Supporting Information

Cobalt-Catalyzed Carbonylative Cycloaddition of Substituted Diynes to Access Complexed Polycyclic Compounds

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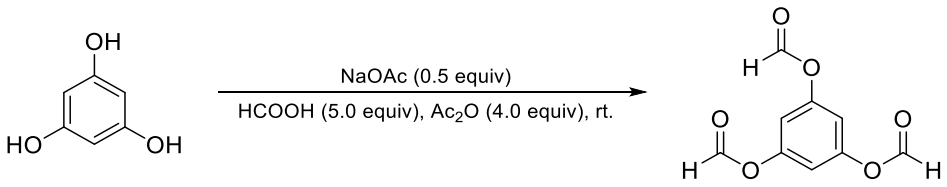
1. General experimental information

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. All commercially available reagents were used without further purification. All of the solvents were treated according to known methods. Column chromatography was performed on silica gel (200-400 mesh). ^{1}H NMR (400 MHz) chemical shifts were reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. ^{13}C NMR (100 MHz) chemical shifts were reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet), coupling constants (Hz) and integration. HRMS measurements were obtained on a TOF analyzer. IR spectra were obtained using a thermo scientific spectrum Nicolet 5700-IR Spectrometer.

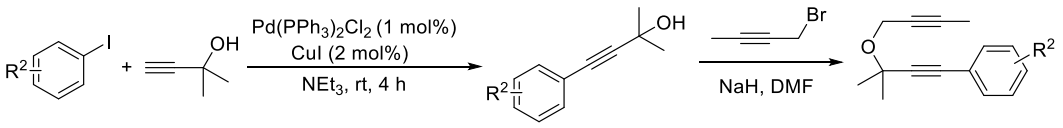
2. Preparation of benzene-1,3,5-triyl triformate (TFBen)[1]



Formic acid (8.4 mL, 222.8 mmol, 5.0 equiv) was added to acetic anhydride (16.8 mL, 178.2 mmol, 4.0 equiv) at rt. The mixture was stirred at 60 °C for 1 h and cooled to rt. The resulting solution was poured into a flask containing 1,3,5-trihydroxybenzene (5.62 g, 44.6 mmol, 1.0 equiv) and AcONa (1.83 g, 22.3 mmol, 0.5 equiv). The mixture was stirred for 4 h in a water bath and then diluted with toluene (100.0 mL), washed with H_2O (50.0 mL) twice. Keep the organic phase in fridge (2-8 °C) for overnight. Then filtered and dried in vacuo to afford the desired product benzene-1,3,5-triyl triformate (TFBen) as a white solid (5.1 g, 55%).

3. General procedure for the synthesis of diynes (1a–t)

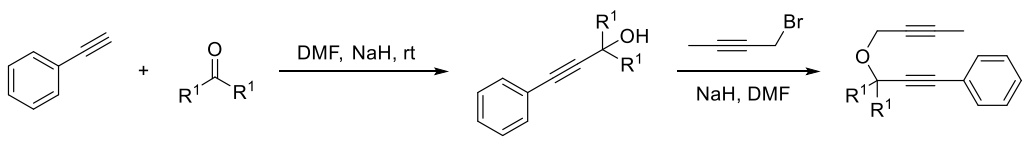
The diynes **1a-o** and **1s** were prepared according to a general procedure reported by Hajela[2] and Snyder[3].



To a solution of Et_3N (10.0 mL), $Pd(PPh_3)_2Cl_2$ (1.0 mol %), CuI (2.0 mol %) and an aryl iodide (6.0 mmol, 1.0 equiv) was added 2-methyl-3-butyn-2-ol (7.2 mmol, 1.2 equiv) under N_2 atmosphere. The mixture was allowed to stir at room temperature for 4 h. After completion of the reaction, it was filtered and the filtrate quenched with saturated NH_4Cl solution and extracted with EtOAc (3 × 15.0 mL). The combined organic layers were washed with brine (10.0 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. The mixture was purified by silica gel column chromatography (petroleum ether / ethyl acetate = 10:1) to give a propargyl alcohol.

To an oven dried round bottom flask was added NaH (60% in mineral oil, 1.2 equiv), which was then purged with argon. Anhydrous DMF (10.0 mL) was then added and the suspension cooled to 0 °C. A propargyl alcohol (4.0 mmol, 1.0 equiv) was added dropwise with stirring, and stirring continued at 0 °C for 1 h, followed by the addition of 1-bromobut-2-yne (4.8 mmol, 1.2 equiv). The solution was stirred at 0 °C for another 30 min, then allowed to warm to rt. After 14 h, the reaction was quenched by the addition of water (20.0 mL), and the mixture poured into a separatory funnel containing brine (50.0 mL). The organic layer was separated, and the aqueous layer extracted with DCM (2 × 15.0 mL). The combined organic layers were dried over Na_2SO_4, filtered, and the solvent was removed in vacuo. The mixture was purified by silica gel column chromatography (petroleum ether / ethyl acetate = 10:1) to give a diyne.

The diynes **1p-r** were prepared according to a general procedure reported by Wu[4] and Snyder[3].

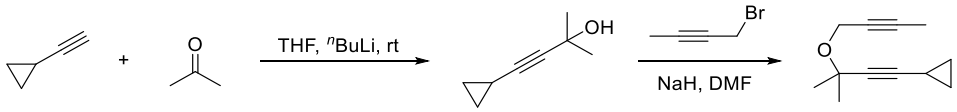


To a 50 mL round-bottom flask was added an alkyne (6 mmol, 1.0 equiv) in DMF (10.0 mL).

The mixture was cooled to 0 °C and stirred for 10 min. Then sodium hydride (60% in mineral oil, 1.2 equiv) was added and the reaction continued at 0 °C for 4 h. A ketone (7.2 mmol, 1.2 equiv) was added and the system was warmed to room temperature for 10 h. After the reaction was completed, the reaction mixture was diluted with saturated sodium bicarbonate solution (30.0 mL) and extracted with ethyl acetate (20.0 mL) three times. The combined organic layers were dried over Na_2SO_4, filtered, and the solvent removed in vacuo. The mixture was purified by silica gel column chromatography (petroleum ether / ethyl acetate = 10:1) to obtain a propargyl alcohol.

To an oven dried round bottom flask was added NaH (60% in mineral oil, 1.2 equiv), which was then purged with argon. Anhydrous DMF (10.0 mL) was then added and the suspension cooled to 0 °C. A propargyl alcohol (4.0 mmol) was added dropwise with stirring, and stirring continued at 0 °C for 1 h, followed by the addition of 1-bromobut-2-yne (4.8 mmol, 1.2 equiv). The solution was stirred at 0 °C for another 30 min, then allowed to warm to rt. After 14 h, the reaction was quenched by the addition of water (20.0 mL), and the mixture poured into a separatory funnel containing brine (50.0 mL). The organic layer was separated, and the aqueous layer extracted with DCM (2 × 15.0 mL). The combined organic layers were dried over Na_2SO_4, filtered, and the solvent was removed in vacuo. The mixture was purified by silica gel column chromatography (petroleum ether / ethyl acetate = 10:1) to give a diyne.

The diyne **1t** was prepared according to a general procedure reported by Denes[5] and Snyder[3].

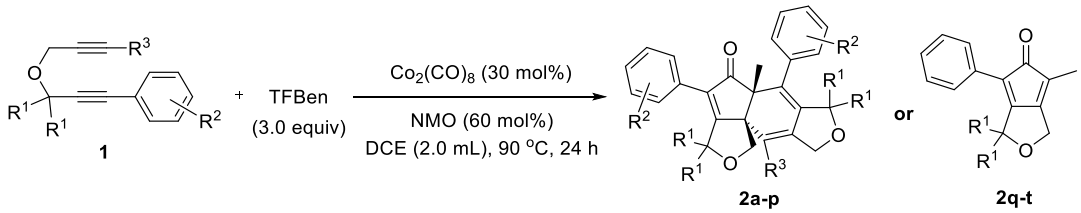


To a solution of ethynylcyclopropane (6.0 mmol, 1.0 equiv) in THF (20.0 mL) at -78 °C, was added ^{n}BuLi (3.0 mL, 2.4 M / hexanes). The solution was warmed to -15 °C and stirred for 1 h and then, after it was recooled to -78 °C, a solution of acetone (7.2 mmol, 1.2 equiv) was added via cannula at -78 °C. After completion of the reaction (TLC monitoring), the solution was allowed to reach -30 °C and quenched with a saturated aqueous solution of NH_4Cl. The mixture was diluted with Et_2O and the aqueous layer was extracted with Et_2O. The organic phase was dried over Na_2SO_4, filtered and concentrated in vacuo. The mixture was purified by silica gel column chromatography (petroleum ether / ethyl acetate = 10:1) to obtain a propargyl alcohol.

To an oven dried round bottom flask was added NaH (60% in mineral oil, 1.2 equiv), which

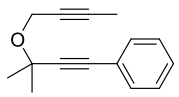
was then purged with argon. Anhydrous DMF (10.0 mL) was then added and the suspension cooled to 0 °C. A propargyl alcohol (4.0 mmol, 1.0 equiv) was added dropwise with stirring, and stirring continued at 0 °C for 1 h, followed by the addition of 1-bromobut-2-yne (4.8 mmol, 1.2 equiv). The solution was stirred at 0 °C for another 30 min, then allowed to warm to rt. After 14 h, the reaction was quenched by the addition of water (20.0 mL), and the mixture poured into a separatory funnel containing brine (50.0 mL). The organic layer was separated, and the aqueous layer extracted with DCM (2 × 15.0 mL). The combined organic layers were dried over Na_2SO_4, filtered, and the solvent was removed in vacuo. The mixture was purified by silica gel column chromatography (petroleum ether / ethyl acetate = 10:1) to give a diyne.

4. General procedure for the synthesis of tetracyclic products (2a-p) and Pauson-Khand products (2q–t)

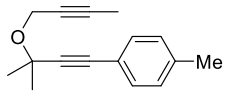


Diyne **1** (0.5 mmol, 1.0 equiv), $Co_2(CO)_8$ (51.3 mg, 0.15 mmol, 30 mol %), NMO (35.1 mg, 0.3 mmol, 60 mol %) and a 1.5 mL vial containing TFBen (315.2 mg, 1.5 mmol, 3.0 equiv) were added to an oven-dried tube (15.0 mL) which was then placed under vacuum and refilled with nitrogen three times. Then DCE (2.0 mL) were added into the tube via syringe. The tube was sealed and stirred at 90 °C for 24 h. Upon the reaction was completed, the resulting mixture was concentrated under vacuum and purified by silica gel column using chromatography (petroleum ether / ethyl acetate = 20:1) to obtain the product **2**.

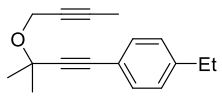
5. Characterization data of compounds 1a-t



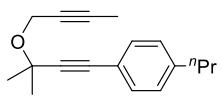
(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)benzene (1a). Yellow oil in 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.41 (m, 2H), 7.31 – 7.29 (m, 3H), 4.31 (q, J = 2.3 Hz, 2H), 1.85 (t, J = 2.4 Hz, 3H), 1.58 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 128.3, 122.7, 90.5, 85.0, 81.9, 76.1, 71.3, 53.2, 28.9, 3.9.



1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-4-methylbenzene (1b). Yellow oil in 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 4.27 (q, J = 2.3 Hz, 2H), 2.29 (s, 3H), 1.81 (t, J = 2.4 Hz, 3H), 1.55 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 131.4, 128.8, 119.4, 89.5, 84.8, 81.4, 76.0, 71.0, 52.8, 28.7, 21.2, 3.5.

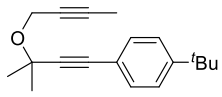


1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-4-ethylbenzene (1c). Yellow oil in 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 4.30 (q, J = 2.3 Hz, 2H), 2.61 (q, J = 7.6 Hz, 2H), 1.83 (t, J = 2.4 Hz, 3H), 1.57 (s, 6H), 1.20 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 131.6, 127.7, 119.7, 89.6, 85.0, 81.6, 76.0, 71.1, 52.9, 28.8, 28.7, 15.3, 3.7.

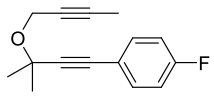


1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-4-propylbenzene (1d). Yellow oil in 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.1 Hz, 2H), 4.29 (q, J = 2.3 Hz, 2H), 2.58 – 2.54 (m, 2H), 1.84 (t, J = 2.3 Hz, 3H), 1.61 (dd, J = 15.1, 7.5 Hz, 2H), 1.57

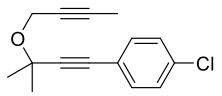
(s, 6H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 131.7, 128.5, 119.9, 89.8, 85.1, 81.8, 76.1, 71.4, 53.1, 38.0, 29.0, 24.5, 13.8, 3.9.



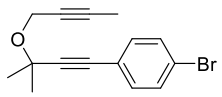
1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-4-(tert-butyl)benzene (1e). Yellow oil in 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 4.26 (q, J = 2.2 Hz, 2H), 1.79 (t, J = 2.3 Hz, 3H), 1.54 (s, 6H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 131.2, 124.9, 119.4, 89.5, 84.7, 81.2, 75.9, 70.9, 52.7, 34.4, 30.9, 28.7, 3.4.



1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-4-fluorobenzene (1f). Yellow oil in 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 6.91 – 6.87 (m, 2H), 4.18 (q, J = 2.3 Hz, 2H), 1.74 (t, J = 2.4 Hz, 3H), 1.47 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, J = 249.5 Hz, 1C), 133.3 (d, J = 8.3 Hz, 1C), 118.5 (d, J = 3.4 Hz, 1C), 115.3 (d, J = 22.1 Hz, 1C), 90.0, 83.5, 81.4, 75.8, 70.9, 52.8, 28.5, 3.4.

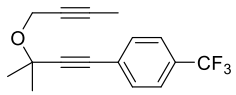


1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-4-chlorobenzene (1g). Yellow oil in 77% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 4.25 (q, J = 2.2 Hz, 2H), 1.81 (t, J = 2.3 Hz, 3H), 1.53 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3, 132.9, 128.5, 121.1, 91.5, 83.7, 81.7, 75.9, 71.1, 53.1, 28.7, 3.7.

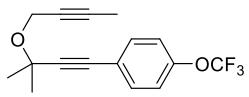


1-bromo-4-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)benzene (1h). Yellow solid in 73% yield, mp 41.0 – 42.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.6

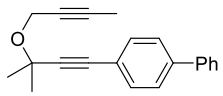
Hz, 2H), 4.32 (q, J = 2.3 Hz, 2H), 1.90 (t, J = 2.4 Hz, 3H), 1.61 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.3, 131.6, 122.7, 121.7, 91.8, 83.9, 82.1, 75.9, 71.3, 53.2, 28.8, 3.9.



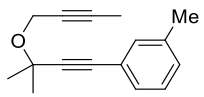
1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-4-(trifluoromethyl)benzene (1i). Yellow oil in 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (q, J = 8.4 Hz, 4H), 4.28 (q, J = 2.3 Hz, 2H), 1.84 (t, J = 2.4 Hz, 3H), 1.58 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.0, 130.2 (q, J = 32.7 Hz, 1C), 126.5, 125.3 (q, J = 3.7 Hz, 1C), 121.3 (q, J = 272.3 Hz, 1C), 93.1, 83.6, 82.1, 75.8, 71.2, 53.3, 28.7, 3.8.



1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-4-(trifluoromethoxy)benzene (1j). Yellow oil in 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 4.27 (q, J = 2.3 Hz, 2H), 1.83 (t, J = 2.4 Hz, 3H), 1.56 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 133.3, 121.5, 120.9, 120.4 (q, J = 257.7 Hz, 1C), 91.4, 83.5, 82.0, 75.9, 71.2, 53.2, 28.8, 3.8.

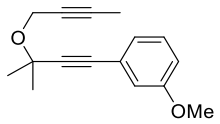


4-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-1,1'-biphenyl (1k). Yellow solid in 77% yield, mp 69.7 – 70.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 2H), 7.53 (dd, J = 19.8, 8.4 Hz, 4H), 7.45 (t, J = 7.5 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H), 4.35 (dd, J = 4.6, 2.2 Hz, 2H), 1.88 (t, J = 2.3 Hz, 3H), 1.62 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 140.3, 132.2, 128.9, 127.7, 127.1, 127.0, 121.6, 91.1, 84.8, 81.9, 76.0, 71.4, 57.0, 53.2, 28.9, 3.9.

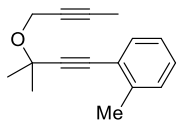


1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-3-methylbenzene (1l). Yellow oil in 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 1H), 7.22 (d, J = 7.7 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.11

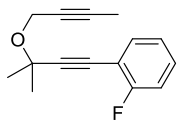
(d, J = 7.4 Hz, 1H), 4.30 (q, J = 2.3 Hz, 2H), 2.31 (s, 3H), 1.85 (t, J = 2.4 Hz, 3H), 1.58 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 132.3, 129.2, 128.7, 128.2, 122.4, 90.0, 85.1, 81.7, 76.0, 71.2, 53.0, 28.8, 21.2, 3.8.



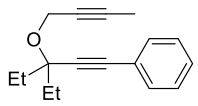
1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-3-methoxybenzene (1m). Yellow oil in 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, J = 8.0 Hz, 1H), 6.99 (d, J = 7.6 Hz, 1H), 6.92 (dd, J = 2.4, 1.4 Hz, 1H), 6.83 (ddd, J = 8.3, 2.6, 0.7 Hz, 1H), 4.27 (q, J = 2.3 Hz, 2H), 3.75 (s, 3H), 1.82 (t, J = 2.4 Hz, 3H), 1.55 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 129.3, 124.2, 123.5, 116.4, 114.9, 90.2, 84.8, 81.7, 75.9, 71.2, 55.2, 53.0, 28.8, 3.7.



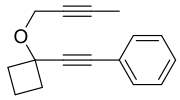
1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-2-methylbenzene (1n). Yellow oil in 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.5 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.14 – 7.11 (m, 1H), 4.33 (d, J = 2.3 Hz, 2H), 2.42 (s, 3H), 1.86 (dd, J = 2.9, 1.7 Hz, 3H), 1.609 (s, 3H), 1.606 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 132.0, 129.5, 128.4, 125.6, 122.5, 94.6, 83.9, 81.9, 76.0, 71.5, 53.2, 29.1, 20.8, 3.9.



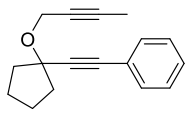
1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-2-fluorobenzene (1o). Yellow oil in 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (td, J = 7.3, 1.7 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.09 – 7.02 (m, 2H), 4.31 (q, J = 2.3 Hz, 2H), 1.84 (t, J = 2.4 Hz, 3H), 1.58 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J = 251.6 Hz, 1C), 133.5, 130.1 (d, J = 7.9 Hz, 1C), 123.9 (d, J = 3.7 Hz, 1C), 115.5 (d, J = 20.9 Hz, 1C), 111.2 (d, J = 15.8 Hz, 1C), 95.8 (d, J = 3.3 Hz, 1C), 81.9, 78.4, 75.9, 71.3, 53.2, 28.8, 3.8.



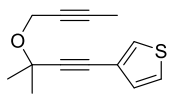
(3-(but-2-yn-1-yloxy)-3-ethylpent-1-yn-1-yl)benzene (1p). Yellow oil in 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.31 – 7.28 (m, 3H), 4.28 (q, J = 2.3 Hz, 2H), 1.84 (t, J = 2.4 Hz, 3H), 1.80 (q, J = 7.4 Hz, 4H), 1.02 (t, J = 7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.7, 128.2, 122.8, 89.2, 86.9, 81.4, 78.3, 76.2, 52.8, 30.6, 8.38, 8.36, 3.8.



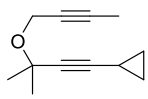
((1-(but-2-yn-1-yloxy)cyclobutyl)ethynyl)benzene (1q). Yellow oil in 49% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.32 – 7.30 (m, 3H), 4.21 (d, J = 1.5 Hz, 2H), 2.46 – 2.37 (m, 4H), 1.97 – 1.88 (m, 2H), 1.85 (d, J = 0.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.9, 128.43, 128.37, 122.8, 89.8, 85.7, 82.1, 75.6, 73.5, 57.1, 53.3, 36.2, 13.5, 3.9.



((1-(but-2-yn-1-yloxy)cyclopentyl)ethynyl)benzene (1r). Yellow oil in 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.41 (m, 2H), 7.31 – 7.29 (m, 3H), 4.28 (q, J = 2.2 Hz, 2H), 2.17 – 2.10 (m, 2H), 2.03 – 1.97 (m, 2H), 1.85 (t, J = 2.3 Hz, 3H), 1.84 – 1.81 (m, 2H), 1.79 – 1.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 128.4, 122.9, 90.1, 85.6, 81.8, 81.4, 76.1, 53.7, 39.8, 23.5, 3.9.

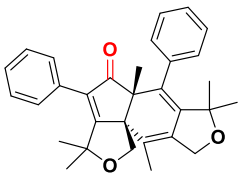


3-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)thiophene (1s). Yellow oil in 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, J = 5.2, 1.1 Hz, 1H), 7.17 (dd, J = 3.6, 1.1 Hz, 1H), 6.95 (dd, J = 5.2, 3.6 Hz, 1H), 4.26 (q, J = 2.3 Hz, 2H), 1.84 (t, J = 2.4 Hz, 3H), 1.56 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2, 127.2, 126.9, 122.5, 94.3, 81.9, 78.2, 75.9, 71.4, 57.0, 53.2, 28.7, 3.8.

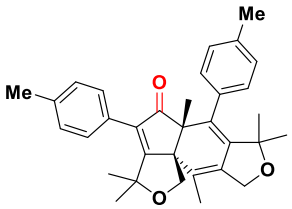


(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)cyclopropane (1t). Yellow oil in 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (q, J = 2.4 Hz, 2H), 1.83 (t, J = 2.4 Hz, 3H), 1.42 (s, 6H), 1.26 – 1.19 (m, 1H), 0.77 – 0.72 (m, 2H), 0.66 – 0.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 88.7, 81.7, 76.7, 76.2, 71.1, 52.8, 29.2, 29.1, 8.4, 3.9, -0.6.

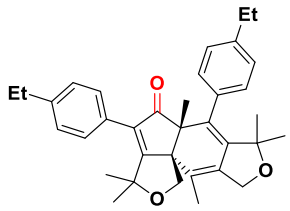
6. Characterization data of products 2a–p, 2q–t and 3a



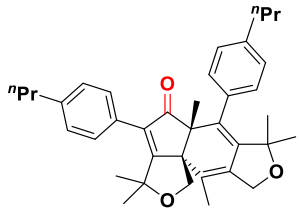
Compound 2a. Yellow solid, 91.7 mg, 81% yield, mp 205.1 – 205.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.7 Hz, 1H), 7.41 – 7.34 (m, 4H), 7.30 – 7.28 (m, 2H), 7.19 (dd, J = 7.9, 1.5 Hz, 2H), 7.03 – 7.01 (m, 1H), 4.53 (dd, J = 12.9, 0.9 Hz, 1H), 4.37 (dd, J = 12.9, 1.3 Hz, 1H), 4.05 (q, J = 9.7 Hz, 2H), 2.02 (s, 3H), 1.83 (s, 3H), 1.12 (s, 6H), 1.07 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.4, 187.0, 140.4, 137.8, 135.5, 132.5, 131.3, 131.2, 130.9, 130.4, 129.2, 128.6, 128.5, 127.9, 127.2, 127.1, 83.9, 80.7, 69.4, 66.5, 65.5, 63.1, 28.1, 27.4, 26.7, 26.4, 23.1, 18.4; HRMS (ESI-TOF) Calcd. for $C_{31}H_{33}O_3^+$ $[M+H]^+$: 453.2424; found: 453.2419. IR ν max cm^{-1}: 2971, 1713, 1594, 1360, 1141, 1120, 1054, 1025, 773, 743, 705, 669 cm^{-1}.



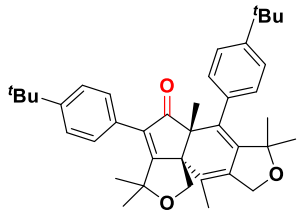
Compound 2b. Yellow oil, 90.1 mg, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 7.8, 1.5 Hz, 1H), 7.20 – 7.17 (m, 3H), 7.10 – 7.06 (m, 3H), 6.90 (dd, J = 7.7, 1.5 Hz, 1H), 4.52 (d, J = 12.8 Hz, 1H), 4.35 (dd, J = 12.8, 1.0 Hz, 1H), 4.03 (q, J = 9.7 Hz, 2H), 2.37 (s, 3H), 2.36 (s, 3H), 2.00 (s, 3H), 1.83 (s, 3H), 1.11 (s, 3H), 1.10 (s, 3H), 1.07 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.6, 186.3, 140.3, 138.5, 136.6, 135.4, 134.7, 132.4, 131.0, 130.8, 130.3, 129.2, 129.0, 128.6, 128.3, 127.7, 84.0, 80.7, 69.5, 66.5, 65.4, 63.0, 28.1, 27.4, 26.7, 26.4, 23.2, 21.5, 21.4, 18.4; HRMS (ESI-TOF) Calcd. for $C_{33}H_{37}O_3^+$ $[M+H]^+$: 481.2737; found: 481.2743. IR ν max cm^{-1}: 2976, 2818, 2360, 1711, 1600, 1511, 1457, 1381, 1352, 1144, 1021, 736, 669 cm^{-1}



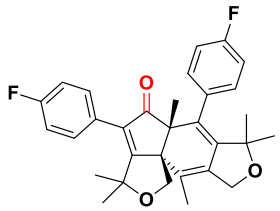
Compound 2c. Yellow solid, 80.1 mg, 63% yield. mp 136.9 – 137.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 7.9, 1.7 Hz, 1H), 7.22 – 7.19 (m, 3H), 7.10 (d, J = 8.1 Hz, 3H), 6.91 (dd, J = 7.7, 1.7 Hz, 1H), 4.52 (dd, J = 12.8, 0.9 Hz, 1H), 4.35 (dd, J = 12.8, 1.3 Hz, 1H), 4.03 (q, J = 9.6 Hz, 2H), 2.70 – 2.63 (m, 4H), 2.01 (s, 3H), 1.84 (s, 3H), 1.26 (t, J = 6.0 Hz, 3H), 1.23 (t, J = 6.0 Hz, 3H), 1.12 (s, 3H), 1.11 (s, 3H), 1.06 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.7, 186.3, 144.8, 143.0, 140.2, 135.5, 134.9, 132.4, 131.1, 130.8, 130.3, 129.3, 129.1, 128.5, 128.0, 127.3, 126.4, 84.0, 80.7, 69.5, 66.5, 65.4, 63.1, 28.8, 28.7, 28.1, 27.4, 26.7, 26.4, 23.2, 18.5, 15.64, 15.59; HRMS (ESI-TOF) Calcd. for $C_{33}H_{41}O_3^+$ $[M+H]^+$: 509.3050; found: 509.3055. IR ν max cm^{-1}: 2961, 2930, 2891, 1709, 1660, 1593, 1509, 1461, 1361, 1146, 1040, 1013, 836, 817 cm^{-1}.



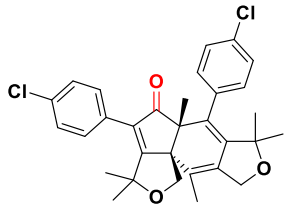
Compound 2d. Yellow oil, 68.4 mg, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 7.9, 1.6 Hz, 1H), 7.19 – 7.17 (m, 3H), 7.11 – 7.07 (m, 3H), 6.91 (dd, J = 7.7, 1.6 Hz, 1H), 4.51 (d, J = 12.0 Hz, 1H), 4.35 (dd, J = 12.8, 1.2 Hz, 1H), 4.03 (q, J = 9.6 Hz, 2H), 2.59 (dd, J = 14.6, 6.4 Hz, 4H), 2.00 (s, 3H), 1.84 (s, 3H), 1.69 – 1.65 (m, 2H), 1.63 – 1.60 (m, 2H), 1.12 (s, 3H), 1.11 (s, 3H), 1.05 (s, 3H), 0.96 (s, 3H), 0.93 (td, J = 7.4, 5.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.8, 186.3, 143.3, 141.4, 140.2, 135.5, 134.9, 132.4, 131.0, 130.7, 130.2, 129.3, 129.0, 128.7, 128.5, 127.9, 127.1, 84.0, 80.7, 69.5, 66.5, 65.4, 63.1, 38.0, 37.9, 28.2, 27.4, 26.7, 26.4, 24.61, 24.56, 23.2, 18.4, 13.9; HRMS (ESI-TOF) Calcd. for $C_{37}H_{45}O_3^+$ $[M+H]^+$: 537.3363; found: 537.3369. IR ν max cm^{-1}: 1590, 1384, 1353, 773, 620 cm^{-1}.



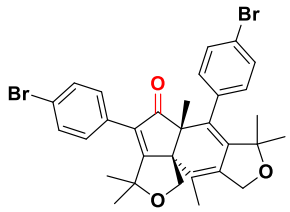
Compound 2e. Yellow solid, 70.6 mg, 50% yield, mp 245.6 – 247.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.85 (m, 1H), 7.38 (d, J = 2.8 Hz, 4H), 7.13 (d, J = 3.2 Hz, 2H), 6.93 – 6.91 (m, 1H), 4.52 (d, J = 11.7 Hz, 1H), 4.35 (d, J = 11.5 Hz, 1H), 4.04 (d, J = 7.5 Hz, 2H), 2.01 (s, 3H), 1.85 (s, 3H), 1.34 (s, 9H), 1.31 (s, 9H), 1.14 (s, 3H), 1.12 (s, 3H), 1.05 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.8, 186.3, 151.6, 150.0, 140.2, 135.4, 134.6, 132.4, 130.7, 130.5, 130.2, 129.4, 128.9, 128.2, 125.5, 124.7, 123.7, 84.0, 80.7, 69.5, 66.5, 65.4, 63.1, 34.8, 34.6, 31.6, 31.4, 28.2, 27.3, 26.7, 26.5, 23.2, 18.5; HRMS (ESI-TOF) Calcd. for $C_{39}H_{49}O_3^+$ $[M+H]^+$: 565.3676; found: 565.3673. IR ν max cm^{-1}: 2968, 1716, 1593, 1378, 1353, 1020, 838, 759, 725, 704, 687, 598, 559 cm^{-1}.



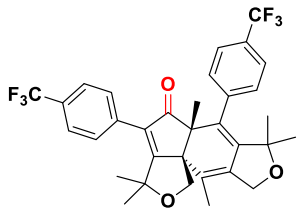
Compound 2f. Yellow solid, 95.3 mg, 78% yield, mp 210.5 – 211.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 1H), 7.19 – 7.16 (m, 2H), 7.08 (t, J = 8.5 Hz, 3H), 6.99 (d, J = 6.7 Hz, 2H), 4.51 (d, J = 12.9 Hz, 1H), 4.35 (d, J = 12.9 Hz, 1H), 4.03 (q, J = 9.8 Hz, 2H), 2.01 (s, 3H), 1.82 (s, 3H), 1.12 (s, 3H), 1.09 (d, J = 4.4 Hz, 3H), 1.06 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.5, 187.5, 163.0 (d, J = 248.7 Hz, 1C), 162.1 (d, J = 246.1 Hz, 1C), 141.1, 134.5, 133.4 (d, J = 3.3 Hz, 1C), 133.0 (d, J = 7.8 Hz, 1C), 132.44, 132.35 (d, J = 7.8 Hz, 1C), 131.0 (d, J = 8.2 Hz, 1C), 130.7, 128.0, 127.2, 115.8 (d, J = 21.6 Hz, 1C), 114.9 (d, J = 20.9 Hz, 1C), 114.1 (d, J = 21.0 Hz, 1C), 83.9, 80.6, 69.4, 66.5, 65.6, 62.8, 28.1, 27.4, 26.7, 26.4, 23.2, 18.5; HRMS (ESI-TOF) Calcd. for $C_{31}H_{31}F_2O_3^+$ $[M+H]^+$: 489.2236; found: 489.2229. IR ν max cm^{-1}: 2831, 1593, 1353, 1090, 776, 743, 619 cm^{-1}.



