Supporting information

Visible-Light-Promoted Synthesis of *gem*-Dihaloenones

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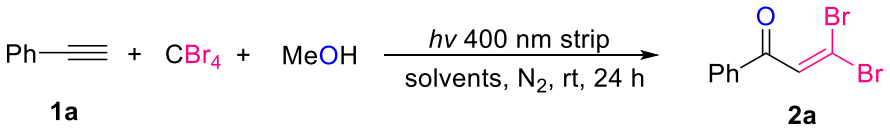
1. General information

Unless otherwise stated, all experimental procedures were performed under nitrogen atmosphere using Schlenk techniques. All solvents and materials were purchased from commercial suppliers and used without further purification. Flash chromatography was carried out using silica gel (200−300 mesh). Reactions were monitored by Thin Layer Chromatography (TLC) using UV light (254nm) for detection. The NMR spectra were recorded using a Bruker Avance III HD 400 spectrometer using TMS as the internal standard (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR 376 MHz for ^{19}F NMR). Mass spectroscopy data were collected by using a Waters UPLC G2-XS Qtof mass spectrometer. The LED strip light (5050SMD, 0.5 m, 14 W, 400 nm) was purchased from Prime LED Co. Ltd.

2. Optimization of methanol concentration

Table S1. Optimization of methanol concentration [a]



1a 2a

Entry	Solvent	CH_3OH (X μL)	Yield (%)[b]
1	H_2O (1 mL)	CH_3OH (40 μL)	<5
2	H_2O (1 mL)	CH_3OH (80 μL)	13
3	H_2O (1 mL)	CH_3OH (120 μL)	16
4	H_2O (1 mL)	CH_3OH (160 μL)	27
5	H_2O (1 mL)	CH_3OH (200 μL)	31
6	CH_3CN (1 mL)	CH_3OH (40 μL)	36
7	CH_3CN (1 mL)	CH_3OH (80 μL)	49
8	CH_3CN (1 mL)	CH_3OH (120 μL)	56
9	CH_3CN (1 mL)	CH_3OH (160 μL)	59
10	CH_3CN (1 mL)	CH_3OH (200 μL)	60

[a] Reaction conditions: phenylacetylene (0.4 mmol), CBr_4 (0.5 mmol), CH_3OH (loading amount as indicated in **Table S1**) in solvents (1 mL) with irradiation using a 14-W 400-nm strip under a N_2 atmosphere at room temperature for 24 h. [b] Isolated yield.

3. General procedure for the synthesis of *gem*-dibromoenones compounds 2

Reaction condition 1:

CBr_4 (165 mg, 0.5 mmol) was taken in a 25 mL reaction tube with a stir bar, the reaction tube was vacuumed and then filled with nitrogen three times. Subsequently, alkynes (0.4 mmol), H_2O (350 μL) and dimethyl sulfoxide (1 mL) were added to the reaction tube. The mixture was irradiated by 400-nm of purple light strip at room temperature for 24 h. Then pour brine (30 mL) into the reaction tube and extracted three times with dichloromethane (3 × 15 mL), organic layer was concentrated under vacuum and products were obtained by column chromatography (petroleum ether/ethyl acetate).

Reaction condition 2:

CBr_4 (165 mg, 0.5 mmol) was taken in a 25 mL reaction tube with a stir bar, the reaction tube was vacuumed and then filled with nitrogen three times. Subsequently, alkynes (0.4 mmol) and CH_3OH (1 mL) were added to the reaction tube. The mixture was irradiated by 400-nm of purple light strip at room temperature for 24 h. Then the mixture was concentrated under vacuum and products were obtained by column chromatography (petroleum ether/ethyl acetate).

General procedure for the synthesis of *gem*-dichloroenones compounds 3

Reaction condition 1:

In a 25 mL reaction tube with a stir bar, the reaction tube was vacuumed and then filled with nitrogen three times. Subsequently, CCl_3Br (92 μL, 1.0 mmol), alkynes (0.4 mmol), H_2O (350 μL) and dimethyl sulfoxide (1 mL) were added to the reaction tube. The mixture was irradiated by 400-nm of purple light strip at room temperature for 24 h. Then pour brine (30 mL) into the reaction tube and extracted three times with dichloromethane (3 × 15 mL), organic layer was concentrated under vacuum and products were obtained by column chromatography (petroleum ether/ethyl acetate).

