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

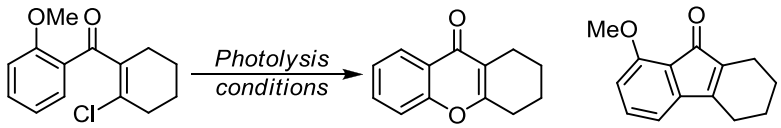
Zheming Xiao, Shujun Cai, Yingbo Shi, Baochao Yang, Shuanhu Gao *

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663N Zhongshan Road, Shanghai 200062, China.

Email: shgao@chem.ecnu.edu.cn
Fax: (+) 86-21-62604784

Supporting Information

Condition Screening:

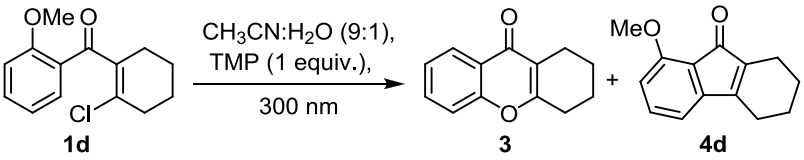


1d **3** **4d**

entry	λ	sol.	base	time	conversion	yield (**3**)[a]	yield (**4d**)[a]
1	300 nm	CH_3CN	none	2 h	88 %	17 %	trace
2	300 nm	CH_3CN	$^iPr_2NH$ (1 equiv.)	40 min	100 %	62 %	11 %
3	300 nm	CH_3CN	NEt_3 (1 equiv.)	40 min	100 %	42 %	trace
4	300 nm	DCE	none	2 h 10 min	100 %	trace	12 %
5	300 nm	DCE	$^iPr_2NH$ (1 equiv.)	45 min	100 %	48 %	18 %
6	300 nm	DCE	NEt_3 (1 equiv.)	45 min	100 %	46 %	6 %
7	300 nm	CH_3CN	TMP (1 equiv.)	40 min	100 %	66 %	9 %
8	300 nm	DCE	TMP (1 equiv.)	40 min	100 %	60 %	22 %
9	300 nm	THF	TMP (1 equiv.)	40 min	100 %	14 %	trace
10	300 nm	Toluene	TMP (1 equiv.)	40 min	100 %	32 %	20 %
11	300 nm	DMF	TMP (1 equiv.)	40 min	100 %	19 %	trace
12	300 nm	CH_3CN:H_2O (9:1)	TMP (1 equiv.)	40 min	100 %	82 %	5 %
13	300 nm	CH_3CN:H_2O (4:1)	TMP (1 equiv.)	40 min	100 %	74 %	5 %
14	300 nm	CH_3CN:H_2O (3:1)	TMP (1 equiv.)	40 min	100 %	75 %	7 %
15	300 nm	CH_3CN:H_2O (5:3)	TMP (1 equiv.)	50 min	100 %	67 %	9 %
16	300 nm	CH_3CN:H_2O (9:1)	$^iPr_2NH$ (1 equiv.)	40 min	100 %	74 %	6 %
17	300 nm	CH_3CN:H_2O (9:1)	NEt_3 (1 equiv.)	40 min	100 %	31 %	trace
18	300 nm	CH_3CN:H_2O (9:1)	DABCO (1 equiv.)	40 min	100 %	78 %	9 %
19	300 nm	CH_3CN:H_2O (9:1)	K_2CO_3 (1 equiv.)	50 min	100 %	69 %	trace
20	300 nm	CH_3CN:H_2O (9:1)	None	1 h 20 min	100 %	37 %	trace
21	300 nm	CH_3CN:H_2O (9:1)	HCl (1 equiv.)	1 h 30 min	91 %	32 %[b]	trace
22	300 nm	CH_3CN:H_2O (9:1)	TMP (0.2 equiv.)	40 min	100 %	64 %	trace
23	300 nm	CH_3CN:H_2O (9:1)	TMP (0.5 equiv.)	40 min	100 %	77 %	trace
24	300 nm	CH_3CN:H_2O (9:1)	TMP (5 equiv.)	40 min	100 %	85 %	4 %
25	300 nm	CH_3CN:H_2O (9:1)	TMP (10 equiv.)	40 min	100 %	82 %	10 %
26	254 nm	CH_3CN:H_2O (9:1)	TMP (1 equiv.)	40 min	100 %	79 %	5 %
27	366 nm	CH_3CN:H_2O (9:1)	TMP (1 equiv.)	3 h	100 %	84 %	8 %

[a] Yields were determined by ^1H NMR crude analysis using CH_2Br_2 as an internal standard, unless otherwise noted. [b] Based on conversion.

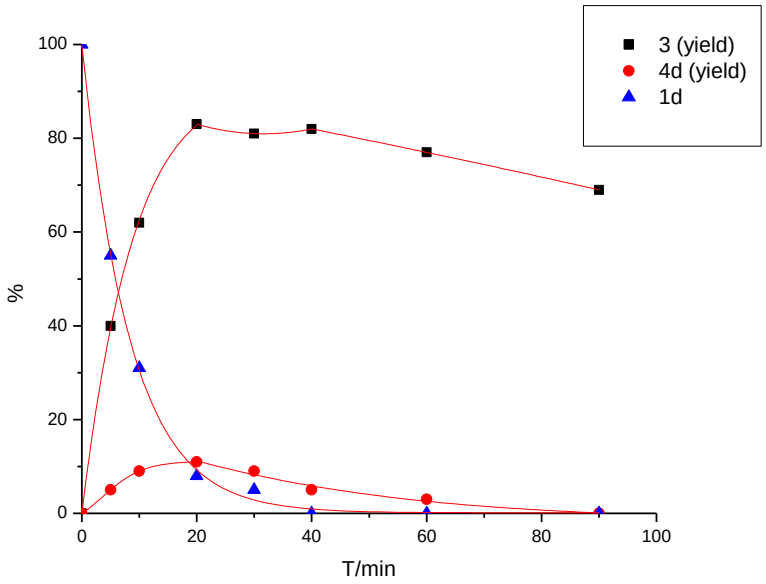
A Curve of the Progress of the Reaction for the Photolysis:

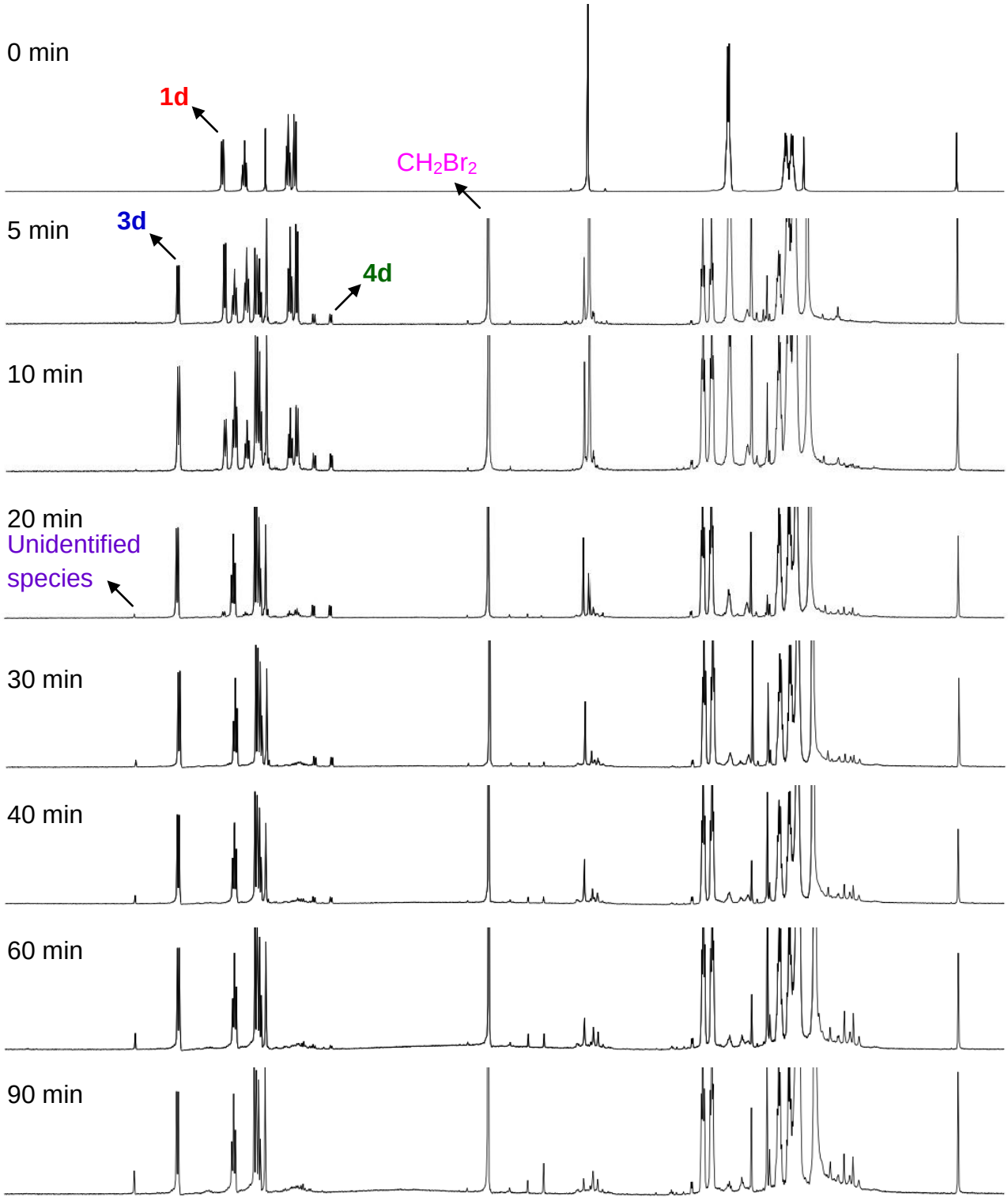


1d **3** **4d**

entry	time	conversion	yield **(3)**[a]	yield **(4d)**[a]
1	5 min	45 %	40 % (88 %)[b]	5 % (10 %)[b]
2	10 min	69 %	62 % (89 %)[b]	9 % (13 %)[b]
3	20 min	92 %	83 % (90 %)[b]	11 % (11 %)[b]
4	30 min	95 %	81 % (85 %)[b]	9 % (9 %)[b]
5	40 min	100 %	82 %	5 %
6	1 h	100 %	77 %	3 %
7	1.5 h	100 %	69 %	0

[a] Yields were determined by ^{1}H NMR crude analysis using CH_2Br_2 as an internal standard, unless otherwise noted. [b] Based on conversion.

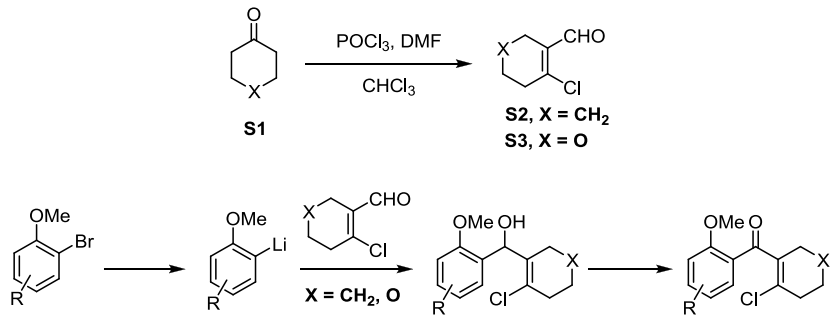




General Experimental Procedures:

All reactions were carried out under nitrogen except noted. Anhydrous dichloromethane (CH_2Cl_2) was 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 $HSGF_{254}$ 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 ^{13}C NMR spectra were recorded on a Bruker-500, 400 spectrometer. Chemical shifts for ^1H and ^{13}C NMR spectra are reported in ppm (δ) relative to residue protium in the solvent ($CDCl_3$: δ 7.26, 77.00 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 preparation of substrates:

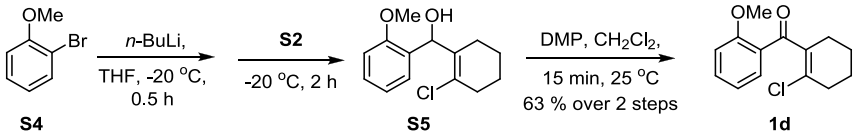


S2 and **S3** were prepared according to the known procedure. [1,2]

To a solution of Brominated (1.0 ~ 1.5 equiv.) in dry THF was added *n*-BuLi (1.0 ~ 1.5 equiv.) at 0 ^oC ~ -83 ^oC dropwised. After about 10 min ~ 1 h, aldehyde (1.0 equiv.) in dry THF was added dropwised at the same temperature. TLC monitored the reaction and showed all aldehyde was consumed, the reaction was quenched with water. It was extracted with EtOAc, and the organic layer was washed with water and brine. The combined organic phase was dried over Na_2SO_4,

filtered, concentrated, and purified by silica gel column chromatography to give the corresponding alcohol.

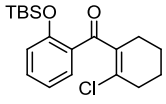
To a solution of fresh prepared alcohol (1.0 equiv.) in dry CH_2Cl_2 was added DMP (1.5 equiv.) at 25 ^oC. After stirring for 5 min, water solution (1 μL water / 1 mL CH_2Cl_2) was added. TLC showed all alcohol was consumed, CH_2Cl_2 was evaporated, then EtOAc and an aqueous solution of 1:1 10% $Na_2S_2O_3$ to saturated $NaHCO_3$ was then added. After stirring for another 10 min, the biphasic mixture was extracted with EtOAc, the combined organic phase was washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, concentrated, and purified by silica gel column chromatography to give the precursor of the photolysis.



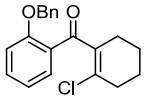
To a solution of **S4** (1.40 g, 7.5 mmol, 1.5 equiv.) in dry THF (40 mL) was added *n*-BuLi (3.1 mL, 1.6 M solution in pentane, 5.0 mmol, 1.0 equiv.) dropwise at -20 ^oC. After 0.5 h, **S2** (0.72 g, 5.0 mmol, 1.0 equiv.) was added dropwise. After about 2 h, TLC showed all **S2** was consumed; the reaction was quenched with water (10 mL). It was extracted with EtOAc (15 mL×3), and the organic layer was washed with water (25 mL) and brine (25 mL). The organic phase was dried over Na_2SO_4, filtered, concentrated, and purified by silica gel column chromatography (2 % ~ 5 % ethyl acetate–hexanes) to give **S5** as a colorless liquid (0.94 g).

To a solution of the **S5** (0.94 g, 4.2 mmol, 1.0 equiv.) in dry CH_2Cl_2 (30 mL) was added DMP (2.7 g, 6.3 mmol, 1.5 equiv.) at 25 ^oC. After stirring for 5 min, water solution (1 μL water /1 mL CH_2Cl_2, 30 μL) was added. After about 10 min, TLC showed all **S5** was consumed, CH_2Cl_2 was evaporated, then EtOAc (20 mL) and an aqueous solution of 1:1 10% $Na_2S_2O_3$ to saturated $NaHCO_3$ (20 mL) was then added. After stirring for another 10 min, the biphasic mixture was extracted with EtOAc (15 mL×3), the combined organic phase was washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried over Na_2SO_4, filtered, concentrated, and purified by silica gel column chromatography

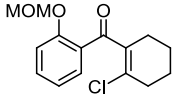
(3% ethyl acetate–hexanes) to give enone **1d** as a white solid (668 mg, 63 % over 2 steps). R_f = 0.37 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.48 (td, *J* = 8.1, 1.2 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 3.87 (s, 3H), 2.78 – 2.15 (m, 4H), 1.84 – 1.67 (m, 4H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7 , 159.0, 136.8, 133.9, 131.2, 129.1, 127.5, 120.8, 111.8, 56.0, 33.7, 28.0, 23.5, 21.7 ppm. MS (m/z): EI [M] calcd for $C_{14}H_{15}O_2Cl$ $[M]^+$: 250, Found 250 (15 %), 235 (2 %), 215 (40 %).



Enone **1b** was prepared using the general procedure (using the *t*-BuLi instead of *n*-BuLi) in 57 % yield over 2 steps, purified by silica gel column chromatography (1 % ethyl acetate-petroleum ether) as a colorless liquid. R_f = 0.39 (5 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.34 (td, *J* = 8.2, 1.8 Hz, 1H), 6.98 (t, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 2.52 – 2.34 (m, 4H), 1.86 – 1.64 (m, 4H), 0.99 (s, 9H), 0.24 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 154.7, 135.4, 133.0, 132.9, 131.1, 130.1, 121.0, 120.5, 34.3, 28.3, 25.8 (3 C), 23.3, 21.5, 18.4, -4.1 (2 C) ppm. MS (m/z): ESI [M] calcd for $C_{19}H_{27}O_2ClSi$ $[M]^+$: 350, Found 351 $[M+H]^+$.

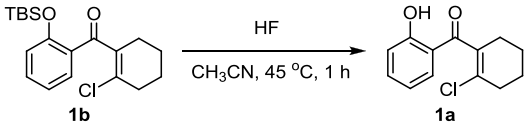


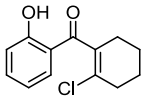
Enone **1e** was prepared using the general procedure in 47 % yield over 2 steps, purified by silica gel column chromatography (1 % ~ 2 % ethyl acetate-petroleum ether) as a white solid. R_f = 0.22 (5 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.52 – 7.32 (m, 6H), 7.08 – 6.98 (m, 2H), 5.08 (s, 2H), 2.29 – 2.21 (m, 2H), 2.21 – 2.12 (m, 2H), 1.47 – 1.31 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 158.0, 136.8, 136.2, 133.8, 131.2, 129.5, 128.6 (2C), 128.3, 128.0 (3C), 121.0, 112.4, 70.8, 33.6, 27.9, 22.9, 21.1 ppm. HRMS (m/z): EI [M] calcd for $C_{20}H_{19}O_2Cl$ $[M]^+$: 326.1074, Found 326.1080.



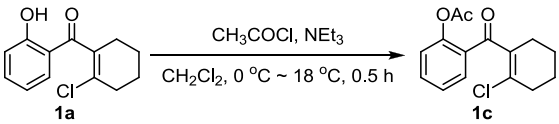
Enone **1f** was prepared using the gerneral procedure in 72 % yield over 2 steps, purified by silica gel column chromatography (2 % ~ 3 % ethyl acetate-petroleum ether) as a white solid. R_f = 0.37 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.15 (d, *J* = 8.3 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 5.21 (s, 2H), 3.49 (s, 3H), 2.45 – 2.37 (m, 4H), 1.83 – 1.69 (m, 4H) ppm. ^{13}C NMR (100 MHz,

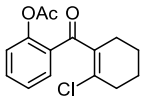
$CDCl_3$) δ 196.6, 156.3, 136.9, 133.6, 130.8, 129.6, 128.6, 121.9, 114.9, 94.7, 56.2, 33.9, 28.1, 23.5, 21.7 ppm. MS (m/z): EI [M] calcd for $C_{15}H_{17}O_3Cl$ $[M]^+$: 280, Found 280 (0.6 %) 249 (2 %) 245 (54 %).





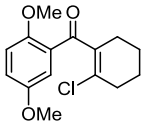
Enone **1a** was prepared from enone **1b**. *Procedure*: To a solution of enone **1b** (250.5 mg, 0.7 mmol) in CH_3CN (5 mL) was added 40 % HF aqueous solution (500 μL) at 45 °C. After 1 h, TLC showed all enone **1b** was consumed, it was quenched by TMSOMe (2 mL), and saturated $NaHCO_3$ was added until no gas generated, then extracted with EtOAc (20 mL), the combined organic phase was washed with saturated $NaHCO_3$ (10 mL) and brine (10 mL), dried over Na_2SO_4, filtered, concentrated, and purified by silica gel column chromatography (20 % ~ 25 % dichloromethane-petroleum ether) as a white solid (168.7 mg, 100 %). R_f = 0.41 (50 % toluene-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.90 (s, 1H), 7.60 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 2.53 – 2.45 (m, 2H), 2.40 – 2.32 (m, 2H), 1.92 – 1.82 (m, 2H), 1.82 – 1.74 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.9, 163.1, 136.9, 133.2, 132.4, 130.2, 119.2, 118.4, 118.0, 32.9, 28.8, 23.3, 21.3 ppm. MS (M/Z): EI [M] calcd for $C_{13}H_{13}O_2Cl$ $[M]^+$: 236, Found 236 (2 %) 201 (100 %) 121 (21 %).



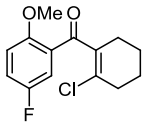


Enone **1c** was prepared from enone **1a**. *Procedure*: To a solution of enone **1a** (222.3 mg, 0.94 mmol) in CH_2Cl_2 was added NEt_3 (197 μL, 1.4 mmol, 1.5 equiv.) at 0 °C, then added CH_3COCl (80 μL, 1.1 mmol, 1.2 equiv.) dropwise, then warmed to r.t.. After TLC showed all enone **1a** was consumed, it was quenched by NH_4Cl, then extracted with EtOAc (20 mL), the combined organic phase was washed with saturated NH_4Cl (10 mL) and brine (10 mL),

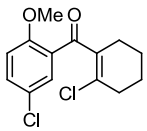
dried over Na_2SO_4, filtered, concentrated, and purified by silica gel column chromatography (5 % ethyl acetate-petroleum ether) as a white solid (219.4 mg, 84 %). R_f = 0.18 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.56 (td, *J* = 8.0, 1.7 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 2.50 – 2.43 (m, 2H), 2.38 – 2.32 (m, 5H), 1.85 – 1.78 (m, 2H), 1.76 – 1.69 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 169.3, 149.7, 135.1, 133.7, 132.1, 131.6, 129.2, 126.1, 123.9, 33.7, 28.4, 23.4, 21.4, 21.0 ppm. HRMS (M/Z): EI [M] calcd for $C_{15}H_{15}O_3Cl$ $[M]^+$: 278.0710, Found 278.0712.



Enone **S6** was prepared using the general procedure in 55 % yield over 2 steps, purified by silica gel column chromatography (2 % ~ 3 % ethyl acetate-petroleum ether) as a colorless liquid. R_f = 0.27 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 3.2 Hz, 1H), 7.04 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 2.48 – 2.30 (m, 4H), 1.86 – 1.64 (m, 4H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 153.7, 153.6, 137.0, 128.6, 127.9, 120.6, 114.3, 113.7, 56.75, 55.8, 33.6, 28.0, 23.5, 21.7 ppm. HRMS (m/z): EI [M] calcd for $C_{15}H_{17}O_3Cl$ $[M]^+$: 280.0866, Found 280.0867.

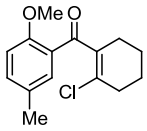


Enone **S7** was prepared using the general procedure in 25 % yield over 2 steps, purified by silica gel column chromatography (2 % ~ 3 % ethyl acetate-petroleum ether) as a white solid. R_f = 0.42 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.6, 3.2 Hz, 1H), 7.16 (ddd, *J* = 9.0, 7.6, 3.2 Hz, 1H), 6.89 (dd, *J* = 9.0, 4.0 Hz, 1H), 3.84 (s, 3H), 2.54 – 2.21 (m, 4H), 1.90 – 1.62 (m, 4H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4 (d, *J* = 1.4 Hz), 156.9 (d, *J* = 240.4 Hz), 155.1 (d, *J* = 1.8 Hz), 136.3, 130.0, 128.8 (d, *J* = 5.9 Hz), 120.1 (d, *J* = 23.4 Hz), 116.9 (d, *J* = 24.0 Hz), 113.3 (d, *J* = 7.5 Hz), 56.6, 33.7, 27.9, 23.4, 21.6 ppm. HRMS (M/Z): EI [M] calcd for $C_{14}H_{14}O_2FCl$ $[M]^+$: 268.0666, Found 268.0667.

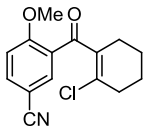


Enone **S8** was prepared using the general procedure in 42 % yield over 2 steps, purified by silica gel column chromatography (2 % ~ 3 % ethyl acetate-petroleum ether) as a colorless liquid. R_f = 0.47 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.7 Hz, 1H), 7.41 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.88 (d, *J* = 8.8 Hz,

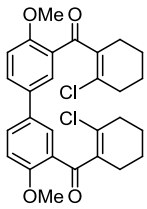
1H), 3.85 (s, 3H), 2.44 – 2.30 (m, 4H), 1.83 – 1.66 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 157.3, 136.2, 133.2, 130.4, 130.3, 129.2, 126.1, 113.3, 56.3, 33.8, 27.9, 23.4, 21.6 ppm. HRMS (M/Z): EI [M] calcd for $C_{14}H_{14}O_2Cl_2$ $[M]^+$: 284.0371, Found 284.0369.



Enone **S9** was prepared using the general procedure in 58 % yield over 2 steps, purified by silica gel column chromatography (2 % ~ 3 % ethyl acetate-petroleum ether) as a colorless liquid. R_f = 0.47 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 2.2 Hz, 1H), 7.27 (dd, J = 8.4, 2.2 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 3.83 (s, 3H), 2.42 – 2.34 (m, 4H), 2.31 (s, 3H), 1.87 – 1.68 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 157.1, 137.0, 134.6, 131.2, 130.2, 128.6, 127.2, 112.0, 56.1, 33.6, 28.0, 23.5, 21.7, 20.3 ppm. HRMS (m/z): EI [M] calcd for $C_{15}H_{17}O_2Cl$ $[M]^+$: 264, Found 264 (30 %) 249 (28 %) 149 (100 %).

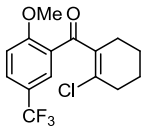


Enone **S10** was prepared using almost the general procedure (the equiv. of DMP is 4 instead of 1.5) in 18 % yield over 2 steps, purified by silica gel column chromatography (70 % dichloromethane-petroleum ether) as a white solid. R_f = 0.26 (pure dichloromethane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 2.0 Hz, 1H), 7.72 (dd, J = 8.7, 2.0 Hz, 1H), 7.01 (d, J = 8.7 Hz, 1H), 3.92 (s, 3H), 2.51 – 2.34 (m, 4H), 1.85 – 1.68 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 161.2, 137.0, 135.5, 134.7, 132.4, 129.4, 118.3, 112.4, 104.5, 56.3, 34.0, 27.8, 23.3, 21.5 ppm. HRMS (M/Z): EI [M] calcd for $C_{15}H_{14}NO_2Cl$ $[M]^+$: 275.0714, Found 275.0713.

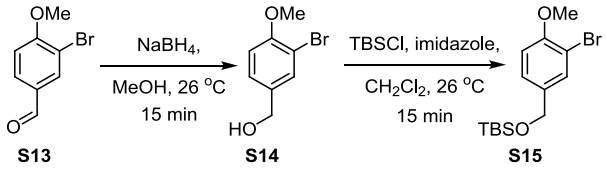


Enone **S11** was prepared using the general procedure in 59 % yield over 2 steps, purified by silica gel column chromatography (15 % ~ 20 % ethyl acetate-petroleum ether) as a white solid. R_f = 0.26 (20 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 2.1 Hz, 2H), 7.69 (dd, J = 8.6, 2.1 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 3.89 (s, 6H), 2.47 – 2.30 (m, 8H), 1.85 – 1.66 (m, 8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4 (2 C), 158.3 (2 C), 136.8 (2 C), 132.5 (2 C), 131.9 (2 C), 129.3 (2 C), 128.9 (2 C),

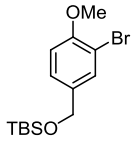
127.8 (2 C), 112.3 (2 C), 56.1 (2 C), 33.7 (2 C), 28.0 (2 C), 23.5 (2 C), 21.7 (2 C) ppm. HRMS (M/Z): EI [M] calcd for $C_{28}H_{28}O_4Cl_2$ $[M]^+$: 498.1365, Found 498.1368.



Enone **S12** was prepared using the general procedure in 49 % yield over 2 steps, purified by silica gel column chromatography (2 % ~ 4 % ethyl acetate-petroleum ether) as a white solid. R_f = 0.46 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 1.8 Hz, 1H), 7.70 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 1H), 3.91 (s, 3H), 2.46 – 2.31 (m, 4H), 1.87 – 1.54 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 160.8, 136.0, 131.0, 130.5 (q, *J* = 3.5 Hz), 128.3, 128.1 (q, *J* = 3.7 Hz), 123.9 (d, *J* = 271.5 Hz), 123.2 (q, *J* = 33.4 Hz), 111.8, 56.2, 33.9, 27.9, 23.4, 21.6 ppm. HRMS (M/Z): EI [M] calcd for $C_{15}H_{14}O_2F_3Cl$ $[M]^+$: 318.0634, Found 318.0635.

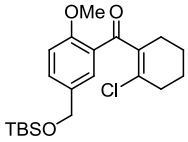


S13 **S14** **S15**

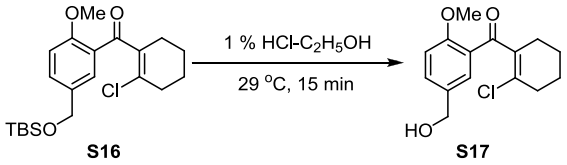


Substrate **S15** was prepared from **S13** in 98 % yield over 2 steps. *Procedure*: **Step 1:** To a solution of **S13** (1.1242g, 5 mmol, 1 equiv.) in MeOH (25 mL) was added $NaBH_4$ (237 mg, 6 mmol, 1.2 equiv.) at 26 °C, after 15 min, TLC showed **S13** was completely consumed, it was quenched by saturated NH_4Cl, MeOH was evaporated, extracted with EtOAc (20 mL), washed with brine (20 mL), dried over Na_2SO_4, filtered, concentrated, and the crude product was used in the next step without purification. **Step 2:** To a solution of **S14** in CH_2Cl_2 (30 mL) was added imidazole (890 mg, 13 mmol, 2.5 equiv.) and TBSCl (946 mg, 6.3 mmol, 1.2 equiv.) at 26 °C, after 15 min, TLC showed All **S14** was completely consumed, it was quenched by saturated NH_4Cl, extracted with EtOAc (30 mL), washed with brine (20 mL), dried over Na_2SO_4, filtered, concentrated, and purified by silica gel column chromatography (2 % ethyl acetate-petroleum ether) as a white solid (1.696 g, 98 %). R_f = 0.67 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 1.8 Hz, 1H), 7.22 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 4.65 (s, 2H), 3.88 (s, 3H), 0.93 (s, 9H), 0.09 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 135.1,

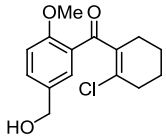
131.3, 126.2, 111.7, 111.4, 64.0, 56.3, 25.9 (3 C), 18.4, -5.3 (2 C) ppm. MS (M/Z): EI [M] calcd for $C_{14}H_{23}BrO_2Si$ $[M]^+$: 330, Found 330 (4 %) 273 (63 %) 199 (100 %).



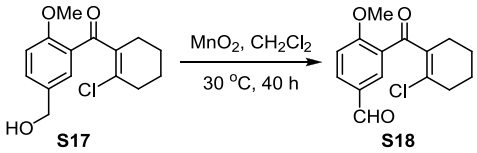
Enone **S16** was prepared using the general procedure in 70 % yield over 2 steps, purified by silica gel column chromatography (2 % ~ 3 % ethyl acetate-petroleum ether) as a white solid. R_f = 0.53 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 1.9 Hz, 1H), 7.46 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 4.70 (s, 2H), 3.86 (s, 3H), 2.52 - 2.26 (m, 4H), 1.91 – 1.65 (m, 4H), 0.93 (s, 9H), 0.08 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 158.2, 136.8, 133.8, 131.9, 129.0, 129.0, 127.0, 111.9, 64.2, 56.1, 33.7, 28.1, 25.9 (3 C), 23.5, 21.7, 18.3, -5.2 (2 C) ppm. MS (M/Z): ESI [M] calcd for $C_{21}H_{31}O_3ClSi$ $[M]^+$: 394, Found 395 $[M+H]^+$.

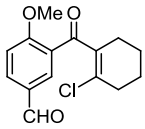


S16 **S17**

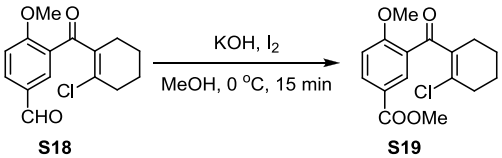


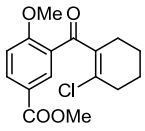
Enone **S17** was prepared from enone **S16**. *Procedure*: To a solution of enone **S16** (379.2 mg, 0.96 mmol) in C_2H_5OH (2 mL) was added 1 % HCl-C_2H_5OH (5 mL) at 29 °C. After 15 min, TLC showed all enone **S16** was consumed, saturated $NaHCO_3$ was added until no gas generated, then extracted with EtOAc (30 mL), the combined organic phase was washed with saturated $NaHCO_3$ (10 mL) and brine (10 mL), dried over Na_2SO_4, filtered, concentrated, and purified by silica gel column chromatography (30 ~ 35 % ethyl acetate-petroleum ether) as a light yellow liquid (252.4 mg, 94 %). R_f = 0.4 (40 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 4.66 (s, 2H), 3.87 (s, 3H), 2.45 – 2.34 (m, 4H), 1.84 – 1.69 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 158.5, 136.7, 133.4, 132.9, 129.7, 129.3, 127.5, 112.1, 64.4, 56.1, 33.7, 28.0, 23.5, 21.7 ppm. HRMS (M/Z): EI [M] calcd for $C_{15}H_{17}O_3Cl$ $[M]^+$: 280.0866, Found 280.0863.





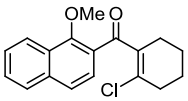
Enone **S18** was prepared from enone **S17**. *Procedure*: To a solution of enone **S17** (125.2 mg, 0.45 mmol, 1 equiv.) in CH_2Cl_2 (10 mL) was added MnO_2 (390 mg, 4.5 mmol, 10 equiv.) at 30 ^oC. After 40 h, TLC showed all enone **S17** was consumed, it was filtered through celite, washed with EtOAc, concentrated, and purified by silica gel column chromatography (15 % ethyl acetate-petroleum ether) as a light yellow solid (252.4 mg, 94 %). R_f = 0.34 (20 % ethyl acetate-petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.12 (d, *J* = 2.0 Hz, 1H), 7.99 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 1H), 3.94 (s, 3H), 2.45 – 2.33 (m, 4H), 1.93 – 1.57 (m, 4H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 190.2, 163.0, 135.9, 134.3, 133.3, 131.5, 129.7, 128.7, 112.0, 56.3, 33.9, 27.9, 23.4, 21.6 ppm. HRMS (M/Z): EI [M] calcd for $C_{15}H_{15}O_3Cl$ $[M]^+$: 278.0710, Found 278.0709.



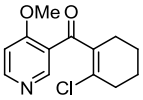


Enone **S19** was prepared from enone **S18**[3]. *Procedure*: To a solution of enone **S18** (76.4 mg, 0.27 mmol, 1 equiv.) in MeOH (2 mL) was added KOH (92.1 mg, 1.64 mmol, 6 equiv.) and I_2 (208.7 mg, 0.82 mmol, 3 equiv.) at 0 ^oC. After 20 min, TLC showed all enone **S18** was consumed, it was quenched by an aqueous solution of 1:1 10% $Na_2S_2O_3$ to saturated $NaHCO_3$ (5 mL) then exctracted with EtOAc (20 mL), washed with brine (10 mL), dried over Na_2SO_4, filtered, concentrated and purified by silica gel column chromatography (12 % ethyl acetate-petroleum ether) as a white solid (252.4 mg, 94 %). R_f = 0.36 (20 % ethyl acetate-petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 2.2 Hz, 1H), 8.14 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 2.60 – 2.29 (m, 4H), 1.83 – 1.67 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 166.1, 161.9, 136.1, 135.0, 132.5, 131.0, 128.0,

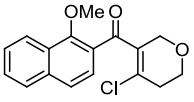
122.8, 111.3, 56.2, 52.0, 33.9, 28.0, 23.4, 21.6 ppm. MS (M/Z): EI [M] calcd for $C_{16}H_{17}O_4Cl$ $[M]^+$: 308, Found 308 (20 %) 293 (5 %) 249 (87 %).



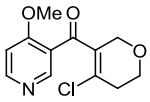
Enone **S20** was prepared using the general procedure in 52 % yield over 2 steps, purified by silica gel column chromatography (3 % ethyl acetate-petroleum ether) as a colorless liquid. R_f = 0.48 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.21 (m, 1H), 7.88 – 7.83 (m, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.61 – 7.52 (m, 2H), 4.03 (s, 3H), 2.53 – 2.44 (m, 4H), 1.92 – 1.73 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 157.6, 137.1, 137.0, 130.7, 128.4, 128.1 (2C), 126.5 (2C), 126.1, 124.1, 123.6, 63.8, 33.9, 28.4, 23.5, 21.8 ppm. MS (M/Z): EI [M] calcd for $C_{18}H_{17}O_2Cl$ $[M]^+$: 300, Found 300 (73 %) 285 (15 %) 265 (41 %).



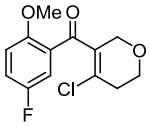
Enone **S21** was prepared using the general procedure in 30 % yield over 2 steps, purified by silica gel column chromatography (40 % ethyl acetate-petroleum ether) as a white solid. R_f = 0.38 (2 % methanol-dichloromethane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.55 (d, *J* = 5.0 Hz, 1H), 6.86 (d, *J* = 5.8 Hz, 1H), 3.91 (d, *J* = 0.8 Hz, 3H), 2.39 (d, *J* = 5.8 Hz, 4H), 1.74 (dd, *J* = 25.3, 5.7 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 164.3, 154.3, 152.1, 135.7, 131.8, 123.8, 107.0, 55.8, 33.9, 27.9, 23.4, 21.6 ppm. MS (M/Z): EI [M] calcd for $C_{13}H_{14}NO_2Cl$ $[M]^+$: 251, Found 251 (34 %) 236 (25 %) 216 (58 %).



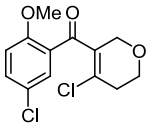
Enone **S22** was prepared using the general procedure in 43 % yield over 2 steps, purified by silica gel column chromatography (8 % ~ 12 % ethyl acetate-petroleum ether) as a yellow liquid. R_f = 0.53 (20 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.21 (m, 1H), 7.88 – 7.84 (m, 1H), 7.65 (s, 2H), 7.63 – 7.54 (m, 2H), 4.51 (t, *J* = 2.4 Hz, 2H), 4.03 (s, 3H), 3.97 (t, *J* = 5.6 Hz, 2H), 2.66 – 2.56 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 157.2, 137.0, 135.8, 130.1, 128.5, 128.1, 127.9, 127.0, 126.6, 125.6, 124.2, 123.5, 67.2, 64.8, 64.0, 33.6 ppm. MS (M/Z): EI [M] calcd for $C_{17}H_{15}O_3Cl$ $[M]^+$: 302, Found 302 (76 %) 267 (24 %) 185 (100 %).



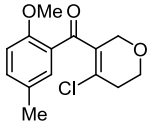
Enone **S23** was prepared using the general procedure in 27 % yield over 2 steps, purified by silica gel column chromatography (50 % ethyl acetate-petroleum ether) as a white solid. R_f = 0.28 (50 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.57 (d, *J* = 5.9 Hz, 1H), 6.86 (d, *J* = 5.9 Hz, 1H), 4.43 (t, *J* = 2.4 Hz, 2H), 3.92 (s, 3H), 3.88 (t, *J* = 5.6 Hz, 2H), 2.55 – 2.49 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 164.0, 154.3, 151.2, 134.6, 131.8, 124.8, 106.9, 66.7, 64.7, 55.9, 33.7 ppm. MS (M/Z): EI [M] calcd for $C_{12}H_{12}NO_3Cl$ $[M]^+$: 253, Found 253 (19 %) 218 (30 %) 136 (100 %).



Enone **S24** was prepared using the general procedure in 29 % yield over 2 steps, purified by silica gel column chromatography (5 % ethyl acetate-petroleum ether) as a white solid. R_f = 0.22 (50 % dichloromethane-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.4, 3.1 Hz, 1H), 7.21 – 7.14 (m, 1H), 6.90 (dd, *J* = 9.0, 3.9 Hz, 1H), 4.42 (s, 2H), 3.90 (t, *J* = 5.5 Hz, 2H), 3.85 (s, 3H), 2.57 – 2.48 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8 (d, *J* = 1.6 Hz), 156.9 (d, *J* = 240.9 Hz), 154.7 (d, *J* = 1.9 Hz), 135.2, 129.6, 129.4 (d, *J* = 6.2 Hz), 120.0 (d, *J* = 23.4 Hz), 116.4 (d, *J* = 24.2 Hz), 113.0 (d, *J* = 7.5 Hz), 66.8, 64.7, 56.6, 33.5 ppm. MS (M/Z): EI [M] calcd for $C_{13}H_{12}O_3FCl$ $[M]^+$: 270, Found 270 (16 %) 235 (26 %) 153 (100 %).

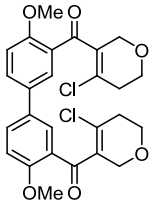


Enone **S25** was prepared using the general procedure in 34 % yield over 2 steps, purified by silica gel column chromatography (6 % ~ 8 % ethyl acetate-petroleum ether) as a white solid. R_f = 0.33 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 2.7 Hz, 1H), 7.41 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 4.42 (t, *J* = 2.5 Hz, 2H), 3.89 (t, *J* = 5.6 Hz, 2H), 3.85 (s, 3H), 2.56 – 2.48 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 157.0, 135.0, 133.2, 130.1, 129.8, 129.7, 126.2, 113.1, 66.8, 64.7, 56.3, 33.6 ppm. MS (M/Z): EI [M] calcd for $C_{13}H_{12}O_3Cl_2$ $[M]^+$: 286, Found 286 (13 %) 251 (27 %) 169 (100 %).



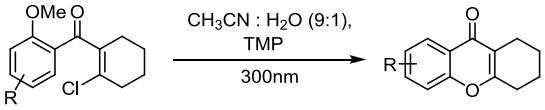
Enone **S26** was prepared using the general procedure in 20 % yield over 2 steps, purified by silica gel column chromatography (5 % ~ 8 % ethyl acetate-petroleum ether) as a white solid. R_f = 0.41 (20 % ethyl acetate-petroleum ether). ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.41 (d, *J* = 2.1 Hz, 1H), 7.30 – 7.25 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 4.40 (t, *J* = 2.4 Hz, 2H), 3.89 (t, *J* = 5.5 Hz, 2H), 3.83 (s, 3H), 2.54 – 2.45 (m, 2H), 2.30 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 156.8, 135.9, 134.5, 130.6, 130.3, 127.8 (2C), 111.7, 66.9, 64.7, 56.1, 33.4, 20.2 ppm. MS (M/Z): EI [M] calcd for $C_{14}H_{15}O_2Cl$ $[M]^+$: 266, Found 266 (15 %) 231 (29 %) 149 (100 %).

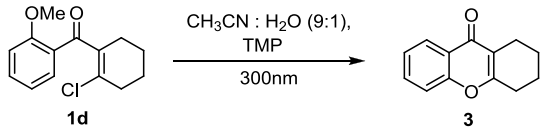


Enone **S27** was prepared using the general procedure in 12 % yield over 2 steps, purified by silica gel column chromatography (25 % ~ 35 % ethyl acetate-petroleum ether) as a white solid. R_f = 0.31 (30 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 2.4 Hz, 2H), 7.69 (dd, *J* = 8.6, 2.4 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H), 4.45 (t, *J* = 2.3 Hz, 4H), 3.95 – 3.88 (m, 10H), 2.59 – 2.48 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9 (2 C), 158.0 (2 C), 135.6 (2 C), 132.7 (2 C), 131.9 (2 C), 129.0 (2 C), 128.6 (2 C), 128.3 (2 C), 112.2 (2 C), 66.9 (2 C), 64.8 (2 C), 56.2 (2 C), 33.5 (2 C) ppm. HRMS (M/Z): EI [M] calcd for $C_{26}H_{24}O_6Cl_2$ $[M]^+$: 502.0950, Found 502.0953.

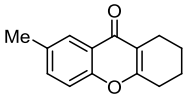
General procedure for the photolysis of substrates:



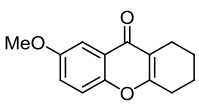
To a solution of substrate in a co-solvent of acetonitrile/H_2O (9:1, v/v) (0.01 M) in quartz tube was added the base TMP (1.0 equiv.). After homogeneous mixing, the solution was photolyzed at r.t. in a Rayonet chamber reactor at 300 nm for 25 min ~ 70 min shown in table 3. TLC showed all substrate consumed, then CH_3CN was evaporated, an saturated NH_4Cl solution was added, then extracted with EtOAc, the combined organic phase was washed with brine, dried over Na_2SO_4, filtered, concentrated, and purified by silica gel column chromatography to give corresponding products.



To a solution of substrate in a co-solvent of acetonitrile/H_2O (9:1, v/v) (0.01 M) in quartz tube was added the base TMP (1.0 equiv.). After all substrate dissolved, the solution was photolyzed at r.t. in a Rayonet chamber reactor at 300 nm for 40 min. TLC showed all **1d** consumed, then CH_3CN was evaporated, an saturated NH_4Cl solution was added, then extracted with EtOAc (10 mL), the combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, filtered, concentrated, and purified by silica gel column chromatography (1 % acetone-petroleum ether). The product **3** was generated in 78 % yield as a white solid (37.8 mg). R_f = 0.25 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.61 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.43 – 7.30 (m, 2H), 2.68 (t, *J* = 6.4 Hz, 2H), 2.58 (t, *J* = 6.2 Hz, 2H), 1.88 (m, 2H), 1.82 – 1.72 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 163.7, 155.8, 132.8, 125.6, 124.3, 123.0, 118.3, 117.5, 28.1, 21.8, 21.5, 20.9 ppm. The NMR data is same as reported.[4] MS (M/Z): EI [M] calcd for $C_{13}H_{12}O_2$ [M]$^+$: 200, Found 200 (86 %) 199 (100 %) 185 (72 %).

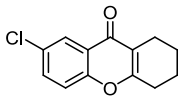


Ketone **5** was prepared according to the general procedure in 69 % yield. The reaction time is 40 min under 300 nm light. The product was isolated through silica gel flash chromatography (2 % ~ 4 % ethyl acetate-petroleum ether) as a white solid (47.3 mg): R_f = 0.39 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.2 Hz, 1H), 7.40 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 1H), 2.65 (t, *J* = 6.3 Hz, 2H), 2.57 (t, *J* = 6.2 Hz, 2H), 2.43 (s, 3H), 1.89 – 1.82 (m, 2H), 1.79 – 1.71 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 163.6, 154.2, 134.1, 134.1, 125.0, 122.8, 118.2, 117.3, 28.1, 21.9, 21.7, 21.0, 20.9 ppm. MS (m/z): EI [M] calcd for $C_{14}H_{14}O_2$ [M]$^+$: 214, Found 214 (85 %) 213 (100 %) 199 (57 %).

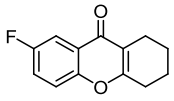


Ketone **6** was prepared according to the general procedure in 72 % yield. The reaction time is 40 min under 300 nm light. The product was isolated through silica gel flash chromatography (1 % acetone-petroleum ether)as a white solid (50.1 mg): R_f = 0.10 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 3.0 Hz, 1H), 7.30

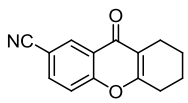
(d, *J* = 9.1 Hz, 1H), 7.18 (dd, *J* = 9.1, 3.0 Hz, 1H), 3.87 (s, 3H), 2.65 (t, *J* = 6.1 Hz, 2H), 2.57 (t, *J* = 6.0 Hz, 2H), 1.91 – 1.81 (m, 2H), 1.78 – 1.69 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 163.6, 156.3, 150.7, 123.6, 123.0, 119.0, 117.6, 104.8, 55.8, 28.1, 21.9, 21.7, 21.0 ppm. The NMR data is same as reported.[5] HRMS (M/Z): EI [M] calcd for $C_{14}H_{14}O_3$ $[M]^+$: 230.0943, Found 230.0945.



