

Supporting Information

Diastereoselective Synthesis of Polysubstituted Spiro Cyclopenta[c]furans by Gold-Catalyzed Cascade Reaction

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1. General Information

Unless otherwise noted, analytic grade solvents were used for the chromatography, and all the reagents were obtained commercially and used without further purification. Reactions were monitored by TLC. Solvents were dried with CaH_2 . All NMR spectra were recorded on Bruker-500 MHz spectrometer. The chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz respectively. HRMS were measured on the Q-TOF6510 instruments.

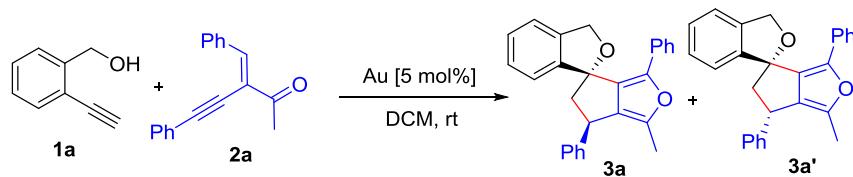
2. Preparation of Starting Materials

1 was prepared according to reported procedures¹

2 was prepared according to reported procedures²

3. Optimization of reaction condition

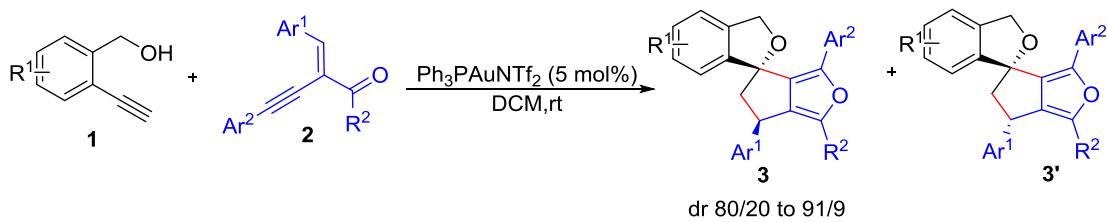
Table S1. Optimization of gold catalysts^a



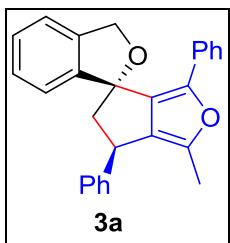
entry	[Au]	yield (%) ^b	dr (3a/3a') ^c
1	BINAPAu ₂ NTf ₂	96	57/43
2	(4-CH ₃ Ph) ₃ AuNTf ₂	80	88/12
3	(2,4-tBu ₂ -PhO) ₃ PAuNTf ₂	82	72/28
4	sphosAuNTf ₂	72	72/28
5	BrettphosAuNTf ₂	50	50/50
6	xphos(CH ₃ CN)AuNTf ₂	64	50/50
7	ItBuAuNTf ₂	21	67/33
8	IMeSAuCl/AgOTf	trace	-
9	ICyAuCl/AgOTf	31	33/67

^aReaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol), catalyst (5 mol%), solvent (1 mL), room temperature, 2 h. ^b Combined yields of the two diastereomers (**3a** and **3a'**), determined by ¹H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard. Combined isolated for all isomers were indicated in parentheses are. ^c Determined by ¹H NMR analysis of the crude reaction mixtures.

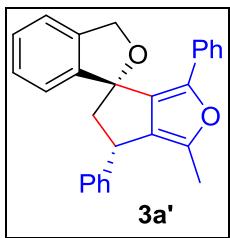
4. Preparation and Characterization of Compound 3 .



To a mixture of alkynyl alcohol **1** (0.3 mmol), enynones **2** (0.2 mmol), $\text{Ph}_3\text{PAuNTf}_2$ (0.01 mmol, 5 mol %), 2 mL DCM was added. The reaction system was stirred at 25 °C for 1-2 hours. After the reaction was completed (determined by TLC analysis), the reaction mixture was filtered and evaporated under reduced pressure, and purified by column chromatography (silica gel, Petroleum ether/ EtOAc: 100/1 to 50/1) to afford the desired product **3**.

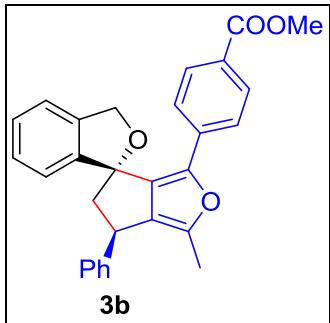


60.5 mg. Yield: 80%, 88/12 d.r. (Colorless oil.) ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.38 – 7.32 (m, 4H), 7.32 – 7.27 (m, 2H), 7.27 – 7.23 (m, 1H), 7.21 – 7.18 (m, 1H), 7.11 (d, J = 7.6 Hz, 1H), 7.05 – 6.89 (m, 5H), 5.27 – 5.19 (m, 2H), 4.59 – 4.46 (m, 1H), 3.15 (dd, J = 13.6, 7.0 Hz, 1H), 2.62 (dd, J = 13.7, 9.6 Hz, 1H), 2.01 (d, J = 1.5 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 143.8, 142.6, 142.6, 142.4, 139.7, 132.4, 131.5, 130.5, 128.6, 128.0, 127.9, 127.6, 126.6, 126.4, 124.6, 122.0, 121.0, 91.2, 71.7, 59.2, 41.7, 12.3. HRMS (ESI, m/z) calcd for $\text{C}_{27}\text{H}_{22}\text{O}_2$ [M+H]⁺ 379.1698, found 379.1699.

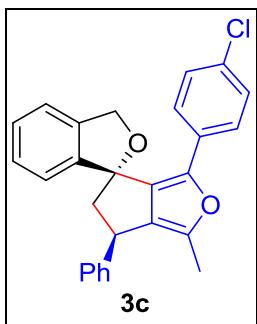


(Colorless oil.) ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.42 – 7.37 (m, 2H), 7.36 – 7.31 (m, 2H), 7.32 – 7.27 (m, 4H), 7.26 – 7.22 (m, 2H), 7.18 – 7.13 (m, 3H), 7.10 – 7.04 (m, 1H), 5.33 – 5.20 (m, 2H), 4.42 – 4.29 (m, 1H), 3.07 (dd, J = 13.5, 8.1 Hz, 1H),

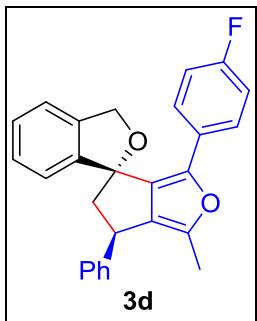
2.93 (dd, $J = 13.4, 7.3$ Hz, 1H), 2.08 (d, $J = 1.3$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 144.4, 143.4, 142.4, 138.4, 131.7, 130.8, 128.6, 128.2, 128.0, 127.8, 127.7, 126.4, 126.3, 124.5, 121.2, 121.0, 91.4, 72.1, 58.5, 41.0, 12.3. HRMS (ESI, m/z) calcd for $\text{C}_{27}\text{H}_{22}\text{O}_2$ [M+H]⁺ 379.1698, found 379.1697.



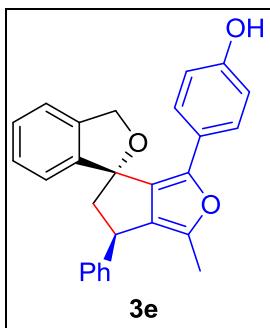
71.5 mg. Yield: 82%, 91/9 d.r. (Colorless oil.) ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.73 – 7.67 (m, 2H), 7.38 – 7.30 (m, 6H), 7.28 – 7.19 (m, 2H), 7.11 (d, $J = 7.6$ Hz, 1H), 7.05 – 7.00 (m, 2H), 5.35 – 5.14 (m, 2H), 4.54 – 4.51 (m, 1H), 3.84 (s, 3H), 3.17 (dd, $J = 13.8, 7.0$ Hz, 1H), 2.63 (dd, $J = 13.8, 9.5$ Hz, 1H), 2.03 (d, $J = 1.4$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 166.9, 143.9, 142.8, 142.3, 139.6, 134.4, 134.0, 133.0, 129.5, 128.7, 128.2, 128.2, 127.5, 127.4, 126.7, 124.0, 121.9, 121.2, 91.2, 71.9, 59.1, 52.0, 41.7, 12.4. HRMS (ESI, m/z) calcd for $\text{C}_{29}\text{H}_{24}\text{O}_4$ [M+H]⁺ 437.1747, found 437.1748.



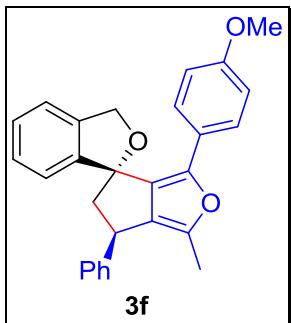
68.4 mg. Yield: 83%, 88/12 d.r. (Colorless oil.). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.37 – 7.29 (m, 6H), 7.27 – 7.20 (m, 2H), 7.10 (d, $J = 7.6$ Hz, 1H), 7.02 – 6.97 (m, 2H), 6.92 – 6.88 (m, 2H), 5.26 – 5.13 (m, 2H), 4.53 – 4.50 (m, 1H), 3.15 (dd, $J = 13.7, 7.0$ Hz, 1H), 2.61 (dd, $J = 13.7, 9.6$ Hz, 1H), 2.00 (d, $J = 1.5$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 142.8, 142.7, 142.4, 142.4, 139.6, 132.6, 132.1, 132.0, 128.9, 128.7, 128.3, 128.2, 128.1, 127.6, 126.7, 125.7, 122.0, 121.1, 91.1, 71.7, 59.1, 41.7, 12.3. HRMS (ESI, m/z) calcd for $\text{C}_{27}\text{H}_{21}\text{ClO}_2$ [M+H]⁺ 413.1303, found 413.1296.



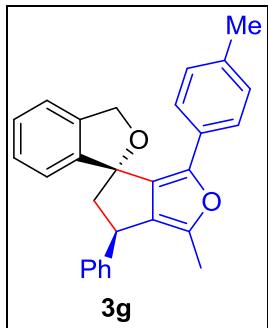
59.2 mg. Yield: 81%, 88/12 d.r. (Colorless oil.). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.38 – 7.17 (m, 8H), 7.10 (d, $J = 7.5$ Hz, 1H), 7.03 – 6.87 (m, 2H), 6.82 – 6.64 (m, 2H), 5.31 – 5.13 (m, 2H), 4.53 – 4.50 (m, 1H), 3.15 (dd, $J = 13.7, 7.0$ Hz, 1H), 2.61 (dd, $J = 13.7, 9.7$ Hz, 1H), 2.00 (d, $J = 1.5$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 162.5, 160.5, 143.0, 142.5, 142.4, 142.4, 139.7, 132.3, 131.1, 128.7, 128.1 (d, $J = 7.1$ Hz), 127.6, 126.8 (d, $J = 3.2$ Hz), 126.7, 126.3 (d, $J = 7.9$ Hz), 122.0, 121.1, 115.1 (d, $J = 21.7$ Hz), 91.1, 71.7, 59.1, 41.7, 12.3. HRMS (ESI, m/z) calcd for $\text{C}_{27}\text{H}_{21}\text{FO}_2$ [M+H] $^+$ 397.1598, found 397.1592.



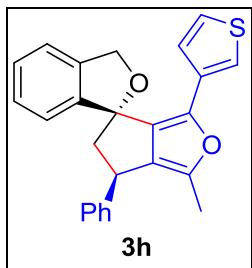
70.2 mg. Yield: 89%, 88/12 d.r. (Colorless oil.). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.31 – 7.13 (m, 9H), 7.07 (d, $J = 7.6$ Hz, 1H), 6.79 (t, $J = 7.9$ Hz, 1H), 6.47 – 6.40 (m, 2H), 6.26 (s, 1H), 5.18 – 5.08 (m, 2H), 4.46 – 4.42 (m, 1H), 3.07 (dd, $J = 13.3, 6.6$ Hz, 1H), 2.56 (dd, $J = 13.7, 9.7$ Hz, 1H), 1.89 (d, $J = 1.5$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 155.3, 143.4, 142.6, 142.6, 142.5, 139.7, 132.3, 131.8, 129.3, 128.7, 128.6, 128.2, 128.0, 127.7, 127.6, 126.7, 122.2, 121.1, 117.1, 113.6, 111.4, 91.3, 71.7, 59.0, 41.6, 12.3. HRMS (ESI, m/z) calcd for $\text{C}_{27}\text{H}_{22}\text{O}_3$ [M+H] $^+$ 395.1642, found 395.1643.



49.8 mg. Yield: 61%, 80/20 d.r. (Colorless oil.). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.38 – 7.18 (m, 8H), 7.11 (d, J = 7.5 Hz, 1H), 6.99 – 6.87 (m, 2H), 6.64 – 6.51 (m, 2H), 5.31 – 5.15 (m, 2H), 4.56 – 4.47 (m, 1H), 3.70 (s, 3H), 3.14 (dd, J = 13.6, 7.0 Hz, 1H), 2.61 (dd, J = 13.7, 9.7 Hz, 1H), 2.00 (d, J = 1.5 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 158.3, 143.9, 142.7, 142.6, 141.6, 139.7, 132.1, 129.8, 128.6, 128.0, 127.9, 127.6, 126.6, 126.0, 123.6, 122.0, 121.0, 113.5, 91.2, 71.6, 59.2, 55.1, 41.7, 12.3. HRMS (ESI, m/z) calcd for $\text{C}_{28}\text{H}_{24}\text{O}_3$ [M+H] $^+$ 409.1798, found 409.1797.

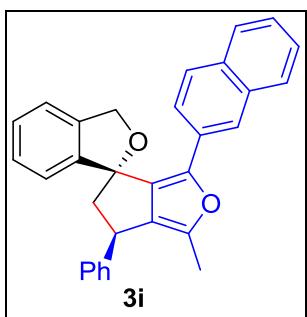


55.5 mg. Yield: 71%, 88/12 d.r. (Colorless oil.). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.37 – 7.28 (m, 6H), 7.26 – 7.19 (m, 2H), 7.11 (d, J = 7.5 Hz, 1H), 6.98 – 6.74 (m, 4H), 5.32 – 5.13 (m, 2H), 4.53 – 4.49 (m, 1H), 3.14 (dd, J = 13.7, 7.0 Hz, 1H), 2.62 (dd, J = 13.6, 9.6 Hz, 1H), 2.20 (s, 3H), 2.00 (d, J = 1.5 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 144.0, 142.7, 142.6, 141.9, 139.7, 136.2, 132.2, 130.7, 128.8, 128.6, 128.0, 127.9, 127.8, 127.6, 126.6, 124.5, 122.1, 121.0, 91.2, 71.7, 59.3, 41.7, 21.1, 12.3. HRMS (ESI, m/z) calcd for $\text{C}_{28}\text{H}_{24}\text{O}_2$ [M+H] $^+$ 393.1855, found 393.1857.

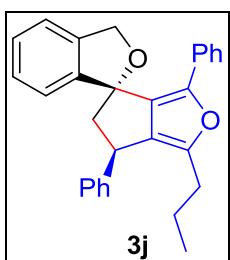


60.5 mg. Yield: 74%, 83/17 d.r. (Colorless oil.). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.36 – 7.31 (m, 6H), 7.29 – 7.23 (m, 2H), 7.19 (d, J = 7.7 Hz, 1H), 7.00 (dd, J = 5.1, 3.0 Hz, 1H), 6.65 – 6.47 (m, 2H), 5.19 (s, 2H), 4.54 – 4.50 (m, 1H), 3.12 (dd, J = 13.7, 7.0 Hz, 1H), 2.64 (dd, J = 13.6, 9.7 Hz, 1H), 1.99 (d, J = 1.5 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 142.6, 142.5, 141.7, 140.9, 139.7, 132.0, 131.6, 130.4, 128.7, 128.1, 127.6, 126.6, 125.1, 124.9, 122.2, 121.2, 119.0, 90.9, 71.7, 59.2,

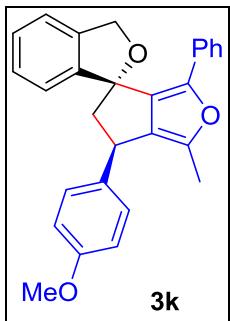
41.8 , 12.3 . HRMS (ESI, m/z) calcd for C₂₅H₂₀O₂S [M+H]⁺ 385.1257, found 385.1261.



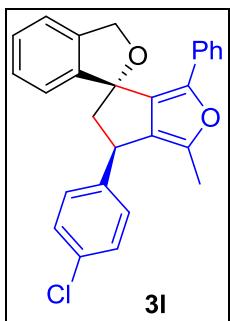
60.1 mg. Yield: 70%, 91/9 d.r. (Colorless oil.). ¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.67 – 7.62 (m, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.42 – 7.15 (m, 14H), 5.33 – 5.19 (m, 2H), 4.58 – 4.54 (m, 1H), 3.19 (dd, *J* = 13.6, 7.0 Hz, 1H), 2.69 (dd, *J* = 13.6, 9.7 Hz, 1H), 2.06 (d, *J* = 1.4 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 143.9 , 142.8 , 142.6 , 142.6 , 139.9 , 133.3 , 132.6 , 132.2 , 132.1 , 128.7 , 128.2 , 128.1 , 128.1 , 127.9 , 127.6 , 127.6 , 127.5 , 126.7 , 126.0 , 125.5 , 123.3 , 122.9 , 122.2 , 121.2 , 91.4 , 71.9 , 59.3 , 41.7 , 12.4 . HRMS (ESI, m/z) calcd for C₃₁H₂₄O₂ [M+H]⁺ 429.1849, found 429.1852.



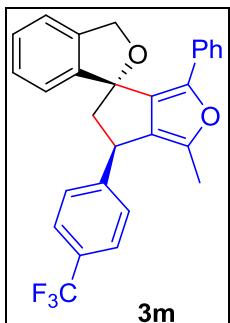
76.4 mg. Yield: 94%, 88/12 d.r. (Colorless oil.). ¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.30 – 7.19 (m, 6H), 7.19 – 7.09 (m, 2H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.98 – 6.89 (m, 5H), 5.16 (q, *J* = 12.4 Hz, 2H), 4.45 (t, *J* = 8.3 Hz, 1H), 3.09 (dd, *J* = 13.8, 7.1 Hz, 1H), 2.56 (dd, *J* = 13.7, 9.5 Hz, 1H), 2.20 (ddt, *J* = 63.7, 14.9, 7.4 Hz, 2H), 1.44 (qd, *J* = 7.4, 1.6 Hz, 2H), 0.75 (td, *J* = 7.4, 1.6 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 145.5 , 142.6 , 141.9 , 141.6 , 138.6 , 131.4 , 130.3 , 129.5 , 127.5 , 127.0 , 126.9 , 126.6 , 125.6 , 125.3 , 123.5 , 121.0 , 119.9 , 90.2 , 70.7 , 58.2 , 40.7 , 27.8 , 20.4 , 12.8 . HRMS (ESI, m/z) calcd for C₂₉H₂₆O₂ [M+H]⁺ 407.2006, found 407.2010.



63.7 mg. Yield: 78%, 88/12 d.r. (Colorless oil.). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.32 – 7.24 (m, 4H), 7.22 – 7.17 (m, 1H), 7.10 (d, J = 7.5 Hz, 1H), 7.05 – 6.97 (m, 5H), 6.95 – 6.85 (m, 2H), 5.26 – 5.19 (m, 2H), 4.50 – 4.46 (m, 1H), 3.80 (s, 3H), 3.12 (dd, J = 13.7, 6.9 Hz, 1H), 2.58 (dd, J = 13.7, 9.6 Hz, 1H), 2.02 (d, J = 1.4 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 158.3, 143.8, 142.6, 142.4, 139.7, 134.6, 132.7, 131.5, 130.4, 128.5, 128.0, 127.9, 126.4, 124.5, 122.0, 121.0, 114.0, 91.2, 71.7, 59.3, 55.3, 40.9, 12.3. HRMS (ESI, m/z) calcd for $\text{C}_{28}\text{H}_{24}\text{O}_3$ [M+H] $^+$ 409.1798, found 409.1797.

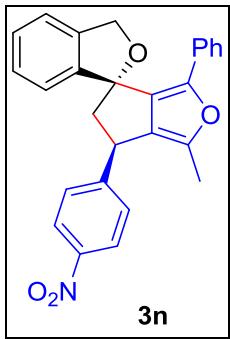


69.8 mg. Yield: 85%, 88/12 d.r. (Colorless oil.). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.33 – 7.26 (m, 6H), 7.21 – 7.18 (m, 1H), 7.09 (d, J = 7.5 Hz, 1H), 7.05 – 6.97 (m, 5H), 5.26 – 5.19 (m, 2H), 4.55 – 4.45 (m, 1H), 3.13 (dd, J = 13.7, 7.0 Hz, 1H), 2.55 (dd, J = 13.7, 9.6 Hz, 1H), 2.02 (d, J = 1.5 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 144.0, 142.4, 142.3, 141.2, 139.7, 132.3, 132.0, 131.3, 130.3, 129.0, 128.8, 128.1, 128.1, 128.0, 126.6, 124.6, 122.0, 121.1, 91.1, 71.8, 59.3, 41.1, 12.4. HRMS (ESI, m/z) calcd for $\text{C}_{27}\text{H}_{21}\text{ClO}_2$ [M+H] $^+$ 413.1303, found 413.1305.

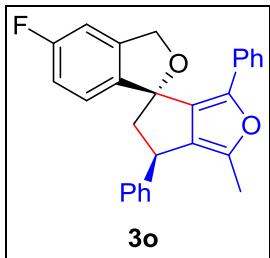


66.8 mg. Yield: 75%, 89/11 d.r. (Colorless oil.). ^1H NMR (500 MHz, CDCl_3) δ (ppm)

7.61 (d, $J = 8.1$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.34 – 7.30 (m, 2H), 7.22 – 7.19 (m, 1H), 7.10 (d, $J = 7.6$ Hz, 1H), 7.06 – 6.97 (m, 5H), 5.27 – 5.20 (m, 2H), 4.60 – 4.56 (m, 1H), 3.17 (dd, $J = 13.7, 7.0$ Hz, 1H), 2.58 (dd, $J = 13.7, 9.6$ Hz, 1H), 2.02 (d, $J = 1.4$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 146.9, 144.1, 142.4, 142.2, 139.7, 131.6, 131.3, 130.2, 129.1, 128.9, 128.1 (d, $J = 5.0$ Hz), 127.9, 126.6, 125.7 (q, $J = 3.8$ Hz), 125.3, 124.6, 123.2, 121.9, 121.1, 91.1, 71.8, 59.2, 41.5, 12.4. HRMS (ESI, m/z) calcd for $\text{C}_{28}\text{H}_{21}\text{F}_3\text{O}_2$ [$\text{M}+\text{H}]^+$ 447.1566, found 447.1557.

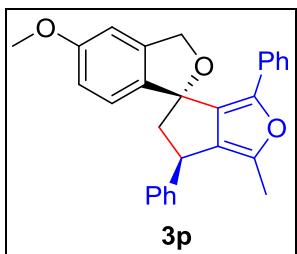


61.1 mg. Yield: 72%, 89/11 d.r. (Orange oil.). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 8.29 – 8.16 (m, 2H), 7.57 – 7.50 (m, 2H), 7.36 – 7.31 (m, 2H), 7.23 – 7.20 (m, 1H), 7.13 – 6.98 (m, 6H), 5.28 – 5.20 (m, 2H), 4.65 – 4.61 (m, 1H), 3.19 (dd, $J = 13.7, 7.1$ Hz, 1H), 2.58 (dd, $J = 13.7, 9.6$ Hz, 1H), 2.03 (d, $J = 1.4$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 150.6, 146.9, 144.3, 142.4, 141.9, 139.7, 131.3, 131.1, 130.1, 128.4, 128.2, 128.2, 128.1, 126.8, 124.6, 124.1, 121.9, 121.1, 91.0, 71.8, 59.1, 41.6, 12.4. HRMS (ESI, m/z) calcd for $\text{C}_{27}\text{H}_{21}\text{NO}_4$ [$\text{M}+\text{H}]^+$ 424.1543, found 424.1543.

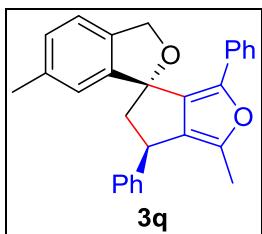


55.5 mg. Yield: 70%, 86/14 d.r. (Colorless oil.) ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.38 – 7.31 (m, 4H), 7.28 – 7.22 (m, 1H), 7.10 – 6.97 (m, 7H), 6.88 (td, $J = 8.7, 2.4$ Hz, 1H), 5.23 – 5.15 (m, 2H), 4.52 – 4.49 (m, 1H), 3.14 (dd, $J = 13.7, 7.0$ Hz, 1H), 2.56 (dd, $J = 13.7, 9.6$ Hz, 1H), 2.02 (d, $J = 1.5$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 163.9, 161.9, 143.9, 142.5 (d, $J = 17.1$ Hz), 141.9 (d, $J = 8.6$ Hz), 138.2, 138.2, 132.2, 131.1, 130.3, 128.7, 128.1, 127.6, 126.7 (d, $J = 9.1$ Hz), 124.6, 123.3 (d, $J = 9.2$ Hz), 115.4 (d, $J = 2.7$ Hz), 108.3 (d, $J = 23.8$ Hz), 90.9, 71.3 (d, $J = 2.7$ Hz), 59.3, 41.6, 12.3. HRMS (ESI, m/z) calcd for $\text{C}_{27}\text{H}_{21}\text{FO}_2$ [$\text{M}+\text{H}]^+$ 397.1598, S9

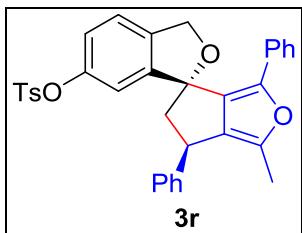
found 397.1602.



65.4 mg. Yield: 80%, 86/14 d.r. (White solid) ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.34 (d, $J = 4.3$ Hz, 4H), 7.27 – 7.22 (m, 1H), 7.09 – 6.97 (m, 6H), 6.83 (d, $J = 2.2$ Hz, 1H), 6.74 (dd, $J = 8.3, 2.3$ Hz, 1H), 5.28 – 5.08 (m, 2H), 4.51 – 4.48 (m, 1H), 3.80 (s, 3H), 3.12 (dd, $J = 13.7, 7.0$ Hz, 1H), 2.58 (dd, $J = 13.7, 9.6$ Hz, 1H), 2.01 (d, $J = 1.4$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 160.0, 143.7, 142.6, 142.4, 141.4, 134.7, 132.3, 131.6, 130.5, 128.6, 128.1, 127.6, 126.6, 126.4, 124.6, 122.8, 114.2, 106.2, 91.0, 71.6, 59.3, 55.6, 41.6, 12.3. HRMS (ESI, m/z) calcd for $\text{C}_{28}\text{H}_{24}\text{O}_3$ [M+H] $^+$ 409.1798, found 409.1801.

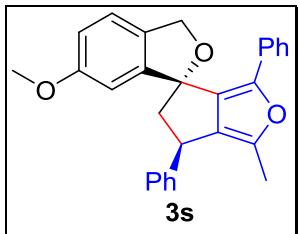


63.6 mg. Yield: 81%, 89/11 d.r. (Colorless oil.) ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.38 – 7.31 (m, 4H), 7.28 – 7.22 (m, 1H), 7.18 (d, $J = 7.7$ Hz, 1H), 7.10 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.06 – 6.99 (m, 5H), 6.92 (s, 1H), 5.29 – 5.06 (m, 2H), 4.53 – 4.49 (m, 1H), 3.13 (dd, $J = 13.7, 7.1$ Hz, 1H), 2.63 (dd, $J = 13.7, 9.6$ Hz, 1H), 2.23 (s, 3H), 2.02 (d, $J = 1.4$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 143.7, 142.9, 142.7, 142.4, 137.8, 136.8, 132.3, 131.7, 130.5, 128.9, 128.6, 128.1, 127.6, 126.6, 126.4, 124.6, 122.5, 120.7, 91.1, 71.7, 59.3, 41.6, 21.3, 12.4. HRMS (ESI, m/z) calcd for $\text{C}_{28}\text{H}_{24}\text{O}_2$ [M+H] $^+$ 393.1849, found 393.1851.

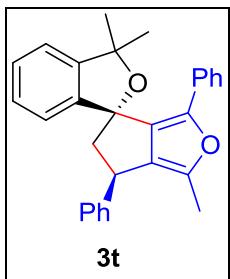


66.5 mg. Yield: 61%, 82/17 d.r. (Colorless oil.) ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.67 – 7.61 (m, 2H), 7.37 – 7.29 (m, 4H), 7.27 – 7.18 (m, 4H), 7.12 – 7.08 (m, 3H),

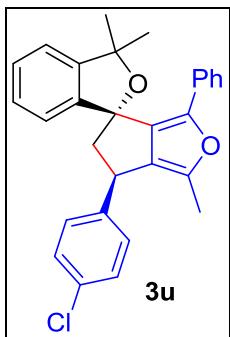
7.02 (dd, $J = 7.6$, 1.9 Hz, 2H), 6.92 (d, $J = 8.2$ Hz, 1H), 6.55 (dd, $J = 8.3$, 2.0 Hz, 1H), 5.29 – 5.10 (m, 2H), 4.51 – 4.48 (m, 1H), 3.14 (dd, $J = 13.8$, 7.0 Hz, 1H), 2.52 (dd, $J = 13.8$, 9.6 Hz, 1H), 2.41 (s, 3H), 2.00 (d, $J = 1.4$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 149.5, 145.4, 144.0, 142.6, 142.3, 141.6, 141.6, 132.2, 132.2, 131.1, 130.3, 129.7, 128.7, 128.6, 128.1, 127.5, 126.7, 126.7, 124.6, 122.8, 122.1, 115.9, 90.8, 71.2, 59.2, 41.6, 21.7, 12.3. HRMS (ESI, m/z) calcd for $\text{C}_{34}\text{H}_{28}\text{O}_5\text{S} [\text{M}+\text{H}]^+$ 549.1730, found 549.1733.



