Supporting Information

Synthesis of Fused Tricyclic Indolizines by Intramolecular Silver-Mediated Double Cyclization of 2-(Pyridin-2-yl)acetic Acid Propargyl Esters

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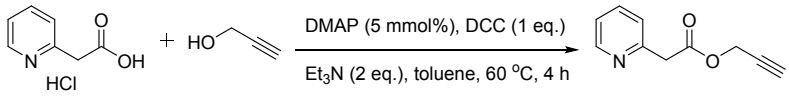
Experimental

General methods and materials.

Proton nuclear magnetic resonance spectra (^{1}H NMR) and carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 400 MHz and 100 MHz, respectively, using $CDCl_3$ as reference standard (δ 7.26 ppm) for ^{1}H 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 F-254 were used for analytical thin-layer chromatography. Column chromatography was performed on silica gel (300-400 mesh). The enantiomeric excesses were determined by Agilent-1200 series HPLC system using a chiral stationary phase column. (column: CHIRALCEL OD-H, eluent: 2-propanol/*n*-hexane=5/95). Starting materials were readily prepared according to literature procedures. Unless otherwise noted, all reagents were obtained commercially and used without further purification.

General procedure for the synthesis of substrate 1a



1a

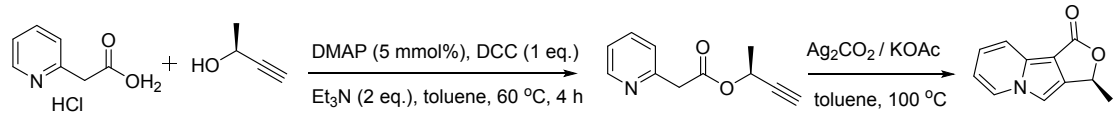
Following a modified procedure from B. Sahoo et al., triethyl amine (0.15 mL, 1.1 mmol) and 1,3-dicyclohexylcarbodiimide (DCC) (0.21 g, 1 mmol), 4-(dimethylamino)pyridine (DMAP) (6.1 mg, 0.05 mmol) were added to a suspension of 2-pyridylacetic acid hydrochloride (0.173 g, 1 mmol) and prop-2-yn-1-ol (0.056 g, 1 mmol) in toluene (10 mL) at 60 °C. The reaction mixture was stirred 4 h at 60 °C. The reaction mixture was filtered to remove 1,3-dicyclohexylurea. The filtrate was washed with water (3 × 10 mL), dried with $MgSO_4$ and concentrated under reduced pressure**,** the crude product was purified by column chromatography on silica gel using a mixture of ethyl acetate and petroleum ether to afford **1a** as a light yellow oil.

General procedure for the synthesis of fused tricyclic indolizine 2

Substrate **1** (0.5 mmol) were added to a suspension of Ag_2CO_3 (0.276 g, 2 equiv.) and KOAc (0.098g, 2 equiv.) in toluene (2.0 mL). The reaction mixture was allowed to stir at 100 °C for 6 h in a sealed tube. The resulting solution was cooled and

evaporated under reduced pressure. The target product **2** was purified by column chromatography on silica gel using a mixture of ethyl acetate and petroleum ether.

Determination of optical rotation of 2h



(*S*)-but-3-yn-2-ol

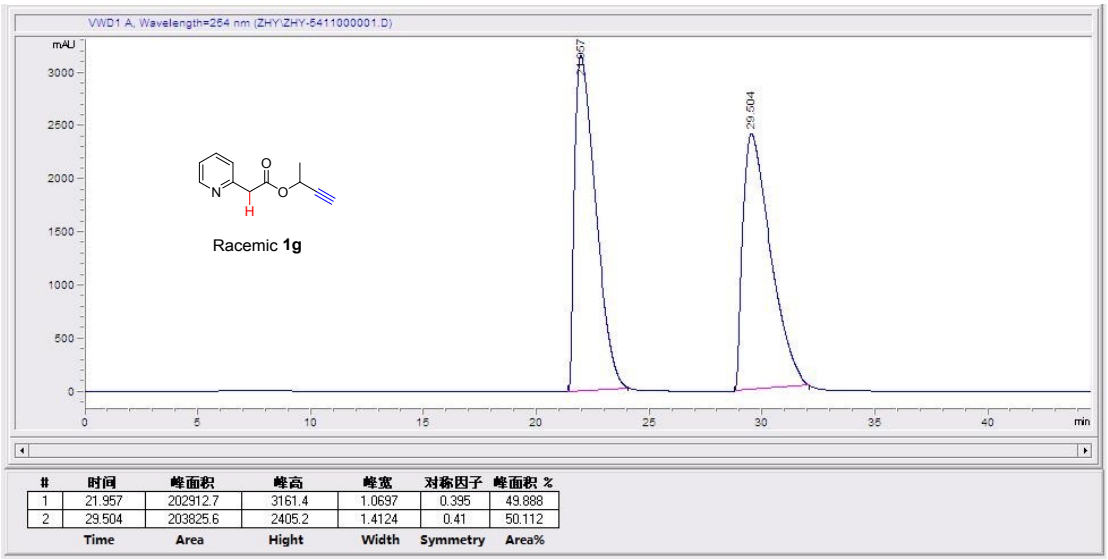
(*S*)-but-3-yn-2-yl 2-(pyridin-2-yl)acetate

(*S*)-3-methyl-1*H*,3*H*-furo[3,4-*a*]indolizin-1-one

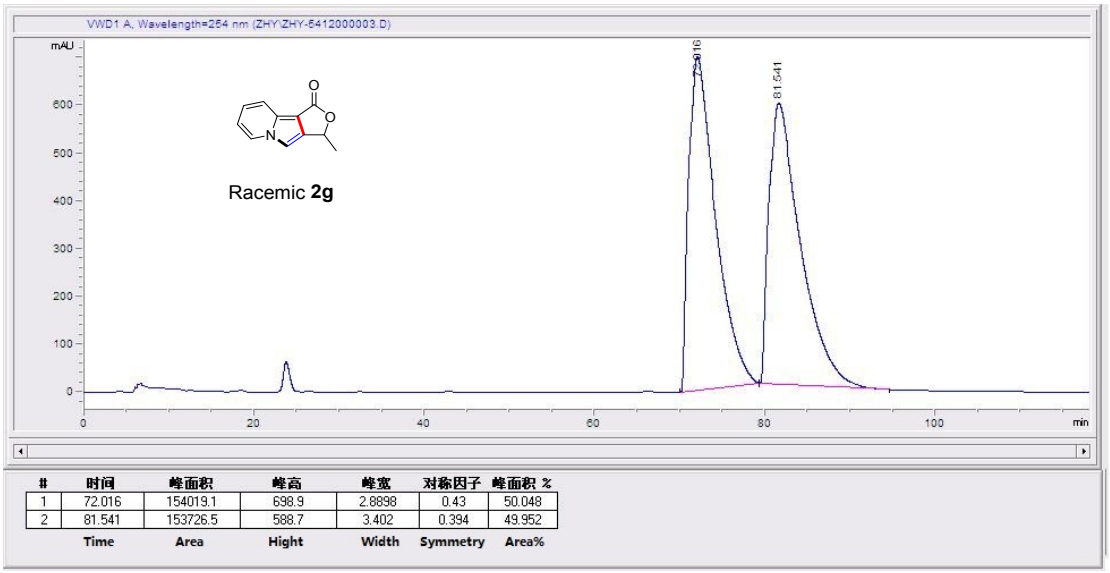
Optical rotation	standard: 45°	found: 55°	found: 63°
	found: 43°		

2h (9.3 mg) was dissolved in 3.10 mL MeOH (AR): 0.3 g/100 mL, 20 °C.

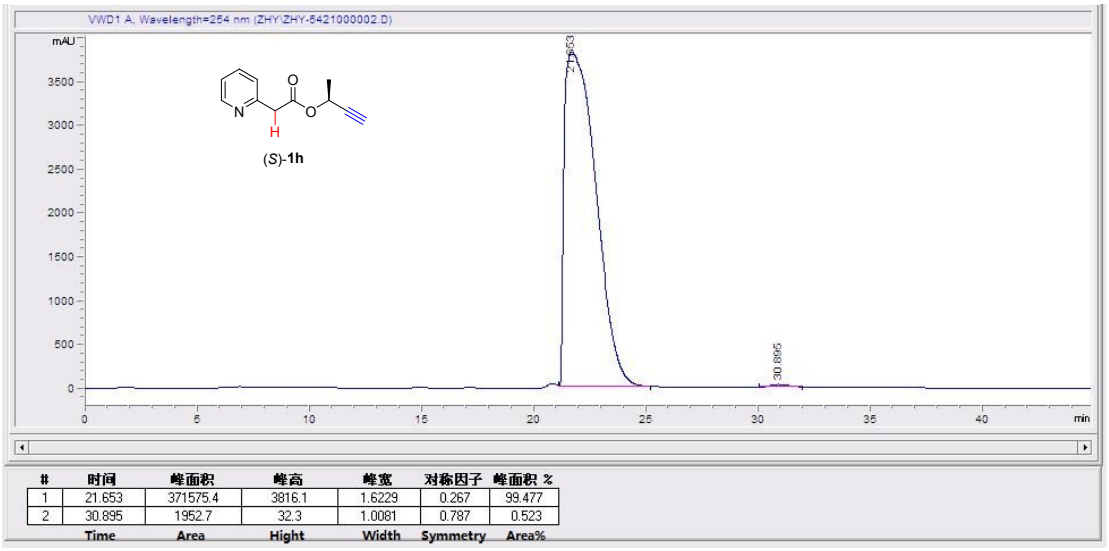
Chiral HPLC experiments



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	21.957	202912.7	3161.4	1.0697	0.395	49.888
2	29.504	203825.6	2405.2	1.4124	0.41	50.112
	Time	Area	Hight	Width	Symmetry	Area%



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	72.016	154019.1	698.9	2.8898	0.43	50.048
2	81.541	153726.5	588.7	3.402	0.394	49.952
	Time	Area	Hight	Width	Symmetry	Area%



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	21.653	371575.4	3816.1	1.6229	0.267	99.477
2	30.895	1952.7	32.3	1.0081	0.787	0.523
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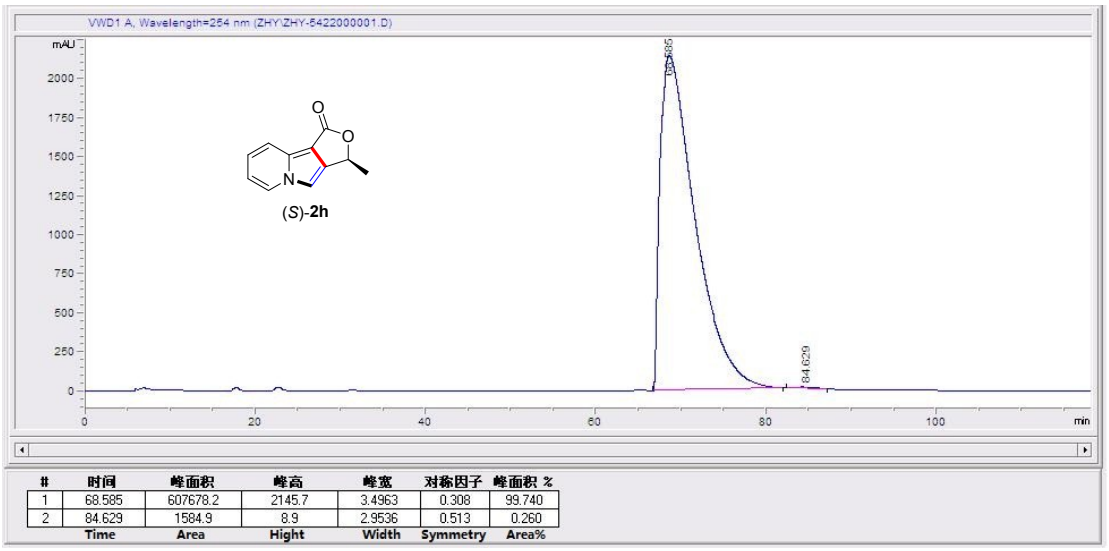

#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	68.585	607678.2	2145.7	3.4963	0.308	99.740
2	84.629	1584.9	8.9	2.9536	0.513	0.260
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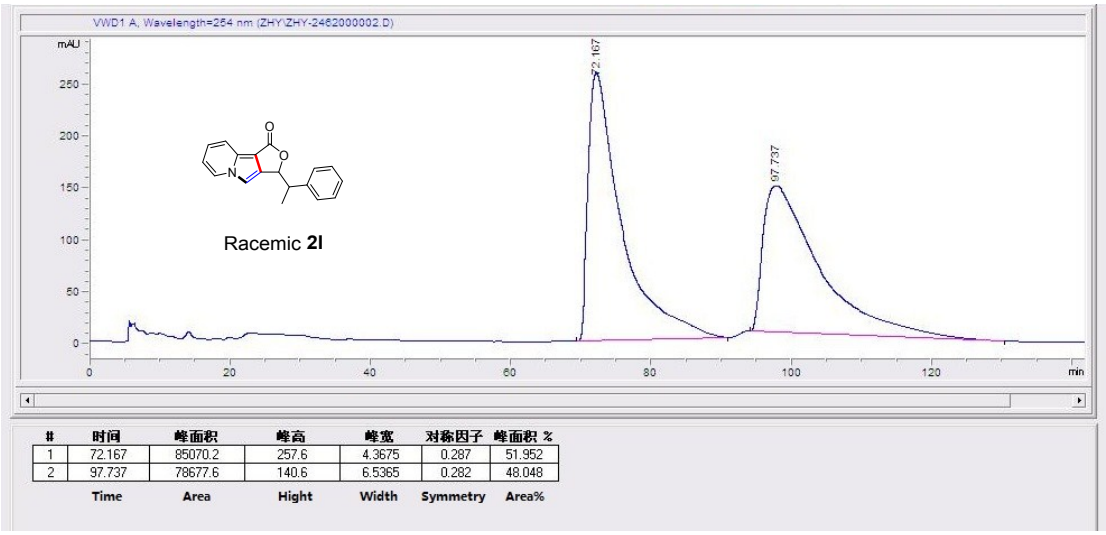
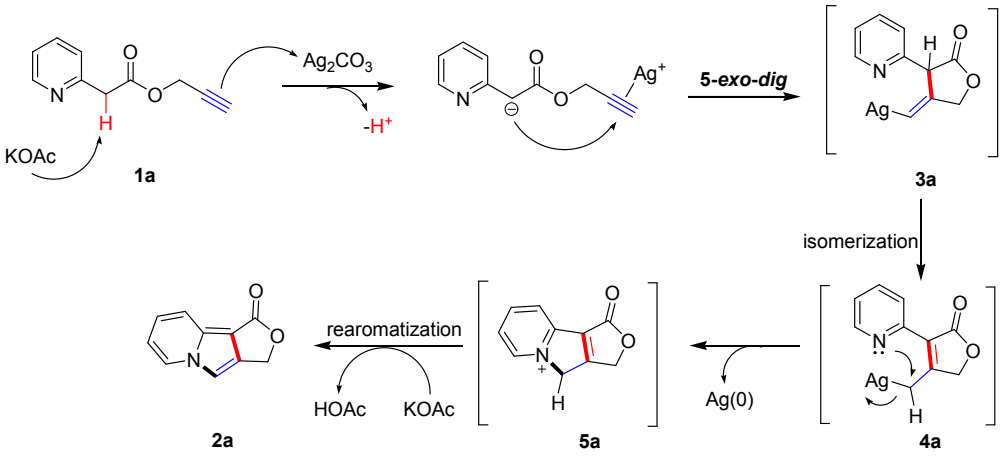
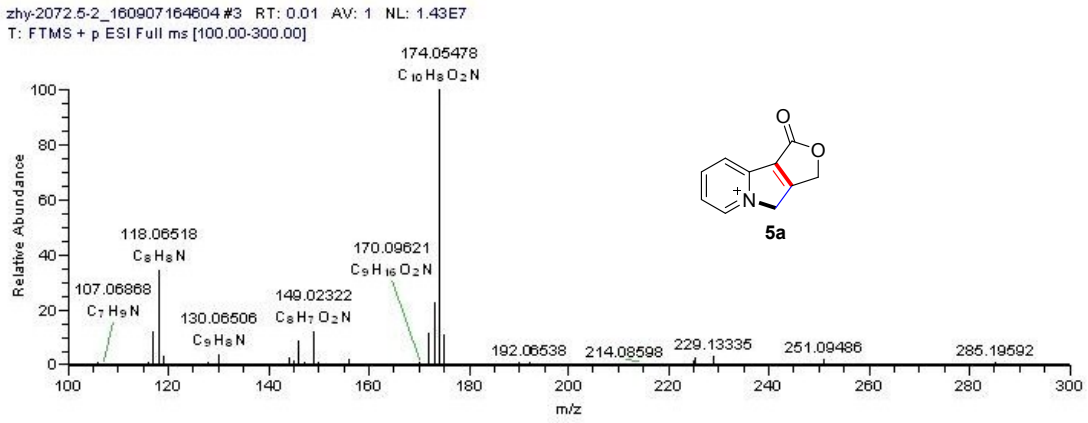


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	72.167	85070.2	257.6	4.3675	0.287	51.952
2	97.737	78677.6	140.6	6.5365	0.282	48.048
	Time	Area	Hight	Width	Symmetry	Area%

ESI/MS experiments

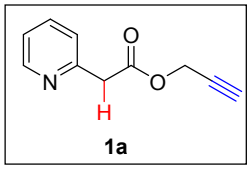
Under the standard condiction, a mixture of **1a** (0.5 mmol), Ag_2CO_3 (0.276 g, 2 equiv.) and KOAc (0.098g, 2 equiv.) in toluene (1 mL) was reacted at 100 °C for 30 min and 50 μL of the mixture was used for the ESI analysis in CH_3CN.





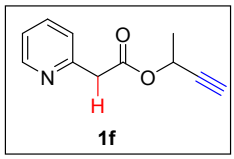
5a

Spectral data of all compounds



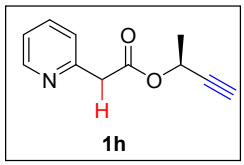
1a

prop-2-yn-1-yl 2-(pyridin-2-yl)acetate (1a) Light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.53 (dd, *J* = 4.9, 0.8 Hz, 1H), 7.67–7.62 (m, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.22–7.07 (m, 1H), 4.71 (t, *J* = 3.9 Hz, 2H), 3.88 (d, *J* = 5.1 Hz, 2H), 2.54 (t, *J* = 2.5 Hz, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.7, 153.8, 149.4, 136.6, 123.8, 122.2, 75.2, 52.3, 43.4 ppm; **HRMS** (*m/z*) (ESI): calcd for $C_{10}H_7NO_2$ 176.0706 [M+H$^+$]; found 176.0699.