Ketone **7** was prepared according to the general procedure in 73 % yield. The reaction time is 40 min under 300 nm light. The product was isolated through silica gel flash chromatography (2 % ~ 4 % ethyl acetate-petroleum ether) as a white solid (47.3 mg): R_f = 0.39 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 2.3 Hz, 1H), 7.54 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 2.71 – 2.61 (m, 2H), 2.61 – 2.52 (m, 2H), 1.95 – 1.87 (m, 2H), 1.81 – 1.68 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 164.1, 154.2, 133.2, 130.2, 125.1, 124.1, 119.4, 118.6, 28.1, 21.8, 21.5, 21.0 ppm. HRMS (M/Z): EI [M] calcd for $C_{13}H_{11}O_2Cl$ $[M]^+$: 234.0448, Found 234.0447.

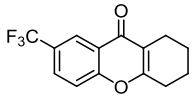


Ketone **8** was prepared according to the general procedure in 71 % yield. The reaction time is 50 min under 300 nm light. The product was isolated through silica gel flash chromatography (3 % ethyl acetate-petroleum ether)as a white solid (30.0 mg): R_f = 0.34 (10 % ethyl acetate-petroleum ether).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.4, 2.9 Hz, 1H), 7.32 (m, 2H), 2.65 (t, *J* = 6.3 Hz, 2H), 2.55 (t, *J* = 6.1 Hz, 2H), 1.93 – 1.81 (m, 2H), 1.79 – 1.70 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9 (d, *J* = 2.2 Hz), 164.2, 159.0 (d, *J* = 245.2 Hz), 152.0 (d, J = 1.4 Hz), 124.1 (d, *J* = 7.2 Hz), 121.1 (d, *J* = 25.5 Hz), 119.6 (d, *J* = 8.0 Hz), 117.8, 110.3 (d, *J* = 23.4 Hz), 28.1, 21.8, 21.5, 20.9 ppm. HRMS (M/Z): EI [M] calcd for $C_{13}H_{11}O_2F$ $[M]^+$: 218.0743, Found 218.0741.

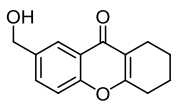


Ketone **9** was prepared according to the general procedure in 67 % yield. The reaction time is 50 min under 300 nm light. The product was isolated through silica gel flash chromatography (60 % ~ 80 % dichloromethane-petroleum ether) as a white solid (36.0 mg): R_f = 0.24 (67 % dichloromethane-petroleum ether).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H),

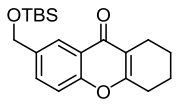
7.81 (d, *J* = 8.6 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 2.69 (t, *J* = 5.7 Hz, 2H), 2.57 (t, *J* = 5.4 Hz, 2H), 1.95 – 1.83 (m, 2H), 1.84 – 1.72 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 164.6, 157.6, 135.2, 131.5, 123.5, 119.6, 119.3, 117.8, 108.5, 28.0, 21.7, 21.3, 20.9 ppm. HRMS (M/Z): EI [M] calcd for $C_{14}H_{11}NO_2$ $[M]^+$: 225.0790, Found 225.0791.



Ketone **10** was prepared according to the general procedure in 66 % yield. The reaction time is 40 min under 300 nm light. The product was isolated through silica gel flash chromatography (2 % ~ 5 % dichloromethane-petroleum ether) as a white solid (42.1 mg): R_f = 0.30 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 1.9 Hz, 1H), 7.81 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 2.69 (t, *J* = 6.3 Hz, 2H), 2.57 (t, *J* = 6.2 Hz, 2H), 1.92 – 1.84 (m, 2H), 1.81 – 1.72 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 164.4, 157.3, 129.3 (q, *J* = 3.2 Hz), 126.8 (q, *J* = 33.5 Hz), 123.6 (q, *J* = 270.5 Hz), 123.9 (q, *J* = 4.0 Hz), 122.9, 119.2, 118.7, 28.1, 21.7, 21.4, 20.9 ppm. HRMS (M/Z): EI [M] calcd for $C_{14}H_{11}O_2F_3$ $[M]^+$: 268.0711, Found 268.0712.

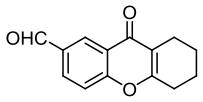


Ketone **11** was prepared according to the general procedure in 75 % yield. The reaction time is 25 min under 300 nm light. The product was isolated through silica gel flash chromatography (30 % ~ 35 % ethyl acetate-petroleum ether) as a white solid (28.2 mg): R_f = 0.19 (40 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.69 – 7.55 (m, 1H), 7.31 (d, *J* = 8.5 Hz, 1H),4.74 (s, 2H) 2.64 (t, *J* = 6.1 Hz, 2H), 2.54 (t, *J* = 5.5 Hz, 2H), 1.88-1.82 (m, 2H), 1.79 – 1.71 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 164.0, 155.2, 137.6, 132.1, 123.6, 122.7, 118.3, 117.8, 64.4, 28.1, 21.8, 21.6, 21.0 ppm. HRMS (M/Z): EI [M] calcd for $C_{14}H_{14}O_3$ $[M]^+$: 230.0943, Found 230.0945.

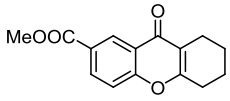


Ketone **12** was prepared according to the general procedure in 64 % yield. The reaction time is 40 min under 300 nm light. The product was isolated through silica gel flash chromatography (2 % ~ 4 % ethyl acetate-petroleum ether) as a white solid (35.9 mg): R_f = 0.45 (10 % ethyl acetate-petroleum ether).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 2.0 Hz, 1H), 7.63 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 4.80 (s, 2H), 2.66 (t, *J* = 6.3 Hz, 2H), 2.58 (t,

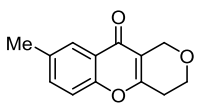
J = 6.1 Hz, 2H), 1.92 – 1.83 (m, 2H), 1.79-1.72 (m, 2H), 0.94 (s, 9H), 0.10 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 163.7, 155.0, 137.8, 131.2, 122.7, 122.6, 118.3, 117.6, 64.4, 28.1, 25.9 (3 C), 21.9, 21.7, 21.0, 18.4, -5.3 (2 C) ppm. MS (M/Z): ESI [M] calcd for $C_{20}H_{28}O_3Si$ $[M]^+$: 344, Found 345 $[M+H]^+$.



Ketone **13** was prepared according to the general procedure in 48 % yield. The reaction time is 50 min under 300 nm light. The product was isolated through silica gel flash chromatography (50 % ~ 70 % dichloromethane-petroleum ether) as a white solid (26.4 mg): R_f = 0.32 (pure dichloromethane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.68 (d, *J* = 1.7 Hz, 1H), 8.15 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 2.70 (t, *J* = 6.2 Hz, 2H), 2.60 (t, *J* = 5.9 Hz, 2H), 1.97 – 1.85 (m, 2H), 1.81-1.75 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 176.9, 164.4, 159.3, 132.8, 131.1, 131.0, 123.2, 119.4, 119.1, 28.1, 21.8, 21.4, 20.9 ppm. HRMS (M/Z): EI [M] calcd for $C_{14}H_{12}O_3$ $[M]^+$: 228.0786, Found 228.0787.

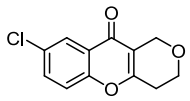


Ketone **14** was prepared according to the general procedure in 67 % yield. The reaction time is 45 min under 300 nm light. The product was isolated through silica gel flash chromatography (70 % ~ 80 % dichloromethane-petroleum ether) as a white solid (41.5 mg): R_f = 0.29 (pure dichloromethane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 2.0 Hz, 1H), 8.22 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 1H), 3.92 (s, 3H), 2.65 (t, *J* = 6.3 Hz, 2H), 2.55 (t, *J* = 6.2 Hz, 2H),1.91 – 1.82 (m, 2H), 1.81 – 1.68 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 165.9, 164.0, 158.3, 133.5, 128.3, 126.4, 122.7, 119.0, 118.0, 52.3, 28.0, 21.7, 21.4, 20.9 ppm. MS (m/z): EI [M] calcd for $C_{15}H_{14}O_2$ $[M]^+$: 258, Found 258 (100 %) 257 (85 %) 243 (48 %).

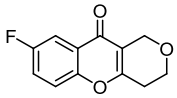


Ketone **15** was prepared according to the general procedure in 75 % yield. The reaction time is 45 min under 300 nm light. The product was isolated through silica gel flash chromatography (8 % ~ 10 % ethyl acetate-petroleum ether) as a white solid (33.4 mg): R_f = 0.31 (20 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 4.65 (s, 2H), 4.00 (t, *J* = 5.5 Hz, 2H), 2.81 – 2.71 (m, 2H), 2.43 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 160.5, 154.3, 134.8, 134.6, 124.8,

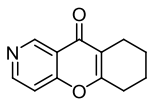
123.1, 117.5, 116.8, 63.8, 62.7, 27.6, 20.9 ppm. MS (m/z): EI [M] calcd for $C_{13}H_{12}O_3$ $[M]^+$: 216, Found 216 (30 %) 188 (58 %) 187 (100 %).



Ketone **16** was prepared according to the general procedure in 74 % yield. The reaction time is 35 min under 300 nm light. The product was isolated through silica gel flash chromatography (8 % ~ 12 % ethyl acetate-petroleum ether) as a white solid (42.4mg): R_f = 0.17 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 1H), 4.63 (s, 2H), 4.01 (t, *J* = 5.3 Hz, 2H), 2.82 – 2.72 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 161.1, 154.3, 133.6, 130.8, 125.0, 124.4, 119.5, 117.2, 63.7, 62.5, 27.6 ppm. MS (m/z): EI [M] calcd for $C_{12}H_9O_3Cl$ $[M]^+$: 236, Found 236 (31 %) 208 (67 %) 207 (100 %).

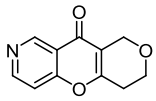


Ketone **17** was prepared according to the general procedure in 77 % yield. The reaction time is 30 min under 300 nm light. The product was isolated through silica gel flash chromatography (9 % ~ 15 % ethyl acetate-petroleum ether) as a white solid (33.4 mg): R_f = 0.32 (20 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.2, 3.0 Hz, 1H), 7.42 (dd, *J* = 9.1, 4.3 Hz, 1H), 7.39 – 7.32 (m, 1H), 4.64 (s, 2H), 4.01 (t, *J* = 5.6 Hz, 2H), 2.81 – 2.74 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8 (d, *J* = 2.4 Hz), 161.1, 159.3 (d, *J* = 246.4 Hz), 152.2 (d, *J* = 1.6 Hz), 124.6 (d, *J* = 7.3 Hz), 121.6 (d, *J* = 25.5 Hz), 119.8 (d, *J* = 8.0 Hz), 116.5, 110.4 (d, *J* = 23.6 Hz), 63.7, 62.5, 27.6 ppm. MS (m/z): EI [M] calcd for $C_{12}H_9FO_3$ $[M]^+$: 220, Found 220 (29 %) 192 (66 %) 191 (100 %).

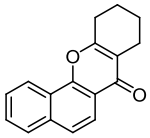


Ketone **18** was prepared according to the general procedure in 52 % yield. The reaction time is 70 min under 300 nm light. The product was isolated through silica gel flash chromatography (0.5 % ~ 2 % methanol-dichloromethane) as a white solid (25.2 mg): R_f = 0.53 (2 % methanol-dichloromethane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.69 (d, *J* = 5.9 Hz, 1H), 7.25 (d, *J* = 5.6 Hz, 1H), 2.67 (t, *J* = 6.3 Hz, 2H), 2.56 (t, *J* = 6.2 Hz, 2H), 1.94 – 1.83 (m, 2H), 1.80 – 1.71 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 164.3, 160.6, 152.4, 150.0,

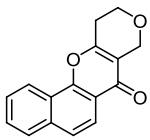
120.9, 118.7, 112.1, 28.0, 21.7, 21.3, 20.8 ppm. MS (m/z): EI [M] calcd for $C_{12}H_{11}NO_2$ $[M]^+$: 201, Found 201 (100 %) 200 (84 %) 186 (63 %).



Ketone **19** was prepared according to the general procedure in 45 % yield. The reaction time is 70 min under 300 nm light. The product was isolated through silica gel flash chromatography (0.5 % ~ 2 % methanol-dichloromethane) as a white solid (21.2 mg): R_f = 0.44 (2 % methanol-dichloromethane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.74 (d, *J* = 5.9 Hz, 1H), 7.30 (d, *J* = 5.9 Hz, 1H), 4.62 (t, *J* = 1.6 Hz, 2H), 4.01 (t, *J* = 5.6 Hz, 2H), 2.81 – 2.74 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 161.3, 160.7, 152.9, 149.8, 119.5, 119.0, 112.2, 63.6, 62.2, 27.5 ppm. MS (m/z): EI [M] calcd for $C_{11}H_9NO_3$ $[M]^+$: 203, Found 203 (29 %) 175 (87 %) 174 (100 %).

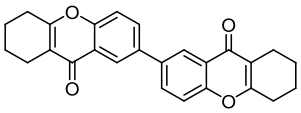


Ketone **20** was prepared according to the general procedure in 71 % yield. The reaction time is 40 min under 300 nm light. The product was isolated through silica gel flash chromatography (4 % ~ 8 % ethyl acetate-petroleum ether) as a white solid (42.6 mg): R_f = 0.30 (10 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 7.6 Hz, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.72 – 7.58 (m, 3H), 2.81 (t, *J* = 6.0 Hz, 2H), 2.64 (t, *J* = 6.0 Hz, 2H), 1.97 – 1.89 (m, 2H), 1.84 – 1.77 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 163.0, 153.1, 135.5, 128.8, 128.0, 126.7, 124.4, 124.0, 122.1, 121.1, 119.8, 119.2, 28.0, 21.9, 21.6, 21.1 ppm. MS (m/z): EI [M] calcd for $C_{17}H_{14}O_2$ $[M]^+$: 250, Found 250 (100 %) 249 (98 %) 235 (32 %).

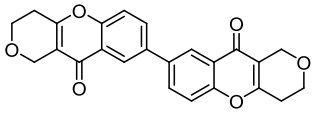


Ketone **21** was prepared according to the general procedure in 93 % yield. The reaction time is 40 min under 300 nm light. The product was isolated through silica gel flash chromatography (10 % ~ 12 % ethyl acetate-petroleum ether) as a white solid (56 mg): R_f = 0.29 (20 % ethyl acetate-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 7.9 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.76 – 7.60 (m, 3H), 4.72 (s, 2H), 4.07 (t, *J* = 5.5 Hz, 2H), 2.97 – 2.88 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 159.8,

153.4, 135.7, 129.1, 128.1, 127.0, 124.9, 123.8, 122.1, 120.6, 119.6, 118.4, 63.8, 62.7, 27.5 ppm. MS (m/z): EI [M] calcd for $C_{16}H_{12}O_3$ $[M]^+$: 252, Found 252 (49 %) 224 (79 %) 223 (100 %).



Ketone **22** was prepared according to the general procedure in 56 % yield. The reaction time is 60 min under 300 nm light. The product was isolated through silica gel flash chromatography (30 % ~ 40 % dichloromethane-petroleum ether) as a white solid (33.6 mg): R_f = 0.14 (20 % ethyl acetate-petroleum ether).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 2.2 Hz, 2H), 7.95 (dd, *J* = 8.7, 2.2 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 2.70 (t, *J* = 6.1 Hz, 4H), 2.61 (t, *J* = 5.9 Hz, 4H), 1.94 – 1.83 (m, 4H), 1.82 – 1.74 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6 (2 C), 164.0 (2 C), 155.5 (2 C), 136.0 (2 C), 131.9 (2 C), 123.7 (2 C), 123.3 (2 C), 118.6 (2 C), 118.4 (2 C), 28.2 (2 C), 21.9 (2 C), 21.6 (2 C), 21.1 (2 C) ppm. HRMS (M/Z): EI [M] calcd for $C_{26}H_{22}O_4$ $[M]^+$: 398.1518, Found 398.1514.



Ketone **23** was prepared according to the general procedure in 73 % yield. The reaction time is 60 min under 300 nm light. The product was isolated through silica gel flash chromatography (10 % ~ 20 % ethyl acetate-dichloromethane) as a white solid (33.4 mg): R_f = 0.36 (20 % ethyl acetate-dichloromethane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 2.3 Hz, 2H), 7.95 (dd, *J* = 8.7, 2.3 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 4.67 (s, 4H), 4.03 (t, *J* = 5.6 Hz, 4H), 2.80 (t, *J* = 5.5 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4 (2 C), 160.9 (2 C), 155.6 (2 C), 136.2 (2 C), 132.2 (2 C), 123.7 (2 C), 123.5 (2 C), 118.6 (2 C), 117.2 (2 C), 63.7 (2 C), 62.6 (2 C), 27.6 (2 C) ppm. HRMS (m/z): EI [M] calcd for $C_{24}H_{18}O_6$ $[M]^+$: 402.1103, Found 402.1102.

Large Scale experiments:

To a solution of substrate **1d** (502.0 mg, 2 mmol) in a co-solvent of acetonitrile/H_2O (9:1, v/v) (0.2 M) 10 mL in quartz tube was added TMP (338 μL, 2 mmol, 1.0 equiv.). After all substrate dissolved, the solution was photolyzed at r.t. in a Rayonet chamber reactor at 300 nm for 5 h 20 min, then CH_3CN was evaporated, an saturated NH_4Cl solution was added, then extracted with EtOAc

(20 mL), the combined organic phase was washed with brine (15 mL), dried over Na_2SO_4, filtered, concentrated, and purified by silica gel column chromatography (1 % ~ 2 % acetone-petroleum ether). The product **3** were generated as a white solid in 81 % yield (325.2 mg).

Repeat the reaction of **1d** at a scale of 507.6 mg in a co-solvent of acetonitrile/H_2O (9:1, v/v) (0.2 M) 10 mL, after irradiation at 300 nm for 5 h 30 min, we isolated product **3** in 79 % yield (318.1 mg).

We then scaled up the reaction to a gram scale (1.29 g, 5.2 mmol) in a co-solvent of acetonitrile/H_2O (9:1, v/v) (0.5 M) 10 mL, after irradiation at 300 nm for 13 h 10 min, we isolated product **3** in 80 % yield (828.0 mg).

To a solution of substrate **S7** (330.4 mg, 1.2 mmol) in a co-solvent of acetonitrile/H_2O (9:1, v/v) (0.15 M) 8 mL in quartz tube was added TMP (208 μL, 1.2 mmol, 1.0 equiv.). After all substrate dissolved, the solution was photolyzed at r.t. in a Rayonet chamber reactor at 300 nm for 3 h 20 min, then CH_3CN was evaporated, an saturated NH_4Cl solution was added, then extracted with EtOAc (20 mL), the combined organic phase was washed with brine (15 mL), dried over Na_2SO_4, filtered, concentrated, and purified by silica gel column chromatography (3 % ~ 4 % ethyl acetate-petroleum ether). The product **8** were generated as a white solid in 90 % yield (241.2 mg).
Repeat the reaction of **S7** at a scale of 322.5 mg in a co-solvent of acetonitrile/H_2O (9:1, v/v) (0.15 M) 8 mL, after irradiation at 300 nm for 3 h 30 min, we isolated product **8** in 86 % yield (225.5 mg).

Reference:

[1] P. R. Giles, and C. M. Marson, *Tetrahedron Lett.*, 1990, **31**, 5227–5230.

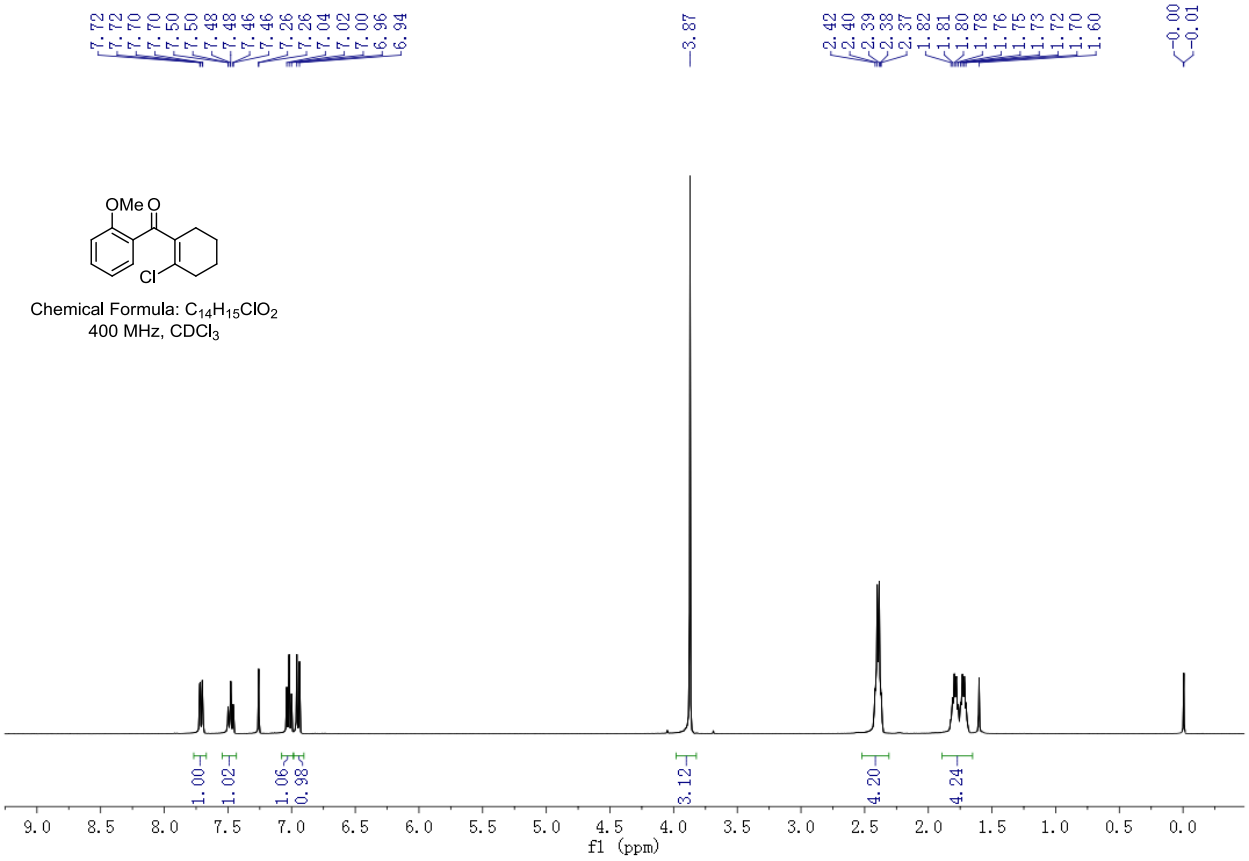
[2] P. R. Giles, and C. M. Marson, *Tetrahedron*, 1991, **47**, 1303–1310.

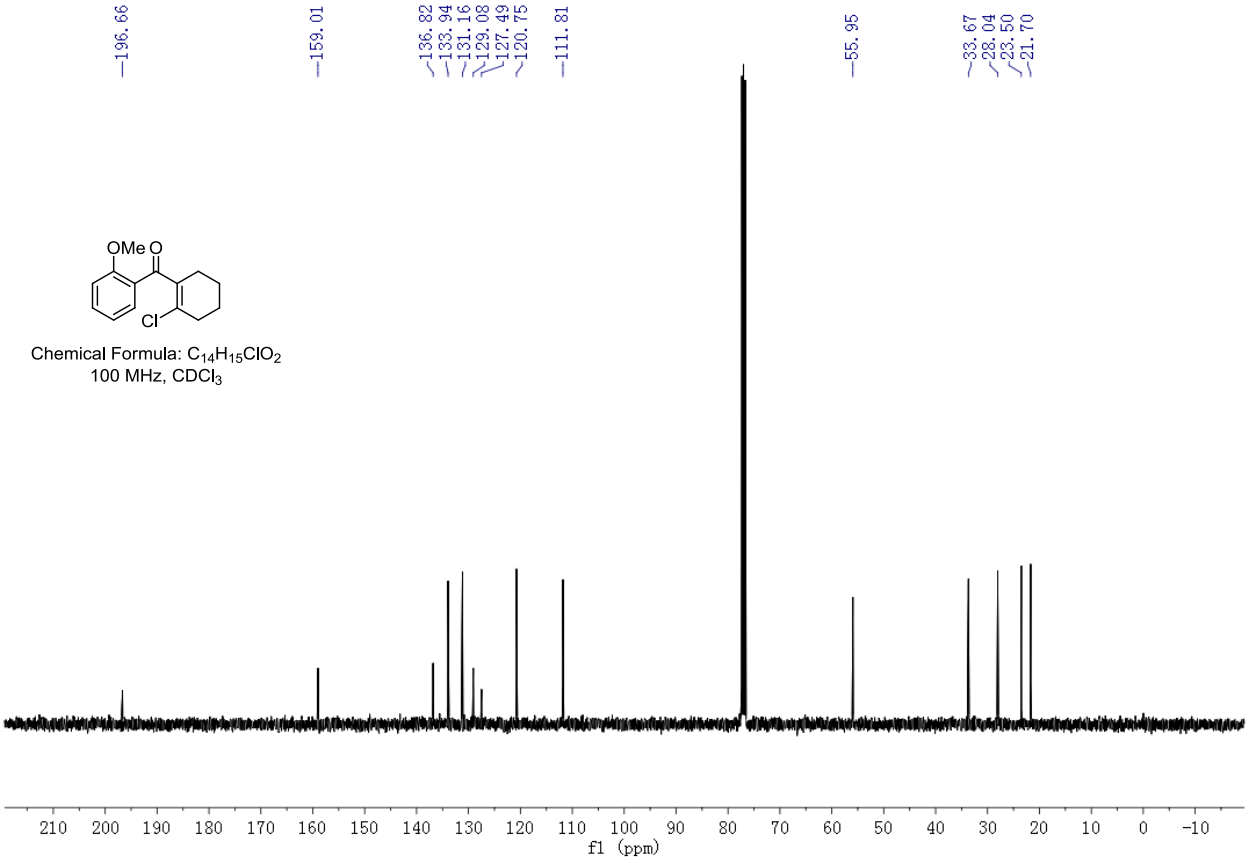
[3] S. Yamada, D. Morizono, and K. Yamamoto, *Tetrahedron Lett.*, 1992, **33**, 4329–4332.

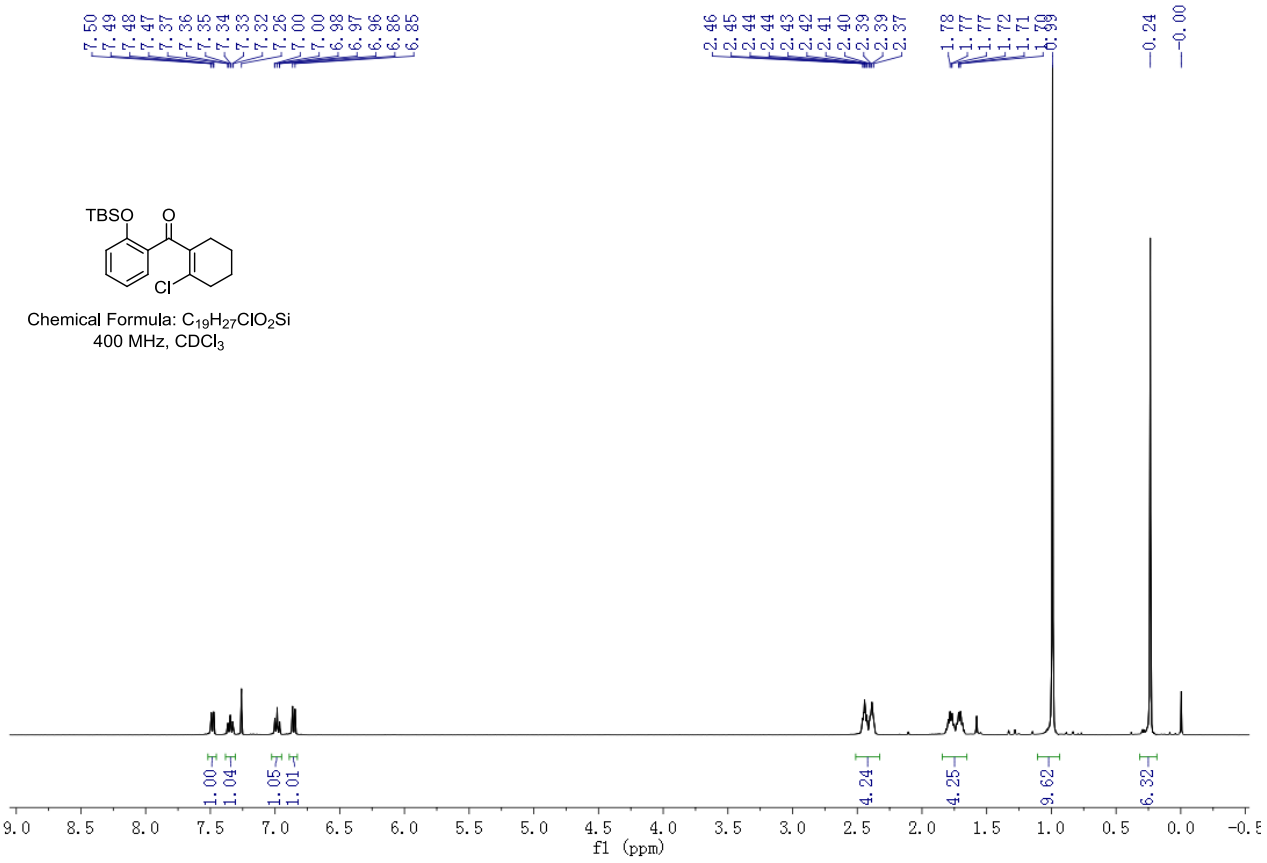
[4] A. V. Dubrovskiy and R. C. Larock, *Tetrahedron*, 2013, **69**, 2789–2798.

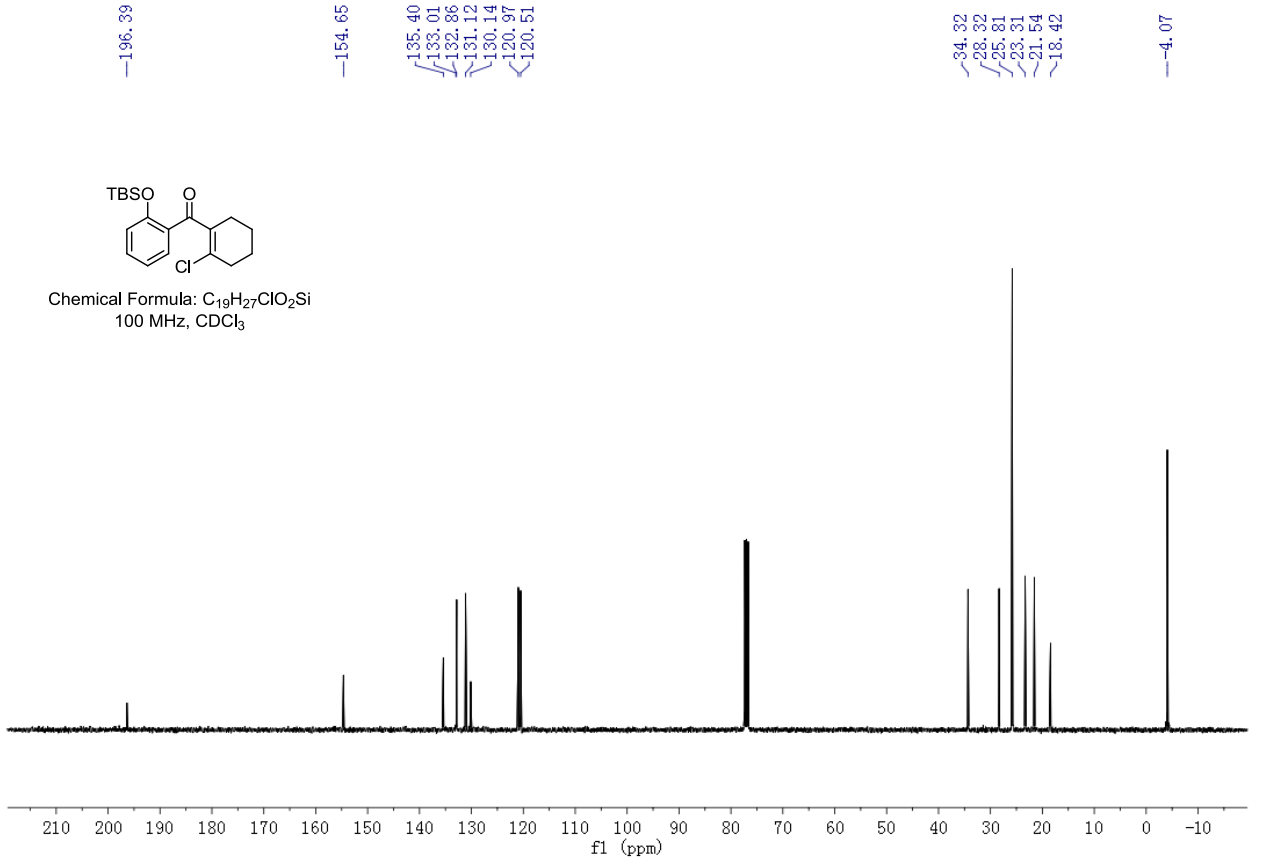
[5] P. A. Turner, E. M. Griffin, J. L. Whatmore, and M. Shipman, *Org. Lett.*, 2011, **13** , 1056–1059.

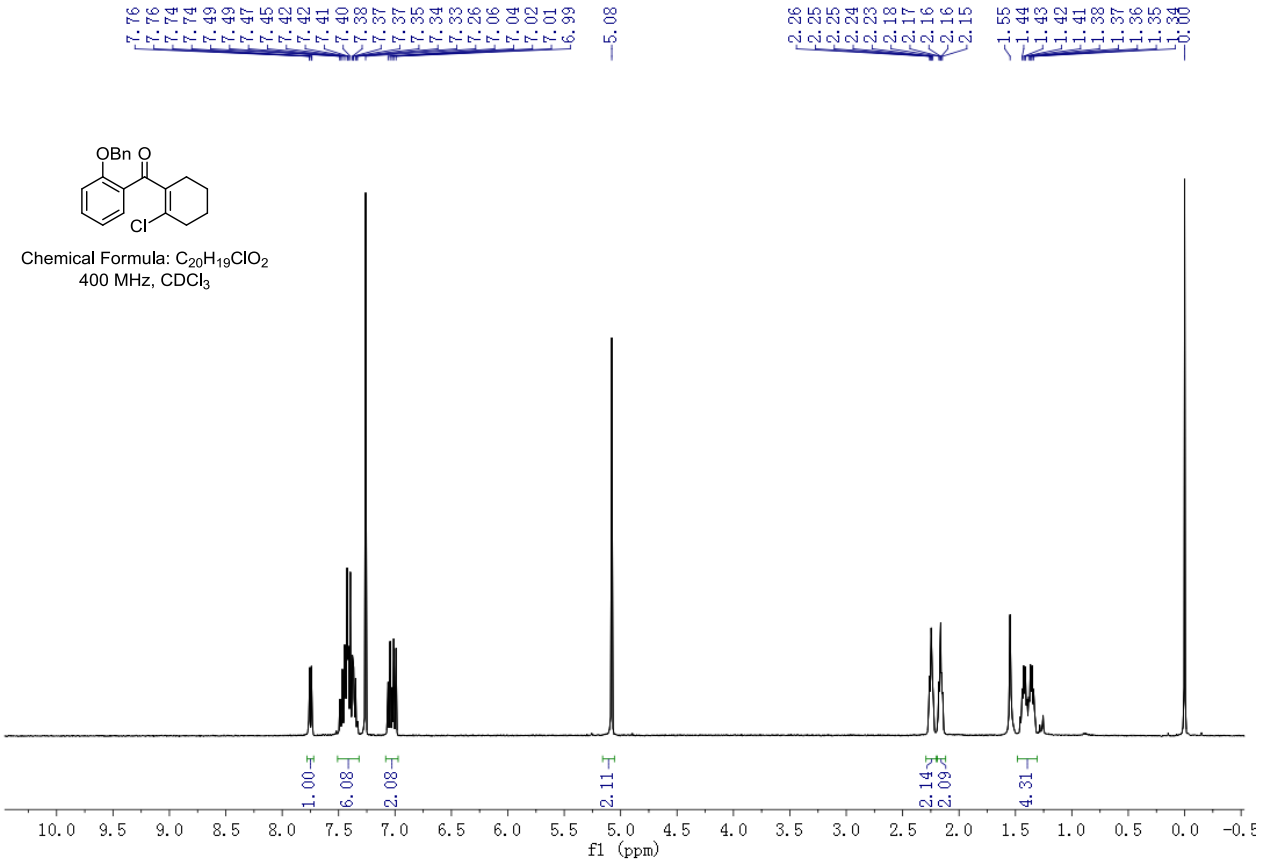
^{1}H and ^{13}C NMR Spectra of the Synthetic Intermediates and Products:

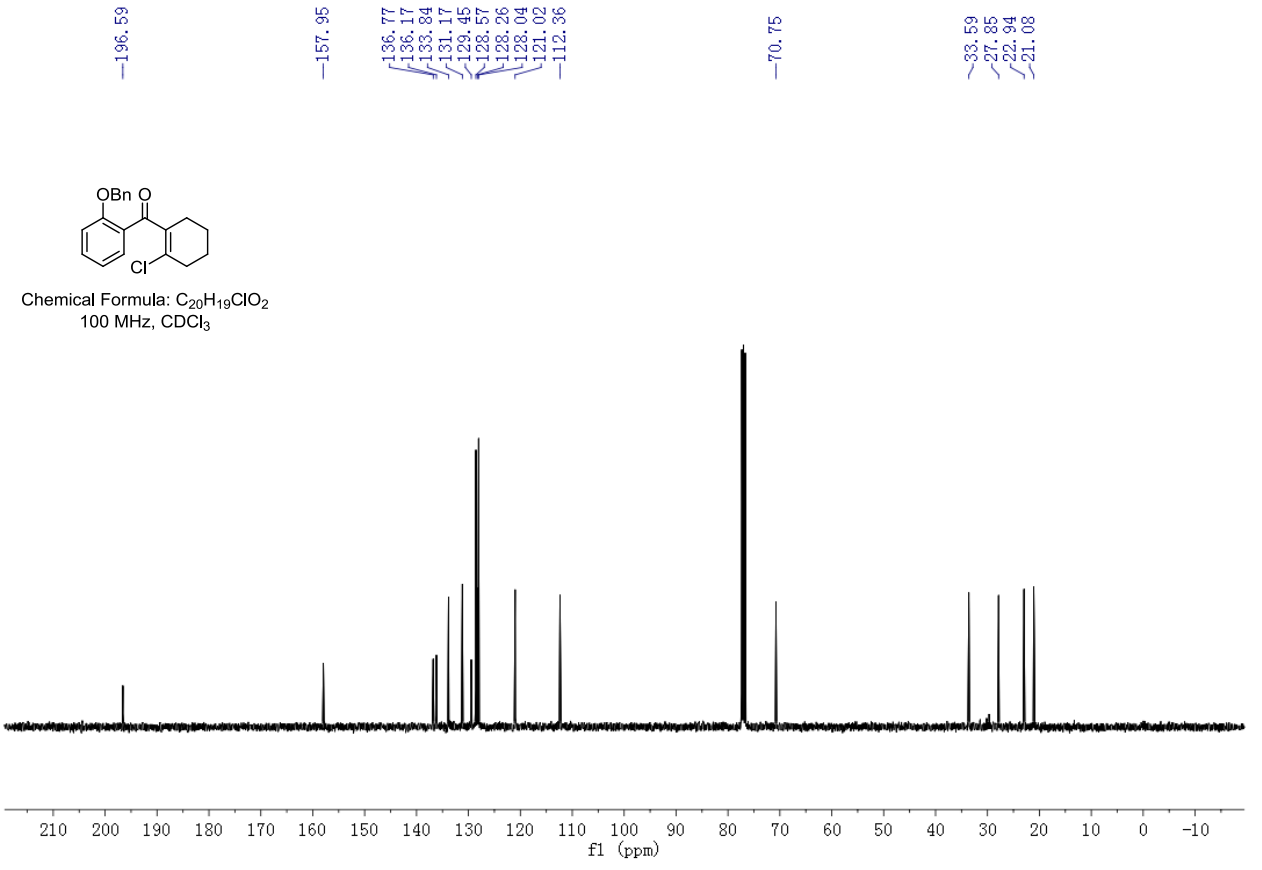


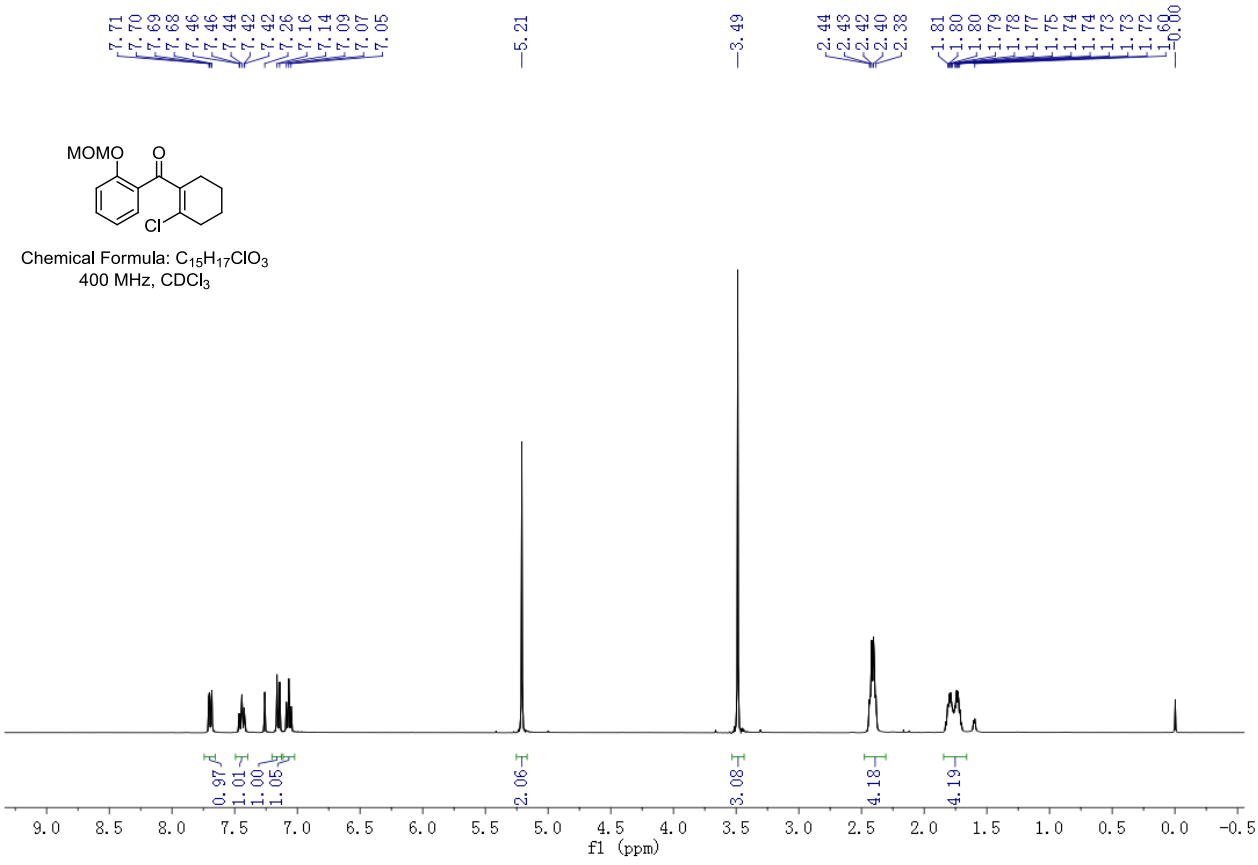



TBSO
O
Cl
Chemical Formula: C19H27ClO2Si
400 MHz, CDCl3
f1 (ppm)

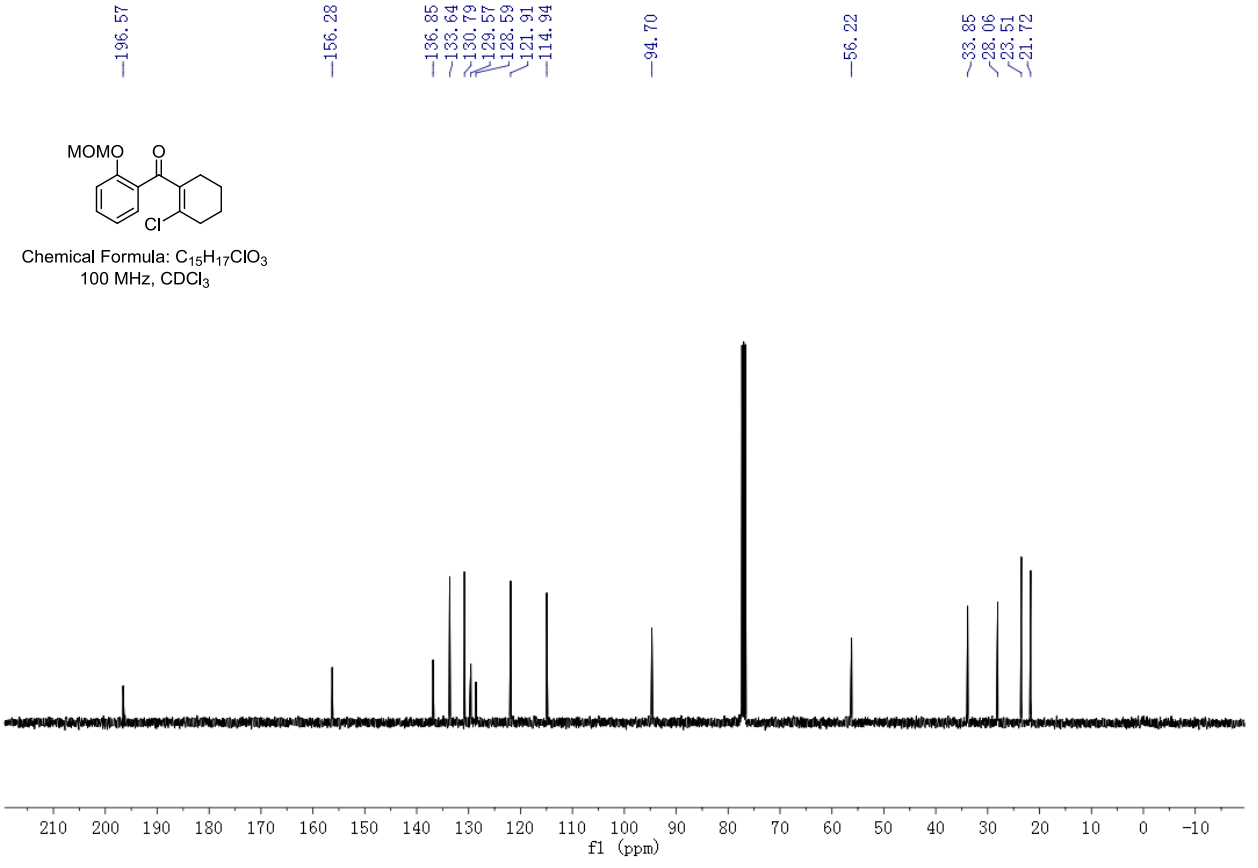

TBSO
O
Cl
Chemical Formula: C19H27ClO2Si
100 MHz, CDCl3
f1 (ppm)


7.76
7.76
7.74
7.74
7.49
7.49
7.47
7.45
7.42
7.42
7.41
7.40
7.38
7.37
7.37
7.35
7.34
7.33
7.26
7.06
7.04
7.02
7.01
6.99
5.08
2.26
2.25
2.25
2.24
2.23
2.18
2.17
2.16
2.16
2.15
1.55
1.44
1.43
1.42
1.41
1.38
1.37
1.36
1.35
1.34
0.80
OBn O
Cl
Chemical Formula: C20H19ClO2
400 MHz, CDCl3
1.00
6.08
2.08
2.11
2.14
2.09
4.31
f1 (ppm)

