Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
This journal is © The Royal Society of Chemistry 2019

Supporting Information

Copper-catalyzed carbene/alkyne metathesis terminated with Buchner reaction: Synthesis of dihydrocyclohepta[*b*]indoles

Qian Zeng,[a] Kuiyong Dong,[a] Jingjing Huang,[b] Lihua Qiu*[a] and Xinfang Xu*[ab]

[a] Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

[b] School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou, 510006, China

E-mail: xinfangxu@suda.edu.cn;

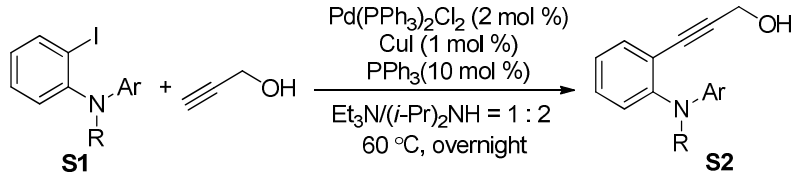
qiulihua@suda.edu.cn

Table of Contents

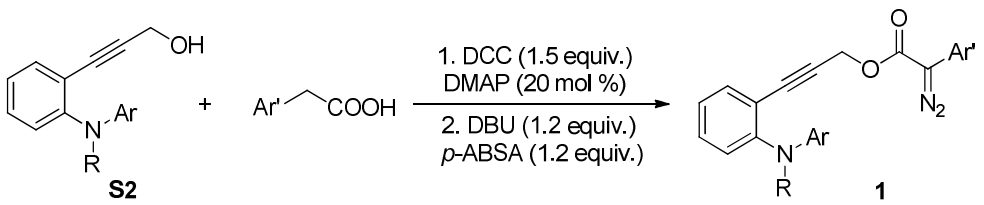
General Information

All reactions were performed in oven-dried (140 °C) glassware under argon atmosphere. DCM (dichloromethane) was distilled prior to use kept over activated 4 Å molecular sieves. Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). Liquid chromatography was performed using flash chromatography of the indicated system on silica gel (300-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 400 NMR spectrometer; chemical shifts were reported in ppm with the solvent signals as reference, and coupling constants (*J*) were given in Hertz. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (ESI Source).

General Procedure for the Preparation of Diazo Compound 1.

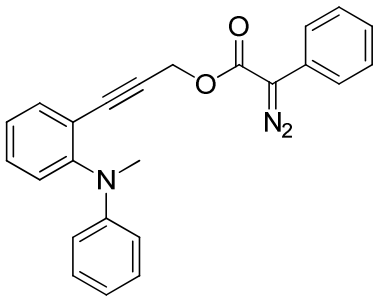


Synthesis of S2:[1] To a 50-mL oven-dried flask containing a magnetic stirring bar, and **S1** (5 mmol) in Et_3N (10 mL) and diisopropylamine (20 mL), was added CuI (9.5 mg，1.0 mol %), $Pd(PPh_3)_2Cl_2$ (70.2 mg, 2 mol %), PPh_3 (131 mg, 10 mol %), and 2-propyn-1-ol (336 mg, 6 mmol) in sequence under argon atmosphere. The reaction mixture was stirred at 60 ℃ for 12 h. Then the reaction mixture was filtered through a short pad of Celite and the solid was washed with ethyl acetate. The combined organic layers were concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **S2** in high yields.



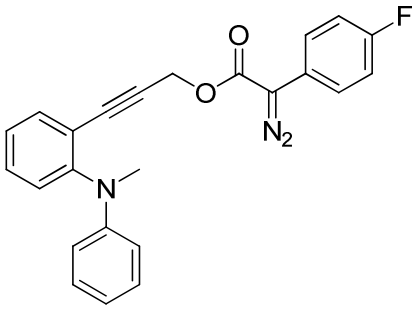
Synthesis of 1:[2] To a solution of **S2** (4.2 mmol), phenylacetic acid (6.3 mmol), and DMAP (103 mg, 0.84 mmol) in dry DCM (20 mL), was added a solution of DCC (1.298 g, 6.3 mmol) in dry DCM (10 mL) slowly over 20 min at 0℃. The resulting mixture was allowed to warm to room temperature over 1 h, and a yellow solid was formed in this period of time. The reaction solution was filtered. After evaporating the solvent in vacuo, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to provide the corresponding ester products as orange oil or solid depend on the substrate (> 90% yields).

To a solution of above obtained ester (3.8 mmol), and *p*-ABSA (1.113 g, 4.6 mmol) in dry CH_3CN (15 mL), was added DBU (699 mg, 4.6 mmol) dropwise at 0℃. The resulting mixture was allowed to warm to room temperature over 30 min and stirred for additional 10 h. The reaction was quenched with aqueous NH_4Cl solution (60 mL) and then extracted with diethyl ether (20 mL), and the organic phase was dried over anhydrous Na_2SO_4. After evaporating the solvent after filtration, the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to give **1** as yellow oil or solid depend on the substrate in 60-80% yields.

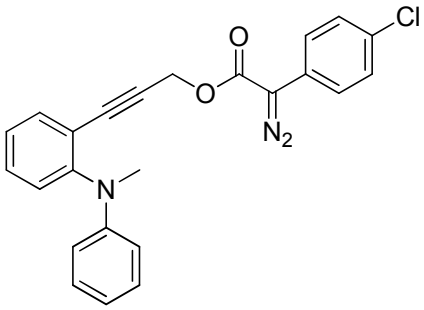


3-(2-(Methyl(phenyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-phenylacetate (1a). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.54-7.49 (comp, 3H), 7.44-7.33 (comp, 3H), 7.27-7.14 (comp, 5H), 6.76 (comp, 3H), 4.94 (s, 2H), 3.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 150.9, 149.2, 134.2,

130.2, 129.1, 128.9, 127.4, 126.0, 125.4, 125.0, 124.1, 120.5, 118.4, 115.2, 88.0, 84.6, 53.1, 39.9. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{19}N_3NaO_2$ [M+Na]$^+$: 404.1369, found 404.1382.

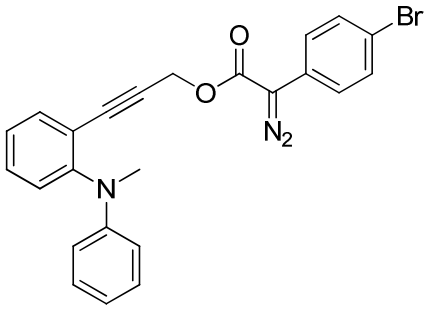


3-(2-(Methyl(phenyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-(4-fluorophenyl)acetate (1b). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.58-7.54 (m, 1H), 7.51-7.44 (m, 2H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.24-7.12 (comp, 5H), 6.85-6.73 (comp, 3H), 4.96 (s, 2H), 3.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 161.2 (d, *J* = 246.4 Hz), 150.9, 149.2, 134.2, 130.2, 128.8, 127.4, 126.0 (d, *J* = 8.0 Hz), 125.0, 121.1 (d, *J* = 3.2 Hz), 120.4, 118.4, 116.1 (d, *J* = 22.0 Hz), 115.2, 88.0, 84.7, 53.2, 39.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.94. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{18}FN_3NaO_2$ [M+Na]$^+$: 422.1275, found 422.1293.

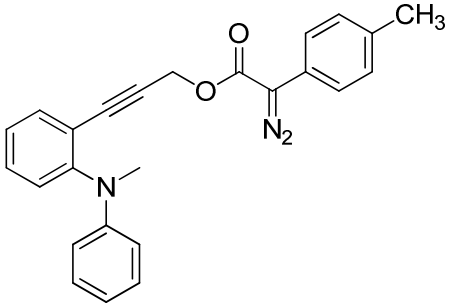


3-(2-(Methyl(phenyl)amino)phenyl)prop-2-yn-1-yl-2-(4-chlorophenyl)-2-diazoacetate (1c). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.52 (d, *J* = 7.7 Hz, 1H), 7.45-7.39 (m, 2H), 7.39-7.33 (comp, 3H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.20-7.13 (comp, 3H), 6.81-6.66 (comp, 3H), 4.93 (s, 2H), 3.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 150.9, 149.2, 134.1, 131.7, 130.3, 129.2, 128.9,

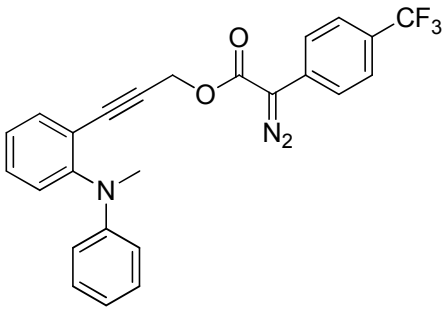
127.4, 125.2, 125.1, 124.0, 120.4, 118.4, 115.2, 87.8, 84.8, 53.2, 39.9. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{18}ClN_3NaO_2$ [M+Na]$^+$: 438.0980, found 438.0976.



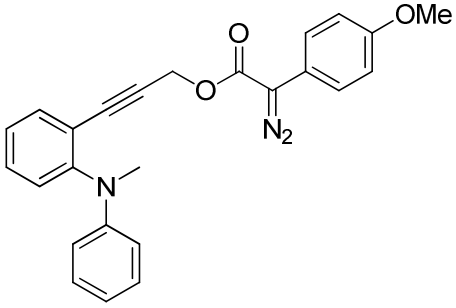
3-(2-(Methyl(phenyl)amino)phenyl)prop-2-yn-1-yl-2-(4-bromophenyl)-2-diazoacetate (1d). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53-7.50 (comp, 3H), 7.38-7.35 (comp, 3H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.17-7.14 (comp, 3H), 6.77-6.71 (comp, 3H), 4.92 (s, 2H), 3.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 150.9, 149.2, 134.2, 132.1, 130.3, 128.8, 127.4, 125.4, 125.0, 124.6, 120.4, 119.5, 118.4, 115.2, 87.8, 84.8, 53.2, 39.9. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{18}BrN_3NaO_2$ [M+Na]$^+$: 482.0475, found 482.0490.



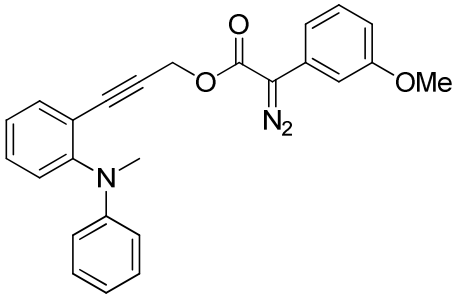
3-(2-(Methyl(phenyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-(*p*-tolyl)acetate (1e). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 1H), 7.41-7.36 (comp, 3H), 7.27-7.16 (comp, 6H), 6.82-6.75 (comp, 3H), 4.95 (s, 2H), 3.36 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 150.9, 149.2, 135.9, 134.2, 130.1, 129.8, 128.8, 127.3, 125.0, 124.2, 122.0, 120.5, 118.4, 115.2, 88.1, 84.5, 53.0, 39.9, 21.1. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{21}N_3NaO_2$ [M+Na]$^+$: 418.1526, found 418.1523.



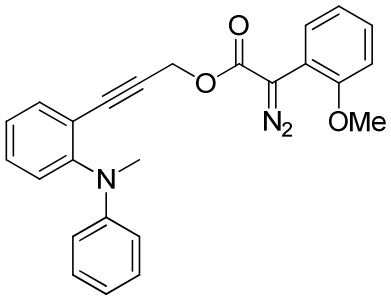
3-(2-(Methyl(phenyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-(4-(trifluoromethyl)phenyl) acetate (1f). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.65-7.59 (comp, 4H), 7.51(m, 1H), 7.38-7.34 (m, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.18-7.14 (comp, 3H), 6.76-6.70 (comp, 3H), 4.94 (s, 2H), 3.32 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 163.6, 150.9, 149.2, 134.3, 130.4, 130.0, 128.9, 127.6, 127.4, 126.0 (q, *J* = 3.7 Hz), 125.1, 123.6, 122.8, 120.4, 118.4, 115.3, 87.7, 84.9, 53.4, 40.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{18}F_3N_3NaO_2$ $[M+Na]^+$: 472.1243,found 472.1255.



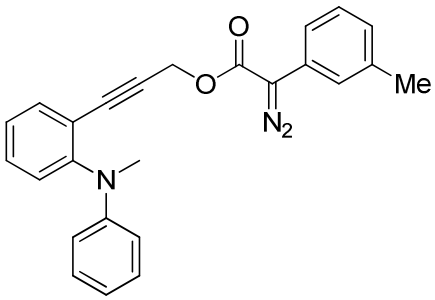
3-(2-(Methyl(phenyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-(4-methoxyphenyl)acetate (1g). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.55 (d, *J* = 7.7 Hz, 1H), 7.42-7.36 (comp, 3H), 7.28-7.16 (comp, 4H), 7.00-6.97 (m, 2H), 6.81-6.75 (comp, 3H), 4.94 (s, 2H), 3.85 (s, 3H), 3.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 158.3, 150.9, 149.2, 134.2, 130.2, 128.9, 127.4, 126.1, 125.0, 120.5, 118.4, 116.7, 115.2, 114.7, 88.1, 84.5, 55.4, 53.1, 39.9. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{21}N_3NaO_3$ $[M+Na]^+$: 434.1475, found 434.1467.



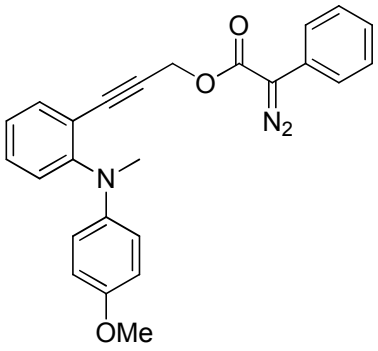
3-(2-(Methyl(phenyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-(3-methoxyphenyl)acetate (1h). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.60 (d, *J* = 7.7 Hz, 1H), 7.45-7.36 (m, 2H), 7.32-7.21 (comp, 5H), 7.07 (dd, *J* = 7.9, 0.8 Hz, 1H), 6.86-6.80 (comp, 4H), 5.00 (s, 2H), 3.90 (s, 3H), 3.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 160.1, 150.8, 149.1, 134.2, 130.1, 129.9, 128.8, 127.3, 126.7, 125.0, 120.4, 118.4, 115.9, 115.2, 111.6, 109.7, 88.0, 84.6, 55.3, 53.0, 39.8. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{21}N_3NaO_3$ $[M+Na]^+$: 434.1475, found 434.1477.



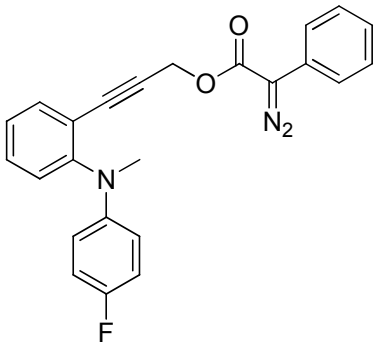
3-(2-(Methyl(phenyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-(2-methoxyphenyl)acetate (1i). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.61-7.55 (m, 2H), 7.40-7.17 (comp, 6H), 7.10-7.05 (m, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.85-6.78 (comp, 3H), 4.94 (s, 2H), 3.89 (s, 3H), 3.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 155.5, 150.8, 149.2, 134.2, 130.2, 130.0, 128.80, 128.77, 127.3, 124.9, 121.2, 120.5, 118.4, 115.2, 113.4, 110.9, 88.3, 84.3, 55.6, 53.0, 39.8. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{21}N_3NaO_3$ $[M+Na]^+$: 434.1475, found 434.1488.



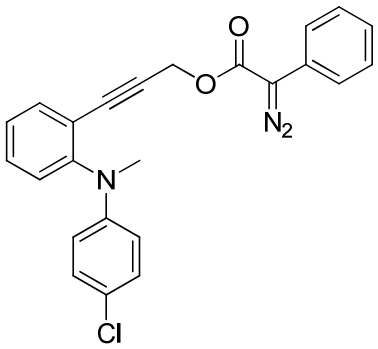
3-(2-(Methyl(phenyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-(*m*-tolyl)acetate (1j). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.54 (m, 1H), 7.41-7.31 (comp, 4H), 7.28-7.17 (comp, 4H), 7.01-7.05 (m, 1H), 6.83-6.75 (comp, 3H), 4.96 (s, 2H), 3.36 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 150.8, 149.2, 138.7, 134.2, 130.1, 128.9, 128.8, 127.3, 126.9, 125.1, 125.0, 124.6, 121.2, 120.4, 118.4, 115.2, 88.1, 84.6, 53.0, 39.9, 21.7. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{21}N_3NaO_2$ $[M+Na]^+$: 418.1526, found 418.1506.



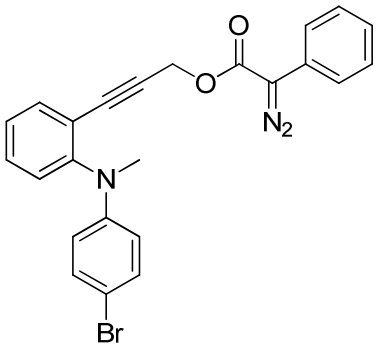
3-(2-((4-Methoxyphenyl)(methyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-phenylacetate (1k). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51-7.46 (comp, 3H), 7.43-7.39 (m, 2H), 7.34-7.29 (m, 1H), 7.23-7.19 (m, 1H), 7.14 (d, J = 8.0 Hz, 1H), 7.11-6.99 (m, 1H), 6.80 (comp, 4H), 4.93 (s, 2H), 3.72 (s, 3H), 3.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 153.6, 151.9, 143.9, 134.4, 130.0, 129.0, 126.0, 125.4, 124.6, 124.0, 123.4, 119.2, 118.4, 114.3, 88.3, 85.1, 55.6, 53.2, 41.0. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{21}N_3NaO_3$ $[M+Na]^+$: 434.1475, found 434.1495.



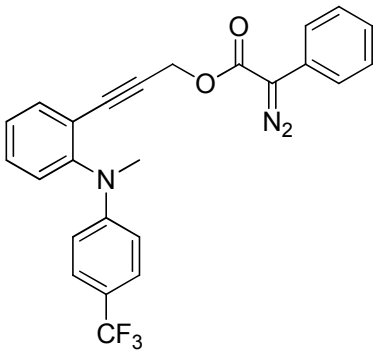
3-(2-((4-Fluorophenyl)(methyl)amino)phenyl)prop-2-yn-1-yl-2-diazo-2-phenylacetate (1l). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.52-7.49(comp, 3H), 7.43-7.40 (m, 2H), 7.38-7.34 (m, 1H), 7.24-7.18 (m, 2H), 7.16-7.11 (m, 1H), 6.91-6.87 (m, 2H), 6.71-6.68 (m, 2H), 4.94 (s, 2H), 3.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 156.6 (d, J = 237.5 Hz), 151.1, 145.9, 134.3, 130.3, 129.0, 126.3, 126.0, 125.3, 124.6, 124.0, 119.8, 117.2 (d, J = 7.5 Hz), 115.3 (d, J = 22.2 Hz), 88.3, 84.6, 53.0, 40.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.02. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{18}FN_3NaO_2$ $[M+Na]^+$: 422.1275, found 422.1281.



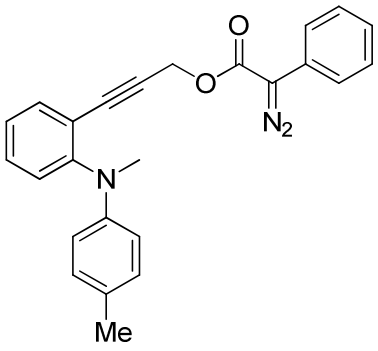
3-(2-((4-Chlorophenyl)(methyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-phenylacetate (1m). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.55-7.49 (comp, 3H), 7.44-7.35 (comp, 3H), 7.24-7.18 (comp, 3H), 7.12-7.10 (m, 2H), 6.61 (m, 2H), 4.95 (s, 2H), 3.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 150.3, 147.8, 134.2, 130.4, 129.0, 128.7, 127.6, 126.0, 125.6, 125.2, 124.0, 122.9, 120.8, 115.8, 88.2, 84.2, 53.0, 39.9. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{18}ClN_3NaO_2$ $[M+Na]^+$: 438.0980, found 438.0991.



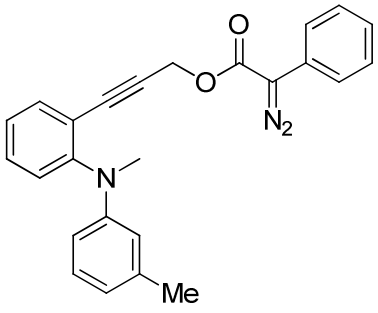
3-(2-((4-Bromophenyl)(methyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-phenylacetate (1n). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.60-7.56 (comp, 3H), 7.45-7.37 (comp, 3H), 7.29-7.20 (comp, 5H), 6.61-6.57 (m, 2H), 4.97 (s, 2H), 3.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 149.9, 147.9, 134.0, 131.3, 130.2, 128.8, 127.5, 125.7, 125.5, 125.0, 123.7, 120.6, 116.0, 109.9, 88.1, 84.0, 52.7, 39.5. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{18}BrN_3NaO_2$ $[M+Na]^+$: 482.0475, found 482.0493.



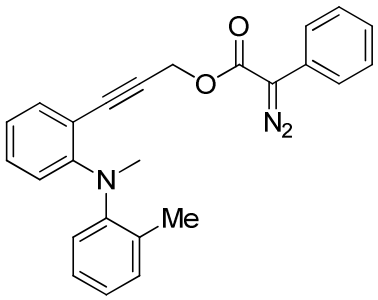
3-(2-(Methyl(4-(trifluoromethyl)phenyl)amino) phenyl)prop-2-yn-1-yl 2-diazo-2-phenylacetate (1o). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.60 (d, J = 7.7 Hz, 1H), 7.52-7.50 (m, 2H), 7.45-7.39 (comp, 5H), 7.31-7.22 (comp, 3H), 6.65 (d, J = 8.6 Hz, 2H), 4.96 (s, 2H), 3.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 151.3, 149.3, 134.3, 130.5, 129.1, 128.6, 126.7, 126.2 (q, J = 3.7 Hz), 126.1, 125.2, 124.0, 121.6, 119.2, 118.8, 112.9, 88.2, 83.8, 52.9, 39.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.91. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{18}F_3N_3NaO_2$ $[M+Na]^+$: 472.1243, found 472.1234.



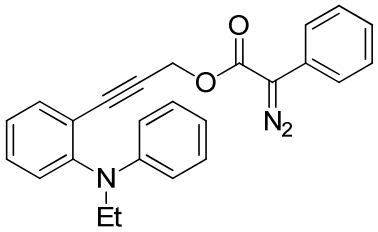
3-(2-(Methyl(*p*-tolyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-phenylacetate (1p). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.70-7.66 (comp, 3H), 7.60-7.53 (m, 2H), 7.52-7.45 (m, 1H), 7.41-7.33 (m, 2H), 7.30-7.26 (m, 1H), 7.19-7.17 (d, J = 8.0 Hz, 2H), 6.89-6.86 (m, 2H), 5.11 (s, 2H), 3.49 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 151.3, 147.1, 134.1, 130.0, 129.3, 128.9, 127.9, 126.5, 125.9, 125.2, 124.3, 123.9, 119.8, 116.0, 87.9, 84.8, 53.0, 40.1, 20.4. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{21}N_3NaO_2$ $[M+Na]^+$: 418.1526, found 418.1524.



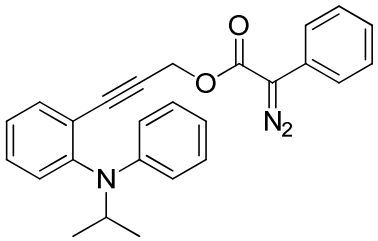
3-(2-(Methyl(m-tolyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-phenylacetate (1q). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.58-7.51 (comp, 3H), 7.47-7.33 (comp, 3H), 7.27-7.16 (comp, 3H), 7.13-7.09 (m, 1H), 6.67-6.56 (comp, 3H), 4.98 (s, 2H), 3.40-3.29 (m, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 151.0, 149.2, 138.5, 134.2, 130.1, 129.0, 128.7, 127.4, 126.0, 125.3, 124.9, 124.0, 120.4, 119.4, 116.0, 112.5, 87.9, 84.7, 53.1, 39.9, 21.8. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{22}N_3O_2$ $[M+H]^+$: 396.1707, found 396.1688.



3-(2-(Methyl(o-tolyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-phenylacetate (1r). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.58 (d, *J* = 7.8 Hz, 2H), 7.49-7.45 (comp, 3H), 7.36-7.31 (m, 1H), 7.30-7.21 (comp, 3H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 4.90 (s, 2H), 3.32 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 152.6, 149.4, 134.8, 134.5, 131.0, 129.8, 129.0, 126.8, 125.9, 125.3, 124.53, 124.49, 123.9, 120.5, 118.7, 114.0, 87.9, 9.18, 53.1, 41.3, 18.5. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{22}N_3O_2$ $[M+H]^+$: 396.1707, found 396.1695.

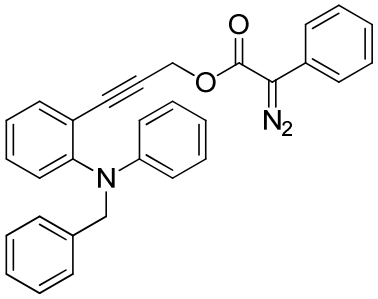


3-(2-(Ethyl(phenyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-phenylacetate (1s). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.64 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.52-7.43 (comp, 3H), 7.32-7.24 (comp, 5H), 6.85-6.79 (m, 3H), 5.02 (s, 2H), 3.91 (q, *J* = 7.0 Hz, 2H), 1.35 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 149.4, 148.2, 134.2, 130.1, 129.0, 128.9, 128.7, 126.0, 125.3, 125.1, 124.0, 121.3, 117.9, 115.2, 87.8, 84.8, 53.0, 46.2, 12.9. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{21}N_3NaO_2$ $[M+Na]^+$: 418.1526 found 418.1539.

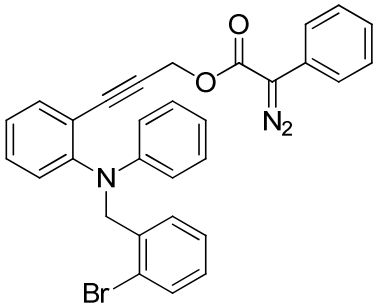


3-(2-(Isopropyl(phenyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-phenylacetate (1t). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.55

(dd, J = 7.7, 1.6 Hz, 1H), 7.48-7.46 (m, 2H), 7.42-7.37 (comp, 3H), 7.28-7.24 (m, 1H), 7.22-7.18 (m, 1H), 7.16 (dd, J = 7.9, 1.0 Hz, 1H), 7.12-7.07 (m, 2H), 6.64 (t, J = 7.3 Hz, 1H), 6.53 (d, J = 7.9 Hz, 2H), 4.88 (s, 2H), 4.37-4.30 (m, 1H), 1.22 (d, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 148.5, 146.2, 134.0, 131.9, 123.0, 129.0, 128.8, 126.4, 126.0, 125.4, 125.0, 124.0, 117.1, 114.8, 86.8, 85.4, 53.0, 49.5, 21.2. HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{23}N_3NaO_2$ $[M+Na]^+$: 432.1682, found 432.1695.



3-(2-(Benzyl(phenyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-phenylacetate (1u). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.62-7.54 (comp, 3H), 7.49-7.43 (comp, 4H), 7.38-7.33 (comp, 4H), 7.27-7.24 (m, 2H), 7.22-7.15 (comp, 3H), 6.83-6.76 (comp, 3H), 5.09-5.08 (m, 2H), 4.91-4.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 150.1, 148.5, 139.2, 134.4, 130.2, 129.0, 128.8, 128.5, 128.3, 126.83, 126.79, 126.0, 125.3, 125.6, 124.0, 120.7, 118.7, 115.9, 88.7, 84.8, 56.5, 53.0. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{23}N_3NaO_2$ $[M+Na]^+$: 480.1682, found 480.1672.

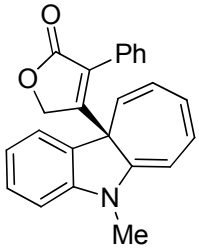


3-(2-((2-Bromobenzyl)(phenyl)amino)phenyl)prop-2-yn-1-yl 2-diazo-2-phenylacetate (1v). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.64 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 7.9 Hz, 2H), 7.48-7.46 (m, 2H), 7.42-7.37

(m, 2H), 7.35-7.32 (m, 2H), 7.25-7.07 (comp, 6H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 2H), 5.01 (s, 2H), 4.80 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 150.0, 148.1, 137.5, 134.5, 132.7, 130.3, 129.1, 128.93, 128.90, 128.4, 127.8, 127.4, 126.0, 125.34, 125.26, 124.1, 122.4, 120.6, 119.1, 116.0, 89.0, 84.7, 57.3, 53.0. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}BrN_3NaO_2$ $[M+Na]^+$: 558.0788, found 558.0796.

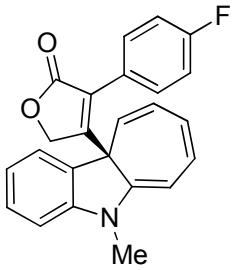
General Procedure for Copper-Catalyzed Cascade Reaction.

To a 10-mL oven-dried vial containing a magnetic stirring bar, $Cu(hfacac)_2$ (2.4 mg, 2.5 mol %), and 4Å MS (100 mg) in DCM (1.0 mL), diazo compound **1** (0.2 mmol) in DCM (1.0 mL) was added *via* a syringe pump over 1 h under argon atmosphere at room temperature. After addition, the reaction mixture was stirred under these conditions until consumption of the material (monitored by TLC, about 2~3 hours). Then the reaction mixture was purified by column chromatography on silica gel without any additional treatment (Hexanes : EtOAc = 15:1 to 10:1) to give the pure products **2** in moderate to high yields.

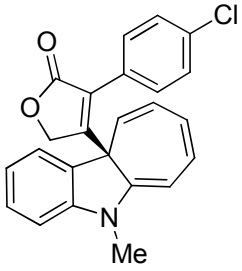


4-(5-Methylcyclohepta[*b*]indol-10a(5*H*)-yl)-3-phenylfuran-2(5*H*)-one (2a). 71.3 mg, 95% yield. Yellow solid; mp: 169-170 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.40 (d, *J* = 7.4 Hz, 1H), 7.33-7.29 (m, 1H), 7.28-7.18 (comp, 3H), 7.00-6.96 (m, 1H), 6.63-6.60 (comp, 3H), 6.56-6.51 (m, 1H), 6.32-6.28 (m, 1H), 6.12-6.08 (m, 1H), 5.23 (d, *J* = 9.4 Hz, 1H), 5.03 (d, *J* = 7.3 Hz, 1H), 4.89 (d, *J* = 17.6 Hz, 1H), 4.49 (d, *J* = 17.6 Hz, 1H), 2.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 161.8, 145.7, 142.0, 134.0, 130.6, 130.4, 129.4, 129.1, 128.9, 128.0, 127.7, 127.4, 123.1, 120.5, 119.9,

110.2, 107.5, 95.2, 72.4, 52.8, 29.2. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{20}NO_2$ $[M+H]^+$: 376.1308 found 376.1299.

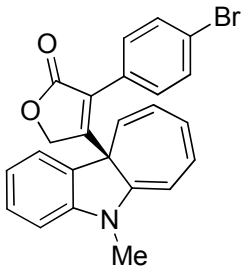


3-(4-Fluorophenyl)-4-(5-methylcyclohepta[*b*]indol-10a(5*H*)-yl) furan-2(5*H*)-one (2b). 61.6 mg, 83% yield. Yellow solid; mp: 66-67 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.40 (d, *J* = 7.4 Hz, 1H), 7.36-7.32 (m, 1H), 7.02- 6.98 (m, 1H), 6.95-6.90 (m, 2H), 6.66-6.57 (comp, 3H), 6.55-6.53 (m, 1H), 6.35-6.31 (m, 1H), 6.14-6.10 (m, 1H), 5.24 (d, *J* = 9.5 Hz, 1H), 5.10 (d, *J* = 7.3 Hz, 1H), 4.91 (d, *J* = 17.7 Hz, 1H), 4.50 (d, *J* = 17.7 Hz, 1H), 2.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 163.8, 162.4, 161.4, 145.6, 142.0, 133.8, 130.8 (d, *J* = 8.2 Hz), 130.3, 129.5, 128.2, 127.8, 126.6 (d, *J* = 3.4 Hz), 123.1, 120.4 (d, *J* = 59.0 Hz), 114.5 (d, *J* = 21.6 Hz), 110.2, 107.5, 95.2, 72.5, 52.8, 29.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.56. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{19}FNO_2$ $[M+H]^+$: 372.1394, found 372.1405.

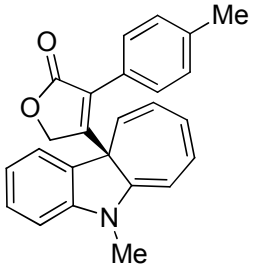


3-(4-Chlorophenyl)-4-(5-methylcyclohepta[*b*]indol-10a(5*H*)-yl)furan-2(5*H*)-one (2c). 66.6 mg, 86% yield. Yellow solid; mp: 145-146 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.40 (d, *J* = 7.4 Hz, 1H), 7.39-7.33 (m, 1H), 7.22-7.20 (m, 2H), 7.02-6.99 (m, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 6.59-6.57 (m, 2H), 6.56-6.52 (m, 1H), 6.33 (dd, *J* = 9.4, 6.4 Hz, 1H), 6.14-6.10 (m, 1H), 5.24 (d, *J* = 9.4 Hz, 1H), 5.09 (d, *J* = 7.3 Hz, 1H), 4.91 (d, *J* = 17.7 Hz, 1H), 4.50 (d, *J* = 17.7 Hz, 1H), 2.78 (s, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 173.6, 162.5, 145.6, 141.9, 134.1, 133.7, 130.4, 130.3, 129.6, 129.2, 128.0, 127.8, 127.6, 123.1, 120.7, 120.1, 110.2, 107.6, 95.3, 72.4, 52.8, 29.4. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{18}ClNNaO_2$ $[M+Na]^+$: 410.0918, found 410.0929.

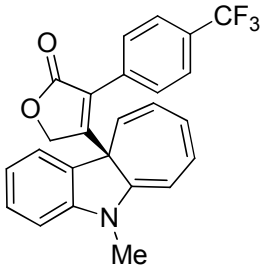


3-(4-Bromophenyl)-4-(5-methylcyclohepta[*b*]indol-10a(5*H*)-yl)furan-2(5*H*)-one (2d). 68.1 mg, 79% yield. Yellow solid; mp: 160-161 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.41-7.32 (comp, 4H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 6.57-6.49 (comp, 3H), 6.35-6.31 (m, 1H), 6.14-6.10 (m, 1H), 5.24 (d, *J* = 9.4 Hz, 1H), 5.09 (d, *J* = 7.3 Hz, 1H), 4.90 (d, *J* = 17.7 Hz, 1H), 4.50 (d, *J* = 17.7 Hz, 1H), 2.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 162.6, 145.6, 141.9, 133.7, 130.63, 130.57, 130.3, 129.61, 129.57, 128.0, 127.8, 123.1, 122.3, 120.7, 120.1, 110.2, 107.6, 95.3, 72.5, 52.8, 29.4. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{18}BrNNaO_2$ $[M+Na]^+$: 454.0413, found 454.0432.

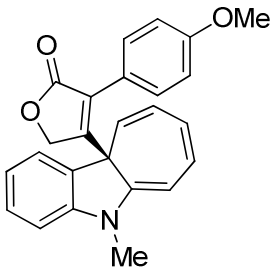


4-(5-Methylcyclohepta[*b*]indol-10a(5*H*)-yl)-3-(*p*-tolyl)furan-2(5*H*)-one (2e). 52.1 mg, 71% yield. Yellow solid; mp: 77-78 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.41 (d, *J* = 7.0 Hz, 1H), 7.35-7.31 (m, 1H), 7.04 (d, *J* = 7.9 Hz, 2H), 7.03-6.98 (m, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.57- 6.52 (comp, 3H), 6.32-6.28 (m, 1H), 6.13-6.09 (m, 1H), 5.25 (d, *J* = 9.4 Hz, 1H), 5.08 (d, *J* = 7.3 Hz, 1H), 4.88 (d, *J* = 17.6 Hz, 1H), 4.49 (d, *J* = 17.6 Hz, 1H), 2.75 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 161.2,

145.7, 142.0, 137.7, 134.0, 130.3, 129.3, 129.0, 128.7, 128.1, 127.7, 127.6, 123.1, 120.5, 119.9, 110.3, 107.4, 95.2, 72.2, 52.8, 29.2, 21.4. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{21}NNaO_2$ $[M+Na]^+$: 390.1465, found 390.1449.