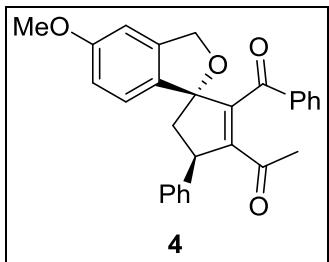
57.2 mg. Yield: 70%, 83/17 d.r. (Colorless oil.). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.40 – 7.31 (m, 4H), 7.27 – 7.24 (m, 1H), 7.18 (d, $J = 8.3$ Hz, 1H), 7.09 – 7.01 (m, 5H), 6.84 (dd, $J = 8.3$, 2.3 Hz, 1H), 6.58 (d, $J = 2.3$ Hz, 1H), 5.25 – 5.10 (m, 2H), 4.53 – 4.50 (m, 1H), 3.62 (s, 3H), 3.16 (dd, $J = 13.7$, 7.1 Hz, 1H), 2.62 (dd, $J = 13.6$, 9.2 Hz, 1H), 2.04 (d, $J = 1.4$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 160.1, 144.3, 143.9, 142.6, 142.5, 132.2, 131.5, 131.4, 130.5, 128.7, 128.1, 127.6, 126.6, 126.5, 124.6, 121.7, 114.8, 106.7, 91.2, 71.5, 59.0, 55.6, 41.5, 12.4. HRMS (ESI, m/z) calcd for $\text{C}_{28}\text{H}_{24}\text{O}_3 [\text{M}+\text{H}]^+$ 409.1798, found 409.1793.



75.1 mg. Yield: 92%, 86/14 d.r. (Colorless oil.) ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.39 – 7.30 (m, 5H), 7.27 – 7.19 (m, 3H), 7.13 (d, $J = 7.6$ Hz, 1H), 7.04 – 6.90 (m, 5H), 4.57 – 4.53 (m, 1H), 3.11 (dd, $J = 13.5$, 7.0 Hz, 1H), 2.73 (dd, $J = 13.5$, 9.7 Hz, 1H), 1.99 (d, $J = 1.5$ Hz, 3H), 1.59 (s, 3H), 1.53 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 147.3, 143.3, 142.8, 142.4, 142.3, 132.5, 132.4, 130.6, 128.7, 128.3, 128.2, 127.9, 127.6, 126.6, 126.3, 124.7, 122.2, 120.9, 89.5, 84.7, 61.9, 41.7, 31.2, 28.8, 12.3. HRMS (ESI, m/z) calcd for $\text{C}_{29}\text{H}_{26}\text{O}_2 [\text{M}+\text{H}]^+$ 407.2006, found 407.2009.



72.9 mg. Yield: 83%, 91/9 d.r. (Colorless oil.). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.37 – 7.34 (m, 1H), 7.33 – 7.27 (m, 4H), 7.26 – 7.21 (m, 2H), 7.12 (d, J = 7.5 Hz, 1H), 7.01 – 6.99 (m, 3H), 6.96 – 6.88 (m, 2H), 4.54 – 4.50 (m, 1H), 3.09 (dd, J = 13.5, 7.0 Hz, 1H), 2.66 (dd, J = 13.4, 9.7 Hz, 1H), 2.00 (d, J = 1.4 Hz, 3H), 1.59 (s, 3H), 1.53 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 147.2, 143.5, 142.3, 142.1, 141.3, 132.3, 132.2, 132.0, 130.4, 129.0, 128.8, 128.3, 128.2, 127.9, 126.4, 124.7, 122.1, 120.9, 89.4, 84.8, 61.8, 41.0, 31.1, 28.8, 12.3. HRMS (ESI, m/z) calcd for $\text{C}_{29}\text{H}_{25}\text{ClO}_2$ [M+H] $^+$ 441.1616, found 441.1616.



68.5 mg. Yield: 81%. (Colorless oil.). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.99 – 7.90 (m, 2H), 7.55 – 7.47 (m, 1H), 7.42 – 7.35 (m, 4H), 7.33 – 7.21 (m, 4H), 6.82 (dd, J = 8.4, 2.4 Hz, 1H), 6.55 (d, J = 2.2 Hz, 1H), 4.92 (d, J = 12.3 Hz, 1H), 4.75 (t, J = 7.3 Hz, 1H), 4.62 (d, J = 12.2 Hz, 1H), 3.73 (s, 3H), 3.05 (dd, J = 14.6, 7.8 Hz, 1H), 2.39 (dd, J = 14.6, 6.8 Hz, 1H), 1.87 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 197.3, 195.5, 160.2, 152.1, 145.8, 143.2, 140.7, 136.4, 133.5, 129.3, 129.2, 128.5, 127.2, 127.2, 124.1, 114.1, 105.7, 100.0, 72.3, 55.4, 50.6, 49.6, 29.5.

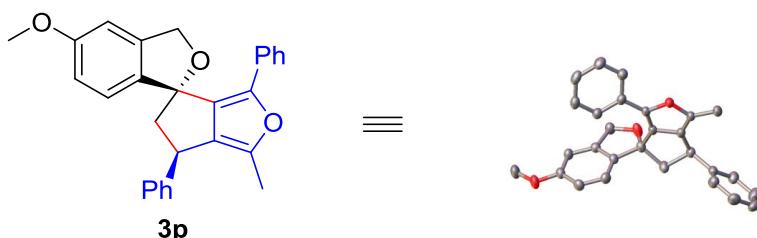
5. Reference

- (1) a) J. W. Wang, and Z. H. Xu. *Org. Lett.* 2017, **19**, 2526; b) H. Wang, and Z. X. *Org. Lett.* 2014, **16**, 22.
- (2) W. B. Li, X. Z. Yu, Z. T. Yue, and J. L. Zhang. *Org. Lett.* 2016, **18**, 3972.

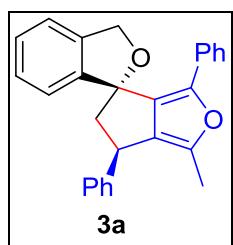
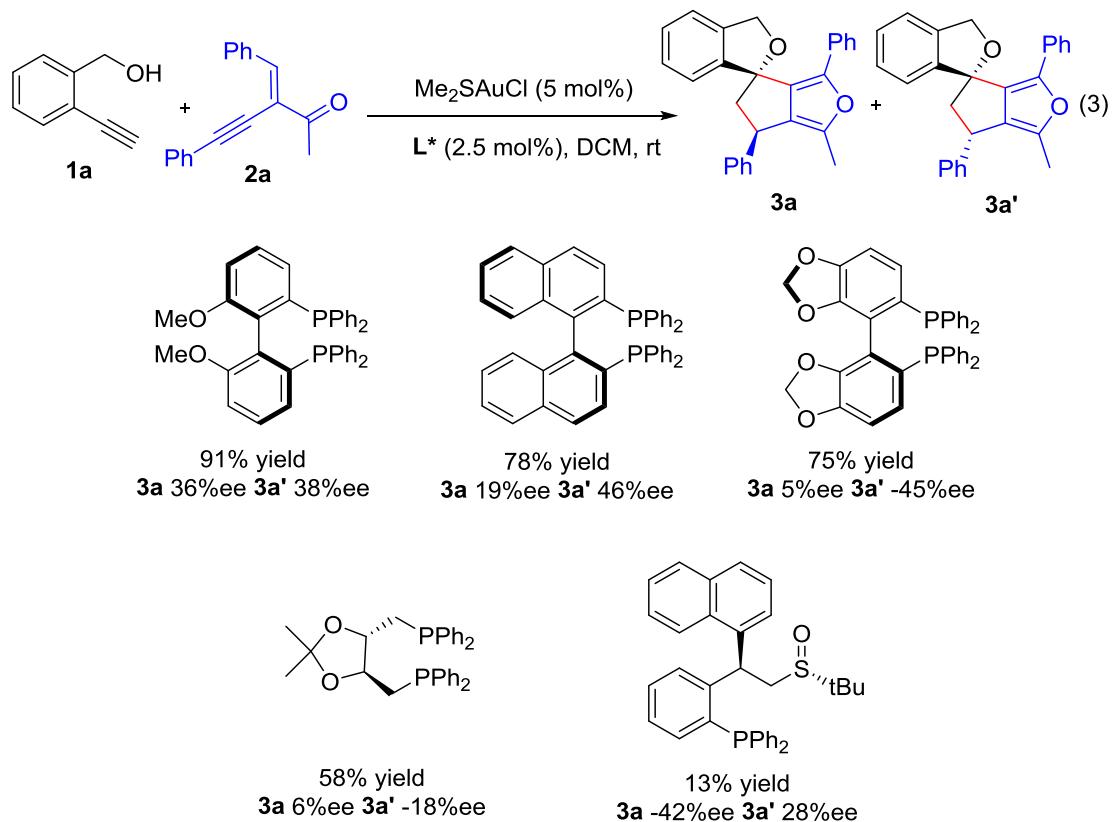
6. X-ray Crystallography

The crystal of **3p** suitable for XRD analysis was prepared by recrystallization from a mixed solvent of DCM and petroleum ether.

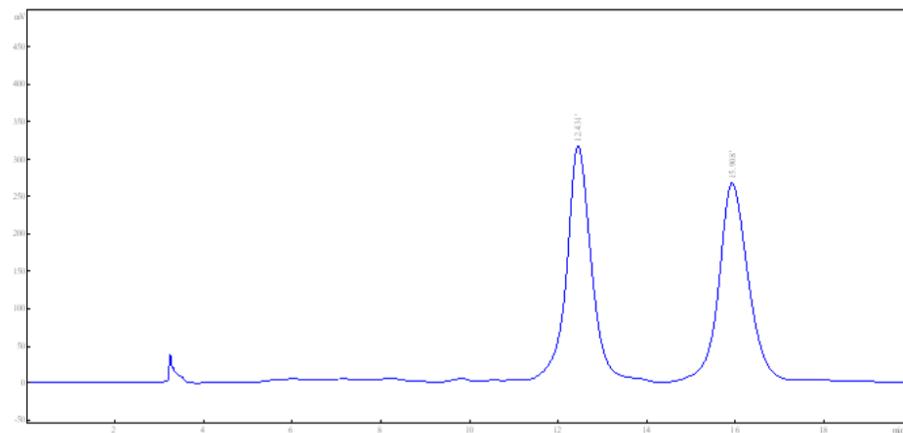
CCDC 1876395 (**3p**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



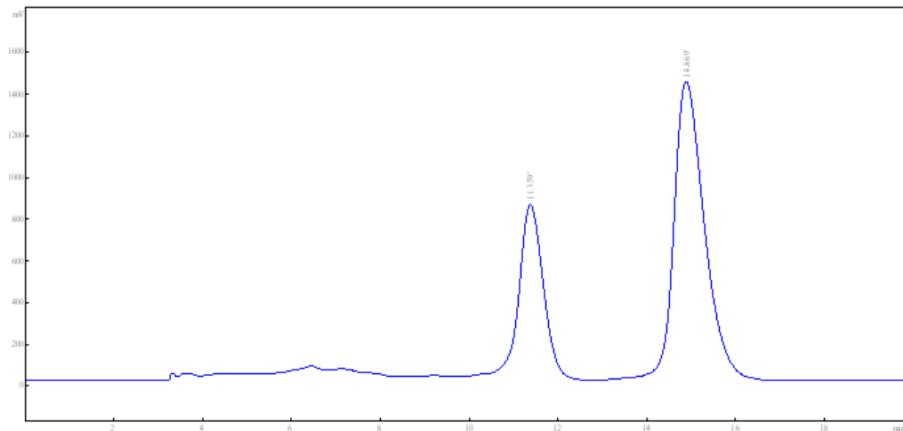
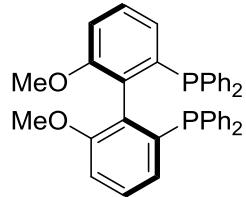
7. Catalytic Enantioselective Reaction



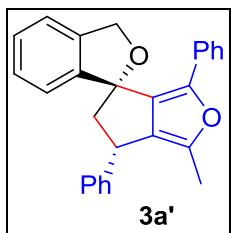
Chiral HPLC analysis of the product: Chiralcel OD-H 250X4.6 mm 5u column; hexane/2-propanol =99/1, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 12.4 min , 15.9 min .



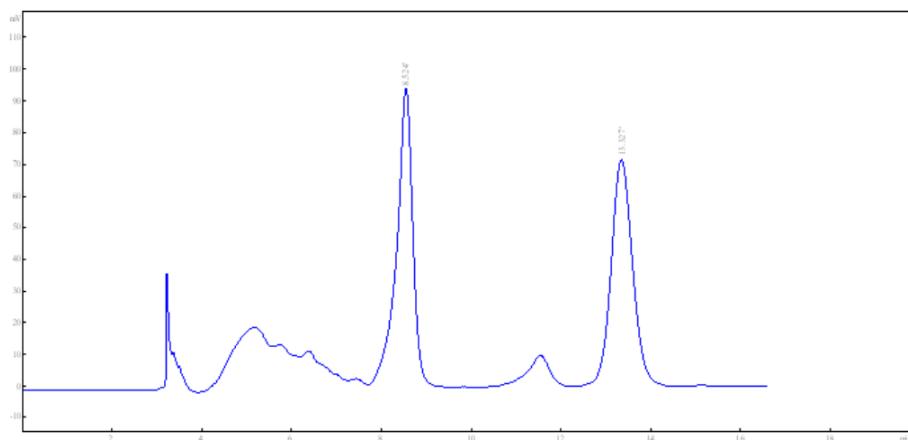
Peak#	Ret.Time	Area	Area %
1	12.431	12094954	50.08
2	15.908	12055714	49.92
Total		24150668	100



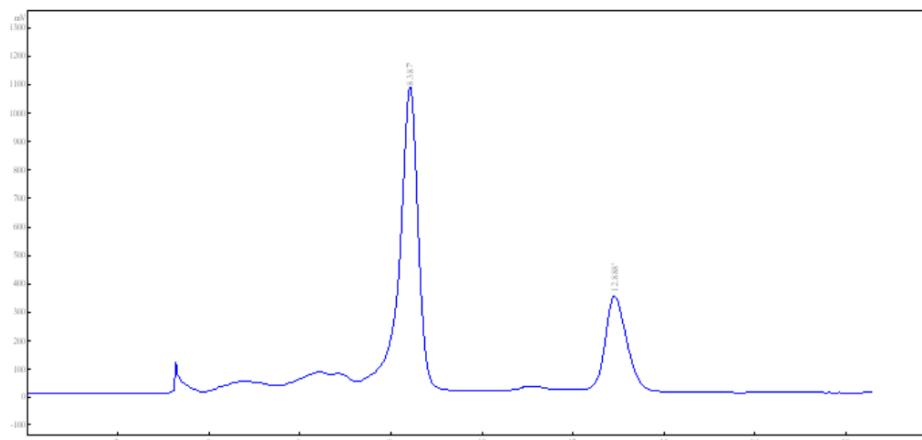
Peak#	Ret.Time	Area	Area %
1	11.359	32056698	31.94
2	14.869	68303245	68.06
Total		100359943	100



Chiral HPLC analysis of the product: Chiralcel OD-H 250X4.6 mm 5u column; hexane/2-propanol =99/1, detected at 254 nm, Flow rate = 1 mL/min, Retention times: 8.5 min , 13.3 min .

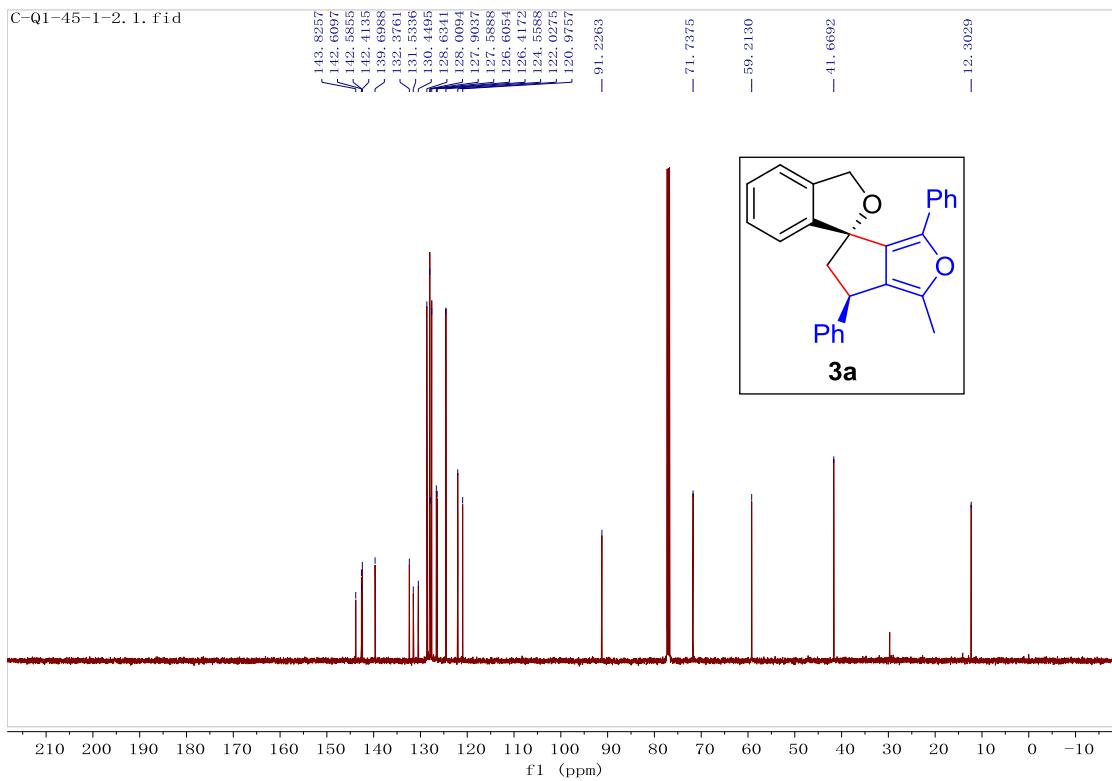
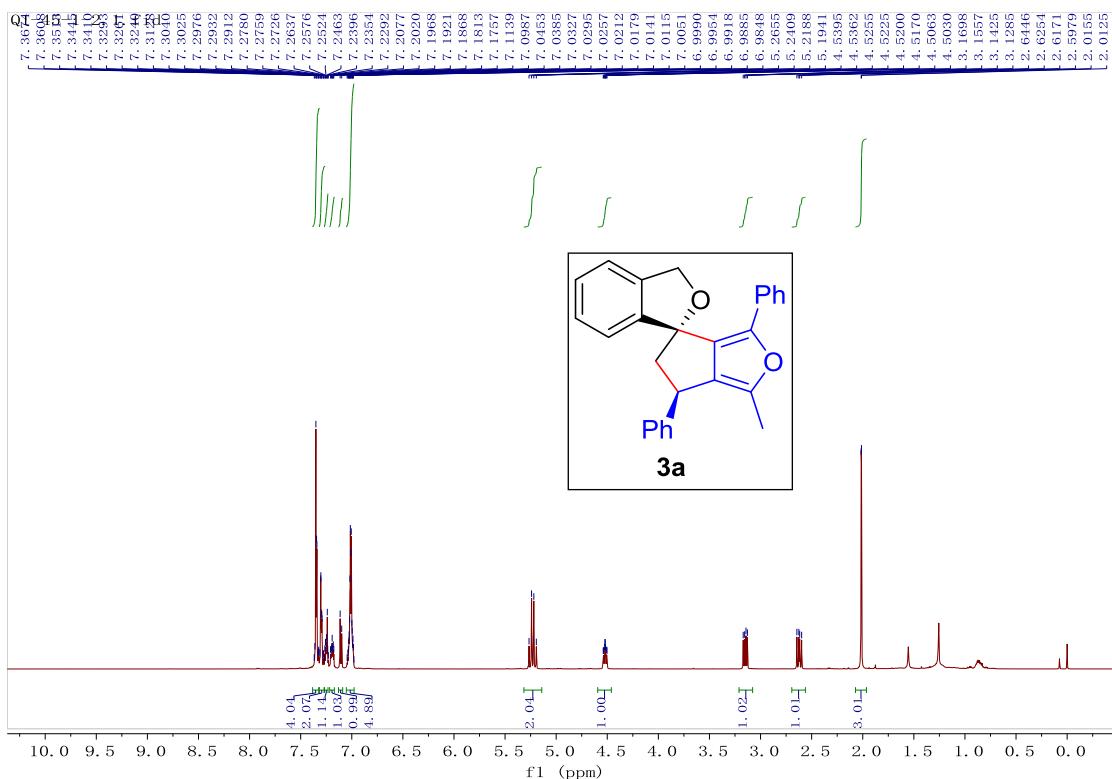


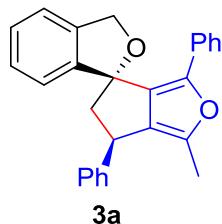
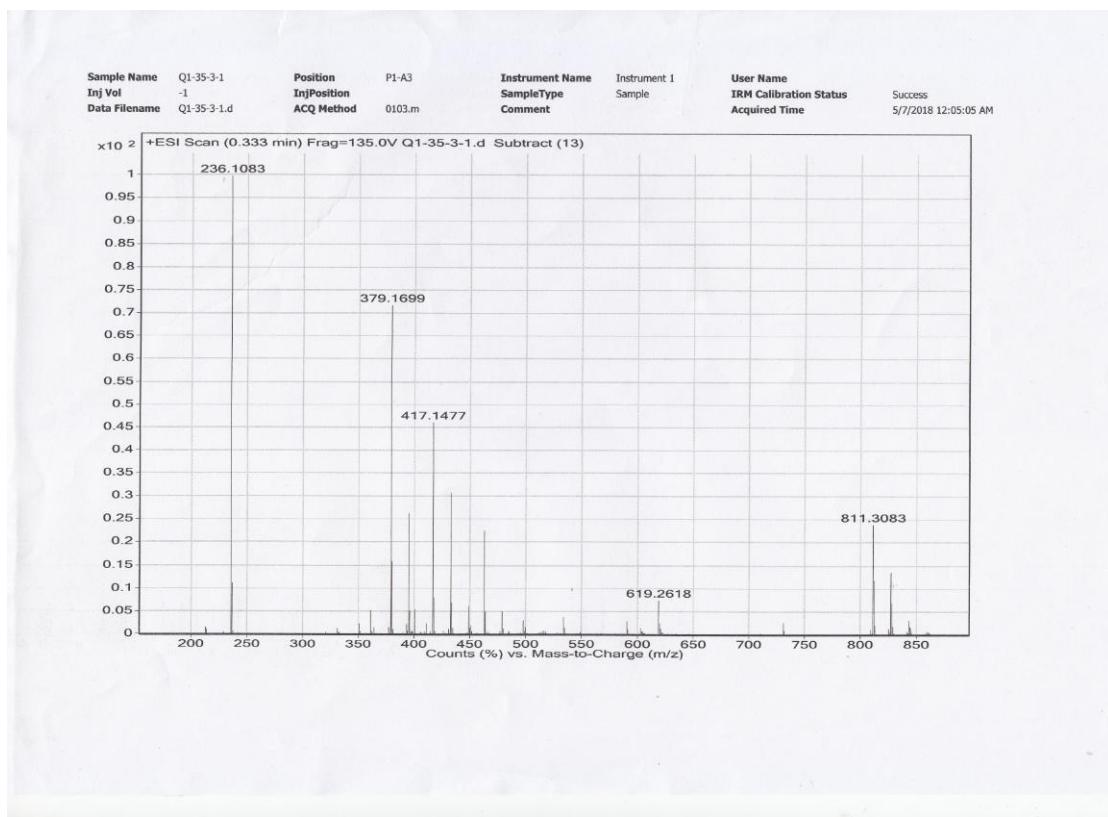
Peak#	Ret.Time	Area	Area %
1	8.524	2347713	49.70
2	13.327	2376234	50.30
Total		4723947	100



Peak#	Ret.Time	Area	Area %
1	8.387	33027613	68.79
2	12.888	14983101	31.21
Total		48010714	100

8. NMR and HRMS Spectra of All Compounds





Chemical Formula: C₂₇H₂₂O₂

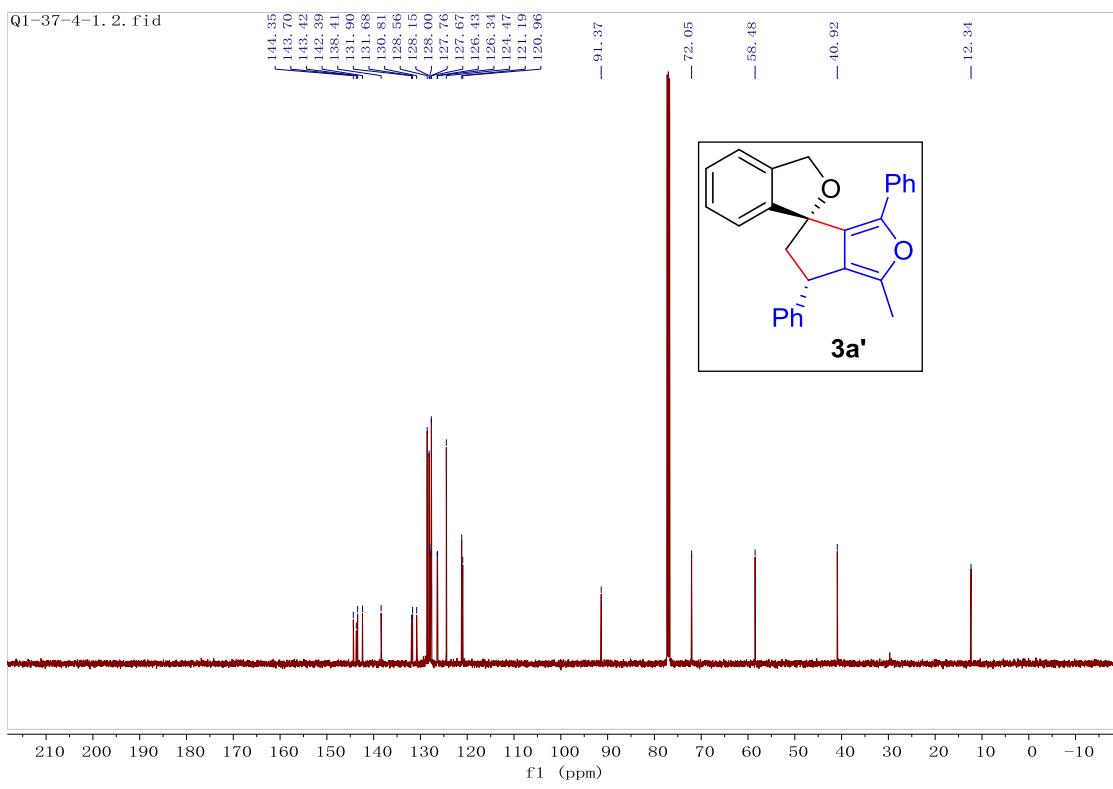
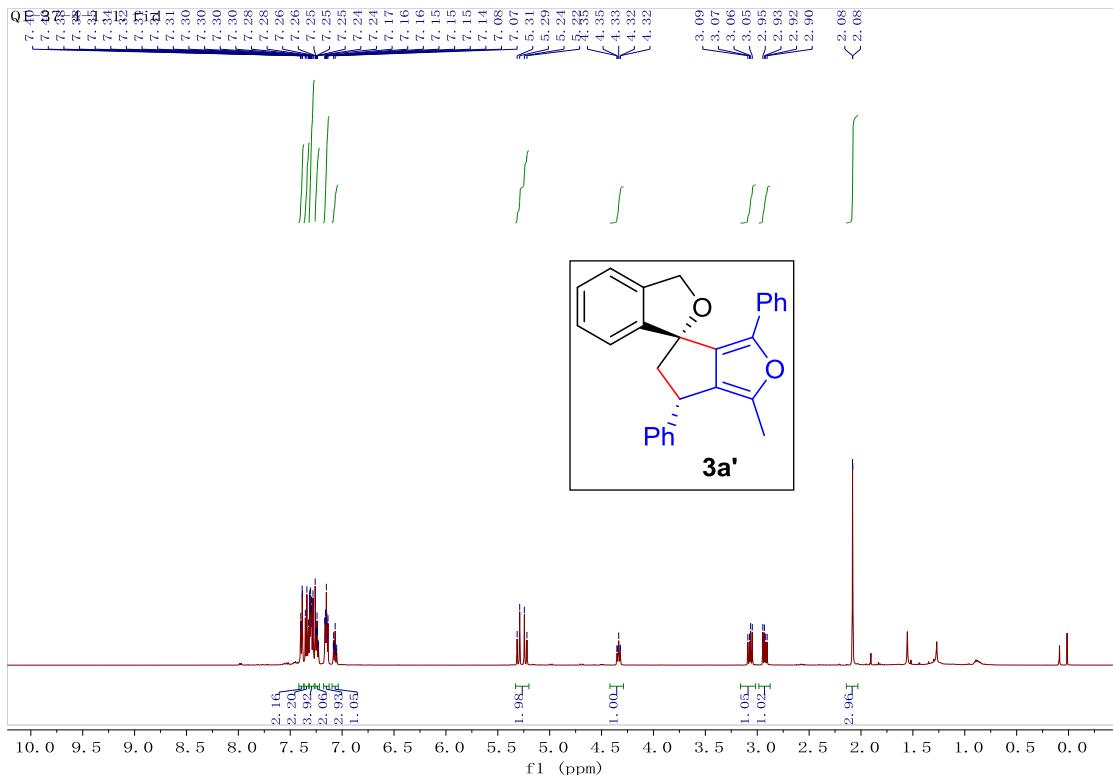
Exact Mass: 378.1620

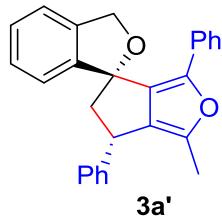
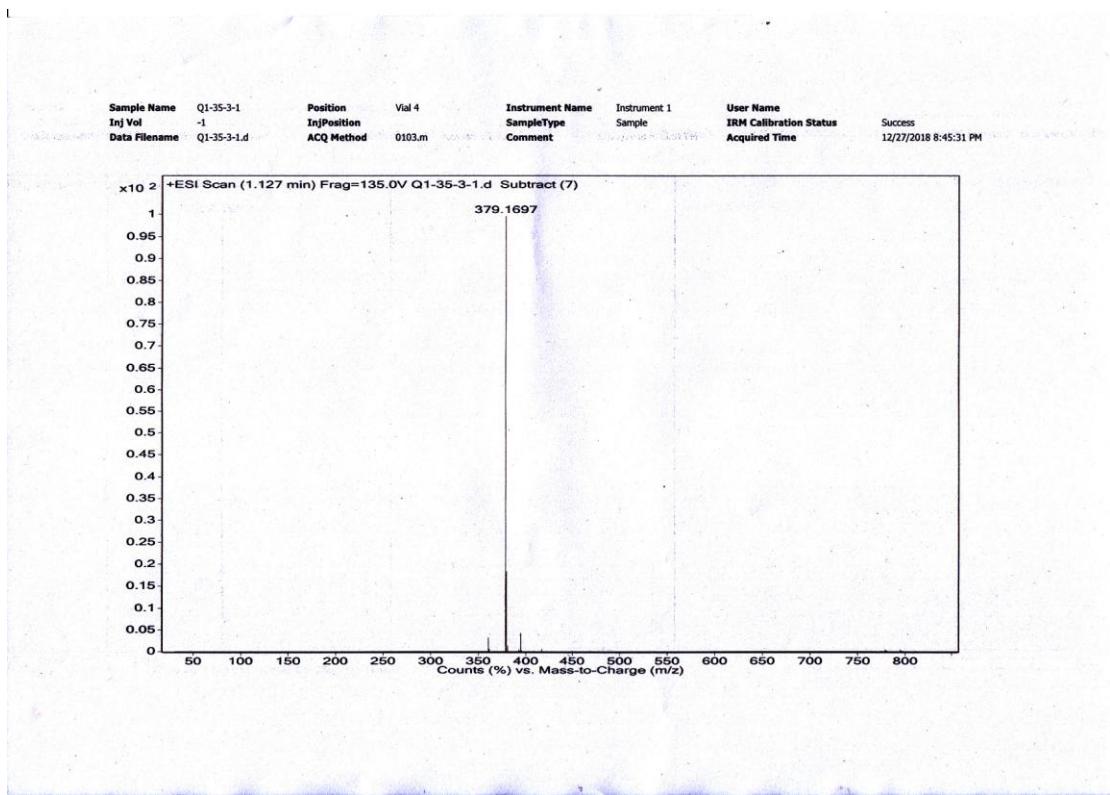
Molecular Weight: 378.4710

m/z: 378.1620 (100.0%), 379.1653 (29.2%), 380.1687 (2.7%), 380.1687 (1.4%)

Elemental Analysis: C, 85.69; H, 5.86; O, 8.45

HRMS (ESI, m/z) calcd for C₂₇H₂₂O₂ [M+H]⁺ 379.1698, found 379.1699.