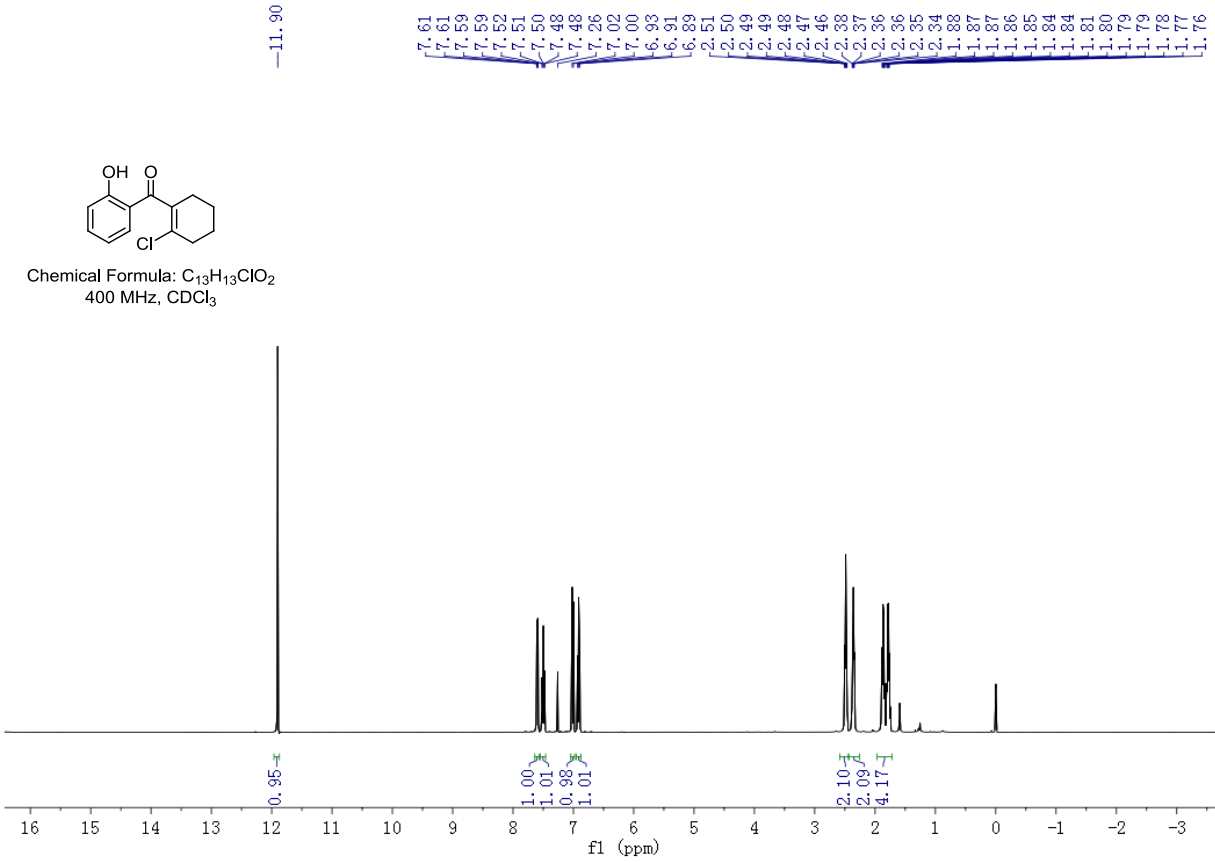

196.59
157.95
136.77
136.17
133.84
131.17
129.45
128.57
128.26
128.04
121.02
112.36
70.75
33.59
27.85
22.94
21.08
OBn O
Cl
Chemical Formula: C20H19ClO2
100 MHz, CDCl3
f1 (ppm)

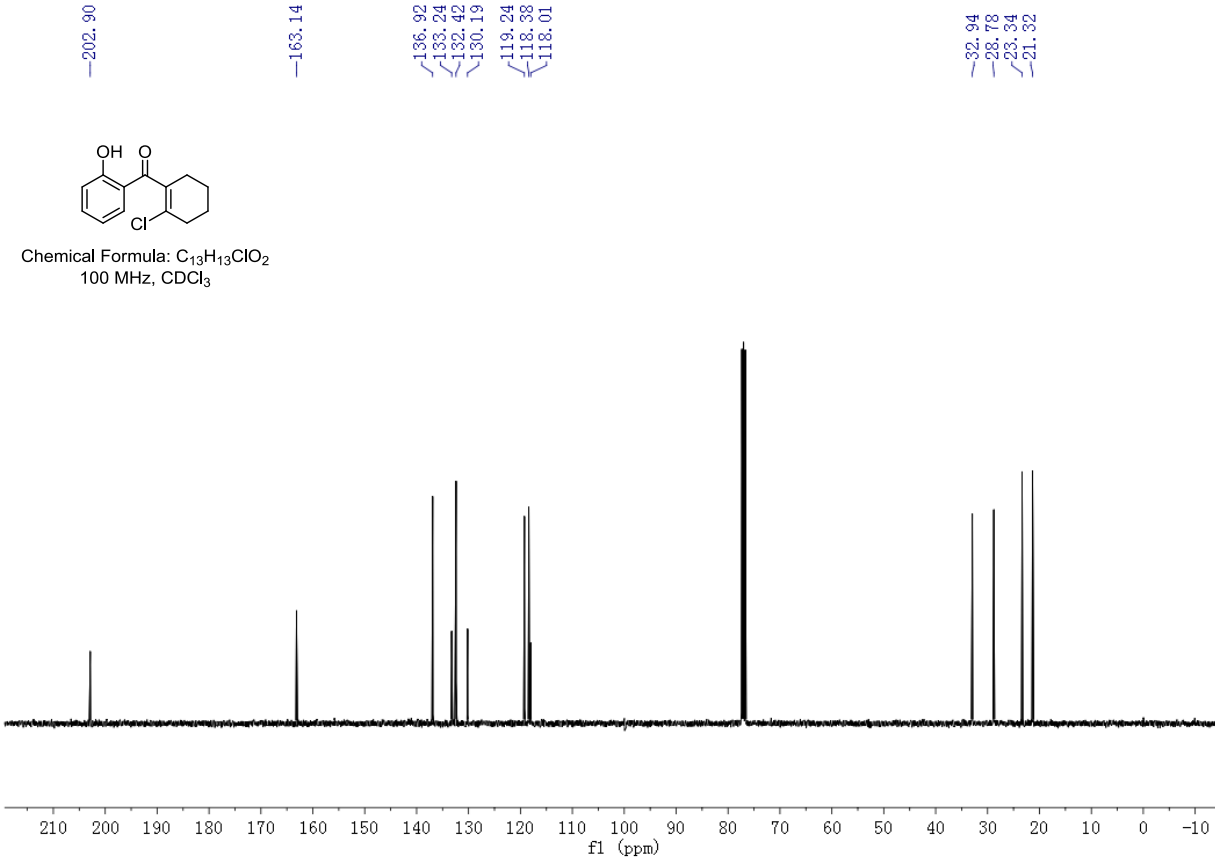


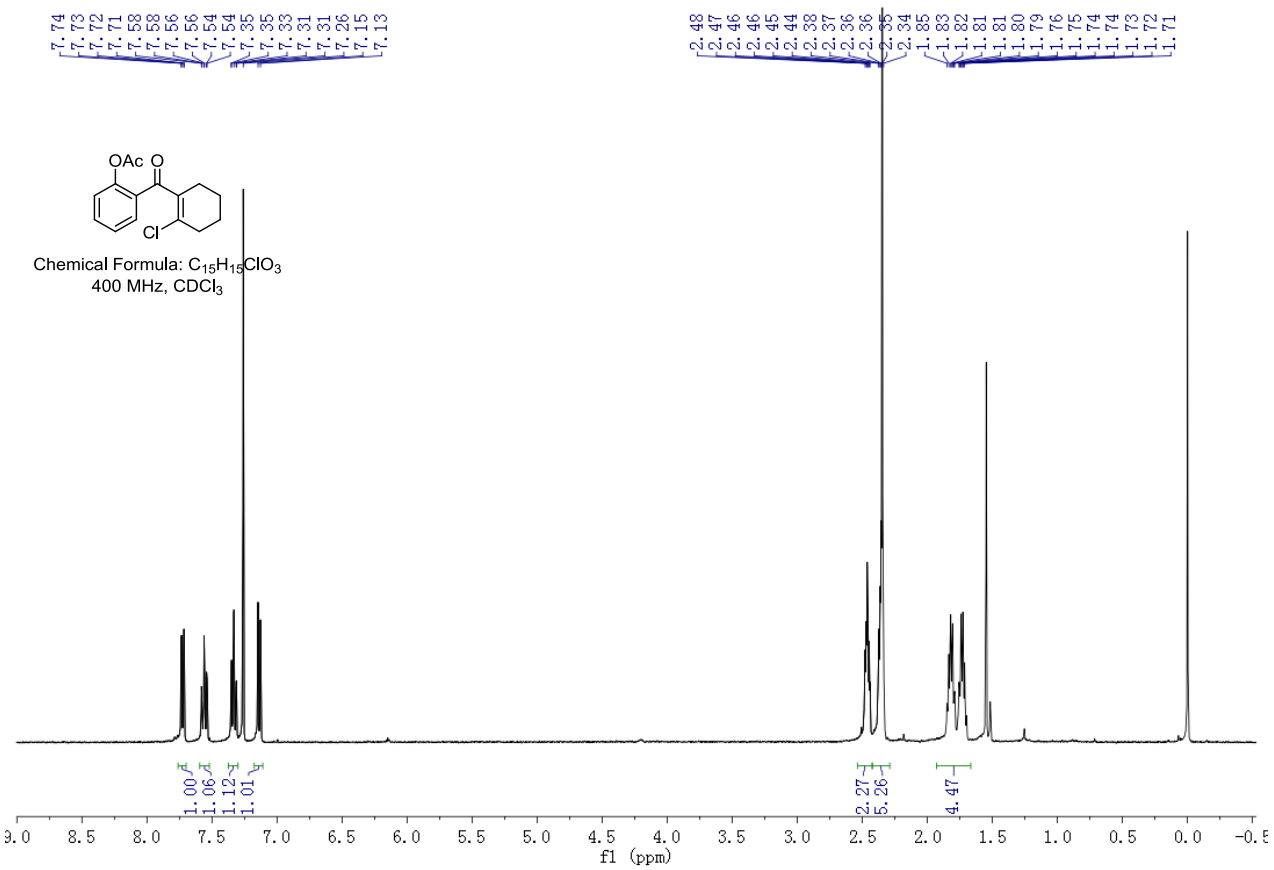
Chemical Formula: $C_{15}H_{17}ClO_3$
400 MHz, $CDCl_3$

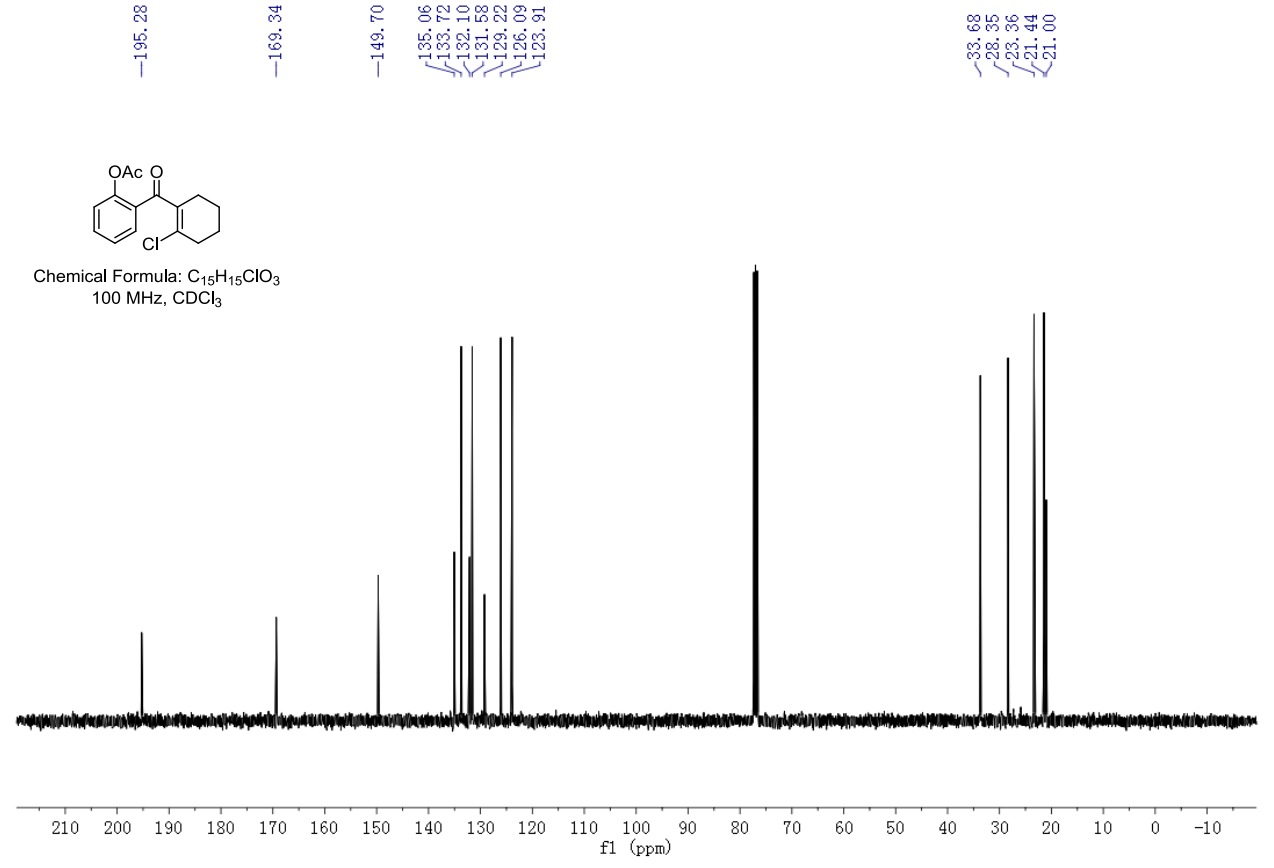


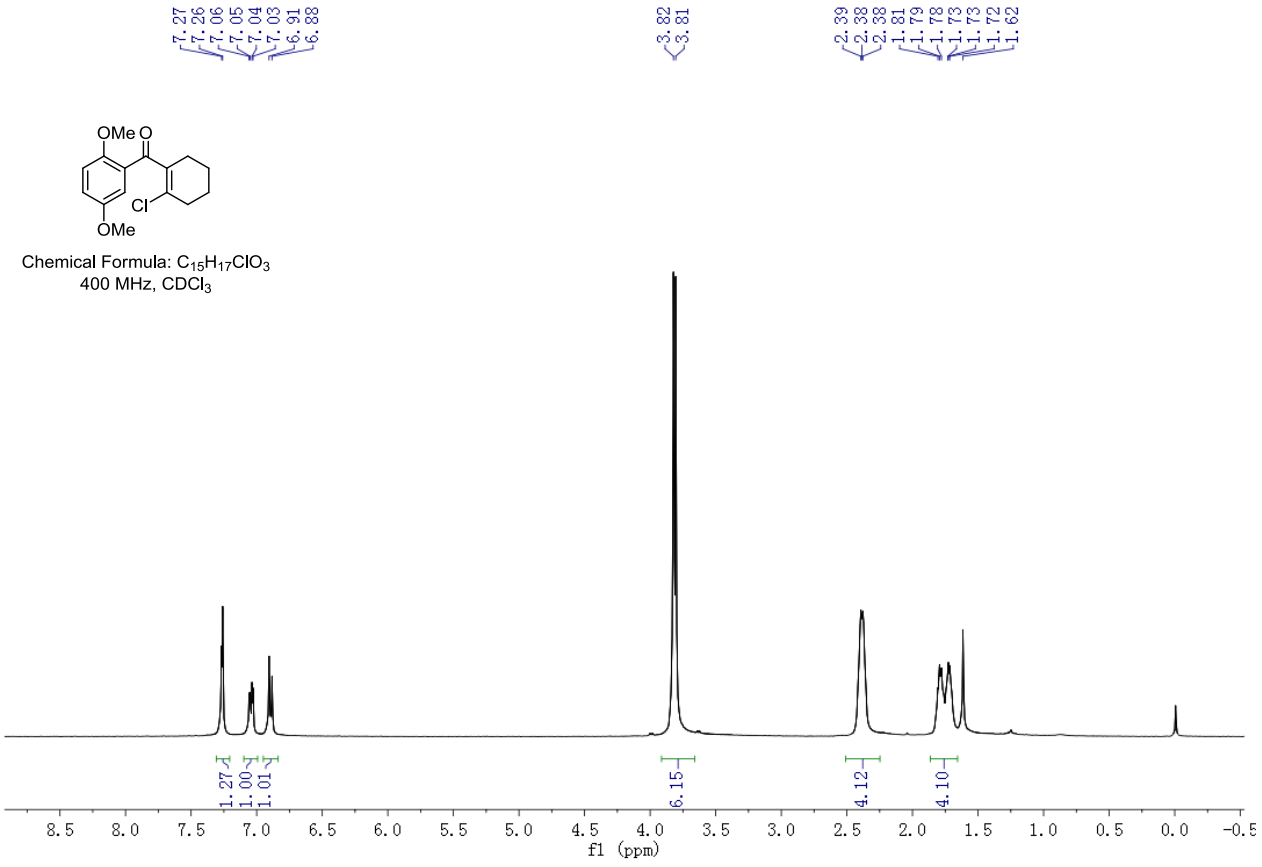
Chemical Formula: $C_{15}H_{17}ClO_3$
100 MHz, $CDCl_3$

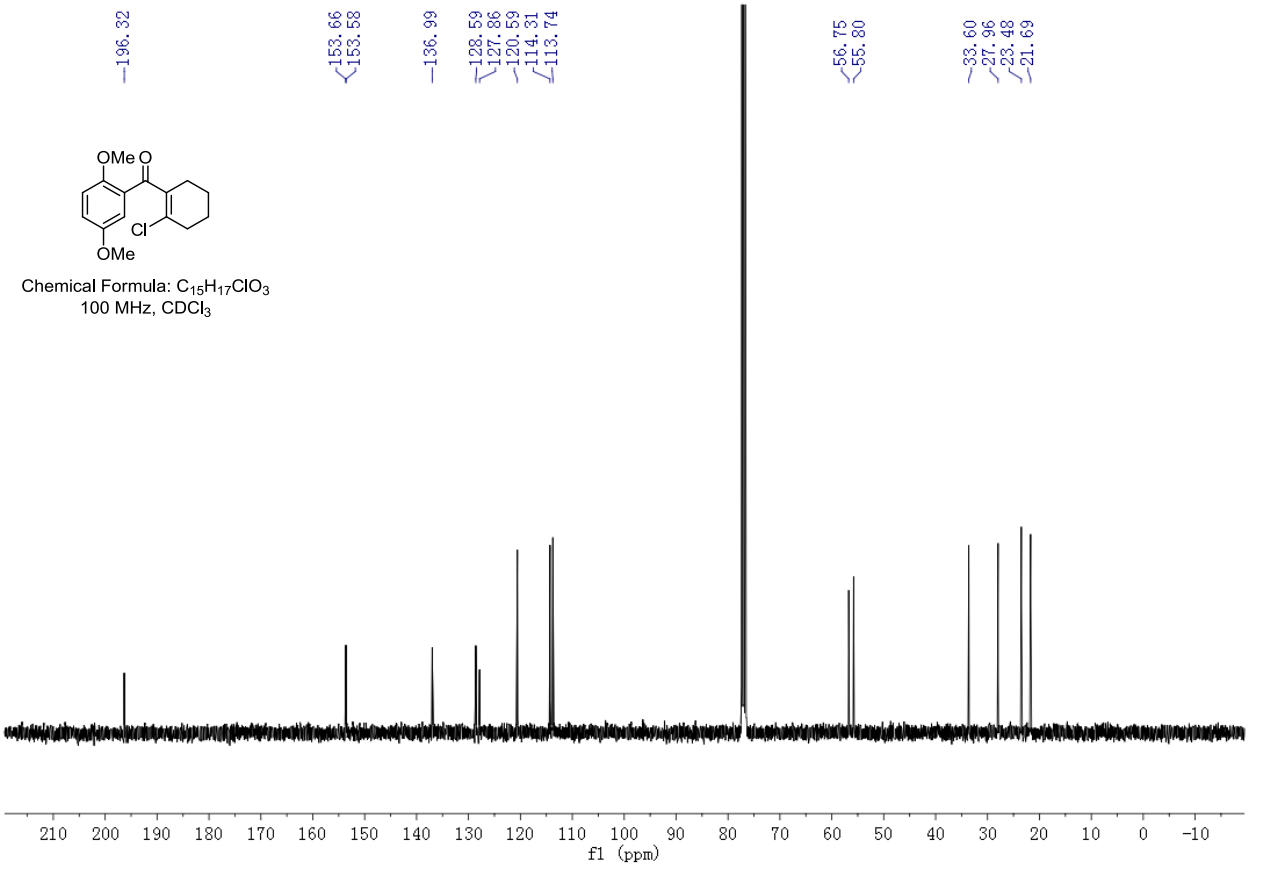

11.90
7.61
7.61
7.59
7.59
7.52
7.51
7.50
7.48
7.48
7.26
7.02
7.00
6.93
6.91
6.89
2.51
2.50
2.49
2.49
2.48
2.47
2.46
2.38
2.37
2.36
2.36
2.35
2.34
1.88
1.87
1.87
1.86
1.85
1.84
1.84
1.81
1.80
1.79
1.79
1.78
1.77
1.76
OH
O
Cl
Chemical Formula: C13H13ClO2
400 MHz, CDCl3
0.95
1.00
1.01
0.98
1.01
2.10
2.09
4.17
f1 (ppm)

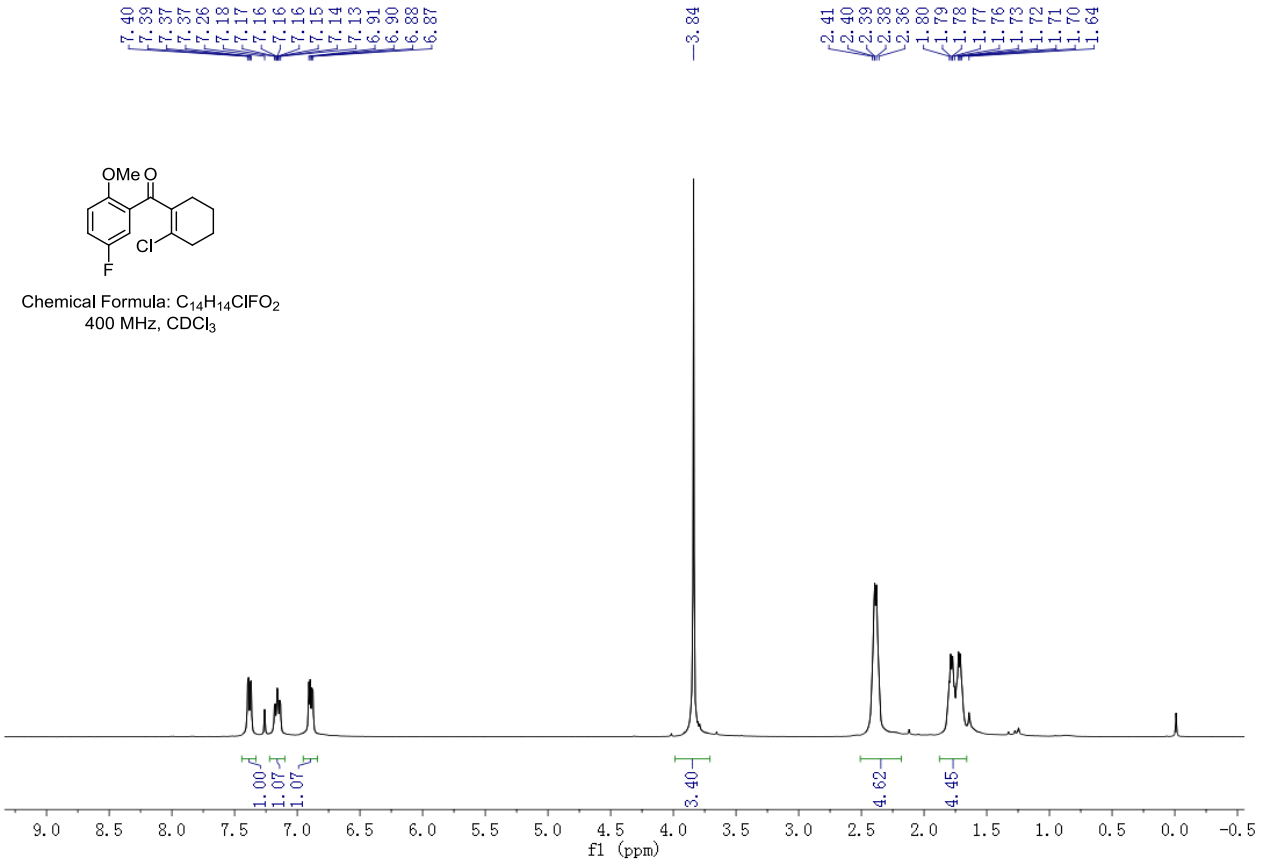

202.90
163.14
136.92
133.24
132.42
130.19
119.24
118.38
118.01
32.94
28.78
23.34
21.32
OH
O
Cl
Chemical Formula: C13H13ClO2
100 MHz, CDCl3
f1 (ppm)


7.74
7.73
7.72
7.71
7.58
7.58
7.56
7.56
7.54
7.54
7.35
7.35
7.33
7.31
7.31
7.26
7.15
7.13
2.48
2.47
2.46
2.46
2.45
2.44
2.38
2.37
2.36
2.36
2.35
2.34
1.85
1.83
1.82
1.81
1.81
1.80
1.79
1.76
1.75
1.74
1.74
1.73
1.72
1.71
OAc O
Cl
Chemical Formula: C15H15ClO3
400 MHz, CDCl3
1.00
1.06
1.12
1.01
2.27
5.26
4.47
f1 (ppm)

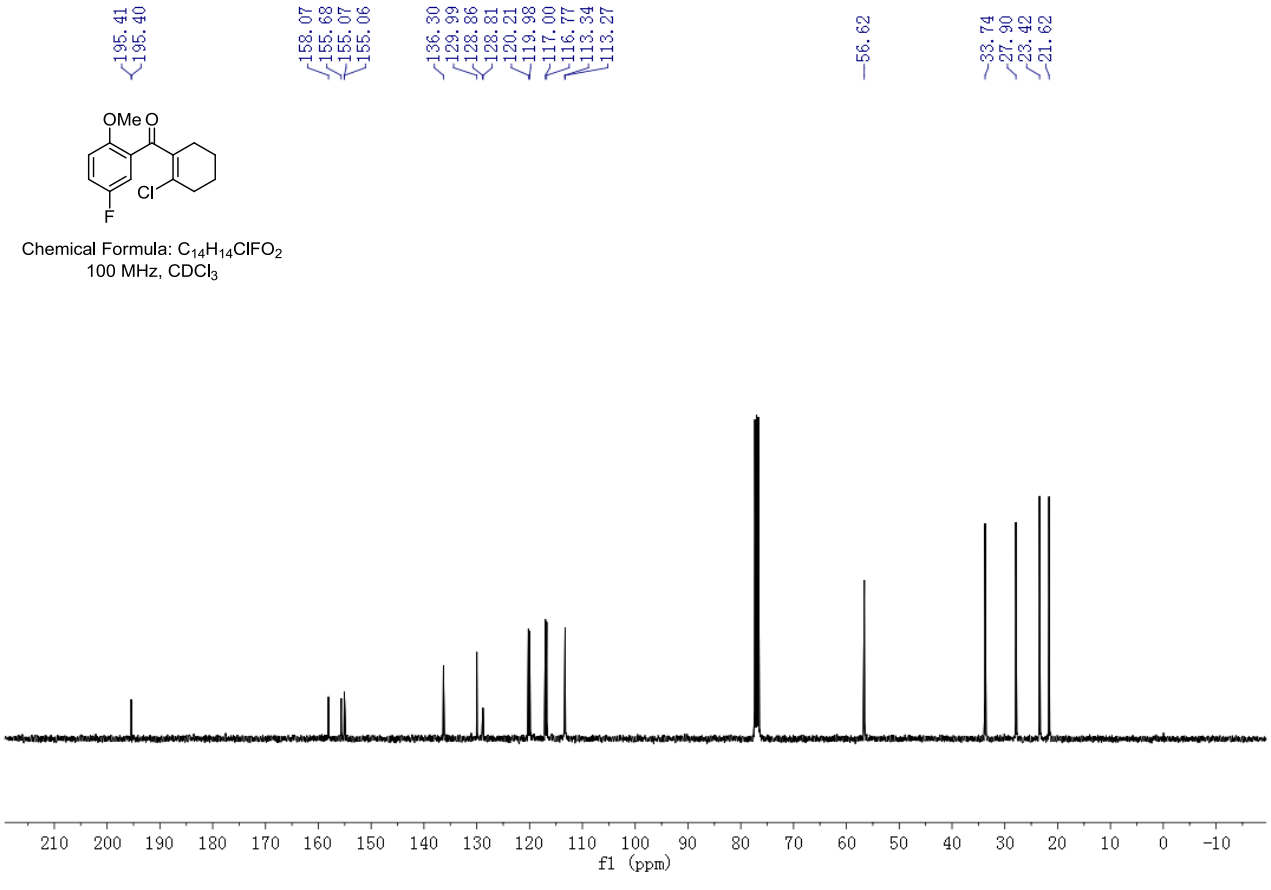

195.28
169.34
149.70
135.06
133.72
132.10
131.58
129.22
126.09
123.91
33.68
28.35
23.36
21.44
21.00
OAc O
Cl
Chemical Formula: C15H15ClO3
100 MHz, CDCl3
f1 (ppm)


7.27
7.26
7.06
7.05
7.04
7.03
6.91
6.88
3.82
3.81
2.39
2.38
2.38
1.81
1.79
1.78
1.73
1.73
1.72
1.62
OMe O
Cl
OMe
Chemical Formula: C15H17ClO3
400 MHz, CDCl3
1.27
1.00
1.01
6.15
4.12
4.10
f1 (ppm)

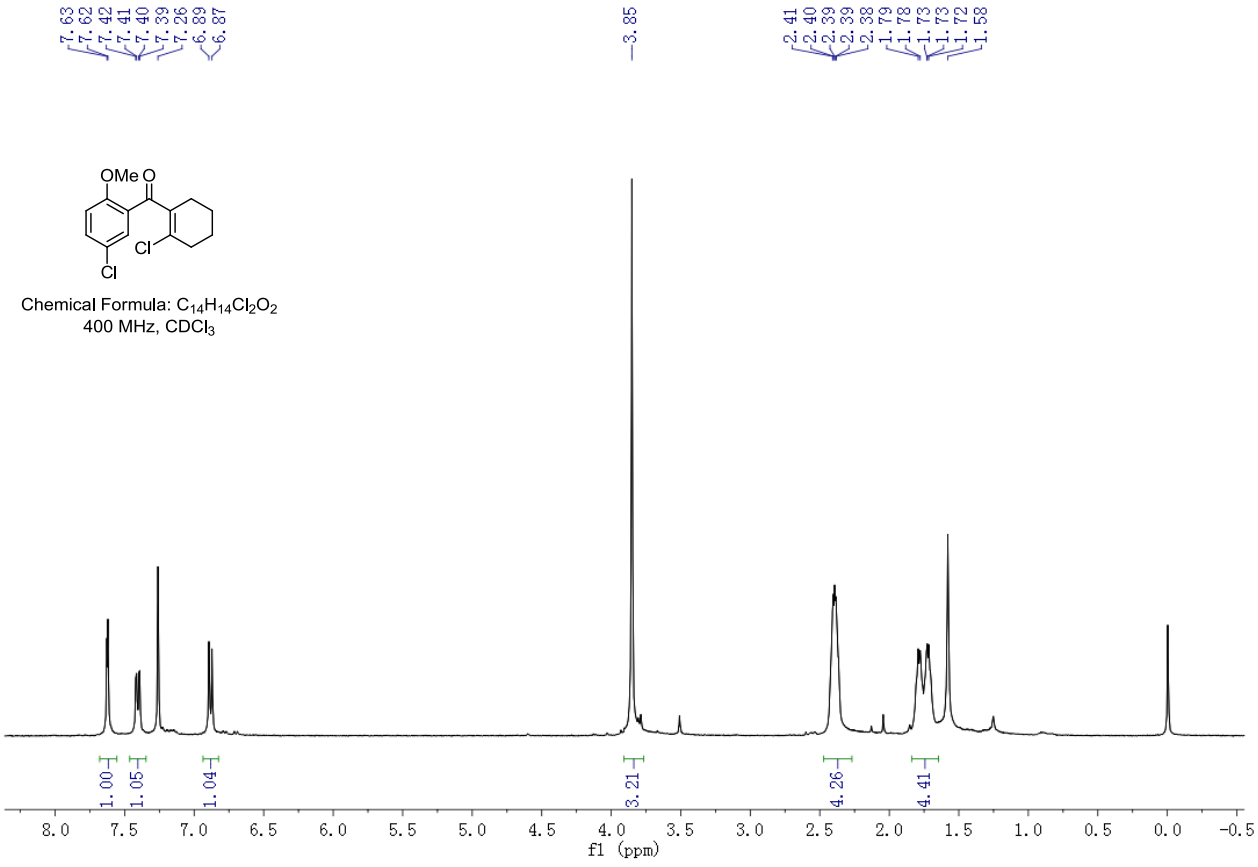

196.32
153.66
153.58
136.99
128.59
127.86
120.59
114.31
113.74
56.75
55.80
33.60
27.96
23.48
21.69
OMe O
Cl
OMe
Chemical Formula: C15H17ClO3
100 MHz, CDCl3
f1 (ppm)

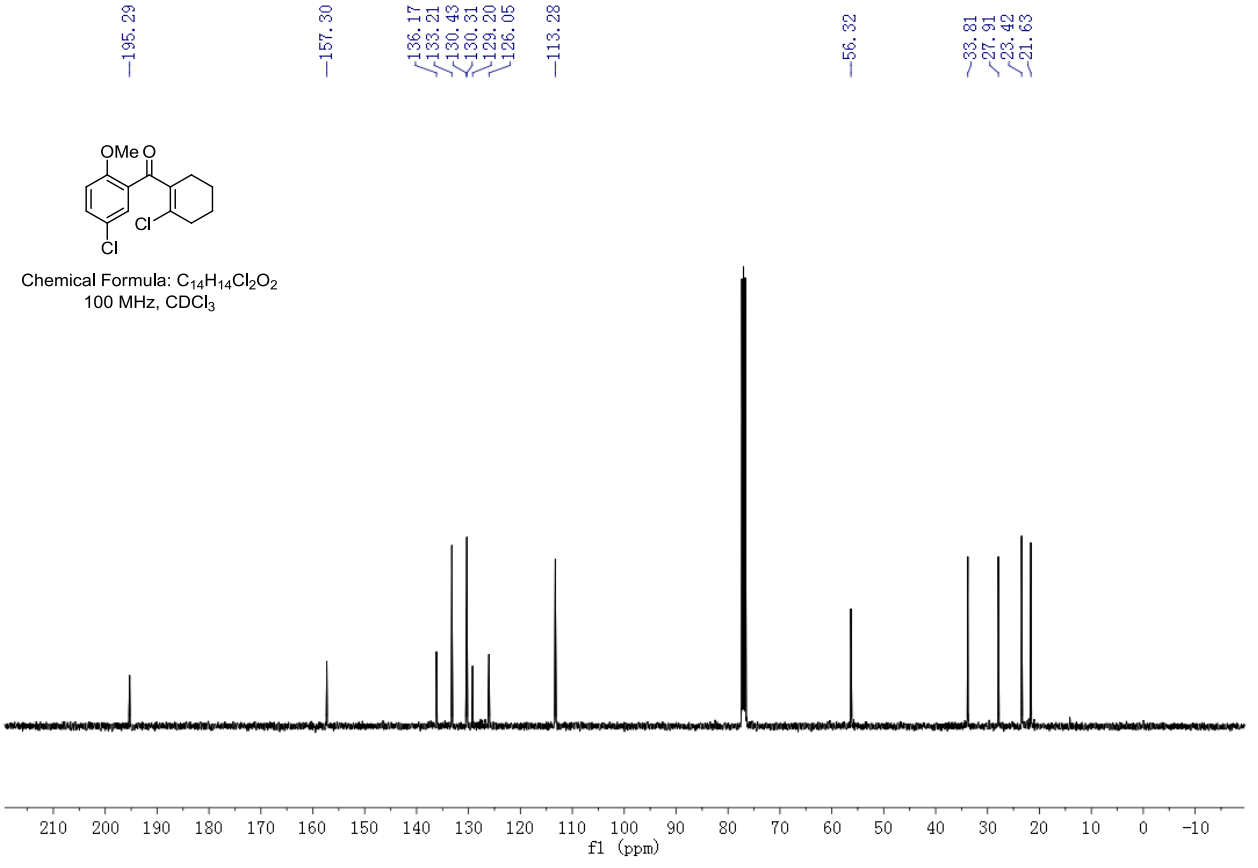


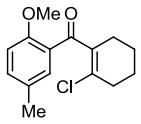
Chemical Formula: $C_{14}H_{14}ClFO_2$
400 MHz, $CDCl_3$



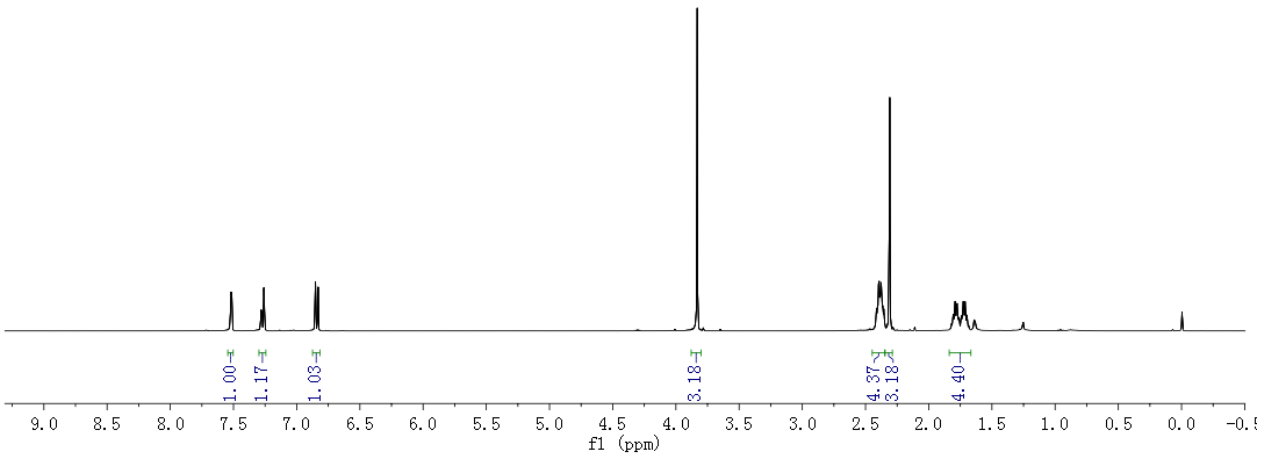
Chemical Formula: $C_{14}H_{14}ClFO_2$
100 MHz, $CDCl_3$

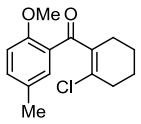

7.63
7.62
7.42
7.41
7.40
7.39
7.26
6.89
6.87
3.85
2.41
2.40
2.39
2.39
2.38
1.79
1.78
1.73
1.73
1.72
1.58
OMe O
Cl
Cl
Chemical Formula: C14H14Cl2O2
400 MHz, CDCl3
1.00
1.05
1.04
3.21
4.26
4.41
f1 (ppm)


195.29
157.30
136.17
133.21
130.43
130.31
129.20
126.05
113.28
56.32
33.81
27.91
23.42
21.63
OMe O
Cl
Cl
Chemical Formula: C14H14Cl2O2
100 MHz, CDCl3
f1 (ppm)

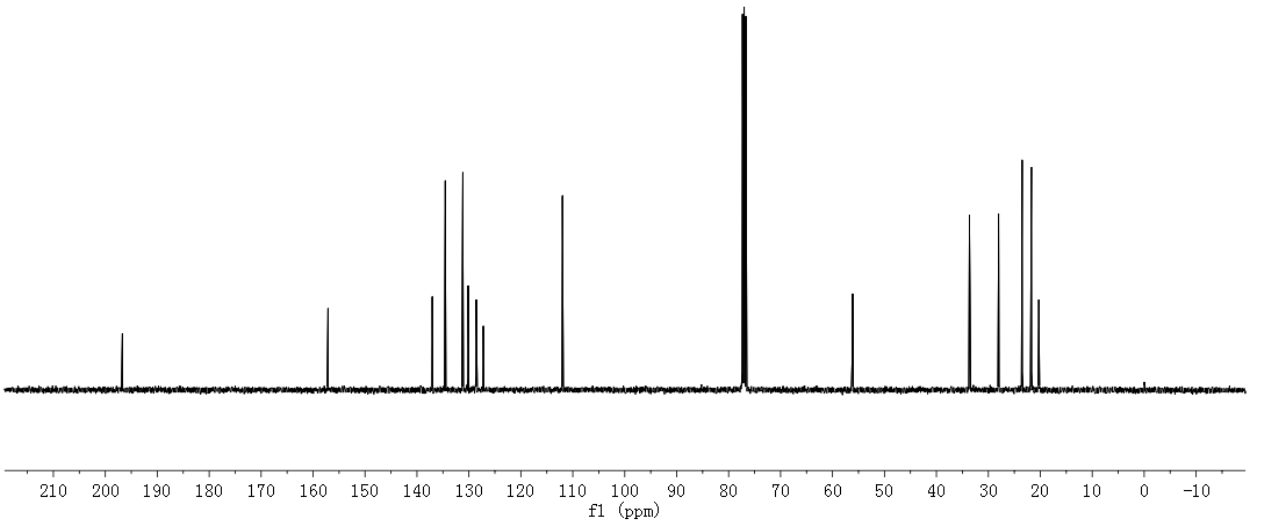


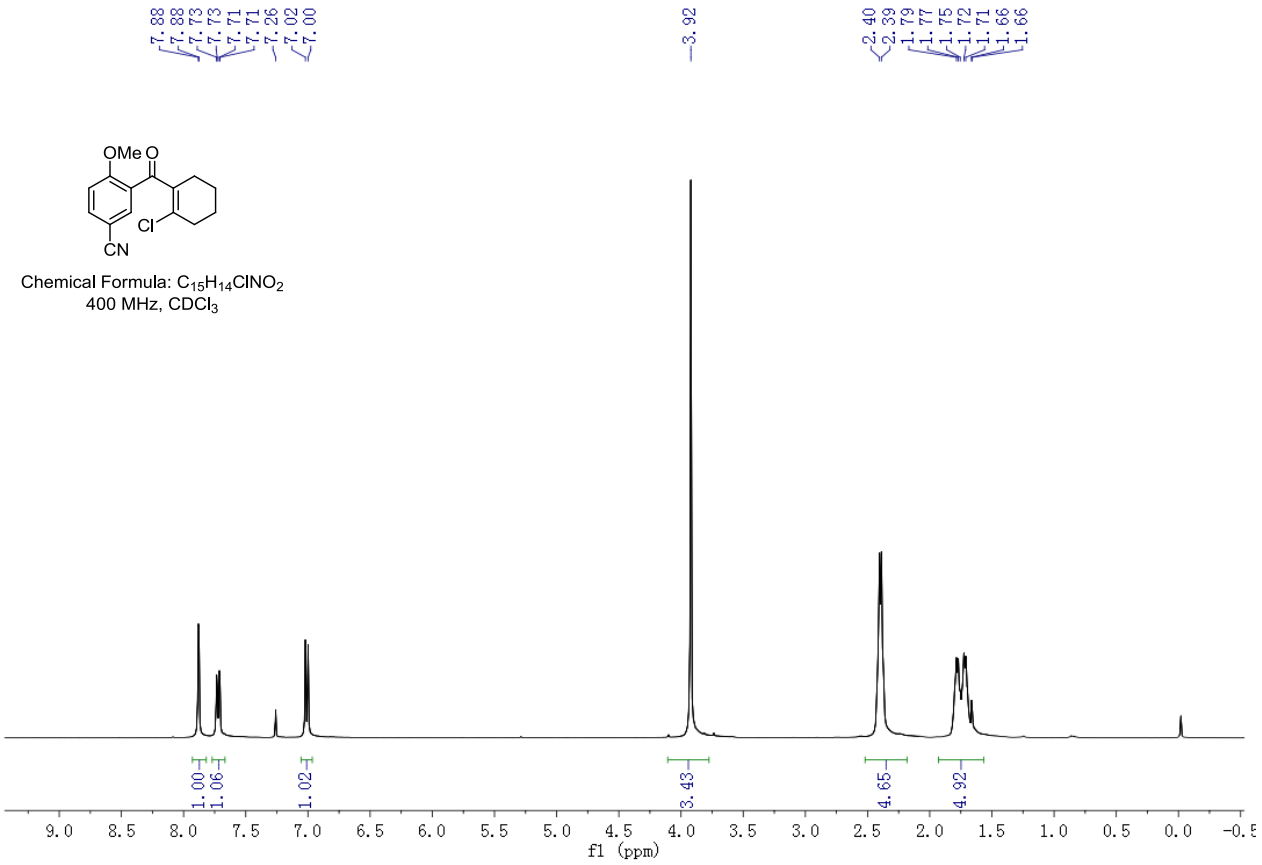
Chemical Formula: $C_{15}H_{17}ClO_2$
400 MHz, $CDCl_3$



