

Supporting Information

Gold Vs. Rhodium Catalysis: Tuning Reactivity through Catalyst Control in the C-H Alkynylation of Isoquinolones

Aslam C. Shaikh, Dinesh R. Shinde and Nitin T. Patil *

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1. General information

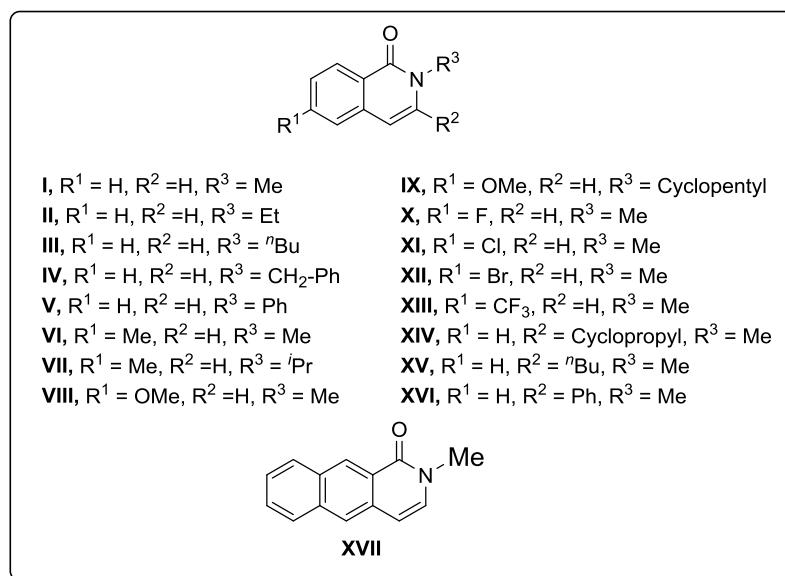
Unless otherwise specified, all reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under argon atmosphere. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccators. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining KMnO₄ and charring on a hot plate. Solvents were removed in vacuo and heated with a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in pet. ether and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump.

Melting points are uncorrected and recorded using digital Buchi Melting Point Apparatus B-540. ¹H NMR spectra and ¹³C NMR spectra were recorded on Bruker AV, 400/500, JEOL 400 MHz spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of ¹H NMR signals are designated as s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), quin (quintet), m (multiplet)... etc. HRMS (ESI) data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. Single-crystal data was collected on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoK_α= 0.71073 Å) radiation.

2. General procedures

2.1 General procedure for preparation of various *N*-substituted isoquinolones

The literature known isoquinolones¹ were converted to *N*-substituted isoquinolones using following procedure: In a 10 mL round-bottom flask isoquinolin-1(2H)-ones (80 mmol, 1.0 equiv), selected alkyl or aryl halide (120 mmol, 1.5 equiv), and cesium carbonate (120 mmol, 1.5 equiv) in DMF (5 mL) was added. The reaction was heated to 50 °C in an oil bath for 3 h. The reaction mixture was allowed to warm to ambient temperature. The reaction mixture was diluted with EtOAc (10 mL). The organic layer was washed with water (2 x 10 mL) and dried over Na₂SO₄. The suspension was filtered, and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography (silica gel, pet. ether/EtOAc) to give the desired *N*-substituted isoquinolones as product.



¹ a) Webb, N. J.; Marsden, S. P.; Raw, S. A.; *Org. Lett.* **2014**, *16*, 4718-4721; b) Guimond, N.; Gorelsky, S. I.; Fagnou, K.; *J. Am. Chem. Soc.* **2011**, *133*, 6449-6457; c) Gao, H.; Zhang, J.; *Adv. Synth. Catal.* **2009**, *351*, 85-88.

2.2 General procedure for gold catalyzed C-H alkynylation of isoquinolones

To a screw-cap vial containing a stir bar were added isoquinolones (0.15 mmol, 1.0 equiv), TIPS-EBX (0.18 mmol, 1.2 equiv), AuCl (10 mol %) and dry CH₃CN (2 mL). The reaction vial was fitted with a cap, evacuated, and filled with nitrogen and heated at 50 °C for 24 h. The reaction mixture was allowed to warm to ambient temperature. The reaction mixture was diluted with CH₂Cl₂ and concentrated under reduced pressure. The residue was diluted with CH₂Cl₂ and wash with NaHCO₃ followed by brine. The collected organic layer dried over Na₂SO₄, concentrated under reduced pressure, and the resulting residue was purified by column chromatography (silica gel, pet. ether/EtOAc) to give the desired products **3**.

2.3 General procedure for rhodium catalyzed C-H alkynylation of isoquinolones

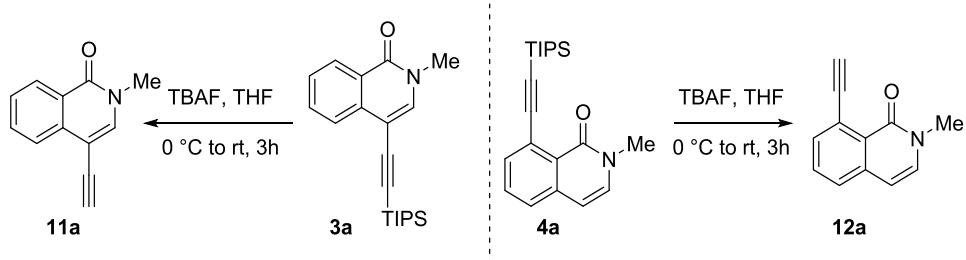
An oven dried sealed tube equipped with a stirring bar, filled with argon. Isoquinolones (0.15 mmol, 1.0 equiv), TIPS-EBX (0.18 mmol, 1.2 equiv), [Cp*RhCl₂]₂ (2.5 mol %) and AgSbF₆ (10 mol %), dry DCE (2.0 mL) were added under a stream of argon flow in the reaction vessel. The reaction was allowed to stir at 80 °C for 16 h until the complete conversion of starting material as monitored by TLC analysis. The reaction mixture was then diluted with EtOAc (10 mL) and washed with NaHCO₃. The combined organic layer was wash with brine, dried over Na₂SO₄ and the resulting residue was purified by column chromatography (silica gel, pet. ether/EtOAc) to give the desired products **4**.

2.4 Procedure for dialkynylation of isoquinolone (1a**)**

An oven dried sealed tube equipped with a stirring bar, filled with argon. *N*-methyl isoquinolone (0.15 mmol, 1.0 equiv), TIPS-EBX (0.38 mmol, 2.5 equiv), AuCl (10 mol %), [Cp*RhCl₂]₂ (2.5 mol %) and AgSbF₆ (10 mol %), dry DCE (3.0 mL) were added under a stream of argon flow in the reaction vessel. The reaction was allowed to stir at 80 °C for 24 h until the complete conversion of starting material as monitored by TLC analysis. The reaction mixture was then diluted with EtOAc (10 mL) and washed with NaHCO₃. The combined organic layer was wash with brine, dried over Na₂SO₄ and the resulting residue was purified by column chromatography (silica gel, pet. ether/EtOAc) to give the desired products **5** (yield 32%).

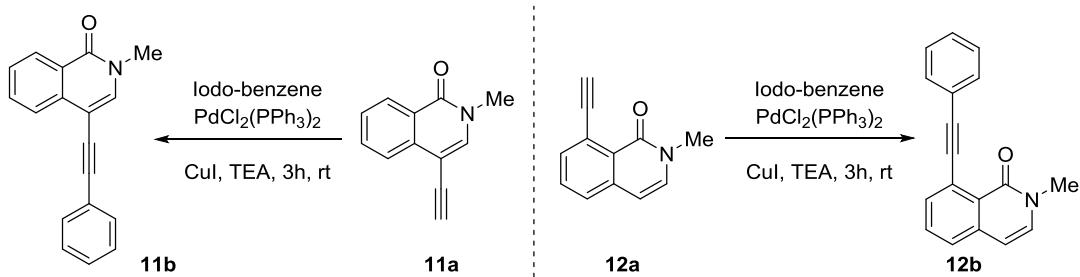
2.5 Procedure for synthetic transformations

a) Procedure for synthesis of **11a** and **12a**



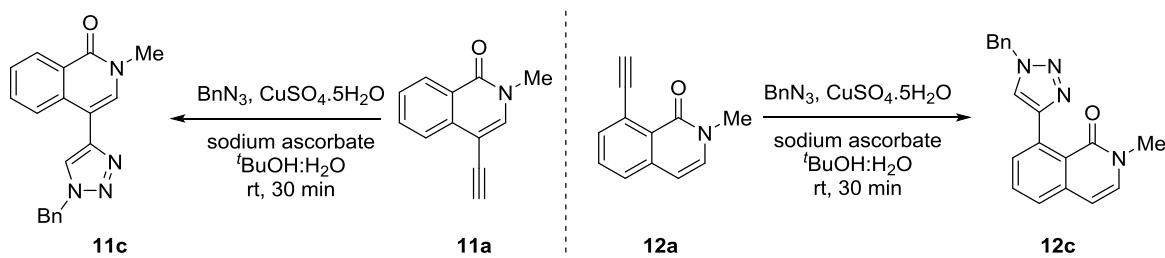
The substrates **3a/4a** (50 mg, 0.15 mmol) was dissolved in THF (3 mL) and TBAF (1.0 M in THF, 0.2 mL, 0.20 mmol) was added at 0 °C. The reaction mixture was stirred for 3 h at room temperature. The mixture was quenched by addition of water. The reaction mixture was extracted with EtOAc (3×5 mL) and the combined organic layers were washed with brine (10 mL), dried over Na₂SO₄ and evaporated in vacuo. The obtained crude product was purified by column chromatography to afford the desired terminal alkynes **11a/12a** (91% and 88%) as a white solid.

b) Procedure for synthesis of **11b** and **12b**



To a stirred solution of iodo-benzene (40 mg, 0.20 mmol), PdCl₂(PPh₃)₂ (2.8 mg, 0.004 mmol, 2 mol %), CuI (1.15 mg, 0.006 mmol, 3 mol%) in dry Et₃N (3 mL) was added **11a/12a** (35 mg, 0.20 mmol). The mixture was stirred at room temperature for 3 h. After completion of the reaction, the reaction mixture was diluted with EtOAc (2×5 mL). The combined organic layers were washed with brine, dried over Na₂SO₄ and evaporated in vacuo. The crude product was purified by column chromatography (silica gel, pet. ether/EtOAc) to give the desired a product **11b/12b** (91% and 90%) as a white solid.

c) Procedure for synthesis of **11c** and **12c**



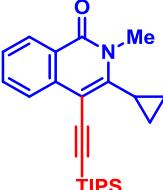
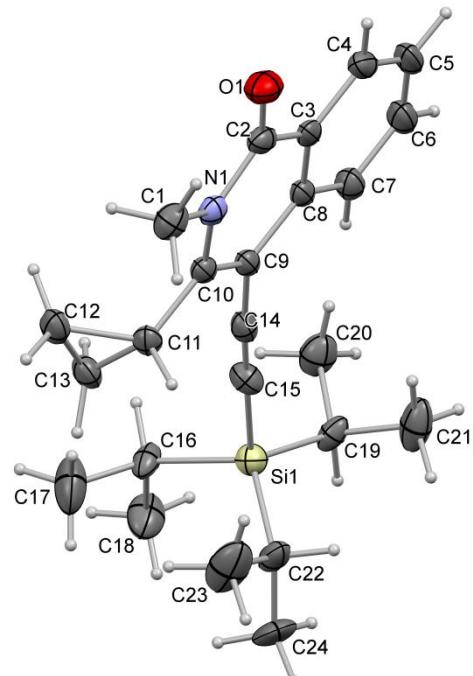
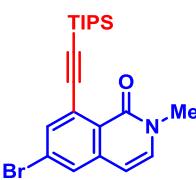
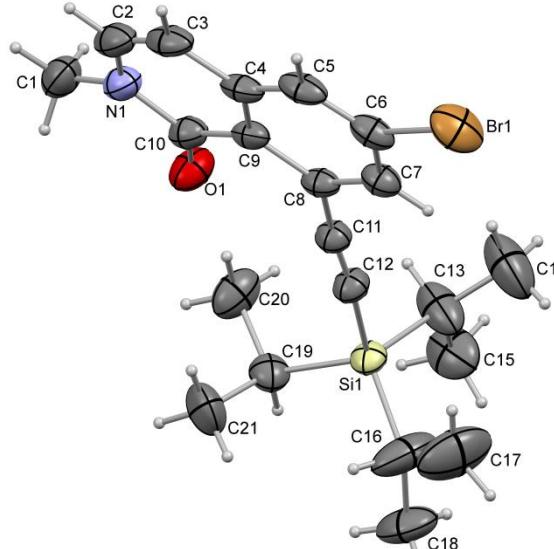
To a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (5.0 mg, 0.02 mmol), sodium ascorbate (7.9 mg, 0.04 mmol), in ${}^t\text{BuOH}/\text{H}_2\text{O}$ (1:2 v/v, 2.0 mL) was added a mixture of alkyne **11a**/**12a** (20 mg, 0.11 mmol) and benzyl azide (15 mg, 0.11 mmol) at room temperature. The resultant mixture was stirred continuously until the reaction system solidified completely (30 min). Then CH_2Cl_2 (5 mL) was added to dissolve the crude product. The organic layer was washed with H_2O followed by brine, dried over Na_2SO_4 and evaporated in vacuo. The crude product was purified by a column chromatography (silica gel, pet. ether/EtOAc) to give **11c**/**12c** (88% and 90%) as an off-white solid.

3. X-ray crystallography

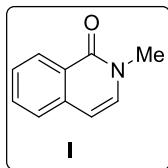
X-ray intensity data measurements of compounds **3n** and **4l** were carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized ($\text{MoK}_{\alpha}=0.71073\text{\AA}$) radiation. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 10 sec for **3n** and **4l** keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX2 program (Bruker, 2006).² All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on F^2 .³ All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms. An ORTEP view of all five compounds were drawn with 50% probability displacement ellipsoids and H atoms are shown as small spheres of arbitrary radii.

² Bruker (2006). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.

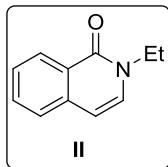
³ Sheldrick, G. M.; *Acta Crystallogr.*, 2008, A64, 112.

Sr. No	Compound Structure	ORTEP Diagram
1	<p style="text-align: center;">3n</p> <p>CCDC No - 1448277</p> 	
2	<p style="text-align: center;">4l</p> <p>CCDC No - 1448276</p> 	

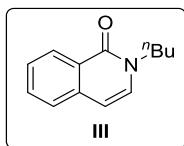
4. Characterization data



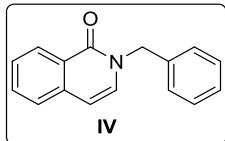
(I): thick liquid, 180 mg, 92 % yield; $R_f = 0.70$ (pet. ether/EtOAc = 80/20); **$^1\text{H NMR}$ (400 MHz, CDCl_3)** $\delta = 8.40$ (d, $J = 8.2$ Hz, 1 H), 7.61 - 7.51 (m, 1 H), 7.49 - 7.39 (m, 2 H), 7.01 (d, $J = 7.3$ Hz, 1 H), 6.43 (d, $J = 7.3$ Hz, 1 H), 3.56 (s, 3 H) ; **$^{13}\text{C NMR}$ (100 MHz, CDCl_3)** $\delta = 162.4$, 137.0, 132.3, 131.8, 127.4, 126.6, 125.9, 125.7, 105.8, 36.8; **HRMS (ESI)** calcd for $\text{C}_{10}\text{H}_{10}\text{ON}$ ($\text{M}^+ + \text{H}$) 160.0757, found 160.0755.



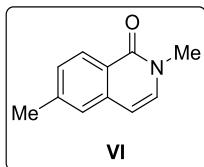
(II): thick liquid, 178 mg, 90 % yield; $R_f = 0.70$ (pet. ether/EtOAc = 80/20); **$^1\text{H NMR}$ (400 MHz, CDCl_3)** $\delta = 8.42$ (d, $J = 8.2$ Hz, 1 H), 7.65 - 7.54 (m, 1 H), 7.51 - 7.38 (m, 2 H), 7.10 - 6.99 (m, 1 H), 6.54 - 6.41 (m, 1 H), 4.08 - 3.98 (m, 2 H), 1.38 - 1.32 (m, 3 H) ; **$^{13}\text{C NMR}$ (100 MHz, CDCl_3)** $\delta = 161.8$, 136.9, 131.9, 131.1, 127.6, 126.6, 126.2, 125.7, 106.1, 44.2, 14.5; **HRMS (ESI)** calcd for $\text{C}_{11}\text{H}_{12}\text{ON}$ ($\text{M}^+ + \text{H}$) 174.0913, found 174.0910.



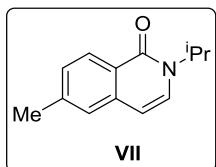
(III): thick liquid, 186 mg, 92 % yield; $R_f = 0.70$ (pet. ether/EtOAc = 80/20); **$^1\text{H NMR}$ (400 MHz, CDCl_3)** $\delta = 8.49$ - 8.34 (m, 1 H), 7.57 (d, $J = 7.8$ Hz, 1 H), 7.51 - 7.37 (m, 2 H), 7.02 (dd, $J = 2.7$, 7.3 Hz, 1 H), 6.45 (dd, $J = 2.7$, 7.3 Hz, 1 H), 4.03 - 3.91 (m, 2 H), 1.83 - 1.68 (m, 2 H), 1.43 - 1.29 (m, 2 H), 0.93 (dt, $J = 2.7$, 7.3 Hz, 3 H); **$^{13}\text{C NMR}$ (100 MHz, CDCl_3)** $\delta = 161.9$, 136.9, 131.8, 131.6, 127.6, 126.5, 126.2, 125.7, 105.8, 49.0, 31.2, 19.8, 13.6; **HRMS (ESI)** calcd for $\text{C}_{13}\text{H}_{16}\text{ON}$ ($\text{M}^+ + \text{H}$) 202.1226, found 202.1224.



