Supporting Information

Photocatalyst-free Visible Light Driven Synthesis of *gem*-dihaloenones from Alkynes, Tetrahalomethanes and Water

Fuqing Zhang,[a] Zixiang Wei,[a] Wei Wu,[b] Na Liu,[a,b] Xinhan Li,[a] Luqian Zou,[a] Kaiming Wang,[a] Jianbin Xu*[a, b] and Baomin Fan*[a, b]

[a] School of Chemistry and Environment, Yunnan Minzu University, Kunming, 650500, China.

[b] Key Laboratory of Chemistry in Ethnic Medicinal Resources, State Ethnic Affairs Commission & Ministry of Education, Yunnan Minzu University, Kunming, Yunnan, 650504, China

E-mail addresses: xujianbin@ymu.edu.cn (Dr. Jianbin Xu); adams.bmf@hotmail.com (Prof. Baomin Fan).

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1. General information

All commercially available reagents were obtained from commercial suppliers and used without further purification. All catalytic experiments were performed under an atmosphere of argon by using Glove Box. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker NMR spectrometer in $CDCl_3$ using TMS as an internal reference with chemical shift values reported in ppm. Abbreviations used in the NMR follow-up experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

HRESIMS data were recorded on an LCMS-IT-TOF mass spectrometer (Shimadzu, Kyoto, Japan).

2. General procedure for the synthesis of *α- gem*-dihaloenones

To an oven dried Schlenk-tube, CBr_4 (0.4 mmol), Methanol (1.5 mL) were added under argon atmosphere. phenylacetylene (0.2 mmol) and ultrapure water (100 μL) was added to the reaction mixture. The reaction mixture was stirred under the irradiation of 30 W LEDs (460 nm - 470 nm) at room temperature. After completion of the reaction (indicated by GC), the solution was concentrated in vacuum and the product was purified by silica gel column chromatography.

3. Control Experiment with $H_2{}^{18}O$

To an oven dried Schlenk-tube, CBr_4 (0.4 mmol), Methanol (1.5 mL) were added under argon atmosphere. phenylacetylene (0.2 mmol) and $H_2{}^{18}O$ (100 μL) was added to the reaction mixture. The reaction mixture was stirred under the irradiation of 30 W LEDs (460 nm - 470 nm) at room temperature. After completion of the reaction (indicated by GC), the solution was concentrated in vacuum and the product was purified by silica gel column chromatography to obtain **3a-^{18}O**.

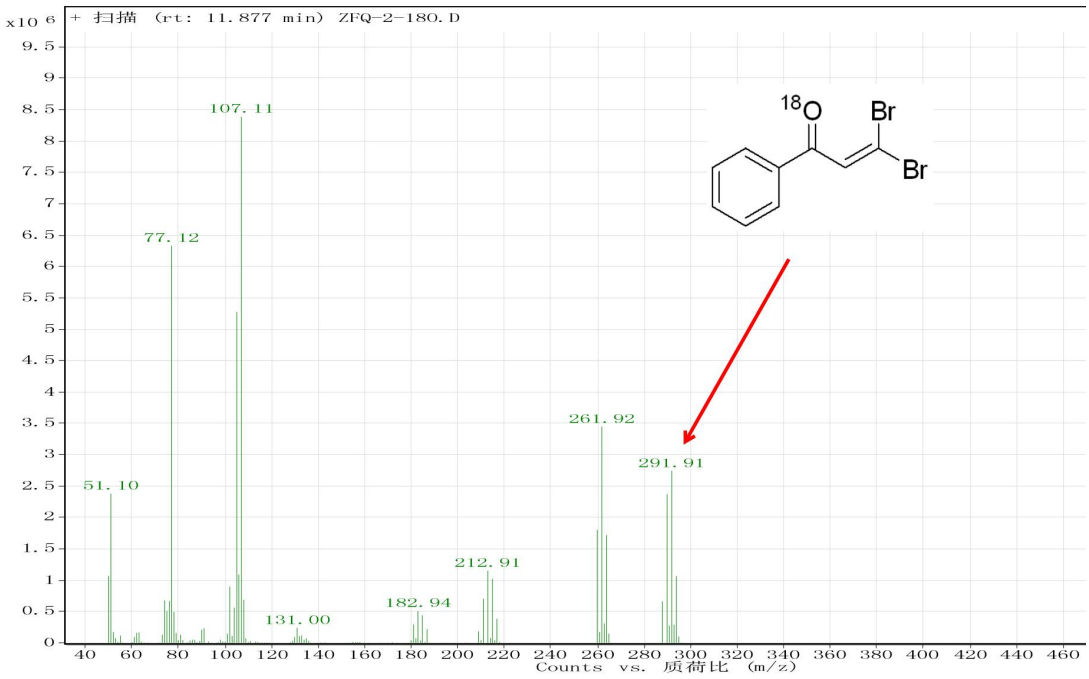


Figure S2. GC spectrum of **3a-^{18}O**

4. UV-Vis Absorption Spectra

The UV-Vis Absorption Spectra of phenylacetylene and CBr_4 in Methanol was introduced to a 1 cm path length quartz cuvette and analyzed using a Agilent Technologies Cary 8454 UV/ViS. The UV/vis spectrum of phenylacetylene showed no absorption. The ultraviolet/visible spectra of CBr_4 show weak absorption.

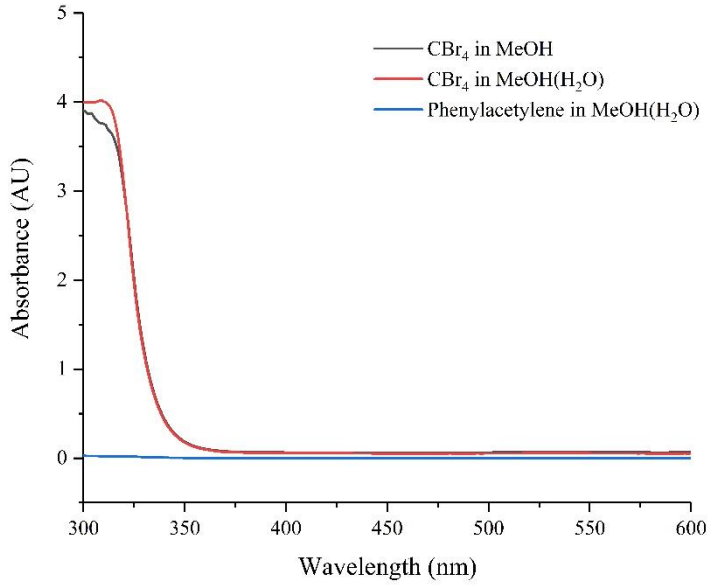
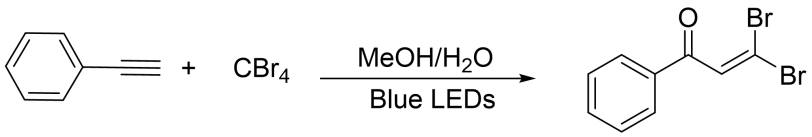


Figure S2. UV-Vis absorption spectra of phenylacetylene and CBr_4

5. Light/Dark experiment



1a **2a** **3a**

To an oven dried Schlenk-tube, CBr_4 (0.4 mmol), Methanol (1.5 mL) were added under argon atmosphere. phenylacetylene (0.2 mmol) and ultrapure water (100 µL) was added to the reaction mixture. The reaction mixture was stirred under the irradiation of 30 W LEDs (460 nm - 470 nm) at room temperature. The reaction tube was wrapped in tin foil and a 10 µL sample of the reaction mixture was taken with a syringe and measured by GC. After being stirred for 4 hours in dark, a 10 µL sample of the reaction mixture was taken with a syringe and measured by GC. The reaction mixture was then irradiated with a 30 W blue LEDs lamp and stirred for 4 hours. This process was repeated three times.

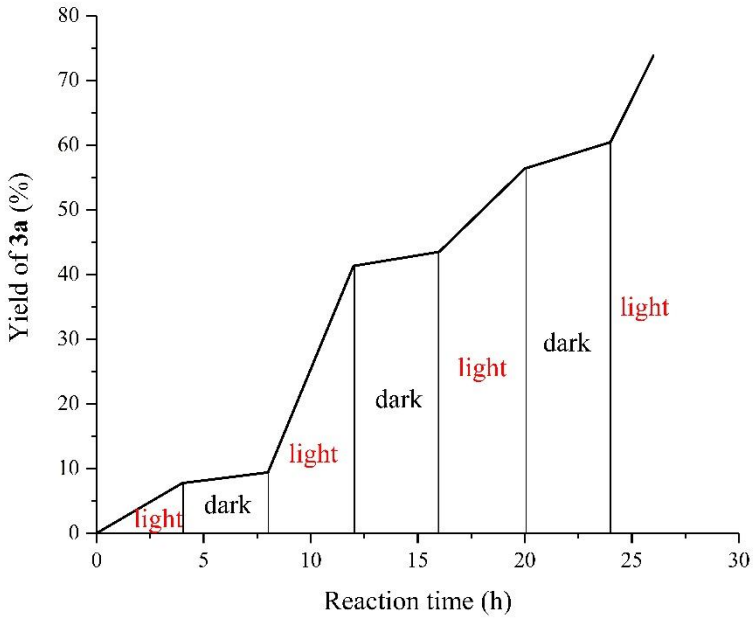


Figure S3. Light/Dark experiment

6. Emission spectrum of LED lamp

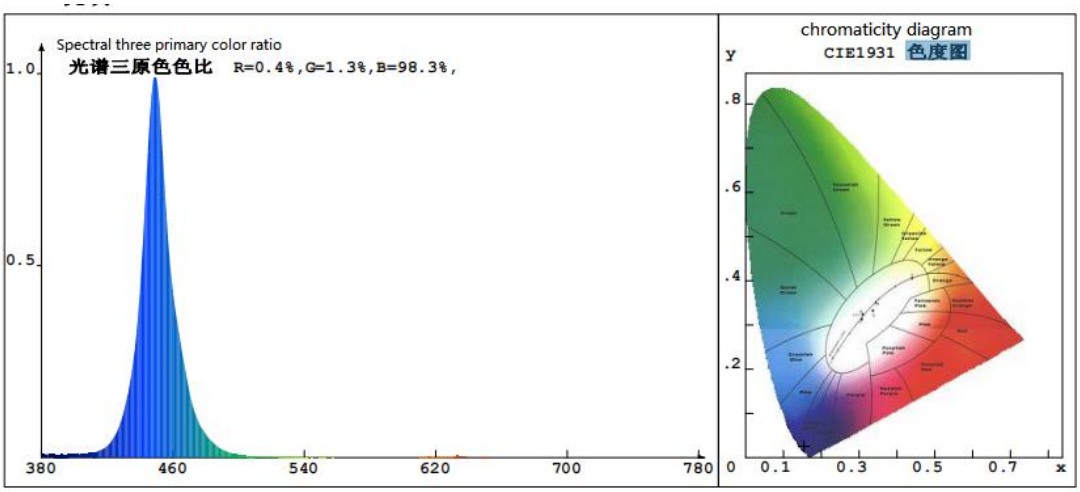
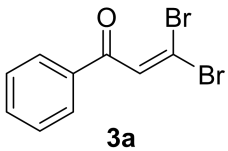


Figure S4. Emission spectrum

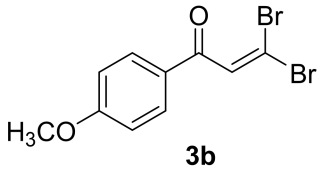
7. Spectral data of products



3a

3,3-dibromo-1-phenylprop-2-en-1-one (**3a**)[1]

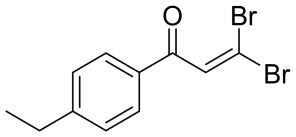
Purified by silica gel chromatography (petroleum), the desired product **3a** was obtained as a yellow oil. Yield: 42.2 mg (73%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.85 (s, 1H), 7.64 – 7.59 (m, 1H), 7.50 (dd, *J* = 8.3, 7.0 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.9, 136.5, 134.0, 132.7, 129.0, 128.8, 103.6.



3b

3,3-dibromo-1-(4-methoxyphenyl)prop-2-en-1-one (**3b**)[1]

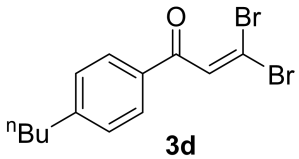
Purified by silica gel chromatography (petroleum), the desired product **3b** was obtained as a yellow oil. Yield: 54.3 mg (85%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.9 Hz, 2H), 7.76 (s, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.7, 164.3, 133.2, 131.3, 129.3, 114.2, 101.7, 55.7.



3c

3,3-dibromo-1-(4-ethylphenyl)prop-2-en-1-one (**3c**)[1]

Purified by silica gel chromatography (petroleum), the desired product **3c** was obtained as a colorless oil. Yield: 52.6 mg (83%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.82 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.6, 151.2, 134.1, 132.9, 129.1, 128.5, 102.7, 29.1, 15.2.

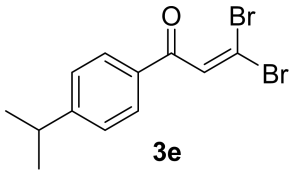


3d

3,3-dibromo-1-(4-butylphenyl)prop-2-en-1-one (**3d**)[1]

Purified by silica gel chromatography (petroleum), the desired product **3d** was obtained as a yellow oil. Yield: 57.4 mg (83%). ^{1}H NMR (400 MHz, Chloroform-d) δ

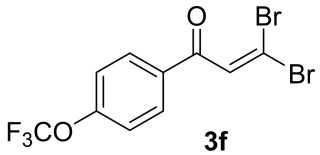
7.83 (d, J = 8.0 Hz, 3H), 7.33 – 7.26 (m, 2H), 2.72 – 2.63 (m, 2H), 1.61 (pd, J = 7.6, 1.5 Hz, 2H), 1.35 (ddd, J = 14.9, 7.4, 1.5 Hz, 2H), 0.97 – 0.89 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.5, 150.0, 134.1, 132.9, 129.0, 129.0, 102.7, 35.9, 33.3, 22.4, 14.0.



3e

3,3-dibromo-1-(4-isopropylphenyl)prop-2-en-1-one (**3e**)

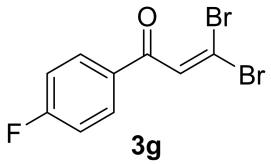
Purified by silica gel chromatography (petroleum), the desired product **3e** was obtained as a yellow oil. Yield: 50.8 mg (76%). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.91 – 7.85 (m, 2H), 7.83 (d, J = 1.1 Hz, 1H), 7.53 – 7.47 (m, 2H), 1.34 (d, J = 1.2 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 187.5, 158.0, 133.9, 132.9, 128.8, 126.0, 102.8, 35.4, 31.2. HRMS (ESI) calcd for $C_{12}H_{13}Br_2O^+$ $[M+H]^+$ 330.9328, found 330.9324



3f

3,3-dibromo-1-(4-(trifluoromethoxy)phenyl)prop-2-en-1-one (**3f**)

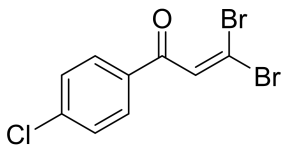
Purified by silica gel chromatography (petroleum), the desired product **3f** was obtained as a yellow solid. Yield: 45.9 mg (61%). M.P. 39-41 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.9 Hz, 2H), 7.82 (s, 1H), 7.32 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.4, 153.3 (q, *J* = 11.1 Hz), 134.7, 132.1, 130.9, 120.7, 104.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -57.6. HRMS (ESI) calcd for $C_{10}H_6Br_2F_3O_2^+$ $[M+H]^+$ 372.8681, found 372.8686



3g

3,3-dibromo-1-(4-fluorophenyl)prop-2-en-1-one (**3g**)[1]

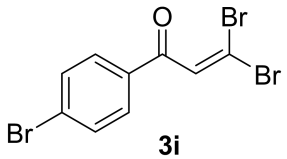
Purified by silica gel chromatography (petroleum), the desired product **3g** was obtained as a yellow oil. Yield: 31.7 mg (51%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.79 (s, 1H), 7.20 – 7.13 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.4, 167.6, 165.0, 132.9 (d, *J* = 3.1 Hz), 132.5, 131.6 (d, *J* = 9.5 Hz), 116.3 (d, *J* = 22.0 Hz), 103.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.3.



3h

3,3-dibromo-1-(4-chlorophenyl)prop-2-en-1-one (**3h**)[1]

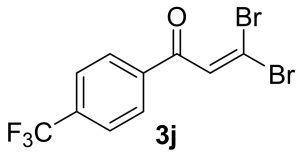
Purified by silica gel chromatography (petroleum), the desired product **3h** was obtained as a yellow solid. Yield: 31.9 mg (49%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.80 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.7, 140.6, 134.9, 132.2, 130.2, 129.4, 104.3.



3i

3,3-dibromo-1-(4-bromophenyl)prop-2-en-1-one (**3i**)[1]

Purified by silica gel chromatography (petroleum), the desired product **3i** was obtained as a yellow oil. Yield: 49.4 mg (67%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (t, *J* = 4.3 Hz, 3H), 7.64 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.9, 135.2, 132.4, 132.1, 130.2, 129.3, 104.5.

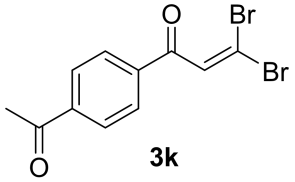


3j

3,3-dibromo-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (**3j**)[1]

Purified by silica gel chromatography (petroleum), the desired product **3j** was obtained as a yellow solid. Yield: 27.3 mg (38%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (dt, *J* = 8.0, 0.9 Hz, 2H), 7.86 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.8, 139.4 (d, *J* = 1.4 Hz), 135.1 (q, *J* = 32.8 Hz), 131.9,

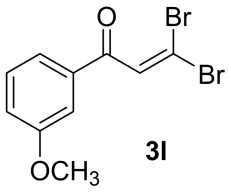
130.4, 129.1, 128.8, 126.1 (q, J = 3.7 Hz), 124.9 (d, J = 2.7 Hz), 122.2, 105.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.2.



3k

1-(4-acetylphenyl)-3,3-dibromoprop-2-en-1-one (**3k**)

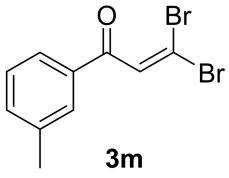
Purified by silica gel chromatography (petroleum), the desired product **3k** was obtained as a colorless oil. Yield: 34.1 mg (51%). M.P. 62-63 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.99 (m, 4H), 7.87 (s, 1H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.4, 187.1, 140.7, 139.8, 132.1, 128.9, 105.3, 27.0. HRMS (ESI) calcd for $C_{11}H_9Br_2O_2^+$ $[M+H]^+$ 330.8964, found 330.8966



3l

3,3-dibromo-1-(3-methoxyphenyl)prop-2-en-1-one (**3l**)[2]

Purified by silica gel chromatography (petroleum), the desired product **3l** was obtained as a yellow oil. Yield: 39.4 mg (62%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.50 – 7.45 (m, 2H), 7.39 (t, J = 7.9 Hz, 1H), 7.16 – 7.12 (m, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.6, 160.1, 137.8, 132.7, 130.0, 121.4, 120.6, 112.8, 103.6, 55.6.

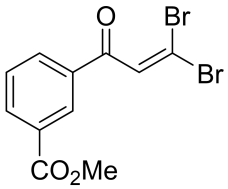


3m

3,3-dibromo-1-(*m*-tolyl)prop-2-en-1-one (**3m**)[1]

Purified by silica gel chromatography (petroleum), the desired product **3m** was obtained as a yellow oil. Yield: 43.9 mg (72%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.75 – 7.71 (m, 2H), 7.44 – 7.35 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.0, 138.9, 136.5, 134.8, 132.9, 129.2, 128.9, 126.1, 103.2,

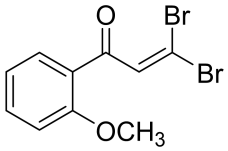
21.5.