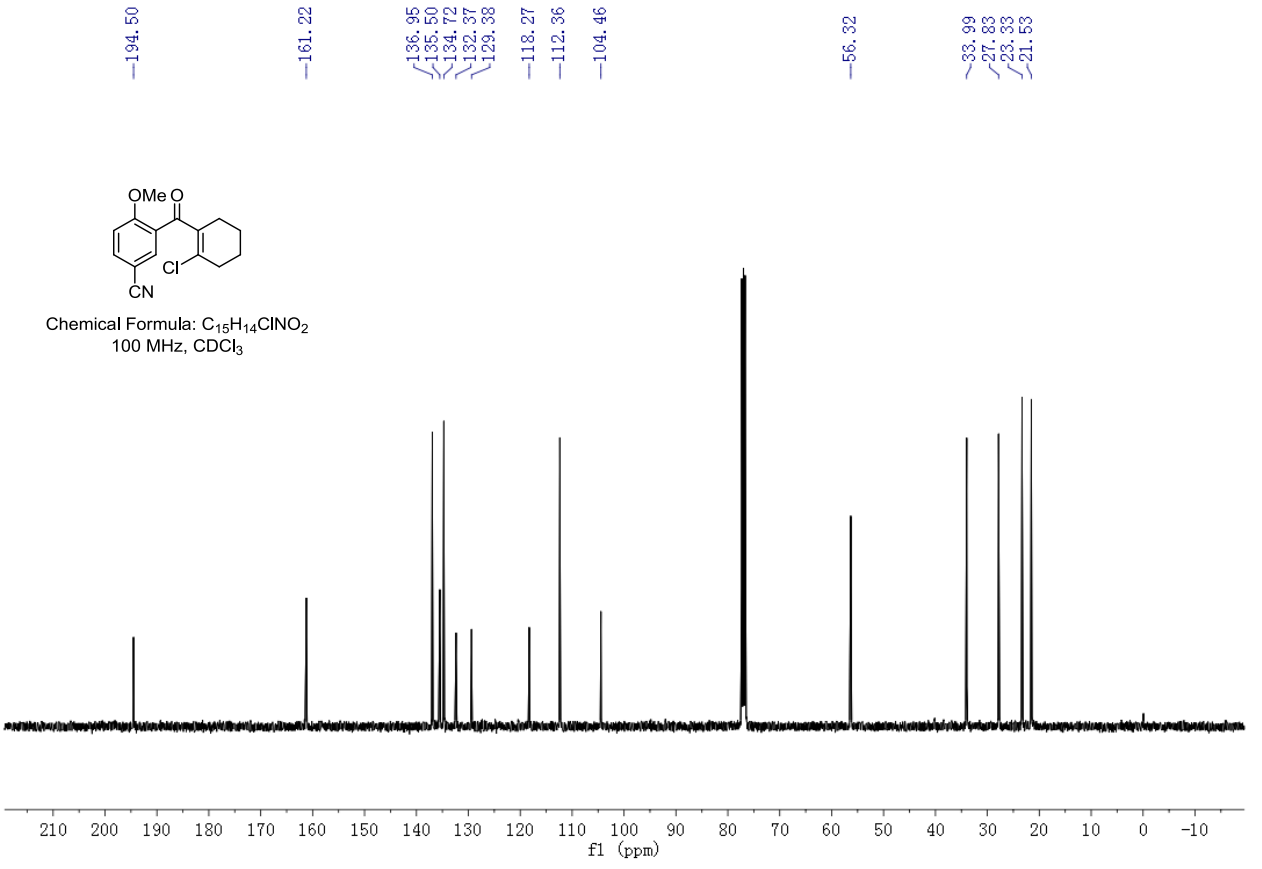


Chemical Formula: $C_{15}H_{17}ClO_2$
100 MHz, $CDCl_3$

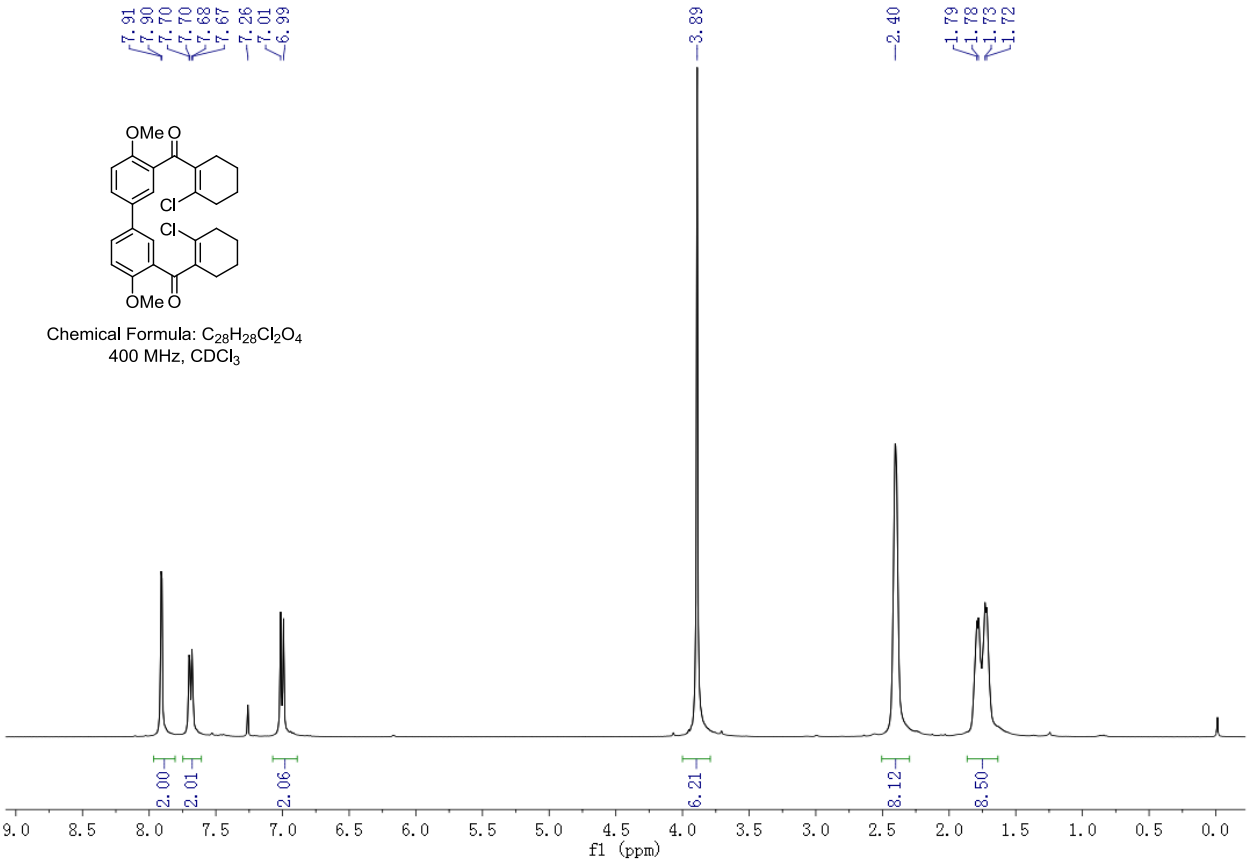




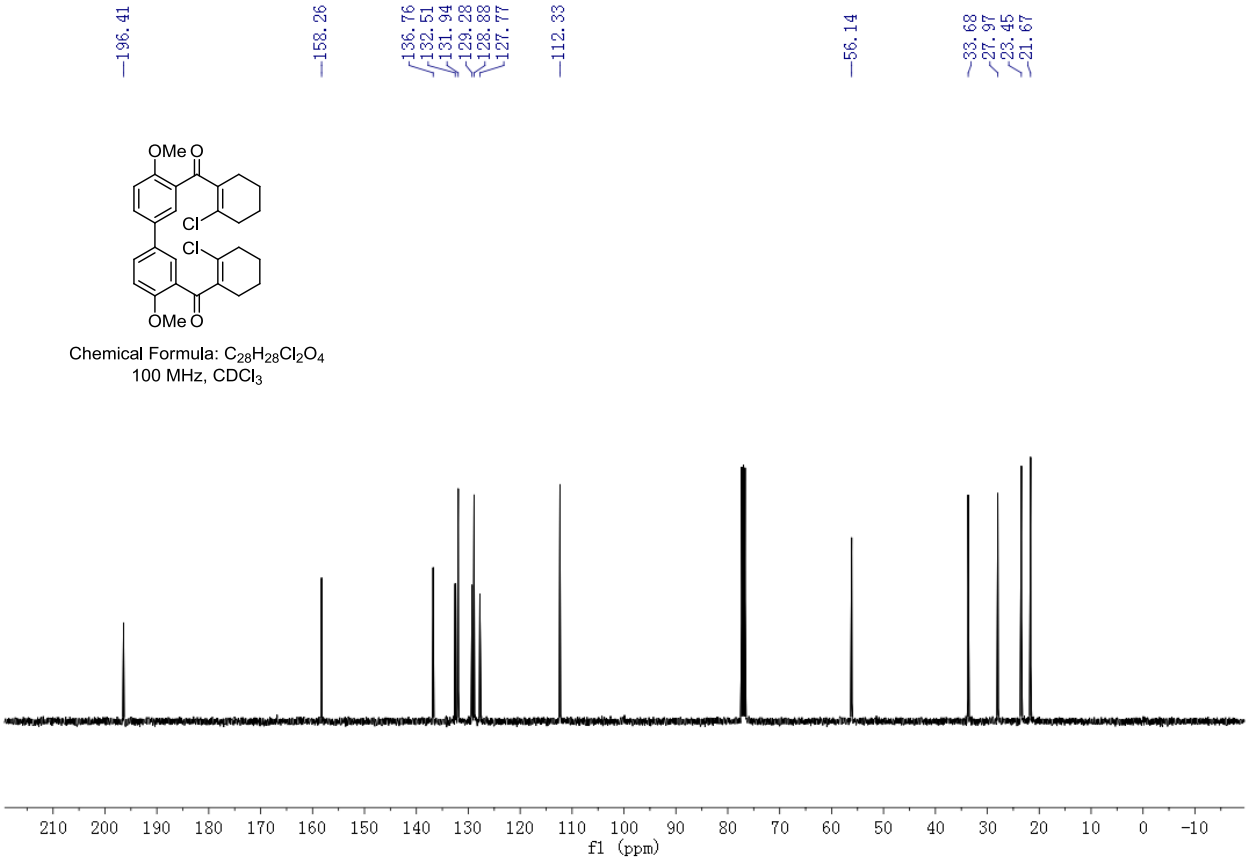
Chemical Formula: $C_{15}H_{14}ClNO_2$
400 MHz, $CDCl_3$



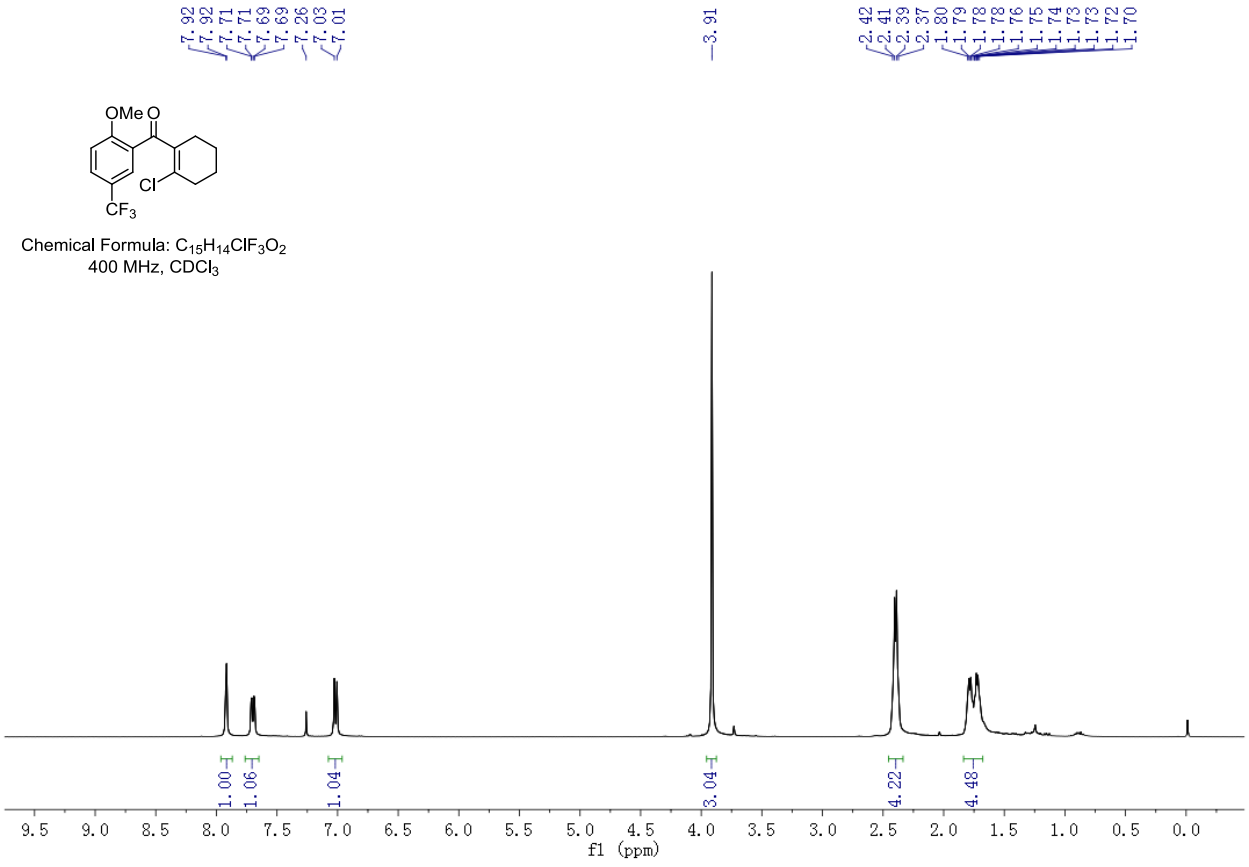
Chemical Formula: $C_{15}H_{14}ClNO_2$
100 MHz, $CDCl_3$



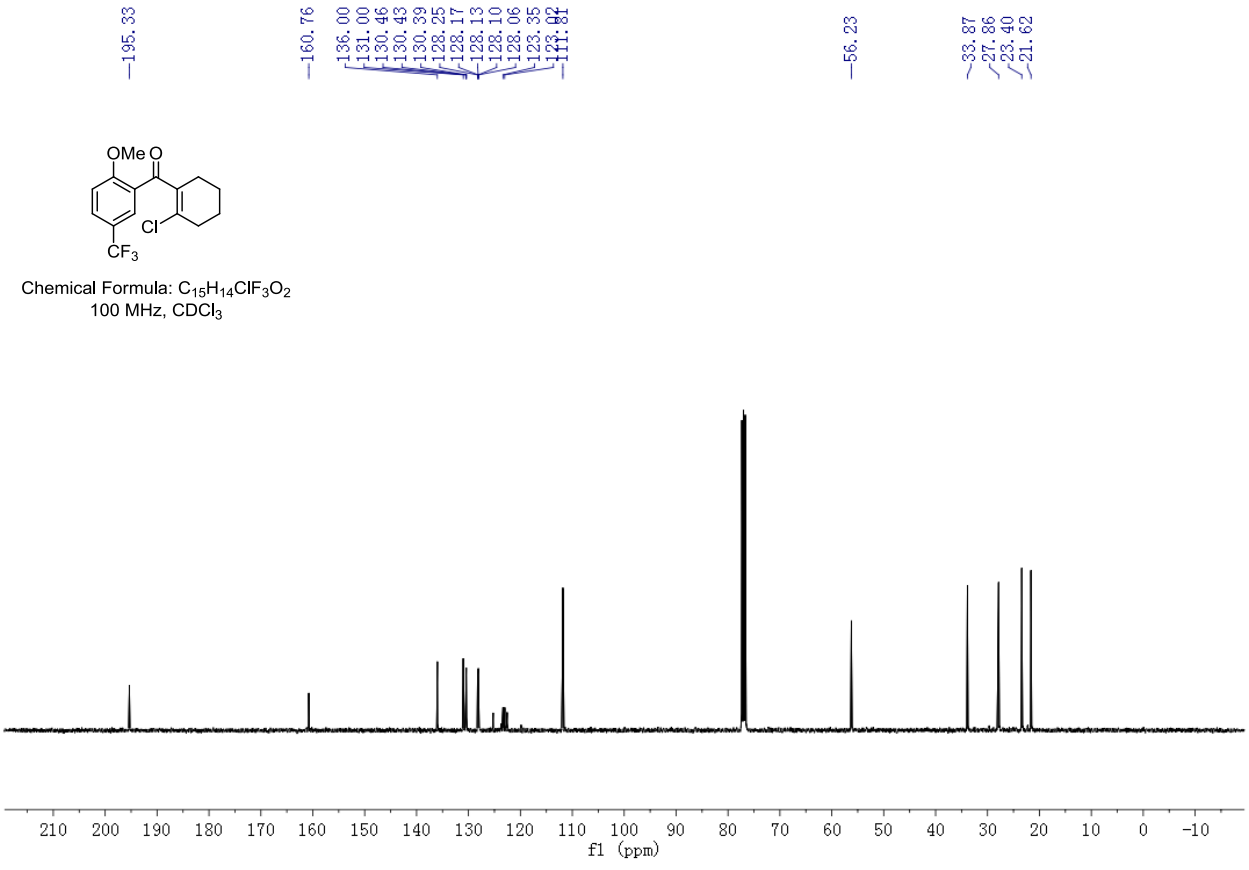
Chemical Formula: $C_{28}H_{28}Cl_2O_4$
400 MHz, $CDCl_3$



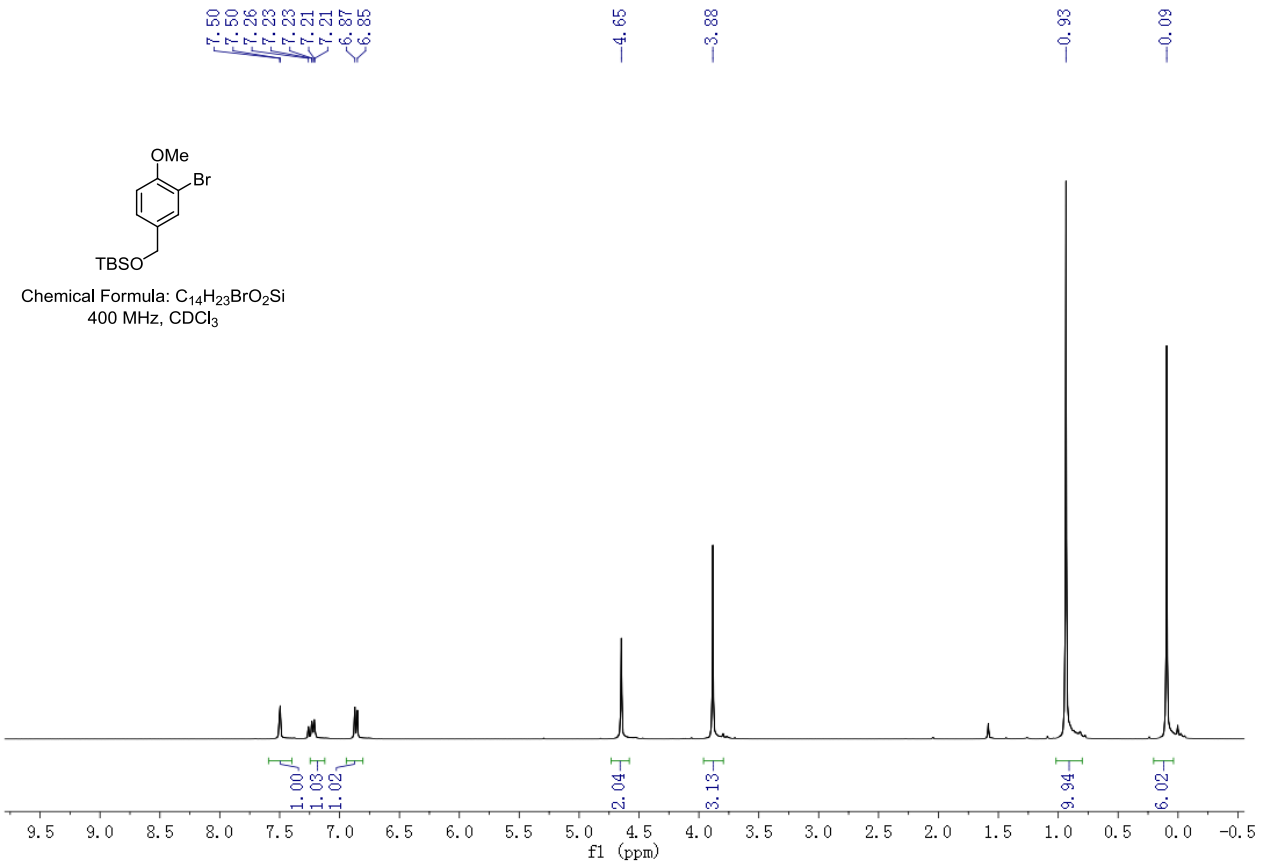
Chemical Formula: $C_{28}H_{28}Cl_2O_4$
100 MHz, $CDCl_3$

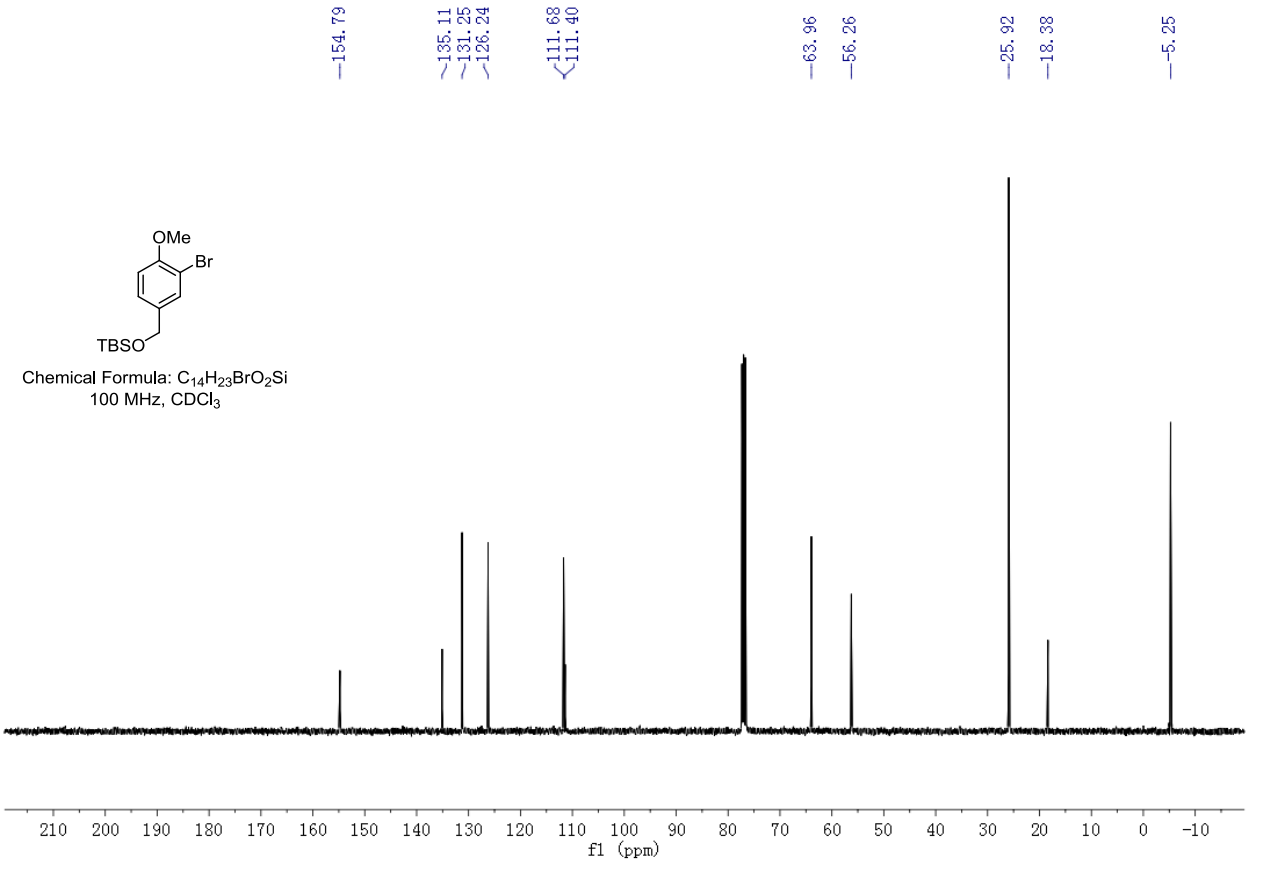


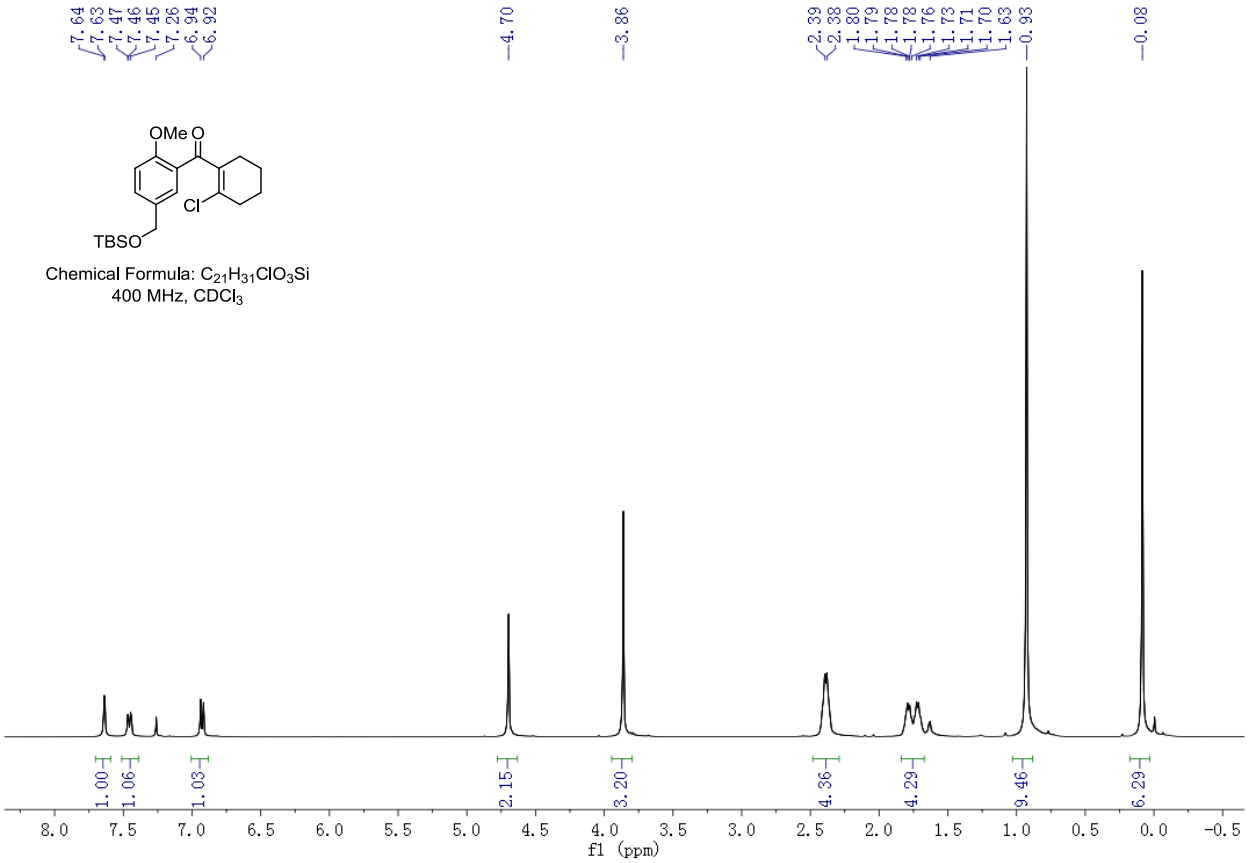
Chemical Formula: $C_{15}H_{14}ClF_3O_2$
400 MHz, $CDCl_3$

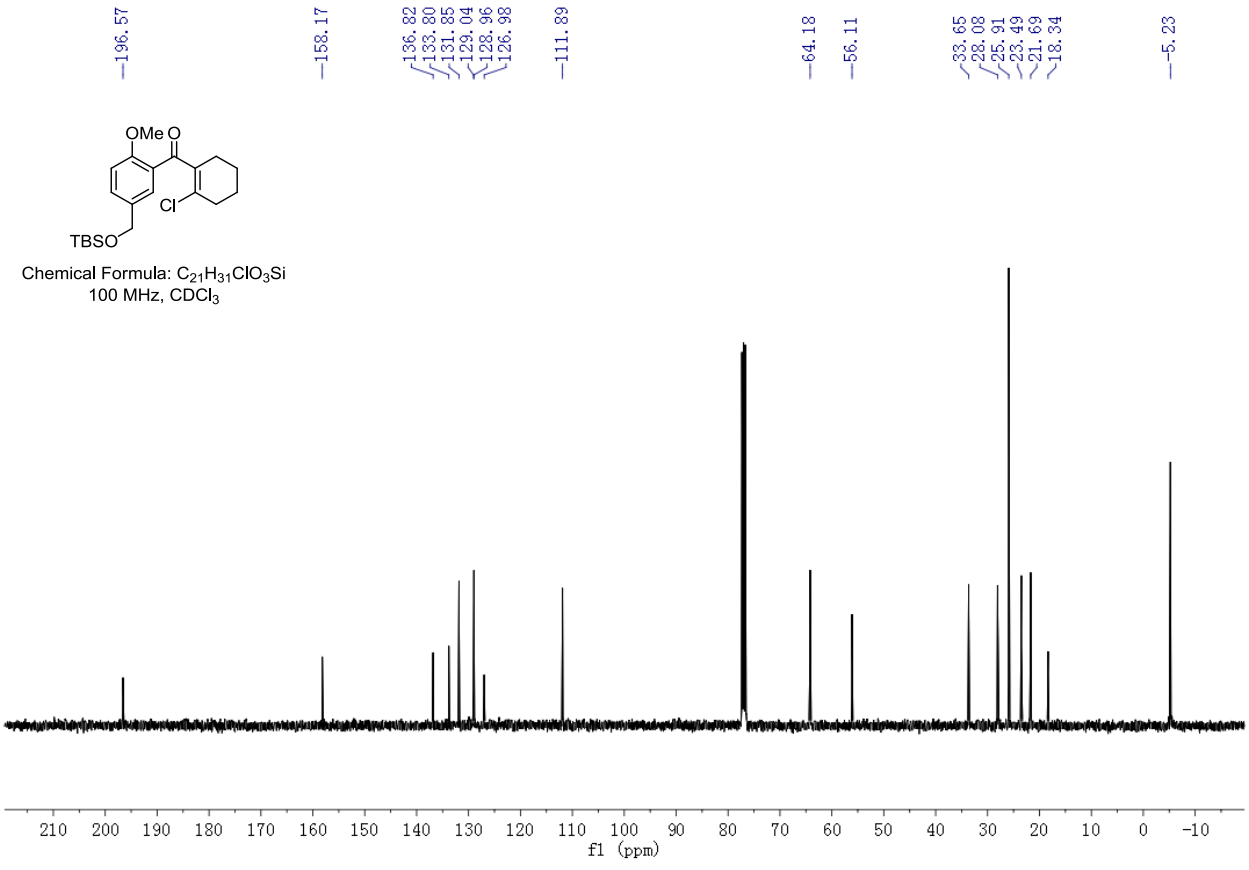


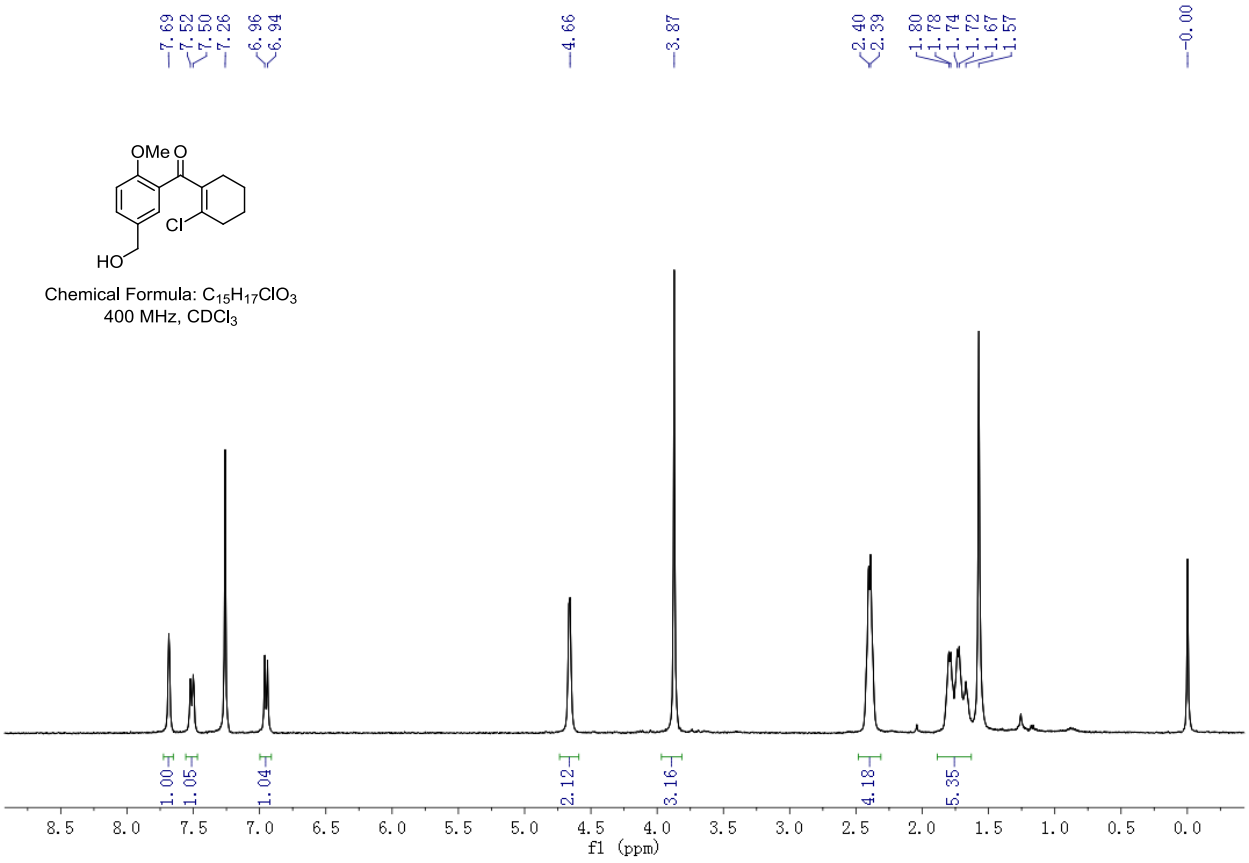
Chemical Formula: $C_{15}H_{14}ClF_3O_2$
100 MHz, $CDCl_3$

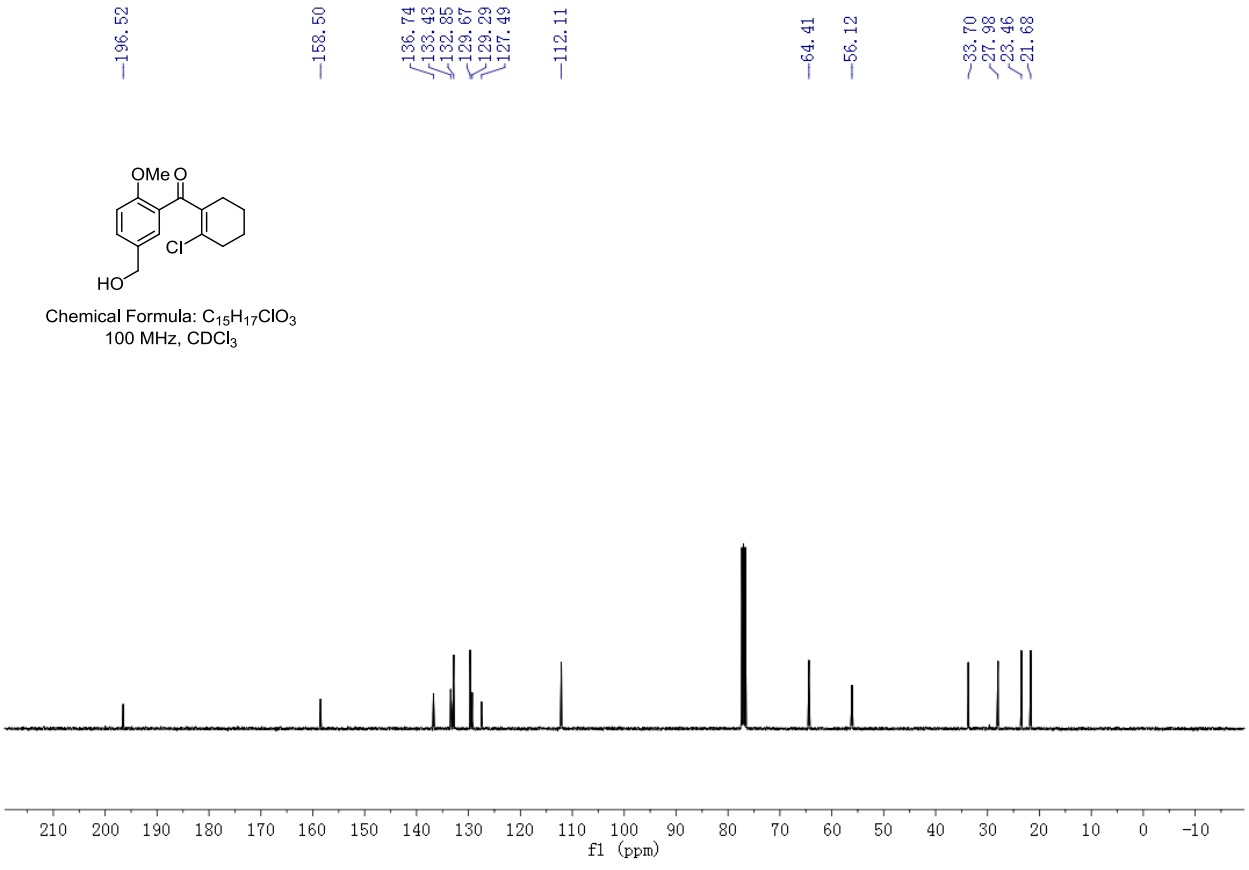

7.50
7.50
7.26
7.23
7.23
7.21
7.21
6.87
6.85
4.65
3.88
0.93
0.09
OMe
Br
TBSO
Chemical Formula: C14H23BrO2Si
400 MHz, CDCl3
1.00
1.03
1.02
2.04
3.13
9.94
6.02
f1 (ppm)

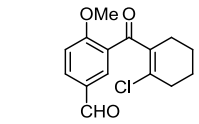

154.79
135.11
131.25
126.24
111.68
111.40
63.96
56.26
25.92
18.38
5.25
OMe
Br
TBSO
Chemical Formula: C14H23BrO2Si
100 MHz, CDCl3
f1 (ppm)


7.64
7.63
7.47
7.46
7.45
7.26
6.94
6.92
4.70
3.86
2.39
2.38
1.80
1.79
1.78
1.78
1.76
1.73
1.71
1.70
1.63
0.93
0.08
OMe O
Cl
TBSO
Chemical Formula: C21H31ClO3Si
400 MHz, CDCl3
1.00
1.06
1.03
2.15
3.20
4.36
4.29
9.46
6.29
f1 (ppm)

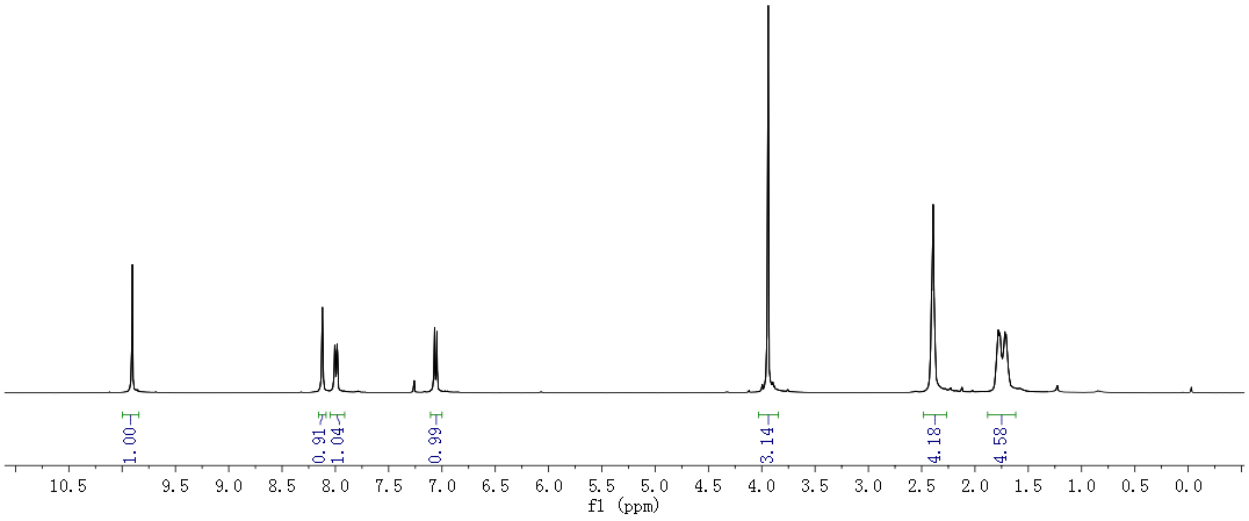

196.57
158.17
136.82
133.80
131.85
129.04
128.96
126.98
111.89
64.18
56.11
33.65
28.08
25.91
23.49
21.69
18.34
-5.23
OMe O
Cl
TBSO
Chemical Formula: C21H31ClO3Si
100 MHz, CDCl3
f1 (ppm)

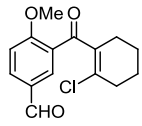

7.69
7.52
7.50
7.26
6.96
6.94
4.66
3.87
2.40
2.39
1.80
1.78
1.74
1.72
1.67
1.57
0.00
OMe O
Cl
HO
Chemical Formula: C15H17ClO3
400 MHz, CDCl3
1.00
1.05
1.04
2.12
3.16
4.18
5.35
f1 (ppm)


196.52
158.50
136.74
133.43
132.85
129.67
129.29
127.49
112.11
64.41
56.12
33.70
27.98
23.46
21.68
OMe O
Cl
HO
Chemical Formula: C15H17ClO3
100 MHz, CDCl3
f1 (ppm)

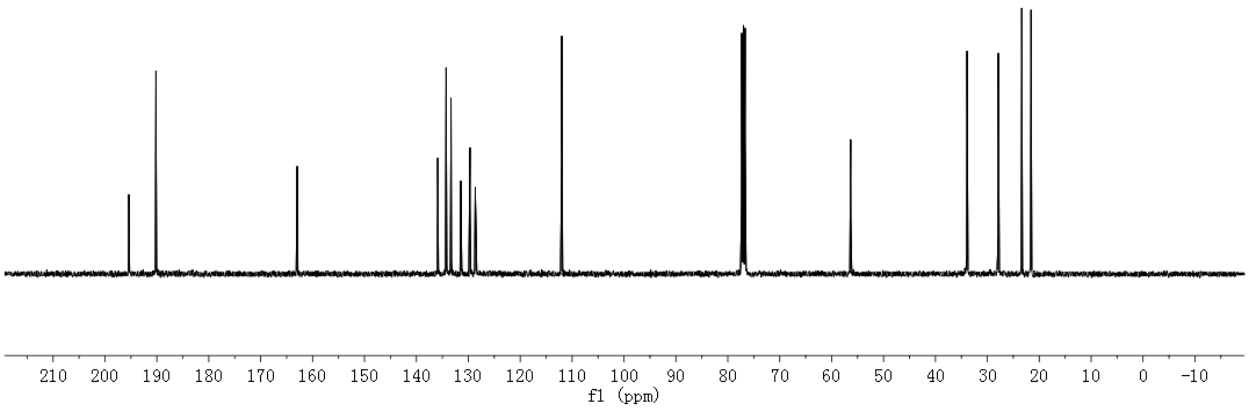


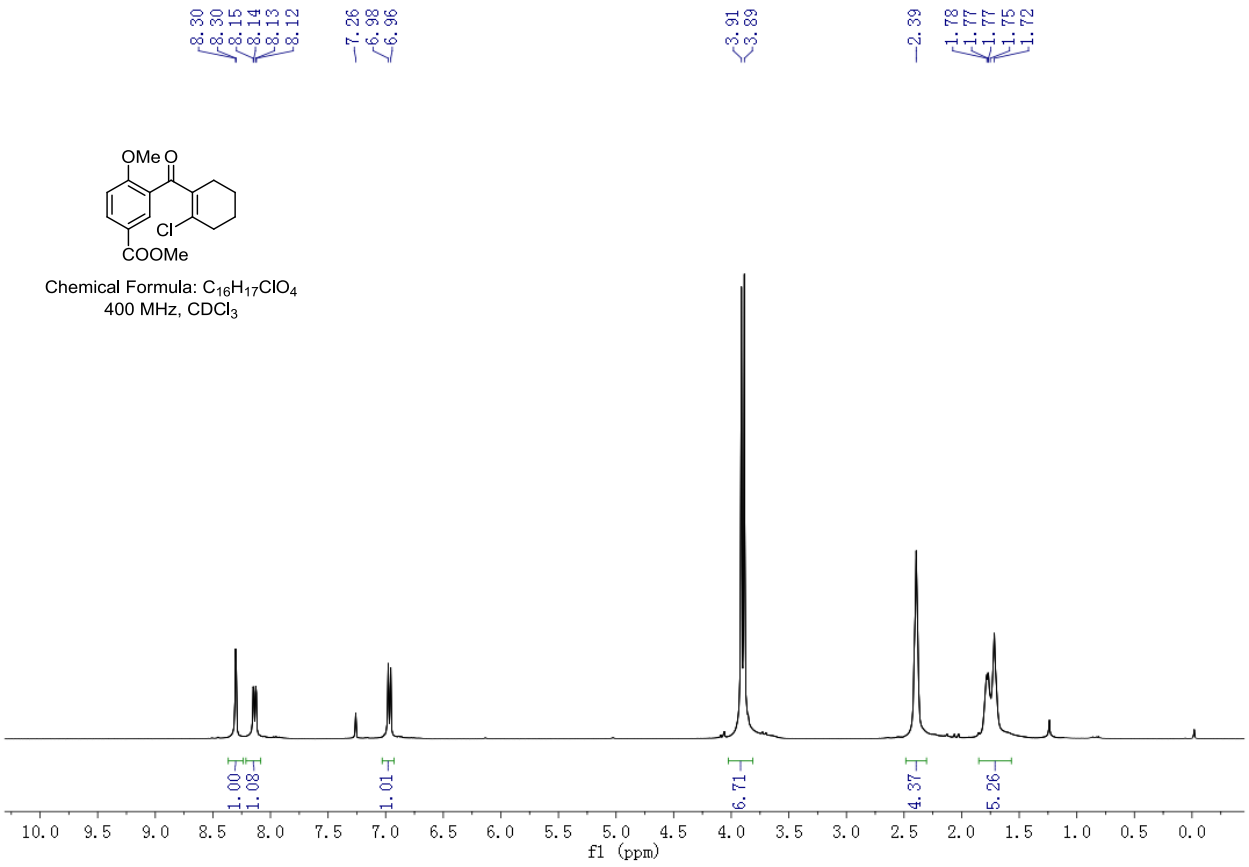
Chemical Formula: $C_{15}H_{15}ClO_3$
400 MHz, $CDCl_3$

