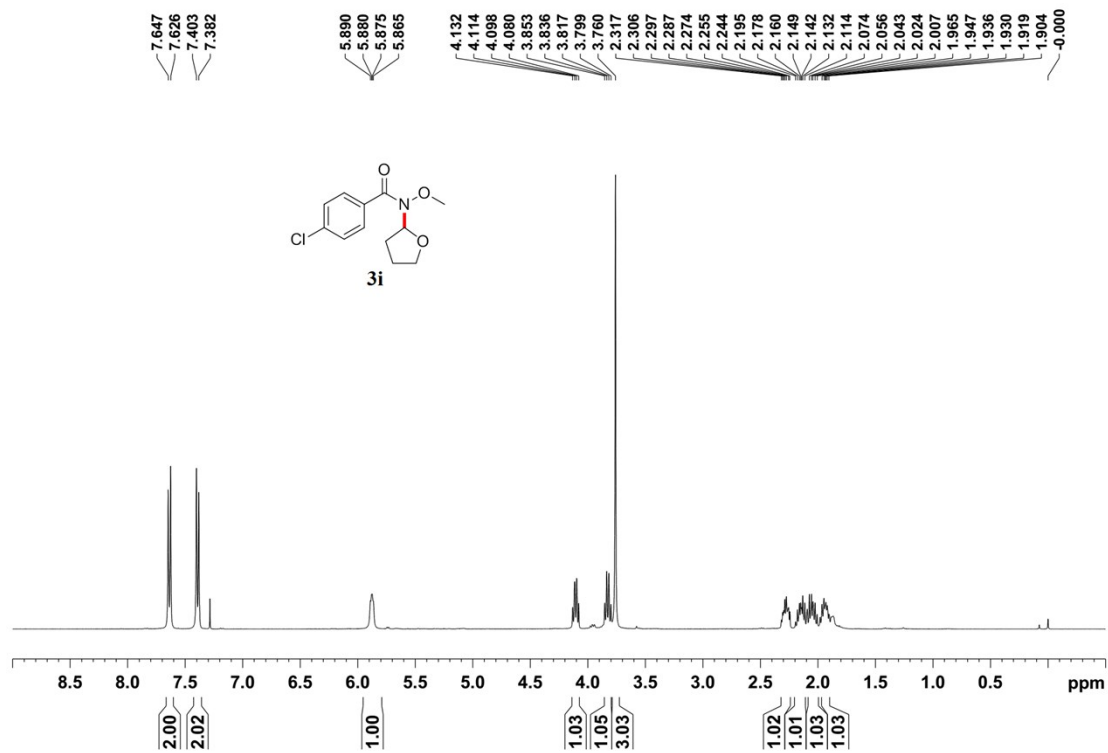


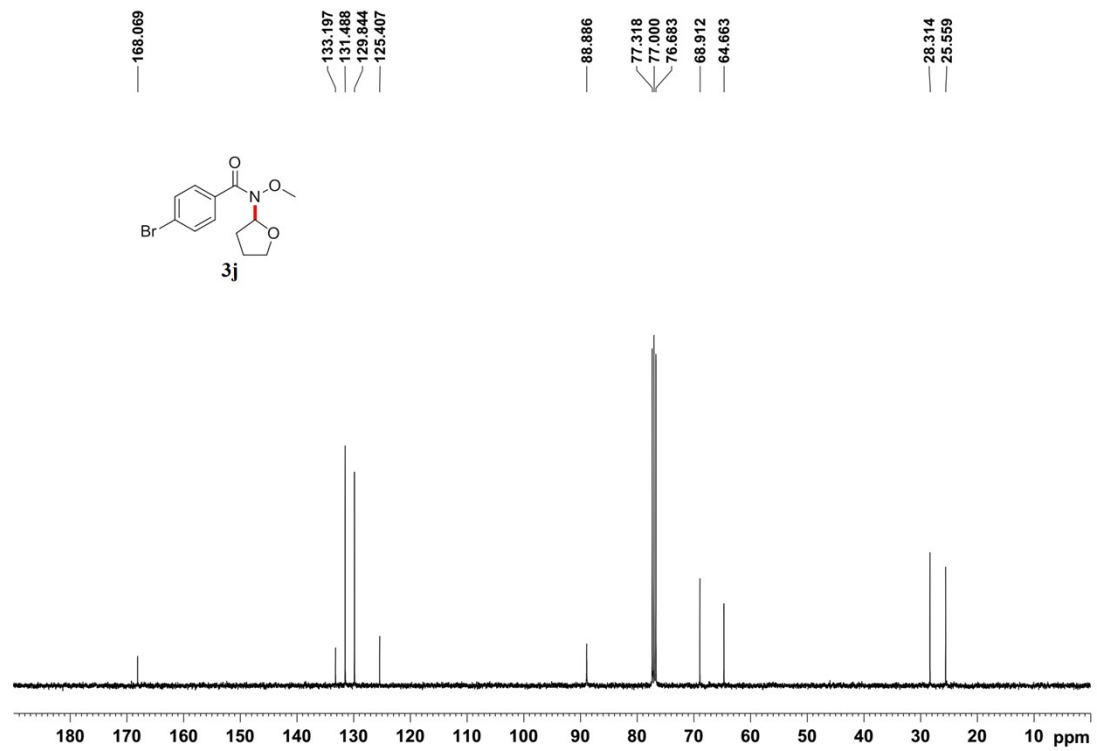
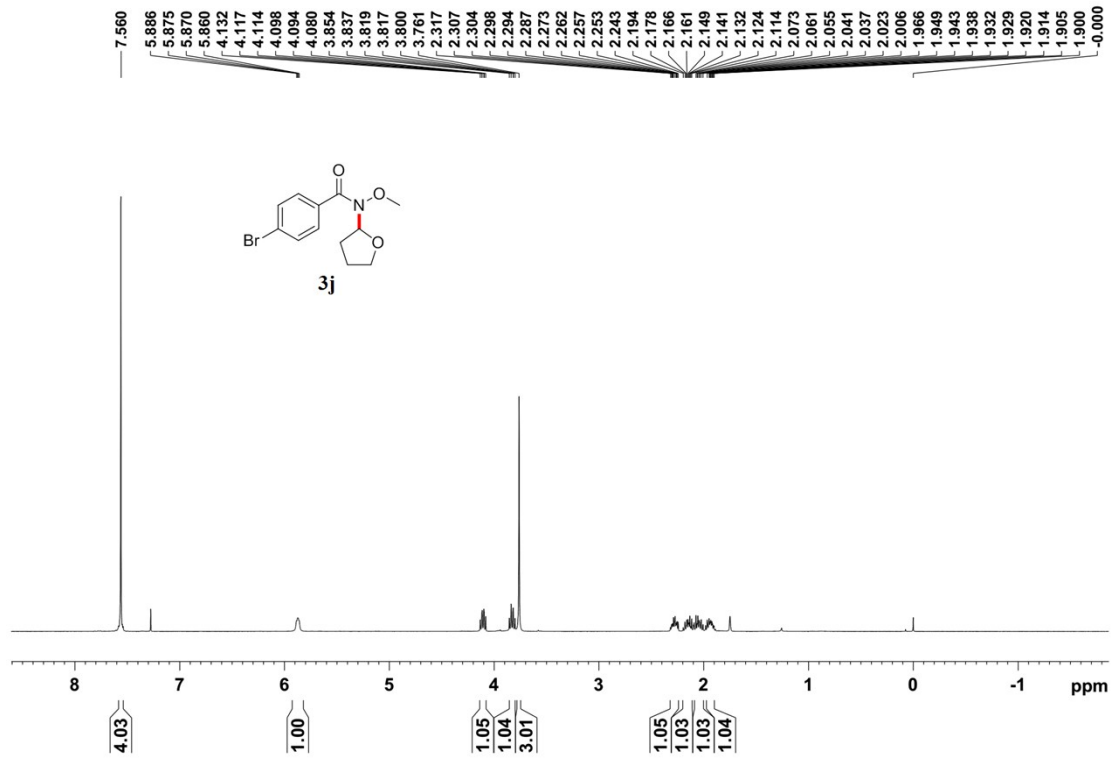


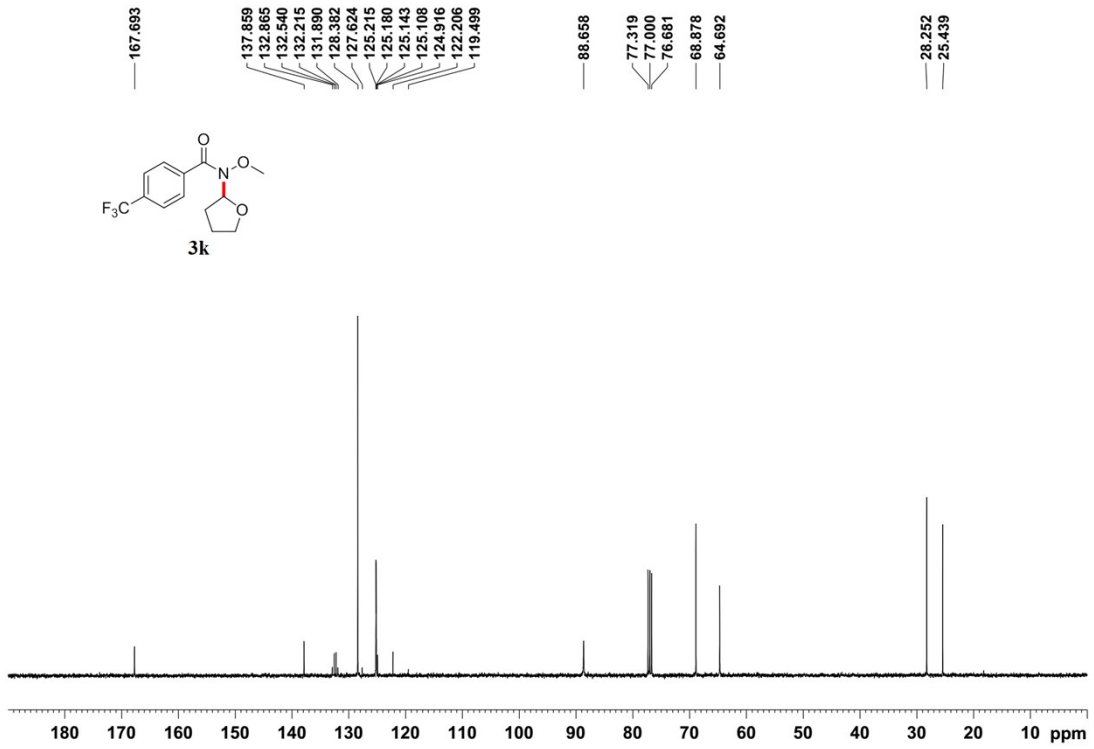
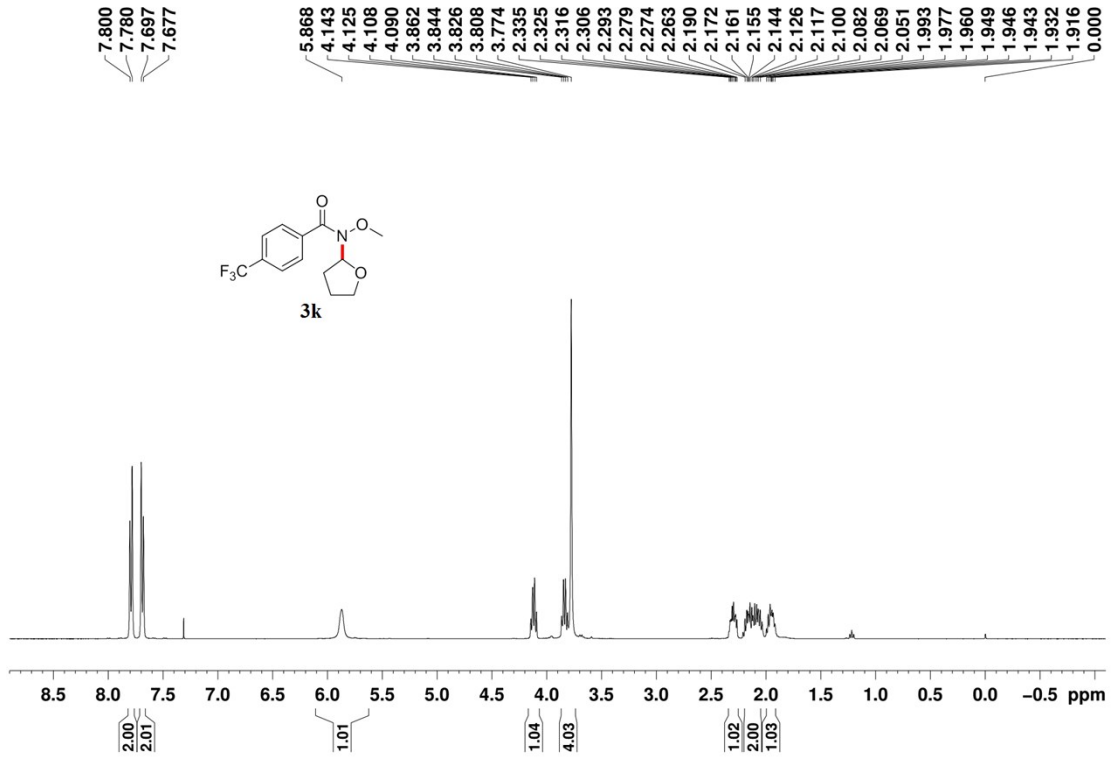