3n

methyl 3-(3,3-dibromoacryloyl)benzoate (**3n**)

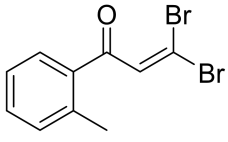
Purified by silica gel chromatography (petroleum), the desired product **3n** was obtained as a yellow solid. Yield: 38.6 mg (55%). M.P. 94-96 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (t, *J* = 1.5 Hz, 1H), 8.27 (dt, *J* = 7.8, 1.4 Hz, 1H), 8.15 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.91 (s, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.8, 166.1, 136.9, 134.6, 132.8, 132.0, 131.1, 129.6, 129.3, 105.0, 52.6. HRMS (ESI) calcd for $C_{11}H_9Br_2O_3^+$ $[M+H]^+$ 346.8913, found 346.8916



3o

3,3-dibromo-1-(2-methoxyphenyl)prop-2-en-1-one (**3o**)

Purified by silica gel chromatography (petroleum), the desired product **3o** was obtained as a yellow oil. Yield: 20.8 mg (87%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.70 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.49 (ddd, *J* = 8.4, 7.3, 1.9 Hz, 1H), 7.05 – 6.99 (m, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.1, 158.7, 136.2, 134.6, 131.2, 127.7, 121.1, 111.9, 101.6, 56.0. HRMS (ESI) calcd for $C_{10}H_9Br_2O_2^+$ $[M+H]^+$ 318.8964, found 318.8969

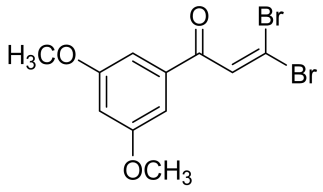


3p

3,3-dibromo-1-(o-tolyl)prop-2-en-1-one (**3p**)[1]

Purified by silica gel chromatography (petroleum), the desired product **3p** was obtained as a yellow oil. Yield: 20.9 mg (34%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.42 (td, *J* = 7.5, 1.5 Hz, 1H), 7.29 (dd, *J* = 11.5,

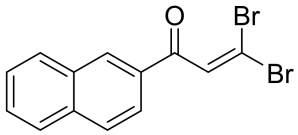
7.9 Hz, 2H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.0, 139.4, 136.7, 135.4, 132.3, 132.2, 129.6, 126.0, 103.0, 21.2.



3q

3,3-dibromo-1-(3,5-dimethoxyphenyl)prop-2-en-1-one (**3q**)

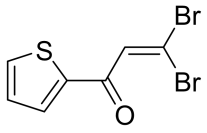
Purified by silica gel chromatography (petroleum), the desired product **3q** was obtained as a yellow oil. Yield: 43.6 mg (62%). M.P. 68-60℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.05 (d, *J* = 2.1 Hz, 2H), 6.67 (s, 1H), 3.84 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.5, 161.2, 138.4, 132.6, 106.5, 106.2, 103.7, 55.8.



3r

3,3-dibromo-1-(naphthalen-2-yl)prop-2-en-1-one (**3r**)[3]

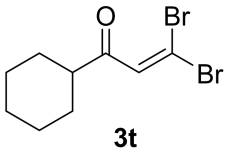
Purified by silica gel chromatography (petroleum), the desired product **3r** was obtained as a yellow oil. Yield: 42.1 mg (62%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 (s, 1H), 8.03 – 7.97 (m, 3H), 7.91 (dd, *J* = 13.0, 8.4 Hz, 2H), 7.66 – 7.55 (m, 2H). ^{113}C NMR (101 MHz, Chloroform-*d*) δ 187.9, 136.0, 133.9, 132.9, 132.6, 131.0, 129.8, 129.2, 129.1, 128.0, 127.2, 124.0, 103.2.



3s

3,3-dibromo-1-(thiophen-2-yl)prop-2-en-1-one (**3s**)[1]

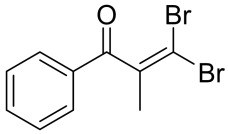
Purified by silica gel chromatography (petroleum), the desired product **3s** was obtained as a yellow solid. Yield: 12.2 mg (21%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.75 – 7.71 (m, 2H), 7.17 (dd, *J* = 4.9, 3.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.4, 144.4, 135.4, 132.7, 131.4, 128.6, 105.0.



3t

3,3-dibromo-1-cyclohexylprop-2-en-1-one (**3t**)

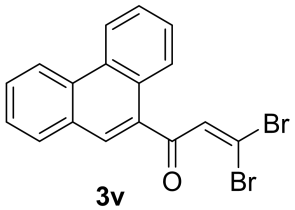
Purified by silica gel chromatography (petroleum), the desired product **3t** was obtained as a colorless oil. Yield: 20%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (s, 1H), 2.37 (tt, *J* = 11.0, 3.4 Hz, 1H), 1.90 – 1.76 (m, 4H), 1.67 (ddd, *J* = 11.3, 3.5, 2.1 Hz, 1H), 1.40 – 1.21 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.4, 133.4, 103.5, 51.6, 28.1, 25.9, 25.6. HRMS (ESI) calcd for $C_9H_{13}Br_2O^+$ $[M+H]^+$ 294.9328, found 294.9324.



3u

3,3-dibromo-2-methyl-1-phenylprop-2-en-1-one (**3u**)[2]

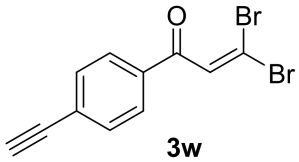
Purified by silica gel chromatography (petroleum), the desired product **3u** was obtained as a colorless oil. Yield: 19 mg (31%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.91 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.52 (dd, *J* = 8.3, 7.0 Hz, 2H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.1, 142.6, 134.4, 133.8, 129.7, 129.2, 88.8, 22.4.



3v

3,3-dibromo-1-(phenanthren-9-yl)prop-2-en-1-one (**3v**)

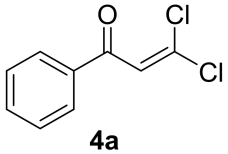
Purified by silica gel chromatography (petroleum), the desired product **3v** was obtained as a yellow solid. Yield: 11.9 mg (15%). M.P. 113-114℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.76 – 8.61 (m, 3H), 8.17 (s, 1H), 7.99 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.85 (s, 1H), 7.78 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.75 – 7.63 (m, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.7, 135.7, 133.8, 132.4, 132.1, 131.0, 130.3, 129.9, 129.6, 128.4, 127.9, 127.6, 127.4, 126.5, 123.1, 122.9, 103.9.



3w

3,3-dibromo-1-(4-ethynylphenyl)prop-2-en-1-one (**3w**)

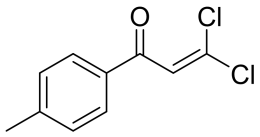
Purified by silica gel chromatography (petroleum), the desired product **3w** was obtained as a yellow solid. Yield: 11.4 mg (18%). M.P. 77-78°C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.82 (s, 1H), 7.60 (d, *J* = 8.5 Hz, 2H), 3.29 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 187.0, 136.2, 132.7, 132.3, 128.7, 127.8, 104.4, 82.7, 81.2.



4a

3,3-dichloro-1-phenylprop-2-en-1-one (**4a**)[2]

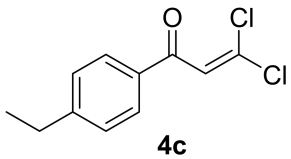
Purified by silica gel chromatography (petroleum), the desired product **4a** was obtained as a colorless oil. Yield: 20 mg (50%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 7.0 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.28 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.8, 137.1, 135.7, 133.9, 129.0, 128.6, 124.2.



4b

3,3-dichloro-1-(*p*-tolyl)prop-2-en-1-one (**4b**)[2]

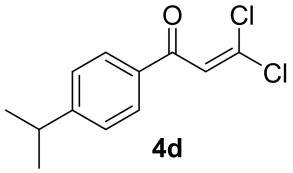
Purified by silica gel chromatography (petroleum), the desired product **4b** was obtained as a colorless oil. Yield: 26.0 mg (60%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 7.0 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.28 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.8, 137.1, 135.7, 133.9, 129.0, 128.6, 124.2.



4c

3,3-dichloro-1-(4-ethylphenyl)prop-2-en-1-one (**4c**)[2]

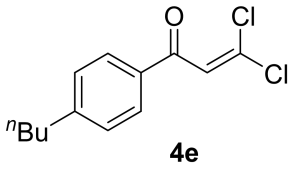
Purified by silica gel chromatography (petroleum), the desired product **4c** was obtained as a colorless oil. Yield: 32.0 mg (70%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.25 (s, 1H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.5, 151.1, 135.0, 134.7, 128.9, 128.5, 124.4, 29.1, 15.2.



4d

3,3-dichloro-1-(4-isopropylphenyl)prop-2-en-1-one (**4d**)

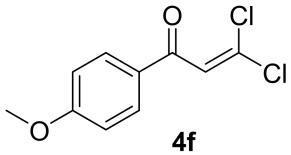
Purified by silica gel chromatography (petroleum), the desired product **4d** was obtained as a colorless oil. Yield: 31.8 mg (65%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.25 (s, 1H), 2.97 (hept, *J* = 7.0 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.4, 155.6, 134.9, 134.9, 129.0, 127.1, 124.4, 34.5, 23.7. HRMS (ESI) calcd for $C_{12}H_{13}Cl_2O^+$ $[M+H]^+$ 243.0338, found 243.0332.



4e

1-(4-butylphenyl)-3,3-dichloroprop-2-en-1-one (**4e**)

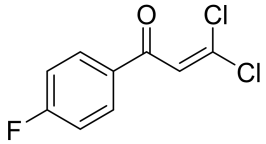
Purified by silica gel chromatography (petroleum), the desired product **4e** was obtained as a colorless oil. Yield: 36.1 mg (70%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.25 (s, 1H), 2.71 – 2.64 (m, 2H), 1.62 (p, *J* = 7.5 Hz, 2H), 1.36 (h, *J* = 7.3 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.4, 149.8, 134.9, 134.7, 129.0, 128.8, 124.4, 35.9, 33.3, 22.4, 14.0. HRMS (ESI) calcd for $C_{13}H_{15}Cl_2O^+$ $[M+H]^+$ 257.0494, found 254.0498.



4f

3,3-dichloro-1-(4-methoxyphenyl)prop-2-en-1-one (**4f**)[2]

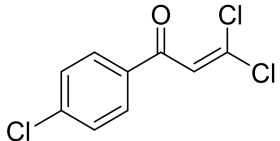
Purified by silica gel chromatography (petroleum), the desired product **4f** was obtained as a colorless oil. Yield: 37.6 mg (81%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 9.0 Hz, 2H), 7.20 (s, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 185.5, 164.2, 131.1, 129.9, 124.5, 114.2, 55.7.



4g

3,3-dichloro-1-(4-fluorophenyl)prop-2-en-1-one (**4g**)[2]

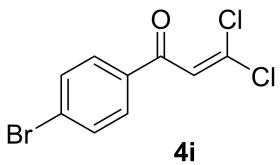
Purified by silica gel chromatography (petroleum), the desired product **4g** was obtained as a yellow oil. Yield: 15.2 mg (35%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.24 (s, 1H), 7.17 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 185.3, 167.5, 165.0, 135.9, 133.4 (d, *J* = 3.0 Hz), 131.4 (d, *J* = 9.5 Hz), 123.9, 116.2 (d, *J* = 22.0 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.6.



4h

3,3-dichloro-1-(4-chlorophenyl)prop-2-en-1-one (**4h**)[2]

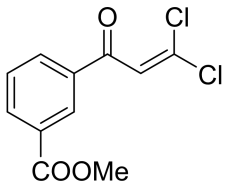
Purified by silica gel chromatography (petroleum), the desired product **4h** was obtained as a colorless oil. Yield: 20.3 mg (43%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.22 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 185.6, 140.4, 136.4, 135.4, 130.0, 129.4, 123.7.



4i

1-(4-bromophenyl)-3,3-dichloroprop-2-en-1-one (**4i**)[4]

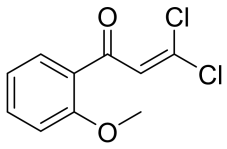
Purified by silica gel chromatography (petroleum), the desired product **4i** was obtained as a colorless oil. Yield: 19.6 mg (35%).[1]H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.76 (m, 2H), 7.66 – 7.61 (m, 2H), 7.21 (s, 1H). [13]C NMR (101 MHz, Chloroform-*d*) δ 185.7, 136.5, 135.8, 132.4, 130.1, 129.2, 123.6.



4j

methyl 3-(3,3-dichloroacryloyl)benzoate (**4j**)

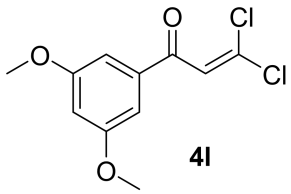
Purified by silica gel chromatography (petroleum), the desired product **4j** was obtained as a colorless oil. Yield: 21.3 mg (41%). [1]H NMR (400 MHz, Chloroform-*d*) δ 8.53 (t, *J* = 1.8 Hz, 1H), 8.26 (dt, *J* = 7.7, 1.4 Hz, 1H), 8.13 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.32 (s, 1H), 3.96 (s, 3H). [13]C NMR (101 MHz, Chloroform-*d*) δ 185.8, 166.2, 137.4, 136.9, 134.5, 132.7, 131.1, 129., 129.3, 123.6, 52.6.



4k

3,3-dichloro-1-(2-methoxyphenyl)prop-2-en-1-one (**4k**)

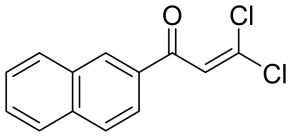
Purified by silica gel chromatography (petroleum), the desired product **4k** was obtained as a colorless oil. Yield: 37.8 mg (82%).[1]H NMR (400 MHz, Chloroform-*d*) δ 7.69 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.49 (ddd, *J* = 8.4, 7.4, 1.9 Hz, 1H), 7.31 (s, 1H), 7.03 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.96 (dd, *J* = 8.4, 1.0 Hz, 1H), 3.91 (s, 3H). [13]C NMR (101 MHz, Chloroform-*d*) δ 187.4, 158.6, 134.4, 133.8, 131.1, 128.1, 128.0, 121.1, 111.8, 55.9. HRMS (ESI) calcd for $C_{10}H_9Cl_2O_2^+$ $[M+H]^+$ 230.9974, found 230.9971.



4l

3,3-dichloro-1-(3,5-dimethoxyphenyl)prop-2-en-1-one (**4l**)

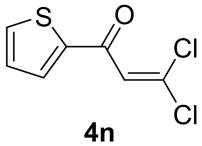
Purified by silica gel chromatography (petroleum), the desired product **4l** was obtained as a colorless oil. Yield: 23.4 mg (45%). M.P. 36-37℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (s, 1H), 7.03 (d, *J* = 2.3 Hz, 2H), 6.67 (t, *J* = 2.3 Hz, 1H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.3, 161.2, 139.0, 135.7, 124.2, 106.4, 106.1, 55.8. HRMS (ESI) calcd for $C_{11}H_{11}Cl_2O_3^+$ $[M+H]^+$ 261.0080, found261.0076.



4m

3,3-dichloro-1-(naphthalen-2-yl)prop-2-en-1-one (**4m**)

Purified by silica gel chromatography (petroleum), the desired product **4m** was obtained as a colorless oil. Yield: 18.1 mg (36%). M.P. 51-53℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 – 8.39 (m, 1H), 8.03 – 7.96 (m, 2H), 7.94 – 7.87 (m, 2H), 7.60 (dddd, *J* = 21.6, 8.2, 6.8, 1.4 Hz, 2H), 7.41 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.7, 136.0, 135.5, 134.4, 132.6, 130.7, 129.8, 129.1, 129.0, 128.0, 127.2, 124.4, 124.0. HRMS (ESI) calcd for $C_{13}H_9Cl_2O^+$ $[M+H]^+$ 251.0025, found 251.0022.

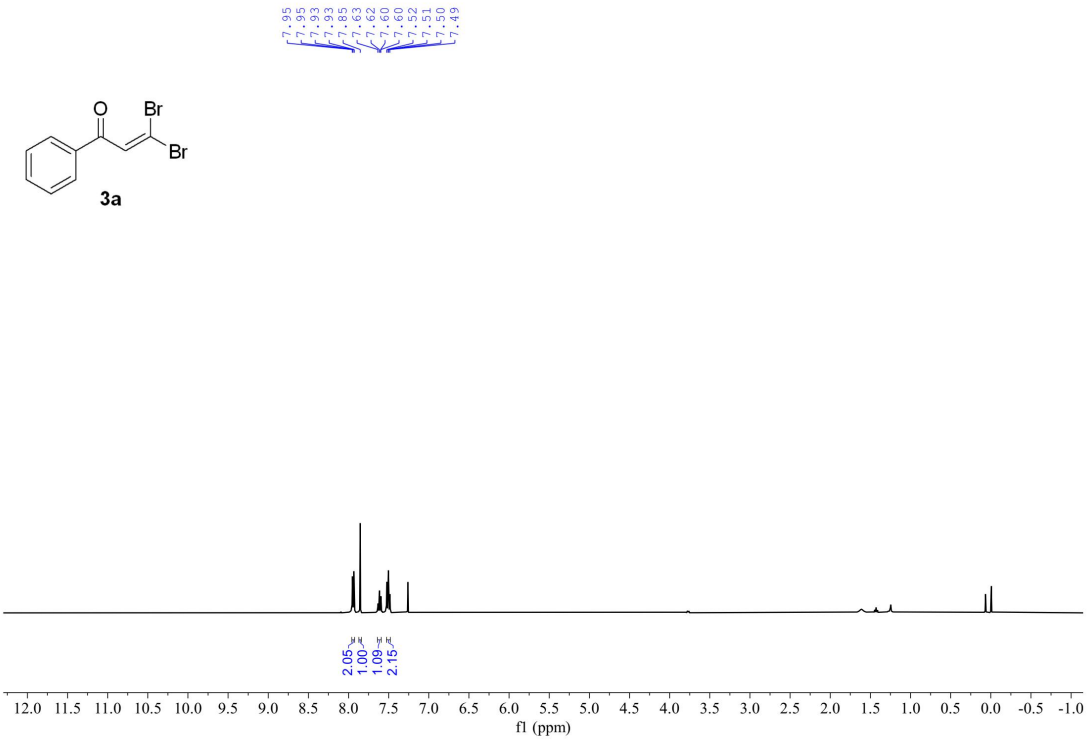


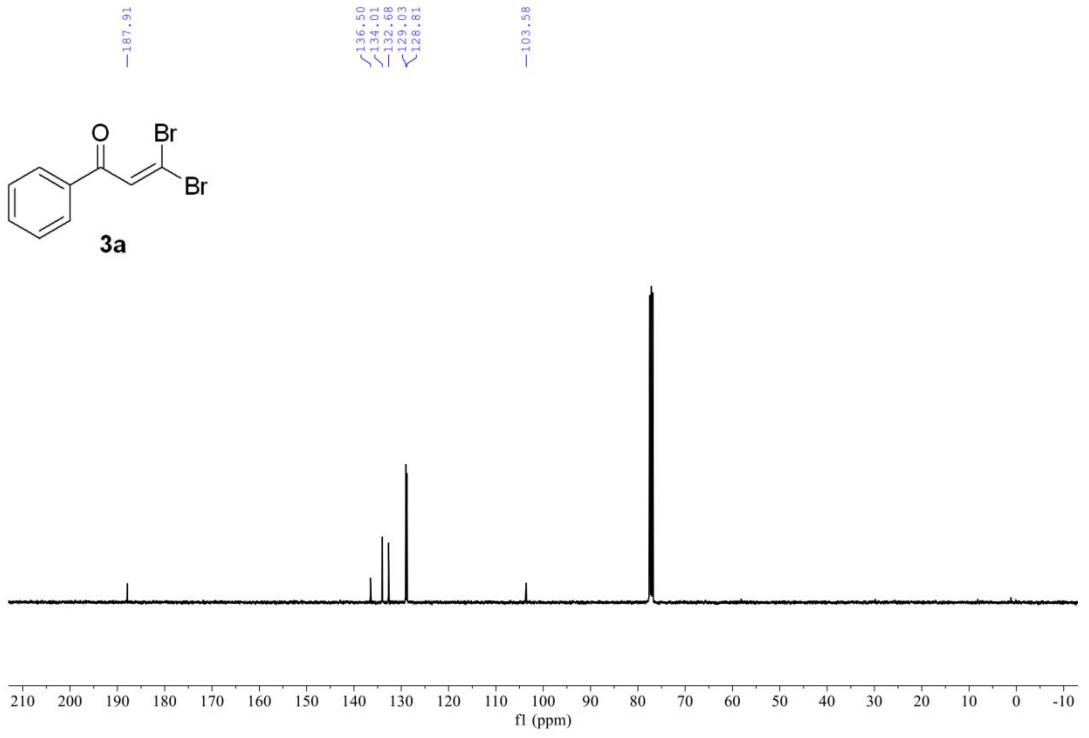
4n

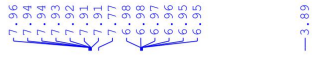
3,3-dichloro-1-(thiophen-2-yl)prop-2-en-1-one (**4n**)[2]

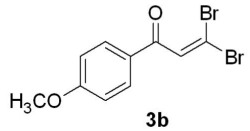
Purified by silica gel chromatography (petroleum), the desired product **4n** was obtained as a colorless solid. Yield: 4.2 mg (10%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.70 (m, 2H), 7.23 (s, 1H), 7.17 (dd, *J* = 4.9, 3.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.5, 144.8, 136.6, 135.2, 132.4, 128.5, 123.3.

