

Supporting Information

Palladium(II)-Catalyzed C-C and C-O Bonds Formation for the Synthesis of C₁-Benzoyl Isoquinolines from Isoquinoline N- Oxides and Nitro Alkenes

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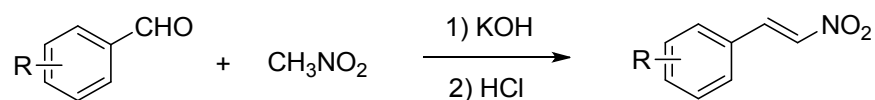
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Experimental

General methods and materials. Proton nuclear magnetic resonance spectra (^1H NMR) and carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 400 MHz and 100 MHz or 500 MHz and 125 MHz, respectively, using CDCl_3 as reference standard (δ 7.26 ppm) for ^1H NMR and (δ 77.04 ppm) for ^{13}C NMR. HRMS (ion trap) were recorded using APCI or ESI. Melting points were uncorrected. Precoated silica gel plates GF-254 were used for analytical thin-layer chromatography. Column chromatography was performed on silica gel (300-400 mesh). Starting materials were readily prepared according to literature procedures. Unless otherwise noted, all reagents were obtained commercially and used without further purification.

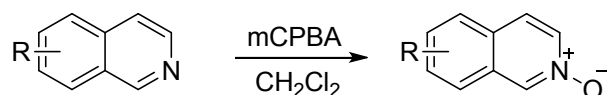
General experimental procedure

Procedure for synthesis of aromatic nitro olefins:



Aryl aldehyde (5 mmol), nitromethane (5 mmol) and MeOH (4 mL) were added in round-bottom flask and then stirred vigorously. 1 ml of 10.5 mol/L KOH solution was added dropwise in an ice bath, a larger number of white or yellow solid would precipitated, stirring continued for 15 min. Distilled water was added until the solution became clear, then 3mL concentrated HCl was added dropwise to the solution and yellow solid would precipitated. The yellow solid were filtered and washed with water, then evaporation under vacuum drying oven. After recrystallization from ethanol, yellow needle-like crystalloid was obtained.

Procedure for synthesis of isoquinoline N-Oxides:

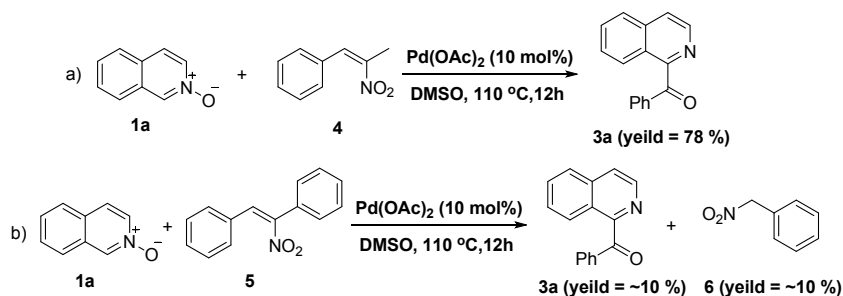


Isoquinoline substituents (2.4 mmol), mCPBA (2mmol), and DCM (15 mL) were added in round-bottom flask and stirred vigorously at room temperature. Then the mixture was monitored by TLC till the mCPBA disappeared and concentrated *in*

vacuo. The residue was washed with ether and filtered to give the light brown solid product.

General procedure for the synthesis of C₁- benzoyl isoquinoline 3. A mixture of isoquinoline N-Oxides **1** (0.6 mmol, 1.2equiv), aromatic nitro alkenes **2** (0.5 mmol, 1equiv), Pd(OAc)₂ and 1.5mL of DMSO was added in sealing and stirred at 110 °C for 12-16 h. The progress of the reaction was monitored by thin-layer chromatography. After cooling down , water (20 mL) was added and mixture was extracted with DCM (3 × 20 mL), combined organic phases were washed with brine and dried with MgSO₄.The residue was evaporated under reduced pressure and purified by flash column chromatography (petroleum ether/ethyl acetate 10:1) to give the pure product **3**.

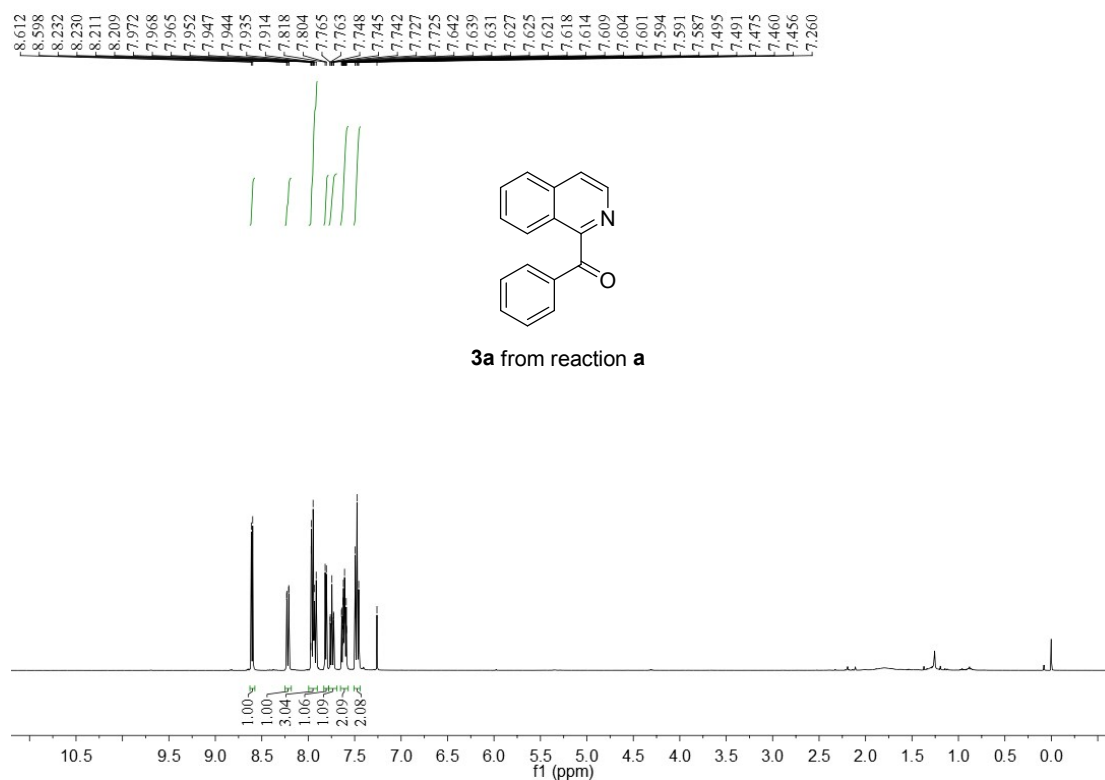
Control experiments



Reaction conditions: **1a** (0.6 mmol), **5** (0.5 mmol), DMSO (1.5 mL), 110 °C, 12h. Isolated. The compound **6** was determined by ¹H NMR and HRMS.

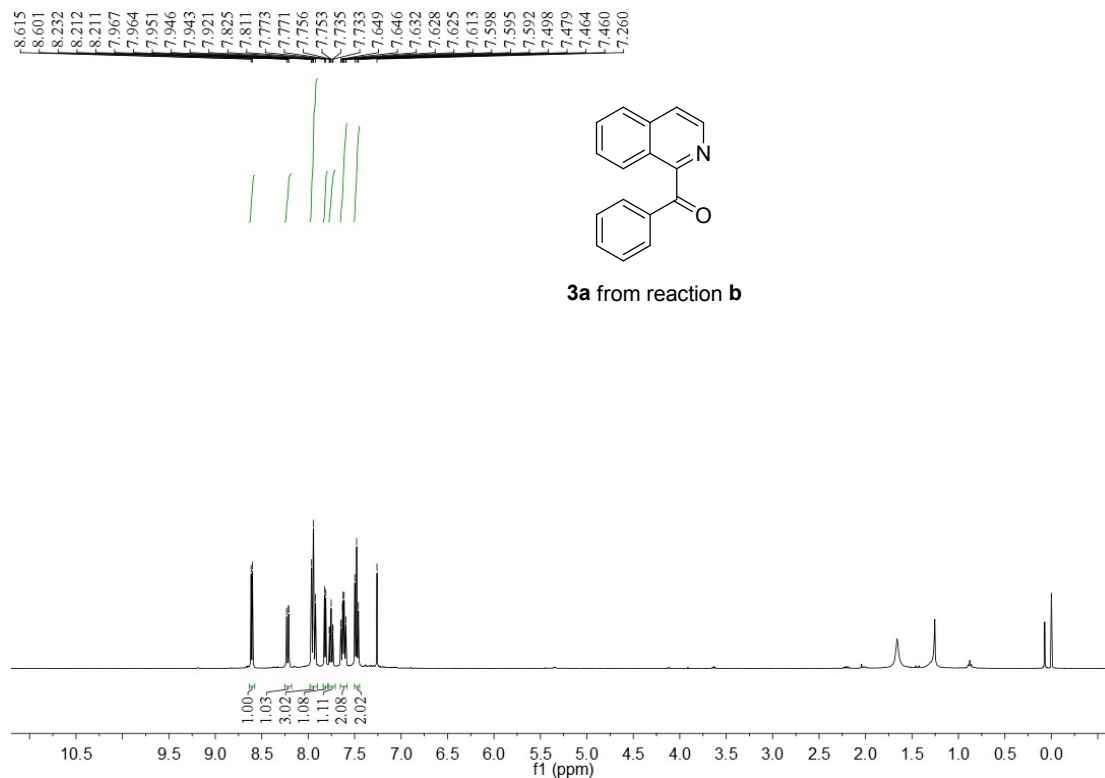
The ¹H NMR spectra of compound **3a** for the reaction **a**.

¹H NMR (400 MHz, CDCl₃): δ 8.61 (d, *J* = 5.6 Hz, 1H), 8.22 (dd, *J* = 8.5, 0.8 Hz, 1H), 8.00-7.90 (m, 3H), 7.81 (d, *J* = 5.3 Hz, 1H), 7.75 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.65 -7.57 (m, 2H), 7.51-7.44 (m, 2H) ppm.



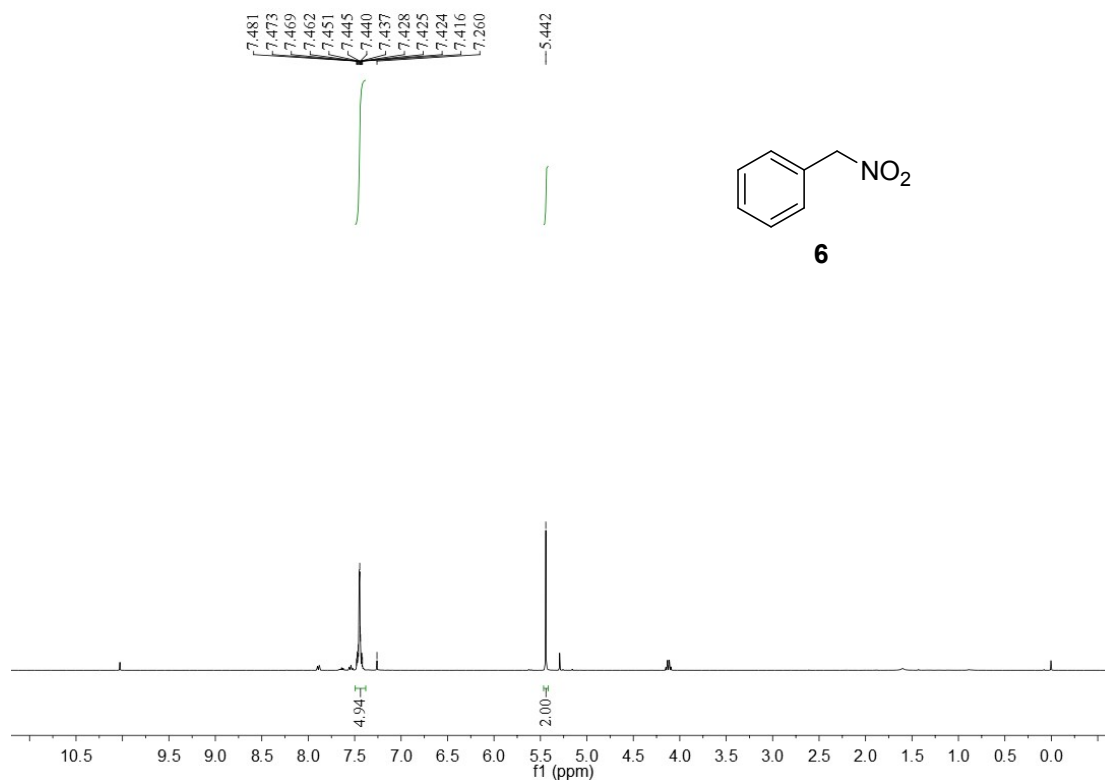
The ^1H NMR spectra of compound **3a** for the reaction **b**.

^1H NMR (400 MHz, CDCl_3): δ 8.61 (d, $J = 5.6$ Hz, 1H), 8.25- 8.18 (m, 1H), 7.95 (dt, $J = 12.0, 4.8$ Hz, 3H), 7.82 (d, $J = 5.5$ Hz, 1H), 7.78-7.71 (m, 1H), 7.65-7.58 (m, 2H), 7.50-7.46 (m, 2H) ppm.

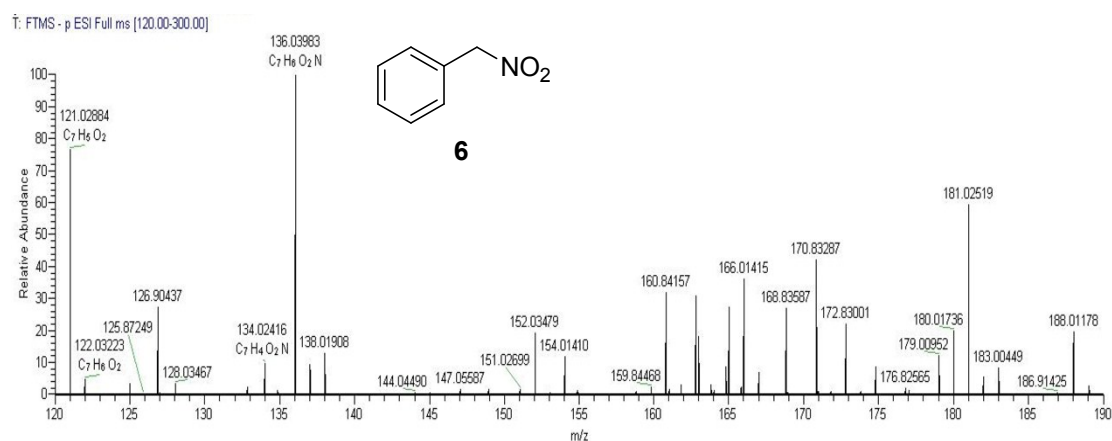


The ^1H NMR spectra of compound **6** for the reaction **b**.

^1H NMR (400 MHz, CDCl_3): δ 7.49-7.38 (m, 5H), 5.44 (s, 2H) ppm; HRMS (m/z) (ESI): calcd for $\text{C}_7\text{H}_6\text{NO}_2$ 136.0399 [M-H $^+$]; found 136.0398.

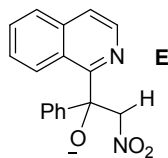
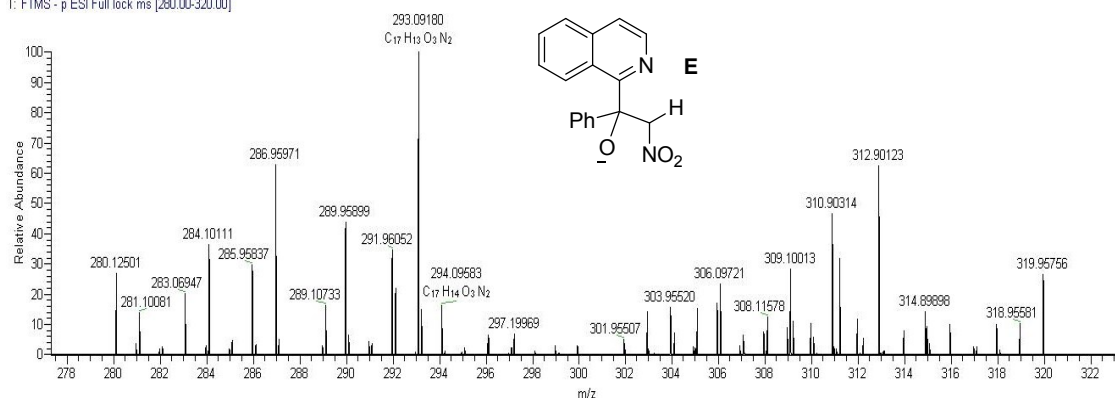


The HRMS spectra of compound **6** for the reaction **b**.

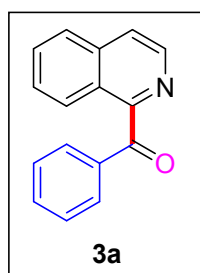


ESI/MS experiments

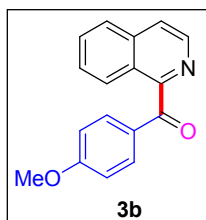
A mixture of the model reaction of isoquinoline N-oxides **1a** with aryl nitro-olefin **2a** was reacted under the standard conditions for 4h and 50 μL of the mixture was used for the ESI analysis in CH_3OH .



Spectral data of all compounds

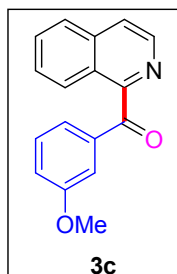


isoquinolin-1-yl(phenyl)methanone (3a): Derived from isoquinoline 2-oxide (**1a**) (87.1 mg, 0.6 mmol, 1.2 equiv.) and 2-nitrovinylbenzene (**2a**) (74.6 mg, 0.5 mmol, 1.0 equiv.); Brown oil (93.3 mg, 80%); ¹H NMR (500 MHz, CDCl₃): δ 8.60 (dd, *J* = 5.6, 1.2 Hz, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 7.98-7.94 (m, 2H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 5.6 Hz, 1H), 7.74 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.64-7.58 (m, 2H), 7.47 (dd, *J* = 11.4, 4.1 Hz, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 194.77, 156.48, 141.20, 136.73, 136.67, 133.69, 130.77, 130.74, 128.49, 128.34, 127.13, 126.44, 126.19, 122.61 ppm; HRMS (m/z) (ESI): calcd for C₁₆H₁₂NO 234.0919 [M+H⁺]; found 234.0911.



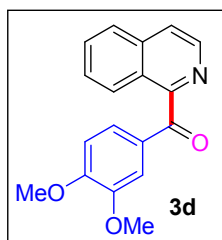
isoquinolin-1-yl(4-methoxyphenyl)methanone (3b): Derived from isoquinoline 2-oxide (**1a**) (87.1 mg, 0.6 mmol, 1.2 equiv.) and 1-methoxy-4-(2-nitrovinyl)benzene (**2b**) (89.6 mg, 0.5 mmol, 1.0 equiv.); Brown solid (98.7 mg, 75%), m.p. 73-75 °C, (lit.², 74 °C); ¹H NMR (500 MHz, CDCl₃): δ 8.59 (d, *J* = 5.6 Hz, 1H), 8.17 (dd, *J* = 8.5, 0.6 Hz, 1H), 7.96-7.92 (m, 2H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 5.6 Hz, 1H), 7.73 (ddd, *J* = 8.2, 6.0, 1.1 Hz, 1H), 7.60 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 6.97-6.92 (m, 2H), 3.87 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 193.39, 164.15, 157.14, 141.21, 136.68,

133.16, 130.66, 129.60, 128.13, 127.04, 126.36, 126.32, 122.23, 113.82, 55.55 ppm;
HRMS (m/z) (ESI): calcd for C₁₇H₁₄NO₂ 264.1025 [M+H⁺]; found 264.1017.



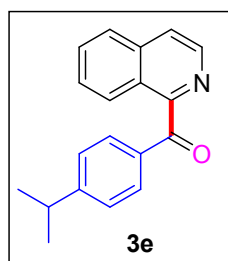
isoquinolin-1-yl(3-methoxyphenyl)methanone (3c): Derived from isoquinoline 2-oxide (**1a**) (87.1 mg, 0.6 mmol, 1.2 equiv.) and 1-methoxy-3-(2-nitrovinyl)benzene (**2c**) (89.6 mg, 0.5 mmol, 1.0 equiv.); Brown solid (96.1 mg, 73%), m.p. 61-63 °C, (lit.², 59 °C); **¹H NMR** (400 MHz, CDCl₃): δ 8.59 (d, *J* = 5.6 Hz, 1H), 8.19 (d, *J* = 8.5

Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 5.6 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.60 (dd, *J* = 14.2, 6.5 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.16 (dd, *J* = 8.1, 2.6 Hz, 1H), 3.85 (s, 3H) ppm; **¹³C NMR** (100 MHz, CDCl₃): δ 194.62, 159.75, 156.55, 141.22, 137.97, 136.69, 130.74, 129.48, 128.33, 127.12, 126.39, 126.16, 123.99, 122.58, 120.46, 114.33, 55.51 ppm; **HRMS** (m/z) (ESI): calcd for C₁₇H₁₄NO₂ 264.1025 [M+H⁺]; found 264.1015.



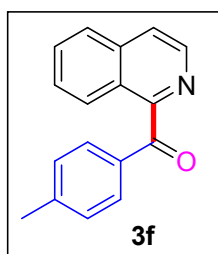
(3,4-dimethoxyphenyl)(isoquinolin-1-yl)methanone (3d):

Derived from isoquinoline 2-oxide (**1a**) (87.1 mg, 0.6 mmol, 1.2 equiv.) and 1,2-dimethoxy-4-(2-nitrovinyl)benzene (**2d**) (104.6 mg, 0.5 mmol, 1.0 equiv.); Brown solid (102.6 mg, 70%), 128-130 °C; **¹H NMR** (400 MHz, CDCl₃): δ 8.58 (d, *J* = 5.7 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 5.6 Hz, 1H), 7.74-7.68 (m, 2H), 7.64-7.54 (m, 1H), 7.35 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H) ppm; **¹³C NMR** (100 MHz, CDCl₃): δ 192.45, 156.03, 153.01, 148.15, 140.13, 135.61, 129.68, 128.60, 127.13, 126.03, 125.95, 125.33, 125.24, 121.25, 110.54, 108.95, 55.11, 55.03 ppm; **HRMS** (m/z) (ESI): calcd for C₁₈H₁₆NO₃ 294.1130 [M+H⁺]; found 294.1115.