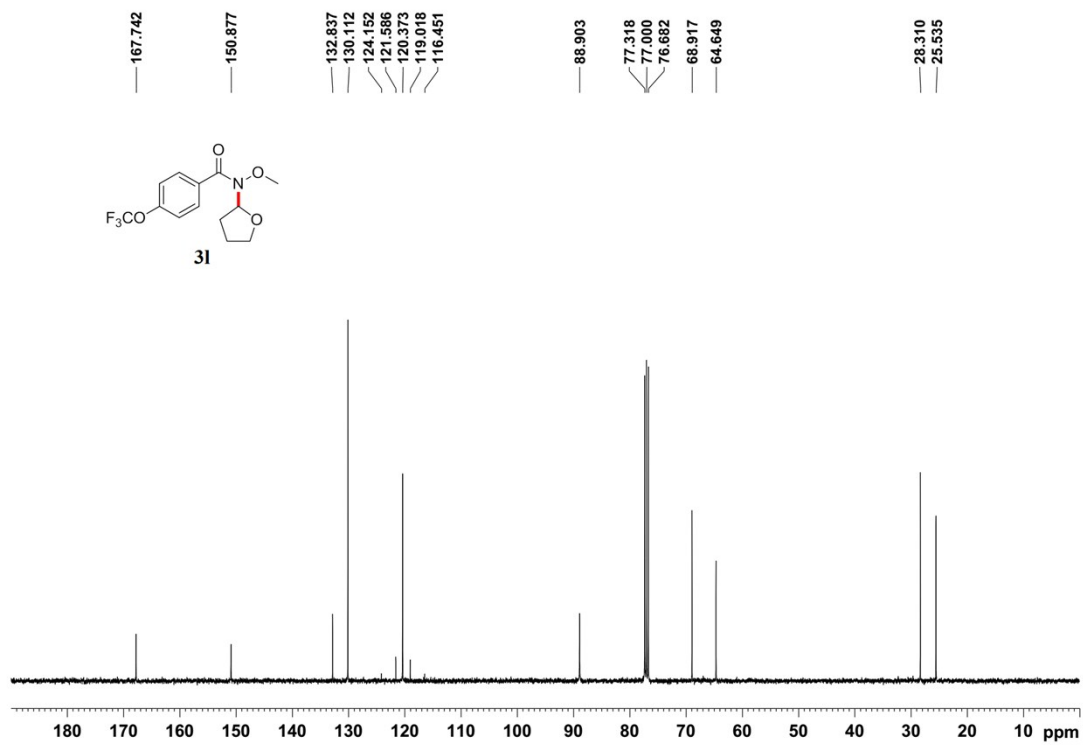
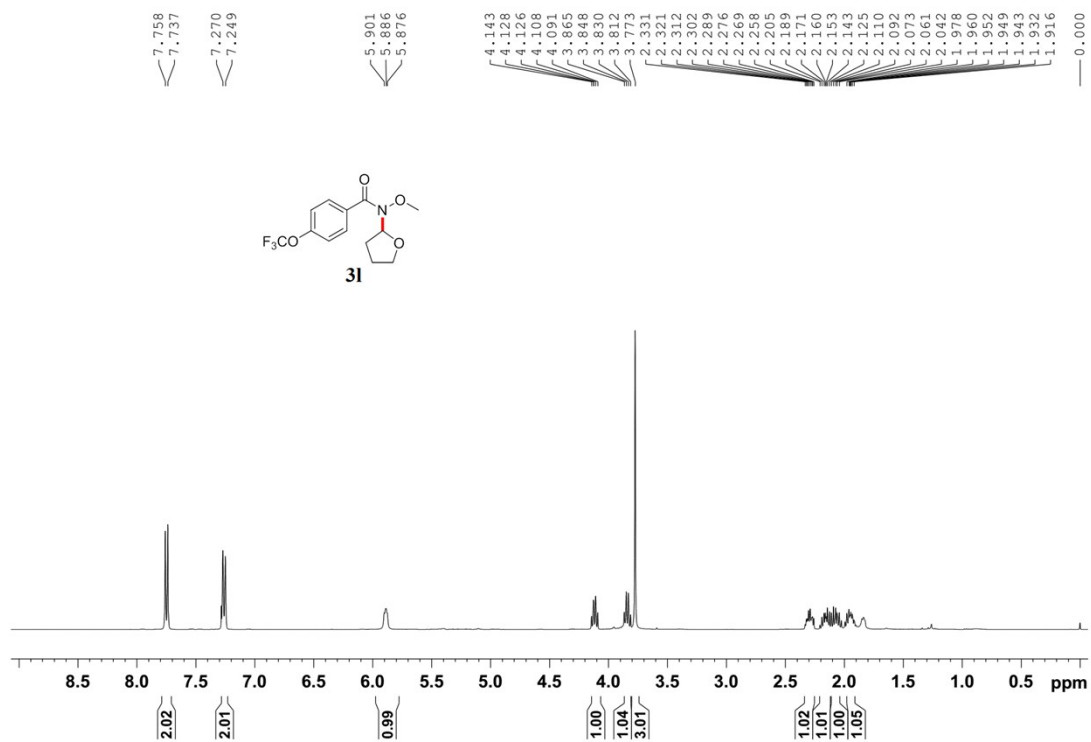


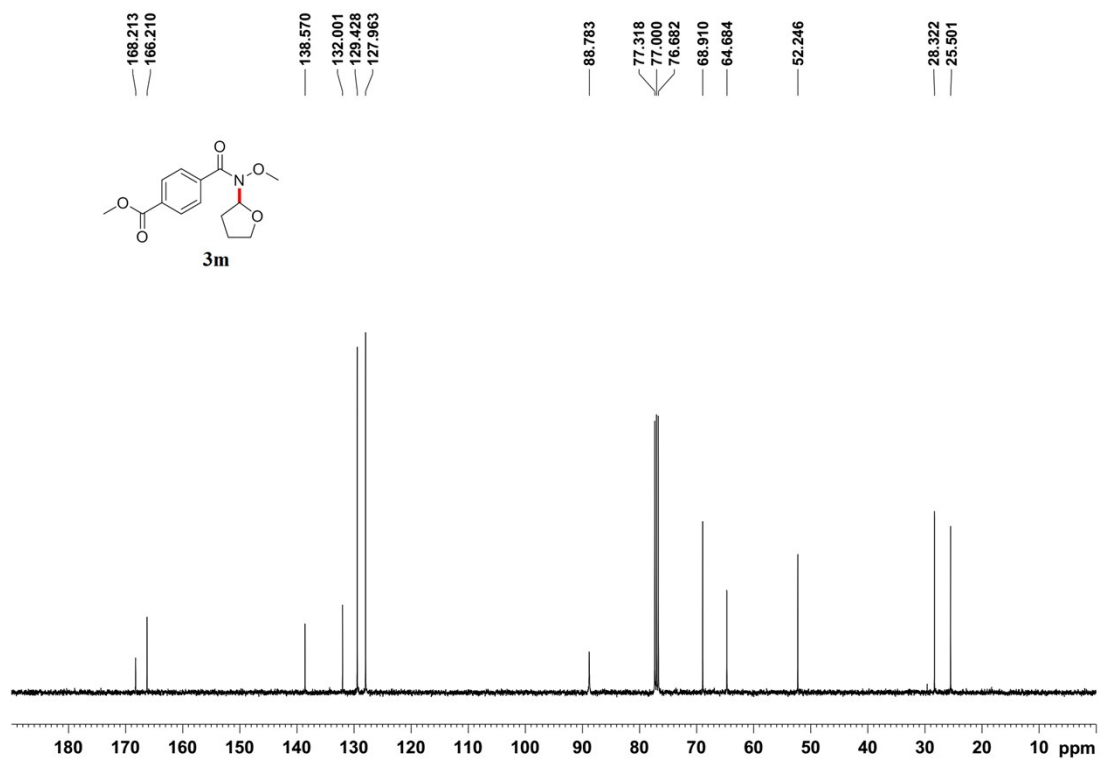
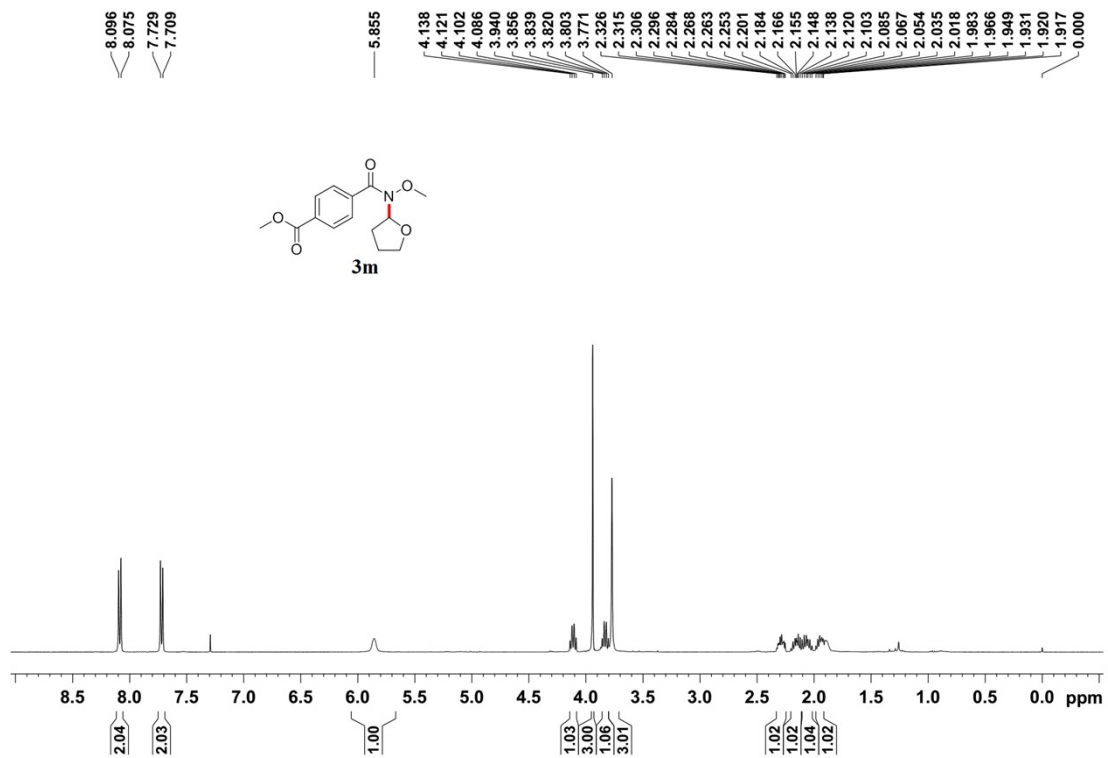


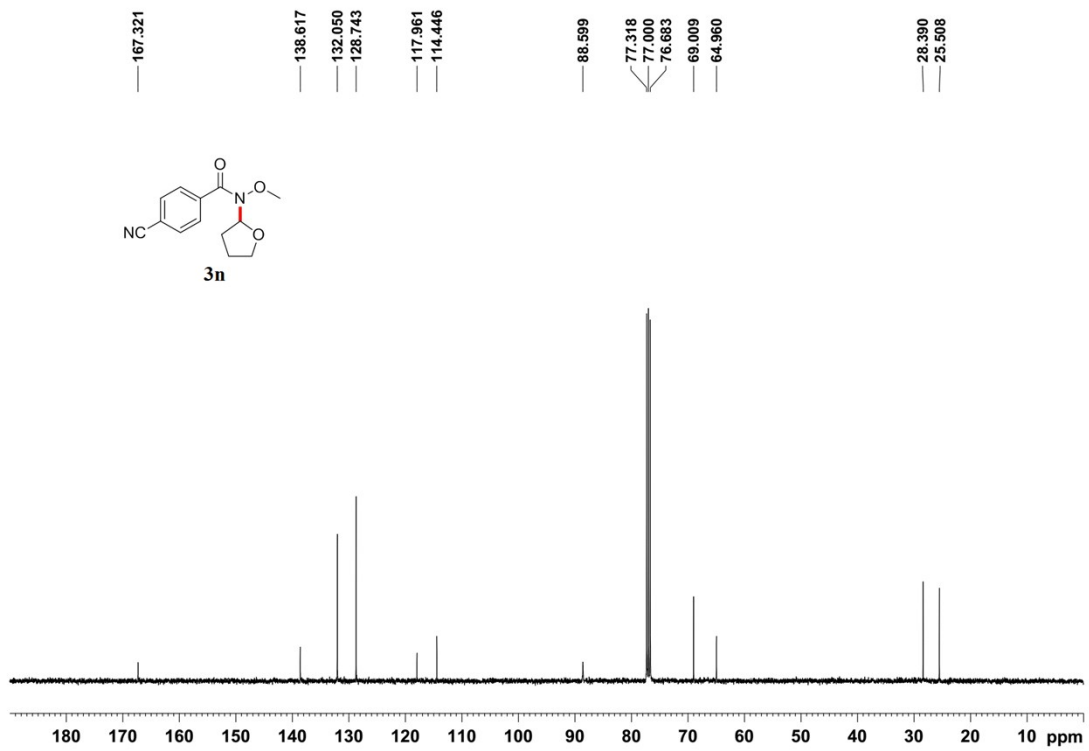
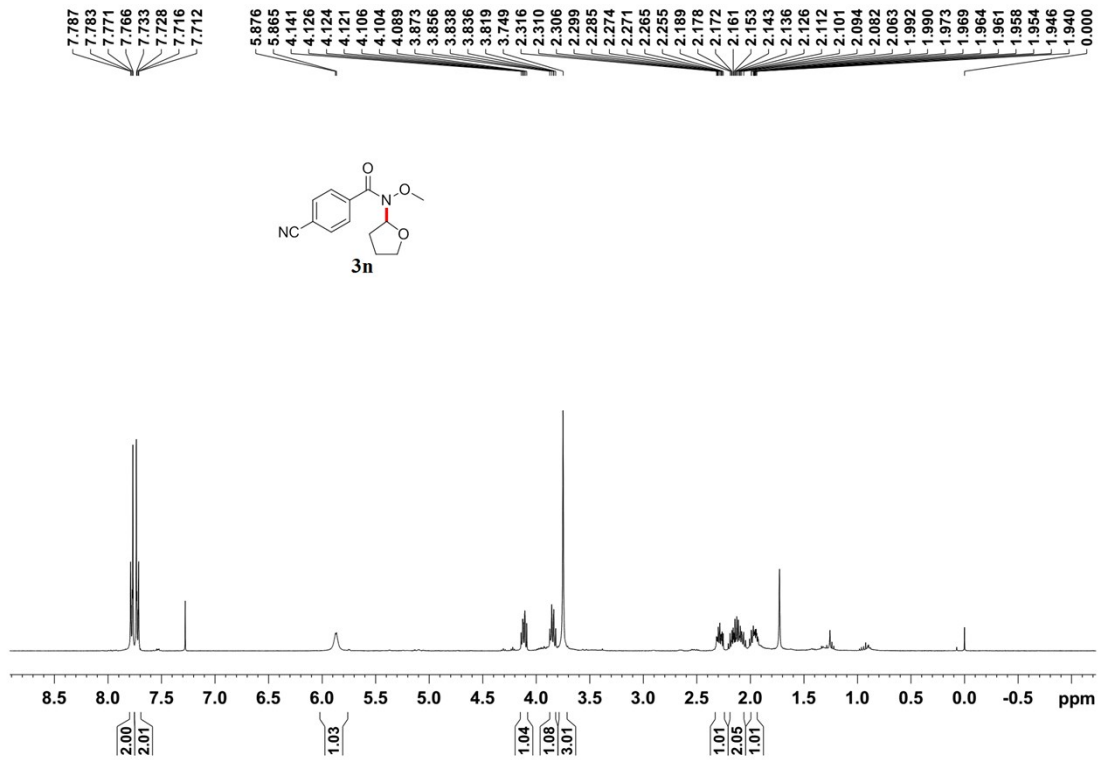