Reaction condition 3:

In a 25 mL reaction tube with a stir bar, the reaction tube was vacuumed and then filled with nitrogen three times. Subsequently, alkynes (0.4 mmol), CCl_3Br (92 μL, 1.0 mmol) and CH_3CH_2OH (1 mL) were added to the reaction tube. The mixture was irradiated by 400-nm of purple light strip at room temperature for 24 h. Then the mixture was concentrated under vacuum and products were obtained by column chromatography (petroleum ether/ethyl acetate).

4. Procedure for the scale-up experiments

4.1 Procedure for the scale-up experiments for synthesizing 3,3-dibromo-1-phenylprop-2-en-1-one (**2a**)

Reaction condition 1:

CBr_4 (2.068 g, 6.25 mmol) was taken in a 50 mL reaction tube with a stir bar, the reaction tube was vacuumed and then filled with nitrogen three times. Subsequently, phenylacetylene (5.0 mmol), H_2O (5 mL) and dimethyl sulfoxide (10 mL) were added to the reaction tube. The mixture was irradiated by 400-nm of purple light strip at room temperature for 36 h. Then pour brine (50 mL) into the reaction tube and extracted three times with dichloromethane (3 × 20 mL), organic layer was concentrated under vacuum and *gem*-dibromoenone **2a** (76%, 1.09g) were obtained by column chromatography (petroleum ether/ethyl acetate).

Reaction condition 2:

CBr_4 (2.068 g, 6.25 mmol) were taken in a 50 mL reaction tube with a stir bar, the reaction tube was vacuumed and then filled with nitrogen three times. Subsequently, phenylacetylene (5.0 mmol) and CH_3OH (5 mL) were added to the reaction tube. The mixture was irradiated by 400-nm of purple light strip at room temperature for 36 h. Then the mixture was concentrated under vacuum and *gem*-dibromoenone **2a** (71%, 1.02g) were obtained by column chromatography (petroleum ether/ethyl acetate).

4.2 Procedure for the scale-up experiments for synthesizing 3,3-dichloro-1-phenylprop-2-en-1-one (**3a**)

Reaction condition 1:

In a 50 mL reaction tube with a stir bar, the reaction tube was vacuumed and then filled with nitrogen three times. Subsequently, CCl_3Br (2.478 g, 12.5 mmol), phenylacetylene (5.0 mmol), H_2O (5 mL) and dimethyl sulfoxide (10 mL) were added to the reaction tube. The mixture was irradiated by 400-nm of purple light strip at room temperature for 36 h. Then pour brine (50 mL) into the reaction tube and extracted three times with dichloromethane (3 × 20 mL), organic layer was concentrated under vacuum and *gem*-dichloroenone **3a** (78%, 0.78g) were obtained by column chromatography (petroleum ether/ethyl acetate).

Reaction condition 3:

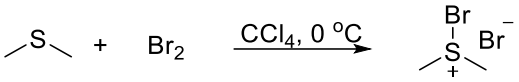
In a 50 mL reaction tube with a stir bar, the reaction tube was vacuumed and then filled with nitrogen three times. Subsequently, CCl_3Br (2.478 g, 12.5 mmol), phenylacetylene (5.0 mmol), and CH_3CH_2OH (5 mL) were added to the reaction tube. The mixture was irradiated by 400-nm of purple light strip at room temperature for 36 h. Then the mixture was concentrated under vacuum and *gem*-dichloroenone **3a** (81%, 0.81g) were obtained by column chromatography (petroleum ether/ethyl acetate).

5. Preparation of DMS^{18}O and [O]–Labeling Experiments with DMS^{18}O and $H_2{}^{18}O$

5.1 Preparation of DMS^{18}O[1]

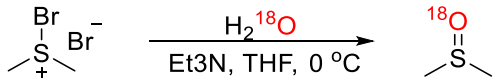
(1) Preparation of bromodimethylsulfoniumbromide (BDMS)

7.2 mL (132 mmol) Bromine was added drop wise to an ice-cooled solution of 9.68 mL (132 mmol) dimethyl sulfide in 120 mL carbon tetrachloride and the mixture was stirred for 2 h. Yellow orange crystals were formed, then filtered and washed with cold carbon tetrachloride. The solid (28 g) was recrystallized in carbon tetrachloride and provided yellow solid BDMS.



Scheme S1. Synthesis of BDMS

(2) Preparation of DMS^{18}O: In a stirred solution of dry triethylamine (25.2 mL, 180 mmol) and H^{18}O (97 atom %^{18}O; 0.80 mL, 44 mmol) in 60 mL of dry tetrahydrofuran at 0 °C, solid BDMS (20.0 g, 90 mmol) was added portion wise over 30 min. Trimethylamine hydrobromide was precipitated and removed by centrifugation and then filtered. Dried the yellow filtrate to remove the solvent. The DMS^{18}O (2.2 g, 75 atom % ^{18}O) was obtained as brownish liquid.