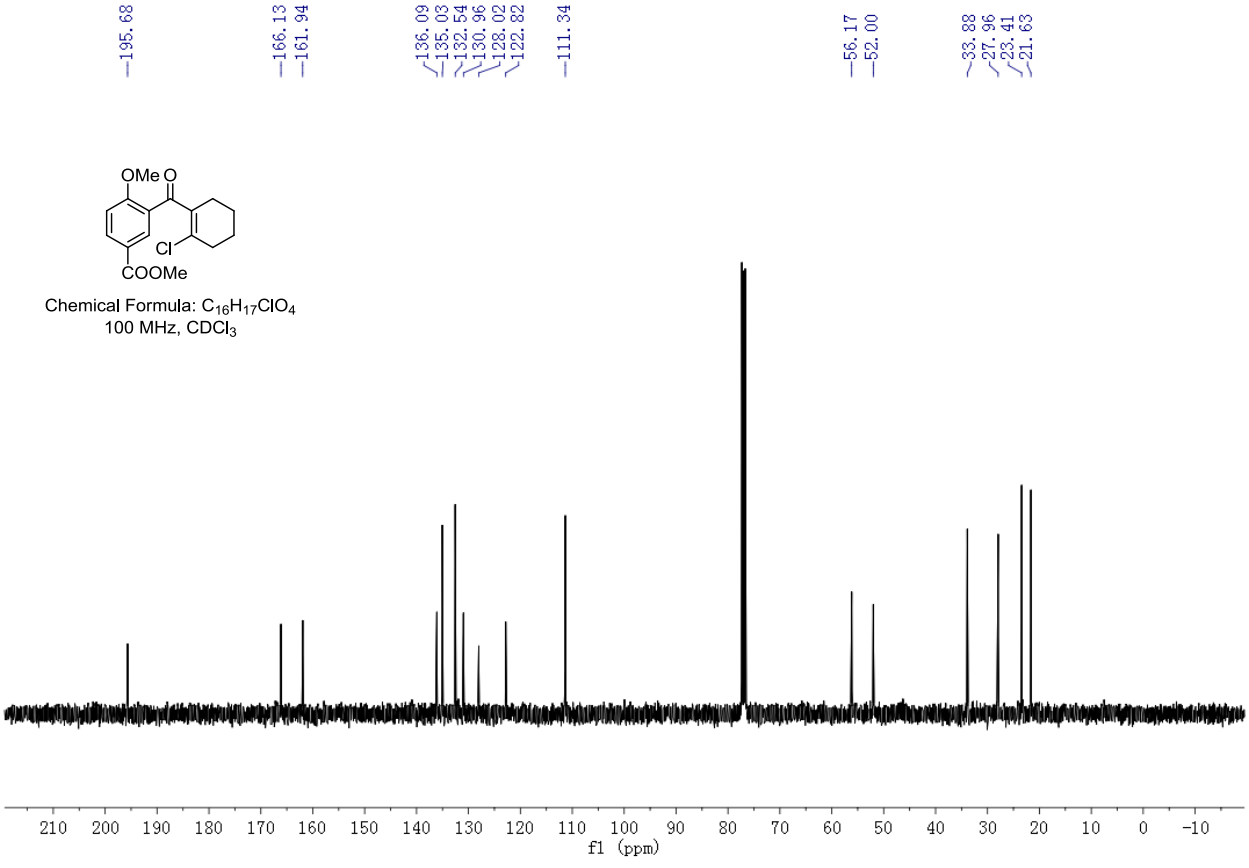


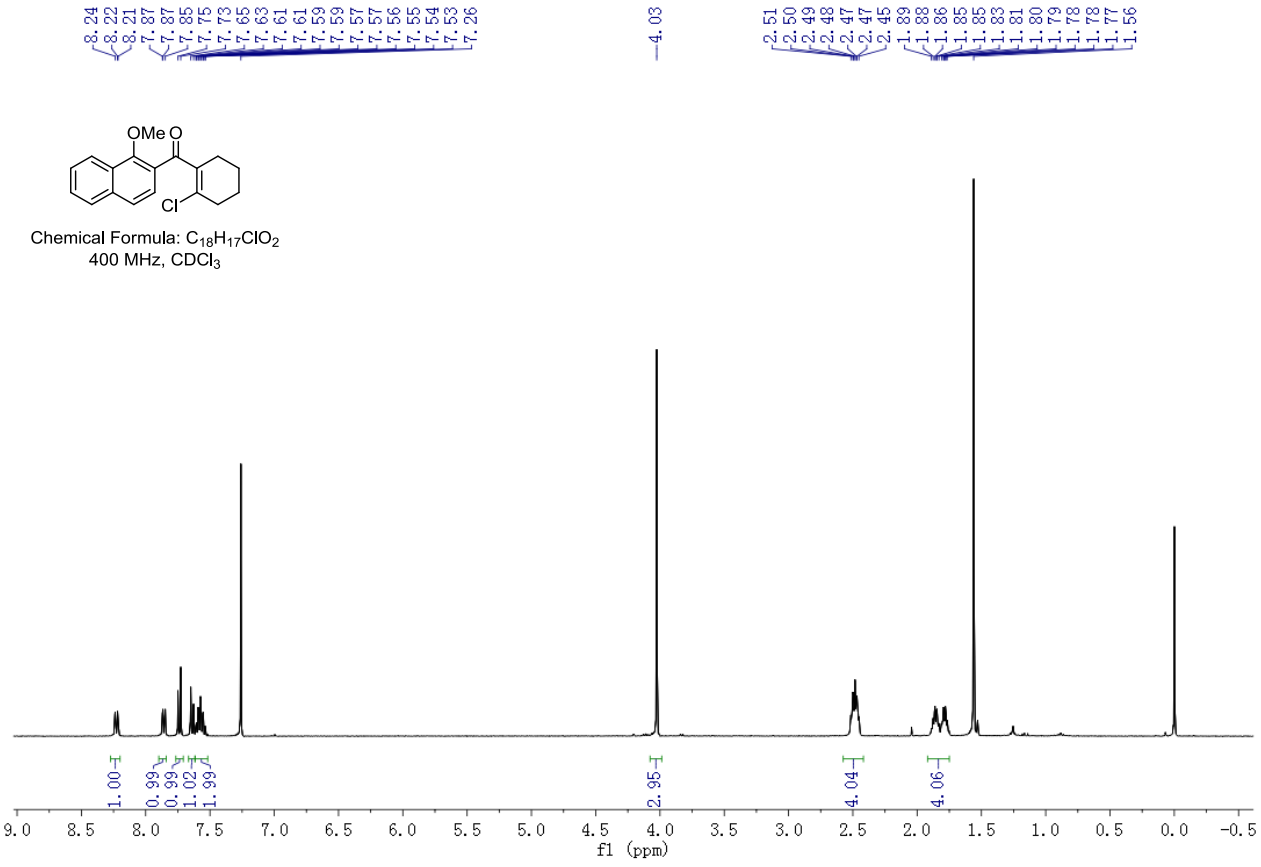


Chemical Formula: $C_{15}H_{15}ClO_3$
100 MHz, $CDCl_3$

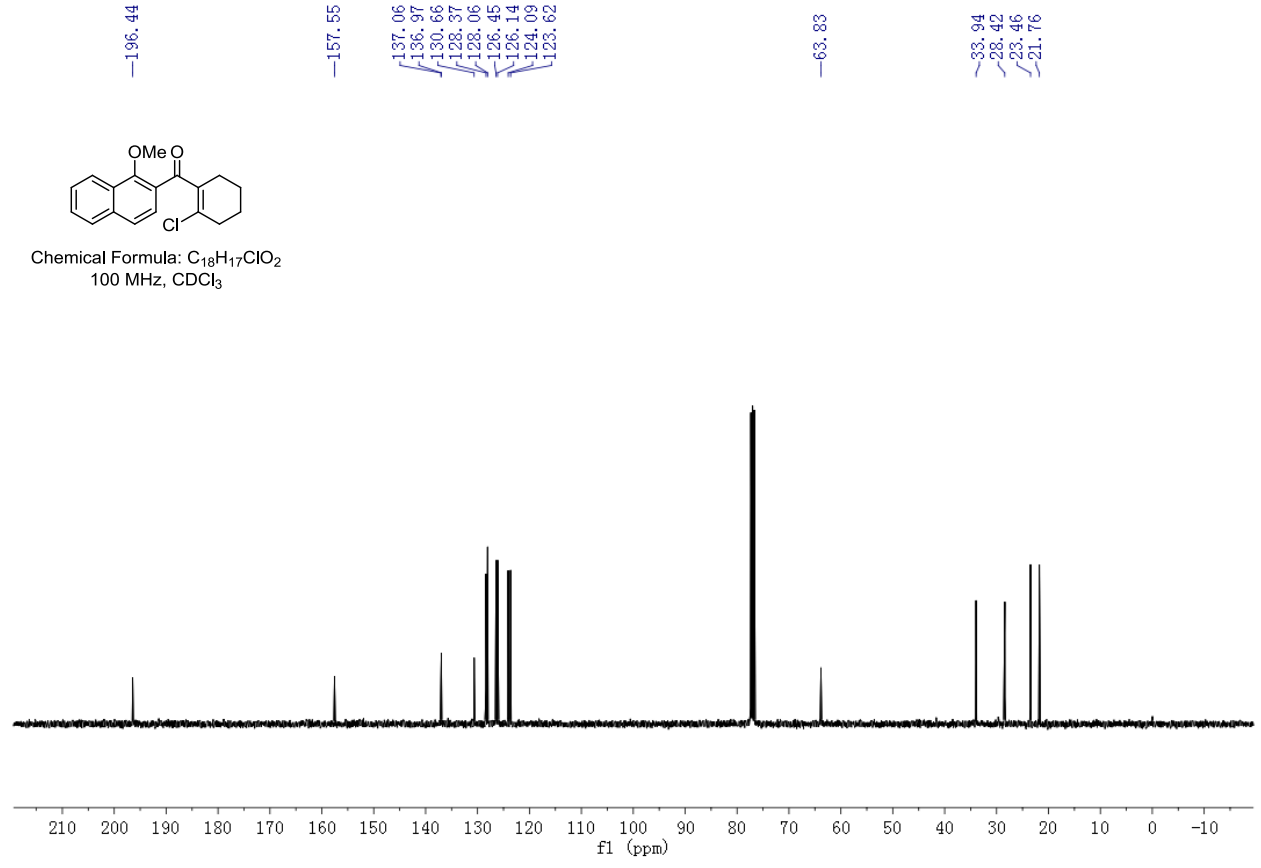



8.30
8.30
8.15
8.14
8.13
8.12
7.26
6.98
6.96
3.91
3.89
2.39
1.78
1.77
1.77
1.75
1.72
OMe O
Cl
COOMe
Chemical Formula: C16H17ClO4
400 MHz, CDCl3
1.00
1.08
1.01
6.71
4.37
5.26
f1 (ppm)

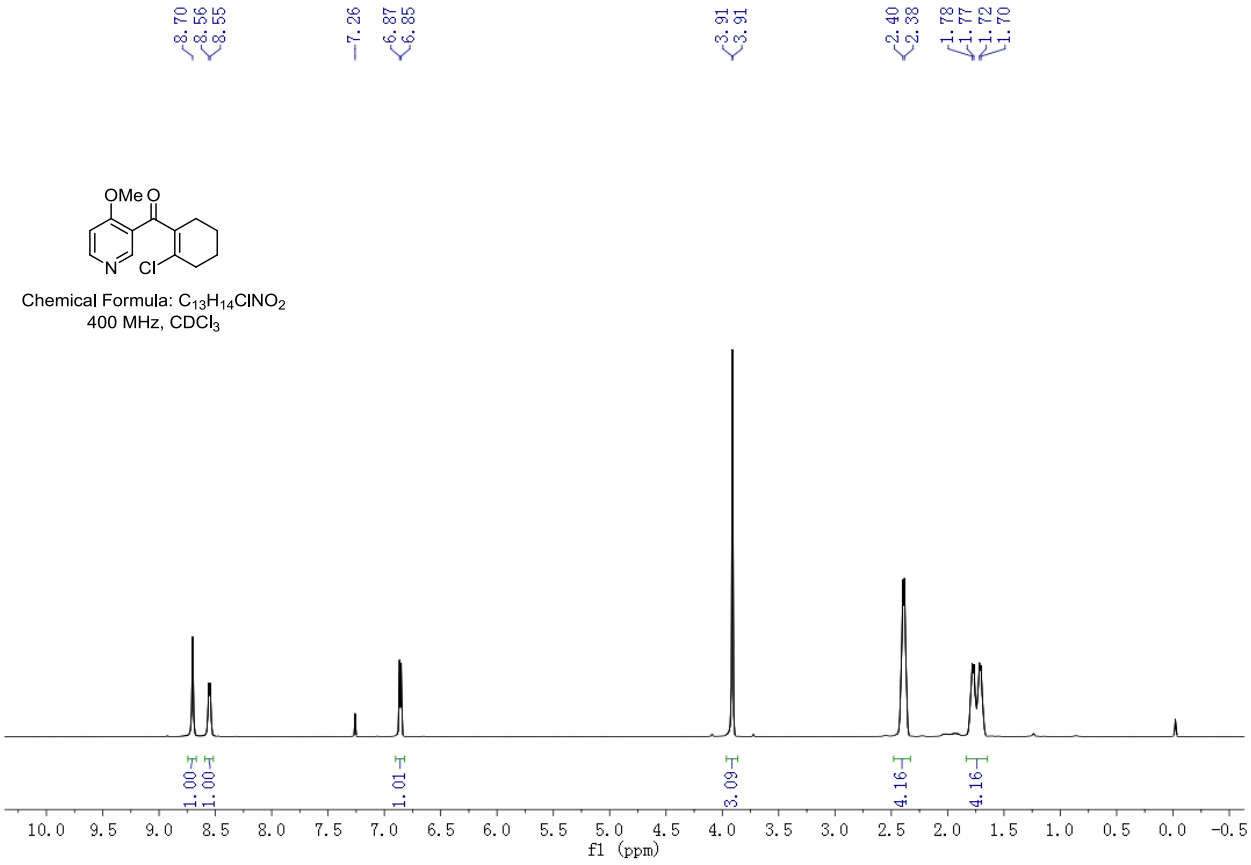

195.68
166.13
161.94
136.09
135.03
132.54
130.96
128.02
122.82
111.34
56.17
52.00
33.88
27.96
23.41
21.63
OMe O
Cl
COOMe
Chemical Formula: C16H17ClO4
100 MHz, CDCl3
f1 (ppm)



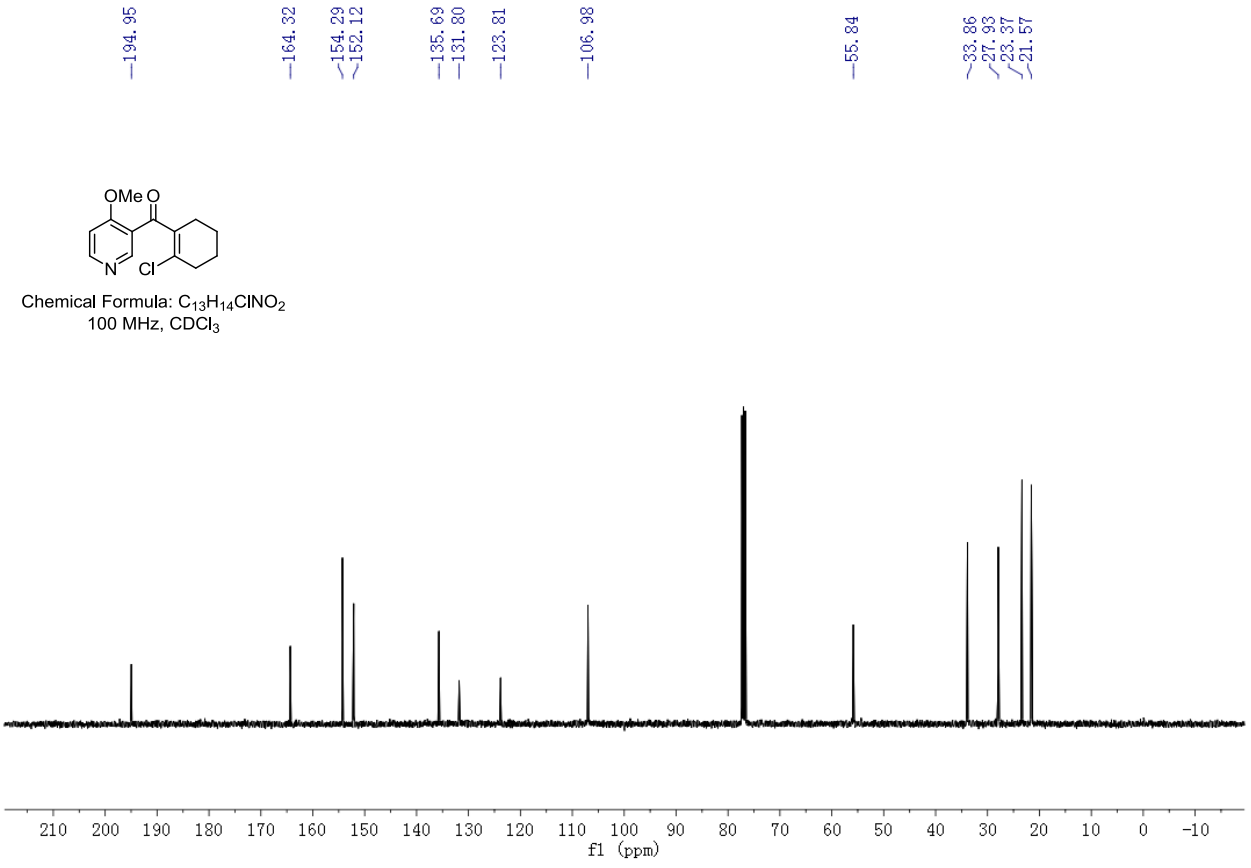
Chemical Formula: $C_{18}H_{17}ClO_2$
400 MHz, $CDCl_3$



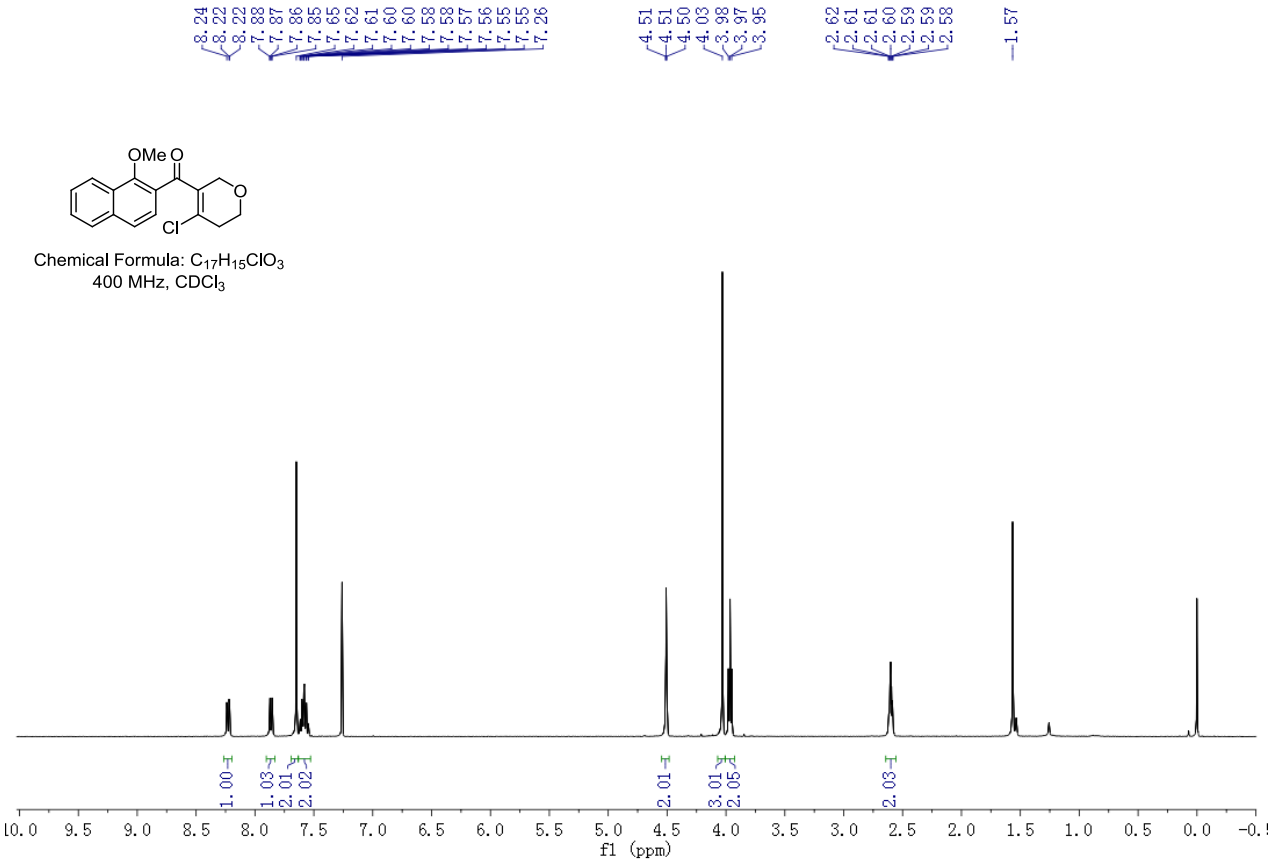
Chemical Formula: $C_{18}H_{17}ClO_2$
100 MHz, $CDCl_3$

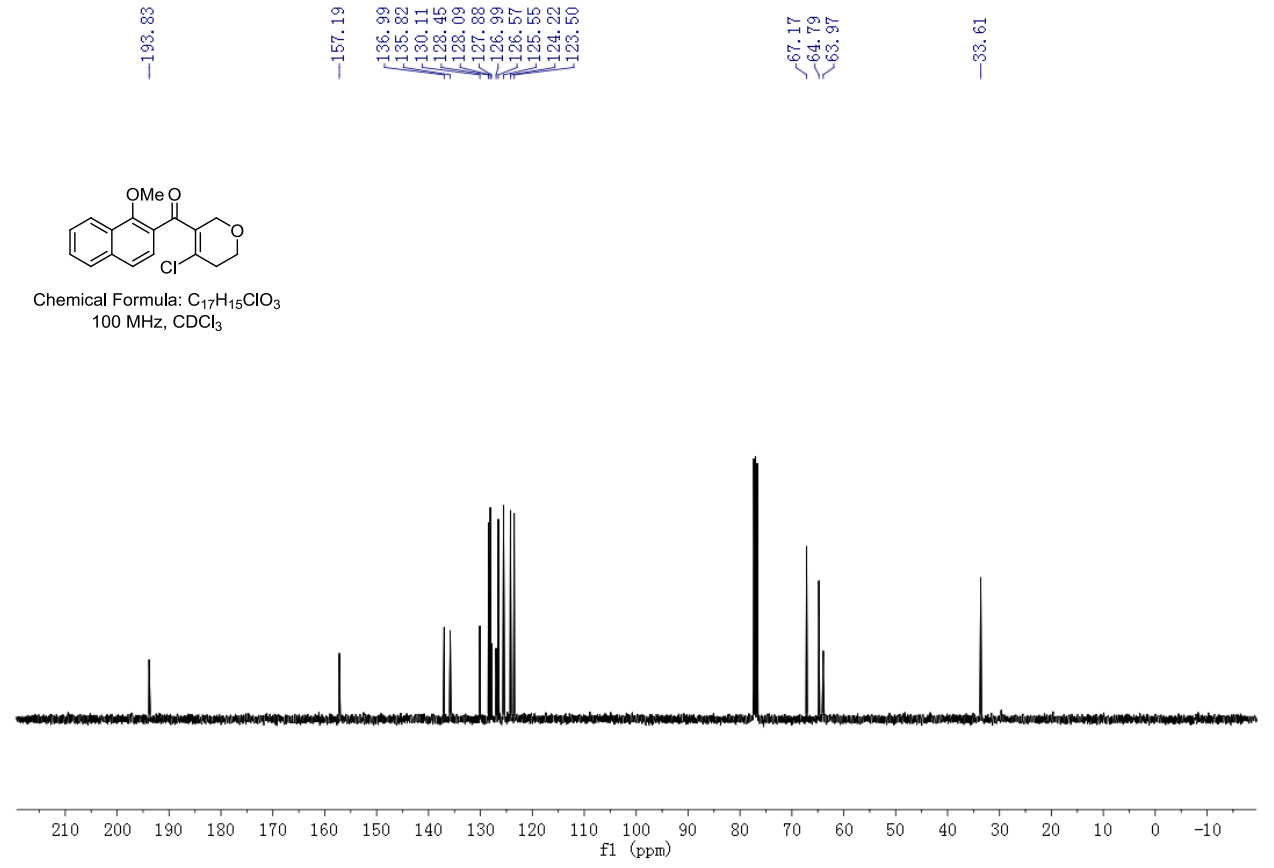


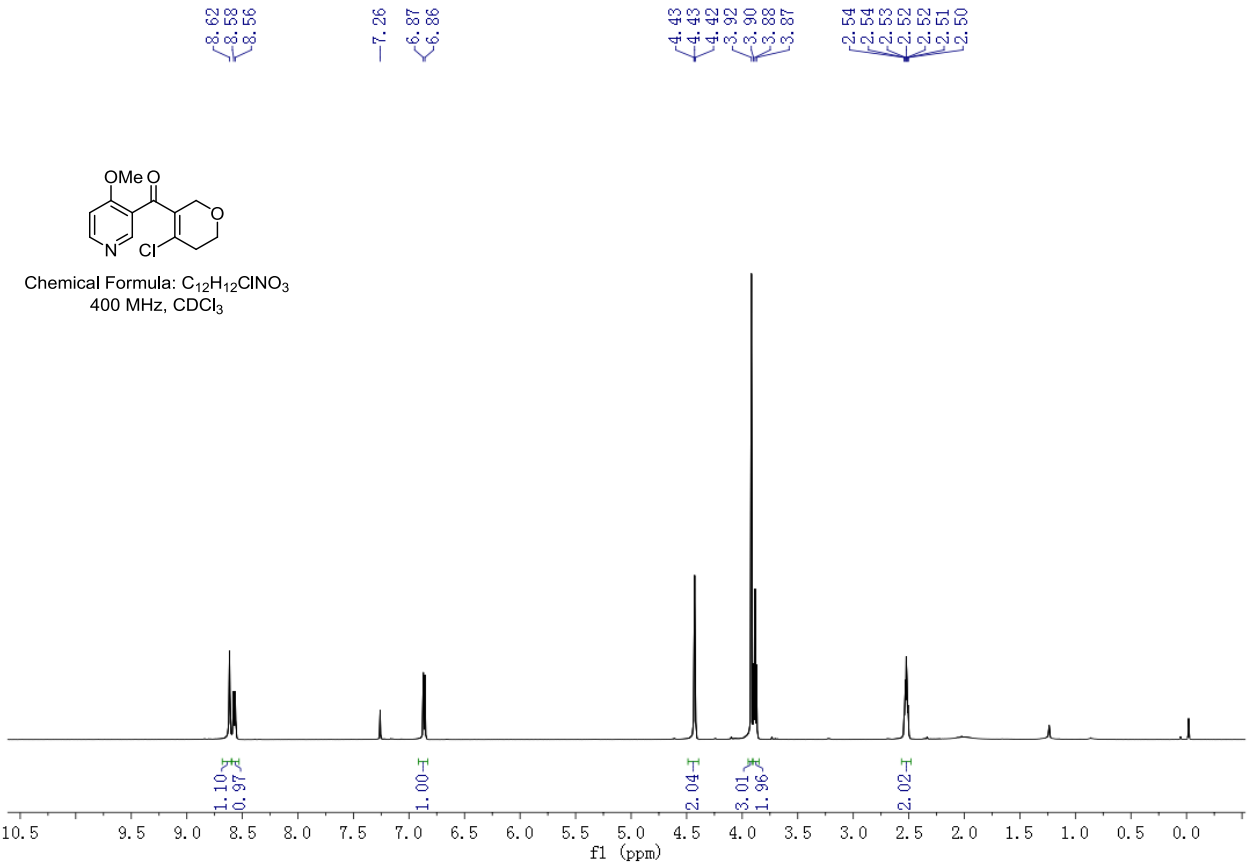
Chemical Formula: $C_{13}H_{14}ClNO_2$
400 MHz, $CDCl_3$

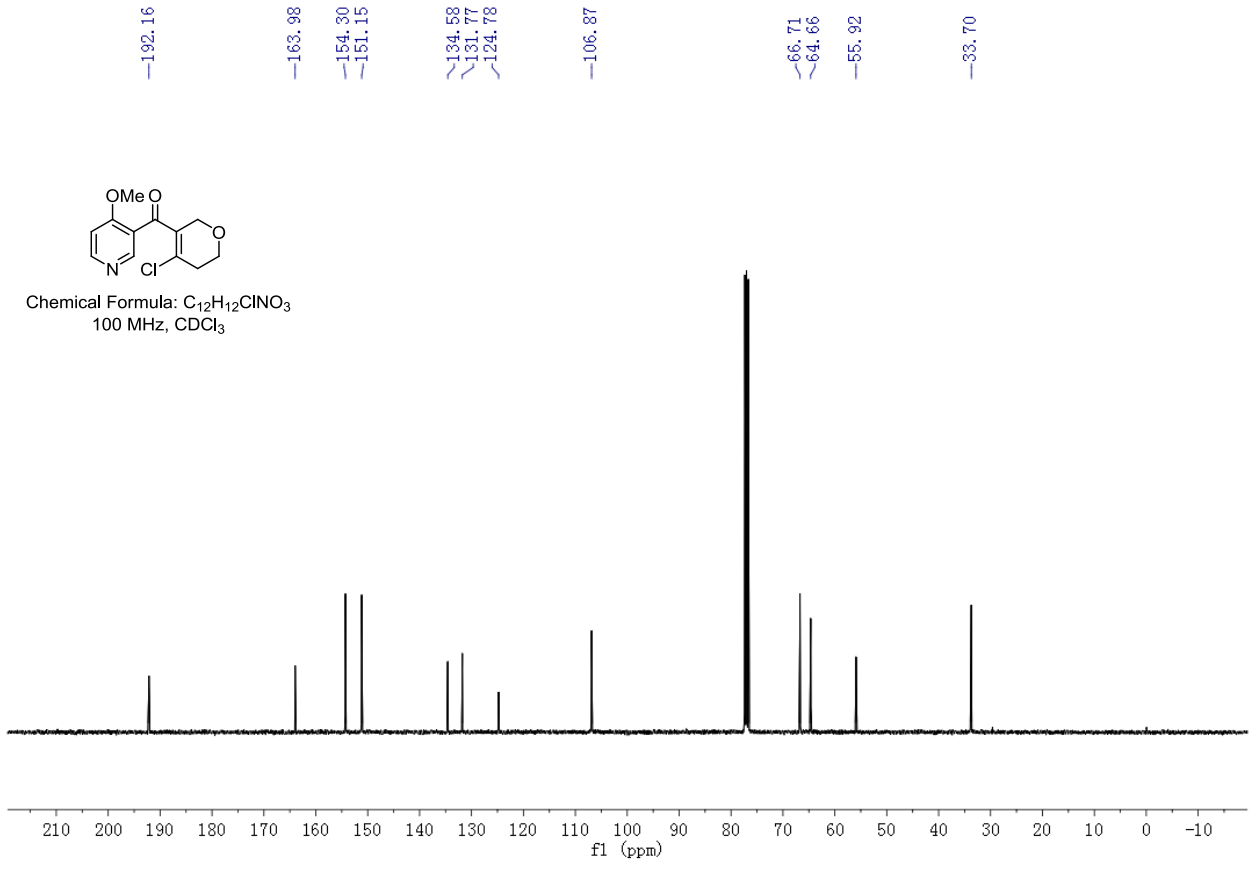


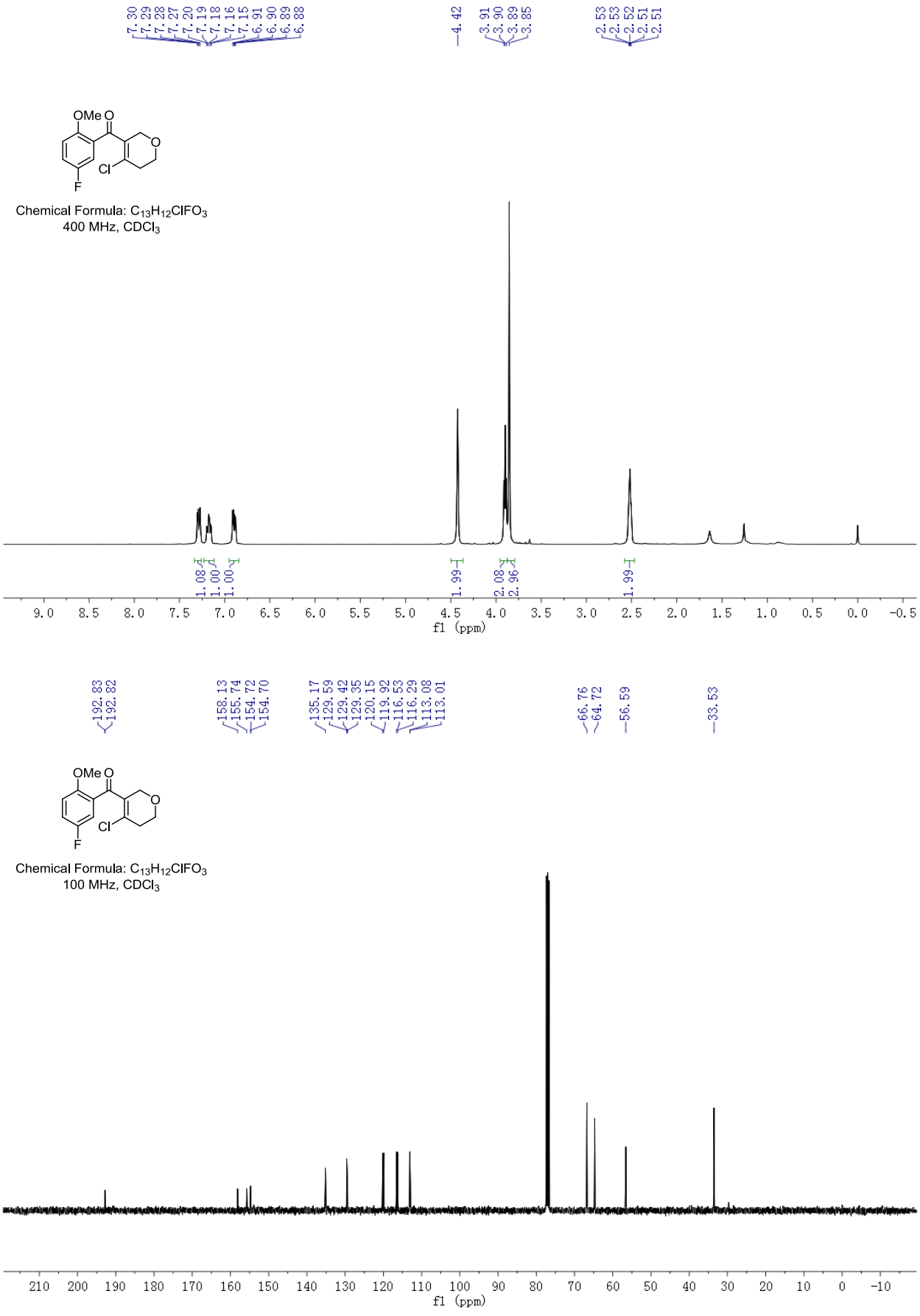
Chemical Formula: $C_{13}H_{14}ClNO_2$
100 MHz, $CDCl_3$

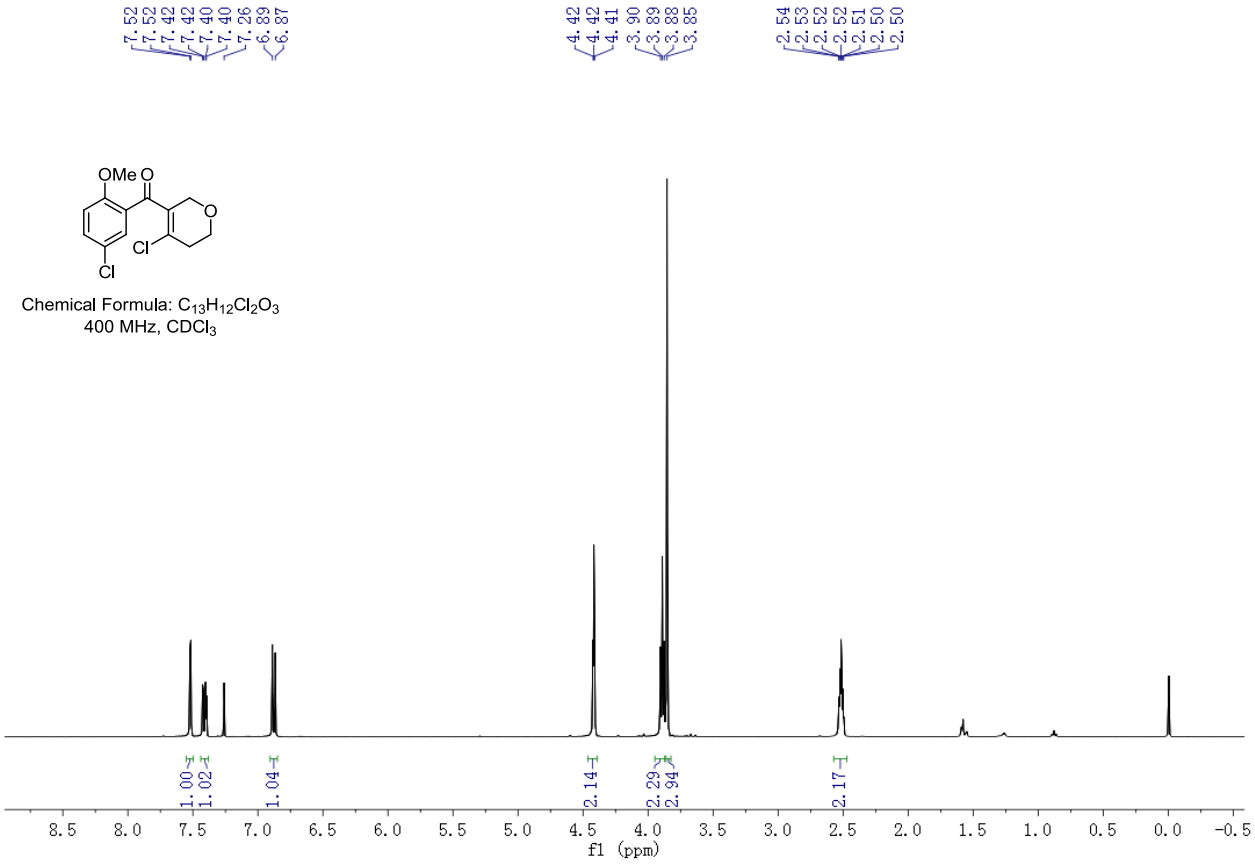

8.24
8.22
8.22
7.88
7.87
7.86
7.85
7.65
7.62
7.61
7.60
7.60
7.58
7.58
7.57
7.56
7.55
7.55
7.26
4.51
4.51
4.50
4.03
3.98
3.97
3.95
2.62
2.61
2.61
2.60
2.59
2.59
2.58
1.57
OMe O
O
Cl
Chemical Formula: C17H15ClO3
400 MHz, CDCl3
1.00
1.03
2.01
2.02
2.01
3.01
2.05
2.03
f1 (ppm)


193.83
157.19
136.99
135.82
130.11
128.45
128.09
127.88
126.99
126.57
125.55
124.22
123.50
67.17
64.79
63.97
33.61
OMe O
O
Cl
Chemical Formula: C17H15ClO3
100 MHz, CDCl3
f1 (ppm)

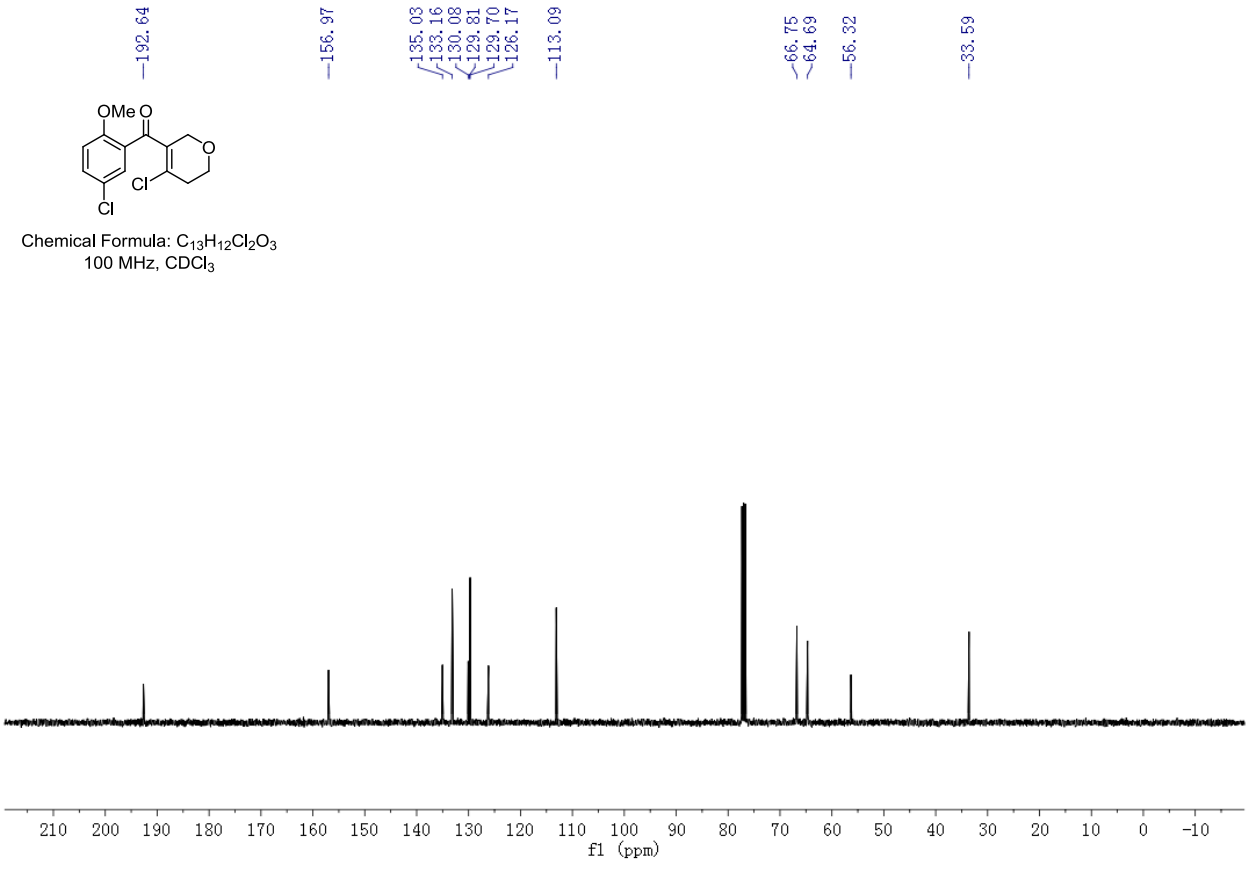

8.62
8.58
8.56
7.26
6.87
6.86
4.43
4.43
4.42
3.92
3.90
3.88
3.87
2.54
2.54
2.53
2.52
2.52
2.51
2.50
OMe O
O
N
Cl
Chemical Formula: C12H12ClNO3
400 MHz, CDCl3
1.10
0.97
1.00
2.04
3.01
1.96
2.02
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


192.16
163.98
154.30
151.15
134.58
131.77
124.78
106.87
66.71
64.66
55.92
33.70
OMe O
O
N
Cl
Chemical Formula: C12H12ClNO3
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

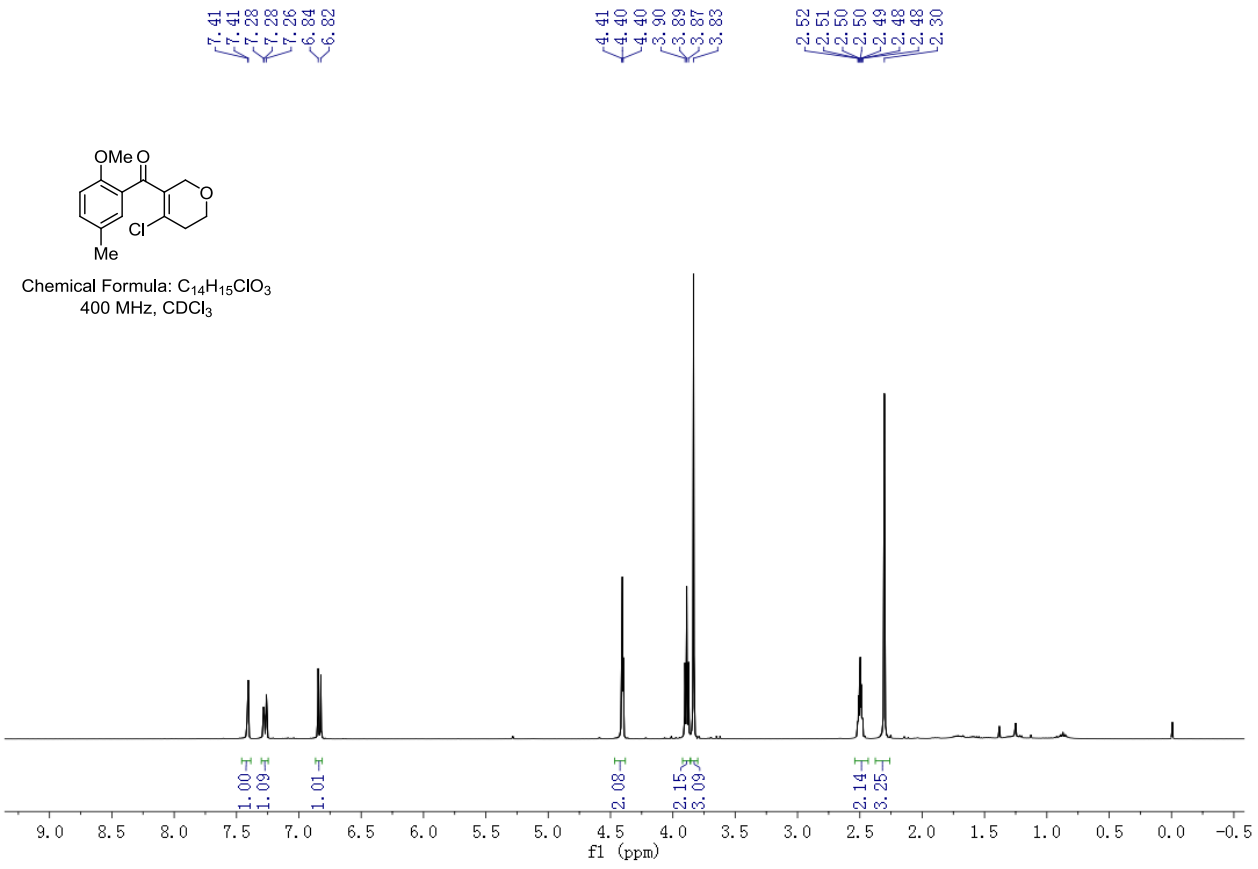

7.30
7.29
7.28
7.27
7.20
7.19
7.18
7.16
7.15
6.91
6.90
6.89
6.88
4.42
3.91
3.90
3.89
3.85
2.53
2.53
2.52
2.51
2.51
OMe O
O
Cl
F
Chemical Formula: C13H12ClFO3
400 MHz, CDCl3
1.08
1.00
1.00
1.99
2.08
2.96
1.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
192.83
192.82
158.13
155.74
154.72
154.70
135.17
129.59
129.42
129.35
120.15
119.92
116.53
116.29
113.08
113.01
66.76
64.72
56.59
33.53
OMe O
O
Cl
F
Chemical Formula: C13H12ClFO3
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



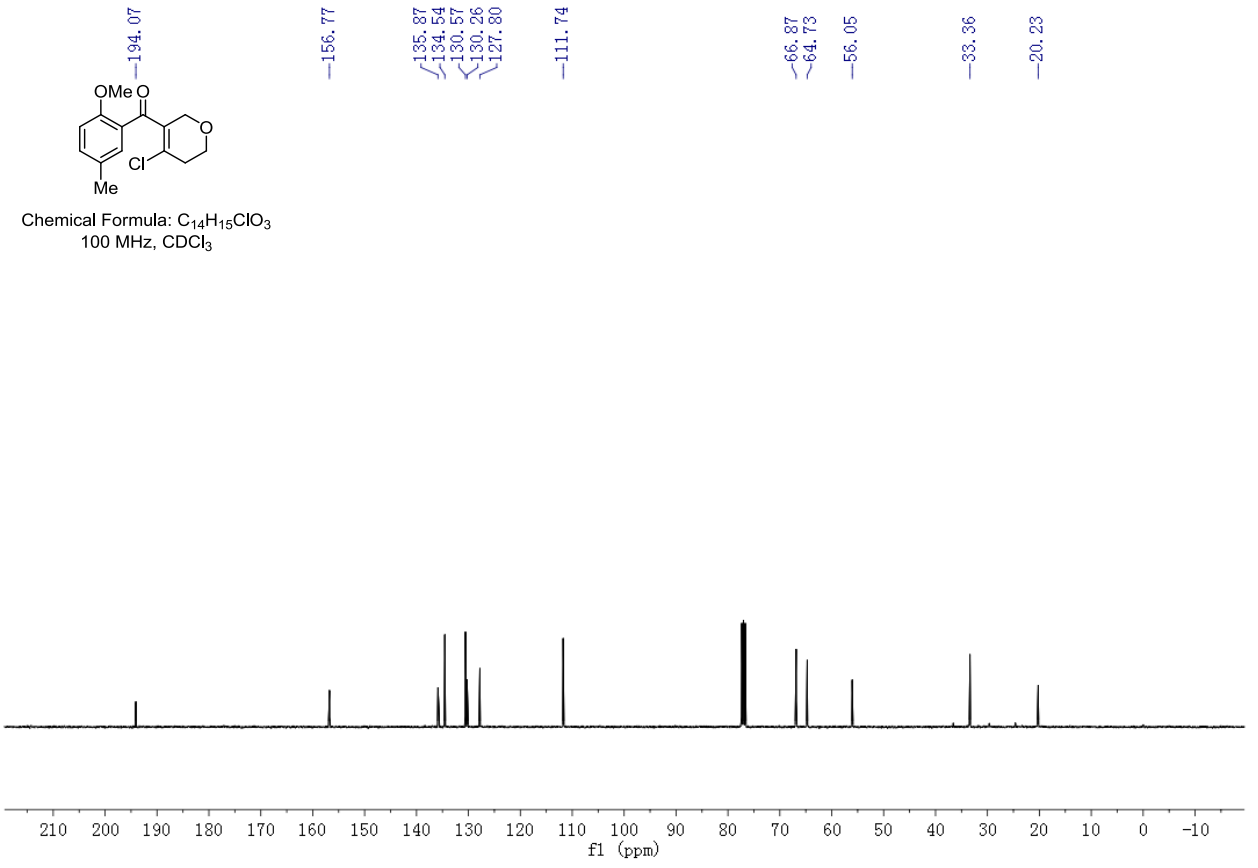
Chemical Formula: $C_{13}H_{12}Cl_2O_3$
400 MHz, $CDCl_3$