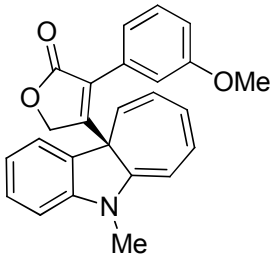


4-(5-Methylcyclohepta[*b*]indol-10a(5*H*)-yl)-3-(4-(trifluoromethyl)phenyl)furan-2(5*H*)-one (2f). 42.1 mg, 50% yield. Yellow solid; mp: 168-170 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.38-7.33 (m, 1H), 7.04-7.00 (m, 1H), 6.75 (d, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.58-6.53 (m, 1H), 6.36-6.32 (m, 1H), 6.16-6.12 (m, 1H), 5.25 (d, *J* = 9.4 Hz, 1H), 5.05 (d, *J* = 7.3 Hz, 1H), 4.95 (d, *J* = 17.8 Hz, 1H), 4.54 (d, *J* = 17.8 Hz, 1H), 2.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 163.4, 145.6, 141.9, 134.50, 134.51, 133.6, 130.3, 129.7, 129.4, 128.0, 127.9, 124.3 (q, *J* = 3.7 Hz), 123.1, 122.8 (q, *J* = 270.5 Hz), 120.8, 120.2, 110.2, 107.6, 95.3, 72.7, 52.8, 29.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.62. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{19}F_3NO_2$ $[M+H]^+$: 422.1362, found 422.1383.

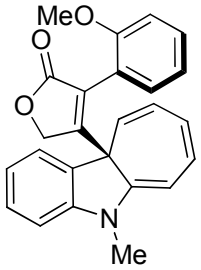


3-(4-Methoxyphenyl)-4-(5-methylcyclohepta[*b*]indol-10a(5*H*)-yl)furan-2(5*H*)-one (2g). 69.7 mg, 91% yield. Yellow solid; mp: 60-61 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm):7.42-7.40 (m, 1H), 7.35-7.31 (m, 1H), 7.01-6.97 (m, 1H), 6.79-6.75 (m, 2H), 6.65 (d, *J* = 7.9 Hz, 1H), 6.60-6.52 (comp, 3H), 6.33-6.29 (m, 1H), 6.13-6.08 (m, 1H), 5.24 (d, *J* = 9.4 Hz, 1H), 5.10 (d, *J* = 7.3 Hz, 1H), 4.88 (d, *J* = 17.6 Hz, 1H), 4.48 (d, *J*

= 17.6 Hz, 1H), 3.81 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 161.2, 159.4, 145.7, 142.0, 133.9, 130.3, 130.1, 129.4, 128.7, 127.6, 123.1, 123.0, 120.5, 119.9, 113.0, 110.3, 107.4, 95.1, 72.2, 55.4, 52.9, 29.4. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{22}NO_3$ $[M+H]^+$: 384.1594, found 384.1601.

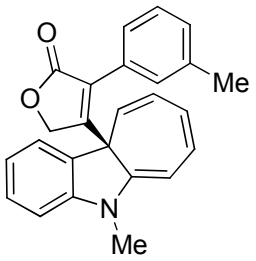


3-(3-Methoxyphenyl)-4-(5-methylcyclohepta[*b*]indol-10a(5*H*)-yl)furan-2(5*H*)-one (2h). 62.0 mg, 81% yield. Yellow solid; mp: 70-71 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42-7.40 (m, 1H), 7.34-7.30 (m, 1H), 7.16-7.12 (m, 1H), 7.01-6.97 (m, 1H), 6.85-6.82 (m, 1H), 6.63 (d, *J* = 7.9 Hz, 1H), 6.58-6.54 (m, 1H), 6.34-6.27 (m, 2H), 6.17-6.10 (m, 2H), 5.24 (d, *J* = 9.4 Hz, 1H), 5.11 (d, *J* = 7.3 Hz, 1H), 4.91 (d, *J* = 17.6 Hz, 1H), 4.51 (d, *J* = 17.6 Hz, 1H), 3.68 (s, 3H), 2.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 161.9, 158.9, 145.6, 142.0, 133.8, 131.8, 130.4, 129.3, 129.0, 128.4, 127.7, 123.1, 121.4, 120.5, 119.9, 114.2, 113.9, 110.2, 107.5, 95.3, 72.4, 55.2, 52.8, 29.2. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{22}NO_3$ $[M+H]^+$: 384.1594, found 384.1585.

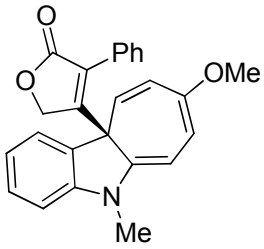


3-(2-Methoxyphenyl)-4-(5-methylcyclohepta[*b*]indol-10a(5*H*)-yl)furan-2(5*H*)-one (2i). 39.8 mg, 52% yield (dr 1.5:1). Yellow solid; mp: 88-89 °C. ^{1}H NMR for the major diastereomer (400 MHz, $CDCl_3$) δ (ppm): 7.42 (dd, *J* = 7.4, 0.7 Hz, 1H), 7.35-7.30 (m, 1H), 7.28-7.24 (m, 1H), 7.00-6.96 (m, 1H), 6.90-6.84 (m, 1H), 6.70-6.61 (m, 2H),

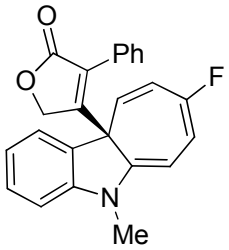
6.57-6.53(m, 1H), 6.30-6.26 (m, 1H), 6.11-6.06 (m, 1H), 6.00 (dd, *J* = 7.4, 1.7 Hz, 1H), 5.24 (d, *J* = 9.5 Hz, 1H), 5.05 (d, *J* = 7.3 Hz, 1H), 4.86 (d, *J* = 17.4 Hz, 1H), 4.53-4.48 (m, 1H), 3.79 (s, 3H), 2.66 (s, 3H). selected ^{1}H NMR for the minor diastereomer (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 1H), 7.19 (m, 2H), 7.00-6.95 (m, 1H), 6.95-6.91 (m, 1H), 6.90-6.83 (m, 1H), 6.70-6.61(m, 1H), 6.57-6.55 (m, 1H), 6.40 (d, *J* = 7.9 Hz, 1H), 6.35-6.34 (m, 1H), 6.17-6.13 (m 1H), 5.31 (d, *J* = 7.4 Hz, 1H), 5.25-5.22 (m, 1H), 4.95 (d, *J* = 17.7 Hz, 1H), 4.53-4.48 (m, 1H), 3.16 (s, 3H), 2.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 173.4, 163.3, 162.3, 157.2, 156.9, 145.7, 145.5, 143.4, 142.0, 134.3, 133.5, 131.0, 130.9, 130.2, 130.1, 129.7, 129.3, 128.5, 127.7, 126.9, 126.8, 123.2, 123.1, 120.3, 120.1, 120.0, 119.7, 119.6, 119.3, 119.1, 118.7, 110.4, 110.3, 110.1, 109.4, 107.4, 106.5, 95.5, 94.9, 73.5, 72.4, 55.4, 54.7, 52.8, 52.7, 29.22, 29.15. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{22}NO_3$ $[M+H]^+$: 384.1594, found 384.1584.



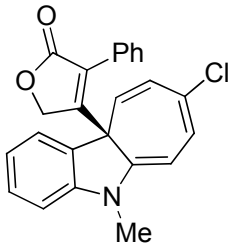
4-(5-Methylcyclohepta[b]indol-10a(5*H*)-yl)-3-(*m*-tolyl)furan-2(5*H*)-one (2j). 58.7 mg, 80% yield. Yellow solid; mp: 134-135 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.4 Hz, 1H), 7.36-7.32(m, 1H), 7.15-7.08 (m, 2H), 7.02-6.98 (m, 1H), 6.63 (d, *J* = 7.9 Hz, 1H), 6.58-6.51 (m, 2H), 6.35-6.31 (m, 2H), 6.14-6.10 (m, 1H), 5.25 (d, *J* = 9.4 Hz, 1H), 5.06 (d, *J* = 7.3 Hz, 1H), 4.92 (d, *J* = 17.6 Hz, 1H), 4.50 (d, *J* = 17.6 Hz, 1H), 2.71 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 161.7, 145.7, 142.1, 136.9, 134.1, 130.43, 130.38, 129.4, 129.3, 129.2, 128.7, 127.7, 127.3, 125.9, 123.0, 120.4, 119.8, 110.1, 107.3, 95.1, 72.5, 52.7, 29.1, 21.5. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{21}NNaO_2$ $[M+Na]^+$: 390.1465, found 390.1458.



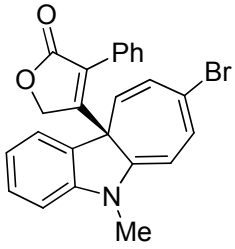
4-(8-Methoxy-5-methylcyclohepta[*b*]indol-10a(5*H*)-yl)-3-phenylfuran-2(5*H*)-one (2k). 68.9 mg, 90% yield. Yellow solid; mp: 158-159 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.38-7.36 (m, 1H), 7.33-7.24 (comp, 4H), 6.96-6.92 (m, 1H), 6.75-6.72 (m, 2H), 6.58 (d, *J* = 7.9 Hz, 1H), 6.17 (dd, *J* = 10.1, 1.6 Hz, 1H), 5.89 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.43 (d, *J* = 10.1 Hz, 1H), 4.95 (d, *J* = 7.9 Hz, 1H), 4.89 (d, *J* = 17.6 Hz, 1H), 4.58 (d, *J* = 17.6 Hz, 1H), 3.65 (s, 3H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 162.2, 152.2, 146.2, 138.6, 133.0, 130.6, 129.4, 129.00, 128.96, 128.0, 127.4, 124.6, 123.2, 119.7, 114.9, 106.8, 104.8, 92.2, 71.6, 55.3, 52.0, 29.2. HRMS (TOF MS ESI^{+}) calculated for $C_{25}H_{22}NO_3$ $[M+H]^{+}$: 384.1594, found 384.1576.



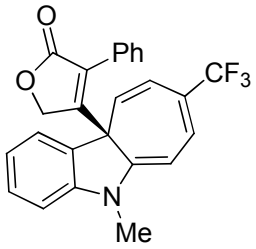
4-(8-Fluoro-5-methylcyclohepta[*b*]indol-10a(5*H*)-yl)-3-phenylfuran-2(5*H*)-one (2l). 63.1 mg, 85% yield. Yellow solid; mp: 79-80 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.38 (d, *J* = 7.4 Hz, 1H), 7.32-7.28 (m, 1H), 7.25-7.19 (comp, 3H), 6.98-6.94 (m, 1H), 6.67-6.65 (m, 2H), 6.60 (d, *J* = 7.9 Hz, 1H), 6.34-6.28 (m, 1H), 6.24-6.19 (m, 1H), 5.28-5.25 (m, 1H), 4.90-4.87 (m, 1H), 4.83 (d, *J* = 17.6 Hz, 1H), 4.49 (d, *J* = 17.6 Hz, 1H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 160.9, 154.6 (d, *J* = 233.2 Hz), 145.7, 139.2 (d, *J* = 2.5 Hz), 133.0, 130.5, 129.7, 129.5, 128.9, 128.2, 127.6, 123.2, 121.2 (d, *J* = 34.3 Hz), 120.5, 112.2 (d, *J* = 12.8 Hz), 111.7 (d, *J* = 28.1 Hz), 107.5, 90.8 (d, *J* = 10.8 Hz), 71.3, 52.7, 29.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.29. HRMS (TOF MS ESI^{+}) calculated for $C_{24}H_{18}FNNaO_2$ $[M+Na]^{+}$: 394.1214, found 394.1219.



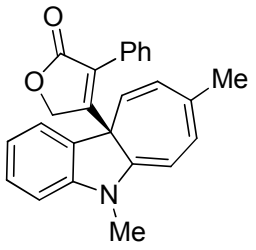
4-(8-Chloro-5-methylcyclohepta[*b*]indol-10a(5*H*)-yl)-3-phenylfuran-2(5*H*)-one (2m). 61.1 mg, 79% yield. Yellow solid; mp: 177-178 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42 (d, *J* = 7.4 Hz, 1H), 7.36-7.32 (m, 1H), 7.30-7.21(comp, 3H), 7.04-7.00(m, 1H), 6.73-6.70 (m, 1H), 6.67-6.63(comp, 3H), 6.27 (d, *J* = 9.8 Hz, 1H), 5.23 (d, *J* = 9.8 Hz, 1H), 4.99 (d, *J* = 8.0 Hz, 1H), 4.88 (d, *J* = 17.7 Hz, 1H), 4.53 (d, *J* = 17.7 Hz, 1H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 161.0, 145.5, 142.3, 133.4, 130.3, 129.7, 129.6, 129.0, 128.9, 128.8, 128.2, 127.5, 123.18, 123.16, 121.0, 111.5, 107.7, 93.4, 71.5, 52.7, 29.4. HRMS (TOF MS ESI^{+}) calculated for $C_{24}H_{19}ClNO_2$ $[M+H]^{+}$: 388.1099, found 388.1087.



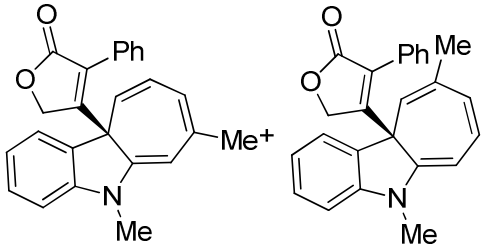
4-(8-Bromo-5-methylcyclohepta[*b*]indol-10a(5*H*)-yl)-3-phenylfuran-2(5*H*)-one (2n). 71.5 mg, 83% yield. Yellow solid; mp: 162-163 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.40-7.38 (m ,1H), 7.34-7.30 (m, 1H), 7.25-7.18 (comp, 3H), 7.03-6.99 (m, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.64-6.61 (comp, 3H), 6.37 (d, *J* = 9.7 Hz, 1H), 5.13 (d, *J* = 9.7 Hz, 1H), 4.93 (d, *J* = 7.9 Hz, 1H), 4.86 (d, *J* = 17.7 Hz, 1H), 4.51 (d, *J* = 17.7 Hz, 1H), 2.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 161.0, 145.5, 142.9, 133.5, 132.5, 130.7, 130.3, 129.71, 129.66, 128.9, 128.2, 127.5, 123.2, 121.1, 111.7, 111.5, 107.8, 94.4, 71.6, 52.8. HRMS (TOF MS ESI^{+}) calculated for $C_{24}H_{18}BrNNaO_2$ $[M+Na]^{+}$: 454.0413, found 454.0411.



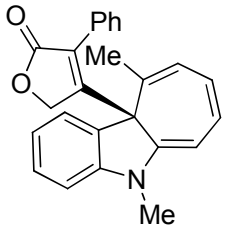
4-(5-Methyl-8-(trifluoromethyl)cyclohepta[*b*]indol-10a(5*H*)-yl)-3-phenylfuran-2(5*H*)-one (2o). 53.4 mg, 61% yield. Yellow solid; mp: 148-149 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.48-7.46 (m, 1H), 7.42-7.38 (m, 1H), 7.29-7.27 (m, 1H), 7.23-7.19 (m, 2H), 7.12-7.08 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.57-6.55 (m, 3H), 5.37 (d, *J* = 9.7 Hz, 1H), 5.08 (d, *J* = 8.0 Hz, 1H), 4.92 (d, *J* = 17.8 Hz, 1H), 4.52 (d, *J* = 17.8 Hz, 1H), 2.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 160.5, 145.4, 145.0, 134.1, 130.1, 123.0 (q, *J* = 5.3 Hz), 129.8, 128.8, 128.3, 127.6, 125.0 (q, *J* = 272.2 Hz), 123.8 (q, *J* = 2.3 Hz), 123.1, 121.9, 119.4 (q, *J* = 29.5 Hz), 110.6, 108.4, 93.4, 71.7, 53.1, 29.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.25. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{18}F_3NNaO_2$ $[M+Na]^+$: 444.1182, found 444.1168.



4-(5,8-Dimethylcyclohepta[*b*]indol-10a(5*H*)-yl)-3-phenylfuran-2(5*H*)-one (2p). 63.9 mg, 87% yield. Yellow solid; mp: 159-160 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):7.36 (d, *J* = 7.4 Hz, 1H), 7.31-7.19 (comp, 4H), 6.96-6.92 (m, 1H), 6.68-6.66 (m, 2H), 6.56 (d, *J* = 7.9 Hz, 1H), 6.32 (d, *J* = 7.3 Hz, 1H), 6.08 (d, *J* = 9.7 Hz, 1H), 5.23 (d, *J* = 9.6 Hz, 1H), 4.97 (d, *J* = 7.3 Hz, 1H), 4.85 (d, *J* = 17.6 Hz, 1H), 4.42 (d, *J* = 17.6 Hz, 1H), 2.69 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 162.3, 146.0, 140.8, 133.7, 130.5, 130.4, 129.3, 129.0, 128.9, 128.6, 128.0, 127.5, 127.4, 123.1, 120.1, 111.0, 107.1, 94.6, 71.8, 52.3, 29.2, 24.2. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{21}NNaO_2$ $[M+Na]^+$: 390.1465, found 390.1483.

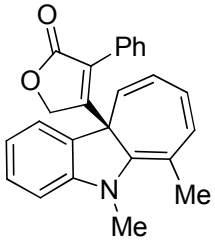


2q and 2q' (5:1), 59.5 mg, 81% yield. Yellow solid; mp: 167-168 °C. (These two isomers cannot be separated from each other by column chromatography on silica gel). ^{1}H NMR for the major isomer **2q** (400 MHz, $CDCl_3$) δ (ppm): 7.42-7.22 (comp, 5H), 7.02-6.98 (m, 1H), 6.68-6.64 (comp, 3H), 6.24 (dd, *J* = 9.4, 6.4 Hz, 1H), 5.97 (d, *J* = 6.4 Hz, 1H), 5.21 (d, *J* = 9.4 Hz, 1H), 4.96 (d, *J* = 17.6 Hz, 1H), 4.87 (s, 1H), 4.60 (d, *J* = 17.6 Hz, 1H), 2.72 (s, 3H), 2.06 (s, 3H). ^{1}HNMR for the minor isomer **2q'** (400 MHz, $CDCl_3$) δ (ppm): 7.42-7.22 (comp, 5H), 6.96-6.91 (m, 1H), 6.80-6.75 (comp, 3H), 6.45 (dd, *J* = 11.2, 7.1 Hz, 1H), 6.02 (d, *J* = 11.2 Hz, 1H), 5.10 (s, 1H), 5.04 (t, *J* = 7.1 Hz, 1H), 4.93 (d, *J* = 17.4 Hz, 1H), 4.46 (d, *J* = 17.4 Hz, 1H), 2.79 (s, 3H), 1.84 (d, *J* = 1.0 Hz, 3H). Combined ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 174.0, 162.28, 162.26, 145.8, 145.7, 143.8, 141.1, 140.0, 135.9, 134.0, 133.8, 130.8, 130.7, 129.4, 129.32, 129.27, 129.0, 128.9, 128.8, 128.6, 128.0, 127.9, 127.7, 127.5, 127.3, 123.4, 123.2, 123.0, 120.4, 120.3, 118.3, 109.7, 109.6, 107.3, 98.0, 94.1, 72.3, 72.2, 52.4, 52.2, 29.1, 29.0, 25.8, 22.2. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{21}NNaO_2$ $[M+Na]^+$: 390.1465, found 390.1456.

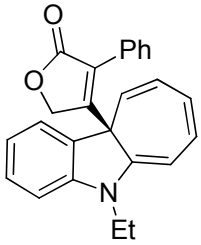


4-(5,10-Dimethylcyclohepta[*b*]indol-10a(5*H*)-yl)-3-phenylfuran-2(5*H*)-one (2r). 25.0 mg, 34% yield. Yellow solid; mp: 162-163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.4 Hz, 1H), 7.33-7.29 (m, 1H), 7.26-7.19 (comp, 3H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.65-6.60 (comp, 3H), 6.43-6.39 (m,1H), 6.18-6.17 (m, 1H), 6.01-5.97 (m, 1H), 4.91-4.83 (m, 2H), 4.52 (d, *J* = 17.4 Hz, 1H), 2.75 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100

MHz, $CDCl_3$) δ 174.0, 161.7, 146.8, 141.5, 131.9, 131.1, 129.6, 128.8, 128.18, 128.16, 127.9, 127.5, 126.0, 125.2, 120.3, 119.7, 117.2, 107.1, 94.2, 72.4, 56.3, 29.3, 23.7. HRMS (TOF MS ESI^+) calculated for $C_{25}H_{21}NNaO_2$ $[M+Na]^+$: 390.1465, found 390.1477.

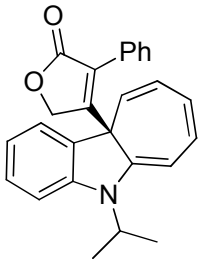


4-(5,6-Dimethylcyclohepta[*b*]indol-10a(5*H*)-yl)-3-phenylfuran-2(5*H*)-one (2r'). 16.9 mg, 23% yield. Yellow solid; mp:159-160 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.37 (m, 2H), 7.26-7.21 (comp, 3H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.64-6.63 (m, 2H), 6.34 (d, *J* = 11.0 Hz, 1H), 6.31-6.27 (m, 1H), 6.12-6.08 (m, 1H), 5.16 (d, *J* = 9.0 Hz, 1H), 4.87 (d, *J* = 11.8 Hz, 1H), 4.38 (d, *J* = 17.6 Hz, 1H), 3.06 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 162.4, 148.1, 137.1, 136.4, 134.7, 130.9, 129.5, 129.0, 128.9, 127.8, 127.6, 126.0, 122.9, 121.3, 120.1, 110.1, 109.2, 105.2, 72.2, 53.8, 35.9, 19.6. HRMS (TOF MS ESI^+) calculated for $C_{25}H_{21}NNaO_2$ $[M+Na]^+$: 390.1465, found 390.1482.

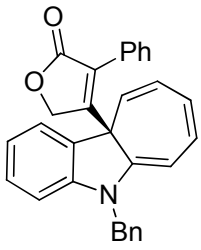


4-(5-Ethylcyclohepta[*b*]indol-10a(5*H*)-yl)-3-phenylfuran-2(5*H*)-one (2s). 60.9 mg, 83% yield. Yellow solid; mp: 142-143 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45-7.43 (m, 1H), 7.36-7.32 (m, 1H), 7.30-7.21 (comp, 3H), 7.04-7.00 (m, 1H), 6.69-6.64 (comp, 3H), 6.60-6.56 (m, 1H), 6.31-6.27 (m, 1H), 6.15-6.11 (m, 1H), 5.24-5.20 (m, 2H), 4.90 (d, *J* = 17.6 Hz, 1H), 4.48 (d, *J* = 17.6 Hz, 1H), 3.38-3.29 (m, 1H), 3.26-3.17 (m, 1H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1,

161.7, 145.2, 141.0, 134.3, 130.8, 130.2, 129.3, 129.0, 128.0, 127.6, 127.5, 123.3, 120.5, 120.0, 110.1, 107.6, 94.9, 72.4, 53.1, 38.2, 11.3. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{21}NNaO_2$ $[M+Na]^+$: 390.1465, found 390.1482.

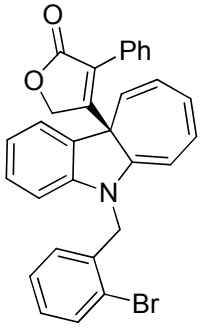


4-(5-Isopropylcyclohepta[*b*]indol-10a(5*H*)-yl)-3-phenylfuran-2(5*H*)-one (2t). 34.3 mg, 45% yield. Yellow solid; mp: 187-188 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.44-7.42 (m, 1H), 7.32-7.28 (m, 1H), 7.25-7.19 (comp, 3H), 7.03-6.99 (m, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.64-6.61 (m, 2H), 6.59-6.55 (m, 1H), 6.30-6.26(m, 1H), 6.15-6.12 (m, 1H), 5.35 (d, J = 7.4 Hz, 1H), 5.13 (d, J = 9.2 Hz, 1H), 4.86 (d, J = 17.6 Hz, 1H), 4.40 (d, J = 17.6 Hz, 1H), 3.95-3.87 (m, 1H), 1.15-1.12 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 161.8, 144.8, 140.3, 135.2, 131.0, 130.2, 129.2, 129.1, 129.0, 128.0, 127.9, 127.2, 123.4, 120.6, 119.9, 110.3, 109.2, 96.1, 72.7, 53.6, 48.0, 19.0, 18.7. HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{23}NNaO_2$ $[M+Na]^+$: 404.1621, found 404.1622.

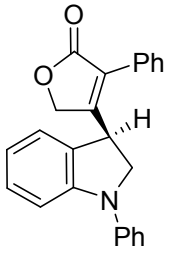


4-(5-Benzylcyclohepta[*b*]indol-10a(5*H*)-yl)-3-phenylfuran-2(5*H*)-one (2u). 40.7 mg, 50% yield. Yellow solid; mp: 102-103 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50 (d, J = 7.3 Hz, 1H), 7.40-7.26 (comp, 7H), 7.10-7.02 (comp, 3H), 6.83 (d, J = 6.9 Hz, 2H), 6.67 (d, J = 7.9 Hz, 1H), 6.55-6.50 (m, 1H), 6.26-6.22 (m, 1H), 6.18-6.14 (m, 1H), 5.33-5.28 (m, 2H), 4.87 (d, J = 17.5 Hz, 1H), 4.51 (d, J = 4.3 Hz, 1H), 4.47 (d, J = 3.8

Hz, 1H), 4.38 (d, J = 17.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 161.3, 145.7, 141.5, 135.8, 133.9, 130.9, 129.8, 129.5, 129.2, 129.0, 128.9, 128.2, 127.7, 127.6, 127.5, 126.5, 123.5, 121.1, 121.0, 111.4, 108.2, 96.1, 72.1, 53.3, 47.4. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{24}NO_2$ $[M+H]^+$: 430.1802, found 430.1789.

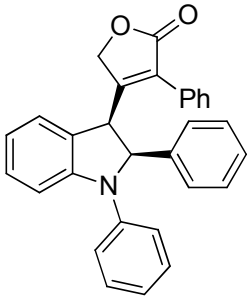


4-(5-(2-Bromobenzyl)cyclohepta[b]indol-10a(5*H*)-yl)-3-phenylfuran-2(5*H*)-one (2v). 67.9 mg, 67% yield. Yellow solid; mp: 100-101 ^{o}C. ^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm): 7.56-7.53 (m, 1H), 7.50-7.47 (m, 1H), 7.40-7.36 (m, 1H), 7.34-7.27 (comp, 3H), 7.10-7.04 (comp, 3H), 6.78-6.76 (m, 2H), 6.58-6.54 (m, 2H), 6.52-6.47 (m, 1H), 6.29-6.25 (m, 1H), 6.17-6.13 (m, 1H), 5.32 (d, J = 9.4 Hz, 1H), 5.17 (d, J = 7.2 Hz, 1H), 4.89 (d, J = 17.5 Hz, 1H), 4.52-4.45 (m, 2H), 4.27 (d, J = 18.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 161.4, 145.5, 141.4, 134.3, 134.0, 133.0, 130.8, 129.9, 129.6, 129.22, 129.15, 129.0, 128.3, 127.9, 127.82, 127.77, 127.1, 123.5, 122.5, 121.3, 121.2, 111.7, 108.1, 96.3, 72.3, 53.1, 49.0. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}BrNNaO_2$ $[M+Na]^+$: 530.0726, found 530.0709.

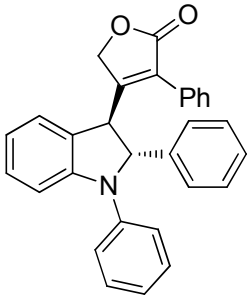


3-Phenyl-4-(1-phenylindolin-3-yl)furan-2(5H)-one (3a). Yellow solid; mp: 72-73 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.44 (comp, 5H), 7.40-7.36 (m, 2H), 7.24-7.21 (m, 2H), 7.17-7.13 (m, 2H), 7.10-7.04 (m, 2H), 6.83-6.79 (m, 1H), 4.91-4.84 (m, 2H), 4.71 (d, J = 17.8 Hz, 1H), 4.27 (t, J = 9.4 Hz, 1H), 3.92-3.88 (m, 1H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 173.0, 161.0, 147.2, 143.2, 123.0, 129.58, 129.55, 129.14, 129.07, 129.0, 128.2, 125.1, 122.5, 120.0, 118.5, 113.6, 109.2, 69.2, 57.8, 39.4. HRMS (TOF MS ESI^+) calculated for $C_{24}H_{20}NO_2$ $[M+H]^+$: 354.1489 found 354.1478.

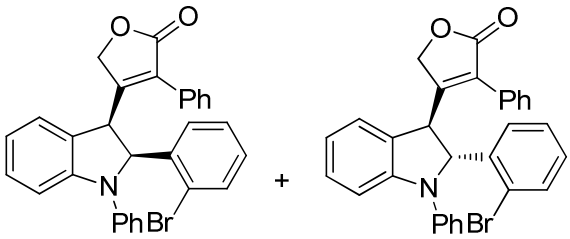


4-((2*S,3*R**)-1,2-Diphenylindolin-3-yl)-3-phenylfuran-2(5*H*)-one (3u).**[2] 24.3 mg, 28% yield. Yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50-7.41 (comp, 5H), 7.29-7.27 (comp, 3H), 7.26-7.22 (comp, 4H), 7.18-7.13 (comp, 4H), 7.01- 6.97 (m, 2H), 6.88-6.84 (m, 1H), 5.46 (d, *J* = 9.4 Hz, 1H), 5.36 (d, *J* = 9.4 Hz, 1H), 4.43 (d, *J* = 18.0 Hz, 1H), 3.37 (d, *J* = 18.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 159.3, 148.2, 142.9, 137.9, 131.4, 129.7, 129.43, 129.37, 129.14, 129.05, 128.97, 128.95, 128.7, 128.6, 126.7, 125.5, 122.6, 120.5, 118.9, 109.9, 72.2, 70.2, 47.1. HRMS (TOF MS ESI^+) calculated for $C_{30}H_{24}NO_2$ $[M+H]^+$: 430.1802, found 430.1799.



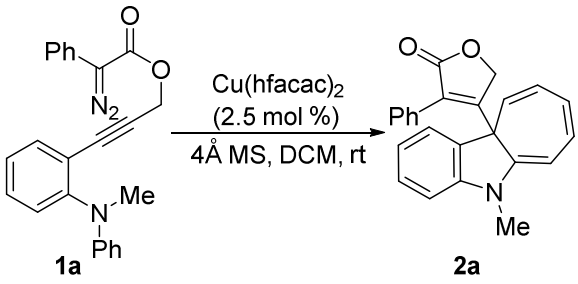
4-((2*R,3*R**)-1,2-Diphenylindolin-3-yl)-3-phenylfuran-2(5*H*)-one (3u').**[2] 14.3 mg, 17 % yield. Yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 14.3 mg, 17 % yield. Yellow oil. 7.34-7.27 (comp, 7H), 7.24-7.22 (comp, 3H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.14-7.07 (comp, 5H), 7.03-6.97 (m, 2H), 6.84-6.81 (m, 1H), 5.10 (d, *J* = 6.7 Hz, 1H), 4.95 (d, *J* = 17.7 Hz, 1H), 4.78 (d, *J* = 17.7 Hz, 1H), 4.63 (d, *J* = 6.7 Hz, 1H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 173.1, 159.8, 148.0, 142.7, 140.4, 129.5, 129.4, 129.3, 129.22, 129.18, 129.02, 128.96, 128.6, 128.4, 128.3, 126.6, 125.1, 123.4, 120.43, 120.36, 109.6, 74.1, 69.5, 50.7. HRMS (TOF MS ESI^+) calculated for $C_{30}H_{24}NO_2$ $[M+H]^+$: 430.1802, found 430.1794.



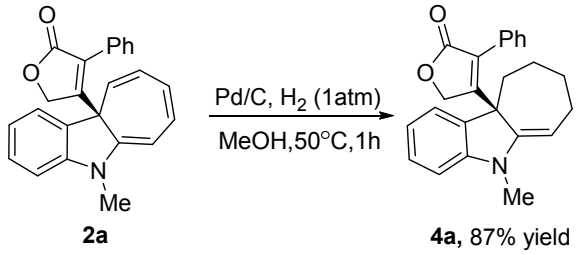
4-(2-(2-Bromophenyl)-1-phenylindolin-3-yl)-3-phenylfuran-2(5*H*)-one (3v and 3v', 1.7:1).[2] 28.4 mg, 28 % yield. Yellow oil. (These two isomers cannot be separated from each other by column chromatography on silica gel). ^1H NMR for the major diastereomer of **3v** (400 MHz, $CDCl_3$) ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.49-6.93 (comp, 18H), 5.93 (d, *J* = 8.9 Hz, 1H), 5.52 (d, *J* = 8.9 Hz, 1H), 4.40 (d, *J* = 17.9 Hz, 1H), 4.02 (d, *J* = 17.9 Hz, 1H). ^1H NMR for the minor diastereomer of **3v'** (400 MHz, $CDCl_3$) ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.49-6.93 (comp, 18H), 5.57 (d, *J* = 4.9 Hz, 1H), 5.06 (d, *J* = 17.5 Hz, 1H), 4.78 (d, *J* = 17.5 Hz, 1H), 4.62-4.60 (m, 1H). Combined ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 172.8, 159.5, 158.7, 148.8, 146.9, 142.3, 142.0, 139.0, 136.2, 133.6, 133.4, 131.1, 129.9, 129.7, 129.54, 129.45, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.1, 128.0, 125.33, 125.25, 123.5, 123.3, 122.8, 122.5, 120.9, 120.7, 120.2, 118.7, 109.8, 109.7, 71.6, 70.9, 70.3, 69.5, 49.3, 44.5. HRMS (TOF MS ESI^+) calculated for $C_{30}H_{22}BrNNaO_2$ $[M+Na]^+$: 530.0726, found 530.0718.

General Procedure for the Scale Up.



To a 10-mL oven-dried vial containing a magnetic stirring bar, $Cu(hfacac)_2$(40 mg, 2.5 mol %), and 4Å MS (1.5 g) in DCM (20.0 ml), diazo compound **1a** (1.305 g, 3.4 mmol) was added as a solution in DCM (10.0 ml) *via* a syringe pump over 1 h under argon atmosphere at room temperature. After addition, the reaction mixture was stirred at room temperature for additional 12 h. Then the solvent was evaporated in vacuo, the residue was purified by column chromatography on silica gel (Hexanes: EtOAc = 15:1 to 10:1) to give 1.07 g of pure product **2a** in yield 89%.