Scheme S2. Synthesis of DMS^{18}O

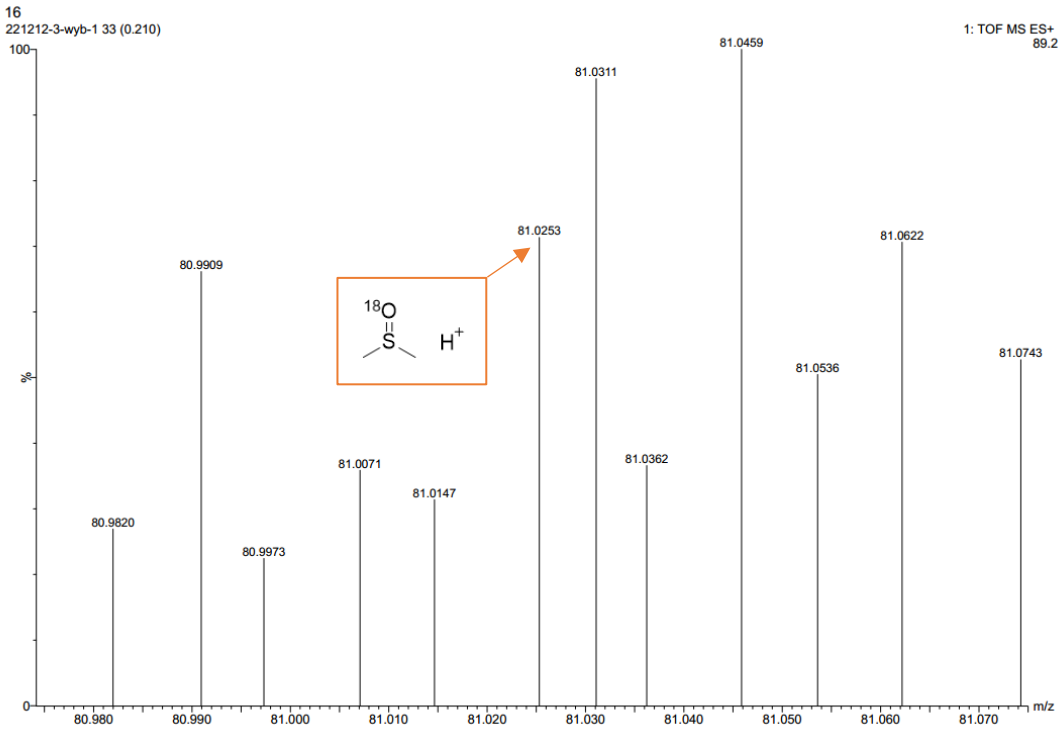
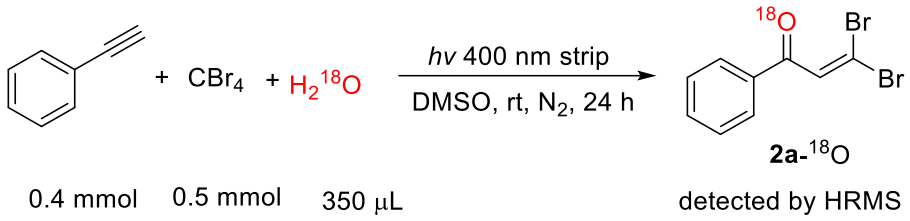


Figure S1. HRMS Spectra of DMS^{18}O

5.2 [O]–Labeling Experiments with $H_2{}^{18}O$

CBr_4 (165 mg, 0.5 mmol) was taken in a 25 mL reaction tube with a stir bar, the reaction tube was vacuumed and then filled with nitrogen three times. Subsequently, phenylacetylene (0.4 mmol), $H_2{}^{18}O$ (350 μL) and dimethyl sulfoxide (1 mL) were added to the reaction tube. The mixture was irradiated by 400-nm of purple light strip at room temperature for 24 h. Then pour brine (30 mL) into the reaction tube and extracted three times with dichloromethane (3 × 15 mL), organic layer was concentrated under vacuum and products were obtained by column chromatography (petroleum ether/ethyl acetate) to deliver the **2a-**^{18}O.



