

Supporting Information

Palladium-catalyzed carbene/alkyne metathesis with enynone as carbene precursor: synthesis of fused polyheterocycles

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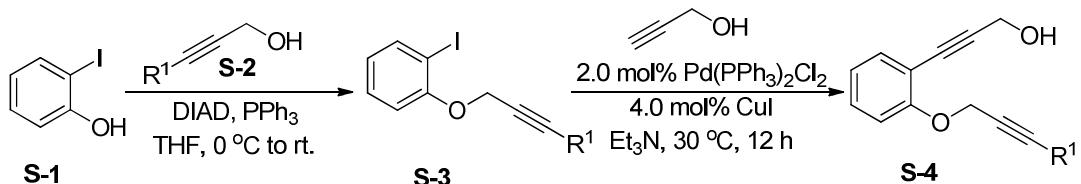
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General Information

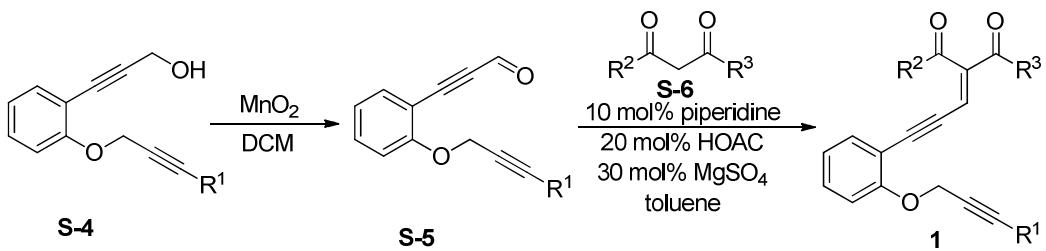
All reactions were performed in oven-dried (140 °C) glassware under an atmosphere of dry N₂. Metal catalysts, alcohols used in this reaction were purchased from commercial sources and used without further purification. DCE (1,2-dichloroethane) was distilled prior to use kept over activated 3 Å molecular 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 (230-400 mesh) or neutral alumina (100-200 mesh). ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on a Varian Inova-400 NMR spectrometer; chemical shifts are reported in ppm with the solvent signals as reference, and coupling constants (*J*) are given in Hertz. The peak information is 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 Enynones 1.



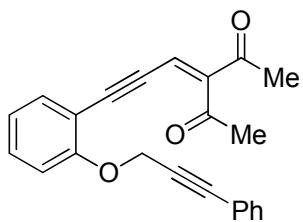
Synthesis of S-3: To an 100-mL oven-dried flask containing a magnetic stirring bar, **S-1** (2.75 g, 12.5 mmol), PPh₃ (3.29 g, 12.5 mmol), and **S-2** (13.5 mmol) in distilled THF (30 mL), DIAD (diisopropyl azodicarboxylate, 2.5 mL) was added dropwise at 0 °C under nitrogen. Then the solution stirred for 30 minutes and the temperature was warmed to room temperature slowly. The reaction was quenched by adding aqueous sodium hydroxide solution (0.5 M, 50 mL). The mixture was then diluted with Et₂O (50 mL) and washed with NaOH (0.5 M, 50 mL) and brine (50 mL) in sequence. The combined organic layers were dried with Na₂SO₄, and concentrated *in vacuo* after filtration. The residue was purified by flash chromatography on silica gel (eluted with petroleum ether/ethyl acetate = 20:1) to give pure products **S-3**.

Synthesis of S-4: To an 100-mL oven-dried flask containing a magnetic stirring bar, **S-3** (11.0 mmol), propargyl alcohol (740.5 mg, 13.2 mmol), CuI (83.6 mg, 4 mol%), Pd(PPh₃)₂Cl₂ (154.4 mg, 2 mol%), and Et₃N (30 mL) were added in sequence under argon atmosphere, and the reaction mixture was stirred at 30 °C for 12 h. After the reaction was completed, the mixture was diluted with H₂O, and extracted with CH₂Cl₂. The organic phase was dried with Na₂SO₄ and evaporated *in vacuo* after filtration. The residue was purified by column chromatography on silica gel (eluted with petroleum ether/ethyl acetate = 3:1) to afford pure products **S-4** (50 – 70% for the two steps).

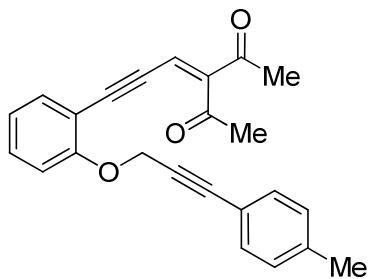


Synthesis of S-5: To an 100-mL oven-dried flask containing a magnetic stirring bar, and **S-4** (2.0 mmol) in DCM (40 mL), was added MnO₂ (3.48 g, 40.0 mmol) at room temperature. The resulting reaction mixture was stirred overnight under these conditions. After **S-4** was completely consumed (monitored by TLC), the reaction mixture was filtered through a short pad of Celite and concentrated *in vacuo* after filtration. The residue was purified by column chromatography on silica gel (eluted with petroleum ether/AcOEt = 10:1) to give pure products **S-5** (60-80%).

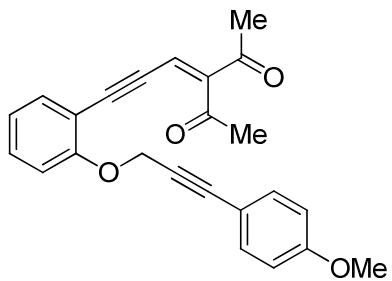
Synthesis of 1: To an 100-mL oven-dried flask containing a magnetic stirring bar, and **S-6** (1.2 mmol) in toluene (20 mL), was added **S-5** (1.0 mmol), HOAc (12.0 mg, 20 mol%), piperidine (8.5 mg, 10 mol%), and MgSO₄ (36.1 mg, 30 mol%) in sequence at room temperature. The reaction was stirred under these conditions and monitored by TLC. After the reaction was completed, the reaction mixture was extracted with ethyl acetate (30 mL), and washed with brine (30 mL). The organic phase was dried with Na₂SO₄ and evaporated *in vacuo* after filtration. The resulting residue was purified by column chromatography on silica gel (eluted with petroleum ether/AcOEt = 10:1) to give **1** in 70–85% yields.



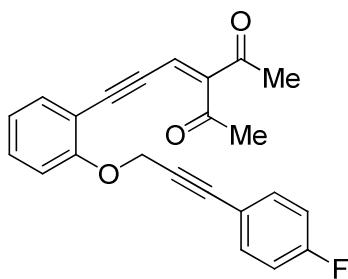
3-{3-[2-((3-Phenylprop-2-yn-1-yl)oxy)phenyl]prop-2-yn-1-ylidene}pentane-2,4-dione (1a**)**. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.48-7.38 (comp, 4H), 7.35-7.28 (comp, 3H), 7.12 (d, $J = 8.3$ Hz, 1H), 7.03 (s, 1H), 7.02-6.97 (m, 1H), 4.99 (s, 2H), 2.67 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 201.3, 195.9, 159.1, 148.7, 134.3, 131.94, 131.85, 129.0, 128.5, 123.0, 122.2, 121.6, 112.8, 111.8, 104.3, 89.9, 88.0, 83.2, 57.4, 31.4, 27.9. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{23}\text{H}_{19}\text{O}_3$ $[\text{M}+\text{H}]^+$: 434.1329, found 434.1333.



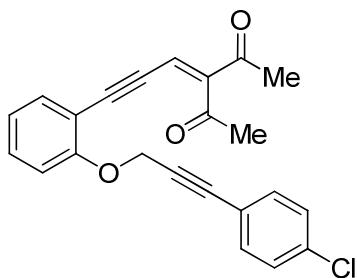
3-{3-[2-((3-(p-Tolyl)prop-2-yn-1-yl)oxy)phenyl]prop-2-yn-1-ylidene}pentane-2,4-dione (1b**)**. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.46-7.44 (m, 1H), 7.42-7.38 (m, 1H), 7.32 (d, $J = 8.1$ Hz, 2H), 7.15-7.09 (comp, 3H), 7.03 (s, 1H), 7.01-6.96 (m, 1H), 4.98 (s, 2H), 2.67 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 201.3, 195.9, 159.1, 148.6, 139.2, 134.3, 131.8, 129.3, 123.0, 121.5, 119.1, 112.8, 111.8, 104.4, 89.9, 88.2, 82.6, 57.5, 31.4, 27.9, 21.6. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{24}\text{H}_{20}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 379.1310, found 379.1314.



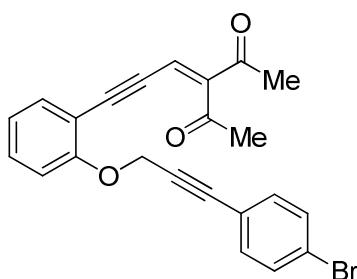
3-[3-{2-((3-(4-Methoxyphenyl)prop-2-yn-1-yl)oxy)phenyl]prop-2-yn-1-ylidene}pentane-2,4-dione (1c). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.45-7.35 (comp, 4H), 7.11-7.09 (m, 1H), 7.02 (s, 1H), 7.00-6.96 (m, 1H), 6.84-6.81 (m, 2H), 4.96 (s, 2H), 3.79 (s, 3H), 2.66 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 201.4, 195.9, 160.1, 159.1, 148.6, 134.3, 133.5, 131.8, 123.0, 121.4, 114.2, 114.1, 112.7, 111.7, 104.4, 89.8, 88.0, 81.9, 57.5, 55.4, 31.4, 27.8. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{24}\text{H}_{20}\text{O}_4\text{Na} [\text{M}+\text{Na}]^+$: 395.1259, found 395.1253.



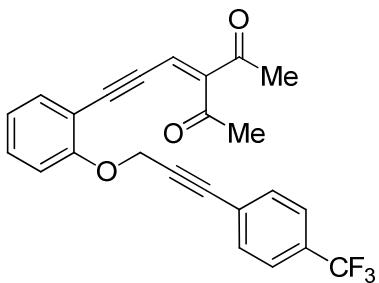
3-[3-{2-((3-(4-Fluorophenyl)prop-2-yn-1-yl)oxy)phenyl]prop-2-yn-1-ylidene}pentane-2,4-dione (1d). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.48-7.37 (comp, 4H), 7.09 (d, $J = 8.3$ Hz, 1H), 7.04-6.96 (comp, 4H), 4.97 (s, 2H), 2.66 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 201.3, 195.9, 159.0, 148.71, 134.4, 133.9 (d, $J = 8.5$ Hz), 131.8, 122.9, 121.6, 118.2 (d, $J = 3.5$ Hz), 115.9, 115.7, 112.7, 111.8, 104.2, 89.9, 86.9, 83.0, 57.3, 31.4, 27.9. ^{19}F NMR (376 MHz, CDCl_3) (δ , ppm) -109.8 (s). HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{23}\text{H}_{17}\text{FO}_3\text{Na} [\text{M}+\text{Na}]^+$: 383.1059, found 383.1049.



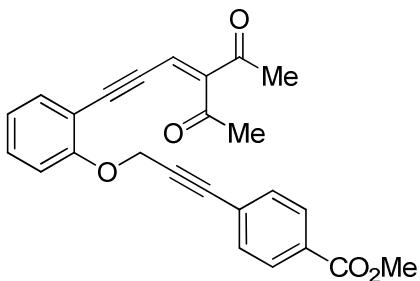
3-[3-{2-((3-(4-Chlorophenyl)prop-2-yn-1-yl)oxy)phenyl]prop-2-yn-1-ylidene}pentane-2,4-dione (1e). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.48-7.34 (comp, 4H), 7.31-7.27 (m, 2H), 7.09 (d, $J = 8.3$ Hz, 1H), 7.04-6.98 (comp, 2H), 4.97 (s, 2H), 2.65 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 201.3, 195.9, 159.0, 148.8, 135.1, 134.4, 133.2, 131.9, 128.9, 122.9, 121.7, 120.6, 112.7, 111.8, 104.2, 89.9, 86.9, 84.2, 57.3, 31.4, 27.9. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{23}\text{H}_{17}\text{ClO}_3\text{Na} [\text{M}+\text{Na}]^+$: 399.0764, found 399.0765.



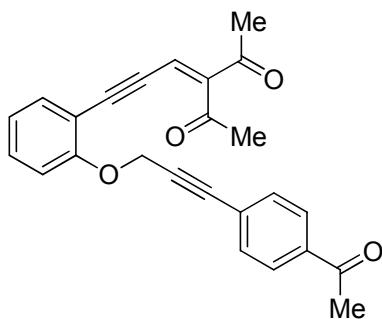
3-[3-{2-((3-(4-Bromophenyl)prop-2-yn-1-yl)oxy)phenyl]prop-2-yn-1-ylidene}pentane-2,4-dione (1f). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.48-7.37(comp, 4H), 7.32-7.27 (m, 2H), 7.09 (d, $J = 8.4$ Hz, 1H), 7.04-6.97 (comp, 2H), 4.97 (s, 2H), 2.65 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 201.3, 195.9, 159.0, 148.8, 134.4, 133.4, 131.9, 131.8, 123.4, 122.9, 121.7, 121.1, 112.7, 111.8, 104.2, 89.9, 86.9, 84.4, 57.3, 31.4, 27.9. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{23}\text{H}_{18}\text{BrO}_3 [\text{M}+\text{H}]^+$: 421.0439, found 421.0423.



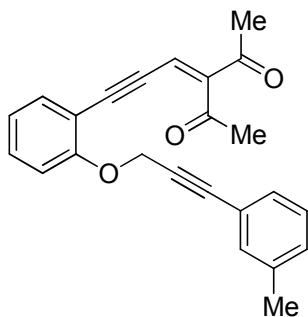
3-{3-[2-((3-(4-(Trifluoromethyl)phenyl)prop-2-yn-1-yl)oxy)phenyl]prop-2-yn-1-yl idene}pentane-2,4-dione (1g). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.60-7.51 (comp, 4H), 7.48-7.38(m, 2H), 7.09 (d, $J = 8.4$ Hz, 1H), 7.06-6.97 (comp, 2H), 5.00 (s, 2H), 2.66 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 201.3, 195.8, 158.9, 148.8, 134.4, 132.2, 131.9, 130.6, 125.93, 125.90, 125.4 (q, $J = 3.7$ Hz), 122.8, 121.8, 112.7, 111.9, 104.0, 89.9, 86.6, 85.7, 57.2, 31.3, 27.8. ^{19}F NMR (376 MHz, CDCl_3) (δ , ppm) -62.0 (s). HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{24}\text{H}_{18}\text{F}_3\text{O}_3$ [$\text{M}+\text{H}]^+$: 411.1208, found 411.1207.



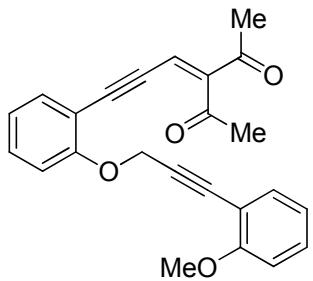
Methyl-4-{3-[2-(4-acetyl-5-oxohex-3-en-1-yn-1-yl)phenoxy]prop-1-yn-1-yl}benzoate (1h). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.98 (d, $J = 8.2$ Hz, 1H), 7.53-7.37 (comp, 4H), 7.10 (d, $J = 8.4$ Hz, 2H), 7.05- 6.98 (comp, 2H), 5.00 (s, 2H), 3.91 (s, 3H), 2.65 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 201.3, 195.8, 166.5, 158.9, 148.8, 134.4, 131.9, 130.3, 129.6, 126.74, 126.71, 122.9, 121.7, 112.7, 111.9, 104.1, 89.9, 87.2, 86.1, 57.2, 52.4, 31.4, 27.9. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{25}\text{H}_{20}\text{O}_5\text{Na}$ [$\text{M}+\text{Na}]^+$: 423.1208, found 423.1212.



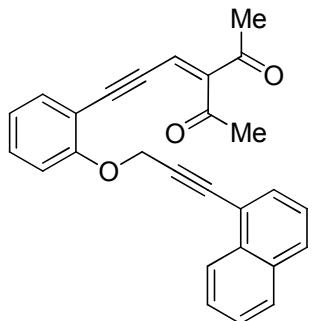
3-{3-[2-[(3-(4-Acetylphenyl)prop-2-yn-1-yl)oxy]phenyl]prop-2-yn-1-ylidene}pentane-2,4-dione (1i). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.90 (d, $J = 8.4$ Hz, 2H), 7.51 (d, $J = 8.4$ Hz, 2H), 7.48-7.38 (m, 2H), 7.09 (d, $J = 8.4$ Hz, 1H), 7.04-6.97 (comp, 2H), 5.00 (s, 2H), 2.65 (s, 3H), 2.59 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 201.3, 197.4, 195.8, 158.9, 148.8, 136.9, 134.4, 132.1, 131.9, 128.4, 126.9, 122.9, 121.8, 112.7, 111.9, 104.1, 89.9, 87.1, 86.5, 57.3, 31.4, 27.8, 26.8. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{25}\text{H}_{21}\text{O}_4$ [$\text{M}+\text{H}]^+$: 385.1440, found 385.1442.



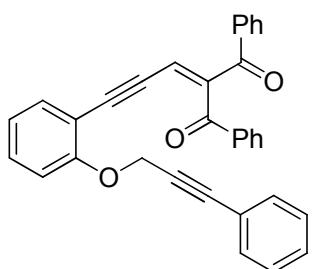
3-{3-[2-((3-(m-Tolyl)prop-2-yn-1-yl)oxy)phenyl]prop-2-yn-1-ylidene}pentane-2,4-dione (1j). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.46-7.39 (m, 2H), 7.25-7.11 (comp, 5H), 7.03-6.99 (comp, 2H), 4.98 (s, 2H), 2.67 (s, 3H), 2.36 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 201.3, 195.9, 159.1, 148.7, 138.2, 134.3, 132.5, 131.9, 129.9, 129.0, 128.4, 123.0, 121.9, 121.5, 112.8, 111.8, 104.4, 89.9, 88.2, 82.9, 57.38, 31.4, 27.9, 21.3. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{24}\text{H}_{20}\text{O}_3$ [$\text{M}+\text{Na}]^+$: 379.1310, found 379.1305.



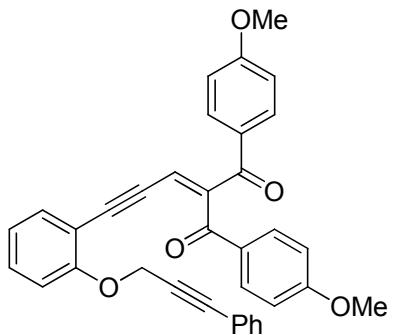
3-[3-{2-((3-(2-Methoxyphenyl)prop-2-yn-1-yl)oxy)phenyl}prop-2-yn-1-ylidene]pentane-2,4-dione (1k) ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.47-7.36 (comp, 3H), 7.33-7.27 (m, 1H), 7.18 (d, $J = 8.4$ Hz, 1H), 7.03 (s, 1H), 7.01-6.96 (m, 1H), 6.92-6.84 (comp, 2H), 5.03 (s, 2H), 3.85 (s, 3H), 2.67 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 201.3, 196.0, 160.4, 159.1, 148.6, 134.2, 133.9, 131.8, 130.5, 123.1, 121.4, 120.6, 113.0, 111.8, 111.3, 110.8, 104.5, 89.8, 87.2, 84.5, 57.6, 55.9, 31.4, 27.9. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{24}\text{H}_{21}\text{O}_4[\text{M}+\text{H}]^+$: 373.1440, found 373.1444.



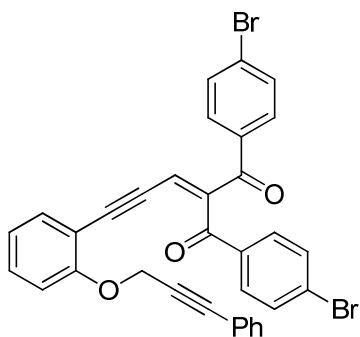
3-[3-{2-((3-(Naphthalen-1-yl)prop-2-yn-1-yl)oxy)phenyl}prop-2-yn-1-ylidene]pentane-2,4-dione (1l). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.19-8.16 (m, 1H), 7.83 (d, $J = 8.9$ Hz, 2H), 7.66 (d, $J = 7.1$ Hz, 1H), 7.54-7.36 (comp, 5H), 7.28-7.21 (m, 1H), 7.05-6.98 (comp, 2H), 5.15 (s, 2H), 2.65 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 201.3, 195.90, 159.0, 148.8, 134.4, 133.4, 133.2, 131.8, 131.0, 129.5, 128.5, 127.1, 126.6, 126.0, 125.3, 123.0, 121.7, 119.8, 113.1, 112.0, 104.3, 89.9, 88.1, 86.3, 57.6, 31.4, 27.8. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{27}\text{H}_{21}\text{O}_3[\text{M}+\text{H}]^+$: 393.1491, found 393.1505



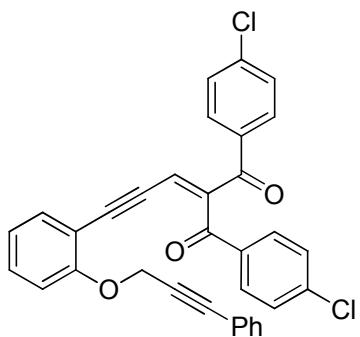
1,3-Diphenyl-2-{3-[2-((3-phenylprop-2-yn-1-yl)oxy)phenyl]prop-2-yn-1-ylidene}propane-1,3-dione (1m). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.11 (d, $J = 7.4$ Hz, 2H), 7.88 (d, $J = 7.4$ Hz, 2H), 7.66-7.43 (comp, 9H), 7.38-7.30 (comp, 3H), 7.12-7.06 (comp, 2H), 7.01-6.96(m, 1H), 6.92-6.86 (m, 1H), 4.89 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 194.3, 193.2, 158.6, 147.4, 136.9, 136.4, 134.2, 133.7, 132.9, 131.9, 131.4, 129.7, 129.3, 128.8, 128.6, 128.3, 127.2, 124.9, 122.1, 121.2, 112.9, 111.7, 103.4, 89.6, 87.8, 83.5, 57.2. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{33}\text{H}_{23}\text{O}_3$ [$\text{M}+\text{H}]^+$: 467.1647, found 467.1645.



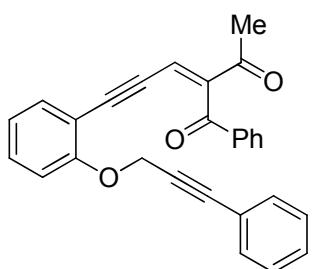
1,3-Bis(4-methoxyphenyl)-2-{3-[2-((3-phenylprop-2-yn-1-yl)oxy)phenyl]prop-2-yn-1-ylidene}propane-1,3-dione (1n). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.03-7.98 (m, 2H), 7.86-7.80 (m, 2H), 7.40-7.34 (m, 2H), 7.28-7.21 (comp, 4H), 7.03-6.95 (m, 2H), 6.92-6.78 (comp, 6H), 4.82 (s, 2H), 3.78 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 192.8, 191.4, 164.1, 163.6, 158.6, 148.3, 134.1, 132.3, 131.9, 131.8, 131.1, 129.62, 129.58, 129.1, 128.8, 128.3, 122.7, 122.2, 121.2, 114.0, 113.9, 113.0, 112.0, 101.4, 89.7, 87.7, 83.5, 57.2, 55.5. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{35}\text{H}_{27}\text{O}_5$ [$\text{M}+\text{H}]^+$: 527.1858, found 372.1845.



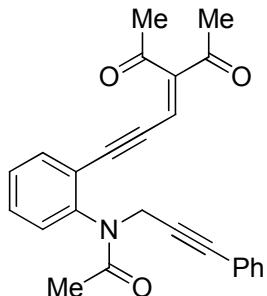
1,3-Bis(4-bromophenyl)-2-{3-[2-((3-phenylprop-2-yn-1-yl)oxy)phenyl]prop-2-yn-1-ylidene}propane-1,3-dione (1o). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.88 (d, $J = 8.4$ Hz, 2H), 7.70-7.57 (comp, 6H), 7.44-7.39 (m, 2H), 7.37-7.28 (comp, 4H), 7.06 (d, $J = 8.4$ Hz, 1H), 7.02 (s, 1H), 6.99-6.94 (m, 1H), 6.92-6.85 (m, 1H), 4.86 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 193.2, 192.0, 158.8, 146.4, 135.7, 135.2, 134.3, 132.3, 132.1, 131.9, 131.8, 131.3, 130.9, 129.3, 129.0, 128.5, 128.3, 125.4, 122.2, 121.4, 112.9, 111.6, 104.4, 89.4, 87.9, 83.4, 57.3. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{33}\text{H}_{20}\text{Br}_2\text{O}_3\text{Na} [\text{M}+\text{Na}]^+$: 646.9656 found 646.9667.



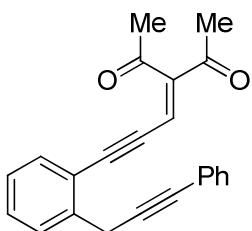
1,3-Bis(4-chlorophenyl)-2-{3-[2-((3-phenylprop-2-yn-1-yl)oxy)phenyl]prop-2-yn-1-ylidene}propane-1,3-dione (1p). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.00-7.93 (m, 2H), 7.79-7.71 (m, 2H), 7.48-7.39 (comp, 6H), 7.35-7.28 (comp, 4H), 7.06 (d, $J = 8.4$ Hz, 1H), 7.01 (s, 1H), 7.00-6.96 (m, 1H), 6.91-6.85 (m, 1H), 4.86 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 193.0, 191.8, 158.8, 146.5, 140.4, 139.6, 135.2, 134.8, 134.2, 131.9, 131.7, 131.2, 130.8, 129.2, 129.1, 128.9, 128.4, 125.2, 122.2, 121.4, 112.9, 111.5, 104.3, 89.4, 87.9, 83.3, 57.3. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{33}\text{H}_{20}\text{Cl}_2\text{O}_3\text{Na} [\text{M}+\text{Na}]^+$: 557.0687, found 557.0690.



(Z)-1-Phenyl-2-{3-[2-((3-phenylprop-2-yn-1-yl)oxy)phenyl]prop-2-yn-1-ylidene}butane-1,3-dione (1q). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.01 (d, $J = 7.6$ Hz, 2H), 7.61-7.57 (m, 1H), 7.51-7.44 (m, 2H), 7.43-7.39 (comp, 2H), 7.34-7.25 (comp, 4H), 7.21 (s, 1H), 7.02 (d, $J = 8.4$ Hz, 1H), 6.88-6.86 (m, 1H), 6.83-6.79 (m, 1H), 4.79(s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 195.3, 194.5, 158.7, 147.5, 136.2, 134.1, 134.0, 131.8, 131.4, 129.6, 128.85, 128.83, 128.4, 122.8, 122.1, 121.2, 112.9, 111.6, 103.2, 89.6, 87.7, 83.4, 57.1 27.4. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{28}\text{H}_{21}\text{O}_3$ [$\text{M}+\text{H}]^+$: 405.1491, found 405.1488.