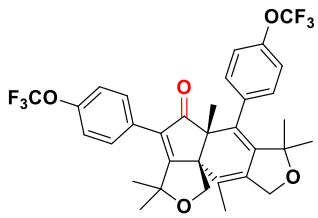
Compound 2g. Yellow solid, 97.8 mg, 75% yield, mp 105.6 – 107.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 8.3, 2.1 Hz, 1H), 7.39 – 7.35 (m, 3H), 7.28 (dd, J = 8.1, 2.2 Hz, 1H), 7.14 – 7.12 (m, 2H), 6.97 (dd, J = 8.1, 2.1 Hz, 1H), 4.51 (dd, J = 12.9, 1.0 Hz, 1H), 4.36 (dd, J = 12.9, 1.3 Hz, 1H), 4.05 – 4.00 (m, 2H), 2.00 (s, 3H), 1.82 (s, 3H), 1.12 (s, 3H), 1.08 (s, 3H), 1.07 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.1, 188.0, 141.1, 136.1, 134.8, 134.3, 133.3, 132.7, 132.5, 132.2, 130.8, 130.5, 129.6, 128.9, 128.2, 127.7, 127.4, 83.8, 80.7, 69.4, 66.5, 65.6, 62.8, 28.0, 27.4, 26.7, 26.4, 23.1, 18.5; HRMS (ESI-TOF) Calcd. for $C_{31}H_{31}Cl_2O_3^+$ $[M+H]^+$: 521.1645; found: 521.1666. IR v max cm^{-1}: 1593, 1508, 1383, 1352, 844, 822, 770, 557, 525 cm^{-1}.



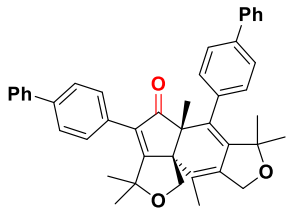
Compound 2h. Yellow solid, 117.5 mg, 77% yield, mp 198.5 – 199.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 8.3, 2.1 Hz, 1H), 7.54 – 7.51 (m, 3H), 7.44 (dd, J = 8.1, 2.1 Hz, 1H), 7.08 – 7.04 (m, 2H), 6.91 (dd, J = 8.1, 2.1 Hz, 1H), 4.53 – 4.50 (m, 1H), 4.36 (dd, J = 12.9, 1.3 Hz, 1H), 4.05 – 3.99 (m, 2H), 2.00 (s, 3H), 1.82 (s, 3H), 1.12 (s, 3H), 1.08 (s, 3H), 1.07 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.0, 188.1, 141.1, 136.6, 134.4, 133.1, 132.5, 131.9, 131.2, 130.8, 130.7, 130.4, 130.1, 127.7, 123.0, 121.5, 83.8, 80.7, 69.4, 66.5, 65.6, 62.8, 28.0, 27.4, 26.7, 26.5, 23.1, 18.5; HRMS (ESI-TOF) Calcd. for $C_{31}H_{31}Br_2O_3^+$ $[M+H]^+$: 611.0614; found: 611.0609. IR v max cm^{-1}: 2980, 1710, 1590, 1488, 1380, 1352, 836, 818, 773, 737, 707, 680, 563, 509 cm^{-1}.



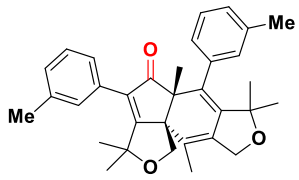
Compound 2i. Yellow solid, 76.5 mg, 52% yield, mp 147.6 – 148.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 1H), 7.68 – 7.64 (m, 3H), 7.58 (d, J = 7.8 Hz, 1H), 7.31 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 7.8 Hz, 1H), 4.54 (d, J = 12.8 Hz, 1H), 4.38 (d, J = 12.9 Hz, 1H), 4.06 (s, 2H), 2.04 (s, 3H), 1.84 (s, 3H), 1.12 (s, 3H), 1.10 (s, 3H), 1.06 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.6, 189.3, 141.5 (q, J = 17.7 Hz, 1C), 134.9, 134.2, 132.6, 131.8, 131.2, 131.0, 130.8 (q, J = 32.7 Hz, 1C), 129.6 (q, J = 32.3 Hz, 1C), 129.5, 128.9, 125.6 (q, J = 3.6 Hz, 1C), 124.9 (q, J = 3.6 Hz, 1C), 124.3 (q, J = 3.7 Hz, 1C), 83.7, 80.7, 69.4, 66.5, 65.8, 62.9, 29.9, 28.0, 27.3, 26.7, 23.1, 18.5; HRMS (ESI-TOF) Calcd. for $C_{33}H_{30}F_6O_3Na^+$ [M+Na]$^+$: 611.1991; found: 611.1985. IR v max cm^{-1}: 2829, 1593, 1354, 1122, 1067, 765, 619 cm^{-1}.



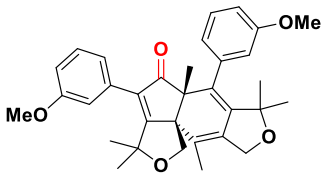
Compound 2j. Yellow solid, 94.6 mg, 61% yield, mp 186.0 – 187.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.5, 1.7 Hz, 1H), 7.27 (s, 1H), 7.24 (s, 4H), 7.16 (d, J = 8.3 Hz, 1H), 7.06 (dd, J = 8.3, 1.7 Hz, 1H), 4.53 (d, J = 12.8 Hz, 1H), 4.37 (d, J = 12.6 Hz, 1H), 4.08 – 4.02 (m, 2H), 2.02 (s, 3H), 1.84 (s, 3H), 1.14 (s, 3H), 1.10 (s, 3H), 1.07 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.2, 188.4, 149.5, 148.6, 141.3, 136.2, 134.1, 132.9, 132.5, 132.2, 130.9, 130.7, 129.8, 127.6, 121.9 (q, J = 8.1 Hz, 1C), 121.1, 120.4, 119.6, 119.3 (d, J = 8.9 Hz. 1C), 83.8, 80.7, 69.4, 66.5, 65.7, 62.8, 28.0, 27.3, 26.7, 26.5, 23.2, 18.5; HRMS (ESI-TOF) Calcd. for $C_{33}H_{31}F_6O_5^+$ [M+H]$^+$: 621.2070; found: 621.2078. IR v max cm^{-1}: 2989, 1712, 1593, 1383, 1352, 1279, 1206, 1169, 1142, 668 cm^{-1}.



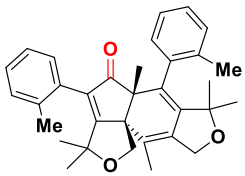
Compound 2k. Yellow solid, 90.7 mg, 60% yield, mp 112.0 – 113.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.1, 1.6 Hz, 1H), 7.68 – 7.65 (m, 3H), 7.63 – 7.60 (m, 4H), 7.56 (dd, J = 7.9, 1.9 Hz, 1H), 7.46 (td, J = 7.6, 2.4 Hz, 4H), 7.39 – 7.34 (m, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.11 (dd, J = 7.9, 1.6 Hz, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.40 (dd, J = 12.9, 1.2 Hz, 1H), 4.09 (q, J = 9.7 Hz, 2H), 2.06 (s, 3H), 1.90 (s, 3H), 1.20 (s, 3H), 1.19 (s, 3H), 1.13 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.6, 187.2, 141.4, 140.8, 140.63, 140.58, 139.8, 136.8, 135.1, 132.5, 131.7, 131.3, 130.5, 130.2, 129.6, 129.0, 128.98, 128.92, 127.7, 127.4, 127.3, 127.2, 127.1, 126.5, 125.7, 84.0, 80.8, 69.5, 66.5, 65.6, 63.1, 28.2, 27.5, 26.8, 26.5, 23.3, 18.6; HRMS (ESI-TOF) Calcd. for $C_{43}H_{41}O_3^+$ $[M+H]^+$: 605.3050; found: 605.3055. IR ν max cm^{-1}: 2816, 1600, 1488, 1354, 766, 697, 619 cm^{-}



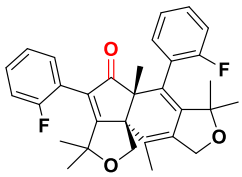
Compound 2l. Yellow oil, 94.9 mg, 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.29 – 7.26 (m, 1H), 7.24 (d, J = 2.8 Hz, 1H), 7.15 (dd, J = 7.3, 5.2 Hz, 2H), 7.10 (d, J = 7.3 Hz, 1H), 6.98 (d, J = 5.3 Hz, 2H), 6.83 – 6.79 (m, 1H), 4.52 (dd, J = 12.8, 0.9 Hz, 1H), 4.36 (d, J = 12.9 Hz, 1H), 4.08 – 4.00 (m, 2H), 2.38 (d, J = 18.9 Hz, 3H), 2.35 (s, 3H), 2.02 (s, 3H), 1.82 (d, J = 3.3 Hz, 3H), 1.12 (s, 6H), 1.06 (d, J = 12.4 Hz, 3H), 0.97 (d, J = 8.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.4, 186.7, 140.1, 138.1, 137.7, 137.3, 136.5, 135.6, 132.5, 131.7, 131.2, 130.3, 129.7, 129.4, 128.4, 128.2, 128.1, 127.8, 126.9, 126.3, 84.0, 80.7, 69.4, 66.5, 65.4, 63.1, 28.1, 27.3, 26.7, 26.5, 23.1, 21.6, 21.5, 18.4; HRMS (ESI-TOF) Calcd. for $C_{33}H_{37}O_3^+$ $[M+H]^+$: 481.2737; found: 481.2739. IR ν max cm^{-1}: 2976, 1597, 1382, 1352, 765, 724, 620 cm^{-1}.



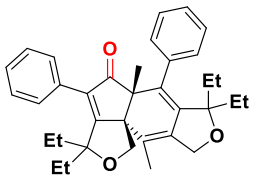
Compound 2m. Yellow oil, 59.0 mg, 46% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 1H), 7.33 – 7.28 (m, 1H), 7.19 (t, J = 7.9 Hz, 1H), 6.90 – 6.84 (m, 2H), 6.77 (d, J = 7.5 Hz, 1H), 6.71 (s, 1H), 6.61 – 6.56 (m, 1H), 4.52 (d, J = 12.9 Hz, 1H), 4.37 (d, J = 12.9 Hz, 1H), 4.07 – 4.00 (m, 2H), 3.83 (d, J = 15.9 Hz, 3H), 3.80 (s, 3H), 2.01 (s, 3H), 1.83 (d, J = 3.4 Hz, 3H), 1.13 (d, J = 3.6 Hz, 6H), 1.10 (d, J = 11.3 Hz, 3H), 0.99 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.1, 187.0, 159.6, 159.1, 158.6, 140.2, 139.1, 135.4, 132.6, 129.6, 128.9, 128.1, 123.8, 123.5, 121.7, 117.2, 116.0, 115.0, 113.9, 113.5, 112.0, 84.0, 80.7, 69.4, 66.5, 65.4, 63.1, 55.4, 27.9, 27.3, 26.8, 26.5, 22.9, 18.4; HRMS (ESI-TOF) Calcd. for $C_{33}H_{37}O_5^+$ $[M+H]^+$: 513.2636; found: 513.2637. IR ν max cm^{-1}: 1594, 1384, 1354, 765, 620 cm^{-1}.



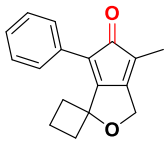
Compound 2n. Yellow oil, 54.1 mg, 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 1H), 7.24 – 7.18 (m, 6H), 7.02 – 7.00 (m, 1H), 4.56 (d, J = 12.8 Hz, 1H), 4.40 – 4.34 (m, 1H), 4.06 (s, 2H), 2.15 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 1.69 (s, 3H), 1.17 (s, 3H), 1.15 (s, 3H), 1.07 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.1, 187.7, 140.1, 137.0, 136.7, 136.6, 132.4, 131.5, 131.4, 130.7, 129.5, 128.9, 128.7, 128.4, 127.8, 127.4, 125.8, 125.7, 125.3, 83.9, 80.4, 68.9, 66.7, 64.8, 64.0, 29.8, 27.1, 26.9, 26.3, 25.1, 21.9, 20.8, 18.5; HRMS (ESI-TOF) Calcd. for $C_{33}H_{37}O_3^+$ $[M+H]^+$: 481.2737; found: 481.2722. IR ν max cm^{-1}: 2828, 1594, 1354, 765, 750, 620 cm^{-1}.



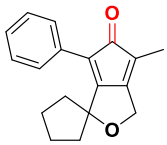
Compound 2o. Yellow solid, 81.8 mg, 67% yield, mp 180.8 – 182.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (td, J = 7.6, 1.8 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.32 – 7.27 (m, 1H), 7.19 – 7.15 (m, 2H), 7.11 – 7.07 (m, 2H), 7.06 – 7.01 (m, 1H), 4.55 (dd, J = 12.8, 1.0 Hz, 1H), 4.37 (dd, J = 12.8, 1.4 Hz, 1H), 4.09 (q, J = 9.8 Hz, 2H), 2.02 (s, 3H), 1.71 (s, 3H), 1.21 (s, 3H), 1.16 (s, 3H), 1.04 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.3, 189.6, 160.3 (d, J = 242.0 Hz, 1C), 160.0 (d, J = 248.1 Hz, 1C), 142.2, 133.8 (d, J = 1.8 Hz, 1C), 132.3, 131.5 (d, J = 2.9 Hz, 1C), 130.9 (d, J = 33.1 Hz, 1C), 130.5 (d, J = 32.5 Hz, 1C), 129.5, 129.4, 125.1 (d, J = 17.2 Hz, 1C), 124.2 (d, J = 3.5 Hz, 1C), 123.7 (d, J = 3.2 Hz, 1C), 122.1, 119.2 (d, J = 16.1 Hz, 1C), 116.0 (d, J = 21.6 Hz, 1C), 114.9 (d, J = 23.0 Hz, 1C), 83.8, 80.5, 69.4, 66.6, 65.3, 63.5, 26.8, 26.5, 26.2, 25.6, 21.5, 18.5; HRMS (ESI-TOF) Calcd. for $C_{31}H_{31}F_2O_3^+$ $[M+H]^+$: 489.2236; found: 489.2238. IR ν max cm^{-1}: 2819, 1593, 1492, 1383, 1352, 1105, 760, 620 cm^{-1}.



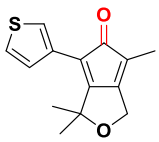
Compound 2p. Yellow oil, 63.6 mg, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.7 Hz, 1H), 7.39 – 7.33 (m, 4H), 7.29 – 7.27 (m, 2H), 7.21 – 7.19 (m, 2H), 7.00 – 6.98 (m, 1H), 4.62 (d, J = 12.2 Hz, 1H), 4.46 (dd, J = 12.9, 1.1 Hz, 1H), 4.03 (d, J = 9.6 Hz, 1H), 3.94 (d, J = 9.6 Hz, 1H), 2.42 (dq, J = 15.1, 7.6 Hz, 1H), 2.09 (dq, J = 14.4, 7.3 Hz, 1H), 1.98 (s, 3H), 1.63 – 1.57 (m, 1H), 1.55 – 1.51 (m, 1H), 1.41 (dd, J = 14.2, 7.3 Hz, 1H), 1.36 – 1.29 (m, 2H), 1.10 (s, 3H), 1.06 (t, J = 7.5 Hz, 3H), 0.99 (dd, J = 14.2, 7.2 Hz, 1H), 0.84 (t, J = 7.3 Hz, 3H), 0.76 (t, J = 7.2 Hz, 3H), 0.65 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.0, 187.1, 137.8, 136.6, 135.1, 134.4, 132.4, 130.3, 130.2, 130.0, 129.5, 128.4, 127.9, 127.2, 127.1, 91.1, 85.3, 69.8, 68.8, 65.8, 63.3, 33.7, 32.0, 29.9, 29.8, 23.2, 18.2, 9.1, 8.8, 8.5, 8.2; HRMS (ESI-TOF) Calcd. for $C_{35}H_{41}O_3^+$ $[M+H]^+$: 509.3050; found: 509.3056. IR ν max cm^{-1}: 2816, 1594, 1353, 774, 620 cm^{-1}.



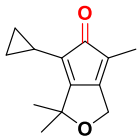
4'-methyl-6'-phenylspiro[cyclobutane-1,1'-cyclopenta[c]furan]-5'(3'*H*)-one (2q). Yellow solid, 79.5 mg, 63% yield, mp 120.3 – 121.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 5H), 3.99 (d, J = 9.4 Hz, 1H), 3.56 (d, J = 9.4 Hz, 1H), 2.93 – 2.78 (m, 2H), 2.14 (t, J = 8.2 Hz, 2H), 2.00 – 1.89 (m, 1H), 1.69 – 1.65 (m, 1H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 181.8, 137.7, 130.8, 129.4, 129.2, 128.6, 83.5, 68.8, 65.6, 53.1, 35.6, 34.2, 13.7, 13.2; HRMS (ESI-TOF) Calcd. for $C_{17}H_{17}O_2^+$ $[M+H]^+$: 253.1223; found: 253.1226.



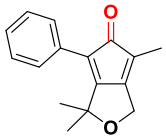
4'-methyl-6'-phenylspiro[cyclopentane-1,1'-cyclopenta[c]furan]-5'(3'*H*)-one (2r). Yellow solid, 93.2 mg, 70% yield, mp 115.1 – 116.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 5H), 4.14 (d, J = 9.6 Hz, 1H), 3.50 (d, J = 9.7 Hz, 1H), 2.64 – 2.58 (m, 1H), 2.40 – 2.33 (m, 1H), 1.96 – 1.89 (m, 1H), 1.75 – 1.65 (m, 2H), 1.55 – 1.45 (m, 3H), 1.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7, 184.1, 137.4, 131.0, 129.4, 129.0, 128.6, 90.9, 67.7, 66.1, 53.2, 40.2, 37.5, 25.5, 25.1, 13.7; HRMS (ESI-TOF) Calcd. for $C_{18}H_{19}O_2^+$ $[M+H]^+$: 267.1380; found: 267.1378.



1,1,4-trimethyl-6-(thiophen-3-yl)-1H-cyclopenta[c]furan-5(3*H*)-one (2s). Yellow oil, 50.5 mg, 41% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.54 (m, 1H), 7.49 (dd, J = 5.0, 0.7 Hz, 1H), 7.16 (dd, J = 5.0, 3.8 Hz, 1H), 4.04 (d, J = 10.0 Hz, 1H), 3.56 (d, J = 10.0 Hz, 1H), 1.96 (s, 3H), 1.39 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 181.6, 131.1, 130.0, 129.1, 128.1, 127.5, 81.5, 68.1, 67.2, 52.8, 26.2, 24.3, 13.6; HRMS (ESI-TOF) Calcd. for $C_{14}H_{15}O_2S^+$ $[M+H]^+$: 247.0787; found: 247.0787.



6-cyclopropyl-1,1,4-trimethyl-1H-cyclopenta[c]furan-5(3*H*)-one (2t). Yellow solid, 48.0 mg, 47% yield, mp 135.6 – 137.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (d, J = 9.7 Hz, 1H), 3.42 (d, J = 9.7 Hz, 1H), 1.66 (s, 3H), 1.49 (s, 3H), 1.46 – 1.40 (m, 2H), 1.02 – 0.96 (m, 1H), 0.88 (s, 3H), 0.85 – 0.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.0, 182.8, 136.8, 80.4, 67.1, 66.2, 52.8, 26.5, 24.3, 13.3, 8.2, 6.1, 5.0; HRMS (ESI-TOF) Calcd. for $C_{13}H_{17}O_2^+$ $[M+H]^+$: 205.1223; found: 205.1223.



1,1,4-trimethyl-6-phenyl-1H-cyclopenta[c]furan-5(3*H*)-one (3a). Yellow oil, 32.4 mg, 27% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 3H), 7.37 (d, J = 6.8 Hz, 2H), 4.15 (d, J = 10.0 Hz, 1H), 3.62 (d, J = 10.0 Hz, 1H), 1.86 (s, 3H), 1.11 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 184.3, 138.1, 130.7, 129.2, 129.1, 128.6, 81.2, 67.3, 66.8, 53.5, 29.7, 27.2, 25.4, 13.4.

7. References

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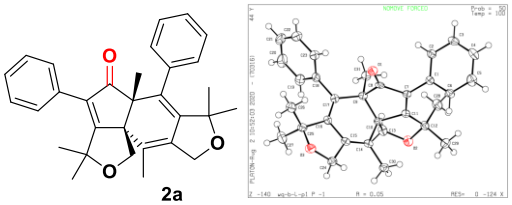
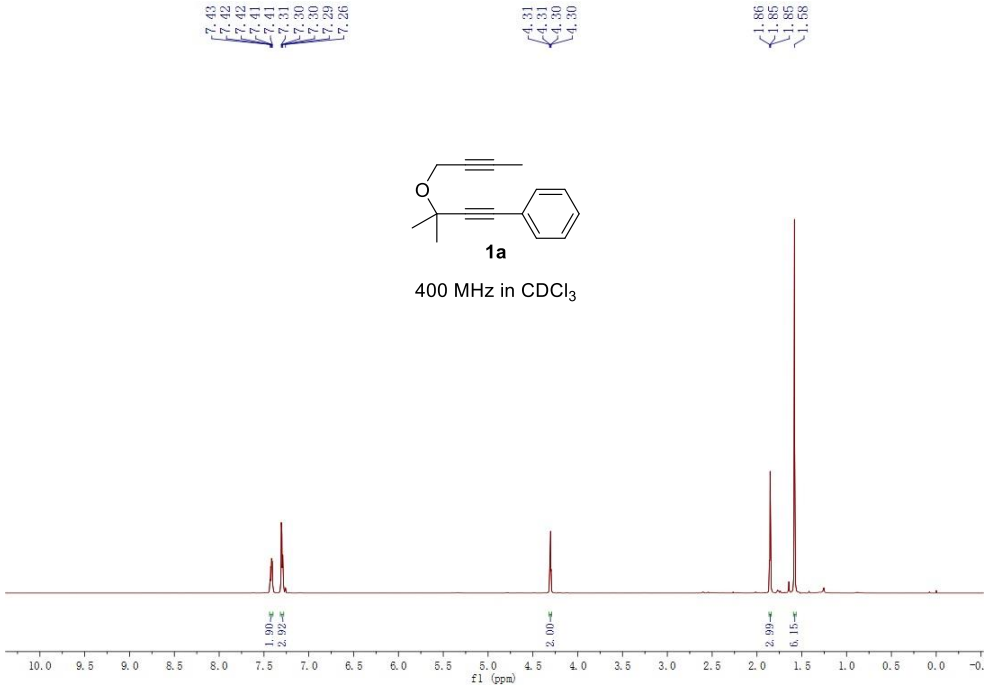
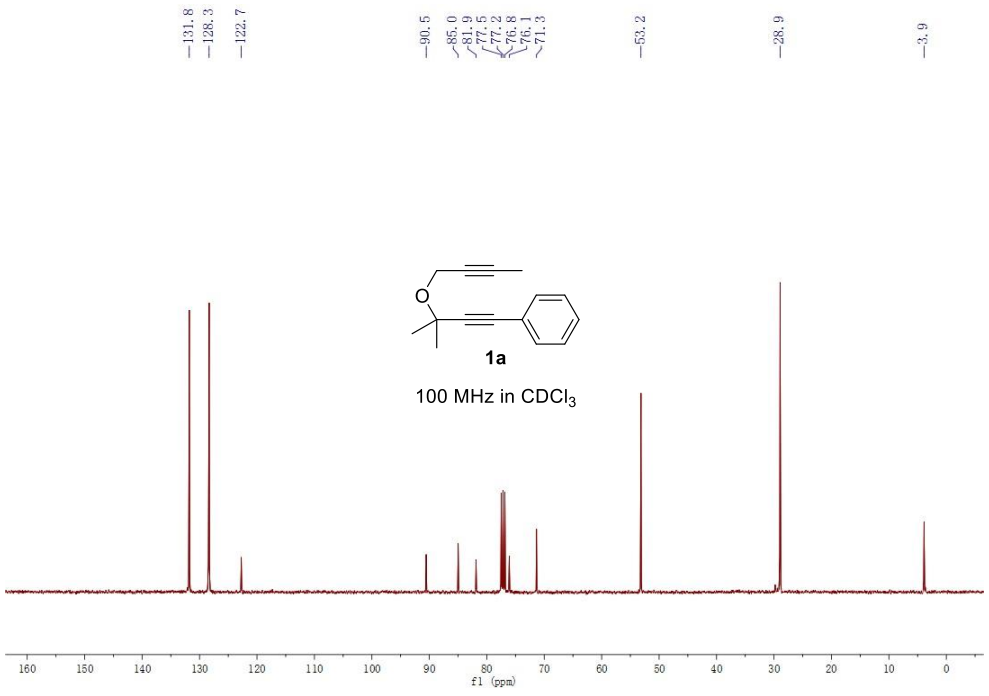
8. X-ray crystal data for compound 2a (CCDC: 2057915)

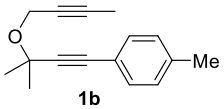


Compound	**2a**
Empirical formula	$C_{31}H_{32}O_3$
Formula weight	452.56
Temperature/K	100.00(11)
Crystal system	triclinic
Space group	P-1
a/Å	9.2372(9)
b/Å	9.8969(9)
c/Å	14.1848(12)
α/°	74.639(8)
β/°	82.413(8)
γ/°	82.113(8)
Volume/Å^3	1232.4(2)
Z	2
ρ_{calc}g/cm^3	1.220
μ/mm^{-1}	0.077
F(000)	484.0
Crystal size/mm^3	0.12 × 0.11 × 0.09
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.292 to 49.996
Index ranges	-9 ≤ h ≤ 10, -11 ≤ k ≤ 11, -16 ≤ l ≤ 15
Reflections collected	7997
Independent reflections	4321 [R_{int} = 0.0378, R_{sigma} = 0.0678]
Data/restraints/parameters	4321/0/313
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0548, wR_2 = 0.1125
Final R indexes [all data]	R_1 = 0.0804, wR_2 = 0.1253
Largest diff. peak/hole / e Å^{-3}	0.24/-0.20

9. ^{1}H, ^{13}C spectra of 1a–t, 2a–p, 2q–t and 3a

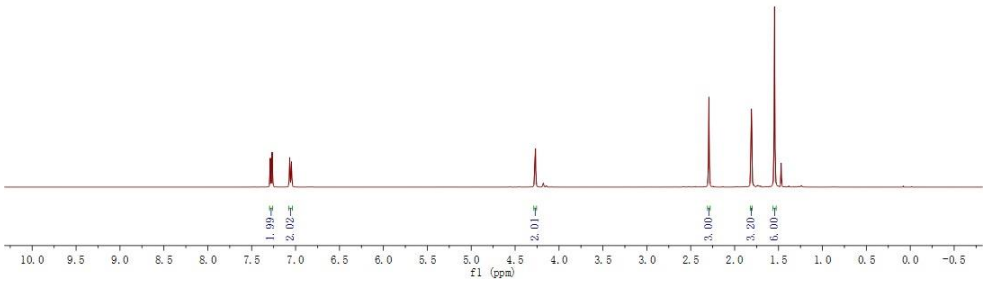


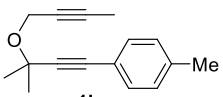




1b

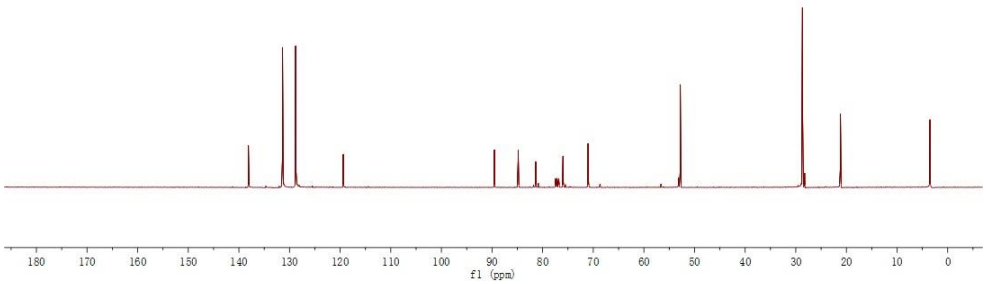
400 MHz in $CDCl_3$

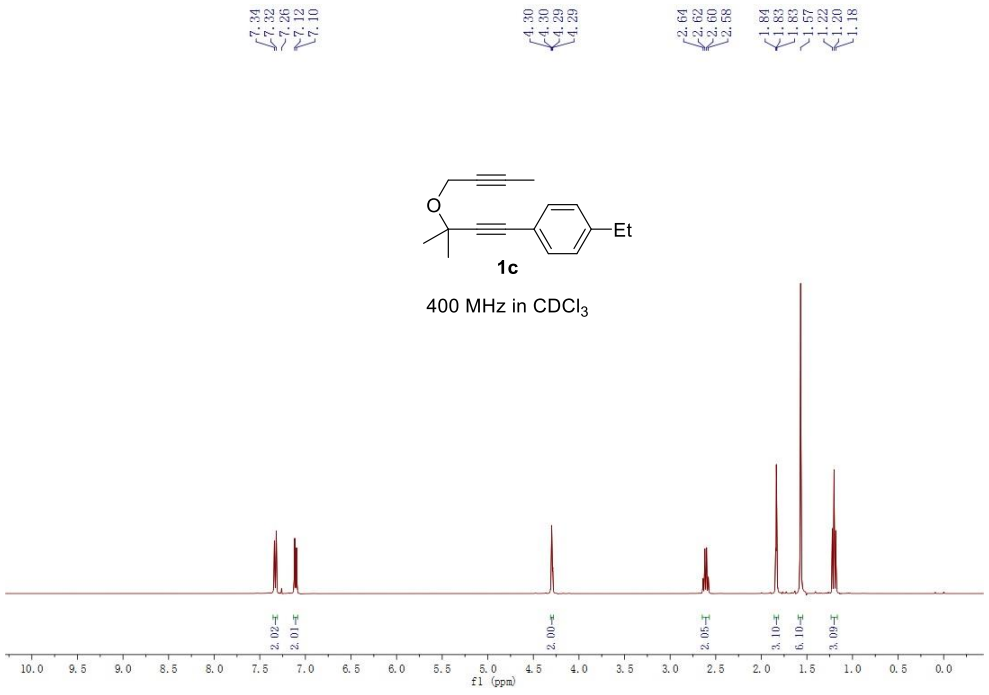


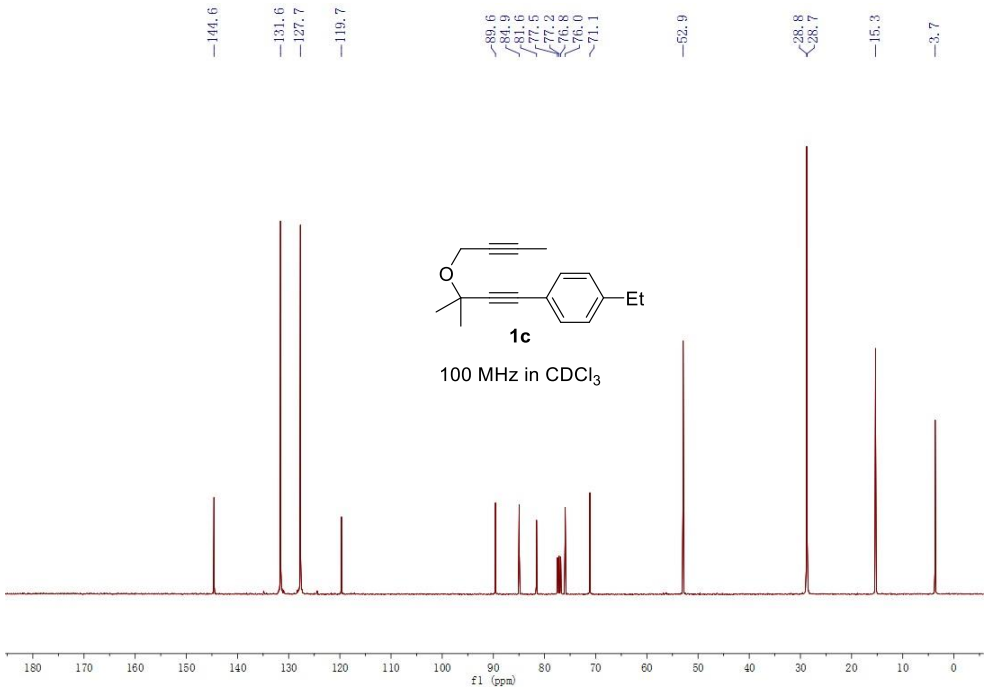


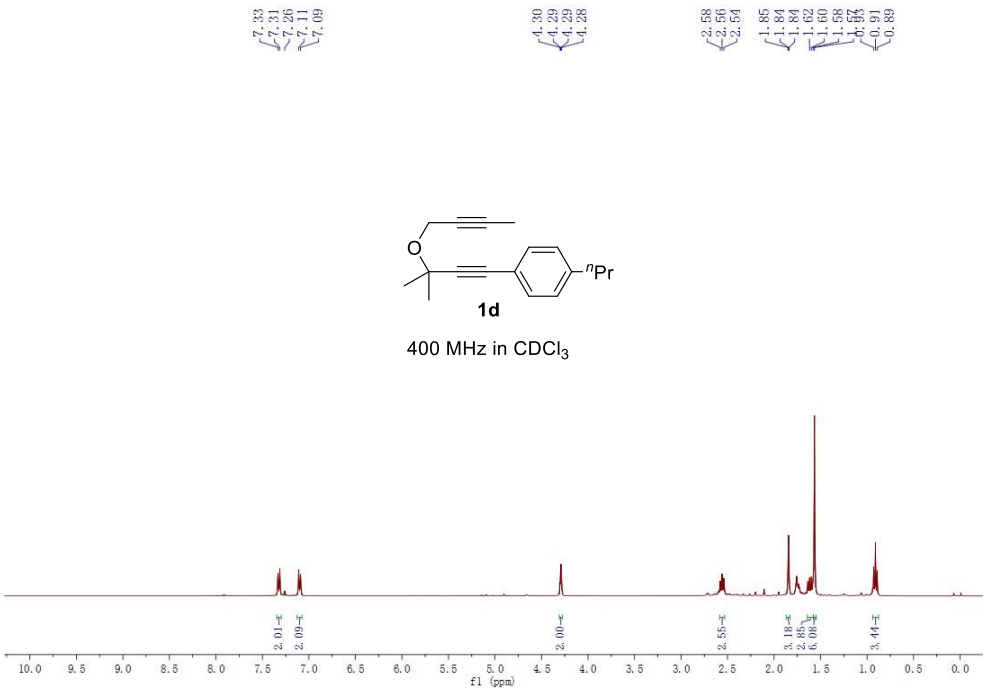
1b

100 MHz in $CDCl_3$

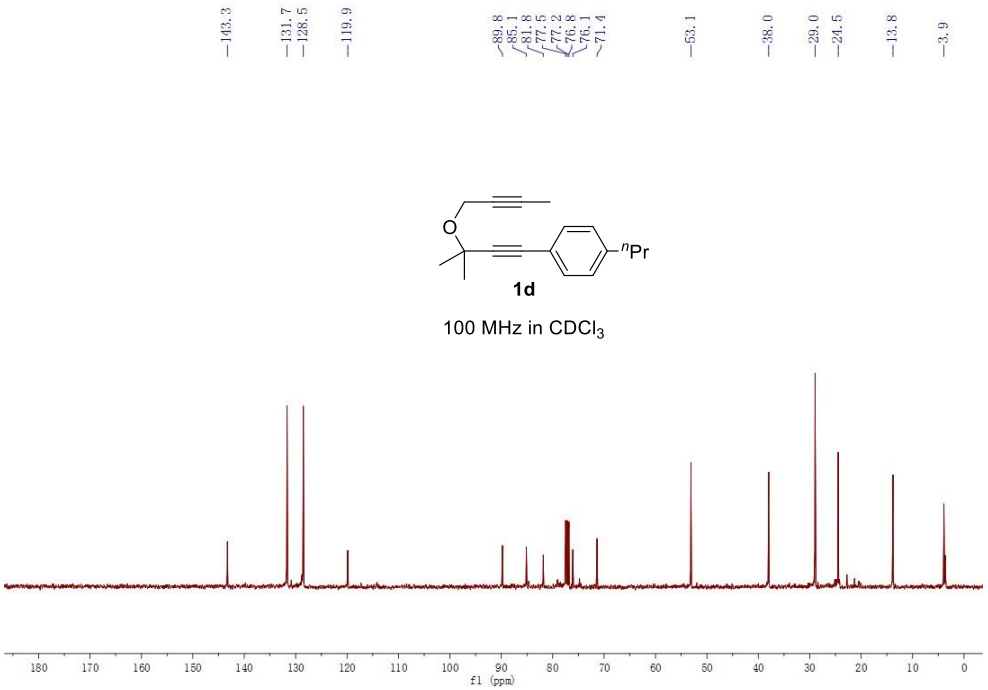



7.34
7.32
7.26
7.12
7.10
4.30
4.30
4.29
4.29
2.64
2.62
2.60
2.58
1.84
1.83
1.83
1.57
1.22
1.20
1.18
O
Et
1c
400 MHz in CDCl3
2.02
2.01
2.00
2.05
3.10
6.10
3.09
f1 (ppm)