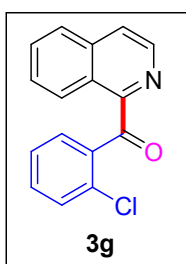


(4-isopropylphenyl)(isoquinolin-1-yl)methanone (3e): Derived from isoquinoline 2-oxide (**1a**) (87.1 mg, 0.6 mmol, 1.2 equiv.) and 1-isopropyl-4-(2-nitrovinyl)benzene (**2e**) (95.6 mg, 0.5 mmol,

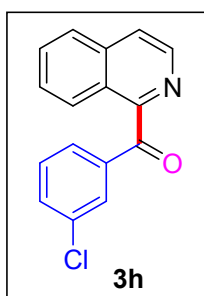
1.0 equiv.); Brown oil (99.1 mg, 72%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.60 (d, $J = 5.6$ Hz, 1H), 8.21 (d, $J = 8.5$ Hz, 1H), 7.90 (dd, $J = 11.9, 8.3$ Hz, 3H), 7.80 (d, $J = 5.6$ Hz, 1H), 7.74 (t, $J = 7.6$ Hz, 1H), 7.65-7.57 (m, 1H), 7.33 (d, $J = 8.0$ Hz, 2H), 2.98 (dt, $J = 13.8, 6.9$ Hz, 1H), 1.27 (d, $J = 6.9$ Hz, 6H) ppm; $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 194.46, 156.85, 155.40, 141.20, 136.71, 134.47, 131.06, 130.70, 128.24, 127.07, 126.68, 126.42, 126.29, 122.43, 34.43, 23.65 ppm; **HRMS** (m/z) (ESI): calcd for $\text{C}_{19}\text{H}_{18}\text{NO}$ 276.1388 [$\text{M}+\text{H}^+$]; found 276.1380.



isoquinolin-1-yl(p-tolyl)methanone (3f): Derived from isoquinoline 2-oxide (**1a**) (87.1 mg, 0.6 mmol, 1.2 equiv.) and 1-methyl-4-(2-nitrovinyl)benzene (**2f**) (81.6 mg, 0.5 mmol, 1.0 equiv.); Brown oil (96.4 mg, 78%); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 8.59 (d, $J = 5.6$ Hz, 1H), 8.19 (d, $J = 8.5$ Hz, 1H), 7.91 (d, $J = 8.3$ Hz, 1H), 7.85 (d, $J = 8.2$ Hz, 2H), 7.79 (d, $J = 5.6$ Hz, 1H), 7.76-7.70 (m, 1H), 7.60 (ddd, $J = 8.2, 7.0, 1.0$ Hz, 1H), 7.27 (d, $J = 8.4$ Hz, 2H), 2.42 (s, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 194.49, 156.87, 144.72, 141.22, 136.69, 134.18, 130.88, 130.68, 129.21, 128.21, 127.07, 126.38, 126.26, 122.38, 21.79 ppm; **HRMS** (m/z) (ESI): calcd for $\text{C}_{17}\text{H}_{14}\text{NO}$ 248.1075 [$\text{M}+\text{H}^+$]; found 248.1057.

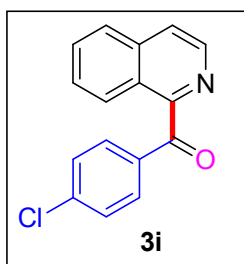


(2-chlorophenyl)(isoquinolin-1-yl)methanone (3g): Derived from isoquinoline 2-oxide (**1a**) (87.1 mg, 0.6 mmol, 1.2 equiv.) and 1-chloro-2-(2-nitrovinyl)benzene (**2g**) (91.8 mg, 0.5 mmol, 1.0 equiv.); brown solid (91.0 mg, 68%), m.p. 98-100 °C, (lit.³, 100-103 °C); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 8.74 (d, $J = 8.4$ Hz, 1H), 8.53 (d, $J = 5.6$ Hz, 1H), 7.92 (d, $J = 7.9$ Hz, 1H), 7.81 (d, $J = 5.5$ Hz, 1H), 7.79-7.71 (m, 3H), 7.48-7.39 (m, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 196.06, 154.53, 141.33, 139.14, 136.97, 132.54, 132.23, 131.01, 130.62, 130.11, 129.01, 127.12, 126.86, 126.43, 126.38, 123.92 ppm; **HRMS** (m/z) (ESI): calcd for $\text{C}_{16}\text{H}_{11}\text{ClNO}$ 268.0529 [$\text{M}+\text{H}^+$]; found 268.0520.



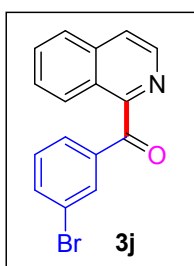
(3-chlorophenyl)(isoquinolin-1-yl)methanone (3h): Derived from isoquinoline 2-oxide (**1a**) (87.1 mg, 0.6 mmol, 1.2 equiv.) and 1-chloro-3-(2-nitrovinyl)benzene (**2h**) (91.8 mg, 0.5 mmol, 1.0 equiv.); brown solid (97.7 mg, 73%), m.p. 101-103 °C, (lit.³, 104-105 °C); ¹H NMR (500 MHz, CDCl₃): δ 8.61 (d, *J* = 5.6 Hz, 1H),

8.26 (d, *J* = 8.5 Hz, 1H), 7.97-7.92 (m, 2H), 7.84 (dd, *J* = 5.4, 3.4 Hz, 2H), 7.78-7.74 (m, 1H), 7.65 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.57 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 193.25, 155.34, 141.12, 138.37, 136.83, 134.72, 133.46, 130.86, 130.67, 129.76, 128.95, 128.62, 127.20, 126.51, 126.03, 123.13 ppm; HRMS (m/z) (ESI): calcd for C₁₆H₁₁ClNO 268.0529 [M+H⁺]; found 268.0524.



(4-chlorophenyl)(isoquinolin-1-yl)methanone (3i): Derived from isoquinoline 2-oxide (**1a**) (87.1 mg, 0.6 mmol, 1.2 equiv.) and 1-chloro-4-(2-nitrovinyl)benzene (**2i**) (91.8 mg, 0.5 mmol, 1.0 equiv.); Brown solid (115.1 mg, 86%), m.p. 72-74 °C (lit.¹ 73-75 °C); ¹H NMR (400 MHz, CDCl₃): δ 8.60 (d, *J* = 5.6 Hz,

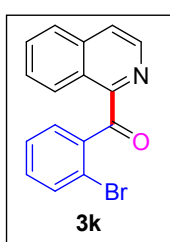
1H), 8.25 (d, *J* = 8.5 Hz, 1H), 7.92 (dd, *J* = 7.8, 5.8 Hz, 3H), 7.83 (d, *J* = 5.6 Hz, 1H), 7.78-7.72 (m, 1H), 7.67-7.61 (m, 1H), 7.45 (d, *J* = 8.6 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 193.41, 155.65, 141.11, 140.19, 136.81, 135.06, 132.20, 130.85, 128.81, 128.56, 127.19, 126.49, 126.09, 122.99 ppm; HRMS (m/z) (ESI): calcd for C₁₆H₁₁ClNO 268.0529 [M+H⁺]; found 268.0538.



(3-bromophenyl)(isoquinolin-1-yl)methanone (3j): Derived from isoquinoline 2-oxide (**1a**) (87.1 mg, 0.6 mmol, 1.2 equiv.) and 1-bromo-3-(2-nitrovinyl)benzene (**2j**) (114.0 mg, 0.5 mmol, 1.0 equiv.); brown solid (118.6 mg, 76%) m.p. 112-114 °C (lit.⁴, 115-116 °C); ¹H NMR (500 MHz, CDCl₃): δ 8.60 (d, *J* = 5.6 Hz, 1H),

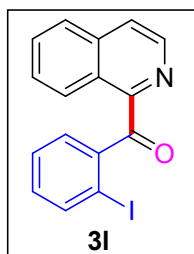
8.26 (d, *J* = 8.5 Hz, 1H), 8.11 (t, *J* = 1.7 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* =

7.9 Hz, 1H), 7.83 (d, $J = 5.6$ Hz, 1H), 7.77-7.71 (m, 2H), 7.66-7.63 (m, 1H), 7.35 (t, $J = 7.9$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 193.15, 155.28, 141.12, 138.60, 136.83, 136.35, 133.56, 130.86, 130.00, 129.41, 128.63, 127.21, 126.51, 126.03, 123.15, 122.72 ppm; HRMS (m/z) (ESI): calcd for $\text{C}_{16}\text{H}_{11}\text{BrNO}$ 312.0024,314.0004 [$\text{M}+\text{H}^+$]; found 312.0013,313.9992.



(2-bromophenyl)(isoquinolin-1-yl)methanone (3k): Derived from isoquinoline 2-oxide (**1a**) (87.1 mg, 0.6 mmol, 1.2 equiv.) and 1-bromo-2-(2-nitrovinyl)benzene (**2k**) (114.0 mg, 0.5 mmol, 1.0 equiv.); brown solid (101.4 mg, 65%), m.p. 112-114 °C (lit.⁴, 115-116 °C); ^1H NMR (400 MHz, CDCl_3): δ 8.83-8.74 (m, 1H), 8.53 (d, $J = 5.6$ Hz,

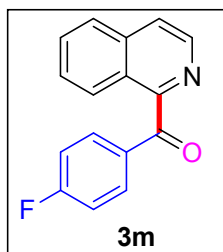
1H), 7.92 (dd, $J = 7.2, 2.0$ Hz, 1H), 7.82 (d, $J = 5.9$ Hz, 1H), 7.80-7.72 (m, 2H), 7.67 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.60 (dd, $J = 8.0, 1.0$ Hz, 1H), 7.47 (td, $J = 7.5, 1.1$ Hz, 1H), 7.38 (td, $J = 7.7, 1.8$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 196.77, 154.00, 141.34, 141.26, 136.97, 133.21, 132.15, 131.05, 130.65, 129.10, 127.40, 127.15, 126.79, 126.49, 124.06, 120.68 ppm; HRMS (m/z) (ESI): calcd for $\text{C}_{16}\text{H}_{11}\text{BrNO}$ 312.0024,314.0004 [$\text{M}+\text{H}^+$]; found 312.0036,314.0015.



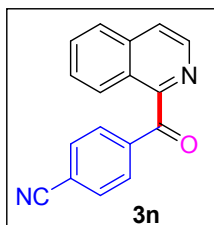
(2-iodophenyl)(isoquinolin-1-yl)methanone (3l): Derived from isoquinoline 2-oxide (**1a**) (87.1 mg, 0.6 mmol, 1.2 equiv.) and 1-iodo-2-(2-nitrovinyl)benzene (**2l**) (137.5 mg, 0.5 mmol, 1.0 equiv.); Yellow solid (111.3 mg, 62%), m.p. 98-100 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.86-8.79 (m, 1H), 8.54 (d, $J = 5.6$ Hz, 1H), 7.95-

7.88 (m, 2H), 7.83 (d, $J = 5.5$ Hz, 1H), 7.80-7.72 (m, 2H), 7.57 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.49 (td, $J = 7.5, 1.0$ Hz, 1H), 7.20 (td, $J = 7.7, 1.7$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 197.71, 153.23, 144.57, 141.38, 139.87, 136.95, 132.01, 130.89, 130.67, 129.14, 127.98, 127.46, 127.18, 126.60, 124.16, 93.19 ppm; HRMS (m/z)

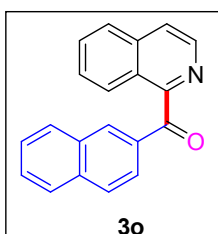
(ESI): calcd for C₁₆H₁₁INO 359.9885 [M+H⁺]; found 359.9873.



(4-fluorophenyl)(isoquinolin-1-yl)methanone (3m): Derived from isoquinoline 2-oxide (**1a**) (87.1 mg, 0.6 mmol, 1.2 equiv.) and 1-fluoro-4-(2-nitrovinyl)benzene (**2m**) (83.6 mg, 0.5 mmol, 1.0 equiv.); Brown solid (104.3 mg, 83%), m.p. 94-95 °C, (lit.², 92 °C); ¹H NMR (500 MHz, CDCl₃): δ 8.59 (d, *J* = 5.6 Hz, 1H), 8.23 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.05-7.97 (m, 2H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 5.6 Hz, 1H), 7.77-7.72 (m, 1H), 7.65-7.60 (m, 1H), 7.18-7.10 (m, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 193.06, 166.14(d, ¹*J*_{CF} = 254.5 Hz), 156.00, 141.09, 136.79, 133.54(d, ³*J*_{CF} = 9.5 Hz), 133.05(d, ⁴*J*_{CF} = 2.9 Hz), 130.82, 128.46, 127.16, 126.44, 126.11, 122.82, 115.67(d, ²*J*_{CF} = 22.0 Hz) ppm; HRMS (m/z) (ESI): calcd for C₁₆H₁₁FNO 252.0825 [M+H⁺]; found 252.0814.

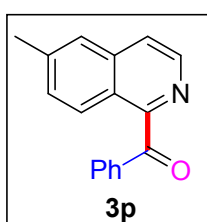


4-(isoquinoline-1-carbonyl)benzotrile (3n): Derived from isoquinoline 2-oxide (**1a**) (87.1 mg, 0.6 mmol, 1.2 equiv.) and 4-(2-nitrovinyl)benzotrile (**2n**) (87.1 mg, 0.5 mmol, 1.0 equiv.); Yellow solid (103.3 mg, 80%), m.p. 138-140 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.61 (d, *J* = 5.6 Hz, 1H), 8.38 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 5.6 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 3H), 7.73-7.65 (m, 1H) ppm; ¹³C NMR (100MHz, CDCl₃): δ 192.98, 154.24, 141.02, 140.29, 136.96, 132.12, 131.15, 130.99, 128.97, 127.29, 126.72, 125.96, 123.73, 118.07, 116.40 ppm; HRMS (m/z) (ESI): calcd for C₁₇H₁₁N₂O 259.0871 [M+H⁺]; found 259.0863.



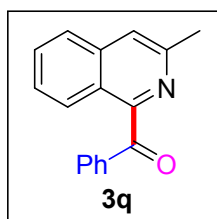
isoquinolin-1-yl(naphthalen-2-yl)methanone (3o): Derived from isoquinoline 2-oxide (**1a**) (87.1 mg, 0.6 mmol, 1.2 equiv.) and 2-(2-nitrovinyl)naphthalene (**2o**) (99.6 mg, 0.5 mmol, 1.0 equiv.); Brown solid (106.2 mg, 75%), m.p. 108-110 °C; ¹H NMR (400

MHz, CDCl₃): δ 8.65 (d, J = 5.6 Hz, 1H), 8.35 (s, 1H), 8.25 (dd, J = 8.5, 0.8 Hz, 1H), 8.15 (dd, J = 8.6, 1.7 Hz, 1H), 7.95 (d, J = 8.5 Hz, 2H), 7.90-7.83 (m, 3H), 7.76 (ddd, J = 8.2, 6.9, 1.1 Hz, 1H), 7.65-7.58 (m, 2H), 7.50 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H) ppm; **¹³C NMR** (100 MHz, CDCl₃): δ 194.81, 156.74, 141.28, 136.78, 135.95, 134.01, 133.76, 132.39, 130.81, 129.89, 128.89, 128.49, 128.39, 127.83, 127.17, 126.75, 126.53, 126.27, 125.29, 122.64 ppm; **HRMS** (m/z) (ESI): calcd for C₂₀H₁₄NO 284.1075 [M+H⁺]; found 284.1063.



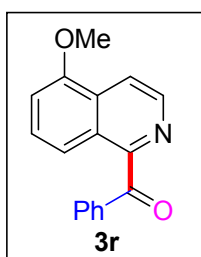
(6-methylisoquinolin-1-yl)(phenyl)methanone (3p): Derived from 6-methylisoquinoline 2-oxide (**1b**) (95.5 mg, 0.6 mmol, 1.2 equiv.) and 2-nitrovinylbenzene (**2a**) (74.6 mg, 0.5 mmol, 1.0 equiv.); Brown oil (98.9 mg, 80%); **¹H NMR** (400 MHz, CDCl₃): δ

8.56 (d, J = 5.6 Hz, 1H), 8.11 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 7.3 Hz, 2H), 7.72 (d, J = 5.6 Hz, 1H), 7.69 (s, 1H), 7.60 (t, J = 7.4 Hz, 1H), 7.50-7.42 (m, 3H), 2.56 (s, 3H) ppm; **¹³C NMR** (100 MHz, CDCl₃): δ 194.85, 156.08, 141.32, 141.18, 137.12, 136.72, 133.64, 130.76, 130.69, 128.47, 125.99, 125.95, 124.89, 122.15, 22.02 ppm; **HRMS** (m/z) (ESI): calcd for C₁₇H₁₄NO 248.1075 [M+H⁺]; found 248.1067.



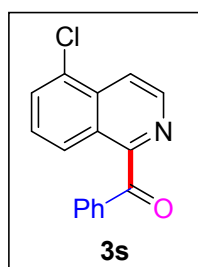
(3-methylisoquinolin-1-yl)(phenyl)methanone (3q): Derived from 3-methylisoquinoline 2-oxide (**1c**) (95.5 mg, 0.6 mmol, 1.2 equiv.) and 2-nitrovinylbenzene (**2a**) (74.6 mg, 0.5 mmol, 1.0 equiv.); Brown solid (106.3 mg, 86%), m.p. 96-98 °C, (lit.¹ 95-97

°C); **¹H NMR** (400 MHz, CDCl₃): δ 8.06 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 7.9 Hz, 2H), 7.80 (d, J = 8.3 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.62-7.56 (m, 2H), 7.47 (dt, J = 15.3, 7.8 Hz, 3H), 2.73 (s, 3H) ppm; **¹³C NMR** (100 MHz, CDCl₃): δ 194.95, 156.33, 150.31, 137.39, 136.52, 133.71, 130.86, 130.60, 128.45, 127.21, 126.52, 125.99, 124.44, 120.46, 24.14 ppm; **HRMS** (m/z) (ESI): calcd for C₁₇H₁₄NO 248.1075 [M+H⁺]; found 248.1063.

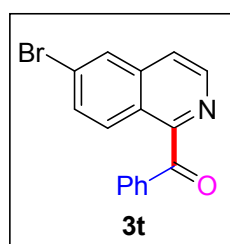


(5-methoxyisoquinolin-1-yl)(phenyl)methanone (3r): Derived

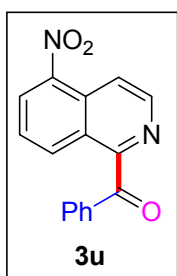
from 5-methoxyisoquinoline 2-oxide (**1d**) (105.1 mg, 0.6 mmol, 1.2 equiv.) and 2-nitrovinylbenzene (**2a**) (74.6 mg, 0.5 mmol, 1.0 equiv.); Yellow solid (102.7 mg, 78%), m.p. 118-120 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.60 (d, *J* = 5.7 Hz, 1H), 8.20 (d, *J* = 5.7 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.49 (dt, *J* = 15.8, 7.9 Hz, 3H), 7.04 (d, *J* = 7.7 Hz, 1H), 4.05 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 194.95, 155.87, 154.71, 140.89, 136.69, 133.63, 130.73, 129.53, 128.47, 128.43, 127.08, 117.78, 117.04, 107.79, 55.79 ppm; HRMS (m/z) (ESI): calcd for C₁₇H₁₄NO₂ 264.1025 [M+H⁺]; found 264.1017.



(5-chloroisoquinolin-1-yl)(phenyl)methanone (3s): Derived from 5-chloroisoquinoline 2-oxide (**1e**) (107.8 mg, 0.6 mmol, 1.2 equiv.) and 2-nitrovinylbenzene (**2a**) (74.6 mg, 0.5 mmol, 1.0 equiv.); Brown solid (104.4 mg, 78%), m.p. 125-127 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.71 (d, *J* = 5.9 Hz, 1H), 8.21 (dd, *J* = 5.9, 0.9 Hz, 1H), 8.16-8.10 (m, 1H), 7.96-7.90 (m, 2H), 7.82 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.65-7.59 (m, 1H), 7.53 (dd, *J* = 8.5, 7.6 Hz, 1H), 7.50-7.45 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 194.36, 156.78, 142.35, 136.36, 134.58, 133.93, 131.59, 130.76, 130.70, 128.58, 128.17, 127.30, 125.25, 118.90 ppm; HRMS (m/z) (APCI): calcd for C₁₆H₁₁ClNO 268.0529 [M+H⁺]; found 268.0510.



(6-bromoisoquinolin-1-yl)(phenyl)methanone (3t): Derived from 6-bromoisoquinoline 2-oxide (**1f**) (134.4 mg, 0.6 mmol, 1.2 equiv.) and 2-nitrovinylbenzene (**2a**) (74.6 mg, 0.5 mmol, 1.0 equiv.); White solid (109.3 mg, 70%), m.p. 116-118 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.62 (d, *J* = 5.6 Hz, 1H), 8.11 (dd, *J* = 8.1, 5.4 Hz, 2H), 7.96-7.91 (m, 2H), 7.74-7.67 (m, 2H), 7.64-7.59 (m, 1H), 7.48 (t, *J* = 7.8 Hz, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 194.22, 156.49, 142.21, 137.82, 136.43, 133.82, 131.95, 130.78, 129.25, 128.52, 127.99, 125.72, 124.90, 121.52 ppm; HRMS (m/z) (ESI): calcd for C₁₆H₁₁BrNO 312.0024, 314.0004 [M+H⁺]; found 312.0014, 313.9992.