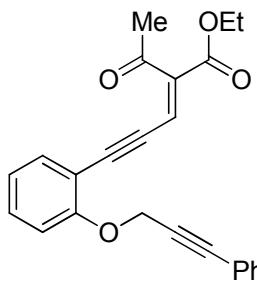


***N*-(2-(4-Acetyl-5-oxohex-3-en-1-yl)phenyl)-*N*-(3-phenylprop-2-yn-1-yl)acetamide (1r).** ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.42-7.23 (comp, 9H), 6.77 (s, 1H), 5.03 (d, $J = 17.4$ Hz, 1H), 4.40 (d, $J = 17.4$ Hz, 1H), 2.44 (s, 3H), 2.29 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 200.7, 195.6, 169.7, 150.5, 143.4, 134.1, 131.6, 131.4, 129.9, 128.9, 128.4, 128.3, 122.8, 122.0, 121.0, 101.7, 89.3, 84.6, 84.3, 38.3, 30.9, 27.0, 22.3. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{25}\text{H}_{22}\text{NO}_3$ [$\text{M}+\text{H}]^+$: 384.1600, found 384.1608.



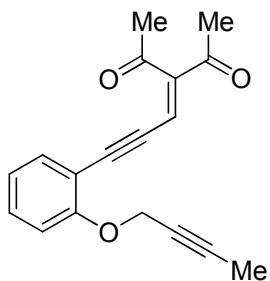
3-(3-(2-(3-Phenylprop-2-yn-1-yl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1s).

¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.69-7.26 (comp, 9H), 6.96 (s, 1H), 3.96 (s, 2H), 2.56 (s, 3H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ , ppm) 201.0, 195.7, 149.6, 139.7, 133.0, 131.8, 130.8, 128.6, 128.4, 128.1, 127.0, 123.6, 122.1, 120.8, 104.9, 89.8, 86.5, 83.6, 31.2, 27.3, 24.7. HRMS (TOF MS ESI⁺) calculated for C₂₃H₁₉O₂ [M+H]⁺: 327.1385, found 327.1376.



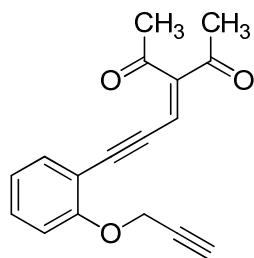
(E)-Ethyl 2-Acetyl-5-(2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)pent-2-en-4-ynoate (1t).

¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.48-7.29 (comp, 7H), 7.14-7.10 (m, 1H), 7.11 (s, 1H), 7.02-6.97 (m, 1H), 5.00 (s, 2H), 4.29 (q, J = 7.1 Hz, 2H), 2.60 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ , ppm) 199.1, 164.1, 159.0, 141.9, 134.4, 131.9, 131.6, 128.9, 128.4, 123.4, 122.2, 121.5, 112.9, 111.9, 102.2, 89.4, 87.9, 83.4, 61.7, 57.4, 30.8, 14.2. HRMS (TOF MS ESI⁺) calculated for C₂₄H₂₁O₄ [M+H]⁺: 373.1440, found 373.1451.



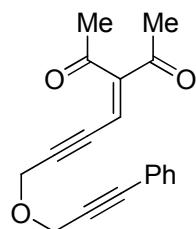
3-(3-(2-(But-2-yn-1-yloxy)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1u).

¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.41-7.33 (comp, 2H), 7.00 (s, 1H), 6.98-6.92 (comp, 2H), 4.68 (dd, J = 4.4, 2.2 Hz, 2H), 2.63 (s, 3H), 2.33 (s, 3H), 1.82 (t, J = 2.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ , ppm) 201.2, 195.8, 159.0, 148.4, 134.1, 131.8, 122.9, 121.2, 112.4, 111.4, 104.4, 89.7, 84.5, 73.4, 57.0, 31.2, 27.8, 3.7. HRMS (TOF MS ESI⁺) calculated for C₁₈H₁₇O₃ [M+H]⁺: 281.1178, found 281.1177.



3-(3-(2-(Prop-2-yn-1-yloxy)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1v).

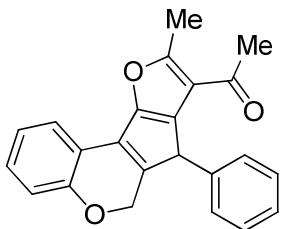
¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.40-7.31 (comp, 2H), 6.99-6.92 (comp, 2H), 6.95 (s, 1H), 4.71 (d, J = 2.4 Hz, 2H), 2.59 (s, 3H), 2.54 (t, J = 2.4 Hz, 1H), 2.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ , ppm) 201.1, 195.7, 158.5, 148.6, 134.1, 131.7, 122.6, 121.5, 112.4, 111.5, 103.9, 89.7, 77.8, 76.4, 56.2, 31.2, 27.6. HRMS (TOF MS ESI⁺) calculated for C₁₇H₁₅O₃ [M+H]⁺: 267.1021, found 267.1020.



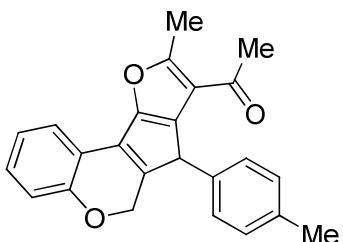
3-{4-[(3-Phenylprop-2-yn-1-yl)oxy]but-2-yn-1-ylidene}pentane-2,4-dione1 (8). ¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.46-7.40 (m, 2H), 7.35-7.27 (comp, 3H), 6.68 (t, J = 1.9 Hz, 1H), 4.52 (d, J = 2.0 Hz, 2H), 4.46 (s, 2H), 2.46 (s, 3H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ , ppm) 200.9, 195.6, 150.7, 131.9, 128.8, 128.4, 122.3, 121.1, 102.6, 87.4, 83.8, 82.2, 57.8, 57.2, 31.0, 27.2. HRMS (TOF MS ESI⁺) calculated for C₁₈H₁₇O₃ [M+H]⁺: 281.1178, found 281.1177.

General Procedure for the Pd₂(dba)₃-Catalyzed Cascade Reaction.

To an 10-mL oven-dried vial containing a magnetic stirring bar, 4Å MS (30 mg), and Pd₂(dba)₃ (9.2 mg, 5.0 mol%) in DCE (1.5 mL), was added enynone **1** (0.2 mmol) in DCE (1.5 mL) over 1.0 h *via* a syringe pump under argon atmosphere at room temperature. Then the reaction mixture was stirred for additional 3.0 h. After the reaction was completed, the solvent was evaporated *in vacuo* and the residue was purified by column chromatography on neutral alumina (Hexanes: EtOAc = 10:1 to 5:1) to afford the pure products **2a-q**.

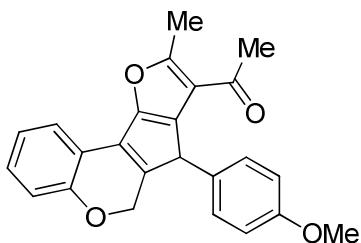


1-{9-Methyl-7-phenyl-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromen-8-yl}ethanone (2a). 48.0 mg, 70% yield. Yellow solid; mp: 155.7-158.2 °C. ¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.61-7.56 (m, 1H), 7.31-7.24 (comp, 3H), 7.21-7.14 (m, 1H), 7.11-7.06 (m, 2H), 7.02-6.96 (m, 1H), 6.83 (d, J = 8.1 Hz, 1H), 5.14 (d, J = 15.4 Hz, 1H), 4.79 (d, J = 15.4 Hz, 1H), 4.46 (s, 1H), 2.73 (s, 3H), 2.06 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ , ppm) 194.6, 161.4, 157.0, 153.0, 139.8, 135.9, 130.2, 129.9, 129.3, 127.9, 127.8, 124.6, 124.5, 121.6, 120.5, 117.7, 116.1, 66.3, 49.9, 31.1, 15.4. HRMS (TOF MS ESI⁺) calculated for C₂₃H₁₈O₃Na [M+Na]⁺: 365.1154, found 365.1169.

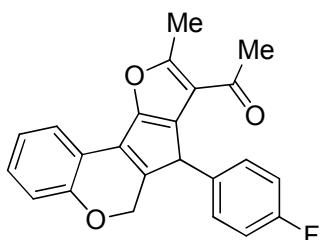


1-{9-Methyl-7-(p-tolyl)-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromen-8-yl}ethanone (2b). 47.0 mg, 66% yield. Yellow solid; mp: 161.6-162.4 °C. ¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.57 (d, J = 7.2 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.08 (d, J =

7.6 Hz, 2H), 6.97 (dd, J = 13.2, 7.5 Hz, 3H), 6.83 (d, J = 8.0 Hz, 1H), 5.11 (d, J = 15.4 Hz, 1H), 4.79 (d, J = 15.4 Hz, 1H), 4.40 (s, 1H), 2.73 (s, 3H), 2.31 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 194.7, 161.2, 156.9, 153.0, 140.0, 137.40, 132.6, 130.3, 129.9, 129.8, 127.7, 124.4, 124.3, 121.6, 120.5, 117.8, 116.1, 66.4, 49.5, 31.1, 21.2, 15.4. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{24}\text{H}_{20}\text{O}_3\text{Na}$ [M+Na] $^+$: 379.1310, found 379.1302.

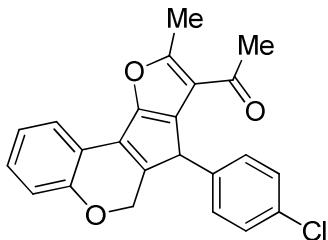


1-(7-(4-Methoxyphenyl)-9-methyl-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromen-8-yl)ethanone (2c). 55.9 mg, 75% yield. Yellow solid; mp: 149.2-151.1 °C. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.57 (d, J = 6.8 Hz, 1H), 7.20-7.13 (m, 1H), 7.05-6.94 (comp, 3H), 6.87-6.77 (comp, 3H), 5.12 (d, J = 15.3 Hz, 1H), 4.79 (d, J = 15.3 Hz, 1H), 4.41 (s, 1H), 3.78 (s, 3H), 2.72 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 194.7, 161.3, 159.1, 156.8, 153.0, 140.2, 130.4, 129.8, 128.9, 127.5, 124.4, 124.3, 121.6, 120.5, 117.8, 116.1, 114.7, 66.4, 55.4, 49.1, 31.1, 15.4. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{24}\text{H}_{20}\text{O}_4\text{Na}$ [M+Na] $^+$: 395.1259, found 395.1250.

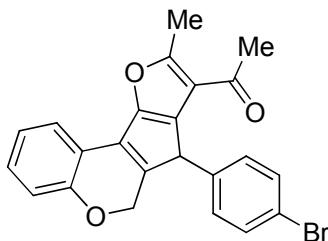


1-(7-(4-Fluorophenyl)-9-methyl-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromen-8-yl)ethanone (2d). 44.7 mg, 62% yield. Yellow solid; mp: 165.0-167.2 °C. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.57 (dd, J = 7.5, 1.4 Hz, 1H), 7.21-7.15 (m, 1H), 7.08-6.95 (m, 5H), 6.84 (d, J = 8.0 Hz, 1H), 5.11 (d, J = 15.4 Hz, 1H), 4.77 (d, J = 15.4 Hz, 1H), 4.41 (s, 1H), 2.73 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ ,

ppm) 193.6, 161.6 (d, $J = 246.4$ Hz), 160.8, 156.3, 152.4, 139.0, 131.0 (d, $J = 3.3$ Hz), 129.7, 129.4, 128.8 (d, $J = 8.0$ Hz), 124.1, 123.9, 121.0, 119.9, 117.0, 115.7, 115.5 (d, $J = 5.1$ Hz), 65.6, 48.3, 30.4, 14.8. ^{19}F NMR (376 MHz, CDCl_3) (δ , ppm) -114.5 (s). HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{23}\text{H}_{17}\text{FO}_3\text{Na} [\text{M}+\text{Na}]^+$: 383.1059, found 383.1045.

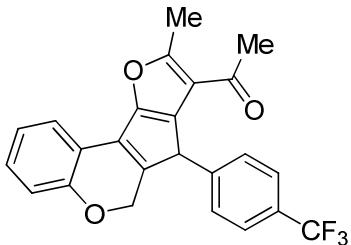


1-(7-(4-Chlorophenyl)-9-methyl-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromen-8-yl)ethanone (2e). 42.9 mg, 57% yield. Yellow solid; mp: 151.1-152.4 °C. ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.60-7.55 (m, 1H), 7.29-7.24 (comp, 2H), 7.21-7.15 (m, 1H), 7.16-6.96 (comp, 3H), 6.84 (d, $J = 8.1$ Hz, 1H), 5.11 (d, $J = 15.4$ Hz, 1H), 4.76 (d, $J = 15.4$ Hz, 1H), 4.42 (s, 1H), 2.73 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 194.1, 161.4, 157.0, 153.0, 139.3, 134.5, 133.5, 130.1, 130.0, 129.5, 129.2, 124.9, 124.5, 121.7, 120.6, 117.5, 116.2, 66.1, 49.0, 31.0, 15.4. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{23}\text{H}_{17}\text{ClO}_3\text{Na} [\text{M}+\text{Na}]^+$: 399.0764, found 399.0769.

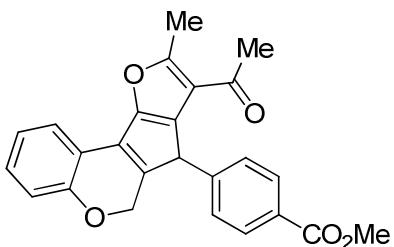


1-(7-(4-Bromophenyl)-9-methyl-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromen-8-yl)ethanone (2f). 46.3 mg, 55% yield. Yellow solid; mp: 155.4-156.5 °C. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.59-7.54 (m, 1H), 7.41 (d, $J = 8.3$ Hz, 2H), 7.21-7.15 (m 1H), 6.99-6.94 (comp, 3H), 6.83 (d, $J = 8.0$ Hz, 1H), 5.10 (d, $J = 15.4$ Hz, 1H), 4.76 (d, $J = 15.4$ Hz, 1H), 4.38 (s, 1H), 2.72 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 194.1, 161.4, 157.0, 153.0, 139.2, 135.1, 132.4, 130.04,

130.02, 129.6, 124.9 124.5, 121.8, 121.6, 120.5, 117.5, 116.2, 66.1, 49.1, 31.0, 15.4. HRMS (TOF MS ESI⁺) calculated for C₂₃H₁₈BrO₃ [M+H]⁺: 421.0439, found 421.0423.

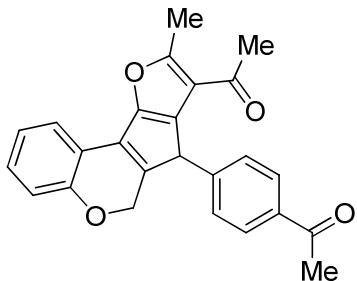


1-(9-Methyl-7-(4-(trifluoromethyl)phenyl)-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromen-8-yl)ethanone (2g). 36.9 mg, 45% yield. Yellow solid; mp: 116.1-119.3 °C. ¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.62-7.52(comp, 3H), 7.25-7.17 (comp, 3H), 7.02-6.97 (m, 1H), 6.84 (d, J = 8.1 Hz, 1H), 5.12 (d, J = 15.4 Hz, 1H), 4.75 (d, J = 15.4 Hz, 1H), 4.49(s, 1H), 2.74 (s, 3H), 2.08 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ , ppm) 193.8, 161.5, 157.1, 153.0, 140.4, 139.0, 130.22, 130.16, 130.1, 129.9, 128.3, 126.3 (q, J = 3.7 Hz), 125.3, 124.6, 121.7, 120.7, 117.4, 116.2, 66.0, 49.3, 30.9, 15.5. ¹⁹F NMR (376 MHz, CDCl₃) (δ , ppm) -62.6 (s). HRMS (TOF MS ESI⁺) calculated for C₂₄H₁₇F₃O₃Na [M+Na]⁺: 433.1027, found 433.1032.

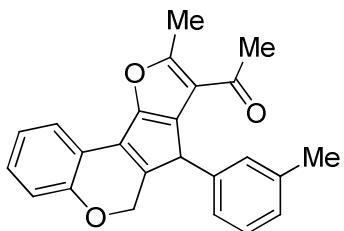


Methyl 4-(8-acetyl-9-methyl-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromen-7-yl)benzoate (2h). 50.5 mg, 63% yield. Yellow solid; mp: 154.1-156.9 °C. ¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.96 (d, J = 8.2 Hz, 1H), 7.60-7.54 (m, 1H), 7.2-7.12 (comp, 3H), 7.02-6.96 (m, 1H), 6.83 (d, J = 8.0 Hz, 1H), 5.11 (d, J = 15.4 Hz, 1H), 4.73 (d, J = 15.4 Hz, 1H), 4.48 (s, 1H), 3.89 (s, 3H), 2.73 (s, 3H), 2.04 (s, 3H); ¹³C NMR (100MHz, CDCl₃) (δ , ppm) 194.0, 166.7, 161.5, 157.1, 153.0, 141.5, 139.0,

130.6, 130.1, 130.0, 129.7, 127.9, 125.1, 124.5, 121.7, 120.5, 117.5, 116.2, 66.1, 52.3, 49.5, 30.9, 15.4. HRMS (TOF MS ESI⁺) calculated for C₂₅H₂₀O₅Na [M+Na]⁺: 423.1208, found 423.1207.

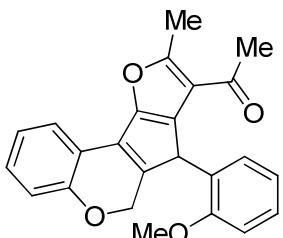


1-(4-(8-Acetyl-9-methyl-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromen-7-yl)phenyl)ethanone (2i). 39.9 mg, 52% yield. Yellow solid; ¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.93 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 7.3 Hz, 1H), 7.26-7.20 (m, 3H), 7.07-7.01 (m, 1H), 6.88 (d, J = 8.0 Hz, 1H), 5.17 (d, J = 15.3 Hz, 1H), 4.19 (d, J = 15.3 Hz, 1H), 4.55 (s, 1H), 2.78 (s, 3H), 2.62 (s, 3H), 2.11 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ , ppm) 197.5, 193.9, 161.5, 157.1, 153.0, 141.8, 139.0, 136.7, 130.1, 130.0, 129.4, 128.1, 125.2, 124.6, 121.7, 120.6, 117.4, 116.2, 66.1, 49.4, 30.9, 26.7, 15.4. HRMS (TOF MS ESI⁺) calculated for C₂₅H₂₀O₄Na [M+Na]⁺: 407.1259, found 407.1246.

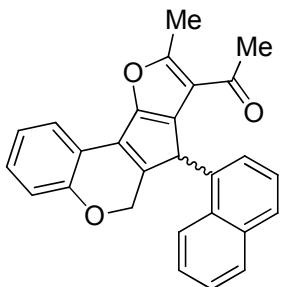


1-(9-Methyl-7-(m-tolyl)-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromen-8-yl)ethanone (2j). 47.0 mg, 66% yield. Yellow solid; mp: 158.6-160.5 °C. ¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.60-7.55 (m, 1H), 7.20-7.14 (m, 2H), 7.05 (d, J = 7.6 Hz, 1H), 7.01-6.96 (m, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.86-6.80 (m, 2H), 5.12 (d, J = 15.4 Hz, 1H), 4.79 (d, J = 15.4 Hz, 1H), 4.38 (s, 1H), 2.73 (s, 3H), 2.28 (s, 3H), 2.06 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ , ppm) 194.7, 161.2, 156.0, 153.0, 139.9, 139.0, 135.6, 130.2, 129.8, 129.1, 128.5, 128.2, 125.1, 124.42, 124.33, 121.5, 120.4, 117.7, 116.1,

66.4, 49.8, 31.1, 21.5, 15.4. HRMS (TOF MS ESI⁺) calculated for C₂₄H₂₀O₃ [M+Na]⁺: 379.1310, found 379.1300.

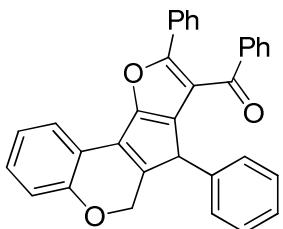


1-(7-(2-Methoxyphenyl)-9-methyl-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromen-8-yl)ethanone (2k). 49.9 mg, 67% yield. Yellow solid; mp: 159.5-161.7 °C. ¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.57-7.53 (m, 1H), 7.25-7.19 (m, 1H), 7.17-7.11 (m, 1H), 6.99-6.93 (m, 2H), 6.83-6.72 (comp, 3H), 5.20 (d, J = 15.6 Hz, 1H), 5.10 (s, 1H), 4.78 (d, J = 15.6 Hz, 1H), 3.92 (s, 3H), 2.74 (s, 3H), 2.03 (s, 3H); ¹³C NMR (100 MHz) (δ , ppm) 194.9, 161.3, 157.3, 157.1, 153.0, 140.3, 129.5, 129.4, 128.8, 127.4, 124.2, 124.0, 123.8, 121.44, 121.41, 120.4, 117.8, 115.9, 110.9, 66.6, 55.6, 42.6, 30.5, 15.3. HRMS (TOF MS ESI⁺) calculated for C₂₄H₂₀O₄ Na [M+Na]⁺: 395.1259 found 395.1244.

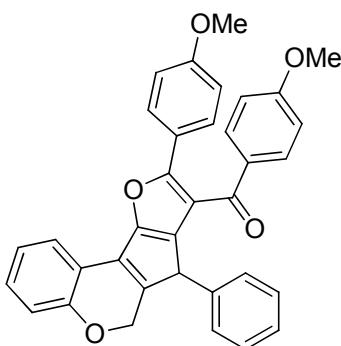


1-(9-Methyl-7-(naphthalen-1-yl)-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromen-8-yl)ethanone (2l). 62.8 mg, 80% yield. Yellow solid; mp: 152.3-151.5 °C. ¹H NMR (400 MHz, CDCl₃) (δ , ppm) *one isomer*: 8.06-6.68 (comp, 11H), 5.26 (s, 1H), 5.02 (d, J = 15.6 Hz, 1H), 4.43 (d, J = 15.6 Hz, 1H), 2.68 (s, 3H), 1.75 (s, 3H); *the other isomer*: 8.06-6.68 (comp, 11H), 4.97 (d, J = 16.0 Hz, 1H), 4.63 (s, 1H), 4.57 (d, J = 16.0 Hz, 1H), 2.62 (s, 3H), 1.69 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ , ppm) combination of two isomers: 194.7, 194.6, 161.7, 161.6, 157.2, 155.8, 153.3, 153.0,

140.4, 139.6, 134.4, 134.0, 132.0, 131.9, 131.8, 131.6, 130.5, 130.1, 130.0, 129.9, 129.8, 129.6, 129.2, 128.7, 128.3, 127.0, 126.6, 126.3, 126.1, 126.0, 125.4, 124.6, 124.5, 124.4, 124.1, 123.9, 123.6, 122.7, 121.60, 121.58, 120.8, 120.4, 117.7, 116.3, 116.1, 66.5, 66.4, 52.0, 44.5, 31.4, 30.6, 15.4. HRMS (TOF MS ESI⁺) calculated for C₂₇H₂₀O₃Na [M+Na]⁺: 415.1310 found 415.1298.

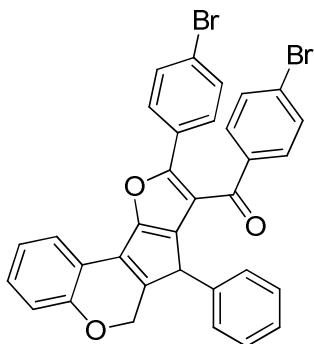


7,9-Diphenyl-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromen-8-yl(phenyl)methanone (2m). 60.7 mg, 65% yield. Yellow solid; mp: 152.3-151.5 °C. ¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.89-7.69 (comp, 5H), 7.58-7.50 (m, 1H), 7.42-7.25 (comp, 6H), 7.17-7.09 (comp, 4H), 6.94 (d, J = 8.0 Hz, 1H), 6.75 (d, J = 6.3 Hz, 2H), 5.16 (d, J = 15.6 Hz, 1H), 4.93 (d, J = 15.6 Hz, 1H), 4.38 (s, 1H). ¹³C NMR (100MHz, CDCl₃) (δ , ppm) 191.9, 157.7, 157.4, 153.2, 140.9, 138.3, 135.0, 134.6, 133.0, 130.4, 130.0, 129.5, 128.8, 128.7, 128.6, 128.3, 127.6, 127.4, 126.9, 125.5, 124.6, 121.71, 120.0, 117.6, 116.2, 66.4, 49.6. HRMS (TOF MS ESI⁺) calculated for C₃₃H₂₃O₃ [M+H]⁺: 467.1647, found 467.1642.

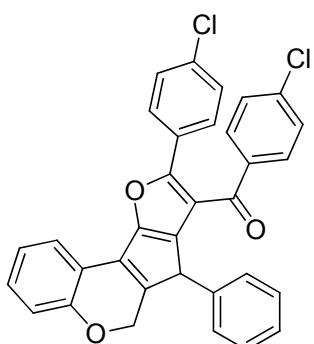


(4-Methoxyphenyl){9-(4-methoxyphenyl)-7-phenyl-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromen-8-yl}methanone (2n). 75.8 mg, 72% yield. Yellow solid; mp: 148.6-146.8 °C. ¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.76-7.64 (m, 5H), 7.24-7.18

(m, 1H), 7.11-7.02 (comp, 4H), 6.90-6.84 (comp, 3H), 6.79-6.72 (comp, 3H), 5.11 (d, J = 15.6 Hz, 1H), 4.88 (d, J = 15.6 Hz, 1H), 4.33 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 190.7, 163.5, 159.9, 157.3, 156.6, 153.2, 140.2, 135.3, 134.5, 131.8, 131.2, 129.9, 128.8, 128.3, 127.6, 127.2, 125.6, 124.6, 123.4, 121.7, 119.0, 117.8, 116.2, 114.0, 113.5, 66.5, 55.6, 55.4, 49.6. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{35}\text{H}_{26}\text{O}_5\text{Na} [\text{M}+\text{Na}]^+$: 549.1678 found 549.1670.

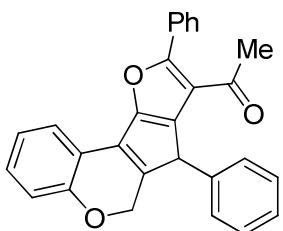


(4-Bromophenyl){9-(4-bromophenyl)-7-phenyl-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromen-8-yl}methanone (2o). 74.9 mg, 60% yield. Yellow solid; mp: 158.5-165.3 °C. ^1H NMR(400 MHz, CDCl_3) (δ , ppm) 7.70-7.62(comp, 3H), 7.50-7.45 (comp, 4H), 7.42-7.37 (m, 2H), 7.25-7.20 (m, 1H), 7.16-7.00 (comp, 4H), 6.87 (t, J = 8.6 Hz, 1H), 6.69 (d, J = 6.9 Hz, 2H), 5.08 (d, J = 15.7 Hz, 1H), 4.85 (d, J = 15.7 Hz, 1H), 4.26 (s, 1H). ^{13}C NMR (100MHz, CDCl_3) (δ , ppm) 190.9, 157.9, 156.5, 153.2, 141.5, 136.9, 134.7, 134.3, 131.9, 131.7, 130.8, 130.2, 129.2, 129.0, 128.3, 128.2, 127.5, 125.5, 124.5, 123.1, 121.8, 120.0, 117.4, 116.3, 66.3, 49.7. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{33}\text{H}_{20}\text{Br}_2\text{O}_3\text{Na} [\text{M}+\text{Na}]^+$: 646.9656 found 646.9670.

