Supporting Information

Cooperative Interplay of Brønsted Acid and Lewis Acid Sites in MIL-101(Cr) for Cross-Dehydrogenative Coupling of C−H Bonds

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Chemicals and materials

Chromium nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, 99%) was purchased from Sigma-Aldrich. Monosodium 2-sulfoterephthalate (>98%), 2-chlorobenzoic acid (>98%), potassium carbonate (>99%), $BH_3 \cdot THF$ solution (0.9 M in THF) were purchased from TCI. Hydrofluoric acid (40%), sulfonic acid (95.0～98.0%), methanol (>99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (5*S*)-2,2,3-Trimethyl-5-(phenylmethyl)-4-imidazolidinone (98%) was provide by Daicel Chiral Technologies Co., Ltd. Xanthene (98%), 2,6-di-*tert*-butyl-4-methylphenol (99%), ketones, aldehydes and other nucleophiles were analytic-grade and provided by aladdin. Copper(II) oxide (99.9% metal basis) was purchased from Macklin. Aniline was provided by J&K Scientific. *n*-Butyllithium (1.6 M in hexane), methyliodide (99.5%) were purchased from energy-chemical. 9*H*-Thioxanthen-9-one (98%) was provided by Bidepharm.

Characterization

The Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 FT-IR spectrometer in the range of 400-4000 cm^{-1}. MIL-101(Cr) and MIL-101(Cr)-SO_3H were degassed at 423 K and 393 K respectively for 12 h before measuring the N_2 sorption isotherms on a Micromeritics 3Flex 3.01 instrument at 77 K. The powder X-ray diffraction (XRD) patterns were obtained using a PANalytical X'Pert PRO diffractometer with Cu Kα radiation operated at 40 kV, 40 mA. ^1H NMR and ^{13}C NMR spectra were measured using a Bruker Avance III device with a frequency of 400 MHz. Time of flight mass spectrometry (TOF MS) spectra was conducted on a Waters GCT Premier Time of Flight mass spectrometer. Thermogravimetric analysis (TGA) was

conducted on TA Q500 instrument under a 100 mL/min flow of 60% O_2/N_2, ramping from 50 °C to 800 °C at a rate of 10 °C/min. Scanning electron microscopy (SEM) images were recorded on Hitachi SU-8010 instrument. The inductively coupled plasma optical emission spectrometry (ICP-OES) was performed by a Varian-730ES atomic absorption spectrometer. The samples for ICP-OES measurement were digested in HNO_3 aqueous solution at 200 °C for 2 h.

The acid capacities of catalysts were determined by acid-base titration.[1] Generally, 0.5 g of catalysts was suspended in saturated NaCl aqueous solution (200 mL). The suspension was stirred at room temperature until equilibrium was reached (24 h), the supernatant was collected by centrifugation, and titrated with 0.05 M NaOH.

Catalytic CDC reaction procedure for xanthene and malonate

The reaction under oxygen flow was carried out in a three-necked round-bottom flask (10 mL) fixed with a condenser. To make sure the fully contact of oxygen bubble with the reaction mixture, the reaction was enlarged to 10 times. Specifically, xanthene (2 mmol), malonate (5 equiv), and MIL-101(Cr)-SO_3H was added into the three-necked round-bottom flask successively. Oxygen was bubbled into the reaction mixture continuously in a flow rate of 3.0 mL/min. After the reaction completed, the catalyst was removed by centrifugation and the product was purified by column chromatography.

Kinetic study

For kinetic studies, 1 mmol of xanthene was used and followed the standard procedure described above. Aliquots of the mixture was taken out and analyzed by ^{1}H NMR with dimethyl terephthalate as internal standard at different reaction time.

Filtration test

To check if the CDC reaction was promoted in a heterogeneous way, we conducted a filtration test. Under the standard reaction conditions, 2 mmol of xanthene was used for the CDC reaction. After a reaction time of 7 h, the catalyst was removed from the reaction mixture by filtration using a 0.22 μm syringe-driven filter, and the filtrate was divided into two equal portions. One portion was stirred continuously under the same conditions. To the other portion of filtrate, a known amount of dimethyl terephthalate was added as external standard and the yield of product was measured by ^{1}H NMR immediately. After a total reaction time of 24 h, the yield of the filtrate was measured as described above.

Recycling test

The catalyst was recovered by centrifugation, washed with ethanol and dried before going to the next cycle. The recovered catalyst was introduced to a mixture of xanthene and cyclopentanone again, the yield of product was determined by ^{1}H NMR with dimethyl terephthalate as the internal standard. After that, the procedure was repeated for another four times. To measure the acid content

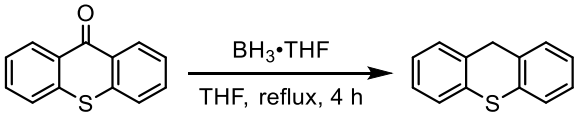
of the recycled catalyst, the recycling test was scaled-up for 75 times to get enough material for acid capacity test.

Asymmetric CDC reactions

Generally, xanthene (0.2 mmol), aldehydes (5 equiv), CH_3NO_2 (1 mL) and MIL-101(Cr)-SO_3H (21 mg), chiral imidazolidinone co-catalyst was added into a reaction tube. The reactor was flushed with oxygen to eliminate the air. Then, the mixture was stirred at 5 °C for 5 d under 1 bar of O_2. The yield of product was determined by ^1H NMR with dimethyl terephthalate as the internal standard. Enantiomeric excess (ee) value was measured by HPLC with Daicel Chiralpak AD-H column at 25 °C: hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm.

Synthesis of thioxanthene[2]

Scheme 1. Hydrogenation of Acridine-9(10*H*)-one

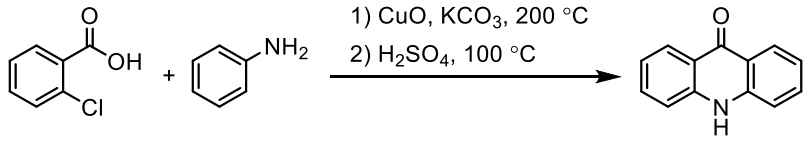


To a slurry of acridine-9(10*H*)-one (425 mg, 2 mmol) in THF (8 mL), BH_3·THF solution (~0.9 M in THF; 4.4 mL) was added dropwise and the mixture was refluxed for 4 h under N_2 atmosphere. Then the mixture was cooled to 0 °C and brine (4 mL) was cautiously added followed by 2 M aq. NaOH (1 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (2 × 5 mL). The organic layer was combined and washed with conc. aq. $NaHCO_3$ (1 × 5

mL), dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica.

Synthesis of Acridine-9(10*H*)-one

Scheme 2. Reaction of 2-Chlorobenzoic Acid and Aniline for the synthesis of Acridine-9(10*H*)-one

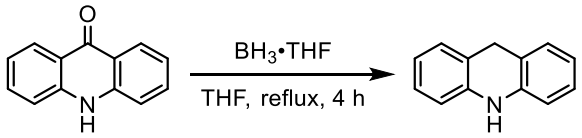


This compound was prepared according to a method reported in literature with slight modifications.[3] 2-Chlorobenzoic acid (7.83 g, 50.0 mmol), potassium carbonate (7.95 g, 57.5 mmol), copper(II) oxide (0.2 g, 2.5 mmol) and aniline (18.2 mL, 200.0 mmol) was added into a three-necked round-bottomed flask (250 mL) equipped with a mechanical stirrer and reflux condenser. The mixture was heated to 200 °C and refluxed for further 2 hours. The dark brown solution was cooled down, and the reflux condenser was replaced by a distillation condenser. Then 175 mL H_2O was added, and about 120 mL liquid was distilled off for complete removal of the excessive aniline. The residue was then treated with charcoal (5 g), refluxed for additional 20 minutes and filtered while hot. The charcoal was additionally washed with hot water (2 × 25 mL). Then, the filtrate was added to HCl solution (4 M, 19 mL) and stirred vigorously. The resulting thick suspension was filtered on a glass filtration funnel, washed with cold H_2O (2 × 25 mL) and dried in vacuo to obtain crude 2-phenylamino benzoic acid as a grey powder.

To a round-bottomed flask was added 2-phenylamino benzoic acid (8.244 g, 35.35 mmol) and conc. sulfuric acid (17.7 mL, ca. 900 mmol), then the mixture was vigorous stirring at 100°C for 4 h. On completion, the resulting green mixture was cooled and poured into 150 mL H_2O with stirring. The resulting green suspension was boiled for 30 minutes then allowed to settle, the solid was collected by filtration, and washed by H_2O (2 × 25 mL). The solid was added into 70 mL of Na_2CO_3 solution (5.375 g, 50.0 mmol) and was neutralized by stirring and boiling for 5 minutes. The resulting suspension was centrifuged and washed with H_2O (2 × 50 mL). The solids were combined and dried in vacuum to obtain acridine-9(10*H*)-one as a yellow powder.

Synthesis of *N*-Phenylacridane[2]

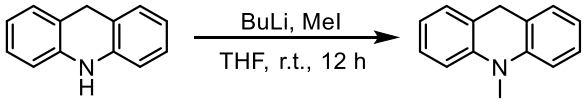
Scheme 3. Reduction of Acridine-9(10*H*)-one



To a slurry of acridine-9(10*H*)-one (391.3 mg, 2 mmol) in THF (8 mL), BH_3·THF solution (~0.9 M in THF; 4.4 mL) was added dropwise and the mixture was refluxed for 4 h under N_2 atmosphere. Then the mixture was cooled to 0 °C and brine (4 mL) was cautiously added followed by 2 M aq. NaOH (1 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (2 × 5 mL). The organic layer was combined and washed with conc. aq. $NaHCO_3$ (1 × 5 mL), dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica.

Synthesis of *N*-Methylacridane

Scheme 4. *N*-Methylation of Acridine



This compound was synthesized according to the known literature method.[4] A Schlenk-tube was charged with a solution of acridane (0.544 g, 3.0 mmol) in THF (20 mL), then a solution of *n*-BuLi (1.6 M in hexanes; 0.69 mL) was added dropwise at 0-5 °C under N_2. The mixture was stirred for 60 minutes, followed by the addition of methyliodide (0.065 mL) in THF (0.7 mL). The mixture was then stirred at 0 °C for additional 2 h and warm to room temperature and stirred overnight. The reaction was quenched by pouring into H_2O (10 mL), and the product was extracted with EtOAc (3 × 10 mL). The organic layer was combined and washed with brine (1 × 30 mL), dried over $MgSO_4$, filtered and concentrated. The crude product was purified by column chromatography on silica to afford *N*-methylacridane as a white solid.

Characterization of catalysts

Table S1 Specific Surface Area, Pore Volume and Chromium Content of Catalysts

catalyst	BET surface area (m^2/g)	pore volume (cm^3/g)	Cr (mmol/g)
MIL-101(Cr)	3517	1.75	4.39
MIL-101(Cr)-SO_3H	2362	1.33	3.07
Amberlyst-15	44	0.003	–

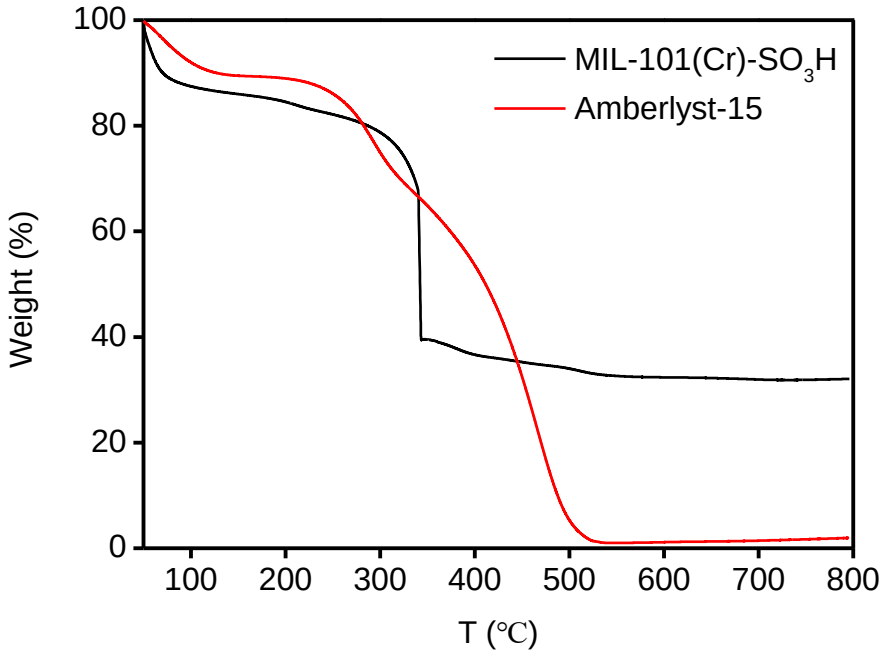


Figure S1. TGA curves of the solid acid catalysts collected under 60% O_2/N_2 atmosphere.

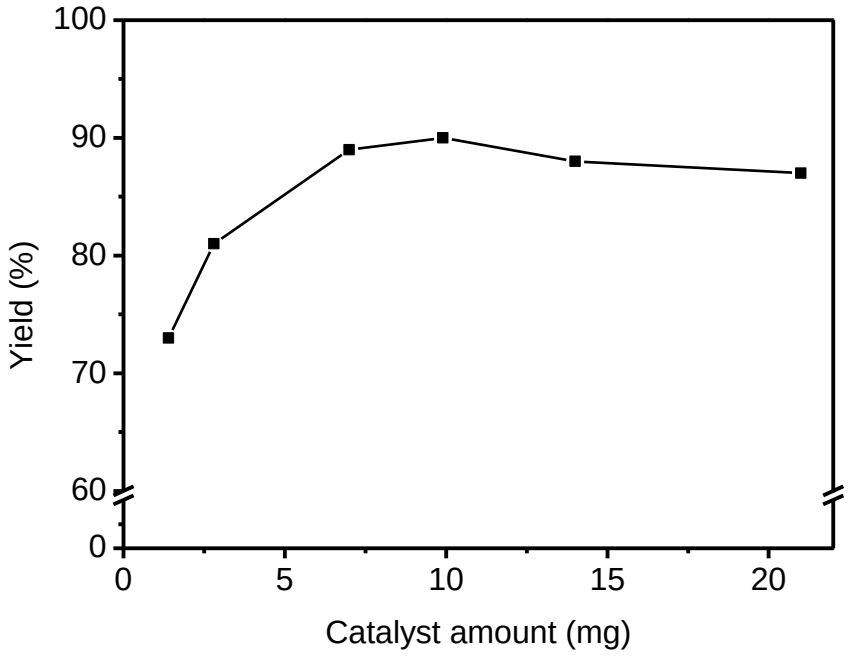


Figure S2. Influence of MIL-101(Cr)-SO_3H amount on the CDC reaction of xanthene and cyclopentanone. Reaction conditions: xanthene (0.2 mmol), cyclopentanone (1 mmol), MIL-101(Cr)-SO_3H, O_2 (1 bar), 40 °C, 24 h.

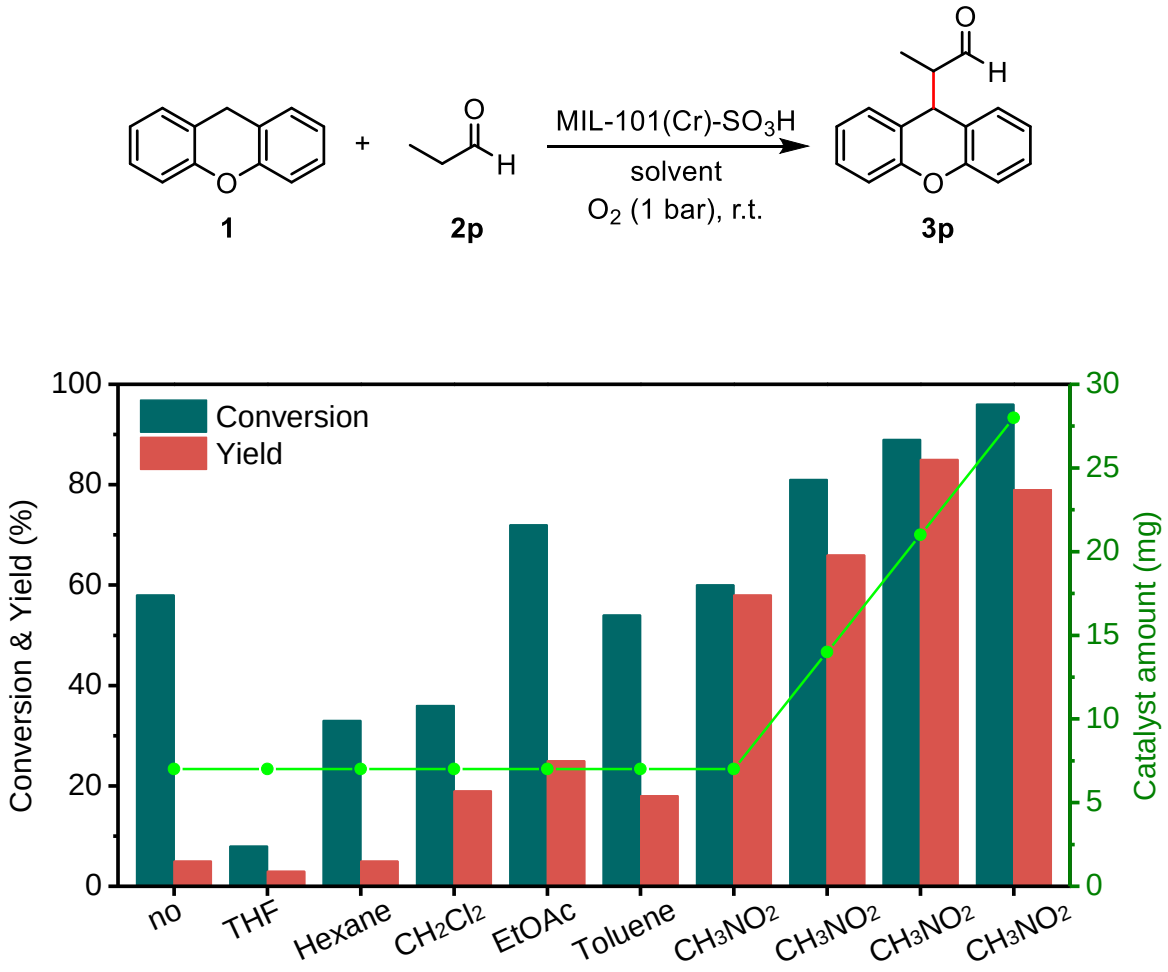


Figure S3. Investigation of the influence of reaction conditions on the CDC reaction of xanthene (**1**) and propionaldehyde (**2p**). Reaction conditions: **1** (0.2 mmol), **2p** (1 mmol), MIL-101(Cr)-SO_3H, solvent (1.0 mL), O_2 (1 bar), r.t., 3 d. Yield of product and conversion of xanthene were determined by ^1H NMR with dimethyl terephthalate as the internal standard.

Table S2 Filtration Test of MIL-101(Cr)-SO_3H Catalyzed CDC Reaction [a]

entry	time (h)	yield (%)
1[b]	7	32
2[c]	24	33

[a] Reaction conditions: xanthene (1.0 mmol), cyclopentanone (5.0 mmol), MIL-101(Cr)-SO_3H (5 mol%), O_2 (1 bar), 40 °C. [b] Reaction time: 7 h; [c] Filtrate of 7 h and reacted till 24 h.

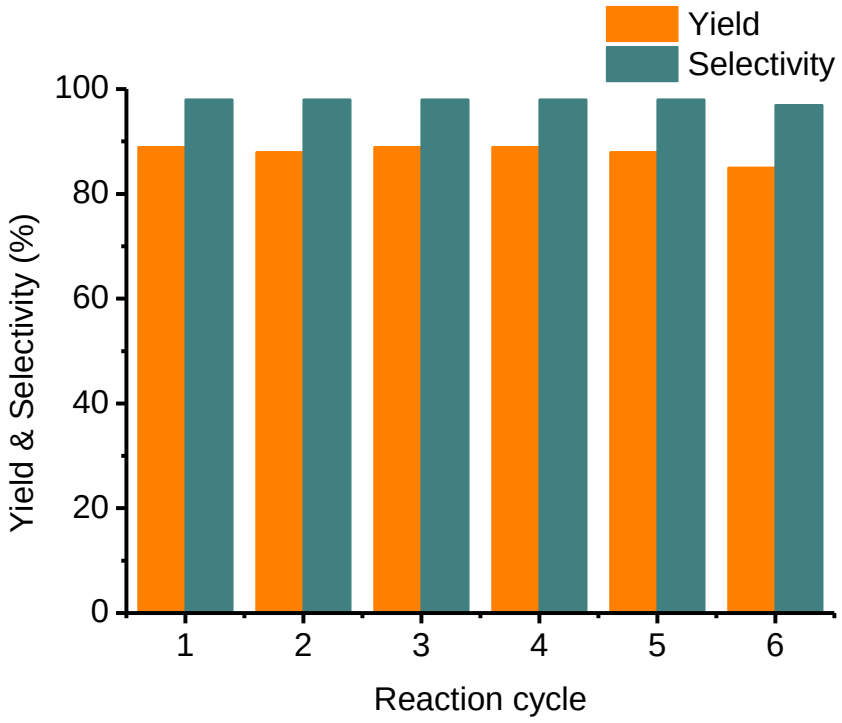


Figure S4. Recycling test of MIL-101(Cr)-SO_3H in catalyzing the CDC reaction of xanthene and cyclopentanone. Reaction conditions: xanthene (0.2 mmol), cyclopentanone (1.0 mmol), MIL-101(Cr)-SO_3H (7 mg), O_2 (1 bar), 40 °C, 24 h.

