A Photo-induced C-C Bond Formation Methodology to Construct

Tetrahydrofluorenones and Related Structures

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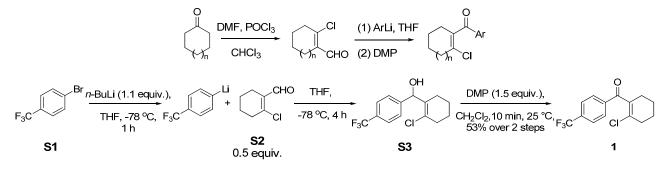
Supporting Information

General Experimental Procedures. All reactions were carried out under nitrogen except noted. Anhydrous dichloromethane (CH₂Cl₂) and 1,2-dichloroethane (DCE) were distilled from calcium hydride. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl, and anhydrous toluene was prepared from sodium. Flash column chromatography was performed as described by Still (Still, W. C.; Kahn, M.; Mitra, A. J. Org. Chem. **1978**, *43*, 2923–2925), employing Qingdao Haiyang silica gel 60 (200–300 mesh) TLC analyses were performed on EMD 250 µm Silica Gel HSGF₂₅₄ plates and visualized by quenching of UV fluorescence (λ_{max} = 254 nm), or by staining ceric ammonium molybdate, ammonium molybdate, or potassium permanganate. ¹H and ¹³C NMR spectra are reported in ppm (δ) relative to residue protium in the solvent (CDCl₃: δ 7.26, 77.0 ppm;) and the multiplicities are presented as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS) were acquired on a waters GCT premier. The photo reactor used for this photolysis is Rayonet RPR-200 (Southern New England Ultraviolet Company).

General procedure for the photolysis:

A solution of substrate and diisopropylamine (4 μ L / mL) in anhydrous 1,2-dichloroethane (4 mg / mL) was added in a quartz tube. This mixture was degassed by bubbling nitrogen through the solution for 0.5 h. It was then photolyzed at 25 °C in a Rayonet chamber reactor (16 lamps, 50/60 Hz, photos of 254 nm ultraviolet--1.65 × 10¹⁶ sec/cm³) at 254 nm for indicated time shown in tables. TLC showed all substrate consumed (**Cautions**: **Turn off the photo reactor before checking the reaction. Serious eye and skin burns will result from exposure to the direct or indirect rays.**), then 1,2-dichloroethane was evaporated. The residue was purified by silica gel column chromatography to give product.

General procedure for preparation of the precursors of the photolysis:

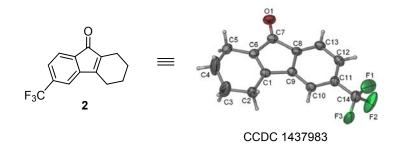


To a solution of **S1** (1.05 mL, 7.5 mmol, 2.0 equiv.) in anhydrous tetrahydrofuran (40 mL) was added *n*-BuLi (3.3 mL, 2.5 M solution in pentane, 8.2 mmol, 2.2 equiv.) at -78 °C over 10 min. After 1 h, a solution of **S2** (549.5 mg, 3.8 mmol, 1.0 equiv.) in anhydrous tetrahydrofuran (5 mL) was added to the above mixture over 10 min at the same temperature. After 6 h, TLC showed all **S2** consumed, the reaction was quenched with water (20 mL). The aqueous phase was extracted with ethyl acetate (20 mL×3), and the organic layer was washed with water (25 mL) and brine (25 mL). The organic phase was dried over anhydrous sodium sulfate, filtered, concentrated, and purified by silica gel column chromatography (10% ethyl acetate–hexane) to give **S3** as colorless oil (790 mg, 72%): R_f = 0.46 (10% ethyl acetate-petroleum ether). The product **S3** was found to be unstable and was carried on to the oxidation step without full characterization.

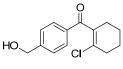
To a solution of **S3** (790 mg, 2.7 mmol, 1.0 equiv.) in anhydrous dichloromethane (18 mL) was added Dess-Martin Periodinane (1746 mg, 4.1 mmol, 1.5 equiv.) at 25 °C. After stirring for 5 min, a solution of water in dichloromethane (1 μ L water /1 mL CH₂Cl₂, 75 μ L, 4.1 mmol, 1.5 equiv.) was added. After about 10 min, TLC showed all **S3** consumed, then dichloromethane was evaporated and ethyl acetate (20 mL) and an aqueous solution of 1:1 10% sodium thiosulphate to saturated sodium bicarbonate (20 mL) was then added. After stirring for another 10 min, the biphasic mixture was extracted with ethyl acetate (20 mL×3), the combined organic phase was washed with saturated sodium bicarbonate (20 mL), dried over anhydrous sodium sulfate, filtered, concentrated, and purified by silica gel column chromatography (4% ethyl acetate–hexane) to **1** as white solid (570 mg, 74%): R_f = 0.59 (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 2.58 – 2.43 (m, 2H), 2.43 – 2.28 (m, 2H), 1.95 – 1.83 (m, 2H), 1.83 – 1.71 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.1, 138.2, 134.7 (q, *J* = 34.0

Hz), 133.9, 131.4, 129.6, 125.8 (q, *J* = 4.0 Hz), 123.6 (q, *J* = 271.0 Hz), 33.2, 28.5, 23.3, 21.3 ppm; MS (m/z) (%): EI [M] calcd for C₁₄H₁₂ClF₃O [M]⁺: 288.05, found 290 (3), 288 (9), 221 (33), 219 (100), 173 (71), 145 (87), 79 (31).

Ketone **2** (40 mg) was prepared according to the general procedure of the photo reaction from **1** in 79% yield. The reaction time is 2 h under 254 nm light. The products were isolated through silica gel flash chromatography (5% ethyl acetate-petroleum ether) as yellow solid: R_f = 0.58 (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.42 (m, 2H), 7.14 (s, 1H), 2.52 – 2.44 (m, 2H), 2.29 – 2.24 (m, 2H), 1.89 – 1.80 (m, 2H), 1.80 – 1.70 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 195.8, 157.7, 145.7, 135.4, 134.7 (q, *J* = 34.0 Hz), 134.4, 125.8 (q, *J* = 4.0 Hz), 123.7 (q, *J* = 271.0 Hz), 121.3, 114.7 (q, *J* = 4.0 Hz), 22.9, 21.7, 21.7, 19.7 ppm; HRMS (EI): Exact mass calcd for C₁₄H₁₁F₃O [M]⁺: 252.0762; found 252.0763. Recrystallization of **2** from ethyl acetate–hexane gave single crystals suitable for X-ray analysis (CCDC: 1437983).

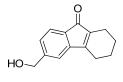


Ketone **3** was isolated through silica gel flash chromatography (7% ethyl acetate-petroleum ether) as yellow solid: $R_f = 0.31$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, J = 8.0 Hz, 1H), 7.78 (s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.02 – 6.90 (m, 1H), 3.57 (d, J = 10.6 Hz, 1H), 2.62 – 2.43 (m, 2H), 2.46 – 2.25 (m, 1H), 2.19 – 2.02 (m, 1H), 1.92 – 1.77 (m, 1H), 1.32 – 1.18 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 191.4, 153.1, 141.2, 140.9, 135.6, 135.5 (q, J = 32.0 Hz), 124.6 (q, J = 4.0 Hz), 124.5, 123.7 (q, J = 271.0 Hz), 122.0 (q, J = 4.0 Hz), 39.6, 26.6, 25.6, 22.3 ppm; HRMS (EI): Exact mass calcd for C₁₄H₁₁F₃O [M]⁺: 252.0762; found 252.0761.



Enone S14 was prepared as colorless oil: $R_f = 0.25$ (30% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 4.72 (s, 2H), 2.88 (s, 1H), 2.52 – 2.39 (m, 2H), 2.37 – 2.25 (m, 2H), 1.87 – 1.78 (m, 2H), 1.78 – 1.65 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ

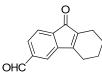
197.2, 147.1, 134.4, 134.1, 129.9, 129.6 (2C), 126.7 (2C), 64.3, 33.0, 28.6, 23.3, 21.3 ppm; MS (m/z) (%): EI [M] calcd for C₁₄H₁₅ClO₂ [M]⁺: 250.08, found 252 (1), 250 (2), 221 (34), 219 (100), 135 (62), 89 (28), 77 (42).



Ketone 4 (51 mg) was prepared according to the general procedure of the photo reaction from S4 in 93% yield. The reaction time is 4 h under 254 nm light. The products were isolated through silica gel flash chromatography (15% ethyl

acetate-petroleum ether) as yellow solid: $R_f = 0.24$ (30% ethyl acetate-petroleum ether); ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3) \delta 7.27 \text{ (d, } J = 7.4 \text{ Hz}, 1\text{H}), 7.08 \text{ (d, } J = 7.2 \text{ Hz}, 1\text{H}), 6.93 \text{ (s, 1H)}, 4.64 \text{ (s, 2H)},$ 2.46 – 2.32 (m, 2H), 2.25 – 2.13 (m, 2H), 1.83 – 1.75 (m, 2H), 1.75 – 1.62 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.3, 157.9, 146.5, 145.5, 134.3, 130.9, 125.9, 121.6, 116.9, 64.9, 22.8, 21.8, 21.8, 19.6 ppm; HRMS (EI): Exact mass calcd for C₁₄H₁₄O₂ [M]⁺: 214.0994; found 214.0993.

Enone S5 was prepared as white solid: $R_{\rm f} = 0.43$ (30% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 10.08 (s, 1H), 8.02 (d, J = 8.2 Hz, 2H), 7.96 (d, J = 8.2 Hz, 2H), 2.53 – 2.40 (m, 2H), 2.40 – 2.28 (m, 2H), 1.93 – 1.80 (m, 2H), 1.80 – 1.64 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.5, 191.5, 139.7, 139.1, 133.9, 131.5, 129.8 (2C), 129.67 (2C), 33.2, 28.5, 23.3, 21.3 ppm; MS (m/z) (%): EI [M] calcd for C₁₄H₁₃ClO₂ [M]⁺: 248.06, found 250 (19), 248 (60), 221 (25), 219 (78), 133 (99), 105 (58), 86 (49), 84 (75), 79 (46), 77 (100).



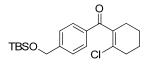
Ketone 5 (58 mg) was prepared according to the general procedure of the photo reaction from S5 in 70% vield. The reaction time is 4.5 h under 254 nm light. The products were isolated through silica gel flash chromatography (10% ethyl

acetate-petroleum ether) as yellow solid: $R_f = 0.42$ (10% ethyl acetate-petroleum ether); ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3) \delta 9.99 \text{ (s, 1H)}, 7.70 \text{ (d, } J = 7.1 \text{ Hz}, 1\text{H}), 7.52 \text{ (d, } J = 7.1 \text{ Hz}, 1\text{H}), 7.47 \text{ (s, 1H)}, 7.47 \text{ (s, 1H)$ 2.54 - 2.46 (m, 2H), 2.32 - 2.24 (m, 2H), 1.91 - 1.80 (m, 2H), 1.80 - 1.71 (m, 2H) ppm; 13 C NMR (100 MHz, CDCl₃) δ 195.9, 191.6, 158.2, 145.5, 140.2, 136.6, 135.8, 133.7, 121.6, 116.2, 23.0, 21.7,
21.7, 19.7 ppm; HRMS (EI): Exact mass calcd for C₁₄H₁₂O₂ [M]⁺: 212.0837; found 212.0836.

Enone S6 was prepared as colorless oil: $R_f = 0.67$ (20% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 3.91 (s, 3H), 2.55 – 2.39 (m, 2H), 2.39 – 2.25 (m, 2H), 1.91 – 1.80 (m, 2H), 1.80 – 1.63 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.6, 166.1, 138.7, 134.1, 134.1, 131.1, 129.9 (2C), 129.1 (2C), 52.3, 33.2, 28.5, 23.3, 21.3 ppm; MS (m/z) (%): EI [M] calcd for C₁₅H₁₅ClO₃ [M]⁺: 278.07, found 280 (2), 278 (5), 219 (100), 163 (40), 77 (19).

Ketone 6 (48 mg) was prepared according to the general procedure of the photo
reaction from S6 in 65% yield. The reaction time is 4 h under 254 nm light.
The products were isolated through silica gel flash chromatography (8% ethyl)

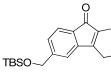
acetate-petroleum ether) as red solid: $R_{\rm f}$ = 0.67 (20% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 7.4 Hz, 1H), 7.56 (s, 1H), 7.40 (d, J = 7.4 Hz, 1H), 3.92 (s, 3H), 2.59 – 2.41 (m, 2H), 2.31 – 2.15 (m, 2H), 1.91 – 1.79 (m, 2H), 1.79 – 1.66 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.3, 166.4, 158.3, 145.0, 135.3, 134.9, 134.3, 130.7, 121.1, 118.6, 52.4, 23.0, 21.8, 21.8, 19.7 ppm; HRMS (EI): Exact mass calcd for C₁₅H₁₄O₃ [M]⁺: 242.0943; found 242.0942.



MeOO

Enone **S7** was prepared as colorless oil: $R_f = 0.41$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 4.80 (s, 2H), 2.57 – 2.42 (m, 2H), 2.42 – 2.25

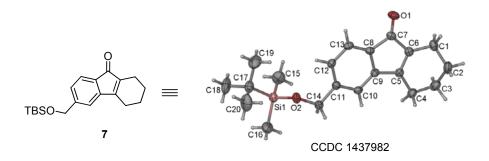
(m, 2H), 1.93 – 1.81 (m, 2H), 1.81 – 1.68 (m, 2H), 0.95 (s, 9H), 0.11 (s, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.0, 147.7, 134.6, 133.8, 129.7, 129.5 (2C), 126.0 (2C), 64.4, 33.1, 28.7, 25.9, 23.5, 21.4, 18.3, -5.4 ppm; MS(ES)⁺ calcd for C₂₀H₂₉ClO₂Si (M+H)⁺ 365.17, found 365.23.



Ketone 7 (50 mg) was prepared according to the general procedure of the photo reaction from **S7** in 86% yield. The reaction time is 4 h under 254 nm light. The products were isolated through silica gel flash chromatography (4%

ethyl acetate-petroleum ether) as yellow solid: $R_f = 0.42$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, J = 7.3 Hz, 1H), 7.08 (d, J = 7.3 Hz, 1H), 6.92 (s, 1H), 4.70 (s,

2H), 2.46 - 2.39 (m, 2H), 2.28 - 2.19 (m, 2H), 1.85 - 1.77 (m, 2H), 1.77 - 1.68 (m, 2H), 0.95 (s, 9H), 0.11 (s, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.3, 157.7, 147.2, 145.3, 134.2, 130.6, 125.0, 121.5, 116.2, 64.8, 25.9, 22.8, 21.9, 21.9, 19.7, 18.4, -5.3 ppm; HRMS (EI): Exact mass calcd for C₂₀H₂₈SiO₂ [M]⁺: 328.1859; found 328.1861. Recrystallization of **7** from ethyl acetate–hexane gave single crystals suitable for X-ray analysis (CCDC: 1437982).



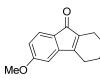
Enone **S8** was prepared as colorless oil: $R_f = 0.41$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 2.56 – 2.42 (m, 2H), 2.42 – 2.27 (m, 2H), 1.94 – 1.83 (m, 2H), 1.83 – 1.68 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.3, 135.2, 134.5, 133.6, 130.0, 129.4 (2C), 128.7 (2C), 33.2, 28.7, 23.5, 21.4 ppm; MS (m/z) (%): EI [M] calcd for C₁₃H₁₃ClO [M]⁺: 220.07, found 222 (16), 220 (48), 185 (44), 143 (22), 105 (88), 77 (100).

Ketone **8** (35 mg) was prepared according to the general procedure of the photo reaction from **S8** in 79% yield. The reaction time is 3.5 h under 254 nm light. The

products were isolated through silica gel flash chromatography (5% ethyl acetate-petroleum ether) as yellow solid: $R_f = 0.42$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, J = 7.0 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.15 (t, J = 7.4 Hz, 1H), 6.94 (d, J = 7.1 Hz, 1H), 2.49 – 2.39 (m, 2H), 2.28 – 2.19 (m, 2H), 1.88 – 1.77 (m, 2H), 1.77 – 1.69 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.5, 158.1, 145.0, 133.7, 133.0, 131.7, 128.1, 121.6, 118.1, 22.9, 21.9, 21.9, 19.6 ppm; HRMS (EI): Exact mass calcd for C₁₃H₁₂O [M]⁺: 184.0888; found 184.0890.

Enone **S9** was prepared as yellow oil: $R_f = 0.33$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8

Hz, 2H), 3.87 (s, 3H), 2.50 – 2.40 (m, 2H), 2.38 – 2.30 (m, 2H), 1.91 – 1.80 (m, 2H), 1.80 – 1.70 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 195.9, 164.0, 134.7, 131.8 (2C), 129.2, 128.1, 114.0 (2C), 55.5, 33.1, 28.7, 23.5, 21.5 ppm; MS (m/z) (%): EI [M] calcd for C₁₄H₁₅ClO₂ [M]⁺: 250.08, found 252 (7), 250 (20), 219 (34), 215 (20), 135 (100), 92 (20), 77 (37).



Ketone **9** (49 mg) was prepared according to the general procedure of the photo reaction from **S9** in 89% yield. The reaction time is 6 h under 254 nm light. The products were isolated through silica gel flash chromatography (4% ethyl

acetate-petroleum ether) as yellow solid: $R_f = 0.32$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, J = 8.3 Hz, 1H), 6.53 – 6.49 (m, 2H), 3.82 (s, 3H), 2.43 – 2.33 (m, 2H), 2.24 – 2.19 (m, 2H), 1.84 – 1.76 (m, 2H), 1.76 – 1.64 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.4, 164.2, 155.6, 147.6, 135.4, 124.3, 123.3, 108.8, 107.7, 55.6, 22.6, 21.9, 21.9, 19.8 ppm; HRMS (EI): Exact mass calcd for C₁₄H₁₄O₂ [M]⁺: 214.0994; found 214.0995.

Enone **S10** was prepared as colorless oil: $R_f = 0.32$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.94 (dd, J = 8.5, 5.5 Hz, 2H), 7.14 (t, J = 8.5 Hz, 2H), 2.50 – 2.43 (m, 2H), 2.38 – 2.30 (m, 2H), 1.90 – 1.81 (m, 2H), 1.79 – 1.71 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 195.7, 166.1 (d, J = 254.0 Hz), 134.2, 132.1 (d, J = 10.0 Hz), 131.6 (d, J = 3.0 Hz), 130.2, 115.9 (d, J = 22.0 Hz), 33.1, 28.6, 23.4, 21.4 ppm; MS (m/z) (%): EI [M] calcd for C₁₃H₁₂ClFO [M]⁺: 238.06, found 240 (7), 238 (23), 237 (27), 203 (33), 123 (100), 95 (62), 79 (18), 77 (21).

Ketone 10 (37 mg) was prepared according to the general procedure of the photo
reaction from S10 in 70% yield. The reaction time is 5 h under 254 nm light. The products were isolated through silica gel flash chromatography (5% ethyl)

acetate-petroleum ether) as yellow solid: $R_f = 0.32$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.32 (dd, J = 7.8, 5.2 Hz, 1H), 6.81 – 6.73 (m, 1H), 6.65 (dd, J = 8.1, 1.6 Hz, 1H), 2.44 – 2.36 (m, 2H), 2.26 – 2.20 (m, 2H), 1.85 – 1.77 (m, 2H), 1.77 – 1.69 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 195.7, 166.5 (d, J = 251.0 Hz), 155.8, 148.3 (d, J = 10.0 Hz), 135.6, 127.4 (d, J = 3.0 Hz), 123.2 (d, J = 10.0 Hz), 113.1 (d, J = 23.0 Hz), 107.3 (d, J = 25.0 Hz), 22.7, 21.8, 21.7, 19.7 ppm; HRMS (EI): Exact mass calcd for C₁₃H₁₁FO [M]⁺: 202.0794; found 202.0795.

Enone **S11** was prepared as colorless oil: $R_f = 0.42$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.77 (m, 2H), 7.55 – 7.38 (m, 2H), 2.56 – 2.41 (m, 2H), 2.41 – 2.26 (m, 2H), 1.91 – 1.81 (m, 2H), 1.81 – 1.67 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.1, 140.1, 134.1, 133.6, 130.8 (2C), 130.6, 129.1 (2C), 33.2, 28.6, 23.4, 21.4 ppm; MS (m/z) (%): EI [M] calcd for C₁₃H₁₂Cl₂O [M]⁺: 254.03, found 256 (5), 254 (8), 221 (33), 219 (100), 139 (89), 111 (58), 79 (23), 77 (24), 75 (31).

Ketone **11** (39 mg) was prepared according to the general procedure of the photo reaction from **S11** in 78% yield. The reaction time is 4.5 h under 254 nm light. The products were isolated through silica gel flash chromatography (5% ethyl acetate-petroleum ether) as yellow solid: R_f = 0.42 (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, *J* = 7.5 Hz, 1H), 7.12 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.90 (d, *J* = 1.5 Hz, 1H), 2.45 – 2.36 (m, 2H), 2.29 – 2.18 (m, 2H), 1.87 – 1.78 (m, 2H), 1.78 – 1.67 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 195.9, 156.8, 146.9, 139.2, 135.3, 129.8, 127.5, 122.5, 119.1, 22.8, 21.8, 21.7, 19.7 ppm; HRMS (EI): Exact mass calcd for C₁₃H₁₁ClO [M]⁺: 218.0498; found 218.0499.

> Ketone **12** (38 mg) was prepared according to the general procedure of the photo reaction from **S12** in 69% yield. The reaction time is 6 h under 254 nm light. The products were isolated through silica gel flash chromatography (6%

the light. The products were isolated through silica gel flash chromatography (6%) ethyl acetate-petroleum ether) as red solid: $R_f = 0.38$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 6.67 (d, J = 2.0 Hz, 1H), 6.37 (d, J = 2.0 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 2.67 – 2.60 (m, 2H), 2.21 – 2.13 (m, 2H), 1.78 – 1.70 (m, 2H), 1.70 – 1.61 (m, 2H) ppm; ¹³C NMR

MeC

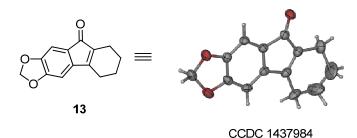
(100 MHz, CDCl₃) δ 197.3, 162.0, 160.9, 153.8, 134.9, 129.9, 122.4, 102.6, 101.9, 55.8, 55.5, 26.5, 22.4, 21.8, 19.7 ppm; HRMS (EI): Exact mass calcd for C₁₅H₁₆O₃ [M]⁺: 244.1099; found 244.1100.

Enone **S13** was prepared as colorless oil: $R_f = 0.29$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.45 (m, 1H), 7.38 (d, J = 1.1 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H), 6.03 (s, 2H), 2.47 – 2.39 (m, 2H), 2.35 – 2.27 (m, 2H), 1.87 – 1.78 (m, 2H), 1.78 – 1.66 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 195.5, 152.3,

148.4, 134.6, 129.9, 129.4, 126.5, 108.5, 108.1, 101.9, 33.0, 28.7, 23.4, 21.4 ppm; MS (m/z) (%): EI [M] calcd for C₁₄H₁₃ClO₃ [M]⁺: 264.06, found 266 (13), 264 (38), 234 (18), 229 (29), 149 (100), 121 (29).

Ketone **13** (43 mg) was prepared according to the general procedure of the photo reaction from **S13** in 76% yield. The reaction time is 4 h under 254 nm light. The products were isolated through silica gel flash chromatography (6% ethyl

acetate-petroleum ether) as orange solid: R_f = 0.29 (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 6.90 (s, 1H), 6.48 (s, 1H), 5.97 (s, 2H), 2.41 – 2.28 (m, 2H), 2.27 – 2.12 (m, 2H), 1.83 – 1.74 (m, 2H), 1.74 – 1.64 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.2, 156.1, 151.1, 146.8, 141.4, 132.7, 125.5, 104.7, 101.7, 101.4, 22.8, 21.9, 21.9, 19.6 ppm; HRMS (EI): Exact mass calcd for C₁₄H₁₂O₃ [M]⁺: 228.0786; found 228.0784. Recrystallization of **13** from ethyl acetate–hexane gave single crystals suitable for X-ray analysis (CCDC: 1437984).

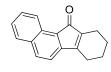


Enone S14 was prepared as colorless oil: $R_f = 0.49$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 7.6 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.36 – 7.29 (m, 1H), 2.53 – 2.37 (m, 4H), 1.83 – 1.66 (m, 4H) ppm; ¹³C NMR (100

MHz, CDCl₃) δ 196.2, 138.6, 135.5, 134.6, 132.0, 131.9, 130.4, 130.3, 126.9, 34.6, 28.1, 23.2, 21.5 ppm; MS (m/z) (%): EI [M] calcd for C₁₃H₁₂Cl₂O [M]⁺: 254.03, found 256 (8), 254 (10), 221 (34), 219 (100), 139 (93), 111 (55), 79 (39), 77(45), 75 (38).

Ketone 14 (39 mg) was prepared according to the general procedure of the photo reaction from S14 in 68% yield. The reaction time is 4.5 h under 254 nm light. The products were isolated through silica gel flash chromatography (5% ethyl acetate-petroleum ether) as yellow solid: $R_f = 0.49$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.21 (t, J = 8.2 Hz, 1H), 7.06 (d, J = 8.2 Hz, 1H), 6.85 (d, J = 7.0 Hz, 1H), 2.47 – 2.38 (m, 2H), 2.29 – 2.21 (m, 2H), 1.85 – 1.78 (m, 2H), 1.78 – 1.68 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 194.3, 156.2, 147.1, 134.6, 133.9, 130.2, 130.0, 126.7, 116.7, 22.7, 21.9, 21.8, 19.7 ppm; HRMS (EI): Exact mass calcd for C₁₃H₁₁ClO [M]⁺: 218.0498; found 218.0497.

Enone **S15** was prepared as white solid: *R*_f = 0.43 (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.90 (d, *J* = 8.6 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.95 – 7.86 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.60 – 7.44 (m, 2H), 2.56 – 2.40 (m, 4H), 1.91 – 1.83 (m, 2H), 1.83 – 1.75 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 199.1, 136.3, 134.1, 133.6, 133.4, 132.1, 130.8 (2 C), 128.4, 128.3, 126.5, 125.9, 124.5, 33.7, 29.0, 23.5, 21.6 ppm; MS (m/z) (%): EI [M] calcd for C₁₇H₁₅ClO [M]⁺: 270.08, found 272 (13), 270 (36), 235 (55), 155 (62), 127 (100), 77 (29).



Ketone **15** (55 mg) was prepared according to the general procedure of the photo reaction from **S15** in 92% yield. The reaction time is 5 h under 254 nm light. The products were isolated through silica gel flash chromatography (4% ethyl

acetate-petroleum ether) as red solid: $R_f = 0.45$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.67 (d, J = 8.6 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 2.51 – 2.41 (m, 2H), 2.29 – 2.18 (m, 2H), 1.89 – 1.79 (m, 2H), 1.79 – 1.70 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 199.8, 156.2, 146.0, 134.3, 133.9, 132.5, 128.9, 128.7, 128.3, 125.3, 123.6, 123.2, 117.0, 22.8, 22.1, 22.0, 19.5 ppm; HRMS (EI): Exact mass calcd for C₁₇H₁₄O [M]⁺: 234.1045; found 234.1048.

Enone **S16** was prepared as white solid: $R_f = 0.43$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.41 (s, 1H), 8.00 (dd, J = 11.9, 8.4 Hz, 2H), 7.90 (dd, J = 13.2, 8.4 Hz, 2H), 7.58 (dt, J = 14.8, 7.1 Hz, 2H), 2.61 – 2.50 (m, 2H), 2.49 –

2.39 (m, 2H), 1.97 – 1.87 (m, 2H), 1.87 – 1.77 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.3, 135.9, 134.6, 132.6, 132.6, 131.7, 130.1, 129.7, 128.6, 128.6, 127.8, 126.7, 124.4, 33.2, 28.8, 23.5, 21.4 ppm; MS (m/z) (%): EI [M] calcd for C₁₇H₁₅ClO [M]⁺: 270.08, found 272 (17), 270 (51), 235 (62), 155 (70), 127 (100), 77 (27).