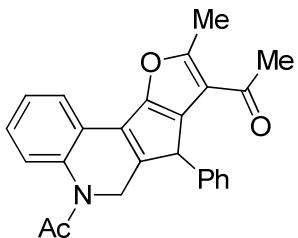


(4-Chlorophenyl){9-(4-chlorophenyl)-7-phenyl-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromen-8-yl}methanone.

nta[1,2-*c*]chromen-8-yl}methanone1 (2p). 67.5 mg, 63% yield. Yellow solid; mp: 154.7-161.3 °C. ¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.77- 7.66 (comp, 3H), 7.56 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 7.25-7.20 (comp, 3H), 7.13-7.03 (comp, 4H), 6.88 (d, J = 8.0 Hz, 1H), 6.70 (d, J = 6.9 Hz, 2H), 5.09 (d, J = 15.7 Hz, 1H), 4.85 (d, J = 15.7 Hz, 1H), 4.27 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) (δ , ppm) 190.7, 157.8, 156.4, 153.2, 141.4, 139.6, 136.4, 134.7, 134.3, 130.7, 130.2, 129.0, 128.9, 128.8, 128.7, 128.0, 127.52, 127.50, 125.5, 124.5, 121.7, 120.0, 117.4, 116.3, 66.3, 49.6. HRMS (TOF MS ESI⁺) calculated for C₃₃H₂₁O₃Cl₂ [M+H]⁺: 535.0868, found 535.0856.



1-{7,9-Diphenyl-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-*c*]chromen-8-yl}ethanone (2q). 50.2 mg, 62% yield. Yellow solid; mp: 156.5-153.8 °C. ¹H NMR (400 MHz, CDCl₃) (δ , ppm): 8.01 (d, J = 7.2 Hz, 1H), 7.70 (d, J = 7.2 Hz, 1H), 7.59-7.45 (m, 3H), 7.40-7.29 (m, 3H), 7.28-7.15 (m, 3H), 7.07 (d, J = 7.3 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 5.22 (d, J = 15.5 Hz, 1H), 4.88 (d, J = 15.5 Hz, 1H), 4.60 (s, 1H), 2.20 (s, 3H); ¹³C NMR (100MHz, CDCl₃) (δ , ppm): 194.4, 158.7, 158.5, 153.1, 141.3, 135.6, 132.2, 130.7, 130.0, 129.5, 129.3, 128.5, 128.4, 127.9, 127.85, 127.81, 124.5, 121.7, 121.4, 117.5, 116.2, 66.4, 50.1, 31.2. HRMS (TOF MS ESI⁺) calculated for C₂₈H₂₁O₃ [M+H]⁺: 405.1491, found 405.1496.



1,1'-(9-Methyl-7-phenyl-5H-furo[2',3':3,4]cyclopenta[1,2-*c*]quinoline-5,8(6*H*,7*H*)-diyl)diethanone (2r). This product was decomposed into a complex mixture during

the isolation on column chromatography, and see the proton NMR of the crude reaction mixture (Figure S1).

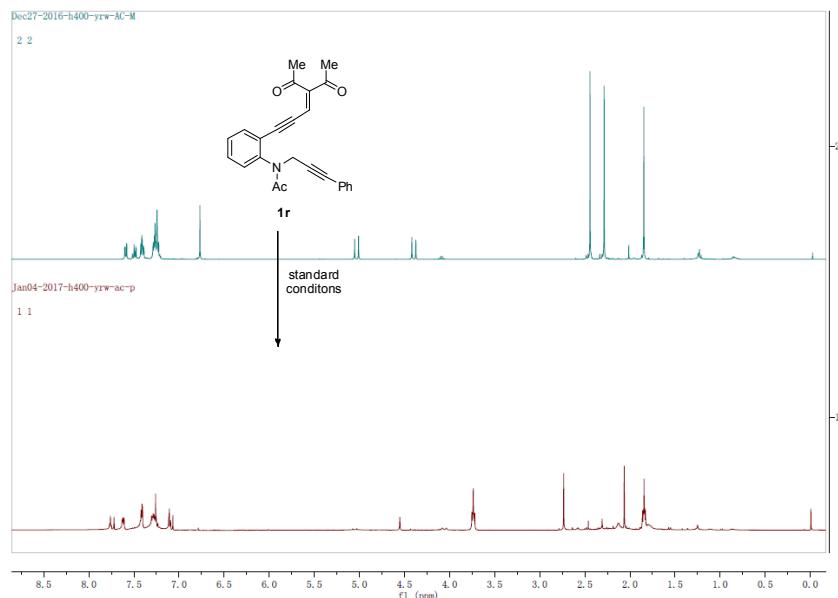
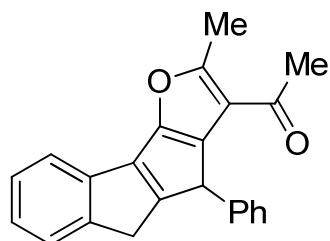
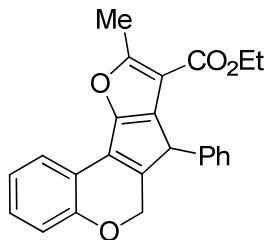


Figure S1. Proton NMR of the crude reaction mixture of **Ir**.

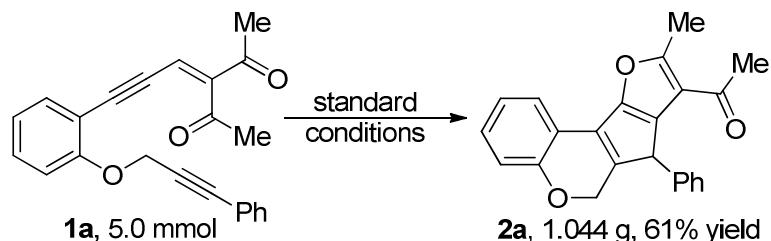


1-(2-Methyl-4-phenyl-4,5-dihydrobenzo[5,6]furan-3-yl)ethanone (2s**)**. 35.8 mg, 55% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.57 (d, $J = 7.5$ Hz, 1H), 7.38-7.19 (comp, 7H), 7.03 (d, $J = 7.4$ Hz, 1H), 5.74 (s, 1H), 2.93 (d, $J = 18.4$ Hz, 1H), 2.32 (dd, $J = 18.4, 2.9$ Hz, 1H), 2.21 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 195.2, 168.4, 145.4, 145.3, 138.7, 138.6, 136.4, 128.6, 127.9, 127.8, 126.2, 125.8, 125.0, 114.7, 96.9, 62.0, 31.0, 29.6, 15.5. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{23}\text{H}_{19}\text{O}_2$ [$\text{M}+\text{H}]^+$: 327.1385, found 327.1388.



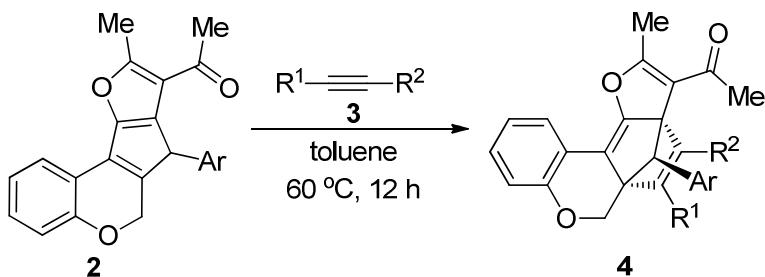
Ethyl 9-Methyl-7-phenyl-6,7-dihydrofuro[2',3':3,4]cyclopenta[1,2-c]chromene-8-carboxylate (2t). 39.4 mg, 53% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.58-6.82 (comp, 9H), 5.13 (d, $J = 15.4$ Hz, 1H), 4.83 (d, $J = 15.4$ Hz, 1H), 4.44 (s, 1H), 4.14-3.86 (m, 2H), 2.73 (s, 3H), 0.97 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 164.0, 161.8, 156.7, 153.1, 139.8, 136.3, 131.3, 129.7, 128.7, 128.0, 127.2, 124.9, 124.4, 121.5, 117.9, 116.1, 112.9, 66.5, 60.0, 49.6, 44.6, 44.0. HRMS (TOF MS ESI $^+$) calculated for $\text{C}_{24}\text{H}_{21}\text{O}_4$ [$\text{M}+\text{H}]^+$: 373.1440, found 373.1438.

General Procedure for the Scale Up.

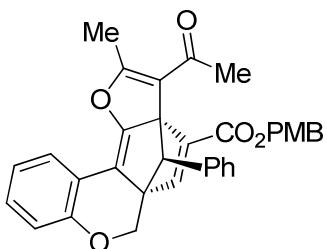


To an 10-mL oven-dried vial containing a magnetic stirring bar, 4Å MS (750 mg), and $\text{Pd}_2(\text{dba})_3$ (230 mg, 5.0 mol%) in DCE (37.5 mL), was added enynone **1a** (1.712 g, 5.0 mmol) in DCE (37.5 mL) over 1.0 h *via* a syringe pump under argon atmosphere at room temperature. Then the reaction mixture was stirred for additional 3.0 h. After the reaction was completed, the solvent was evaporated *in vacuo* and the residue was purified by column chromatography on neutral alumina (Hexanes: EtOAc = 10:1 to 5:1) to afford the pure product **2a** in 61% yield (1.044 g).

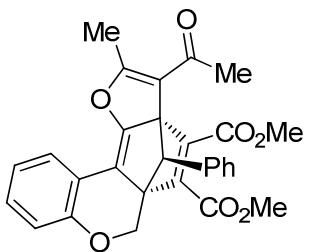
General Procedure for the [4+2] Cycloaddition.



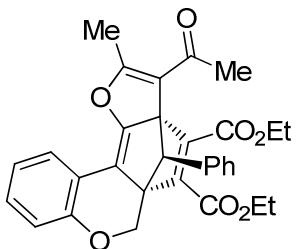
To an 10-mL oven-dried vial containing a magnetic stirring bar, **2** (0.2 mmol), alkyne **3** (0.3 mmol), and toluene (3.0 mL) were added in sequence, then the reaction mixture was stirred for 12 h at 60 °C. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel (Hexanes: EtOAc = 10:1 to 3:1) to afford the pure products **4a-4d**.



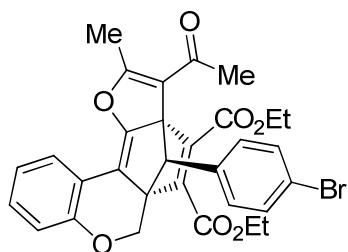
4-Methoxybenzyl 3-acetyl-2-methyl-12-phenyl-6H-3a,5a-methanobenzofuro[6,7-c]chromene-4-carboxylate(4a). 55.4 mg, 52% yield. Yellow oil. ¹H NMR (400 MHz, CDCl₃) (δ , ppm) 8.02 (s, 1H), 7.43 (d, J = 7.4 Hz, 1H), 7.30-7.25 (comp, 2H), 7.22-7.15 (comp, 3H), 7.11-7.02 (comp, 3H), 6.99-6.93 (m, 1H), 6.90-6.85 (comp, 3H), 5.08 (s, 2H), 4.52 (d, J = 11.4 Hz, 1H), 4.41 (s, 1H), 4.06 (d, J = 11.4 Hz, 1H), 3.80 (s, 3H), 2.48 (s, 3H), 2.09 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ , ppm) 194.3, 170.4, 163.3, 163.0, 159.8, 156.4, 152.8, 151.6, 135.3, 130.5, 129.0, 128.7, 128.2, 127.92, 127.78, 127.32, 122.4, 118.7, 117.4, 116.1, 114.1, 104.2, 95.8, 73.4, 66.3, 66.2, 66.0, 55.4, 30.1, 15.7. HRMS (TOF MS ESI⁺) calculated for C₃₄H₂₈O₆Na [M+Na]⁺: 555.1784, found 555.1773.



Dimethyl 3-acetyl-2-methyl-12-phenyl-6H-3a,5a-methanobenzofuro[6,7-c]chromene-4,5-dicarboxylate (4b). 63.0 mg, 65% yield. Yellow solid; mp: 151.9-154.4 °C. ¹H NMR (400 MHz, CDCl₃) (δ , ppm): 7.49-7.45(m, 1H), 7.24-7.16 (comp, 3H), 7.11-7.03 (comp, 3H), 7.00-6.95 (m, 1H), 6.88 (d, J = 8.1 Hz, 1H), 4.80 (d, J = 11.7 Hz, 1H), 4.52 (s, 1H), 3.99 (d, J = 11.7 Hz, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 2.53 (s, 3H), 2.17 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ , ppm): 193.8, 171.2, 166.2, 163.4, 162.1, 154.5, 152.9, 150.5, 134.7, 128.9, 128.9, 128.5, 128.2, 127.5, 122.3, 118.0, 117.6, 115.3, 104.7, 95.3, 73.7, 68.6, 64.2, 52.6, 52.3, 30.0, 15.9. HRMS (TOF MS ESI⁺) calculated for C₂₉H₂₅O₇ [M+H]⁺: 485.1600, found 485.1588.

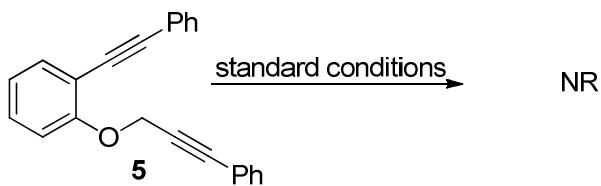


Diethyl 3-acetyl-2-methyl-12-phenyl-6H-3a,5a-methanobenzofuro[6,7-c]chromene-4,5-dicarboxylate (4c). 59.5 mg, 58% yield. Yellow solid; mp: 154.9-153.4 °C. ¹H NMR (400 MHz, CDCl₃) (δ , ppm): 7.50-7.44 (m, 1H), 7.24-7.17 (comp, 3H), 7.12-7.02 (comp, 3H), 7.00-6.93 (m, 1H), 6.89-6.83 (m, 1H), 4.79 (d, J = 11.6 Hz, 1H), 4.51 (s, 1H), 4.39-4.12 (m, 4H), 3.99 (d, J = 11.6 Hz, 1H), 2.53 (s, 3H), 2.16 (s, 3H), 1.28-1.20 (comp, 6H); ¹³C NMR (100 MHz, CDCl₃) (δ , ppm): 193.9, 171.3, 165.8, 162.9, 162.2, 154.9, 152.8, 150.1, 134.7, 128.9, 128.8, 128.5, 128.1, 127.5, 122.2, 118.0, 117.5, 115.2, 104.7, 94.9, 73.5, 68.6, 64.2, 61.7, 61.3, 30.1, 15.8, 14.10, 14.09. HRMS (TOF MS ESI⁺) calculated for C₃₁H₂₈O₇Na [M+Na]⁺: 535.1733, found 535.1727.

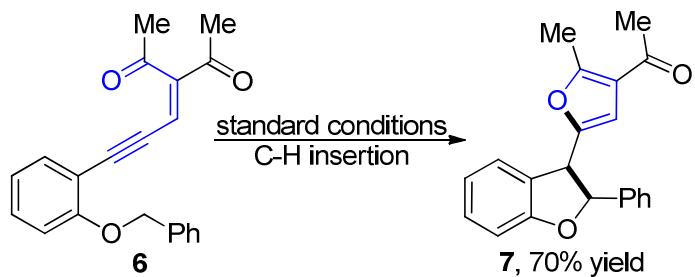


Diethyl 3-acetyl-12-(4-bromophenyl)-2-methyl-6*H*-3*a*,5*a*-methanobenzofuro[6,7-*c*]chromene-4,5-dicarboxylate (4d**).** 59.1 mg, 50% yield. Yellow solid; mp: 190.5-192.9 °C. ¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.48-7.43 (m, 1H), 7.33 (d, J = 8.5 Hz, 2H), 7.11-7.04 (m, 1H), 7.01-6.95 (comp, 3H), 6.88 (d, J = 8.1 Hz, 1H), 4.78 (d, J = 11.7 Hz, 1H), 4.48 (s, 1H), 4.32-4.18 (comp, 4H), 3.99 (d, J = 11.7 Hz, 1H), 2.51 (s, 3H), 2.18 (s, 3H), 1.27-1.20 (comp, 6H); ¹³C NMR (100 MHz, CDCl₃) (δ , ppm) 193.6, 171.1, 165.6, 162.7, 161.9, 154.5, 152.9, 149.9, 133.7, 132.0, 130.5, 128.3, 127.5, 122.7, 122.4, 117.8, 117.6, 115.4, 104.7, 93.9, 73.6, 68.3, 64.0, 61.8, 61.3, 30.0, 15.9, 14.08, 14.07. HRMS (TOF MS ESI⁺) calculated for C₃₁H₂₇O₇BrNa [M+Na]⁺: 613.0838, found 613.0837.

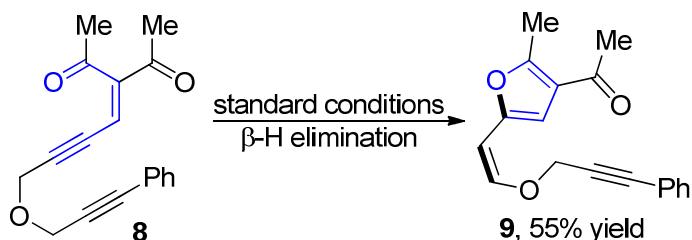
Control Experiments:



To an 10-mL oven-dried vial containing a magnetic stirring bar, 4Å MS (30 mg), and Pd₂(dba)₃ (9.2 mg, 5.0 mol%) in DCE (1.5 mL), was added **5** (61.7 mg, 0.2 mmol) in DCE (1.5 mL) over 1.0 h *via* a syringe pump under argon atmosphere at room temperature. Then the reaction mixture was stirred for additional 3.0 h. According to the TLC results and proton NMR analysis of the crude reaction mixture, most of the material remained intact.



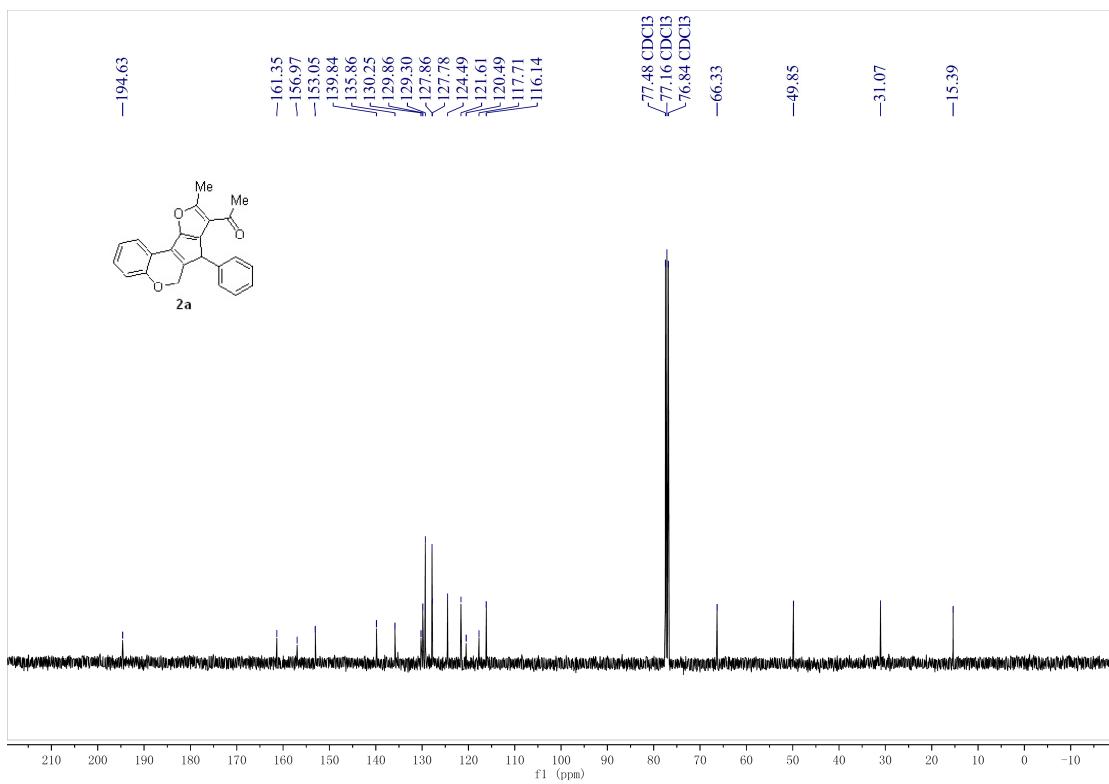
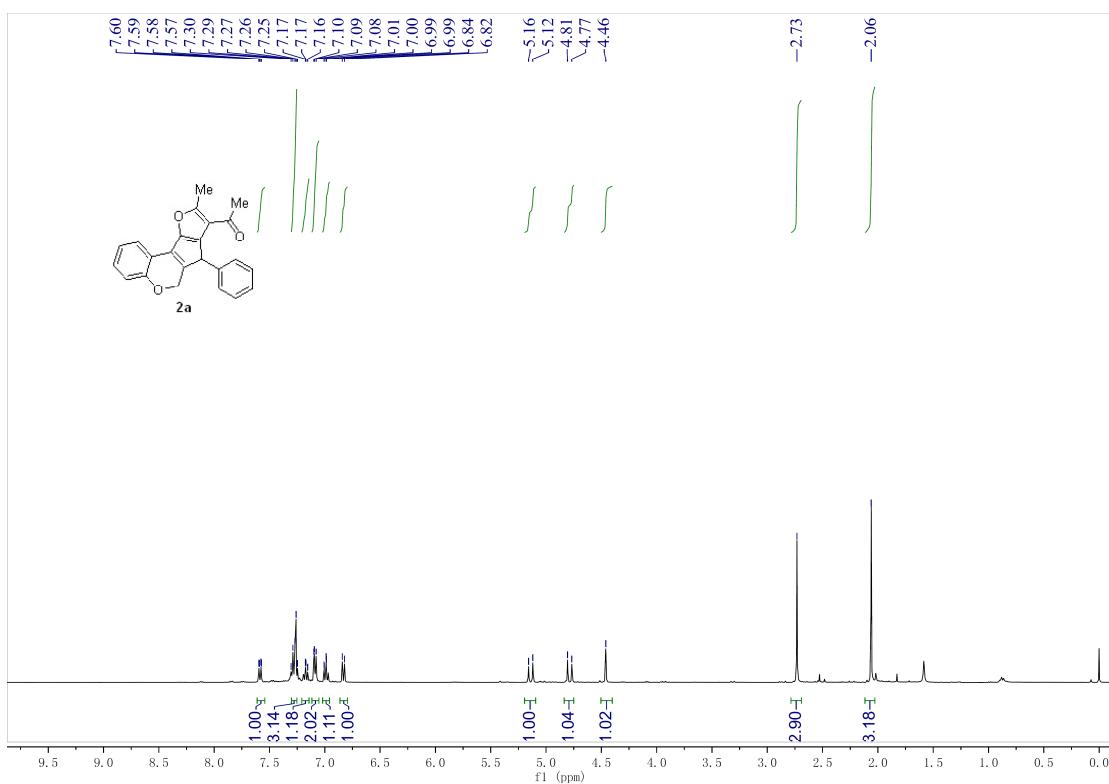
To an 10-mL oven-dried vial containing a magnetic stirring bar, 4Å MS (30 mg), and Pd₂(dba)₃ (9.2 mg, 5.0 mol%) in DCE (1.5 mL), was added enynone **6** (63.6 mg, 0.2 mmol) in DCE (1.5 mL) over 1.0 h *via* a syringe pump under argon atmosphere at room temperature. Then the reaction mixture was stirred for additional 3.0 h. After the reaction was completed, the solvent was evaporated *in vacuo* and the residue was purified by column chromatography on silica gel (Hexanes: EtOAc = 10:1 to 5:1) to afford the pure product **7** in 70% yield (44.6 mg). The physical and spectral properties of **7** are identical to those earlier reported.¹