8. NMR Spectral of α-gem-dihalovinyl ketones

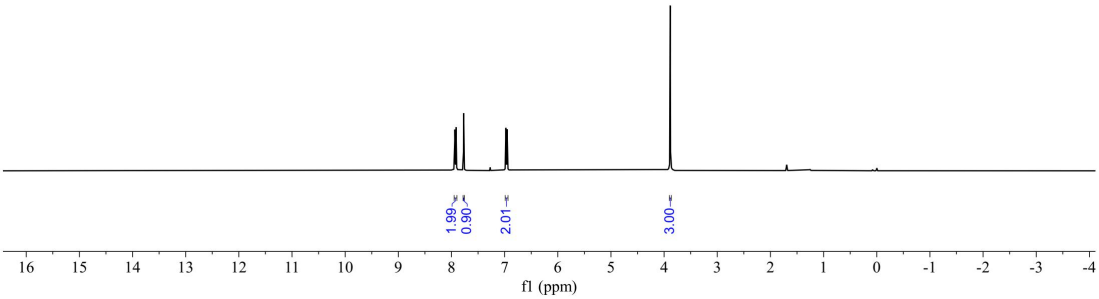





7.96
7.94
7.94
7.93
7.92
7.91
7.91
7.77
6.98
6.98
6.97
6.96
6.95
6.95
3.89


O
Br
Br
H3CO

3b


1.99
0.90
2.01
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)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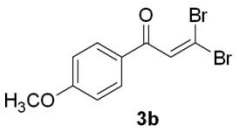
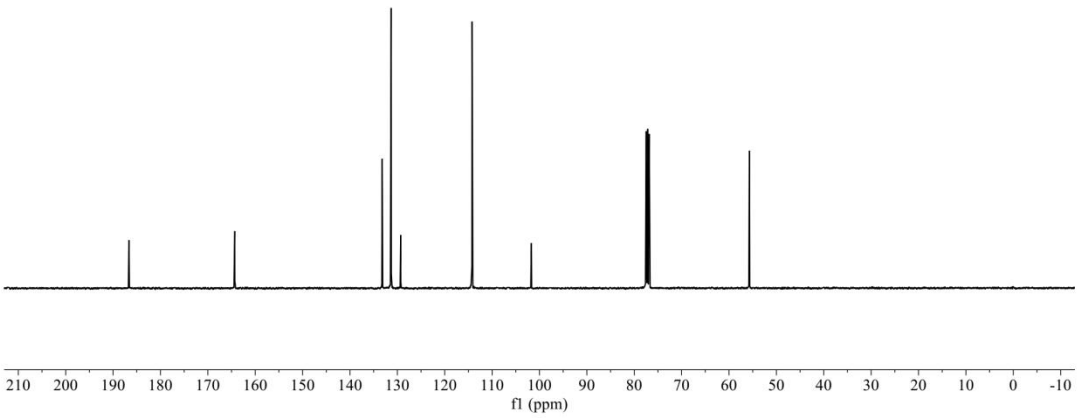
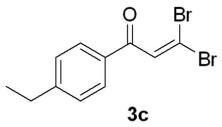
164.32
133.20
131.31
129.29
114.23
101.71
55.70


O
Br
Br
H3CO

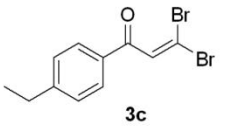
3b


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)


O
Br
Br

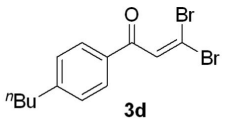
3c

7.87
7.85
7.82
7.32
7.30
2.74
2.72
2.70
2.68
1.28
1.26
1.24
2.01
0.94
2.01
2.02
3.00
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)


O
Br
Br

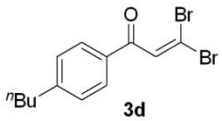
3c

187.55
151.21
134.11
132.92
129.05
128.51
102.71
29.14
15.24
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)


O
Br
Br
nBu

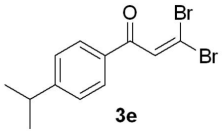
3d

7.85
7.83
7.31
7.31
7.29
1.66
1.65
1.64
1.64
1.63
1.62
1.62
1.61
1.61
1.60
1.60
1.58
1.58
1.41
1.40
1.39
1.38
1.37
1.36
1.35
1.35
1.33
1.31
0.95
0.95
0.93
0.93
0.92
3.02
1.91
1.98
2.04
2.07
3.00
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)


O
Br
Br
nBu

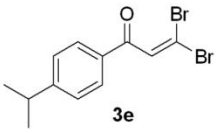
3d

187.52
149.97
134.10
132.92
129.04
128.96
102.72
35.88
33.27
22.42
14.02
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)


O
Br
Br

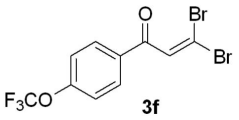
3e

7.88
7.86
7.81
7.35
7.33
3.02
3.00
2.99
2.97
2.95
2.94
2.92
1.28
1.26
1.94
0.83
1.93
1.02
6.00
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)


O
Br
Br

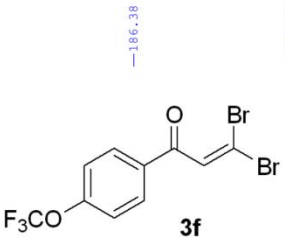
3e

187.51
155.72
134.31
133.01
129.09
127.10
102.55
34.44
23.71
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)


O
Br
Br
F3CO

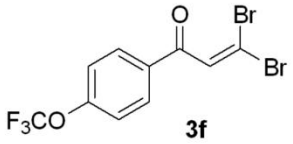
3f

8.01
7.99
7.82
7.33
7.32
2.09
1.00
2.09
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)


O
Br
Br
F3CO

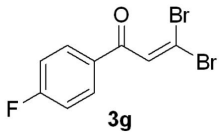
3f

186.38
153.27
134.70
132.14
130.88
120.73
104.58
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)


O
Br
Br
F3CO

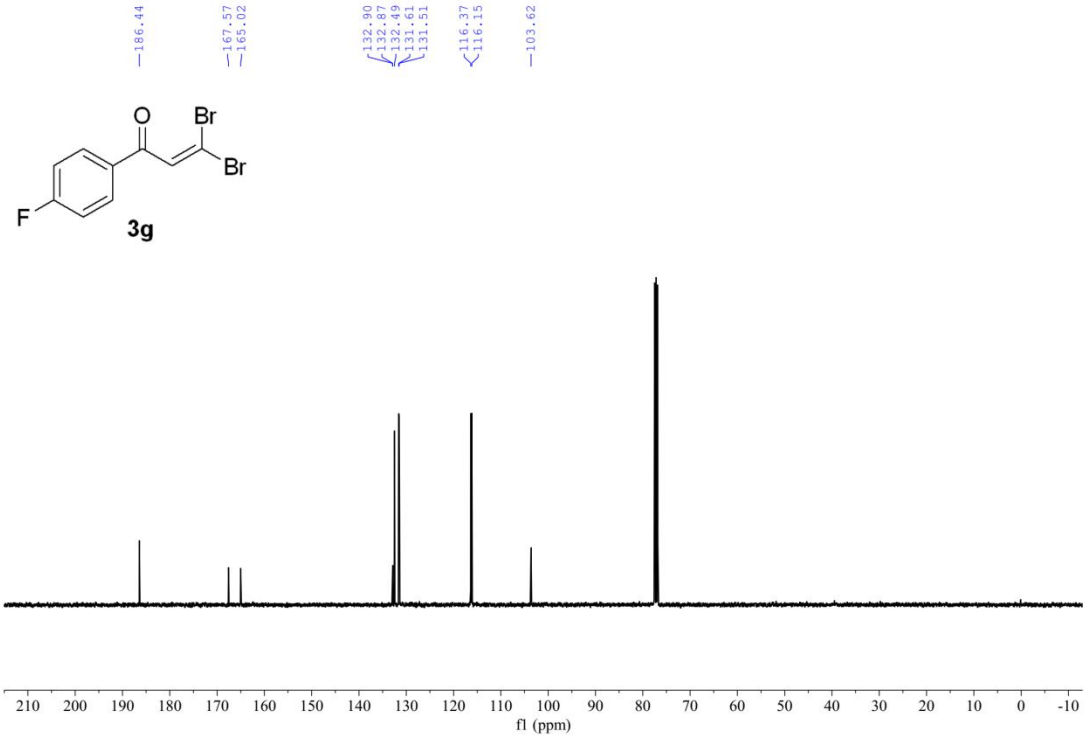
3f

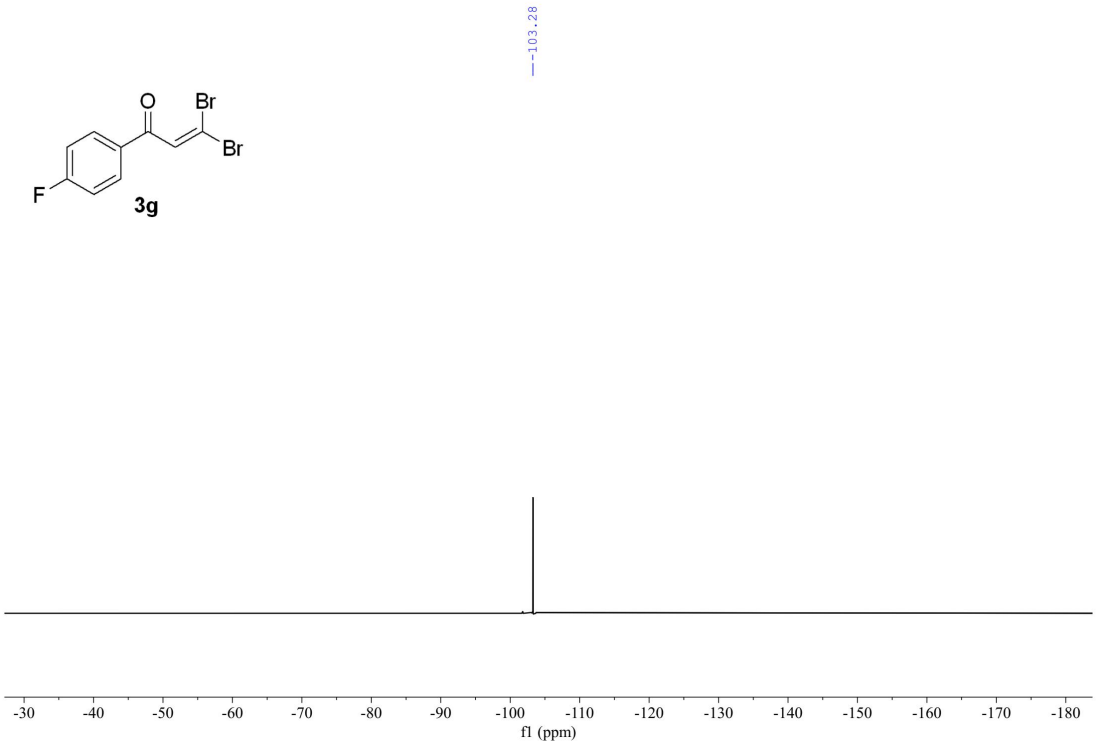
-57.56
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

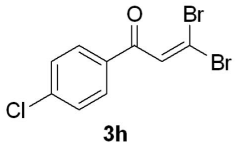

O
Br
Br
F

3g

8.00
7.98
7.97
7.96
7.81
7.20
7.18
7.16
2.10
1.00
2.14
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)

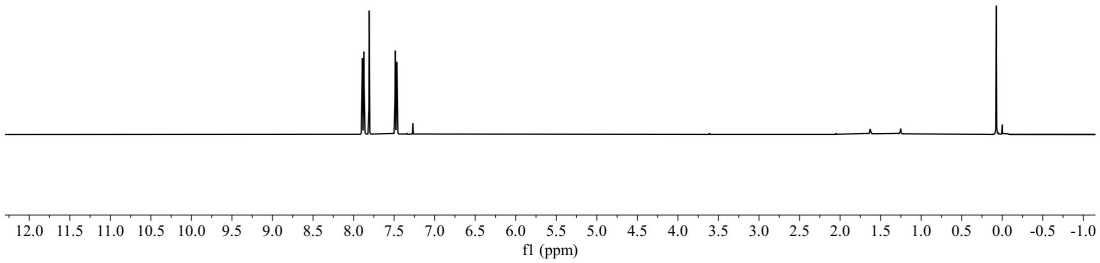

186.44
167.57
165.02
132.90
132.87
132.49
131.61
131.51
116.37
116.15
103.62
O
Br
Br
F
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-103.28
O
Br
Br
F
3g
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)


O
Br
Br
Cl

3h

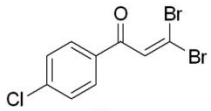

7.89
7.87
7.81
7.49
7.47


12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)

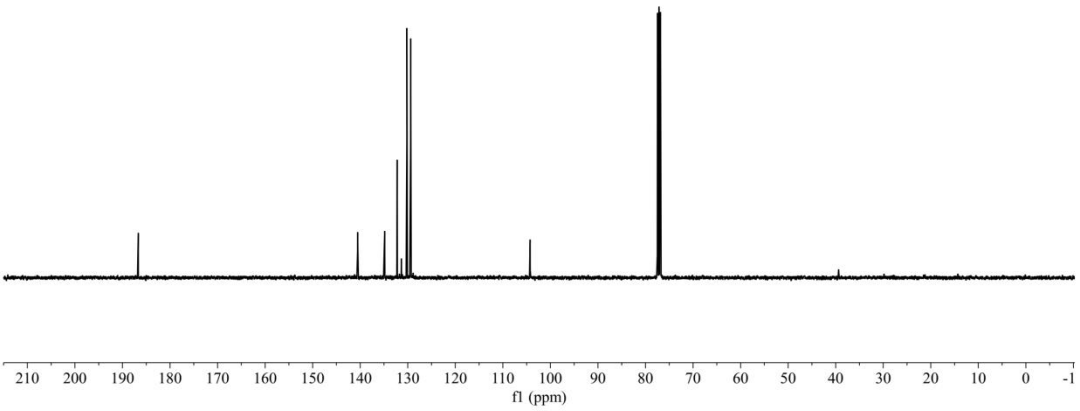
186.68

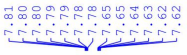

140.56
134.85
132.22
130.18
129.38

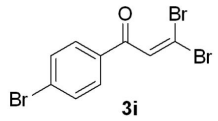
104.26


O
Br
Br
Cl

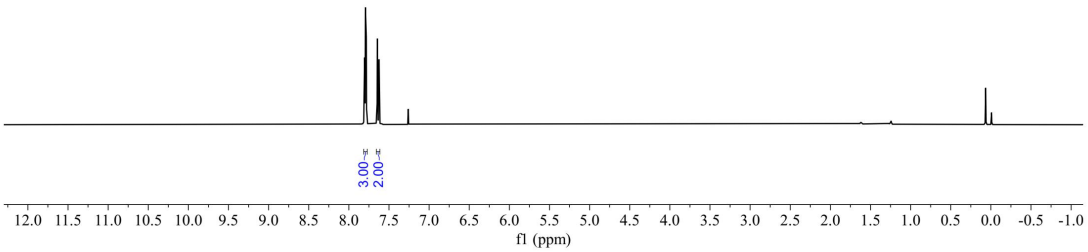
3h


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.81
7.80
7.80
7.79
7.79
7.78
7.78
7.65
7.65
7.64
7.63
7.62
7.62


O
Br
Br
Br

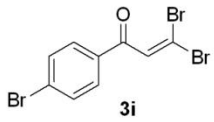
3i


3.00
2.00
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)

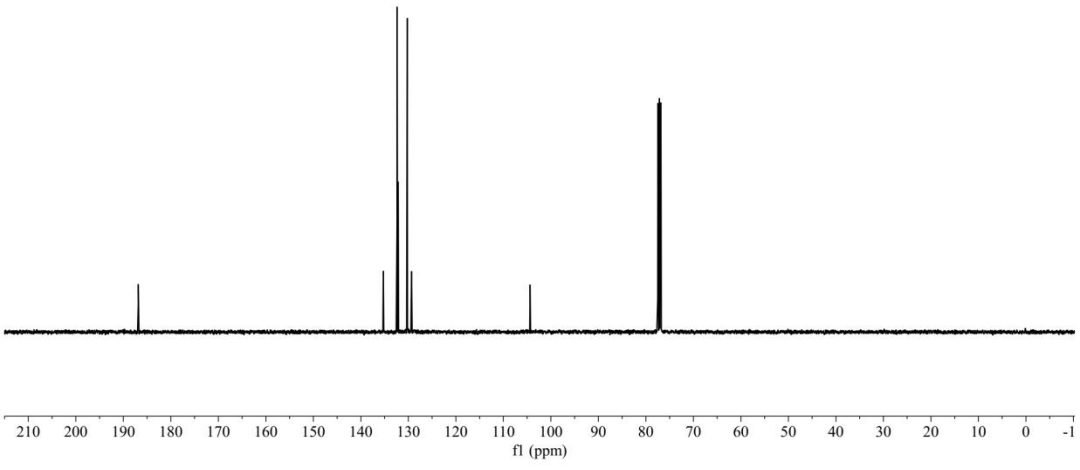
186.85

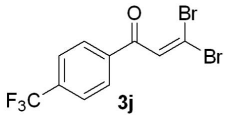

135.27
132.37
132.14
130.24
129.33

104.38

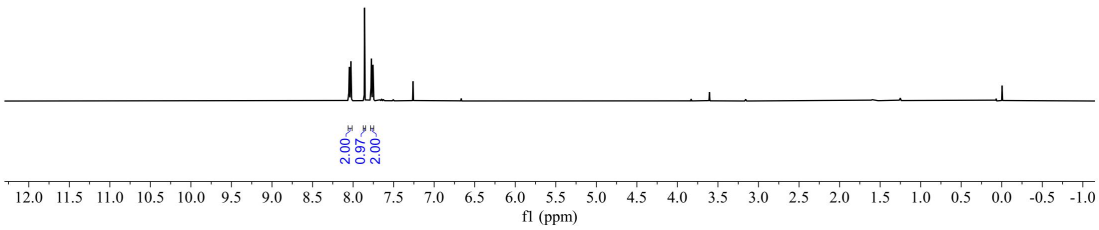

O
Br
Br
Br

3i

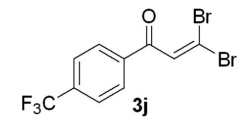

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


O
Br
Br
F3C

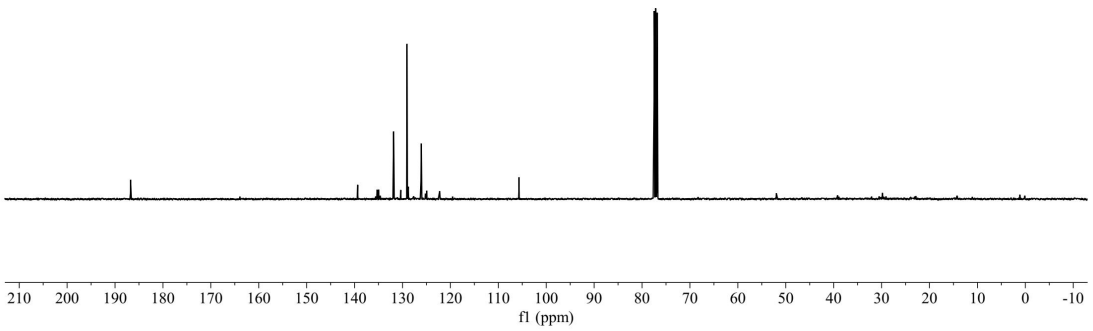
3j

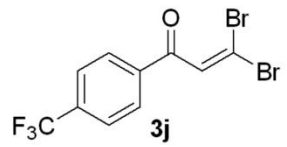

8.05
8.05
8.04
8.03
8.03
8.02
7.77
7.75
2.00
0.97
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


186.76
139.37
139.36
135.61
135.28
134.95
134.63
131.85
130.36
129.06
128.80
126.14
126.11
126.07
126.03
124.95
124.92
122.23
105.70