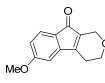


Ketone **16** (40 mg) was prepared according to the general procedure of the photo reaction from **S16** in 91% yield. The reaction time is 3.5 h under 254 nm light. The products were isolated through silica gel flash chromatography (5% ethyl

acetate-petroleum ether) as red solid: $R_f = 0.42$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.16 – 8.09 (m, 1H), 7.79 – 7.70 (m, 1H), 7.66 – 7.59 (m, 1H), 7.52 – 7.45 (m, 1H), 7.43 – 7.35 (m, 2H), 3.07 – 2.96 (m, 2H), 2.32 – 2.23 (m, 2H), 1.94 – 1.85 (m, 2H), 1.78 – 1.69 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 198.9, 158.3, 143.1, 137.8, 132.8, 129.4, 128.4, 128.1, 127.8, 127.1, 126.8, 124.3, 118.5, 27.4, 22.9, 21.3, 19.9 ppm; HRMS (EI): Exact mass calcd for C₁₇H₁₄O [M]⁺: 234.1045; found 234.1046.

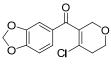
Enone S17 was prepared as colorless oil: $R_f = 0.37$ (20% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.86 (m, 2H), 6.95 (dd, J = 6.8, 4.8 Hz, 2H), 4.34 (t, J = 2.5 Hz, 2H), 3.94 (t, J = 5.6 Hz, 2H), 3.86 (s, 3H), 2.60 – 2.51 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 192.8, 164.3, 134.3, 131.9 (2C), 128.2, 126.9, 114.0 (2C), 67.1, 64.9, 55.5, 32.6 ppm; MS (m/z) (%): EI [M] calcd for

C₁₃H₁₃ClO₃ [M]⁺: 252.05, found 254 (7), 252 (22), 217 (19), 189 (27), 135 (100), 92 (25).



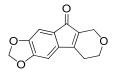
Ketone **17** (48 mg) was prepared according to the general procedure of the photo reaction from **S17** in 65% yield. The reaction time is 4 h under 254 nm light. The products were isolated through silica gel flash chromatography (10% ethyl

acetate-petroleum ether) as yellow solid: R_f = 0.36 (20% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, *J* = 7.8 Hz, 1H), 6.59 – 6.53 (m, 2H), 4.41 (t, *J* = 2.9 Hz, 2H), 3.91 (t, *J* = 5.4 Hz, 2H), 3.84 (s, 3H), 2.58 – 2.48 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 193.7, 164.4, 153.2, 146.3, 133.7, 130.2, 124.0, 109.6, 108.2, 63.4, 62.5, 55.7, 23.3 ppm; HRMS (EI): Exact mass calcd for C₁₃H₁₂O₃ [M]⁺: 216.0786; found 216.0790.



Enone **S18** was prepared as colorless oil: $R_f = 0.43$ (20% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.53 (dd, J = 8.1, 1.3 Hz, 1H), 7.39 (d, J = 1.3 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 6.05 (s, 2H), 4.33 (t, J = 2.4 Hz, 2H), 3.95

 $(t, J = 5.5 \text{ Hz}, 2\text{H}), 2.66 - 2.46 \text{ (m, 2H) ppm}; {}^{13}\text{C NMR} (100 \text{ MHz}, \text{CDCl}_3) \delta 192.4, 152.7, 148.5, 134.3, 130.1, 127.2, 126.8, 108.4, 108.2, 102.0, 67.1, 64.9, 32.7 ppm; MS (m/z) (%): EI [M] calcd for C_{13}H_{11}ClO_4 [M]^+: 266.03, found 268 (3), 266 (9), 149 (22), 86 (66), 84 (100), 49 (74).$



Ketone **18** (46 mg) was prepared according to the general procedure of the photo reaction from **S18** in 96% yield. The reaction time is 4 h under 254 nm light. The products were isolated through silica gel flash chromatography (10% ethyl

acetate-petroleum ether) as red solid: $R_f = 0.41$ (20% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 6.91 (s, 1H), 6.51 (s, 1H), 6.00 (s, 2H), 4.37 (t, J = 3.0 Hz, 2H), 3.90 (t, J = 5.4 Hz, 2H), 2.54 – 2.38 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 193.5, 153.9, 151.3, 147.4, 140.0, 131.0, 125.3, 105.1, 102.0, 101.7, 63.3, 62.4, 23.5 ppm; HRMS (EI): Exact mass calcd for C₁₃H₁₀O₄ [M]⁺: 230.0579; found 230.0580.

Enone **S19** was prepared as colorless oil: $R_f = 0.41$ (20% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.74 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H), 7.96 – 7.85 (m, 2H), 7.63 (ddd, J = 8.5, 6.9, 1.3 Hz, 1H), 7.60 – 7.48 (m, 2H), 4.54 (t, J = 2.5 Hz, 2H), 3.97 (t, J = 5.6 Hz, 2H), 2.64 – 2.53 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.0, 135.4, 134.0, 133.9, 133.7, 131.1, 130.5, 130.4, 128.5, 128.3, 126.6, 125.6, 124.6, 67.5, 64.8, 33.4 ppm; MS (m/z) (%): EI [M] calcd for C₁₆H₁₃ClO₂ [M]⁺: 272.06, found 274 (6), 272 (17), 237 (49), 207 (20), 155 (42), 127 (100).

Ketone **19** (45 mg) was prepared according to the general procedure of the photo reaction from **S19** in 75% yield. The reaction time is 4 h under 254 nm light. The products were isolated through silica gel flash chromatography (10% ethyl acetate-petroleum ether) as orange solid: $R_f = 0.39$ (20% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.63 (d, J = 8.6 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 8.3 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 4.43 (t, J = 3.1 Hz, 2H), 3.95 (t, J = 5.3 Hz, 2H), 2.64 – 2.51 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.0, 154.0, 144.5, 134.7, 134.2, 130.9, 129.0 (2 C), 128.3, 125.7, 123.5, 123.1, 117.0, 63.5, 62.4, 23.5 ppm; HRMS (EI): Exact mass calcd for C₁₆H₁₂O₂ [M]⁺: 236.0837; found 236.0838.

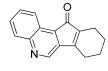
Enone **S20** was prepared as colorless oil: $R_f = 0.38$ (30% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 9.03 (s, 1H), 8.75 (d, J = 1.2 Hz, 1H), 8.25 – 8.03 (m, 1H), 7.47 – 7.33 (m, 1H), 2.56 – 2.40 (m, 2H), 2.40 – 2.27 (m, 2H), 1.89 –

1.79 (m, 2H), 1.79 – 1.67 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 195.9, 153.7, 151.1, 136.3, 133.6, 131.8, 130.8, 123.7, 33.2, 28.4, 23.3, 21.3 ppm; MS (m/z) (%): EI [M] calcd for C₁₂H₁₂ClNO [M]⁺: 221.06, found 223 (16), 221 (48), 193 (26), 186 (52), 143 (53), 106 (84), 78 (100), 51 (64).

Ketone **20** (51 mg) was prepared according to the general procedure of the photo reaction from **S20** in 57% yield. The reaction time is 6 h under 254 nm light. The products were isolated through silica gel flash chromatography (15% ethyl

acetate-petroleum ether) as yellow solid: $R_f = 0.38$ (30% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, J = 5.3 Hz, 1H), 7.55 (d, J = 7.1 Hz, 1H), 7.10 – 6.93 (m, 1H), 2.62 – 2.53 (m, 2H), 2.33 – 2.24 (m, 2H), 1.87 – 1.71 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 195.1, 166.7, 158.3, 151.6, 138.2, 128.0, 125.9, 122.0, 21.7, 21.7, 21.7, 19.7 ppm; HRMS (EI): Exact mass calcd for C₁₂H₁₁NO [M]⁺: 185.0841; found 185.0839.

Enone S21 was prepared as colorless oil: R_f = 0.59 (50% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.98 (d, J = 4.4 Hz, 1H), 8.40 (dd, J = 8.5, 0.7 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.72 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.60 (ddd, J = 8.3, 6.9, 1.2 Hz, 1H), 7.50 (d, J = 4.4 Hz, 1H), 2.56 - 2.36 (m, 4H), 1.85 - 1.54 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.6, 149.8, 149.0, 142.4, 136.4, 135.0, 129.8, 129.7, 128.1, 125.3, 124.2, 120.4, 34.2, 28.4, 23.2, 21.4 ppm; MS (m/z) (%): EI [M] calcd for C₁₆H₁₄ClNO [M]⁺: 271.08, found 273 (8), 271 (22), 236 (100), 143 (38), 128 (47), 101 (34), 79 (29).



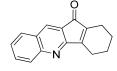
Ketone **21** (38 mg) was prepared according to the general procedure of the photo reaction from **S21**in 84% yield. The reaction time is 3.5 h under 254 nm light. The products were isolated through silica gel flash chromatography (25% ethyl

acetate-petroleum ether) as red solid: $R_f = 0.61$ (50% ethyl acetate-petroleum ether); ¹H NMR (400

MHz, CDCl₃) δ 8.64 (s, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.7 Hz, 1H), 7.63 – 7.55 (m, 1H), 7.51 (dd, *J* = 10.0, 5.3 Hz, 1H), 2.58 – 2.48 (m, 2H), 2.27 – 2.23 (m, 2H), 1.95 – 1.82 (m, 2H), 1.82 – 1.57 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 198.7, 157.7, 151.2, 140.7, 137.2, 132.8, 130.7, 129.6, 129.4, 129.0, 123.8, 122.4, 23.2, 21.9, 21.7, 19.6 ppm; HRMS (EI): Exact mass calcd for C₁₆H₁₃NO [M]⁺: 235.0997; found 235.0995.

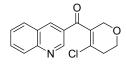
> Enone S22 was prepared as white solid: $R_f = 0.45$ (50% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 9.36 (d, J = 2.1 Hz, 1H), 8.66 (d, J = 1.8Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.91 – 7.75 (m, 1H),

7.69 – 7.55 (m, 1H), 2.56 – 2.48 (m, 2H), 2.47 – 2.40 (m, 2H), 1.95 – 1.86 (m, 2H), 1.86 – 1.75 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.0, 150.0, 149.9, 138.6, 133.8, 132.2, 131.8, 129.5 (2 C), 127.9, 127.5, 127.1, 33.3, 28.6, 23.4, 21.4 ppm; MS (m/z) (%): EI [M] calcd for C₁₆H₁₄ClNO [M]⁺: 271.08, found 273 (21), 271 (62), 236 (54), 156 (67), 128 (100), 101 (55), 79 (36), 77 (36).



Ketone **22** (38 mg) was prepared according to the general procedure of the photo reaction from **S22** in 78% yield. The reaction time is 4.5 h under 254 nm light. The products were isolated through silica gel flash chromatography (30% ethyl

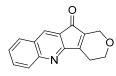
acetate-petroleum ether) as orange solid: $R_f = 0.44$ (50% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.81 – 8.72 (m, 1H), 8.08 – 7.92 (m, 2H), 7.72 – 7.60 (m, 1H), 7.49 – 7.38 (m, 1H), 3.00 – 2.87 (m, 2H), 2.32 – 2.20 (m, 2H), 1.95 – 1.83 (m, 2H), 1.78 – 1.68 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.2, 155.5, 153.1, 152.7, 141.7, 135.7, 131.5, 130.5, 127.3, 124.5, 122.7, 120.9, 26.6, 22.5, 20.9, 20.0 ppm; HRMS (EI): Exact mass calcd for C₁₆H₁₃NO [M]⁺: 235.0997; found 235.0998.



Enone **S23** was prepared as colorless oil: $R_f = 0.49$ (50% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 9.33 (s, 1H), 8.63 (s,

1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.88 – 7.72 (m, 1H),

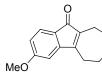
7.64 – 7.49 (m, 1H), 4.44 (d, J = 1.2 Hz, 2H), 3.97 (t, J = 4.6 Hz, 2H), 2.61 (d, J = 2.4 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 192.9, 149.8, 149.4, 138.7, 133.3, 132.2, 130.2, 129.4, 129.3, 128.1, 127.5, 126.8, 66.9, 64.7, 32.9 ppm; MS (m/z) (%): EI [M] calcd for C1₅H1₂ClNO₂ [M]⁺: 273.06, found 275 (16), 273 (47), 238 (50), 210 (35), 156 (71), 128 (100), 101 (48).



Ketone **23** (31 mg) was prepared according to the general procedure of the photo reaction from **S23** in 56% yield. The reaction time is 2 h under 254 nm light. The products were isolated through silica gel flash chromatography (30% ethyl

acetate-petroleum ether) as orange solid: R_f = 0.46 (50% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.89 (s, 1H), 8.07 (t, *J* = 9.4 Hz, 2H), 7.90 – 7.63 (m, 1H), 7.63 – 7.46 (m, 1H), 4.52 (t, *J* = 3.3 Hz, 2H), 4.02 (t, *J* = 5.3 Hz, 2H), 3.26 – 2.97 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 194.9, 153.4, 153.0, 151.4, 142.3, 133.9, 131.9, 130.9, 127.8, 124.1, 122.7, 120.8, 63.6, 62.6, 27.1 ppm; HRMS (EI): Exact mass calcd for C₁₅H₁₁NO₂ [M]⁺: 237.0790; found 237.0788.

Enone **S24** was prepared as colorless oil: $R_f = 0.31$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.83 (m, 2H), 7.01 – 6.89 (m, 2H), 3.94 – 3.76 (m, 3H), 2.75 – 2.62 (m, 2H), 2.43 – 2.26 (m, 2H), 1.85 – 1.65 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.0, 163.8, 138.7, 133.2, 131.7 (2C), 127.8, 113.9 (2C), 55.4, 39.1, 31.0, 30.6, 26.2, 25.2 ppm; MS (m/z) (%): EI [M] calcd for C₁₅H₁₇ClO₂ [M]⁺: 264.09, found 266 (7), 264 (19), 229 (19), 149 (30), 135 (100), 77 (34).



Ketone **24** (49 mg) was prepared according to the general procedure of the photo reaction from **S24** in 71% yield. The reaction time is 4 h under 254 nm light. The products were isolated through silica gel flash chromatography (5% ethyl

acetate-petroleum ether) as yellow solid: $R_f = 0.31$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, J = 7.9 Hz, 1H), 6.58 (d, J = 2.1 Hz, 1H), 6.51 (dd, J = 7.9, 2.1 Hz, 1H), 3.83 (s, 3H), 2.61 – 2.47 (m, 2H), 2.43 – 2.31 (m, 2H), 1.89 – 1.78 (m, 2H), 1.78 – 1.67 (m, 2H), 1.67 – 1.49 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.4, 164.3, 157.2, 148.8, 138.1, 123.7, 123.5, 108.6, 107.9, 55.6, 30.9, 26.9, 26.9, 26.5, 23.4 ppm; HRMS (EI): Exact mass calcd for C₁₅H₁₆O₂ [M]⁺: 228.1150; found 228.1152.

Enone S25 was prepared as colorless oil: $R_f = 0.48$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 7.78 (m, 2H), 7.21 – 6.95 (m, 2H), 2.83 – 2.59 (m, 2H), 2.47 – 2.18 (m, 2H), 1.91 – 1.59 (m, 6H) ppm; ¹³C NMR

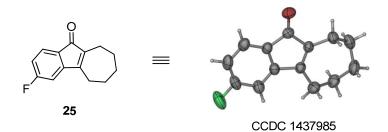
(100 MHz, CDCl₃) δ 195.8, 166.0 (d, *J* = 254 Hz), 138.3, 134.4, 132.0 (d, *J* = 9 Hz), 131.6 (d, *J* = 3

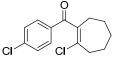
Hz), 115.8 (d, J = 22 Hz), 39.3, 31.0, 30.6, 26.3, 25.2 ppm; MS (m/z) (%): EI [M] calcd for C₁₄H₁₄ClFO [M]⁺: 252.07, found 254 (8), 252 (23), 217 (35), 123 (100), 95 (47).



Ketone 25 (49 mg) was prepared according to the general procedure of the photo reaction from S25 in 54% yield. The reaction time is 2 h under 254 nm light. The products were isolated through silica gel flash chromatography (10% ethyl

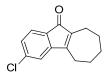
acetate-petroleum ether) as orange solid: $R_{\rm f} = 0.52$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.37 - 7.30 (m, 1H), 6.80 - 6.70 (m, 2H), 2.60 - 2.51 (m, 2H), 2.45 - 2.38 (m, 2H), 1.87 – 1.79 (m, 2H), 1.79 – 1.71 (m, 2H), 1.62 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 195.8, 166.6 (d, J = 251 Hz), 157.3 (d, J = 2 Hz), 149.6 (d, J = 9 Hz), 138.2, 126.6 (d, J = 3 Hz), 123.6 (d, J = 10 Hz), 112.9 (d, J = 13 Hz), 107.6 (d, J = 26 Hz), 30.7, 27.1, 26.8, 26.4, 23.4 ppm; HRMS (EI): Exact mass calcd for C₁₄H₁₃FO [M]⁺: 216.0950; found 216.0948. Recrystallization of 25 from ethyl acetate-hexane gave single crystals suitable for X-ray analysis (CCDC: 1437985).





Enone **S26** was prepared as colorless oil: $R_{\rm f} = 0.45$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4Hz, 2H), 2.81 - 2.65 (m, 2H), 2.46 - 2.30 (m, 2H), 1.90 - 1.63 (m, 6H) ppm; ${}^{13}C$ NMR (100 MHz, CDCl₃) δ 196.1, 139.9, 138.1, 134.8, 133.6, 130.8 (2C), 129.1 (2C), 39.3, 30.9, 30.7, 26.3, 25.2 ppm; MS (m/z) (%): EI [M] calcd for C₁₄H₁₄Cl₂O [M]⁺: 268.04, found 268 (4), 233

(60), 159 (100), 139 (99), 111 (55), 95 (33).



Ketone 26 (41 mg) was prepared according to the general procedure of the photo reaction from S26 in 63% yield. The reaction time is 4 h under 254 nm light. The products were isolated through silica gel flash chromatography (4% ethyl

acetate-petroleum ether) as yellow solid: $R_f = 0.42$ (10% ethyl acetate-petroleum ether); ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3) \delta 7.28 \text{ (d, } J = 7.6 \text{ Hz}, 1\text{H}), 7.12 \text{ (d, } J = 7.6 \text{ Hz}, 1\text{H}), 6.99 \text{ (s, 1H)}, 2.60 - 2.53 \text{ (m, 1H)}, 2.60 - 2.53 \text{ (m, 2H)}, 2.60 - 2.53 \text{ (m, 2H)}$ 2H), 2.46 - 2.37 (m, 2H), 1.88 - 1.79 (m, 2H), 1.79 - 1.70 (m, 2H), 1.66 - 1.58 (m, 2H) ppm; ${}^{13}C$

NMR (100 MHz, CDCl₃) δ 196.0, 158.4, 148.2, 139.4, 138.0, 129.0, 127.3, 122.8, 119.4, 30.7, 27.1, 26.8, 26.4, 23.4 ppm; HRMS (EI): Exact mass calcd for C₁₄H₁₃ClO [M]⁺: 232.0655; found 232.0657.

Enone S27 was prepared as colorless oil: $R_f = 0.67$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H), 2.82 – 2.69 (m, 2H), 2.46 – 2.34 (m, 2H), 1.92 – 1.69 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.4, 138.2, 138.0, 135.7, 134.6 (q, J = 33.0Hz), 129.7, 125.8 (q, J = 4.0 Hz), 123.6 (q, J = 271.0 Hz), 39.5, 31.0, 30.7, 26.3, 25.2 ppm; MS (m/z) (%): EI [M] calcd for C₁₅H₁₄ClF₃O [M]⁺: 302.07, found 304 (2), 302 (6), 233 (91), 173 (100), 145 (97), 77 (18).

Enone S28 was prepared as yellow oil: $R_f = 0.25$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.05 (d, J = 2.3 Hz, 2H), 6.64 (t, J = 2.3Hz, 1H), 3.80 (s, 6H), 2.73 – 2.65 (m, 2H), 2.38 – 2.26 (m, 2H), 1.84 – 1.64

(m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.8, 160.9 (2C), 138.5, 136.9, 134.0, 106.9 (2C), 105.6, 55.4, 55.4, 39.2, 30.8, 30.6, 26.2, 25.2 ppm; MS (m/z) (%): EI [M] calcd for C₁₆H₁₉ClO₃ [M]⁺: 294.10, found 296 (3), 294 (9), 259 (100), 165 (34), 137 (24), 122 (29), 77 (24).

MeO

Ketone **28** (42 mg) was prepared according to the general procedure of the photo reaction from **S28** in 92% yield. The reaction time is 2.5 h under 254 nm light. The products were isolated through silica gel flash chromatography (3% ethyl acetate-petroleum ether) as red solid: R_f = 0.24 (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 6.68 (d, *J* = 1.9 Hz, 1H), 6.38 (d, *J* = 1.8 Hz, 1H), 3.80 (d, *J* = 2.6 Hz, 6H), 3.03 – 2.85 (m, 2H), 2.41 – 2.18 (m, 2H), 1.86 – 1.65 (m, 4H), 1.61 – 1.53 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.3, 164.1, 161.8, 154.3, 134.7, 134.0, 123.0, 103.0, 102.0, 55.8, 55.6, 30.9, 30.0, 26.7, 26.3, 22.6 ppm; HRMS (EI): Exact mass calcd for C₁₆H₁₈O₃ [M]⁺: 258.1256; found 258.1254.

> Enone **S29** was prepared as colorless oil: $R_f = 0.67$ (20% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.45 (m, 1H),

7.39 (s, 1H), 6.92 – 6.77 (m, 1H), 6.03 (d, *J* = 1.1 Hz, 2H), 2.77 – 2.60 (m, 2H), 2.42 – 2.27 (m, 2H), 1.83 – 1.65 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 195.6, 152.2, 148.3, 138.6, 133.5, 129.8, 126.3, 108.6, 108.1, 101.9, 39.2, 31.0, 30.6, 26.2, 25.2 ppm; MS (m/z) (%): EI [M] calcd for C₁₅H₁₅ClO₃ [M]⁺: 278.07, found 280 (2), 278 (6), 149 (22), 123 (20), 86 (67), 84 (100).

Ketone **29** (57 mg) was prepared according to the general procedure of the photo reaction from **S29** in 93% yield. The reaction time is 4 h under 254 nm light. The products were isolated through silica gel flash chromatography (5% ethyl acetate-petroleum ether) as orange solid: $R_f = 0.65$ (20% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 6.88 (s, 1H), 6.54 (s, 1H), 5.96 (s, 2H), 2.54 – 2.42 (m, 2H), 2.39 – 2.26 (m, 2H), 1.82 – 1.75 (m, 2H), 1.75 – 1.65 (m, 2H), 1.65 – 1.44 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.2, 157.5, 151.3, 146.7, 142.8, 135.3, 124.6, 104.7, 101.8, 101.6, 30.7, 27.2, 27.0, 26.5, 23.3 ppm; HRMS (EI): Exact mass calcd for C₁₅H₁₄O₃ [M]⁺: 242.0943; found 242.0941.

Enone **S30** was pr ether); ¹H NMR (4 111), 7.08 (4, L = S

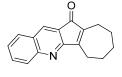
Enone **S30** was prepared as white solid: $R_f = 0.43$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.42 (s, 1H), 8.03 (dd, J = 8.6, 1.6 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.6 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H),

7.63 – 7.57 (m, 1H), 7.57 – 7.51 (m, 1H), 2.84 – 2.74 (m, 2H), 2.49 – 2.39 (m, 2H), 1.89 – 1.74 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.4, 138.7, 135.8, 134.3, 132.6, 132.5, 131.7, 129.6, 128.6, 128.6, 127.8, 126.7, 124.5, 39.3, 31.1, 30.7, 26.3, 25.3 ppm; MS (m/z) (%): EI [M] calcd for C₁₈H₁₇ClO [M]⁺: 284.10, found 286 (8), 284 (22), 249 (45), 155 (87), 135 (29), 127 (100), 77 (31).

Ketone **30** (43 mg) was prepared according to the general procedure of the photo reaction from **S30** in 74% yield. The reaction time is 4.5 h under 254 nm light. The products were isolated through silica gel flash chromatography (4% ethyl

acetate-petroleum ether) as red solid: $R_f = 0.42$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.28 – 8.21 (m, 1H), 7.78 – 7.71 (m, 1H), 7.64 (d, J = 7.9 Hz, 1H), 7.49 (d, J = 7.9 Hz, 1H), 7.44 – 7.37 (m, 2H), 3.27 – 3.17 (m, 2H), 2.51 – 2.38 (m, 2H), 2.00 – 1.91 (m, 2H), 1.91 – 1.80 (m, 2H), 1.80 – 1.69 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 198.7, 161.3, 144.0, 138.2, 135.8, 129.6, 128.7, 127.9, 127.9, 126.8, 126.8, 124.4, 118.4, 31.6, 28.6, 26.0, 25.4, 21.2 ppm; HRMS (EI): Exact mass calcd for C₁₈H₁₆O [M]⁺: 248.1201; found 248.1202.

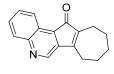
Enone **S31** was prepared as colorless oil: $R_f = 0.79$ (50% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 9.36 (d, J = 2.1 Hz, 1H), 8.66 (d, J = 1.9 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.89 – 7.75 (m, 1H), 7.71 – 7.52 (m, 1H), 2.97 – 2.66 (m, 2H), 2.58 – 2.29 (m, 2H), 1.92 – 1.65 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.1, 150.1, 149.9, 138.6, 137.9, 136.1, 132.1, 129.5, 129.4, 127.9, 127.5, 127.1, 39.5, 31.1, 30.7, 26.3, 25.2 ppm; MS (m/z) (%): EI [M] calcd for C₁₇H₁₆CINO [M]⁺: 285.09, found 287 (13), 285 (39), 250 (47), 156 (88), 128 (100), 101 (45).



Ketone **31** (20 mg) was prepared according to the general procedure of the photo reaction from **S31** in 72% yield. The reaction time is 4 h under 254 nm light. The products were isolated through silica gel flash chromatography (20% ethyl

acetate-petroleum ether) as orange solid: $R_f = 0.77$ (50% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.84 (s, 1H), 8.29 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.71 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.51 (ddd, J = 8.3, 6.8, 1.2 Hz, 1H), 3.36 – 3.12 (m, 2H), 2.60 – 2.39 (m, 2H), 2.08 – 1.92 (m, 2H), 1.92 – 1.80 (m, 2H), 1.80 – 1.71 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.4, 158.6, 153.9, 153.6, 142.0, 138.5, 131.3, 131.0, 127.3, 124.7, 123.2, 120.9, 31.1, 28.7, 25.8, 25.5, 21.6 ppm; HRMS (EI): Exact mass calcd for C₁₇H₁₅NO [M]⁺: 249.1154; found 249.1155.

Enone **S32** was prepared as colorless oil: $R_f = 0.62$ (50% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 9.00 (d, J = 4.3 Hz, 1H), 8.46 (d, J = 8.5 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.75 (t, J = 7.7 Hz, 1H), 7.68 – 7.54 (m, 1H), 7.53 (d, J = 4.3 Hz, 1H), 2.84 – 2.64 (m, 2H), 2.63 – 2.45 (m, 2H), 1.86 – 1.78 (m, 2H), 1.76 – 1.57 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 198.0, 149.8, 149.1, 142.3, 140.4, 139.5, 129.9, 129.8, 128.1, 125.5, 124.4, 120.2, 40.2, 30.9 (2 C), 26.3, 24.9 ppm; MS (m/z) (%): EI [M] calcd for C₁₇H₁₆CINO [M]⁺: 285.09, found 287 (4), 285 (12), 250 (100), 128 (66), 101 (33).