General Procedure for the Synthesis of 4a[3]



To a 10-mL oven-dried vial containing a magnetic stirring bar, **2a** (53 mg, 0.15 mmol), 10 % Pd/C (10 mg), and CH_3OH (2.0 mL) were added in sequence, and the reaction was stirred at 50℃ for 2 h under H_2 atmosphere (with hydrogen balloon, ~1 atm). Then the solution was filtered through a short Celite pad and the filtrate was concentrated under reduced pressure. The crude residue was purified by column

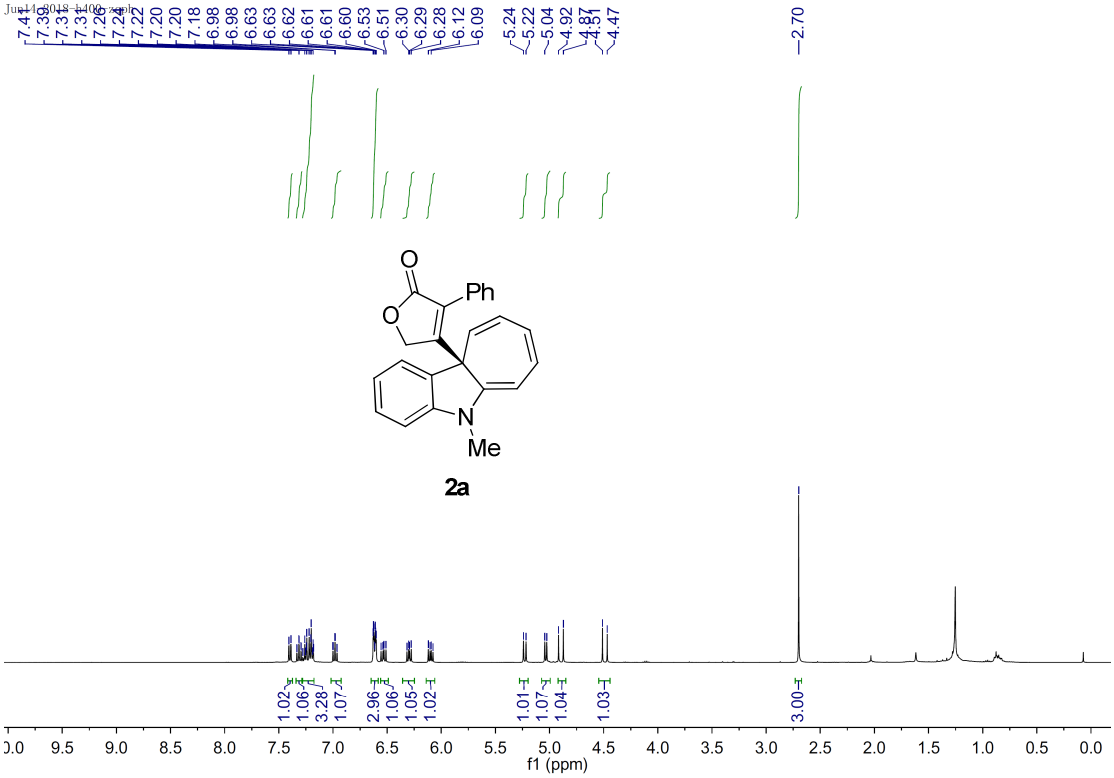
chromatography on silica gel (hexanes : EtOAc = 10:1) to yield 46.6 mg pure product **4a** in 87% yield as yellow solid. mp: 88-89 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 3H), 7.18-7.14 (m, 1H), 7.08 (d, *J* = 6.7 Hz, 2H), 7.01-6.99 (m, 1H), 6.71-6.67 (m, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.14 (d, *J* = 17.1 Hz, 1H), 5.02 (d, *J* = 17.1 Hz, 1H), 4.23-4.20 (m, 1H), 2.60 (s, 3H), 2.29-2.25 (m, 1H), 2.02-1.95 (m, 3H), 1.82-1.74 (m, 3H), 1.38-1.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 160.2, 150.2, 147.0, 131.9, 131.2, 129.4, 129.1, 128.2, 128.0, 127.5, 122.6, 118.0, 105.3, 97.9, 70.5, 54.3, 35.6, 29.7, 29.1, 28.0, 26.2. HRMS (TOF MS ESI^{+}) calculated for $C_{24}H_{24}NO_2$ $[M+H]^{+}$: 358.1802, found 358.1800.

References:

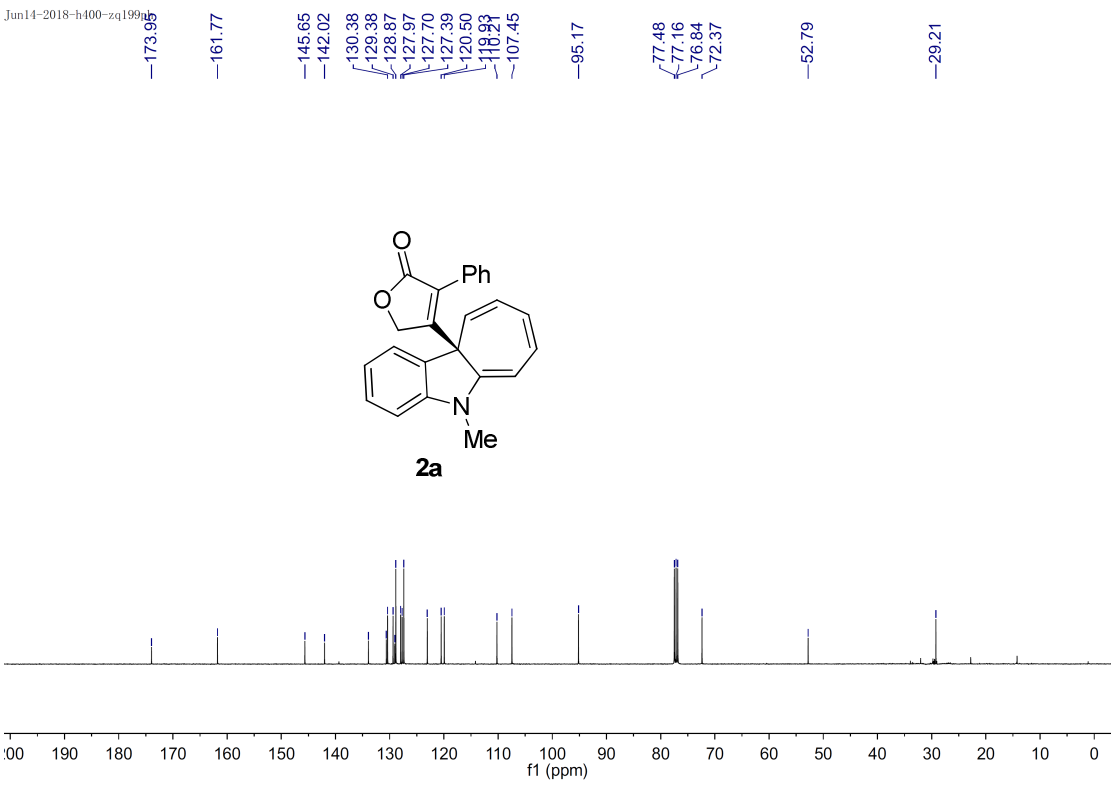
(1) Y. Chen, J. Chen, N. Zhang, L. Ye, X. Zhang and M. Yan, *Tetrahedron Lett.*, 2015, **56**, 478.

(2) K.-Y. Dong, C. Pei, Q. Zeng, H.-L. Wei, M. P. Doyle and X.-F. Xu, *ACS Catal*., 2018, **8**, 9543.

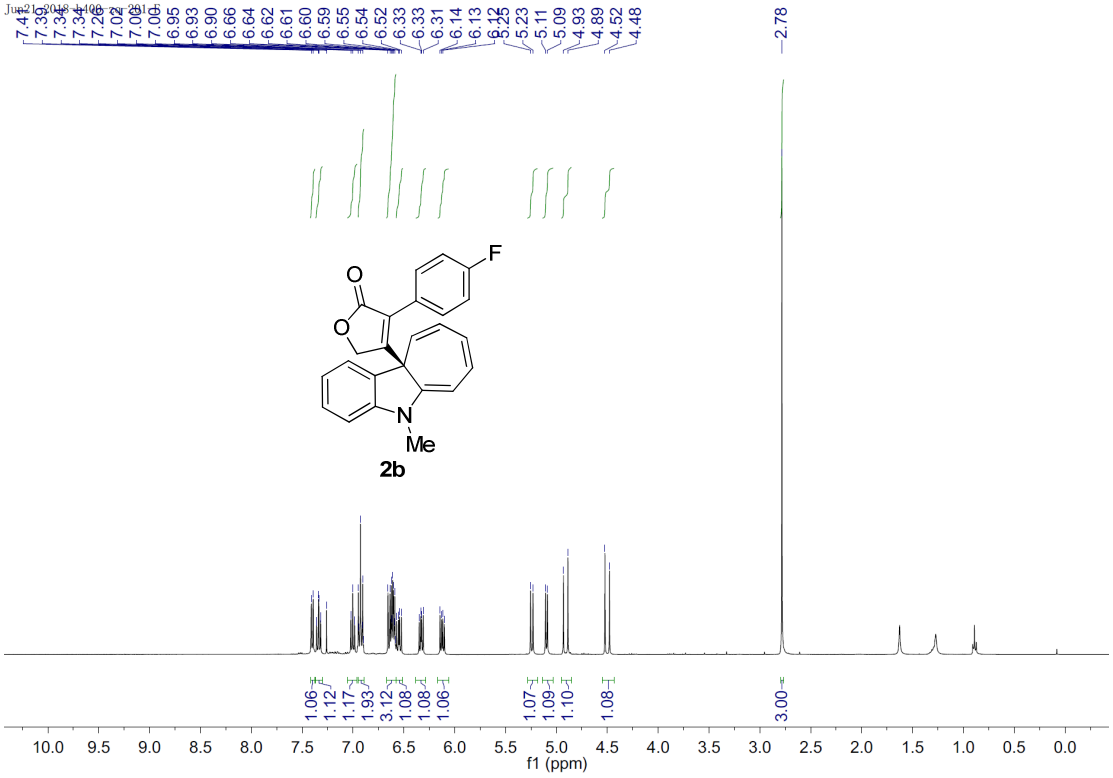
(3) P. D. Jadhav, X. Lu and R.-S. Liu, *ACS Catal.,* 2018, **8**, 9697.

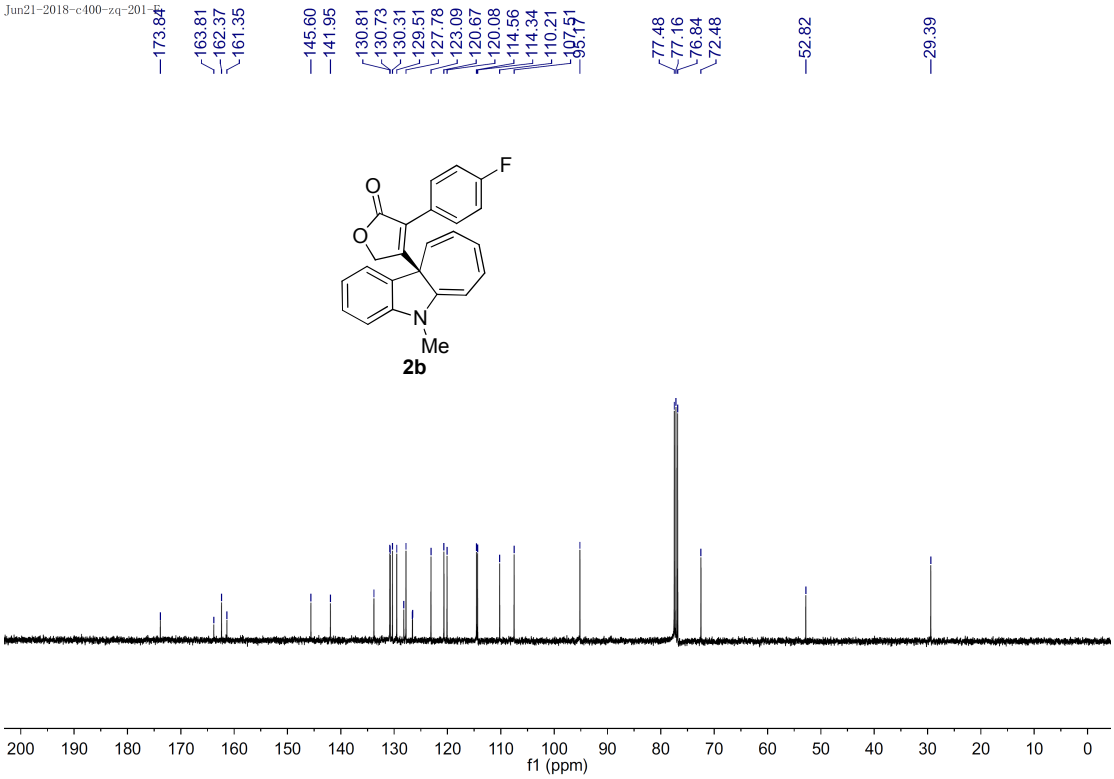

7.41
7.39
7.31
7.26
7.22
7.20
7.20
7.18
6.98
6.98
6.63
6.62
6.61
6.61
6.60
6.53
6.51
6.30
6.29
6.28
6.12
6.09
5.24
5.22
5.04
4.92
4.87
4.51
4.47
2.70
O
Ph
O
N
Me
1.02
1.06
3.28
1.07
2.96
1.06
1.05
1.02
1.01
1.07
1.04
1.03
3.00
f1 (ppm)

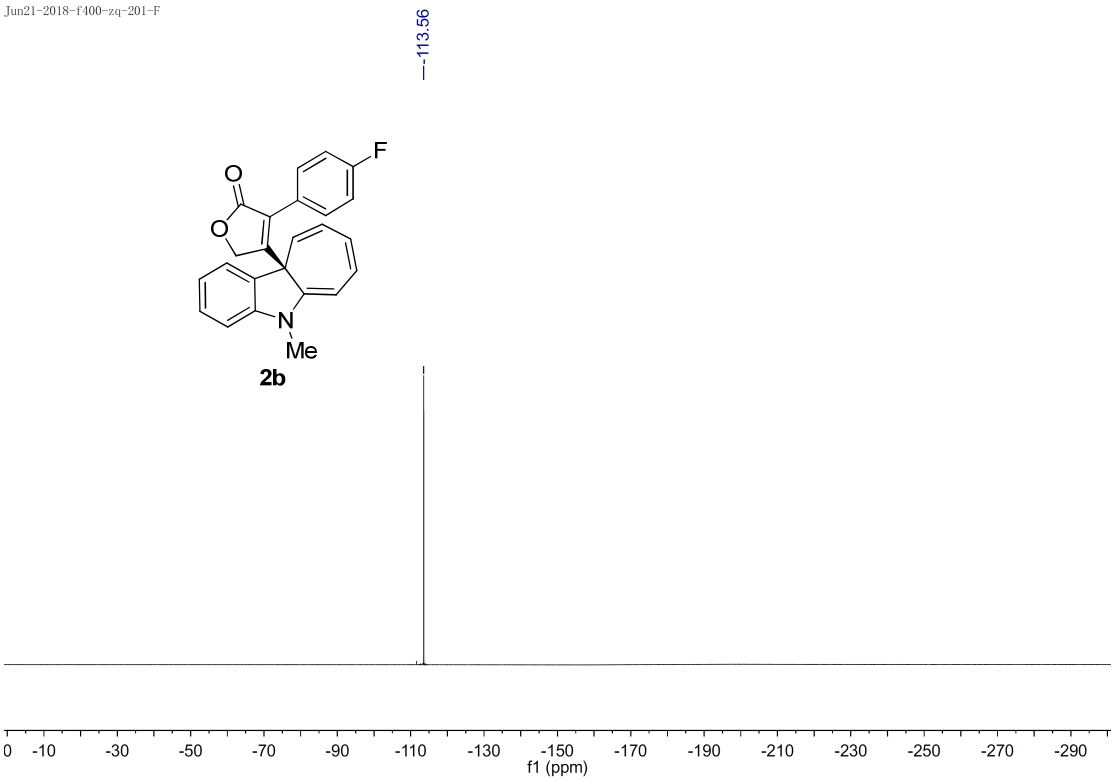
2a

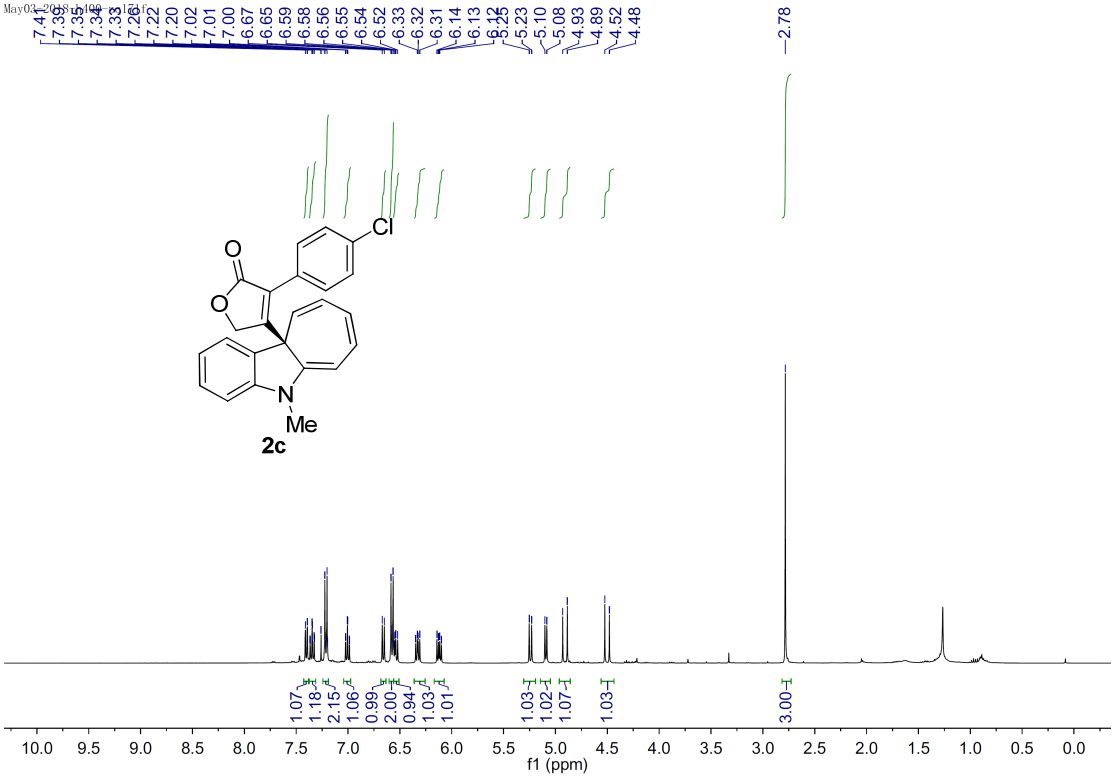

173.95
161.77
145.65
142.02
130.38
129.38
128.87
127.97
127.70
127.39
120.50
110.21
107.45
95.17
77.48
77.16
76.84
72.37
52.79
29.21
O
Ph
O
N
Me
f1 (ppm)

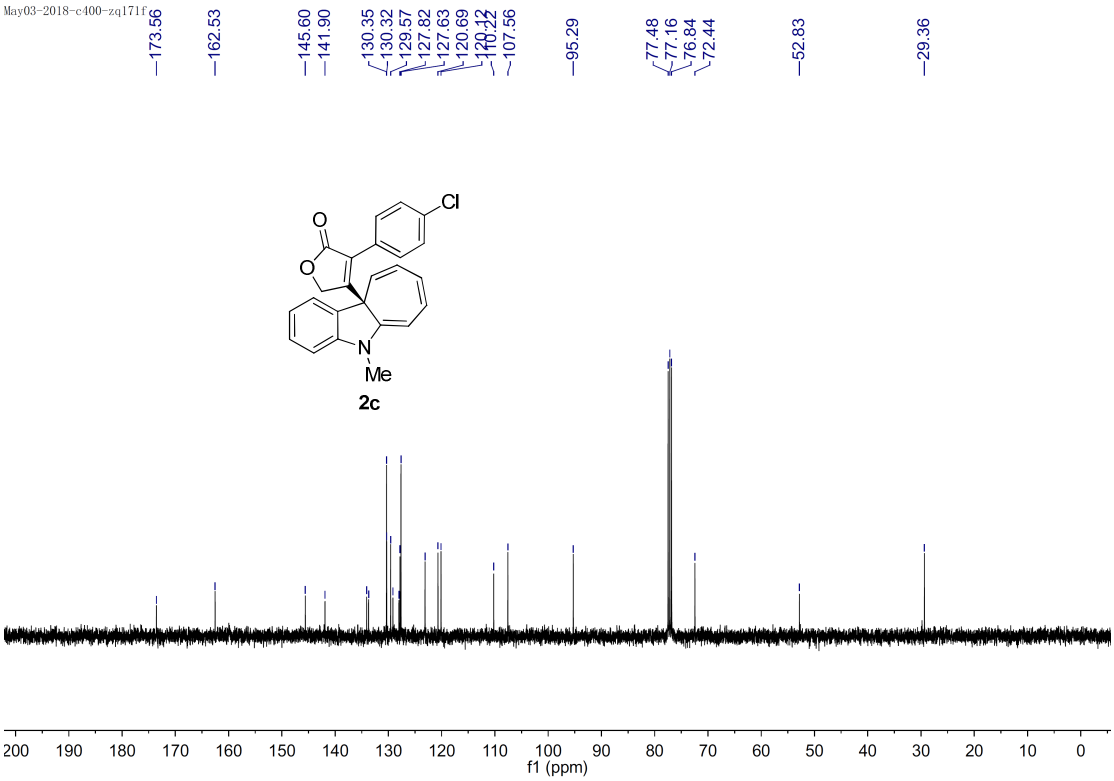
2a

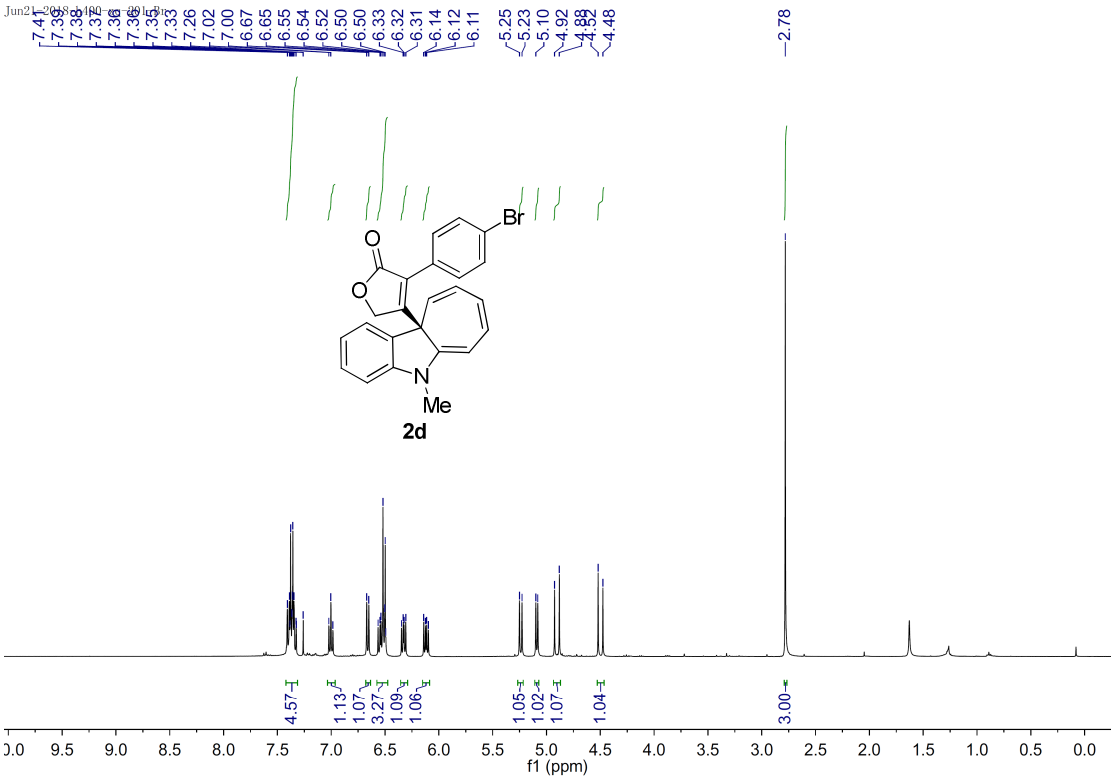

7.41
7.39
7.34
7.26
7.02
7.00
6.95
6.93
6.90
6.66
6.64
6.62
6.61
6.60
6.59
6.55
6.54
6.52
6.33
6.31
6.14
6.13
5.23
5.11
5.09
4.93
4.89
4.52
4.48
2.78
F
O
O
N
Me
2b
1.06
1.12
1.17
1.93
3.12
1.08
1.08
1.06
1.07
1.09
1.10
1.08
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

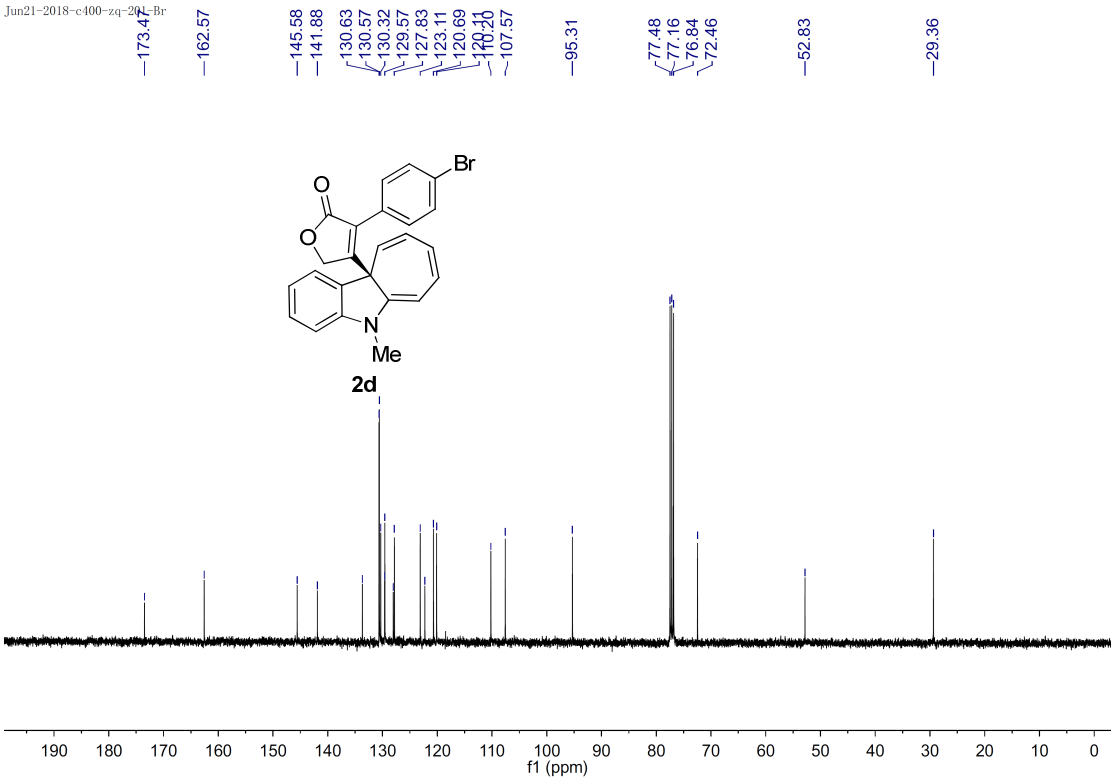

Jun21-2018-c400-zq-201-f
173.84
163.81
162.37
161.35
145.60
141.95
130.81
130.73
130.31
129.51
127.78
123.09
120.67
120.08
114.56
114.34
110.21
107.51
95.17
77.48
77.16
76.84
72.48
52.82
29.39
F
O
O
N
Me
2b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

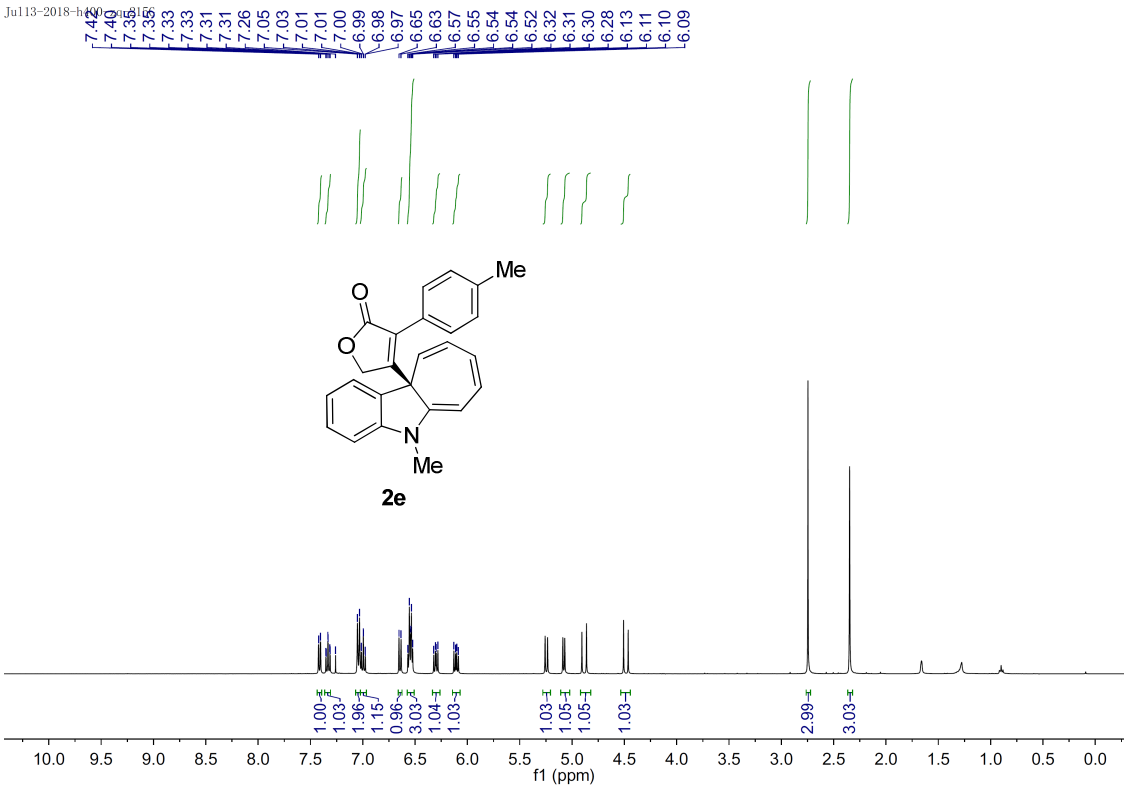

Jun21-2018-f400-zq-201-F
-113.56
F
O
O
N
Me
2b
0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

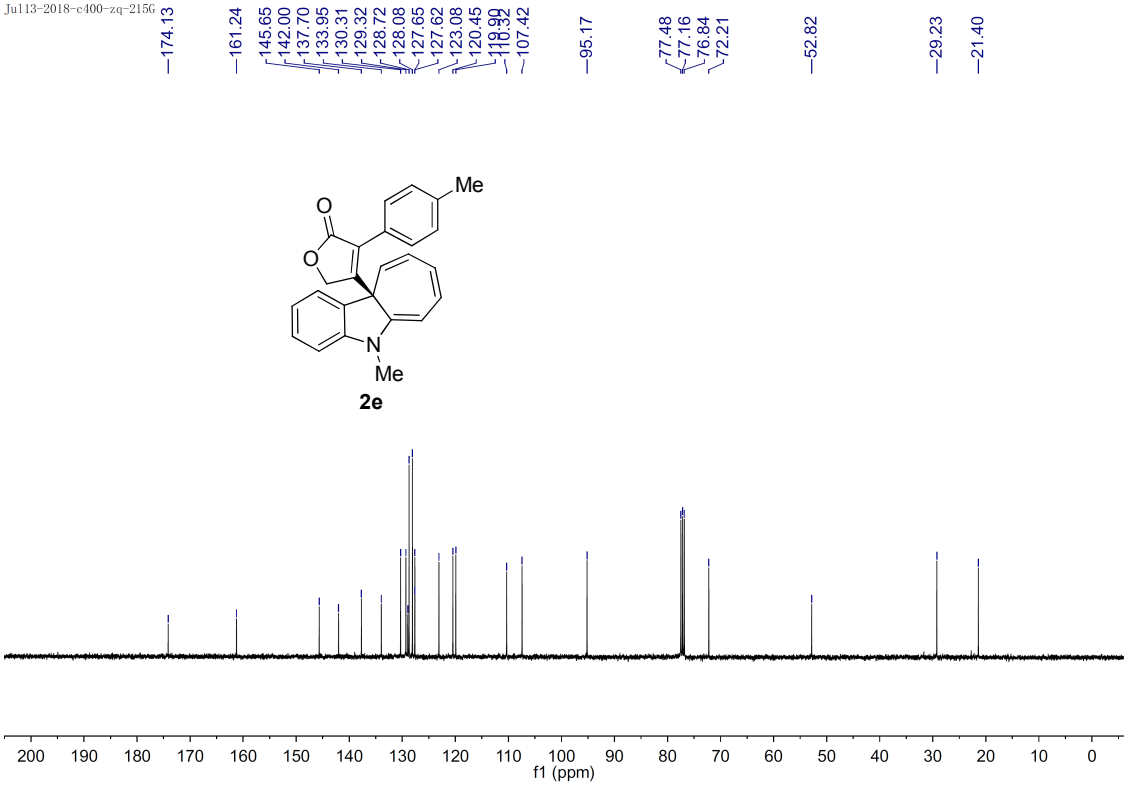

7.41 7.39 7.35 7.34 7.33 7.26 7.22 7.20 7.02 7.01 7.00 6.67 6.65 6.59 6.58 6.56 6.55 6.54 6.52 6.33 6.32 6.31 6.14 6.13 5.23 5.10 5.08 4.93 4.89 4.52 4.48
2.78
Cl
O
O
N
Me
2c
1.07 1.18 2.15 1.06 0.99 2.00 0.94 1.03 1.01 1.03 1.02 1.07 1.03 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

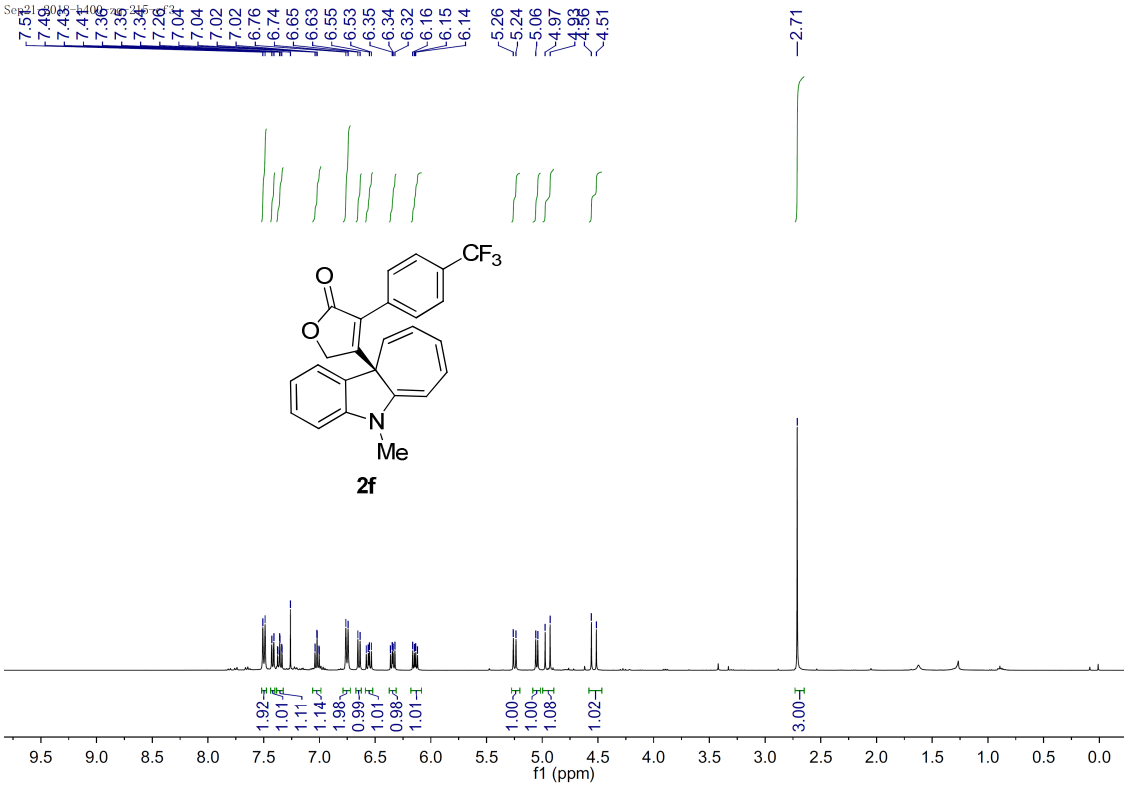

May03-2018-c400-zq171f
173.56
162.53
145.60
141.90
130.35
130.32
129.57
127.82
127.63
120.69
110.22
107.56
95.29
77.48
77.16
76.84
72.44
52.83
29.36
Cl
O
O
N
Me
2c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.41
7.39
7.38
7.37
7.36
7.35
7.33
7.26
7.02
7.00
6.67
6.65
6.55
6.54
6.52
6.50
6.50
6.33
6.32
6.31
6.14
6.12
6.11
5.25
5.23
5.10
4.92
4.88
4.52
4.48
2.78
Br
O
O
N
Me
2d
4.57
1.13
1.07
3.27
1.09
1.06
1.05
1.02
1.07
1.04
3.00
0.0 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)