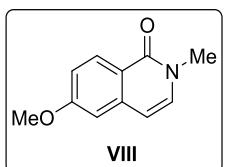
(IV): off white solid, 210 mg, 94 % yield; mp = 55-56 °C; R_f = 0.65 (pet. ether/EtOAc = 80/20); **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ = 8.53 - 8.38 (m, 1 H), 7.65 - 7.59 (m, 1 H), 7.53 - 7.44 (m, 2 H), 7.35 - 7.24 (m, 5 H), 7.08 (d, J = 7.3 Hz, 1 H), 6.47 (d, J = 7.3 Hz, 1 H), 5.22 (s, 2 H); **$^{13}\text{C NMR}$ (100 MHz, CDCl_3)** δ = 162.2, 136.9, 136.8, 132.2, 131.2, 128.7, 128.0, 127.9, 127.8, 126.8, 126.2, 125.9, 106.4, 51.6; **HRMS (ESI)** calcd for $\text{C}_{16}\text{H}_{14}\text{ON}$ ($\text{M}^+ + \text{H}$) 236.1070, found 236.1066.



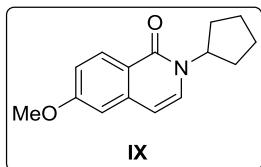
(VI): off white solid, 185 mg, 88 % yield; mp = 88-89 °C; R_f = 0.75 (pet. ether/EtOAc = 80/20); **$^1\text{H NMR}$ (500 MHz, CDCl_3)** δ = 8.28 (d, J = 8.2 Hz, 1 H), 7.28 - 7.20 (m, 2 H), 7.00 (d, J = 7.3 Hz, 1 H), 6.38 (d, J = 7.3 Hz, 1 H), 3.55 (s, 3 H), 2.43 (s, 3 H); **$^{13}\text{C NMR}$ (125 MHz, CDCl_3)** δ = 158.5, 139.3, 134.3, 129.7, 125.9, 125.1, 123.2, 121.6, 104.4, 38.8, 24.3; **HRMS (ESI)** calcd for $\text{C}_{11}\text{H}_{12}\text{ON}$ ($\text{M}^+ + \text{H}$) 174.0913, found 174.0911.



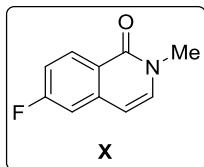
(VII): off white solid, 160 mg, 82 % yield; mp = 72-73 °C; R_f = 0.75 (pet. ether/EtOAc = 80/20); **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ = 8.32 (d, J = 8.3 Hz, 1 H), 7.31 - 7.15 (m, 2 H), 7.09 (d, J = 7.3 Hz, 1 H), 6.46 (d, J = 7.3 Hz, 1 H), 5.46 - 5.30 (m, 1 H), 2.43 (br. s., 3 H), 1.35 (d, J = 6.8 Hz, 6 H); **$^{13}\text{C NMR}$ (100 MHz, CDCl_3)** δ = 161.5, 142.3, 136.4, 128.1, 127.8, 126.5, 125.2, 123.8, 106.0, 45.4, 21.6, 21.5; **HRMS (ESI)** calcd for $\text{C}_{13}\text{H}_{16}\text{ON}$ ($\text{M}^+ + \text{H}$) 202.1226, found 202.1222.



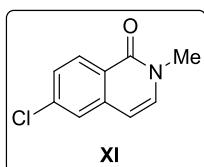
(VIII): white solid, 185 mg, 92 % yield; mp = 90-91 °C; R_f = 0.65 (pet. ether/EtOAc = 80/20); **$^1\text{H NMR}$ (500 MHz, CDCl_3)** δ = 8.31 (d, J = 9.2 Hz, 1 H), 7.09 - 6.94 (m, 2 H), 6.82 (d, J = 2.7 Hz, 1 H), 6.37 (d, J = 7.3 Hz, 1 H), 3.87 (s, 3 H), 3.54 (s, 3 H); **$^{13}\text{C NMR}$ (125 MHz, CDCl_3)** δ = 162.4, 162.2, 139.1, 133.0, 129.5, 119.9, 116.2, 106.5, 105.6, 55.3, 36.7; **HRMS (ESI)** calcd for $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}$ ($\text{M}^+ + \text{H}$) 190.0863, found 190.0859.



(IX): white solid, 170 mg, 88 % yield; mp = 84-85 °C; R_f = 0.65 (pet. ether/EtOAc = 80/20); **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ = 8.35 (d, J = 8.7 Hz, 1 H), 7.13 - 7.08 (m, 1 H), 7.04 (dd, J = 2.7, 9.2 Hz, 1 H), 6.84 (d, J = 2.3 Hz, 1 H), 6.48 - 6.41 (m, 1 H), 5.50 - 5.34 (m, 1 H), 3.89 (s, 3 H), 2.22 - 2.09 (m, 2 H), 1.91 - 1.83 (m, 2 H), 1.78 - 1.63 (m, 4 H); **$^{13}\text{C NMR}$ (100 MHz, CDCl_3)** δ = 162.5, 162.0, 138.4, 130.1, 128.3, 119.9, 116.1, 106.4, 106.1, 55.4, 55.4, 31.9, 24.6; **HRMS (ESI)** calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2\text{N}$ ($\text{M}^+ + \text{H}$) 244.1332, found 244.1327.

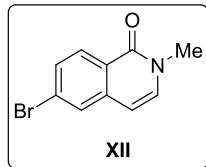


(X): off white solid, 155 mg, 85 % yield; mp = 198-199 °C; R_f = 0.70 (pet. ether/EtOAc = 80/20); **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ = 8.53 - 8.26 (m, 1 H), 7.22 - 6.98 (m, 3 H), 6.41 (d, J = 7.3 Hz, 1 H), 3.58 (s, 3 H); **$^{13}\text{C NMR}$ (100 MHz, CDCl_3)** δ = 166.2 (d, J = 252.3 Hz) 161.9, 139.3 (d, J = 10.0 Hz), 133.7, 130.9 (d, J = 10.0 Hz), 122.7, 115.5 (d, J = 23.9 Hz), 110.7 (d, J = 21.6 Hz), 105.3 (d, J = 3.1 Hz), 37.0; **HRMS (ESI)** calcd for $\text{C}_{10}\text{H}_9\text{ONF}$ ($\text{M}^+ + \text{H}$) 178.0663, found 178.0660.

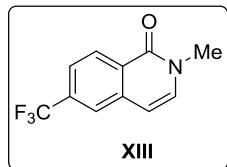


(XI): off white solid, 150 mg, 80 % yield; mp = 127-128 °C; R_f = 0.70 (pet. ether/EtOAc = 80/20); **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ = 8.35 (d, J = 8.8 Hz, 1 H), 7.54 - 7.46 (m, 1 H), 7.42

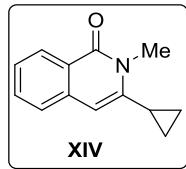
(dd, $J = 2.2, 8.6$ Hz, 1 H), 7.10 (d, $J = 7.3$ Hz, 1 H), 6.41 (d, $J = 7.3$ Hz, 1 H), 3.60 (s, 3 H); ^{13}C NMR (100 MHz, CDCl₃) δ = 162.0, 138.5, 138.3, 133.7, 129.5, 127.3, 125.1, 124.4, 104.9, 37.1; HRMS (ESI) calcd for C₁₀H₉ONCl (M⁺ + H) 194.0367, found 194.0366.



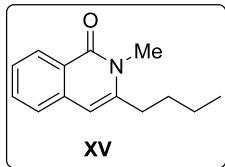
(XII): brown solid, 140 mg, 84 % yield; mp = 152-153 °C; R_f = 0.75 (pet. ether/EtOAc = 80/20); ^1H NMR (500 MHz, CDCl₃) δ = 8.29 - 8.20 (m, 1 H), 7.68 - 7.62 (m, 1 H), 7.58 - 7.49 (m, 1 H), 7.11 - 7.03 (m, 1 H), 6.41 - 6.32 (m, 1 H), 3.61 - 3.53 (m, 3 H); ^{13}C NMR (125 MHz, CDCl₃) δ = 162.1, 138.5, 133.7, 130.0, 129.5, 128.2, 127.1, 124.6, 104.7, 37.1; HRMS (ESI) calcd for C₁₀H₉ONBr (M⁺ + H) 237.9862, found 237.9860.



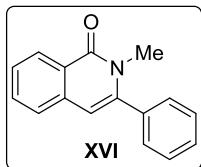
(XIII): off white solid, 157 mg, 90 % yield; 73% yield; mp = 114-115 °C; R_f = 0.65 (pet. ether/EtOAc = 80/20); ^1H NMR (500 MHz, CDCl₃) δ = 8.49 (d, $J = 8.2$ Hz, 1 H), 7.74 (s, 1 H), 7.67 - 7.57 (m, 1 H), 7.14 (d, $J = 7.3$ Hz, 1 H), 6.49 (d, $J = 7.3$ Hz, 1 H), 3.60 (s, 3 H); ^{13}C NMR (125 MHz, CDCl₃) δ = 161.7, 136.9, 133.8 (d, $J = 32.5$ Hz), 133.6, 133.4, 127.9, 124.7, 123.1 (dd, $J = 7.6, 3.8$ Hz), 105.4, 37.1; HRMS (ESI) calcd for C₁₁H₉ONF₃ (M⁺ + H) 228.0631, found 228.0626.



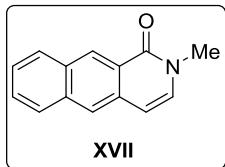
(XIV): white solid, 130 mg, 70 % yield; mp = 69-70 °C; R_f = 0.70 (pet. ether/EtOAc = 80/20); ^1H NMR (400 MHz, CDCl₃) δ = 8.47 - 8.27 (m, 1 H), 7.62 - 7.53 (m, 1 H), 7.45 - 7.36 (m, 2 H), 6.34 (s, 1 H), 3.79 (s, 3 H), 1.93 - 1.82 (m, 1 H), 1.10 - 1.01 (m, 2 H), 0.84 - 0.78 (m, 2 H); ^{13}C NMR (100 MHz, CDCl₃) δ = 163.3, 144.3, 136.5, 131.9, 127.8, 126.0, 125.3, 124.4, 104.3, 30.8, 14.5, 6.7; HRMS (ESI) calcd for C₁₃H₁₄ON (M⁺ + H) 200.1070, found 200.1067.



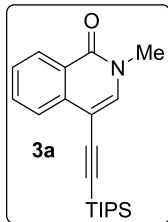
(XV): white solid, 125 mg, 68 % yield; mp = 74-75 °C; R_f = 0.70 (pet. ether/EtOAc = 80/20); **$^1\text{H NMR}$ (500 MHz, CDCl₃)** δ = 8.38 (d, J = 8.2 Hz, 1 H), 7.61 - 7.55 (m, 1 H), 7.44 - 7.37 (m, 2 H), 6.35 (s, 1 H), 3.61 (s, 3 H), 2.69 - 2.63 (m, 2 H), 1.71 - 1.61 (m, 2 H), 1.47 (qd, J = 7.4, 14.8 Hz, 2 H), 0.99 (t, J = 7.3 Hz, 3 H); **$^{13}\text{C NMR}$ (125 MHz, CDCl₃)** δ = 163.5, 143.4, 136.5, 132.0, 127.7, 125.8, 125.1, 124.1, 104.8, 33.3, 30.6, 30.4, 22.4, 13.8; **HRMS (ESI)** calcd for C₁₄H₁₈ON (M⁺ + H) 216.1383, found 216.1379.



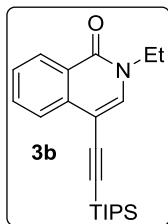
(XVI): white solid, 120 mg, 88 % yield; mp = 62-63 °C; R_f = 0.75 (pet. ether/EtOAc = 80/20); **$^1\text{H NMR}$ (400 MHz, CDCl₃)** δ = 8.46 (d, J = 8.3 Hz, 1 H), 7.63 (t, J = 7.6 Hz, 1 H), 7.54 - 7.45 (m, 5 H), 7.45 - 7.37 (m, 2 H), 6.46 (s, 1 H), 3.43 (s, 3 H); **$^{13}\text{C NMR}$ (100 MHz, CDCl₃)** δ = 163.3, 143.8, 136.3, 136.1, 132.2, 128.9, 128.7, 128.6, 127.8, 126.5, 125.8, 124.8, 107.5, 34.1; **HRMS (ESI)** calcd for C₁₆H₁₄ON (M⁺ + H) 236.1070, found 236.1066.



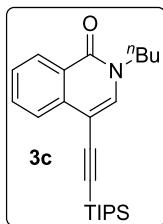
(XVII): light yellow solid, 142 mg, 78 % yield; mp = 154-155 °C; R_f = 0.50 (pet. ether/EtOAc = 80/20); **$^1\text{H NMR}$ (400 MHz, CDCl₃)** δ = 9.03 (s, 1 H), 8.05 (d, J = 8.3 Hz, 1 H), 7.95 (s, 1 H), 7.90 (d, J = 8.3 Hz, 1 H), 7.60 - 7.53 (m, 1 H), 7.50 (d, J = 7.8 Hz, 1 H), 6.95 (d, J = 7.3 Hz, 1 H), 6.57 (d, J = 7.3 Hz, 1 H), 3.59 (s, 3 H); **$^{13}\text{C NMR}$ (100 MHz, CDCl₃)** δ = 163.0, 135.1, 133.1, 131.8, 131.4, 129.5, 128.8, 127.9, 127.4, 125.8, 124.5, 124.0, 106.0, 36.6; **HRMS (ESI)** calcd for C₁₄H₁₂ON (M⁺ + H) 210.0913, found 210.0910.



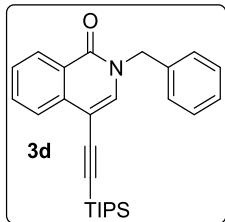
(3a): thick liquid, 48 mg, 92 % yield; $R_f = 0.80$ (pet. ether/EtOAc = 90/10); **1H NMR (400 MHz, CDCl₃)** δ = 8.43 (d, J = 8.3 Hz, 1 H), 8.04 - 7.91 (m, 1 H), 7.80 - 7.68 (m, 1 H), 7.60 - 7.49 (m, 1 H), 7.45 (s, 1 H), 3.63 (s, 3 H), 1.18 (s, 21 H); **13C NMR (100 MHz, CDCl₃)** δ = 161.8, 137.3, 136.3, 132.6, 127.8, 127.4, 125.3, 125.0, 101.5, 100.8, 94.5, 37.2, 18.7, 11.3; **HRMS (ESI)** calcd for C₂₁H₃₀ONSi (M⁺ + H) 340.2091, found 340.2093.



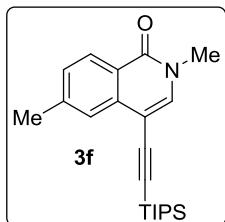
(3b): thick liquid, 43 mg, 88 % yield; $R_f = 0.82$ (pet. ether/EtOAc = 90/10); **1H NMR (400 MHz, CDCl₃)** δ = 8.43 (d, J = 7.8 Hz, 1 H), 7.97 (d, J = 8.3 Hz, 1 H), 7.73 (t, J = 7.6 Hz, 1 H), 7.54 (t, J = 7.8 Hz, 1 H), 7.45 (s, 1 H), 4.08 (q, J = 6.8 Hz, 2 H), 1.41 (t, J = 7.1 Hz, 3 H), 1.18 (s, 21 H); **13C NMR (100 MHz, CDCl₃)** δ = 161.2, 136.2, 132.5, 127.8, 127.3, 125.5, 124.9, 101.7, 100.9, 94.4, 44.7, 18.7, 14.6, 11.3; **HRMS (ESI)** calcd for C₂₂H₃₂ONSi (M⁺ + H) 354.2248, found 354.2249.



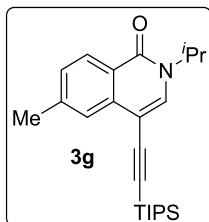
(3c): thick liquid, 40 mg, 86 % yield; $R_f = 0.82$ (pet. ether/EtOAc = 90/10); **1H NMR (400 MHz, CDCl₃)** δ = 8.46 - 8.39 (m, 1 H), 7.99 - 7.92 (m, 1 H), 7.77 - 7.69 (m, 1 H), 7.57 - 7.50 (m, 1 H), 7.42 (s, 1 H), 4.04 - 3.98 (m, 2 H), 1.83 - 1.74 (m, 2 H), 1.46 - 1.39 (m, 2 H), 1.18 (s, 21 H), 0.98 (t, J = 7.3 Hz, 3 H); **13C NMR (100 MHz, CDCl₃)** δ = 161.3, 136.6, 136.2, 132.5, 127.9, 127.3, 125.5, 124.9, 101.4, 101.0, 94.4, 49.5, 31.4, 20.0, 18.7, 13.7, 11.3; **HRMS (ESI)** calcd for C₂₄H₃₆ONSi (M⁺ + H) 382.2561, found 382.2563.



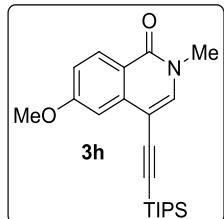
(3d): off white solid, 36 mg, 82 % yield; mp = 88-89 °C; R_f = 0.80 (pet. ether/EtOAc = 90/10); **1H NMR (500 MHz, CDCl₃)** δ = 8.46 (d, J = 7.9 Hz, 1 H), 7.98 (d, J = 7.9 Hz, 1 H), 7.79 - 7.70 (m, 1 H), 7.58 - 7.51 (m, 1 H), 7.46 (s, 1 H), 7.39 - 7.29 (m, 5 H), 5.23 (s, 2 H), 1.16 (s, 21 H); **13C NMR (125 MHz, CDCl₃)** δ = 161.5, 136.4, 136.2, 132.8, 128.9, 128.1, 128.0, 127.9, 127.5, 125.5, 125.0, 102.0, 100.7, 94.7, 52.1, 18.7, 11.3; **HRMS (ESI)** calcd for C₂₇H₃₄ONSi (M⁺ + H) 416.2404, found 416.2407.



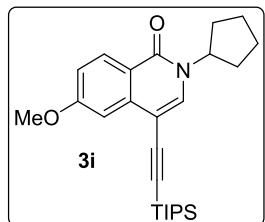
(3f): thick liquid, 46 mg, 90 % yield; R_f = 0.75 (pet. ether/EtOAc = 90/10); **1H NMR (500 MHz, CDCl₃)** δ = 8.30 (d, J = 7.9 Hz, 1 H), 7.77 (s, 1 H), 7.43 (s, 1 H), 7.35 (td, J = 0.8, 8.5 Hz, 1 H), 3.61 (s, 3 H), 2.51 (s, 3 H), 1.18 (s, 21 H); **13C NMR (125 MHz, CDCl₃)** δ = 161.8, 143.1, 137.3, 136.4, 128.9, 127.7, 124.9, 123.0, 101.3, 101.0, 94.4, 37.1, 22.0, 18.7, 11.3; **HRMS (ESI)** calcd for C₂₂H₃₂ONSi (M⁺ + H) 354.2248, found 354.2249.