Ketone **32** (20 mg) was prepared according to the general procedure of the photo reaction from **S32** in 76% yield. The reaction time is 4 h under 254 nm light. The products were isolated through silica gel flash chromatography (25% ethyl

acetate-petroleum ether) as red solid: $R_f = 0.61$ (50% ethyl acetate-petroleum ether); ¹H NMR (400

MHz, CDCl₃) δ 8.77 (s, 1H), 8.55 (dd, J = 8.4, 0.8 Hz, 1H), 7.97 (d, J = 8.6 Hz, 1H), 7.59 (ddd, J = 8.5, 6.8, 1.5 Hz, 1H), 7.53 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 2.86 – 2.62 (m, 2H), 2.48 – 2.34 (m, 2H), 1.91 – 1.78 (m, 4H), 1.71 – 1.50 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 199.0, 159.0, 150.9, 140.9, 138.7, 135.5, 130.1, 129.5, 129.5, 129.1, 123.7, 122.3, 30.5, 27.7, 26.9, 26.6, 23.3 ppm; HRMS (EI): Exact mass calcd for C₁₇H₁₅NO [M]⁺: 249.1154; found 249.1156.

Enone **S33** was prepared as yellow oil: $R_f = 0.56$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.1 Hz, 2H), 2.74 – 2.49 (m, 2H), 2.45 – 2.25 (m, 2H), 1.98 – 1.63 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.4, 137.4, 137.1, 134.7 (q, J = 34.0 Hz), 129.8, 125.8 (q, J = 4.0 Hz), 123.6 (q, J =271.0 Hz), 121.4, 35.6, 29.5, 24.2, 21.3 ppm; MS (m/z) (%): EI [M] calcd for C₁₄H₁₂BrF₃O [M]⁺: 332.00, found 334 (7), 332 (7), 263 (53), 253 (66), 173 (100), 145 (99), 79 (36).

Enone **S34** was prepared as colorless oil: $R_f = 0.34$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.03 – 7.89 (m, 2H), 7.20 – 7.12 (m, 2H), 2.67 – 2.54 (m, 2H), 2.40 – 2.28 (m, 2H), 1.93 – 1.71 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.0, 166.1 (d, J = 255.0 Hz), 137.5, 132.3 (d, J = 10.0 Hz), 131.0 (d, J = 3.0 Hz), 120.5, 116.0 (d, J = 22.0 Hz), 35.6, 29.6, 24.2, 21.3 ppm; MS (m/z) (%): EI [M] calcd for C₁₃H₁₂BrFO [M]⁺: 282.01, found 284 (14), 284 (14), 203 (52), 123(100), 95 (54).

Enone **S35** was prepared as white solid: $R_f = 0.44$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.99 (d, J = 8.6 Hz, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 7.2 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.54 (dt, J = 17.8, 7.9 Hz, 2H), 2.73 – 2.56 (m, 2H), 2.56 – 2.40 (m, 2H), 1.96 – 1.75 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 199.5, 139.4, 134.1, 133.9, 132.3, 131.4, 131.0, 128.5, 128.4, 126.5, 126.1, 124.5, 122.0, 36.0, 30.1, 24.3, 21.5 ppm; MS (m/z) (%): EI [M] calcd for C₁₇H₁₅BrO [M]⁺: 314.03, found 316 (17), 314 (17), 235 (100), 155 (67), 127 (100), 77 (25).

Enone **S36** was prepared as yellow oil: $R_f = 0.33$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 3.86 (s, 3H), 2.65 – 2.56 (m, 2H), 2.40 – 2.26 (m, 2H), 1.91 – 1.69 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.2, 164.0, 137.9, 131.9 (2C), 127.4, 119.5, 114.0 (2C), 55.4, 35.4, 29.6, 24.2, 21.3 ppm; MS (m/z) (%): EI [M] calcd for C₁₄H₁₅BrO₂ [M]⁺: 294.03, found 296 (10), 294 (10), 263 (15), 215 (33), 135 (100), 92 (30), 77 (51).

Enone **S37** was prepared as white solid: $R_f = 0.41$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.42 (s, 1H), 8.07 – 7.97 (m, 2H), 7.97 – 7.84 (m, 2H), 7.67 – 7.50 (m, 2H), 2.73 – 2.63 (m, 2H), 2.47 – 2.38 (m, 2H), 1.98 – 1.80 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.6, 137.9, 135.9, 132.6, 131.9, 131.9, 129.70 128.7, 128.7, 127.8, 126.7, 124.5, 120.3, 35.6, 29.7, 24.2, 21.4 ppm; MS (m/z) (%): EI [M] calcd for C₁₇H₁₅BrO [M]⁺: 314.03, found 316 (18), 314 (18), 235 (49), 155 (44), 127 (100), 77 (32).

Enone **S38** was prepared as colorless oil: $R_f = 0.39$ (30% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 9.06 (s, 1H), 8.77 (d, J = 4.1 Hz, 1H), 8.20 (d, J = 7.9 Hz, 1H), 7.42 (dd, J = 7.9, 4.8 Hz, 1H), 2.69 – 2.53 (m, 2H), 2.45 – 2.23 (m, 2H), 1.89 – 1.69 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.3, 153.7, 151.2, 136.8, 136.5, 130.1, 123.8, 121.8, 35.6, 29.4, 24.1, 21.2 ppm; MS (m/z) (%): EI [M] calcd for C₁₂H₁₂BrNO [M]⁺: 265.01, found 267 (32), 265 (32), 186 (87), 106 (100), 78 (89), 51 (54).

Enone **S39** was prepared as white solid: $R_f = 0.47$ (50% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 9.37 (d, J = 1.9 Hz, 1H), 8.67 (d, J = 1.9 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.89 – 7.79 (m, 1H), 7.62 (t, J = 7.5 Hz, 1H), 2.71 – 2.61 (m, 2H), 2.45 – 2.35 (m, 2H), 1.94 – 1.78 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.2, 150.0, 149.9, 138.8, 136.9, 132.2, 129.4, 129.4, 127.5, 127.1, 127.0, 121.8, 35.6, 29.5, 24.1, 21.3 ppm; MS (m/z) (%): EI [M] calcd for C₁₆H₁₄BrNO [M]⁺: 315.03, found 317 (44), 315 (44), 236 (82), 156 (81), 128 (100), 101 (52), 79 (31), 77 (26).

Enone **S40** was prepared as colorless oil: $R_f = 0.60$ (50% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 9.01 (d, J = 4.4 Hz, 1H), 8.56 (dd, J = 8.5, 0.7 Hz, 1H), 8.15 (d, J = 8.3 Hz, 1H), 7.84 – 7.70 (m, 1H), 7.68 – 7.60 (m, 1H), 7.58 (d, J = 4.4 Hz, 1H), 2.67 – 2.53 (m, 2H), 2.52 – 2.41 (m, 2H), 1.90 – 1.70 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 198.4, 149.8, 149.1, 140.8, 138.1, 129.8, 129.8, 128.4, 125.54, 125.3, 124.4, 121.2, 36.4,

29.7, 24.1, 21.4 ppm; MS (m/z) (%): EI [M] calcd for C₁₆H₁₄BrNO [M]⁺: 315.03, found 317 (12), 315 (12), 235 (96), 155 (68), 127 (100), 79 (36), 77 (42).

Enone **S41** was prepared as colorless oil: $R_f = 0.32$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, J = 8.3 Hz, 2H), 6.96 (d, J = 8.2 Hz, 2H), 3.87 (s, 3H), 2.97 – 2.71 (m, 2H), 2.44 – 2.27 (m, 2H), 1.95 – 1.63 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.5, 163.9, 142.2, 132.0 (2C), 127.1, 123.2, 114.0 (2C), 55.5, 41.6, 31.9, 30.7, 26.1, 25.6 ppm; MS (m/z) (%): EI [M] calcd for C₁₅H₁₇BrO₂ [M]⁺: 308.04, found 310 (8), 308 (8), 229 (31), 135 (100), 77 (21).

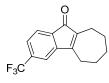
Enone **S42** was prepared as yellow oil: $R_f = 0.27$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.10 (d, J = 1.7 Hz, 2H), 6.68 (s, 1H), 3.84 (s, 6H), 2.97 – 2.81 (m, 2H), 2.43 – 2.28 (m, 2H), 1.87 – 1.68 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.2, 161.0, 142.0, 136.4, 123.8, 107.3, 105.9, 55.6, 41.7, 31.9, 30.7, 26.1, 25.7 ppm; MS (m/z) (%): EI [M] calcd for C₁₆H₁₉BrO₃ [M]⁺: 338.05, found 340 (3), 338 (3), 259 (100), 165 (27), 137 (18), 122 (23), 77 (19).

Enone **S43** was prepared as colorless oil: $R_f = 0.47$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 7.87 (m, 2H), 7.21 – 7.08 (m, 2H), 2.94 – 2.83 (m, 2H), 2.44 – 2.21 (m, 2H), 1.95 – 1.66 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.1, 166.0 (d, J = 254 Hz), 141.7, 132.3 (d, J = 9 Hz), 130.8 (d, J = 3 Hz), 124.1, 116.0 (d, J = 22 Hz), 41.7, 31.9, 30.7, 26.1, 25.6 ppm; MS (m/z) (%): EI [M] calcd for C₁₄H₁₄BrFO [M]⁺: 296.02, found 298 (7), 286 (7), 217 (35), 123 (100), 95 (43).

Enone S44 was prepared as colorless oil: $R_f = 0.43$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J*=8.6, 2H), 7.46 (d, *J*=8.6, 2H), 2.99 – 2.83 (m, 2H), 2.46 – 2.26 (m, 2H), 1.90 – 1.64 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.3, 141.6, 140.0, 132.8, 131.0 (2C), 129.1 (2C), 124.4, 41.7, 31.9, 30.6, 26.1, 25.6 ppm; MS (m/z) (%): EI [M] calcd for C₁₄H₁₄BrClO [M]⁺: 311.99, found 314 (4), 312 (4), 277 (20), 233 (25), 139 (100), 111 (48).

Enone S45 was prepared as white solid: $R_f = 0.42$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.43 (s, 1H), 8.09 – 7.96 (m, 2H), 7.91 (dd, J=13.9, 8.4, 2H), 7.59 (ddd, J=21.7, 14.3, 7.3, 2H), 3.03 – 2.89 (m, 2H), 2.52 – 2.37 (m, 2H), 1.94 – 1.74 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.7, 142.2, 135.9, 132.7, 132.0, 131.8, 129.7, 128.8, 128.7, 127.9, 126.7, 124.7, 124.1, 41.8, 32.1, 30.8, 26.2, 25.7 ppm; MS (m/z) (%): EI [M] calcd for C₁₈H₁₇BrO [M]⁺: 328.05, found 330 (12), 328 (12), 249 (85), 155 (94), 127 (100), 77 (16).

Enone **S46** was prepared as colorless oil: $R_f = 0.68$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.3 Hz, 2H), 2.97 – 2.83 (m, 2H), 2.44 – 2.28 (m, 2H), 1.92 – 1.68 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.5, 141.4, 137.3, 134.6 (q, J = 33.0 Hz), 129.9, 125.9 (q, J = 4.0 Hz), 125.2, 123.6 (q, J = 271.0 Hz), 41.8, 31.9, 30.7, 26.1, 25.6 ppm; MS (m/z) (%): EI [M] calcd for C₁₅H₁₄BrF₃O [M]⁺: 346.02, found 348 (6), 346 (6), 267 (50), 173 (100), 145 (84), 77 (15).



Ketone **27** (30 mg) was prepared according to the general procedure of the photo reaction from **S46** in 69% yield. The reaction time is 3 h under 254 nm light. The products were isolated through silica gel flash chromatography (3% ethyl

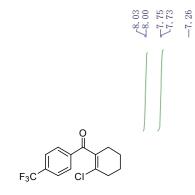
acetate-petroleum ether) as yellow solid: $R_f = 0.67$ (10% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.45 (s, 2H), 7.23 (s, 1H), 2.69 – 2.60 (m, 2H), 2.48 – 2.40 (m, 2H), 1.91 – 1.81 (m, 2H), 1.81 – 1.72 (m, 2H), 1.67 – 1.59 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.1, 159.4, 146.9, 138.1, 134.7 (q, J = 32.0 Hz), 133.6, 125.6 (q, J = 4.0 Hz), 123.7 (q, J = 271.0 Hz), 121.7, 115.0 (q, J = 4.0 Hz), 30.7, 27.2, 26.7, 26.3, 23.3 ppm; HRMS (EI): Exact mass calcd for C₁₅H₁₃F₃O [M]⁺: 266.0918; found 266.0916.

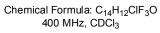
Enone S47 was prepared as colorless oil: $R_f = 0.62$ (50% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 9.07 (s, 1H), 8.77 (d, J = 4.6 Hz, 1H), 8.21 (d, J = 7.9 Hz, 1H), 7.42 (dd, J = 7.9, 4.8 Hz, 1H), 3.00 – 2.74 (m, 2H), 2.44 – 2.28 (m, 2H), 1.94 – 1.59 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.3, 153.7, 151.3, 141.1, 136.6, 130.0, 125.5, 123.8, 41.8, 31.8, 30.6, 26.0, 25.5 ppm; MS (m/z) (%): EI [M] calcd for C₁₃H₁₄BrNO [M]⁺: 279.03, found 281 (12), 279 (12), 200 (65), 106 (100), 78 (71), 51 (32).



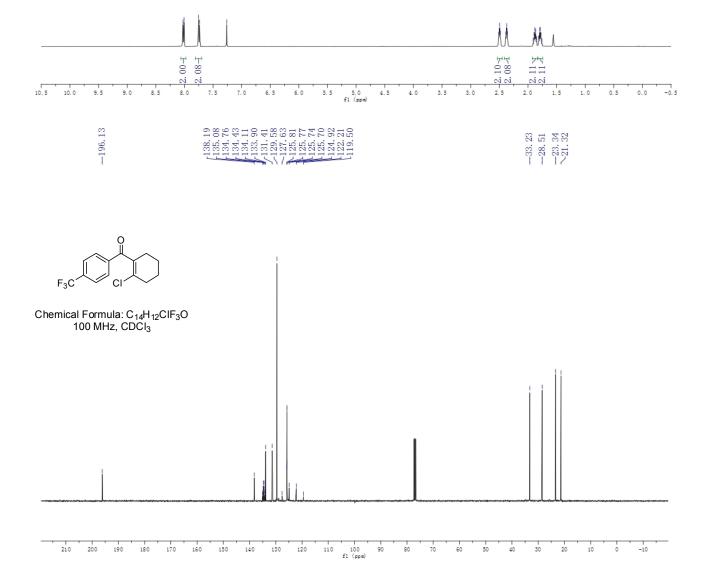
Ketone **33** (18 mg) was prepared according to the general procedure of the photo reaction from **S47** in 76% yield. The reaction time is 2.5 h under 254 nm light. The products were isolated through silica gel flash chromatography (20% ethyl

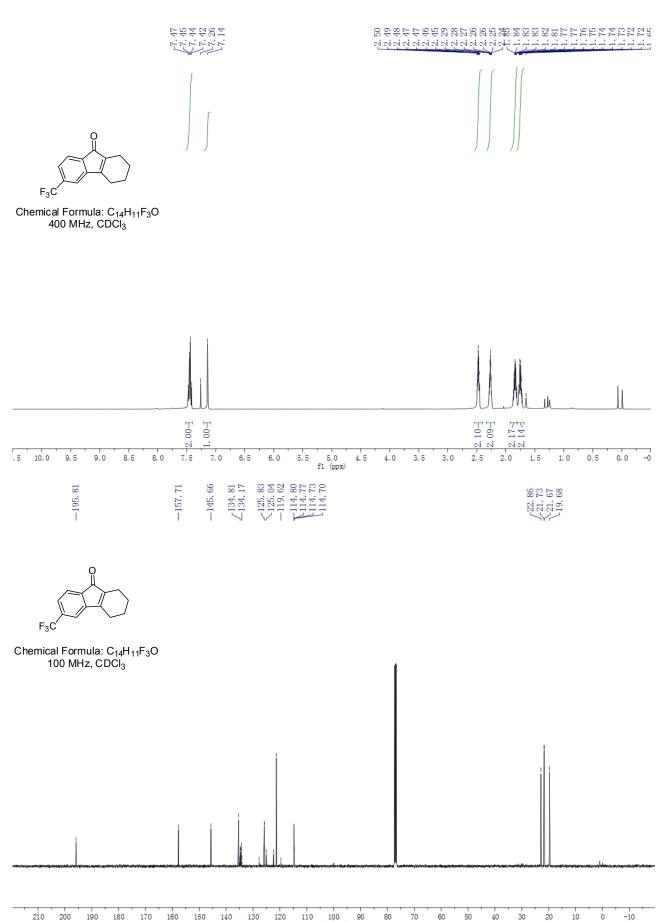
acetate-petroleum ether) as yellow solid: $R_f = 0.63$ (50% ethyl acetate-petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.38 (d, J = 5.3 Hz, 1H), 7.55 (d, J = 7.1 Hz, 1H), 7.02 (dd, J = 6.9, 5.5 Hz, 1H), 2.92 – 2.69 (m, 2H), 2.57 – 2.34 (m, 2H), 1.89 – 1.80 (m, 2H), 1.83 – 1.70 (m, 2H), 1.70 – 1.45 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 195.5, 167.5, 159.8, 151.6, 140.5, 128.2, 124.7, 121.9, 30.8, 26.8, 26.4, 25.5, 23.5 ppm; HRMS (EI): Exact mass calcd for C₁₃H₁₃NO [M]⁺: 199.0997; found 199.0995.



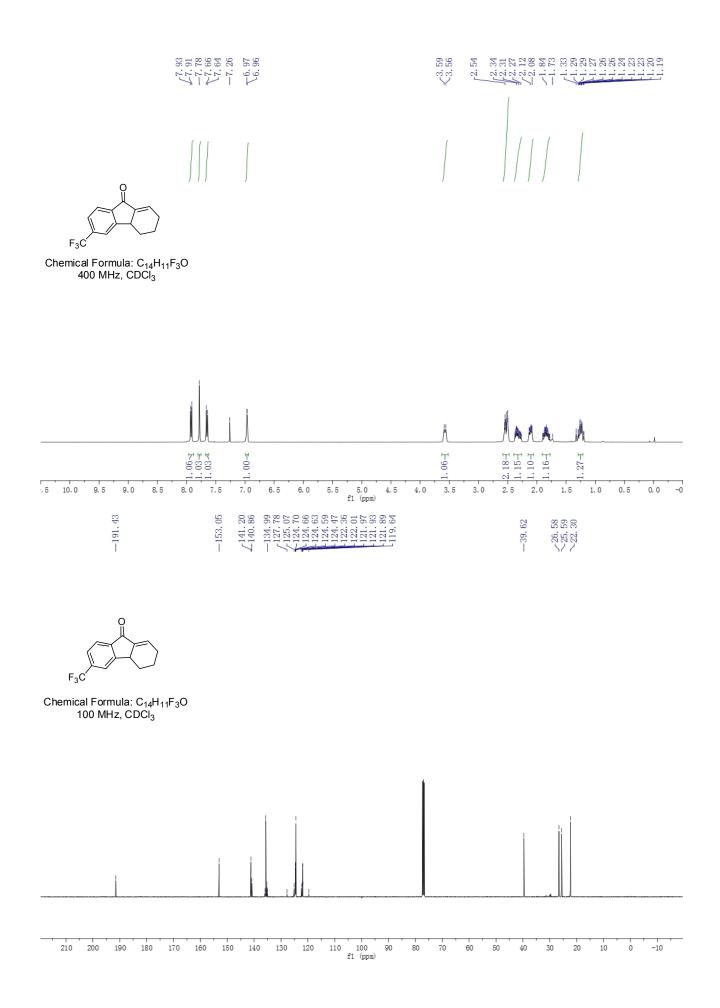


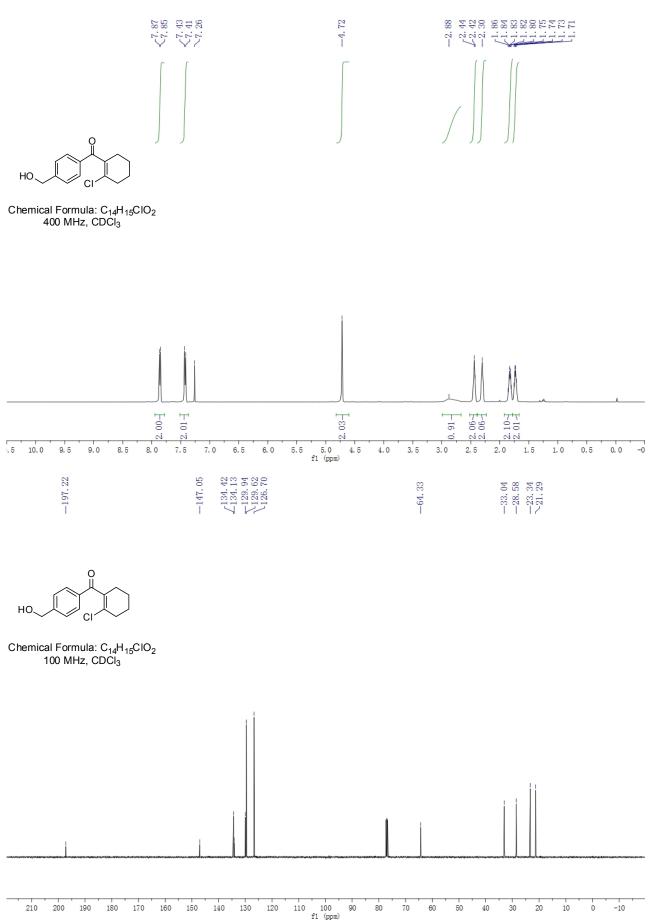


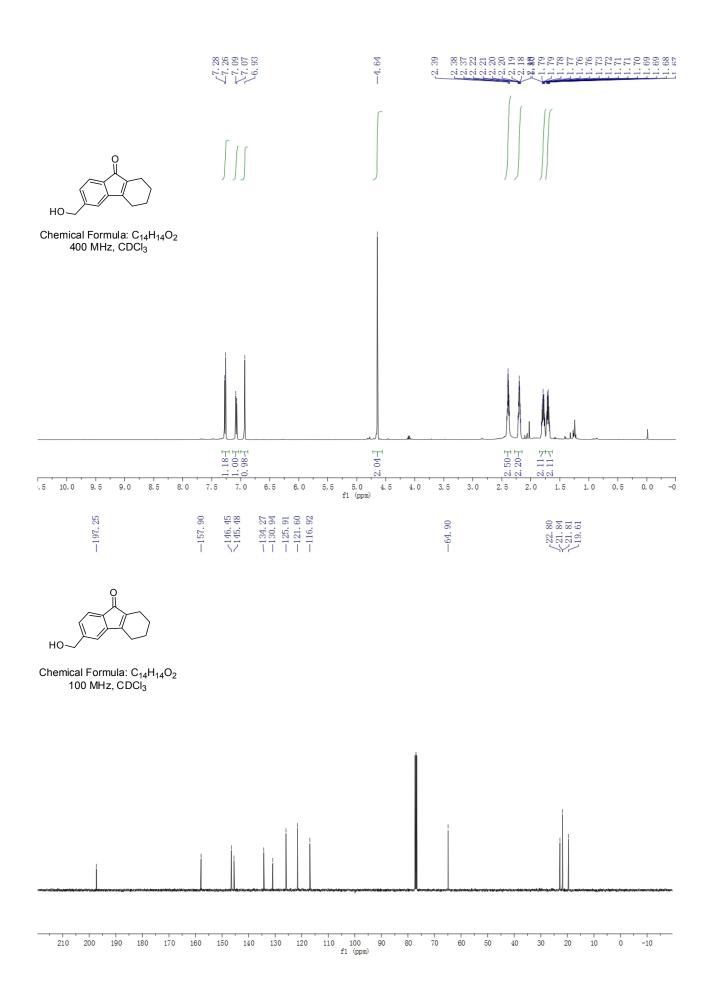


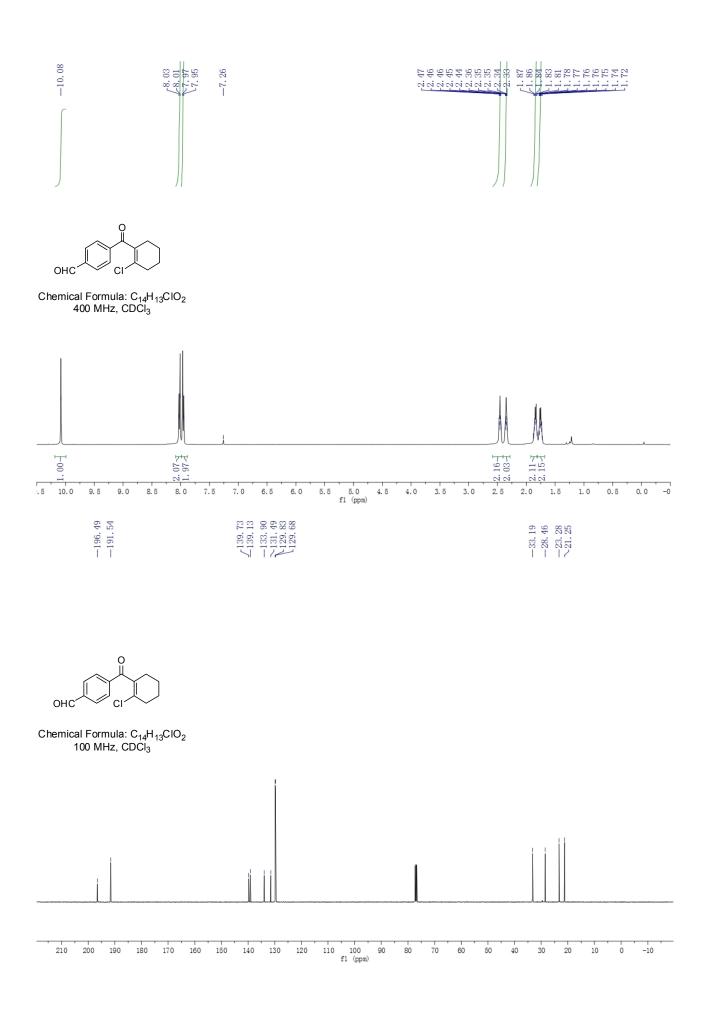


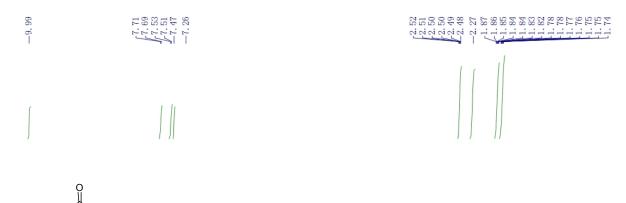
f1 (ppm)