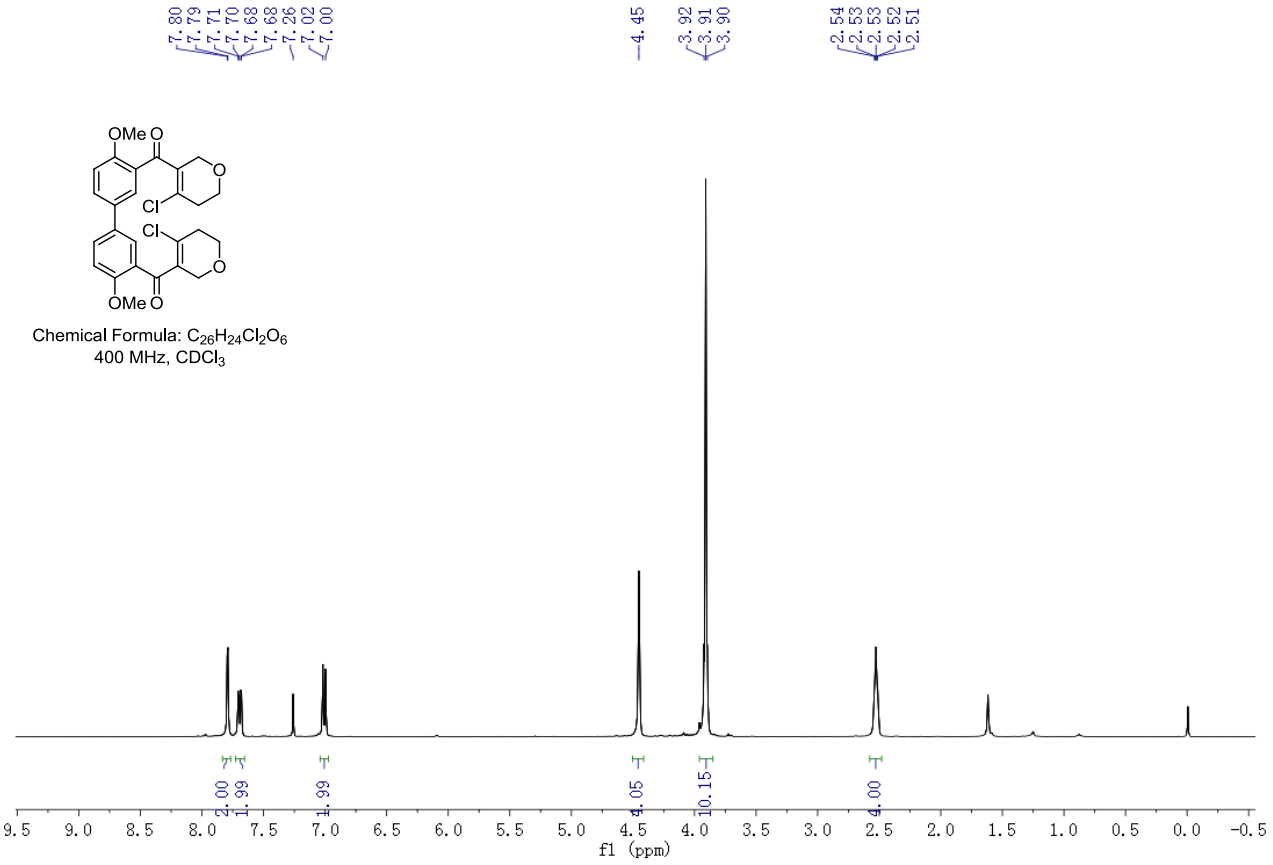
Chemical Formula: $C_{13}H_{12}Cl_2O_3$
100 MHz, $CDCl_3$



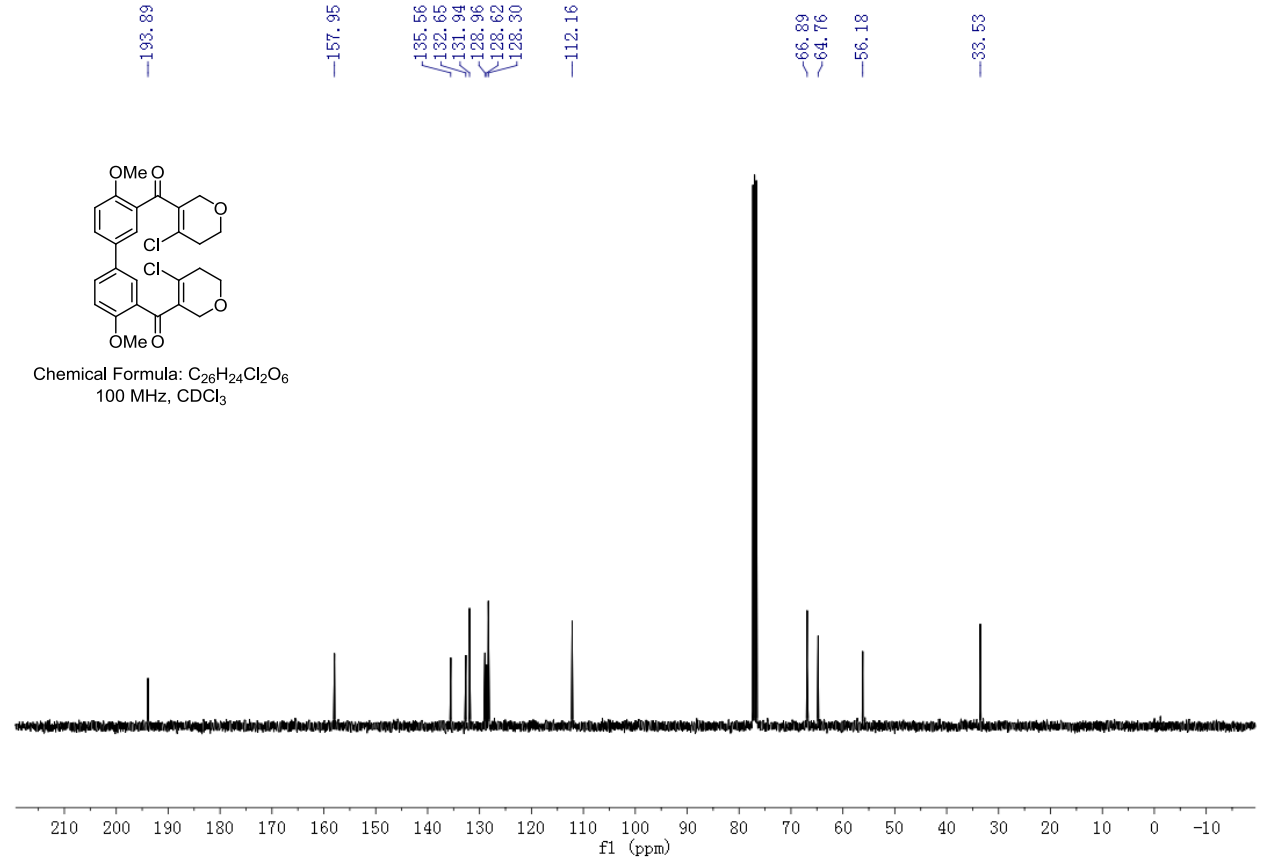
Chemical Formula: $C_{14}H_{15}ClO_3$
400 MHz, $CDCl_3$



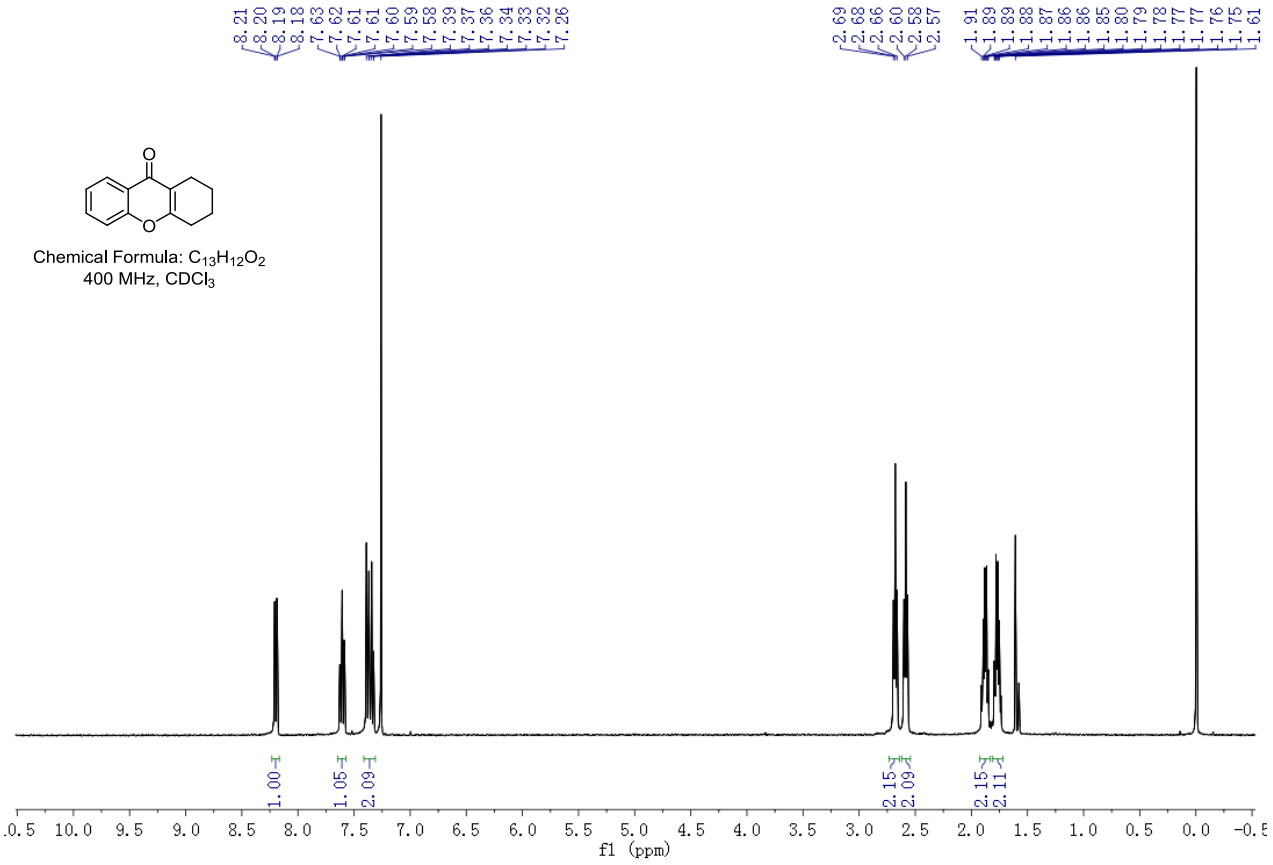
Chemical Formula: $C_{14}H_{15}ClO_3$
100 MHz, $CDCl_3$

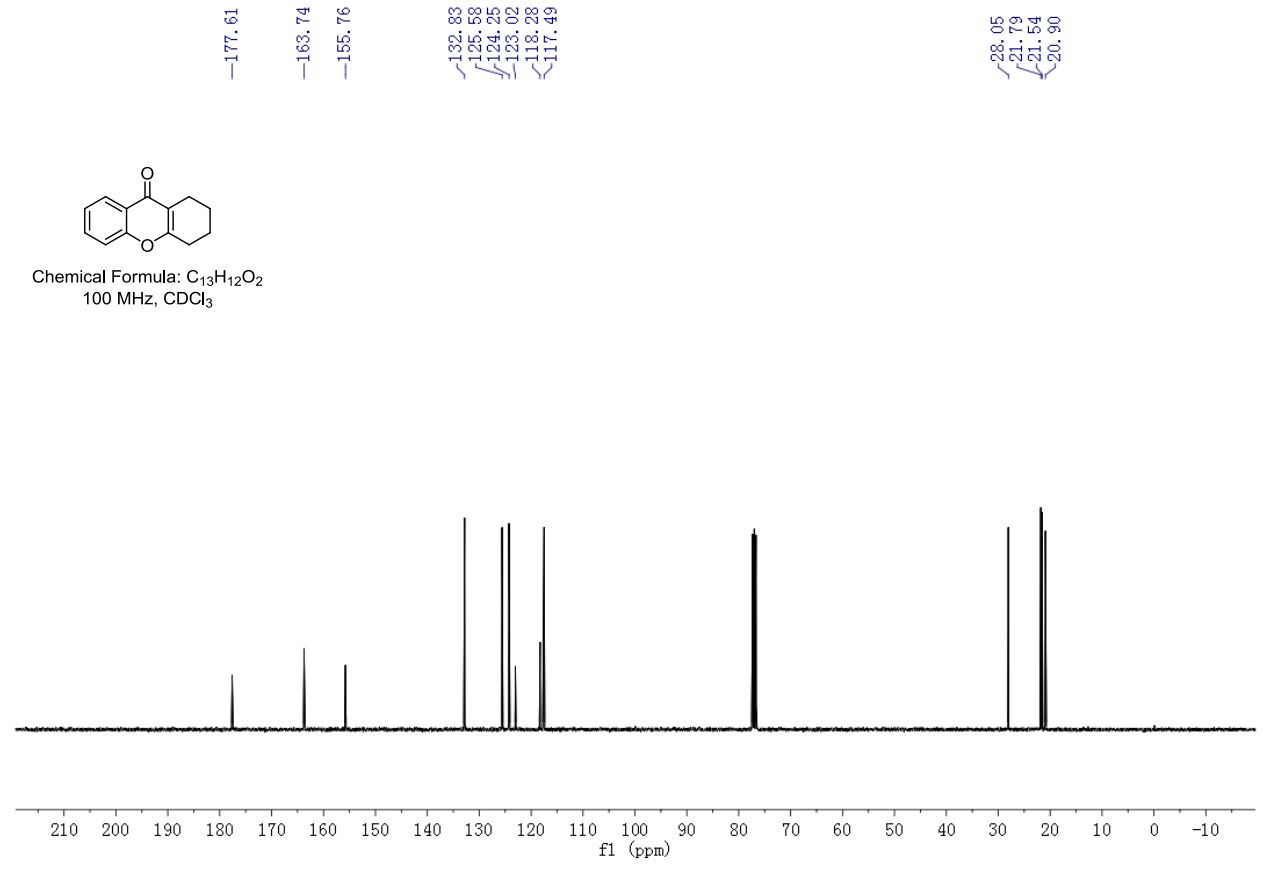


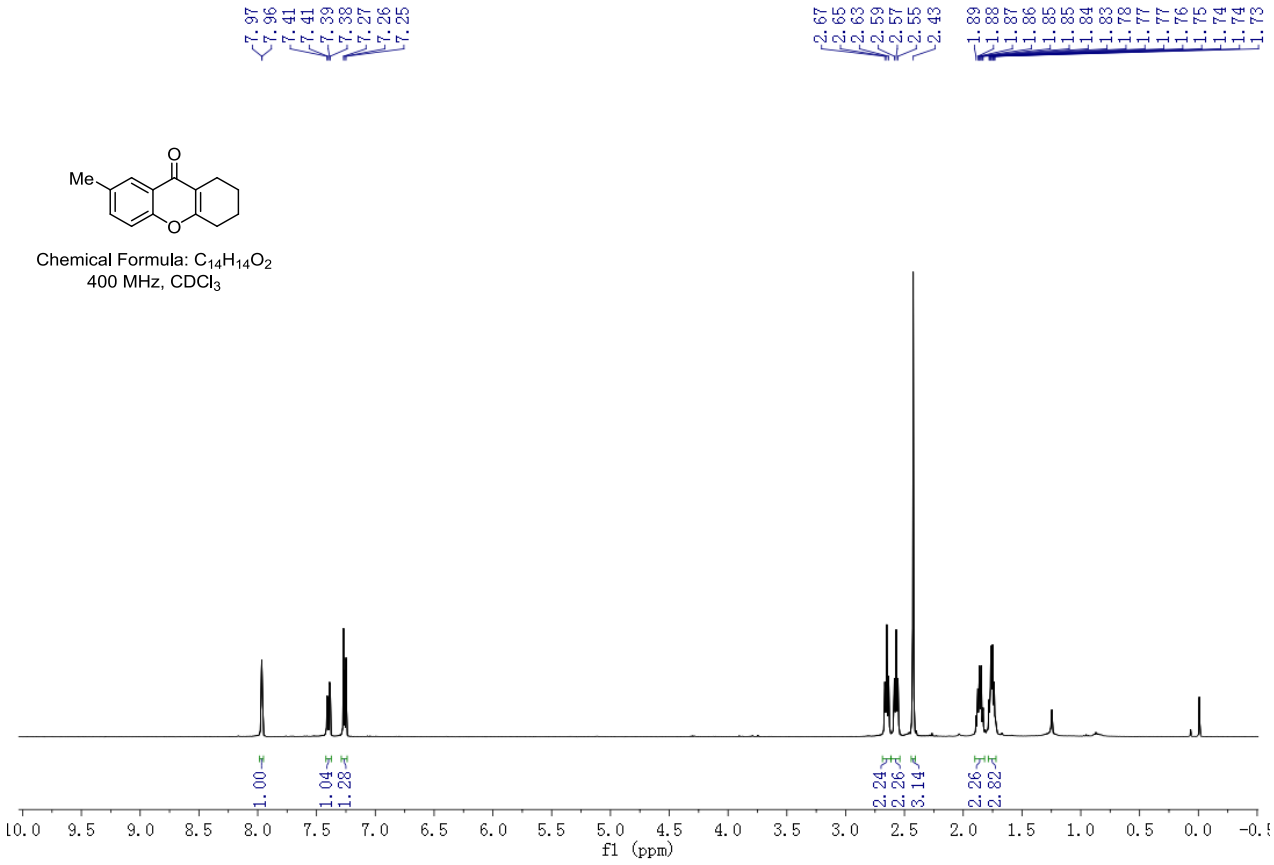
Chemical Formula: $C_{26}H_{24}Cl_2O_6$
400 MHz, $CDCl_3$

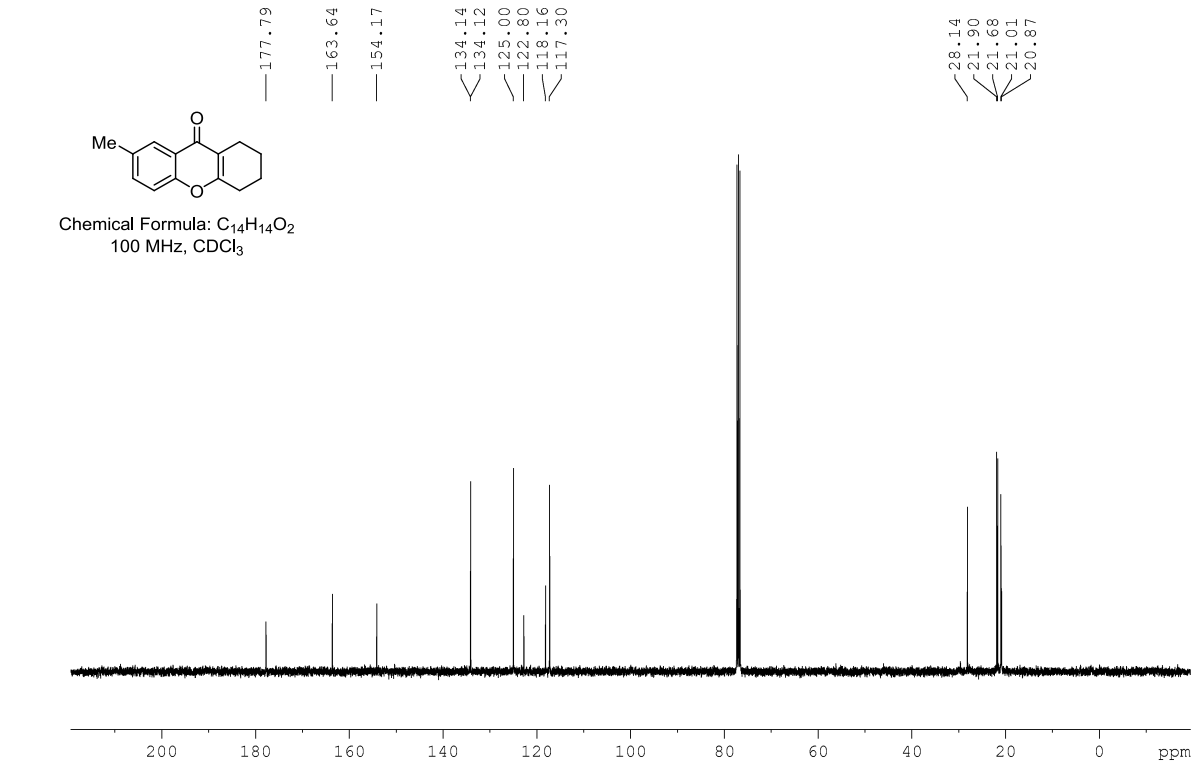


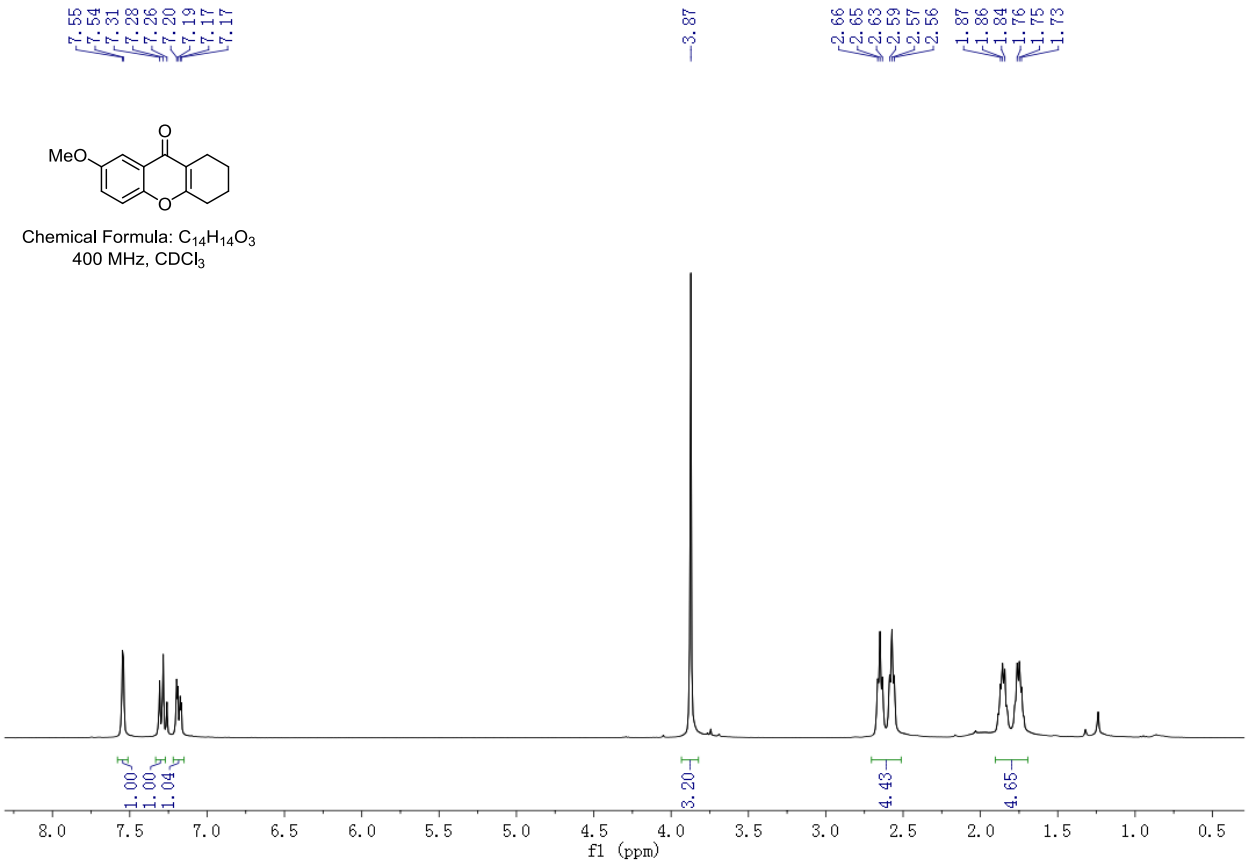
Chemical Formula: $C_{26}H_{24}Cl_2O_6$
100 MHz, $CDCl_3$

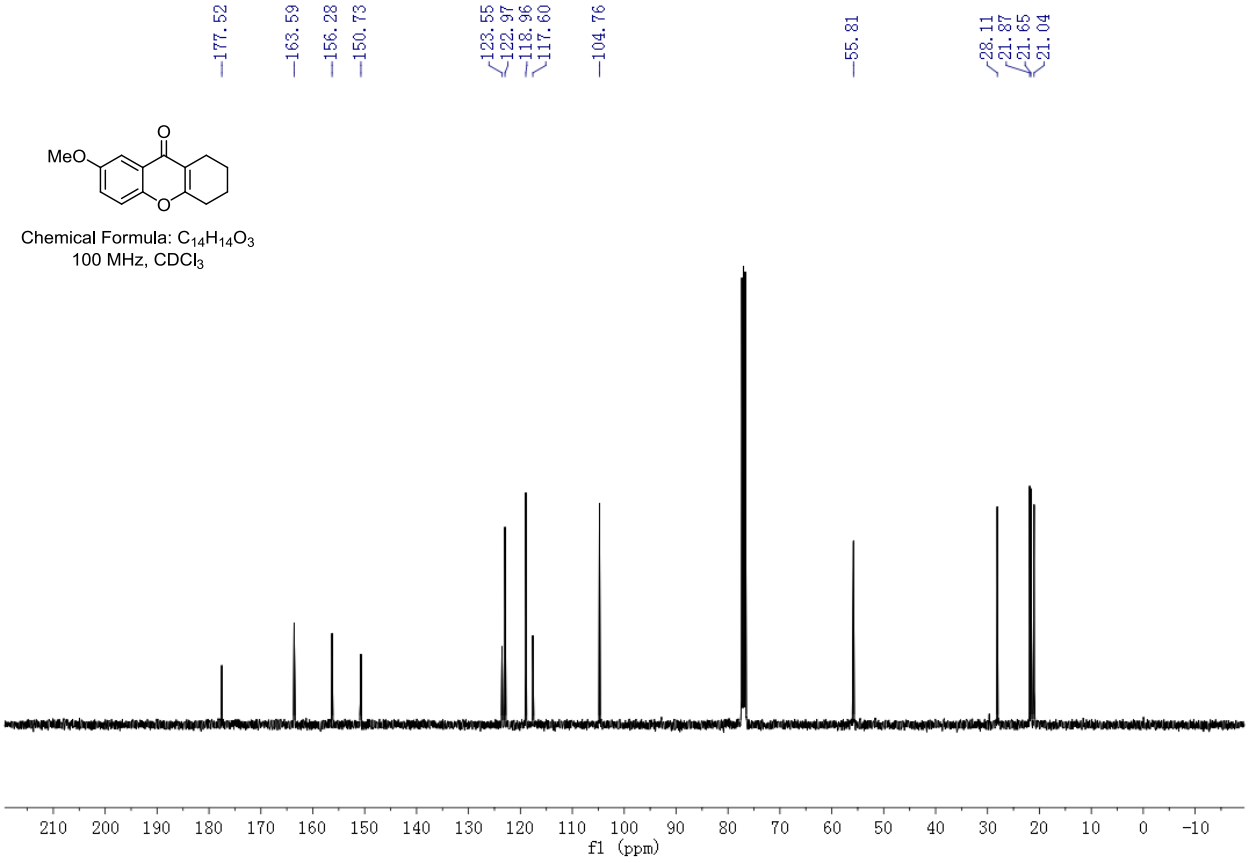

8.21
8.20
8.19
8.18
7.63
7.62
7.61
7.61
7.60
7.59
7.58
7.39
7.37
7.36
7.34
7.33
7.32
7.26
2.69
2.68
2.66
2.60
2.58
2.57
1.91
1.89
1.89
1.88
1.87
1.86
1.86
1.85
1.80
1.79
1.78
1.77
1.77
1.76
1.75
1.61
O
O
Chemical Formula: C13H12O2
400 MHz, CDCl3
1.00
1.05
2.09
2.15
2.09
2.15
2.11
f1 (ppm)

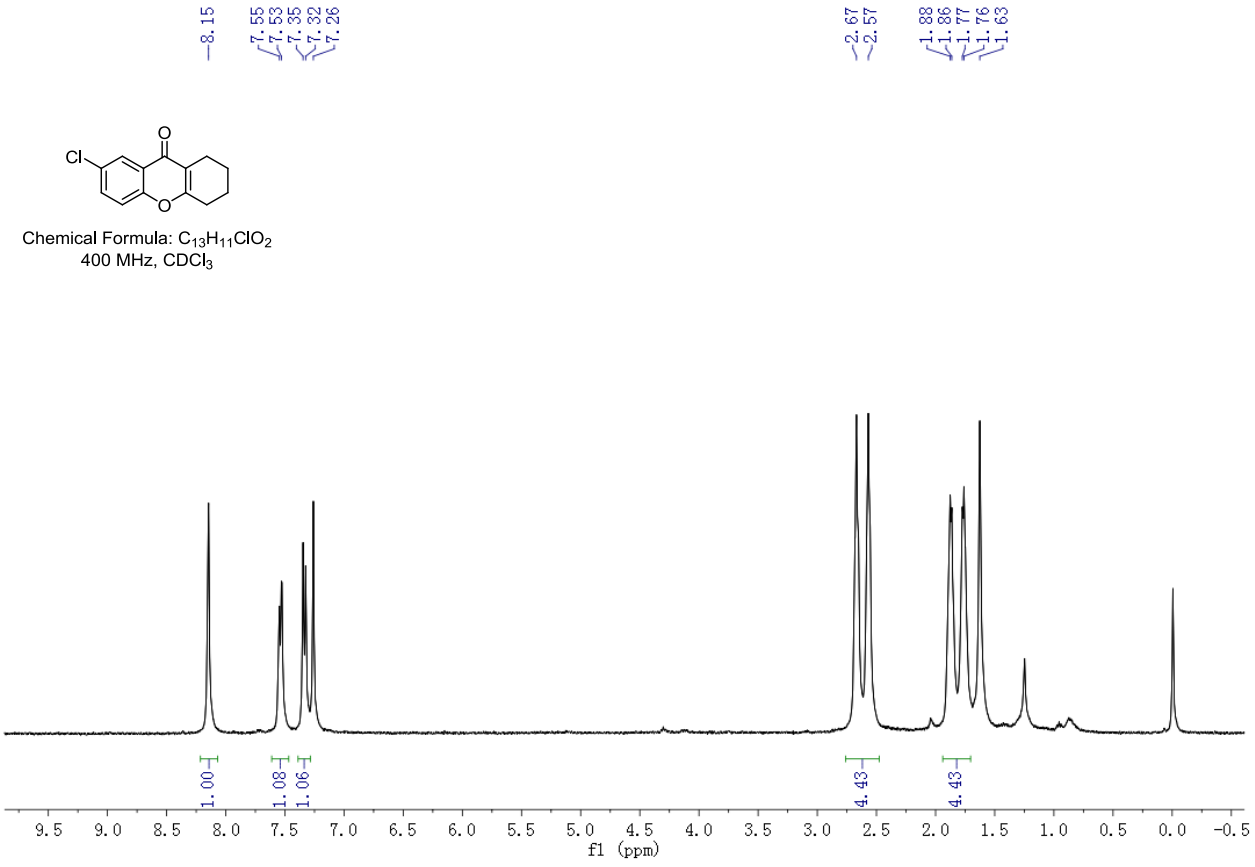

177.61
163.74
155.76
132.83
125.58
124.25
123.02
118.28
117.49
28.05
21.79
21.54
20.90
O
O
Chemical Formula: C13H12O2
100 MHz, CDCl3
f1 (ppm)

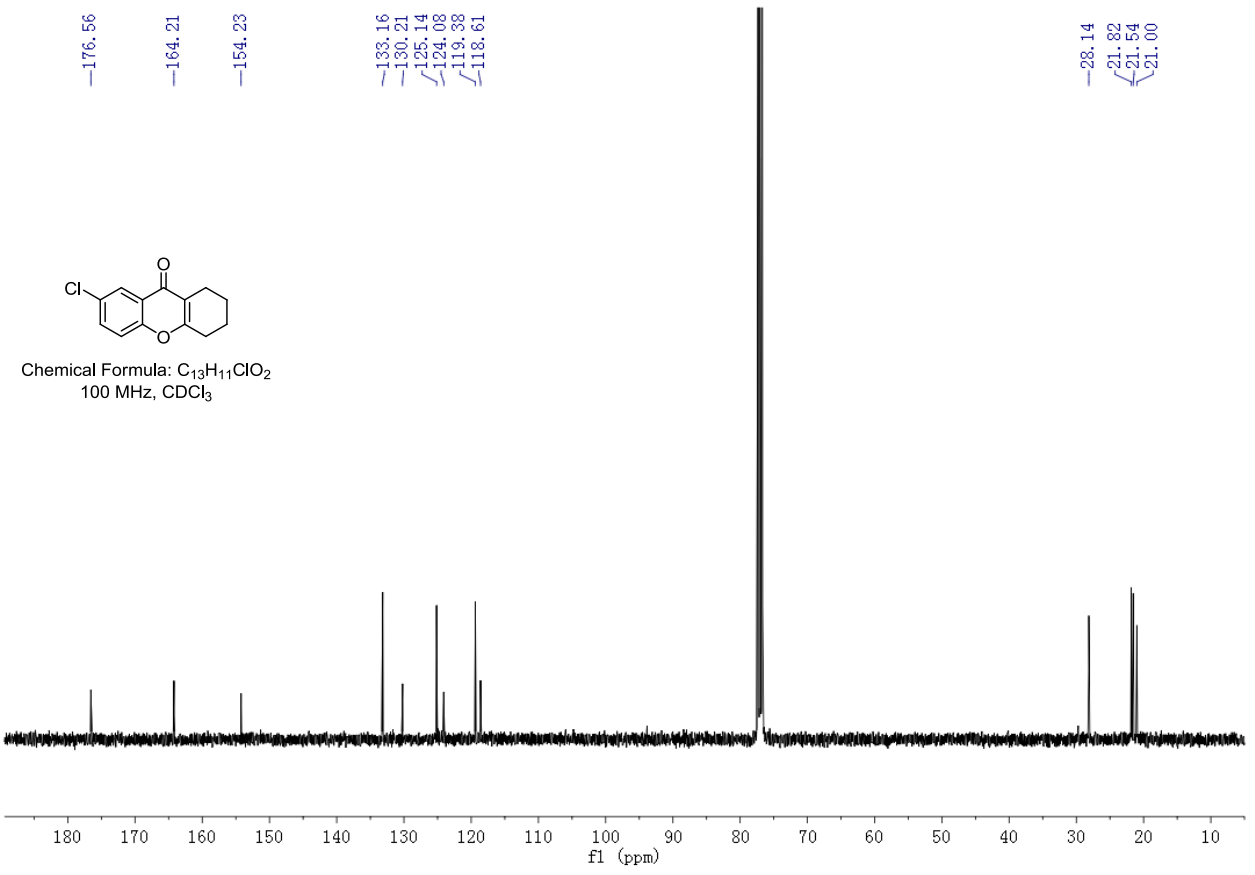

7.97
7.96
7.41
7.41
7.39
7.38
7.27
7.26
7.25
2.67
2.65
2.63
2.59
2.57
2.55
2.43
1.89
1.88
1.87
1.86
1.85
1.85
1.84
1.83
1.78
1.77
1.77
1.76
1.75
1.74
1.74
1.73
Me
O
O
Chemical Formula: C14H14O2
400 MHz, CDCl3
1.00
1.04
1.28
2.24
2.26
3.14
2.26
2.82
f1 (ppm)

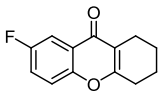

177.79
163.64
154.17
134.14
134.12
125.00
122.80
118.16
117.30
28.14
21.90
21.68
21.01
20.87
Me
O
O
Chemical Formula: C14H14O2
100 MHz, CDCl3
ppm


7.55
7.54
7.31
7.28
7.26
7.20
7.19
7.17
7.17
7.17
3.87
2.66
2.65
2.63
2.59
2.57
2.56
1.87
1.86
1.84
1.76
1.75
1.73
MeO
O
O
Chemical Formula: C14H14O3
400 MHz, CDCl3
1.00
1.00
1.04
3.20
4.43
4.65
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

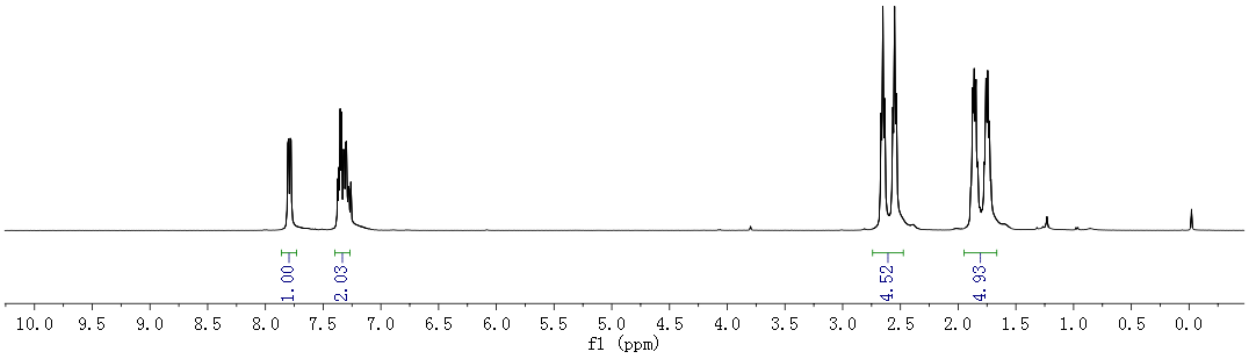

177.52
163.59
156.28
150.73
123.55
122.97
118.96
117.60
104.76
55.81
28.11
21.87
21.65
21.04
MeO
O
O
Chemical Formula: C14H14O3
100 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

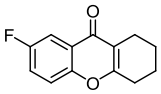

8.15
7.55
7.53
7.35
7.32
7.26
2.67
2.57
1.88
1.86
1.77
1.76
1.63
Cl
O
O
Chemical Formula: C13H11ClO2
400 MHz, CDCl3
1.00
1.08
1.06
4.43
4.43
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


176.56
164.21
154.23
133.16
130.21
125.14
124.08
119.38
118.61
28.14
21.82
21.54
21.00
Cl
O
O
Chemical Formula: C13H11ClO2
100 MHz, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

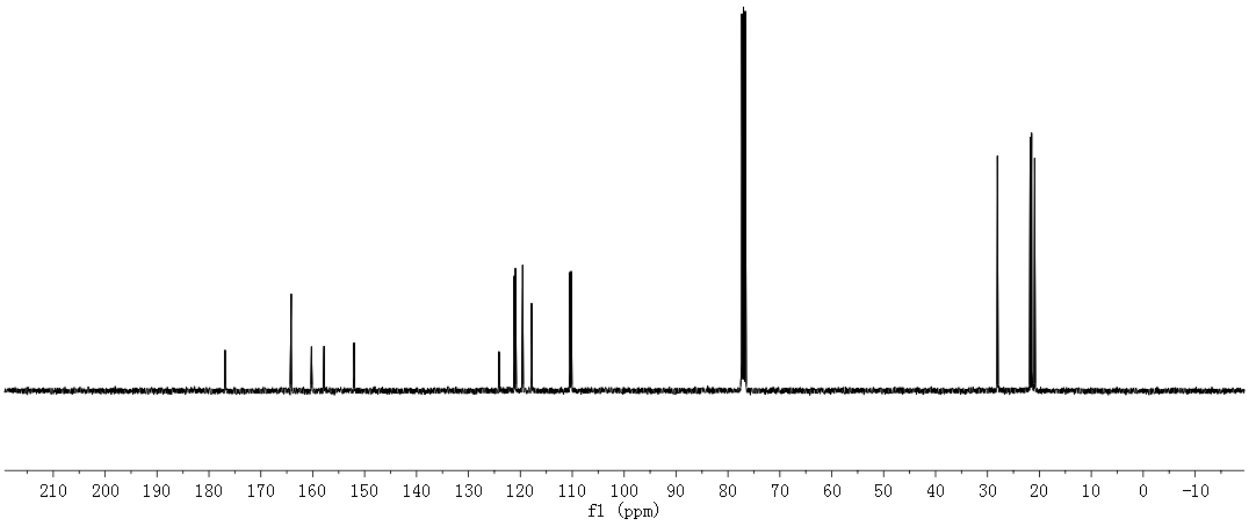


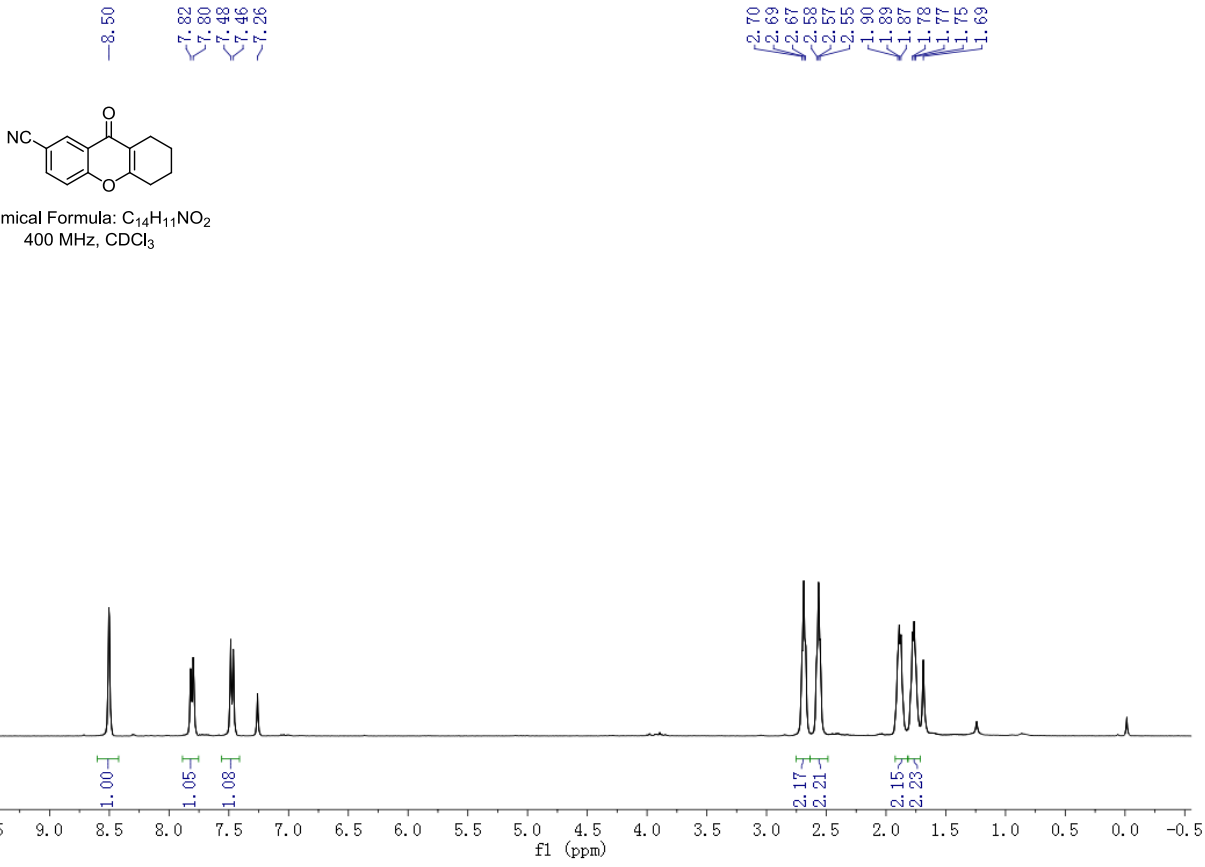
Chemical Formula: $C_{13}H_{11}FO_2$
400 MHz, $CDCl_3$