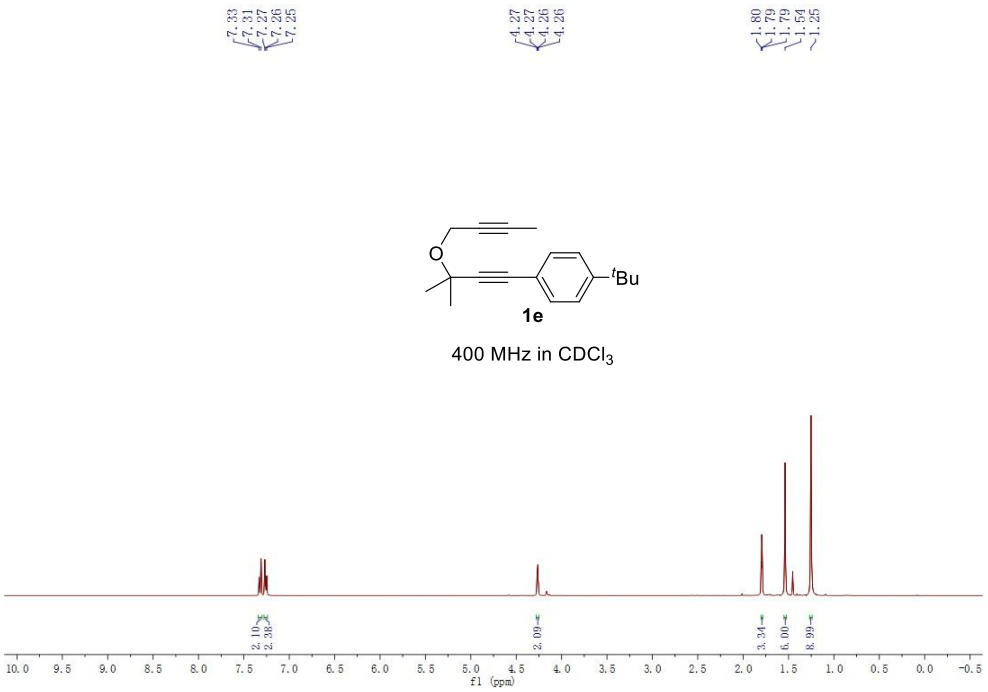

144.6
131.6
127.7
119.7
89.6
84.9
81.6
77.5
77.2
76.8
76.0
71.1
52.9
28.8
28.7
15.3
3.7
O
Et
1c
100 MHz in CDCl3
f1 (ppm)

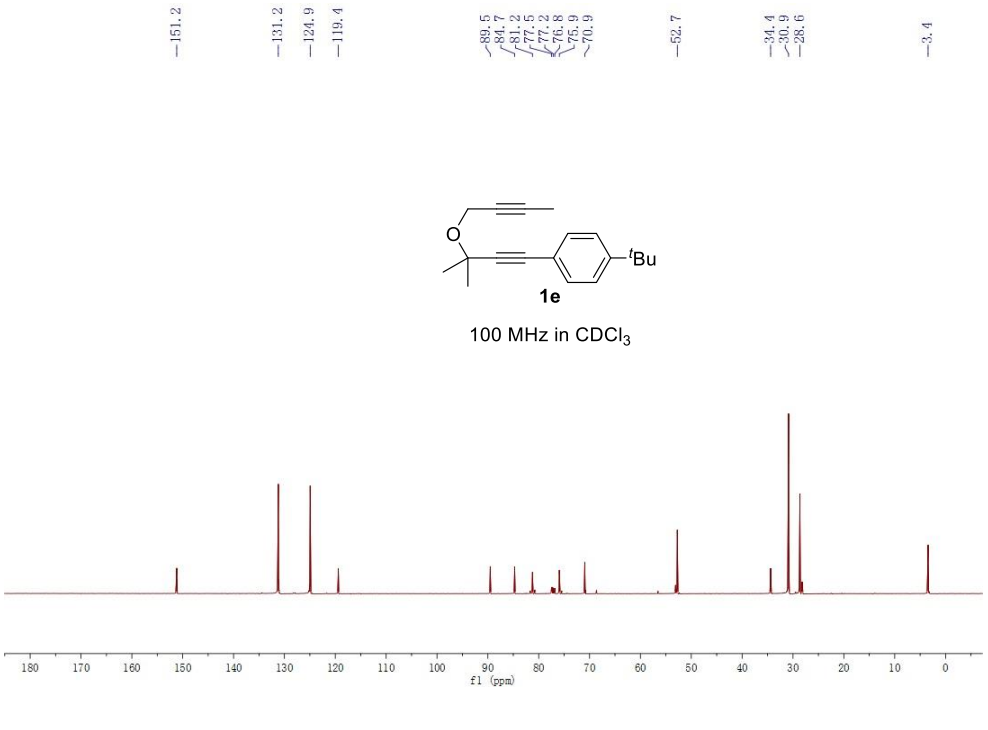


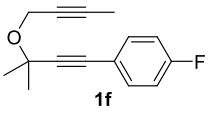
400 MHz in $CDCl_3$



100 MHz in $CDCl_3$

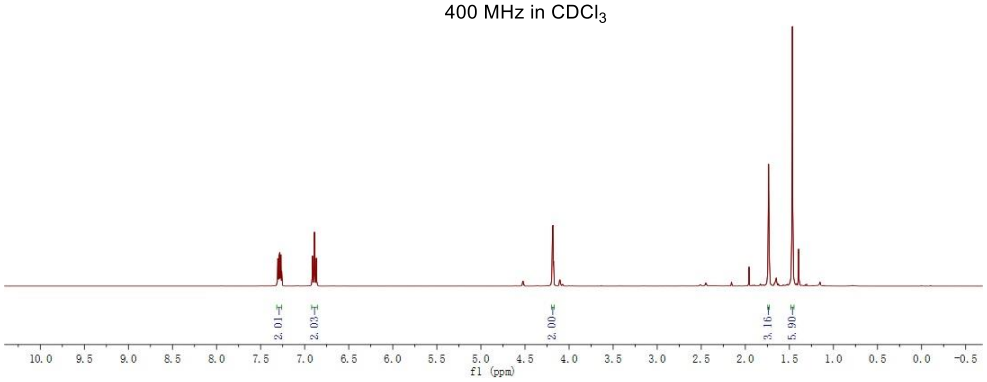

7.33
7.31
7.27
7.26
7.25
4.27
4.27
4.26
4.26
1.80
1.79
1.79
1.54
1.25
O
tBu
1e
400 MHz in CDCl3
2.10
2.38
2.09
3.34
6.00
8.99
f1 (ppm)

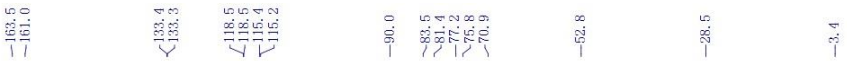

151.2
131.2
124.9
119.4
89.5
84.7
81.2
77.5
77.2
76.8
75.9
70.9
52.7
34.4
30.9
28.6
3.4
O
tBu
1e
100 MHz in CDCl3
f1 (ppm)

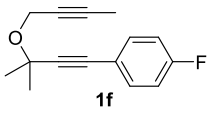


1f

400 MHz in $CDCl_3$

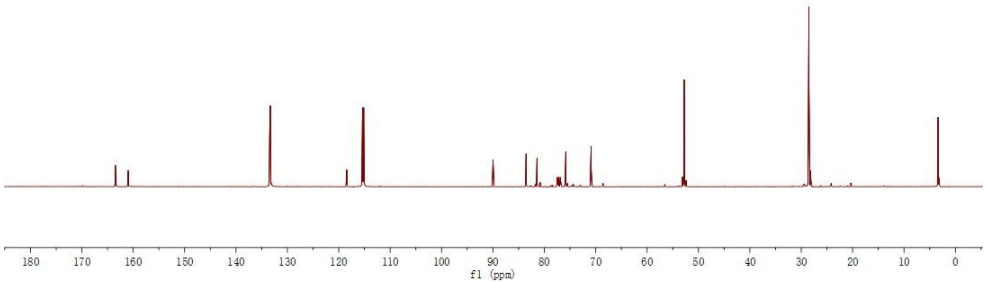


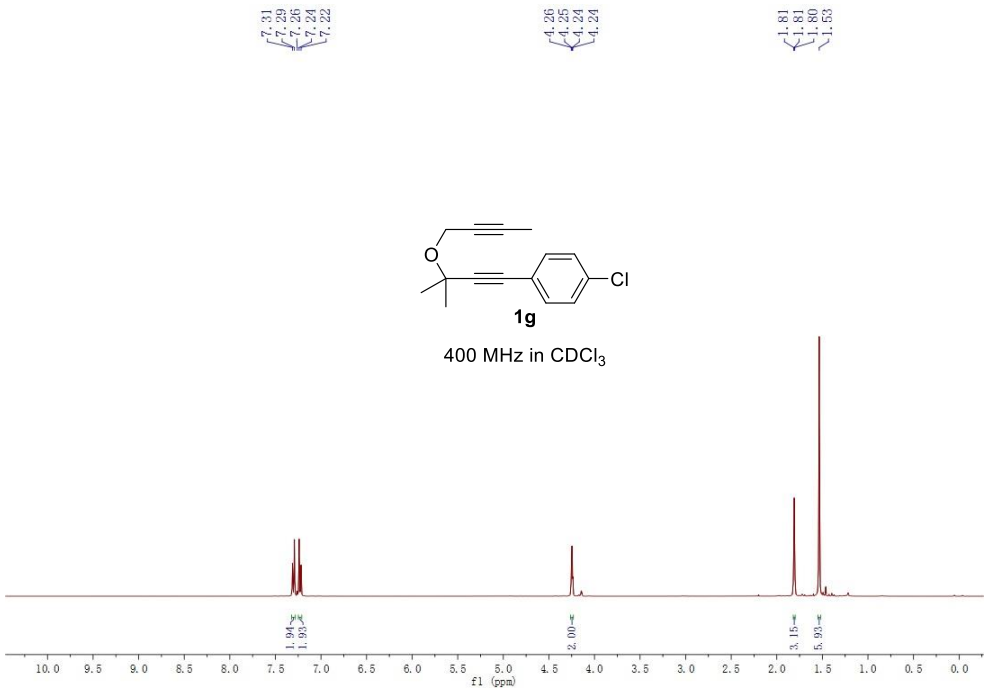


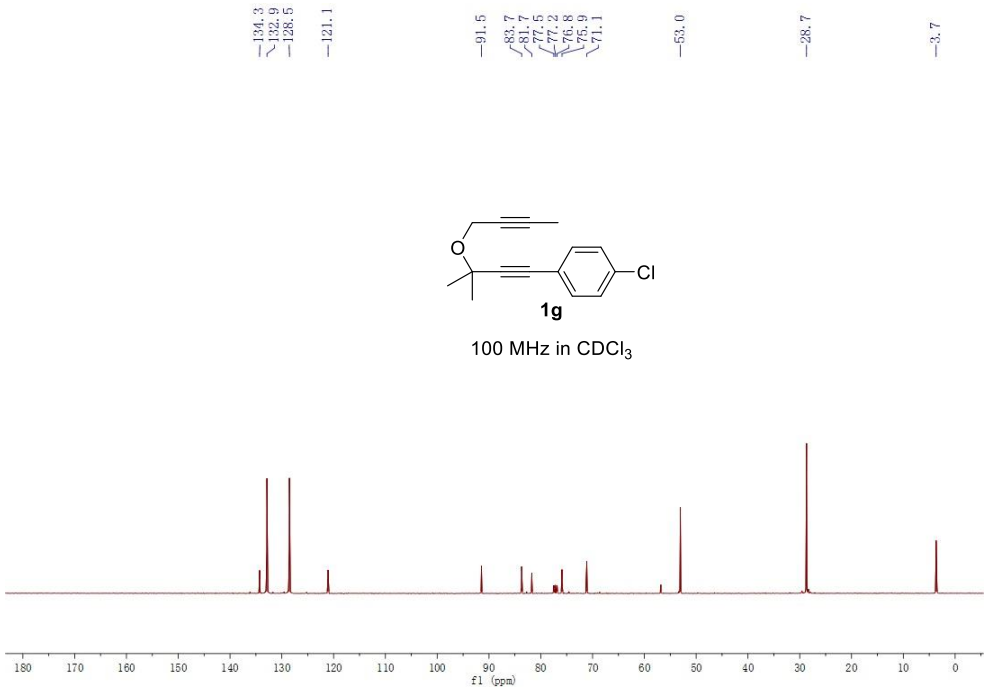


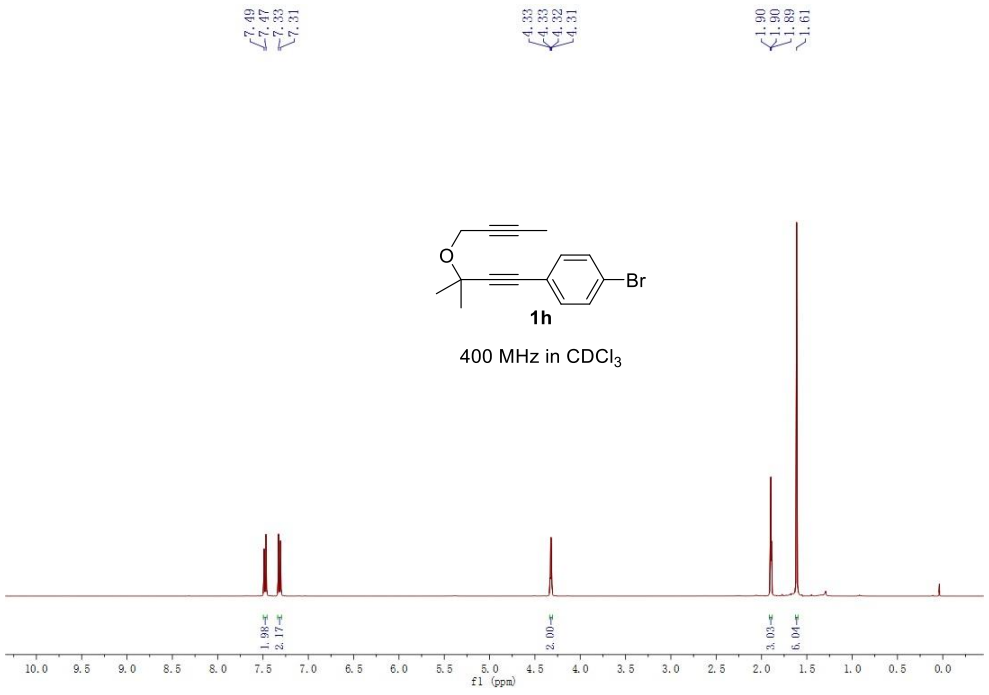
1f

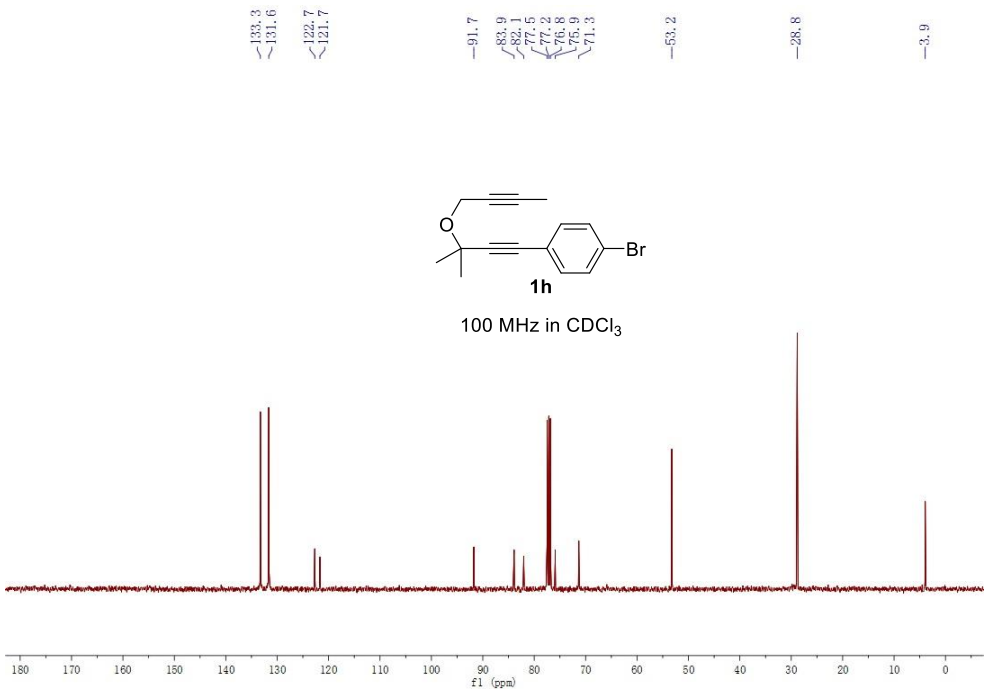
100 MHz in $CDCl_3$

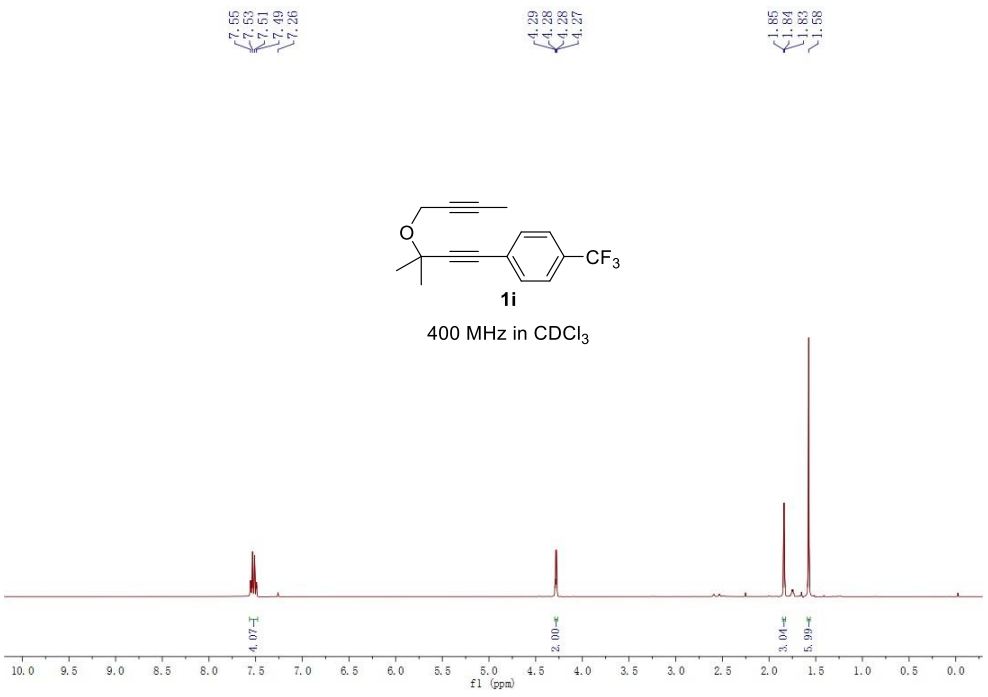


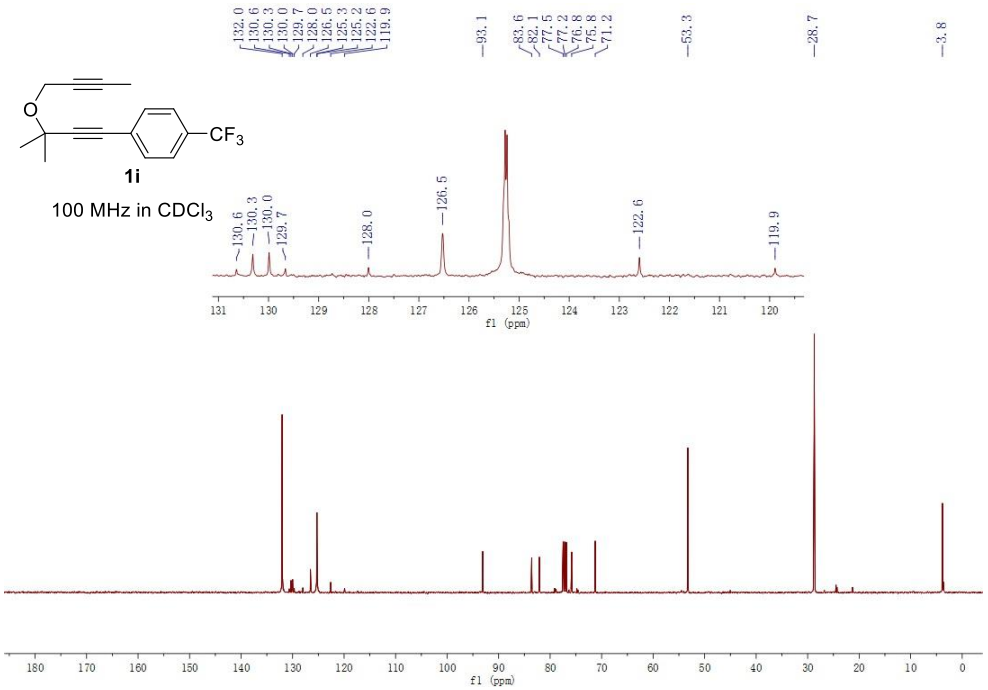

7.31
7.29
7.26
7.24
7.22
4.26
4.25
4.24
4.24
1.81
1.81
1.80
1.53
O
Cl
1g
400 MHz in CDCl3
1.94
1.93
2.00
3.15
5.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

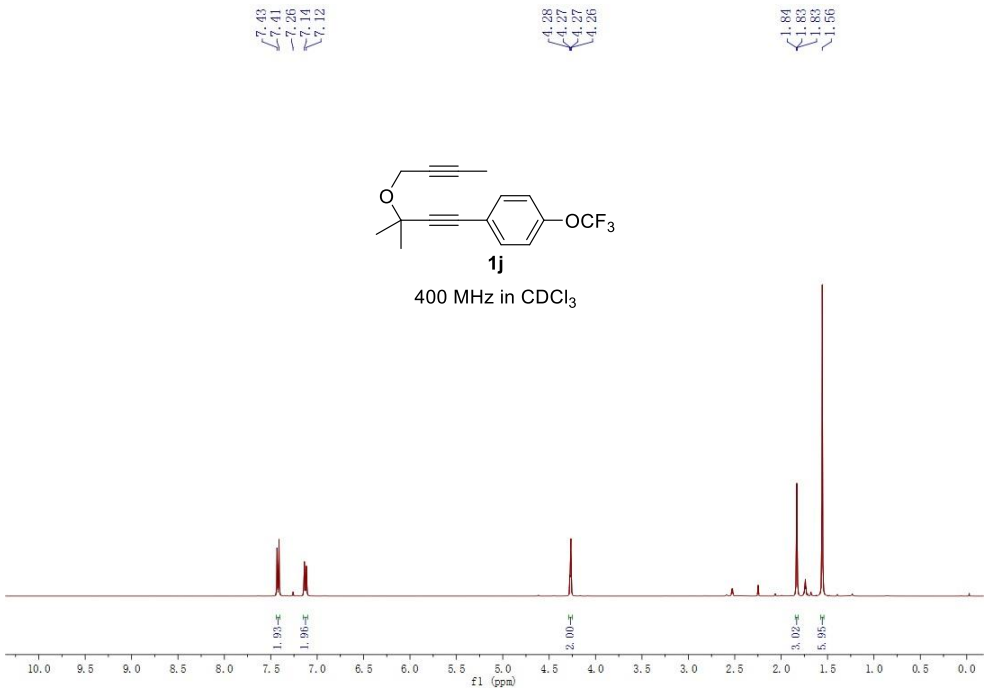

134.3
132.9
128.5
121.1
91.5
83.7
81.7
77.5
77.2
76.8
75.9
71.1
53.0
28.7
3.7
O
Cl
1g
100 MHz in CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

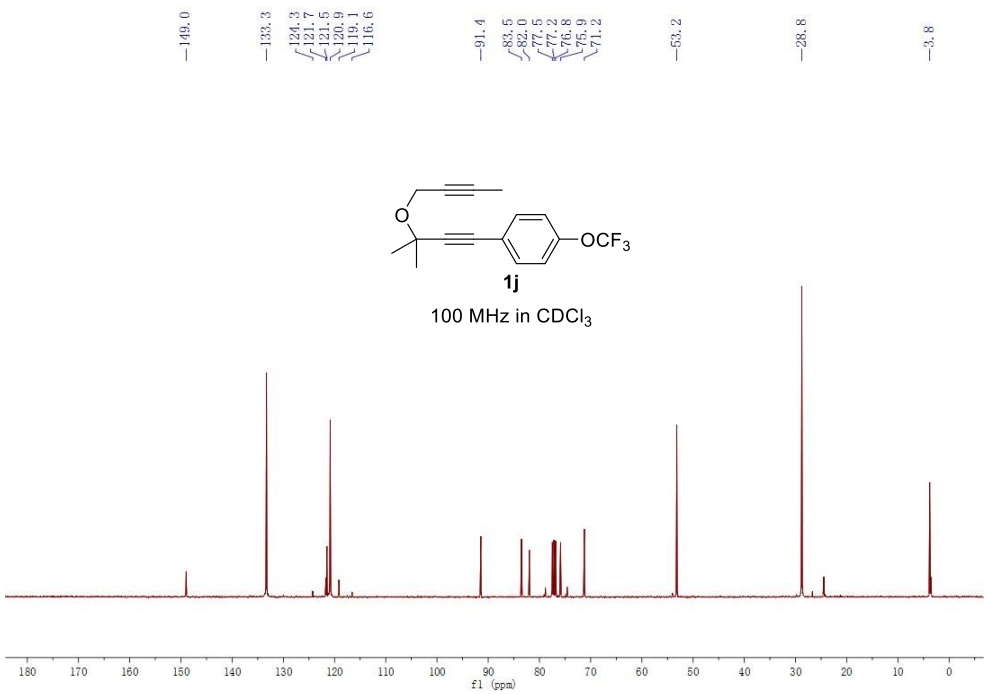

7.49
7.47
7.33
7.31
4.33
4.33
4.32
4.31
1.90
1.90
1.89
1.61
O
Br
1h
400 MHz in CDCl3
1.98
2.17
2.00
3.03
6.04
f1 (ppm)

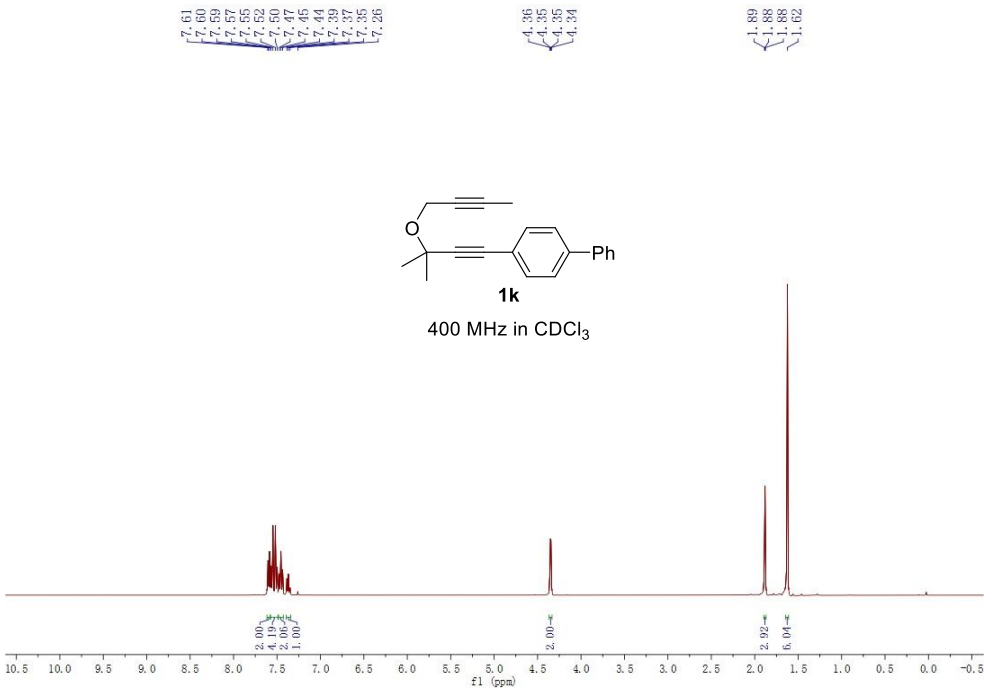

133.3
131.6
122.7
121.7
91.7
83.9
82.1
77.5
77.2
76.8
75.9
71.3
53.2
28.8
3.9
O
Br
1h
100 MHz in CDCl3
f1 (ppm)