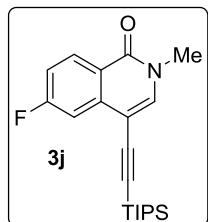
(3g): thick liquid, 40 mg, 86 % yield; R_f = 0.75 (pet. ether/EtOAc = 90/10); **1H NMR (500 MHz, CDCl₃)** δ = 8.32 (d, J = 8.2 Hz, 1 H), 7.78 (s, 1 H), 7.44 (s, 1 H), 7.34 (td, J = 0.8, 8.5 Hz, 1 H), 5.38 (td, J = 6.9, 13.7 Hz, 1 H), 2.51 (s, 3 H), 1.41 (d, J = 6.7 Hz, 6 H), 1.20 (s, 21 H); **13C NMR (125 MHz, CDCl₃)** δ = 161.0, 143.1, 135.8, 131.8, 128.8, 128.0, 124.7, 123.1, 101.5, 101.5, 94.2, 46.3, 22.0, 21.8, 18.7, 11.4; **HRMS (ESI)** calcd for C₂₄H₃₆ONSi (M⁺ + H) 382.2561, found 382.2563.



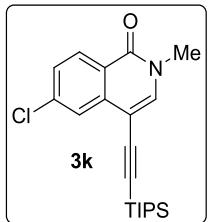
(3h): white solid, 43 mg, 88 % yield; mp = 64-65 °C; R_f = 0.70 (pet. ether/EtOAc = 90/10); **¹H NMR (500 MHz, CDCl₃)** δ = 8.32 (d, J = 8.9 Hz, 1 H), 7.45 (s, 1 H), 7.35 (d, J = 2.4 Hz, 1 H), 7.08 (dd, J = 2.6, 9.0 Hz, 1 H), 3.91 (s, 3 H), 3.60 (s, 3 H), 1.17 (s, 21 H); **¹³C NMR (125 MHz, CDCl₃)** δ = 163.0, 161.5, 138.6, 137.9, 129.7, 119.0, 117.5, 105.4, 101.1, 94.3, 55.4, 37.0, 18.7, 11.3; **HRMS (ESI)** calcd for C₂₂H₃₂O₂NSi (M⁺ + H) 370.2197, found 370.2195.



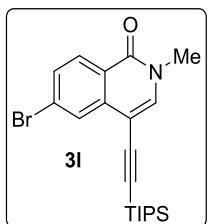
(3i): white solid, 37 mg, 85 % yield; mp = 73-75 °C; R_f = 0.70 (pet. ether/EtOAc = 90/10); **¹H NMR (400 MHz, CDCl₃)** δ = 8.33 (d, J = 9.2 Hz, 1 H), 7.45 (s, 1 H), 7.35 (d, J = 2.7 Hz, 1 H), 7.08 (dd, J = 3.0, 8.9 Hz, 1 H), 5.39 (quin, J = 8.0 Hz, 1 H), 3.91 (s, 3 H), 2.23 - 2.10 (m, 2 H), 1.96 - 1.86 (m, 2 H), 1.81 - 1.70 (m, 4 H), 1.19 (s, 21 H); **¹³C NMR (100 MHz, CDCl₃)** δ = 163.1, 161.2, 138.0, 133.4, 130.1, 119.1, 117.4, 105.3, 101.6, 101.4, 94.1, 56.1, 55.5, 31.9, 24.4, 18.8, 11.3; **HRMS (ESI)** calcd for C₂₆H₃₈O₂NSi (M⁺ + H) 424.2666, found 424.2668.



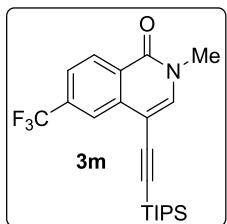
(3j): thick liquid, 13 mg, 40 % yield; R_f = 0.70 (pet. ether/EtOAc = 90/10); **¹H NMR (500 MHz, CDCl₃)** δ = 8.44 (dd, J = 5.8, 8.9 Hz, 1 H), 7.58 (dd, J = 2.4, 9.8 Hz, 1 H), 7.47 (s, 1 H), 7.23 (dt, J = 2.1, 8.5 Hz, 1 H), 3.62 (s, 3 H), 1.17 (s, 21 H); **¹³C NMR (125 MHz, CDCl₃)** δ = 166.5 (d, J = 253.6 Hz), 161.1, 138.9, 138.4, 131.1 (d, J = 9.5 Hz), 121.9, 116.2 (d, J = 23.8 Hz), 110.4 (d, J = 22.8 Hz), 101.0 (d, J = 2.8 Hz), 95.1, 37.2, 18.7, 11.3; **HRMS (ESI)** calcd for C₂₁H₂₉ONFSi (M⁺ + H) 358.1997, found 358.1993.



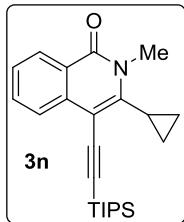
(3k): light yellow solid, 20 mg, 42 % yield; mp = 96-97 °C; R_f = 0.70 (pet. ether/EtOAc = 90/10); **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ = 8.35 (d, J = 8.3 Hz, 1 H), 7.96 (d, J = 2.0 Hz, 1 H), 7.56 - 7.42 (m, 2 H), 3.61 (s, 3 H), 1.18 (s, 21 H); **$^{13}\text{C NMR}$ (100 MHz, CDCl_3)** δ = 161.2, 139.4, 138.3, 137.7, 129.6, 128.0, 124.7, 123.6, 100.7, 100.0, 95.4, 37.2, 18.7, 11.3; **HRMS (ESI)** calcd for $\text{C}_{21}\text{H}_{29}\text{ONFSi}$ ($\text{M}^+ + \text{H}$) 374.1701, found 374.1704.



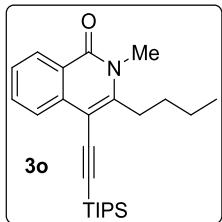
(3l): light brown solid, 28 mg, 64 % yield; mp = 105-106 °C; R_f = 0.75 (pet. ether/EtOAc = 90/10); **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ = 8.27 (d, J = 8.3 Hz, 1 H), 8.21 - 8.03 (m, 1 H), 7.63 (dd, J = 2.0, 8.8 Hz, 1 H), 7.46 (s, 1 H), 3.61 (s, 3 H), 1.18 (s, 21 H); **$^{13}\text{C NMR}$ (100 MHz, CDCl_3)** δ = 161.3, 138.2, 137.9, 130.7, 129.6, 128.1, 127.9, 123.9, 100.6, 100.0, 95.5, 37.3, 18.7, 11.3; **HRMS (ESI)** calcd for $\text{C}_{21}\text{H}_{29}\text{ONBrSi}$ ($\text{M}^+ + \text{H}$) 418.1196, found 418.1197.



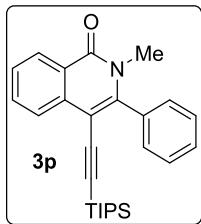
(3m): light yellow solid, 26 mg, 58 % yield; mp = 89-90 °C; R_f = 0.75 (pet. ether/EtOAc = 90/10); **$^1\text{H NMR}$ (500 MHz, CDCl_3)** δ = 8.54 (d, J = 8.5 Hz, 1 H), 8.31 (s, 1 H), 7.78 - 7.67 (m, 1 H), 7.53 (s, 1 H), 3.65 (s, 3 H), 1.18 (s, 21 H); **$^{13}\text{C NMR}$ (125 MHz, CDCl_3)** δ = 161.0, 138.1, 136.5, 134.3 (d, J = 32.4 Hz), 134.0, 128.9, 127.3, 124.7, 123.5 (d, J = 2.8 Hz), 122. (d, J = 3.8 Hz), 101.4, 99.6, 96.1, 37.4, 18.6, 11.2; **HRMS (ESI)** calcd for $\text{C}_{22}\text{H}_{29}\text{ONF}_3\text{Si}$ ($\text{M}^+ + \text{H}$) 408.1965, found 408.1964.



(3n): white solid, 43 mg, 90 % yield; mp = 75-76 °C; R_f = 0.80 (pet. ether/EtOAc = 90/10); **^1H NMR (400 MHz, CDCl_3)** δ = 8.39 (d, J = 8.1 Hz, 1 H), 8.08 (d, J = 8.1 Hz, 1 H), 7.69 (t, J = 7.7 Hz, 1 H), 7.48 (t, J = 7.6 Hz, 1 H), 3.81 (s, 3 H), 2.02 - 1.93 (m, 1 H), 1.23 (d, J = 4.9 Hz, 2 H), 1.20 (s, 21 H), 1.12 (q, J = 5.7 Hz, 2 H); **^{13}C NMR (100 MHz, CDCl_3)** δ = 162.3, 148.1, 136.2, 132.5, 127.6, 126.8, 124.6, 124.0, 102.6, 101.2, 99.6, 32.0, 18.8, 14.2, 11.4, 10.2; **HRMS (ESI)** calcd for $\text{C}_{24}\text{H}_{34}\text{ONSi}$ ($\text{M}^+ + \text{H}$) 380.2404, found 380.2303.

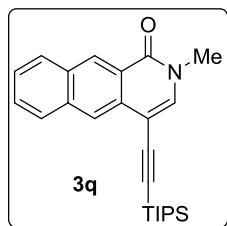


(3o): white solid, 38 mg, 85 % yield; mp = 91-92 °C; R_f = 0.82 (pet. ether/EtOAc = 90/10); **^1H NMR (500 MHz, CDCl_3)** δ = 8.43 - 8.34 (m, 1 H), 8.01 (d, J = 7.9 Hz, 1 H), 7.70 (dt, J = 1.4, 7.6 Hz, 1 H), 7.50 - 7.41 (m, 1 H), 3.68 (s, 3 H), 3.14 - 3.04 (m, 2 H), 1.68 (td, J = 7.9, 15.9 Hz, 2 H), 1.51 (qd, J = 7.4, 14.9 Hz, 2 H), 1.22 - 1.14 (m, 21 H), 0.99 (t, J = 7.3 Hz, 3 H); **^{13}C NMR (125 MHz, CDCl_3)** δ = 162.5, 149.3, 136.0, 132.6, 127.8, 126.5, 124.6, 123.5, 101.7, 100.4, 97.1, 32.7, 31.5, 30.6, 22.9, 18.8, 13.9, 11.4; **HRMS (ESI)** calcd for $\text{C}_{25}\text{H}_{38}\text{ONSi}$ ($\text{M}^+ + \text{H}$) 396.2717, found 396.2713.

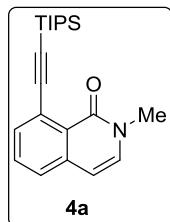


(3p): white solid, 38 mg, 88 % yield; mp = 100-101 °C; R_f = 0.80 (pet. ether/EtOAc = 90/10); **^1H NMR (500 MHz, CDCl_3)** δ = 8.48 (d, J = 7.8 Hz, 1 H), 8.08 (d, J = 8.3 Hz, 1 H), 7.80 - 7.68 (m, 1 H), 7.55 (t, J = 7.6 Hz, 1 H), 7.52 - 7.44 (m, 3 H), 7.44 - 7.35 (m, 2 H), 3.35 (s, 3 H), 0.95 (s, 21 H); **^{13}C NMR (125 MHz, CDCl_3)** δ = 162.3, 148.1, 135.9, 135.3, 132.7, 129.2, 129.1, 128.8,

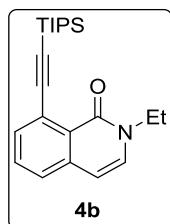
127.8, 127.2, 125.2, 124.4, 101.8, 101.4, 97.1, 34.5, 18.5, 11.1; **HRMS (ESI)** calcd for C₂₇H₃₄ONSi (M⁺ + H) 416.2404, found 416.2404.



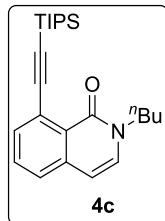
(3q): light yellow solid, 35 mg, 76 % yield; mp = 86-87 °C; R_f = 0.60 (pet. ether/EtOAc = 90/10); **¹H NMR (500 MHz, CDCl₃)** δ = 9.03 (s, 1 H), 8.45 (s, 1 H), 8.08 (d, J = 8.5 Hz, 1 H), 7.96 (d, J = 8.5 Hz, 1 H), 7.65 - 7.59 (m, 1 H), 7.58 - 7.51 (m, 1 H), 7.41 (s, 1 H), 3.64 (s, 3 H), 1.25 - 1.19 (m, 21 H); **¹³C NMR (125 MHz, CDCl₃)** δ = 162.4, 136.4, 135.1, 132.1, 132.0, 129.4, 129.1, 128.3, 128.0, 126.3, 124.0, 123.5, 101.5, 101.2, 94.6, 36.9, 18.8, 11.4; **HRMS (ESI)** calcd for C₂₅H₃₂ONSi (M⁺ + H) 390.2248, found 390.2247.



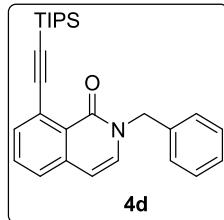
(4a): white solid, 46 mg, 88 % yield; mp = 84-86 °C; R_f = 0.80 (pet. ether/EtOAc = 85/15); **¹H NMR (400 MHz, CDCl₃)** δ = 7.69 - 7.63 (m, 1 H), 7.48 (t, J = 7.8 Hz, 1 H), 7.42 - 7.34 (m, 1 H), 7.04 (d, J = 7.3 Hz, 1 H), 6.36 (d, J = 6.9 Hz, 1 H), 3.56 (s, 3 H), 1.21 - 1.18 (m, 21 H); **¹³C NMR (100 MHz, CDCl₃)** δ = 161.3, 138.3, 135.0, 133.0, 130.7, 126.0, 126.0, 123.8, 107.0, 105.3, 97.6, 37.3, 18.8, 11.5; **HRMS (ESI)** calcd for C₂₁H₃₀ONSi (M⁺ + H) 340.2091, found 340.2092.



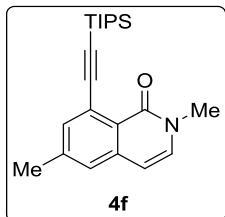
(4b): white solid, 42 mg, 86 % yield; mp = 73-74 °C; R_f = 0.80 (pet. ether/EtOAc = 85/15); **$^1\text{H NMR}$** (**500 MHz, CDCl₃**) δ = 7.66 (dd, J = 1.5, 7.6 Hz, 1 H), 7.48 (t, J = 7.6 Hz, 1 H), 7.39 (dd, J = 1.5, 7.9 Hz, 1 H), 7.05 (d, J = 7.0 Hz, 1 H), 6.38 (d, J = 7.3 Hz, 1 H), 4.03 (q, J = 7.3 Hz, 2 H), 1.36 (t, J = 7.2 Hz, 3 H), 1.22 - 1.17 (m, 21 H); **$^{13}\text{C NMR}$** (**125 MHz, CDCl₃**) δ = 160.5, 138.2, 135.0, 131.7, 130.6, 126.3, 126.0, 123.9, 107.1, 105.4, 97.6, 43.9, 18.8, 14.5, 11.5; **HRMS (ESI)** calcd for C₂₂H₃₁ONSi (M⁺ + H) 354.2248 found 354.2248.



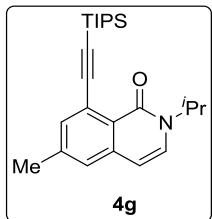
(4c): thick liquid, 36 mg, 78 % yield; R_f = 0.80 (pet. ether/EtOAc = 90/10); **$^1\text{H NMR}$** (**500 MHz, CDCl₃**) δ = 7.65 (dd, J = 1.4, 7.5 Hz, 1 H), 7.47 (t, J = 7.6 Hz, 1 H), 7.38 (dd, J = 1.5, 7.9 Hz, 1 H), 7.03 (d, J = 7.3 Hz, 1 H), 6.35 (d, J = 7.0 Hz, 1 H), 3.96 (t, J = 7.3 Hz, 2 H), 1.78 - 1.71 (m, 2 H), 1.44 - 1.34 (m, 2 H), 1.22 - 1.18 (m, 21 H), 0.96 (t, J = 7.3 Hz, 3 H); **$^{13}\text{C NMR}$** (**125 MHz, CDCl₃**) δ = 160.6, 138.2, 134.8, 132.3, 130.6, 126.4, 125.9, 123.9, 107.1, 104.9, 97.6, 48.8, 31.2, 19.9, 18.8, 13.7, 11.5; **HRMS (ESI)** calcd for C₂₄H₃₆ONSi (M⁺ + H) 382.2561 found 382.2562.



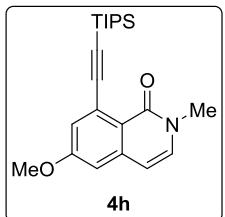
(4d): white solid, 36 mg, 82 % yield; mp = 74-75 °C; R_f = 0.90 (pet. ether/EtOAc = 90/10); **$^1\text{H NMR}$** (**400 MHz, CDCl₃**) δ = 7.67 (d, J = 7.3 Hz, 1 H), 7.48 (t, J = 7.8 Hz, 1 H), 7.40 - 7.22 (m, 6 H), 7.02 (d, J = 7.3 Hz, 1 H), 6.33 (d, J = 7.3 Hz, 1 H), 5.19 (s, 2 H), 1.22 (s, 21 H); **$^{13}\text{C NMR}$** (**100 MHz, CDCl₃**) δ = 160.7, 138.1, 137.0, 134.9, 131.7, 130.8, 128.7, 128.5, 127.7, 126.4, 126.0, 124.2, 107.0, 105.5, 97.9, 51.3, 18.8, 11.5; **HRMS (ESI)** calcd for C₂₇H₃₄ONSi (M⁺ + H) 416.2404, found 416.2404.