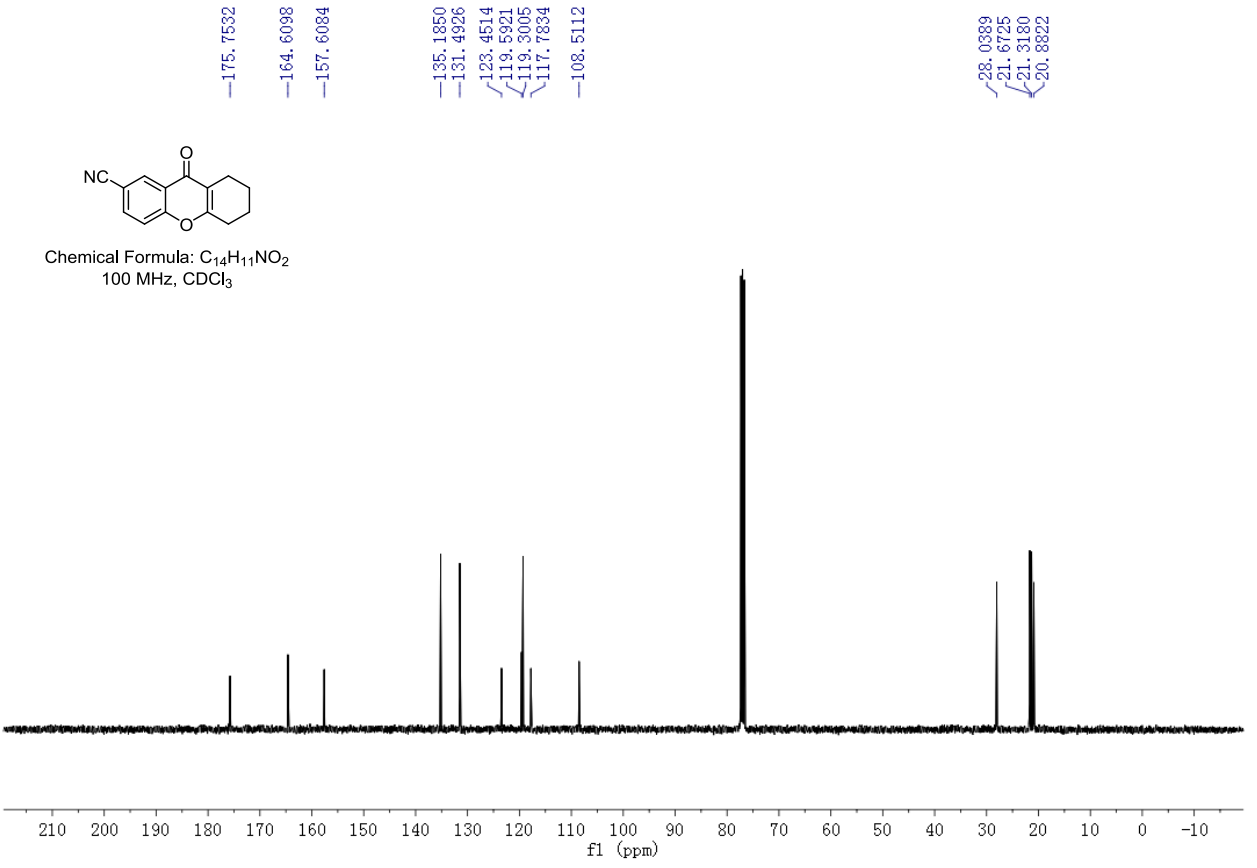


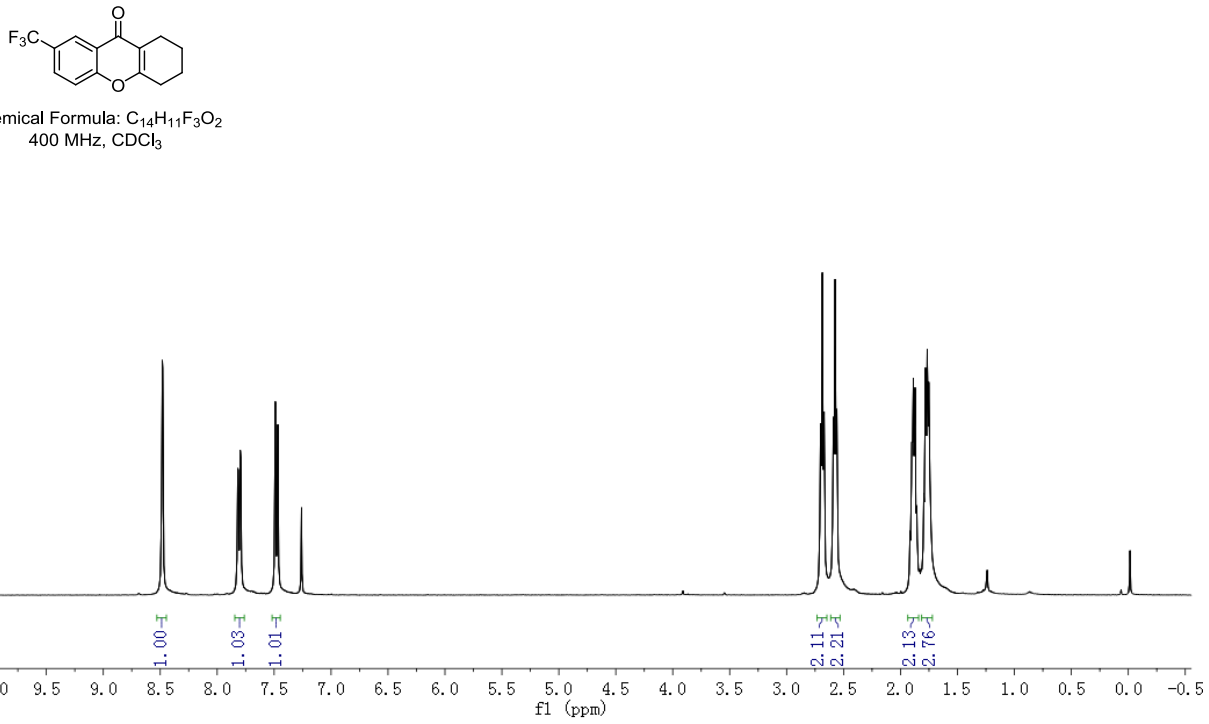


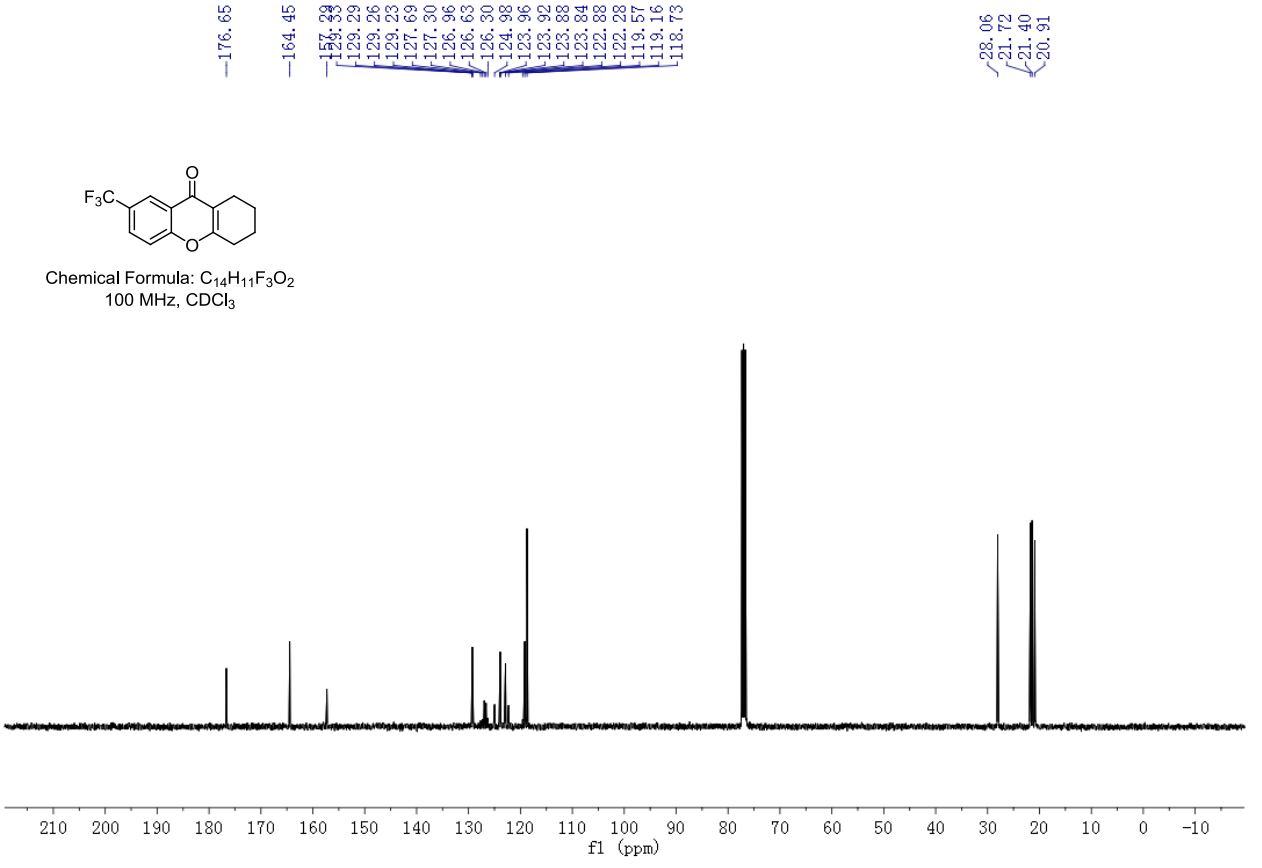
Chemical Formula: $C_{13}H_{11}FO_2$
100 MHz, $CDCl_3$

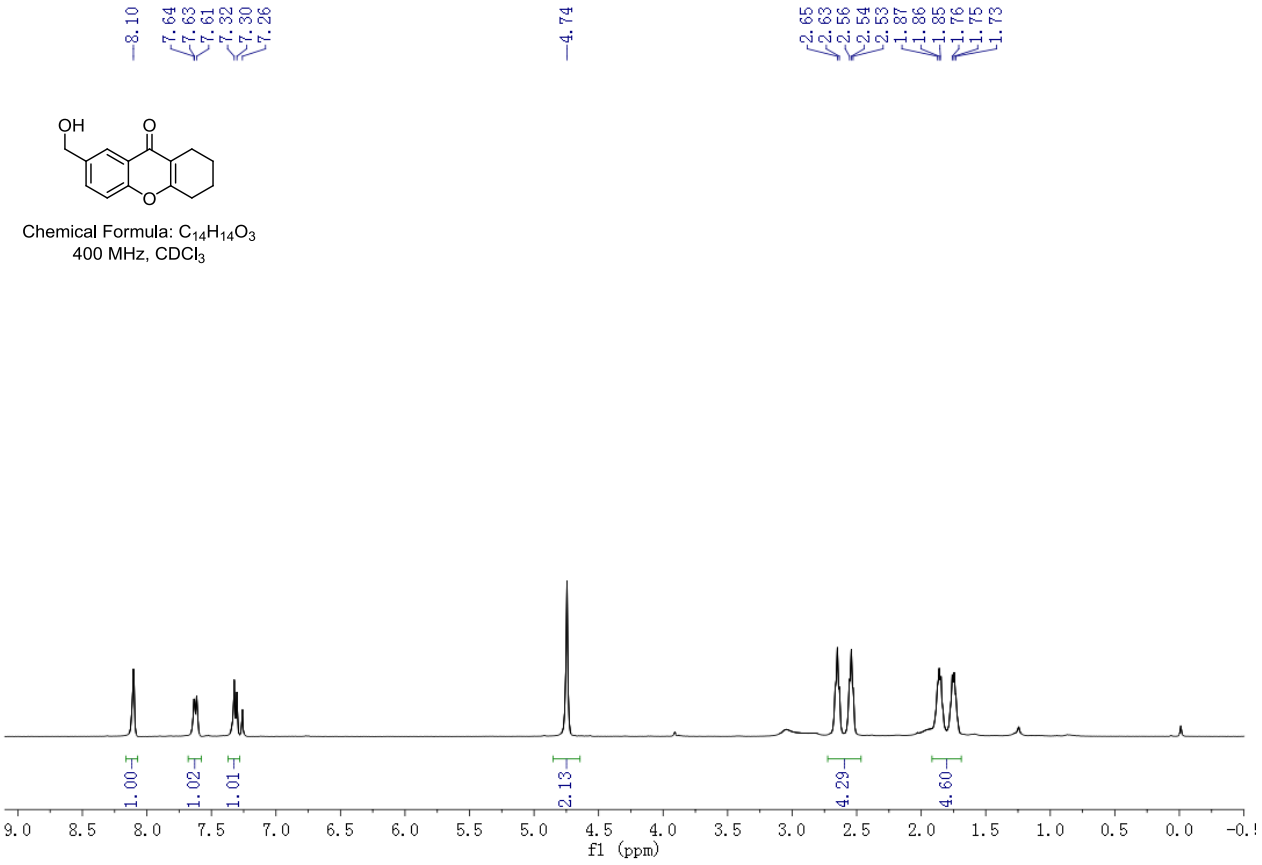


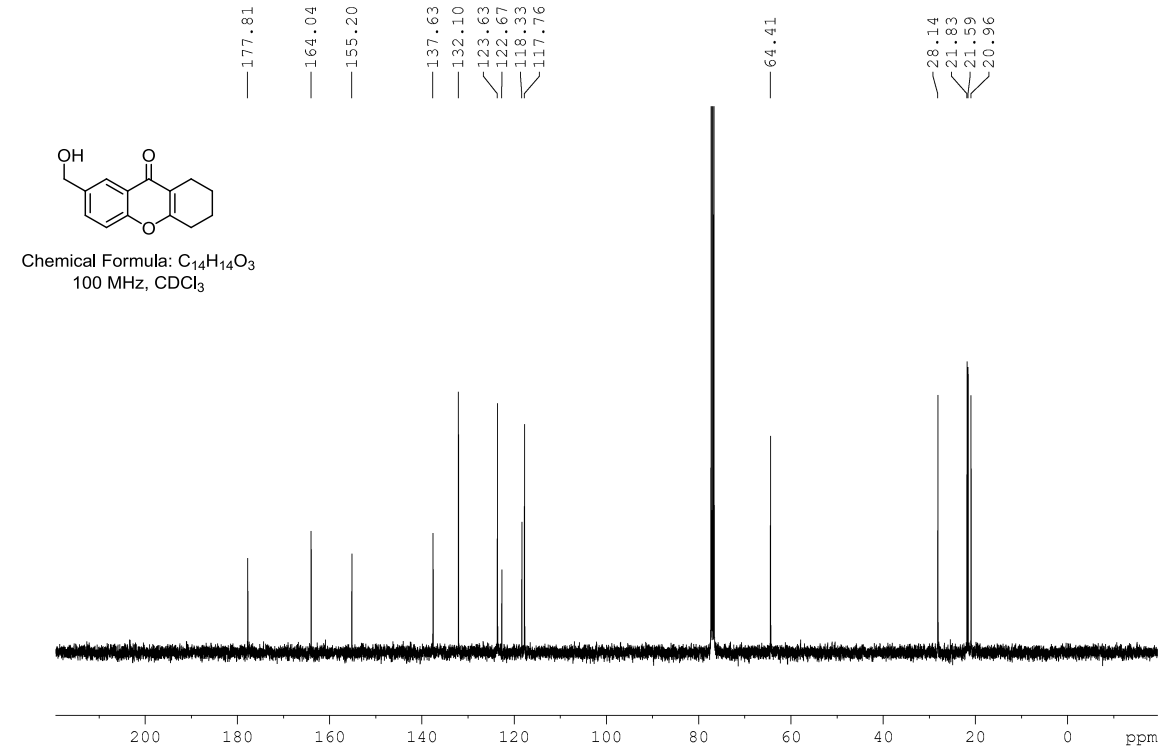

8.50
7.82
7.80
7.48
7.46
7.26
2.70
2.69
2.67
2.58
2.57
2.55
1.90
1.89
1.87
1.78
1.77
1.75
1.69
NC
O
O
Chemical Formula: C14H11NO2
400 MHz, CDCl3
1.00
1.05
1.08
2.17
2.21
2.15
2.23
f1 (ppm)

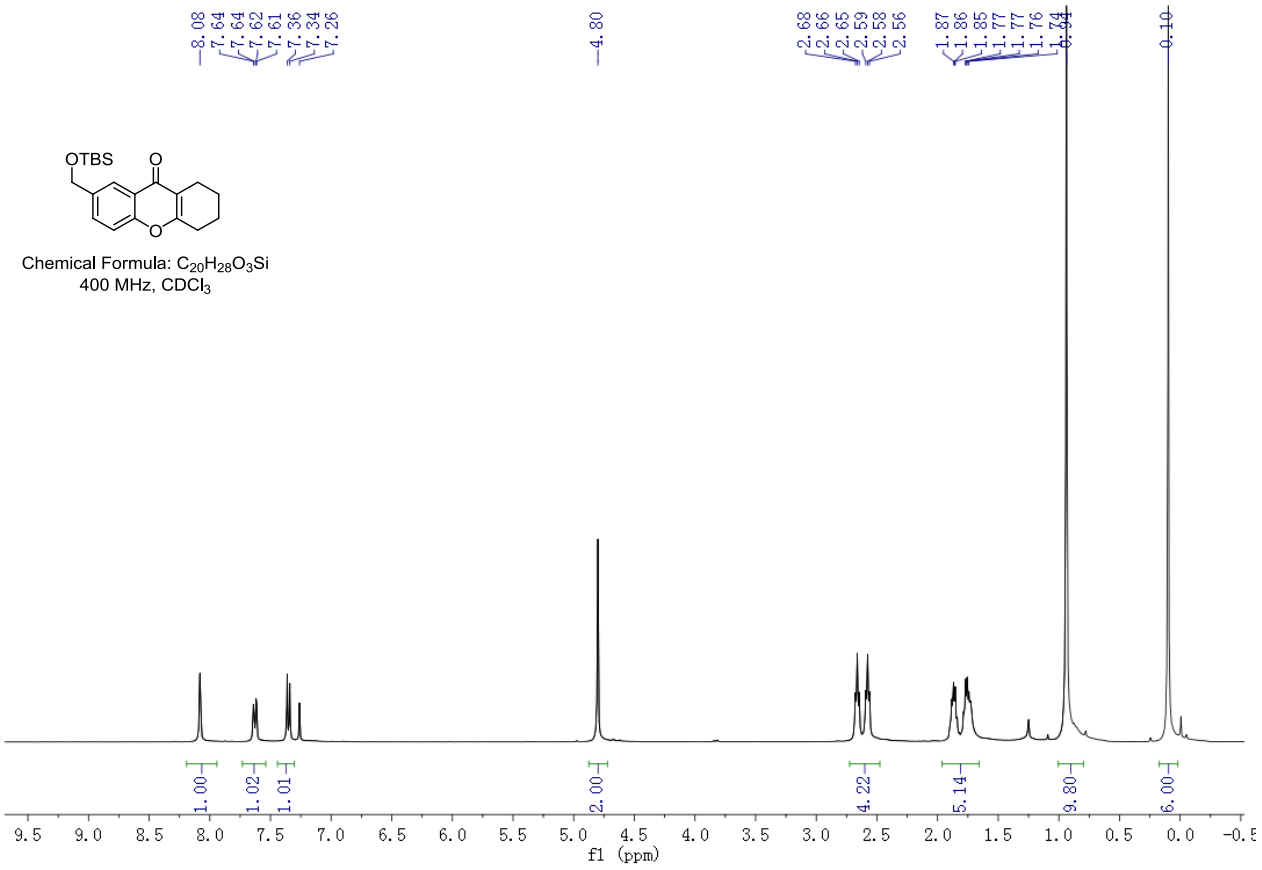

175.7532
164.6098
157.6084
135.1850
131.4926
123.4514
119.5921
119.3005
117.7834
108.5112
28.0389
21.6725
21.3180
20.8822
NC
O
O
Chemical Formula: C14H11NO2
100 MHz, CDCl3
f1 (ppm)


8.48
7.82
7.81
7.80
7.79
7.49
7.47
7.26
2.70
2.69
2.67
2.59
2.57
2.56
1.92
1.90
1.89
1.88
1.87
1.86
1.86
1.80
1.79
1.78
1.78
1.77
1.76
1.75
1.74
F3C
O
O
Chemical Formula: C14H11F3O2
400 MHz, CDCl3
1.00
1.03
1.01
2.11
2.21
2.13
2.76
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

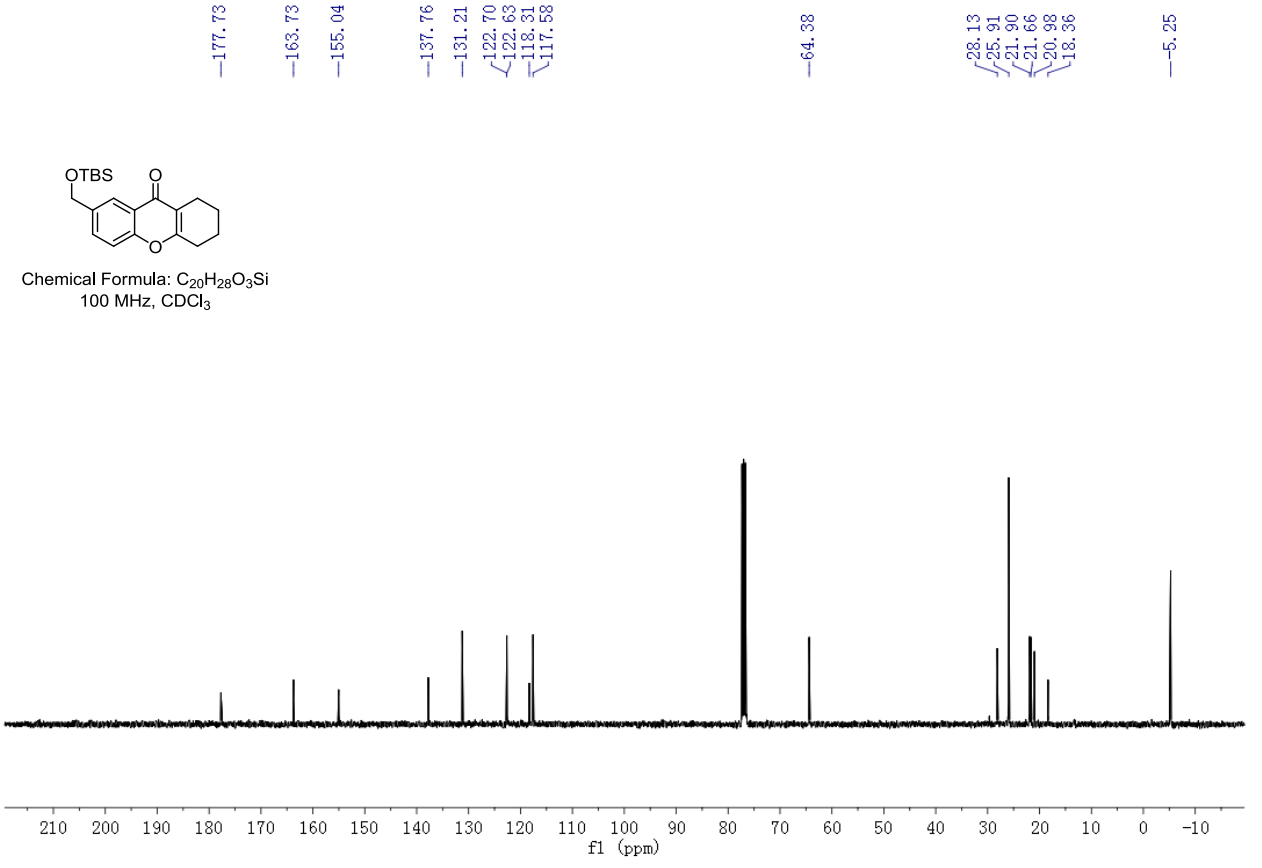

176.65
164.45
157.29
157.33
129.29
129.26
129.23
127.69
127.30
126.96
126.63
126.30
124.98
123.96
123.92
123.88
123.84
122.88
122.28
119.57
119.16
118.73
28.06
21.72
21.40
20.91
F3C
O
O
Chemical Formula: C14H11F3O2
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.10
7.64
7.63
7.61
7.32
7.30
7.26
4.74
2.65
2.63
2.56
2.54
2.53
1.87
1.86
1.85
1.76
1.75
1.73
OH
O
O
Chemical Formula: C14H14O3
400 MHz, CDCl3
1.00
1.02
1.01
2.13
4.29
4.60
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

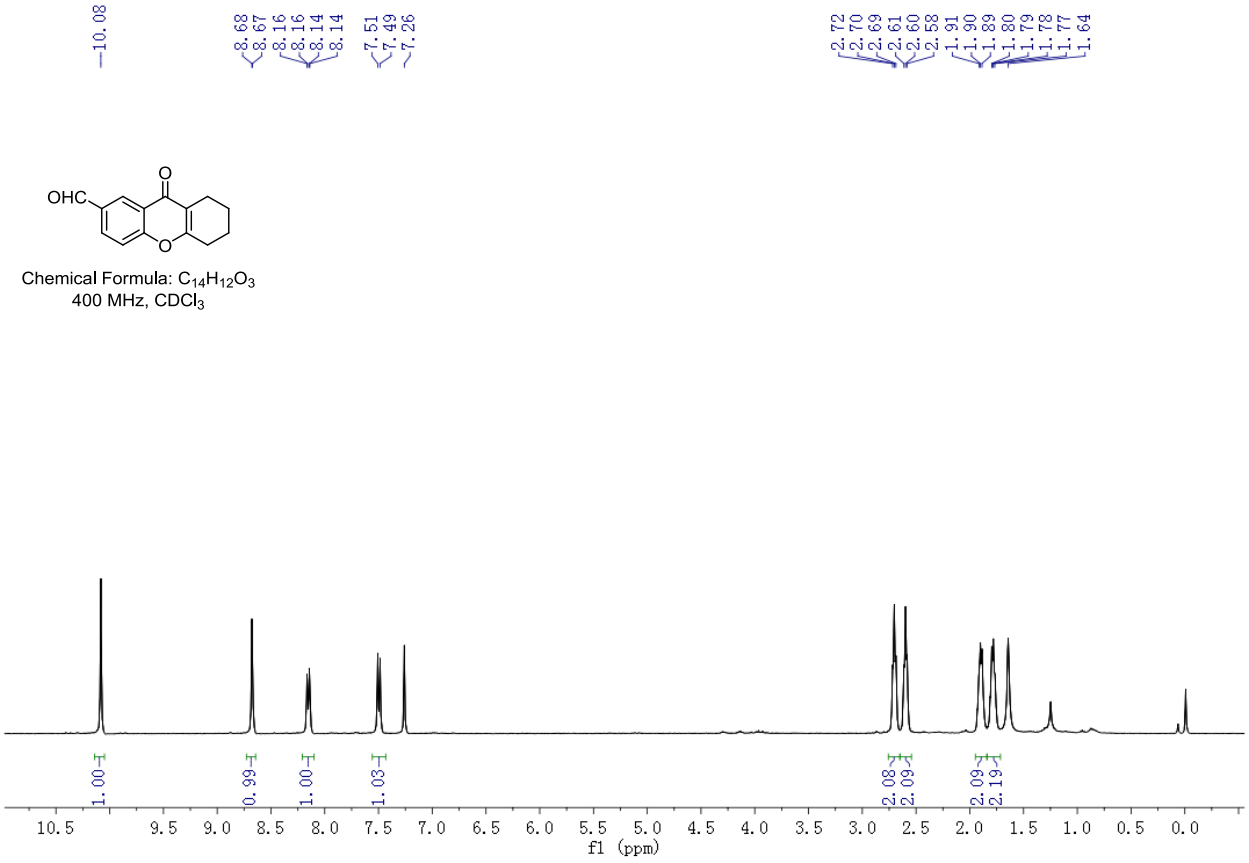

177.81
164.04
155.20
137.63
132.10
123.63
122.67
118.33
117.76
64.41
28.14
21.83
21.59
20.96
OH
O
O
Chemical Formula: C14H14O3
100 MHz, CDCl3
200 180 160 140 120 100 80 60 40 20 0
ppm

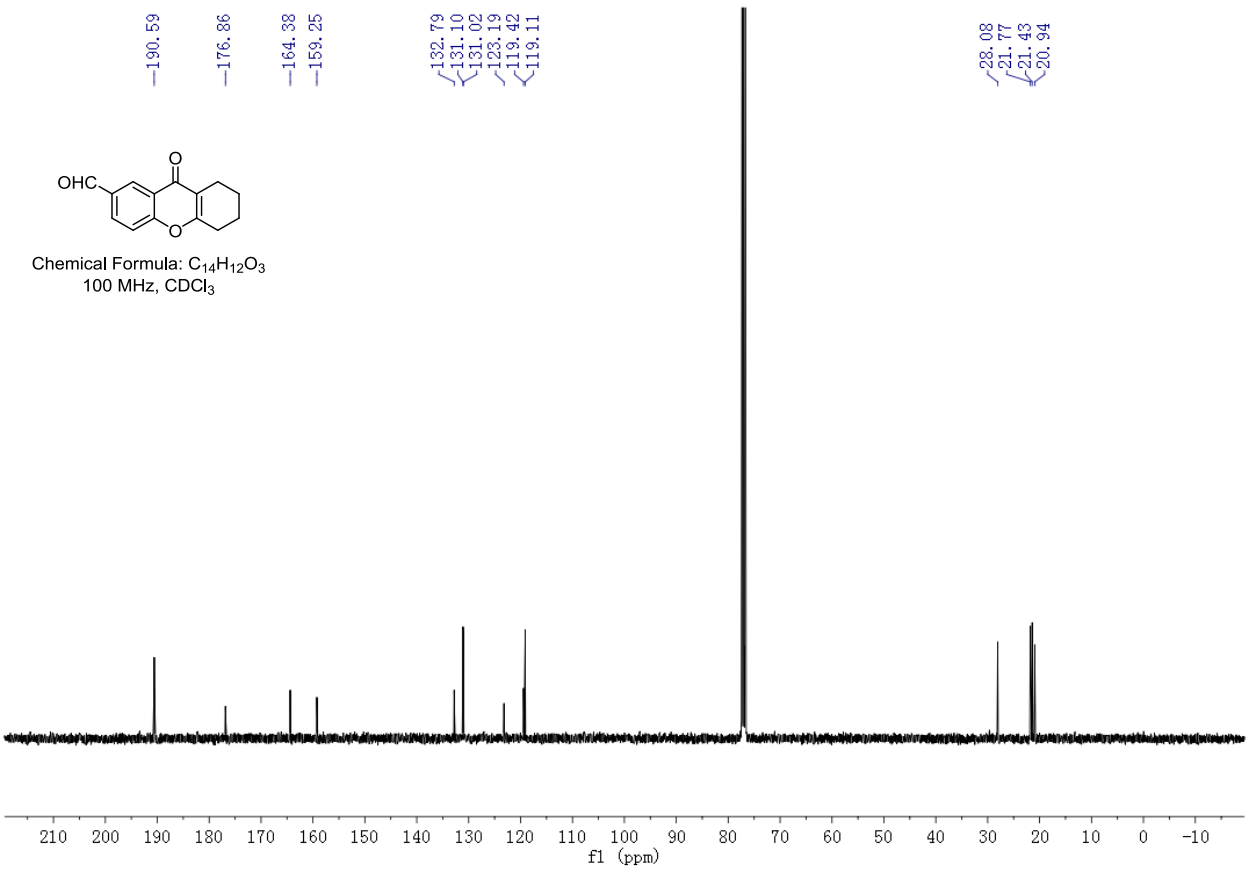


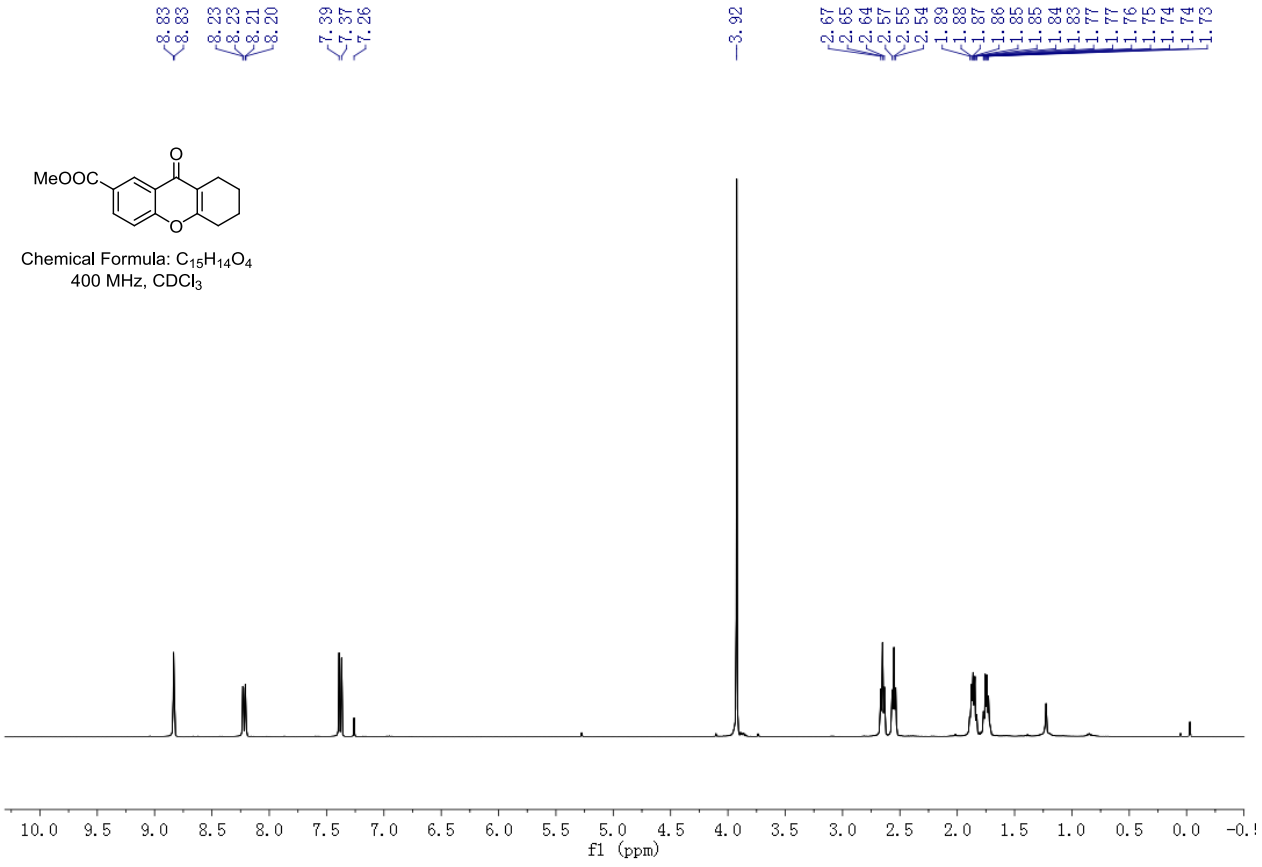
Chemical Formula: $C_{20}H_{28}O_3Si$
400 MHz, $CDCl_3$

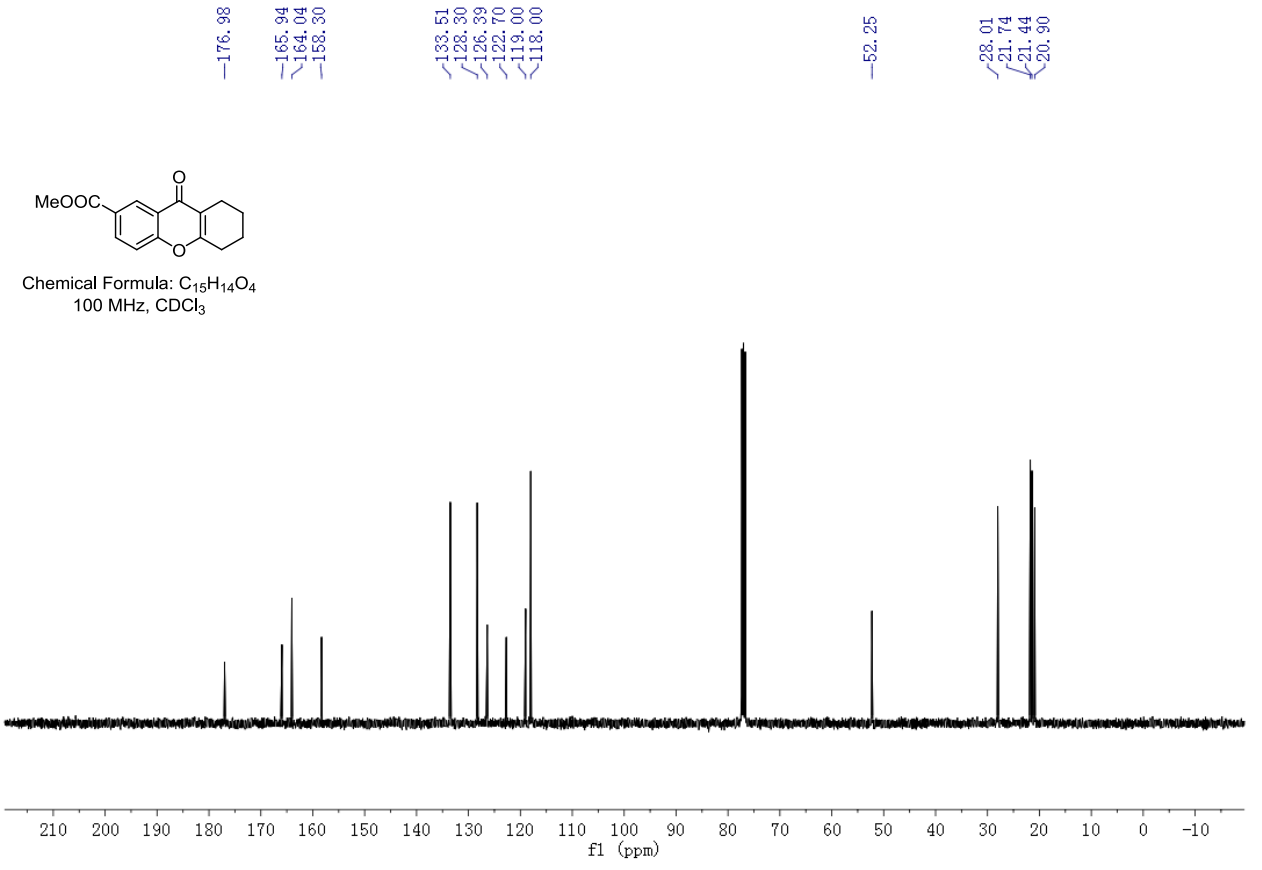


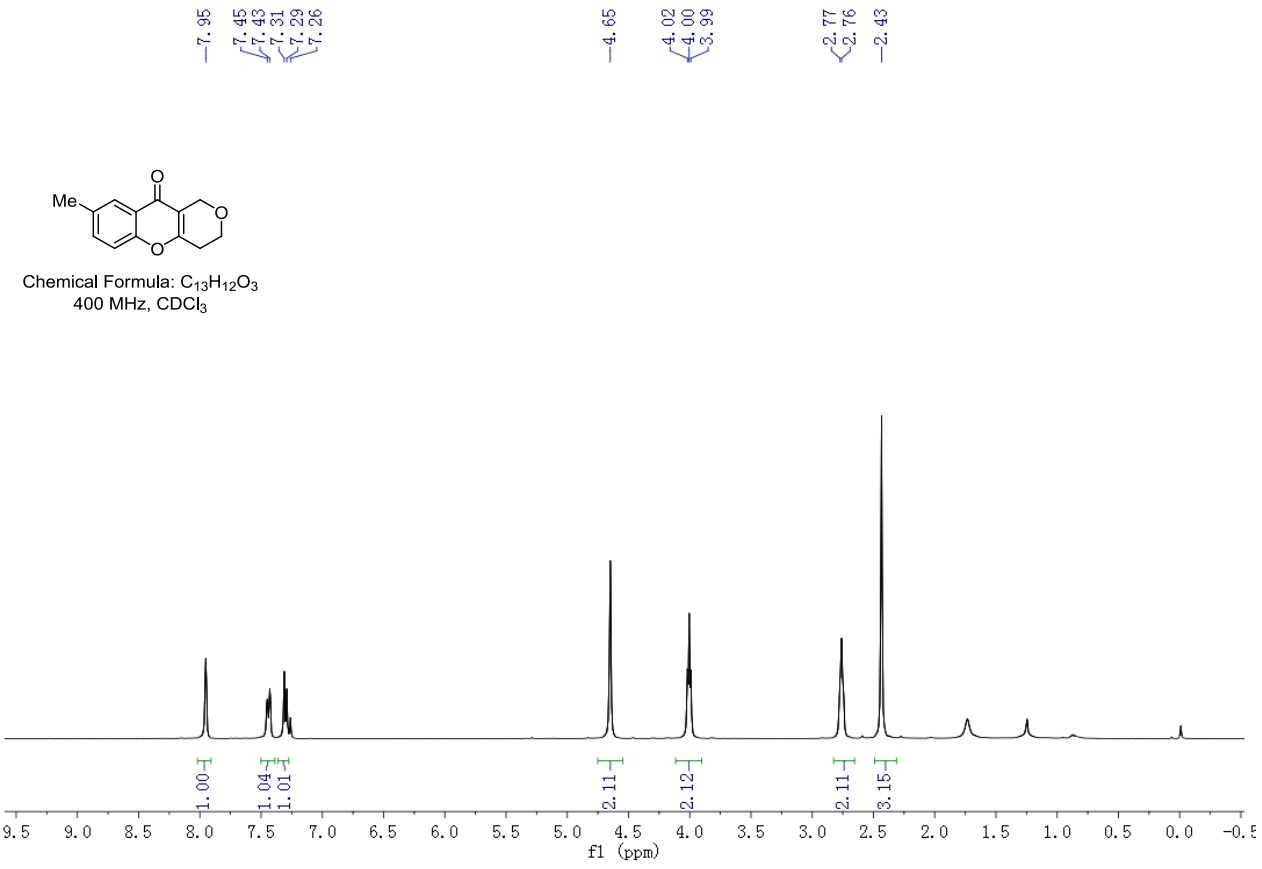
Chemical Formula: $C_{20}H_{28}O_3Si$
100 MHz, $CDCl_3$

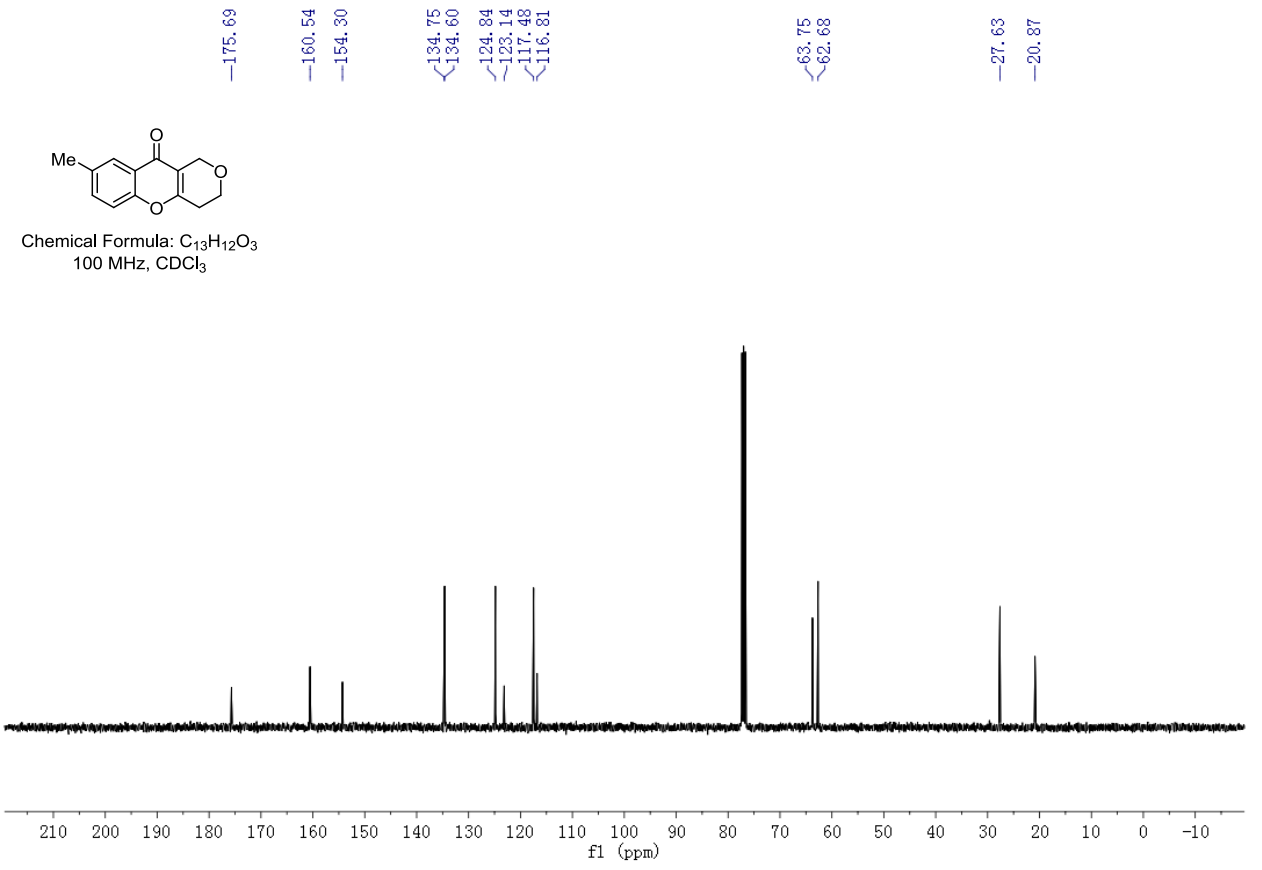

10.08
8.68
8.67
8.16
8.16
8.14
8.14
7.51
7.49
7.26
2.72
2.70
2.69
2.61
2.60
2.58
1.91
1.90
1.89
1.80
1.79
1.78
1.77
1.64
OHC
O
O
Chemical Formula: C14H12O3
400 MHz, CDCl3
1.00
0.99
1.00
1.03
2.08
2.09
2.09
2.19
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

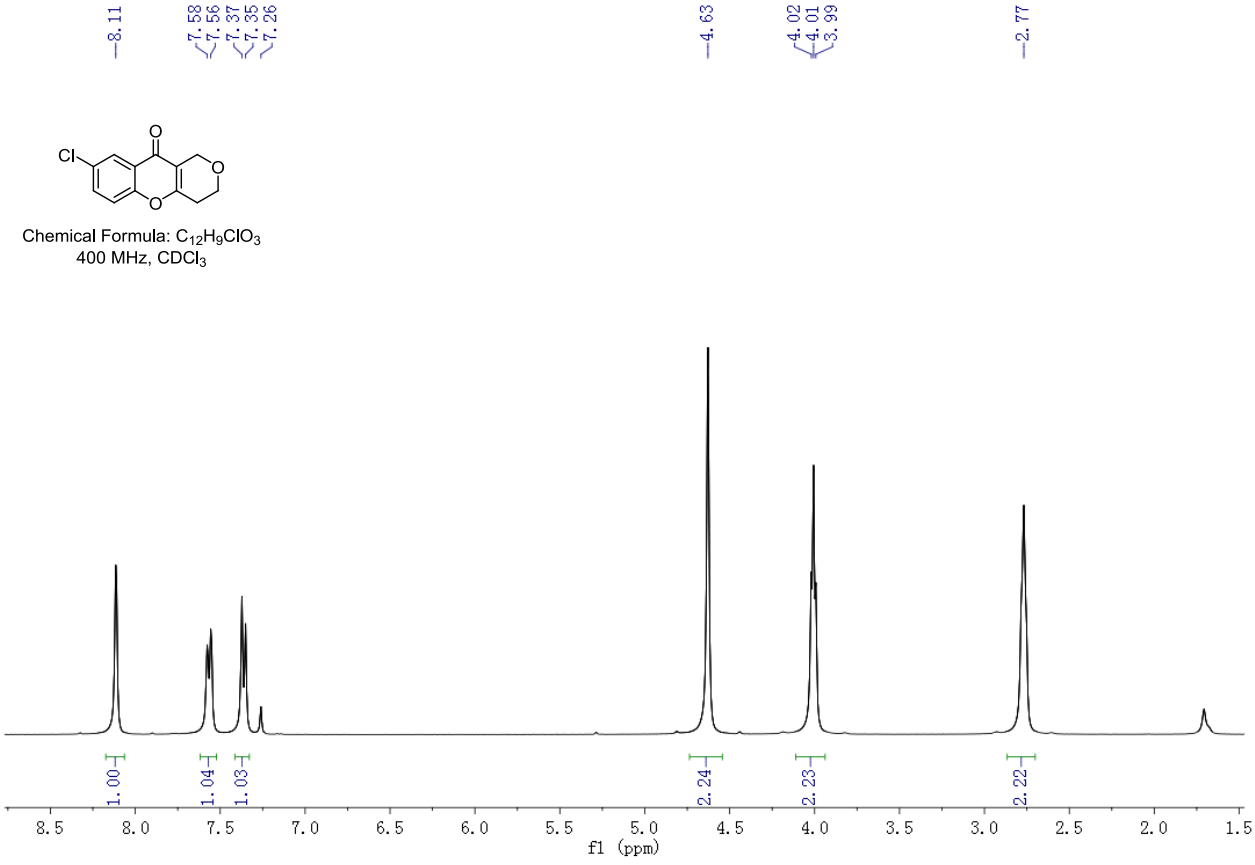

190.59
176.86
164.38
159.25
132.79
131.10
131.02
123.19
119.42
119.11
28.08
21.77
21.43
20.94
OHC
O
O
Chemical Formula: C14H12O3
100 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