Jun21-2018-c400-zq-2d-Br
173.47
162.57
145.58
141.88
130.63
130.57
130.32
129.57
127.83
123.11
120.69
120.11
120.00
107.57
95.31
77.48
77.16
76.84
72.46
52.83
29.36
Br
O
O
N
Me
2d
f1 (ppm)

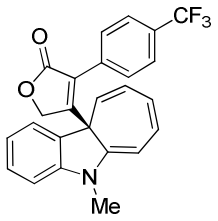

Ju113-2018-h400-zq-2e
7.42
7.40
7.35
7.33
7.33
7.31
7.31
7.26
7.05
7.03
7.01
7.01
7.00
6.99
6.98
6.97
6.65
6.63
6.57
6.55
6.54
6.54
6.52
6.32
6.31
6.30
6.28
6.13
6.11
6.10
6.09
Me
O
O
N
Me
2e
1.00
1.03
1.96
1.15
0.96
3.03
1.04
1.03
1.03
1.05
1.05
1.03
2.99
3.03
f1 (ppm)


Jul13-2018-c400-zq-215G
174.13
161.24
145.65
142.00
137.70
133.95
130.31
129.32
128.72
128.08
127.65
127.62
123.08
120.45
118.99
118.32
107.42
95.17
77.48
77.16
76.84
72.21
52.82
29.23
21.40
Me
O
O
N
Me
2e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

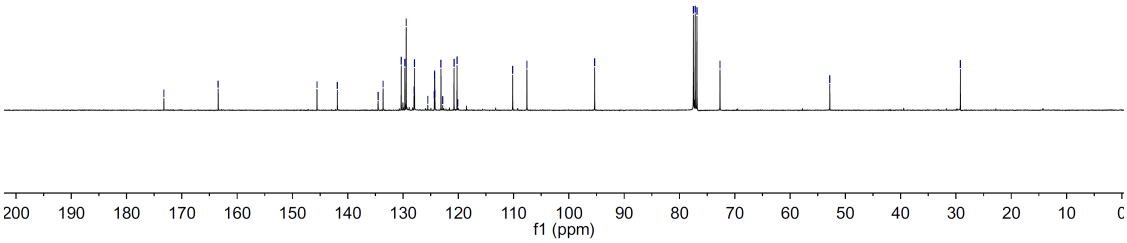

7.57
7.49
7.43
7.41
7.36
7.35
7.34
7.26
7.04
7.04
7.02
7.02
6.76
6.74
6.65
6.63
6.55
6.53
6.35
6.34
6.32
6.16
6.15
6.14
5.26
5.24
5.06
4.97
4.93
4.56
4.51
2.71
CF3
O
O
N
Me
2f
1.92
1.01
1.11
1.14
1.98
0.99
1.01
0.98
1.01
1.00
1.00
1.08
1.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

Sep21-2018-c400-zq-215-c13

173.25
163.43
145.56
141.88
130.32
129.67
129.43
127.92
124.26
123.13
120.78
110.23
110.17
107.59
95.34
77.48
77.16
76.84
72.67
52.81
29.19

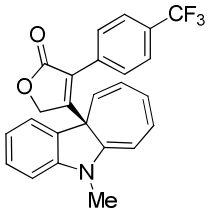


2f

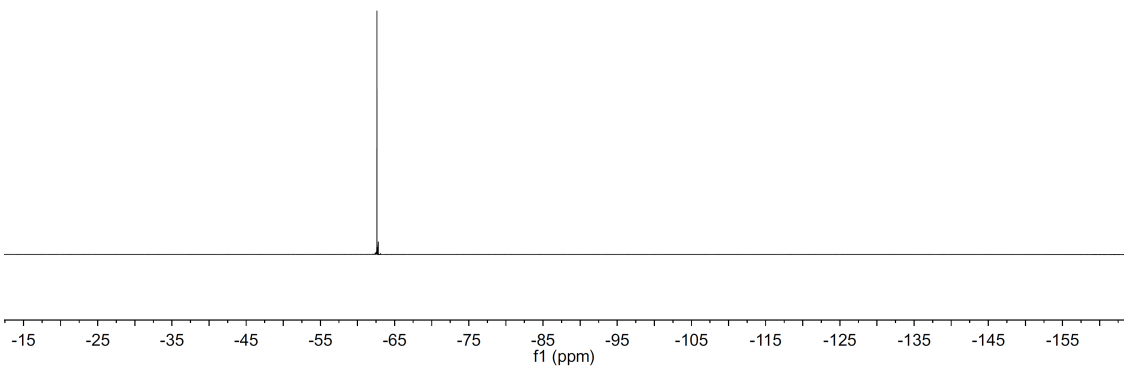


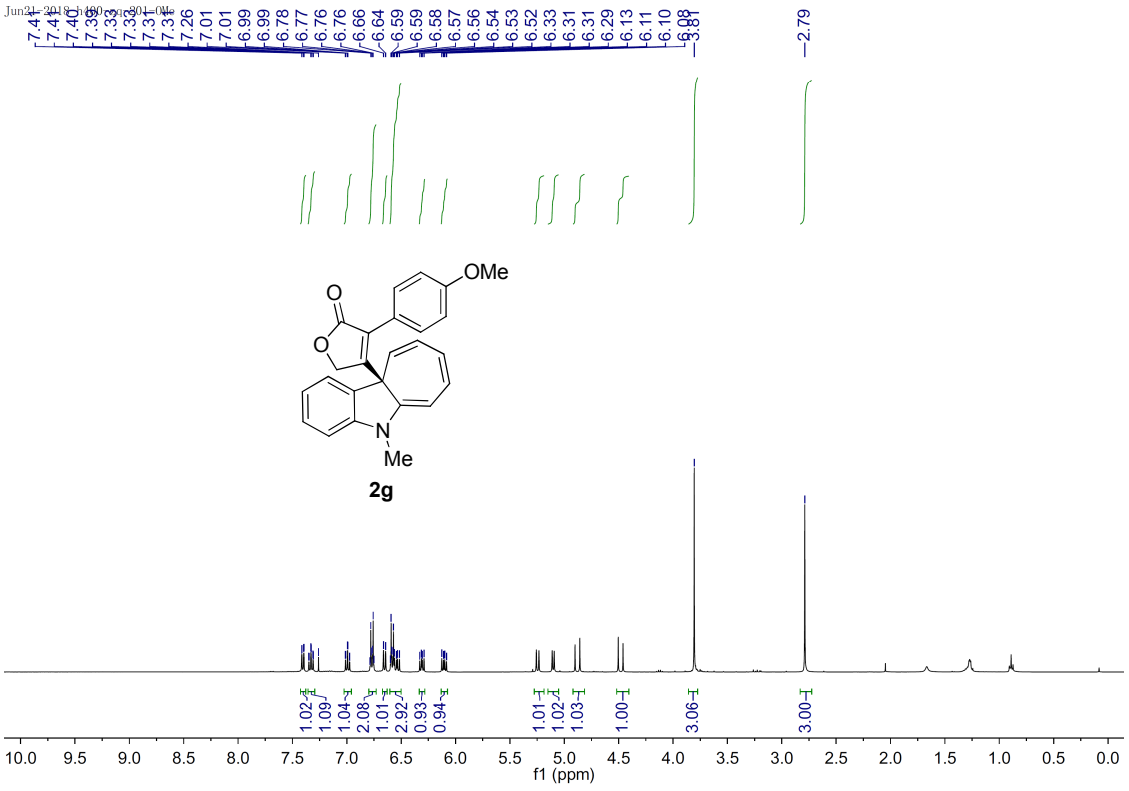
Sep21-2018-f400-zq-215-cf3

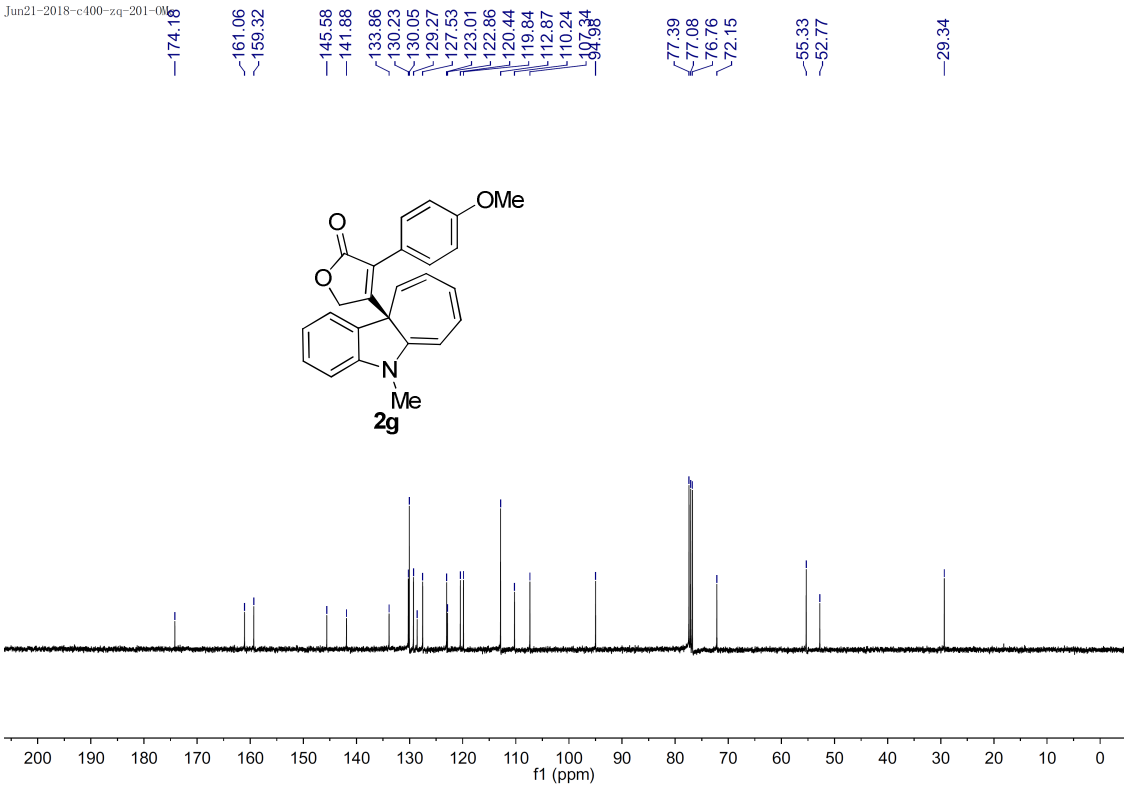
62.62

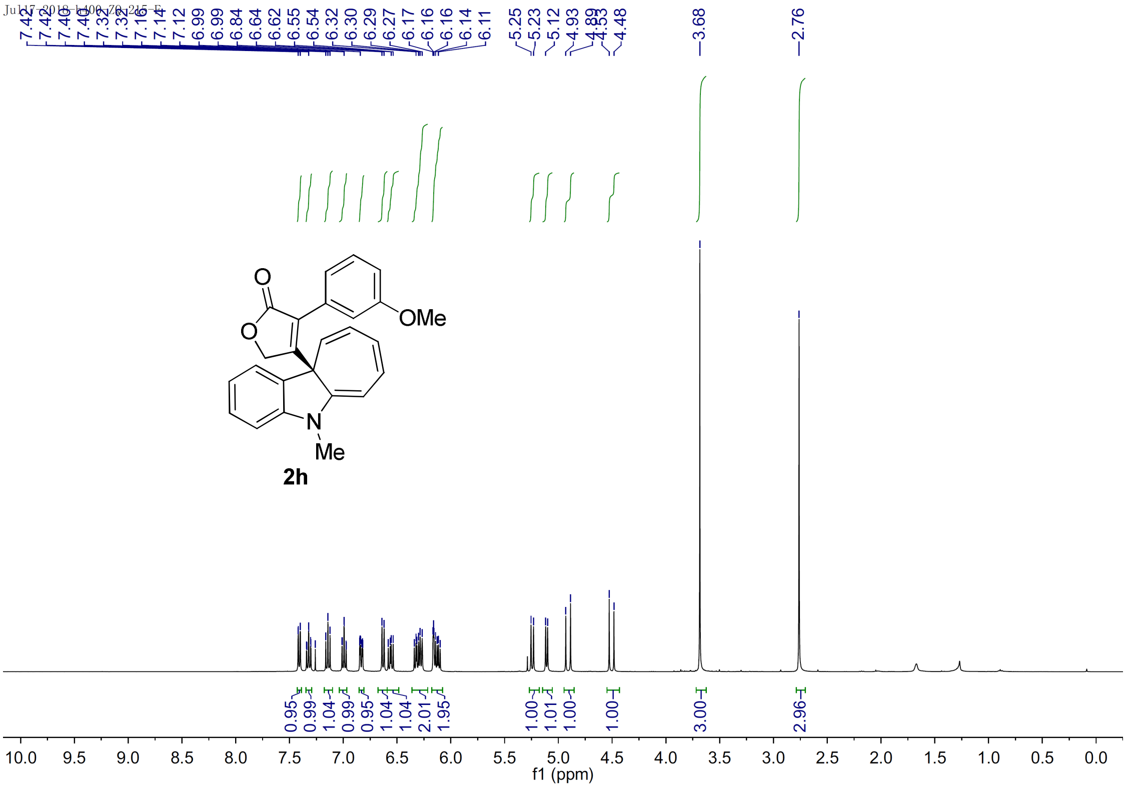


2f

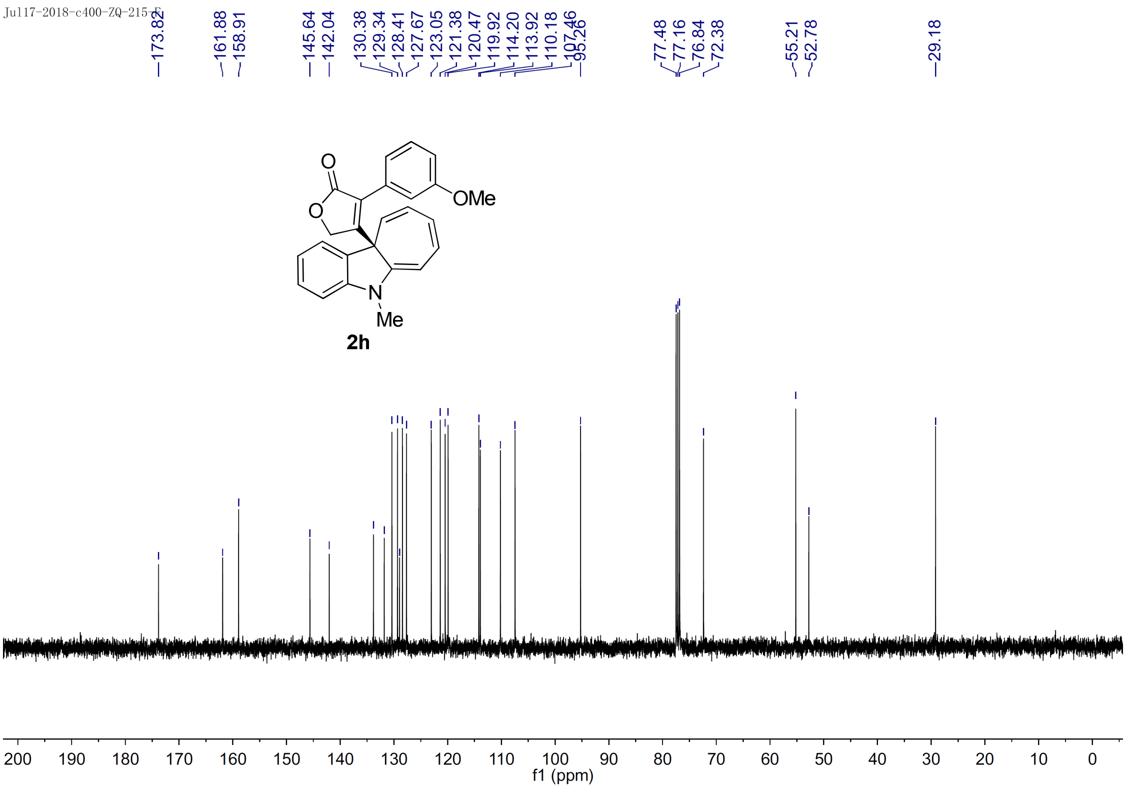



Jun21-2018-c400-zq-201-OMe
7.41
7.41
7.40
7.39
7.33
7.32
7.31
7.31
7.26
7.01
7.01
6.99
6.99
6.78
6.77
6.76
6.76
6.66
6.64
6.59
6.59
6.58
6.57
6.56
6.54
6.53
6.52
6.33
6.31
6.31
6.29
6.13
6.11
6.10
6.08
3.81
2.79
O
O
N
Me
OMe
2g
1.02
1.09
1.04
2.08
1.01
2.92
0.93
0.94
1.01
1.02
1.03
1.00
3.06
3.00
10.0 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)

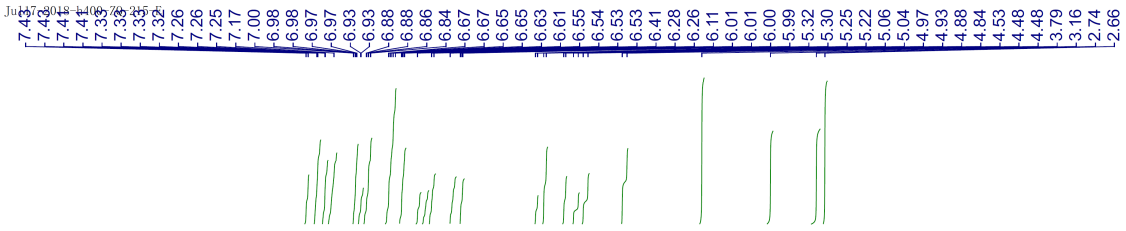

Jun21-2018-c400-zq-201-OMe
174.18
161.06
159.32
145.58
141.88
133.86
130.23
130.05
129.27
127.53
123.01
122.86
120.44
119.84
112.87
110.24
107.34
94.98
77.39
77.08
76.76
72.15
55.33
52.77
29.34
O
O
N
Me
OMe
2g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

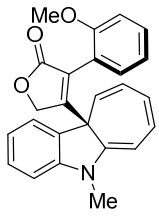


7.42
7.42
7.40
7.40
7.32
7.32
7.16
7.14
7.12
6.99
6.99
6.84
6.64
6.62
6.55
6.54
6.32
6.30
6.29
6.27
6.17
6.16
6.16
6.14
6.11
5.25
5.23
5.12
4.93
4.89
4.53
4.48
3.68
2.76
O
O
OMe
N
Me
2h
0.95
0.99
1.04
0.99
0.95
1.04
1.04
2.01
1.95
1.00
1.01
1.00
1.00
3.00
2.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

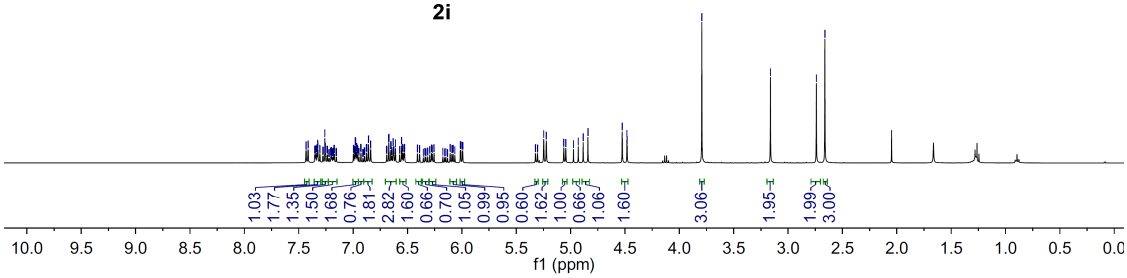


Jul17-2018-c400-ZQ-215-F
173.82
161.88
158.91
145.64
142.04
130.38
129.34
128.41
127.67
123.05
121.38
120.47
119.92
114.20
113.92
110.18
107.46
95.26
77.48
77.16
76.84
72.38
55.21
52.78
29.18
O
O
OMe
N
Me
2h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

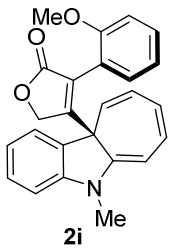



MeO
O
O
N
Me

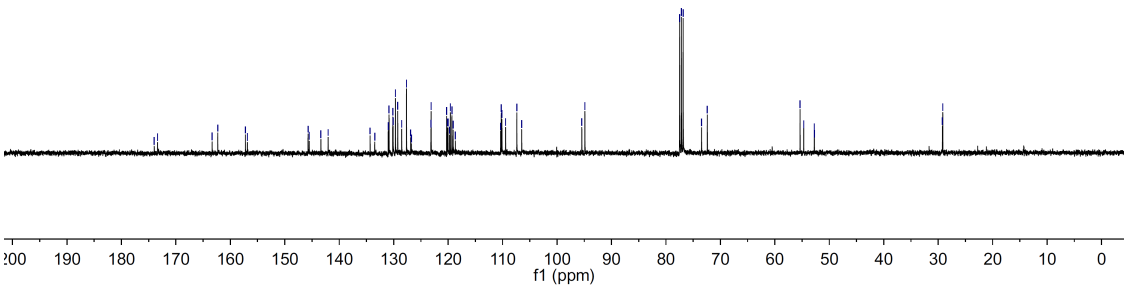
2i

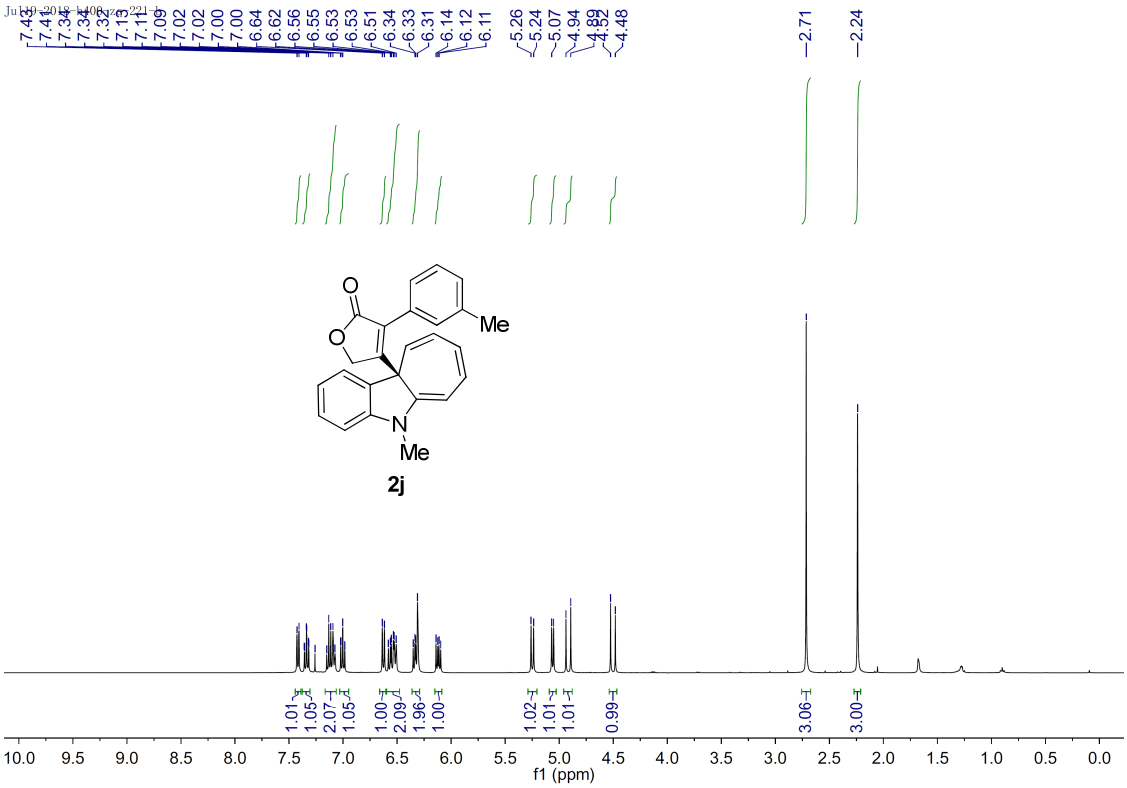

1.03
1.77
1.35
1.50
1.68
0.76
1.81
2.82
1.60
0.66
0.70
1.05
0.99
0.95
0.60
1.62
1.00
0.66
1.06
1.60
3.06
1.95
1.99
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

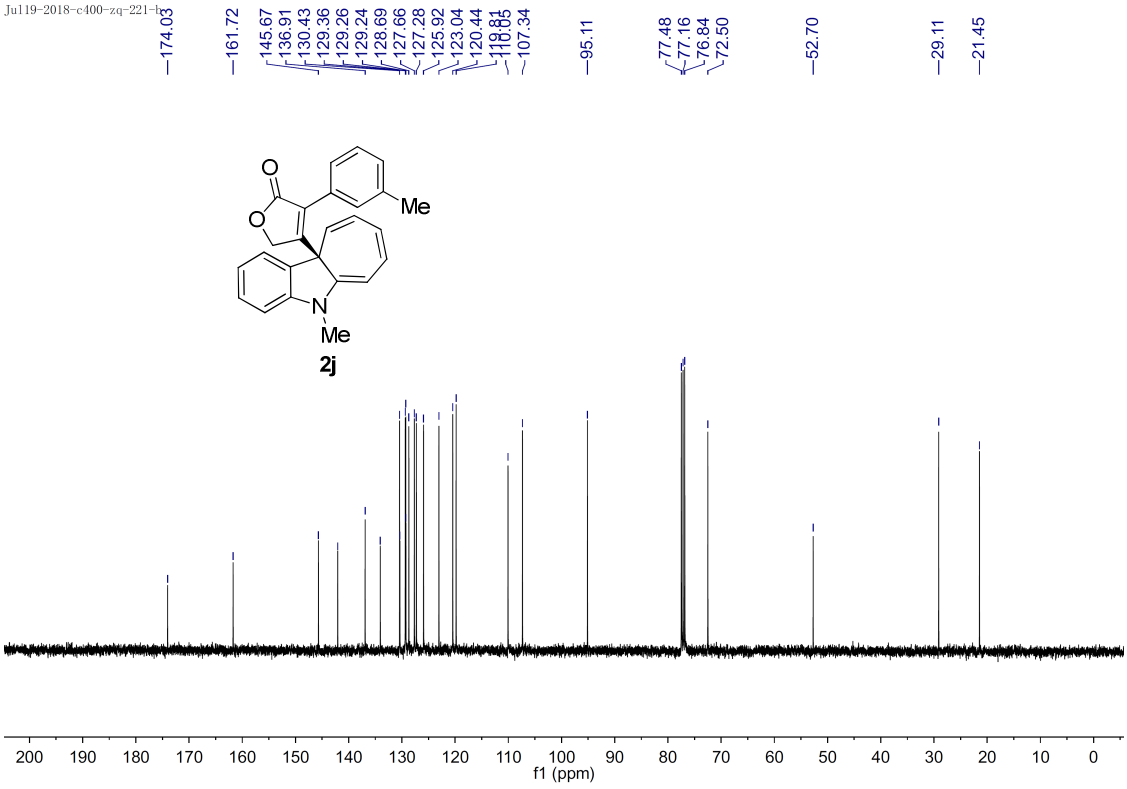

173.96
173.36
163.34
162.30
157.22
156.87
145.72
145.51
143.36
142.03
130.85
129.68
129.25
127.65
123.12
119.59
110.25
110.12
109.44
107.38
94.45
94.88
77.48
77.16
76.84
73.46
72.40
55.36
54.69
52.75
52.73
29.22
29.15

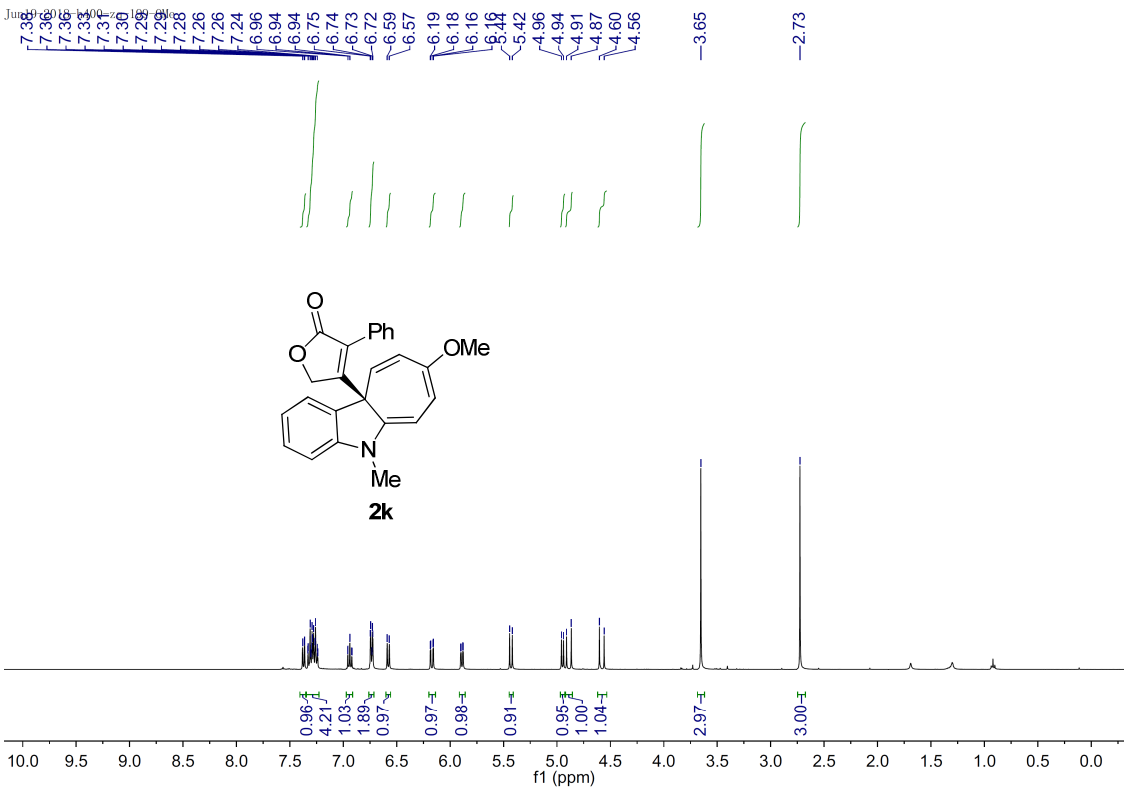

MeO
O
O
N
Me

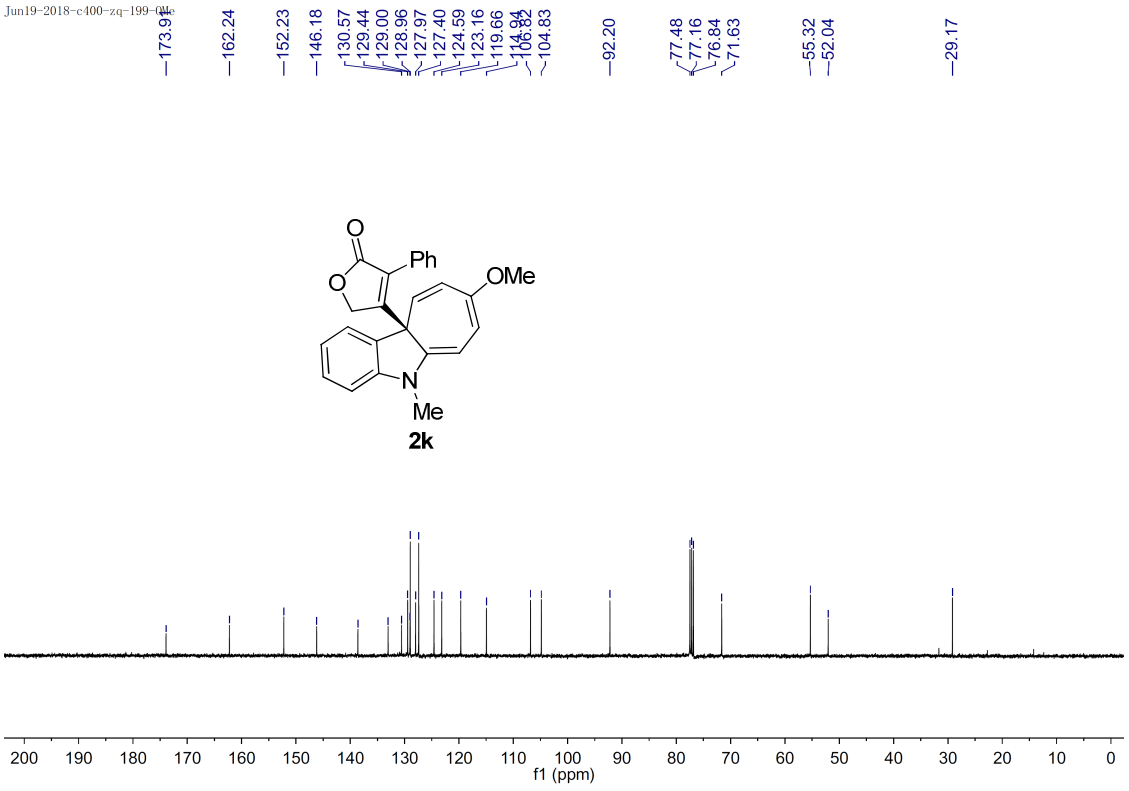
2i

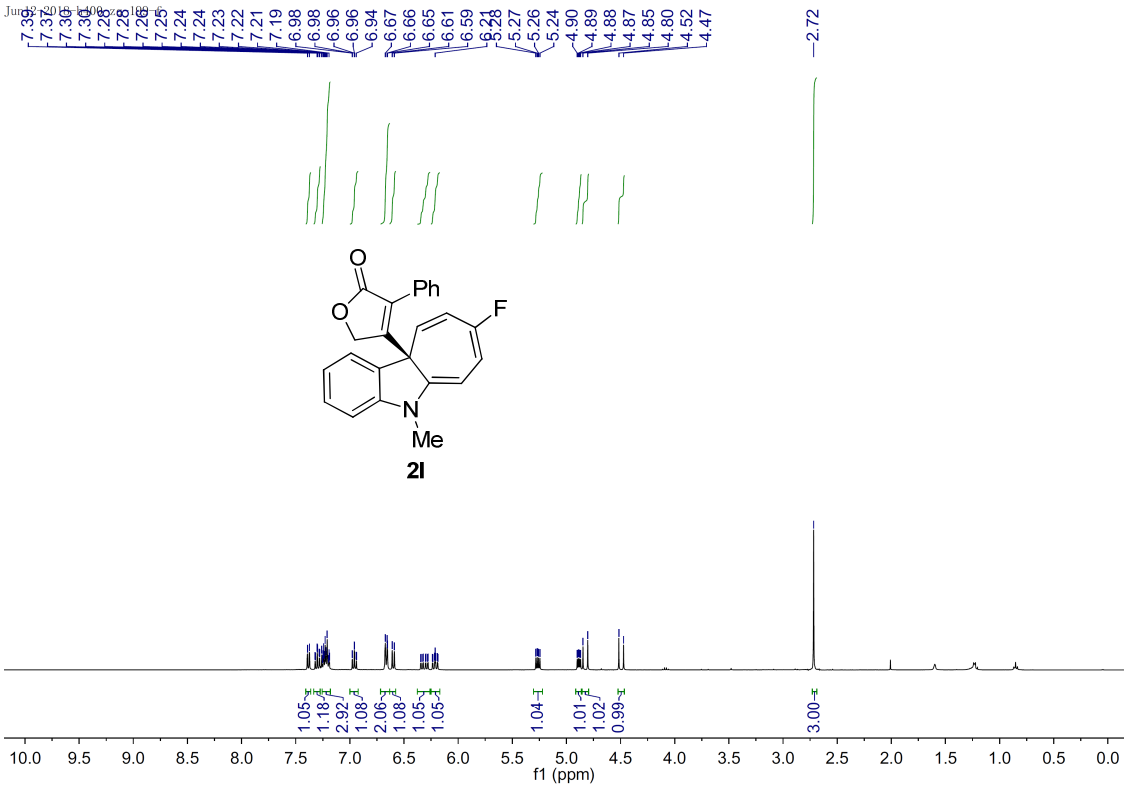

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

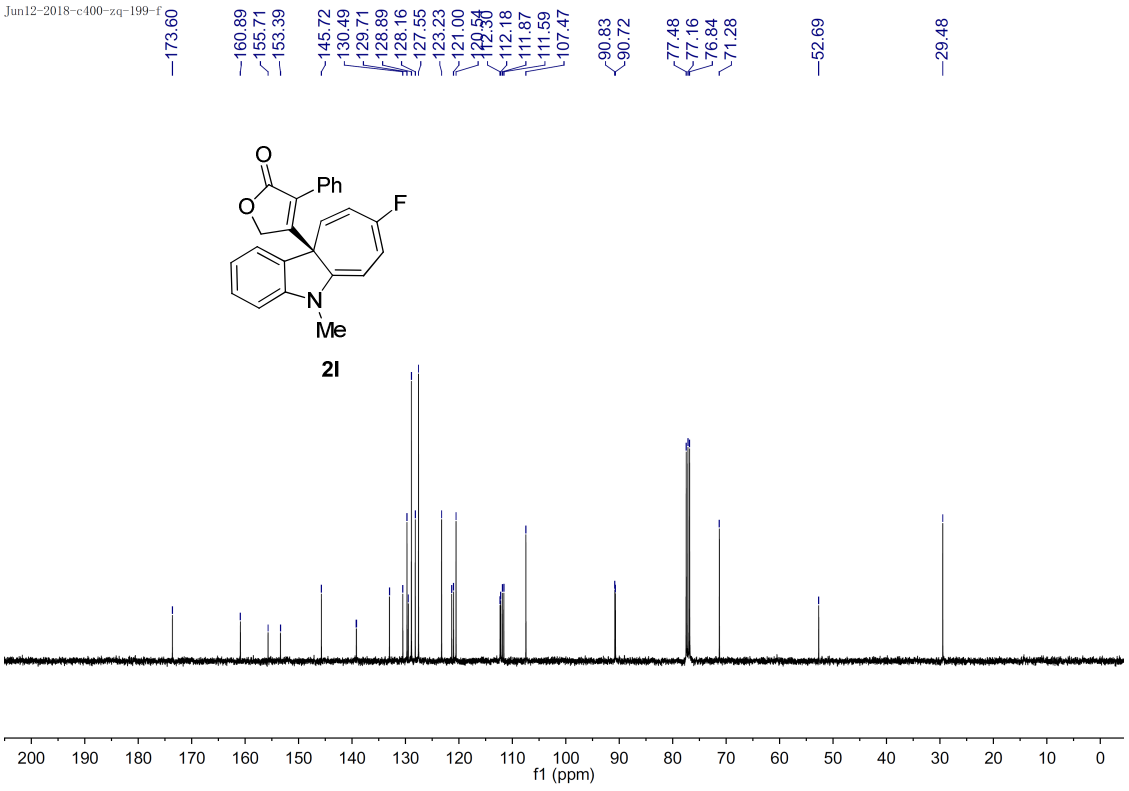

Me
O
O
N
Me
2j
f1 (ppm)