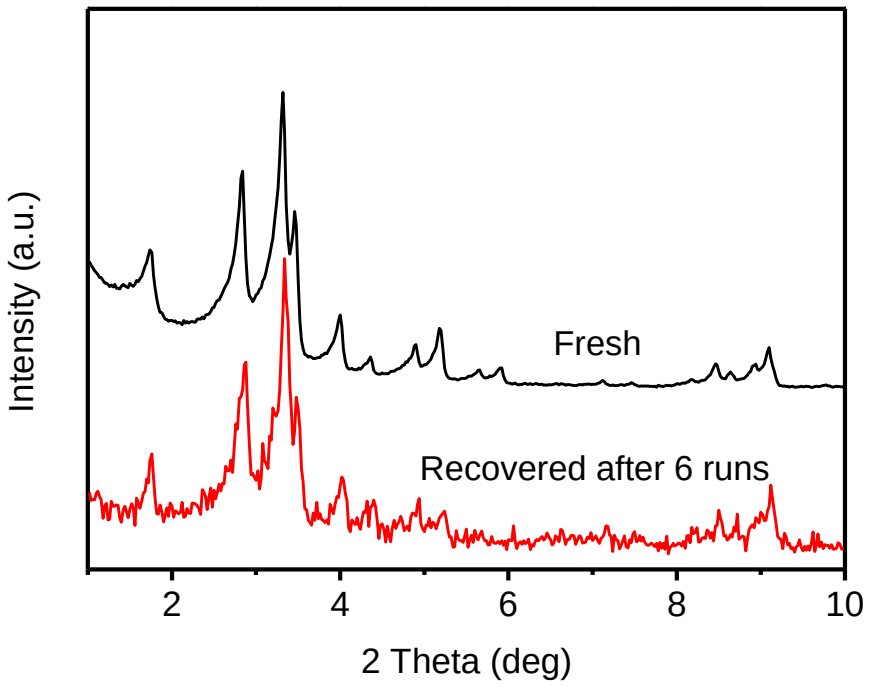


Figure S5. PXRD patterns of MIL-101(Cr)-SO_3H before and after six runs.

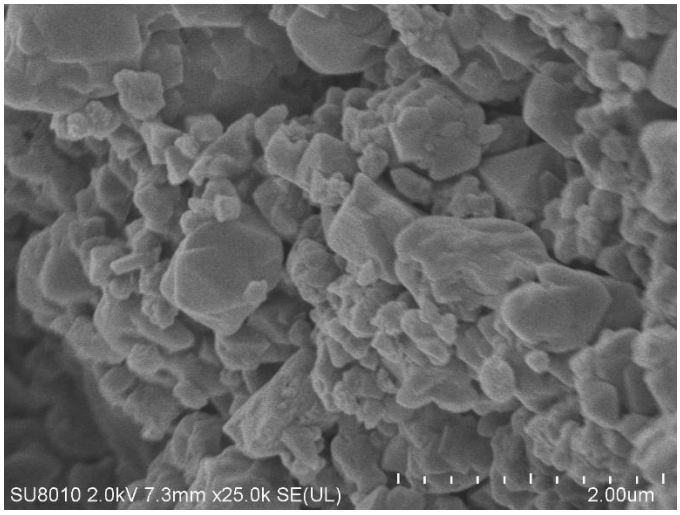


Figure S6. SEM image of MIL-101(Cr)-SO_3H after six runs.

Table S3 Cr Content and H^+ Loading of the Recycled MIL-101(Cr)-SO_3H

material	Cr (mmol/g)	H^+ loading (mmol/g)
MIL-101(Cr)-SO_3H	3.07	1.42
recycled MIL-101(Cr)-SO_3H	2.99	1.20

Color change experiment

To a sodium iodide solution (10 mg/mL in methanol), 100 μL of filtrate of the reaction mixture was added. Yellow color appeared immediately when adding the CDC reaction mixture catalyzed by MIL-101(Cr)-SO_3H. When there is no catalyst, the color change was less obvious. However, such color change was not observed with dichloromethane as the solvent. No color change was observed for the pure sodium iodide solution (a in Figure S7), which excludes the color change through the oxidation of sodium iodide by air. Besides, the pure filtrate (c in Figure S7) is colorless, which indicated that the yellow color was caused by the oxidation of sodium iodide to iodide. This phenomenon indicated that ketone benefits for the autoxidation of xanthene, therefore, the reaction with excess amount of ketone as solvent is more favorable than that of solvent free reaction conditions (Table 2).

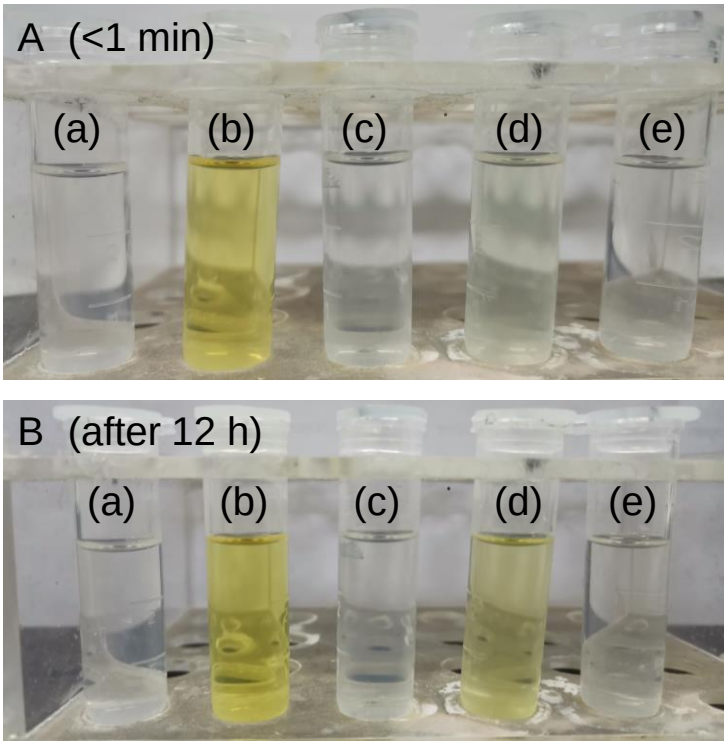
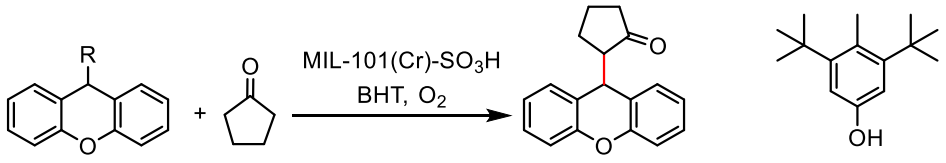


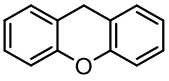
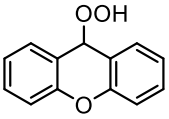
Figure S7. Sodium iodide solution (a) and after adding filtrate of the CDC reaction mixture catalyzed by MIL-101(Cr)-SO_3H (b), filtrate in methanol (c), sodium iodide solution after adding xanthene in cyclopentanone (d) and xanthene in dichloromethane (e) within 1 min and after 12 h.

Quenching experiment

The quenching experiment was conducted under standard reaction conditions, 3 equivalents of 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added into the reaction mixture as a radical inhibitor. The reaction mixture composition was analyzed by ^{1}H NMR.

Table S4 CDC Reaction of Xanthene and Xanthene Hydroperoxide in the Presence of BHT



entry	substrate	conversion (%)	yield (%)
1[a]		6	2
2[b]		100	82

[a] Reaction conditions: xanthene (0.2 mmol), cyclopentanone (1.0 mmol), MIL-101(Cr)-SO_3H (7 mg), BHT (0.6 mmol), O_2 (1 bar), 40 °C, 24 h. [b] Reaction conditions: xanthene hydroperoxide (0.2 mmol), cyclopentanone (1.0 mmol), MIL-101(Cr)-SO_3H (7 mg), BHT (0.6 mmol), O_2 (1 bar), 40 °C, 2 h. Conversion and yield were determined by ^{1}H NMR analysis.

References

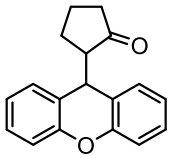
(1) Leveneur, S.; Murzin, D. Y.; Salmi, T. Application of Linear Free-Energy Relationships to Perhydrolysis of Different Carboxylic Acids over Homogeneous and Heterogeneous Catalysts. *J. Mol. Catal. A: Chem.* **2009,** *303*, 148-155.

(2) Pintér, Á.; Sud, A.; Sureshkumar, D.; Klussmann, M. Autoxidative Carbon–Carbon Bond Formation from Carbon–Hydrogen Bonds. *Angew. Chem., Int. Ed.* **2010,** *49*, 5004-5007.

(3) Allen, C. F. H.; Mckee, G. H. W. Acridone. *Org. Synth.* **1939,** *19*, 6-9.

(4) Mulder, P.; Litwinienko, G.; Lin, S. Q.; Maclean, P. D.; Barclay, L. R. C.; Ingold, K. U. The L-type calcium channel blockers, Hantzsch 1,4-dihydropyridines, are not peroxyl radical-trapping, chain-breaking antioxidants. *Chem. Res. Toxicol.* **2006,** *19*, 79-85.

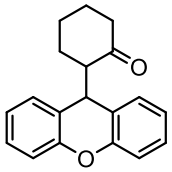
Characterization data of the CDC products



3a

rac-9-(1'-Oxocyclopent-2'-yl)xanthene. Yield: 89% as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.20 (m, 3 H), 7.12-7.07 (m, 4 H), 6.99 (t, *J* = 7.4 Hz, 1 H), 4.77 (d, *J* = 2.6 Hz, 1 H), 2.45 (td, *J* = 9.6, 2.2 Hz, 1 H), 2.25 (dd, *J* = 18.6, 7.4 Hz, 1 H), 1.83-1.73 (m, 2 H), 1.68-1.61 (m, 1 H), 1.58-1.50 (m, 1H), 1.46-1.36 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 219.3, 153.2, 152.6, 129.3, 128.30, 128.27, 127.9, 124.6, 123.8, 123.6, 122.0, 116.5, 116.4, 60.0, 39.4, 38.1, 24.1, 20.4 ppm. IR (cm^{-1}): 3041, 2970, 2882, 2835, 1732, 1600, 1576, 1477, 1467, 754. TOF MS (EI^+) m/z: calcd. for $C_{18}H_{16}O_2$: 264.1150; found: 264.1150.

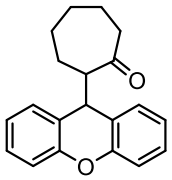


3b

rac-9-(1'-Oxocyclohex-2'-yl)xanthene. Yield: 91% as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.6 Hz, 1 H), 7.25-7.18 (m, 3 H), 7.08-7.00 (m, 4 H), 4.93 (d, *J* = 3.0 Hz, 1 H), 2.51 (ddd, *J* = 12.7, 4.4, 3.6 Hz, 1 H), 2.42 (d, *J* = 14.6 Hz, 1 H), 2.24 (td, *J* = 13.2, 6.0 Hz, 1 H), 1.94-1.89 (m, 1 H), 1.78-1.68 (m, 2H), 1.52-1.36 (m, 2 H), 1.10 (ddd, *J* = 25.6, 12.8, 3.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.8, 153.4, 153.1, 130.6, 128.9, 127.9, 127.7, 125.7, 123.6, 123.3, 123.0, 116.4, 116.2, 60.7, 42.2, 36.8, 27.7, 26.8, 24.8

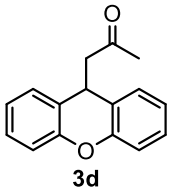
ppm. IR (cm^{-1}): 2920, 2852, 1701, 1646, 1574, 1478, 753. TOF MS (EI^+) m/z: calcd. for $C_{19}H_{18}O_2$: 278.1307; found: 278.1306.



3c

rac-9-(1'-Oxocyclohept-2'-yl)xanthene. Yield: 61% as a white solid.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.27-7.21 (m, 3 H), 7.12-7.05 (m, 4 H), 7.01 (td, *J* = 7.6, 1.2 Hz, 1 H), 4.65 (d, *J* = 4.4 Hz, 1 H), 2.59 (dt, *J* = 11.8, 3.8 Hz, 1 H), 2.36 (ddd, *J* = 12.4, 6.8, 1.8 Hz, 1 H), 2.10 (td, *J* = 12.2, 2.4 Hz, 1 H), 1.75-1.73 (br m, 3 H), 1.58-1.55 (br m, 1H), 1.38-1.13 (m, 3 H), 1.06-0.96 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 216.5, 153.3, 153.1, 129.2, 128.8, 128.2, 128.0, 124.6, 123.8, 123.2, 122.0, 116.7, 116.4, 62.6, 44.9, 42.2, 30.0, 28.6, 25.1, 24.9 ppm. IR (cm^{-1}): 2929, 2855, 1687, 1599, 1575, 1249, 750. TOF MS (EI^+) m/z: calcd. for $C_{20}H_{20}O_2$: 292.1463; found: 292.1462.

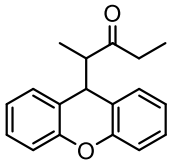


3d

9-(2'-Oxoprop-1'-yl)xanthene. Yield: 41% as a white solid.

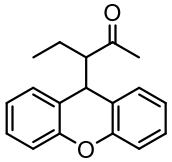
^1H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.19 (m, 4 H), 7.10-7.02 (m, 4 H), 4.61 (t, *J* = 6.6 Hz, 1 H), 2.81 (d, *J* = 6.6 Hz, 2 H), 1.97 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.8, 152.3, 128.7,

128.0, 125.3, 123.6, 116.7, 54.5, 34.5, 31.2 ppm. IR (cm^{-1}): 2921, 2884, 2849, 1702, 1599, 1575, 1479, 1456, 1260, 748. TOF MS (EI^+) m/z: calcd. for $C_{16}H_{14}O_2$: 238.0994; found: 238.0993.



3e

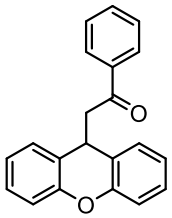
rac-9-(1'-Methyl-2'-oxobut-1'-yl)xanthene. Yield: 63% as a viscous colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.19 (m, 2H), 7.16-7.10 (m, 4H), 7.08-7.00 (m, 2H), 4.23 (d, *J* = 8.0 Hz, 1H), 2.75-2.68 (m, 1H), 2.20 (dq, *J* = 18.2, 7.2 Hz, 1H), 1.90 (dq, *J* = 18.2, 7.2 Hz, 1H), 0.91(d, *J* = 7.0 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.5, 153.3, 153.1, 129.7, 128.9, 128.1, 127.9, 125.1, 123.6, 123.4, 123.1, 116.6, 53.4, 42.5, 37.0, 14.1, 7.4 ppm. IR (cm^{-1}): 2975, 2934, 2875, 1711, 1600, 1567, 1475, 1456, 1249, 747. TOF MS (EI^+) m/z: calcd. for $C_{18}H_{18}O_2$: 266.1307; found: 266.1307.



3f

rac-9-(1'-Ethyl-2'-oxoprop-1'-yl)xanthene. Yield: 56% as a viscous colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.27-7.21 (m, 2H), 7.15-7.02 (m, 6H), 4.07 (d, *J* = 8.6 Hz, 1H), 2.69-2.64 (m, 1H), 1.76 (s, 3H), 1.65-1.53 (m, 1H), 1.40-1.30 (m, 1H), 0.71 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.8, 153.3, 129.7, 128.9, 128.1, 128.0, 124.8, 124.2, 123.6, 123.2,

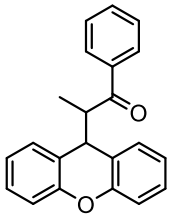
116.78, 116.76, 61.1, 42.8, 33.4, 23.0, 12.0 ppm. IR (cm^{-1}): 2963, 2931, 2875, 1709, 1600, 1577, 1475, 1456, 1246, 753. TOF MS (EI^+) m/z: calcd. for $C_{18}H_{18}O_2$: 266.1307; found: 266.1303.



3g

9-(2'-Phenyl-2'-oxoethyl)xanthene. Yield: 55% as a pale yellow solid.

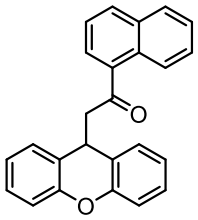
^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.4 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.32 (dd, *J* = 7.4, 1.4 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.11 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.02 (td, *J* = 7.4, 1.2 Hz, 2H), 4.85 (t, *J* = 6.6 Hz, 1H), 3.35 (d, *J* = 6.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.0, 152.5, 137.1, 133.3, 129.0, 128.6, 128.2, 128.0, 125.7, 123.6, 116.7, 49.8, 34.8 ppm. IR (cm^{-1}): 2921, 2896, 2850, 1681, 1597, 1576, 1477, 1459, 1253, 1217, 750, 683. TOF MS (EI^+) m/z: calcd. for $C_{21}H_{16}O_2$: 300.1150; found: 300.1153.



3h

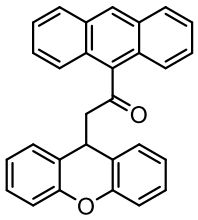
9-(1'-Methyl-2'-phenyl-2'-oxoethyl)xanthene. Yield: 49% as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.28-7.24 (m, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.15-7.05 (m, 5H), 6.92 (td, *J* = 7.0, 1.8 Hz, 1H), 4.40 (d, *J* =

7.6 Hz, 1H), 3.69 (m, 1H), 1.01 (d, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.4, 153.4, 153.2, 137.2, 133.0, 129.9, 129.0, 128.7, 128.22, 128.19, 127.9, 125.2, 123.5, 123.4, 123.1, 116.63, 116.60, 48.7, 42.8, 14.7 ppm. IR (cm^{-1}): 3038, 2968, 2922, 1677, 1596, 1578, 1475, 1457, 1371, 1247, 754, 709. TOF MS (EI^+) m/z: calcd. for $C_{22}H_{18}O_2$: 314.1307; found: 314.1309.



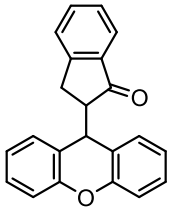
3i

9-(2'-naphthalen-1-yl-2'-oxoethyl)xanthene. Yileld: 14% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.58-7.46 (m, 3H), 7.37 (dd, J = 7.6, 1.2 Hz, 2H), 7.33 (t, J = 7.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 7.04 (t, J = 7.4 Hz, 2H), 4.93 (t, J = 6.8 Hz, 1H), 3.41 (d, J = 6.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.15, 152.5, 136.1, 134.0, 132.9, 130.1, 128.9, 128.6, 128.1, 128.0, 126.6, 125.8, 125.5, 124.4, 123.7, 116.7, 53.2, 35.5 ppm. IR (cm^{-1}): 2921, 2849, 1674, 1598, 1575, 1508, 1478, 1459, 1251, 766, 749. TOF MS (EI^+) m/z: calcd. for $C_{25}H_{18}O_2$: 350.1307; found: 350.1311.



3j

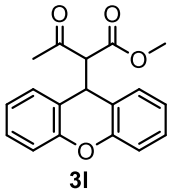
9-(2'- anthracen-9-yl-2'-oxoethyl)xanthene. Yileld: 20%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (s, 1H), 7.92 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.40-7.36 (m, 2H), 7.30-7.23 (m, 6H), 7.16-7.12 (m, 4H), 5.07 (t, *J* = 6.7 Hz, 1H), 3.37 (d, *J* = 6.7 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.8, 152.8, 135.7, 131.0, 129.1, 128.8, 128.5, 128.2, 127.0, 126.8, 125.6, 125.5, 124.0, 123.7, 116.8, 56.6, 34.5 ppm. IR (cm^{-1}): 3050, 2925, 2889, 1700, 1599, 1575, 1477, 1456, 1250, 753, 731. TOF MS (EI^+) m/z: calcd. for $C_{29}H_{20}O_2$: 400.1463; found: 400.1459.



3k

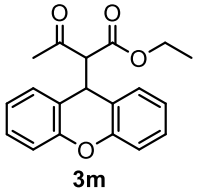
rac-2,3-Dihydro-2-(9*H*-xanthen-9-yl)-1*H*-inden-1-one. Yield: 70% as slightly yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 7.8 Hz, 1H), 7.44-7.37 (m, 2H), 7.28-7.20 (m, 2H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.16-7.04 (m, 4H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.80 (td, *J* = 7.6, 1.2 Hz, 1H), 5.03 (d, *J* = 3.0 Hz, 1H), 3.12-3.08 (m, 1H), 2.89 (dd, *J* = 17.4, 7.8 Hz, 1H), 2.78 (dd, *J* = 17.4, 4.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.6, 154.3, 152.8, 152.5, 137.1, 134.9, 129.7, 128.6, 128.3, 128.1, 127.3, 126.5, 124.2, 123.91, 123.89, 123.5, 120.6, 116.6, 116.4, 58.4, 38.8, 28.0 ppm. IR (cm^{-1}): 3028, 2921, 2890, 2849, 1696, 1602, 1576, 1477, 1456, 1255, 743. TOF MS

(EI$^+$) m/z: calcd. for $C_{22}H_{16}O_2$: 312.1150; found: 312.1154.



3l

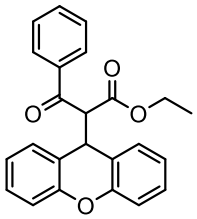
rac-9-(1'-Methoxycarbonyl-2'-oxoprop-1'-yl)xanthene. Yield: 49% as a slightly yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.27-7.21 (m, 3H), 7.15 (ddd, *J* = 8.2, 4.2, 1.2 Hz, 2H), 7.05 (tt, *J* = 7.4, 1.6 Hz, 2H), 4.83 (d, *J* = 9.4 Hz, 1H), 3.80 (d, *J* = 9.4 Hz, 1H), 3.55 (s, 3H), 1.88 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.8, 167.8, 153.4, 129.4, 129.1, 128.58, 128.56, 123.7, 123.6, 123.3, 123.1, 116.9, 116.8, 66.4, 52.5, 39.7, 31.7 ppm. IR (cm^{-1}): 3040, 2952, 2842, 1734, 1061, 1576, 1476, 1457, 1434, 1250, 1143, 754. TOF MS (EI$^+$) m/z: calcd. for $C_{18}H_{16}O_2$: 296.1049; found: 296.1051.



3m

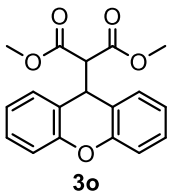
rac-9-(1'-Ethoxycarbonyl-2'-oxoprop-1'-yl)xanthene. Yield: 75% as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.27-7.23 (m, 3H), 7.14 (ddd, *J* = 8.0, 4.4, 1.2 Hz, 2H), 7.04 (tt, *J* = 7.4, 1.3 Hz, 2H), 4.84 (d, *J* = 9.2 Hz, 1H), 4.04-3.93 (m, 2H), 3.78 (d, *J* = 9.2 Hz, 1H), 1.90 (s, 3H), 1.08 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.8, 167.3, 153.4, 153.3, 129.3, 129.2, 128.40, 128.39, 123.6, 123.4, 123.20, 123.16, 116.8, 116.6, 66.5, 61.5,

39.4, 31.4, 13.9 ppm. IR (cm^{-1}): 3039, 2985, 2962, 2922, 1735, 1714, 1644, 1597, 1576, 1475, 1458, 1358, 1243, 1021, 754. TOF MS (EI^+) m/z: calcd. for $C_{19}H_{18}O_4$: 310.1205; found: 310.1209.