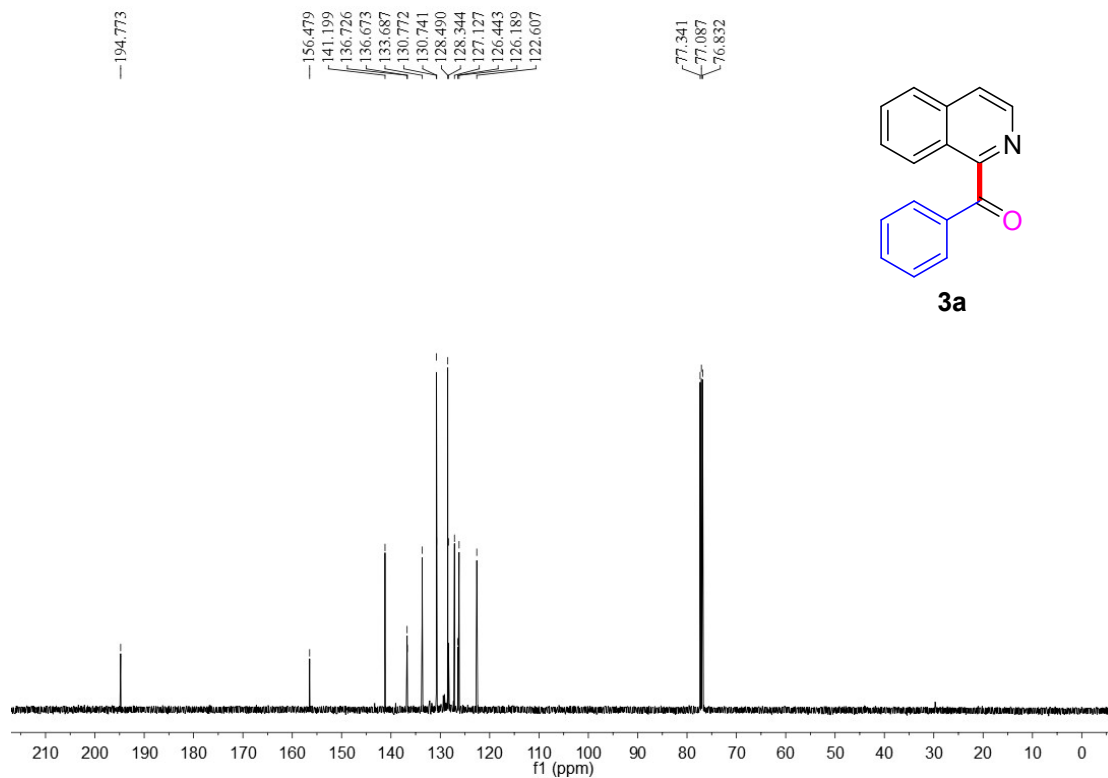
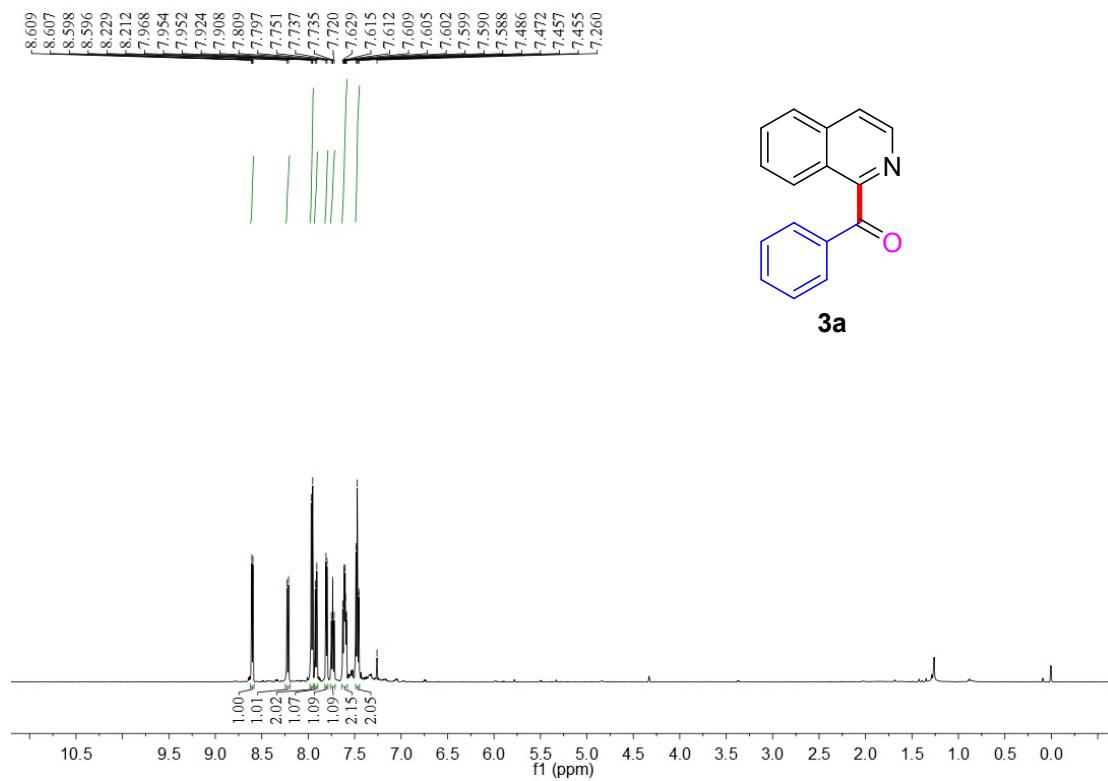
(5-nitroisoquinolin-1-yl)(phenyl)methanone (3u): Derived from 5-nitroisoquinoline 2-oxide (**1g**) (114.1 mg, 0.6 mmol, 1.2 equiv.) and 2-nitrovinylbenzene (**2a**) (74.6 mg, 0.5 mmol, 1.0 equiv.); Light yellow solid (105.8 mg, 76%), m.p. 110-112 °C, (lit.¹, 106-108 °C); ¹H NMR (400 MHz, CDCl₃): δ 8.83 (d, *J* = 6.1 Hz, 1H), 8.63 (d, *J* =

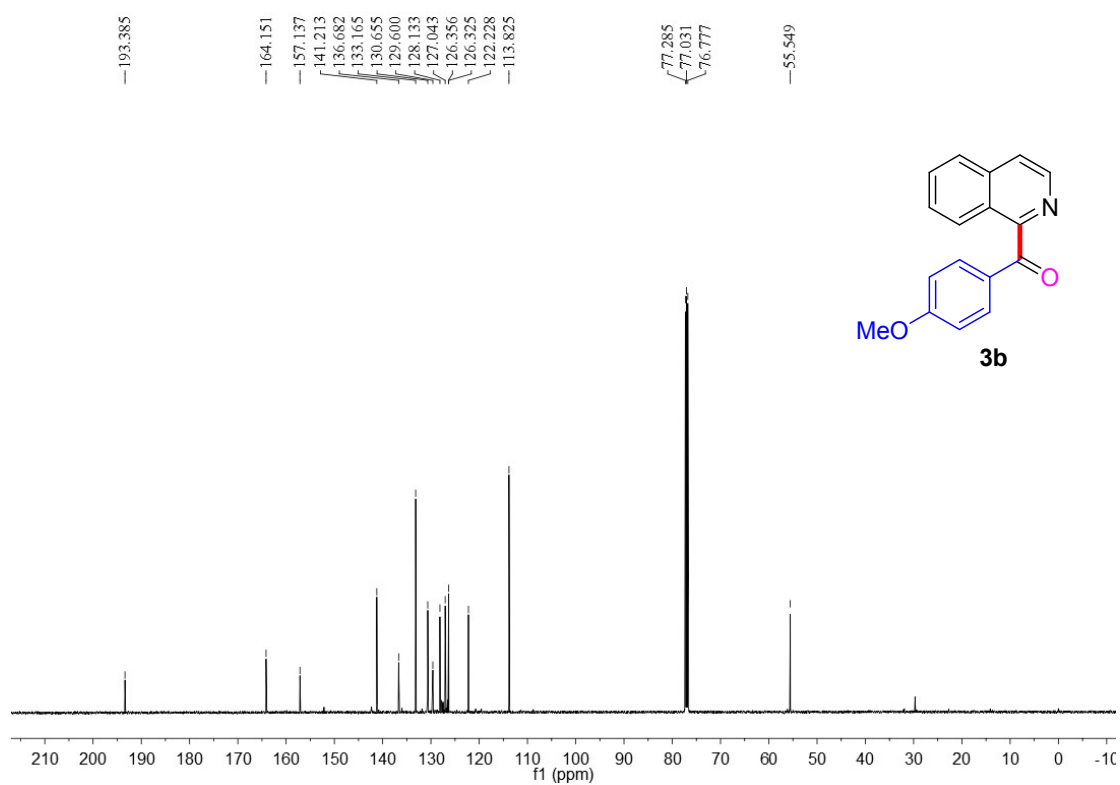
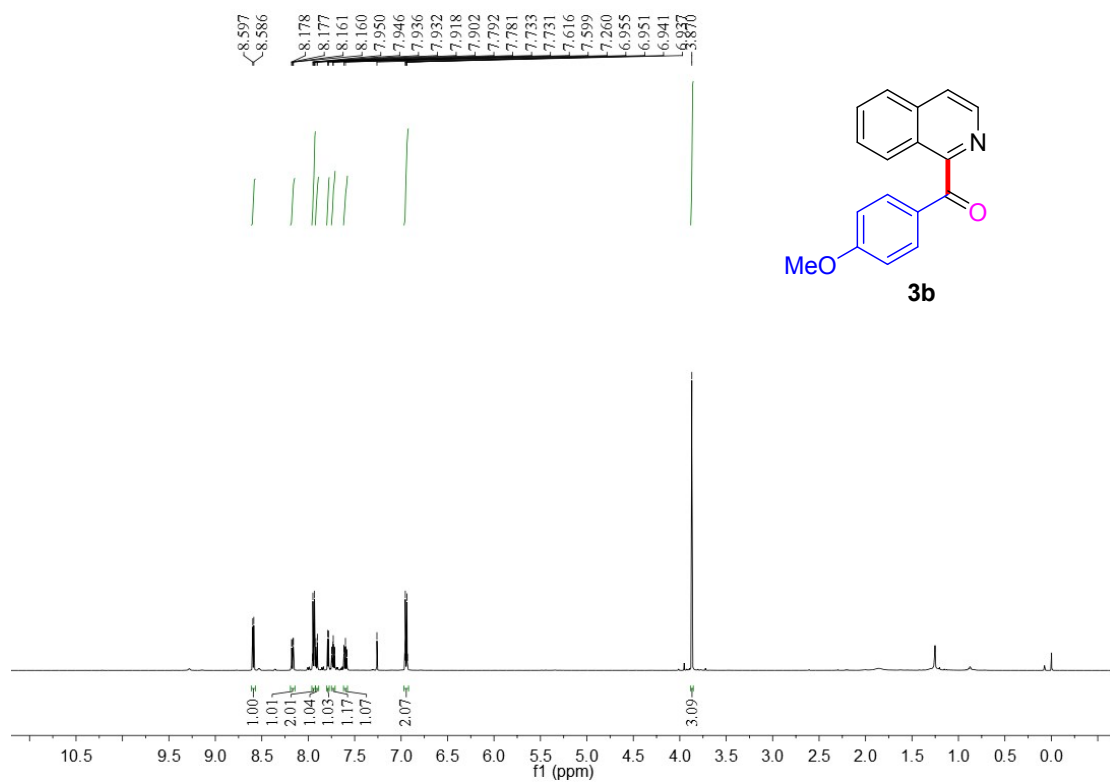
6.1 Hz, 1H), 8.56 (t, *J* = 7.3 Hz, 2H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.74 (t, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 193.80, 157.17, 145.27, 144.45, 136.02, 134.25, 133.24, 130.84, 129.15, 128.69, 128.60, 126.77, 126.75, 117.62 ppm; HRMS (m/z) (ESI): calcd for C₁₆H₁₁N₂O₃ 279.0770 [M+H⁺]; found 279.0756.

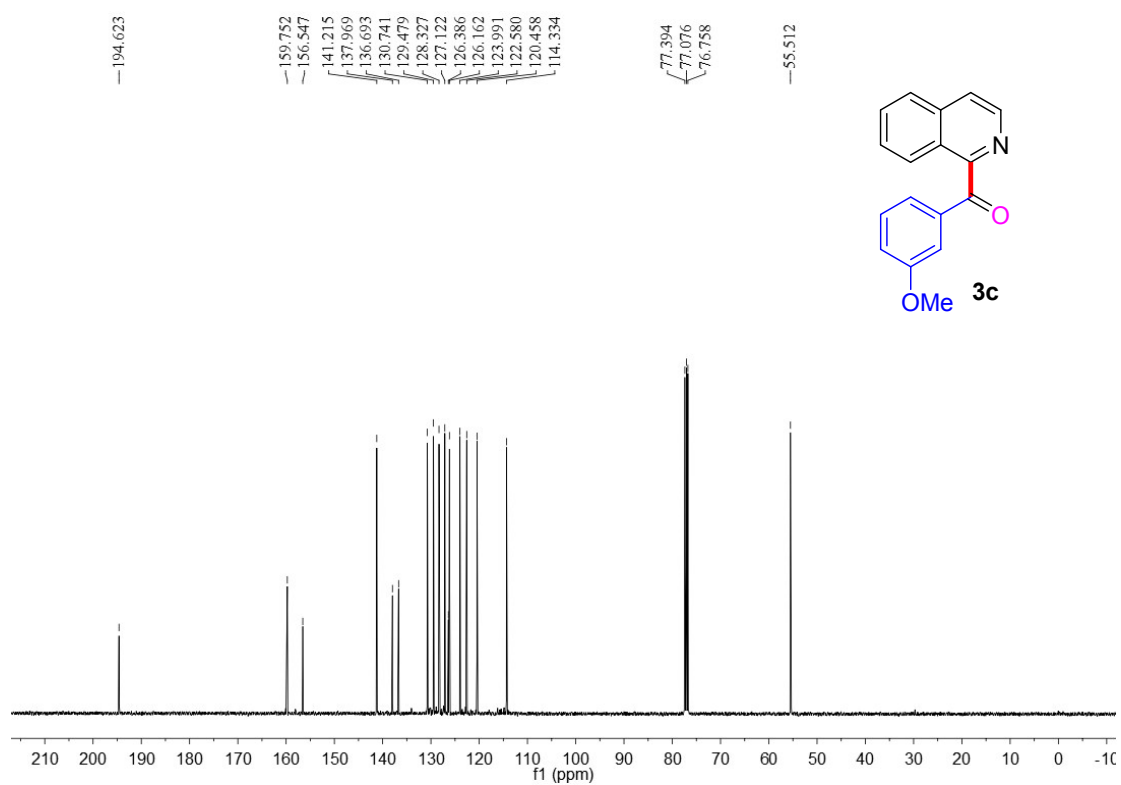
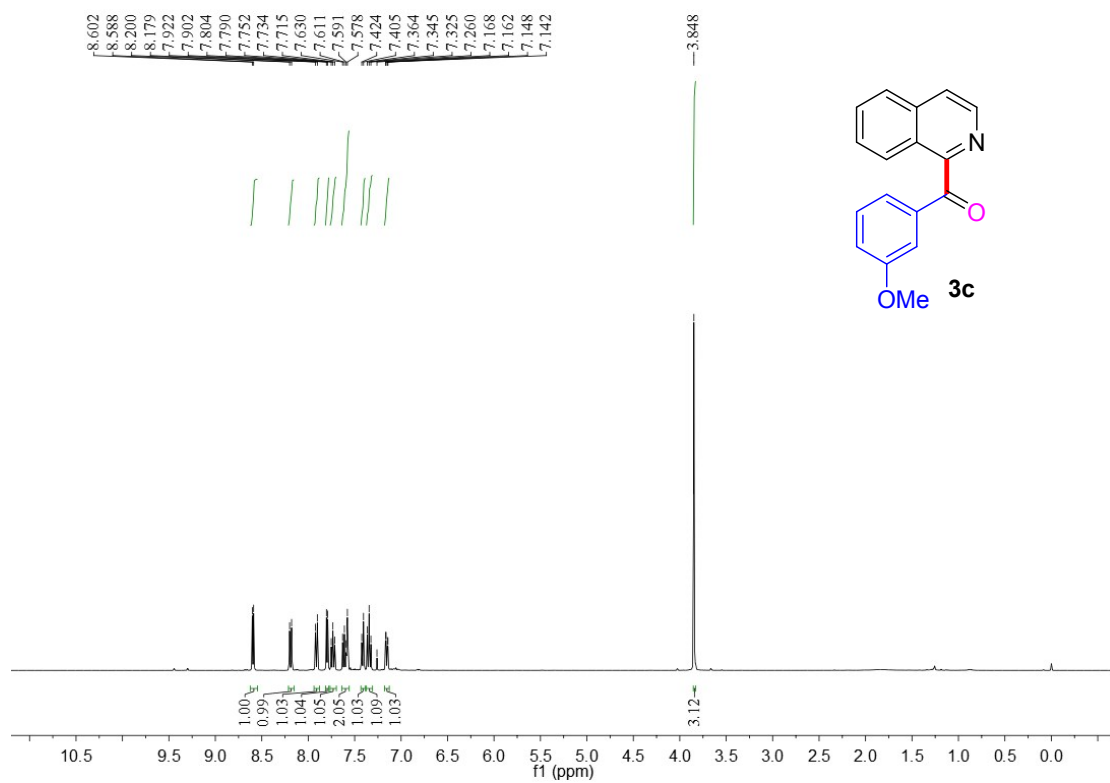
Reference

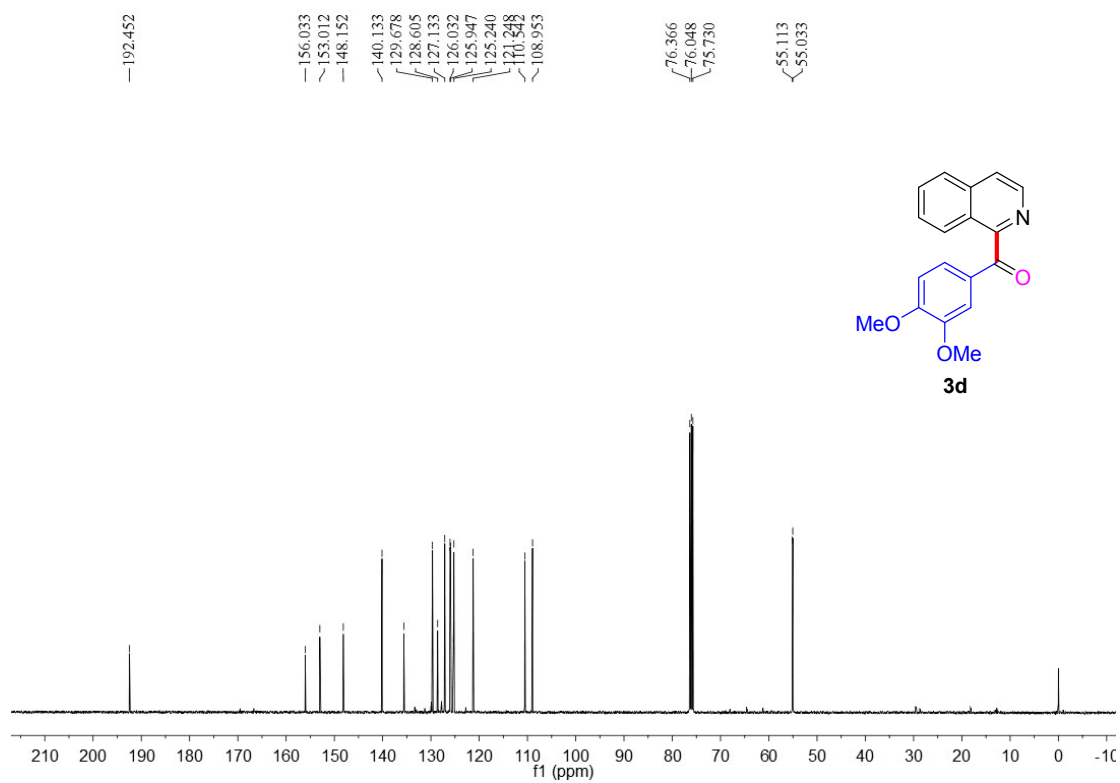
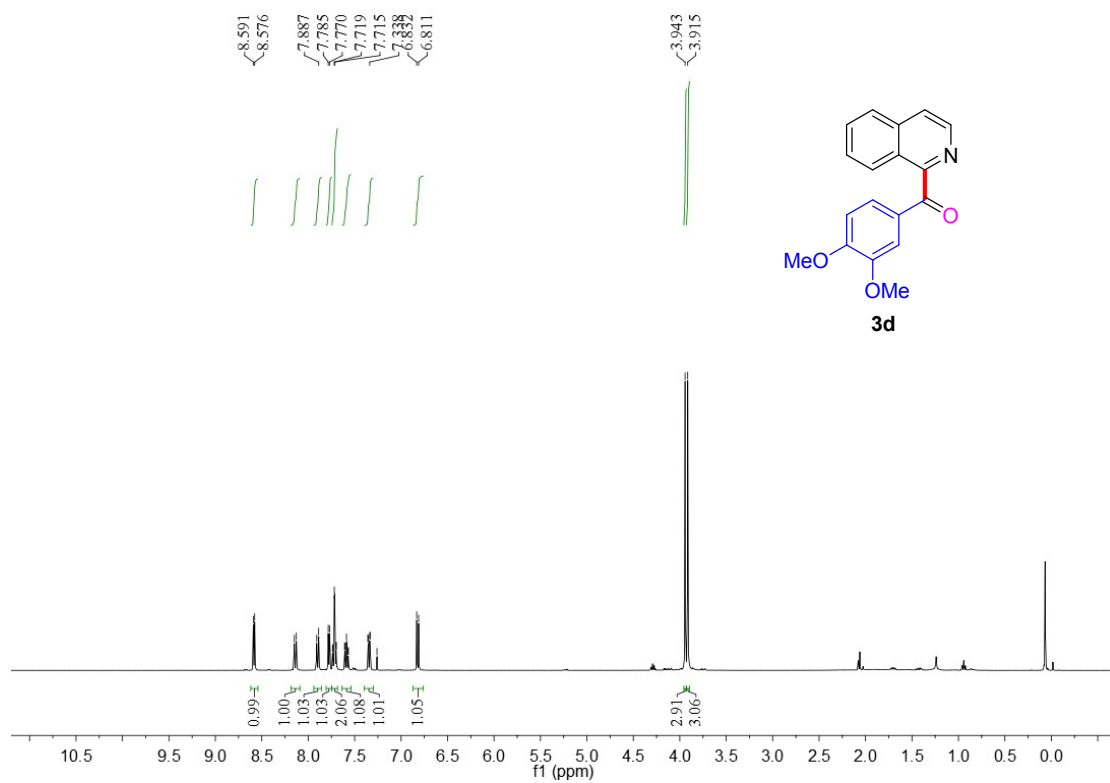
1. W. Ali, A. Behera, S. Guin, B. K. Patel, *J. Org. Chem.* **2015**, *80*, 5625–5632.
2. B. Reux, T. Nevalainen, K. H. Raitio, A. M. P. Koskinen, *Bio. Med. Chem.* **2009**, *17*, 4441-4447.
3. D. P. Aysola, M. S. Gibson, *Can. J. Chem.* **1977**, *55*, 435-437.
4. H. W. Gibson, F. D. Popp, *J. Chem. Soc. C* **1966**, 1860-1864.

