

Cu-Catalyzed C–H Alkenylation of Benzoic Acid and Acrylic Acid Derivatives with Vinyl Boronates

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Table of Contents

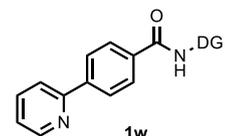
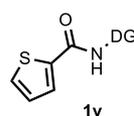
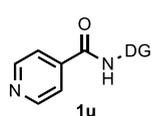
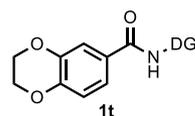
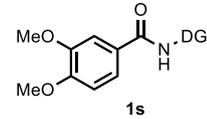
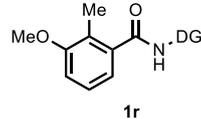
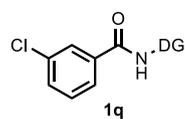
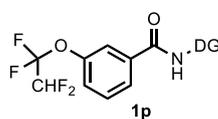
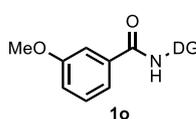
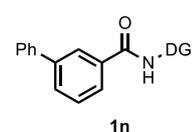
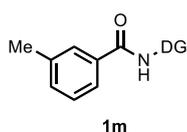
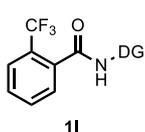
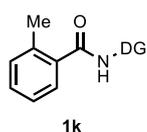
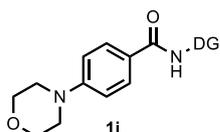
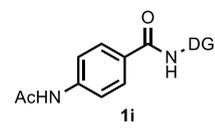
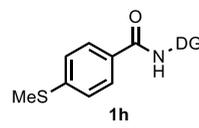
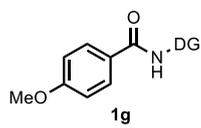
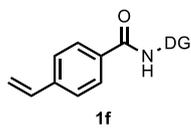
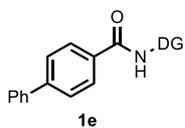
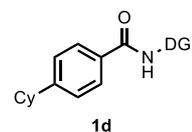
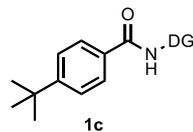
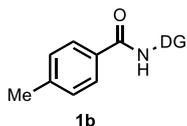
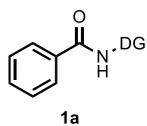
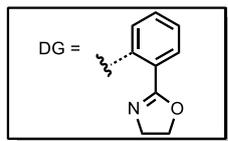
1. General Information	S2
2. Substrate Structures	S3
3. Experimental Section	S4
3.1 General Procedure for Preparation of Copper Salts	S4
3.2 Preparation of Carboxamides	S5
3.3 Preparation of Alkenylboronates	S13
3.4 Optimizations of the Reaction Conditions	S16
3.5 Evaluation of Benzamide Derivatives	S24
3.6 Evaluation of Alkenyl Boronates	S42
3.7 Evaluation of Alkene-Alkene Coupling	S54
3.8 Gram-Scale Reaction	S64
3.9 Directing Group Removal	S65
3.10 Transformations of Alkenylated Benzoic Acid	S66
3.11 Hydrogenation of Heterocyclic Alkenes	S68
3.12 X-Ray Structure of 3a (mono)	S69
4. References	S81
5. NMR Spectra	S82

1. General Information

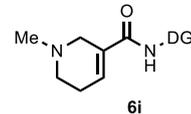
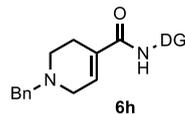
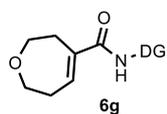
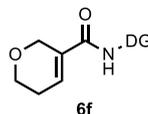
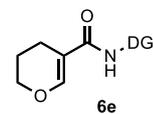
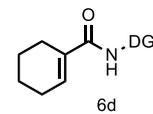
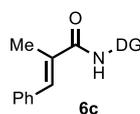
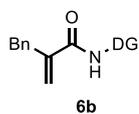
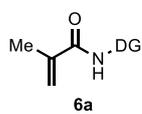
All the commercially available chemicals were obtained accordingly. Copper acetate was purchased from Strem. Dimethyl sulfoxide (DMSO) was purchased from J&K Scientific. Other reagents were purchased from Alfa Aesar, Sigma-Aldrich, Aladdin, Adamas-beta, Bidepharm, Macklin, 9Dingchem, and Energy Chemical of the highest purity grade and used without further purification, unless otherwise indicated. Tetrahydrofuran (THF), acetonitrile (CH₃CN), dichloromethane (CH₂Cl₂) and *N,N*-dimethylformamide (DMF) were dried using the solvent purification system. Other anhydrous solvents were purchased from J&K Scientific. The extent of reaction was monitored by thin-layer chromatography (TLC), was performed on 0.25 mm silica gel HSGF254 plates. Visualization was carried out with ultraviolet light (254 nm) or stained with potassium permanganate followed by gentle heating if necessary. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded at room temperature on a Varian 400, Bruker 400, Agilent 400 (400 Hz for ¹H; 375 Hz for ¹⁹F; 100 Hz for ¹³C), Bruker Avance Neo 500 instrument (500 MHz), Bruker Avance Neo 600 instrument (600 MHz), or JEOL JNM-ECZ600R/S1 (600 MHz) spectrometer. The chemical shifts (δ) were quoted in parts per million (ppm) referenced to tetramethylsilane (TMS) (0.0 ppm for ¹H NMR) and CDCl₃ (77.0 ppm for ¹³C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, and coupling constants (*J* Hz). ¹³C NMR spectra were fully decoupled by broad band proton decoupling. High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF or CI/EL.

2. Substrate Structures

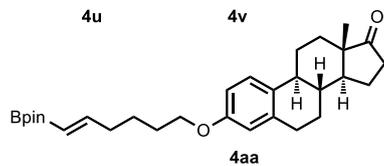
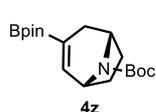
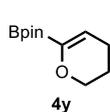
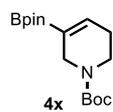
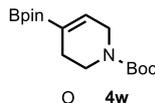
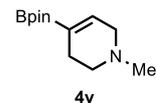
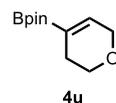
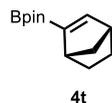
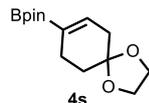
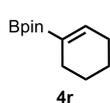
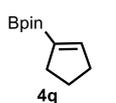
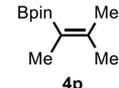
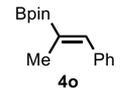
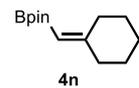
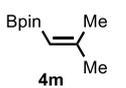
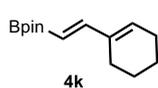
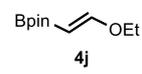
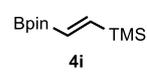
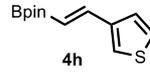
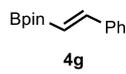
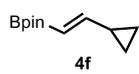
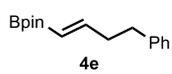
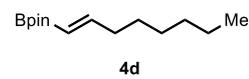
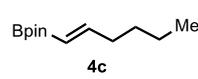
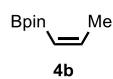
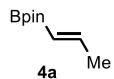
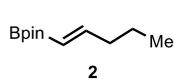
(Hetero)Arene Carboxamides



Vinyl Carboxamides



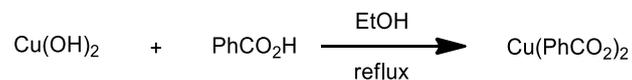
Alkenyl Boronates



3. Experimental Section

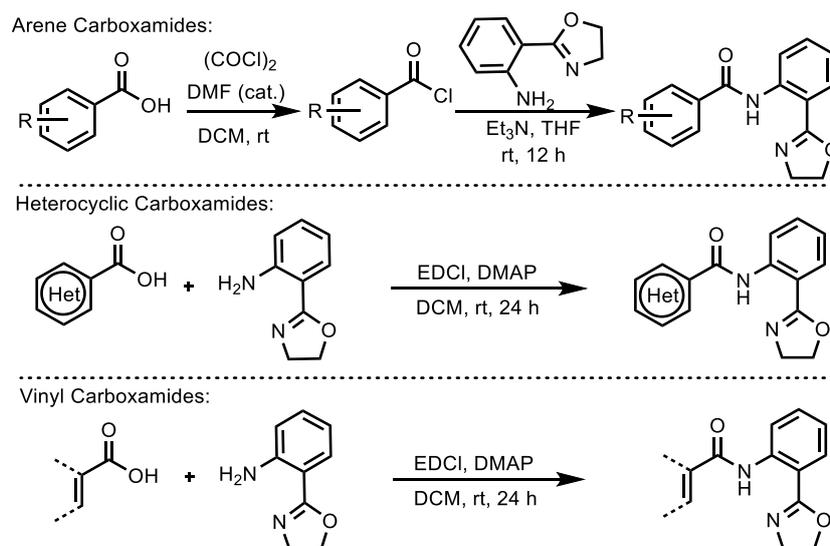
3.1 General Procedure for Preparation of Copper Salts

Copper(II) benzoate was synthesized following literature procedure.¹



An oven dried 100 mL sealed tube charged with Cu(OH)₂ (2.93 g, 30 mmol), PhCO₂H (7.69 g, 63 mmol), EtOH (30 mL), and the reaction mixture was placed into a pre-heated oil bath and reflux for 24 h. The reaction mixture was filtered immediately, and the filter cake was washed with hot EtOH. The filtrate was concentrated under reduced pressure, and the resulting residue was recrystallized in the small amount of EtOH to afford Cu(PhCO₂)₂ as a light-blue crystalline solid (5.58 g, 61%).

3.2 Preparation of Carboxamides



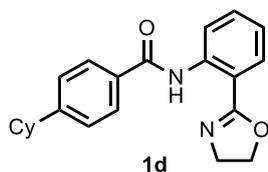
The benzoic acid substrates were synthesized following known procedure.² **1a-1c**, **1f-1g**, **1k-1m**, **1o**, **1q**, and **1u-w** are known in literature.

General Procedure for Synthesis of Arene Carboxamides:

To a solution 2-(4,5-dihydrooxazol-2-yl)aniline (5.0 mmol), Et₃N (7.5 mmol) in THF (20 mL) was slowly added the tetrahydrofuran solution of acid chloride (5.0 mmol), prepared from the corresponding carboxylic acid and oxalyl chloride, under nitrogen at room temperature. The reaction mixture was stirred at room temperature for 12 h. Upon completion, the reaction was quenched with saturated NaHCO₃ (100 mL) and extracted with EtOAc (3 × 150 mL). The combined organic layers were washed with saturated brine, dried over Na₂SO₄, concentrated under vacuum. The crude product was purified by column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate or recrystallized from petroleum ether/ethyl acetate to provide the desired product (**1d-e**, **1h-j**, **1n**, **1p**, **1r-t**).

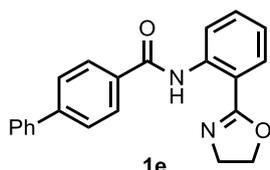
General Procedure for Synthesis of Heterocyclic Carboxamides:

To a solution of heterocyclic carboxylic acid (4.0 mmol), 2-(4,5-dihydrooxazol-2-yl)aniline (5.0 mmol) and DMAP (0.5 mmol) in DCM (20 mL) was added EDCI (6.0 mmol) under nitrogen at 0 °C. The mixture was stirred for 24 h at room temperature. Saturated NaHCO₃ was added to quench reaction, and then extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with saturated brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was recrystallized from petroleum ether/ethyl acetate or isolated by column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate or recrystallized from petroleum ether/ethyl acetate to provide the desired product (**1u-w**).



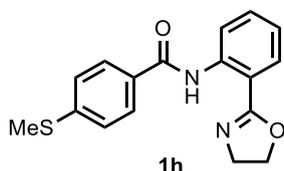
4-Cyclohexyl-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)benzamide (1d)

1d was obtained by recrystallization from petroleum ether/ethyl acetate (50/1) as white solid (450 mg, 65%). mp 164–166 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.96 (s, 1H), 8.97 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 4.38 (t, *J* = 9.1 Hz, 2H), 4.17 (t, *J* = 9.2 Hz, 2H), 2.61–2.52 (m, 1H), 1.90–1.82 (m, 4H), 1.79–1.73 (m, 1H), 1.51–1.34 (m, 4H), 1.32–1.23 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 164.8, 152.0, 140.2, 132.7, 132.5, 129.2, 127.8, 127.0, 122.1, 119.7, 113.4, 66.2, 54.6, 44.5, 34.2, 26.7, 26.0; HRMS (ESI-TOF) *m/z* Calcd for C₂₂H₂₄N₂O₂Na [M+Na]⁺: 371.1730, found: 371.1727.



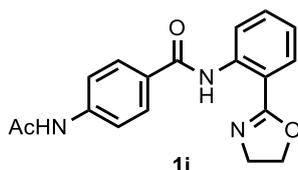
***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-[1,1'-biphenyl]-4-carboxamide (1e)**

1e was obtained by recrystallization from petroleum ether/ethyl acetate (50/1) as yellow solid (410 mg, 65%). mp 137–139 °C; ¹H NMR (400 MHz, CDCl₃) δ 13.08 (s, 1H), 8.99 (d, *J* = 8.5 Hz, 1H), 8.16 (d, *J* = 8.3 Hz, 2H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.11 (t, *J* = 8.0 Hz, 1H), 4.40 (t, *J* = 9.0 Hz, 2H), 4.20 (t, *J* = 9.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 165.8, 164.9, 144.3, 140.2, 140.0, 133.9, 132.6, 129.3, 128.8, 128.2, 127.9, 127.2, 127.2, 122.3, 119.8, 113.5, 66.2, 54.7; HRMS (ESI-TOF) *m/z* Calcd for C₂₂H₁₈N₂O₂Na [M+Na]⁺: 365.1260, found: 365.1256.



***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-4-(methylthio)benzamide (1h)**

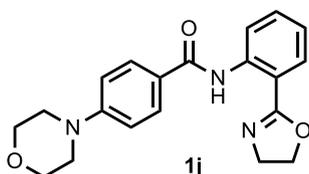
1h was obtained by recrystallization from petroleum ether/ethyl acetate (50/1) as white solid (410 mg, 67%). mp 106–108 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.98 (s, 1H), 8.94 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.09 (t, *J* = 8.0 Hz, 1H), 4.40 (t, *J* = 9.2 Hz, 2H), 4.18 (t, *J* = 9.2 Hz, 2H), 2.53 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.5, 164.9, 143.6, 140.2, 132.6, 131.4, 129.2, 128.1, 125.3, 122.3, 119.7, 113.4, 66.2, 54.6, 14.9; HRMS (ESI-TOF) *m/z* Calcd for C₁₇H₁₆N₂O₂SNa [M+Na]⁺: 335.0825, found: 335.0821.



4-Acetamido-*N*-(2-(4,5-dihydrooxazol-2-yl)phenyl)benzamide (1i)

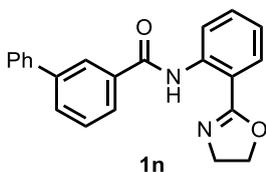
1i was obtained by recrystallization from petroleum ether/ethyl acetate (50/1) as white solid (120 mg, 19%). mp

240–242 °C; ^1H NMR (400 MHz, CDCl_3) δ 13.01 (s, 1H), 8.95 (d, $J = 8.4$ Hz, 1H), 8.08 (d, $J = 8.7$ Hz, 2H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.66 (d, $J = 8.1$ Hz, 2H), 7.52 (t, $J = 8.4$ Hz, 1H), 7.33 (s, 1H), 7.11 (t, $J = 7.5$ Hz, 1H), 4.43 (t, $J = 9.5$ Hz, 2H), 4.22 (t, $J = 9.6$ Hz, 2H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.4, 165.4, 165.0, 140.9, 140.2, 132.7, 130.8, 129.3, 128.9, 122.3, 119.8, 119.0, 113.5, 66.3, 54.7, 24.8; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 346.1162, found: 346.1160.



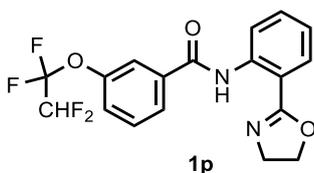
N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-4-morpholinobenzamide (**1j**)

1j was obtained by column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate (2/1) as yellow solid (260 mg, 37%). mp 154–156 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.86 (s, 1H), 8.96 (d, $J = 8.4$ Hz, 1H), 8.03 (d, $J = 9.0$ Hz, 2H), 7.89 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.50 (t, $J = 7.9$ Hz, 1H), 7.08 (t, $J = 8.0$ Hz, 1H), 6.95 (d, $J = 8.9$ Hz, 2H), 4.41 (t, $J = 9.7$ Hz, 2H), 4.20 (t, $J = 9.2$ Hz, 2H), 3.90–3.84 (m, 4H), 3.32–3.25 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.8, 164.9, 153.4, 140.5, 132.6, 129.2, 129.2, 125.5, 121.9, 119.7, 114.0, 113.2, 66.6, 66.2, 54.7, 47.9; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 374.1475, found: 374.1478.



N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-[1,1'-biphenyl]-3-carboxamide (**1n**)

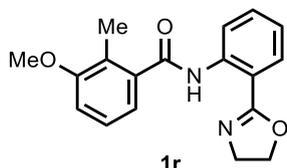
1n was obtained by recrystallization from petroleum ether/ethyl acetate (50/1), as white solid (430 mg, 78%). mp 160–162 °C; ^1H NMR (400 MHz, CDCl_3) δ 13.14 (s, 1H), 8.99 (d, $J = 8.4$ Hz, 1H), 8.37 (s, 1H), 8.07 (d, $J = 7.7$ Hz, 1H), 7.86 (d, $J = 7.8$ Hz, 1H), 7.74 (d, $J = 7.6$ Hz, 1H), 7.66 (d, $J = 7.5$ Hz, 2H), 7.58–7.41 (m, 4H), 7.37 (d, $J = 7.2$ Hz, 1H), 7.07 (t, $J = 7.6$ Hz, 1H), 4.36 (t, $J = 9.5$ Hz, 2H), 4.15 (t, $J = 9.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 164.9, 141.3, 140.3, 140.1, 135.6, 132.6, 130.1, 129.3, 129.1, 128.8, 127.6, 127.1, 126.7, 126.3, 122.3, 119.7, 113.4, 66.2, 54.6; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 365.1260, found: 365.1255.



N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-3-(1,1,2,2-tetrafluoroethoxy)benzamide (**1p**)

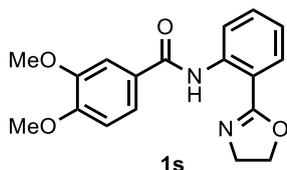
1p was obtained by recrystallization from petroleum ether/ethyl acetate (50/1), as yellow solid (501 mg, 77%). mp 84–86 °C; ^1H NMR (400 MHz, CDCl_3) δ 13.18 (d, $J = 5.4$ Hz, 1H), 8.93 (dd, $J = 8.4, 2.2$ Hz, 1H), 8.05–

7.97 (m, 2H), 7.93–7.83 (m, 1H), 7.56–7.46 (m, 2H), 7.40–7.33 (m, 1H), 7.14–7.06 (m, 1H), 5.96 (tt, $J = 53.1$, 2.7 Hz, 1H), 4.47–4.33 (m, 2H), 4.24–4.09 (m, 2H); ^{13}C NMR (150 MHz, decoupled for ^{19}F , CDCl_3) δ 165.0, 164.4, 148.9, 139.9, 137.2, 132.7, 129.9, 129.3, 126.1, 124.8, 122.6, 120.9, 119.7, 116.5, 113.6, 107.6, 66.3, 54.4; ^{19}F NMR (375 MHz, CDCl_3) δ -88.10–88.17 (m, 2F), -136.81 (dt, $J_{F-F} = 53.1$, 5.6 Hz, 2F); HRMS (ESI-TOF) m/z Calcd for $\text{C}_{18}\text{H}_{14}\text{F}_4\text{N}_2\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 405.0833, found: 405.0823.



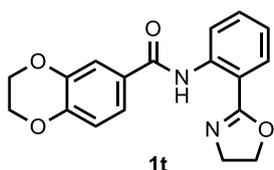
N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-3-methoxy-2-methylbenzamide (**1r**)

1r was obtained by recrystallization from petroleum ether/ethyl acetate (50/1) as white solid (390 mg, 53%). mp 166–168 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.53 (s, 1H), 8.95 (d, $J = 8.4$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.51 (t, $J = 8.0$ Hz, 1H), 7.25–7.16 (m, 2H), 7.10 (t, $J = 7.6$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 4.36–4.27 (m, 2H), 4.04–3.96 (m, 2H), 3.85 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.7, 164.4, 158.0, 139.9, 138.5, 132.4, 129.1, 126.4, 125.3, 122.4, 119.7, 119.3, 113.4, 111.5, 66.1, 55.6, 54.6, 12.7; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 333.1210, found: 333.1203.



N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-3,4-dimethoxybenzamide (**1s**)

1s was obtained by recrystallization from petroleum ether/ethyl acetate (50/1) as white solid (550 mg, 71%). mp 179–181 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.92 (s, 1H), 8.96 (d, $J = 8.5$ Hz, 1H), 7.89–7.83 (m, 1H), 7.74–7.69 (m, 1H), 7.67 (s, 1H), 7.50 (t, $J = 7.9$ Hz, 1H), 7.12–7.04 (m, 1H), 6.96–6.89 (m, 1H), 4.37 (dt, $J = 9.3$, 4.7 Hz, 2H), 4.17 (dd, $J = 9.2$, 3.7 Hz, 2H), 3.97 (d, $J = 2.1$ Hz, 1H), 3.94 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.4, 165.0, 151.8, 148.6, 140.3, 132.6, 129.2, 127.6, 122.0, 121.0, 119.5, 113.2, 110.5, 110.4, 66.1, 55.9, 55.8, 54.6; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 349.1159, found: 349.1155.



N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2,3-dihydrobenzo[b][1,4]dioxine-6-carboxamide (**1t**)

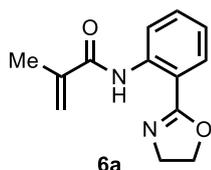
1t was obtained by recrystallization from petroleum ether/ethyl acetate (50/1) as white solid (510 mg, 66%). mp 167–169 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.89 (s, 1H), 8.93 (d, $J = 8.4$ Hz, 1H), 7.84 (dd, $J = 7.9$, 1.5 Hz, 1H), 7.63 (d, $J = 2.1$ Hz, 1H), 7.59 (dd, $J = 8.5$, 2.1 Hz, 1H), 7.48 (t, $J = 8.0$ Hz, 1H), 7.06 (t, $J = 7.6$ Hz, 1H),

6.92 (d, $J = 8.4$ Hz, 1H), 4.35 (t, $J = 9.7$ Hz, 2H), 4.27 (q, $J = 5.0$ Hz, 4H), 4.16 (t, $J = 9.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.2, 164.7, 146.6, 143.2, 140.2, 132.4, 129.1, 128.4, 122.0, 121.1, 119.5, 117.2, 117.1, 113.3, 66.1, 64.5, 64.0, 54.5; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 347.1002, found: 347.0996.

The vinyl carboxylic acids (5,6-dihydro-2*H*-pyran-3-carboxylic acid (**6f-s**), 1-methyl-1,2,5,6-tetrahydropyridine-3-carboxylic acid (**6g-s**), and 2, 3, 6, 7-tetrahydrooxepine-4-carboxylic acid (**6i-s**)) were synthesized following the known procedure.³ Others are commercially available.

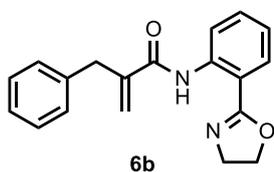
General Procedure for Synthesis of Vinyl Carboxamides:

To a solution of vinyl carboxylic acid (4.0 mmol), 2-(4,5-dihydrooxazol-2-yl)aniline (5.0 mmol) and DMAP (0.5 mmol) in DCM (20 mL) was added EDCI (6.0 mmol) under nitrogen at 0 °C. The mixture was stirred for 24 h at room temperature. Saturated NaHCO_3 was added to quench reaction, and then extracted with EtOAc (3 \times 100 mL). The combined organic layers were washed with saturated brine, dried over Na_2SO_4 , concentrated under reduced pressure. The crude product was recrystallized from petroleum ether/ethyl acetate or isolated by column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate to provide the desired product (**6a-i**).



N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)methacrylamide (**6a**)

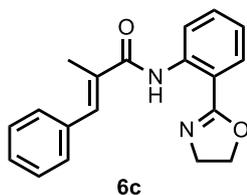
6a was obtained by recrystallization from petroleum ether/ethyl acetate (50/1) as white solid (195 mg, 43%). mp 78–80 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.54 (s, 1H), 8.84 (d, $J = 8.5$ Hz, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.46 (t, $J = 8.0$ Hz, 1H), 7.07 (t, $J = 8.0$ Hz, 1H), 6.01 (s, 1H), 5.50 (s, 1H), 4.36 (t, $J = 9.3$ Hz, 2H), 4.12 (t, $J = 9.6$ Hz, 2H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.1, 164.6, 140.9, 139.9, 132.4, 129.1, 122.2, 120.9, 119.6, 113.3, 66.1, 54.6, 18.7; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 253.0947, found: 253.0943.



2-Benzyl-*N*-(2-(4,5-dihydrooxazol-2-yl)phenyl)acrylamide (**6b**)

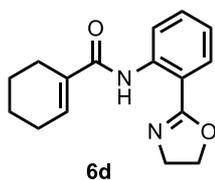
6b was obtained by column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate (20/1) as white solid (570 mg, 62%). mp 76–78 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.62 (s, 1H), 8.82 (d, $J = 8.5$ Hz, 1H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.46 (t, $J = 8.0$ Hz, 1H), 7.34–7.24 (m, 4H), 7.21 (t, $J = 6.9$ Hz, 1H), 7.07 (t, $J = 7.1$ Hz, 1H), 6.09 (s, 1H), 5.37 (s, 1H), 4.38 (t, $J = 9.4$ Hz, 2H), 4.12 (t, $J = 9.5$ Hz, 2H), 3.80 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.9, 164.7, 145.4, 140.0, 138.9, 132.5, 129.2, 129.2, 128.4, 126.3, 122.3, 121.1,

119.8, 113.4, 66.2, 54.7, 38.1; HRMS (ESI-TOF) m/z Calcd for $C_{19}H_{18}N_2O_2Na$ $[M+Na]^+$: 329.1260, found: 329.1254.



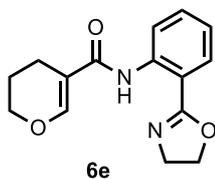
(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2-methyl-3-phenylacrylamide (6c)

6c was obtained by recrystallization from petroleum ether/ethyl acetate (50/1) as yellow solid (169 mg, 28%). mp 120–122 °C; 1H NMR (400 MHz, $CDCl_3$) δ 12.65 (s, 1H), 8.91 (d, $J = 7.9$ Hz, 1H), 7.87 (d, $J = 7.9$ Hz, 1H), 7.62 (s, 1H), 7.48 (t, $J = 7.9$ Hz, 1H), 7.43–7.37 (m, 4H), 7.33–7.28 (m, 1H), 7.07 (t, $J = 7.6$ Hz, 1H), 4.36 (t, $J = 9.6$ Hz, 2H), 4.11 (t, $J = 9.4$ Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 164.7, 140.1, 136.4, 135.1, 133.1, 132.5, 129.4, 129.1, 128.2, 127.8, 122.2, 119.8, 113.4, 66.1, 54.6, 14.3; HRMS (ESI-TOF) m/z Calcd for $C_{19}H_{18}N_2O_2Na$ $[M+Na]^+$: 329.1260, found: 329.1258.



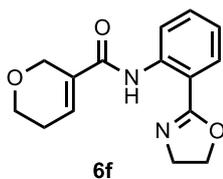
N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)cyclohex-1-enecarboxamide (6d)

6d was obtained by recrystallization from petroleum ether/ethyl acetate (50/1) as yellow solid (160 mg, 30%). mp 127–129 °C; 1H NMR (400 MHz, $CDCl_3$) δ 12.30 (s, 1H), 8.85 (d, $J = 8.5$ Hz, 1H), 7.85 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.45 (t, $J = 8.0$ Hz, 1H), 7.05 (t, $J = 8.0$ Hz, 1H), 6.93–6.85 (m, 1H), 4.36 (t, $J = 9.4$ Hz, 1H), 4.13 (t, $J = 9.6$ Hz, 2H), 2.46–2.39 (m, 2H), 2.28–2.21 (m, 2H), 1.78–1.70 (m, 2H), 1.68–1.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 164.6, 140.2, 135.1, 134.4, 132.4, 129.1, 121.8, 119.8, 113.3, 66.1, 54.6, 25.7, 24.2, 22.3, 21.5; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{18}N_2O_2Na$ $[M+Na]^+$: 293.1260, found: 293.1261.



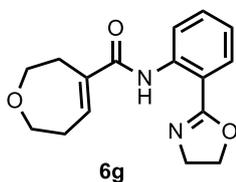
N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-3,4-dihydro-2H-pyran-5-carboxamide (6e)

6e was obtained by recrystallization from petroleum ether/ethyl acetate (50/1) as white solid (200 mg, 37%). mp 109–111 °C; 1H NMR (400 MHz, $CDCl_3$) δ 12.14 (s, 1H), 8.82 (d, $J = 8.5$ Hz, 1H), 7.83 (d, $J = 7.8$ Hz, 1H), 7.64 (s, 1H), 7.45 (d, $J = 7.9$ Hz, 1H), 7.02 (t, $J = 7.6$ Hz, 1H), 4.40–4.30 (m, 2H), 4.16–4.03 (m, 4H), 2.47–2.40 (m, 2H), 2.01–1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 164.6, 152.6, 140.3, 132.3, 129.0, 121.5, 119.6, 112.9, 109.8, 66.2, 66.0, 54.5, 21.3, 19.3; HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{16}N_2O_3Na$ $[M+Na]^+$: 295.1053, found: 295.1050.



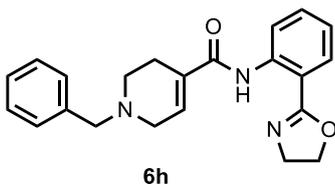
***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5,6-dihydro-2H-pyran-3-carboxamide (6f)**

6f was obtained by column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate (10/1) as yellow solid (595 mg, 22%). mp 113–115 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.44 (s, 1H), 8.78 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 4.52 (s, 2H), 4.40 (t, *J* = 9.4 Hz, 2H), 4.16 (t, *J* = 9.3 Hz, 2H), 3.81 (t, *J* = 5.5 Hz, 2H), 2.38 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 164.9, 164.7, 139.9, 134.3, 132.6, 131.4, 129.2, 122.3, 119.8, 113.2, 66.2, 64.9, 63.4, 54.6, 25.5; HRMS (ESI-TOF) *m/z* Calcd for C₁₅H₁₆N₂O₃Na [M+Na]⁺: 295.1053, found: 295.1051.



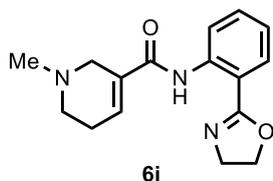
***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2,3,6,7-tetrahydrooxepine-4-carboxamide (6g)**

6g was obtained by column chromatography on silica gel with a gradient eluent of petroleum ether/ethyl acetate (5/1) as white solid (191 mg, 58%). mp 100–102 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.46 (s, 1H), 8.79 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 6.1 Hz, 1H), 4.33 (t, *J* = 9.5 Hz, 2H), 4.07 (t, *J* = 9.5 Hz, 2H), 3.79–3.69 (m, 4H), 2.88–2.81 (m, 2H), 2.56–2.49 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 167.9, 164.6, 140.9, 140.0, 136.6, 132.4, 129.1, 121.9, 119.4, 113.2, 69.6, 68.9, 66.0, 54.5, 32.0, 31.9; HRMS (ESI-TOF) *m/z* Calcd for C₁₆H₁₈N₂O₃Na [M+Na]⁺: 309.1210, found: 309.1205.



1-Benzyl-*N*-(2-(4,5-dihydrooxazol-2-yl)phenyl)-1,2,3,6-tetrahydropyridine-4-carboxamide (6h)

6h was obtained by column chromatography on neutral alumina with a gradient eluent of petroleum ether/ethyl acetate (6/1) as yellow solid (500 mg, 51%). mp 159–161 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.39 (s, 1H), 8.84 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.38–7.30 (m, 4H), 7.30–7.23 (m, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.81 (s, 1H), 4.31 (t, *J* = 9.5 Hz, 2H), 4.05 (t, *J* = 9.5 Hz, 2H), 3.62 (s, 2H), 3.18 (d, *J* = 2.9 Hz, 2H), 2.67 (t, *J* = 5.5 Hz, 2H), 2.57 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 164.5, 140.0, 137.9, 132.7, 132.3, 132.3, 129.1, 129.0, 128.2, 127.1, 121.9, 119.6, 113.2, 66.0, 62.4, 54.5, 52.8, 49.3, 25.2; HRMS (ESI-TOF) *m/z* Calcd for C₂₂H₂₄N₃O₂ [M+H]⁺: 362.1863, found: 362.1863.



***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-1-methyl-1,2,5,6-tetrahydropyridine-3-carboxamide (6i)**

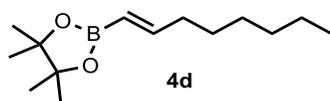
6i was obtained by column chromatography on neutral alumina with a gradient eluent of petroleum ether/ethyl acetate (1/1) as yellow solid (530 mg, 62%). mp 83–85 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.46 (s, 1H), 8.80 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.87 (s, 1H), 4.37 (t, *J* = 9.4 Hz, 2H), 4.13 (t, *J* = 9.0 Hz, 2H), 3.31 (s, 2H), 2.58–2.52 (m, 2H), 2.48–2.38 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 165.5, 164.7, 140.0, 133.5, 132.4, 131.9, 129.1, 122.0, 119.6, 113.2, 66.1, 54.5, 53.5, 50.8, 45.7, 26.5; HRMS (ESI-TOF) *m/z* Calcd for C₁₆H₁₉N₃O₂Na [M+Na]⁺: 308.1369, found: 308.1360.

3.3 Preparation of Alkenylboronates

The alkenylboronates (**2**, **4c**, **4g**, **4l-m**, **4q-s**, and **4u-z**) are commercially available. The alkenylboronates (**4d-f**, **4h-i**, **4k**, **4o**) were synthesized following the general procedure below.⁴ Others (**4a-b**,⁸ **4j**,⁹ **4n**,¹⁰ **4p**,¹¹ **4t**,¹²) were synthesized following the known procedures.

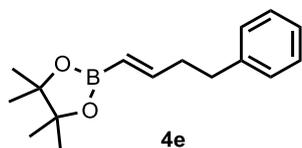
General Procedure for Synthesis of Alkenylboronates (**4d-f**, **4h-i**, **4k**, **4o**):

A stirring bar, B₂Pin₂ (7.5 mmol, 1.9 g), micro copper powder (0.5 mmol, 32.0 mg), and NaOMe (1.0 mmol, 54 mg) were added to an oven dried 100 mL Schlenk tube. Under the nitrogen, alkyne (5.0 mmol) and EtOH (20 mL) were added to the mixture, and the tube was capped tightly. Then the reaction mixture was stirred for 24 h at room temperature. Upon completion, the mixture was poured into water (100 mL), extracted with DCM (3 × 100 mL). The combined organic phases were dried over Na₂SO₄, concentrated under reduced pressure, and purified by flash column chromatography on silica gel to provide the desired product (**4d-f**, **4h-i**, **4k**, **4o**).



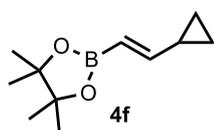
(*E*)-4,4,5,5-Tetramethyl-2-(oct-1-en-1-yl)-1,3,2-dioxaborolane (**4d**)⁴

4d was obtained by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1), as colorless oil (535 mg, 45%). ¹H NMR (400 MHz, CDCl₃) δ 6.68–6.59 (m, 1H), 5.42 (d, *J* = 18.0 Hz, 1H), 2.15 (q, *J* = 6.9 Hz, 2H), 1.45–1.35 (m, 2H), 1.34–1.23 (m, 18H), 0.88 (t, *J* = 6.6 Hz, 3H).



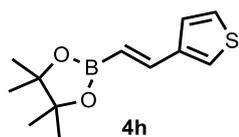
(*E*)-4,4,5,5-Tetramethyl-2-(4-phenylbut-1-en-1-yl)-1,3,2-dioxaborolane (**4e**)^{4,5}

4e was obtained by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1), as colorless oil (645 mg, 50%). ¹H NMR (400 MHz, CDCl₃) δ 7.30–7.23 (m, 2H), 7.21–7.15 (m, 3H), 6.75–6.65 (m, 1H), 5.50 (d, *J* = 18.0 Hz, 1H), 2.74 (t, *J* = 8.0 Hz, 2H), 2.51–2.43 (m, 2H), 1.27 (s, 12H).



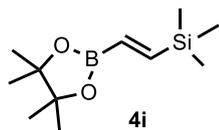
(*E*)-2-(2-Cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4f**)⁴

4f was obtained by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 200/1), as colorless oil (960 mg, 99%). ¹H NMR (400 MHz, CDCl₃) δ 6.07 (dd, *J* = 17.8, 9.3 Hz, 1H), 5.48 (d, *J* = 17.8 Hz, 1H), 1.57–1.46 (m, 1H), 1.25 (s, 12H), 0.83–0.77 (m, 2H), 0.56–0.50 (m, 2H).



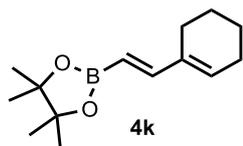
(E)-4,4,5,5-Tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (4h)⁴

4h was obtained by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1), as yellow solid (908 mg, 77%). ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 18.6 Hz, 1H), 7.32–7.24 (m, 3H), 5.94 (d, *J* = 18.1 Hz, 1H), 1.33–1.27 (m, 12H).



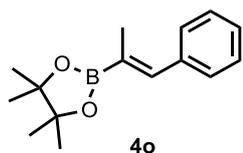
(E)-Trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (4i)^{4,6}

4i was obtained by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1), as colorless oil (226 mg, 20%). ¹H NMR (400 MHz, CDCl₃) δ 7.09 (d, *J* = 21.8 Hz, 1H), 6.21 (d, *J* = 21.8 Hz, 1H), 1.25 (s, 12H), 0.05 (s, 9H).



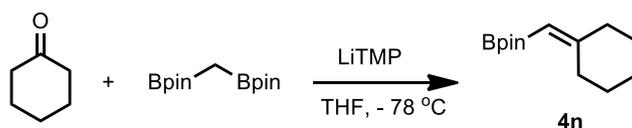
(E)-2-(2-(Cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4k)^{4,7}

4k was obtained by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1), as colorless oil (374 mg, 32%). ¹H NMR (400 MHz, CDCl₃) δ 7.03 (d, *J* = 18.2 Hz, 1H), 5.97 (s, 1H), 5.43 (d, *J* = 18.3 Hz, 1H), 2.19–2.11 (m, 4H), 1.71–1.54 (m, 4H), 1.28 (s, 12H).



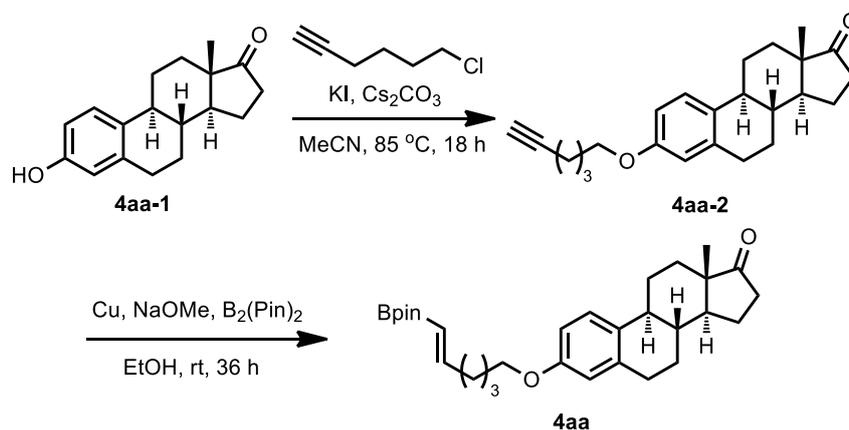
(Z)-4,4,5,5-Tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (4o)⁴

4o was obtained by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80/1), as colorless oil (744 mg, 61%). ¹H NMR (400 MHz, CDCl₃) δ 7.40–7.36 (m, 2H), 7.35–7.30 (m, 2H), 7.26–7.19 (m, 2H), 1.99 (s, 3H), 1.30 (s, 12H).



To a solution of 2, 2, 6, 6-tetramethylpiperidine (339 mg, 2.4 mmol) in THF (4 mL) was slowly added *n*-BuLi (1.0 mL, 2.5 M in hexane, 2.4 mmol) at 0 °C under nitrogen atmosphere, and the mixture was stirred at the same temperature for 10 min. After cooled to -78 °C, a solution of bis[(pinacolato)boryl]methane (643 mg, 2.4 mmol) in THF (5 mL) was added dropwise, and the resulting mixture was stirred at -78 °C for another 30 min. Then, a

solution of cyclohexanone (197 mg, 2.0 mmol) in THF (3 mL) was added dropwise at $-78\text{ }^{\circ}\text{C}$, and stirred at the same temperature for 4 h. The reaction was allowed to slowly warm up to room temperature in 4 hours. At $0\text{ }^{\circ}\text{C}$, saturated aqueous NH_4Cl (50 mL) was added dropwise to quench this reaction. The mixture was stirred for 1 h, filtered and concentrated. Water (50 mL) was added to the obtained residue, and the aqueous layer was extracted with EtOAc ($3 \times 50\text{ mL}$). The combined organic phases were washed with brine (100 mL), dried over Na_2SO_4 , filtered and evaporated. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate = 80/1) to afford **4n** as a colorless oil (370 mg, 83%).¹⁰ $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.01 (s, 1H), 2.50 (t, $J = 6.1\text{ Hz}$, 2H), 2.18 (t, $J = 6.1\text{ Hz}$, 2H), 1.61–1.50 (m, 6H), 1.25 (s, 12H).

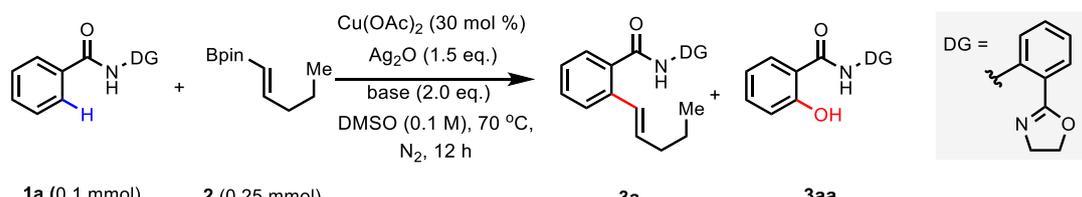


Under nitrogen atmosphere, a reaction mixture of 1,3,5(10)-Estratrien-3-ol-17-one (1.4 g, 5.0 mmol), 5-chloropent-1-yne (641 mg, 5.5 mmol), KI (83 mg, 0.5 mmol) and Cs_2CO_3 (2.5 g, 7.5 mmol) in MeCN (20 mL) was stirred for 18 h at $85\text{ }^{\circ}\text{C}$. The reaction mixture was poured into water (100 mL) and extracted with EtOAc ($3 \times 100\text{ mL}$). The combined organic phases were washed with brine (100 mL), dried over Na_2SO_4 , filtered and evaporated. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to afford **4aa-2** as white solid (1.56 g, 89%). mp $94\text{--}96\text{ }^{\circ}\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.18 (d, $J = 8.5\text{ Hz}$, 1H), 6.69 (d, $J = 8.4\text{ Hz}$, 1H), 6.63 (s, 1H), 3.95 (t, $J = 6.2\text{ Hz}$, 2H), 2.92–2.85 (m, 2H), 2.52–2.45 (m, 1H), 2.40–2.35 (m, 1H), 2.28–1.85 (m, 9H), 1.76–1.40 (m, 8H), 0.90 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 220.8, 156.9, 137.6, 131.9, 126.2, 114.4, 112.0, 84.0, 68.6, 67.1, 50.3, 47.9, 43.9, 38.3, 35.8, 31.5, 29.6, 28.2, 26.5, 25.8, 25.0, 21.5, 18.1, 13.8; HRMS (EI) m/z Calcd for $\text{C}_{24}\text{H}_{30}\text{O}_2$ [M]: 350.2246, found: 350.2245.

A stirring bar, B_2Pin_2 (1.36 g, 5.35 mmol), micro copper powder (29 mg, 0.45 mmol), and NaOMe (49 mg, 0.9 mmol) were added to an oven dried 100 mL Schlenk tube. The tube was capped and back-filled with nitrogen (3 times). Under the nitrogen flow, **4aa-2** (1.56 g, 4.46 mmol) and EtOH (20 mL) were added to the mixture, and the tube was capped tightly again. Then the reaction mixture was stirred for 36 h at room temperature. After that, the mixture was poured into water (100 mL), extracted with DCM ($3 \times 100\text{ mL}$). The combined organic phases were dried over Na_2SO_4 , concentrated under vacuum, and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1) to afford **4aa** as white solid (592 mg, 28%). mp $115\text{--}117\text{ }^{\circ}\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.17 (d, $J = 8.6\text{ Hz}$, 1H), 6.73–6.59 (m, 3H), 5.46 (d, $J = 18.0\text{ Hz}$, 1H), 3.92 (t, $J = 6.4\text{ Hz}$, 2H), 2.92–2.84 (m, 2H), 2.53–2.45 (m, 1H), 2.41–2.35 (m, 1H), 2.28–1.91 (m, 7H), 1.82–1.73 (m, 2H), 1.65–1.41 (m, 8H), 1.26 (s, 12H), 0.90 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 220.7, 157.0, 153.8, 137.5, 131.7, 126.1, 114.4, 112.0, 82.9, 67.5, 50.3, 47.9, 43.9, 38.3, 35.8, 35.3, 31.5, 29.5, 28.7, 26.5, 25.8, 24.7, 24.6, 21.5, 13.8; HRMS (EI) m/z Calcd for $\text{C}_{30}\text{H}_{43}(10)\text{BO}_4$ [M]: 477.3291, found: 477.3286.

3.4 Optimizations of the Reaction Conditions

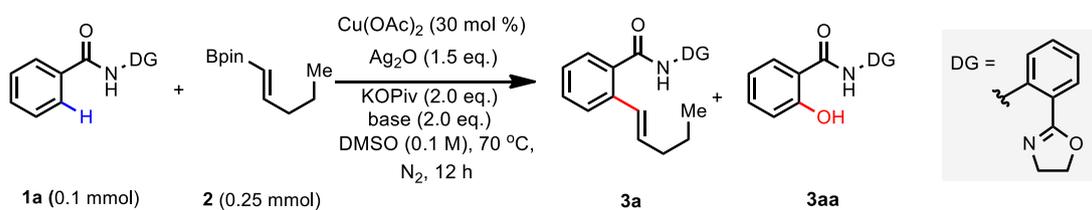
Table S1. Screening of Bases.^{a,b}



Entry	Base	3a (%) (mono/di)	3aa (%)	1a (%)
1	KOAc	40 (3.4/1)	12	27
2	KOPiv	46 (3.2/1)	12	19
3	KHCO ₃	29 (6.3/1)	10	34
4	KO ^t Bu	0	0	50
5	K ₃ PO ₄	32 (5.4/1)	6	35
6	CsF	23 (4.8/1)	0	68
7	NaOPiv	36 (4.1/1)	5	32
8	Na ₂ CO ₃	7 (7.0/0)	11	24
9	LiOTf	0	9	67

^aConditions: **1a** (0.1 mmol), **2** (0.25 mmol), Cu(OAc)₂ (0.03 mmol), Ag₂O (0.2 mmol), base (0.2 mmol), DMSO (1.0 mL), N₂, 70 °C, 12 h; ^bThe yield was determined by ¹H NMR using CH₂Br₂ as an internal standard.

Table S2. Screening of Double Bases.^{a,b}



Entry	Base	3a (%) (mono/di)	3aa (%)	1a (%)	Entry	Base	3a (%) (mono/di)	3aa (%)	1a (%)
1	LiOTf	26 (3.3/1)	16	50	8	NaO ^t Bu	10 (10/0)	0	80
2	Na ₂ CO ₃	62 (2.4/1)	13	18	9	K ₂ CO ₃	58 (2.4/1)	14	20
3	NaHCO ₃	56 (2.5/1)	13	18	10	KHCO ₃	66 (2.1/1)	12	18
4	NaBF ₄	49 (4.4/1)	8	36	11	K ₃ PO ₄	45 (3.5/1)	17	24
5	HCO ₂ Na	5 (5/0)	0	90	12	CsHCO ₃	58 (2.2/1)	13	17
6	NaTFA	27 (3.5/1)	17	30	13	CsF	59 (2.7/1)	13	21
7	NaOH	38 (3.8/1)	16	29	14	DBU	41 (3.6/1)	5	40

^aConditions: **1a** (0.1 mmol), **2** (0.25 mmol), Cu(OAc)₂ (0.03 mmol), Ag₂O (0.2 mmol), KOPiv (0.2 mmol), base (0.2 mmol), DMSO (1.0 mL), N₂, 70 °C, 12 h; ^bThe yield was determined by ¹H NMR using CH₂Br₂ as an internal standard.

Table S3. Screening of the Ratio of the Double Bases.^{a,b}

Entry	Bases	3a (%) (mono/di)	3aa (%)	1a (%)
1	1 eq. KOPiv + 2 eq. KHCO ₃	64 (3/1)	10	22
2	3 eq. KOPiv + 2 eq. KHCO ₃	56 (3/1)	16	20
3	2 eq. KOPiv + 2 eq. KHCO ₃	66 (2.1/1)	12	18
4	2 eq. KOPiv + 1 eq. KHCO ₃	64 (2.2/1)	13	13
5	2 eq. KOPiv + 3 eq. KHCO ₃	63 (2.3/1)	11	17

^aConditions: **1a** (0.1 mmol), **2** (0.25 mmol), Cu(OAc)₂ (0.03 mmol), Ag₂O (0.2 mmol), bases, DMSO (1.0 mL), N₂, 70 °C, 12 h; ^bThe yield was determined by ¹H NMR using CH₂Br₂ as an internal standard.

Table S4. Screening of Cu Salts.^{a,b}

Entry	[Cu]	3a (%) (mono/di)	3aa (%)	1a (%)
1	Cu(OAc) ₂	66 (2.1/1)	12	18
2	Cu(1-AdCO ₂) ₂	58 (1.6/1)	14	17
3	Cu(OPiv) ₂	70 (2.3/1)	12	18
4	Cu(PhCO ₂) ₂	73 (2.2/1)	9	17
5	CuTC	62 (2.6/1)	12	17
6	CuBr	60 (3.6/1)	11	27

^aConditions: **1a** (0.1 mmol), **2** (0.25 mmol), [Cu] (0.03 mmol), Ag₂O (0.2 mmol), KOPIV (0.2 mmol), KHCO₃ (0.2 mmol), DMSO (1.0 mL), N₂, 70 °C, 12 h; ^bThe yield was determined by ¹H NMR using CH₂Br₂ as an internal standard.

Table S5. Screening of Temperature.^{a,b}

Reaction scheme showing the conversion of **1a** (0.1 mmol) and **2** (0.25 mmol) to **3a** and **3aa** under the following conditions: Cu(PhCO₂)₂ (30 mol %), Ag₂O (1.5 eq.), KOPiv (2.0 eq.), KHCO₃ (2.0 eq.), DMSO (0.1 M), T °C, N₂, 12 h.

Entry	T (°C)	3a (%) (mono/di)	3aa (%)	1a (%)
1	30	41 (9.3/1)	0	58
2	40	62 (4.2/1)	0	38
3	45	74 (2.9/1)	trace	24
4	50	70 (2.3/1)	trace	20
5	60	71 (2.0/1)	10	17
6	70	73 (2.2/1)	9	17
7	80	59 (2.1/1)	10	18

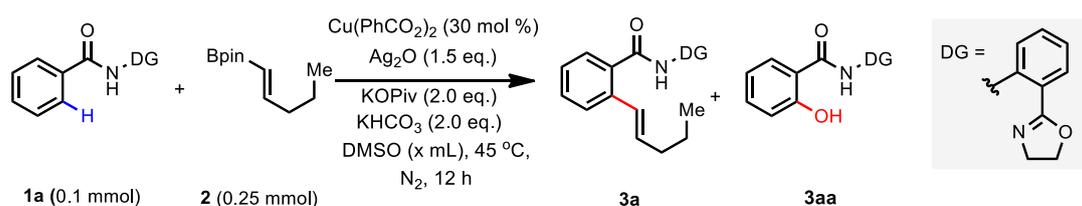
^aConditions: **1a** (0.1 mmol), **2** (0.25 mmol), Cu(PhCO₂)₂ (0.03 mmol), Ag₂O (0.2 mmol), KOPiv (0.2 mmol), KHCO₃ (0.2 mmol), DMSO (1.0 mL), N₂, T °C, 12 h; ^bThe yield was determined by ¹H NMR using CH₂Br₂ as an internal standard.

Table S6. Screening of Solvents.^{a,b}

Reaction scheme showing the conversion of **1a** (0.1 mmol) and **2** (0.25 mmol) to **3a** and **3aa** under the following conditions: Cu(PhCO₂)₂ (30 mol %), Ag₂O (1.5 eq.), KOPiv (2.0 eq.), KHCO₃ (2.0 eq.), Solvent (0.1 M), 45 °C, N₂, 12 h.

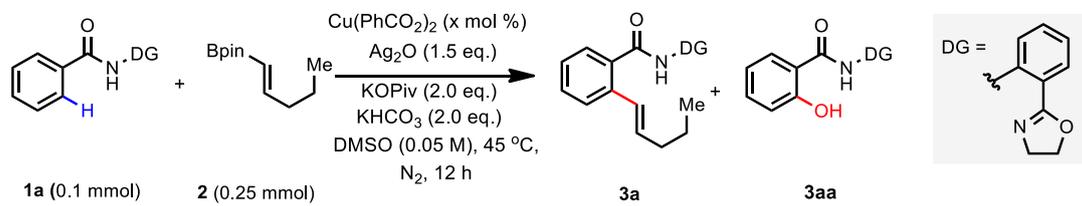
Entry	Solvent	3a (%) (mono/di)	3aa (%)	1a (%)
1	DMSO	74 (2.9/1)	trace	24
2	DMF	34 (4.7/1)	trace	66
3	MeOH	0	0	90
4	dioxane	0	0	99
5	MeCN	0	0	99
6	Toluene	0	0	94
7	DCM	0	0	99

^aConditions: **1a** (0.1 mmol), **2** (0.25 mmol), Cu(PhCO₂)₂ (0.03 mmol), Ag₂O (0.2 mmol), KOPiv (0.2 mmol), KHCO₃ (0.2 mmol), Solvent (1.0 mL), N₂, 45 °C, 12 h; ^bThe yield was determined by ¹H NMR using CH₂Br₂ as an internal standard.

Table S7. Screening of Concentration.^{a,b}


Entry	x (mL)	3a (%) (mono/di)	3aa (%)	1a (%)
1	0.5	61 (4.5/1)	trace	34
2	1.0	74 (2.9/1)	trace	24
3	1.5	75 (2.8/1)	trace	19
4	2.0	77 (2.4/1)	trace	21
5	2.5	75 (2.6/1)	trace	20
6	3.0	74 (3.1/1)	4	19
7	4.0	69 (3.6/1)	7	18

^aConditions: **1a** (0.1 mmol), **2** (0.25 mmol), Cu(PhCO₂)₂ (0.03 mmol), Ag₂O (0.2 mmol), KOPIV (0.2 mmol), KHCO₃ (0.2 mmol), DMSO (x mL), N₂, 45 °C, 12 h; ^bThe yield was determined by ¹H NMR using CH₂Br₂ as an internal standard.

Table S8. Screening of the Loading of Cu(PhCO₂)₂.^{a,b}


Entry	x	3a (%) (mono/di)	3aa (%)	1a (%)
1	20	69 (2.8/1)	trace	25
2	30	77 (2.4/1)	trace	21
3	35	74 (2.2/1)	trace	15

^aConditions: **1a** (0.1 mmol), **2** (0.25 mmol), Cu(PhCO₂)₂, Ag₂O (0.2 mmol), KOPIV (0.2 mmol), KHCO₃ (0.2 mmol), DMSO (2.0 mL), N₂, 45 °C, 12 h; ^bThe yield was determined by ¹H NMR using CH₂Br₂ as an internal standard.

Table S9. Screening of Oxidants.^{a,b}

Entry	[O]	3a (%) (mono/di)	3aa (%)	1a (%)
1	Ag ₂ O	77 (2.4/1)	trace	21
2	AgOAc	25 (4/1)	11	5
3	Ag ₂ CO ₃	43 (4.4/1)	8	38
4	Selectfluor	0	0	99
5	NMO	0	0	99
6	O ₂	0	trace	99
7	Air	0	23	65
8	Ag ₂ O + Air atmosphere	65 (3.1/1)	8	20

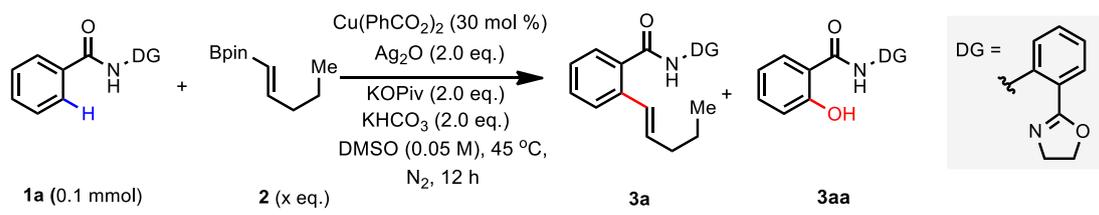
^aConditions: **1a** (0.1 mmol), **2** (0.25 mmol), Cu(PhCO₂)₂ (0.03 mmol), [O] (0.2 mmol), KOPIV (0.2 mmol), KHCO₃ (0.2 mmol), DMSO (2.0 mL), N₂, 45 °C, 12 h; ^bThe yield was determined by ¹H NMR using CH₂Br₂ as an internal standard.

Table S10. Screening of the Loading of Oxidants.^{a,b}

Entry	x	3a (%) (mono/di)	3aa (%)	1a (%)
1	1.0	45 (4.6/1)	10	27
2	1.5	77 (2.4/1)	trace	21
3	2.0	78 (2.4/1)	trace	19
4	2.5	61 (3.1/1)	6	20

^aConditions: **1a** (0.1 mmol), **2** (0.25 mmol), Cu(PhCO₂)₂ (0.03 mmol), Ag₂O, KOPIV (0.2 mmol), KHCO₃ (0.2 mmol), DMSO (2.0 mL), N₂, 45 °C, 12 h; ^bThe yield was determined by ¹H NMR using CH₂Br₂ as an internal standard.

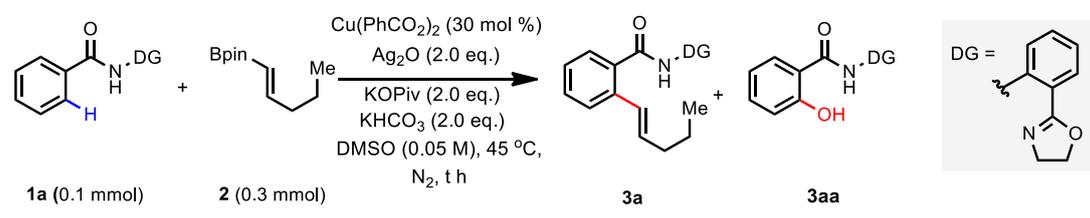
Table S11. Screening of the Loading of **2**.^{a,b}



Entry	x	3a (%) (mono/di)	3aa (%)	1a (%)
1	2.5	78 (2.4/1)	trace	19
2	3.0	86 (2.1/1)	trace	12
3	3.5	84 (2.0/1)	trace	13
4 ^c	3.5	70 (1.0/1)	trace	trace

^aConditions: **1a** (0.1 mmol), **2** (x eq.), Cu(PhCO₂)₂ (0.03 mmol), Ag₂O (0.2 mmol), KOPIV (0.2 mmol), KHCO₃ (0.2 mmol), DMSO (2.0 mL), N₂, 45 °C, 12 h; ^bThe yield was determined by ¹H NMR using CH₂Br₂ as an internal standard; ^c36 h.

Table S12. Screening of the Reaction Time.^{a,b}



Entry	t (h)	3a (%) (mono/di)	3aa (%)	1a (%)
1	3	58 (6.3/1)	0	42
2	6	72 (3.5/1)	0	28
3	9	76 (2.3/1)	trace	22
4	12	86 (2.1/1)	trace	12
5	15	85 (2.1/1)	trace	12
6	18	84 (1.9/1)	trace	11

^aConditions: **1a** (0.1 mmol), **2** (0.3 mmol), Cu(PhCO₂)₂ (0.03 mmol), Ag₂O (0.2 mmol), KOPIV (0.2 mmol), KHCO₃ (0.2 mmol), DMSO (2.0 mL), N₂, 45 °C, t h; ^bThe yield was determined by ¹H NMR using CH₂Br₂ as an internal standard.

Table S13. Re-comparison of Copper Salts.^{a,b}

Reaction scheme showing the conversion of **1a** (0.1 mmol) and **2** (0.3 mmol) to **3a** and **3aa** using copper salts. Conditions: [Cu] (30 mol %), Ag₂O (2.0 eq.), KOPIV (2.0 eq.), KHCO₃ (2.0 eq.), DMSO (0.05 M), 45 °C, N₂, 12 h. The DG group is defined as a benzene ring with a 2-oxazolidinone substituent.

Entry	[Cu]	3a (%) (mono/di)	3aa (%)	1a (%)
1	Cu(PhCO ₂) ₂	86 (2.1/1)	trace	12
2	Cu(OPiv) ₂	83 (2.1/1)	trace	14
3	Cu(OAc) ₂	78 (2.4/1)	trace	17

^aConditions: **1a** (0.1 mmol), **2** (0.3 mmol), [Cu] (0.03 mmol), Ag₂O (0.2 mmol), KOPIV (0.2 mmol), KHCO₃ (0.2 mmol), DMSO (2.0 mL), N₂, 45 °C, 12 h; ^bThe yield was determined by ¹H NMR using CH₂Br₂ as an internal standard.

Table S14. Control Experiments.^{a,b}

Reaction scheme showing the conversion of **1a** (0.1 mmol) and **2a** (0.3 mmol) to **3a** and **4a** using copper salts. Conditions: (PhCO₂)₂Cu (30 mol %), Ag₂O (2.0 equiv), KOPIV (2.0 equiv), KHCO₃ (2.0 equiv), DMSO, N₂, 45 °C, 12 h. The DG group is defined as a benzene ring with a 2-oxazolidinone substituent.

Entry	Deviation from optimal conditions	Yield (%) of 3a (mono/di)	Yield (%) of 4a	Yield (%) of 1a
1	none	86 (2.1/1.0)	trace	12
2	No (PhCO ₂) ₂ Cu	N.D.	0	99
3	No KOPIV	6 (6.0/0)	0	93
4	No KHCO ₃	66 (2.3/1.0)	8	10
5	No bases	0	0	99
6	No Ag ₂ O	trace	0	97
7	air instead of N ₂	70 (2.6/1.0)	6	15
8	air instead of Ag ₂ O	0	23	65
9	selectfluor instead of Ag ₂ O	0	0	99
10	0.1 eq. Ag ₂ O + air instead of Ag ₂ O	15 (15/0)	15	60
11	0.1 eq. Ag ₂ O + O ₂ instead of Ag ₂ O	10 (10/0)	20	45
12	0.1 eq. Ag ₂ O + 2 eq. selectfluor instead of Ag ₂ O	0	0	95
13	0.1 eq. Ag ₂ O + 2 eq. NMO instead of Ag ₂ O	4 (4/0)	trace	83

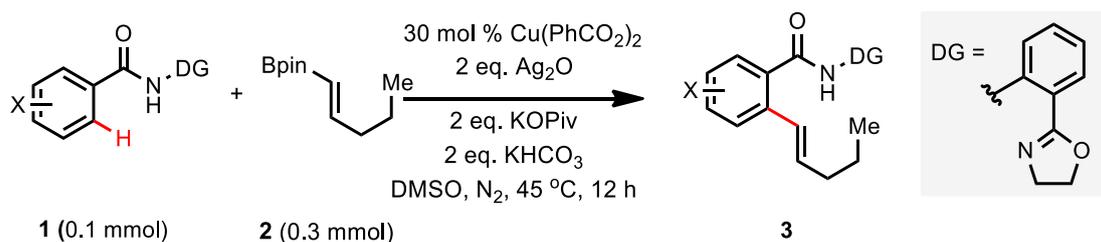
^aThe yield was determined by ¹H NMR using dibromomethane as an internal standard. ^bIsolated yield.

To validate the role of silver salt in our reaction, control experiments were conducted. The reaction cannot proceed in the absence of copper(II) benzoate and bases, and trace amount of the desired alkenylation product

were observed in the absence of Ag₂O. In addition, 23% of hydroxylation byproduct was formed using oxygen as oxidant instead of Ag₂O. The formation of hydroxylation byproduct, probably derived from Cu-catalyzed C–H acetoxylation followed by a rapid hydrolysis (*J. Org. Chem.* **2015**, *80*, 8843), indicated a Cu-involved C–H activation process rather than that of Ag.

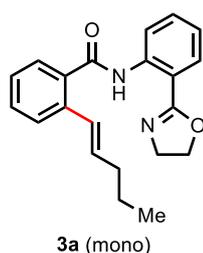
Given that only trace amount of desired product was observed using a catalytic amount of Ag with other oxidants, we hypothesized that the silver could serve as not only an oxidant but also an activator to accelerate the transmetalation of vinyl borons.

3.5 Evaluation of Benzamide Derivatives



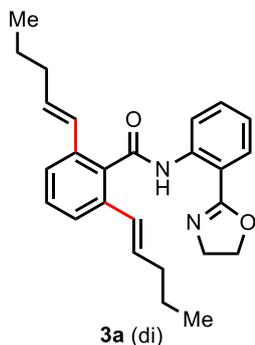
General Procedure A for Alkenylation of Benzamide Derivatives:

An oven dried 25 mL Schlenk tube was charged with substrate **1** (0.1 mmol), $\text{Cu}(\text{PhCO}_2)_2$ (0.03 mmol), Ag_2O (0.2 mmol), KOiPr (0.2 mmol), and KHCO_3 (0.2 mmol), and the tube was capped and back-filled with nitrogen (3 times). Under the nitrogen flow, **2** (0.3 mmol) and DMSO (2 mL) were added to the mixture, and the tube was capped tightly again. Then the reaction mixture was placed into a pre-heated oil bath and stirred at $45\text{ }^\circ\text{C}$ for 12 h. After cooled to room temperature, EtOAc (20 mL) was added to quench the reaction, and organic layer was washed with $\text{NH}_3\cdot\text{H}_2\text{O}$ (20 mL), and the water phase was extracted by EtOAc (20 mL). The combined organic layers were washed with saturated brine, dried over Na_2SO_4 , concentrated under vacuum. The crude product was purified by preparative TLC to afford the desired product **3**.



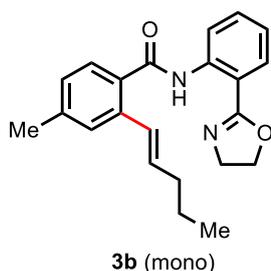
(E) - N -(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2-(pent-1-en-1-yl)benzamide (**3a** (mono))

Substrate **1a** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3a** (mono) was obtained as a white solid (17.1 mg, 52%). mp $98\text{--}100\text{ }^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 12.57 (s, 1H), 8.94 (d, $J = 8.6\text{ Hz}$, 1H), 7.89 (d, $J = 8.0\text{ Hz}$, 1H), 7.60 (d, $J = 7.9\text{ Hz}$, 2H), 7.52 (t, $J = 7.8\text{ Hz}$, 1H), 7.40 (t, $J = 7.6\text{ Hz}$, 1H), 7.31-7.27 (m, 1H), 7.12 (t, $J = 7.7\text{ Hz}$, 1H), 6.91 (d, $J = 15.5\text{ Hz}$, 1H), 6.27-6.17 (m, 1H), 4.34 (t, $J = 9.5\text{ Hz}$, 2H), 4.02 (t, $J = 9.5\text{ Hz}$, 2H), 2.18 (q, $J = 7.4\text{ Hz}$, 2H), 1.52-1.42 (m, 2H), 0.92 (t, $J = 7.4\text{ Hz}$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 164.5, 140.1, 137.0, 135.4, 133.4, 132.5, 130.1, 129.2, 127.7, 127.6, 126.6, 126.5, 122.5, 119.8, 113.5, 66.2, 54.7, 35.5, 22.5, 13.7; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 335.1754, found: 335.1759.



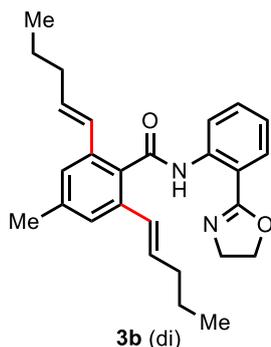
***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2,6-di(*E*)-pent-1-en-1-ylbenzamide (**3a** (di))**

Substrate **1a** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3a** (di) was obtained as a white solid (9.9 mg, 25%). mp 55–57 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.29 (s, 1H), 8.95 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.31–7.27 (m, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.51 (d, *J* = 15.8 Hz, 2H), 6.25–6.13 (m, 2H), 4.29 (t, *J* = 9.5 Hz, 2H), 3.90 (t, *J* = 9.4 Hz, 2H), 2.10 (q, *J* = 7.2 Hz, 4H), 1.45–1.35 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 168.8, 164.0, 139.6, 135.2, 135.0, 133.4, 132.4, 129.1, 128.8, 127.0, 123.9, 122.7, 120.2, 113.7, 66.1, 54.7, 35.2, 22.4, 13.6; HRMS (ESI-TOF) *m/z* Calcd for C₂₆H₃₁N₂O₂ [M+H]⁺: 403.2380, found: 403.2391.



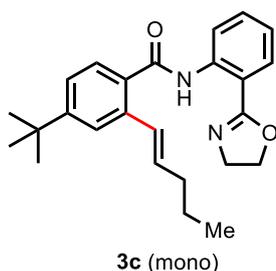
***E*)-*N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-4-methyl-2-(pent-1-en-1-yl)benzamide (**3b** (mono))**

Substrate **1b** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3b** (mono) was obtained as a white solid (15.7 mg, 46%). mp 133–135 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.52 (s, 1H), 8.93 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.96–7.48 (m, 2H), 7.40 (s, 1H), 7.15–7.05 (m, 2H), 6.92 (d, *J* = 15.9 Hz, 1H), 6.25–6.16 (m, 1H), 4.34 (t, *J* = 9.5 Hz, 2H), 4.02 (t, *J* = 9.5 Hz, 2H), 2.39 (s, 3H), 2.18 (q, *J* = 7.3 Hz, 2H), 1.52–1.42 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.5, 164.5, 140.2, 140.2, 137.1, 133.0, 132.6, 132.5, 129.1, 127.9, 127.8, 127.4, 127.1, 122.3, 119.8, 113.4, 66.1, 54.7, 35.3, 22.5, 21.5, 13.8; HRMS (ESI-TOF) *m/z* Calcd for C₂₂H₂₅N₂O₂ [M+H]⁺: 349.1911, found: 349.1920.



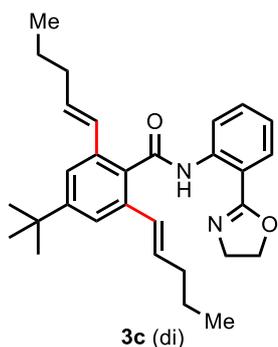
***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-4-methyl-2,6-di((*E*)-pent-1-en-1-yl)benzamide (**3b (di)**)**

Substrate **1b** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3b (di)** was obtained as a white solid (10.5 mg, 26%). mp 57–59 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.24 (s, 1H), 8.95 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.22 (s, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.50 (d, *J* = 15.7 Hz, 2H), 6.23–6.13 (m, 2H), 4.29 (t, *J* = 9.5 Hz, 2H), 3.91 (t, *J* = 9.5 Hz, 2H), 2.36 (s, 3H), 2.09 (q, *J* = 7.0 Hz, 4H), 1.44–1.34 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 169.0, 164.0, 139.7, 138.3, 135.2, 133.0, 132.6, 132.4, 129.1, 127.2, 124.6, 122.6, 120.2, 113.7, 66.1, 54.7, 35.2, 22.5, 21.5, 13.6; HRMS (ESI-TOF) *m/z* Calcd for C₂₇H₃₃N₂O₂ [M+H]⁺: 417.2537, found: 417.2549.



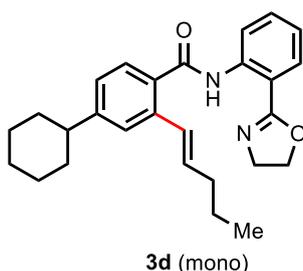
***(E)*-4-(Tert-butyl)-*N*-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-(pent-1-en-1-yl)benzamide (**3c (mono)**)**

Substrate **1c** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3c (mono)** was obtained as a white solid (16.5 mg, 43%). mp 132–134 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.53 (s, 1H), 8.94 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.61–7.55 (m, 2H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 15.8 Hz, 1H), 6.26–6.15 (m, 1H), 4.35 (t, *J* = 9.5 Hz, 2H), 4.05 (t, *J* = 9.5 Hz, 2H), 2.19 (q, *J* = 7.3 Hz, 2H), 1.55–1.43 (m, 2H), 1.37 (s, 9H), 0.93 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.5, 164.5, 153.3, 140.2, 136.9, 132.9, 132.6, 132.5, 129.2, 128.3, 127.7, 123.8, 123.5, 122.3, 119.9, 113.5, 66.1, 54.7, 35.3, 34.8, 31.2, 22.5, 13.8; HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₃₁N₂O₂ [M+H]⁺: 391.2380, found: 391.2390.



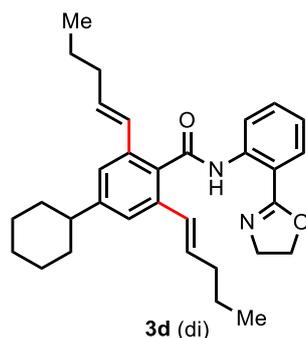
4-(Tert-butyl)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2,6-di((E)-pent-1-en-1-yl)benzamide (3c (di))

Substrate **1c** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3c** (di) was obtained as a white solid (12.3 mg, 27%). mp 107–109 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.23 (s, 1H), 8.95 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.41 (s, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 15.8 Hz, 2H), 6.24–6.13 (m, 2H), 4.29 (t, *J* = 9.5 Hz, 2H), 3.93 (t, *J* = 9.4 Hz, 2H), 2.10 (q, *J* = 7.1 Hz, 4H), 1.47–1.34 (m, 13H), 0.86 (t, *J* = 7.3 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 169.1, 164.0, 151.4, 139.7, 134.8, 132.9, 132.6, 132.4, 129.1, 127.6, 122.6, 121.2, 120.3, 113.7, 66.1, 54.7, 35.2, 34.8, 31.3, 22.5, 13.6; HRMS (ESI-TOF) *m/z* Calcd for C₃₀H₃₉N₂O₂ [M+H]⁺: 459.3006, found: 459.3022.



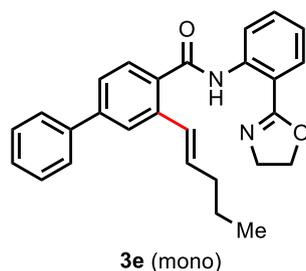
(E)-4-Cyclohexyl-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-(pent-1-en-1-yl)benzamide (3d (mono))

Substrate **1d** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3d** (mono) was obtained as a white solid (16.3 mg, 40%). mp 111–113 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.53 (s, 1H), 8.94 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.42 (s, 1H), 7.14–7.08 (m, 2H), 6.94 (d, *J* = 15.8 Hz, 1H), 6.27–6.16 (m, 1H), 4.35 (t, *J* = 9.5 Hz, 2H), 4.04 (t, *J* = 9.5 Hz, 2H), 2.59–2.50 (m, 1H), 2.18 (q, *J* = 7.3 Hz, 2H), 1.92–1.85 (m, 4H), 1.77 (d, *J* = 12.4 Hz, 1H), 1.55–1.37 (m, 6H), 1.34–1.25 (m, 1H), 0.93 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.5, 164.4, 150.3, 140.2, 137.2, 132.9, 132.8, 132.5, 129.1, 128.0, 127.9, 125.2, 125.1, 122.3, 119.8, 113.4, 66.1, 54.7, 44.6, 35.3, 34.2, 26.8, 26.1, 22.6, 13.8; HRMS (ESI-TOF) *m/z* Calcd for C₂₇H₃₃N₂O₂ [M+H]⁺: 417.2537, found: 417.2549.



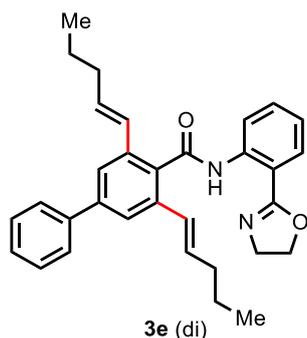
4-Cyclohexyl-*N*-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2,6-di((*E*)-pent-1-en-1-yl)benzamide (3d (di))

Substrate **1d** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3d** (di) was obtained as a white solid (12.2 mg, 26%). mp 100–102 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.23 (s, 1H), 8.94 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.24 (s, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.51 (d, *J* = 15.5 Hz, 2H), 6.23–6.10 (m, 2H), 4.29 (t, *J* = 9.6 Hz, 2H), 3.92 (t, *J* = 9.6 Hz, 2H), 2.57–2.47 (m, 1H), 2.09 (q, *J* = 7.1 Hz, 4H), 1.95–1.85 (m, 4H), 1.77 (d, *J* = 12.4 Hz, 1H), 1.50–1.35 (m, 9H), 0.86 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 169.1, 163.9, 148.5, 139.6, 135.1, 132.9, 132.9, 132.4, 129.1, 127.4, 122.6, 122.6, 120.3, 113.7, 66.1, 54.7, 44.7, 35.2, 34.3, 26.9, 26.1, 22.5, 13.6; HRMS (ESI-TOF) *m/z* Calcd for C₃₂H₄₁N₂O₂ [M+H]⁺: 485.3163, found: 485.3180.



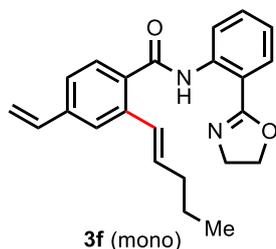
(*E*)-*N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-3-(pent-1-en-1-yl)-[1,1'-biphenyl]-4-carboxamide (3e (mono))

Substrate **1e** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3e** (mono) was obtained as a white solid (17.3 mg, 43%). mp 94–96 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.64 (s, 1H), 8.96 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.81 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.55–7.45 (m, 4H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 15.6 Hz, 1H), 6.35–6.23 (m, 1H), 4.36 (t, *J* = 9.5 Hz, 2H), 4.05 (t, *J* = 9.5 Hz, 2H), 2.21 (q, *J* = 7.1 Hz, 2H), 1.55–1.45 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.2, 164.5, 143.0, 140.5, 140.1, 137.7, 134.1, 133.6, 132.6, 129.2, 128.8, 128.4, 127.8, 127.7, 127.2, 125.4, 125.4, 122.5, 119.9, 113.5, 66.2, 54.7, 35.3, 22.5, 13.8; HRMS (ESI-TOF) *m/z* Calcd for C₂₇H₂₇N₂O₂ [M+H]⁺: 411.2067, found: 411.2082.



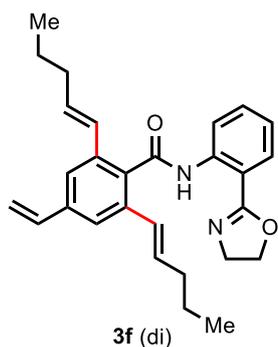
***N*-2-(4,5-Dihydrooxazol-2-yl)phenyl-3,5-di((*E*)-pent-1-en-1-yl)-[1,1'-biphenyl]-4-carboxamide (3e (di))**

Substrate **1e** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3e** (di) was obtained as a white solid (12.5 mg, 26%). mp 122–124 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.36 (s, 1H), 8.97 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.62 (s, 2H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.58 (d, *J* = 15.6 Hz, 2H), 6.33–6.21 (m, 2H), 4.30 (t, *J* = 9.5 Hz, 2H), 3.92 (t, *J* = 9.5 Hz, 2H), 2.12 (q, *J* = 7.2 Hz, 4H), 1.49–1.34 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 168.7, 164.0, 141.7, 141.0, 139.6, 135.7, 133.9, 133.7, 132.5, 129.1, 128.7, 127.5, 127.2, 127.1, 122.9, 122.7, 120.2, 113.7, 66.1, 54.7, 35.2, 22.4, 13.6; HRMS (ESI-TOF) *m/z* Calcd for C₃₂H₃₅N₂O₂ [M+H]⁺: 479.2693, found: 479.2709.



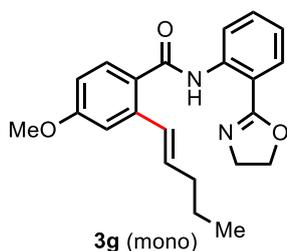
***(E)*-N-2-(4,5-Dihydrooxazol-2-yl)phenyl-2-(pent-1-en-1-yl)-4-vinylbenzamide (3f (mono))**

Substrate **1f** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3f** (mono) was obtained as a white solid (11.7 mg, 33%). mp 110–112 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.59 (s, 1H), 8.93 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.63–7.57 (m, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.12 (t, *J* = 7.1 Hz, 1H), 6.93 (d, *J* = 15.7 Hz, 1H), 6.76 (dd, *J* = 17.6, 10.8 Hz, 1H), 6.29–6.20 (m, 1H), 5.85 (d, *J* = 17.6 Hz, 1H), 5.35 (d, *J* = 10.9 Hz, 1H), 4.35 (t, *J* = 9.6 Hz, 2H), 4.03 (t, *J* = 9.5 Hz, 2H), 2.19 (q, *J* = 6.9 Hz, 2H), 1.53–1.41 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.1, 164.5, 140.1, 139.2, 137.5, 136.3, 134.6, 133.5, 132.5, 129.2, 128.2, 127.6, 124.7, 124.2, 122.4, 119.8, 115.3, 113.5, 66.2, 54.7, 35.3, 22.5, 13.8; HRMS (ESI-TOF) *m/z* Calcd for C₂₃H₂₅N₂O₂ [M+H]⁺: 361.1911, found: 361.1920.



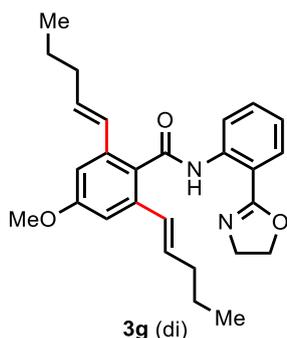
***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2,6-di((*E*)-pent-1-en-1-yl)-4-vinylbenzamide (**3f (di)**)**

Substrate **1f** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3f (di)** was obtained as a white solid (10.3 mg, 24%). mp 78–80 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.30 (s, 1H), 8.95 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.44 (s, 2H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.74 (dd, *J* = 17.6, 11.0 Hz, 1H), 6.51 (d, *J* = 15.7 Hz, 2H), 6.29–6.17 (m, 2H), 5.84 (d, *J* = 17.6 Hz, 1H), 5.32 (d, *J* = 10.9 Hz, 1H), 4.29 (t, *J* = 9.5 Hz, 2H), 3.91 (t, *J* = 9.5 Hz, 2H), 2.11 (q, *J* = 6.9 Hz, 4H), 1.48–1.31 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 168.6, 164.0, 139.5, 137.7, 136.6, 135.5, 134.5, 133.6, 132.4, 129.1, 127.0, 122.7, 121.8, 120.2, 114.7, 113.6, 66.1, 54.7, 35.2, 22.4, 13.6; HRMS (ESI-TOF) *m/z* Calcd for C₂₈H₃₃N₂O₂ [M+H]⁺: 429.2537, found: 429.2550.



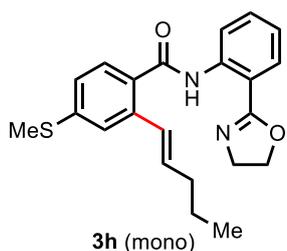
***(E)*-*N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-4-methoxy-2-(pent-1-en-1-yl)benzamide (**3g (mono)**)**

Substrate **1g** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3g (mono)** was obtained as a white solid (14.2 mg, 39%). mp 107–109 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.52 (s, 1H), 8.91 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.14–7.07 (m, 2H), 6.98 (d, *J* = 15.6 Hz, 1H), 6.82 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.26–6.14 (m, 1H), 4.35 (t, *J* = 9.5 Hz, 2H), 4.04 (t, *J* = 9.5 Hz, 2H), 3.87 (s, 3H), 2.19 (q, *J* = 7.6 Hz, 2H), 1.54–1.42 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.1, 164.5, 160.9, 140.2, 139.5, 133.4, 132.5, 129.7, 129.2, 128.1, 127.9, 122.2, 119.7, 113.4, 112.1, 111.6, 66.1, 55.3, 54.7, 35.2, 22.5, 13.8; HRMS (ESI-TOF) *m/z* Calcd for C₂₂H₂₅N₂O₃ [M+H]⁺: 365.1860, found: 365.1867.



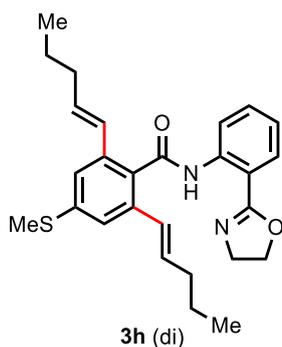
***N*-2-(4,5-Dihydrooxazol-2-yl)phenyl-4-methoxy-2,6-di((*E*)-pent-1-en-1-yl)benzamide (**3g (di)**)**

Substrate **1g** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3g (di)** was obtained as a white solid (11.4 mg, 27%). mp 68–70 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.25 (s, 1H), 8.95 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 6.8 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.93 (s, 2H), 6.51 (d, *J* = 15.6 Hz, 2H), 6.23–6.13 (m, 2H), 4.29 (t, *J* = 9.5 Hz, 2H), 3.91 (t, *J* = 9.5 Hz, 2H), 3.87 (s, 3H), 2.10 (q, *J* = 6.9 Hz, 4H), 1.46–1.33 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 168.8, 164.0, 159.6, 139.7, 137.0, 133.5, 132.4, 129.1, 128.7, 127.1, 122.5, 120.1, 113.6, 109.3, 66.1, 55.3, 54.7, 35.1, 22.4, 13.6; HRMS (ESI-TOF) *m/z* Calcd for C₂₇H₃₃N₂O₃ [M+H]⁺: 433.2486, found: 433.2503.



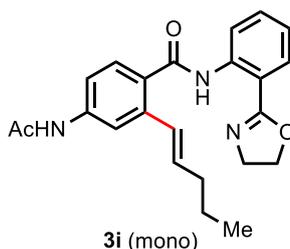
***E*-N**-2-(4,5-Dihydrooxazol-2-yl)phenyl-4-(methylthio)-2-(pent-1-en-1-yl)benzamide (**3h (mono)**)

Substrate **1h** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3h (mono)** was obtained as a white solid (13.8 mg, 37%). mp 83–85 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.56 (s, 1H), 8.91 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.60–7.48 (m, 2H), 7.42 (s, 1H), 7.16–7.08 (m, 2H), 6.92 (d, *J* = 15.7 Hz, 1H), 6.26–6.15 (m, 1H), 4.35 (t, *J* = 9.5 Hz, 2H), 4.03 (t, *J* = 9.5 Hz, 2H), 2.54 (s, 3H), 2.18 (q, *J* = 7.3 Hz, 2H), 1.52–1.41 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.9, 164.5, 141.4, 140.1, 137.8, 133.8, 132.5, 131.9, 129.2, 128.4, 127.5, 123.9, 123.8, 122.4, 119.8, 113.5, 66.2, 54.7, 35.2, 22.5, 15.3, 13.8; HRMS (ESI-TOF) *m/z* Calcd for C₂₂H₂₅N₂O₂S [M+H]⁺: 381.1631, found: 381.1639.



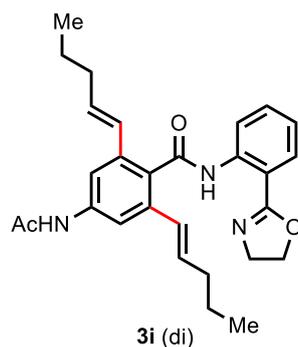
***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-4-(methylthio)-2,6-di((*E*)-pent-1-en-1-yl)benzamide (**3h** (di))**

Substrate **1h** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3h** (di) was obtained as a white solid (10.0 mg, 23%). mp 95–97 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.29 (s, 1H), 8.94 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.27–7.26 (m, 2H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.49 (d, *J* = 15.7 Hz, 2H), 6.26–6.13 (m, 2H), 4.29 (t, *J* = 9.5 Hz, 2H), 3.92 (t, *J* = 9.6 Hz, 2H), 2.54 (s, 3H), 2.10 (q, *J* = 7.2 Hz, 4H), 1.44–1.33 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 168.4, 164.0, 139.5, 139.1, 135.9, 133.9, 132.4, 132.3, 129.1, 126.7, 122.7, 121.7, 120.1, 113.6, 66.1, 54.7, 35.2, 22.4, 15.7, 13.6; HRMS (ESI-TOF) *m/z* Calcd for C₂₇H₃₃N₂O₂S [M+H]⁺: 449.2257, found: 449.2273.



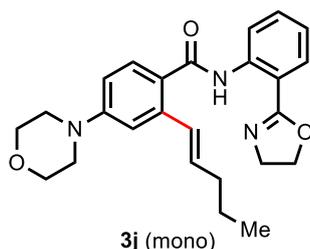
(*E*)-4-Acetamido-*N*-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-(pent-1-en-1-yl)benzamide (3i** (mono))**

Substrate **1i** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 2/1), **3i** (mono) was obtained as a white solid (12.6 mg, 33%). mp 151–153 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.62 (s, 1H), 8.90 (d, *J* = 8.6 Hz, 1H), 7.91–7.85 (m, 2H), 7.61 (s, 1H), 7.58–7.48 (m, 3H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 15.6 Hz, 1H), 6.20–6.09 (m, 1H), 4.34 (t, *J* = 9.4 Hz, 2H), 4.02 (t, *J* = 9.5 Hz, 2H), 2.18 (s, 3H), 2.13 (d, *J* = 7.0 Hz, 2H), 1.48–1.35 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.8, 168.2, 164.4, 134.0, 139.8, 138.2, 133.8, 132.5, 131.0, 129.2, 128.8, 127.2, 122.5, 119.7, 117.9, 117.3, 113.5, 66.2, 54.7, 35.2, 24.6, 22.4, 13.7; HRMS (ESI-TOF) *m/z* Calcd for C₂₃H₂₆N₃O₃ [M+H]⁺: 392.1969, found: 392.1979.



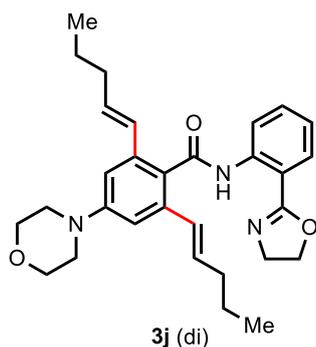
4-Acetamido-*N*-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2,6-di(*E*)-pent-1-en-1-yl)benzamide (3i (di)**)**

Substrate **1i** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 2/1), **3i (di)** was obtained as a white solid (7.3 mg, 16%). mp 71–73 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.37 (s, 1H), 8.94 (d, *J* = 8.5 Hz, 1H), 7.96–7.78 (m, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.42–7.37 (m, 2H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.43 (d, *J* = 15.4 Hz, 2H), 6.23–6.06 (m, 2H), 4.29 (t, *J* = 9.6 Hz, 2H), 3.91 (t, *J* = 9.5 Hz, 2H), 2.18 (s, 3H), 2.08 (q, *J* = 7.2 Hz, 4H), 1.45–1.30 (m, 4H), 0.84 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 169.1, 168.8, 163.9, 139.4, 138.2, 136.0, 133.9, 132.4, 131.1, 129.2, 126.5, 122.8, 120.1, 116.0, 113.8, 66.1, 54.7, 35.2, 24.4, 22.3, 13.6; HRMS (ESI-TOF) *m/z* Calcd for C₂₈H₃₄N₃O₃ [M+H]⁺: 460.2595, found: 460.2609.



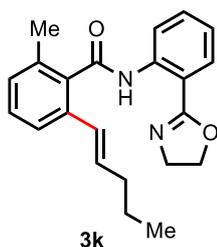
(*E*)-*N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-4-morpholino-2-(pent-1-en-1-yl)benzamide (3j (mono)**)**

Substrate **1j** was alkenylated with alkenyl boronates (**2**) following the general procedure **A** (Cu(OPiv)₂ (30 mol%)). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 4/1), **3j (mono)** was obtained as a white solid (14.1 mg, 34%). mp 83–85 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.50 (s, 1H), 8.91 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.05–6.97 (m, 2H), 6.81 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.20–6.10 (m, 1H), 4.35 (t, *J* = 9.5 Hz, 2H), 4.05 (t, *J* = 9.5 Hz, 2H), 3.91–3.84 (m, 4H), 3.31–3.25 (m, 4H), 2.19 (q, *J* = 7.4 Hz, 2H), 1.52–1.43 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.1, 164.5, 152.4, 140.4, 139.2, 132.8, 132.5, 129.5, 129.1, 128.7, 126.4, 122.1, 119.7, 113.3, 113.1, 112.7, 66.8, 66.1, 54.7, 48.4, 35.2, 22.5, 13.8; HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₂₉N₃O₃Na [M+Na]⁺: 442.2101, found: 442.2111.



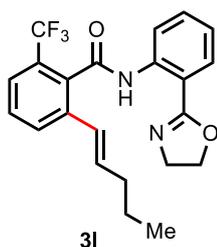
***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-4-morpholino-2,6-di((*E*)-pent-1-en-1-yl)benzamide (**3j** (di))**

Substrate **1j** was alkenylated with alkenyl boronates (**2**) following the general procedure A ($\text{Cu}(\text{OPiv})_2$ (30 mol%). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 4/1), **3j** (mono) was obtained as a white solid (9.5 mg, 20%). mp 103–105 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.22 (s, 1H), 8.95 (d, $J = 8.3$ Hz, 1H), 7.86 (d, $J = 7.8$ Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 1H), 7.12 (t, $J = 7.7$ Hz, 1H), 6.93 (s, 2H), 6.52 (d, $J = 15.6$ Hz, 2H), 6.20–6.10 (m, 2H), 4.29 (t, $J = 9.5$ Hz, 2H), 3.97–3.83 (m, 6H), 3.29–3.21 (m, 4H), 2.09 (q, $J = 7.1$ Hz, 4H), 1.44–1.33 (m, 4H), 0.85 (t, $J = 7.4$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.9, 164.0, 151.3, 139.7, 136.5, 133.1, 132.4, 129.1, 128.0, 127.6, 122.5, 120.1, 113.5, 111.3, 66.9, 66.0, 54.7, 49.2, 35.2, 22.4, 13.6; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{30}\text{H}_{37}\text{N}_3\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 510.2727, found: 510.2747.



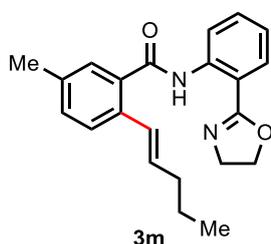
(*E*)-*N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2-methyl-6-(pent-1-en-1-yl)benzamide (3k**)**

Substrate **1k** was alkenylated with alkenyl boronates (**2**) following the general procedure A ($\text{Cu}(\text{OPiv})_2$ (30 mol%), 60 °C). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3k** was obtained as a white solid (16.3 mg, 47%). mp 83–85 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.29 (s, 1H), 8.95 (d, $J = 8.4$ Hz, 1H), 7.91–7.85 (m, 1H), 7.54 (t, $J = 7.9$ Hz, 1H), 7.39 (d, $J = 7.8$ Hz, 1H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 7.09 (d, $J = 7.6$ Hz, 1H), 6.51 (d, $J = 15.7$ Hz, 1H), 6.25–6.14 (m, 1H), 4.30 (t, $J = 9.5$ Hz, 2H), 3.93 (t, $J = 9.5$ Hz, 2H), 2.38 (s, 3H), 2.10 (q, $J = 7.2$ Hz, 2H), 1.44–1.34 (m, 2H), 0.86 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.0, 164.1, 139.5, 136.6, 135.0, 134.4, 133.2, 132.5, 129.2, 128.7, 128.5, 127.1, 122.9, 122.7, 120.1, 113.6, 66.1, 54.7, 35.2, 22.4, 19.5, 13.6; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 349.1911, found: 349.1913.



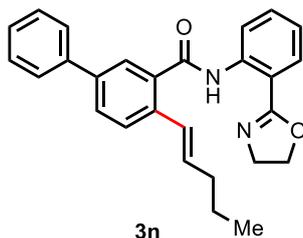
(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2-(pent-1-en-1-yl)-6-(trifluoromethyl)benzamide (3l)

Substrate **1l** was alkenylated with alkenyl boronates (**2**) following the general procedure A ($\text{Cu}(\text{OPiv})_2$ (30 mol%), 60 °C). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3l** was obtained as a white solid (13.0 mg, 33%). mp 52–54 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.48 (s, 1H), 8.88 (d, $J = 8.4$ Hz, 1H), 7.88 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.59–7.51 (m, 2H), 7.47 (t, $J = 7.9$ Hz, 1H), 7.16 (t, $J = 7.3$ Hz, 1H), 6.55 (d, $J = 15.8$ Hz, 1H), 6.34–6.19 (m, 1H), 4.31 (t, $J = 9.5$ Hz, 2H), 3.92 (t, $J = 8.8$ Hz, 2H), 2.13 (q, $J = 7.3$ Hz, 2H), 1.46–1.35 (m, 2H), 0.86 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 164.1, 139.3, 136.7, 135.5, 134.0 (q, $J_{\text{C-F}} = 2.0$ Hz), 132.5, 129.1, 129.1, 129.0, 127.3 (q, $J_{\text{C-F}} = 31.0$ Hz), 125.8, 124.4 (q, $J_{\text{C-F}} = 5.0$ Hz), 123.8 (d, $J_{\text{C-F}} = 273.0$ Hz), 123.0, 120.2, 113.7, 66.1, 54.6, 35.2, 22.3, 13.5; ^{19}F NMR (375 MHz, CDCl_3) δ -59.01 (s, 3F). HRMS (ESI-TOF) m/z Calcd for $\text{C}_{22}\text{H}_{22}\text{F}_3\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 403.1628, found: 403.1640.



(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5-methyl-2-(pent-1-en-1-yl)benzamide (3m)

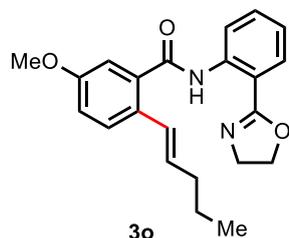
Substrate **1m** was alkenylated with alkenyl boronates (**2**) following the general procedure A ($\text{Cu}(\text{OPiv})_2$ (35 mol%), 50 °C). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3m** was obtained as a white solid (26.8 mg, 77%). mp 130–132 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.54 (s, 1H), 8.93 (d, $J = 8.2$ Hz, 1H), 7.89 (dd, $J = 8.0, 4.0$ Hz, 1H), 7.55–7.47 (m, 2H), 7.44 (s, 1H), 7.21 (d, $J = 8.2$ Hz, 1H), 7.12 (t, $J = 7.1$ Hz, 1H), 6.86 (d, $J = 15.8$ Hz, 1H), 6.23–6.12 (m, 1H), 4.35 (t, $J = 9.5$ Hz, 2H), 4.03 (t, $J = 9.5$ Hz, 2H), 2.37 (s, 3H), 2.16 (q, $J = 6.8$ Hz, 2H), 1.50–1.40 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.6, 164.4, 140.1, 136.3, 135.3, 134.1, 132.5, 132.4, 130.9, 129.1, 128.4, 127.4, 126.4, 122.4, 119.8, 113.4, 66.1, 54.6, 35.3, 22.6, 21.1, 13.7; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 349.1911, found: 349.1914.



(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-4-(pent-1-en-1-yl)-[1,1'-biphenyl]-3-carboxamide (3n)

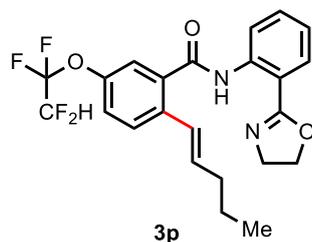
Substrate **1n** was alkenylated with alkenyl boronates (**2**) following the general procedure A ($\text{Cu}(\text{OPiv})_2$ (30 mol%). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3n** was obtained as a white solid (23.4 mg, 57%). mp 108–110 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.70 (s, 1H), 8.97 (d, $J = 8.3$ Hz, 1H), 7.94–7.87 (m, 2H), 7.72–7.62 (m, 4H), 7.53 (t, $J = 7.9$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.34 (t, $J = 7.3$ Hz, 1H), 7.12 (t, $J = 7.4$ Hz, 1H), 6.99 (d, $J = 15.7$ Hz, 1H), 6.33–6.22 (m, 1H), 4.34 (t, $J = 9.5$ Hz, 2H), 4.02 (t, $J = 9.5$ Hz, 2H), 2.21 (q, $J = 7.3$ Hz, 2H), 1.54–1.43 (m, 2H), 0.94 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.2, 164.6, 140.1, 140.1, 139.3, 136.1, 135.5, 133.4, 132.6, 129.2, 128.8,

128.7, 127.5, 127.2, 127.0, 126.8, 126.4, 122.5, 119.8, 113.5, 66.1, 54.7, 35.3, 22.5, 13.8; HRMS (ESI-TOF) m/z Calcd for $C_{27}H_{27}N_2O_2$ $[M+H]^+$: 411.2067, found: 411.2077.



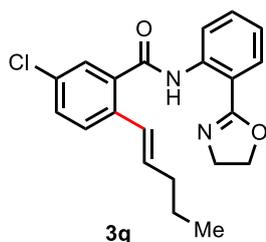
(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5-methoxy-2-(pent-1-en-1-yl)benzamide (3o)

Substrate **1o** was alkenylated with alkenyl boronates (**2**) following the general procedure A ($Cu(OPiv)_2$ (30 mol%). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3o** was obtained as a white solid (27.1 mg, 75%). mp 111–113 °C; 1H NMR (400 MHz, $CDCl_3$) δ 12.58 (s, 1H), 8.94 (d, $J = 8.4$ Hz, 1H), 7.89 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.57–7.49 (m, 2H), 7.19–7.07 (m, 2H), 6.96 (dd, $J = 8.7, 2.6$ Hz, 1H), 6.83 (d, $J = 15.7$ Hz, 1H), 6.10 (dt, $J = 15.6, 7.0$ Hz, 1H), 4.34 (t, $J = 9.4$ Hz, 2H), 4.02 (t, $J = 9.5$ Hz, 2H), 3.84 (s, 3H), 2.20–2.10 (m, 2H), 1.50–1.38 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 164.4, 158.2, 139.9, 136.2, 132.5, 131.4, 129.6, 129.2, 127.8, 126.9, 122.5, 119.8, 116.9, 113.4, 112.0, 66.1, 55.4, 54.7, 35.2, 22.6, 13.7; HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{25}N_2O_3$ $[M+H]^+$: 365.1860, found: 365.1870.



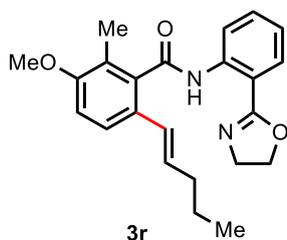
(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2-(pent-1-en-1-yl)-5-(1,1,2,2-tetrafluoroethoxy)benzamide (3p)

Substrate **1p** was alkenylated with alkenyl boronates (**2**) following the general procedure A ($Cu(OPiv)_2$ (30 mol%). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3p** was obtained as a white solid (23.6 mg, 53%). mp 84–86 °C; 1H NMR (400 MHz, $CDCl_3$) δ 12.79 (s, 1H), 8.92 (d, $J = 8.4$ Hz, 1H), 7.90 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.62 (d, $J = 8.7$ Hz, 1H), 7.57–7.50 (m, 2H), 7.26–7.24 (m, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 6.93 (d, $J = 15.8$ Hz, 1H), 6.27–6.16 (m, 1H), 5.93 (tt, $J = 53.1, 12.8$ Hz, 1H), 4.37 (t, $J = 9.6$ Hz, 2H), 4.04 (t, $J = 9.5$ Hz, 2H), 2.20 (q, $J = 7.0$ Hz, 2H), 1.53–1.42 (m, 2H), 0.93 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (150 MHz, decoupled for ^{19}F , $CDCl_3$) δ 166.8, 164.6, 147.0, 139.9, 136.2, 136.0, 134.2, 132.6, 129.2, 128.0, 126.6, 123.6, 122.8, 121.1, 119.8, 116.5, 113.6, 107.7, 66.3, 54.4, 35.2, 22.4, 13.7; ^{19}F NMR (375 MHz, $CDCl_3$) δ -88.16 – -88.22 (m, 2F), -136.78 (dt, $J_{F-F} = 53.1, 5.7$ Hz, 2F); HRMS (ESI-TOF) m/z Calcd for $C_{23}H_{23}F_4N_2O_3$ $[M+H]^+$: 451.1639, found: 451.1652.



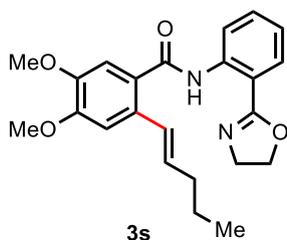
(E)-5-Chloro-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-(pent-1-en-1-yl)benzamide (3q)

Substrate **1q** was alkenylated with alkenyl boronates (**2**) following the general procedure A ($\text{Cu}(\text{OPiv})_2$ (30 mol%). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3q** was obtained as a white solid (13.3 mg, 37%). mp 134–136 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.67 (s, 1H), 8.88 (d, $J = 8.4$ Hz, 1H), 7.89 (d, $J = 7.8$ Hz, 1H), 7.62 (d, $J = 2.1$ Hz, 1H), 7.56–7.50 (m, 2H), 7.36 (dd, $J = 8.5$, 1.7 Hz, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 6.85 (d, $J = 15.7$ Hz, 1H), 6.27–6.16 (m, 1H), 4.37 (t, $J = 9.5$ Hz, 2H), 4.06 (t, $J = 9.6$ Hz, 2H), 2.20–2.14 (m, 2H), 1.50–1.42 (m, 2H), 0.92 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.9, 164.5, 139.7, 136.5, 135.5, 134.0, 132.6, 132.2, 130.2, 129.2, 127.8, 126.5, 122.7, 119.8, 113.6, 66.3, 54.6, 35.2, 22.4, 13.7; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{21}\text{H}_{22}\text{ClN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 369.1364, found: 369.1371.



(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-3-methoxy-2-methyl-6-(pent-1-en-1-yl)benzamide (3r)

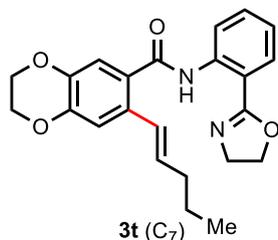
Substrate **1r** was alkenylated with alkenyl boronates (**2**) following the general procedure A ($\text{Cu}(\text{OPiv})_2$ (30 mol%), 60 °C). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3r** was obtained as a white solid (15.1 mg, 40%). mp 104–106 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.27 (s, 1H), 8.94 (d, $J = 8.4$ Hz, 1H), 7.88 (d, $J = 7.8$ Hz, 1H), 7.53 (t, $J = 7.8$ Hz, 1H), 7.37 (d, $J = 8.6$ Hz, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 6.85 (d, $J = 8.6$ Hz, 1H), 6.44 (d, $J = 15.6$ Hz, 1H), 6.13–6.01 (m, 1H), 4.30 (t, $J = 9.5$ Hz, 2H), 3.95 (t, $J = 9.5$ Hz, 2H), 3.85 (s, 3H), 2.23 (s, 3H), 2.08 (q, $J = 7.1$ Hz, 2H), 1.44–1.32 (m, 2H), 0.85 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.8, 164.1, 156.5, 139.5, 137.9, 132.4, 131.1, 129.1, 127.5, 126.8, 123.8, 122.9, 122.7, 120.2, 113.6, 110.9, 66.1, 55.6, 54.7, 35.2, 22.6, 13.6, 12.8; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{23}\text{H}_{27}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 379.2016, found: 379.2025.



(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-4,5-dimethoxy-2-(pent-1-en-1-yl)benzamide (3s)

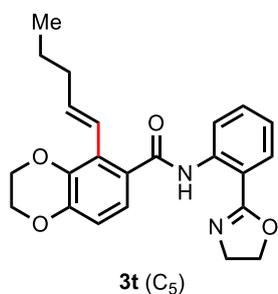
Substrate **1s** was alkenylated with alkenyl boronates (**2**) following the general procedure A ($\text{Cu}(\text{OPiv})_2$ (30 mol%), 9 h). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1),

3s was obtained as a white solid (24.0 mg, 61%). mp 126–128 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.55 (s, 1H), 8.94 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 1H), 7.22 (s, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.06 (s, 1H), 6.97 (d, *J* = 15.7 Hz, 1H), 6.18–6.07 (m, 1H), 4.36 (t, *J* = 9.5 Hz, 2H), 4.03 (t, *J* = 9.5 Hz, 2H), 3.97 (s, 3H), 3.93 (s, 3H), 2.18 (q, *J* = 7.1 Hz, 2H), 1.58–1.41 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.8, 164.6, 150.4, 147.6, 140.2, 132.6, 131.6, 131.1, 129.2, 127.6, 127.4, 122.3, 119.6, 113.3, 110.8, 108.9, 66.1, 55.9, 54.7, 35.2, 22.6, 13.8; HRMS (ESI-TOF) *m/z* Calcd for C₂₃H₂₇N₂O₄ [M+H]⁺: 395.1965, found: 395.1973.



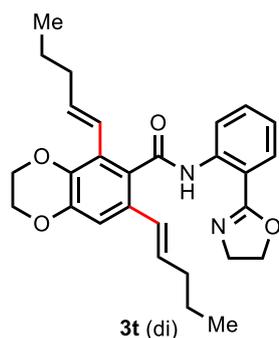
(*E*)-*N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-7-(pent-1-en-1-yl)-2,3-dihydrobenzo[*b*][1,4]dioxine-6-carboxamide (3t** (C₇))**

Substrate **1t** was alkenylated with alkenyl boronates (**2**) following the general procedure **A** (Cu(OPiv)₂ (30 mol%)). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3t** (C₇) was obtained as a white solid (9.7 mg, 25%). mp 138–140 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.49 (s, 1H), 8.89 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.19 (s, 1H), 7.14–7.06 (m, 2H), 6.85 (d, *J* = 15.6 Hz, 1H), 6.12–6.00 (m, 1H), 4.41–4.25 (m, 6H), 4.06 (t, *J* = 9.6 Hz, 2H), 2.15 (q, *J* = 7.2 Hz, 2H), 1.50–1.39 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.6, 164.4, 145.2, 142.1, 140.1, 132.5, 131.8, 131.6, 129.1, 128.7, 127.1, 122.3, 119.8, 117.1, 115.0, 113.5, 66.2, 64.5, 64.4, 54.7, 35.1, 22.6, 13.7; HRMS (ESI-TOF) *m/z* Calcd for C₂₃H₂₅N₂O₄ [M+H]⁺: 393.1809, found: 393.1817.



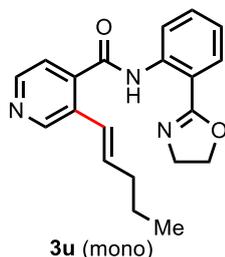
(*E*)-*N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5-(pent-1-en-1-yl)-2,3-dihydrobenzo[*b*][1,4]dioxine-6-carboxamide (3t** (C₅))**

Substrate **1t** was alkenylated with alkenyl boronates (**2**) following the general procedure **A** (Cu(OPiv)₂ (30 mol%)). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3t** (C₅) was obtained as a white solid (4.3 mg, 11%). mp 136–138 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.36 (s, 1H), 8.88 (d, *J* = 8.7 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.49 (t, *J* = 8.2 Hz, 1H), 7.13–7.07 (m, 2H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.25–6.14 (m, 1H), 4.38–4.28 (m, 6H), 4.04 (t, *J* = 9.5 Hz, 2H), 2.10 (q, *J* = 8.0 Hz, 2H), 1.36–1.31 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.7, 164.3, 144.7, 141.4, 140.1, 137.6, 132.5, 130.5, 129.1, 126.3, 122.4, 122.2, 121.1, 119.7, 115.3, 113.3, 66.1, 64.3, 64.1, 54.8, 36.0, 22.3, 13.7; HRMS (ESI-TOF) *m/z* Calcd for C₂₃H₂₅N₂O₄ [M+H]⁺: 393.1809, found: 393.1818.



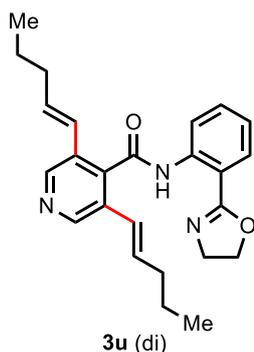
***N*-2-(4,5-Dihydrooxazol-2-yl)phenyl)-5,7-di((*E*)-pent-1-en-1-yl)-2,3-dihydrobenzo[*b*][1,4]dioxine-6-carboxamide (3t (di))**

Substrate **1t** was alkenylated with alkenyl boronates (**2**) following the general procedure **A** using $(\text{Cu}(\text{OPiv})_2$ (30 mol%). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3t** (di) was obtained as a white solid (6.4 mg, 14%). mp 58–60 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.17 (s, 1H), 8.87 (d, $J = 8.5$ Hz, 1H), 7.85 (d, $J = 7.3$ Hz, 1H), 7.51 (t, $J = 7.7$ Hz, 1H), 7.11 (t, $J = 7.5$ Hz, 1H), 6.96 (s, 1H), 6.44 (d, $J = 15.5$ Hz, 1H), 6.37 (d, $J = 16.1$ Hz, 1H), 6.30–6.18 (m, 1H), 6.11–5.99 (m, 1H), 4.35–4.25 (m, 6H), 3.96 (t, $J = 9.5$ Hz, 2H), 2.12–2.00 (m, 4H), 1.45–1.33 (m, 2H), 1.29–1.22 (m, 2H), 0.85 (t, $J = 7.4$ Hz, 3H), 0.76 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 164.0, 143.6, 140.2, 139.7, 137.0, 132.4, 131.7, 129.8, 129.0, 128.7, 126.5, 124.7, 122.5, 122.4, 120.1, 113.6, 112.2, 66.1, 64.5, 64.1, 54.8, 35.9, 35.1, 22.5, 22.3, 13.6, 13.5; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{28}\text{H}_{33}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 461.2435, found: 461.2447.



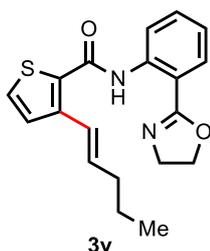
(*E*)-*N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-3-(pent-1-en-1-yl)isonicotinamide (3u (mono))

Substrate **1u** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 6/1), **3u** (mono) was obtained as a white solid (7.8 mg, 24%). mp 122–124 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.79 (s, 1H), 8.89 (d, $J = 8.4$ Hz, 1H), 8.85 (s, 1H), 8.56 (d, $J = 5.0$ Hz, 1H), 7.90 (d, $J = 7.8$ Hz, 1H), 7.54 (t, $J = 7.4$ Hz, 1H), 7.46 (d, $J = 5.0$ Hz, 1H), 7.16 (t, $J = 7.6$ Hz, 1H), 6.82 (d, $J = 15.9$ Hz, 1H), 6.37–6.26 (m, 1H), 4.37 (t, $J = 9.5$ Hz, 2H), 4.03 (t, $J = 9.5$ Hz, 2H), 2.21 (q, $J = 6.9$ Hz, 2H), 1.55–1.43 (m, 2H), 0.93 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 164.6, 148.6, 147.9, 141.2, 139.5, 135.7, 132.6, 131.5, 129.2, 124.5, 123.1, 120.9, 119.9, 113.6, 66.3, 54.5, 35.4, 22.3, 13.7; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{20}\text{H}_{22}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 336.1707, found: 336.1714.



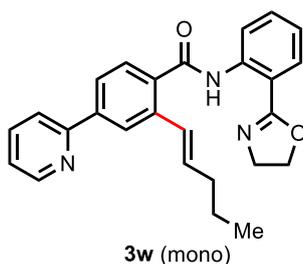
***N*-2-(4,5-Dihydrooxazol-2-yl)phenyl-3,5-di((*E*)-pent-1-en-1-yl)isonicotinamide (3u (di))**

Substrate **1u** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 6/1), **3u** (di) was obtained as a white solid (5.2 mg, 13%). mp 48–50 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.51 (s, 1H), 8.90 (d, $J = 8.4$ Hz, 1H), 8.63 (s, 2H), 7.89 (d, $J = 7.8$ Hz, 1H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.18 (t, $J = 7.3$ Hz, 1H), 6.44 (d, $J = 15.8$ Hz, 2H), 6.34–6.22 (m, 2H), 4.32 (t, $J = 9.5$ Hz, 2H), 3.92 (t, $J = 9.5$ Hz, 2H), 2.13 (q, $J = 6.9$ Hz, 4H), 1.47–1.35 (m, 4H), 0.87 (t, $J = 7.4$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.1, 164.2, 145.6, 140.1, 139.2, 135.8, 132.6, 129.6, 129.2, 123.9, 123.1, 120.2, 113.7, 66.2, 54.6, 35.3, 22.2, 13.5; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{25}\text{H}_{30}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 404.2333, found: 404.2341.



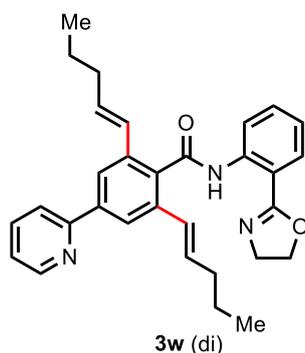
***(E)*-*N*-2-(4,5-Dihydrooxazol-2-yl)phenyl-3-(pent-1-en-1-yl)thiophene-2-carboxamide (3v)**

Substrate **1v** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **3v** was obtained as a white solid (12.5 mg, 37%). mp 53–55 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.77 (s, 1H), 8.81 (d, $J = 8.5$ Hz, 1H), 7.87 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.52–7.45 (m, 1H), 7.35–7.29 (m, 3H), 7.13–7.06 (m, 1H), 6.26 (dt, $J = 15.9, 7.0$ Hz, 1H), 4.39 (t, $J = 9.4$ Hz, 2H), 4.14 (t, $J = 9.6$ Hz, 2H), 2.26–2.18 (m, 2H), 1.55–1.44 (m, 2H), 0.95 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.6, 161.9, 143.8, 140.0, 134.8, 132.4, 130.5, 129.1, 127.3, 126.9, 123.9, 122.4, 120.1, 113.5, 66.3, 54.6, 35.3, 22.5, 13.8; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 341.1318, found: 341.1323



(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2-(pent-1-en-1-yl)-4-(pyridin-2-yl)benzamide (3w (mono))

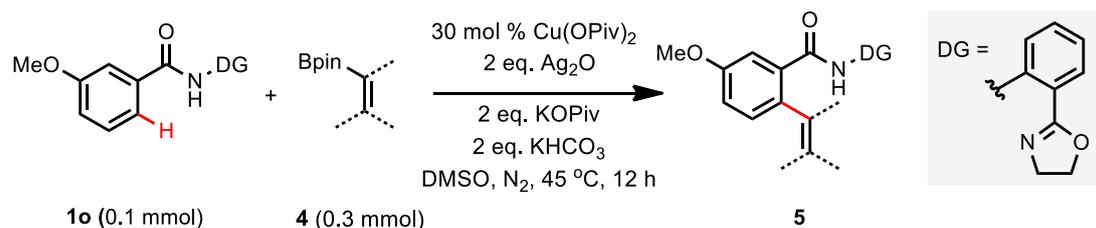
Substrate **1v** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 5/1), **3w** (mono) was obtained as a white solid (19.4 mg, 48%). mp 130–132 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.67 (s, 1H), 8.96 (d, *J* = 8.4 Hz, 1H), 8.73 (d, *J* = 4.6 Hz, 1H), 8.22 (d, *J* = 1.6 Hz, 1H), 7.89 (dt, *J* = 7.9, 1.7 Hz, 2H), 7.80–7.77 (m, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.56–7.50 (m, 1H), 7.29–7.25 (m, 1H), 7.16–7.10 (m, 1H), 6.98 (d, *J* = 15.8 Hz, 1H), 6.37 (dt, *J* = 15.7, 7.0 Hz, 1H), 4.34 (t, *J* = 9.5 Hz, 2H), 4.01 (t, *J* = 9.5 Hz, 2H), 2.25–2.17 (m, 2H), 1.54–1.44 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.2, 164.4, 156.7, 149.7, 140.9, 140.0, 137.5, 136.8, 135.6, 133.9, 132.5, 129.2, 128.3, 127.4, 125.1, 125.0, 122.5, 122.5, 120.9, 119.8, 113.5, 66.2, 54.7, 35.3, 22.5, 13.8; HRMS (ESI-TOF) *m/z* Calcd for C₂₆H₂₆N₃O₂ [M+H]⁺: 412.2020, found: 412.2029.



***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2,6-di((*E*)-pent-1-en-1-yl)-4-(pyridin-2-yl)benzamide (3w (di))**

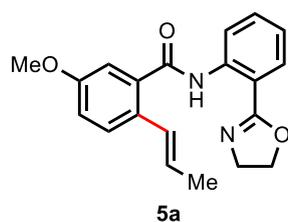
Substrate **1v** was alkenylated with alkenyl boronates (**2**) following the general procedure **A**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 5/1), **3w** (di) was obtained as a white solid (11.7 mg, 25%). mp 165–167 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.38 (s, 1H), 8.98 (d, *J* = 7.9 Hz, 1H), 8.73 (d, *J* = 4.8 Hz, 1H), 8.01 (s, 2H), 7.88 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.81–7.77 (m, 2H), 7.59–7.52 (m, 1H), 7.30–7.25 (m, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 15.7 Hz, 2H), 6.40–6.29 (m, 2H), 4.29 (t, *J* = 9.5 Hz, 2H), 3.90 (t, *J* = 9.5 Hz, 2H), 2.13 (q, *J* = 6.9 Hz, 4H), 1.47–1.35 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 168.6, 164.0, 157.3, 149.7, 139.8, 139.6, 136.8, 135.8, 135.3, 133.9, 132.4, 129.1, 126.9, 122.7, 122.6, 122.4, 121.0, 120.2, 113.7, 66.1, 54.7, 35.3, 22.4, 13.6; HRMS (ESI-TOF) *m/z* Calcd for C₃₁H₃₄N₃O₂ [M+H]⁺: 480.2646, found: 480.2663.

3.6 Evaluation of Alkenyl Boronates



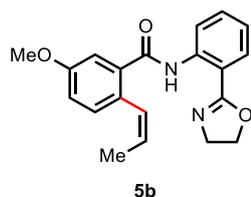
General Procedure B for C-H Alkenylation with Alkenyl Boronates:

A stirring bar, substrate **1o** (0.1 mmol), Cu(OPiv)₂ (0.03 mmol), Ag₂O (0.2 mmol), KOPiv (0.2 mmol), and KHCO₃ (0.2 mmol) were added to an oven dried 25 mL Schlenk tube. The tube was capped and back-filled with nitrogen (3 times). Under the nitrogen flow, **4** (0.3 mmol) and DMSO (2 mL) were added to the mixture, and the tube was capped tightly again. Then the reaction mixture was placed into a pre-heated oil bath and stirred at 45 °C for 12 h. After cooled to room temperature, EtOAc (20 mL) was added to quench the reaction, and organic layer was washed with NH₃·H₂O (20 mL), and the water phase was extracted by EtOAc (20 mL). The combined organic layers were washed with saturated brine, dried over Na₂SO₄, concentrated under vacuum. The crude product was purified by preparative TLC or column chromatography (neutral alumina) to afford the desired product **5**.



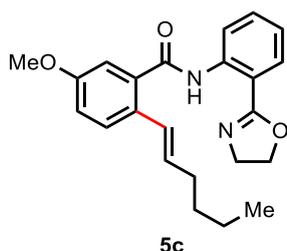
(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5-methoxy-2-(prop-1-en-1-yl)benzamide (**5a**)

Substrate **1o** was alkenylated with alkenyl boronate (**4a**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/toluene = 1/3), **5a** was obtained as a white solid (27.5 mg, 82%). mp 93–95 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.59 (s, 1H), 8.95 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.56–7.47 (m, 2H), 7.19–7.10 (m, 2H), 6.96 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.85 (d, *J* = 14.9 Hz, 1H), 6.16–6.05 (m, 1H), 4.35 (t, *J* = 9.6 Hz, 2H), 4.03 (t, *J* = 9.5 Hz, 2H), 3.84 (s, 3H), 1.85 (dd, *J* = 6.6, 1.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.1, 164.5, 158.2, 134.0, 136.0, 132.6, 129.8, 129.2, 128.2, 127.8, 126.1, 122.5, 119.8, 117.0, 113.5, 112.1, 66.2, 55.4, 54.7, 18.7; HRMS (ESI-TOF) *m/z* Calcd for C₂₀H₂₁N₂O₃ [M+H]⁺: 337.1547, found: 337.1551.



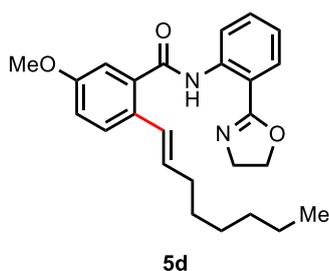
(Z)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-5-methoxy-2-(prop-1-en-1-yl)benzamide (**5b**)

Substrate **1o** was alkenylated with alkenyl boronate (**4b**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/toluene = 1/3), **5b** was obtained as a white solid (22.8 mg, 68%). mp 73–75 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.54 (s, 1H), 8.92 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.30–7.26 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.99 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.69 (d, *J* = 11.6 Hz, 1H), 5.82–5.72 (m, 1H), 4.35 (t, *J* = 9.5 Hz, 2H), 4.04 (t, *J* = 9.5 Hz, 2H), 3.86 (s, 3H), 1.79 (dd, *J* = 7.1, 1.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.9, 164.5, 158.1, 139.9, 137.5, 132.5, 131.6, 129.2, 128.6, 128.0, 126.6, 122.5, 119.9, 116.2, 113.5, 112.6, 66.1, 55.4, 54.7, 14.5; HRMS (ESI-TOF) *m/z* Calcd for C₂₀H₂₁N₂O₃ [M+H]⁺: 337.1547, found: 337.1552.



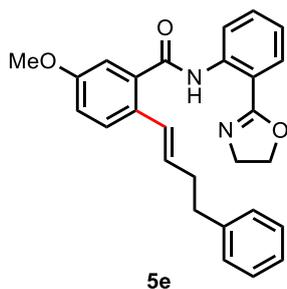
(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2-(hex-1-en-1-yl)-5-methoxybenzamide (5c)

Substrate **1o** was alkenylated with alkenyl boronate (**4c**) following the general procedure **B** (50 °C). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **5c** was obtained as a white solid (25.2 mg, 67%). mp 102–104 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.57 (s, 1H), 8.94 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 6.9 Hz, 1H), 7.52 (t, *J* = 8.3 Hz, 2H), 7.17–7.09 (m, 2H), 6.96 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.82 (d, *J* = 15.8 Hz, 1H), 6.14–6.04 (m, 1H), 4.34 (t, *J* = 9.5 Hz, 2H), 4.01 (t, *J* = 9.5 Hz, 2H), 3.83 (s, 3H), 2.17 (q, *J* = 6.9 Hz, 2H), 1.45–1.28 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.1, 164.4, 158.2, 140.0, 136.2, 132.5, 131.7, 129.6, 129.2, 127.8, 126.8, 122.5, 119.8, 116.9, 113.5, 112.1, 66.1, 55.4, 54.6, 32.8, 31.6, 22.2, 13.9; HRMS (ESI-TOF) *m/z* Calcd for C₂₃H₂₇N₂O₃ [M+H]⁺: 379.2016 found: 379.2024.