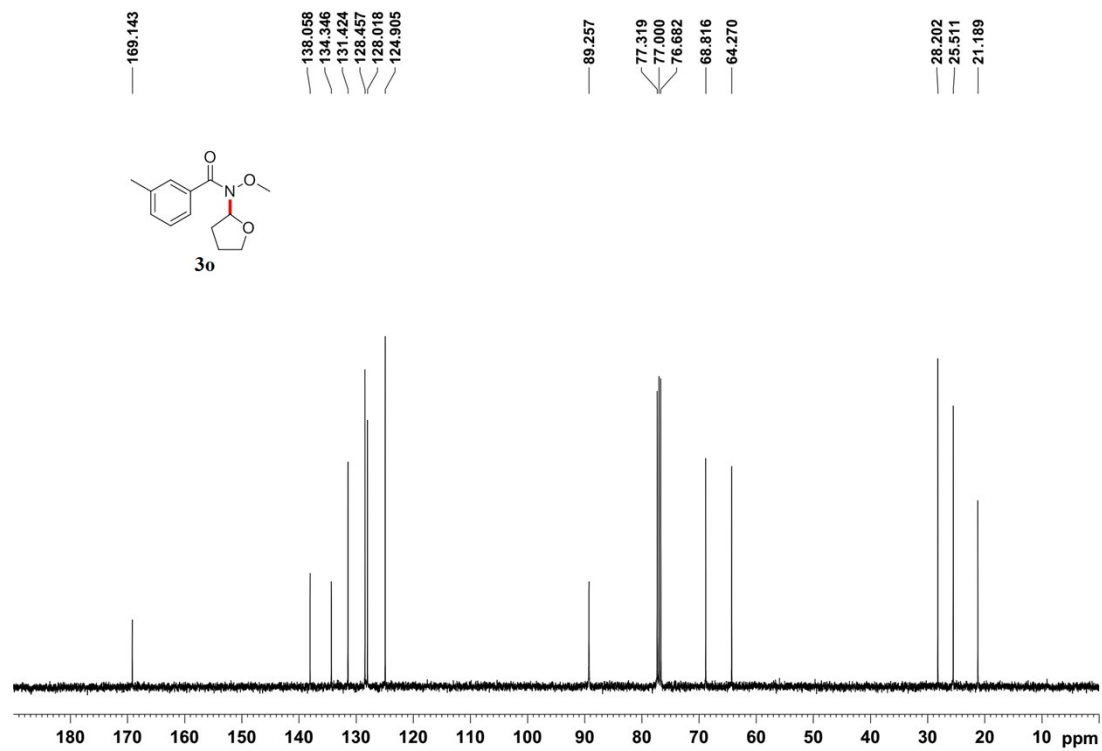
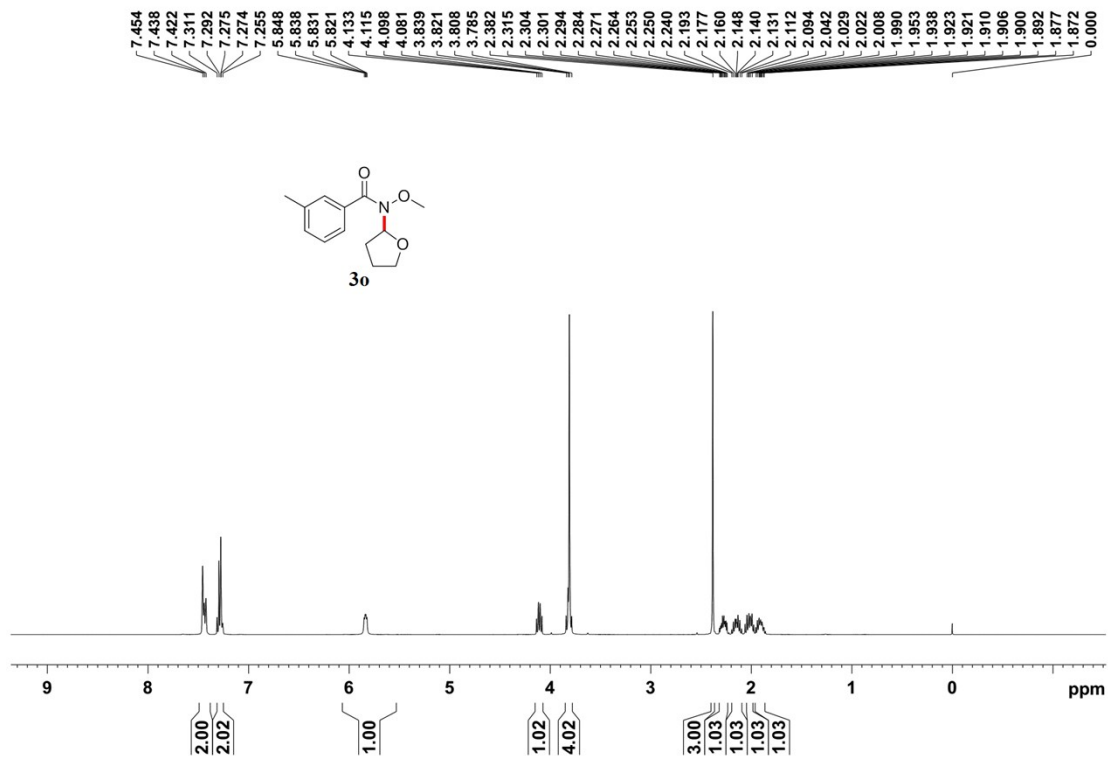


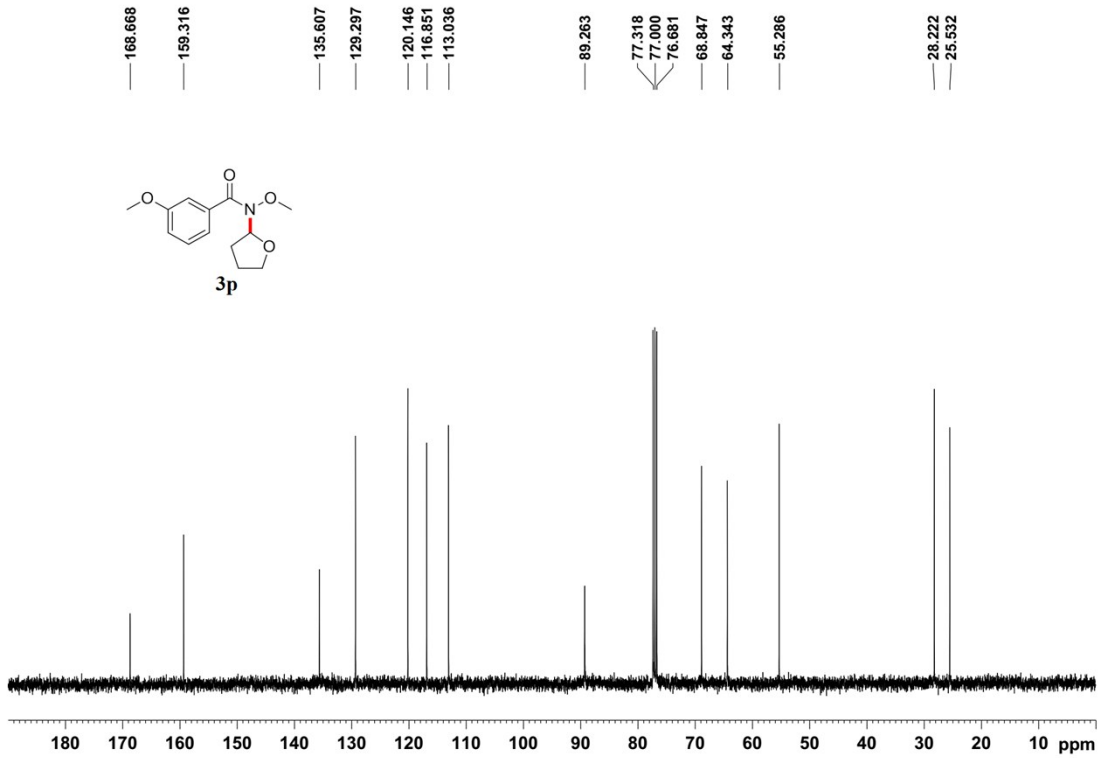
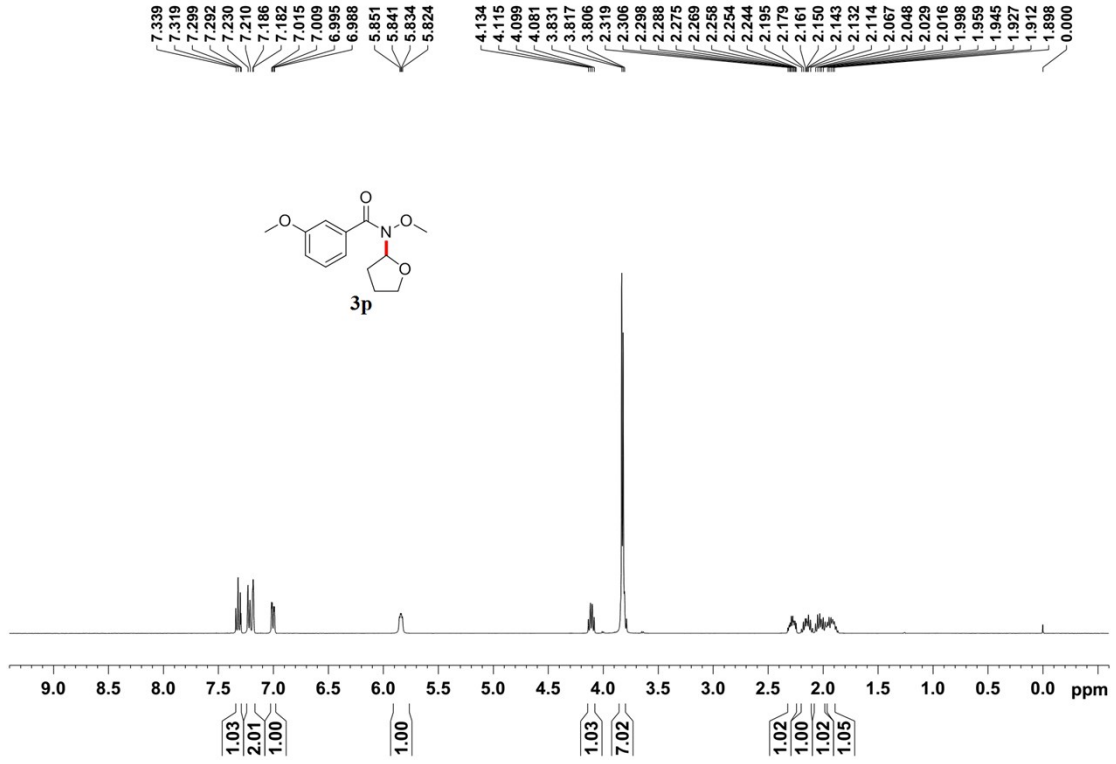


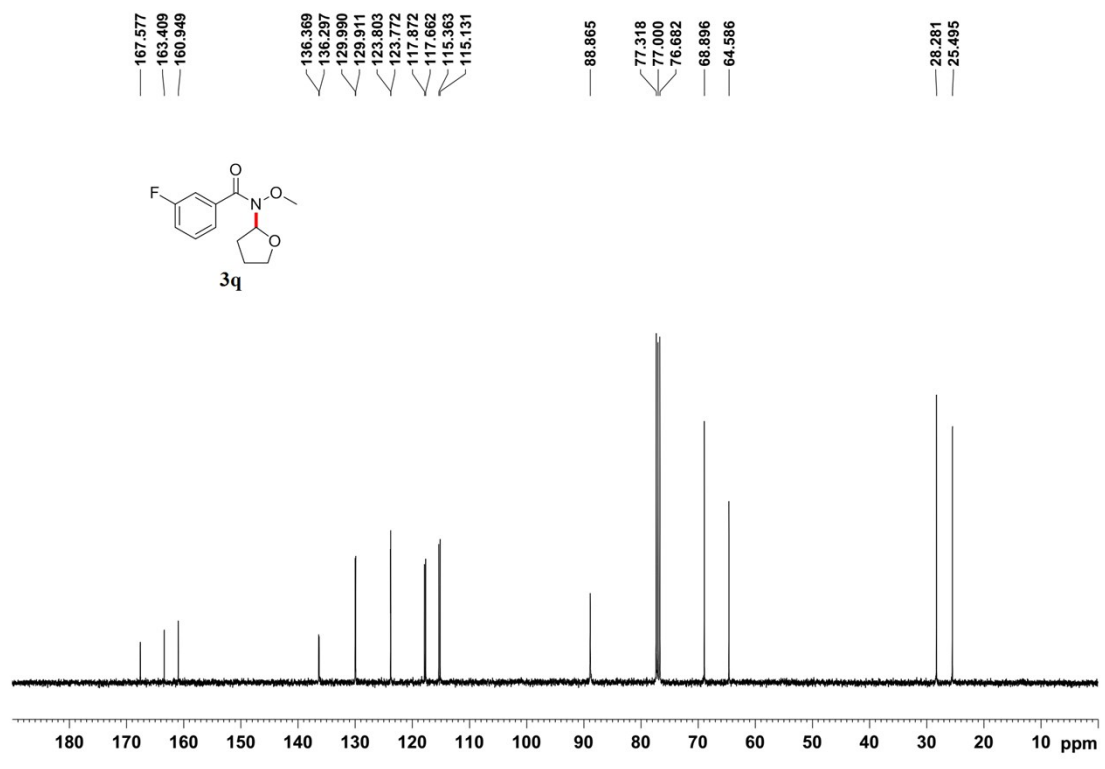
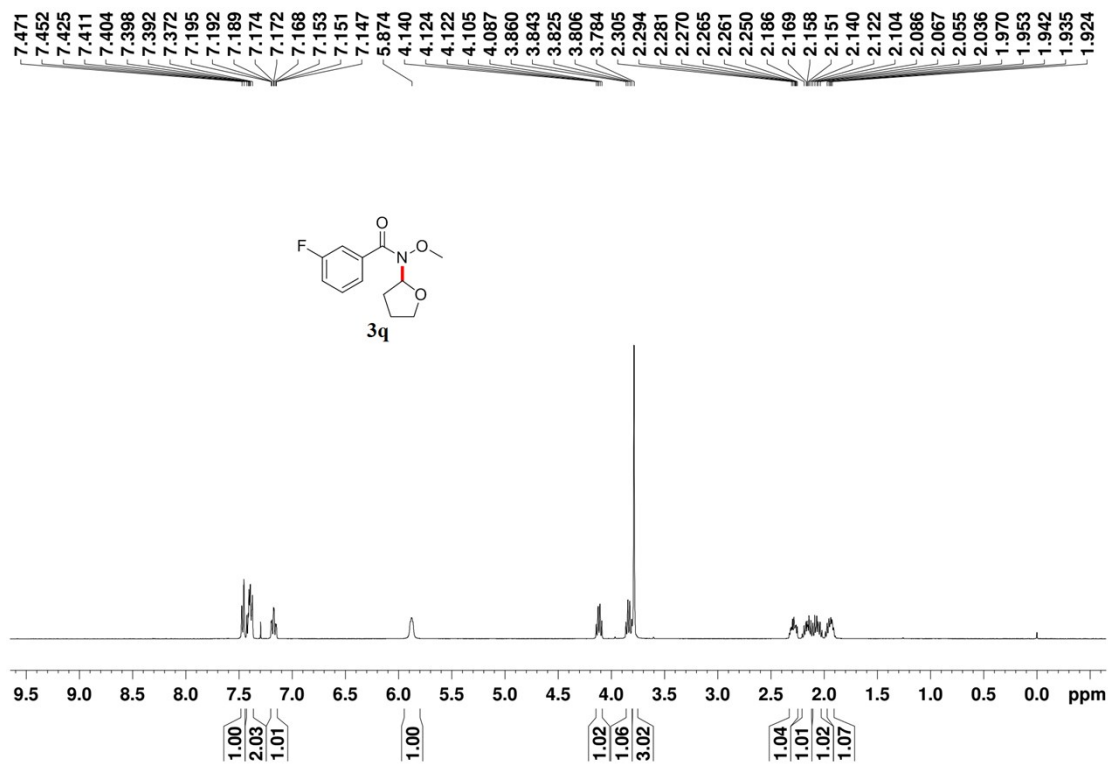