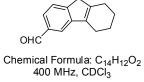


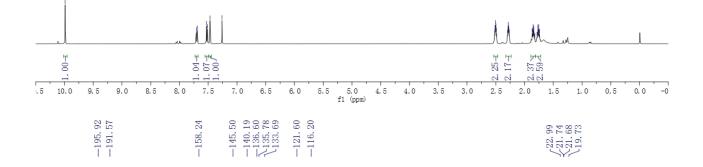


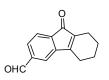


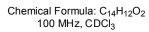


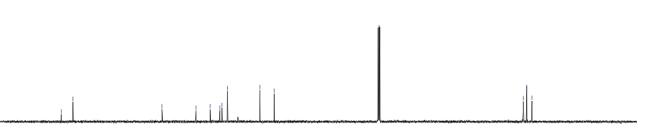




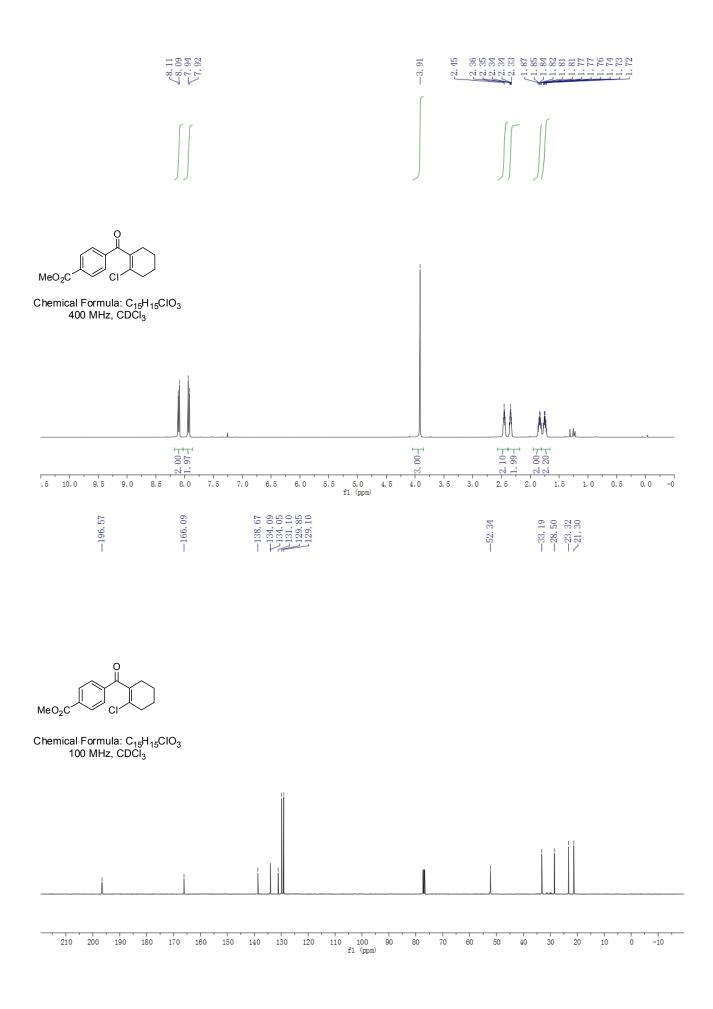


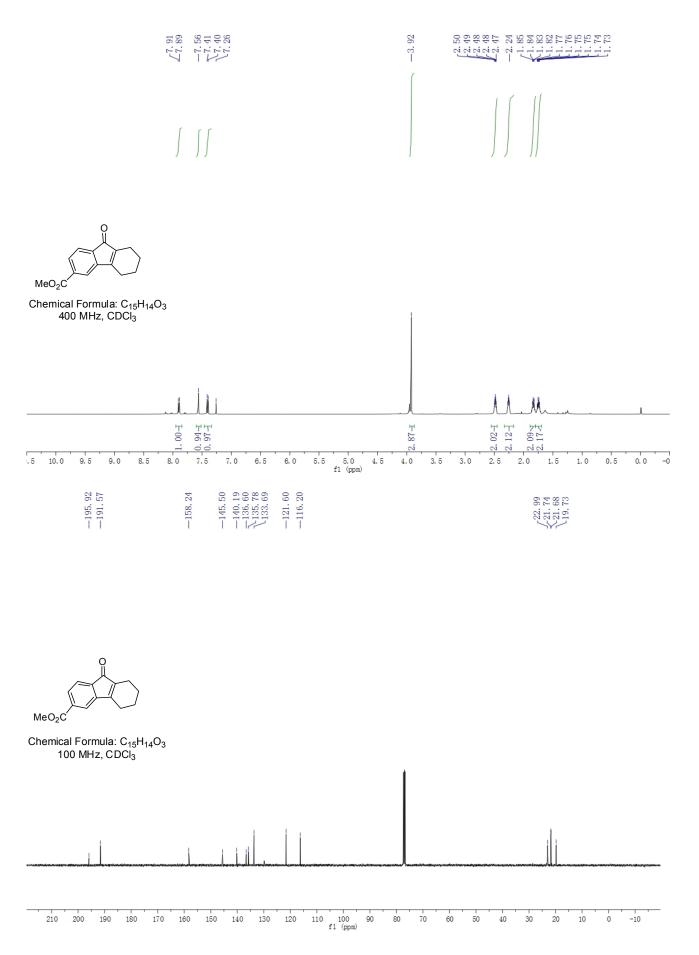


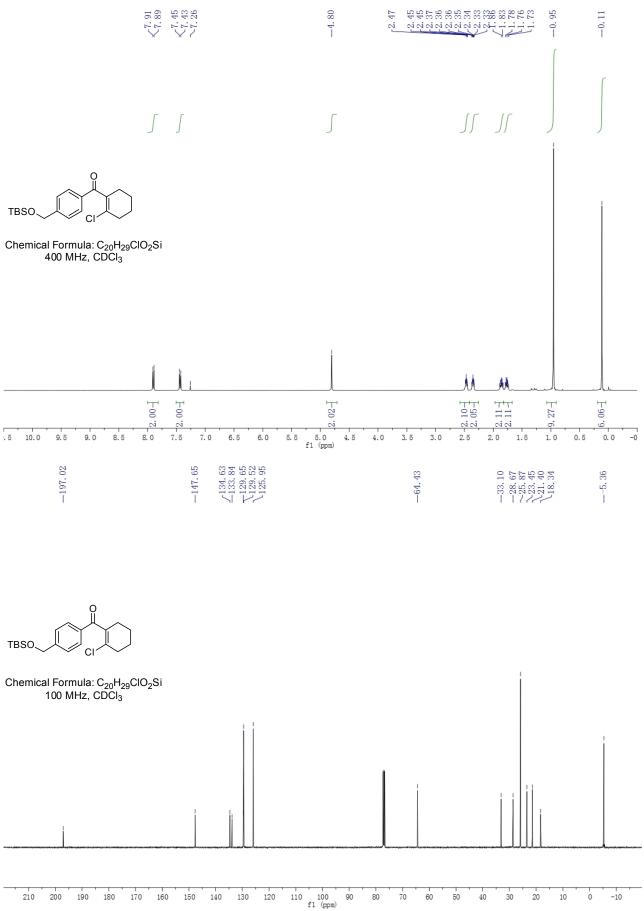


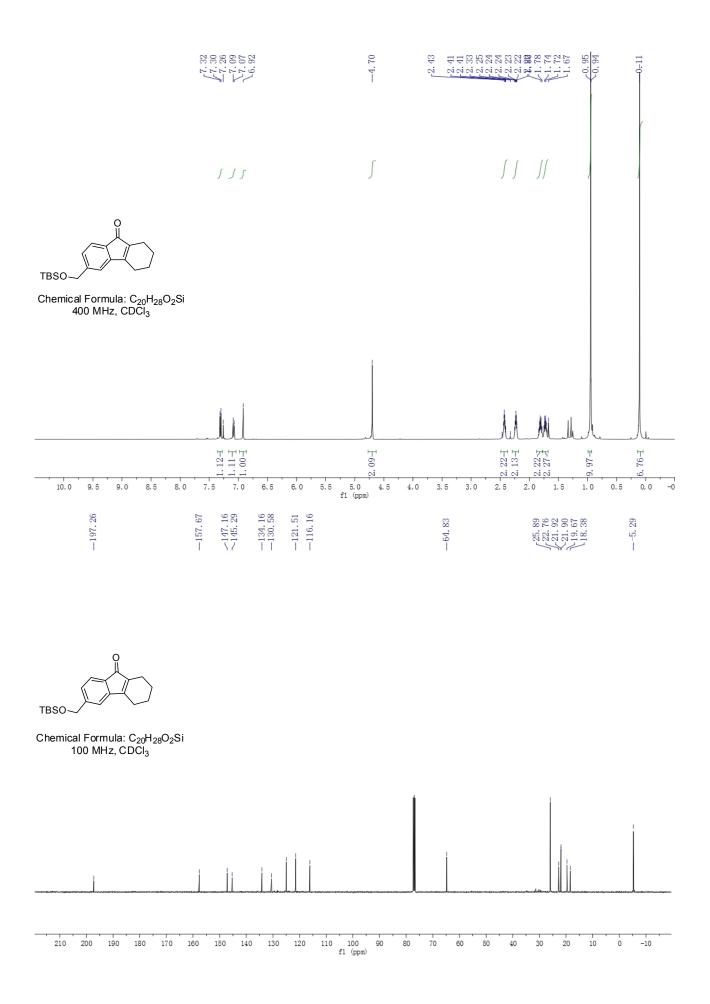


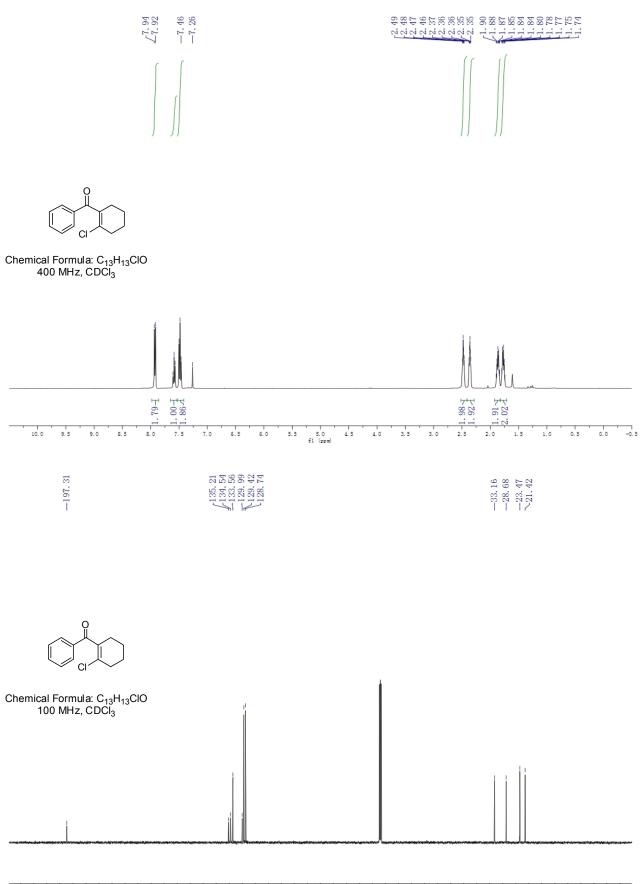
110 100 f1 (ppm) ò -10



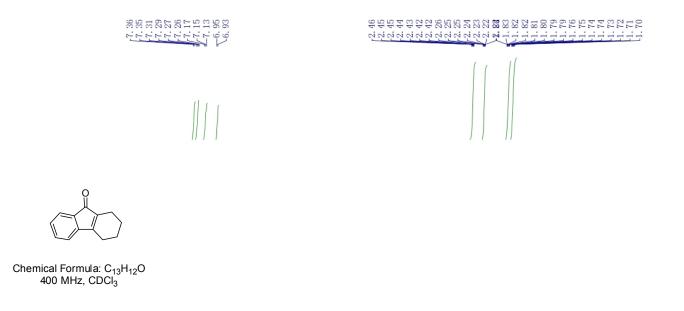


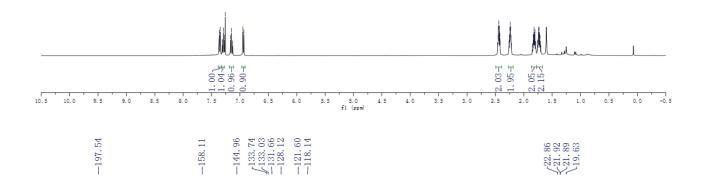


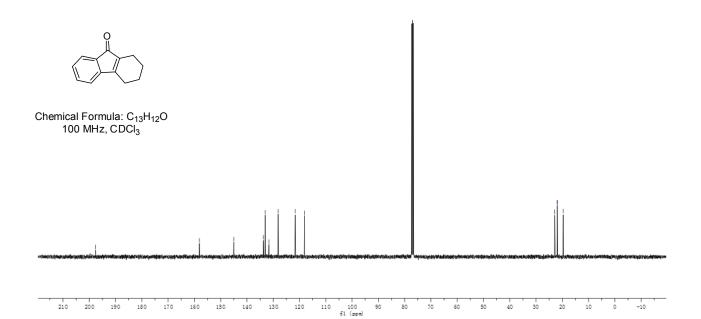


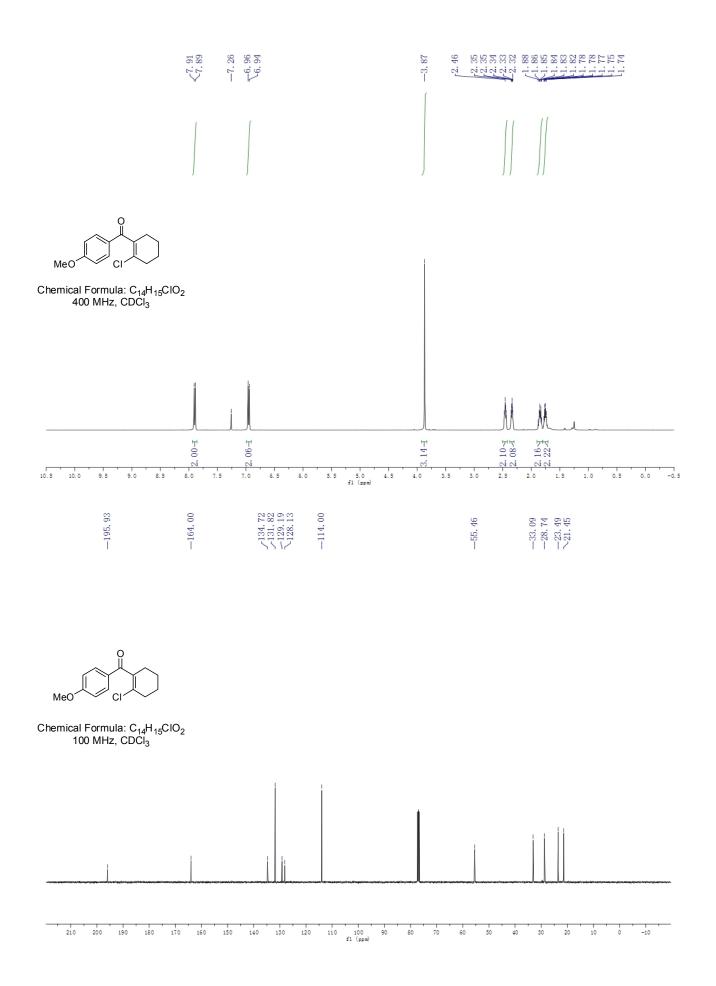


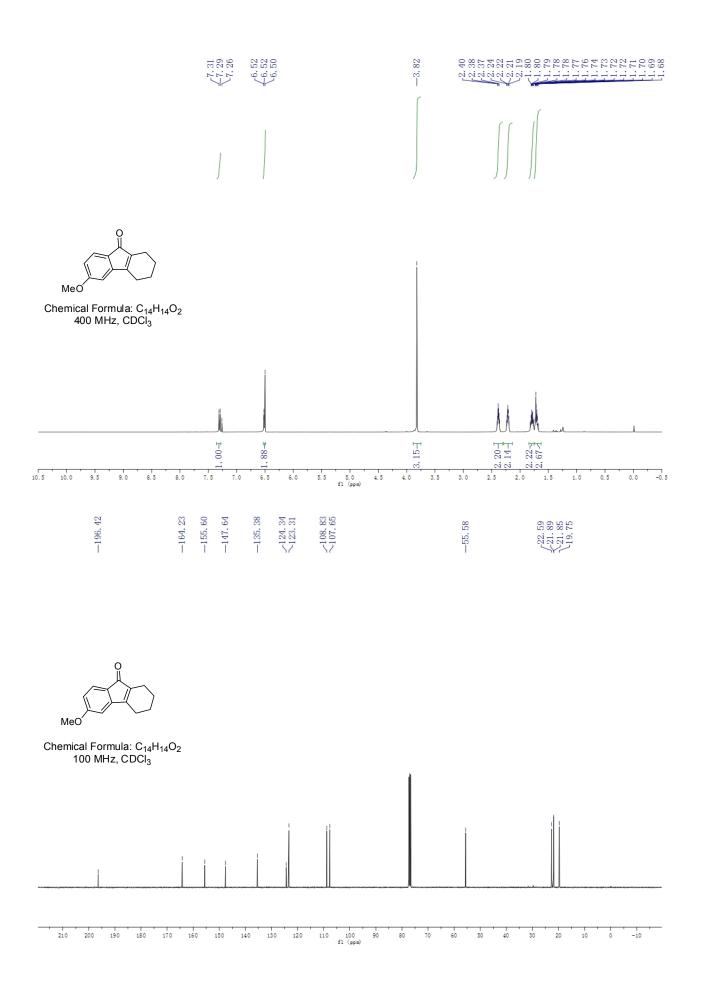
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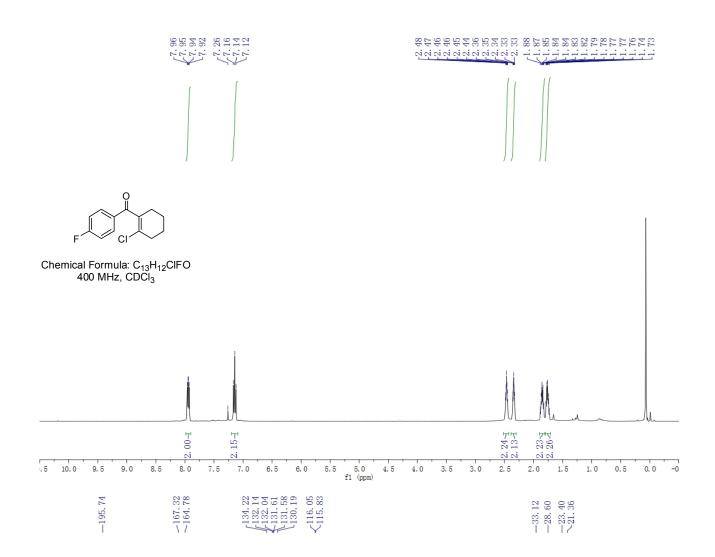


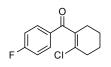




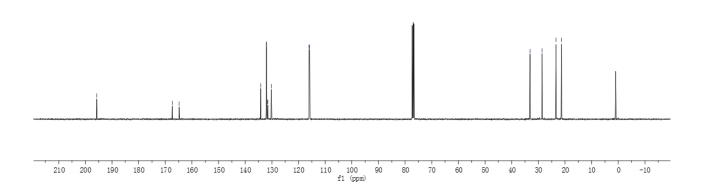


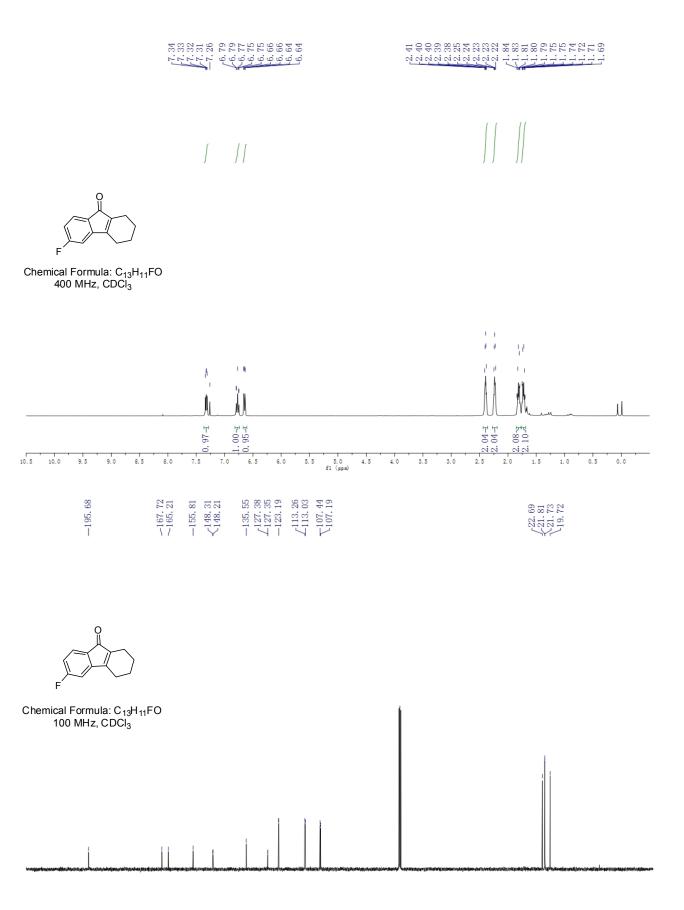




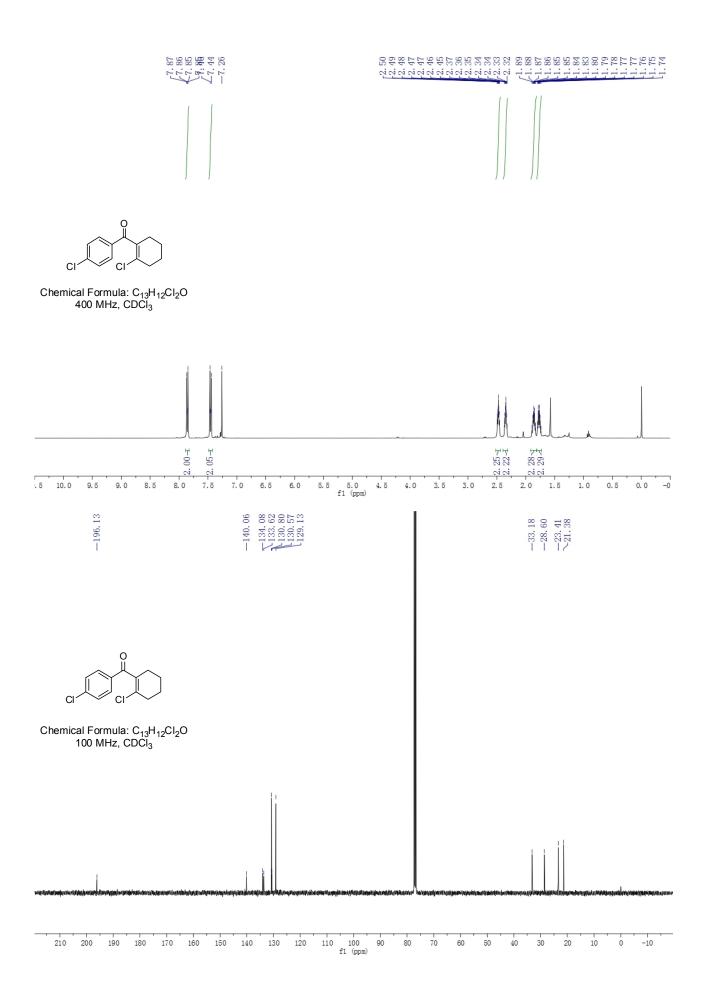


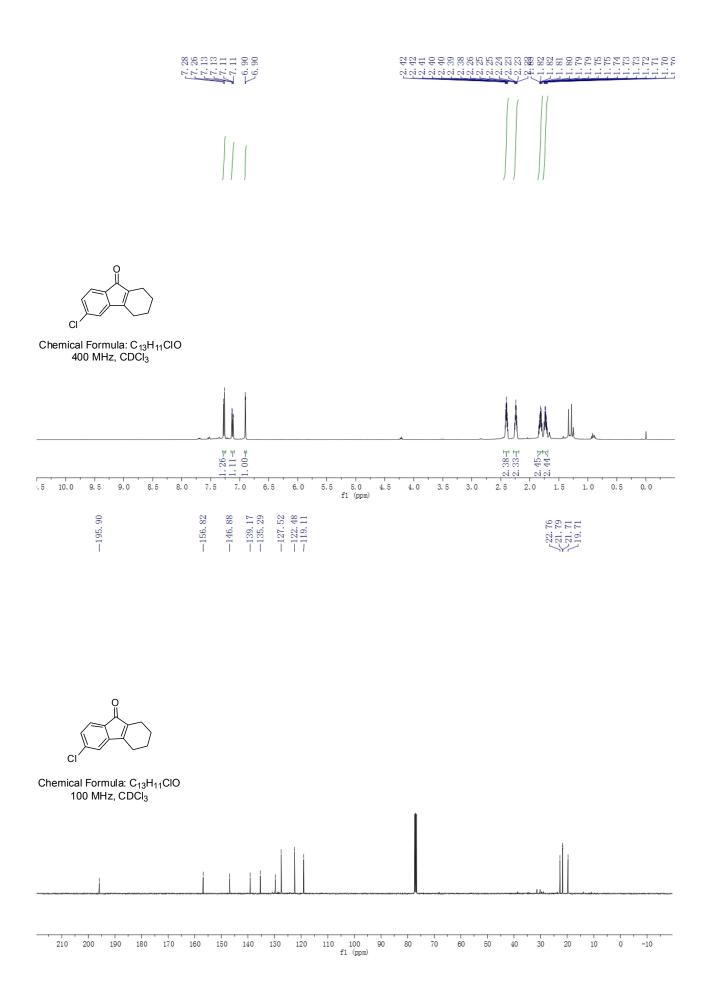
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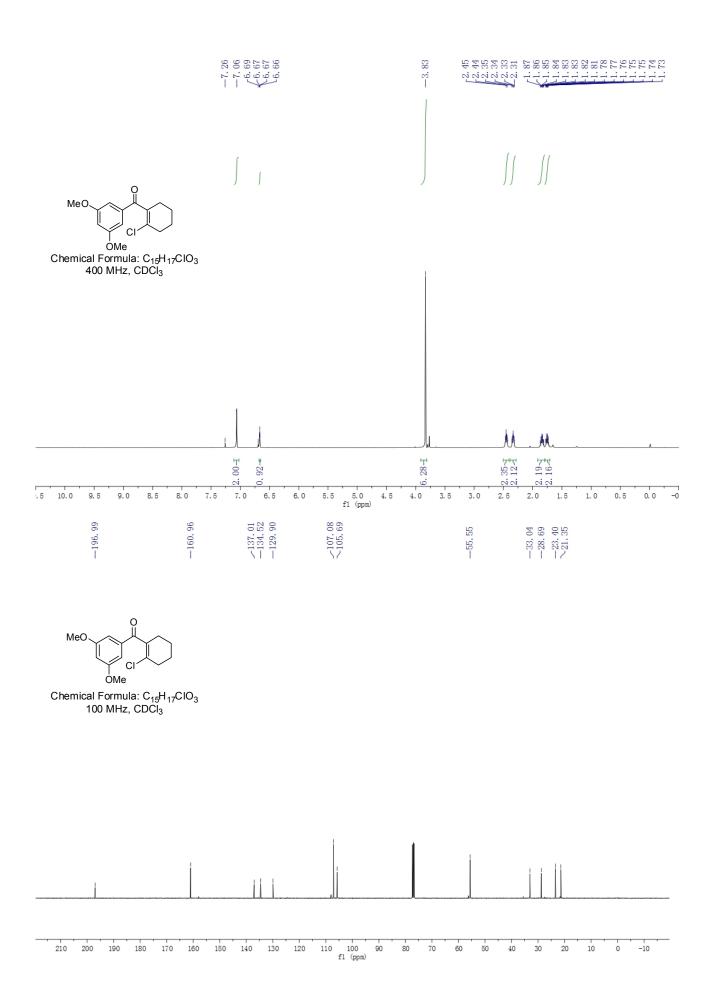