Chemical Formula: $C_{27}H_{22}O_2$

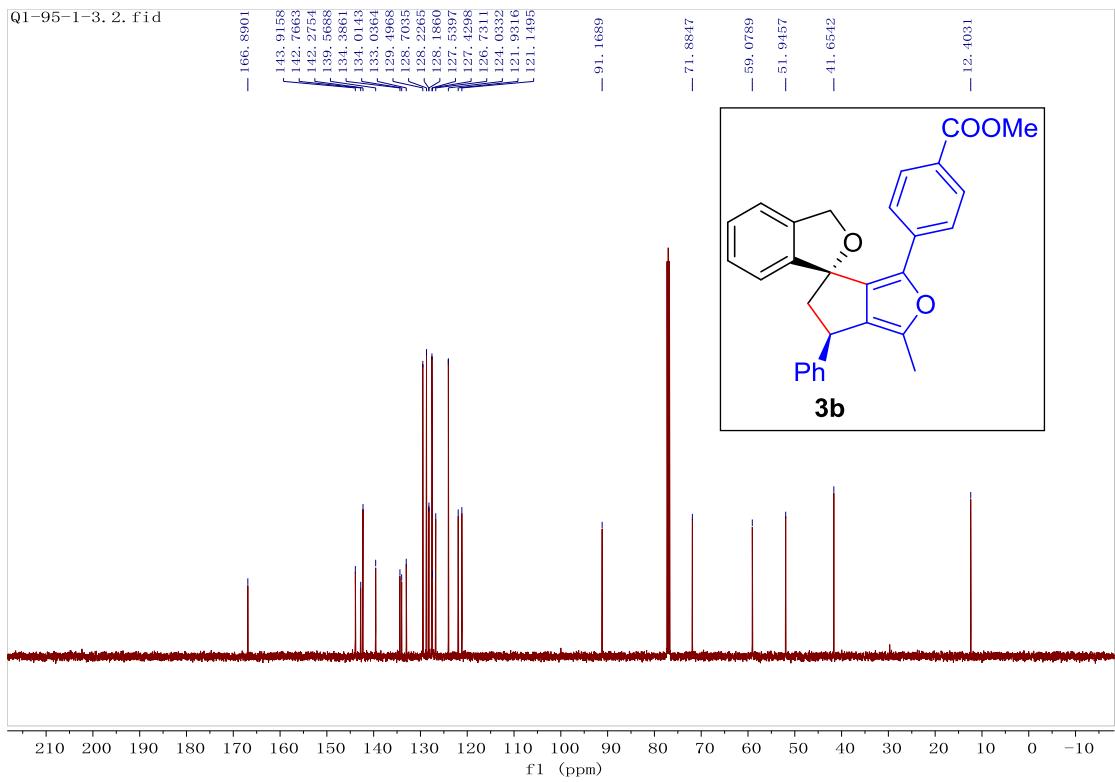
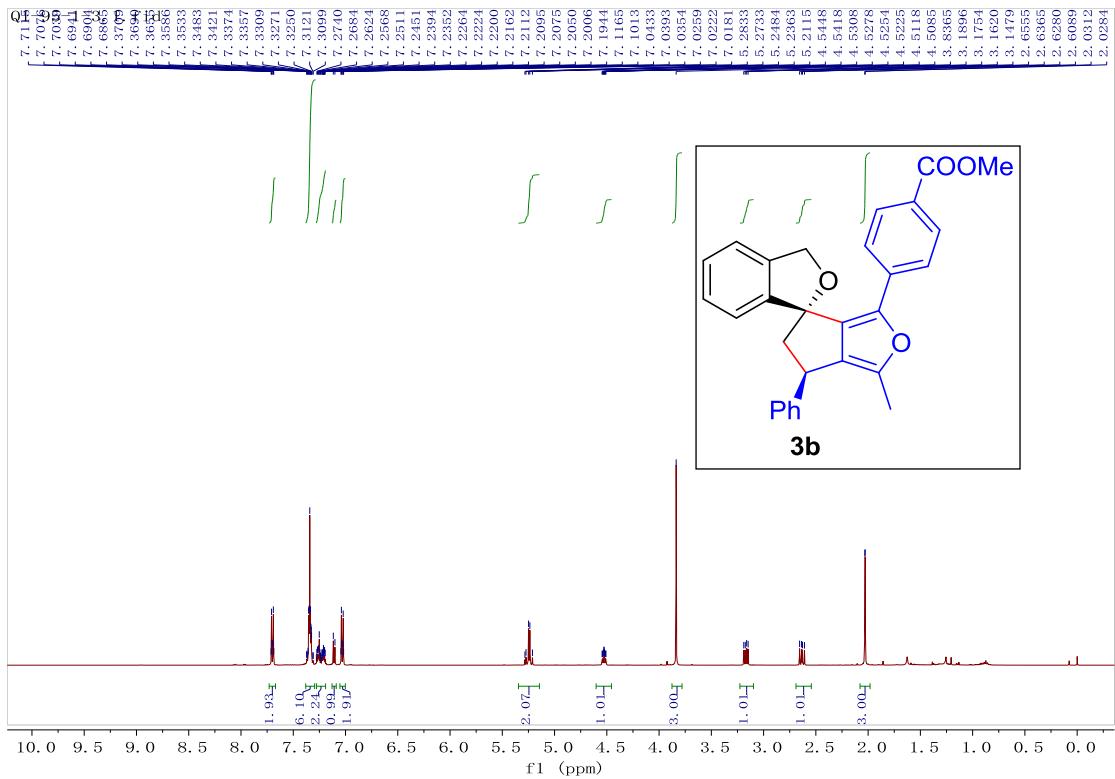
Exact Mass: 378.1620

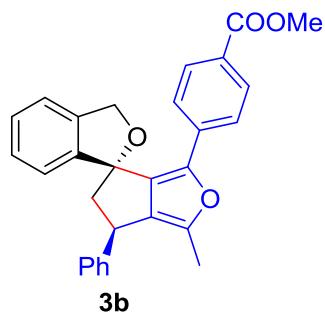
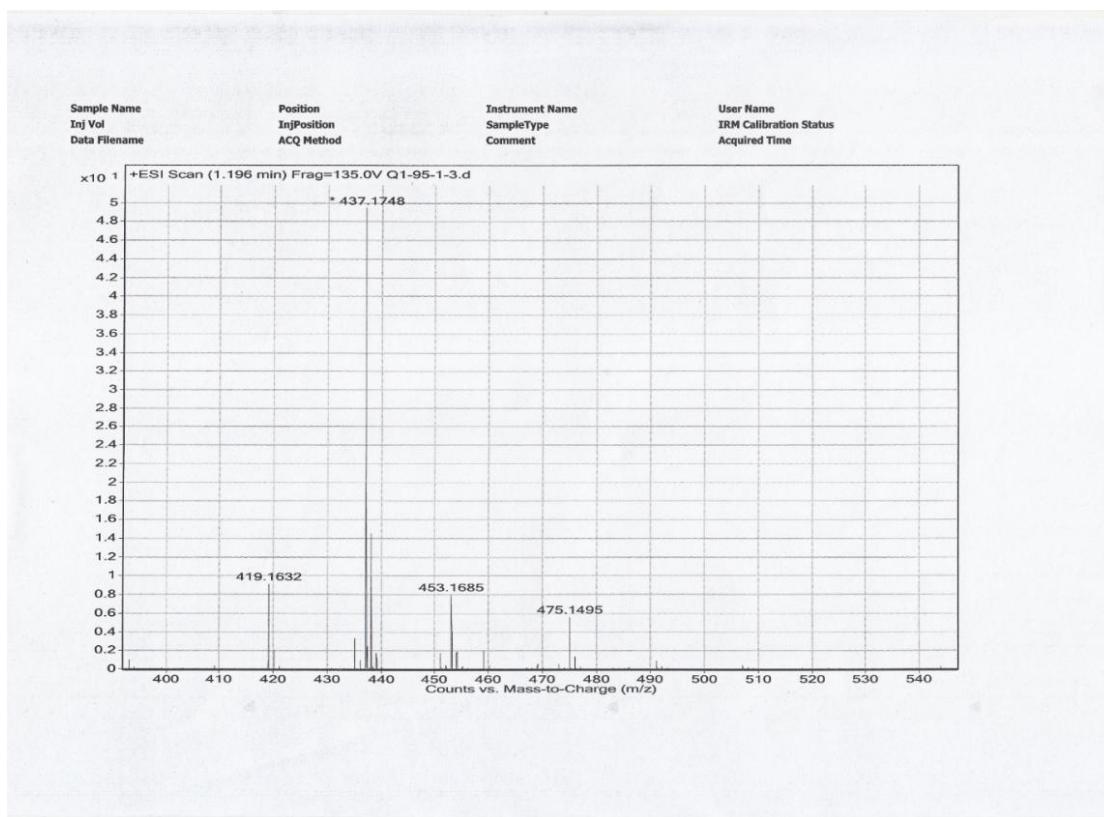
Molecular Weight: 378.4710

m/z: 378.1620 (100.0%), 379.1653 (29.2%), 380.1687 (2.7%), 380.1687 (1.4%)

Elemental Analysis: C, 85.69; H, 5.86; O, 8.45

HRMS (ESI, m/z) calcd for $C_{27}H_{22}O_2 [M+H]^+$ 379.1698, found 379.1697.





Chemical Formula: C₂₉H₂₄O₄

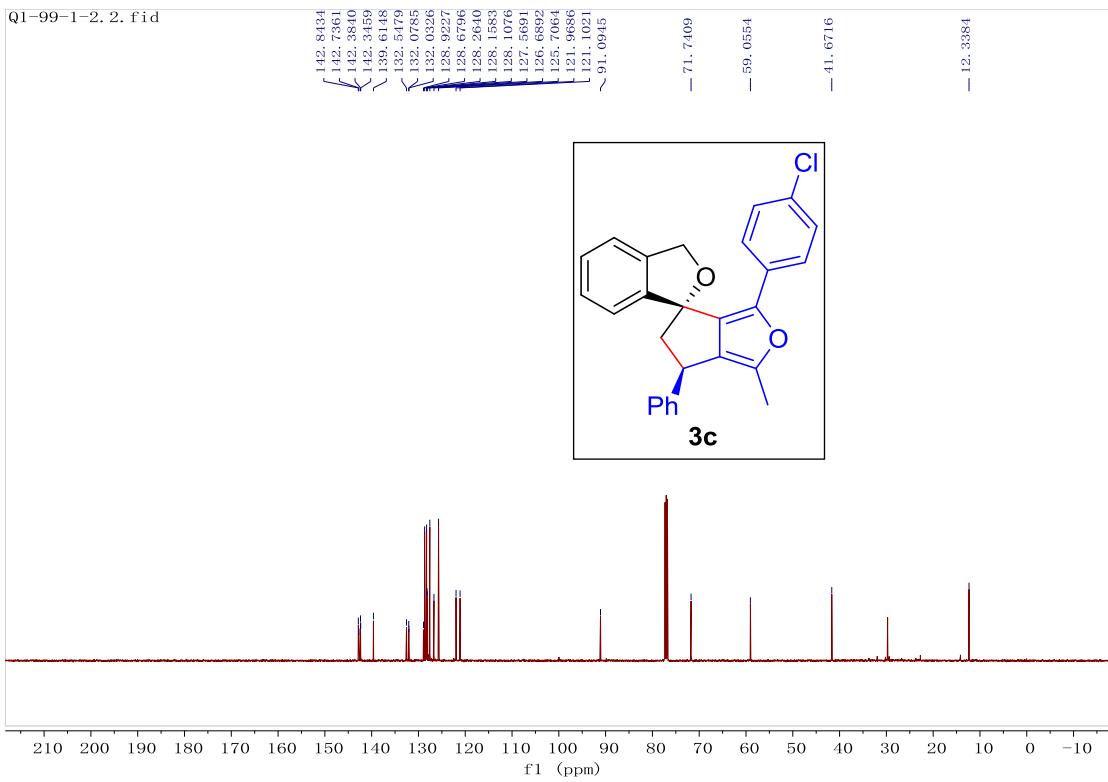
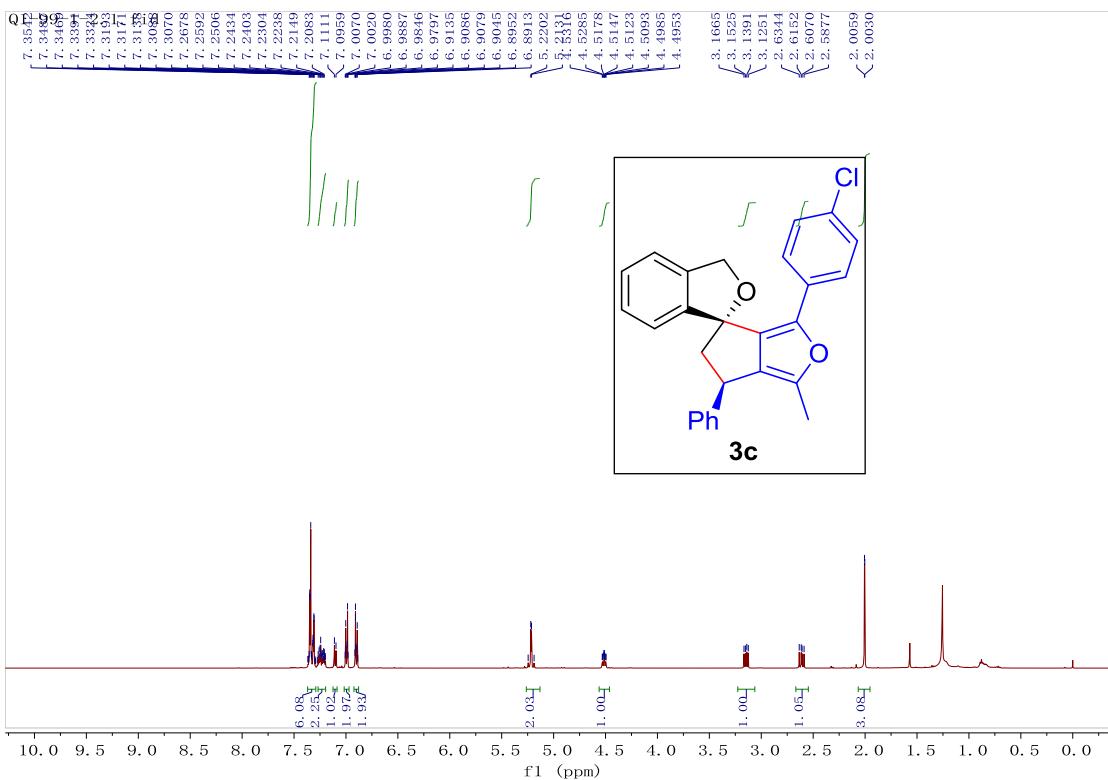
Exact Mass: 436.1675

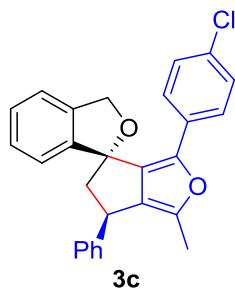
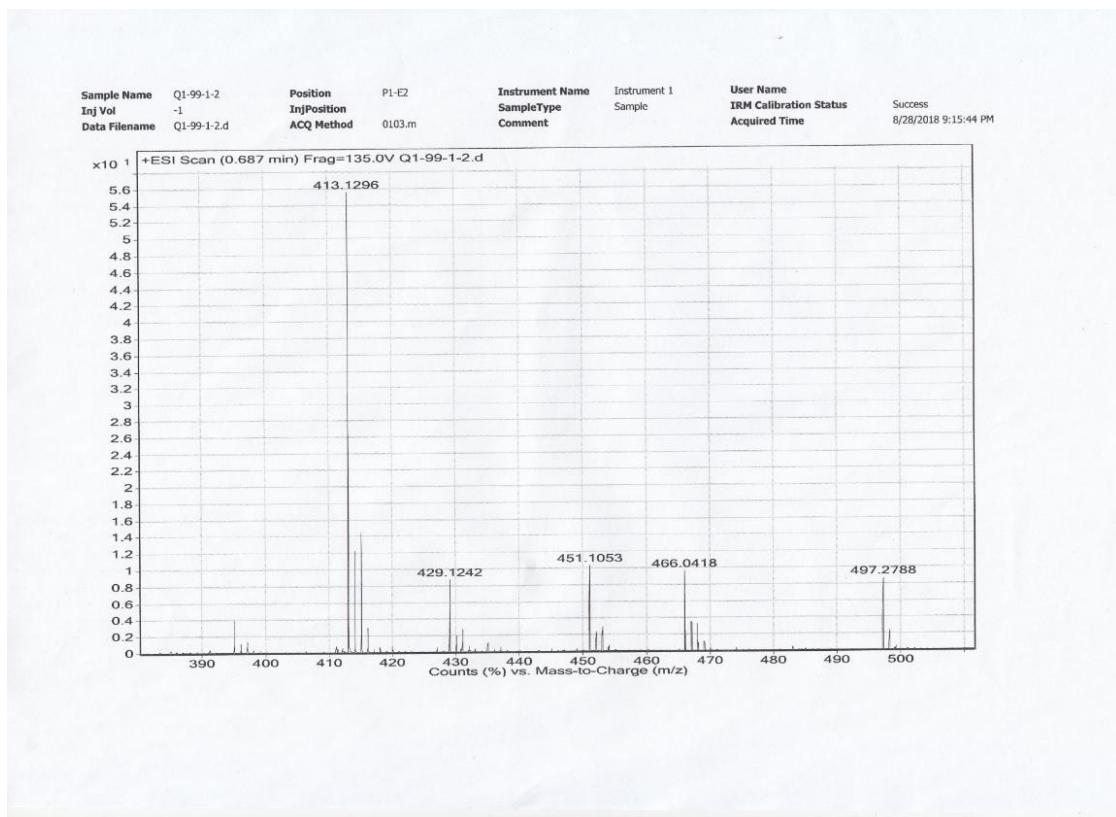
Molecular Weight: 436.5070

m/z: 436.1675 (100.0%), 437.1708 (31.4%), 438.1742 (2.7%), 438.1742 (2.0%)

Elemental Analysis: C, 79.80; H, 5.54; O, 14.66

HRMS (ESI, m/z) calcd for C₂₉H₂₄O₄ [M+H]⁺ 437.1747, found 437.1748.





Chemical Formula: C₂₇H₂₁ClO₂

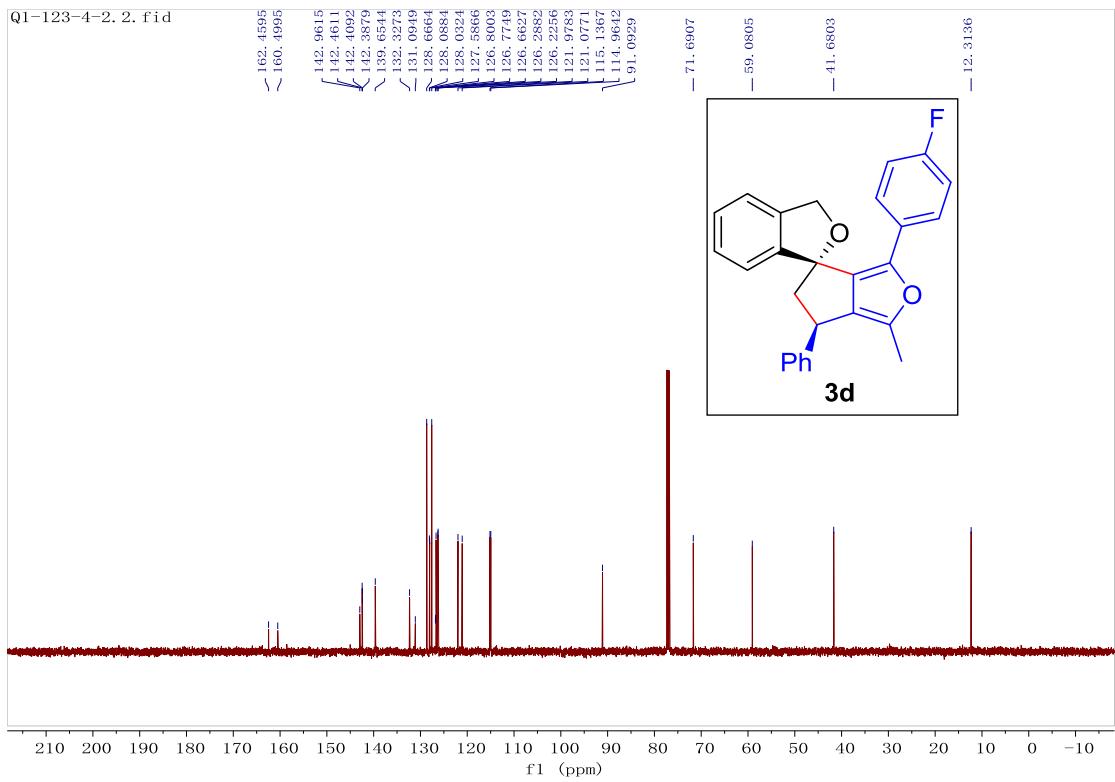
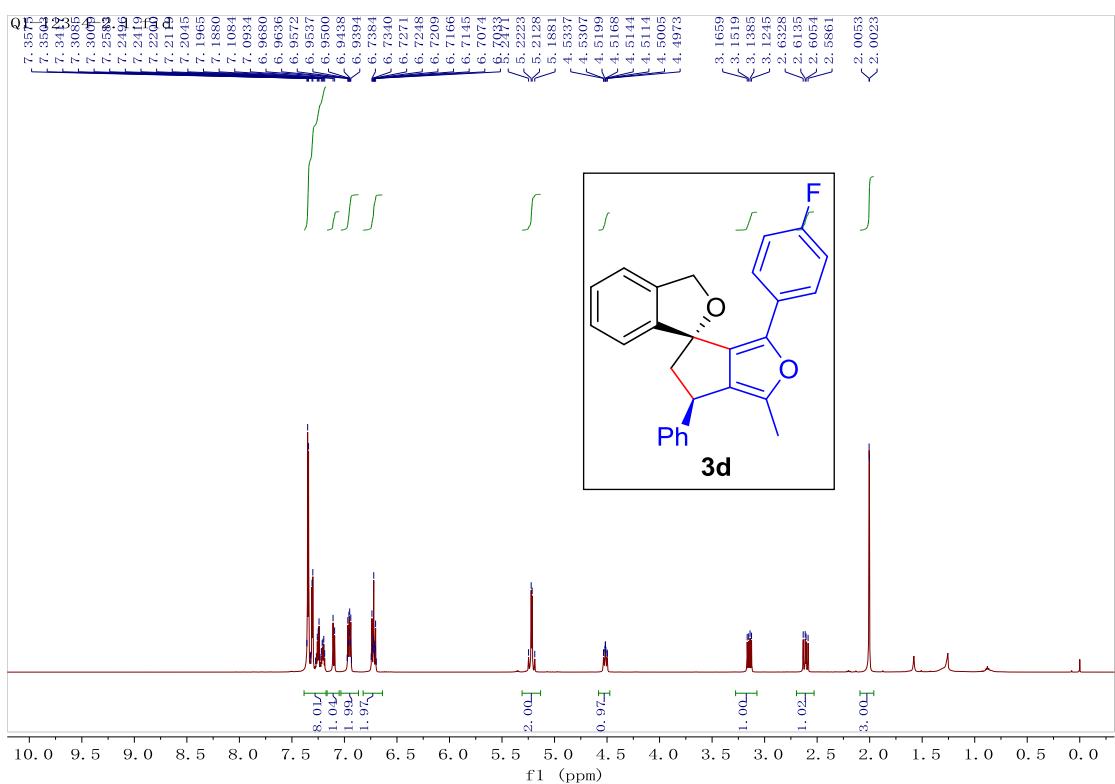
Exact Mass: 412.1230

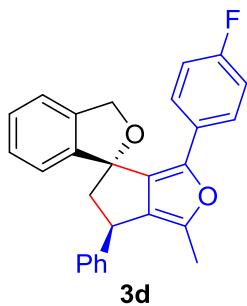
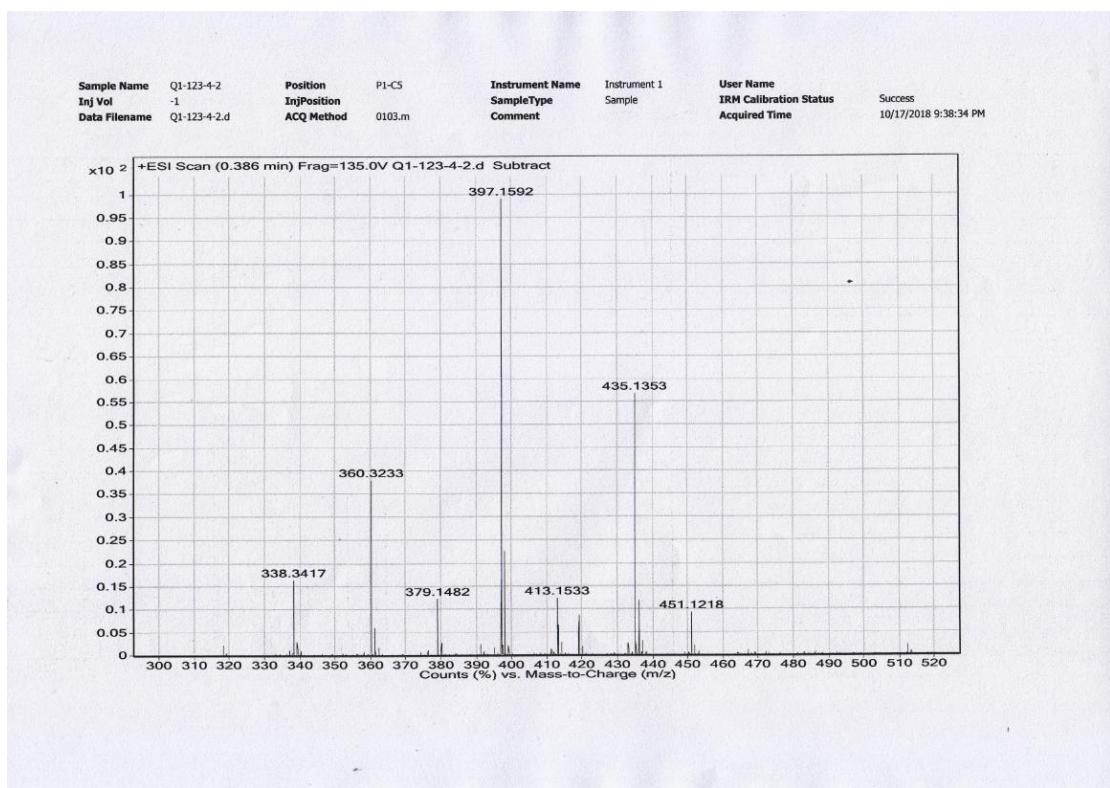
Molecular Weight: 412.9130

m/z: 412.1230 (100.0%), 414.1201 (32.0%), 413.1264 (29.2%), 415.1234 (9.3%), 414.1297 (4.1%)

Elemental Analysis: C, 78.54; H, 5.13; Cl, 8.59; O, 7.75

HRMS (ESI, m/z) calcd for C₂₇H₂₁ClO₂ [M+H]⁺ 413.1303, found 413.1296.