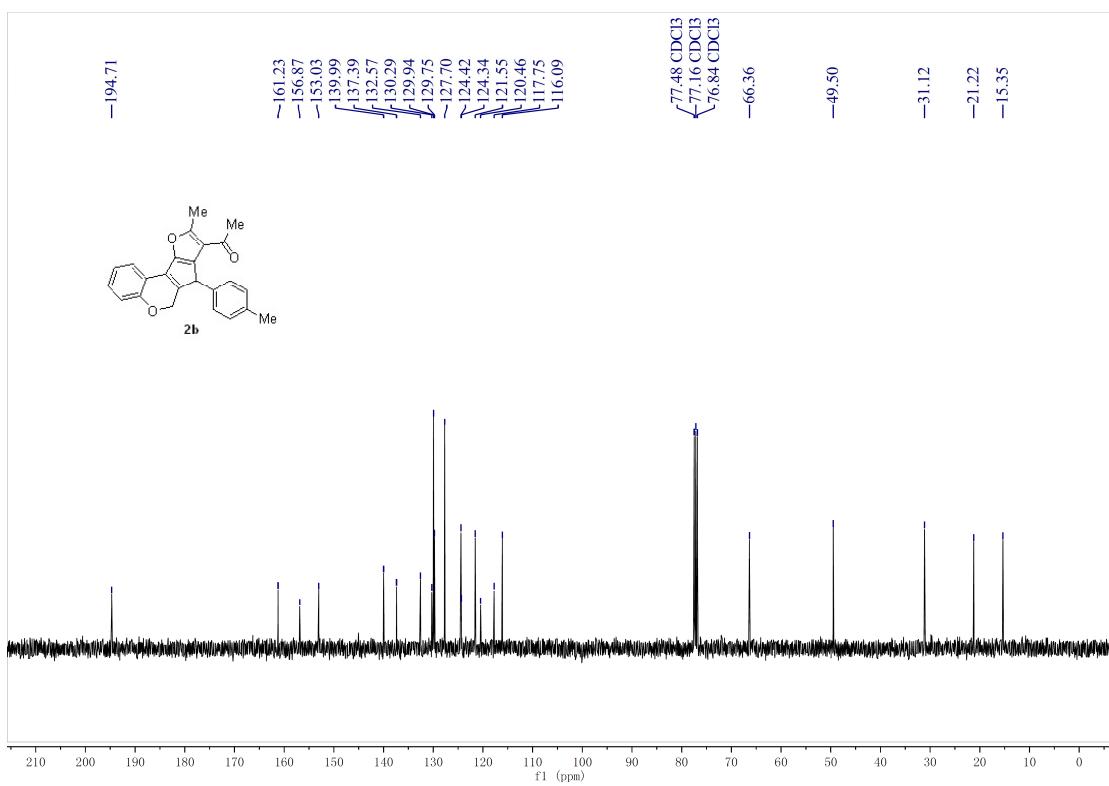
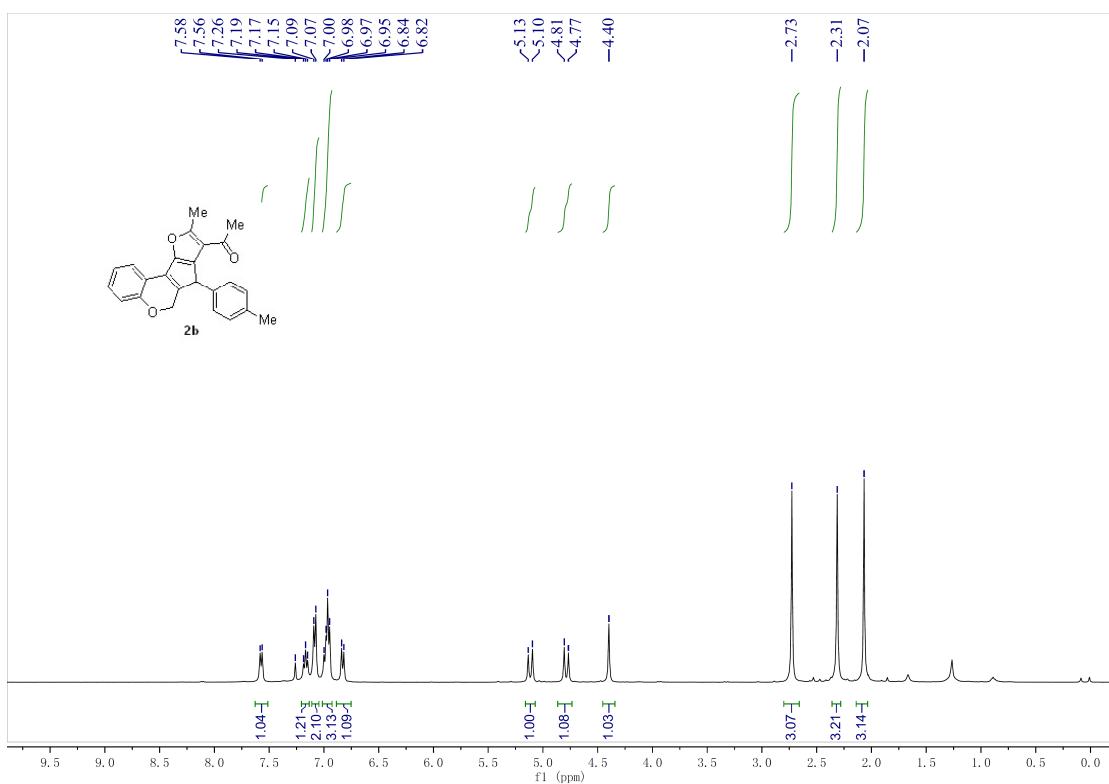


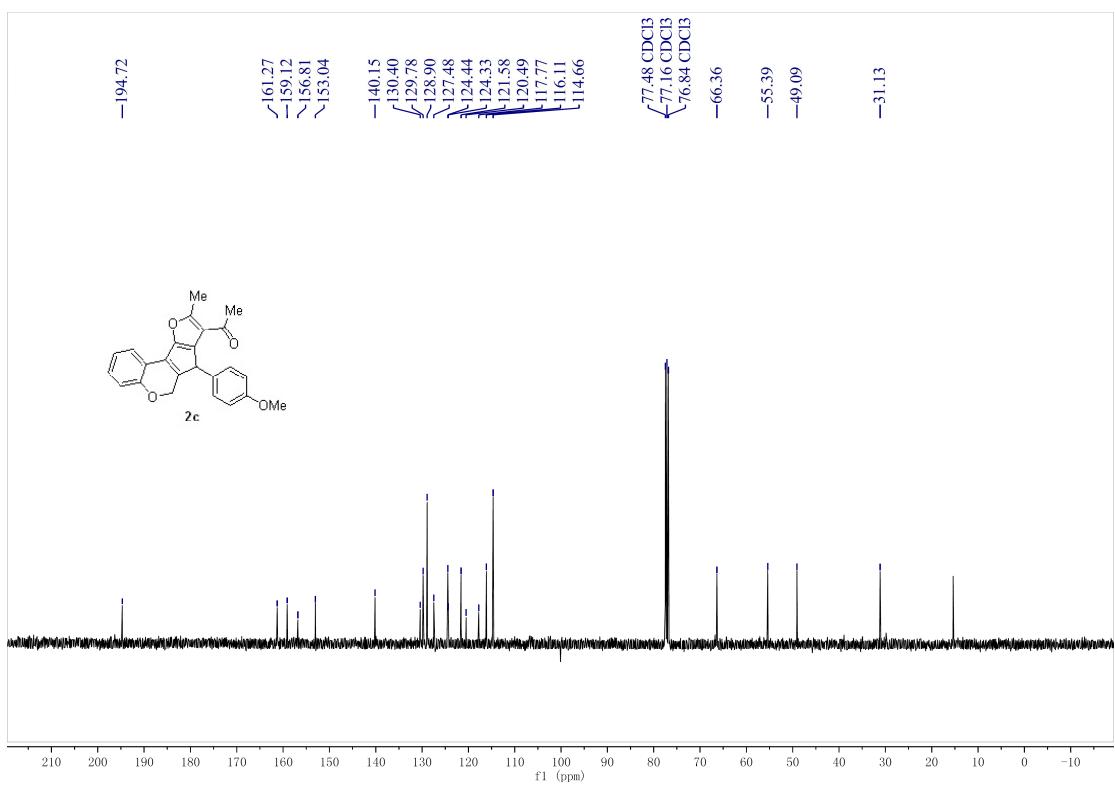
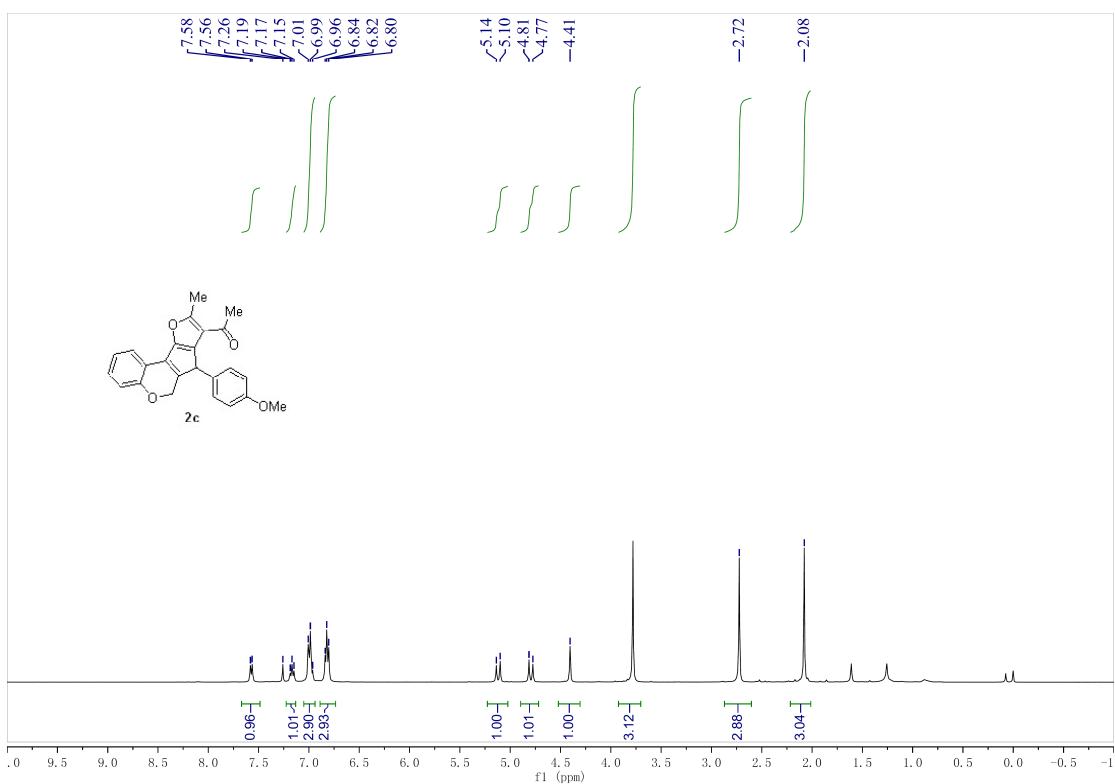
To an 10-mL oven-dried vial containing a magnetic stirring bar, 4Å MS (30 mg), and Pd₂(dba)₃ (9.2 mg, 5.0 mol%) in DCE (1.5 mL), was added enynone **8** (56.0 mg, 0.2 mmol) in DCE (1.5 mL) over 1.0 h *via* a syringe pump under argon atmosphere at room temperature. Then the reaction mixture was stirred for additional 3.0 h. After the reaction was completed, the solvent was evaporated *in vacuo* and the residue was purified by column chromatography on silica gel (Hexanes: EtOAc = 10:1 to 5:1) to afford the pure product **9** in 55% yield (30.8 mg). Yellow oil. ¹H NMR (400 MHz, CDCl₃) (δ , ppm) 7.48-7.44 (m, 2H), 7.35-7.31 (comp, 3H), 6.77 (s, 1H), 6.41 (d, J = 6.8 Hz, 1H), 5.42 (d, J = 6.8 Hz, 1H), 4.82 (s, 2H), 2.57 (s, 3H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ , ppm) 194.8, 156.2, 148.4, 144.2, 132.0, 131.8, 129.1, 128.52, 128.46, 108.6, 96.9, 87.9, 83.5, 60.9, 29.3, 14.4. HRMS (TOF MS ESI⁺) calculated for C₁₈H₁₇O₃ [M+H]⁺: 281.1171, found 281.1178.

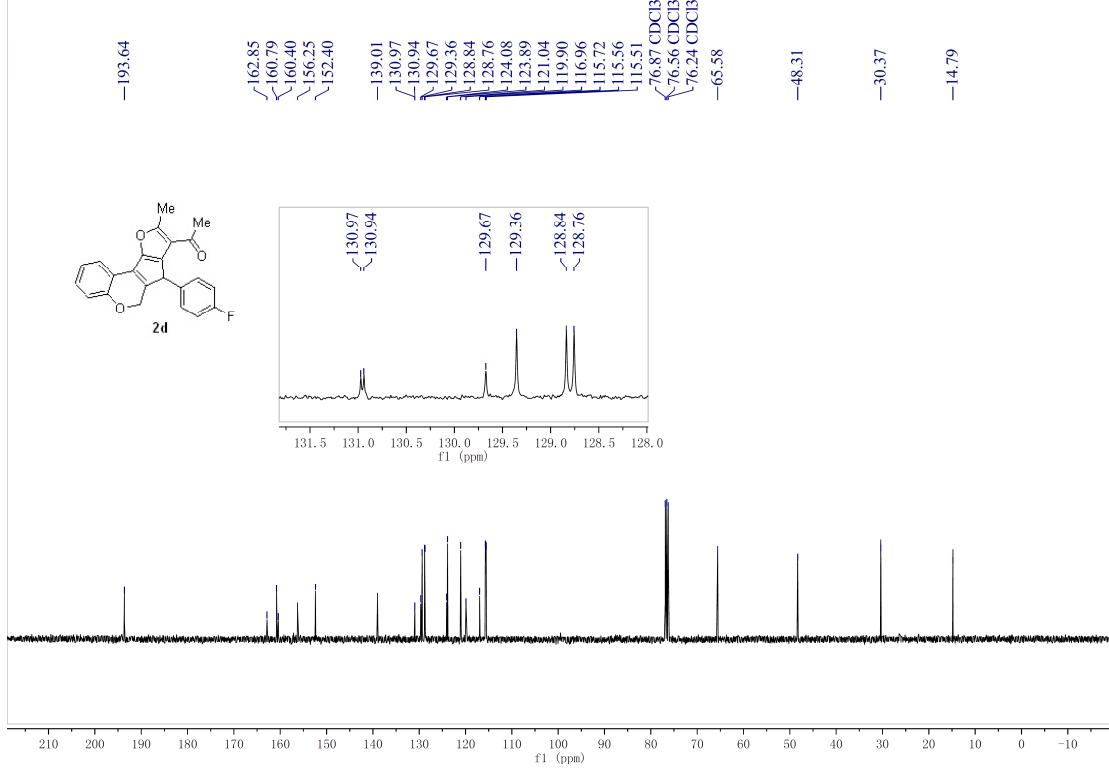
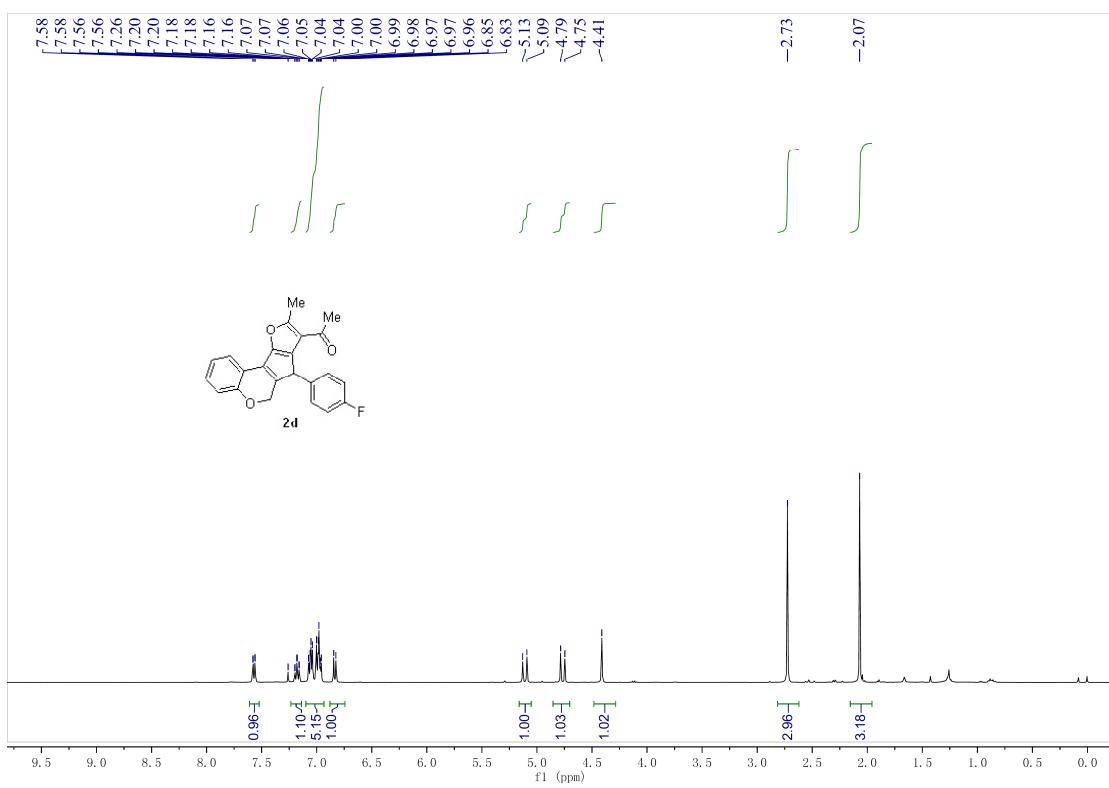
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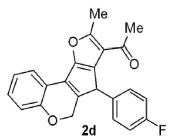
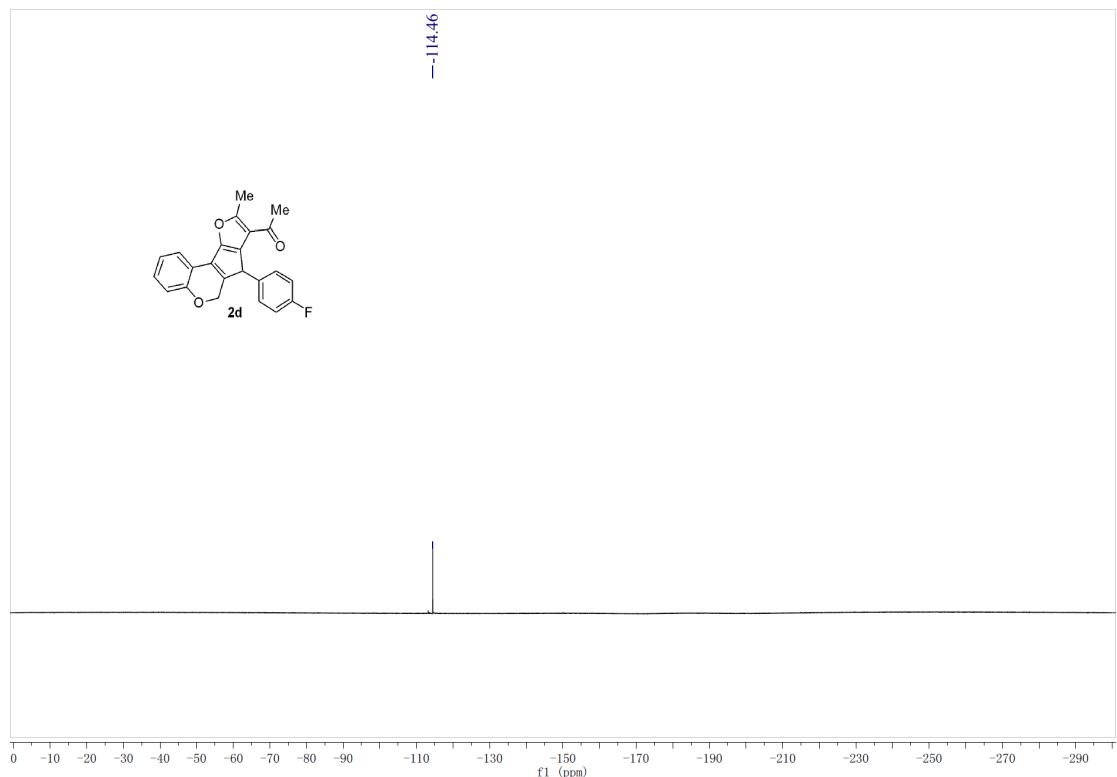
- (1) D. Zhu, J. Ma, K. Luo, H. Fu, L. Zhang and S. Zhu, *Angew. Chem. Int. Ed.*, 2016, **55**, 8452.