Scheme S3. [O]–Labeling Experiments with $H_2{}^{18}O$

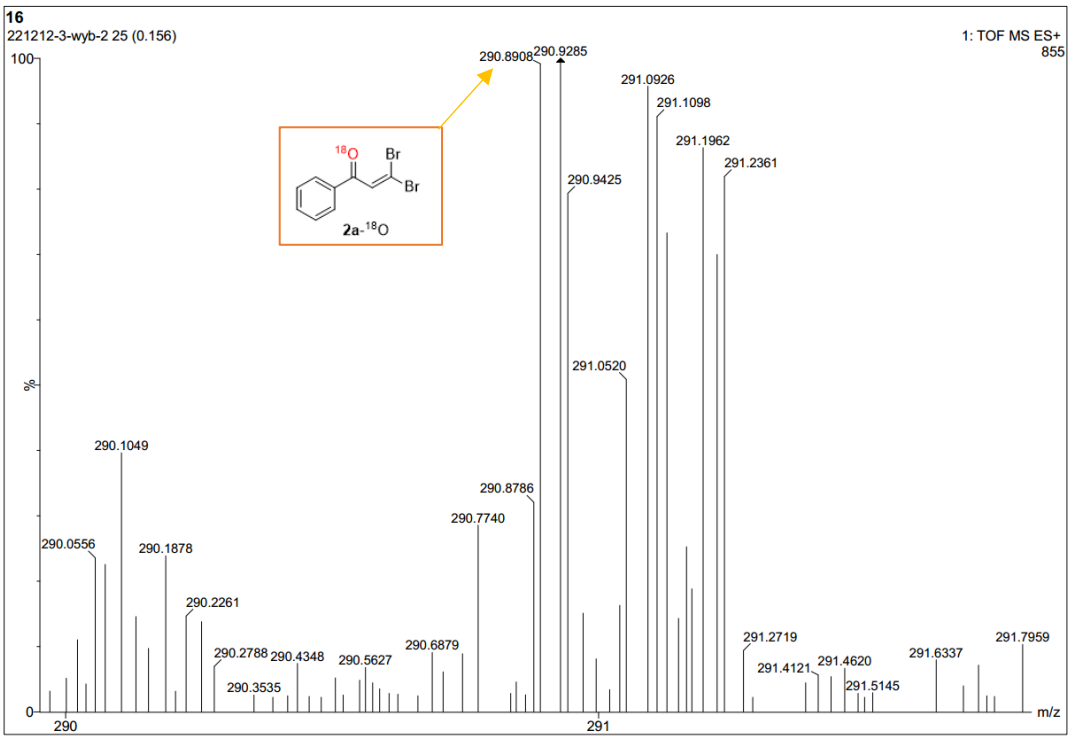
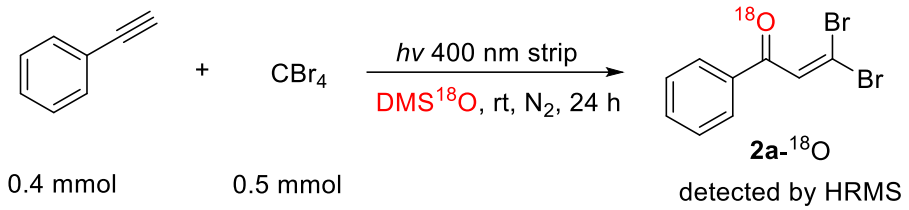


Figure S2. HRMS Spectra of **2a-**^{18}O

5.3 [O]–Labeling Experiments with DMS^{18}O

CBr_4 (165 mg, 0.5 mmol) was taken in a 25 mL reaction tube with a stir bar, the reaction tube was vacuumed and then filled with nitrogen three times. Subsequently, phenylacetylene (0.4 mmol), DMS^{18}O (1 mL) were added to the reaction tube. The mixture was irradiated by 400-nm of purple light strip at room temperature for 24 h. Then pour brine (30 mL) into the reaction tube and extracted three times with dichloromethane (3 × 15 mL), organic layer was concentrated under vacuum and products were obtained by column chromatography (petroleum ether/ethyl acetate) to deliver the **2a-**^{18}**O**.