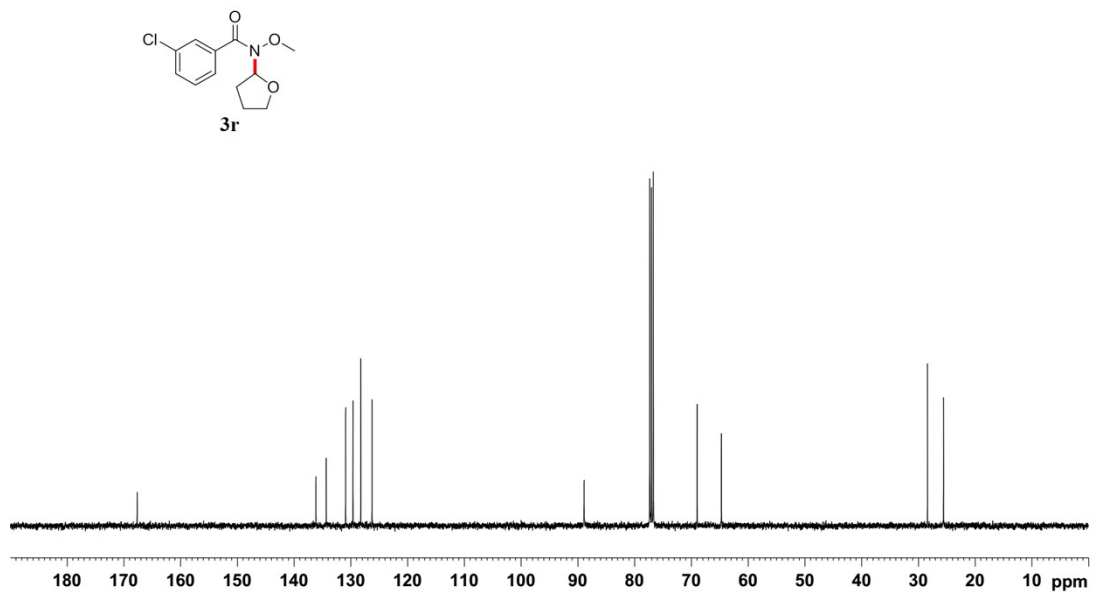
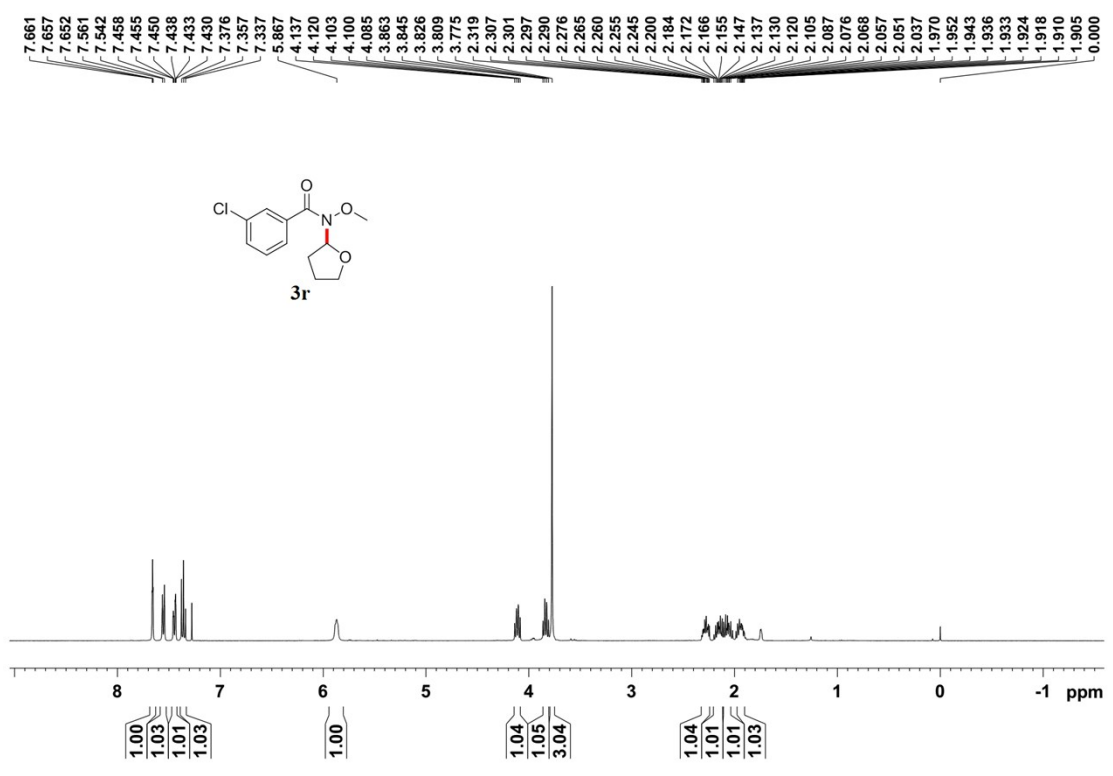


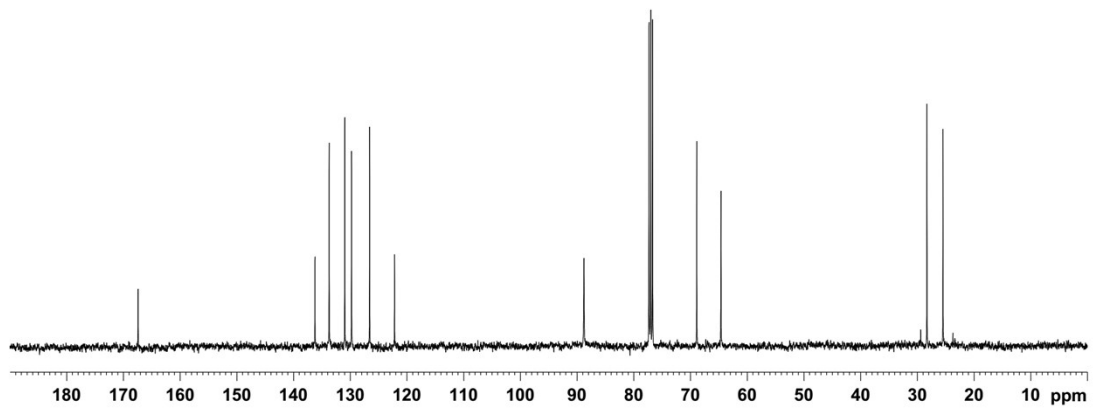
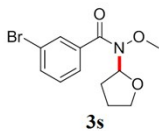
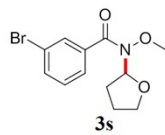
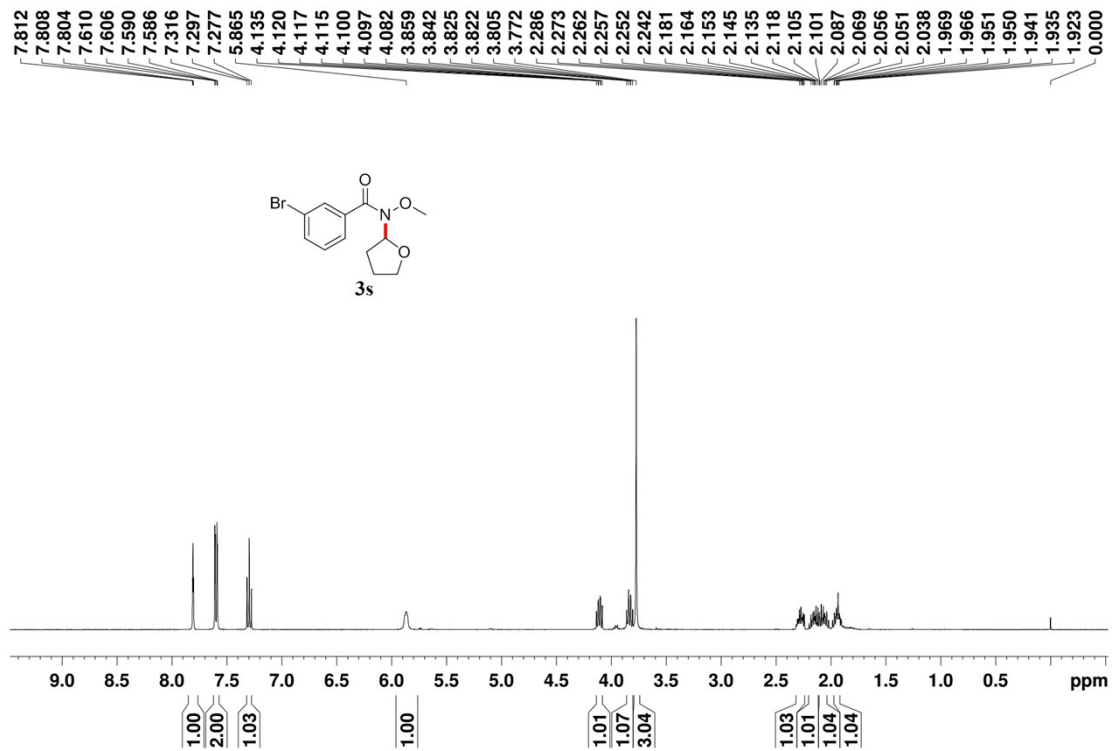


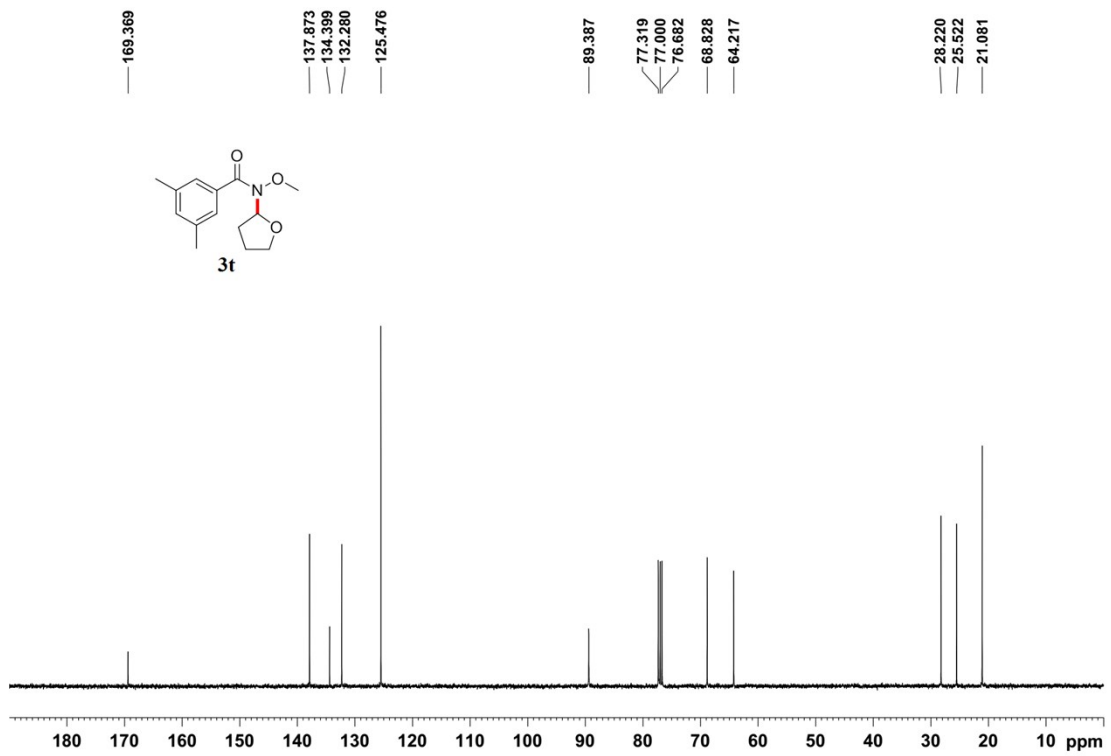
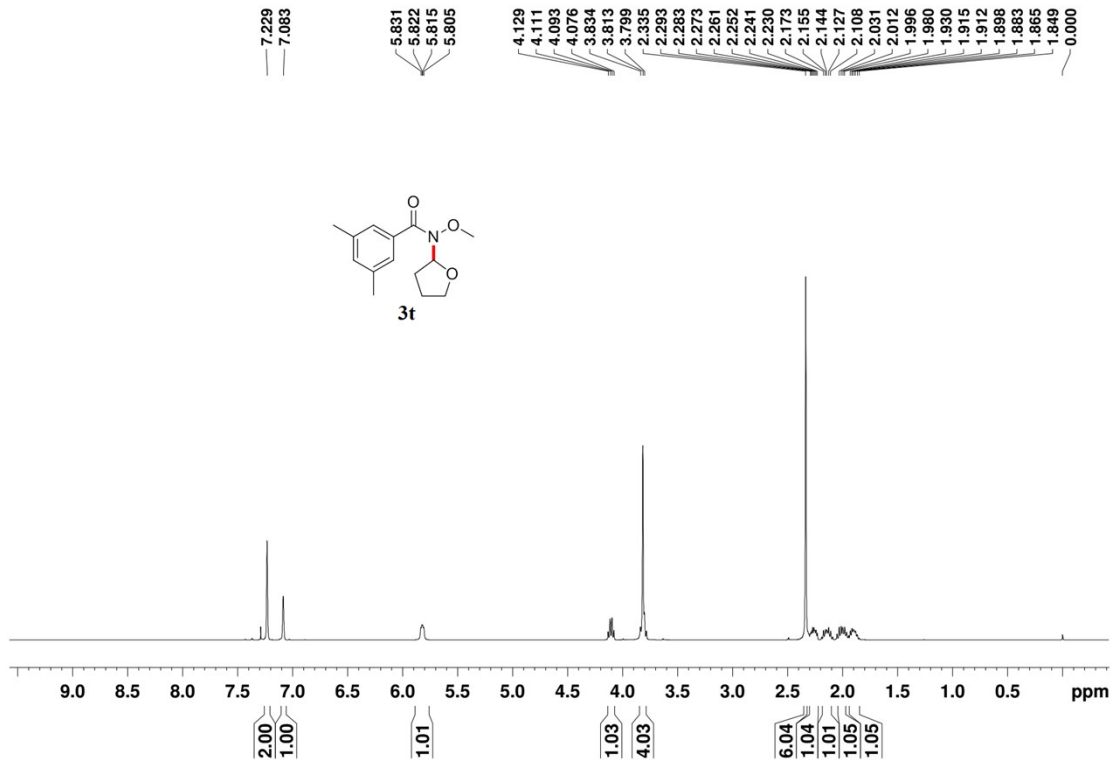