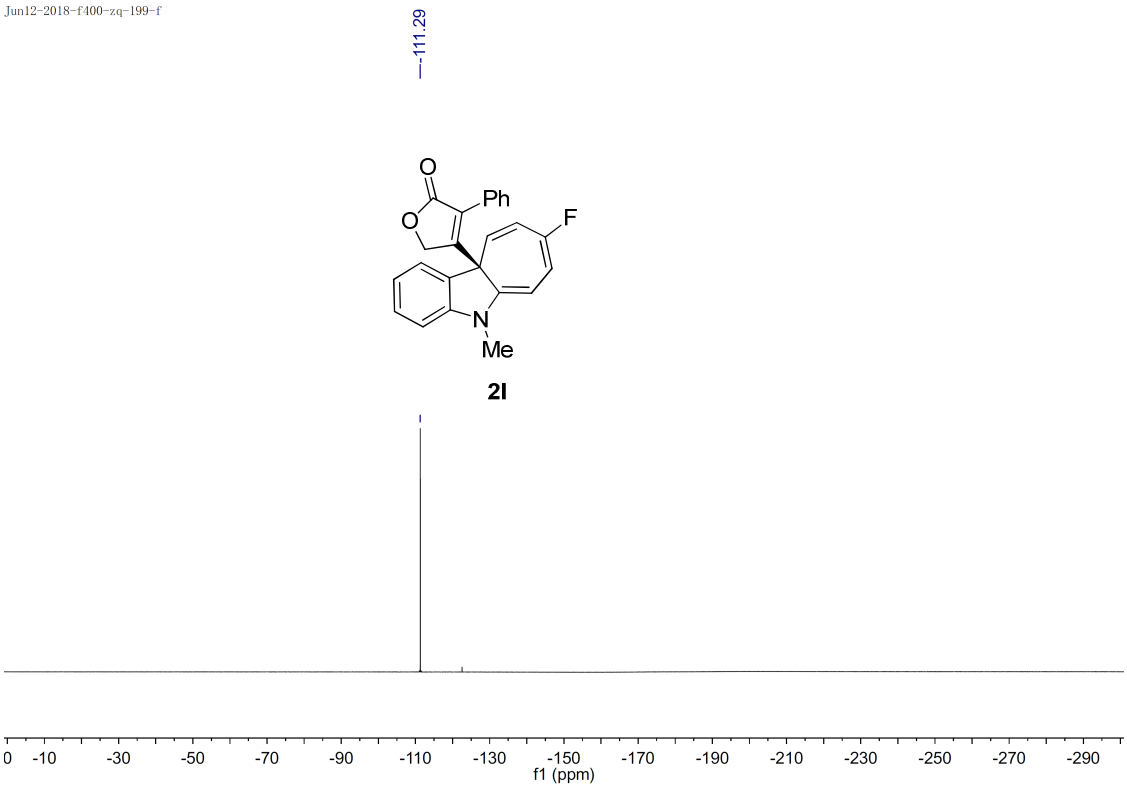

Me
O
O
N
Me
2j
f1 (ppm)

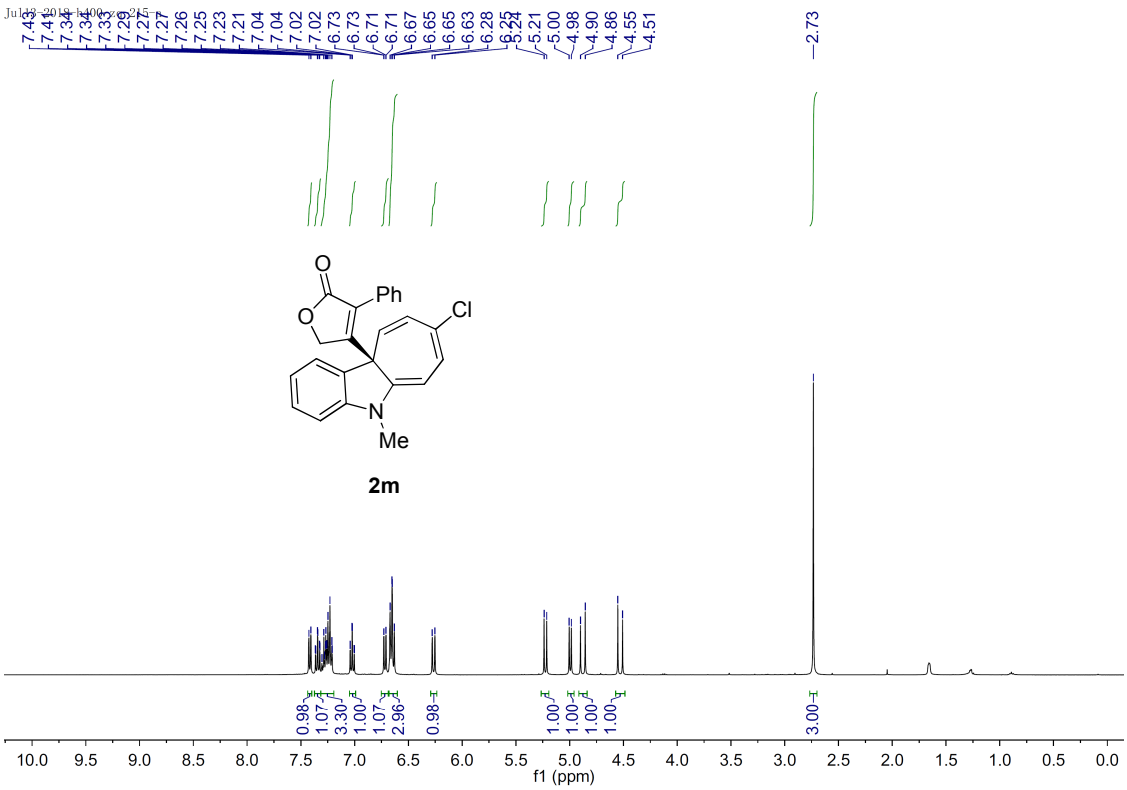

7.38
7.36
7.36
7.33
7.31
7.30
7.29
7.28
7.26
7.26
7.24
6.96
6.94
6.94
6.75
6.74
6.73
6.72
6.59
6.57
6.19
6.18
6.16
6.16
5.42
4.96
4.94
4.91
4.87
4.60
4.56
3.65
2.73
O
Ph
OMe
O
N
Me
2k
0.96
4.21
1.03
1.89
0.97
0.97
0.98
0.91
0.95
1.00
1.04
2.97
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

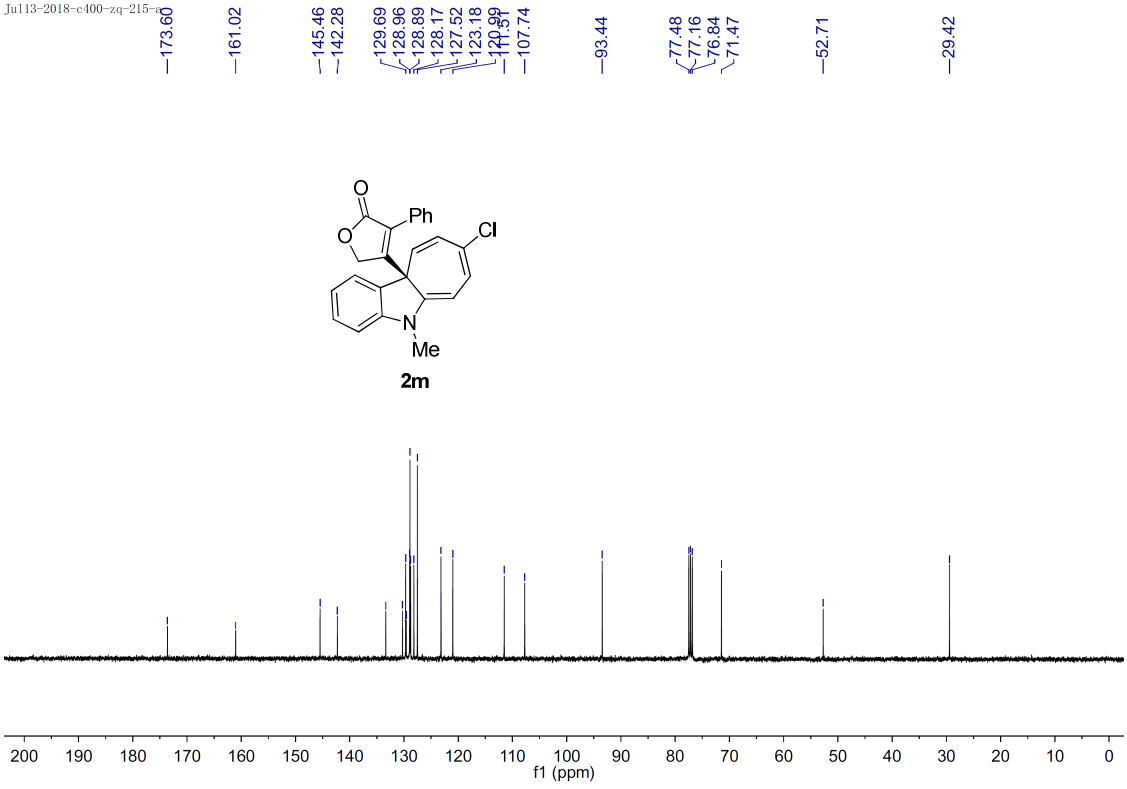

Jun19-2018-c400-zq-199-OMe
173.91
162.24
152.23
146.18
130.57
129.44
129.00
128.96
127.97
127.40
124.59
123.16
119.66
114.94
106.82
104.83
92.20
77.48
77.16
76.84
71.63
55.32
52.04
29.17
O
Ph
OMe
O
N
Me
2k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

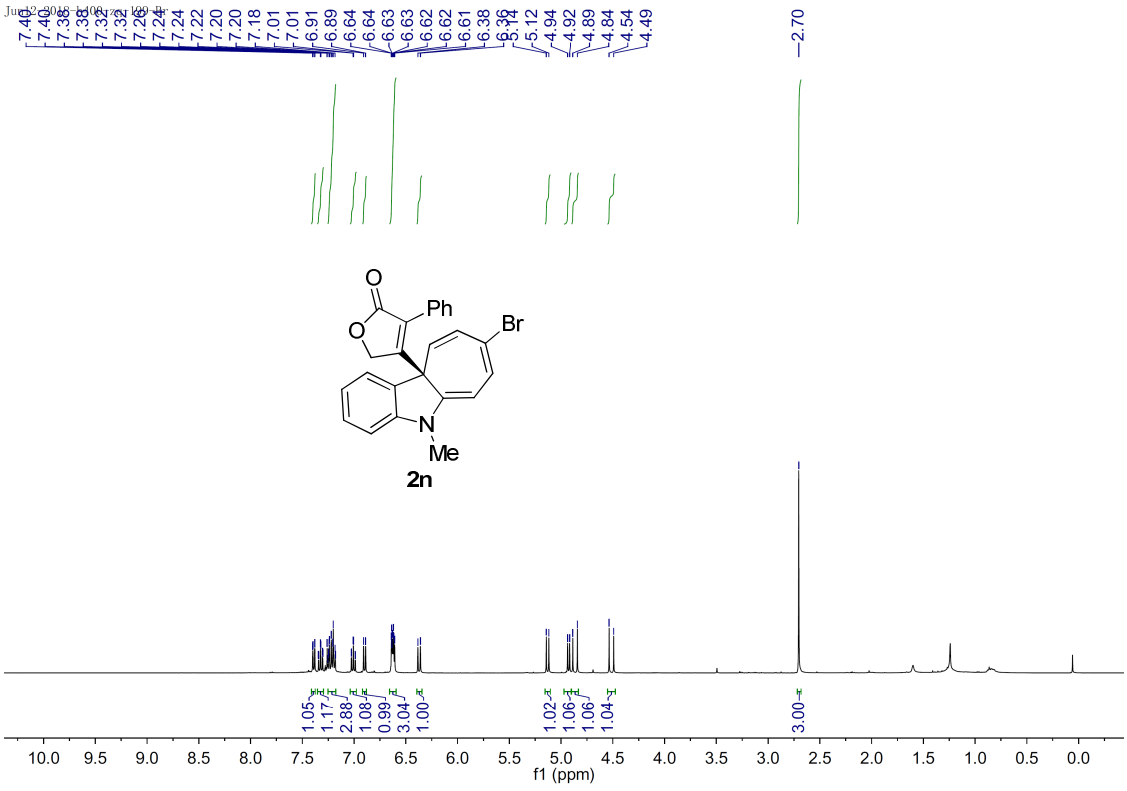

7.39
7.37
7.36
7.36
7.28
7.26
7.25
7.24
7.24
7.23
7.22
7.21
7.19
6.98
6.98
6.96
6.96
6.94
6.67
6.66
6.65
6.61
6.59
6.21
5.28
5.27
5.26
5.24
4.90
4.89
4.88
4.87
4.85
4.80
4.52
4.47
2.72
O
Ph
O
F
N
Me
2l
1.05
1.18
2.92
1.08
2.06
1.08
1.05
1.05
1.04
1.01
1.02
0.99
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 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)

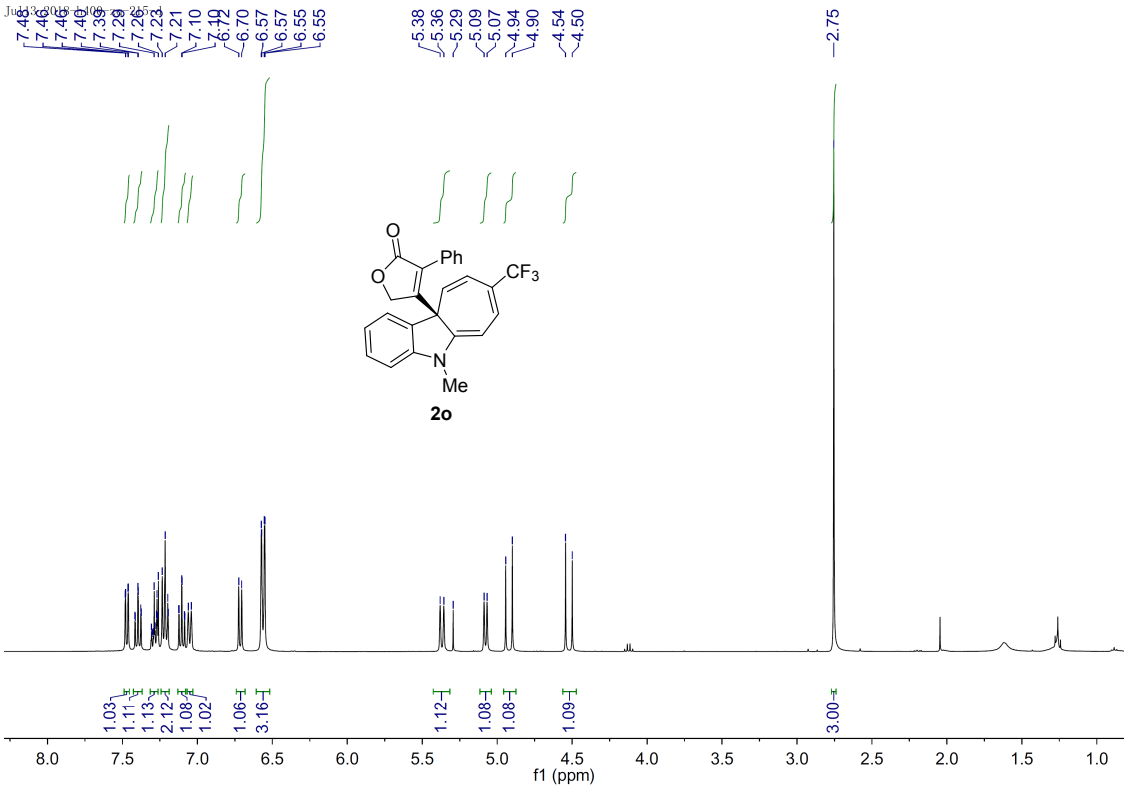

Jun12-2018-c400-zq-199-f
173.60
160.89
155.71
153.39
145.72
130.49
129.71
128.89
128.16
127.55
123.23
121.00
120.54
112.30
112.18
111.87
111.59
107.47
90.83
90.72
77.48
77.16
76.84
71.28
52.69
29.48
O
Ph
O
F
N
Me
2l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

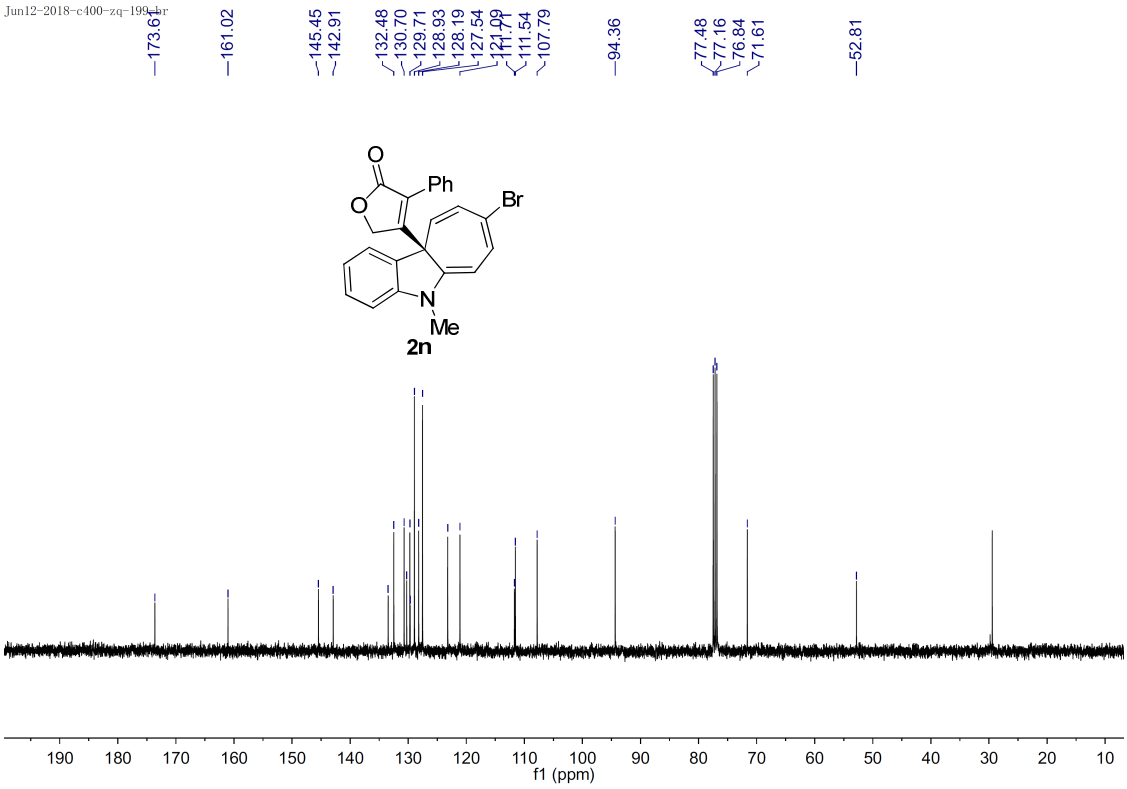

Jun12-2018-f400-zq-199-f
-111.29
O
Ph
O
F
N
Me
2l
0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

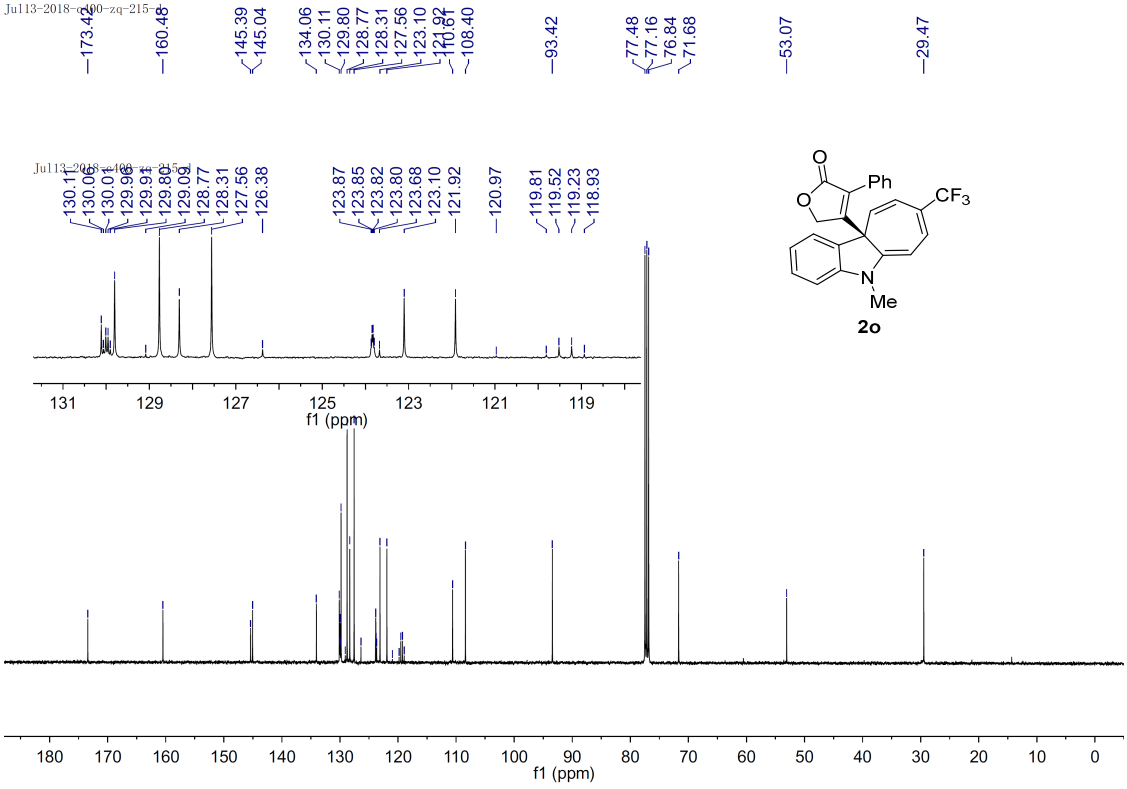

7.45
7.41
7.34
7.33
7.29
7.27
7.26
7.25
7.23
7.21
7.04
7.04
7.02
7.02
6.73
6.71
6.71
6.67
6.65
6.65
6.63
6.28
6.25
5.24
5.21
5.00
4.98
4.90
4.86
4.55
4.51
2.73
O
Ph
O
Cl
N
Me
2m
0.98
1.07
3.30
1.00
1.07
2.96
0.98
1.00
1.00
1.00
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

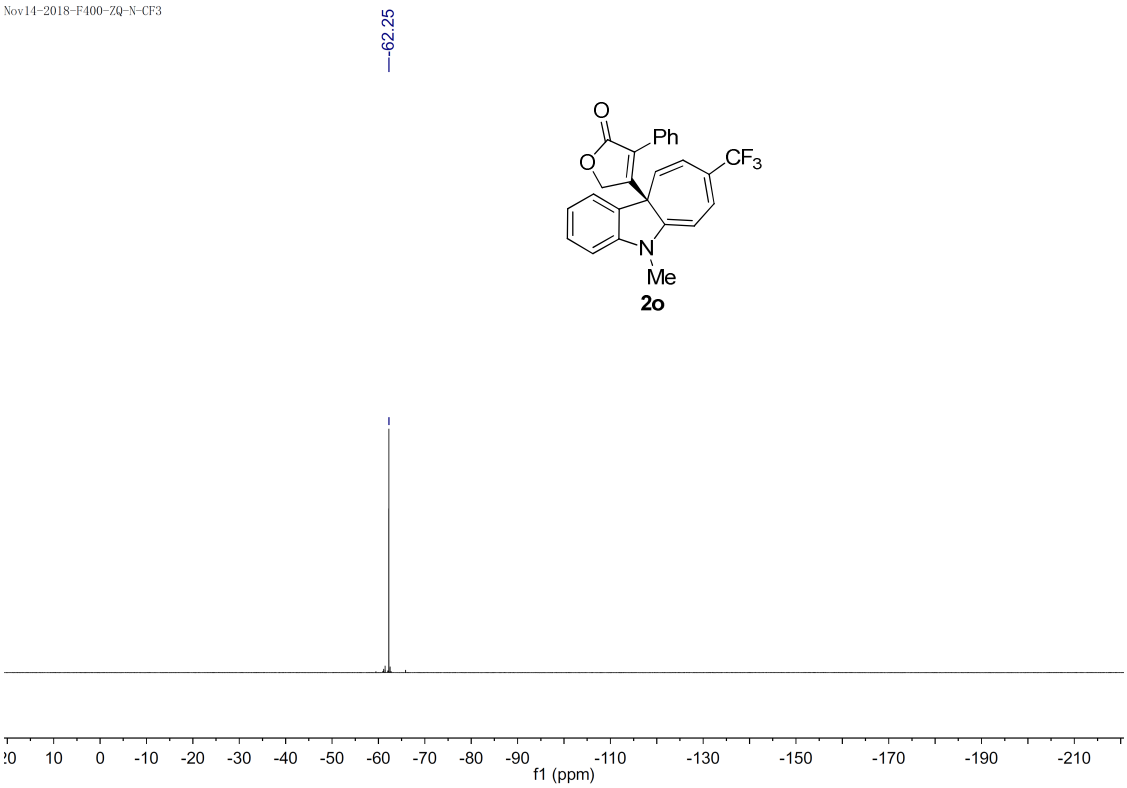

Jul13-2018-c400-zq-215-c
173.60
161.02
145.46
142.28
129.69
128.96
128.89
128.17
127.52
123.18
120.99
111.51
107.74
93.44
77.48
77.16
76.84
71.47
52.71
29.42
O
Ph
O
Cl
N
Me
2m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

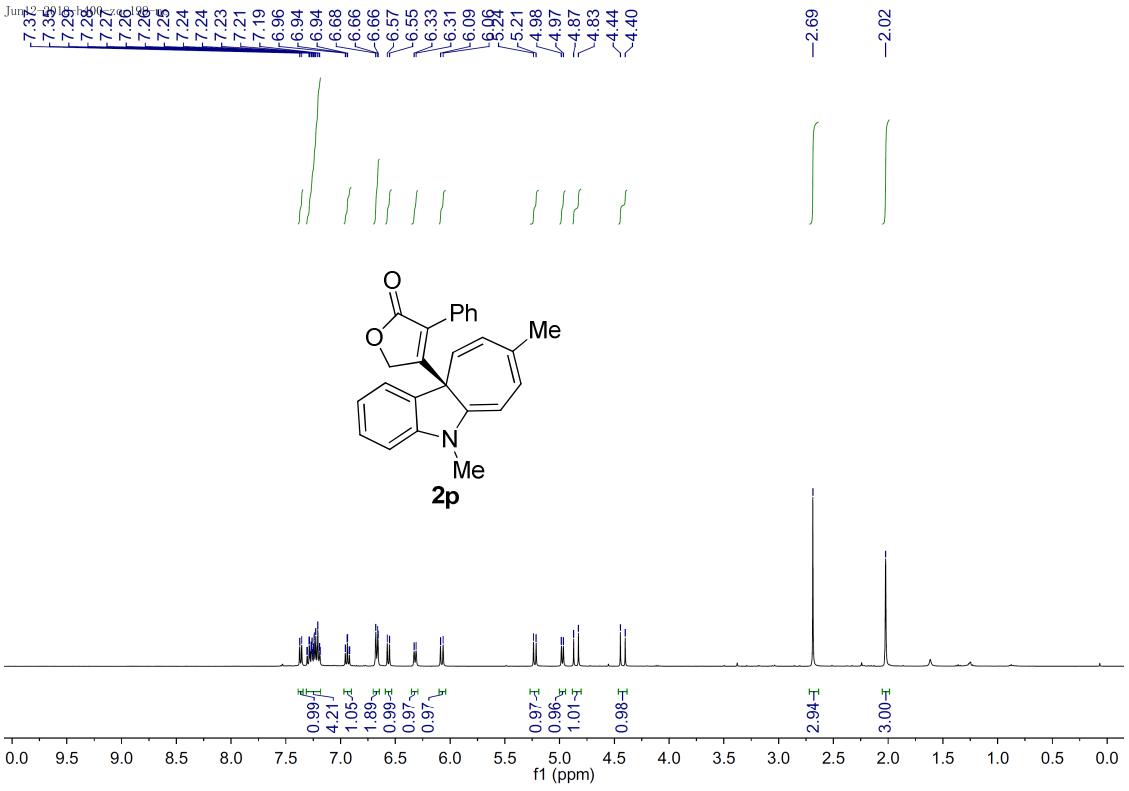

7.46
7.40
7.38
7.32
7.26
7.24
7.22
7.20
7.18
7.01
6.91
6.89
6.64
6.64
6.63
6.63
6.62
6.62
6.61
6.38
6.36
5.14
5.12
4.94
4.92
4.89
4.84
4.54
4.49
2.70
O
Ph
O
Br
N
Me
2n
1.05
1.17
2.88
1.08
0.99
3.04
1.00
1.02
1.06
1.06
1.04
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

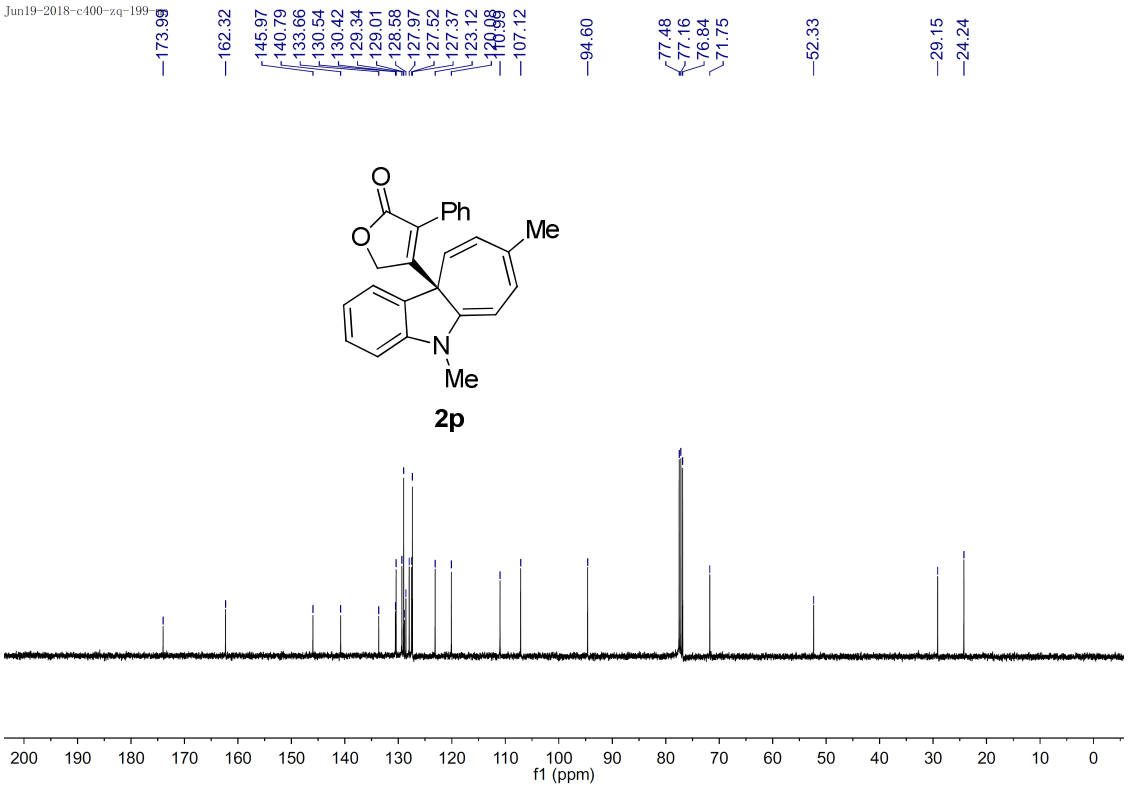

7.46
7.45
7.40
7.39
7.29
7.26
7.23
7.21
7.10
7.12
6.70
6.57
6.57
6.55
6.55
5.38
5.36
5.29
5.09
5.07
4.94
4.90
4.54
4.50
2.75
O
O
Ph
CF3
N
Me
2o
1.03
1.11
1.13
2.12
1.08
1.02
1.06
3.16
1.12
1.08
1.08
1.09
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