O
Br
Br
F3C

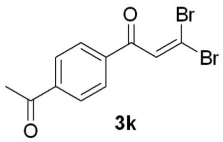
3j


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)


O
Br
Br
F3C

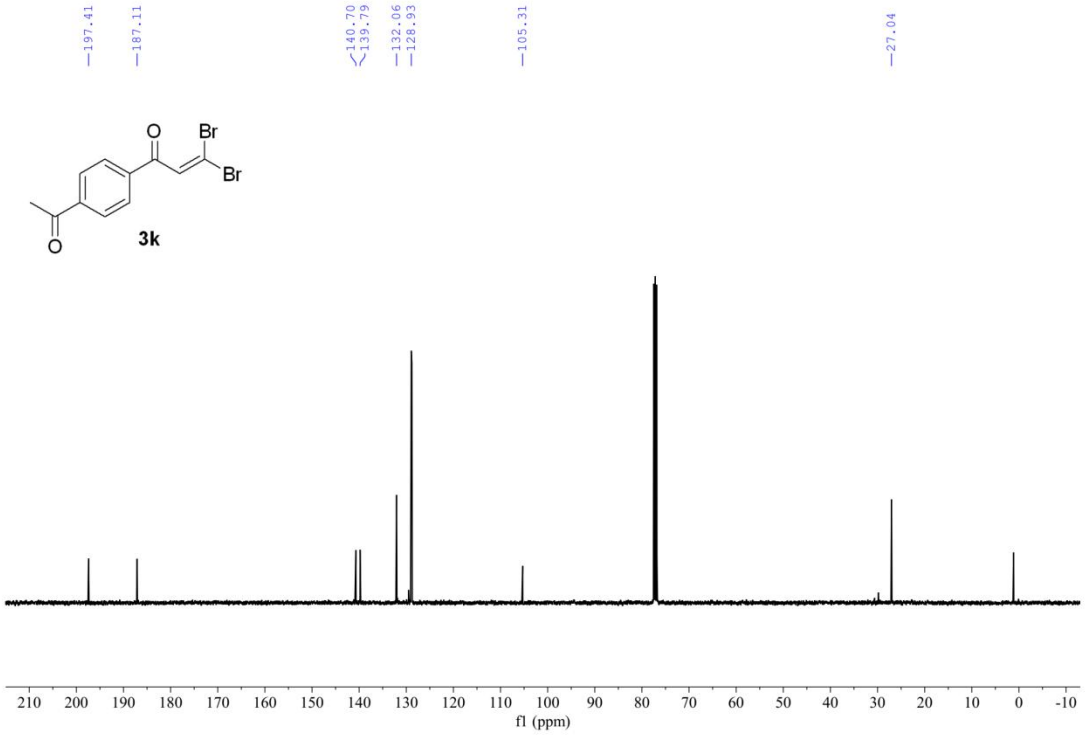
3j

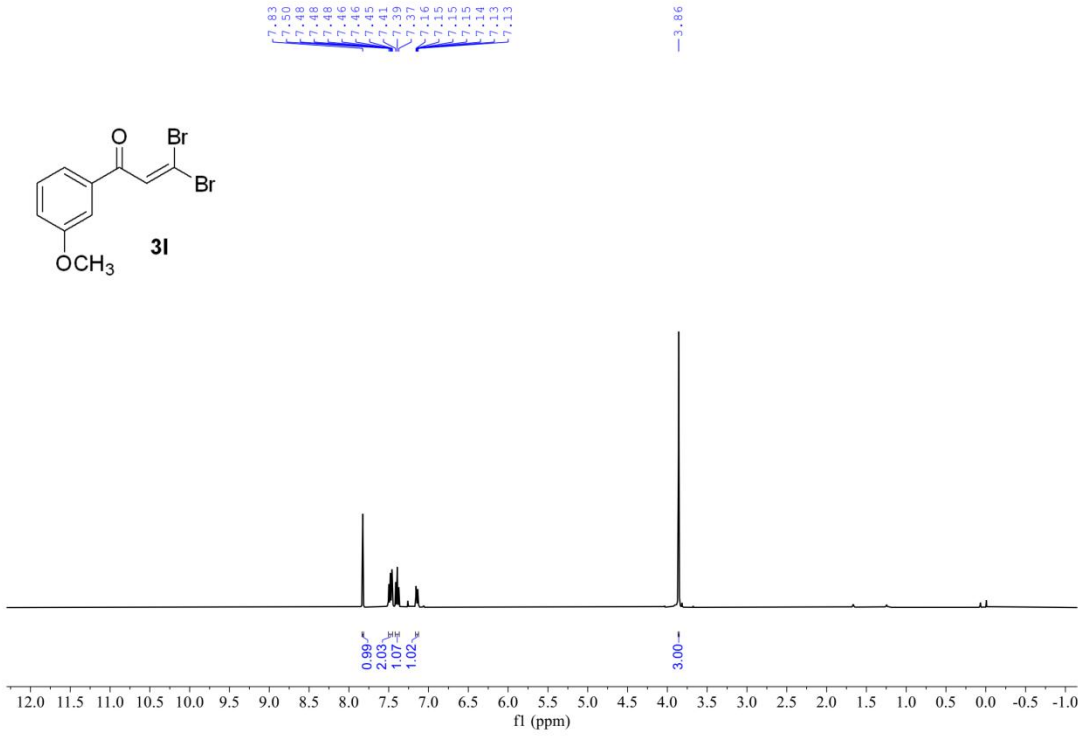
-63.18
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

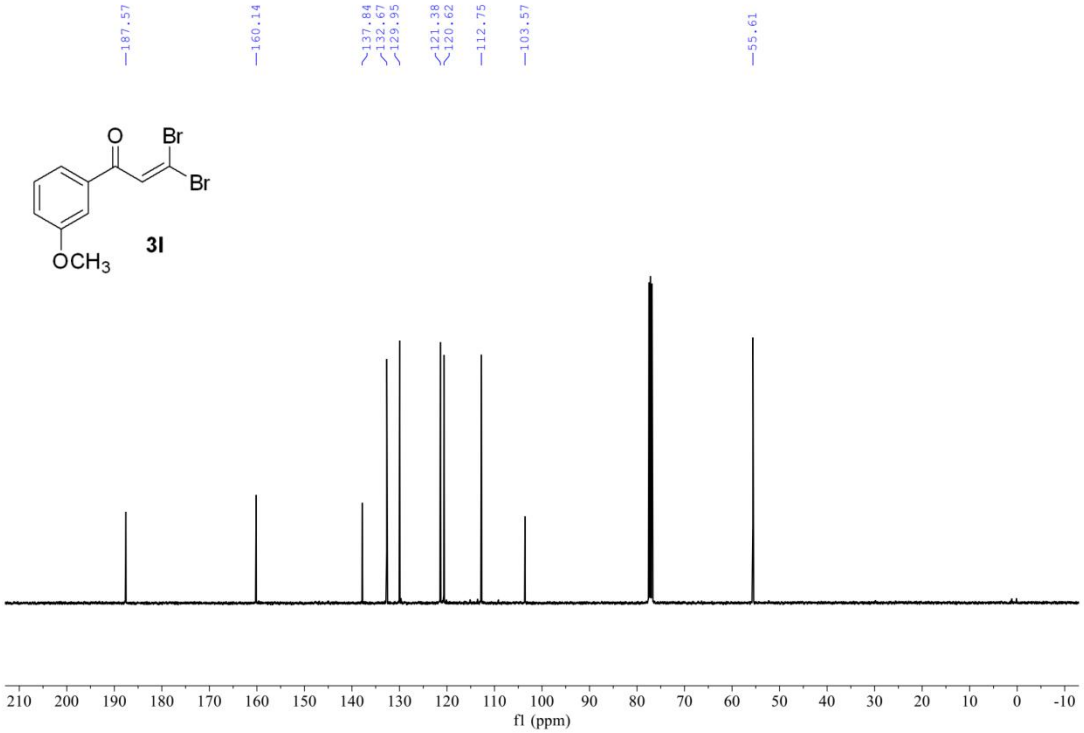

O
Br
Br
O

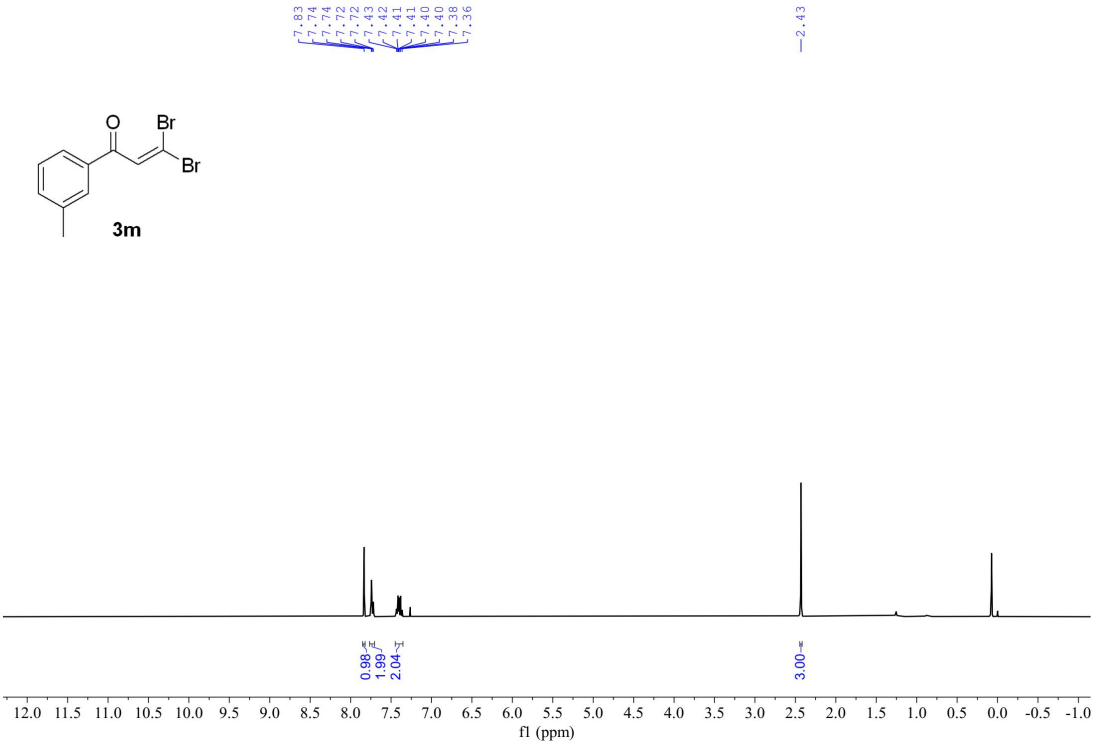
3k

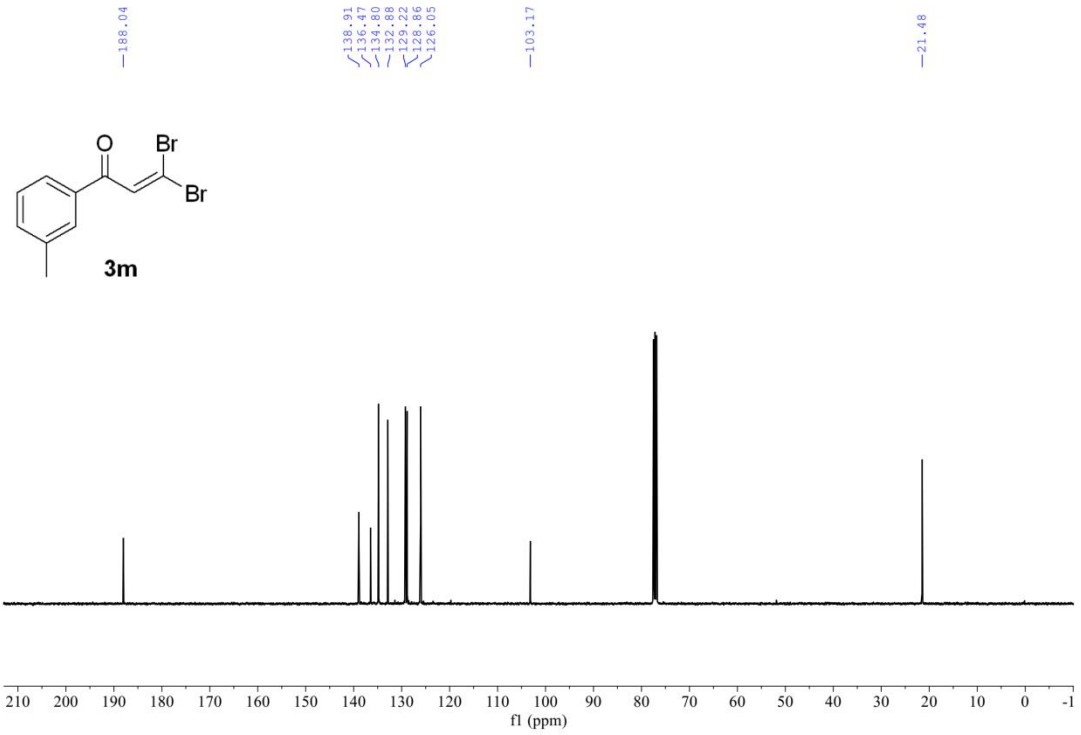
8.06
8.04
8.01
7.99
7.87
2.65
4.06
1.01
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

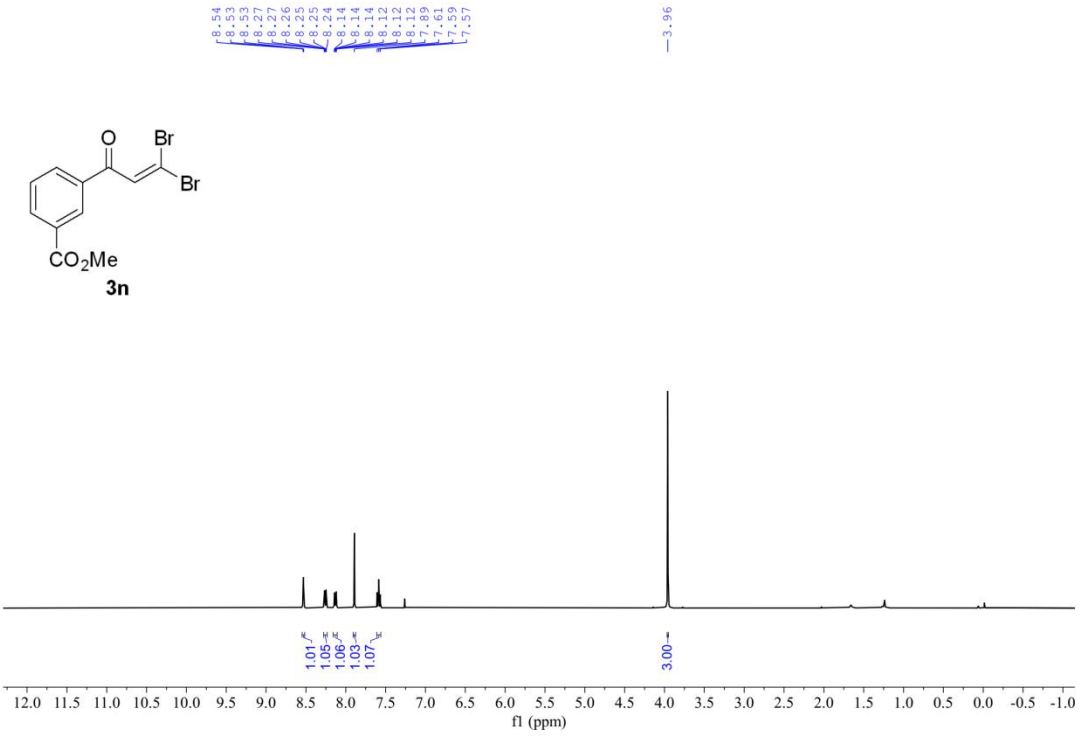

197.41
187.11
140.70
139.79
132.06
128.93
105.31
27.04
O
Br
Br
O
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

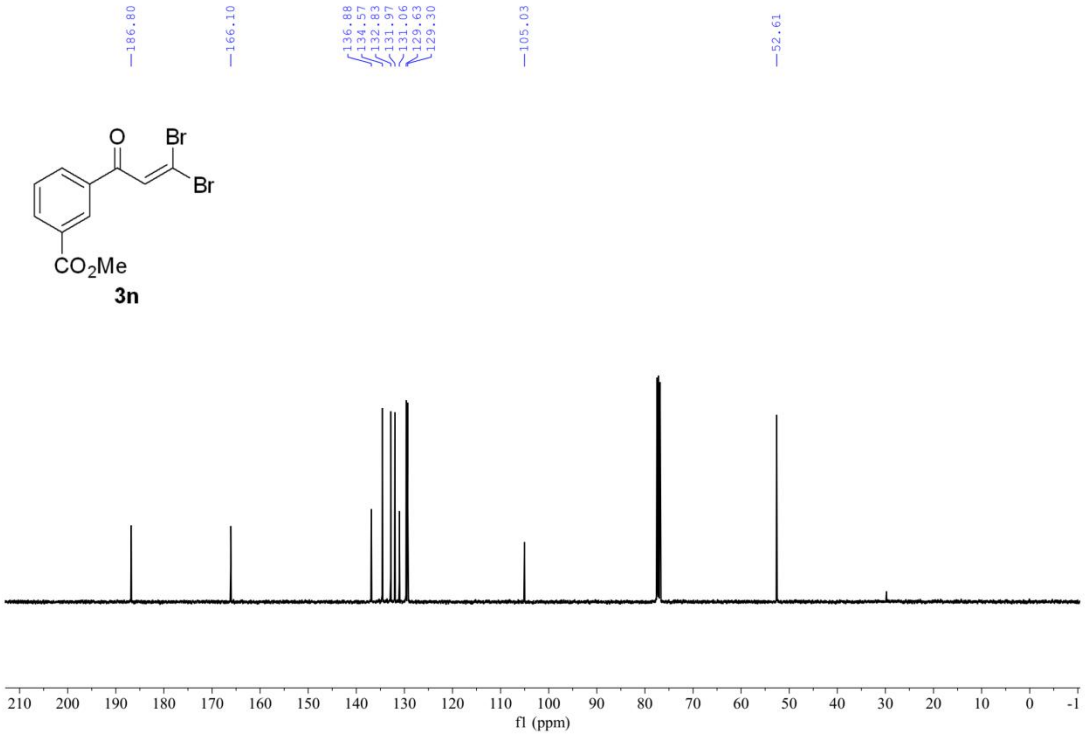

7.83
7.50
7.48
7.48
7.48
7.46
7.46
7.45
7.41
7.39
7.37
7.16
7.15
7.15
7.15
7.14
7.13
7.13
3.86
O
Br
Br
OCH3
3l
0.99
2.03
1.07
1.02
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

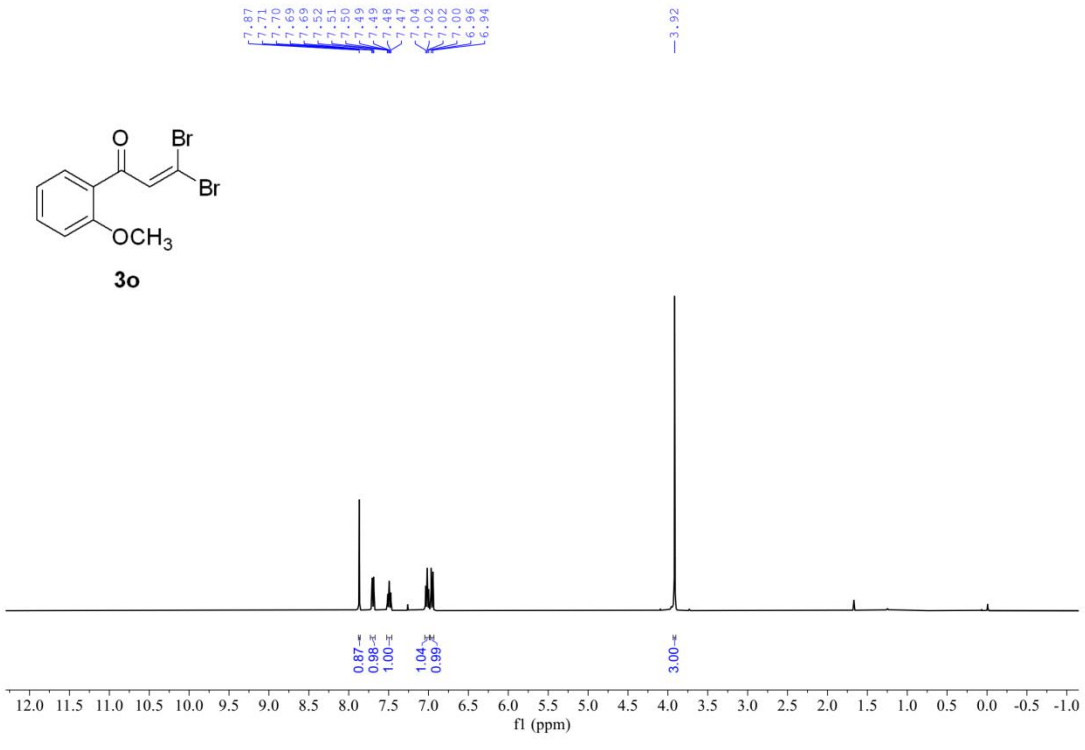

187.57
160.14
137.84
132.67
129.95
121.38
120.62
112.75
103.57
55.61
O
Br
Br
OCH3
3l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