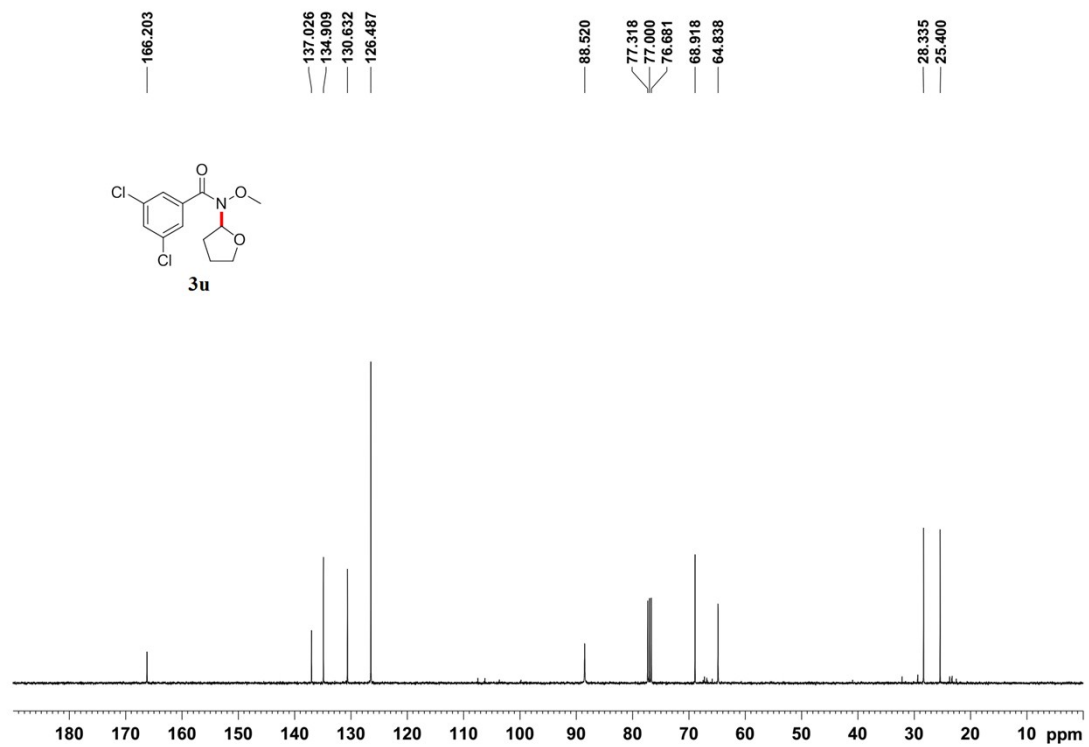
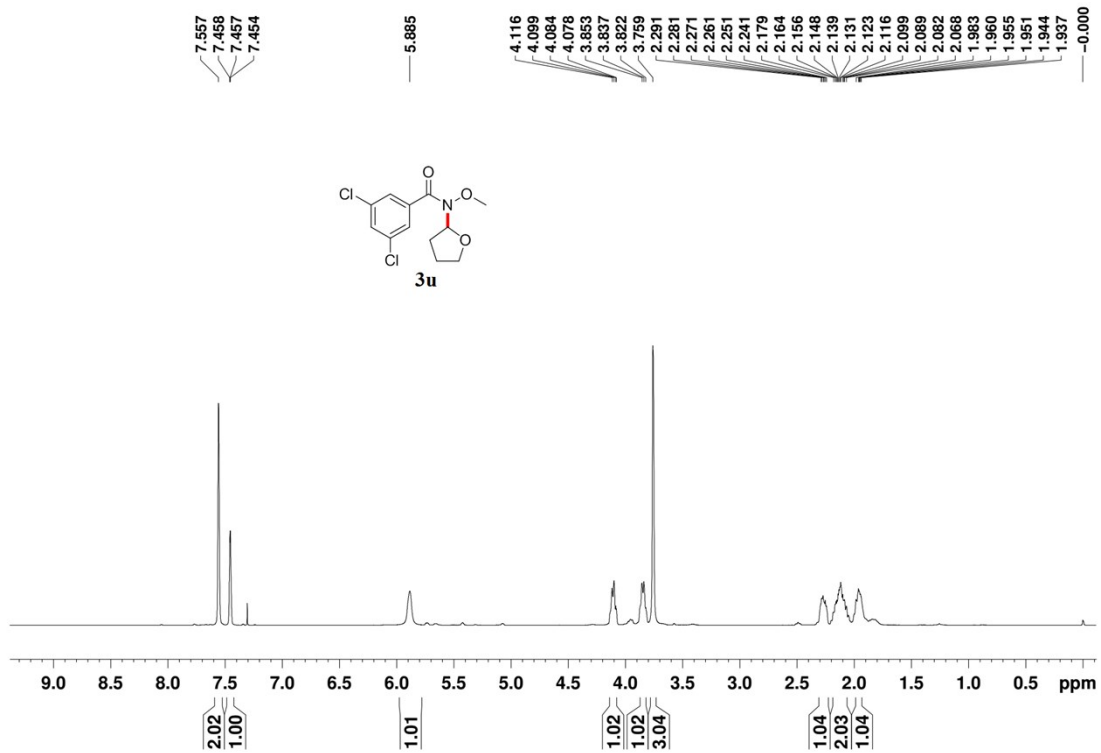


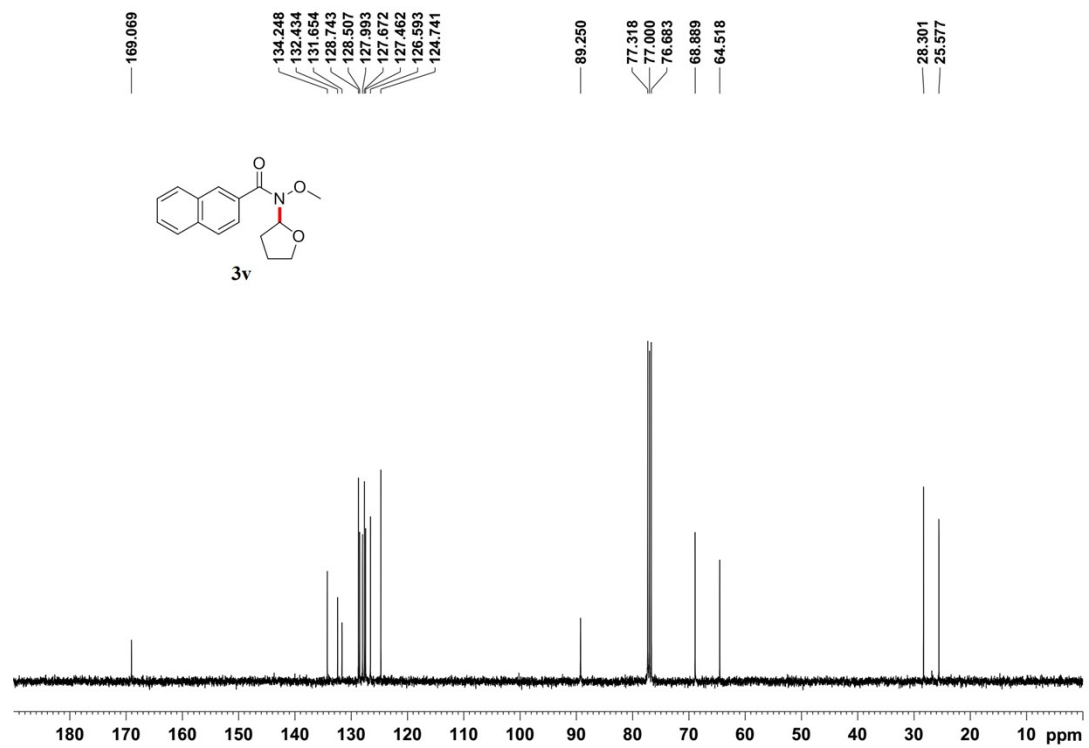
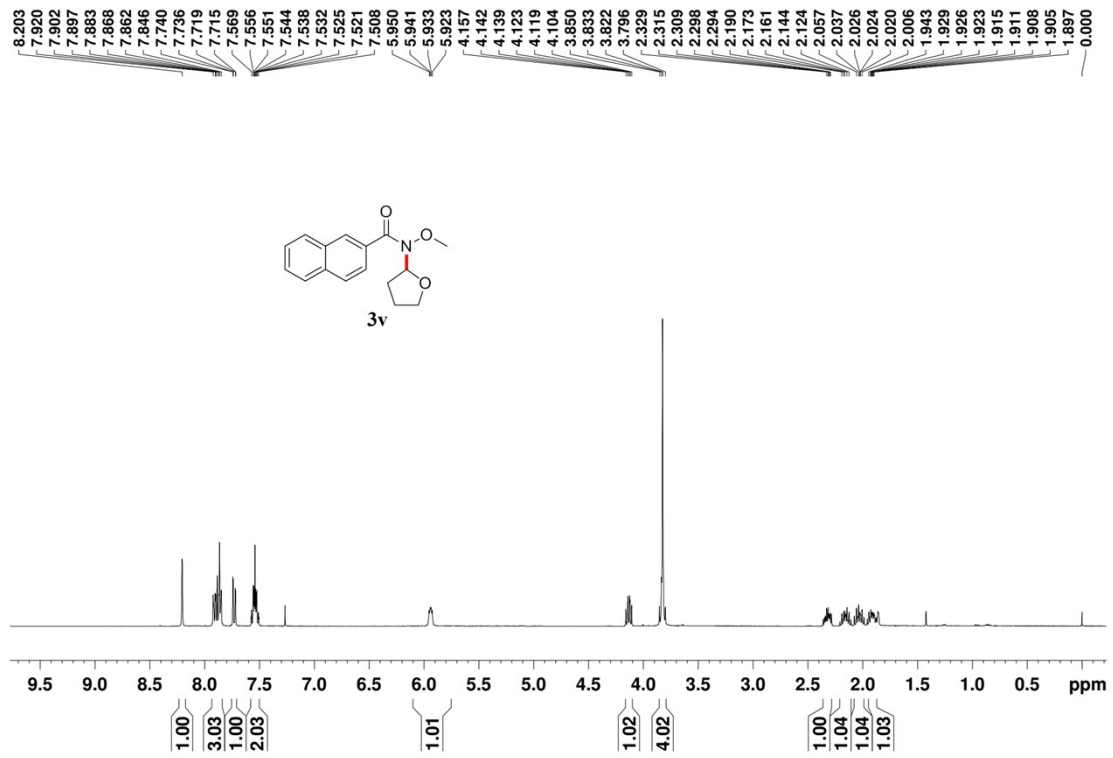


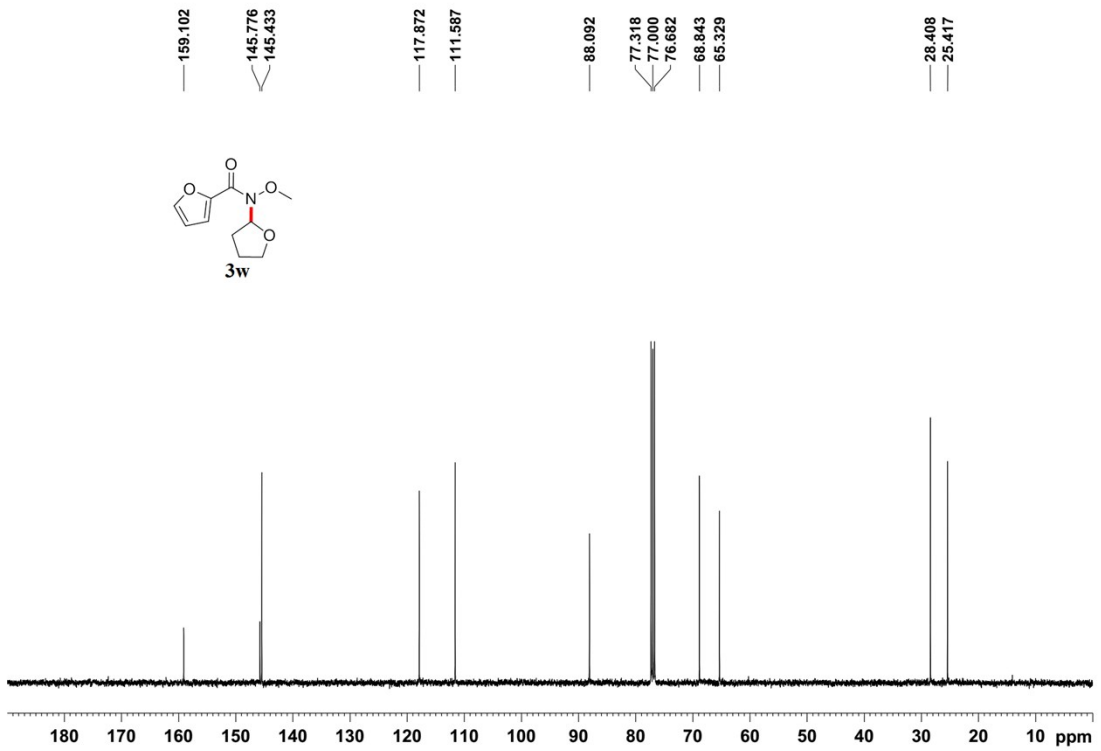
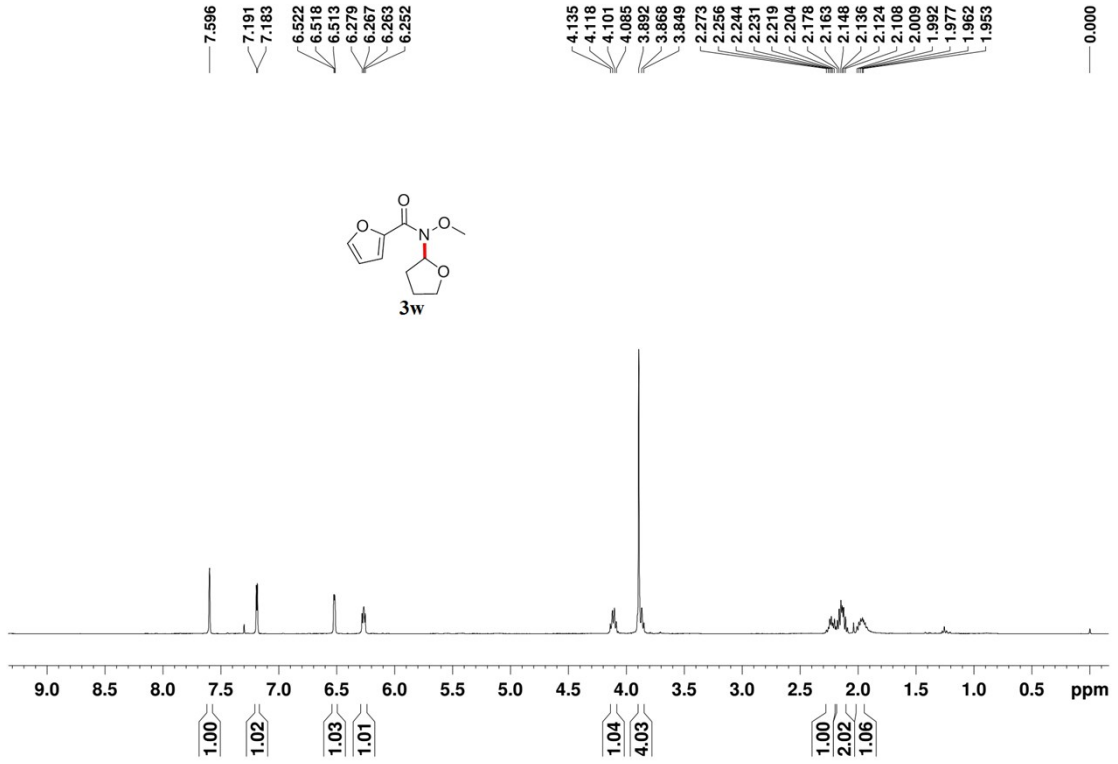