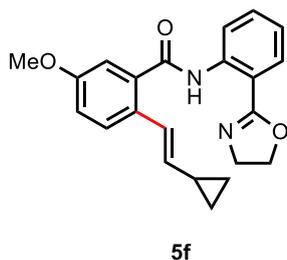
(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5-methoxy-2-(oct-1-en-1-yl)benzamide (5d)

Substrate **1o** was alkenylated with alkenyl boronate (**4d**) following the general procedure **B** (50 °C). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **5d** was obtained as a white solid (27.0 mg, 67%). mp 103–105 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.58 (s, 1H), 8.94 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 6.8 Hz, 1H), 7.56–7.49 (m, 2H), 7.18–7.08 (m, 2H), 6.96 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.82 (d, *J* = 15.6 Hz, 1H), 6.15–6.05 (m, 1H), 4.34 (t, *J* = 9.4 Hz, 2H), 4.02 (t, *J* = 9.5 Hz, 2H), 3.83 (s, 3H), 2.16 (q, *J* = 7.3 Hz, 2H), 1.47–1.36 (m, 2H), 1.35–1.20 (m, 6H), 0.86 (t, *J* = 6.7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.1, 164.4, 158.2, 140.0, 136.2, 132.5, 131.7, 129.7, 129.2, 127.8, 126.8, 122.5, 119.8, 116.9, 113.4, 112.0, 66.1, 55.4, 54.6, 33.2, 31.7, 29.4, 28.9, 22.6, 14.1; HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₃₁N₂O₃ [M+H]⁺: 407.2329, found: 407.2341.



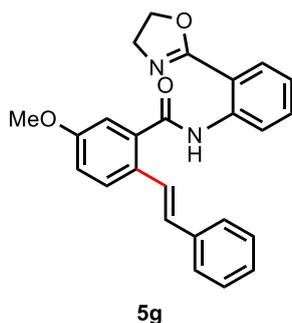
(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5-methoxy-2-(4-phenylbut-1-en-1-yl)benzamide (5e)

Substrate **1o** was alkenylated with alkenyl boronate (**4e**) following the general procedure **B** (50 °C). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **5e** was obtained as a white solid (21.7 mg, 51%). mp 88–90 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.59 (s, 1H), 8.94 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.56–7.47 (m, 2H), 7.29–7.23 (m, 2H), 7.20–7.11 (m, 5H), 6.96 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.91 (d, *J* = 15.6 Hz, 1H), 6.18–6.07 (m, 1H), 4.35 (t, *J* = 9.6 Hz, 2H), 4.02 (t, *J* = 9.5 Hz, 2H), 3.84 (s, 3H), 2.77–2.71 (m, 2H), 2.54–2.45 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 168.1, 164.5, 158.3, 141.8, 140.0, 136.3, 132.6, 130.4, 129.5, 129.2, 128.4, 128.3, 127.9, 127.5, 125.8, 122.6, 119.8, 116.9, 113.5, 112.1, 66.2, 55.4, 54.7, 35.9, 34.9; HRMS (ESI-TOF) *m/z* Calcd for C₂₇H₂₇N₂O₃ [M+H]⁺: 427.2016, found: 427.2028.



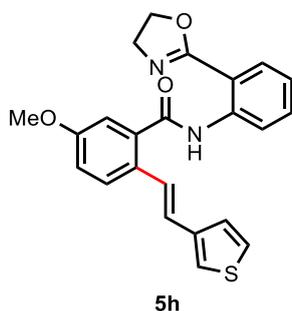
(E)-2-(2-Cyclopropylvinyl)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-5-methoxybenzamide (5f)

Substrate **1o** was alkenylated with alkenyl boronate (**4f**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/toluene = 1/3), **5f** was obtained as a white solid (19.2 mg, 53%). mp 146–148 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.59 (s, 1H), 8.95 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.17–7.09 (m, 2H), 6.96–6.90 (m, 2H), 5.58 (dd, *J* = 15.7, 9.0 Hz, 1H), 4.35 (t, *J* = 9.5 Hz, 2H), 4.03 (t, *J* = 9.5 Hz, 2H), 3.83 (s, 3H), 1.59–1.49 (m, 1H), 0.79–0.73 (m, 2H), 0.47–0.41 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 168.2, 164.5, 158.1, 140.0, 135.8, 135.3, 132.5, 129.5, 129.2, 127.4, 124.5, 122.5, 119.8, 117.0, 113.5, 112.2, 66.2, 55.4, 54.7, 14.7, 7.3; HRMS (ESI-TOF) *m/z* Calcd for C₂₂H₂₃N₂O₃ [M+H]⁺: 363.1703, found: 363.1710.



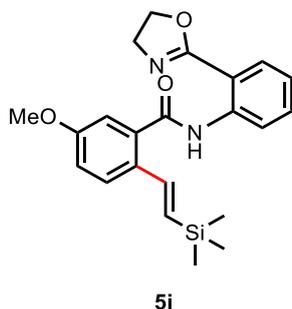
(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5-methoxy-2-styrylbenzamide (5g)

Substrate **1o** was alkenylated with alkenyl boronate (**4g**) following the general procedure **B** (50 °C). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **5g** was obtained as a white solid (18.7 mg, 47%). mp 135–137 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.69 (s, 1H), 8.98 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.4 Hz, 1H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 16.2 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.26–7.23 (m, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.04 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.98 (d, *J* = 16.2 Hz, 1H), 4.19 (t, *J* = 9.5 Hz, 2H), 3.93–3.85 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 167.8, 164.4, 158.9, 139.8, 137.6, 137.1, 132.6, 129.2, 128.8, 128.5, 127.6, 127.4, 126.5, 126.1, 122.6, 119.9, 117.3, 113.6, 112.6, 66.1, 55.5, 54.6; HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₂₃N₂O₃ [M+H]⁺: 399.1703, found: 399.1707.



(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5-methoxy-2-(2-(thiophen-3-yl)vinyl)benzamide (5h)

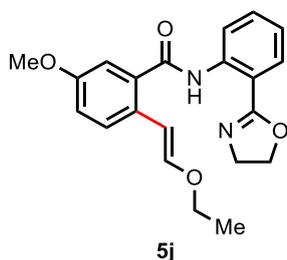
Substrate **1o** was alkenylated with alkenyl boronate (**4h**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **5h** was obtained as a white solid (21.7 mg, 54%). mp 68–70 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.67 (s, 1H), 8.97 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.54 (t, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 16.2 Hz, 1H), 7.27–7.19 (m, 4H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.05–6.97 (m, 2H), 4.22 (t, *J* = 9.5 Hz, 2H), 3.91 (t, *J* = 9.5 Hz, 2H), 3.87 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.9, 164.4, 158.8, 140.5, 139.8, 136.9, 132.6, 129.2, 128.8, 127.4, 126.2, 125.9, 125.2, 123.1, 122.7, 121.9, 119.9, 117.3, 113.6, 112.6, 66.2, 55.5, 54.6; HRMS (ESI-TOF) *m/z* Calcd for C₂₃H₂₁N₂O₃S [M+H]⁺: 405.1267, found: 405.1276.



(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5-methoxy-2-(2-(trimethylsilyl)vinyl)benzamide (5i)

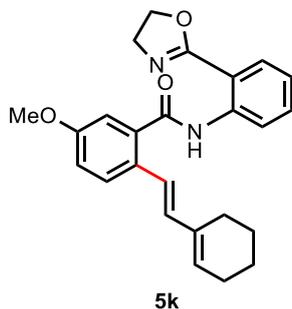
Substrate **1o** was alkenylated with alkenyl boronate (**4i**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **5i** was obtained as a white solid (12.0 mg, 31%). mp 141–143 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.59 (s, 1H), 8.94 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 1.8 Hz, 1H), 7.16 (d, *J* = 2.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.99 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.33 (d, *J* = 19.0 Hz, 1H), 4.34 (t, *J* = 9.6

Hz, 2H), 4.00 (t, $J = 9.5$ Hz, 2H), 3.86 (d, $J = 7.3$ Hz, 3H), 0.07 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.9, 164.5, 159.0, 140.7, 139.9, 137.1, 132.6, 130.2, 129.9, 129.2, 127.8, 122.5, 119.8, 116.9, 113.4, 112.1, 66.1, 55.5, 54.6, -1.3; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 395.1785, found: 395.1794.



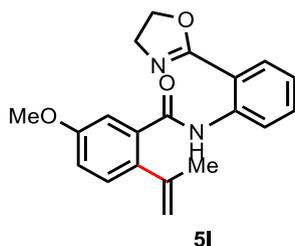
(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2-(2-ethoxyvinyl)-5-methoxybenzamide (5j)

Substrate **1o** was alkenylated with alkenyl boronate (**4j**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **5j** was obtained as a white solid (10.7 mg, 30%). mp 118–120 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.57 (s, 1H), 8.94 (d, $J = 8.4$ Hz, 1H), 7.89 (d, $J = 7.9$ Hz, 1H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.33 (d, $J = 8.7$ Hz, 1H), 7.19 (d, $J = 2.6$ Hz, 1H), 7.12 (t, $J = 7.2$ Hz, 1H), 6.94 (dd, $J = 8.5, 2.5$ Hz, 1H), 6.86 (d, $J = 12.9$ Hz, 1H), 6.33 (d, $J = 12.8$ Hz, 1H), 4.36 (t, $J = 9.5$ Hz, 2H), 4.04 (t, $J = 9.5$ Hz, 2H), 3.87–3.80 (m, 5H), 1.28 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.2, 164.4, 157.6, 148.0, 140.0, 135.6, 132.5, 129.2, 128.0, 127.1, 122.5, 119.8, 117.2, 113.5, 112.6, 103.3, 66.2, 65.0, 55.4, 54.7, 14.7; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 367.1652, found: 367.1660.



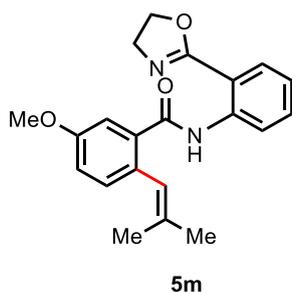
(E)-2-(2-(Cyclohex-1-en-1-yl)vinyl)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-5-methoxybenzamide (5k)

Substrate **1o** was alkenylated with alkenyl boronate (**4k**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 10/1), **5k** was obtained as a white solid (26.2 mg, 65%). mp 103–105 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.59 (s, 1H), 8.96 (d, $J = 8.4$ Hz, 1H), 7.88 (d, $J = 7.9$ Hz, 1H), 7.58 (d, $J = 8.7$ Hz, 1H), 7.53 (t, $J = 7.9$ Hz, 1H), 7.19 (d, $J = 2.7$ Hz, 1H), 7.13 (t, $J = 7.4$ Hz, 1H), 6.98 (dd, $J = 8.7, 2.6$ Hz, 1H), 6.91 (d, $J = 16.1$ Hz, 1H), 6.64 (d, $J = 16.1$ Hz, 1H), 5.85 (s, 1H), 4.33 (t, $J = 9.4$ Hz, 2H), 3.99 (t, $J = 9.5$ Hz, 2H), 3.85 (s, 3H), 2.20–2.13 (m, 4H), 1.70–1.60 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.1, 164.3, 158.3, 139.9, 136.6, 136.4, 133.0, 132.5, 130.1, 129.6, 129.2, 127.4, 122.5, 122.2, 119.9, 117.2, 113.5, 112.4, 66.2, 55.4, 54.6, 26.1, 24.6, 22.6, 22.5; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{25}\text{H}_{27}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 403.2016, found: 403.2027.



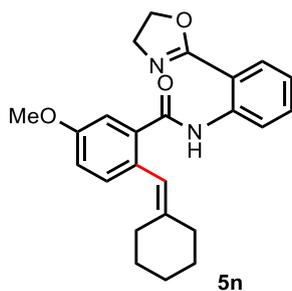
***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5-methoxy-2-(prop-1-en-2-yl)benzamide (5l)**

Substrate **1o** was alkenylated with alkenyl boronate (**4l**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **5l** was obtained as a white solid (18.2 mg, 55%). mp 101–103 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.47 (s, 1H), 8.90 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.17 (d, *J* = 2.6 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.96 (dd, *J* = 8.5, 2.7 Hz, 1H), 5.07 (s, 1H), 5.01 (s, 1H), 4.34 (t, *J* = 9.6 Hz, 2H), 4.02 (t, *J* = 9.4 Hz, 2H), 3.84 (s, 3H), 2.08 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.6, 164.3, 158.5, 144.3, 140.0, 137.0, 134.8, 132.5, 130.1, 129.2, 122.4, 119.7, 116.2, 115.0, 113.4, 112.7, 66.1, 55.4, 54.7, 23.9; HRMS (ESI-TOF) *m/z* Calcd for C₂₀H₂₁N₂O₃ [M+H]⁺: 337.1547, found: 337.1553.



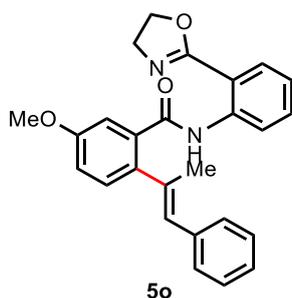
***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5-methoxy-2-(2-methylprop-1-en-1-yl)benzamide (5m)**

Substrate **1o** was alkenylated with alkenyl boronate (**4m**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **5m** was obtained as a white solid (29.0 mg, 83%). mp 72–74 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.44 (s, 1H), 8.91 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 2.7 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.97 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.46 (s, 1H), 4.33 (t, *J* = 9.5 Hz, 2H), 4.02 (t, *J* = 9.5 Hz, 2H), 3.84 (s, 3H), 1.82 (s, 3H), 1.75 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.1, 164.3, 157.7, 139.9, 137.3, 135.3, 132.5, 131.9, 129.6, 129.2, 123.0, 122.9, 122.4, 119.9, 116.3, 113.5, 112.5, 66.1, 55.3, 54.8, 26.3, 19.4; HRMS (ESI-TOF) *m/z* Calcd for C₂₁H₂₃N₂O₃ [M+H]⁺: 351.1703, found: 351.1711.



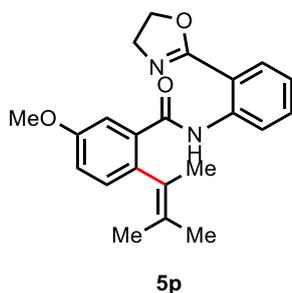
2-(Cyclohexylidenemethyl)-*N*-(2-(4,5-dihydrooxazol-2-yl)phenyl)-5-methoxybenzamide (5n)

Substrate **1o** was alkenylated with alkenyl boronate (**4n**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **5n** was obtained as a white solid (28.2 mg, 73%). mp 128–130 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.41 (s, 1H), 8.90 (d, *J* = 8.4 Hz, 1H), 7.87 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.26–7.23 (m, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.96 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.42 (s, 1H), 4.34 (t, *J* = 9.5 Hz, 2H), 4.04 (t, *J* = 9.5 Hz, 2H), 3.84 (s, 3H), 2.23–2.13 (m, 4H), 1.55–1.45 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 168.2, 164.3, 157.8, 143.3, 139.9, 137.5, 132.5, 131.9, 129.3, 129.2, 122.3, 119.9, 119.7, 116.3, 113.5, 112.5, 66.1, 55.4, 54.8, 37.3, 29.6, 28.4, 27.6, 26.6; HRMS (ESI-TOF) *m/z* Calcd for C₂₄H₂₇N₂O₃ [M+H]⁺: 391.2016, found: 391.2025.



(*E*)-*N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5-methoxy-2-(1-phenylprop-1-en-2-yl)benzamide (5o)

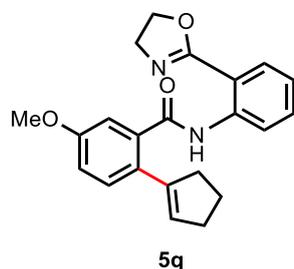
Substrate **1o** was alkenylated with alkenyl boronate (**4o**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **5o** was obtained as a white solid (25.4 mg, 62%). mp 89–90 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.51 (s, 1H), 8.93 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.30–7.22 (m, 3H), 7.23–7.15 (m, 3H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.01 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.58 (s, 1H), 4.15 (t, *J* = 9.5 Hz, 2H), 3.92–3.83 (m, 5H), 2.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.7, 164.2, 158.5, 139.9, 138.1, 137.6, 137.1, 136.7, 132.6, 130.2, 129.7, 129.2, 128.8, 128.0, 126.3, 122.5, 119.7, 116.6, 113.4, 113.0, 66.0, 55.5, 54.6, 19.7; HRMS (ESI-TOF) *m/z* Calcd for C₂₆H₂₅N₂O₃ [M+H]⁺: 413.1860, found: 413.1869.



N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5-methoxy-2-(3-methylbut-2-en-2-yl)benzamide (5p)

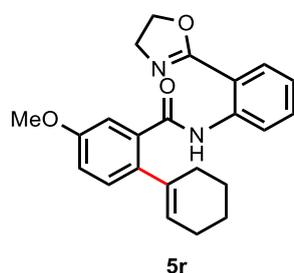
Substrate **1o** was alkenylated with alkenyl boronate (**4p**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **5p** was obtained as a white solid (18.3 mg, 51%). mp 106–108 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.18 (s, 1H), 8.79 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 2.7 Hz, 1H), 7.14–7.05 (m, 2H), 6.97 (dd, *J* = 8.4, 2.7 Hz, 1H), 4.33 (t, *J* = 9.4 Hz, 2H), 4.02 (t, *J* = 9.6 Hz, 2H), 3.84 (s, 3H), 1.95 (s, 3H), 1.70 (s, 3H), 1.53 (s,

3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 164.2, 157.7, 140.0, 137.4, 136.3, 132.4, 131.1, 129.1, 128.3, 128.0, 122.3, 120.1, 116.5, 113.6, 112.3, 66.0, 55.4, 54.8, 22.2, 21.1, 20.3; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 365.1860, found: 365.1869.



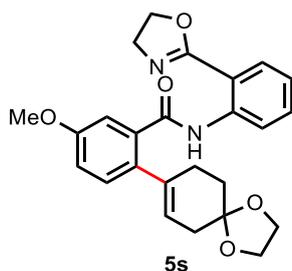
2-(Cyclopent-1-en-1-yl)-*N*-(2-(4,5-dihydrooxazol-2-yl)phenyl)-5-methoxybenzamide (**5q**)

Substrate **1o** was alkenylated with alkenyl boronate (**4q**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **5q** was obtained as a white solid (22.4 mg, 62%). mp 116–118 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.39 (s, 1H), 8.91 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H), 7.28 (d, J = 8.7 Hz, 1H), 7.14–7.08 (mz, 2H), 6.94 (dd, J = 8.6, 2.7 Hz, 1H), 5.82 (s, 1H), 4.33 (t, J = 9.5 Hz, 2H), 3.99 (t, J = 9.5 Hz, 2H), 3.83 (s, 3H), 2.62 (t, J = 6.5 Hz, 2H), 2.35 (t, J = 6.1 Hz, 2H), 1.91–1.80 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.1, 164.2, 158.3, 141.8, 139.9, 137.2, 132.5, 129.8, 129.2, 129.1, 129.0, 122.4, 119.7, 116.1, 113.4, 112.7, 66.1, 55.4, 54.7, 35.6, 33.5, 24.1; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 363.1703, found: 363.1711.



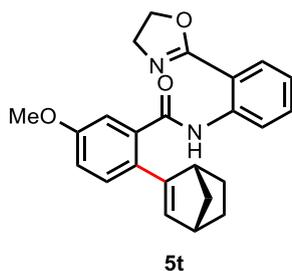
N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-4-methoxy-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-carboxamide (**5r**)

Substrate **1o** was alkenylated with alkenyl boronate (**4r**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **5r** was obtained as a white solid (16.7 mg, 45%). mp 111–113 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.28 (s, 1H), 8.90 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.19–7.15 (m, 2H), 7.10 (t, J = 7.6 Hz, 1H), 6.95 (dd, J = 8.5, 2.7 Hz, 1H), 5.74 (s, 1H), 4.33 (t, J = 9.5 Hz, 2H), 3.99 (t, J = 9.5 Hz, 2H), 3.83 (s, 3H), 2.27 (s, 2H), 2.04–1.97 (m, 2H), 1.59–1.45 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.0, 164.2, 158.1, 140.0, 137.0, 135.5, 132.5, 129.9, 129.2, 127.0, 122.3, 119.6, 116.5, 113.3, 112.8, 66.1, 55.4, 54.7, 29.9, 25.7, 23.0, 21.9; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{23}\text{H}_{25}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 377.1860, found: 377.1869.



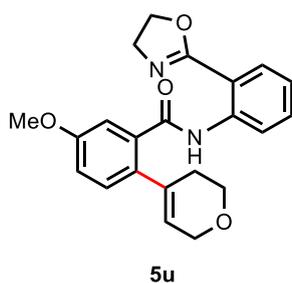
***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5-methoxy-2-(1,4-dioxaspiro[4.5]dec-7-en-8-yl)benzamide (5s)**

Substrate **1o** was alkenylated with alkenyl boronate (**4s**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 10/1), **5s** was obtained as a white solid (25.9 mg, 60%). mp 113–115 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.31 (s, 1H), 8.89 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 6.9 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 2.6 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.95 (dd, *J* = 8.5, 2.7 Hz, 1H), 5.63 (s, 1H), 4.32 (t, *J* = 9.5 Hz, 2H), 3.98 (t, *J* = 9.5 Hz, 2H), 3.87–3.82 (m, 7H), 2.55–2.45 (m, 2H), 2.25 (s, 2H), 1.71 (t, *J* = 6.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 168.8, 164.3, 158.4, 140.0, 137.0, 136.6, 134.1, 132.4, 130.0, 129.1, 124.0, 122.3, 119.5, 116.6, 113.5, 112.9, 107.4, 66.0, 64.2, 55.4, 54.7, 36.0, 31.4, 29.2; HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₂₇N₂O₅ [M+H]⁺: 435.1914, found: 435.1927.



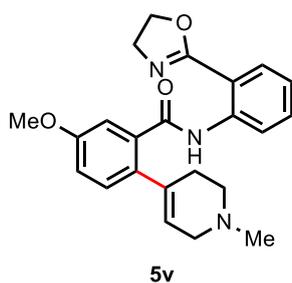
2-((1*R*,4*S*)-Bicyclo[2.2.1]hept-2-en-2-yl)-*N*-(2-(4,5-dihydrooxazol-2-yl)phenyl)-5-methoxybenzamide (5t)

Substrate **1o** was alkenylated with alkenyl boronate (**4t**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/dichloromethane = 1/1), **5t** was obtained as a white solid (28 mg, 72%). mp 88–90 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.40 (s, 1H), 8.92 (d, *J* = 8.4 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 1H), 7.14–7.07 (m, 2H), 6.93 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.03 (d, *J* = 2.8 Hz, 1H), 4.36–4.29 (m, 2H), 3.98 (t, *J* = 9.7 Hz, 2H), 3.83 (s, 3H), 3.10 (s, 1H), 2.84 (s, 1H), 1.71–1.59 (m, 2H), 1.42 (d, *J* = 8.0 Hz, 1H), 1.15–1.00 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.1, 164.1, 158.4, 146.1, 140.0, 137.5, 132.5, 131.2, 129.7, 129.2, 127.4, 122.4, 119.7, 116.1, 113.4, 112.9, 66.1, 55.4, 54.6, 47.9, 46.3, 43.2, 26.2, 24.7; HRMS (ESI-TOF) *m/z* Calcd for C₂₄H₂₅N₂O₃ [M+H]⁺: 389.1860, found: 389.1868.



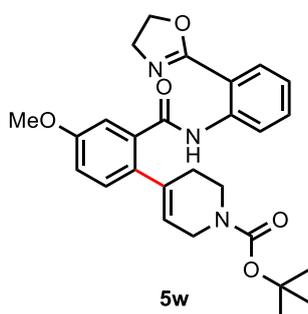
2-(3,6-Dihydro-2H-pyran-4-yl)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-5-methoxybenzamide (5u)

Substrate **1o** was alkenylated with alkenyl boronate (**4u**) following the general procedure **B**. After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 10/1), **5u** was obtained as a white solid (26.3 mg, 70%). mp 115–117 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.45 (s, 1H), 8.88 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.23–7.18 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.98 (dd, *J* = 8.5, 2.7 Hz, 1H), 5.75 (s, 1H), 4.35 (t, *J* = 9.5 Hz, 2H), 4.17 (d, *J* = 2.4 Hz, 2H), 4.00 (t, *J* = 9.5 Hz, 2H), 3.84 (s, 3H), 3.76 (t, *J* = 5.3 Hz, 2H), 2.40 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 168.5, 164.4, 158.6, 139.8, 136.9, 135.0, 133.5, 132.6, 130.0, 129.3, 124.6, 122.5, 119.6, 116.5, 113.3, 113.0, 66.1, 65.7, 64.4, 55.4, 54.7, 29.7; HRMS (ESI-TOF) *m/z* Calcd for C₂₂H₂₃N₂O₄ [M+H]⁺: 379.1652, found: 379.1662.



N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5-methoxy-2-(1-methyl-1,2,3,6-tetrahydropyridin-4-yl)benzamide (5v)

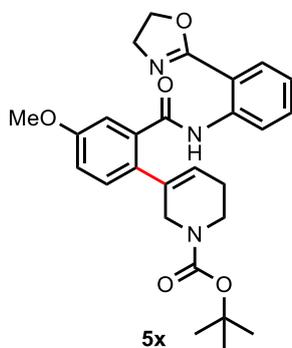
Substrate **1o** was alkenylated with alkenyl boronate (**4v**) following the general procedure **B**. After purification by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 1/1), **5v** was obtained as a white solid (25.6 mg, 66%). mp 117–119 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.41 (s, 1H), 8.89 (d, *J* = 8.5 Hz, 1H), 7.89 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 2.7 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.96 (dd, *J* = 8.5, 2.7 Hz, 1H), 5.69 (s, 1H), 4.35 (t, *J* = 9.5 Hz, 2H), 4.01 (t, *J* = 9.5 Hz, 2H), 3.84 (s, 3H), 2.98–2.95 (m, 2H), 2.52–2.44 (m, 4H), 2.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.5, 164.4, 158.4, 140.0, 136.9, 135.5, 134.1, 132.6, 130.3, 129.2, 124.0, 122.5, 119.7, 116.5, 113.4, 112.9, 66.1, 55.4, 54.8, 54.7, 52.2, 45.6, 30.6; HRMS (ESI-TOF) *m/z* Calcd for C₂₃H₂₆N₃O₃ [M+H]⁺: 392.1969, found: 392.1978.



tert-Butyl 4-(2-((2-(4,5-dihydrooxazol-2-yl)phenyl)carbamoyl)-4-methoxyphenyl)-5,6-dihydropyridine-1(2H)-carboxylate (5w)

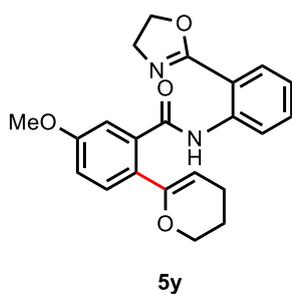
Substrate **1o** was alkenylated with alkenyl boronate (**4w**) following the general procedure **B**. After purification by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 5/1), **5w** was obtained as a white solid (38.4 mg, 81%), rotameric mixture. mp 173–175 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.45 (s, 0.5H), 12.40 (s, 0.5H), 8.88 (d, *J* = 8.4 Hz, 1H), 7.88 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.22–7.16 (m, 2H),

7.11 (t, $J = 7.3$ Hz, 1H), 6.97 (dd, $J = 8.5, 2.7$ Hz, 1H), 5.68 (brs, 1H), 4.35 (t, $J = 9.5$ Hz, 2H), 4.00 (t, $J = 9.5$ Hz, 2H), 3.96–3.86 (m, 2H), 3.84 (s, 3H), 3.52–3.38 (m, 2H), 2.50–2.30 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.5, 164.4, 158.6, 154.8, 139.8, 137.0, 136.7, 136.1, 135.8, 133.7, 133.5, 132.6, 130.4, 129.8, 129.3, 123.0, 122.8, 122.5, 119.6, 116.6, 113.3, 113.0, 79.5, 66.1, 55.4, 54.6, 43.9, 43.2, 41.1, 39.8, 30.0, 29.7, 28.4; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{27}\text{H}_{32}\text{N}_3\text{O}_5$ $[\text{M}+\text{H}]^+$: 478.2336, found: 478.2349.



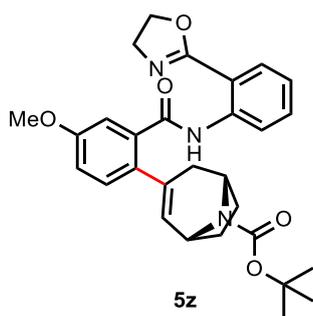
tert-Butyl 3-(2-((2-(4,5-dihydrooxazol-2-yl)phenyl)carbamoyl)-4-methoxyphenyl)-5,6-dihydropyridine-1(2H)-carboxylate (5x)

Substrate **1o** was alkenylated with alkenyl boronate (**4x**) following the general procedure **B**. After purification by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 5/1), **5x** was obtained as a white solid (38.2 mg, 80%), rotameric mixture. mp 117–119 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.39 (s, 1H), 8.89 (d, $J = 8.2$ Hz, 1H), 7.87 (d, $J = 7.9$ Hz, 1H), 7.50 (t, $J = 7.8$ Hz, 1H), 7.26–7.15 (m, 2H), 7.10 (t, $J = 7.6$ Hz, 1H), 6.98 (d, $J = 8.3$ Hz, 1H), 5.84 (s, 1H), 4.34 (t, $J = 9.5$ Hz, 2H), 4.25–4.05 (m, 2H), 4.02 (t, $J = 9.3$ Hz, 2H), 3.84 (s, 3H), 3.37 (s, 2H), 2.13 (brs, 2H), 1.41 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.3, 164.5, 158.9, 154.9, 140.0, 138.0, 135.1, 132.5, 131.6, 130.3, 129.2, 124.9, 122.4, 119.8, 116.4, 113.4, 113.1, 79.5, 66.1, 55.4, 54.7, 46.7, 39.6, 28.4, 25.4; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{27}\text{H}_{31}\text{N}_3\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 500.2156, found: 500.2155.



2-(3,4-Dihydro-2H-pyran-6-yl)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-5-methoxybenzamide (5y)

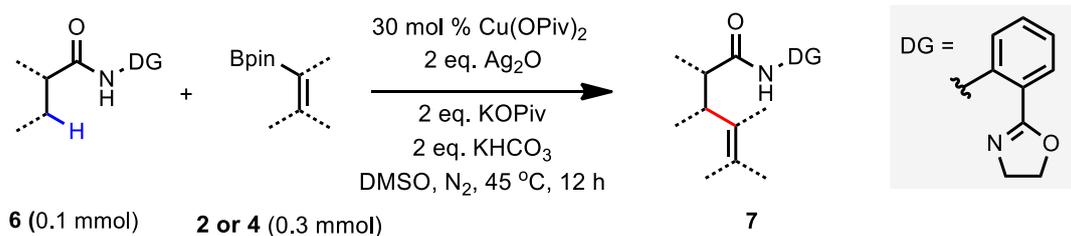
Substrate **1o** was alkenylated with alkenyl boronate (**4y**) following the general procedure **B**. After purification by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 10/1), **5y** was obtained as a white solid (24.2 mg, 65%). mp 127–129 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.38 (s, 1H), 8.93 (d, $J = 8.4$ Hz, 1H), 7.86 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.50 (t, $J = 7.2$ Hz, 1H), 7.37 (d, $J = 8.5$ Hz, 1H), 7.13 (d, $J = 2.6$ Hz, 1H), 7.09 (t, $J = 8.0$ Hz, 1H), 6.92 (dd, $J = 8.5, 2.7$ Hz, 1H), 5.04 (t, $J = 3.8$ Hz, 1H), 4.33 (t, $J = 9.5$ Hz, 2H), 4.01 (t, $J = 9.5$ Hz, 2H), 3.92–3.86 (m, 2H), 3.83 (s, 3H), 2.12–2.05 (m, 2H), 1.80–1.71 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.7, 164.1, 159.3, 152.1, 140.2, 137.5, 132.5, 129.9, 129.0, 128.3, 122.1, 119.6, 115.8, 113.2, 112.7, 99.9, 66.5, 66.1, 55.4, 54.7, 22.1, 20.9; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 379.1652, found: 379.1652.



(1*R*,5*S*)-*tert*-Butyl 3-(2-((2-(4,5-dihydrooxazol-2-yl)phenyl)carbamoyl)-4-methoxyphen-yl)-8-azabicyclo [3.2.1]oct-2-ene-8-carboxylate (5z)

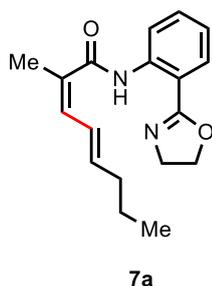
Substrate **1o** was alkenylated with alkenyl boronate (**4z**) following the general procedure **B**. After purification by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 10/1), **5z** was obtained as a white solid (38.8 mg, 77%), rotameric mixture. mp 123–125 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.43 (s, 0.5H), 12.38 (s, 0.5H), 8.89 (d, *J* = 8.4 Hz, 1H), 7.88 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.16–7.07 (m, 3H), 6.93 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.01 (s, 1H), 4.45–4.18 (m, 4H), 4.01 (t, *J* = 9.6 Hz, 2H), 3.83 (s, 3H), 3.18–2.83 (m, 1H), 2.10 (d, *J* = 17.2 Hz, 1H), 2.00–1.80 (m, 2H), 1.73–1.55 (m, 2H), 1.42 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 168.6, 168.4, 164.4, 158.5, 154.0, 139.8, 137.5, 137.4, 134.7, 134.6, 132.9, 132.6, 131.1, 130.8, 130.2, 129.5, 129.3, 122.5, 119.5, 116.2, 113.2, 112.6, 79.1, 66.1, 55.4, 54.6, 53.5, 52.8, 52.6, 51.8, 38.5, 37.8, 34.6, 34.0, 29.5, 28.8, 28.3; HRMS (ESI-TOF) *m/z* Calcd for C₂₉H₃₄N₃O₅ [M+H]⁺: 504.2493, found: 504.2509.

3.7 Evaluation of Alkene-Alkene Coupling



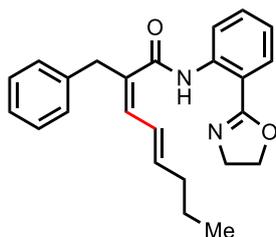
General Procedure C for Alkene-Alkene Coupling:

A stirring bar, substrate **6** (0.1 mmol), Cu(OPiv)₂ (0.03 mmol), Ag₂O (0.2 mmol), KOPiv (0.2 mmol), and KHCO₃ (0.2 mmol) were added to an oven dried 25 mL Schlenk tube. The tube was capped and back-filled with nitrogen (3 times). Under the nitrogen flow, **2** or **4** (0.3 mmol) and DMSO (2 mL) were added to the mixture, and the tube was capped tightly again. Then the reaction mixture was placed into a pre-heated oil bath and stirred at 45 °C. Upon completion (monitored by TLC), the reaction mixture was cooled to room temperature. EtOAc (20 mL) was added to quench the reaction, and organic layer was washed with NH₃·H₂O (20 mL), and the water phase was extracted by EtOAc (20 mL). The combined organic layers were washed with saturated brine, dried over Na₂SO₄, concentrated under vacuum. The crude product was purified by preparative TLC or column chromatography (neutral alumina) to afford the desired product **7**.



(2Z,4E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2-methylocta-2,4-dienamide (**7a**)

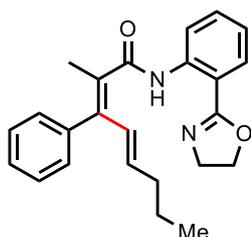
Substrate **6a** was alkenylated with alkenyl boronate (**2**) following the general procedure **C** (6 h). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **7a** was obtained as a white solid (15.0 mg, 51%). mp 87–89 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.29 (s, 1H), 8.87 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.99–6.90 (m, 1H), 6.27 (d, *J* = 11.2 Hz, 1H), 5.89–5.76 (m, 1H), 4.37 (t, *J* = 9.5 Hz, 2H), 4.09 (t, *J* = 9.5 Hz, 2H), 2.14–2.04 (m, 5H), 1.48–1.36 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.1, 164.5, 140.0, 139.3, 136.4, 132.4, 129.2, 129.1, 127.5, 122.2, 120.0, 113.4, 66.1, 54.6, 34.9, 22.4, 21.2, 13.7; HRMS (ESI-TOF) *m/z* Calcd for C₁₈H₂₃N₂O₂ [M+H]⁺: 299.1754, found: 299.1758.



7b

(2Z,4E)-2-Benzyl-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)octa-2,4-dienamide (7b)

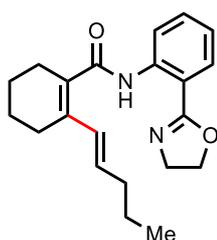
Substrate **6b** was alkenylated with alkenyl boronate (**2**) following the general procedure **C** (3 h). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **7b** was obtained as a white solid (14.6 mg, 40%). mp 67–69 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.36 (s, 1H), 8.81 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.29–7.24 (m, 4H), 7.21–7.14 (m, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.82–6.72 (m, 1H), 6.15 (d, *J* = 11.2 Hz, 1H), 5.87–5.76 (m, 1H), 4.34 (t, *J* = 9.5 Hz, 2H), 4.04 (t, *J* = 9.5 Hz, 2H), 3.80 (s, 2H), 2.07 (q, *J* = 7.3 Hz, 2H), 1.46–1.33 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.7, 164.3, 139.8, 139.5, 138.9, 135.3, 134.1, 132.4, 129.1, 128.9, 128.4, 127.2, 126.2, 122.3, 120.0, 113.3, 66.1, 54.6, 40.5, 34.9, 22.4, 13.7; HRMS (ESI-TOF) *m/z* Calcd for C₂₄H₂₆N₂O₂Na [M+Na]⁺: 397.1886, found: 397.1881.



7c

(2E,4E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2-methyl-3-phenylocta-2,4-dienamide (7c)

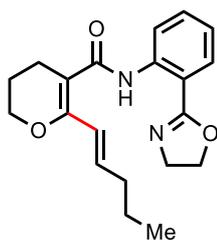
Substrate **6c** was alkenylated with alkenyl boronate (**2**) following the general procedure **C** (6 h). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **7c** was obtained as a white solid (24.5 mg, 66%). mp 83–85 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.45 (s, 1H), 8.90 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.0 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 15.4 Hz, 1H), 5.24–5.15 (m, 1H), 4.37 (t, *J* = 9.4 Hz, 2H), 4.08 (t, *J* = 9.6 Hz, 2H), 1.98 (q, *J* = 7.1 Hz, 2H), 1.84 (s, 3H), 1.33–1.19 (m, 2H), 0.78 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 164.5, 141.8, 139.9, 139.2, 136.8, 132.5, 130.2, 130.1, 129.3, 129.2, 128.1, 126.9, 122.3, 119.9, 113.4, 66.2, 54.6, 35.1, 22.3, 18.2, 13.6; HRMS (ESI-TOF) *m/z* Calcd for C₂₄H₂₇N₂O₂ [M+H]⁺: 375.2067, found: 375.2076.



7d

(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2-(pent-1-en-1-yl)cyclohex-1-enecarboxamide (7d)

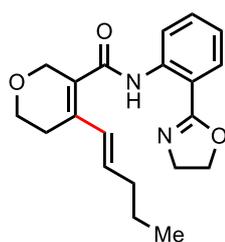
Substrate **6d** was alkenylated with alkenyl boronate (**2**) following the general procedure **C** (12 h). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 30/1), **7d** was obtained as a white solid (19.1 mg, 57%). mp 124–126 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.16 (s, 1H), 8.86 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 15.5 Hz, 1H), 5.83–5.73 (m, 1H), 4.35 (t, *J* = 9.5 Hz, 2H), 4.07 (t, *J* = 9.5 Hz, 2H), 2.47 (s, 2H), 2.30 (s, 2H), 2.09–2.00 (m, 2H), 1.78–1.68 (m, 4H), 1.42–1.32 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.5, 164.3, 139.9, 135.3, 132.4, 132.3, 130.7, 129.2, 129.1, 122.2, 119.9, 113.3, 66.1, 54.7, 35.2, 27.8, 25.4, 22.7, 22.4, 22.2, 13.7; HRMS (ESI-TOF) *m/z* Calcd for C₂₁H₂₇N₂O₂ [M+H]⁺: 339.2067, found: 339.2075.



7e

(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-6-(pent-1-en-1-yl)-3,4-dihydro-2H-pyran-5-carboxamide (7e)

Substrate **6e** was alkenylated with alkenyl boronate (**2**) following the general procedure **C** (3 h). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 15/1), **7e** was obtained as a white solid (14.8 mg, 44%). mp 101–103 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.10 (s, 1H), 8.83 (d, *J* = 8.4 Hz, 1H), 7.85 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 15.4 Hz, 1H), 6.37–6.24 (m, 1H), 4.37 (t, *J* = 9.5 Hz, 2H), 4.14–4.06 (m, 4H), 2.56 (t, *J* = 6.5 Hz, 2H), 2.12 (q, *J* = 7.2 Hz, 2H), 2.01–1.91 (m, 2H), 1.48–1.38 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.4, 164.5, 156.4, 140.4, 134.9, 132.4, 129.1, 123.8, 121.8, 119.9, 113.2, 107.1, 66.1, 65.9, 54.7, 34.9, 22.8, 22.3, 22.0, 13.8; HRMS (ESI-TOF) *m/z* Calcd for C₂₀H₂₄N₂O₃Na [M+Na]⁺: 363.1679, found: 363.1687.

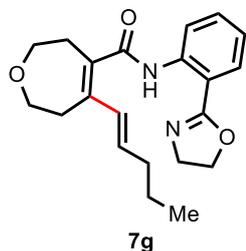


7f

(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-4-(pent-1-en-1-yl)-5,6-dihydro-2H-pyran-3-carboxamide (7f)

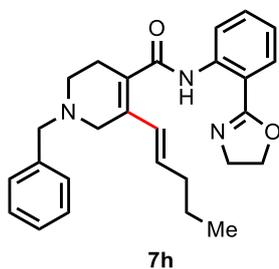
Substrate **6f** was alkenylated with alkenyl boronate (**2**) following the general procedure **C** (6 h). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 15/1), **7f** was obtained as a white solid (14.4 mg, 43%). mp 95–97 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.33 (s, 1H), 8.83 (d, *J* = 8.4 Hz, 1H), 7.87 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 15.6 Hz, 1H), 5.93–5.77 (m, 1H), 4.52 (s, 2H), 4.36 (t, *J* = 9.5 Hz, 2H), 4.07 (t, *J* = 9.5 Hz, 2H), 3.88 (t, *J* = 5.6 Hz, 2H), 2.44–2.38 (m, 2H), 2.09 (q, *J* = 7.2 Hz, 2H), 1.46–1.34 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.6, 164.4, 139.6, 134.4, 132.6, 132.5, 130.2, 129.2, 127.9, 122.5, 120.0, 113.4, 66.3, 66.2, 64.2,

54.6, 35.1, 25.2, 22.5, 13.7; HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{24}N_2O_3Na$ $[M+Na]^+$: 363.1679, found: 363.1677.



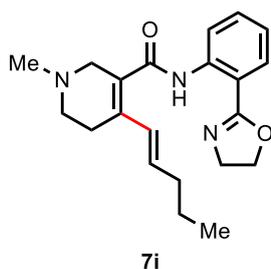
(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-5-(pent-1-en-1-yl)-2,3,6,7-tetrahydrooxepine-4-carboxamide (7g)

Substrate **6g** was alkenylated with alkenyl boronate (**2**) following the general procedure **C** (6 h). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 10/1), **7g** was obtained as a white solid (10.5 mg, 30%). mp 97–99 °C; 1H NMR (400 MHz, $CDCl_3$) δ 12.27 (s, 1H), 8.82 (d, J = 8.4 Hz, 1H), 7.86 (dd, J = 7.9, 1.3 Hz, 1H), 7.49 (t, J = 7.9 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.54 (d, J = 15.6 Hz, 1H), 5.85–5.72 (m, 1H), 4.37 (t, J = 9.5 Hz, 2H), 4.06 (t, J = 9.4 Hz, 2H), 3.83–3.79 (m, 2H), 3.78–3.71 (m, 2H), 2.83–2.76 (m, 2H), 2.74–2.68 (m, 2H), 2.06 (q, J = 7.4 Hz, 2H), 1.41–1.31 (m, 2H), 0.86 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 164.5, 141.7, 139.9, 136.2, 132.5, 132.5, 129.2, 129.0, 122.3, 119.7, 113.3, 69.3, 68.5, 66.2, 54.6, 35.2, 34.9, 32.4, 22.6, 13.7; HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{26}N_2O_3Na$ $[M+Na]^+$: 377.1836, found: 377.1842.



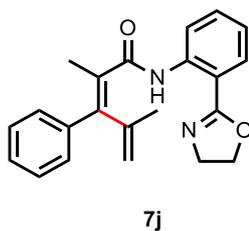
(E)-1-Benzyl-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-5-(pent-1-en-1-yl)-1,2,3,6-tetrahydropyridine-4-carboxamide (7h)

Substrate **6h** was alkenylated with alkenyl boronate (**2**) following the general procedure **C** (6 h). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 10/1), **7h** was obtained as a white solid (27.3 mg, 64%). mp 85–87 °C; 1H NMR (400 MHz, $CDCl_3$) δ 12.25 (s, 1H), 8.86 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.3 Hz, 1H), 7.42–7.32 (m, 4H), 7.31–7.25 (m, 1H), 7.08 (t, J = 7.6 Hz, 1H), 6.65 (d, J = 15.8 Hz, 1H), 5.75–5.62 (m, 1H), 4.34 (t, J = 9.5 Hz, 2H), 4.06 (t, J = 9.5 Hz, 2H), 3.68 (s, 2H), 3.30 (s, 2H), 2.68–2.58 (m, 4H), 2.03 (q, J = 7.1 Hz, 2H), 1.42–1.29 (m, 2H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 164.3, 139.8, 138.0, 134.6, 132.4, 131.1, 129.7, 129.2, 129.1, 128.3, 127.1, 127.0, 122.3, 120.0, 113.4, 66.1, 62.5, 54.7, 53.2, 49.1, 35.3, 27.9, 22.5, 13.7; HRMS (ESI-TOF) m/z Calcd for $C_{27}H_{32}N_3O_2$ $[M+H]^+$: 430.2489, found: 430.2492.



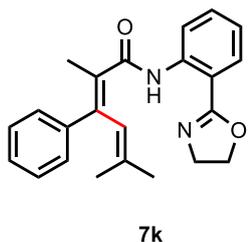
(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-1-methyl-4-(pent-1-en-1-yl)-1,2,5,6-tetrahydropyridine-3-carboxamide (7i)

Substrate **6i** was alkenylated with alkenyl boronate (**2**) following the general procedure **C** (6 h). After purification by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 1/1), **7i** was obtained as a white solid (27.6 mg, 78%). mp 111–113 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.32 (s, 1H), 8.85 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 15.8 Hz, 1H), 5.89–5.78 (m, 1H), 4.35 (t, *J* = 9.4 Hz, 2H), 4.04 (t, *J* = 9.5 Hz, 2H), 3.35 (s, 2H), 2.65–2.60 (m, 2H), 2.50–2.44 (m, 2H), 2.42 (s, 3H), 2.10–2.00 (m, 2H), 1.44–1.31 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.9, 164.3, 139.7, 134.2, 132.4, 132.1, 129.7, 129.1, 128.2, 122.4, 119.9, 113.4, 66.1, 55.9, 54.6, 51.5, 45.5, 35.1, 26.3, 22.6, 13.7; HRMS (ESI-TOF) *m/z* Calcd for C₂₁H₂₇N₃O₂Na [M+Na]⁺: 376.1995, found: 376.1994.



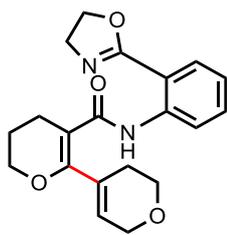
(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2,4-dimethyl-3-phenylpenta-2,4-dienamide (7j)

Substrate **6c** was alkenylated with alkenyl boronate (**4i**) following the general procedure **C** (6 h). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **7j** was obtained as a white solid (10.4 mg, 30%). mp 117–119 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.23 (s, 1H), 8.83 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.34–7.23 (m, 3H), 7.08 (t, *J* = 7.6 Hz, 1H), 5.13 (s, 1H), 4.92 (s, 1H), 4.37 (t, *J* = 9.5 Hz, 2H), 4.11 (t, *J* = 9.4 Hz, 2H), 1.96 (s, 3H), 1.68 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.3, 164.5, 145.2, 144.4, 140.3, 138.7, 132.6, 131.6, 129.2, 128.9, 128.2, 127.4, 122.1, 119.6, 116.1, 113.1, 66.1, 54.7, 22.0, 17.9; HRMS (ESI-TOF) *m/z* Calcd for C₂₂H₂₂N₂O₂Na [M+Na]⁺: 369.1573, found: 369.1576.



(E)-N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-2,5-dimethyl-3-phenylhexa-2,4-dienamide (7k)

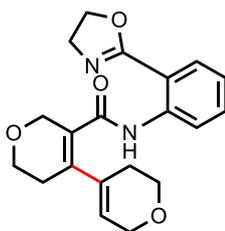
Substrate **6c** was alkenylated with alkenyl boronate (**4m**) following the general procedure **C** (6 h). After purification by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 20/1), **7k** was obtained as a white solid (23.1 mg, 64%). mp 82–84 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.28 (s, 1H), 8.87 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.32–7.22 (m, 3H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.04 (s, 1H), 4.36 (t, *J* = 9.5 Hz, 2H), 4.07 (t, *J* = 9.5 Hz, 2H), 2.01 (s, 3H), 1.65 (s, 3H), 1.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.8, 164.3, 141.0, 140.1, 140.0, 137.3, 132.5, 132.3, 129.1, 128.1, 127.0, 125.2, 122.1, 119.7, 113.3, 66.1, 54.7, 26.4, 19.7, 17.8; HRMS (ESI-TOF) *m/z* Calcd for C₂₃H₂₄N₂O₂Na [M+Na]⁺: 383.1730, found: 383.1716.



7l

***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-3',5,6,6'-tetrahydro-2'*H*,4*H*-[2,4'-bipyran]-3-carboxamide (7l)**

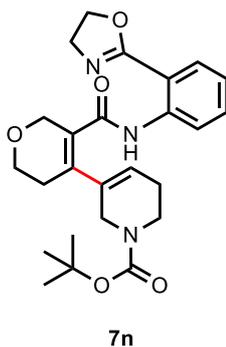
Substrate **6e** was alkenylated with alkenyl boronate (**4u**) following the general procedure **C** (3 h). After purification by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 10/1), **7l** was obtained as a white solid (22.8 mg, 64%). mp 99–101 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.98 (s, 1H), 8.76 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.00 (s, 1H), 4.37 (t, *J* = 9.5 Hz, 2H), 4.14–4.00 (m, 6H), 3.69 (t, *J* = 5.3 Hz, 2H), 2.50 (t, *J* = 6.5 Hz, 2H), 2.33 (s, 2H), 1.97–1.86 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 169.4, 164.5, 157.0, 140.2, 132.5, 131.4, 129.3, 128.3, 121.9, 119.4, 113.0, 109.0, 66.4, 66.0, 65.3, 64.0, 54.8, 26.6, 22.7, 21.9; HRMS (ESI-TOF) *m/z* Calcd for C₂₀H₂₂N₂O₄Na [M+Na]⁺: 377.1472, found: 377.1471.



7m

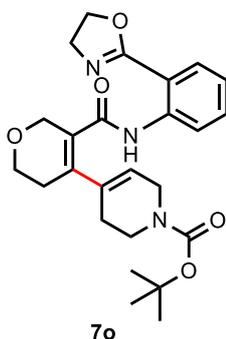
***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-3',5,6,6'-tetrahydro-2*H*,2'*H*-[4,4'-bipyran]-3-carboxamide (7m)**

Substrate **6f** was alkenylated with alkenyl boronate (**4u**) following the general procedure **C** (4.5 h). After purification by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 10/1), **7m** was obtained as a white solid (17.3 mg, 49%). mp 95–97 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.10 (s, 1H), 8.74 (d, *J* = 8.4 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 5.74 (s, 1H), 4.45 (s, 2H), 4.37 (t, *J* = 9.4 Hz, 2H), 4.10–4.01 (m, 4H), 3.87 (t, *J* = 5.5 Hz, 2H), 3.68 (t, *J* = 5.4 Hz, 2H), 2.35–2.29 (m, 2H), 2.28–2.23 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 167.5, 164.5, 139.6, 137.4, 134.6, 132.6, 130.8, 129.3, 124.4, 122.5, 119.6, 113.2, 66.2, 66.1, 65.4, 64.2, 64.0, 54.7, 27.8, 27.2; HRMS (ESI-TOF) *m/z* Calcd for C₂₀H₂₂N₂O₄Na [M+Na]⁺: 377.1472, found: 377.1469.



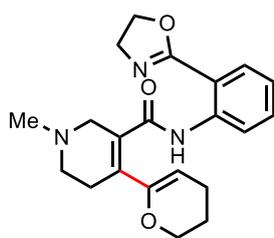
***tert*-Butyl 3-(5-((2-(4,5-dihydrooxazol-2-yl)phenyl)carbamoyl)-3,6-dihydro-2*H*-pyran-4-yl)-5,6-dihydro-pyridine-1(2*H*)-carboxylate (7n)**

Substrate **6f** was alkenylated with alkenyl boronate (**4x**) following the general procedure **C** (4.5 h). After purification by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 10/1), **7n** was obtained as a white solid (32.0 mg, 71%), rotameric mixture. mp 73–75 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.11 (s, 1H), 8.75 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 5.86 (s, 1H), 4.46 (s, 2H), 4.36 (t, *J* = 9.4 Hz, 2H), 4.11 (brs, 2H), 3.99 (brs, 2H), 3.87 (t, *J* = 5.4 Hz, 2H), 3.26 (s, 2H), 2.32 (s, 2H), 2.00 (brs, 2H), 1.42 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 167.5, 167.0, 164.2, 154.8, 139.6, 136.2, 135.0, 132.5, 132.2, 129.2, 124.3, 122.4, 119.5, 113.0, 79.6, 66.1, 64.1, 54.6, 44.7, 43.9, 40.3, 39.0, 28.8, 28.4, 27.9, 25.1; HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₃₁N₃O₅Na [M+Na]⁺: 476.2156, found: 476.2155.



***tert*-Butyl 4-(5-((2-(4,5-dihydrooxazol-2-yl)phenyl)carbamoyl)-3,6-dihydro-2*H*-pyran-4-yl)-5,6-dihydro-pyridine-1(2*H*)-carboxylate (7o)**

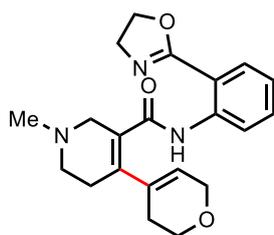
Substrate **6f** was alkenylated with alkenyl boronate (**4w**) following the general procedure **C** (6 h). After purification by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 10/1), **7o** was obtained as a white solid (23.3 mg, 52%), rotameric mixture. mp 73–75 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.06 (brs, 1H), 8.75 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 5.67 (brs, 1H), 4.45 (s, 2H), 4.37 (t, *J* = 9.5 Hz, 2H), 4.07 (t, *J* = 9.4 Hz, 2H), 3.87 (t, *J* = 5.5 Hz, 2H), 3.84–3.70 (s, 2H), 3.40 (brs, 2H), 2.36–2.18 (m, 4H), 1.38 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 167.5, 164.4, 154.7, 139.6, 137.9, 135.6, 132.6, 130.8, 129.3, 122.9, 122.4, 119.5, 113.0, 79.6, 66.1, 66.1, 64.1, 54.7, 43.6, 42.9, 40.7, 39.2, 28.3, 27.6, 27.0; HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₃₁N₃O₅Na [M+Na]⁺: 476.2156, found: 476.2158.



7p

4-(3,4-Dihydro-2H-pyran-6-yl)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-1-methyl-1,2,5,6-tetrahydropyridine-3-carboxamide (7p)

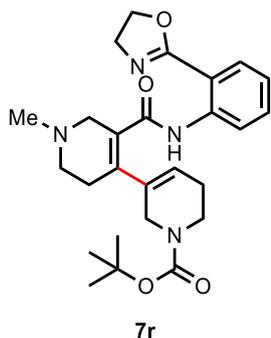
Substrate **6i** was alkenylated with alkenyl boronate (**4y**) following the general procedure **C** (5 h). After purification by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 1.5/1), **7p** was obtained as a white solid (24.3 mg, 67%). mp 68–70 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.07 (s, 1H), 8.78 (d, *J* = 8.6 Hz, 1H), 7.83 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 4.90 (t, *J* = 3.9 Hz, 1H), 4.35 (t, *J* = 9.5 Hz, 2H), 4.07 (t, *J* = 9.5 Hz, 2H), 3.74 (t, *J* = 8.0 Hz, 2H), 3.30 (s, 2H), 2.60 (t, *J* = 5.7 Hz, 2H), 2.43–2.37 (m, 5H), 2.00–1.92 (m, 2H), 1.69–1.60 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 169.4, 164.0, 151.7, 140.0, 132.4, 131.3, 130.5, 129.0, 121.9, 119.7, 113.0, 100.0, 66.1, 65.9, 55.7, 54.7, 51.5, 45.3, 27.3, 22.0, 20.7; HRMS (ESI-TOF) *m/z* Calcd for C₂₁H₂₆N₃O₃ [M+H]⁺: 368.1969, found: 368.1966.



7q

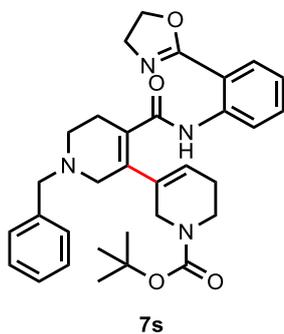
4-(3,6-Dihydro-2H-pyran-4-yl)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-1-methyl-1,2,5,6-tetrahydropyridine-3-carboxamide (7q)

Substrate **6i** was alkenylated with alkenyl boronate (**4u**) following the general procedure **C** (5 h). After purification by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 1/1), **7q** was obtained as a white solid (22.8 mg, 63%). mp 82–84 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.04 (s, 1H), 8.76 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 5.69 (s, 1H), 4.36 (t, *J* = 9.5 Hz, 2H), 4.09–3.97 (m, 4H), 3.66 (t, *J* = 5.3 Hz, 2H), 3.30 (s, 2H), 2.61 (t, *J* = 5.7 Hz, 2H), 2.45–2.34 (m, 5H), 2.24 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 168.5, 164.3, 139.8, 138.1, 135.0, 132.5, 129.8, 129.3, 123.8, 122.3, 119.6, 113.1, 66.0, 65.3, 64.0, 55.3, 54.7, 51.5, 45.4, 29.2, 27.4; HRMS (ESI-TOF) *m/z* Calcd for C₂₁H₂₆N₃O₃ [M+H]⁺: 368.1969, found: 368.1968.



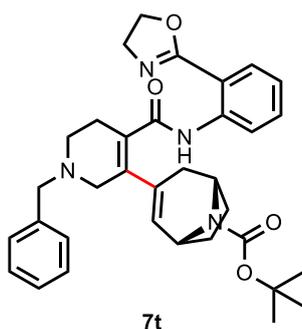
***tert*-Butyl 5'-((2-(4,5-dihydrooxazol-2-yl)phenyl)carbamoyl)-1'-methyl-1',2',3',5,6,6'-hexahydro-[3,4'-bipyridine]-1(2H)-carboxylate (7r)**

Substrate **6i** was alkenylated with alkenyl boronate (**4x**) following the general procedure **C** (5 h). After purification by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 1/1), **7r** was obtained as a white solid (44.0 mg, 87%), rotameric mixture. mp 78–80 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.05 (s, 1H), 8.77 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 5.82 (s, 1H), 4.34 (t, *J* = 9.5 Hz, 2H), 4.10 (brs, 2H), 3.98 (brs, 2H), 3.30 (s, 2H), 3.23 (s, 2H), 2.61 (t, *J* = 5.6 Hz, 2H), 2.46–2.36 (m, 5H), 1.96 (brs, 2H), 1.42 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 168.6, 168.0, 164.1, 154.8, 139.7, 136.6, 135.4, 132.4, 131.3, 129.2, 123.8, 122.2, 119.5, 113.0, 79.5, 66.1, 55.3, 54.6, 51.5, 45.4, 44.9, 44.0, 40.3, 39.0, 30.4, 29.3, 28.4, 25.1; HRMS (ESI-TOF) *m/z* Calcd for C₂₆H₃₄N₄O₄Na [M+Na]⁺: 489.2472, found: 489.2468.



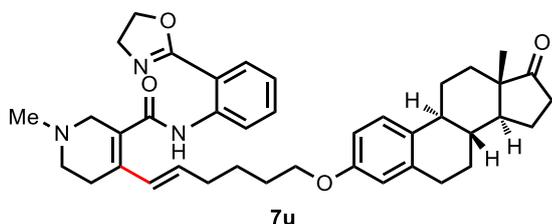
***tert*-Butyl 1'-benzyl-4'-((2-(4,5-dihydrooxazol-2-yl)phenyl)carbamoyl)-1',2',5,5',6,6'-hexahydro-[3,3'-bipyridine]-1(2H)-carboxylate (7s)**

Substrate **6h** was alkenylated with alkenyl boronate (**4x**) following the general procedure **C** (5 h). After purification by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 10/1), **7s** was obtained as a white solid (50.0 mg, 92%), rotameric mixture. mp 87–89 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.04 (s, 1H), 8.80 (d, *J* = 8.4 Hz, 1H), 7.83 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.40–7.31 (m, 4H), 7.30–7.26 (m, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 5.80 (s, 1H), 4.34 (t, *J* = 9.5 Hz, 2H), 4.10 (brs, 2H), 3.91 (brs, 2H), 3.65 (s, 2H), 3.23 (brs, 2H), 3.14 (s, 2H), 2.65 (brs, 2H), 2.57 (brs, 2H), 1.99 (brs, 2H), 1.39 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 169.2, 168.6, 164.1, 154.7, 139.7, 137.5, 137.3, 134.2, 132.4, 131.0, 129.2, 128.3, 127.2, 124.7, 122.2, 119.6, 113.1, 79.5, 66.0, 62.2, 56.3, 55.5, 54.7, 48.9, 45.2, 44.4, 40.2, 38.9, 28.3, 27.1, 25.1, 24.9; HRMS (ESI-TOF) *m/z* Calcd for C₃₂H₃₉N₄O₄ [M+H]⁺: 543.2966, found: 543.2963.



(1*R*,5*S*)-*tert*-Butyl 3-(1-benzyl-4-((2-(4,5-dihydrooxazol-2-yl)phenyl)carbamoyl)-1,2,5,6-tetrahydropyridin-3-yl)-8-azabicyclo[3.2.1]oct-2-ene-8-carboxylate (7t)

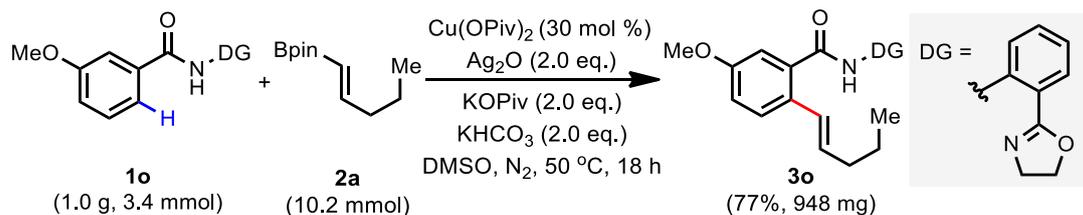
Substrate **6h** was alkenylated with alkenyl boronate (**4z**) following the general procedure **C** (5 h). After purification by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 10/1), **7t** was obtained as a white solid (19.0 mg, 34%), rotameric mixture. mp 83–85 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.00 (brs, 1H), 8.78 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.35–7.25 (m, 5H), 7.06 (t, *J* = 7.6 Hz, 1H), 5.97 (s, 1H), 4.37 (t, *J* = 9.5 Hz, 2H), 4.30–4.05 (m, 4H), 3.70–3.55 (m, 2H), 3.20–3.07 (m, 1H), 3.00–2.75 (m, 2H), 2.70–2.49 (m, 4H), 2.10–1.60 (m, 5H), 1.37 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 169.5, 169.2, 164.3, 154.1, 139.8, 138.7, 138.3, 137.5, 133.9, 133.6, 132.6, 131.3, 130.8, 130.3, 129.3, 129.3, 128.3, 127.2, 122.3, 119.6, 113.0, 79.2, 66.1, 62.2, 55.6, 55.0, 54.8, 53.3, 52.5, 52.4, 51.7, 48.9, 36.6, 35.7, 34.4, 33.8, 29.4, 28.7, 28.3, 27.0; HRMS (ESI-TOF) *m/z* Calcd for C₃₄H₄₀N₄O₄Na [M+Na]⁺: 591.2942, found: 591.2942.



***N*-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-1-methyl-4-((*E*)-6-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)hex-1-en-1-yl)-1,2,5,6-tetrahydropyridine-3-carboxamide (7u)**

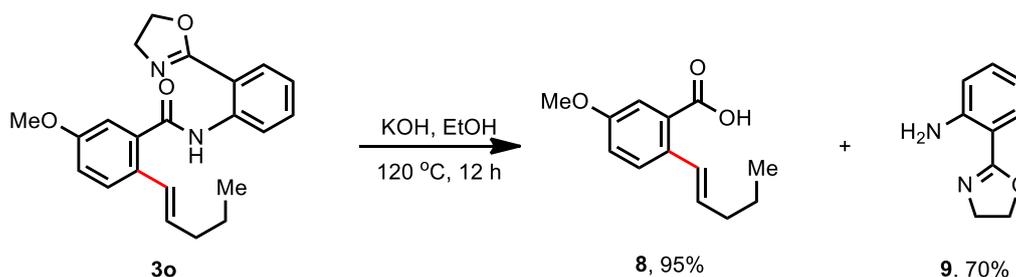
Substrate **6i** was alkenylated with alkenyl boronate (**4aa**) following the general procedure **C** (9 h). After purification by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 2/1), **7u** was obtained as a white solid (31.2 mg, 49%). mp 103–105 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.33 (s, 1H), 8.84 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.73–6.63 (m, 2H), 6.59 (s, 1H), 5.89–5.79 (m, 1H), 4.33 (t, *J* = 9.5 Hz, 2H), 4.04 (t, *J* = 9.4 Hz, 2H), 3.87 (t, *J* = 6.3 Hz, 2H), 3.36 (s, 2H), 2.90–2.83 (m, 2H), 2.62 (t, *J* = 5.8 Hz, 2H), 2.55–2.32 (m, 7H), 2.28–1.91 (m, 8H), 1.76–1.70 (m, 2H), 1.60–1.45 (m, 7H), 0.90 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 221.0, 167.8, 164.3, 157.0, 139.7, 137.6, 134.1, 132.4, 131.8, 131.7, 129.9, 129.1, 128.5, 126.2, 122.4, 119.9, 114.4, 113.4, 112.0, 67.5, 66.1, 55.8, 54.6, 51.4, 50.4, 48.0, 45.4, 43.9, 38.3, 35.8, 32.7, 31.5, 29.6, 28.7, 26.5, 26.2, 25.9, 25.8, 21.5, 13.8; HRMS (ESI-TOF) *m/z* Calcd for C₄₀H₅₀N₃O₄ [M+H]⁺: 636.3796, found: 636.3792.

3.8 Gram-Scale Reaction



A stirring bar, substrate **1o** (1.006 g, 3.4 mmol), Cu(OPiv)_2 (272 mg, 1.02 mmol), Ag_2O (1.57g, 6.8 mmol), KOPiv (952 mg, 6.8 mmol), and KHCO_3 (680 mg, 6.8 mmol) were added to an oven dried 500 mL Schlenk tube. The tube was capped and back-filled with nitrogen (3 times). Under the nitrogen flow, **2a** (1.96 g, 10.2 mmol) and DMSO (68 mL) were added to the mixture, and the tube was capped tightly again. Then the reaction mixture was placed into a pre-heated oil bath and stirred at 50 °C for 18 h (monitored by TLC). After cooled to room temperature, EtOAc (250 mL) was added to quench the reaction, and organic layer was washed with $\text{NH}_3 \cdot \text{H}_2\text{O}$ (250 mL), and the water phase was extracted by EtOAc (250 mL). The combined organic layers were washed with saturated brine, dried over Na_2SO_4 , concentrated under vacuum. The crude product was purified by column chromatography (neutral alumina, petroleum ether/ethyl acetate = 15/1) to afford the desired product **3o** (948 mg, 77%).

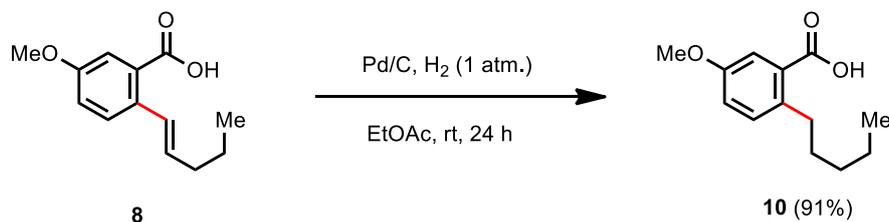
3.9 Directing Group Removal



To a 15 mL sealed tube was added **3o** (36.4 mg, 0.1 mmol), KOH (336 mg, 6.0 mmol), EtOH (2 mL), and the tube was capped tightly. The reaction mixture was placed into a pre-heated oil bath and stirred at 120 °C for 12 h under air. Upon completion (monitored by TLC), the reaction mixture was evaporated to remove solvent. Then the mixture was washed with H₂O (25 mL) and extracted with EtOAc (3 × 25 mL). The combined organic phases were dried over Na₂SO₄ and concentrated under vacuum. The products were purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to give the directing group **9** (11.3 mg, 70%). The water fraction was treated with 1N HCl to adjust the PH ≈ 3-4, and extracted with EtOAc (3 × 25 mL). The organic fractions were dried over Na₂SO₄ and concentrated. The product were purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to give the desired product **8** as white solid (20.8 mg, 95%). mp 54–56 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.53–7.48 (m, 2H), 7.18 (d, *J* = 15.8 Hz, 1H), 7.06 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.11–6.01 (m, 1H), 3.84 (s, 3H), 2.23 (q, *J* = 7.2 Hz, 2H), 1.59–1.44 (m, 2H), 1.00–0.92 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.0, 158.0, 133.5, 132.6, 128.8, 128.1, 127.5, 119.9, 114.8, 55.5, 35.2, 22.5, 13.7; HRMS (ESI-TOF) *m/z* Calcd for C₁₃H₁₅O₃ [M-H]⁻: 219.1027, found: 219.1020.

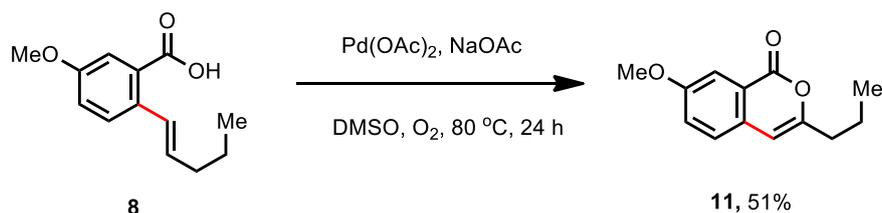
3.10 Transformations of Alkenylated Benzoic Acid

Hydrogenation of Alkenylated Benzoic Acid



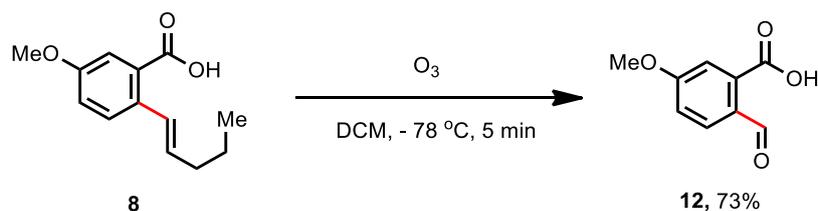
To the oven dried 25 mL round-bottom flask was added **8** (20.8 mg, 0.095 mmol), Pd/C (10 wt. % loading on carbon, 6.0 mg), and EtOAc (2 mL). The reaction flask was back-filled with H₂ (3 times, balloon), and stirred at room temperature for 24 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of Celite, washed with other EtOAc, and concentrated under reduced pressure. The product were purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to give the desired product **10** as white solid (19.0 mg, 91%). mp 53–55 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.26 (brs, 1H), 7.47 (s, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 3.76 (s, 3H), 2.89 (t, *J* = 7.3 Hz, 2H), 1.60–1.48 (m, 2H), 1.34–1.18 (m, 4H), 0.88–0.72 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 157.2, 137.5, 132.0, 130.1, 118.9, 115.3, 55.3, 33.6, 31.7, 31.5, 22.5, 14.0; HRMS (ESI-TOF) *m/z* Calcd for C₁₃H₁₇O₃ [M-H]⁻: 221.1183, found: 221.1181.

Lactonization of Alkenylated Benzoic Acid



An oven dried 25 mL Schlenk tube was charged with substrate **8** (22 mg, 0.1 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol), and NaOAc (16.2 mg, 0.2 mmol) and tube was capped and back-filled with O₂ (3 times). Under the O₂ flow, DMSO (2 mL) were added to the mixture, and the tube was capped tightly again. Then the reaction mixture was placed into a pre-heated oil bath and stirred at 80 °C for 24 h. After cooled to room temperature, EtOAc (20 mL) was added to quench the reaction, and organic layer was washed with water (20 mL), and the water phase was extracted by EtOAc (20 mL). The combined organic layers were washed with saturated brine, dried over Na₂SO₄, concentrated under vacuum. The product were purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to give the desired product **11** as white solid (11.1 mg, 51%). mp 40–42 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 1.8 Hz, 1H), 7.32–7.23 (m, 2H), 6.23 (s, 1H), 3.90 (s, 3H), 2.50 (t, *J* = 7.5 Hz, 2H), 1.80–1.68 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.3, 159.0, 155.9, 131.3, 126.6, 124.6, 121.1, 109.7, 102.6, 55.7, 35.2, 20.3, 13.5; HRMS (ESI-TOF) *m/z* Calcd for C₁₃H₁₅O₃ [M+H]⁺: 219.1016, found: 219.1013.

Ozonolysis of Alkenylated Benzoic Acid



An oven dried 10 mL digestion tube was charged with substrate **8** (22 mg, 0.1 mmol), and DCM (2 mL) and cooled to $-78\text{ }^\circ\text{C}$. Then ozone was introduced into the reaction mixture for 5 min, and the reaction system turned to dark green. Upon completion (monitored by TLC), dimethyl sulfide (2.0 mL) was added to the mixture, and stirred at the room temperature for 4 h. Then EtOAc (20 mL) and water (20 mL) were added. The mixture was extracted, and the water phase was extracted by other EtOAc (20 mL). The combined organic layers were washed with saturated brine, dried over Na_2SO_4 , concentrated under vacuum. The product were purified by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 1/1) to give the desired product **12**¹³ as white solid (13.0 mg, 73%). 1H NMR (400 MHz, CD_3OD) δ 10.31 (s, 1H), 7.83 (d, $J = 8.3$ Hz, 1H), 7.16 (s, 1H), 6.98 (d, $J = 8.0$ Hz, 1H), 3.89 (s, 3H); HRMS (ESI-TOF) m/z Calcd for $C_9H_7O_4$ [M-H] $^-$: 179.0339, found: 179.0335.

3.12 X-Ray Structure of 3a (mono)

General procedure for crystal preparation: Compound **3a** (mono) (around 15 mg) was dissolved in dichloromethane (1.0 mL)/hexane (5.0 mL) in a screw cap vial (5.0 mL), and the vial was capped with an open-top cap. The single crystals were grown in the vial *via* slow evaporation of solvents at room temperature. X-ray data was collected with a Bruker APEX-II CCD diffractometer. The molecular structure and X-ray diffractive data/refinement of **3a** (mono) were shown below.

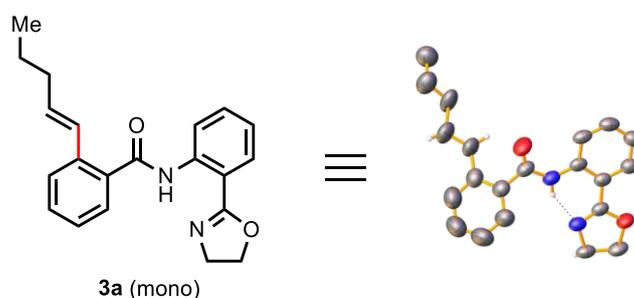


Figure S1. Molecular structure of **3a** (mono) with thermal ellipsoids at 30% probability

Bond precision:	C-C = 0.0036 Å		Wavelength=0.71073
Cell:	a=7.2548(3)	b=9.1568(4)	c=13.7284(7)
	alpha=86.674(2)	beta=89.179(2)	gamma=86.906(2)
Temperature:	293 K		
	Calculated	Reported	
Volume	909.07(7)	909.07(7)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C19.50 H18.50 N2 O2, 0.5(C3 H7)	?	
Sum formula	C21 H22 N2 O2	C21 H22 N2 O2	
Mr	334.41	334.40	
Dx,g cm-3	1.222	1.222	
Z	2	2	
Mu (mm-1)	0.079	0.079	
F000	356.0	356.0	
F000'	356.15		
h,k,lmax	8,11,16	8,11,16	
Nref	3395	3363	
Tmin,Tmax	0.985,0.990	0.673,0.746	
Tmin'	0.985		
Correction method=	# Reported T Limits: Tmin=0.673 Tmax=0.746 AbsCorr = MULTI-SCAN		
Data completeness=	0.991	Theta(max)= 25.499	
R(reflections)=	0.0616(2626)	wR2(reflections)= 0.1799(3363)	
S =	1.043	Npar= 278	

Table 1. Crystal data and structure refinement for mo_d8v19243_0m.

Identification code	mo_d8v19243_0m	
Empirical formula	C ₂₁ H ₂₂ N ₂ O ₂	
Formula weight	334.40	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.2548(3) Å	α = 86.674(2)°.
	b = 9.1568(4) Å	β = 89.179(2)°.
	c = 13.7284(7) Å	γ = 86.906(2)°.
Volume	909.07(7) Å ³	
Z	2	
Density (calculated)	1.222 Mg/m ³	
Absorption coefficient	0.079 mm ⁻¹	
F(000)	356	
Crystal size	0.190 x 0.160 x 0.130 mm ³	
Theta range for data collection	2.973 to 25.499°.	
Index ranges	-8 ≤ h ≤ 8, -11 ≤ k ≤ 11, -16 ≤ l ≤ 16	
Reflections collected	12851	
Independent reflections	3363 [R(int) = 0.0309]	
Completeness to theta = 25.242°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6727	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3363 / 58 / 278	
Goodness-of-fit on F ²	1.043	
Final R indices [I > 2σ(I)]	R1 = 0.0616, wR2 = 0.1662	
R indices (all data)	R1 = 0.0758, wR2 = 0.1799	
Largest diff. peak and hole	0.352 and -0.248 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mo_d8v19243_0m. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	1889(2)	6282(2)	5590(1)	60(1)
N(2)	3146(2)	3471(2)	5862(1)	58(1)
O(1)	1671(2)	7185(1)	4043(1)	74(1)
O(2)	3795(3)	1105(2)	6391(1)	94(1)
C(1)	1198(3)	7806(2)	5660(2)	63(1)
C(2)	1098(3)	8417(2)	4609(2)	71(1)
C(3)	2105(2)	6057(2)	4696(2)	52(1)
C(4)	2803(2)	4696(2)	4268(1)	52(1)
C(5)	3019(3)	4680(2)	3261(2)	63(1)
C(6)	3673(3)	3438(3)	2821(2)	72(1)
C(7)	4102(3)	2186(2)	3390(2)	70(1)
C(8)	3921(2)	2162(2)	4385(2)	61(1)
C(9)	3285(2)	3415(2)	4847(2)	52(1)
C(10)	3431(3)	2383(2)	6564(2)	65(1)
C(11)	3222(3)	2881(2)	7577(2)	69(1)
C(12)	1722(4)	3801(3)	7802(2)	93(1)
C(13)	1451(6)	4253(4)	8738(3)	128(1)
C(14)	2703(6)	3799(5)	9445(3)	134(1)
C(15)	4185(5)	2906(4)	9230(2)	110(1)
C(16)	4494(4)	2406(3)	8301(2)	79(1)
C(17)	6171(14)	1511(14)	8077(7)	88(2)
C(18)	7021(9)	522(8)	8705(5)	103(2)
C(19)	9309(9)	190(9)	8243(5)	107(2)
C(20)	9912(10)	-1138(10)	8736(5)	120(2)
C(21)	11996(15)	-1308(15)	8435(12)	118(3)
C(17')	6130(30)	1450(30)	8085(18)	124(3)
C(18')	7593(12)	1106(9)	8610(8)	131(2)
C(19')	8481(11)	-591(9)	8615(8)	142(2)
C(20')	10293(13)	-104(12)	8506(9)	156(2)
C(21')	11570(20)	-1635(17)	8478(18)	159(4)

Table 3. Bond lengths [Å] and angles [°] for mo_d8v19243_0m.

N(1)-C(3)	1.262(2)
N(1)-C(1)	1.466(2)
N(2)-C(10)	1.355(3)
N(2)-C(9)	1.399(3)
N(2)-H(2)	0.87(2)
O(1)-C(3)	1.355(2)
O(1)-C(2)	1.445(2)
O(2)-C(10)	1.222(2)
C(1)-C(2)	1.518(3)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.472(2)
C(4)-C(5)	1.389(3)
C(4)-C(9)	1.409(3)
C(5)-C(6)	1.377(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.374(3)
C(6)-H(6)	0.9300
C(7)-C(8)	1.370(3)
C(7)-H(7)	0.9300
C(8)-C(9)	1.396(3)
C(8)-H(8)	0.9300
C(10)-C(11)	1.491(3)
C(11)-C(12)	1.383(3)
C(11)-C(16)	1.401(3)
C(12)-C(13)	1.380(4)
C(12)-H(12)	0.9300
C(13)-C(14)	1.370(5)
C(13)-H(13)	0.9300
C(14)-C(15)	1.355(4)
C(14)-H(14)	0.9300
C(15)-C(16)	1.391(4)
C(15)-H(15)	0.9300
C(16)-C(17)	1.468(8)

C(16)-C(17')	1.474(16)
C(17)-C(18)	1.345(11)
C(17)-H(17)	0.9300
C(18)-C(19)	1.785(9)
C(18)-H(18)	0.9300
C(19)-C(20)	1.408(9)
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(20)-C(21)	1.563(12)
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(17')-C(18')	1.306(19)
C(17')-H(17')	0.9300
C(18')-C(19')	1.649(11)
C(18')-H(18')	0.9300
C(19')-C(20')	1.414(11)
C(19')-H(19C)	0.9700
C(19')-H(19D)	0.9700
C(20')-C(21')	1.639(15)
C(20')-H(20C)	0.9700
C(20')-H(20D)	0.9700
C(21')-H(21D)	0.9600
C(21')-H(21E)	0.9600
C(21')-H(21F)	0.9600
C(3)-N(1)-C(1)	107.52(16)
C(10)-N(2)-C(9)	129.30(17)
C(10)-N(2)-H(2)	119.7(14)
C(9)-N(2)-H(2)	111.0(14)
C(3)-O(1)-C(2)	106.22(16)
N(1)-C(1)-C(2)	104.44(16)
N(1)-C(1)-H(1A)	110.9
C(2)-C(1)-H(1A)	110.9
N(1)-C(1)-H(1B)	110.9
C(2)-C(1)-H(1B)	110.9

H(1A)-C(1)-H(1B)	108.9
O(1)-C(2)-C(1)	104.21(15)
O(1)-C(2)-H(2A)	110.9
C(1)-C(2)-H(2A)	110.9
O(1)-C(2)-H(2B)	110.9
C(1)-C(2)-H(2B)	110.9
H(2A)-C(2)-H(2B)	108.9
N(1)-C(3)-O(1)	117.57(16)
N(1)-C(3)-C(4)	127.36(17)
O(1)-C(3)-C(4)	115.07(17)
C(5)-C(4)-C(9)	119.01(17)
C(5)-C(4)-C(3)	118.93(17)
C(9)-C(4)-C(3)	122.05(17)
C(6)-C(5)-C(4)	121.4(2)
C(6)-C(5)-H(5)	119.3
C(4)-C(5)-H(5)	119.3
C(7)-C(6)-C(5)	119.2(2)
C(7)-C(6)-H(6)	120.4
C(5)-C(6)-H(6)	120.4
C(8)-C(7)-C(6)	121.07(19)
C(8)-C(7)-H(7)	119.5
C(6)-C(7)-H(7)	119.5
C(7)-C(8)-C(9)	120.65(19)
C(7)-C(8)-H(8)	119.7
C(9)-C(8)-H(8)	119.7
C(8)-C(9)-N(2)	123.07(18)
C(8)-C(9)-C(4)	118.64(19)
N(2)-C(9)-C(4)	118.27(16)
O(2)-C(10)-N(2)	123.6(2)
O(2)-C(10)-C(11)	122.6(2)
N(2)-C(10)-C(11)	113.77(18)
C(12)-C(11)-C(16)	119.9(2)
C(12)-C(11)-C(10)	119.0(2)
C(16)-C(11)-C(10)	121.1(2)
C(13)-C(12)-C(11)	120.8(3)
C(13)-C(12)-H(12)	119.6
C(11)-C(12)-H(12)	119.6
C(14)-C(13)-C(12)	119.4(3)

C(14)-C(13)-H(13)	120.3
C(12)-C(13)-H(13)	120.3
C(15)-C(14)-C(13)	120.4(3)
C(15)-C(14)-H(14)	119.8
C(13)-C(14)-H(14)	119.8
C(14)-C(15)-C(16)	122.2(3)
C(14)-C(15)-H(15)	118.9
C(16)-C(15)-H(15)	118.9
C(15)-C(16)-C(11)	117.5(3)
C(15)-C(16)-C(17)	120.8(5)
C(11)-C(16)-C(17)	121.5(4)
C(15)-C(16)-C(17')	121.0(10)
C(11)-C(16)-C(17')	121.5(10)
C(18)-C(17)-C(16)	124.8(8)
C(18)-C(17)-H(17)	117.6
C(16)-C(17)-H(17)	117.6
C(17)-C(18)-C(19)	106.8(7)
C(17)-C(18)-H(18)	126.6
C(19)-C(18)-H(18)	126.6
C(20)-C(19)-C(18)	103.7(6)
C(20)-C(19)-H(19A)	111.0
C(18)-C(19)-H(19A)	111.0
C(20)-C(19)-H(19B)	111.0
C(18)-C(19)-H(19B)	111.0
H(19A)-C(19)-H(19B)	109.0
C(19)-C(20)-C(21)	103.2(8)
C(19)-C(20)-H(20A)	111.1
C(21)-C(20)-H(20A)	111.1
C(19)-C(20)-H(20B)	111.1
C(21)-C(20)-H(20B)	111.1
H(20A)-C(20)-H(20B)	109.1
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(18')-C(17')-C(16)	130(2)

C(18')-C(17')-H(17')	115.2
C(16)-C(17')-H(17')	115.2
C(17')-C(18')-C(19')	118.1(13)
C(17')-C(18')-H(18')	121.0
C(19')-C(18')-H(18')	121.0
C(20')-C(19')-C(18')	91.7(8)
C(20')-C(19')-H(19C)	113.3
C(18')-C(19')-H(19C)	113.3
C(20')-C(19')-H(19D)	113.3
C(18')-C(19')-H(19D)	113.3
H(19C)-C(19')-H(19D)	110.7
C(19')-C(20')-C(21')	103.2(10)
C(19')-C(20')-H(20C)	111.1
C(21')-C(20')-H(20C)	111.1
C(19')-C(20')-H(20D)	111.1
C(21')-C(20')-H(20D)	111.1
H(20C)-C(20')-H(20D)	109.1
C(20')-C(21')-H(21D)	109.5
C(20')-C(21')-H(21E)	109.5
H(21D)-C(21')-H(21E)	109.5
C(20')-C(21')-H(21F)	109.5
H(21D)-C(21')-H(21F)	109.5
H(21E)-C(21')-H(21F)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mo_d8v19243_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^* U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
N(1)	55(1)	49(1)	75(1)	-11(1)	-2(1)	3(1)
N(2)	54(1)	44(1)	76(1)	-4(1)	-4(1)	2(1)
O(1)	92(1)	47(1)	79(1)	-2(1)	-1(1)	14(1)
O(2)	132(2)	51(1)	96(1)	0(1)	-15(1)	13(1)
C(1)	52(1)	49(1)	88(2)	-17(1)	-3(1)	5(1)
C(2)	70(1)	43(1)	100(2)	-11(1)	-4(1)	6(1)
C(3)	39(1)	42(1)	74(1)	-4(1)	-3(1)	-2(1)
C(4)	38(1)	46(1)	73(1)	-9(1)	-2(1)	-3(1)
C(5)	58(1)	57(1)	75(1)	-6(1)	1(1)	0(1)
C(6)	69(1)	72(1)	75(1)	-19(1)	3(1)	2(1)
C(7)	57(1)	60(1)	94(2)	-25(1)	0(1)	5(1)
C(8)	47(1)	45(1)	92(2)	-11(1)	-4(1)	2(1)
C(9)	35(1)	46(1)	76(1)	-8(1)	-3(1)	-3(1)
C(10)	60(1)	50(1)	84(2)	1(1)	-9(1)	1(1)
C(11)	70(1)	57(1)	80(2)	4(1)	2(1)	-5(1)
C(12)	90(2)	92(2)	94(2)	3(1)	15(1)	13(1)
C(13)	138(3)	128(3)	111(3)	-5(2)	41(2)	30(2)
C(14)	175(4)	137(3)	85(2)	-10(2)	19(2)	27(3)
C(15)	138(3)	112(2)	79(2)	3(2)	-7(2)	3(2)
C(16)	90(2)	70(1)	76(2)	5(1)	-5(1)	-7(1)
C(17)	81(3)	101(3)	79(3)	1(3)	-26(2)	21(3)
C(18)	89(3)	117(3)	98(3)	11(3)	-35(2)	19(3)
C(19)	73(3)	138(4)	103(3)	37(3)	-18(2)	15(3)
C(20)	97(3)	140(4)	118(4)	24(3)	-2(3)	14(3)
C(21)	96(5)	145(7)	111(5)	-10(5)	6(4)	6(5)
C(17')	107(5)	110(5)	157(6)	-4(5)	-30(5)	-25(5)
C(18')	114(4)	117(4)	164(5)	3(4)	-28(4)	-27(4)
C(19')	124(4)	120(4)	183(5)	7(4)	-29(4)	-29(4)
C(20')	138(5)	139(4)	192(6)	3(4)	8(4)	-34(4)
C(21')	125(8)	167(8)	187(8)	-18(7)	14(7)	-14(6)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for mo_d8v19243_0m.

	x	y	z	U(eq)
H(2)	2850(30)	4360(20)	6028(15)	66(6)
H(1A)	2035	8345	6031	75
H(1B)	-12	7855	5970	75
H(2A)	-149	8774	4447	85
H(2B)	1922	9211	4495	85
H(5)	2715	5525	2877	76
H(6)	3823	3448	2147	86
H(7)	4523	1340	3095	84
H(8)	4224	1304	4757	74
H(12)	886	4119	7318	112
H(13)	429	4859	8887	153
H(14)	2534	4105	10075	160
H(15)	5023	2618	9720	132
H(17)	6682	1637	7454	105
H(18)	6515	95	9272	123
H(19A)	9305	96	7543	129
H(19B)	10090	974	8388	129
H(20A)	9236	-1948	8527	144
H(20B)	9769	-1084	9436	144
H(21A)	12167	-862	7792	177
H(21B)	12373	-2329	8438	177
H(21C)	12725	-837	8890	177
H(17')	6115	1020	7487	149
H(18')	8120	1800	8972	158
H(19C)	8279	-1151	9225	170
H(19D)	8093	-1119	8067	170
H(20C)	10616	454	9053	187
H(20D)	10427	496	7906	187
H(21D)	11457	-2186	9090	239
H(21E)	12835	-1415	8364	239
H(21F)	11160	-2199	7962	239

Table 6. Torsion angles [°] for mo_d8v19243_0m.

C(3)-N(1)-C(1)-C(2)	-1.0(2)
C(3)-O(1)-C(2)-C(1)	-2.2(2)
N(1)-C(1)-C(2)-O(1)	2.0(2)
C(1)-N(1)-C(3)-O(1)	-0.5(2)
C(1)-N(1)-C(3)-C(4)	178.86(16)
C(2)-O(1)-C(3)-N(1)	1.8(2)
C(2)-O(1)-C(3)-C(4)	-177.60(15)
N(1)-C(3)-C(4)-C(5)	-177.22(17)
O(1)-C(3)-C(4)-C(5)	2.1(2)
N(1)-C(3)-C(4)-C(9)	1.8(3)
O(1)-C(3)-C(4)-C(9)	-178.87(15)
C(9)-C(4)-C(5)-C(6)	0.7(3)
C(3)-C(4)-C(5)-C(6)	179.73(17)
C(4)-C(5)-C(6)-C(7)	0.7(3)
C(5)-C(6)-C(7)-C(8)	-1.2(3)
C(6)-C(7)-C(8)-C(9)	0.3(3)
C(7)-C(8)-C(9)-N(2)	-177.26(16)
C(7)-C(8)-C(9)-C(4)	1.1(3)
C(10)-N(2)-C(9)-C(8)	-5.4(3)
C(10)-N(2)-C(9)-C(4)	176.17(17)
C(5)-C(4)-C(9)-C(8)	-1.6(2)
C(3)-C(4)-C(9)-C(8)	179.42(15)
C(5)-C(4)-C(9)-N(2)	176.88(15)
C(3)-C(4)-C(9)-N(2)	-2.1(2)
C(9)-N(2)-C(10)-O(2)	-3.6(3)
C(9)-N(2)-C(10)-C(11)	177.62(17)
O(2)-C(10)-C(11)-C(12)	-133.2(3)
N(2)-C(10)-C(11)-C(12)	45.6(3)
O(2)-C(10)-C(11)-C(16)	45.4(3)
N(2)-C(10)-C(11)-C(16)	-135.8(2)
C(16)-C(11)-C(12)-C(13)	-0.5(4)
C(10)-C(11)-C(12)-C(13)	178.2(3)
C(11)-C(12)-C(13)-C(14)	1.0(5)
C(12)-C(13)-C(14)-C(15)	-0.5(6)
C(13)-C(14)-C(15)-C(16)	-0.5(6)
C(14)-C(15)-C(16)-C(11)	1.1(5)

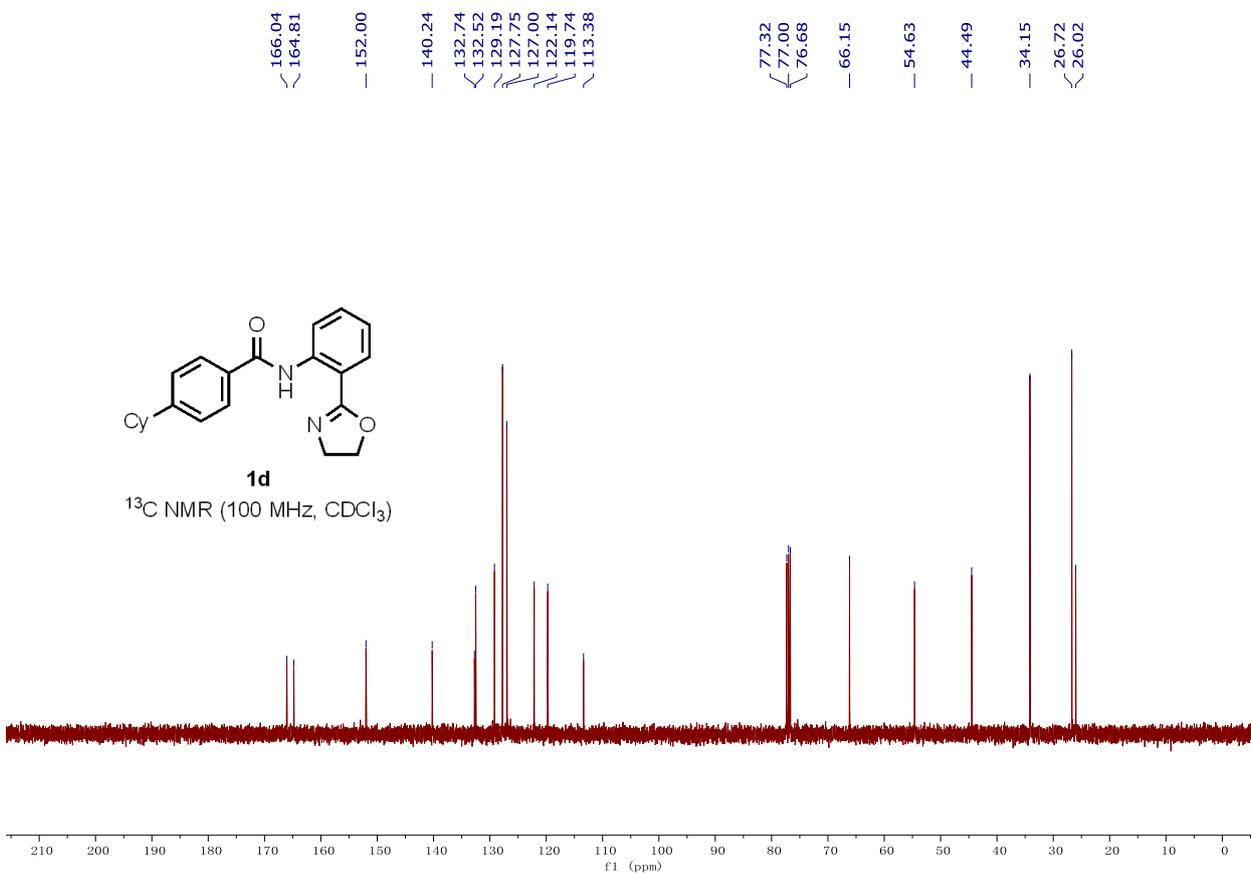
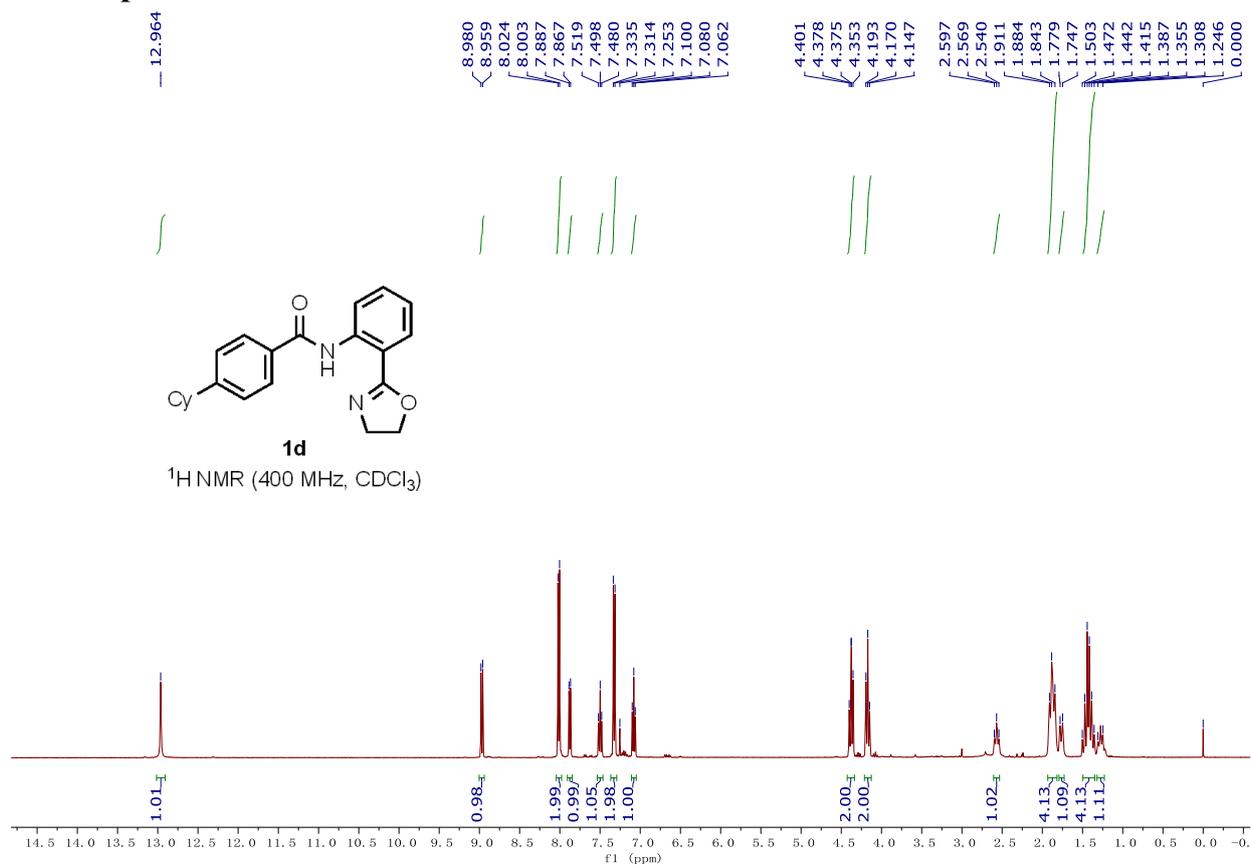
C(14)-C(15)-C(16)-C(17)	176.3(7)
C(14)-C(15)-C(16)-C(17')	179.4(12)
C(12)-C(11)-C(16)-C(15)	-0.5(4)
C(10)-C(11)-C(16)-C(15)	-179.1(2)
C(12)-C(11)-C(16)-C(17)	-175.8(7)
C(10)-C(11)-C(16)-C(17)	5.6(8)
C(12)-C(11)-C(16)-C(17')	-178.9(12)
C(10)-C(11)-C(16)-C(17')	2.5(12)
C(15)-C(16)-C(17)-C(18)	34.7(15)
C(11)-C(16)-C(17)-C(18)	-150.3(9)
C(17')-C(16)-C(17)-C(18)	-60(28)
C(16)-C(17)-C(18)-C(19)	-161.5(10)
C(17)-C(18)-C(19)-C(20)	-162.2(9)
C(18)-C(19)-C(20)-C(21)	-172.6(8)
C(15)-C(16)-C(17')-C(18')	-11(3)
C(11)-C(16)-C(17')-C(18')	167.0(18)
C(17)-C(16)-C(17')-C(18')	76(28)
C(16)-C(17')-C(18')-C(19')	141.4(19)
C(17')-C(18')-C(19')-C(20')	135.4(15)
C(18')-C(19')-C(20')-C(21')	-179.6(11)

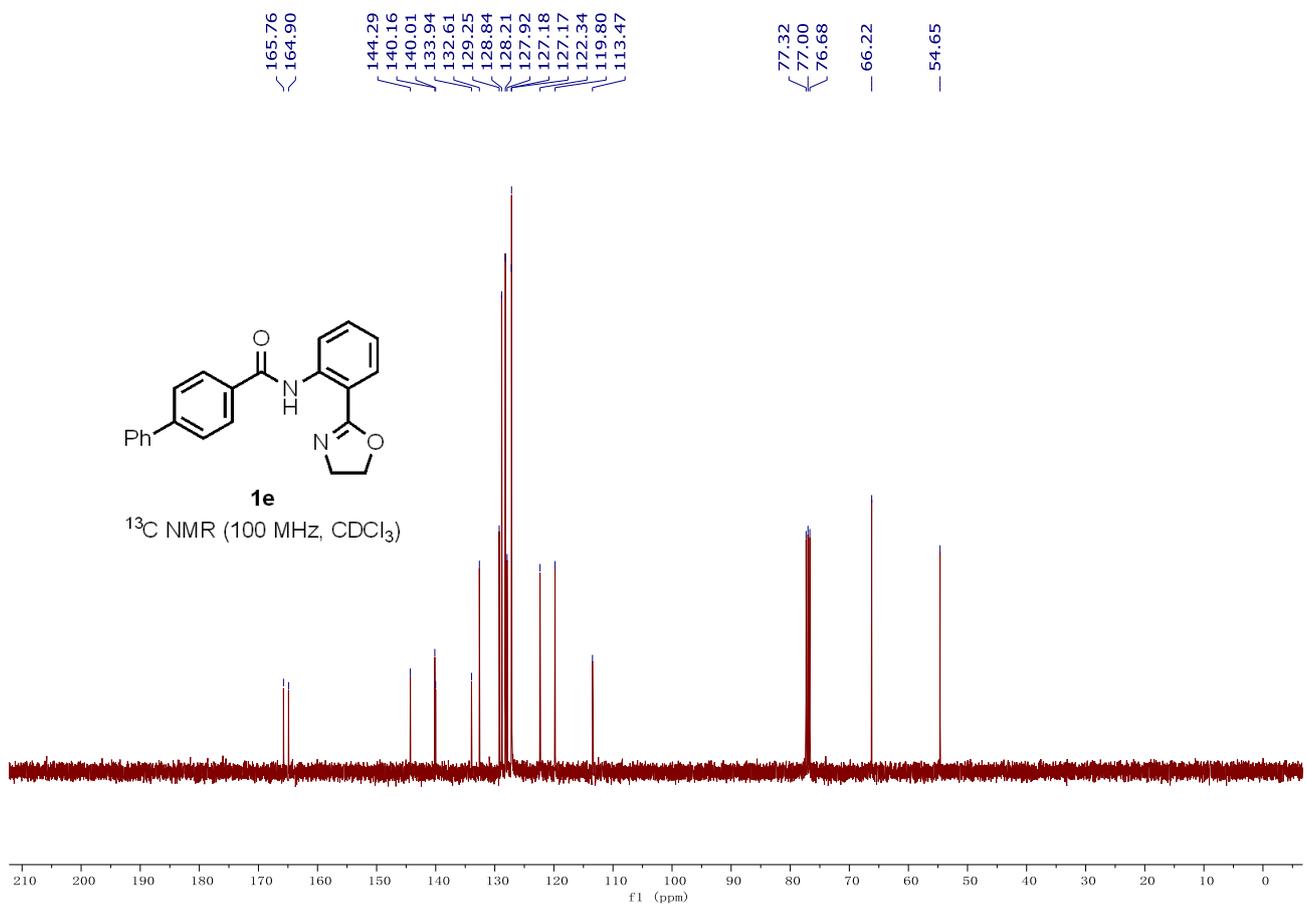
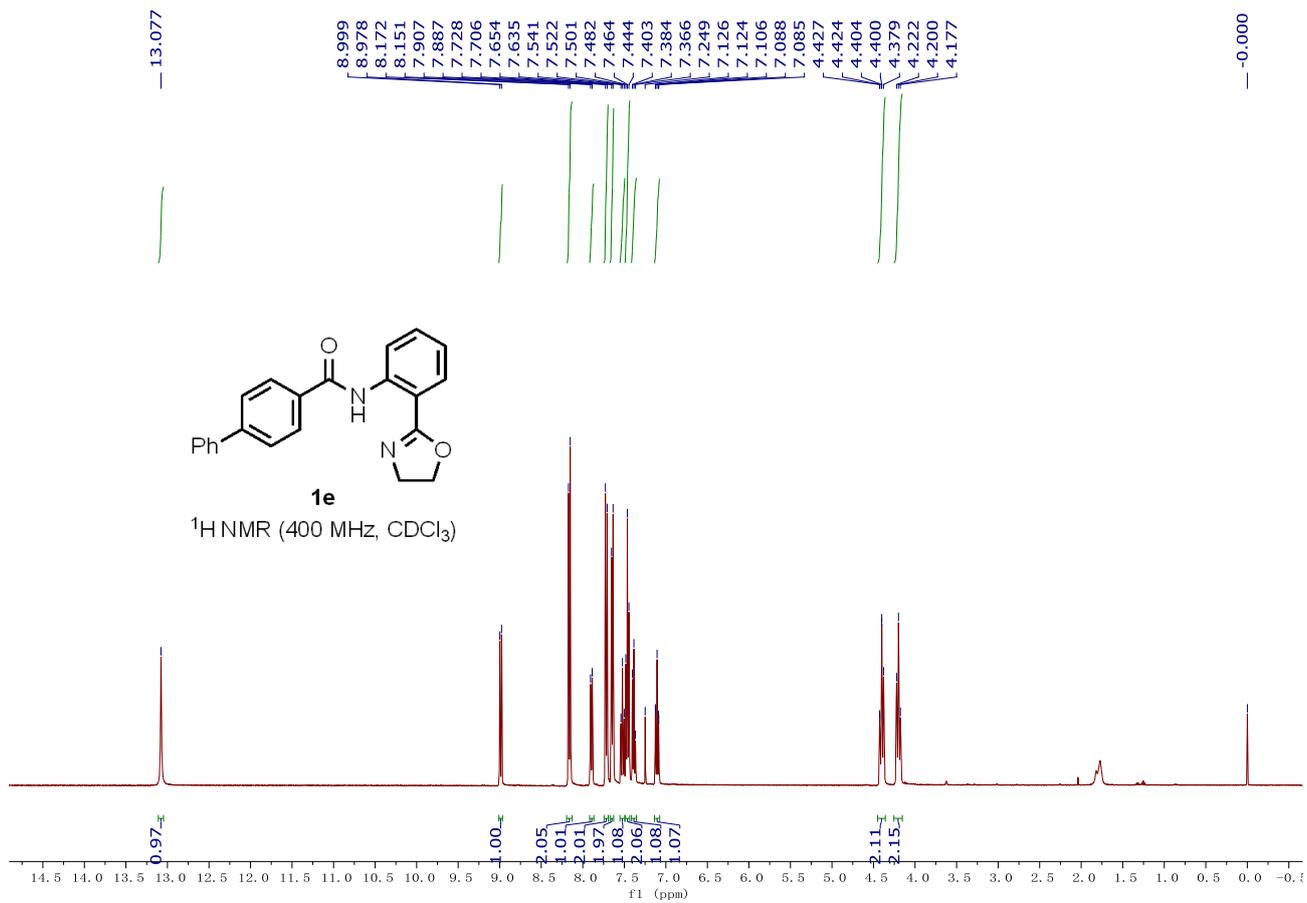
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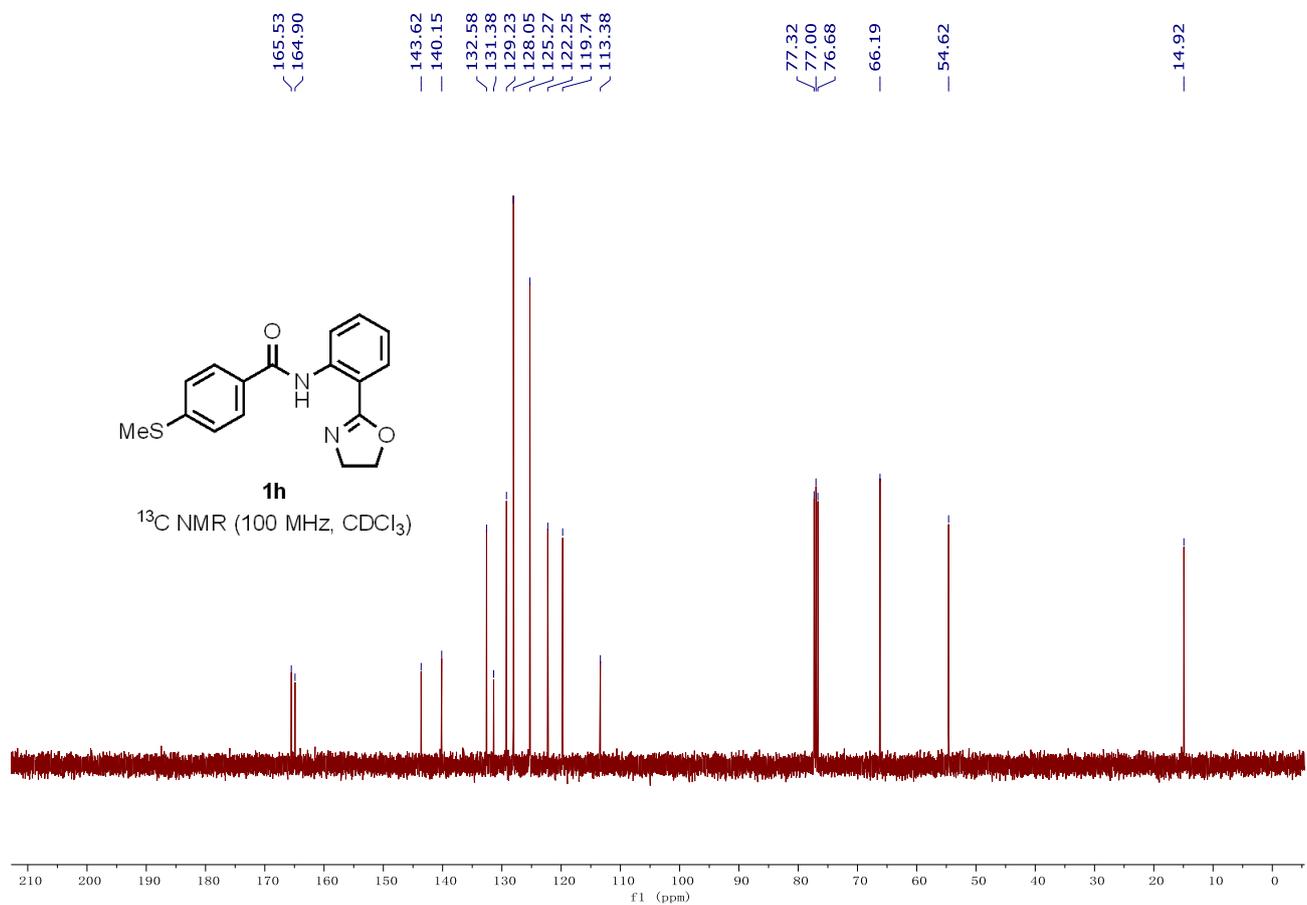
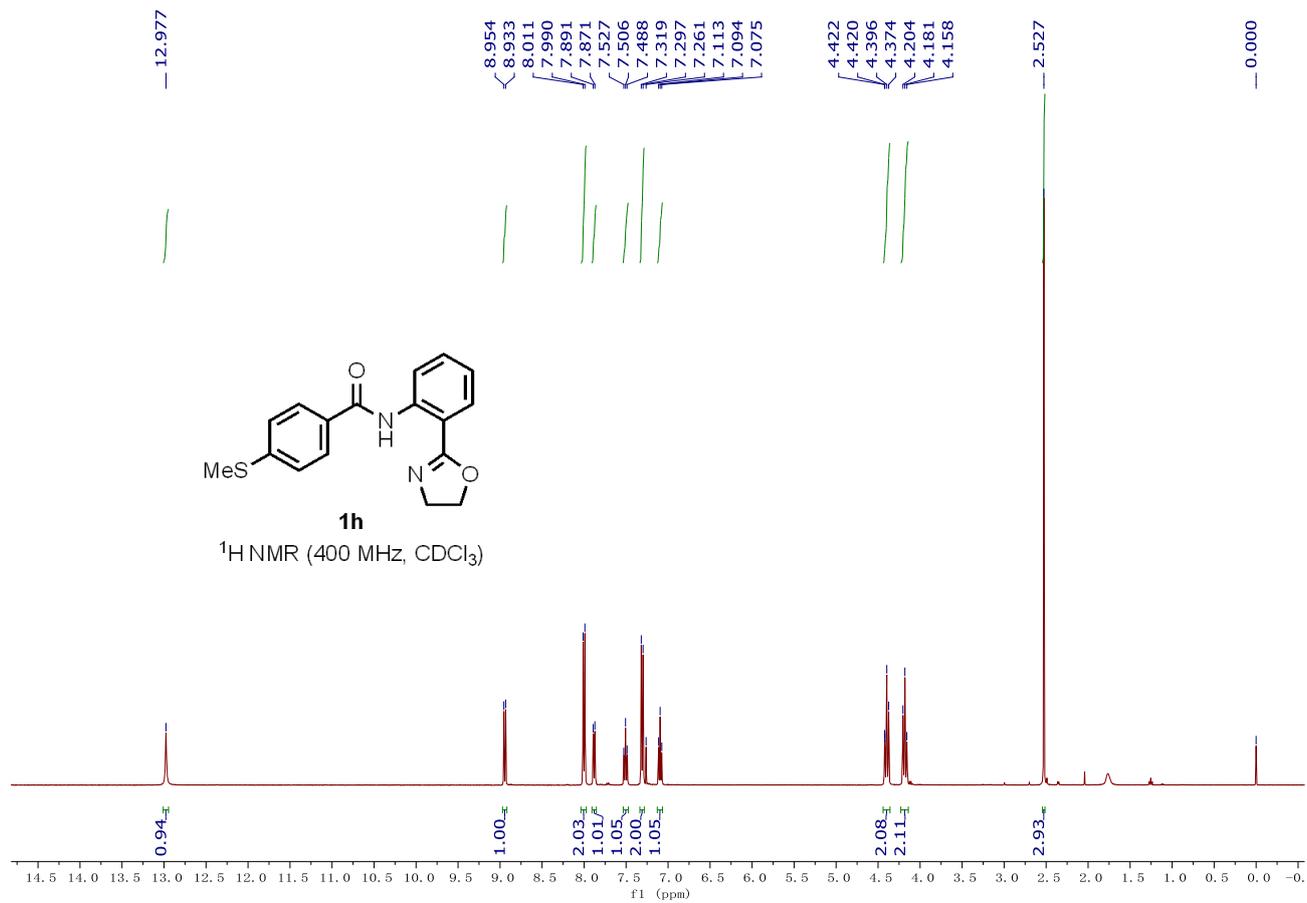
4. References

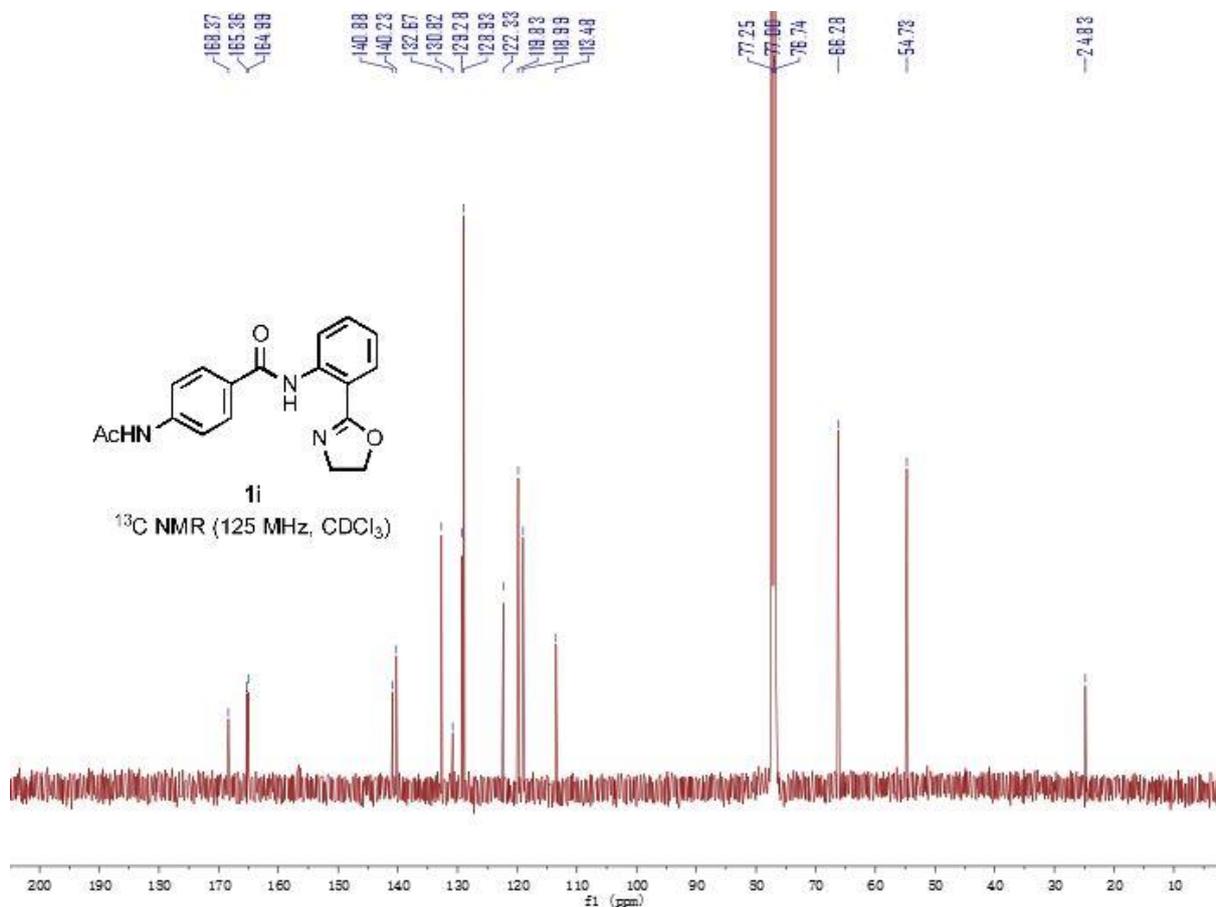
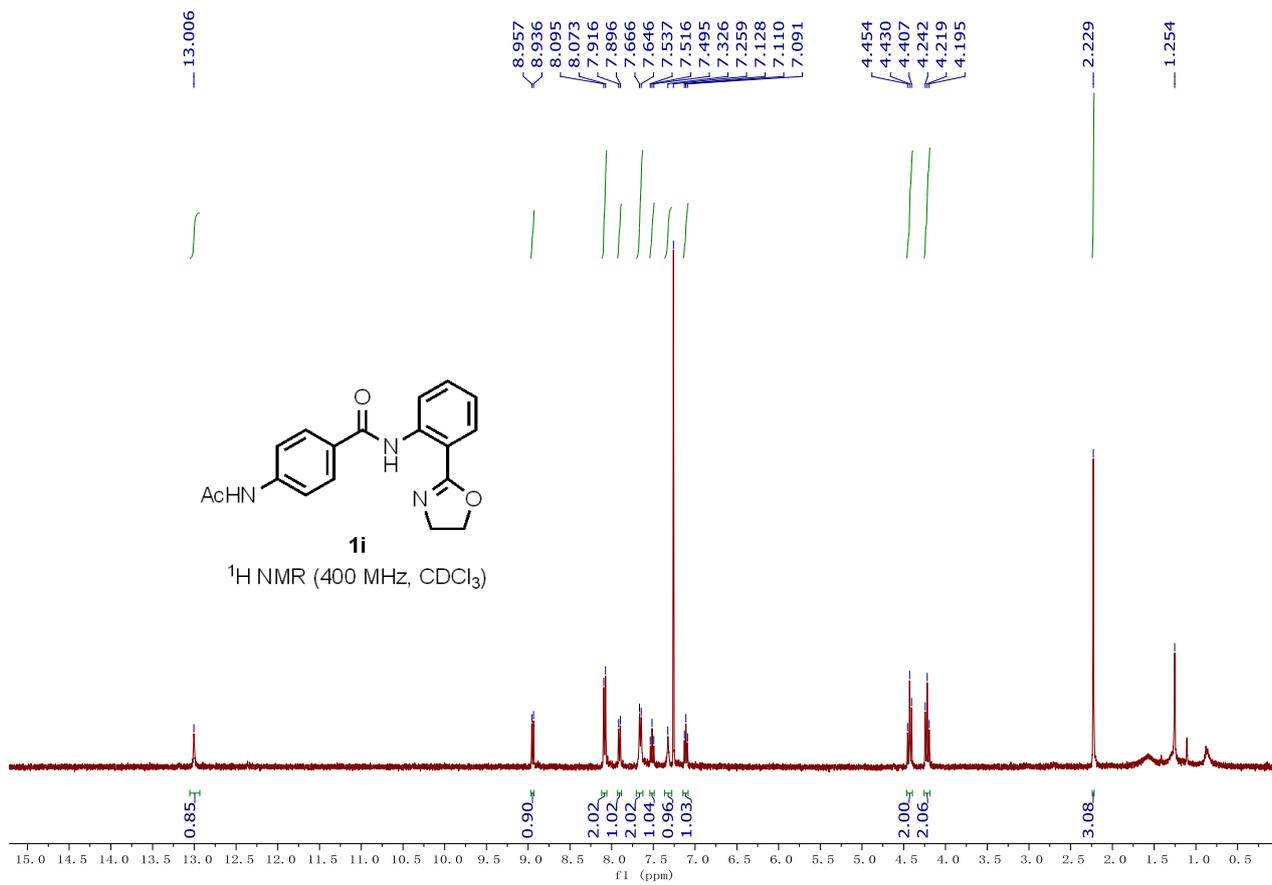
1. (a) Fu, X.-P.; Xuan, Q.-Q.; Liu, L.; Wang, D.; Chen, Y.-J.; Li, C.-J. *Tetrahedron* **2013**, *69*, 4436–4444. (b) Wang, C.-P.; Dong, G.-B. *J. Am. Chem. Soc.* **2018**, *140*, 6057–6066. (b) Yu, J.-F.; Li, J.-J.; Wang, P.; Yu, J.-Q. *Angew. Chem. Int. Ed.* **2019**, 10.1002/anie.201910395.
2. (a) Shang, M.; Sun, S.-Z.; Dai, H.-X.; Yu, J.-Q. *J. Am. Chem. Soc.* **2014**, *136*, 3354–3357. (b) Shang, M.; Wang, M.-M.; Saint-Denis, T.-G.; Li, M.-H.; Dai, H.-X.; Yu, J.-Q. *Angew. Chem. Int. Ed.* **2017**, *56*, 5317–5321.
3. Song S.; Zhu, S.-F.; Pu, L.-Y.; Zhou, Q.-L. *Angew. Chem. Int. Ed.* **2013**, *52*, 6072–6075.
4. Zhao, J.; Niu, Z.-Q.; Fu, H.; Li, Y.-D. *Chem. Commun.* **2014**, *50*, 2058–2060.
5. Gao, G.-L.; Yan, J.-X.; Yang, K.; Fener Chen, F.-E.; Song, Q.-L. *Green Chem.* **2017**, *19*, 3997–4001.
6. Lawson, J.-R; Wilkins, L.-C; Melen, R.-L *Chem. Eur. J.* **2017**, *23*, 10997–11000.
7. Nakajima, K.; Kato, T.; Nishibayashi, Y. *Org. Lett.* **2017**, *19*, 4323–4326.
8. Nakamura, M.; Hatakeyama, T.; Hara, K.; Fukudome, H.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 14344–14345.
9. Crestey, F.; Hooyberghs, G.; Kristensen, J. L. *Tetrahedron* **2012**, *68*, 1417–1421.
10. Kovalenko, M.; Yarmoliuk, D. V.; Serhiichuk, D.; Chernenko, D.; Smyrnov, V.; Breslavskiy, A.; Hryshchuk, O. V.; Kleban, I.; Rassukana, Y.; Tymtsunik, A. V.; Tolmachev, A. A.; Kuchkovska, Y. O.; Grygorenko, O. O. *Eur. J. Org. Chem.* **2019**, 5624–5635.
11. Silvi, M.; Sandford, C.; Aggarwal, V. K. *J. Am. Chem. Soc.* **2017**, *139*, 5736–5739.
12. Kondoh, A.; Jamison, T. F. *Chem. Commun.* **2010**, *46*, 907–909.
13. Koeberle, S. C.; Fischer, S.; Schollmeyer, D.; Schattel, V.; Grütter, C.; Rauh, D.; Laufer, S. A. *J. Med. Chem.* **2012**, *55*, 5868–5877.