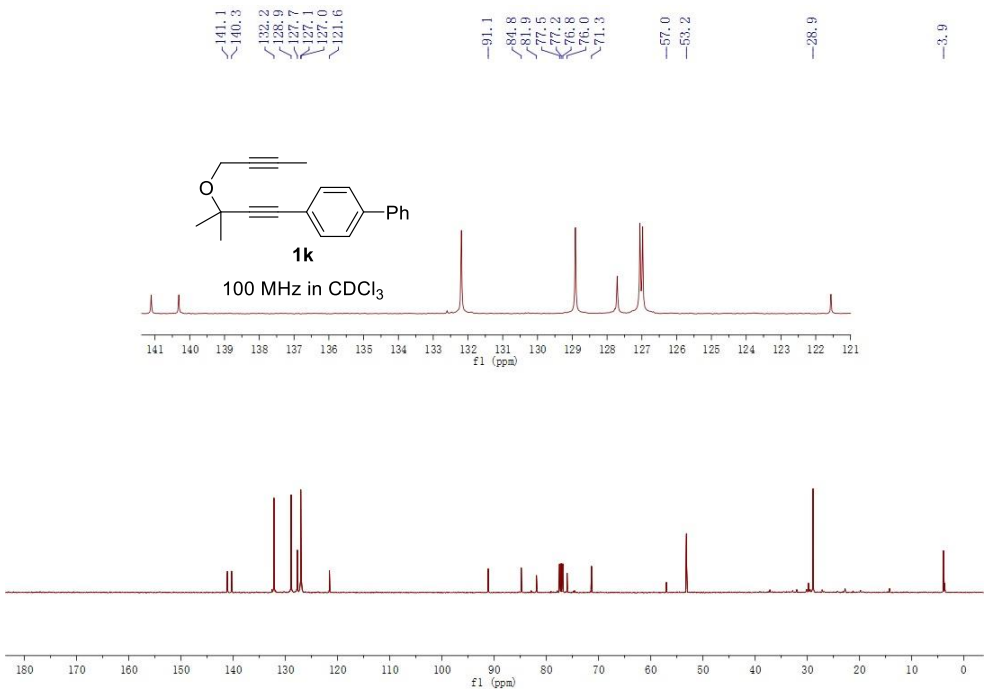

7.55
7.53
7.51
7.49
7.26
4.29
4.28
4.28
4.27
1.85
1.84
1.83
1.58
O
CF3
1i
400 MHz in CDCl3
4.07
2.00
3.04
5.99
f1 (ppm)

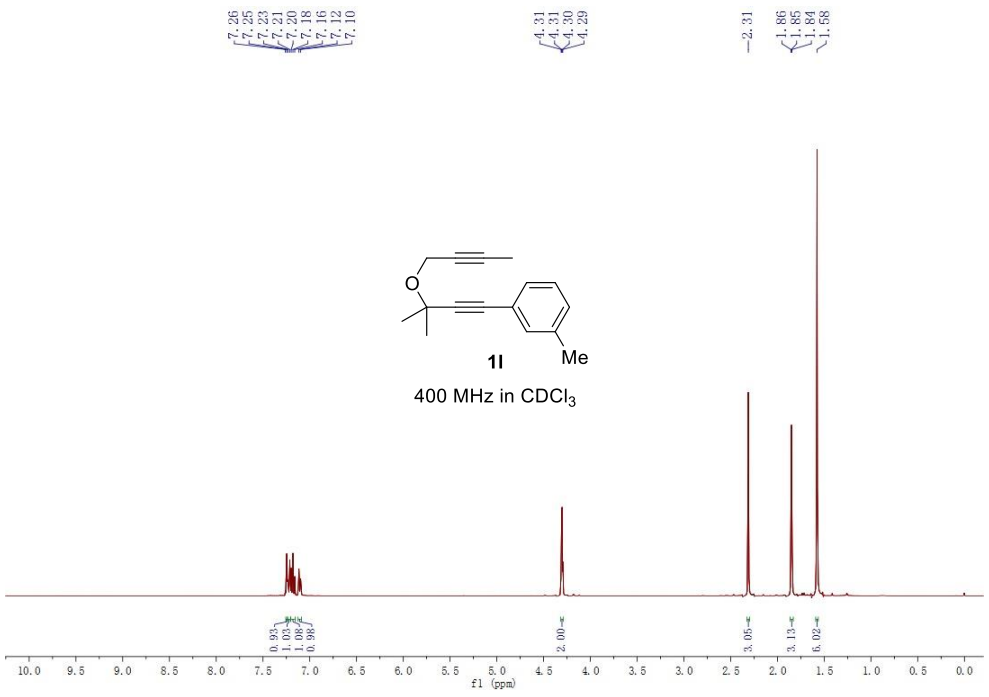

132.0
130.6
130.3
130.0
129.7
128.0
126.5
125.3
125.2
122.6
119.9
93.1
83.6
82.1
77.5
77.2
76.8
75.8
71.2
53.3
28.7
3.8
O
CF3
1i
100 MHz in CDCl3
130.6
130.3
130.0
129.7
128.0
126.5
122.6
119.9
f1 (ppm)

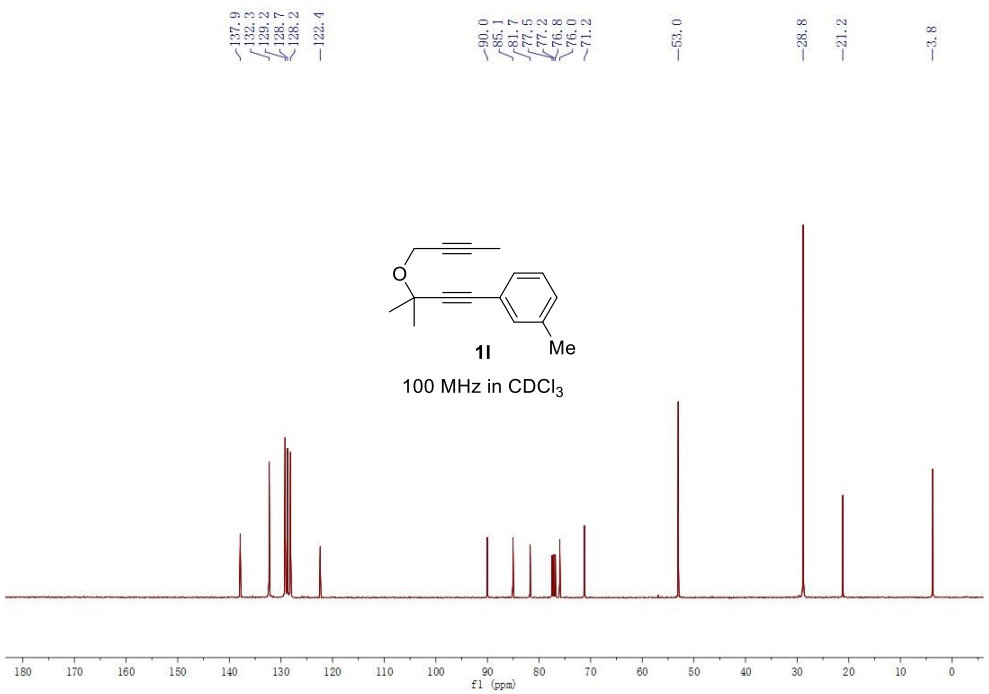

7.43
7.41
7.26
7.14
7.12
4.28
4.27
4.27
4.26
1.84
1.83
1.83
1.56
O
OCF3
1j
400 MHz in CDCl3
1.93
1.96
2.00
3.02
5.95
f1 (ppm)

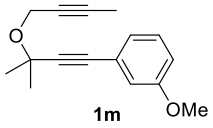

149.0
133.3
124.3
121.7
121.5
120.9
119.1
116.6
91.4
83.5
82.0
77.5
77.2
76.8
75.9
71.2
53.2
28.8
3.8
O
OCF3
1j
100 MHz in CDCl3
f1 (ppm)


7.61
7.60
7.59
7.57
7.55
7.52
7.50
7.47
7.45
7.44
7.39
7.37
7.35
7.26
4.36
4.35
4.34
1.89
1.88
1.88
1.62
O
Ph
1k
400 MHz in CDCl3
2.00
4.19
2.06
1.00
2.00
2.92
6.04
f1 (ppm)


141.1
140.3
132.2
128.9
127.7
127.1
127.0
121.6
91.1
84.8
81.9
77.5
77.2
76.8
76.0
71.3
57.0
53.2
28.9
3.9
O
Ph
1k
100 MHz in CDCl3
f1 (ppm)

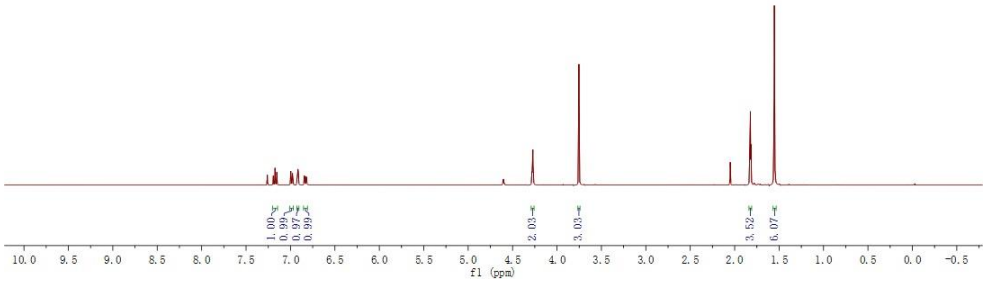

7.26
7.25
7.23
7.21
7.20
7.18
7.16
7.12
7.10
4.31
4.31
4.30
4.29
2.31
1.86
1.85
1.84
1.58
O
Me
1l
400 MHz in CDCl3
0.93
1.03
1.08
0.98
2.00
3.05
3.13
6.02
f1 (ppm)

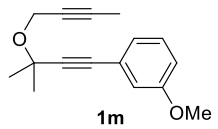

137.9
132.3
129.2
128.7
128.2
122.4
90.0
85.1
81.7
77.5
77.2
76.8
76.0
71.2
53.0
28.8
21.2
3.8
O
Me
1l
100 MHz in CDCl3
f1 (ppm)



1m

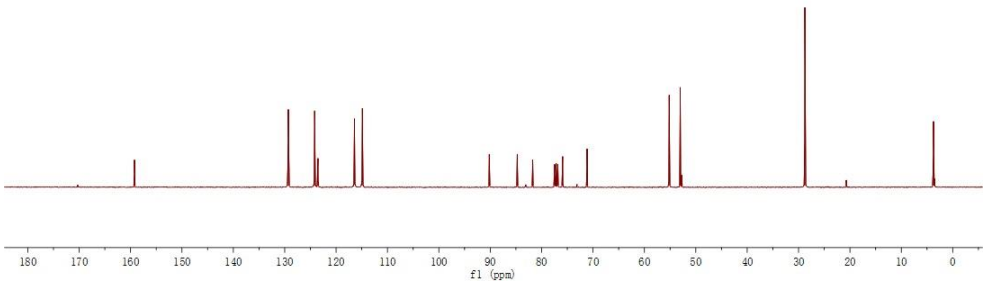
400 MHz in $CDCl_3$

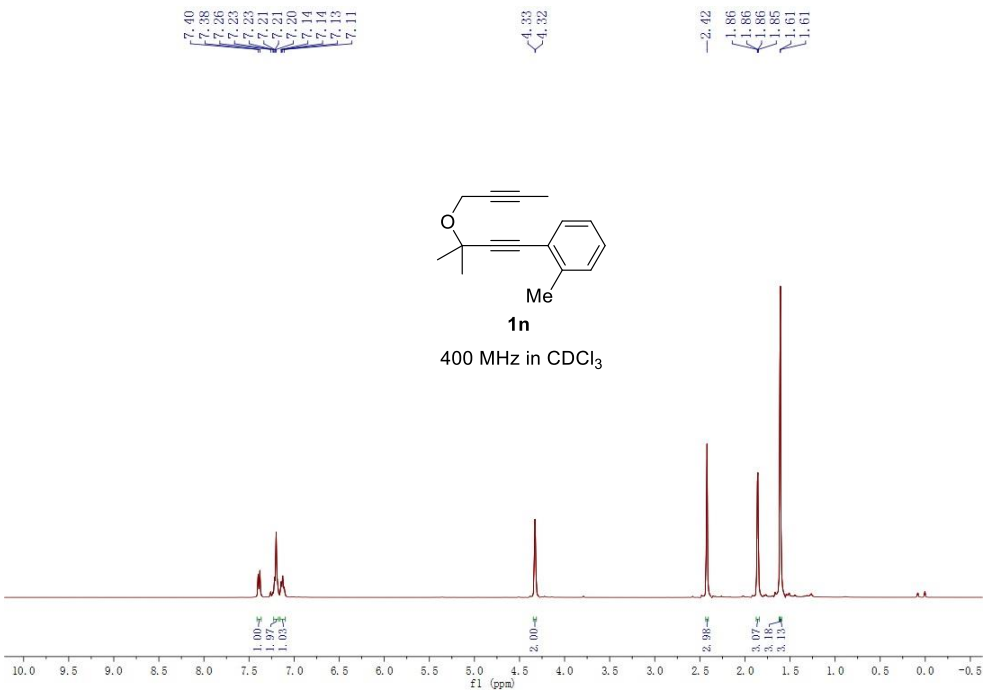




1m

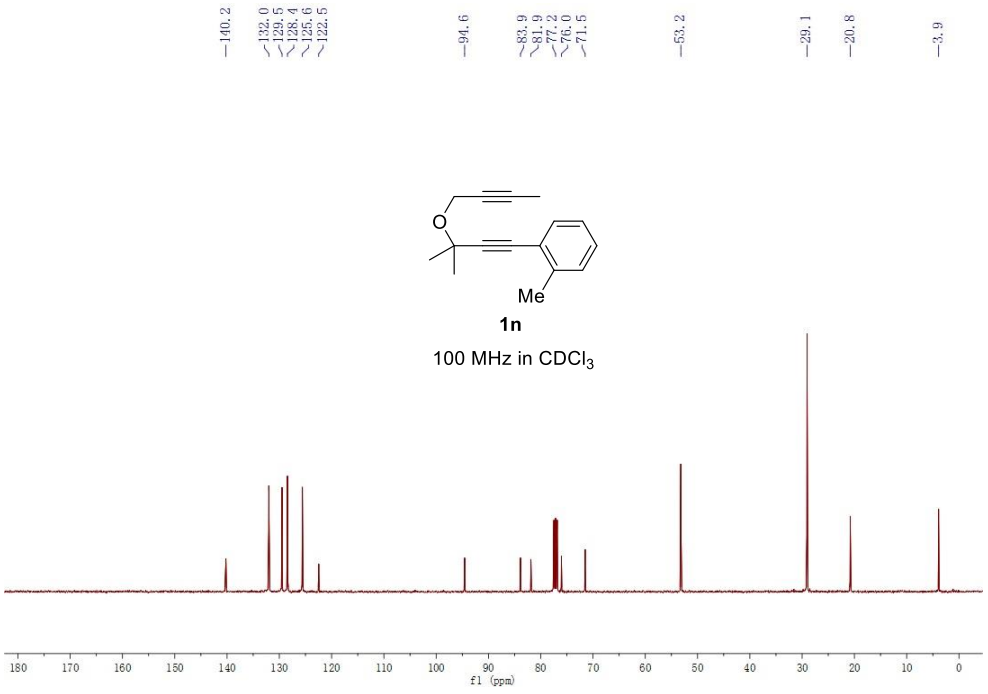
100 MHz in $CDCl_3$





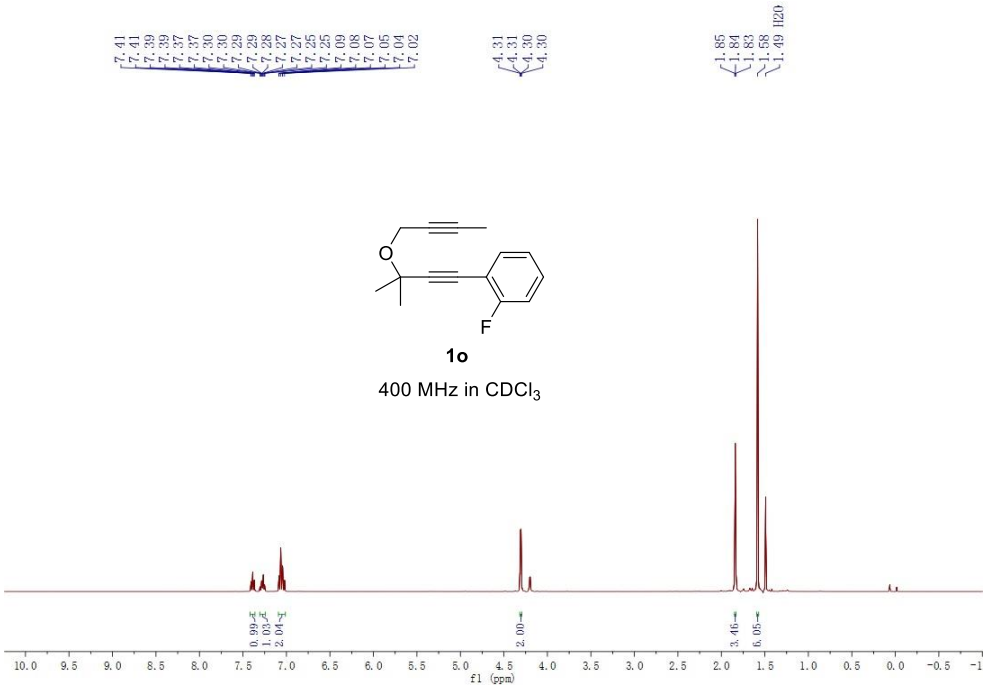
1n

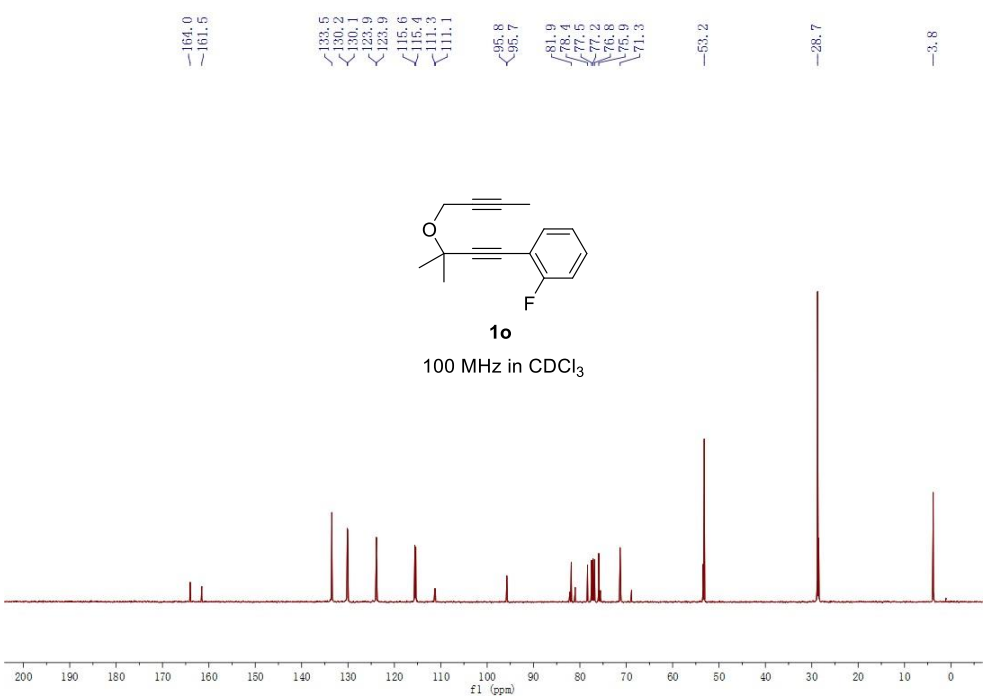
400 MHz in $CDCl_3$

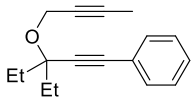


1n

100 MHz in $CDCl_3$

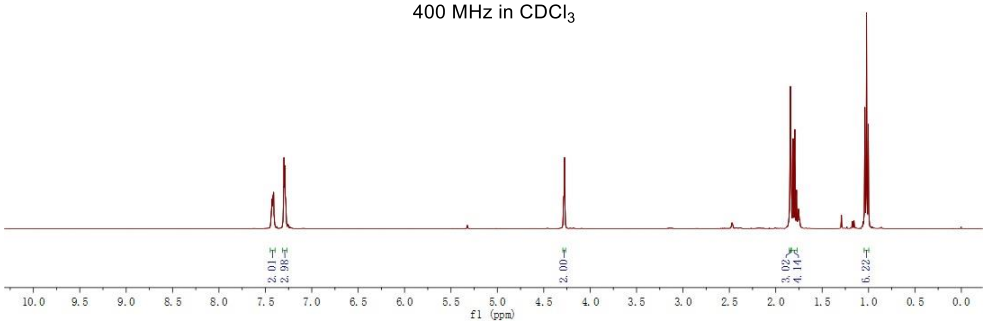

7.41
7.41
7.39
7.39
7.37
7.37
7.30
7.30
7.29
7.29
7.28
7.27
7.27
7.25
7.09
7.08
7.07
7.05
7.04
7.02
4.31
4.31
4.30
4.30
1.85
1.84
1.83
1.58
1.49
H2O
O
F
1o
400 MHz in CDCl3
0.99
1.03
2.04
2.00
3.46
6.05
f1 (ppm)

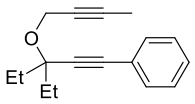

164.0
161.5
133.5
130.2
130.1
123.9
123.9
115.6
115.4
111.3
111.1
95.8
95.7
81.9
78.4
77.5
77.2
76.8
75.9
71.3
53.2
28.7
3.8
O
F
1o
100 MHz in CDCl3
f1 (ppm)



1p

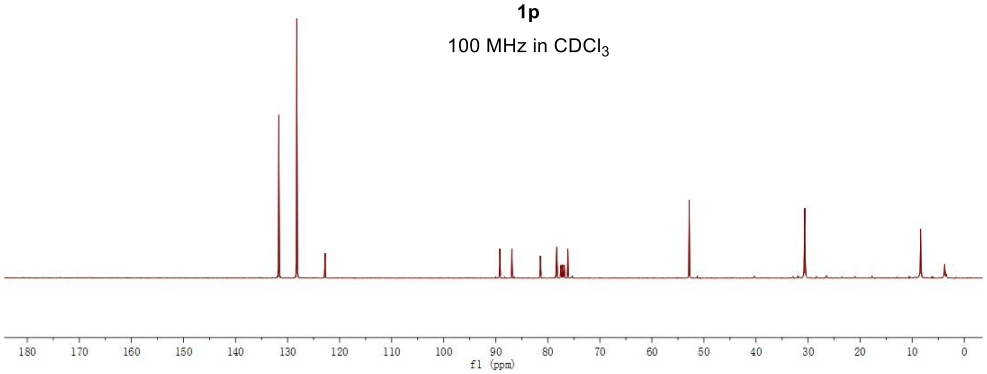
400 MHz in $CDCl_3$

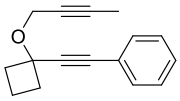




1p

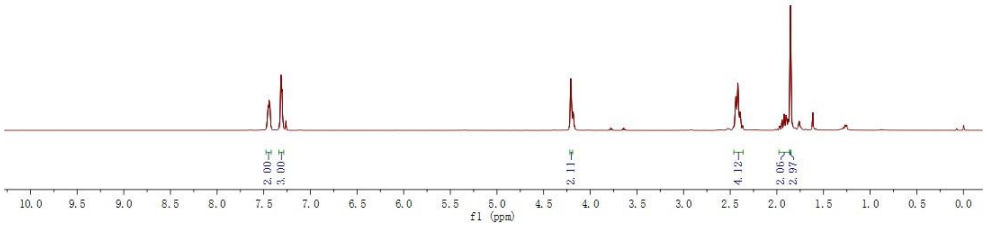
100 MHz in $CDCl_3$

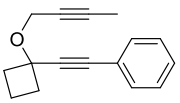




1q

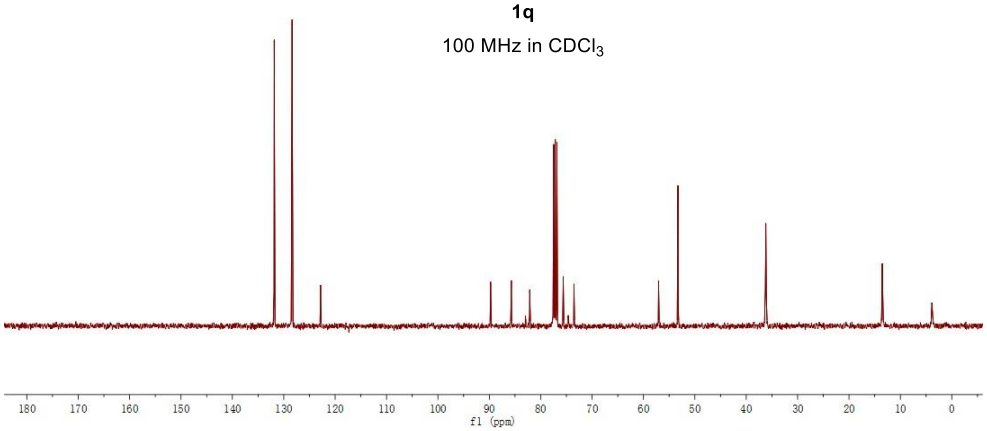
400 MHz in $CDCl_3$

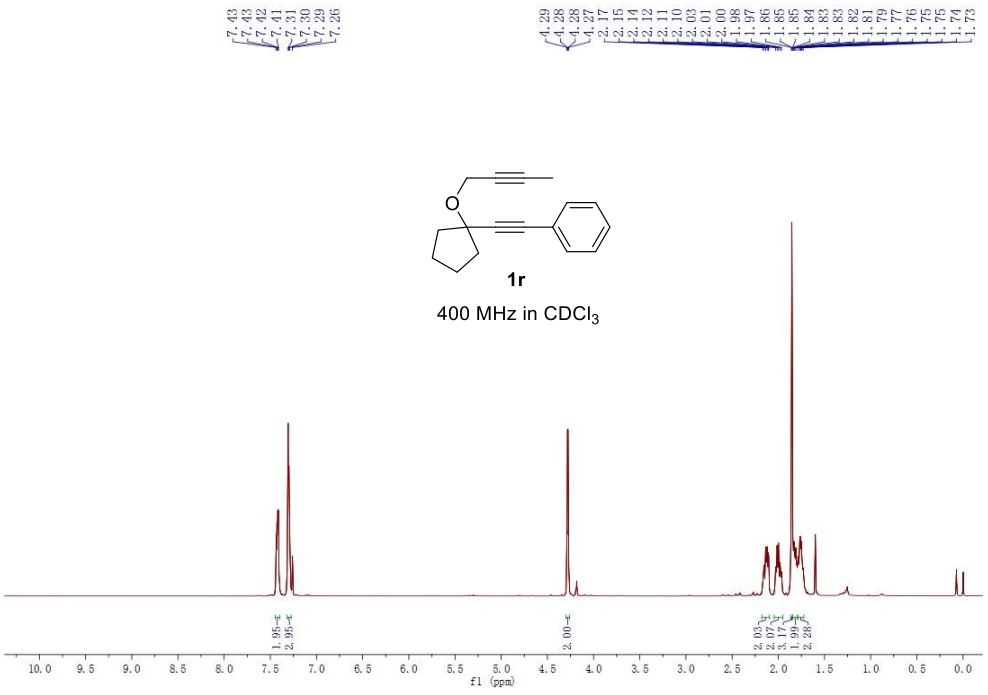


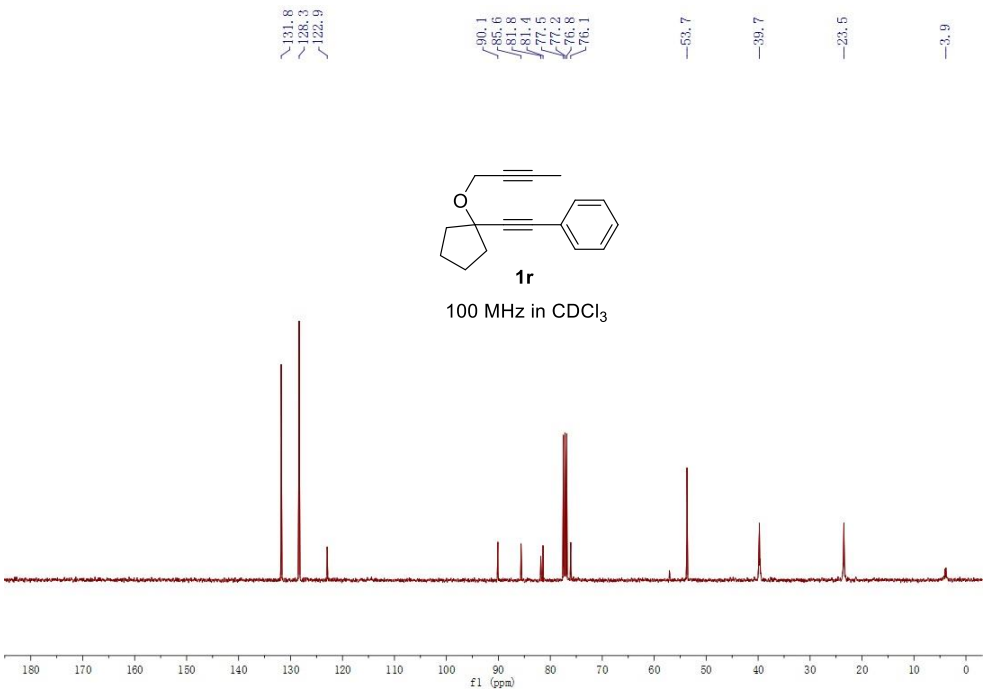


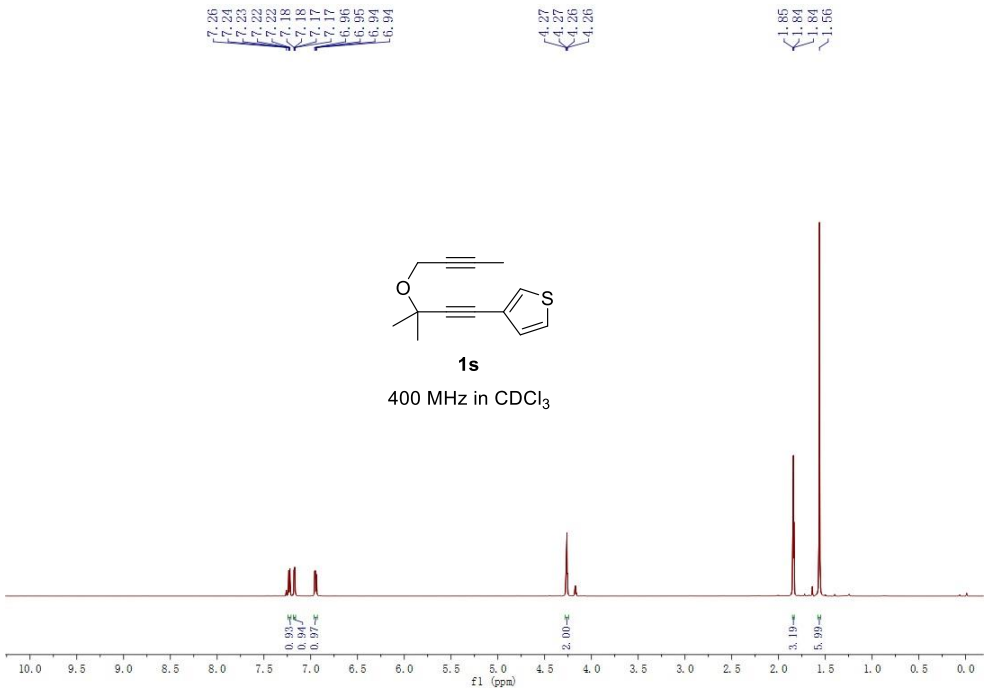
1q

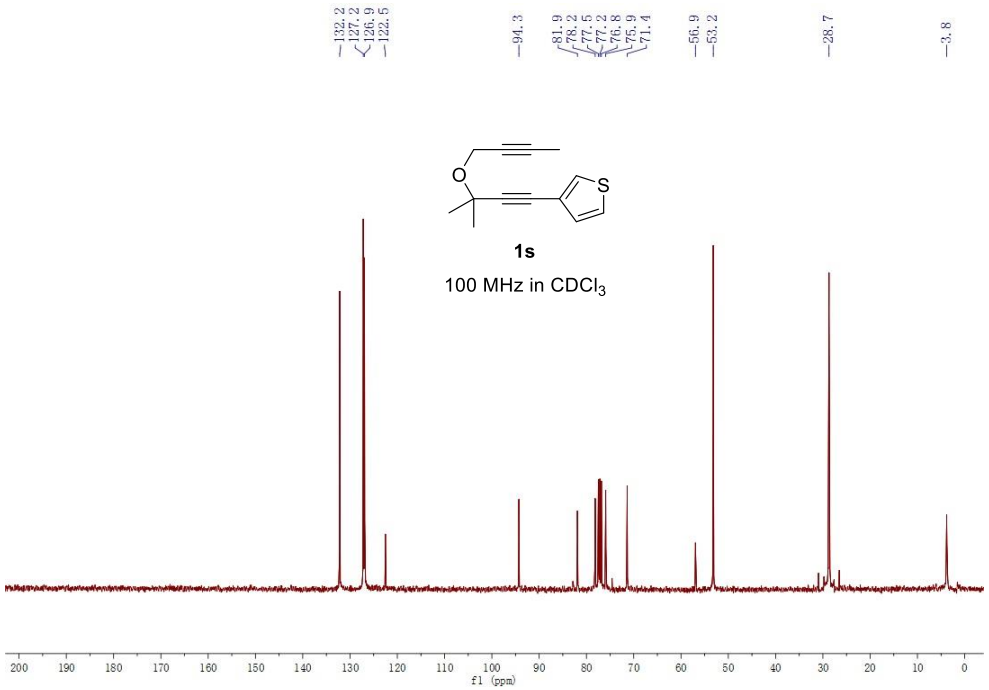
100 MHz in $CDCl_3$

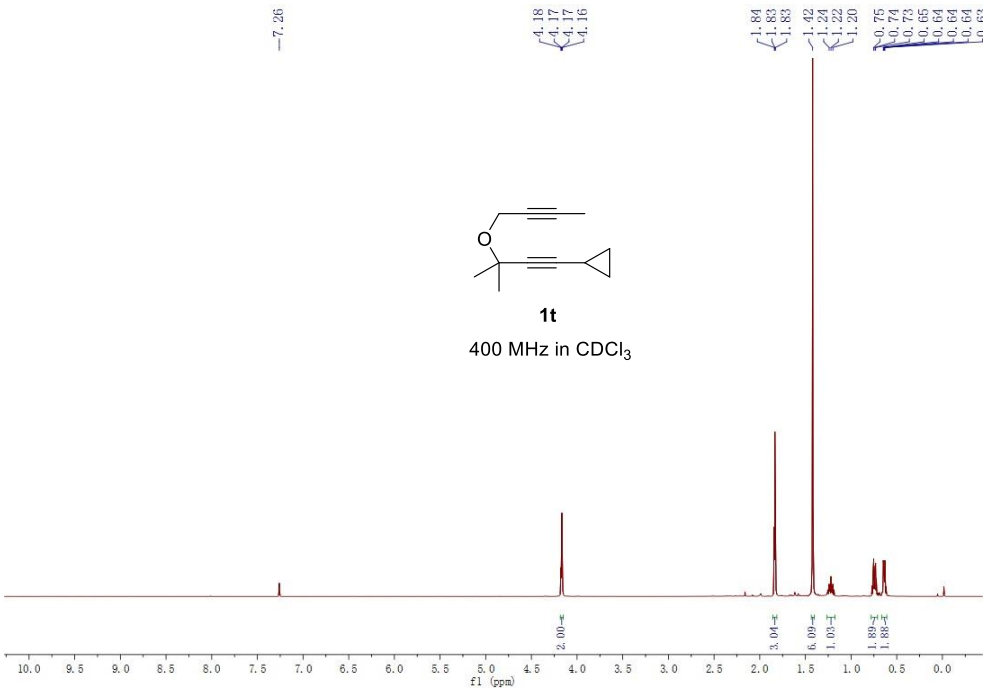



7.43
7.43
7.42
7.41
7.31
7.30
7.29
7.26
4.29
4.28
4.28
4.27
2.17
2.15
2.14
2.12
2.11
2.10
2.03
2.01
2.00
1.98
1.97
1.86
1.85
1.85
1.84
1.83
1.83
1.82
1.81
1.79
1.77
1.76
1.75
1.75
1.74
1.73
1r
400 MHz in CDCl3
1.95
2.95
2.00
2.03
2.07
3.17
1.99
2.28
f1 (ppm)