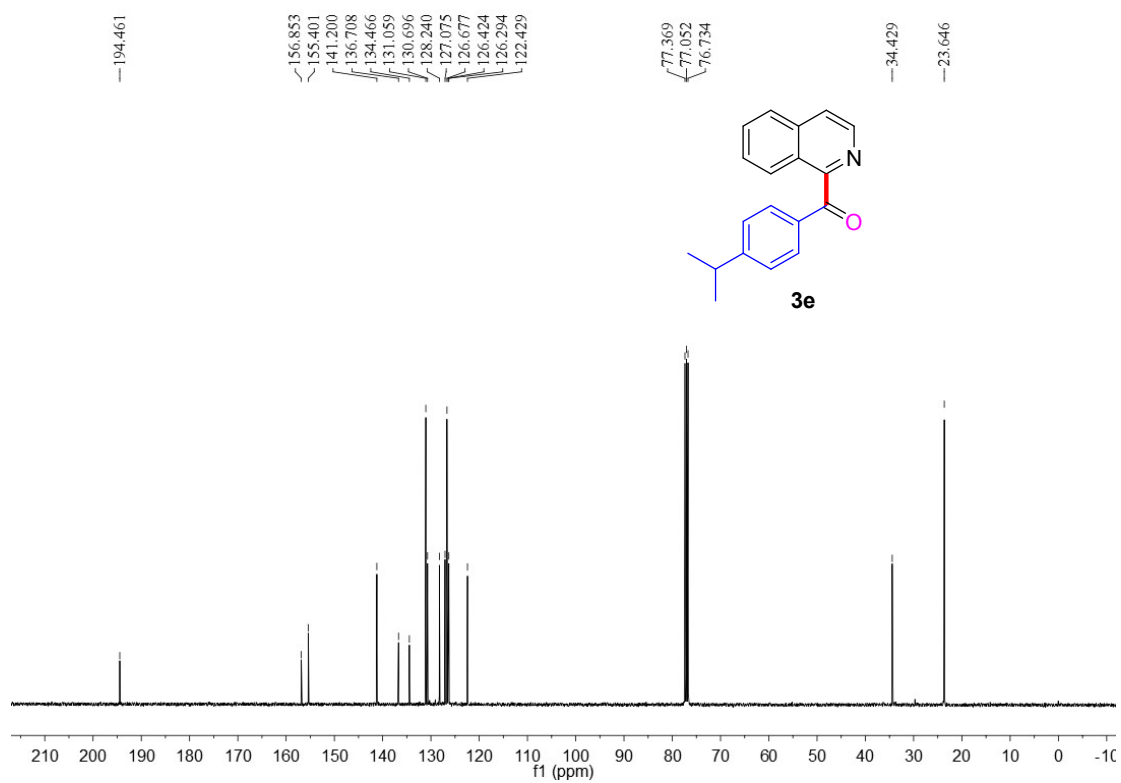
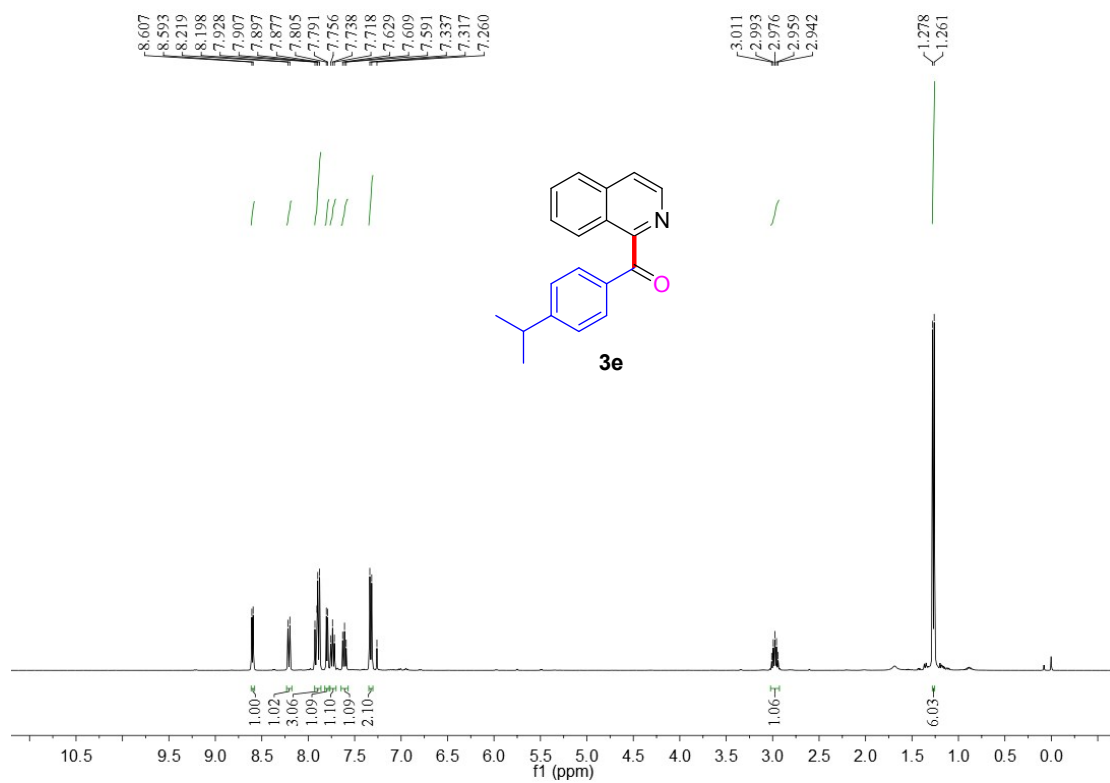
Copies of ¹H NMR and ¹³C NMR Spectra of all compounds

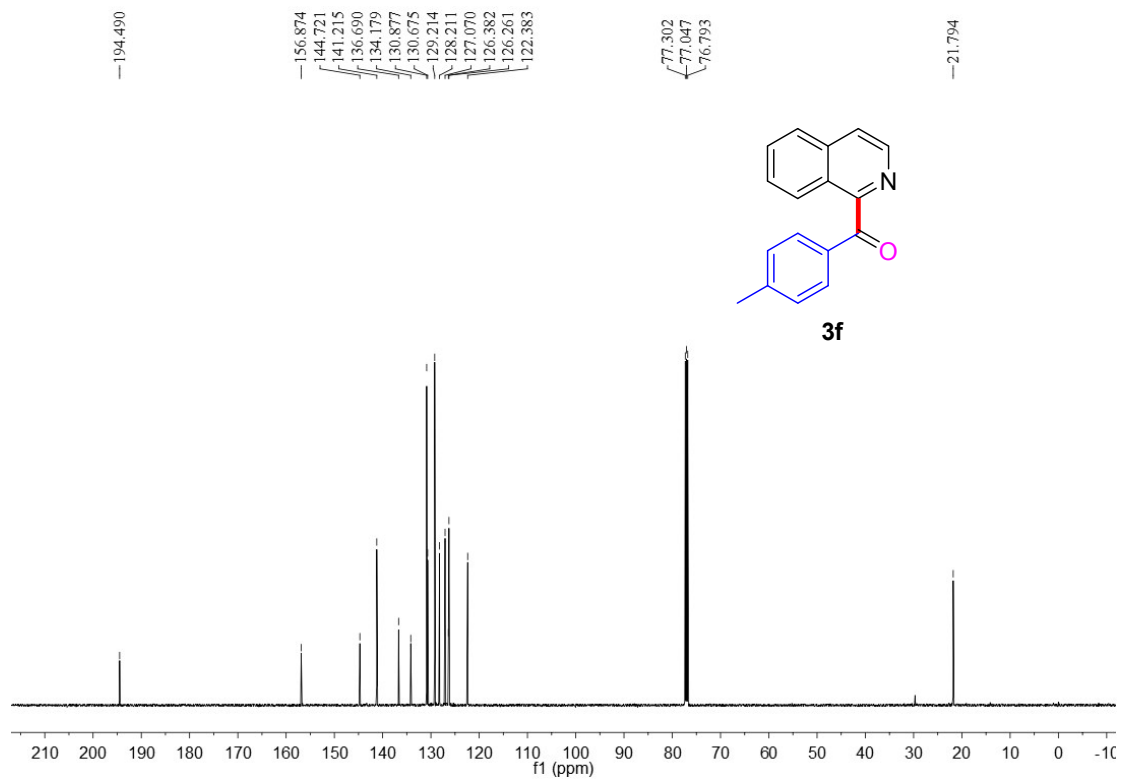
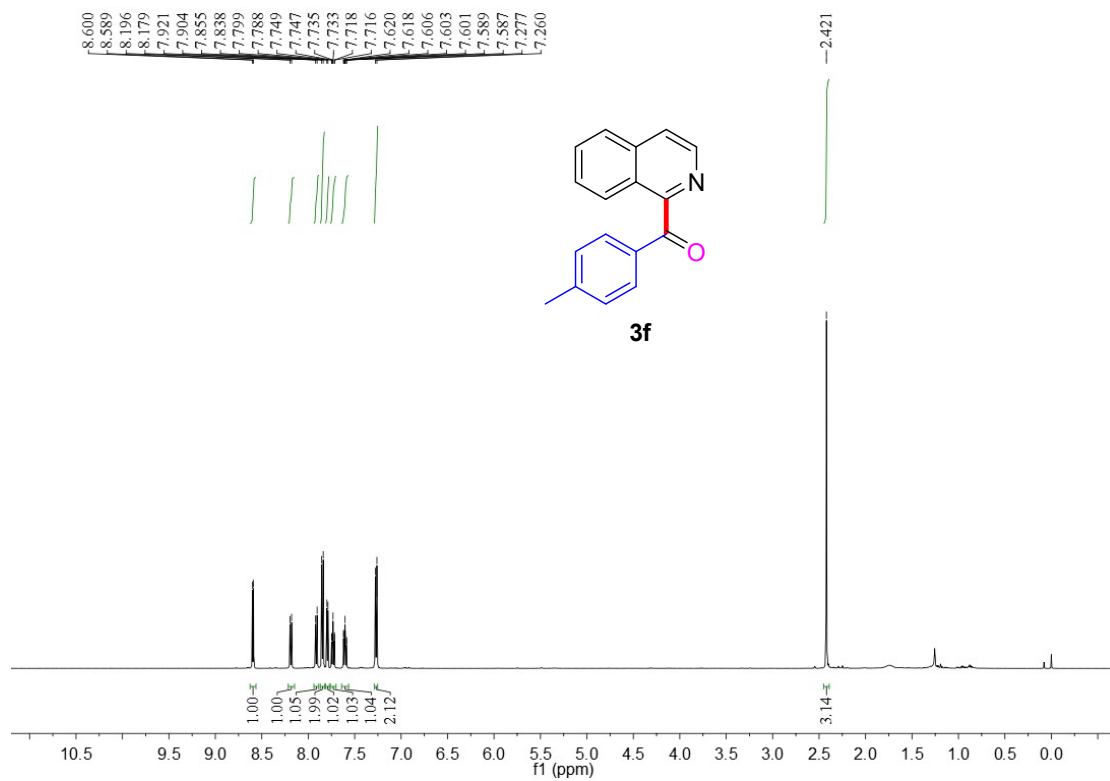


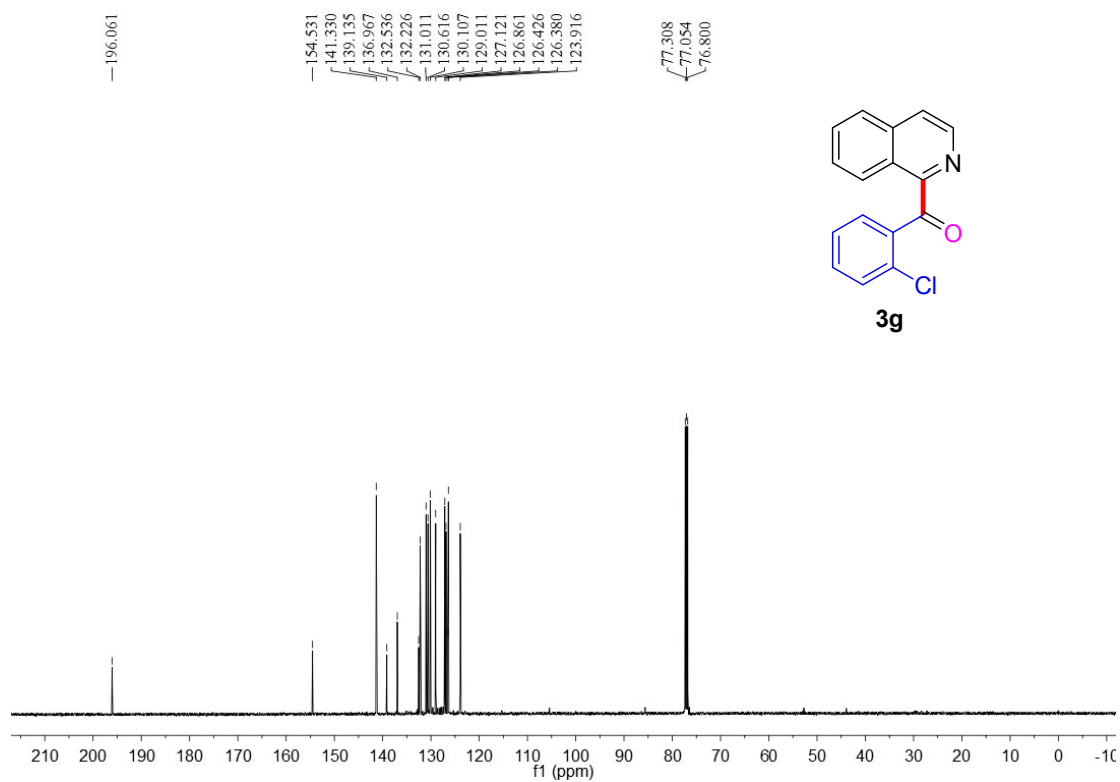
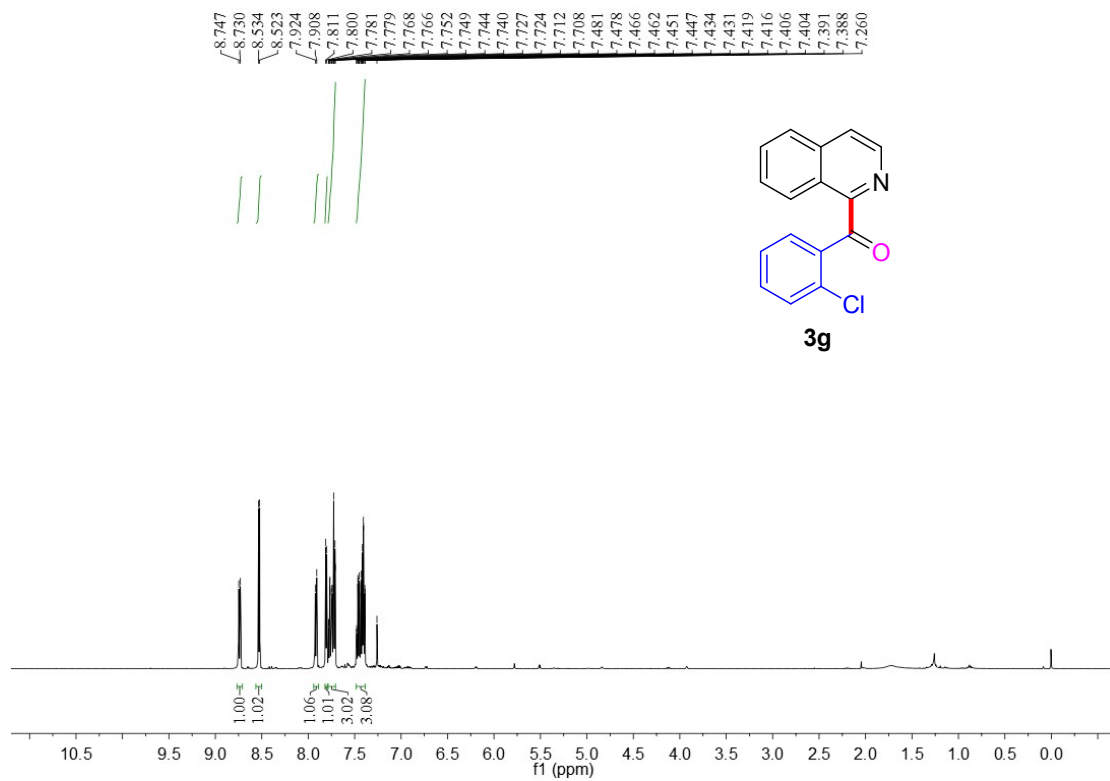


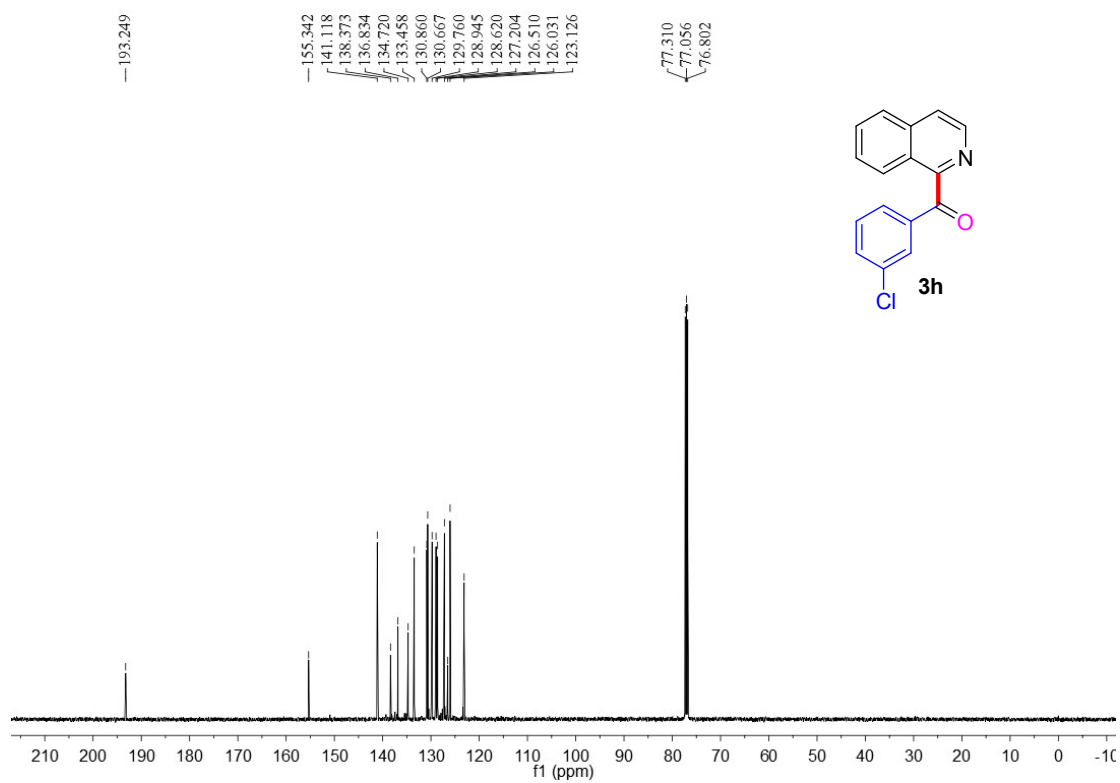
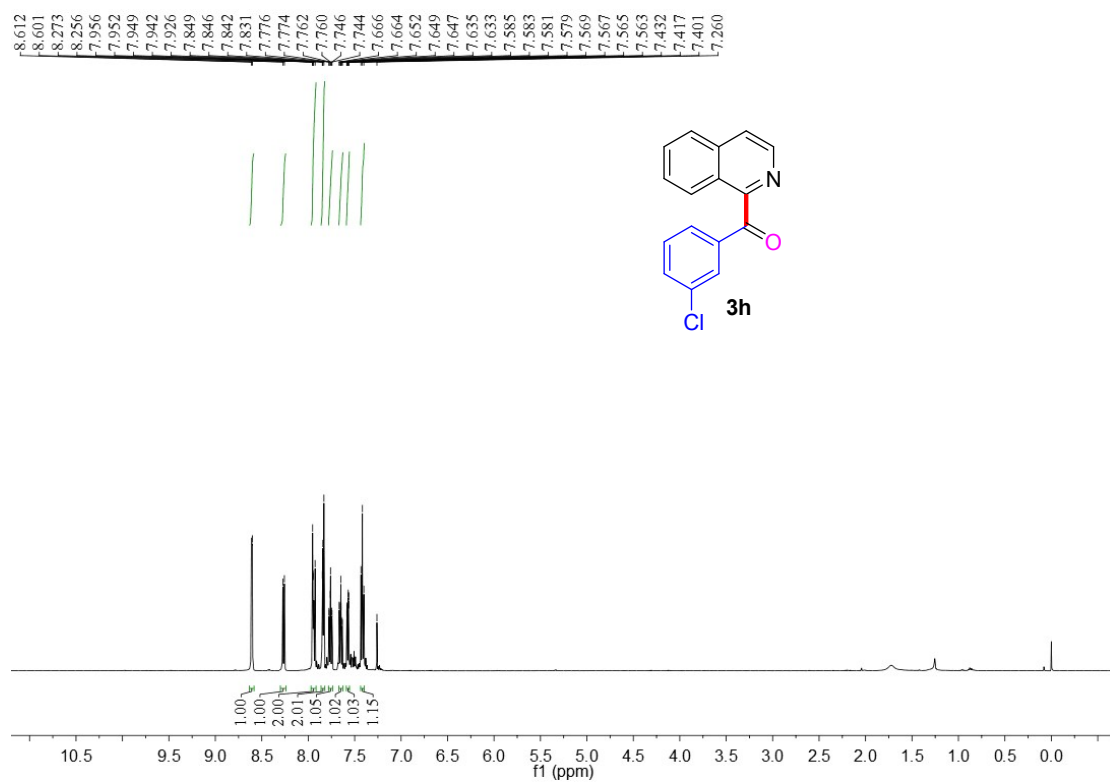


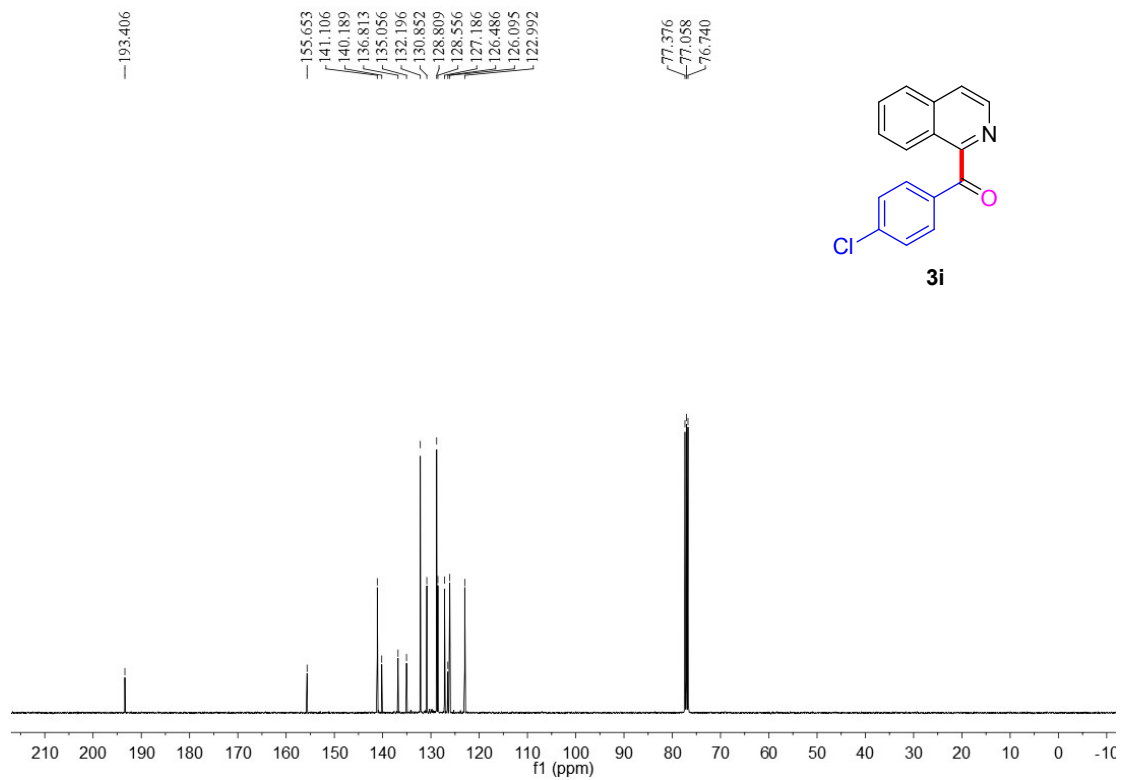
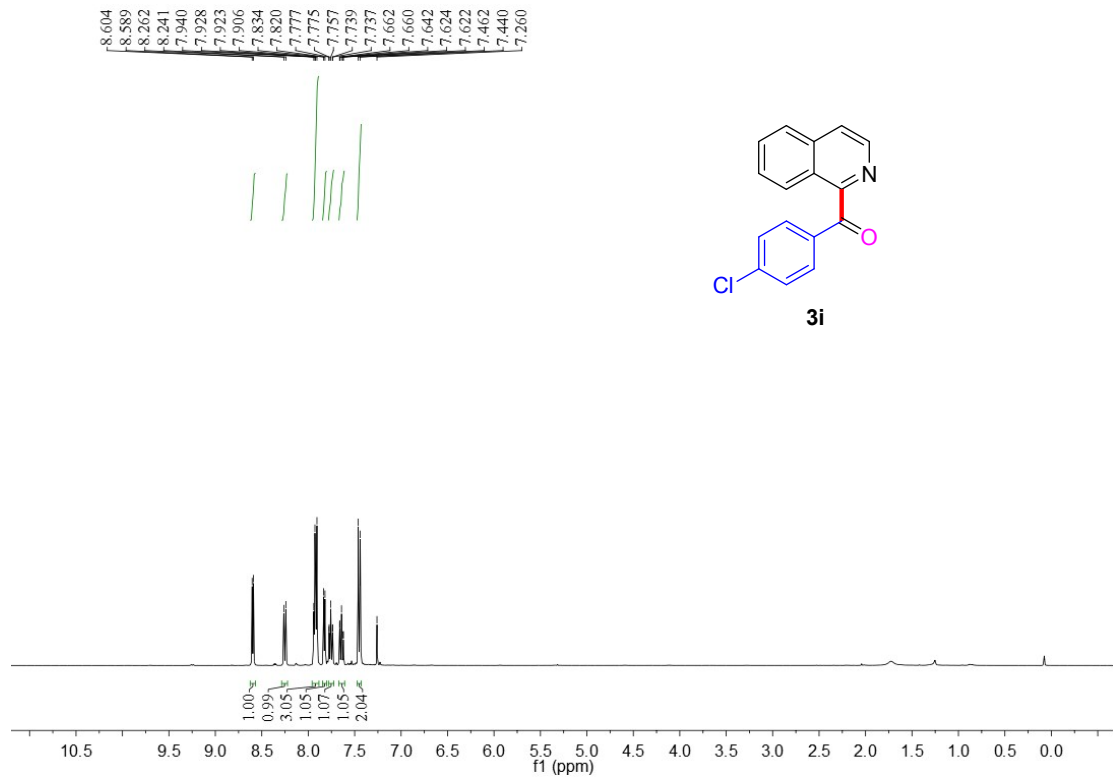