3n

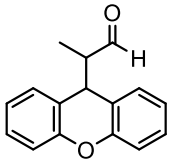
rac-9-(1'-Ethoxycarbonyl-2'-phenyl-2'-oxoeth-1'-yl)xanthene. Yield: 54% as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.6, 1.2 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.38 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.34-7.25 (m, 4H), 7.17 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.12-7.05 (m, 3H), 6.90 (td, *J* = 7.2, 1.8 Hz, 1H), 5.07 (d, *J* = 9.6 Hz, 1H), 4.63 (d, *J* = 9.6 Hz, 1H), 3.99-3.87 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 167.6, 153.8, 153.5, 136.7, 133.6, 129.9, 129.3, 128.6, 128.54, 128.50, 128.3, 123.8, 123.7, 123.6, 123.5, 116.74, 116.70, 61.7, 61.5, 40.0, 13.9 ppm. IR (cm^{-1}): 3066, 2981, 1922, 1850, 1732, 1685, 1597, 1577, 1475, 1458, 1248, 1148, 1031, 751. TOF MS (EI^+) m/z: calcd. for $C_{24}H_{20}O_4$: 372.1362; found: 372.1367.



3o

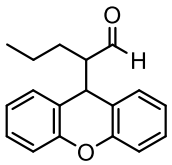
9-(1'-Methoxycarbonyl-2'-oxo-3'-oxabut-1'-yl)xanthene. Yield: 64% as a viscous yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.30 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.26 (td, *J* = 7.6, 1.6 Hz, 2H), 7.15

(dd, J = 8.2, 1.0 Hz, 2H), 7.05 (td, J = 7.4, 1.2 Hz, 2H), 4.82 (d, J = 9.1 Hz, 1H), 3.60 (d, J = 9.1 Hz, 1H), 3.56 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7, 153.2, 128.8, 128.6, 123.4, 122.6, 116.8, 59.9, 52.5, 39.8 ppm. IR (cm^{-1}): 3042, 2952, 2844, 1732, 1656, 1602, 1576, 1476, 1457, 1434, 1340, 1248, 1140, 1031, 752. TOF MS (EI^+) m/z: calcd. for $C_{18}H_{16}O_5$: 312.0998; found: 312.0999.



3p

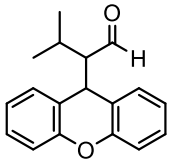
rac-2-(9*H*-xanthen-9-yl)propanal. Yield: 52% as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.76 (d, J = 1.0 Hz, 1H), 7.28-7.22 (m, 3H), 7.12-7.03 (m, 5H), 4.62 (d, J = 4.0 Hz, 1H), 2.71-2.64 (m, 1H), 0.91 (d, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 203.95, 153.23, 153.02, 129.13, 128.71, 128.49, 128.32, 123.71, 123.53, 123.43, 121.56, 116.75, 55.92, 39.79, 9.52 ppm. IR (cm^{-1}): 3041, 2975, 2933, 1717, 1601, 1575, 1477, 1455, 1250, 749. TOF MS (EI^+) m/z: calcd. for $C_{16}H_{14}O_2$: 238.0994; found: 238.0997.



3q

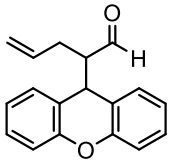
rac-2-(9*H*-xanthen-9-yl)pentanal. Yield: 66% as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.63 (d, J = 2.6 Hz, 1H), 7.26-7.21 (m, 3H), 7.12-7.05 (m, 5H), 4.46 (d, J = 4.5 Hz, 1H), 2.55-2.51

(m, 1H), 1.55-1.47 (m, 1H), 1.36-1.21 (m, 3H), 1.15-1.07 (m, 1H), 0.77 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 204.80, 153.10, 153.03, 129.07, 128.83, 128.45, 128.38, 123.66, 123.52, 123.22, 122.25, 116.91, 116.81, 60.64, 40.21, 27.67, 20.83, 14.10 ppm. IR (cm^{-1}): 3042, 2958, 2930, 2871, 1720, 1601, 1576, 1478, 1456, 1252, 753. TOF MS (EI^+) m/z: calcd. for $C_{18}H_{18}O_2$: 266.1307; found: 266.1303.



3r

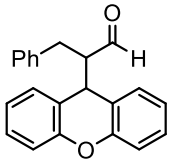
rac-3-methyl-2-(9*H*-xanthen-9-yl)butanal. Yield: 64% as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.50 (d, J = 4.1 Hz, 1H), 7.25-7.22 (m, 4H), 7.11-7.06 (m, 4H), 4.48 (d, J = 5.9 Hz, 1H), 2.31-2.28 (m, 1H), 2.01-1.94 (m, 1H), 1.10 (d, J = 6.8 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 204.63, 153.31, 153.10, 128.99, 128.82, 128.37, 128.30, 124.12, 123.67, 123.50, 123.26, 116.95, 116.91, 66.41, 38.38, 26.22, 21.86, 19.44 ppm. IR (cm^{-1}): 3069, 3041, 2962, 2929, 1716, 1600, 1576, 1475, 1455, 1246, 756. TOF MS (EI^+) m/z: calcd. for $C_{18}H_{18}O_2$: 266.1307; found: 266.1306.



3s

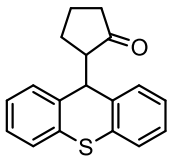
rac-2-(9*H*-xanthen-9-yl)pent-4-enal. Yield: 56% as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ

= 9.63 (d, J = 2.0 Hz, 1H), 7.27-7.22 (m, 3H), 7.13-7.05 (m, 5H), 5.65-5.57 (m, 1H), 4.99-4.95 (m, 2H), 4.55 (d, J = 4.2 Hz, 1H), 2.69-2.65 (m, 1H), 2.29-2.23 (m, 1H), 2.18-2.13 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 204.04, 153.11, 153.01, 135.13, 129.07, 128.83, 128.57, 128.50, 123.73, 123.63, 122.88, 122.02, 117.48, 116.93, 116.86, 60.05, 39.50, 29.78 ppm. IR (cm^{-1}): 3073, 3042, 2924, 2849, 1720, 1640, 1601, 1576, 1477, 1456, 1251, 752. TOF MS (EI^+) m/z: calcd. for $C_{18}H_{16}O_2$: 264.1150; found: 264.1151.



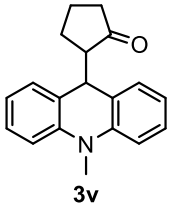
3t

rac-3-phenyl-2-(9*H*-xanthen-9-yl)propanal. Yield: 77% as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.65 (d, J = 1.7 Hz, 1H), 7.29-7.25 (m, 3H), 7.18 (t, J = 7.4 Hz, 2H), 7.14- 7.05 (m, 6H), 6.96 (d, J = 7.3 Hz, 2H), 4.59 (d, J = 3.9 Hz, 1H), 3.00-2.96 (m, 1H), 2.82-2.77 (m, 1H), 2.71-2.67 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 203.64, 153.05, 152.99, 138.89, 129.11, 128.94, 128.76, 128.65, 128.58, 126.45, 123.82, 123.66, 122.77, 121.84, 116.98, 116.92, 62.55, 39.65, 31.37 ppm. IR (cm^{-1}): 3031, 2959, 2928, 2830, 2738, 1719, 1601, 1496, 1477, 1457, 1247, 753, 743, 697. TOF MS (EI^+) m/z: calcd. for $C_{22}H_{18}O_2$: 314.1307; found: 314.1308.



3u

2-(9*H*-thioxanthen-9-yl)cyclopentan-1-one. Yield: 41% as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (dd, *J* = 7.3, 17.1 Hz, 3H), 7.25 – 7.12 (m, 5H), 4.65 (d, *J* = 5.2 Hz, 1H), 2.61 – 2.54 (m, 1H), 2.24 (d, *J* = 6.6, 17.2 Hz, 1H), 1.93 – 1.76 (m, 3H), 1.62 – 1.43 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.94, 137.11, 134.82, 133.69, 132.41, 130.17, 129.87, 127.00, 126.79, 126.69, 126.64, 126.53, 56.25, 46.93, 38.25, 27.00, 20.38 ppm. IR (cm^{-1}): 3059, 3008, 2963, 2937, 2866, 1763, 1463, 1441, 1398, 1172, 746. TOF MS (EI^+) m/z: calcd. for $C_{18}H_{16}OS$: 280.0922; found: 280.0921.



3v

2-(10-methyl-9,10-dihydroacridin-9-yl)cyclopentan-1-one. Yield: 15% as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 3H), 7.14 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.00 (td, *J* = 7.4, 1.1 Hz, 1H), 6.94 – 6.89 (m, 3H), 4.74 (d, *J* = 3.3 Hz, 1H), 3.41 (s, 3H), 2.32 (td, *J* = 9.6, 3.3 Hz, 1H), 2.24 (dd, *J* = 18.0, 7.1 Hz,1H), 1.88 – 1.66 (m, 3H), 1.59 – 1.38 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 219.31, 143.70, 142.94, 129.33, 128.23, 127.54, 127.25, 126.53, 123.73, 120.99, 120.79, 112.16, 112.09, 59.60, 41.96, 38.96, 33.12, 24.72, 20.54 ppm. IR (cm^{-1}): 2954, 1734, 1592, 1478, 1345, 1268, 755. TOF MS (EI^+) m/z: calcd. for $C_{19}H_{19}NO$: 277.1467; found: 277.1466.

NMR spectra of CDC products

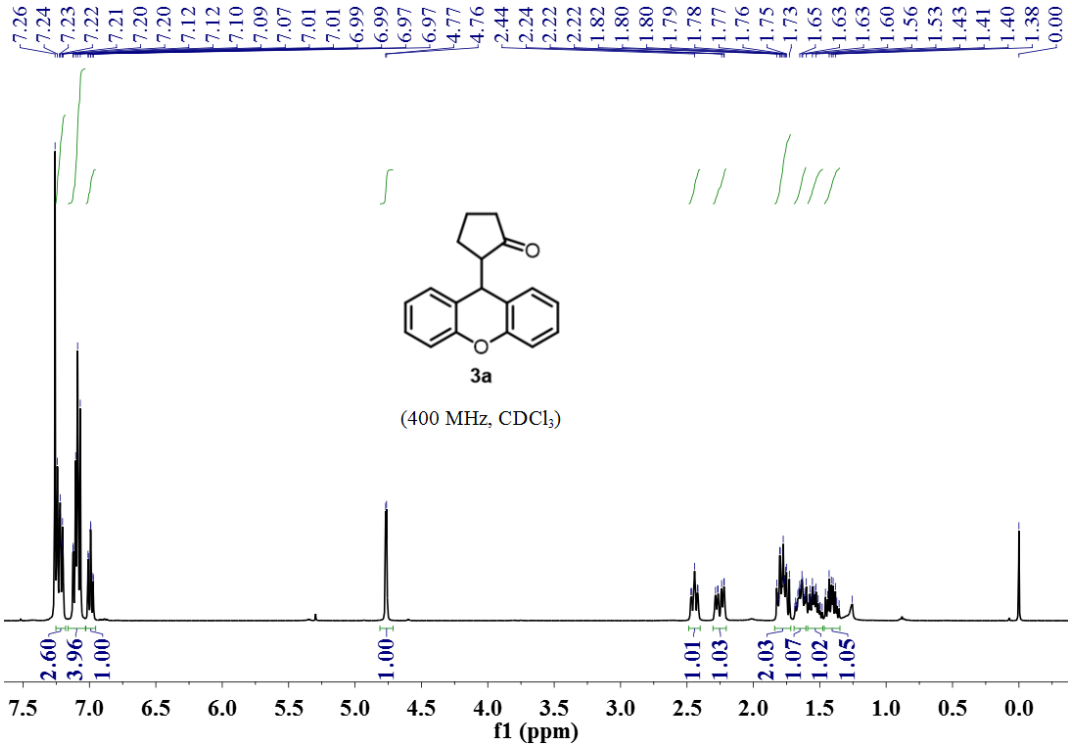


Figure S8. ^{1}H NMR spectrum of **3a**.

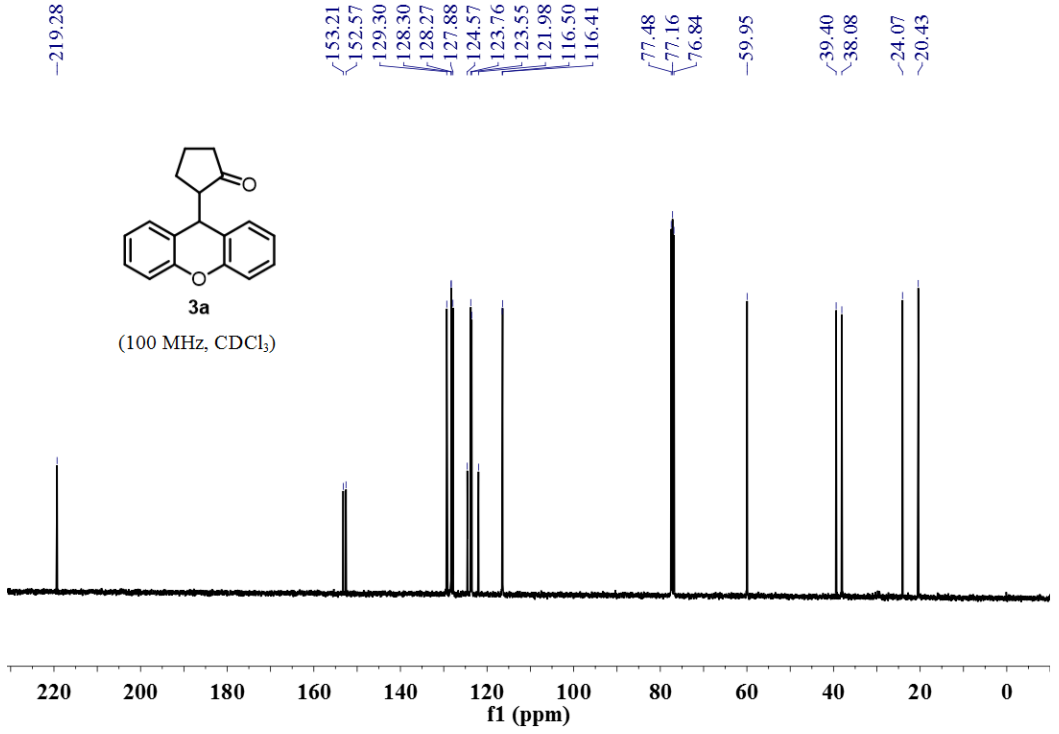


Figure S9. ^{13}C NMR spectrum of **3a**.

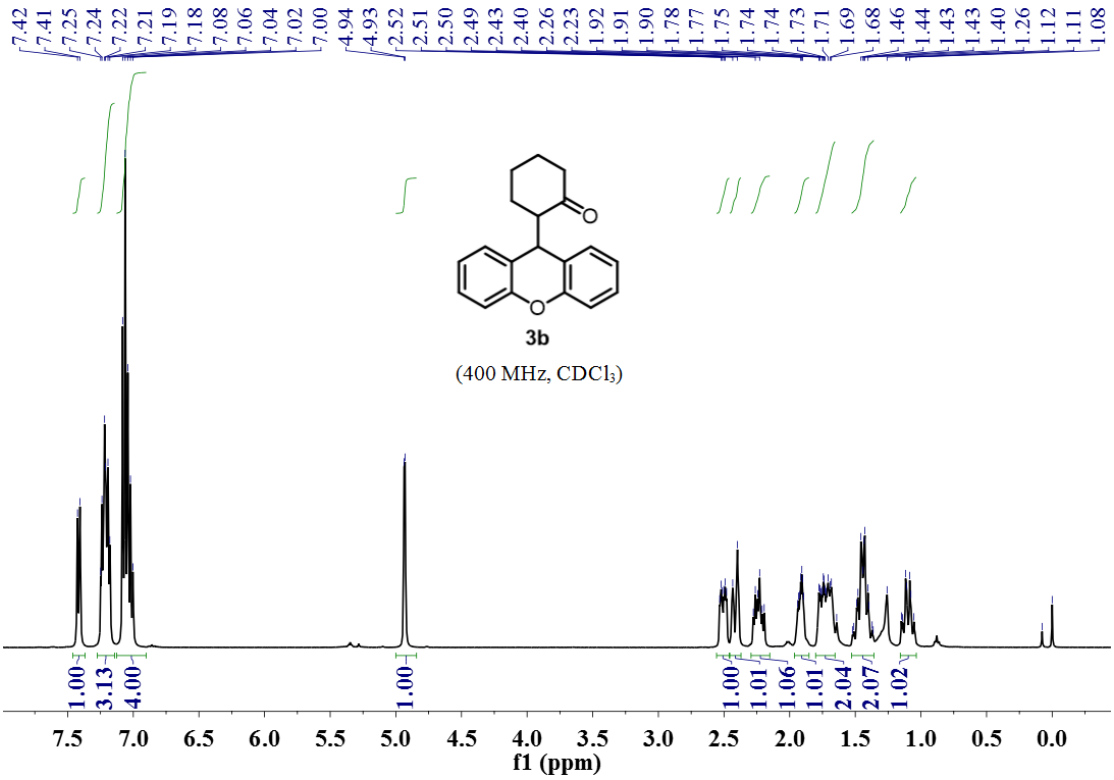


Figure S10. ^{1}H NMR spectrum of **3b**.

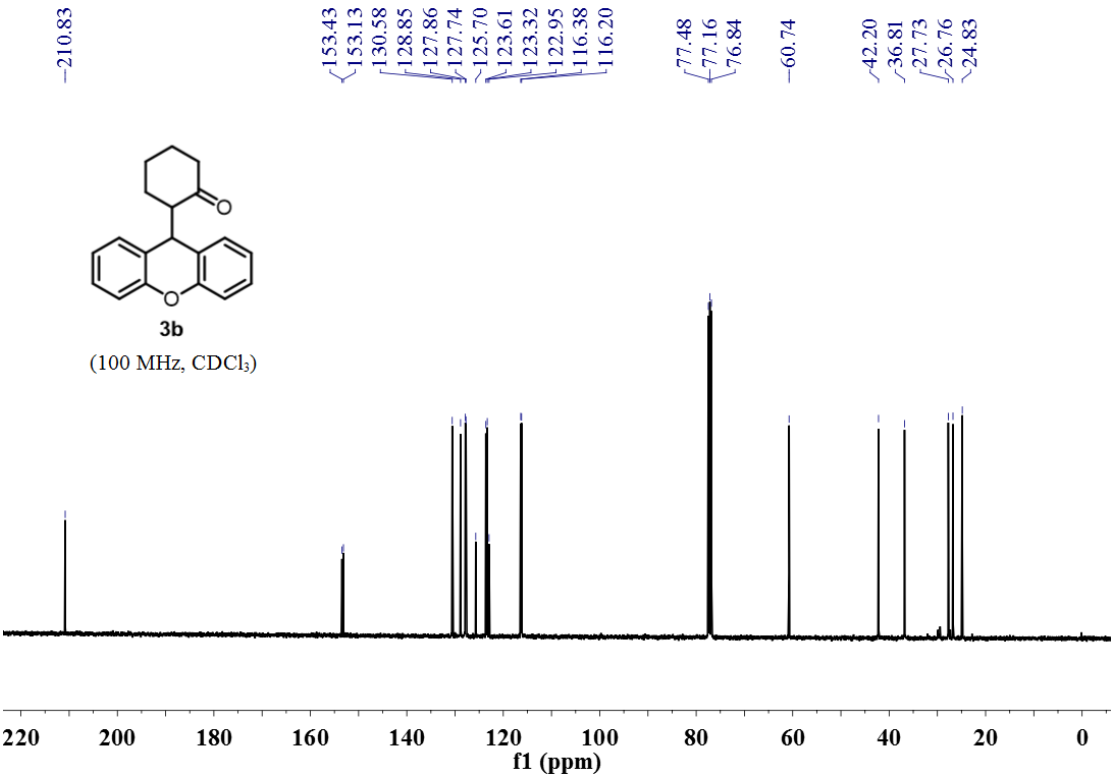


Figure S11. ^{13}C NMR spectrum of **3b**.

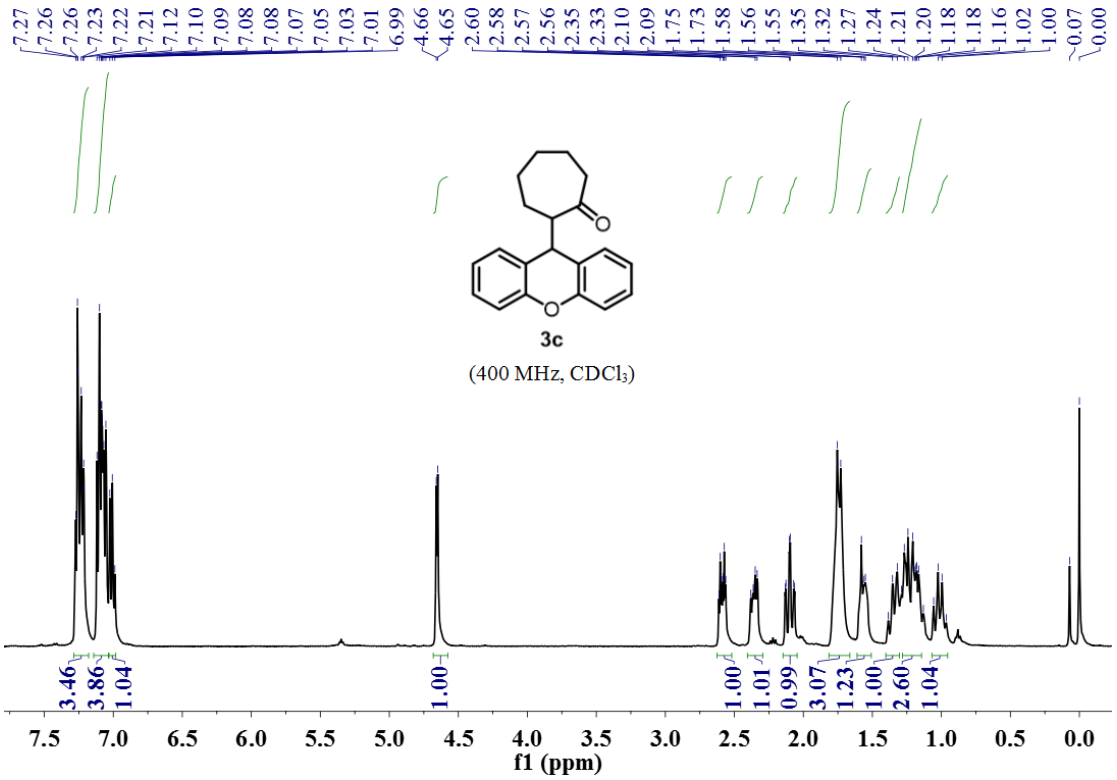


Figure S12. ^{1}H NMR spectrum of **3c**.