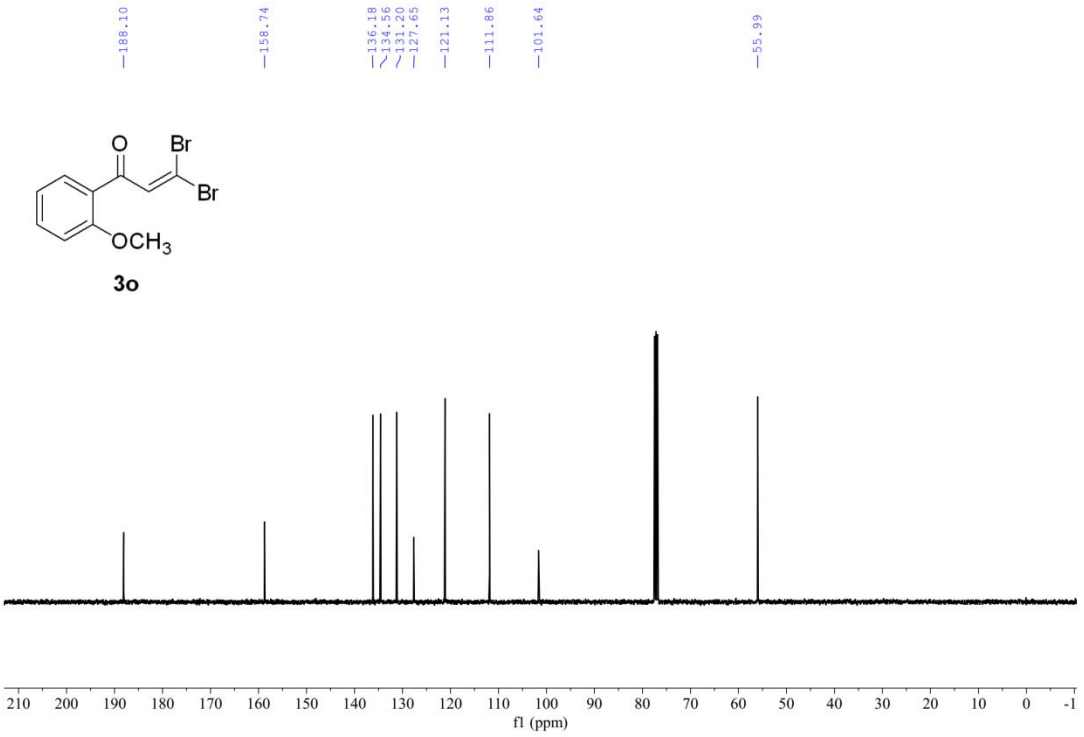

7.83
7.74
7.74
7.72
7.72
7.43
7.42
7.41
7.41
7.40
7.40
7.38
7.36
2.43
O
Br
Br
3m
0.98
1.99
2.04
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


188.04
138.91
136.47
134.80
133.88
129.22
128.66
126.05
103.17
21.48
O
Br
Br
3m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

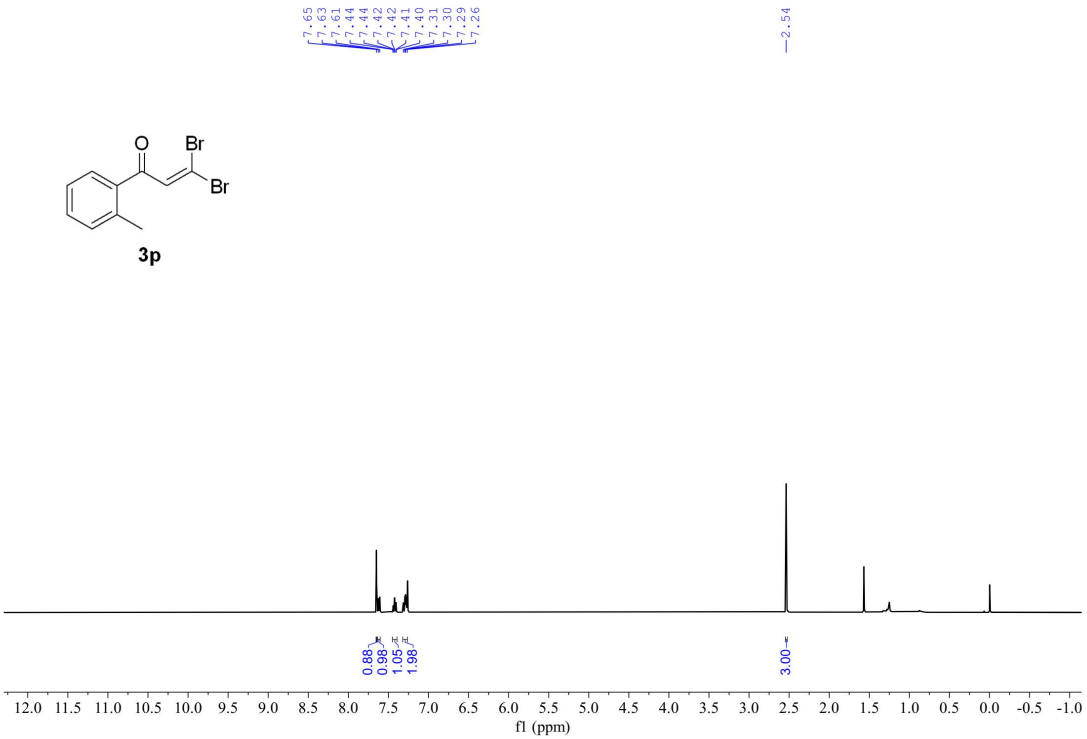

8.54
8.53
8.53
8.27
8.27
8.26
8.25
8.24
8.14
8.14
8.14
8.12
8.12
8.12
7.89
7.61
7.59
7.57
3.96
O
Br
Br
CO2Me
3n
1.01
1.05
1.06
1.03
1.07
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


186.80
166.10
136.88
134.57
132.83
131.97
131.06
129.63
129.30
105.03
52.61
O
Br
Br
CO2Me
3n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

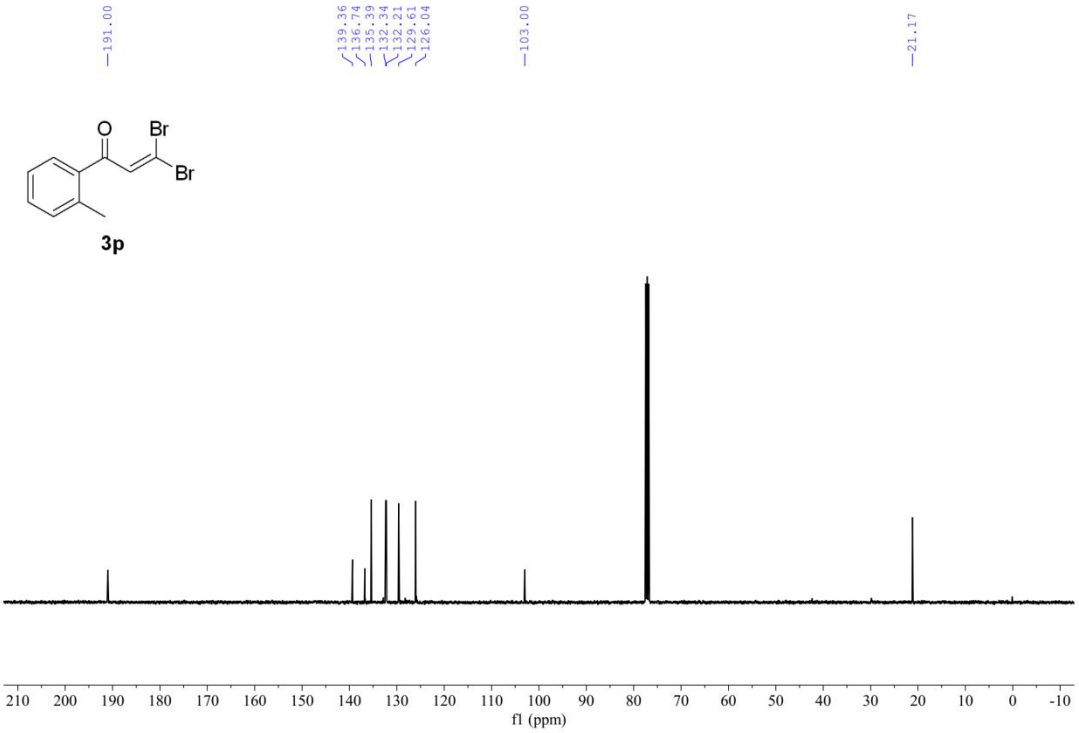

7.87
7.71
7.70
7.69
7.69
7.52
7.51
7.50
7.49
7.49
7.48
7.47
7.04
7.02
7.02
7.00
6.96
6.94
3.92
O
Br
Br
OCH3
3o
0.87
0.98
1.00
1.04
0.99
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

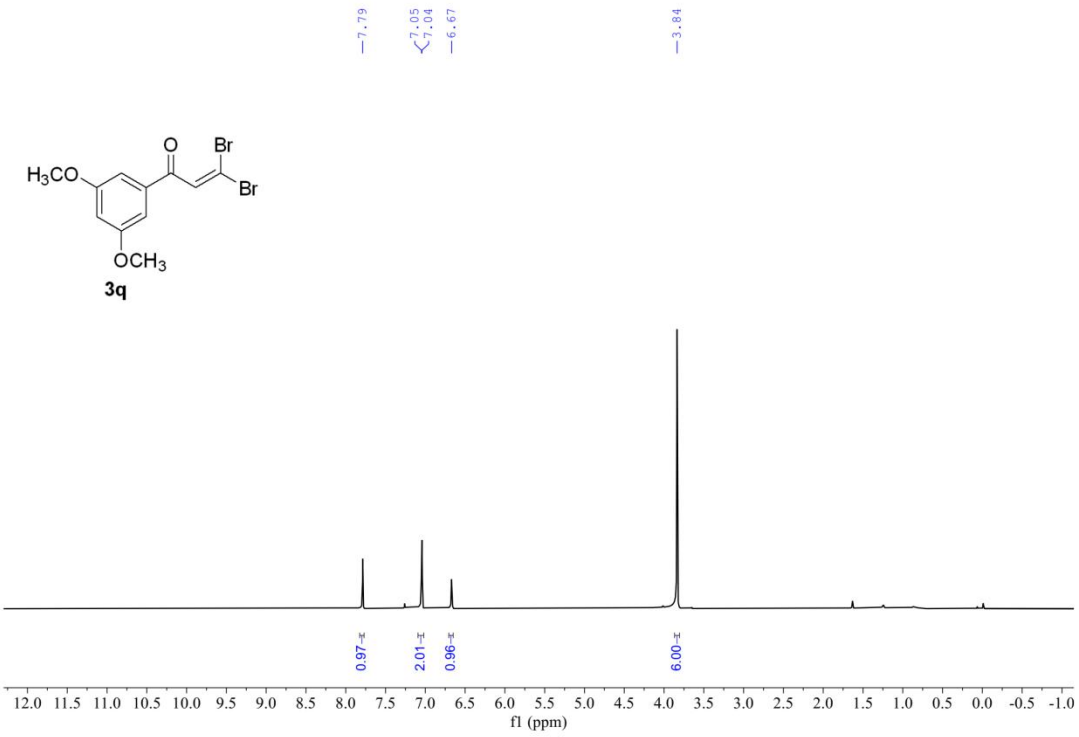

188.10
158.74
136.18
134.56
131.20
127.65
121.13
111.86
101.64
55.99
O
Br
Br
OCH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

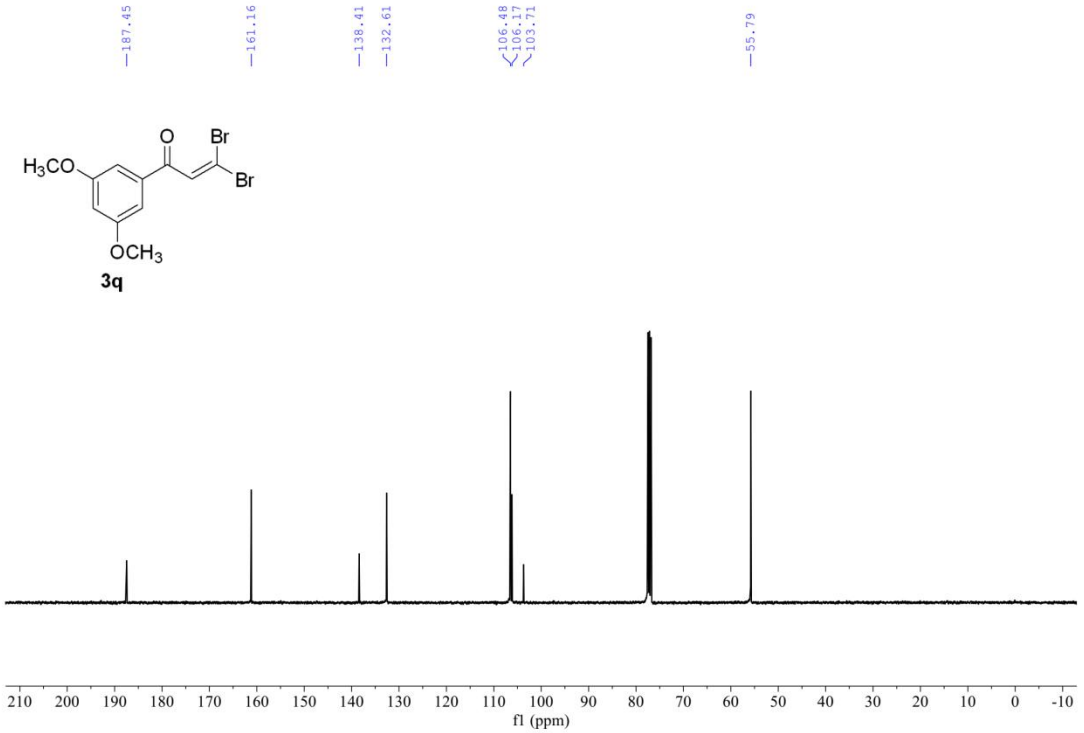
3o

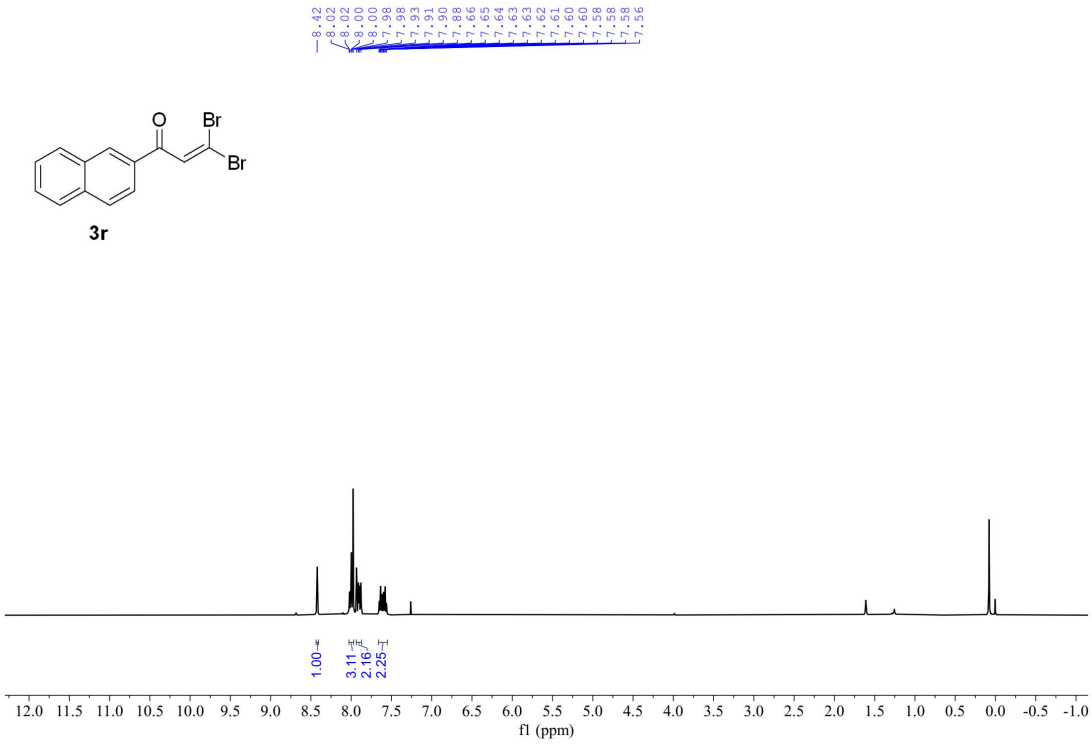

7.65
7.63
7.61
7.44
7.44
7.42
7.42
7.41
7.40
7.31
7.30
7.29
7.26
2.54
O
Br
Br
0.88
0.98
1.05
1.98
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

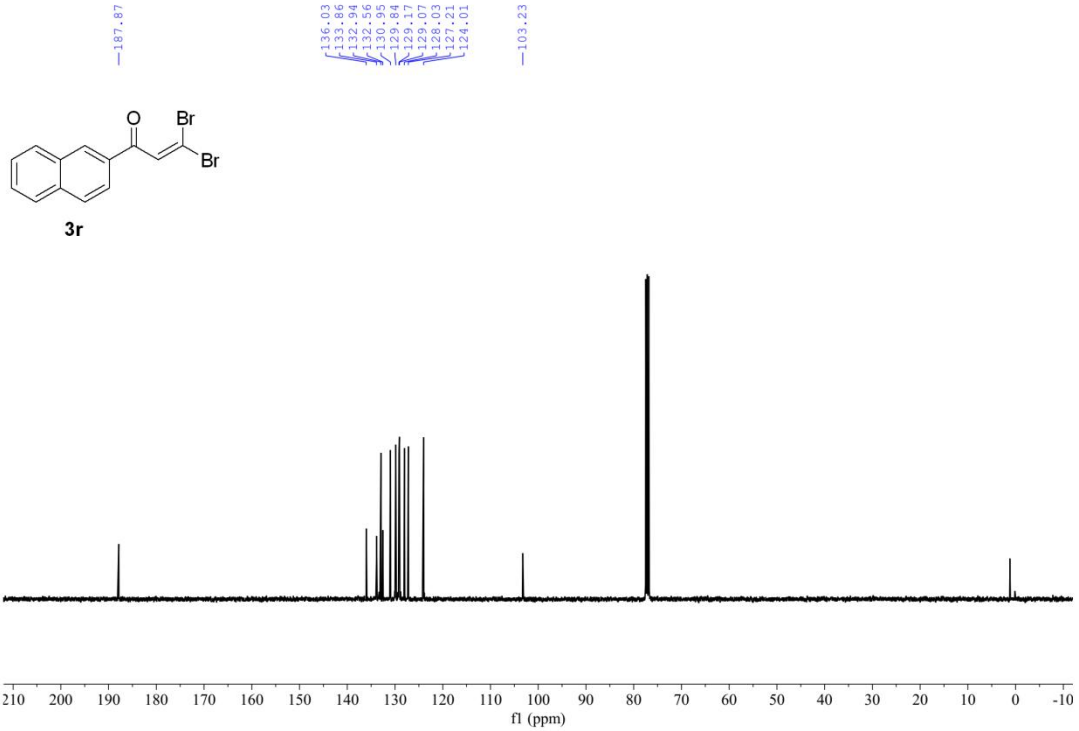
3p

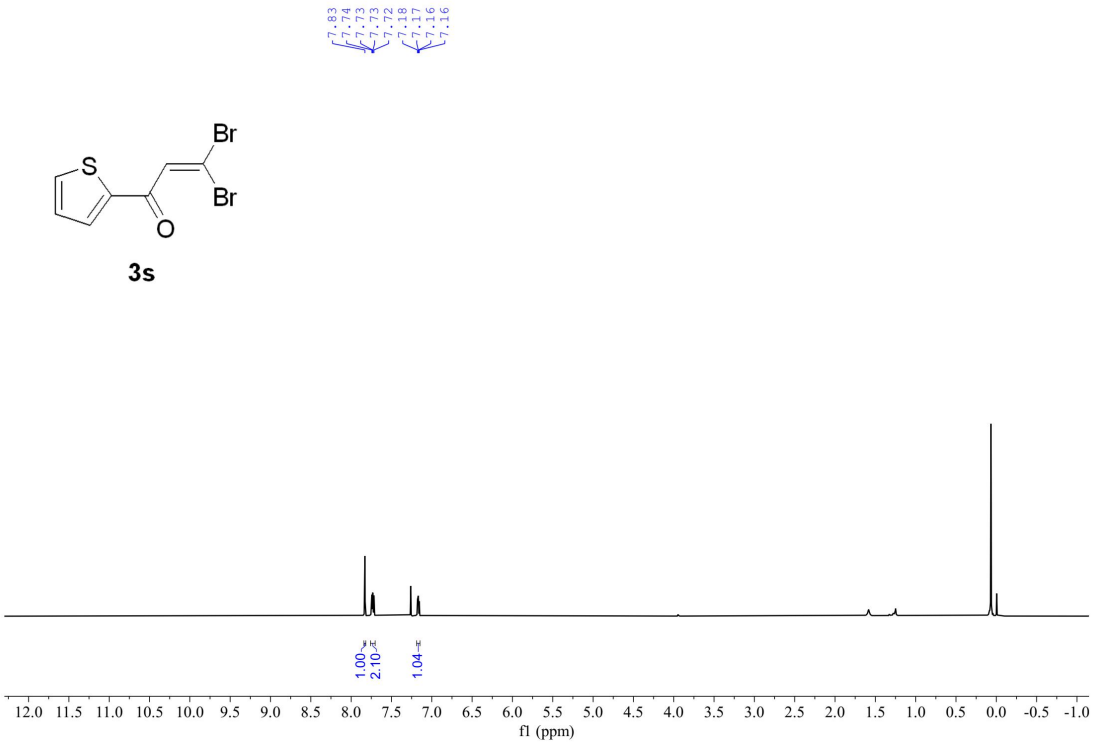

191.00
139.36
136.74
135.39
132.34
132.21
129.61
126.04
103.00
21.17
O
Br
Br
3p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