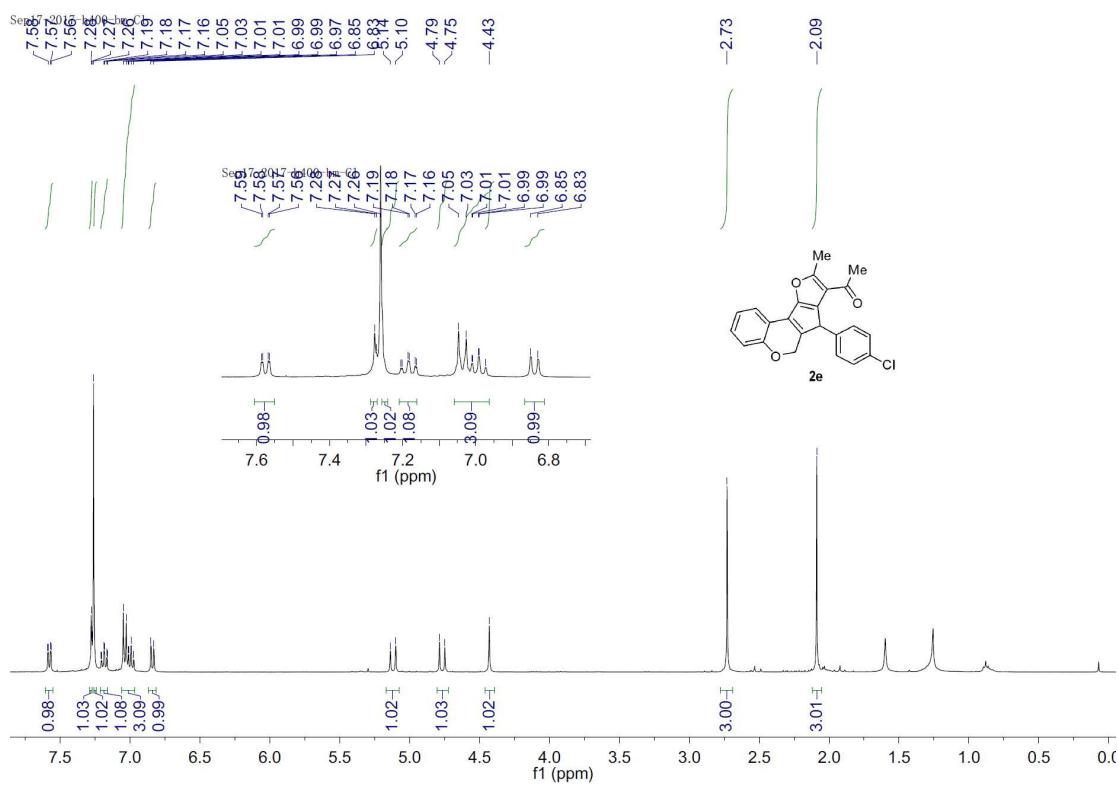


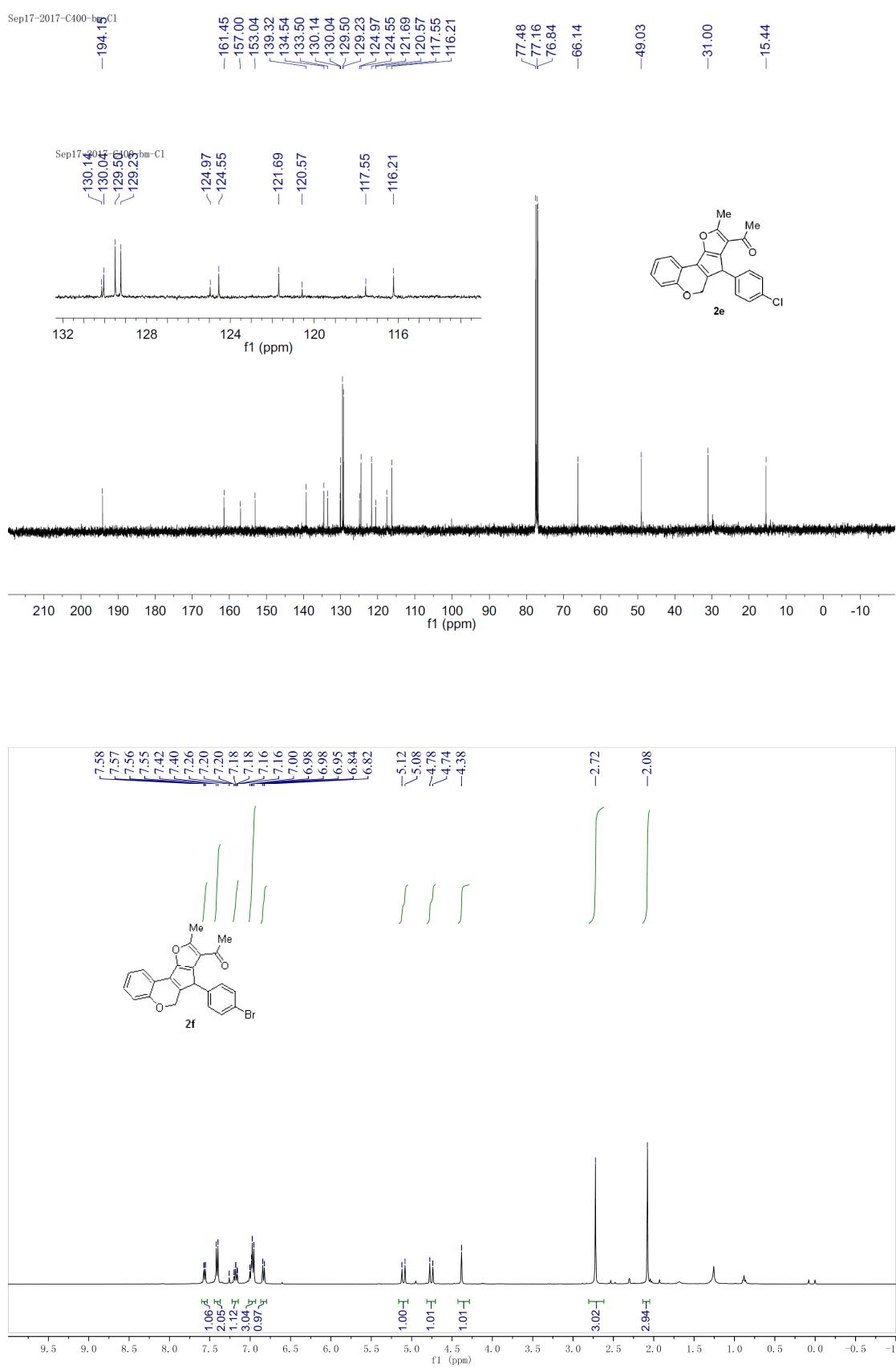


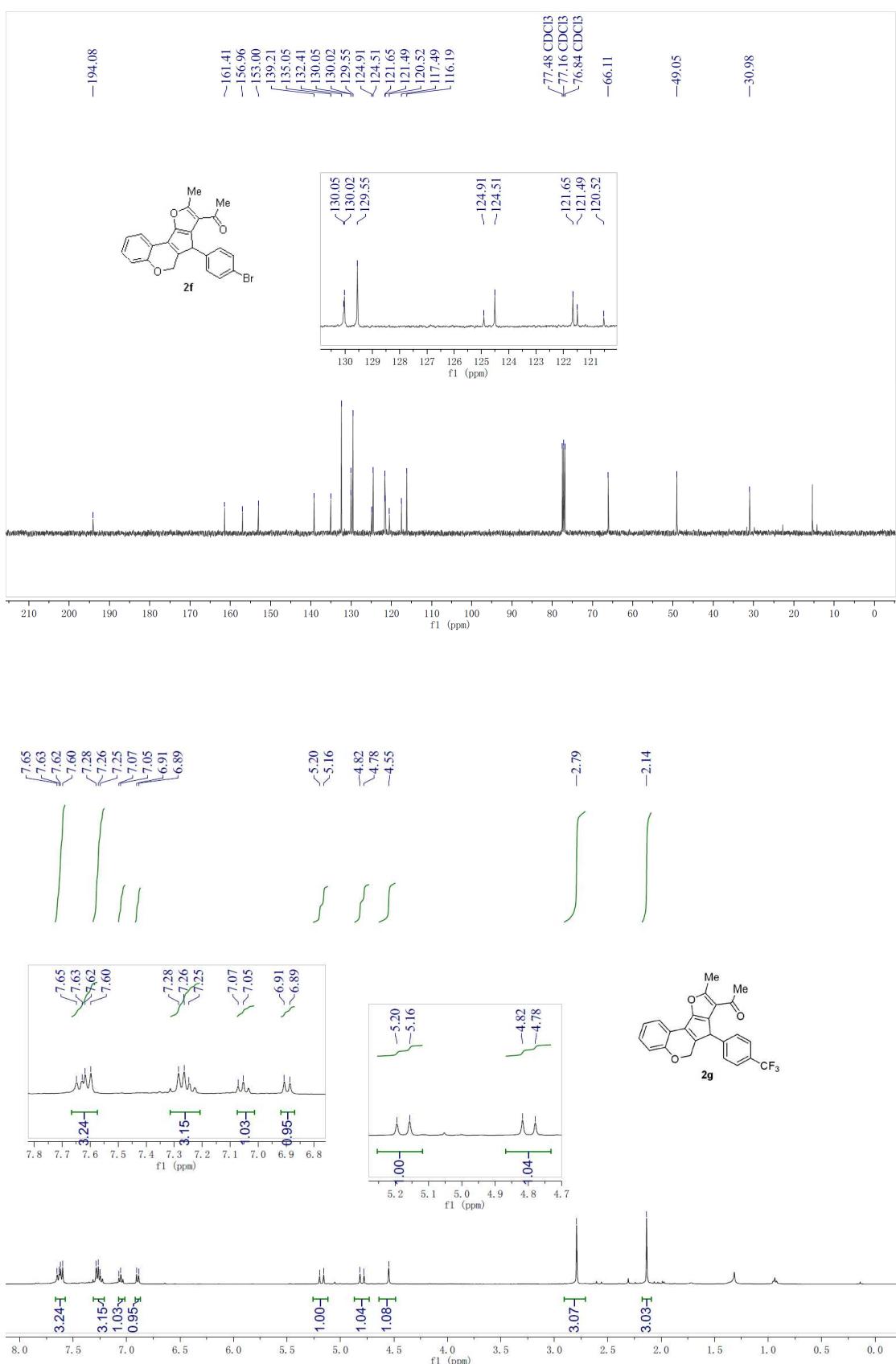


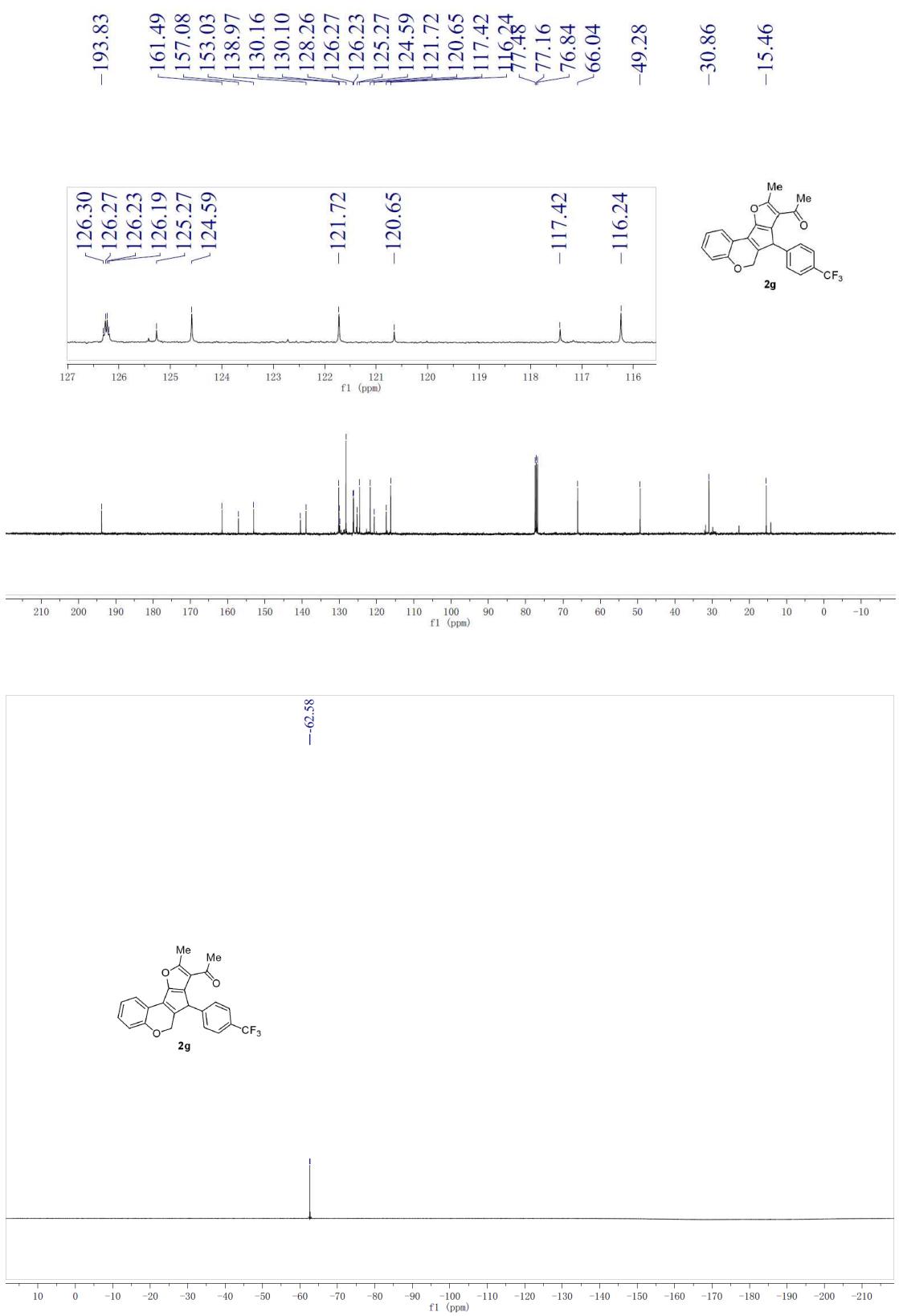


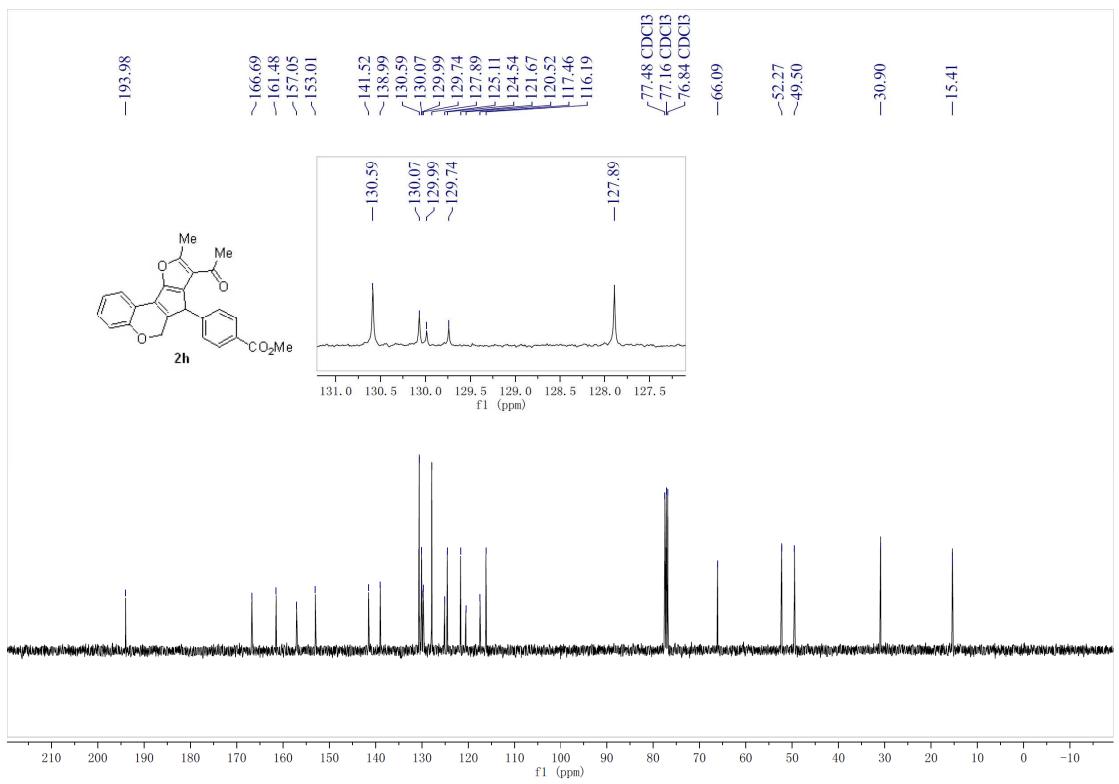
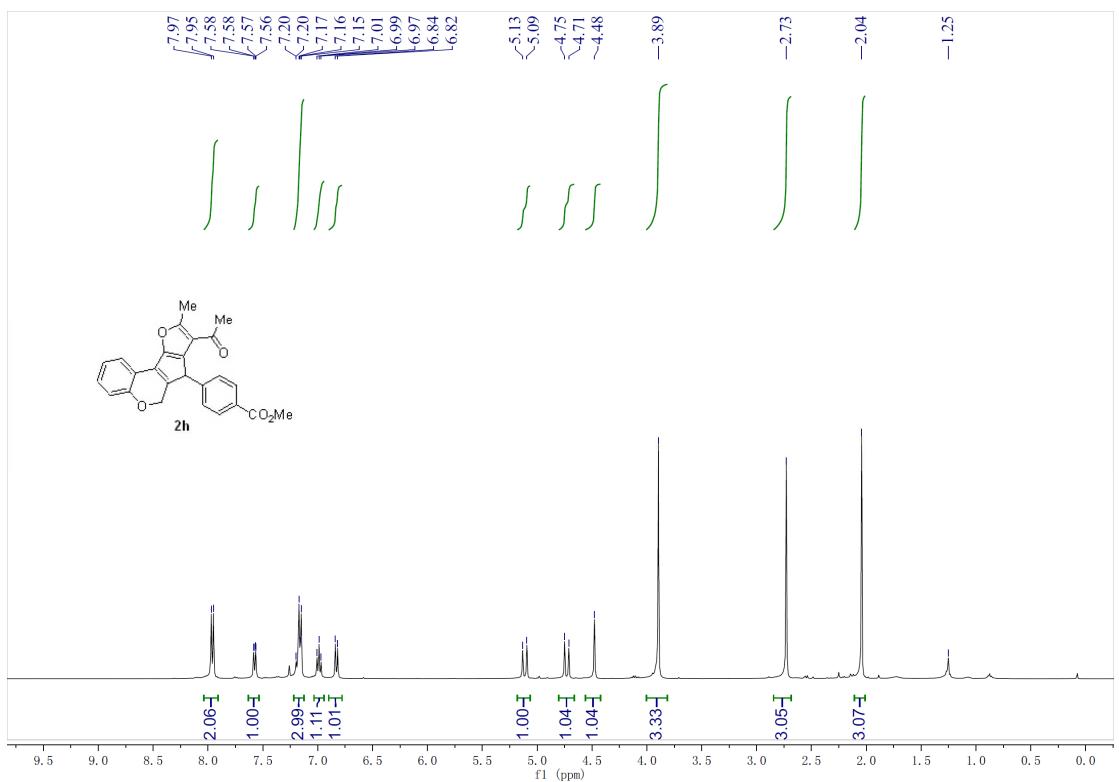
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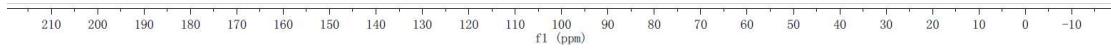
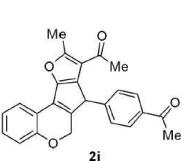
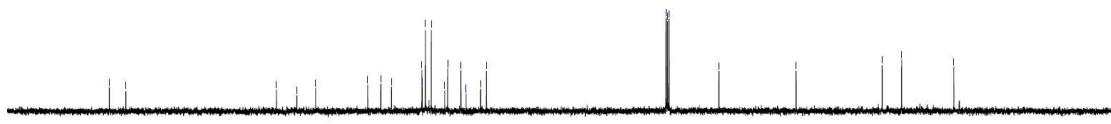
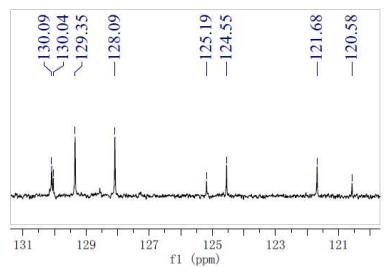
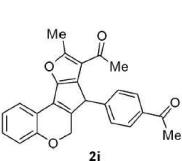
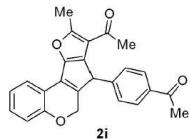
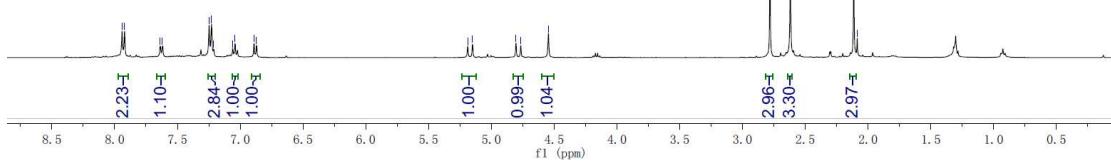
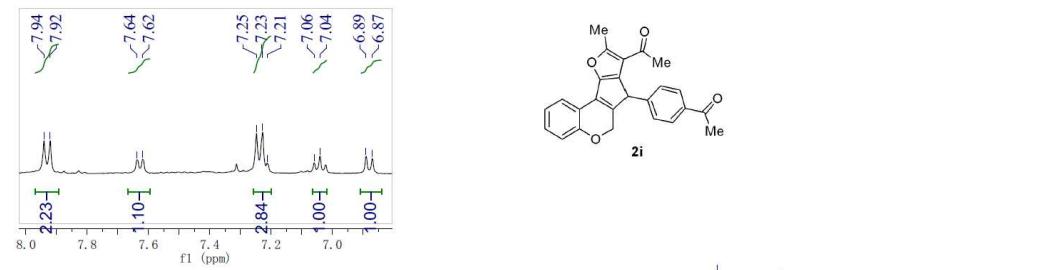
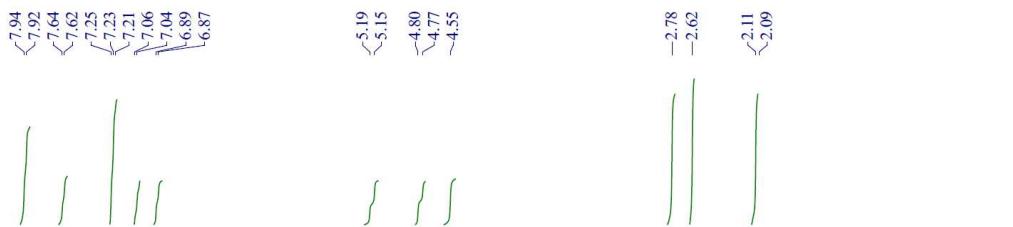


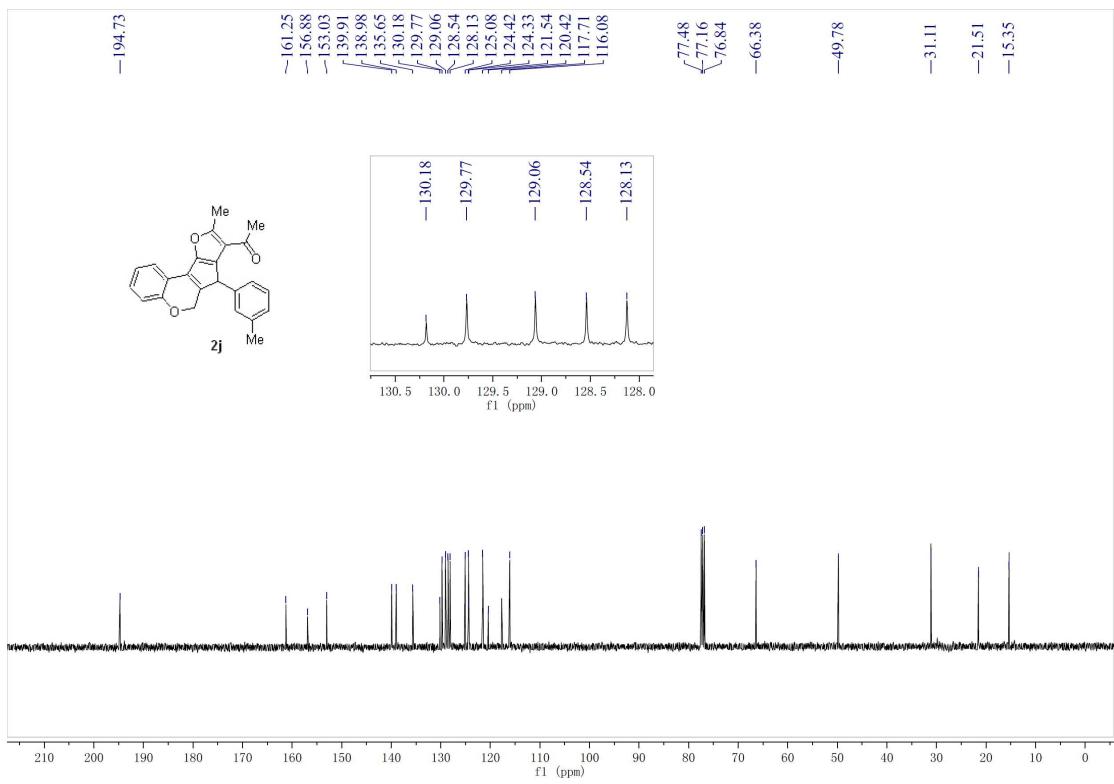
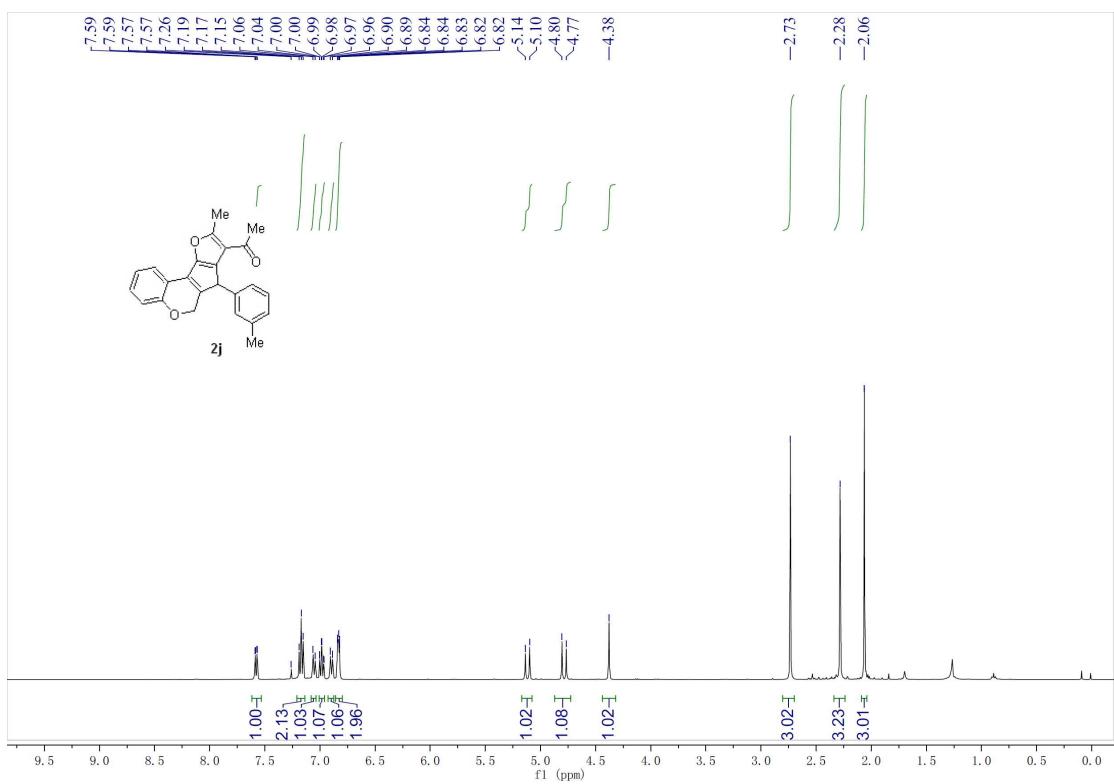


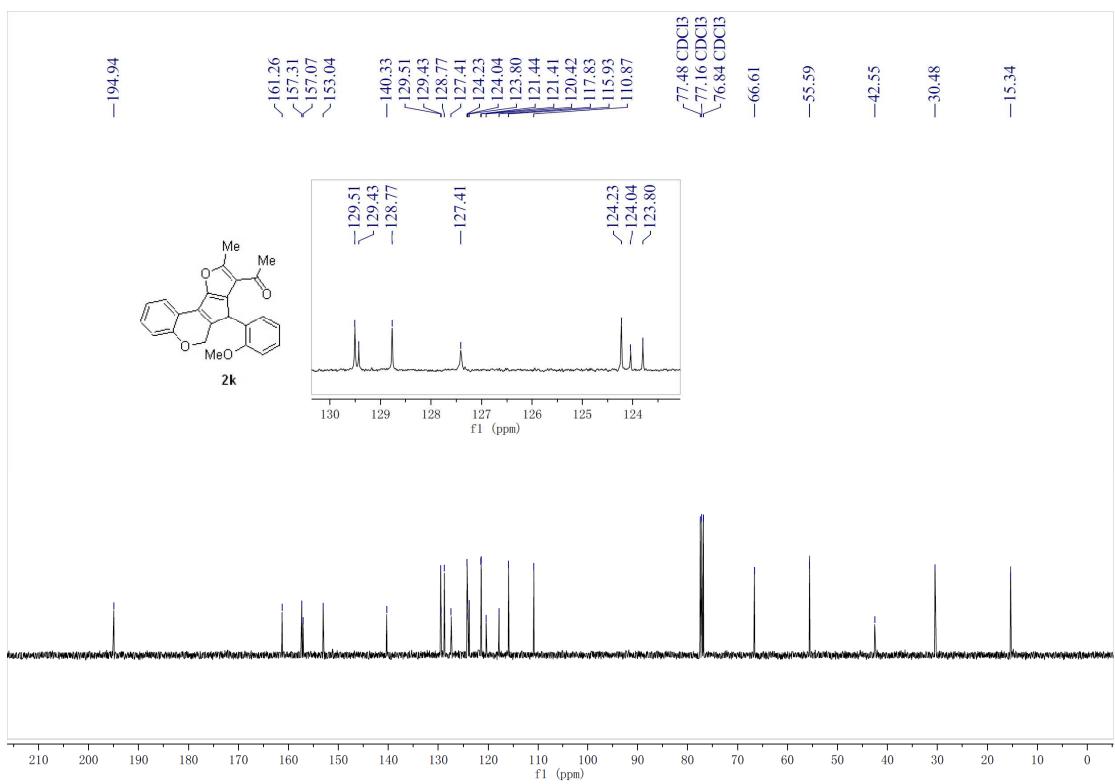
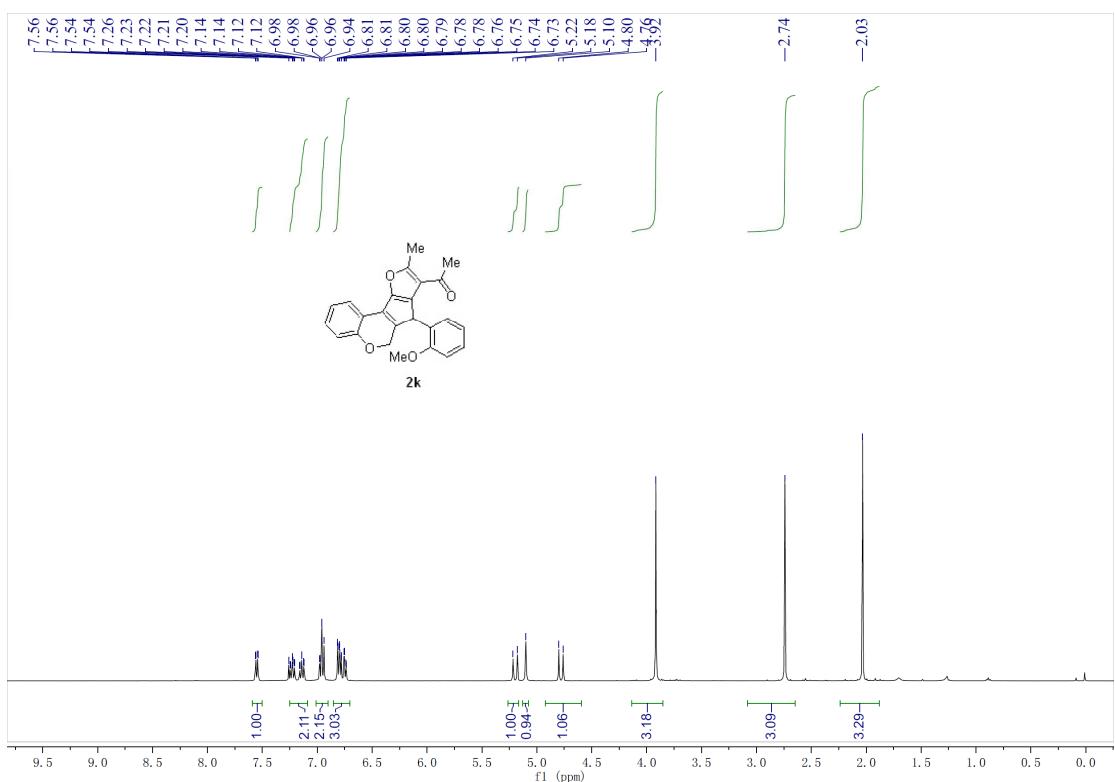