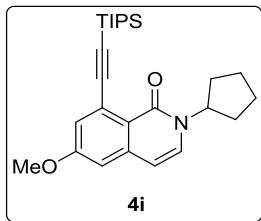
(4f): white solid, 46 mg, 90 % yield; mp = 85-86 °C; R_f = 0.85 (pet. ether/EtOAc = 90/10); **¹H NMR (400 MHz, CDCl₃)** δ = 7.49 - 7.44 (m, 1 H), 7.20 - 7.15 (m, 1 H), 7.00 (d, J = 7.3 Hz, 1 H), 6.29 (d, J = 7.3 Hz, 1 H), 3.54 (s, 3 H), 2.41 (s, 3 H), 1.22 - 1.19 (m, 21 H); **¹³C NMR (100 MHz, CDCl₃)** δ = 161.3, 141.0, 138.5, 136.3, 133.1, 126.1, 123.9, 123.6, 107.1, 105.1, 96.8, 37.1, 21.2, 18.8, 11.5; **HRMS (ESI)** calcd for C₂₂H₃₂ONSi (M⁺ + H) 354.2248 found 354.2248.



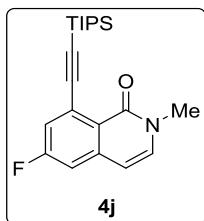
(4g): light yellow solid, 39 mg, 83 % yield; mp = 77-78 °C; R_f = 0.80 (pet. ether/EtOAc = 90/10); **¹H NMR (500 MHz, CDCl₃)** δ = 7.49 - 7.42 (m, 1 H), 7.16 (s, 1 H), 7.06 (d, J = 7.6 Hz, 1 H), 6.34 (d, J = 7.3 Hz, 1 H), 5.41 (td, J = 6.9, 13.7 Hz, 1 H), 2.40 (s, 3 H), 1.33 (d, J = 7.0 Hz, 6 H), 1.22 - 1.18 (m, 21 H); **¹³C NMR (125 MHz, CDCl₃)** δ = 160.2, 140.9, 137.7, 136.3, 127.3, 126.0, 124.1, 123.9, 107.4, 105.3, 96.8, 44.8, 21.9, 21.1, 18.8, 11.5; **HRMS (ESI)** calcd for C₂₄H₃₆ONSi (M⁺ + H) 382.2561, found 382.2562.



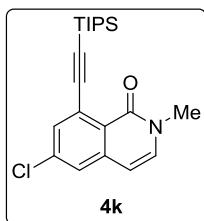
(4h): light yellow solid, 40 mg, 82 % yield; mp = 120-121 °C; R_f = 0.80 (pet. ether/EtOAc = 90/10); **¹H NMR (500 MHz, CDCl₃)** δ = 7.23 (d, J = 2.7 Hz, 1 H), 7.01 (d, J = 7.0 Hz, 1 H), 6.78 (d, J = 2.7 Hz, 1 H), 6.28 (d, J = 7.3 Hz, 1 H), 3.88 (s, 3 H), 3.53 (s, 3 H), 1.21 - 1.18 (m, 21 H); **¹³C NMR (125 MHz, CDCl₃)** δ = 161.1, 160.8, 140.3, 133.6, 125.6, 123.7, 120.1, 107.6, 106.6, 105.0, 97.3, 55.4, 37.1, 18.8, 11.5; **HRMS (ESI)** calcd for C₂₂H₃₂O₂NSi (M⁺ + H) 370.2197, found 370.2195.



(4i): light yellow solid, 37 mg, 85 % yield; mp = 94-95 °C; R_f = 0.82 (pet. ether/EtOAc = 90/10); **$^1\text{H NMR}$ (500 MHz, CDCl_3)** δ = 7.22 (d, J = 2.4 Hz, 1 H), 7.06 (d, J = 7.3 Hz, 1 H), 6.77 (d, J = 2.7 Hz, 1 H), 6.33 (d, J = 7.6 Hz, 1 H), 5.48 (quin, J = 8.3 Hz, 1 H), 3.88 (s, 3 H), 2.22 - 2.13 (m, 2 H), 1.90 - 1.79 (m, 2 H), 1.75 - 1.69 (m, 3 H), 1.65 - 1.56 (m, 2 H), 1.21 - 1.17 (m, 21 H); **$^{13}\text{C NMR}$ (125 MHz, CDCl_3)** δ = 160.7, 160.6, 139.5, 128.9, 125.9, 123.7, 120.1, 107.4, 107.0, 105.4, 97.3, 55.4, 54.6, 32.2, 24.7, 18.8, 11.5; **HRMS (ESI)** calcd for $\text{C}_{26}\text{H}_{38}\text{O}_2\text{NSi}$ ($\text{M}^+ + \text{H}$) 424.2666, found 424.2668.

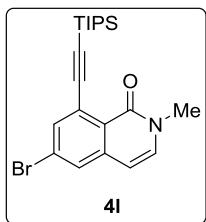


(4j): white solid, 32 mg, 64 % yield; mp = 78-79 °C; R_f = 0.75 (pet. ether/EtOAc = 90/10); **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ = 7.34 (dd, J = 2.7, 9.0 Hz, 1 H), 7.11 - 6.98 (m, 2 H), 6.30 (d, J = 7.3 Hz, 1 H), 3.55 (s, 3 H), 1.20 (s, 21 H); **$^{13}\text{C NMR}$ (100 MHz, CDCl_3)** δ = 164.5 (d, J = 252.0 Hz), 160.7, 140.6 (d, J = 10.8 Hz), 134.2, 127.0 (d, J = 10.8 Hz), 122.9, 122.7 (d, J = 24.7 Hz), 111.3 (d, J = 21.6 Hz), 105.6, 104.7 (d, J = 3.1 Hz), 99.4, 37.2, 18.7, 11.4; **HRMS (ESI)** calcd for $\text{C}_{21}\text{H}_{29}\text{OFNSi}$ ($\text{M}^+ + \text{H}$) 358.1997, found 358.1197.

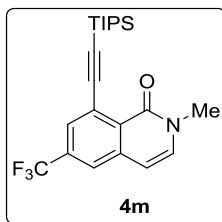


(4k): light yellow solid, 35 mg, 73 % yield; mp = 107-108 °C; R_f = 0.70 (pet. ether/EtOAc = 90/10); **$^1\text{H NMR}$ (500 MHz, CDCl_3)** δ = 7.57 (d, J = 2.1 Hz, 1 H), 7.38 (d, J = 2.4 Hz, 1 H), 7.08 (d, J = 7.3 Hz, 1 H), 6.29 (d, J = 7.3 Hz, 1 H), 3.55 (s, 3 H), 1.21 - 1.18 (m, 21 H); **$^{13}\text{C NMR}$ (125 MHz, CDCl_3)** δ = 160.8, 139.5, 136.8, 134.4, 134.3, 125.8, 125.2, 124.4, 105.5,

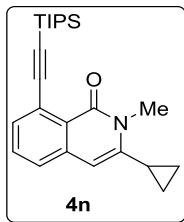
104.3, 99.5, 37.3, 18.8, 11.4; **HRMS (ESI)** calcd for C₂₁H₂₉OClNSi (M⁺ + H) 374.1701, found 374.1706.



(4l): light Brown solid, 35 mg, 82 % yield; mp = 68-69 °C; R_f = 0.70 (pet. ether/EtOAc = 90/10); **¹H NMR (500 MHz, CDCl₃)** δ = 7.78 (s, 1 H), 7.64 (s, 1 H), 7.14 (d, J = 7.3 Hz, 1 H), 6.42 (d, J = 7.3 Hz, 1 H), 3.58 (s, 3 H), 1.23 - 1.18 (m, 21 H); **¹³C NMR (125 MHz, CDCl₃)** δ = 160.5, 138.5, 134.5, 132.8, 130.3, 130.2, 127.9, 125.3, 122.7, 122.7, 105.5, 104.8, 100.1, 37.4, 18.7, 11.5; **HRMS (ESI)** calcd for C₂₁H₂₉OBrNSi (M⁺ + H) 418.1196, found 418.1197.

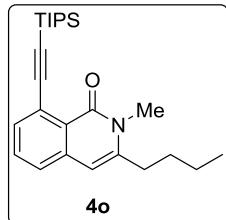


(4m): light yellow solid, 36 mg, 83 % yield; mp = 72-74 °C; R_f = 0.70 (pet. ether/EtOAc = 90/10); **¹H NMR (400 MHz, CDCl₃)** δ = 7.72 (d, J = 2.0 Hz, 1 H), 7.57 - 7.51 (m, 1 H), 7.07 (d, J = 7.3 Hz, 1 H), 6.27 (d, J = 7.3 Hz, 1 H), 3.55 (s, 3 H), 1.20 (s, 21 H); **¹³C NMR (100 MHz, CDCl₃)** δ = 160.8, 139.6, 137.0, 134.3, 128.4, 125.9, 125.2(d, J = 43.1 Hz), 124.8, 123.9, 105.4, 104.1, 99.6, 37.3, 18.8, 11.5; **HRMS (ESI)** calcd for C₂₂H₂₉OF₃NSi (M⁺ + H) 408.1965, found 408.1961.

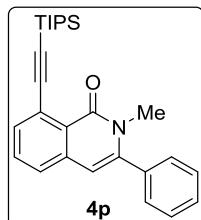


(4n): white solid, 39 mg, 83 % yield; mp = 71-72 °C; R_f = 0.82 (pet. ether/EtOAc = 90/10); **¹H NMR (400 MHz, CDCl₃)** δ = 7.60 (d, J = 7.3 Hz, 1 H), 7.48 - 7.38 (m, 1 H), 7.31 (d, J = 7.8 Hz, 1 H), 6.21 (s, 1 H), 3.75 (s, 3 H), 1.89 - 1.78 (m, 1 H), 1.20 (s, 22 H), 1.07 - 0.97 (m, 2 H), 0.76

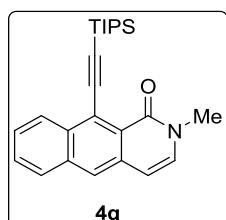
(q, $J = 5.2$ Hz, 2 H); **^{13}C NMR (100 MHz, CDCl_3)** δ = 162.0, 145.0, 137.7, 134.3, 130.6, 125.6, 124.3, 123.8, 107.3, 103.6, 97.3, 30.9, 18.8, 14.4, 11.5, 6.6; **HRMS (ESI)** calcd for $\text{C}_{24}\text{H}_{34}\text{ONSi} (\text{M}^+ + \text{H})$ 380.2404, found 380.2405.



(4o): white solid, 40 mg, 88 % yield; mp = 71-72 °C; R_f = 0.82 (pet. ether/EtOAc = 90/10); **^1H NMR (400 MHz, CDCl_3)** δ = 7.60 (d, $J = 7.3$ Hz, 1 H), 7.44 (t, $J = 7.6$ Hz, 1 H), 7.32 (d, $J = 7.8$ Hz, 1 H), 6.22 (s, 1 H), 3.57 (s, 3 H), 2.62 (dd, $J = 7.3, 8.3$ Hz, 2 H), 1.67 - 1.58 (m, 2 H), 1.50 - 1.39 (m, 2 H), 1.21 (s, 21 H), 1.01 - 0.93 (t, 3 H); **^{13}C NMR (100 MHz, CDCl_3)** δ = 162.2, 144.1, 137.7, 134.1, 130.7, 125.4, 124.1, 123.8, 107.3, 104.2, 97.2, 33.4, 30.8, 30.3, 22.3, 18.8, 13.8, 11.5; **HRMS (ESI)** calcd for $\text{C}_{25}\text{H}_{37}\text{ONSi} (\text{M}^+ + \text{H})$ 396.2644, found 396.2647.

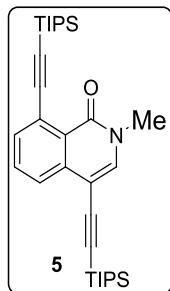


(4p): white solid, 37 mg, 86 % yield; mp = 94-95 °C; R_f = 0.80 (pet. ether/EtOAc = 90/10); **^1H NMR (500 MHz, CDCl_3)** δ = 7.68 (dd, $J = 1.4, 7.5$ Hz, 1 H), 7.52 - 7.45 (m, 4 H), 7.41 - 7.35 (m, 3 H), 6.35 (s, 1 H), 3.40 (s, 3 H), 1.23 - 1.19 (m, 21 H); **^{13}C NMR (125 MHz, CDCl_3)** δ = 162.0, 144.6, 137.5, 136.1, 134.8, 130.9, 128.9, 128.6, 128.6, 126.0, 124.7, 123.9, 107.1, 106.8, 97.6, 34.3, 18.8, 11.5; **HRMS (ESI)** calcd for $\text{C}_{27}\text{H}_{34}\text{ONSi} (\text{M}^+ + \text{H})$ 416.2404, found 416.2401.

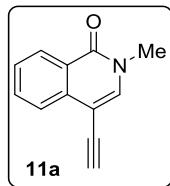


(4q): yellow solid, 36 mg, 79 % yield; mp = 154-155 °C; R_f = 0.60 (pet. ether/EtOAc = 80/20); **^1H NMR (500 MHz, CDCl_3)** δ = 8.88 - 8.80 (m, 1 H), 7.90 - 7.86 (m, 2 H), 7.61 - 7.55 (m, 2 H),

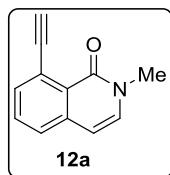
6.98 (d, $J = 7.3$ Hz, 1 H), 6.48 (d, $J = 7.6$ Hz, 1 H), 3.58 (s, 3 H), 1.30 - 1.25 (m, 21 H); **^{13}C NMR (125 MHz, CDCl₃)** δ = 161.9, 134.1, 134.0, 134.0, 131.9, 128.0, 127.9, 127.8, 126.6, 126.0, 124.7, 122.4, 106.3, 105.3, 104.0, 37.0, 18.9, 11.6; **HRMS (ESI)** calcd for C₂₅H₃₂ONSi (M⁺ + H) 390.2248, found 390.2245.



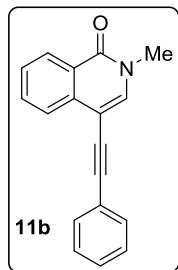
(5): white solid, 28 mg, 75 % yield; mp = 95-96 °C; R_f = 0.80 (pet. ether/EtOAc = 95/05); **^1H NMR (500 MHz, CDCl₃)** δ = 7.95 - 7.88 (m, 1 H), 7.75 - 7.68 (m, 1 H), 7.59 (t, $J = 7.8$ Hz, 1 H), 7.44 (s, 1 H), 3.58 (s, 3 H), 1.22 - 1.18 (m, 21 H), 1.18 - 1.14 (m, 21 H); **^{13}C NMR (125 MHz, CDCl₃)** δ = 160.4, 138.2, 137.4, 137.4, 135.7, 131.2, 125.2, 125.1, 124.0, 106.7, 101.0, 100.5, 98.2, 94.4, 37.4, 18.8, 18.7, 11.5, 11.3; **HRMS (ESI)** calcd for C₃₂H₅₀ONSi₂ (M⁺ + H) 520.3425, found 520.3422.



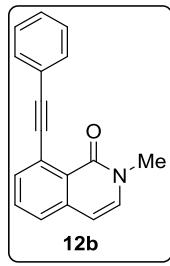
(11a): white solid, 23 mg, 91 % yield; mp = 98-99 °C; R_f = 0.40 (pet. ether/EtOAc = 40/60); **^1H NMR (500 MHz, CDCl₃)** δ = 8.43 (d, $J = 7.9$ Hz, 1 H), 7.95 (d, $J = 7.9$ Hz, 1 H), 7.74 (t, $J = 7.6$ Hz, 1 H), 7.55 (t, $J = 7.5$ Hz, 1 H), 7.46 (s, 1 H), 3.62 (s, 3 H), 3.30 (s, 1 H); **^{13}C NMR (125 MHz, CDCl₃)** δ = 161.8, 137.7, 136.0, 132.6, 127.8, 127.6, 125.3, 124.8, 99.9, 80.8, 78.0, 37.3; **HRMS (ESI)** calcd for C₁₂H₁₀ON (M⁺ + H) 184.0757, found 184.0753.



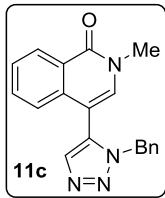
(12a): white solid, 22 mg, 88 % yield; mp = 102-104 °C; R_f = 0.45 (pet. ether/EtOAc = 30/70); **$^1\text{H NMR}$ (500 MHz, CDCl_3)** δ = 7.68 (dd, J = 1.2, 7.3 Hz, 1 H), 7.58 - 7.50 (m, 1 H), 7.49 - 7.40 (m, 1 H), 7.16 - 6.99 (m, 1 H), 6.48 - 6.32 (m, 1 H), 3.58 (s, 3 H), 3.57 (s, 1 H); **$^{13}\text{C NMR}$ (125 MHz, CDCl_3)** δ = 161.4, 138.4, 134.6, 133.1, 131.0, 126.7, 126.1, 122.4, 105.6, 83.5, 82.8, 37.3; **HRMS (ESI)** calcd for $\text{C}_{12}\text{H}_{10}\text{ON}$ ($\text{M}^+ + \text{H}$) 184.0757, found 184.0754.



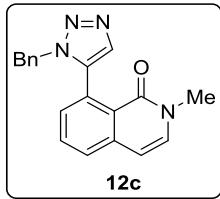
(11b): off white solid, 31 mg, 91 % yield; mp = 122-123 °C; R_f = 0.40 (pet. ether/EtOAc = 40/60); **$^1\text{H NMR}$ (500 MHz, CDCl_3)** δ = 8.48 - 8.39 (m, 1 H), 8.02 (d, J = 8.2 Hz, 1 H), 7.79 - 7.70 (m, 1 H), 7.60 - 7.52 (m, 3 H), 7.50 (s, 1 H), 7.41 - 7.34 (m, 3 H), 3.64 (s, 3 H); **$^{13}\text{C NMR}$ (125 MHz, CDCl_3)** δ = 161.8, 136.6, 136.1, 132.5, 131.4, 128.4, 128.3, 127.7, 127.5, 125.3, 124.9, 123.0, 101.1, 92.9, 83.4, 37.2; **HRMS (ESI)** calcd for $\text{C}_{18}\text{H}_{14}\text{ON}$ ($\text{M}^+ + \text{H}$) 260.1070, found 260.1064.