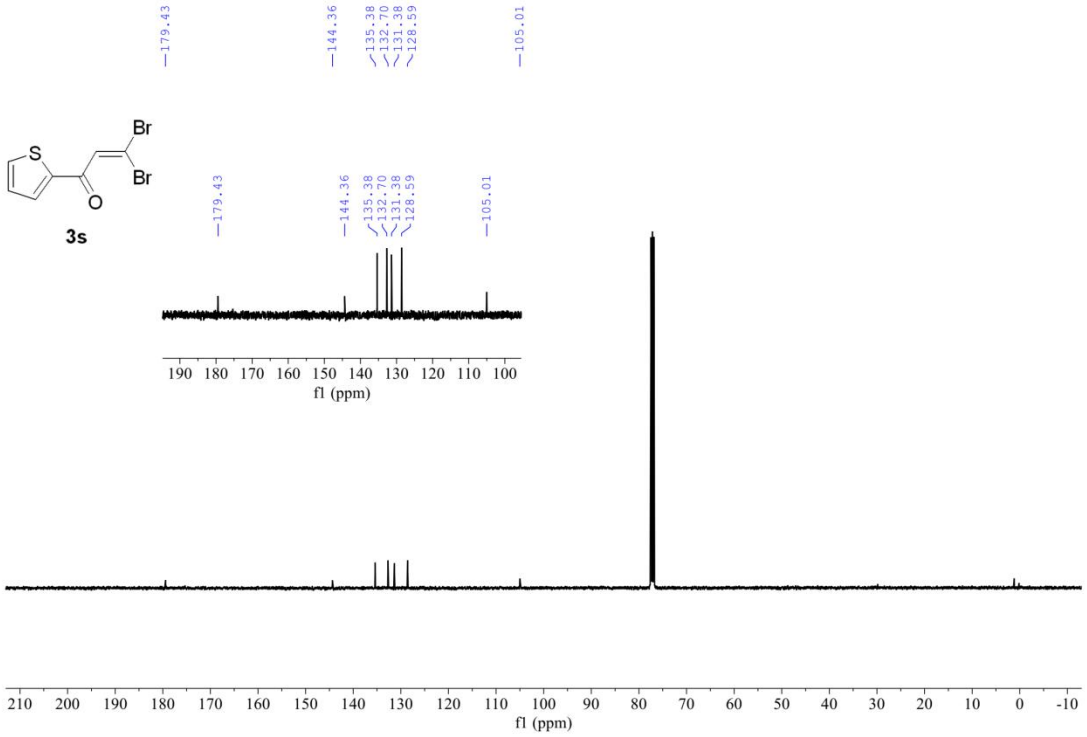

7.79
7.05
7.04
6.67
3.84
O
Br
Br
H3CO
OCH3
3q
0.97
2.01
0.96
6.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

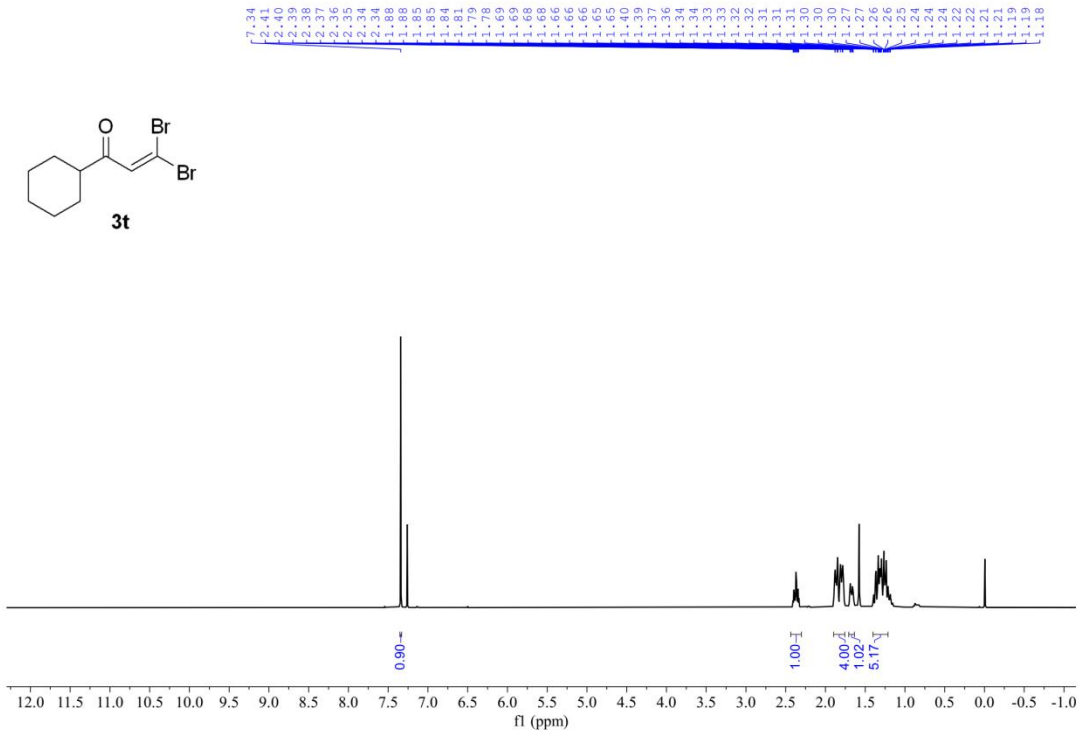

187.45
161.16
138.41
132.61
106.48
106.17
103.71
55.79
O
Br
Br
H3CO
OCH3
3q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

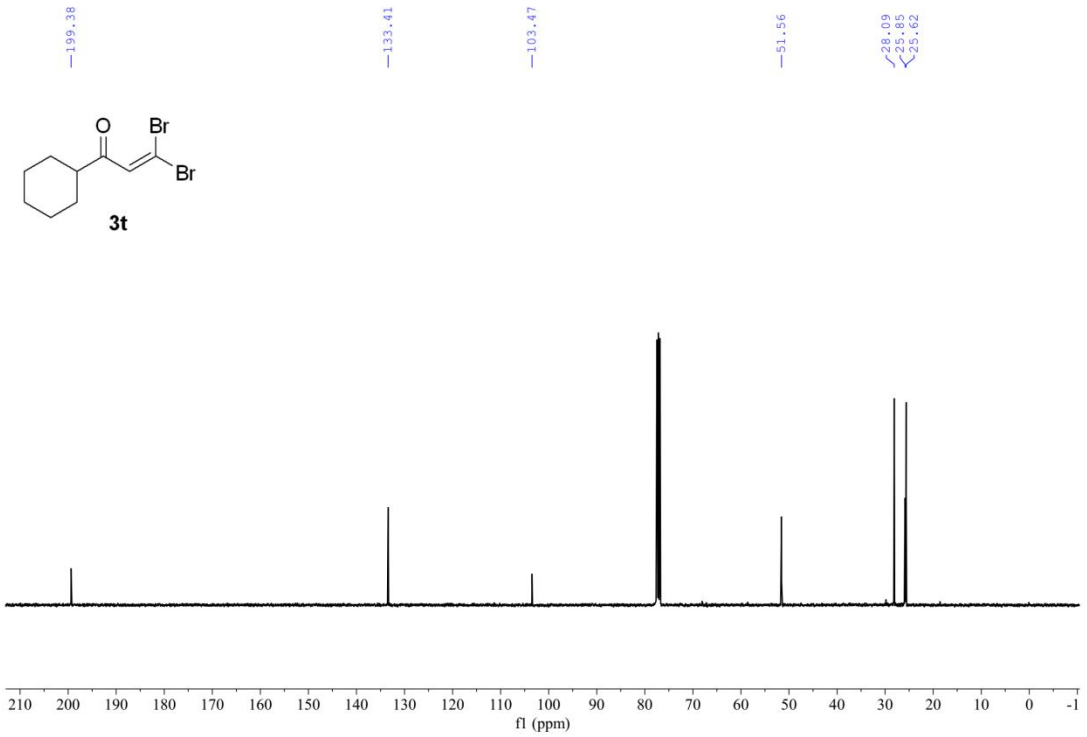

8.42
8.02
8.02
8.00
8.00
7.98
7.98
7.93
7.91
7.90
7.88
7.66
7.65
7.64
7.63
7.63
7.62
7.61
7.60
7.60
7.58
7.58
7.58
7.56
O
Br
Br
3r
1.00
3.11
2.16
2.25
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

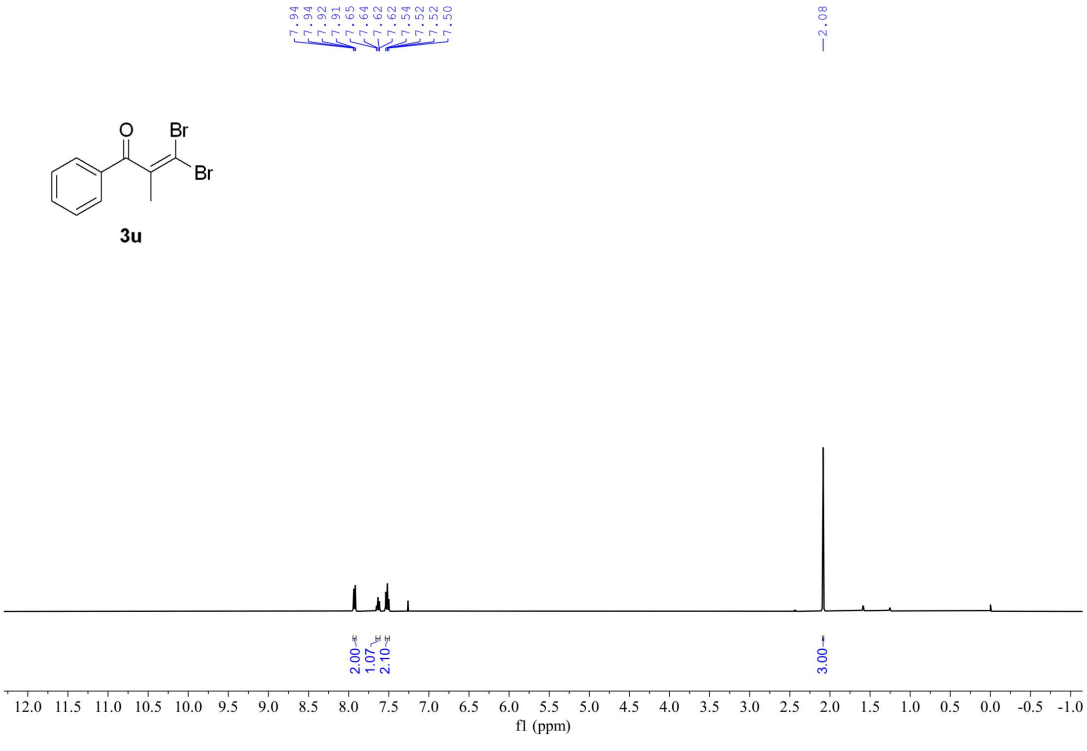

187.87
136.03
133.86
132.94
132.56
130.95
129.84
129.17
129.07
128.03
127.21
124.01
103.23
O
Br
Br
3r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

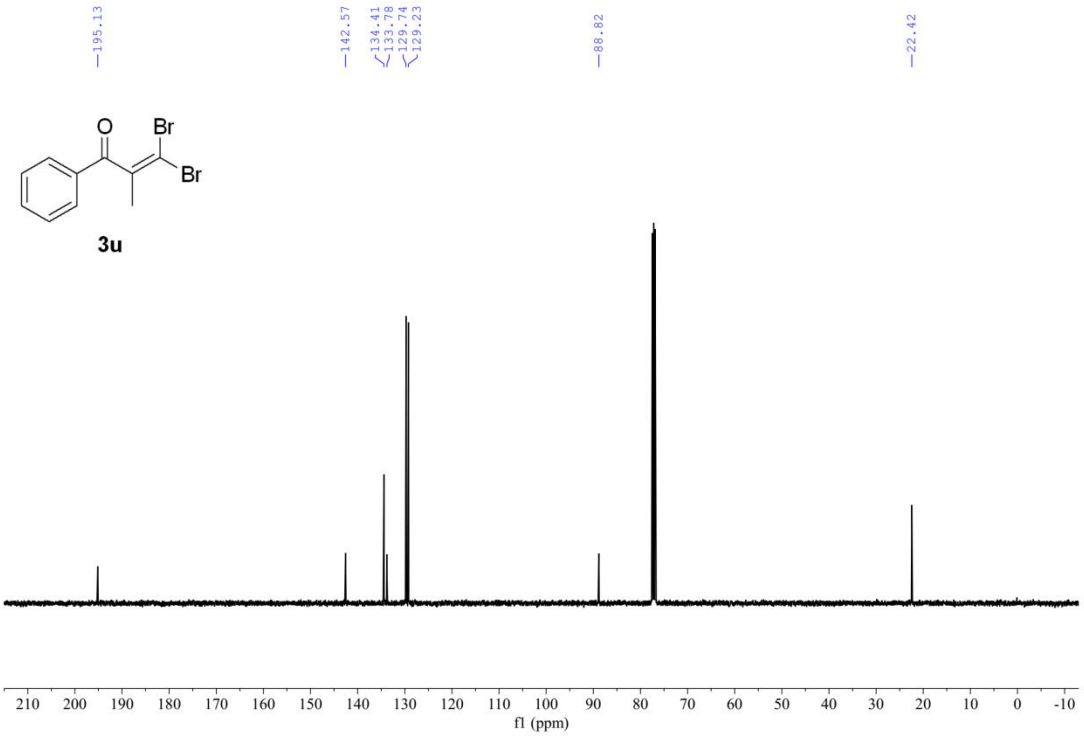

7.83
7.74
7.73
7.73
7.72
7.18
7.17
7.16
7.16
S
Br
Br
O
3s
1.00
2.10
1.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

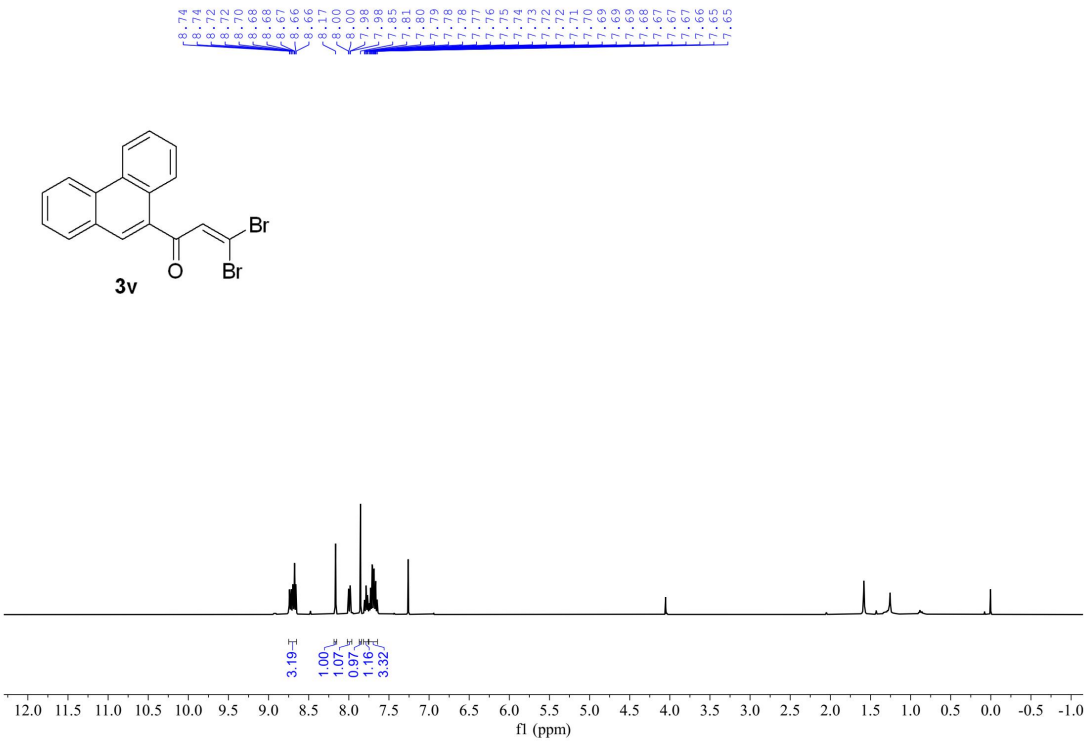

179.43
144.36
135.38
132.70
131.38
128.59
105.01
Br
Br
S
O
3s
fl (ppm)

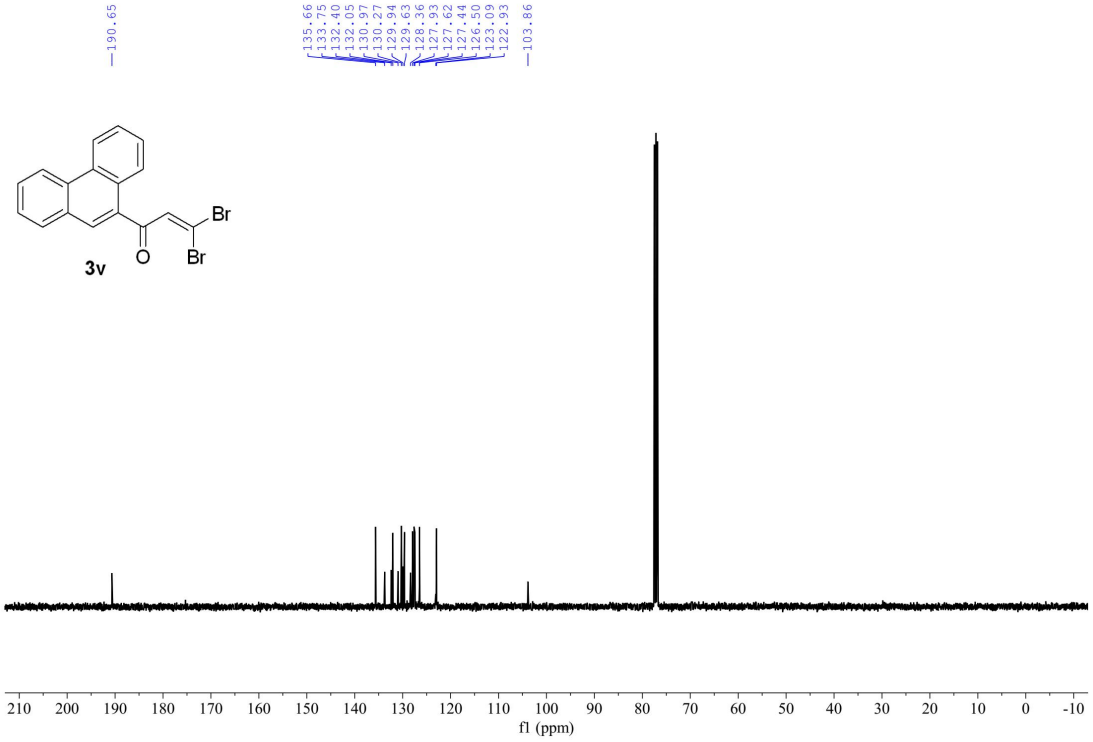

O
Br
Br
3t
0.90
1.00
4.00
1.02
5.17
fl (ppm)