Chemical Formula: $C_{27}H_{21}FO_2$

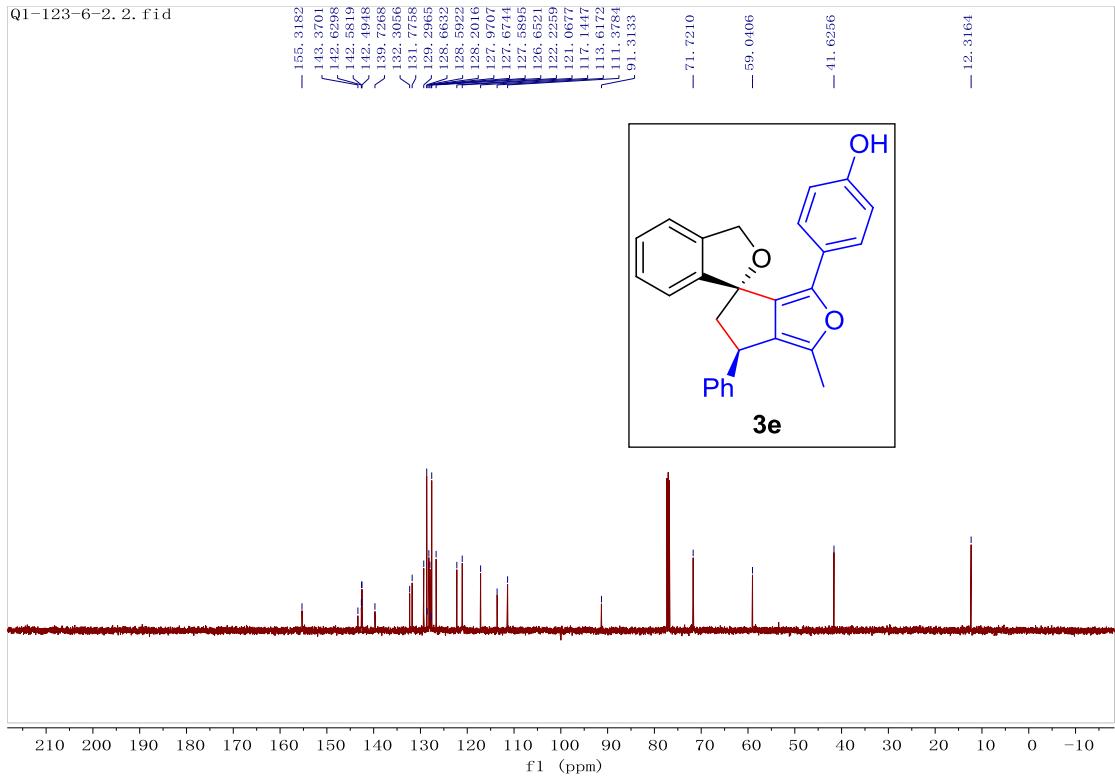
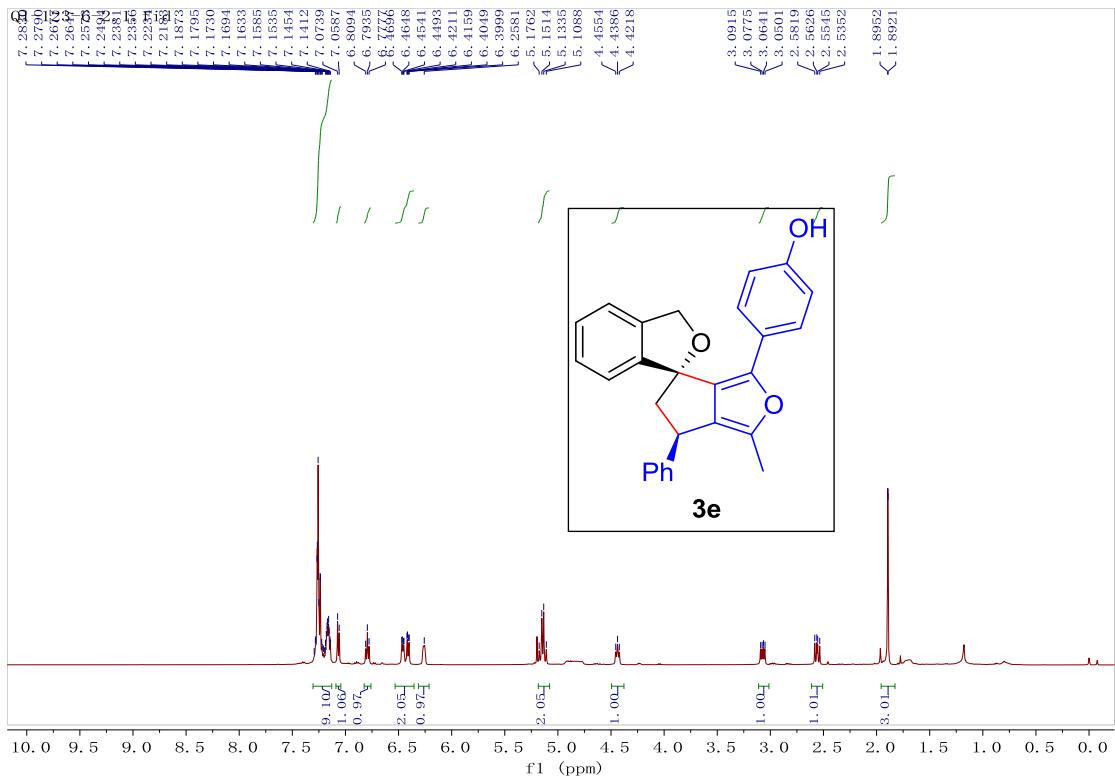
Exact Mass: 396.1526

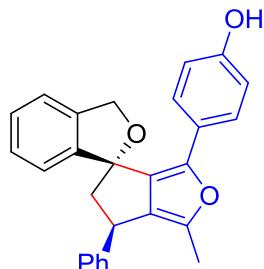
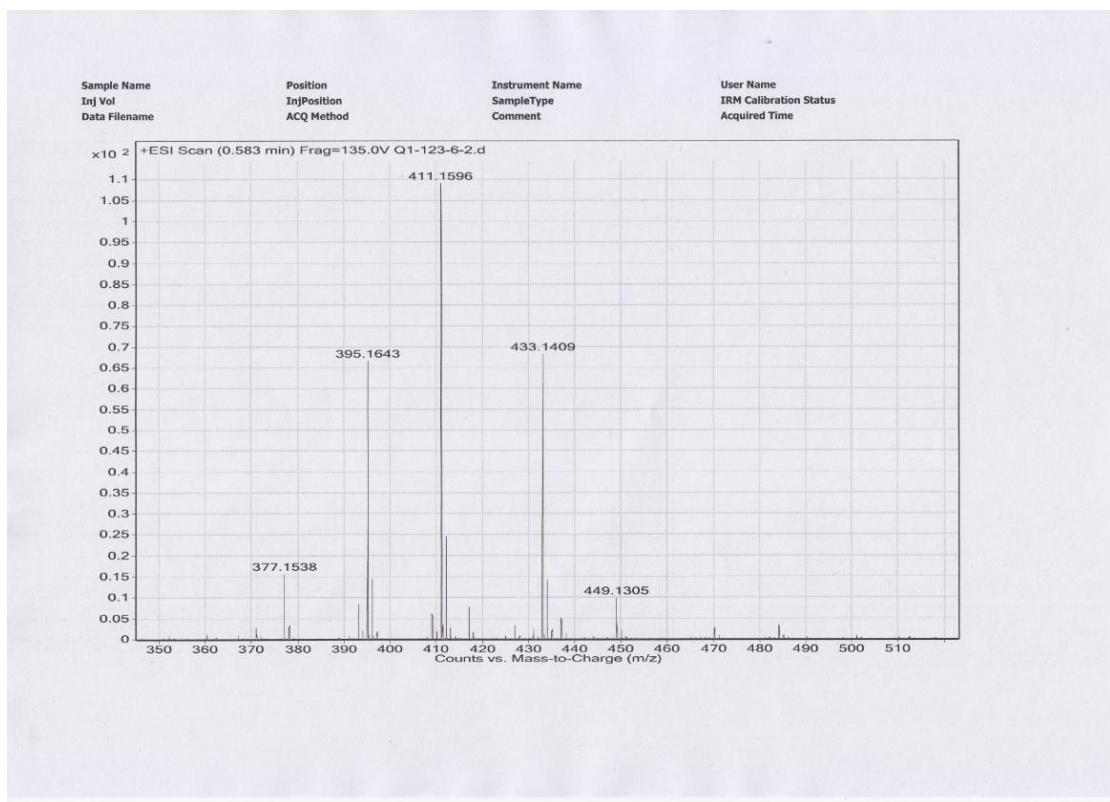
Molecular Weight: 396.4614

m/z : 396.1526 (100.0%), 397.1559 (29.2%), 398.1593 (2.7%), 398.1593 (1.4%)

Elemental Analysis: C, 81.80; H, 5.34; F, 4.79; O, 8.07

HRMS (ESI, m/z) calcd for $C_{27}H_{21}FO_2 [M+H]^+$ 397.1598, found 397.1592.





Chemical Formula: $C_{27}H_{22}O_3$

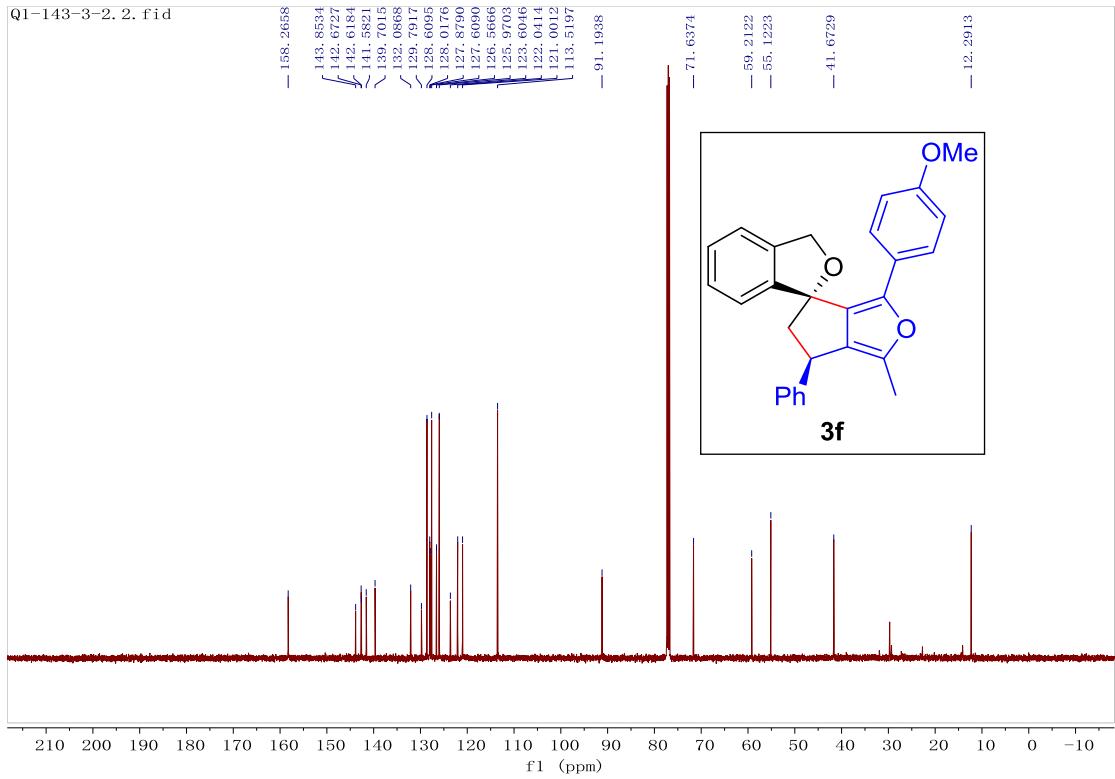
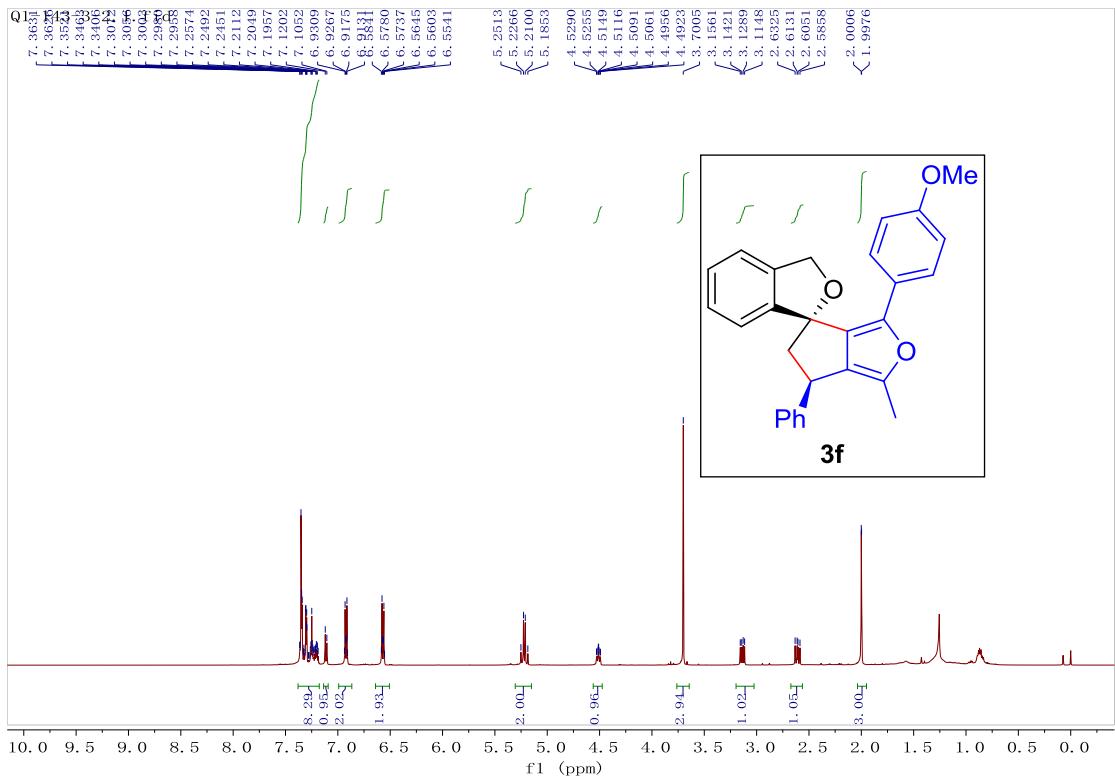
Exact Mass: 394.1569

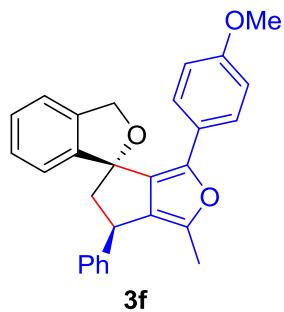
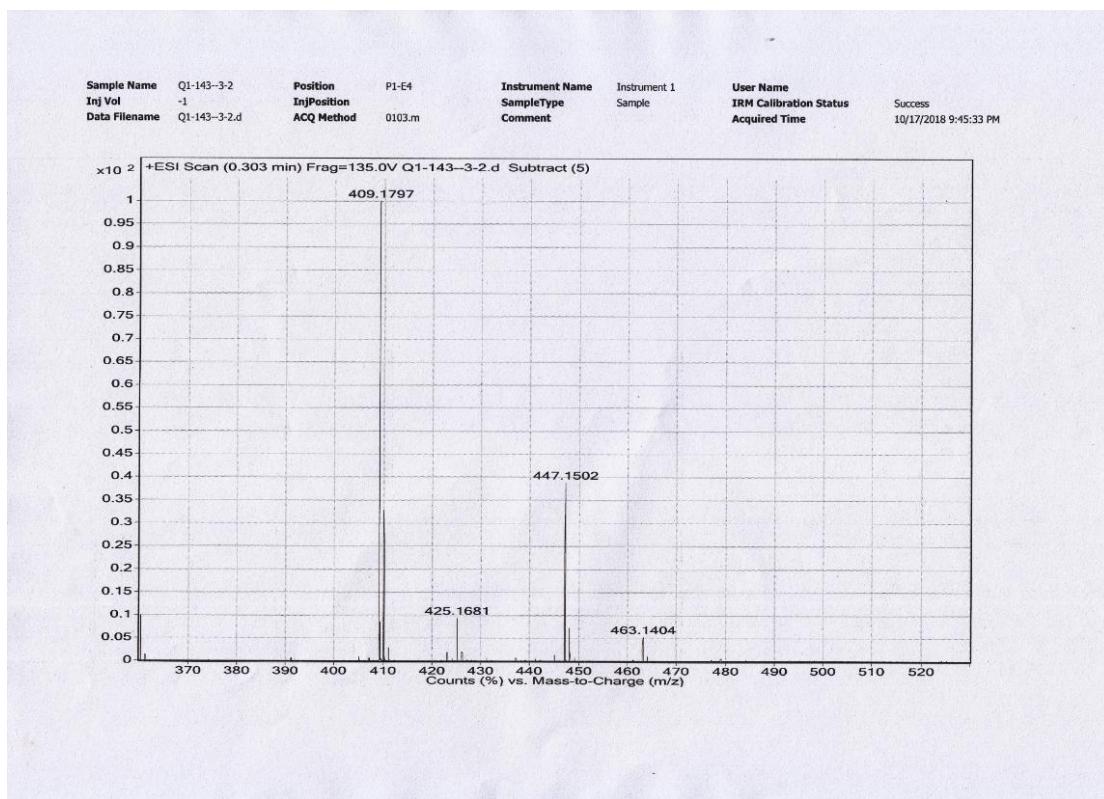
Molecular Weight: 394.4700

m/z : 394.1569 (100.0%), 395.1602 (29.2%), 396.1636 (2.7%), 396.1636 (1.4%)

Elemental Analysis: C, 82.21; H, 5.62; O, 12.17

HRMS (ESI, m/z) calcd for $C_{27}H_{22}O_3 [M+H]^+$ 395.1642, found 395.1643.





Chemical Formula: $C_{28}H_{24}O_3$

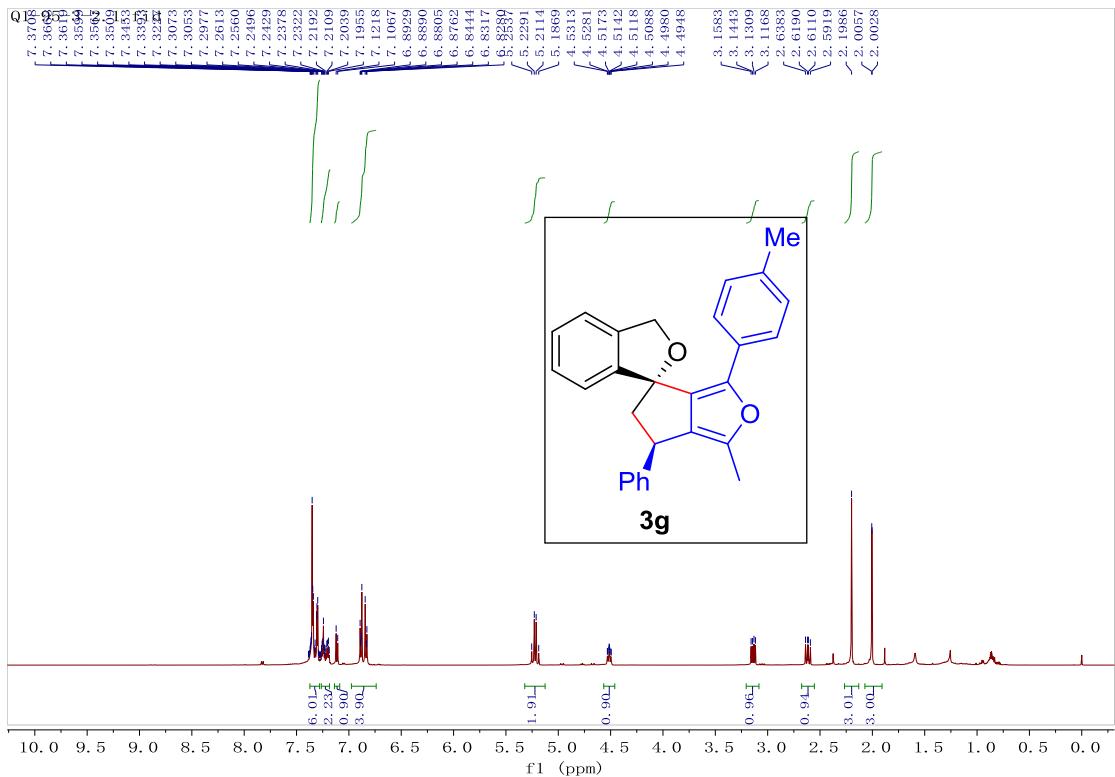
Exact Mass: 408.1725

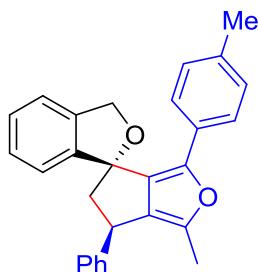
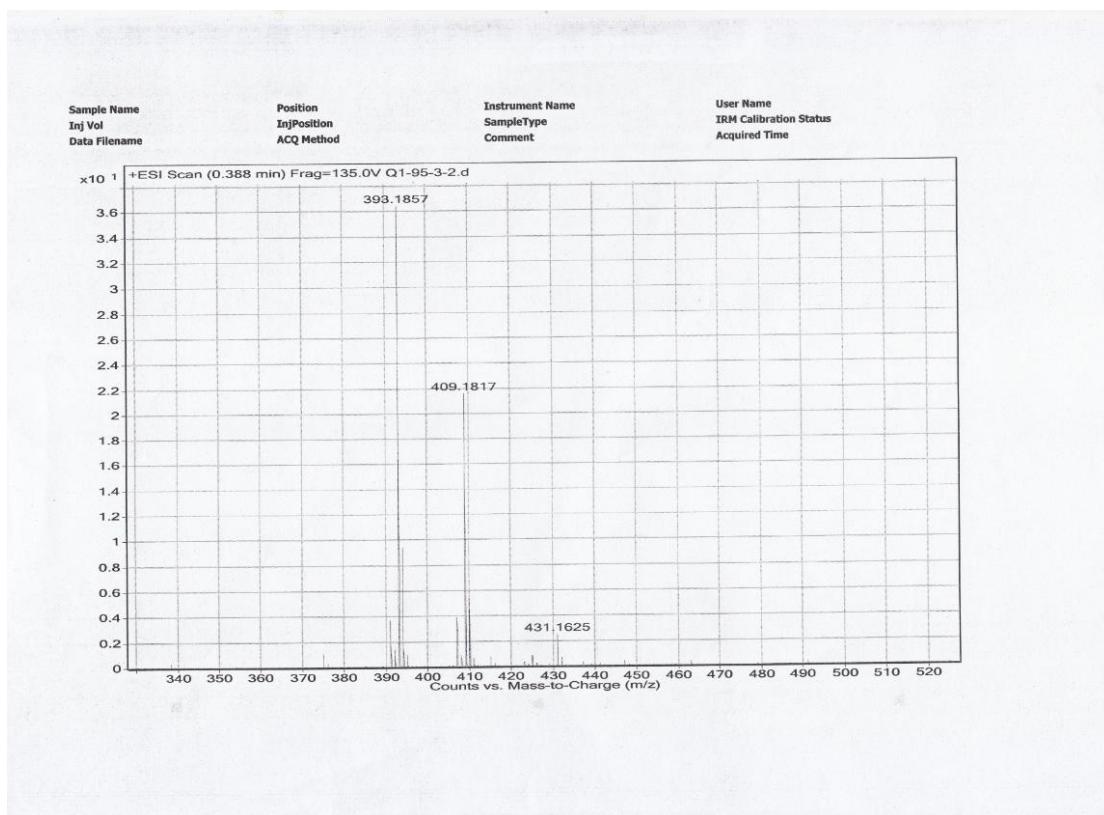
Molecular Weight: 408.4970

m/z : 408.1725 (100.0%), 409.1759 (30.3%), 410.1793 (2.7%), 410.1793 (1.7%)

Elemental Analysis: C, 82.33; H, 5.92; O, 11.75

HRMS (ESI, m/z) calcd for $C_{28}H_{24}O_3 [M+H]^+$ 409.1798, found 409.1797.