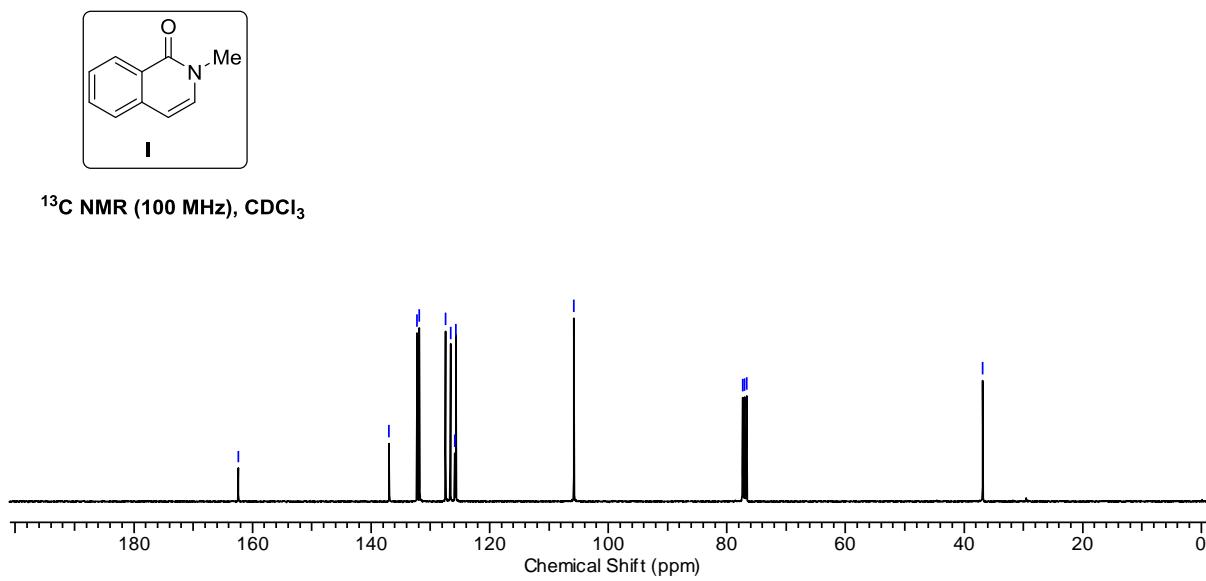
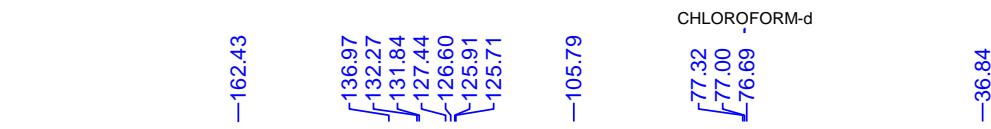
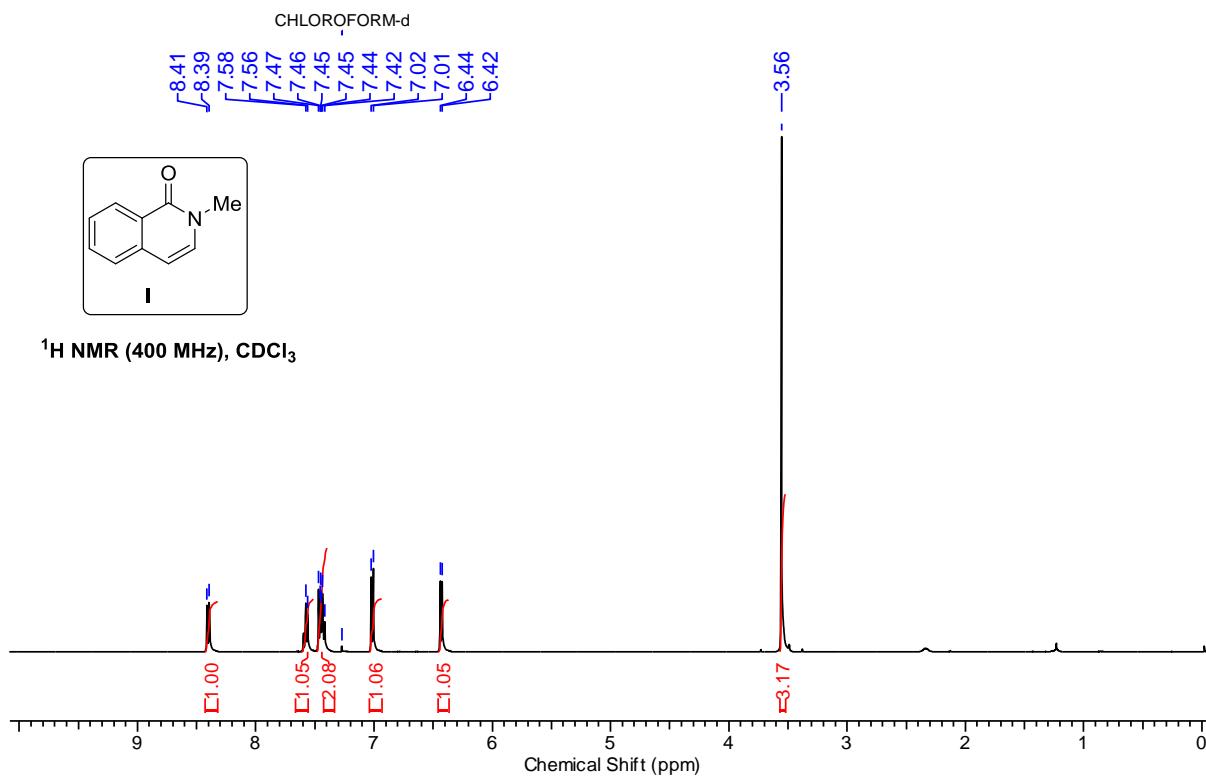
(12b): off white solid, 30 mg, 90 % yield; mp = 109-110 °C; R_f = 0.40 (pet. ether/EtOAc = 50/50); **$^1\text{H NMR}$ (500 MHz, CDCl_3)** δ = 7.74 - 7.64 (m, 3 H), 7.55 (t, J = 7.8 Hz, 1 H), 7.44 (dd, J = 1.1, 8.0 Hz, 1 H), 7.40 - 7.29 (m, 3 H), 7.10 (d, J = 7.3 Hz, 1 H), 6.44 (d, J = 6.9 Hz, 1 H), 3.62 (s, 3 H); **$^{13}\text{C NMR}$ (125 MHz, CDCl_3)** δ = 161.7, 138.6, 133.7, 133.1, 131.9, 131.0, 128.2, 128.2, 126.1, 125.7, 123.8, 123.7, 105.7, 95.0, 90.0, 37.4; **HRMS (ESI)** calcd for $\text{C}_{18}\text{H}_{14}\text{ON}$ ($\text{M}^+ + \text{H}$) 260.1070, found 260.1065.

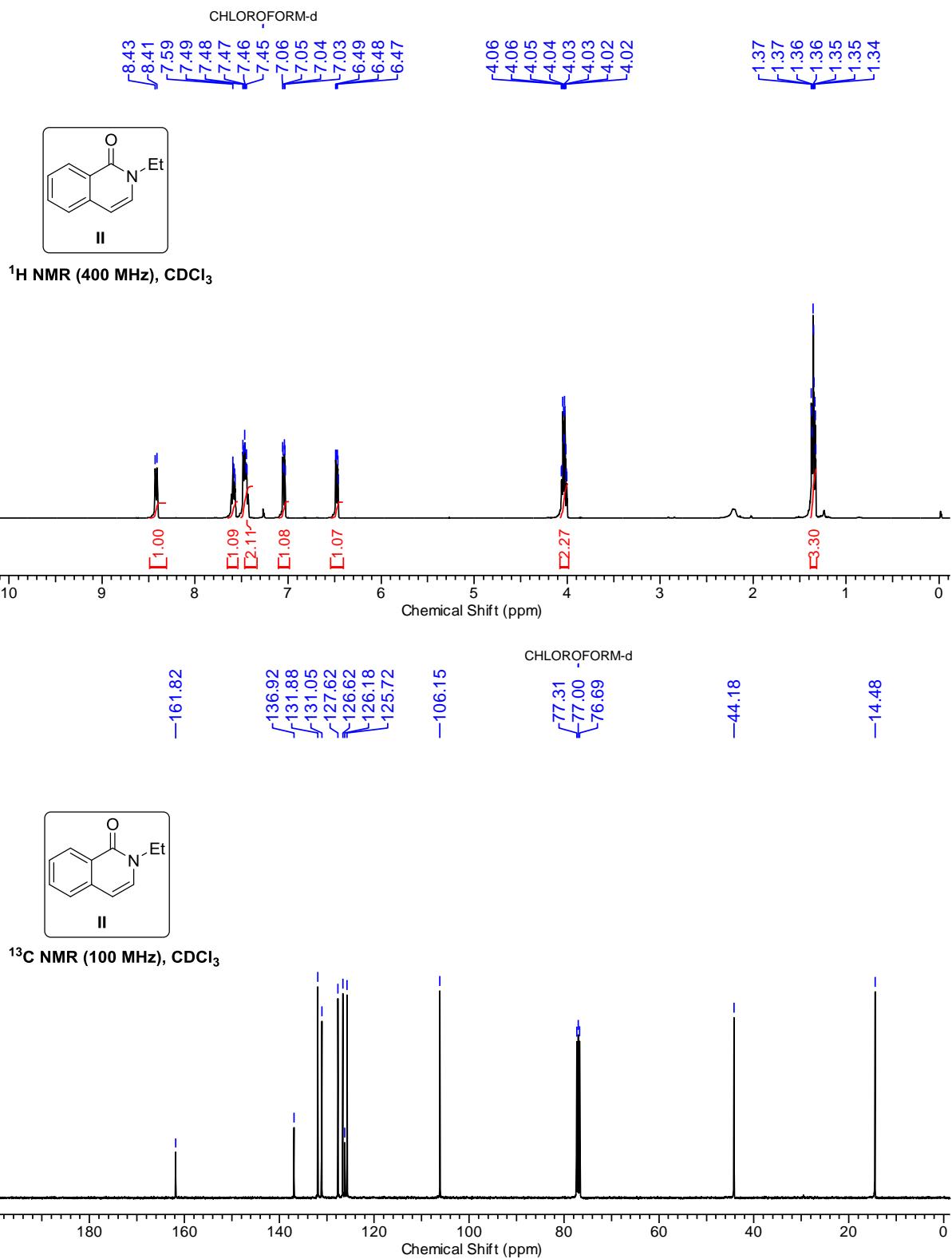


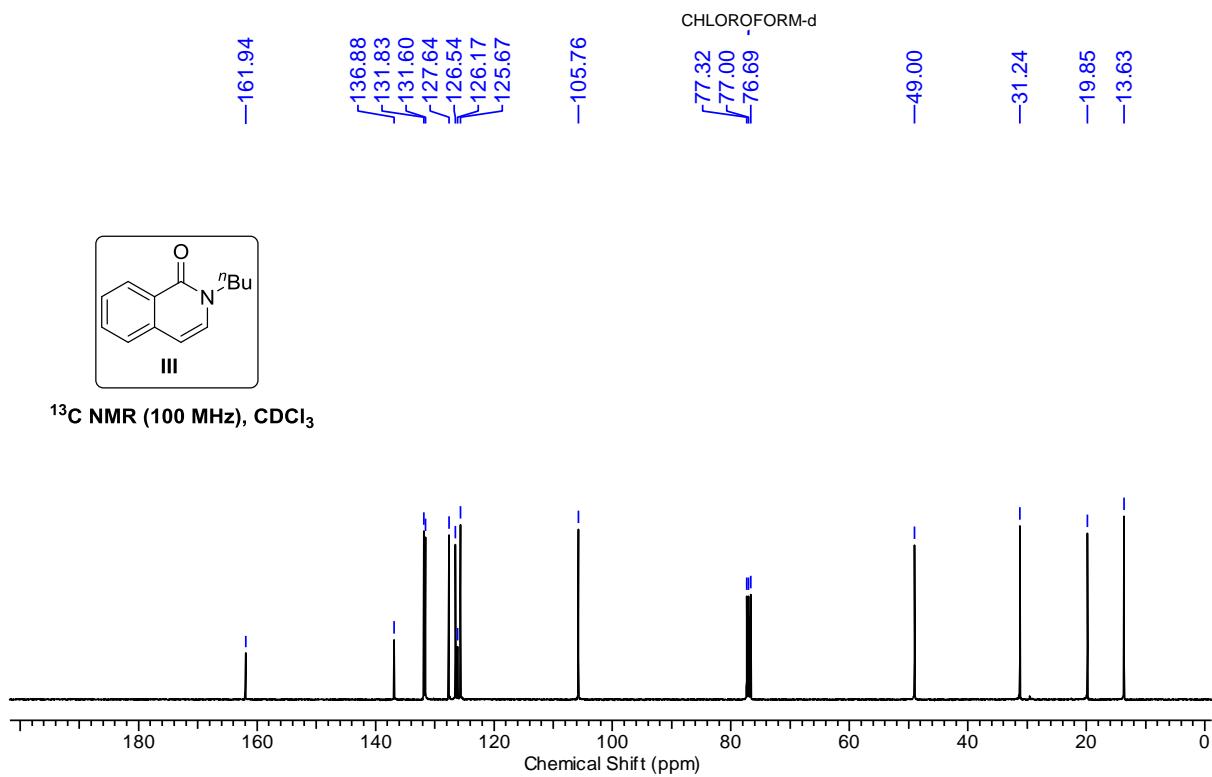
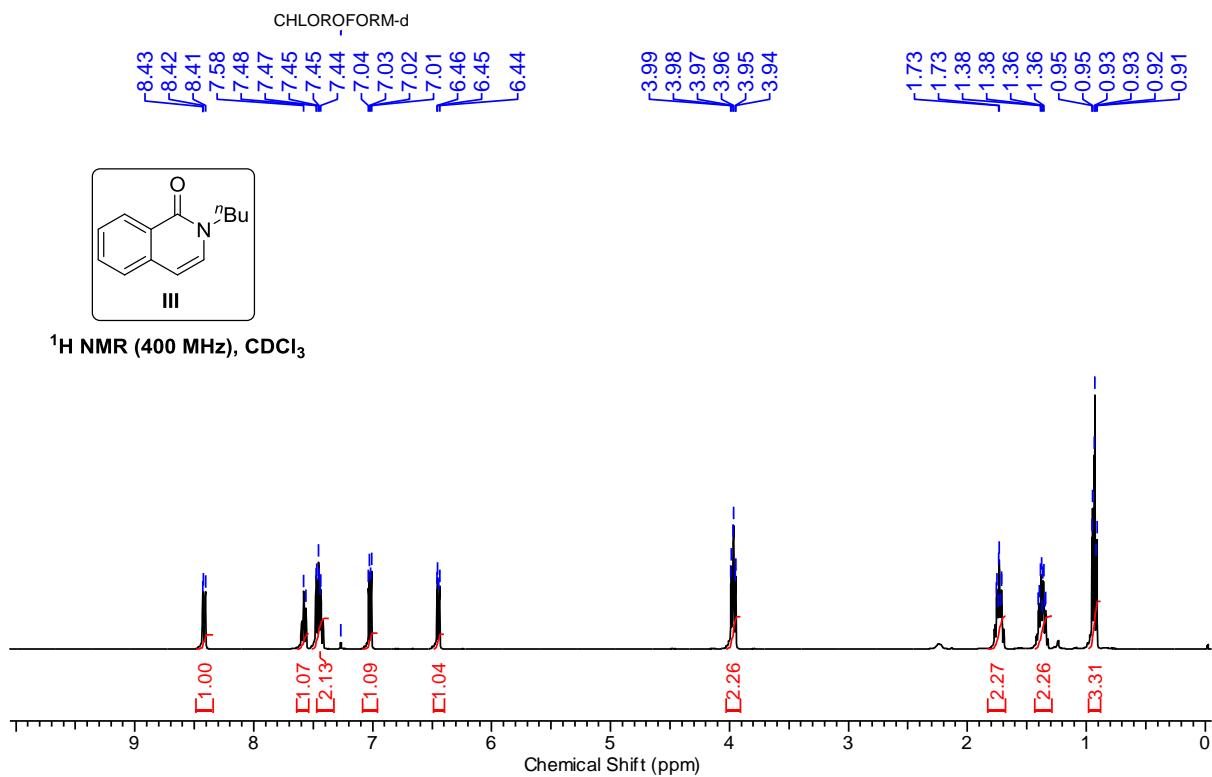
(11c): white solid, 39 mg, 88 % yield; mp = 215-217 °C; R_f = 0.30 (pet. ether/EtOAc = 30/70); **$^1\text{H NMR}$ (500 MHz, CDCl_3)** δ = 7.74 - 7.64 (m, 3 H), 7.55 (t, J = 7.8 Hz, 1 H), 7.44 (dd, J = 1.1, 8.0 Hz, 1 H), 7.40 - 7.29 (m, 3 H), 7.10 (d, J = 7.3 Hz, 1 H), 6.44 (d, J = 6.9 Hz, 1 H), 3.62 (s, 3 H); **$^{13}\text{C NMR}$ (125 MHz, CDCl_3)** δ = 161.7, 138.6, 133.7, 133.1, 131.9, 131.0, 128.2, 128.2, 126.1, 125.7, 123.8, 123.7, 105.7, 95.0, 90.0, 37.4; **HRMS (ESI)** calcd for $\text{C}_{19}\text{H}_{17}\text{ON}_4$ ($\text{M}^+ + \text{H}$) 317.1397, found 317.1394.