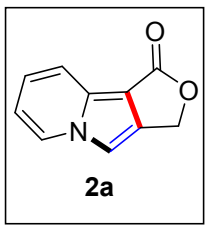
1f

but-3-yn-2-yl 2-(pyridin-2-yl)acetate (1e) light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (dd, *J* = 4.8, 0.7 Hz, 1H), 7.50 (m, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.03 (m, 1H), 5.34 (m, 1H), 3.72 (s, 2H), 2.37 (d, *J* = 2.2 Hz, 1H), 1.35 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 153.6, 149.0, 136.3, 123.5, 121.8, 81.5, 73.0, 60.2, 43.2, 20.8 ppm; HRMS (m/z) (ESI): calcd for $C_{11}H_{12}NO_2$ 190.0863 [M+H+]; found 190.0859.



1h

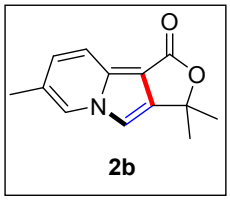
(*S*)-but-3-yn-2-yl 2-(pyridin-2-yl)acetate (1f) Light yellow oil; e.e = 99.0%; $[\alpha]^{20}D$ = -55^{o} (c = 0.3, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (dd, *J* = 4.8, 0.7 Hz, 1H), 7.49 (m, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.02 (m, 1H), 5.33 (qd, *J* = 6.7, 2.1 Hz, 1H), 3.71 (s, 2H), 2.37 (d, *J* = 2.2 Hz, 1H), 1.34 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 153.9, 149.3, 136.6, 123.8, 122.1, 81.8, 73.3, 60.5, 43.5, 21.1 ppm. HRMS (*m/z*) (ESI): calcd for $C_{11}H_{12}NO_2$ 190.0863 [M+H$^+$]; found 190.0859; RT = 21.65 min. (Chiral HPLC, CHIRALCEL OD-H -column and using 5% isopropanol mixture in hexane as eluent, Flow rate: 0.5 mL/min)



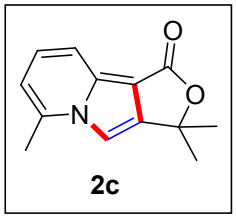
2a

1*H*,3*H*-furo[3,4-a]indolizin-1-one (2a) White solid, m.p. 120-123 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.0 Hz, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.16 (s, 1H), 7.12–7.10 (m, 1H), 6.83–6.82 (m, 1H), 5.30 (d, *J* = 0.8 Hz, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ

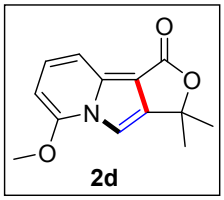
167.0, 138.8, 129.6, 126.6, 122.5, 118.4, 113.6, 104.1, 103.9, 65.8 ppm; **HRMS** (*m/z*) (APCI): calcd for $C_{10}H_7NO_2$ 174.0550 [M+H$^+$]; found 174.0544



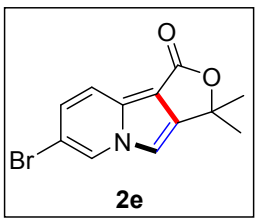
3,3,7-trimethyl-1*H*,3*H*-furo[3,4-a]indolizin-1-one (2b) Light yellow solid, m.p. 131-133 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 1.1 Hz, 1H), 7.60 (d, *J* = 9.0 Hz, 1H), 6.97 (s, 1H), 6.87 (dd, *J* = 9.0, 1.3 Hz, 1H), 2.23 (d, *J* = 0.6 Hz, 1H), 1.59 (s, 2H) ppm; **^{13}C NMR** (100 MHz, CDCl3): δ 165.9, 147.4, 128.0, 125.7, 124.6, 123.2, 117.7, 103.5, 102.7, 82.0, 28.2, 18.3 ppm; **HRMS** (*m/z*) (ESI): calcd for $C_{13}H_{14}NO_2$ 216.1019[M+H$^+$]; found 216.1010.



3,3,6-trimethyl-1*H*,3*H*-furo[3,4-a]indolizin-1-one (2c) Light yellow solid; m.p. 144-146 °C;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.9 Hz, 1H), 7.06 (dd, *J* = 8.8, 6.9 Hz, 1H), 7.00 (s, 1H), 6.68 (d, *J* = 6.9 Hz, 1H), 2.57 (s, 3H), 1.67 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 147.6, 135.0, 129.8, 122.7, 115.8, 112.9, 104.2, 99.9, 82.0, 28.1, 19.1 ppm; **HRMS** (*m/z*) (ESI): calcd for $C_{13}H_{14}NO_2$ 216.1019 [M+H$^+$] found 216.1019.

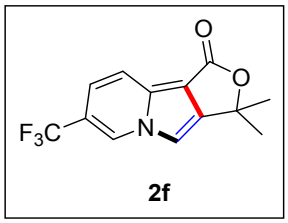


6-methoxy-3,3-dimethyl-1*H*,3*H*-furo[3,4-*a*]indolizin-1-one (2d) White solid, m.p. 142-143 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.8 Hz, 1H), 7.18 (s, 1H), 7.12–6.95 (m, 1H), 6.10 (d, *J* = 7.4 Hz, 1H), 4.05 (s, 3H), 1.63 (s, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.0, 149.6, 146.9, 130.6, 124.4, 110.3, 103.8, 98.3, 89.4, 82.0, 56.5, 28.2 ppm; **HRMS** (*m/z*) (ESI): calcd for $C_{13}H_{14}NO_3$ 232.0974. [M+H$^+$]; found 232.0974.



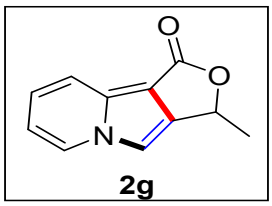
7-bromo-3,3-dimethyl-1*H*,3*H*-furo[3,4-*a*]indolizin-1-one (2e) White solid, m.p. 180-183 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.62 (d, *J* = 9.4 Hz, 1H), 7.15 (s, 1H), 7.08 (dd, *J* = 9.4, 1.6 Hz, 1H), 1.63 (s, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$):

δ 165.4, 148.0, 127.2, 126.8, 125.7, 118.7, 108.1, 105.1, 103.8, 82.3, 28.1 ppm; **HRMS** (*m/z*) (ESI): calcd for $C_{12}H_{11}BrNO_2$ 279.9968 281.9947 [M+H$^+$]; found 279.9968 281.9949.



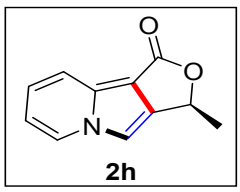
2f

3,3-dimethyl-7-(trifluoromethyl)-1*H*,3*H*-furo[3,4-a]indolizin-1-one (2f) Light yellow solid; m.p. 152-155 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.84 (d, *J* = 9.3 Hz, 1H), 7.33 (s, 1H), 7.18 (d, *J* = 9.3 Hz, 1H), 1.67 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 148.6, 128.6, 125.7 (q, *J* = 3.9 Hz), 123.3 (q, *J* = 270.0 Hz), 118.8, 117.9, 117.5 (q, *J* = 35.5 Hz), 105.9, 105.2, 82.4, 27.9 ppm. **HRMS** (*m/z*) (APCI): calcd for $C_{13}H_{11}F_3NO_2$ 270.0736 [M+H$^+$]; found 270.0735.



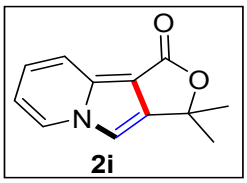
2g

3-methyl-1*H*,3*H*-furo[3,4-*a*]indolizin-1-one (2g) White solid, m.p. 136-137 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.09–8.07 (m, 1H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.13 (s, 1H), 7.07–7.05 (m, 1H), 6.80–6.79 (m, 1H), 5.60–5.54 (m, 1H), 1.60 (d, *J* = 6.6 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.5, 143.7, 129.3, 126.8, 122.6, 118.4, 113.6, 104.0, 103.9, 74.2, 21.5 ppm; **HRMS** (*m/z*) (ESI): calcd for $C_{11}H_{10}NO_2$ 188.0712 [M+H$^+$]; found 188.0706.

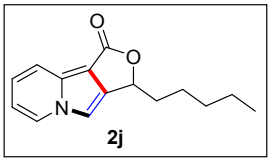


2h

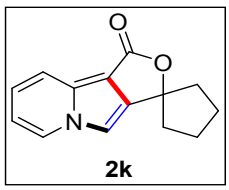
(*S*)-3-methyl-1*H*,3*H*-furo[3,4-*a*]indolizin-1-one (2h) Light yellow oil; e.e = 99.0%; $[\alpha]^{20}D$ = -55^o (c = 0.3, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (dd, *J* = 4.8, 0.7 Hz, 1H), 7.49 (m, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.02 (m, 1H), 5.33 (m, 1H), 3.71 (s, 2H), 2.37 (d, *J* = 2.2 Hz, 1H), 1.34 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 153.9, 149.3, 136.6, 123.8, 122.1, 81.8, 73.3, 60.5, 43.5, 21.1 ppm. HRMS (*m/z*) (ESI): calcd for $C_{11}H_{12}NO_2$ 190.0863 [M+H$^+$]; found 190.0859; RT = 21.65 min. (Chiral HPLC, CHIRALCEL OD-H -column and using 5% isopropanol mixture in hexane as eluent, Flow rate: 0.5 mL/min)



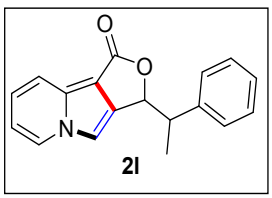
3,3-dimethyl-1*H*,3*H*-furo[3,4-*a*]indolizin-1-one (2i) Light yellow solid, m.p. 121-123 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.0 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.15 (s, 1H), 7.05–7.01 (m, 1H), 6.78–6.76 (m, 1H), 1.62 (s, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.9, 147.3, 129.2, 127.0, 122.7, 118.2, 113.5, 103.7, 103.3, 82.1, 28.1 ppm; **HRMS** (*m/z*) (APCI): calcd for $C_{12}H_{12}NO_2$ 202.0868 [M+H$^+$]; found 202.0856.



3-pentyl-1*H*,3*H*-furo[3,4-*a*]indolizin-1-one (2j) Light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (dt, *J* = 7.0, 1.0 Hz, 1H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.13 (s, 1H), 7.10–7.04 (m, 1H), 6.82–6.79 (m, 1H), 5.44 (t, *J* = 6.6 Hz, 1H), 1.97–1.73 (m, 2H), 1.48 (ddd, *J* = 13.1, 7.7, 4.0 Hz, 2H), 1.37–1.24 (m, 5H), 0.90–0.82 (m, 4H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.7, 142.5, 129.3, 126.7, 122.5, 118.4, 113.5, 104.4, 104.1, 78.0, 35.2, 31.51 (s), 24.4, 22.5, 14.0, 13.9 ppm; **HRMS** (*m/z*) (ESI): calcd for $C_{15}H_{18}NO_2$ 244.1338 [M+H$^+$]; found 244.1333.

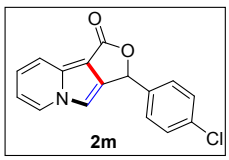


1′*H*-spiro[cyclopentane-1,3′-furo[3,4-*a*]indolizin]-1′-one (2k) White solid, m.p. 126-128 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.06 (d, *J* = 6.9 Hz, 1H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.11 (s, 1H), 7.09–7.04 (m, 1H), 6.78 (dd, *J* = 9.8, 3.9 Hz, 1H), 2.20 (dd, *J* = 10.7, 4.3 Hz, 2H), 2.08–1.97 (m, 4H), 1.95–1.78 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ 166.0, 145.3, 129.2, 126.7, 122.5, 118.4, 113.4, 104.7, 103.0, 91.8, 77.3, 77.1, 76.8, 39.9, 24.4 ppm; **HRMS** (*m/z*) (APCI): calcd for $C_{14}H_{14}NO_2$ 228.1025 [M+H$^+$]; found 228.1009.

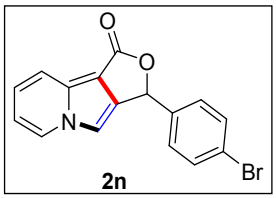


3-(1-phenylethyl)-1*H*,3*H*-furo[3,4-*a*]indolizin-1-one (2l) White solid, m.p. 142-144 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.0 Hz, 1H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.31–7.13 (m,

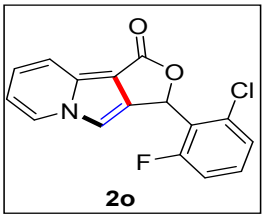
6H), 7.03–6.88 (m, 1H), 6.67 (m, 1H), 6.14 (s, 1H), 5.41 (d, J = 8.9 Hz, 1H), 2.86 (m, 1H), 1.46 (d, J = 6.9 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.40, 140.79, 139.98, 128.08, 127.5, 127.1, 127.0, 126.2, 125.5, 121.4, 117.3, 112.4, 103.9, 103.3, 80.7, 44.4, 17.7 ppm; **HRMS** (*m/z*) (ESI): calcd for $C_{18}H_{16}NO_2$ 278.1181 [M+H$^+$]; found 278.1174.



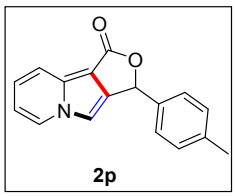
3-(4-chlorophenyl)-1*H*,3*H*-furo[3,4-*a*]indolizin-1-one (2m) White solid, m.p. 155-157 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08–8.06 (m, 1H), 7.89–7.80 (m, 1H), 7.32 (s, 4H), 7.17–7.10 (m, 2H), 6.85–6.84 (m, 1H), 6.42 (d, J = 1.0 Hz, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.9, 141.6, 136.3, 134.8, 129.5, 129.0, 128.2, 126.9, 123.1, 118.60, 113.9, 104.8, 103.9, 77.9 ppm; **HRMS** (*m/z*) (APCI): calcd for $C_{16}H_{11}ClNO_2$ 284.0478 [M+H$^+$]; found 284.0461.



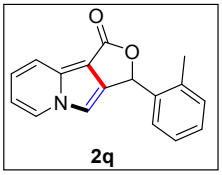
3-(4-bromophenyl)-1*H*, 3*H*-furo[3,4-*a*]indolizin-1-one (2n) White solid, m.p. 116-117 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.00–7.99 (m, 1H), 7.79 (d, J = 9.0 Hz, 1H), 7.49–7.36 (m, 2H), 7.25–7.14 (m, 2H), 7.12–7.00 (m, 2H), 6.79–6.78 (m, 1H), 6.35 (s, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) : δ 164.8, 140.5, 135.8, 130.9, 128.6, 128.5, 127.4, 125.8, 122.0, 121.9, 117.6, 112.9, 103.7, 102.8, 76.9 ppm; **HRMS** (*m/z*) (ESI): calcd for $C_{16}H_{11}BrNO_2$ 327.9968 329.9947 [M+H$^+$]; found 327.9967 327.9900.



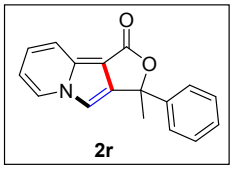
3-(2-chloro-6-fluorophenyl)-1*H*,3*H*-furo[3,4-*a*]indolizin-1-one (2o) White solid, m.p. 163-165 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05–8.04 (m, 1H), 7.90–7.84 (m, 1H), 7.30–7.27 (m, 1H), 7.25-7.21 (m, 1H), 7.17–7.09 (m, 2H), 7.02–6.91 (m, 2H), 6.84 (m, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 162.0 (d, $^1J_{C\text{-}F}$ = 253.0 Hz), 140.6, 134.7, 130.8 (d, $^3J_{C\text{-}F}$ = 10.0 Hz), 129.5, 126.8, 125.9 (d, $^4J_{C\text{-}F}$ = 3.6 Hz), 123.0, 122.8, 118.7, 115.2 (d, $^2J_{C\text{-}F}$ = 22.1 Hz), 113.7, 104.5, 72.3 ppm; **HRMS** (*m/z*) (ESI): calcd for $C_{16}H_{10}ClFNO_2$ 302.0384 [M+H$^+$]; found 302.0378.



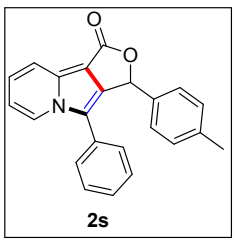
3-(*p*-tolyl)-1*H*,3*H*-furo[3,4-*a*]indolizin-1-one (2p) White solid, m.p. 113-115 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 6.9 Hz, 1H), 7.85 (d, *J* = 8.9 Hz, 1H), 7.34–7.21 (m, 2H), 7.13 (dd, *J* = 19.9, 6.8 Hz, 4H), 6.83 (t, *J* = 6.9 Hz, 1H), 6.43 (s, 1H), 2.34 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.3, 142.1, 138.9, 134.7, 129.4, 129.4, 126.8, 122.8, 118.6, 113.7, 104.8, 104.2, 78.8, 21.2 ppm; **HRMS** (*m/z*) (APCI): calcd for $C_{17}H_{14}NO_2$ 264.1025 [M+H$^+$]; found 264.1007.



3-(o-tolyl)-1*H*,3*H*-furo[3,4-*a*]indolizin-1-one (2q) White solid, m.p. 117-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 –8.05 (m, 1H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.24 (dd, *J* = 12.2, 7.6 Hz, 3H), 7.14–7.11 (m, 3H), 6.89–6.80 (m, 1H), 6.70 (s, 1H), 2.54 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.3, 141.5, 136.4, 135.5, 130.8, 129.5, 128.9, 126.7, 126.3,126.3, 122.8, 118.6, 113.8, 104.9, 104.5, 19.2 ppm; **HRMS** (*m/z*) (ESI): calcd for $C_{17}H_{14}NO_2$ 264.1025 [M+H$^+$]; found 264.1020.

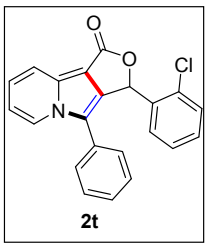


3-methyl-3-phenyl-1*H*,3*H*-furo[3,4-*a*]indolizin-1-one (2r) Light yellow solid, m.p. 124-126 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 6.9 Hz, 1H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 10.2 Hz, 2H), 7.02 (dd, *J* = 8.3, 7.4 Hz, 1H), 6.73 (t, *J* = 6.9 Hz, 1H), 1.92 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.5, 145.3, 141.1, 128.3, 127.5, 126.9, 125.8, 123.9, 121.9, 117.5, 112.7, 103.1, 102.6, 83.7, 28.7 ppm; **HRMS** (*m/z*) (ESI): calcd for $C_{16}H_{11}N_3O$ 286.0844 [M+Na$^+$]; found 286.0839.