3g

Chemical Formula: C₂₈H₂₄O₂

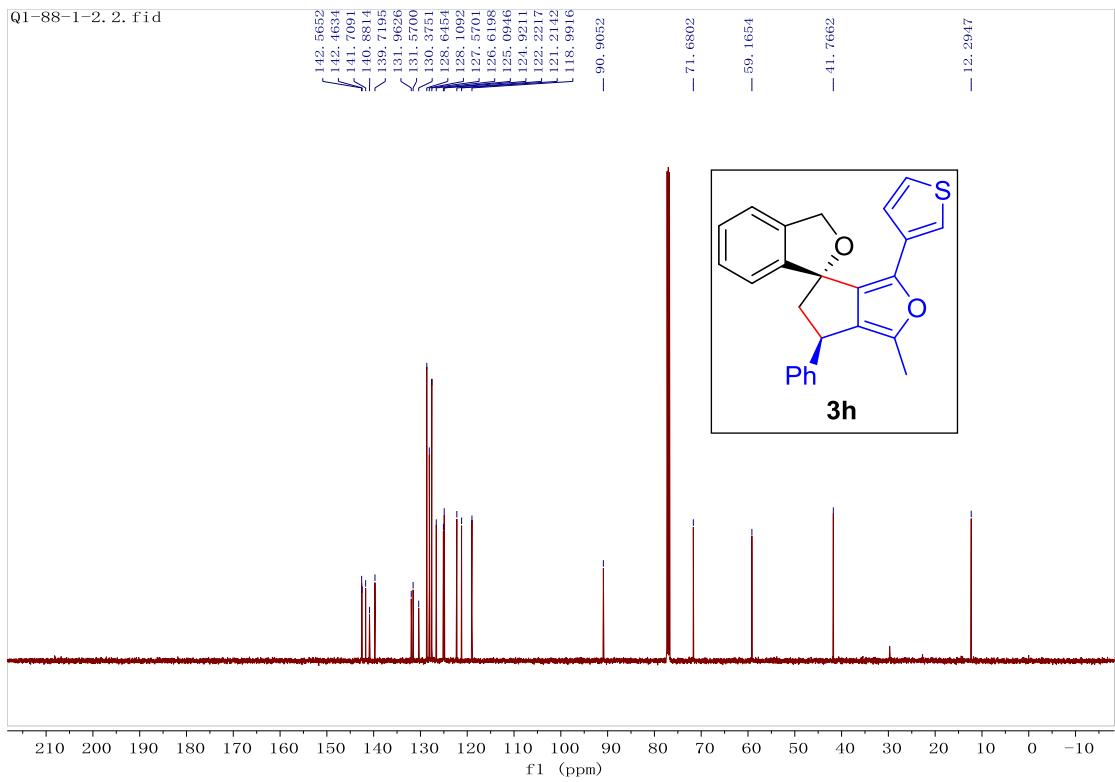
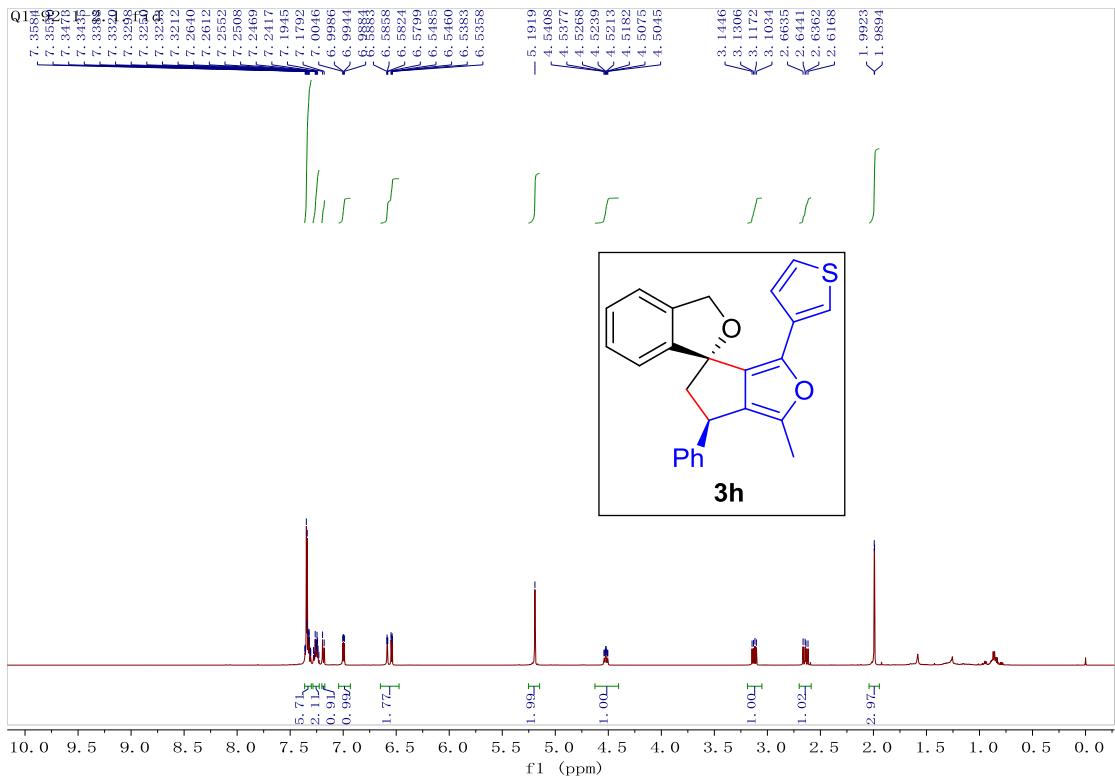
Exact Mass: 392.1776

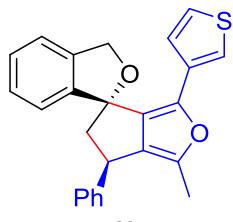
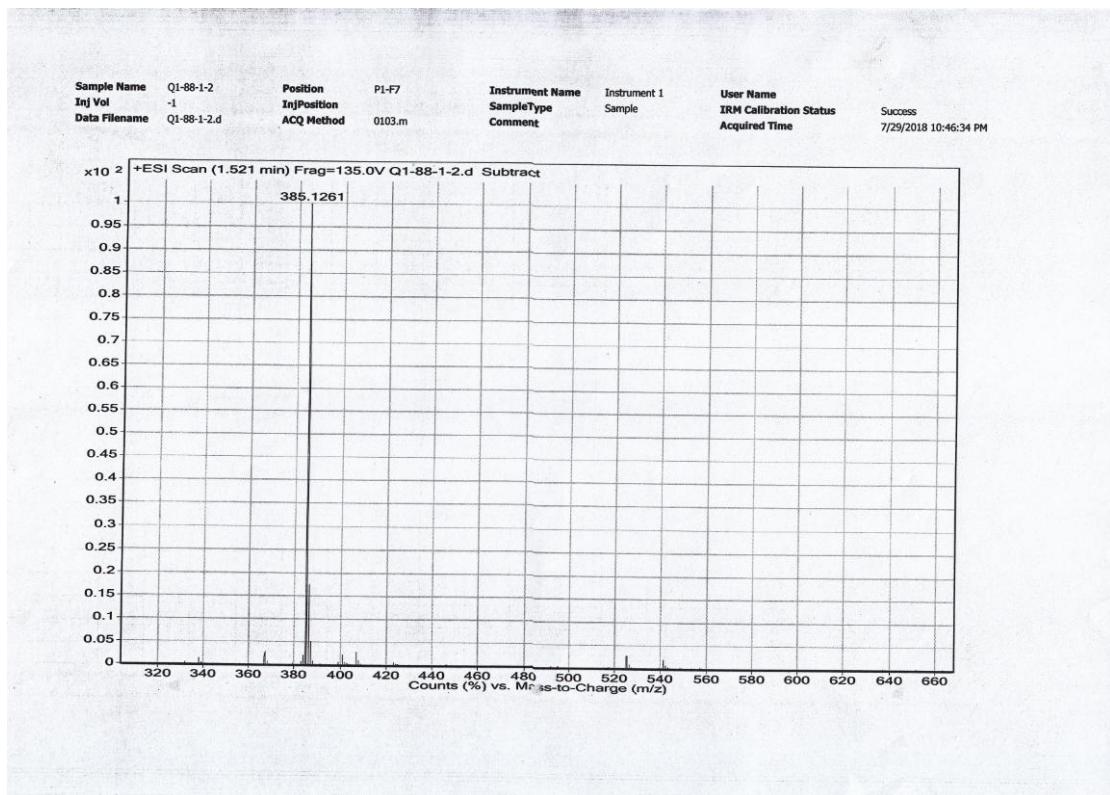
Molecular Weight: 392.4980

m/z: 392.1776 (100.0%), 393.1810 (30.3%), 394.1843 (2.7%), 394.1843 (1.7%)

Elemental Analysis: C, 85.68; H, 6.16; O, 8.15

HRMS (ESI, m/z) calcd for C₂₈H₂₄O₂ [M+H]⁺ 393.1855, found 393.1857.





Chemical Formula: $C_{25}H_{20}O_2S$

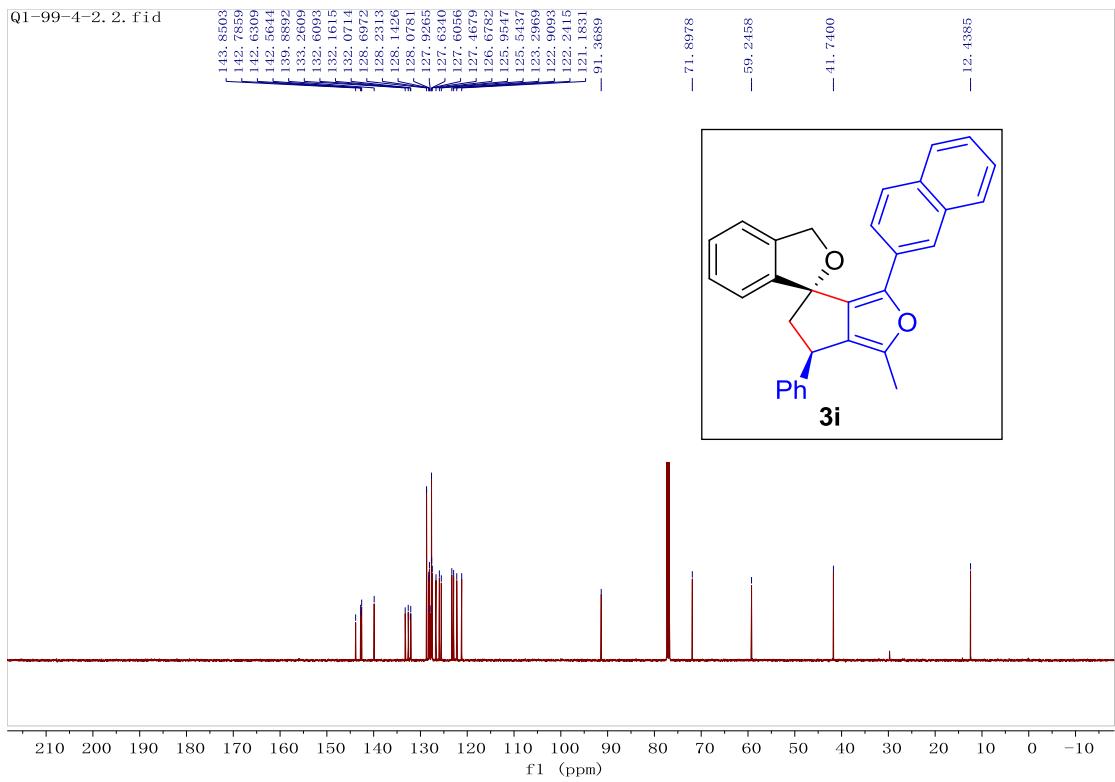
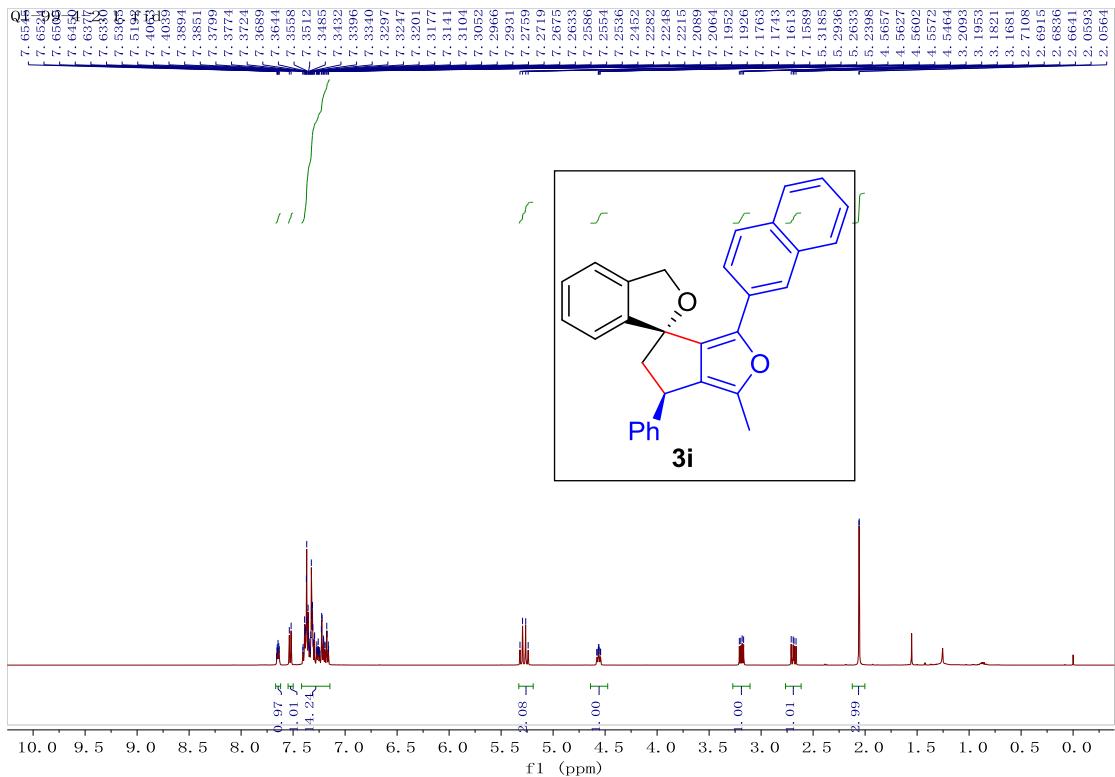
Exact Mass: 384.1184

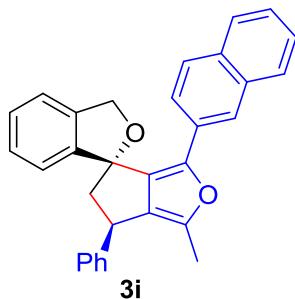
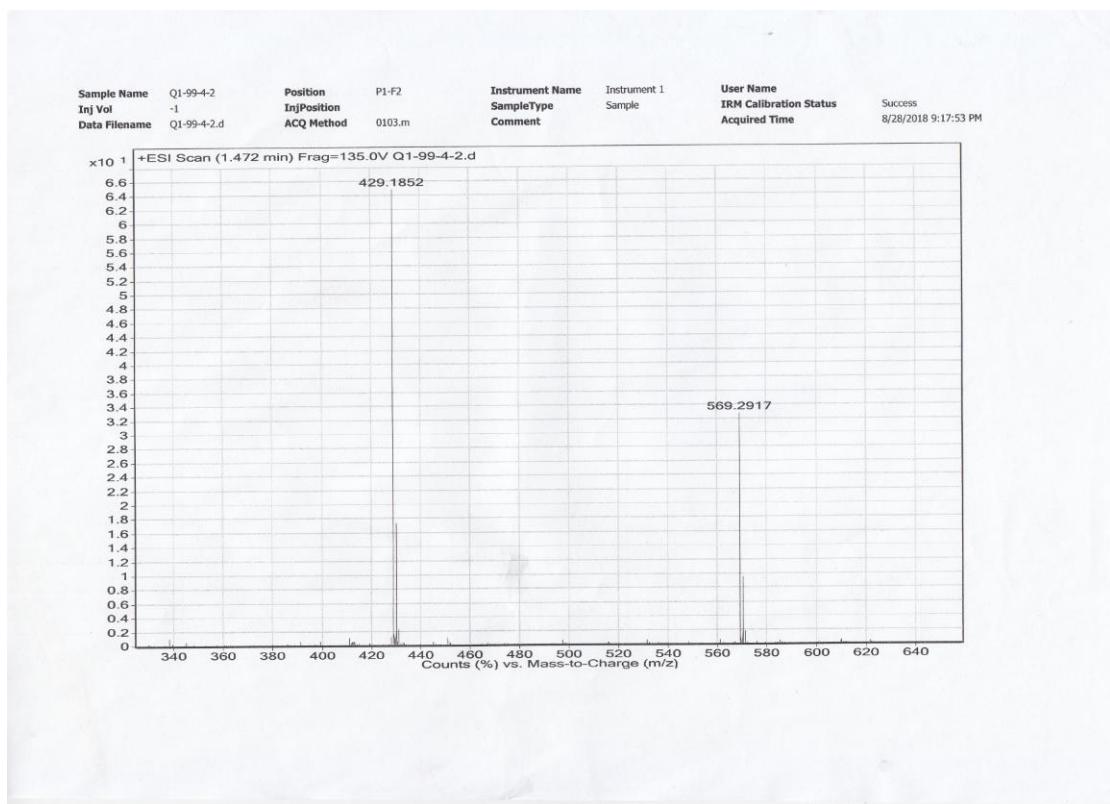
Molecular Weight: 384.4930

m/z : 384.1184 (100.0%), 385.1218 (27.0%), 386.1142 (4.5%), 386.1251 (2.7%), 387.1176 (1.2%)

Elemental Analysis: C, 78.10; H, 5.24; O, 8.32; S, 8.34

HRMS (ESI, m/z) calcd for $C_{25}H_{20}O_2S [M+H]^+$ 385.1257, found 385.1261.





Chemical Formula: $C_{31}H_{24}O_2$

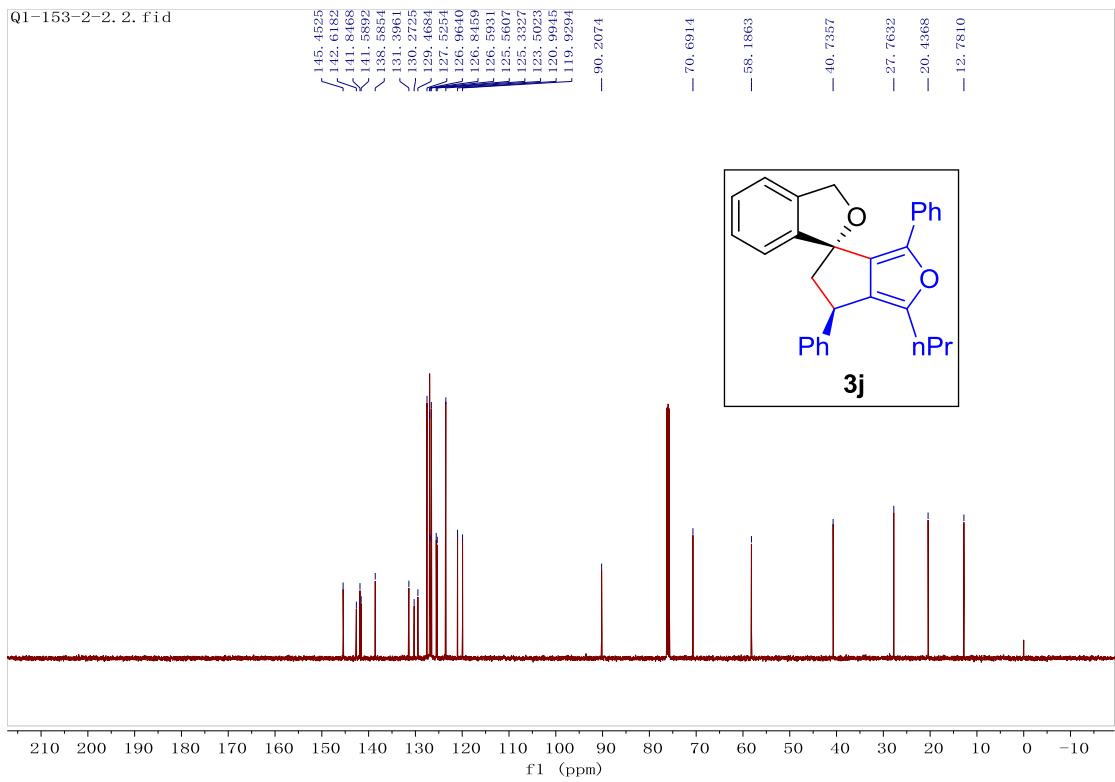
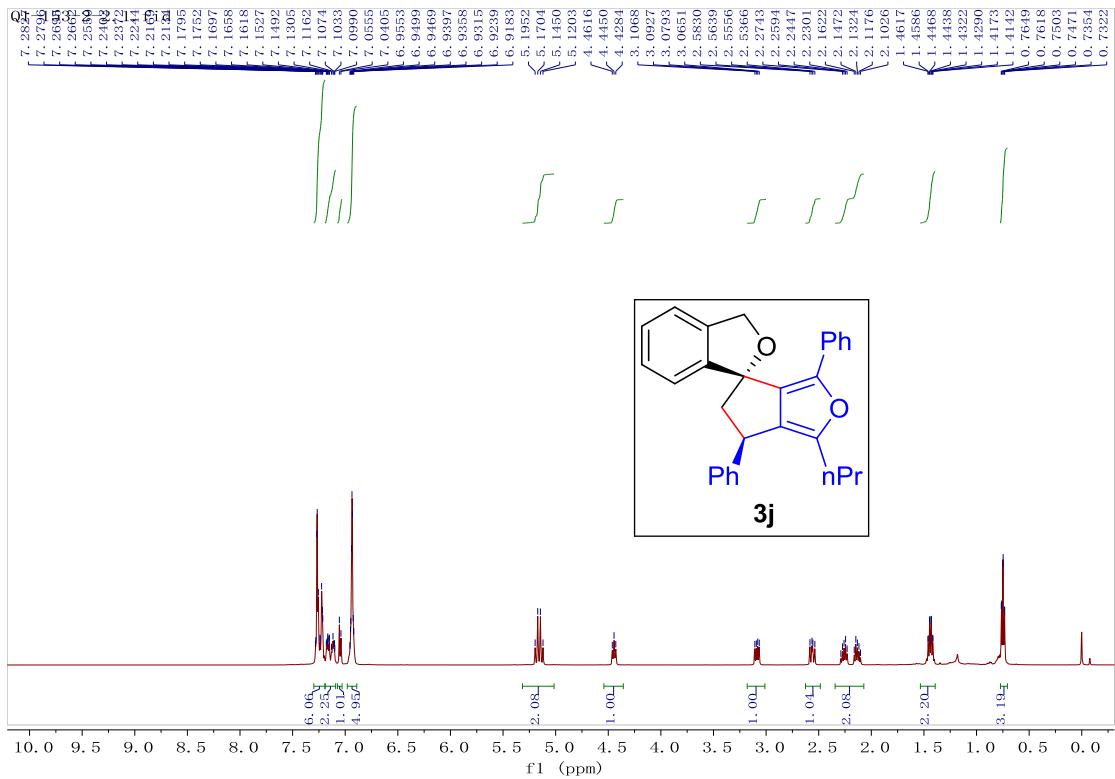
Exact Mass: 428.1776

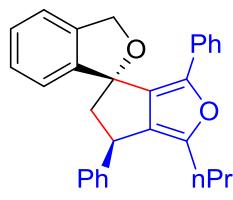
Molecular Weight: 428.5310

m/z : 428.1776 (100.0%), 429.1810 (33.5%), 430.1843 (2.7%), 430.1843 (2.7%)

Elemental Analysis: C, 86.89; H, 5.65; O, 7.47

HRMS (ESI, m/z) calcd for $C_{31}H_{24}O_2 [M+H]^+$ 429.1849, found 429.1852.





Chemical Formula: C₂₉H₂₆O₂

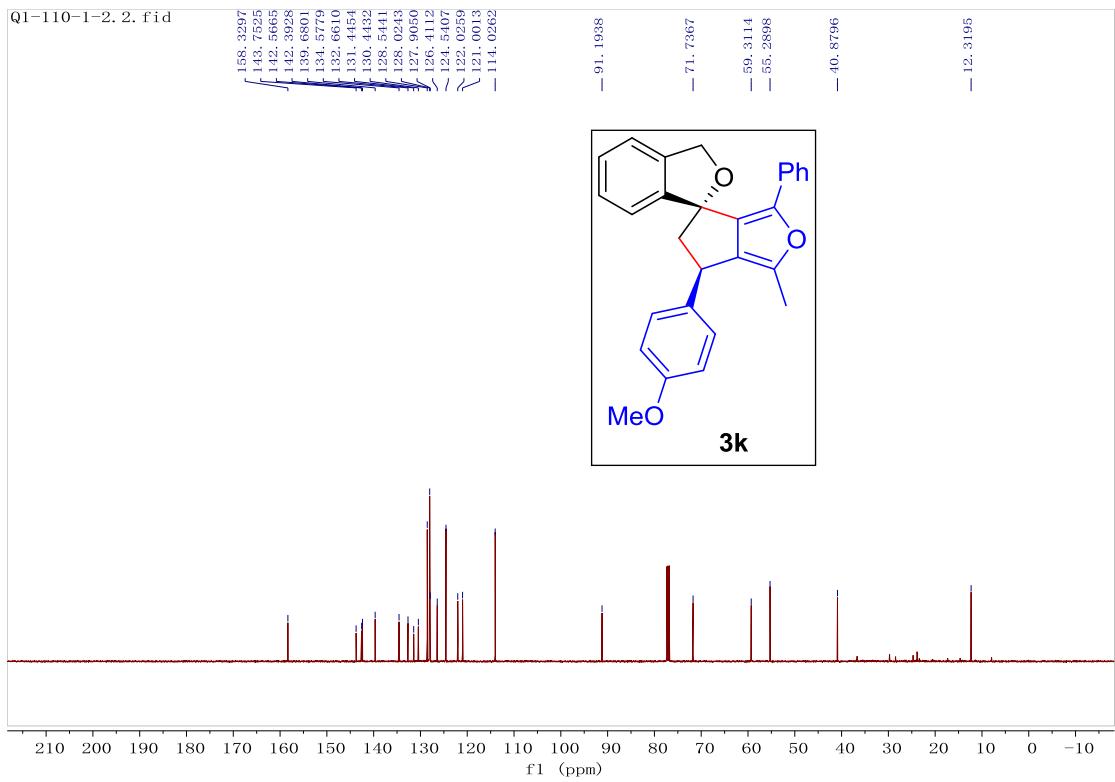
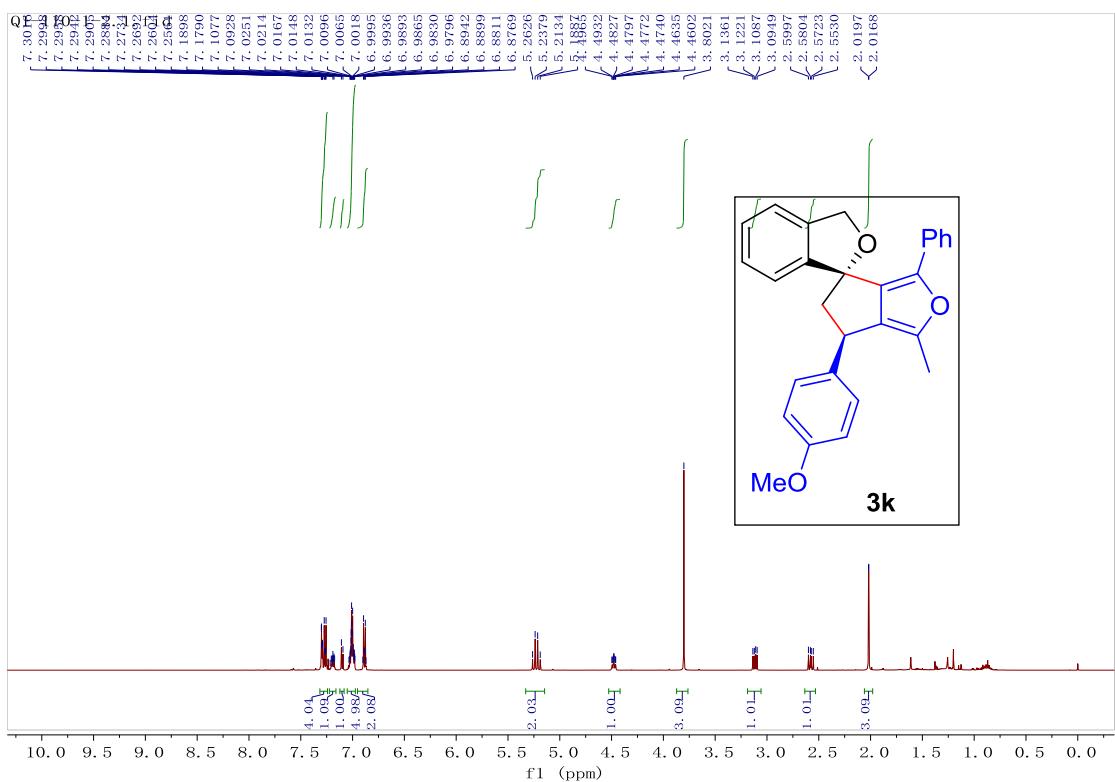
Exact Mass: 406.1933

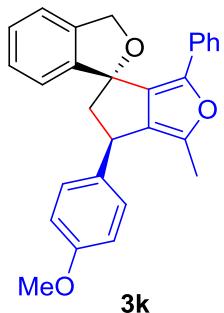
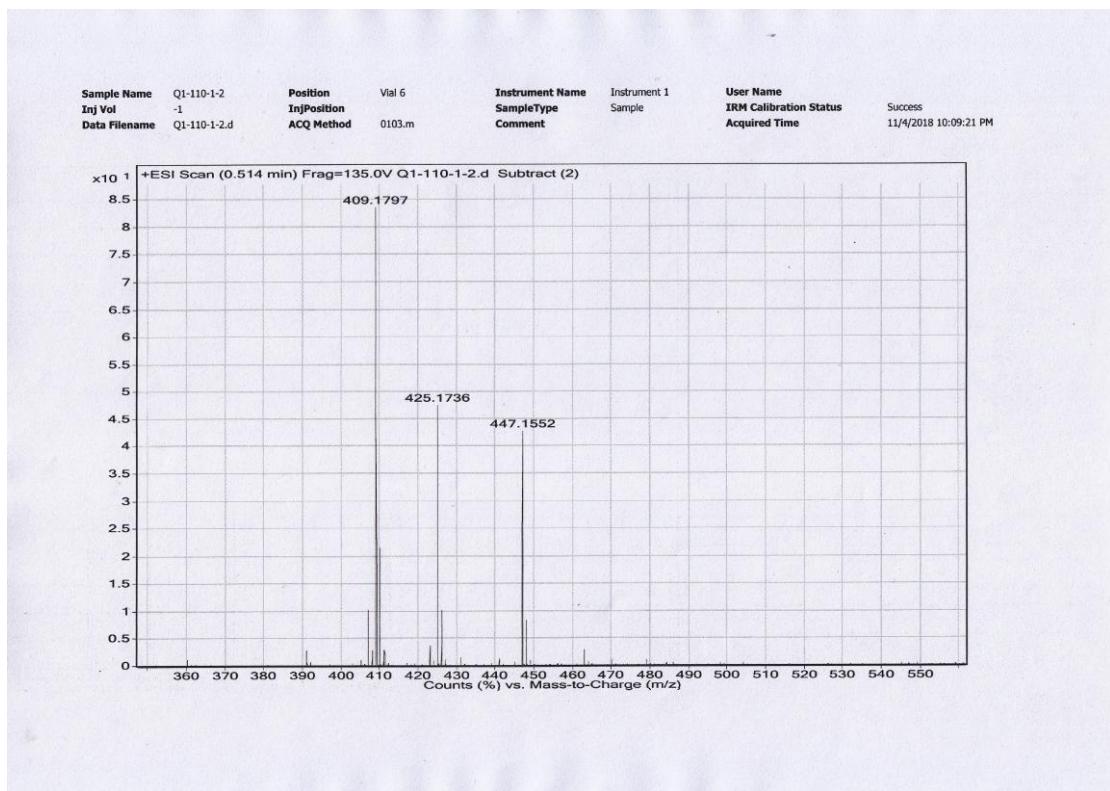
Molecular Weight: 406.5250

m/z: 406.1933 (100.0%), 407.1966 (31.4%), 408.2000 (2.7%), 408.2000 (2.0%)

Elemental Analysis: C, 85.68; H, 6.45; O, 7.87

HRMS (ESI, m/z) calcd for C₂₉H₂₆O₂ [M+H]⁺ 407.2006, found 407.2010.