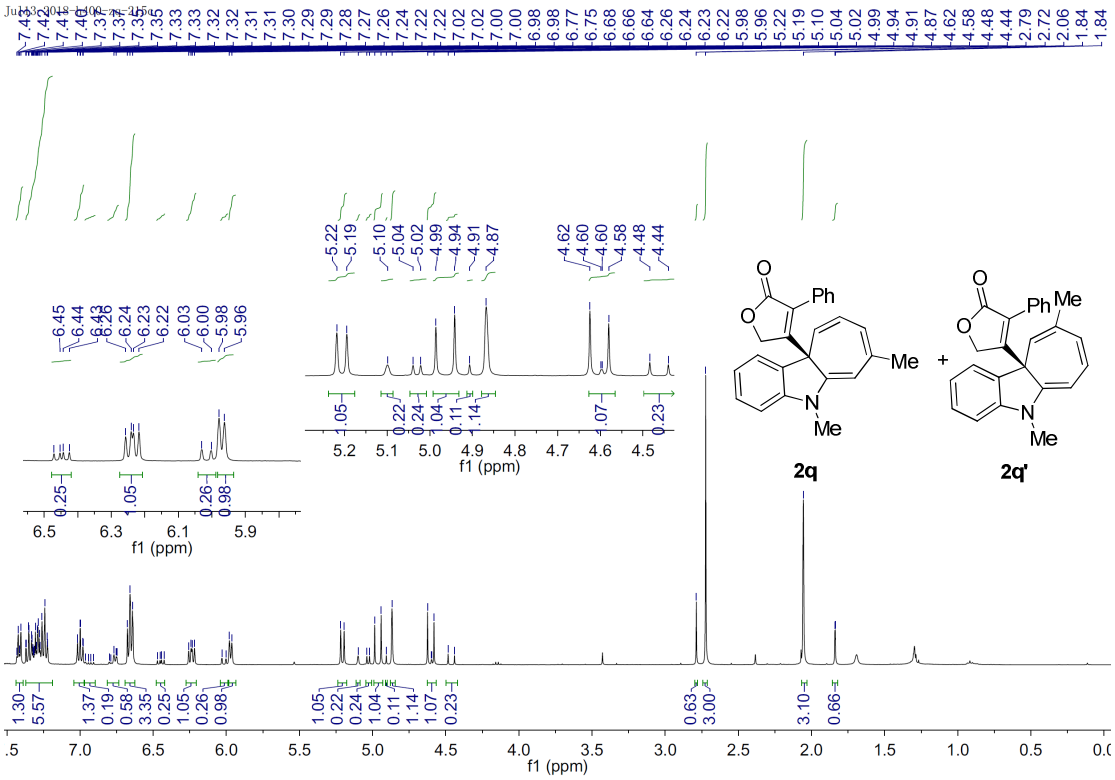

Jun12-2018-c400-zq-199-1H
173.61
161.02
145.45
142.91
132.48
130.70
129.71
128.93
128.19
127.54
111.71
111.54
107.79
94.36
77.48
77.16
76.84
71.61
52.81
O
O
Ph
Br
N
Me
2n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

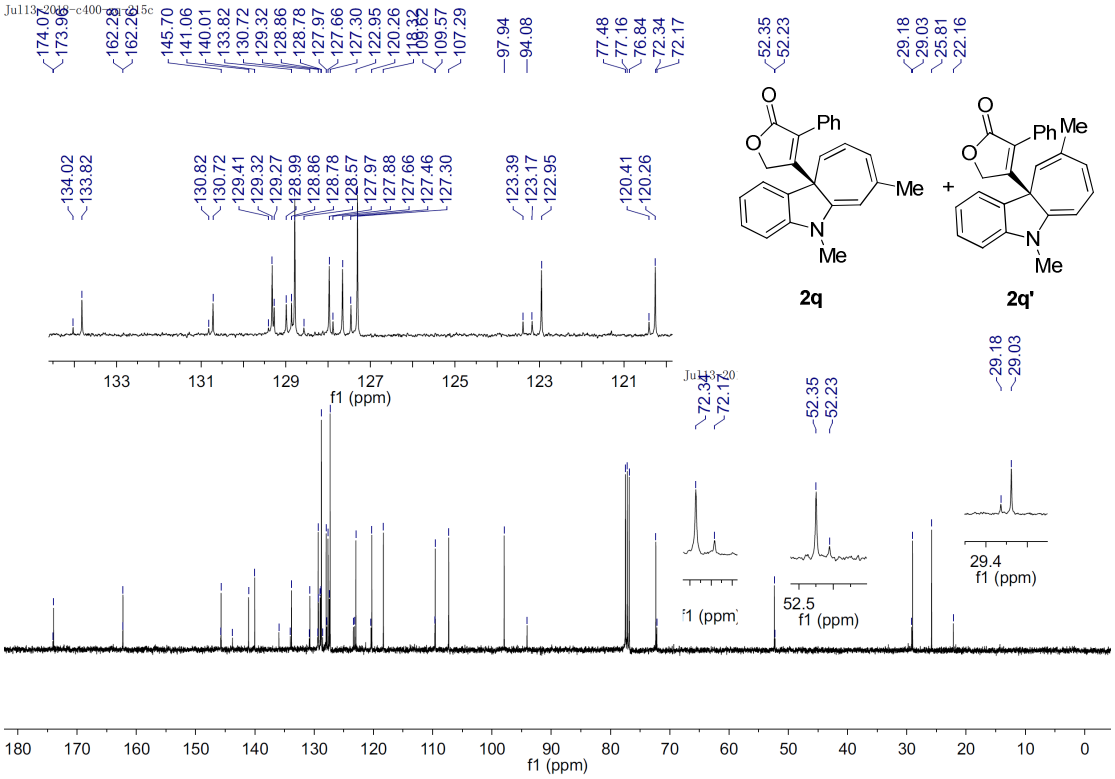

Jul13-2018-c400-zq-215-1
173.42
160.48
145.39
145.04
134.06
130.11
129.80
128.77
128.31
127.56
123.10
110.87
108.40
93.42
77.48
77.16
76.84
71.68
53.07
29.47
130.11
130.06
130.01
129.96
129.93
129.80
129.09
128.77
128.31
127.56
126.38
123.87
123.85
123.82
123.80
123.68
123.10
121.92
120.97
119.81
119.52
119.23
118.93
131
129
127
125
123
121
119
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
Ph
O
CF3
N
Me
2o

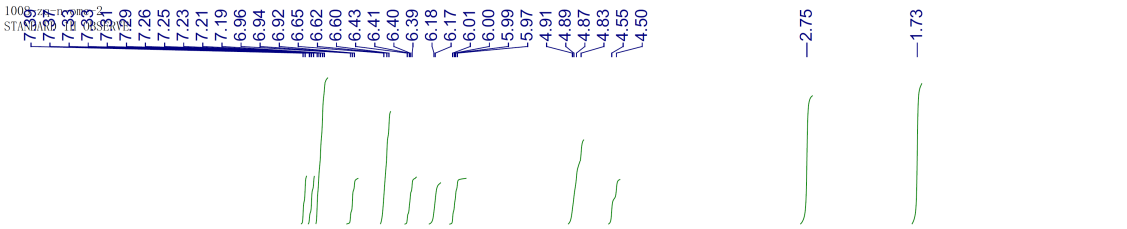

Nov14-2018-F400-ZQ-N-CF3
62.25
O
Ph
O
CF3
N
Me
2o
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

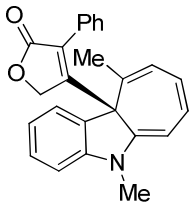

7.37
7.35
7.28
7.27
7.26
7.25
7.24
7.24
7.23
7.21
7.19
6.96
6.94
6.94
6.68
6.66
6.66
6.57
6.55
6.33
6.31
6.09
5.24
5.21
4.98
4.97
4.87
4.83
4.44
4.40
2.69
2.02
O
O
Ph
Me
N
Me
2p
0.99
4.21
1.05
1.89
0.99
0.97
0.97
0.97
0.96
1.01
0.98
2.94
3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Jun19-2018-c400-zq-199-
173.99
162.32
145.97
140.79
133.66
130.54
130.42
129.34
129.01
128.58
127.97
127.52
127.37
123.12
120.08
110.99
107.12
94.60
77.48
77.16
76.84
71.75
52.33
29.15
24.24
O
O
Ph
Me
N
Me
2p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

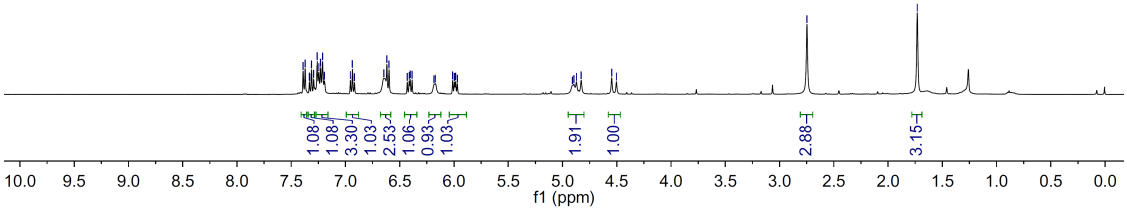

2q
2q'
f1 (ppm)


2q
2q'
f1 (ppm)

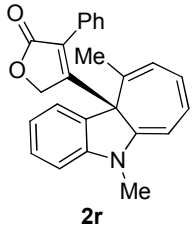

7.33
7.29
7.26
7.25
7.23
7.21
7.19
6.96
6.94
6.92
6.65
6.62
6.60
6.43
6.41
6.40
6.39
6.18
6.17
6.01
6.00
5.99
5.97
4.91
4.89
4.87
4.83
4.55
4.50
2.75
1.73


O
Ph
Me
O
N
Me

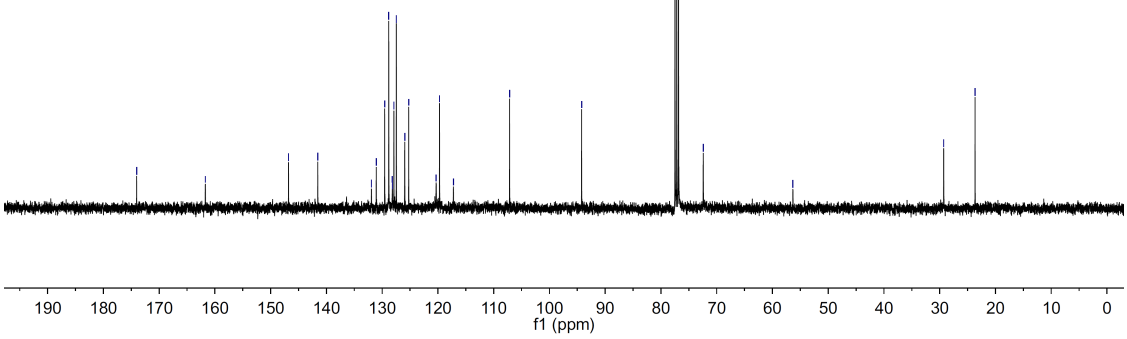
2r

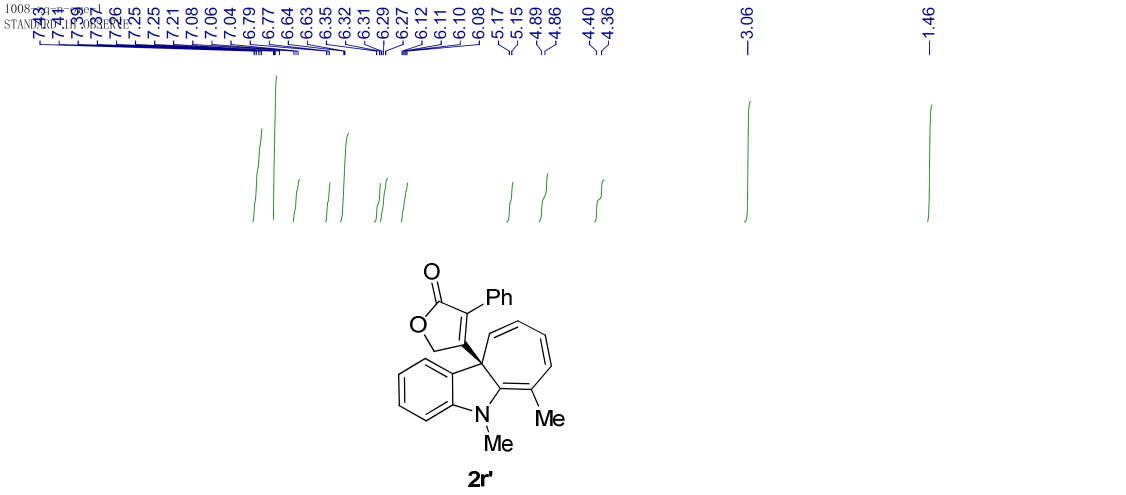

1.08
1.08
3.30
1.03
2.53
1.06
0.93
1.03
1.91
1.00
2.88
3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


174.03
161.72
146.79
141.54
131.06
129.55
128.82
127.90
127.46
125.95
125.23
120.33
119.71
107.14
94.22
77.48
77.16
76.84
72.41
56.34
29.28
23.66


O
Ph
Me
O
N
Me

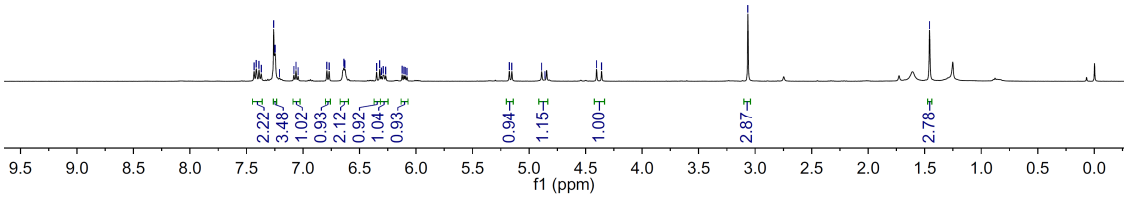
2r

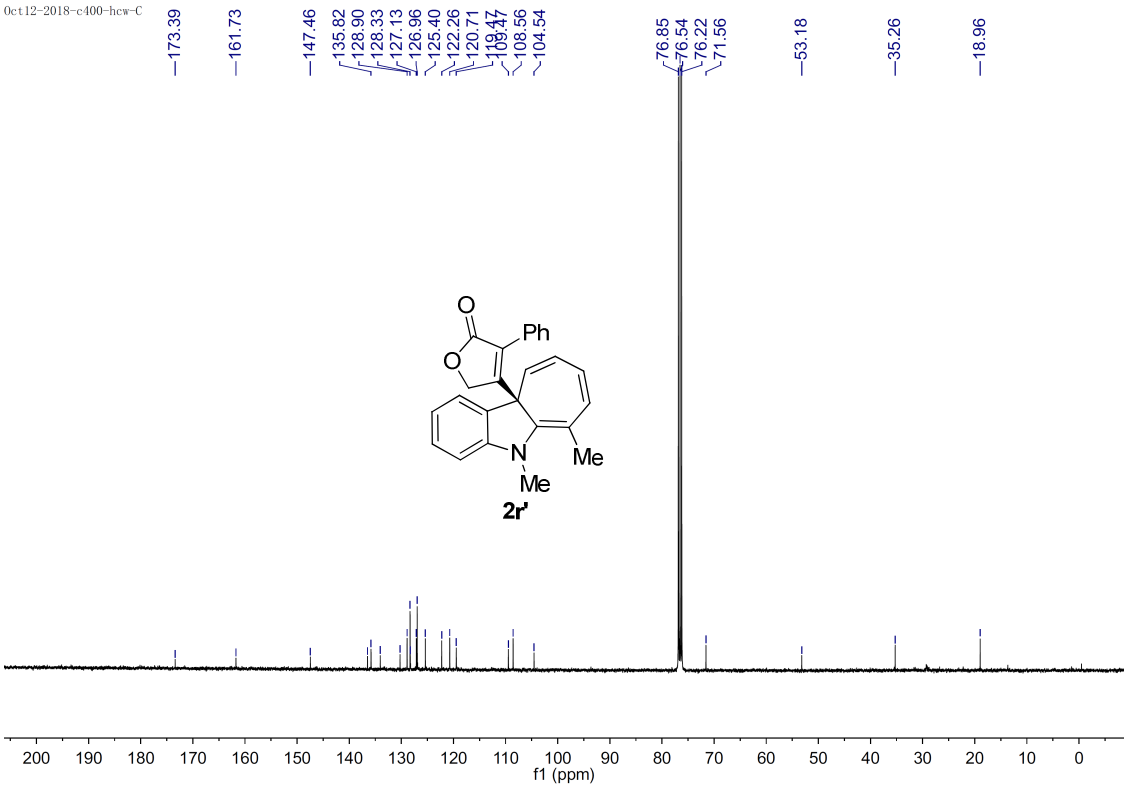

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.43
7.41
7.39
7.37
7.26
7.25
7.25
7.21
7.08
7.06
7.04
6.79
6.77
6.64
6.63
6.35
6.32
6.31
6.29
6.27
6.12
6.11
6.10
6.08
5.17
5.15
4.89
4.86
4.40
4.36
3.06
1.46

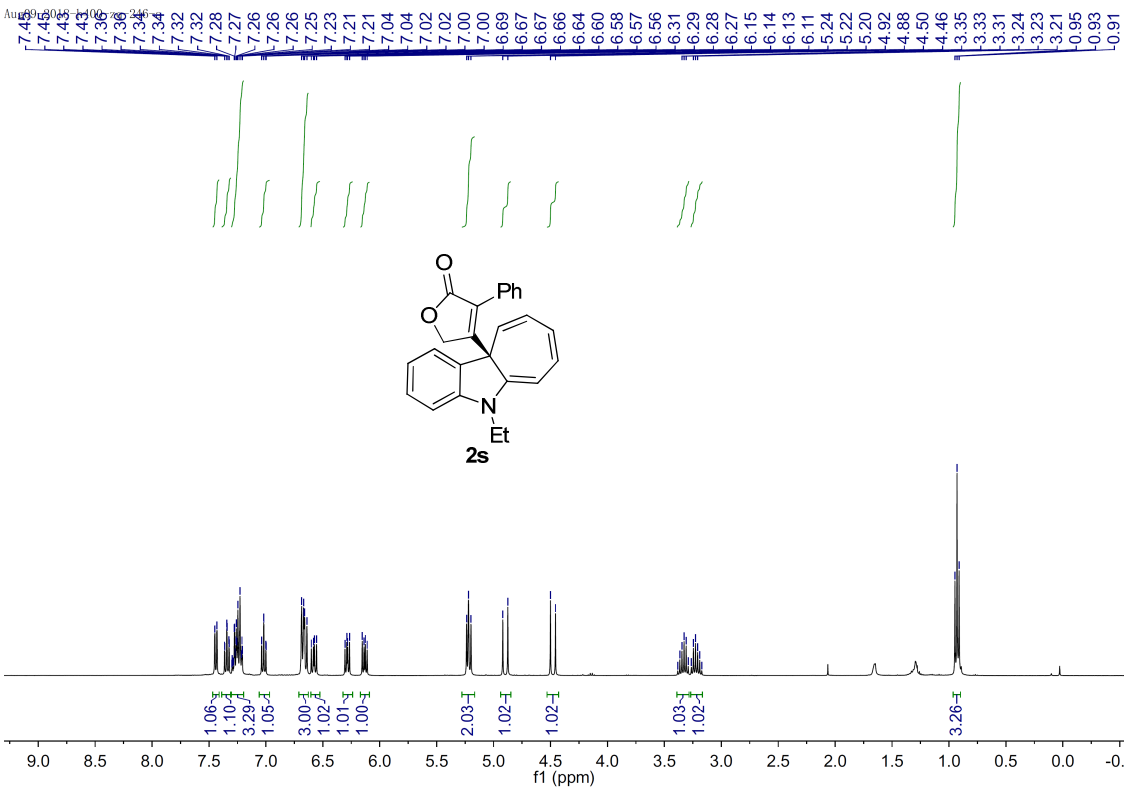
O
Ph
O
N
Me
Me

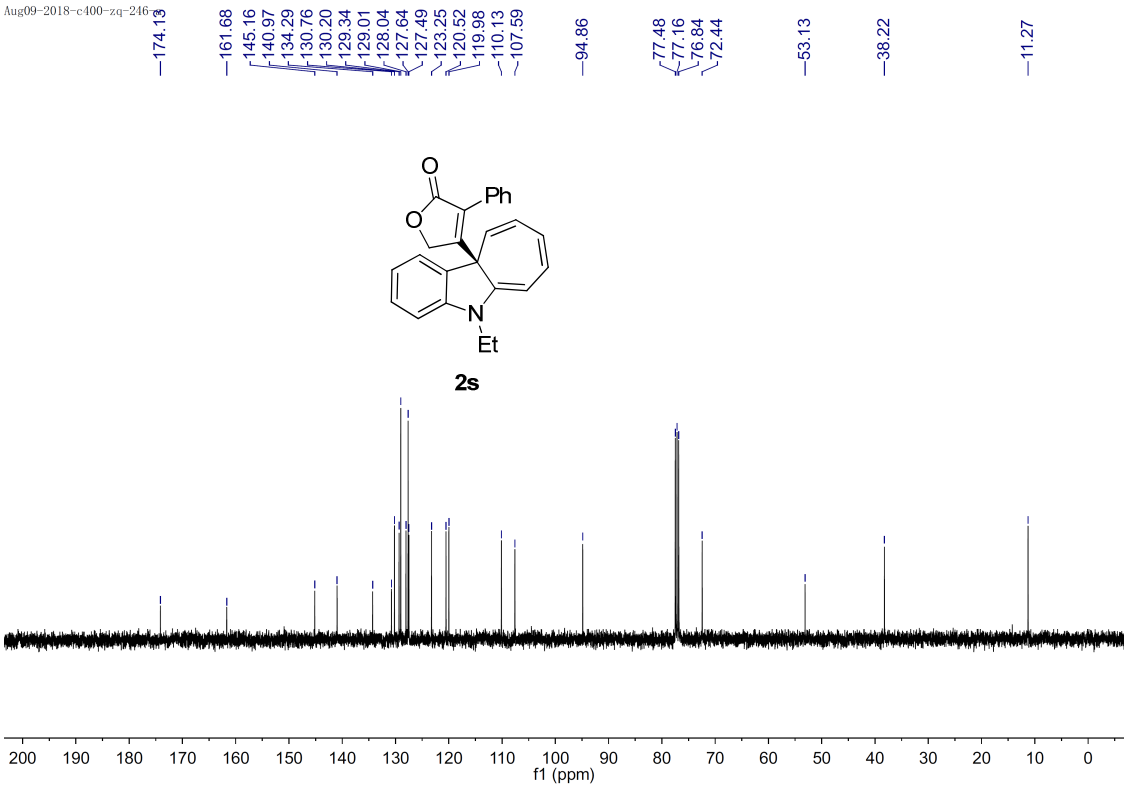
2r'

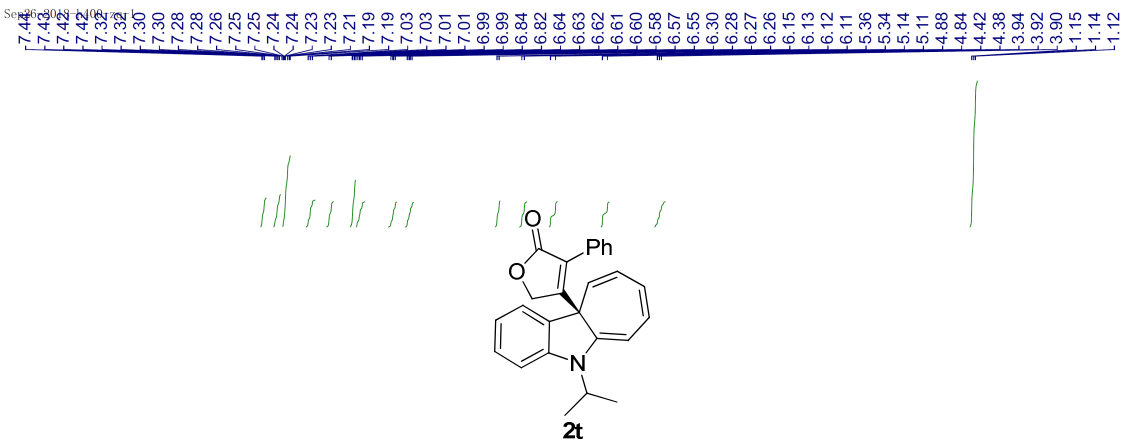

2.22
3.48
1.02
0.93
2.12
0.92
1.04
0.93
0.94
1.15
1.00
2.87
2.78
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

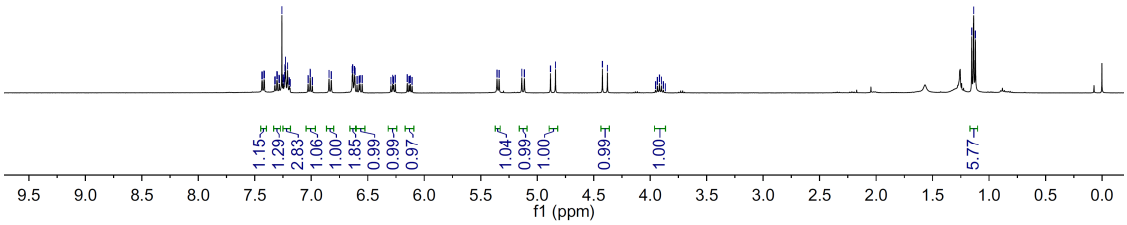

0ct12-2018-c400-hcw-C
173.39
161.73
147.46
135.82
128.90
128.33
127.13
126.96
125.40
122.26
120.71
119.47
109.47
108.56
104.54
76.85
76.54
76.22
71.56
53.18
35.26
18.96
O
Ph
O
N
Me
Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

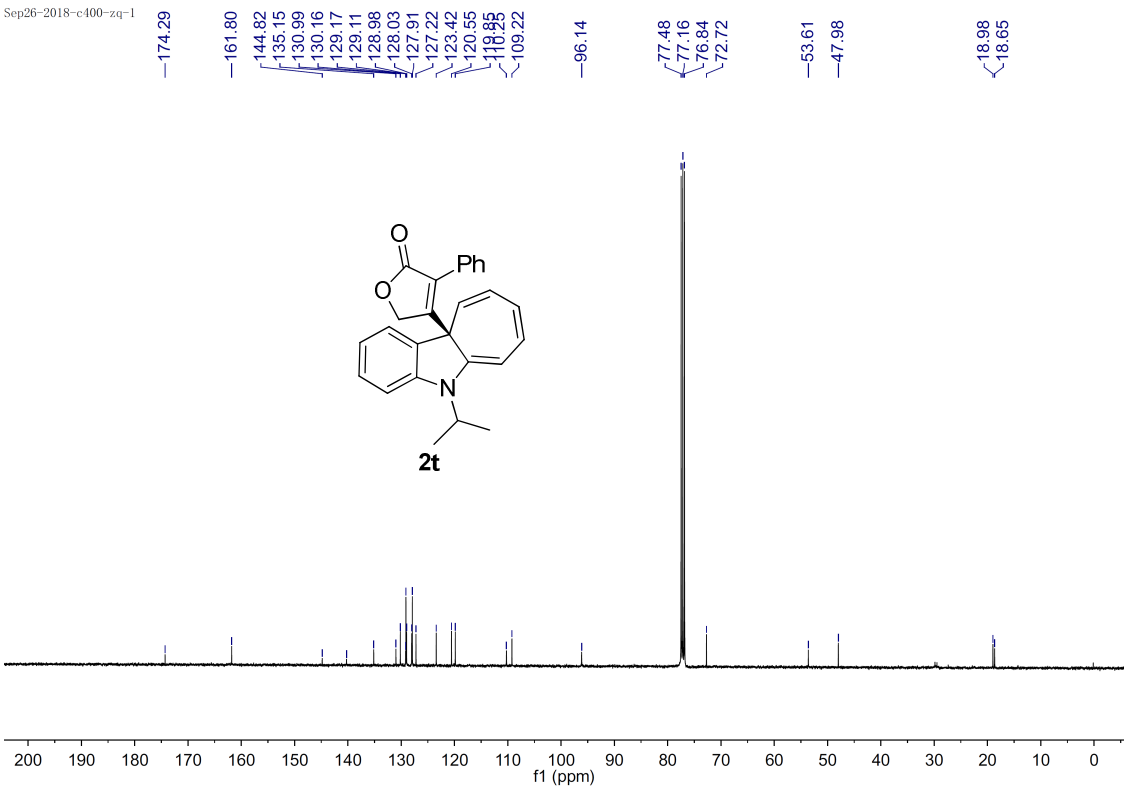
2r'

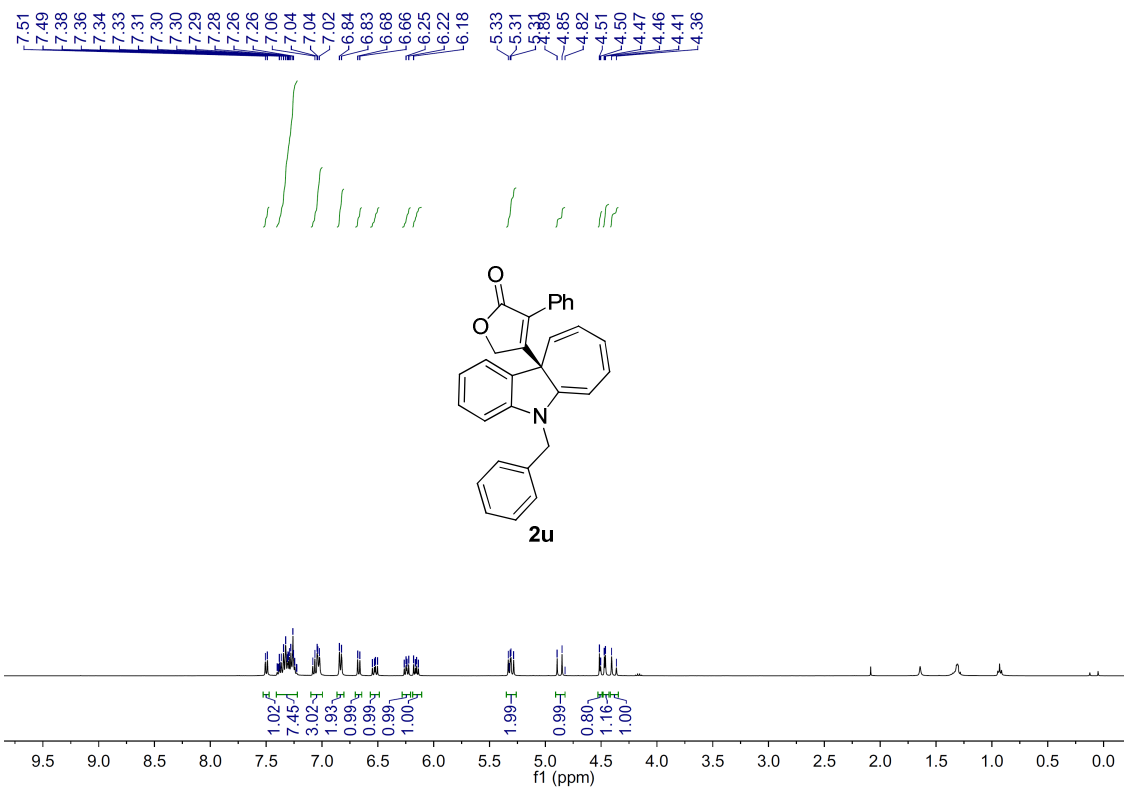

Ph
O
N
Et
2s
1.06
1.10
3.29
1.05
3.00
1.02
1.01
1.00
2.03
1.02
1.02
1.03
1.02
3.26
f1 (ppm)

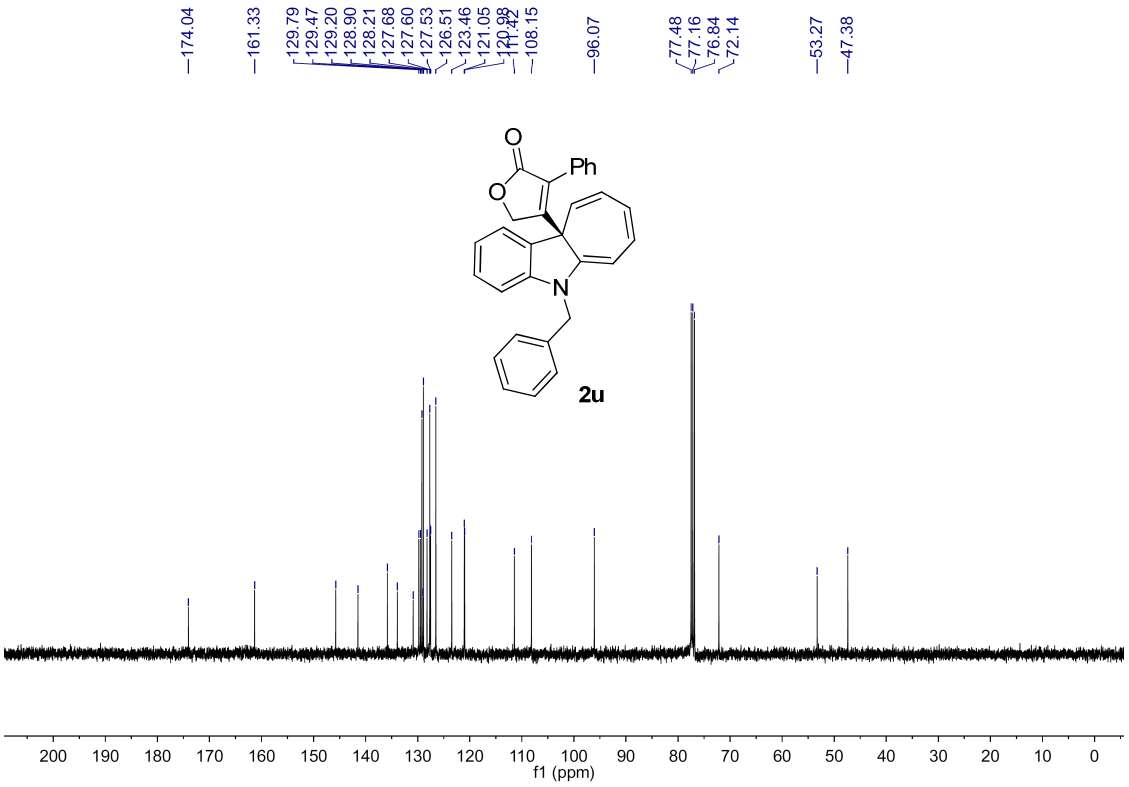

174.13
161.68
145.16
140.97
134.29
130.76
130.20
129.34
129.01
128.04
127.64
127.49
123.25
120.52
119.98
110.13
107.59
94.86
77.48
77.16
76.84
72.44
53.13
38.22
11.27
Ph
O
N
Et
2s
f1 (ppm)