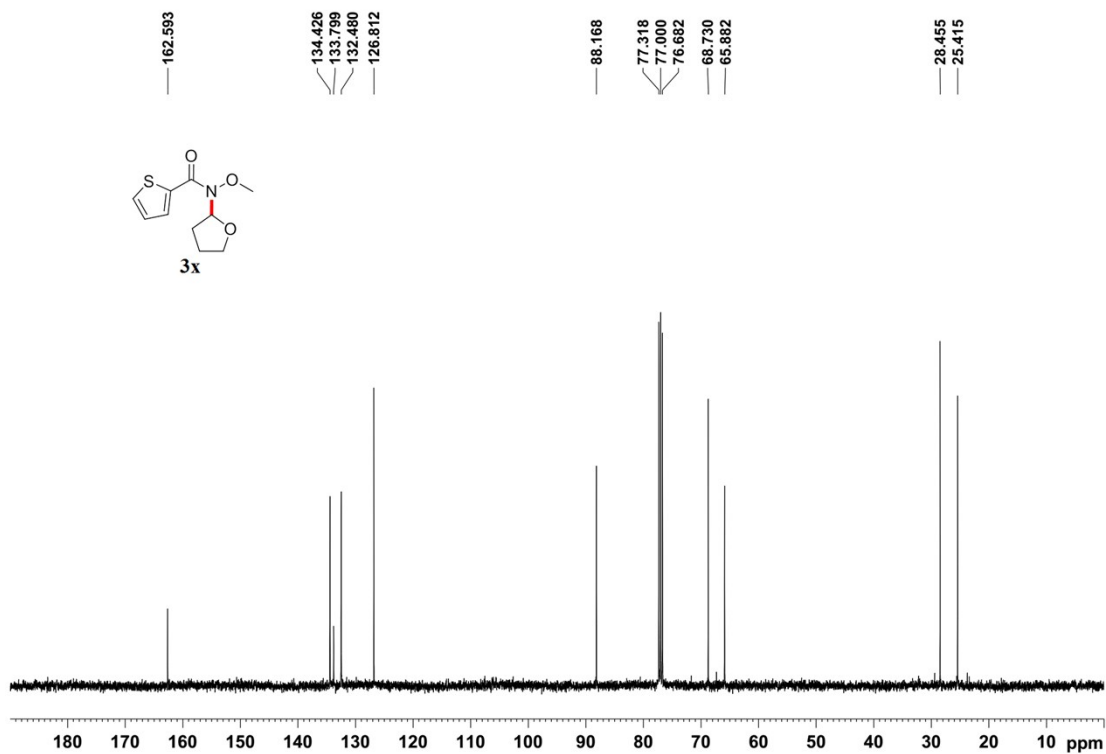
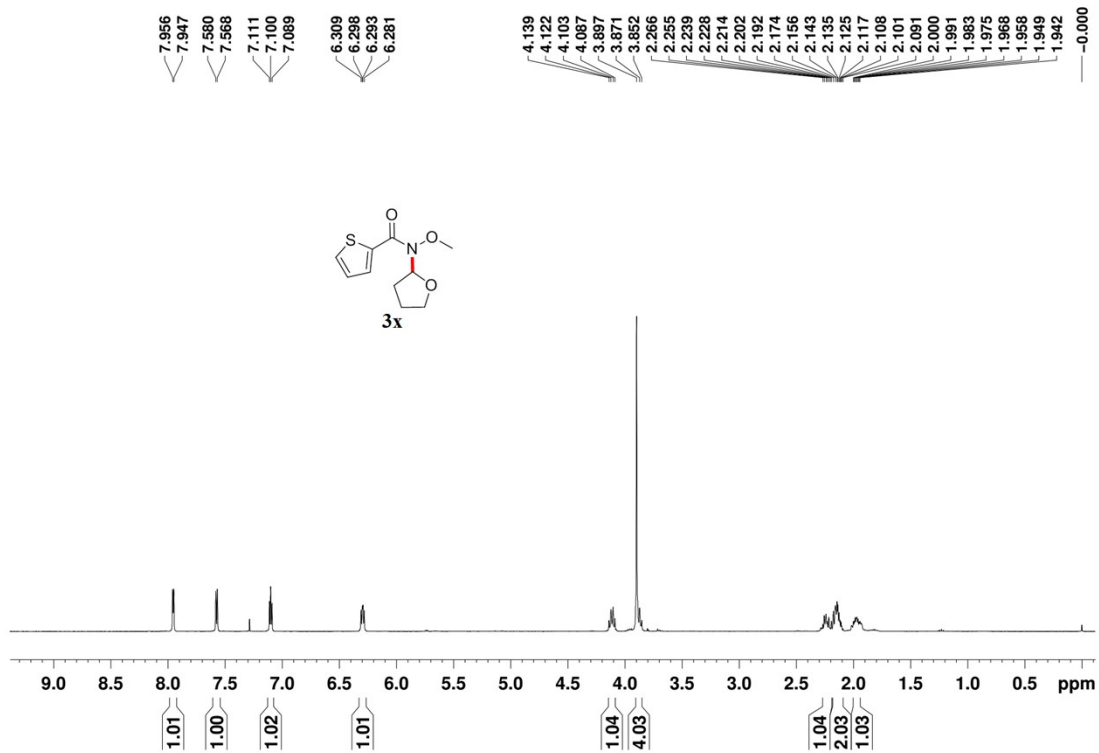


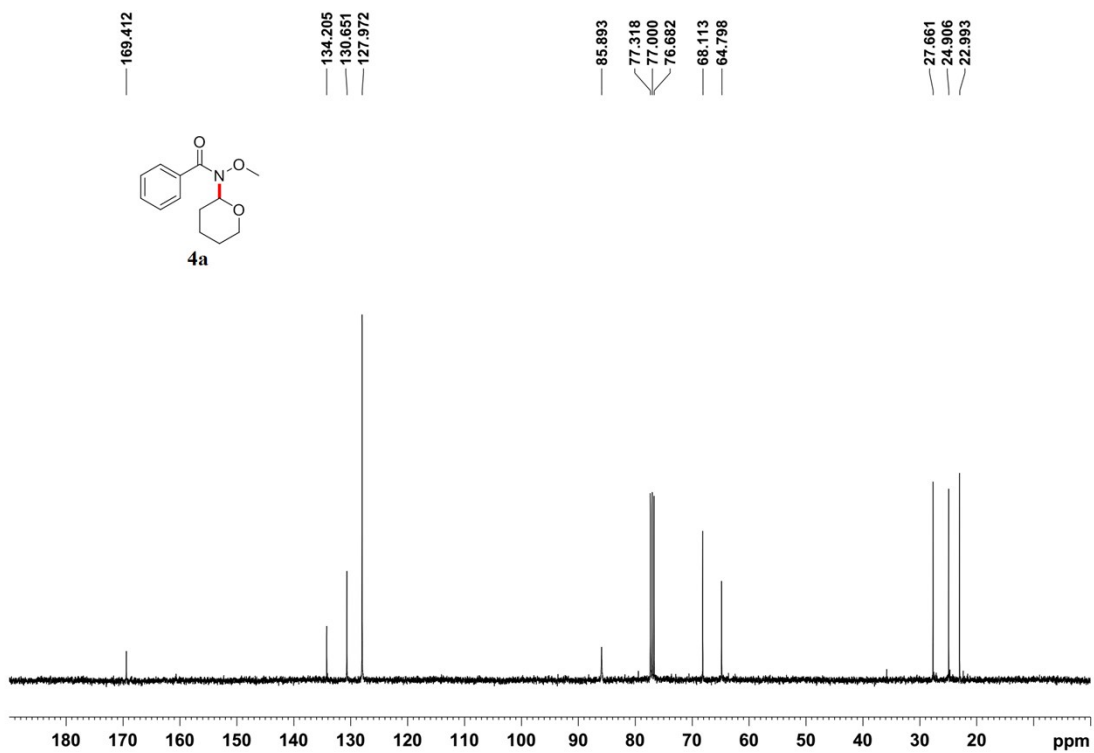
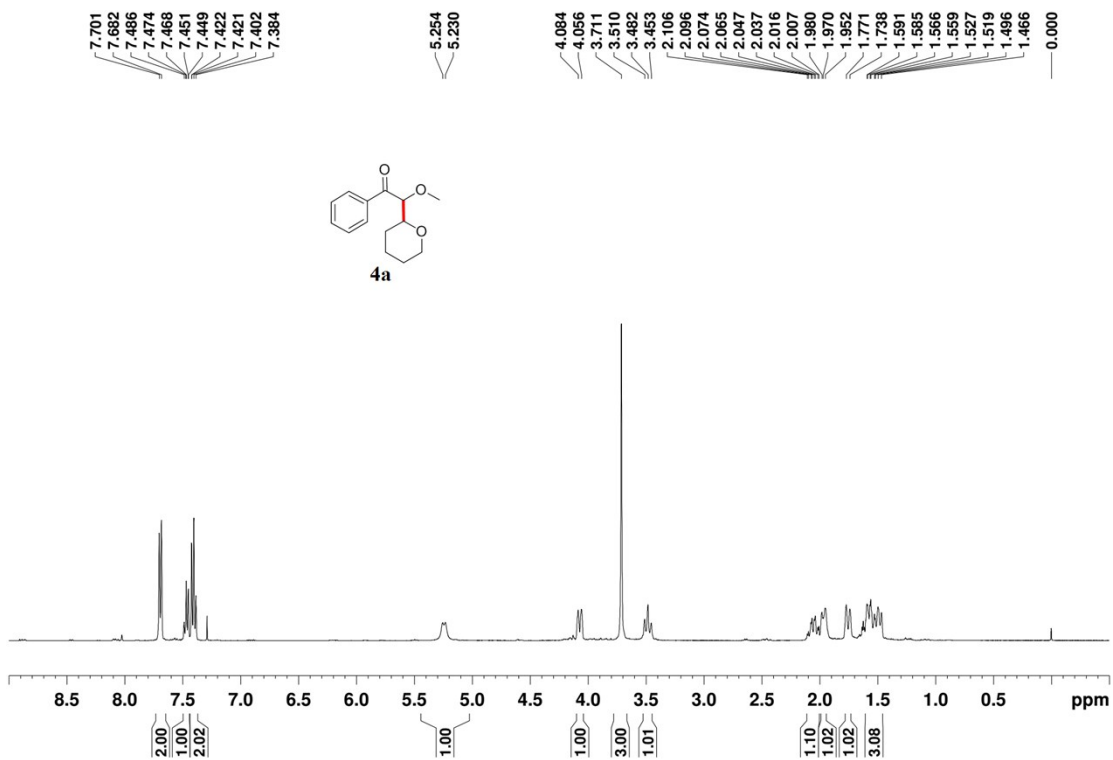


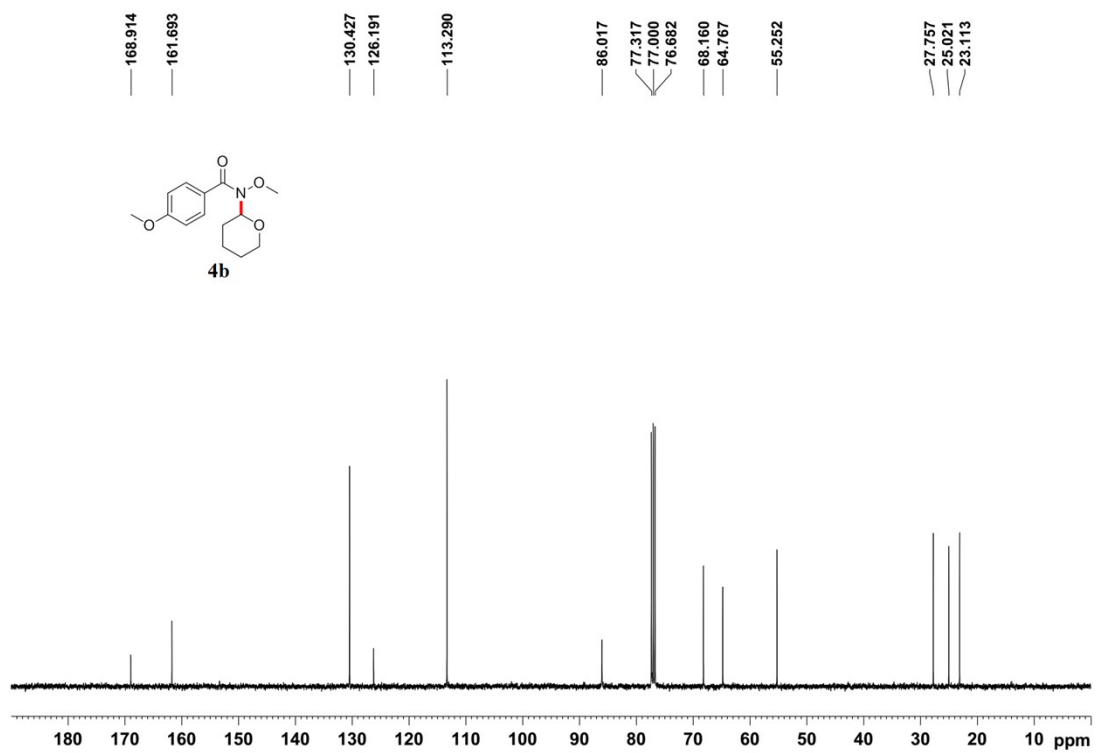
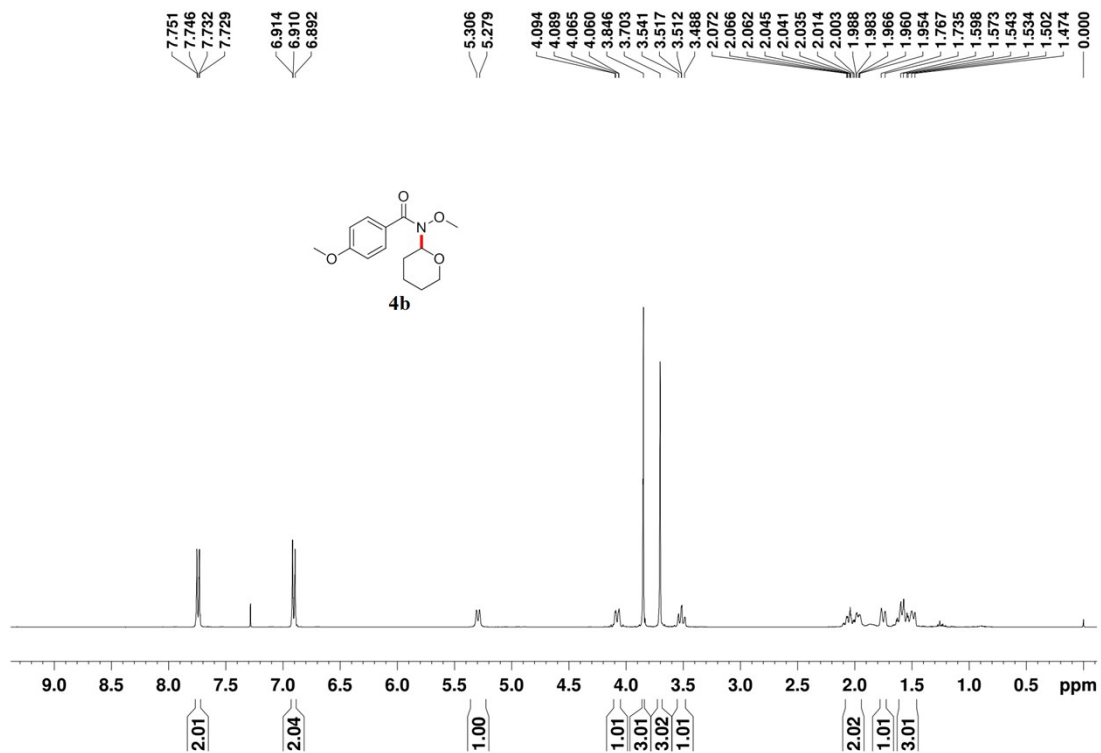