Scheme S4. [O]–Labeling Experiments with $DMS^{18}O$

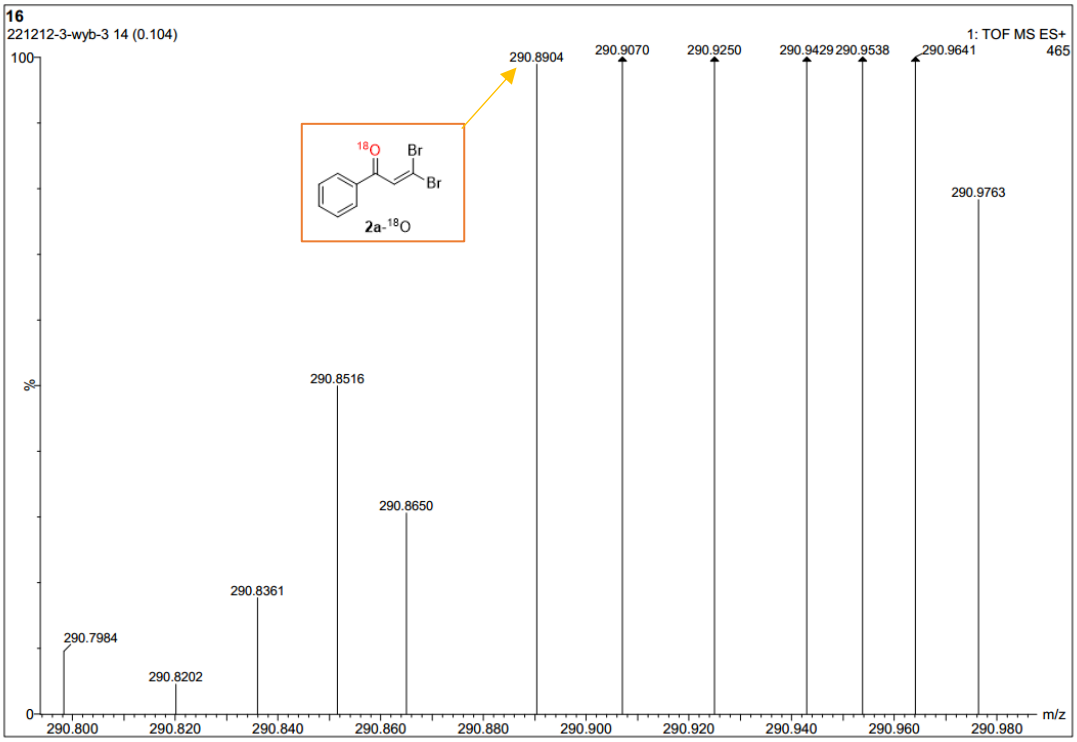
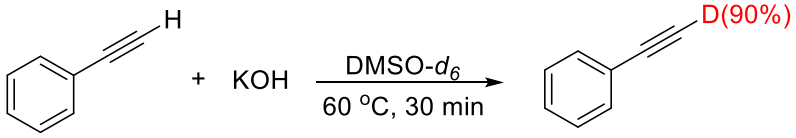


Figure S3. HRMS Spectra of **2a**-^{18}O

6. Deuterated Experiments with phenylacetylene 1a-D

6.1 Preparation of phenylacetylene 1a-D[2]

In an oven-dried reaction tube with a stir bar, phenylacetylene **1a** (0.5 mmol) and 20 mol % of crushed KOH in 0.8 mL of DMSO-d_6 were added. The reaction mixture was stirring at 60 °C for 30 minutes. Then pour brine (30 mL) into the reaction tube and extracted three times with dichloromethane (3 × 10 mL), and dried over Na2SO4, and then the organic layer was concentrated under vacuum. Phenylacetylene **1a-D** (90%-D) was obtained by column chromatography (petroleum ether).