131.8
128.3
122.9
90.1
85.6
81.8
81.4
77.5
77.2
76.8
76.1
53.7
39.7
23.5
3.9
1r
100 MHz in CDCl3
f1 (ppm)

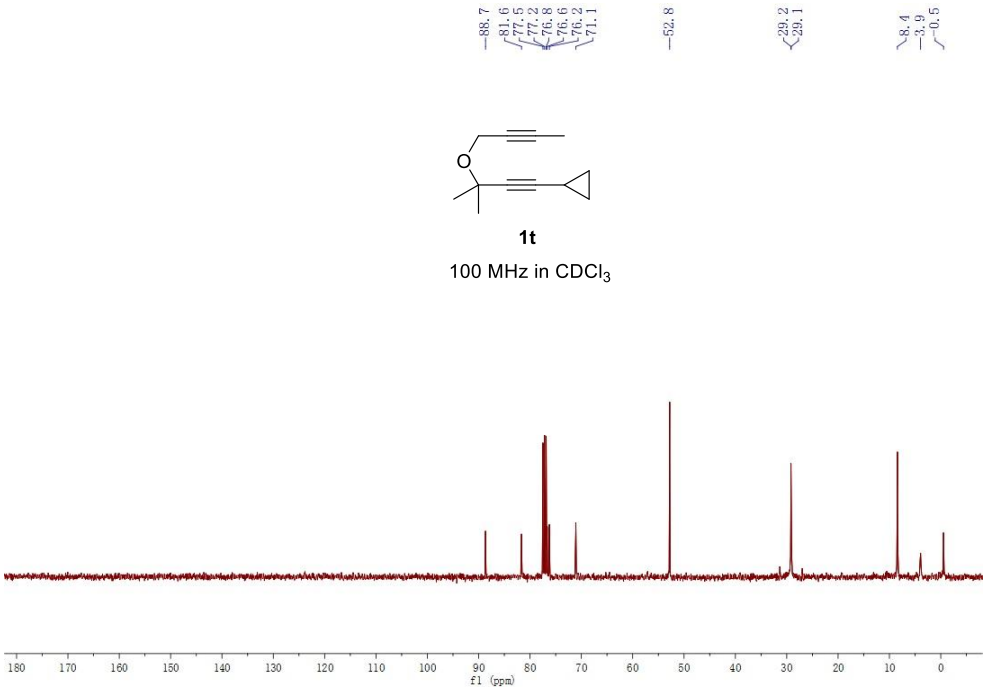

7.26
7.24
7.23
7.22
7.22
7.18
7.18
7.17
7.17
6.96
6.95
6.94
6.94
4.27
4.27
4.26
4.26
1.85
1.84
1.84
1.56
O
S
1s
400 MHz in CDCl3
0.93
0.94
0.97
2.00
3.19
5.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


132.2
127.2
126.9
122.5
94.3
81.9
78.2
77.5
77.2
76.8
75.9
71.4
56.9
53.2
28.7
3.8
O
S
1s
100 MHz in CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



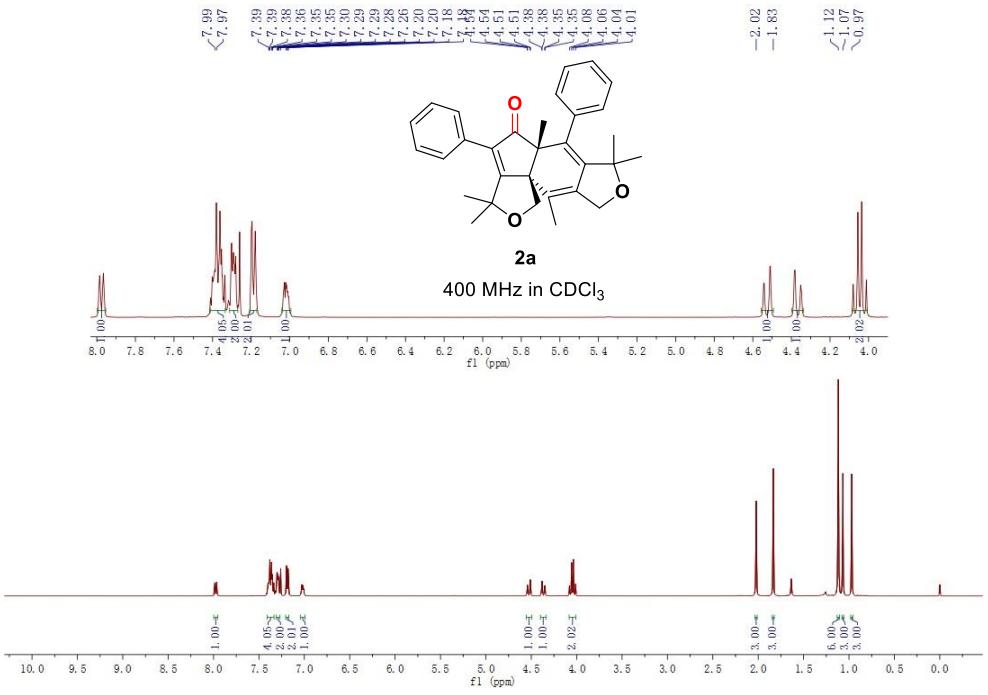
1t

400 MHz in $CDCl_3$

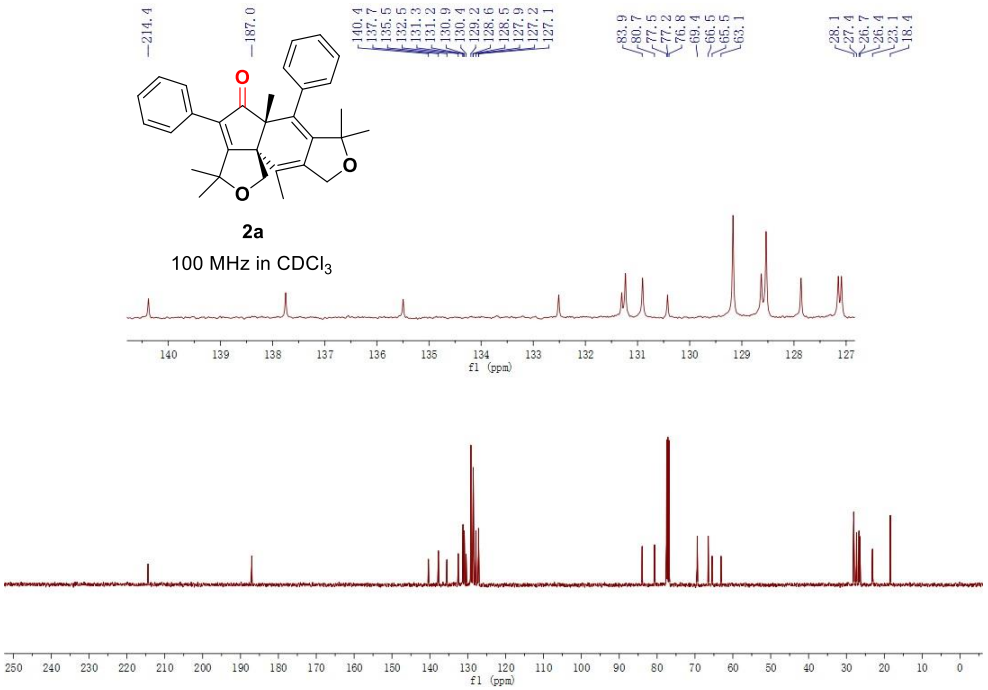


1t

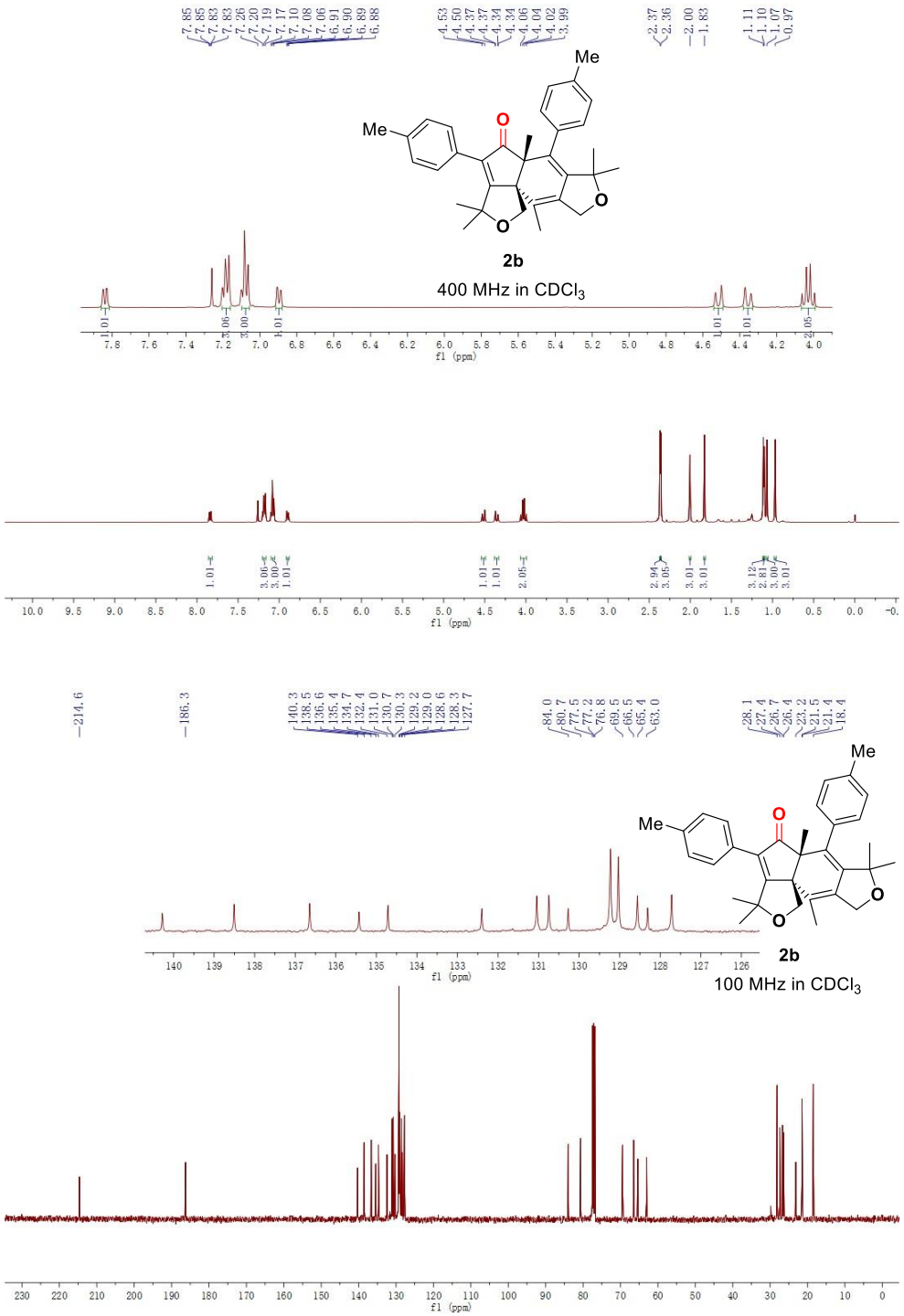
100 MHz in $CDCl_3$

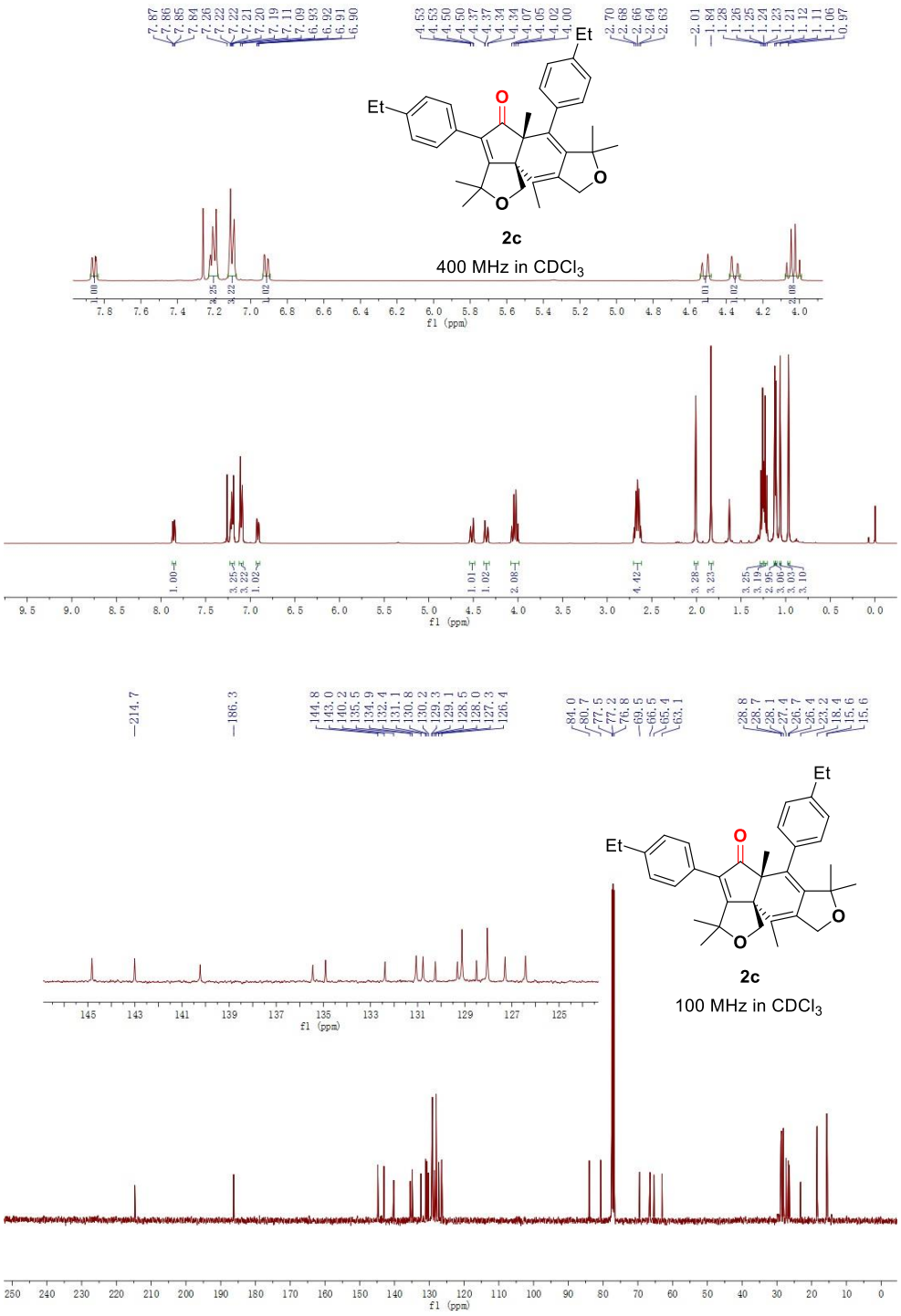

7.99
7.97
7.39
7.39
7.38
7.36
7.35
7.35
7.30
7.29
7.29
7.28
7.26
7.20
7.20
7.18
4.54
4.54
4.51
4.51
4.38
4.38
4.35
4.35
4.08
4.06
4.04
4.01
2.02
1.83
1.12
1.07
0.97
O
O
O
2a
400 MHz in CDCl3
f1 (ppm)

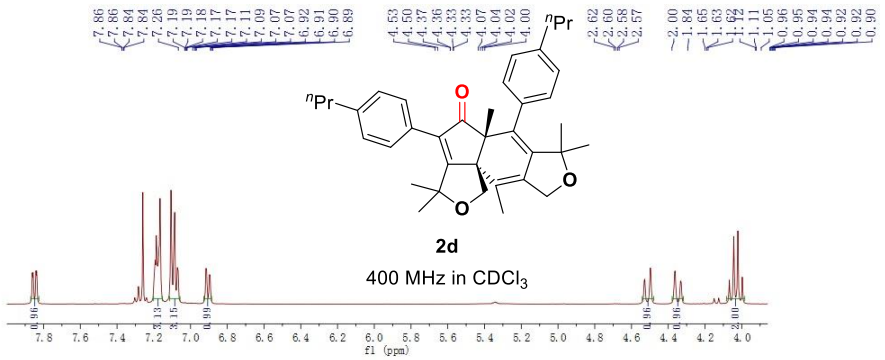
f1 (ppm)

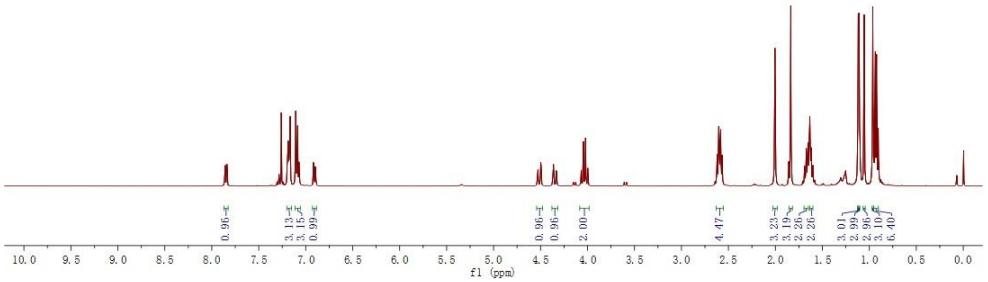

214.4
187.0
140.4
137.7
135.5
132.5
131.3
131.2
130.9
130.4
129.2
128.6
128.5
127.9
127.2
127.1
83.9
80.7
77.5
77.2
76.8
69.4
66.5
65.5
63.1
28.1
27.4
26.7
26.4
23.1
18.4
O
O
O
2a
100 MHz in CDCl3
f1 (ppm)

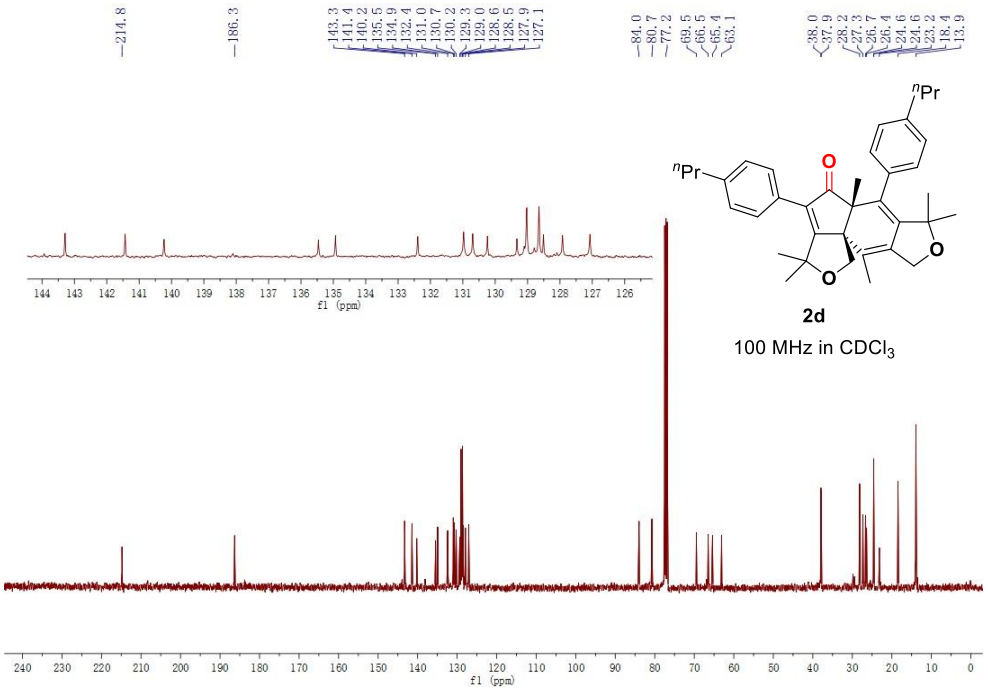
f1 (ppm)

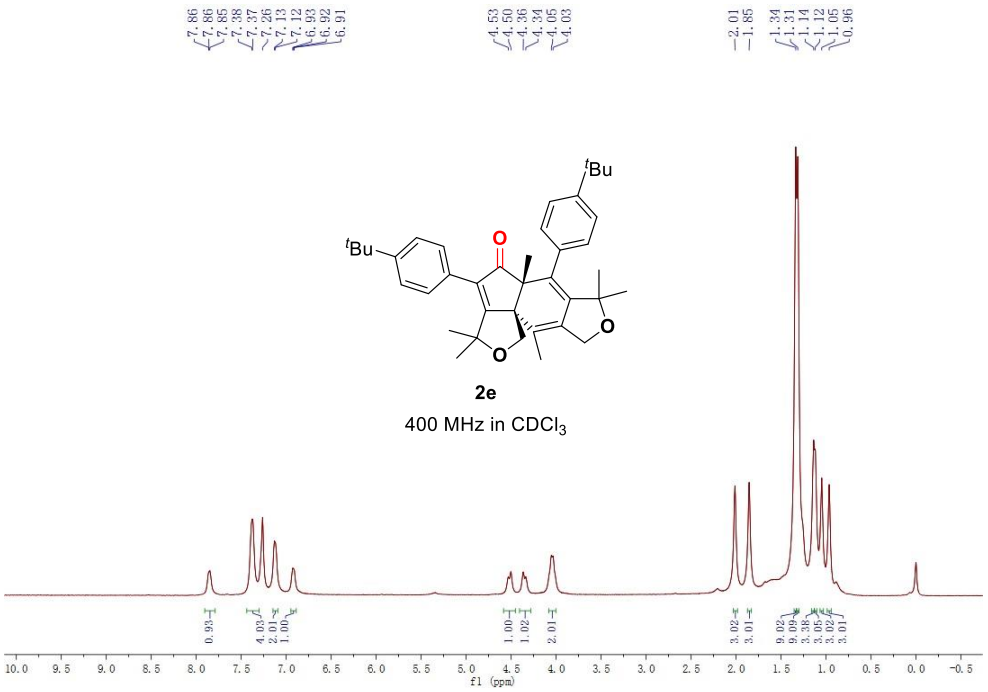

Me
Me
O
O
O
2b
400 MHz in CDCl3
f1 (ppm)
f1 (ppm)
Me
Me
O
O
O
2b
100 MHz in CDCl3
f1 (ppm)
f1 (ppm)

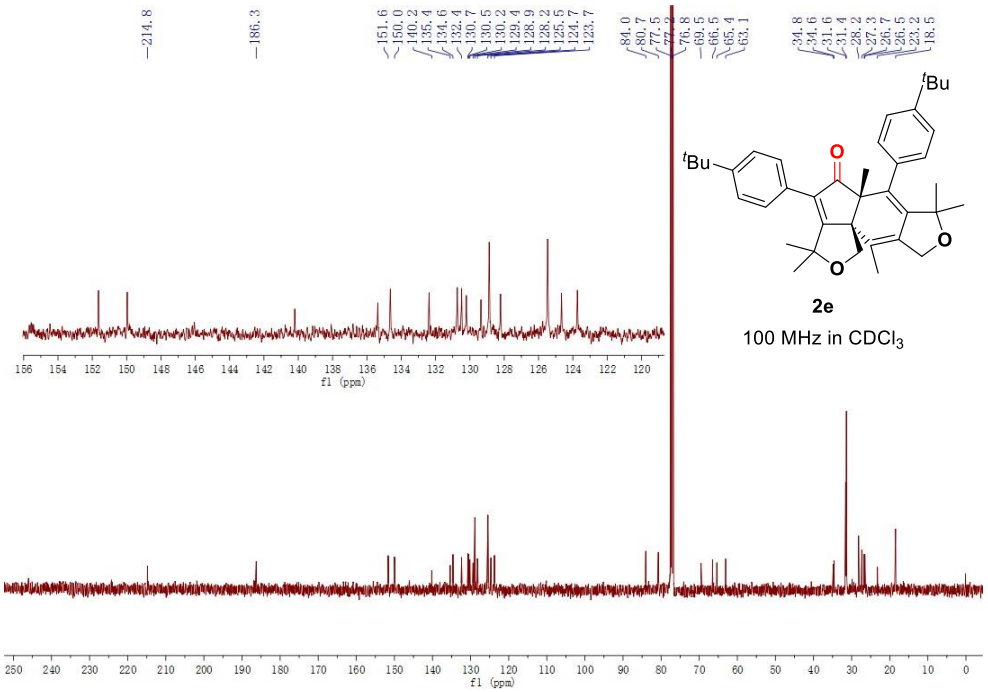

Et
O
Et
O
O
2c
400 MHz in CDCl3
f1 (ppm)
f1 (ppm)
Et
O
Et
O
O
2c
100 MHz in CDCl3
f1 (ppm)
f1 (ppm)

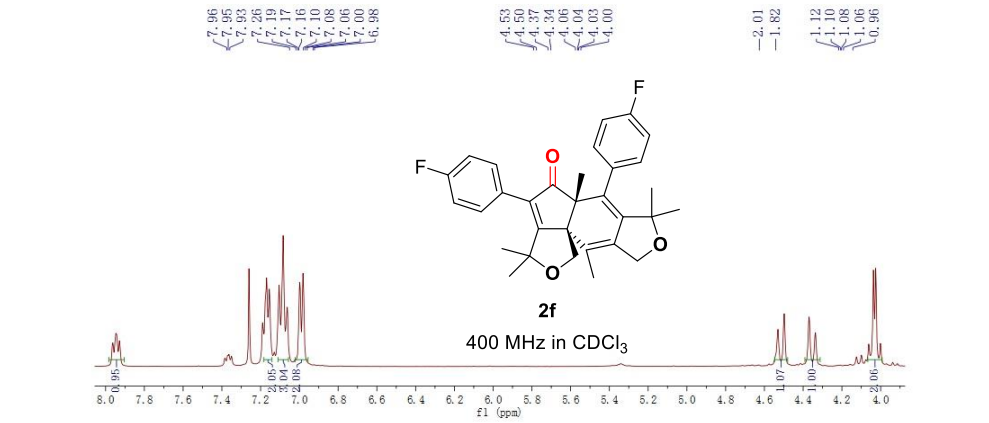

nPr
O
O
O
nPr
2d
400 MHz in CDCl3
f1 (ppm)

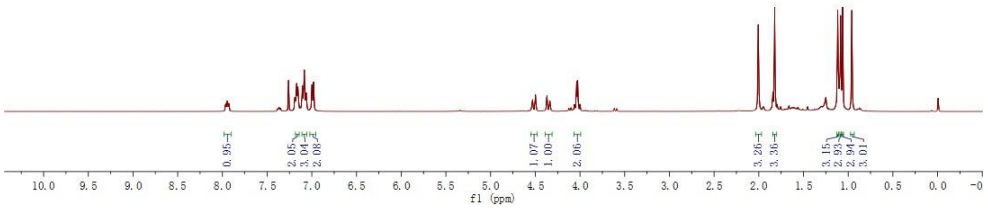

f1 (ppm)

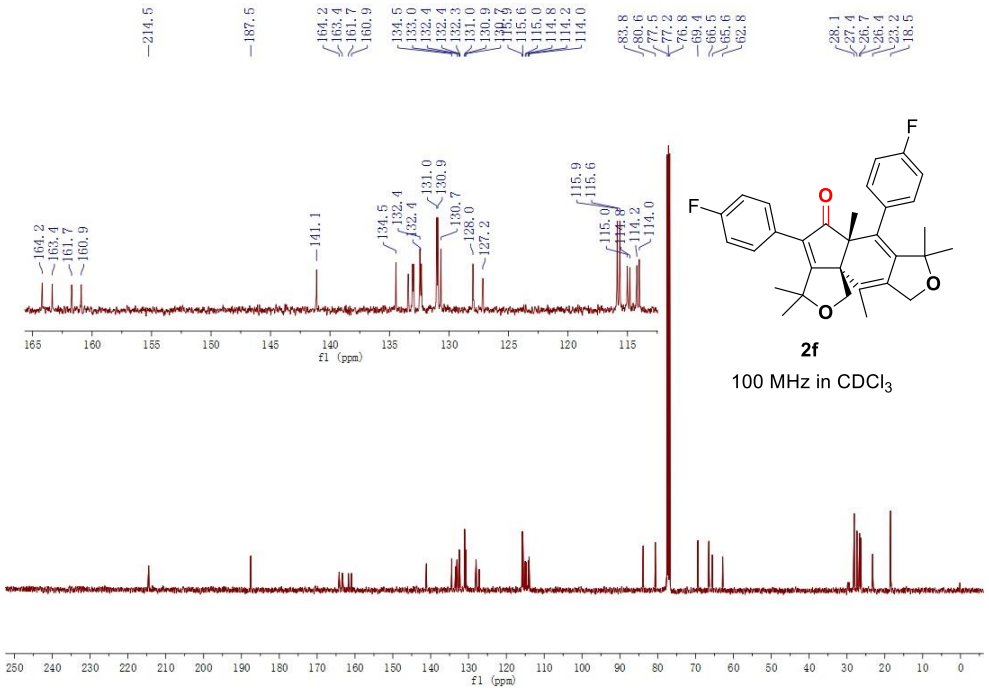

nPr
O
O
O
nPr
2d
100 MHz in CDCl3
f1 (ppm)
f1 (ppm)