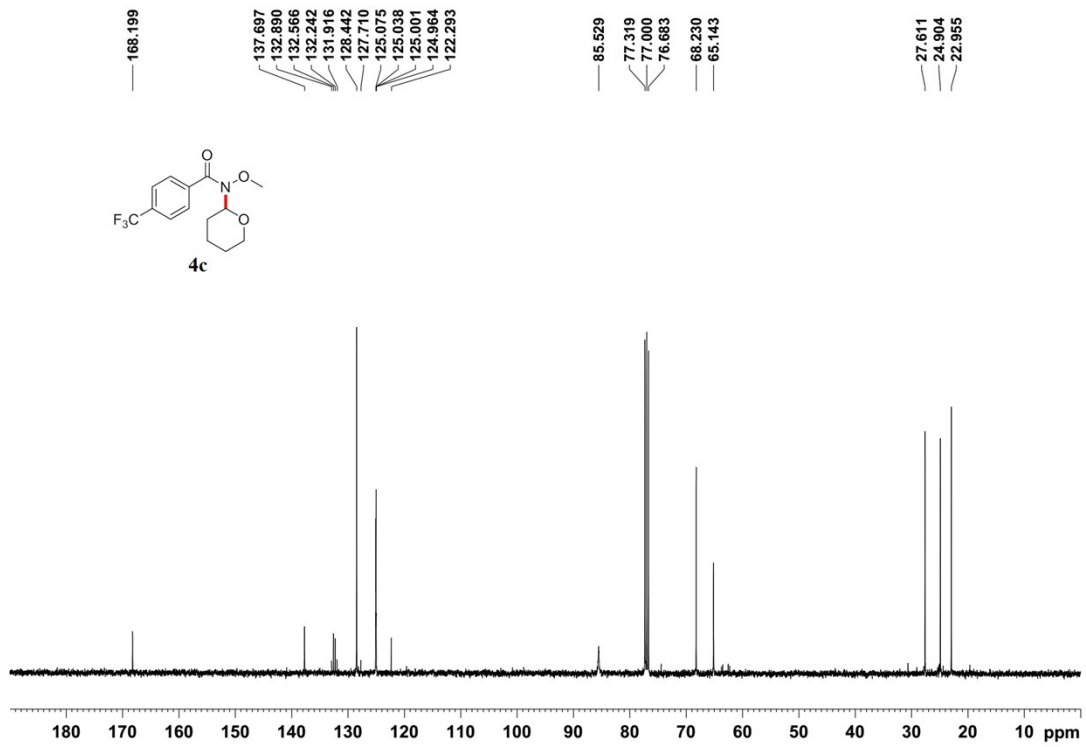
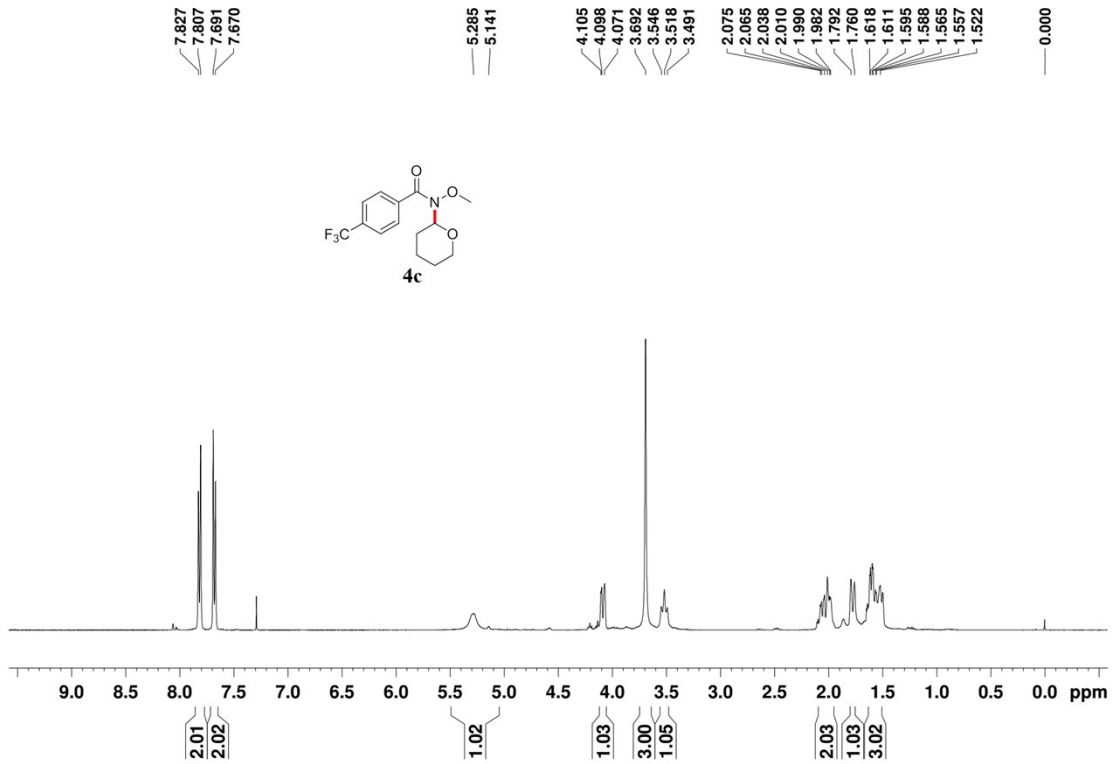


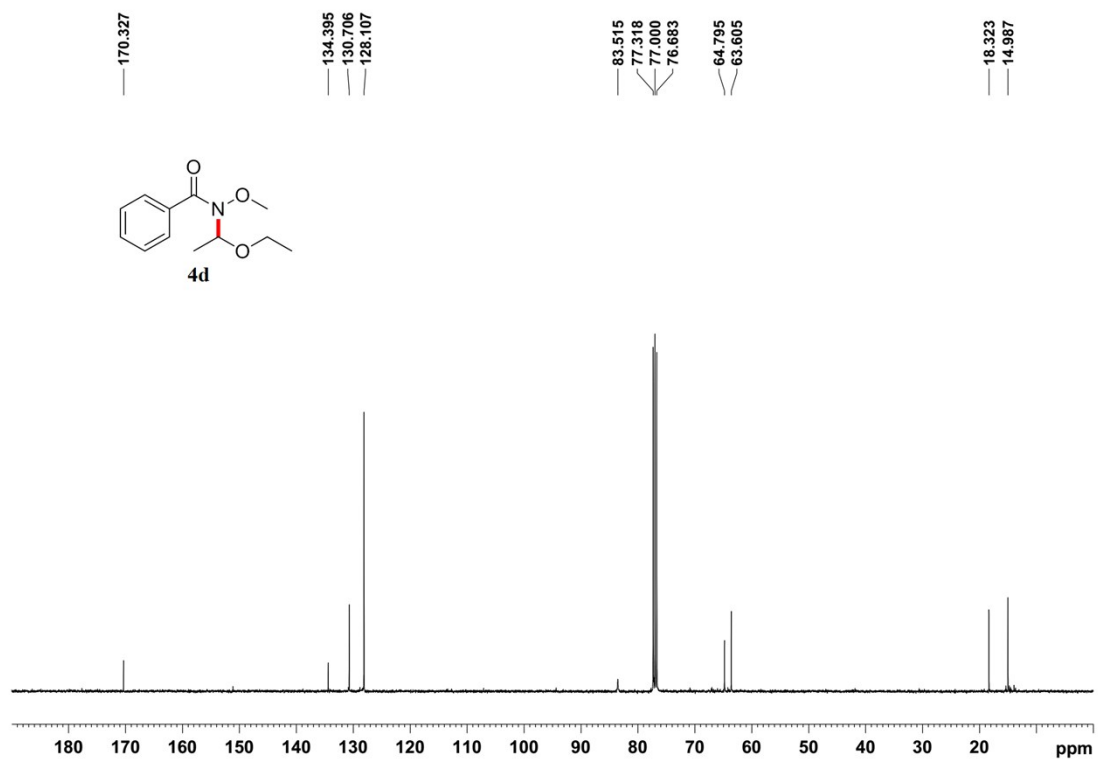
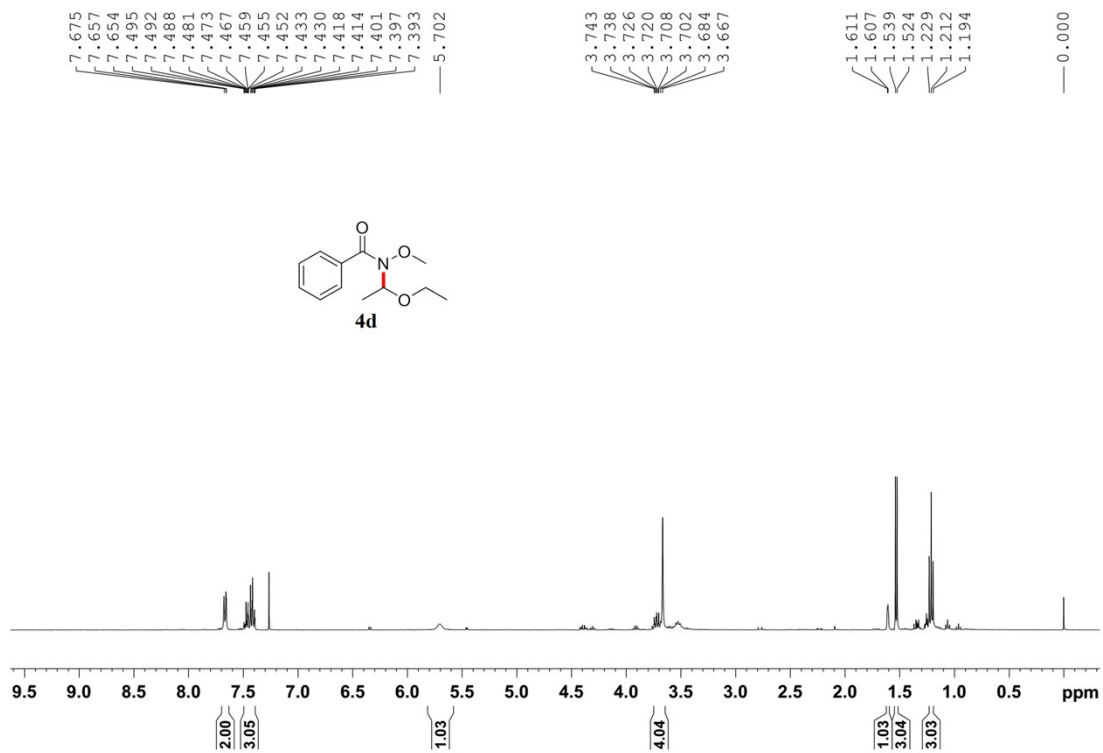