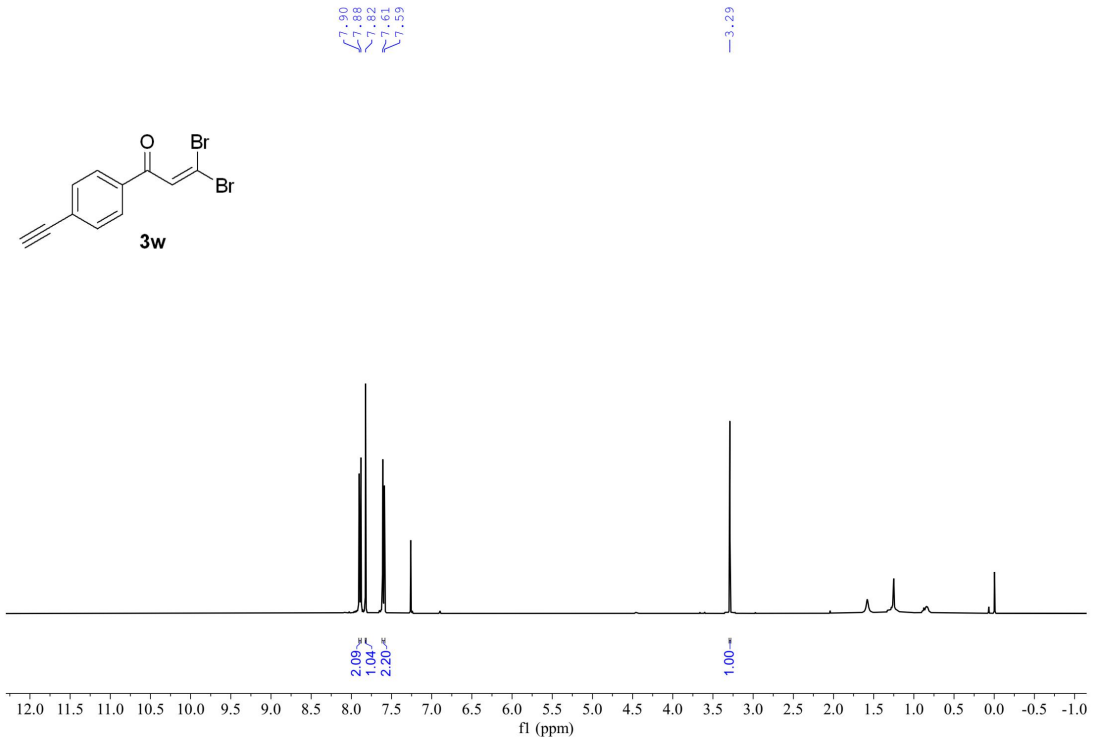

199.38
133.41
103.47
51.56
28.09
25.85
25.62
O
Br
Br
3t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

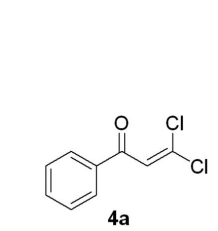

7.94
7.94
7.92
7.91
7.65
7.64
7.62
7.62
7.54
7.52
7.52
7.50
2.08
O
Br
Br
3u
2.00
1.07
2.10
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


195.13
142.57
134.41
133.78
129.74
129.23
88.82
22.42
O
Br
Br
3u
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)


8.74
8.74
8.72
8.72
8.70
8.68
8.68
8.67
8.66
8.66
8.17
8.00
8.00
7.98
7.85
7.81
7.80
7.79
7.78
7.78
7.77
7.76
7.75
7.74
7.73
7.72
7.72
7.71
7.70
7.69
7.69
7.69
7.68
7.67
7.67
7.67
7.66
7.65
7.65
Br
O
Br
3v
3.19
1.00
1.07
0.97
1.16
3.32
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)

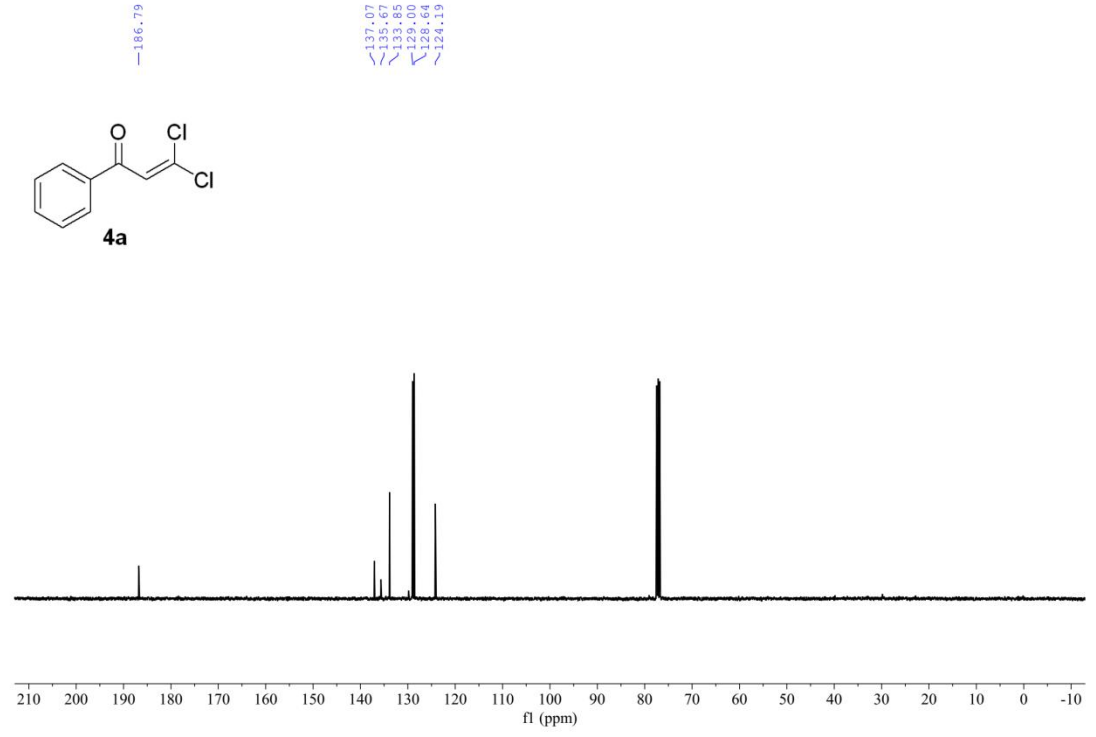

190.65
135.66
133.75
132.40
132.05
130.97
130.27
129.94
129.63
128.36
127.93
127.62
127.44
126.50
123.09
122.93
103.86
Br
O
Br
3v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.90
7.88
7.82
7.61
7.59
3.29
O
Br
Br
3w
2.09
1.04
2.20
1.00
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)

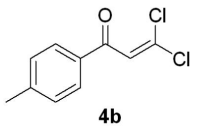

O
Cl
Cl

4a

7.94
7.92
7.63
7.61
7.59
7.52
7.50
7.48
7.29
2.00
1.02
2.04
0.97
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)

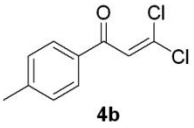

186.79
137.07
135.67
133.85
129.00
128.64
124.19
O
Cl
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4a


O
Cl
Cl

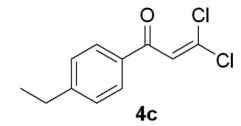
4b

7.83
7.81
7.30
7.27
7.24
2.42
1.94
1.98
0.92
3.00
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)


O
Cl
Cl

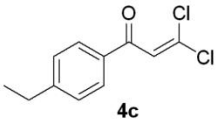
4b

186.47
144.94
134.98
134.53
129.69
128.81
124.40
21.87
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)


O
Cl
Cl

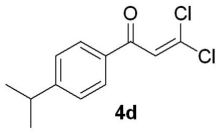
4c

7.86
7.84
7.32
7.30
7.25
2.75
2.73
2.71
2.69
1.28
1.26
1.24
1.91
1.95
0.89
2.01
3.00
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)


O
Cl
Cl

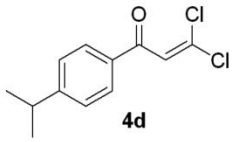
4c

186.48
151.07
134.97
134.74
128.91
128.51
124.41
29.14
15.23
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)


O
Cl
Cl

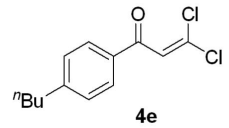
4d

7.87
7.85
7.35
7.33
7.25
3.03
3.01
2.99
2.97
2.96
2.94
2.92
1.28
1.26
1.90
1.91
0.89
0.99
6.00
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)


O
Cl
Cl

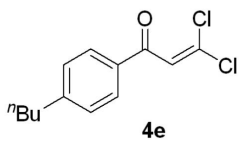
4d

186.44
155.61
134.94
134.89
128.95
127.10
124.42
34.45
23.73
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)


O
Cl
Cl
nBu

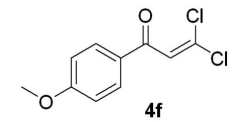
4e

7.85
7.83
7.30
7.28
7.25
2.69
2.67
2.65
1.65
1.64
1.62
1.60
1.58
1.40
1.38
1.37
1.35
1.33
1.31
0.95
0.93
0.91
1.91
1.94
0.90
2.02
2.29
2.12
3.00
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)


O
Cl
Cl
nBu

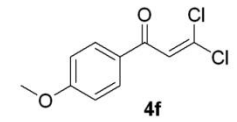
4e

186.44
149.82
134.92
134.71
129.03
128.81
124.42
35.87
33.27
22.43
13.99
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


O
Cl
Cl
O

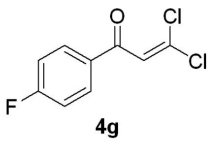
4f

7.92
7.90
7.21
6.97
6.95
3.88
1.96
0.91
1.98
3.00
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)


O
Cl
Cl
O

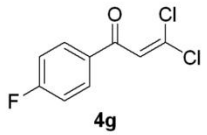
4f

185.48
164.24
131.11
129.90
124.54
114.20
55.68
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)


O
Cl
Cl
F

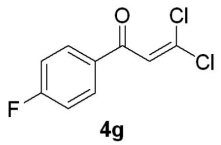
4g

7.98
7.97
7.96
7.95
7.24
7.20
7.17
7.15
2.10
1.00
2.12
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)


O
Cl
Cl
F

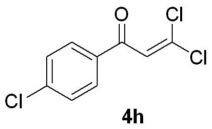
4g

185.33
167.52
164.97
135.90
133.45
133.42
131.43
131.34
123.94
116.35
116.13
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)


O
Cl
Cl
F

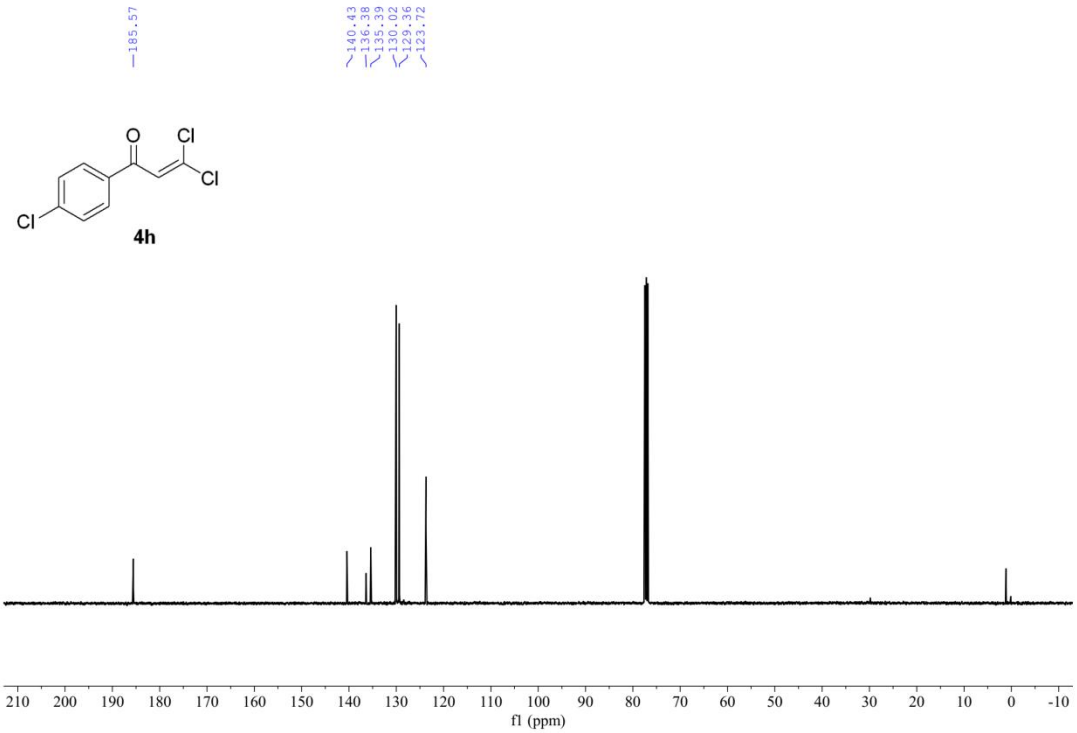
4g

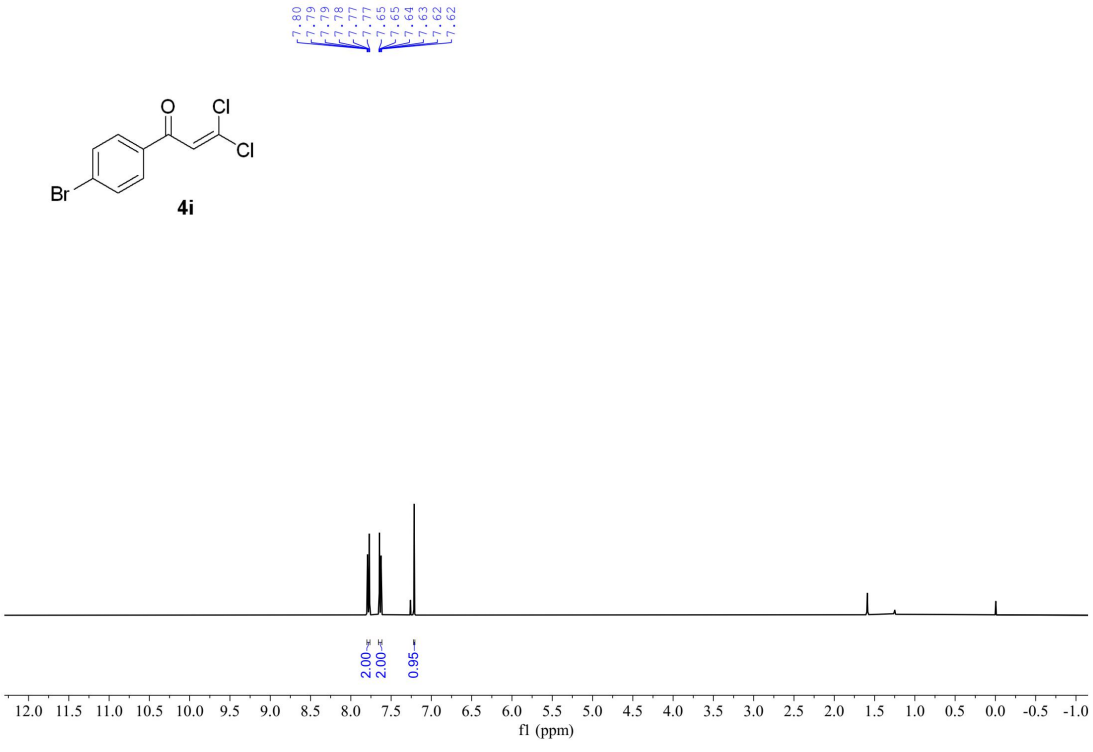
-103.60
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

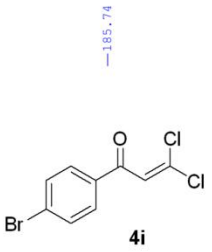

O
Cl
Cl
Cl

4h

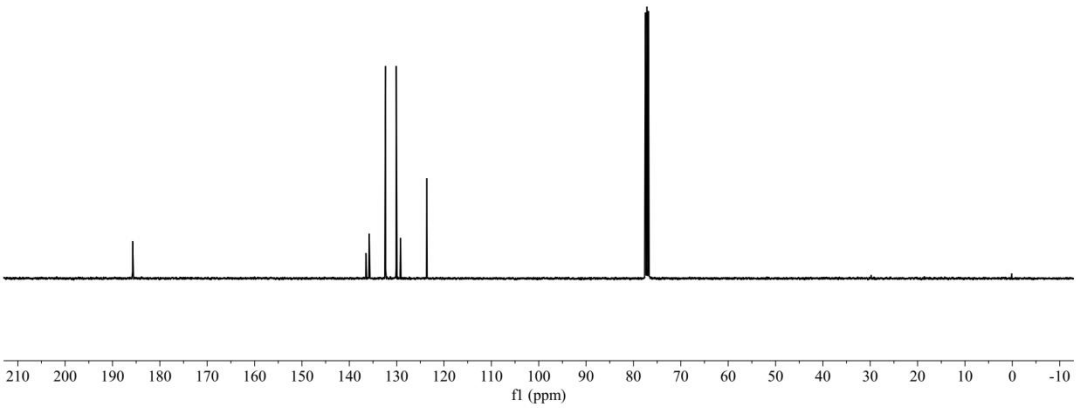
7.87
7.85
7.48
7.46
7.22
2.02
2.00
0.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


185.57
140.43
136.38
135.39
130.02
129.36
123.72
O
Cl
Cl
Cl
4h
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)

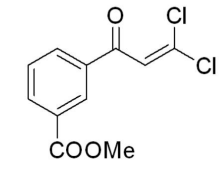

7.80
7.79
7.79
7.78
7.77
7.77
7.65
7.65
7.64
7.63
7.62
7.62
O
Cl
Cl
Br
4i
2.00
2.00
0.95
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