Scheme S5. Synthesis of phenylacetylene **1a-D**

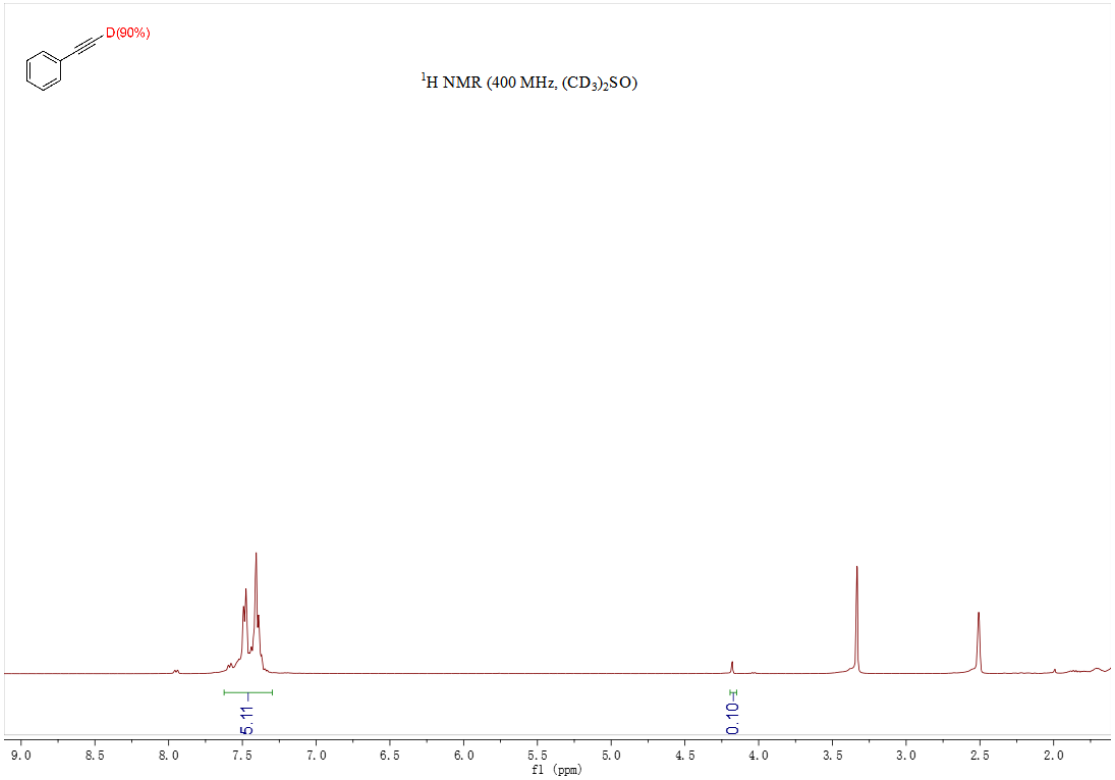


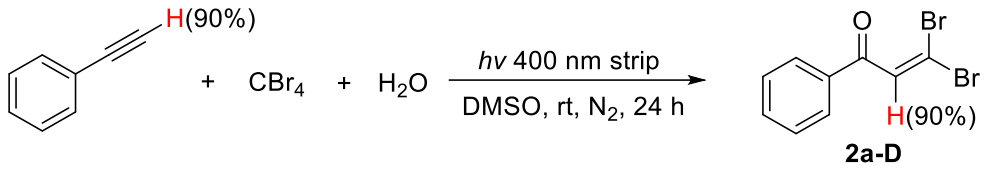
Figure S4. [1]NMR Spectra of **1a-D**

6.2 Deuterated Experiments with phenylacetylene 1a-D

Reaction condition 1:

CBr_4 (165 mg, 0.5 mmol) was taken in a 25 mL reaction tube with a stir bar, the reaction tube was vacuumed and then filled with nitrogen three times. Subsequently, phenylacetylene **1a-D** (0.2 mmol), H_2O (350 μL) and dimethyl sulfoxide (1 mL) were added to the reaction tube. The mixture was irradiated by 400-nm of purple light strip at room temperature for 24 h. Then pour brine (30 mL)

into the reaction tube and extracted three times with dichloromethane (3 × 15 mL), organic layer was concentrated under vacuum and products were obtained by column chromatography (petroleum ether/ethyl acetate) to deliver the **2a-D**.