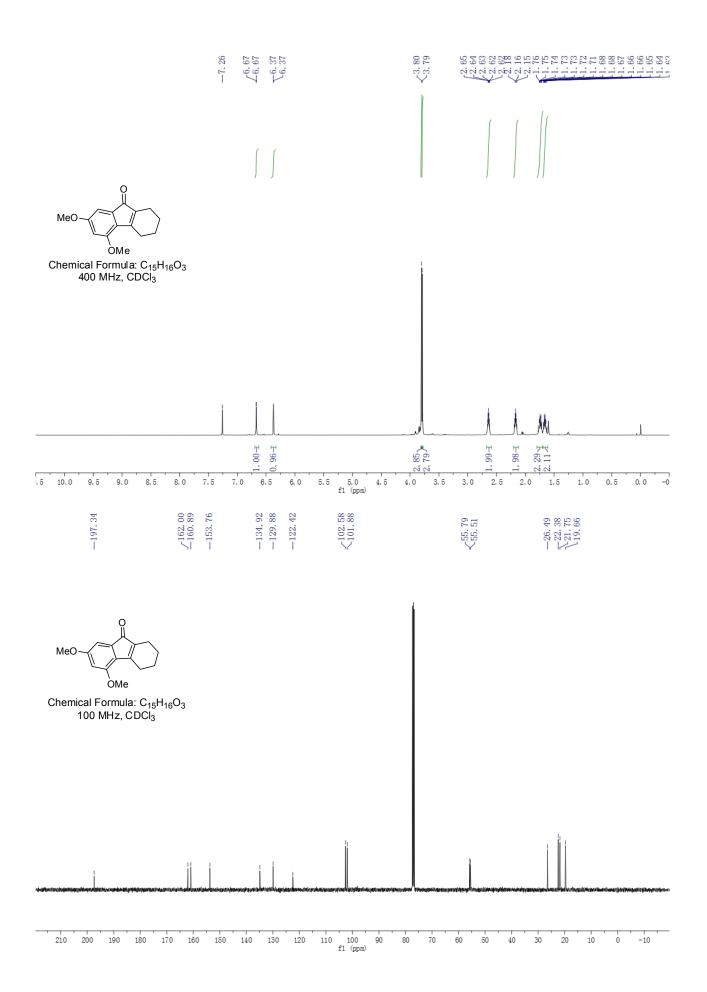


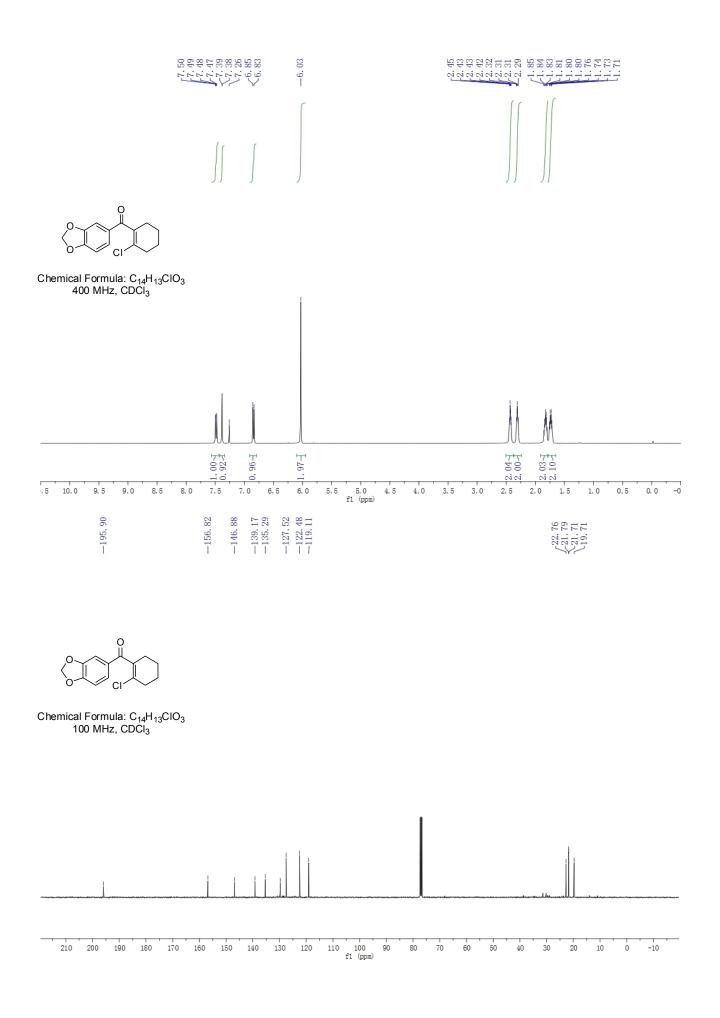
110 100 f1 (ppm) -10



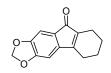




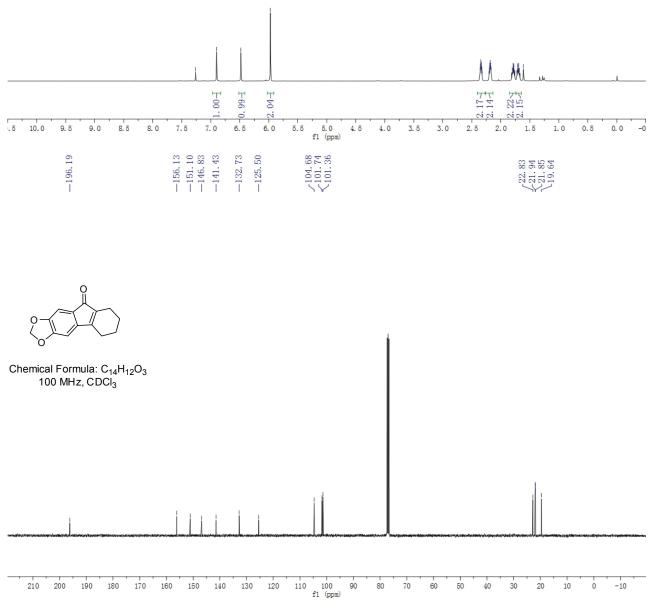


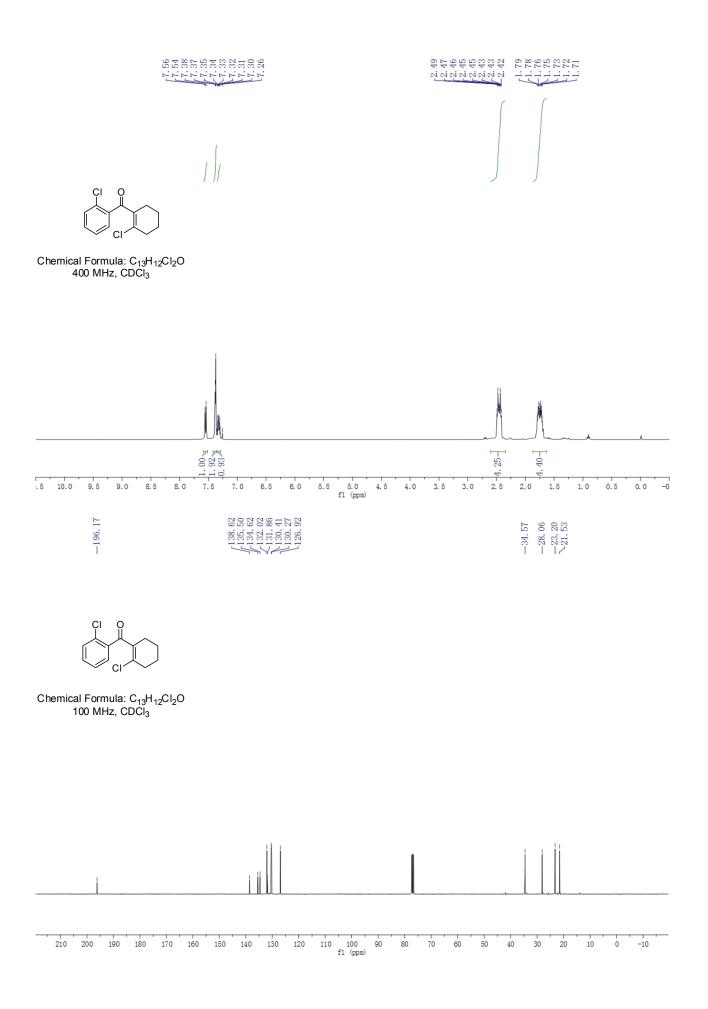


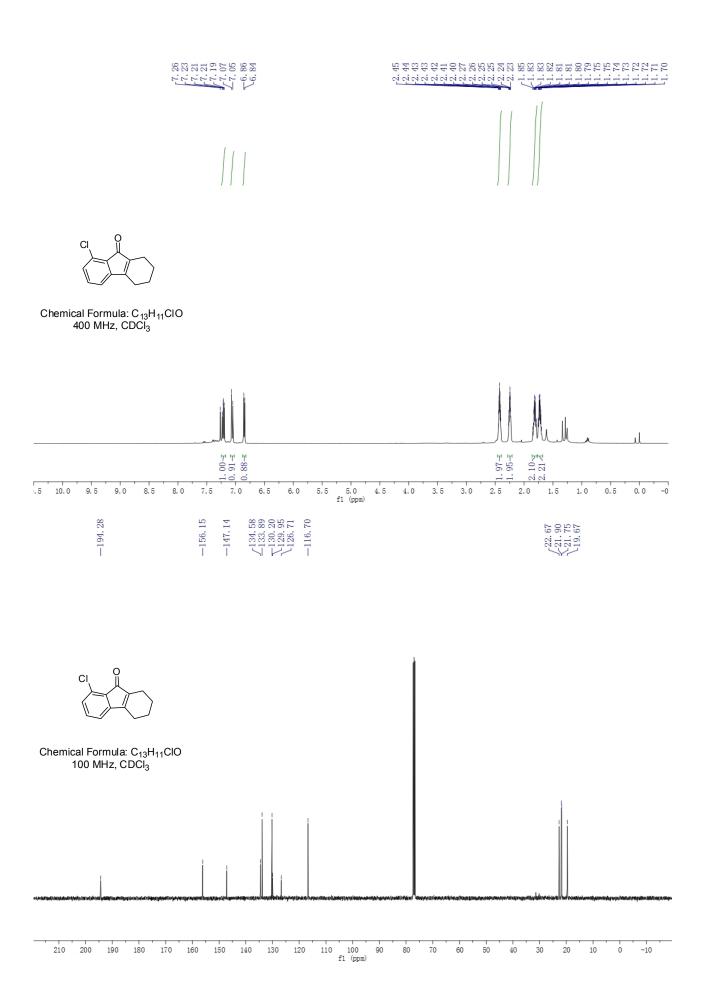


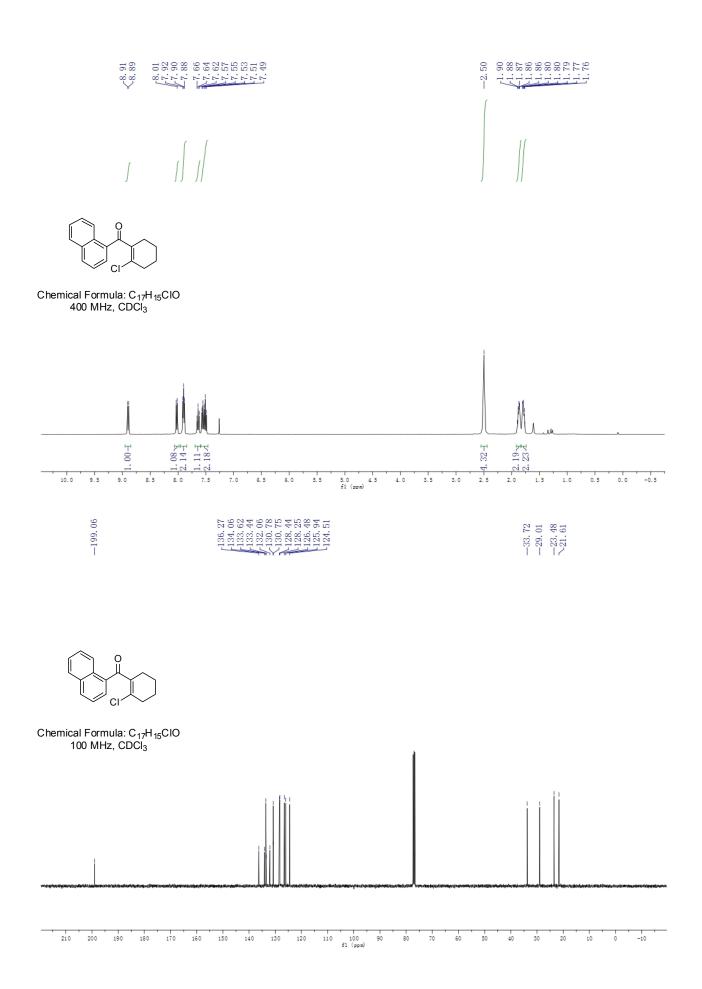


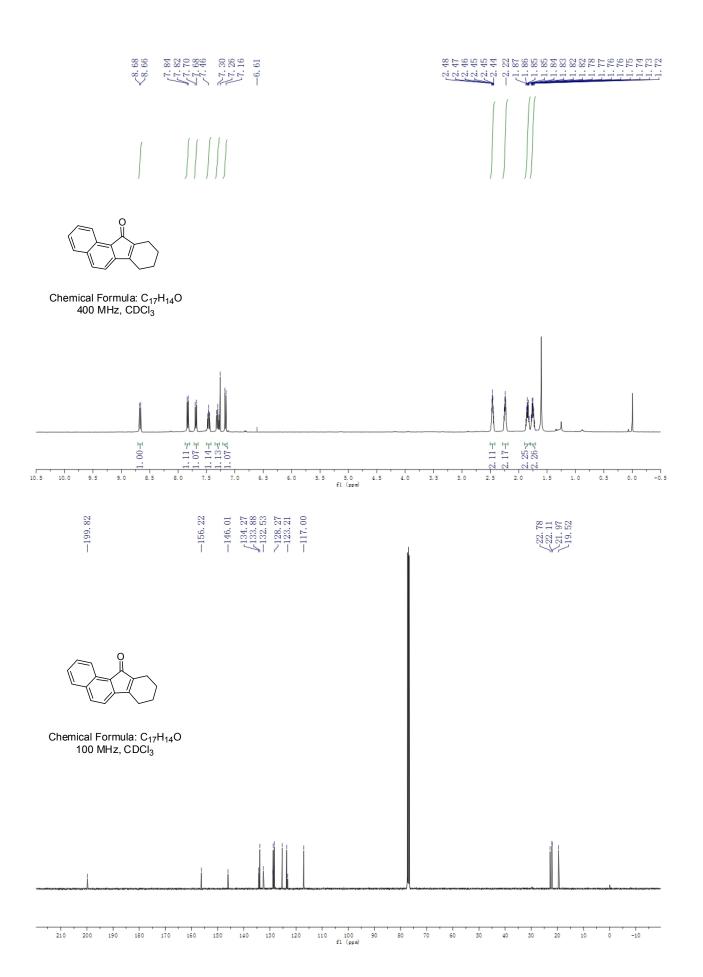
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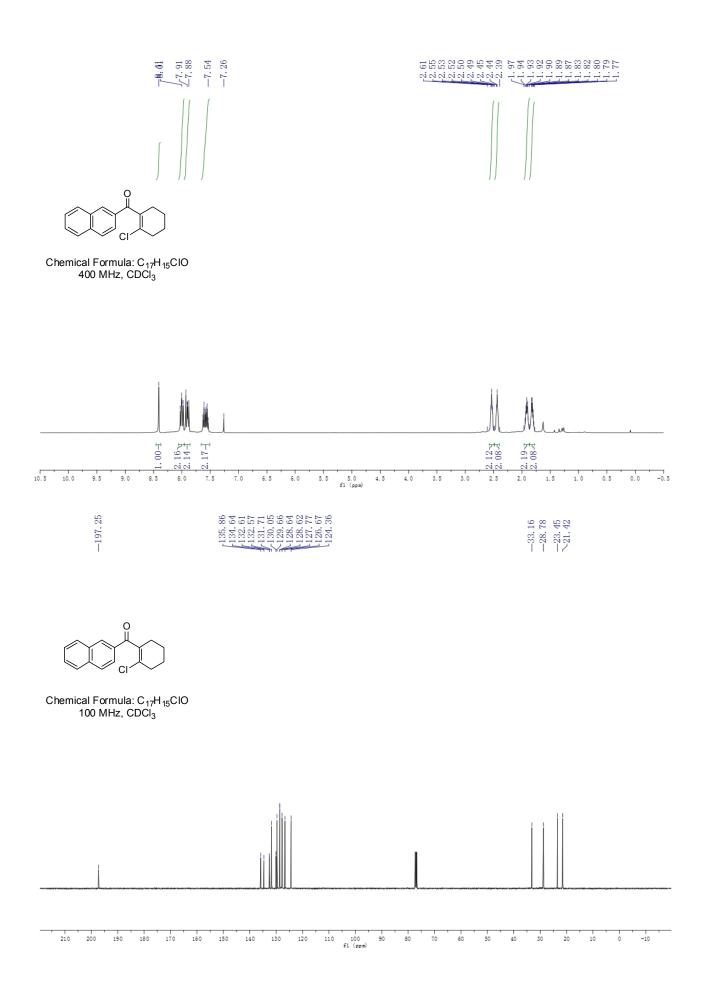


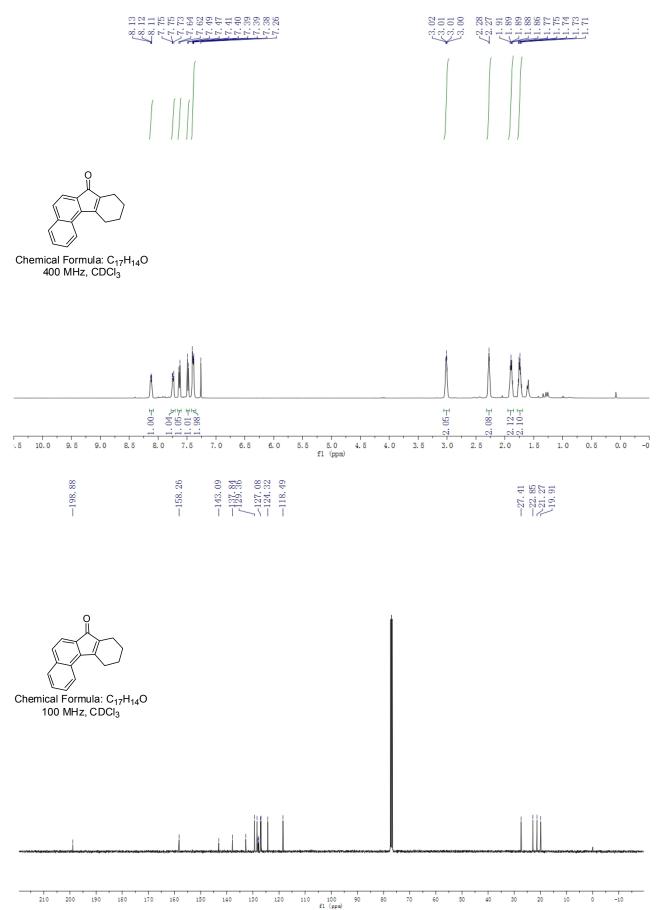


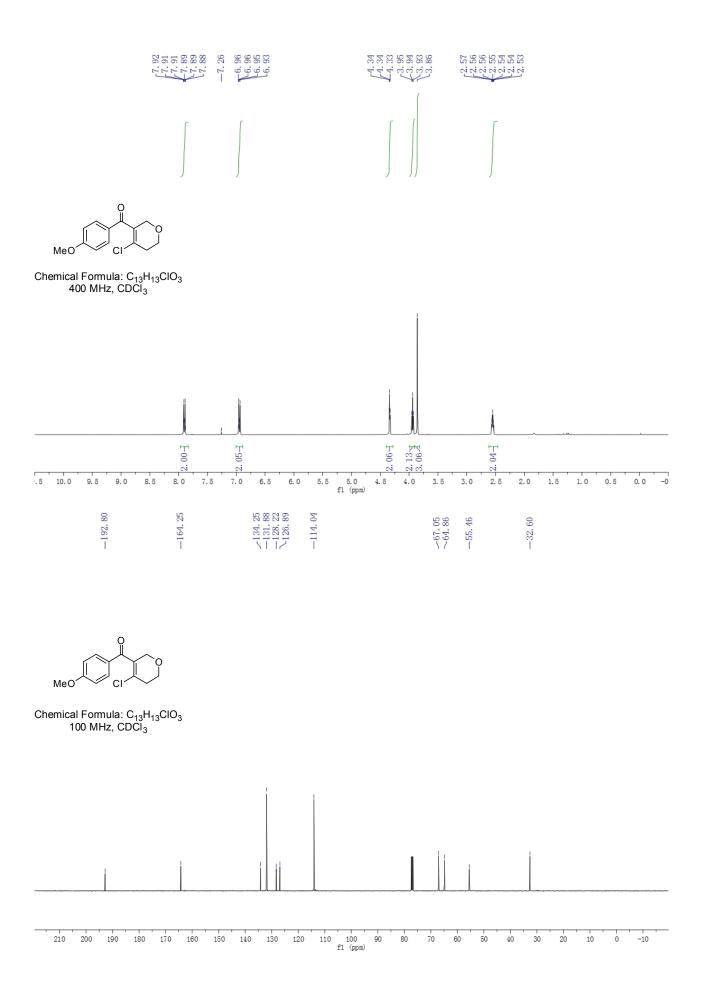


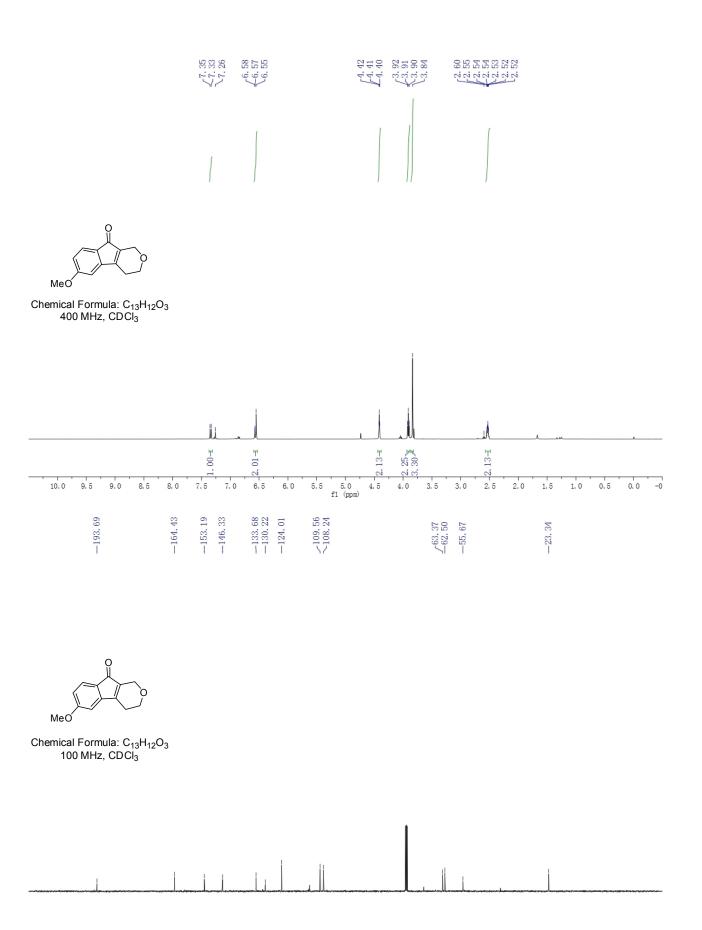


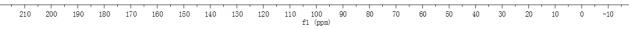


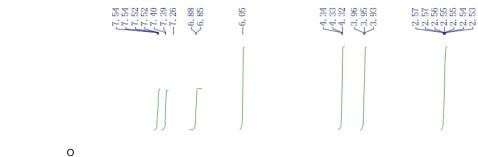






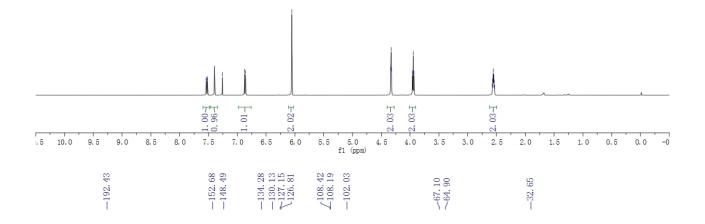






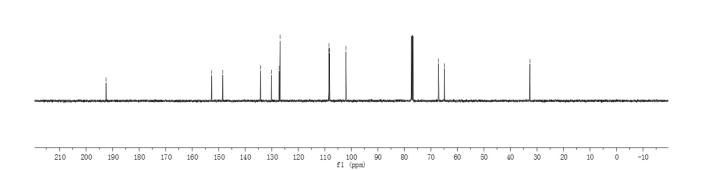
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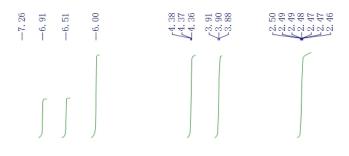
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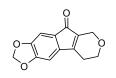


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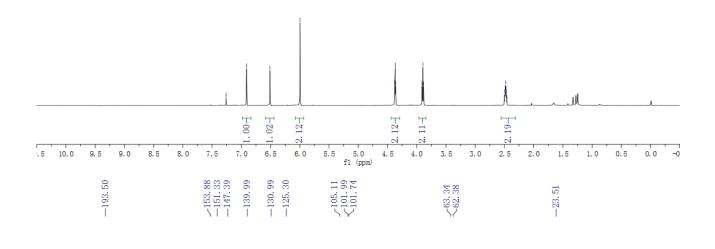
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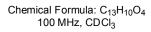


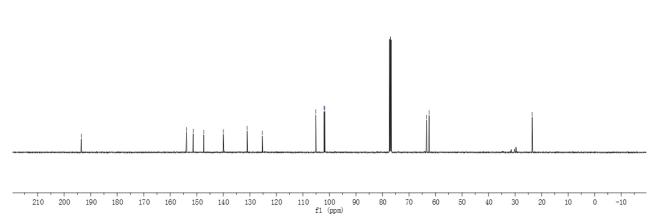


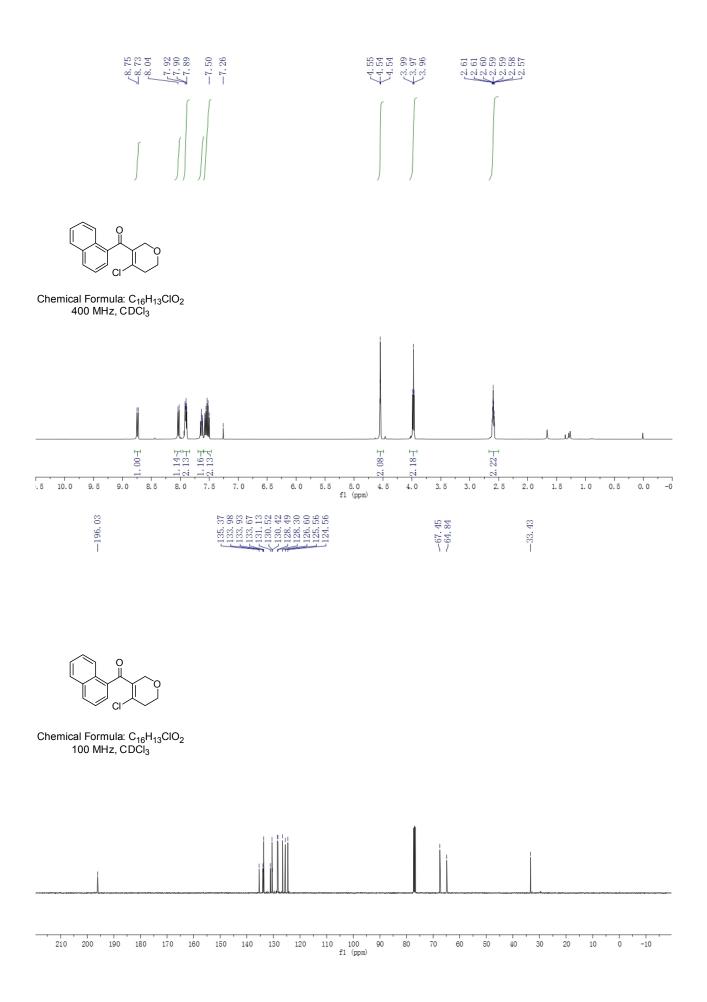
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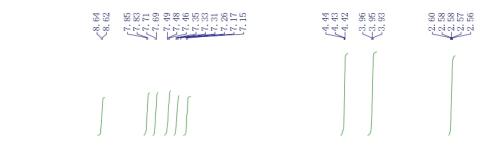