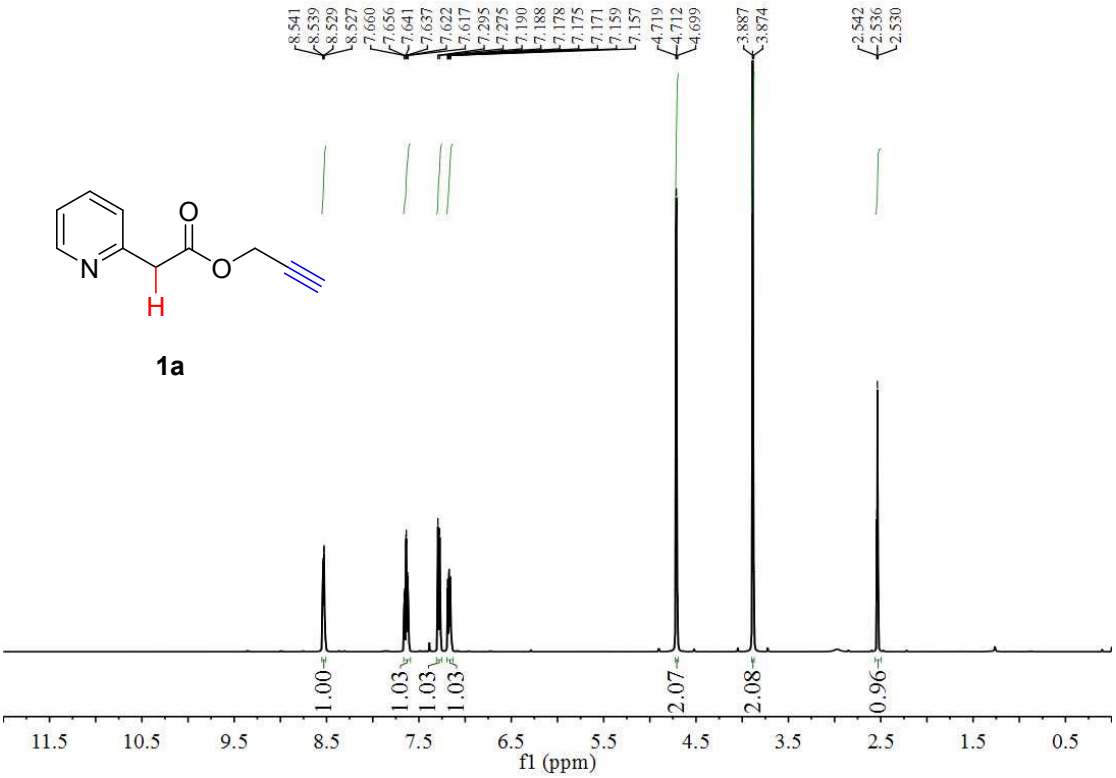
4-phenyl-3-(p-tolyl)-1*H*,3*H*-furo[3,4-*a*]indolizin-1-one (2s) Light yellow solid, m.p. 154-156 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 7.2 Hz, 1H), 7.96–7.93 (m, 1H), 7.41–7.29 (m, 3H), 7.20–7.11 (m, 5H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.82 (td, *J* = 7.0, 1.3 Hz, 1H), 6.44 (s, 1H), 2.31 (s, 3H) ppm; **^{13}C NMR** (100 MHz,

$CDCl_3$): δ 166.5, 140.6, 138.8, 134.6, 129.3, 129.2, 129.2, 129.2, 128.9, 128.4, 127.3, 124.1, 122.8, 118.9, 117.6, 113.8, 104.4, 79.5, 21.3 ppm; **HRMS** (*m/z*) (ESI): calcd for $C_{23}H_{18}NO_2$ 340.1338 [M+H$^+$]; found 340.1332.

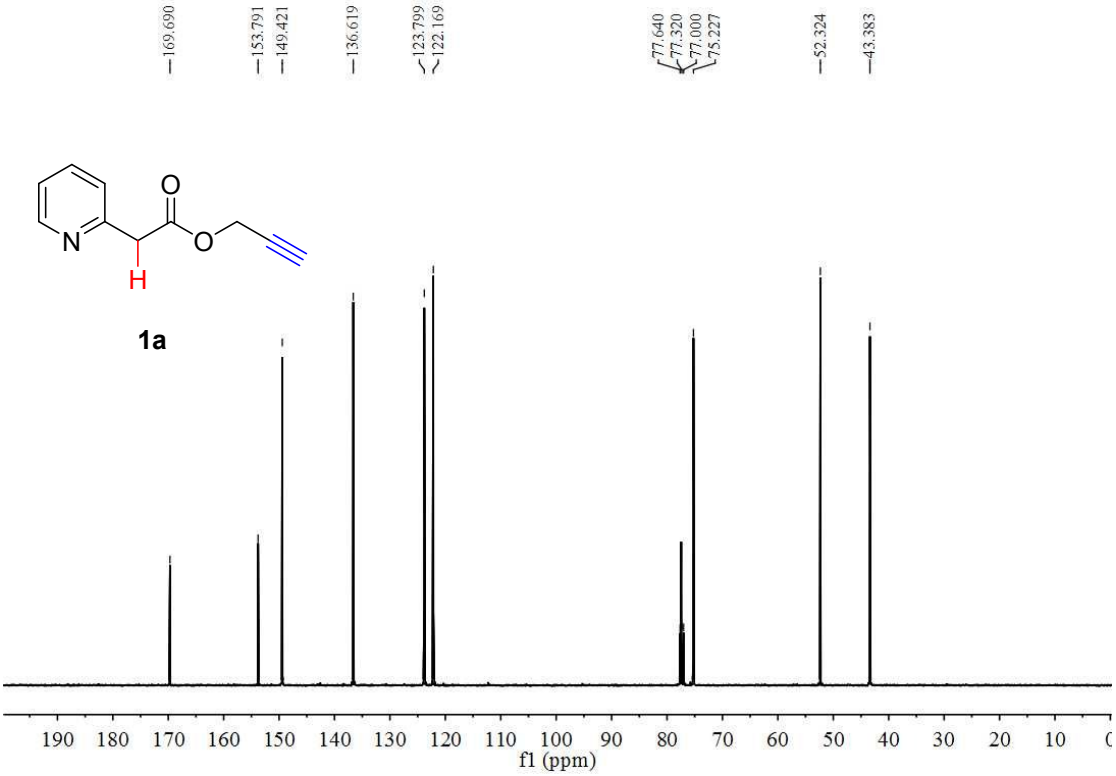


3-(2-chlorophenyl)-4-phenyl-1*H*,3*H*-furo[3,4-*a*]indolizin-1-one (2t) White solid, m.p. 181-183 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 7.1 Hz, 1H), 7.93 (d, *J* = 8.9 Hz, 1H), 7.38–7.28 (m, 4H), 7.23–7.12 (m, 6H), 6.95 (d, *J* = 4.9 Hz, 1H), 6.83 (td, *J* = 7.0, 1.2 Hz, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.3, 139.9, 134.8, 133.8, 130.2, 129.7, 129.4, 129.2, 129.0, 128.8, 128.6, 127.1, 124.3, 123.0, 118.7, 117.7, 114.0, 104.2, 75.8 ppm; **HRMS** (*m/z*) (APCI): calcd for $C_{22}H_{15}NO_2$ 360.0791 [M+H$^+$]; found 360.0769.

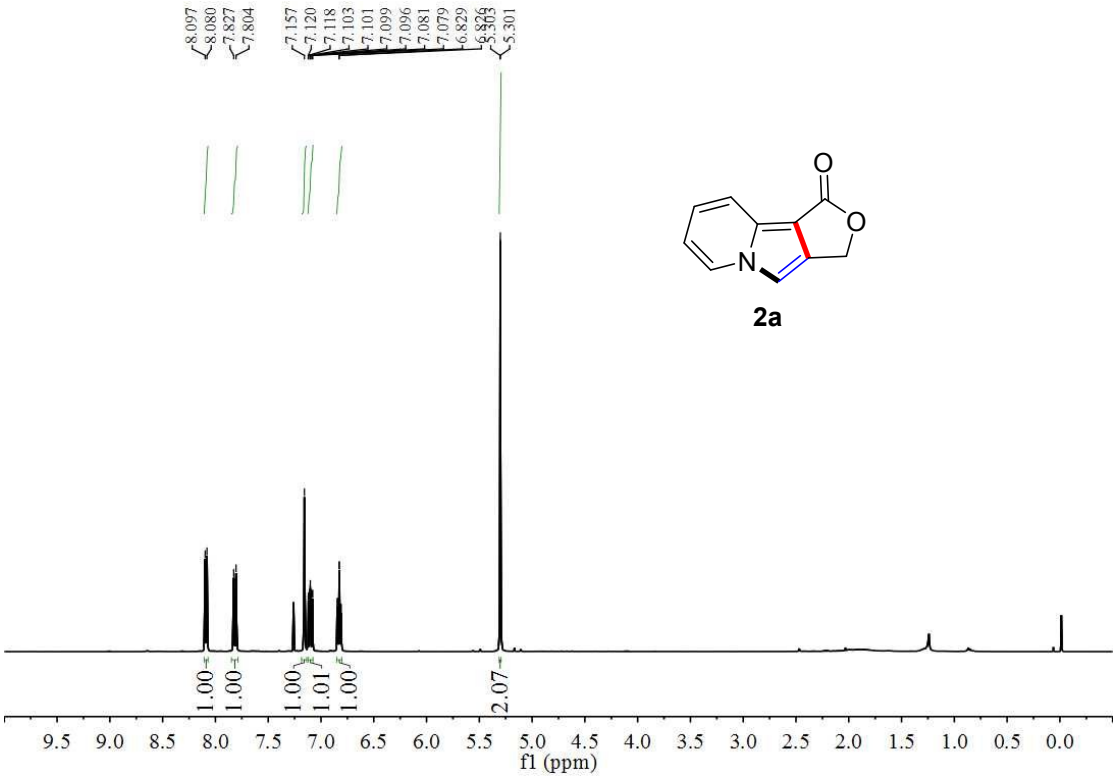
Copies of ^{1}H NMR and ^{13}C NMR Spectra of all compounds



1a



1a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7.804
7.157
7.120
7.118
7.103
7.101
7.099
7.096
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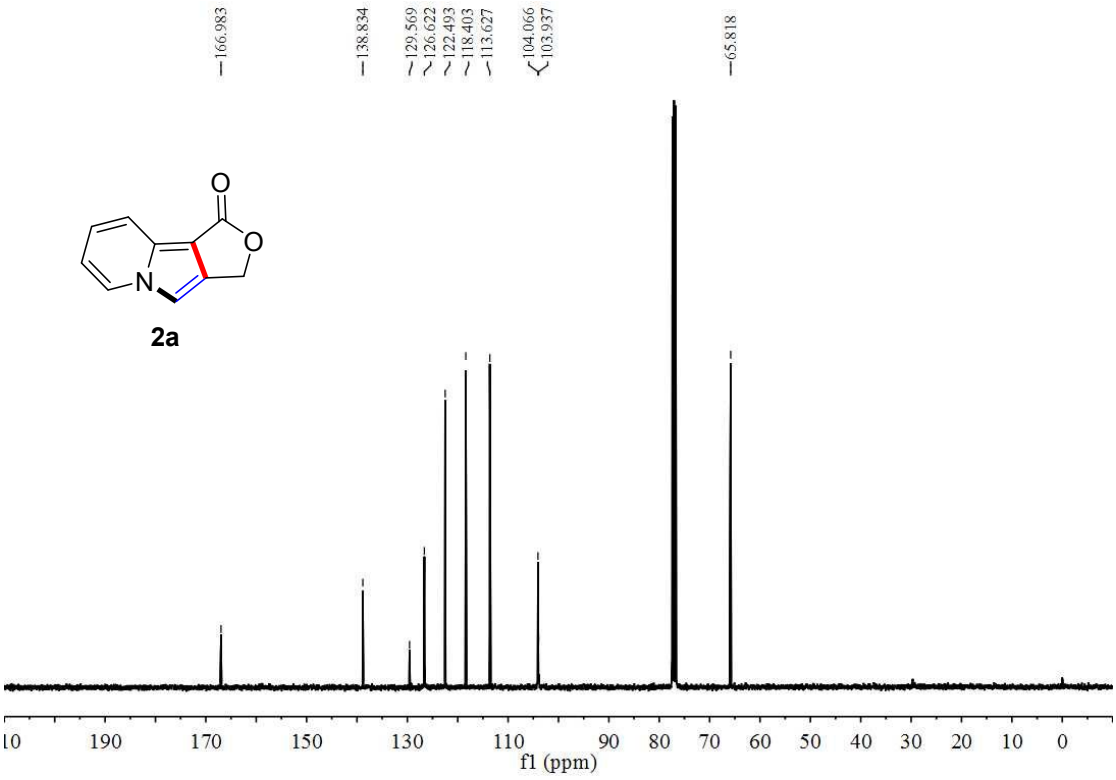
7.079
6.829
5.305
5.301
1.00
1.00
1.00
1.01
1.00
2.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
O
N

2a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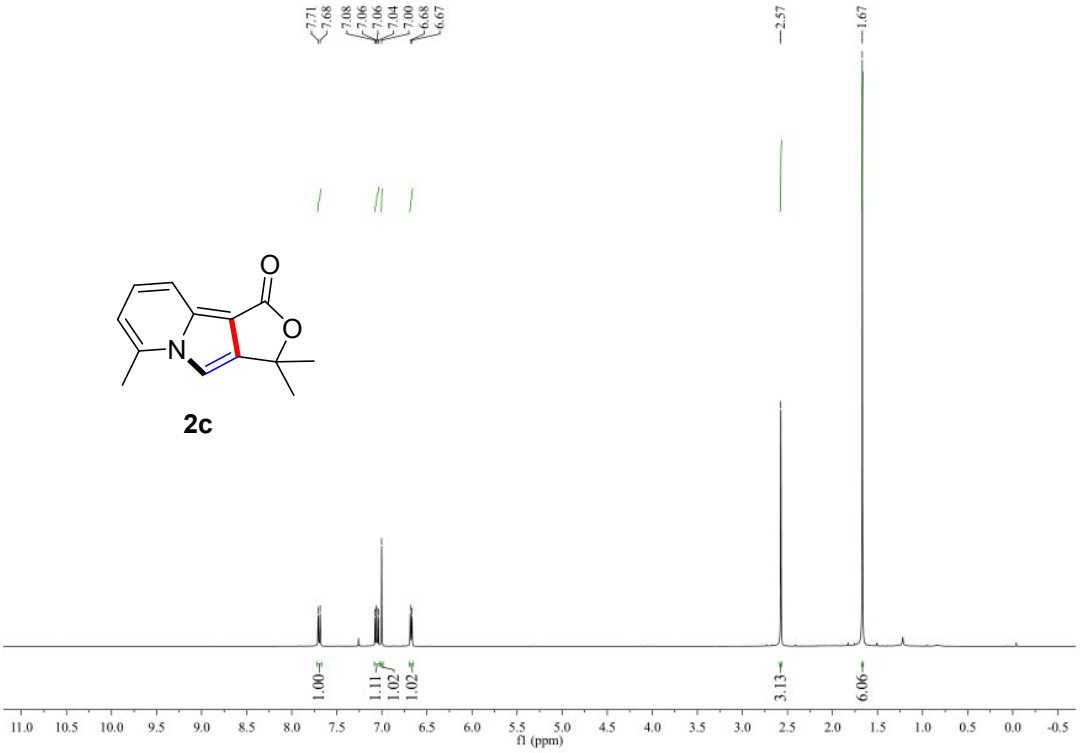
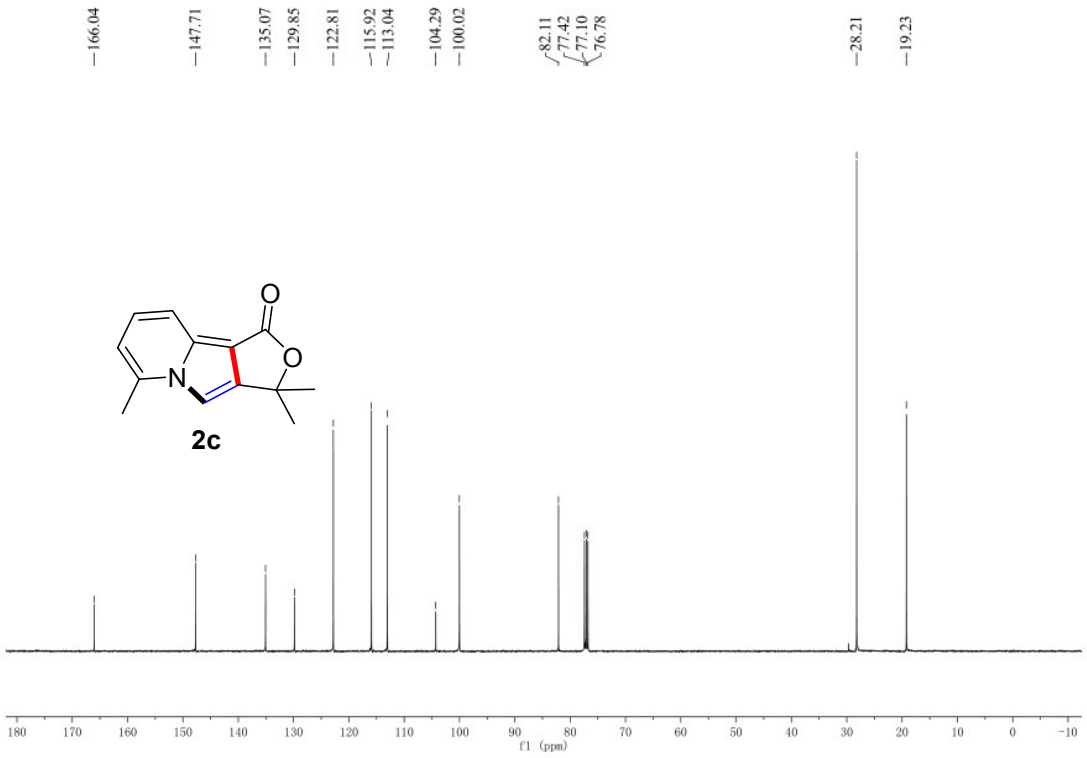
138.834
129.569
126.622
122.493
118.403
113.627
104.066
103.937
65.818
10 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
O
N

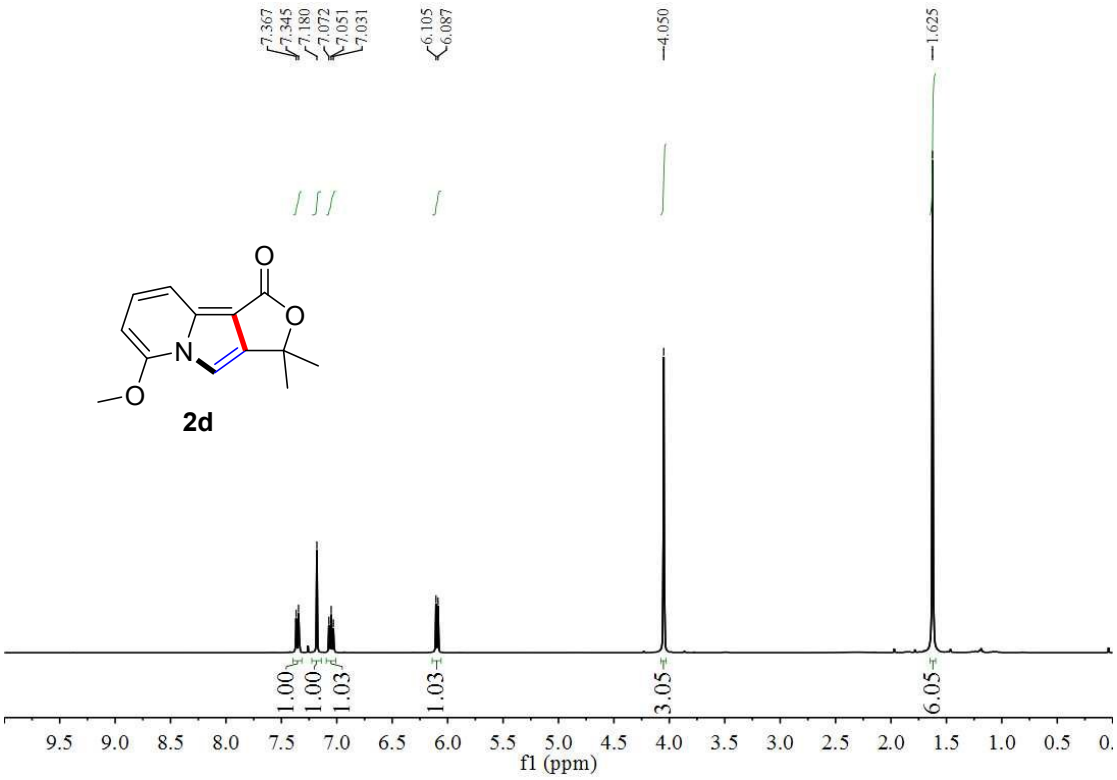
2a


7.71
7.68
7.08
7.06
7.06
7.04
7.00
6.68
6.67
2.57
1.67
O
O
N
1.00
1.11
1.02
1.02
3.13
6.06
f1 (ppm)