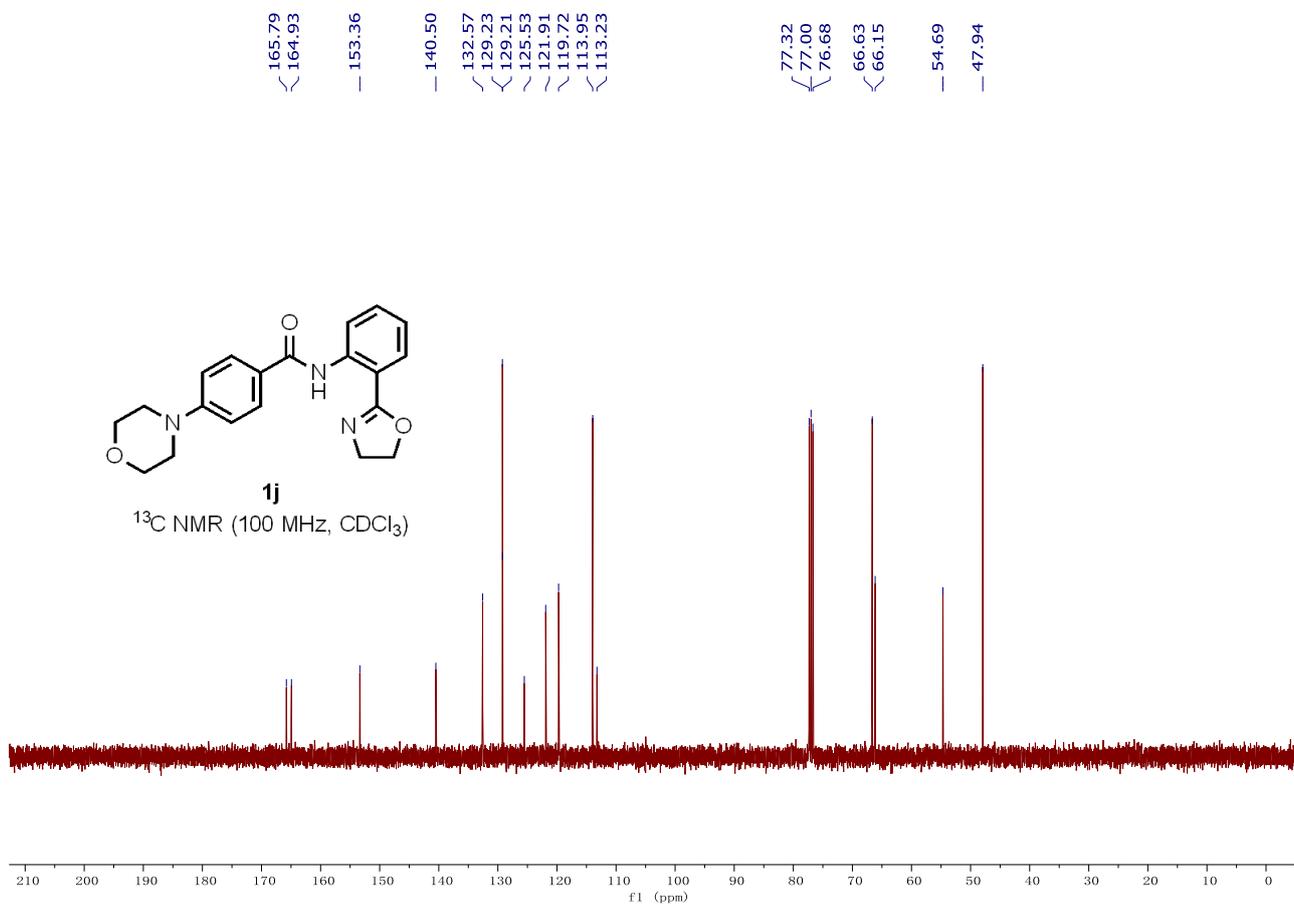
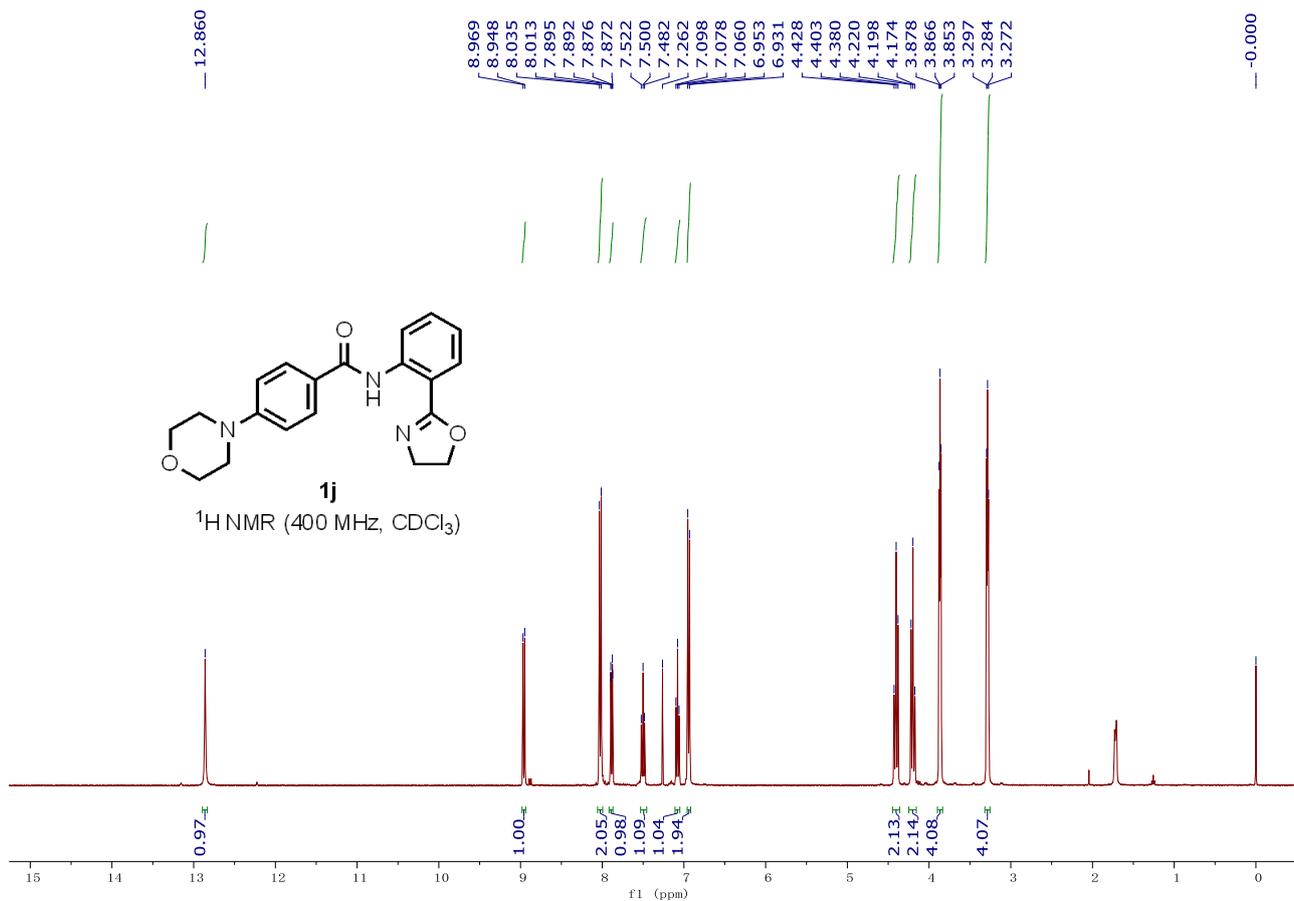
5. NMR Spectra

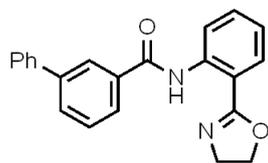






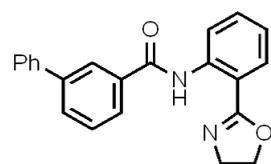
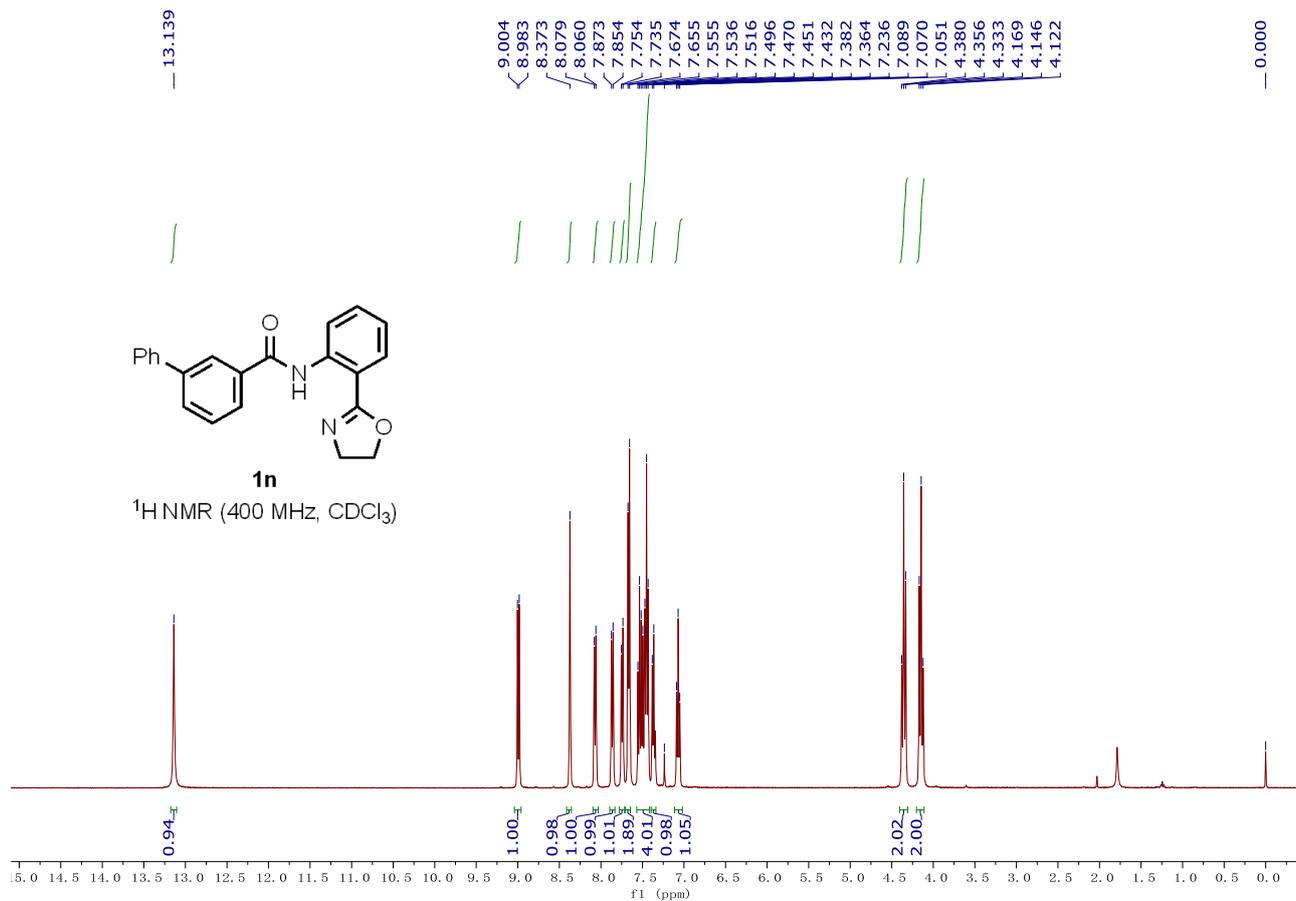






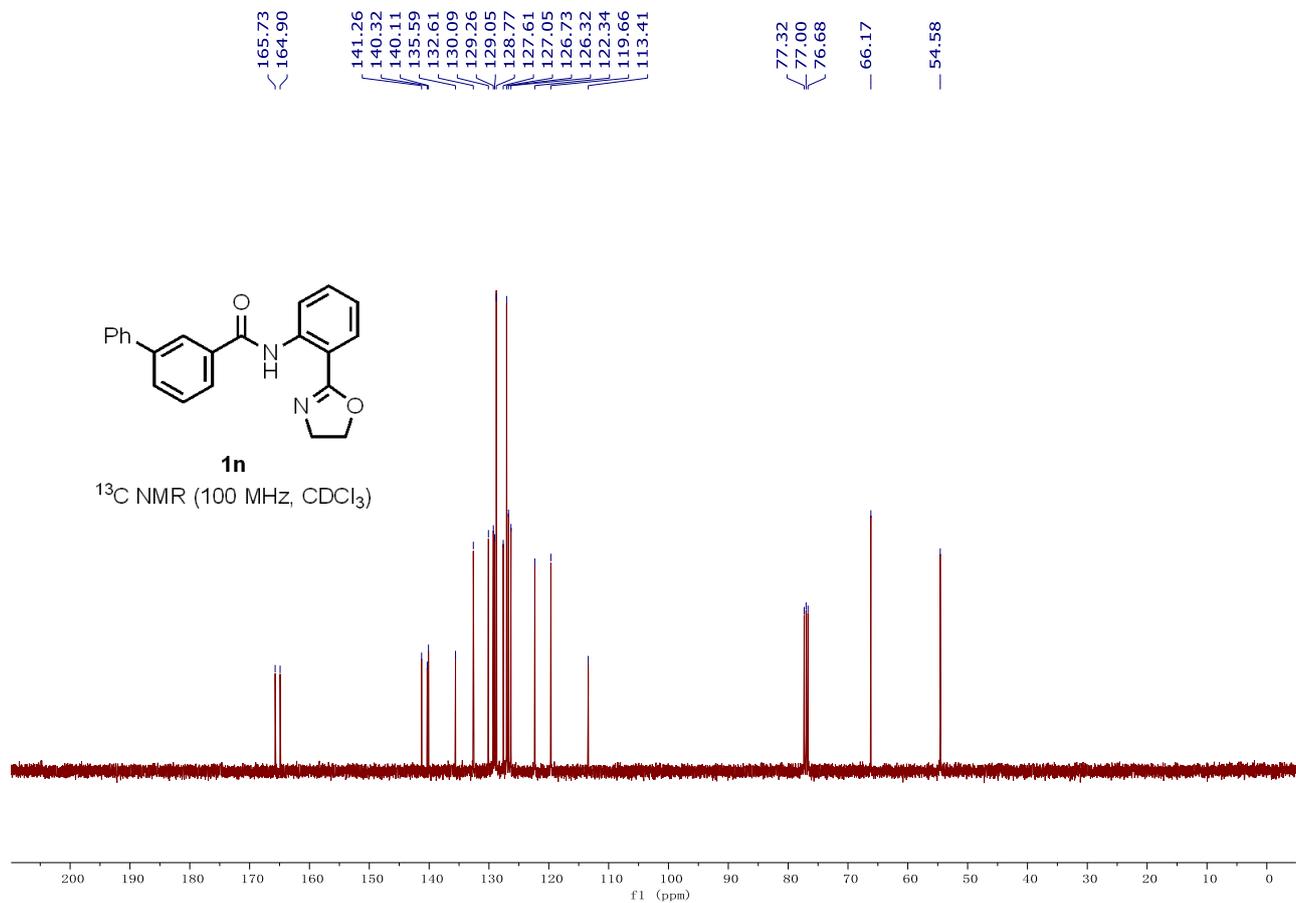
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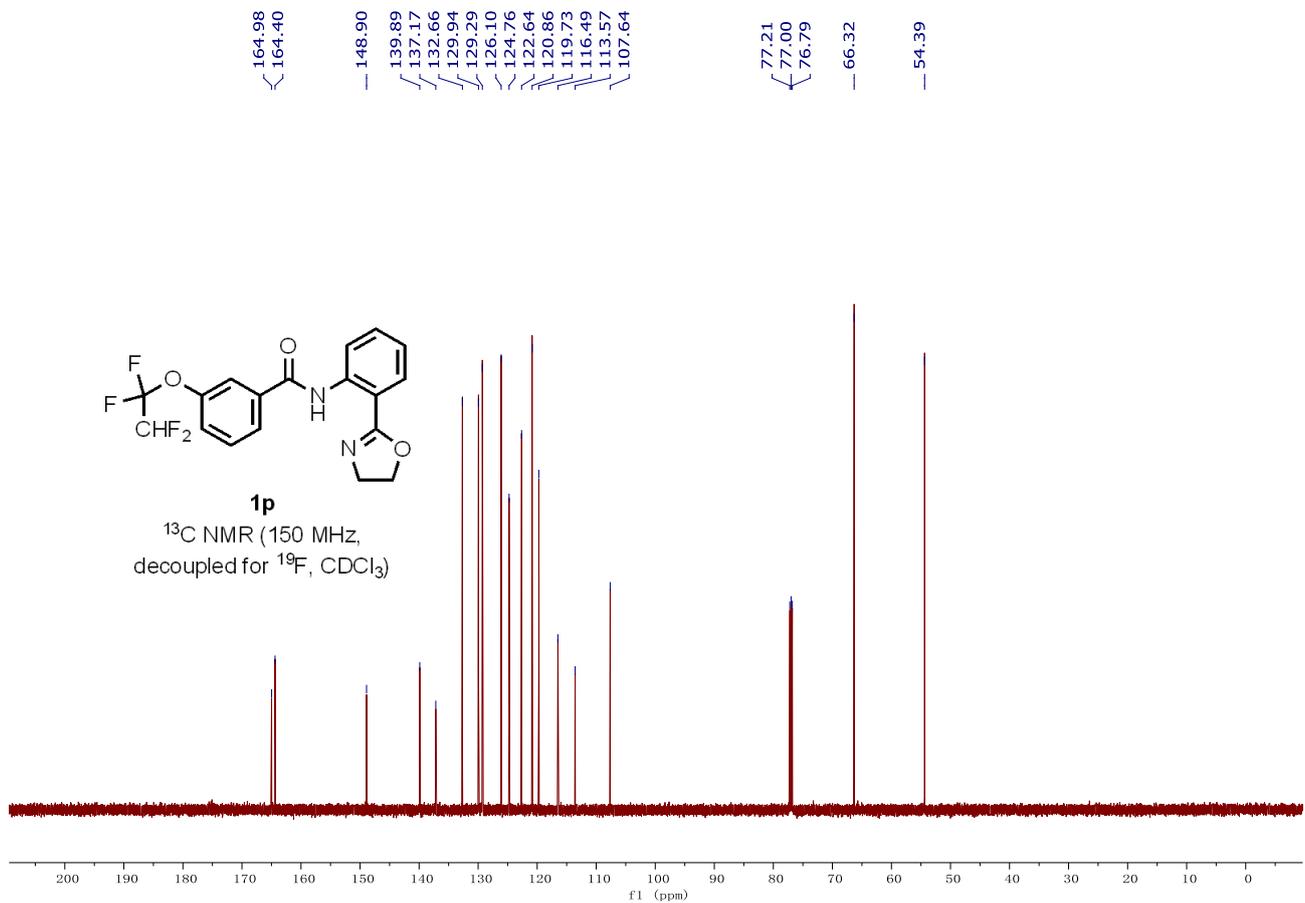
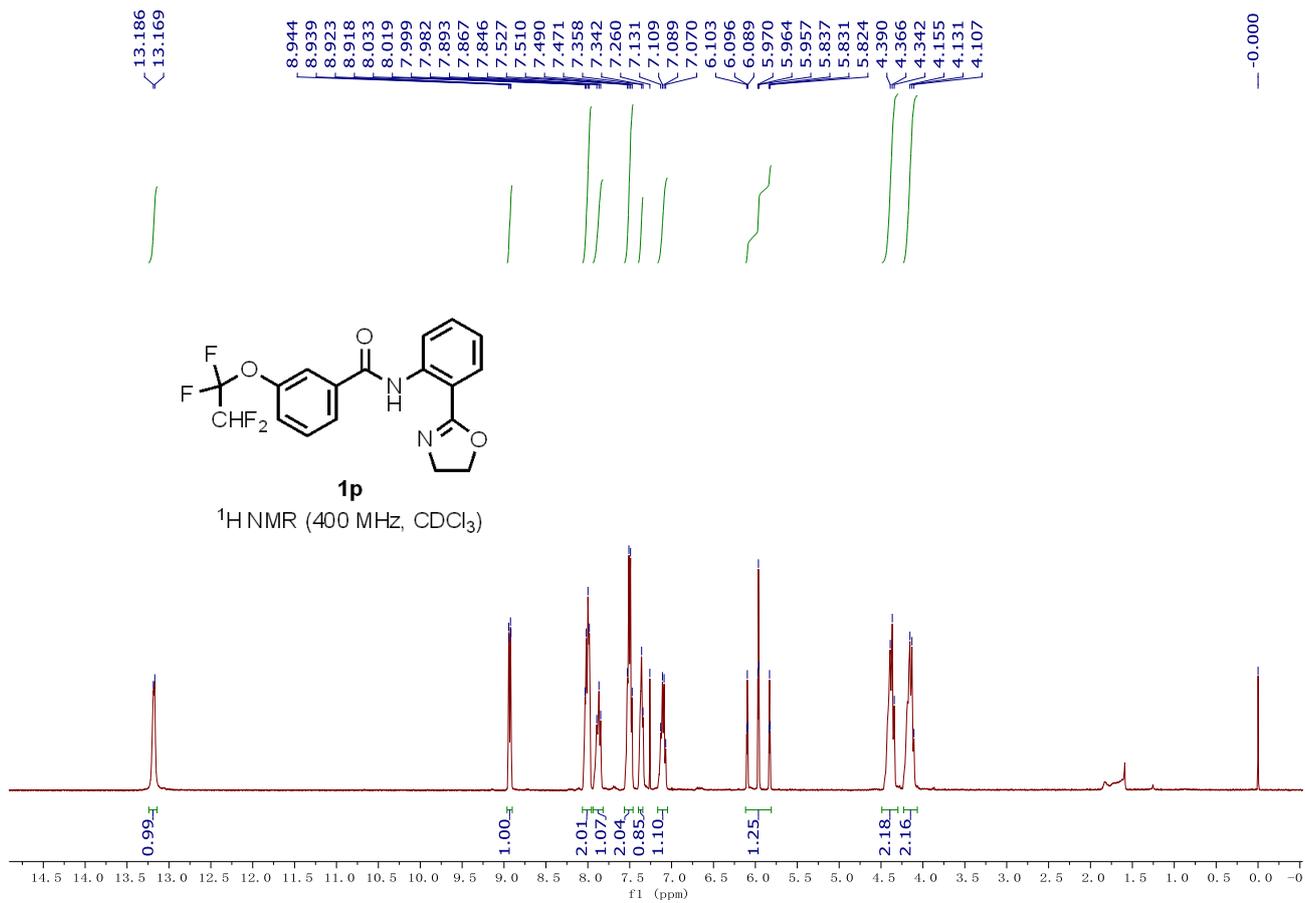
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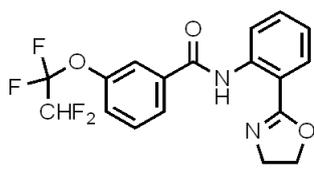
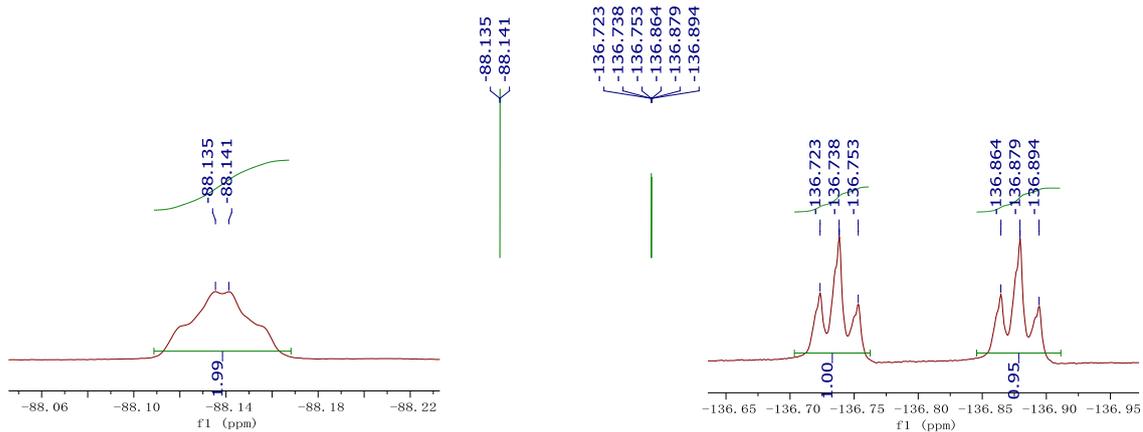


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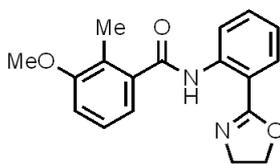
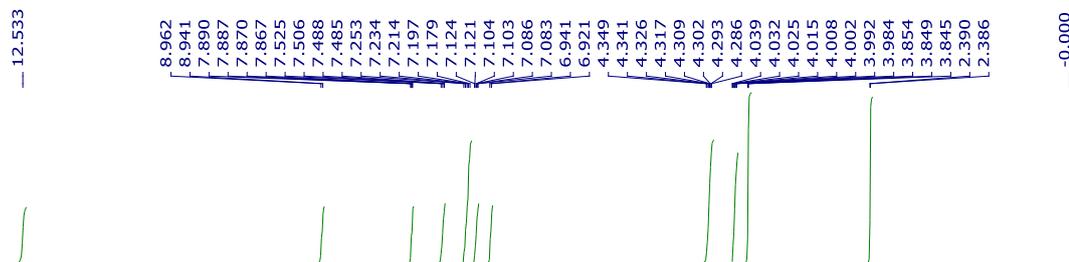
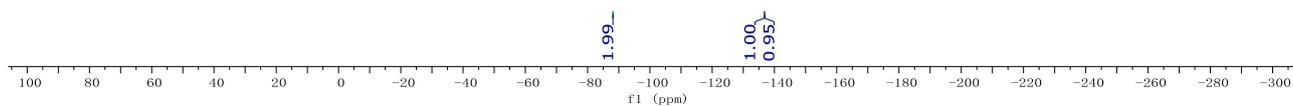
¹³C NMR (100 MHz, CDCl₃)



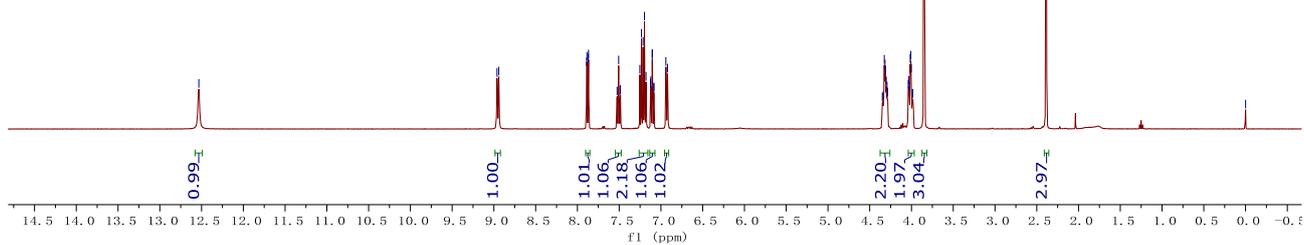


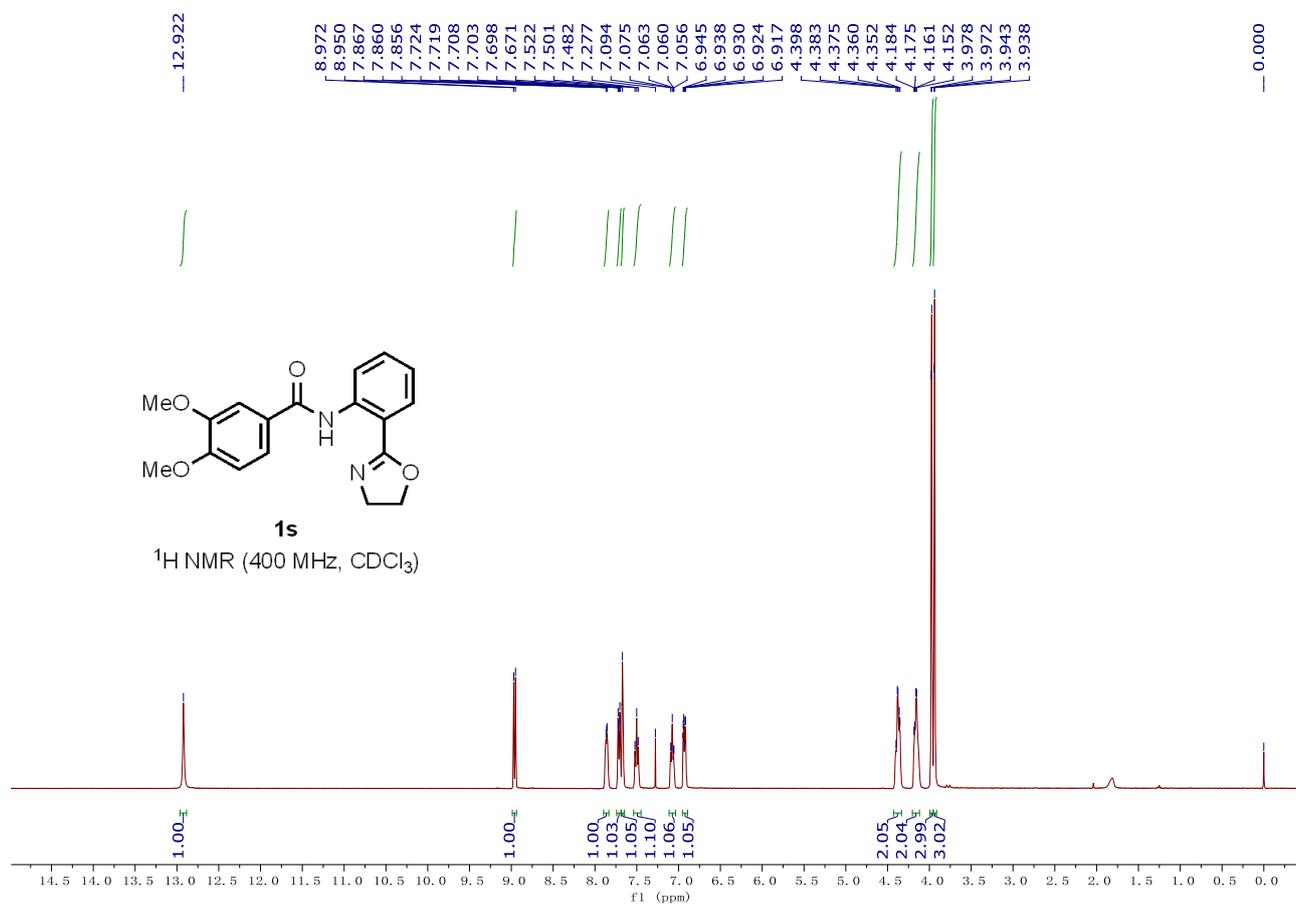
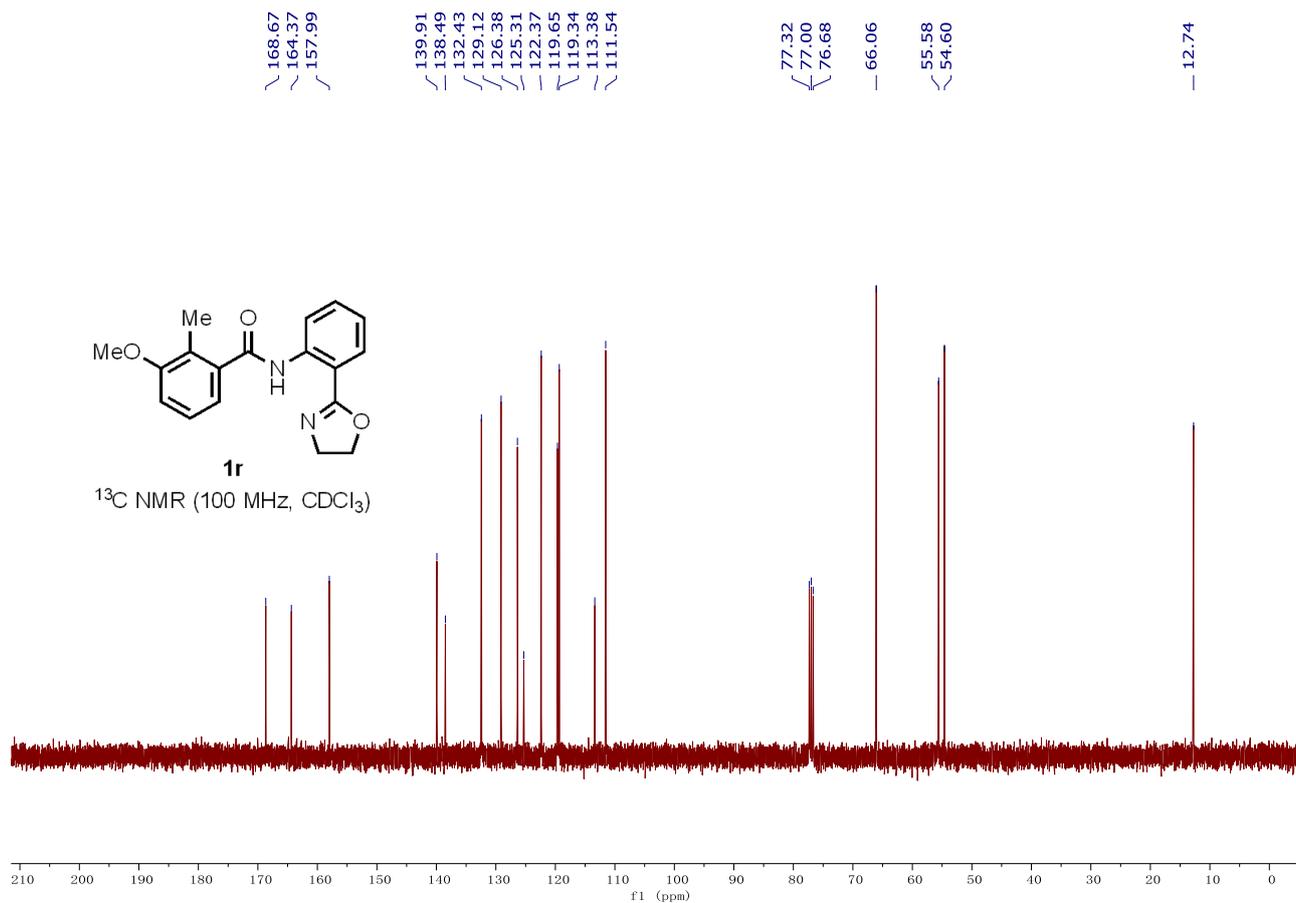


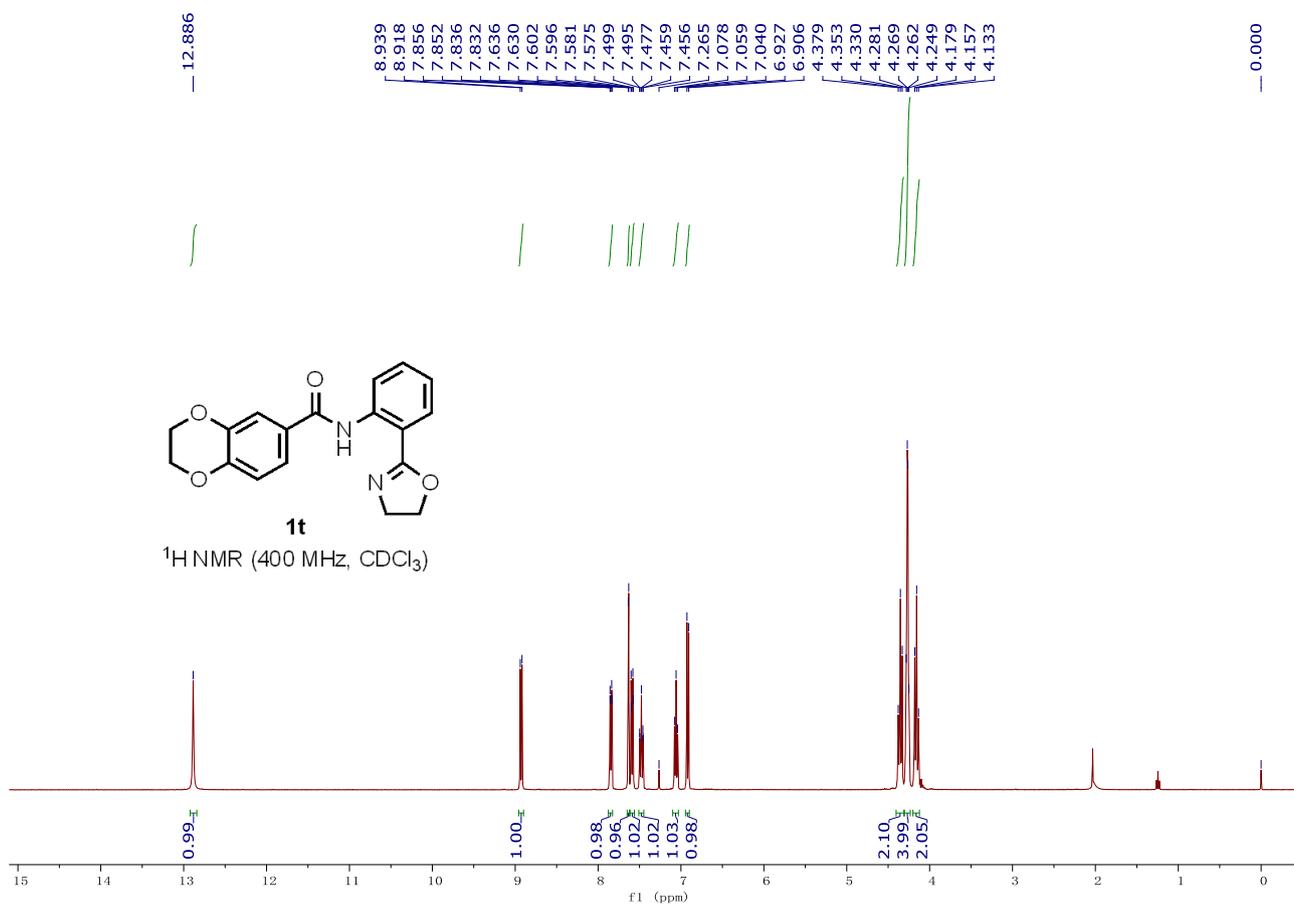
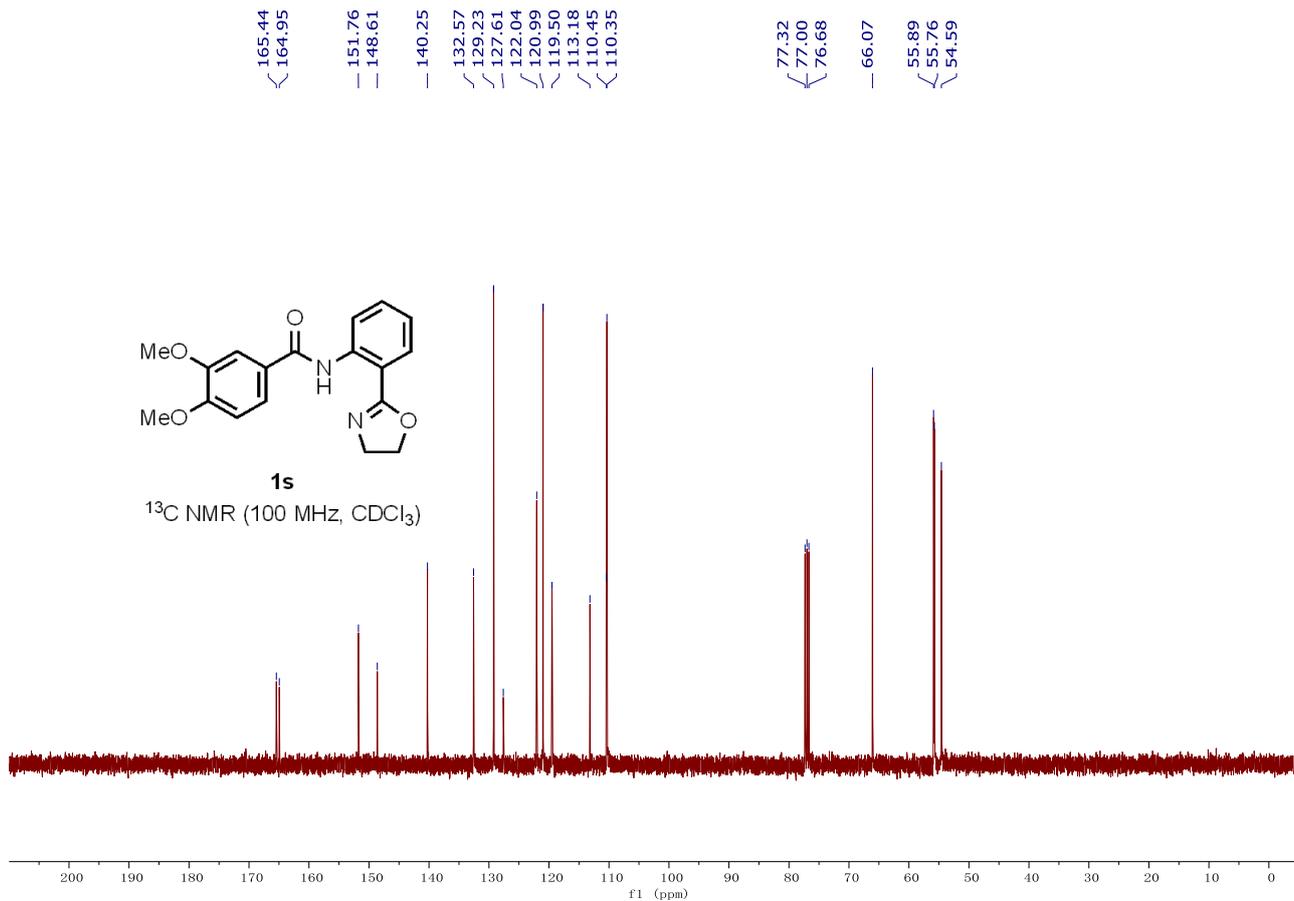
1p
¹⁹F NMR (375 MHz, CDCl₃)

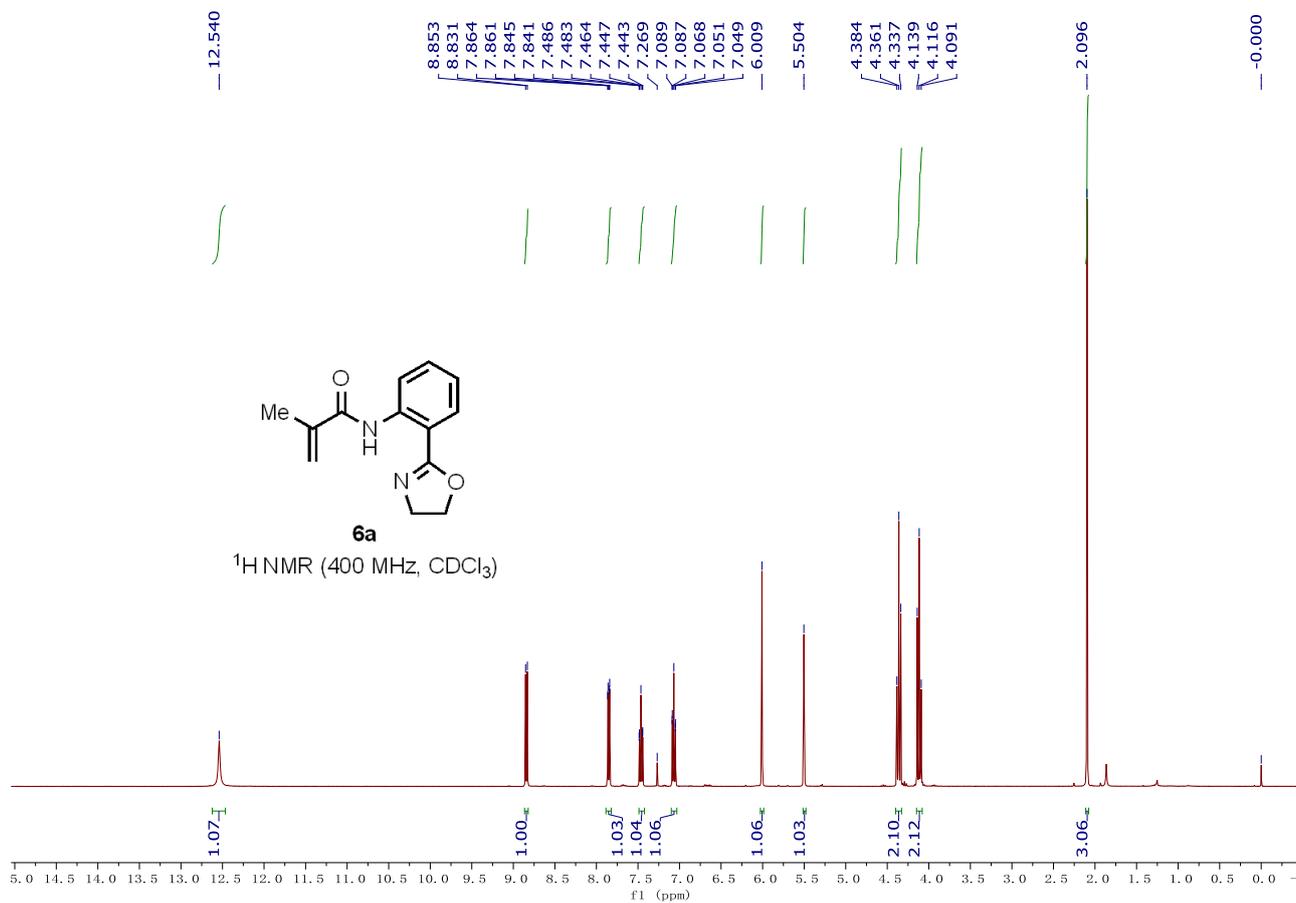
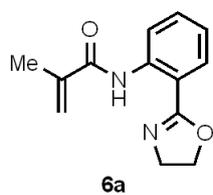
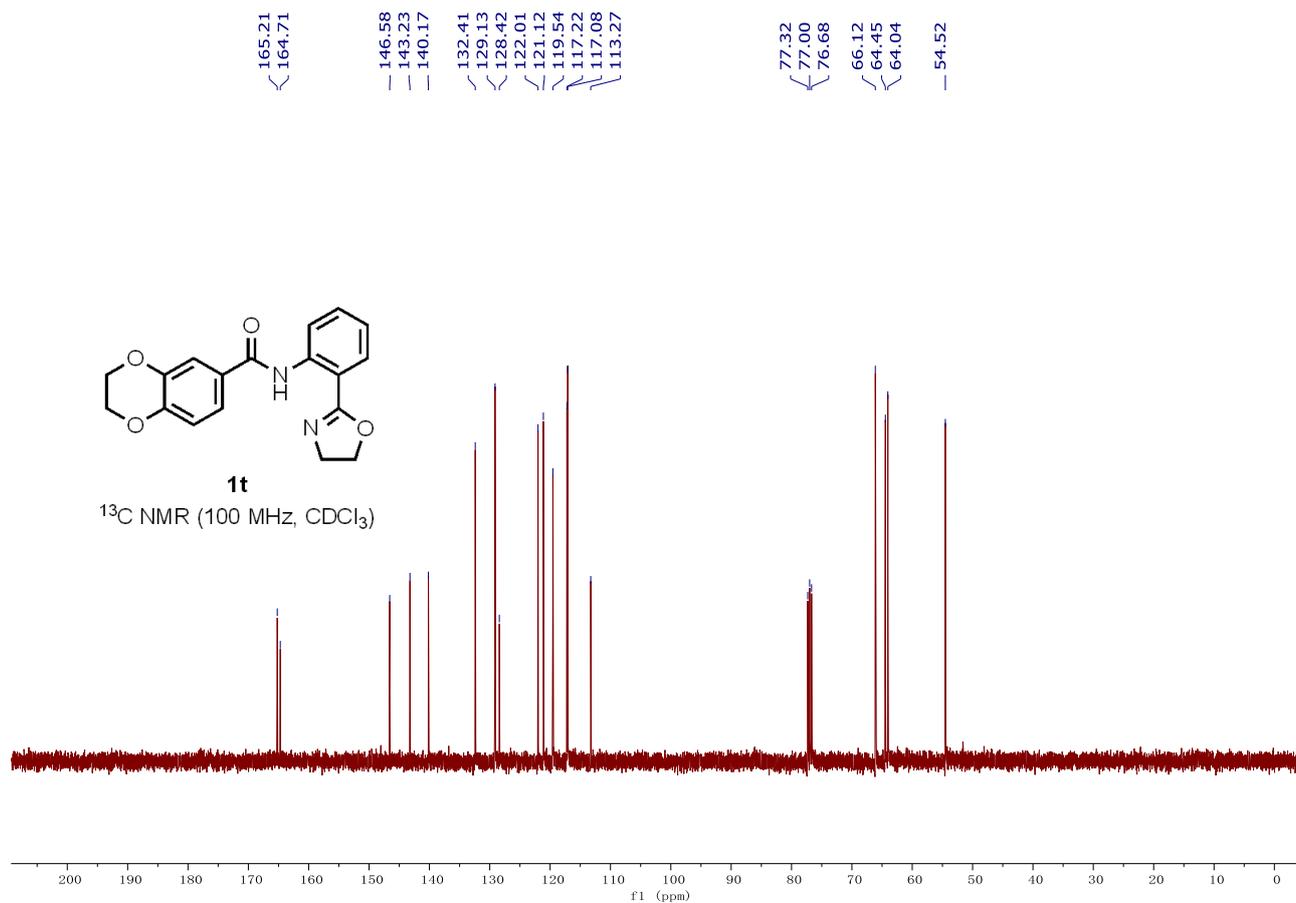
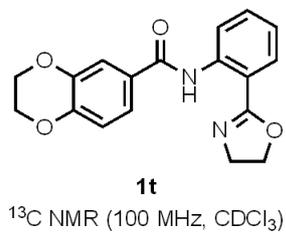


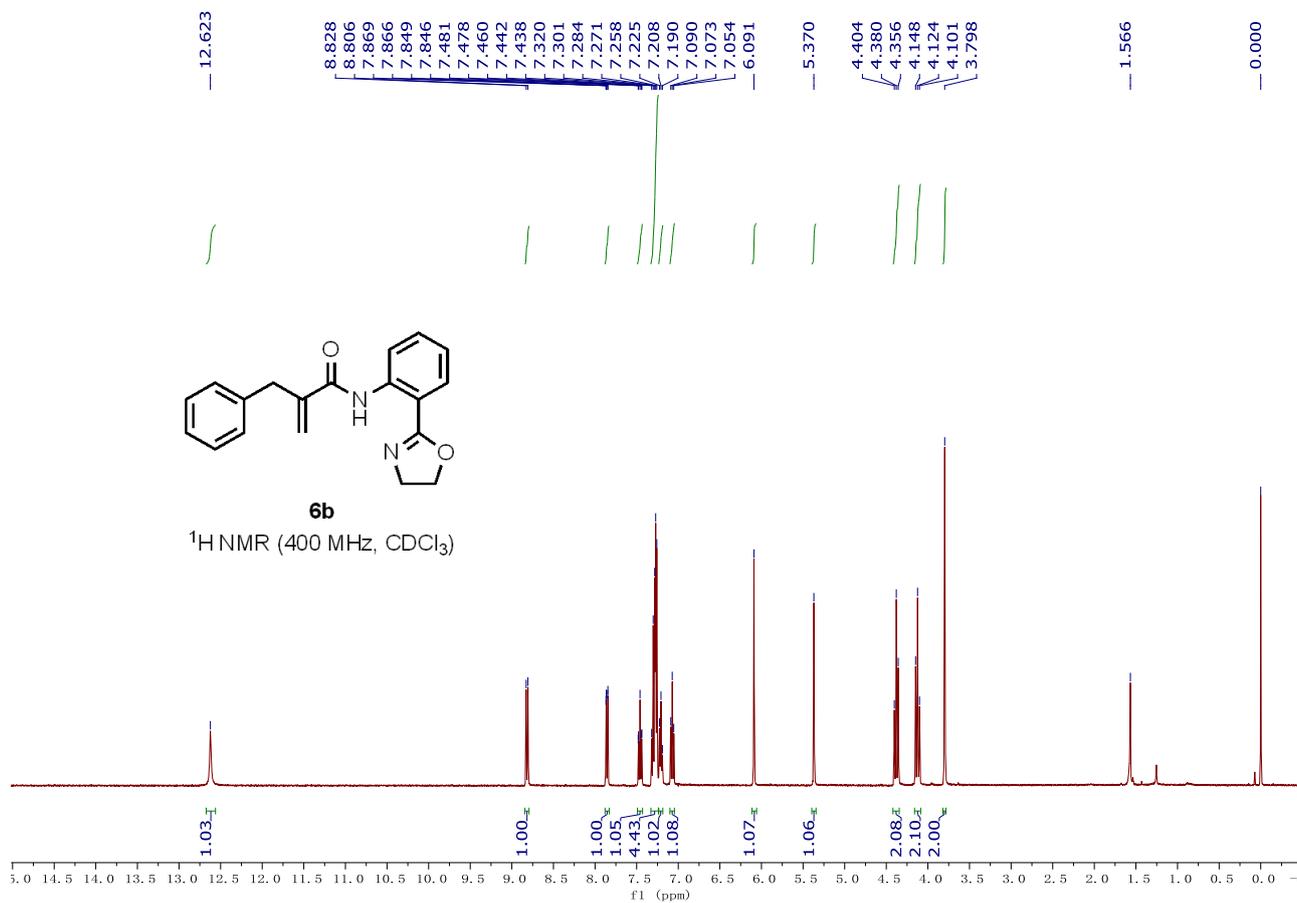
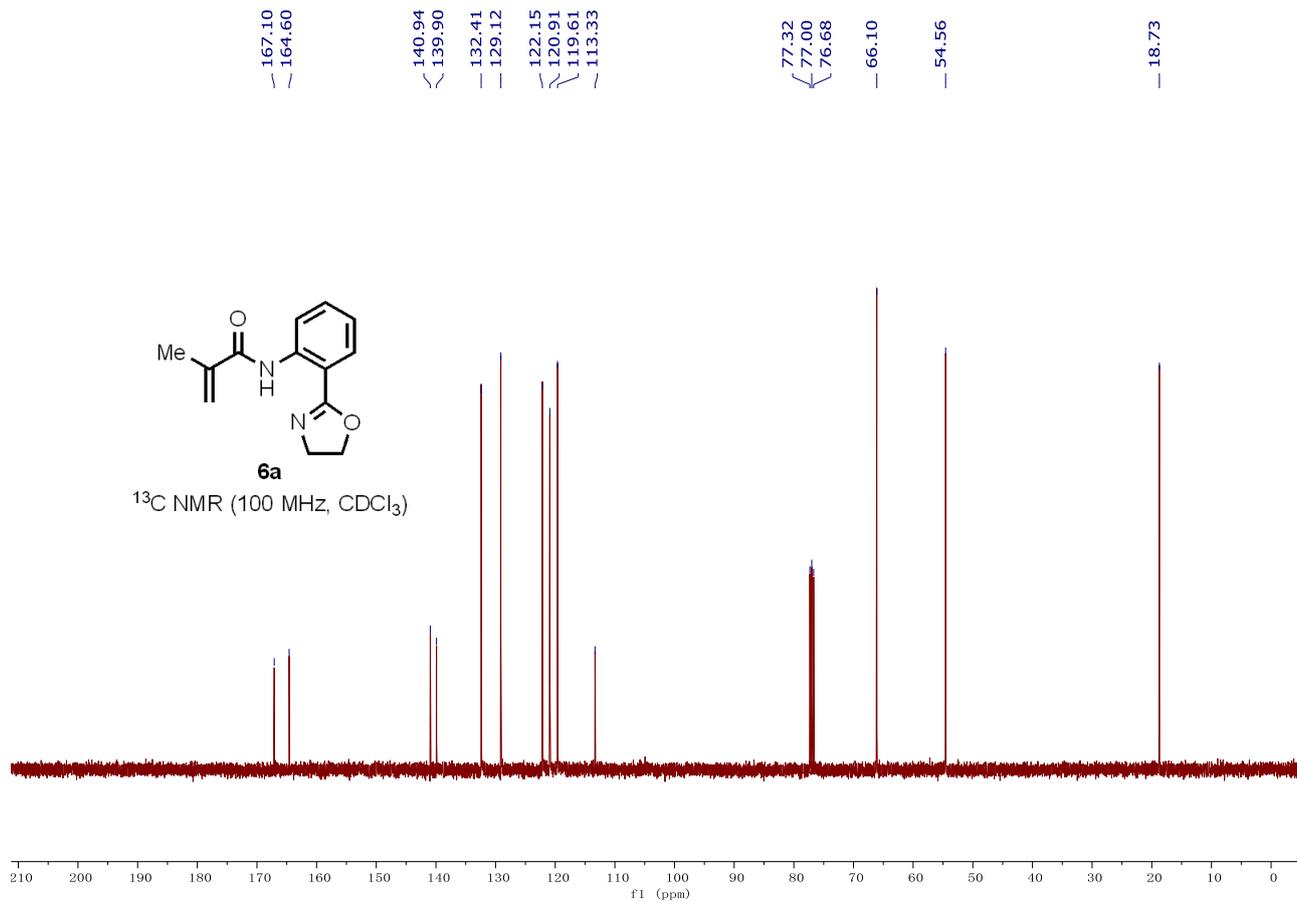
1r
¹H NMR (400 MHz, CDCl₃)

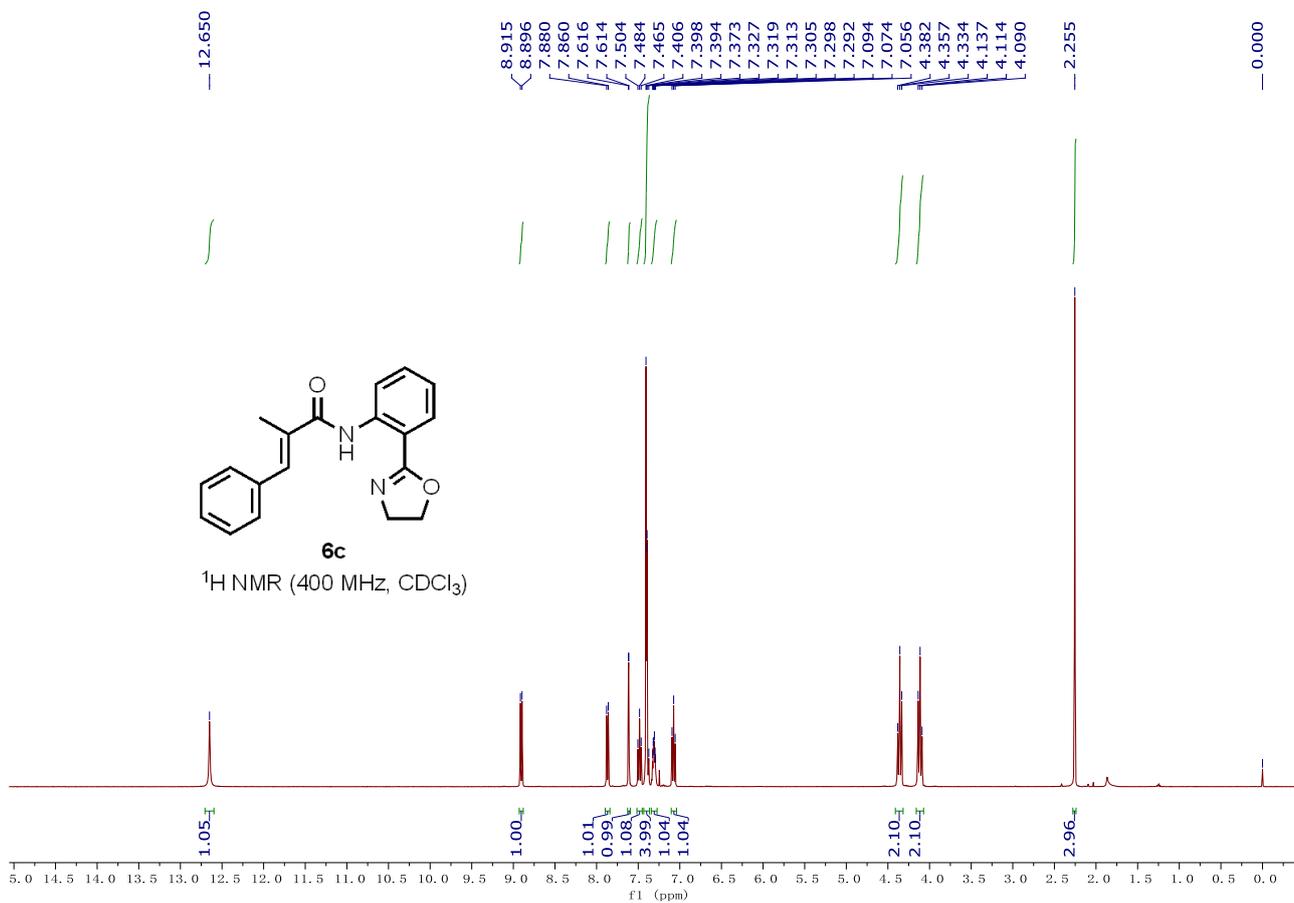
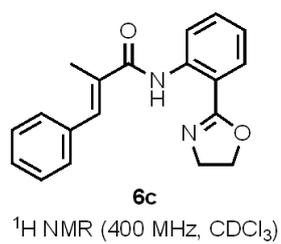
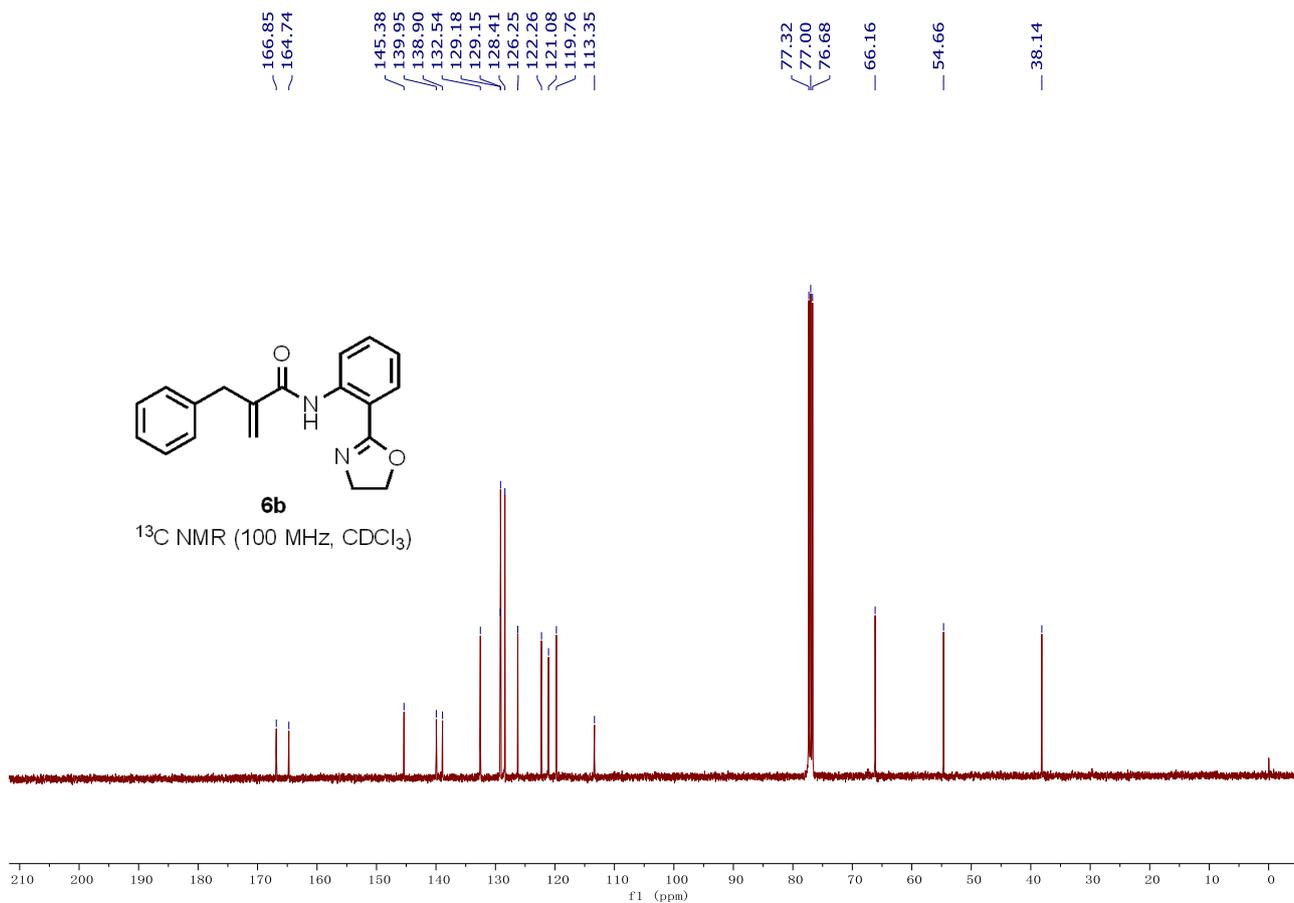
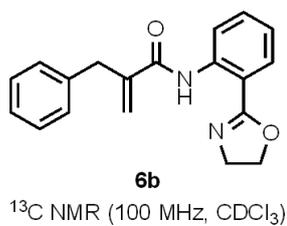


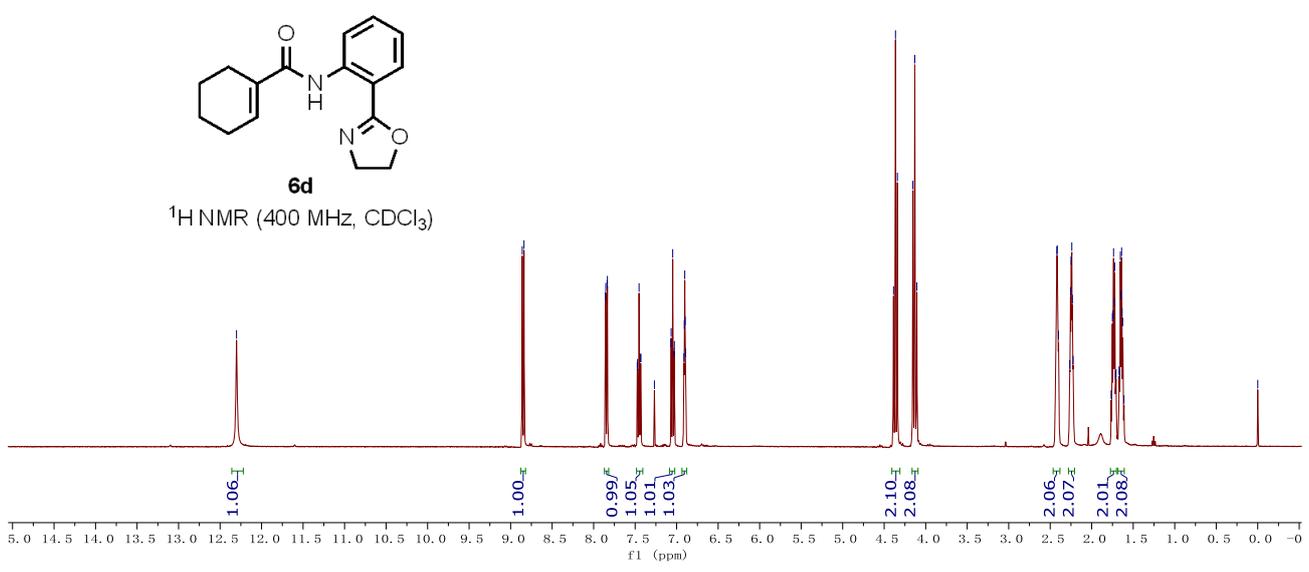
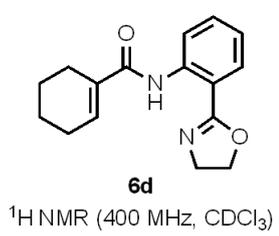
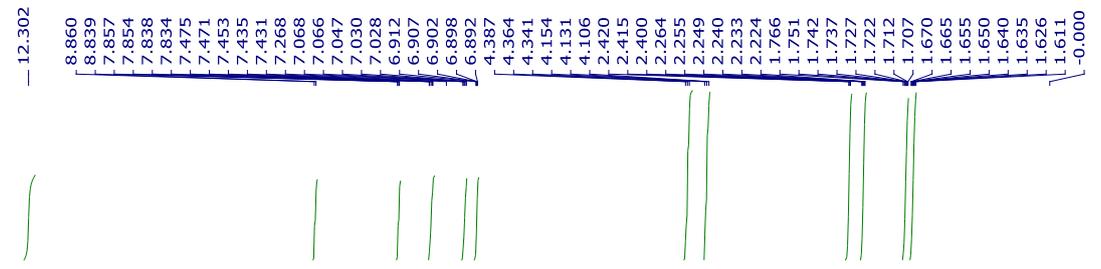
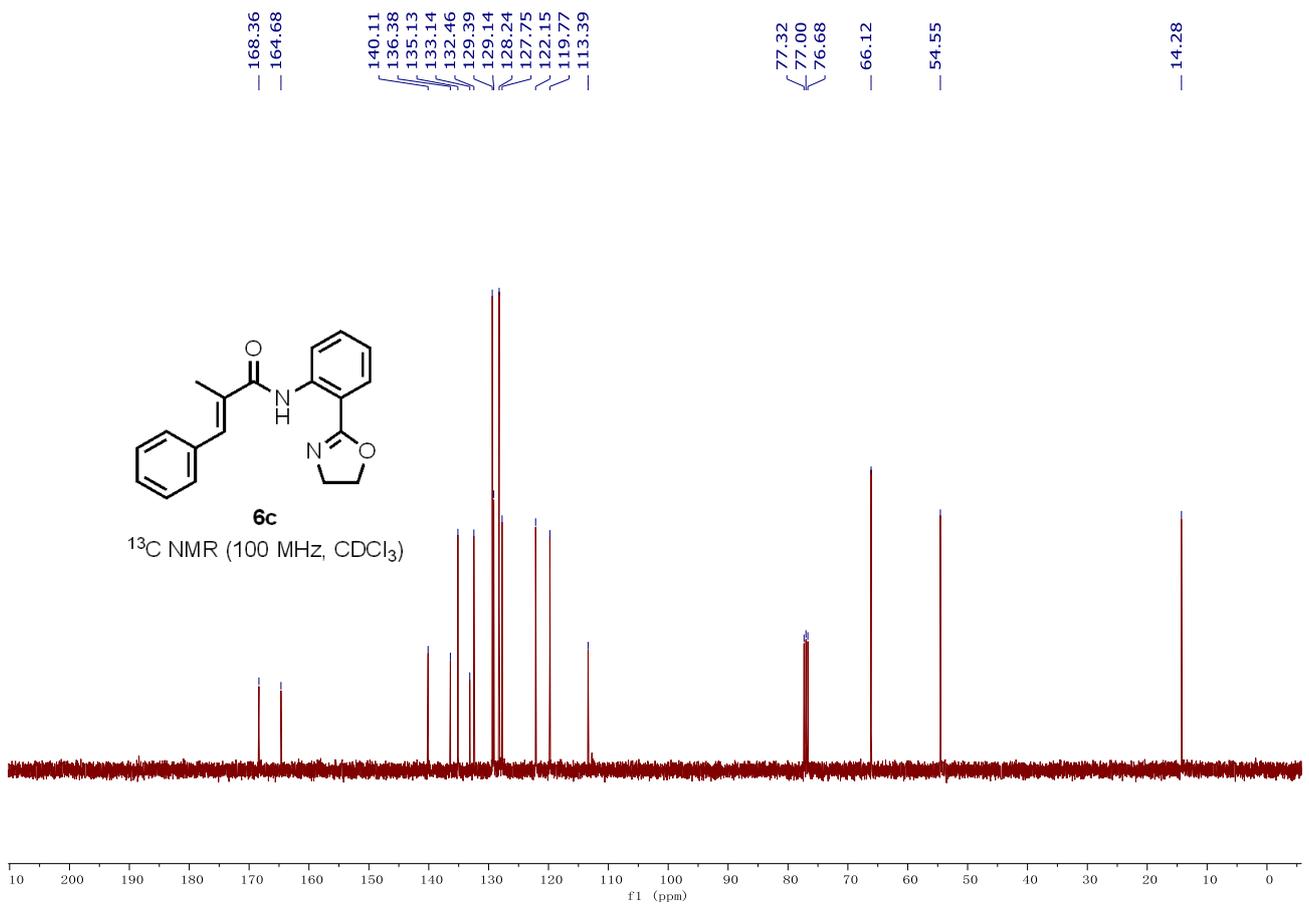
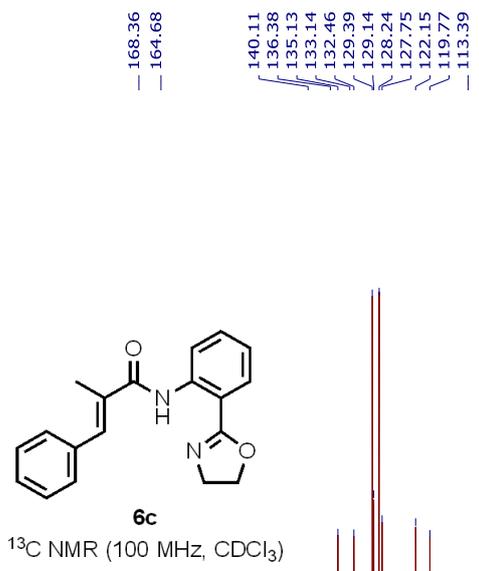


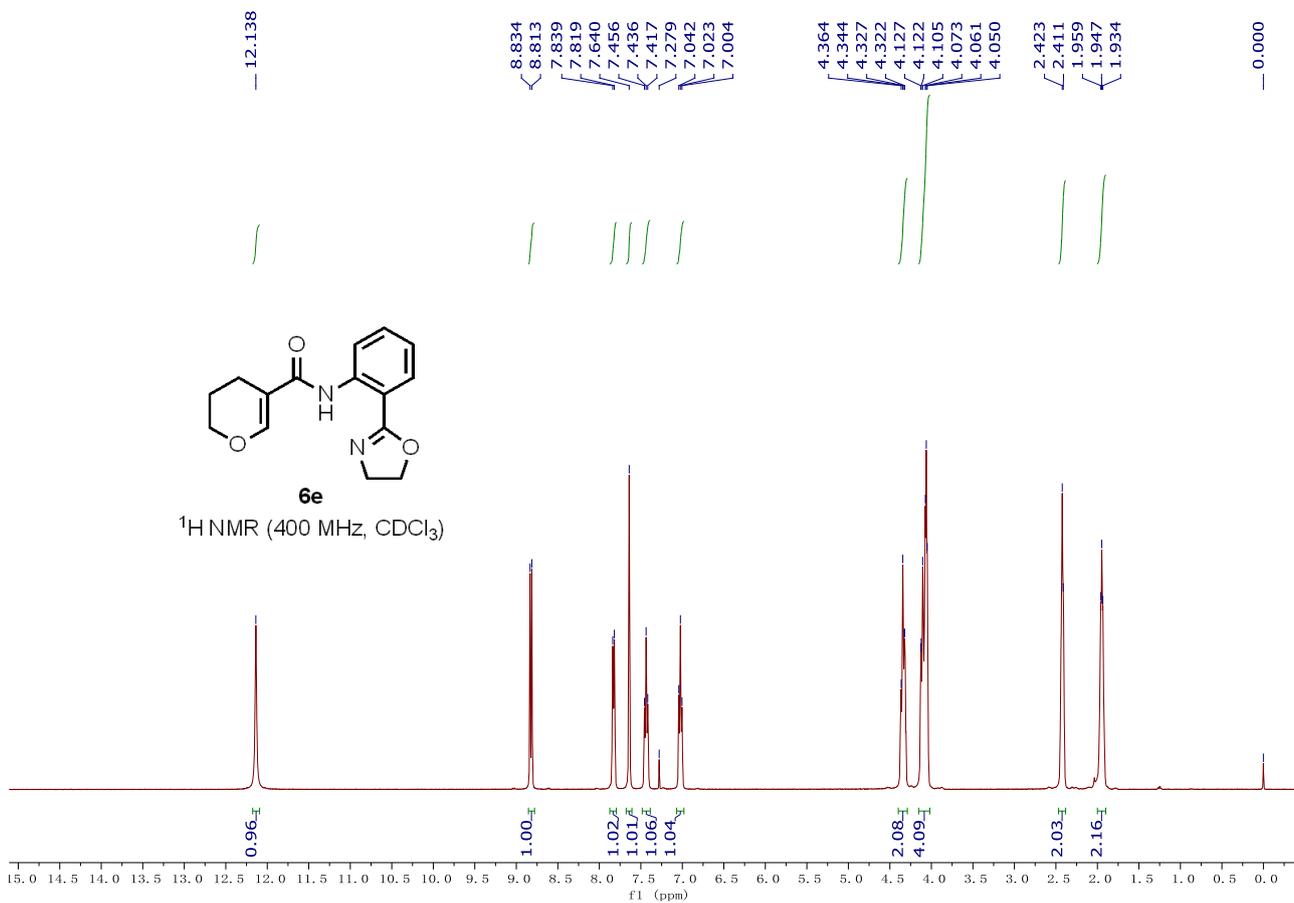
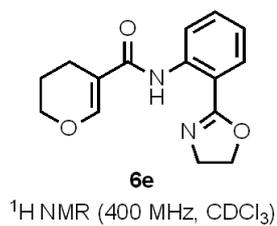
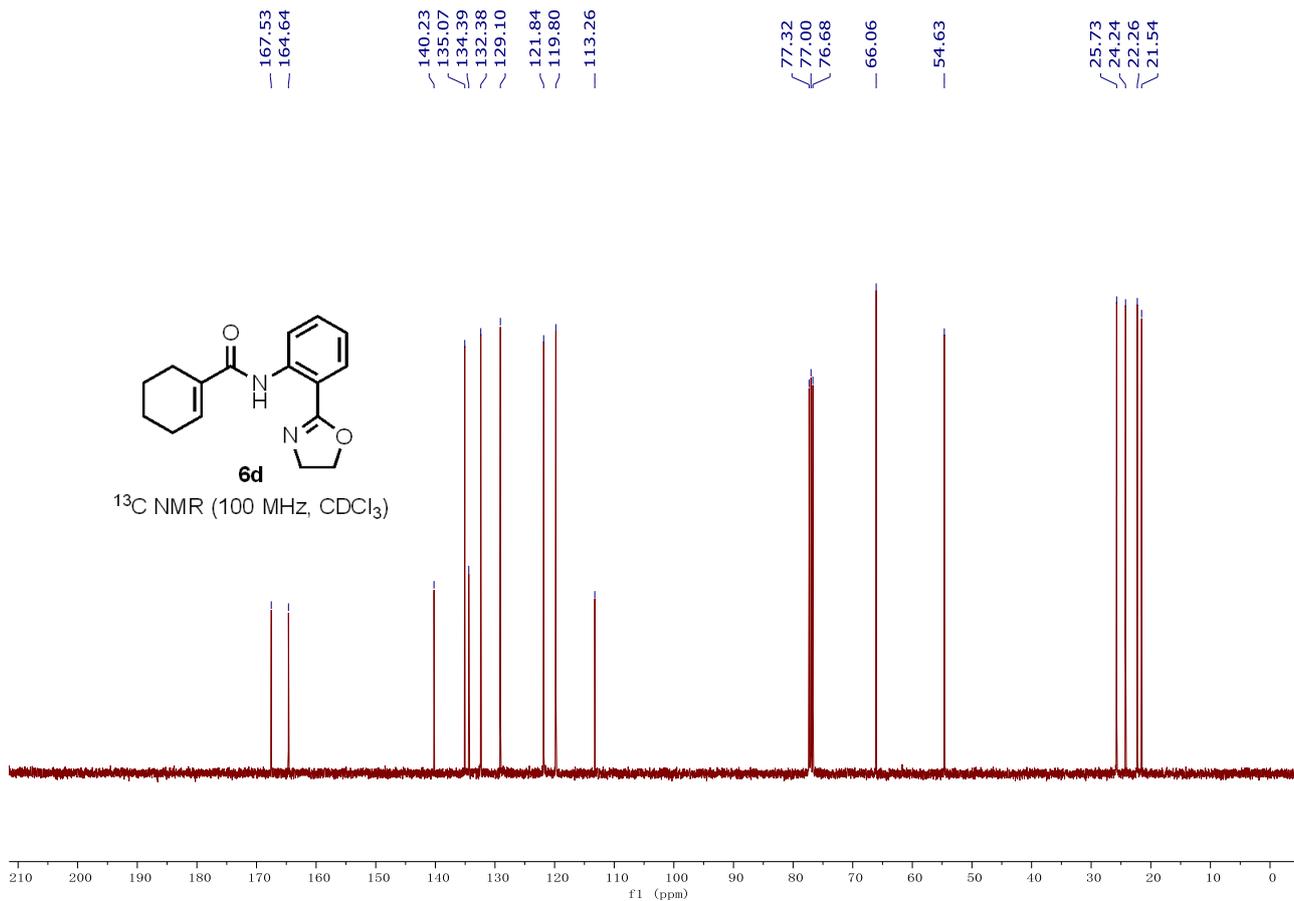
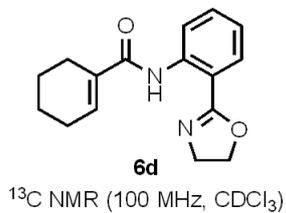


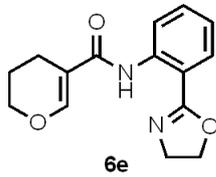




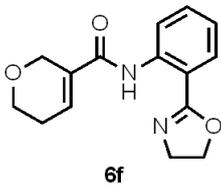
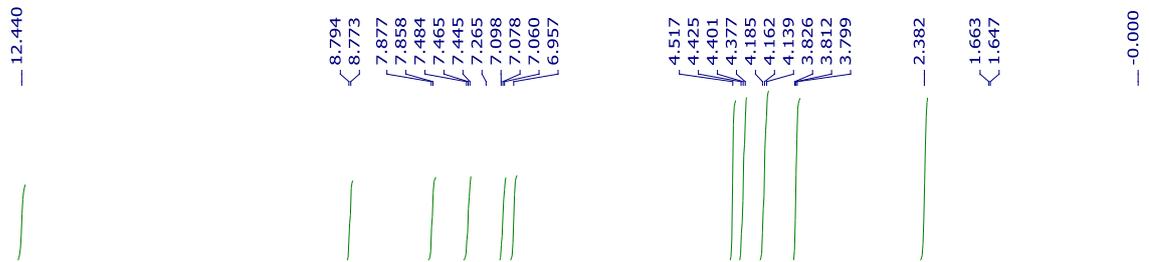
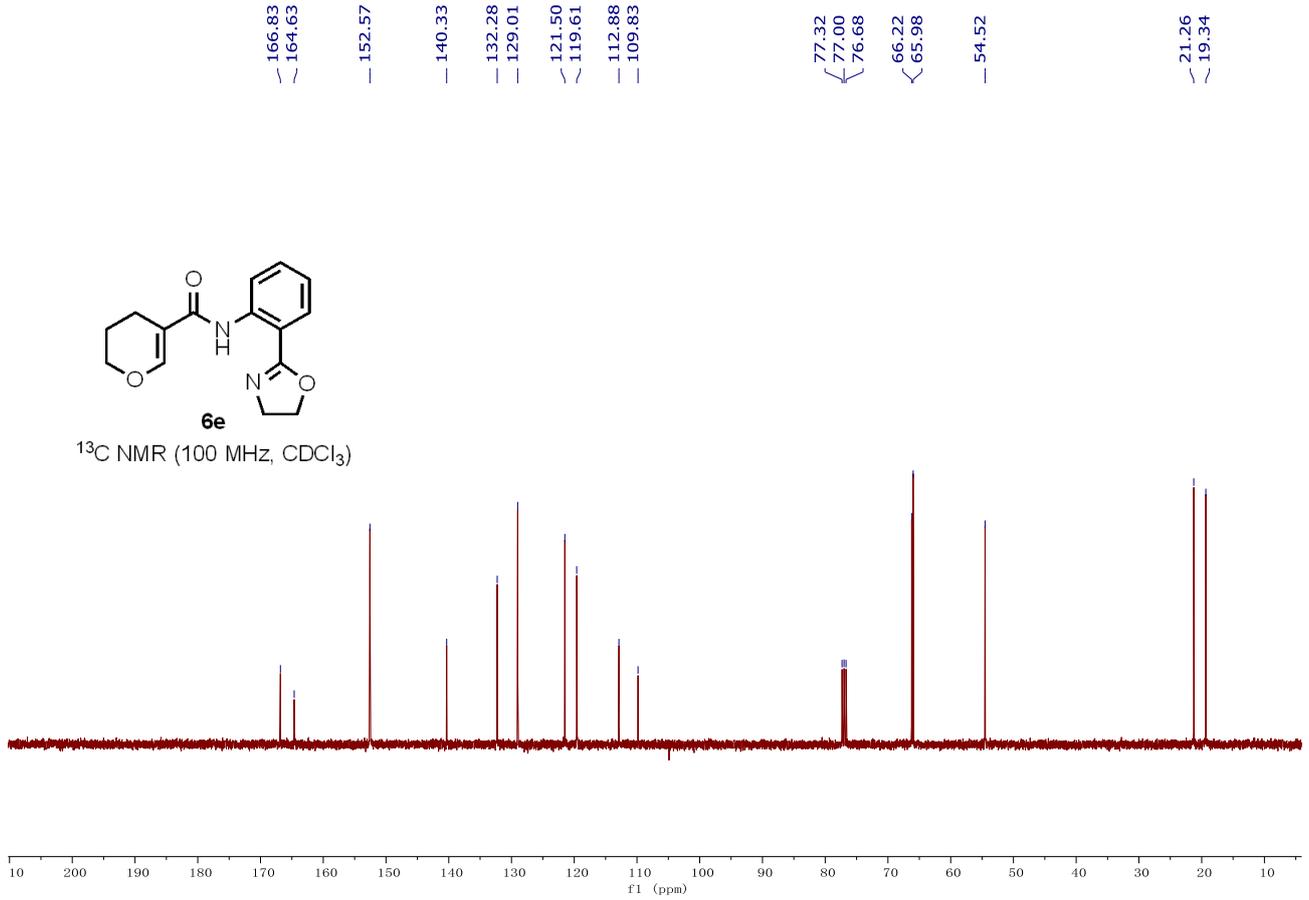




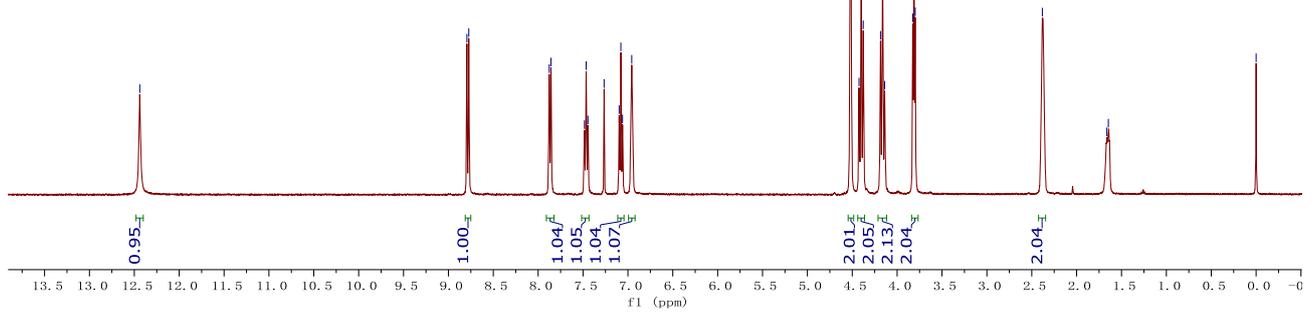


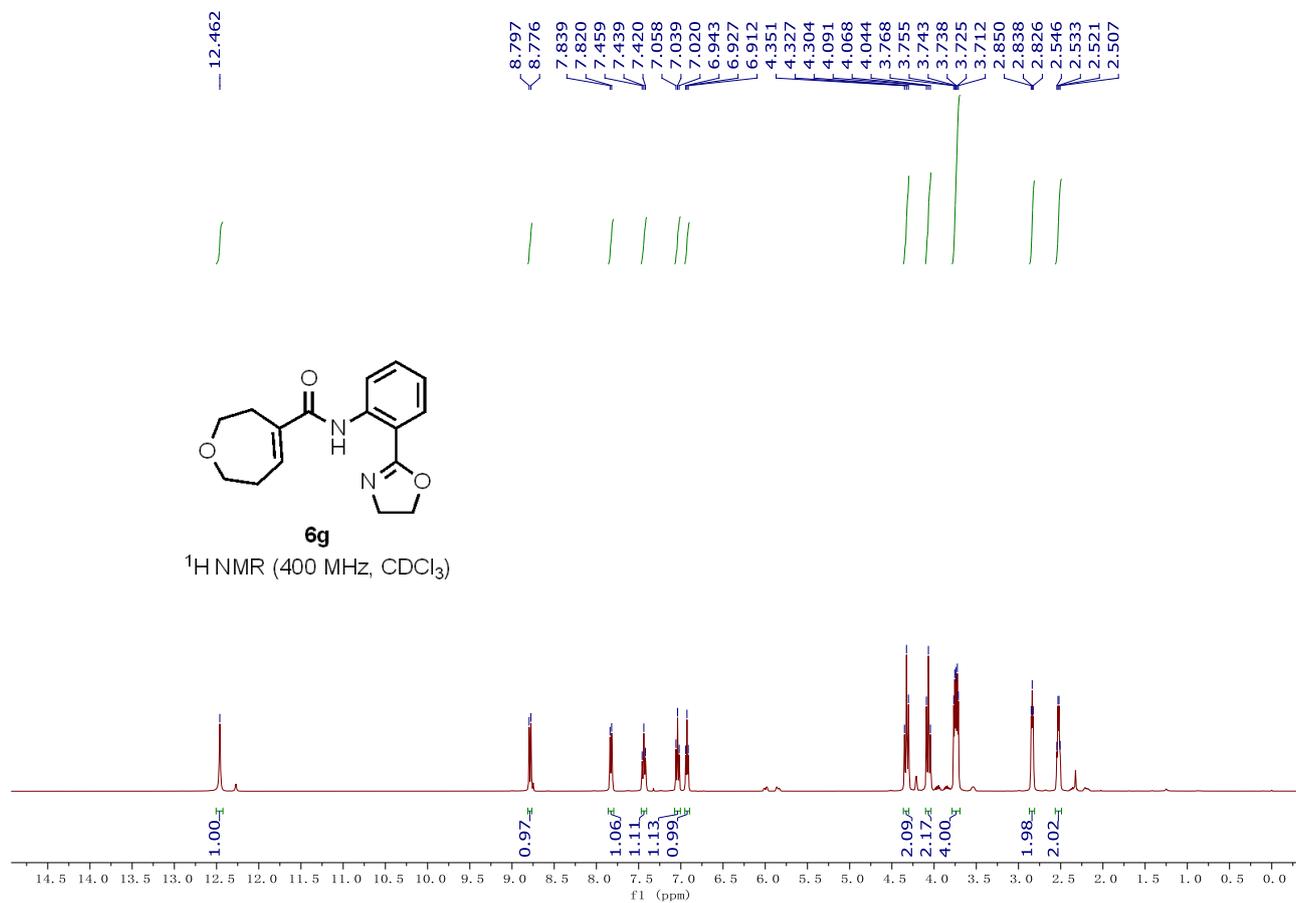
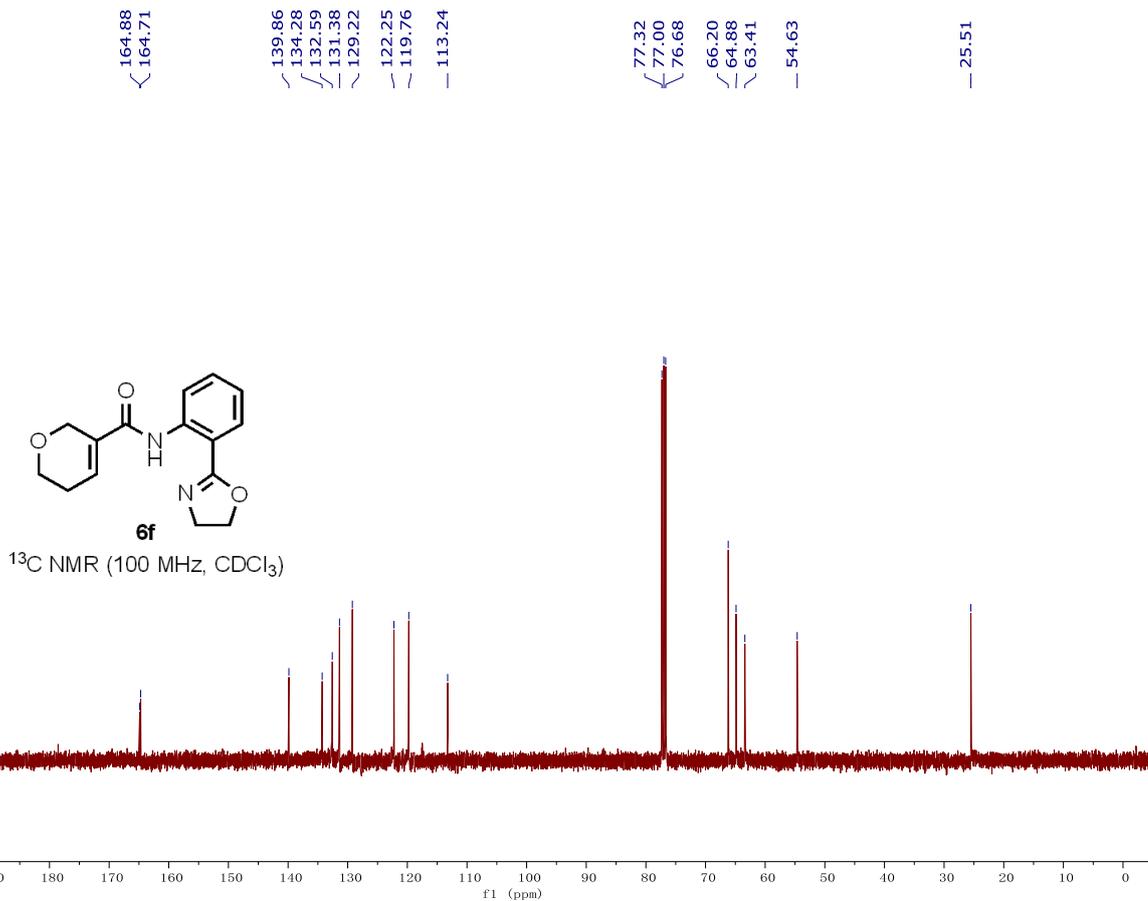


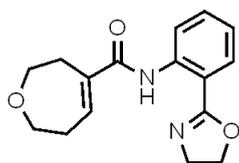
^{13}C NMR (100 MHz, CDCl_3)



^1H NMR (400 MHz, CDCl_3)

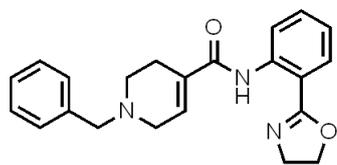
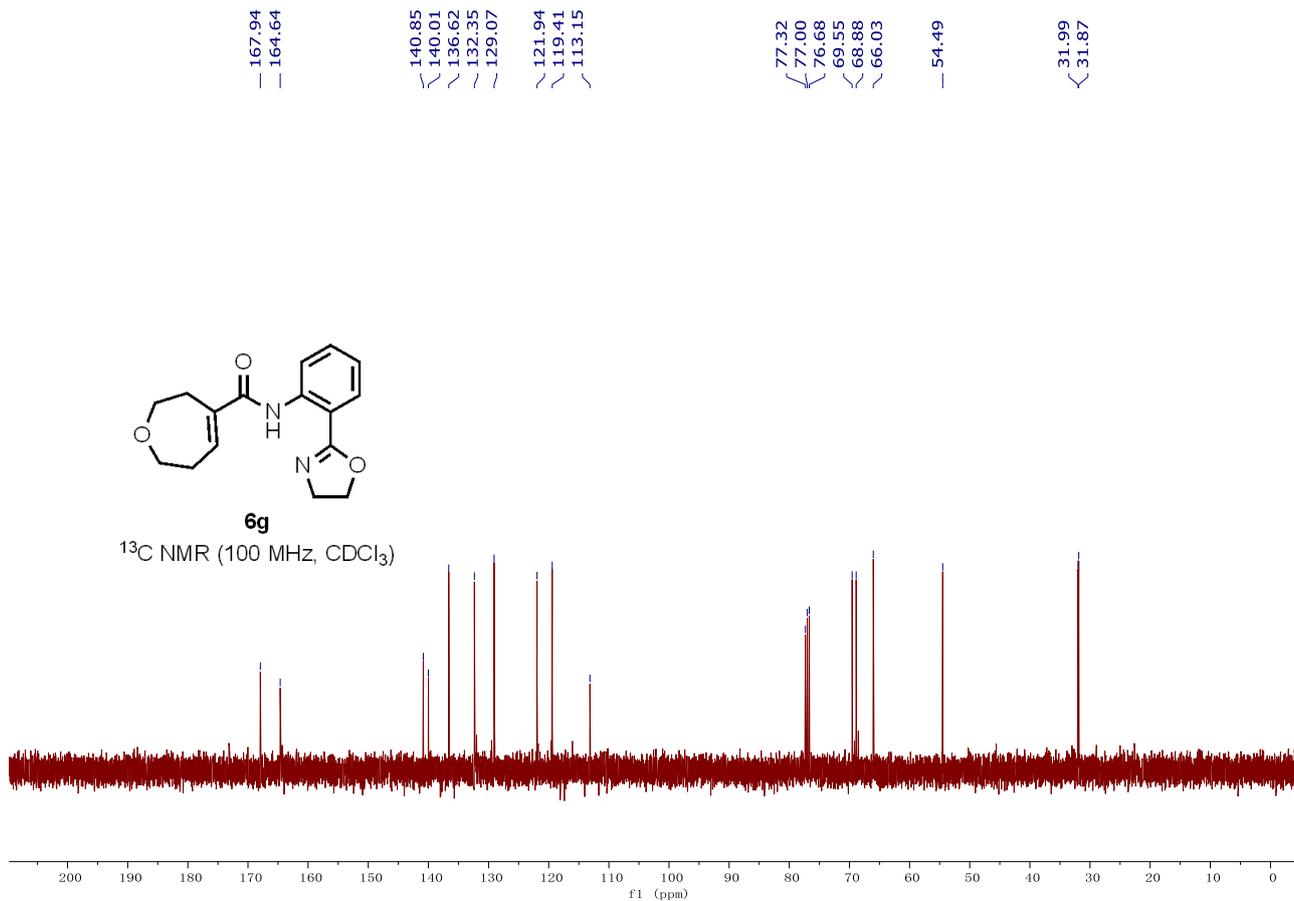






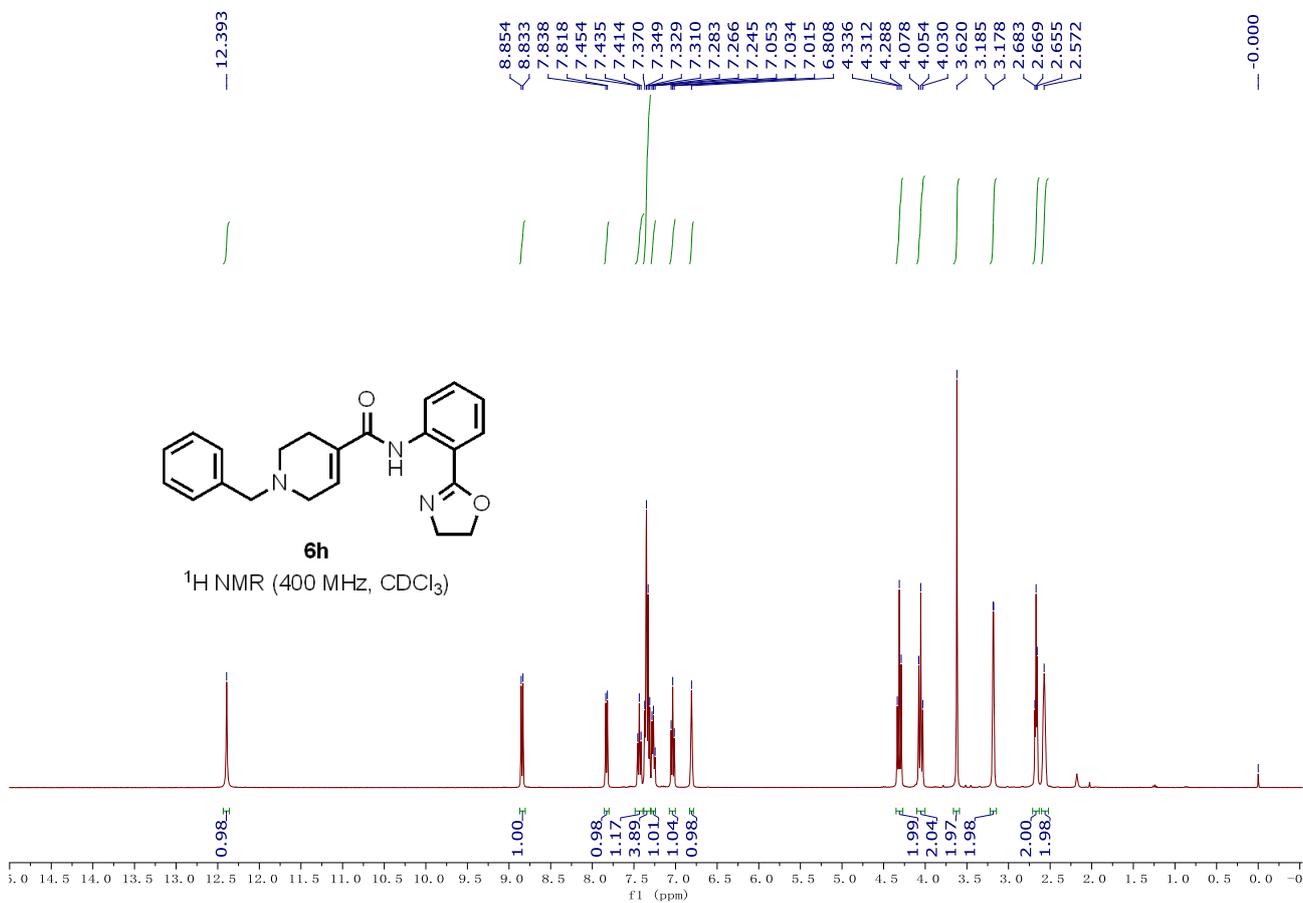
6g

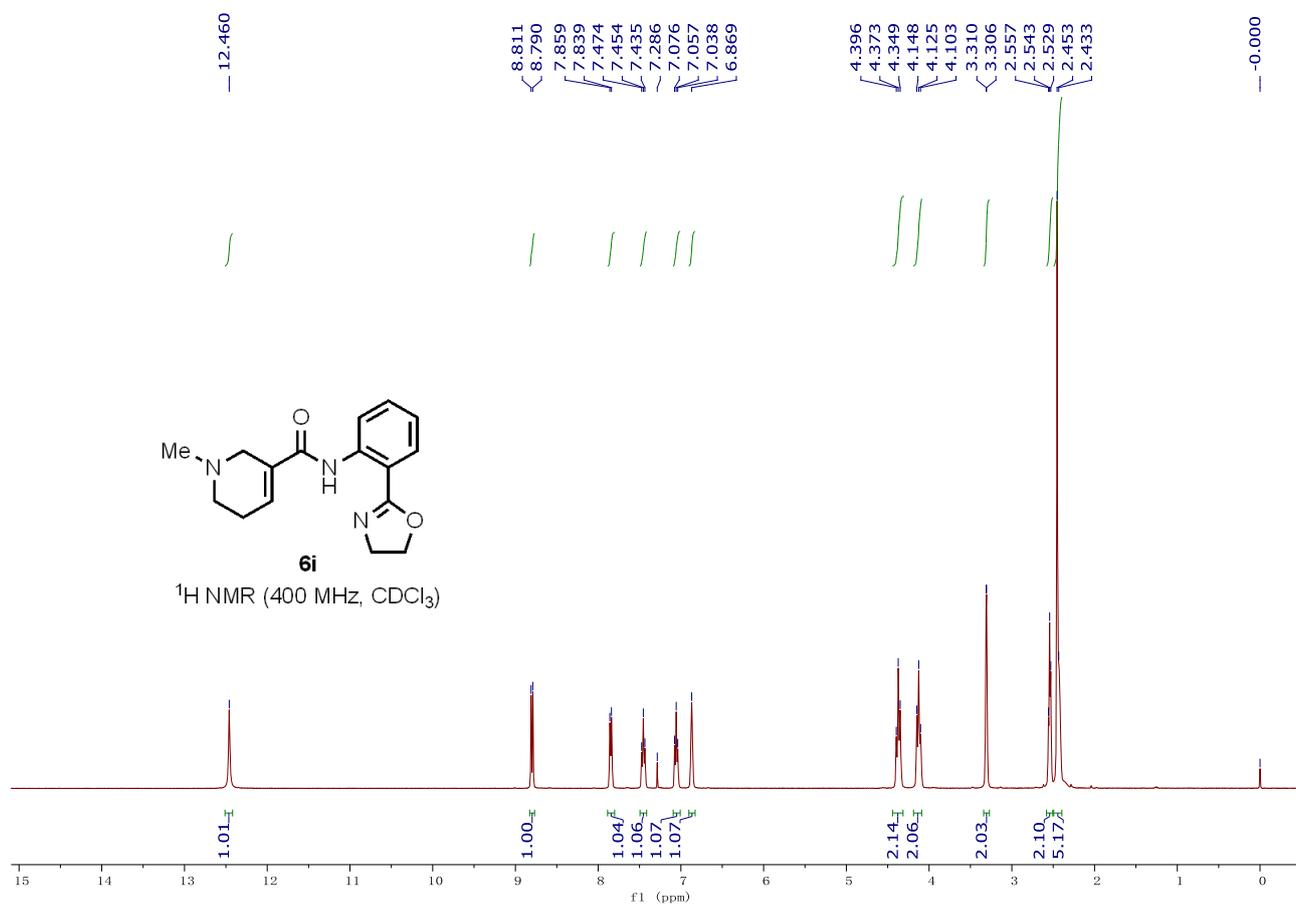
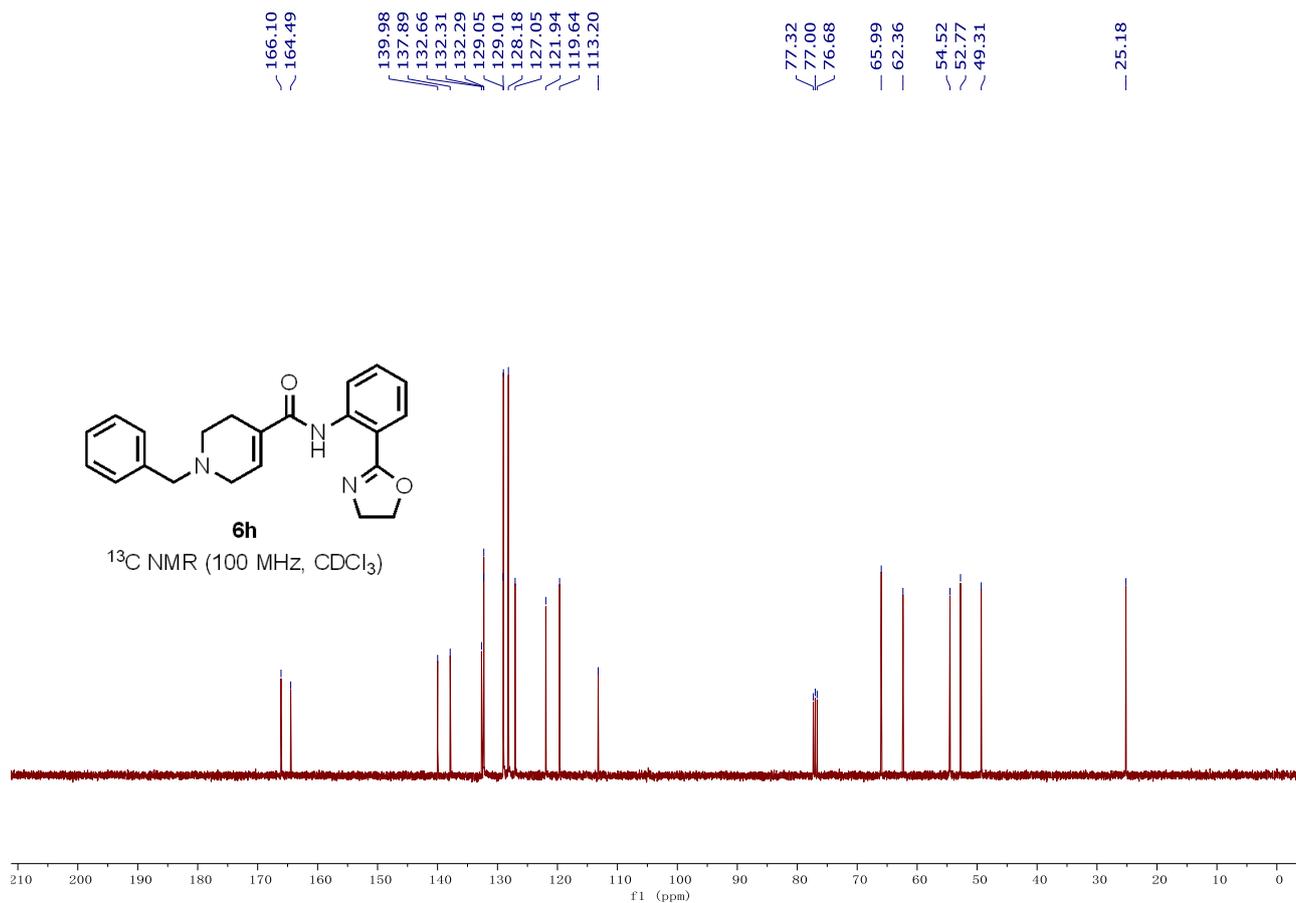
^{13}C NMR (100 MHz, CDCl_3)

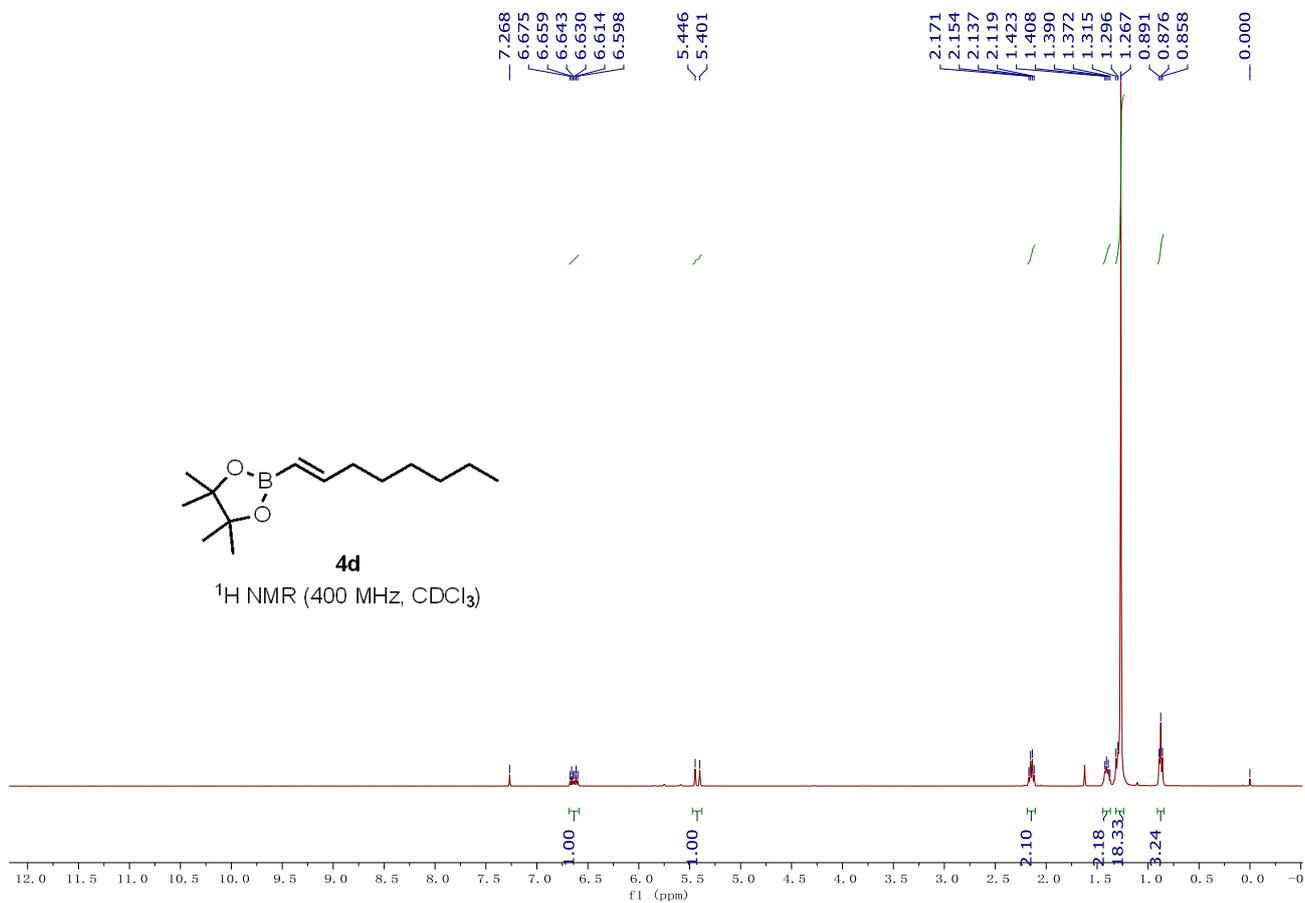
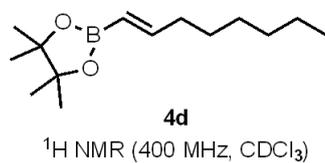
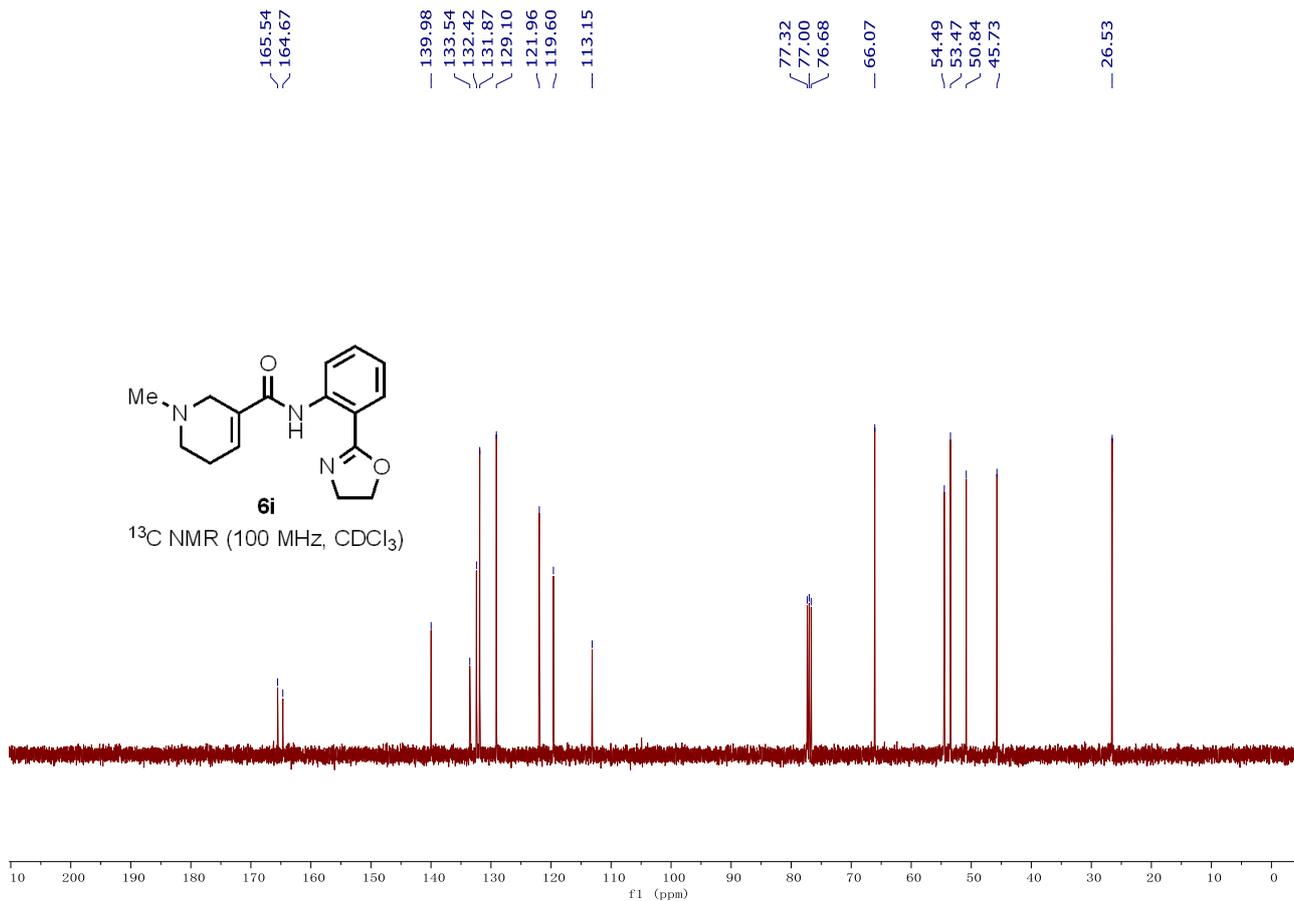
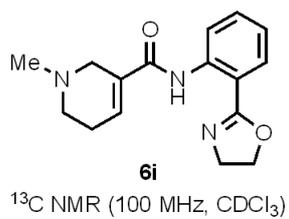


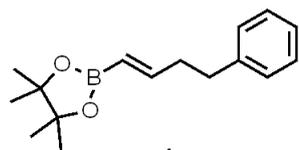
6h

^1H NMR (400 MHz, CDCl_3)



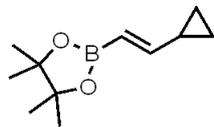
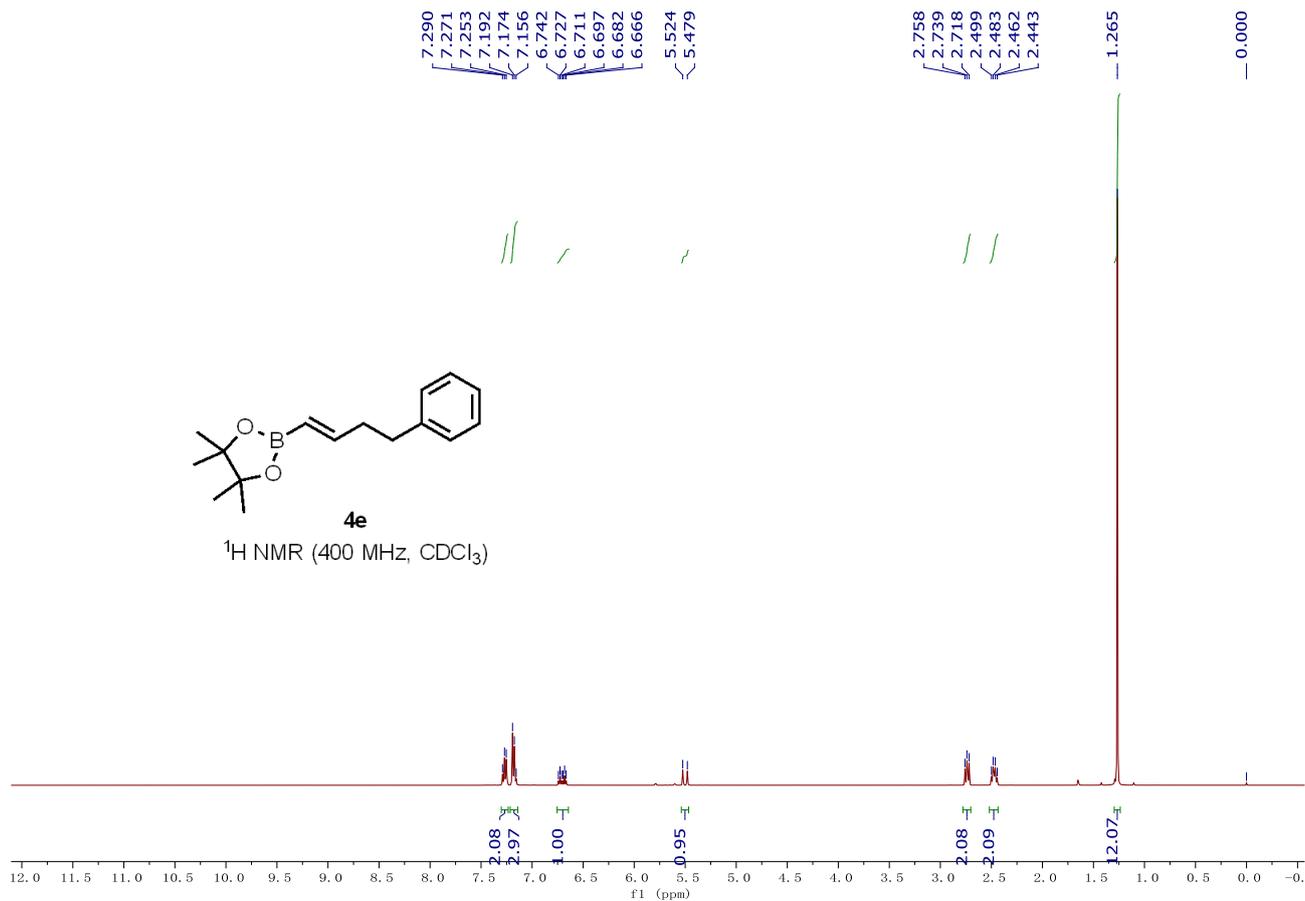