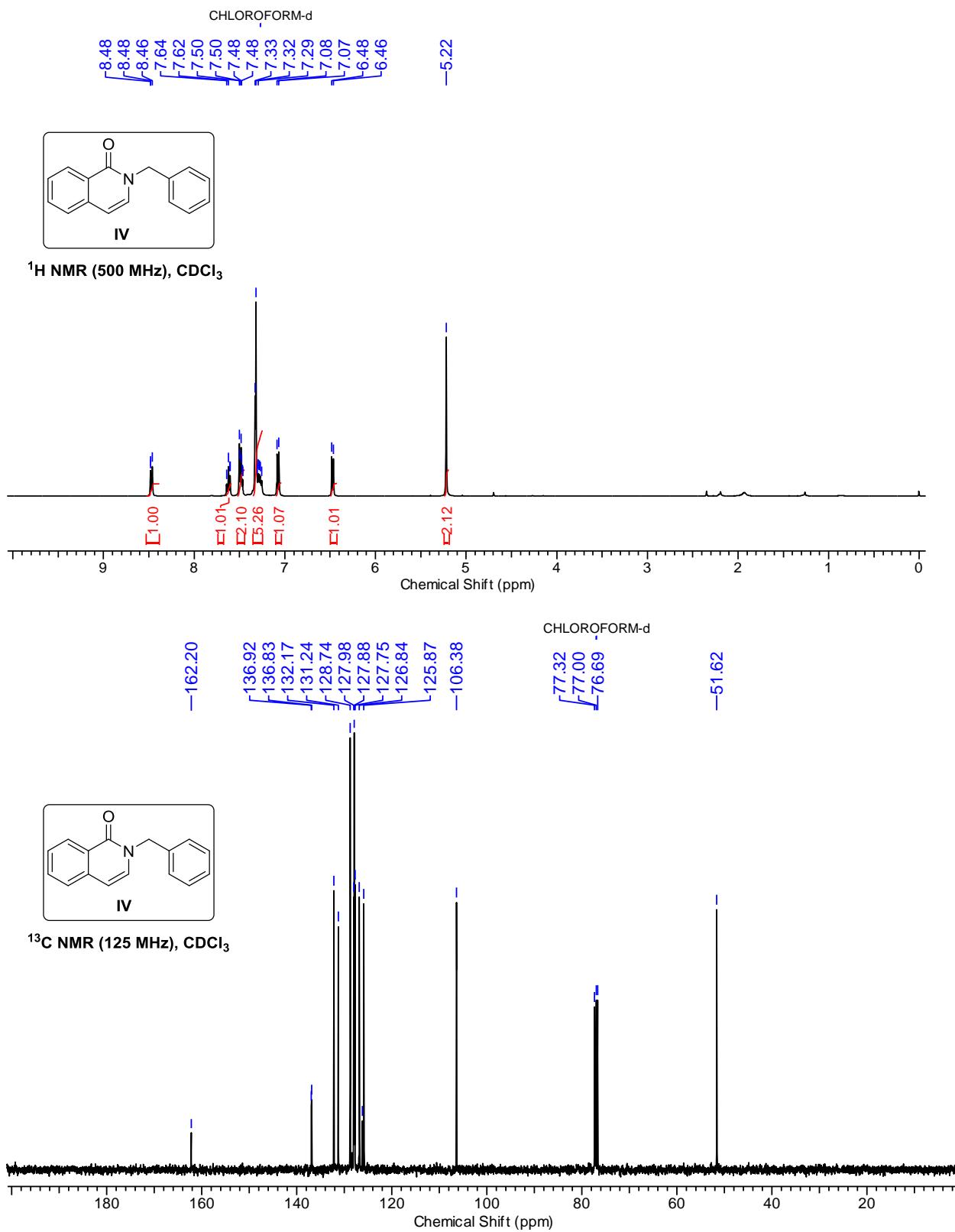


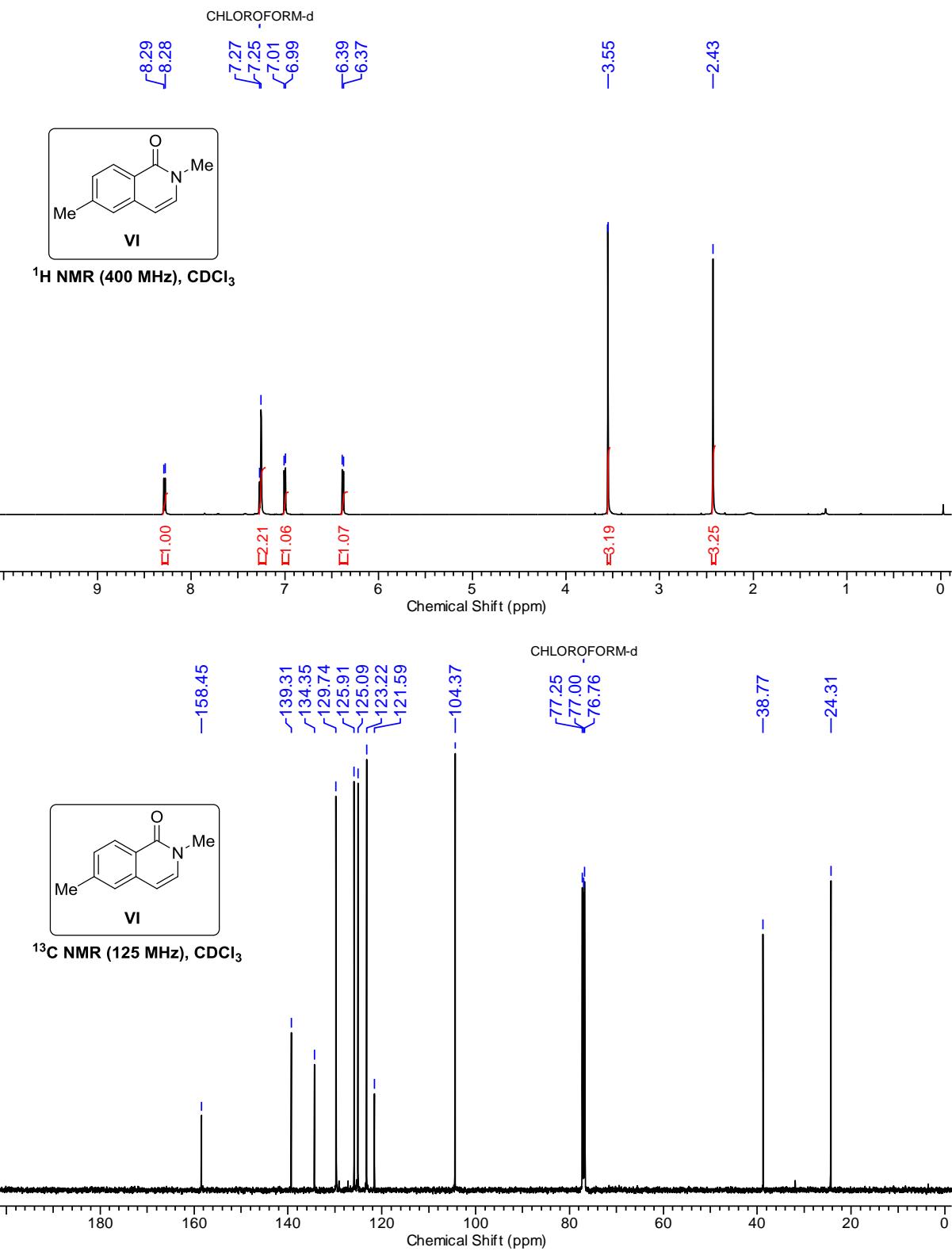
(12c): white solid, 36 mg, 90 % yield; mp = 198-199 °C; R_f = 0.30 (pet. ether/EtOAc = 30/70); **$^1\text{H NMR}$ (500 MHz, CDCl_3)** δ = 7.92 (s, 1 H), 7.78 (d, J = 7.3 Hz, 1 H), 7.63 (t, J = 7.6 Hz, 1 H), 7.53 (d, J = 7.9 Hz, 1 H), 7.44 - 7.31 (m, 5 H), 7.11 (d, J = 7.3 Hz, 1 H), 6.50 (d, J = 7.3 Hz, 1 H), 5.65 (s, 2 H), 3.52 (s, 3 H); **$^{13}\text{C NMR}$ (125 MHz, CDCl_3)** δ = 162.1, 138.9, 135.2, 132.5, 132.3, 131.3, 131.2, 129.0, 128.5, 128.0, 127.0, 124.4, 123.0, 106.2, 54.0, 37.5; **HRMS (ESI)** calcd for $\text{C}_{19}\text{H}_{17}\text{ON}_4$ ($\text{M}^+ + \text{H}$) 317.1397, found 317.1393.