2c


166.04
147.71
135.07
129.85
122.81
115.92
113.04
104.29
100.02
82.11
77.42
77.10
76.78
28.21
19.23
O
O
N
f1 (ppm)

2c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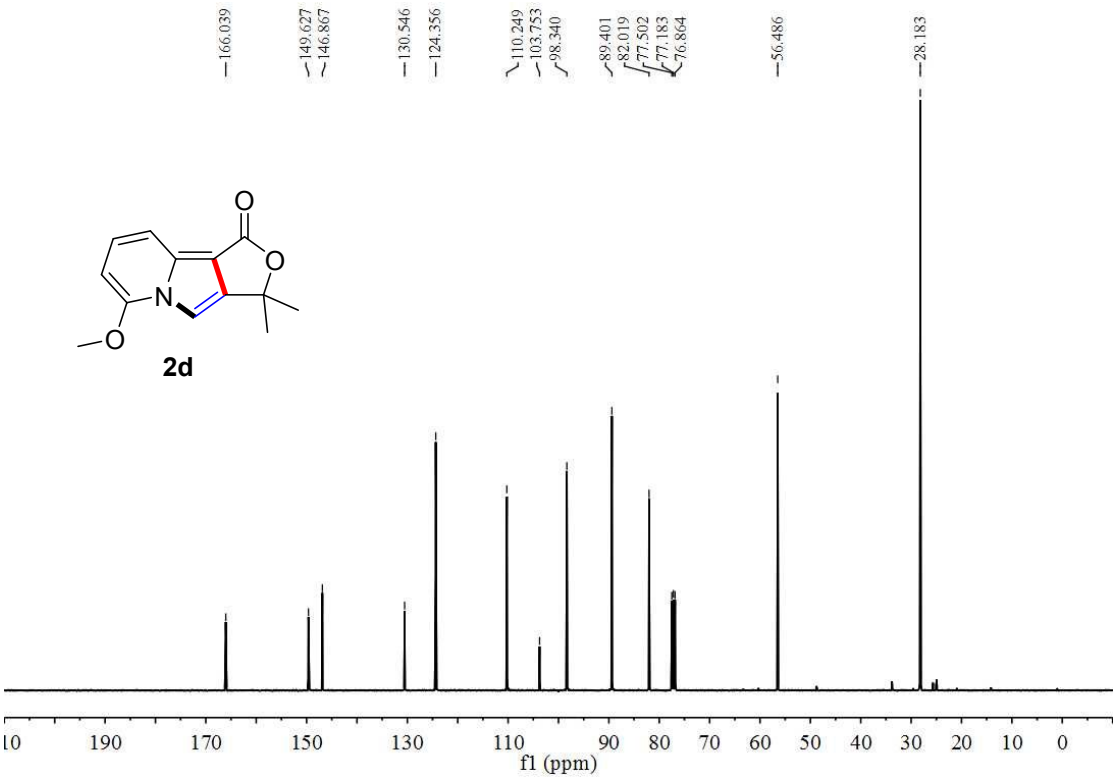
7.345
7.180
7.072
7.051
7.031
6.105
6.087
4.050
1.625
1.00
1.00
1.03
1.03
3.05
6.05
f1 (ppm)

2d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146.867
130.546
124.356
110.249
103.753
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89.401
82.019
77.502
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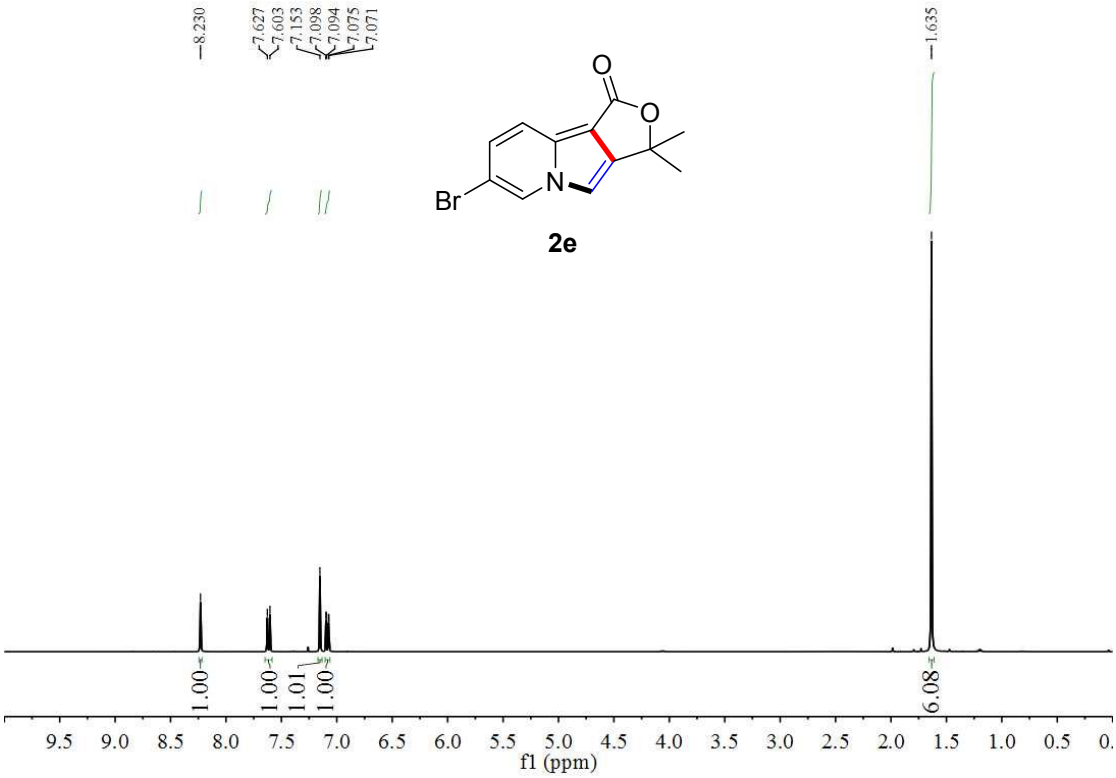
76.864
56.486
28.183
f1 (ppm)

2d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7.153
7.098
7.094
7.075
7.071
1.635
O
O
N
Br
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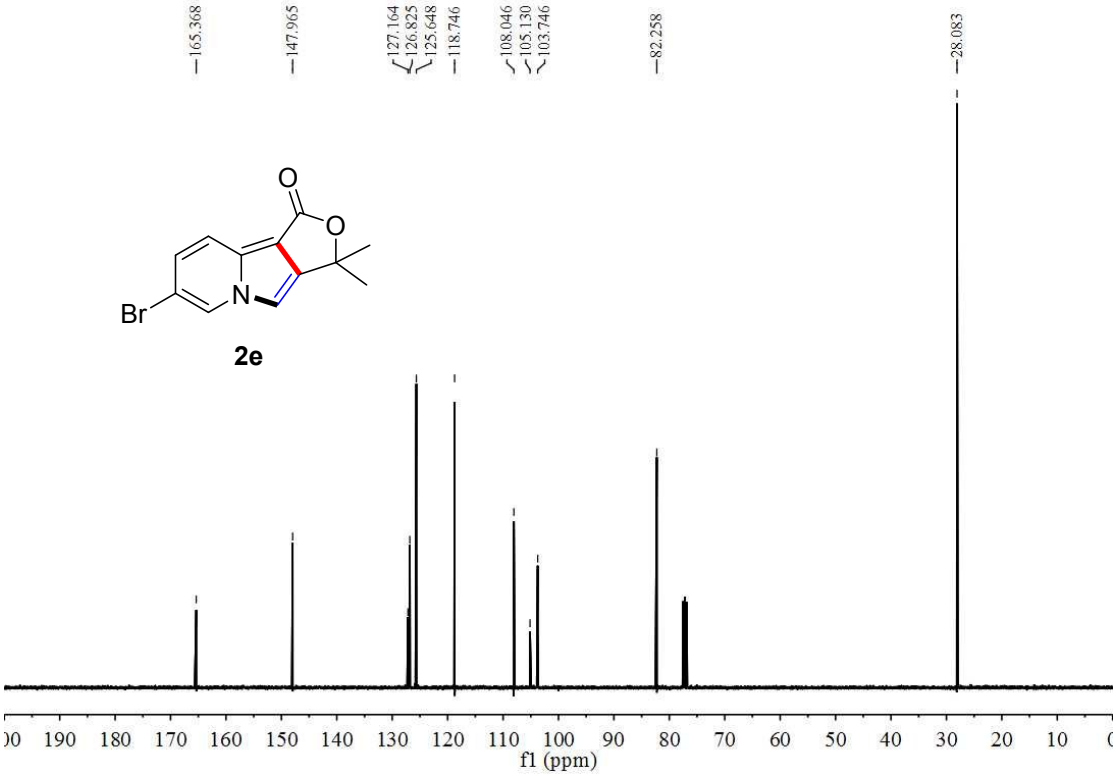
1.00
1.01
1.00
6.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

2e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147.965
127.164
126.825
125.648
118.746
108.046
105.130
103.746
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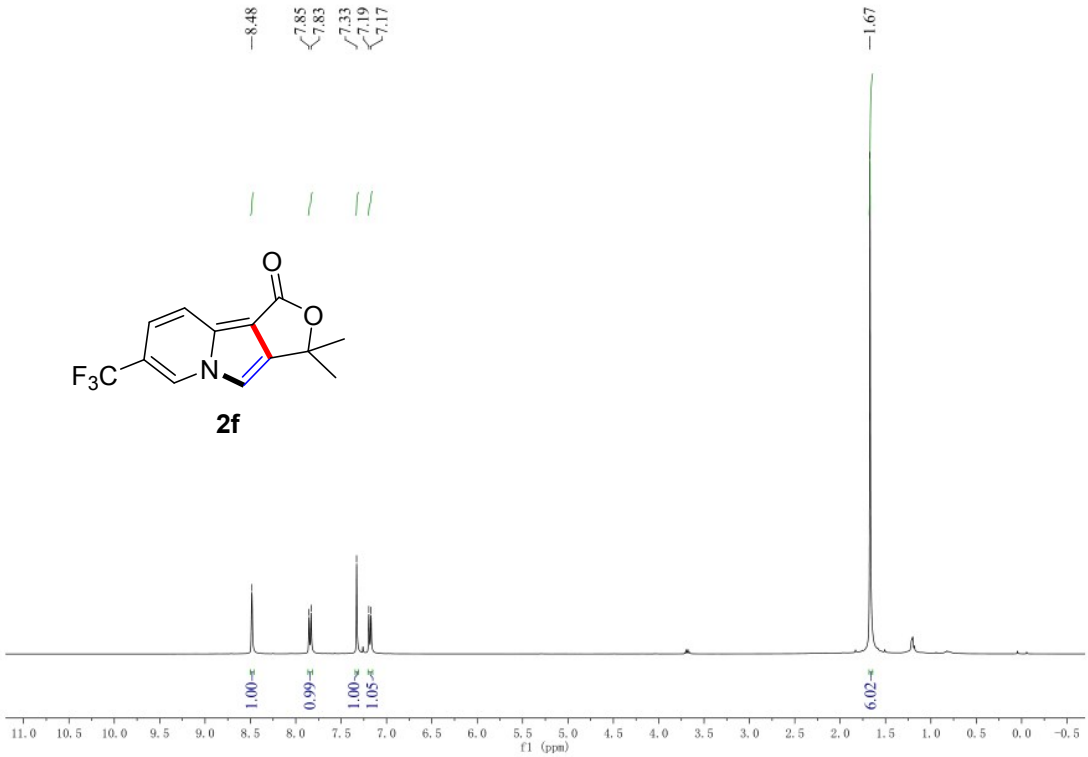
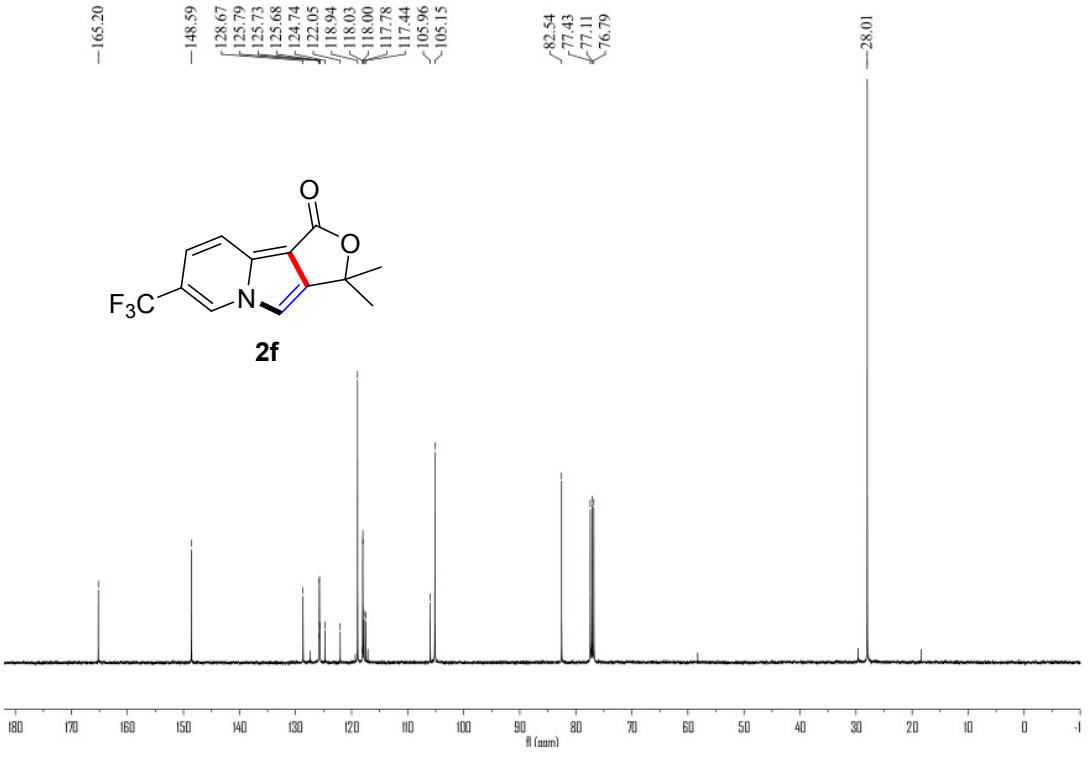
28.083
O
O
N
Br
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