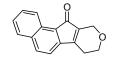
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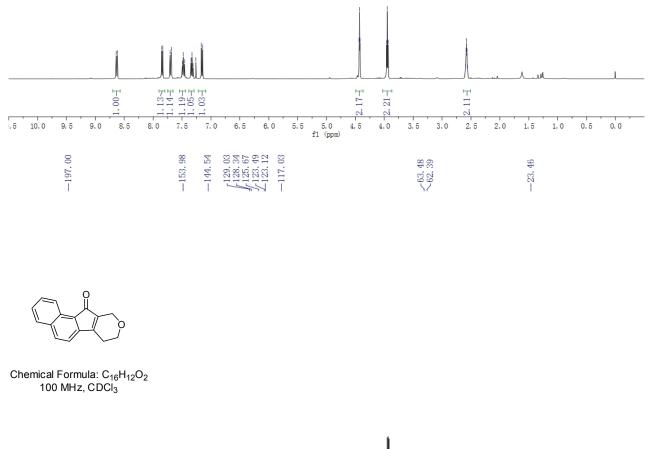


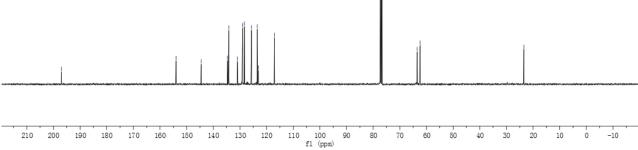






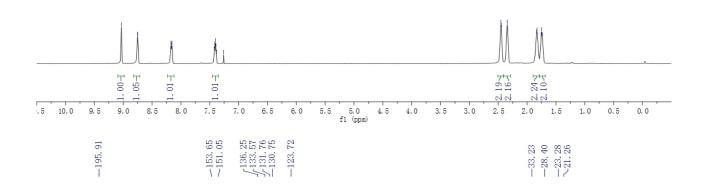
Chemical Formula: C₁₆H₁₂O₂ 400 MHz, CDCl₃





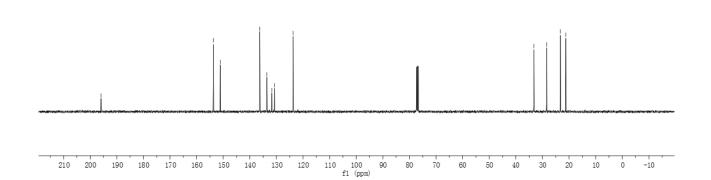


Chemical Formula: C₁₂H₁₂CINO 400 MHz, CDCl₃





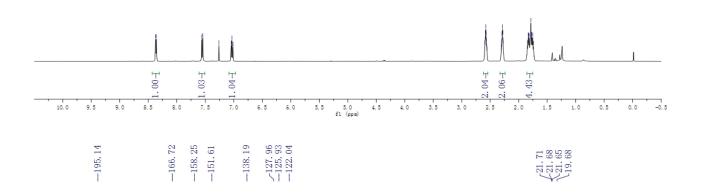
Chemical Formula: C₁₂H₁₂CINO 100 MHz, CDCl₃

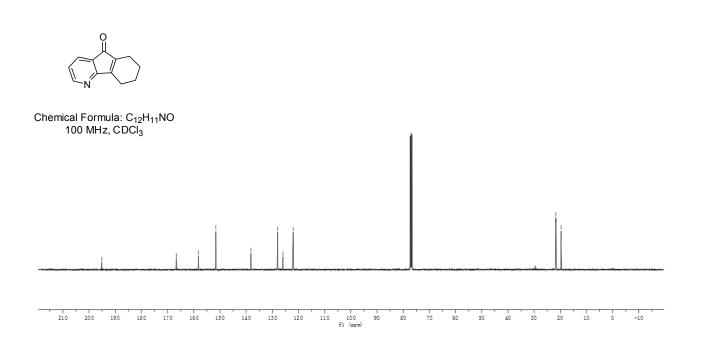


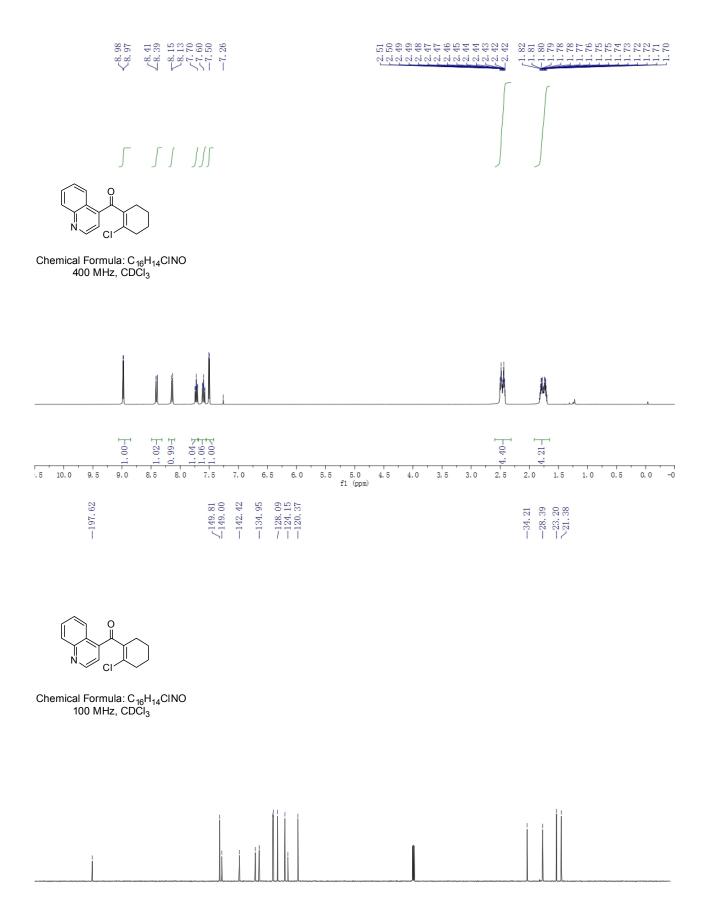




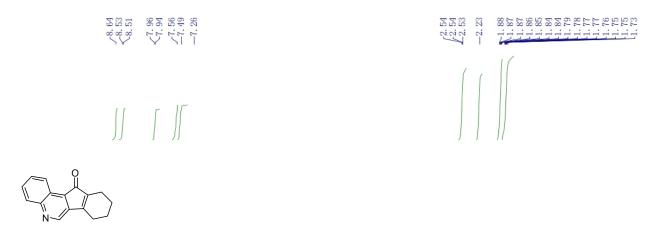
Chemical Formula: C₁₂H₁₁NO 400 MHz, CDCl₃



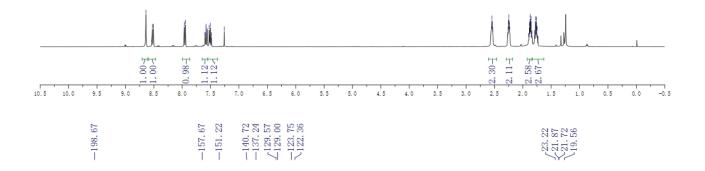


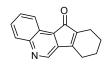


110 100 f1 (ppm) -10

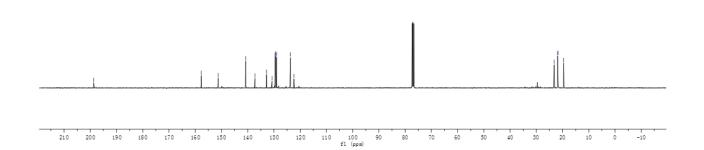


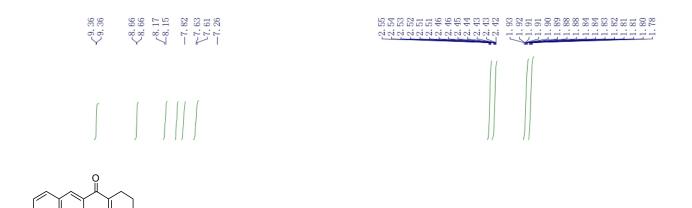
Chemical Formula: C₁₆H₁₃NO 400 MHz, CDCl₃

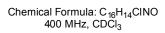




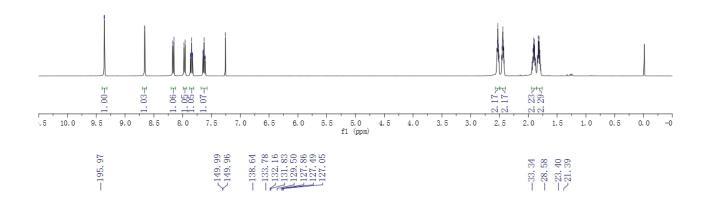
Chemical Formula: C₁₆H₁₃NO 100 MHz, CDCl₃

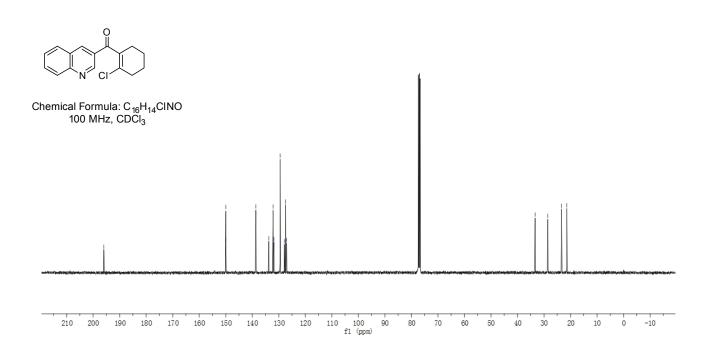


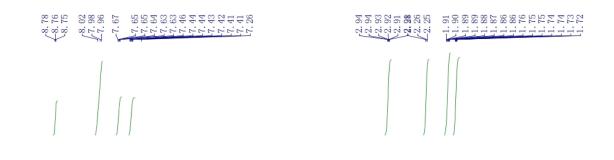


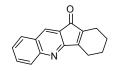


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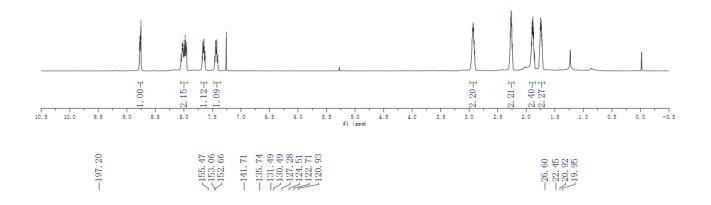




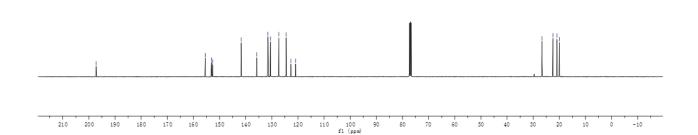


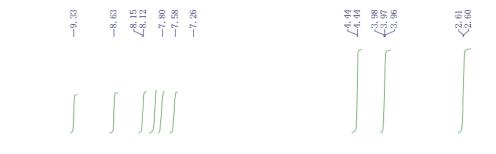


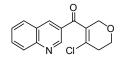
Chemical Formula: C₁₆H₁₃NO 400 MHz, CDCl₃



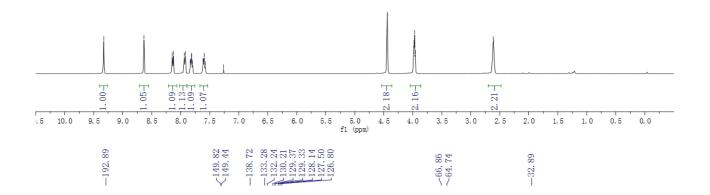
 $\begin{array}{c} \mbox{Chemical Formula: } C_{16} \mbox{H}_{13} \mbox{NO} \\ \mbox{100 MHz, CDCl}_3 \end{array}$

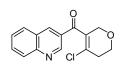




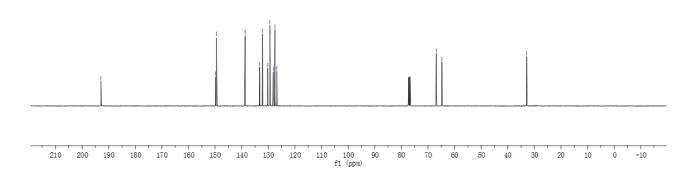


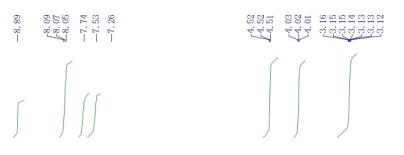
 $\begin{array}{c} \mbox{Chemical Formula: } C_{15} H_{12} CINO_2 \\ \mbox{400 MHz, } CDCl_3 \end{array}$

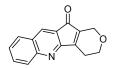




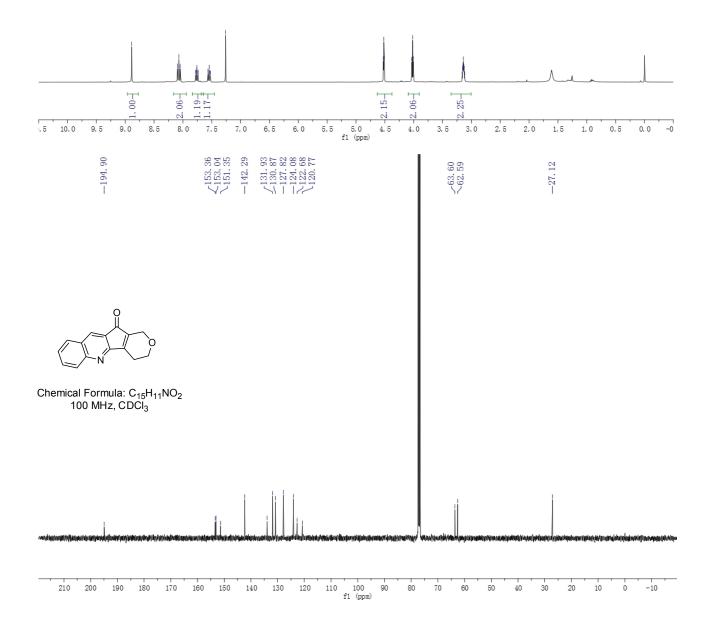
 $\begin{array}{c} \mbox{Chemical Formula: } C_{15}\mbox{H}_{12}\mbox{CINO}_2 \\ \mbox{100 MHz, CDCl}_3 \end{array}$