Chemical Formula: $C_{28}H_{24}O_3$

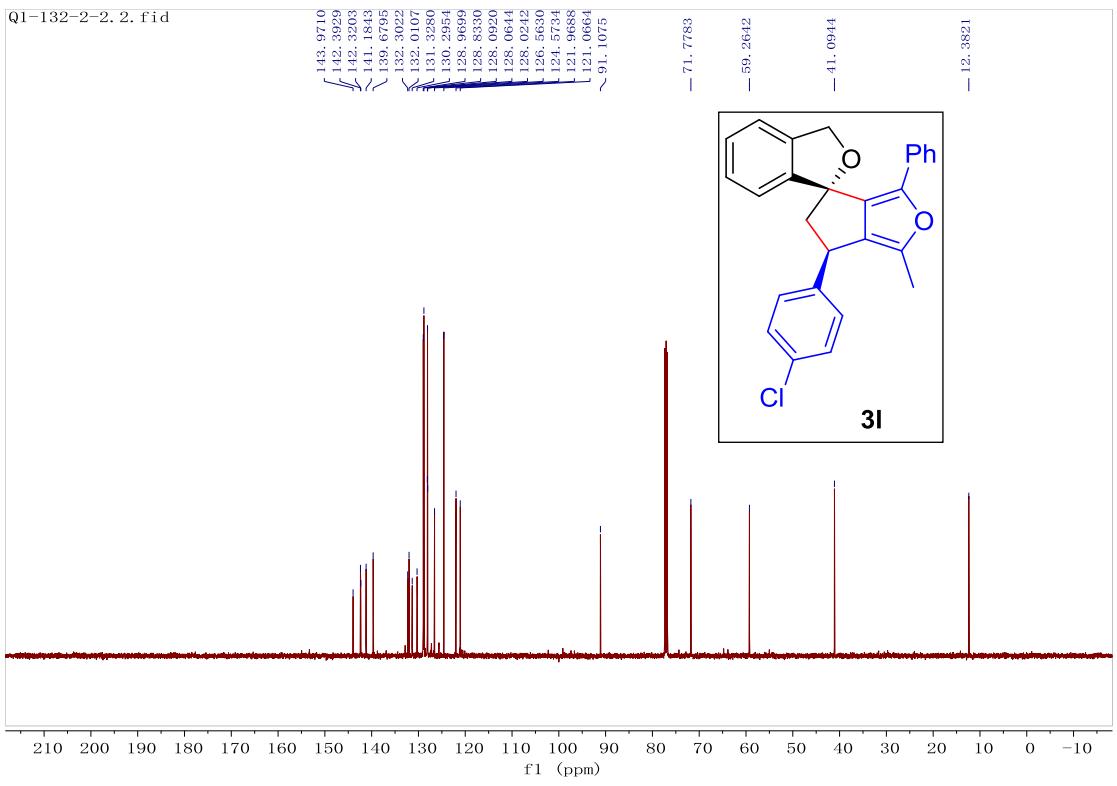
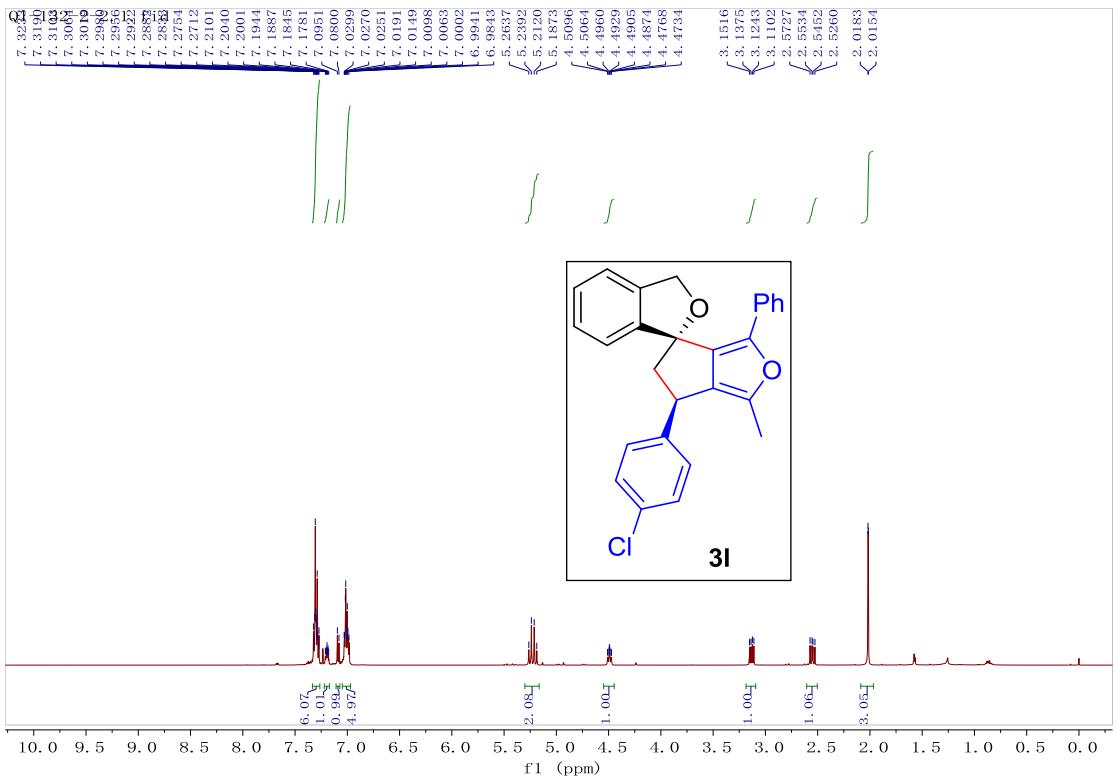
Exact Mass: 408.1725

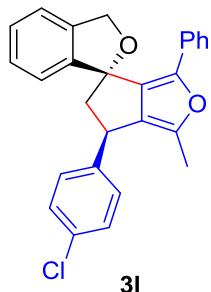
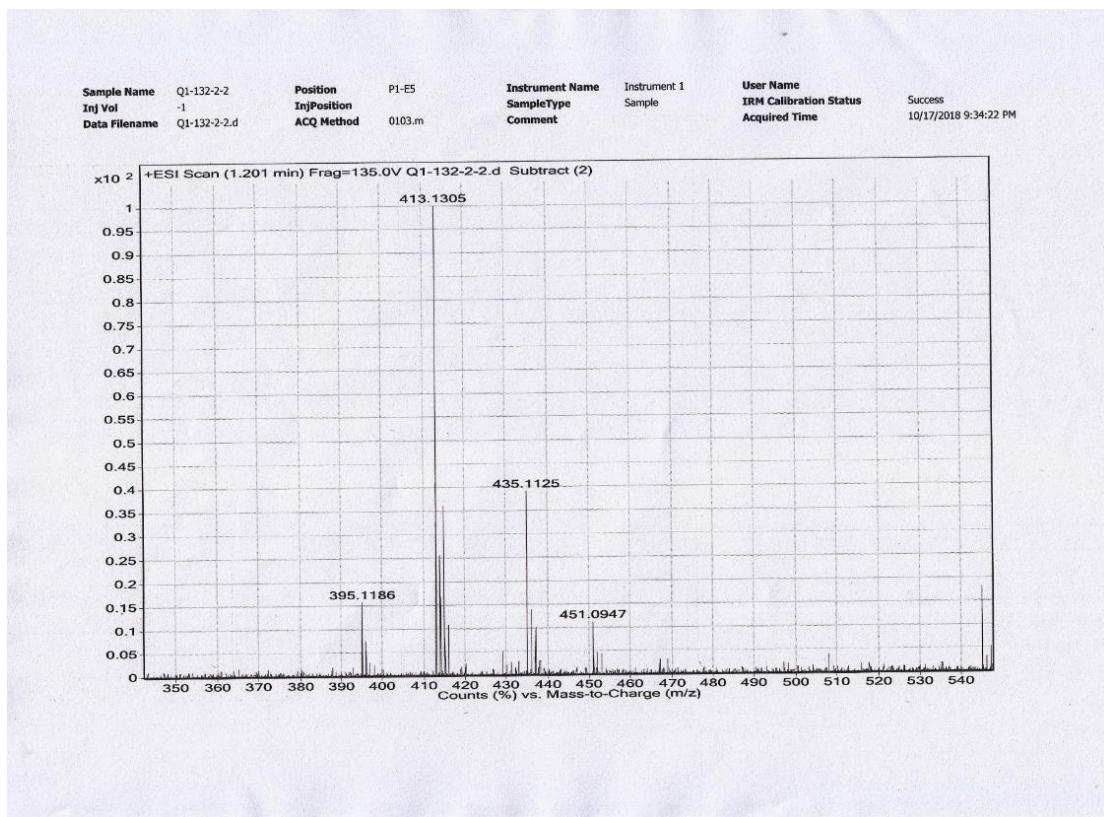
Molecular Weight: 408.4970

m/z : 408.1725 (100.0%), 409.1759 (30.3%), 410.1793 (2.7%), 410.1793 (1.7%)

Elemental Analysis: C, 82.33; H, 5.92; O, 11.75

HRMS (ESI, m/z) calcd for $C_{28}H_{24}O_3 [M+H]^+$ 409.1798, found 409.1797.





Chemical Formula: $C_{27}H_{21}ClO_2$

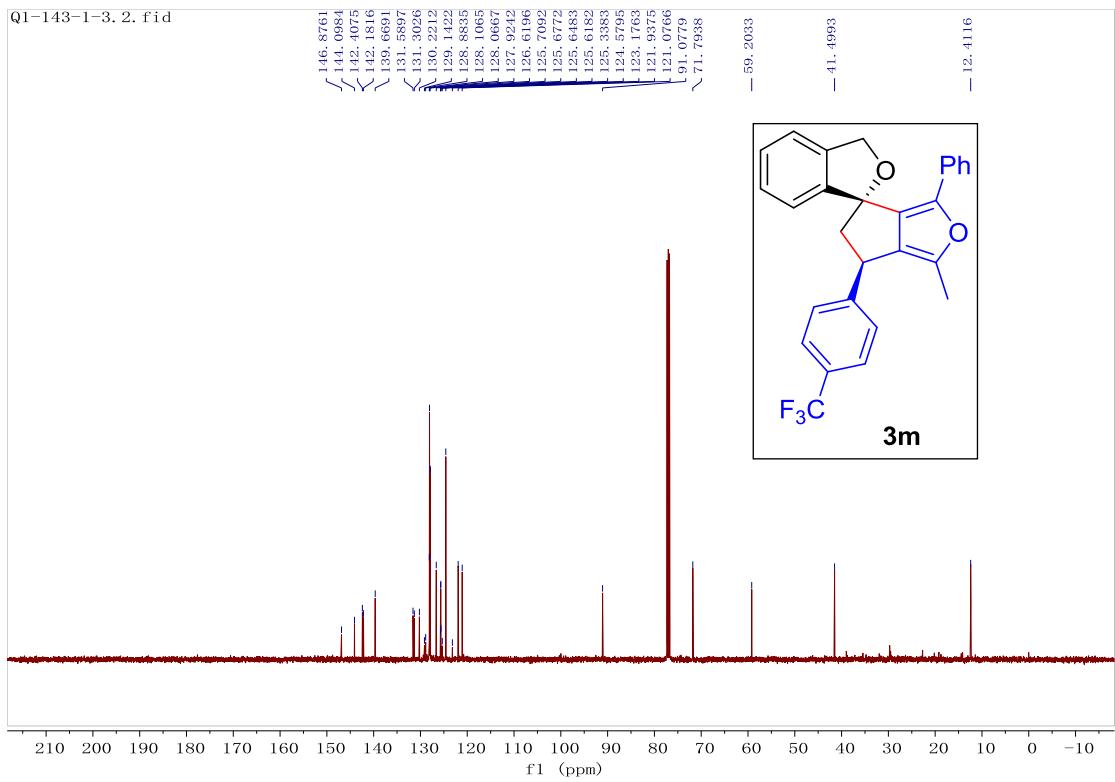
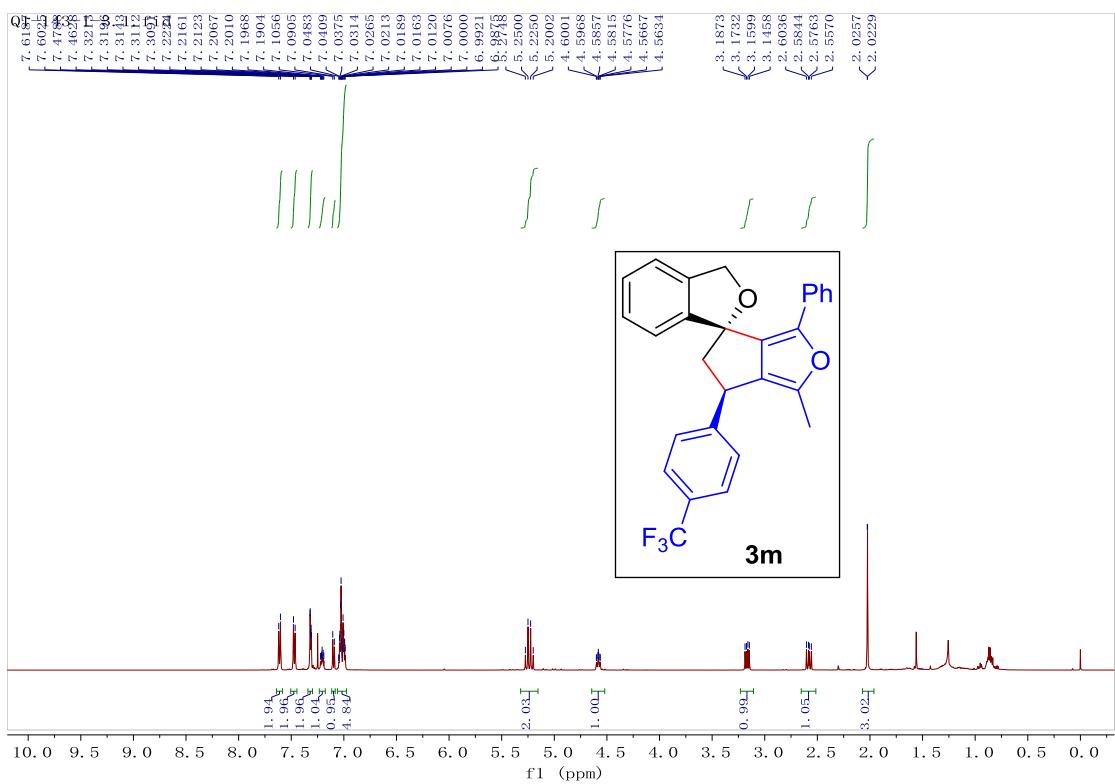
Exact Mass: 412.1230

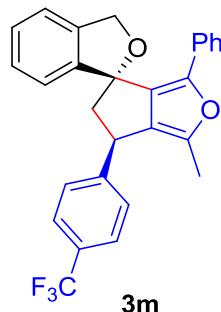
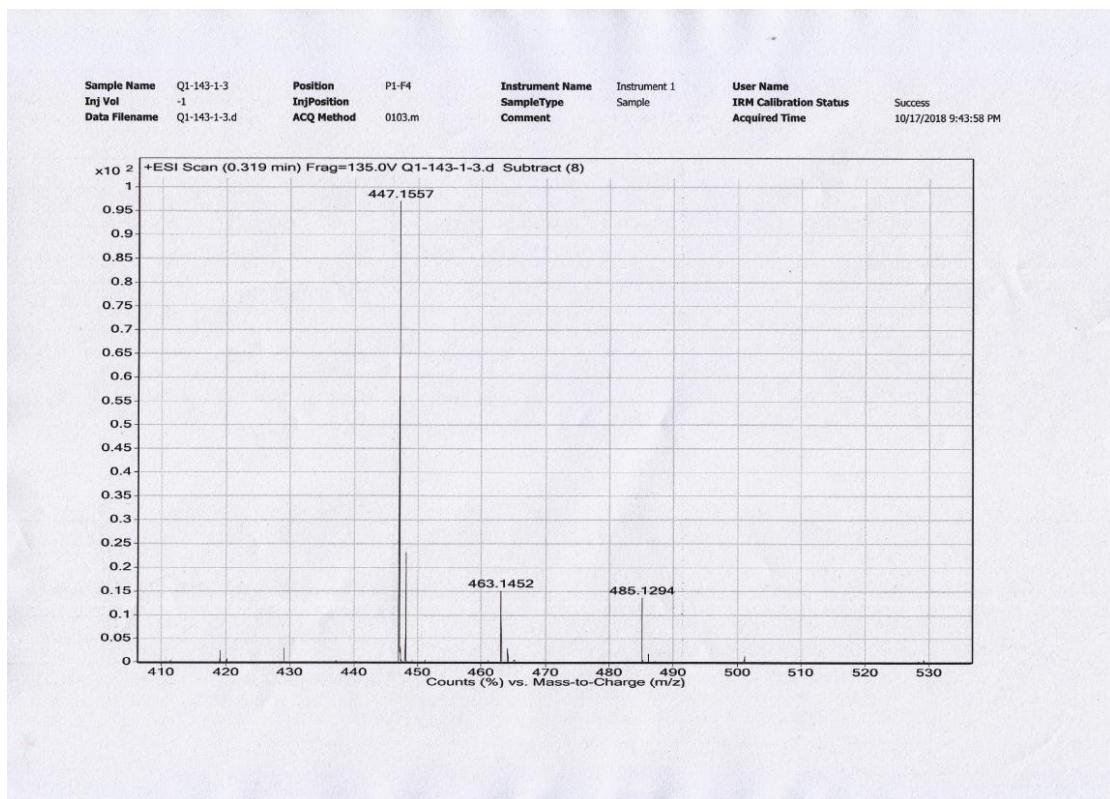
Molecular Weight: 412.9130

m/z: 412.1230 (100.0%), 414.1201 (32.0%), 413.1264 (29.2%), 415.1234 (9.3%), 414.1297 (4.1%)

Elemental Analysis: C, 78.54; H, 5.13; Cl, 8.59; O, 7.75

HRMS (ESI, m/z) calcd for $C_{27}H_{21}ClO_2 [M+H]^+$ 413.1303, found 413.1305.





Chemical Formula: $C_{28}H_{21}F_3O_2$

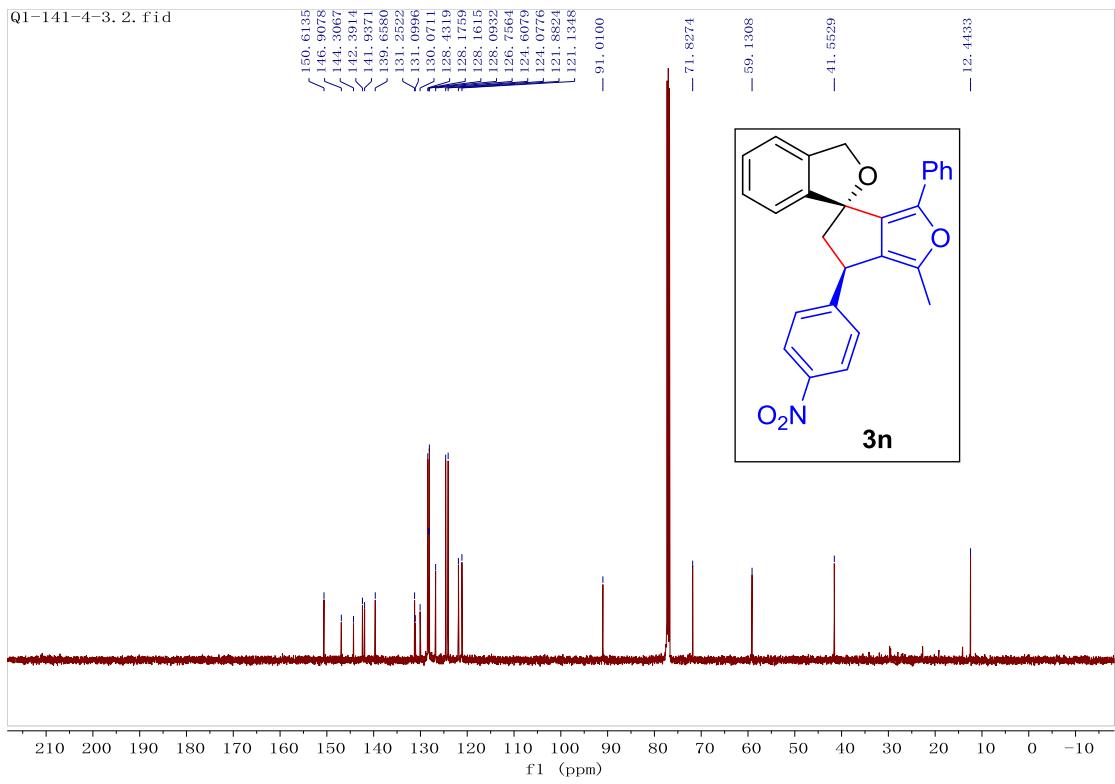
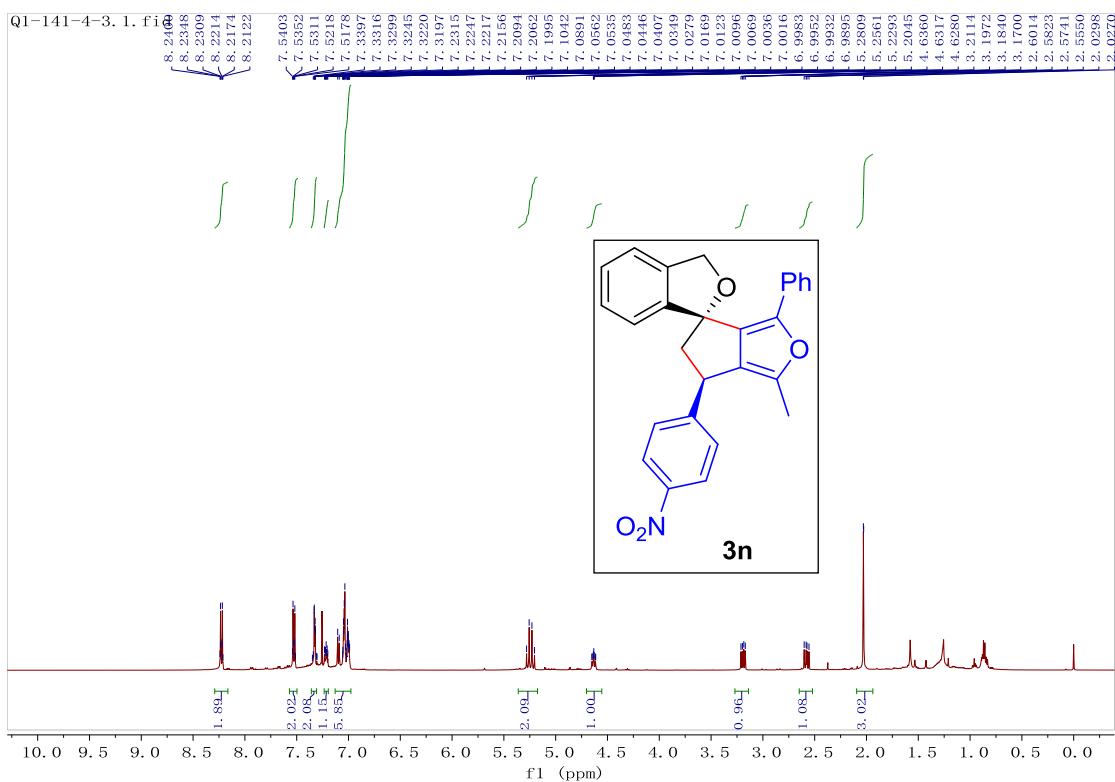
Exact Mass: 446.1494

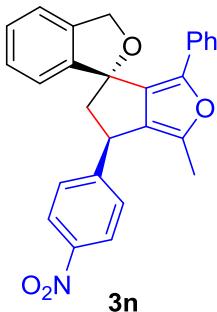
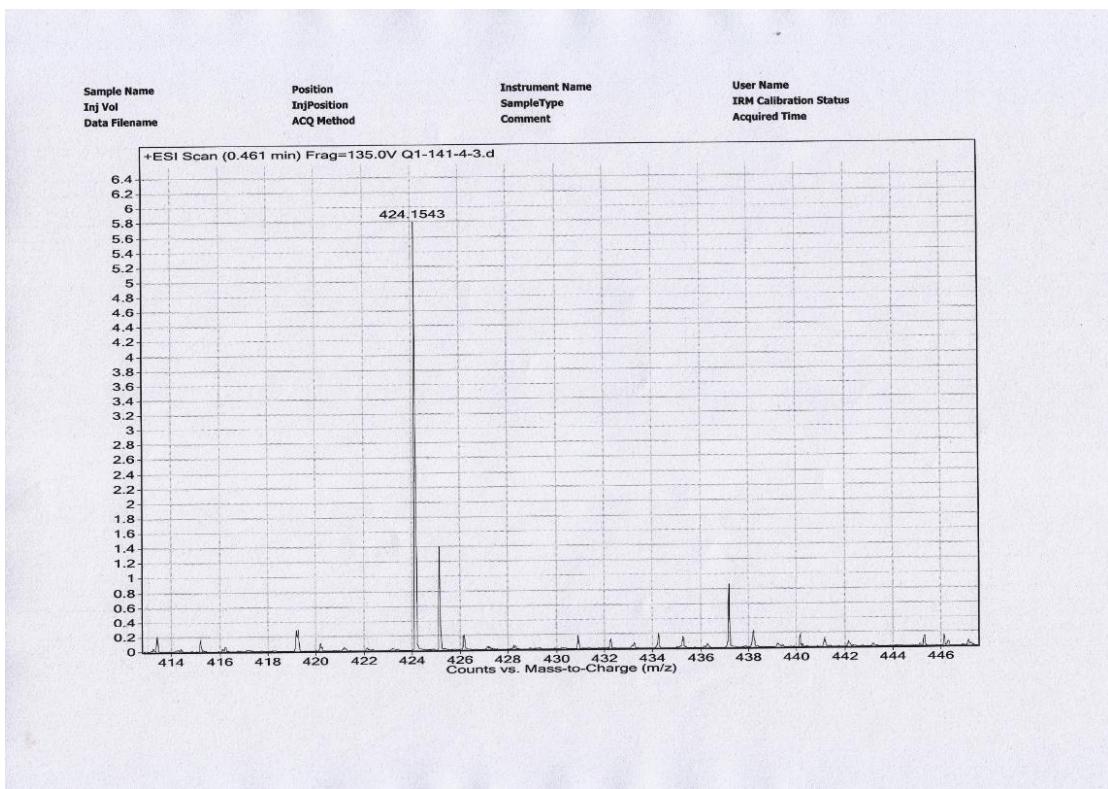
Molecular Weight: 446.4692

m/z: 446.1494 (100.0%), 447.1527 (30.3%), 448.1561 (2.7%), 448.1561 (1.7%)

Elemental Analysis: C, 75.33; H, 4.74; F, 12.77; O, 7.17

HRMS (ESI, m/z) calcd for $C_{28}H_{21}F_3O_2 [M+H]^+$ 447.1566, found 447.1557.