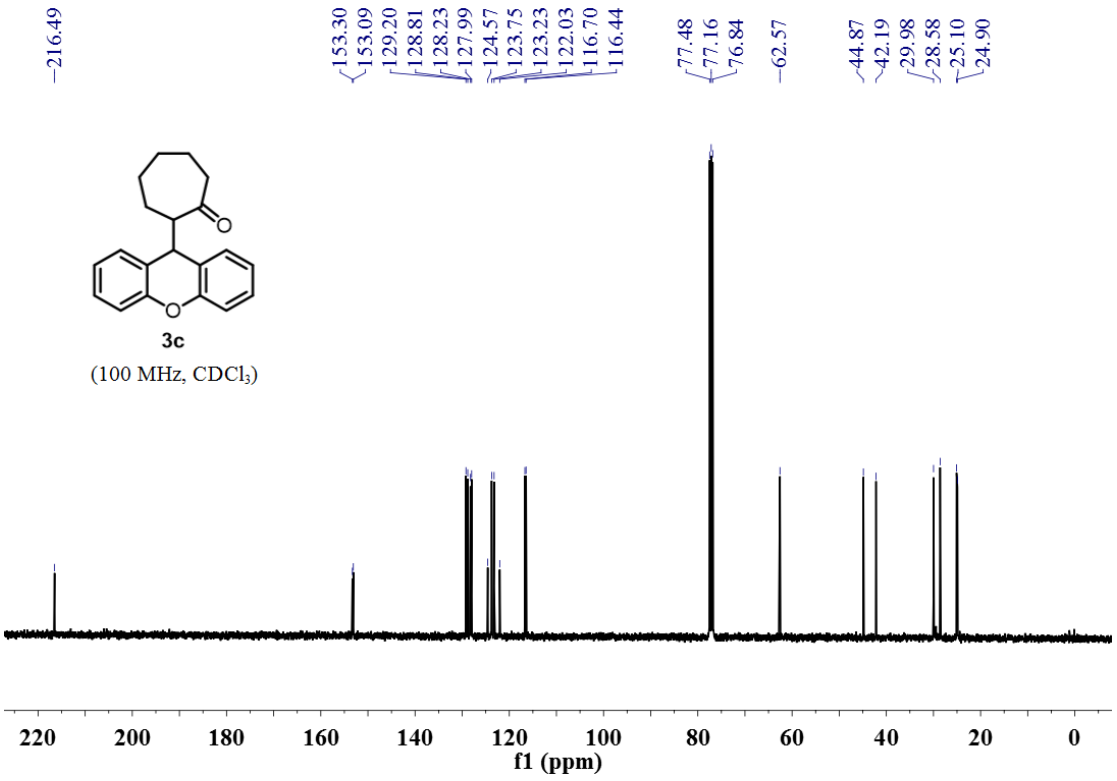


Figure S13. ^{13}C NMR spectrum of **3c**.

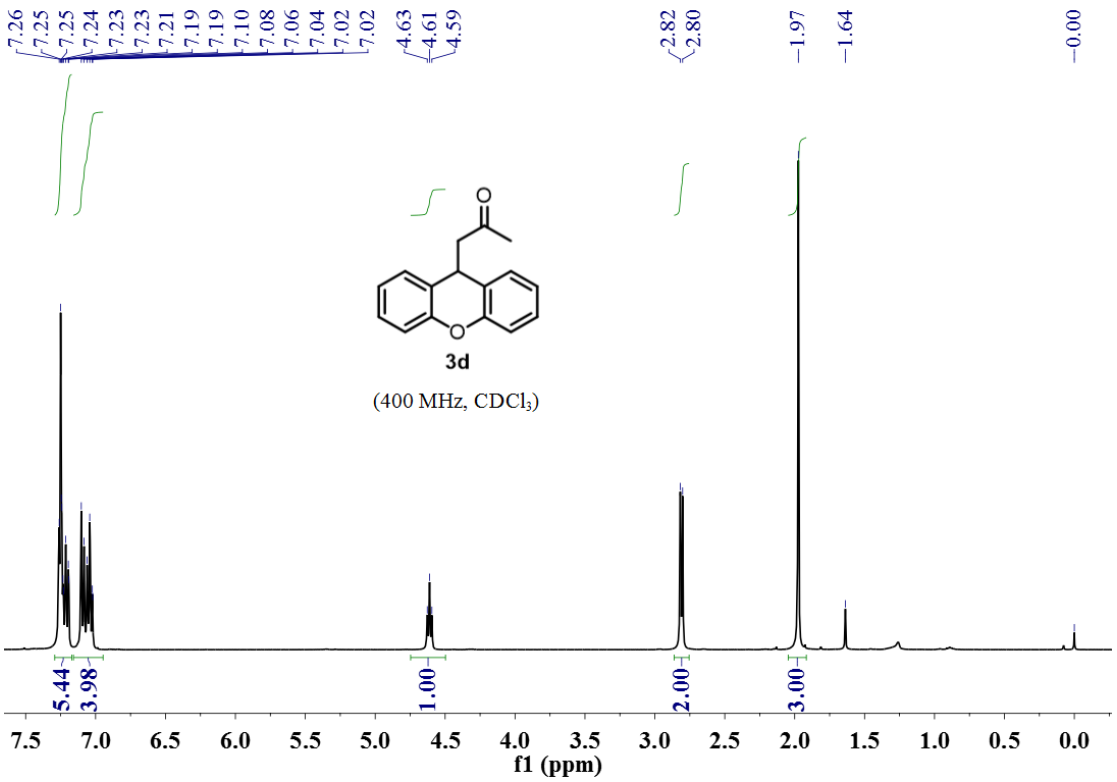


Figure S14. ^{1}H NMR spectrum of **3d**.

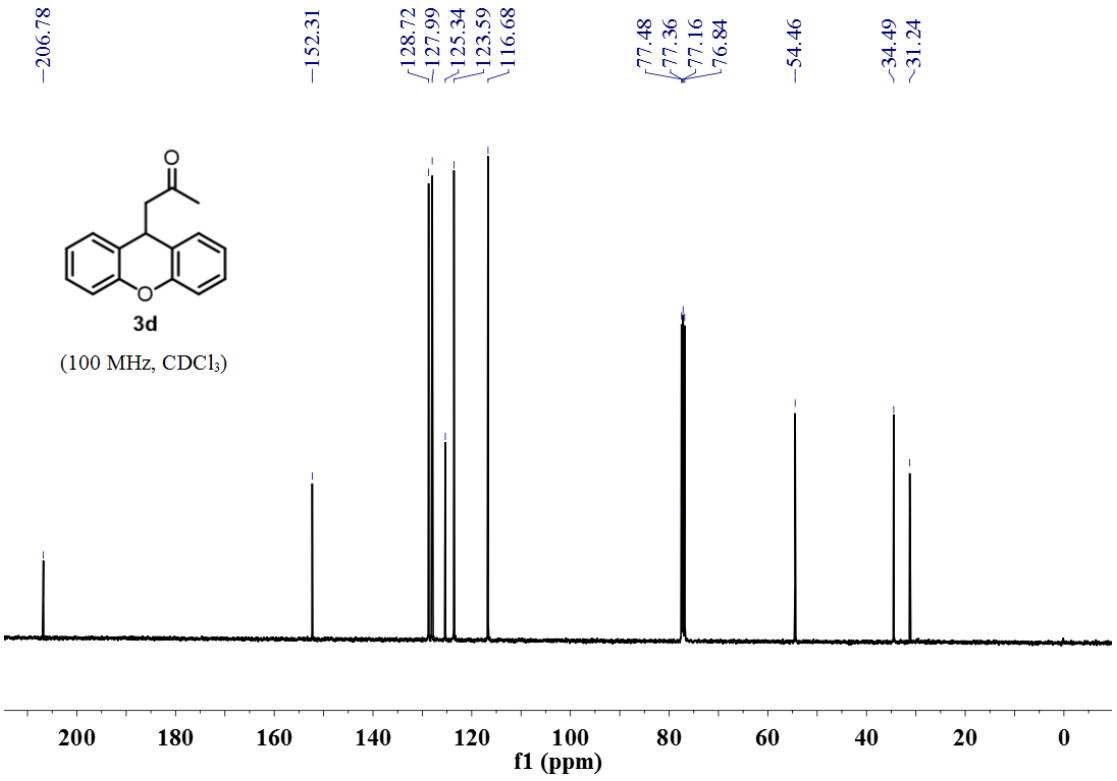


Figure S15. ^{13}C NMR spectrum of **3d**.

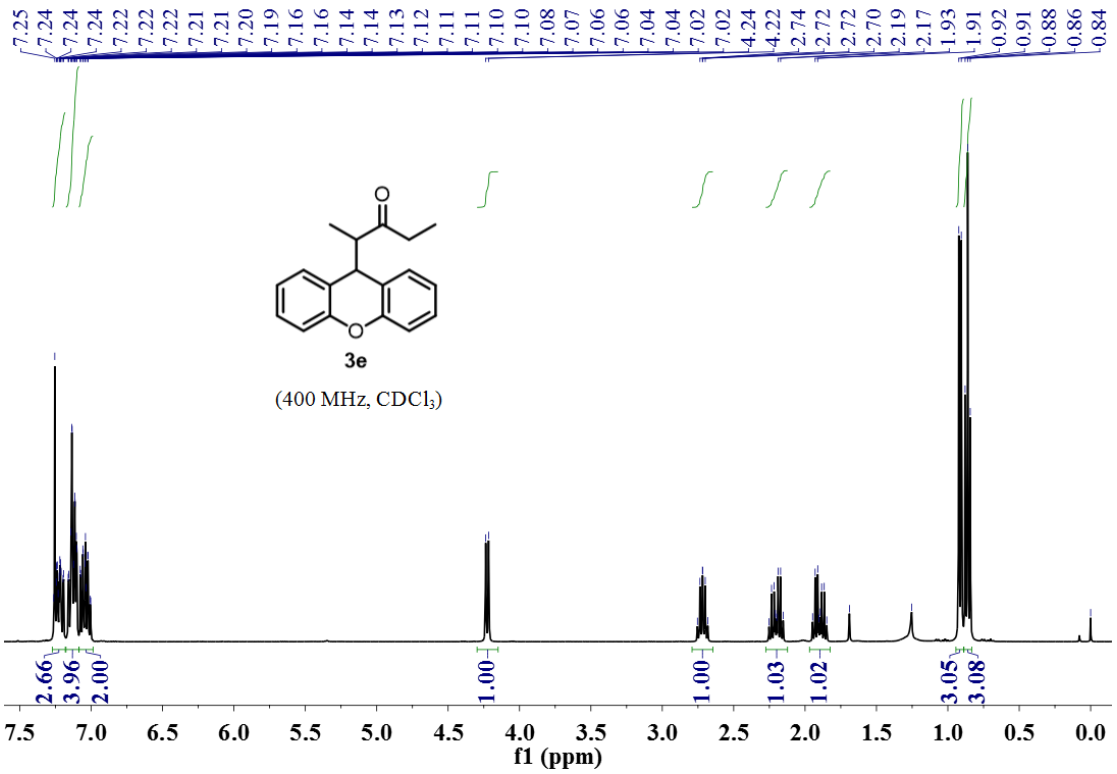


Figure S16. ^{1}H NMR spectrum of **3e**.

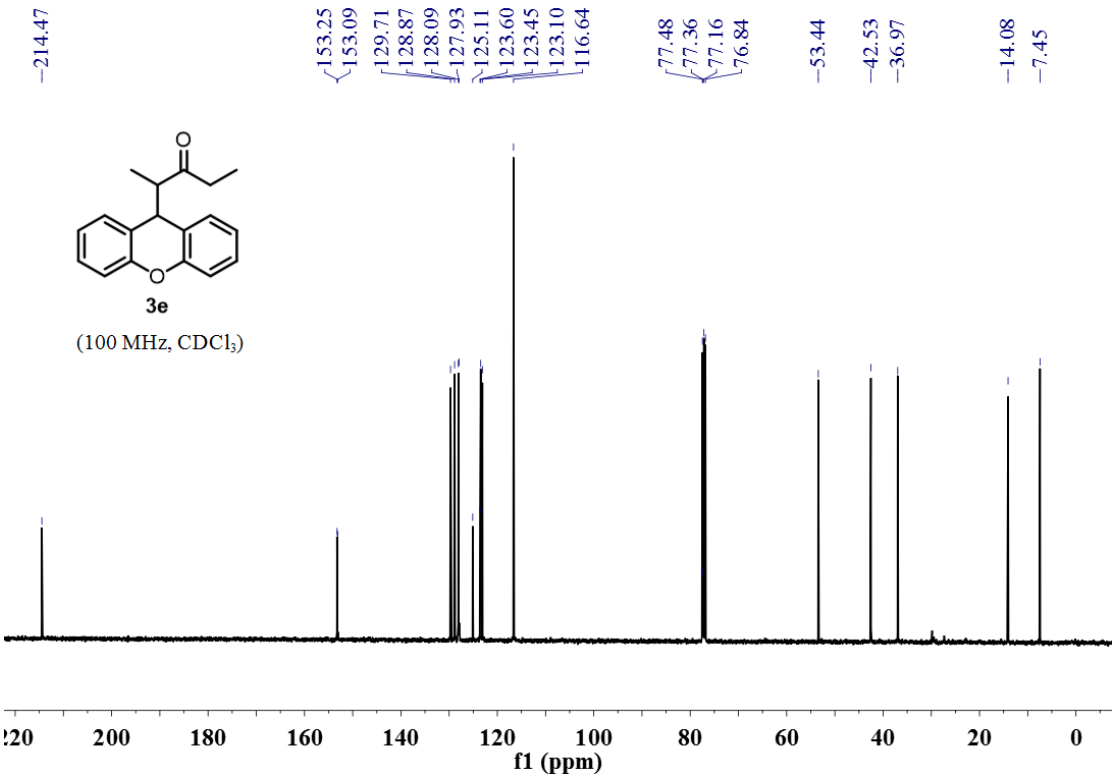


Figure S17. ^{13}C NMR spectrum of **3e**.

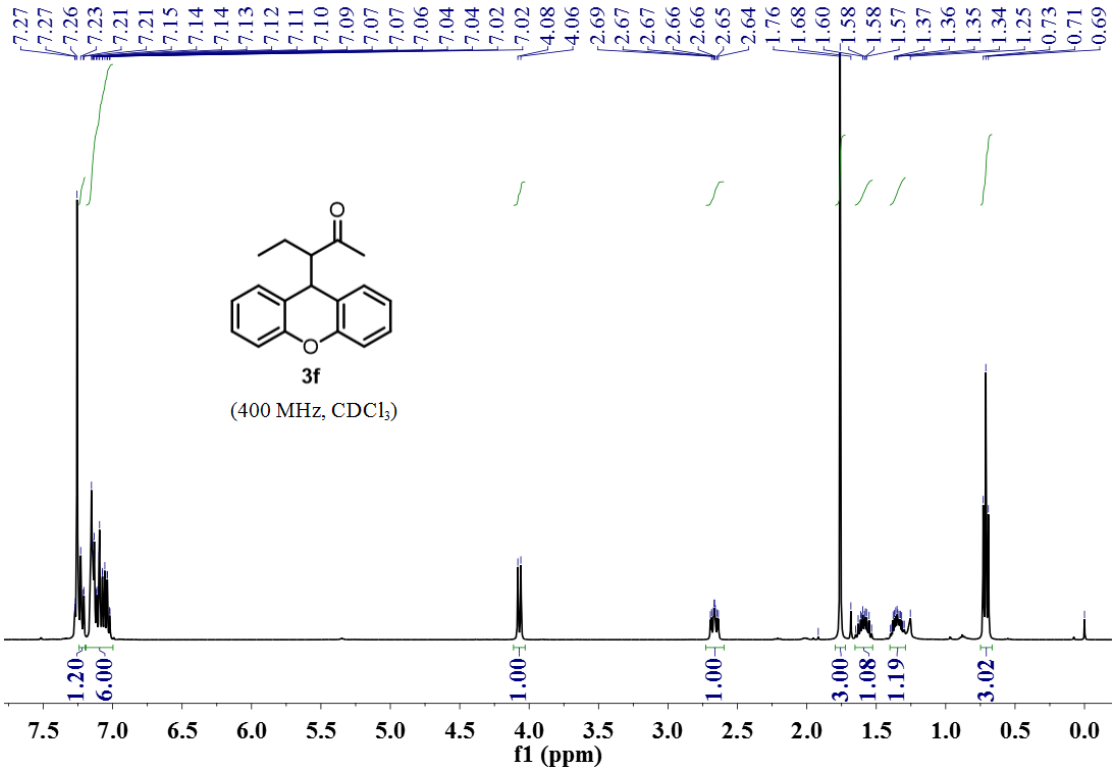


Figure S18. ^{1}H NMR spectrum of **3f**.

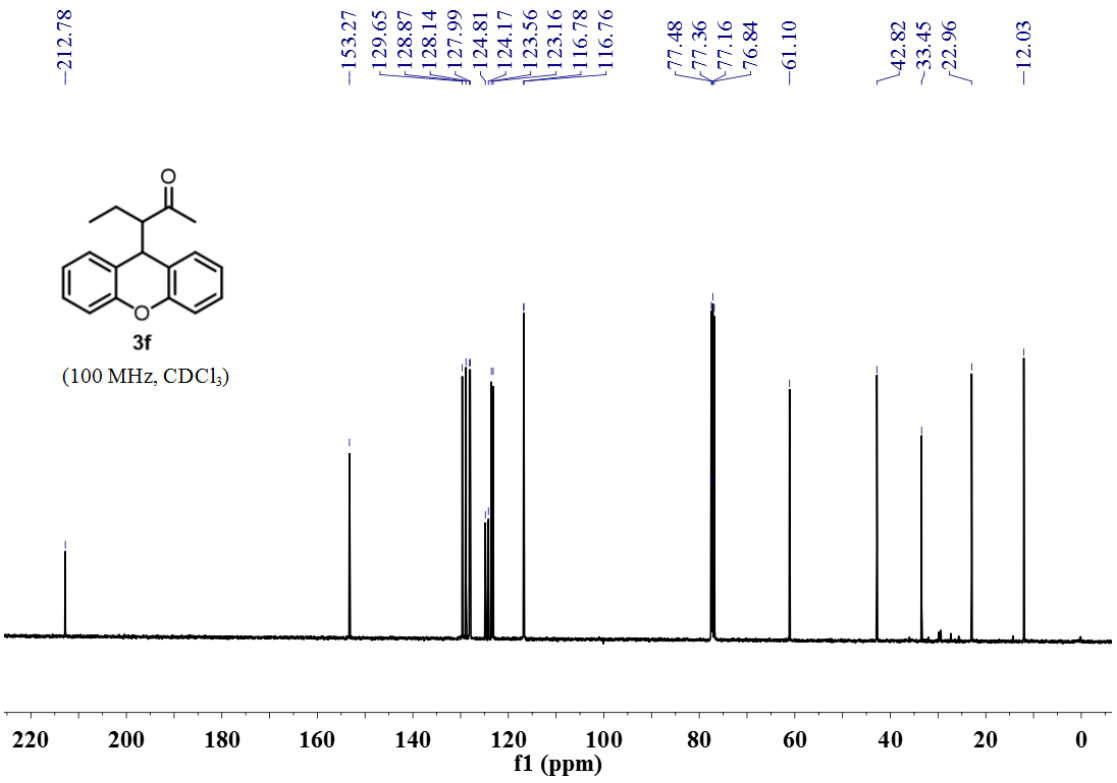


Figure S19. ^{13}C NMR spectrum of **3f**.

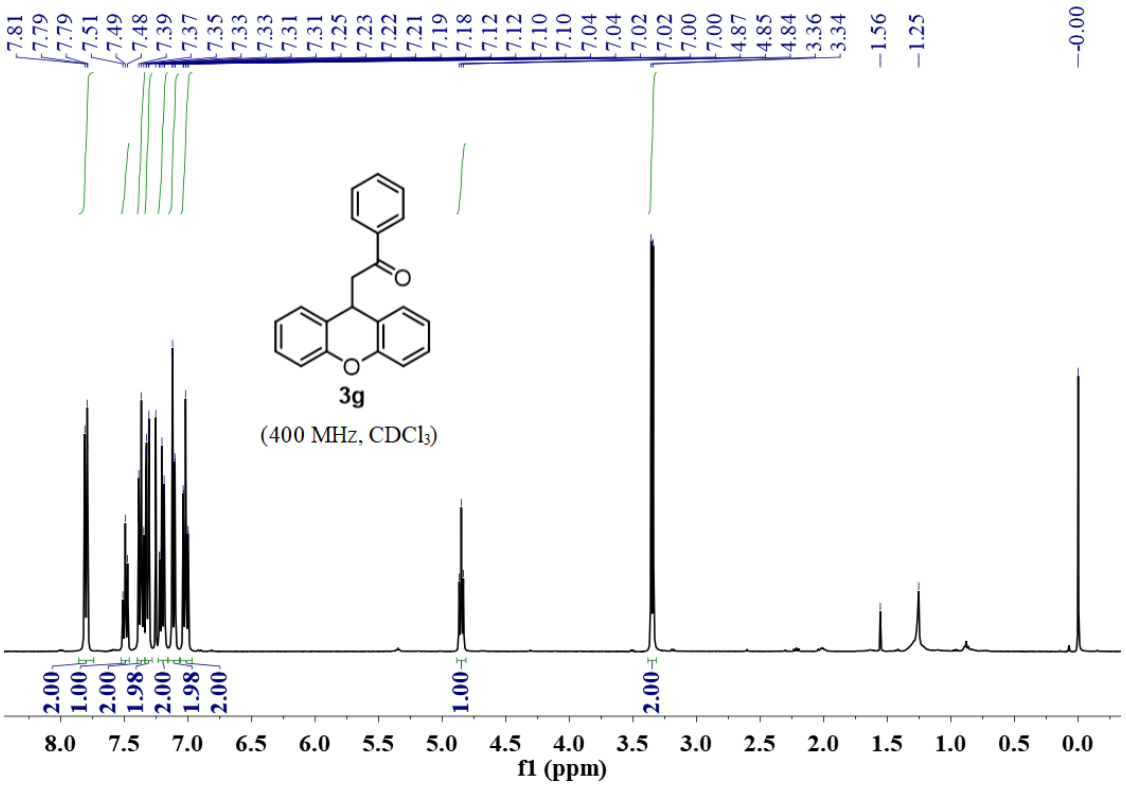


Figure S20. ^{1}H NMR spectrum of **3g**.