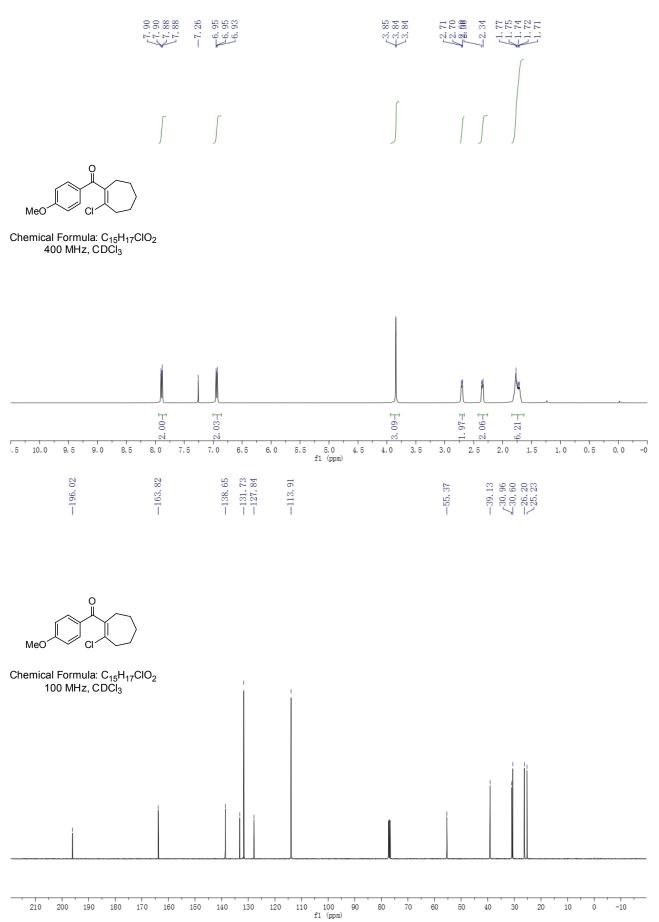


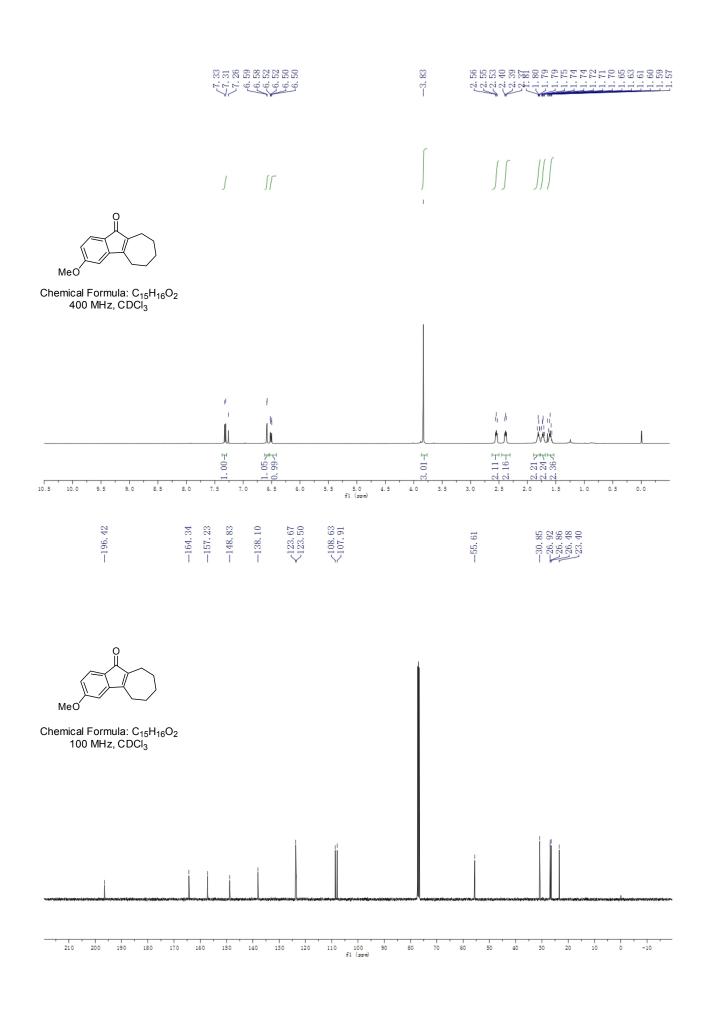


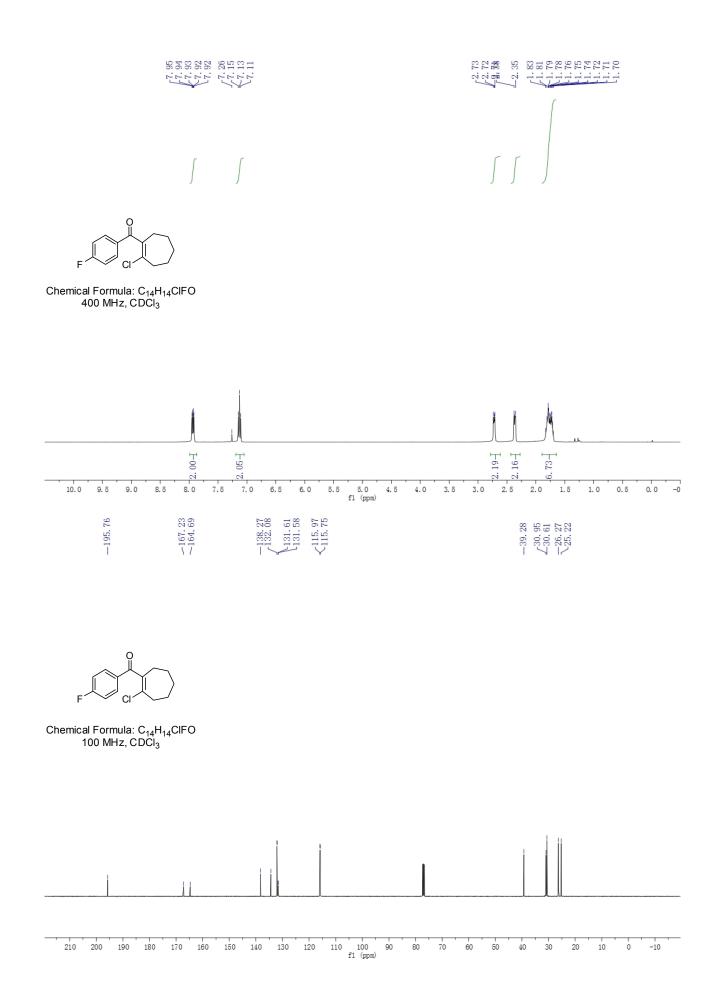


Chemical Formula: C₁₅H₁₁NO₂ 400 MHz, CDCl₃

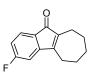


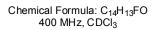


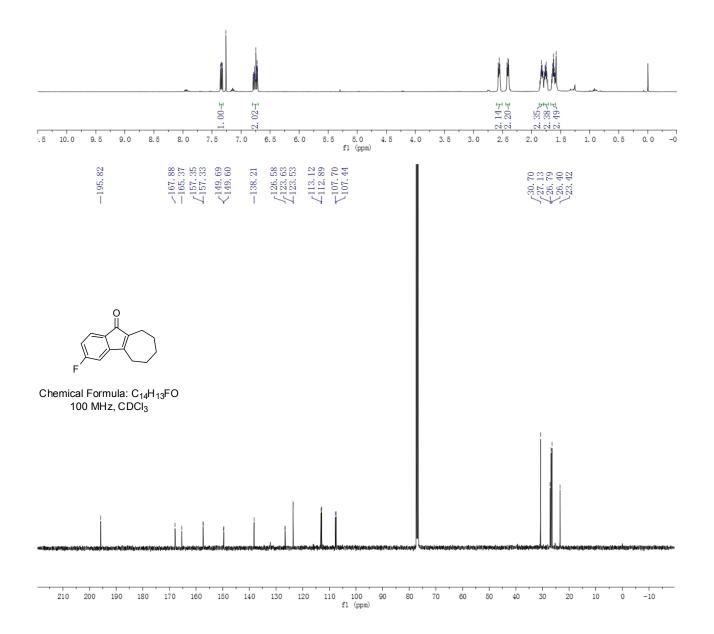


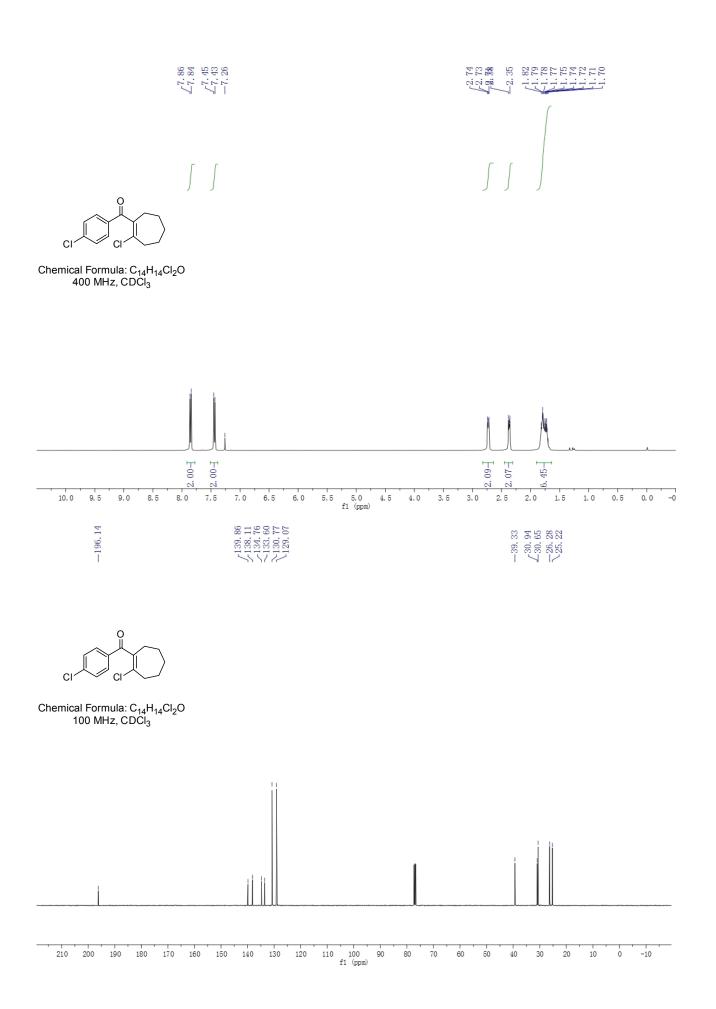


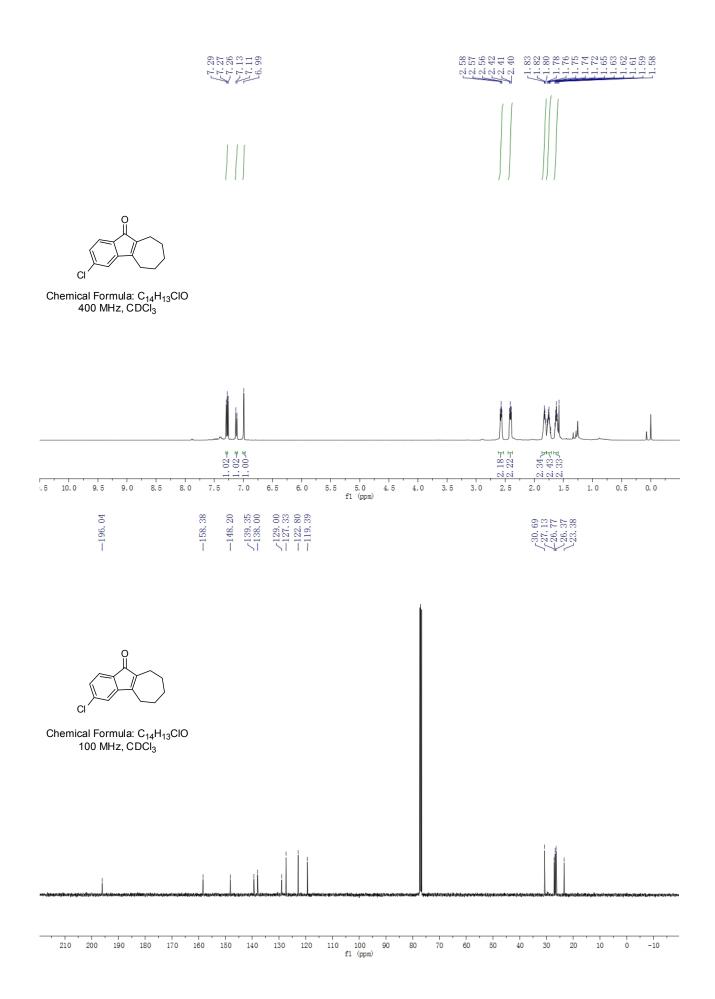


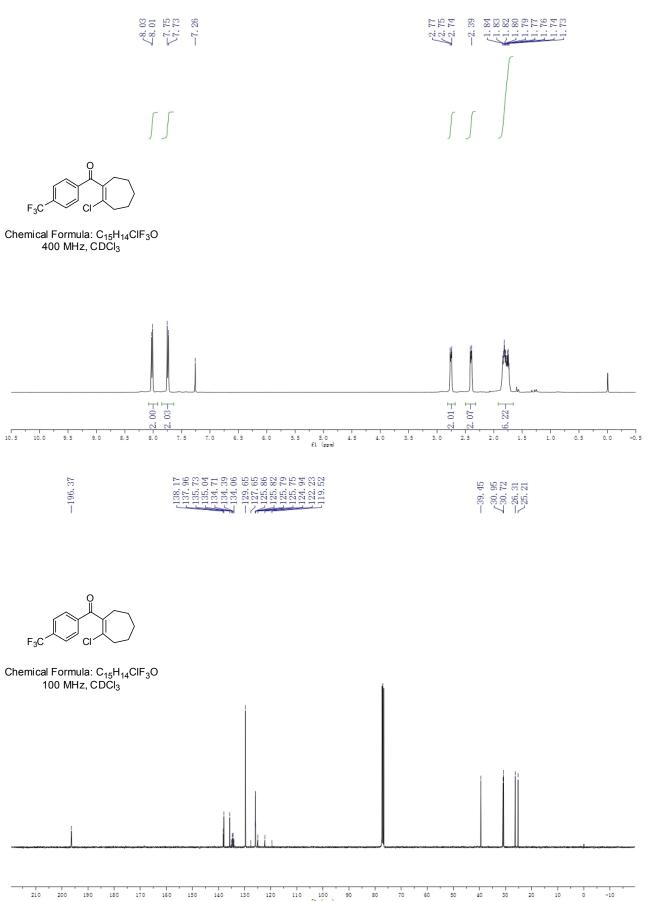




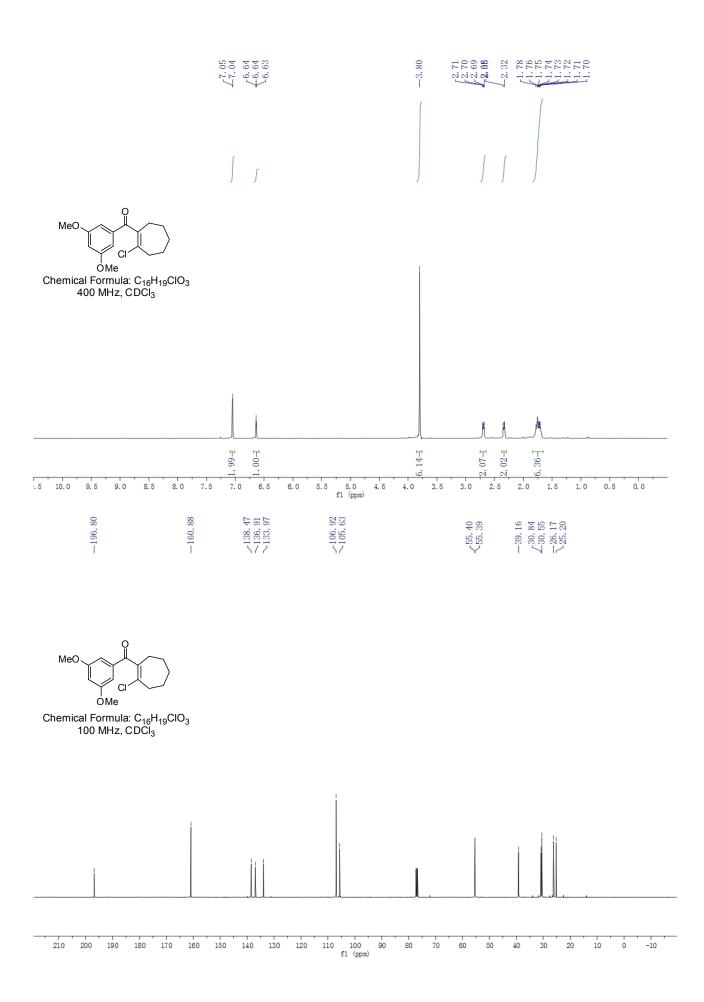


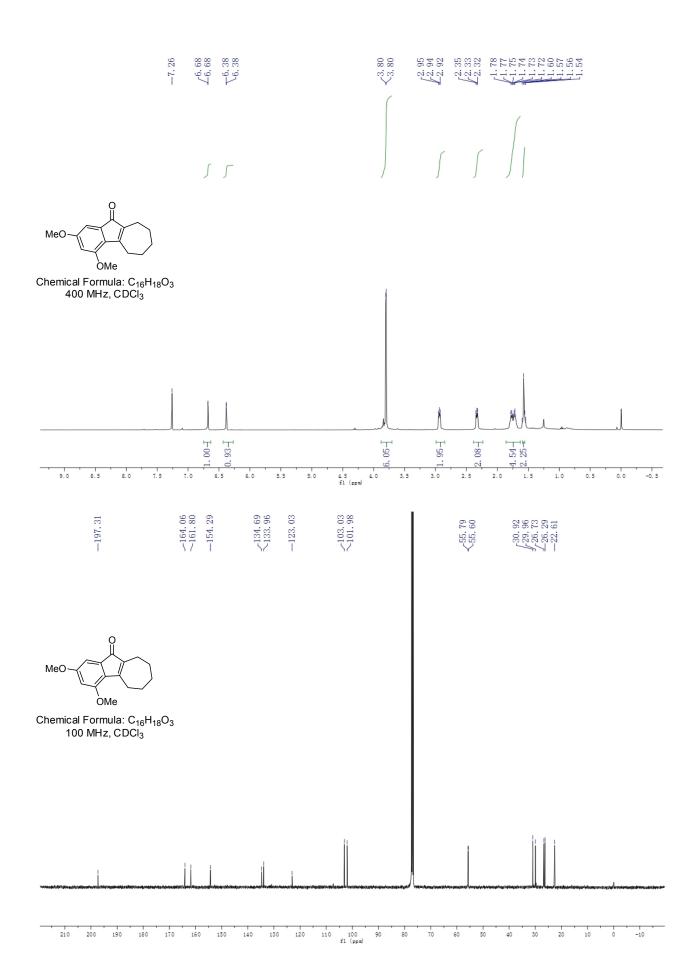


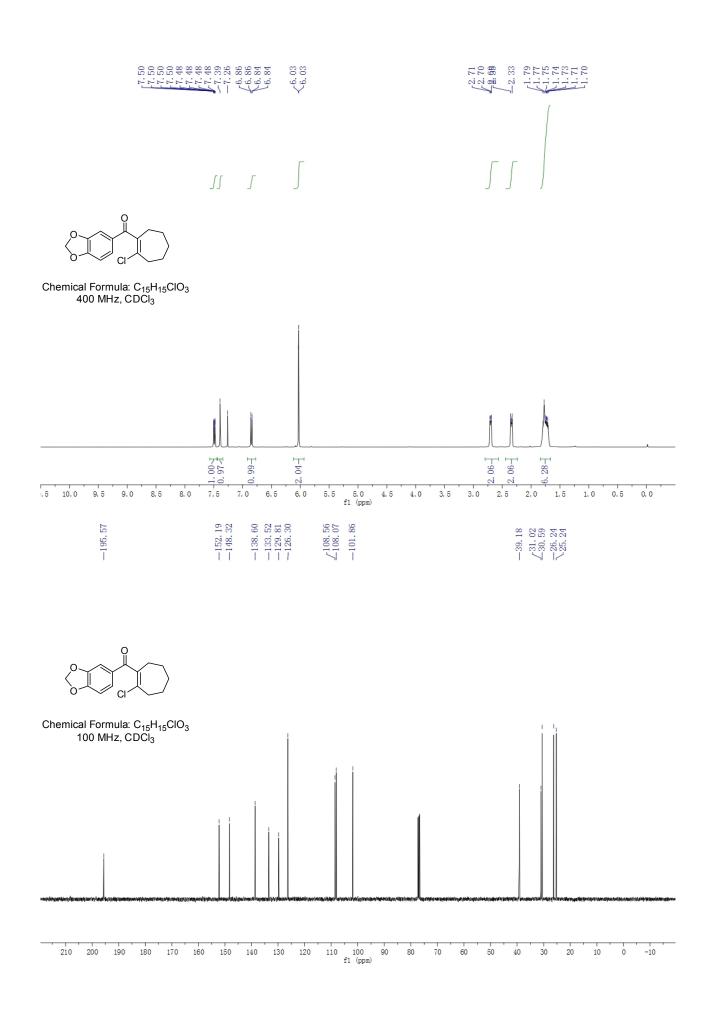


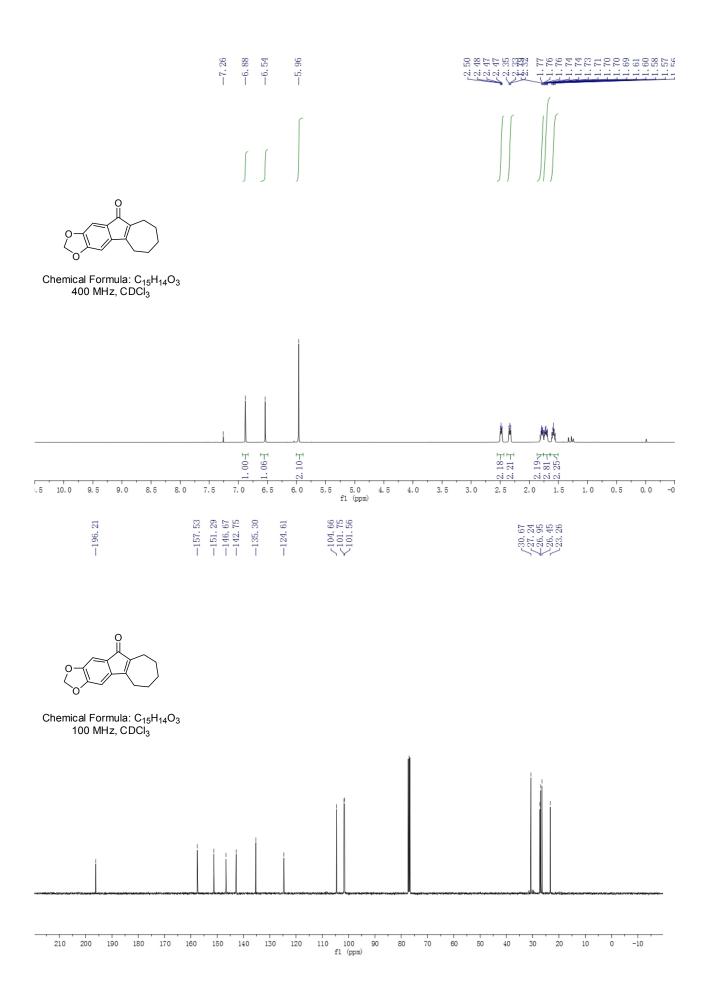


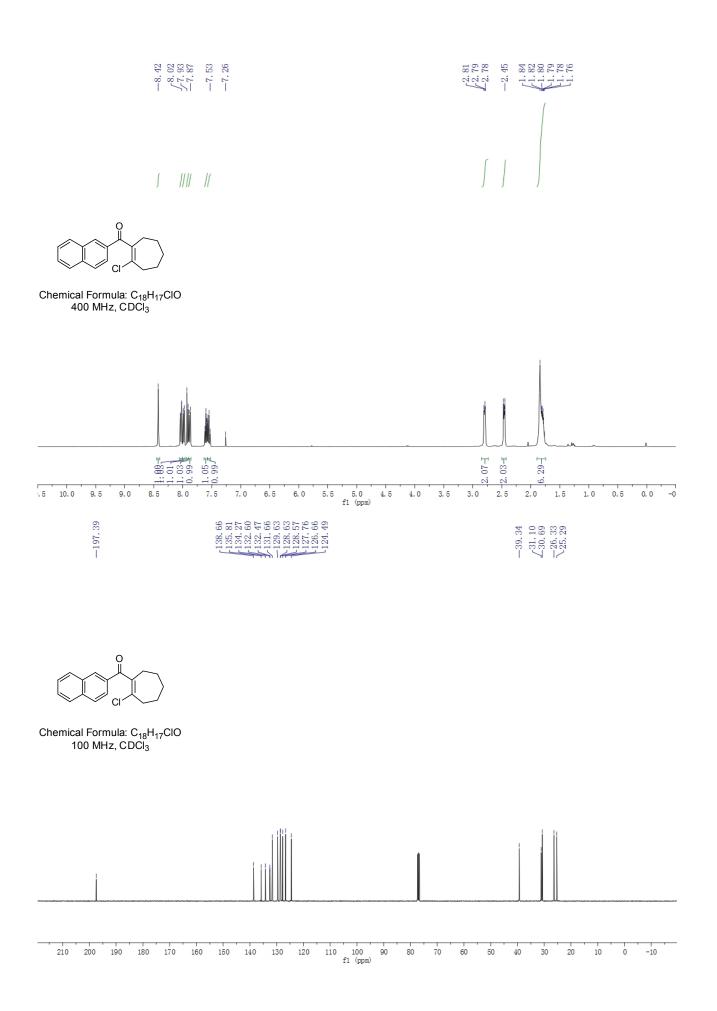
110 100 f1 (ppm) 120

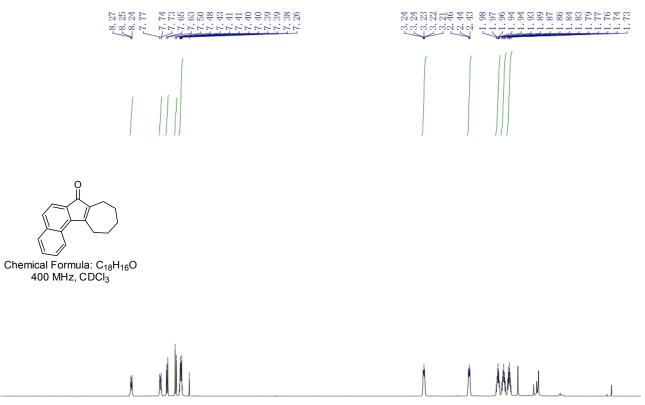


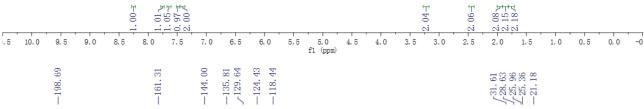


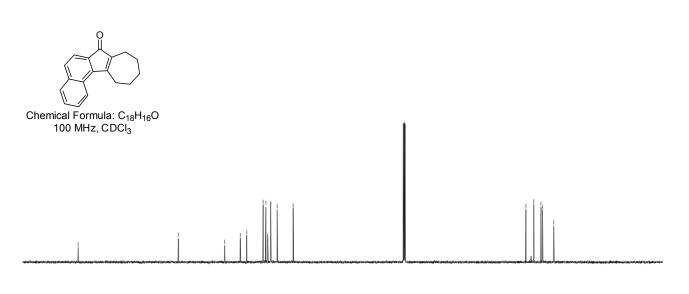




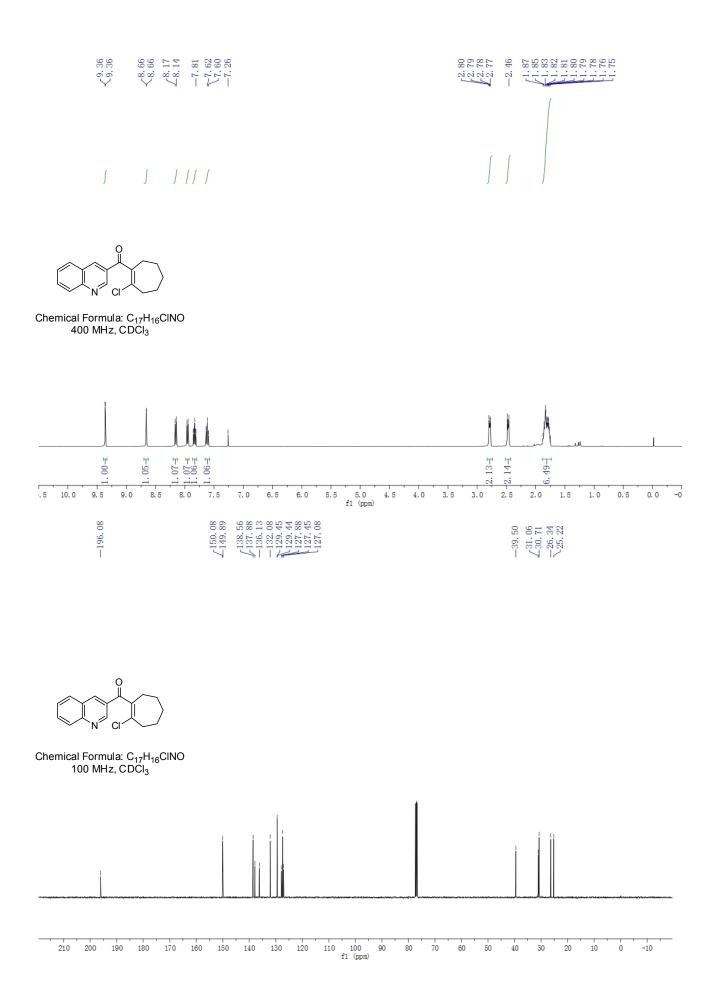


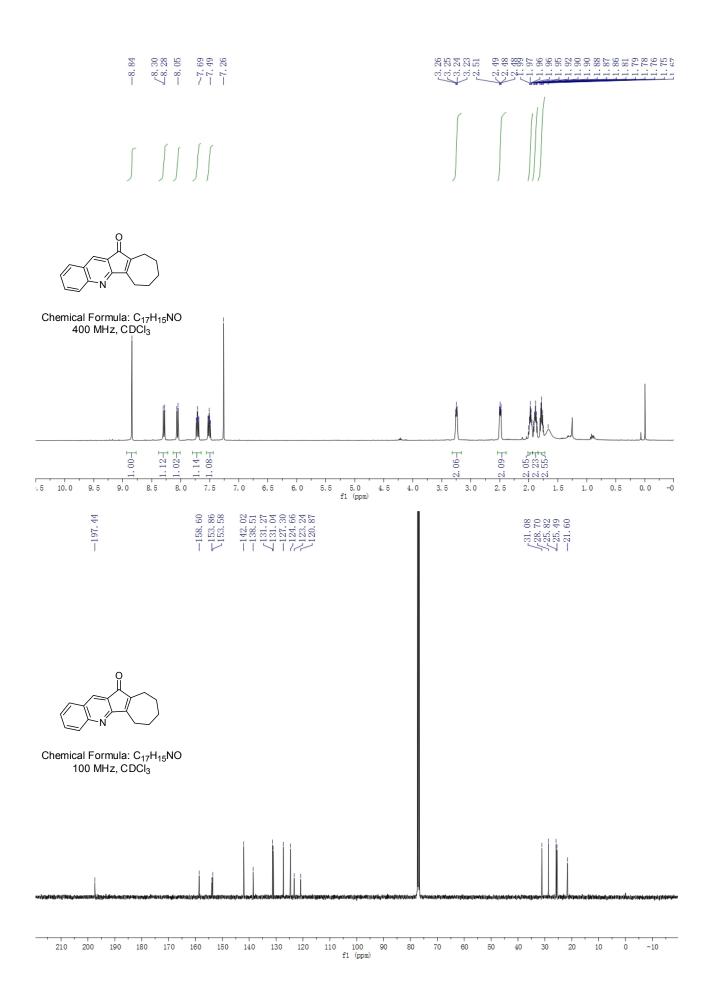


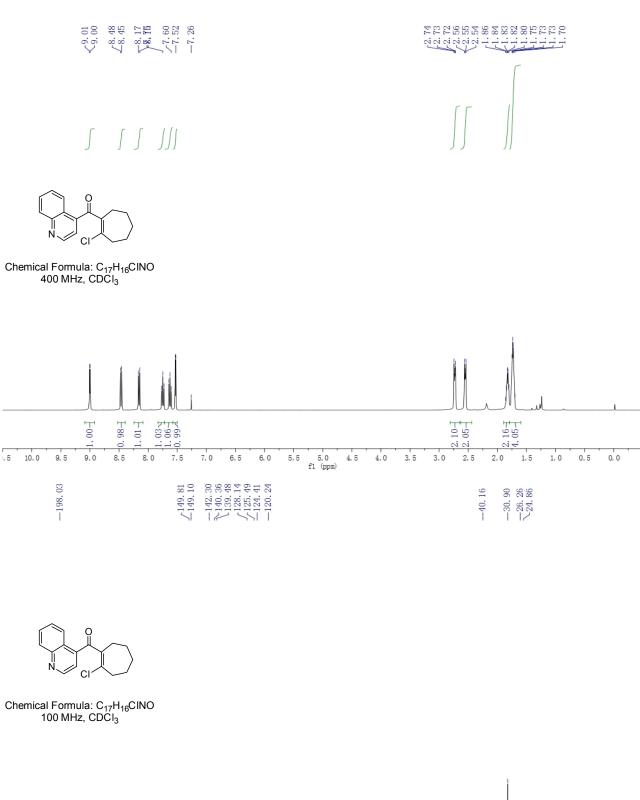


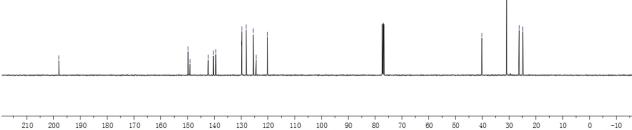


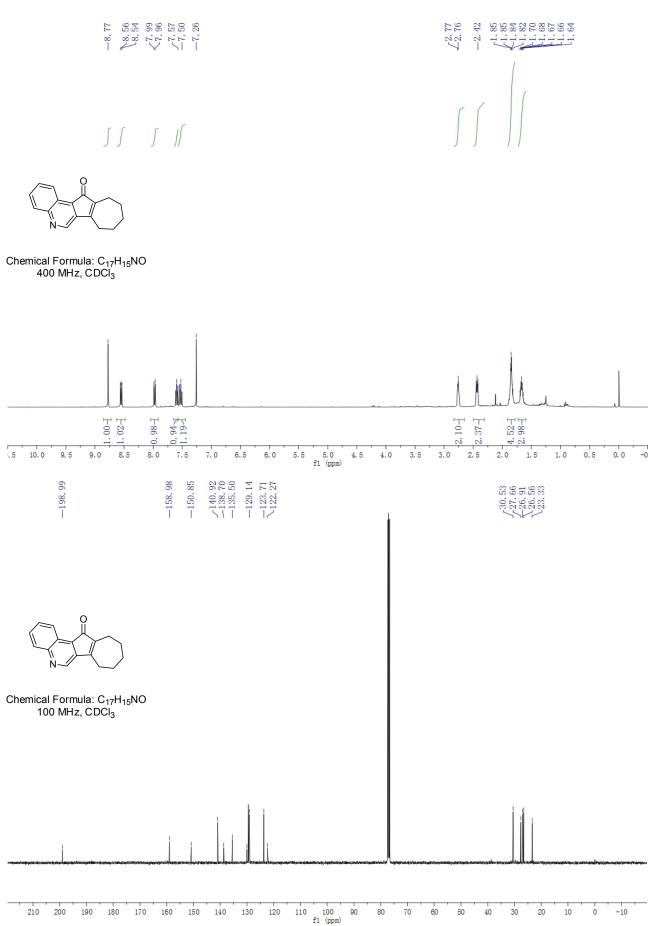
f1 (ppm) -10