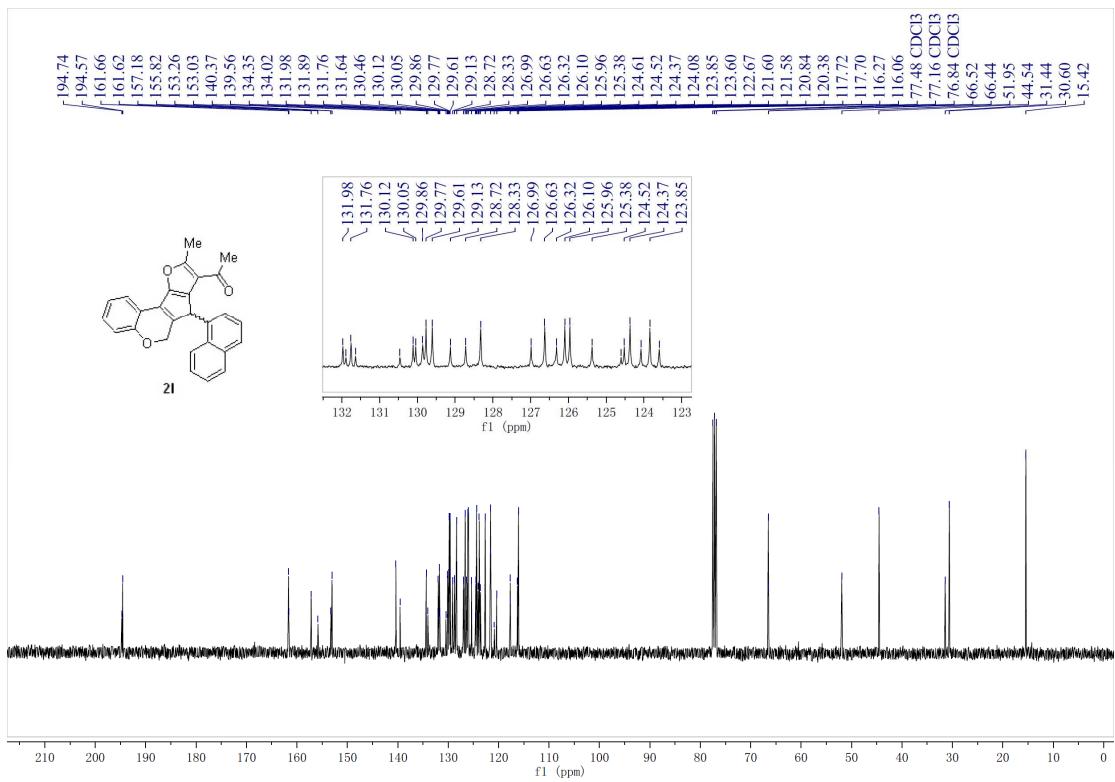
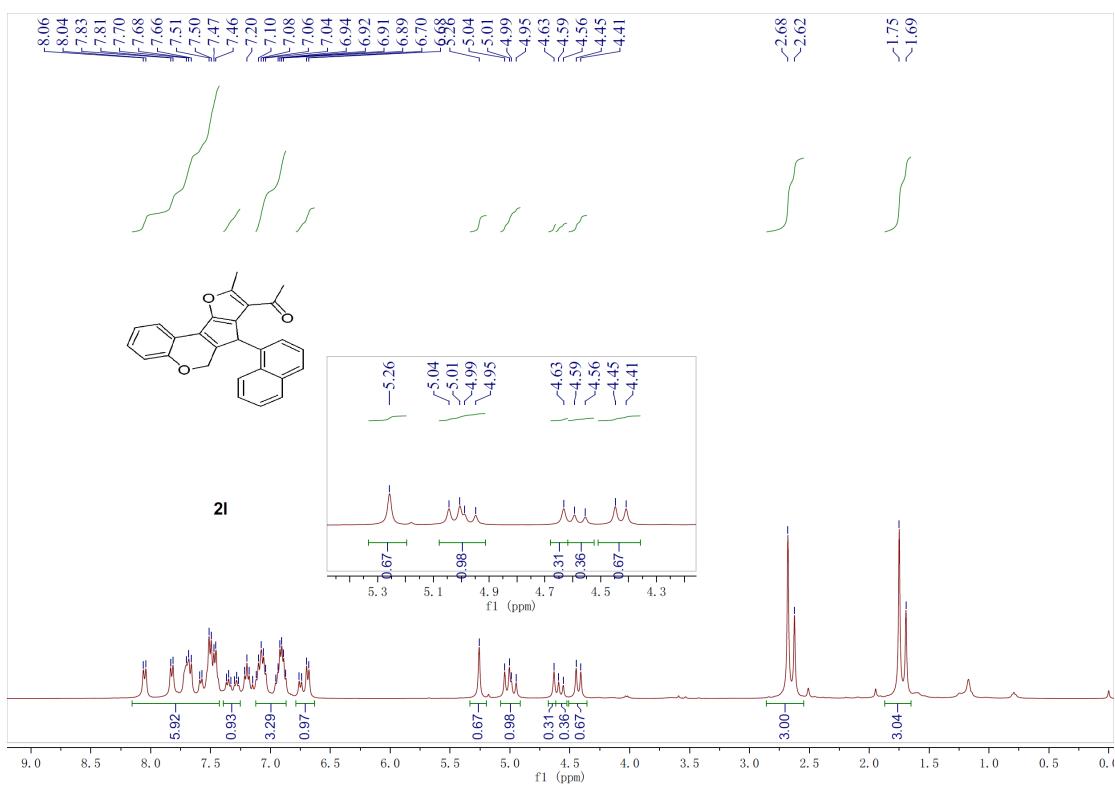


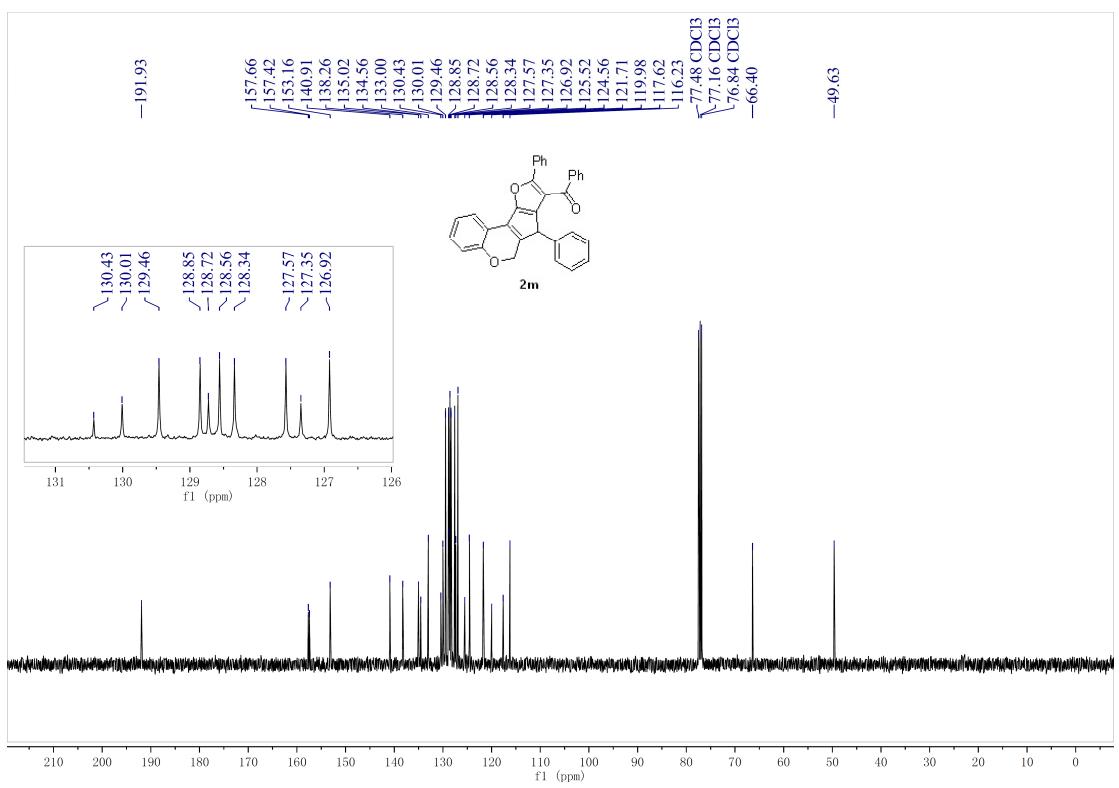
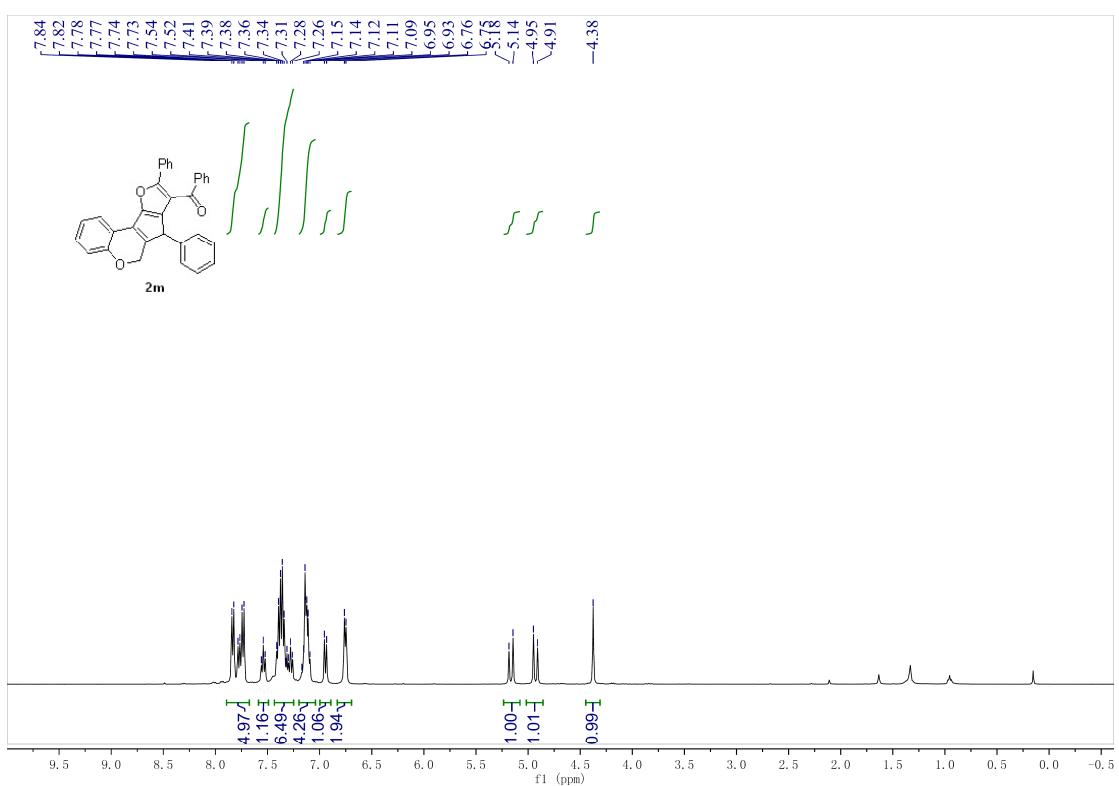


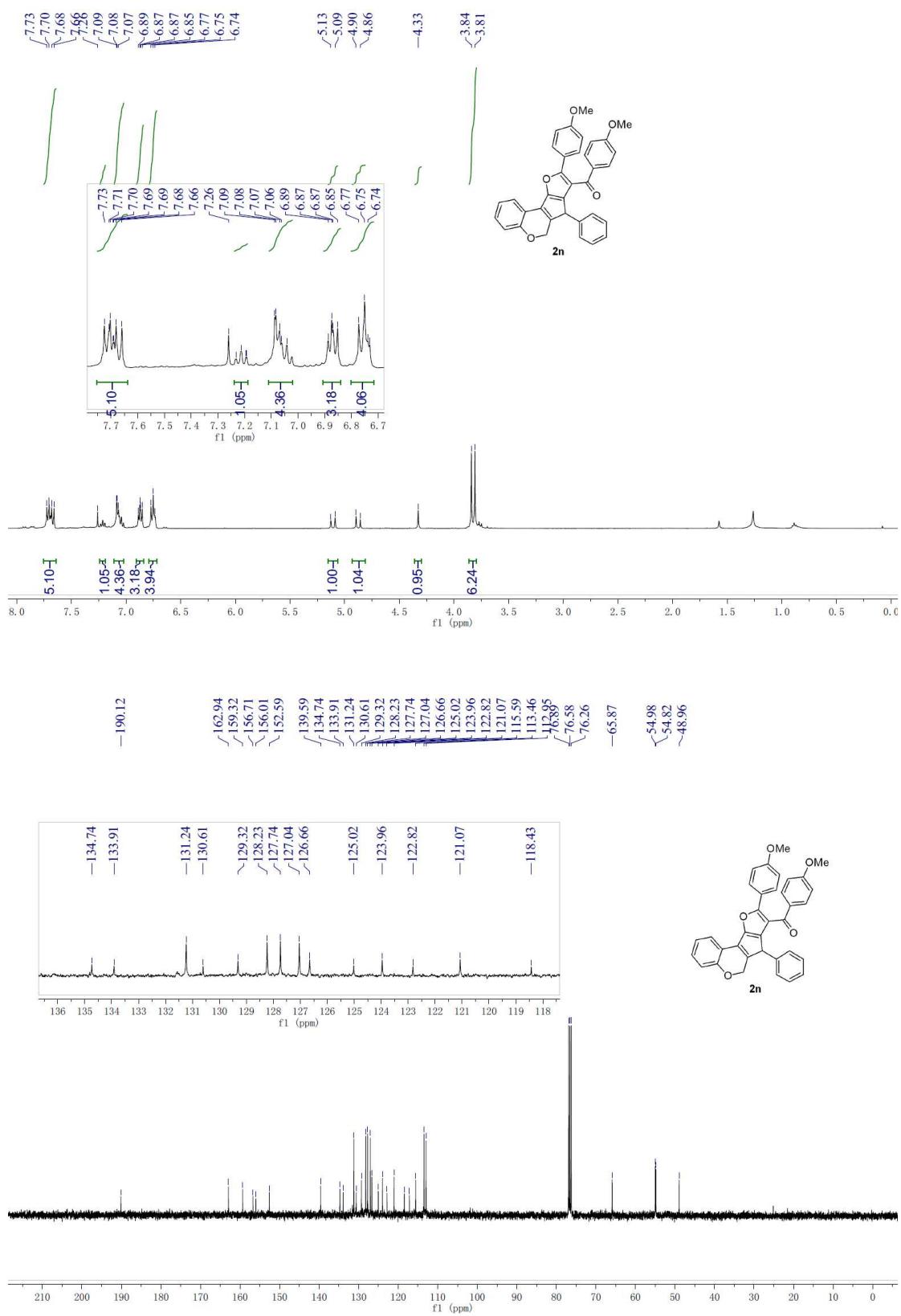


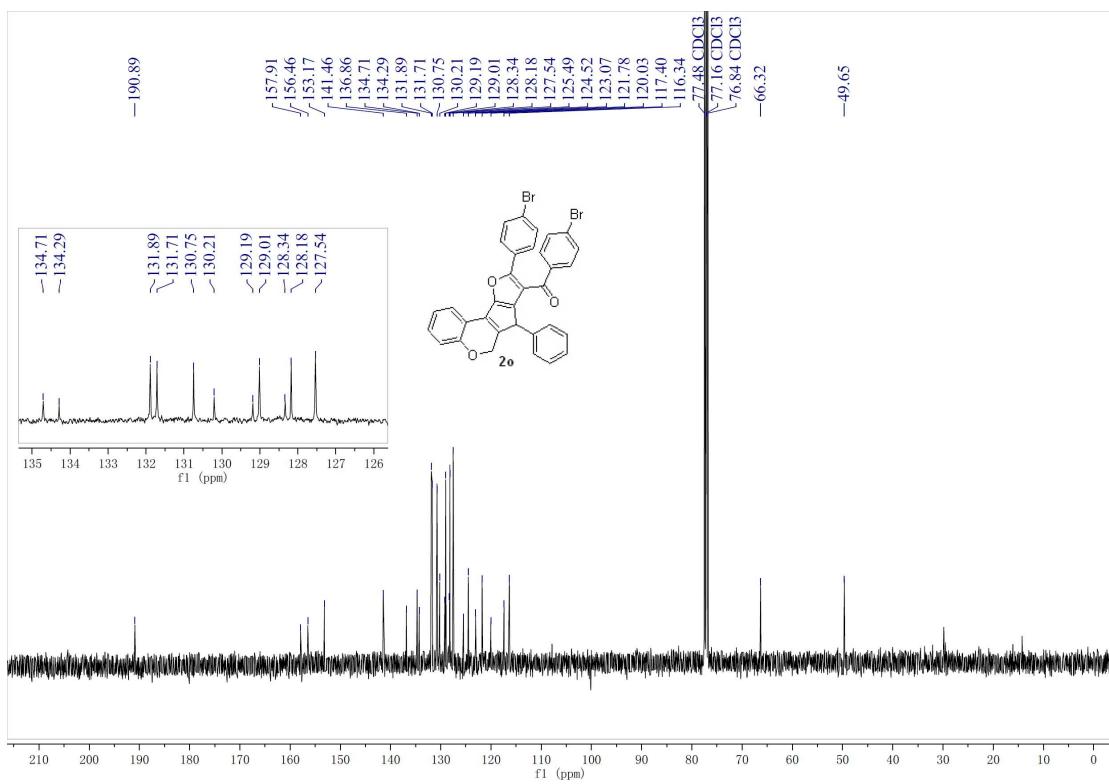
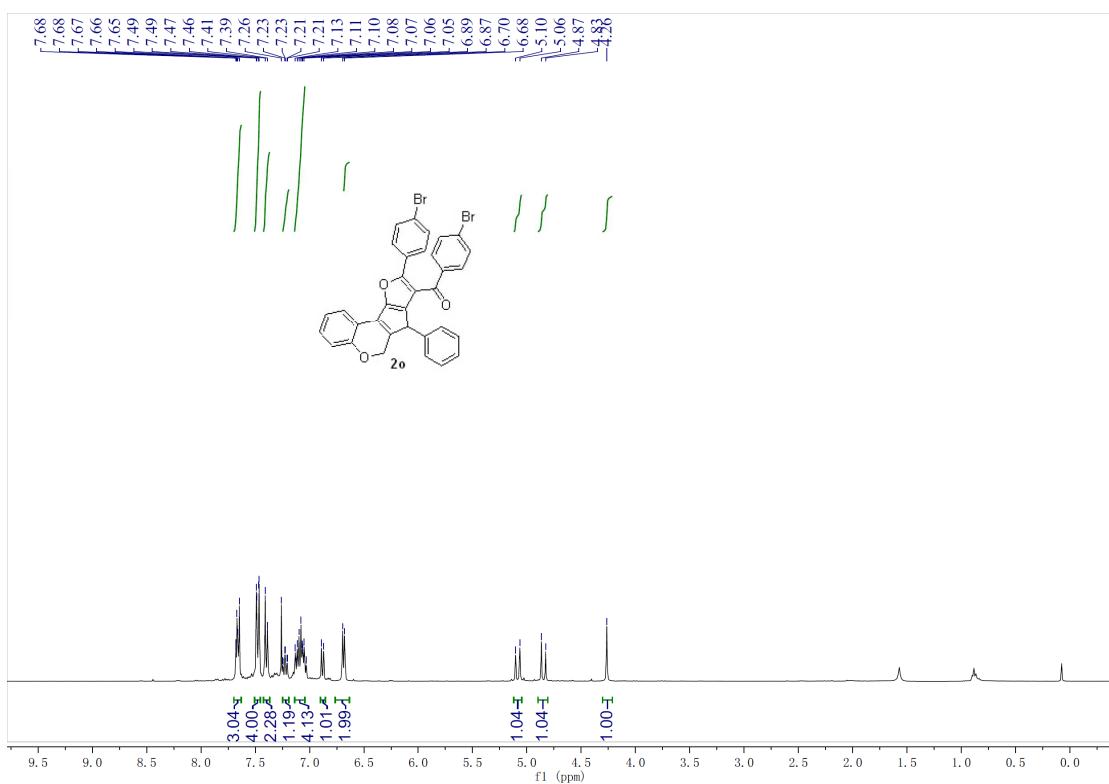


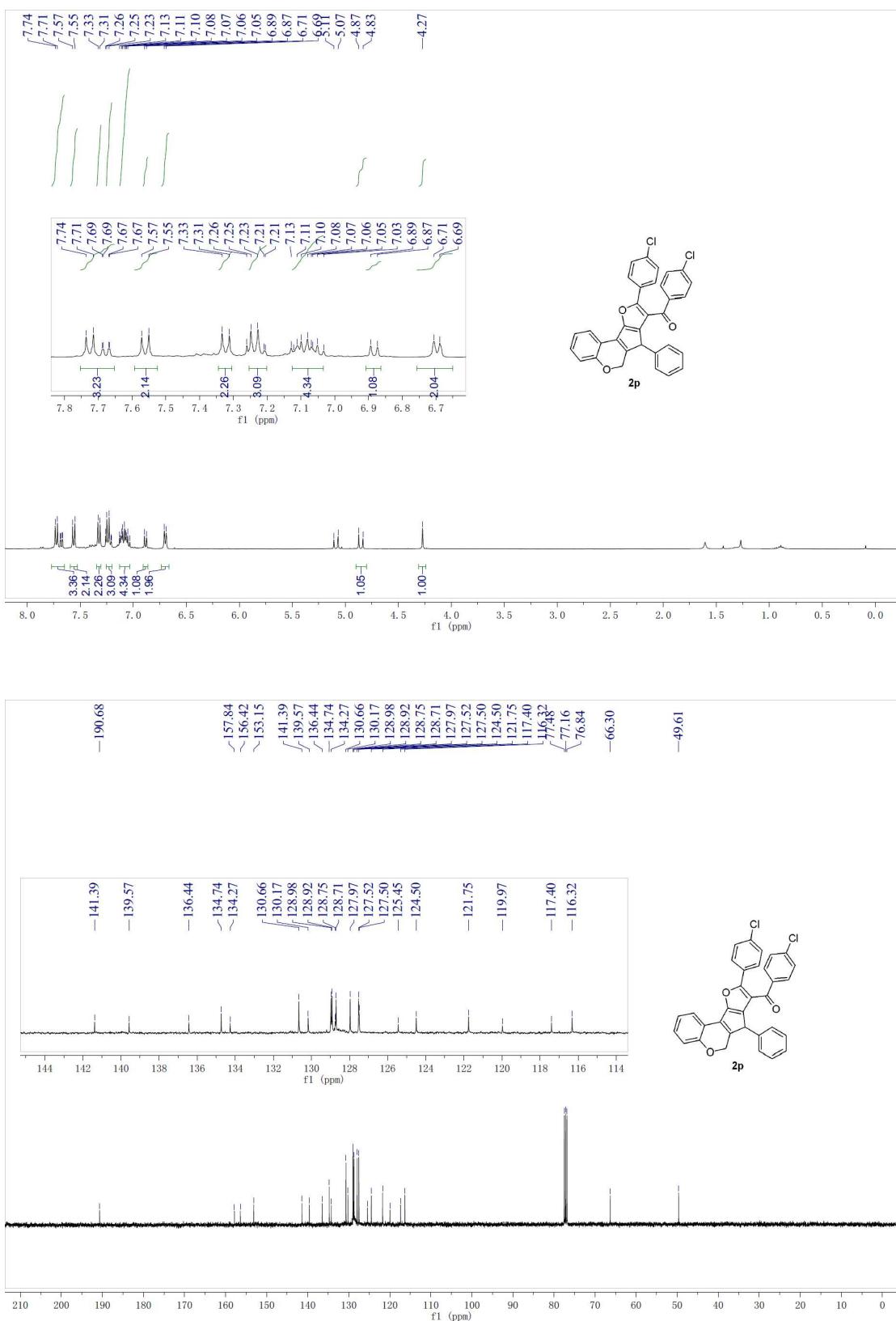


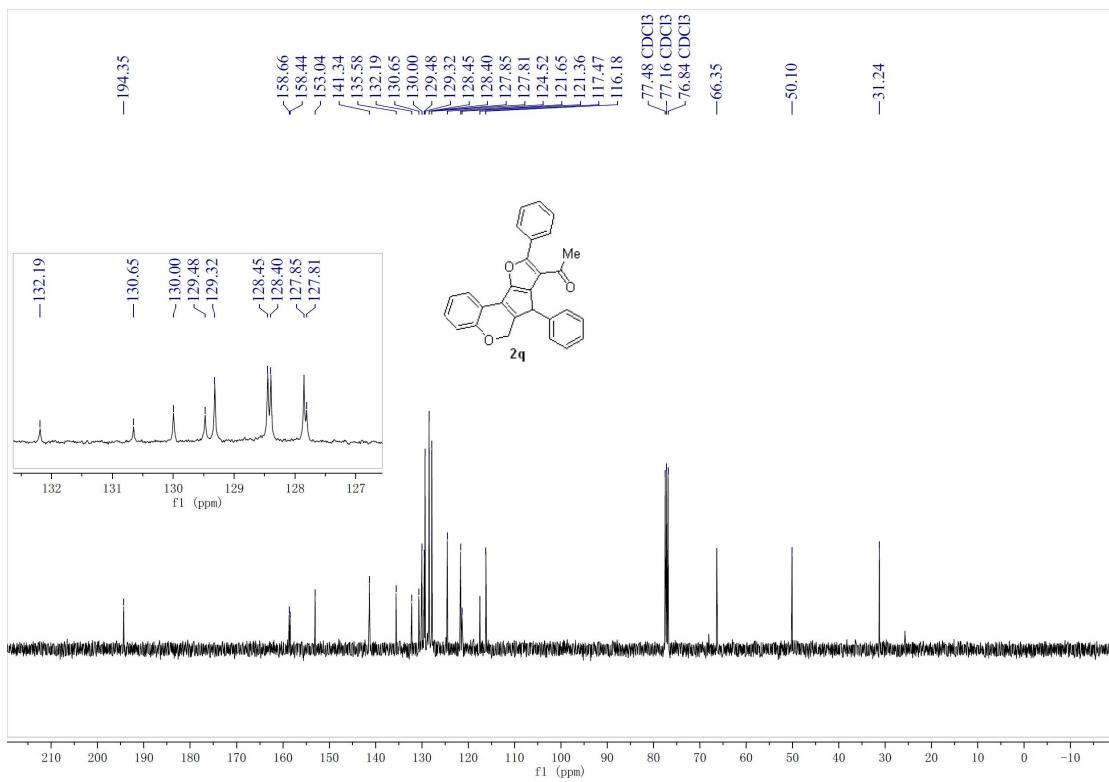
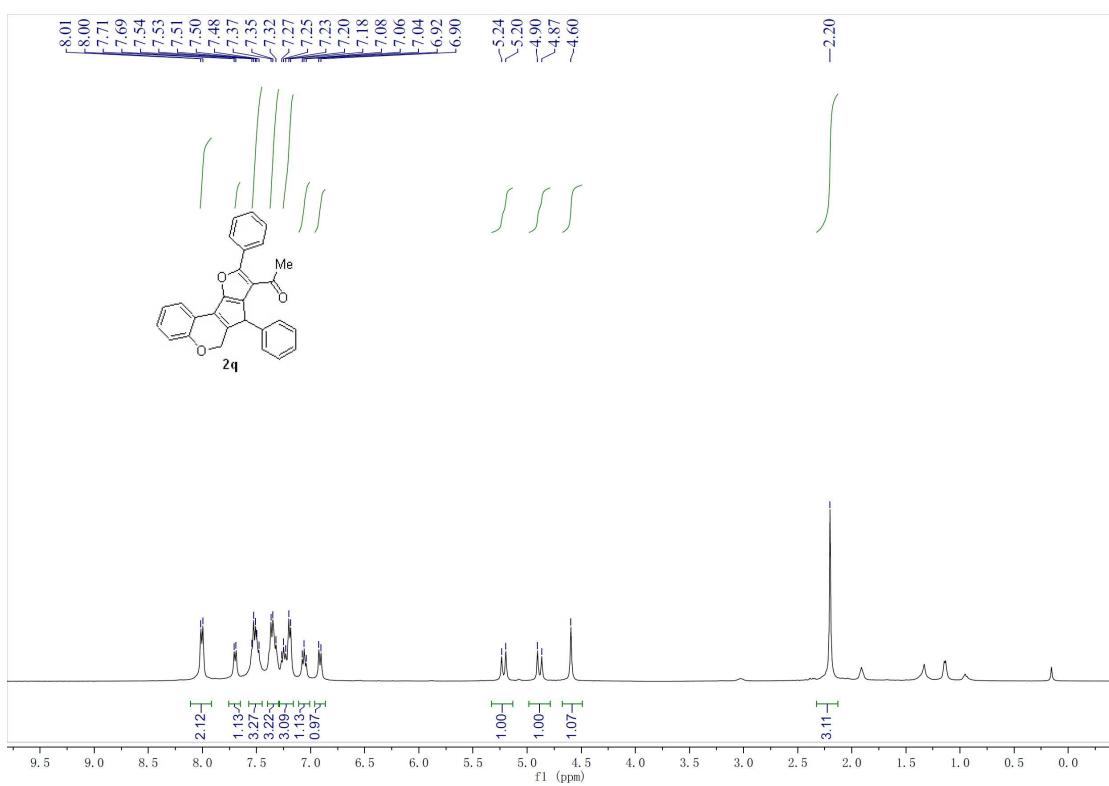