2e


8.48
7.85
7.83
7.33
7.19
7.17
1.67
O
O
N
F3C
2f
1.00
0.99
1.00
1.05
6.02
f1 (ppm)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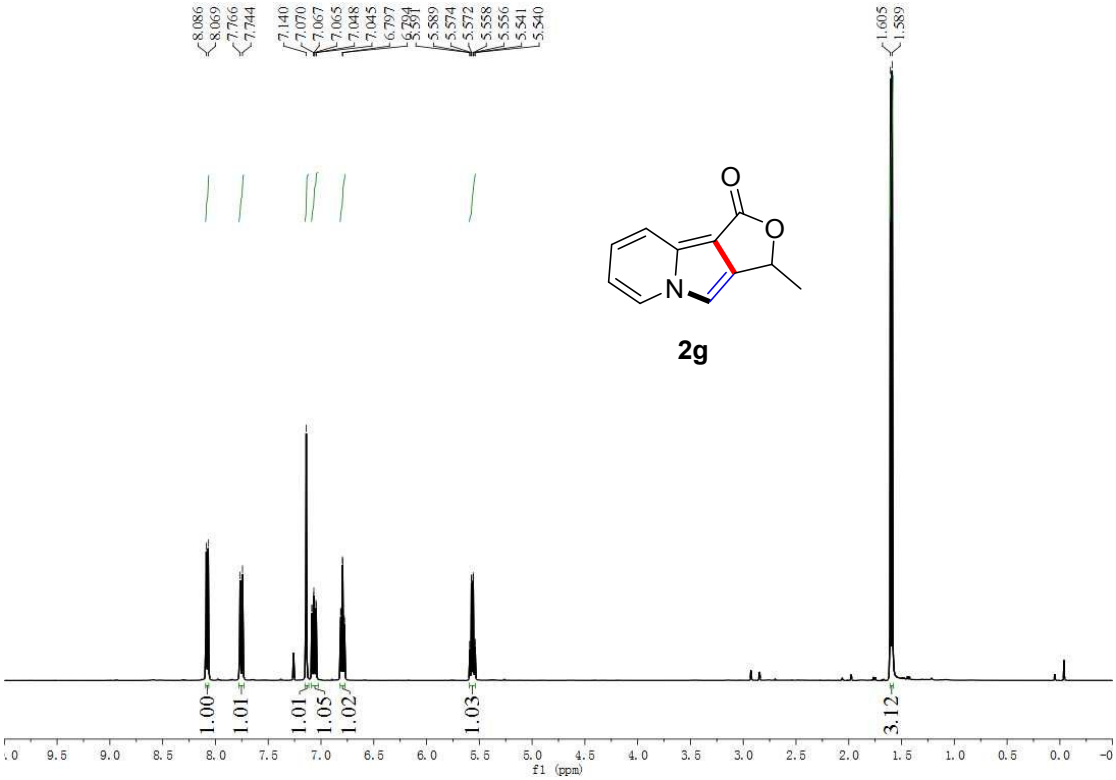
148.59
128.67
125.79
125.73
125.68
124.74
122.05
118.94
118.03
118.00
117.78
117.44
105.96
105.15
82.54
77.43
77.11
76.79
28.01
O
O
N
F3C
2f
f1 (ppm)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8.069
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7.140
7.070
7.067
7.065
7.048
7.045
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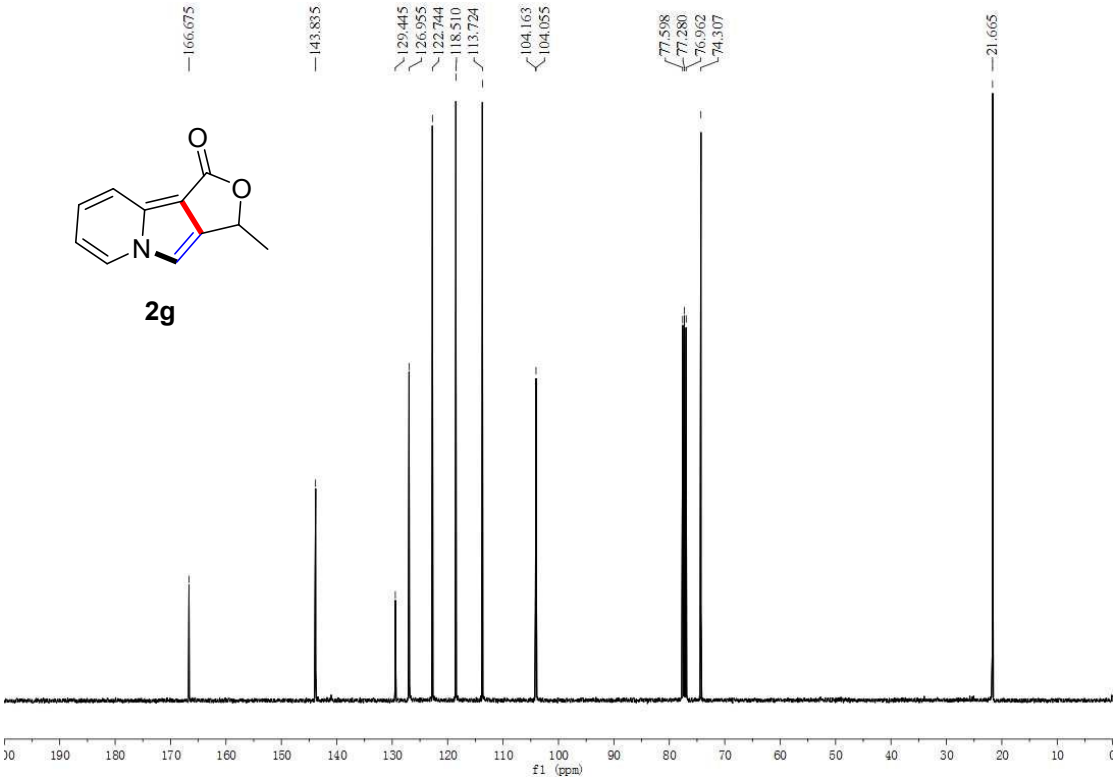
6.794
5.591
5.589
5.574
5.572
5.558
5.556
5.541
5.540
1.605
1.589
O
O
N
2g
1.00
1.01
1.01
1.05
1.02
1.03
3.12
f1 (ppm)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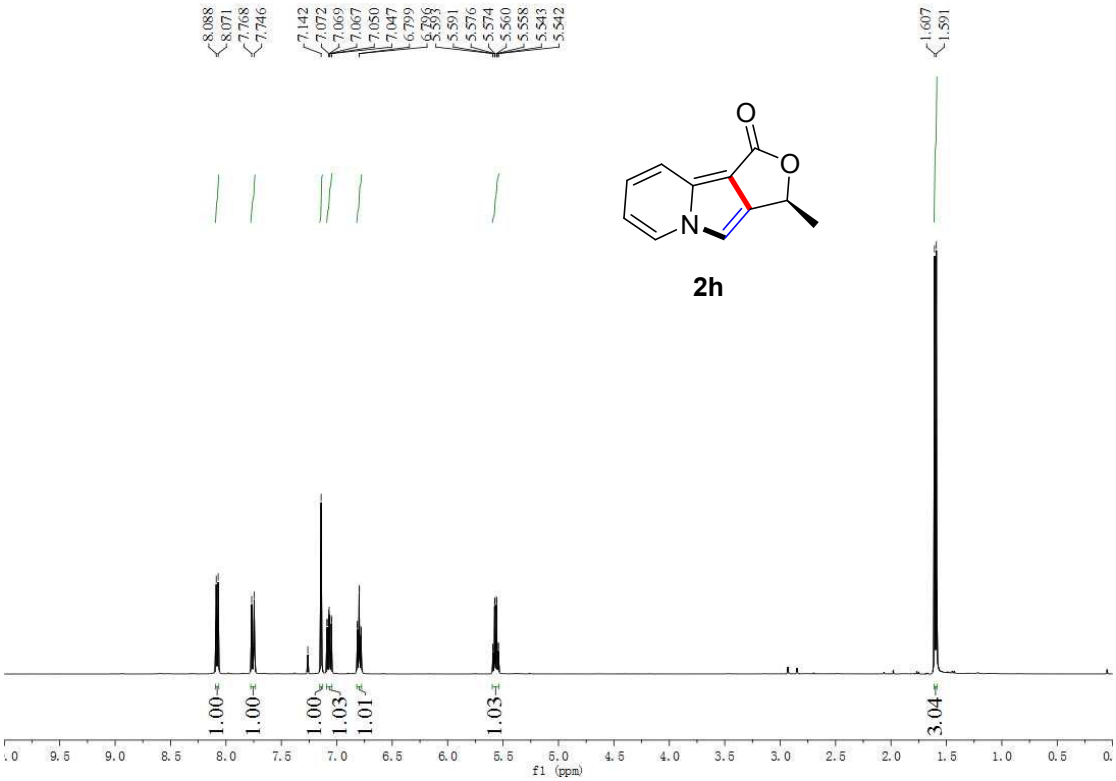
129.445
126.955
122.744
118.510
113.724
104.163
104.055
77.598
77.280
76.962
74.307
21.665
O
O
N
2g
f1 (ppm)


8.088
8.071
7.768
7.746
7.142
7.072
7.069
7.067
7.050
7.047
6.799
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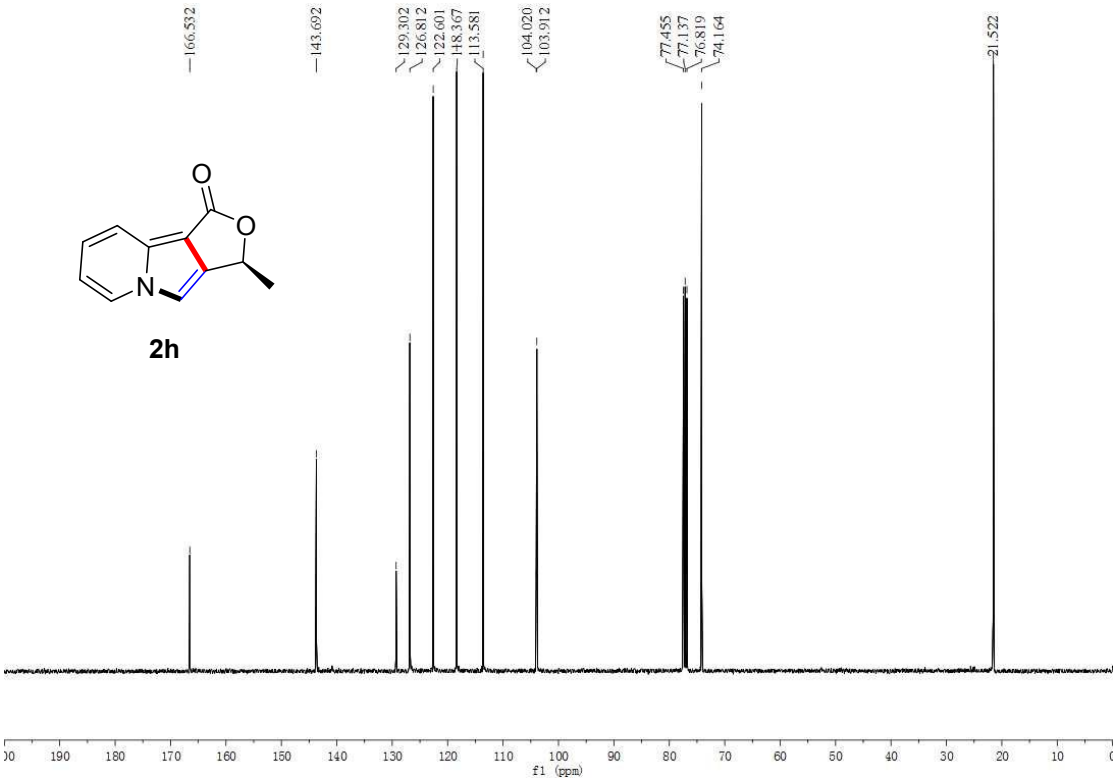
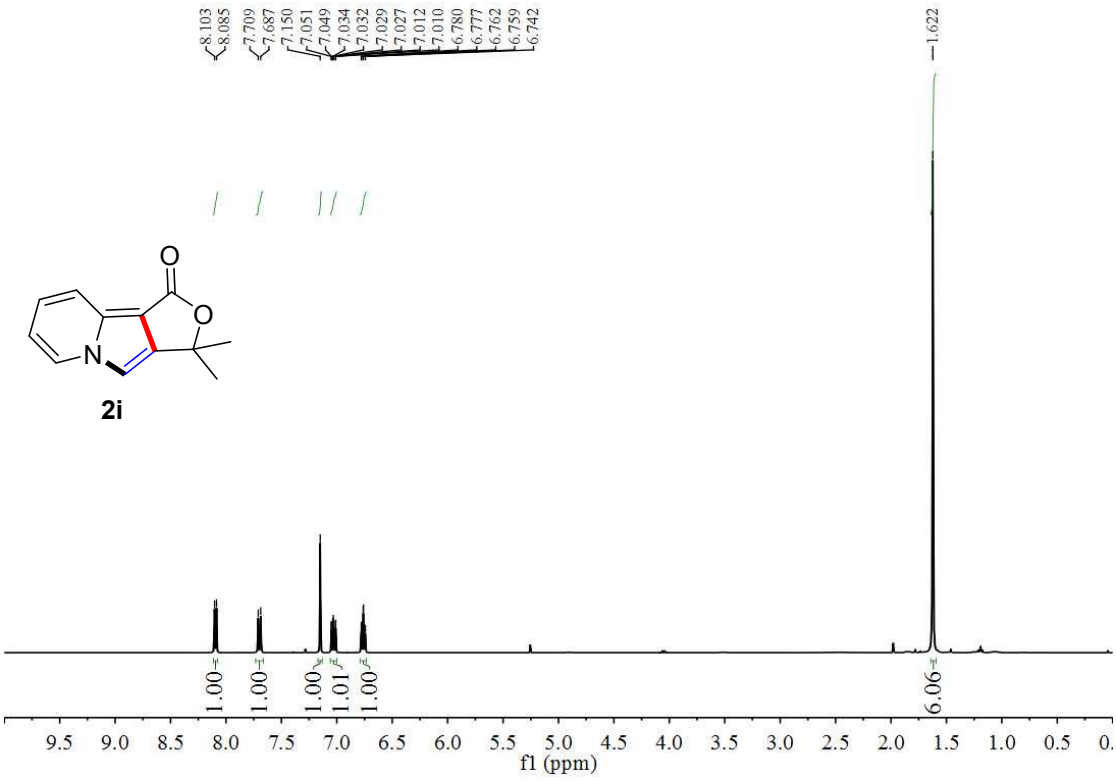
5.576
5.574
5.560
5.558
5.543
5.542
1.607
1.591
1.00
1.00
1.00
1.03
1.01
1.03
3.04
f1 (ppm)

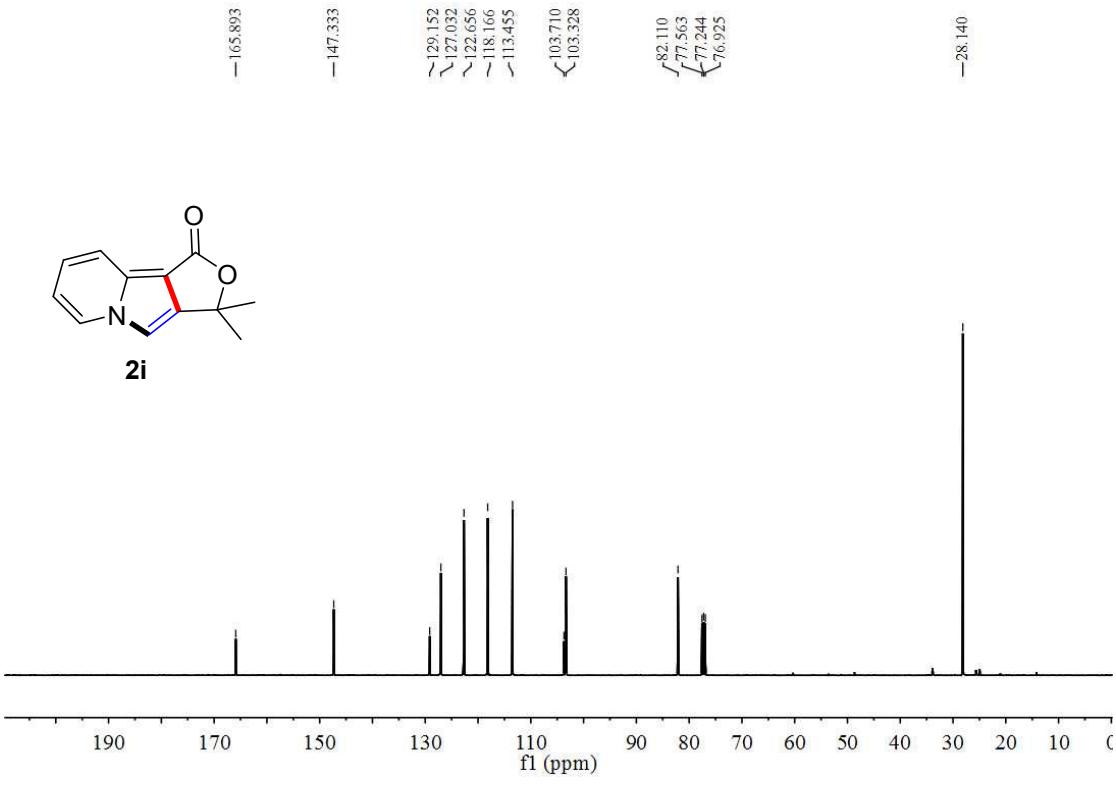
2h


166.532
143.692
129.302
126.812
122.601
118.367
113.581
104.020
103.912
77.455
77.137
76.819
74.164
21.522
f1 (ppm)

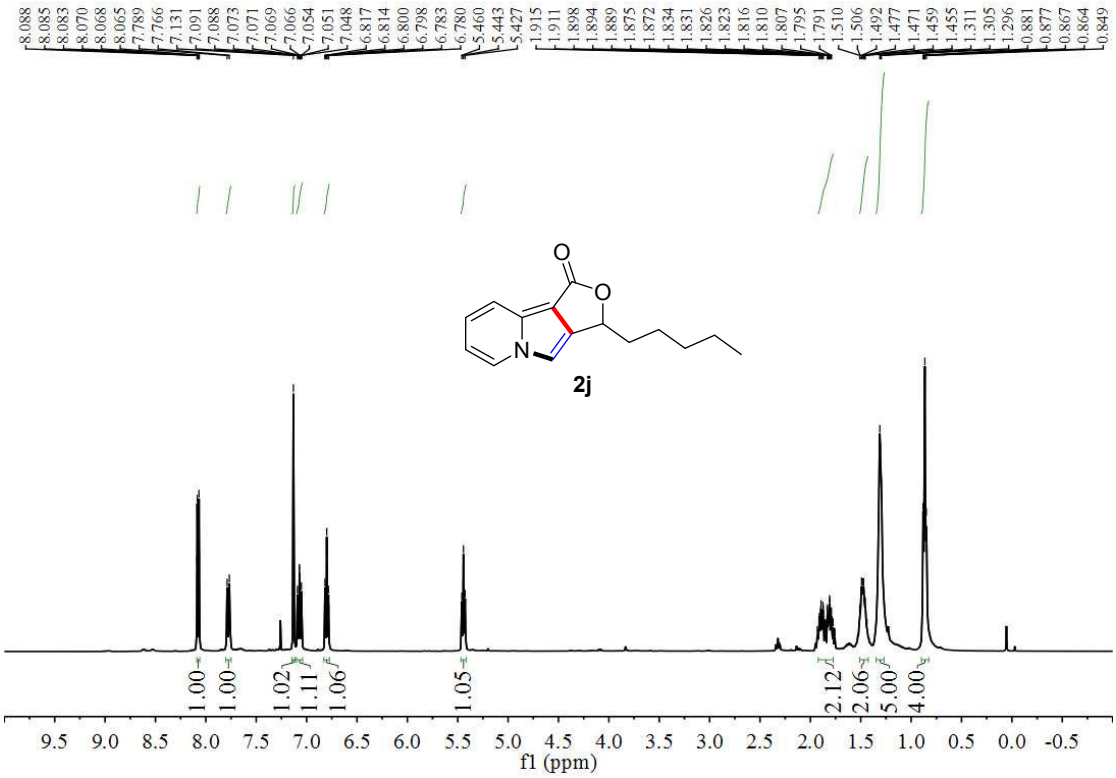
2h


8.103
8.085
7.709
7.687
7.150
7.051
7.049
7.034
7.032
7.029
7.027
7.012
7.010
6.780
6.777
6.762
6.759
6.742
1.622
O
O
N
1.00
1.00
1.00
1.01
1.00
6.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

2i


165.893
147.333
129.152
127.032
122.656
118.166
113.455
103.710
103.328
82.110
77.563
77.244
76.925
28.140
O
O
N
190 170 150 130 110 90 80 70 60 50 40 30 20 10
f1 (ppm)