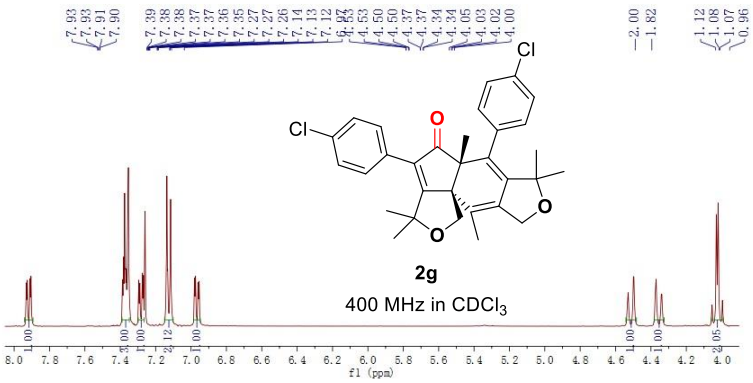

7.86
7.86
7.85
7.38
7.37
7.26
7.13
7.12
6.93
6.92
6.91
4.53
4.50
4.36
4.34
4.05
4.03
2.01
1.85
1.34
1.31
1.14
1.12
1.05
0.96
tBu
tBu
O
O
O
2e
400 MHz in CDCl3
0.93
4.03
2.14
1.00
1.00
1.02
2.01
3.02
3.01
9.02
9.09
3.38
3.08
3.02
3.01
f1 (ppm)

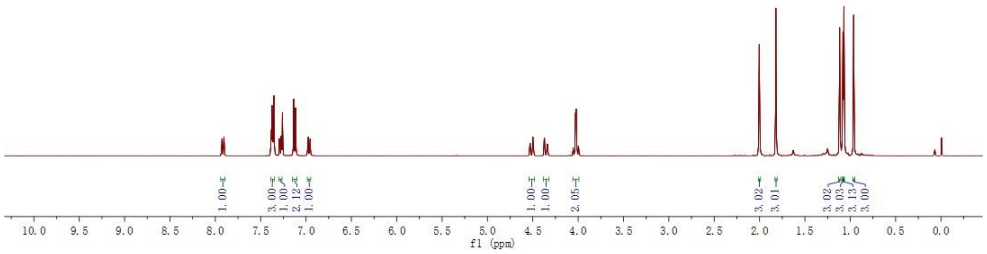

214.8
186.3
151.6
150.0
140.2
135.4
134.6
132.4
130.7
130.5
130.2
129.4
128.9
128.2
125.5
124.7
123.7
84.0
80.7
77.5
77.2
76.8
69.5
66.5
65.4
63.1
34.8
34.6
31.6
31.4
28.2
27.3
26.7
26.5
23.2
18.5
tBu
tBu
O
O
O
2e
100 MHz in CDCl3
f1 (ppm)
f1 (ppm)

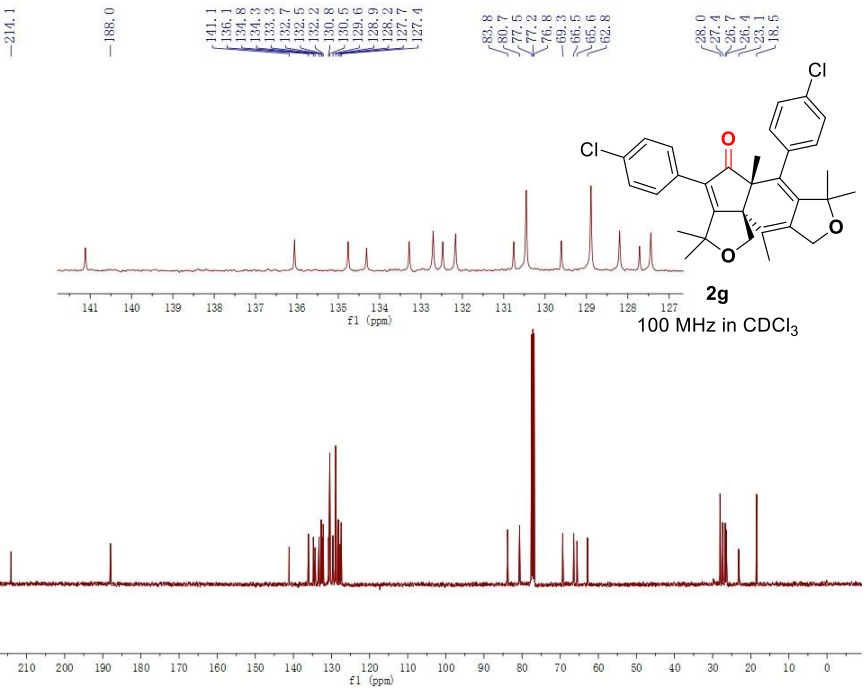

F
F
O
O
O
2f
400 MHz in CDCl3
f1 (ppm)

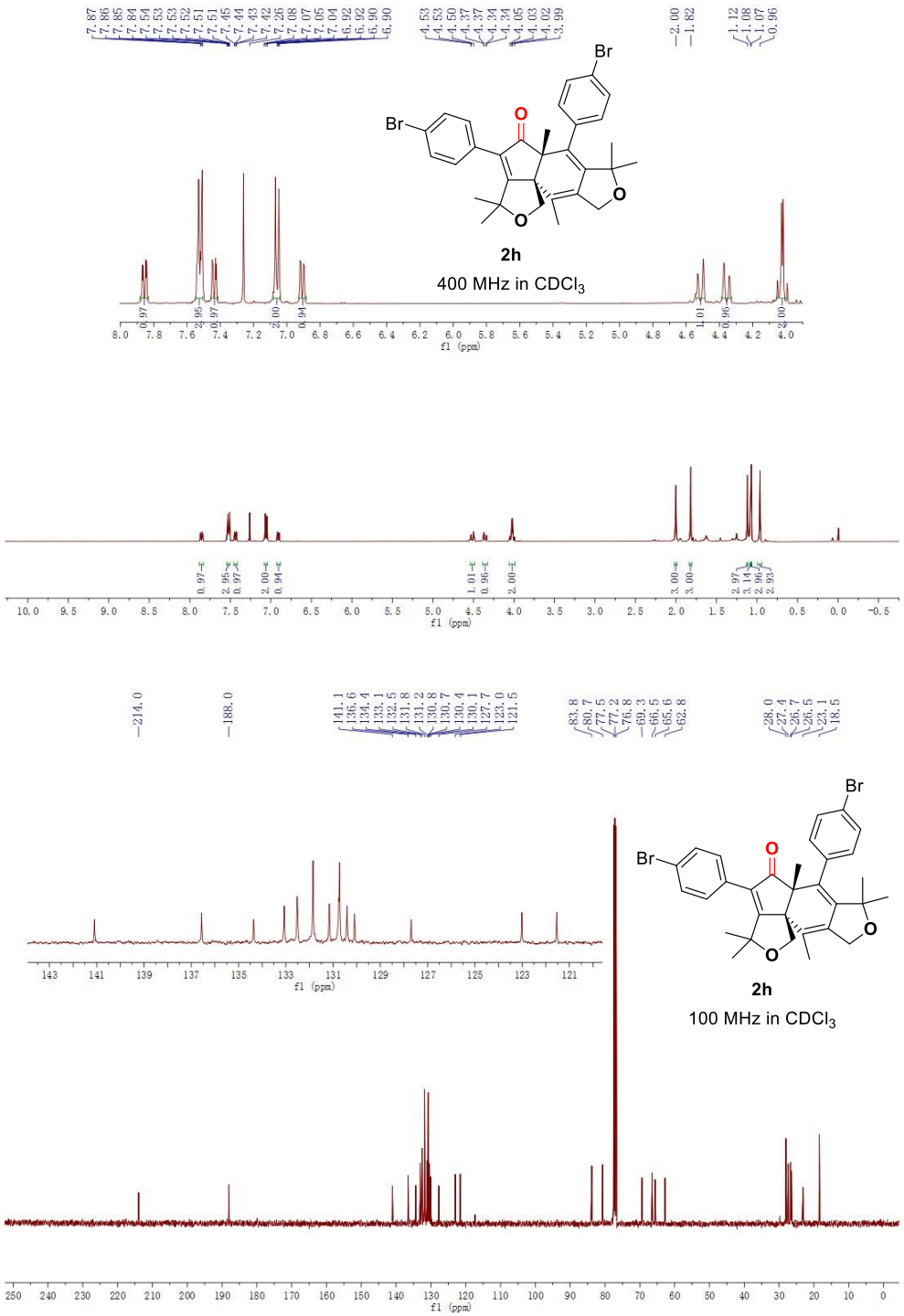

f1 (ppm)

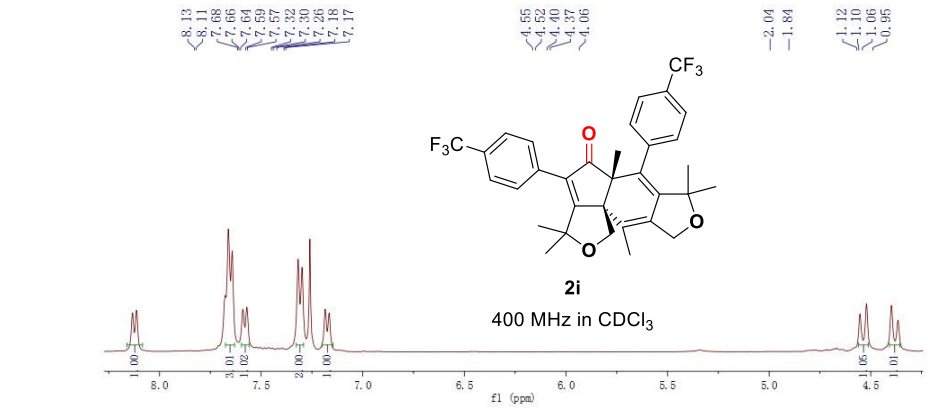

F
F
O
O
O
2f
100 MHz in CDCl3
f1 (ppm)

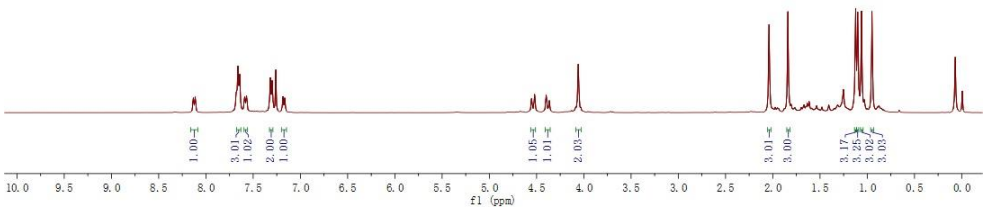

Cl
Cl
O
O
O
2g
400 MHz in CDCl3

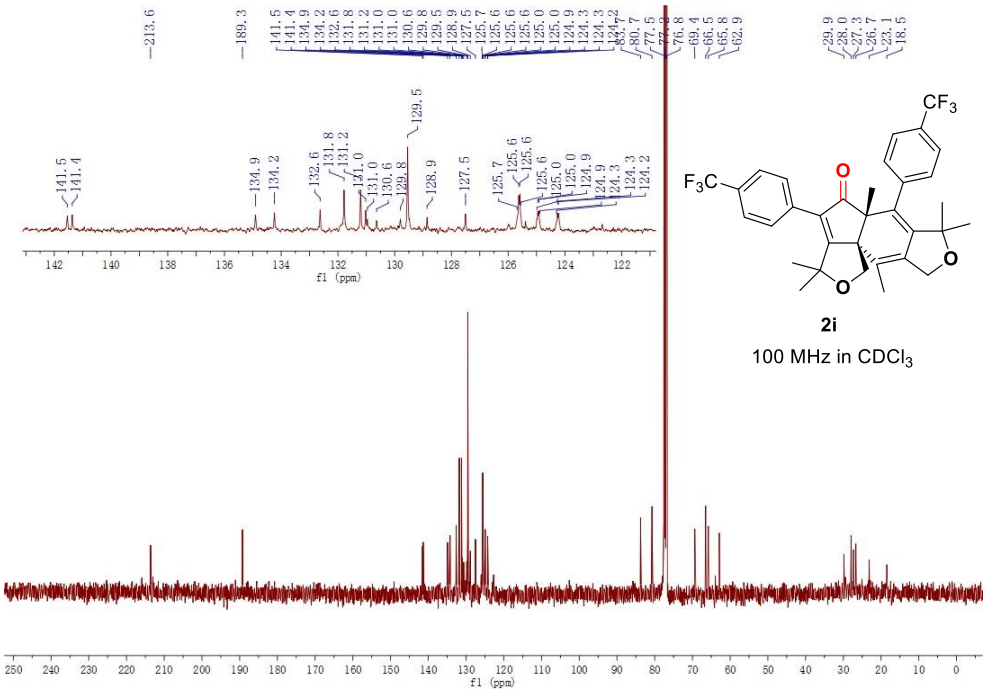


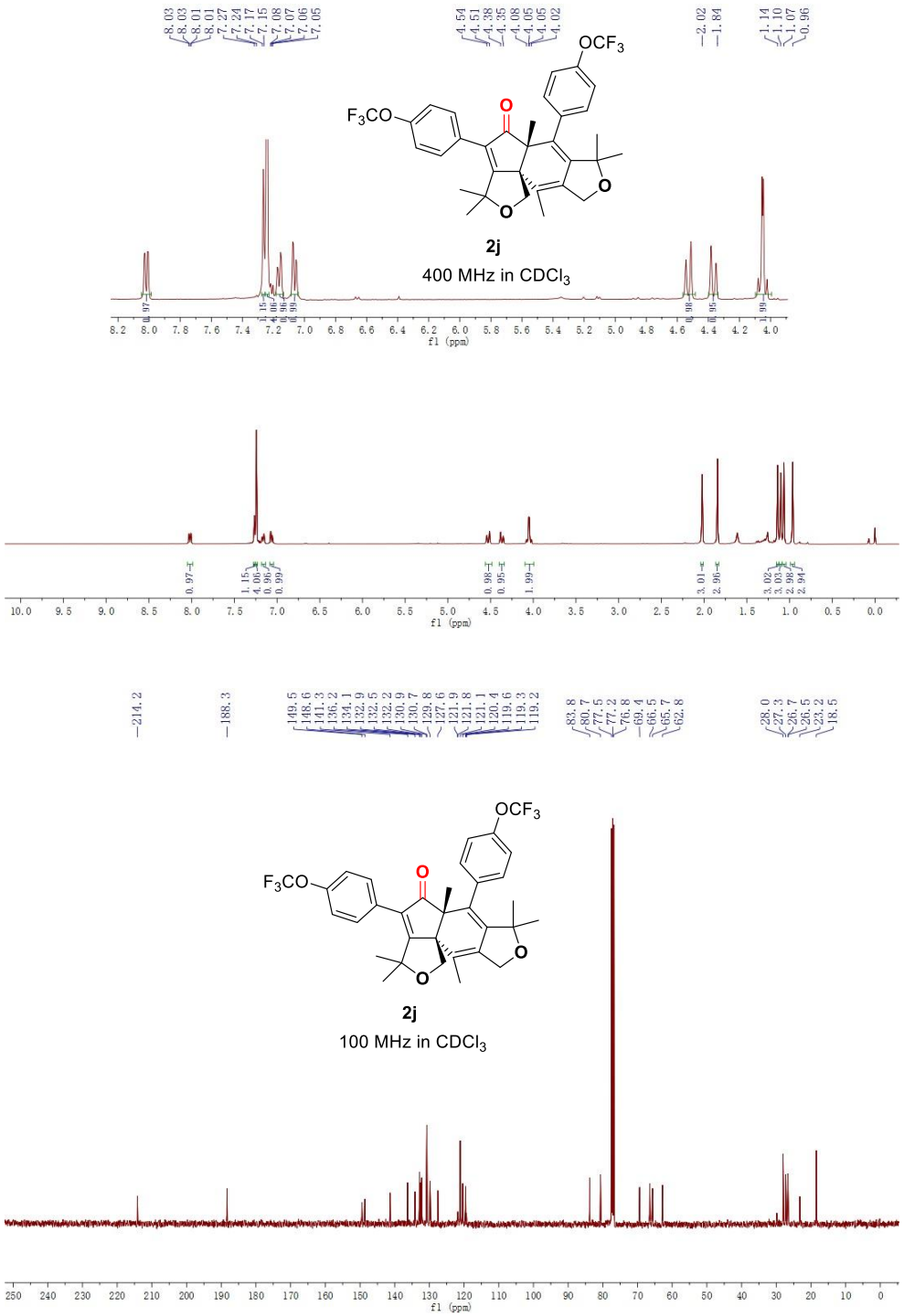

Cl
Cl
O
O
O
2g
100 MHz in CDCl3

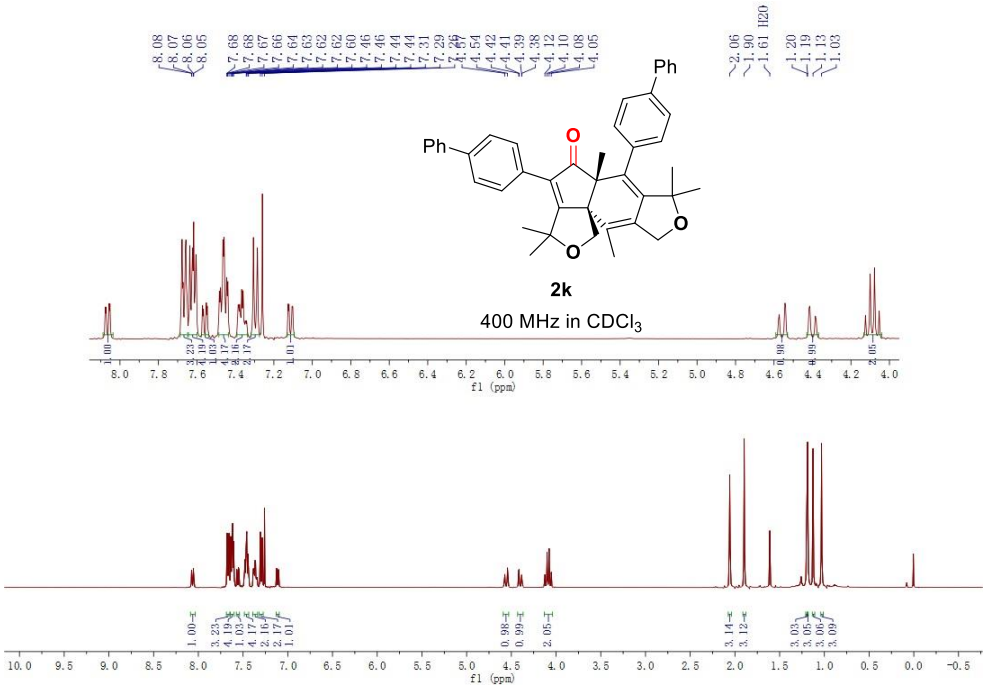

Br
Br
O
O
O
2h
400 MHz in CDCl3
f1 (ppm)
Br
Br
O
O
O
2h
100 MHz in CDCl3
f1 (ppm)

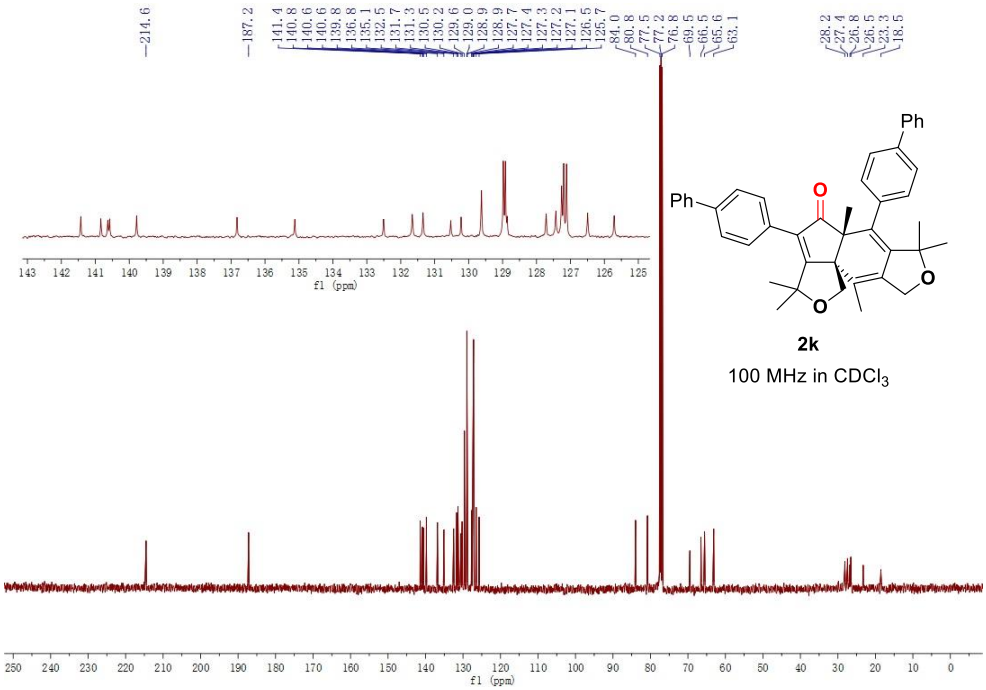

8.13
8.11
7.68
7.66
7.64
7.59
7.57
7.32
7.30
7.26
7.18
7.17
4.55
4.52
4.40
4.37
4.06
2.04
1.84
1.12
1.10
1.06
0.95
CF3
F3C
O
O
O
2i
400 MHz in CDCl3
f1 (ppm)


f1 (ppm)


213.6
189.3
141.5
141.4
134.9
134.2
132.6
131.8
131.2
131.0
130.6
129.8
129.5
128.9
127.5
125.7
125.6
125.0
124.9
124.3
124.2
80.7
77.5
76.8
69.4
66.5
65.8
62.9
29.9
28.0
27.3
26.7
23.1
18.5
CF3
F3C
O
O
O
2i
100 MHz in CDCl3
f1 (ppm)


OCF3
F3CO
O
O
O
2j
400 MHz in CDCl3
f1 (ppm)
2j
100 MHz in CDCl3
f1 (ppm)

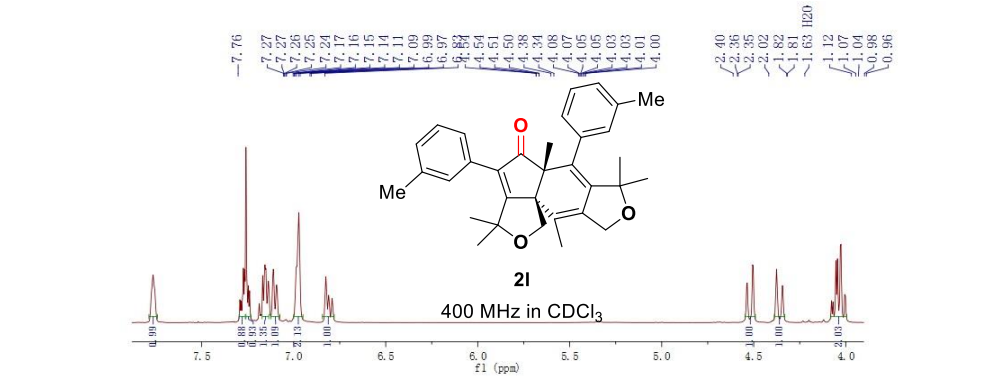

Ph
Ph
O
O
O
2k
400 MHz in CDCl3
f1 (ppm)

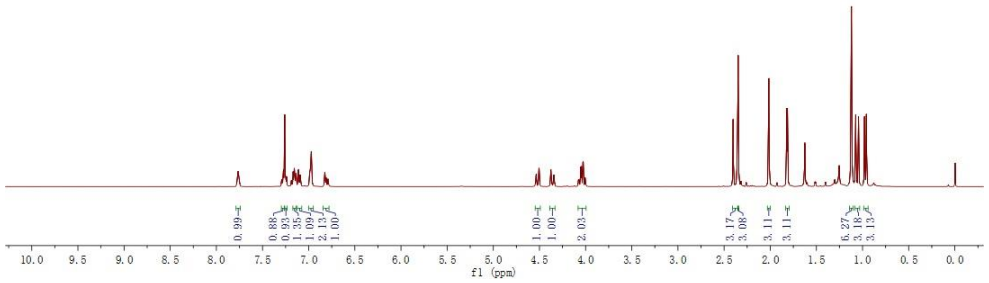

f1 (ppm)

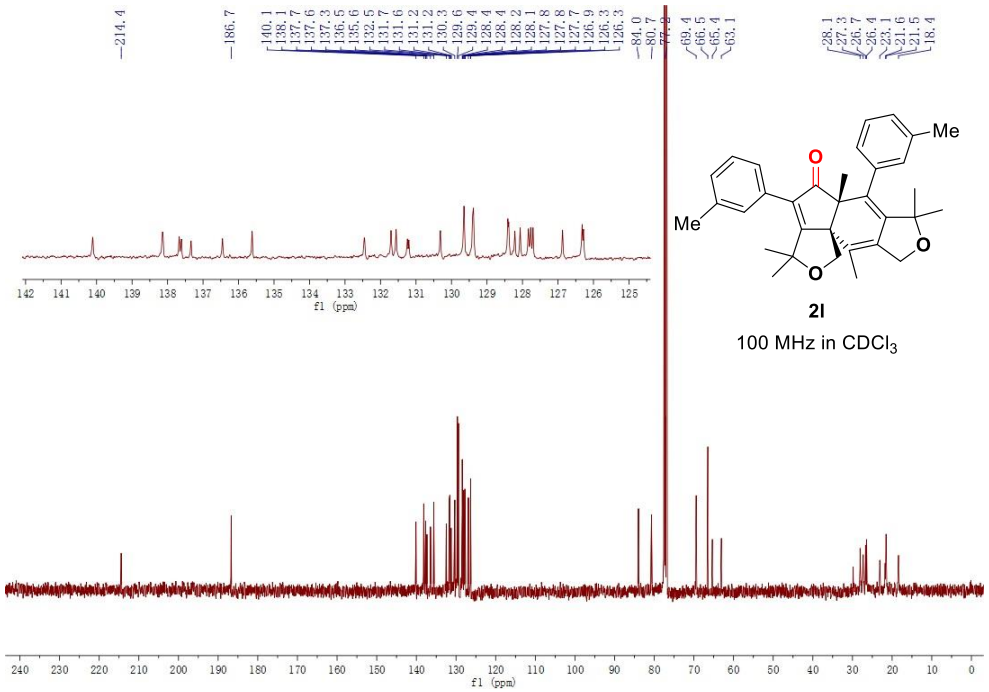
f1 (ppm)

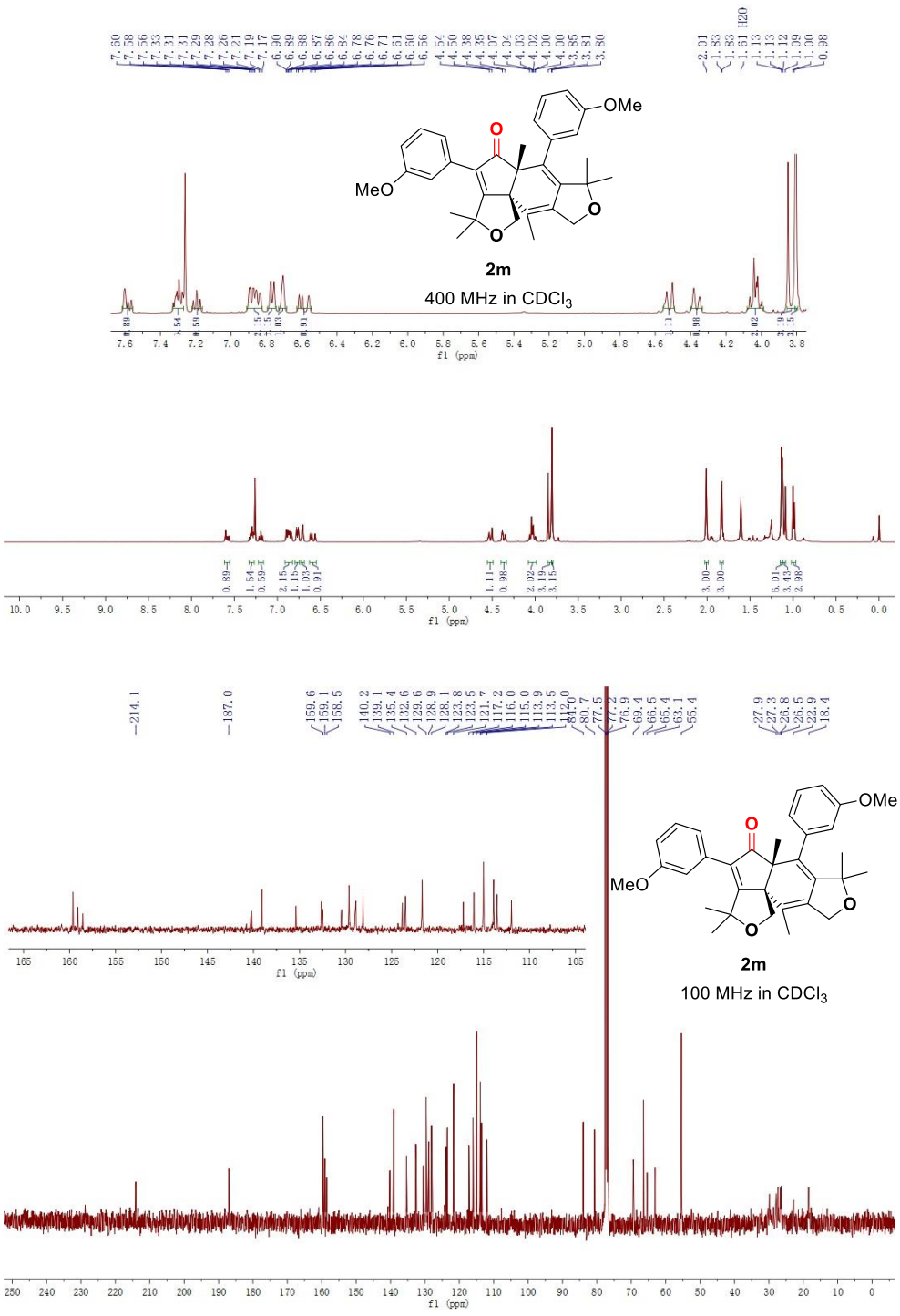
f1 (ppm)

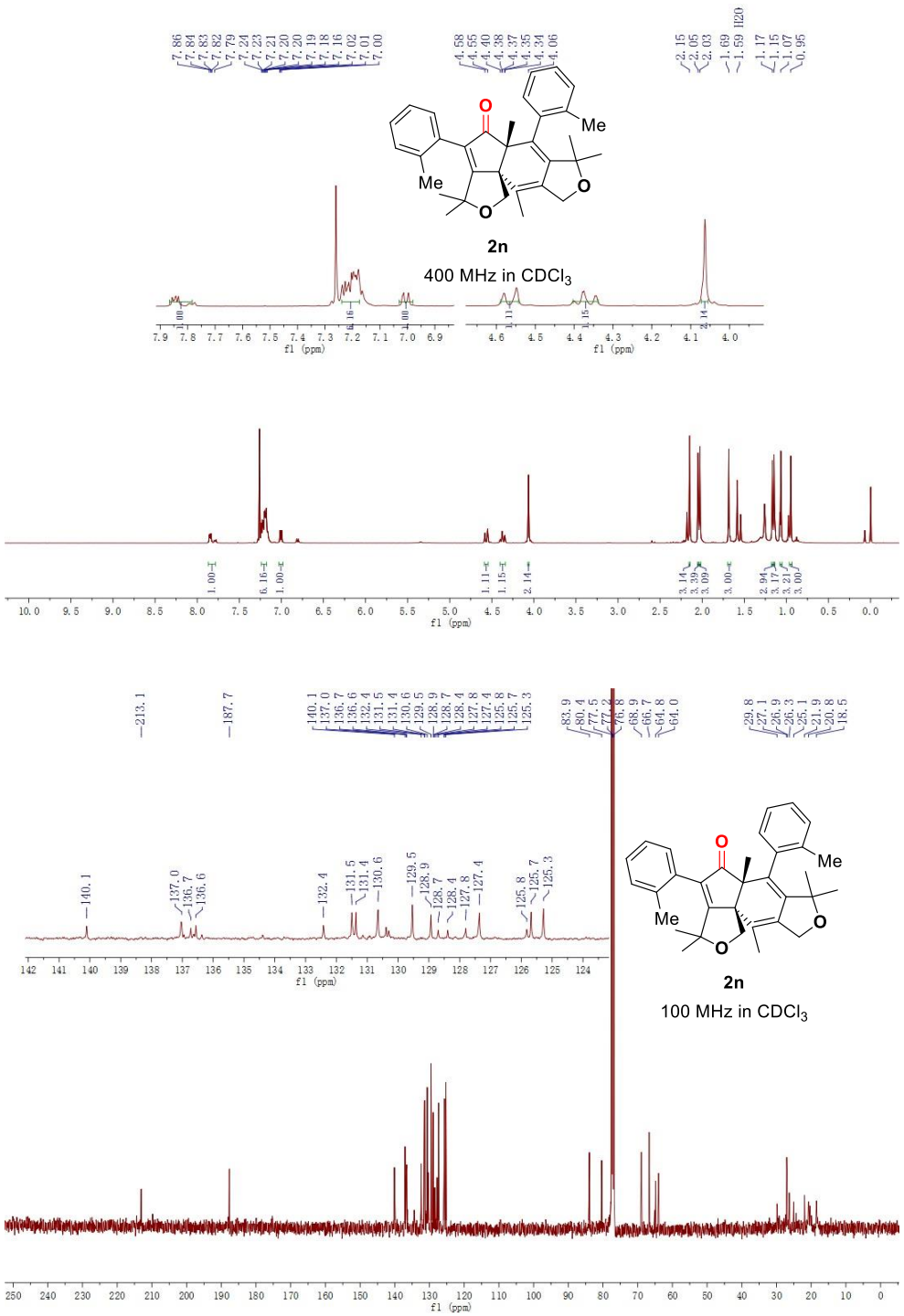
Ph
Ph
O
O
O
2k
100 MHz in CDCl3
f1 (ppm)