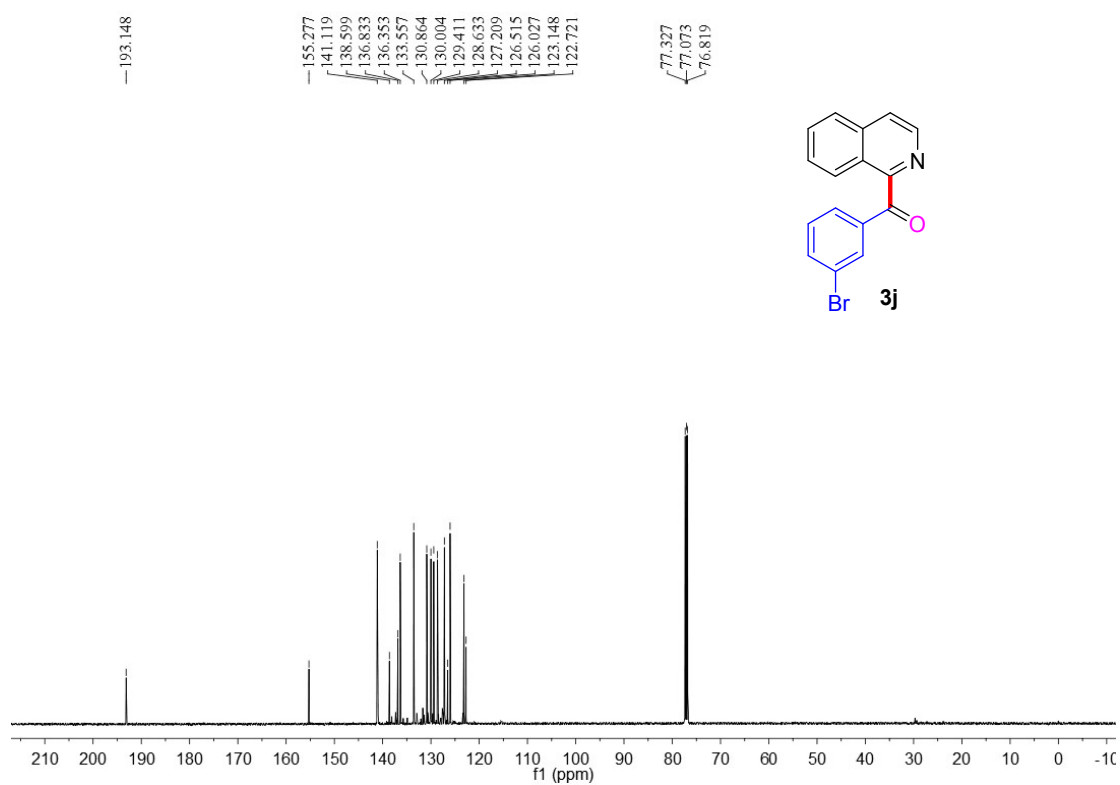
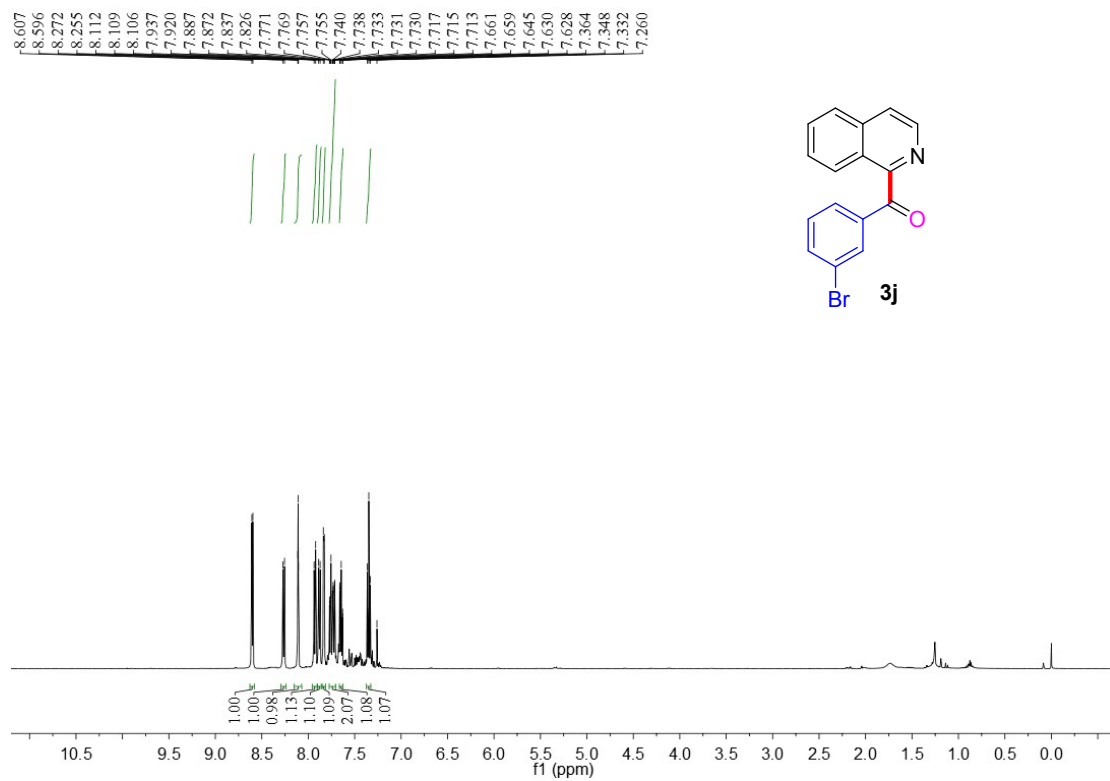


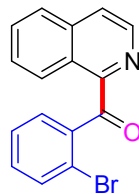
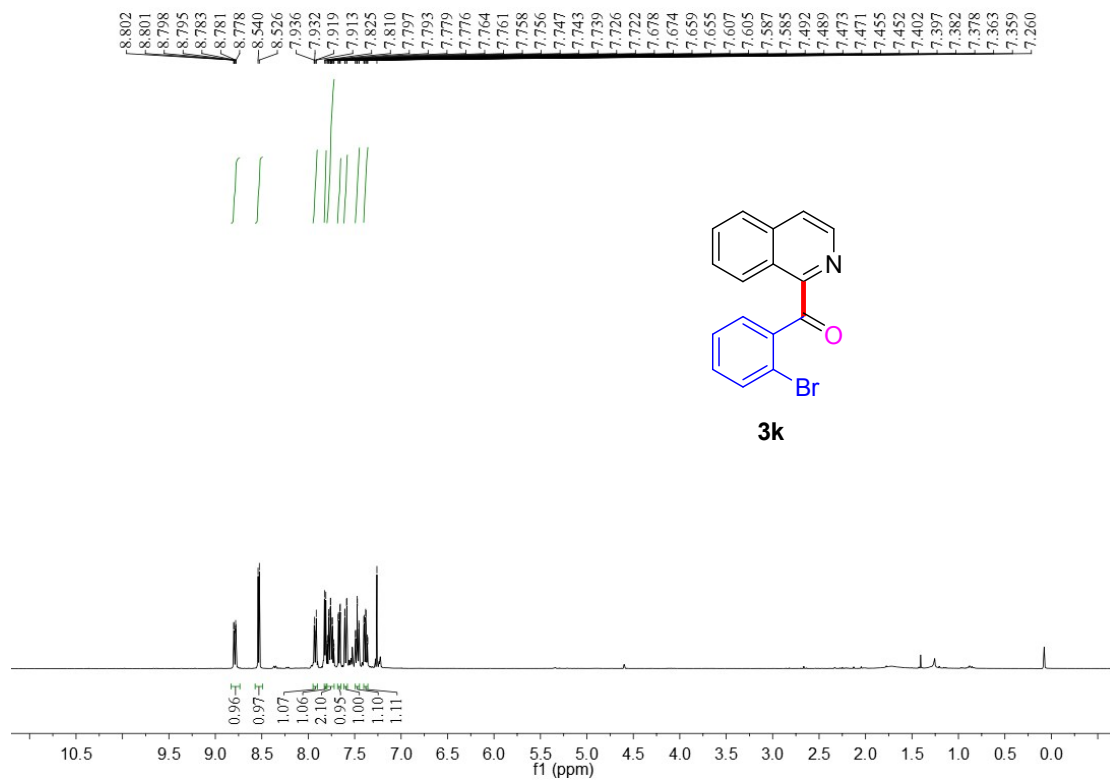




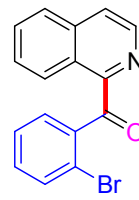
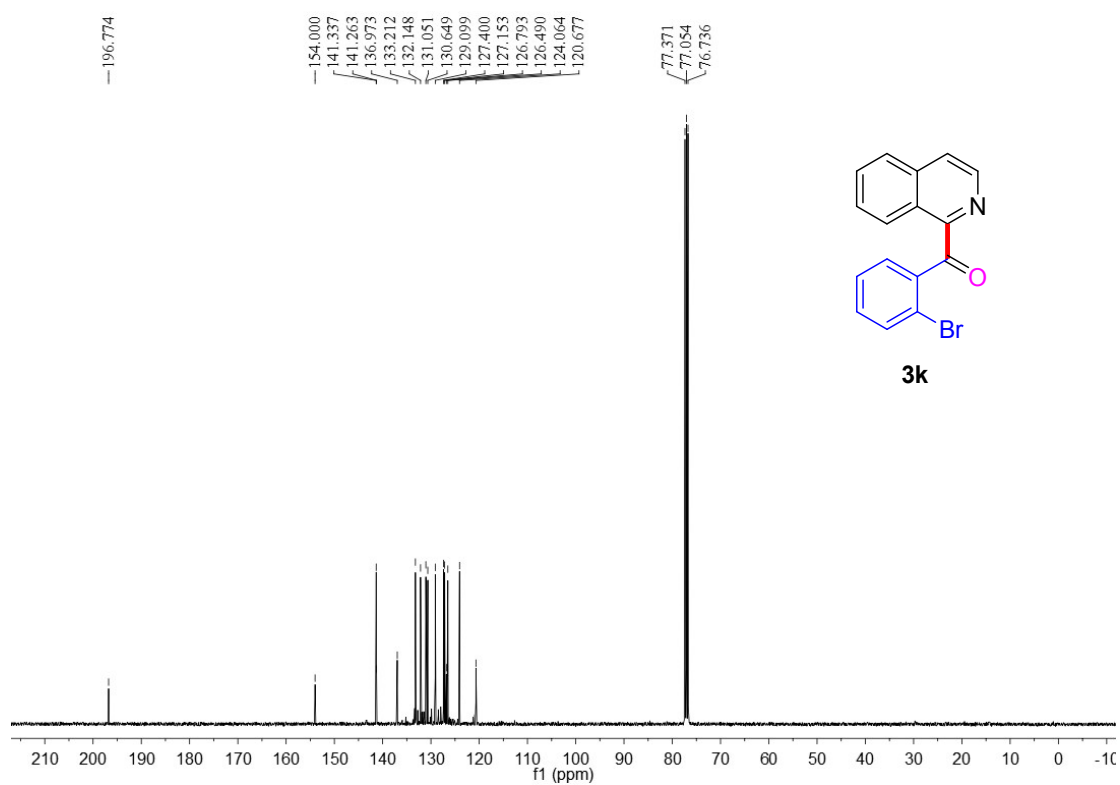




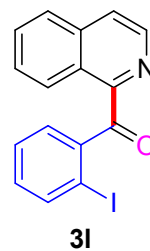
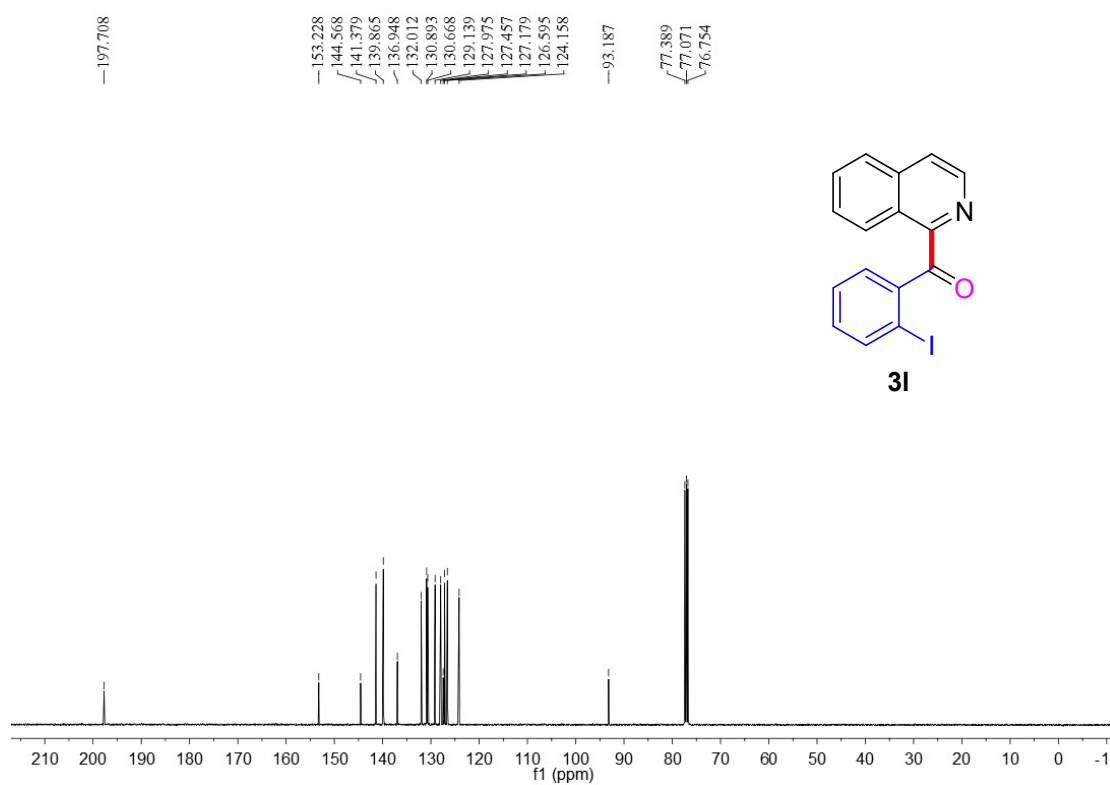
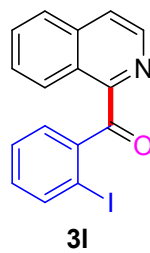
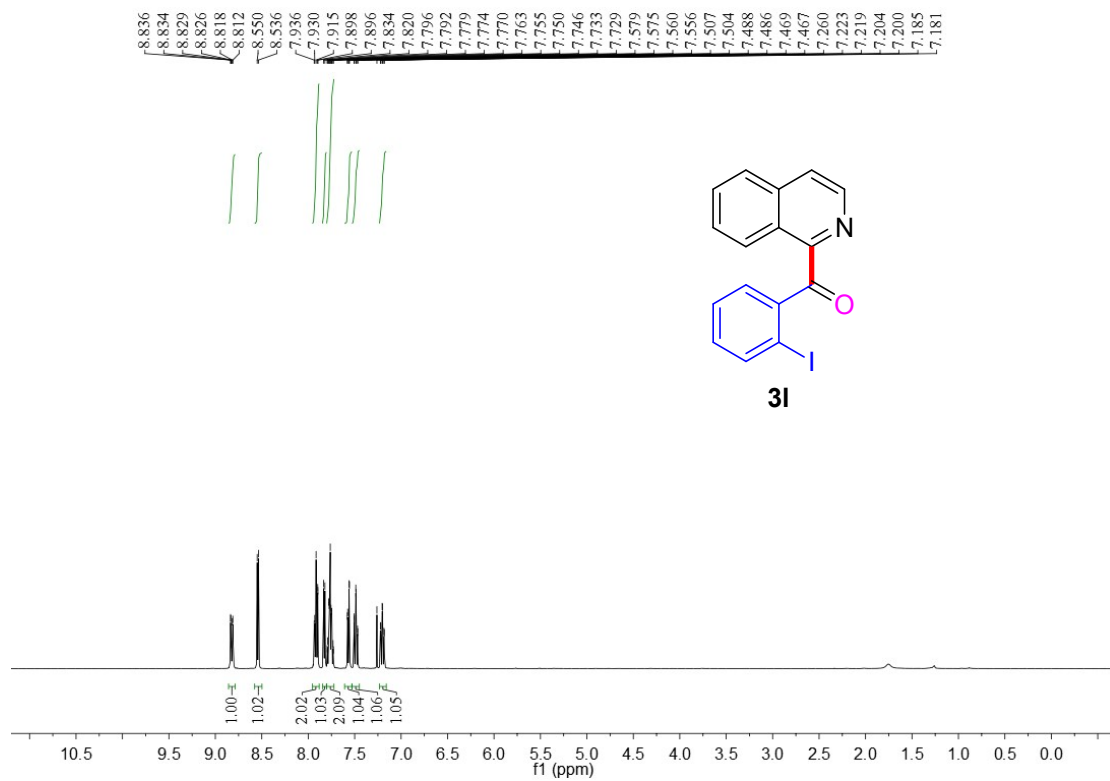


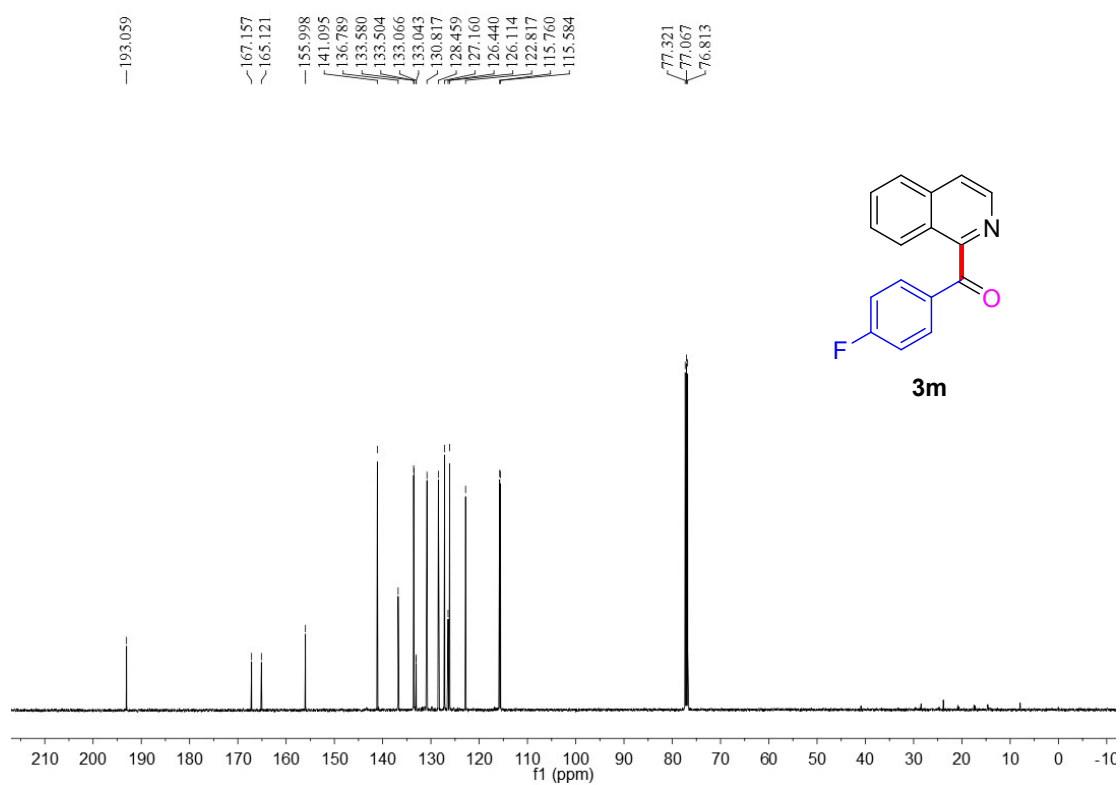
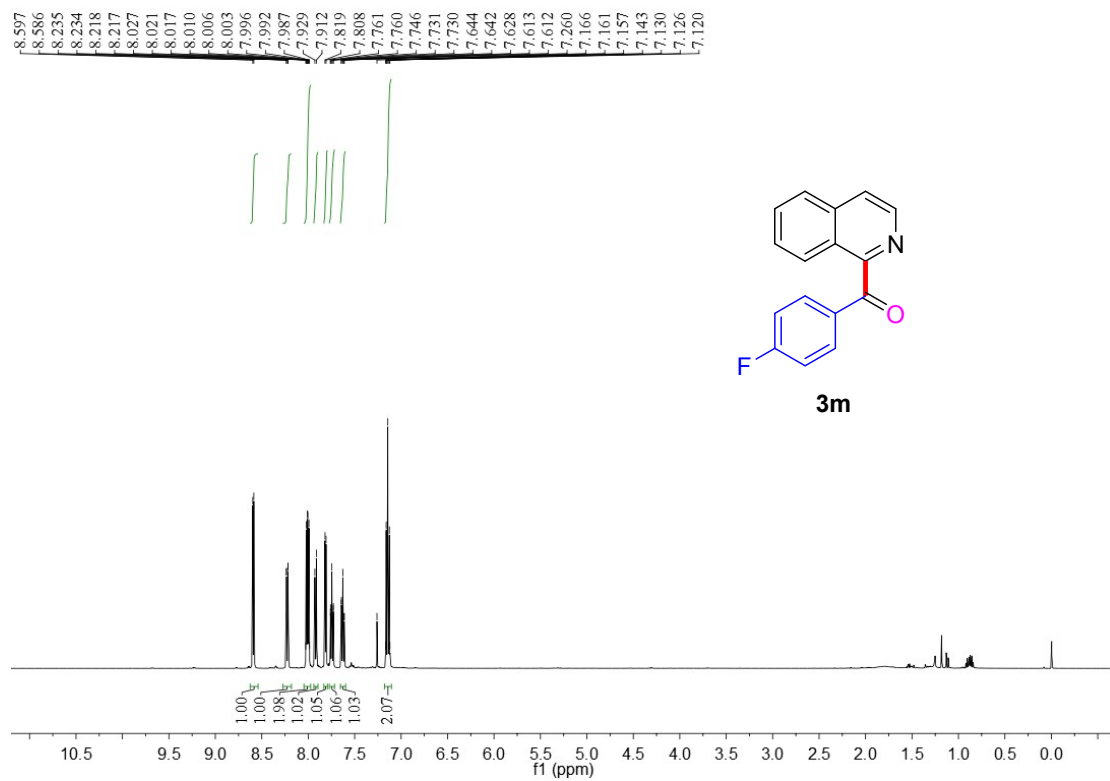