2i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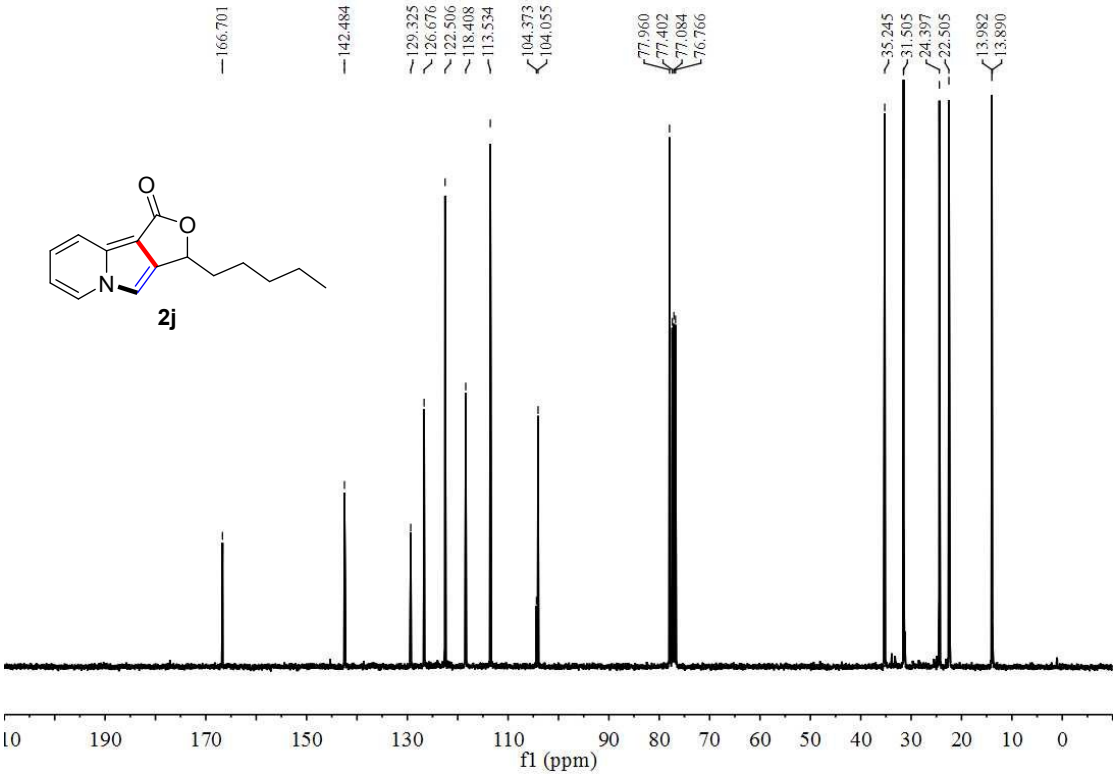
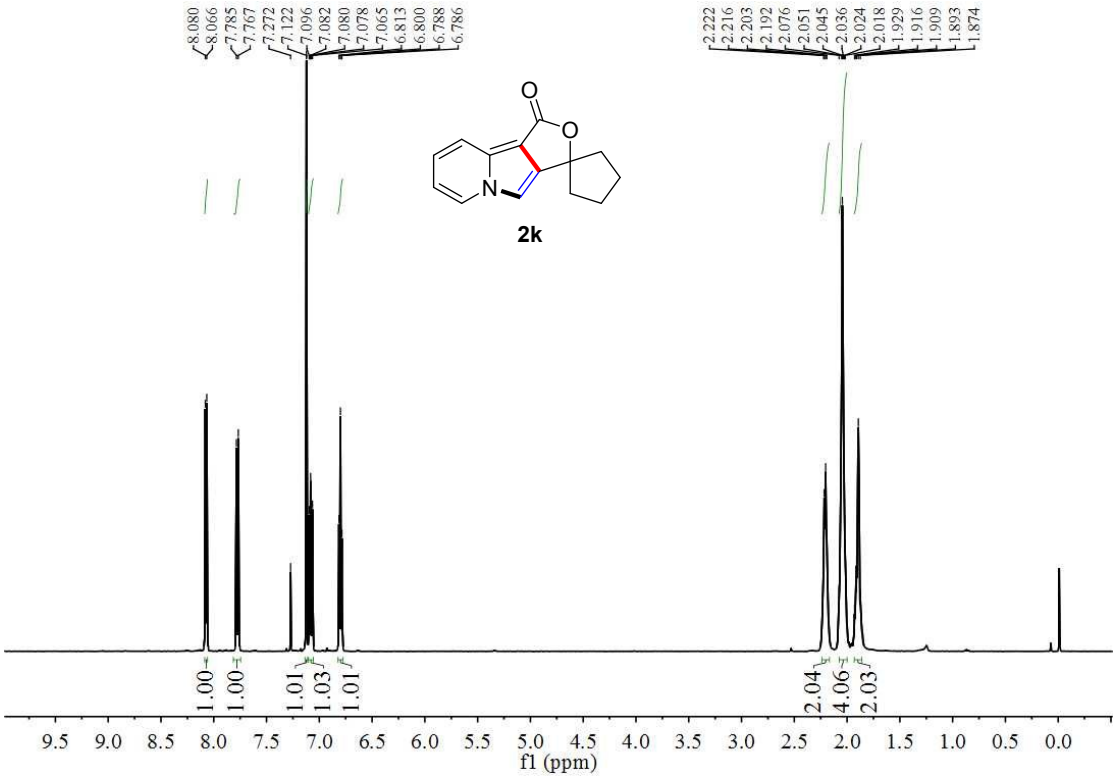
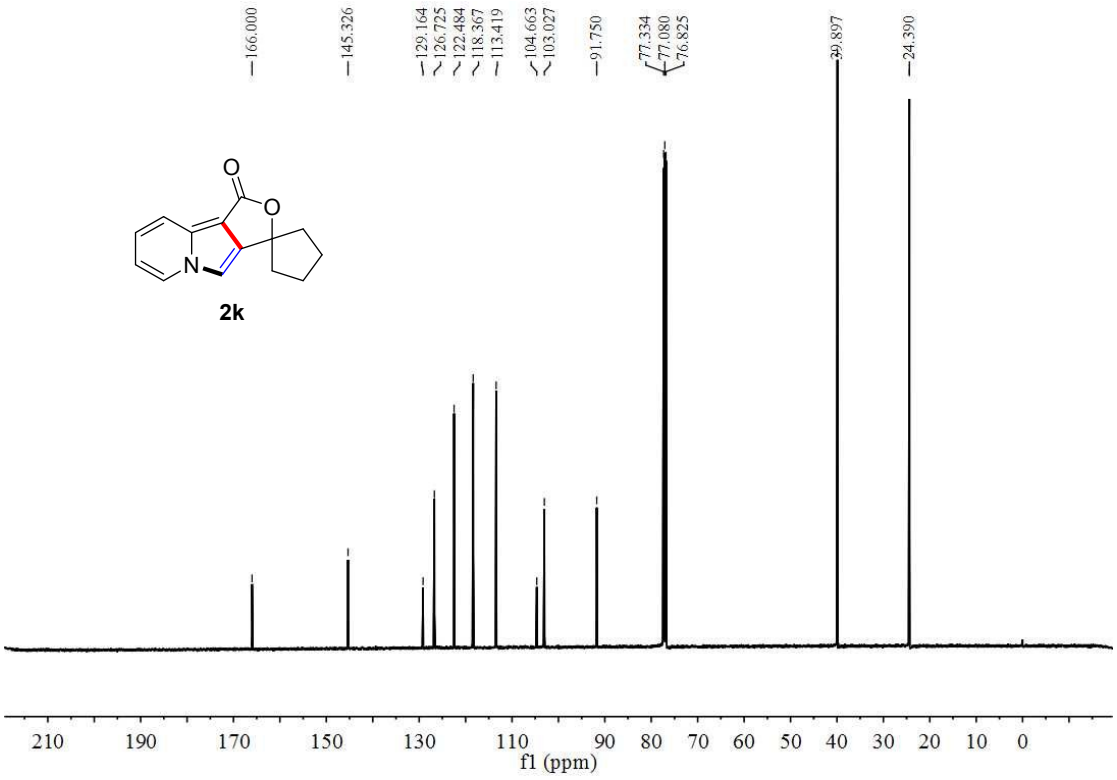
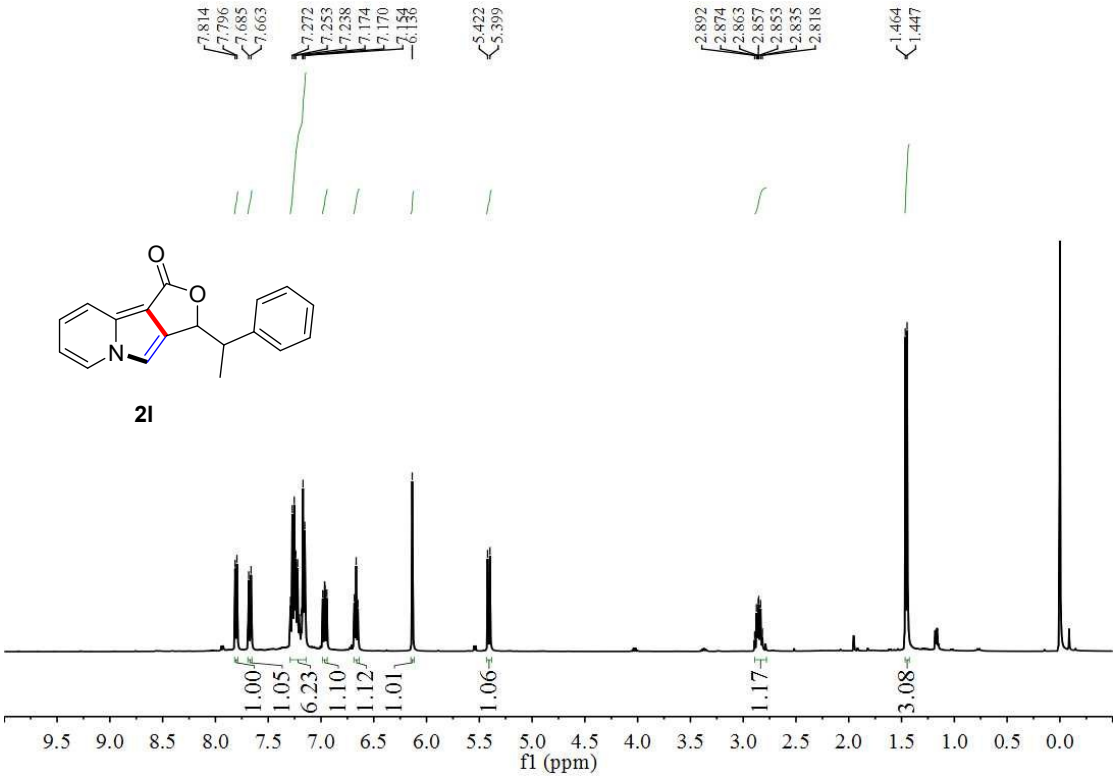
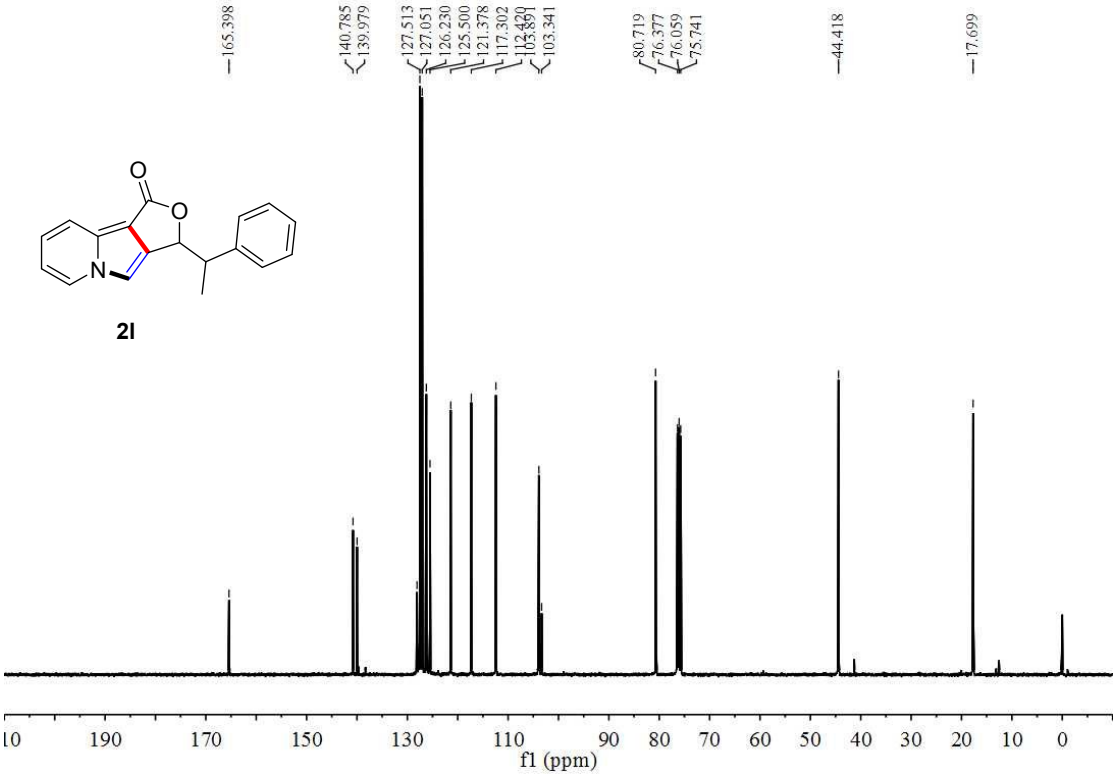
8.085
8.083
8.070
8.068
8.065
7.789
7.766
7.131
7.091
7.088
7.073
7.071
7.069
7.066
7.054
7.051
7.048
6.817
6.814
6.800
6.798
6.783
6.780
5.460
5.443
5.427
1.915
1.911
1.898
1.894
1.889
1.875
1.872
1.834
1.831
1.826
1.823
1.816
1.810
1.807
1.795
1.791
1.510
1.506
1.492
1.477
1.471
1.459
1.455
1.311
1.305
1.296
0.881
0.877
0.867
0.864
0.849
O
O
N
2j
1.00
1.00
1.02
1.11
1.06
1.05
2.12
2.06
5.00
4.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

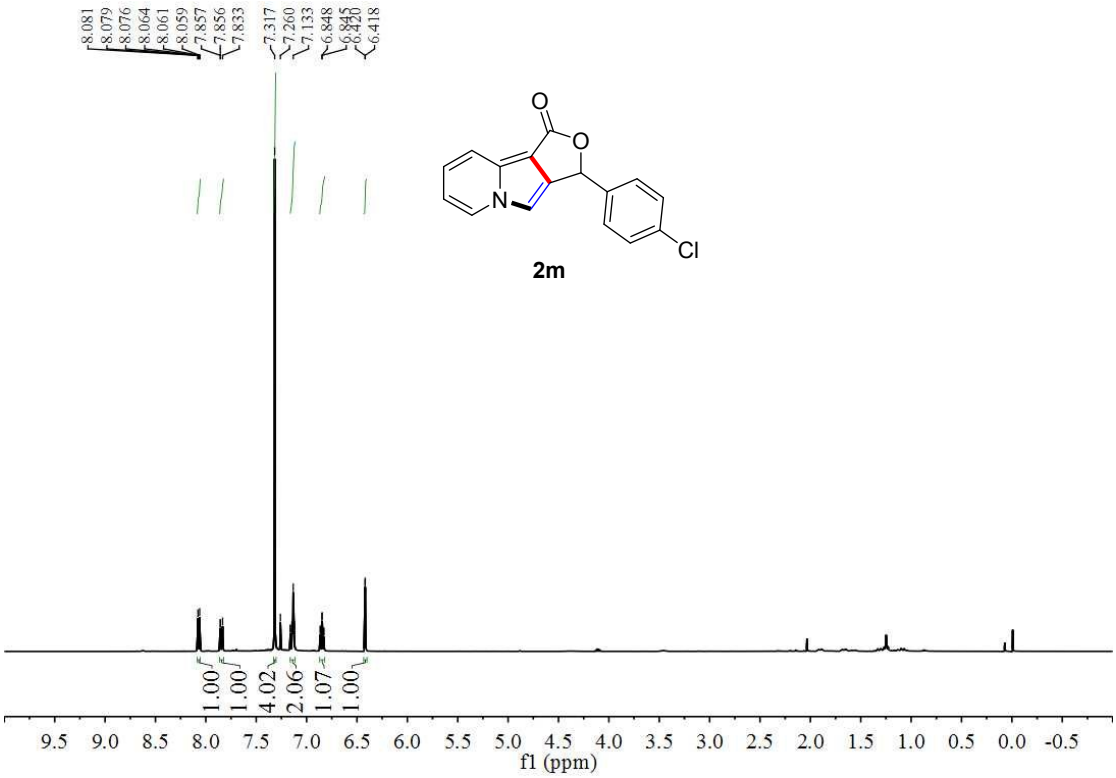

166.701
142.484
129.325
126.676
122.506
118.408
113.534
104.373
104.055
77.960
77.402
77.084
76.766
35.245
31.505
24.397
22.505
13.982
13.890
O
O
N
2j
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

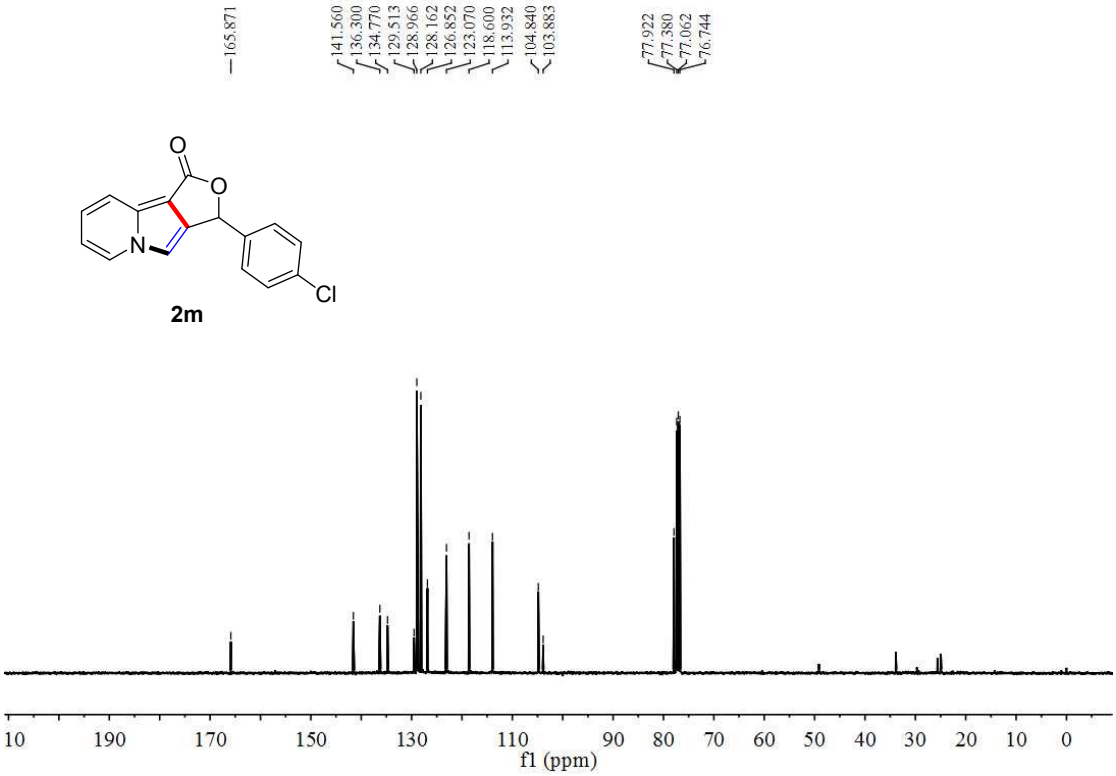

8.080
8.066
7.785
7.767
7.272
7.122
7.096
7.082
7.080
7.078
7.065
6.813
6.800
6.788
6.786
2.222
2.216
2.203
2.192
2.076
2.051
2.045
2.036
2.024
2.018
1.929
1.916
1.909
1.893
1.874
O
O
N
2k
1.00
1.00
1.01
1.03
1.01
2.04
4.06
2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