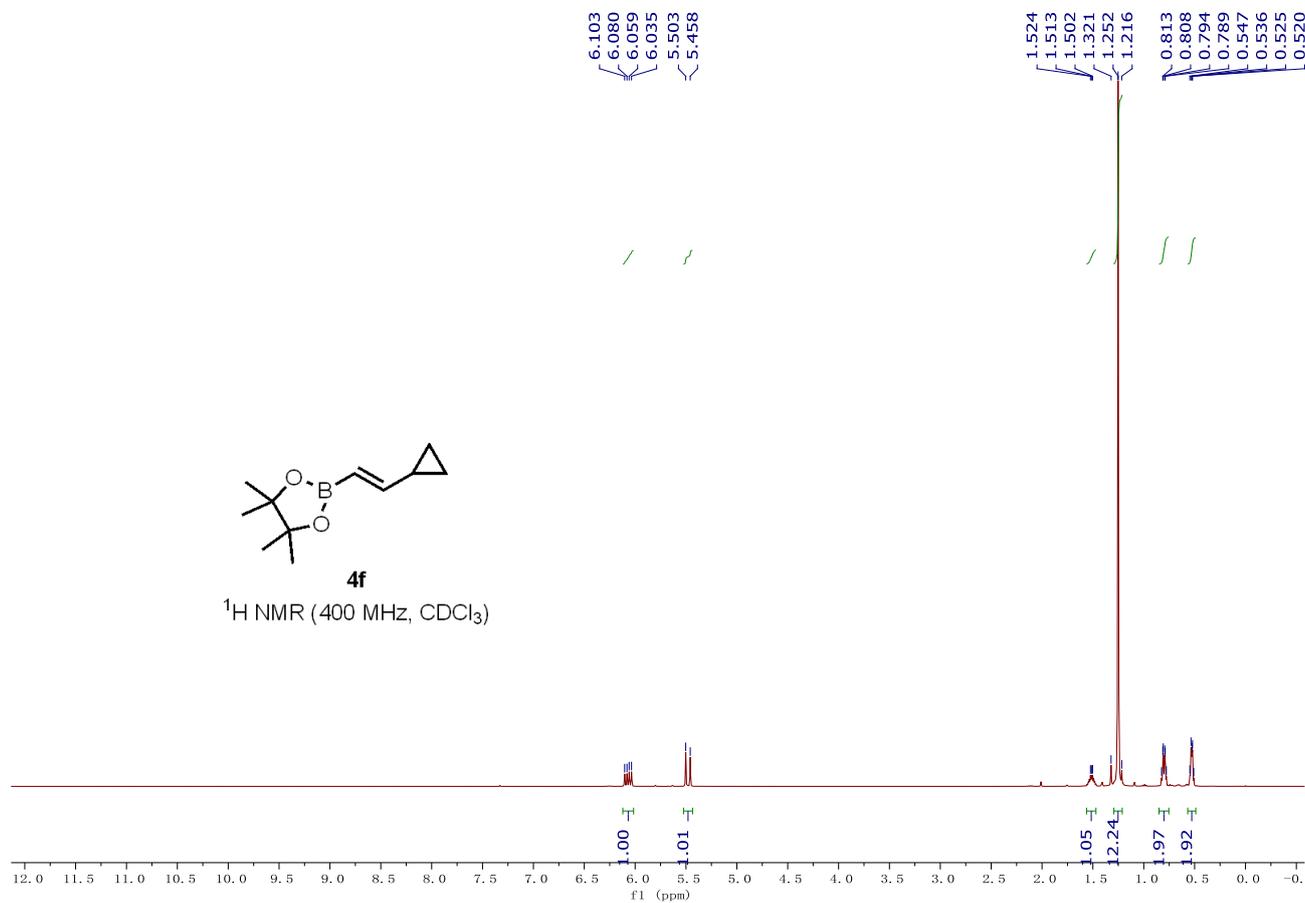
4e

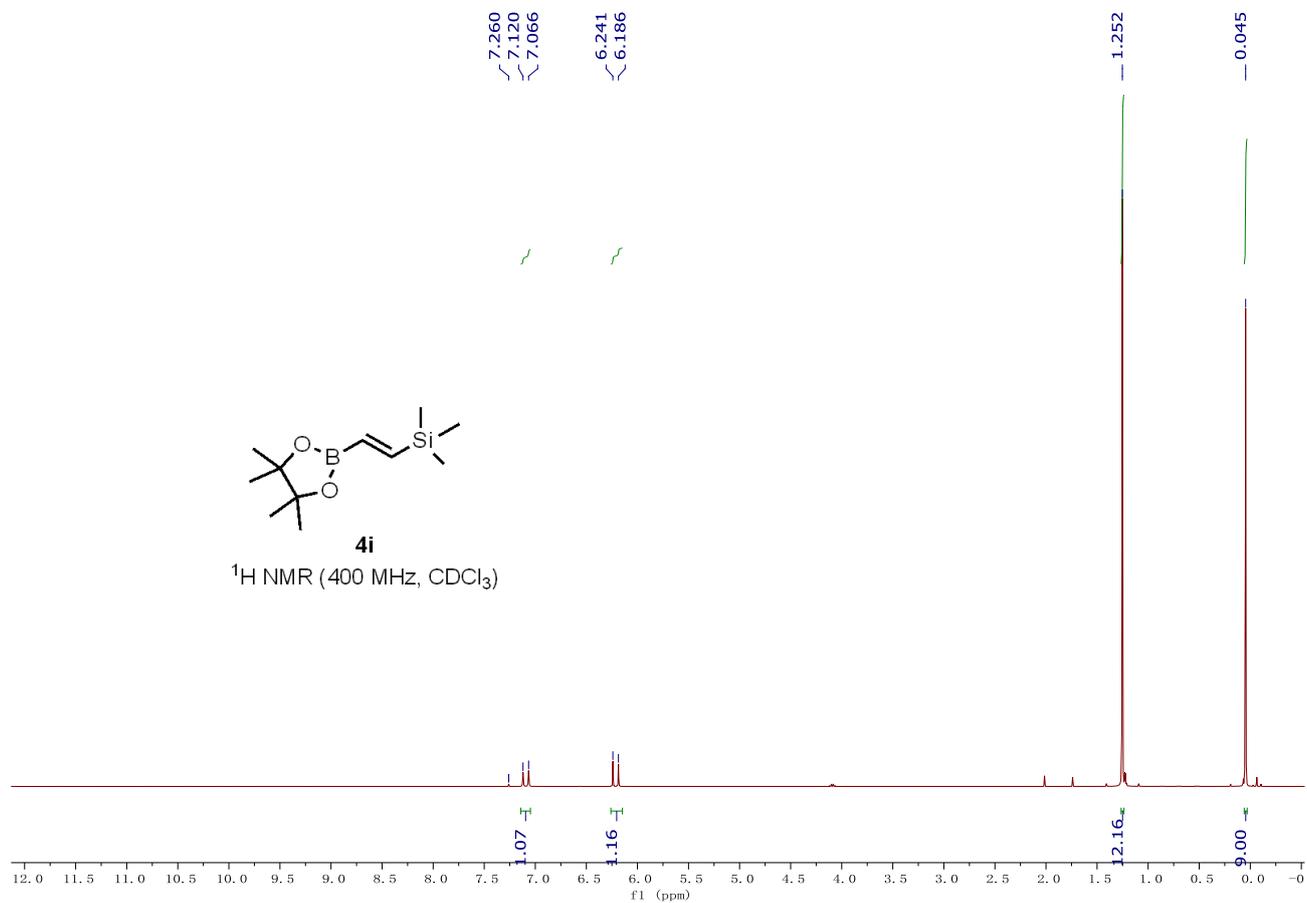
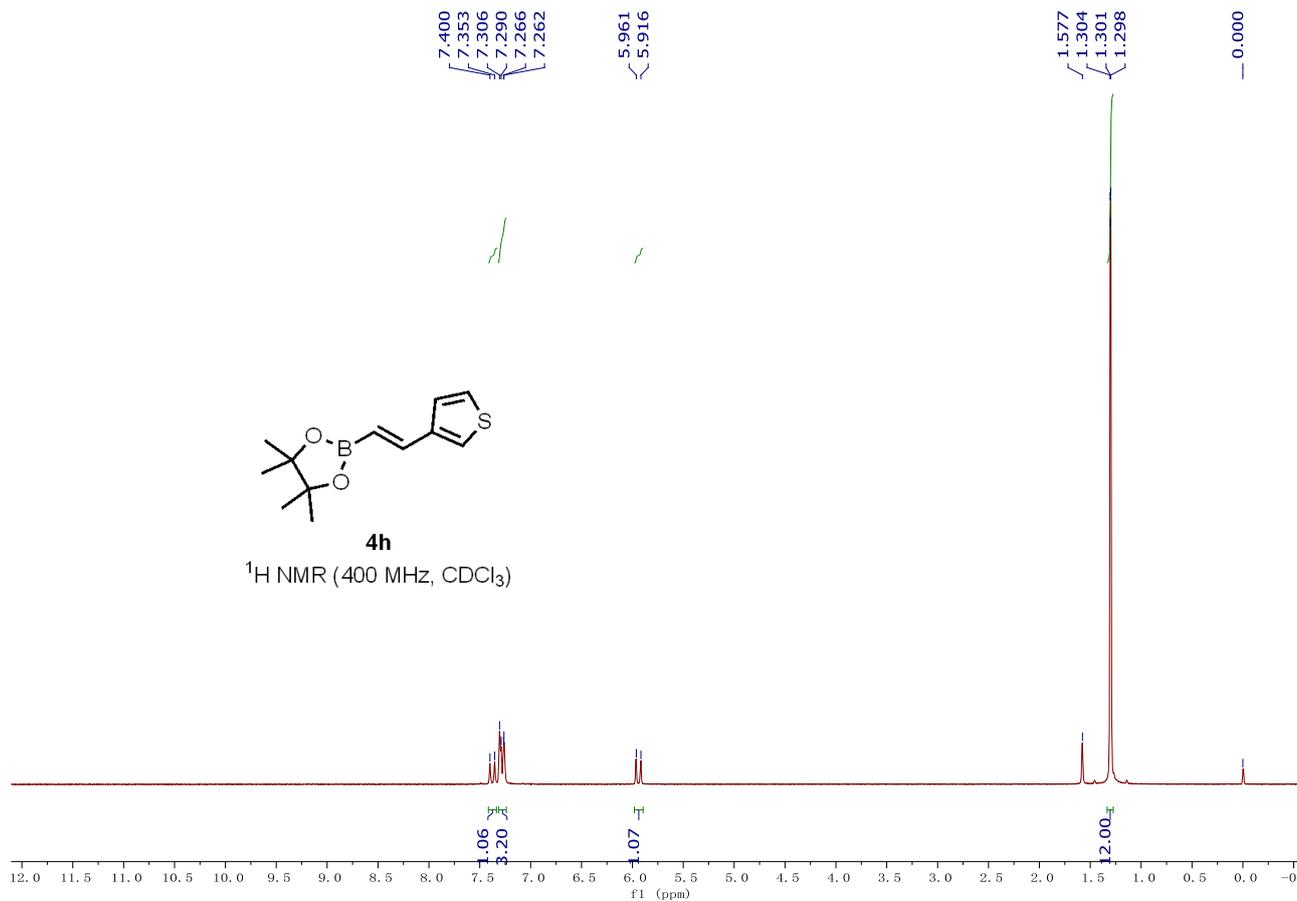
¹H NMR (400 MHz, CDCl₃)

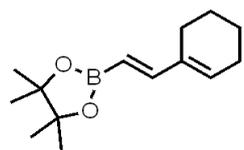


4f

¹H NMR (400 MHz, CDCl₃)

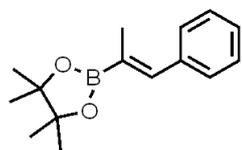
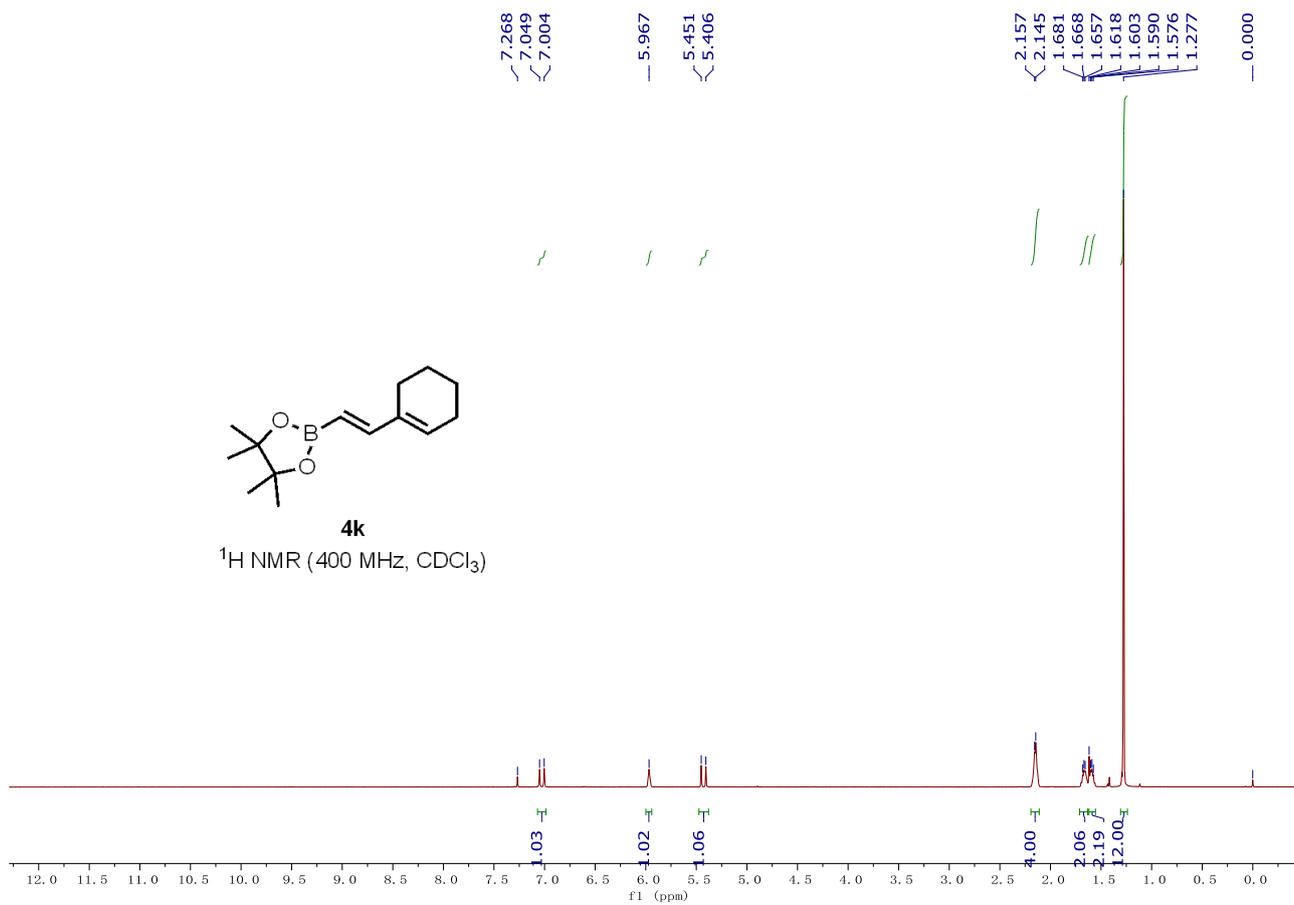






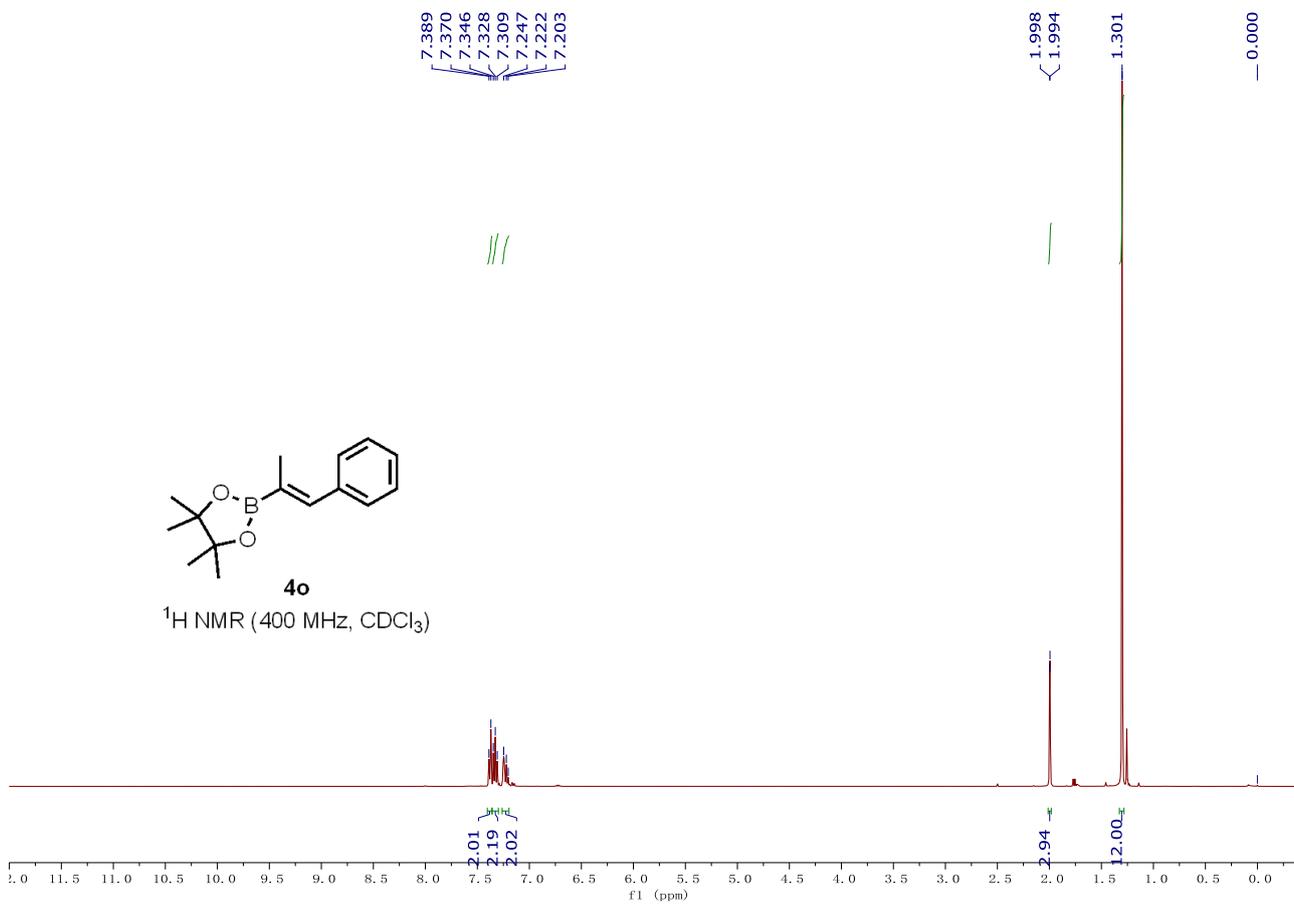
4k

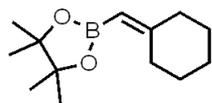
¹H NMR (400 MHz, CDCl₃)



4o

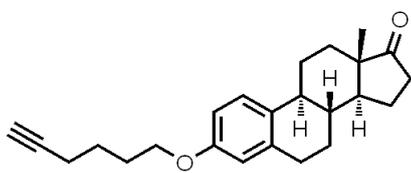
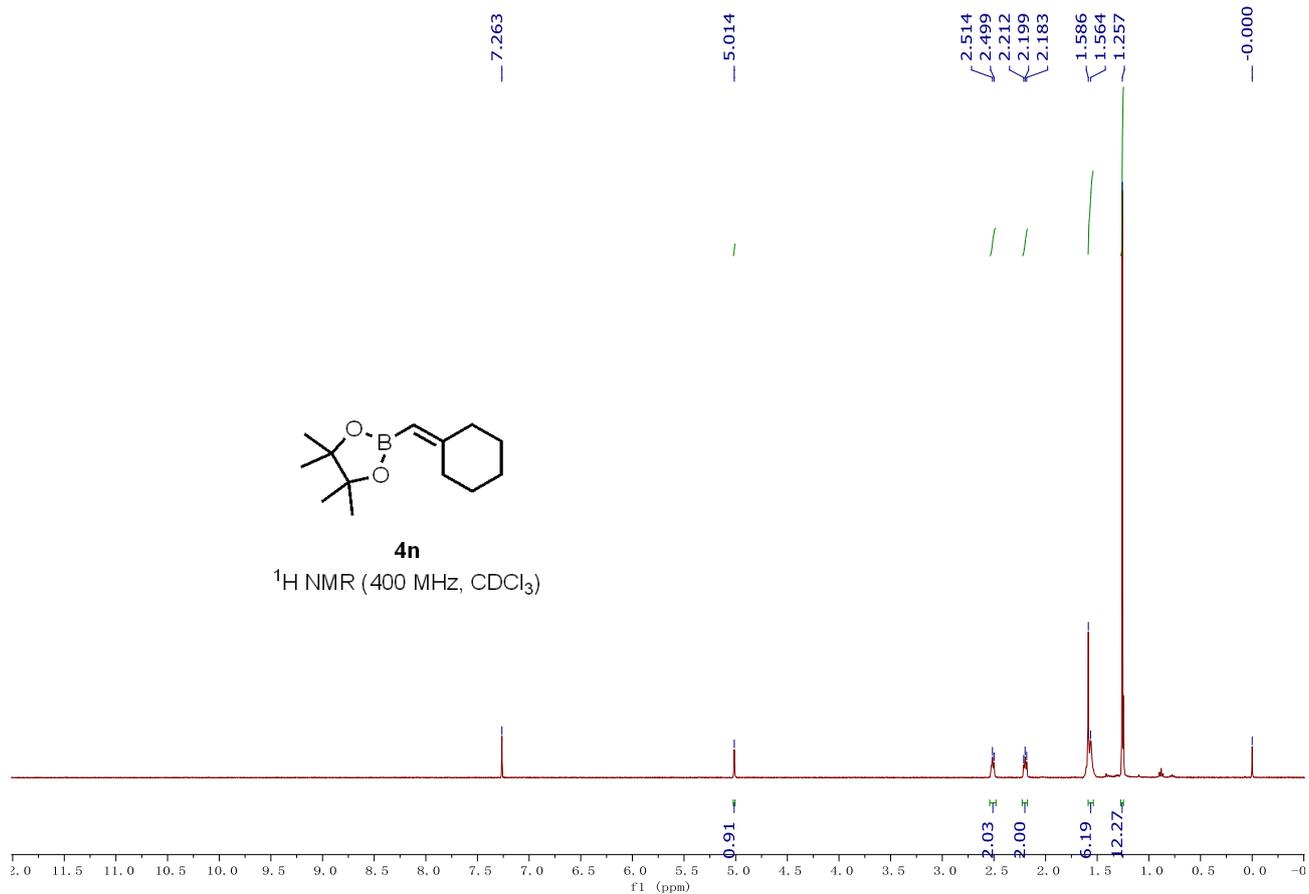
¹H NMR (400 MHz, CDCl₃)





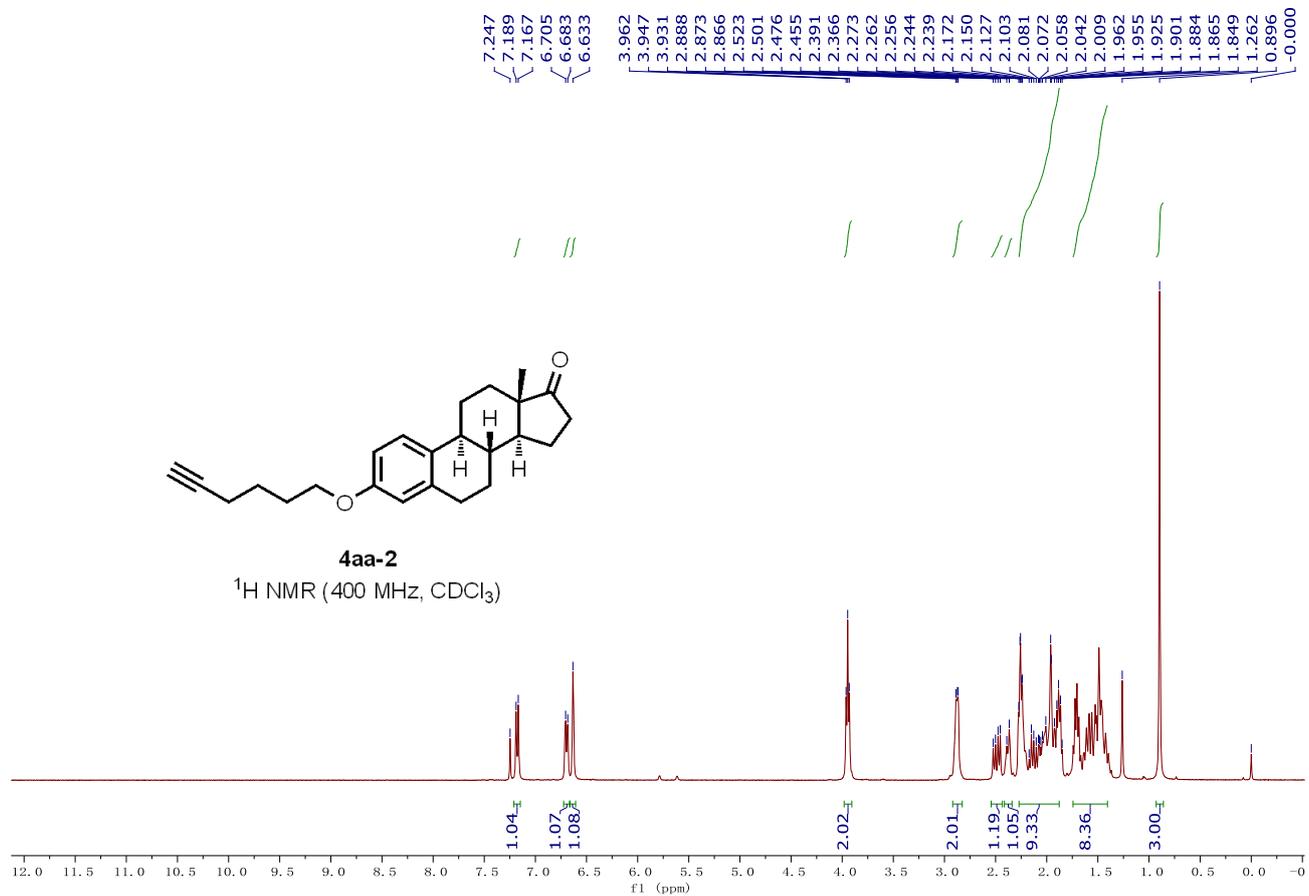
4n

¹H NMR (400 MHz, CDCl₃)



4aa-2

¹H NMR (400 MHz, CDCl₃)



— 220.78

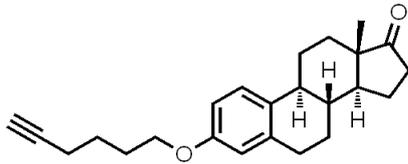
— 156.91

137.60
131.86
126.20

114.43
111.99

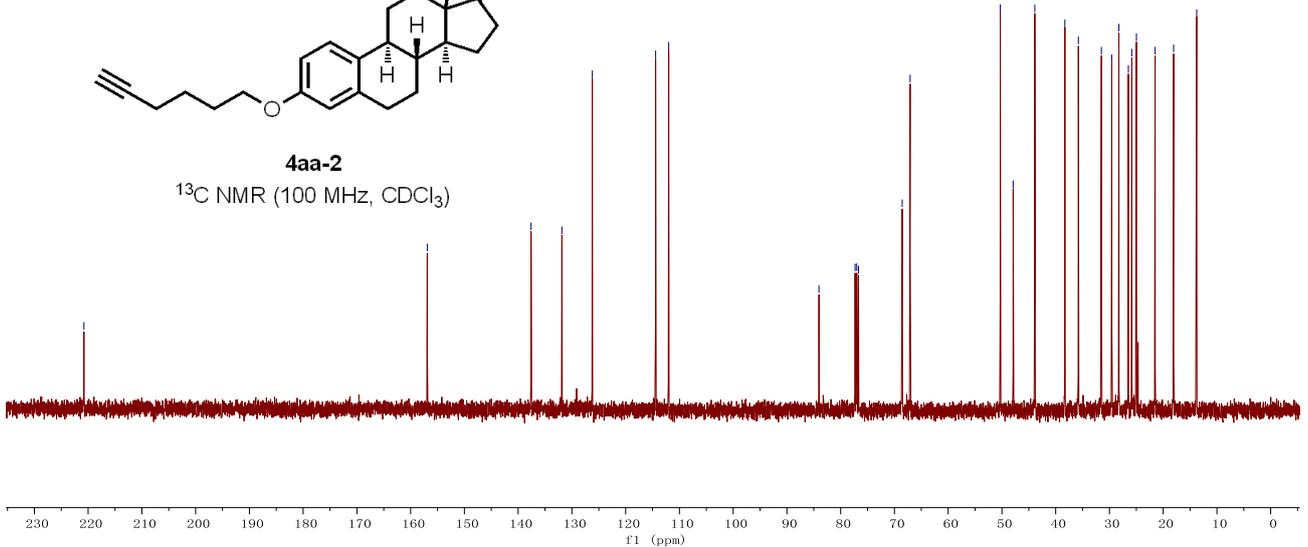
84.04
77.32
77.00
76.68
68.55
67.07

50.30
47.91
43.88
38.29
35.78
31.50
29.56
28.24
26.47
25.84
24.98
21.50
18.05
13.77

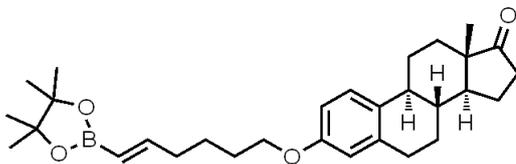


4aa-2

¹³C NMR (100 MHz, CDCl₃)

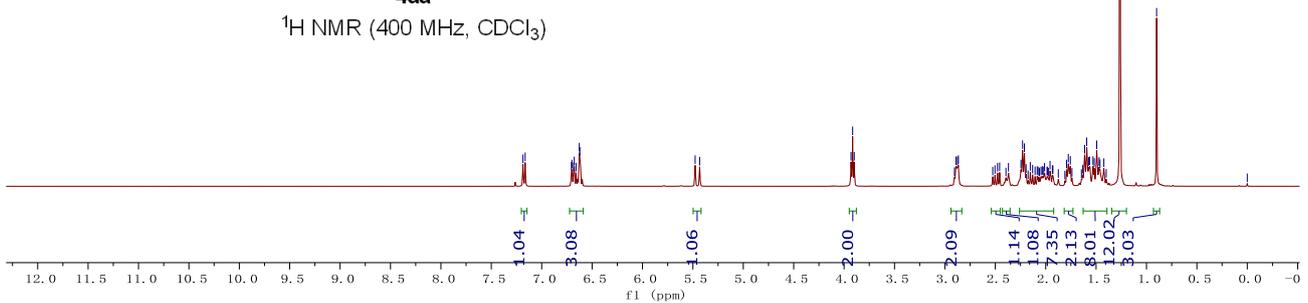


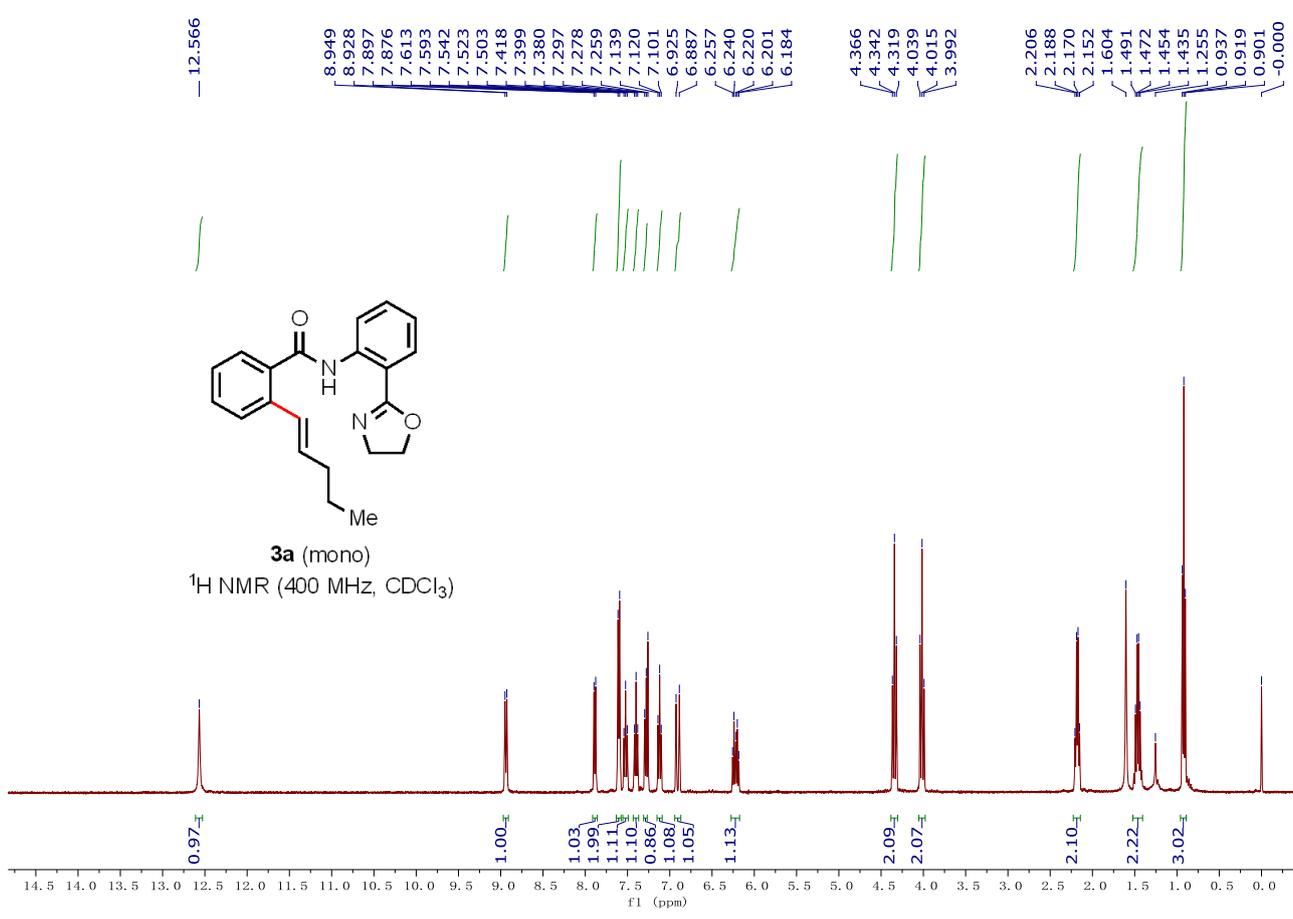
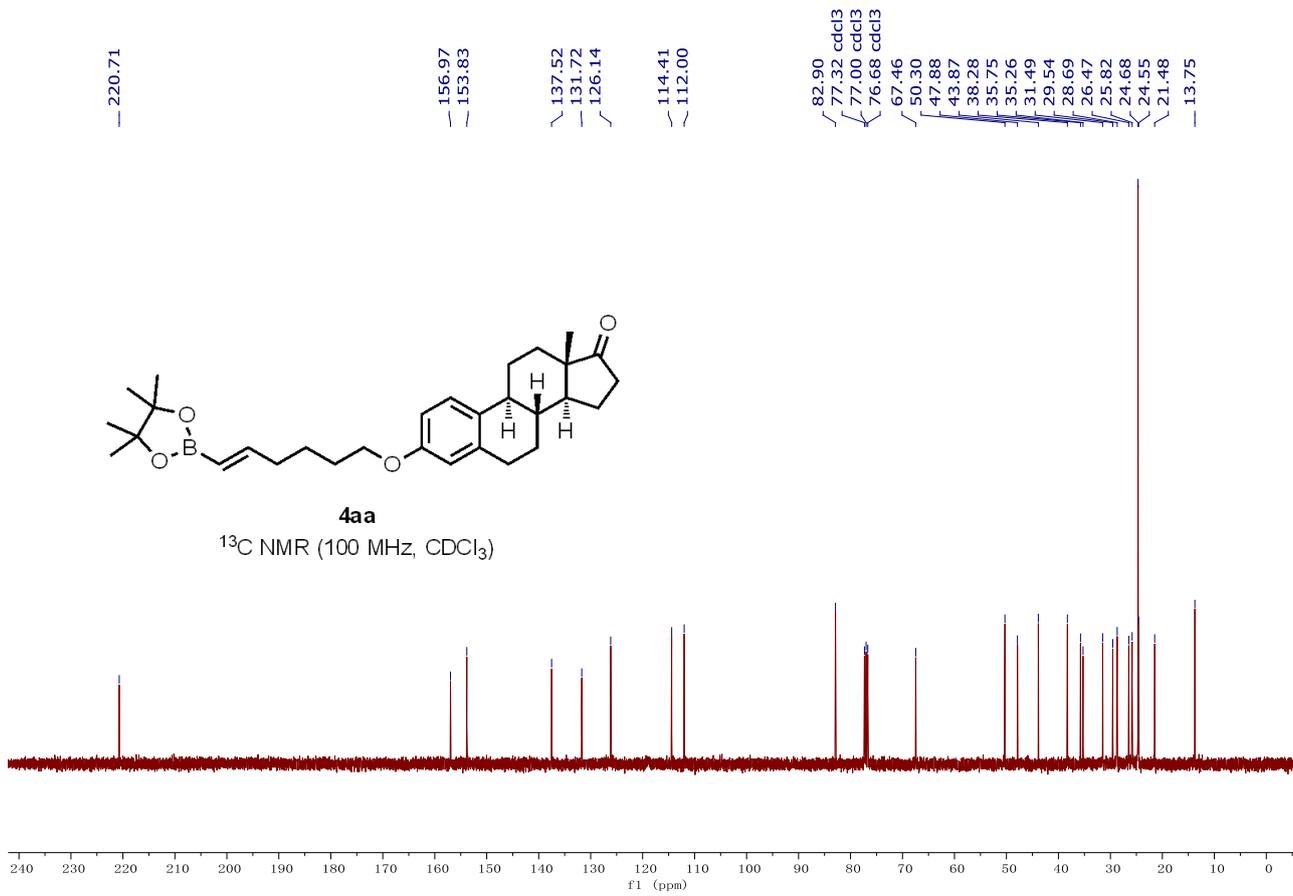
7.186
7.164
6.705
6.699
6.684
6.677
6.659
6.627
6.621
5.478
5.433
3.931
3.915
3.899
2.905
2.890
2.875
2.866
2.525
2.503
2.478
2.457
2.394
2.370
2.245
2.230
2.212
2.195
2.175
2.153
2.130
2.105
2.084
2.075
2.062
2.046
2.034
2.025
2.012
1.987
1.981
1.974
1.957
1.934
1.929
1.875
1.809
1.793
1.776
1.755
1.739
1.739
1.645
1.632
1.614
1.593
1.574
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1.423
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0.000

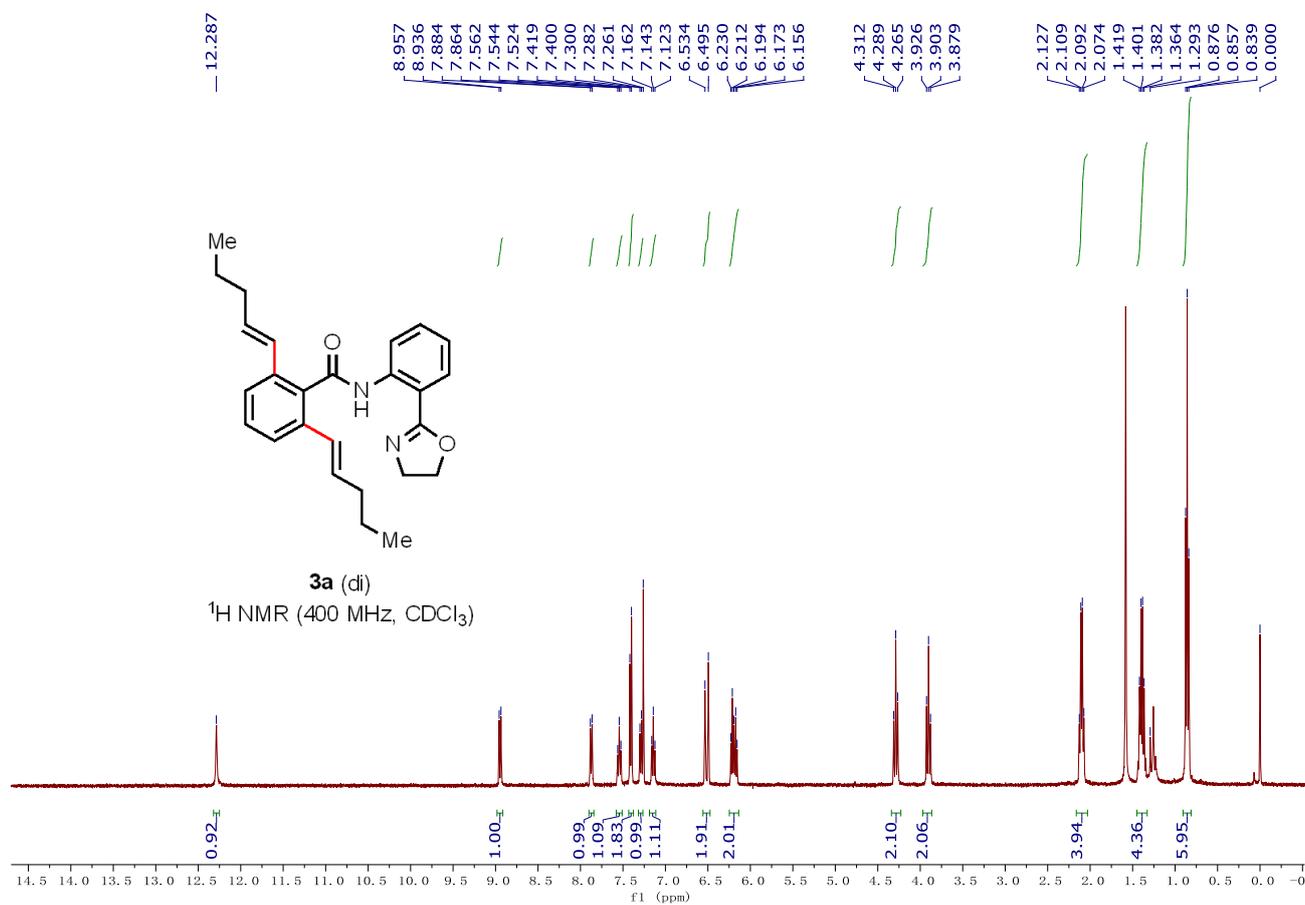
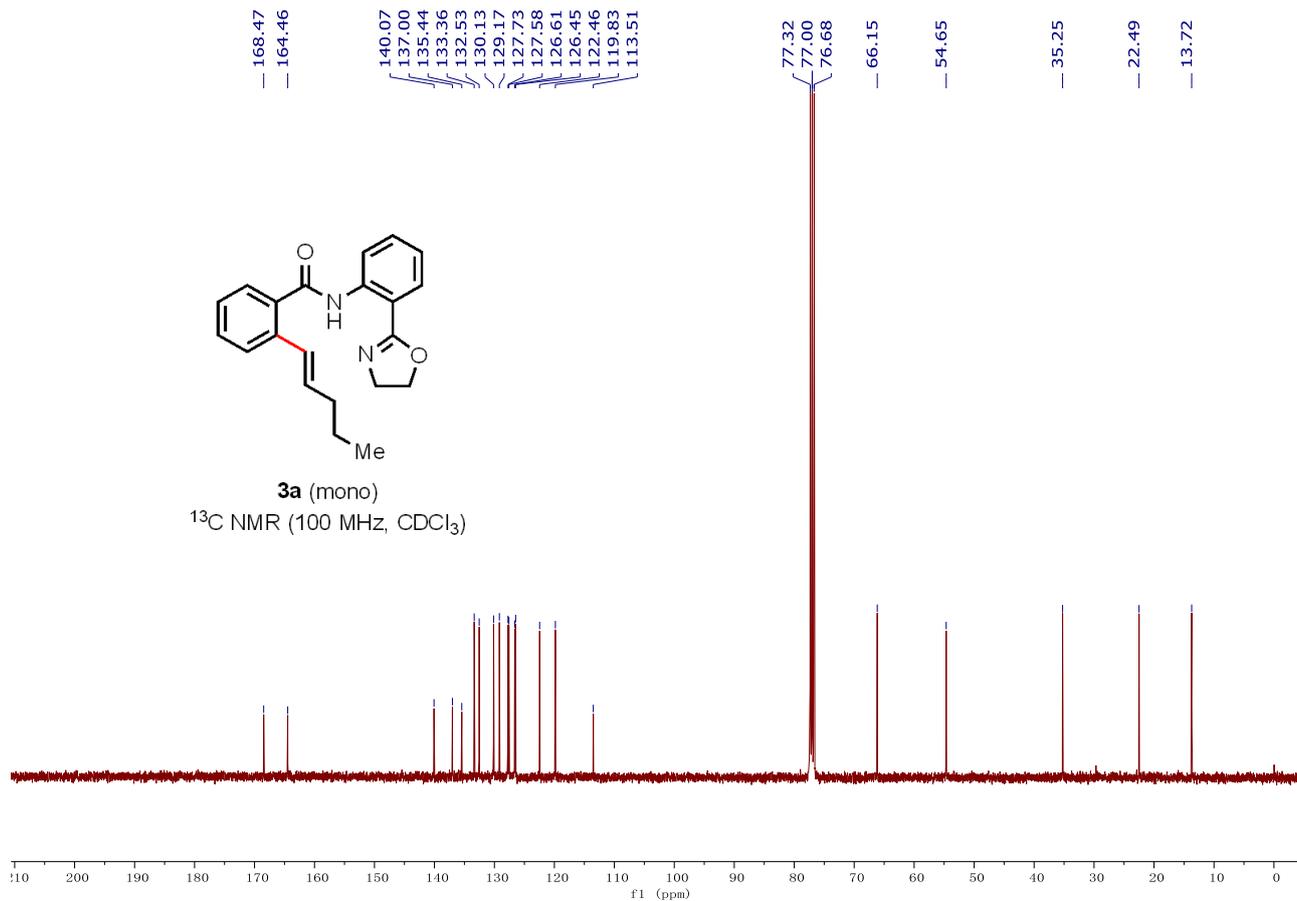


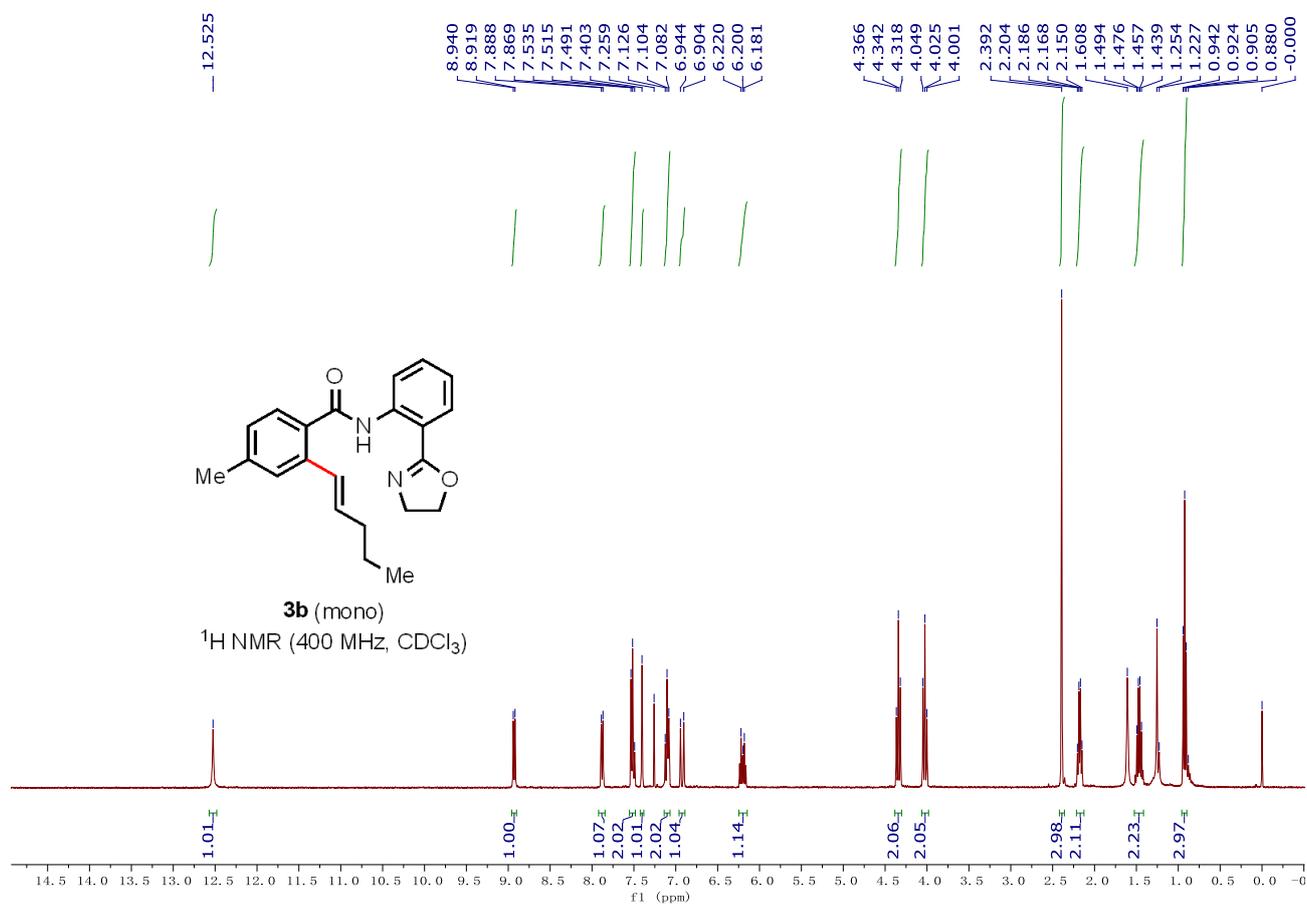
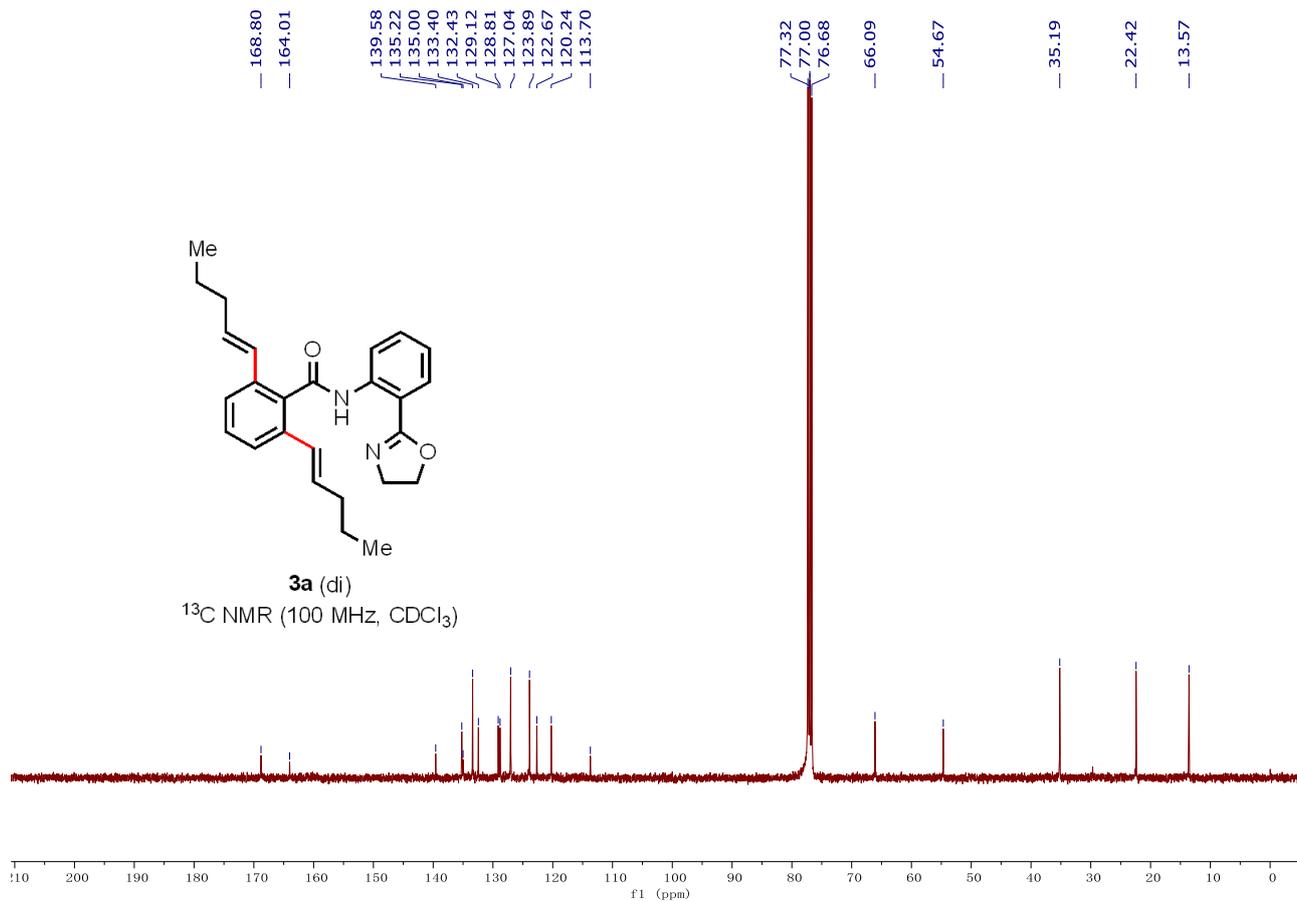
4aa

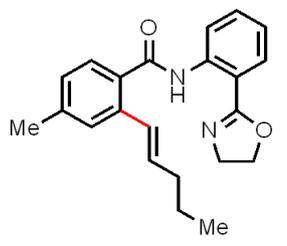
¹H NMR (400 MHz, CDCl₃)



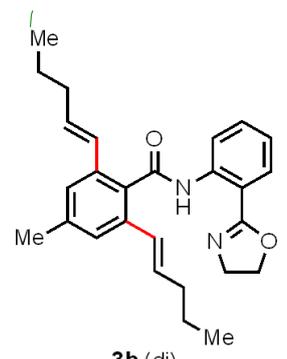
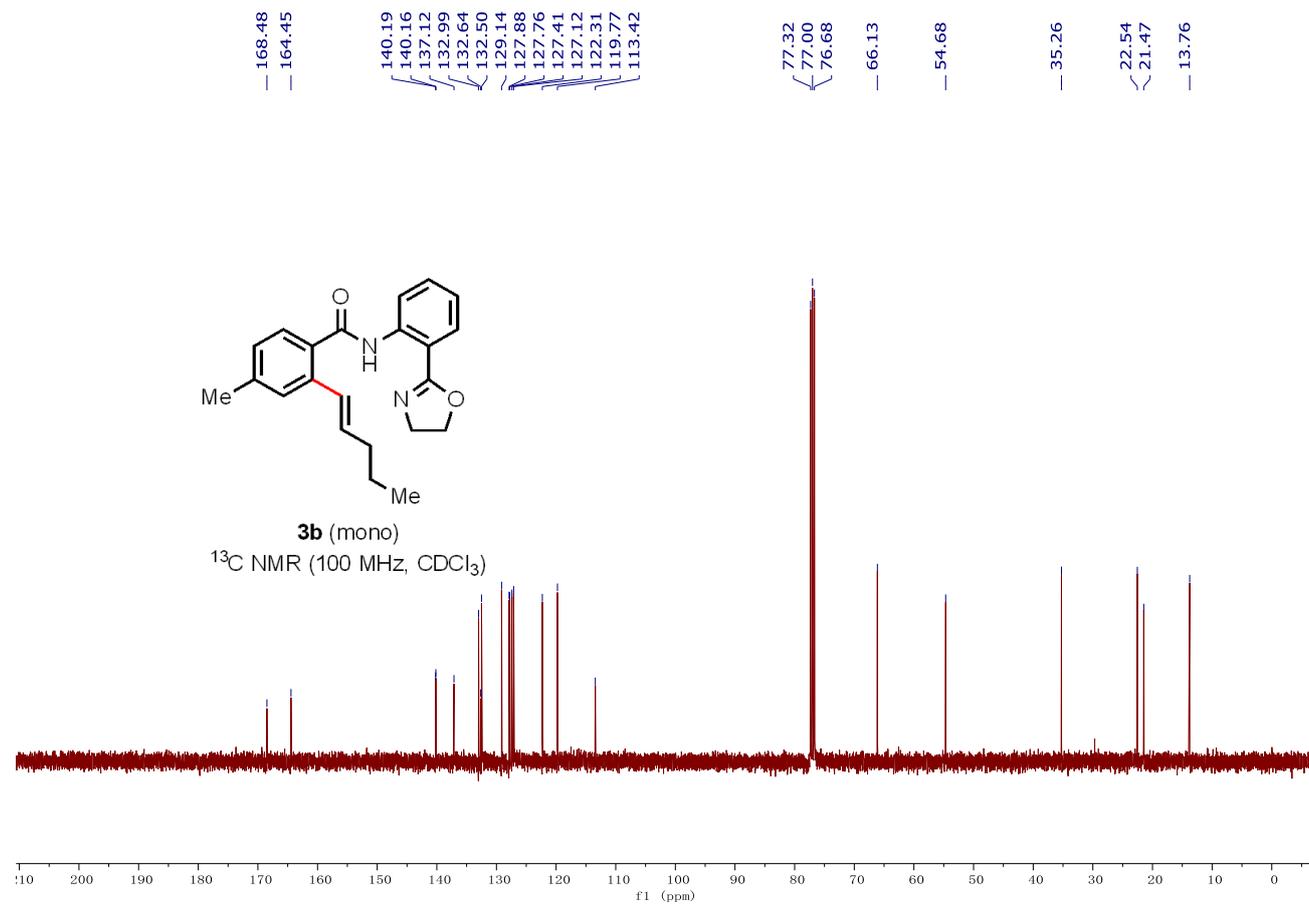




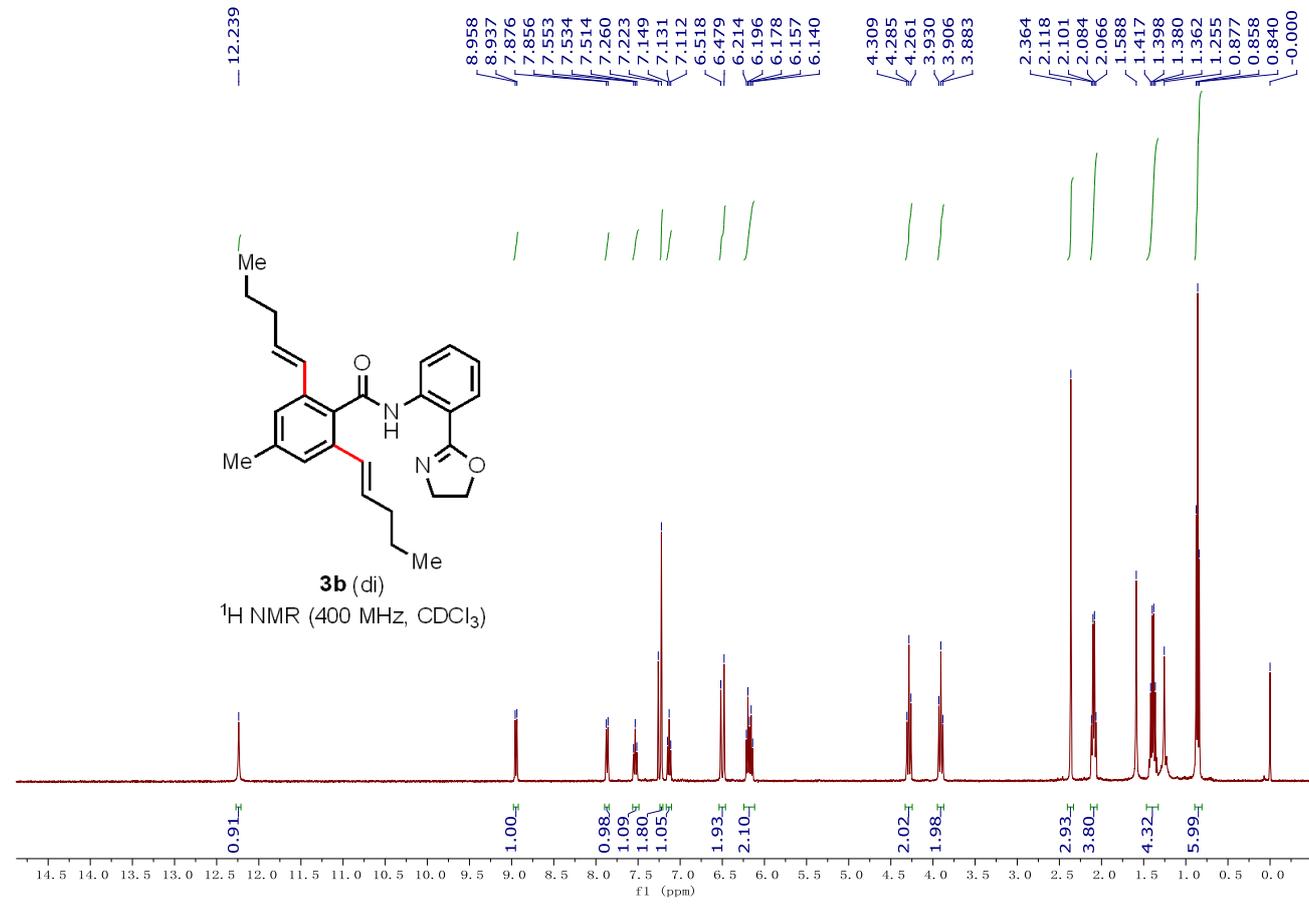


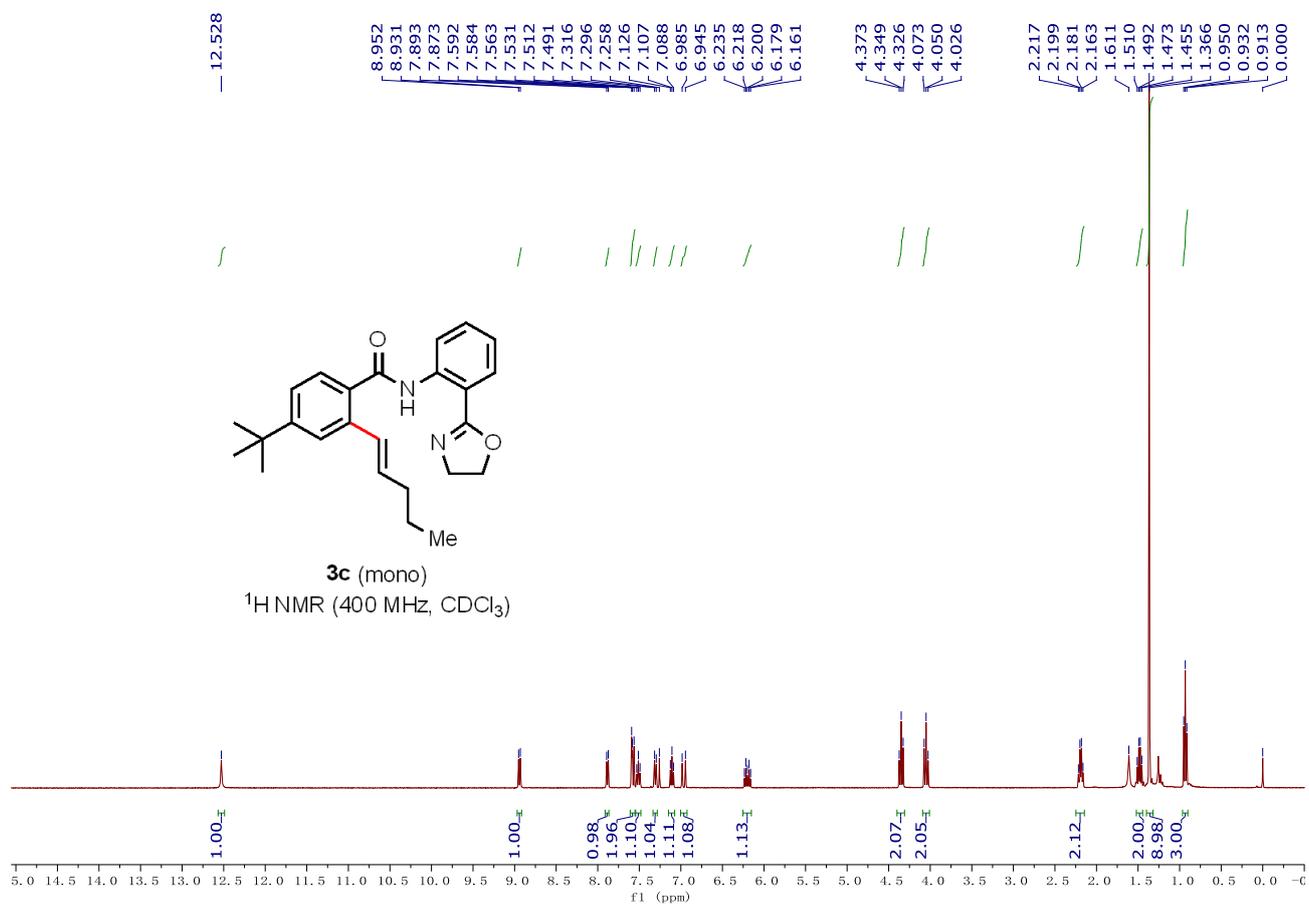
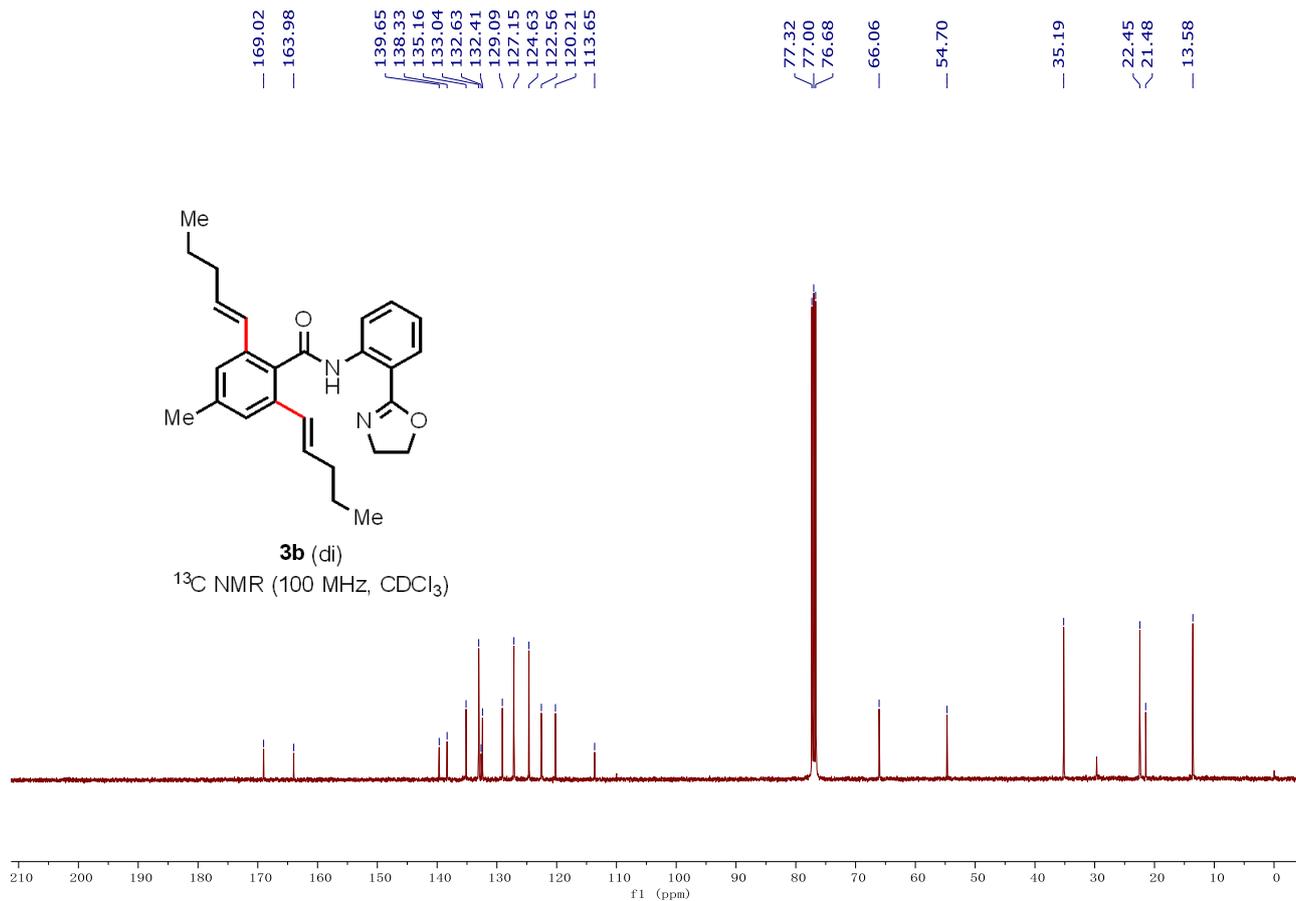


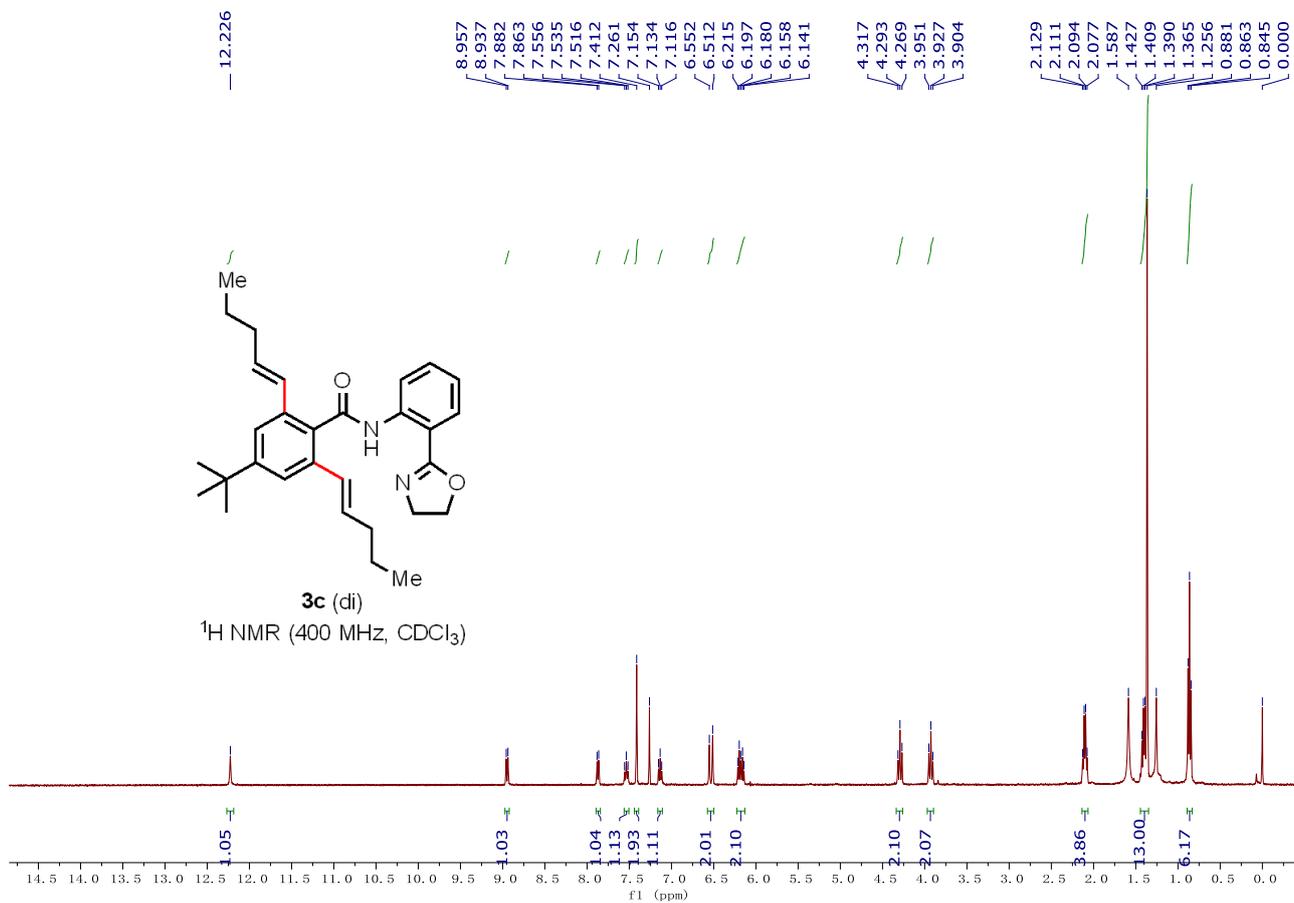
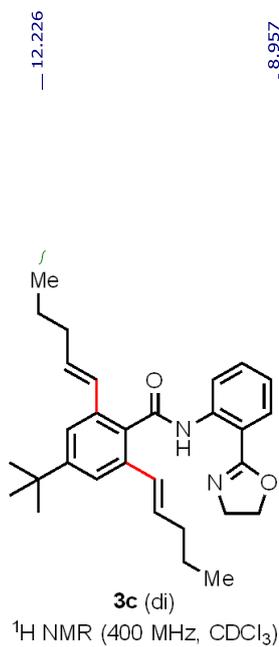
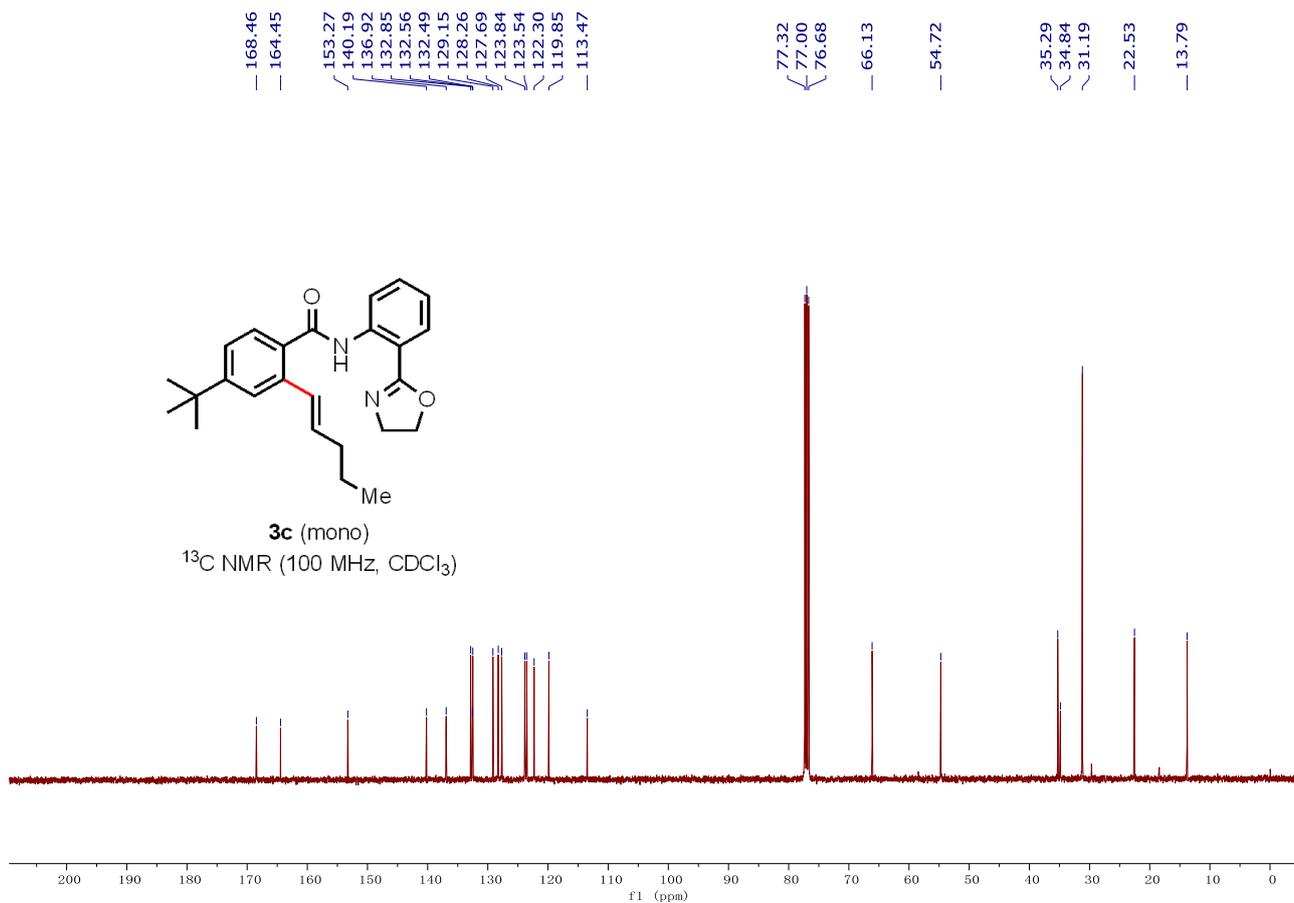
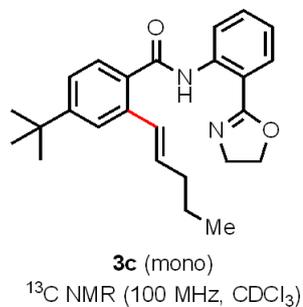
3b (mono)
 ^{13}C NMR (100 MHz, CDCl_3)

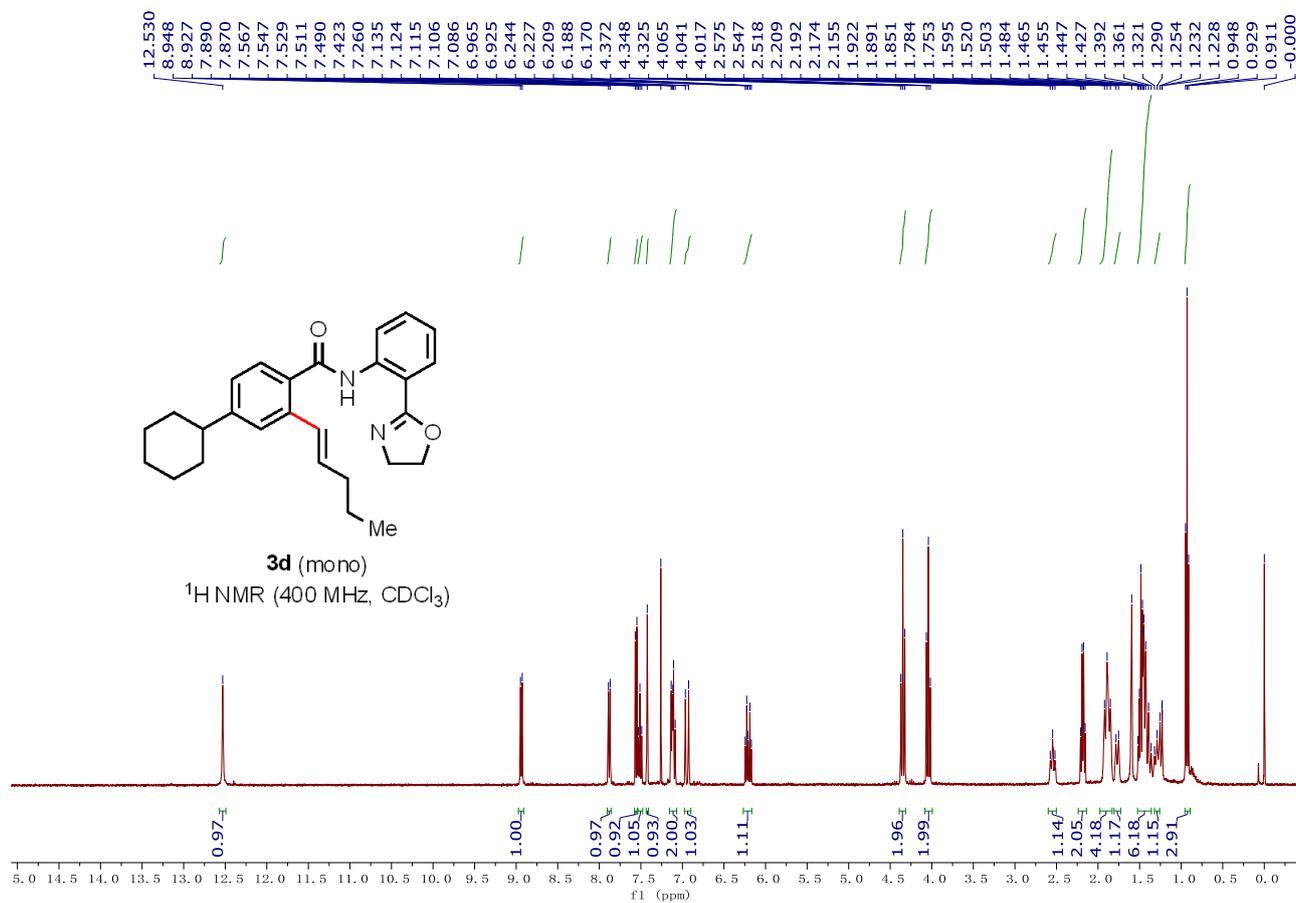
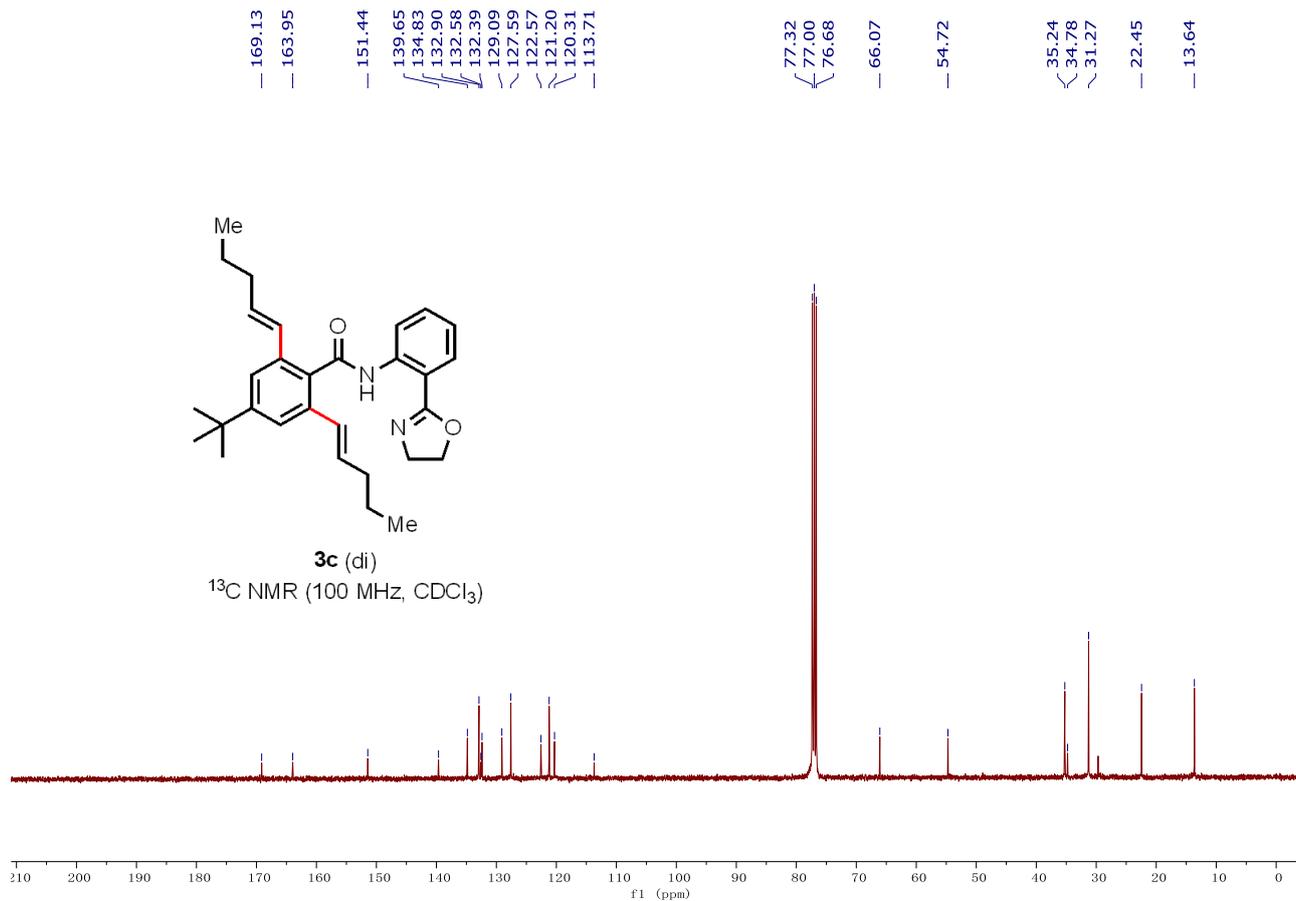


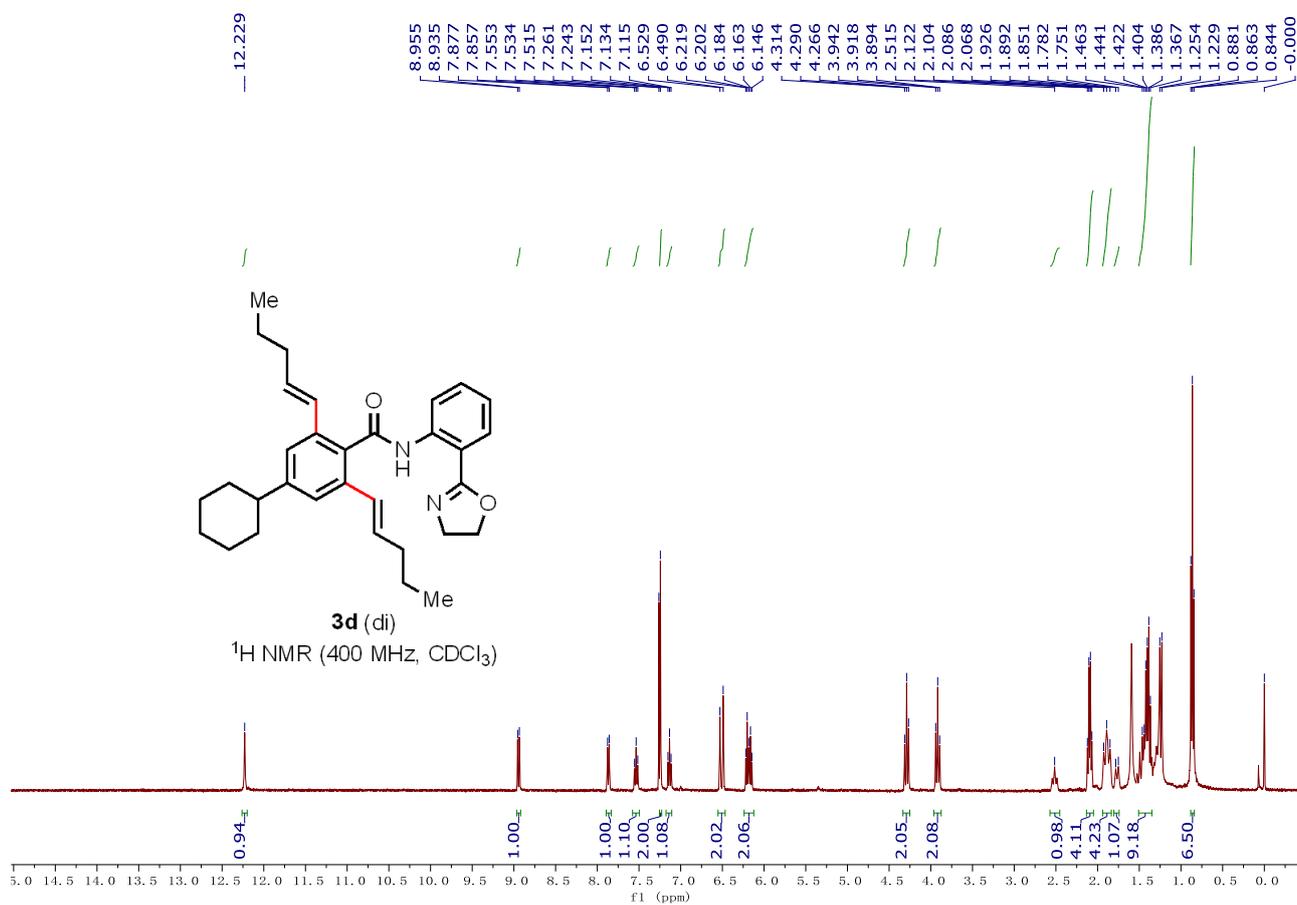
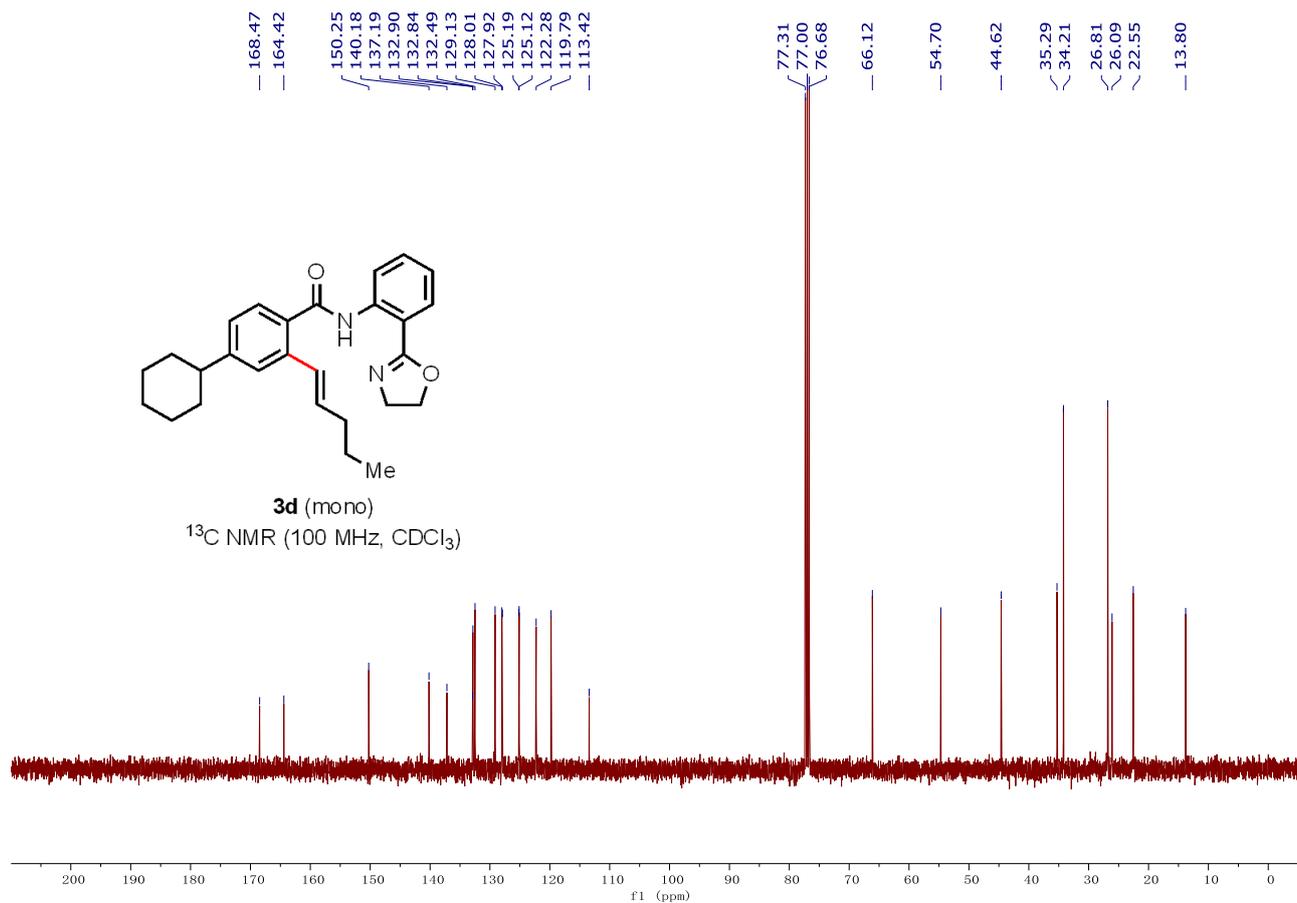
3b (di)
 ^1H NMR (400 MHz, CDCl_3)

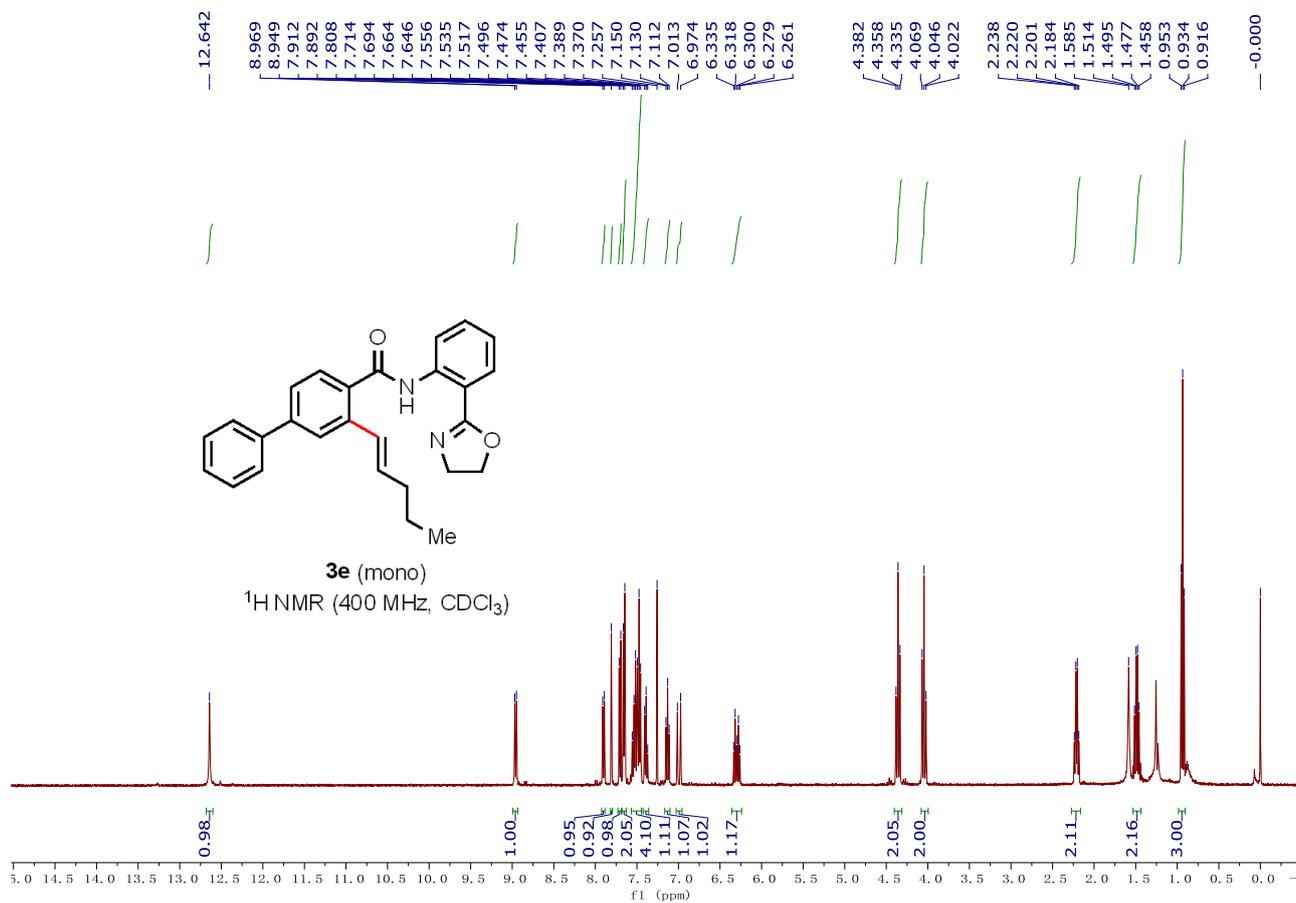
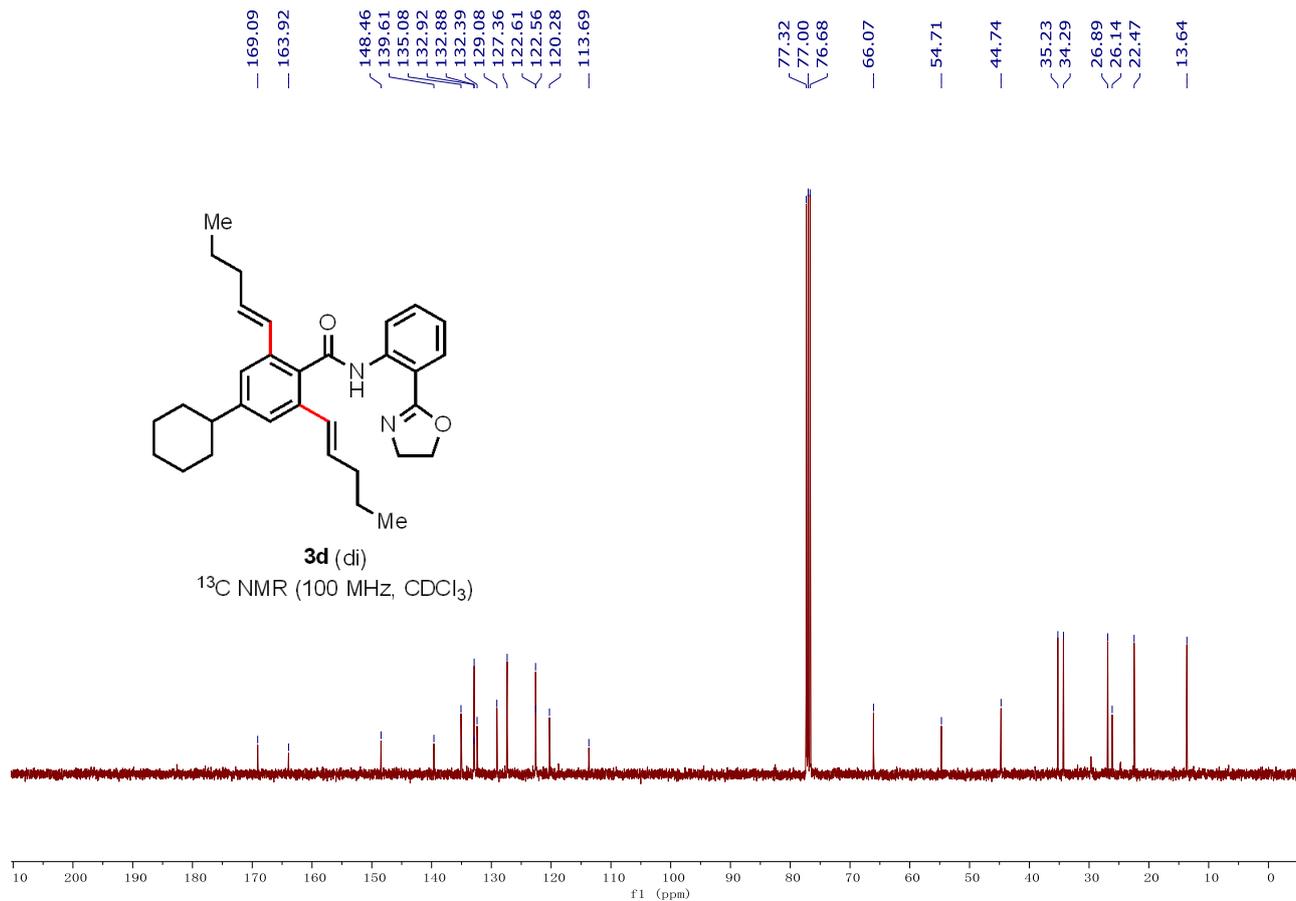


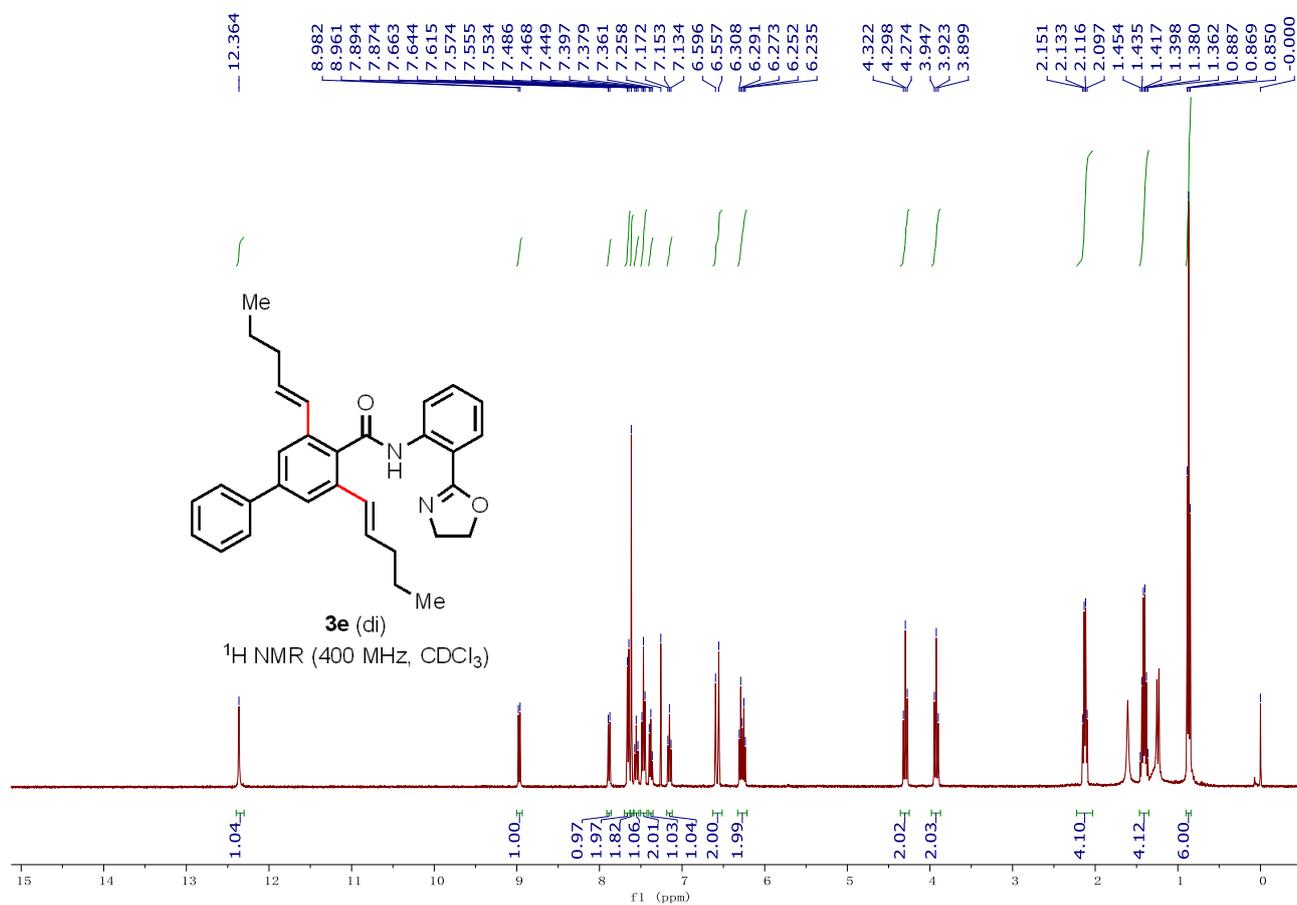
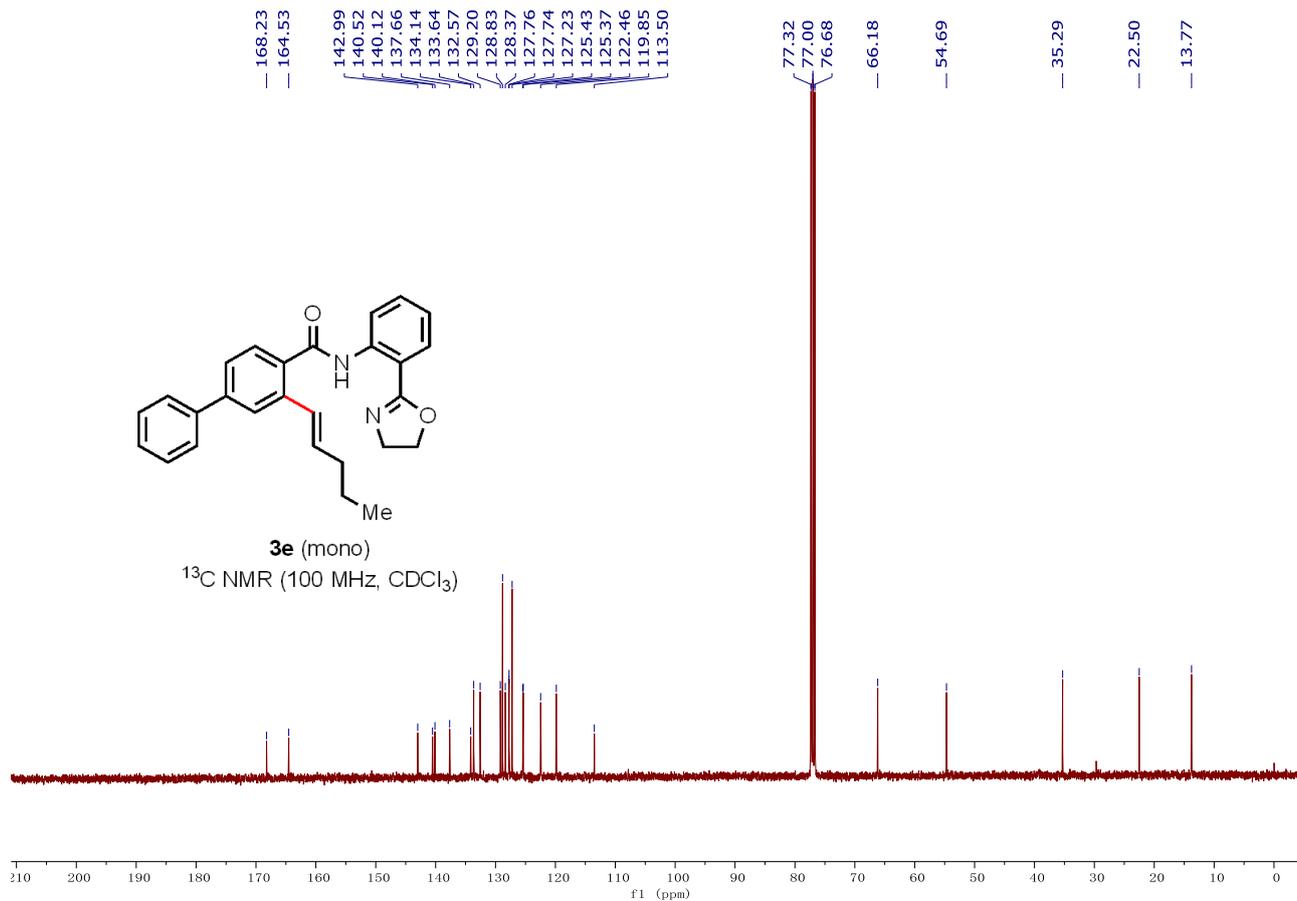


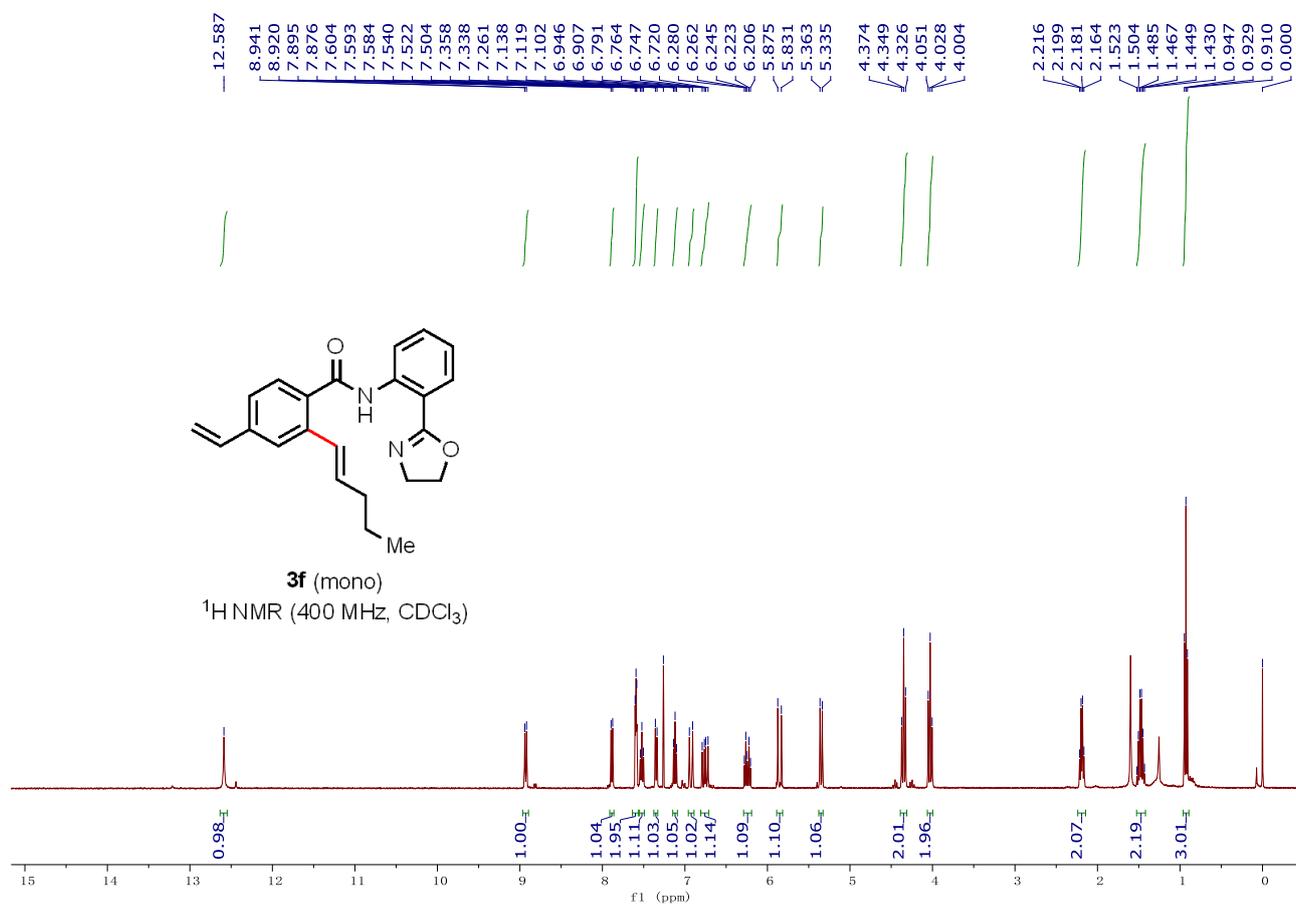
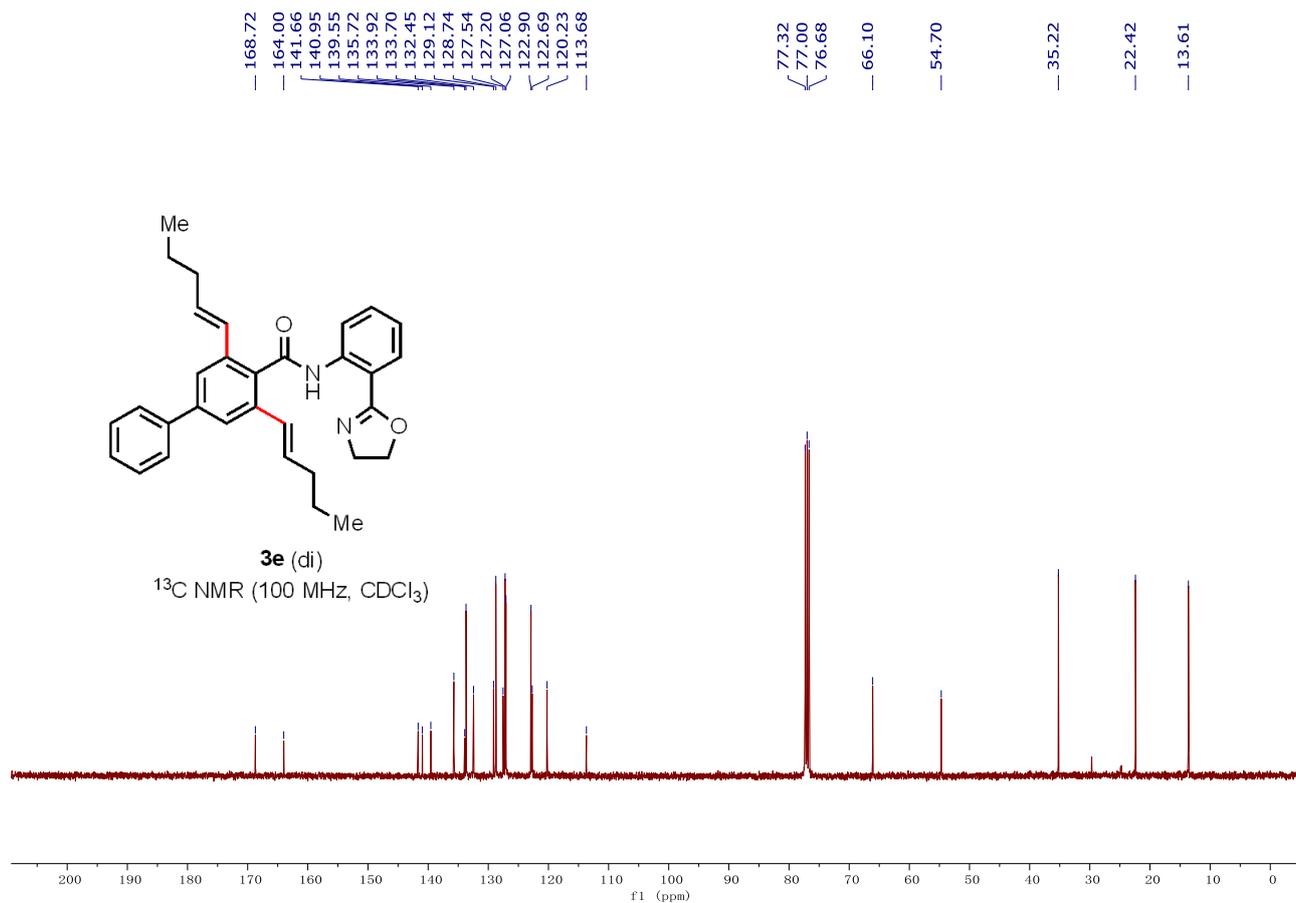


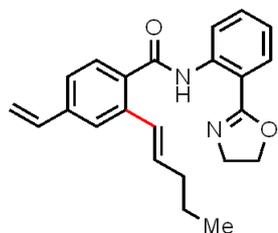






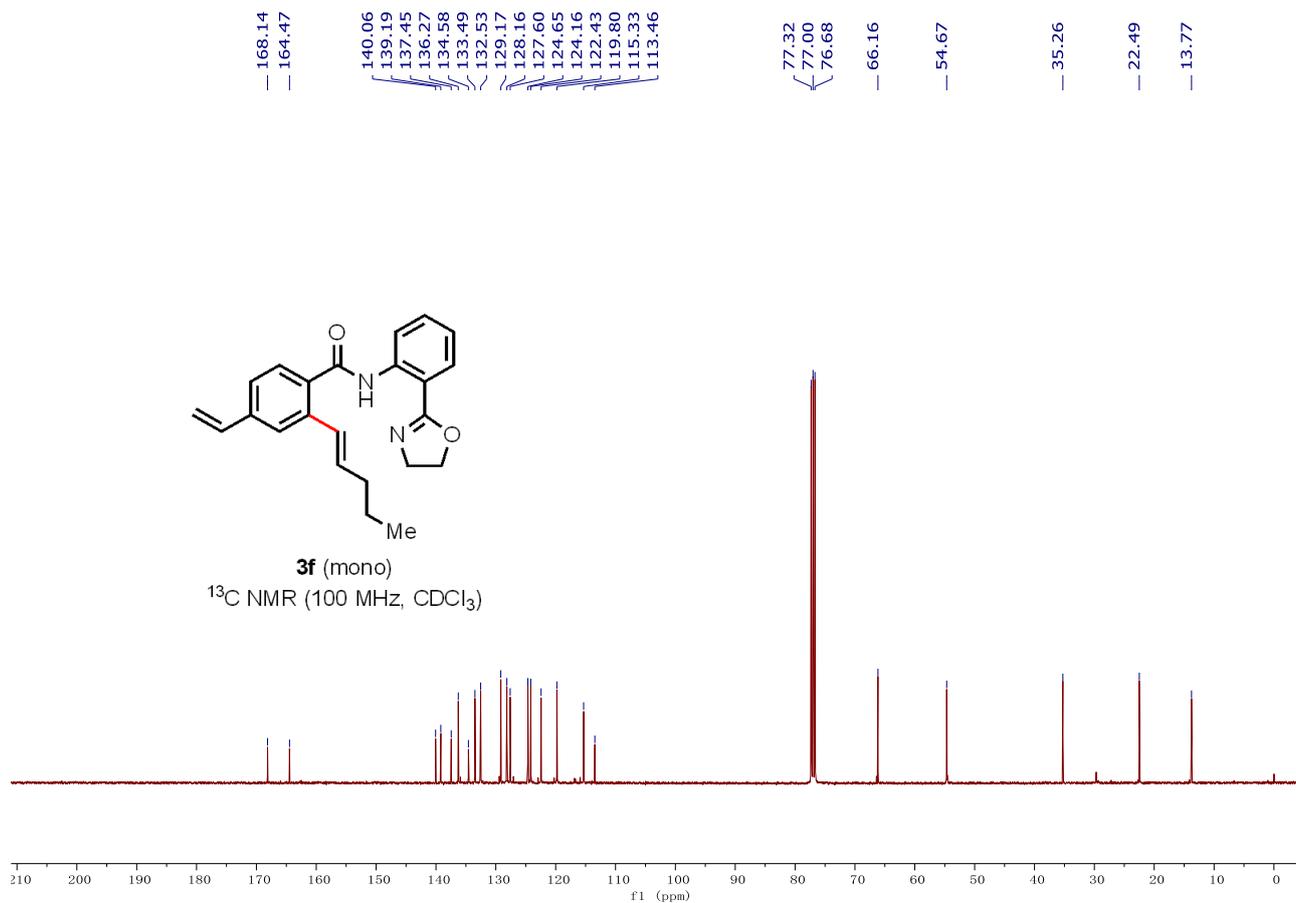






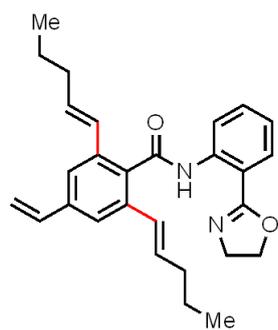
3f (mono)

^{13}C NMR (100 MHz, CDCl_3)



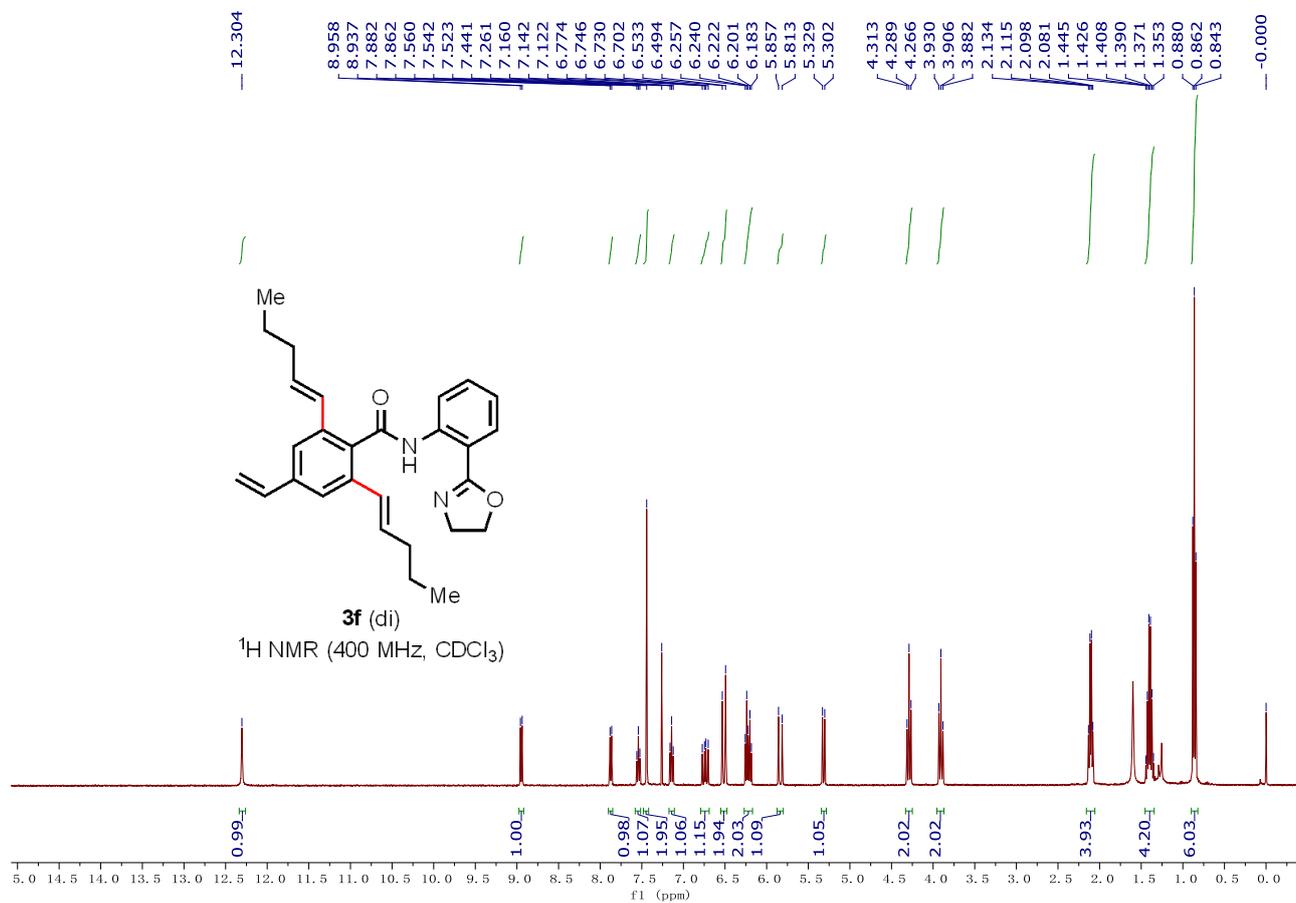
Chemical shift values (ppm) for the ^{13}C NMR spectrum:

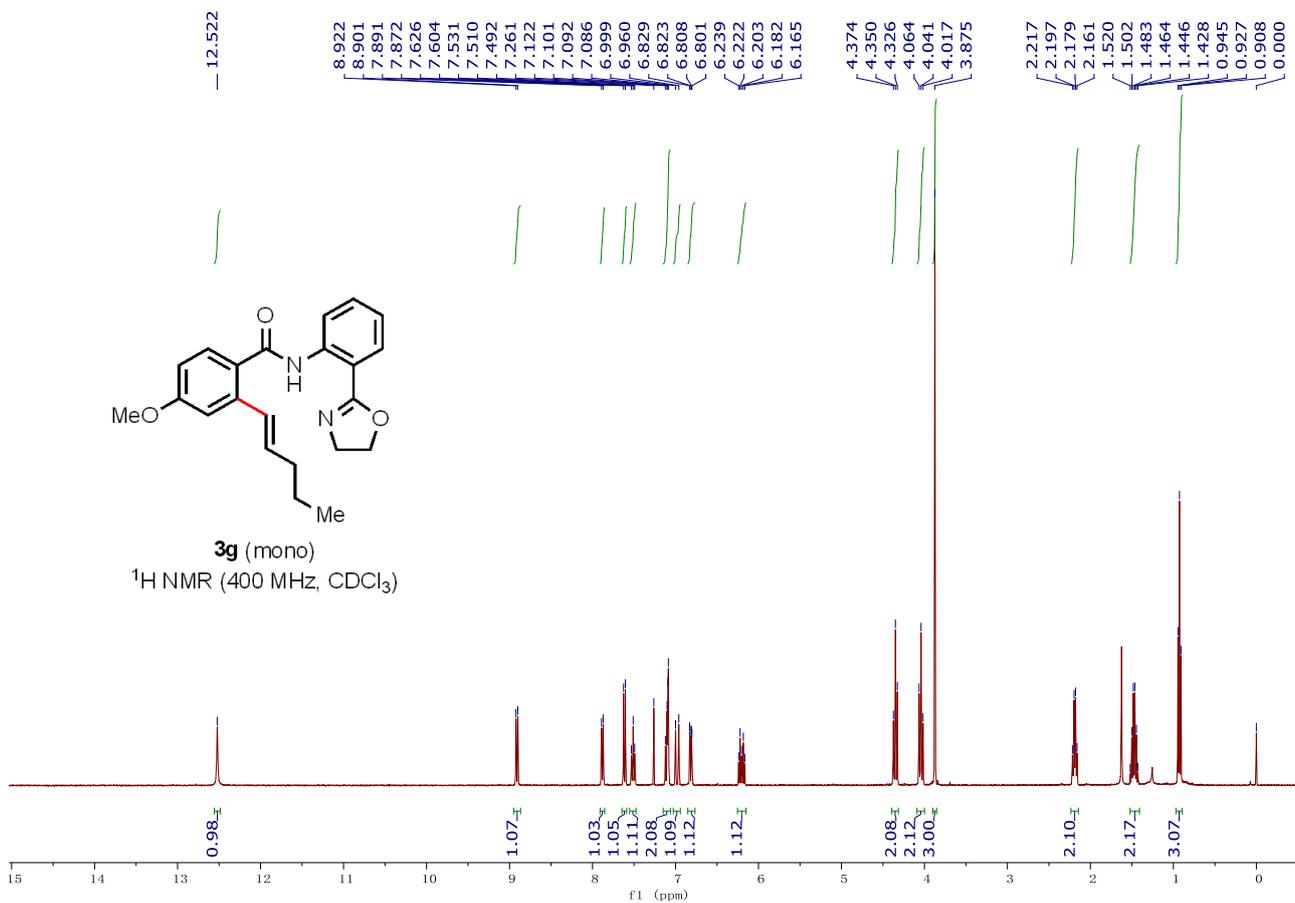
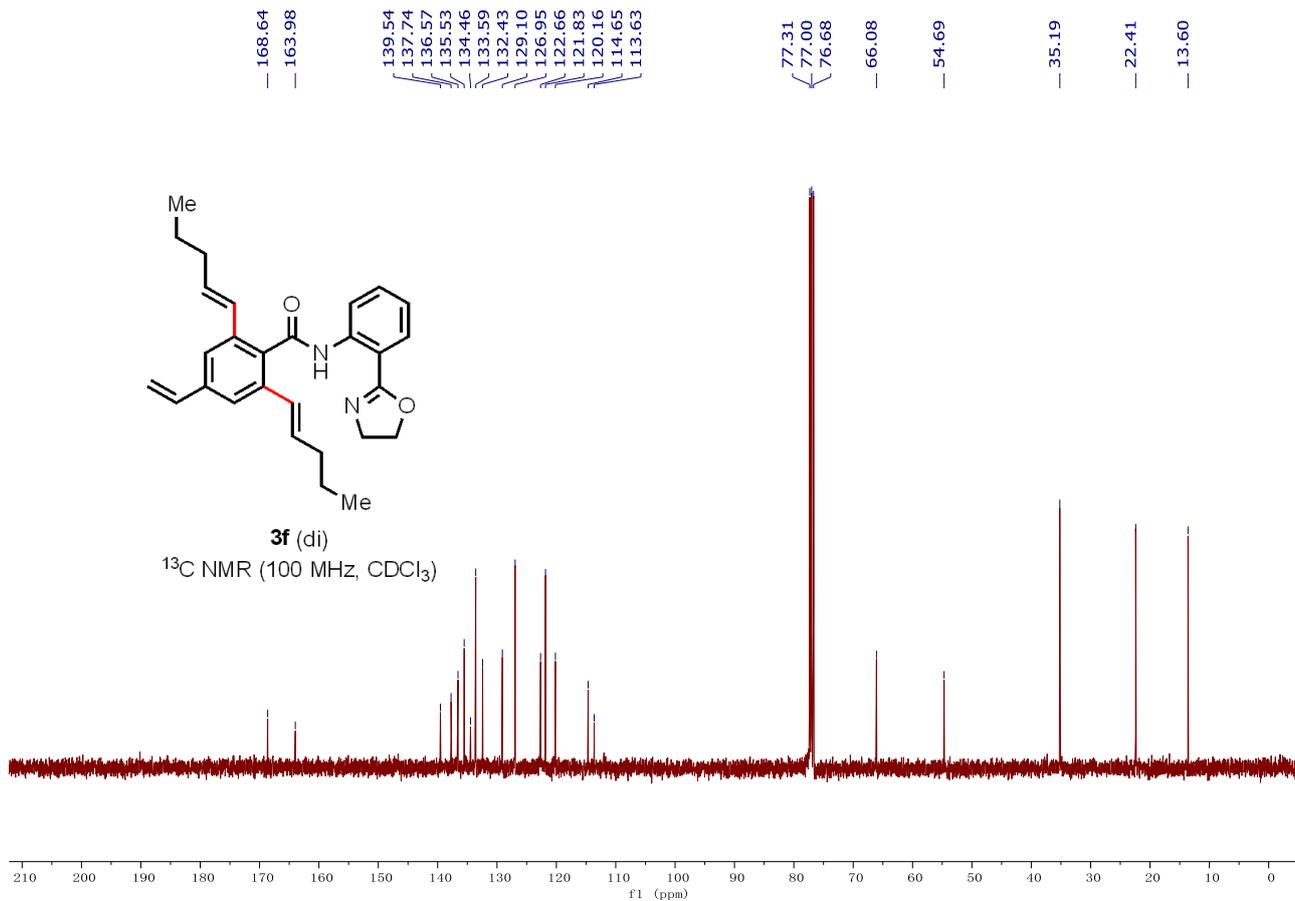
12.304
8.958
8.937
7.882
7.862
7.560
7.542
7.523
7.441
7.261
7.160
7.142
7.122
6.774
6.746
6.730
6.702
6.533
6.494
6.257
6.240
6.222
6.201
6.183
5.857
5.813
5.329
5.302
4.313
4.289
4.266
3.930
3.906
3.882
2.134
2.115
2.098
2.081
1.445
1.426
1.408
1.390
1.371
1.353
0.880
0.862
0.843
-0.000