Chemical Formula: C₂₇H₂₁NO₄

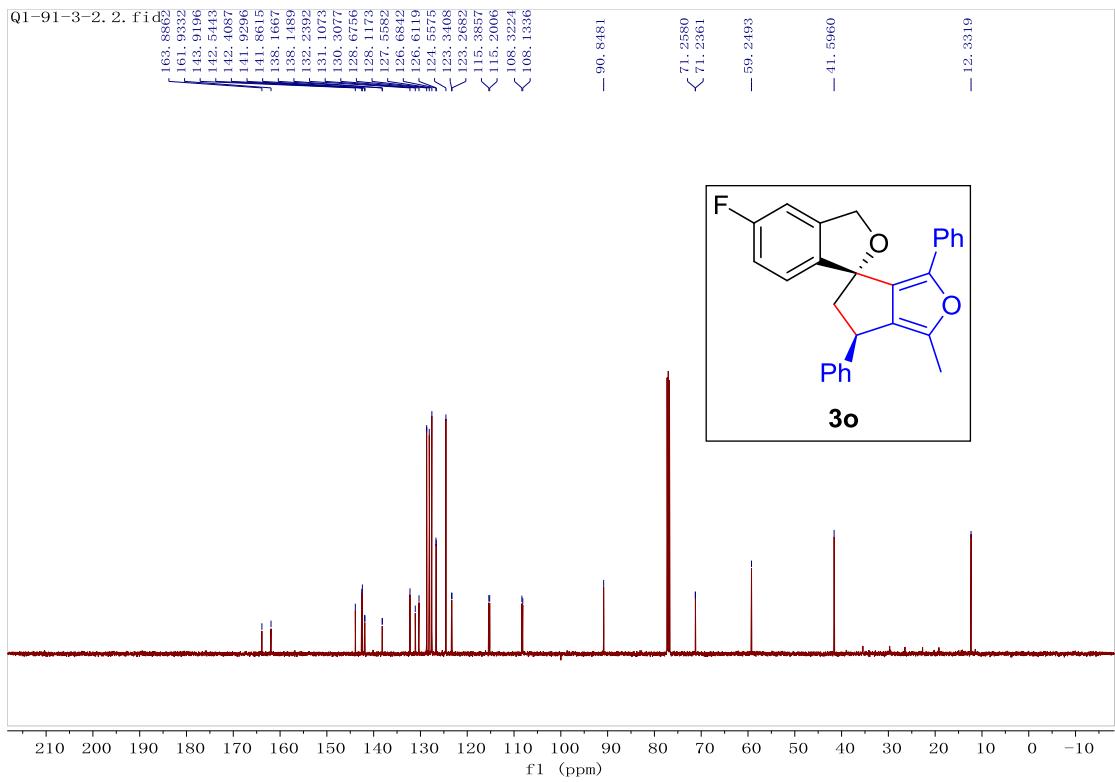
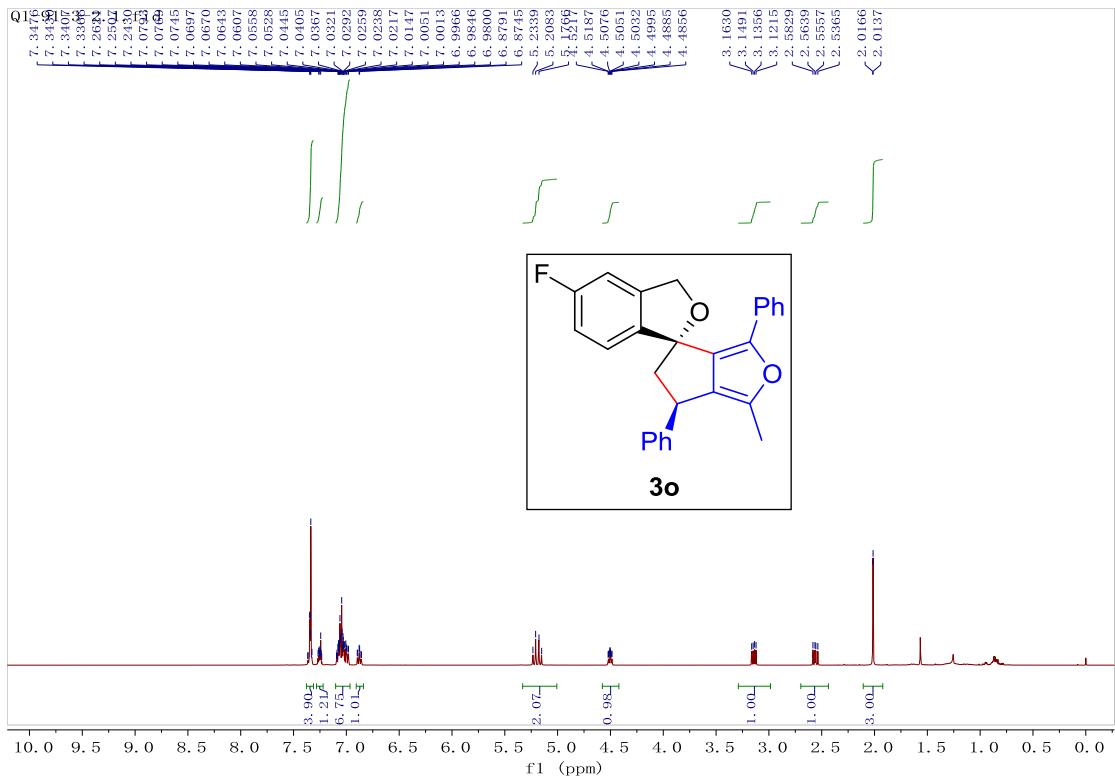
Exact Mass: 423.1471

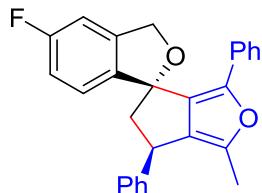
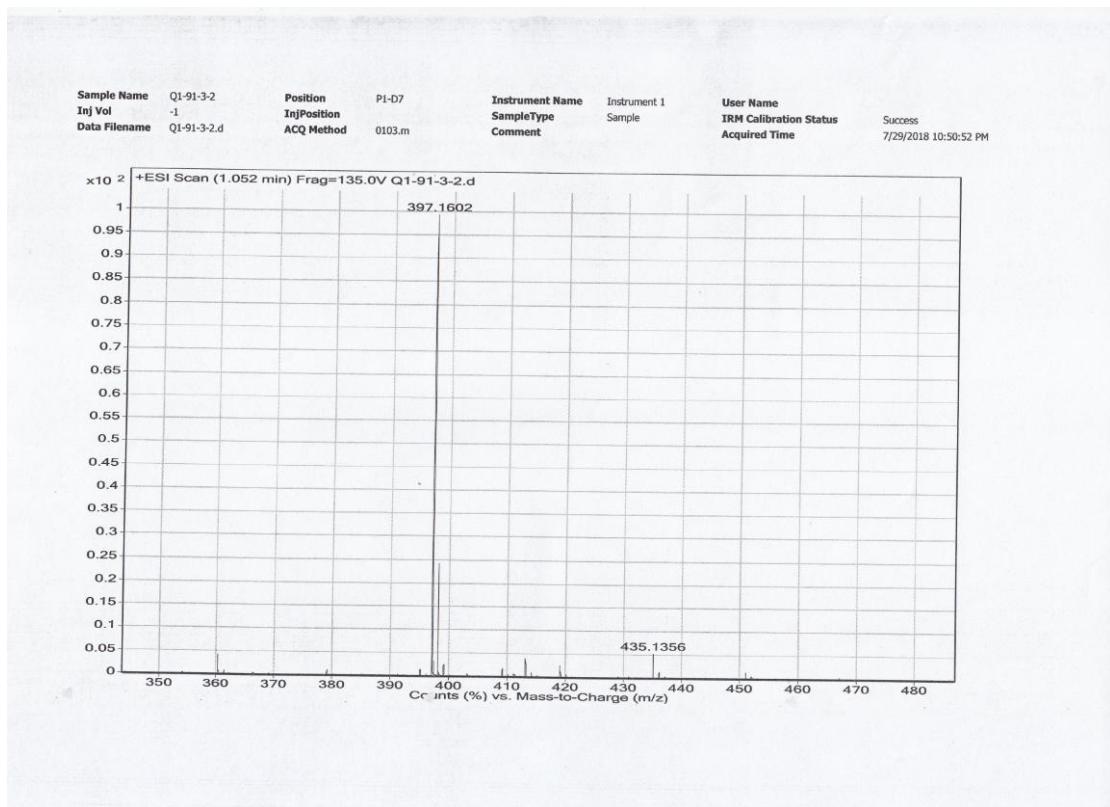
Molecular Weight: 423.4680

m/z: 423.1471 (100.0%), 424.1504 (29.2%), 425.1538 (2.7%), 425.1538 (1.4%)

Elemental Analysis: C, 76.58; H, 5.00; N, 3.31; O, 15.11

HRMS (ESI, m/z) calcd for C₂₇H₂₁NO₄ [M+H]⁺ 424.1543, found 424.1543.





3o

Chemical Formula: C₂₇H₂₁FO₂

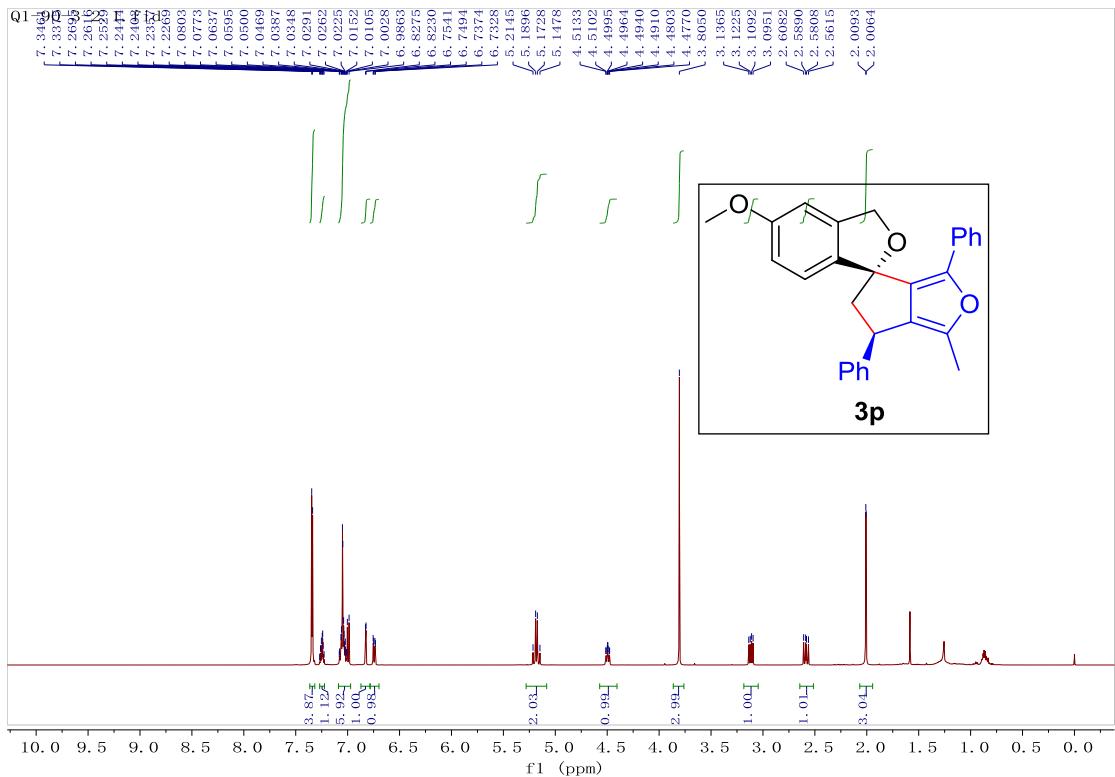
Exact Mass: 396.1526

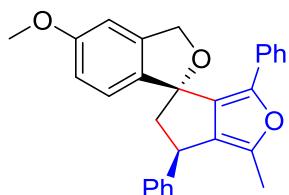
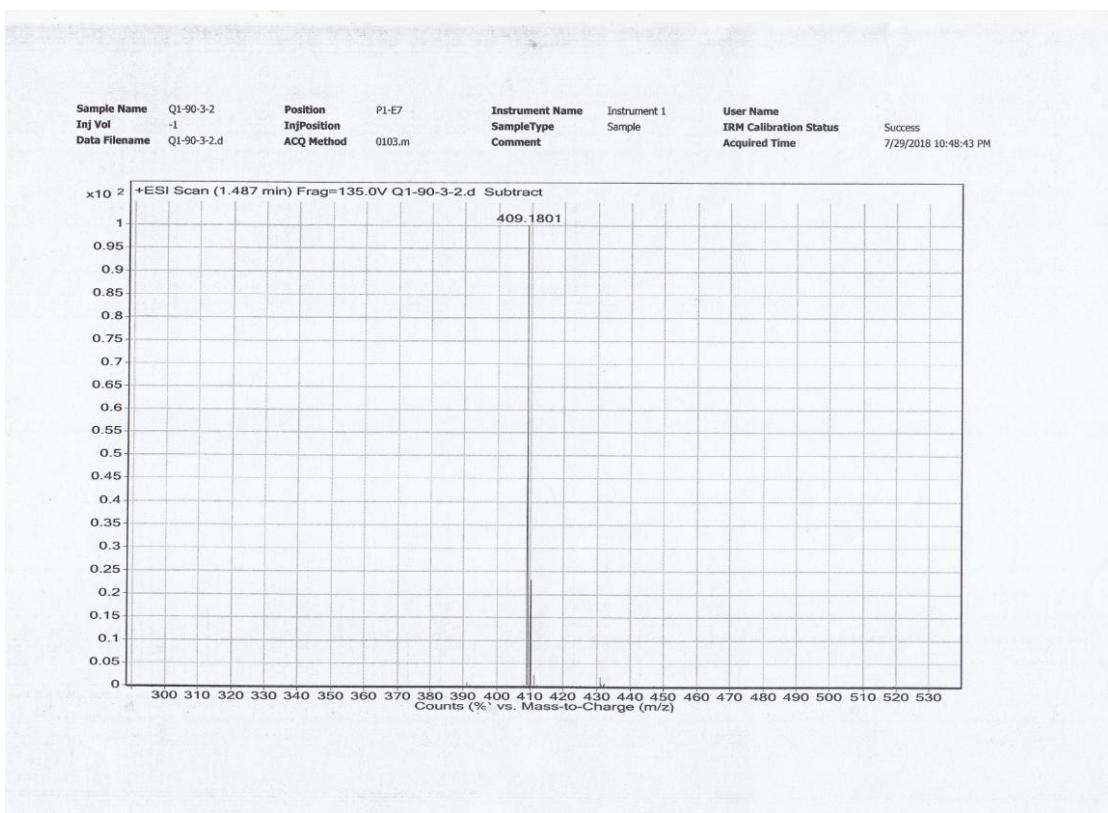
Molecular Weight: 396.4614

m/z: 396.1526 (100.0%), 397.1559 (29.2%), 398.1593 (2.7%), 398.1593 (1.4%)

Elemental Analysis: C, 81.80; H, 5.34; F, 4.79; O, 8.07

HRMS (ESI, m/z) calcd for C₂₇H₂₁FO₂ [M+H]⁺ 397.1598, found 397.1602.





3p

Chemical Formula: C₂₈H₂₄O₃

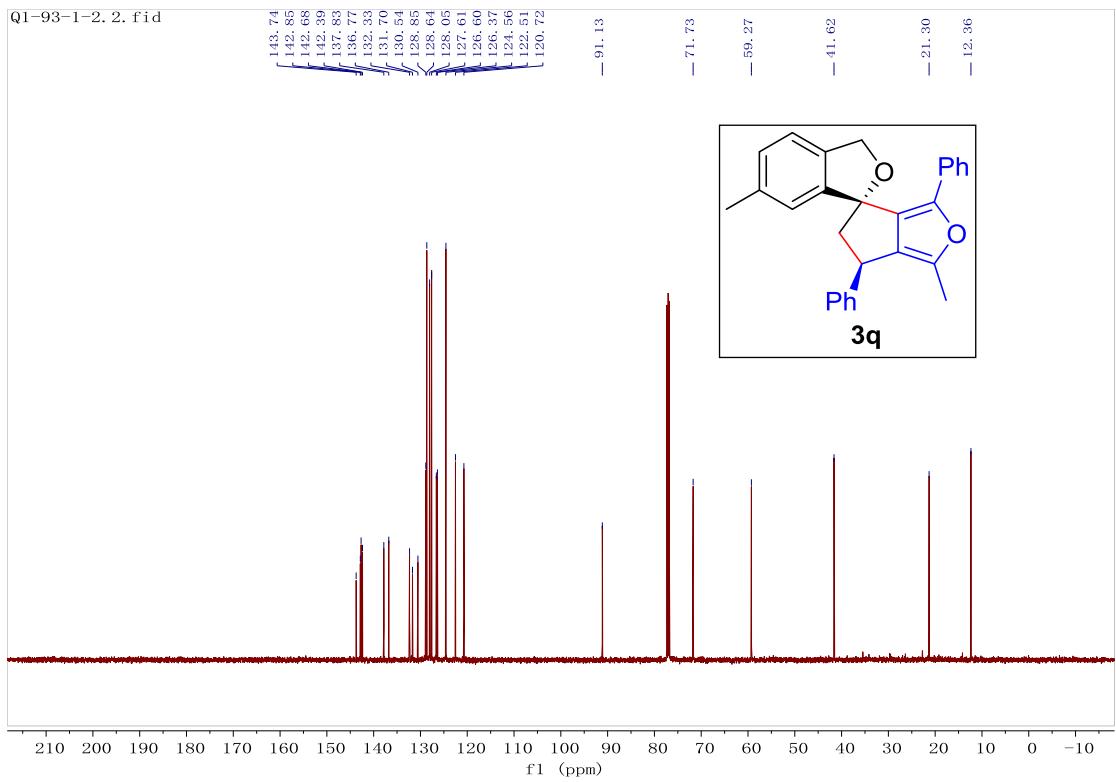
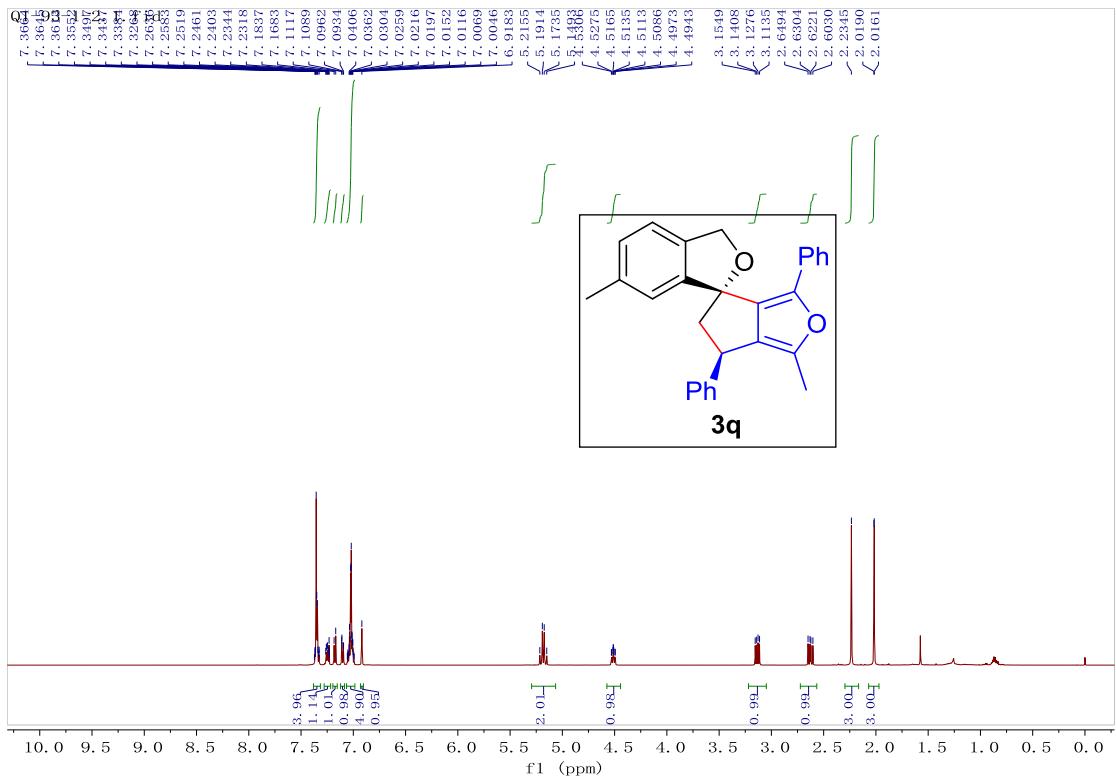
Exact Mass: 408.1725

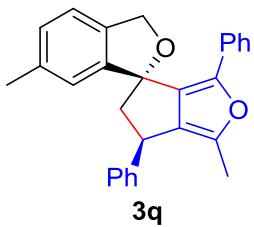
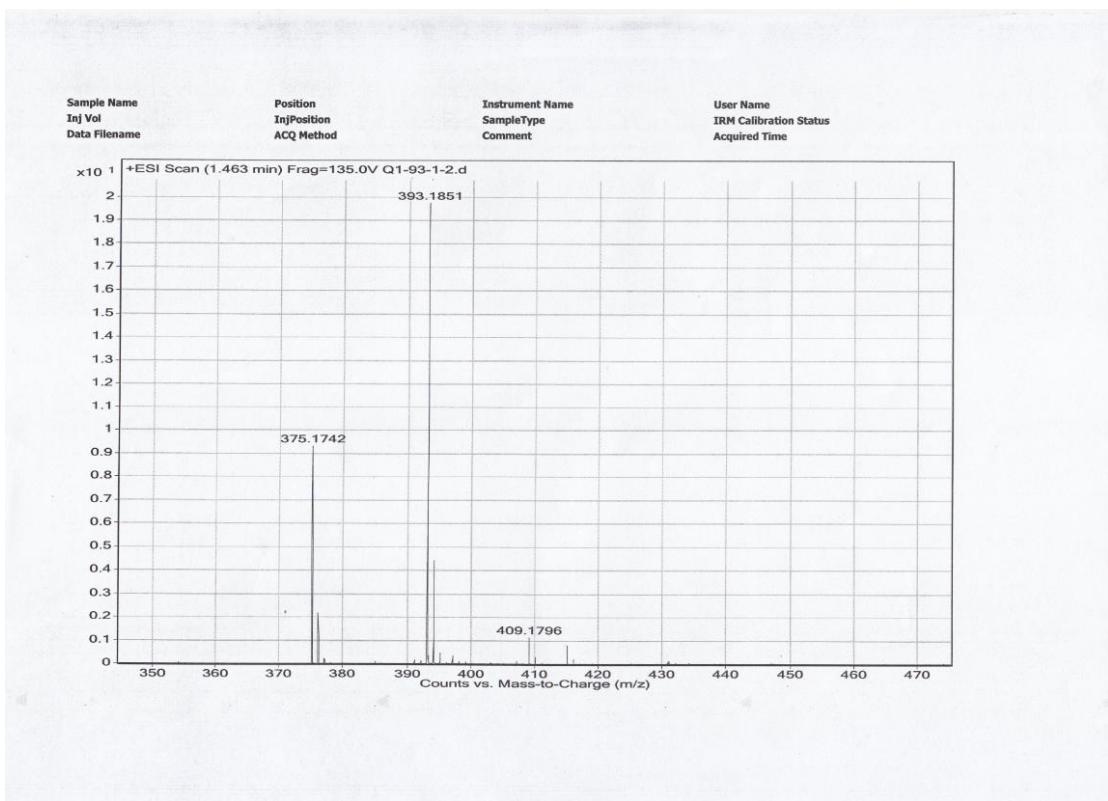
Molecular Weight: 408.4970

m/z: 408.1725 (100.0%), 409.1759 (30.3%), 410.1793 (2.7%), 410.1793 (1.7%)

Elemental Analysis: C, 82.33; H, 5.92; O, 11.75

HRMS (ESI, m/z) calcd for C₂₈H₂₄O₃ [M+H]⁺ 409.1798, found 409.1801.





3q

Chemical Formula: C₂₈H₂₄O₂

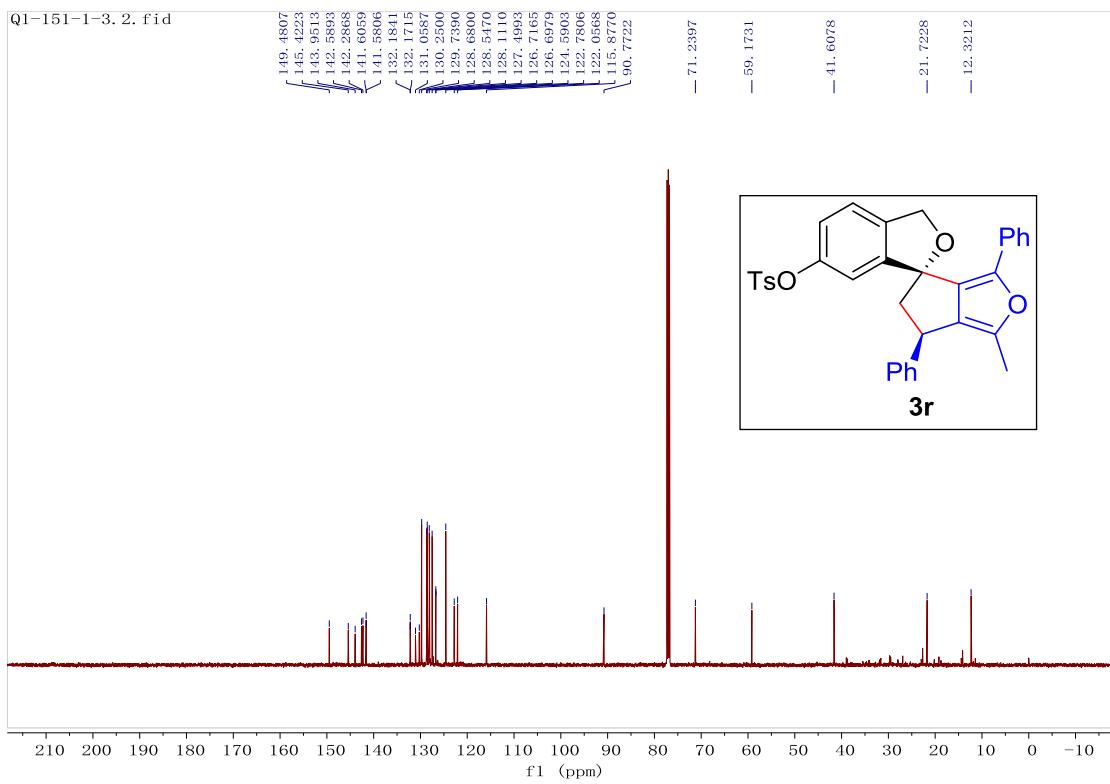
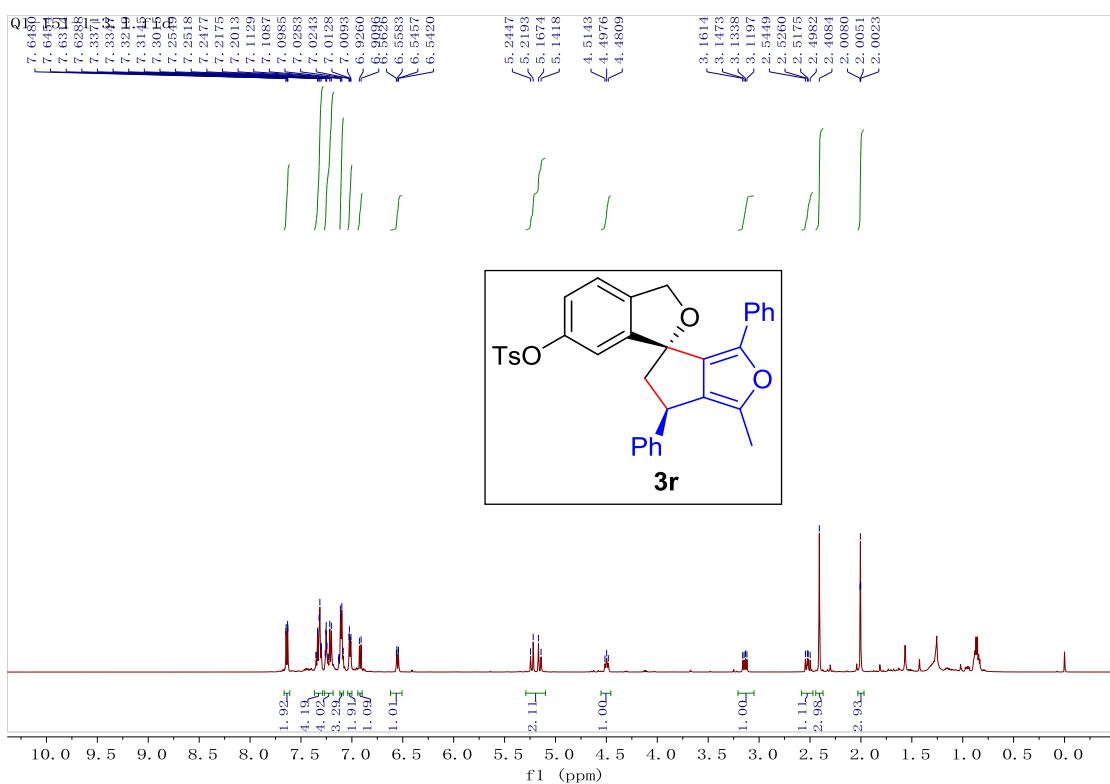
Exact Mass: 392.1776