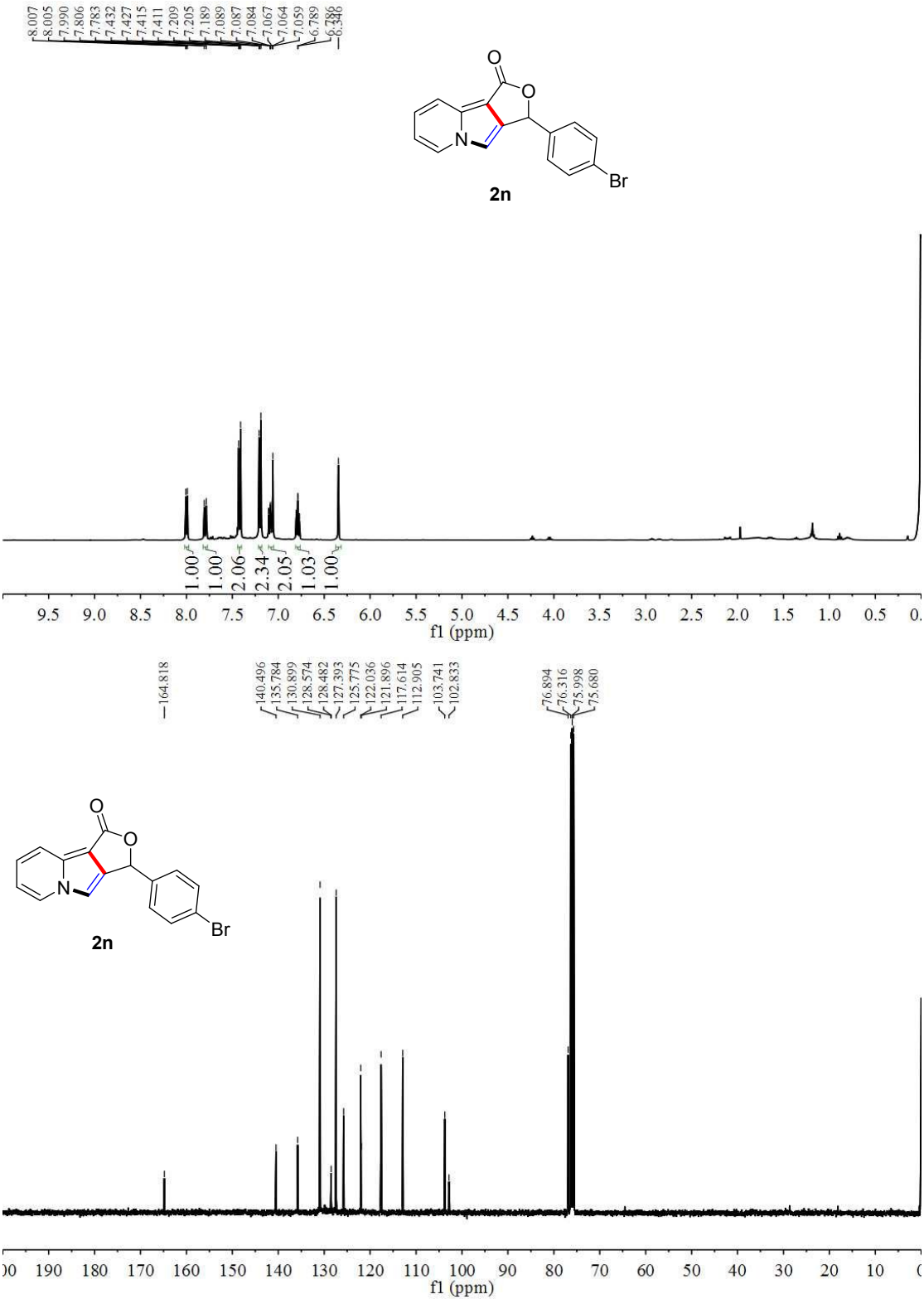

166.000
145.326
129.164
126.725
122.484
118.367
113.419
104.663
103.027
91.750
77.334
77.080
76.825
39.897
24.390
O
O
N
2k
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

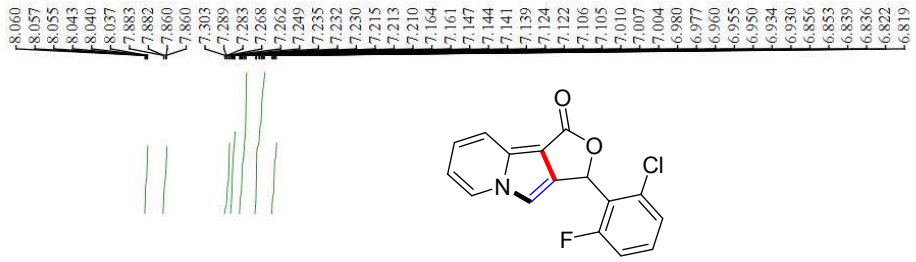

7.814
7.796
7.685
7.663
7.272
7.253
7.238
7.174
7.170
7.154
7.138
5.422
5.399
2.892
2.874
2.863
2.857
2.853
2.835
2.818
1.464
1.447
2I
1.00
1.05
6.23
1.10
1.12
1.01
1.06
1.17
3.08
f1 (ppm)


165.398
140.785
139.979
127.513
127.051
126.230
125.500
121.378
117.302
103.341
80.719
76.377
76.059
75.741
44.418
17.699
2I
f1 (ppm)

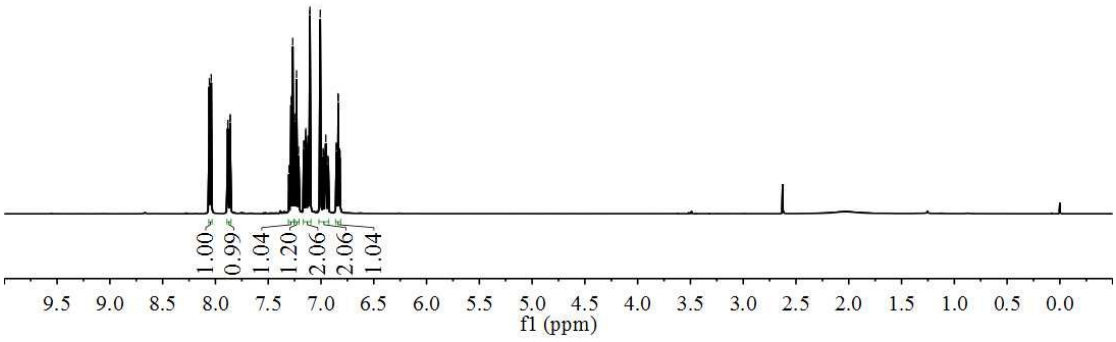

8.081
8.079
8.076
8.064
8.061
8.059
7.857
7.856
7.833
7.317
7.260
7.133
6.848
6.845
6.420
6.418
O
O
N
Cl
2m
1.00
1.00
4.02
2.06
1.07
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

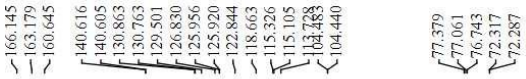

165.871
141.560
136.300
134.770
129.513
128.966
128.162
126.852
123.070
118.600
113.932
104.840
103.883
77.922
77.380
77.062
76.744
O
O
N
Cl
2m
10 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

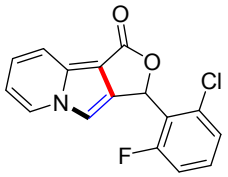

8.007
8.005
7.990
7.806
7.783
7.432
7.427
7.415
7.411
7.209
7.205
7.189
7.089
7.087
7.084
7.067
7.064
7.059
6.789
6.336
6.346
O
O
N
Br
2n
1.00
1.00
2.06
2.34
2.05
1.03
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
164.818
140.496
135.784
130.899
128.574
128.482
127.393
125.775
122.036
121.896
117.614
112.905
103.741
102.833
76.894
76.316
75.998
75.680
O
O
N
Br
2n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


8.060
8.057
8.055
8.043
8.040
8.037
7.883
7.882
7.860
7.860
7.303
7.289
7.283
7.268
7.262
7.249
7.235
7.232
7.230
7.215
7.213
7.210
7.164
7.161
7.147
7.144
7.141
7.139
7.124
7.122
7.106
7.105
7.010
7.007
7.004
6.980
6.977
6.960
6.955
6.950
6.934
6.930
6.856
6.853
6.839
6.836
6.822
6.819
O
O
N
Cl
F

2o

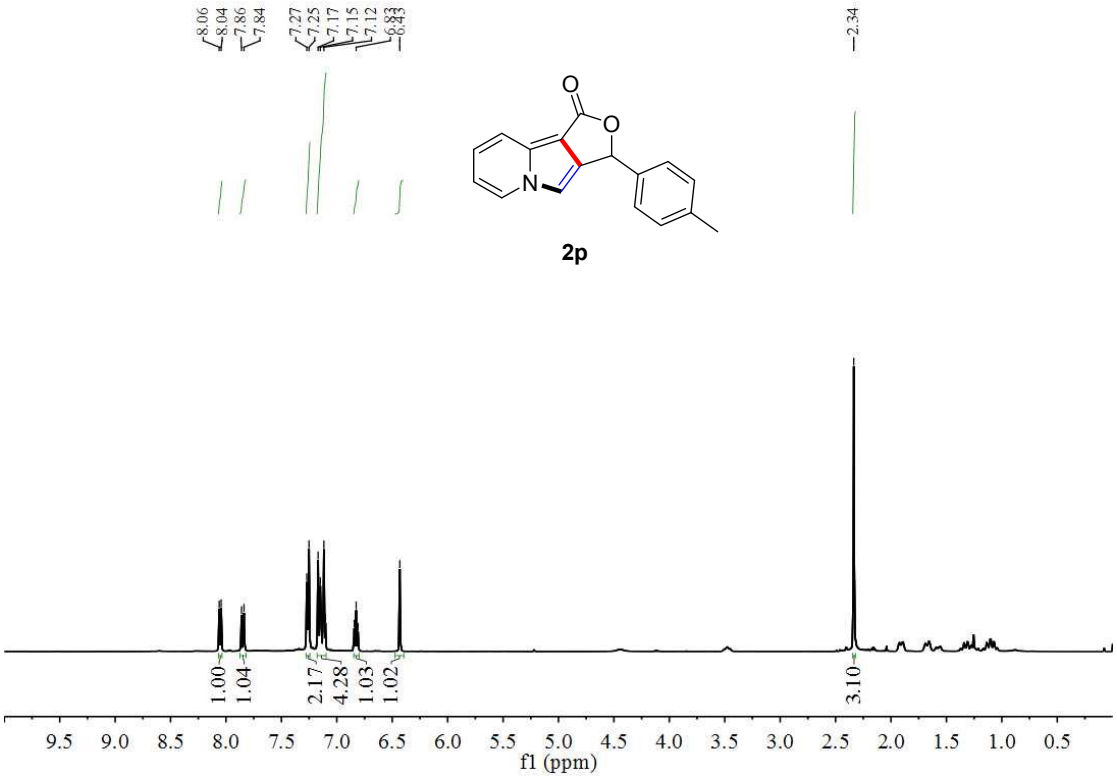

1.00
0.99
1.04
1.20
2.06
2.06
1.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.145
163.179
160.645
140.616
140.605
130.863
130.763
129.501
126.830
125.956
125.920
122.844
118.663
115.326
115.105
113.728
104.483
104.440
77.379
77.061
76.743
72.317
72.287

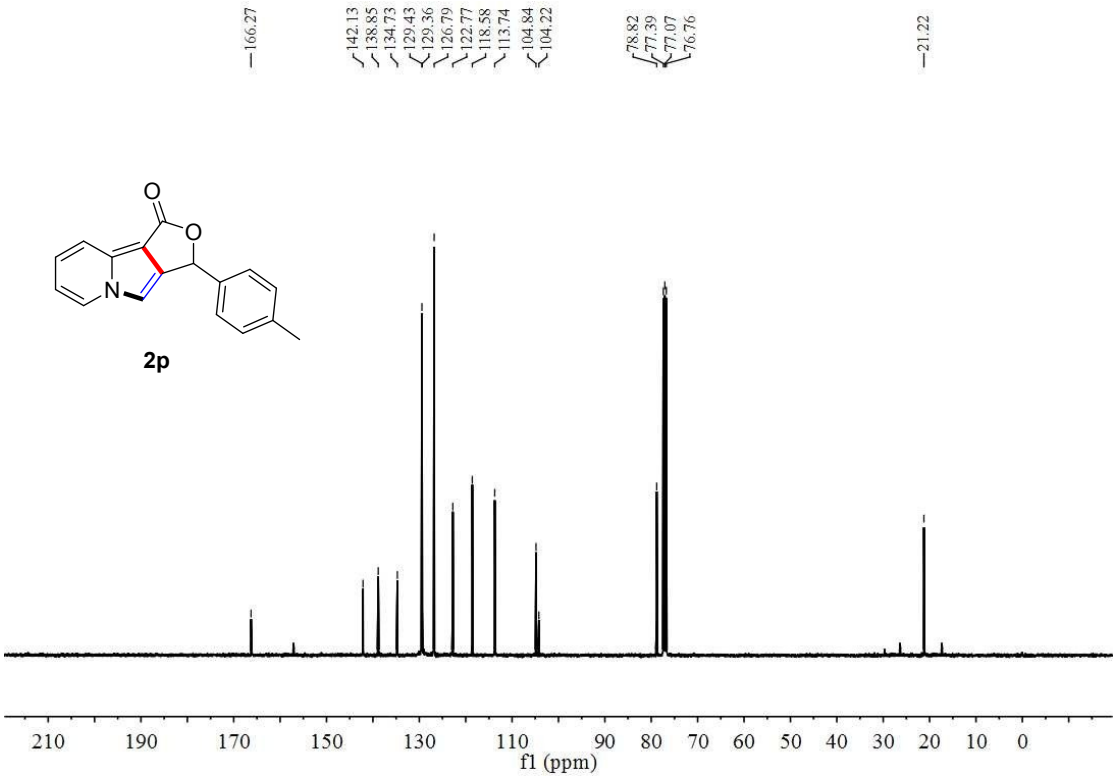

O
O
N
Cl
F

2o

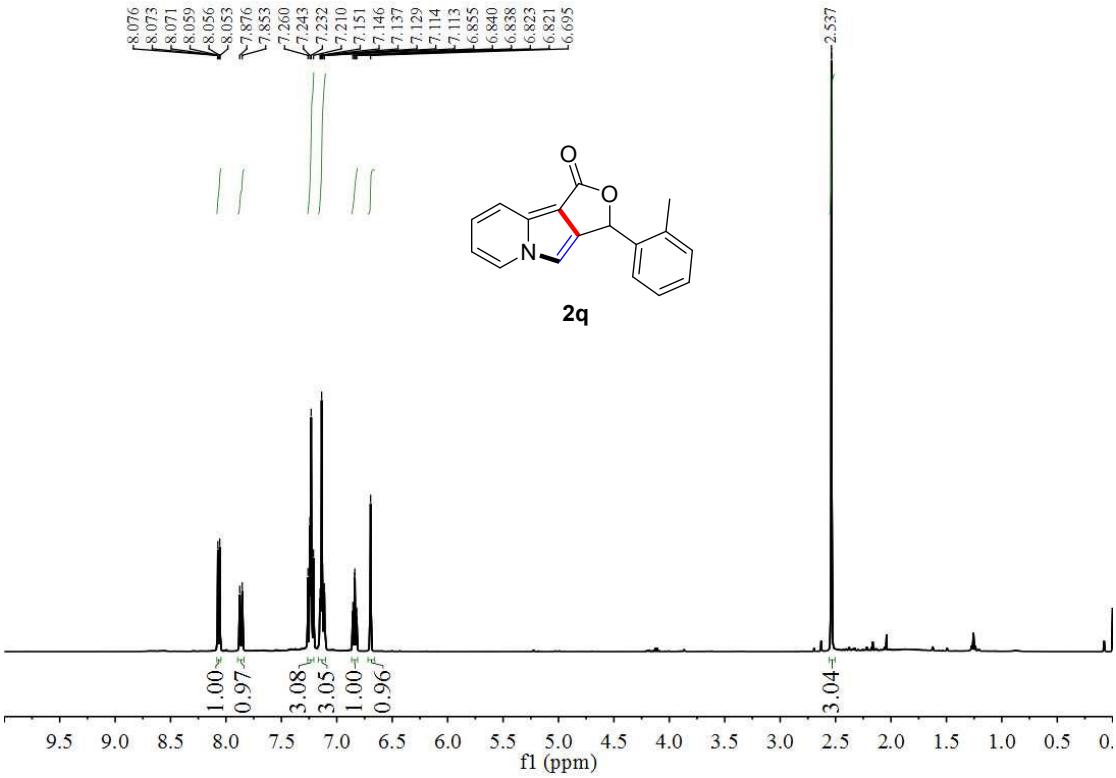
10 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

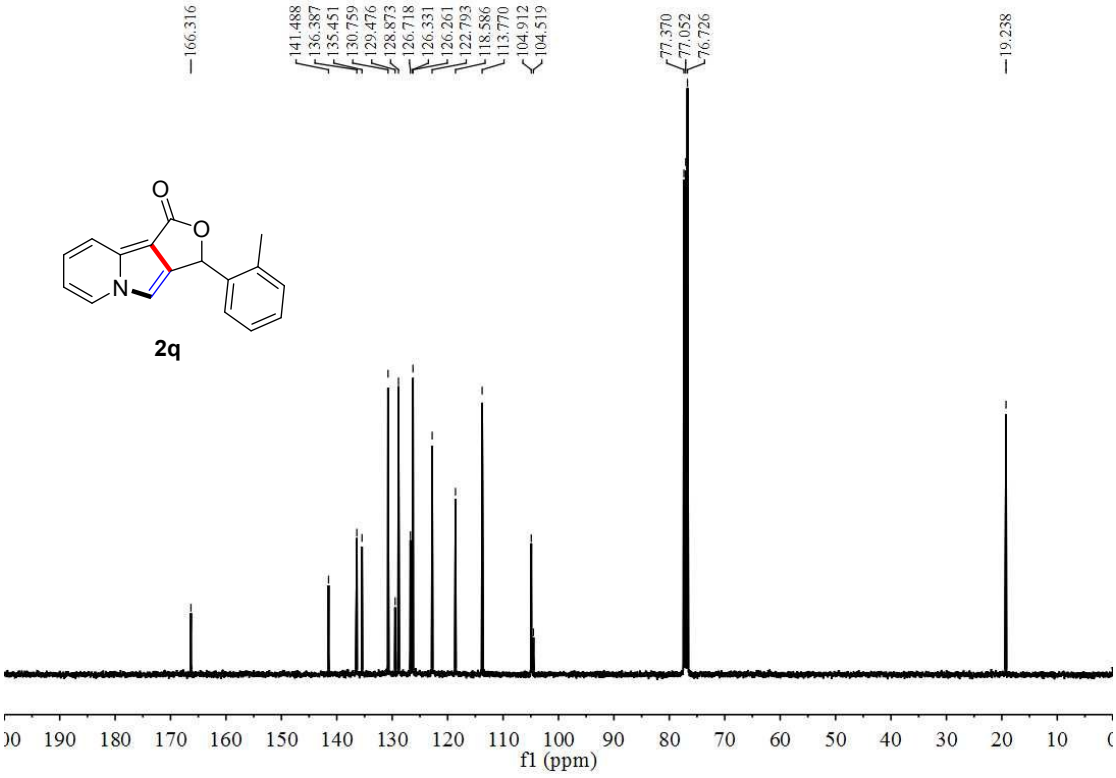

8.06
8.04
7.86
7.84
7.27
7.25
7.17
7.15
7.12
6.83
6.83
2.34
O
O
N
1.00
1.04
2.17
4.28
1.03
1.02
3.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