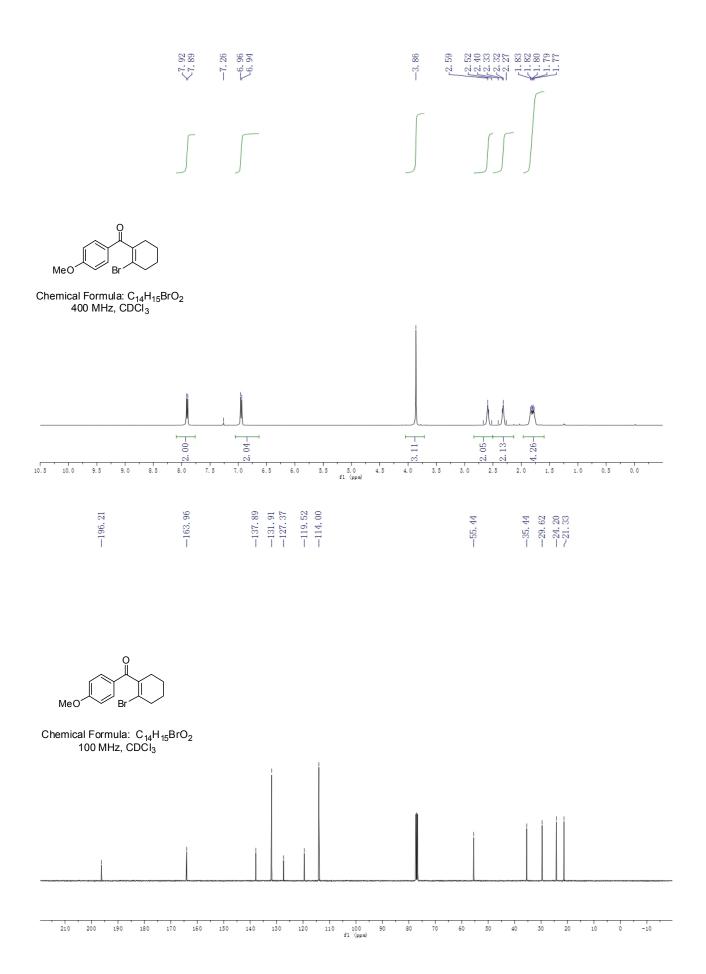


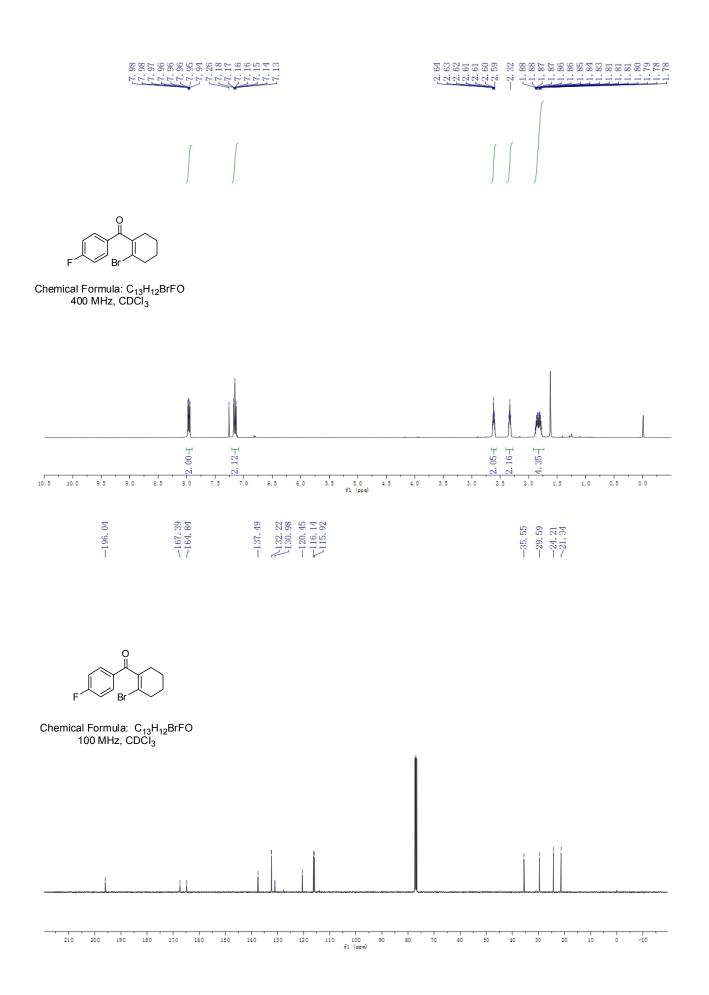


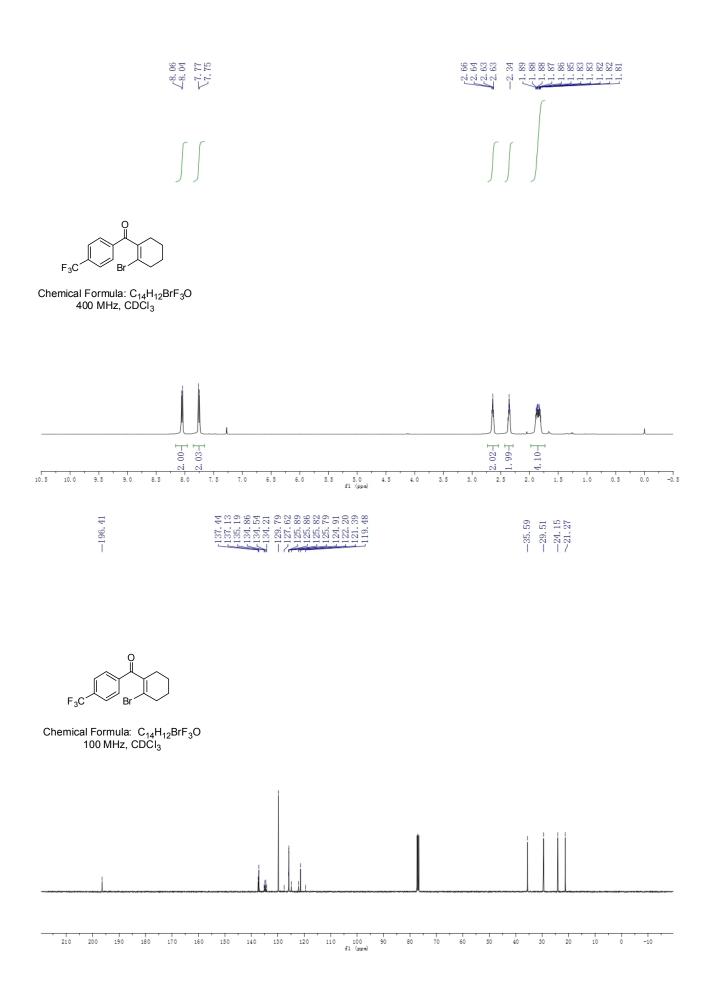




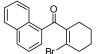




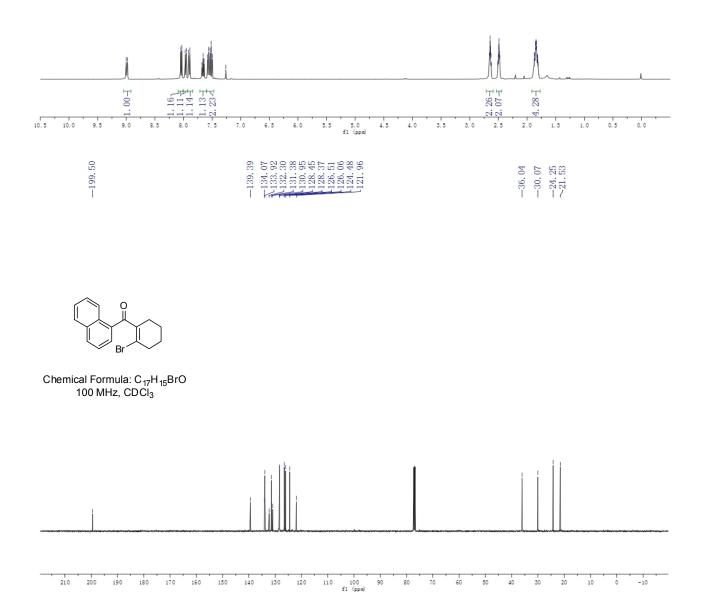


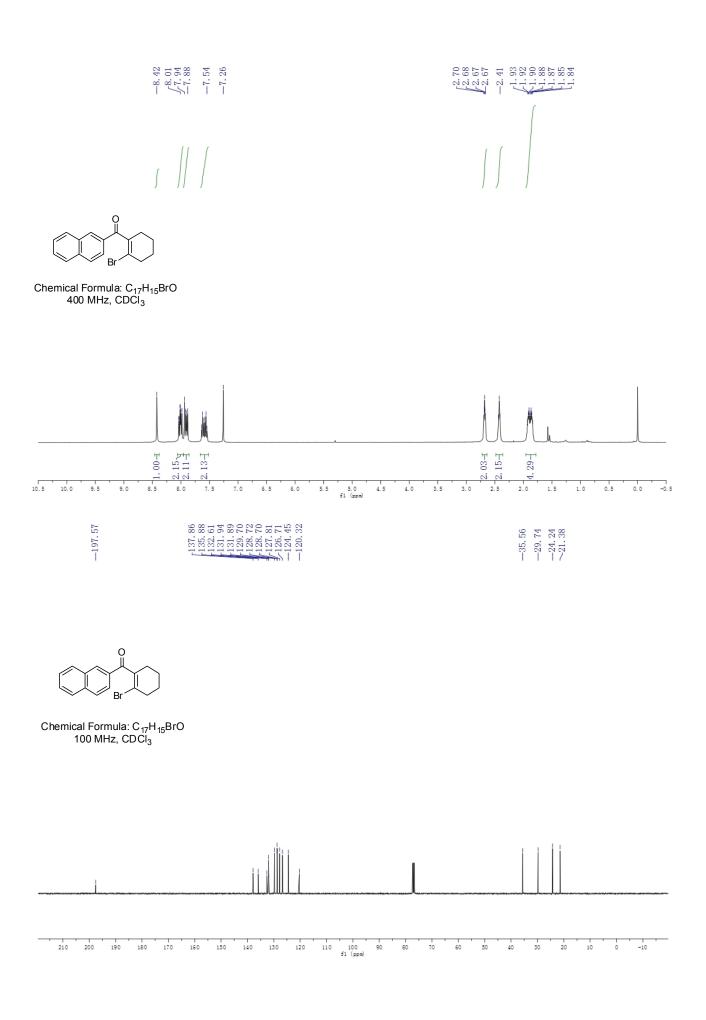


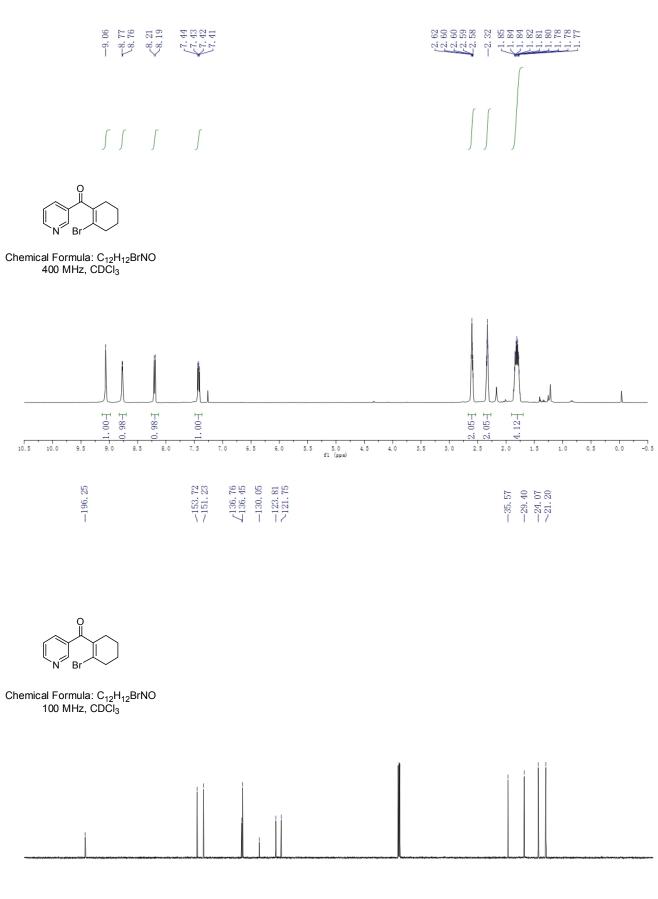




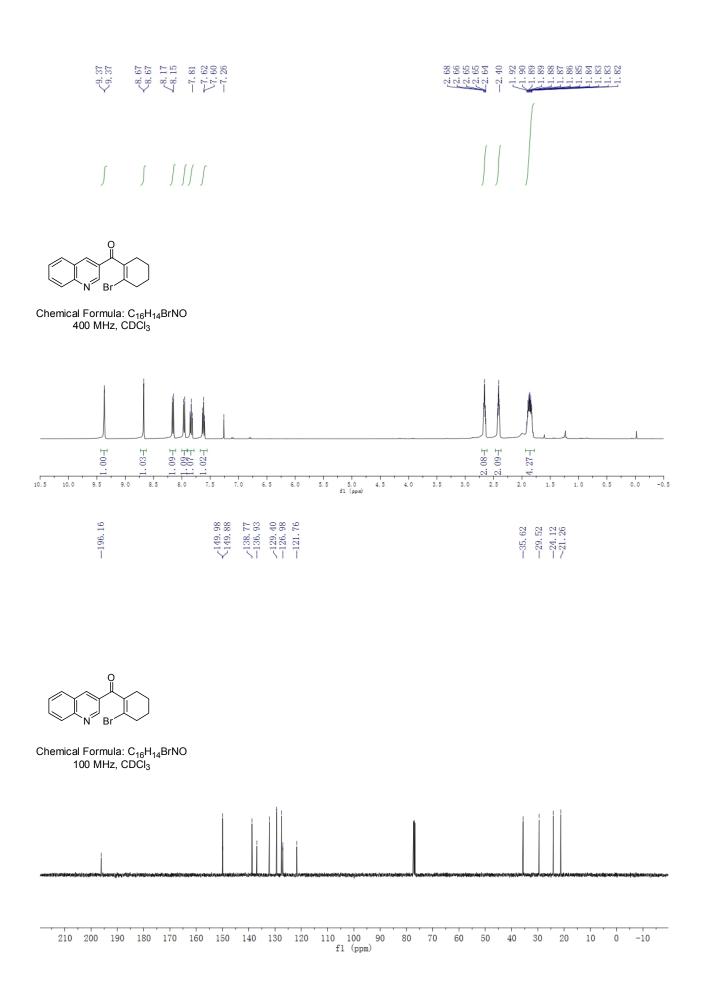
Chemical Formula: C₁₇H₁₅BrO 400 MHz, CDCl₃





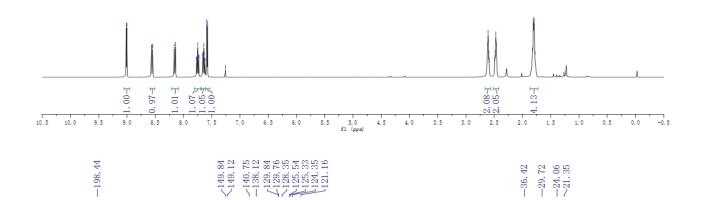


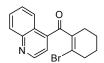
120 110 100 f1 (ppm) -10



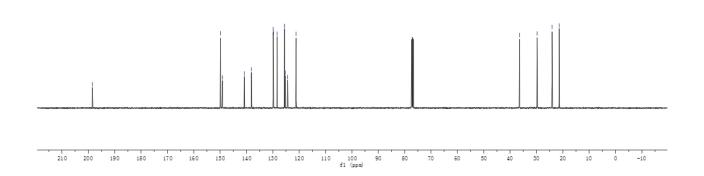


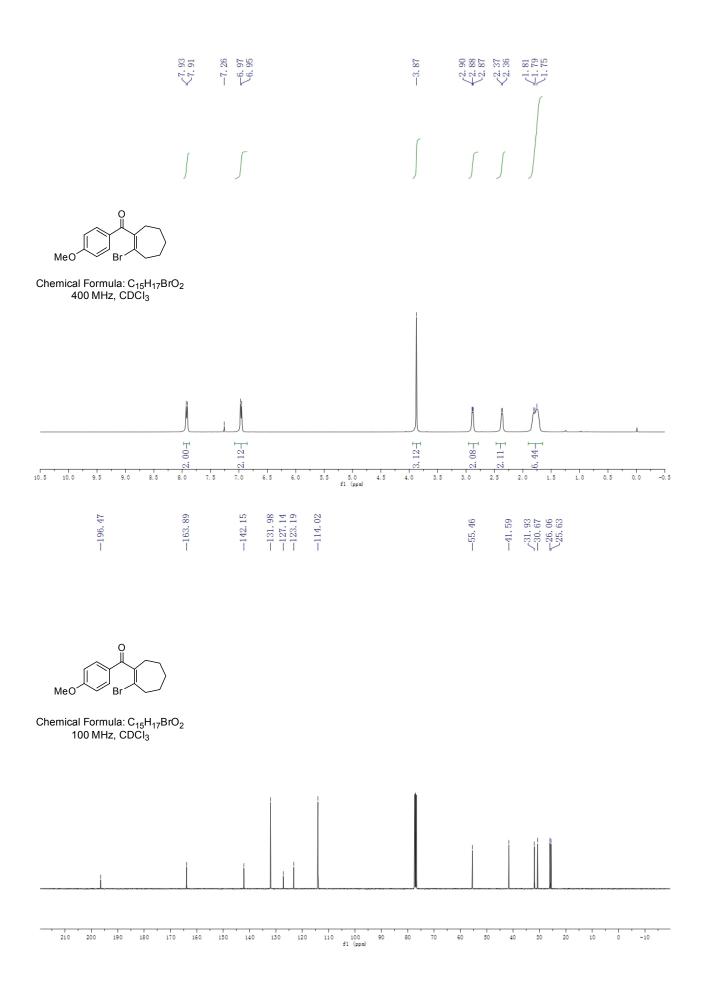
Chemical Formula: C₁₆H₁₄BrNO 400 MHz, CDCl₃

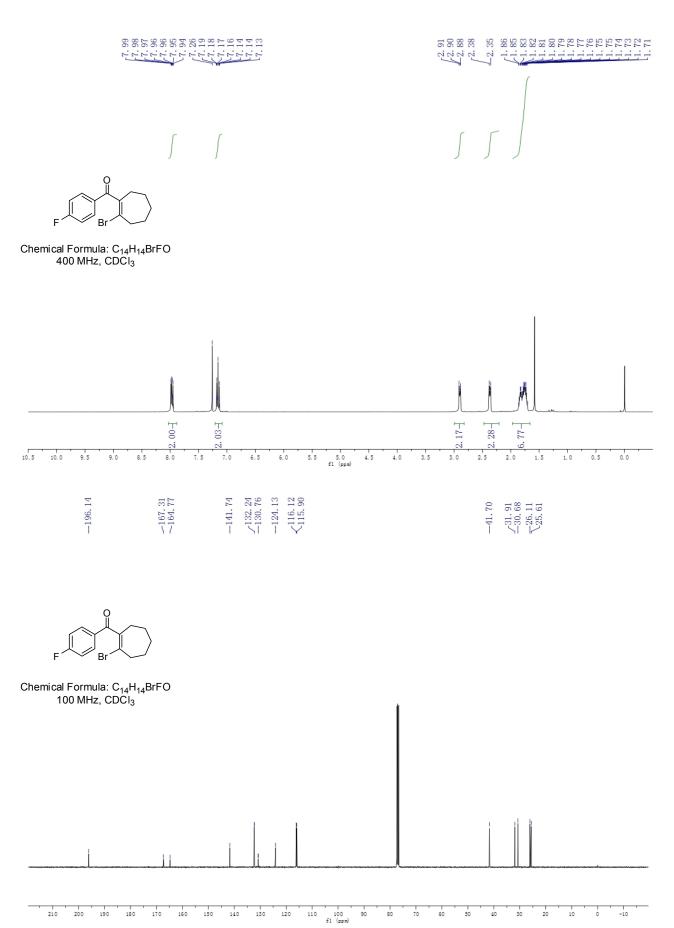


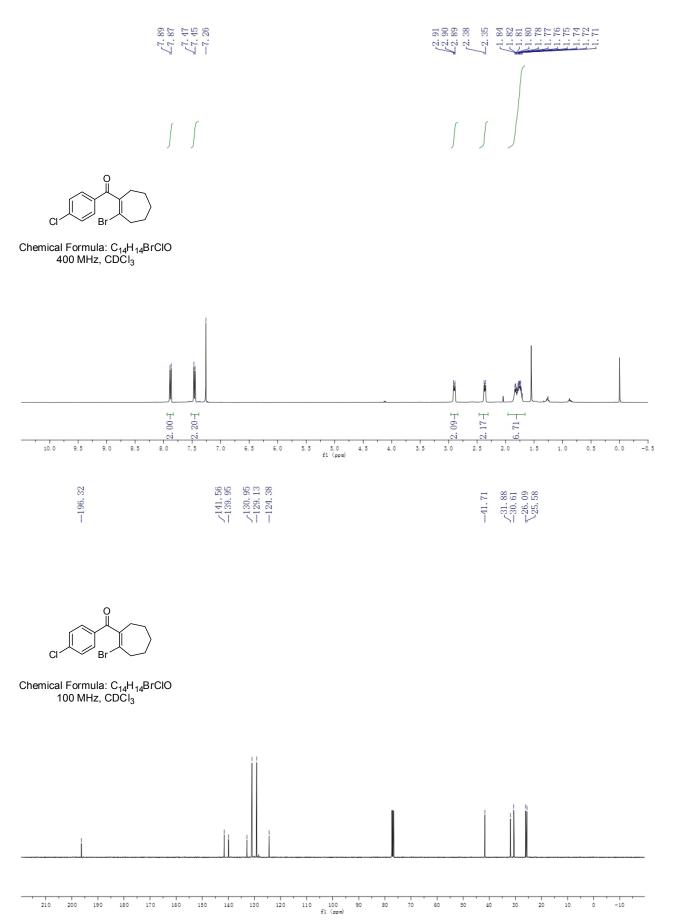


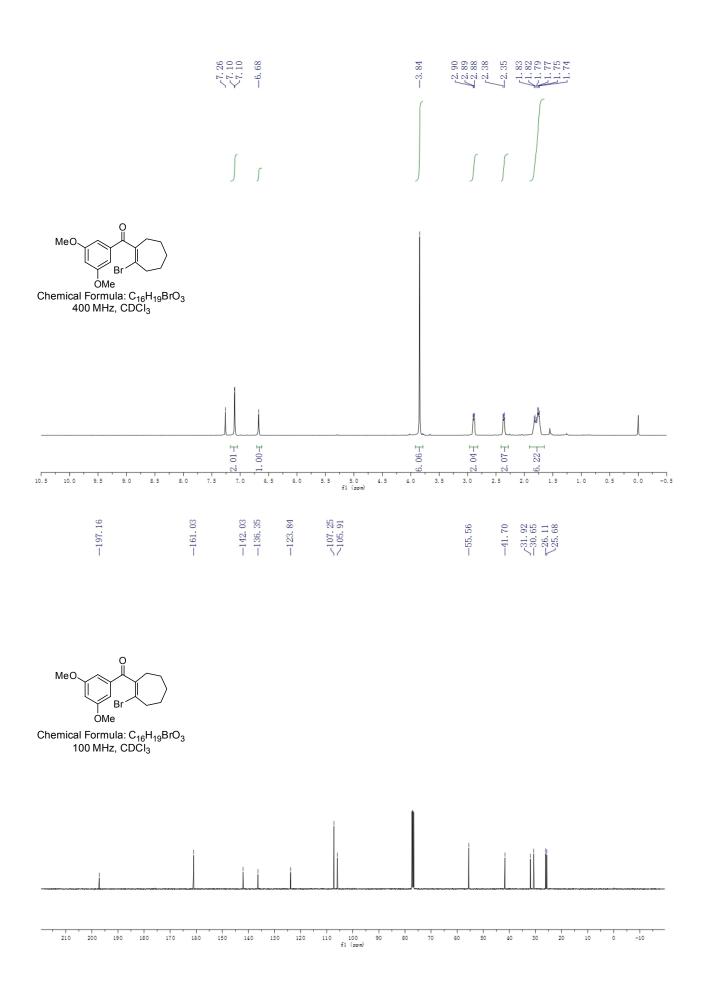
Chemical Formula: C₁₆H₁₄BrNO 100 MHz, CDCl₃

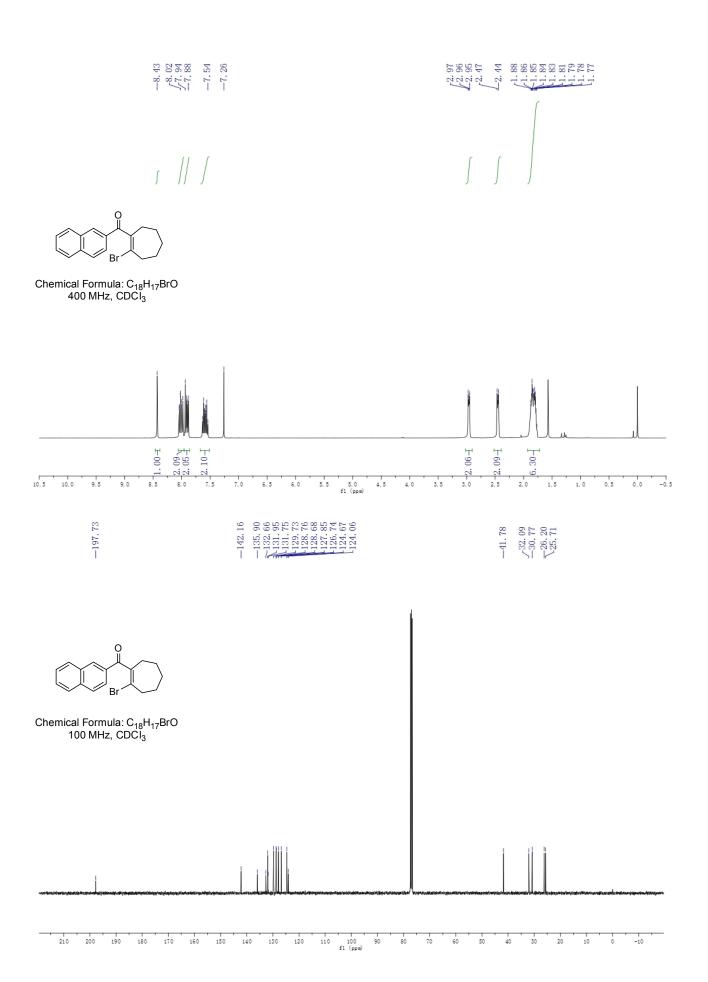


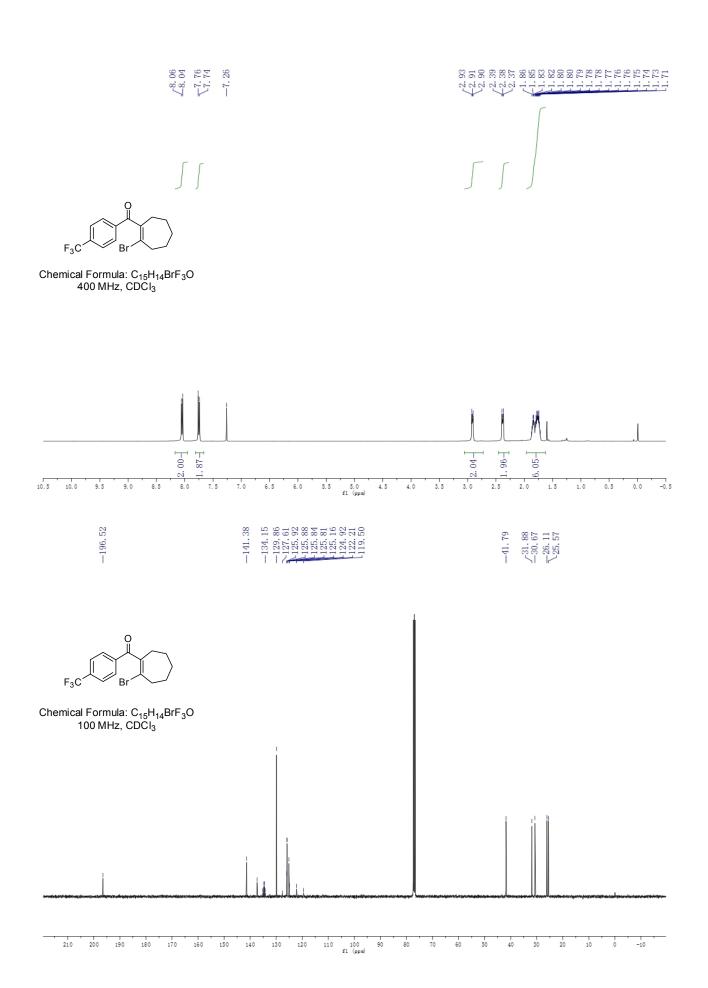


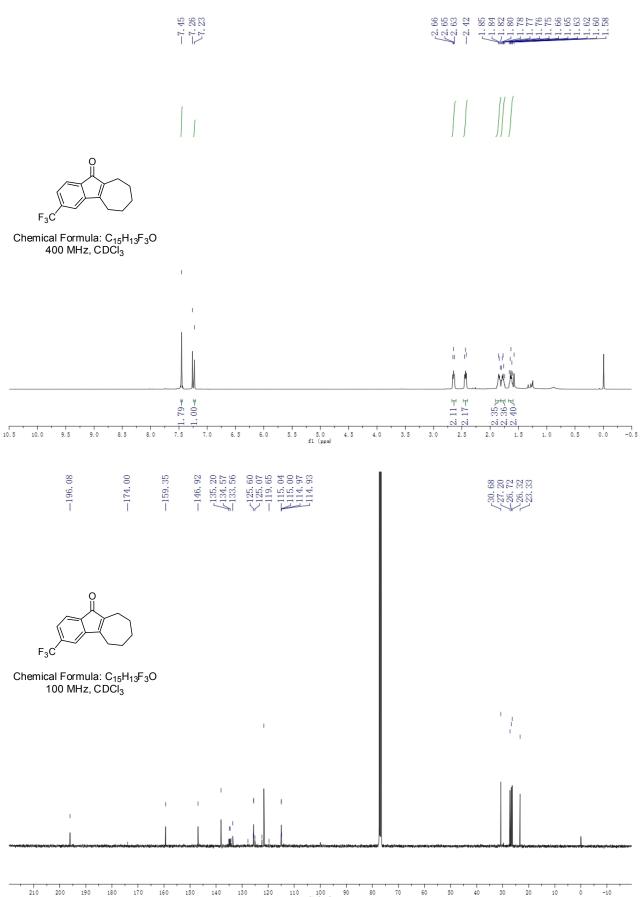


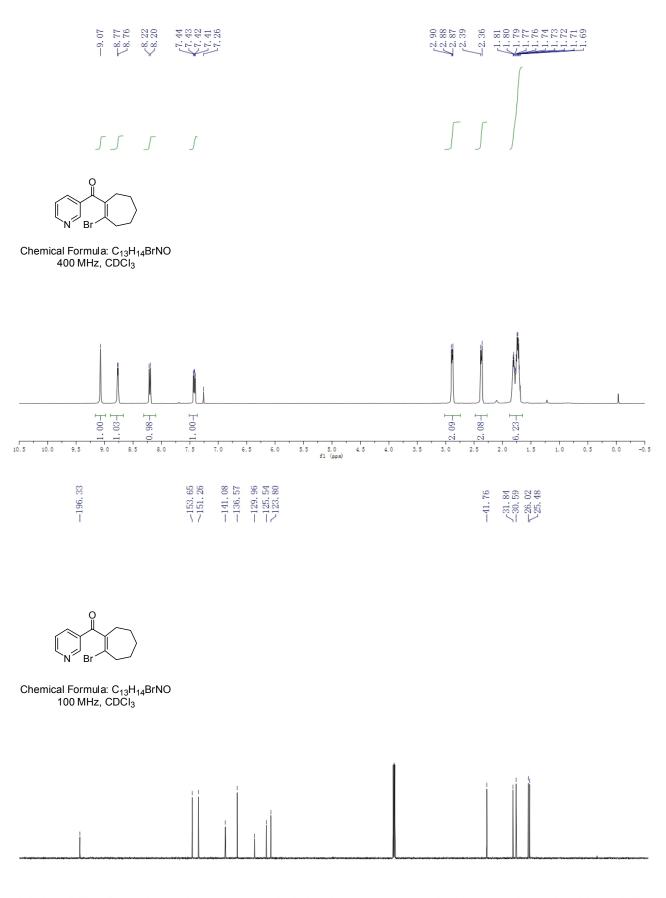












110 100 f1 (ppm) -10