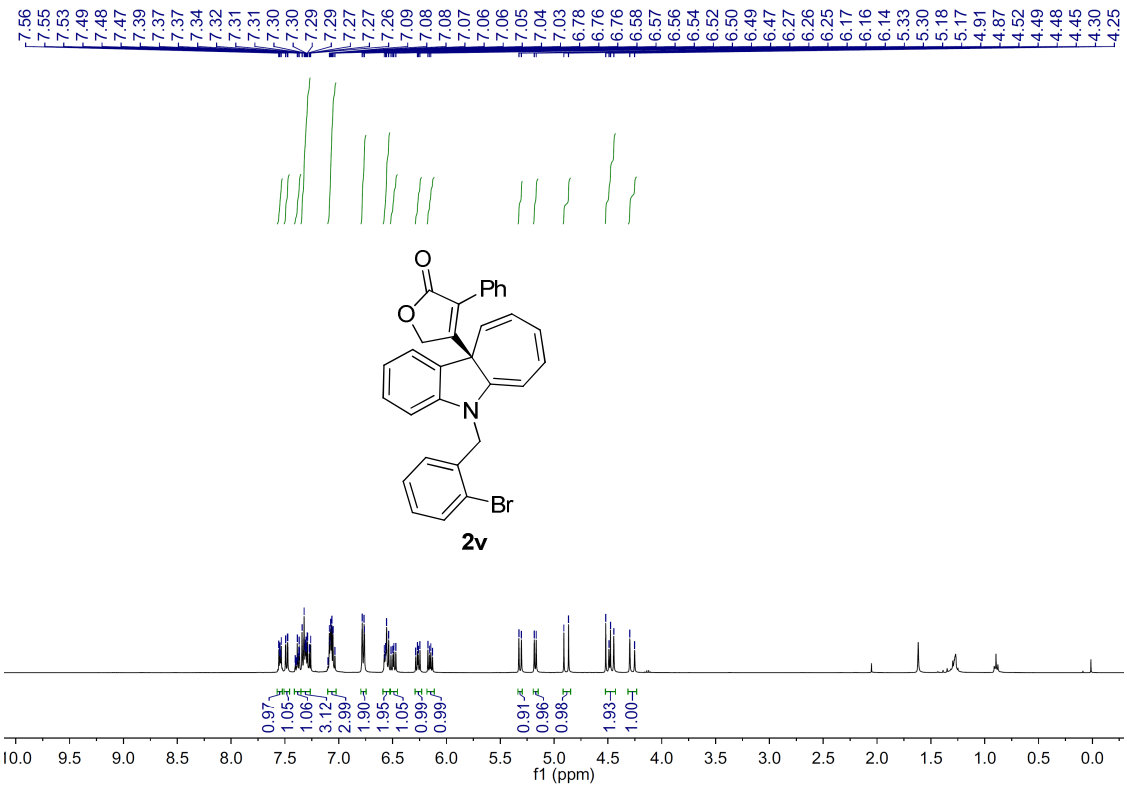

O
Ph
O
N
2t

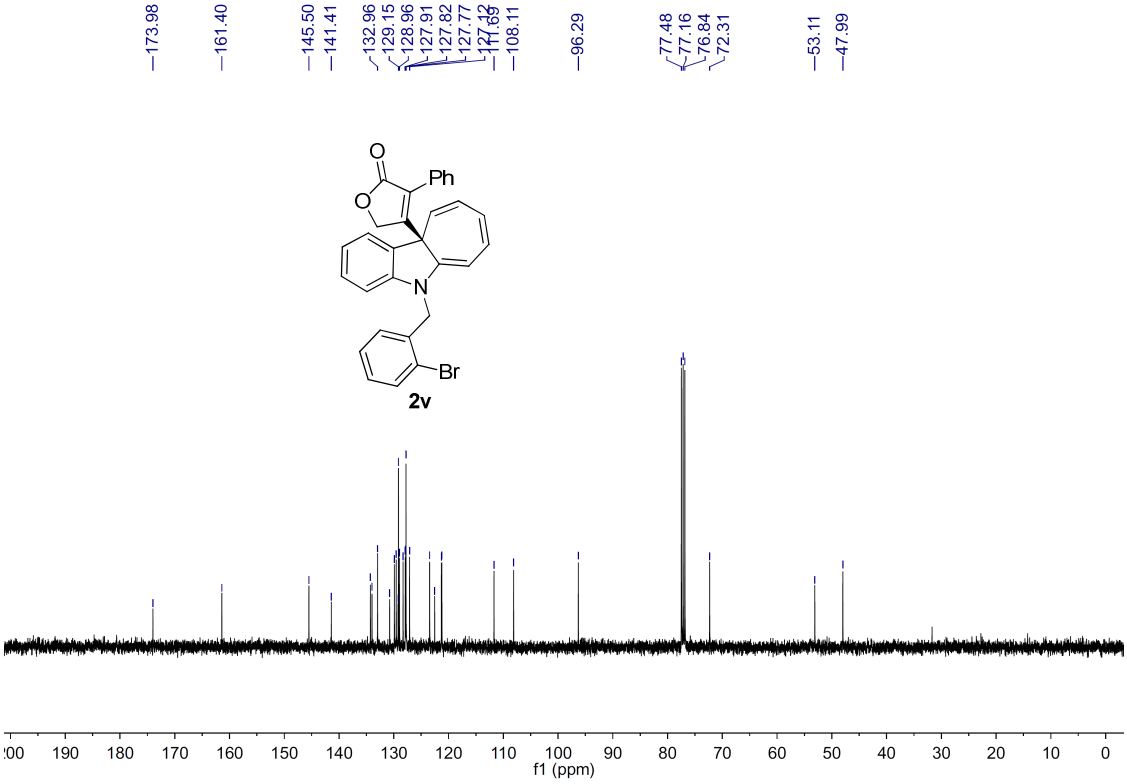

1.15
1.29
2.83
1.06
1.00
1.85
0.99
0.99
0.97
1.04
0.99
1.00
0.99
1.00
5.77
f1 (ppm)

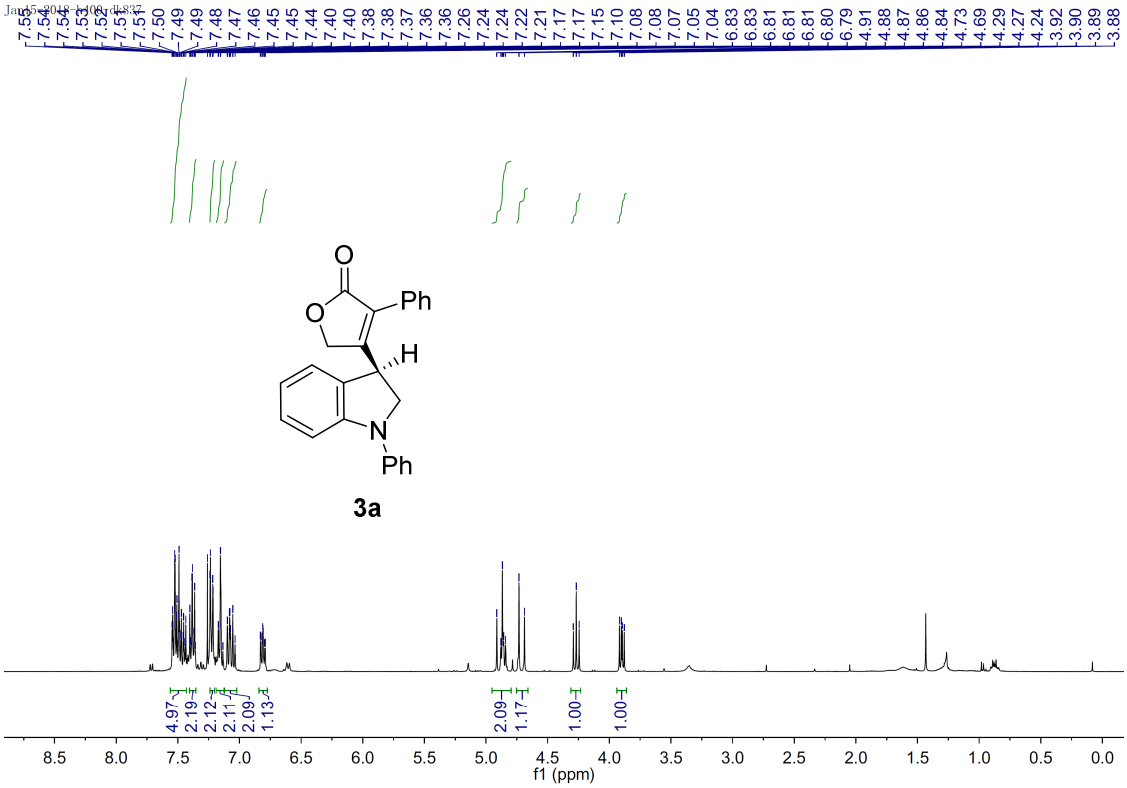

Sep26-2018-c400-zq-1
174.29
161.80
144.82
135.15
130.99
130.16
129.17
129.11
128.98
128.03
127.91
127.22
123.42
120.55
119.85
110.25
109.22
96.14
77.48
77.16
76.84
72.72
53.61
47.98
18.98
18.65
O
Ph
O
N
2t
f1 (ppm)

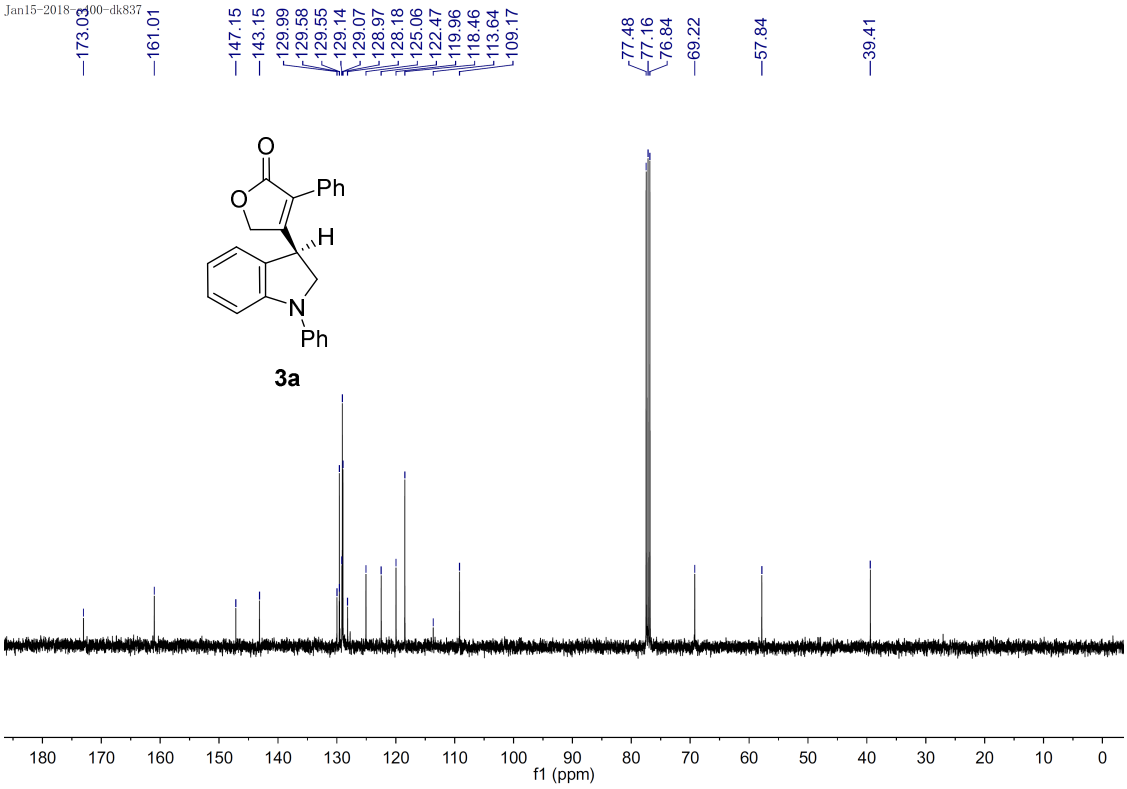

7.51
7.49
7.38
7.36
7.34
7.33
7.31
7.30
7.30
7.29
7.28
7.26
7.26
7.06
7.04
7.04
7.02
6.84
6.83
6.68
6.66
6.25
6.22
6.18
5.33
5.31
5.31
4.89
4.85
4.82
4.51
4.50
4.47
4.46
4.41
4.36
O
Ph
O
N
2u
1.02
7.45
3.02
1.93
0.99
0.99
0.99
1.00
1.99
0.99
0.80
1.16
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

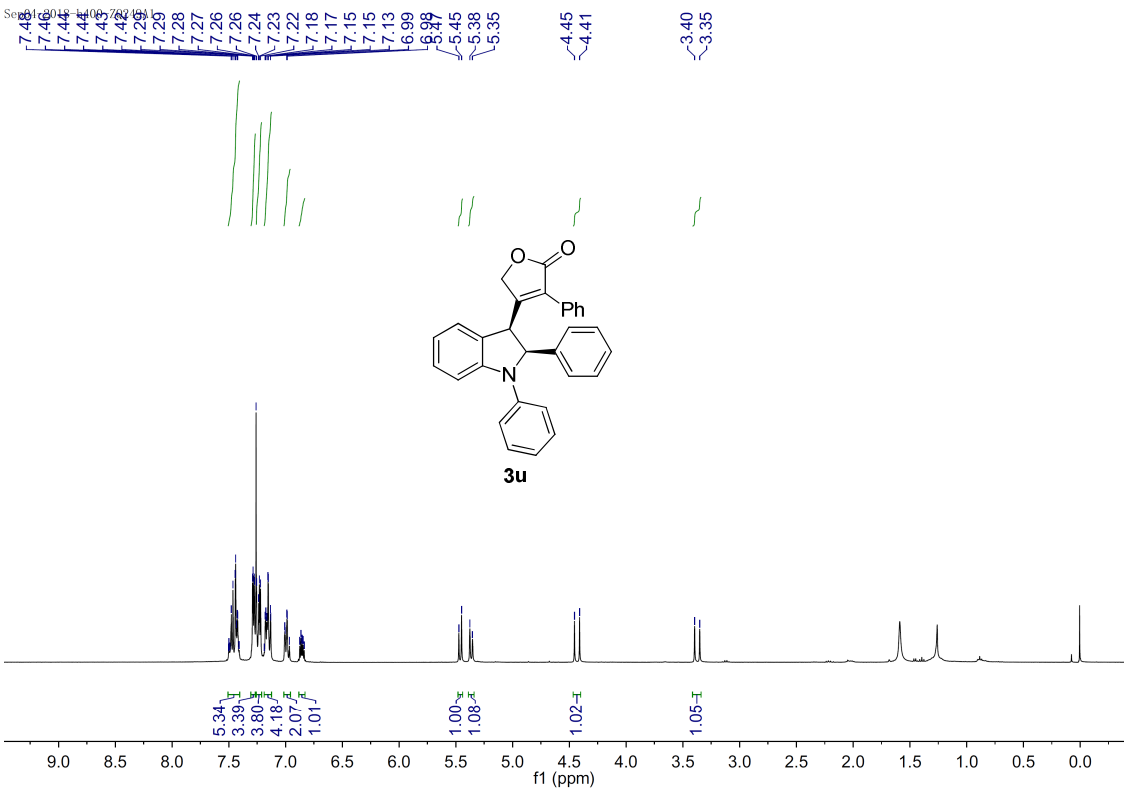

174.04
161.33
129.79
129.47
129.20
128.90
128.21
127.68
127.60
127.53
126.51
123.46
121.05
120.98
111.42
108.15
96.07
77.48
77.16
76.84
72.14
53.27
47.38
O
Ph
O
N
2u
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.56
7.55
7.53
7.49
7.48
7.47
7.39
7.37
7.37
7.34
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.27
7.27
7.26
7.09
7.08
7.08
7.07
7.06
7.06
7.05
7.04
7.03
6.78
6.76
6.76
6.58
6.57
6.56
6.54
6.52
6.50
6.49
6.47
6.27
6.26
6.25
6.17
6.16
6.14
5.33
5.30
5.18
5.17
4.91
4.87
4.52
4.49
4.48
4.45
4.30
4.25
O
Ph
O
N
Br
2v
0.97
1.05
1.06
3.12
2.99
1.90
1.95
1.05
0.99
0.99
0.91
0.96
0.98
1.93
1.00
10.0 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)

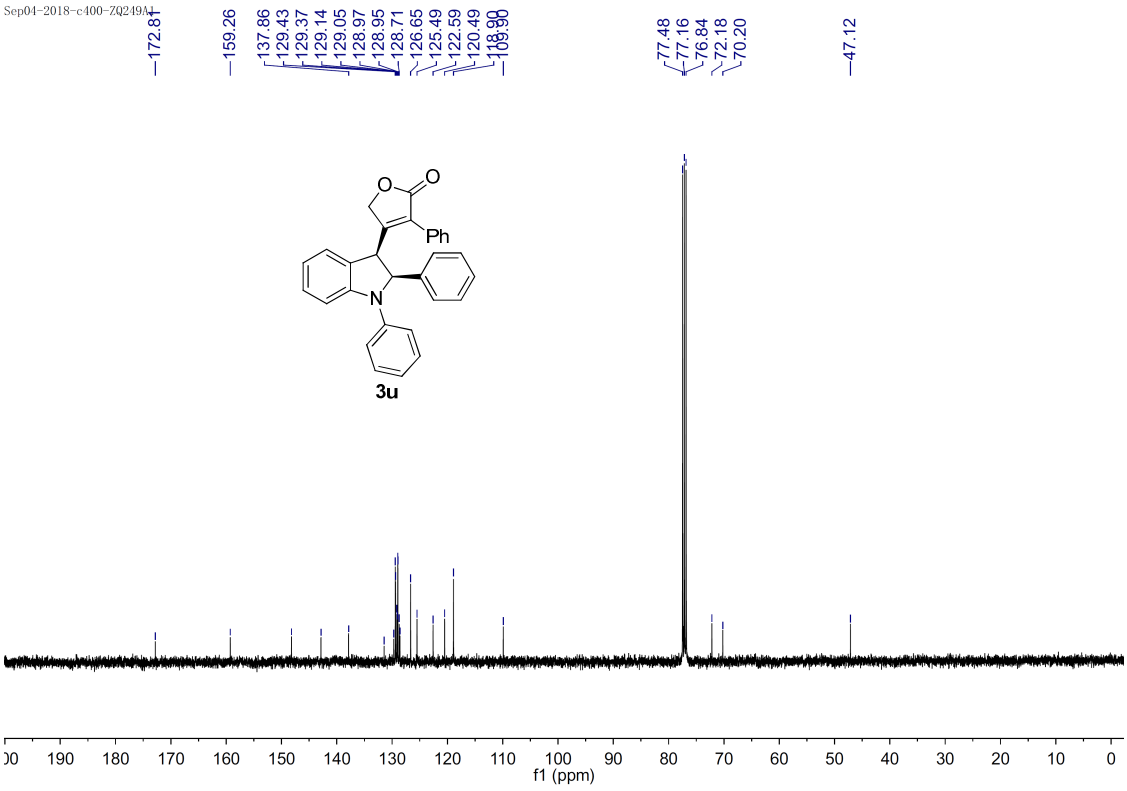

173.98
161.40
145.50
141.41
132.96
129.15
128.96
127.91
127.82
127.77
108.11
96.29
77.48
77.16
76.84
72.31
53.11
47.99
O
Ph
O
N
Br
2v
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.55 7.54 7.54 7.53 7.52 7.51 7.51 7.50 7.49 7.49 7.48 7.47 7.46 7.45 7.45 7.44 7.40 7.40 7.38 7.38 7.37 7.36 7.36 7.26 7.24 7.24 7.22 7.21 7.17 7.17 7.15 7.10 7.08 7.08 7.07 7.05 7.04 6.83 6.83 6.81 6.81 6.80 6.79 4.91 4.88 4.87 4.86 4.84 4.73 4.69 4.29 4.27 4.24 3.92 3.90 3.89 3.88
O
O
Ph
H
N
Ph
3a
4.97 2.19 2.12 2.11 2.09 1.13 2.09 1.17 1.00 1.00
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)

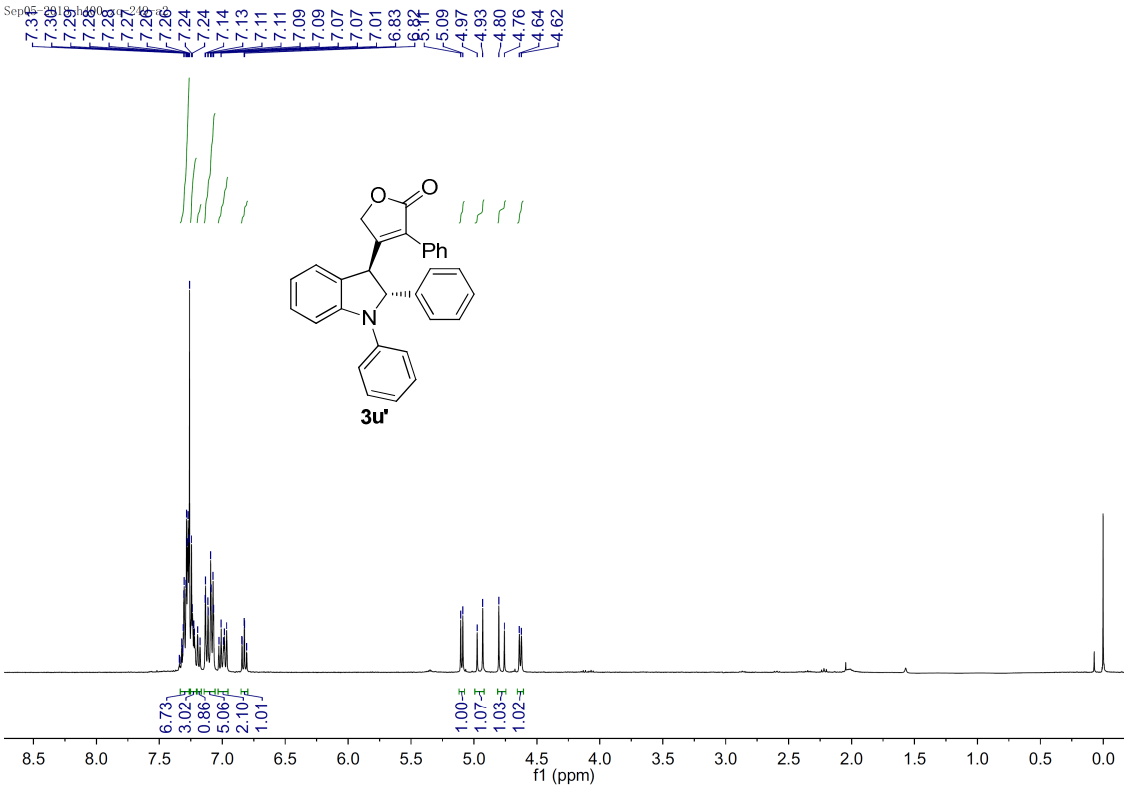

173.03 161.01 147.15 143.15 129.99 129.58 129.55 129.14 129.07 128.97 128.18 125.06 122.47 119.96 118.46 113.64 109.17 77.48 77.16 76.84 69.22 57.84 39.41
O
O
Ph
H
N
Ph
3a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

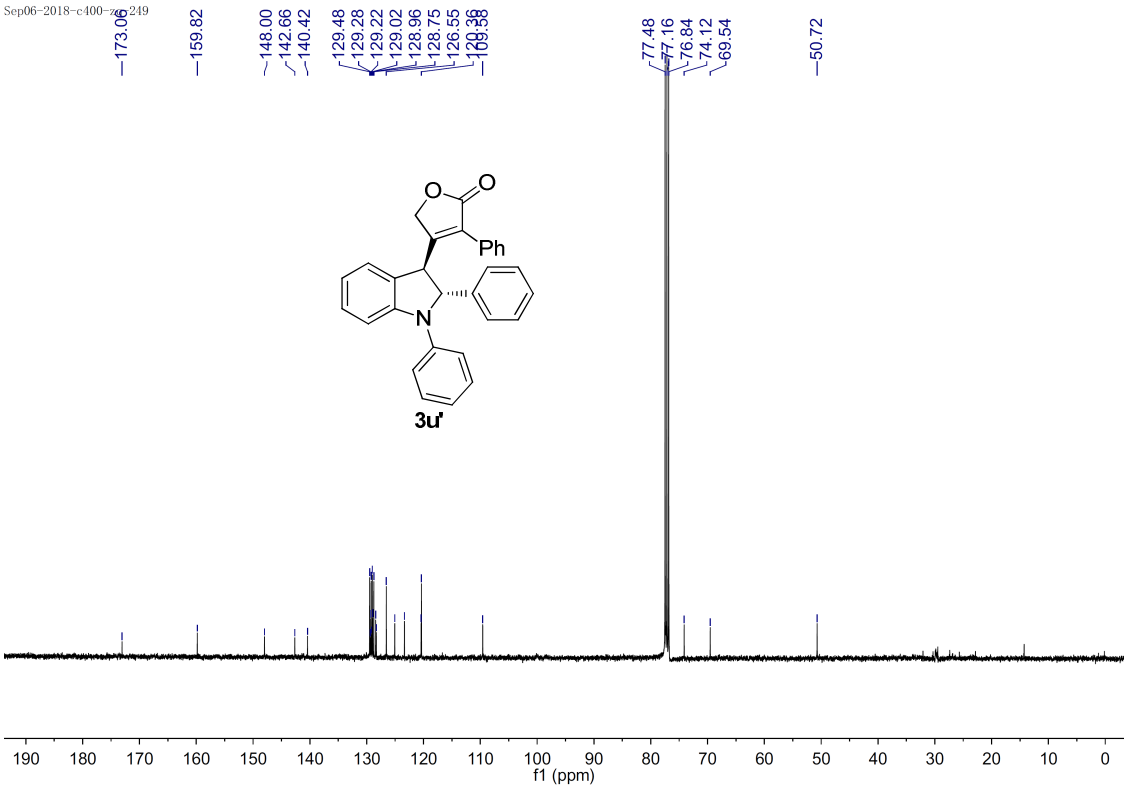

7.48
7.46
7.44
7.44
7.43
7.42
7.29
7.29
7.28
7.27
7.26
7.26
7.24
7.23
7.22
7.18
7.17
7.15
7.15
7.13
6.99
6.98
5.47
5.45
5.38
5.35
4.45
4.41
3.40
3.35
O
O
Ph
N
5.34
3.39
3.80
4.18
2.07
1.01
1.00
1.08
1.02
1.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

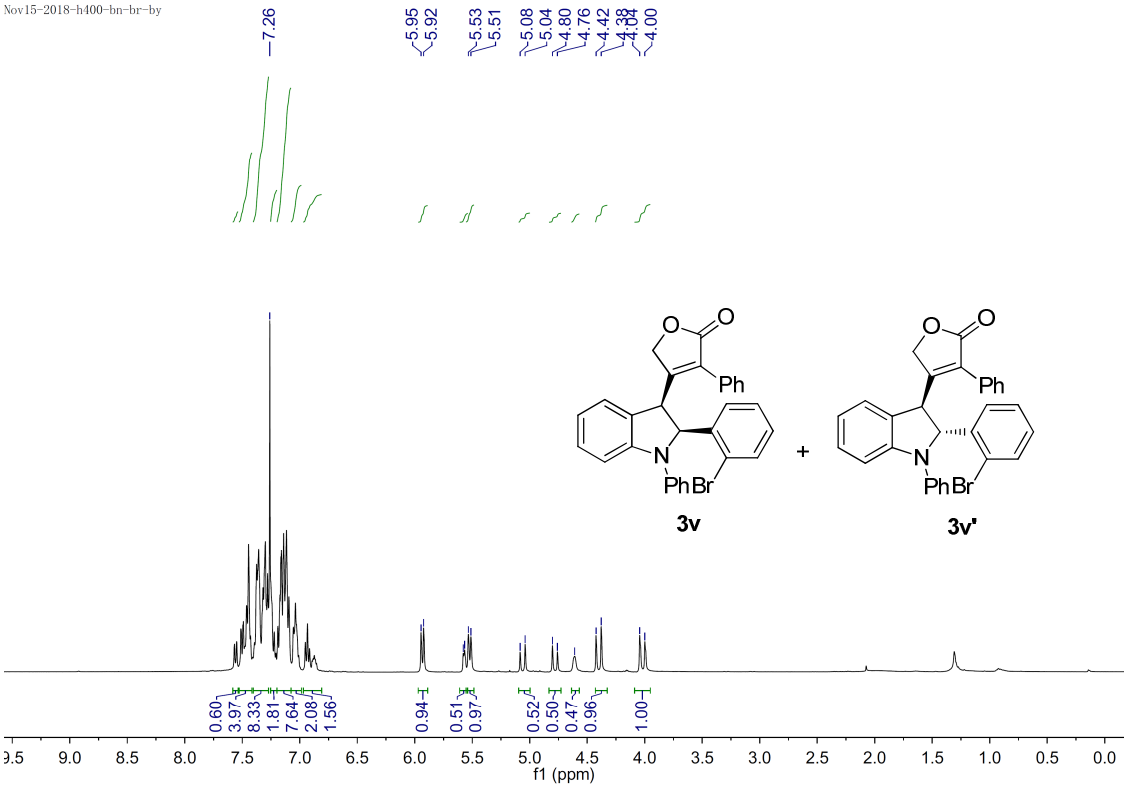
3u

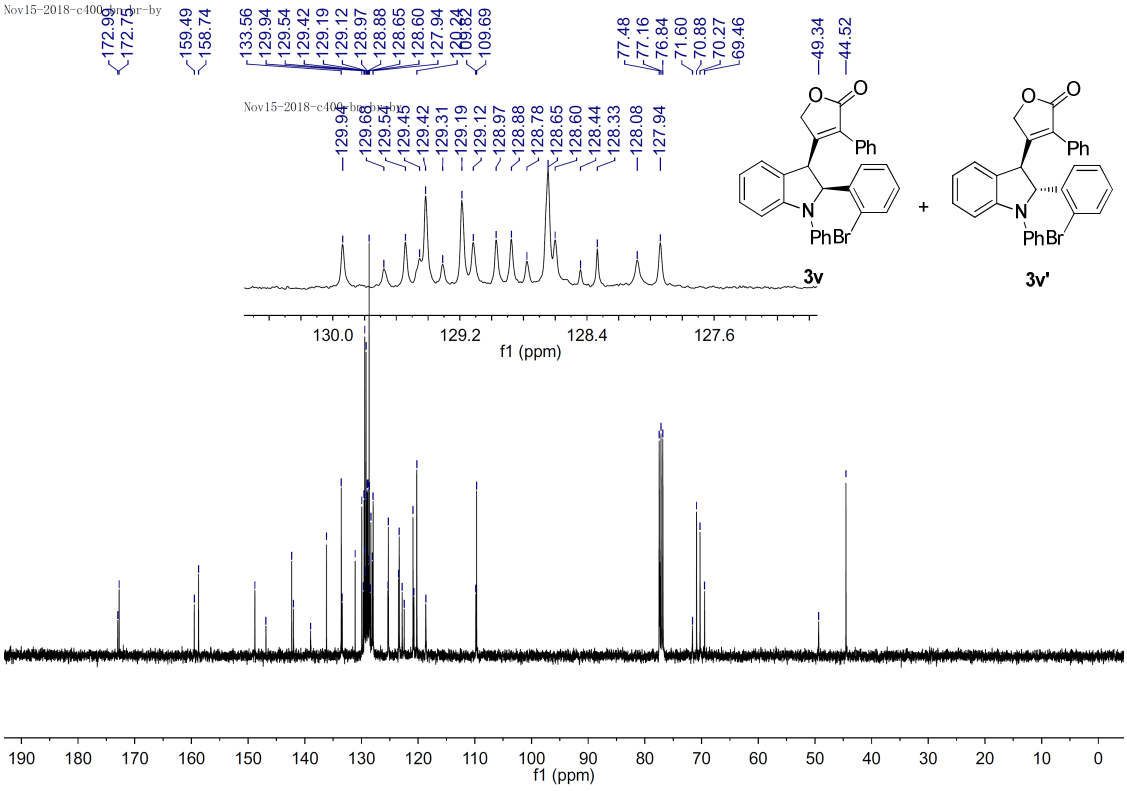

Sep04-2018-c400-ZQ249A1
172.81
159.26
137.86
129.43
129.37
129.14
129.05
128.97
128.95
128.71
126.65
125.49
122.59
120.49
118.90
109.90
77.48
77.16
76.84
72.18
70.20
47.12
O
O
Ph
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3u

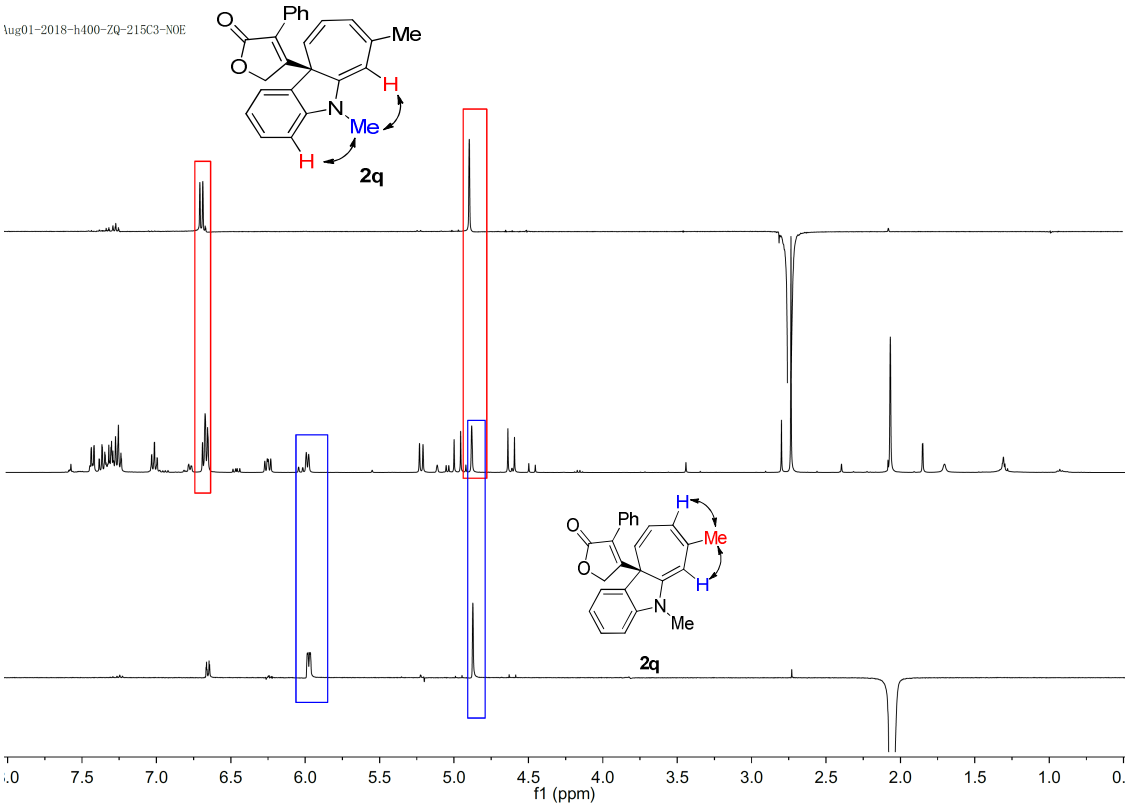

7.31
7.30
7.29
7.28
7.27
7.26
7.24
7.24
7.14
7.13
7.11
7.11
7.09
7.09
7.07
7.07
7.01
6.83
6.82
5.11
5.09
4.97
4.93
4.80
4.76
4.64
4.62
O
O
Ph
N
3u'
6.73
3.02
0.86
5.06
2.10
1.01
1.00
1.07
1.03
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Sep06-2018-c400-zc-249
173.06
159.82
148.00
142.66
140.42
129.48
129.28
129.22
129.02
128.96
128.75
126.55
120.36
109.58
77.48
77.16
76.84
74.12
69.54
50.72
O
O
Ph
N
3u'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

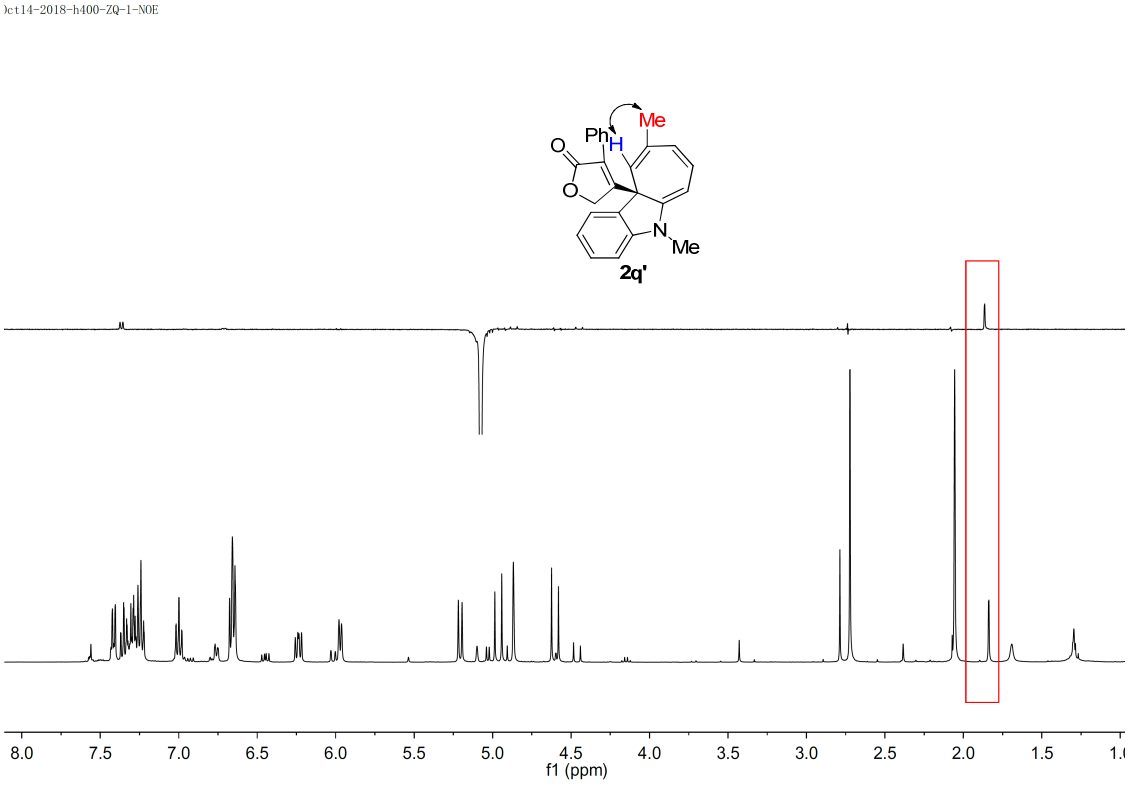

Nov15-2018-h400-bn-br-by
7.26
5.95
5.92
5.53
5.51
5.08
5.04
4.80
4.76
4.42
4.38
4.04
4.00
0.60
3.97
8.33
1.81
7.64
2.08
1.56
0.94
0.51
0.97
0.52
0.50
0.47
0.96
1.00
f1 (ppm)
Ph
PhBr
3v
3v'


Nov15-2018-c400-bn-br-by
172.99
172.75
159.49
158.74
133.56
129.94
129.54
129.42
129.19
129.12
128.97
128.88
128.65
128.60
127.94
109.82
109.69
77.48
77.16
76.84
71.60
70.88
70.27
69.46
49.34
44.52
129.94
129.66
129.54
129.45
129.42
129.31
129.19
129.12
128.97
128.88
128.78
128.65
128.60
128.44
128.33
128.08
127.94
130.0
129.2
128.4
127.6
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
Ph
PhBr
3v
3v'

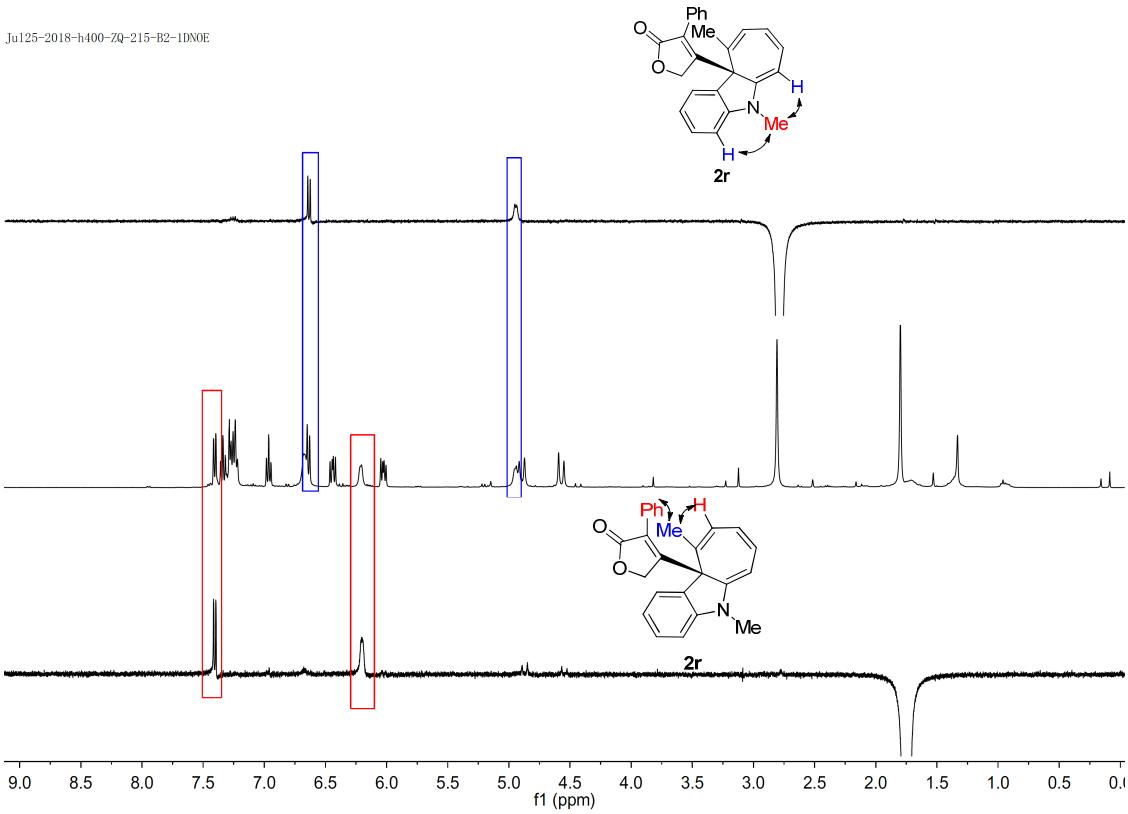
1D NOE NMR Analysis of 2q.