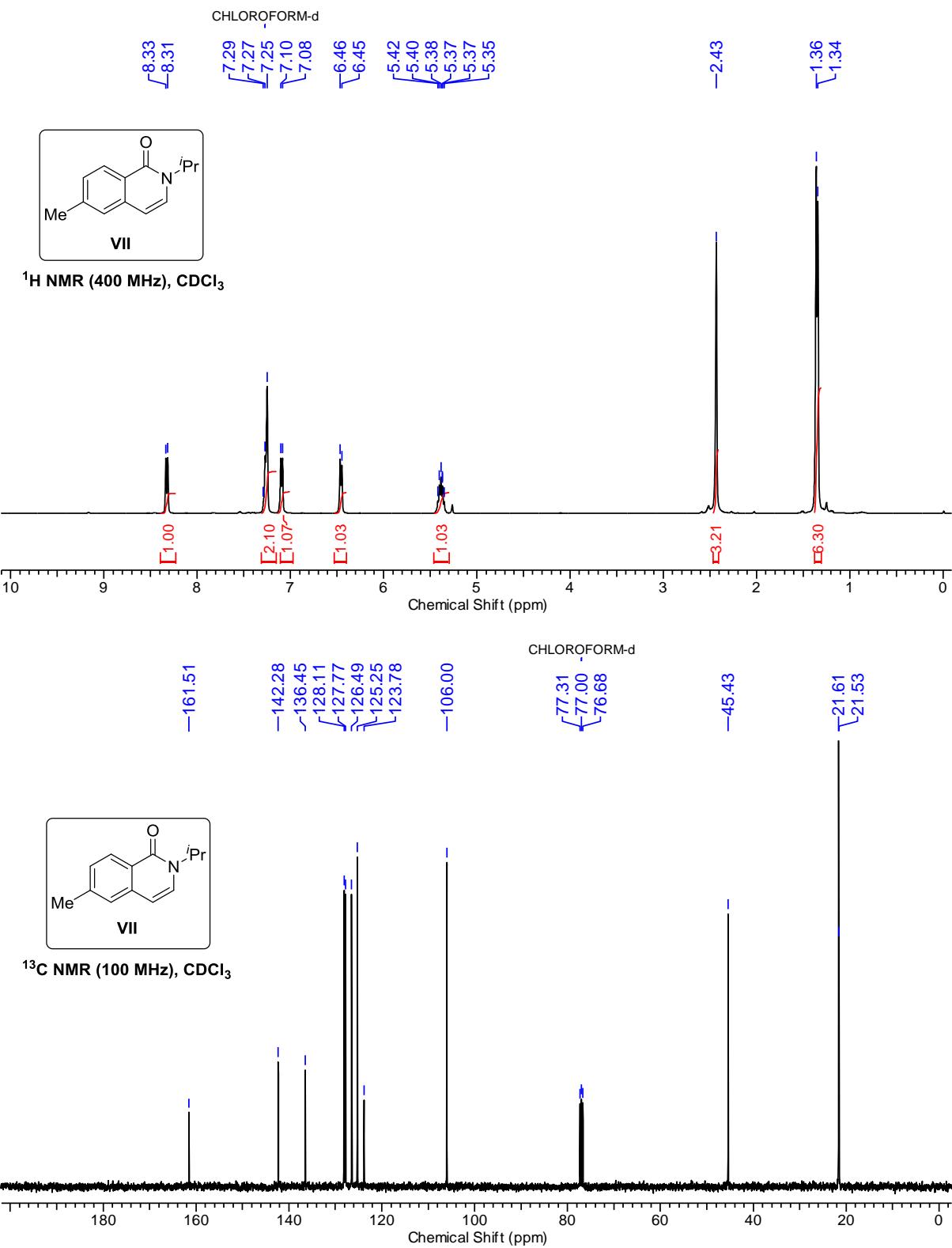


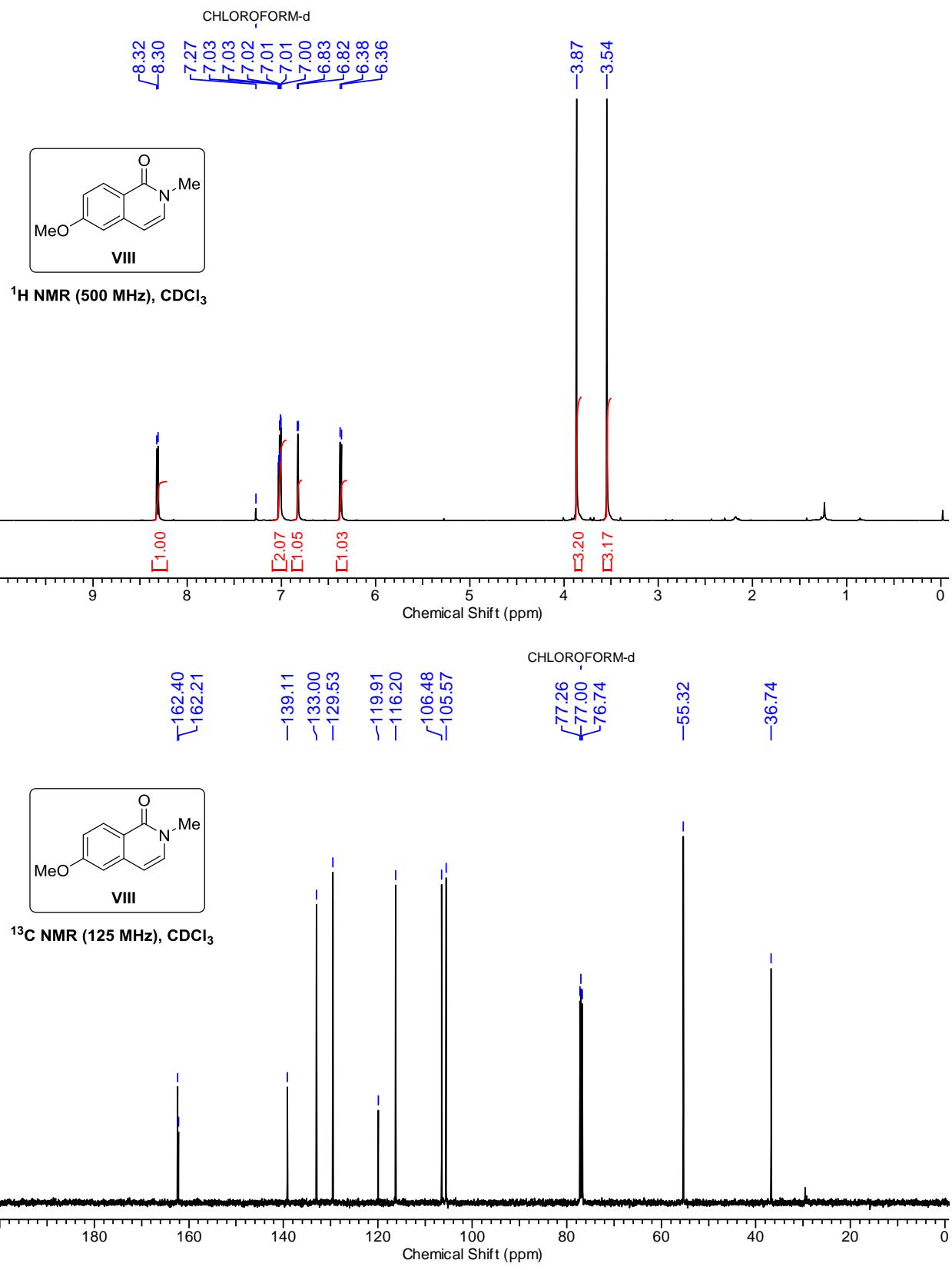


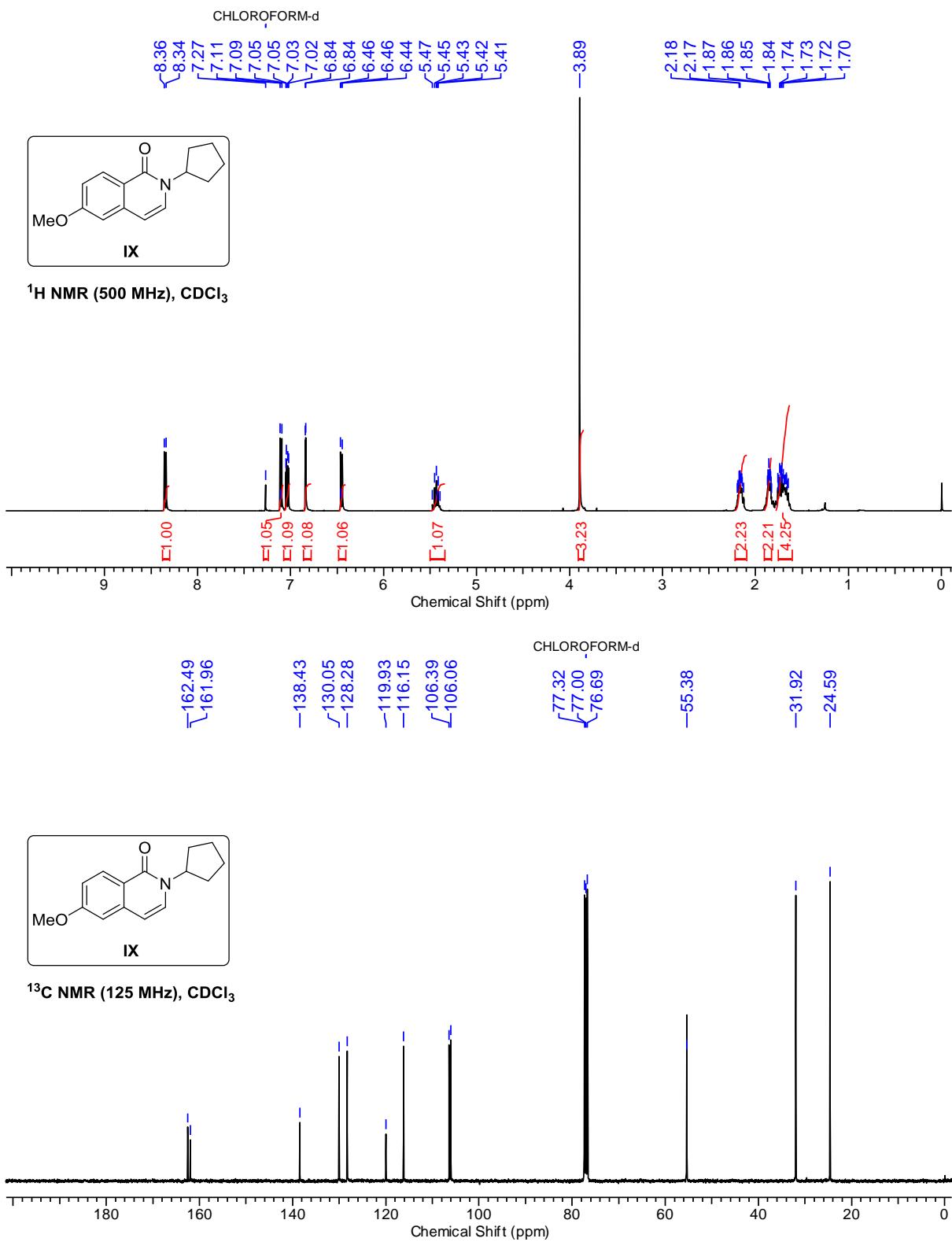


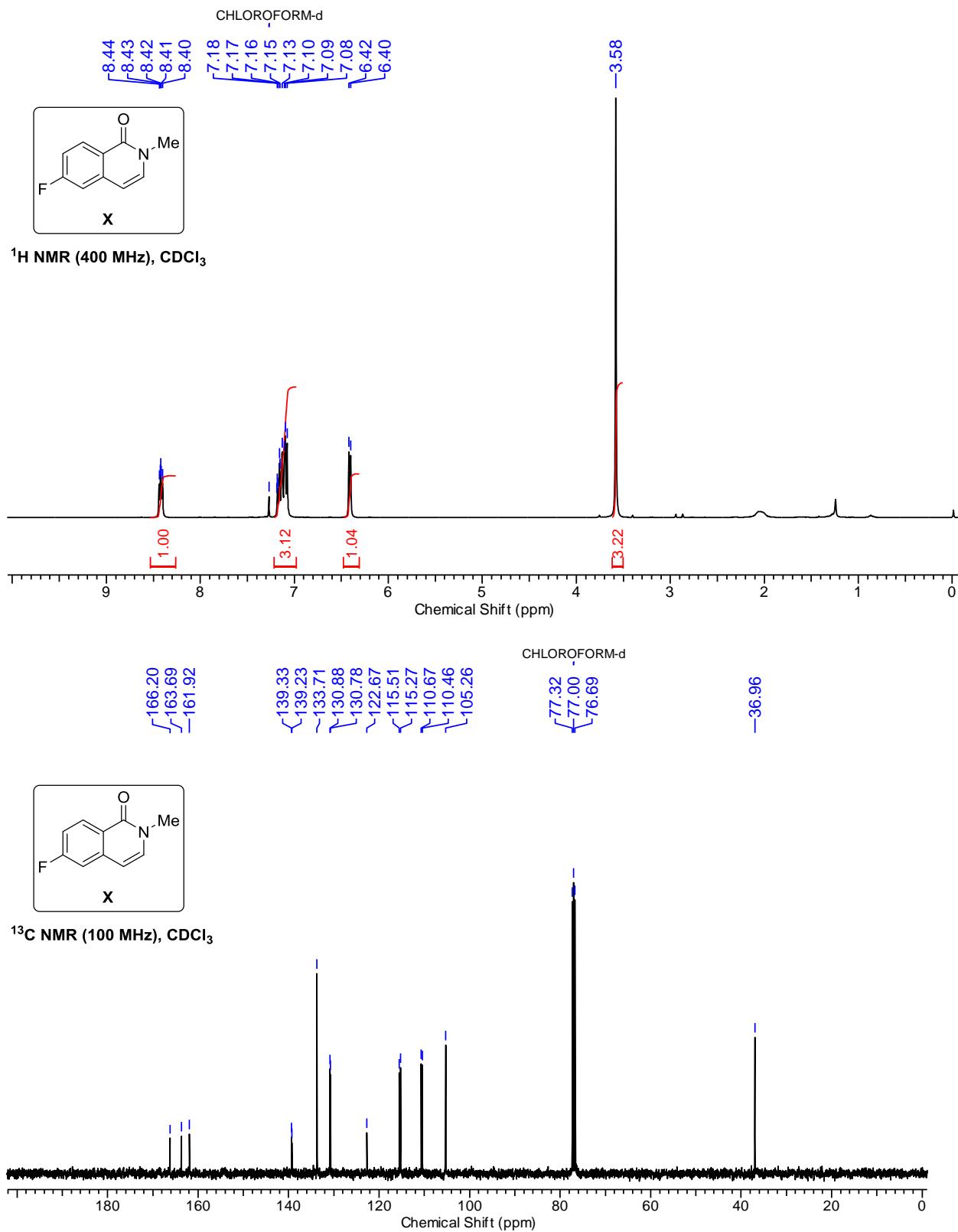


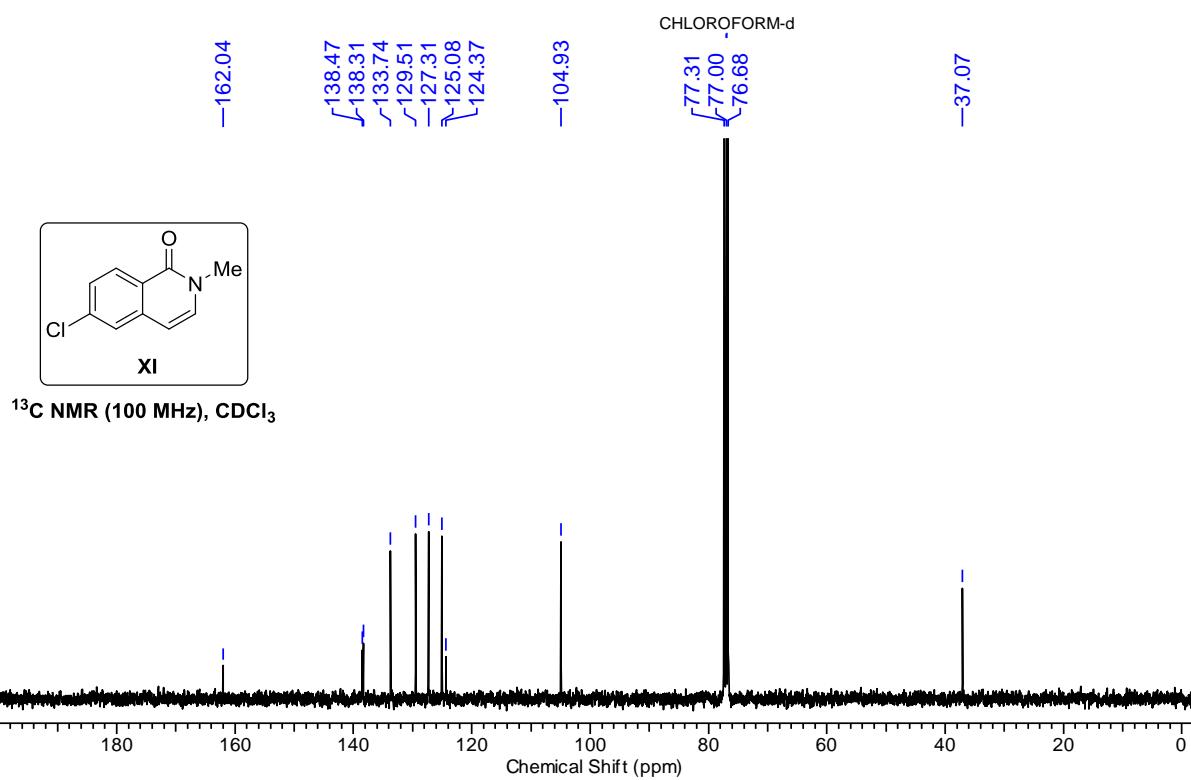
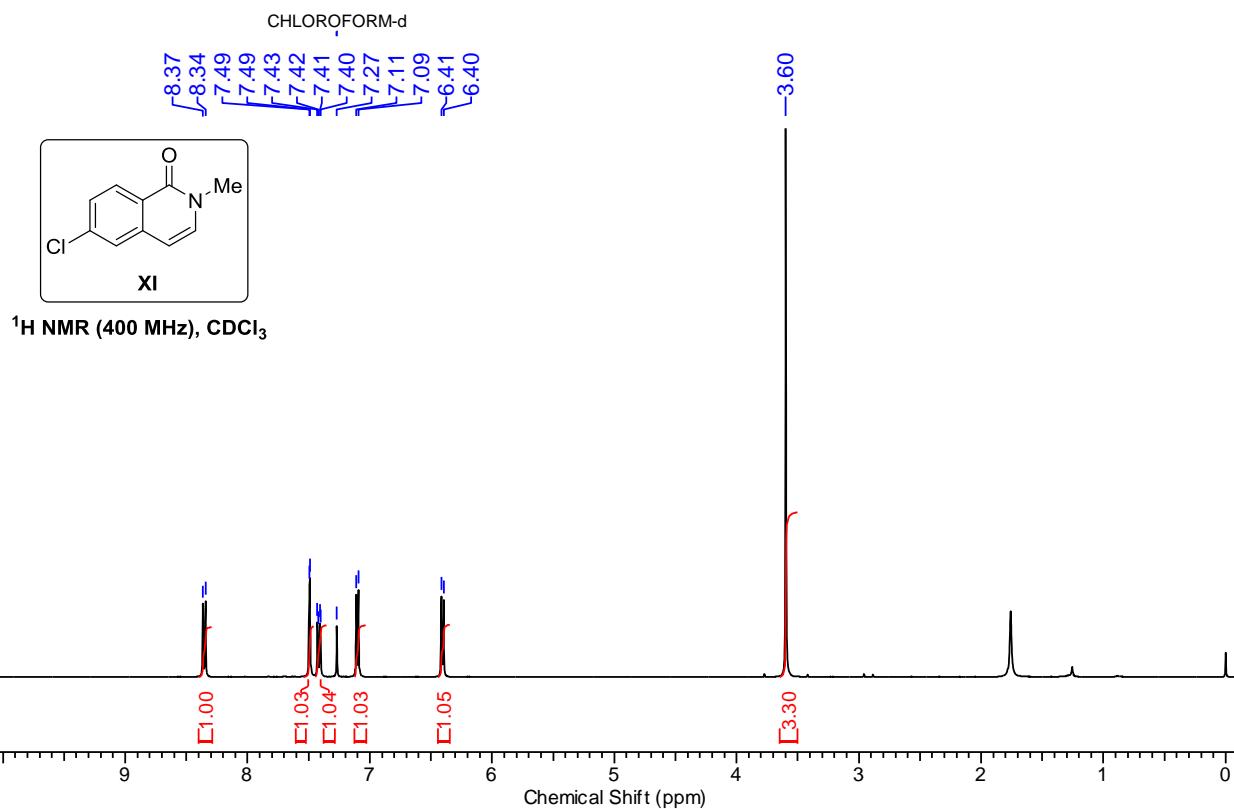


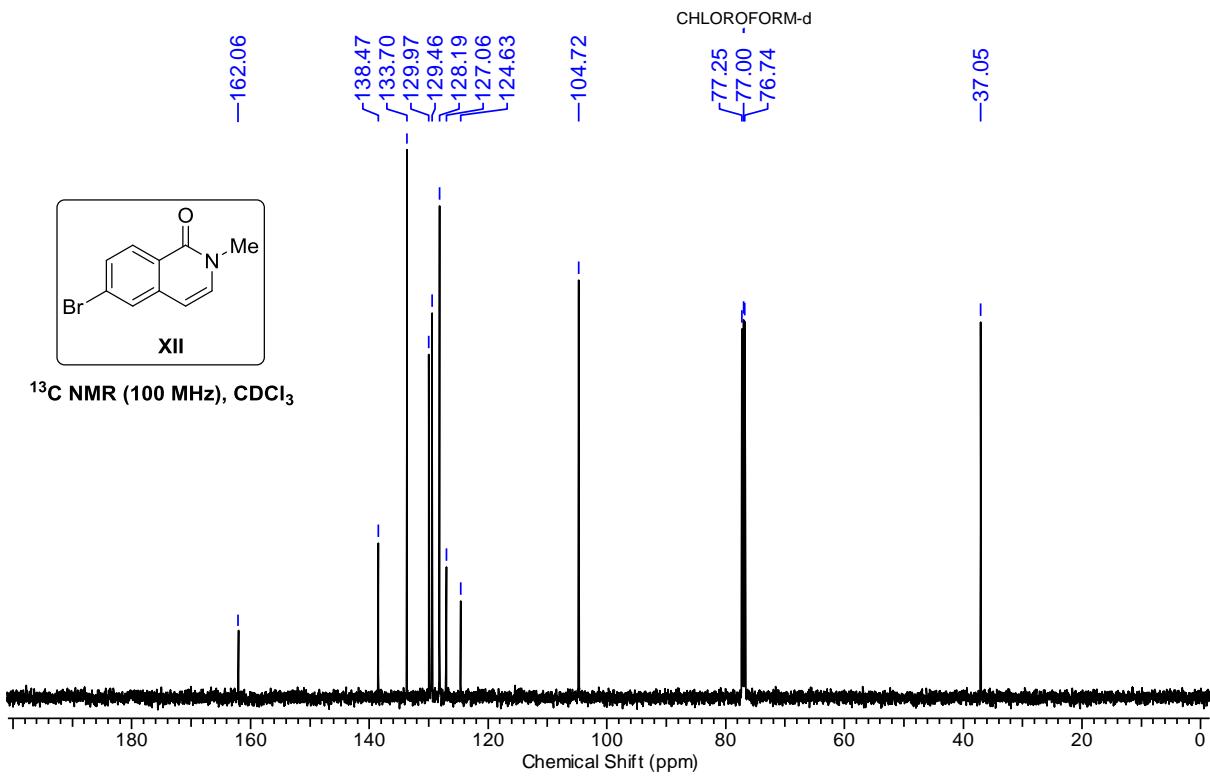
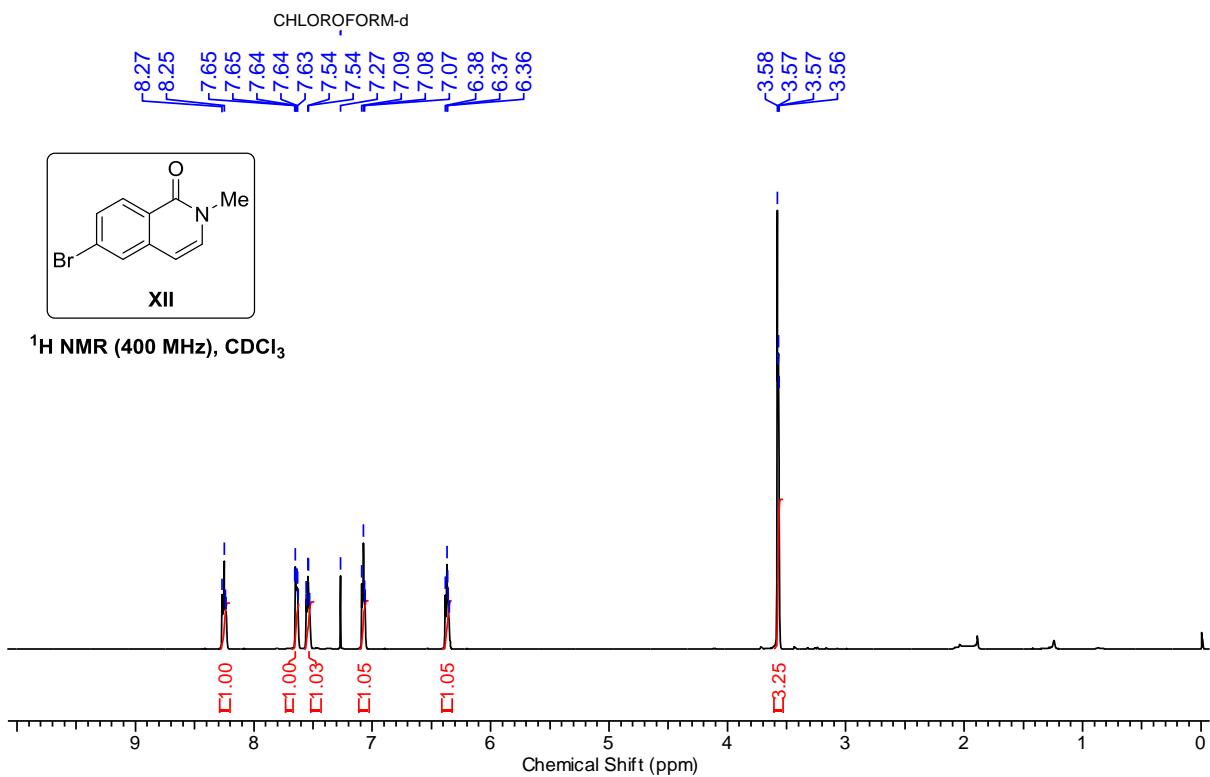