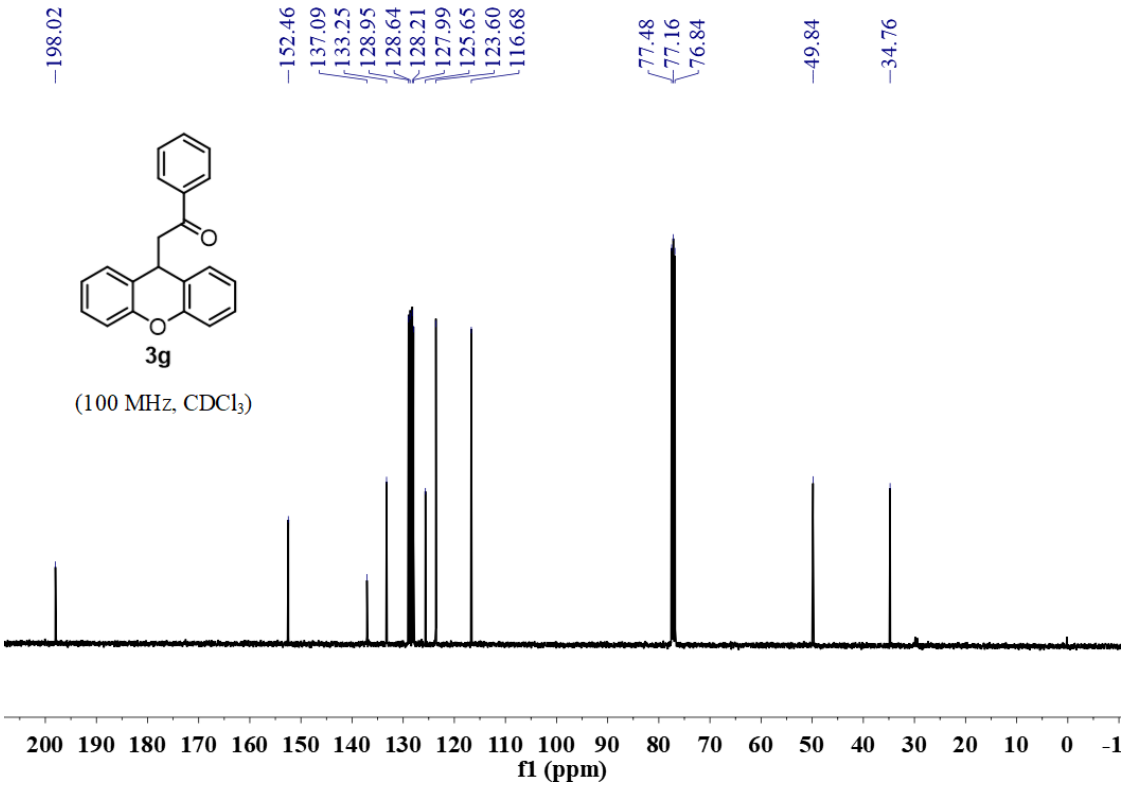


Figure S21. ^{13}C NMR spectrum of **3g**.

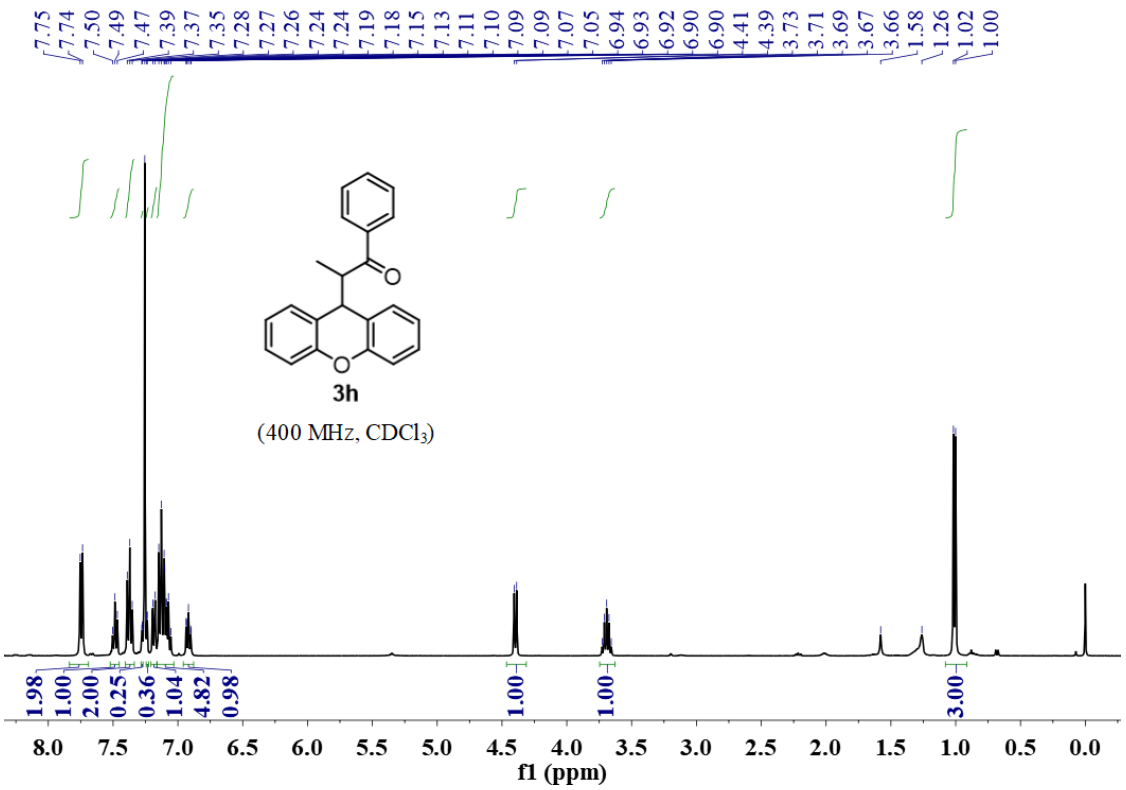


Figure S22. ^{1}H NMR spectrum of **3h**.

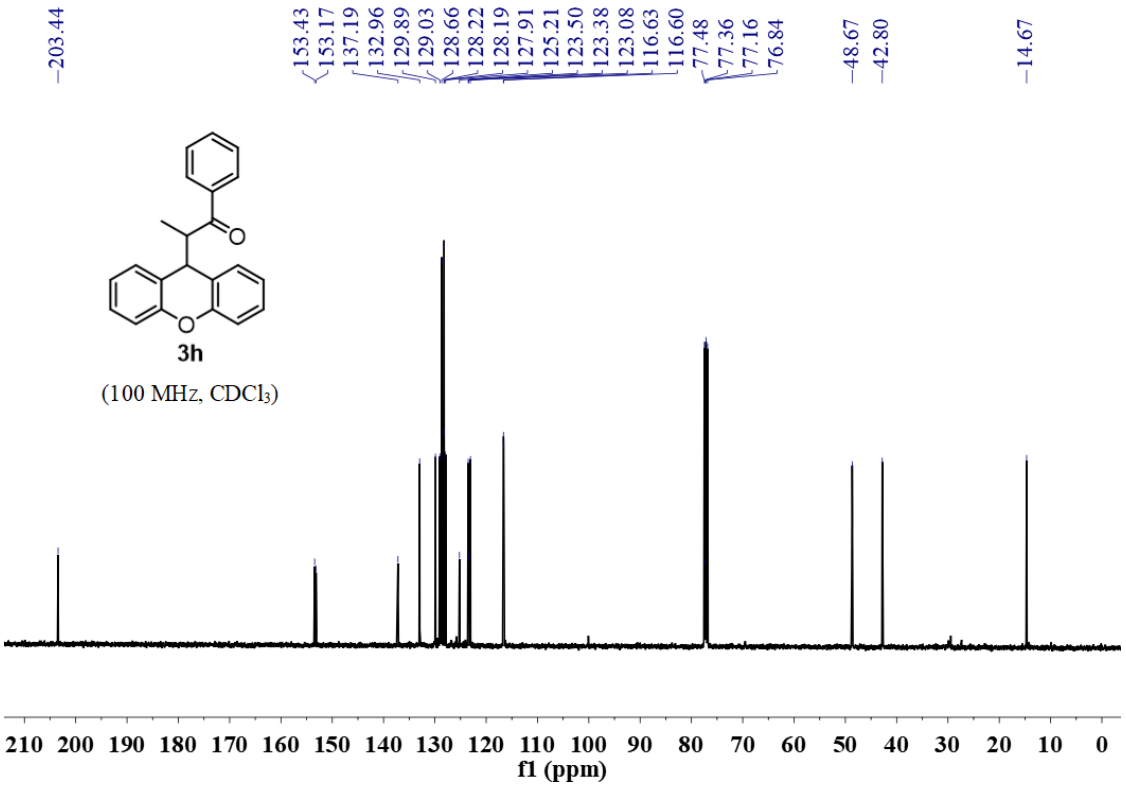


Figure S23. ^{13}C NMR spectrum of **3h**.

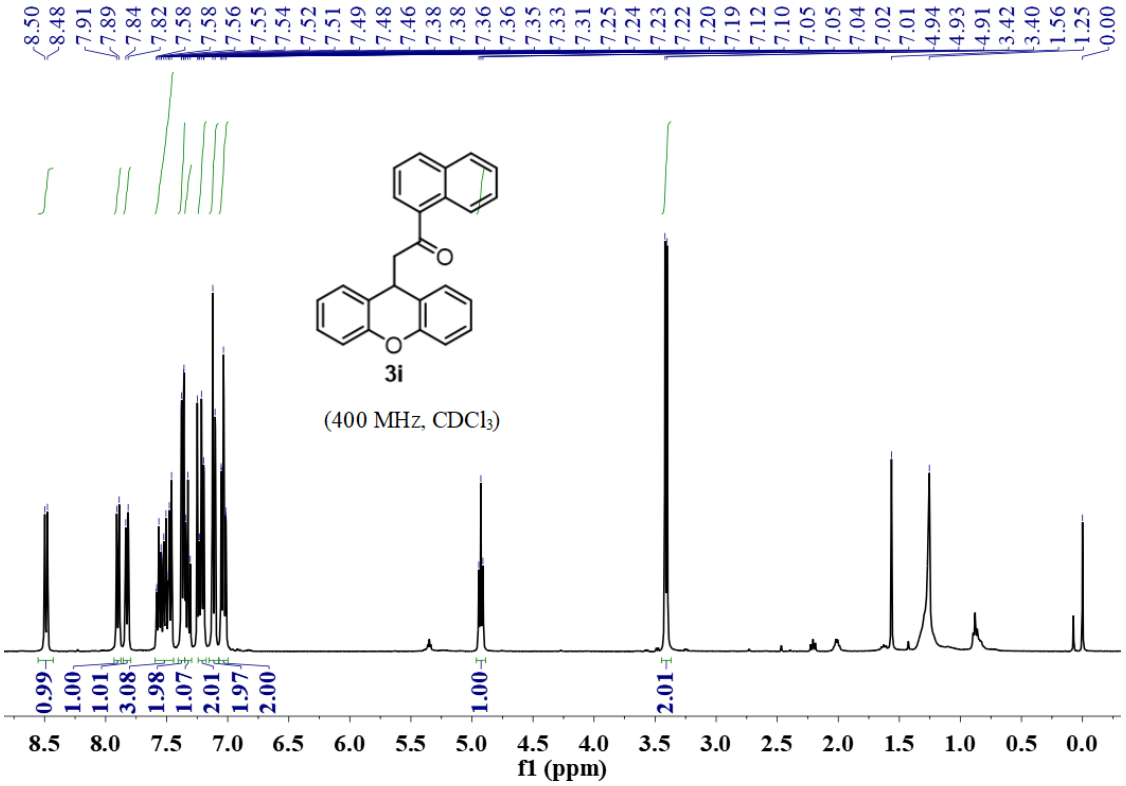


Figure S24. ^{1}H NMR spectrum of **3i**.

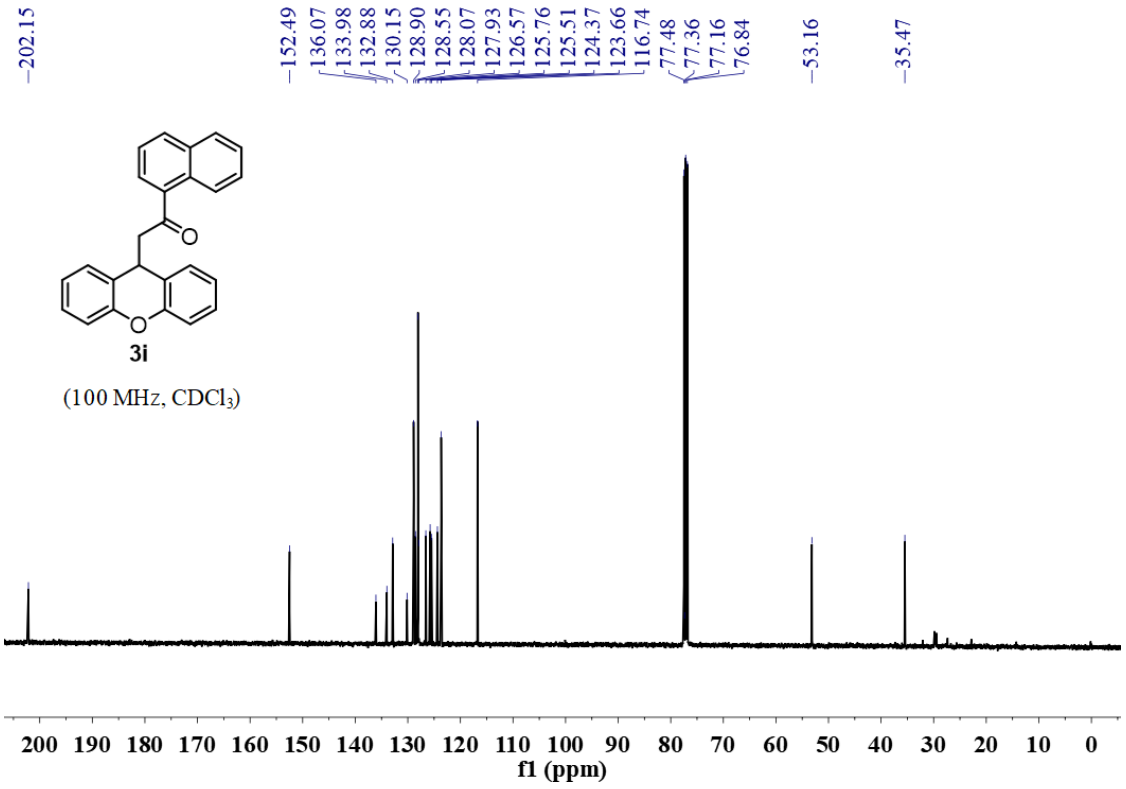


Figure S25. ^{13}C NMR spectrum of **3i**.

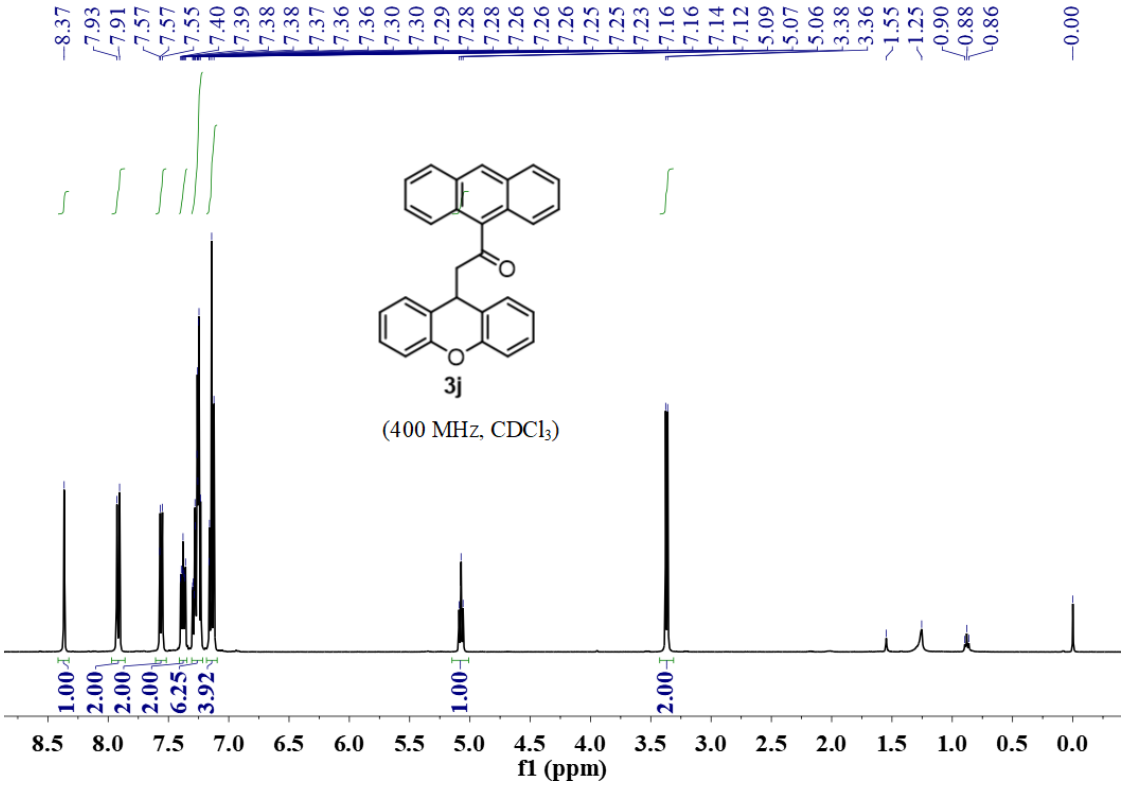


Figure S26. ^{1}H NMR spectrum of **3j**.

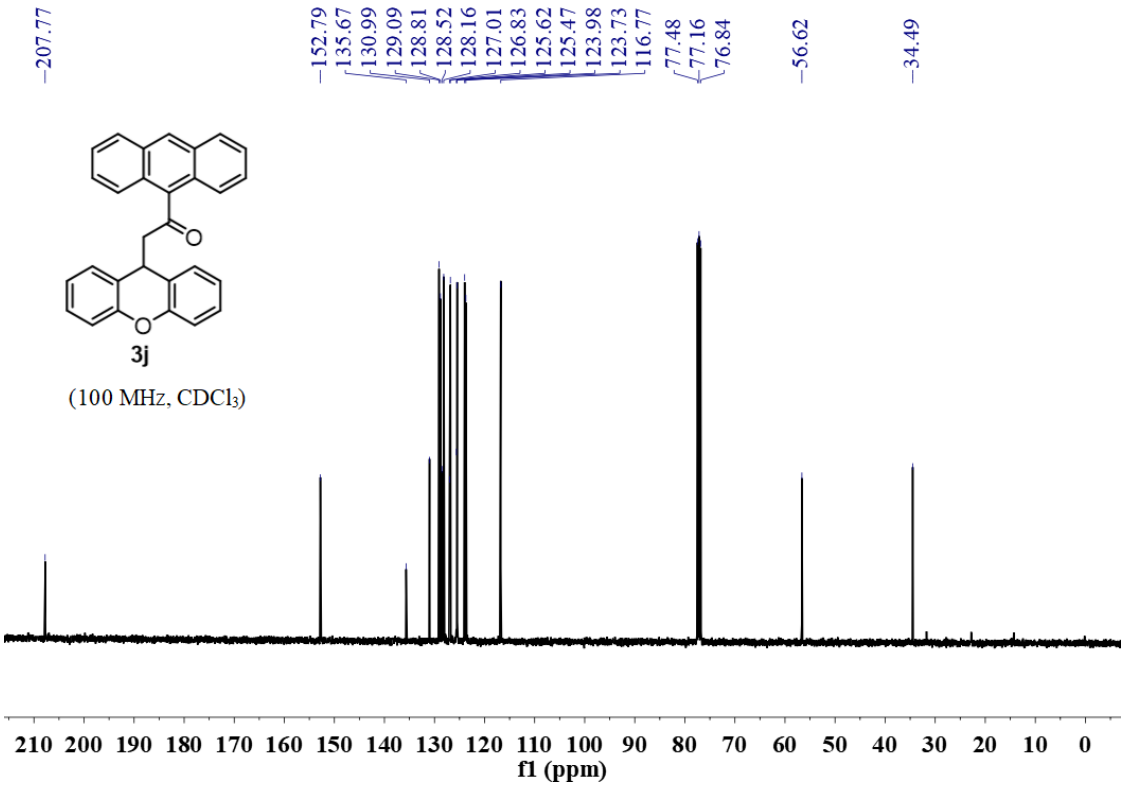


Figure S27. ^{13}C NMR spectrum of **3j**.

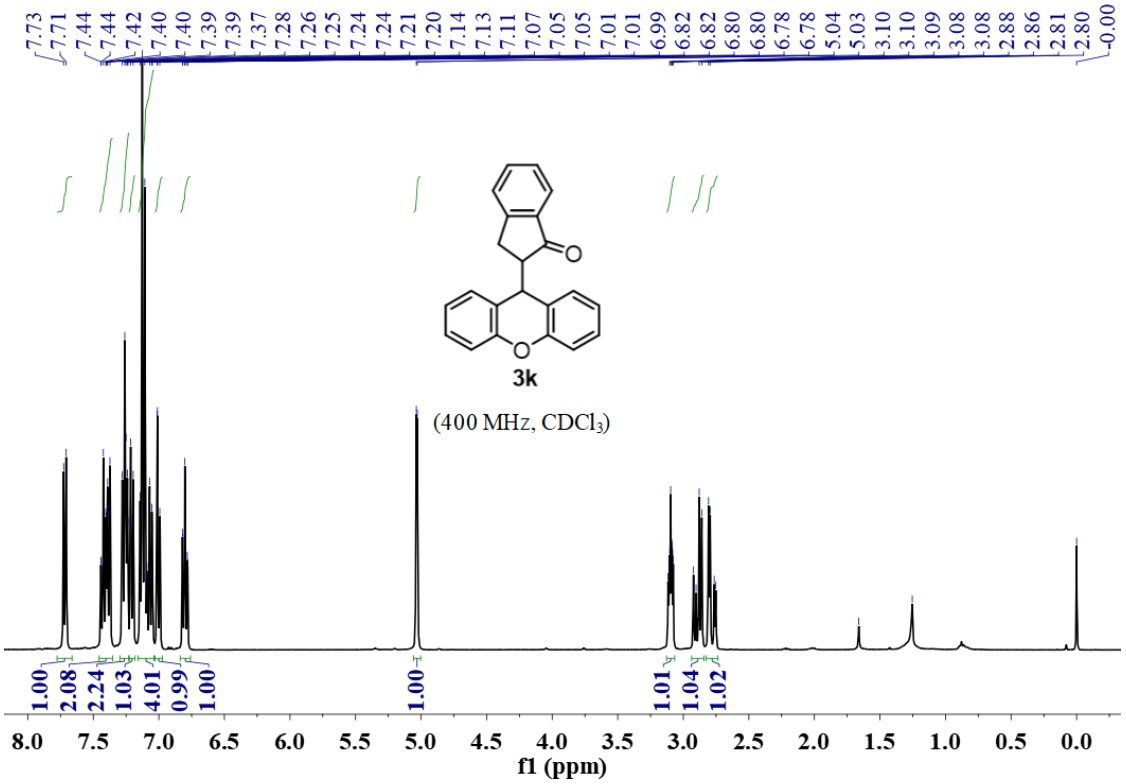


Figure S28. ^{1}H NMR spectrum of **3k**.