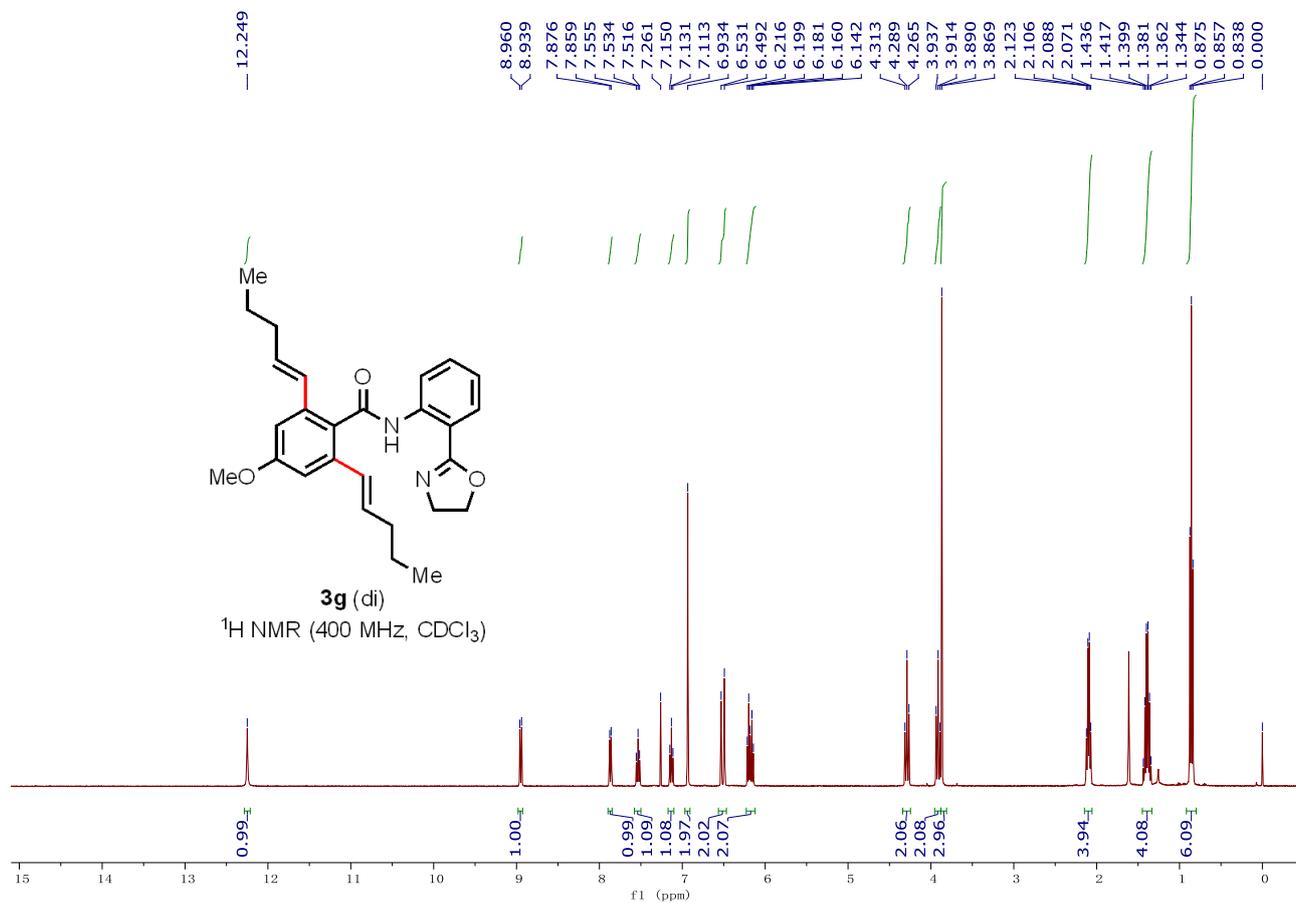
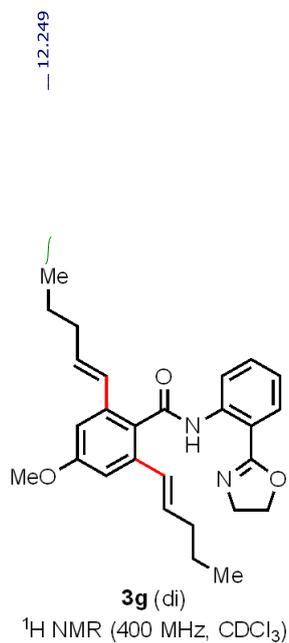
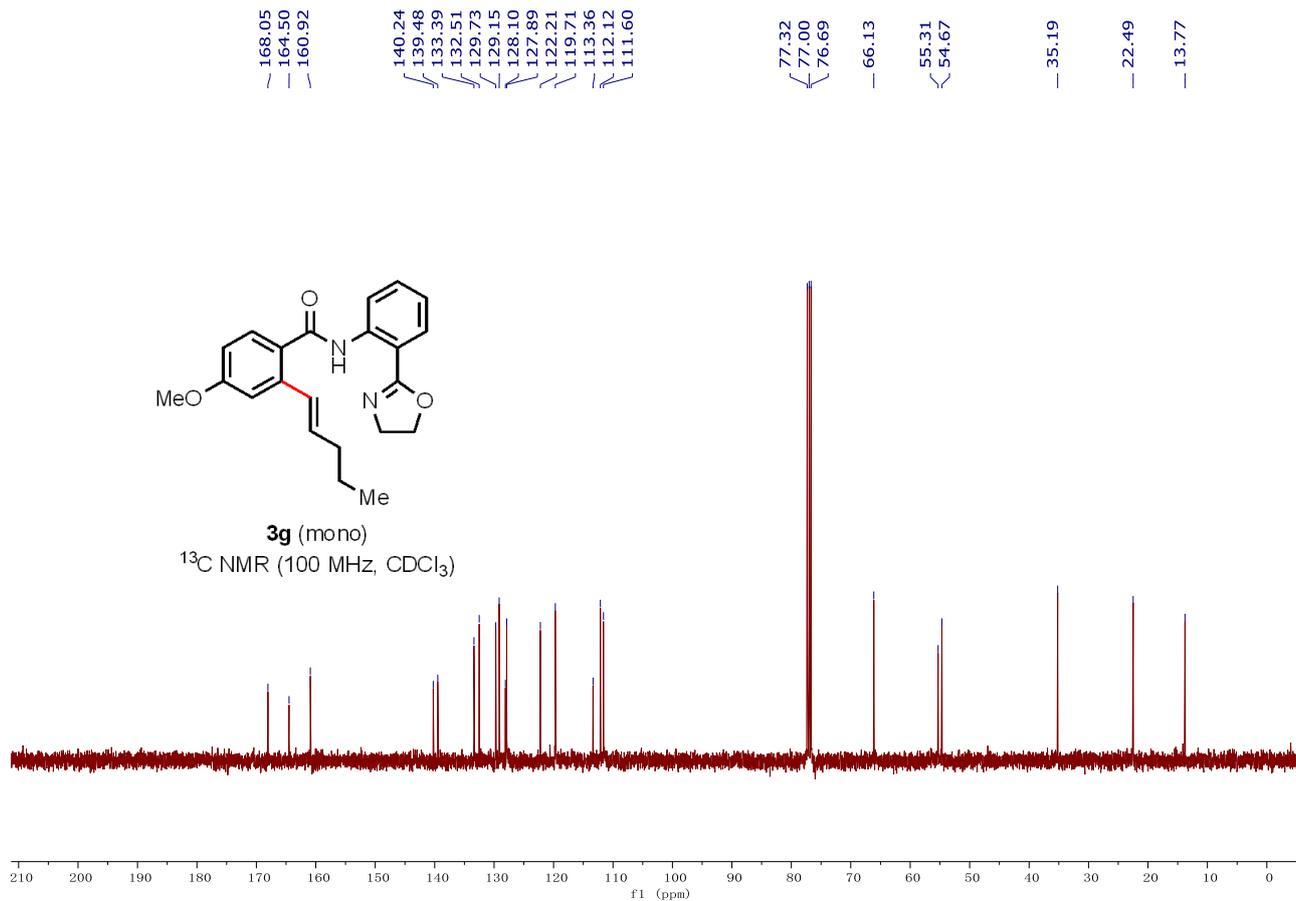
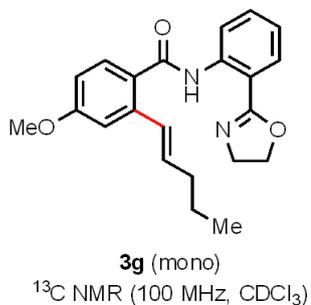


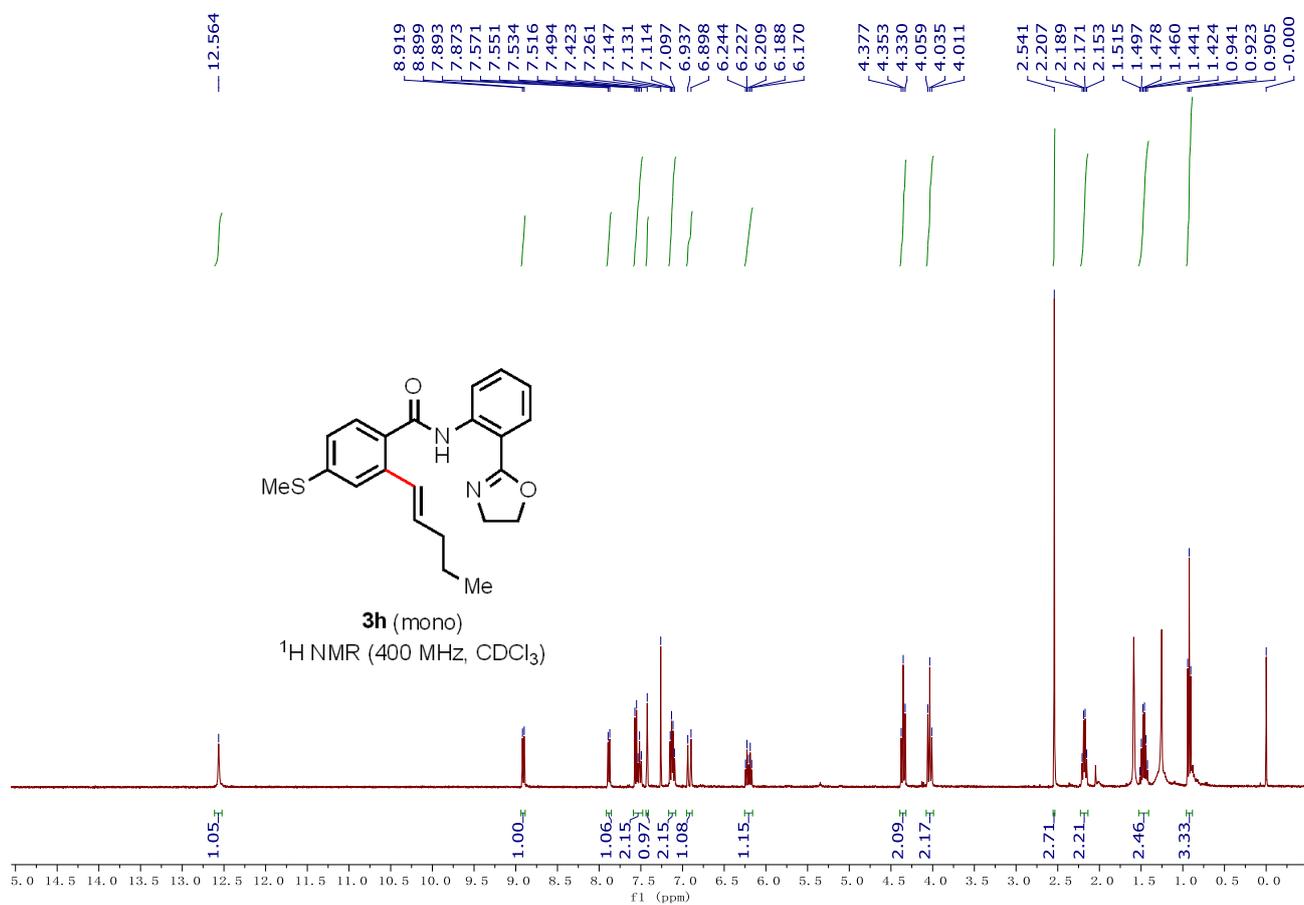
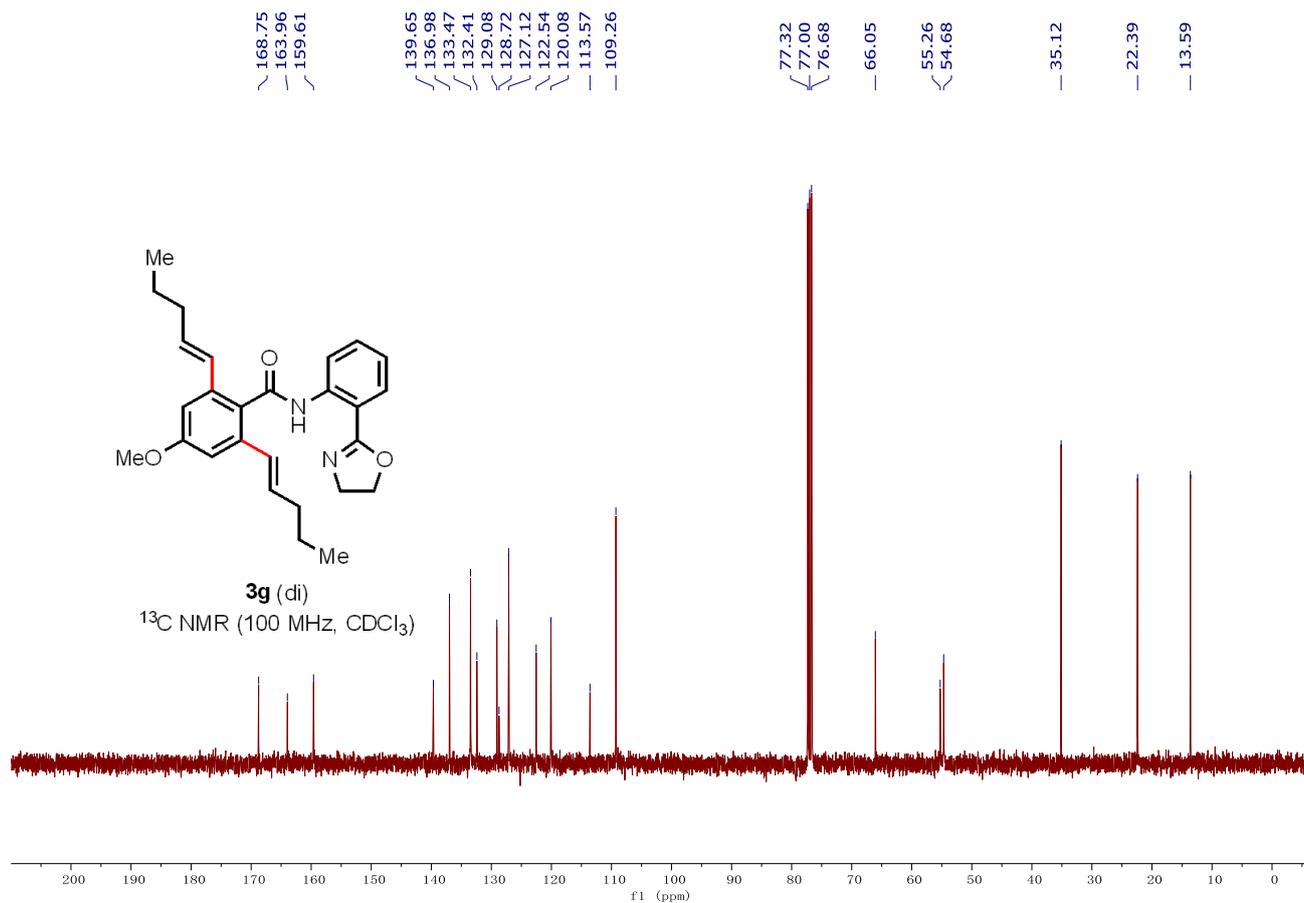
3f (di)

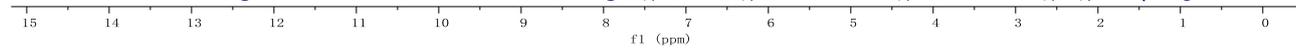
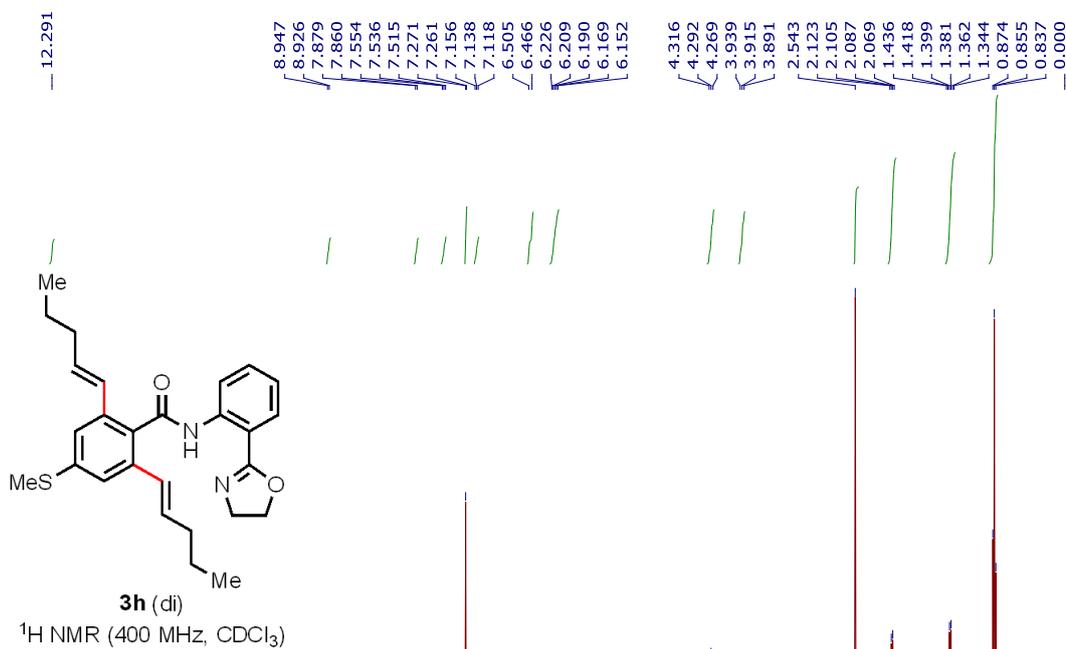
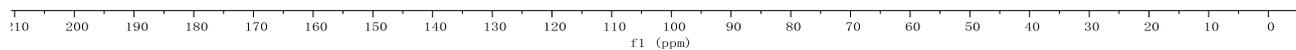
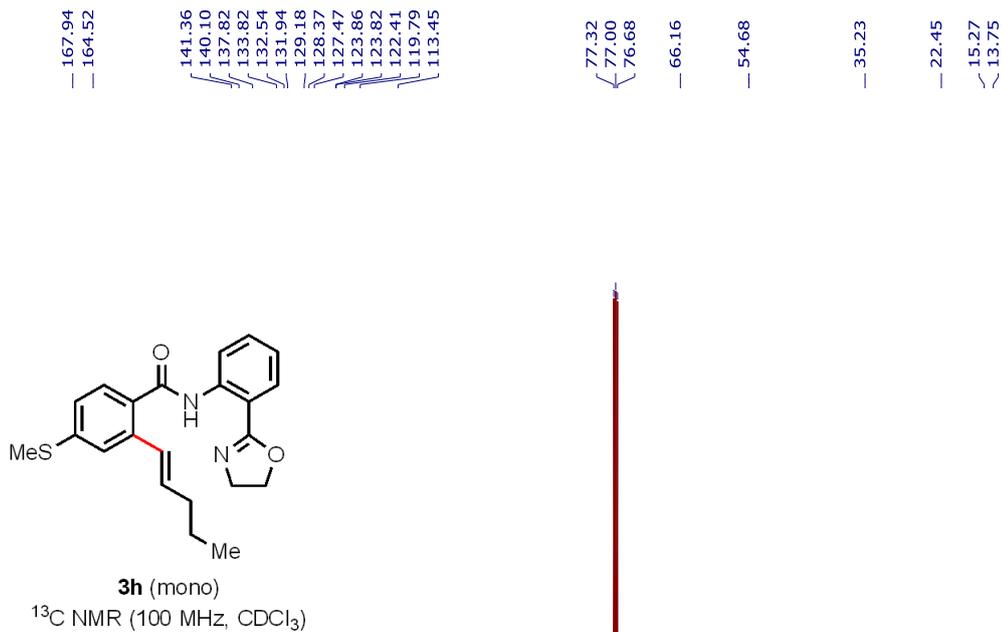
^1H NMR (400 MHz, CDCl_3)

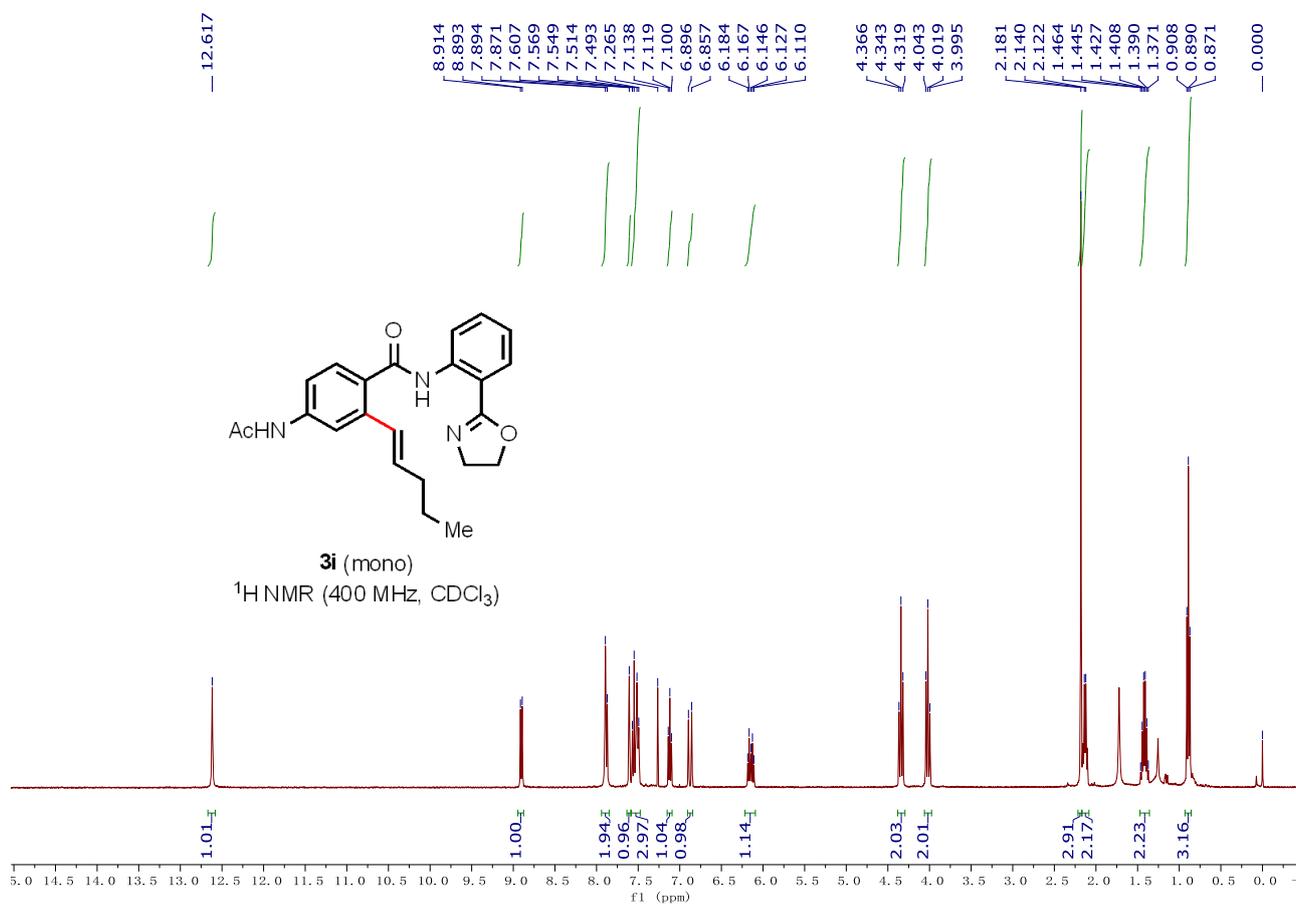
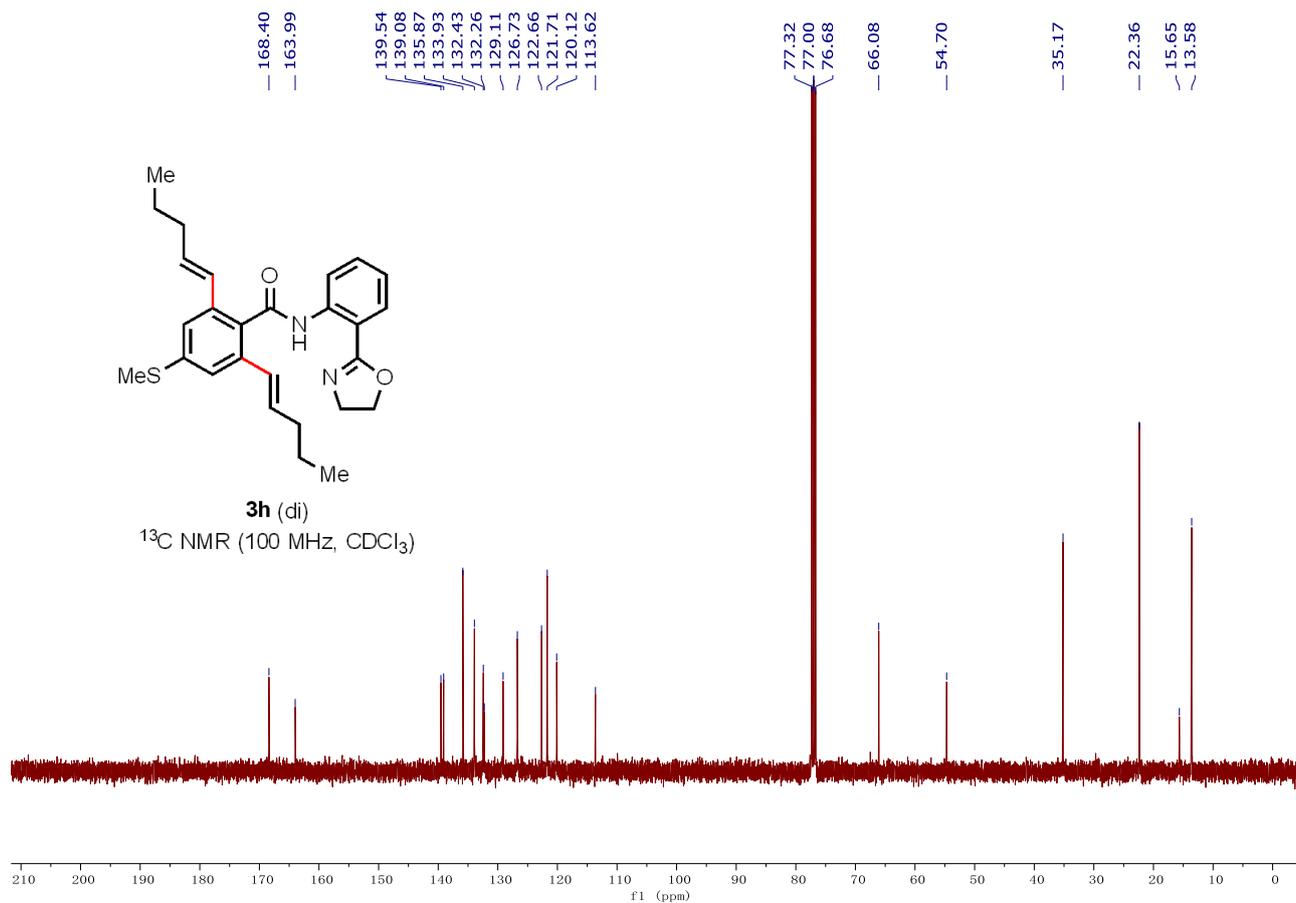


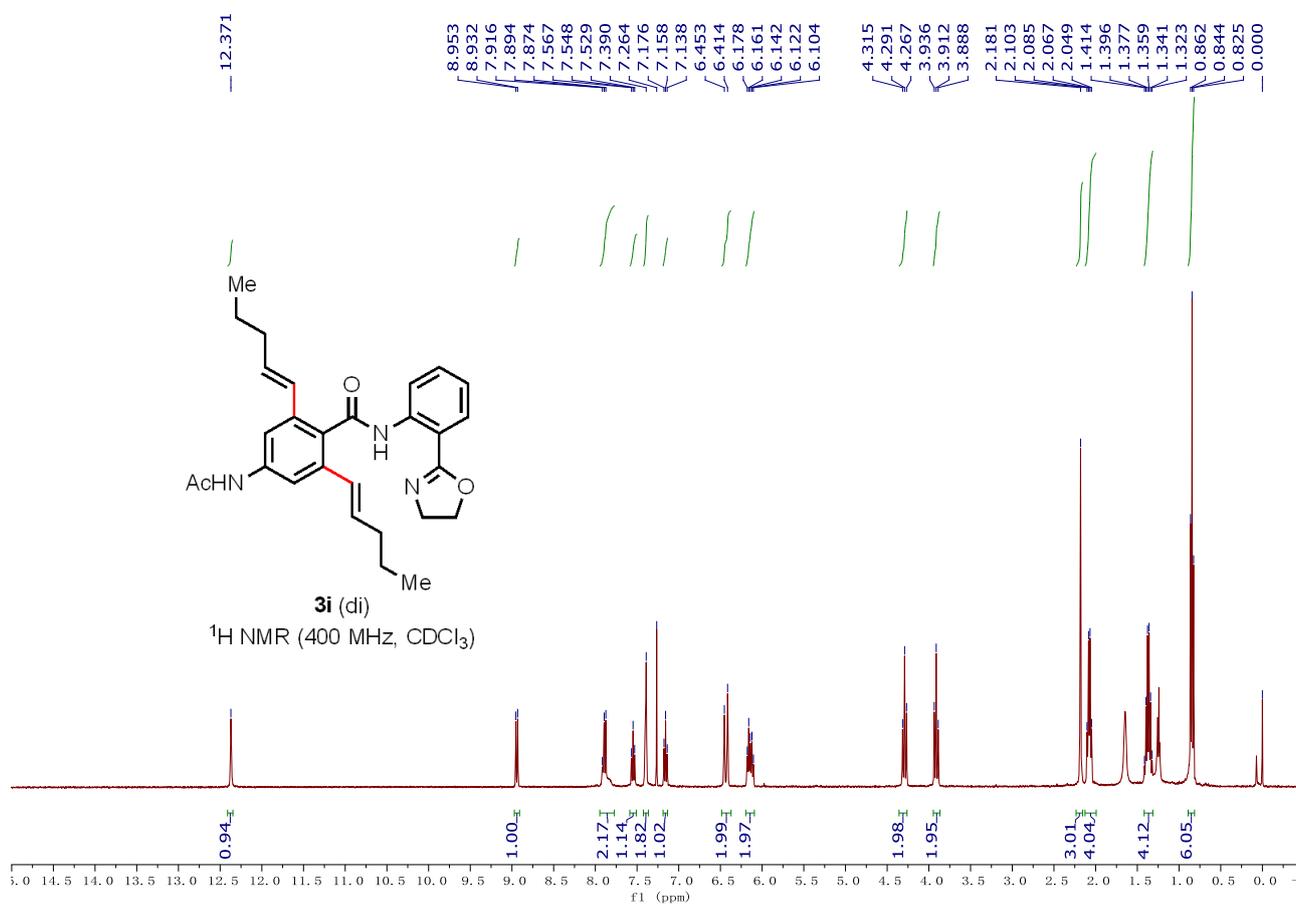
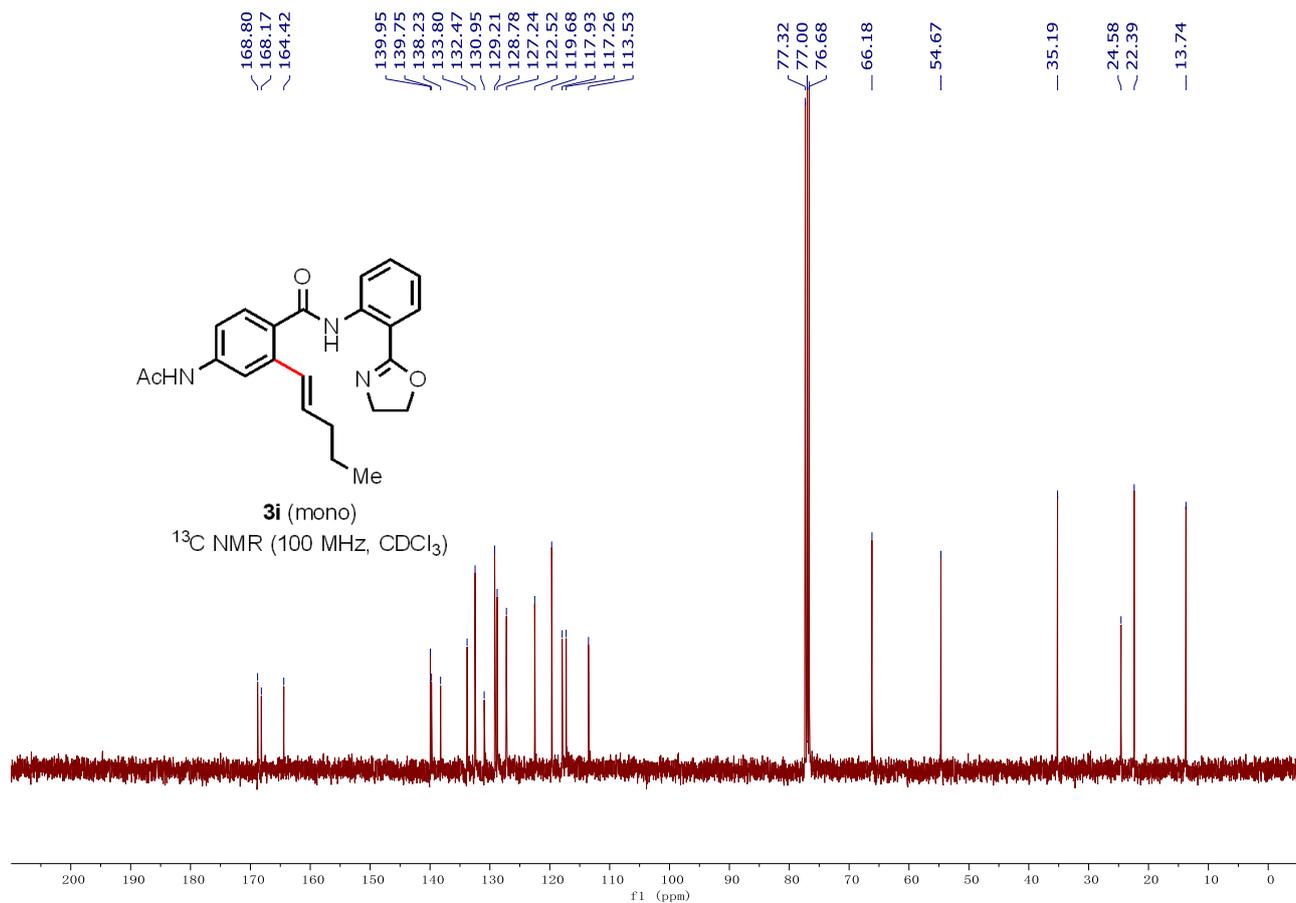


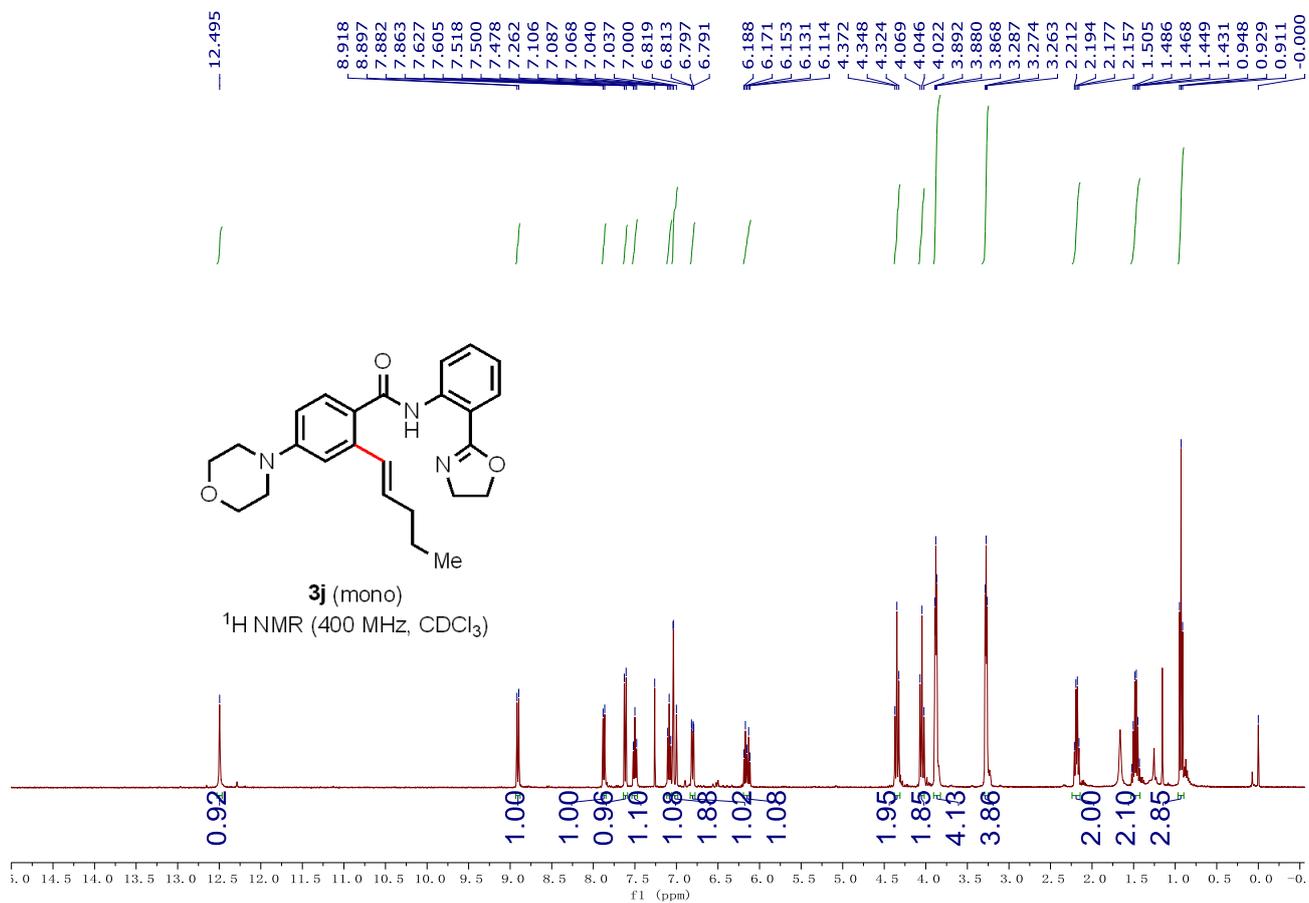
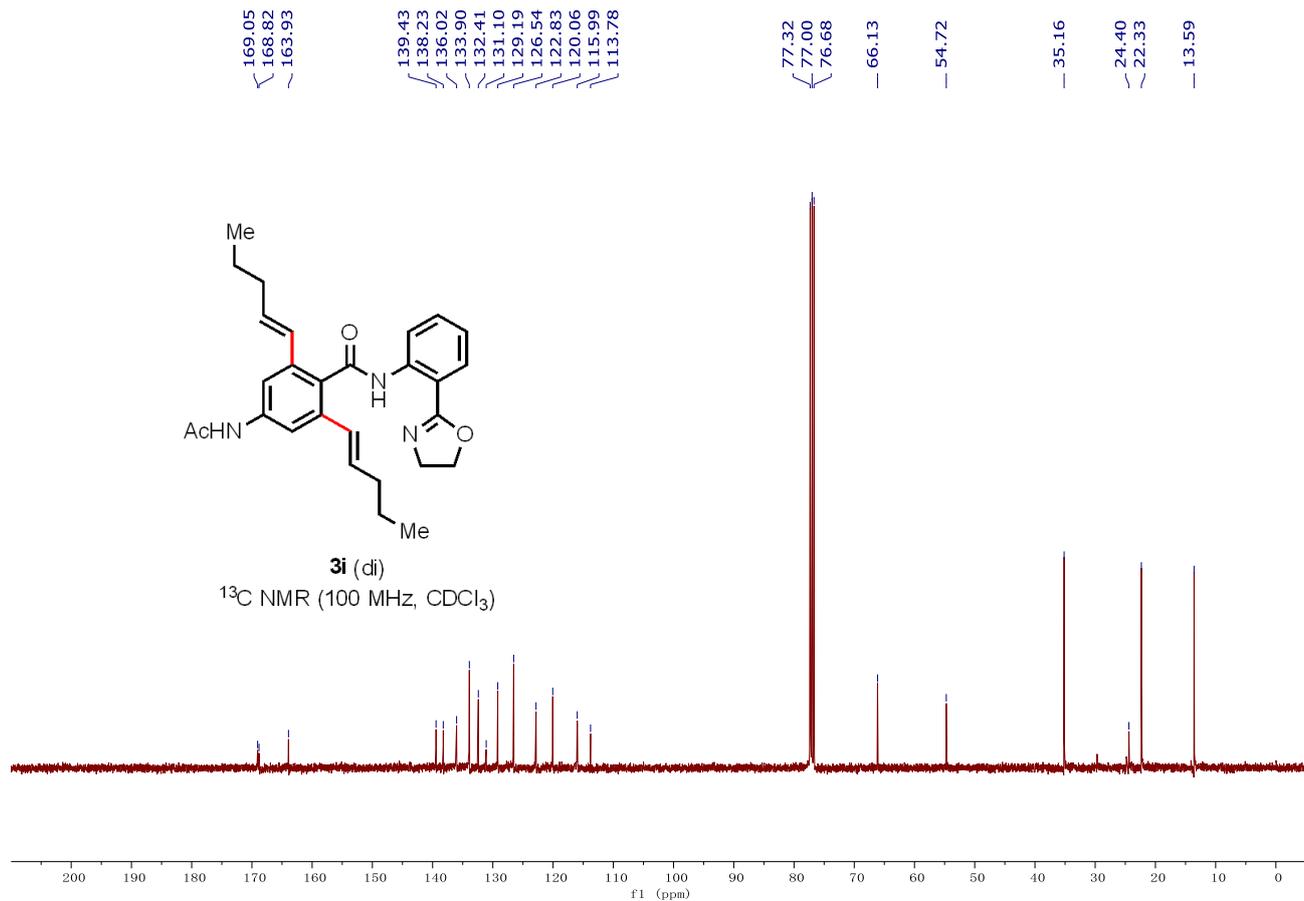


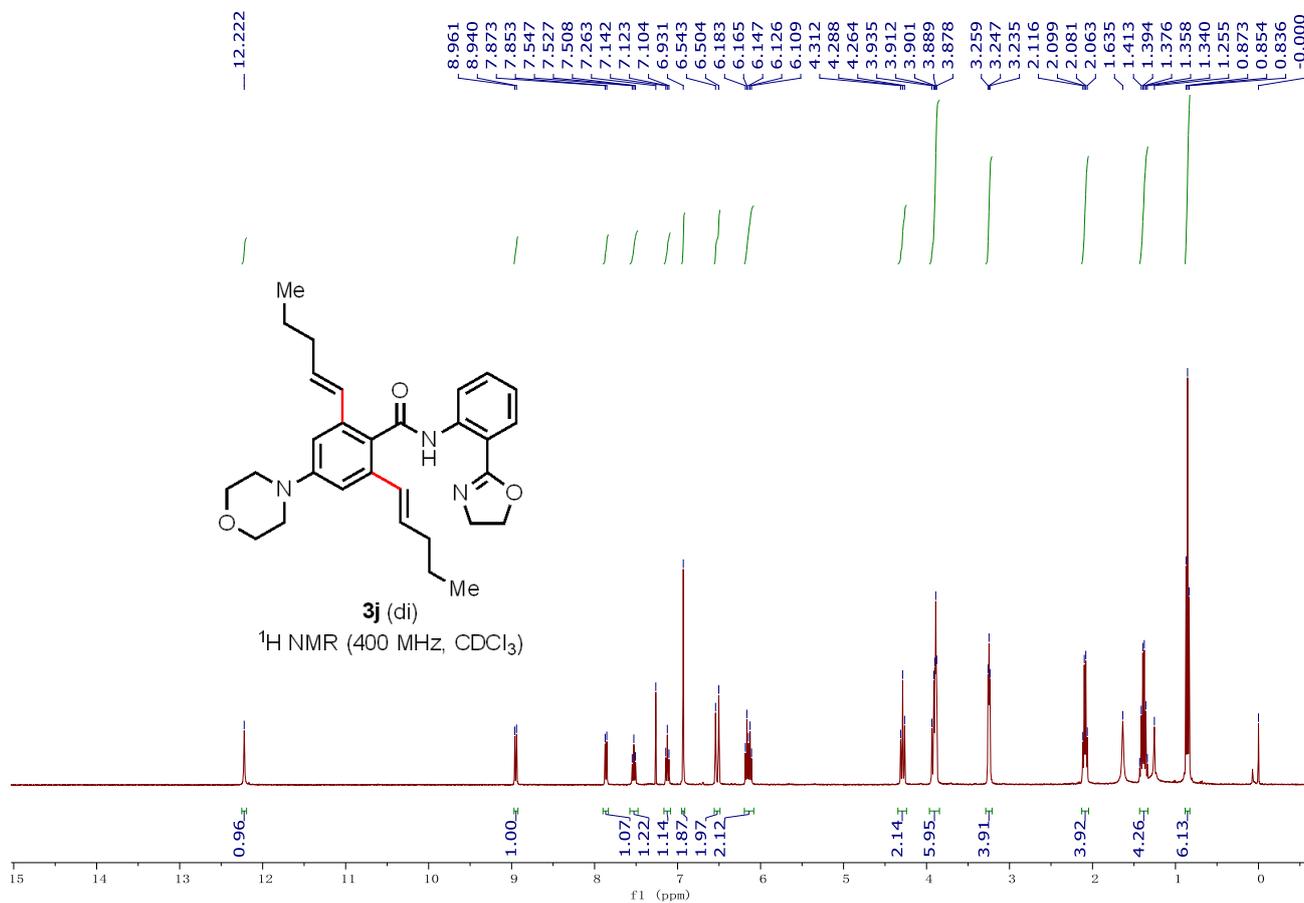
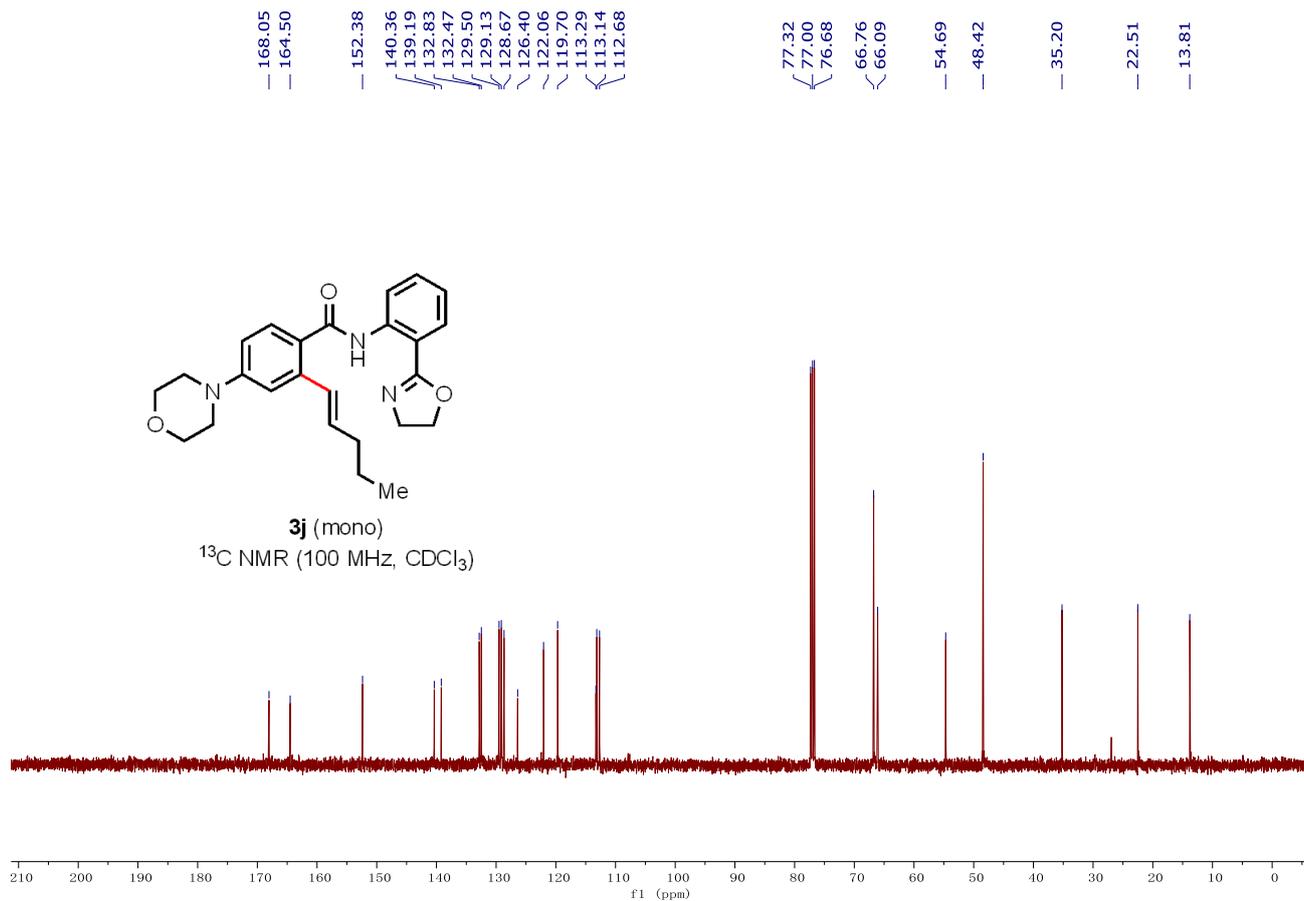


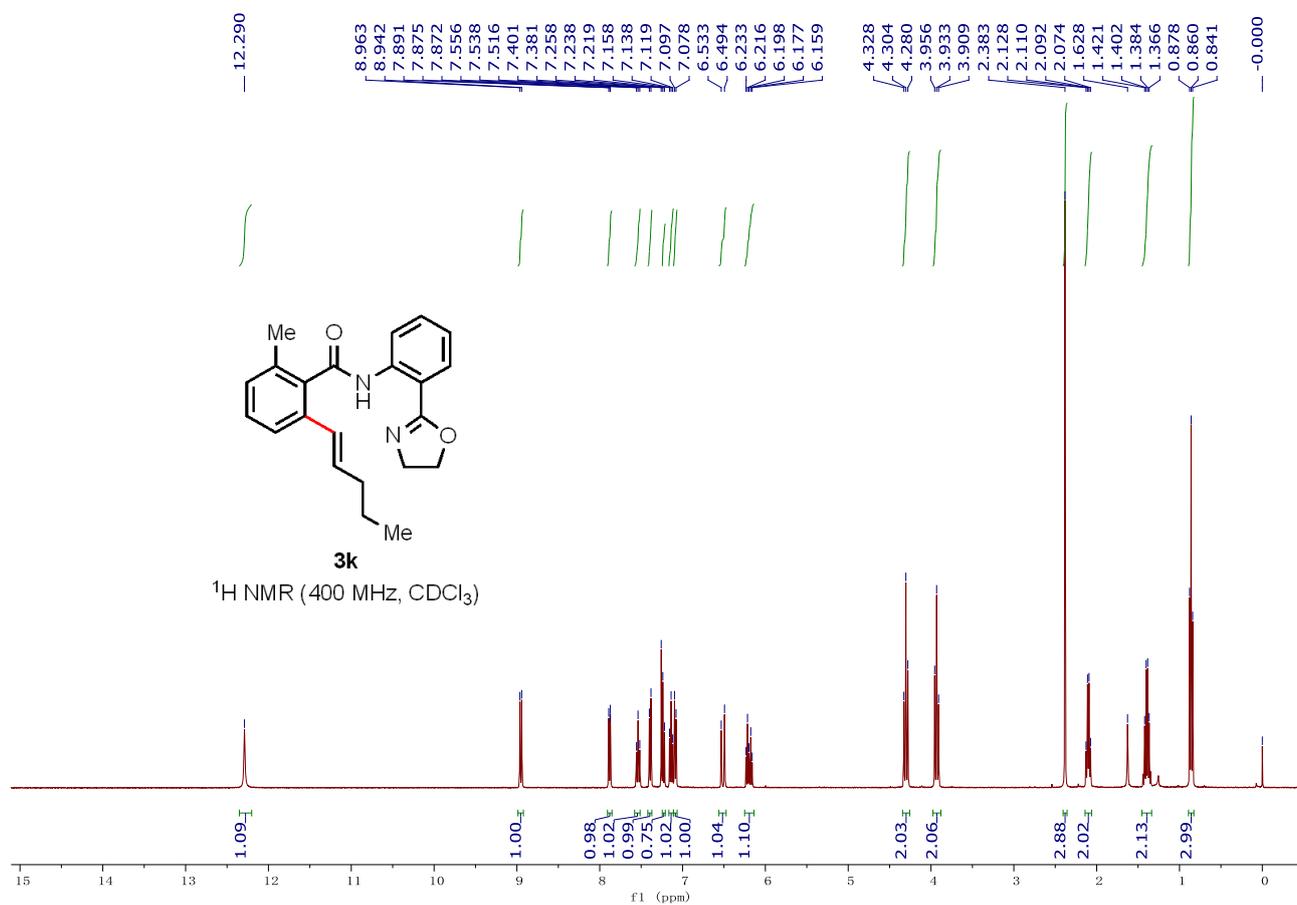
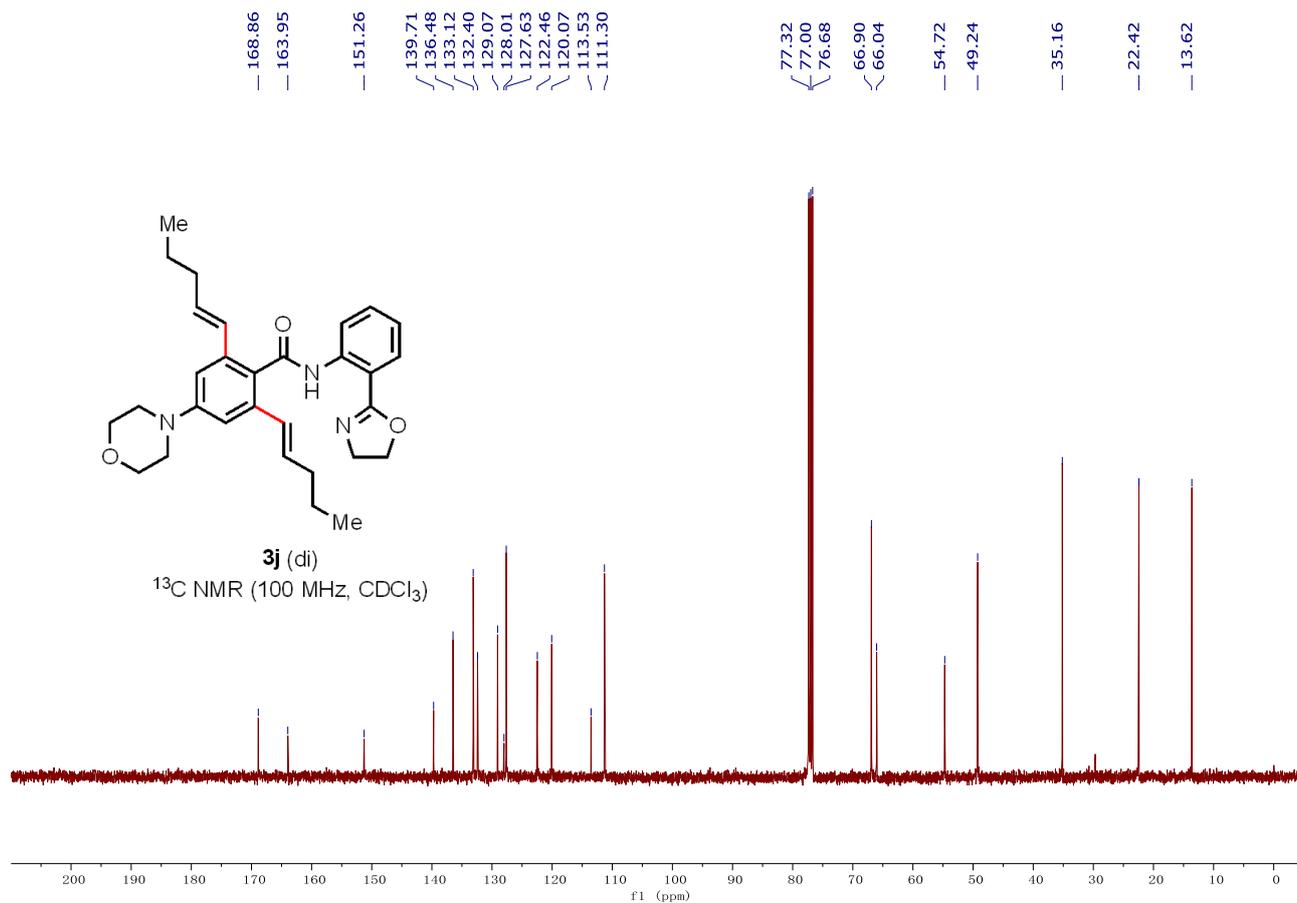


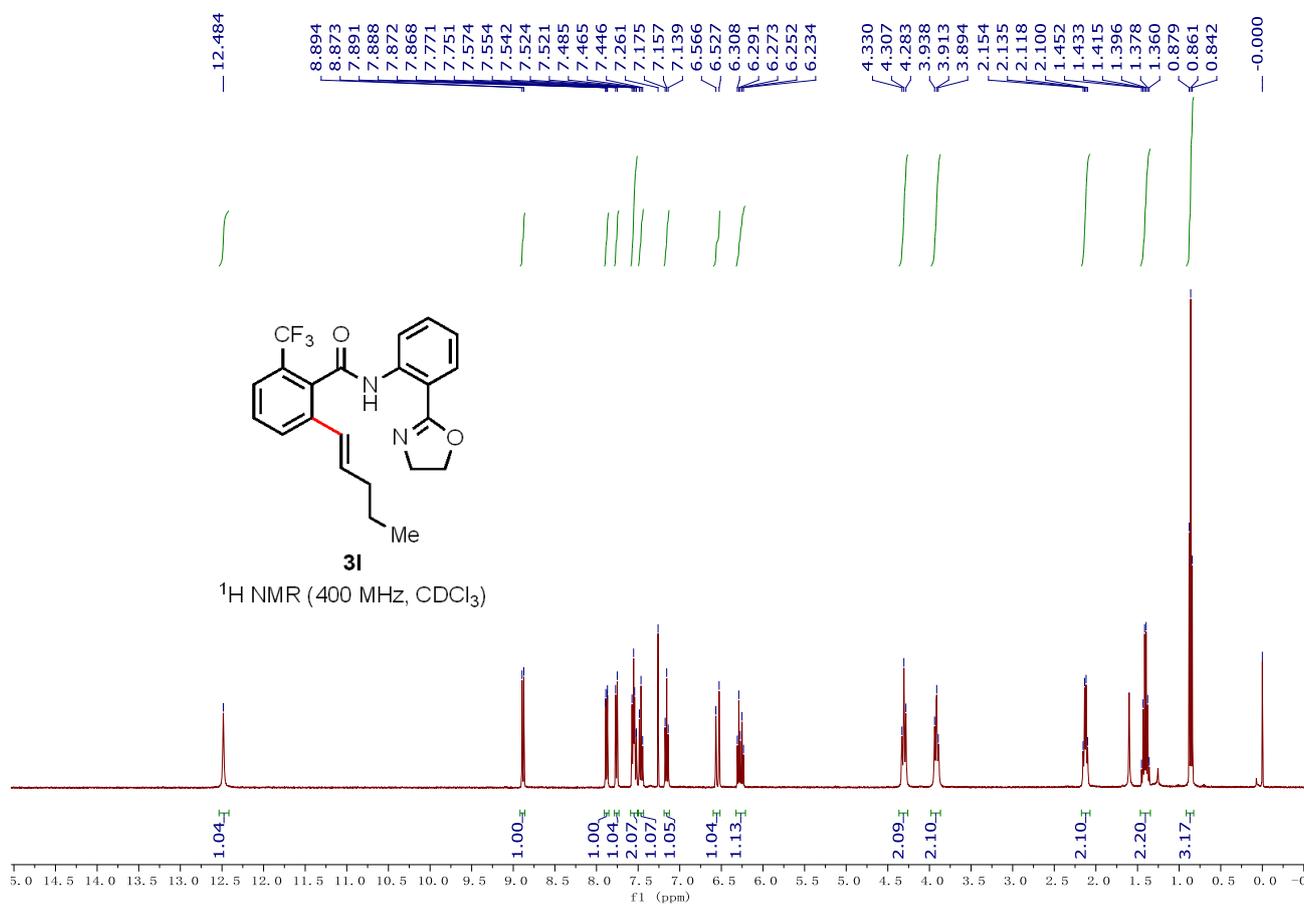
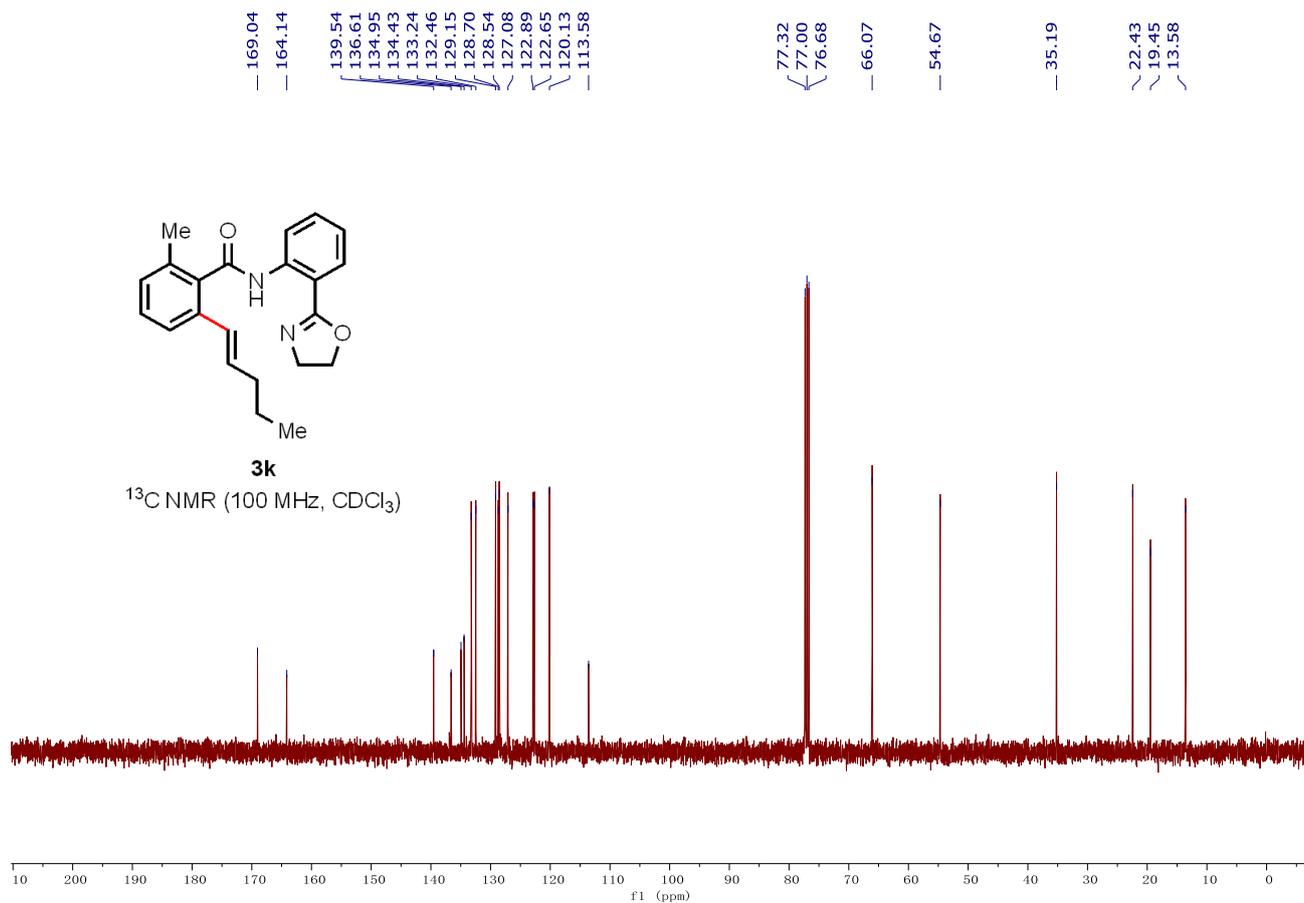


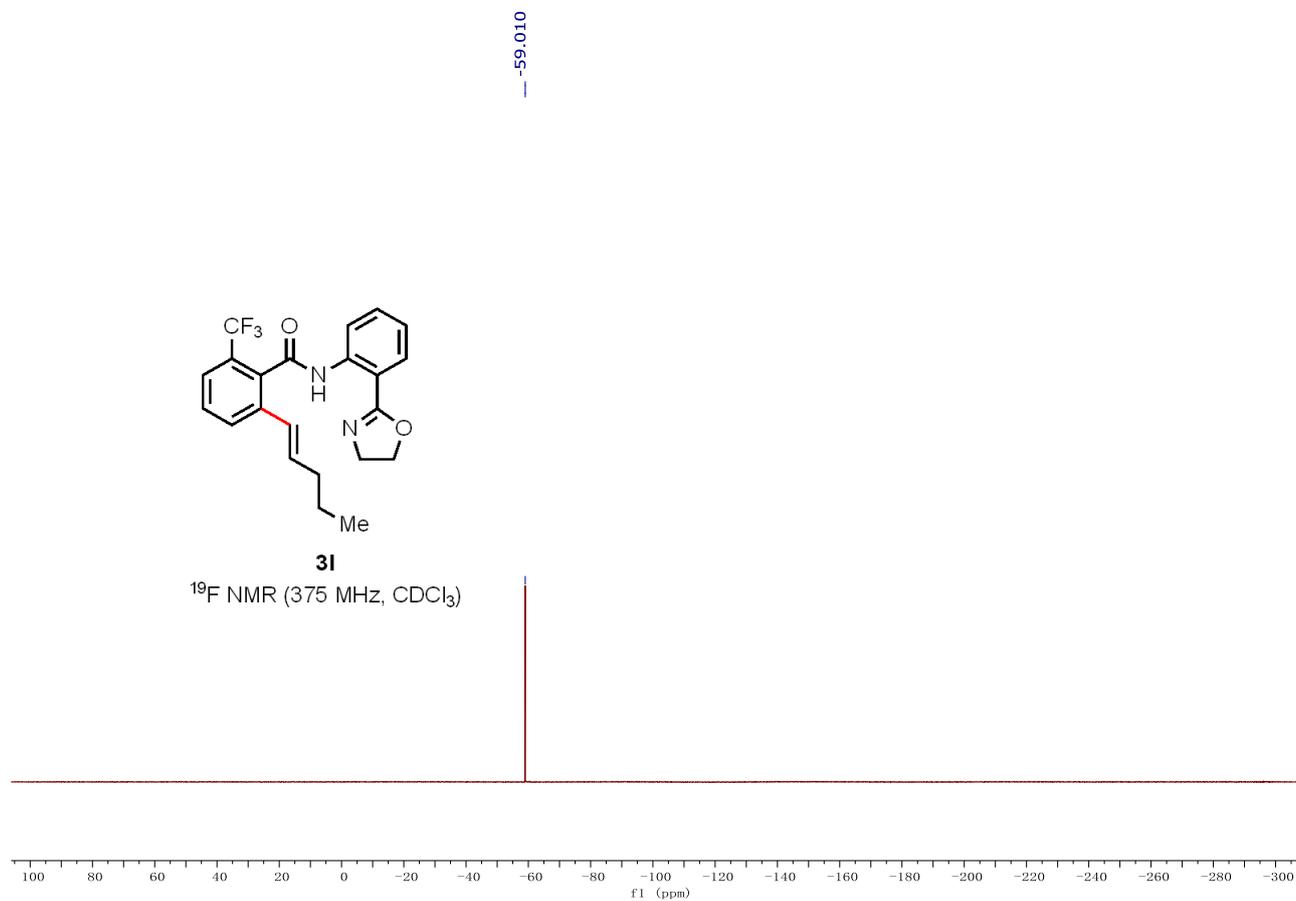
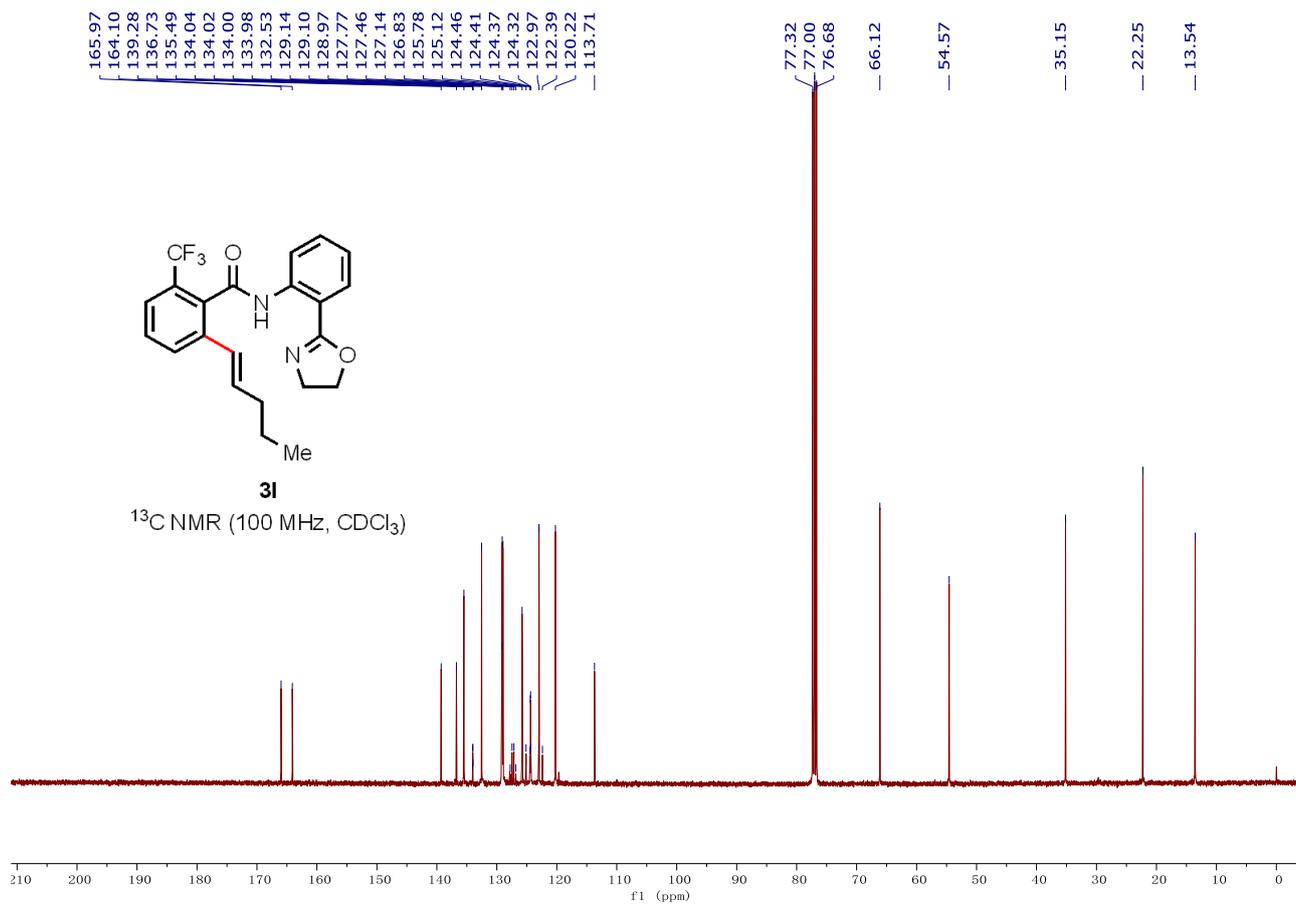


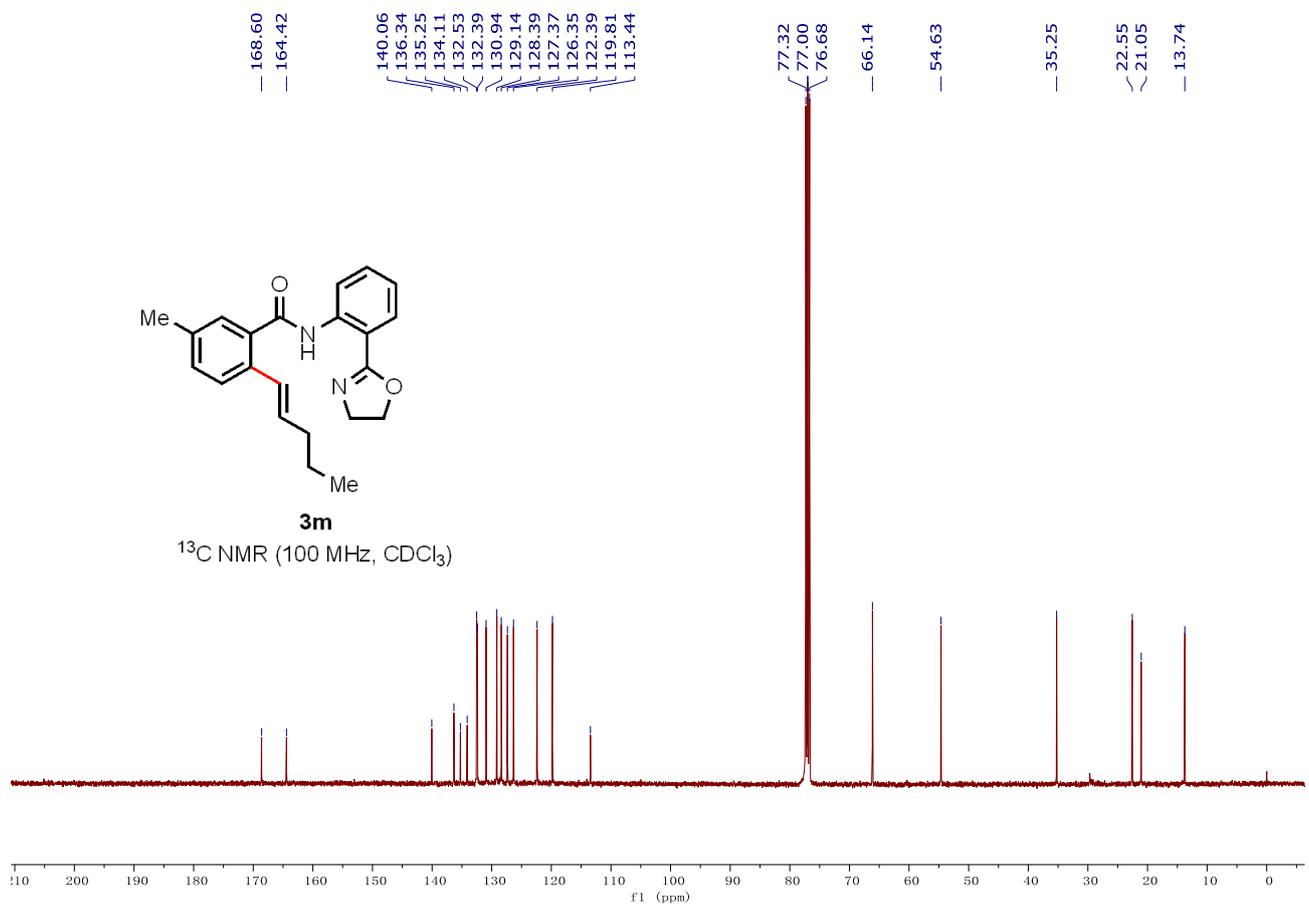
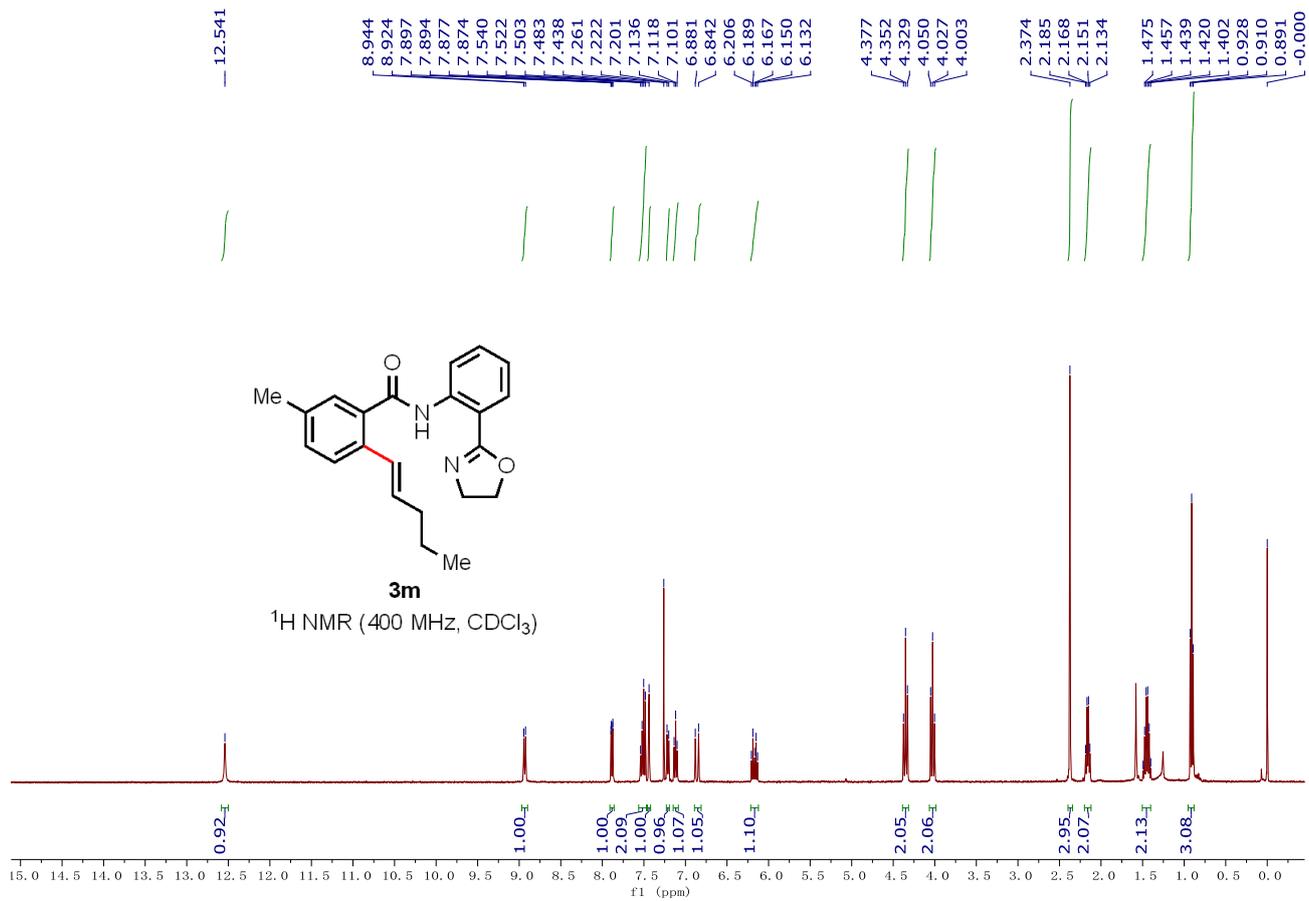


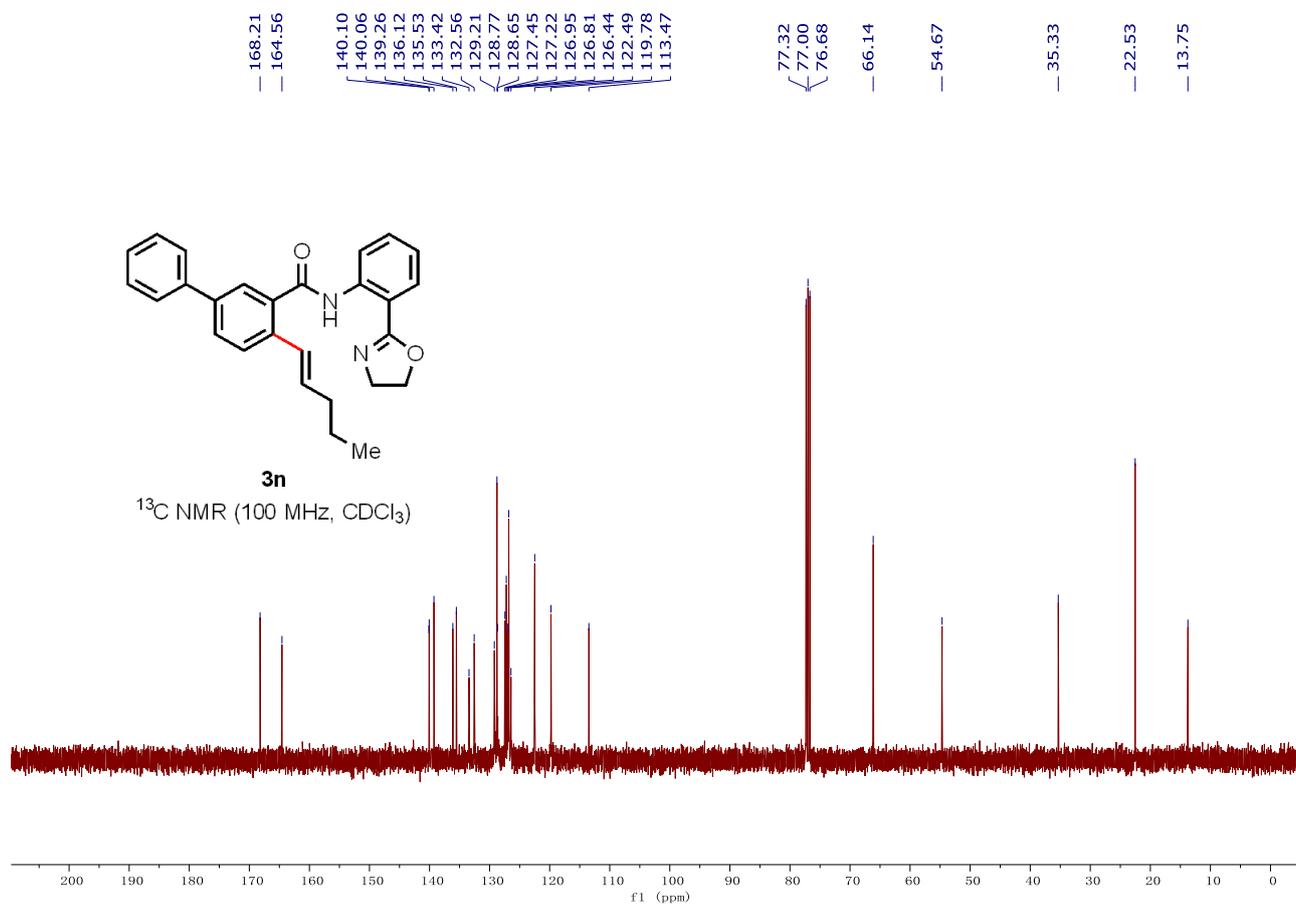
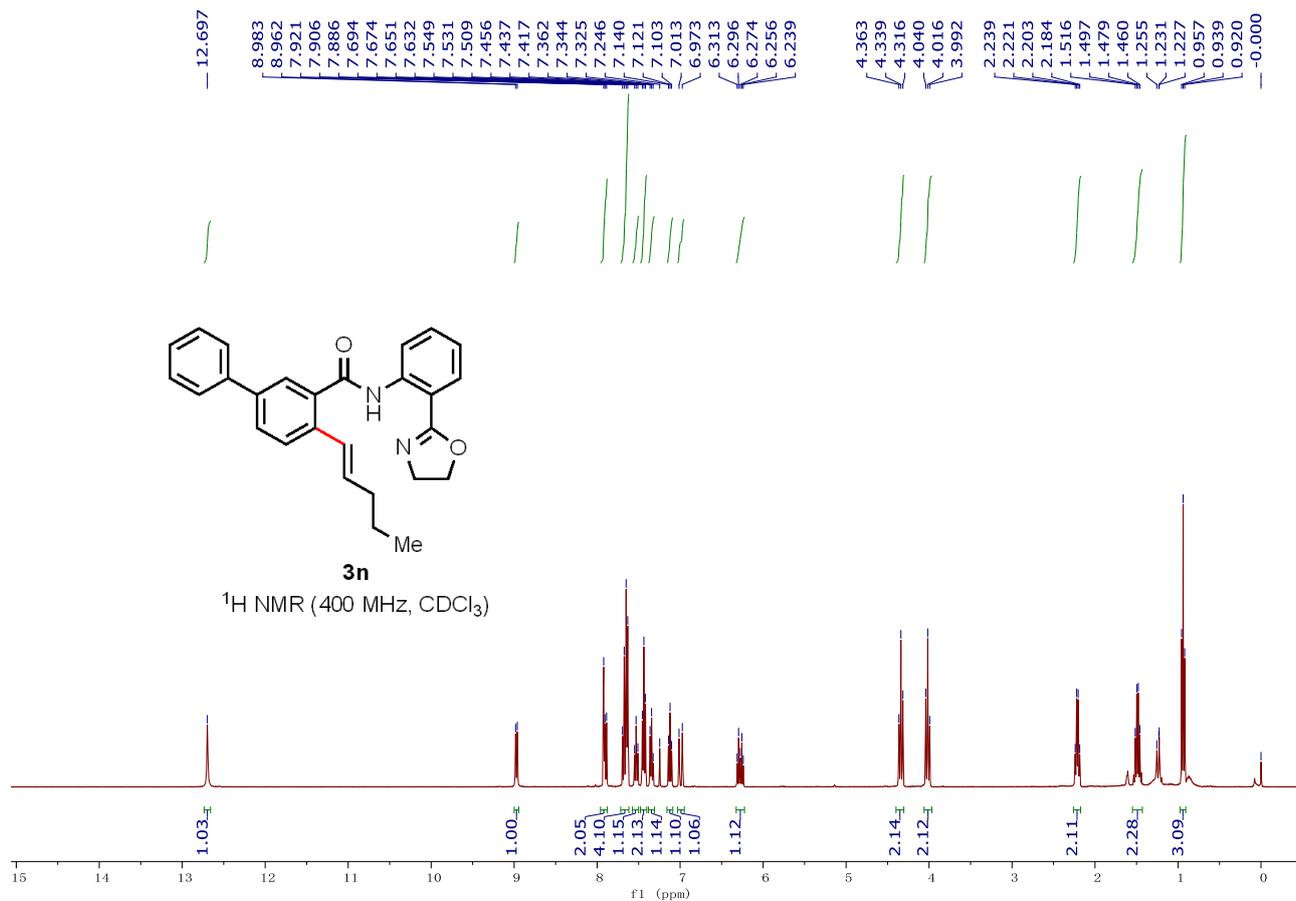


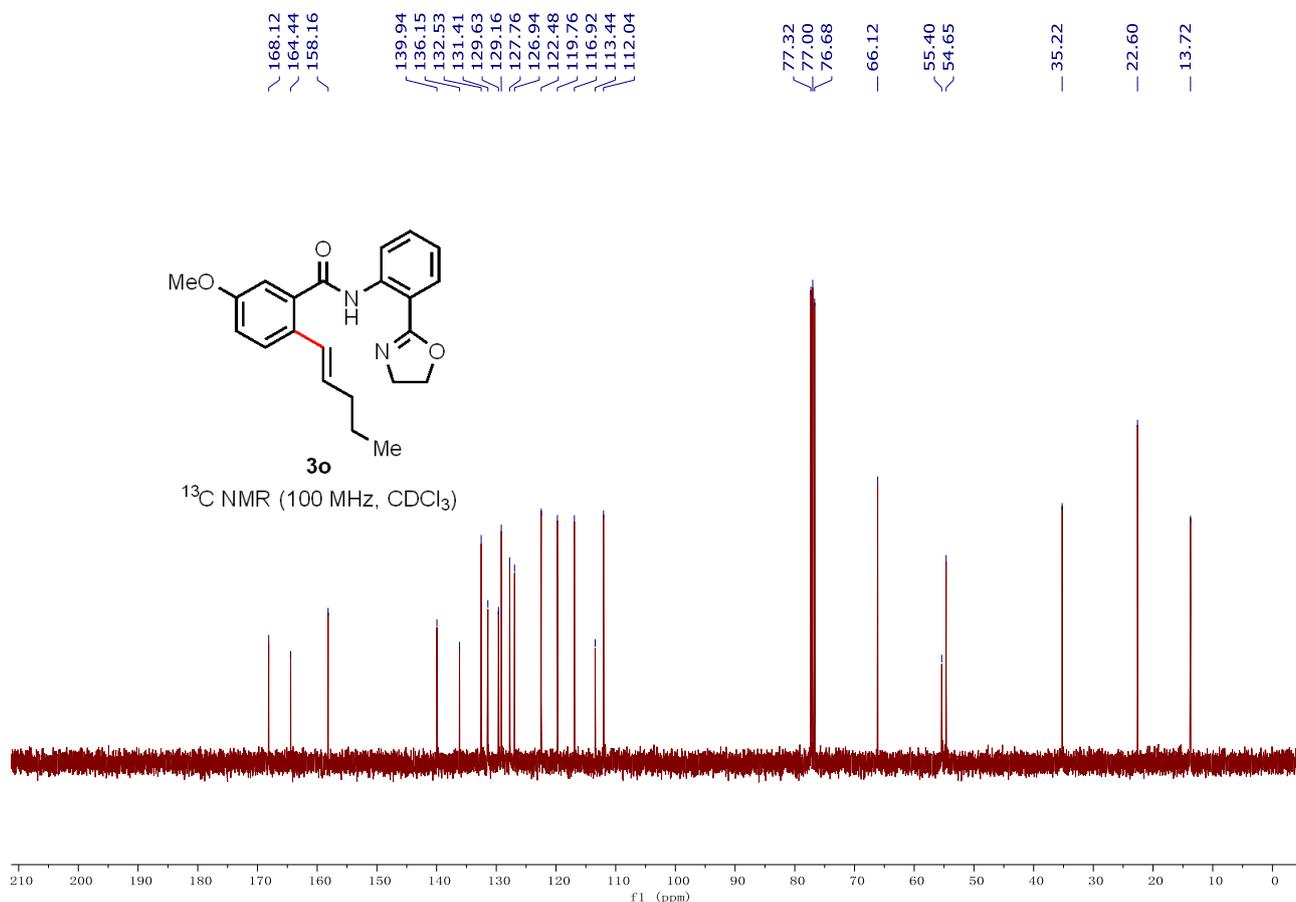
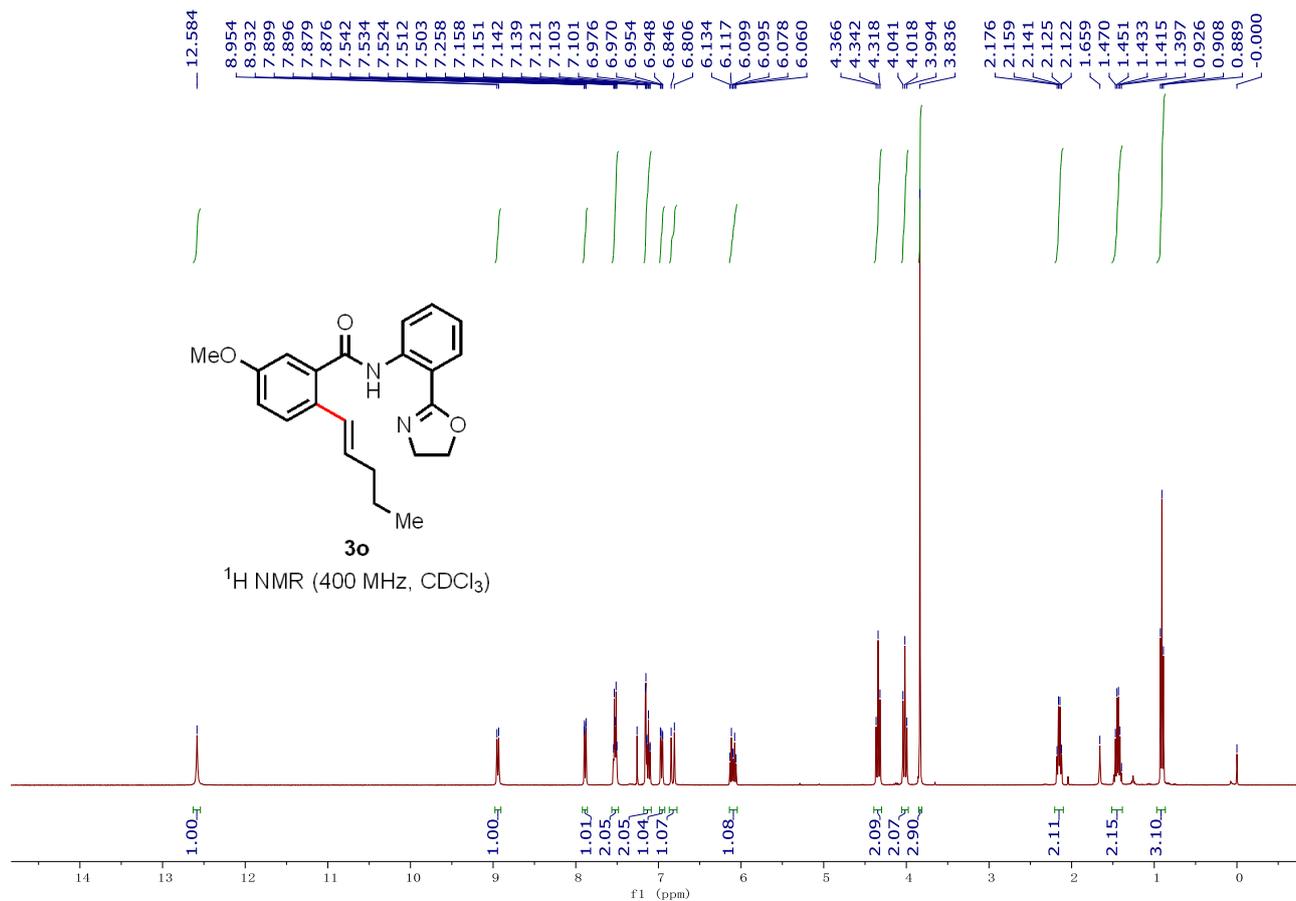


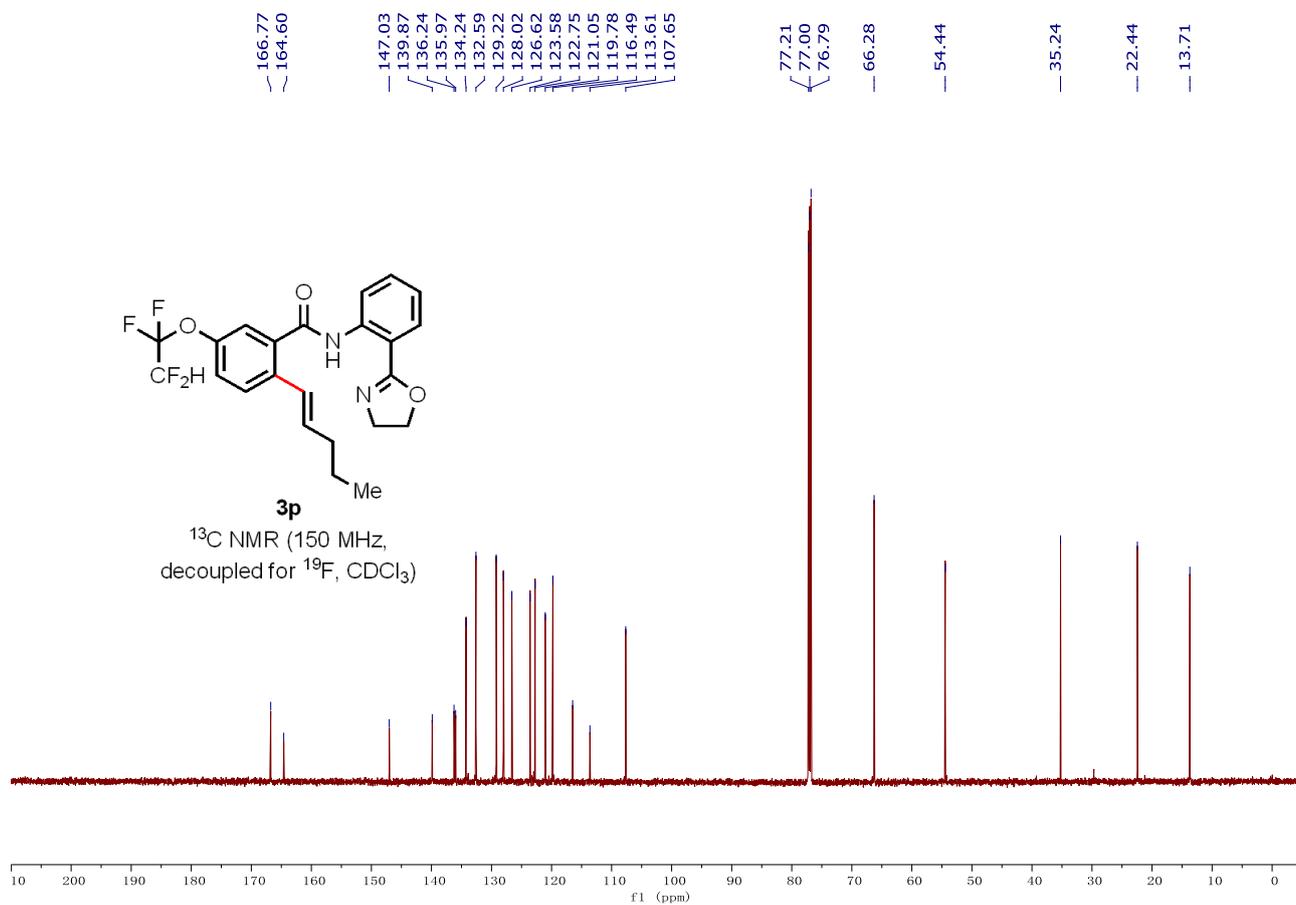
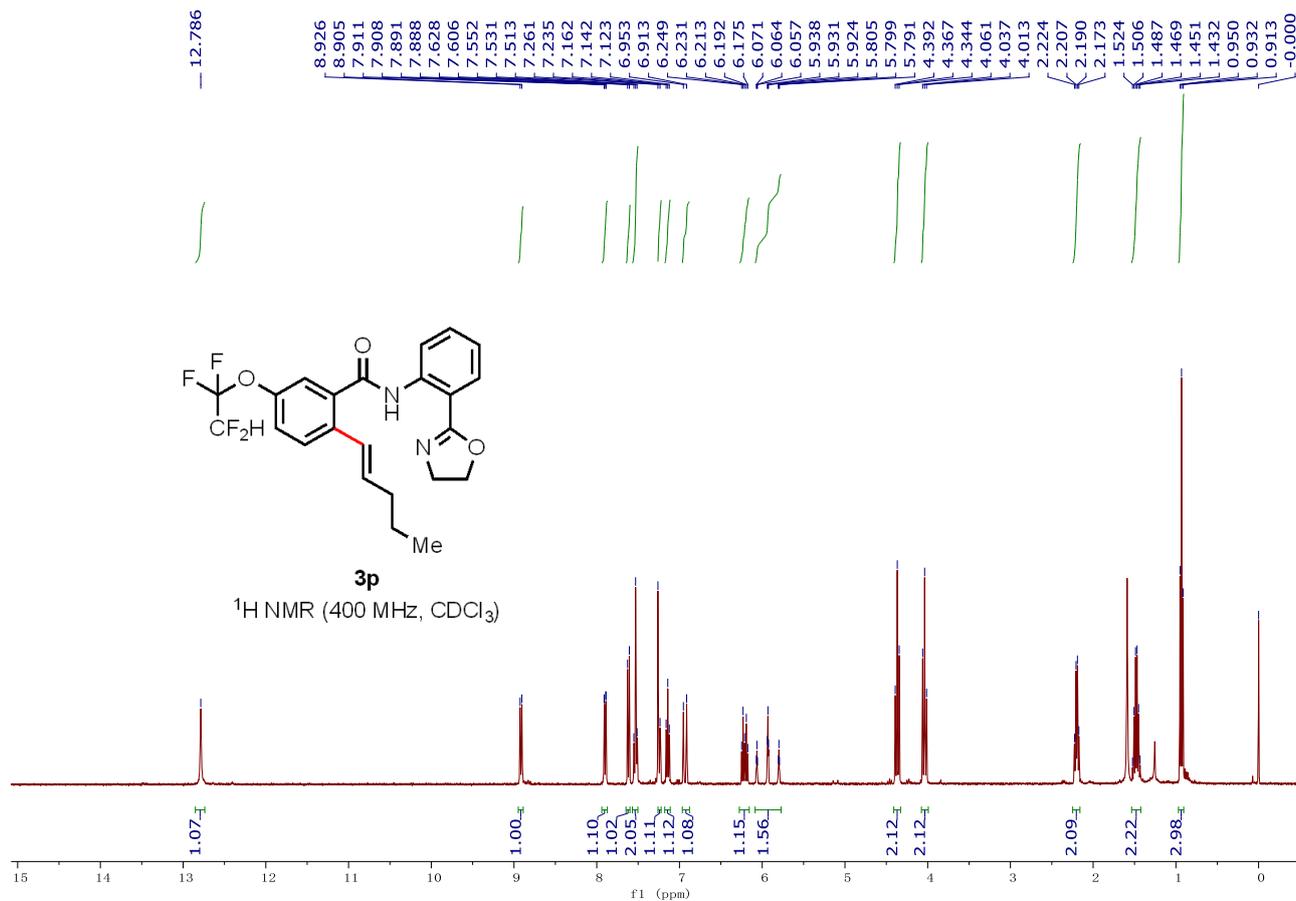


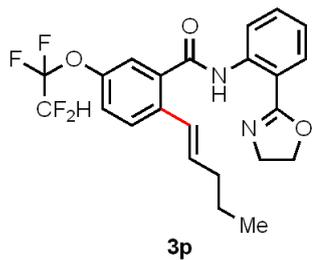
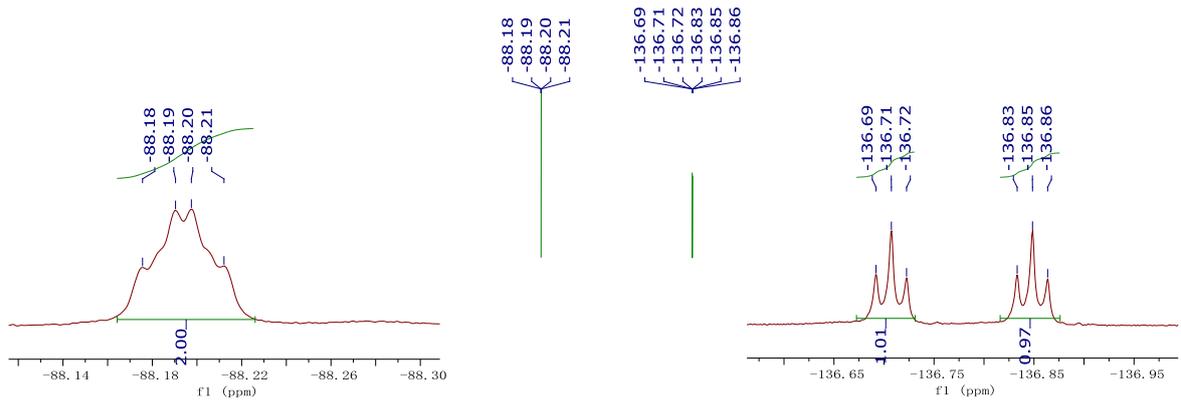




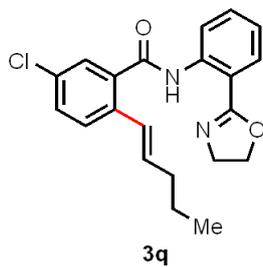
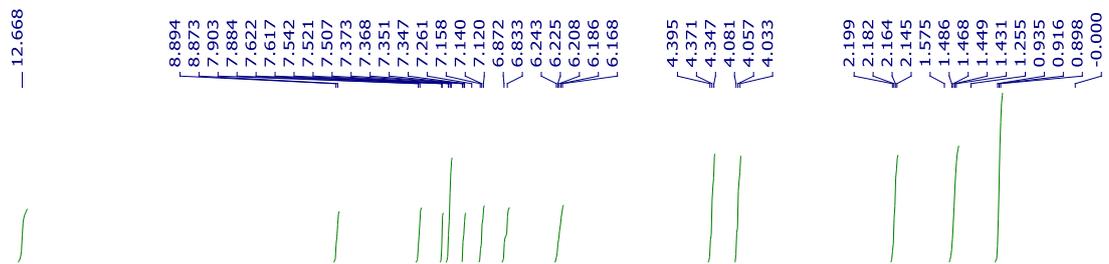
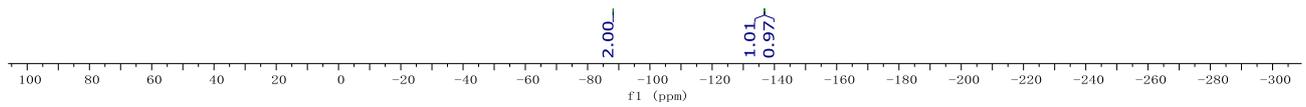




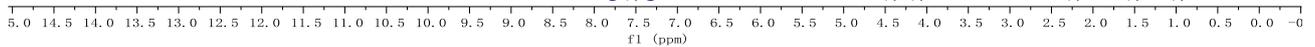


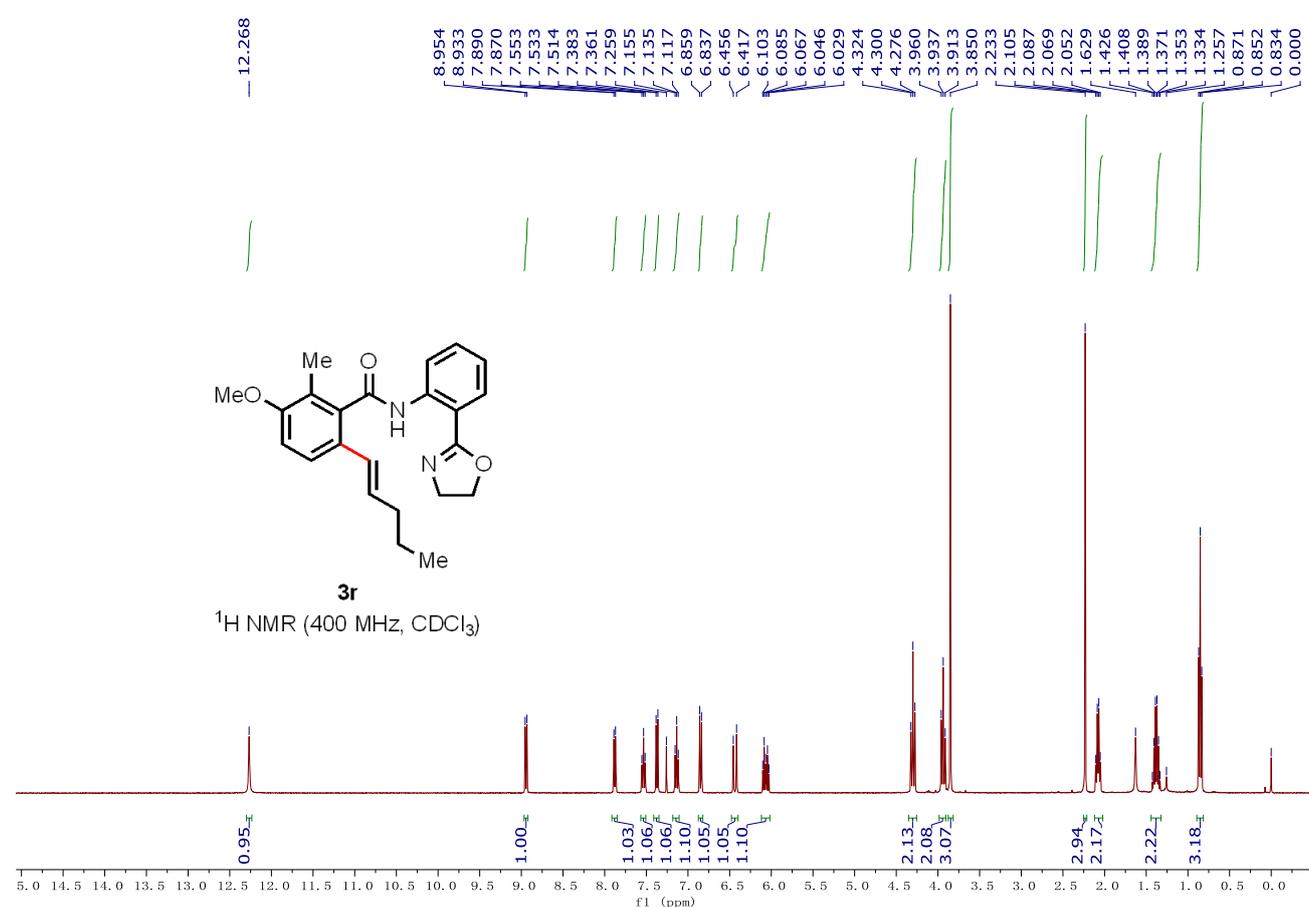
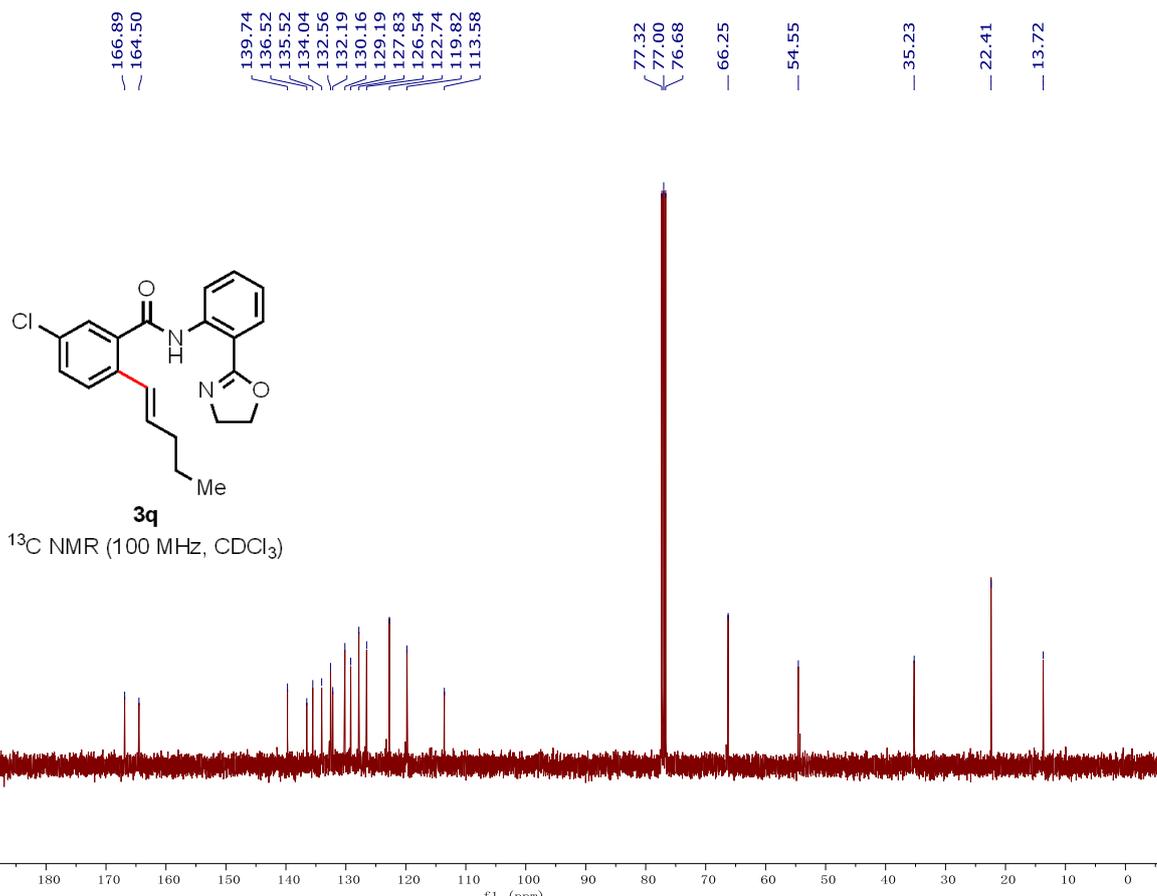


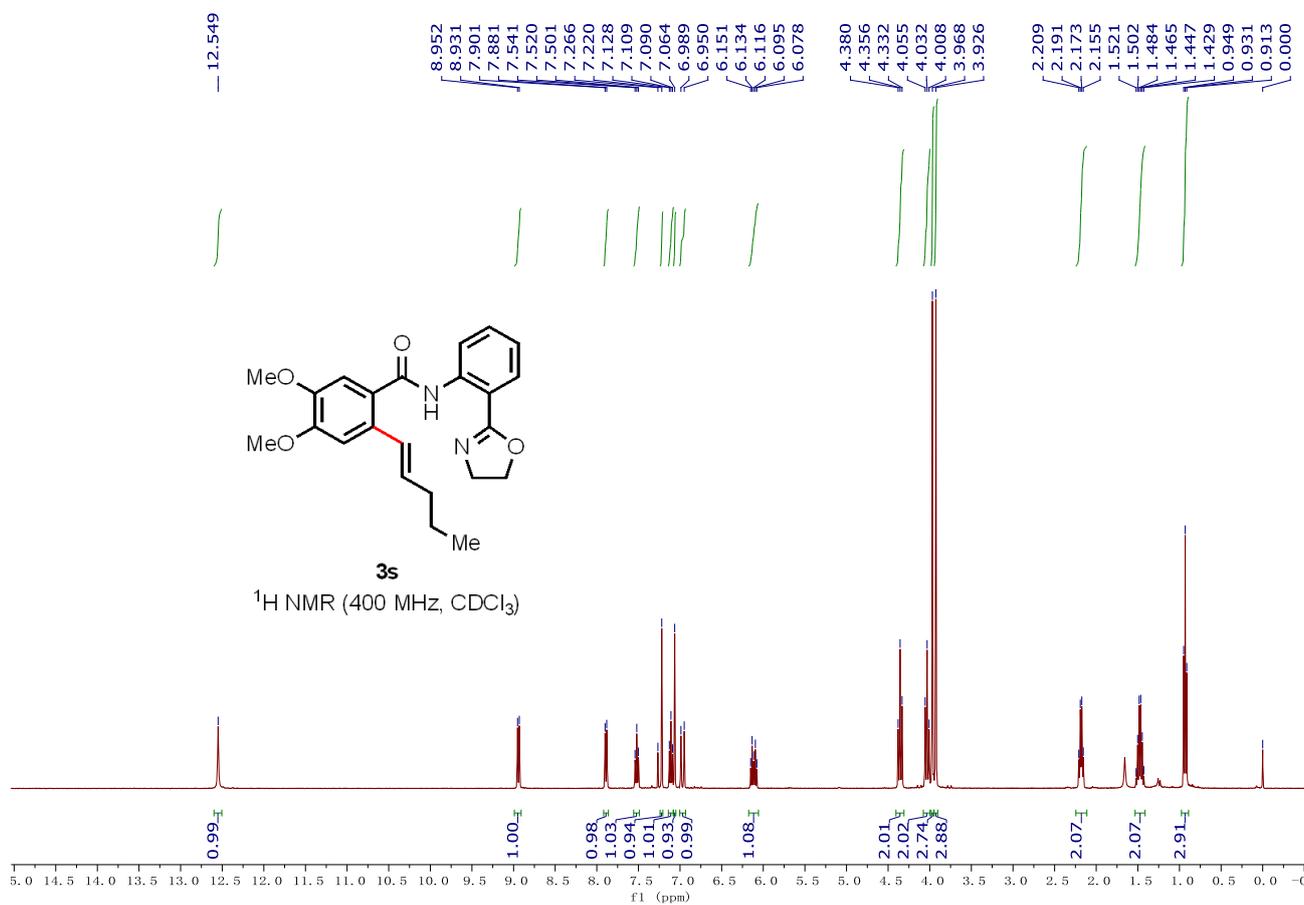
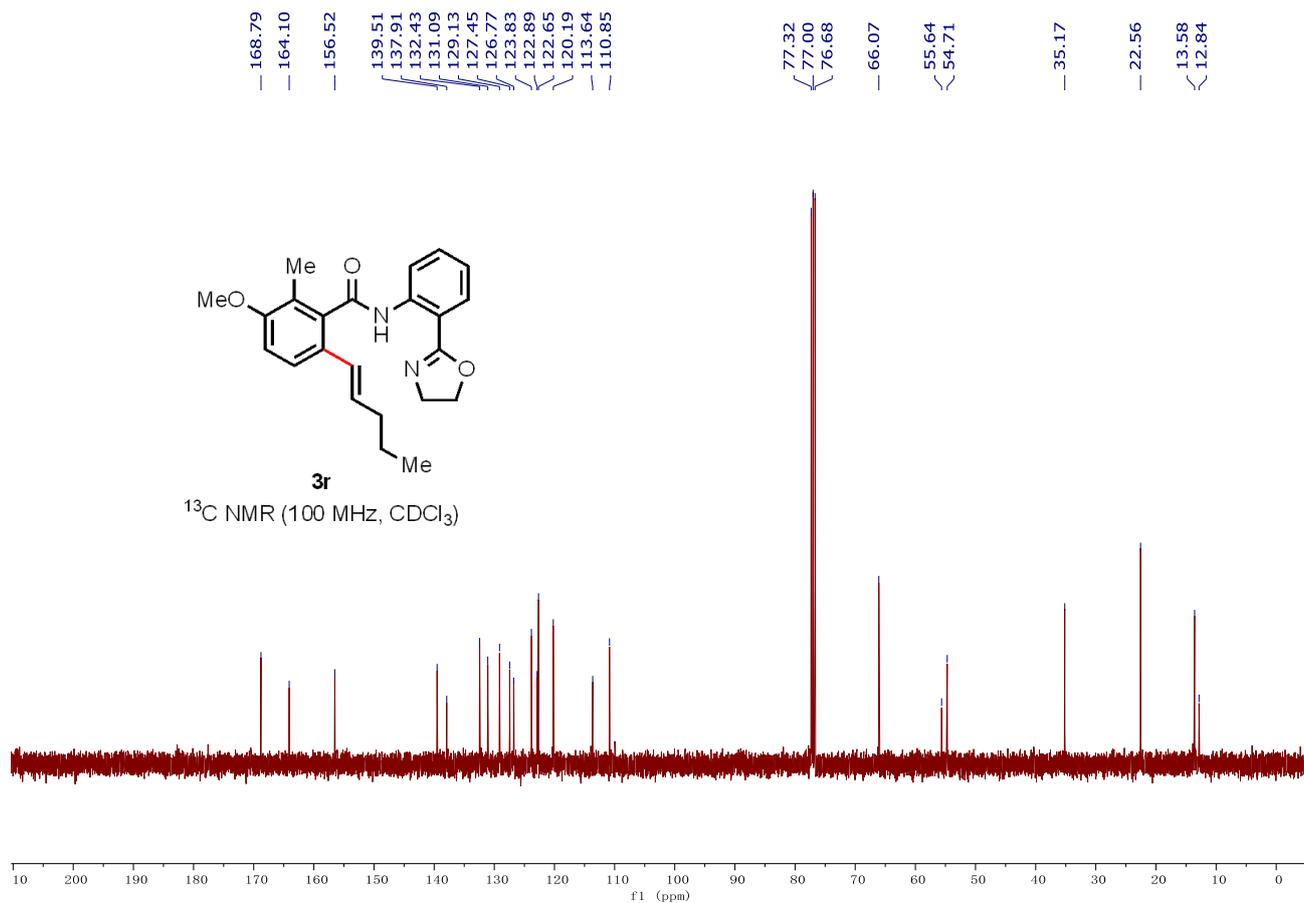
¹⁹F NMR (375 MHz, CDCl₃)

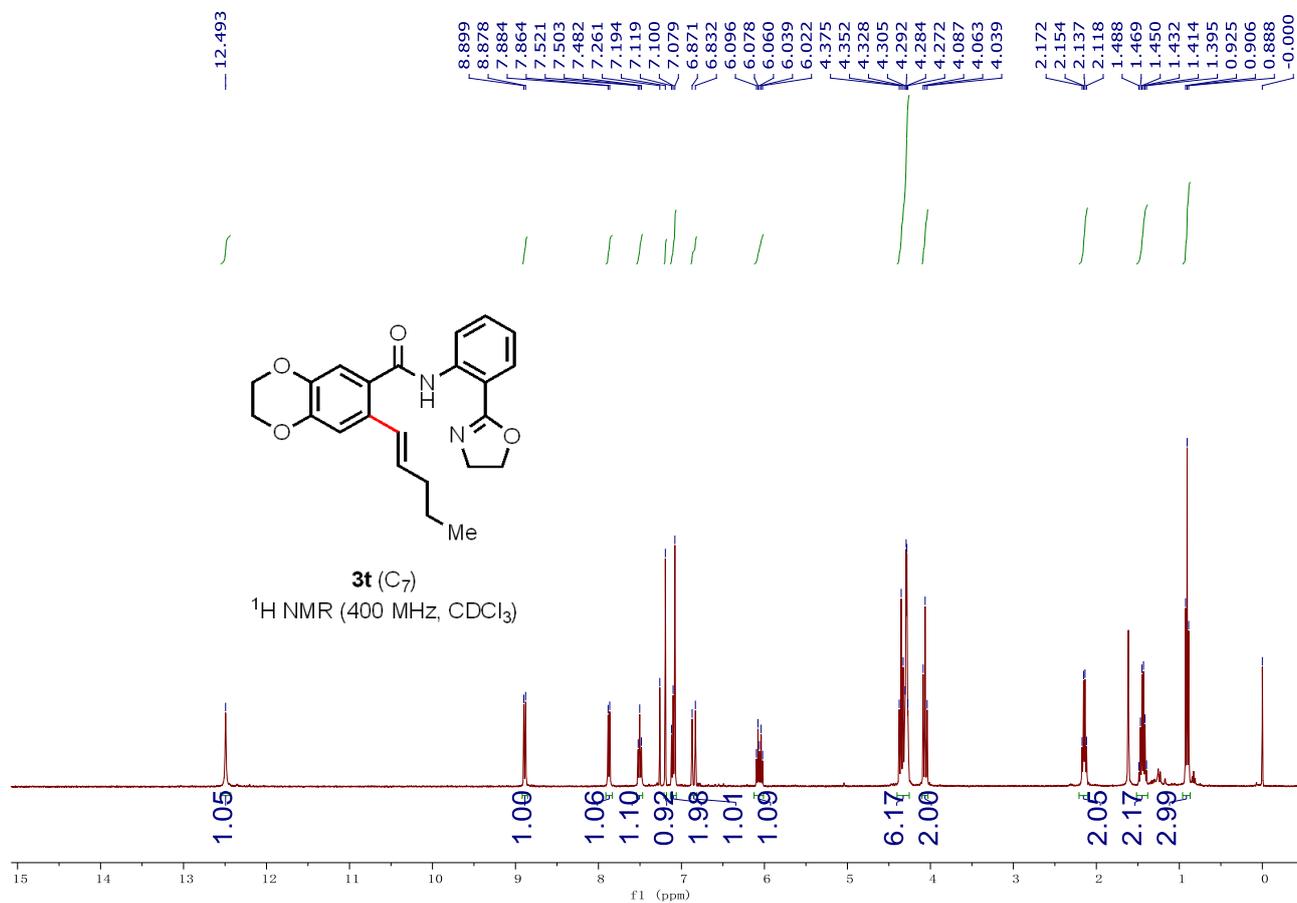
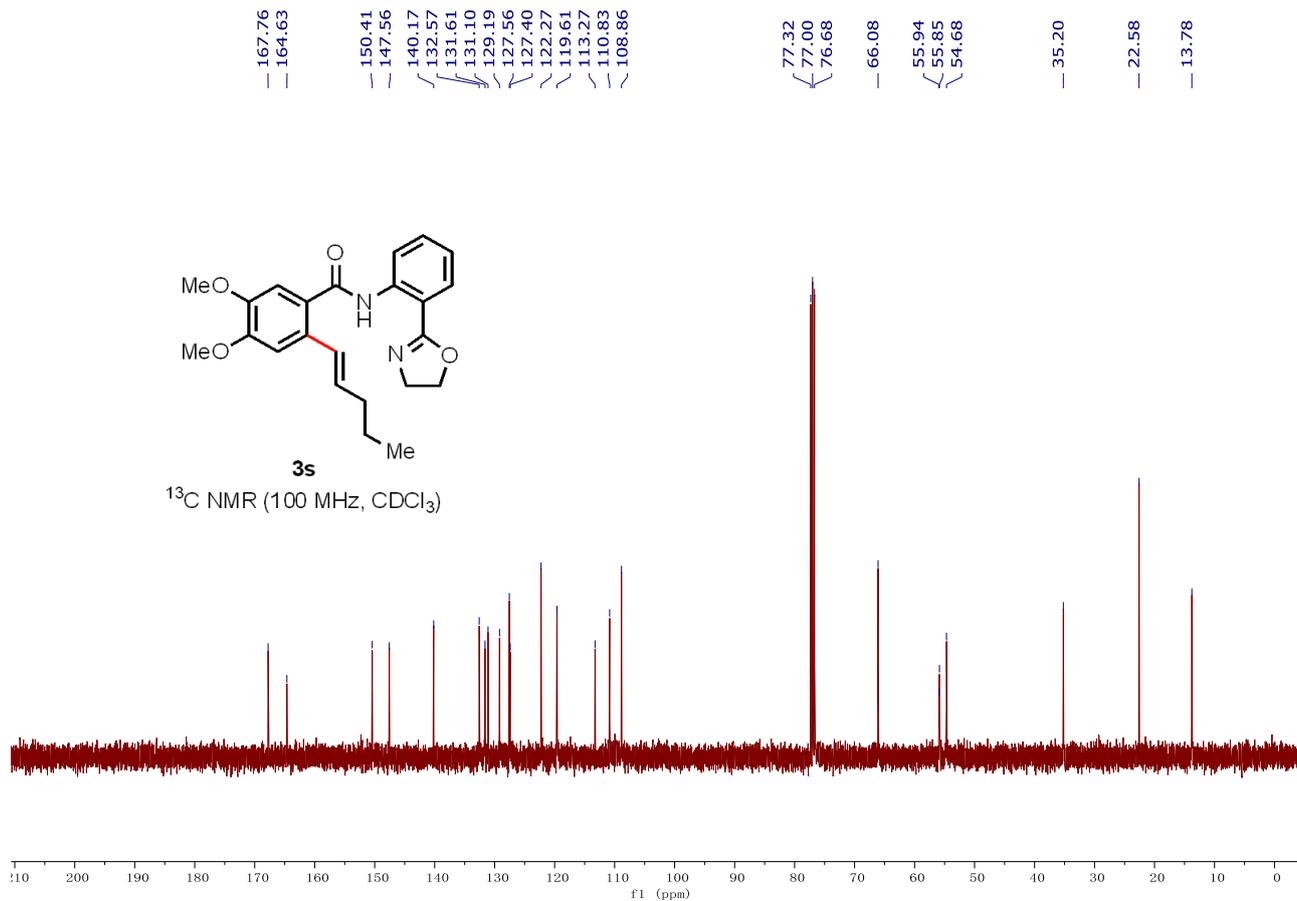