Scheme S6. Deuterated Experiments with phenylacetylene **1a-D**

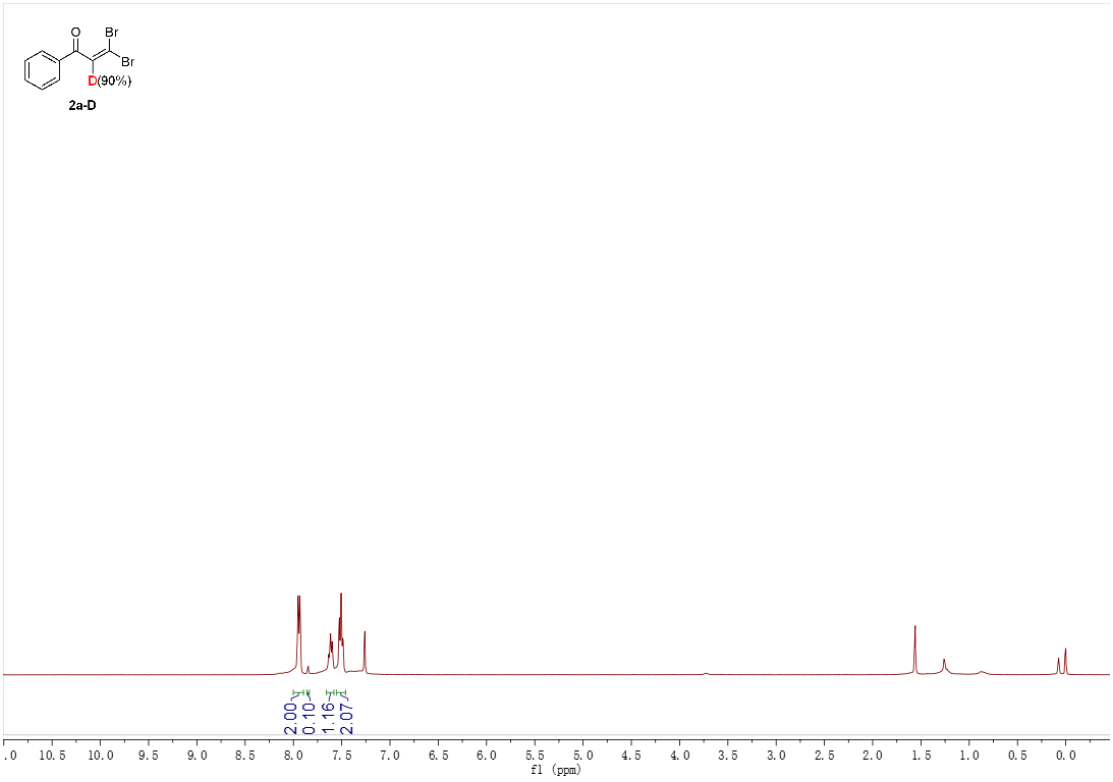
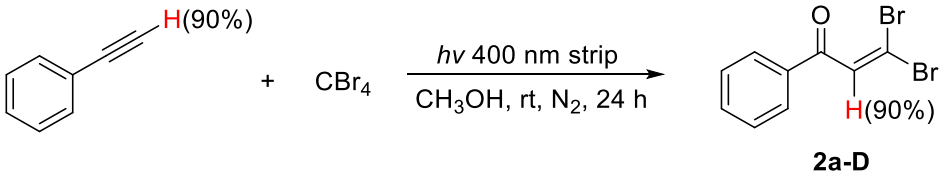


Figure S5. ^{1}NMR Spectra of **2a-D**

Reaction condition 2:

CBr_4 (165 mg, 0.5 mmol) was taken in a 25 mL reaction tube with a stir bar, the reaction tube was vacuumed and then filled with nitrogen three times. Subsequently, phenylacetylene **1a-D** (0.2 mmol) and CH_3OH (1 mL) were added to the reaction tube. The mixture was irradiated by 400-nm of purple light strip at room temperature for 24 h. Then the mixture was concentrated under vacuum and products were obtained by column chromatography (petroleum ether/ethyl acetate) to deliver the **2a-D**.



Scheme S7. Deuterated experiments with phenylacetylene **1a-D**

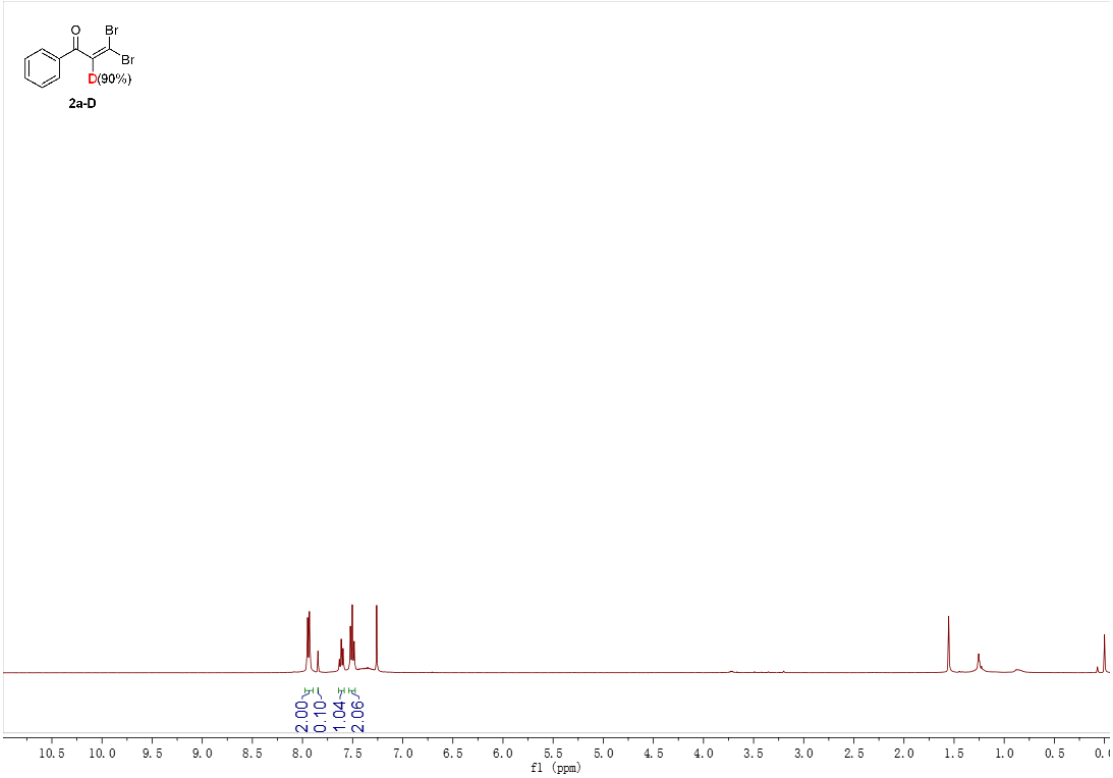
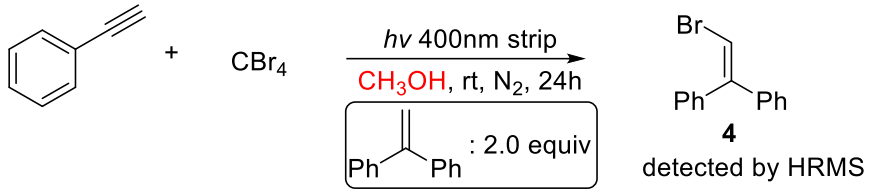