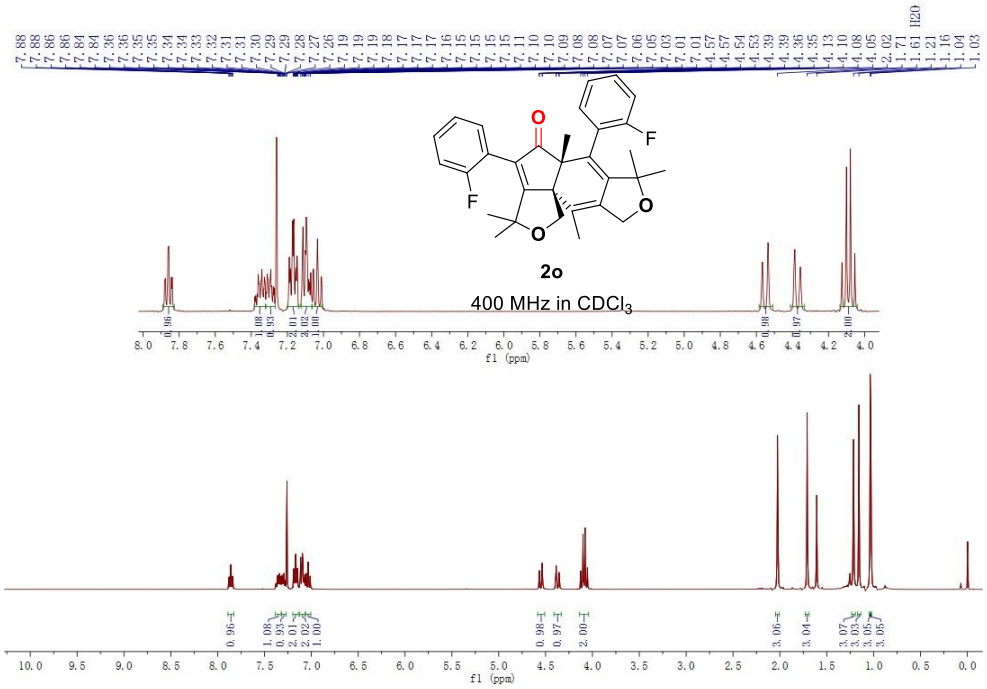

Me
O
Me
O
O
2l
400 MHz in CDCl3

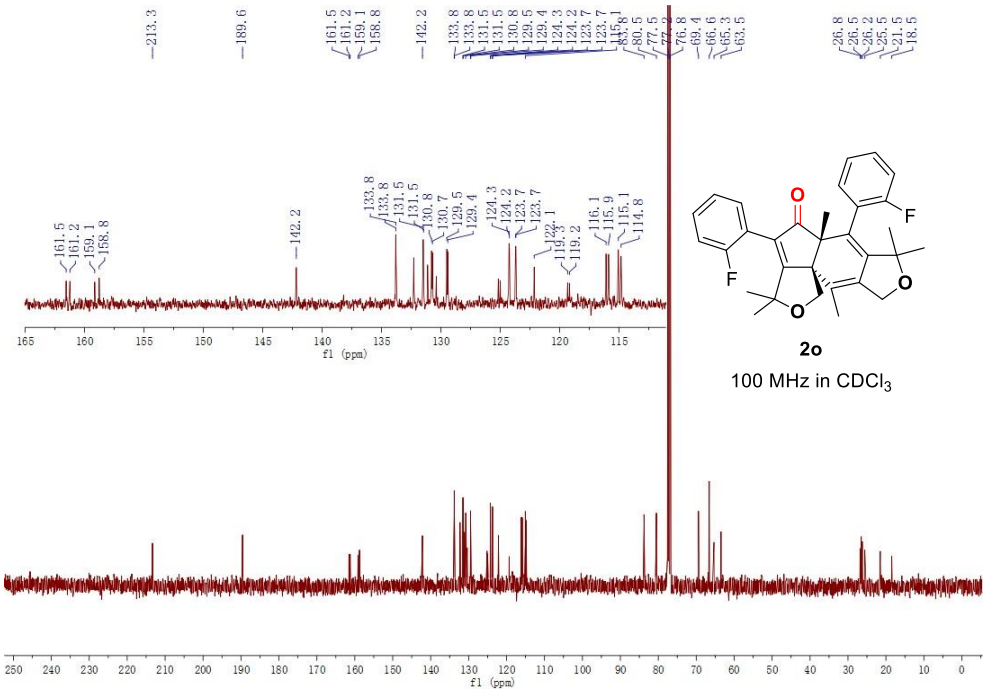


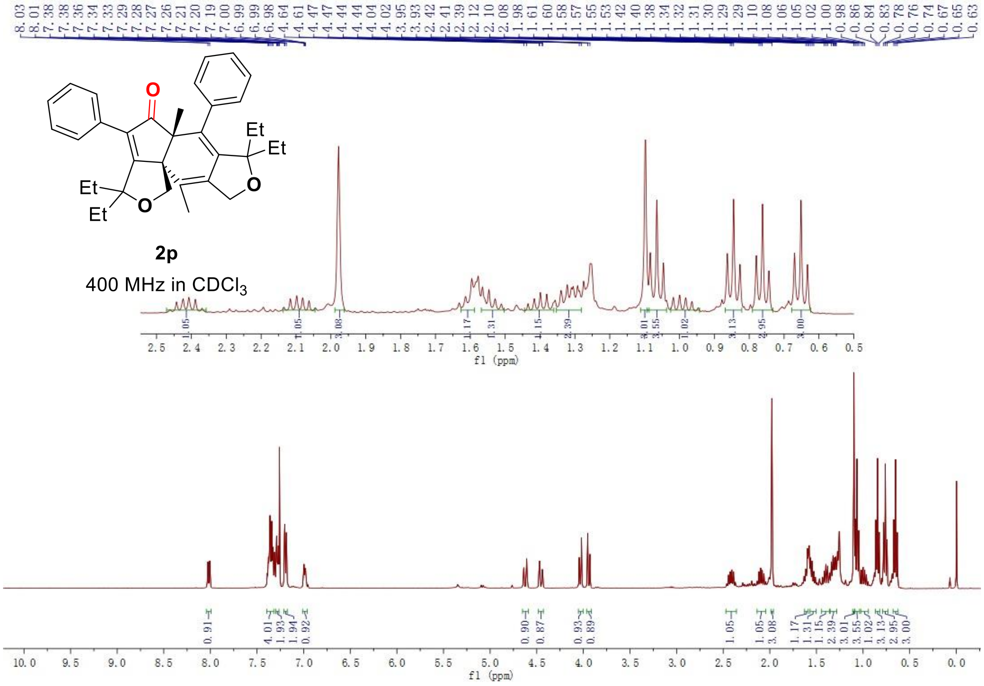

Me
O
Me
O
O
2l
100 MHz in CDCl3

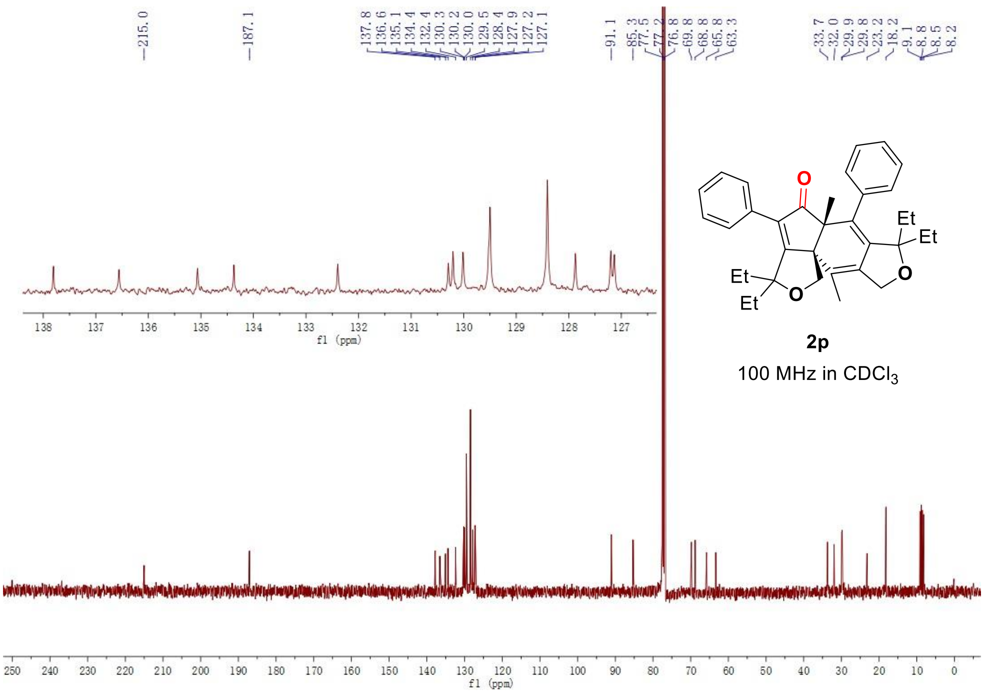

OMe
MeO
O
O
O
2m
400 MHz in CDCl3
f1 (ppm)
f1 (ppm)
OMe
MeO
O
O
O
2m
100 MHz in CDCl3
f1 (ppm)
f1 (ppm)

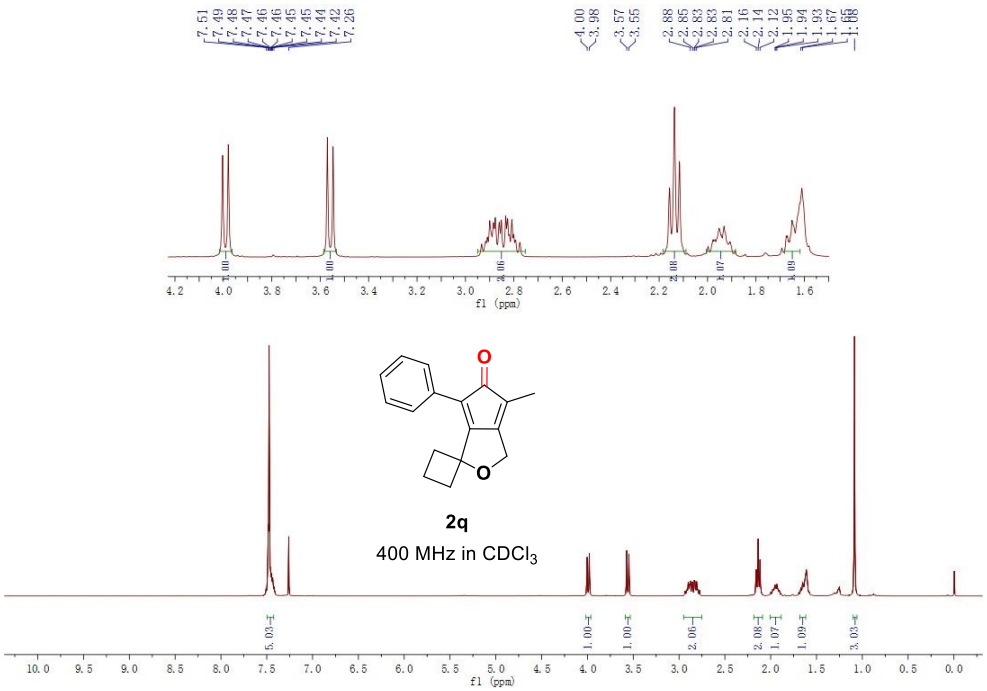

Me
Me
O
O
O
2n
400 MHz in CDCl3
f1 (ppm)
f1 (ppm)
f1 (ppm)
Me
Me
O
O
O
2n
100 MHz in CDCl3
f1 (ppm)
f1 (ppm)

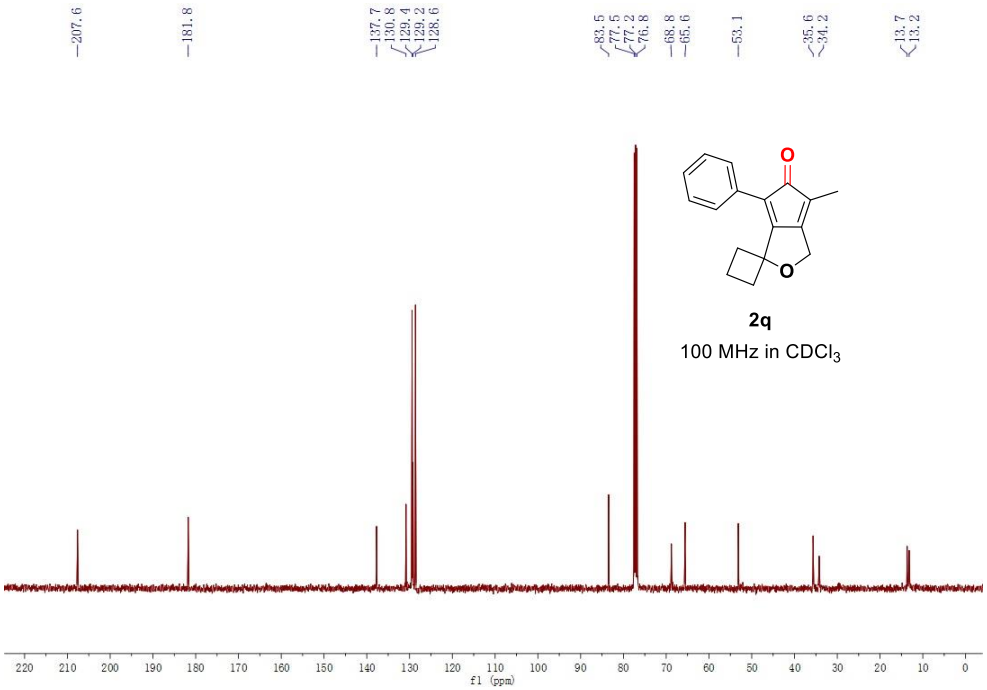

2o
400 MHz in CDCl3
f1 (ppm)

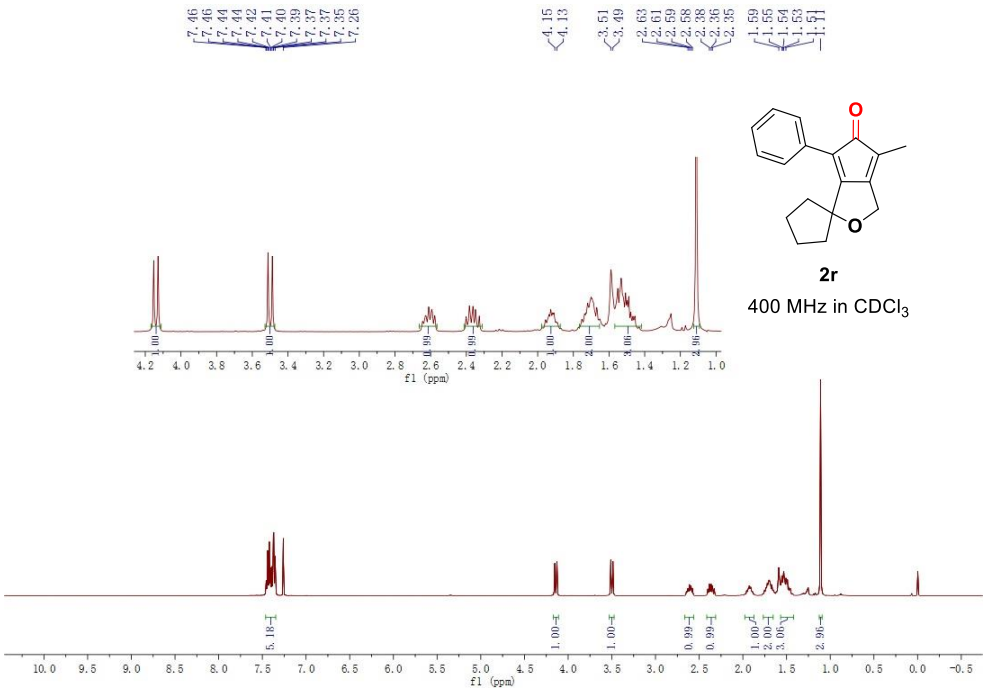

2o
100 MHz in CDCl3
f1 (ppm)


8.03 8.01 7.38 7.38 7.36 7.34 7.33 7.29 7.28 7.27 7.26 7.21 7.20 7.19 7.00 6.99 6.99 6.98 4.64 4.61 4.47 4.47 4.44 4.44 4.04 4.02 3.95 3.93 2.42 2.41 2.39 2.12 2.10 2.08 1.98 1.61 1.60 1.58 1.57 1.55 1.53 1.42 1.40 1.38 1.34 1.32 1.31 1.30 1.29 1.29 1.10 1.08 1.06 1.06 1.05 1.02 1.00 0.98 0.86 0.84 0.83 0.78 0.76 0.74 0.67 0.65 0.63
O
Et
Et
Et
Et
O
O
2p
400 MHz in CDCl3
f1 (ppm)
f1 (ppm)


215.0
187.1
137.8 136.6 135.1 134.4 132.4 130.3 130.2 130.0 129.5 128.4 127.9 127.2 127.1
91.1
85.3 77.5 77.2 76.8 69.8 68.8 65.8 63.3
33.7 32.0 29.9 29.8 23.2 18.2 9.1 8.8 8.5 8.2
O
Et
Et
Et
Et
O
O
2p
100 MHz in CDCl3
f1 (ppm)
f1 (ppm)

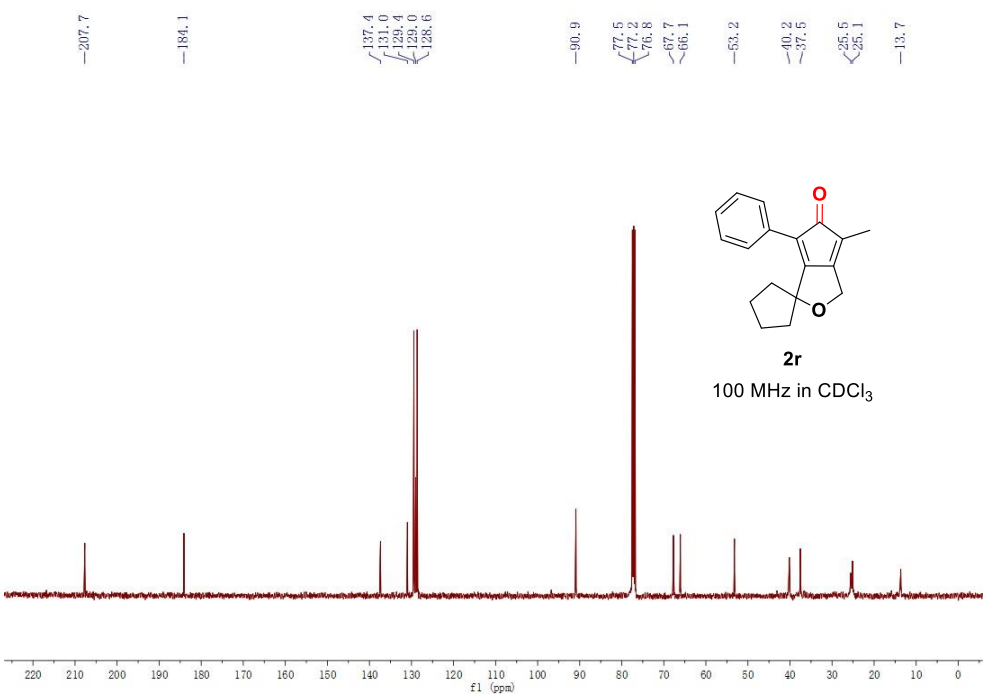

7.51
7.49
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.42
7.26
4.00
3.98
3.57
3.55
2.88
2.85
2.83
2.83
2.81
2.16
2.14
2.12
1.95
1.94
1.93
1.67
f1 (ppm)
O
O
2q
400 MHz in CDCl3
5.03
1.00
1.00
2.06
2.08
1.07
1.09
3.03
f1 (ppm)


207.6
181.8
137.7
130.8
129.4
129.2
128.6
83.5
77.5
77.2
76.8
68.8
65.6
53.1
35.6
34.2
13.7
13.2
O
O
2q
100 MHz in CDCl3
f1 (ppm)