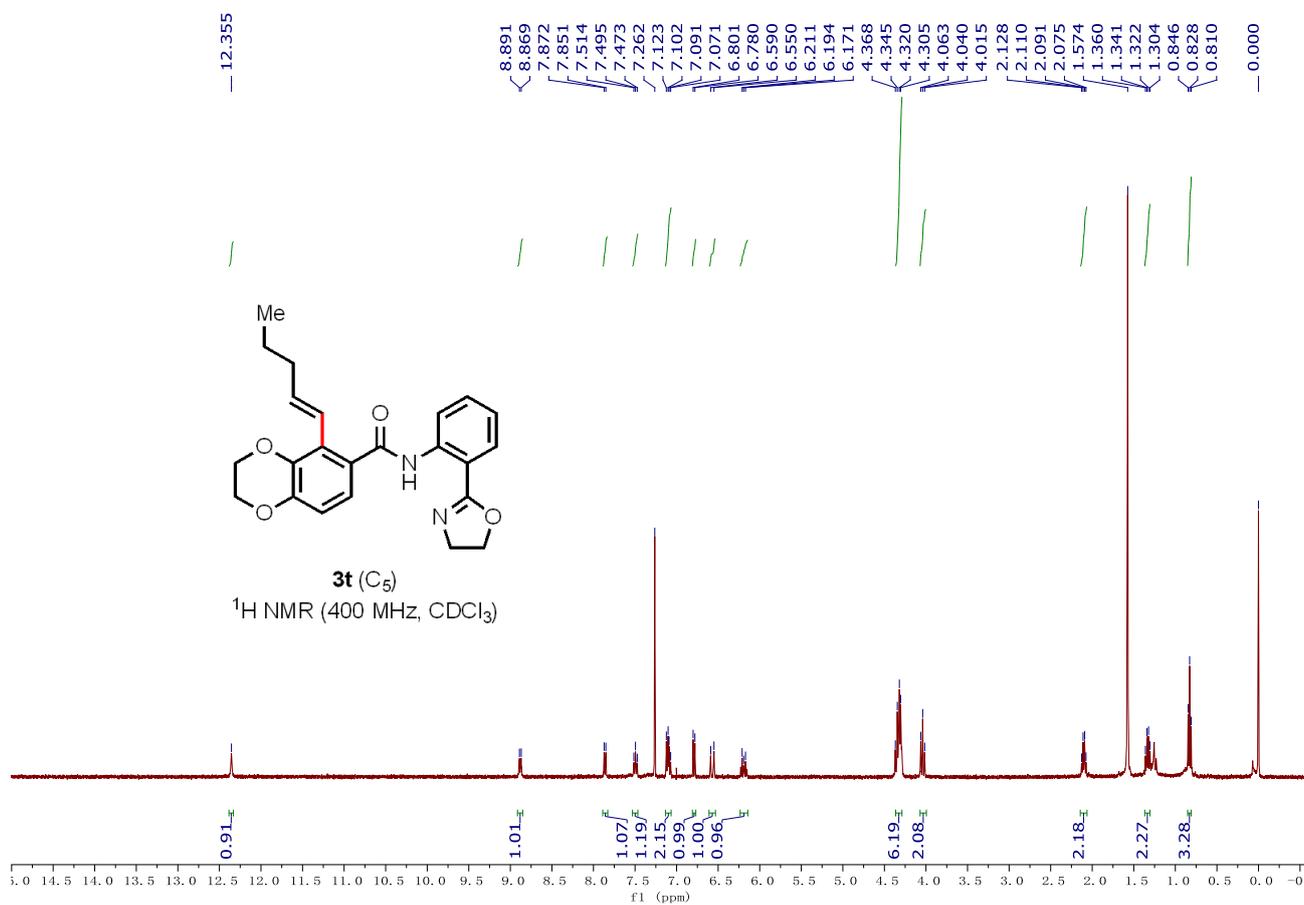
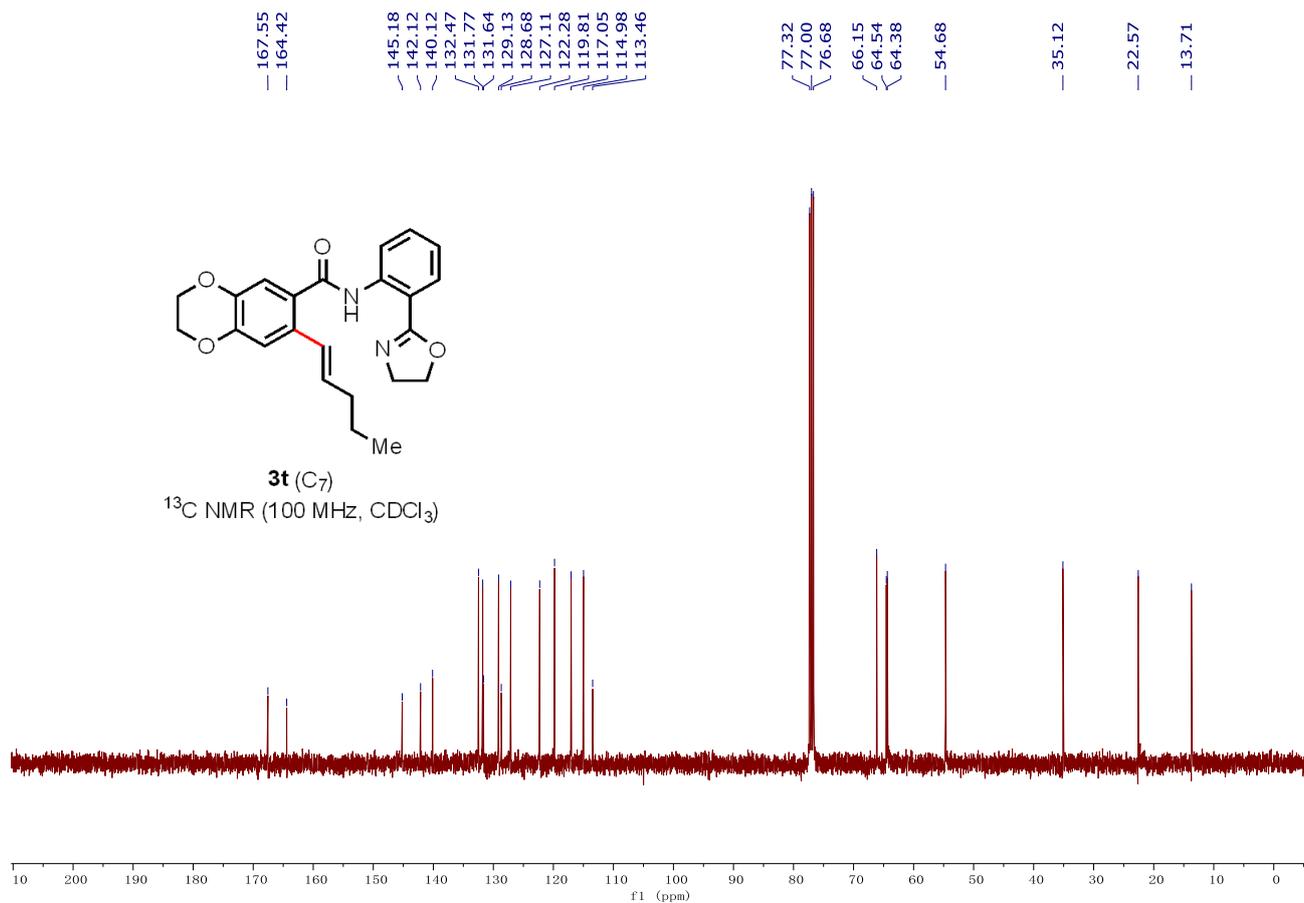
¹H NMR (400 MHz, CDCl₃)

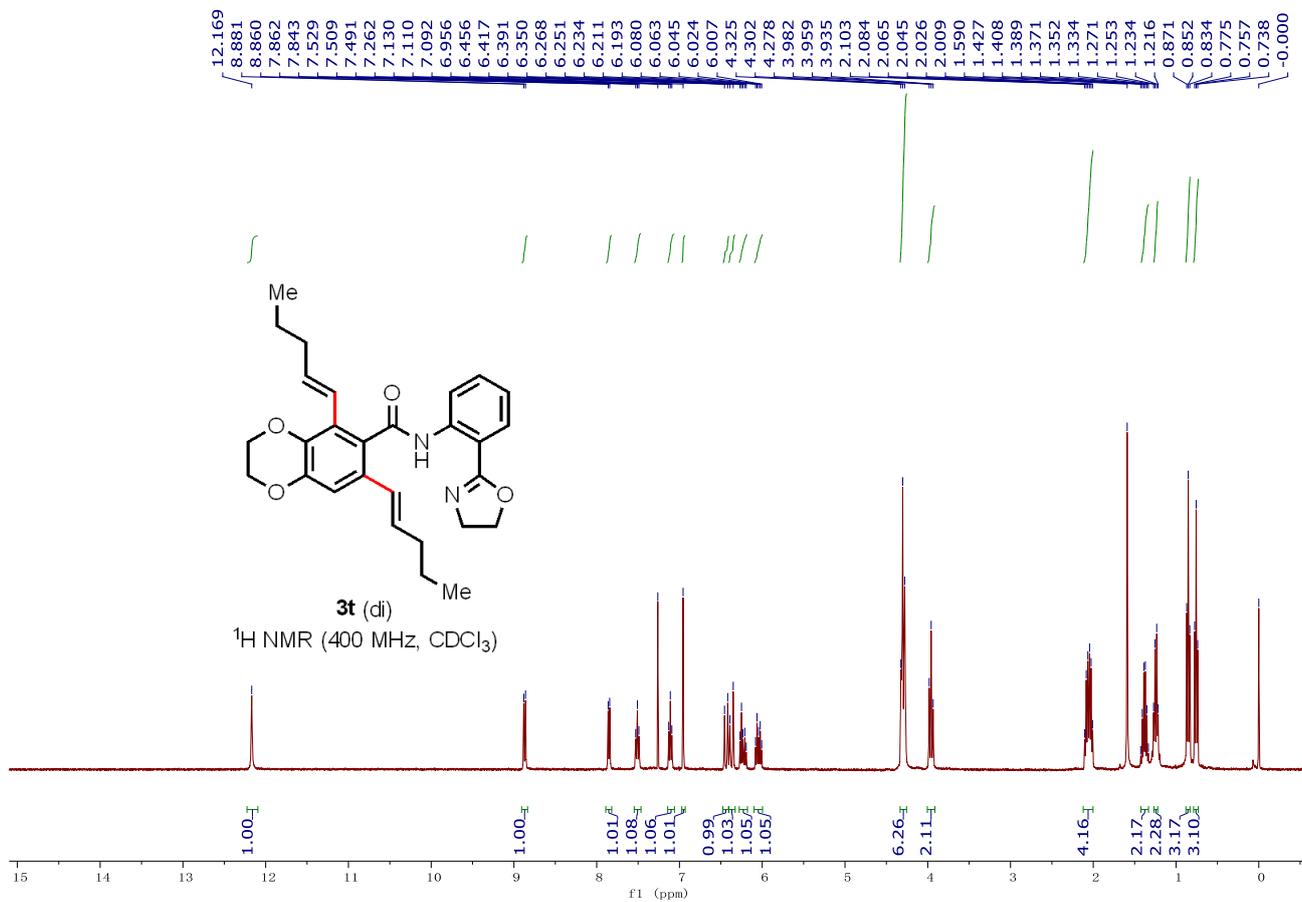
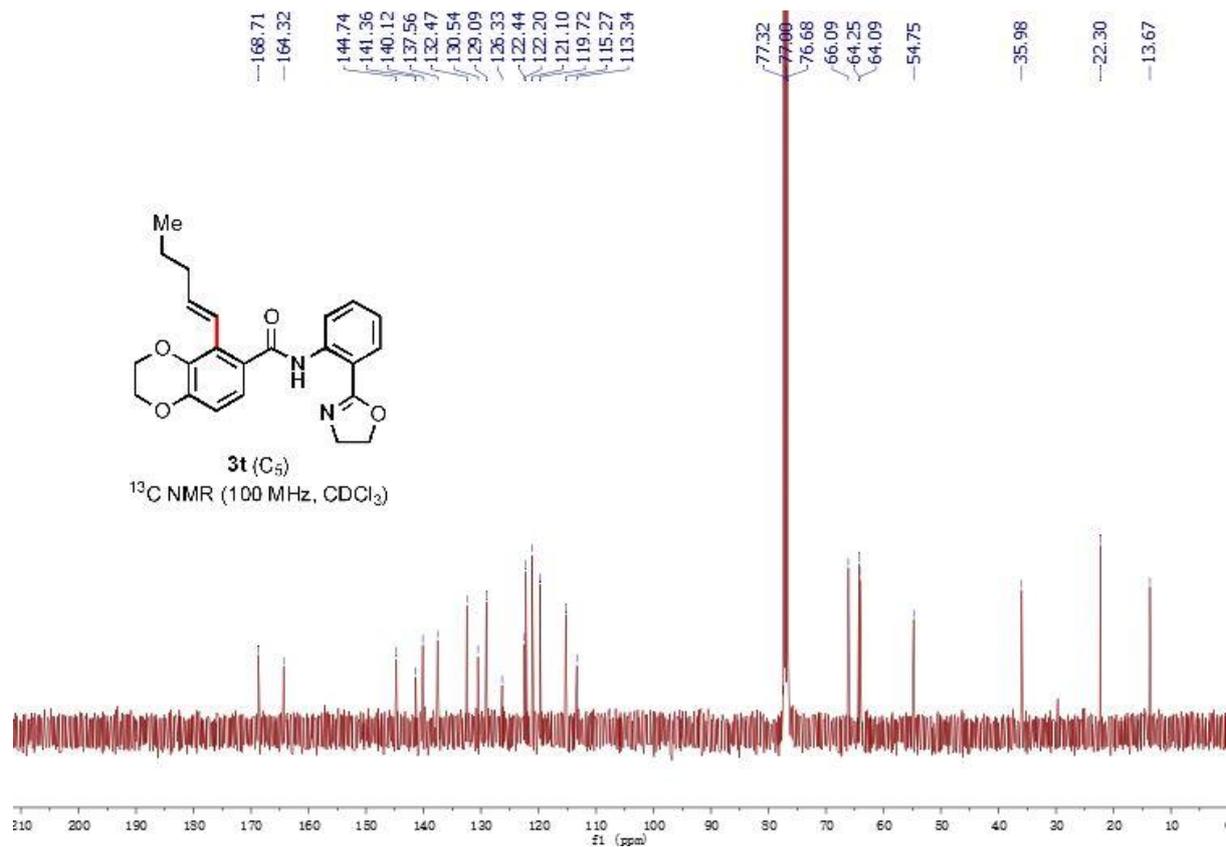


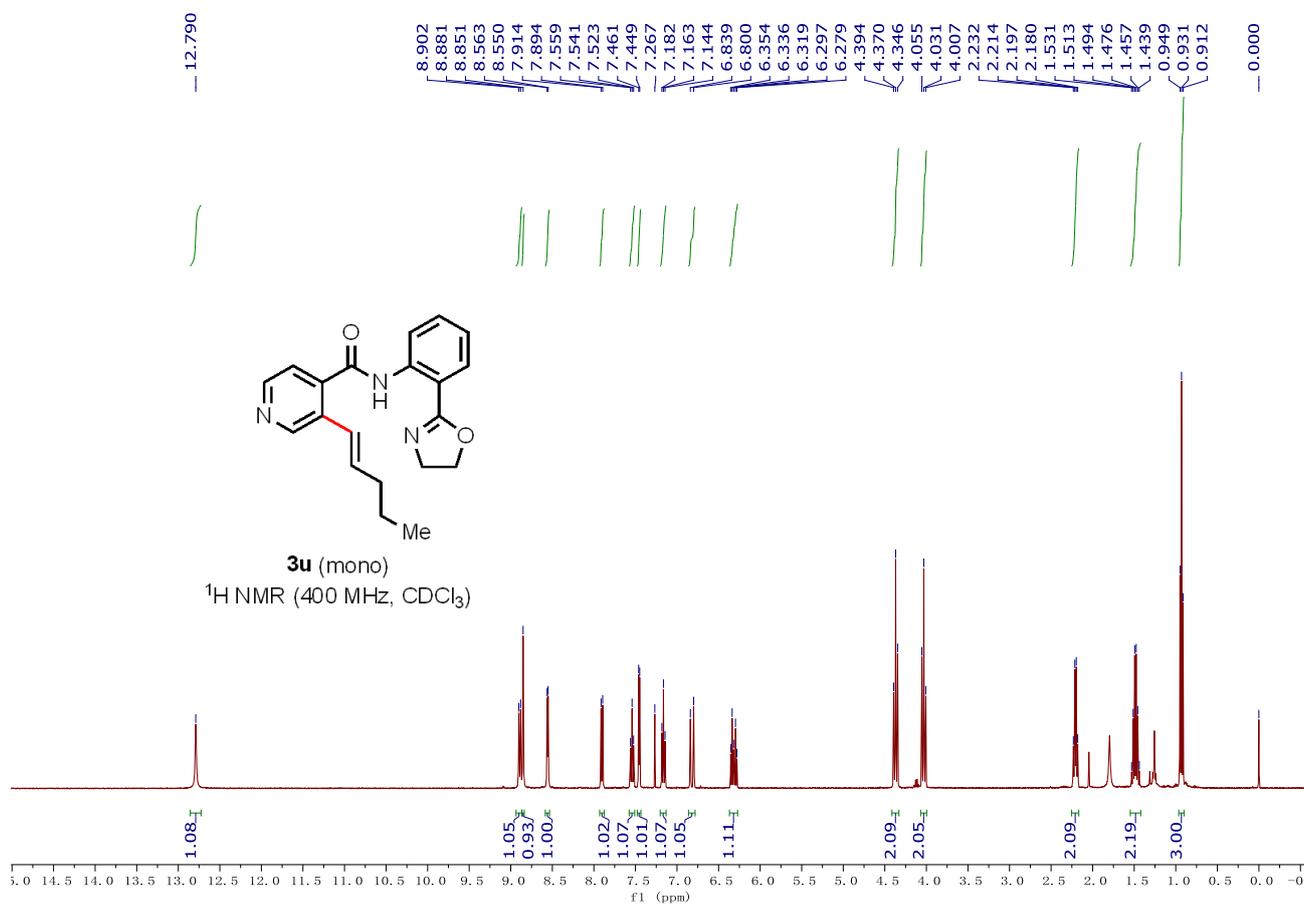
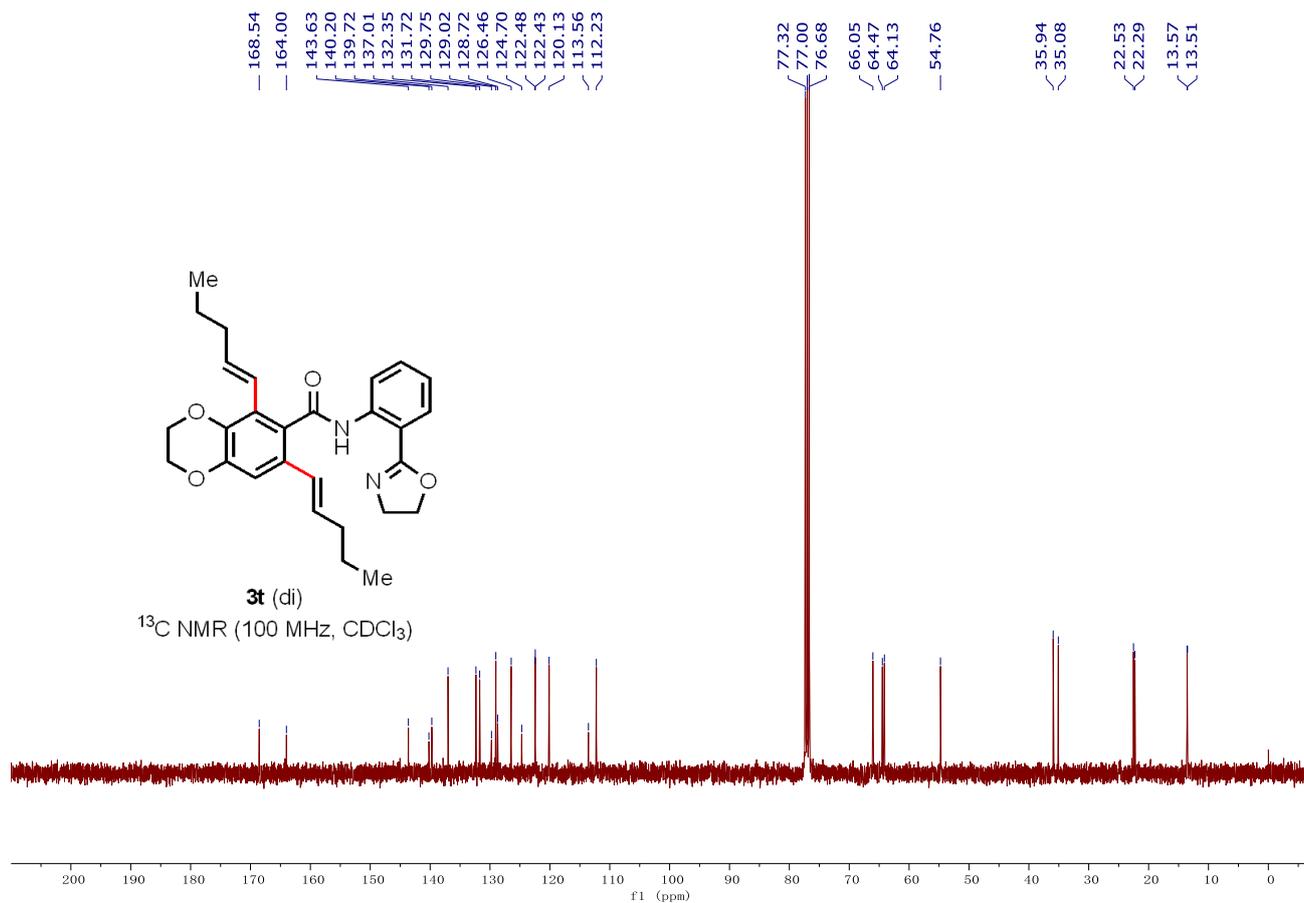


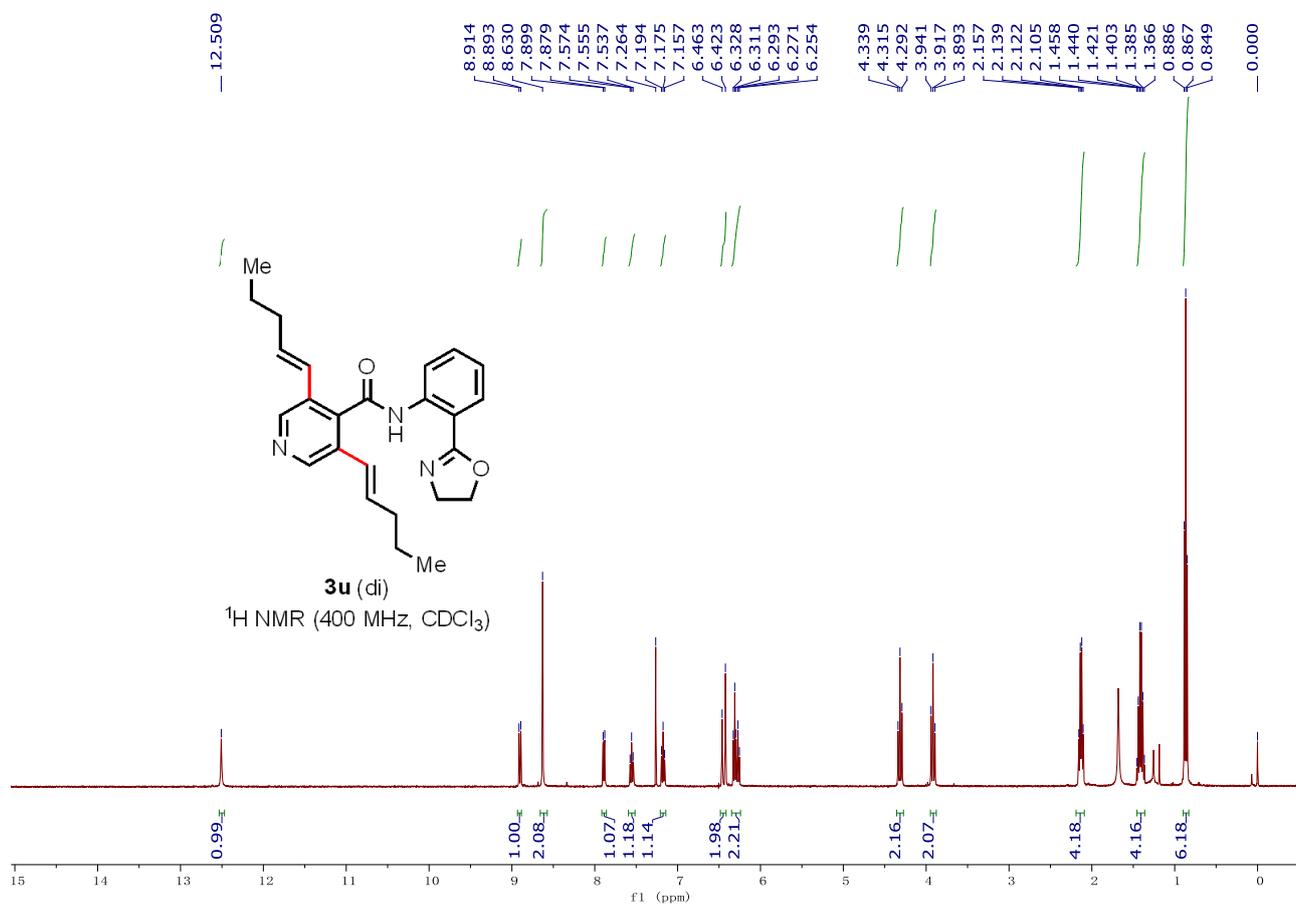
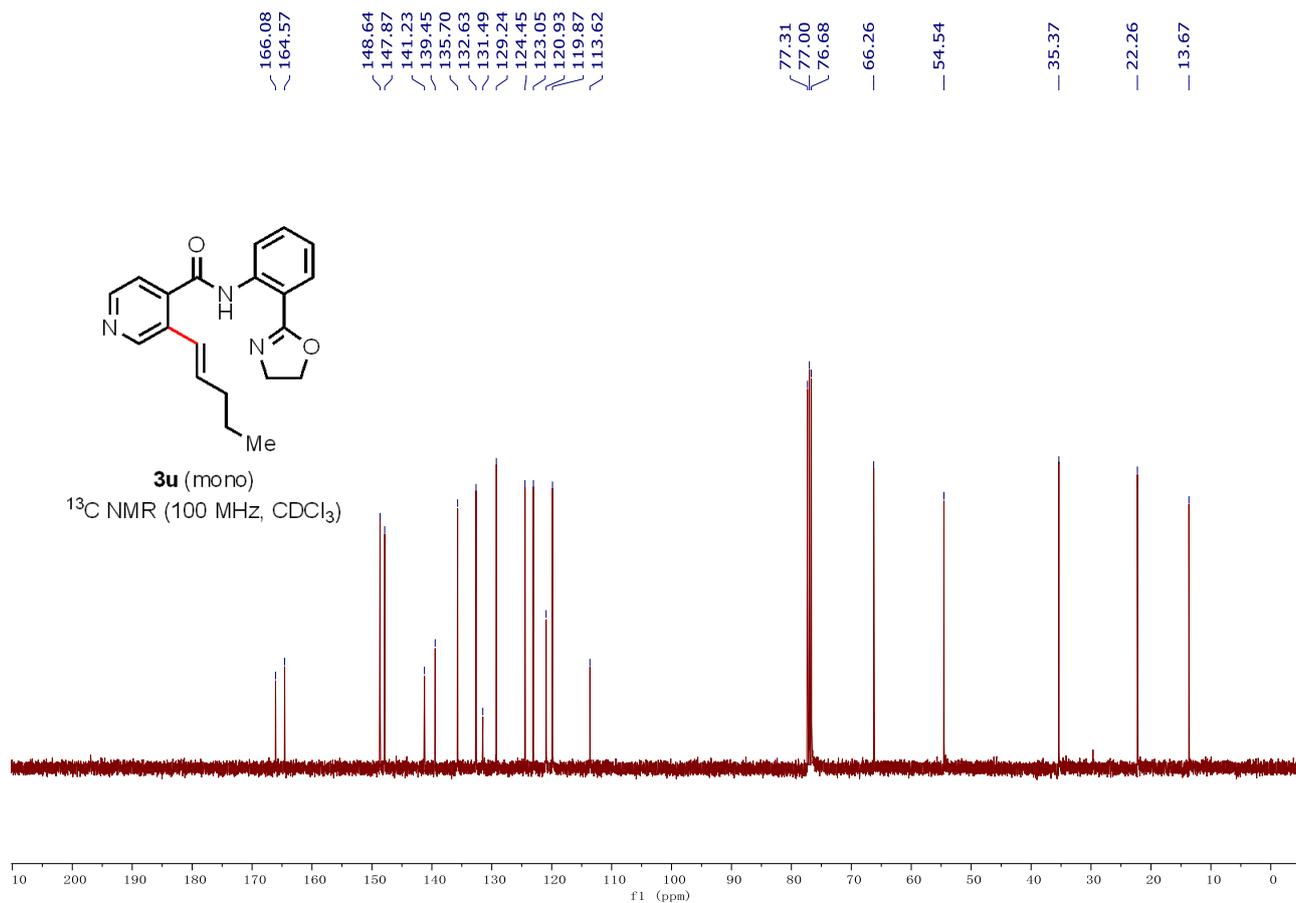


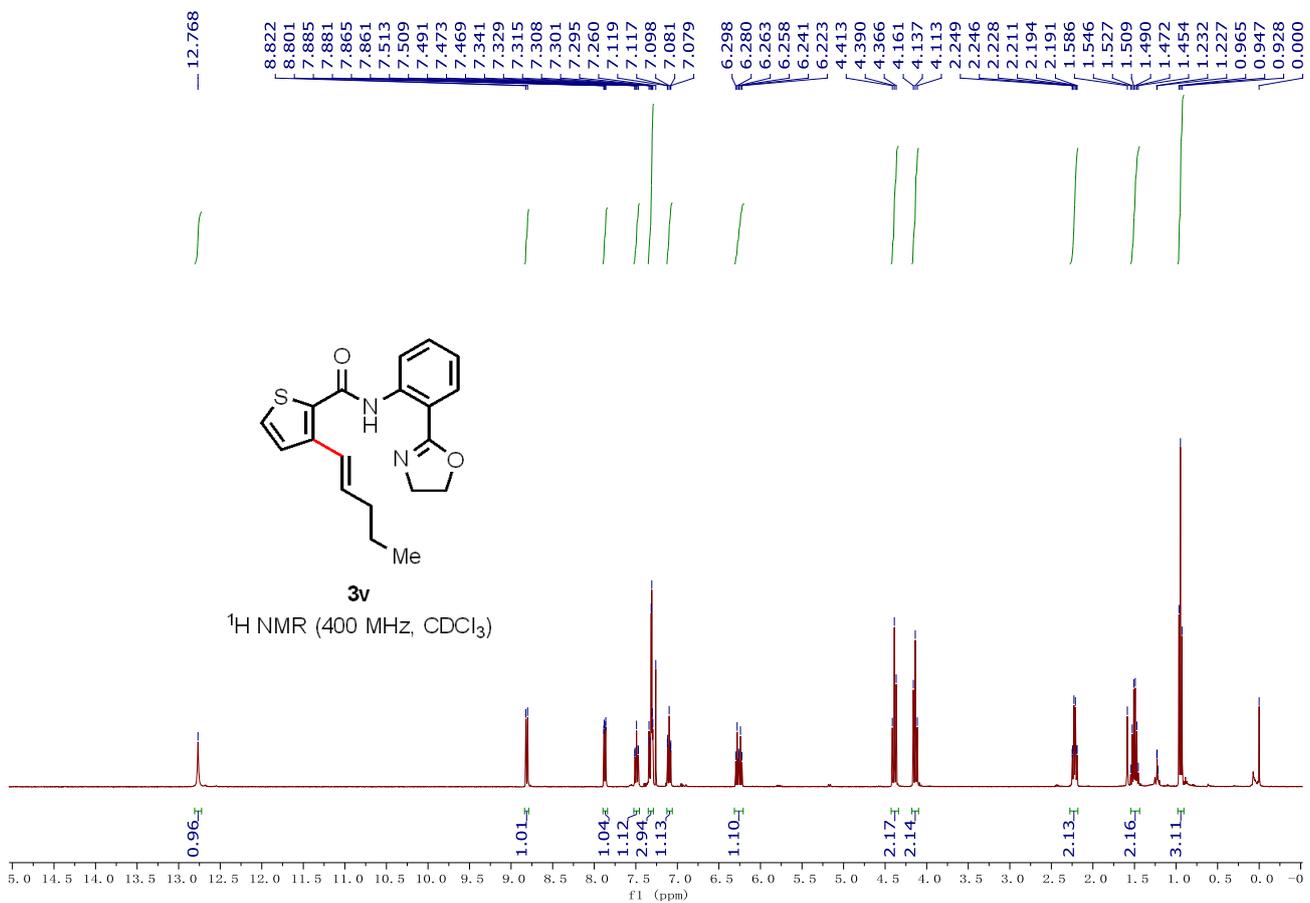
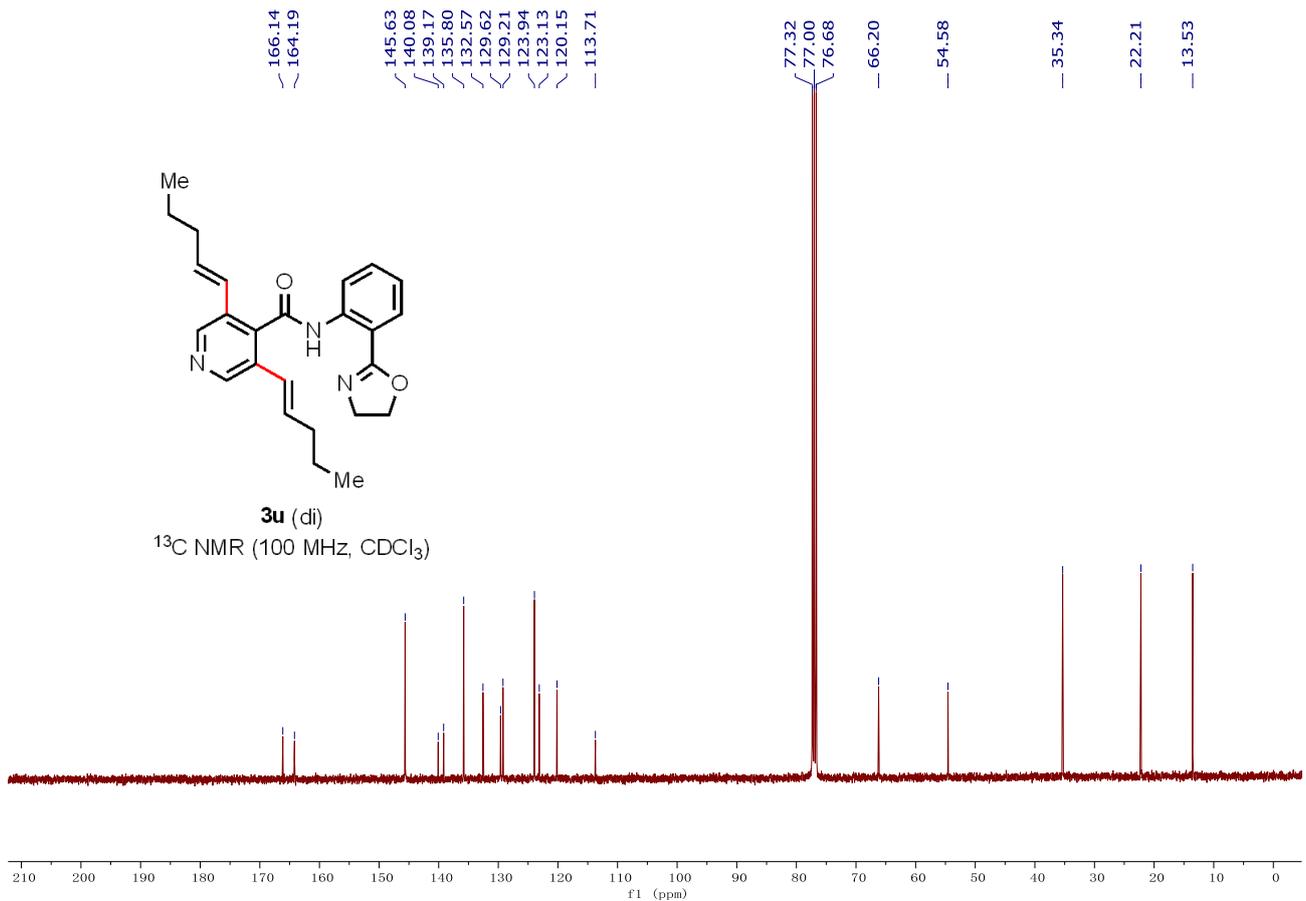


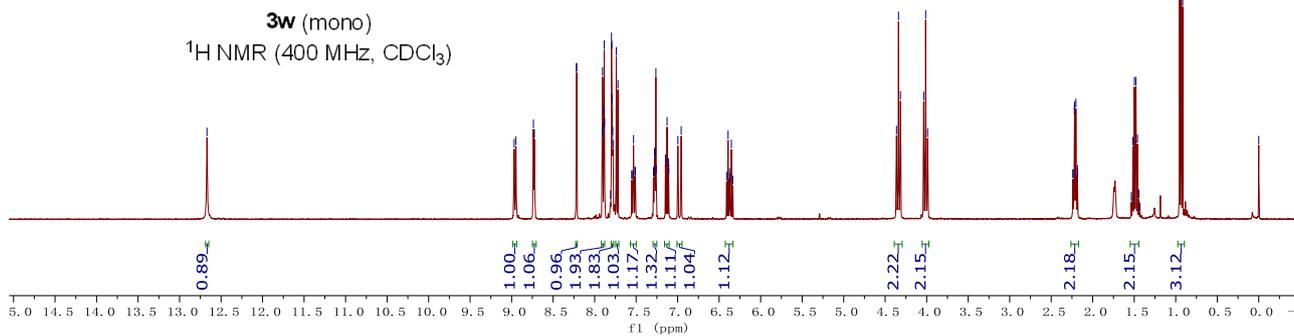
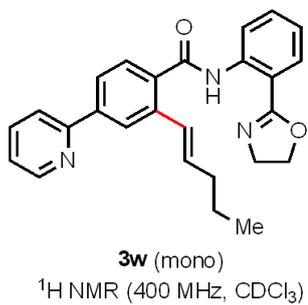
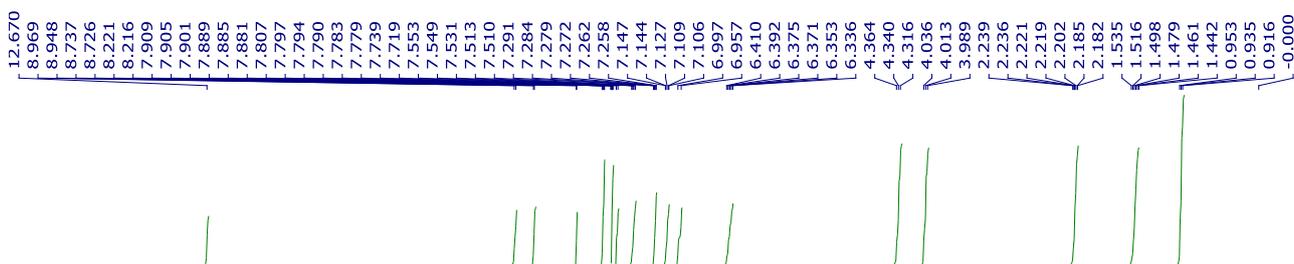
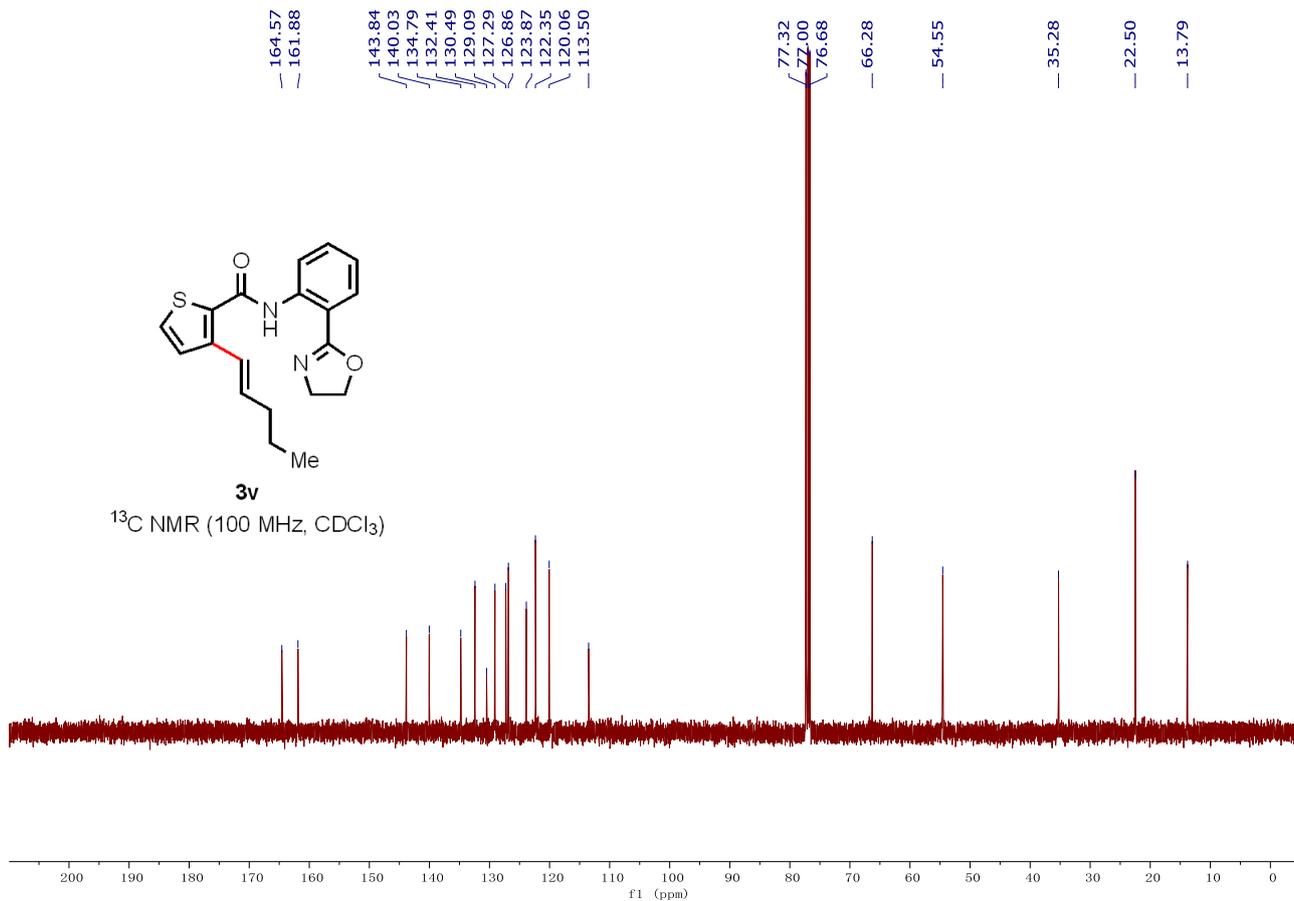
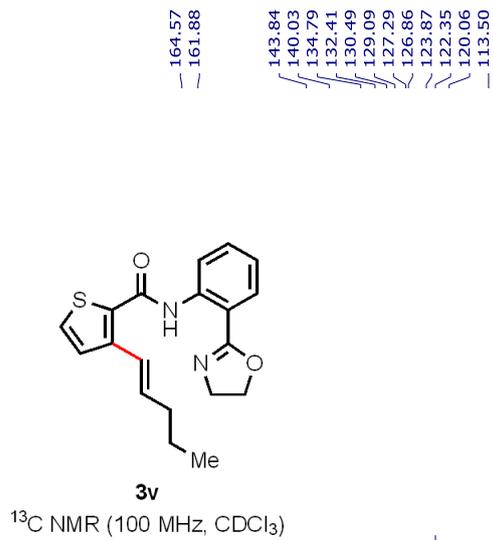


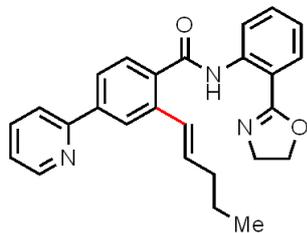




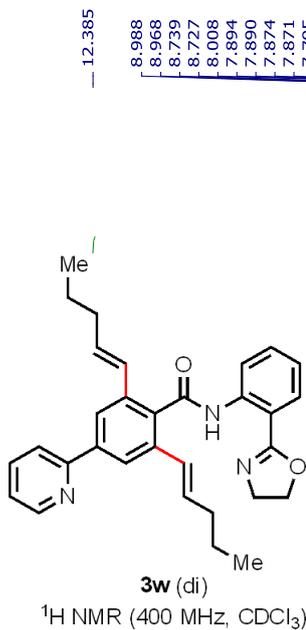
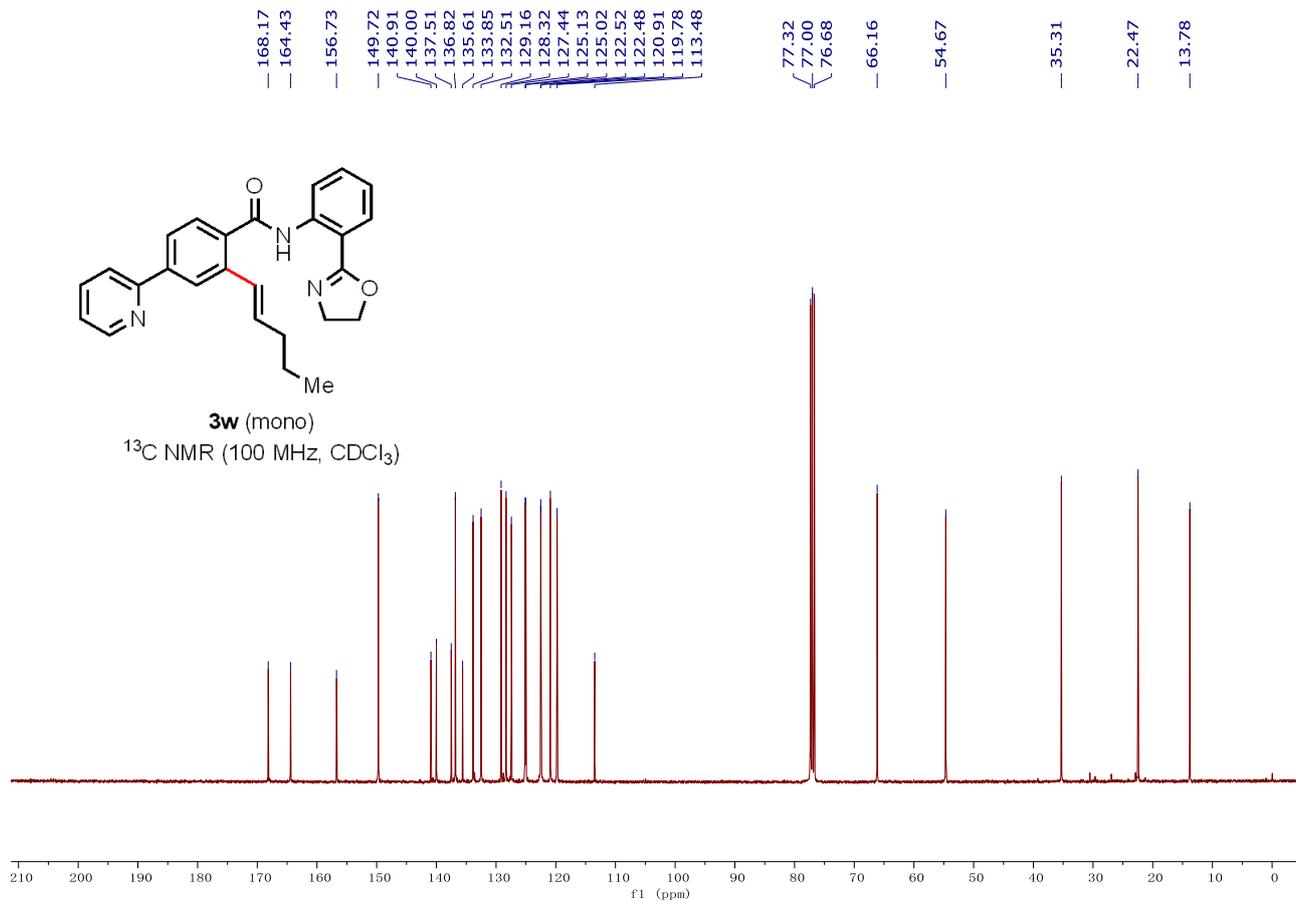




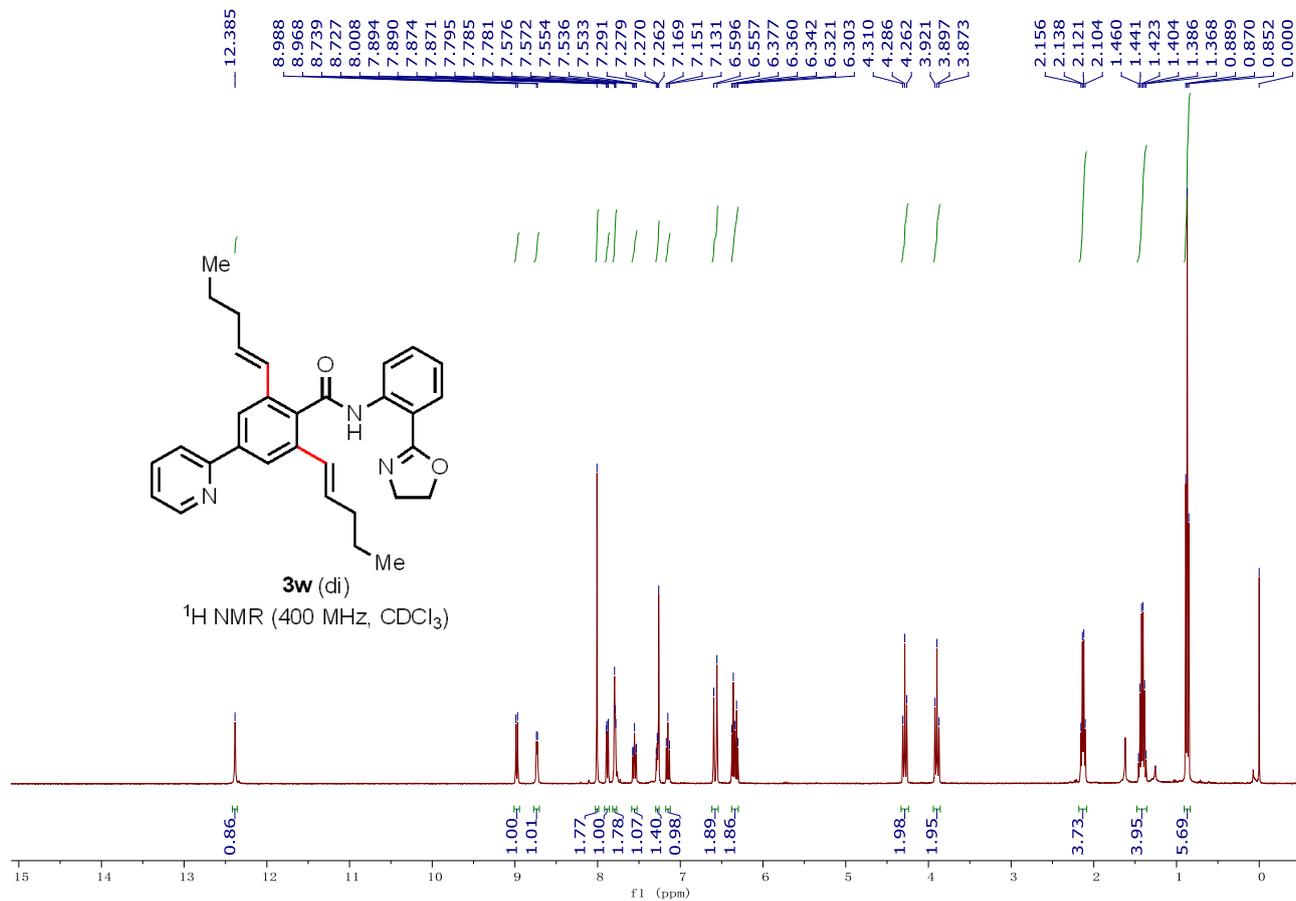


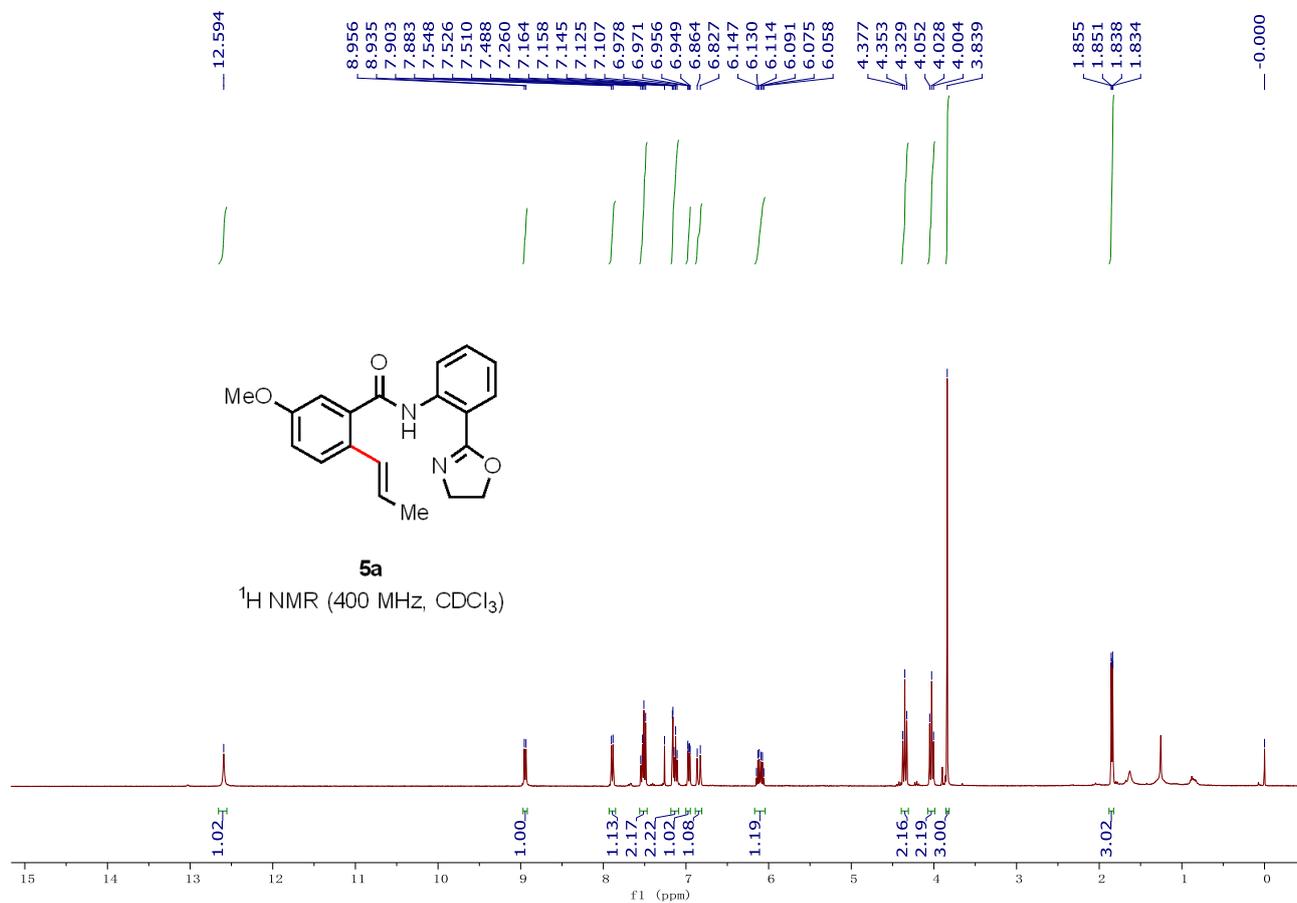
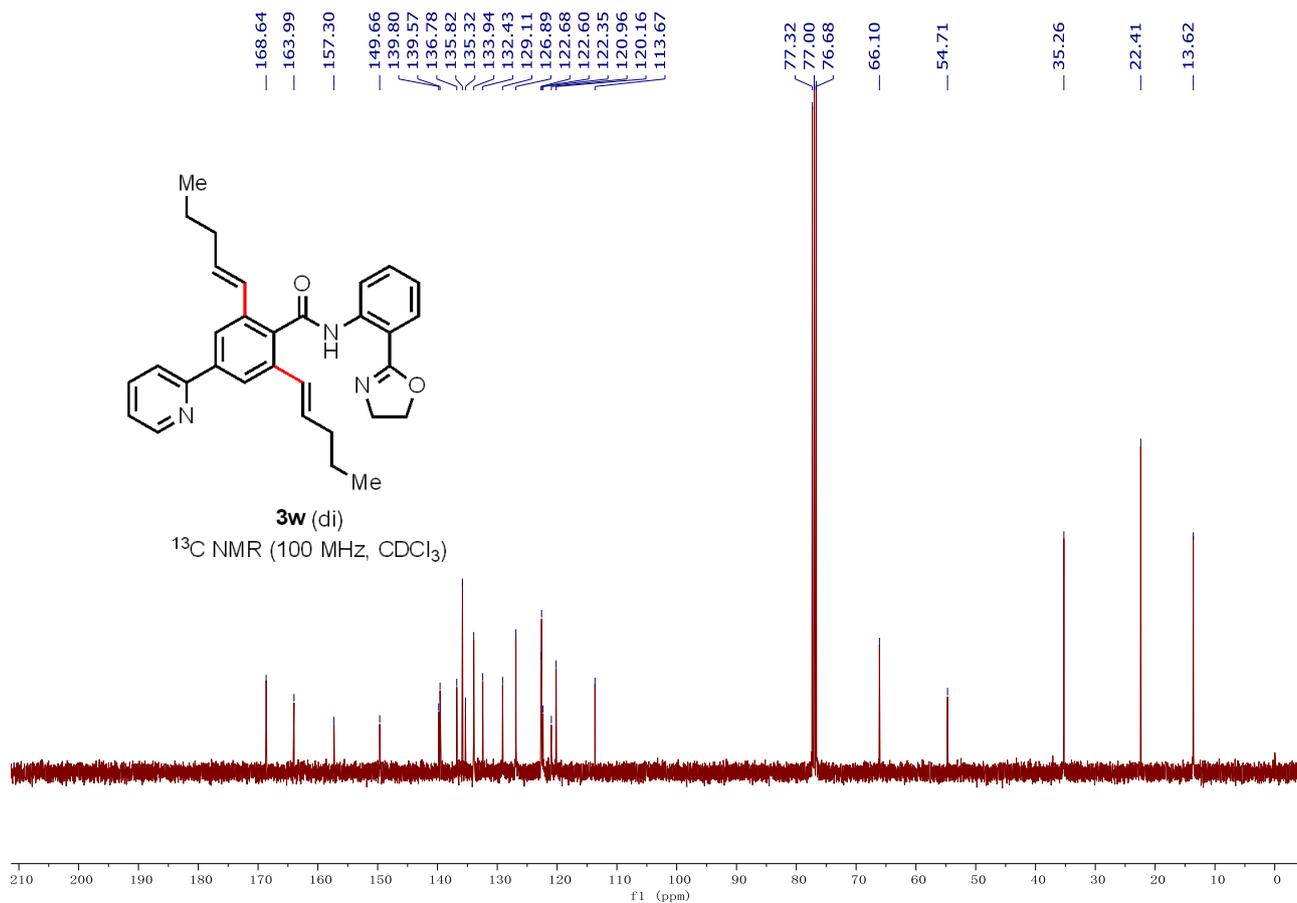


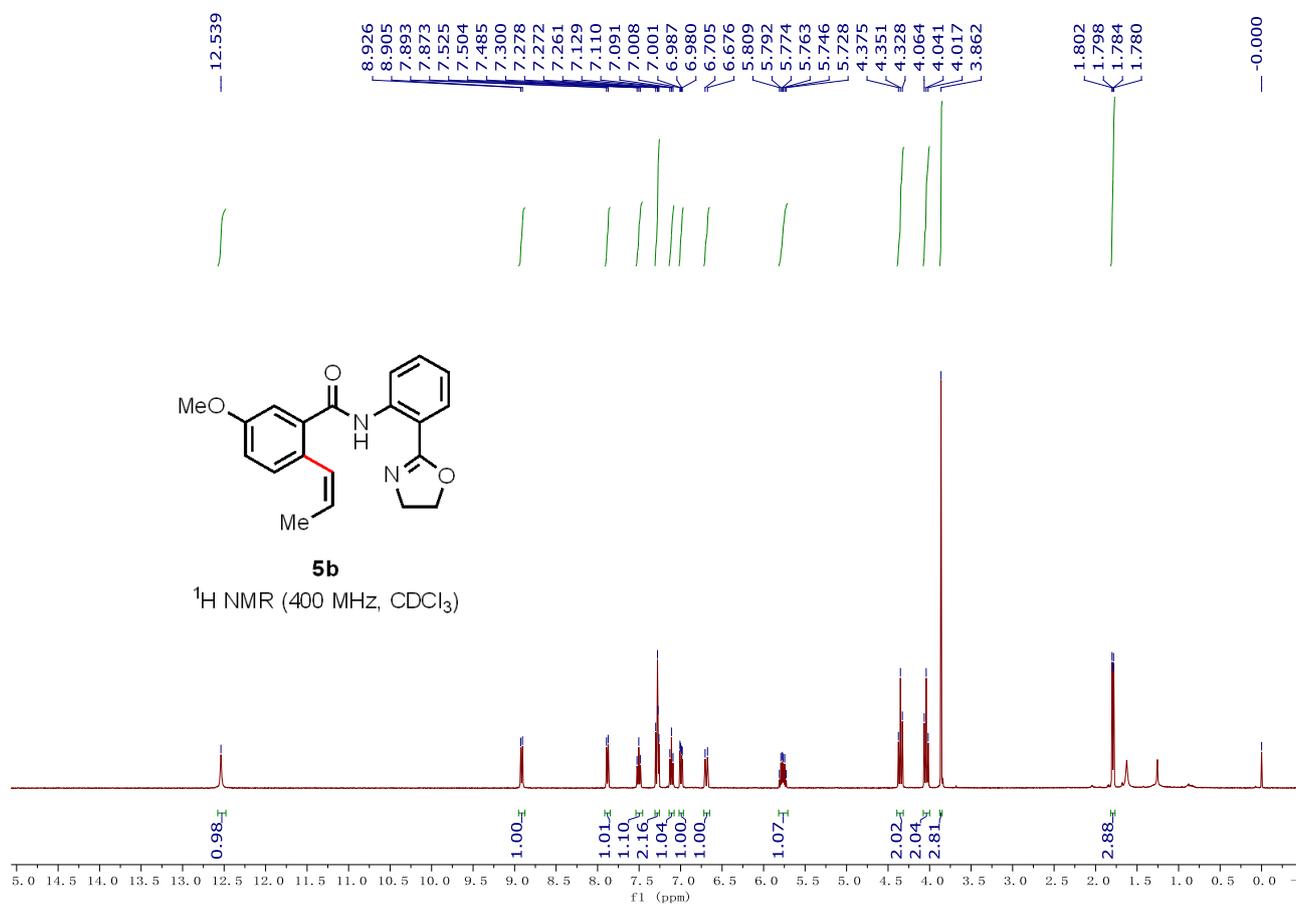
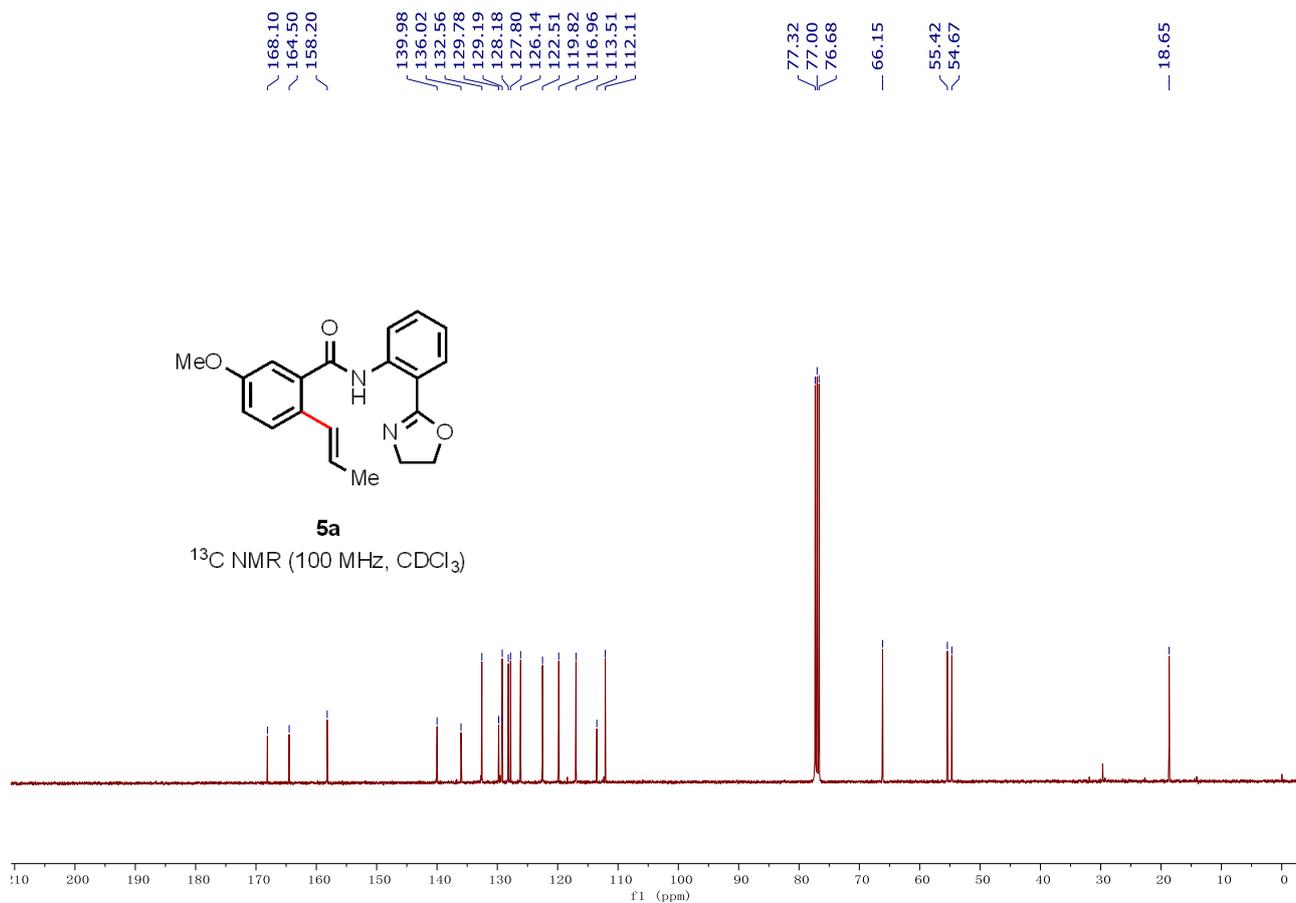
3w (mono)
¹³C NMR (100 MHz, CDCl₃)

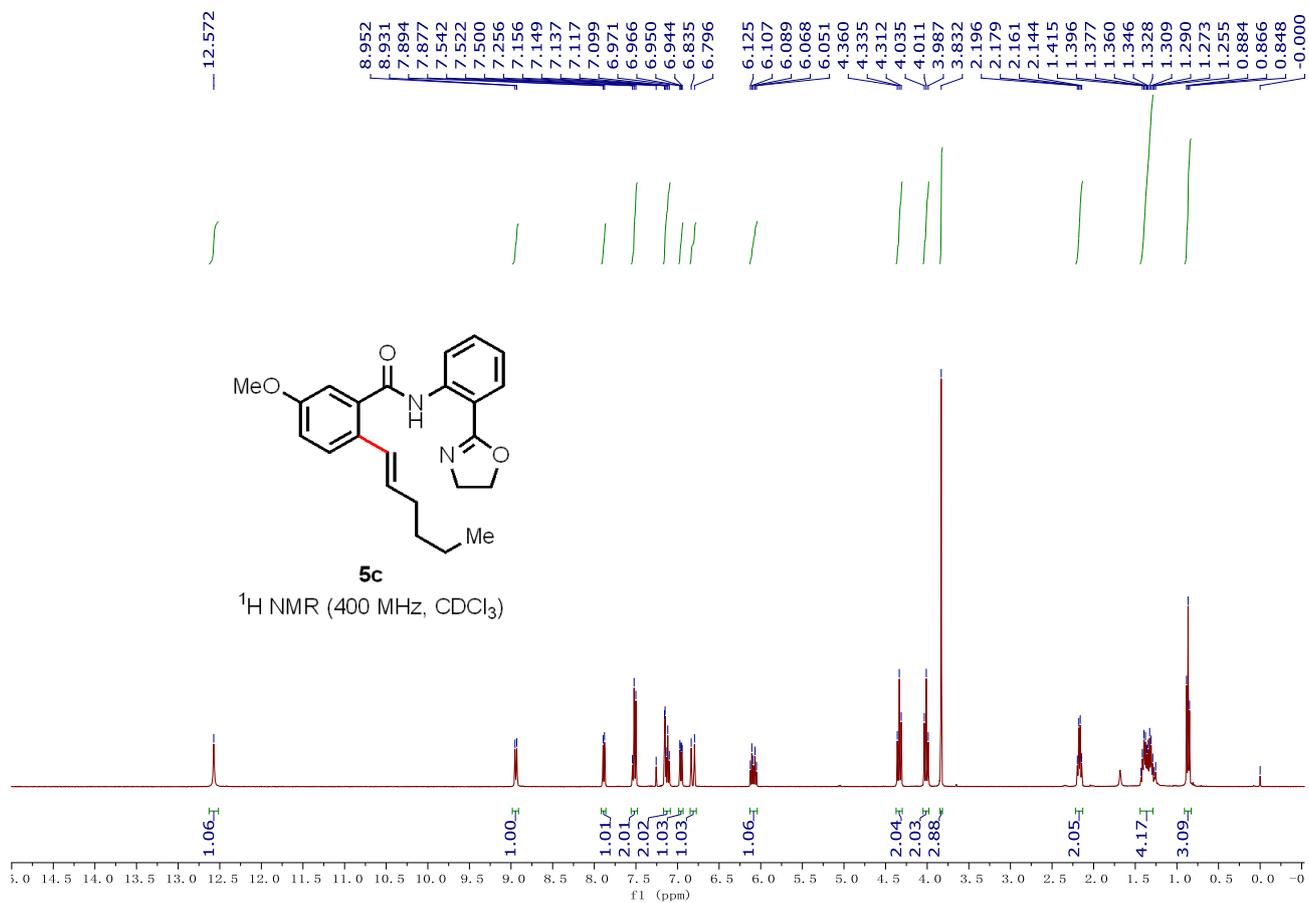
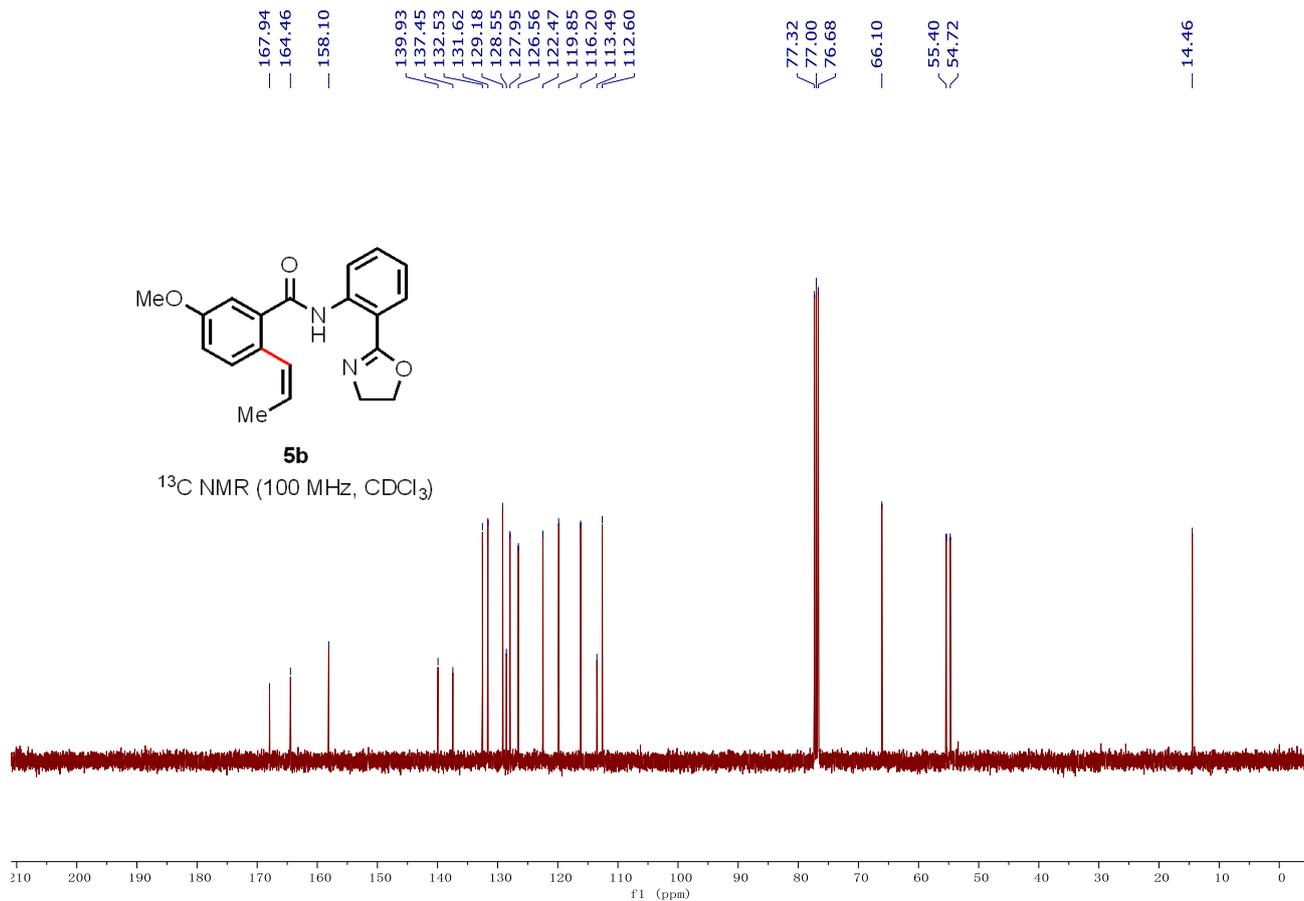


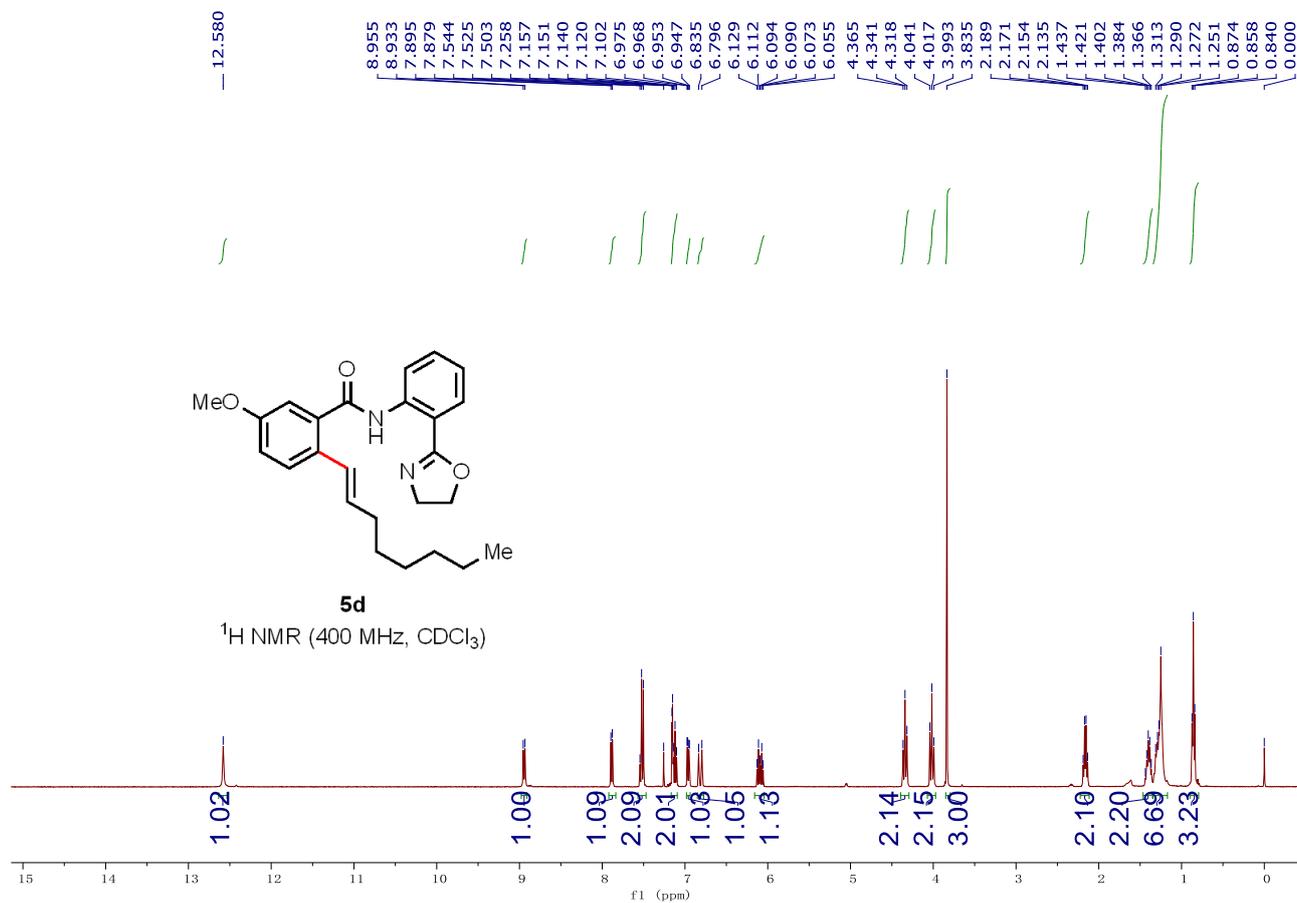
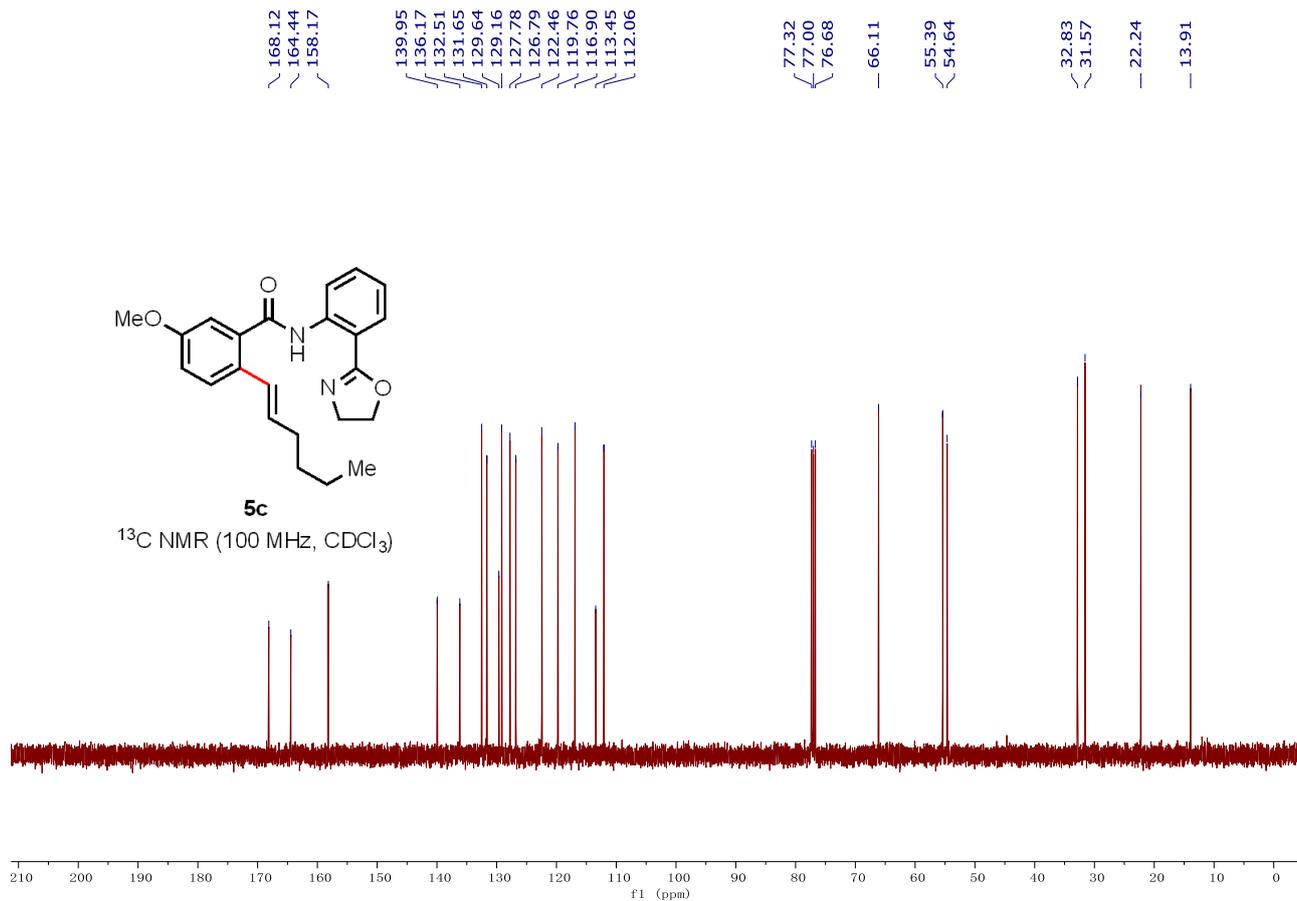
3w (di)
¹H NMR (400 MHz, CDCl₃)

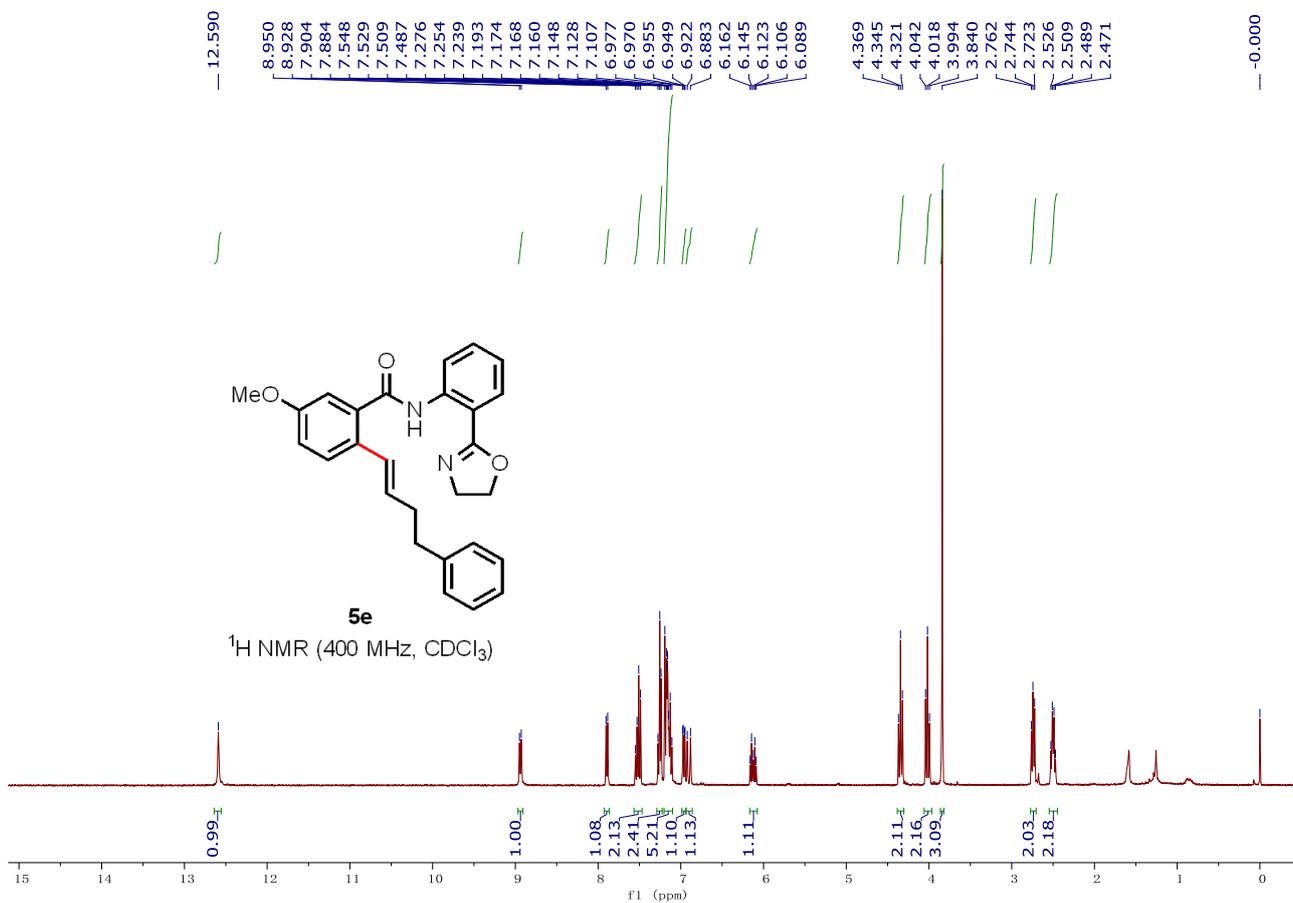
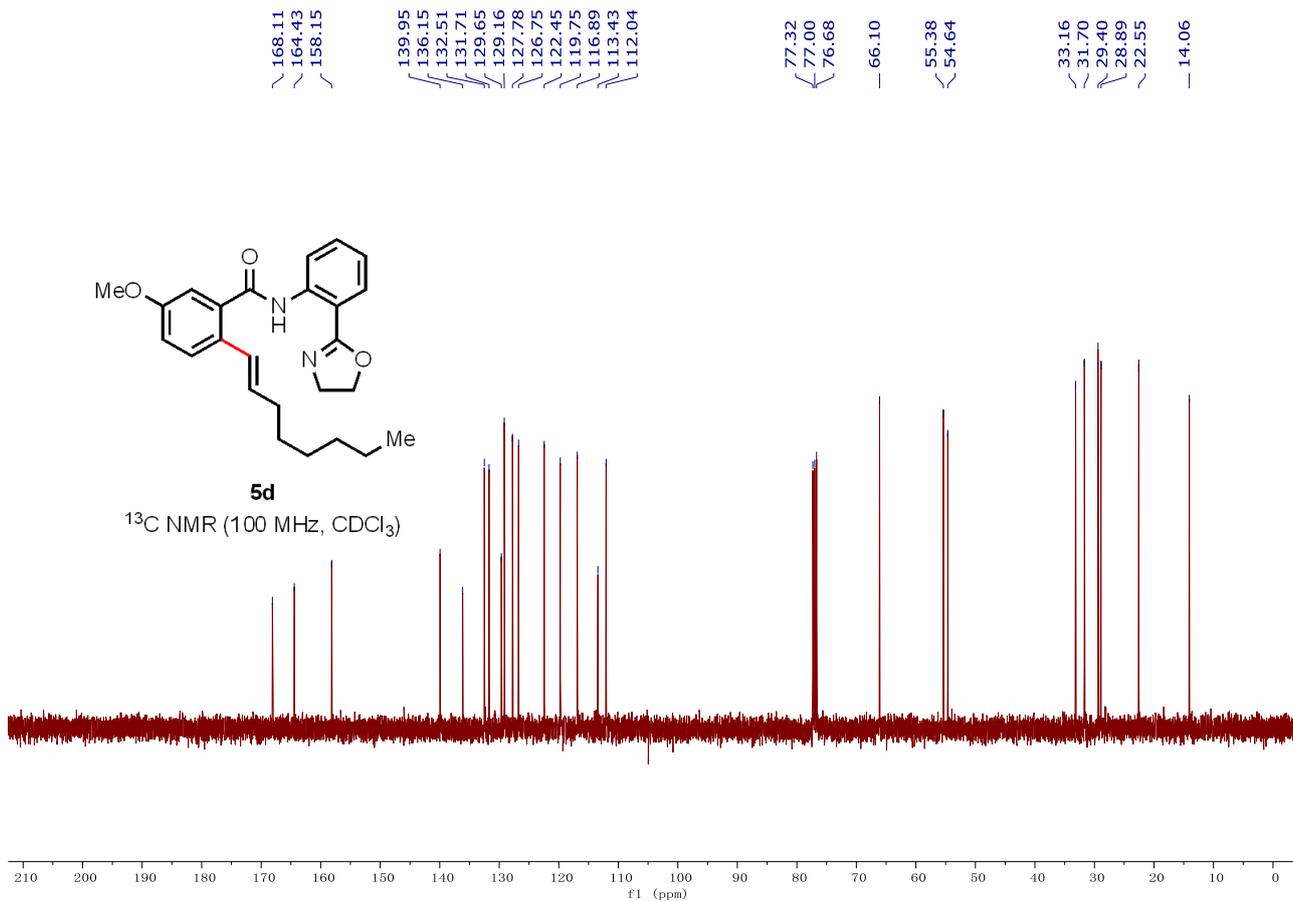


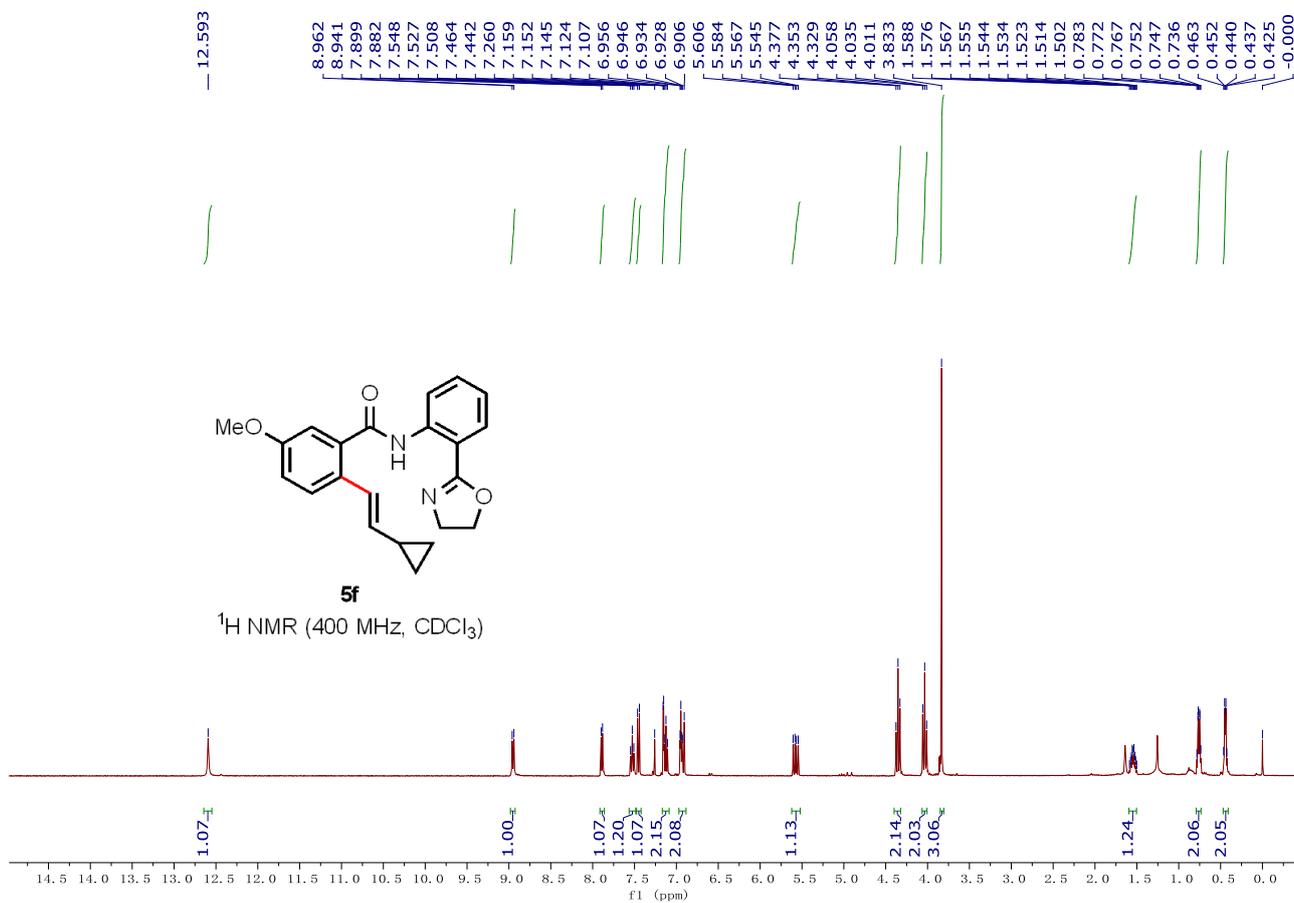
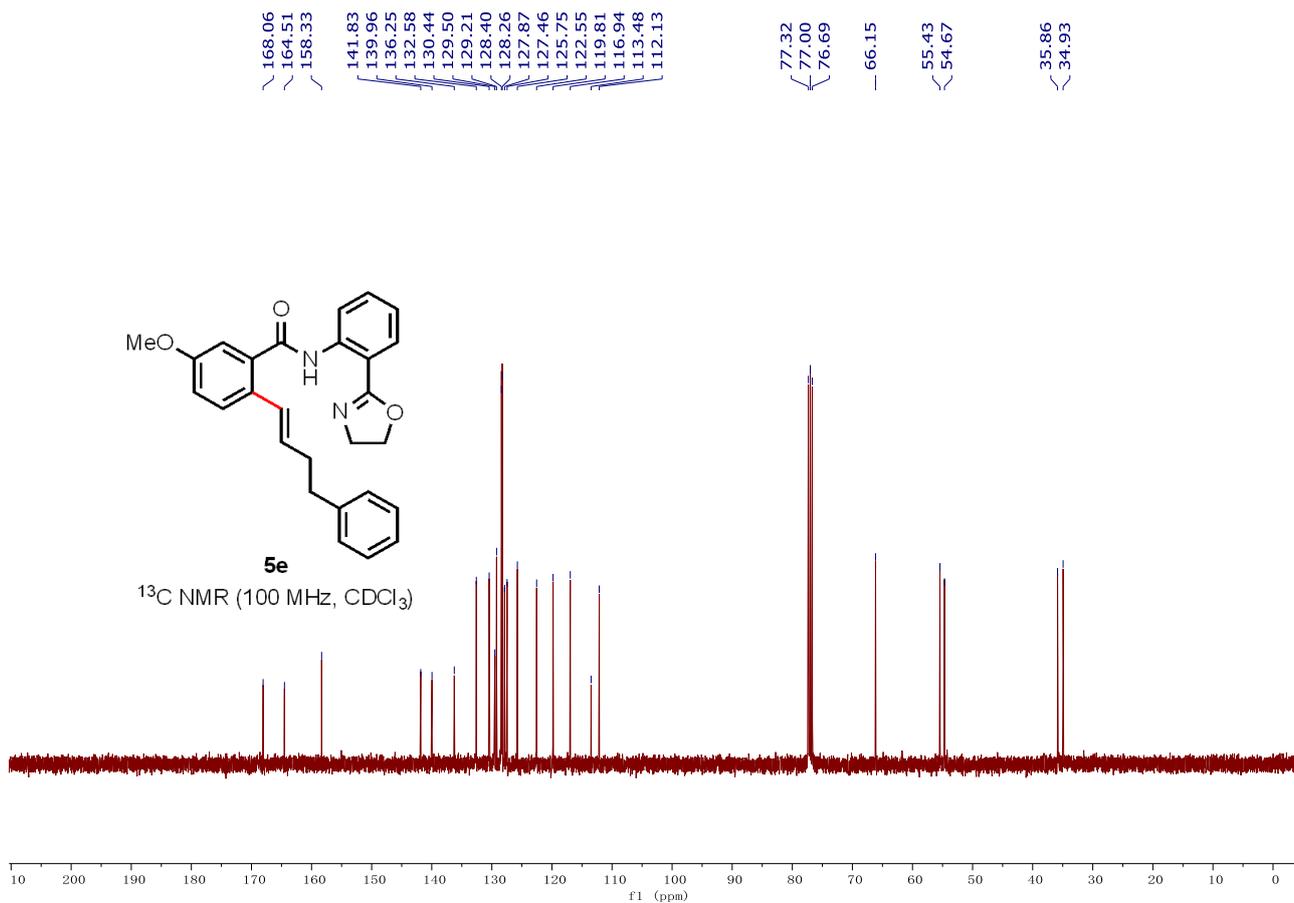




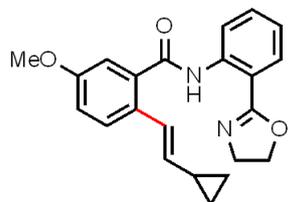






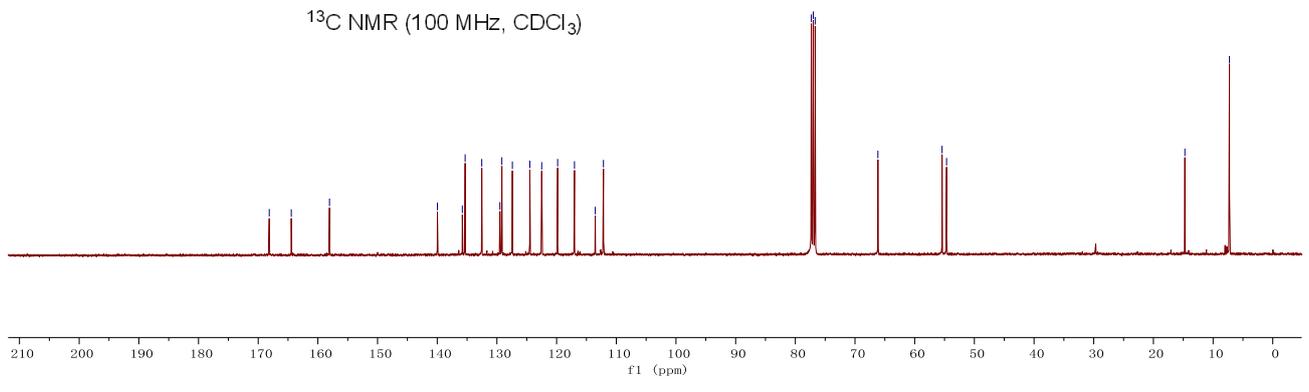


168.15
 164.46
 158.06
 139.98
 135.80
 135.32
 132.54
 129.50
 129.17
 127.41
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 77.00
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 54.66

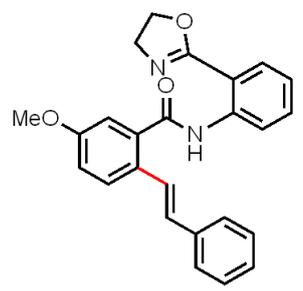


5f

¹³C NMR (100 MHz, CDCl₃)

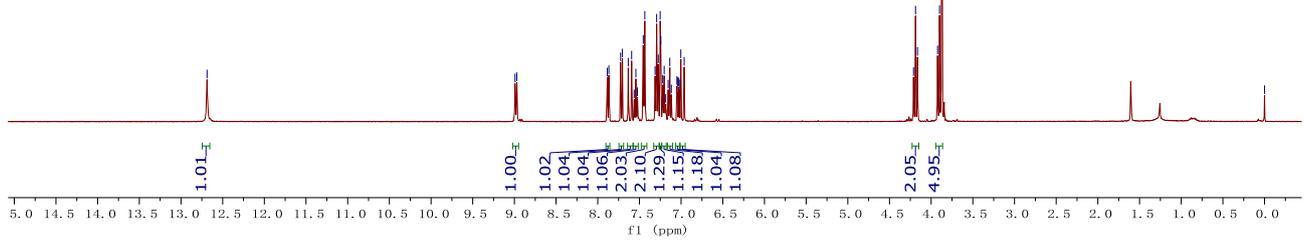


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 7.634
 7.594
 7.563
 7.543
 7.524
 7.454
 7.435
 7.312
 7.293
 7.274
 7.251
 7.244
 7.221
 7.203
 7.184
 7.155
 7.136
 7.117
 7.050
 7.044
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 7.003
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 4.188
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 0.000

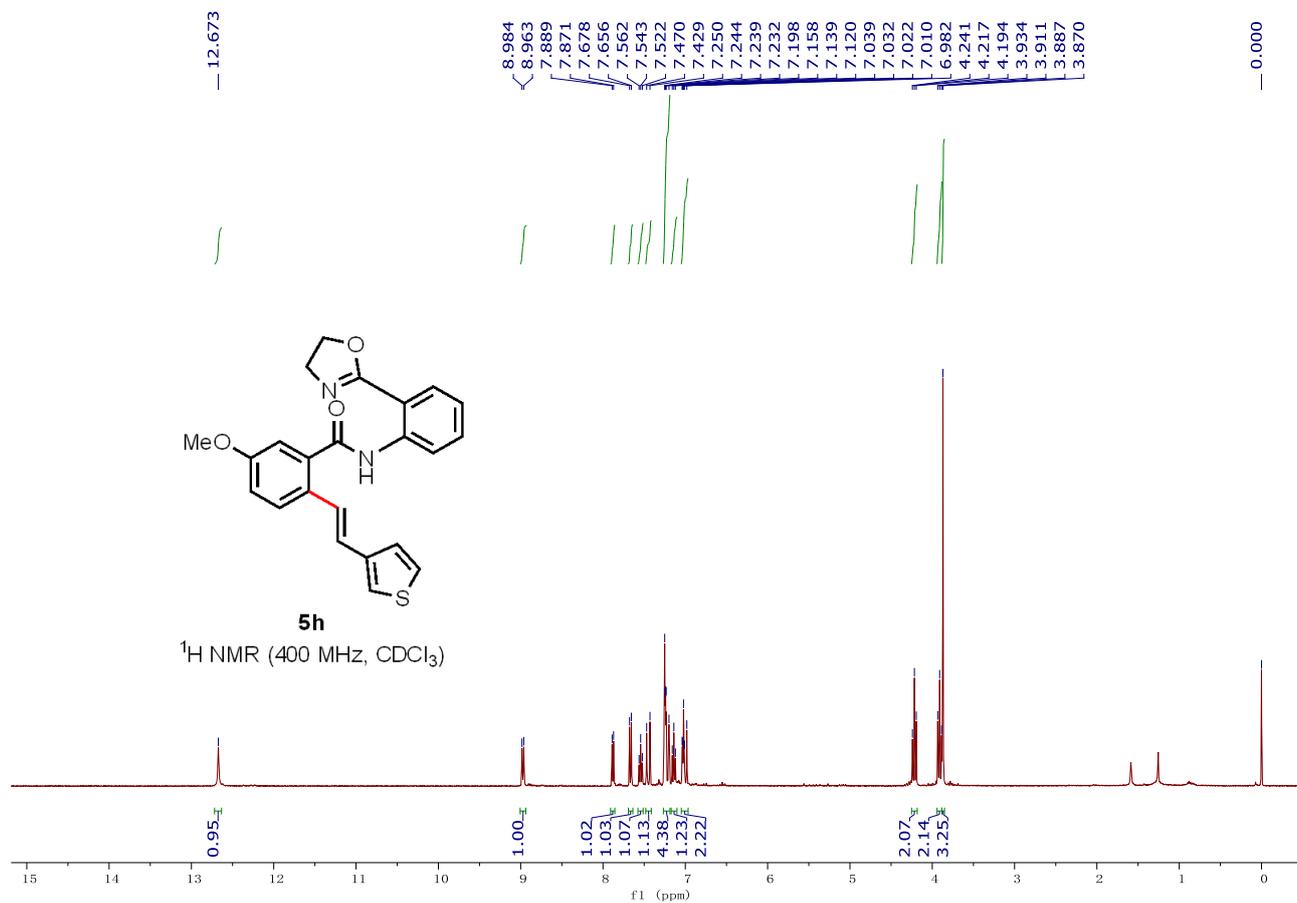
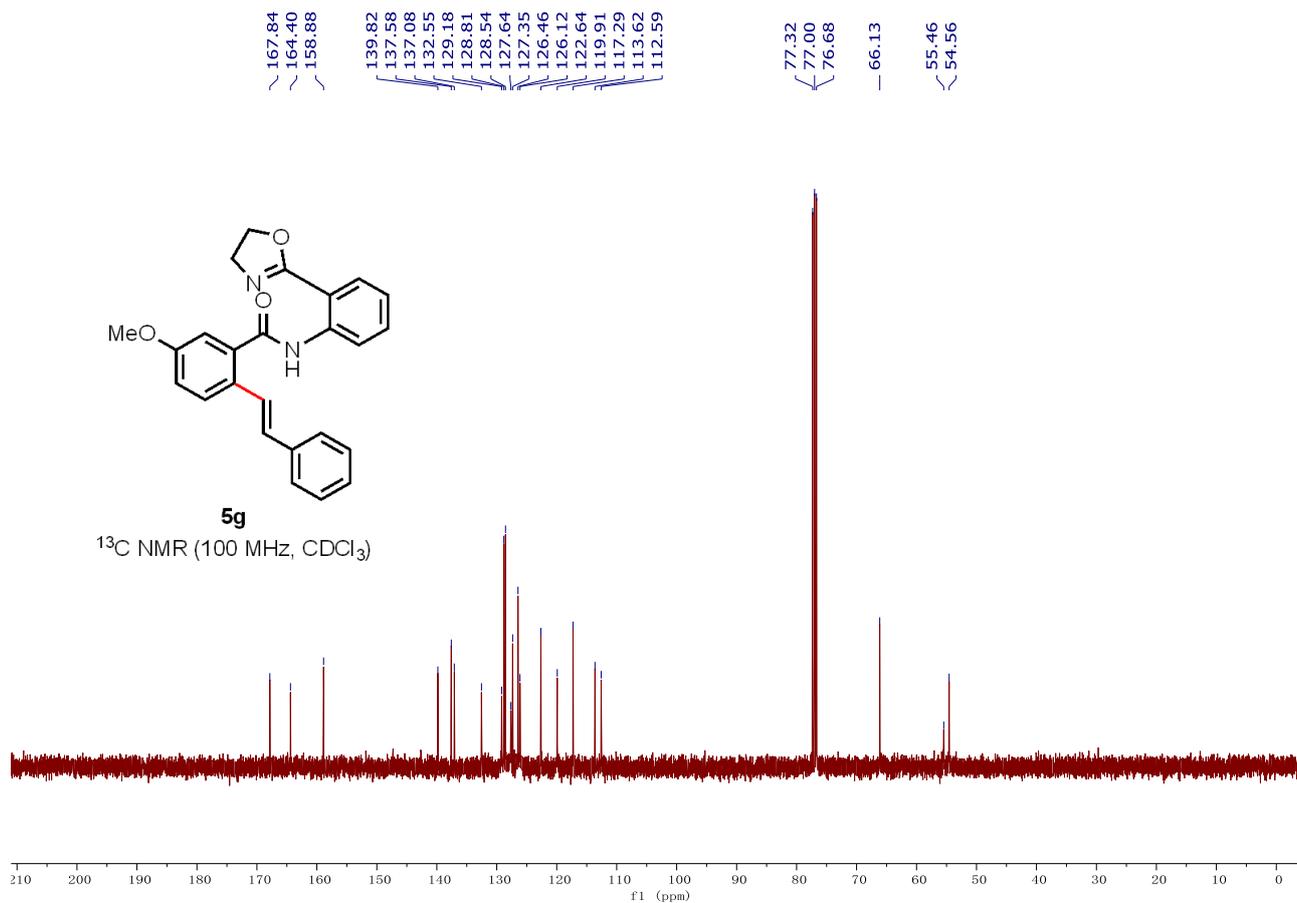


5g

¹H NMR (400 MHz, CDCl₃)

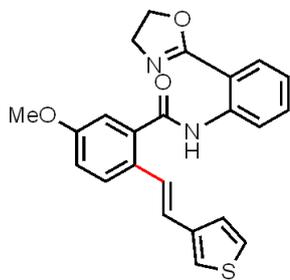


1.01
 1.00
 1.02
 1.04
 1.04
 1.06
 2.03
 2.10
 1.29
 1.15
 1.18
 1.04
 1.08
 2.05
 4.95

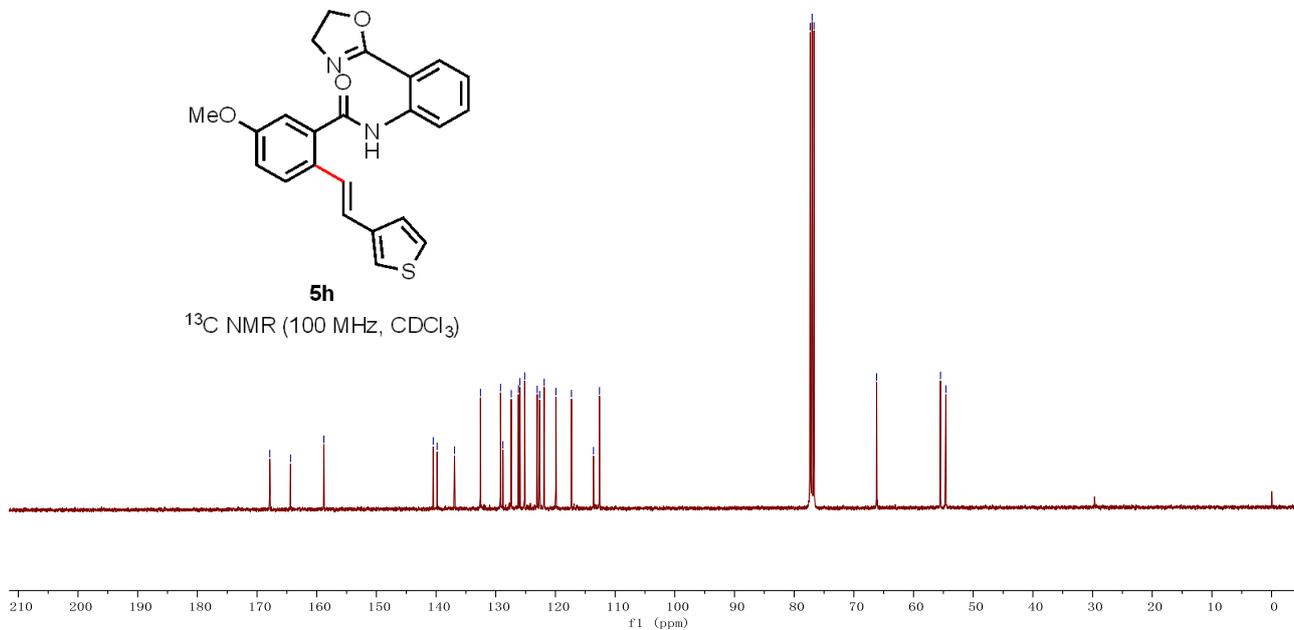


167.86
164.39
158.80
140.48
139.83
136.91
132.57
129.20
128.81
127.40
126.20
125.94
125.16
123.05
122.65
121.88
119.92
117.31
113.62
112.62

77.32
77.00
76.68
66.18
55.48
54.58



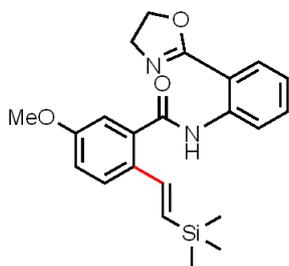
¹³C NMR (100 MHz, CDCl₃)



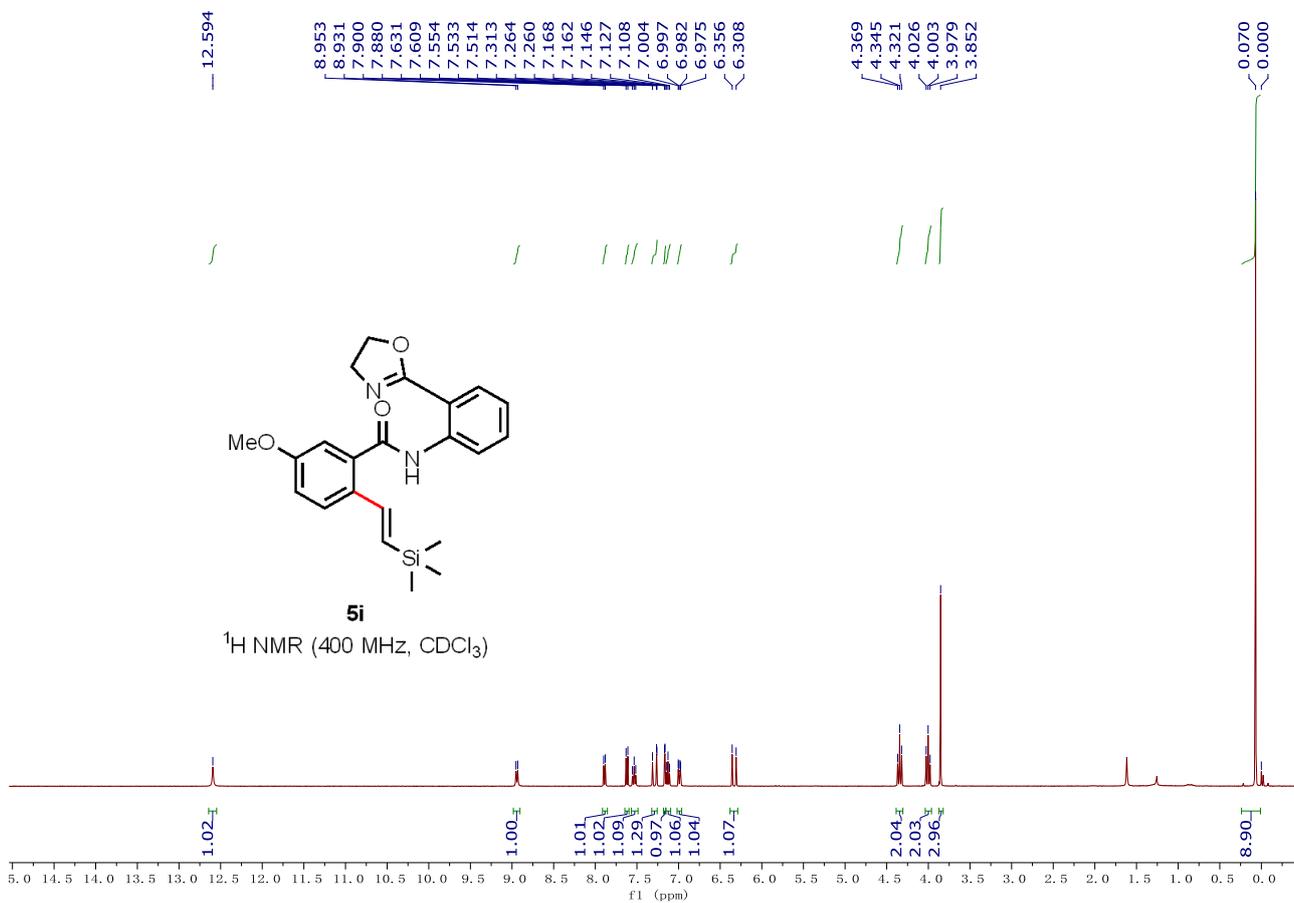
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8.953
8.931
7.900
7.880
7.631
7.609
7.554
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7.514
7.313
7.264
7.260
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7.146
7.127
7.108
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6.982
6.975
6.356
6.308

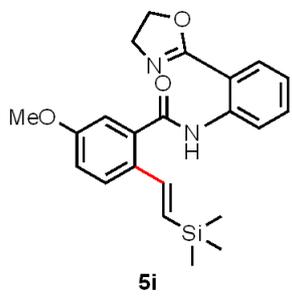
4.369
4.345
4.321
4.026
4.003
3.979
3.852

0.070
0.000

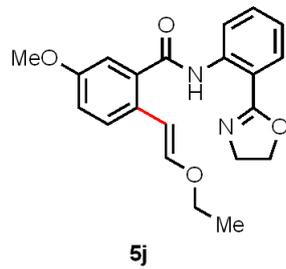
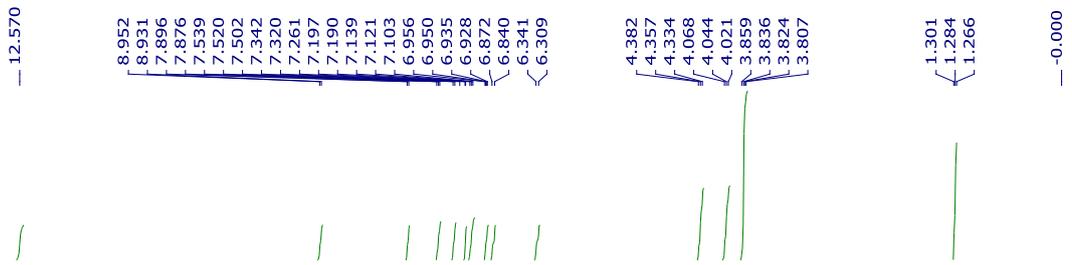
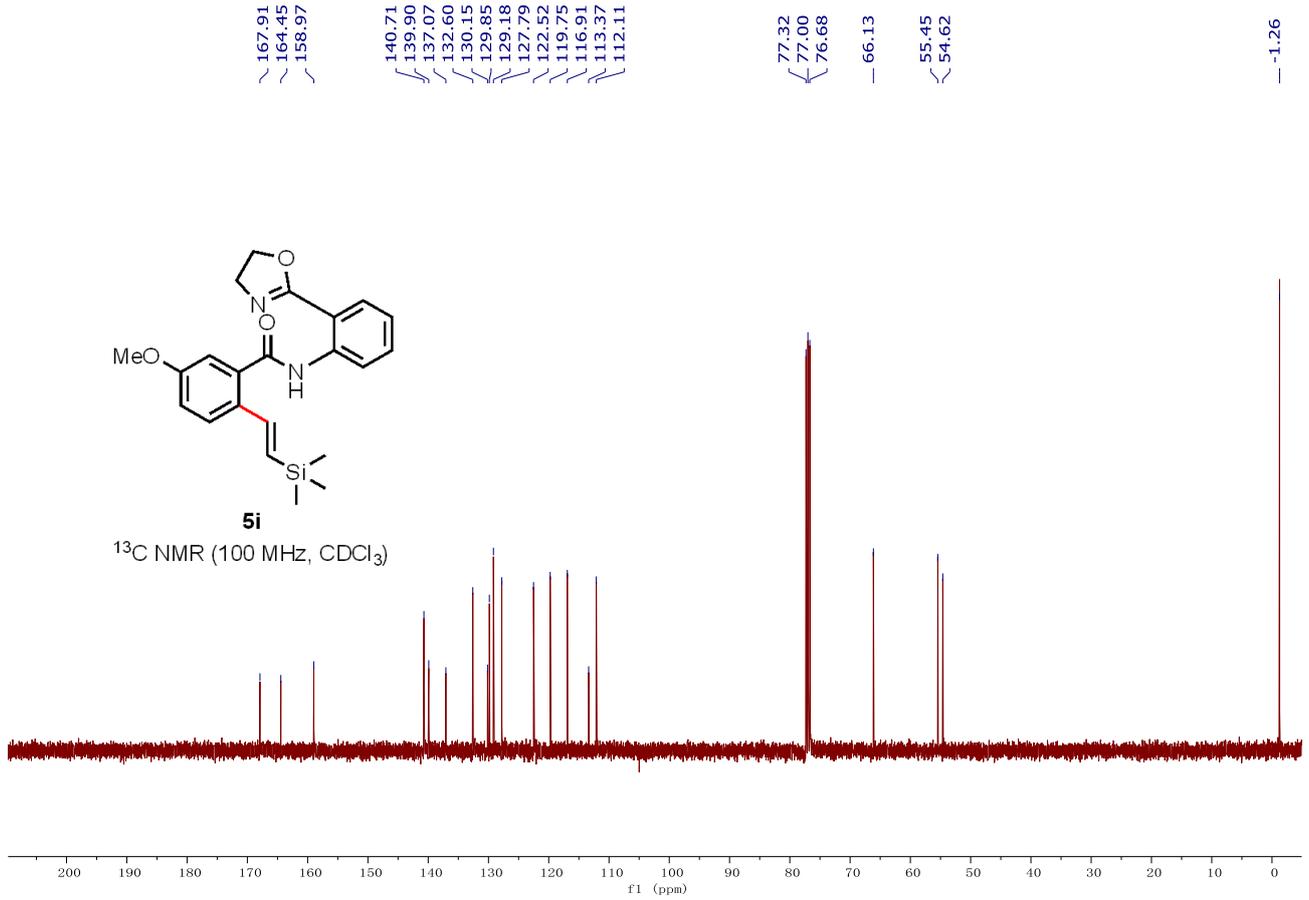


¹H NMR (400 MHz, CDCl₃)

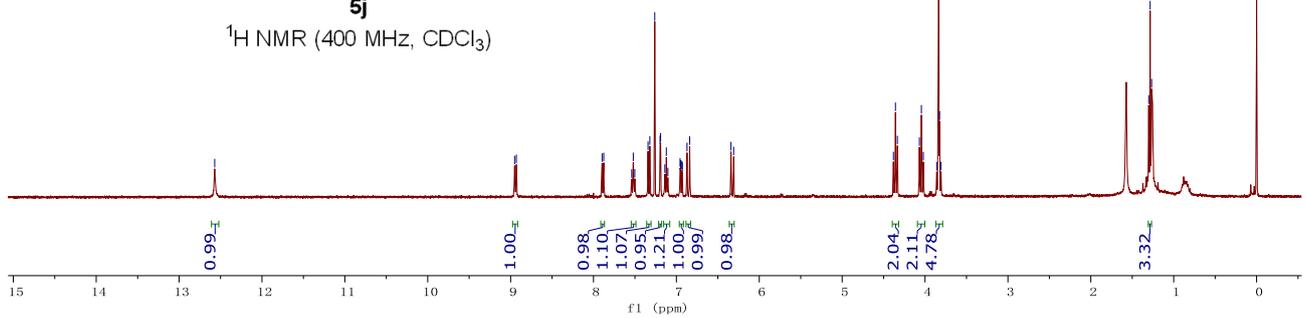


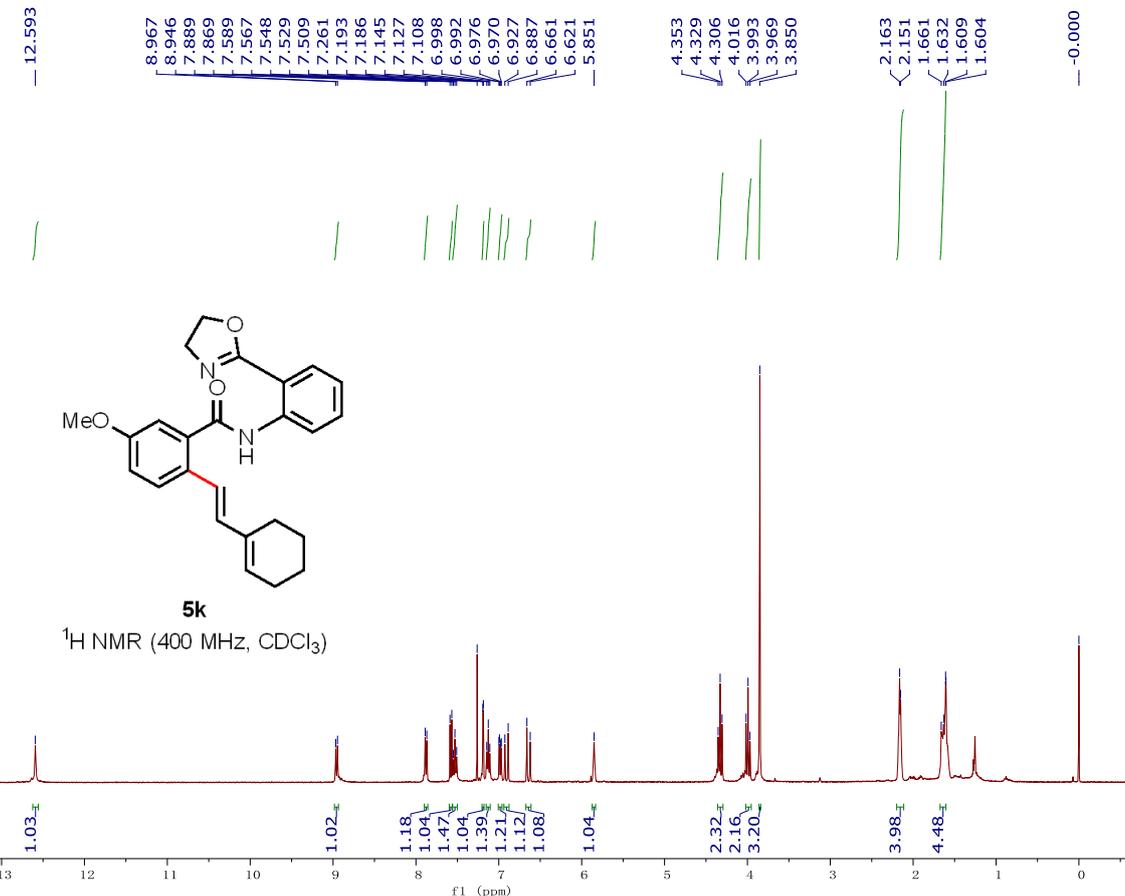
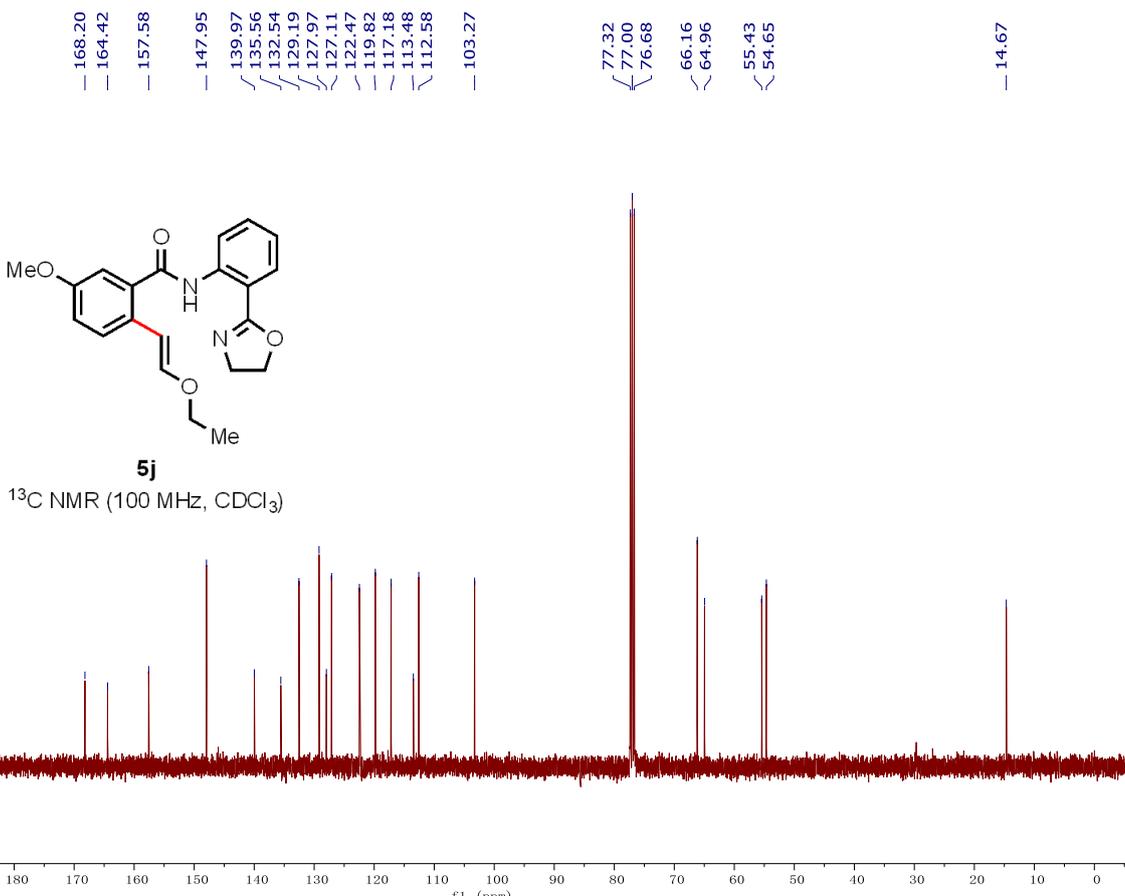