185.74
136.48
133.81
132.35
130.09
129.18
123.64
O
Cl
Cl
Br

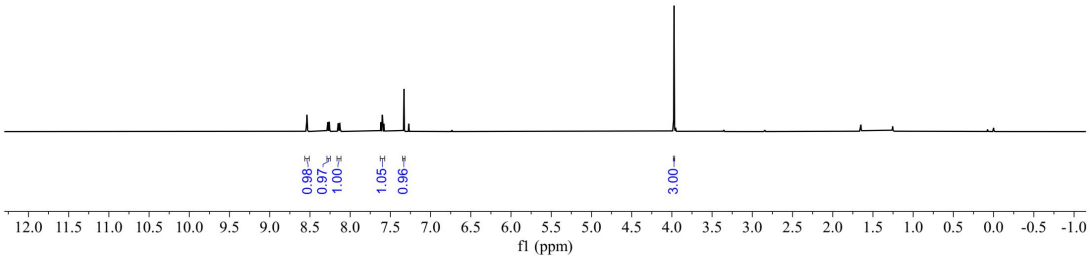
4i

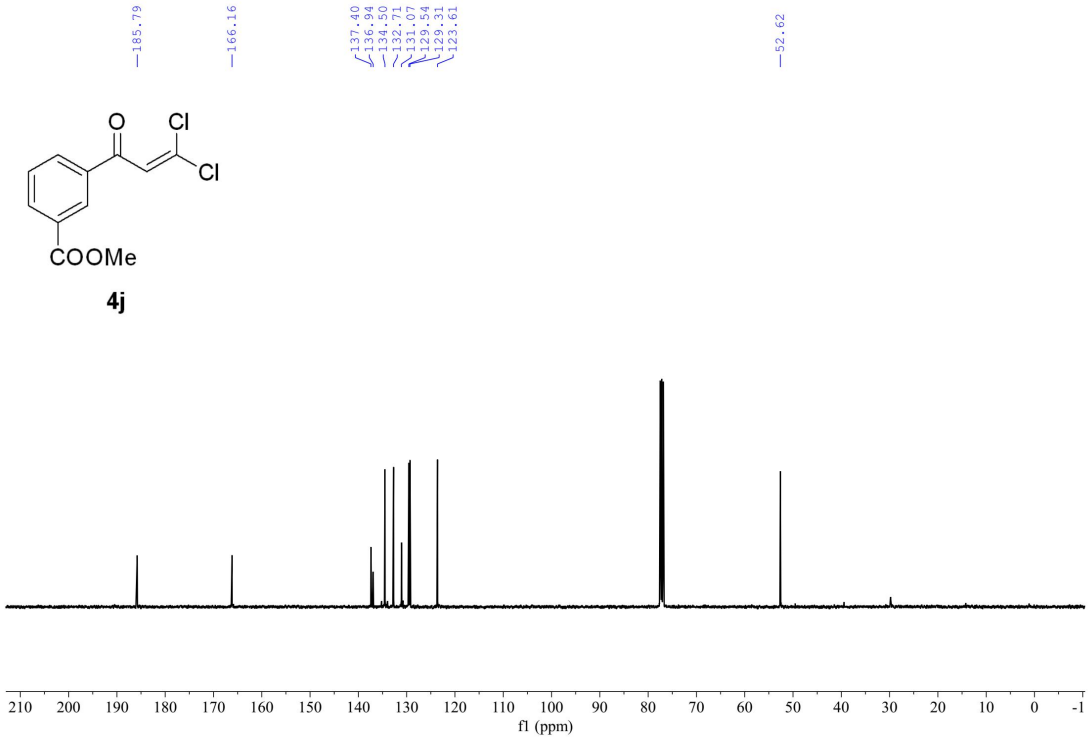

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.54
8.54
8.53
8.28
8.28
8.27
8.26
8.26
8.26
8.15
8.15
8.14
8.13
8.13
8.12
7.62
7.60
7.58
7.33
3.97

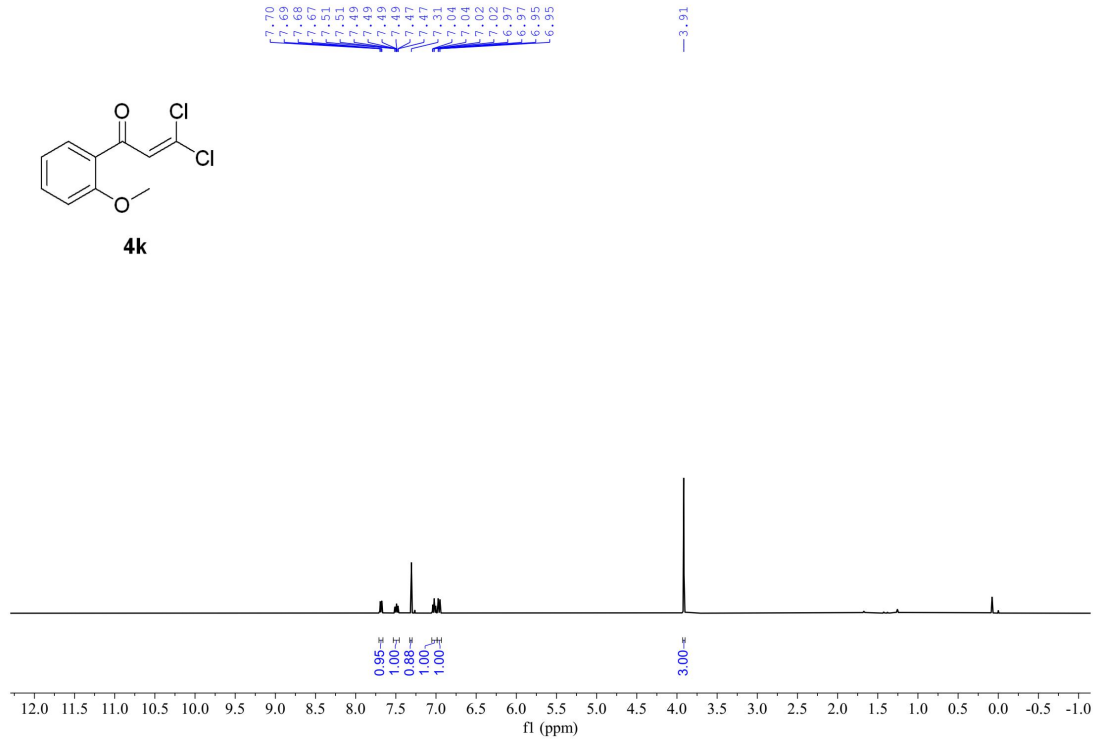

O
Cl
Cl
COOMe

4j

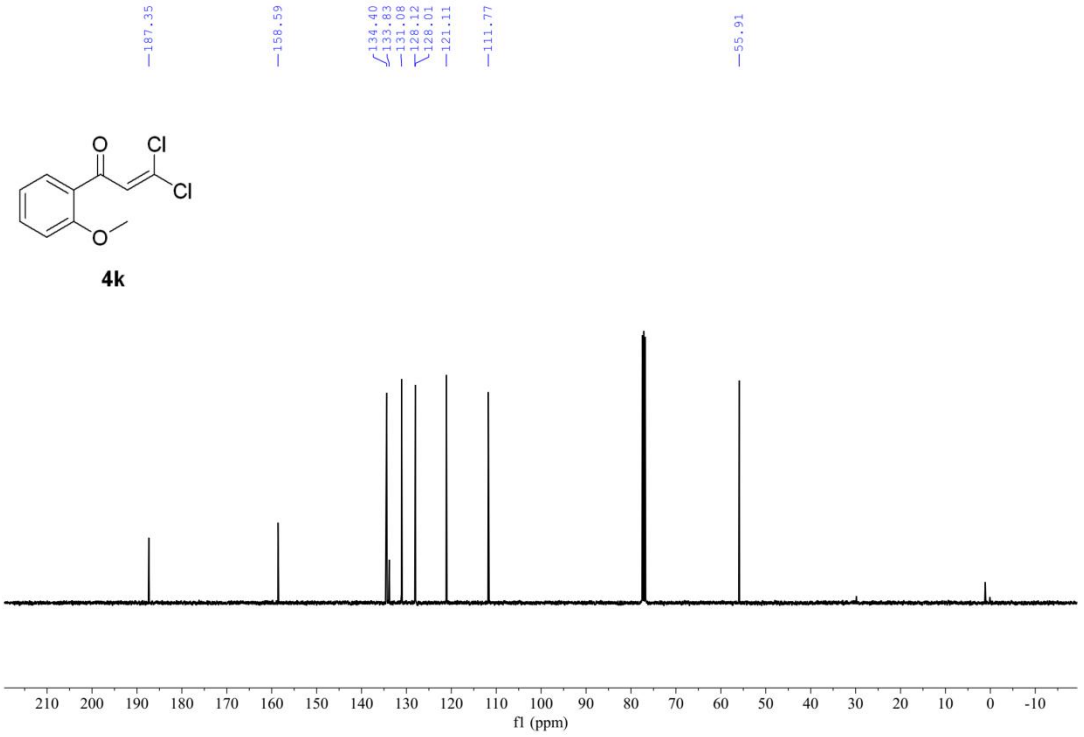

0.98
0.97
1.00
1.05
0.96
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

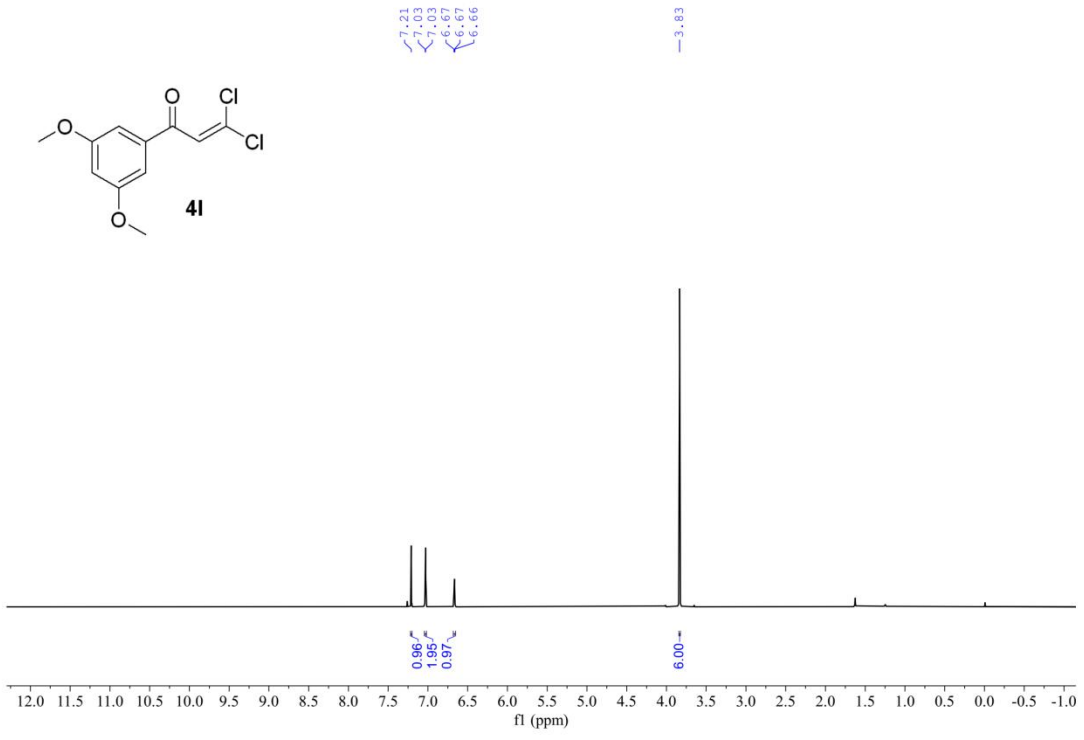

185.79
166.16
137.40
136.94
134.50
132.71
131.07
129.54
129.31
123.61
52.62
O
Cl
Cl
COOMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

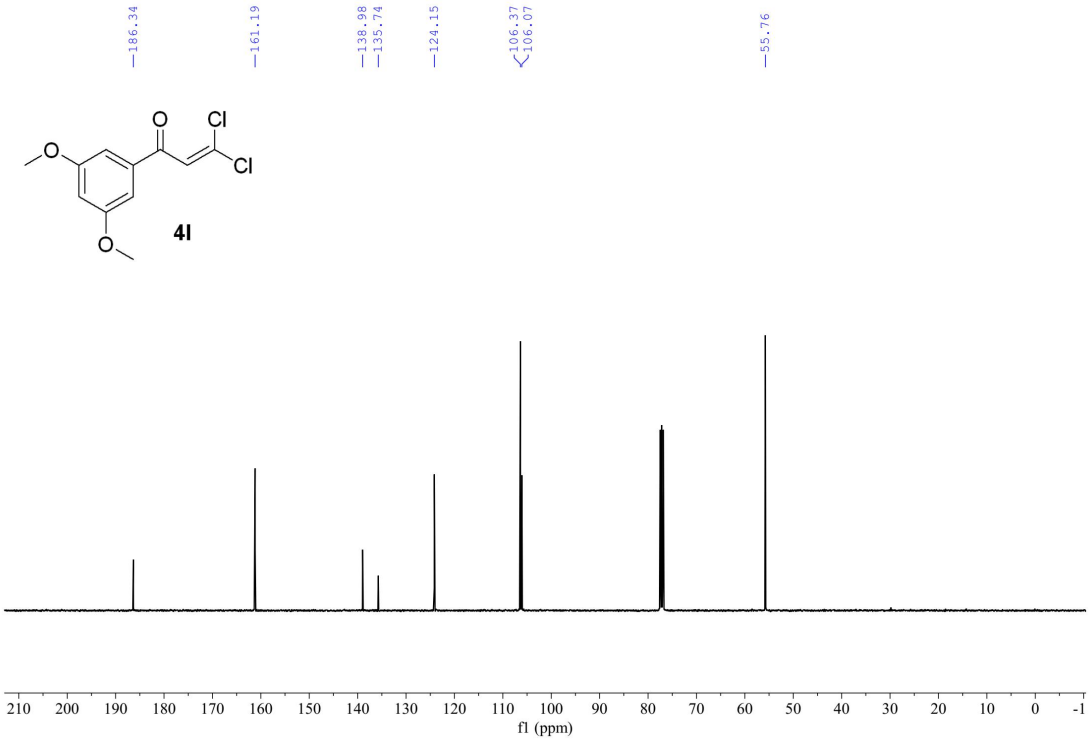
4j

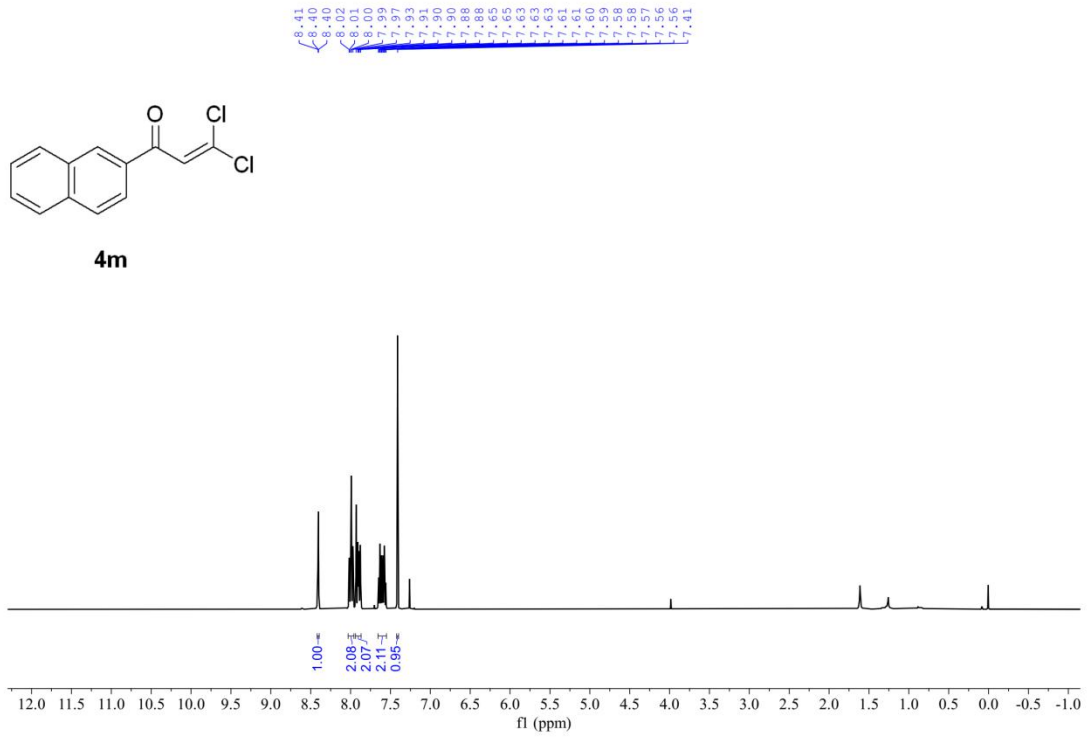

7.70
7.69
7.68
7.67
7.51
7.51
7.49
7.49
7.49
7.49
7.47
7.47
7.31
7.04
7.04
7.02
7.02
6.97
6.95
6.95
3.91
O
Cl
Cl
O
0.95
1.00
0.88
1.00
1.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

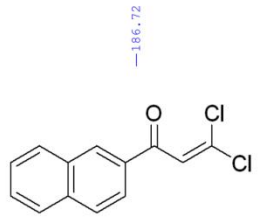
4k


187.35
158.59
134.40
133.83
131.08
128.12
128.01
121.11
111.77
55.91
O
Cl
Cl
O
4k
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)


7.21
7.03
7.03
6.67
6.67
6.66
3.83
O
Cl
Cl
O
O
4l
0.96
1.95
0.97
6.00
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)

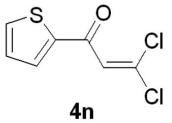

186.34
161.19
138.98
135.74
124.15
106.37
106.07
55.76
O
Cl
Cl
O
O
4l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


8.41
8.40
8.40
8.02
8.01
8.00
7.99
7.97
7.93
7.91
7.90
7.90
7.88
7.88
7.65
7.65
7.63
7.63
7.63
7.63
7.61
7.61
7.60
7.60
7.59
7.58
7.58
7.57
7.56
7.56
7.41
O
Cl
Cl
4m
1.00
2.08
2.07
2.11
0.95
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)


O
Cl
Cl

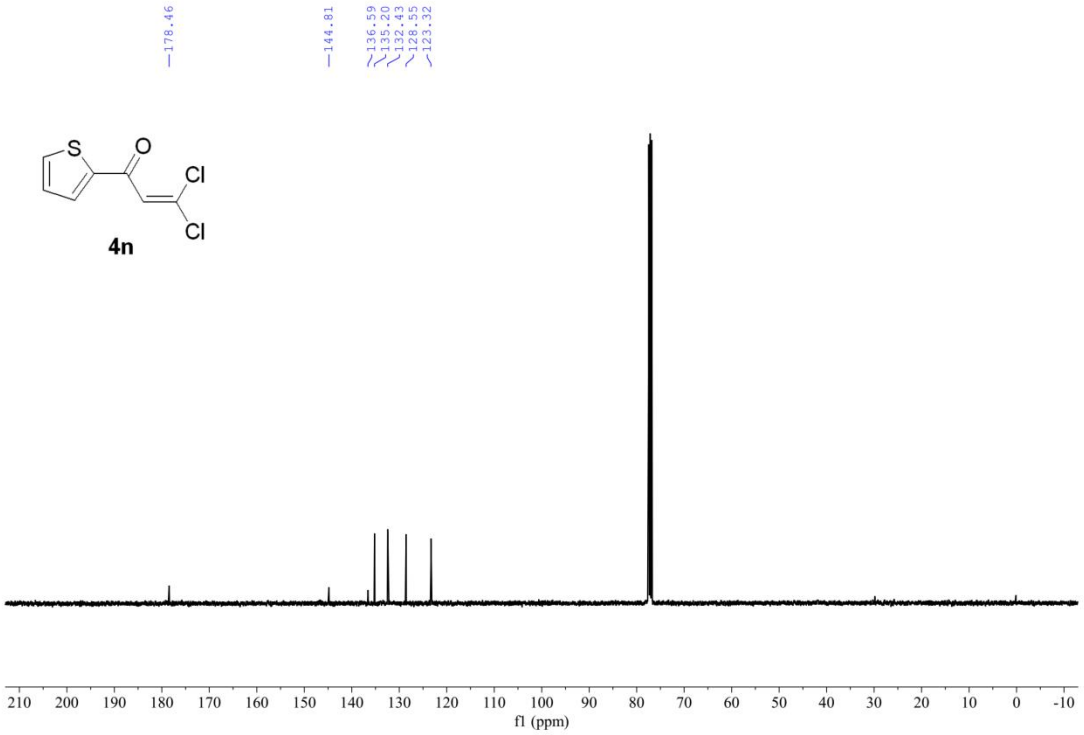
4m

186.72
135.97
135.47
134.42
132.57
130.66
129.80
129.10
129.03
128.02
127.19
124.38
123.97
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)


S
O
Cl
Cl

4n

7.73
7.72
7.72
7.24
7.18
7.17
7.17
7.16
2.18
1.00
1.08
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)


178.46
144.81
136.59
135.20
132.43
128.55
123.32
S
O
Cl
Cl
4n
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. References

1. X. Zeng, Y. Xu, J. Liu , Y. Deng, *Org. Lett.,* **2021**, *23*: 9058-9062.

2. Z. Y. Xu , Y. P. Liu, X. Liu, R. Fu, W. J. Hao, J. S. Tu, B. Jiang, *Adv. Synth. Catal.*, **2022**, *364*, 2666-2672.

3. R. Taylor, S. Beltrán-Rodil, M.Edwards, D.Pugh, M. Reid, *Synlett*, **2009**, *2010*, 602-606.

4. D. K. Li, *Tetrahedron Lett.*, **2021**, *87*: 153551.