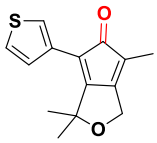
2r

400 MHz in $CDCl_3$



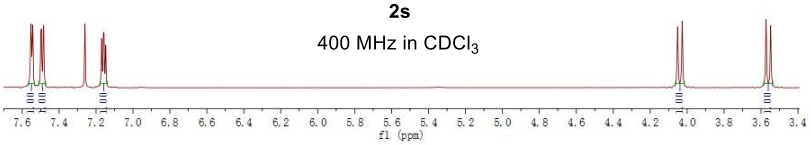
2r

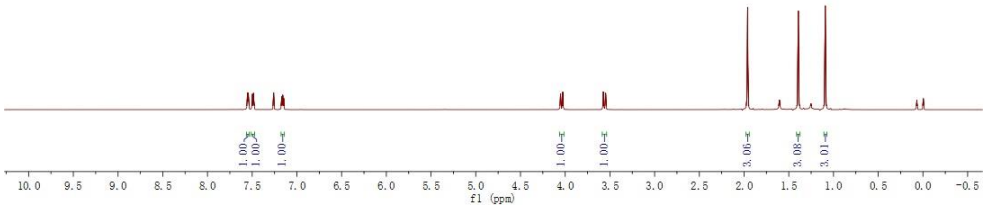
100 MHz in $CDCl_3$

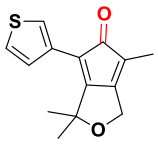


2s

400 MHz in $CDCl_3$

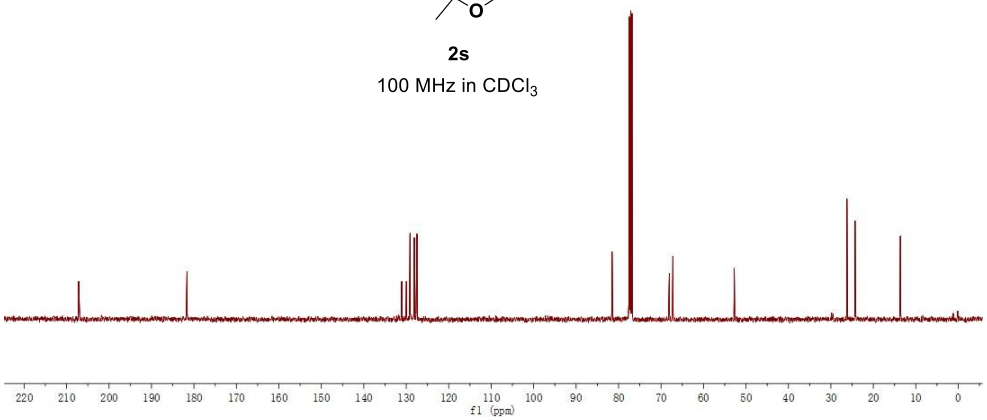


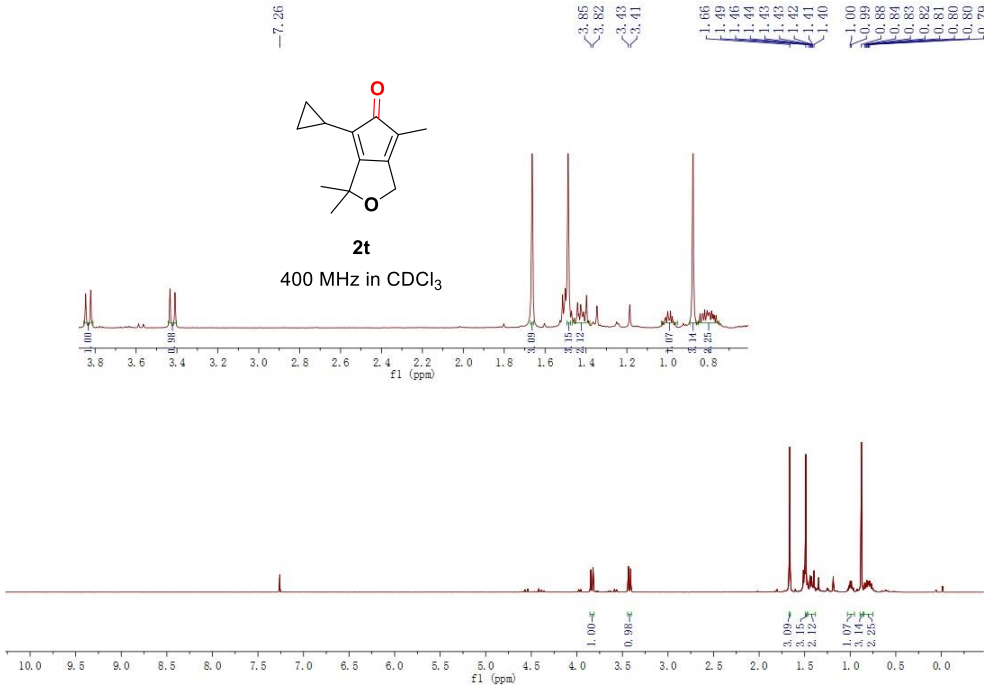




2s

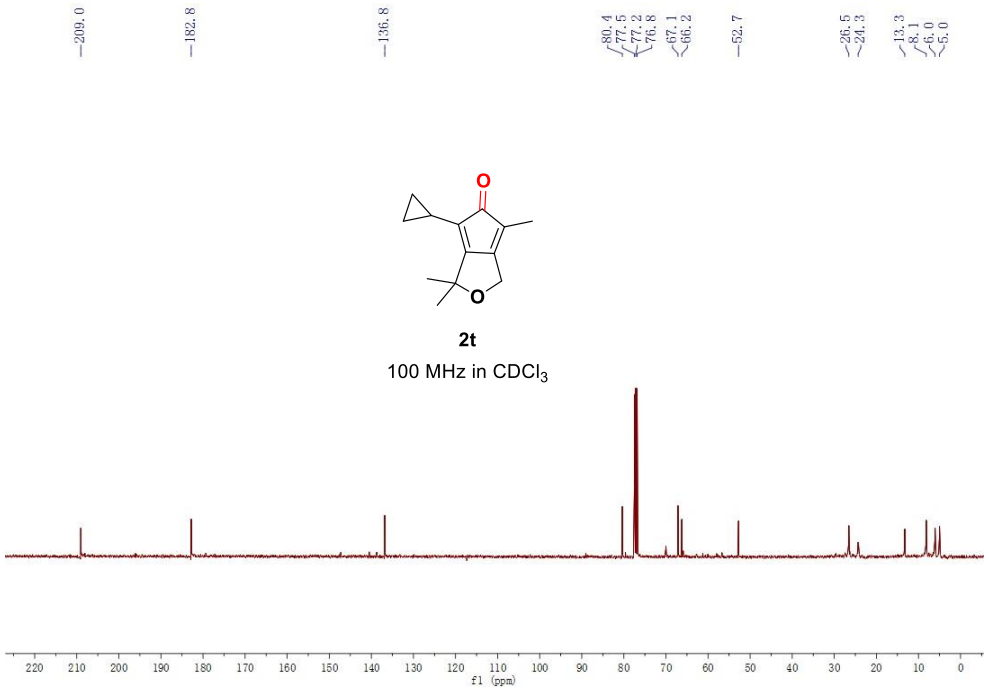
100 MHz in $CDCl_3$





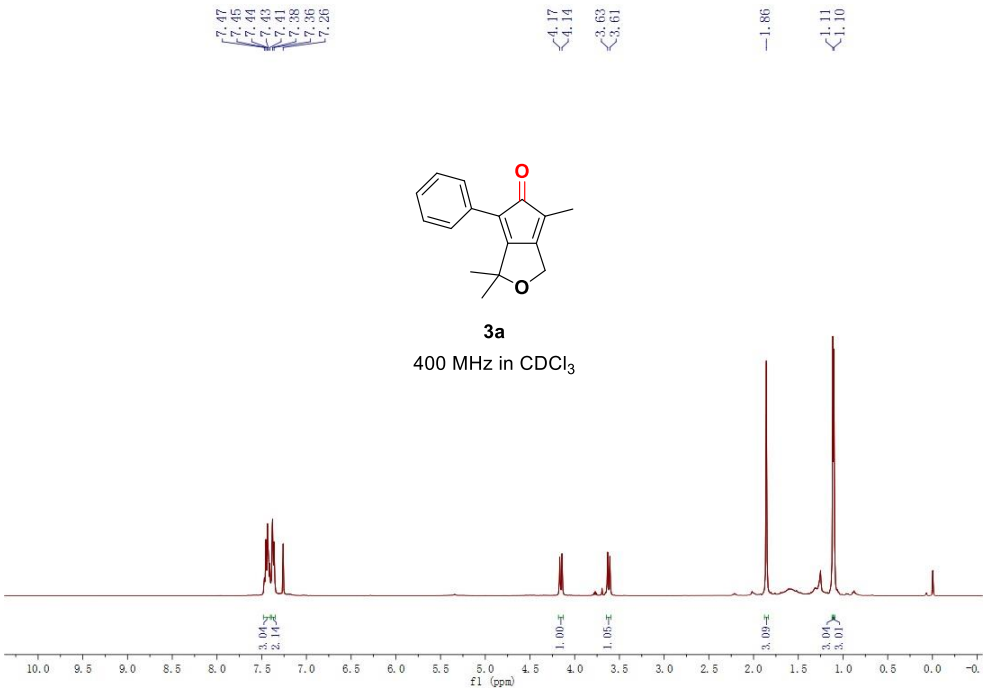
2t

400 MHz in $CDCl_3$



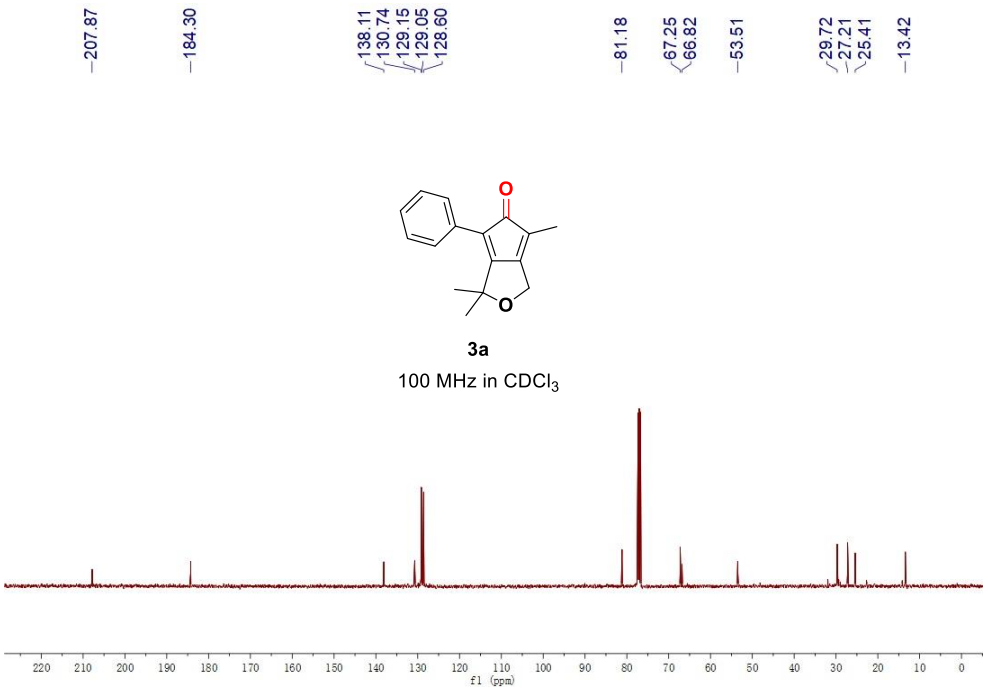
2t

100 MHz in $CDCl_3$



3a

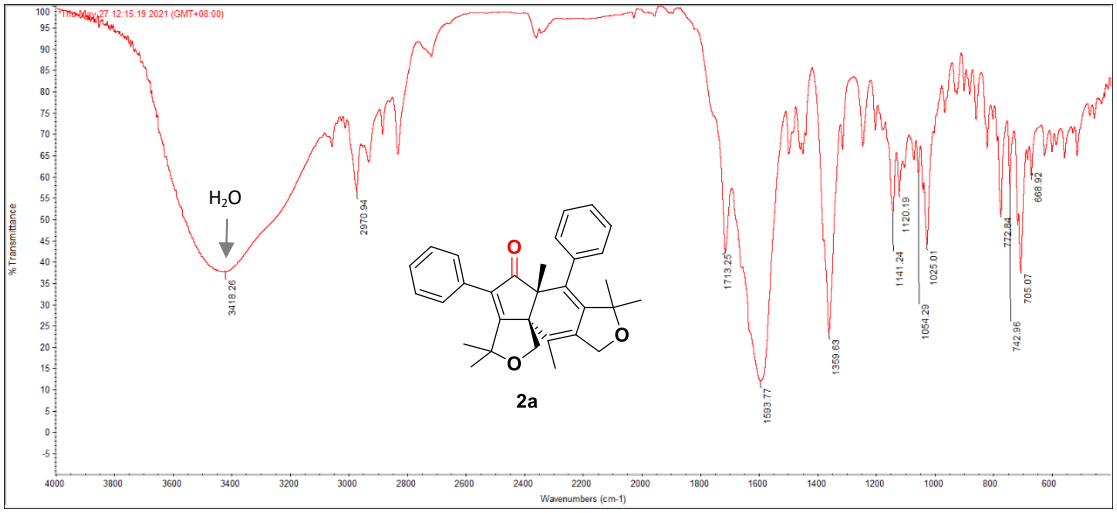
400 MHz in $CDCl_3$

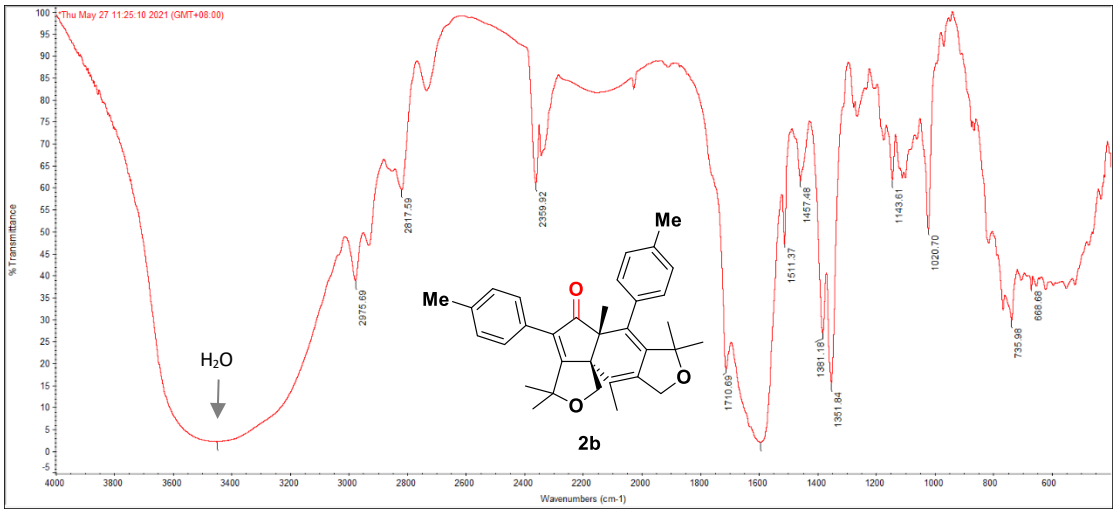


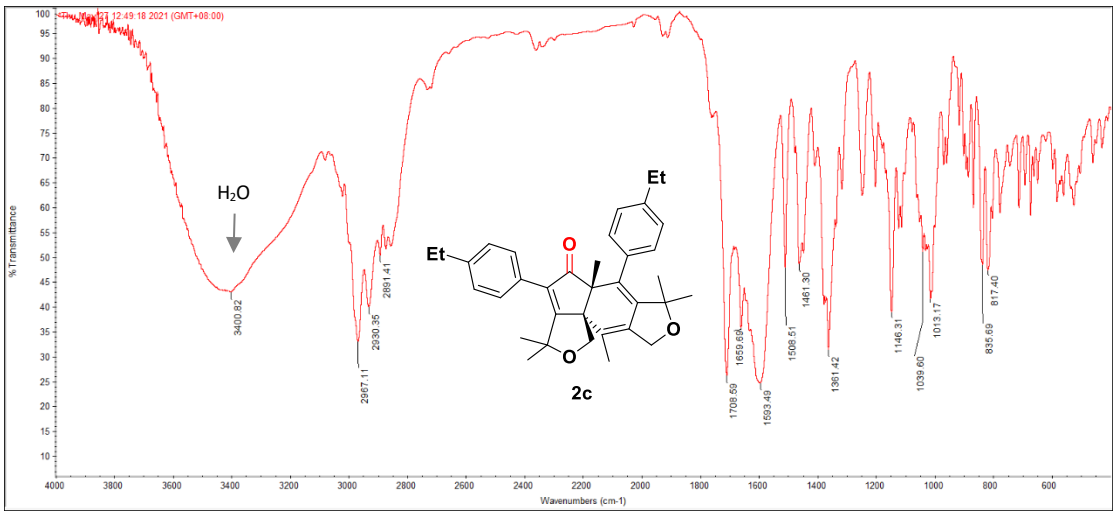
3a

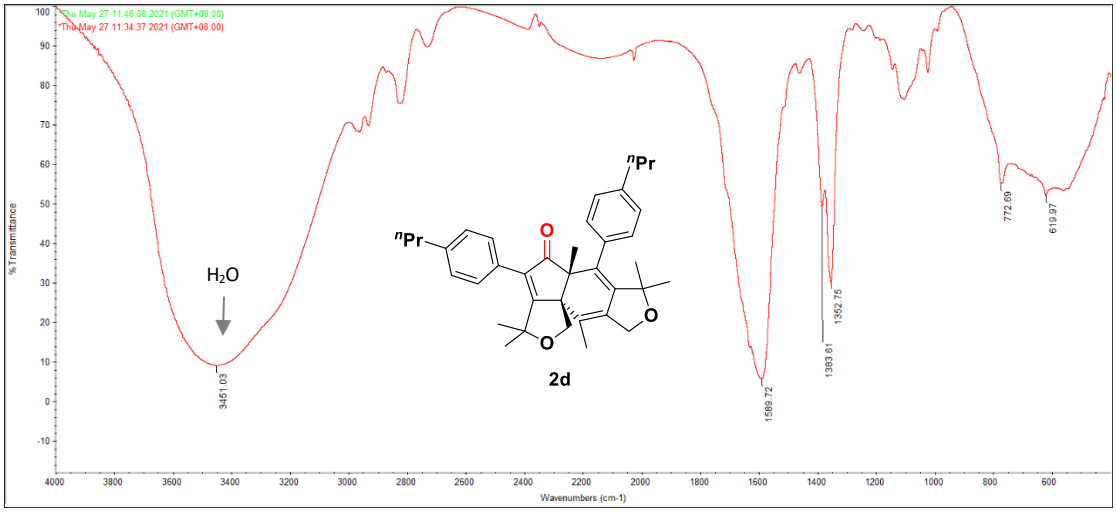
100 MHz in $CDCl_3$

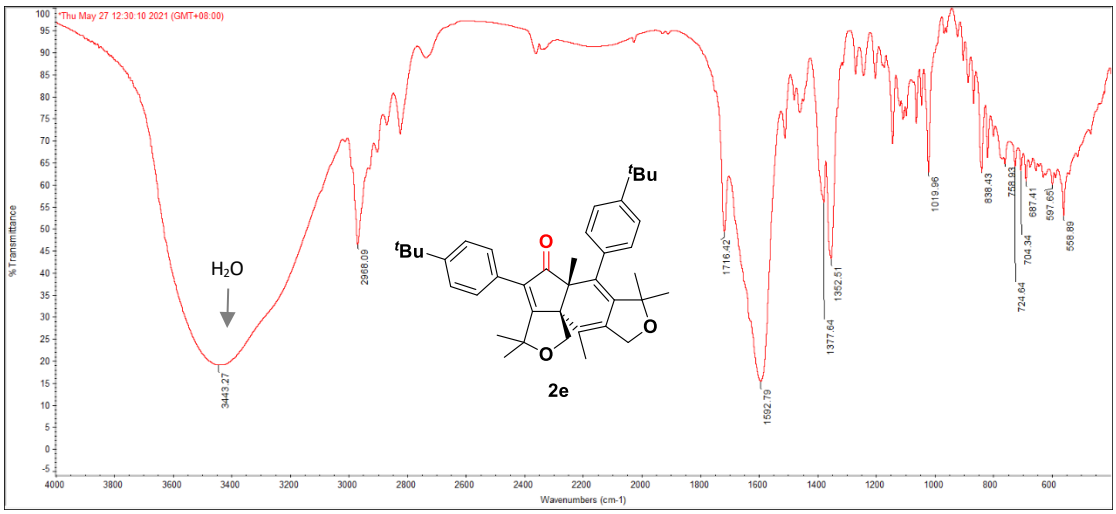
10. IR spectra of 2a–p

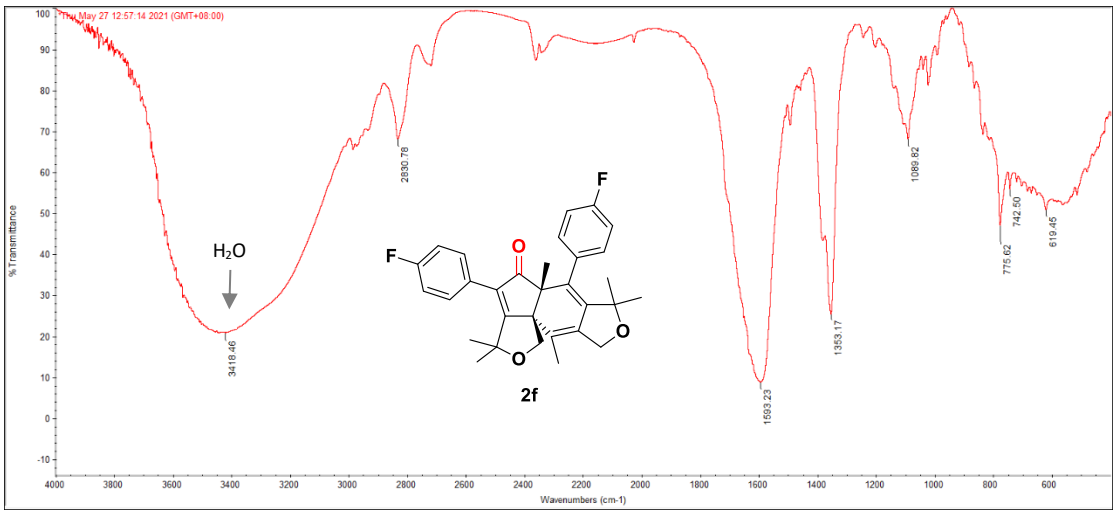


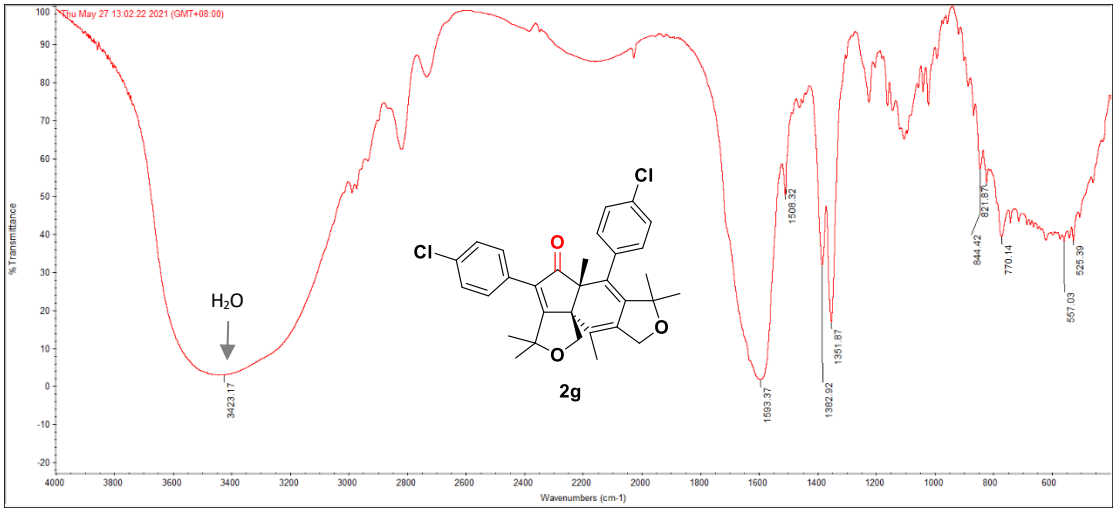


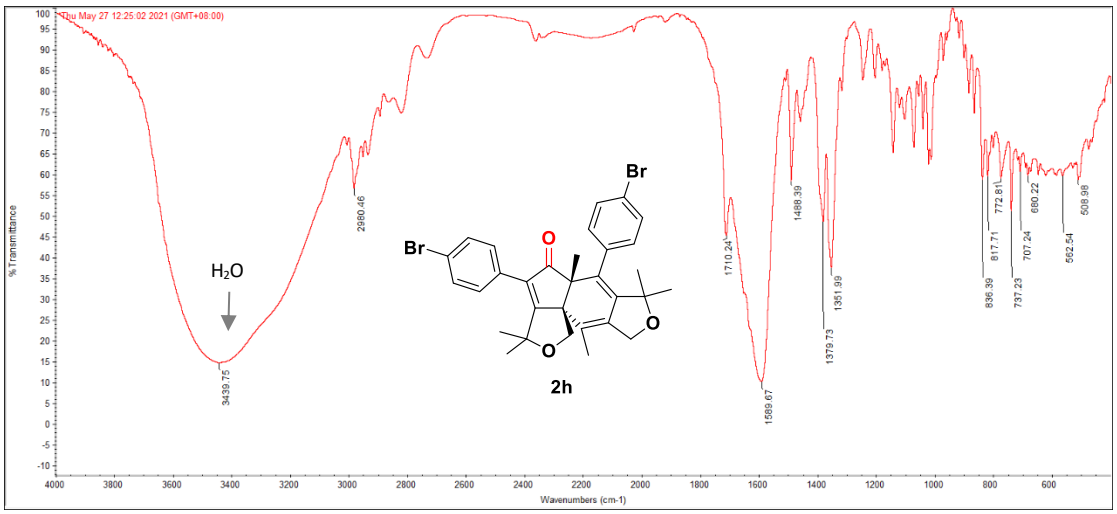


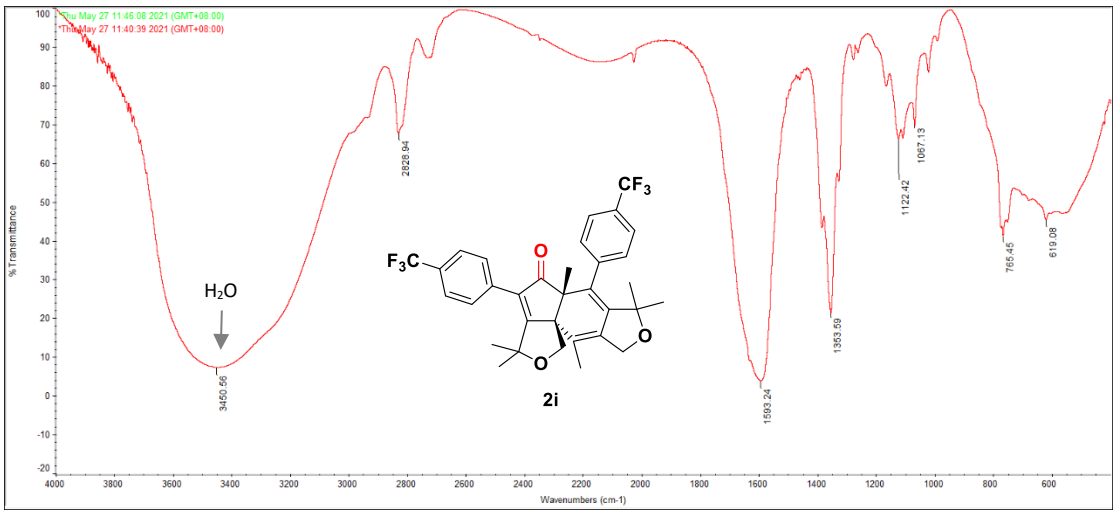

Thu May 27 11:46:08 2021 (GMT+08:00)
Thu May 27 11:34:37 2021 (GMT+08:00)
% Transmittance
Wavenumbers (cm-1)
H2O
3451.03
1589.72
1383.61
1352.75
772.69
619.97
nPr
nPr
O
O
O
2d

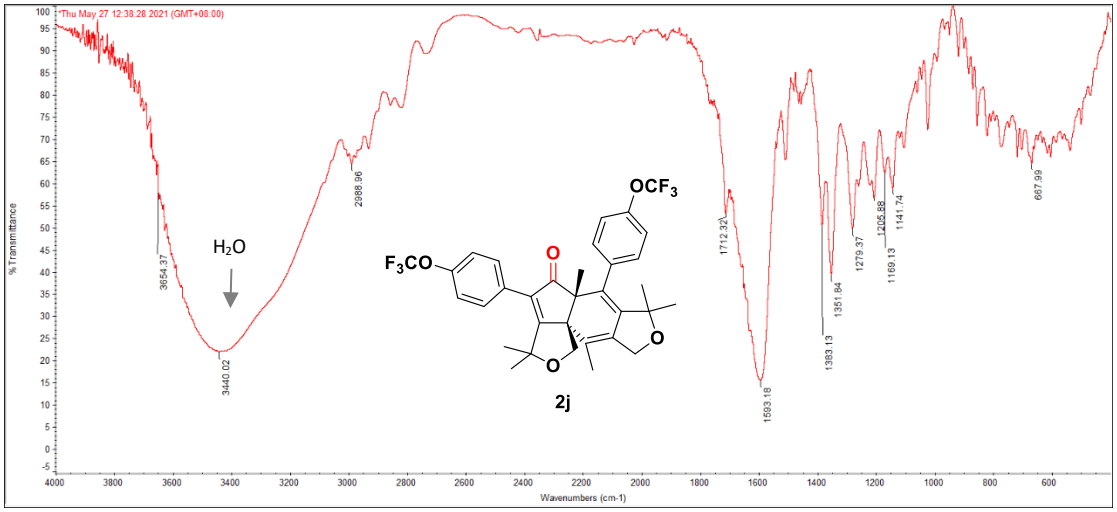

Thu May 27 12:30:10 2021 (GMT+08:00)
% Transmittance
Wavenumbers (cm-1)
H2O
3443.27
2966.09
1716.42
1592.79
1377.64
1352.51
1019.96
838.43
758.93
724.64
704.34
687.41
597.65
556.89
tBu
tBu
O
O
O
2e

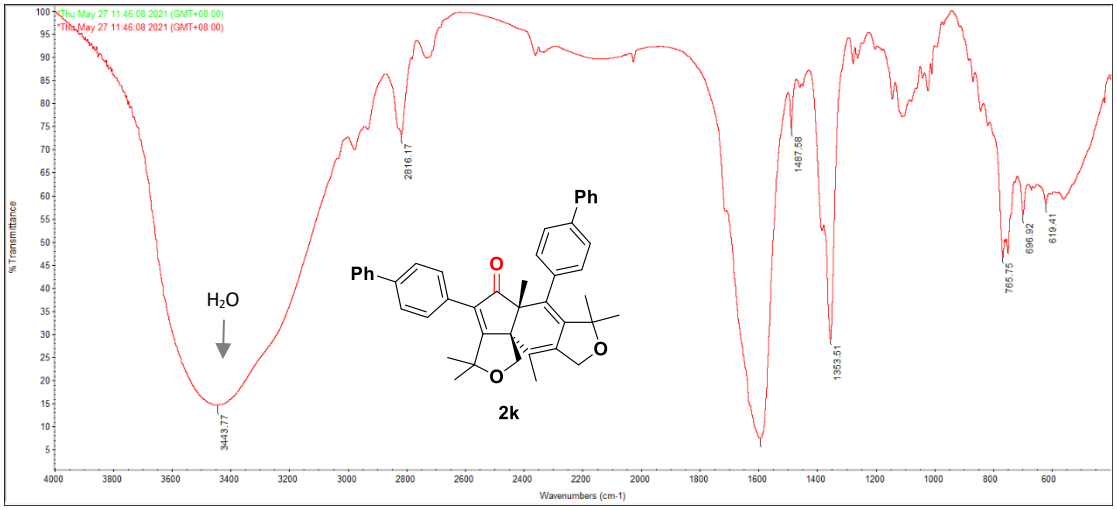

Thu May 27 12:57:14 2021 (GMT+08:00)
% Transmittance
Wavenumbers (cm-1)
H2O
3418.46
2830.78
1593.23
1353.17
1089.82
775.62
742.50
619.45
F
F
O
O
O
2f

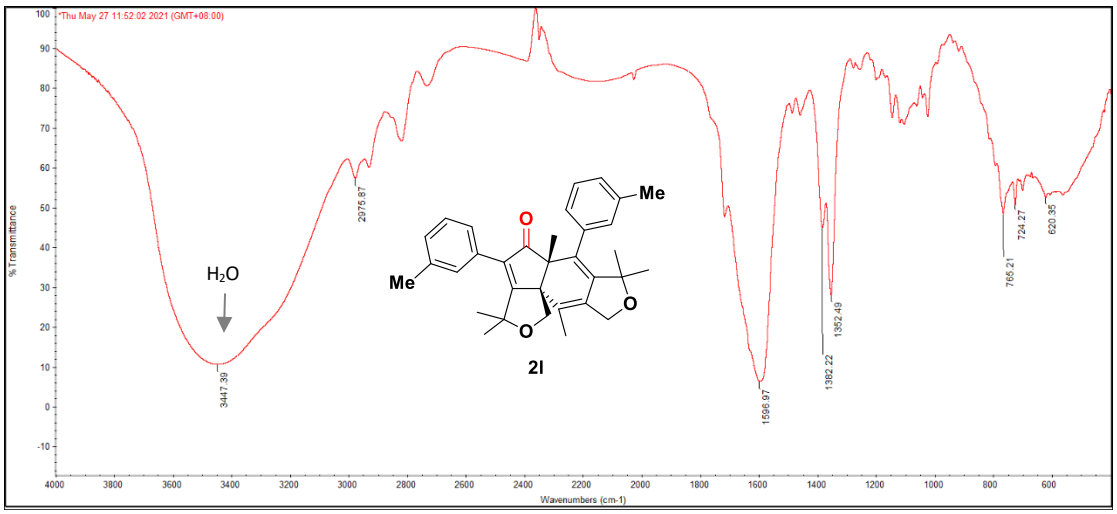

Thu May 27 13:02:22 2021 (GMT+08:00)
% Transmittance
Wavenumbers (cm-1)
H2O
3423.17
1593.37
1508.32
1382.92
1351.87
844.42
821.87
770.14
557.03
525.39
Cl
Cl
O
O
O
2g

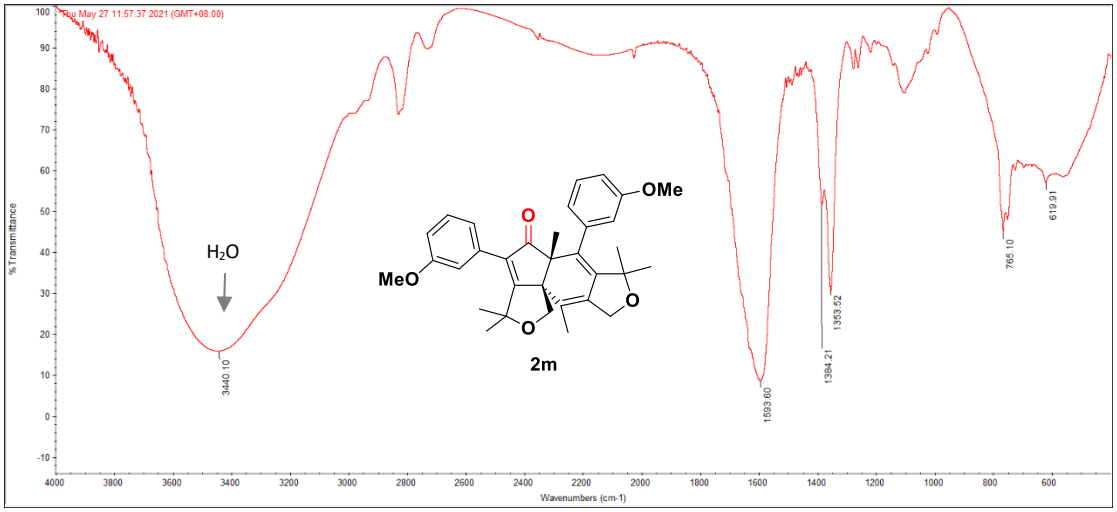

Thu May 27 12:25:02 2021 (GMT+08:00)
% Transmittance
Wavenumbers (cm-1)
H2O
3439.75
2980.46
1710.24
1589.67
1488.39
1379.73
1351.99
836.39
817.71
772.81
737.23
707.24
680.22
562.54
509.98
Br
Br
O
O
O
2h

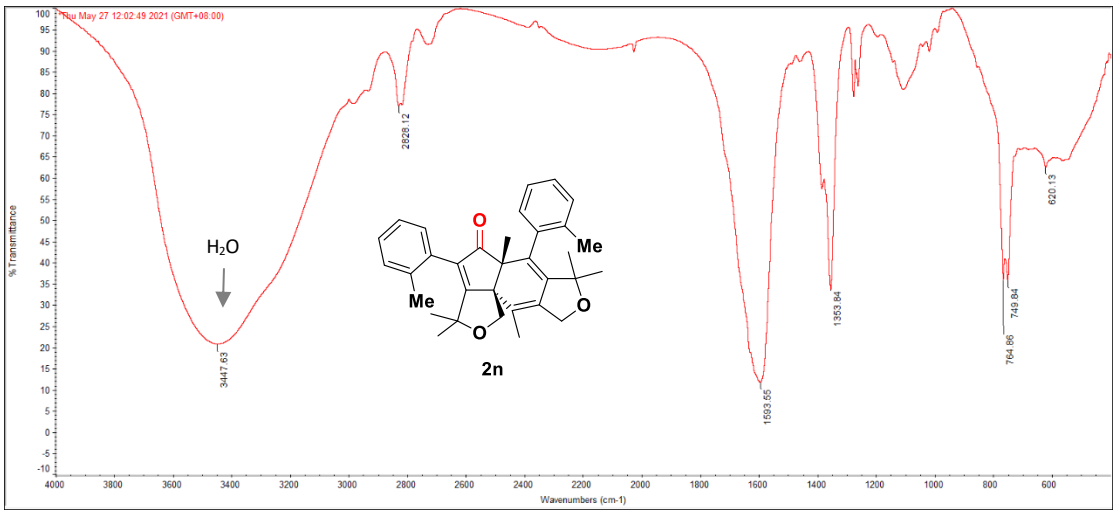

Thu May 27 11:46:08 2021 (GMT+08:00)
Thu May 27 11:40:39 2021 (GMT+08:00)
% Transmittance
Wavenumbers (cm-1)
H2O
3450.56
2826.94
1593.24
1353.59
1122.42
1067.13
765.45
619.08
CF3
F3C
O
O
O
2i

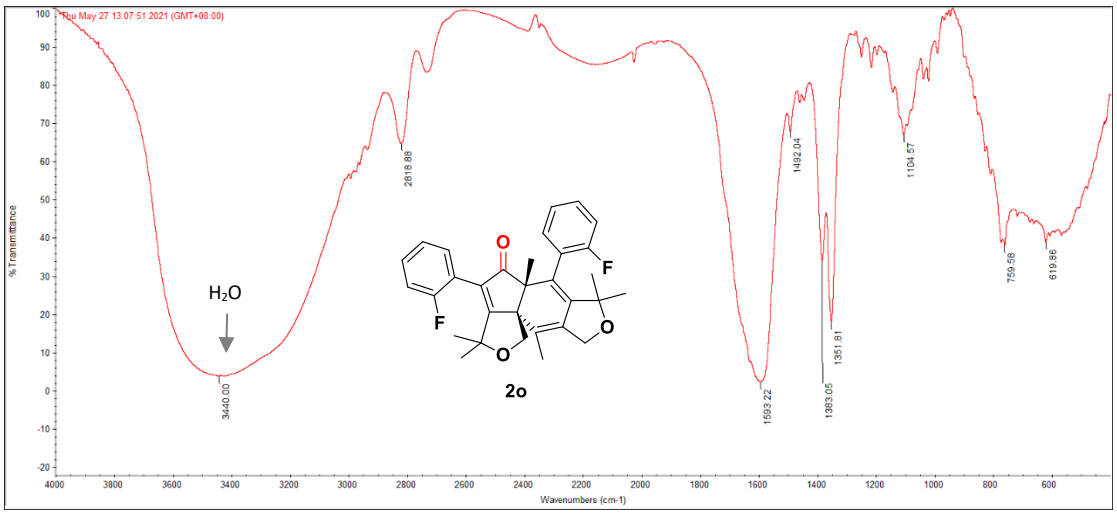

Thu May 27 12:38:28 2021 (GMT+08:00)
% Transmittance
Wavenumbers (cm-1)
3654.37
3440.02
2988.96
1712.32
1593.18
1383.13
1351.84
1279.37
1205.88
1169.13
1141.74
667.99
H2O
F3CO
OCF3
O
O
O
2j

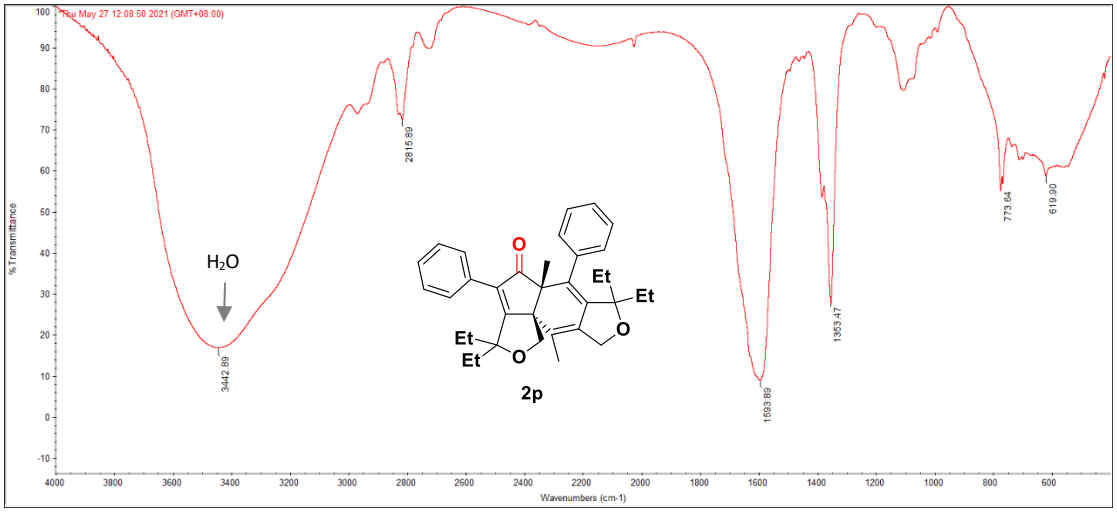

Thu May 27 11:46:08 2021 (GMT+08:00)
Thu May 27 11:46:08 2021 (GMT+08:00)
% Transmittance
Wavenumbers (cm-1)
3443.77
2816.17
1487.68
1353.51
765.75
696.92
619.41
H2O
Ph
Ph
O
O
O
2k


Thu May 27 11:52:02 2021 (GMT+08:00)
% Transmittance
Wavenumbers (cm-1)
3447.39
2975.87
1596.97
1382.22
1352.49
765.21
724.27
620.35
H2O
Me
Me
O
O
O
2l


Thu May 27 11:57:37 2021 (GMT+08:00)
% Transmittance
Wavenumbers (cm-1)
H2O
3440.10
1593.60
1384.21
1353.52
765.10
619.91
MeO
OMe
O
O
O
2m


Thu May 27 12:02:49 2021 (GMT+08:00)
% Transmittance
Wavenumbers (cm-1)
H2O
3447.63
2828.12
1593.55
1353.84
764.66
749.84
620.13
Me
Me
O
O
O
2n


Thu May 27 13:07:51 2021 (GMT+08:00)
% Transmittance
Wavenumbers (cm-1)
H2O
3440.00
2818.86
1593.22
1492.04
1383.05
1351.81
1104.57
759.56
619.86
F
F
O
O
O
2o


Thu May 27 12:08:50 2021 (GMT+08:00)
% Transmittance
Wavenumbers (cm-1)
H2O
3442.89
2815.89
1593.89
1353.47
773.64
619.90
O
Et
Et
Et
Et
O
O
2p