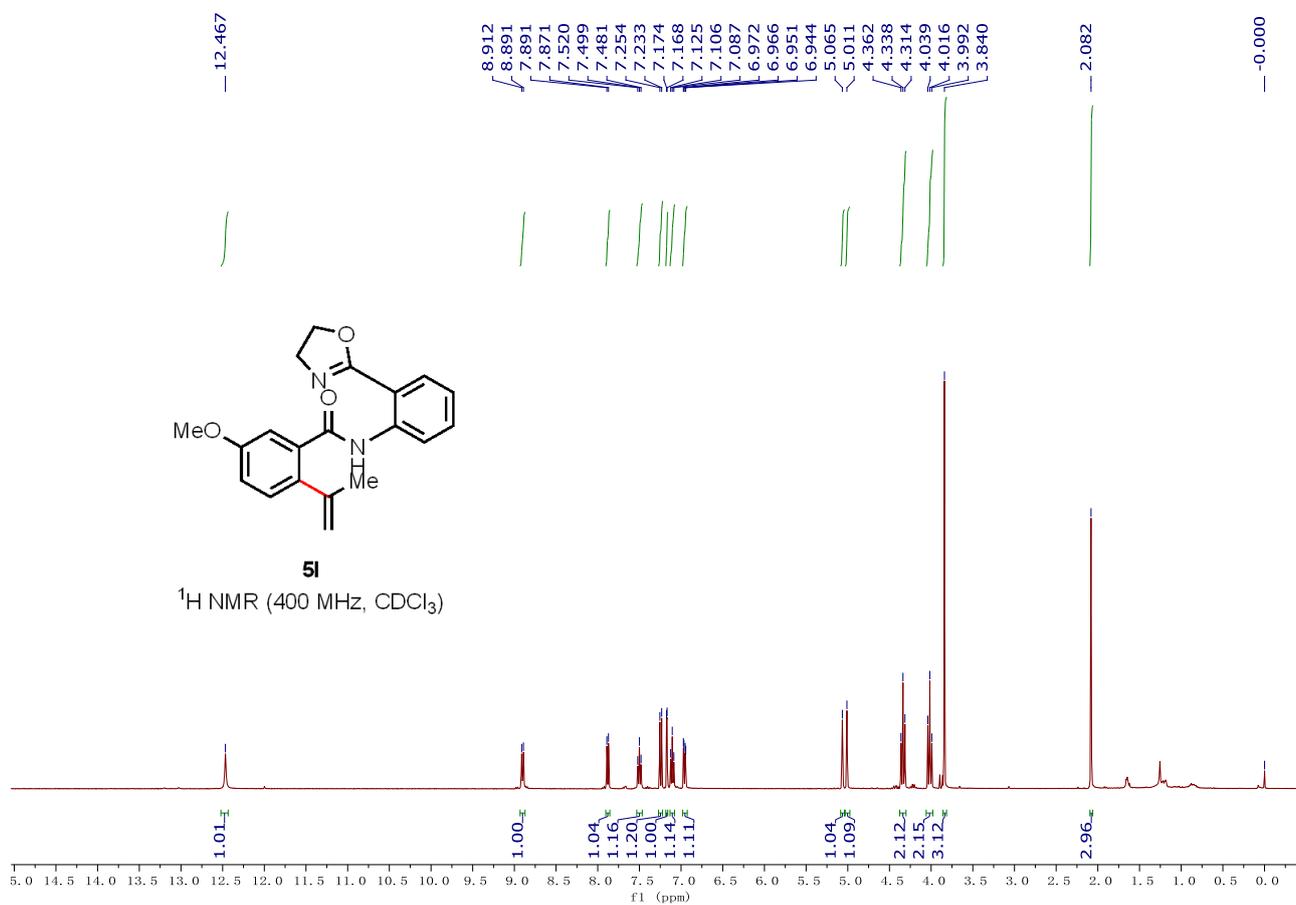
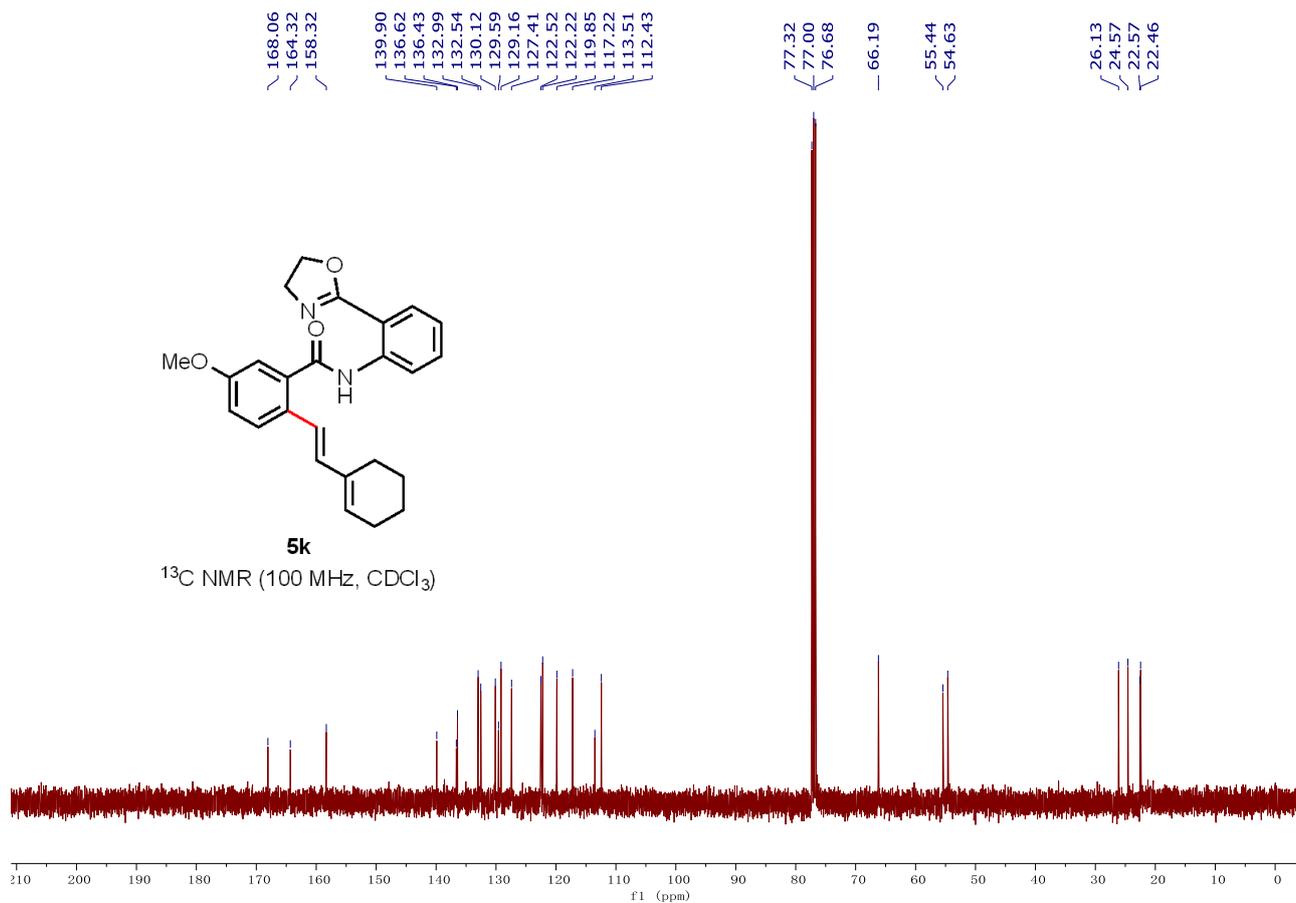
^{13}C NMR (100 MHz, CDCl_3)



^1H NMR (400 MHz, CDCl_3)

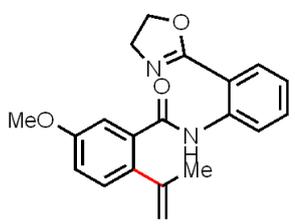






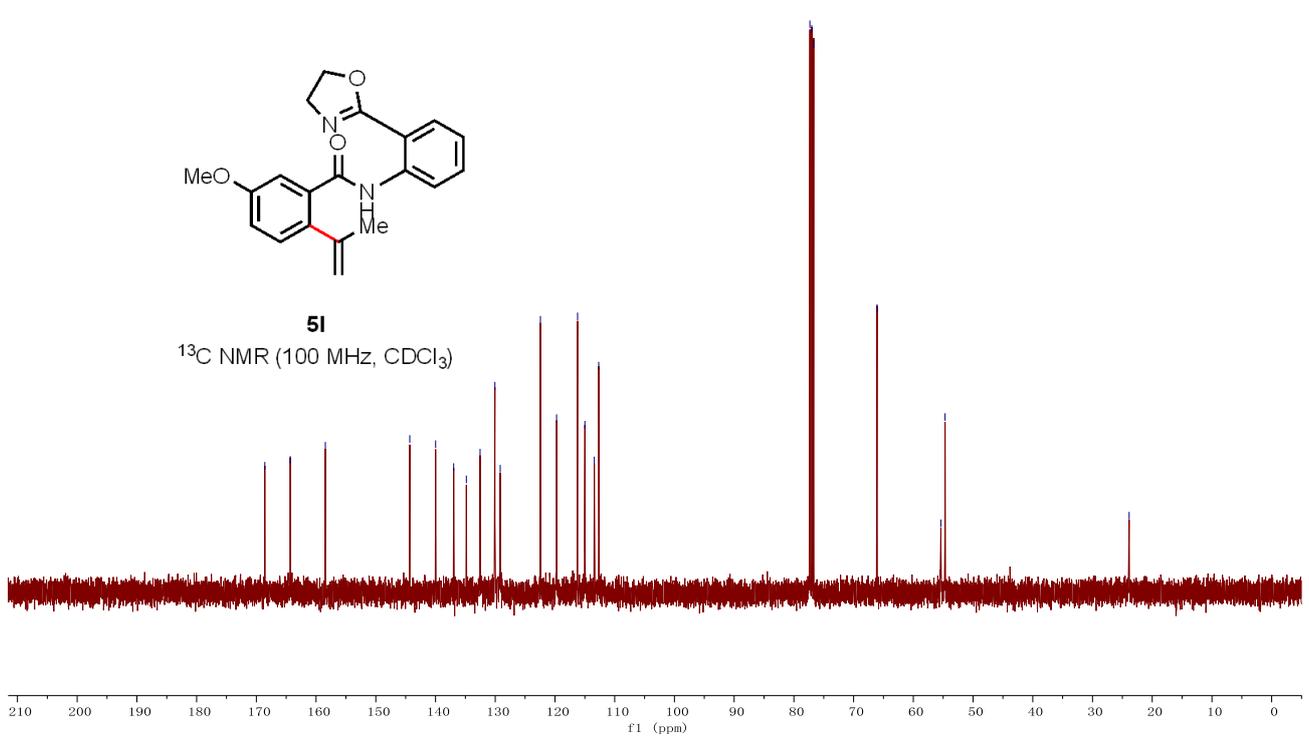
δ 168.58
 δ 164.33
 δ 158.45
 δ 144.31
 δ 139.98
 δ 136.96
 δ 134.84
 δ 132.54
 δ 130.06
 δ 129.17
 δ 122.44
 δ 119.73
 δ 116.22
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δ 77.32
 δ 77.00
 δ 76.68
 δ 66.07
 δ 55.39
 δ 54.68
 δ 23.86

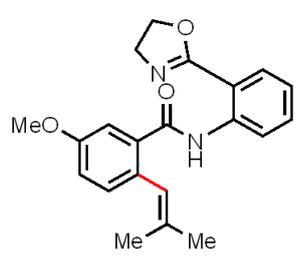


5l

^{13}C NMR (100 MHz, CDCl_3)

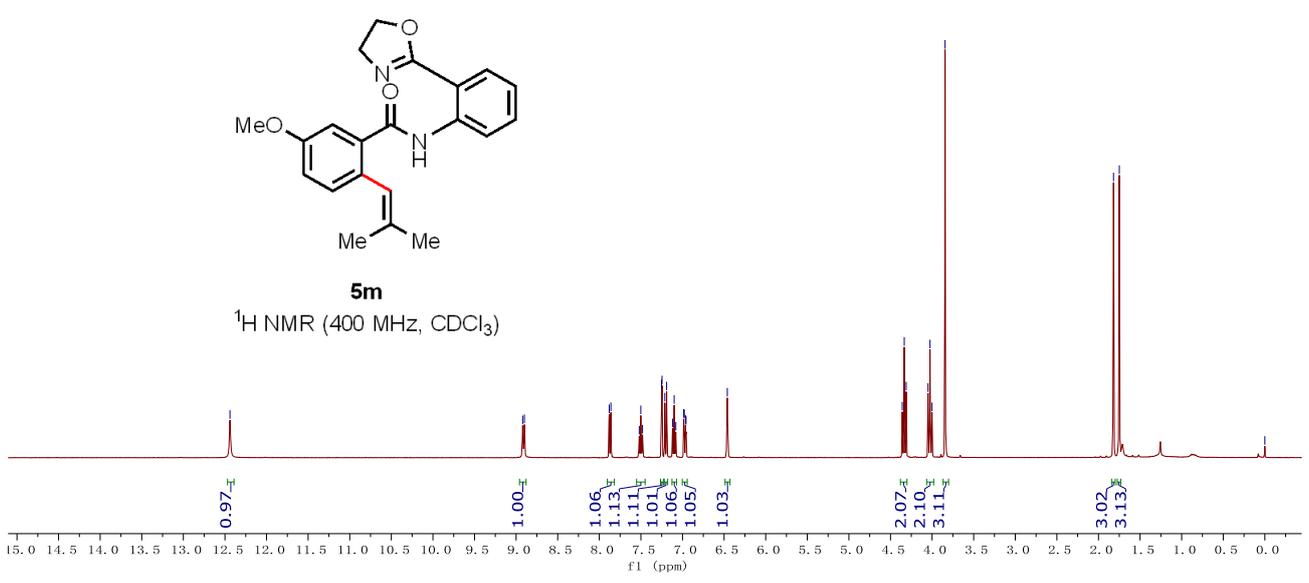


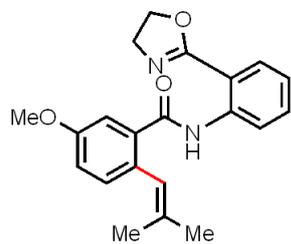
δ 12.440
 δ 8.921
 δ 8.900
 δ 7.881
 δ 7.861
 δ 7.520
 δ 7.501
 δ 7.480
 δ 7.253
 δ 7.246
 δ 7.212
 δ 7.191
 δ 7.119
 δ 7.100
 δ 7.080
 δ 6.985
 δ 6.979
 δ 6.964
 δ 6.957
 δ 6.461
 δ 4.358
 δ 4.335
 δ 4.311
 δ 4.048
 δ 4.025
 δ 4.001
 δ 3.844
 δ 1.819
 δ 1.749
 δ -0.000



5m

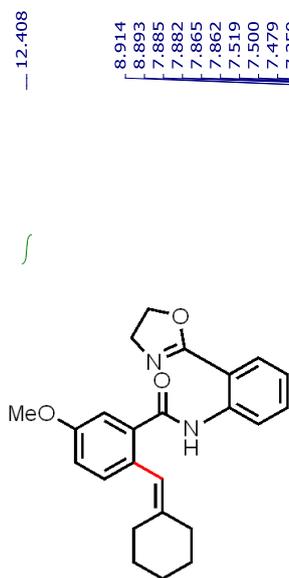
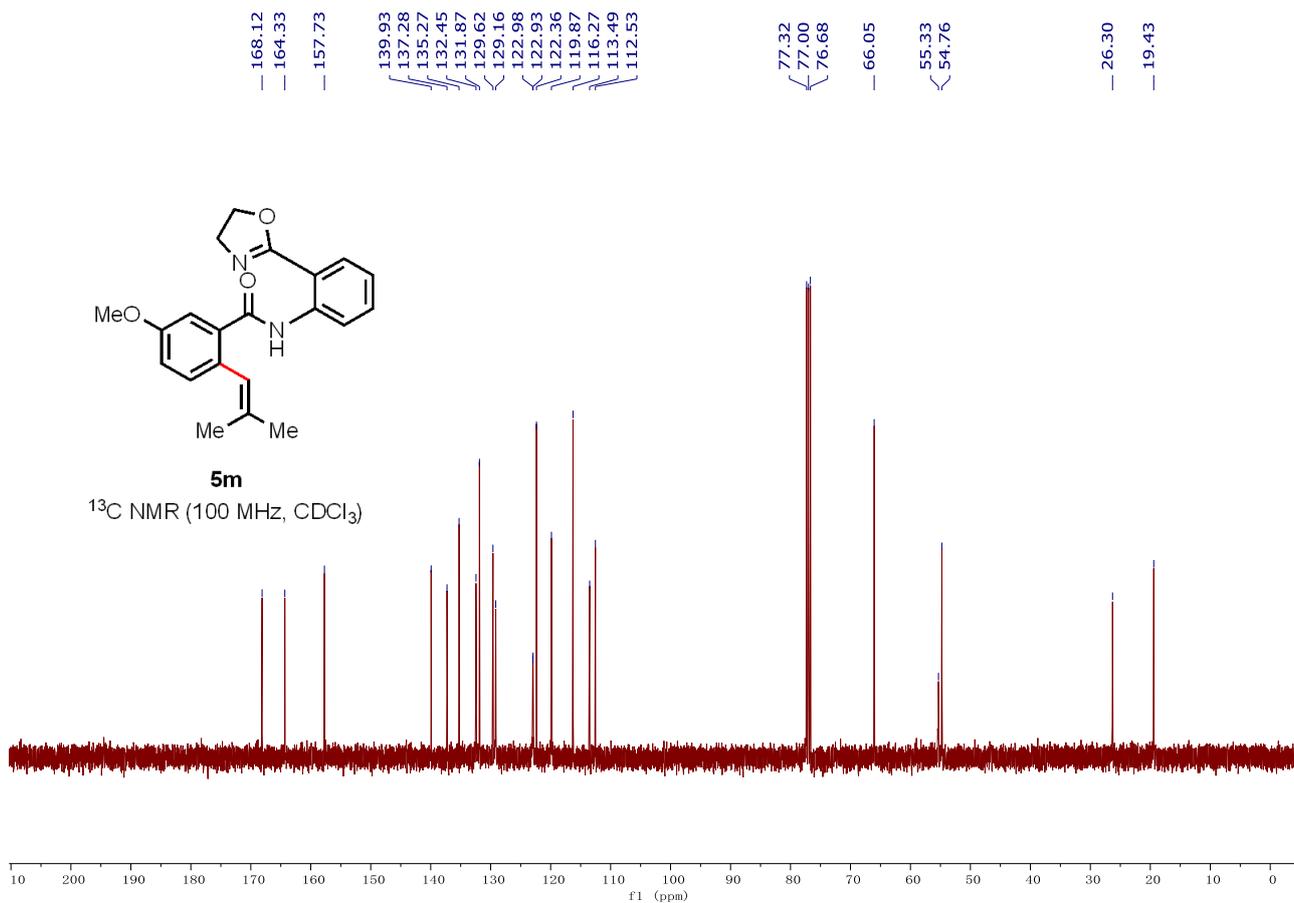
^1H NMR (400 MHz, CDCl_3)





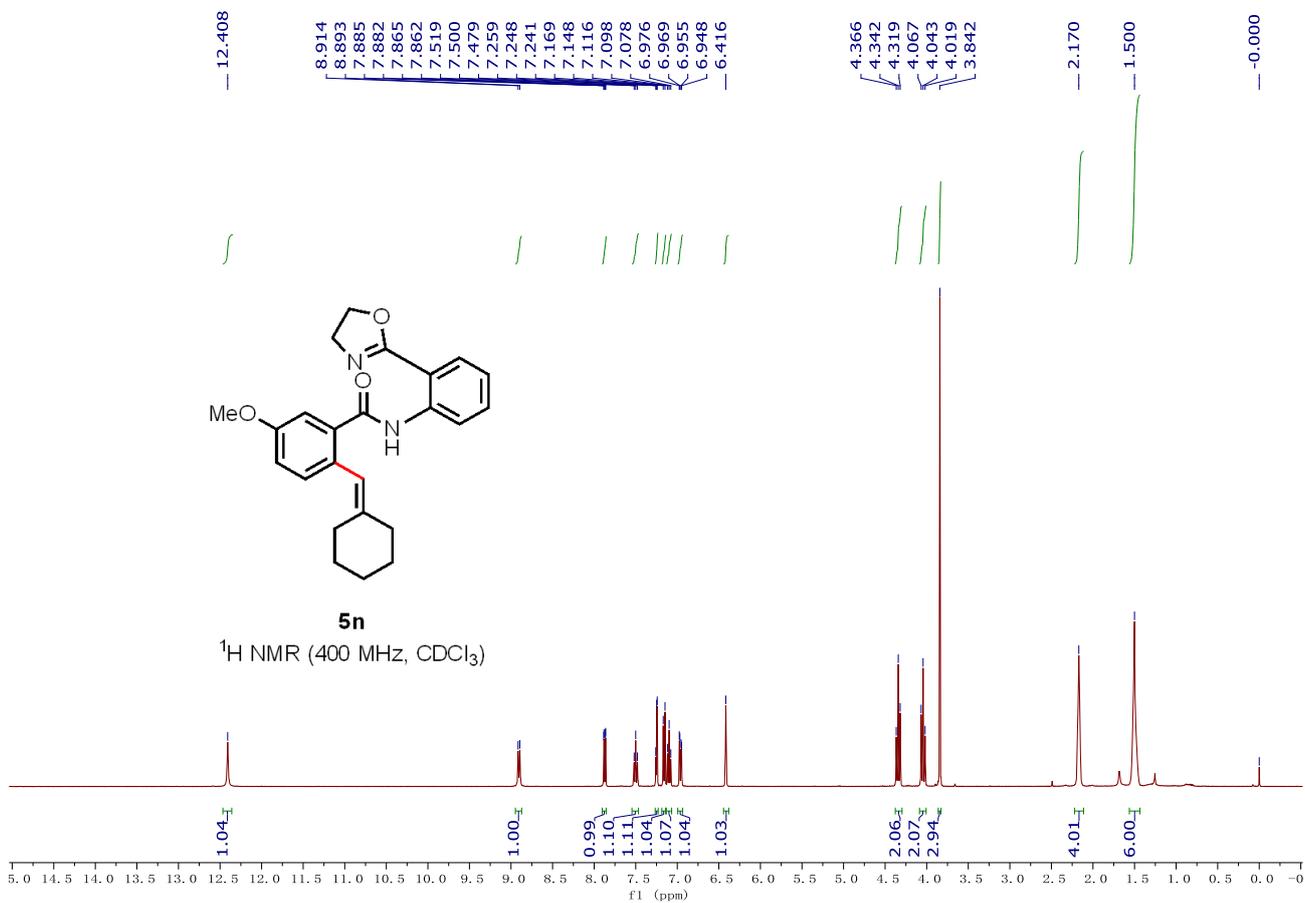
5m

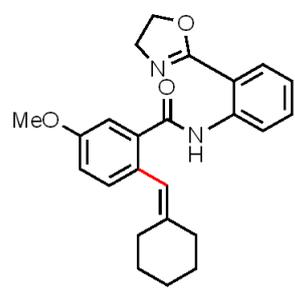
^{13}C NMR (100 MHz, CDCl_3)



5n

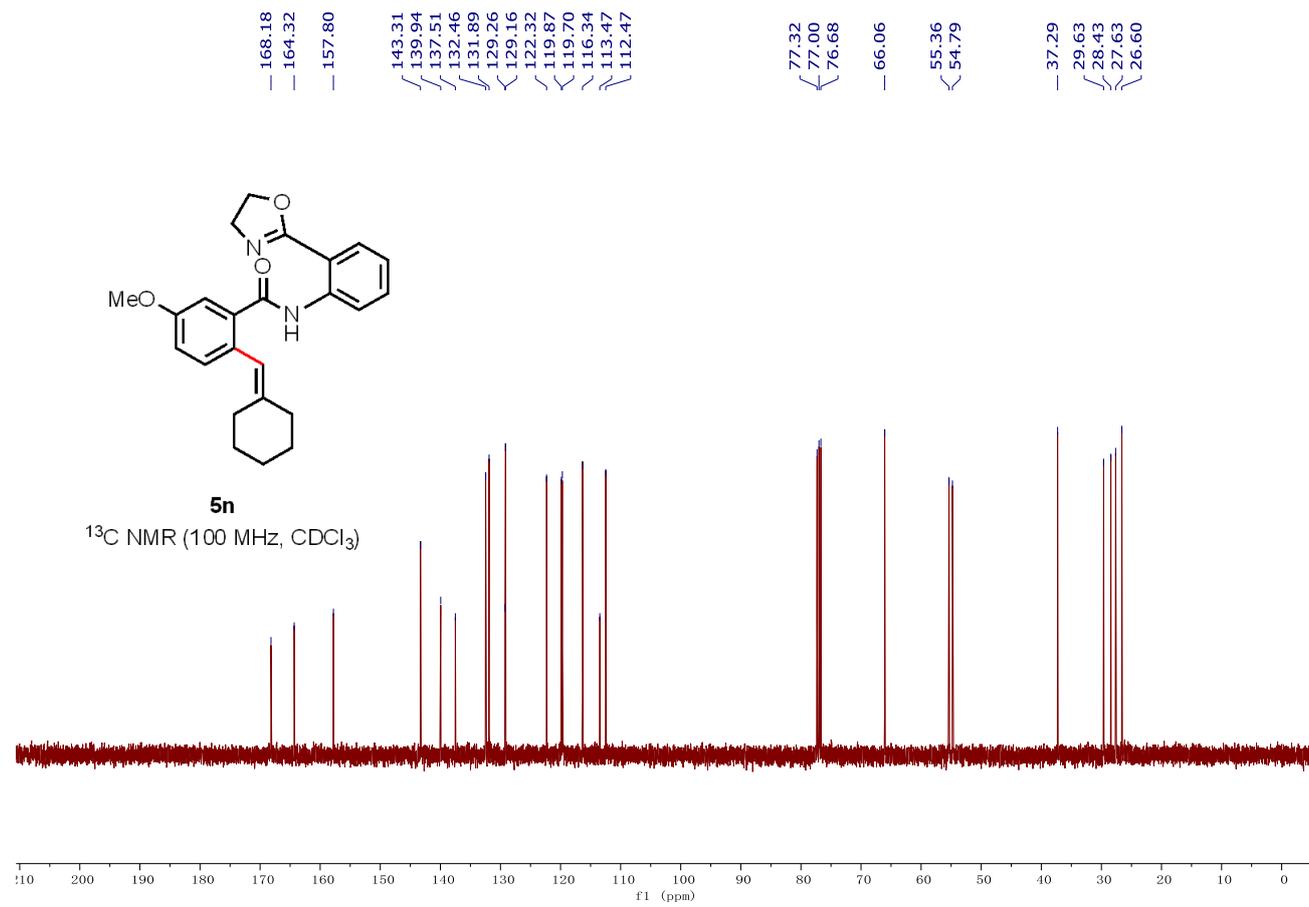
^1H NMR (400 MHz, CDCl_3)





5n

¹³C NMR (100 MHz, CDCl₃)

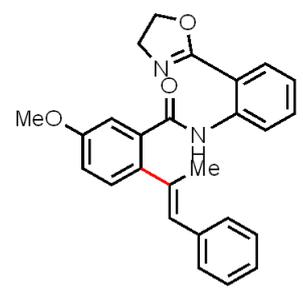


12.506

8.942, 8.921, 7.858, 7.838, 7.517, 7.498, 7.478, 7.353, 7.332, 7.288, 7.269, 7.255, 7.251, 7.239, 7.232, 7.202, 7.184, 7.168, 7.150, 7.119, 7.101, 7.083, 7.026, 7.019, 7.005, 6.998, 6.575, 4.171, 4.147, 4.123, 3.898, 3.867, 3.851

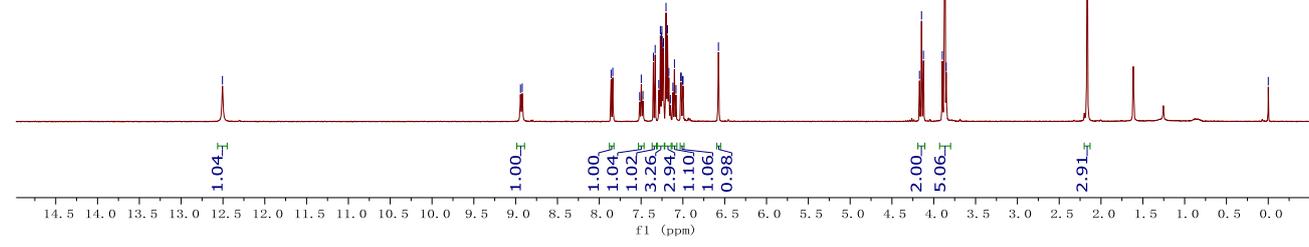
2.166

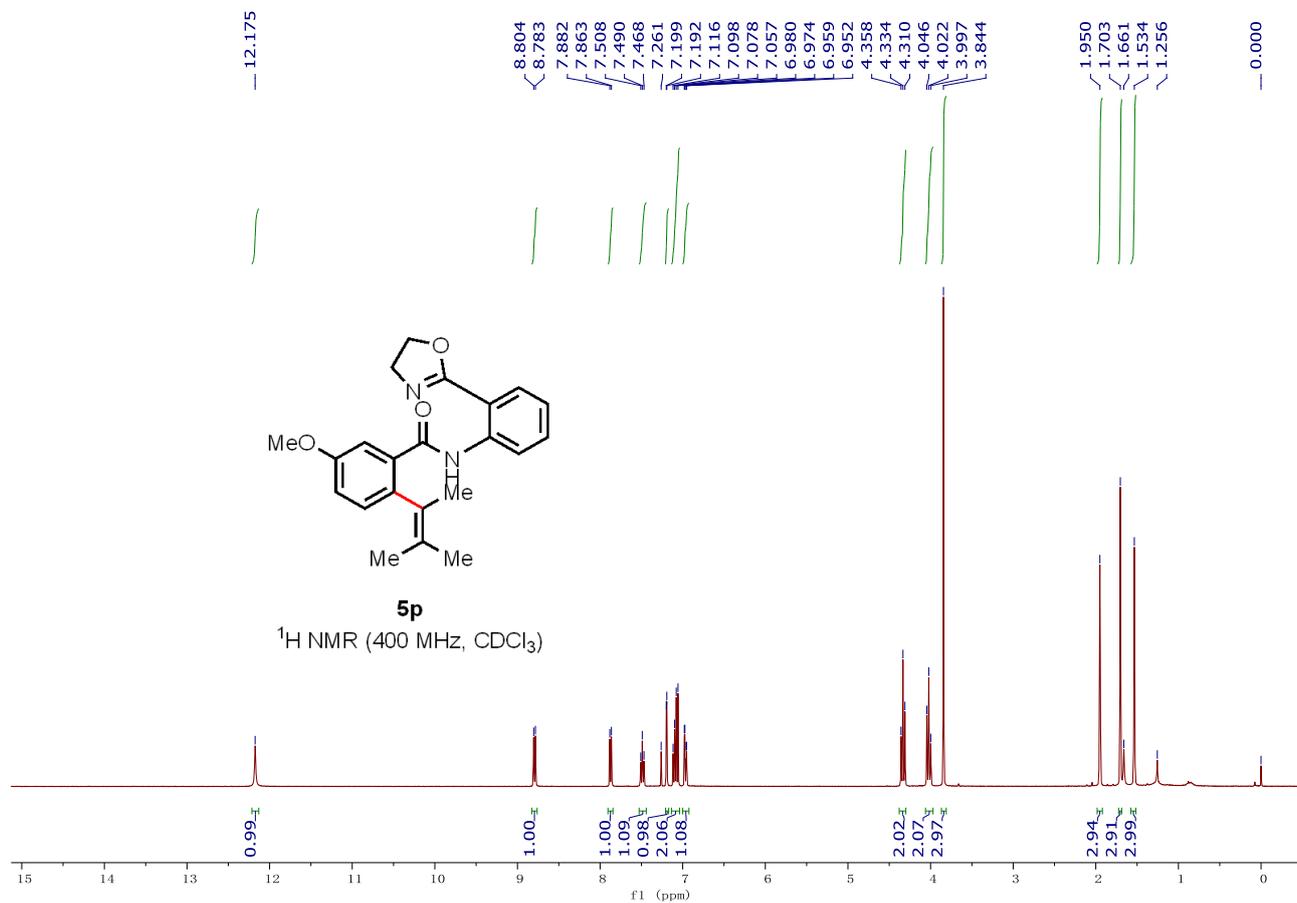
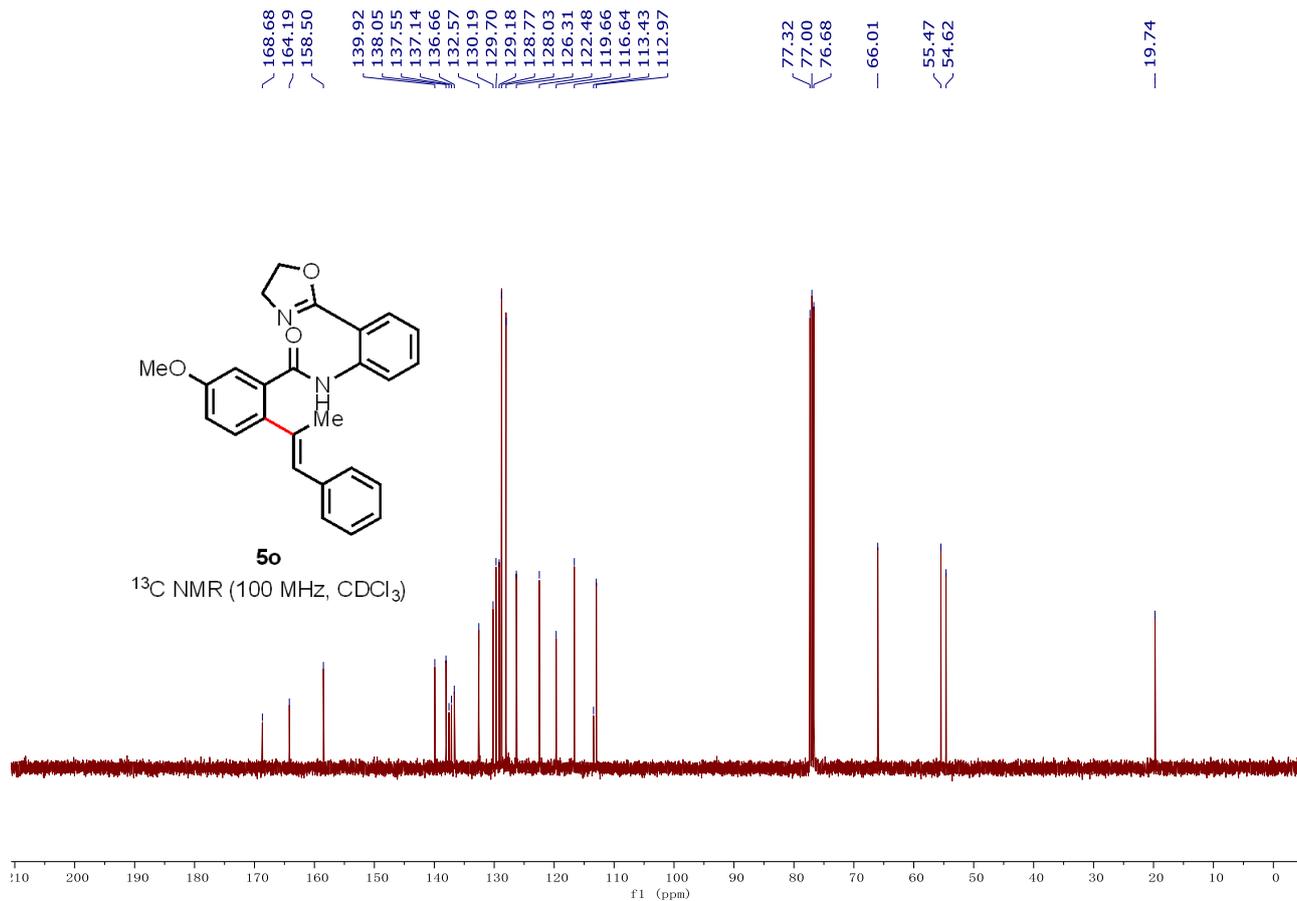
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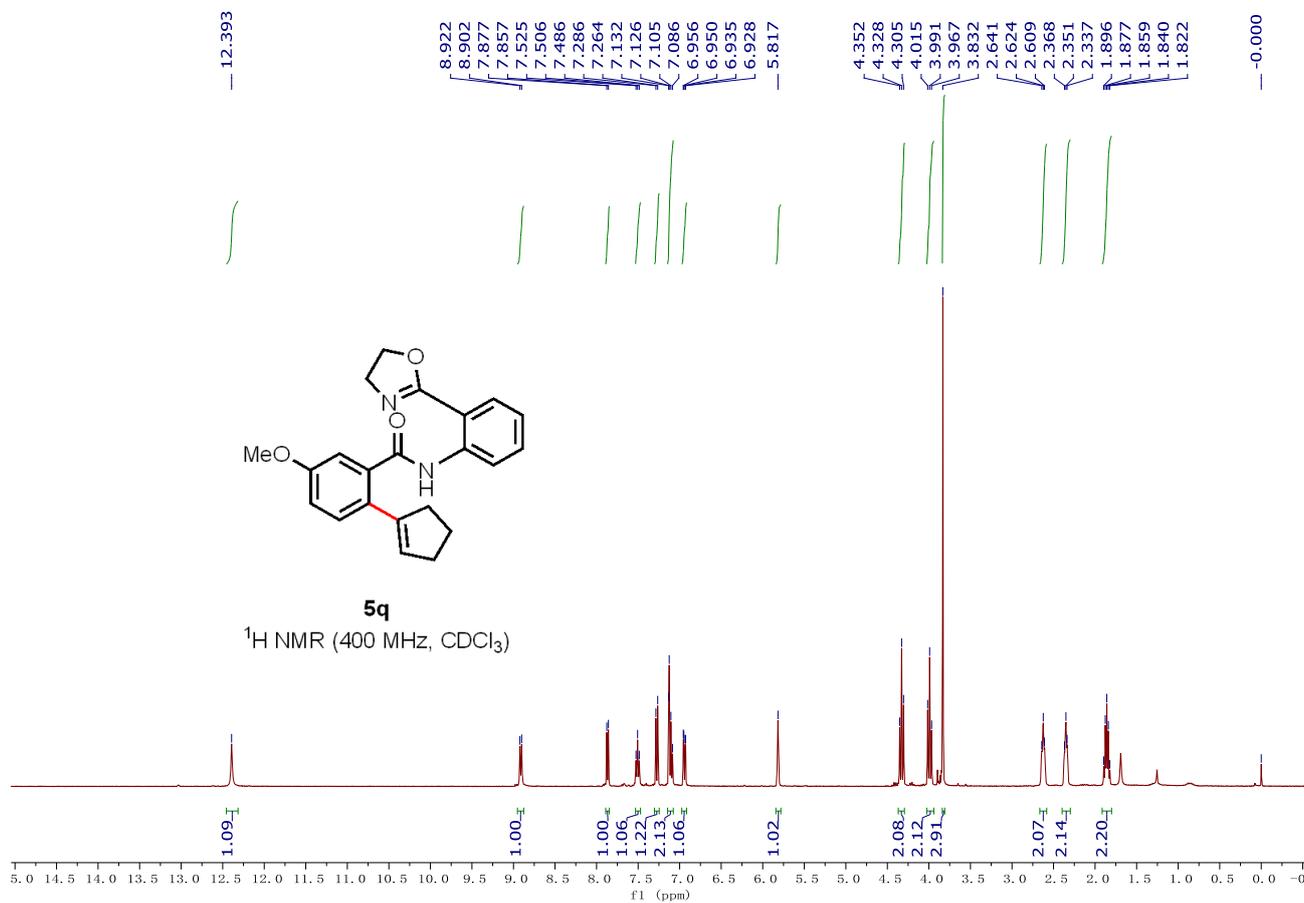
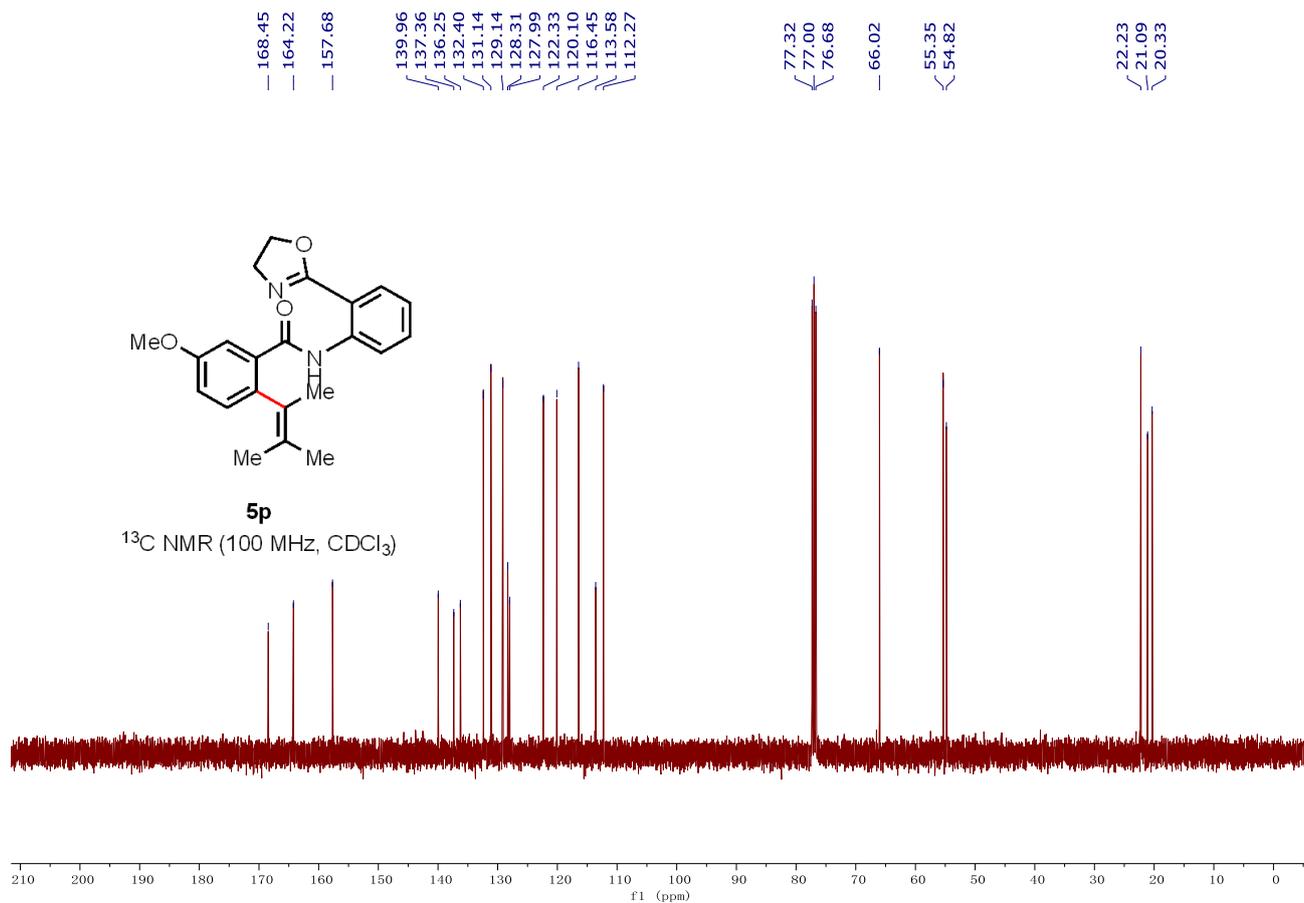


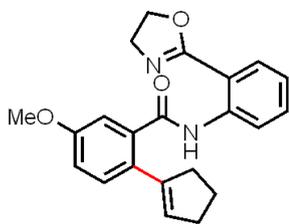
5o

¹H NMR (400 MHz, CDCl₃)



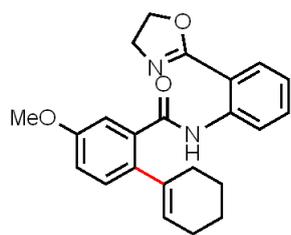
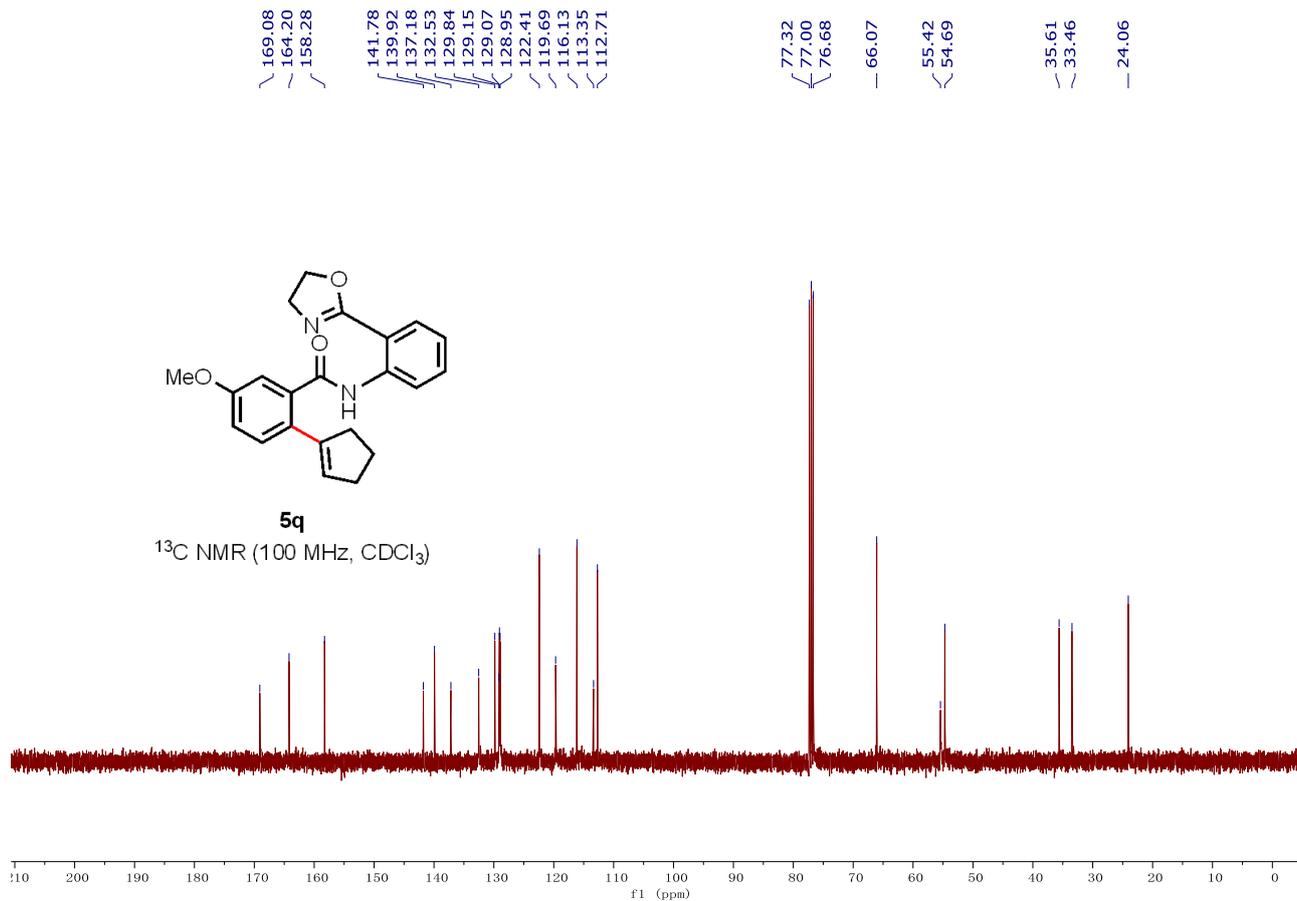






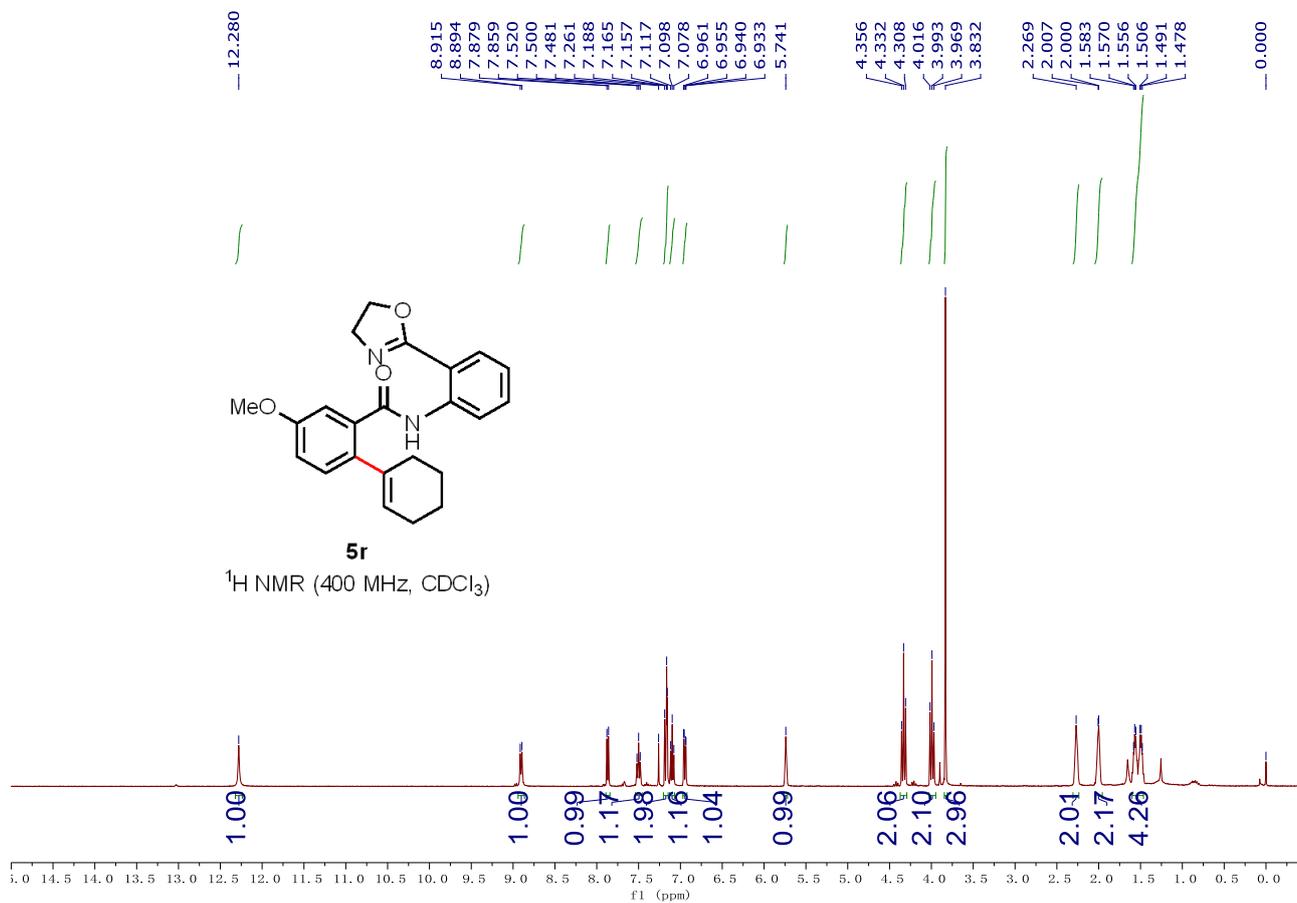
5q

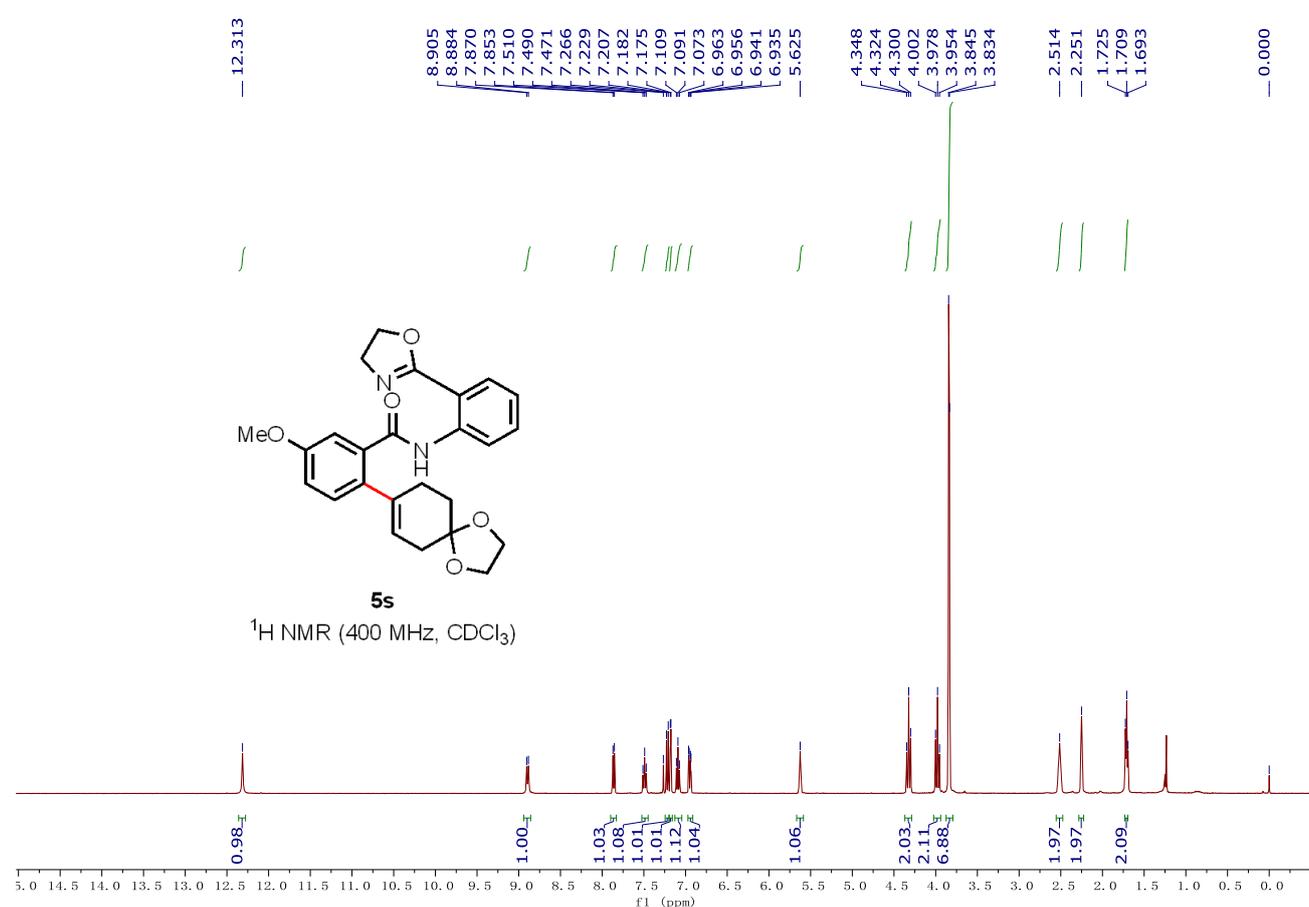
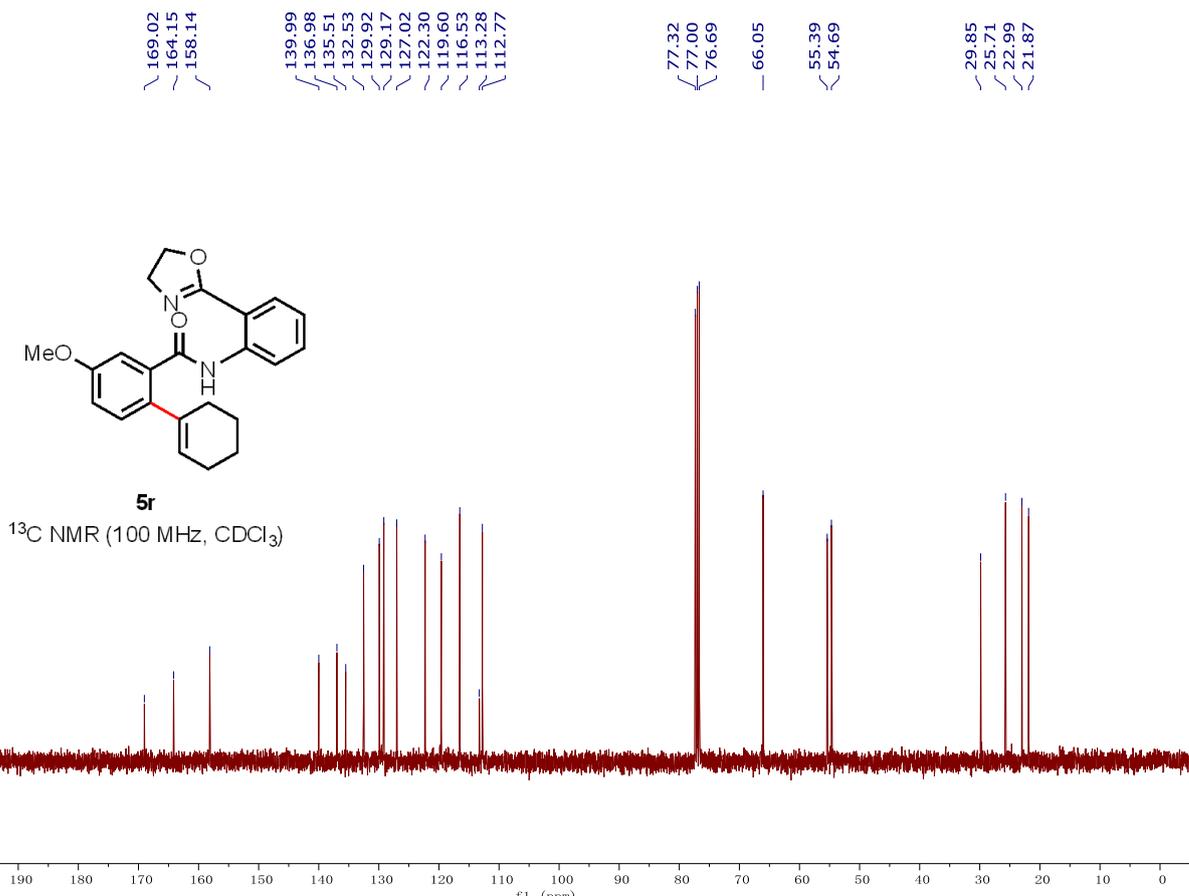
^{13}C NMR (100 MHz, CDCl_3)

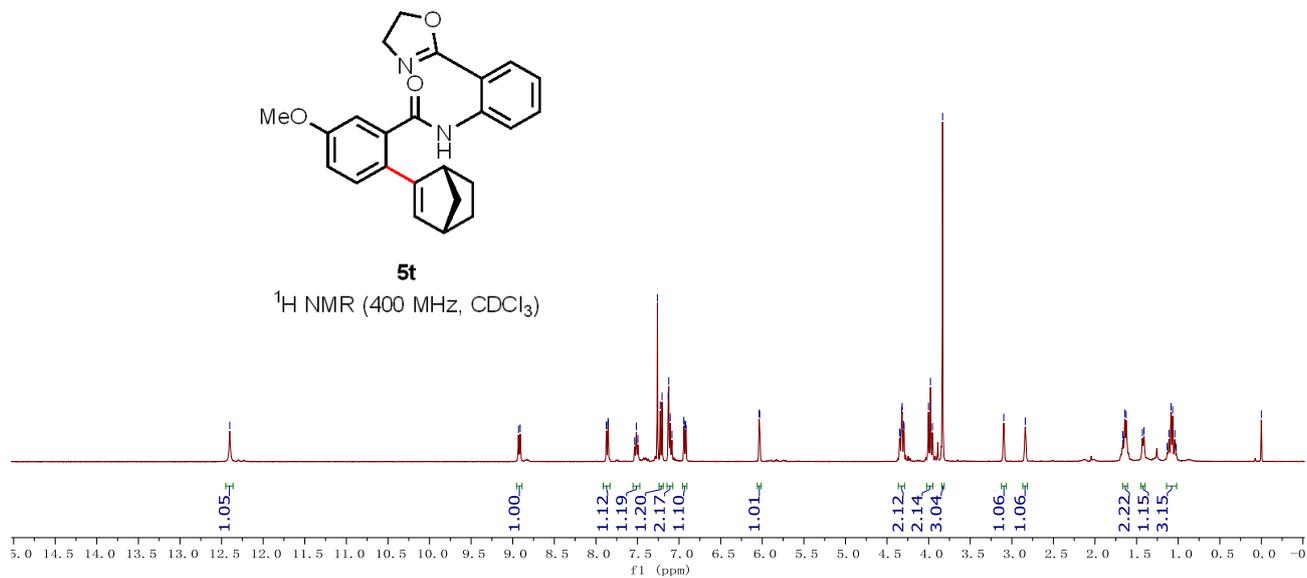
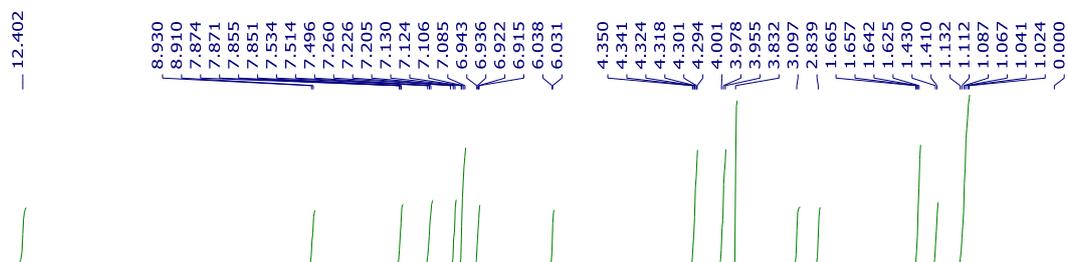
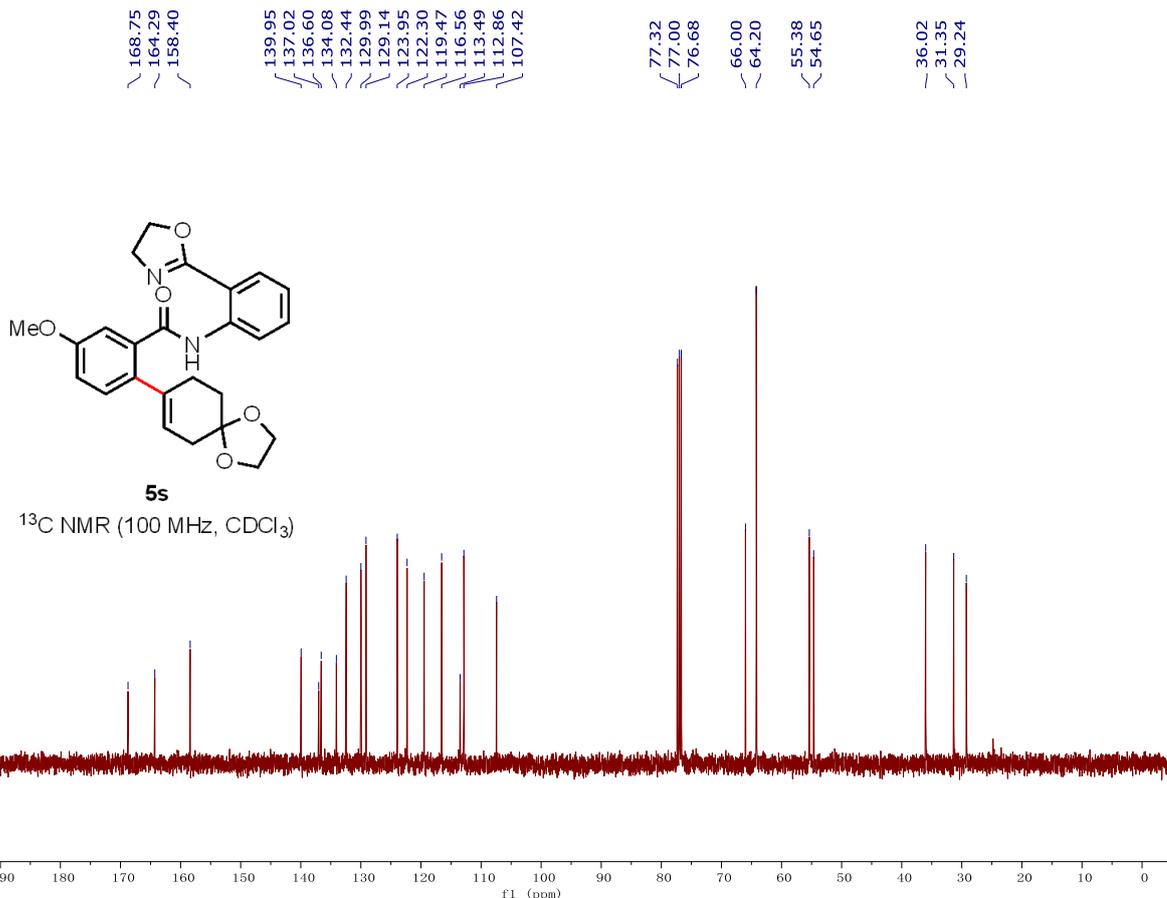


5r

^1H NMR (400 MHz, CDCl_3)

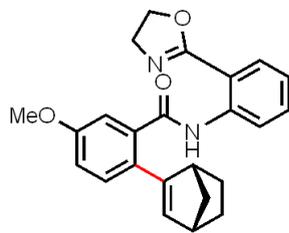






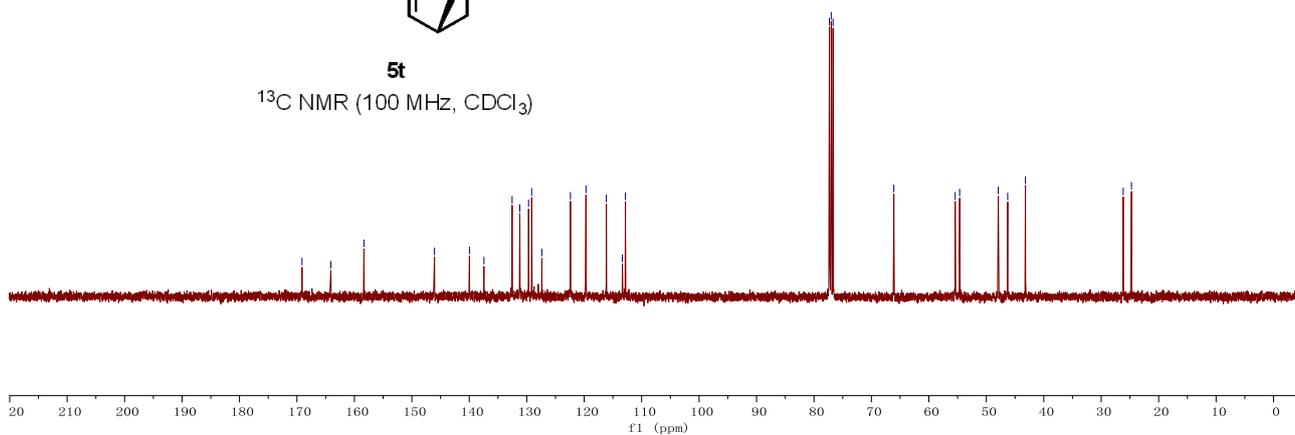
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164.11
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146.06
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137.45
132.54
131.21
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129.14
127.37
122.39
119.70
116.14
113.35
112.82

77.32
77.00
76.68
66.10
55.42
54.64
47.91
46.28
43.19
26.17
24.73

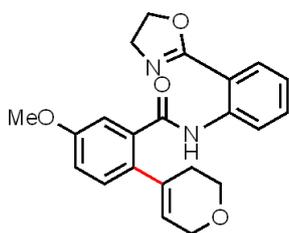


5t

^{13}C NMR (100 MHz, CDCl_3)

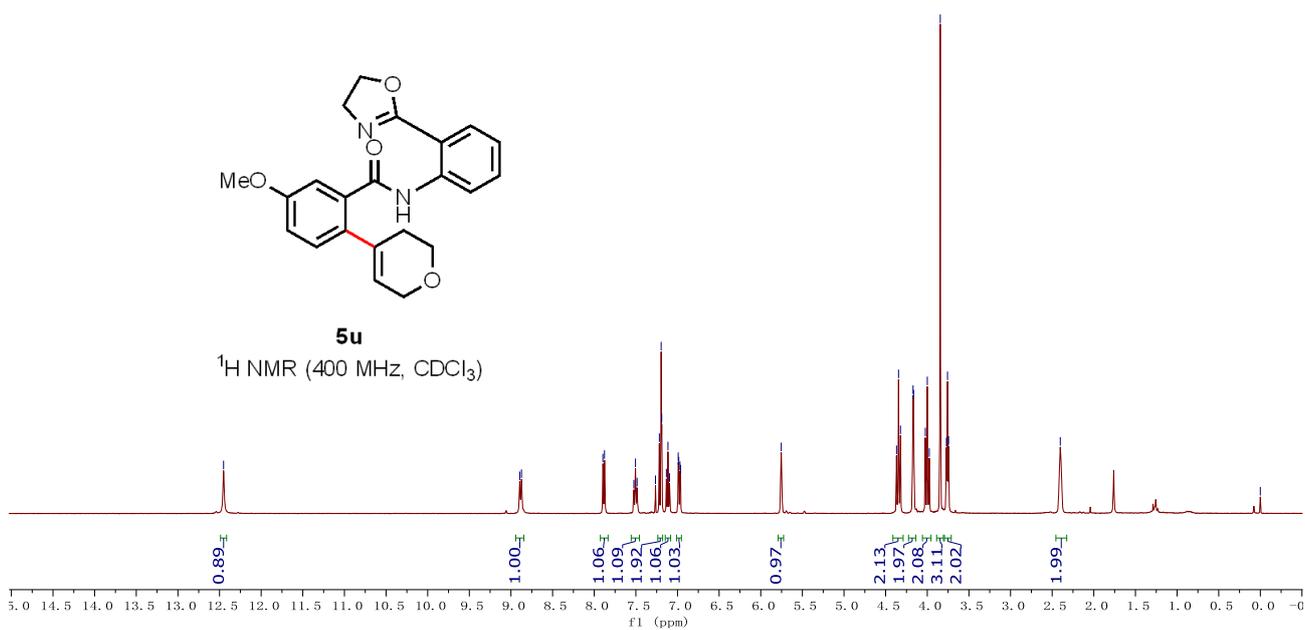


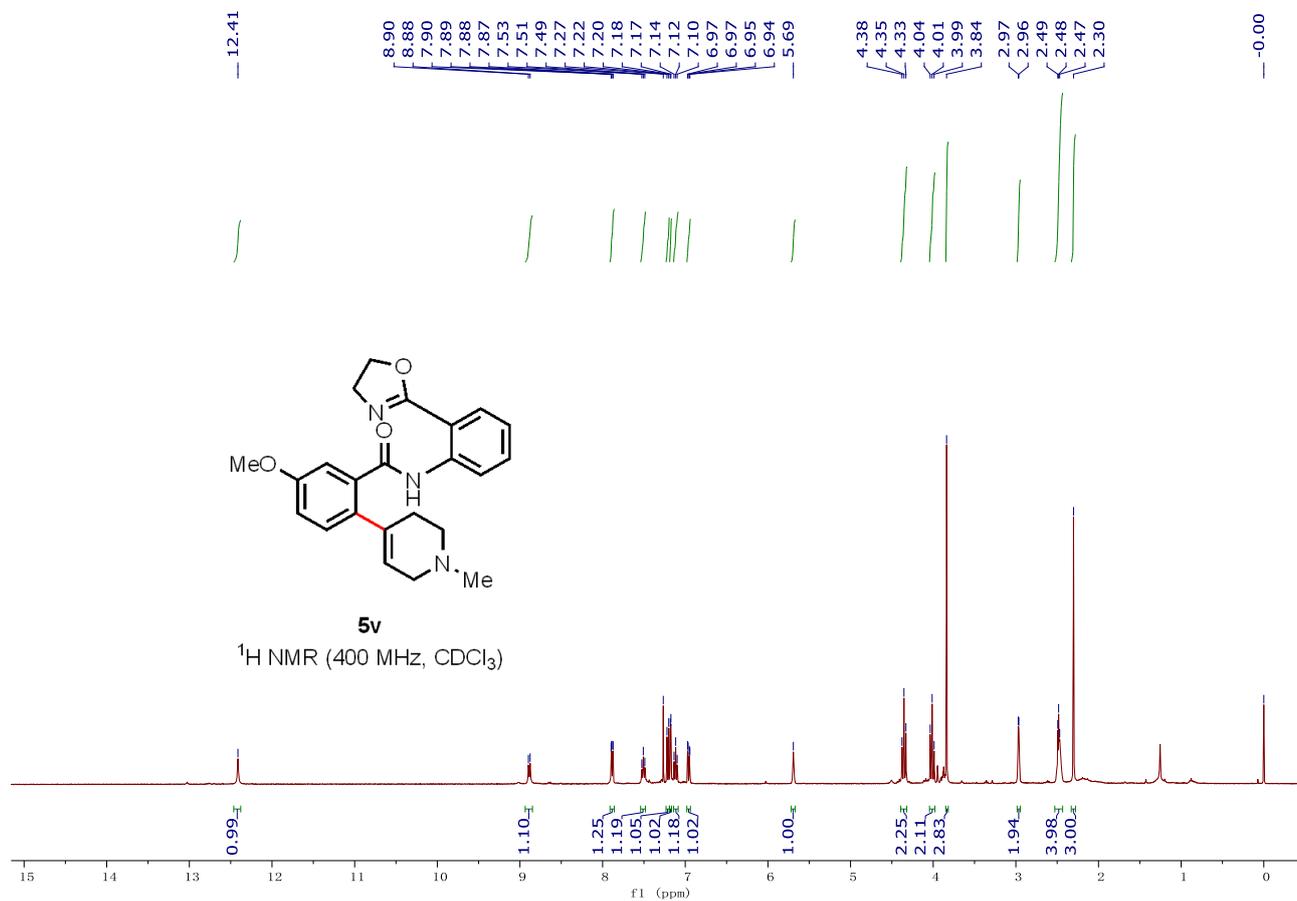
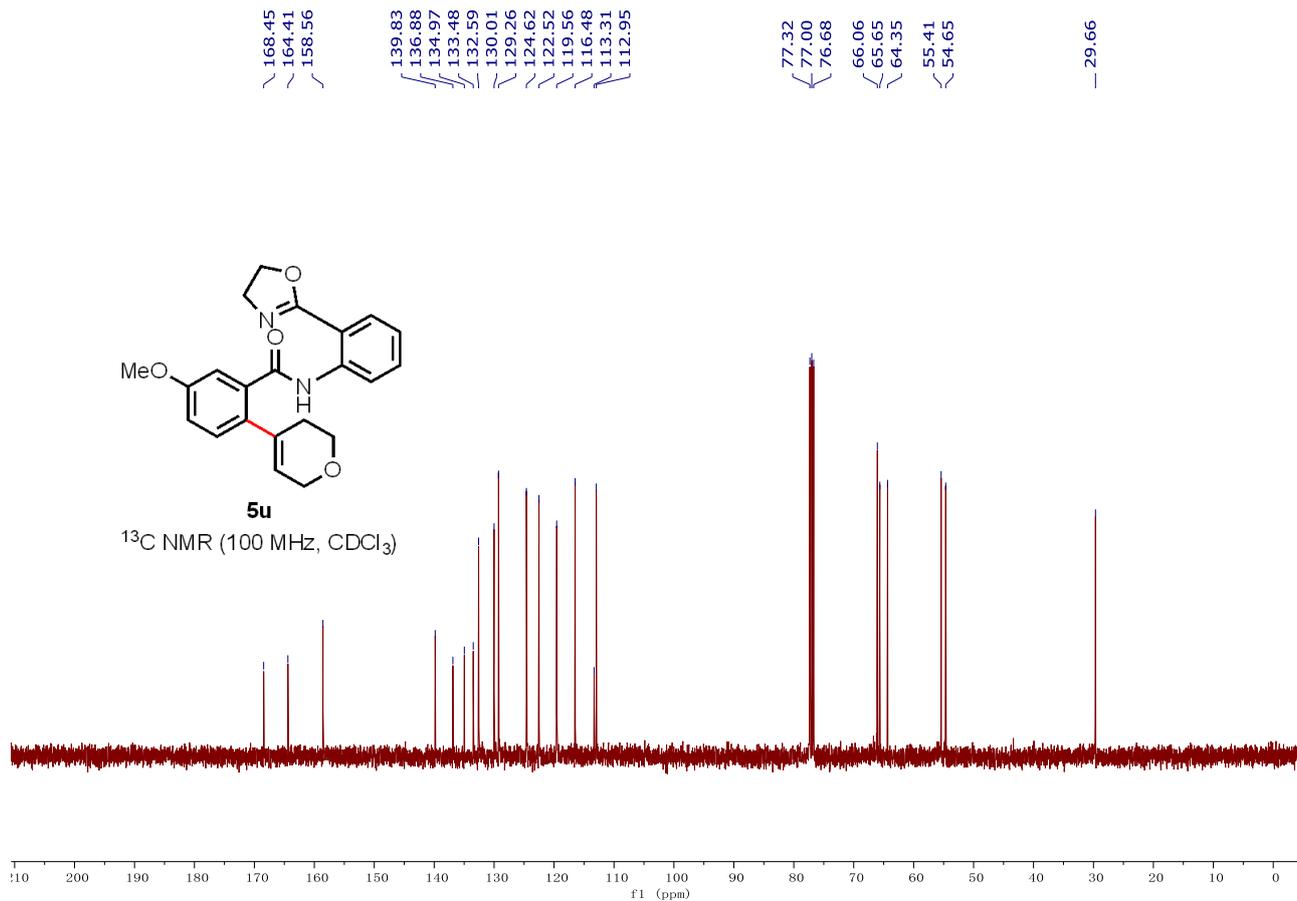
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7.196
7.190
7.133
7.114
7.096
6.991
6.985
6.970
6.963
5.754
4.369
4.345
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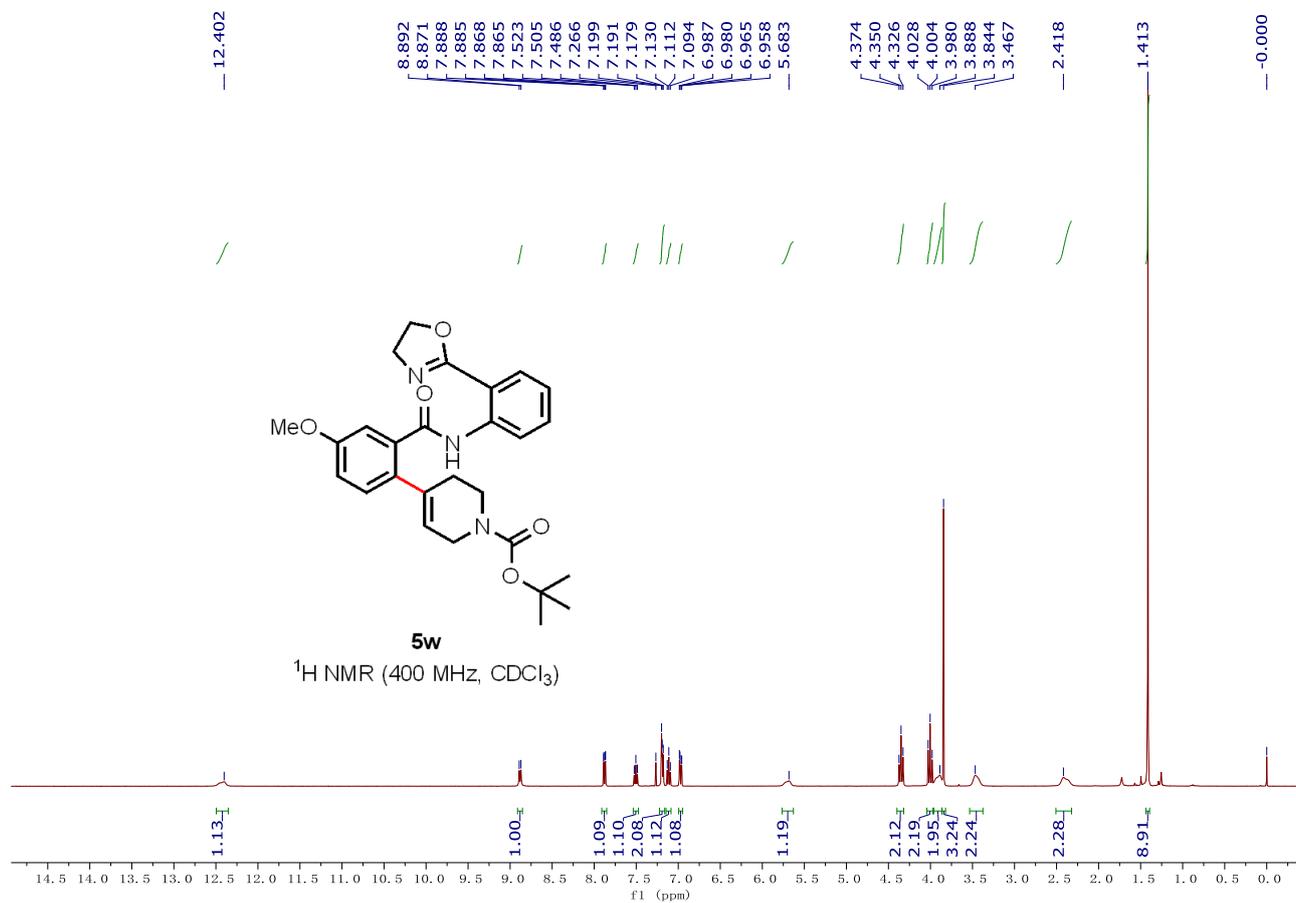
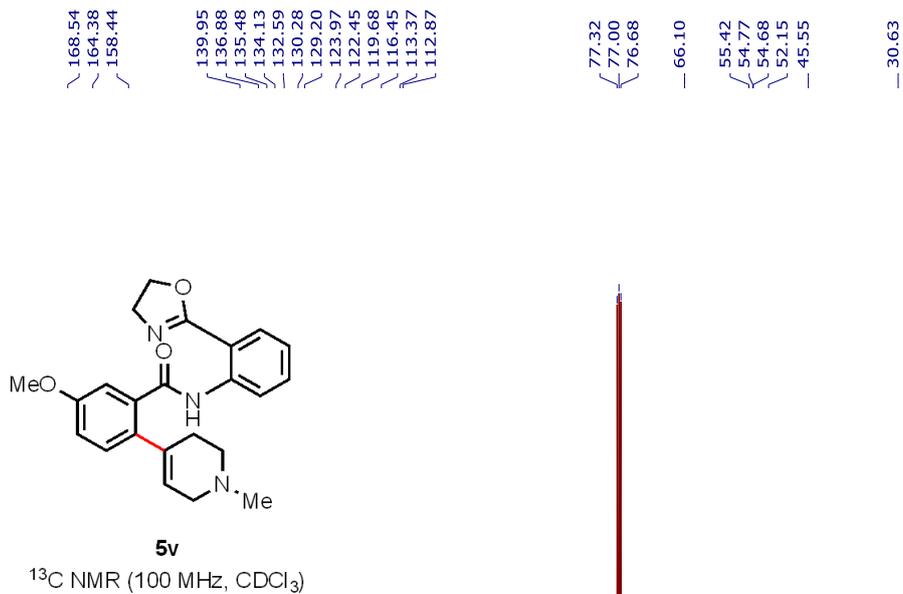


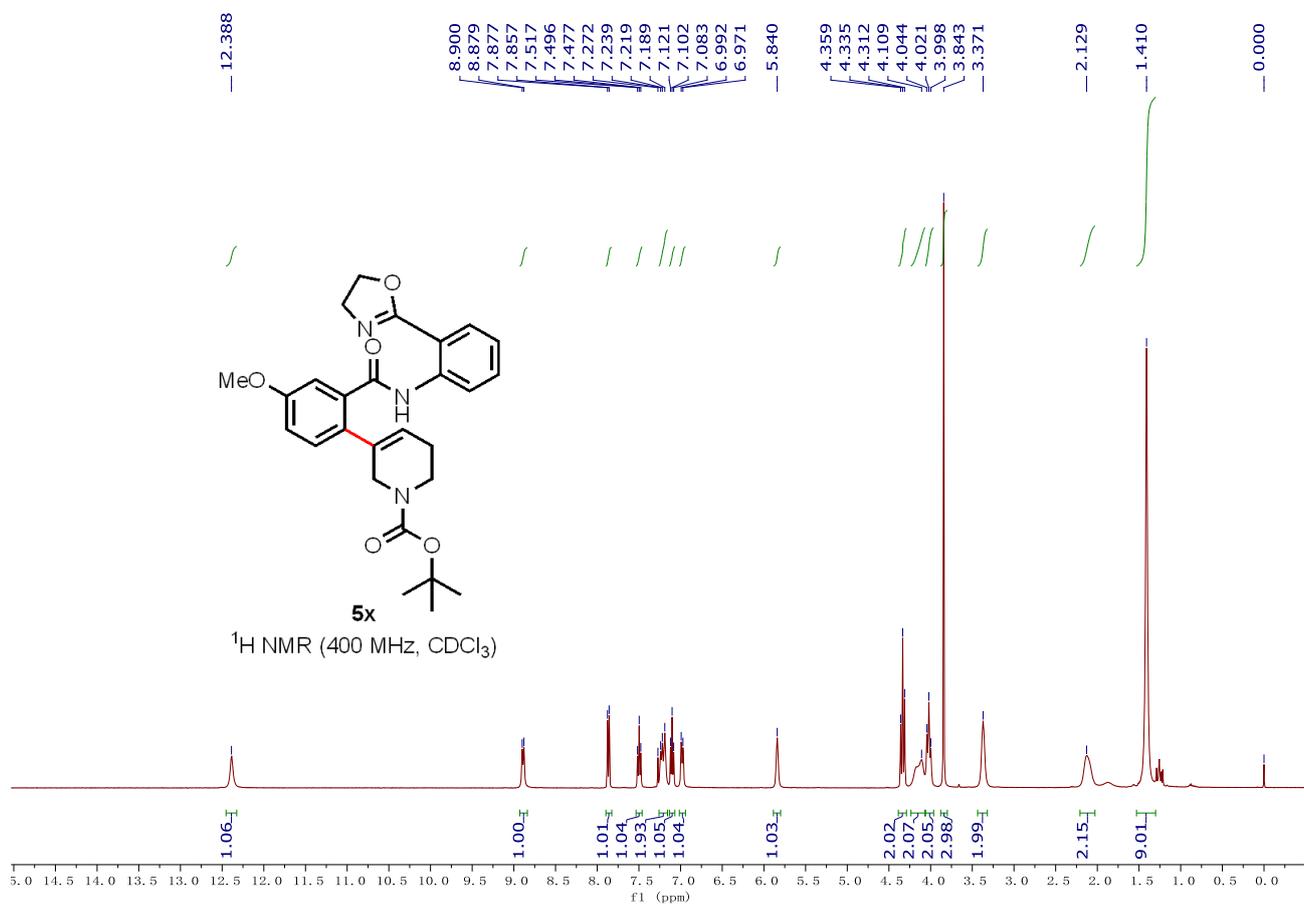
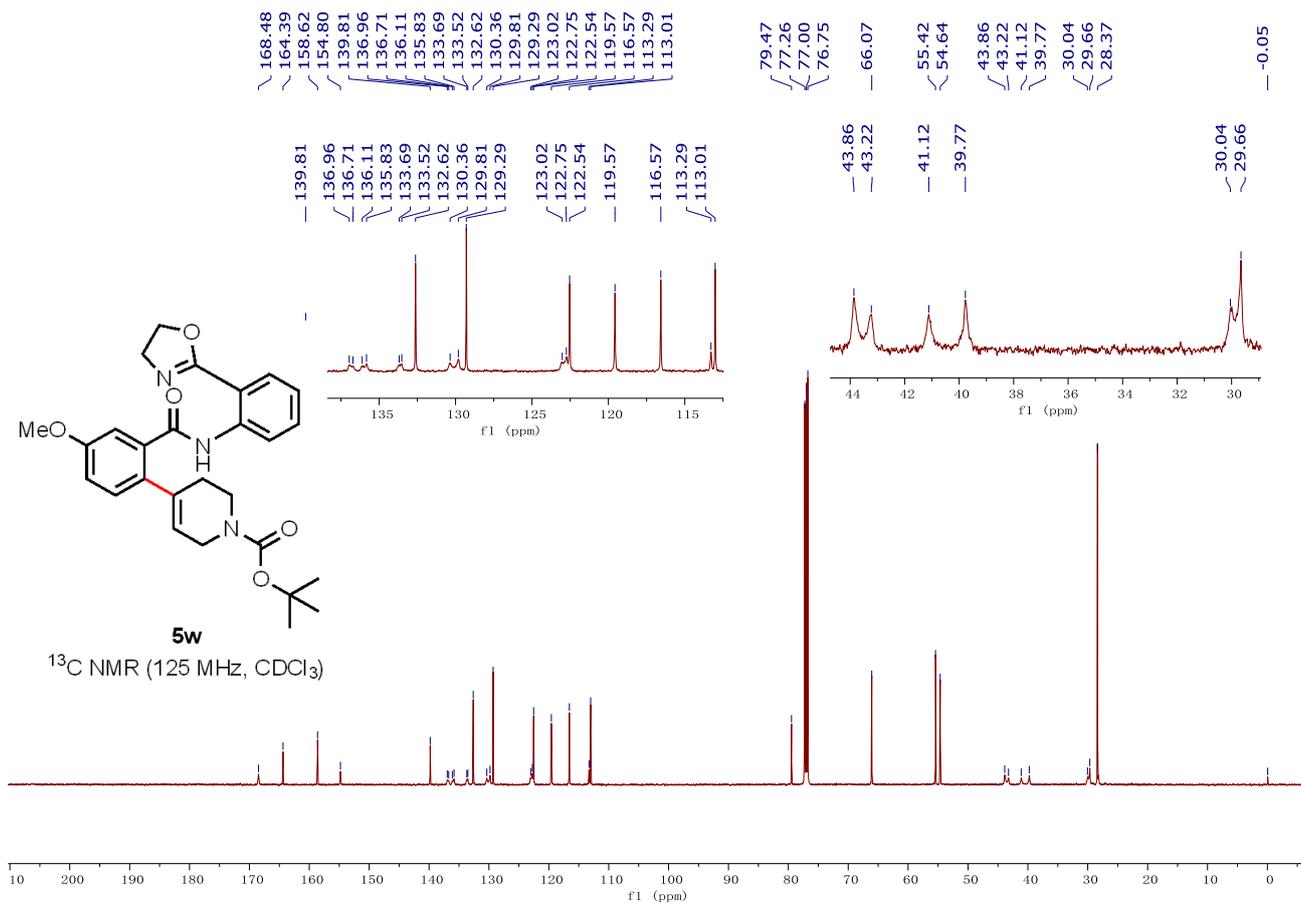
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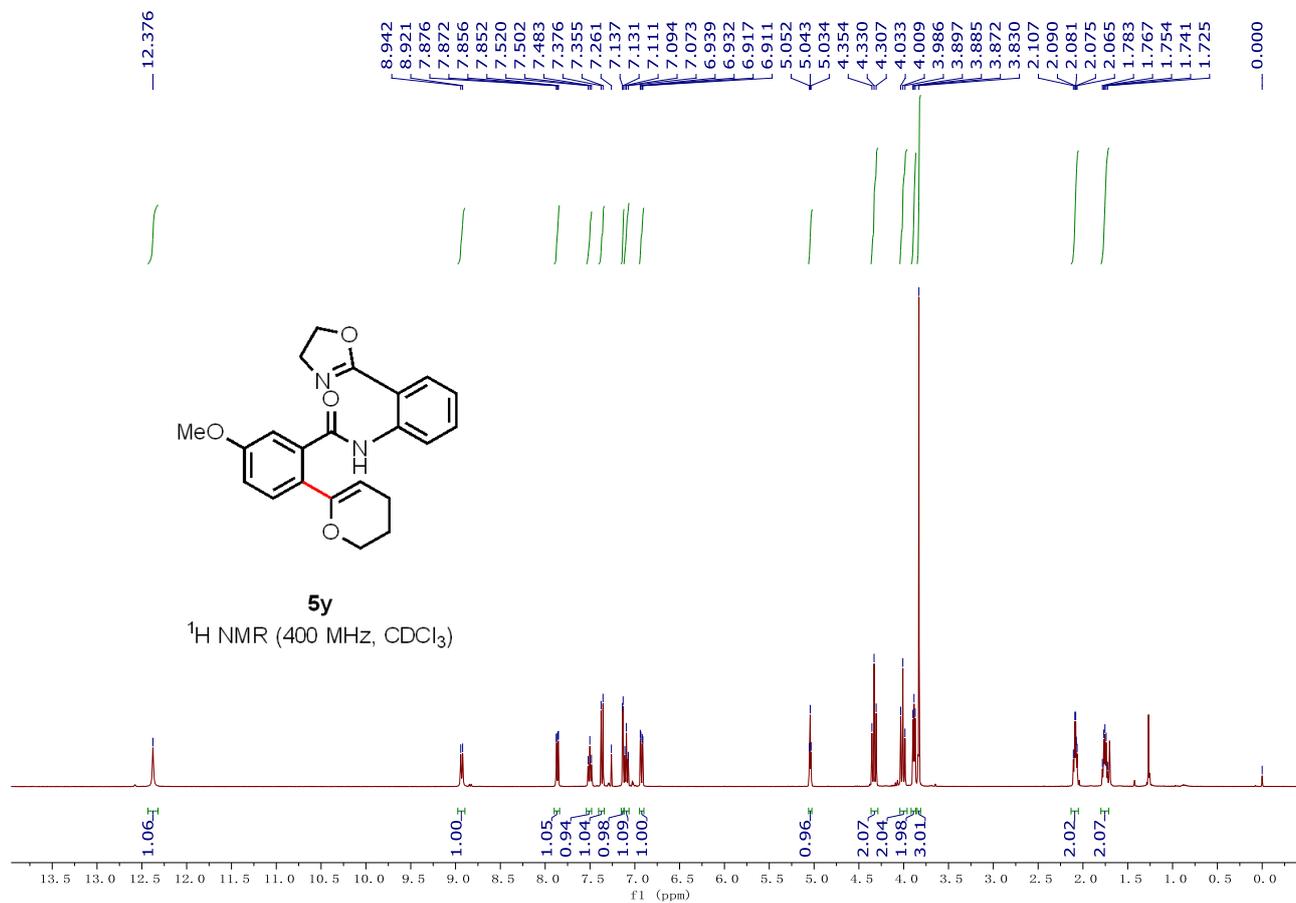
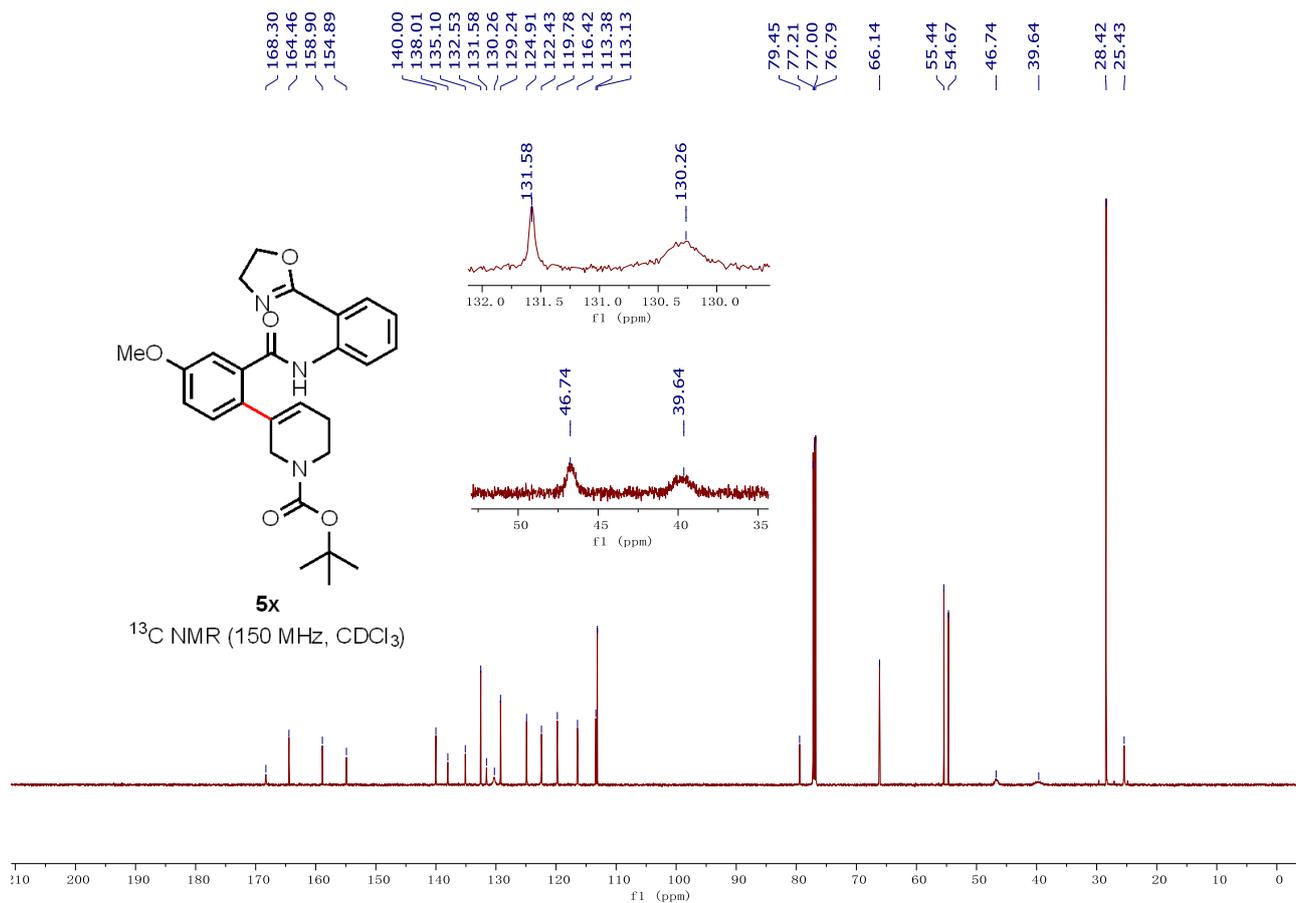
^1H NMR (400 MHz, CDCl_3)

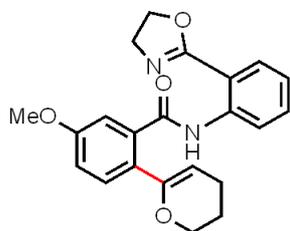








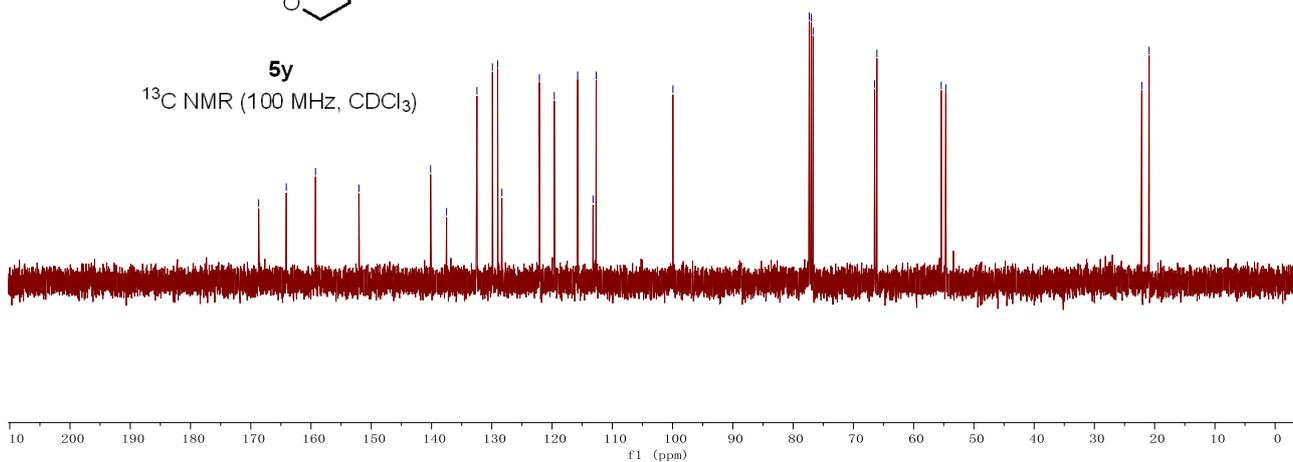




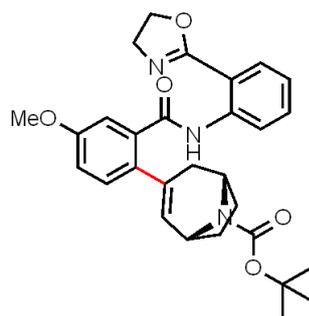
δ 168.69
 δ 164.10
 δ 159.27
 δ 152.06
 δ 140.15
 δ 137.51
 δ 132.46
 δ 129.90
 δ 129.03
 δ 128.32
 δ 122.11
 δ 119.63
 δ 115.76
 δ 113.20
 δ 112.68
 δ 99.94
 δ 77.32
 δ 77.00
 δ 76.68
 δ 66.46
 δ 66.09
 δ 55.41
 δ 54.66
 δ 22.14
 δ 20.91

5y

^{13}C NMR (100 MHz, CDCl_3)

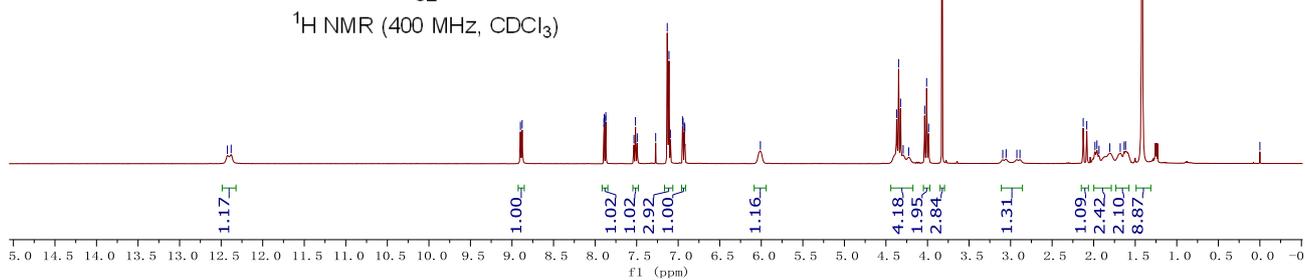


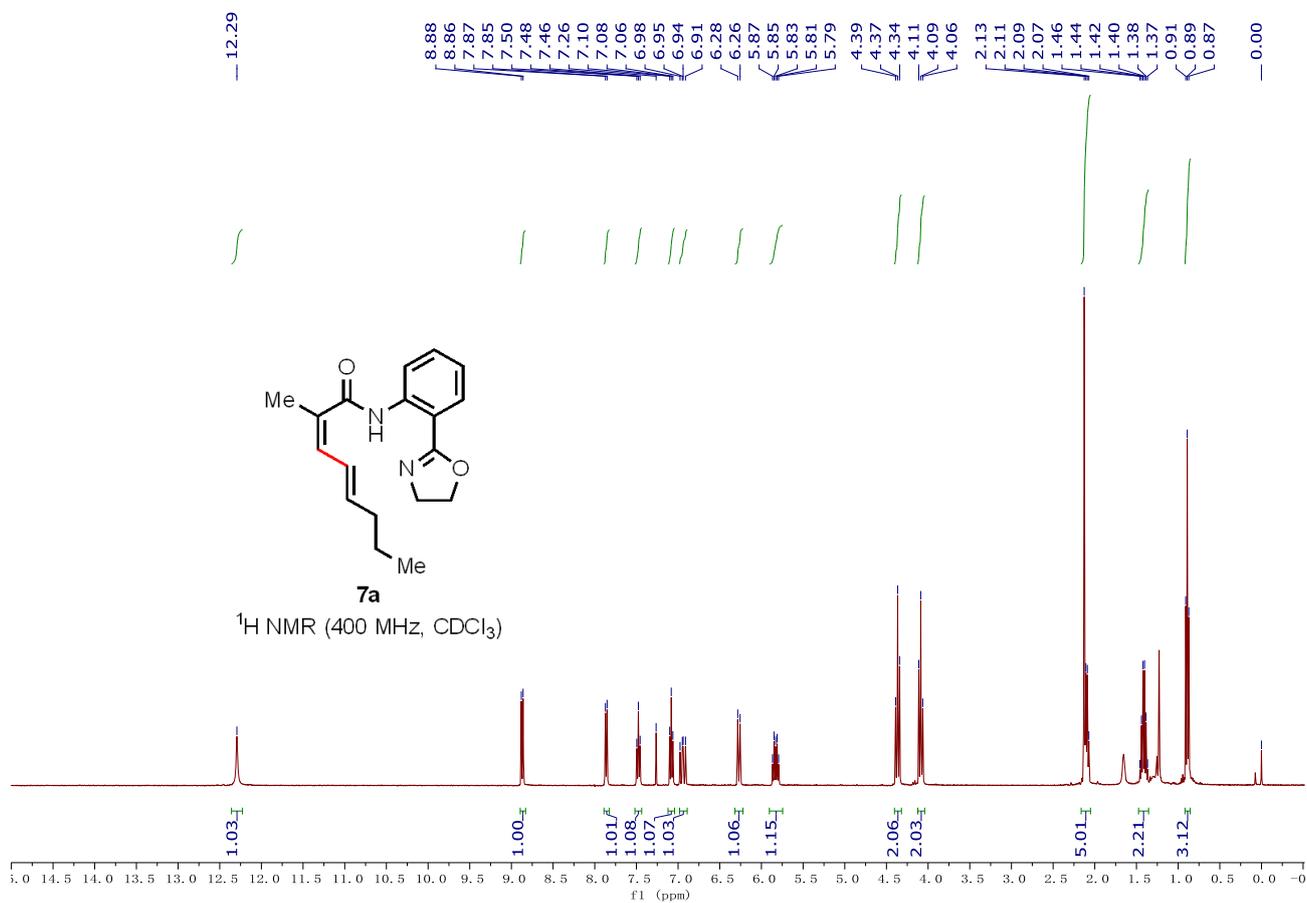
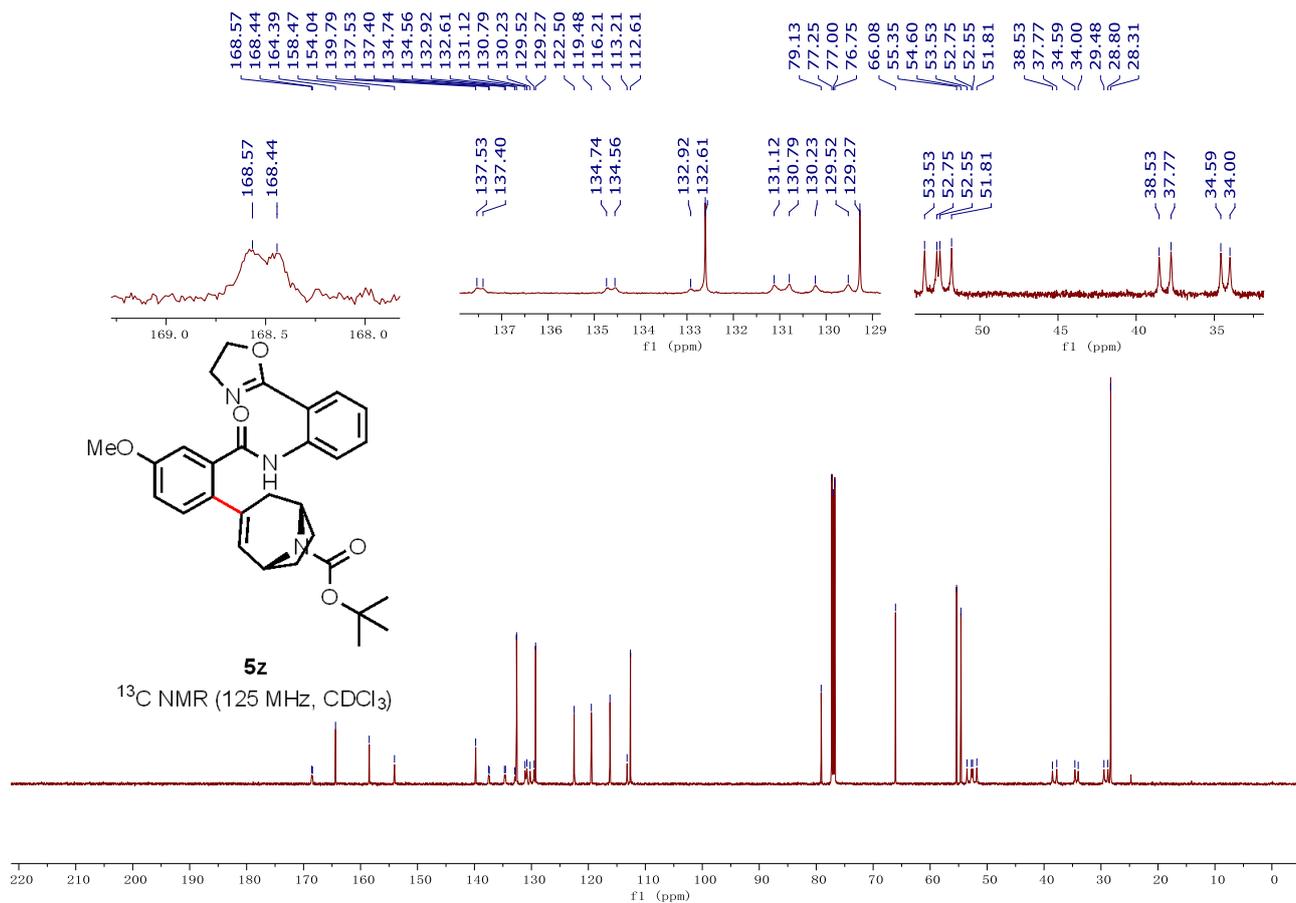
δ 12.425
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 δ 7.894
 δ 7.891
 δ 7.874
 δ 7.871
 δ 7.532
 δ 7.514
 δ 7.493
 δ 7.271
 δ 7.132
 δ 7.111
 δ 7.094
 δ 6.941
 δ 6.927
 δ 6.920
 δ 6.011
 δ 4.371
 δ 4.347
 δ 4.324
 δ 4.292
 δ 4.226
 δ 4.034
 δ 4.010
 δ 3.986
 δ 3.825
 δ 3.094
 δ 3.054
 δ 2.924
 δ 2.887
 δ 2.126
 δ 2.083
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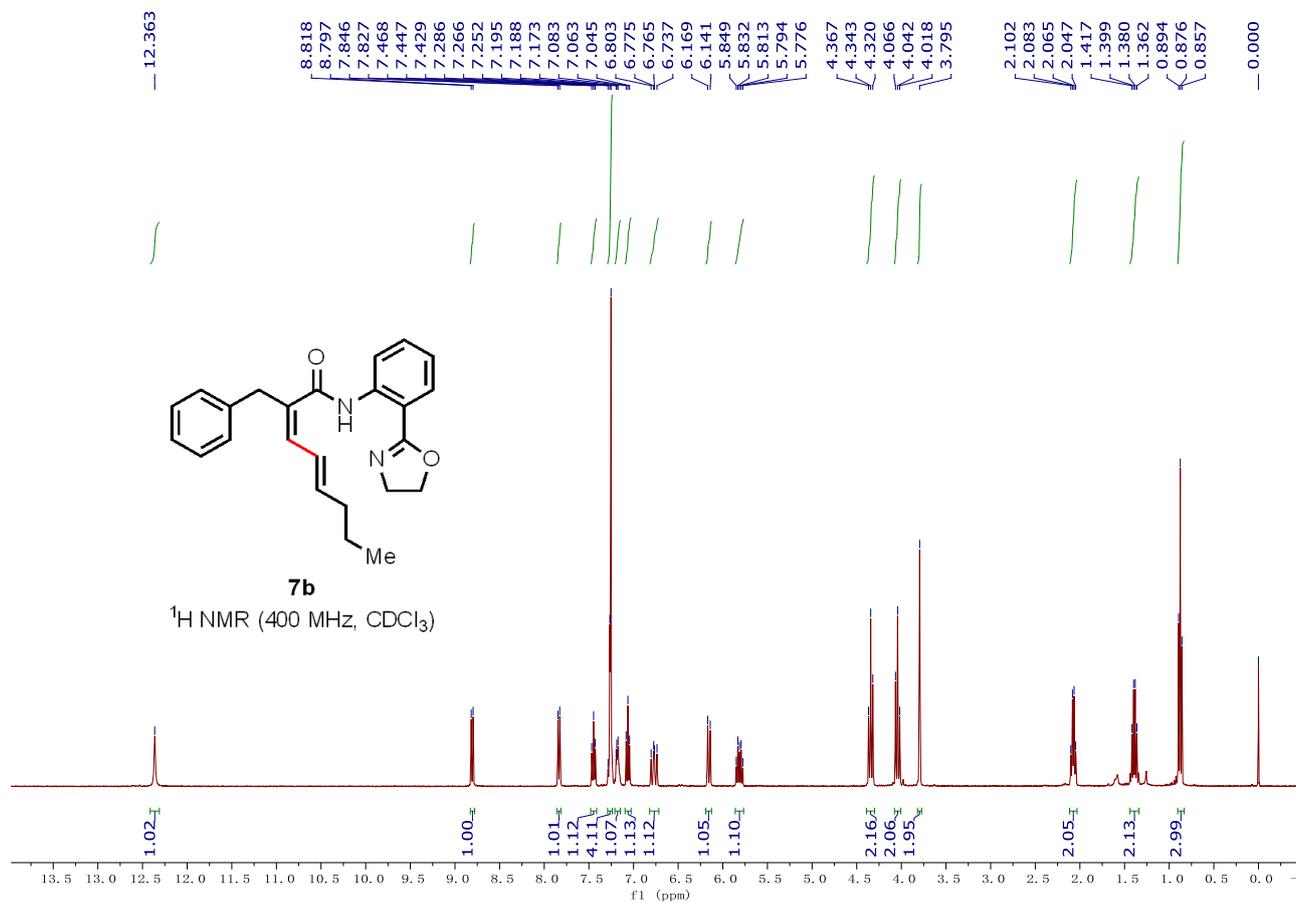
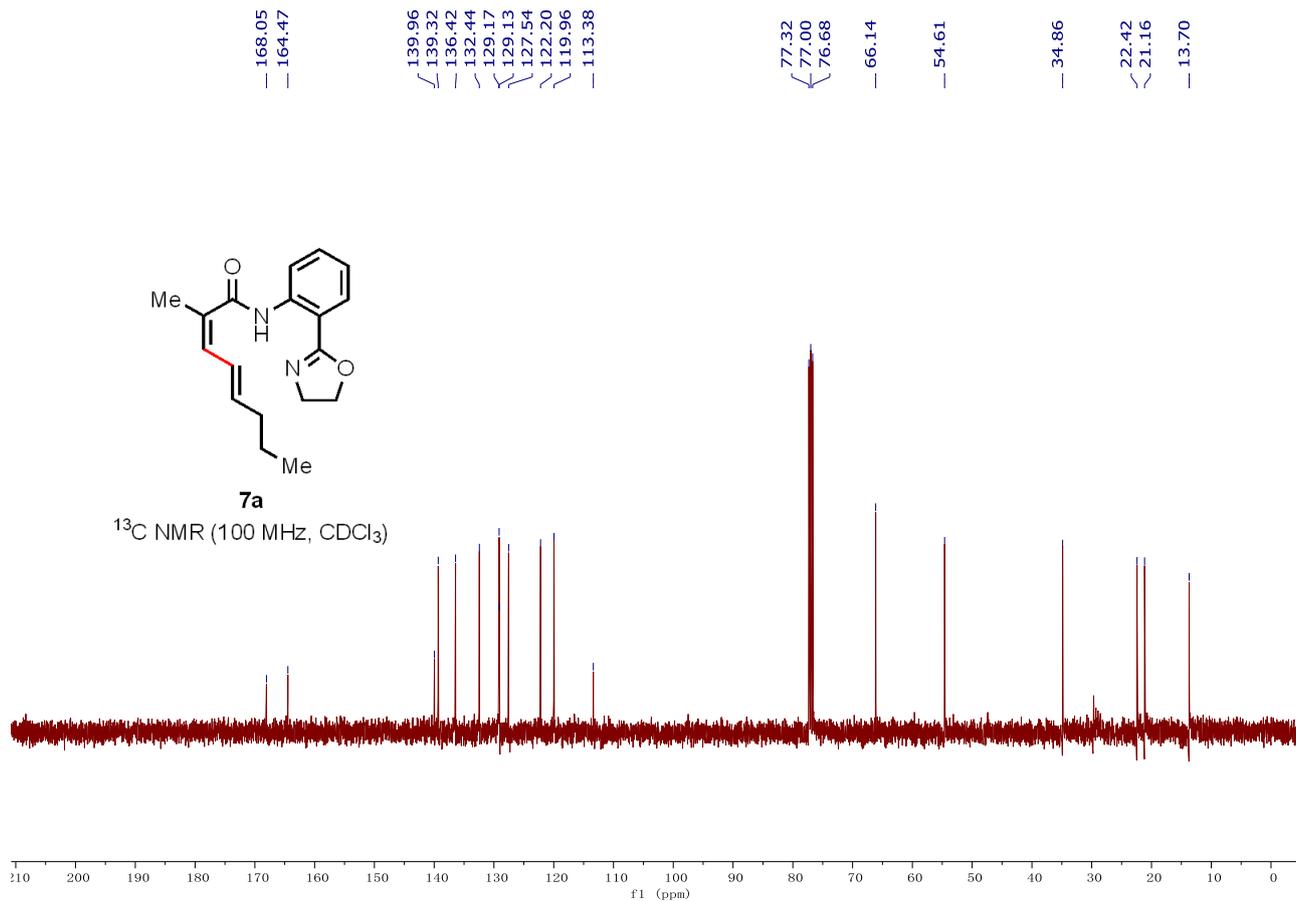


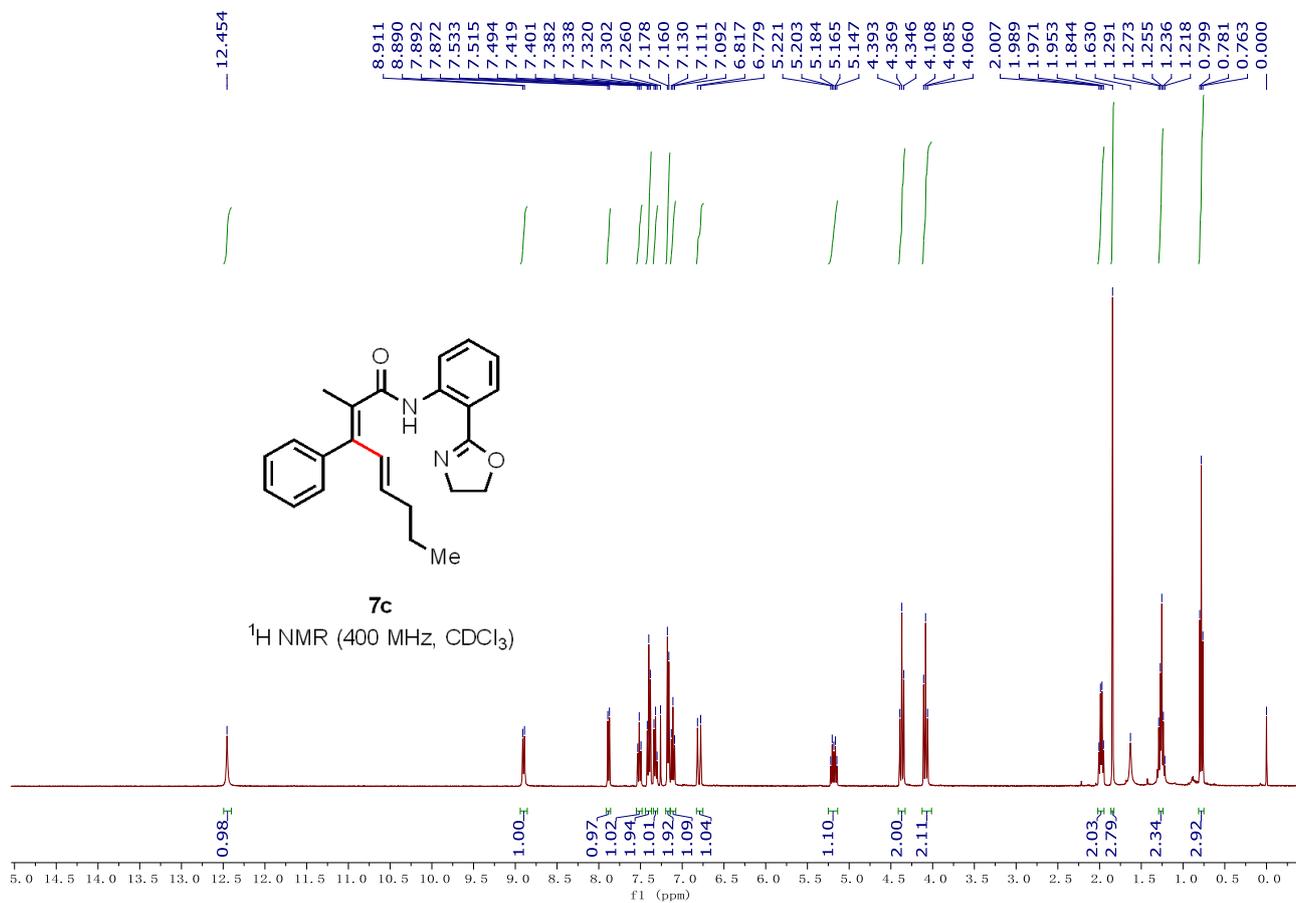
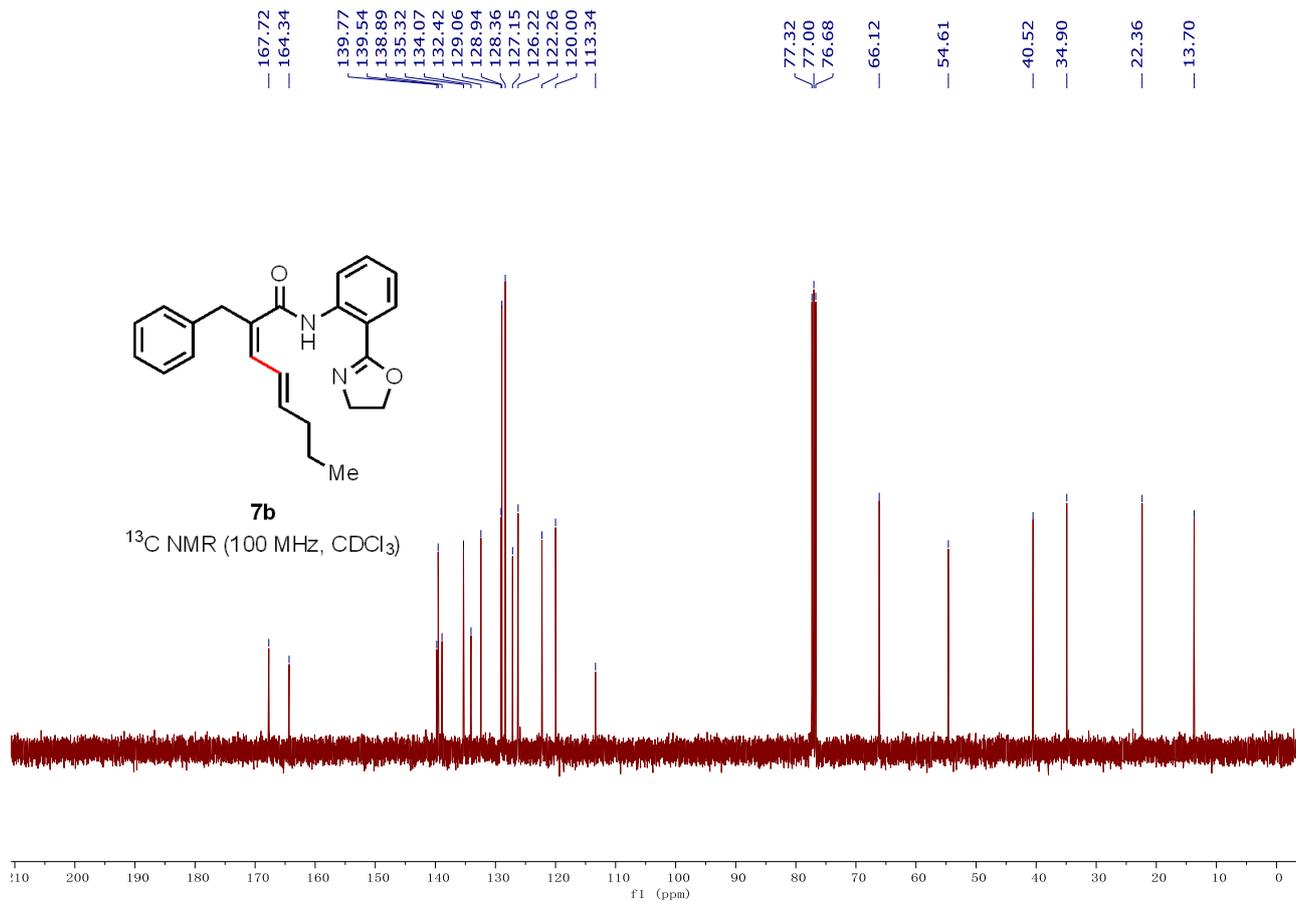
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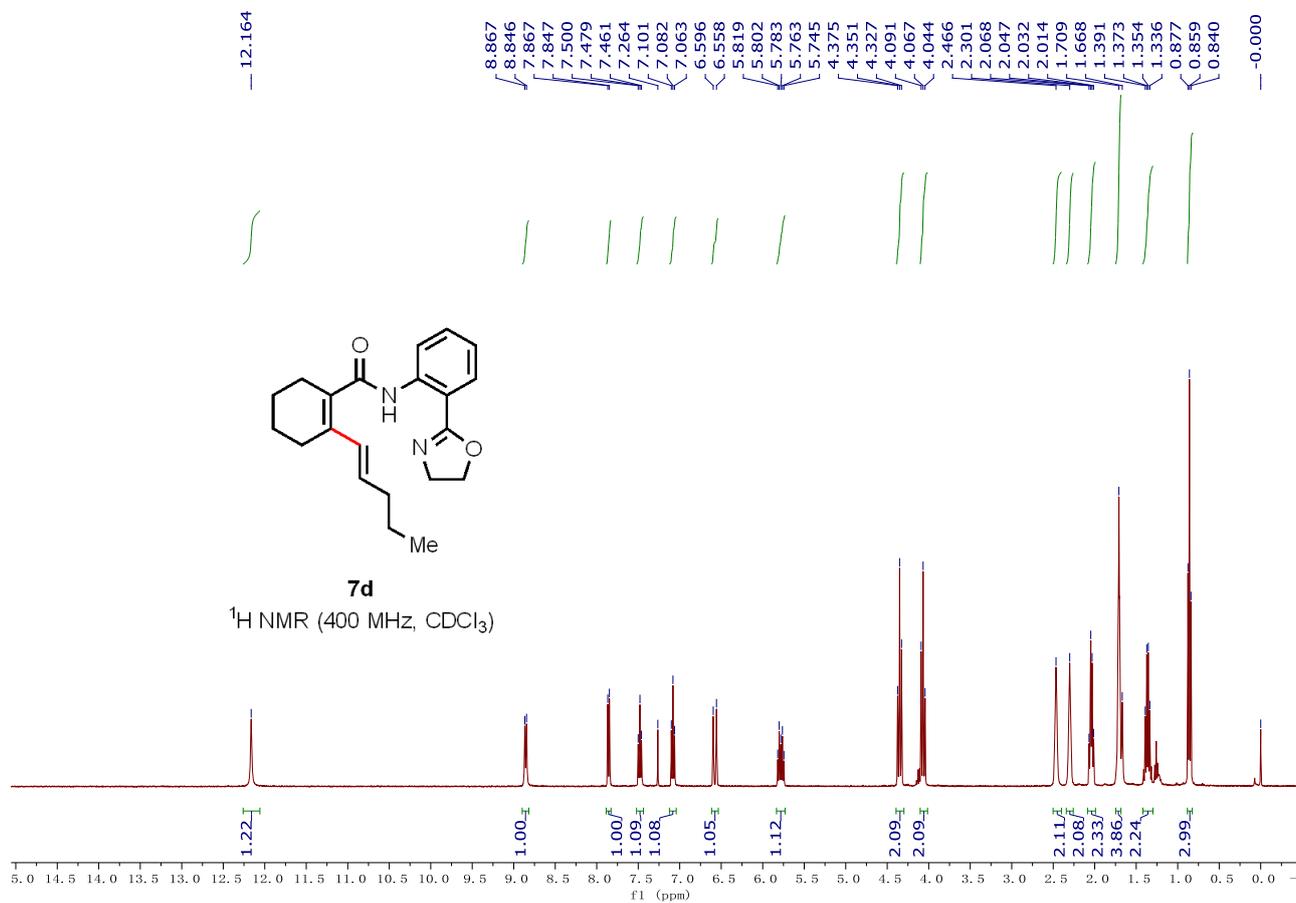
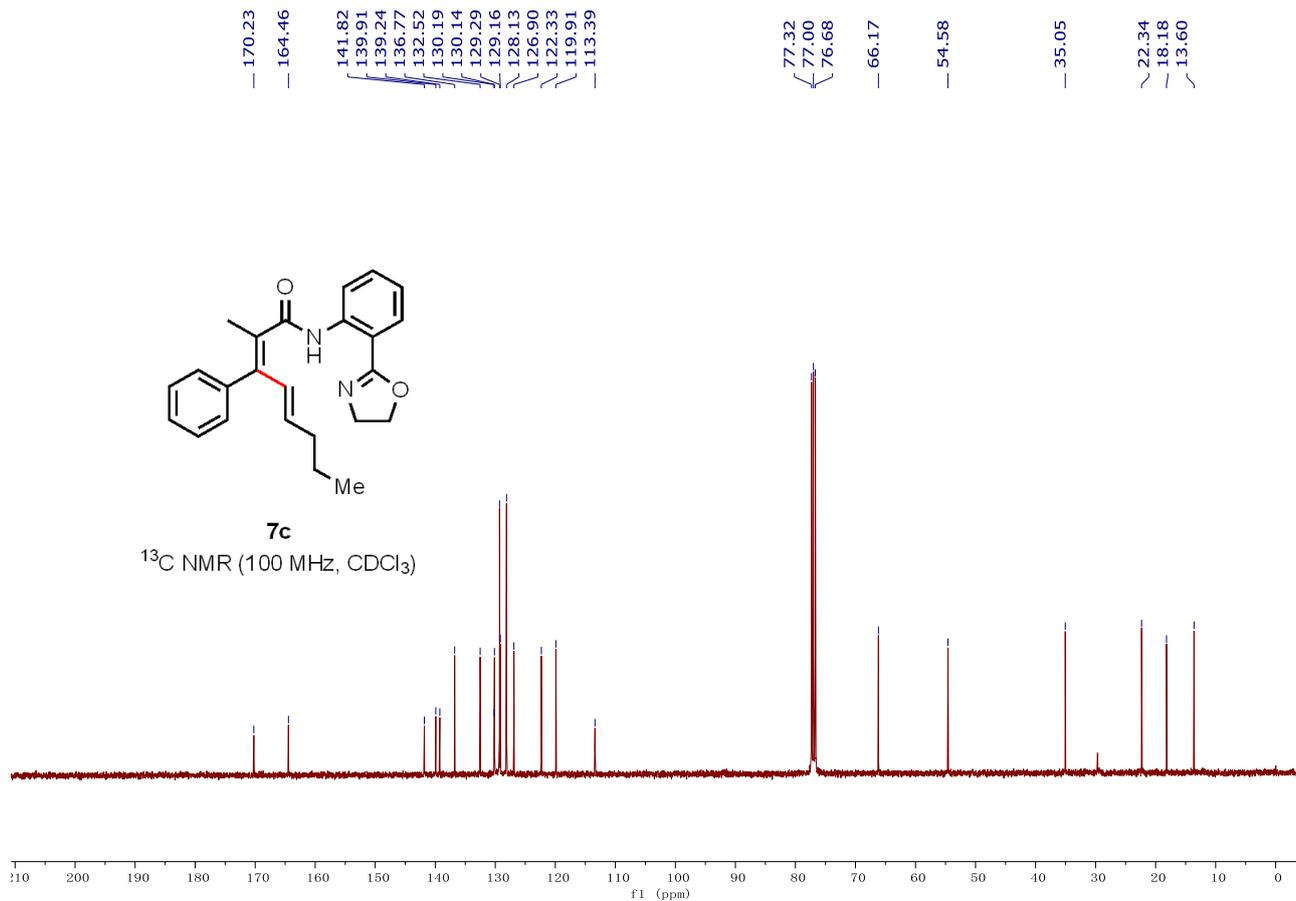
^1H NMR (400 MHz, CDCl_3)