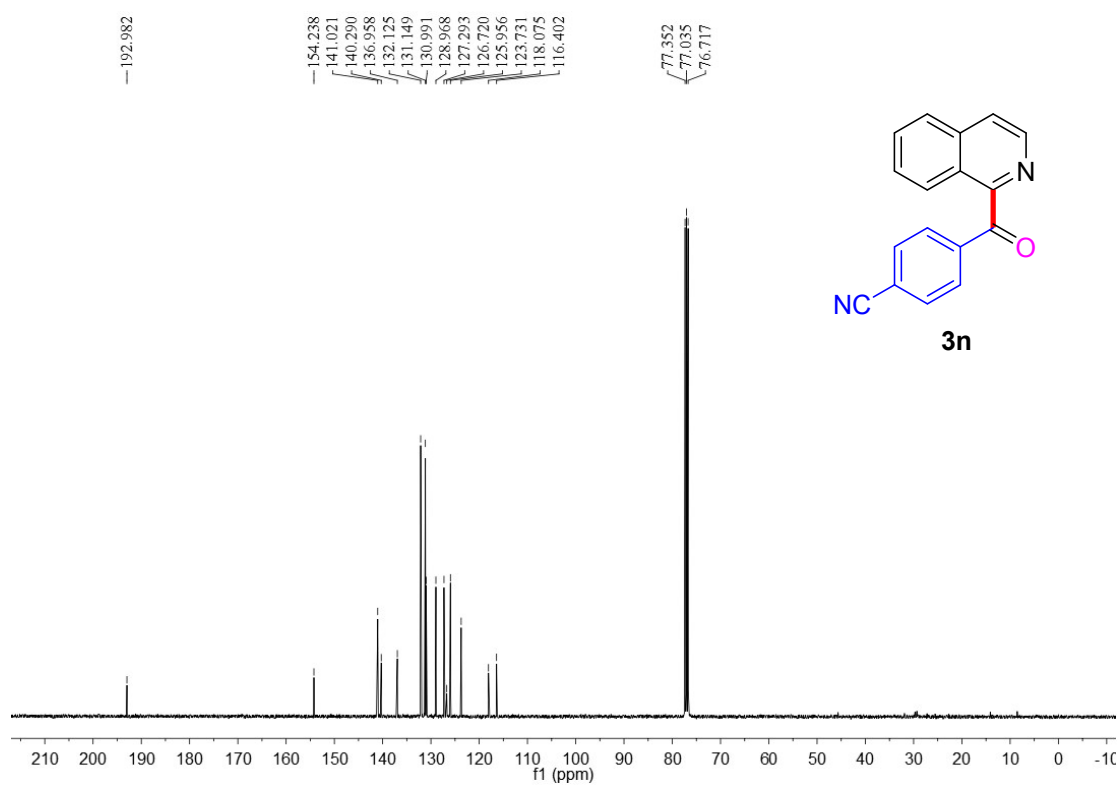
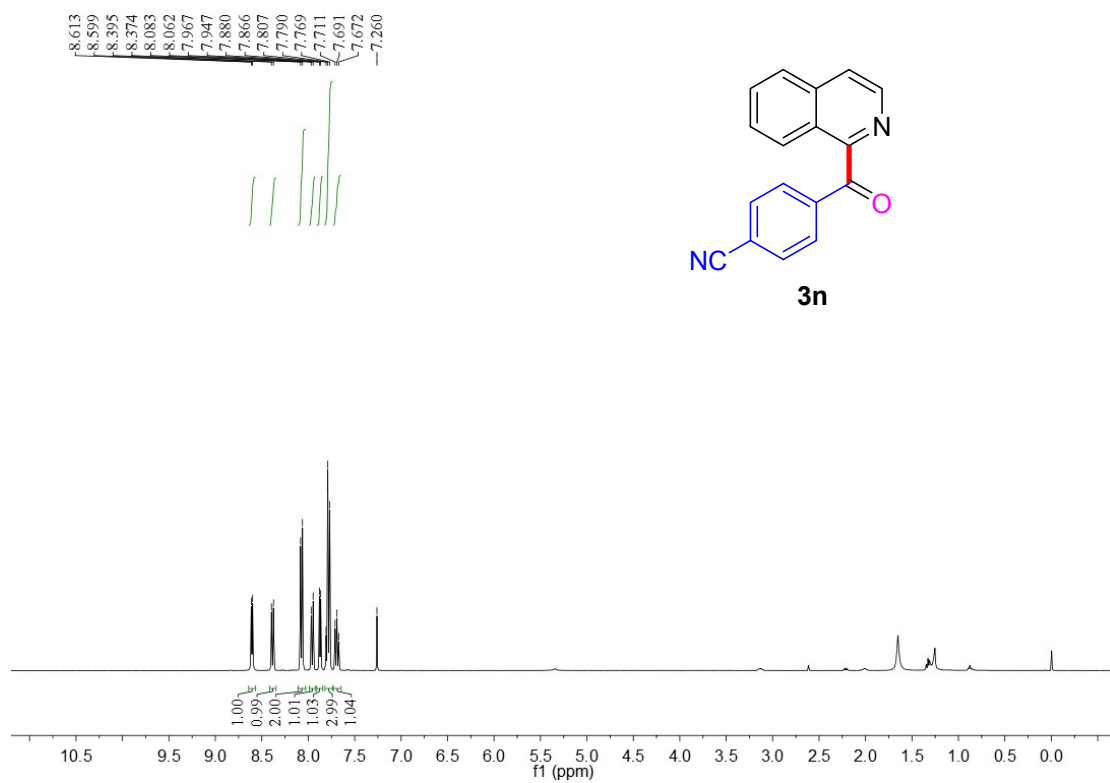
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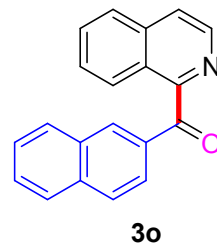
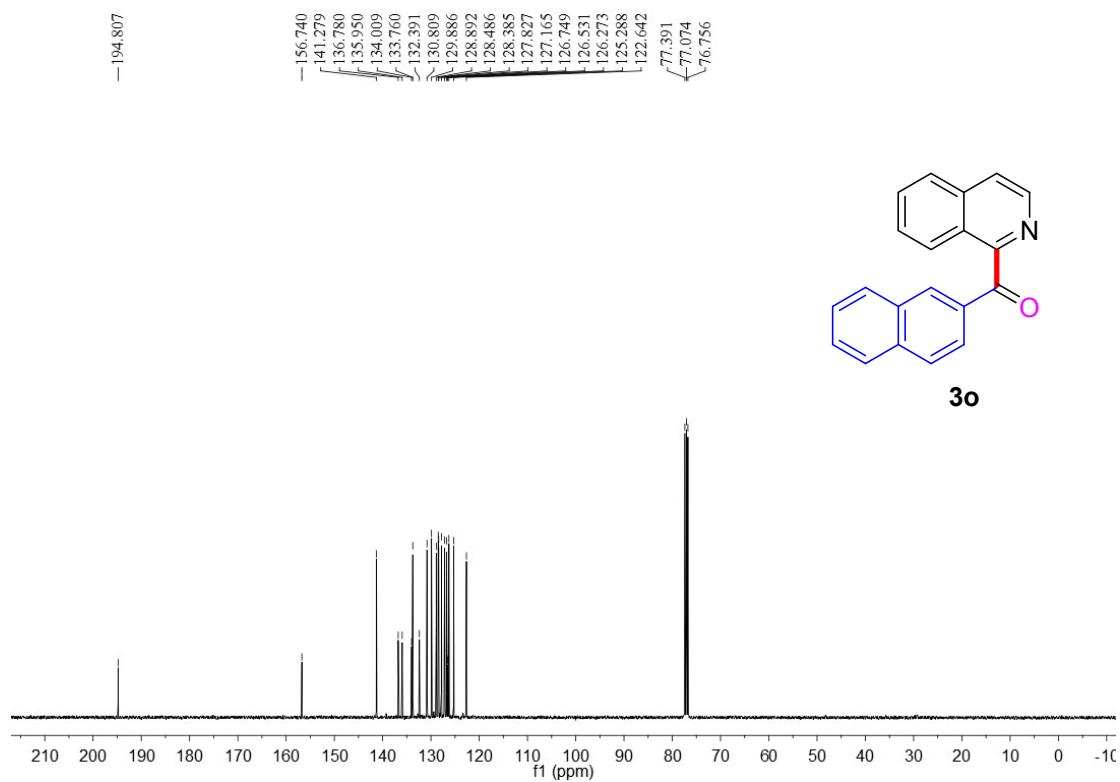
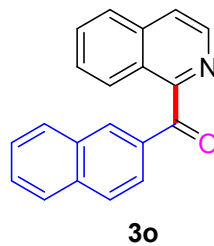
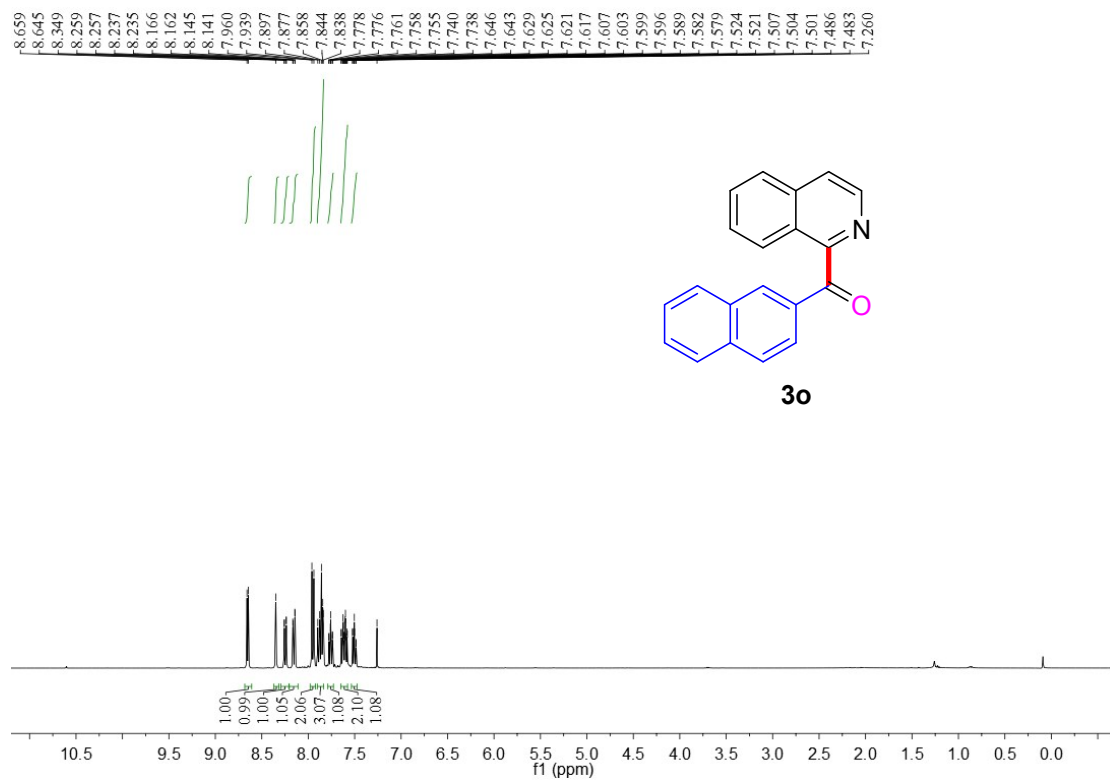


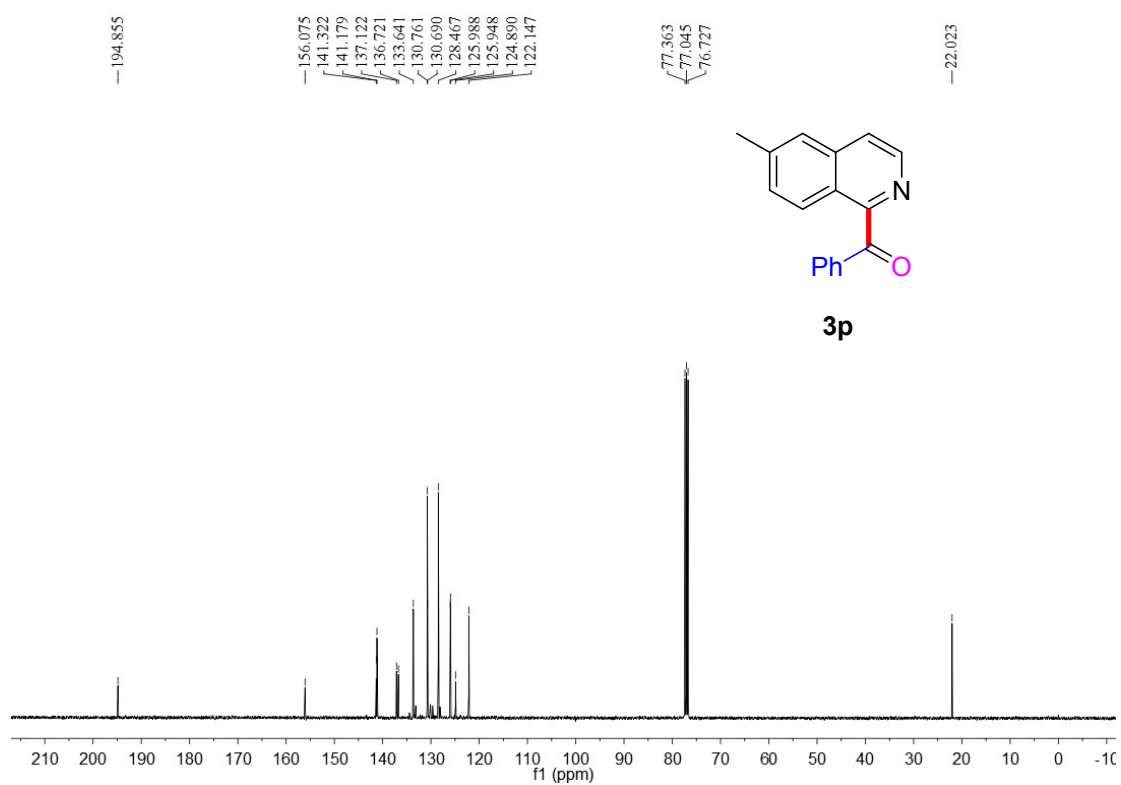
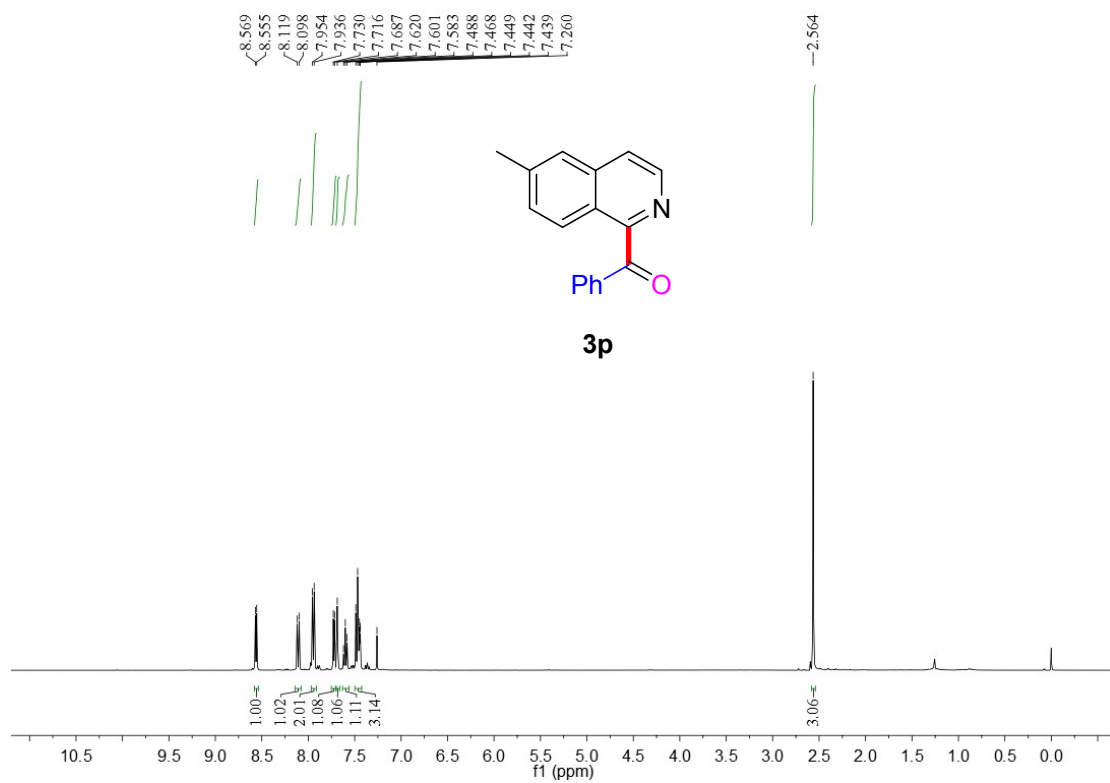
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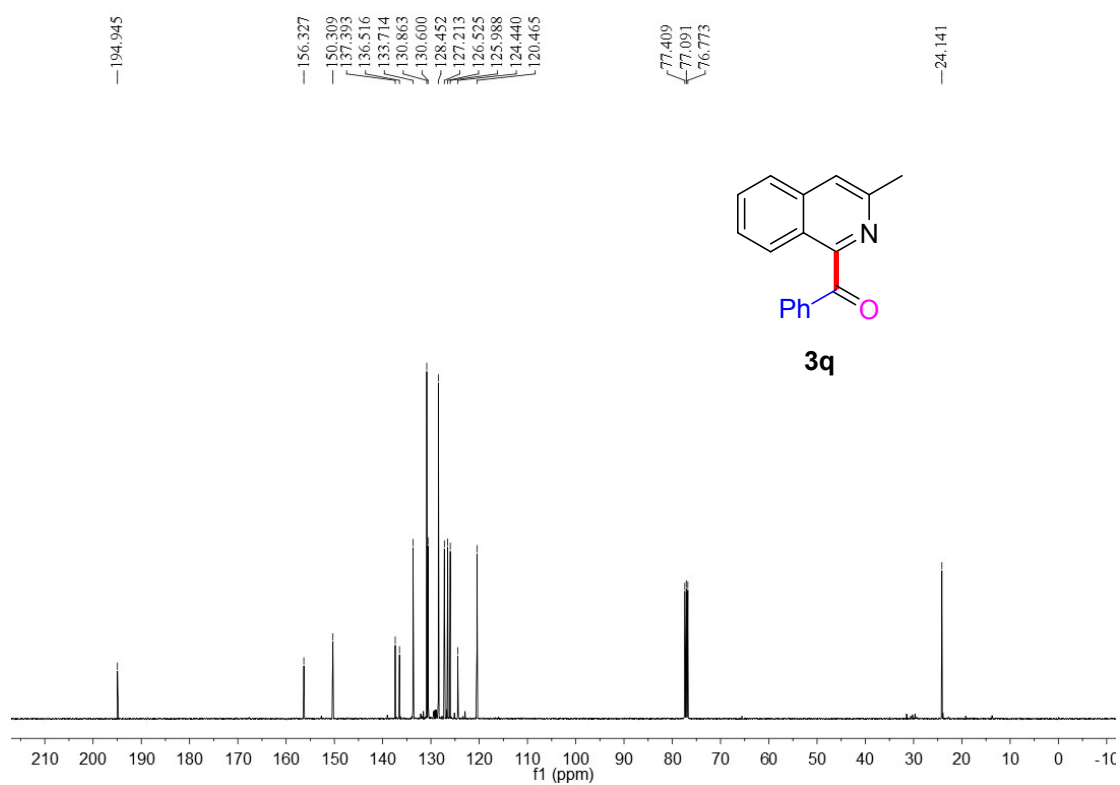
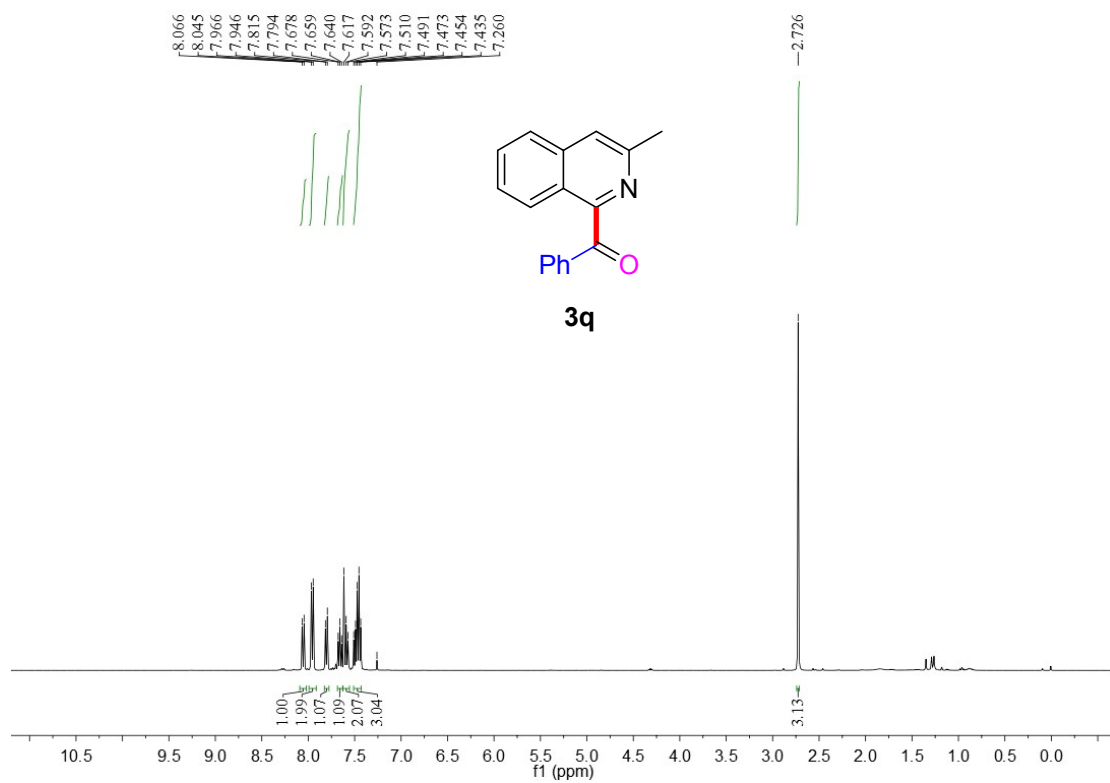