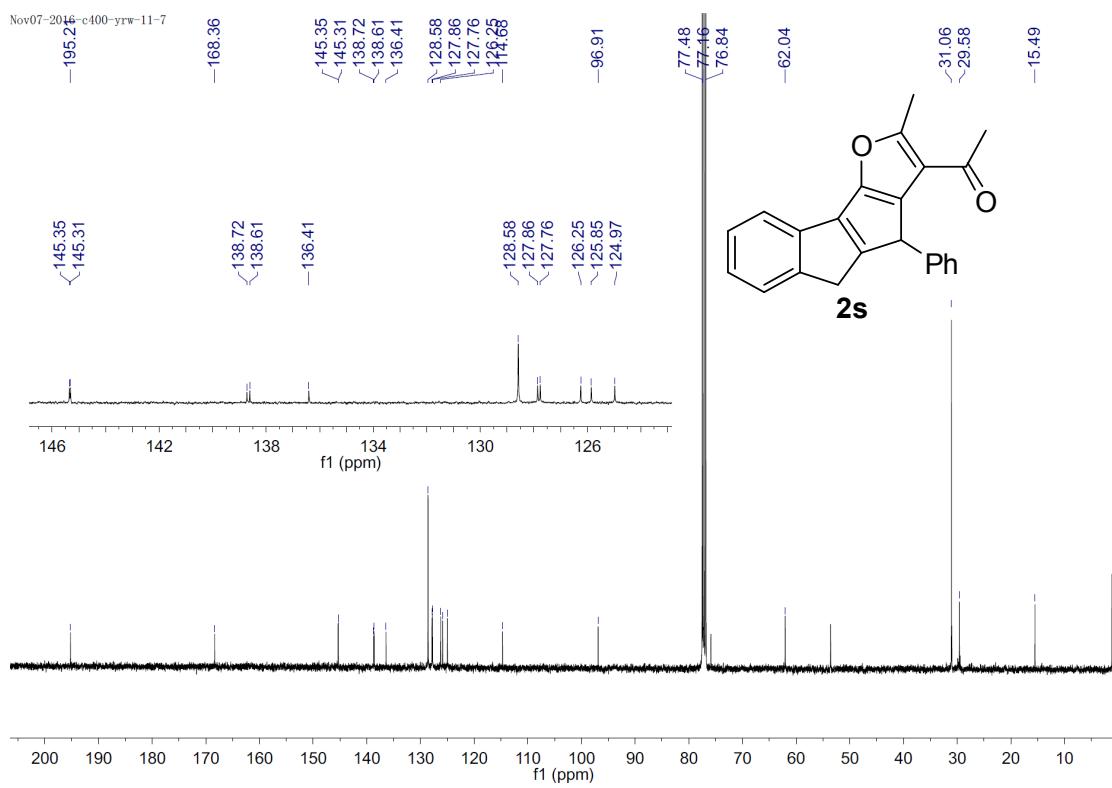
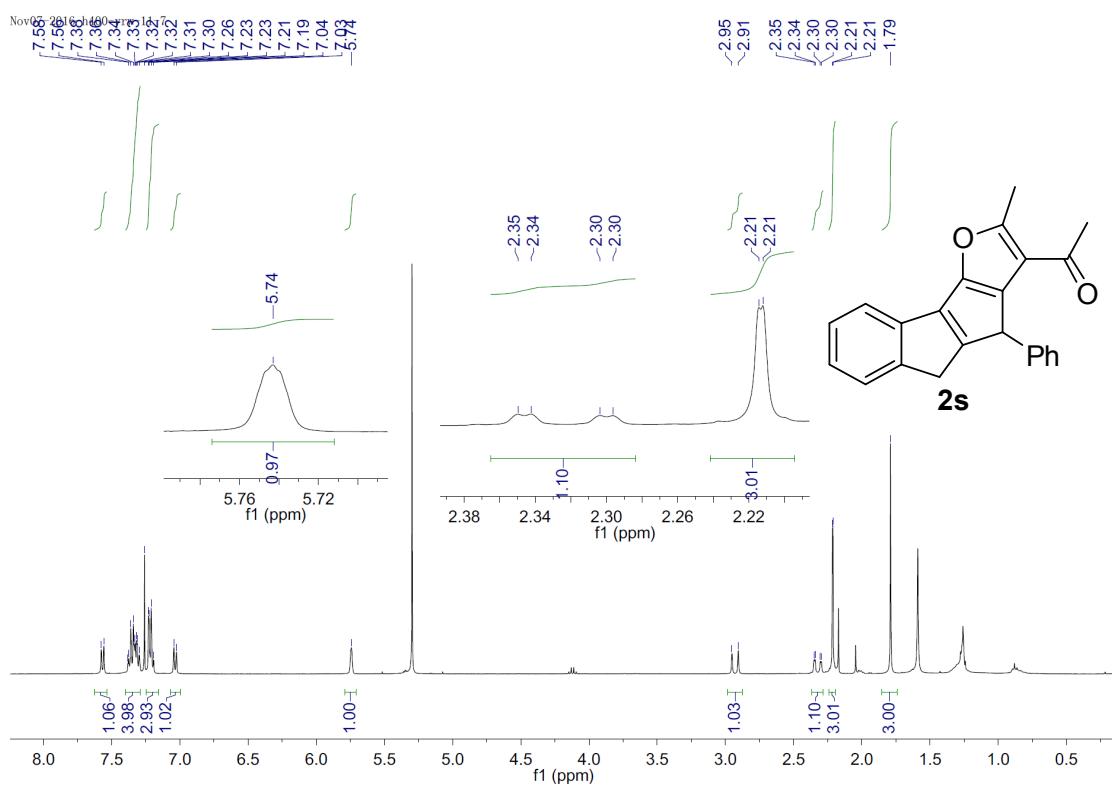


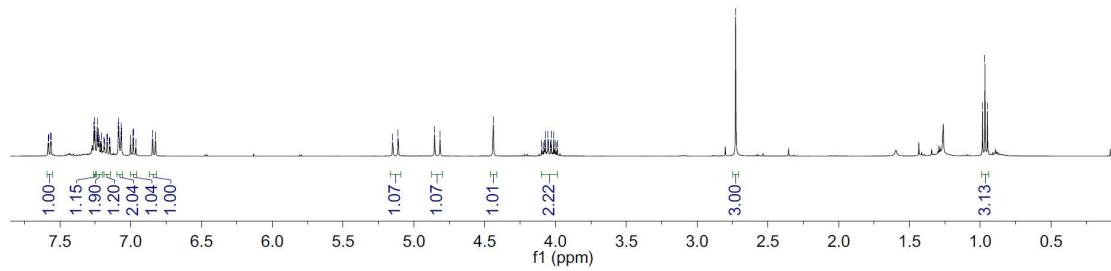
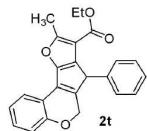
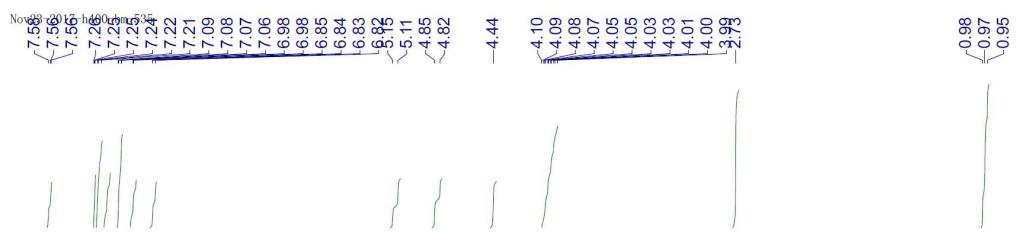








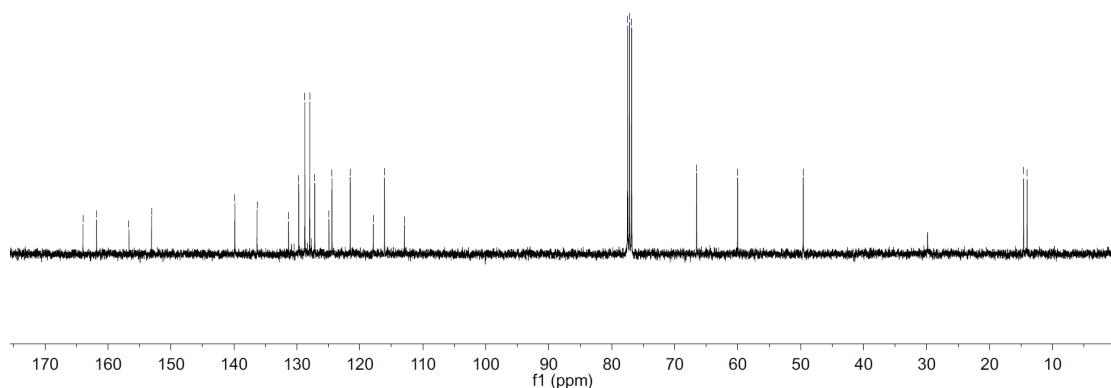
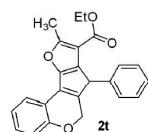


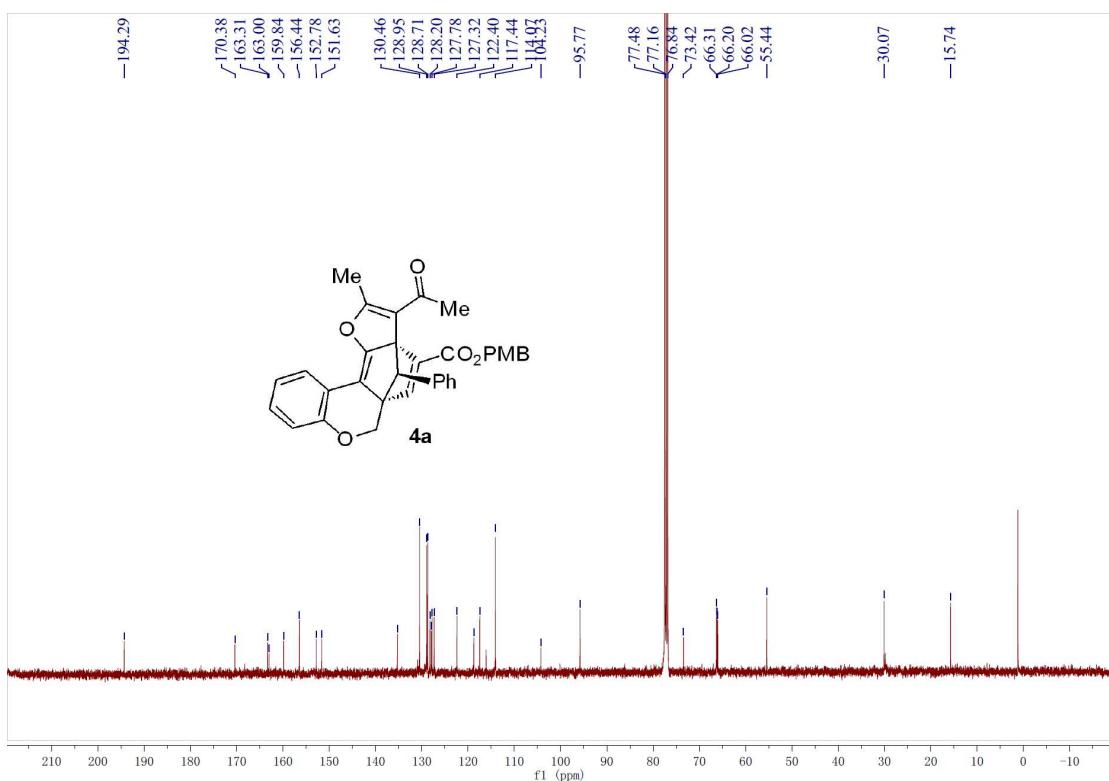
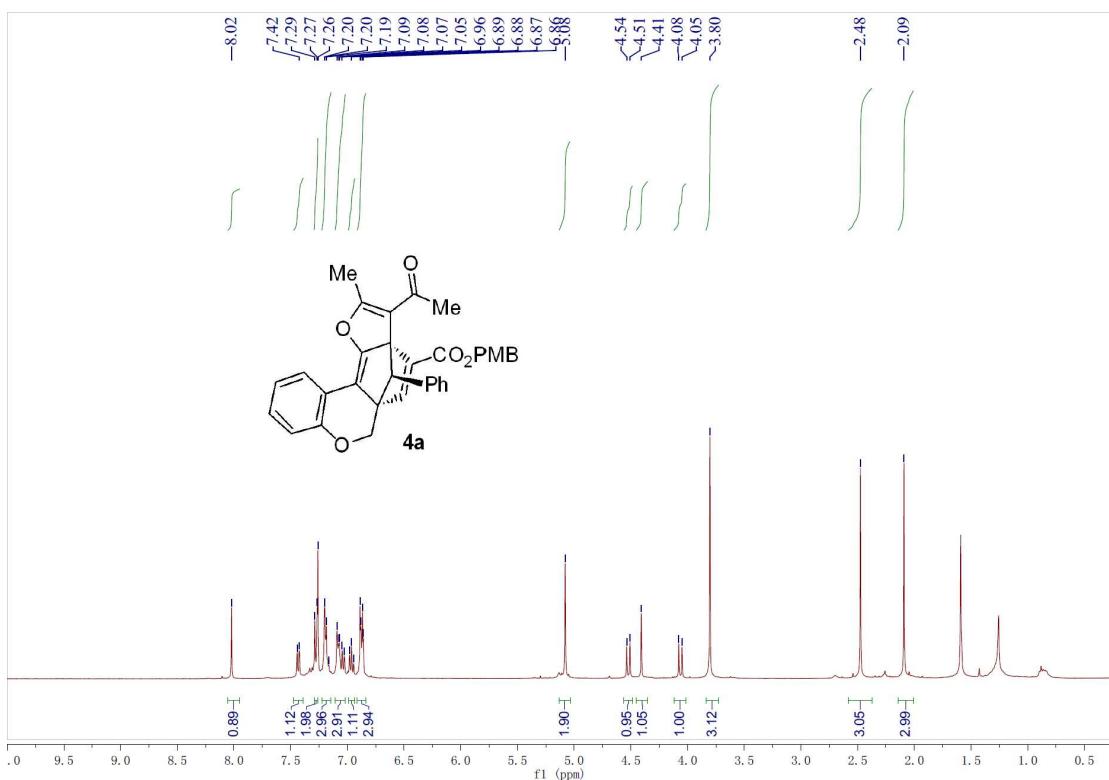


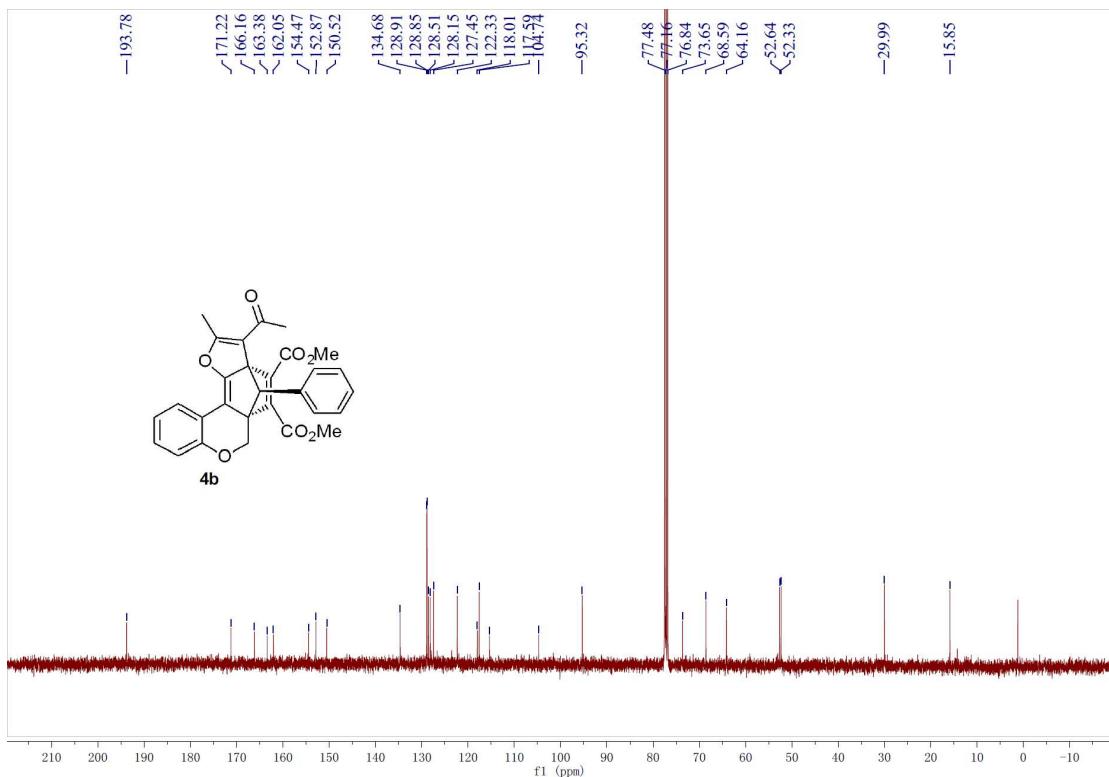
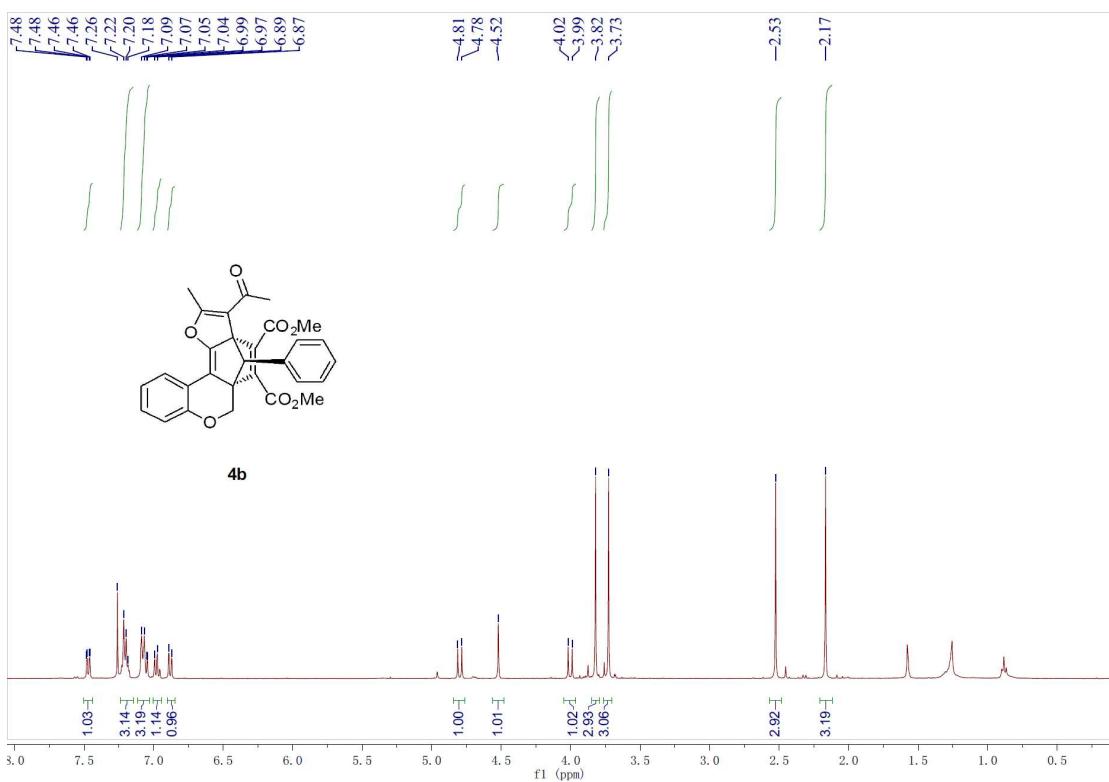
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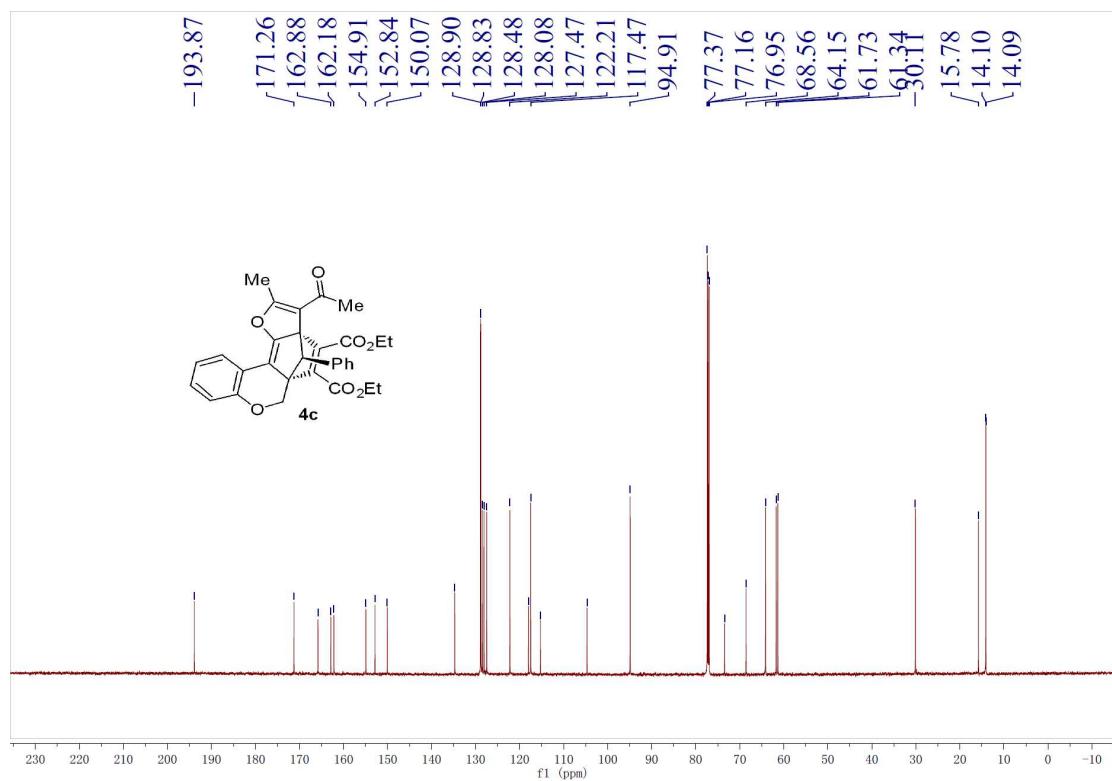
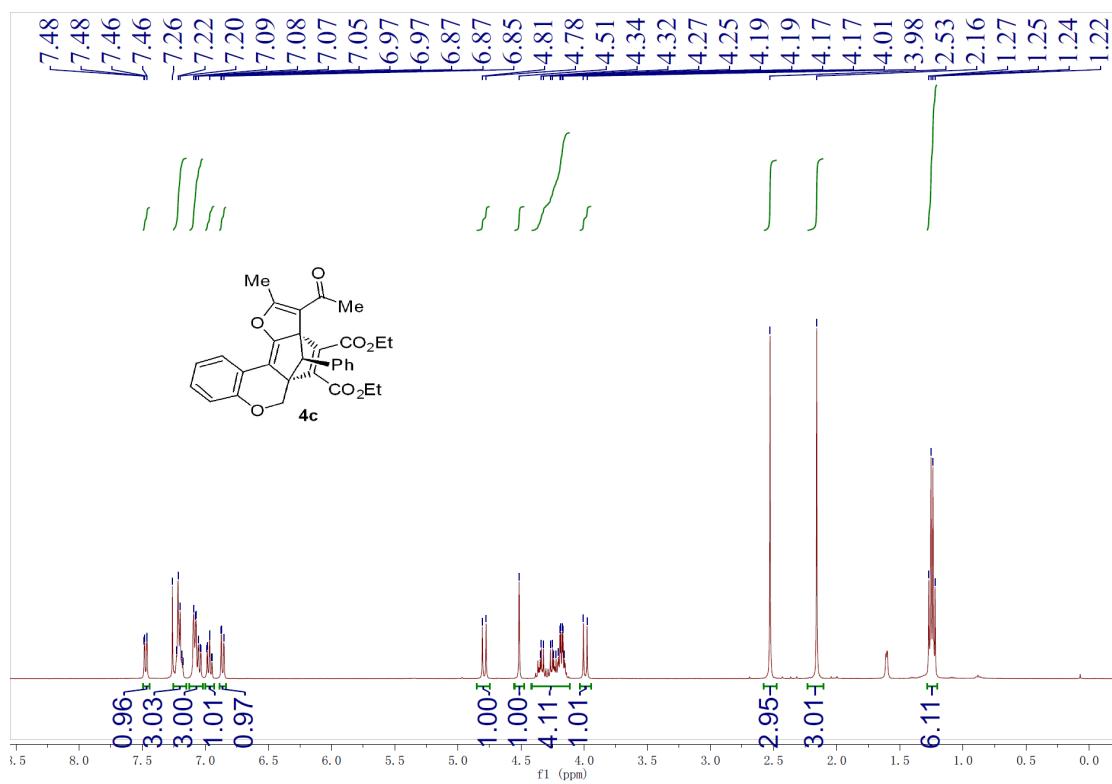
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112.90