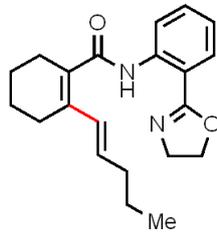






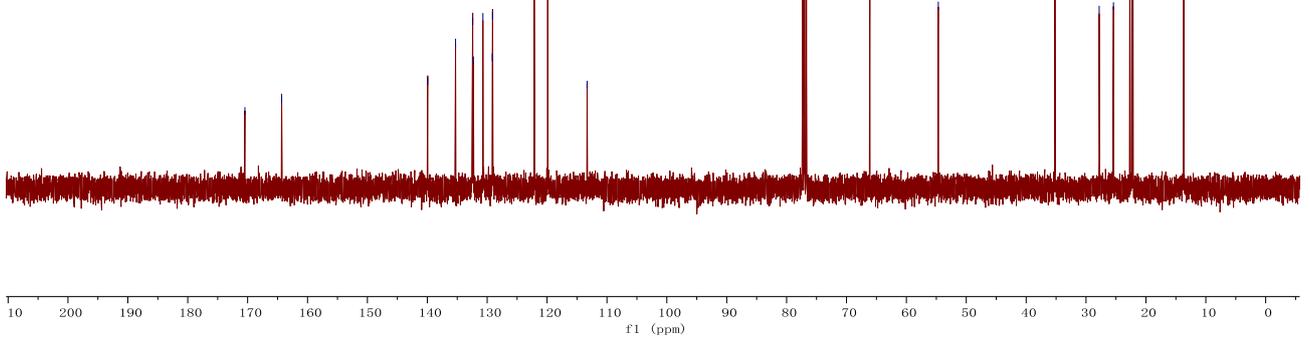


170.46
 164.32
 139.94
 135.28
 132.42
 132.30
 130.71
 129.15
 129.10
 122.15
 119.89
 113.31
 77.32
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 35.19
 27.80
 25.42
 22.69
 22.35
 22.16
 13.69

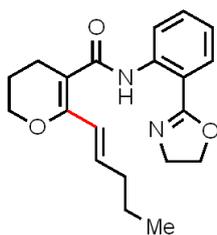


7d

¹³C NMR (100 MHz, CDCl₃)

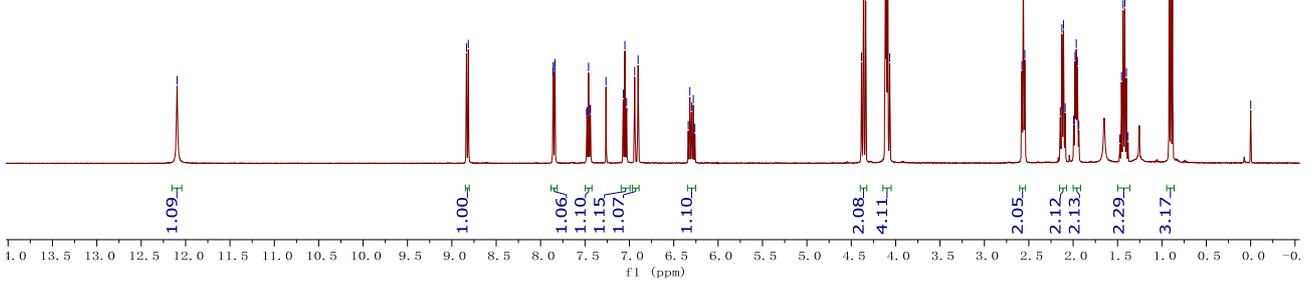


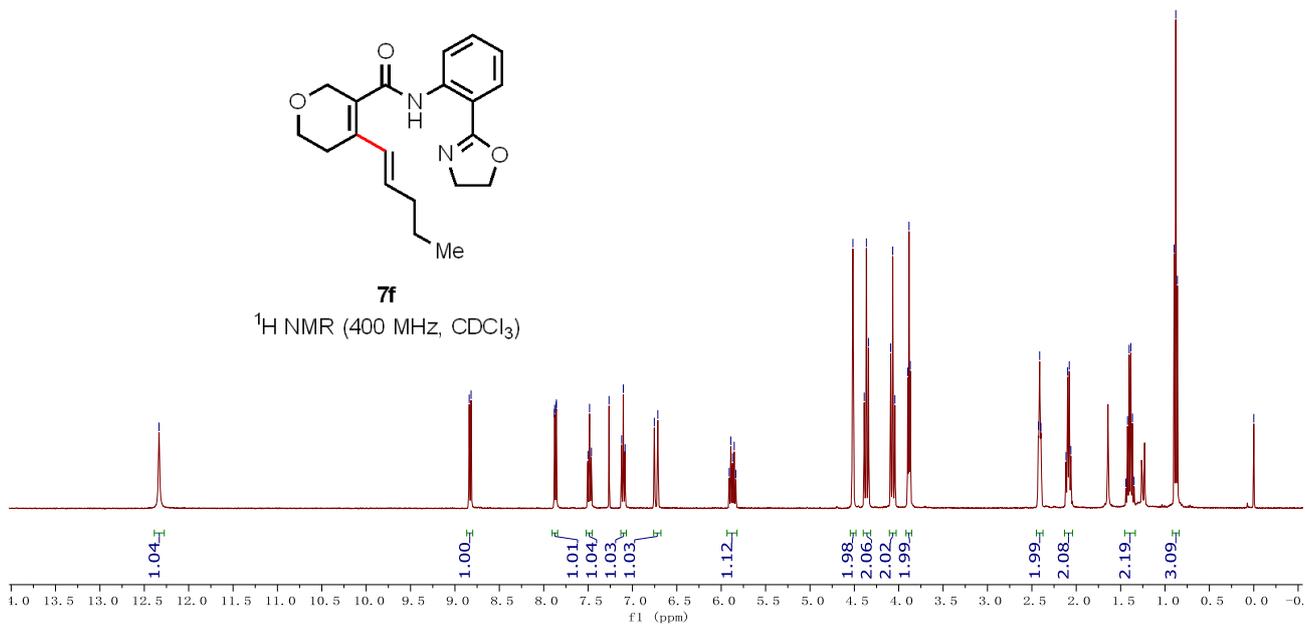
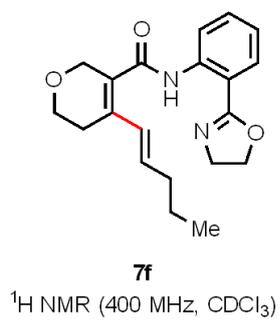
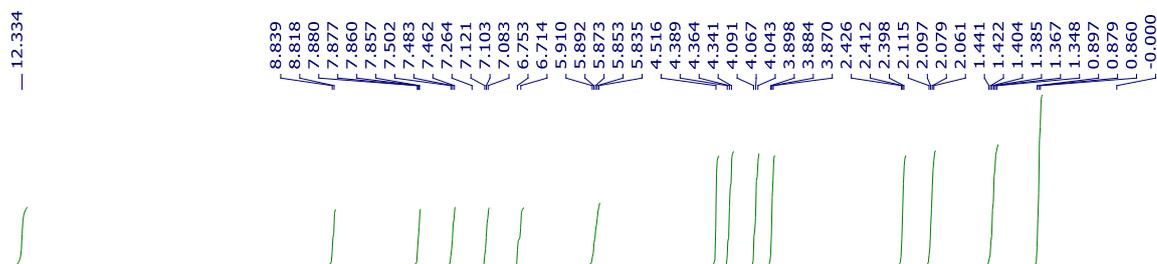
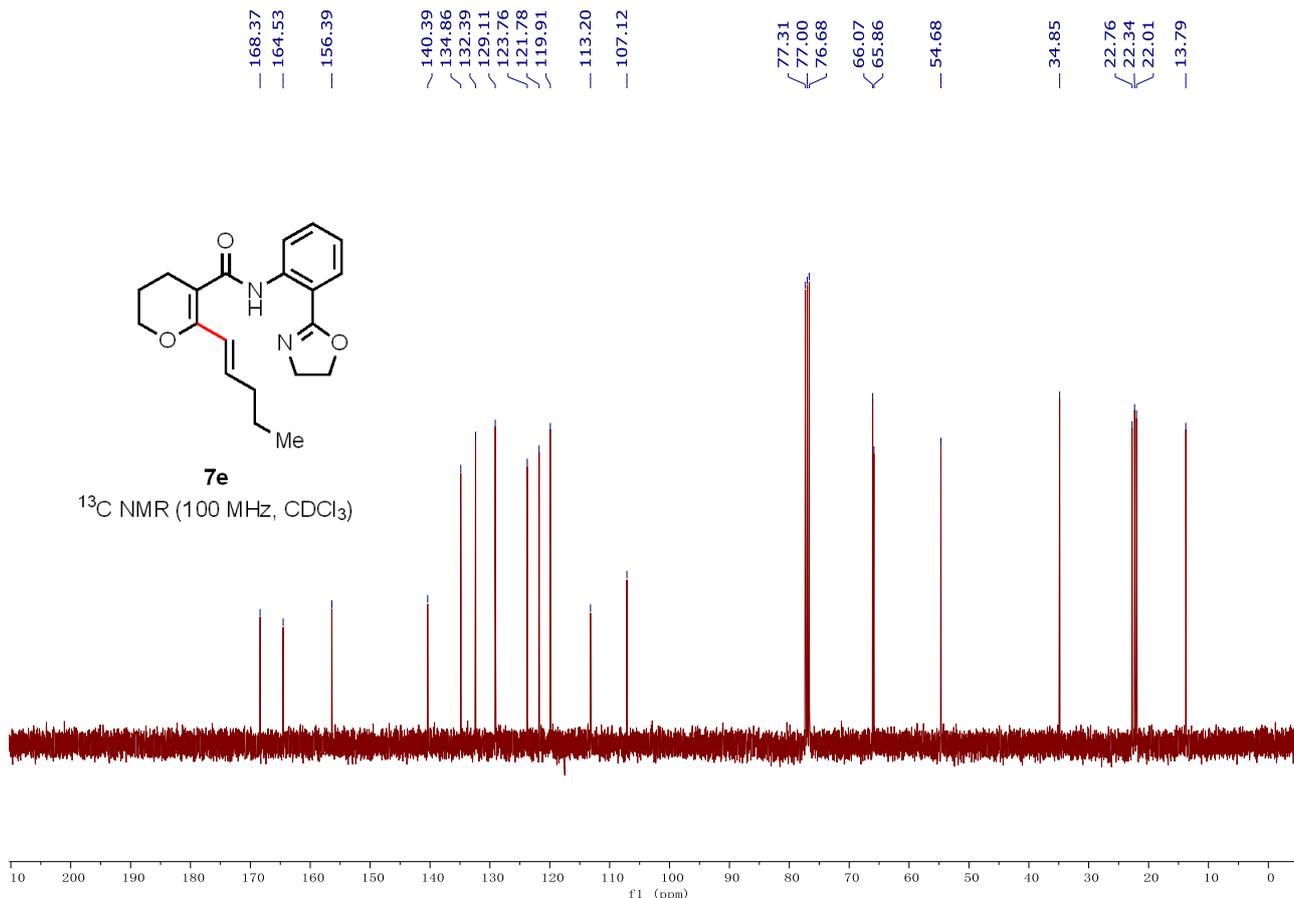
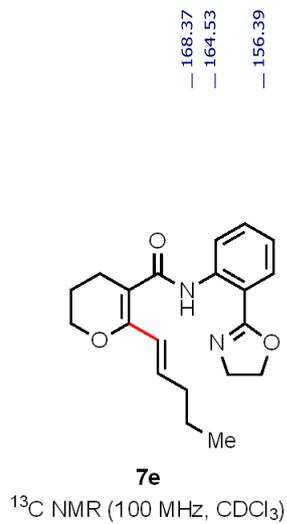
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 8.814
 7.862
 7.858
 7.842
 7.838
 7.481
 7.478
 7.460
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 7.438
 7.264
 7.069
 7.051
 7.031
 6.940
 6.902
 6.336
 6.318
 6.299
 6.280
 6.262
 4.385
 4.361
 4.337
 4.115
 4.104
 4.091
 4.066
 2.578
 2.561
 2.545
 2.145
 2.126
 2.109
 2.090
 1.994
 1.979
 1.965
 1.952
 1.936
 1.455
 1.437
 1.418
 1.400
 1.381
 0.918
 0.900
 0.881
 -0.000

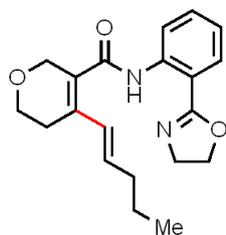


7e

¹H NMR (400 MHz, CDCl₃)

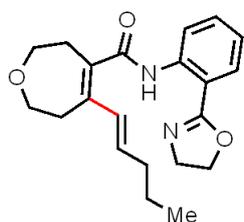
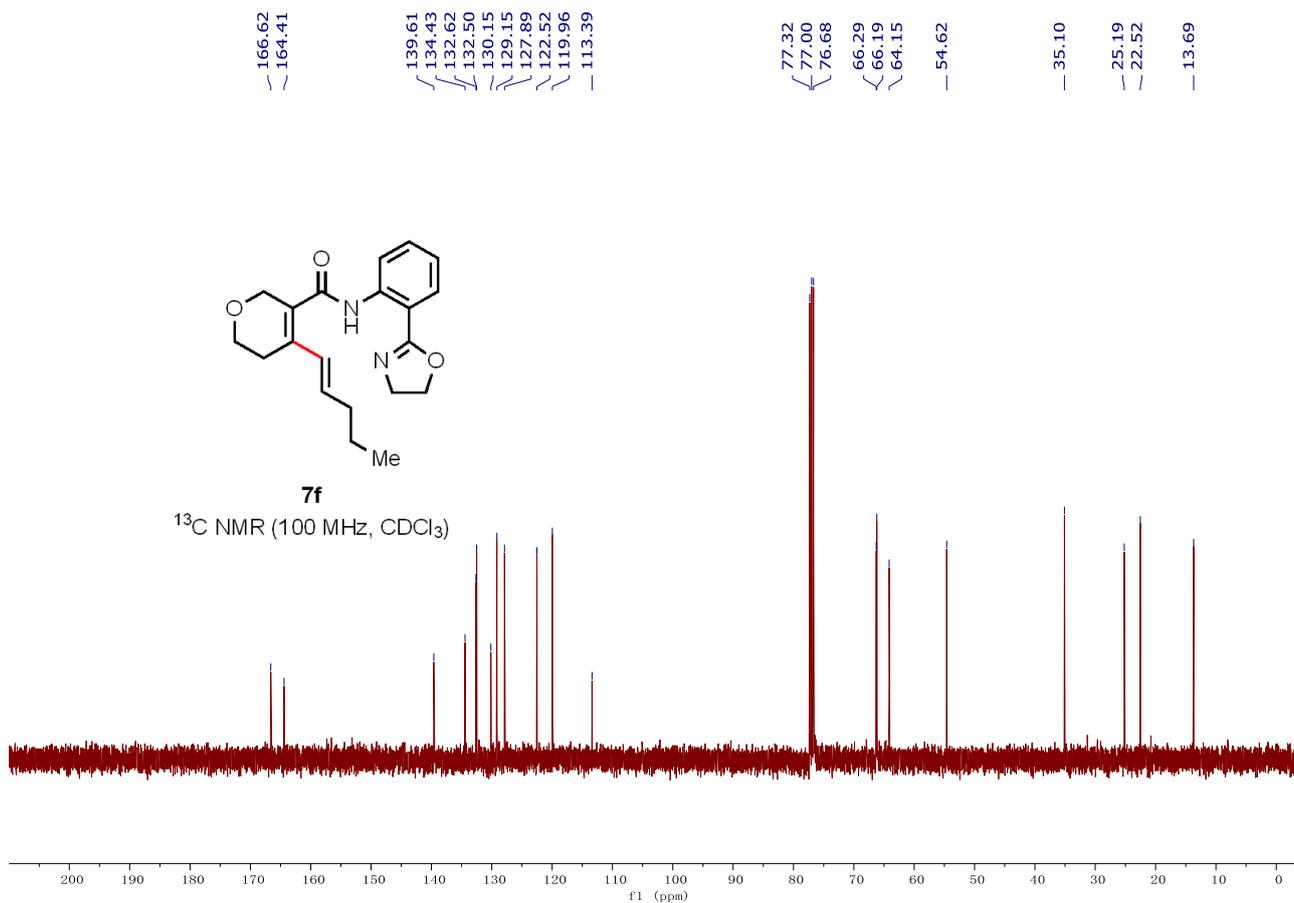






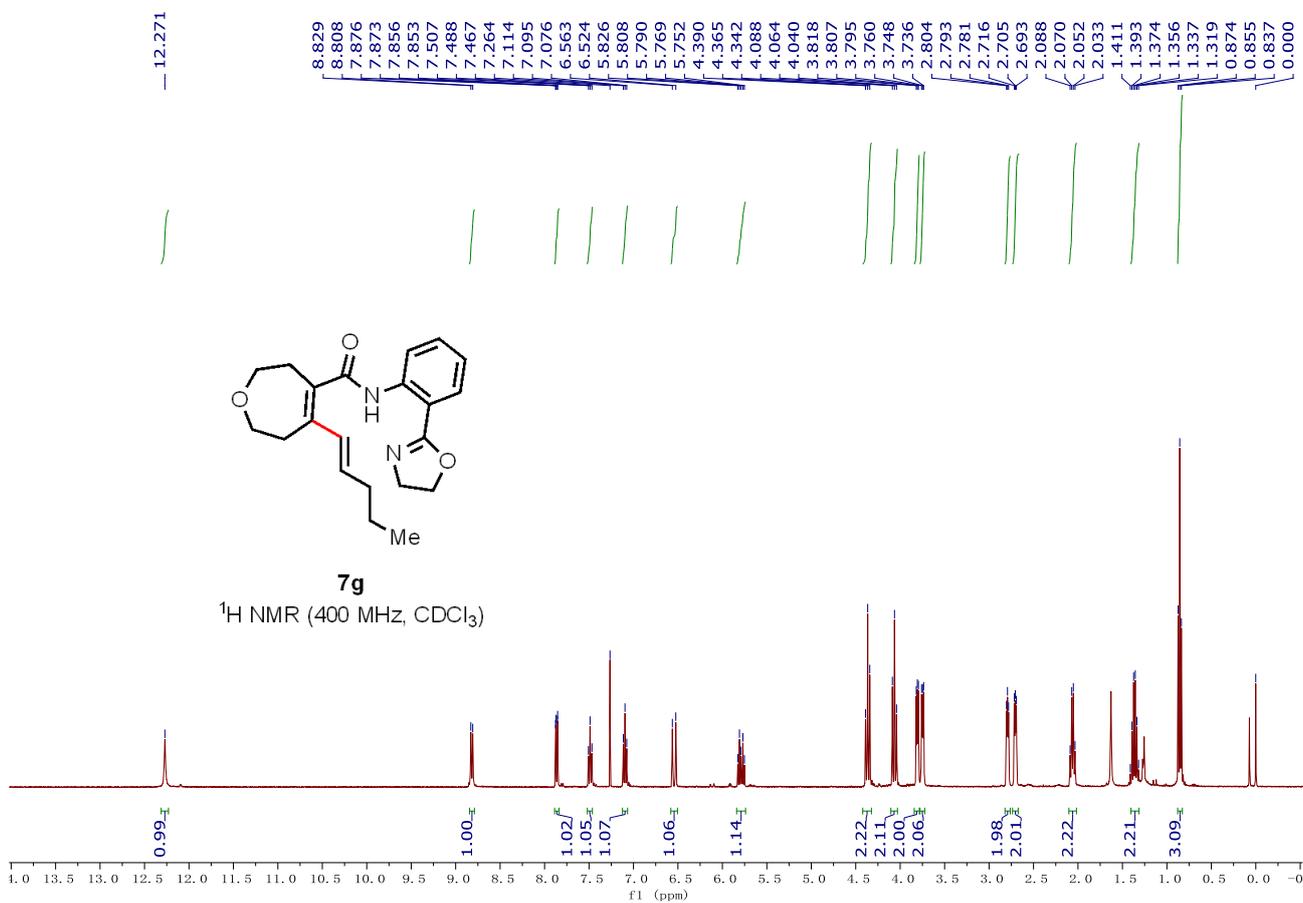
7f

^{13}C NMR (100 MHz, CDCl_3)



7g

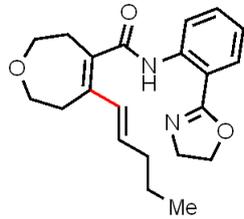
^1H NMR (400 MHz, CDCl_3)



— 170.17
 — 164.49
 / 141.67
 / 139.85
 / 136.15
 / 132.53
 / 132.45
 / 129.16
 / 129.02
 / 122.34
 / 119.74
 — 113.26

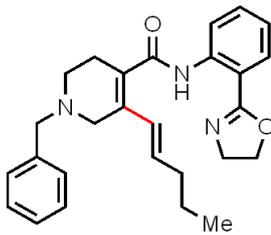
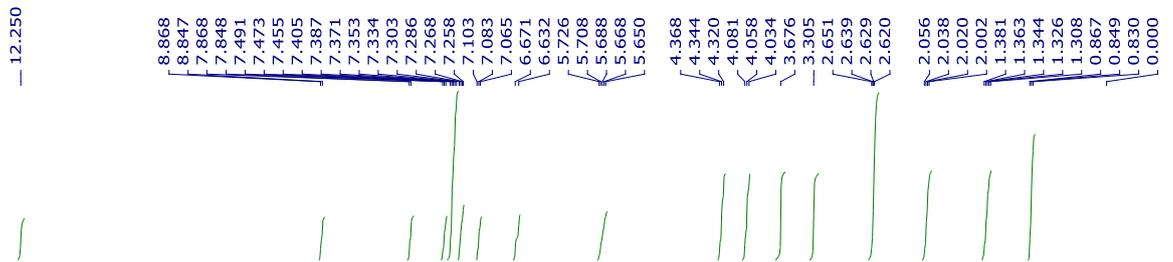
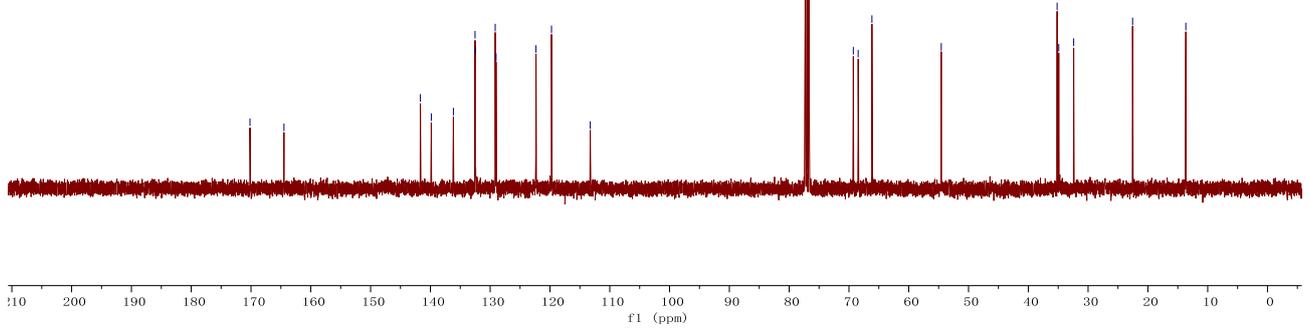
/ 77.32
 / 77.00
 / 76.68
 / 69.27
 / 68.46
 / 66.15
 — 54.56

/ 35.18
 / 34.91
 / 32.41
 — 22.56
 — 13.66



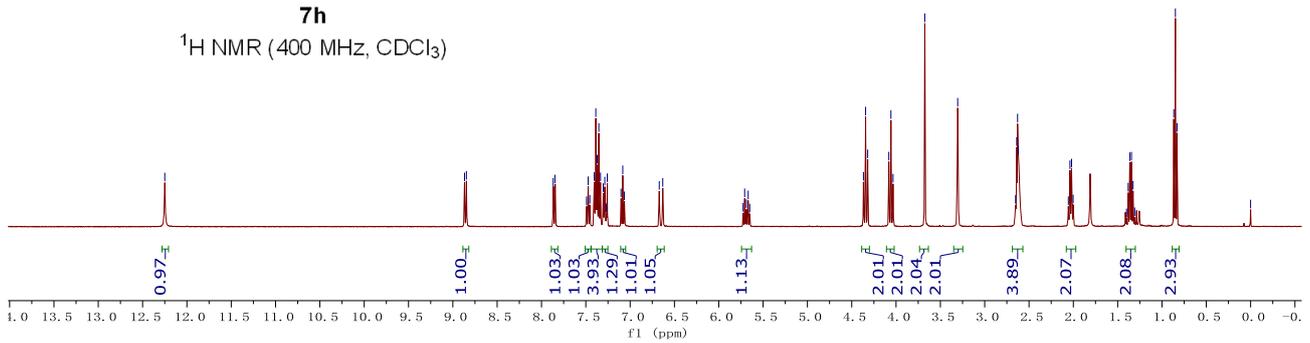
7g

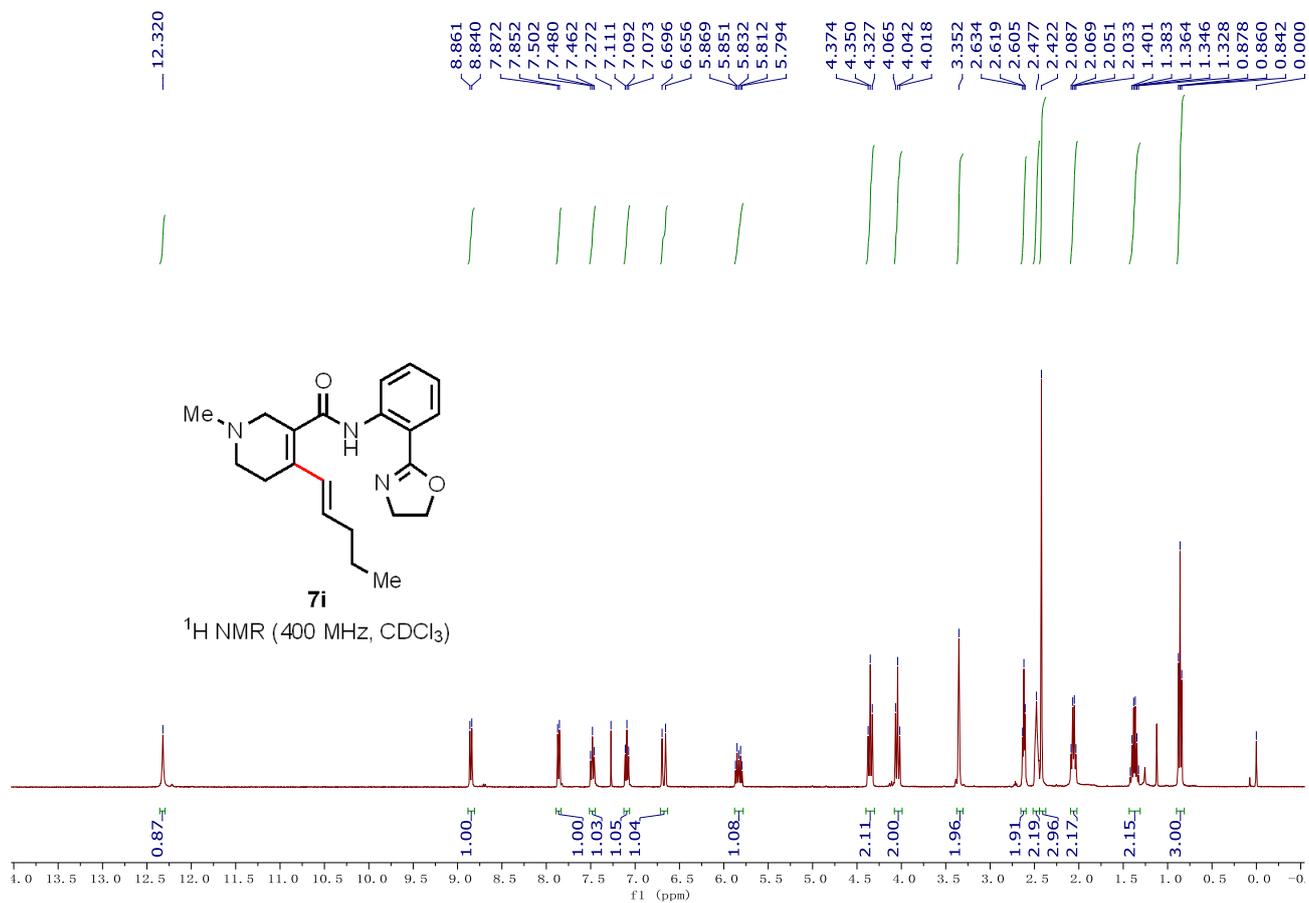
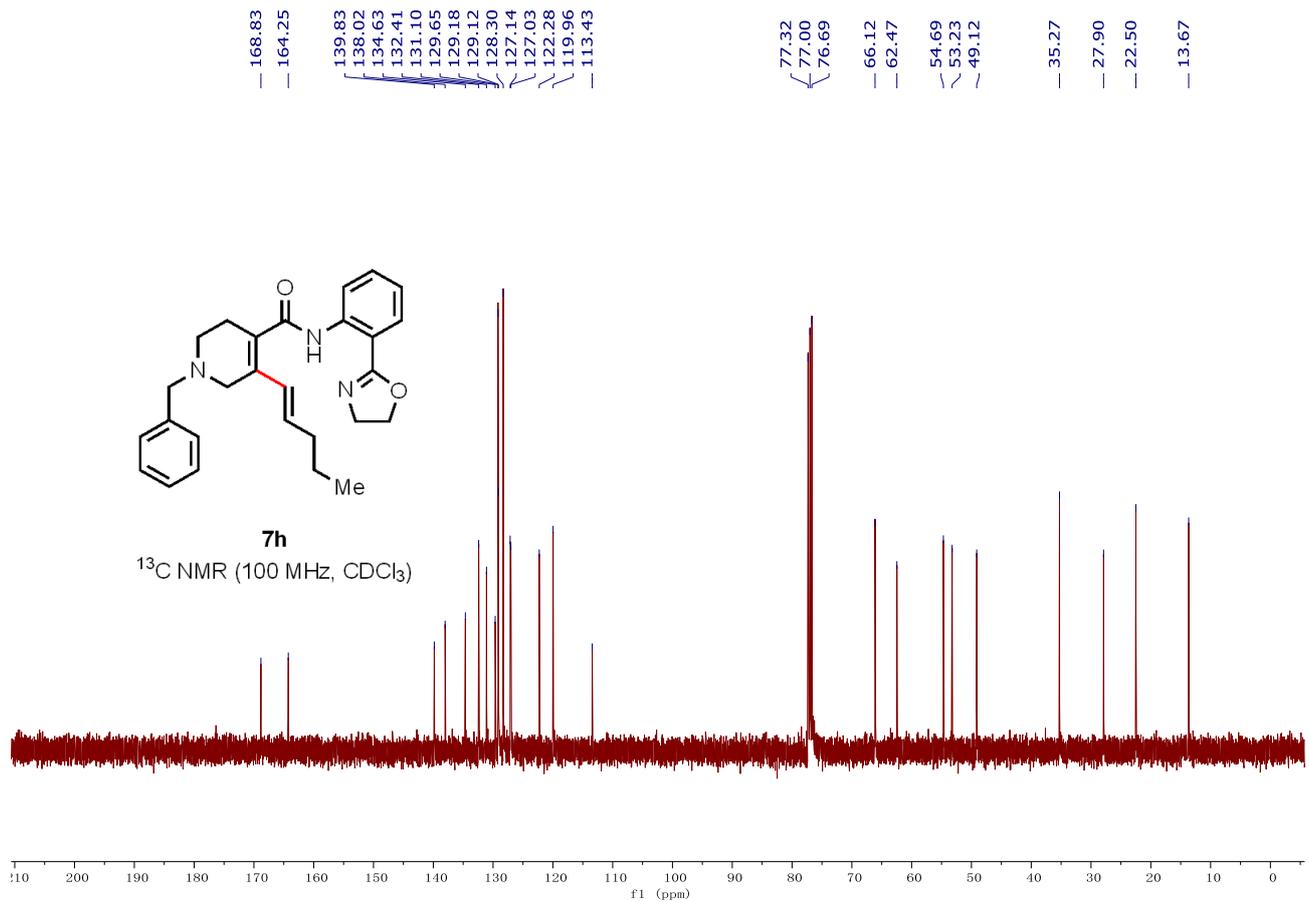
^{13}C NMR (100 Hz, CDCl_3)

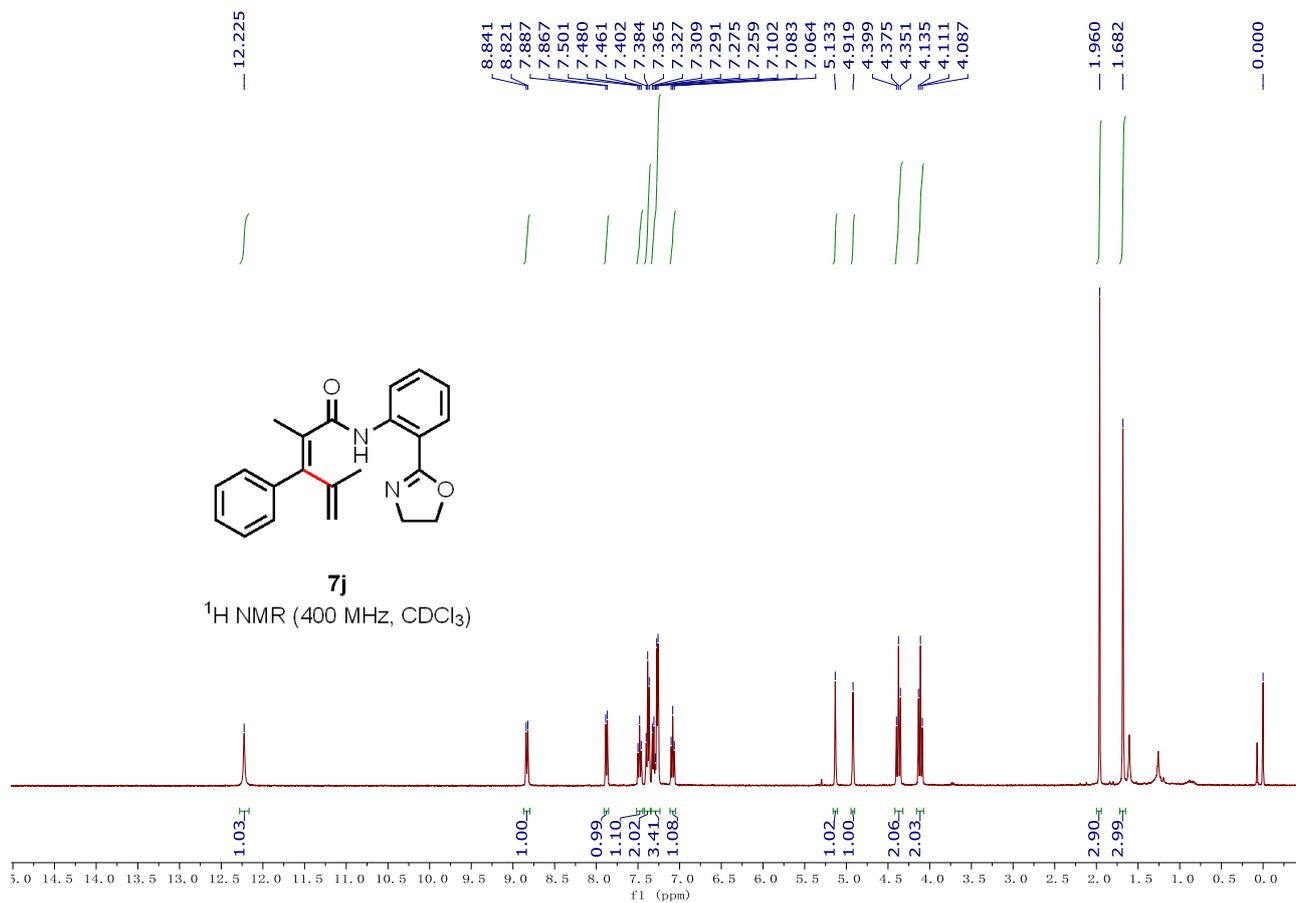
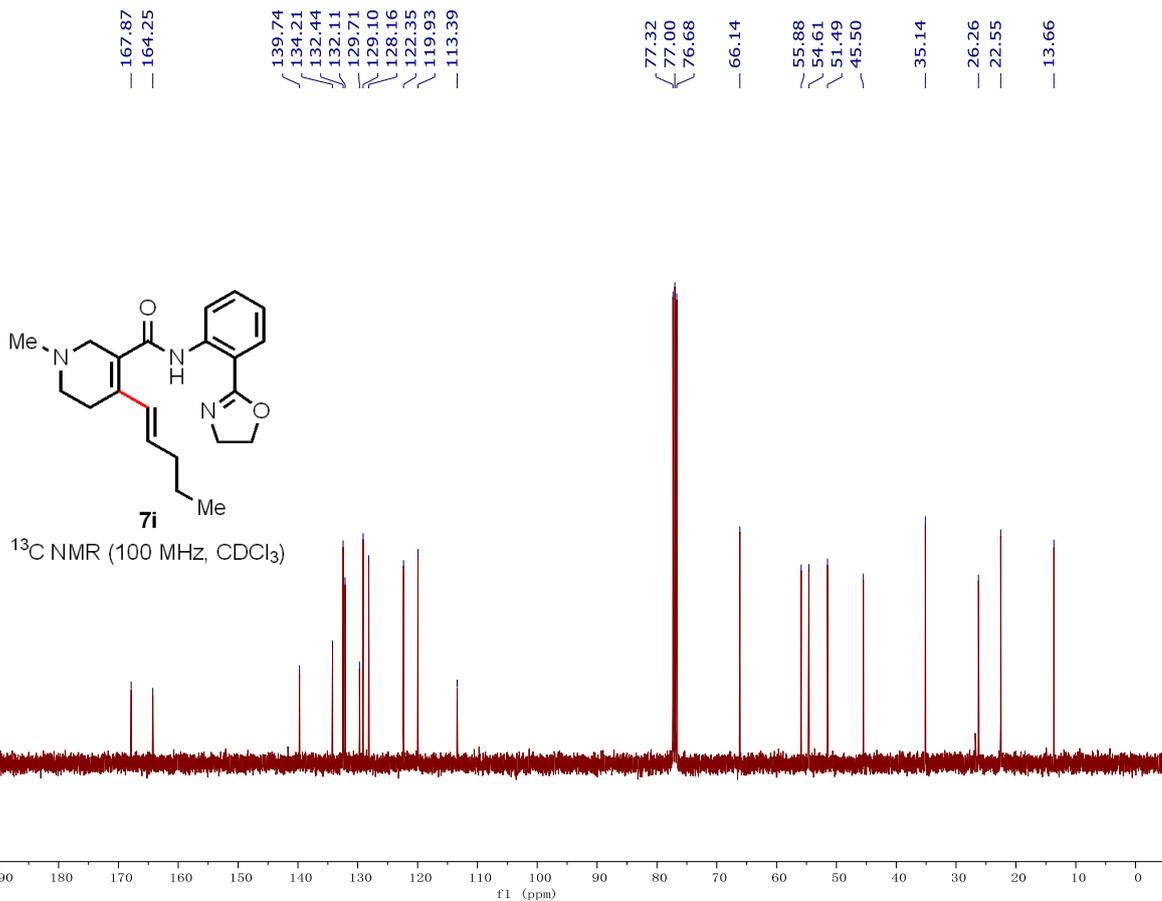


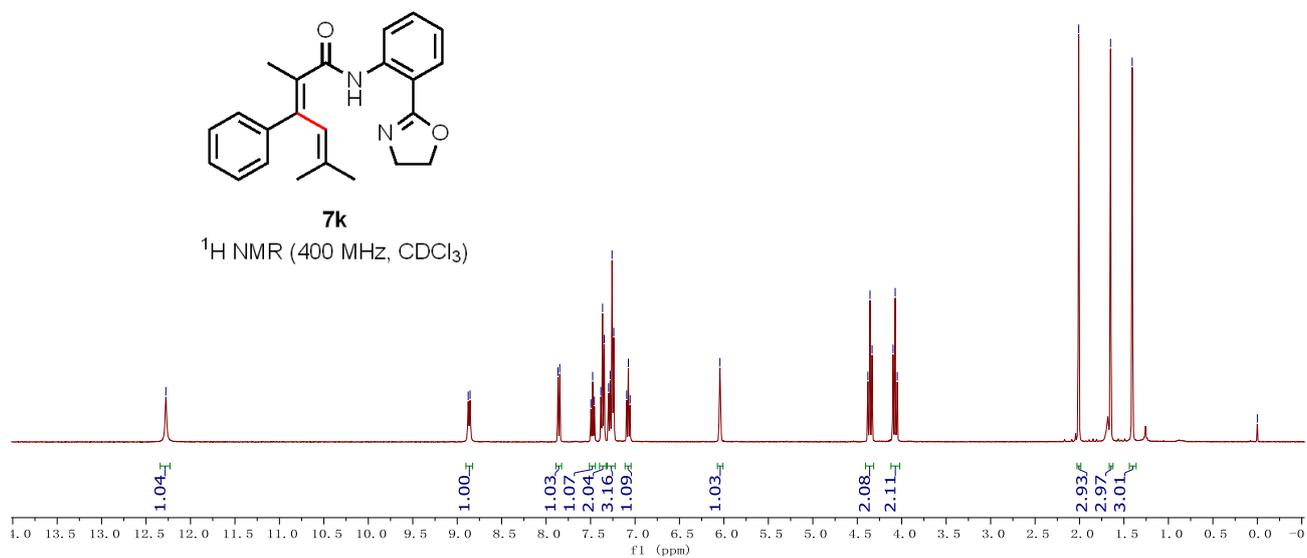
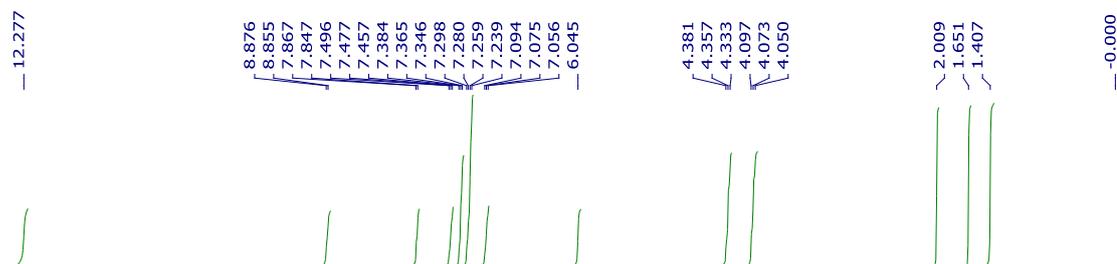
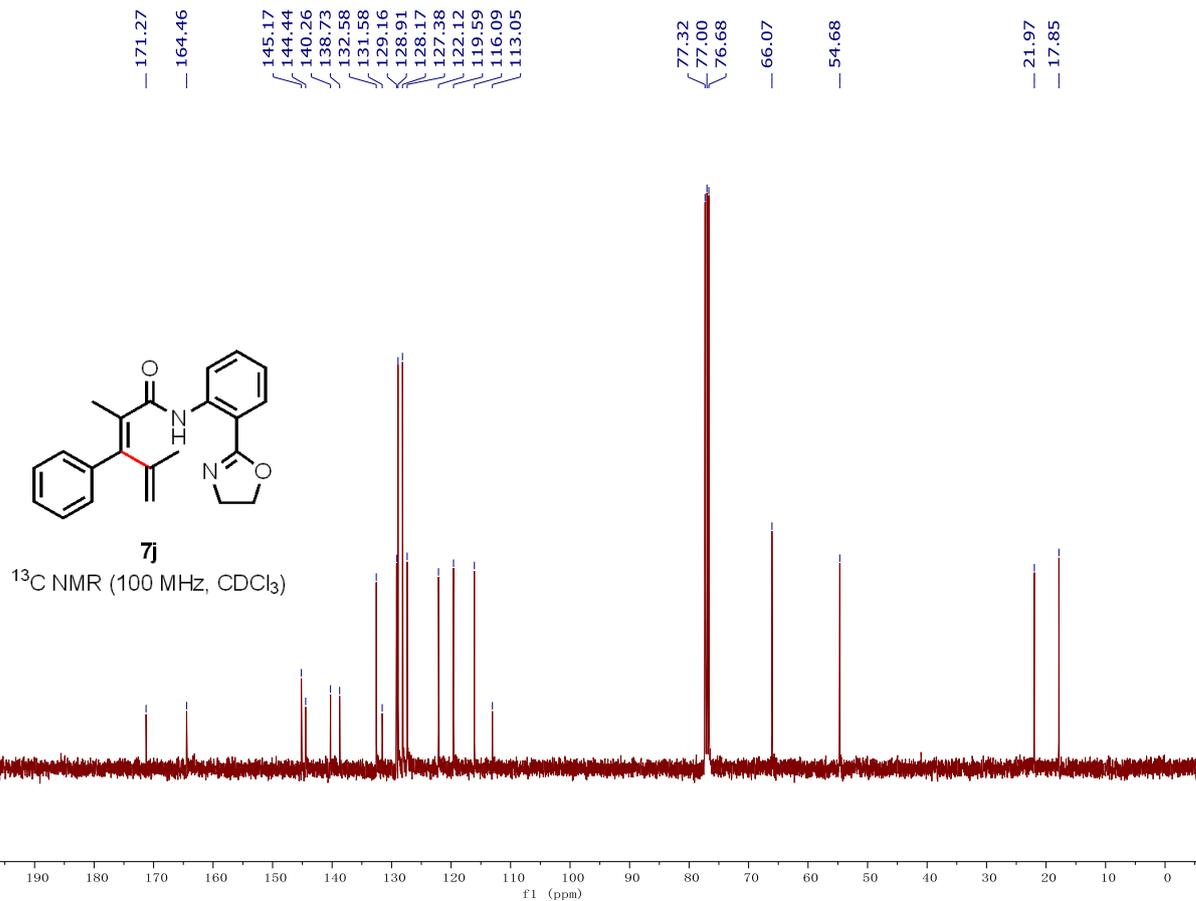
7h

^1H NMR (400 MHz, CDCl_3)



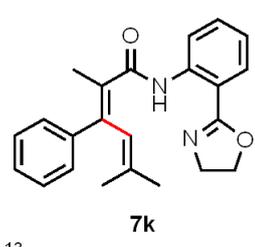




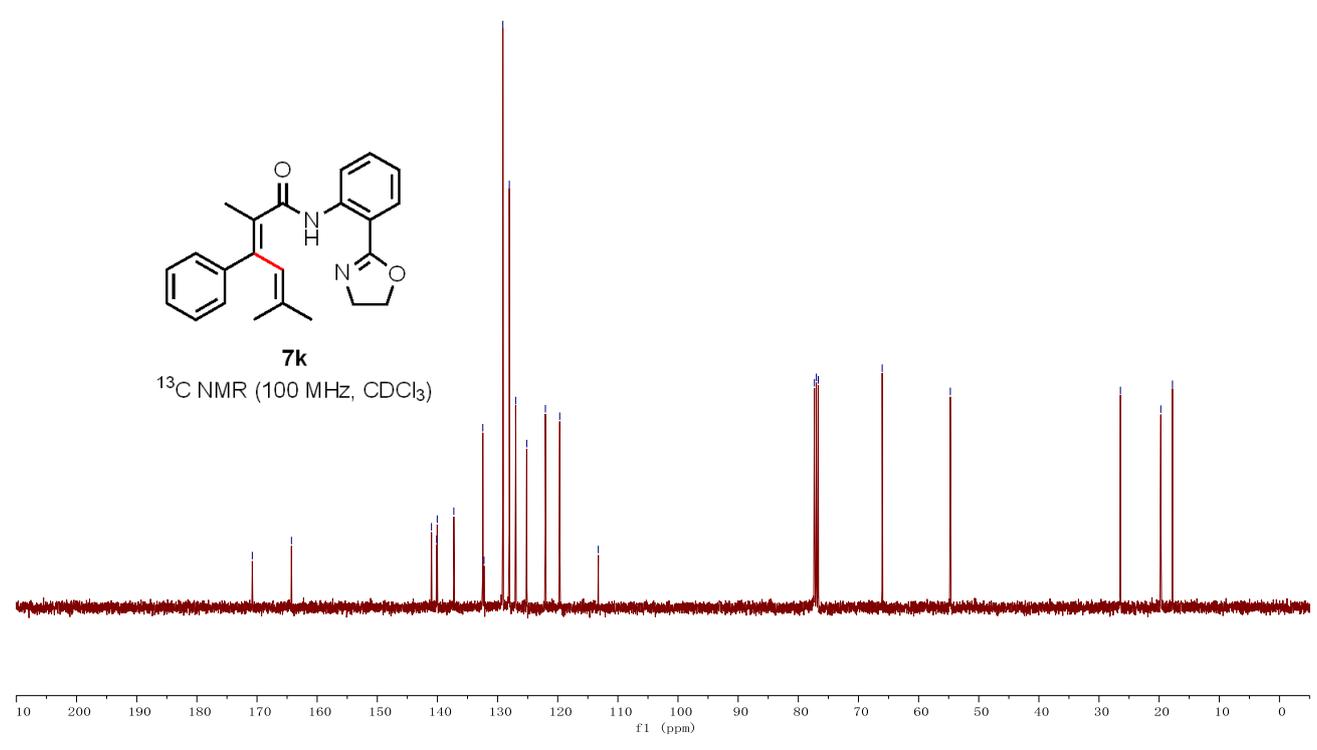


170.78
 164.28
 140.99
 140.14
 140.04
 137.28
 132.46
 132.26
 129.12
 128.05
 127.00
 125.16
 122.05
 119.67
 113.25

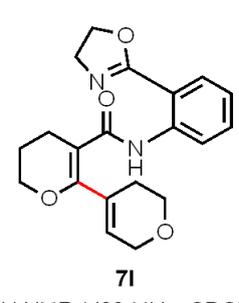
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 76.68
 66.05
 54.72
 26.44
 19.73
 17.79



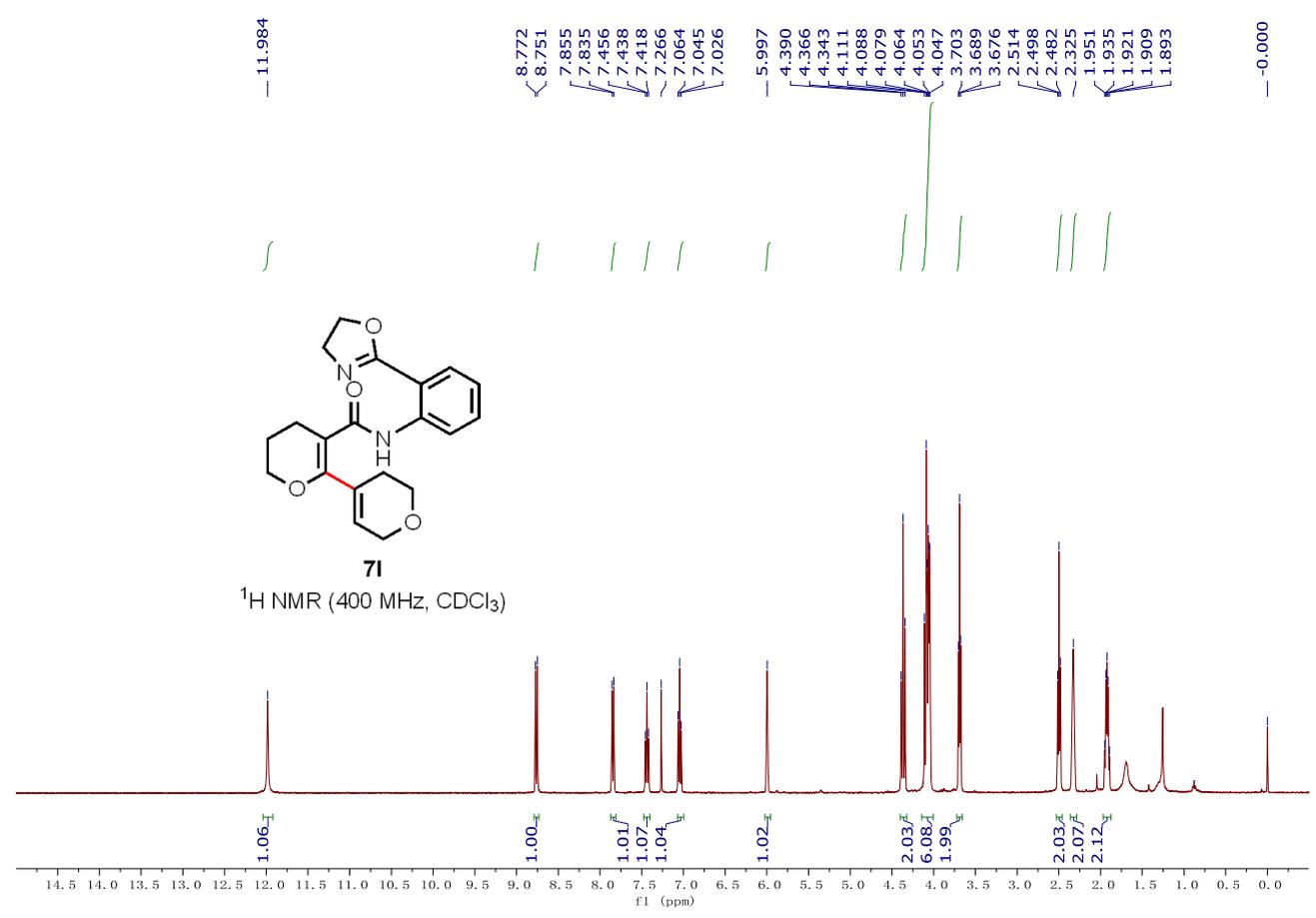
¹³C NMR (100 MHz, CDCl₃)



11.984
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 8.751
 7.855
 7.835
 7.456
 7.438
 7.418
 7.266
 7.064
 7.045
 7.026
 5.997
 4.390
 4.366
 4.343
 4.111
 4.088
 4.079
 4.064
 4.053
 4.047
 3.703
 3.689
 3.676
 2.514
 2.498
 2.482
 2.325
 1.951
 1.935
 1.921
 1.909
 1.893
 -0.000



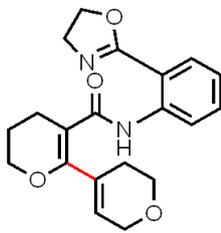
¹H NMR (400 MHz, CDCl₃)



169.35
164.49
156.95
140.20
132.49
131.42
129.25
128.29
121.92
119.41
112.95
108.98

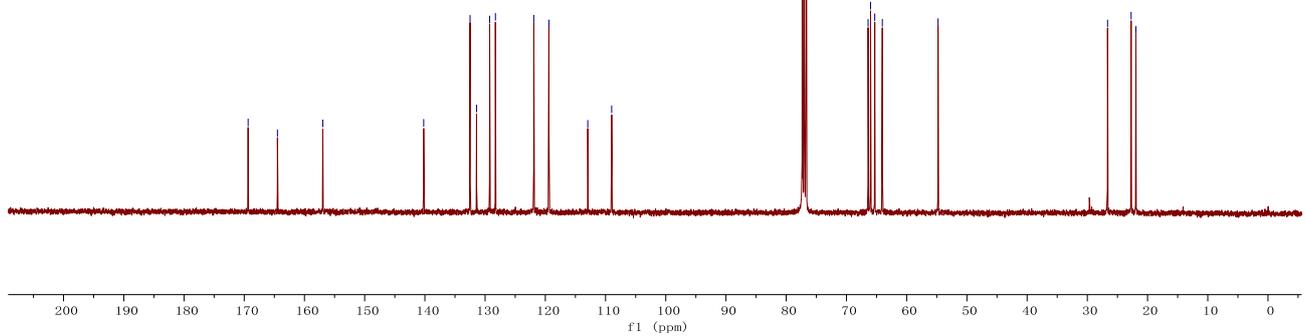
77.32
77.00
76.68
66.40
66.00
65.30
64.04
54.78

26.64
22.72
21.93



7i

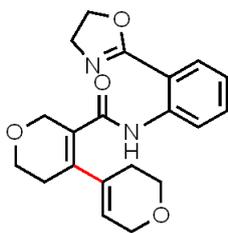
¹³C NMR (100 MHz, CDCl₃)



12.104

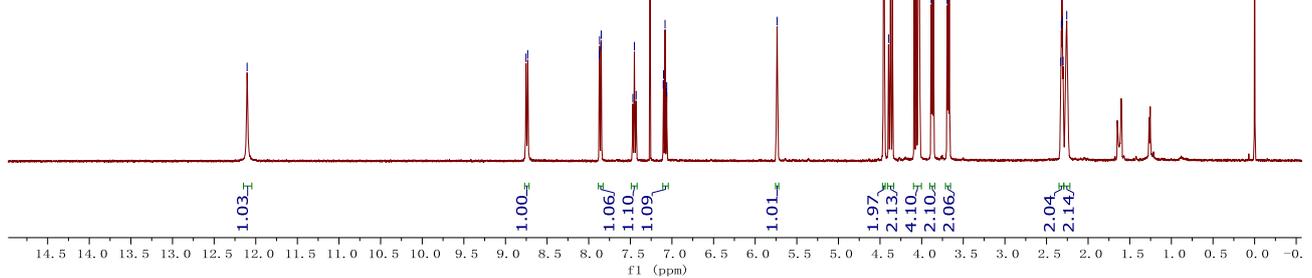
8.754
8.733
7.873
7.869
7.853
7.849
7.470
7.452
7.430
7.263
7.104
7.101
7.083
7.066
7.063
5.737
4.454
4.398
4.374
4.351
4.089
4.065
4.036
4.029
3.886
3.872
3.858
3.695
3.681
3.668
2.329
2.322
2.315
2.309
2.302
2.257

-0.000



7m

¹H NMR (400 MHz, CDCl₃)

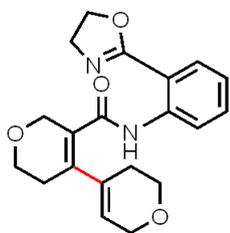


167.51
164.46

139.61
137.44
134.62
132.56
130.78
129.30
124.35
122.48
119.61
113.16

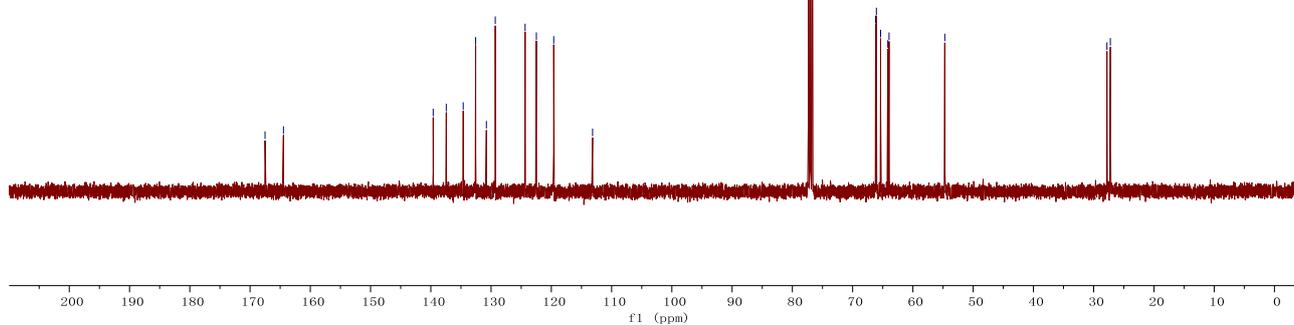
77.32
77.00
76.68
66.19
66.06
65.35
64.16
63.96
54.71

27.80
27.23



7m

¹³C NMR (100 MHz, CDCl₃)



12.111

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7.851
7.831
7.462
7.444
7.423
7.272
7.091
7.072
7.053

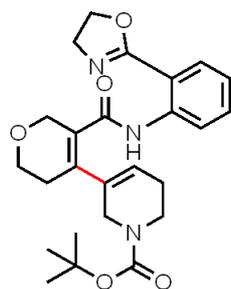
5.858

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4.383
4.359
4.336
4.114
3.993
3.881
3.868
3.854
3.261

2.319
1.998

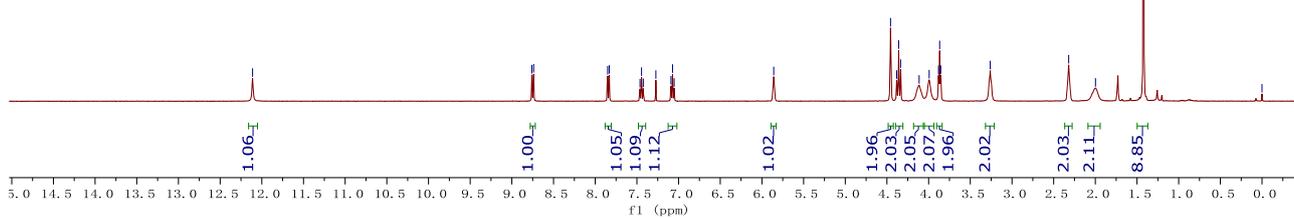
1.422

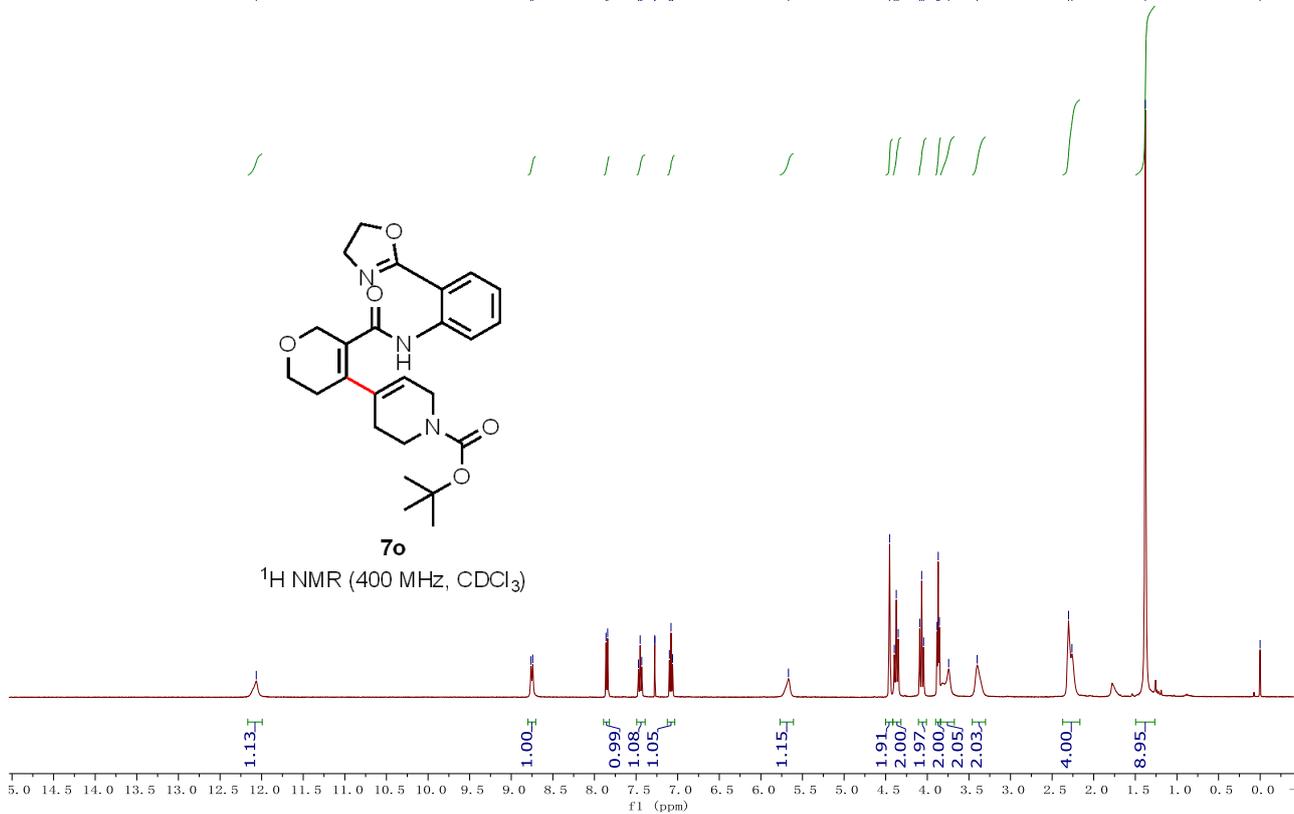
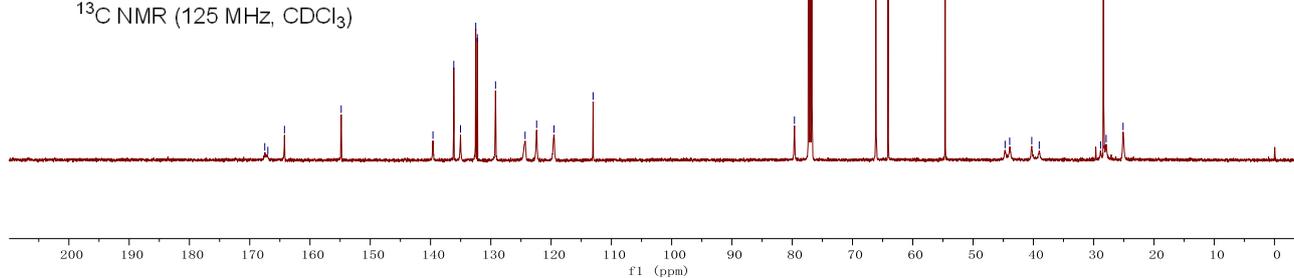
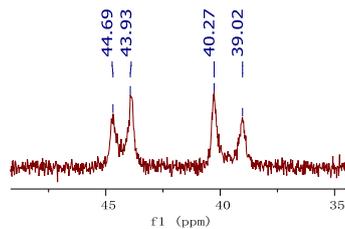
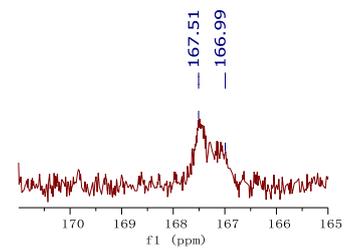
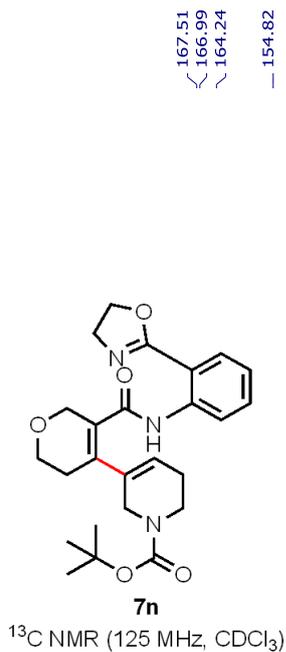
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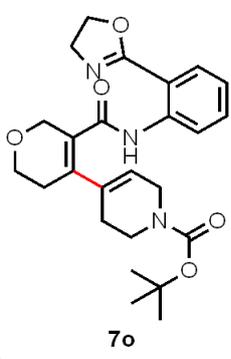


7n

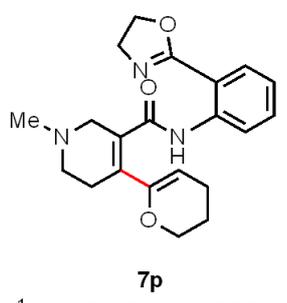
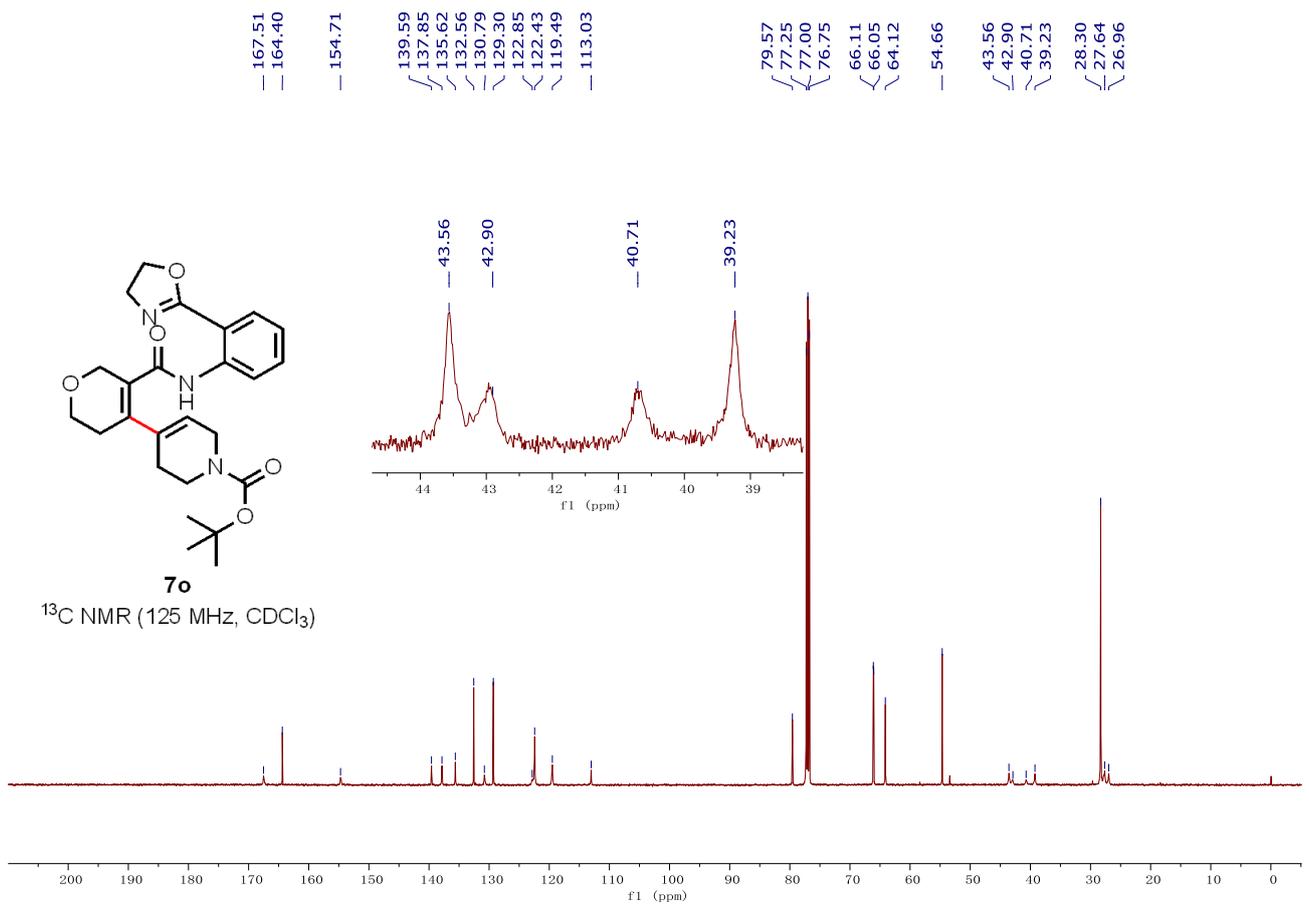
¹H NMR (400 MHz, CDCl₃)



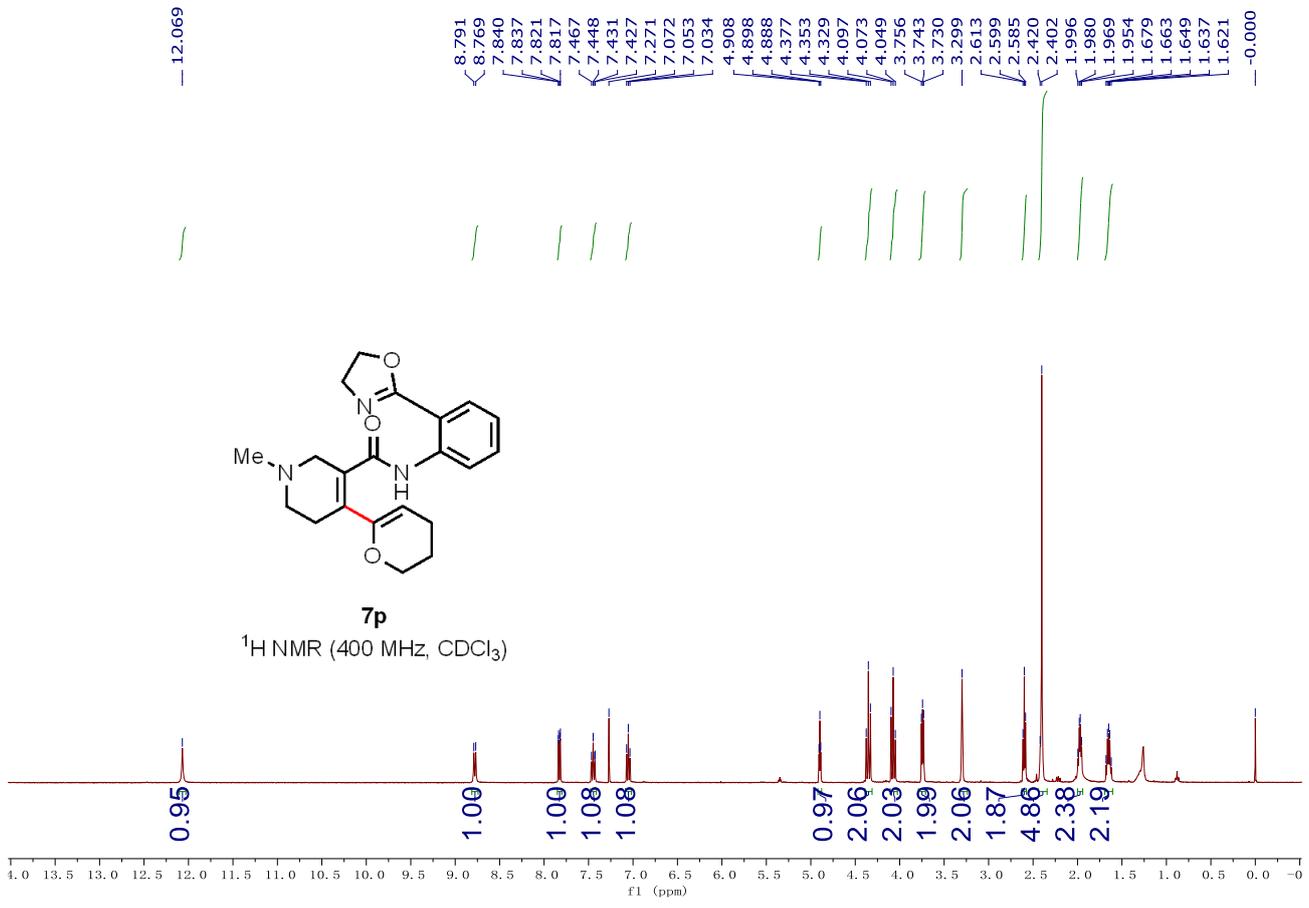




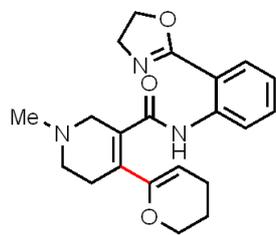
¹³C NMR (125 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)

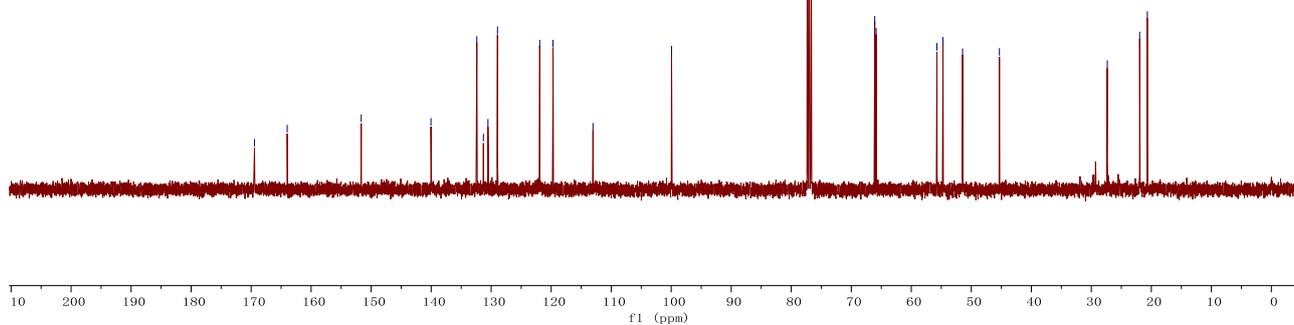


169.44
 163.99
 151.65
 140.04
 132.39
 131.30
 130.53
 128.95
 121.91
 119.70
 113.04
 99.95
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 27.34
 21.95
 20.67

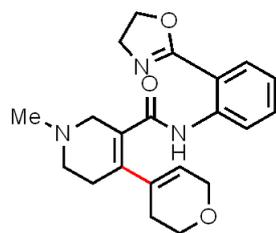


7p

^{13}C NMR (100 MHz, CDCl_3)

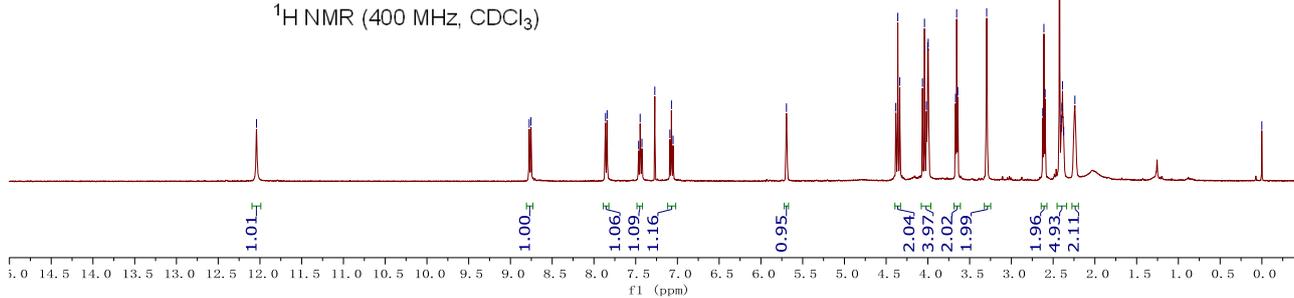


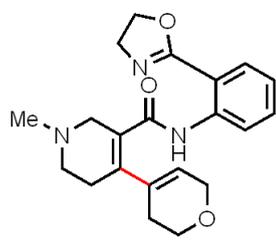
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 8.754
 7.861
 7.842
 7.465
 7.446
 7.425
 7.271
 7.090
 7.071
 7.052
 5.694
 4.384
 4.361
 4.337
 4.065
 4.041
 4.017
 4.002
 3.996
 3.669
 3.656
 3.642
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 2.611
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 2.388
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 2.239
 0.000



7q

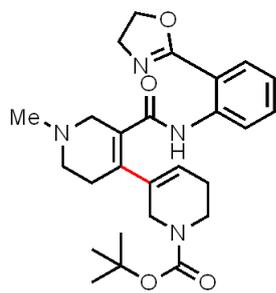
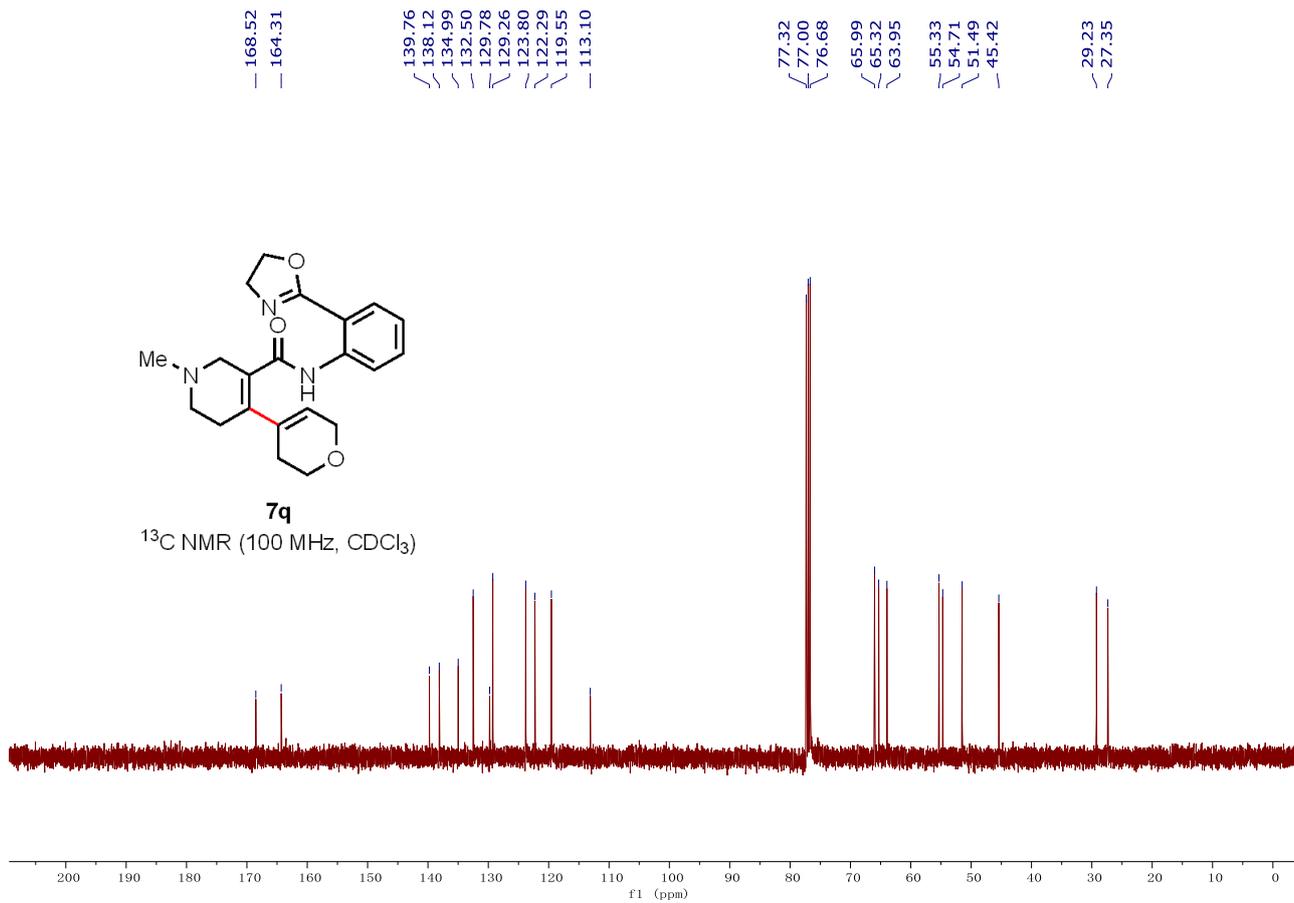
^1H NMR (400 MHz, CDCl_3)





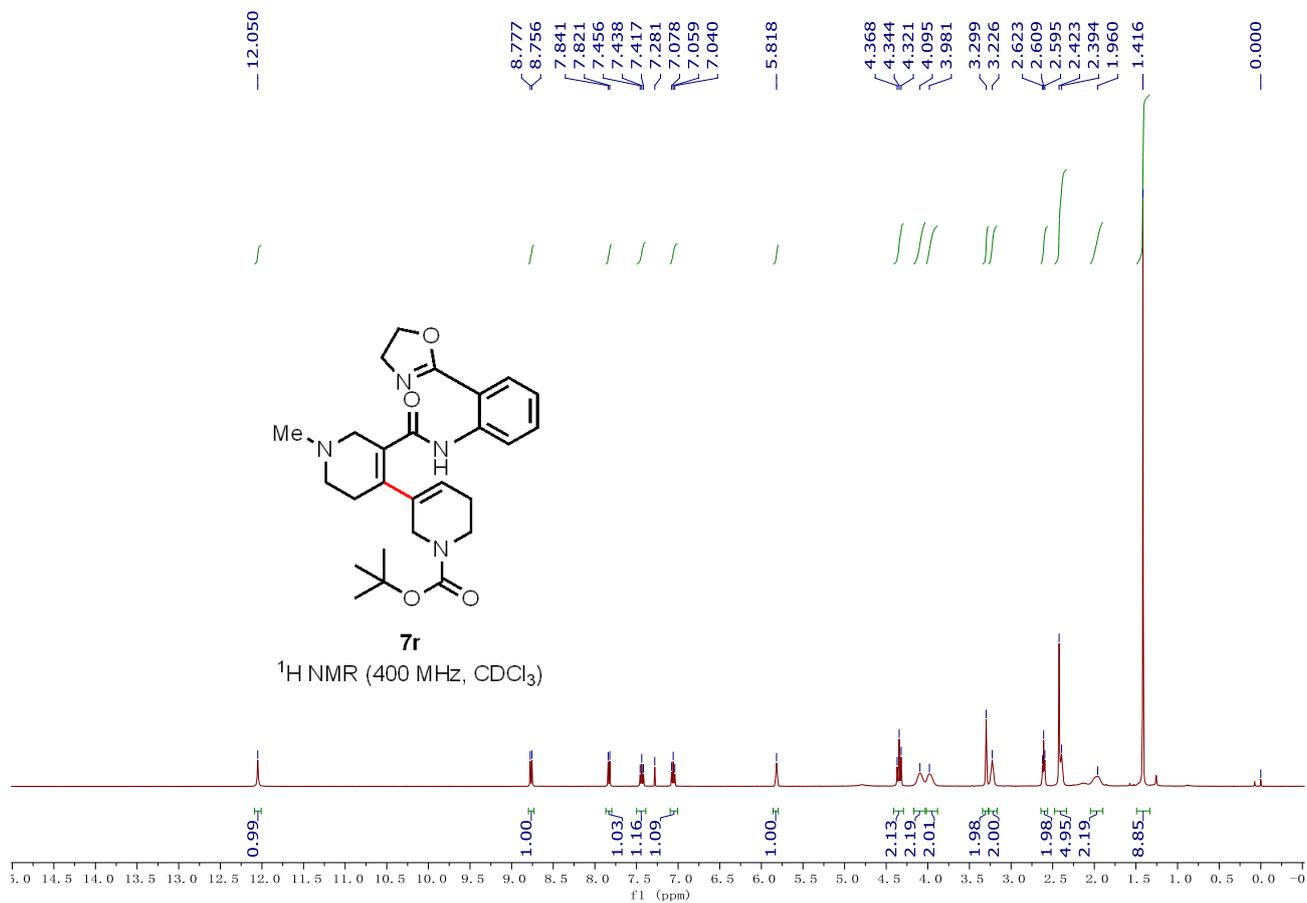
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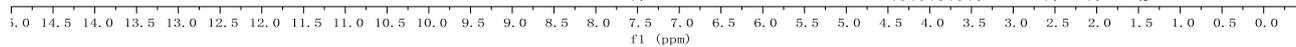
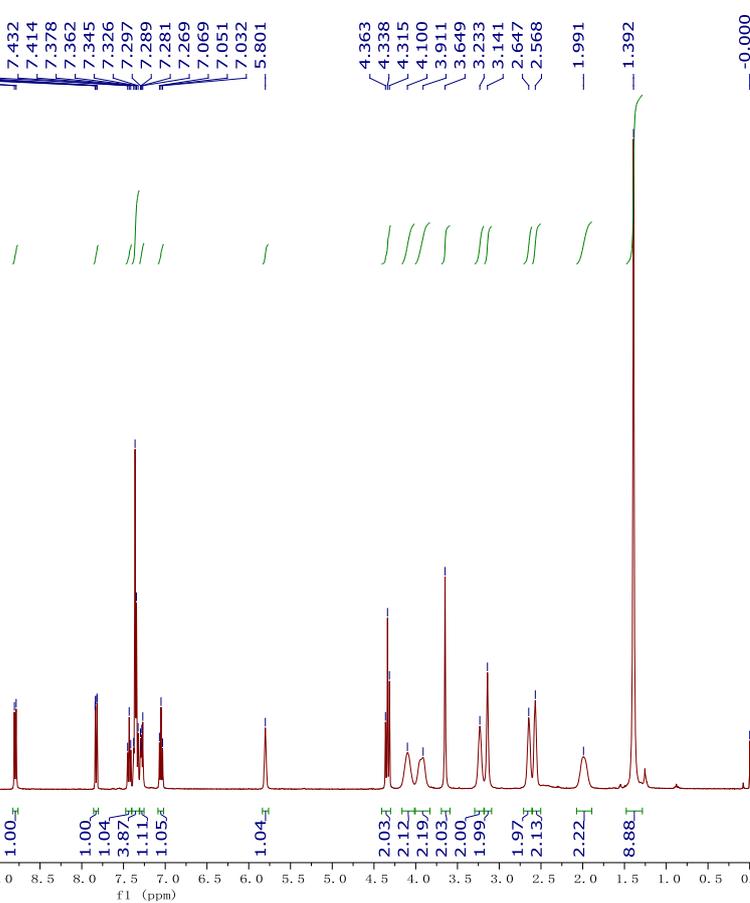
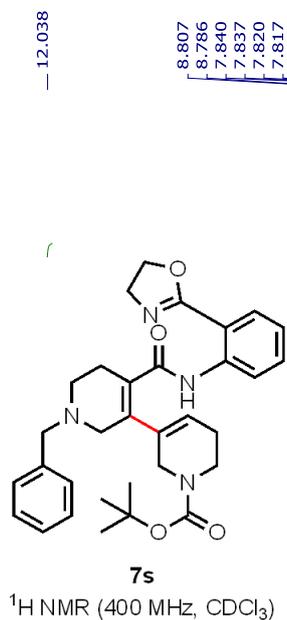
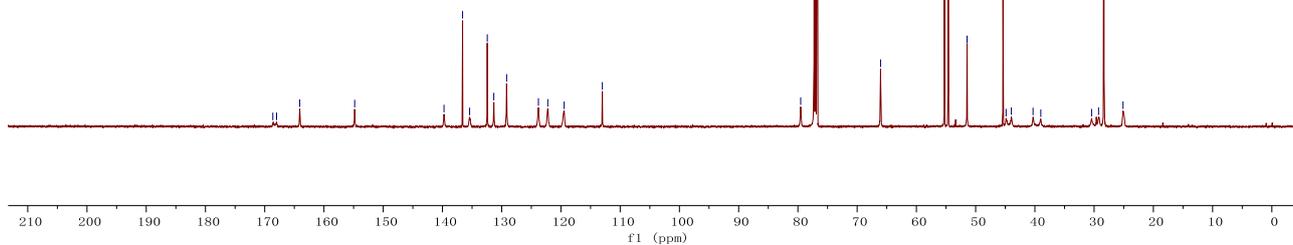
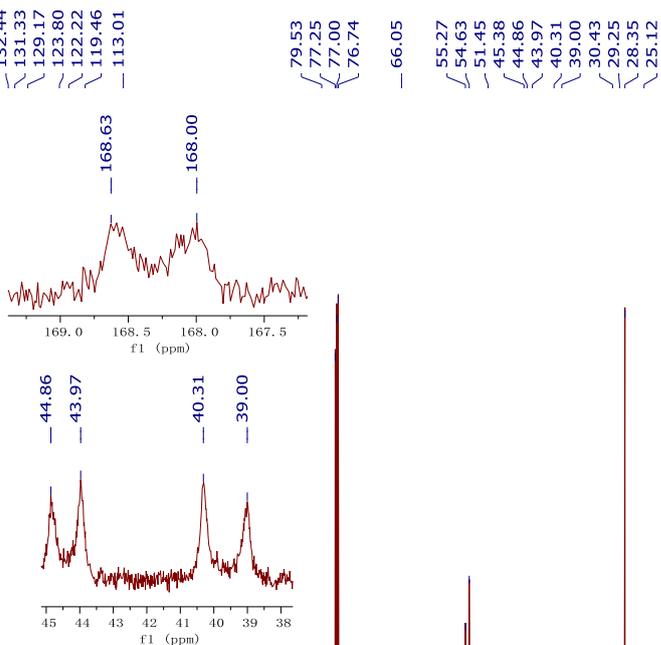
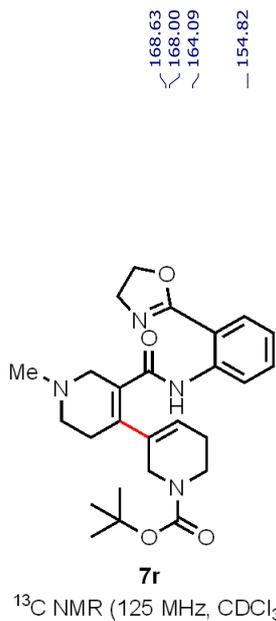
^{13}C NMR (100 MHz, CDCl_3)

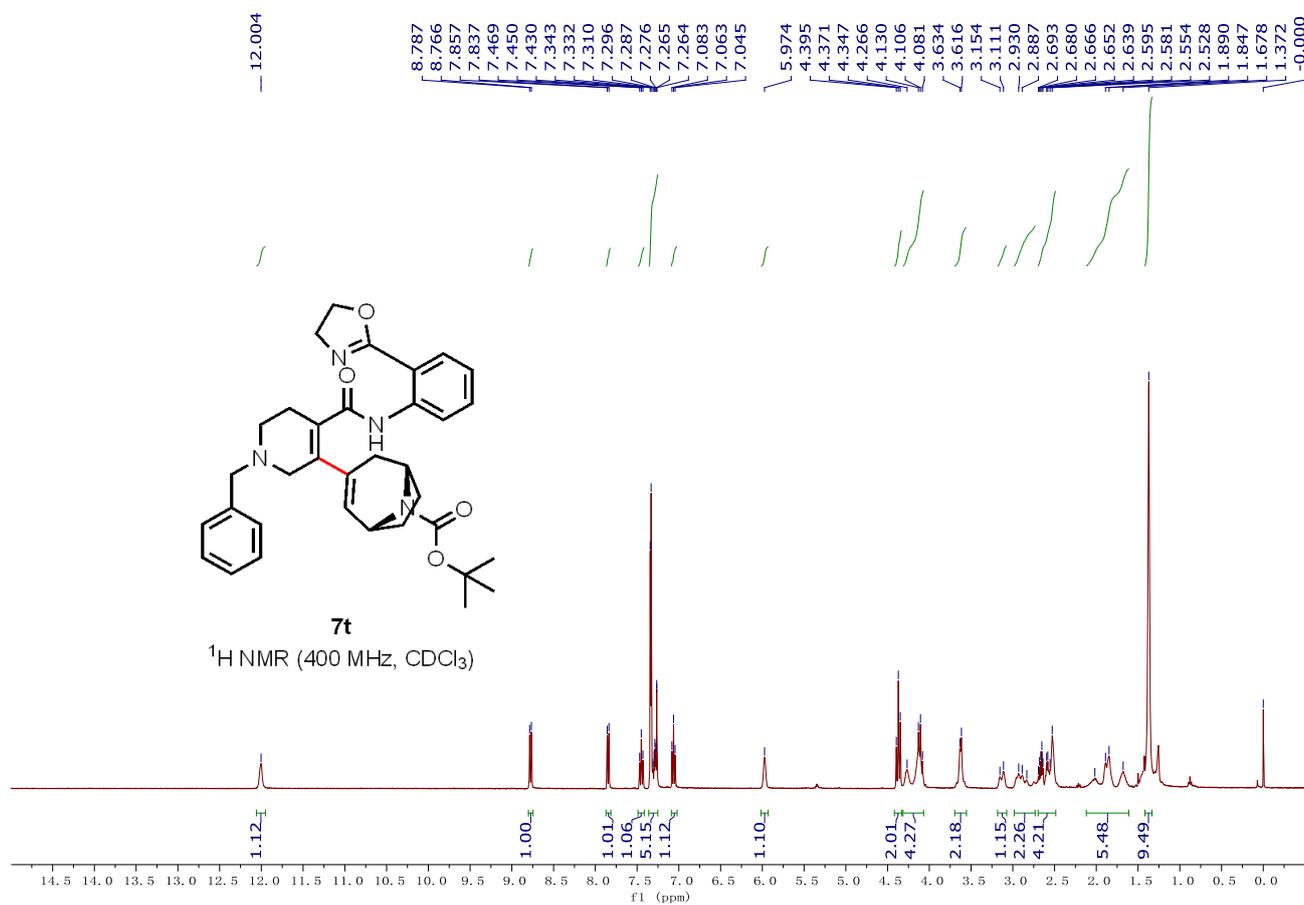
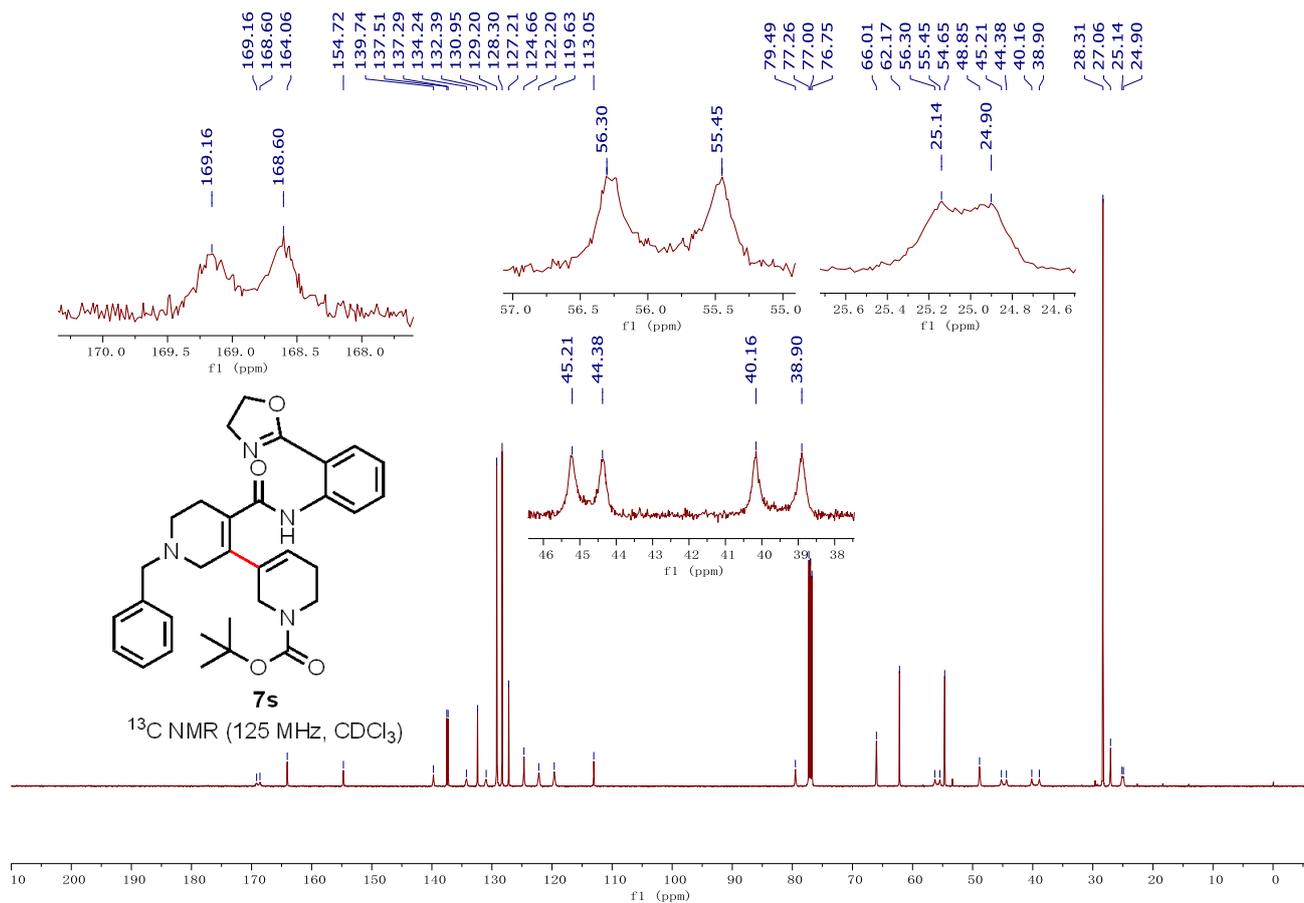


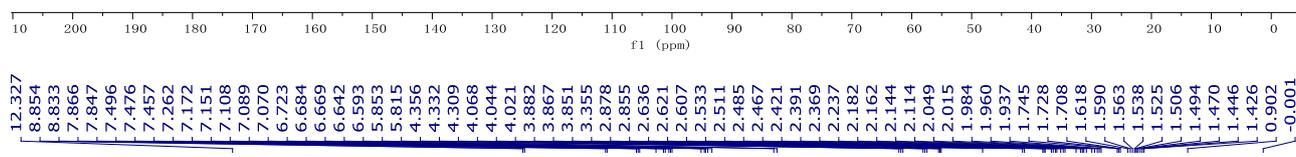
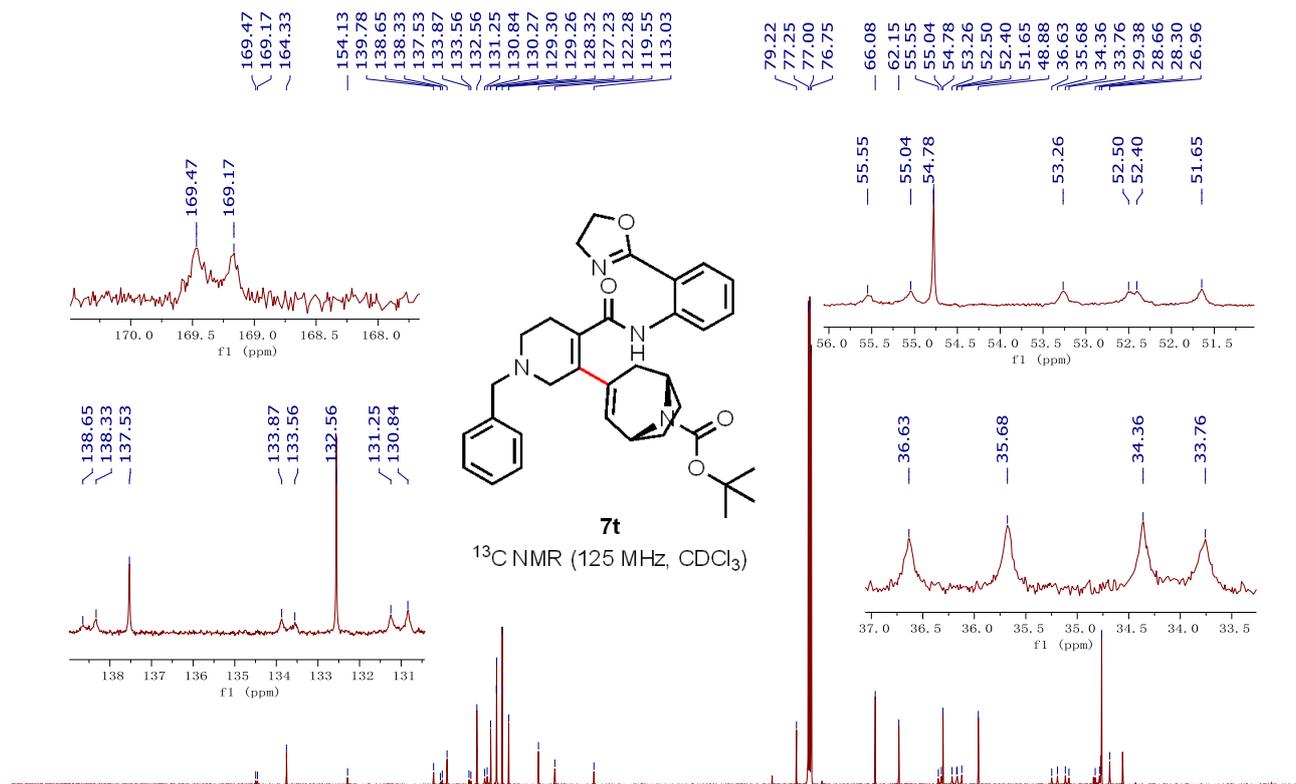
7r

^1H NMR (400 MHz, CDCl_3)







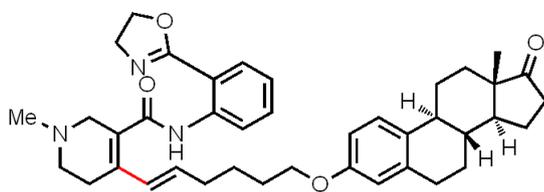


— 220.96

— 167.76
— 164.28
— 156.97
— 139.71
— 137.61
— 134.13
— 132.44
— 131.79
— 131.66
— 129.91
— 129.11
— 128.45
— 126.22
— 122.36
— 119.92
— 114.39
— 113.37
— 112.03

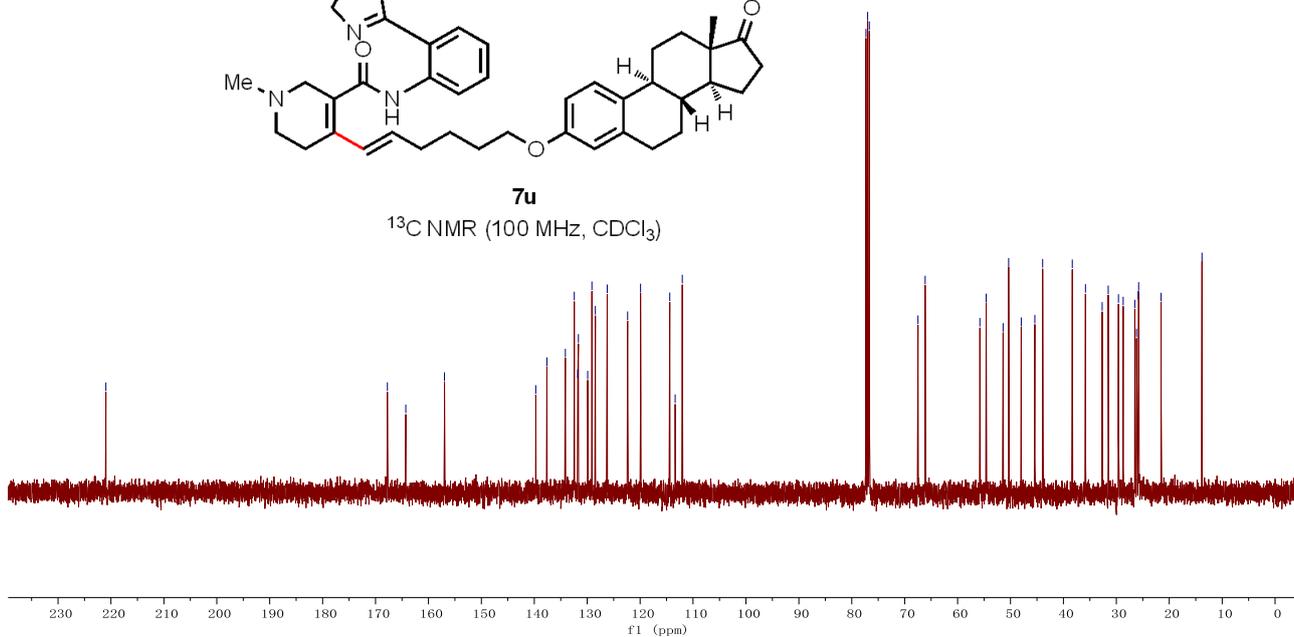
77.32 cdd13
77.00 cdd13
76.68 cdd13
67.48
66.13

55.79
54.60
51.40
50.35
47.97
45.40
43.92
38.33
35.84
32.68
31.53
29.60
28.70
26.51
25.87
21.54
13.82



7u

¹³C NMR (100 MHz, CDCl₃)

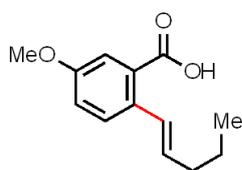


7.521
7.512
7.488
7.258
7.203
7.164
7.077
7.070
7.055
7.048
6.098
6.081
6.061
6.042
6.025

3.849

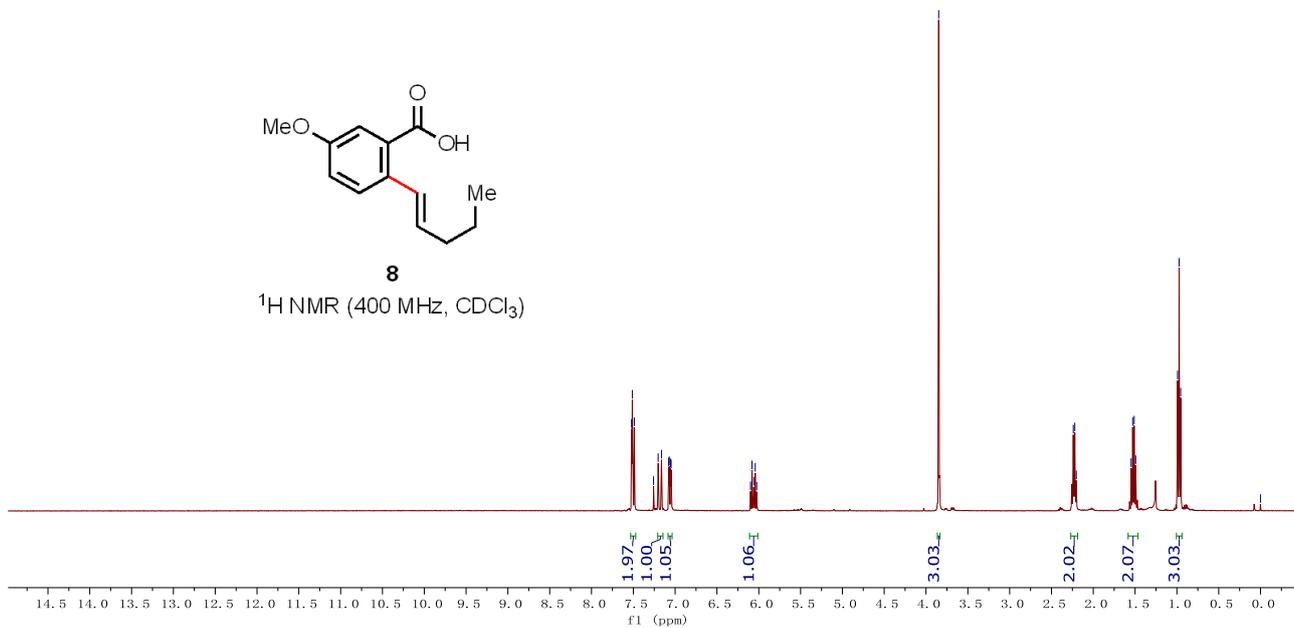
2.239
2.221
2.203
1.548
1.529
1.511
1.492
0.992
0.974
0.955

0.000



8

¹H NMR (400 MHz, CDCl₃)



1.97

1.00

1.05

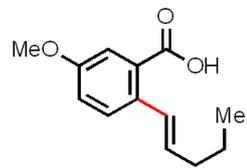
1.06

3.03

2.02

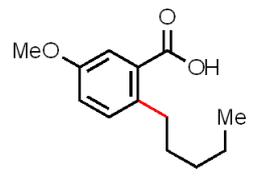
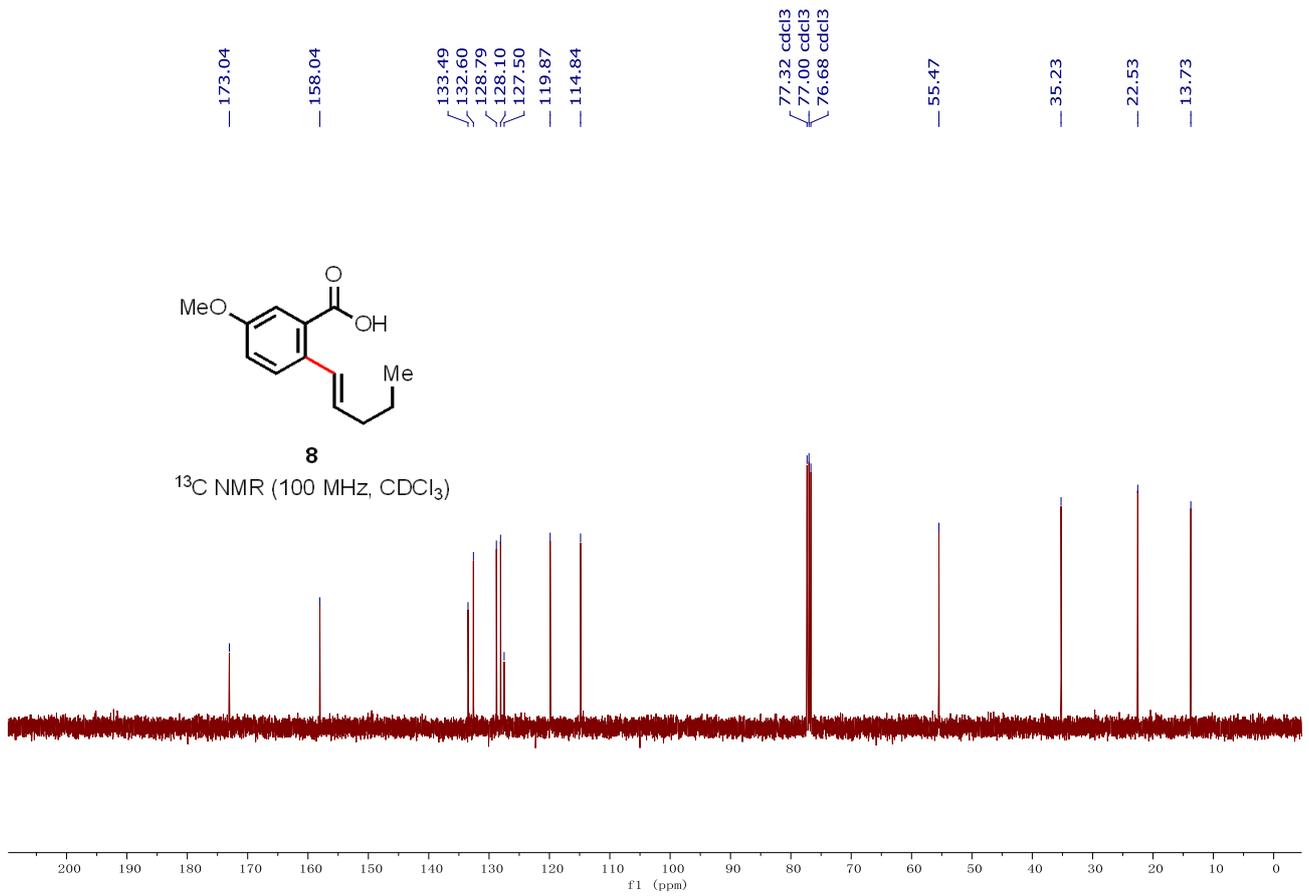
2.07

3.03



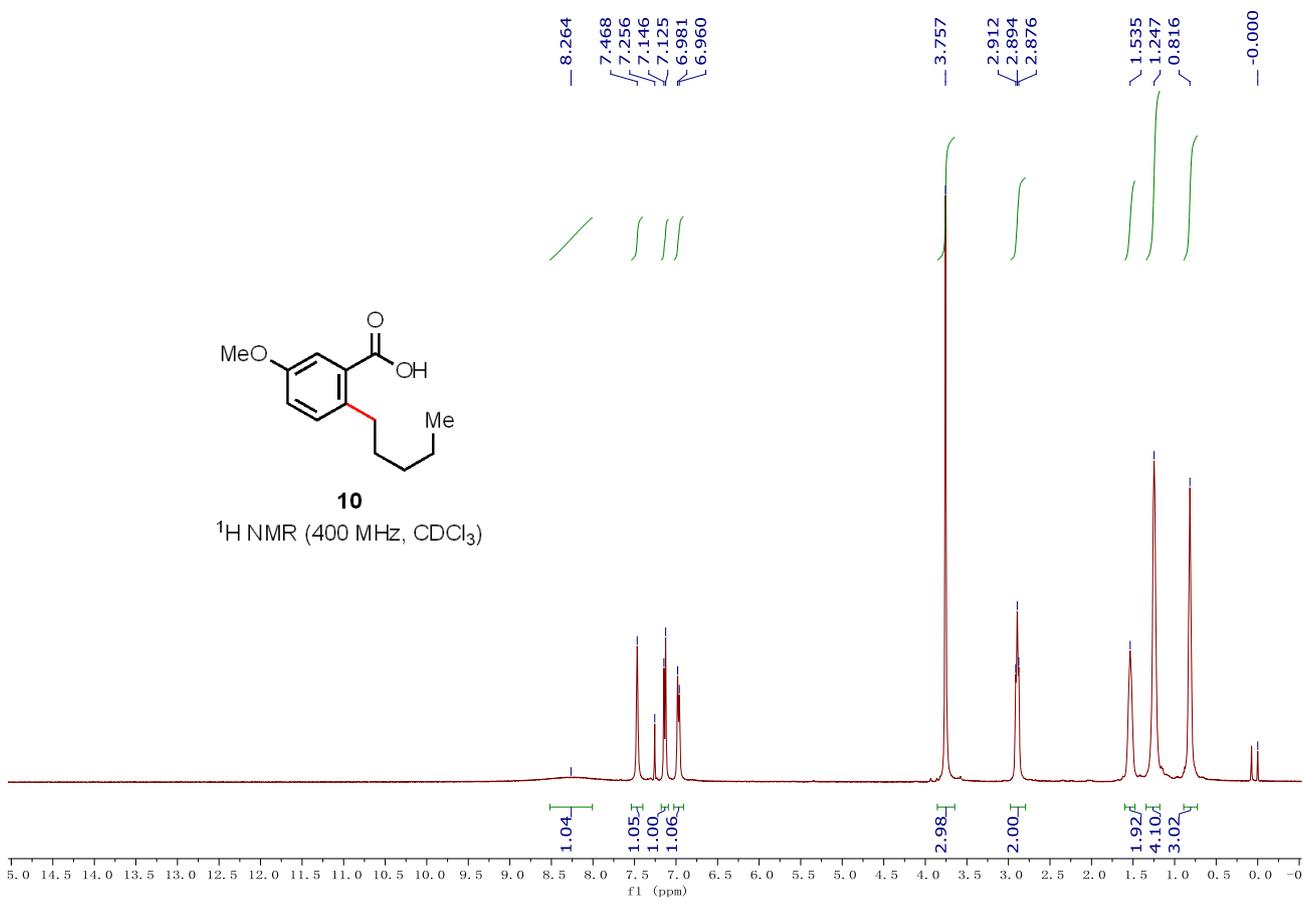
8

¹³C NMR (100 MHz, CDCl₃)

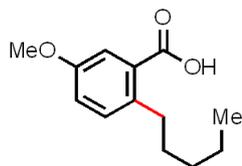


10

¹H NMR (400 MHz, CDCl₃)

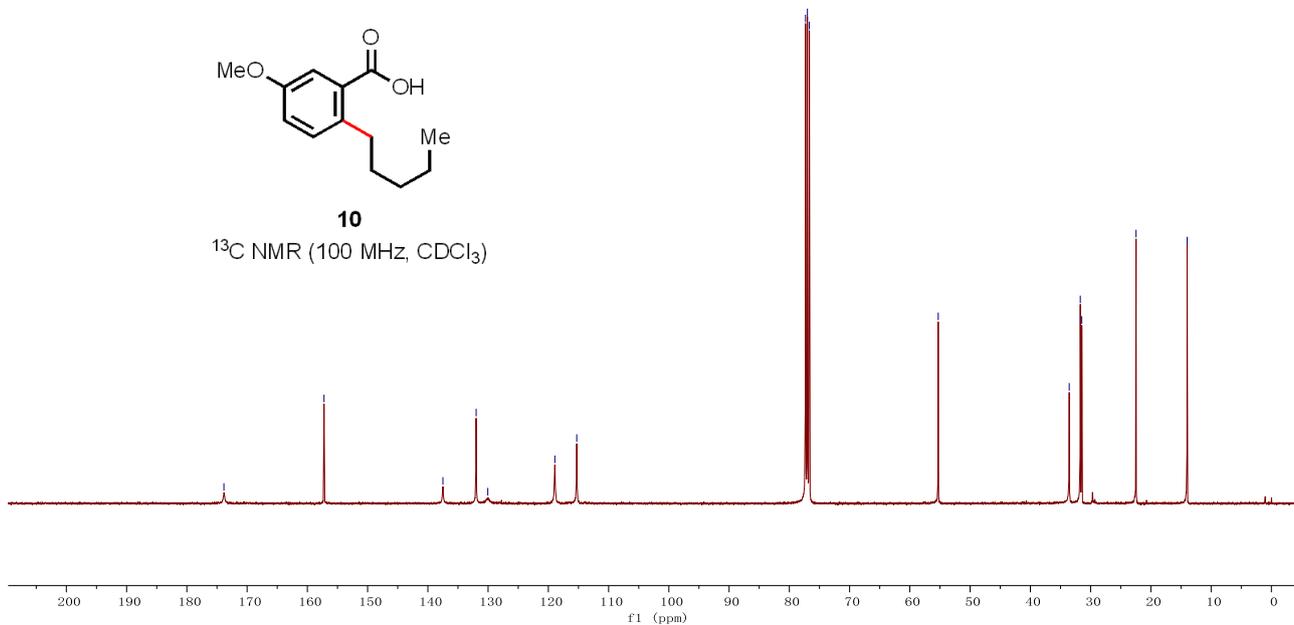


— 173.85
 — 157.23
 — 137.50
 — 131.99
 — 130.05
 — 118.93
 — 115.29
 — 77.32
 — 77.00
 — 76.68
 — 55.29
 — 33.55
 — 31.71
 — 31.46
 — 22.45
 — 13.98

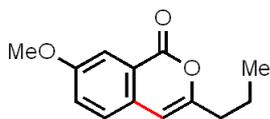


10

¹³C NMR (100 MHz, CDCl₃)



7.673
 7.669
 7.310
 7.288
 7.283
 7.277
 7.269
 7.261
 7.255
 — 6.226
 — 3.895
 2.517
 2.498
 2.479
 1.782
 1.763
 1.745
 1.726
 1.707
 1.689
 1.629
 1.008
 0.989
 0.971
 — 0.000



11

¹H NMR (400 MHz, CDCl₃)