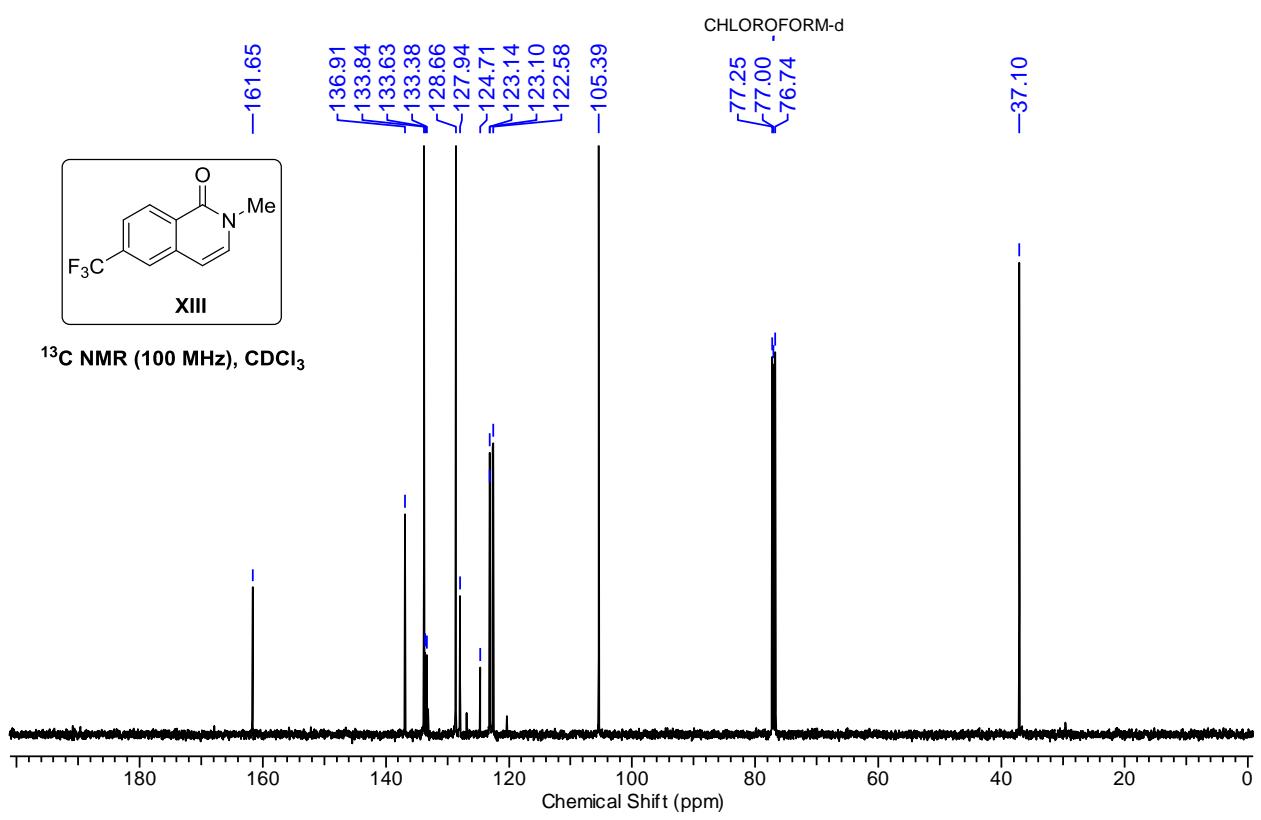
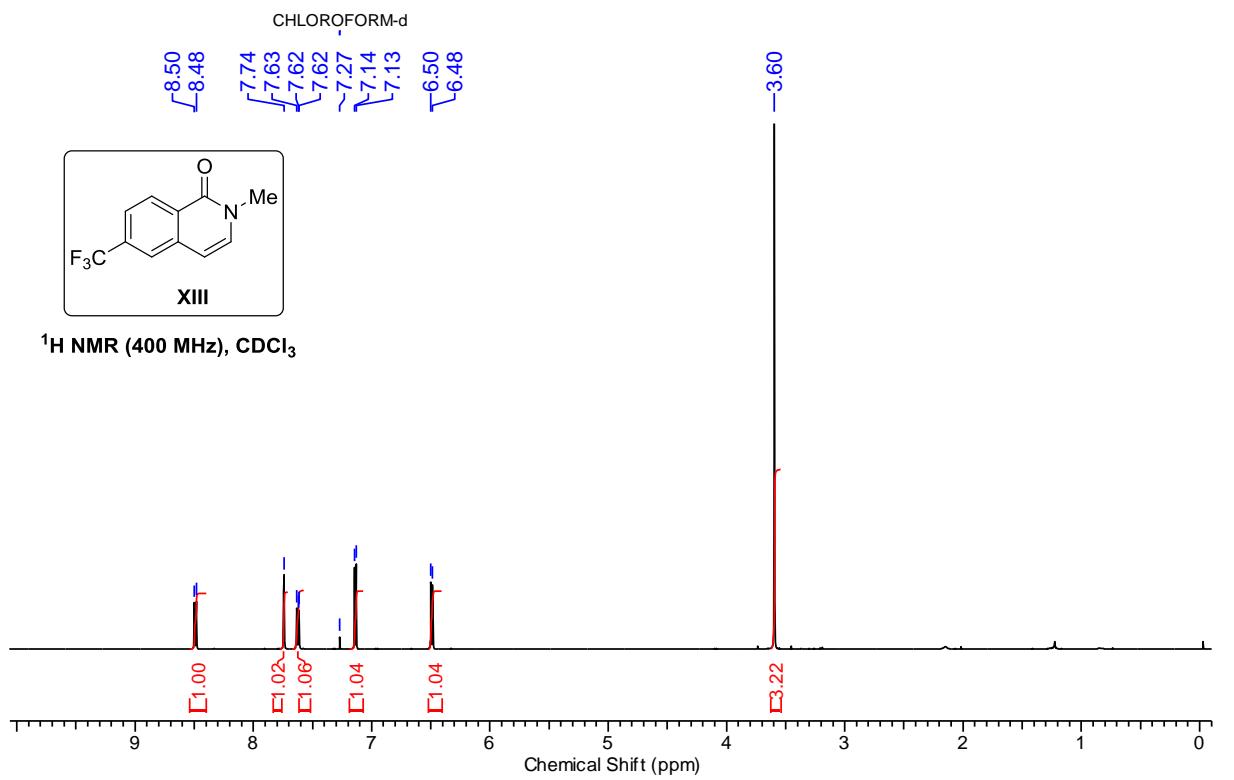


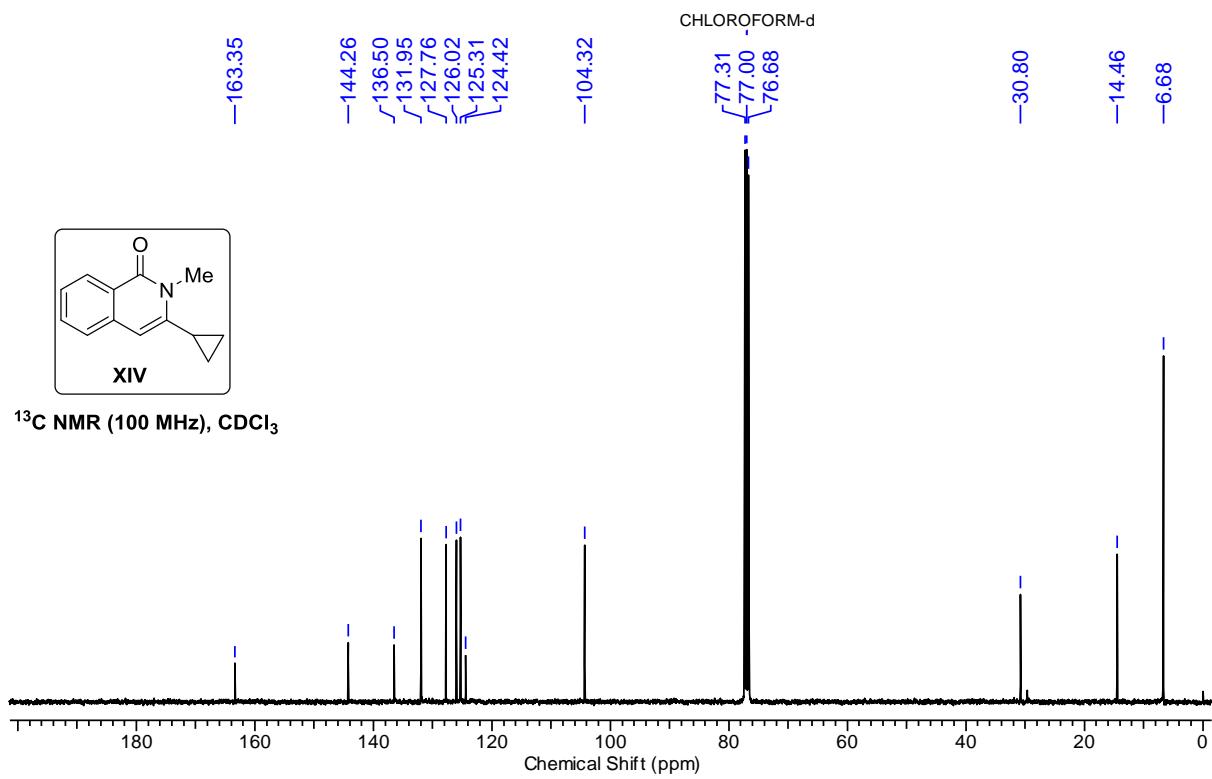
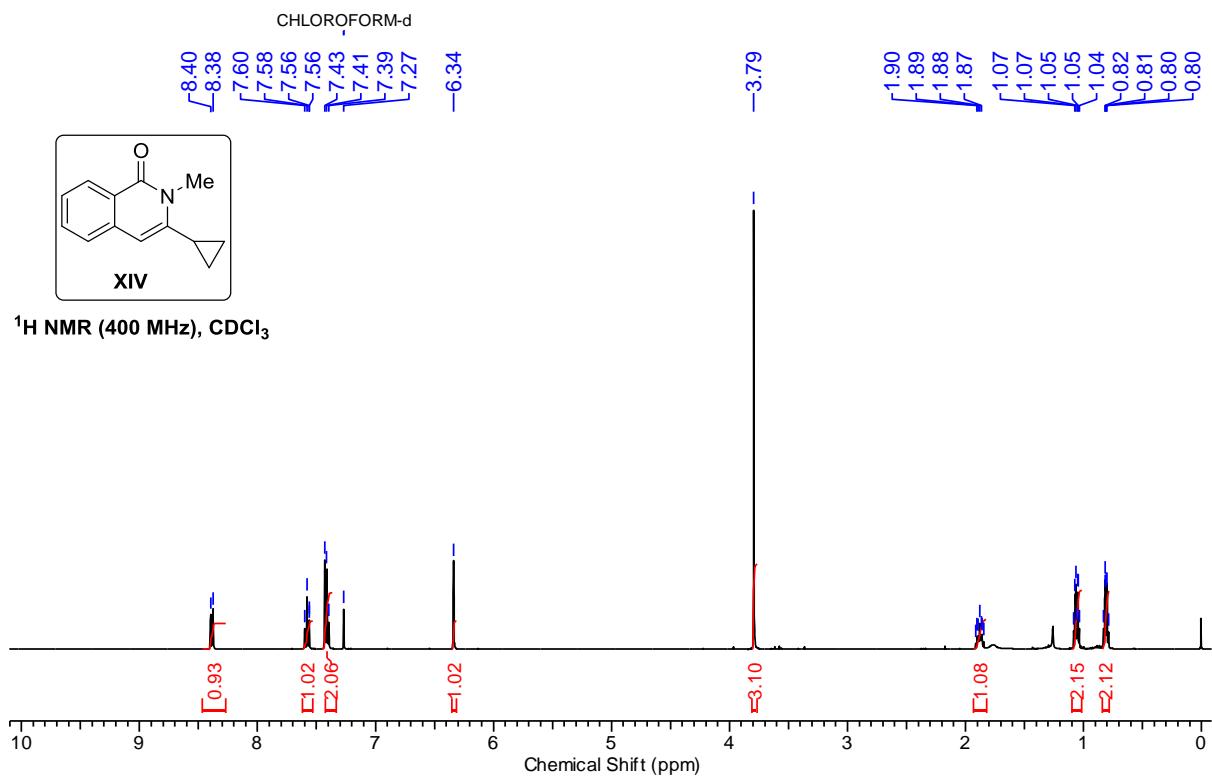


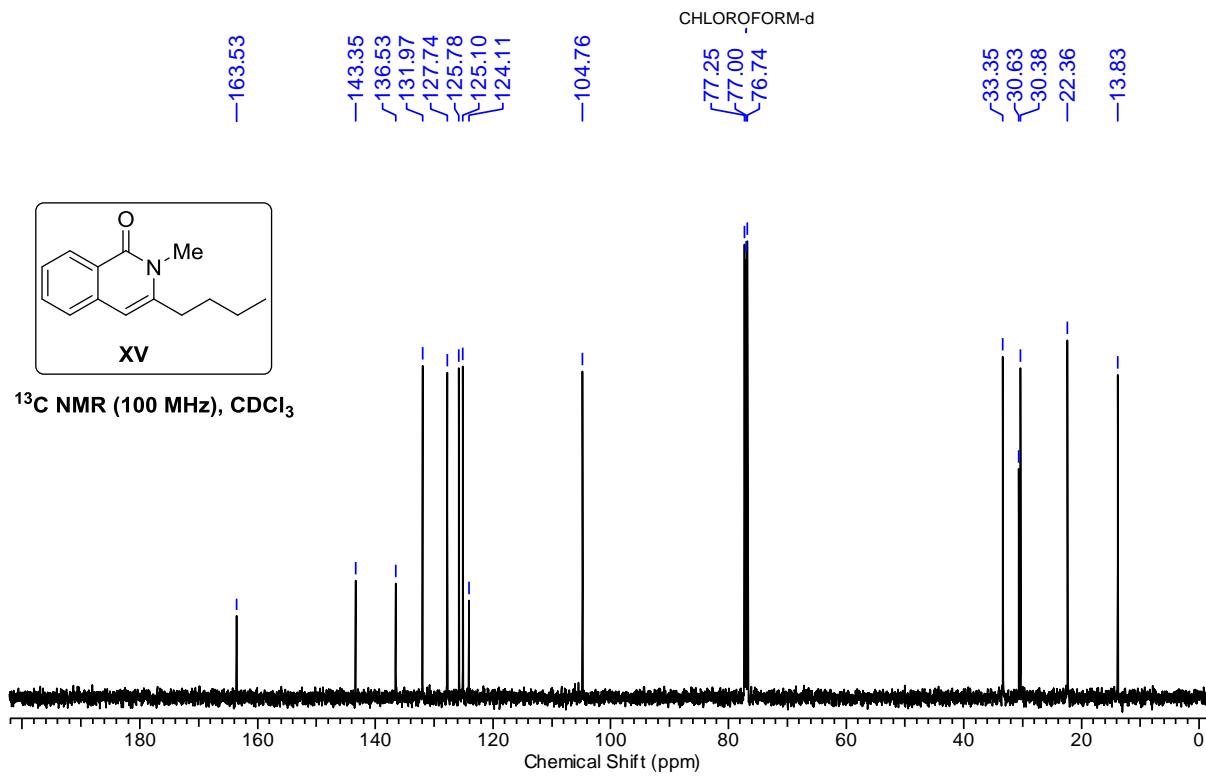
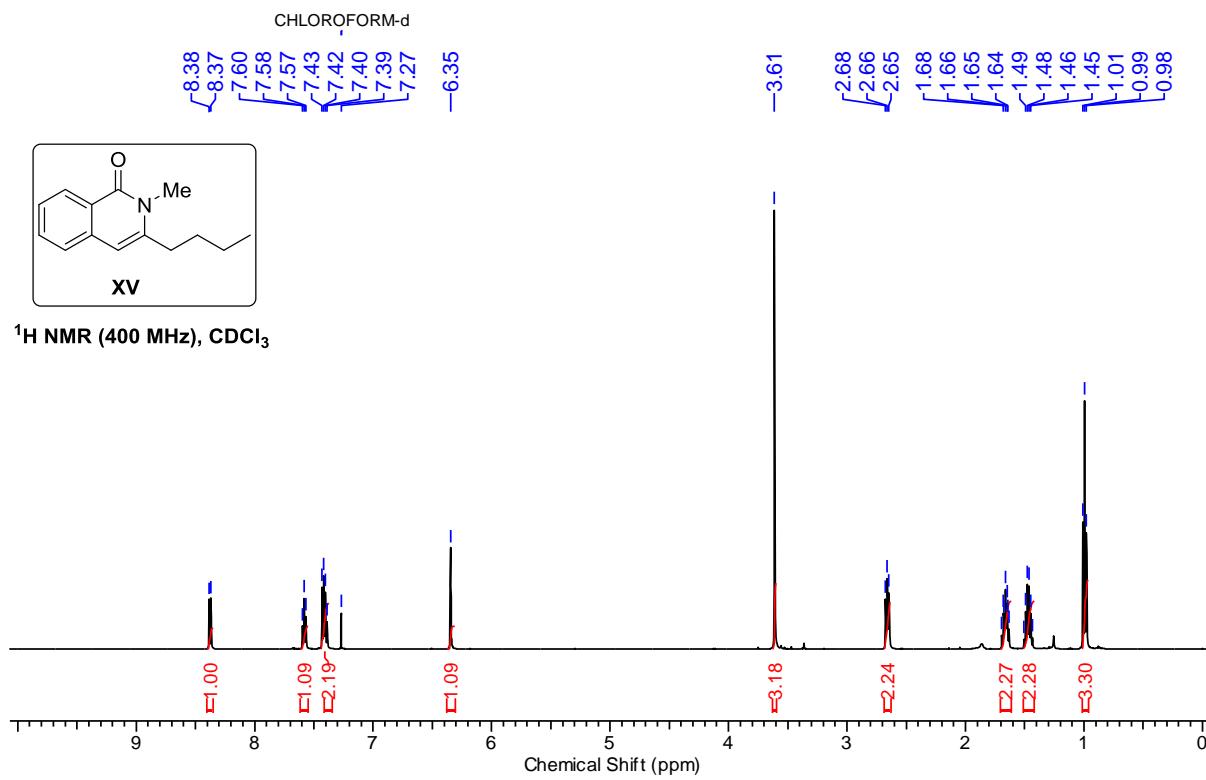


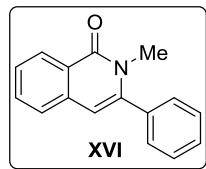
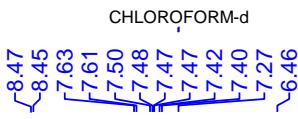




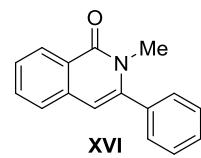
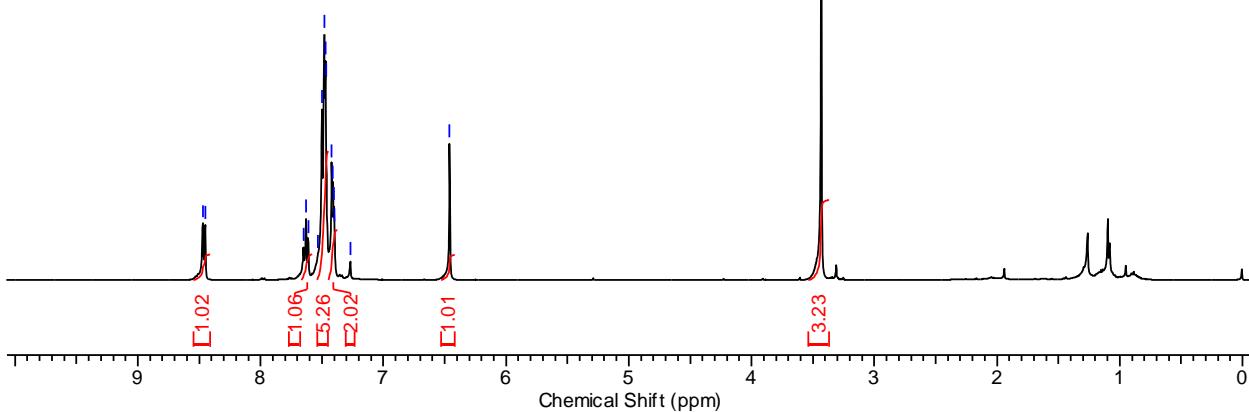








¹H NMR (400 MHz), CDCl₃



¹³C NMR (100 MHz), CDCl₃