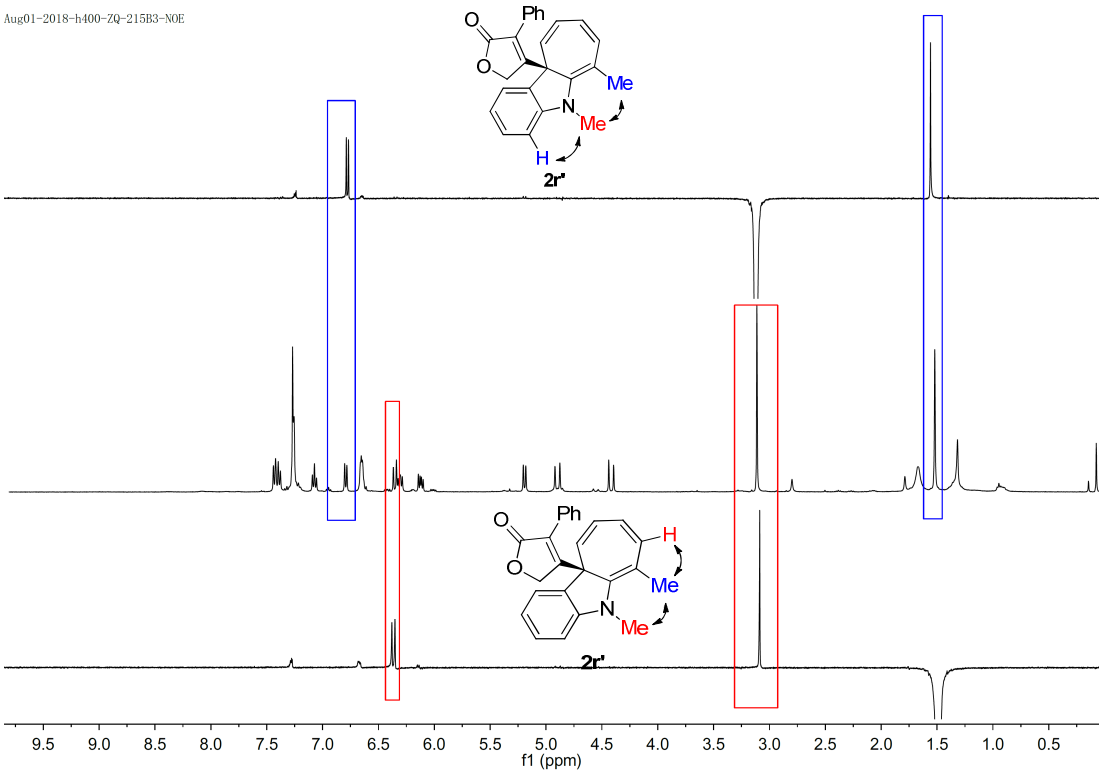
1D NOE NMR Analysis of 2q'.

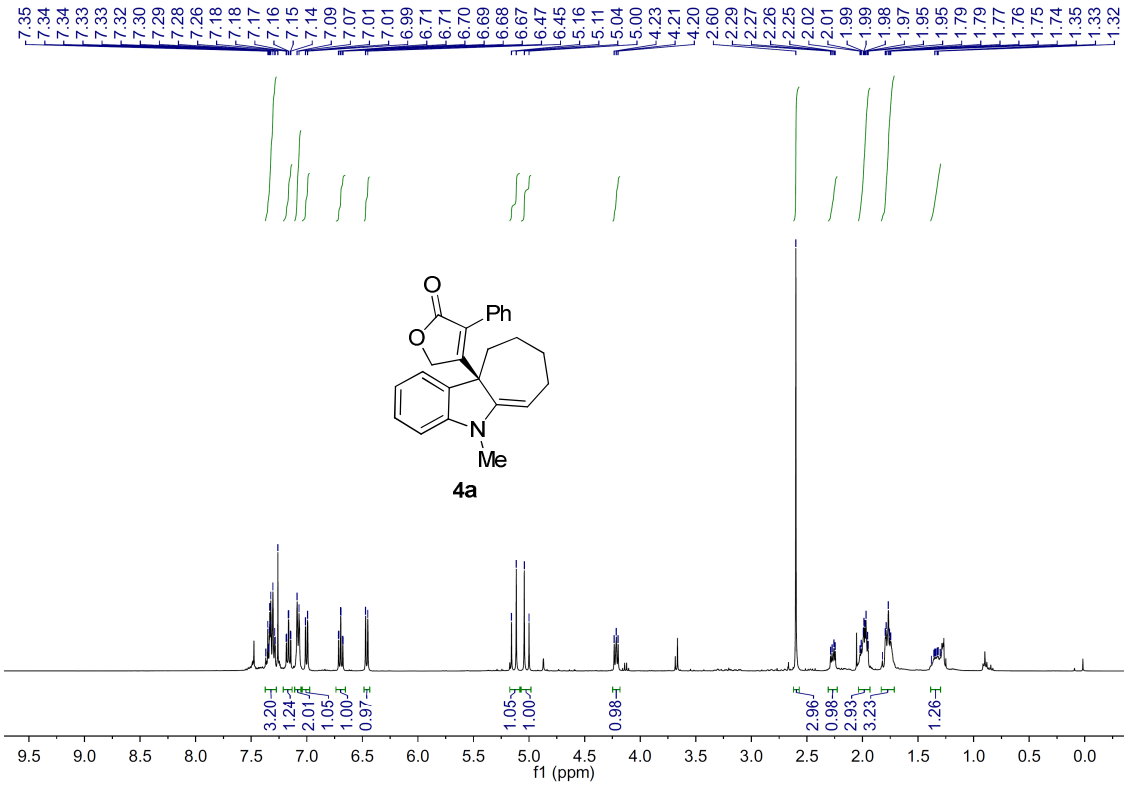


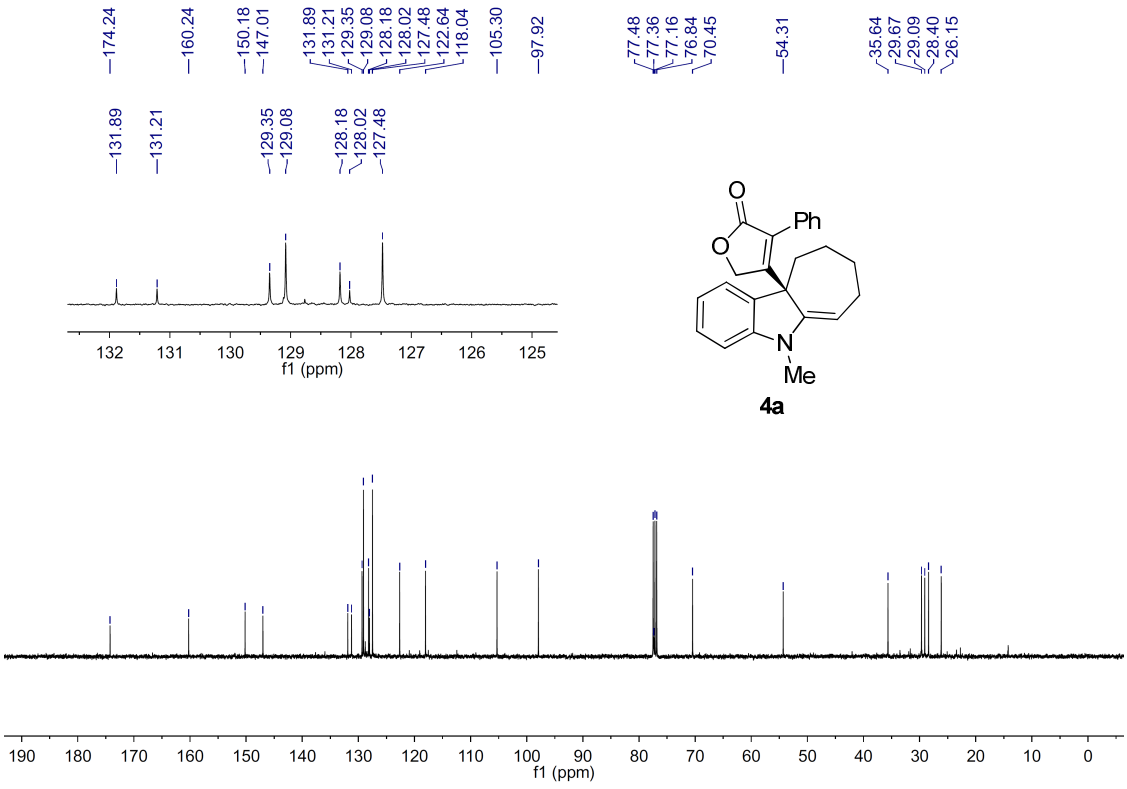
1D NOE NMR Analysis of 2r.



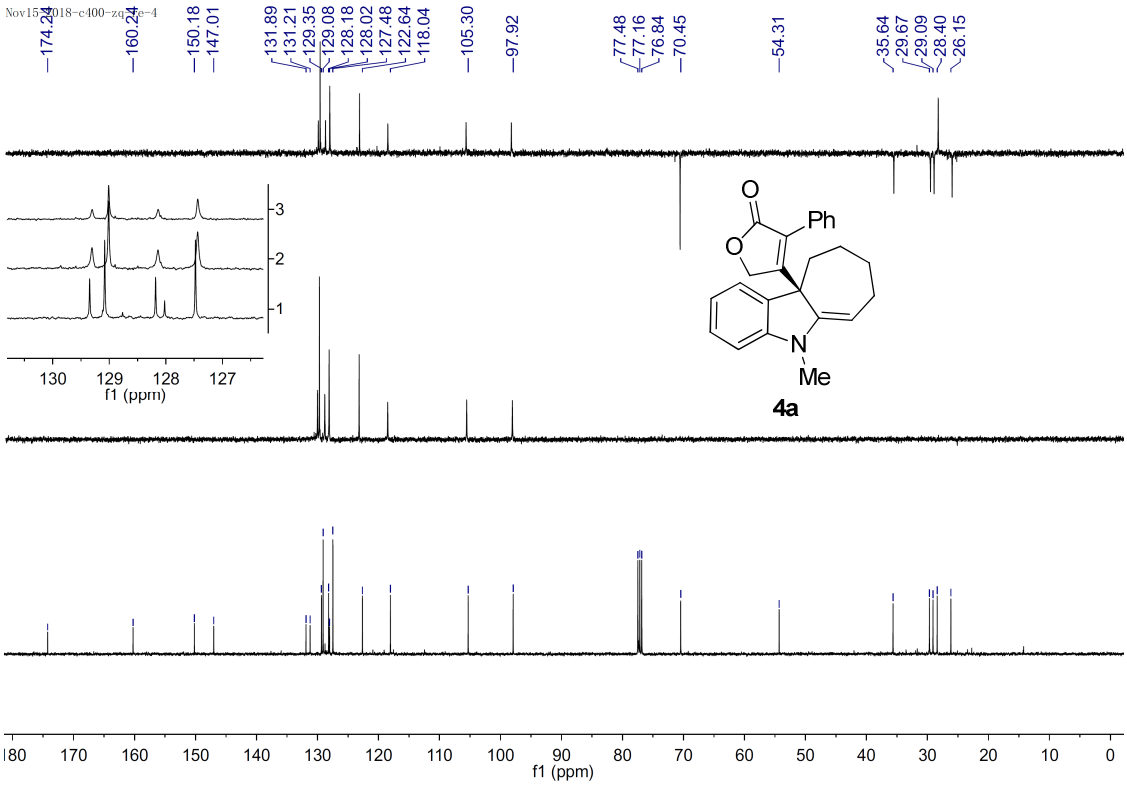
1D NOE NMR Analysis of 2r'

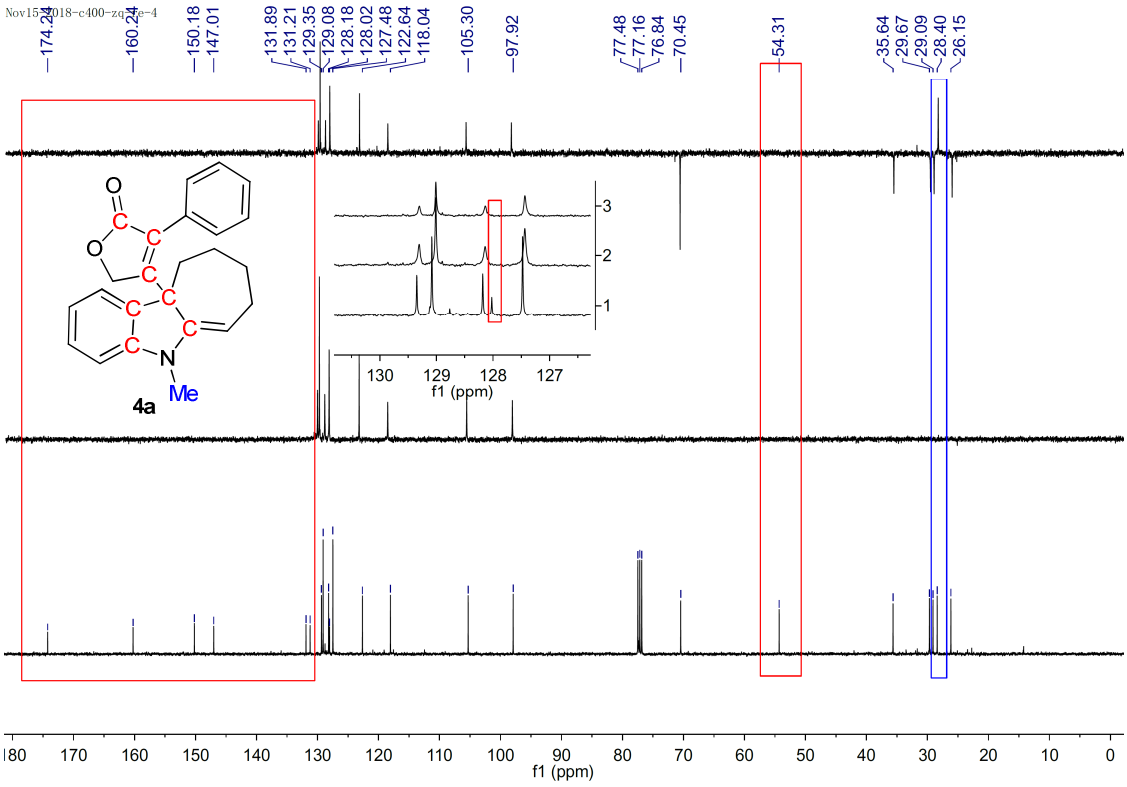


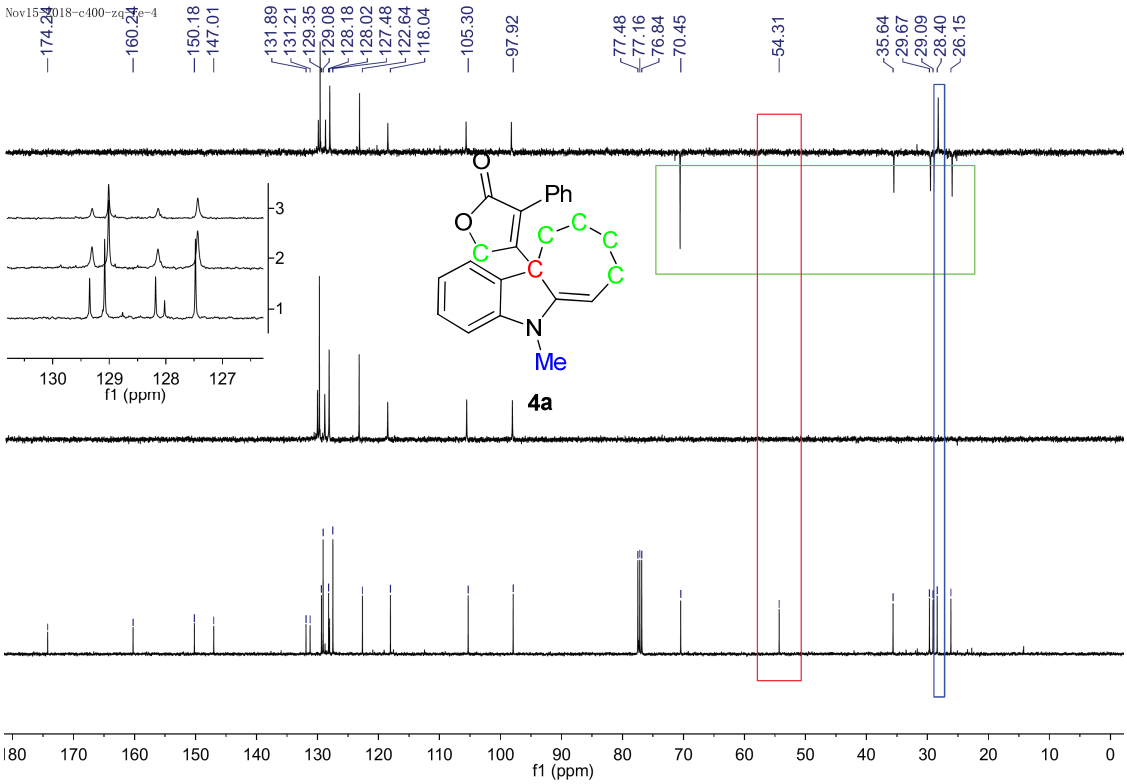

7.35 7.34 7.34 7.33 7.33 7.32 7.30 7.29 7.28 7.26 7.18 7.18 7.17 7.16 7.15 7.14 7.09 7.07 7.01 7.01 6.99 6.71 6.70 6.69 6.68 6.67 6.47 6.45 5.16 5.11 5.04 5.00 4.23 4.21 4.20 2.60 2.29 2.27 2.26 2.25 2.02 2.01 1.99 1.99 1.98 1.97 1.95 1.95 1.79 1.79 1.77 1.76 1.75 1.74 1.35 1.33 1.32
O
Ph
O
N
Me
4a
3.20 1.24 2.01 1.05 1.00 0.97 1.05 1.00 0.98 2.96 0.98 2.93 3.23 1.26
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)


174.24 160.24 150.18 147.01 131.89 131.21 129.35 129.08 128.18 128.02 127.48 122.64 118.04 105.30 97.92 77.48 77.36 77.16 76.84 70.45 54.31 35.64 29.67 29.09 28.40 26.15
131.89 131.21 129.35 129.08 128.18 128.02 127.48
132 131 130 129 128 127 126 125
f1 (ppm)
O
Ph
O
N
Me
4a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

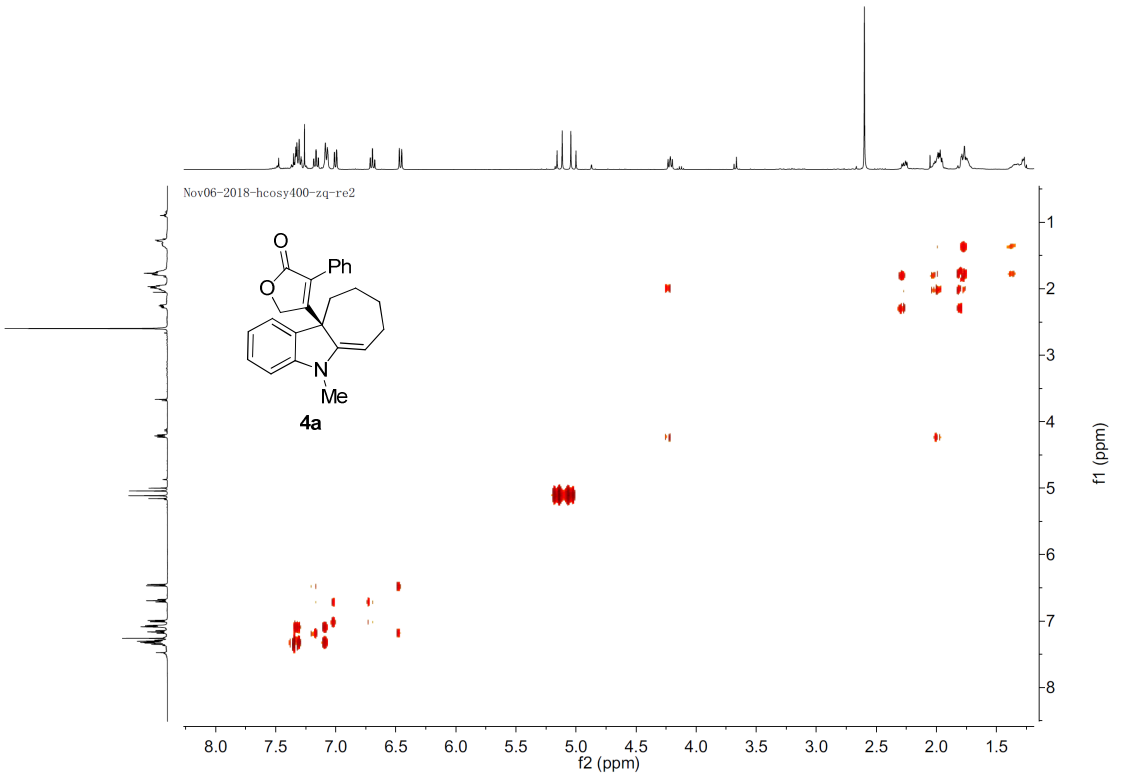
Dapt-135 / 90 NMR spectra of **4a**

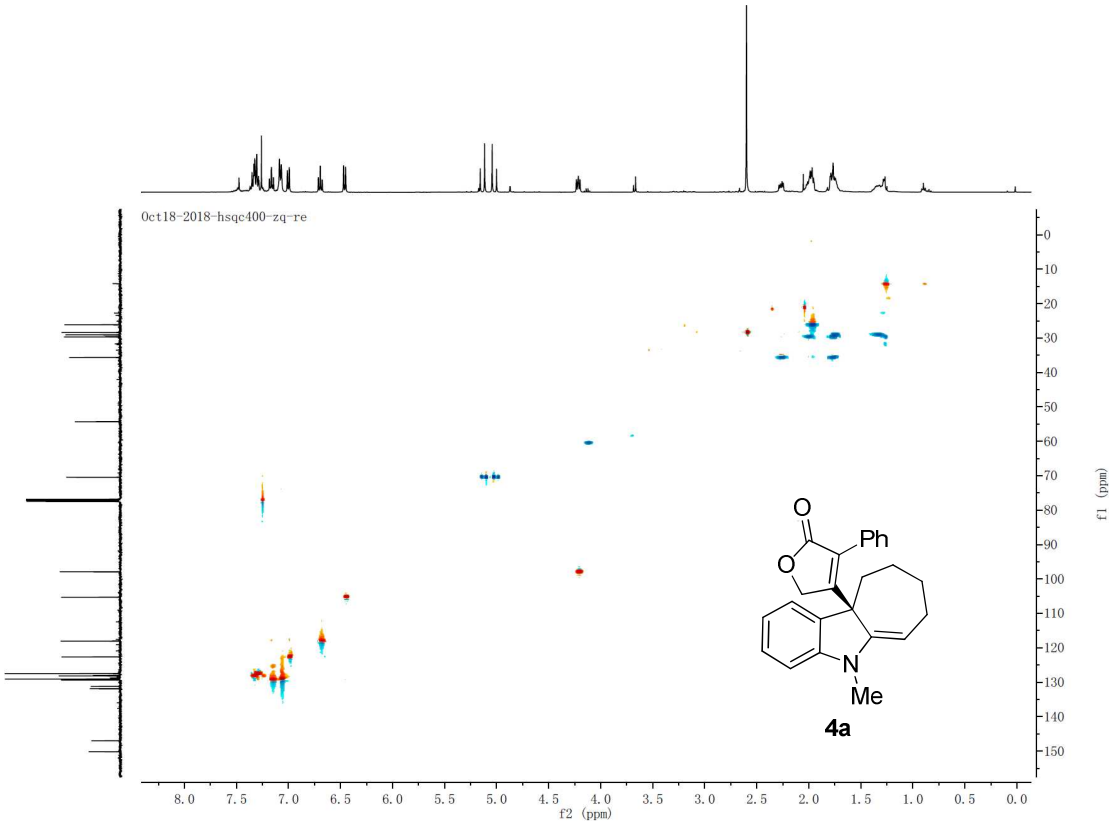




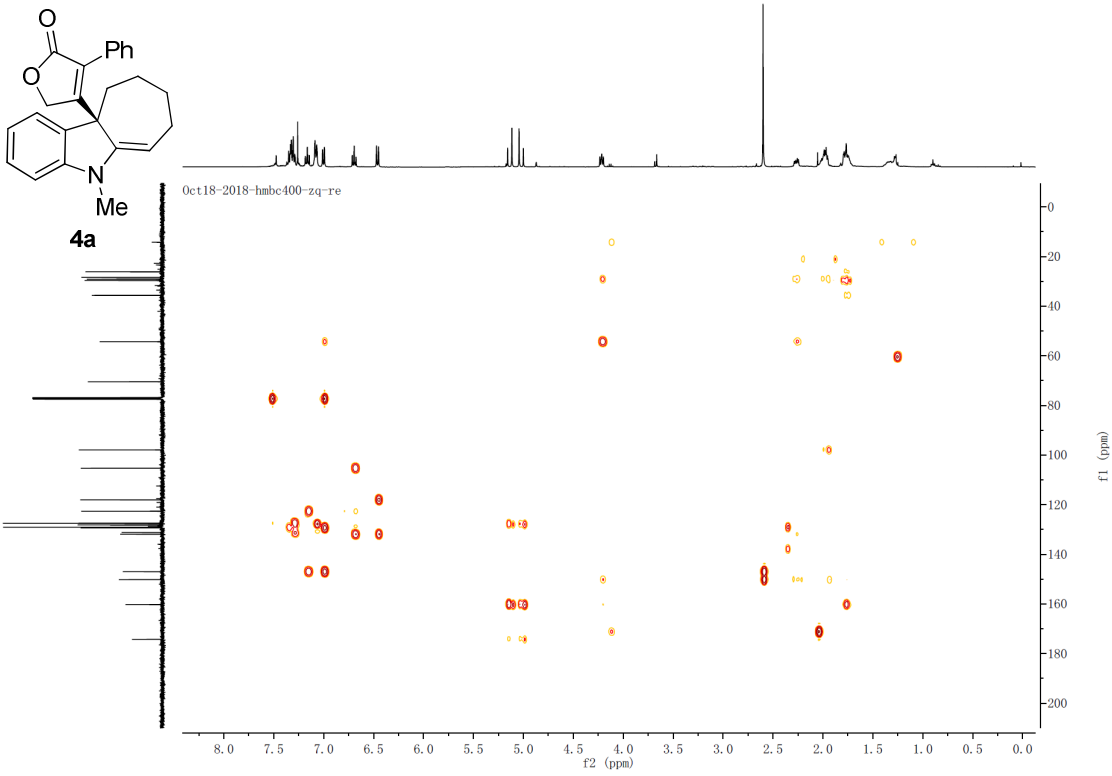


2D NMR Spectrum analysis of 4a:



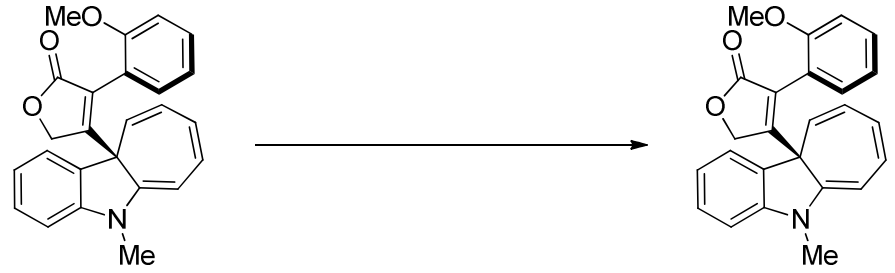


Hsqc NMR spectra of **4a.**

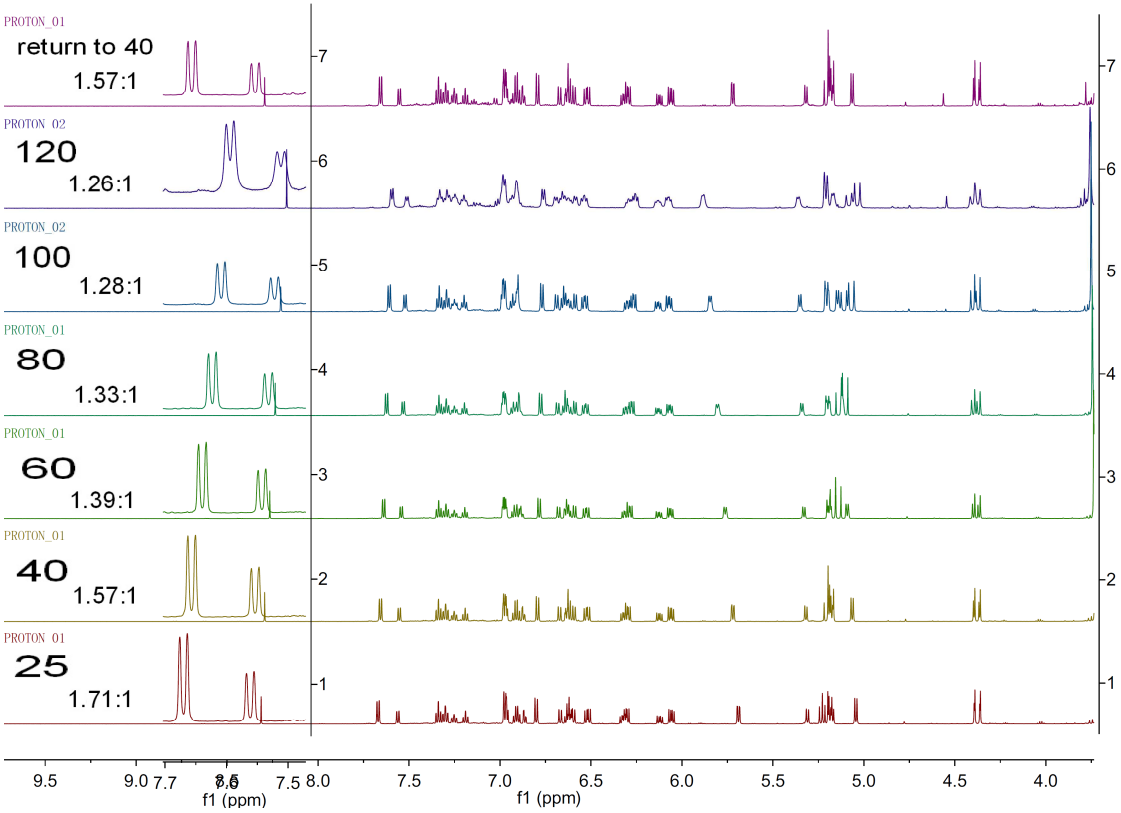


Hmbc NMR spectra of **4a.**

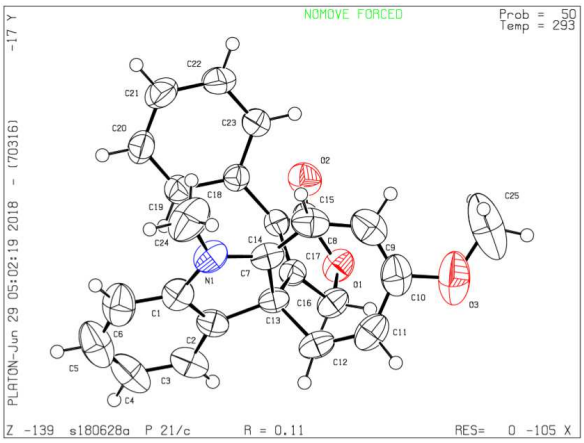
Variable-temperature experiment of 2i

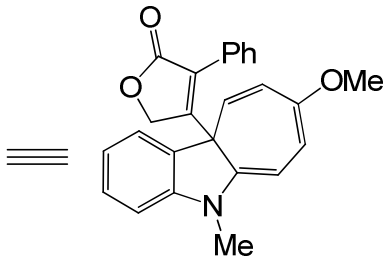


2i, *dr* 1.7:1 (25 °C) **2i**, *dr* 1.26:1 (120 °C)



Crystallographic Data for Compound 2k





2k CCDC 1852858

Bond precision: C-C = 0.0034 A Wavelength=0.71073

Cell: a=11.06500 b=11.52100 c=15.83200
alpha=90 beta=97.7800 gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1999.683	2000
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C25 H21 N O3	?
Sum formula	C25 H21 N O3	C25 H21 N O3
Mr	383.43	383.43
Dx,g cm-3	1.274	1.274
Z	4	4
Mu (mm-1)	0.084	0.084
F000	808.0	808.0
F000'	808.37	
h,k,lmax	17,18,25	17,17,24
Nref	8725	7680
Tmin,Tmax	0.967,0.975	
Tmin'	0.967	

Correction method= Not given

Data completeness= 0.880 Theta(max)= 34.881

R(reflections)= 0.1073(5236) wR2(reflections)= 0.2016(7680)

S = 1.185 Npar= 264