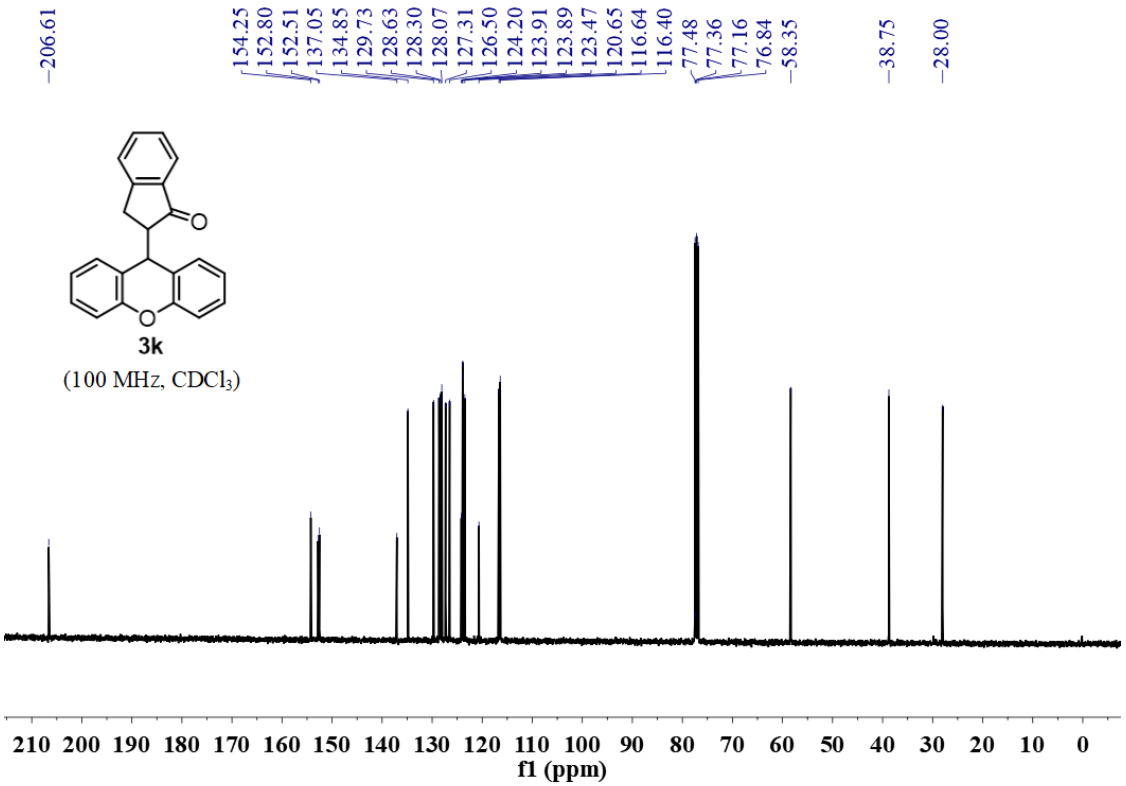


Figure S29. ^{13}C NMR spectrum of **3k**.

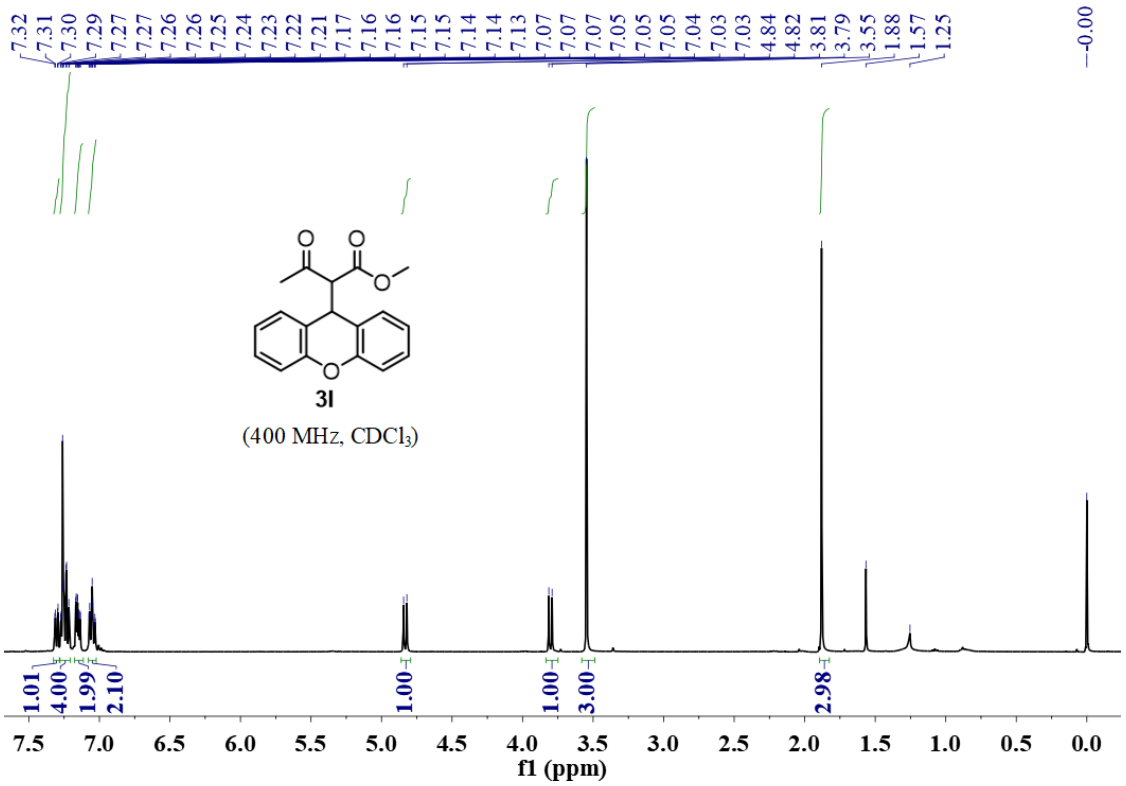


Figure S30. ^{1}H NMR spectrum of **3l**.

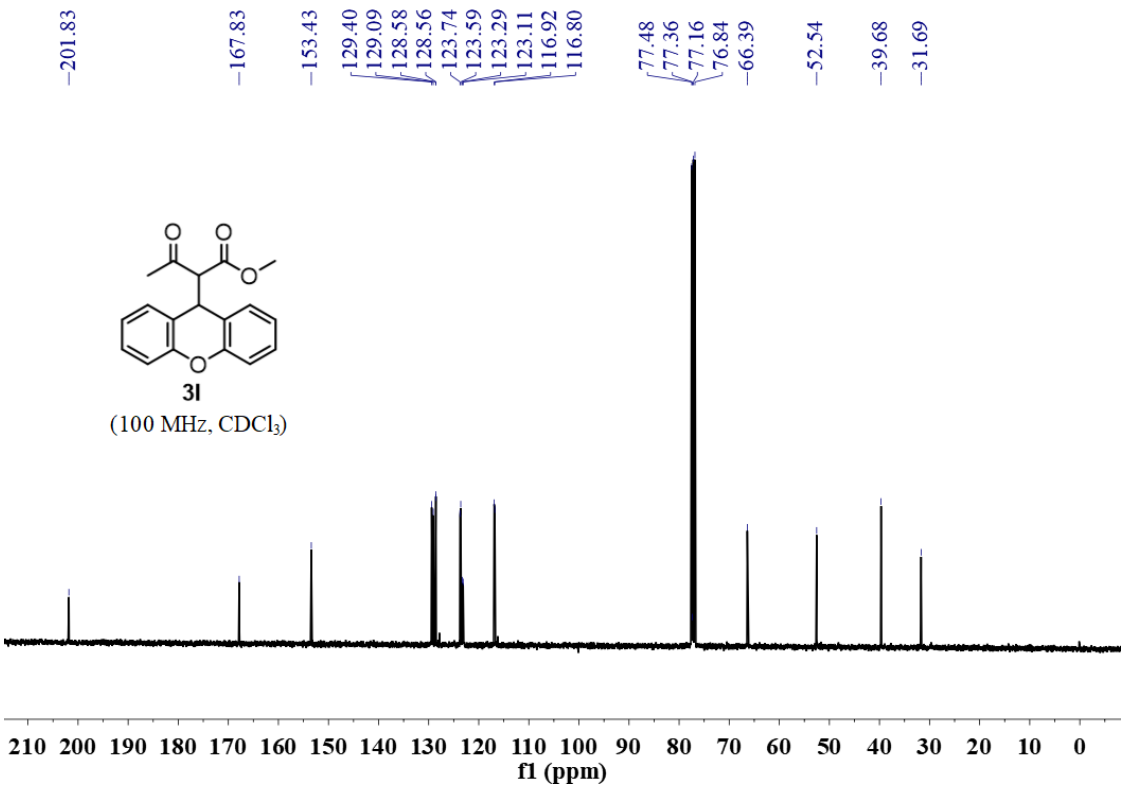


Figure S31. ^{13}C NMR spectrum of **3l**.

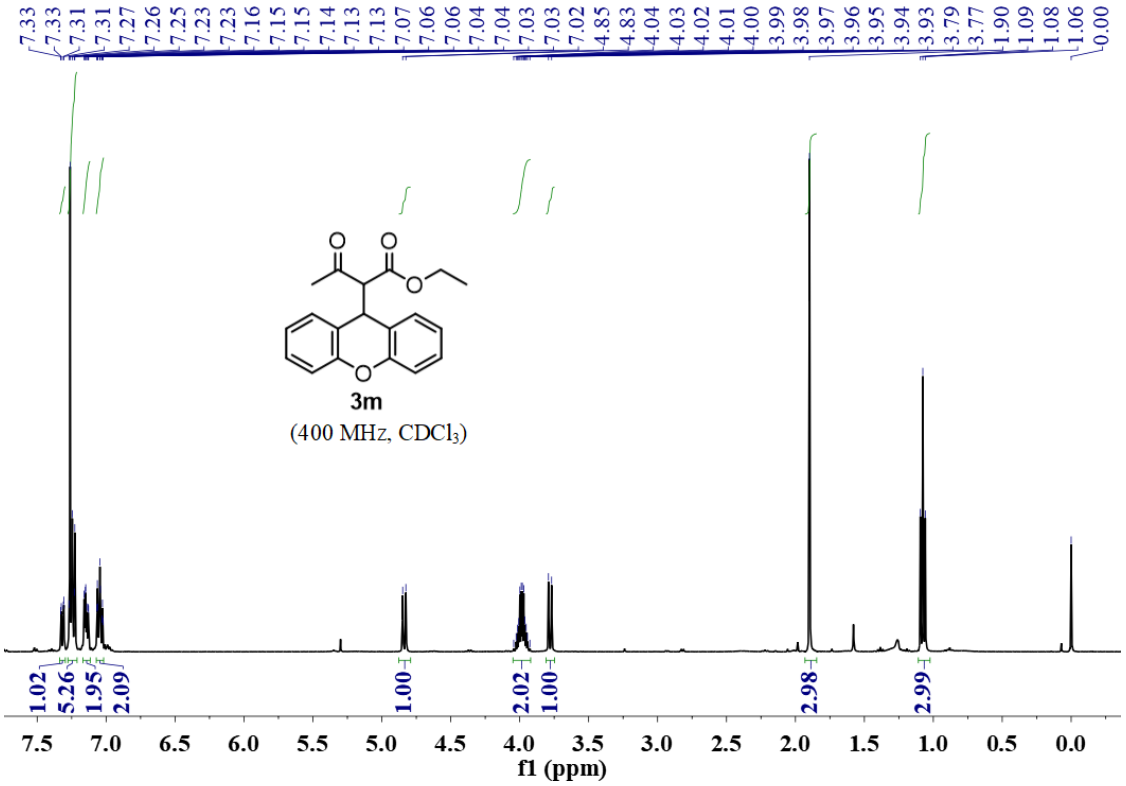


Figure S32. ^{1}H NMR spectrum of **3m**.

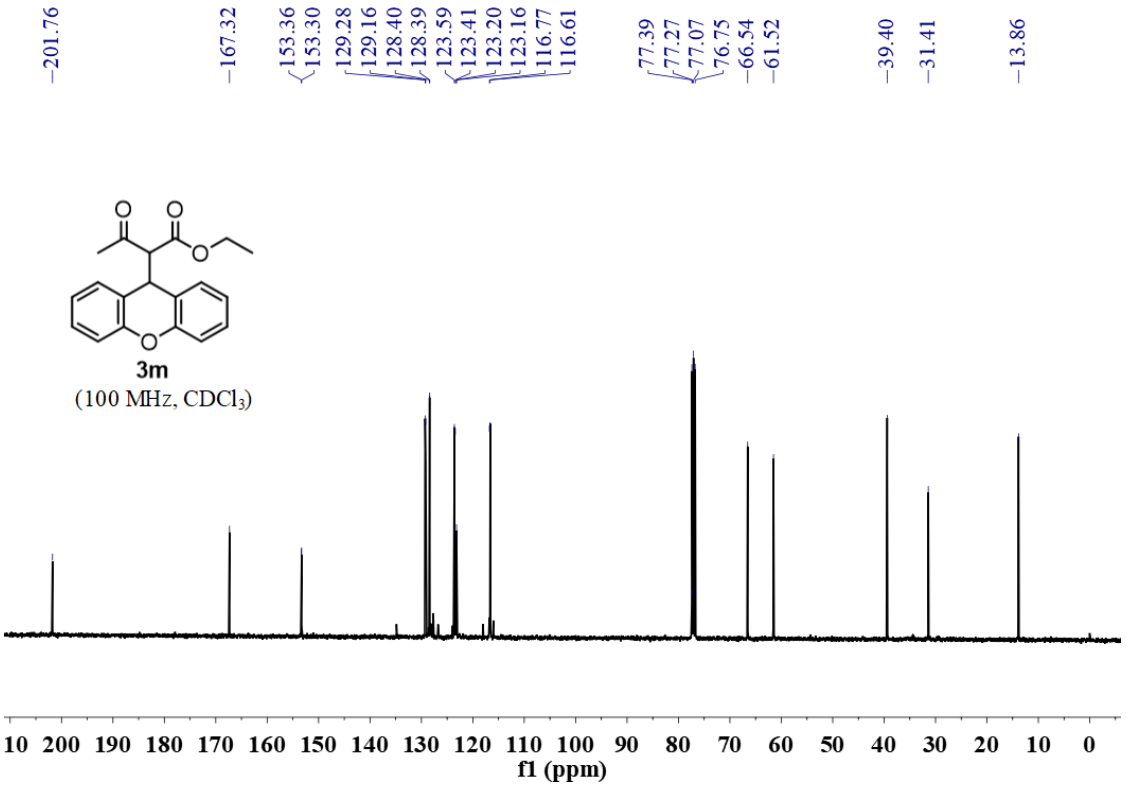


Figure S33. ^{13}C NMR spectrum of **3m**.

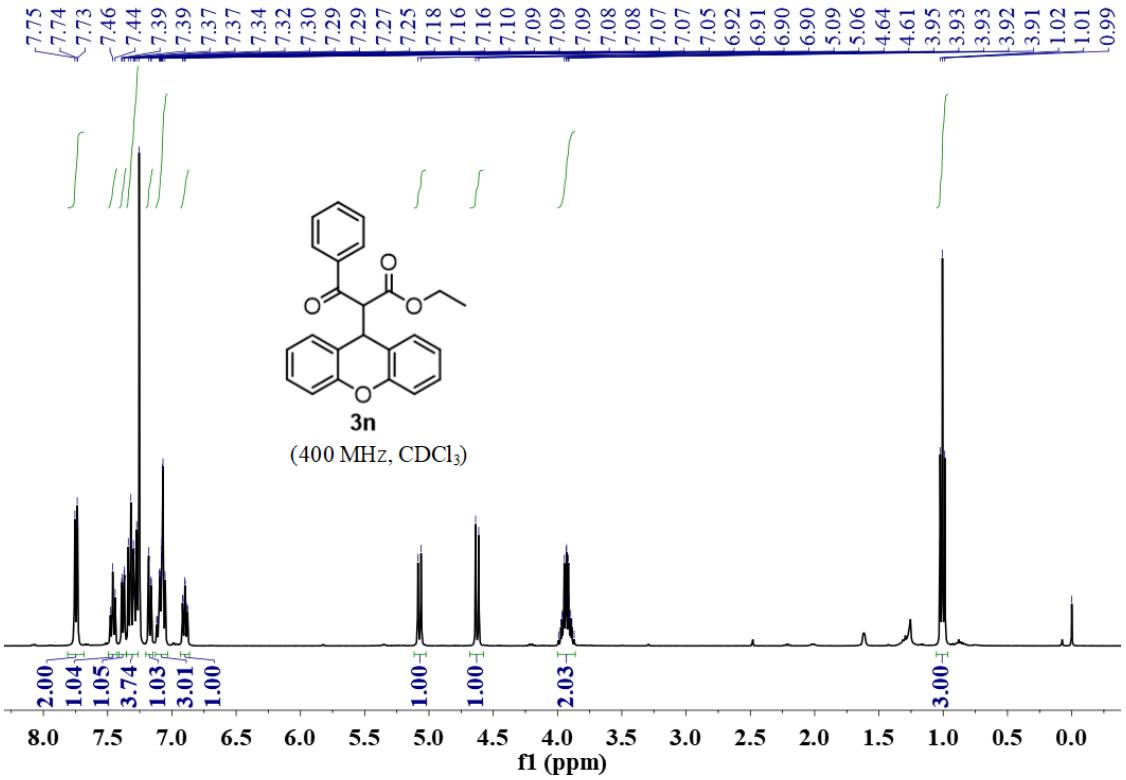


Figure S34. ^{1}H NMR spectrum of **3n**.

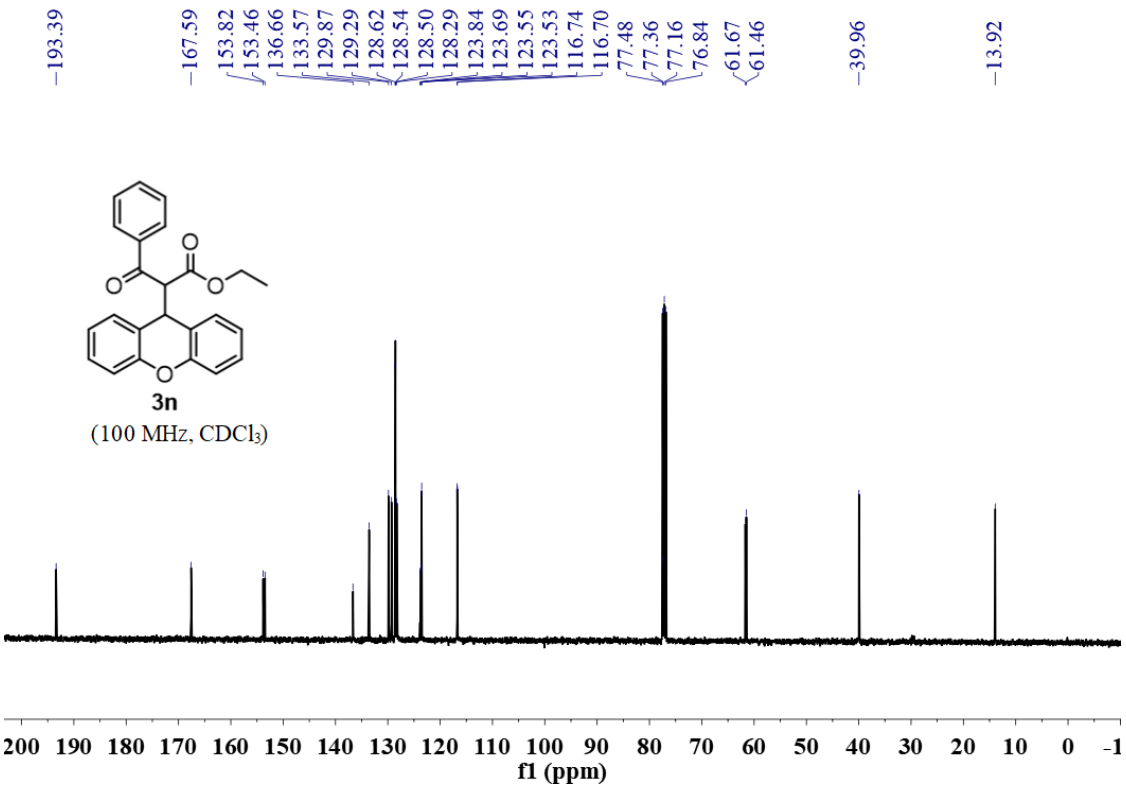


Figure S35. ^{13}C NMR spectrum of **3n**.