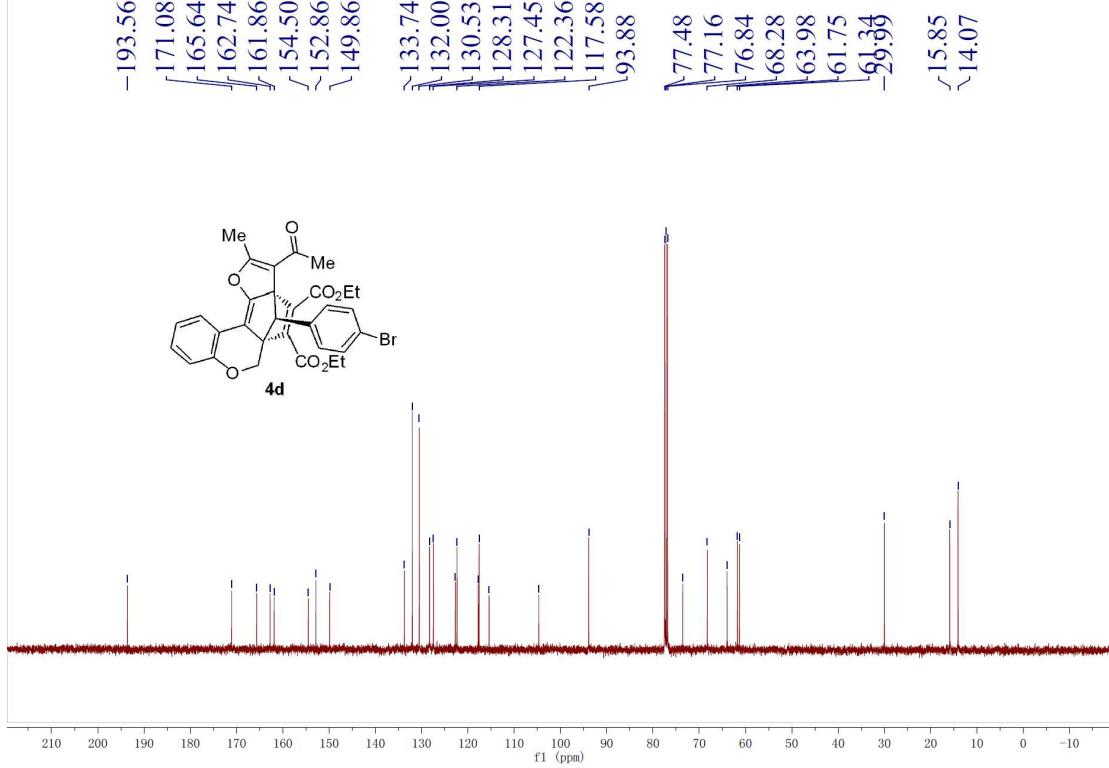
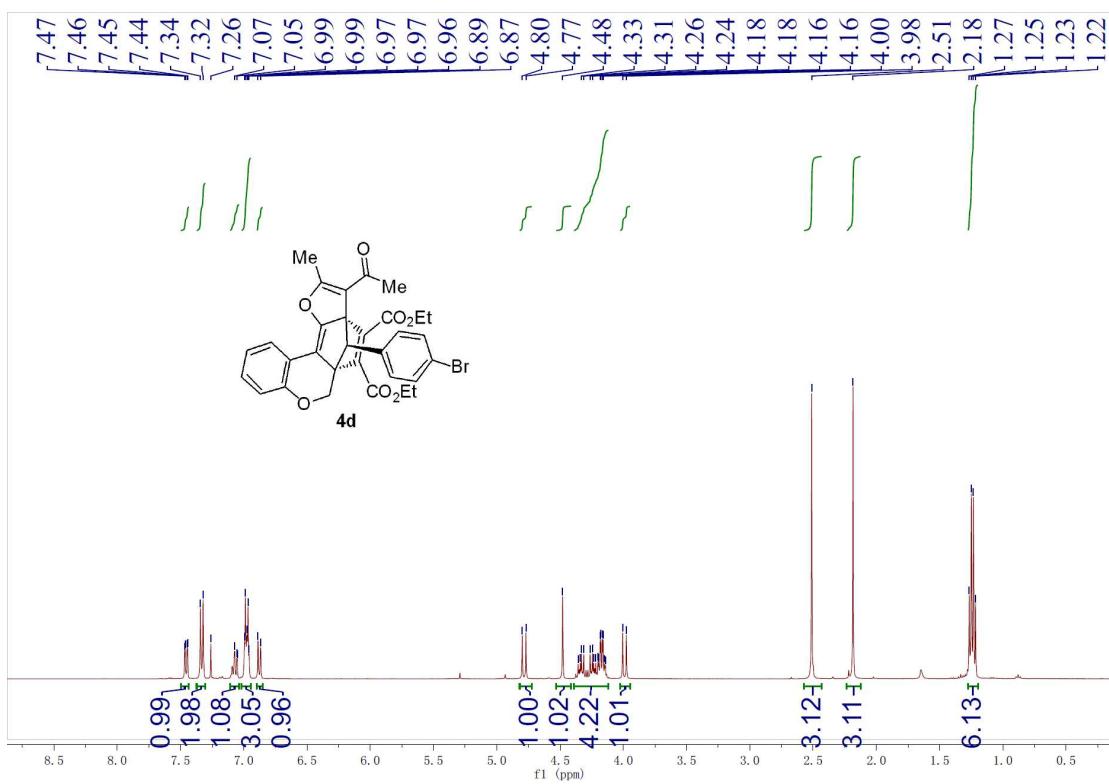
$$\begin{array}{r} 77.48 \\ \swarrow \quad \searrow \\ 77.16 & 76.84 \end{array}$$

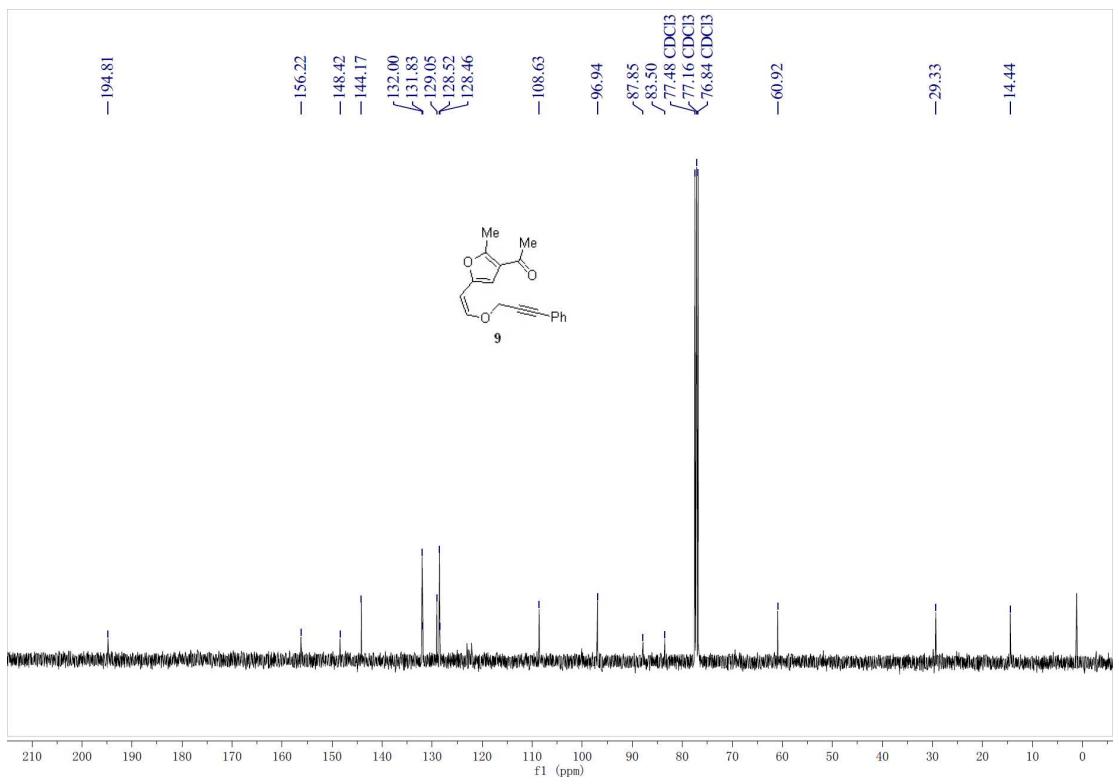
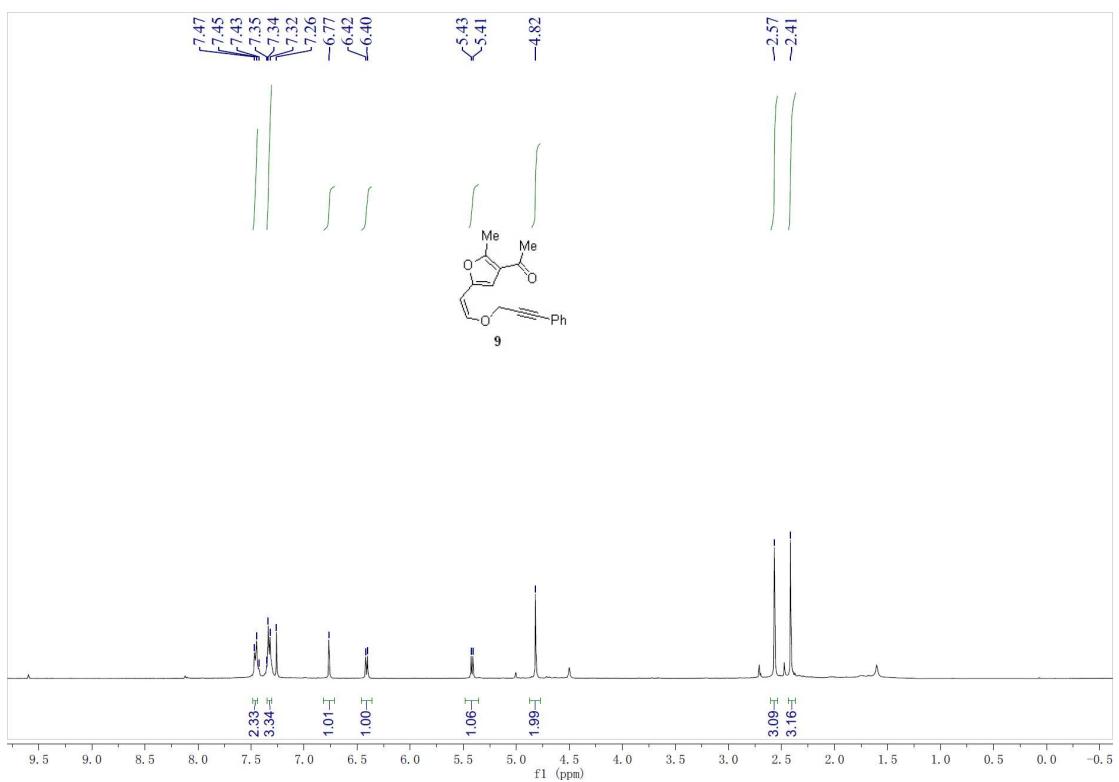




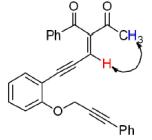
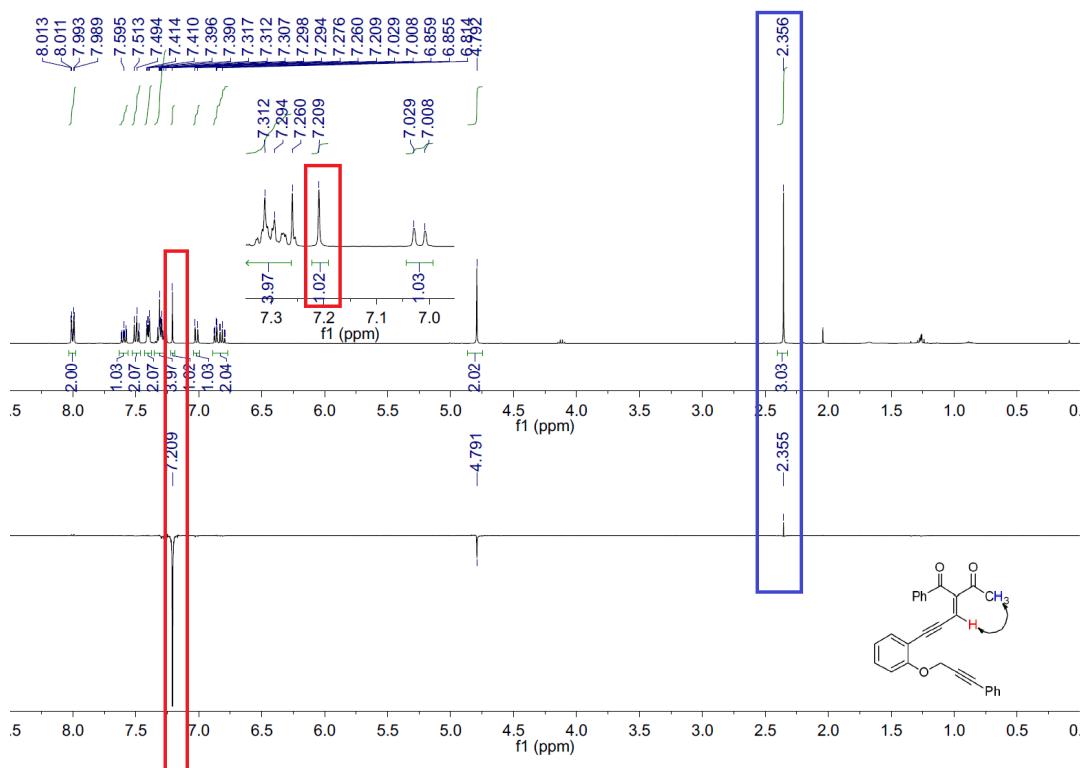
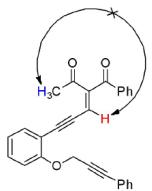
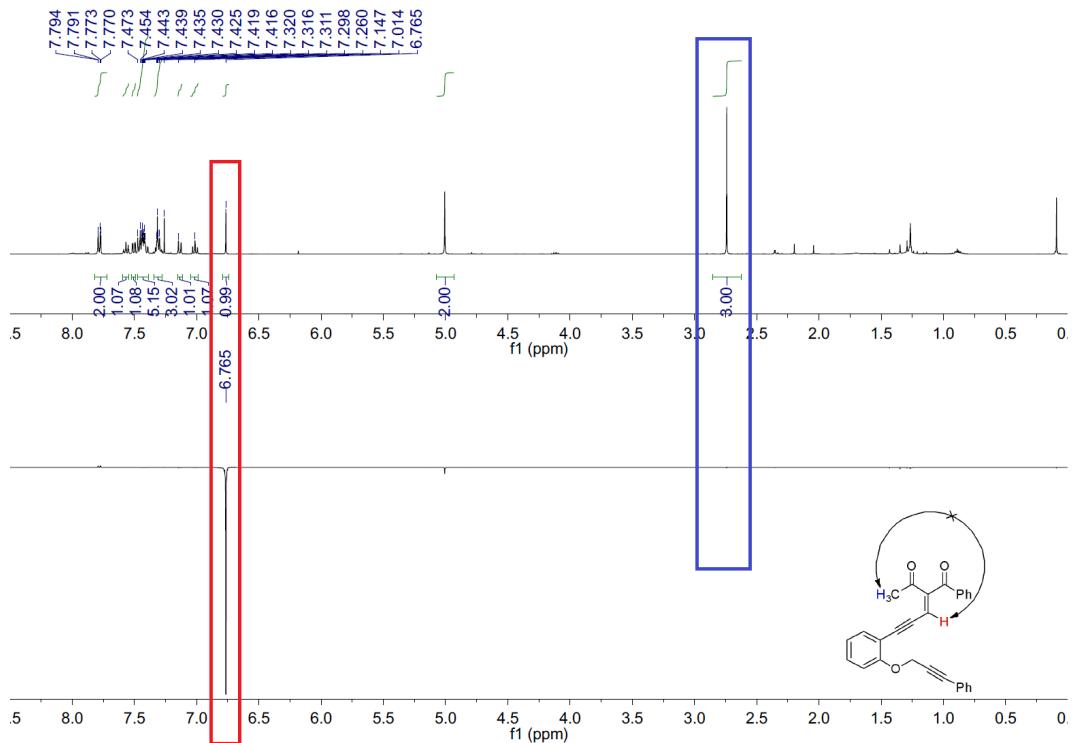




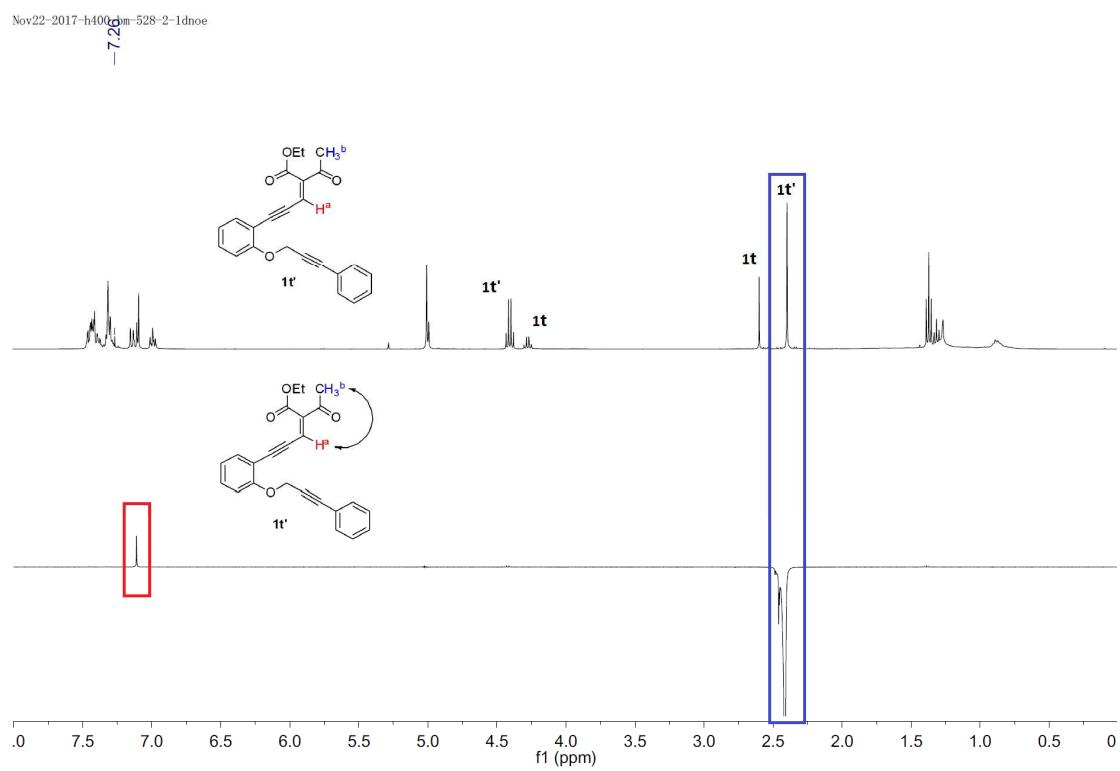
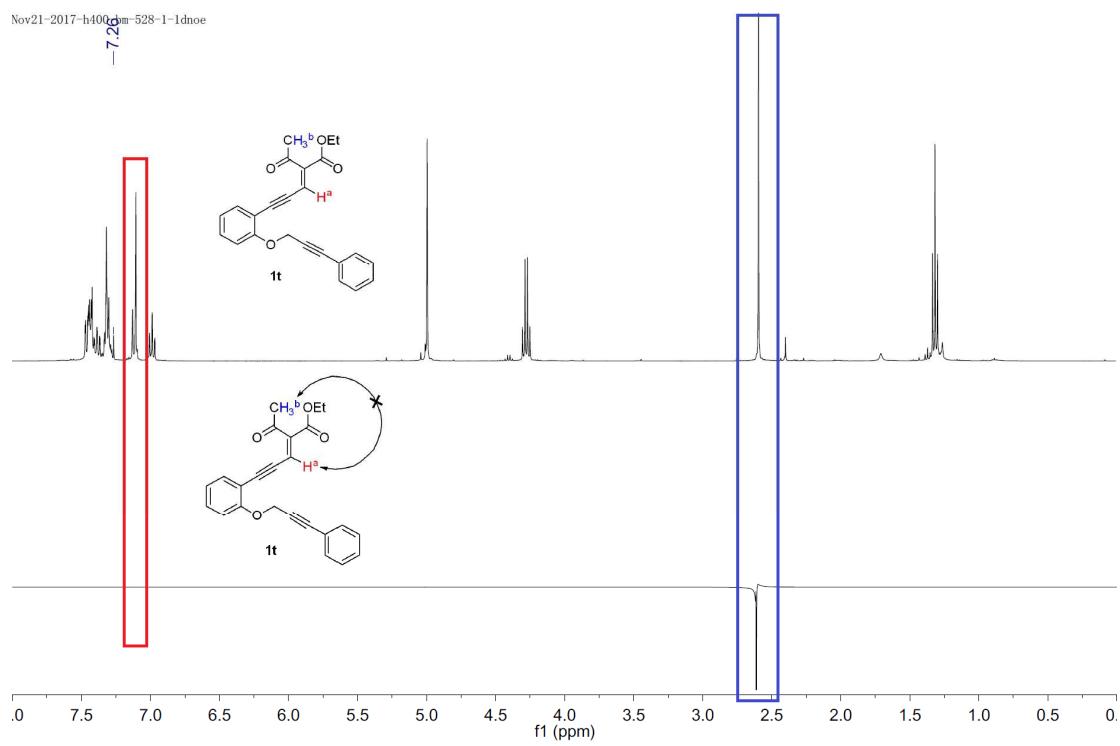




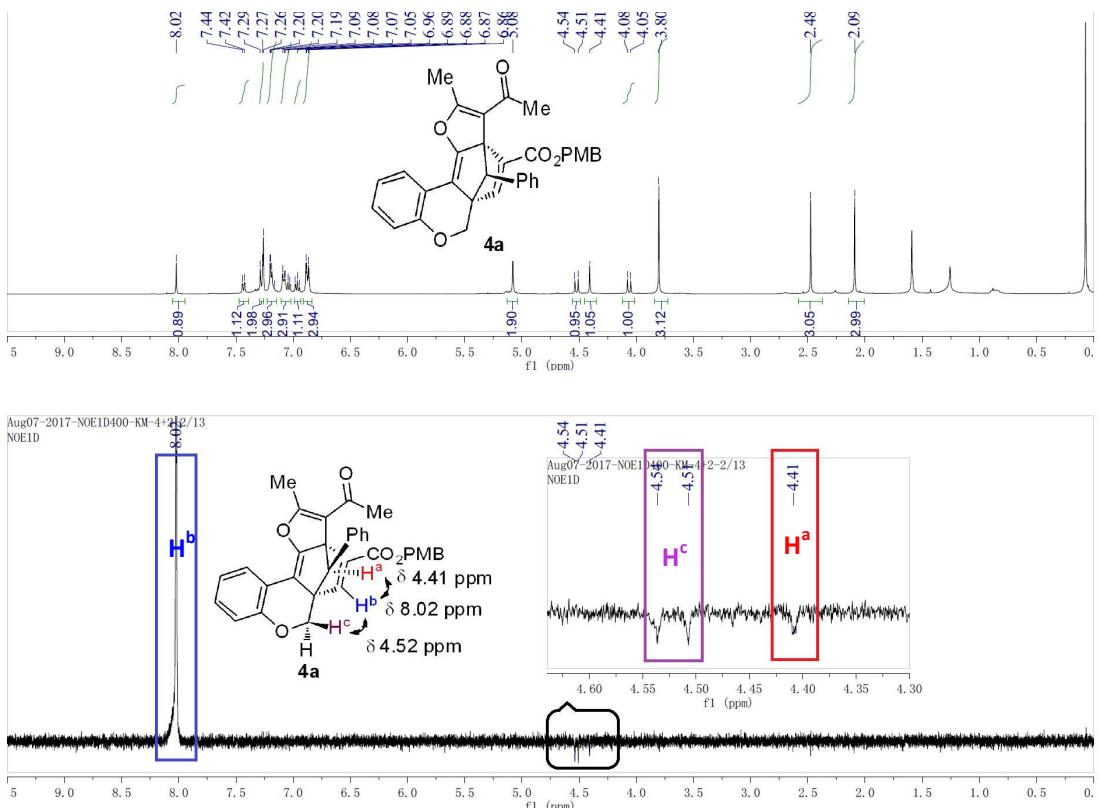
1D-NOE NMR Spectra for Z-1q and E-1q.



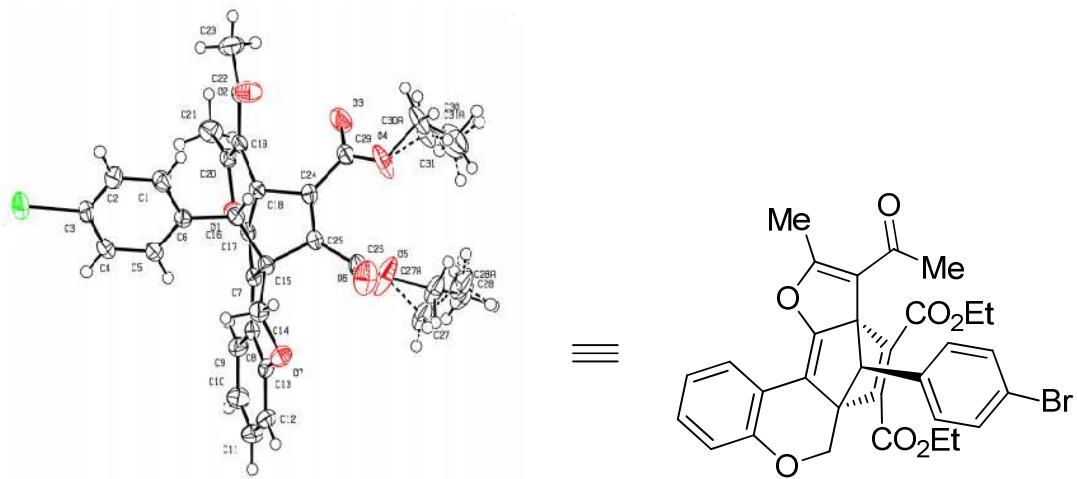
1D-NOE NMR Spectra for Z-1t and E-1t.



1D-NOE NMR Spectra for 4a.



X-ray crystal structures of 4d



Datablock: b170417a_0ma_a_a

Bond precision:	C-C = 0.0032 Å	Wavelength=0.71073
Cell:	a=20.5026 (10)	b=10.6536 (6)
	alpha=90	beta=90.321(2)
Temperature:	120 K	gamma=90
	Calculated	Reported
Volume	2674.7 (3)	2674.7 (3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C ₃₁ H ₂₇ Br O ₇	C ₃₁ H ₂₇ Br O ₇
Sum formula	C ₃₁ H ₂₇ Br O ₇	C ₃₁ H ₂₇ Br O ₇
Mr	591.43	591.44
Dx, g cm ⁻³	1.469	1.469
Z	4	4
Mu (mm ⁻¹)	1.585	1.585
F000	1216.0	1216.0
F000'	1215.44	
h,k,lmax	25,13,15	25,13,15
Nref	5510	5495
Tmin,Tmax	0.628, 0.728	0.589, 0.745
Tmin'	0.615	
Correction method=	# Reported T Limits: Tmin=0.589 Tmax=0.745	
AbsCorr =	MULTI-SCAN	
Data completeness=	0.997	Theta(max)= 26.450
R(reflections)=	0.0478 (4246)	wR2(reflections)= 0.0993 (5495)
S =	1.112	Npar= 372

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.