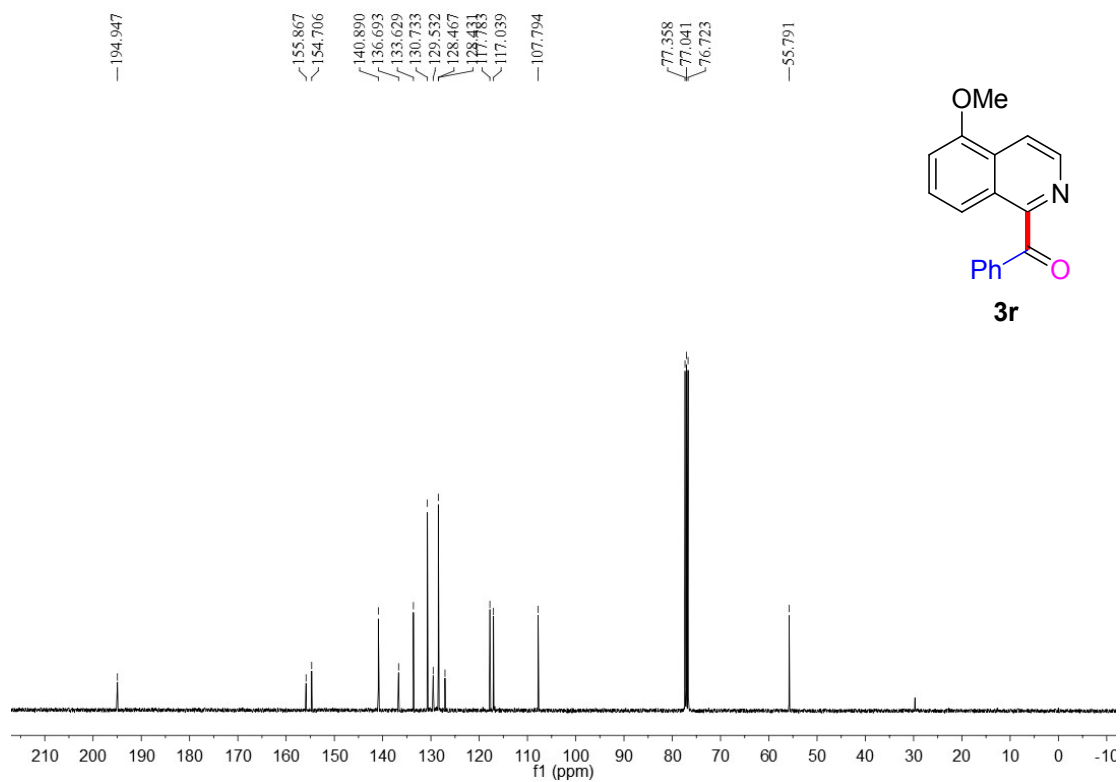
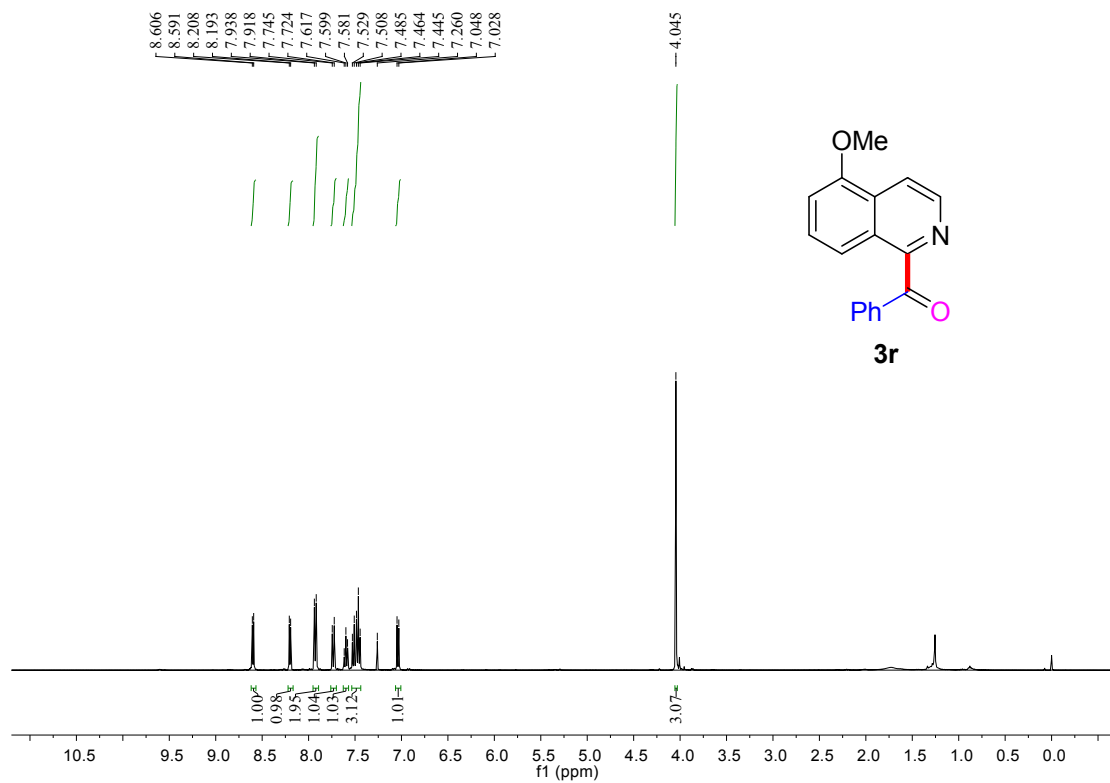


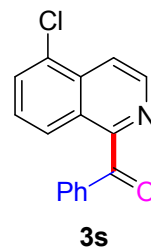
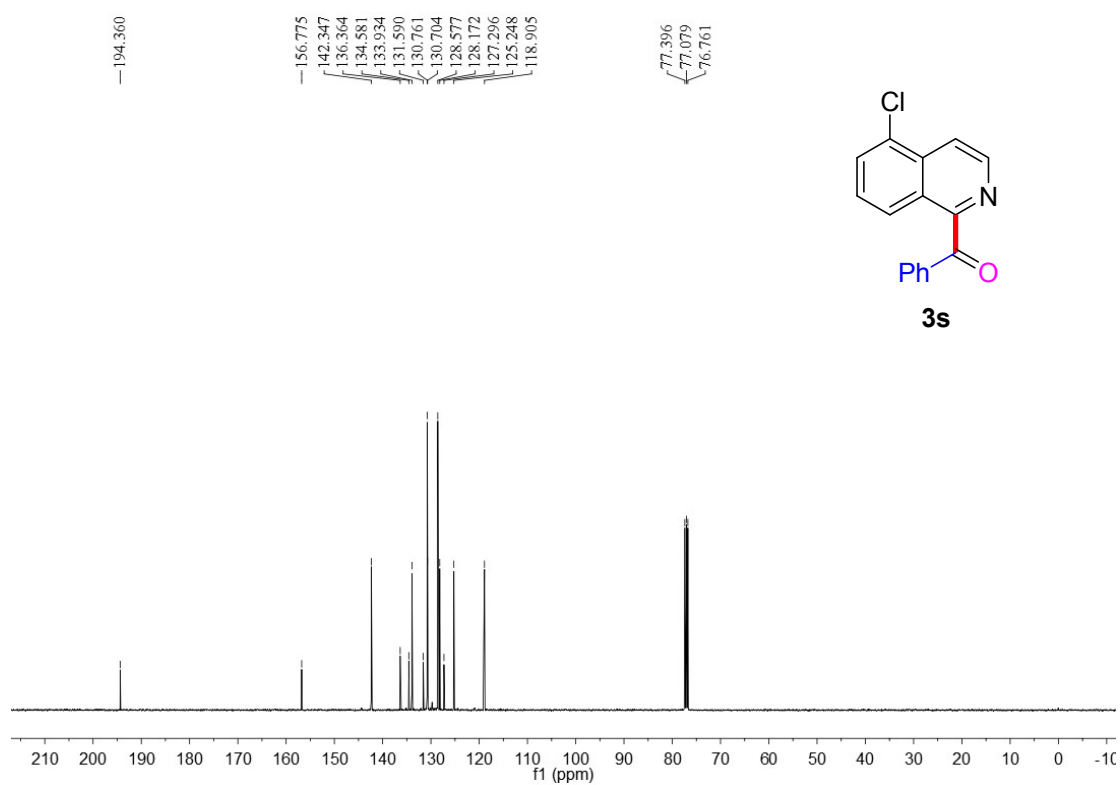
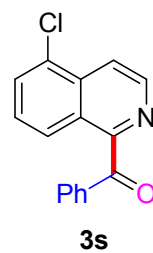
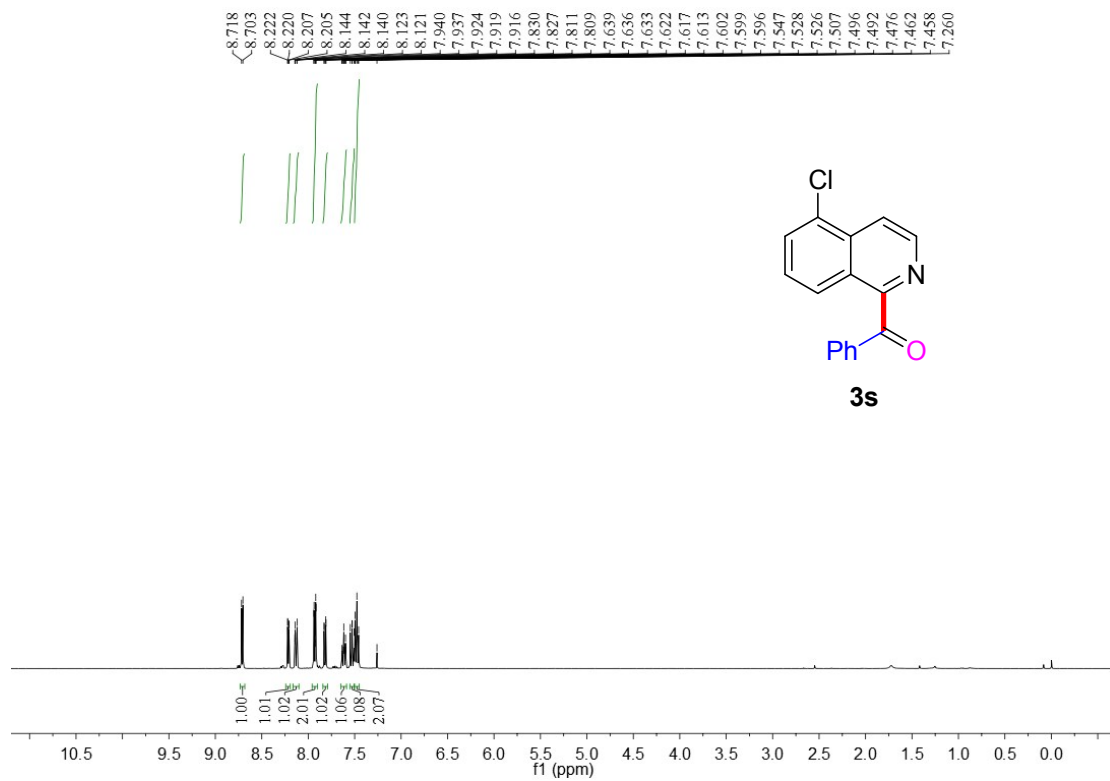


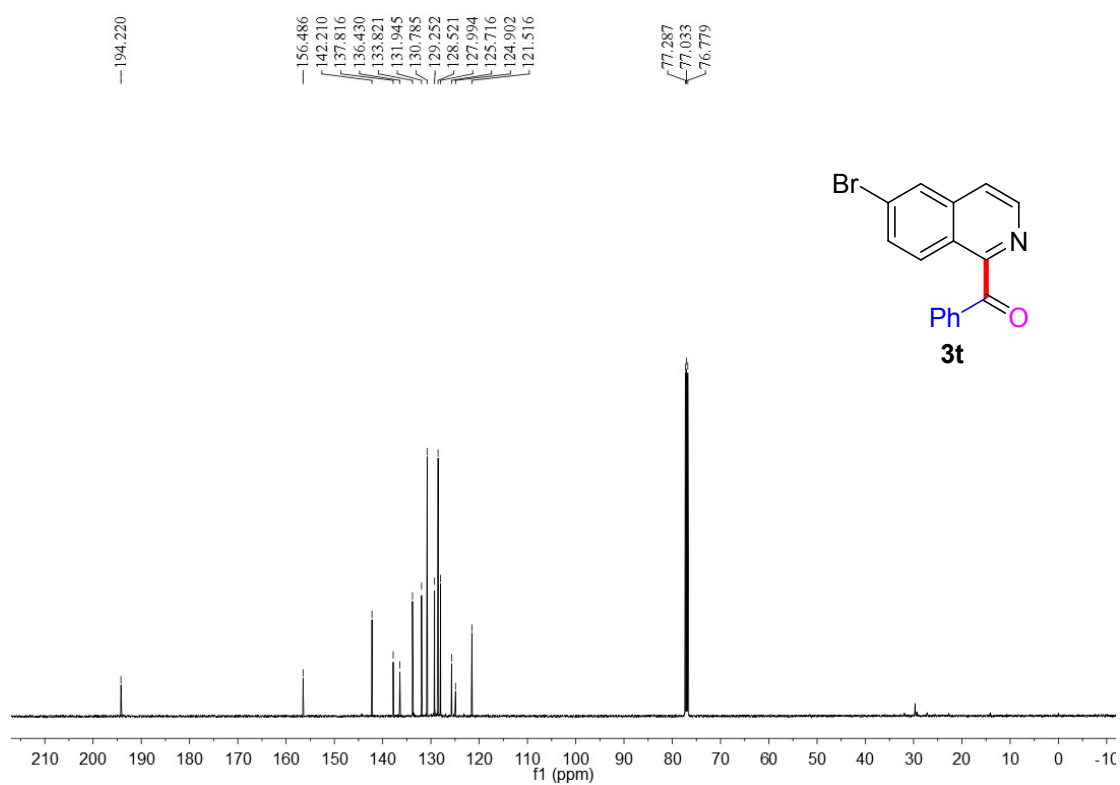
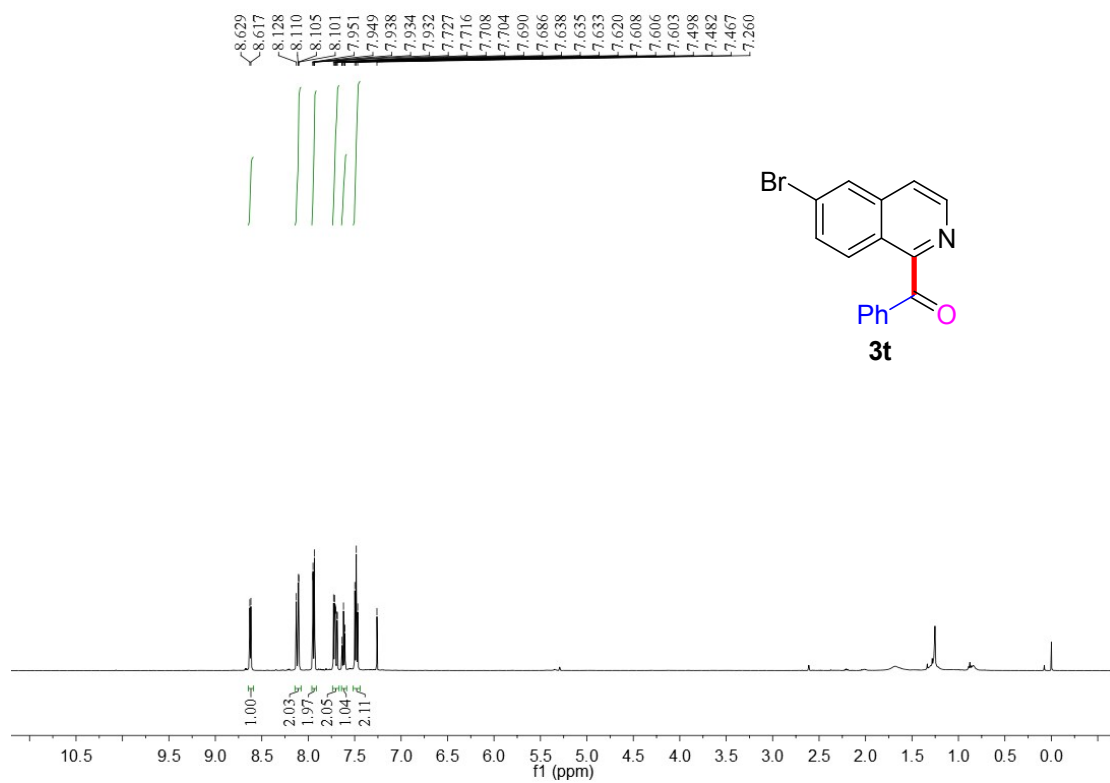


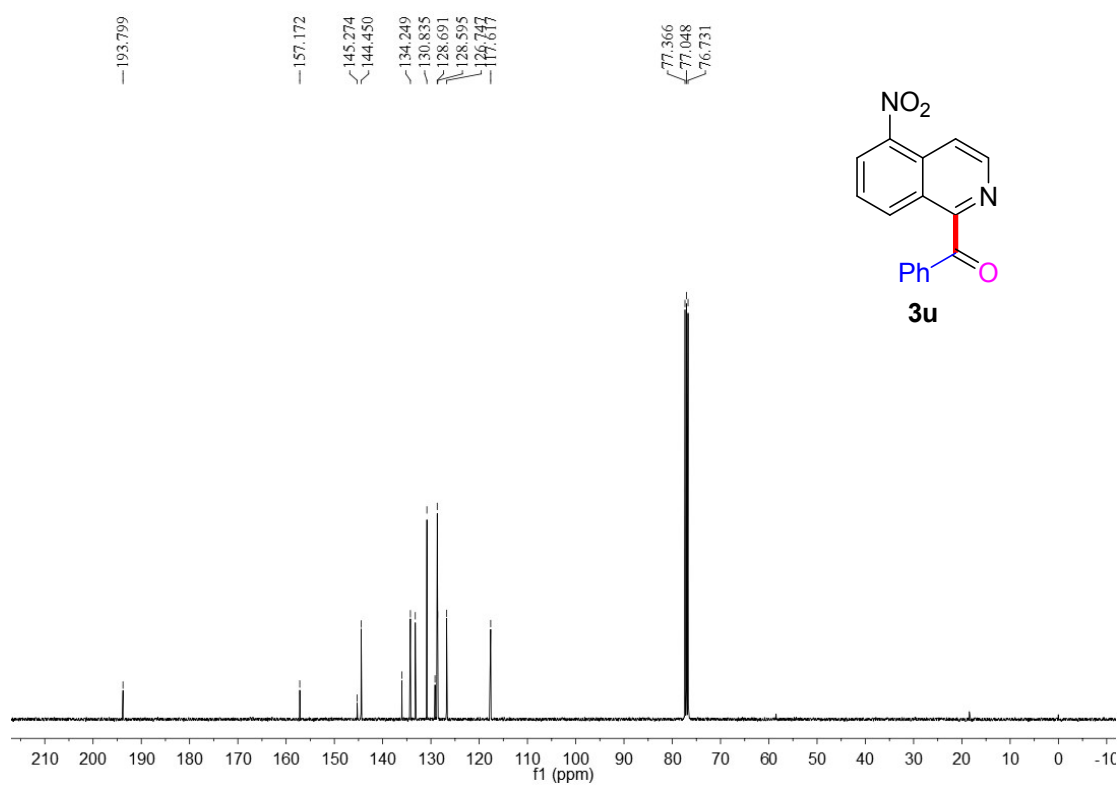
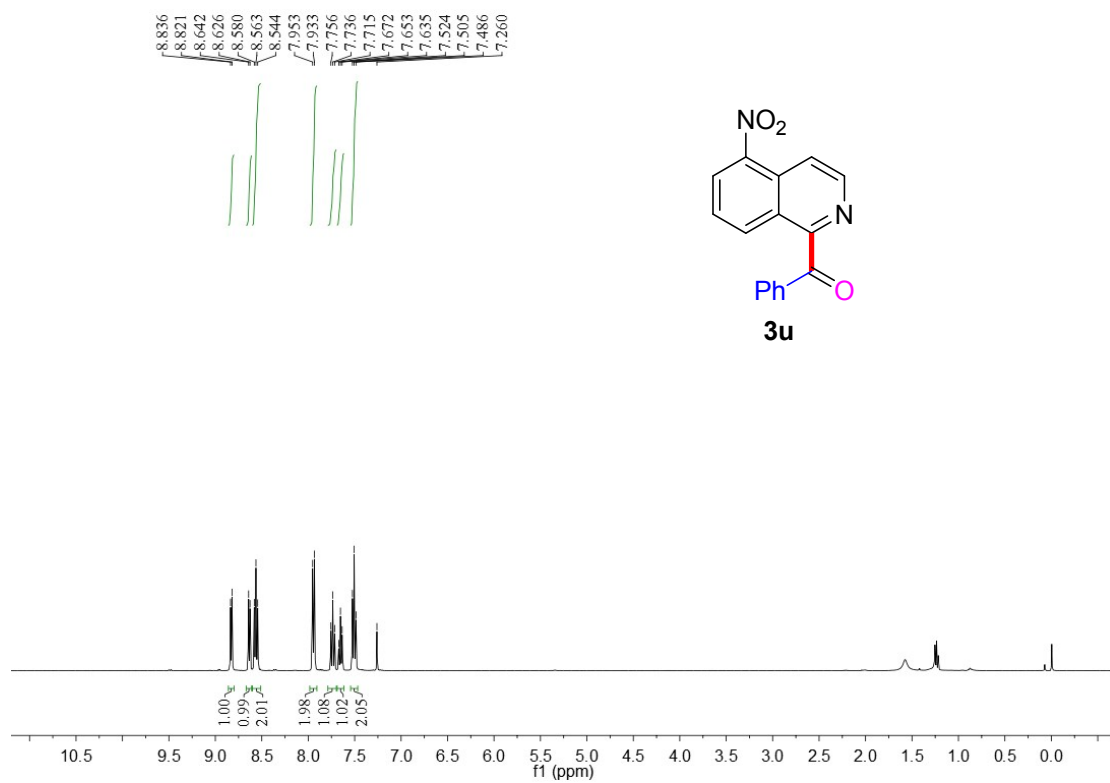






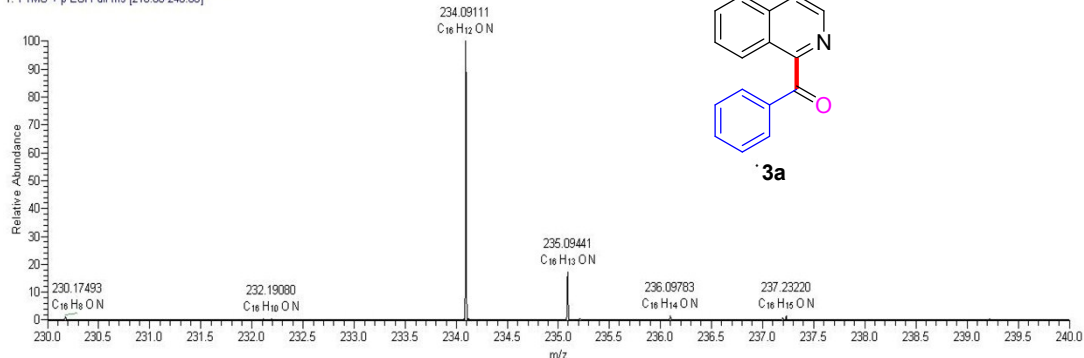




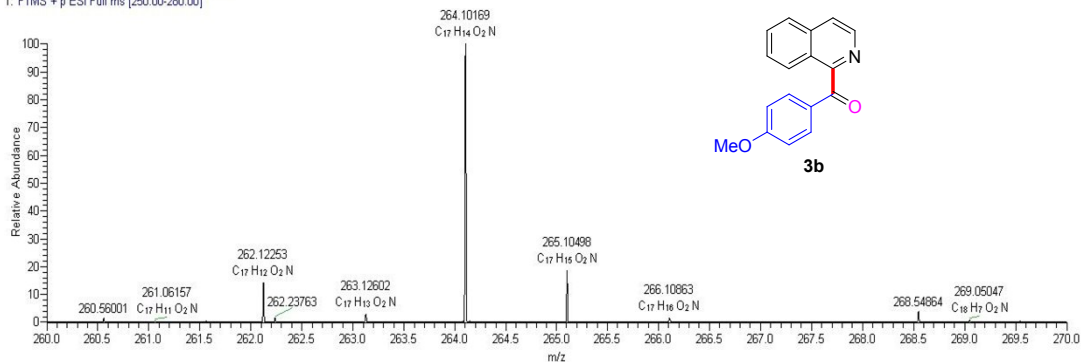


Copies of HRMS Spectra of all compounds

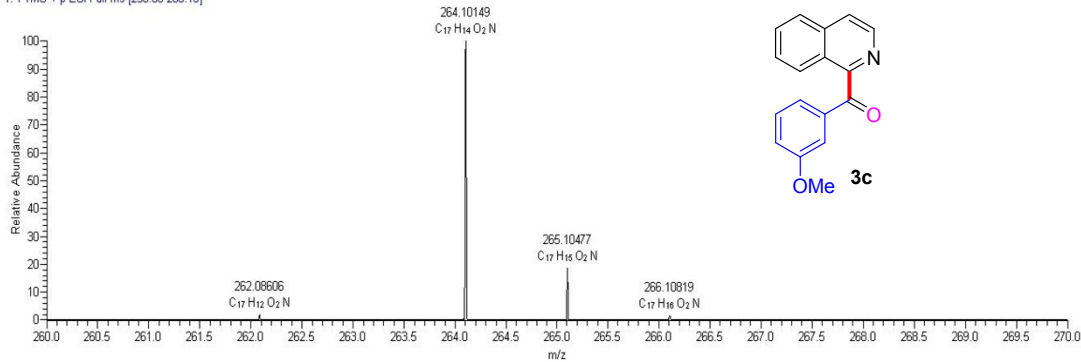
T: FTMS + p ESI Full ms [210.00-240.00]