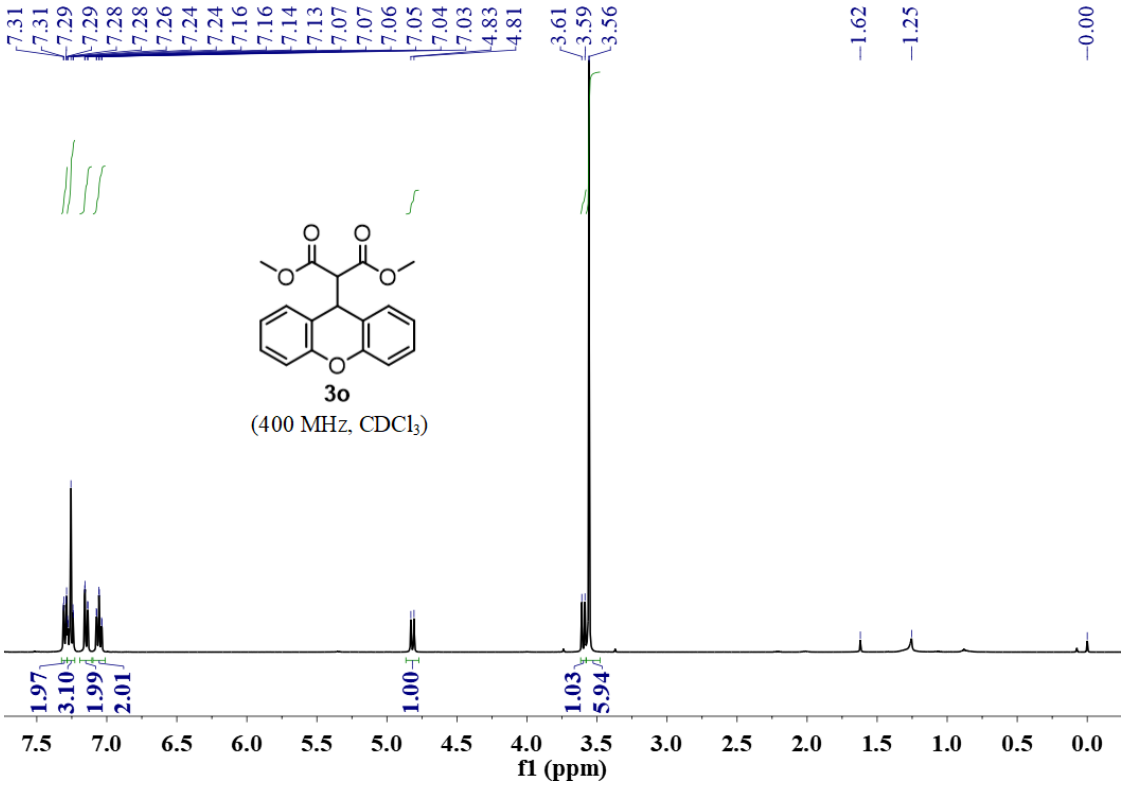


Figure S36. ^{1}H NMR spectrum of **3o**.

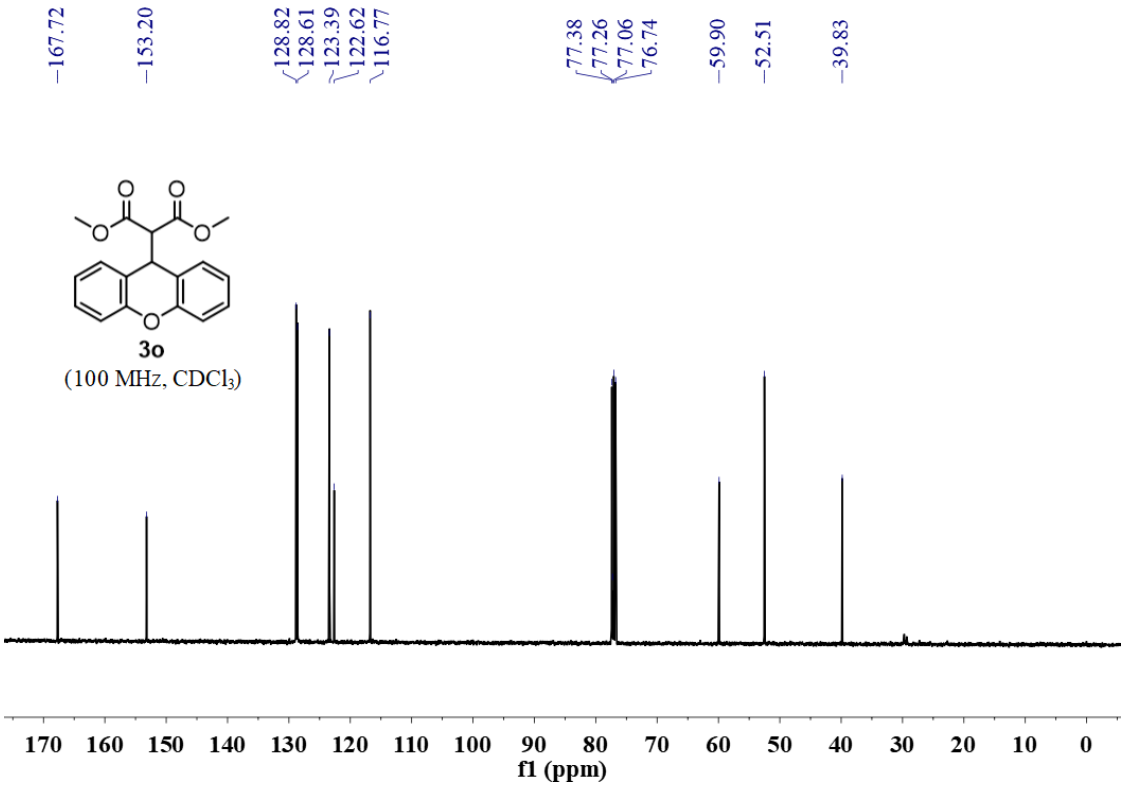


Figure S37. ^{13}C NMR spectrum of **3o**.

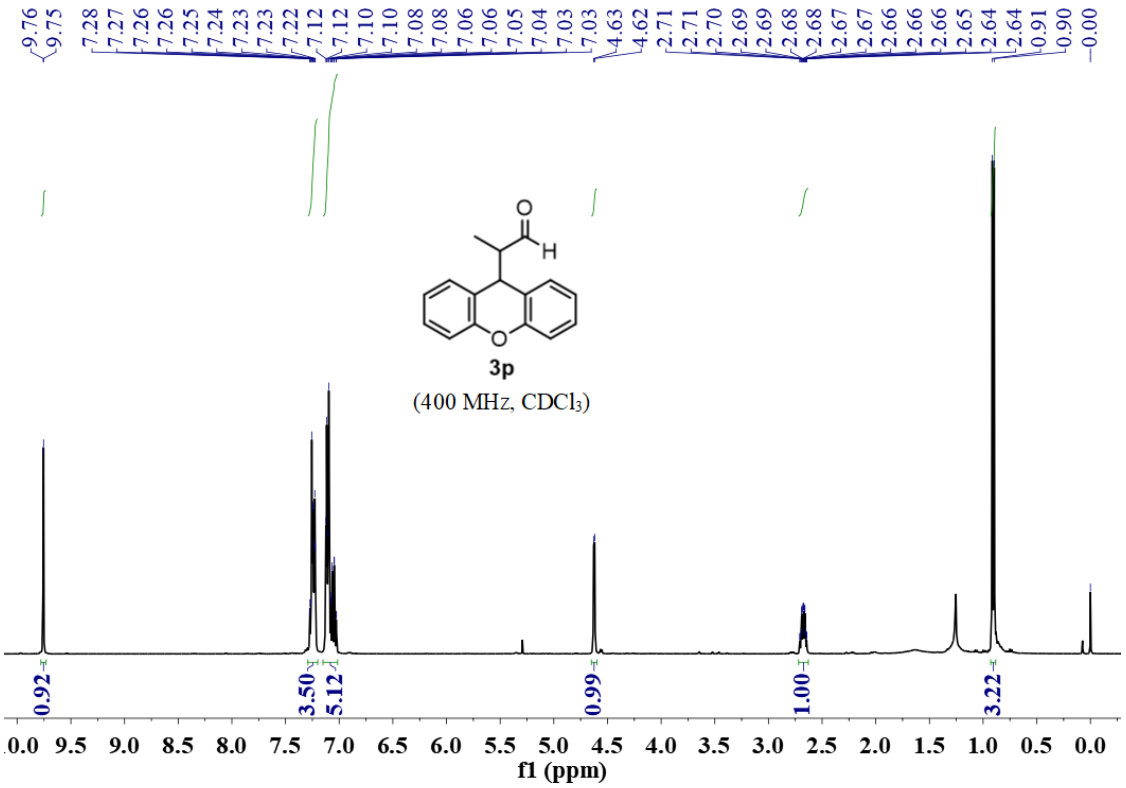


Figure S38. ^{1}H NMR spectrum of **3p**.

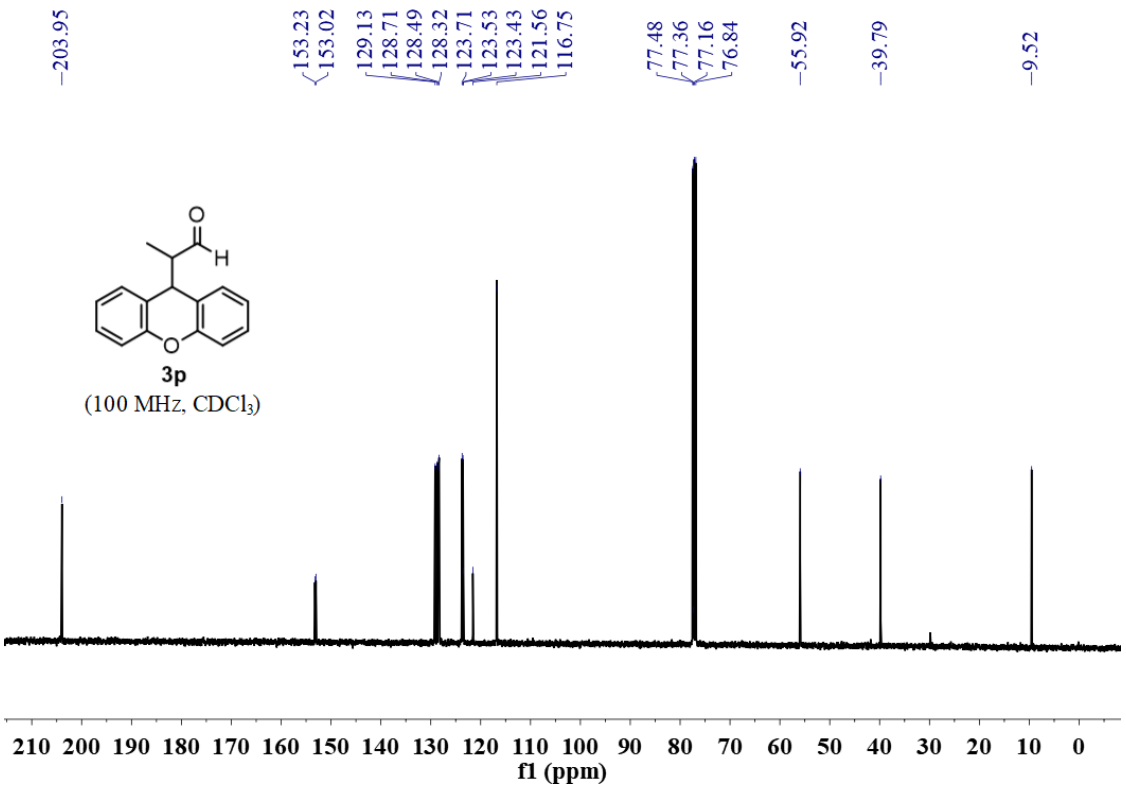


Figure S39. ^{13}C NMR spectrum of **3p**.

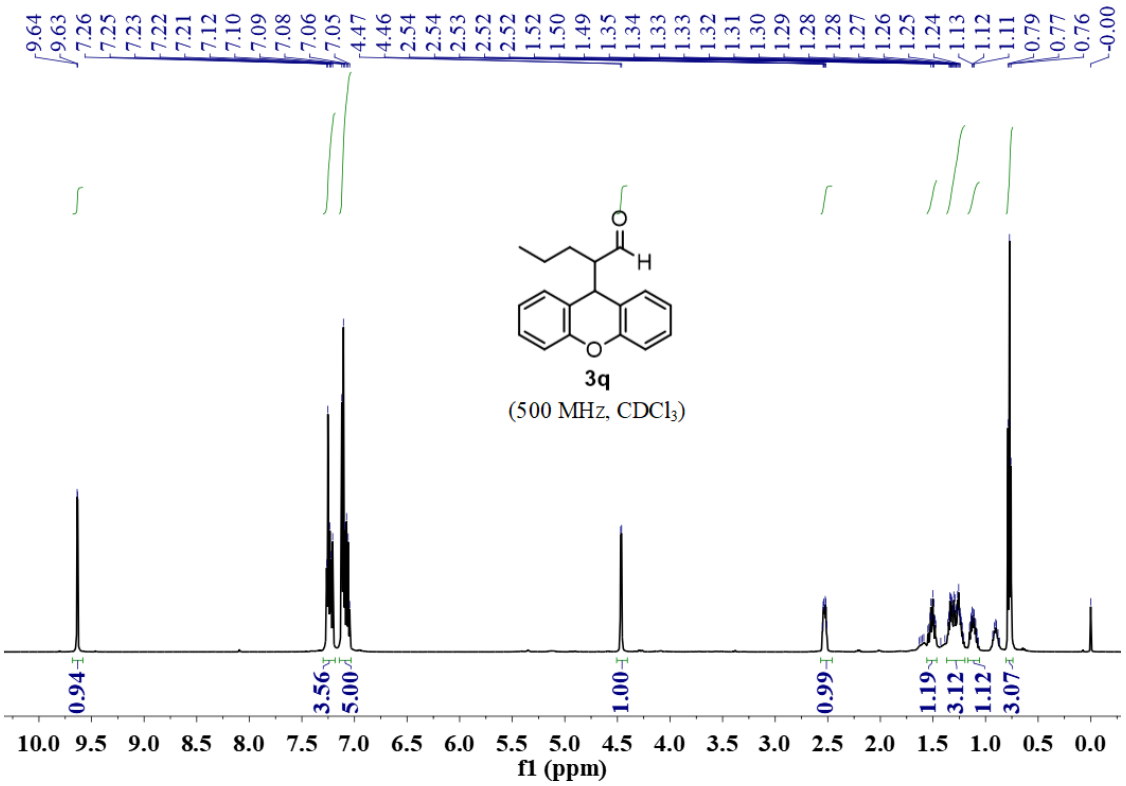


Figure S40. ^{1}H NMR spectrum of **3q**.

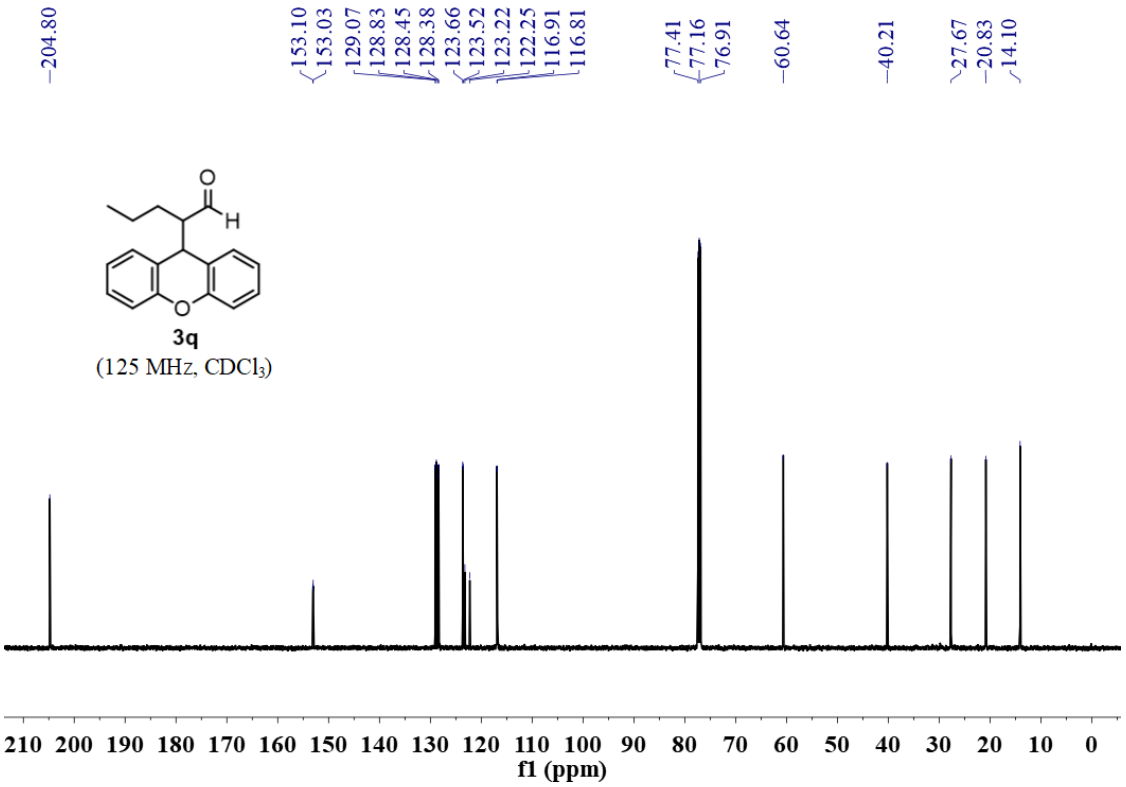


Figure S41. ^{13}C NMR spectrum of **3q**.

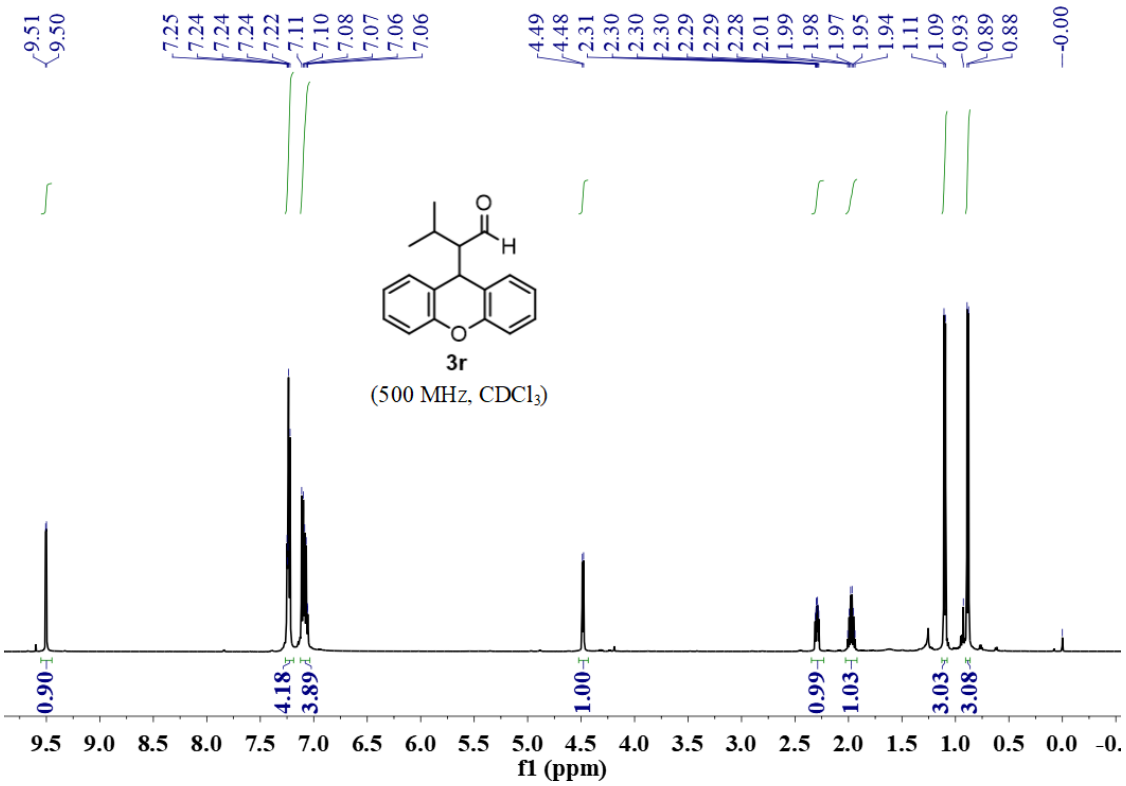


Figure S42. ^{1}H NMR spectrum of **3r**.

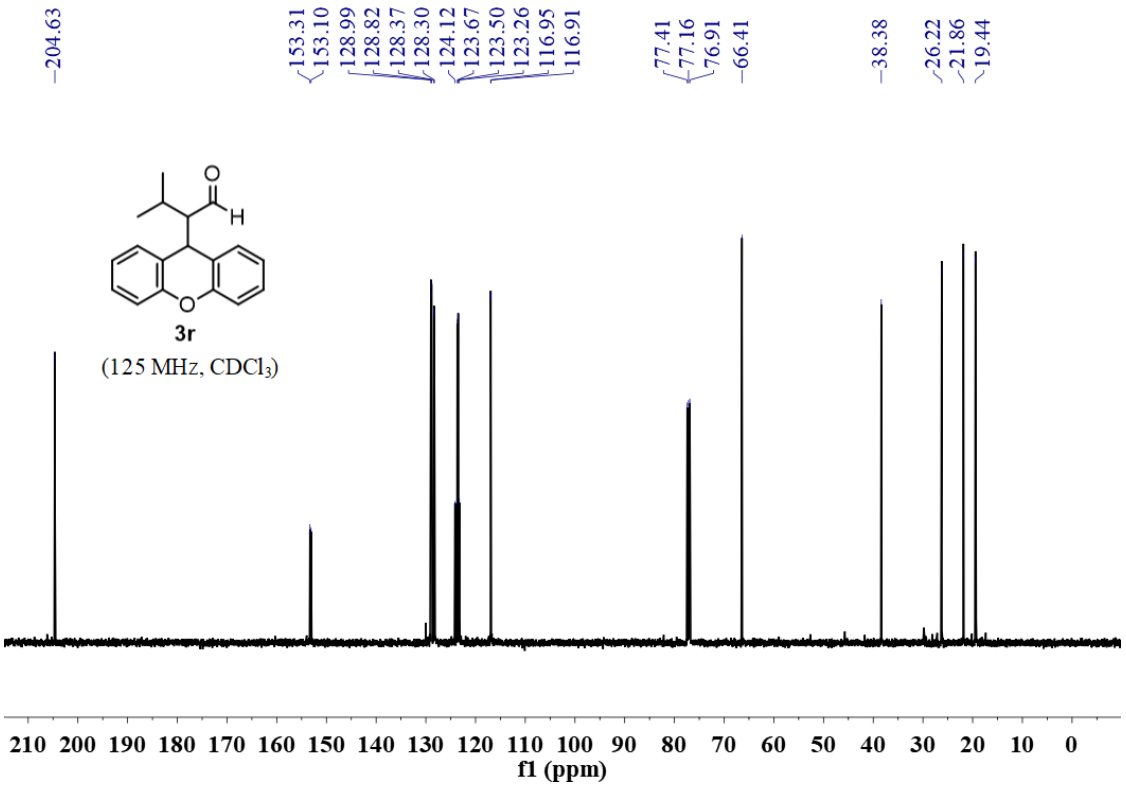


Figure S43. ^{13}C NMR spectrum of **3r**.