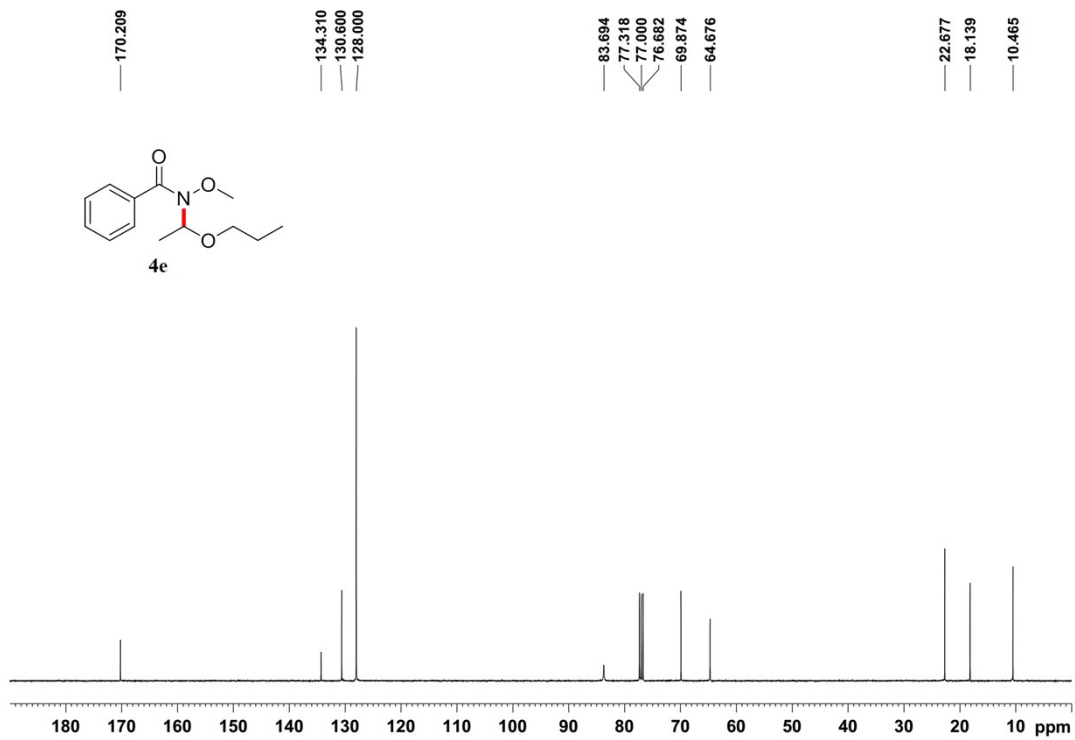
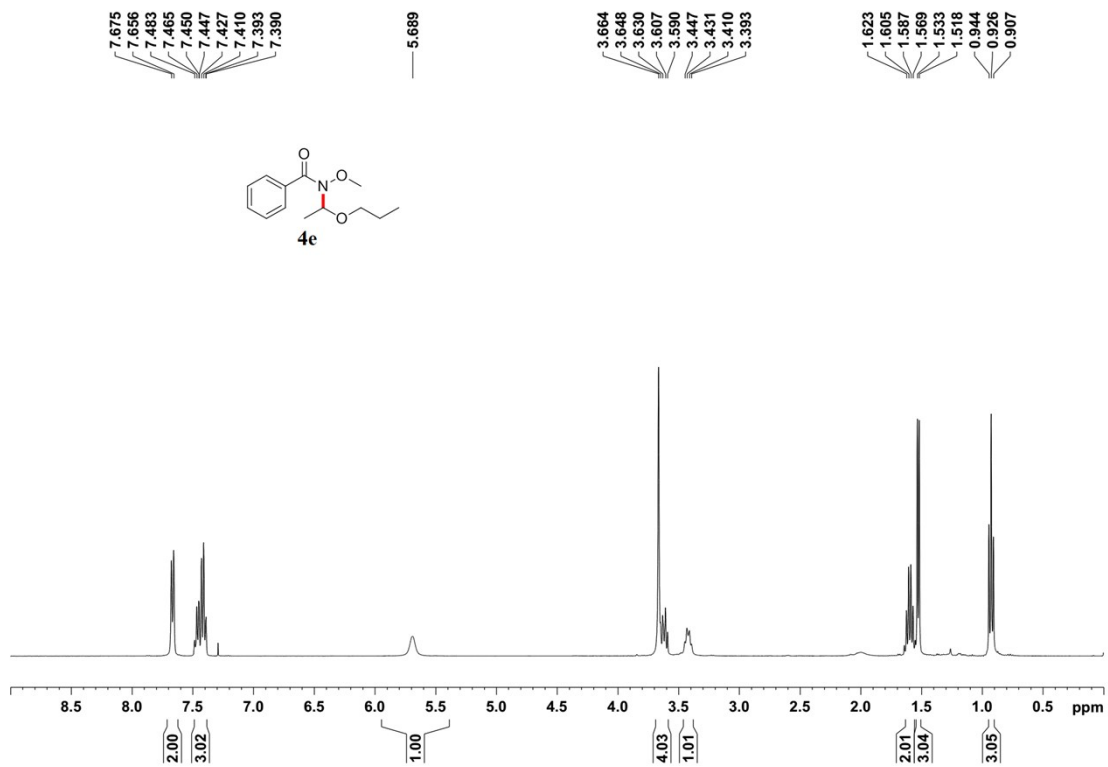


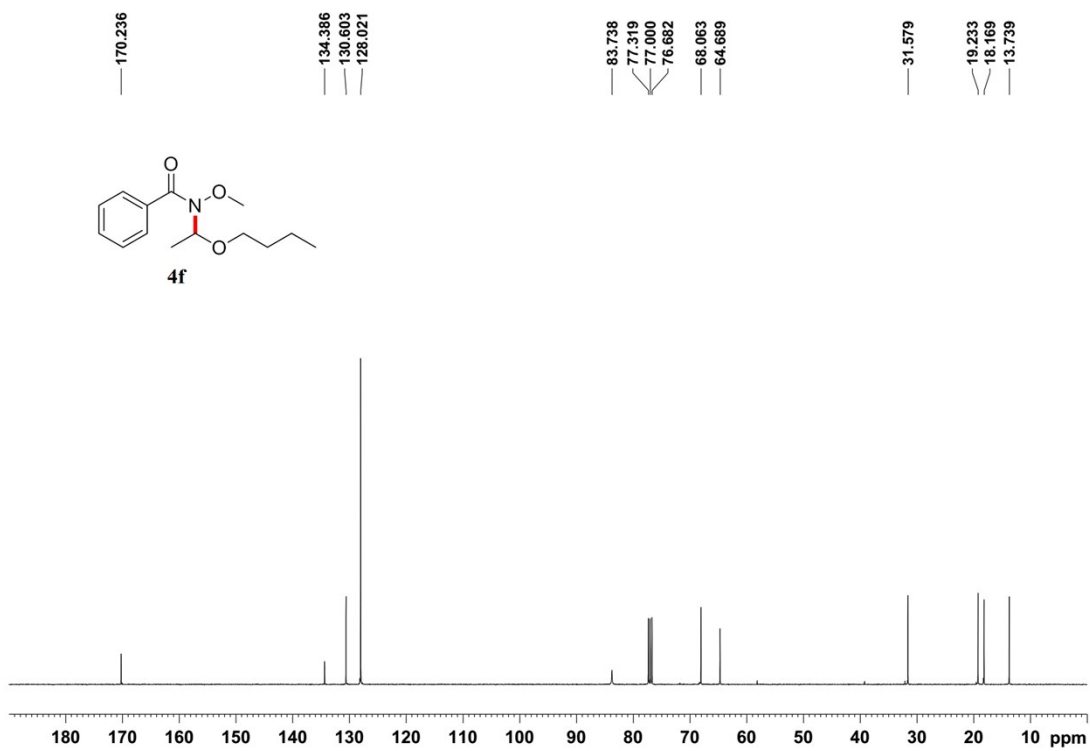
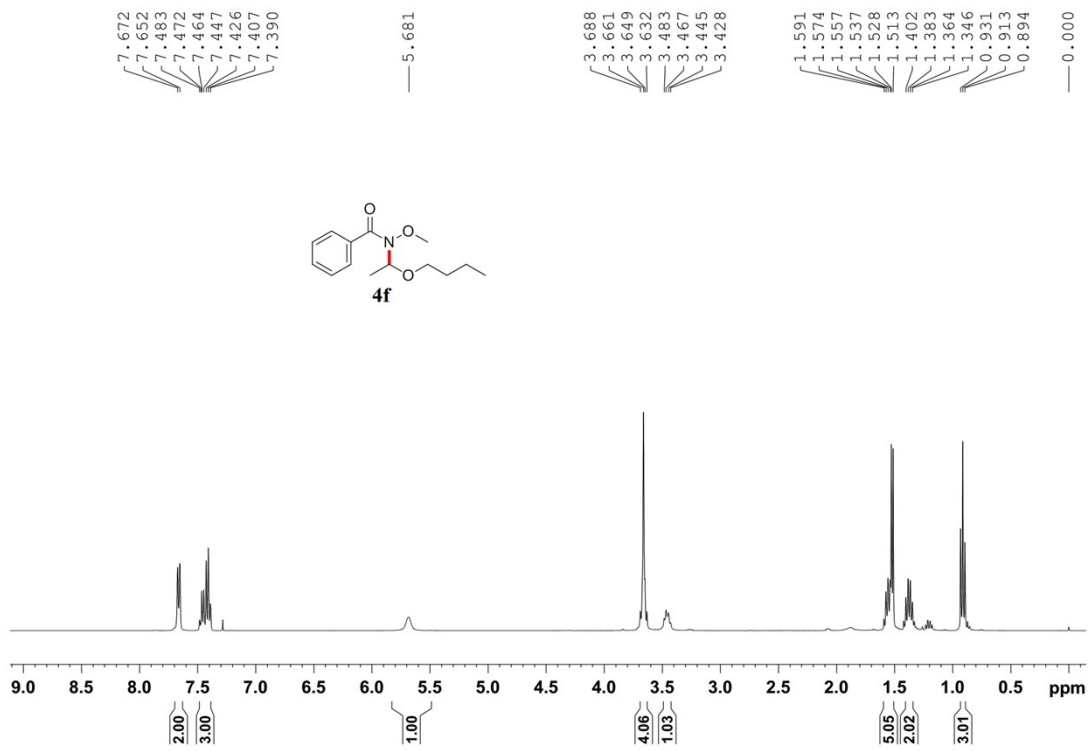


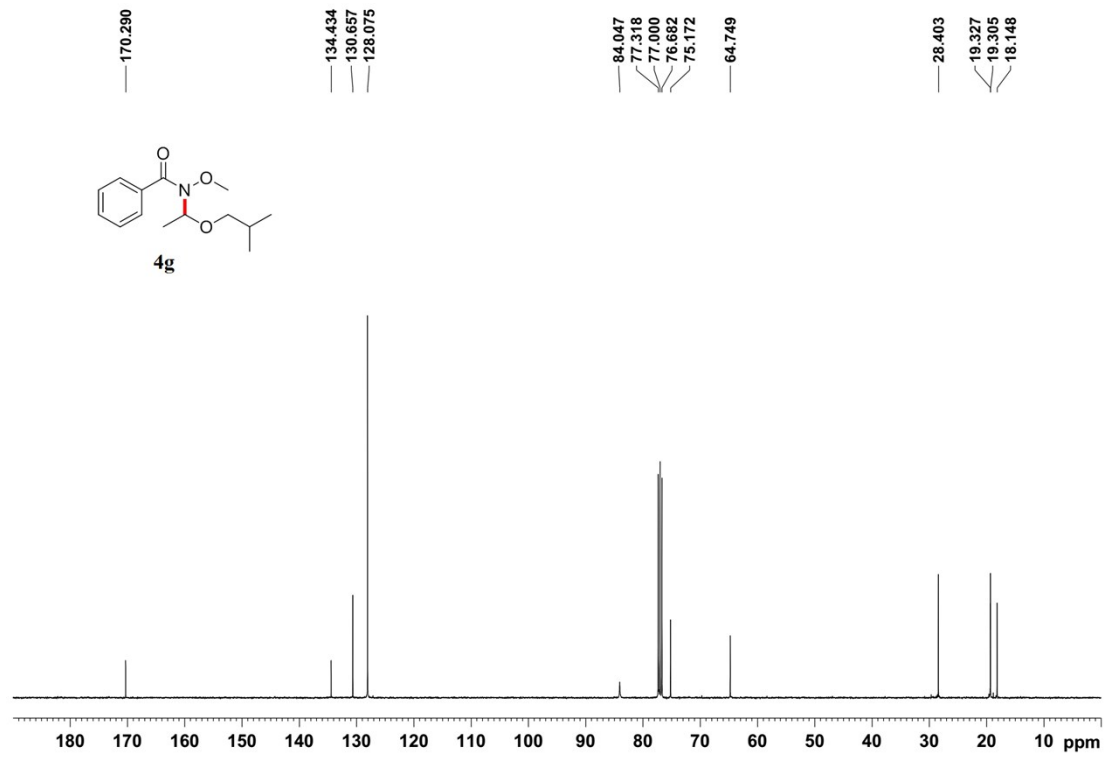
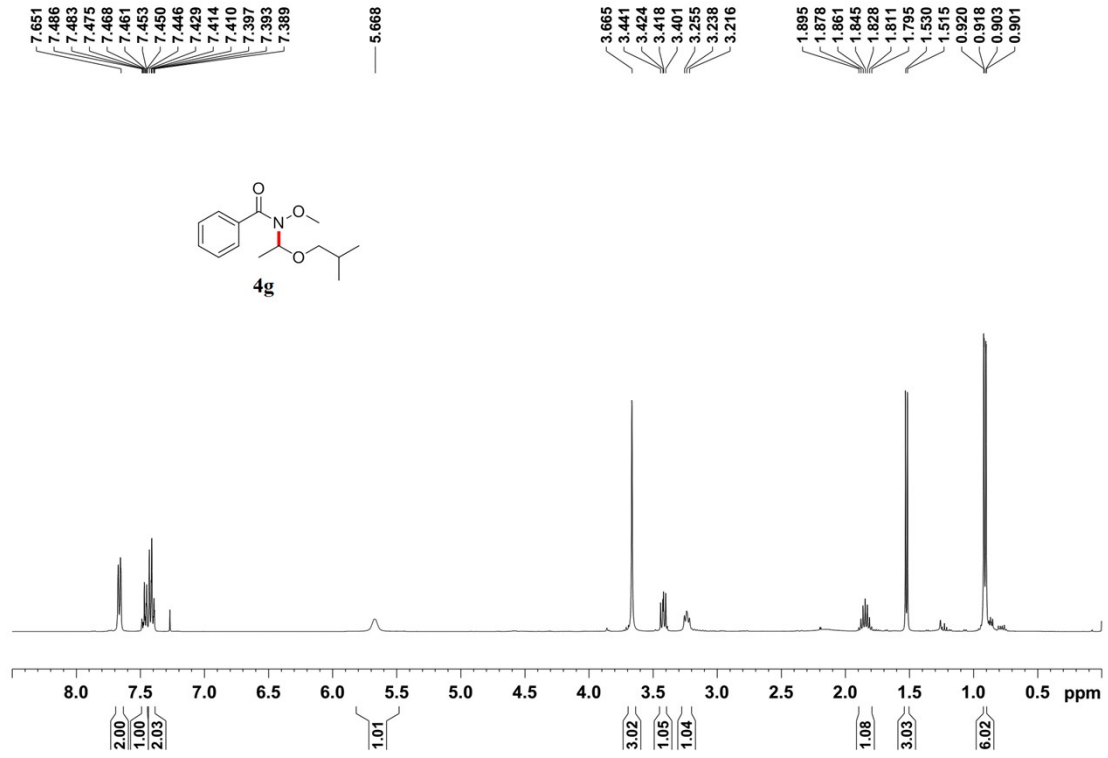










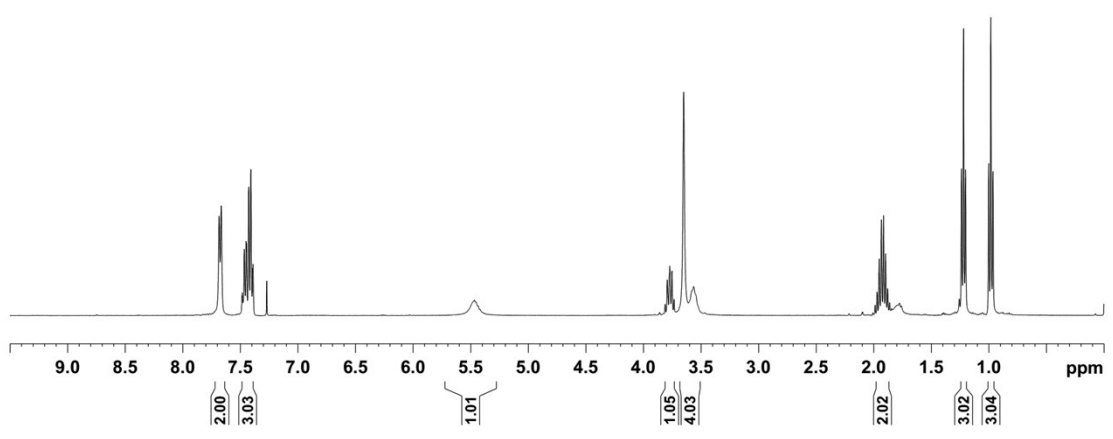
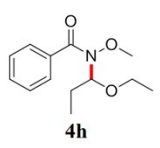


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