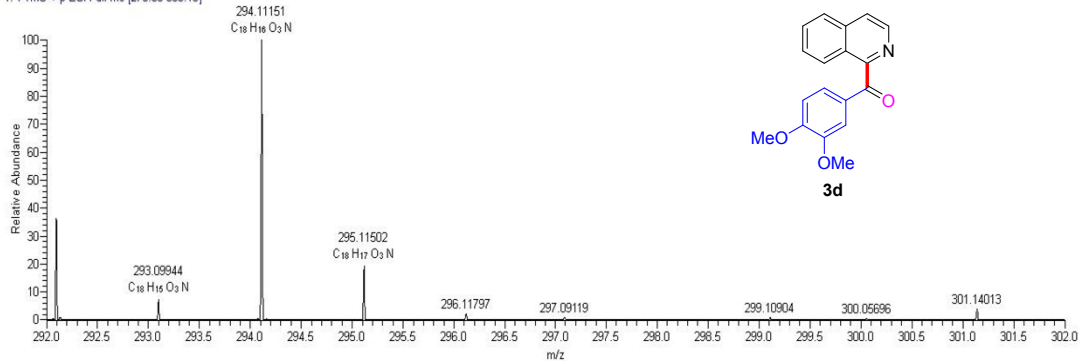
T: FTMS + p ESI Full ms [250.00-280.00]



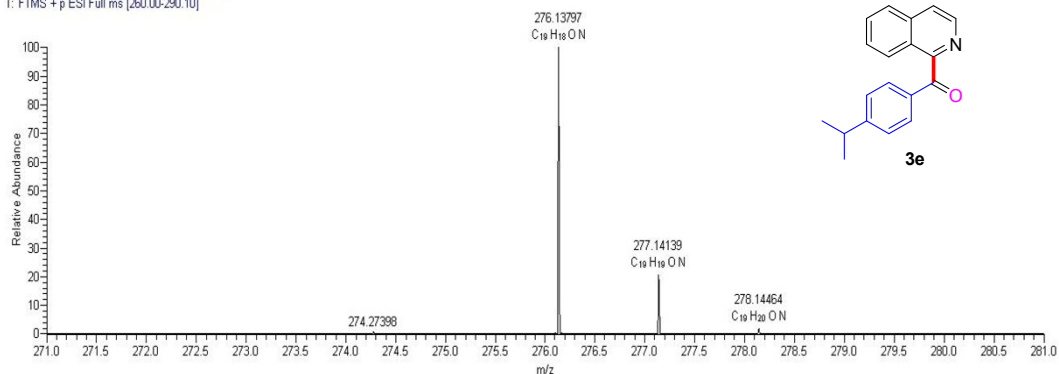
T: FTMS + p ESI Full ms [250.00-280.10]



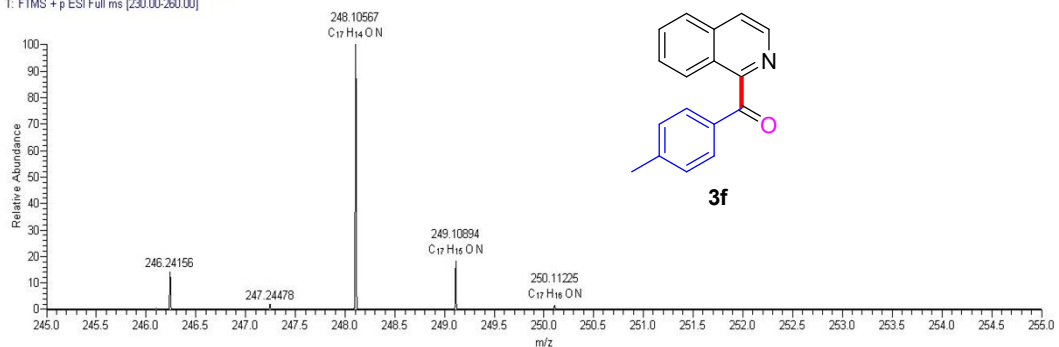
T: FTMS + p ESI Full ms [270.00-330.10]



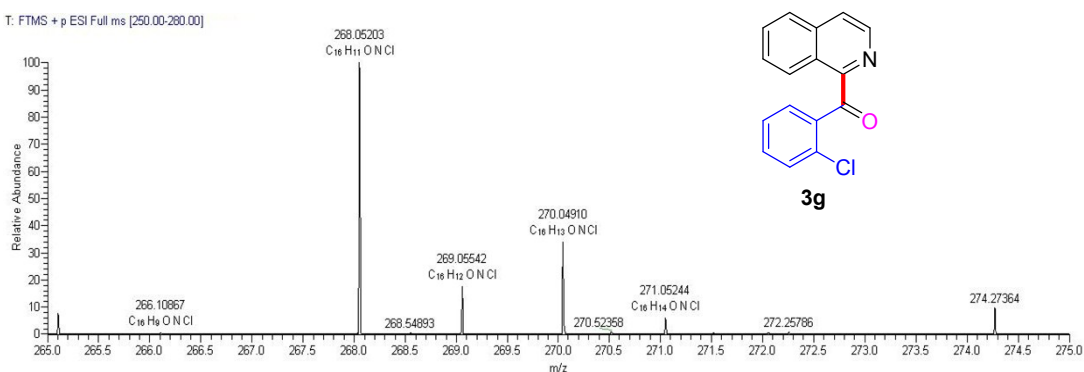
T: FTMS + p ESI Full ms [260.00-290.10]



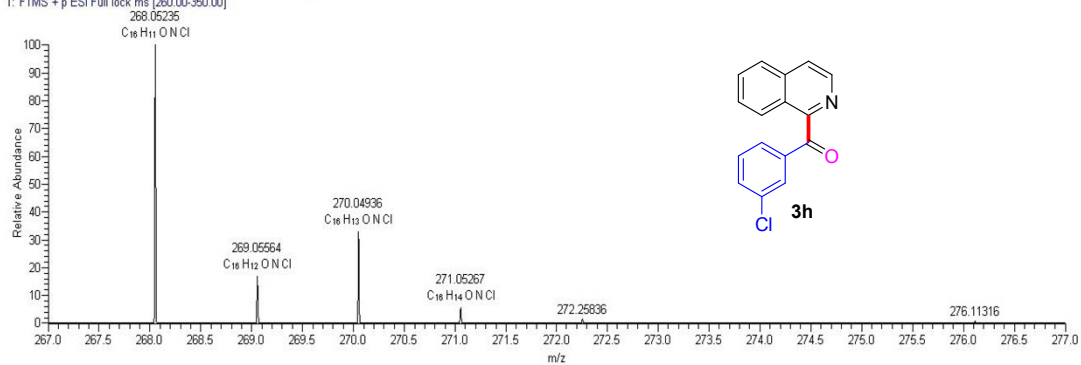
T: FTMS + p ESI Full ms [230.00-260.00]



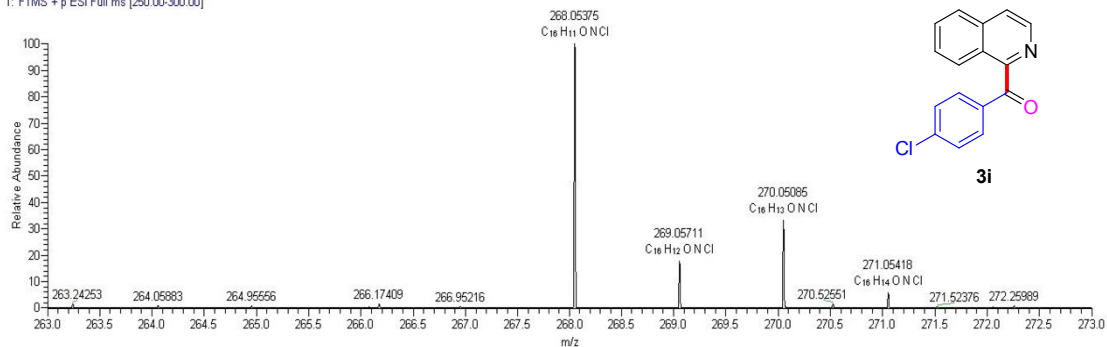
T: FTMS + p ESI Full ms [250.00-280.00]



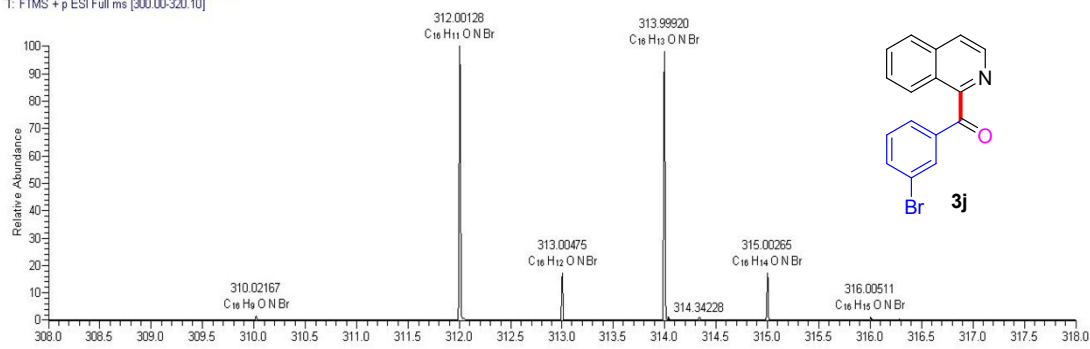
T: FTMS + p ESI Full lock ms [260.00-350.00]



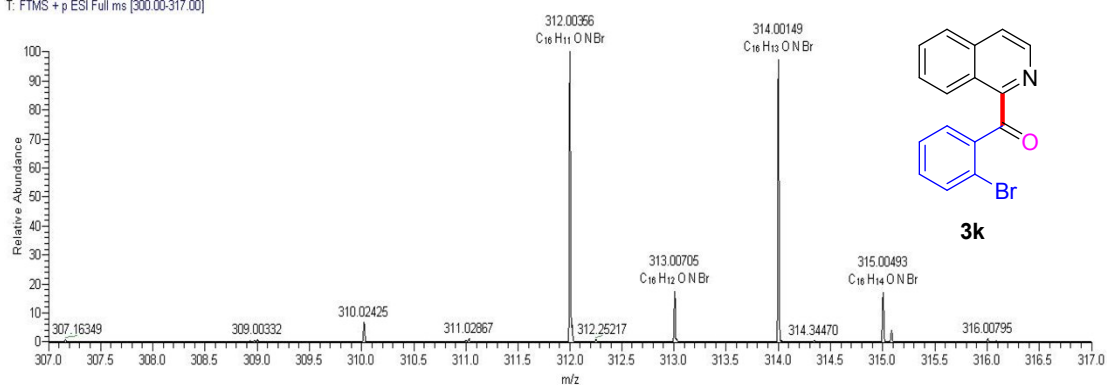
T: FTMS + p ESI Full ms [260.00-300.00]



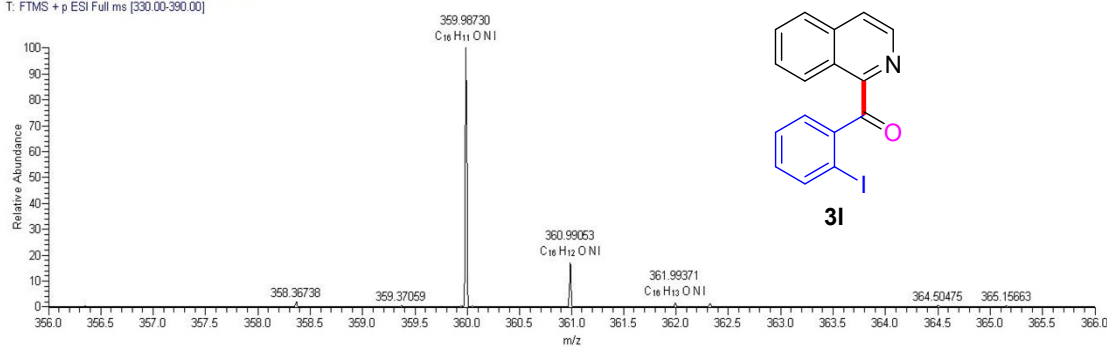
T: FTMS + p ESI Full ms [300.00-320.10]



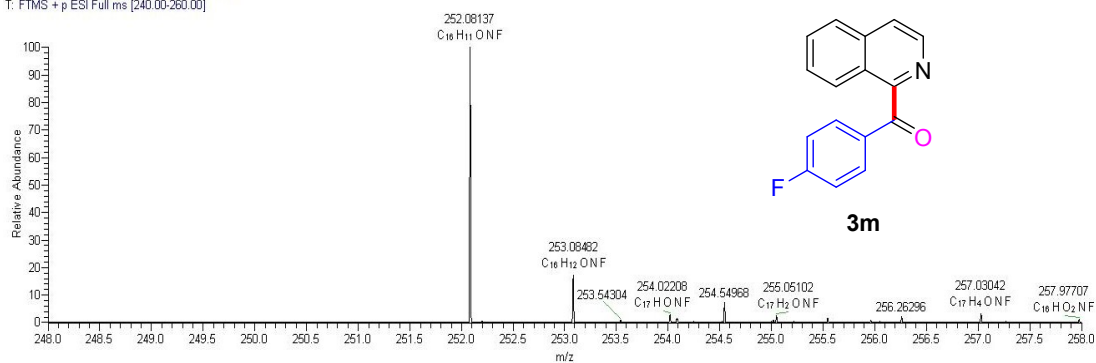
T: FTMS + p ESI Full ms [300.00-317.00]



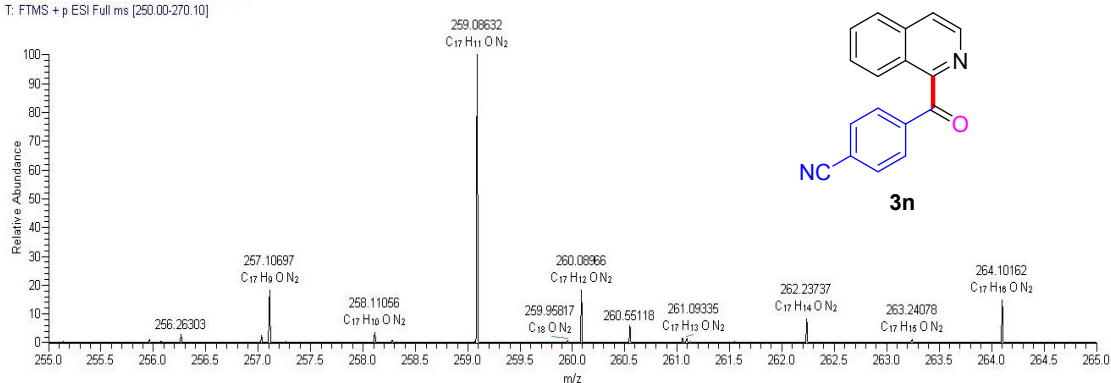
T: FTMS + p ESI Full ms [330.00-390.00]



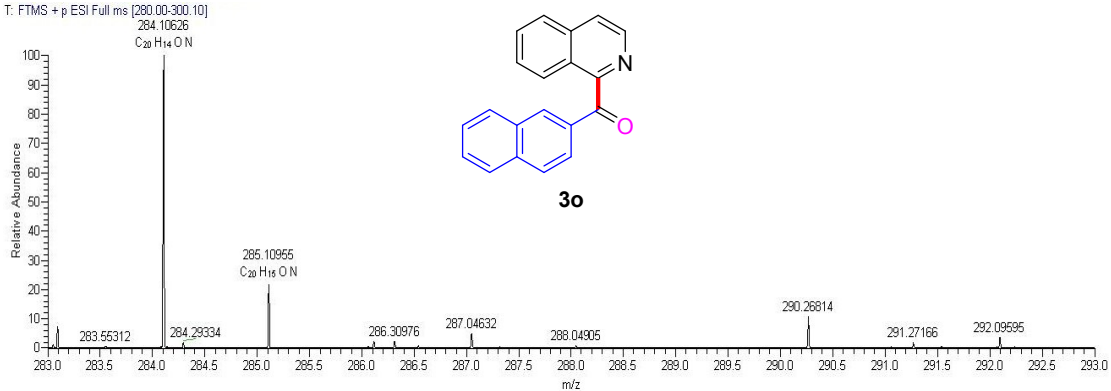
T: FTMS + p ESI Full ms [240.00-260.00]



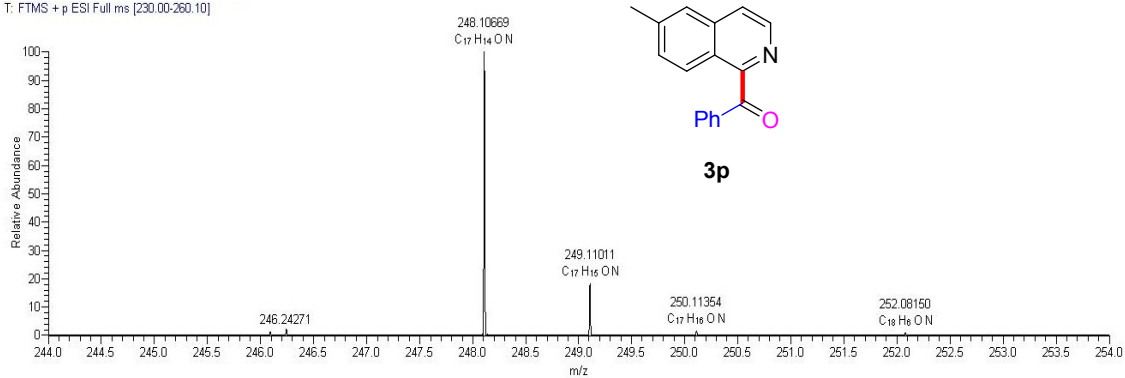
T: FTMS + p ESI Full ms [250.00-270.10]

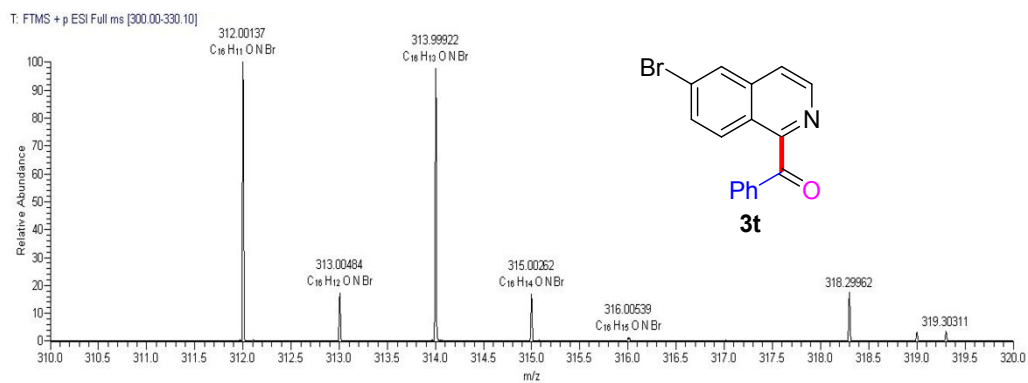
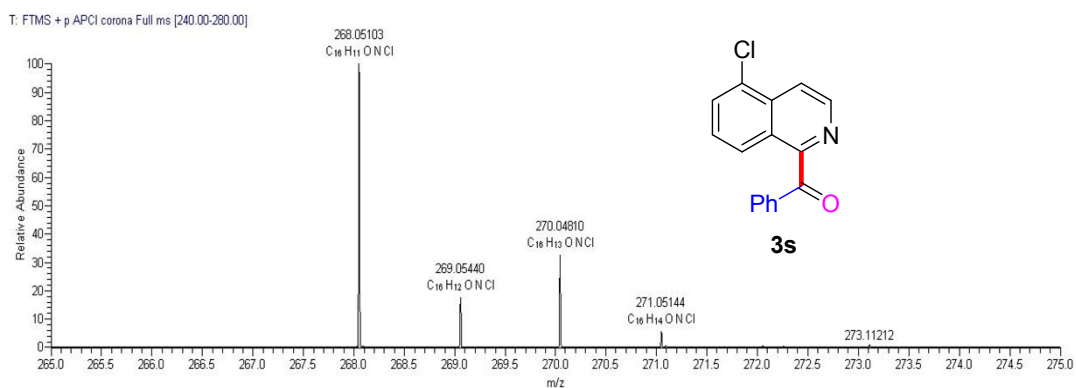
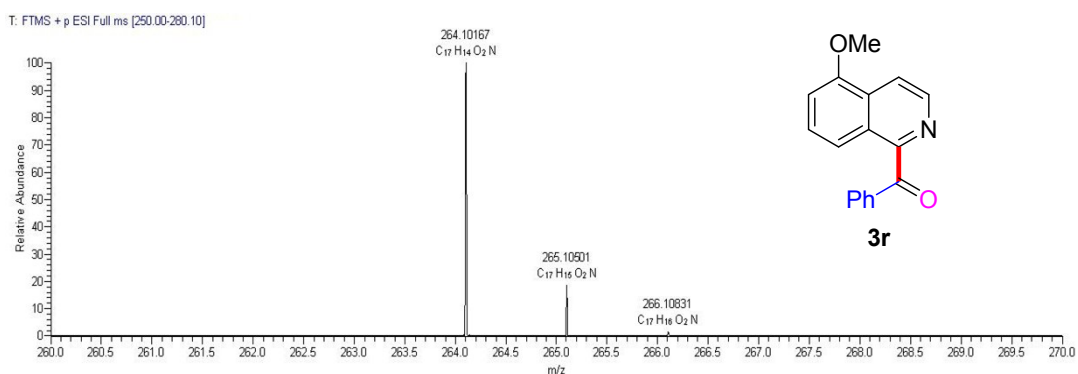
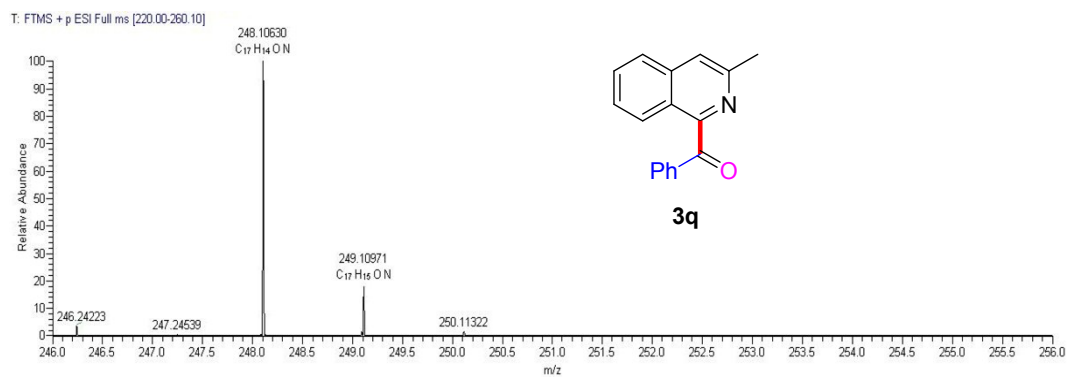


T: FTMS + p ESI Full ms [280.00-300.10]



T: FTMS + p ESI Full ms [230.00-260.10]





T: FTMS +p ESI Full ms [276.00-286.10]