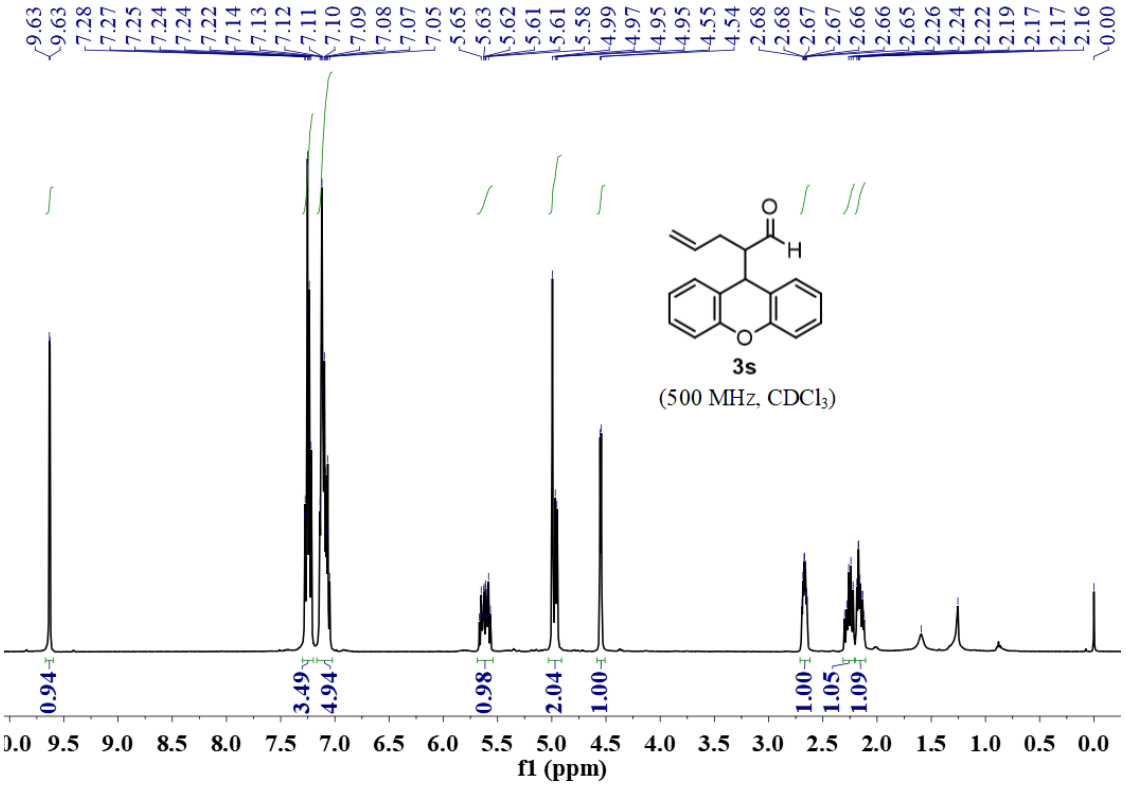


Figure S44. ^{1}H NMR spectrum of **3s**.

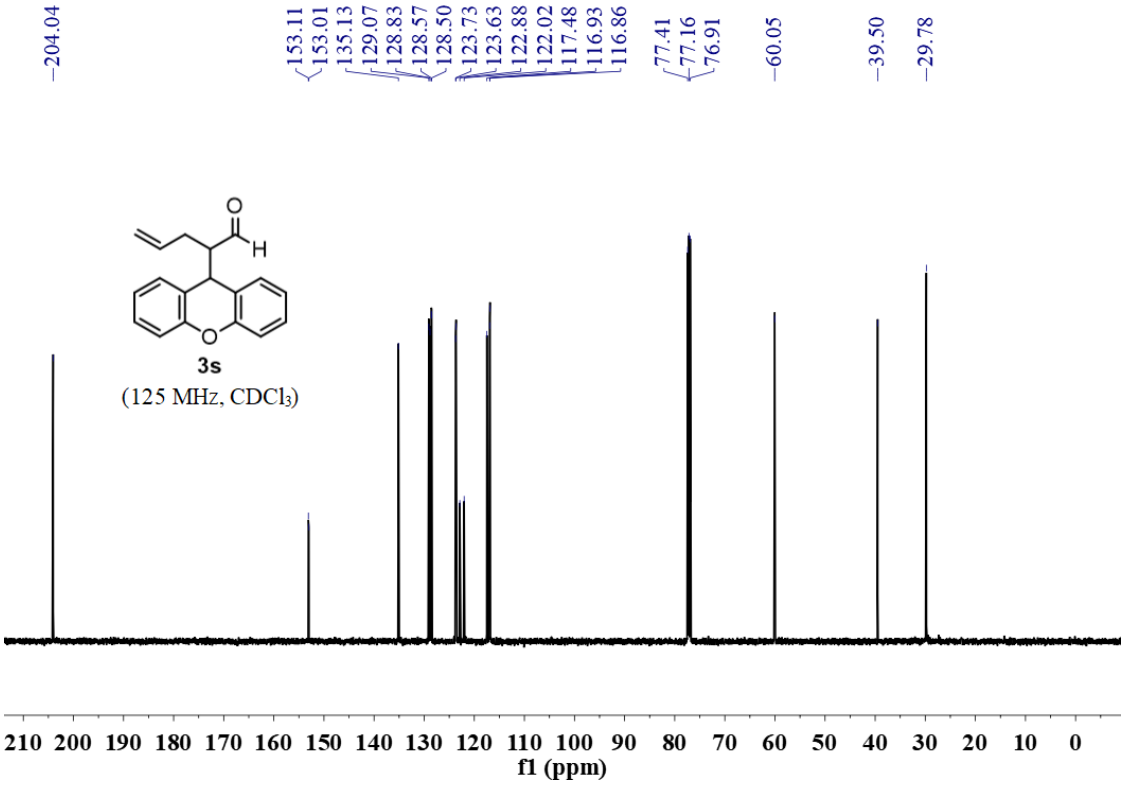


Figure S45. ^{13}C NMR spectrum of **3s**.

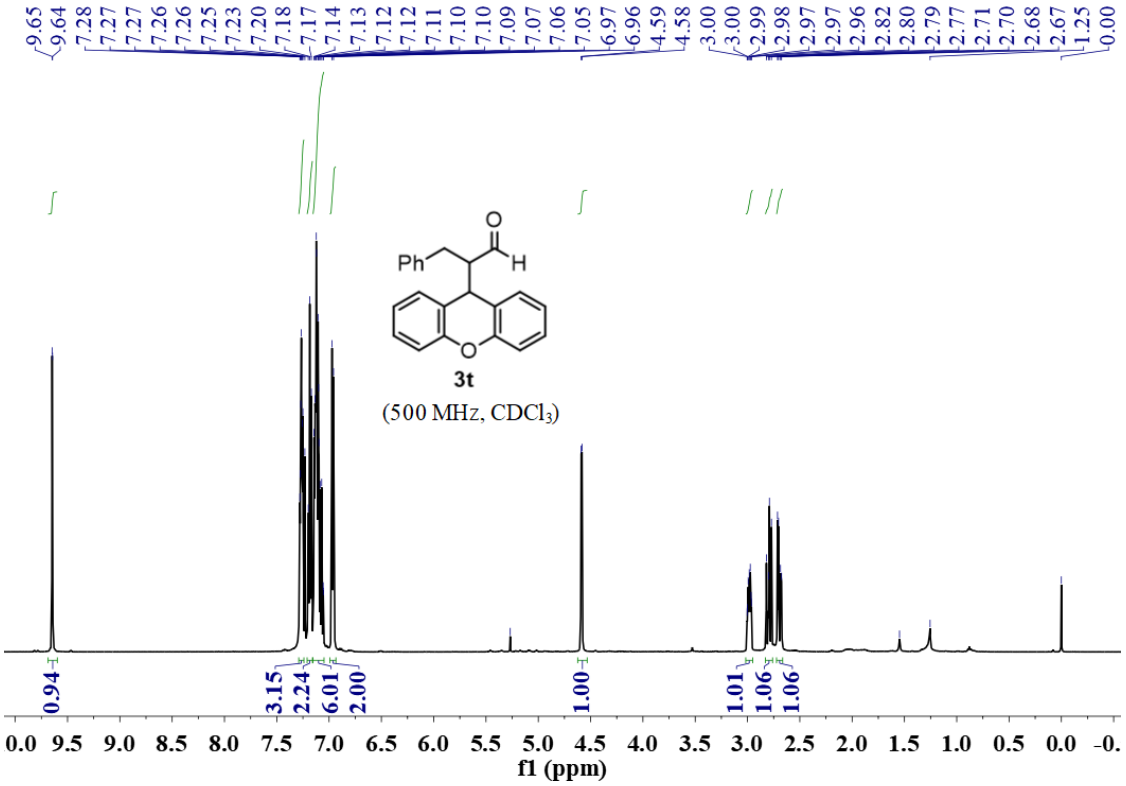


Figure S46. ^{1}H NMR spectrum of **3t**.

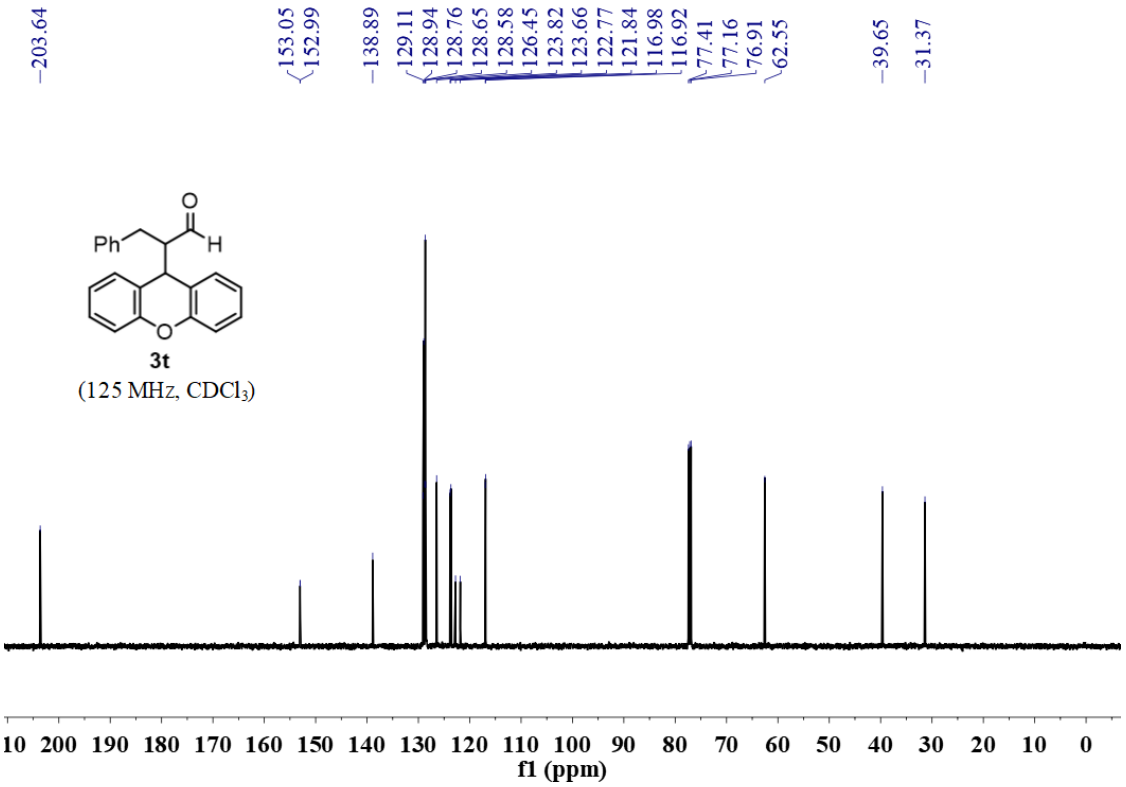


Figure S47. ^{13}C NMR spectrum of **3t**.

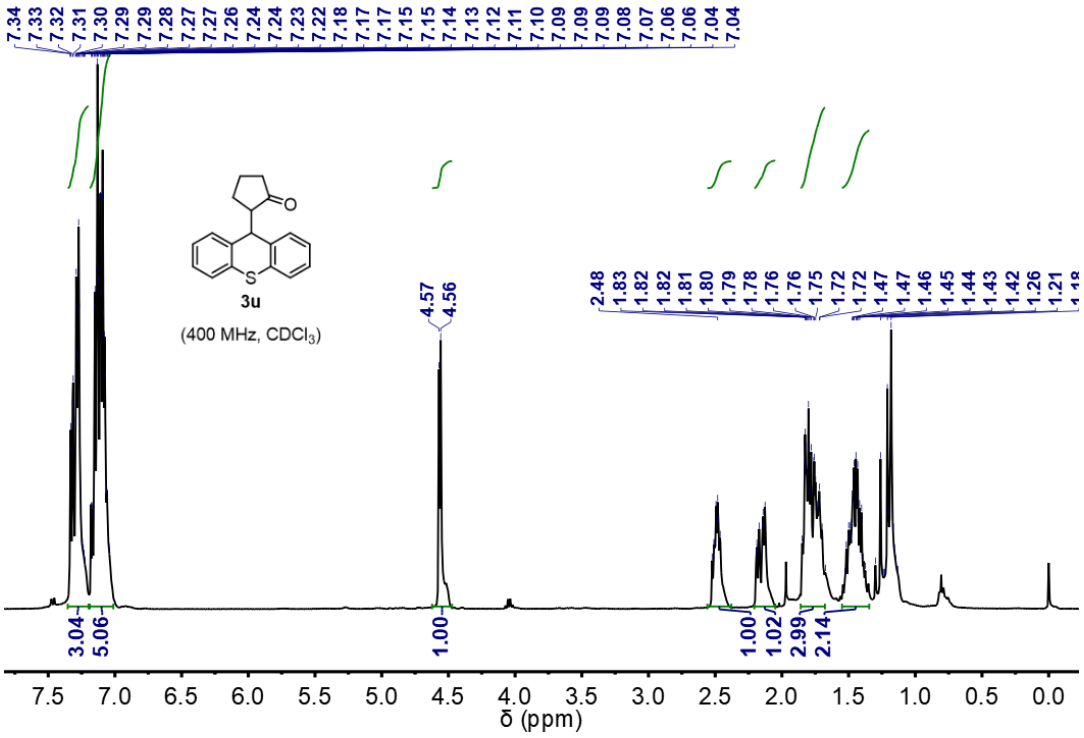


Figure S48. ^{1}H NMR spectrum of **3u**.

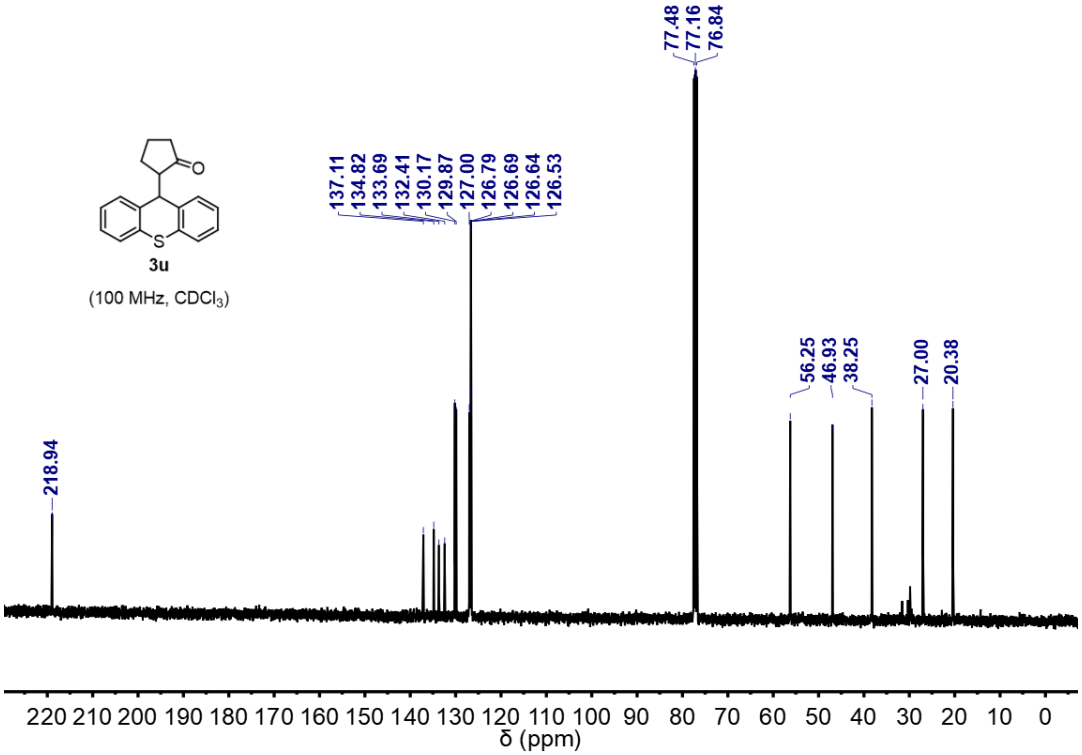


Figure S49. ^{13}C NMR spectrum of **3u**.

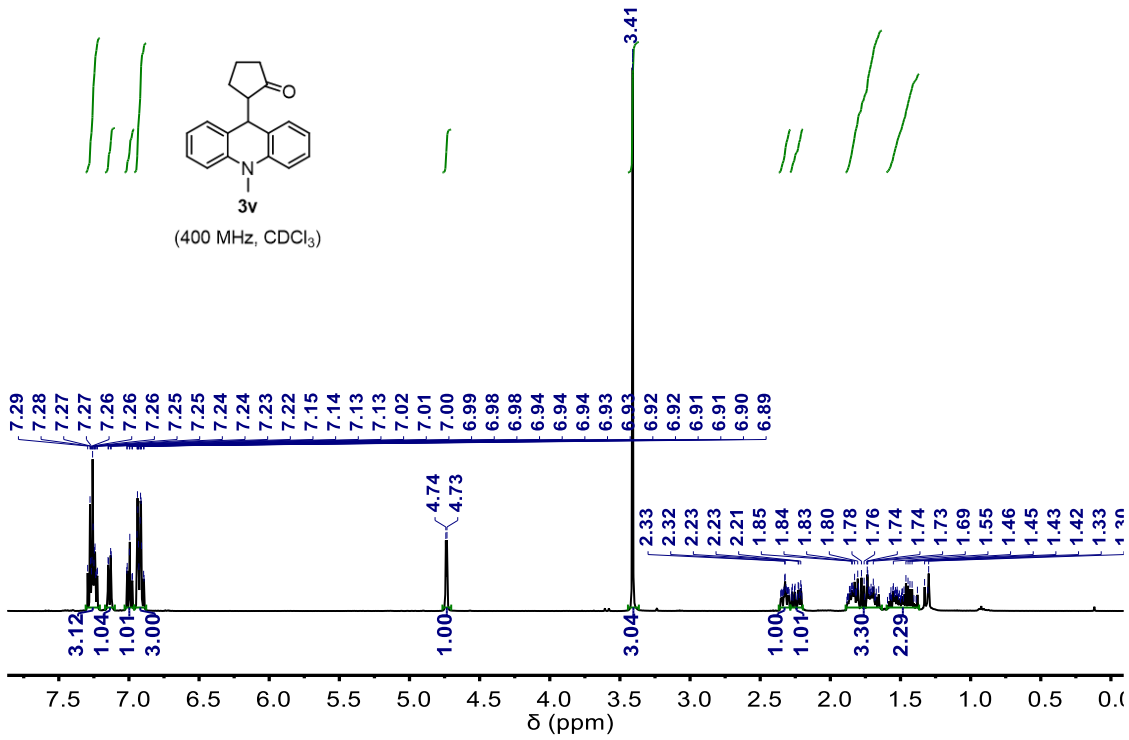


Figure S50. ^{1}H NMR spectrum of **3v**.

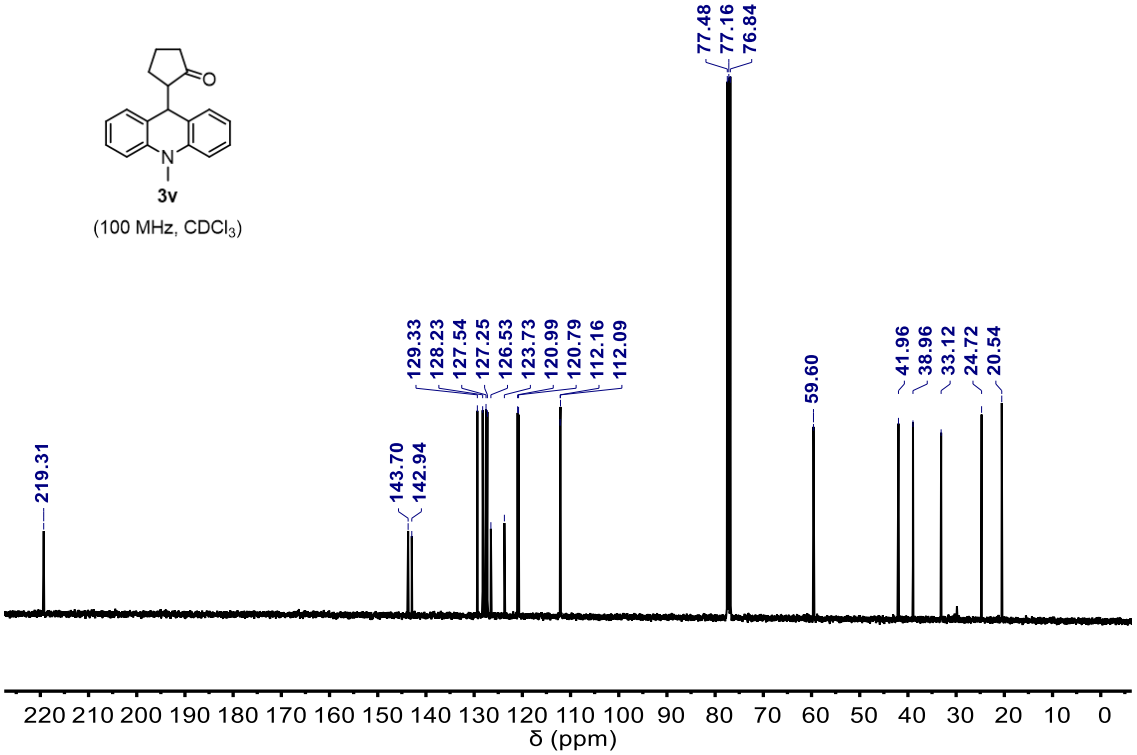


Figure S51. ^{13}C NMR spectrum of **3v**.