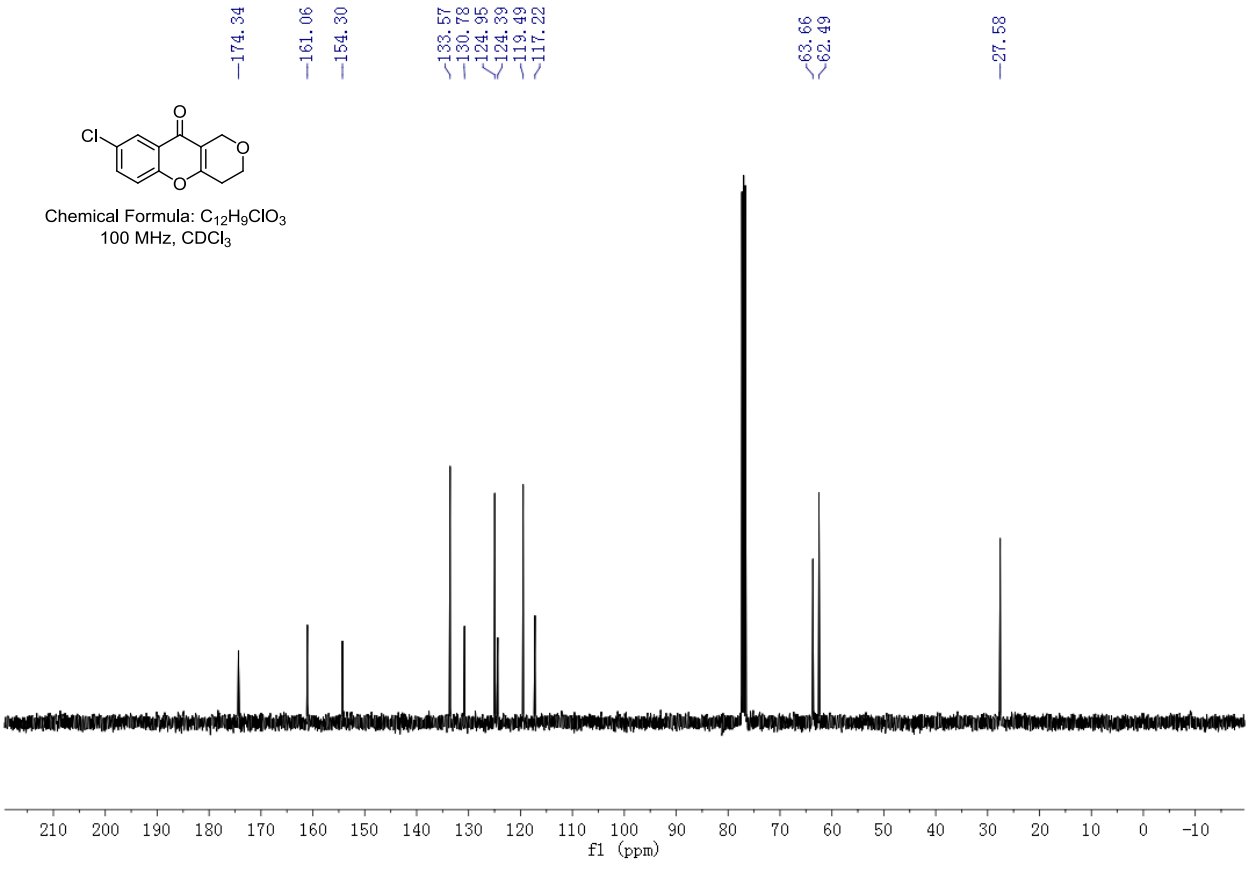

8.83
8.83
8.23
8.23
8.21
8.20
7.39
7.37
7.26
3.92
2.67
2.65
2.64
2.57
2.55
2.54
1.89
1.88
1.87
1.86
1.85
1.85
1.84
1.83
1.77
1.77
1.76
1.75
1.74
1.74
1.73
MeOOC
O
O
Chemical Formula: C15H14O4
400 MHz, CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

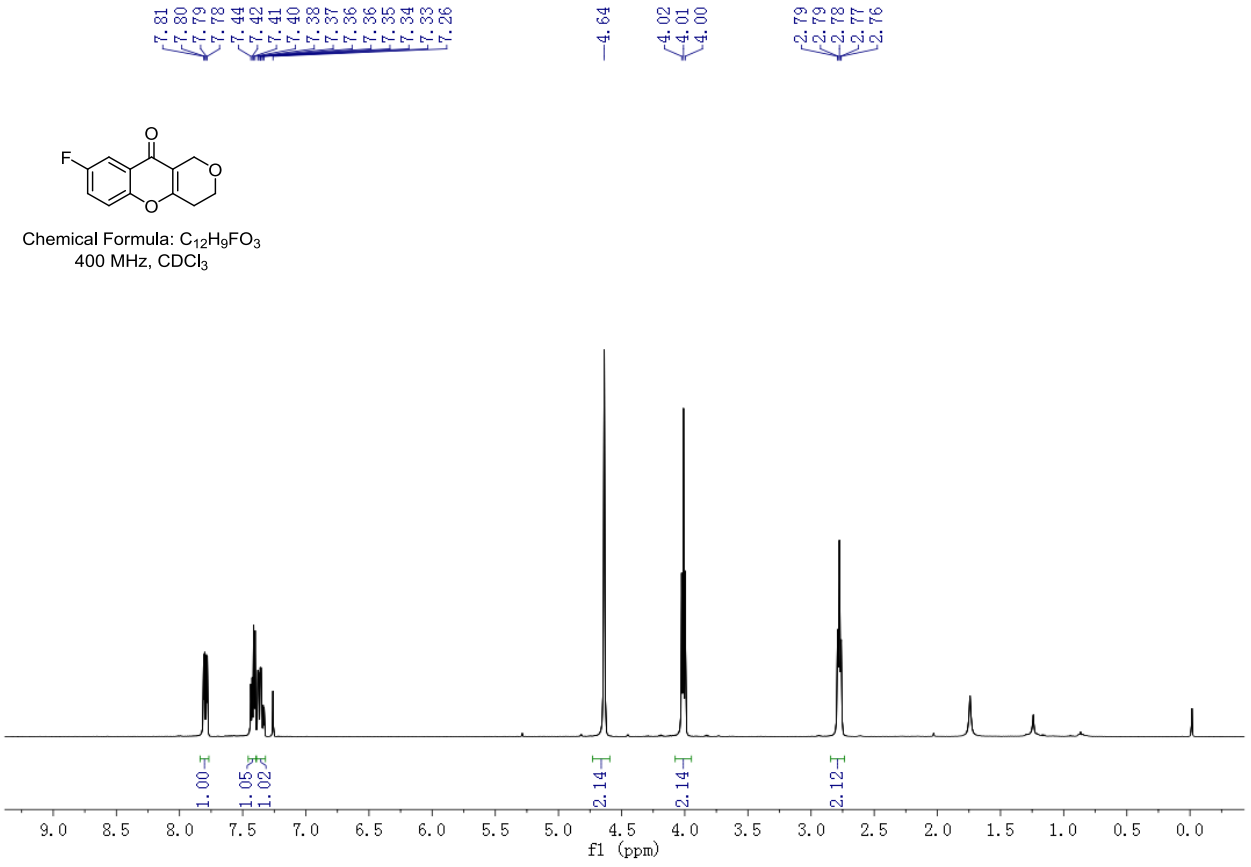

176.98
165.94
164.04
158.30
133.51
128.30
126.39
122.70
119.00
118.00
52.25
28.01
21.74
21.44
20.90
MeOOC
O
O
Chemical Formula: C15H14O4
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

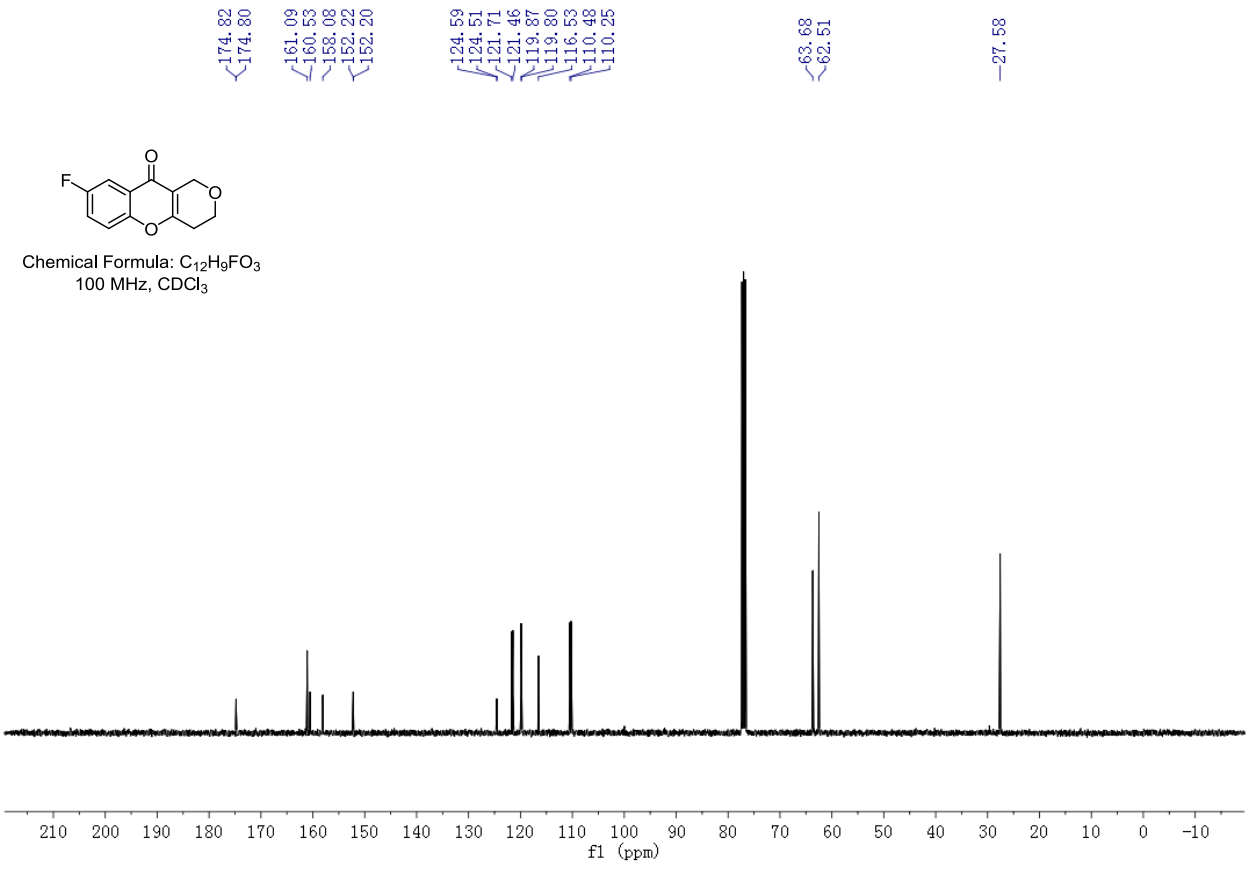

7.95
7.45
7.43
7.31
7.29
7.26
4.65
4.02
4.00
3.99
2.77
2.76
2.43
Me
O
O
O
Chemical Formula: C13H12O3
400 MHz, CDCl3
1.00
1.04
1.01
2.11
2.12
2.11
3.15
f1 (ppm)

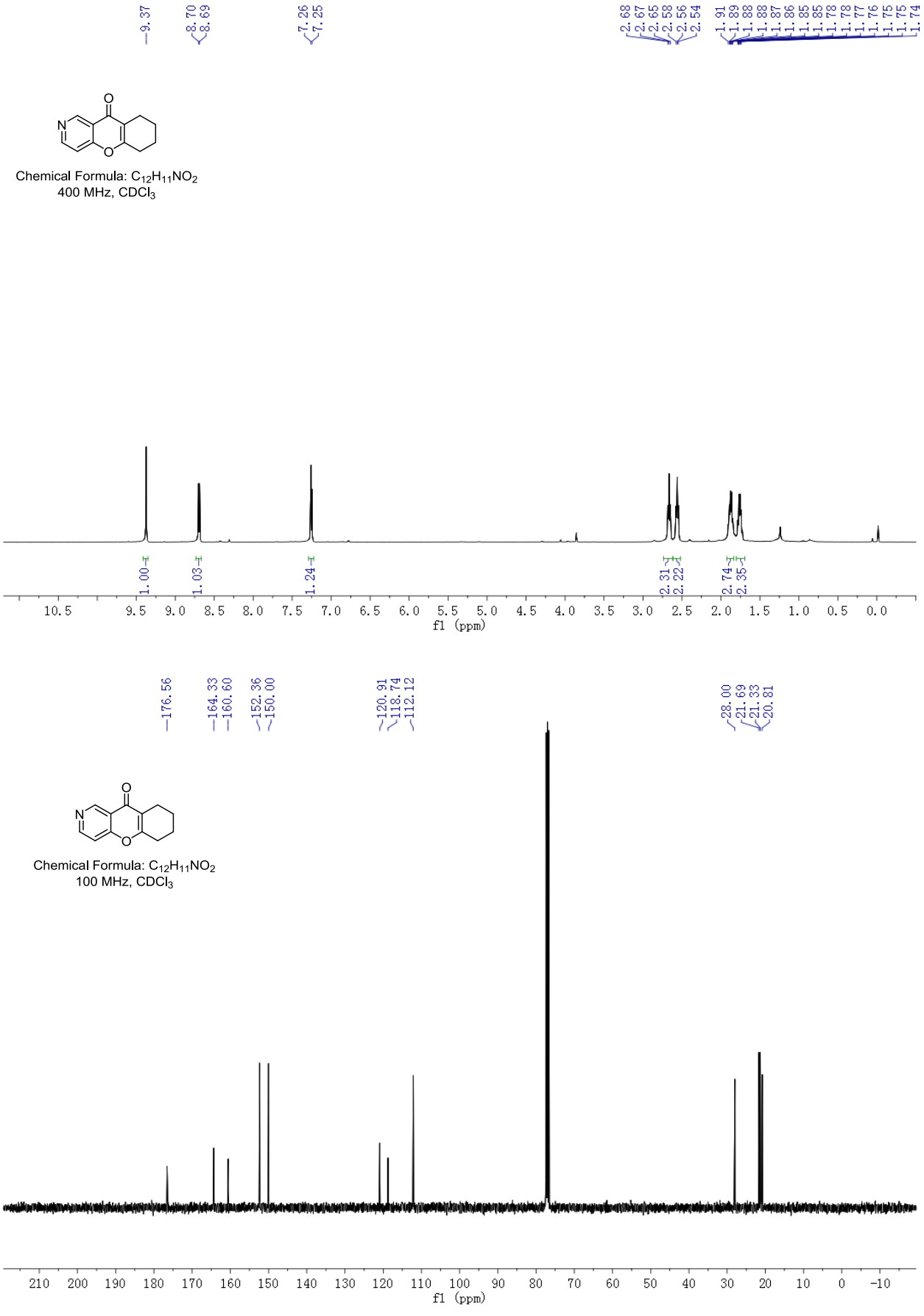

175.69
160.54
154.30
134.75
134.60
124.84
123.14
117.48
116.81
63.75
62.68
27.63
20.87
Me
O
O
O
Chemical Formula: C13H12O3
100 MHz, CDCl3
f1 (ppm)

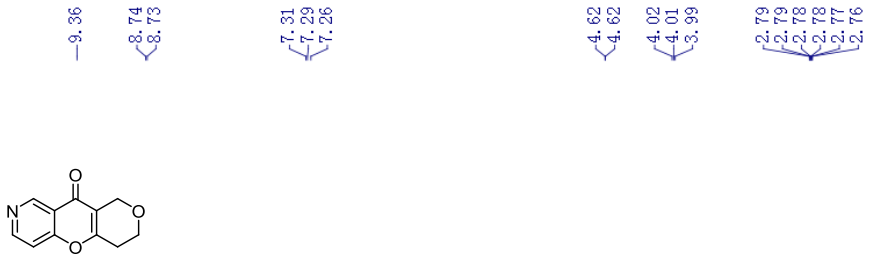

8.11
7.58
7.56
7.37
7.35
7.26
4.63
4.02
4.01
3.99
2.77
Cl
O
O
O
Chemical Formula: C12H9ClO3
400 MHz, CDCl3
1.00
1.04
1.03
2.24
2.23
2.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


174.34
161.06
154.30
133.57
130.78
124.95
124.39
119.49
117.22
63.66
62.49
27.58
Cl
O
O
O
Chemical Formula: C12H9ClO3
100 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

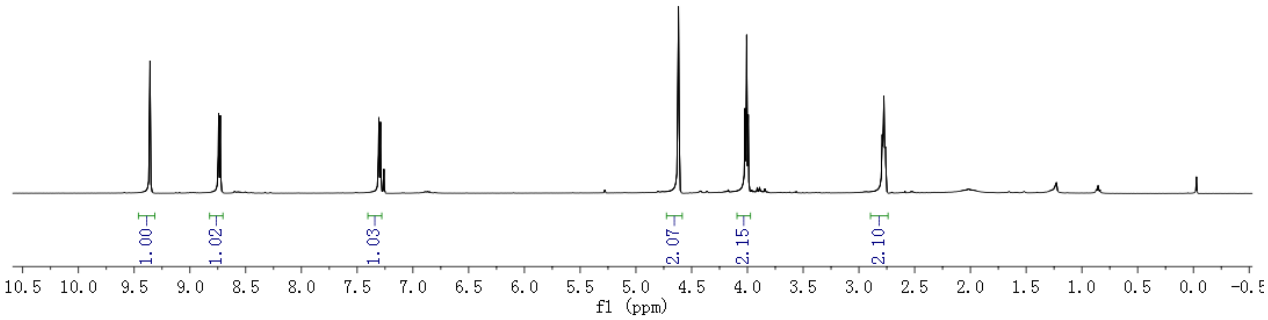

7.81
7.80
7.79
7.78
7.44
7.42
7.41
7.40
7.38
7.37
7.36
7.36
7.35
7.34
7.33
7.26
4.64
4.02
4.01
4.00
2.79
2.79
2.78
2.77
2.76
F
O
O
O
Chemical Formula: C12H9FO3
400 MHz, CDCl3
1.00
1.05
1.02
2.14
2.14
2.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

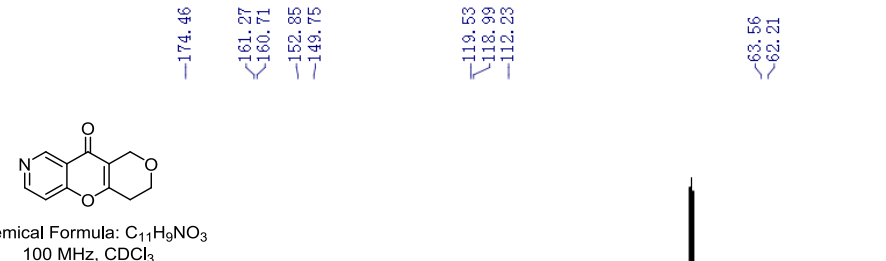

174.82
174.80
161.09
160.53
158.08
152.22
152.20
124.59
124.51
121.71
121.46
119.87
119.80
116.53
110.48
110.25
63.68
62.51
27.58
F
O
O
O
Chemical Formula: C12H9FO3
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.37
8.70
8.69
7.26
7.25
2.68
2.67
2.65
2.58
2.56
2.54
1.91
1.89
1.88
1.88
1.87
1.86
1.85
1.85
1.78
1.78
1.77
1.76
1.75
1.75
1.74
Chemical Formula: C12H11NO2
400 MHz, CDCl3
1.00
1.03
1.24
2.31
2.22
2.74
2.35
f1 (ppm)
176.56
164.33
160.60
152.36
150.00
120.91
118.74
112.12
28.00
21.69
21.33
20.81
Chemical Formula: C12H11NO2
100 MHz, CDCl3
f1 (ppm)

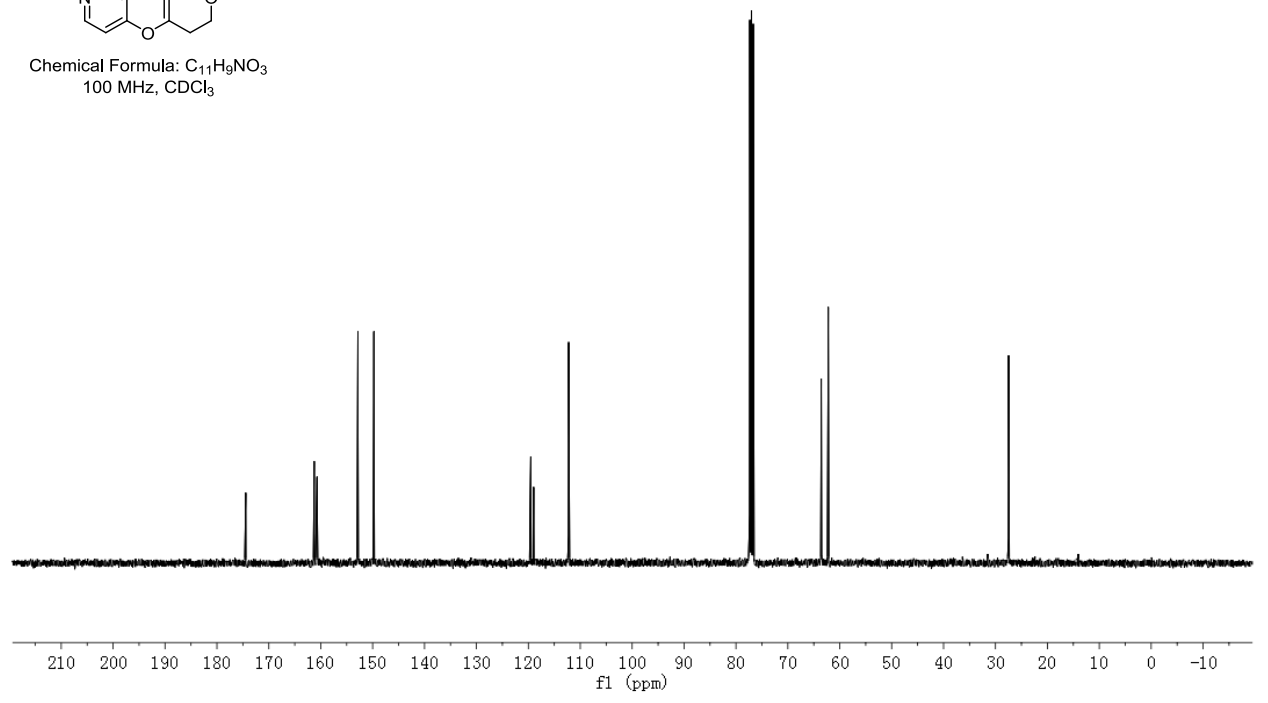


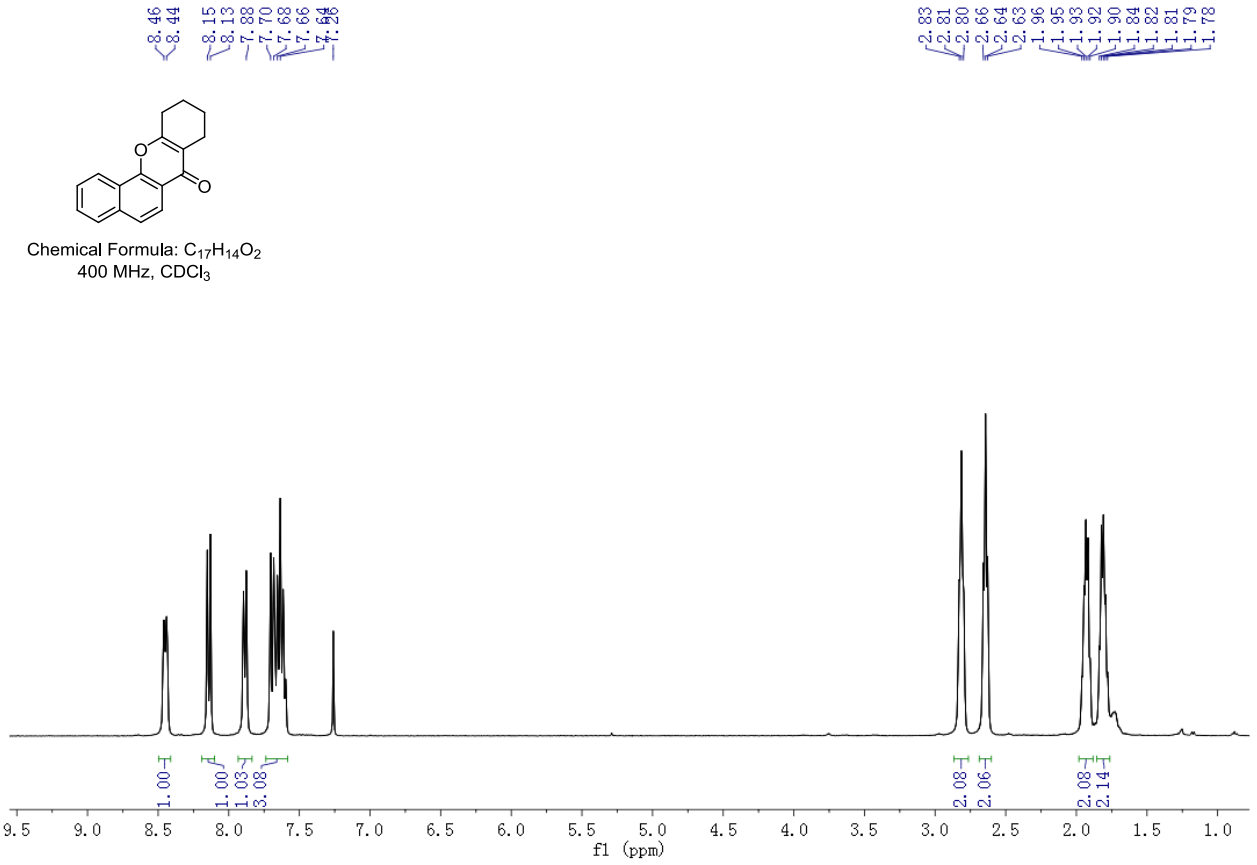
Chemical Formula: $C_{11}H_9NO_3$
400 MHz, $CDCl_3$

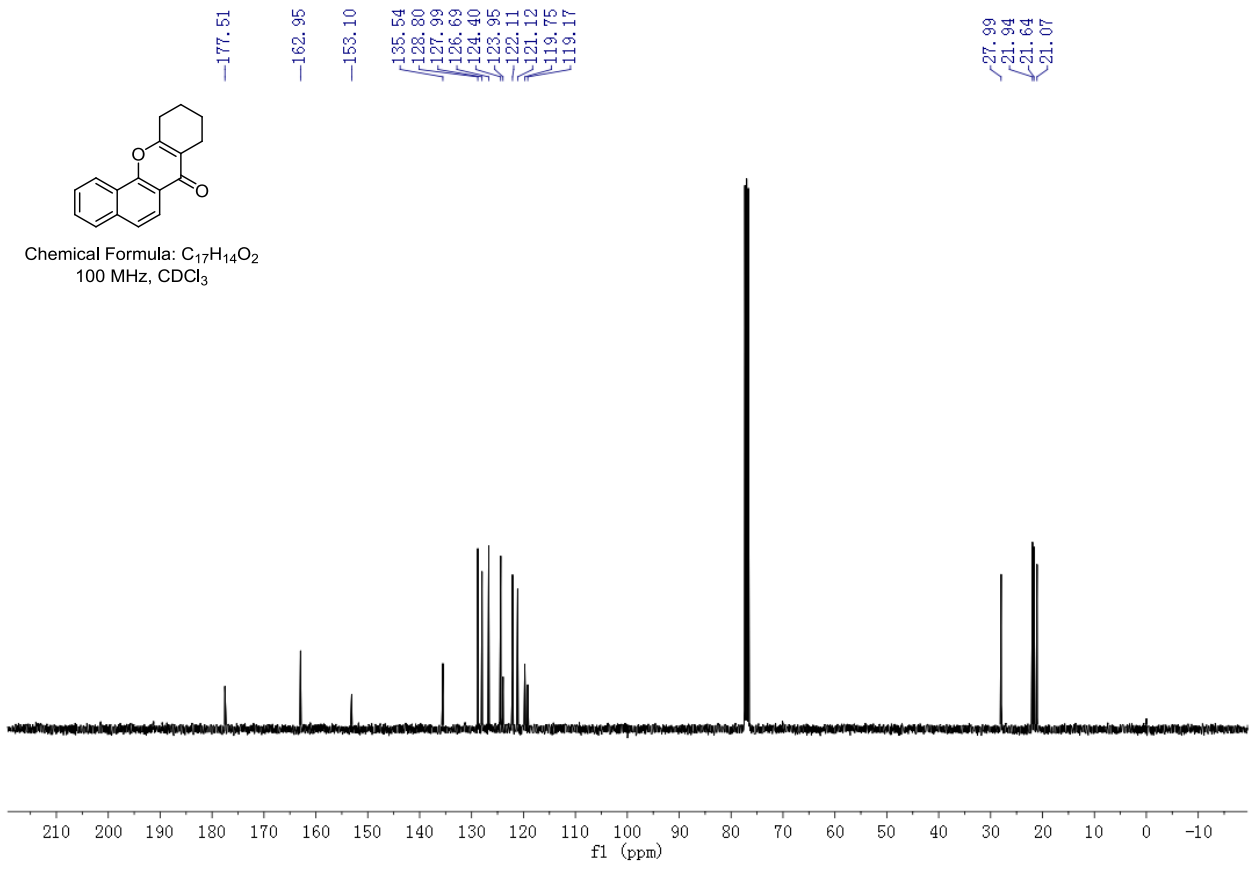


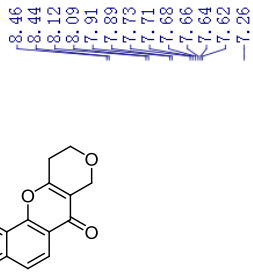


Chemical Formula: $C_{11}H_9NO_3$
100 MHz, $CDCl_3$

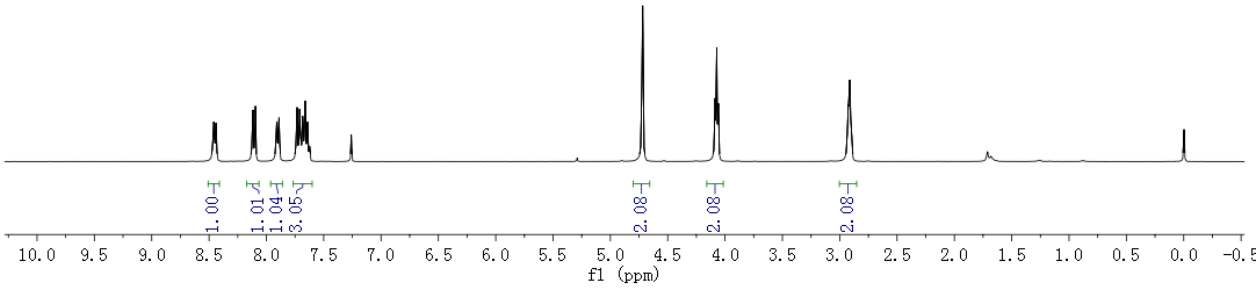


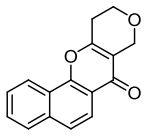

8.46
8.44
8.15
8.13
7.88
7.70
7.68
7.66
7.64
7.26
2.83
2.81
2.80
2.66
2.64
2.63
1.96
1.95
1.93
1.92
1.90
1.84
1.82
1.81
1.79
1.78
O
O
Chemical Formula: C17H14O2
400 MHz, CDCl3
1.00
1.00
1.03
3.08
2.08
2.06
2.08
2.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)


177.51
162.95
153.10
135.54
128.80
127.99
126.69
124.40
123.95
122.11
121.12
119.75
119.17
27.99
21.94
21.64
21.07
O
O
Chemical Formula: C17H14O2
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

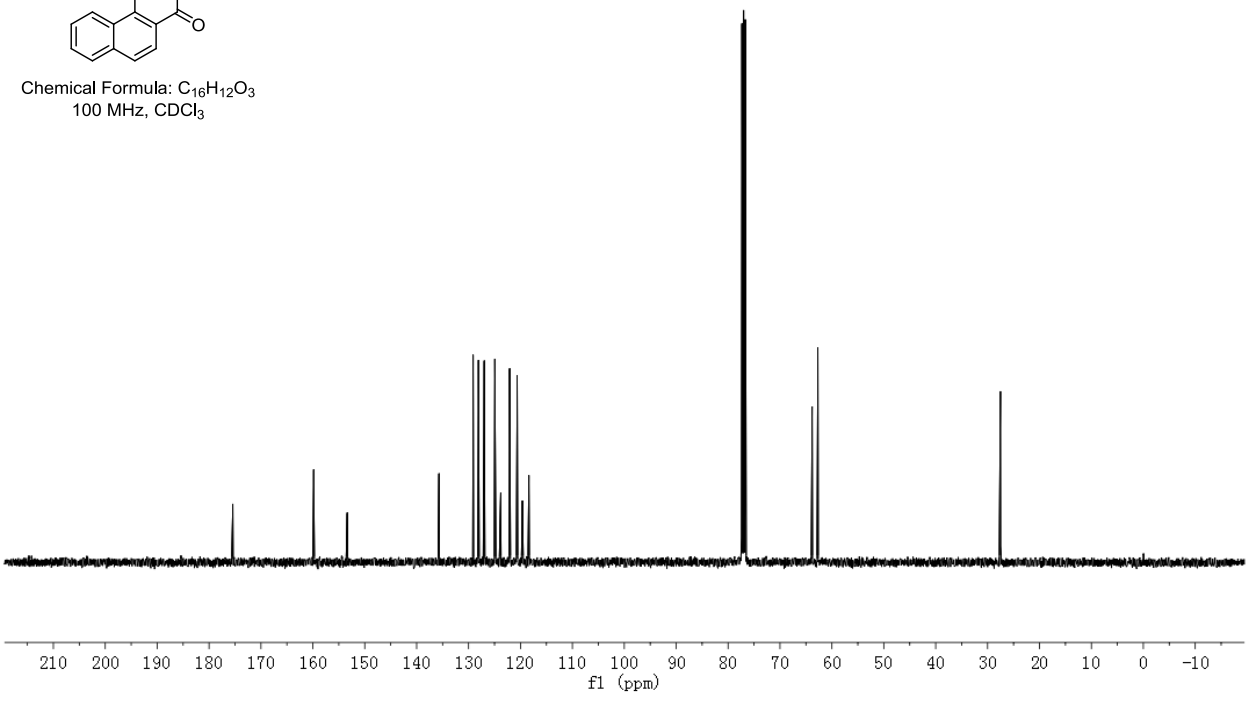


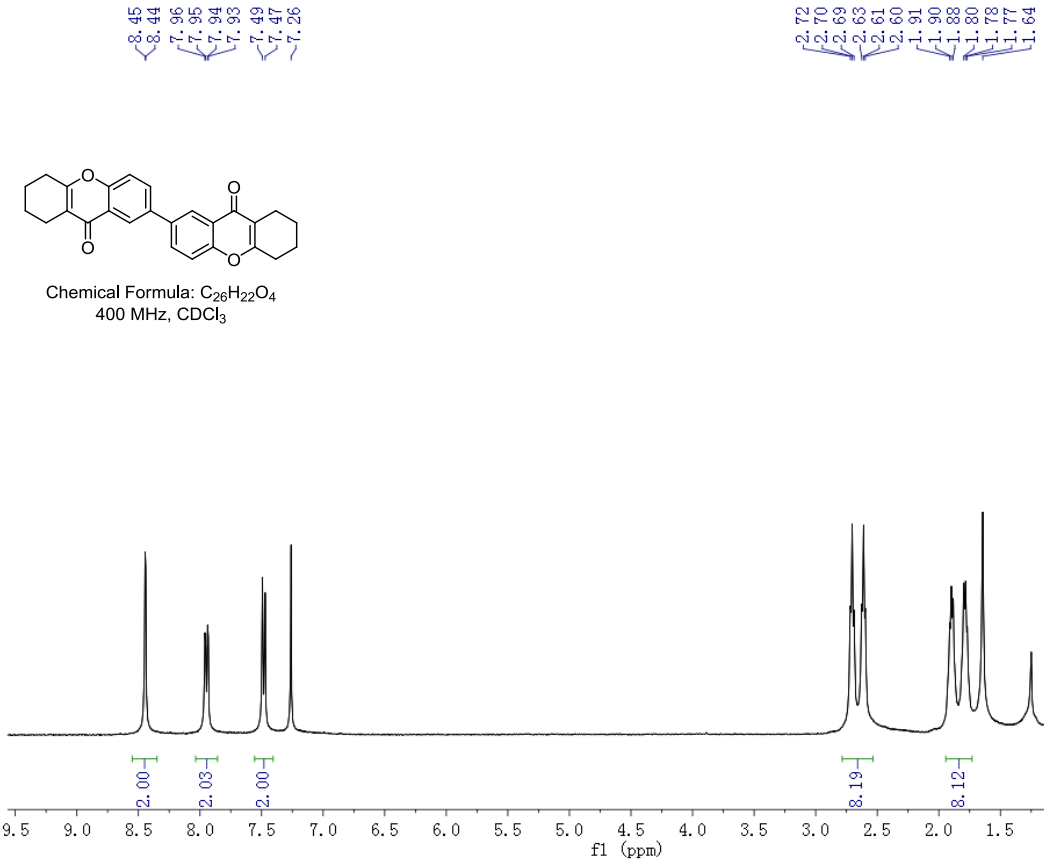
Chemical Formula: $C_{16}H_{12}O_3$
400 MHz, $CDCl_3$

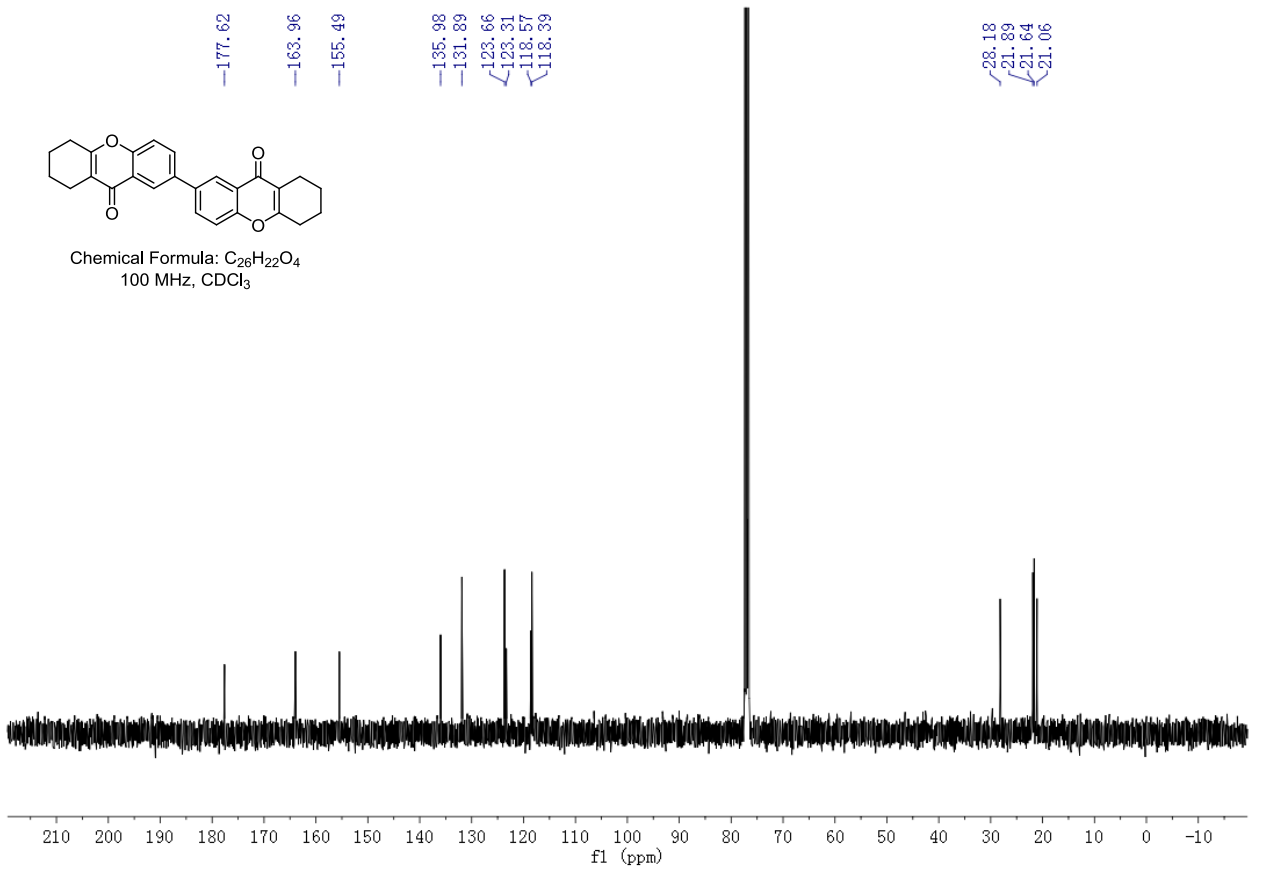


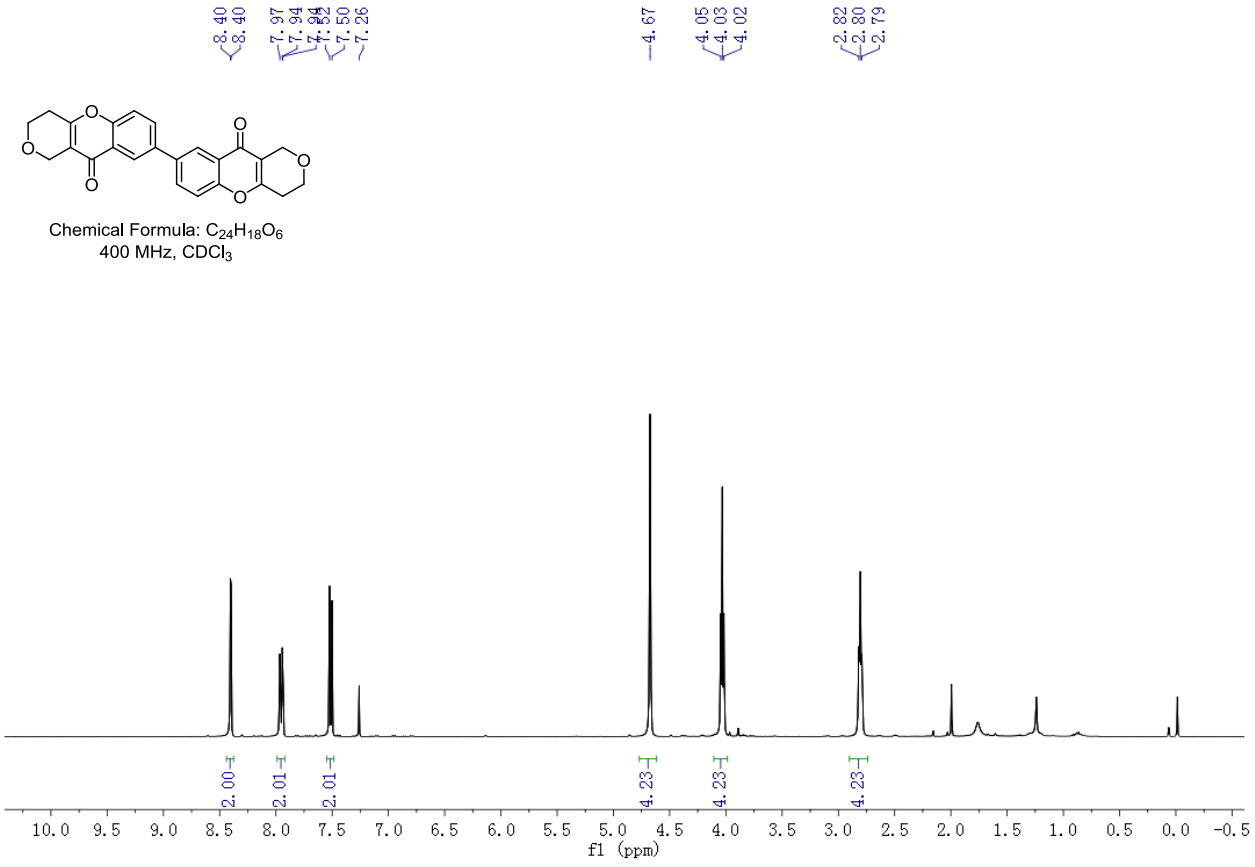


Chemical Formula: $C_{16}H_{12}O_3$
100 MHz, $CDCl_3$

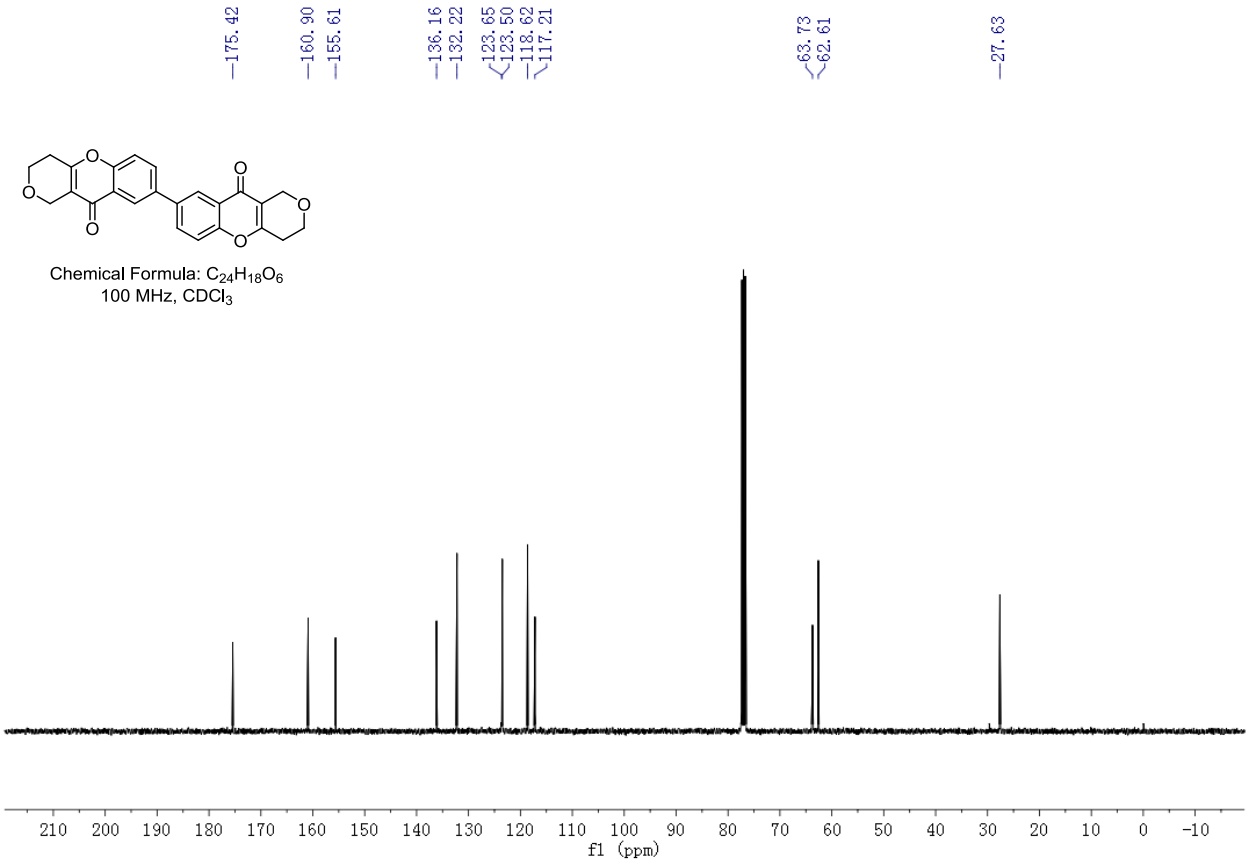



8.45
8.44
7.96
7.95
7.94
7.93
7.49
7.47
7.26
2.72
2.70
2.69
2.63
2.61
2.60
1.91
1.90
1.88
1.80
1.78
1.77
1.64
Chemical Formula: C26H22O4
400 MHz, CDCl3
2.00
2.03
2.00
8.19
8.12
f1 (ppm)


177.62
163.96
155.49
135.98
131.89
123.66
123.31
118.57
118.39
28.18
21.89
21.64
21.06
Chemical Formula: C26H22O4
100 MHz, CDCl3
f1 (ppm)



Chemical Formula: $C_{24}H_{18}O_6$
400 MHz, $CDCl_3$



Chemical Formula: $C_{24}H_{18}O_6$
100 MHz, $CDCl_3$