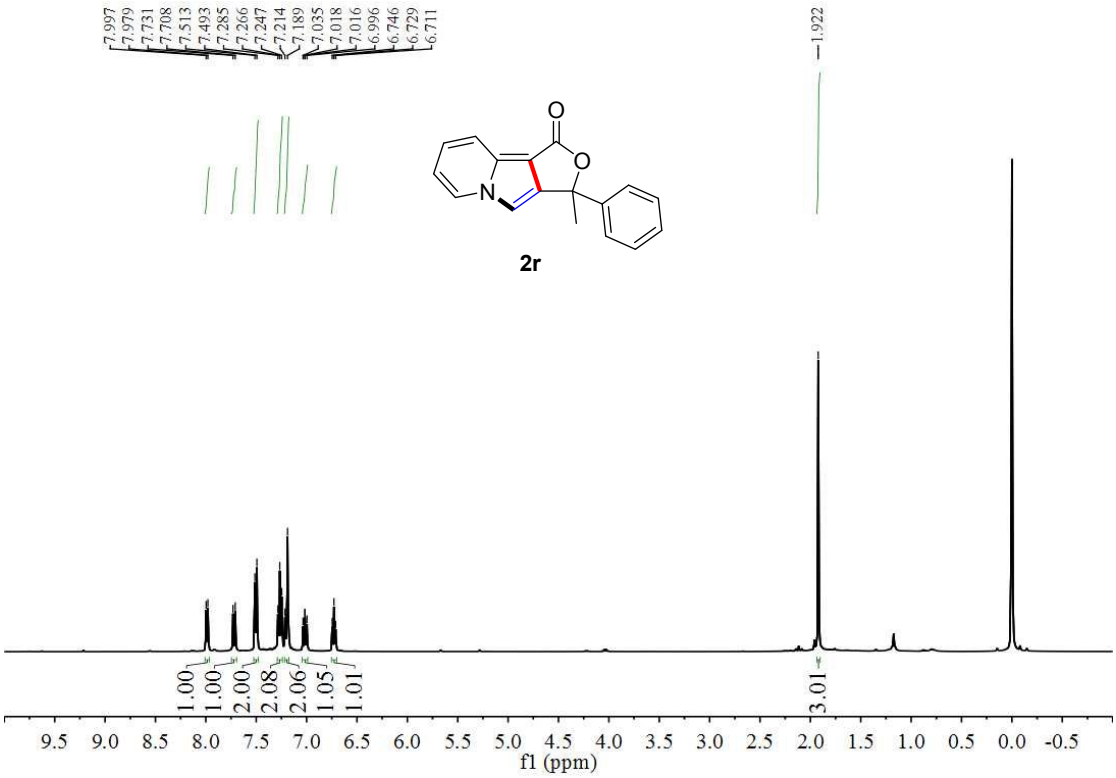
2p

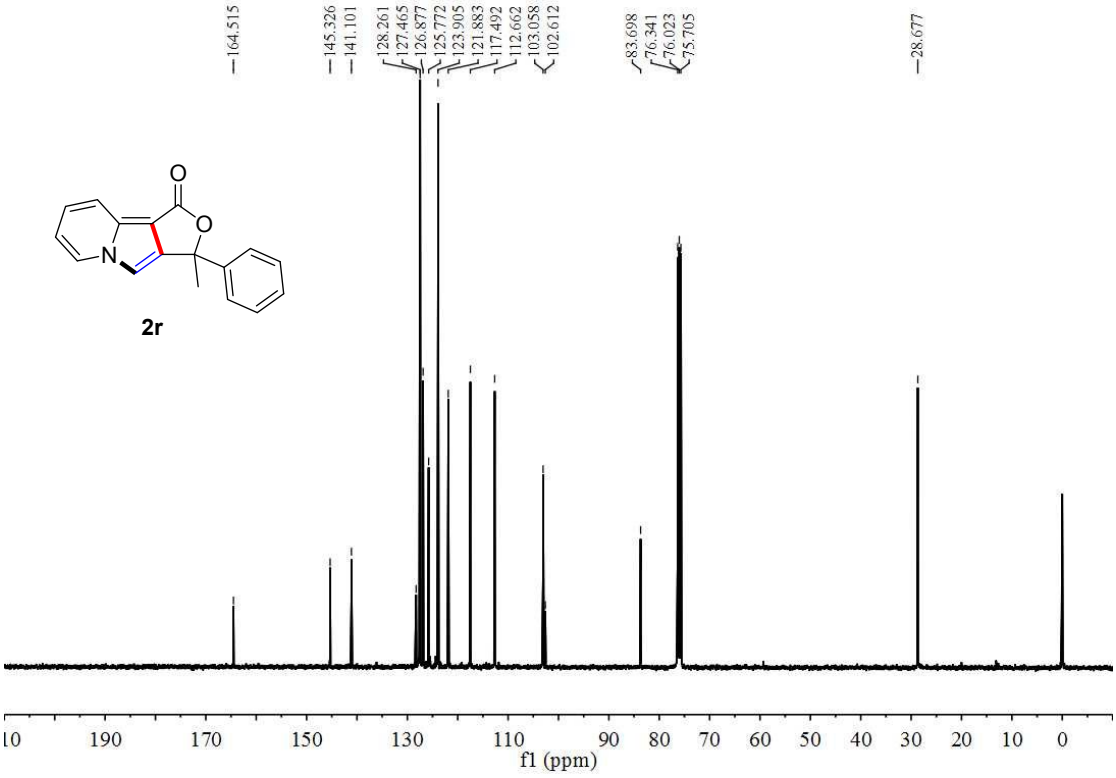

166.27
142.13
138.85
134.73
129.43
129.36
126.79
122.77
118.58
113.74
104.84
104.22
78.82
77.39
77.07
76.76
21.22
O
O
N
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

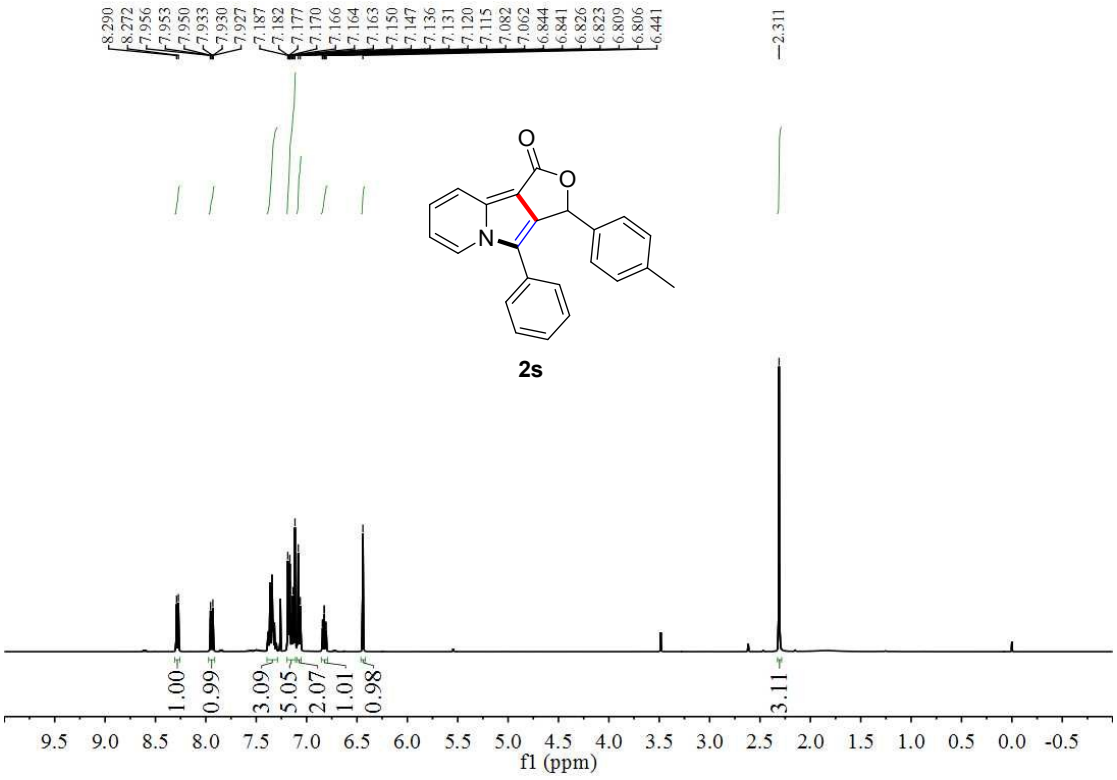
2p


8.076
8.073
8.071
8.059
8.056
8.053
7.876
7.853
7.260
7.243
7.232
7.210
7.151
7.146
7.137
7.129
7.114
7.113
6.855
6.840
6.838
6.823
6.821
6.695
2.537
O
O
N
2q
1.00
0.97
3.08
3.05
1.00
0.96
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


166.316
141.488
136.387
135.451
130.759
129.476
128.873
126.718
126.331
126.261
122.793
118.586
113.770
104.912
104.519
77.370
77.052
76.726
19.238
O
O
N
2q
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.997
7.979
7.731
7.708
7.513
7.493
7.285
7.266
7.247
7.214
7.189
7.035
7.018
7.016
6.996
6.746
6.729
6.711
1.922
2r
1.00
1.00
2.00
2.08
2.06
1.05
1.01
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


164.515
145.326
141.101
128.261
127.465
126.877
125.772
123.905
121.883
117.492
112.662
103.058
102.612
83.698
76.341
76.023
75.705
28.677
2r
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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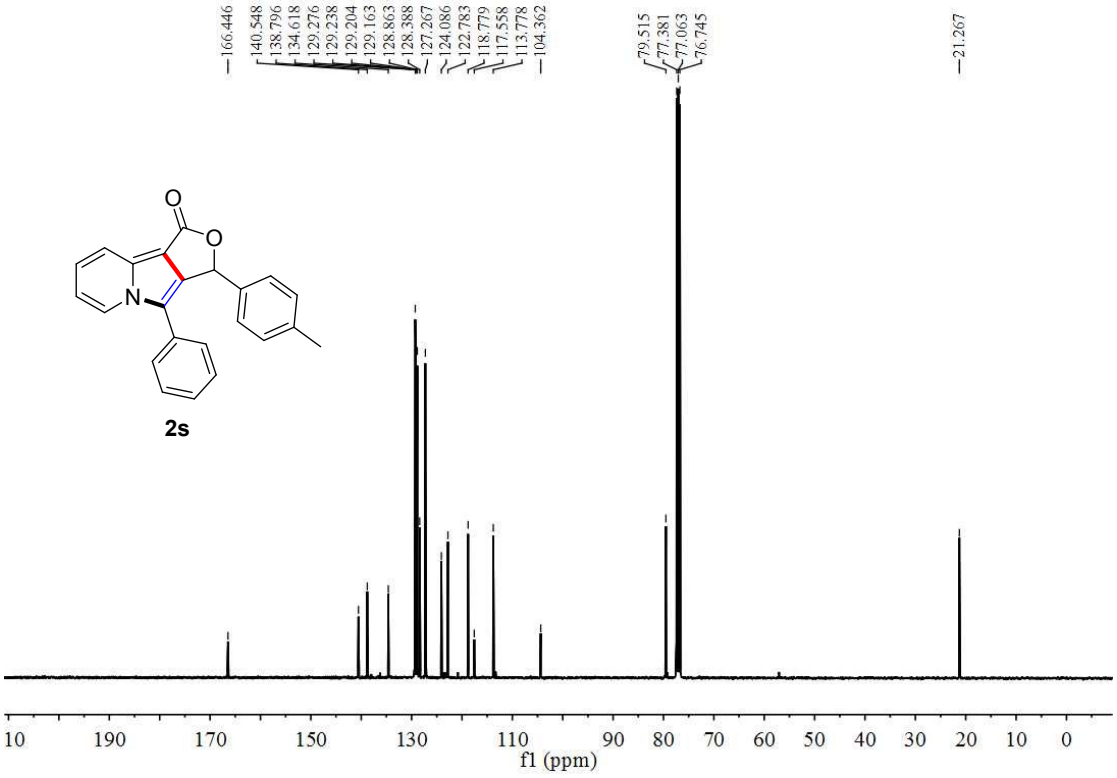
8.272
7.956
7.953
7.950
7.933
7.930
7.927
7.187
7.182
7.177
7.170
7.166
7.164
7.163
7.150
7.147
7.136
7.131
7.120
7.115
7.082
7.062
6.844
6.841
6.826
6.823
6.809
6.806
6.441
2.311
O
O
N
2s
1.00
0.99
3.09
5.05
2.07
1.01
0.98
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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134.618
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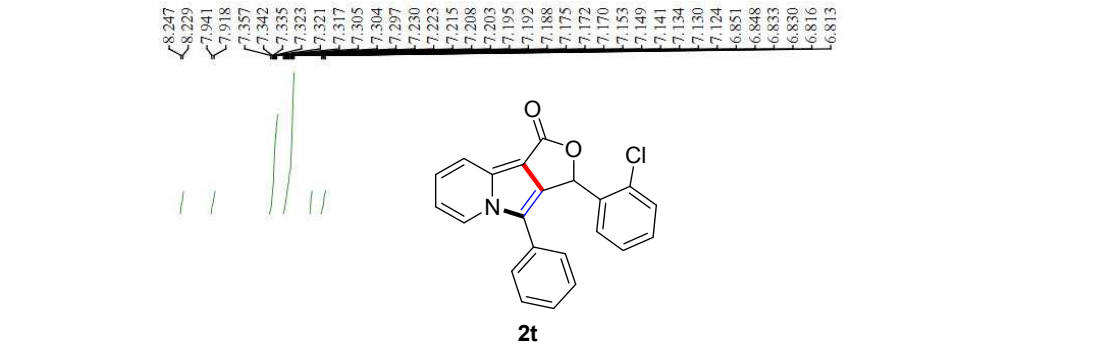
129.238
129.204
129.163
128.863
128.388
127.267
124.086
122.783
118.779
117.558
113.778
104.362
79.515
77.381
77.063
76.745
21.267
O
O
N
2s
10 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.229
7.941
7.918
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7.342
7.335
7.323
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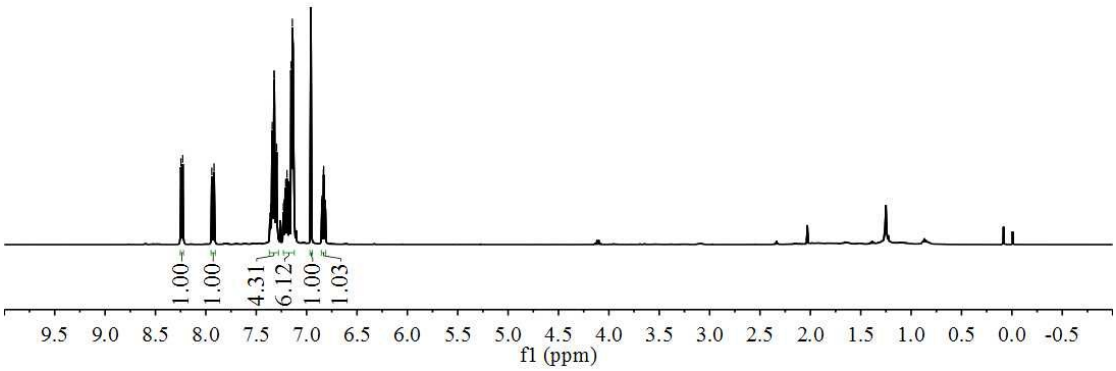
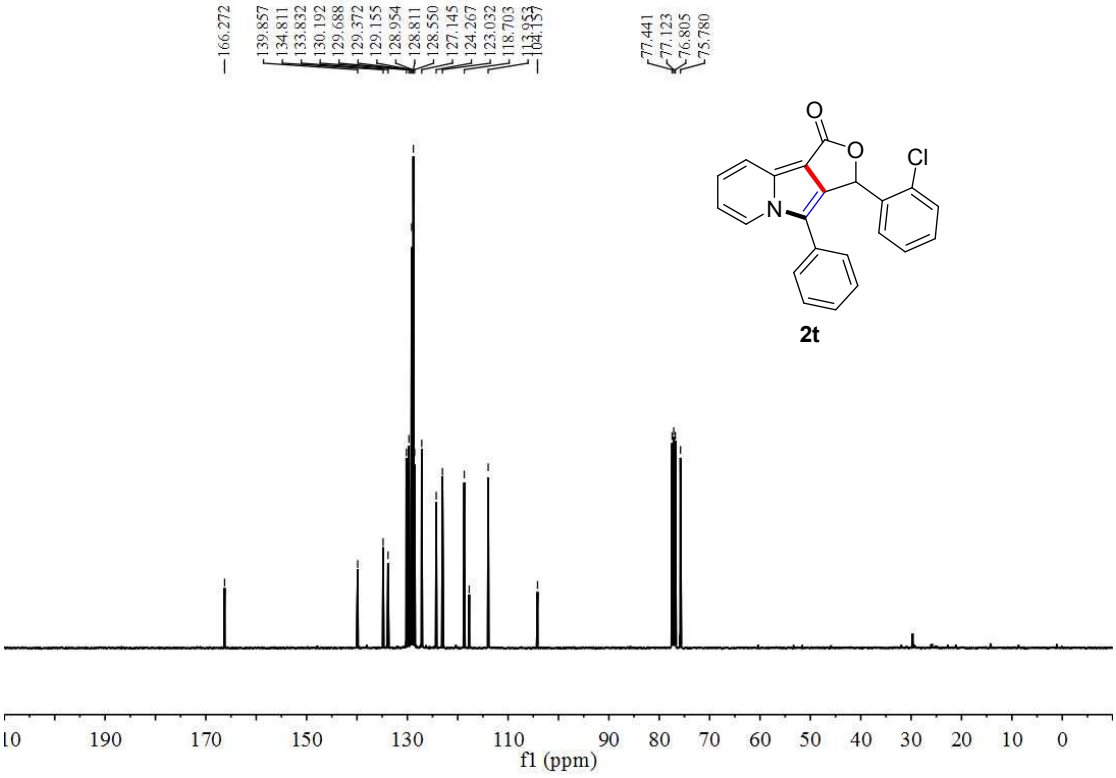
7.297
7.230
7.223
7.215
7.208
7.203
7.195
7.192
7.188
7.175
7.172
7.170
7.153
7.149
7.141
7.134
7.130
7.124
6.851
6.848
6.833
6.830
6.816
6.813
O
O
Cl
N

2t


1.00
1.00
4.31
6.12
1.00
1.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


166.272
139.857
134.811
133.832
130.192
129.688
129.372
129.155
128.954
128.811
128.550
127.145
124.267
123.032
118.703
113.353
104.157
77.441
77.123
76.805
75.780
O
O
Cl
N
10 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2t