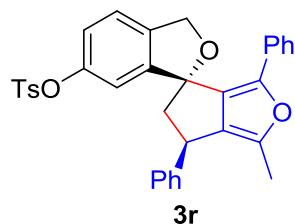
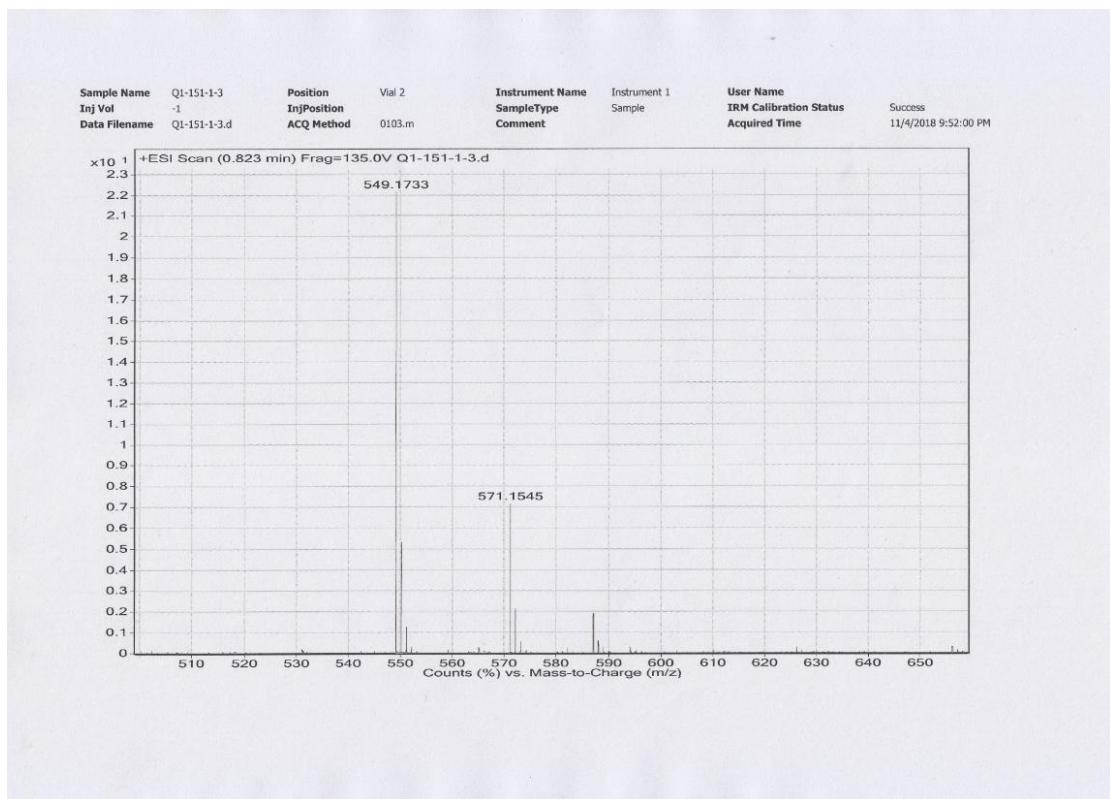
Molecular Weight: 392.4980

m/z: 392.1776 (100.0%), 393.1810 (30.3%), 394.1843 (2.7%), 394.1843 (1.7%)

Elemental Analysis: C, 85.68; H, 6.16; O, 8.15

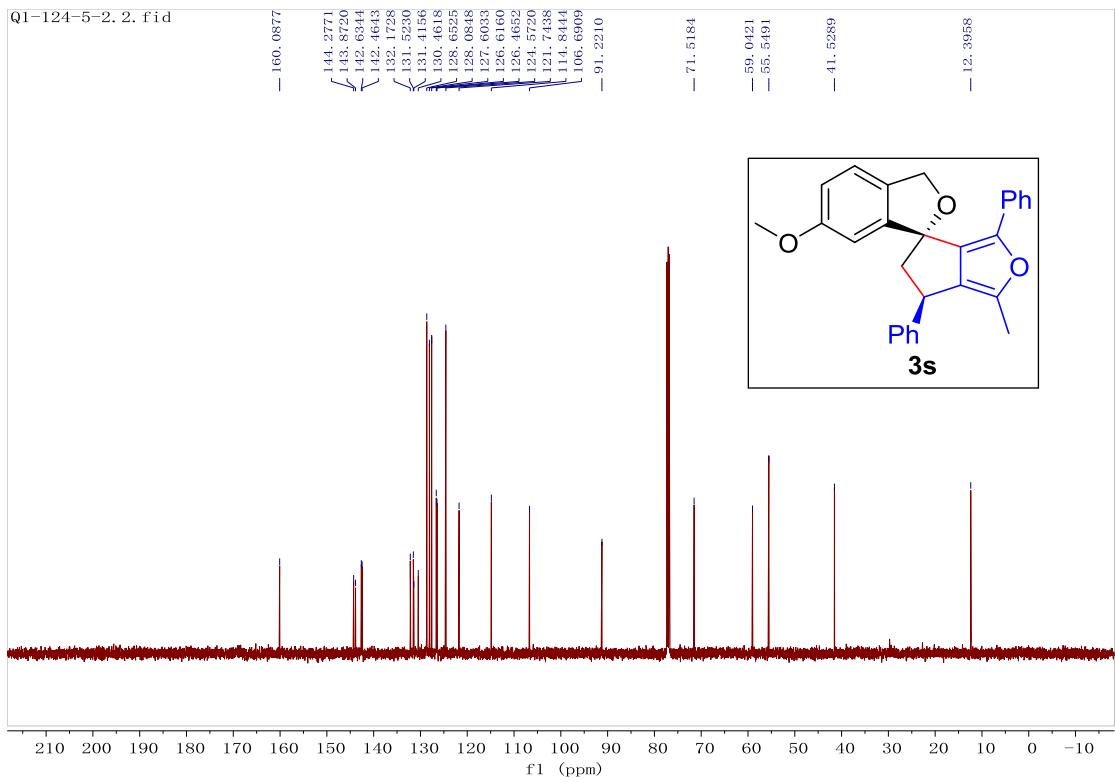
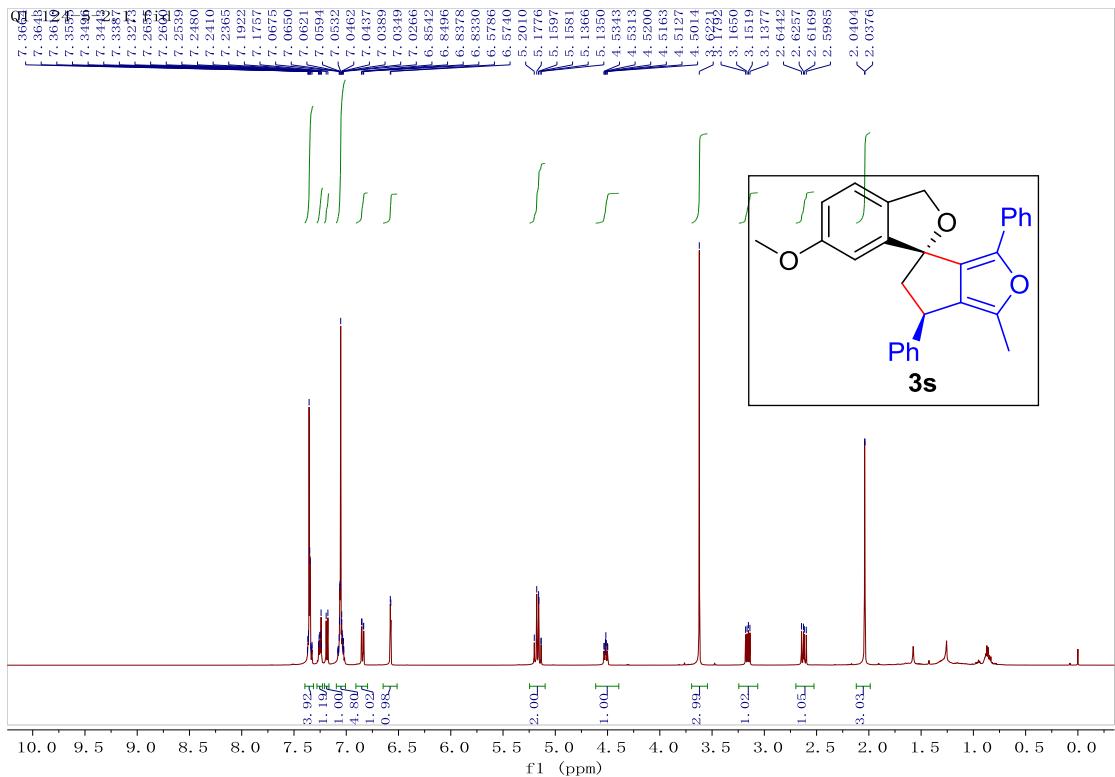
HRMS (ESI, m/z) calcd for C₂₈H₂₄O₂ [M+H]⁺ 393.1849, found 393.1851.

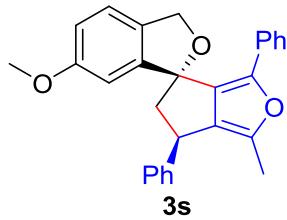
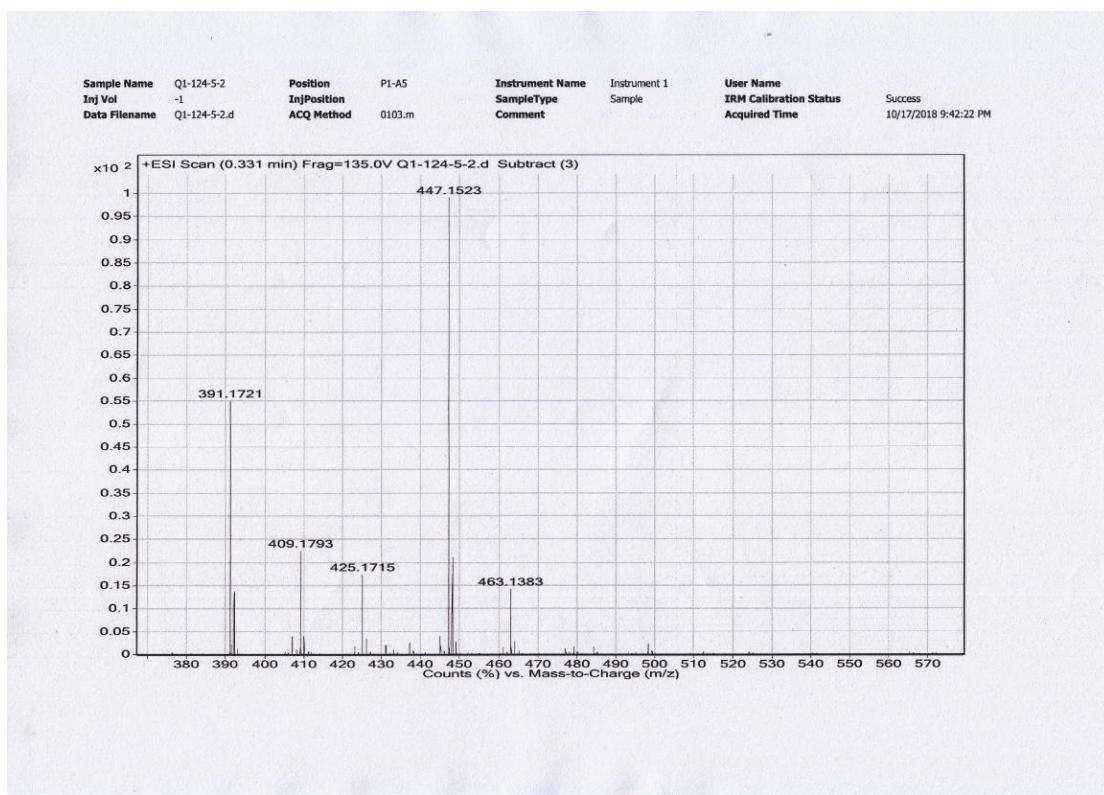




Chemical Formula: C₃₄H₂₈O₅S
 Exact Mass: 548.1657
 Molecular Weight: 548.6530
 m/z: 548.1657 (100.0%), 549.1691 (36.8%), 550.1725 (6.6%),
 550.1615 (4.5%), 551.1649 (1.7%), 550.1700 (1.0%)
 Elemental Analysis: C, 74.43; H, 5.14; O, 14.58; S, 5.84

HRMS (ESI, m/z) calcd for C₃₄H₂₈O₅S [M+H]⁺ 549.1730, found 549.1733.





Chemical Formula: C₂₈H₂₄O₃

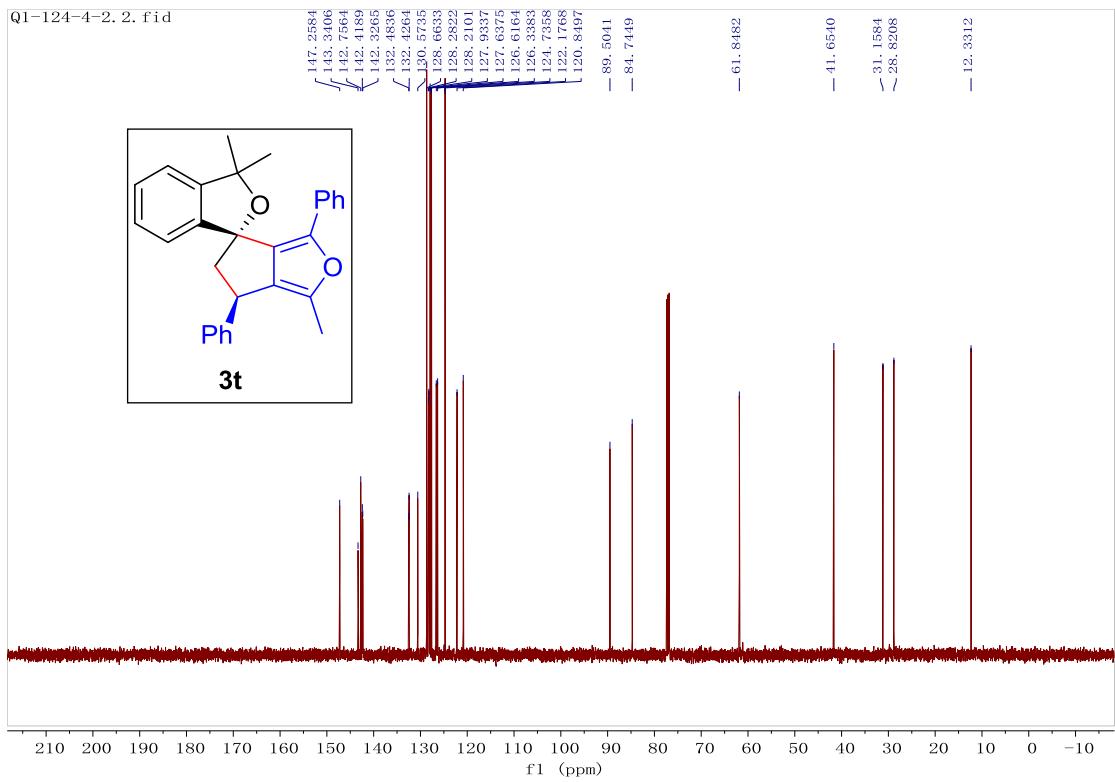
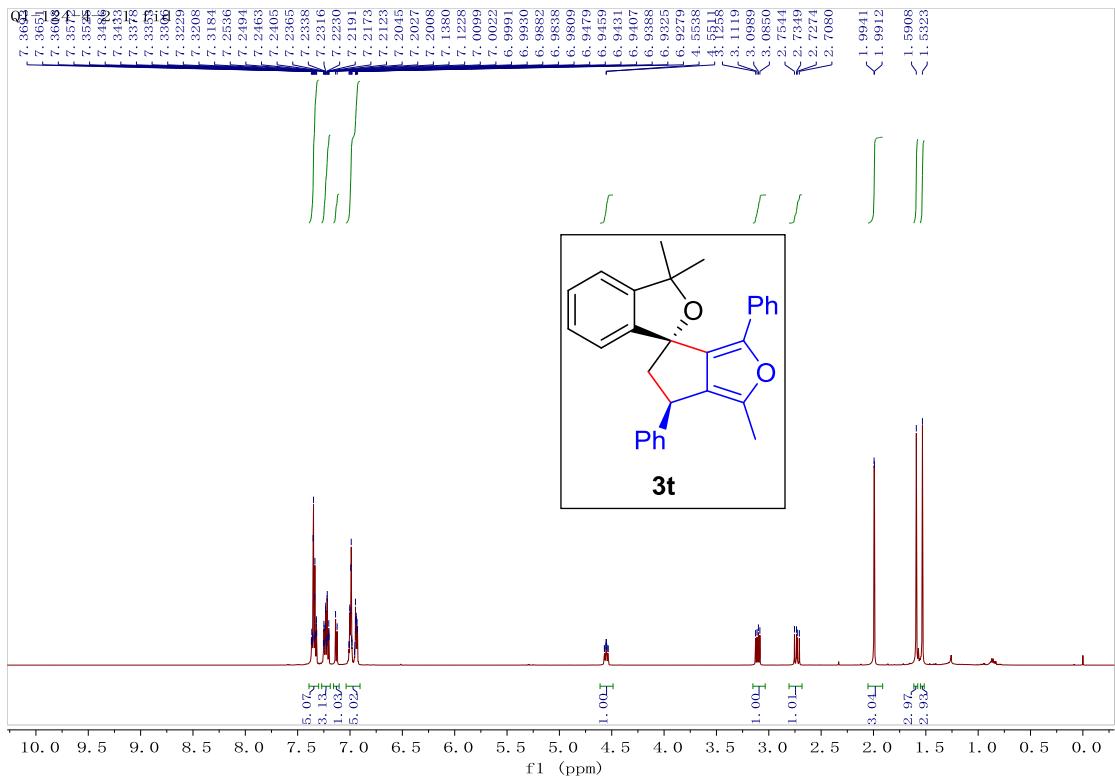
Exact Mass: 408.1725

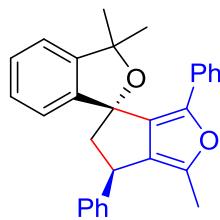
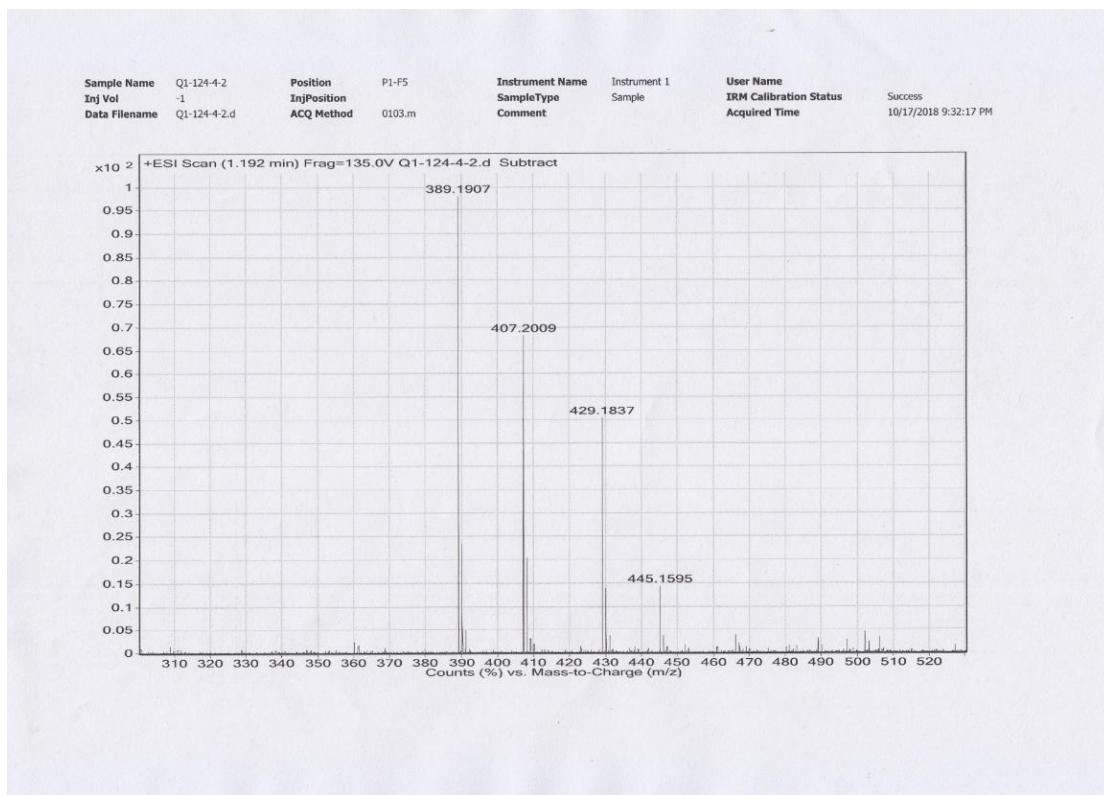
Molecular Weight: 408.4970

m/z: 408.1725 (100.0%), 409.1759 (30.3%), 410.1793 (2.7%), 410.1793 (1.7%)

Elemental Analysis: C, 82.33; H, 5.92; O, 11.75

HRMS (ESI, m/z) calcd for C₂₈H₂₄O₃ [M+H]⁺ 409.1798, found 409.1793.





3t

Chemical Formula: $C_{29}H_{26}O_2$

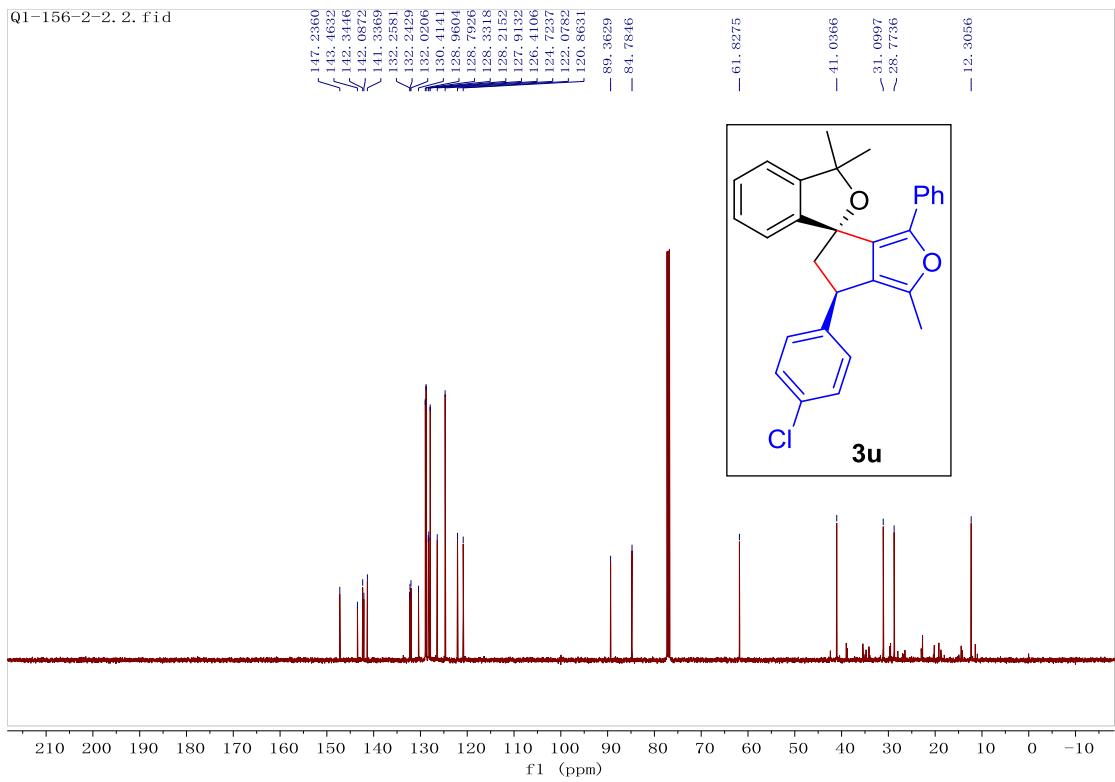
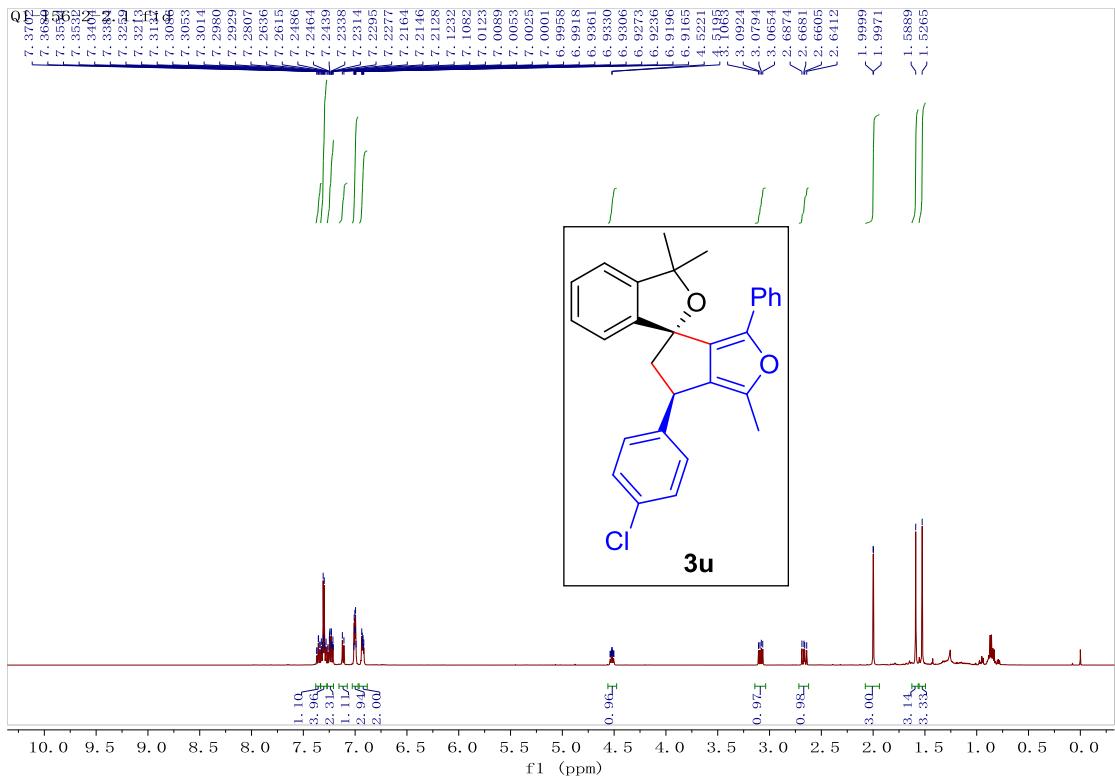
Exact Mass: 406.1933

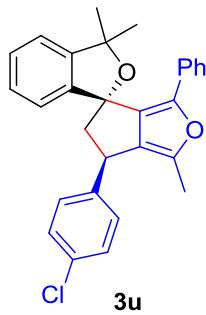
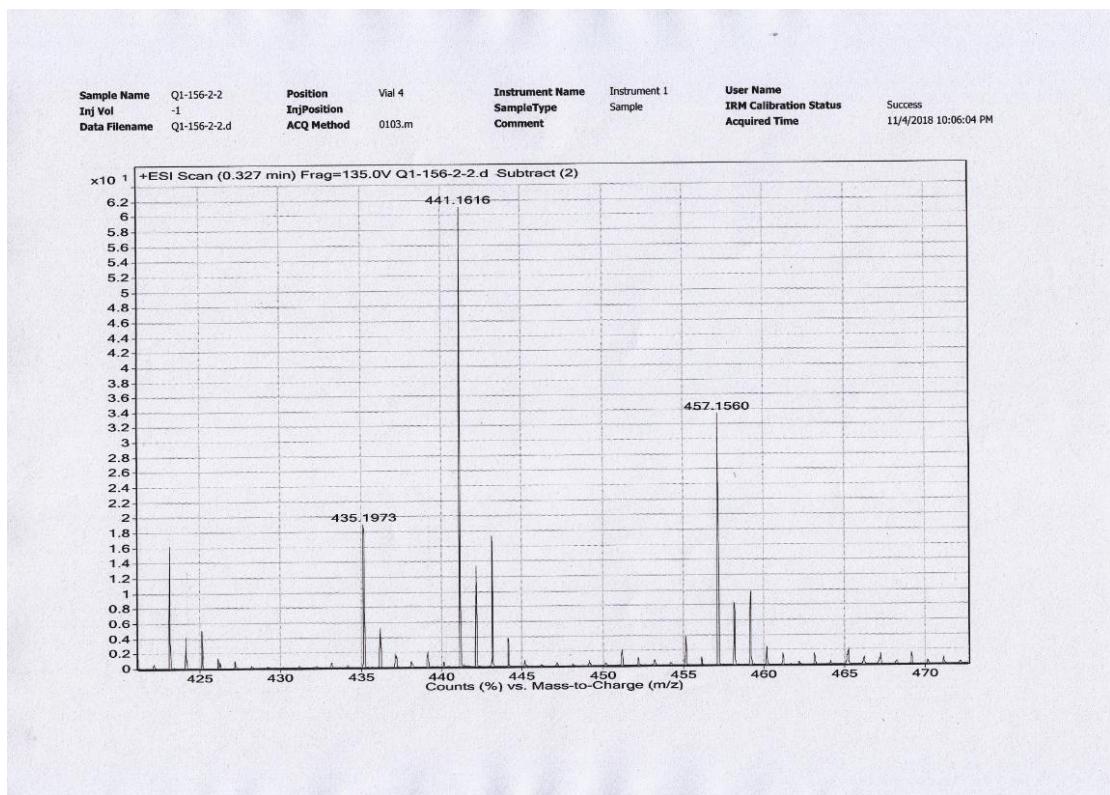
Molecular Weight: 406.5250

m/z : 406.1933 (100.0%), 407.1966 (31.4%), 408.2000 (2.7%), 408.2000 (2.0%)

Elemental Analysis: C, 85.68; H, 6.45; O, 7.87

HRMS (ESI, m/z) calcd for $C_{29}H_{26}O_2 [M+H]^+$ 407.2006, found 407.2009.





Chemical Formula: $C_{29}H_{25}ClO_2$

Exact Mass: 440.1543

Molecular Weight: 440.9670

m/z : 440.1543 (100.0%), 442.1514 (32.0%), 441.1577 (31.4%), 443.1547 (10.0%), 442.1610 (4.7%)

Elemental Analysis: C, 78.99; H, 5.71; Cl, 8.04; O, 7.26

HRMS (ESI, m/z) calcd for $C_{29}H_{25}ClO_2 [M+H]^+$ 441.1616, found 441.1616.