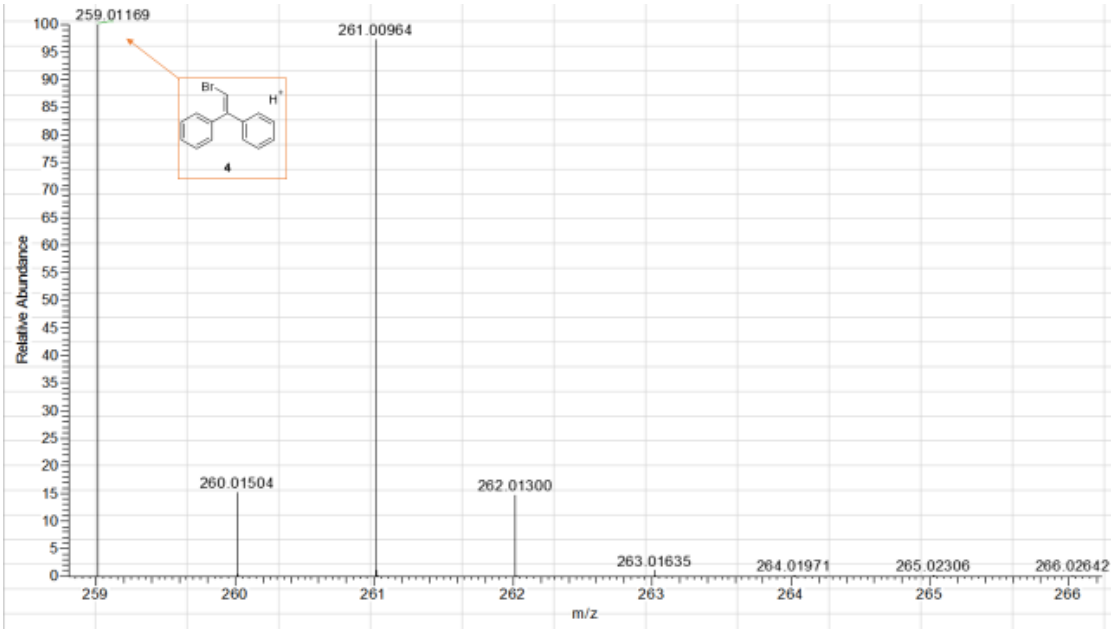
Figure S6. ^{1}NMR Spectra of **2a-D**

7. HRMS Spectrum for Radical Trapping and intermediate 12



Scheme S8. Radical trapping experiments with ethene-1,1-diyldibenzene

CBr_4 (165 mg, 0.5 mmol) and ethene-1,1-diyldibenzene (0.8 mmol, 141 μL, 2.0 equiv.) were taken in a 25 mL reaction tube with a stir bar, the reaction tube was vacuumed and then filled with nitrogen three times. Subsequently, phenylacetylene (0.4 mmol) and CH_3OH (1 mL) were added to the reaction tube. The mixture was irradiated by 400 nm of purple light strip at room temperature for 24 h. The radical captured product **4** could be detected by high resolution mass spectroscopy (HRMS) (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}Br$ 259.0117; found 251.01169.



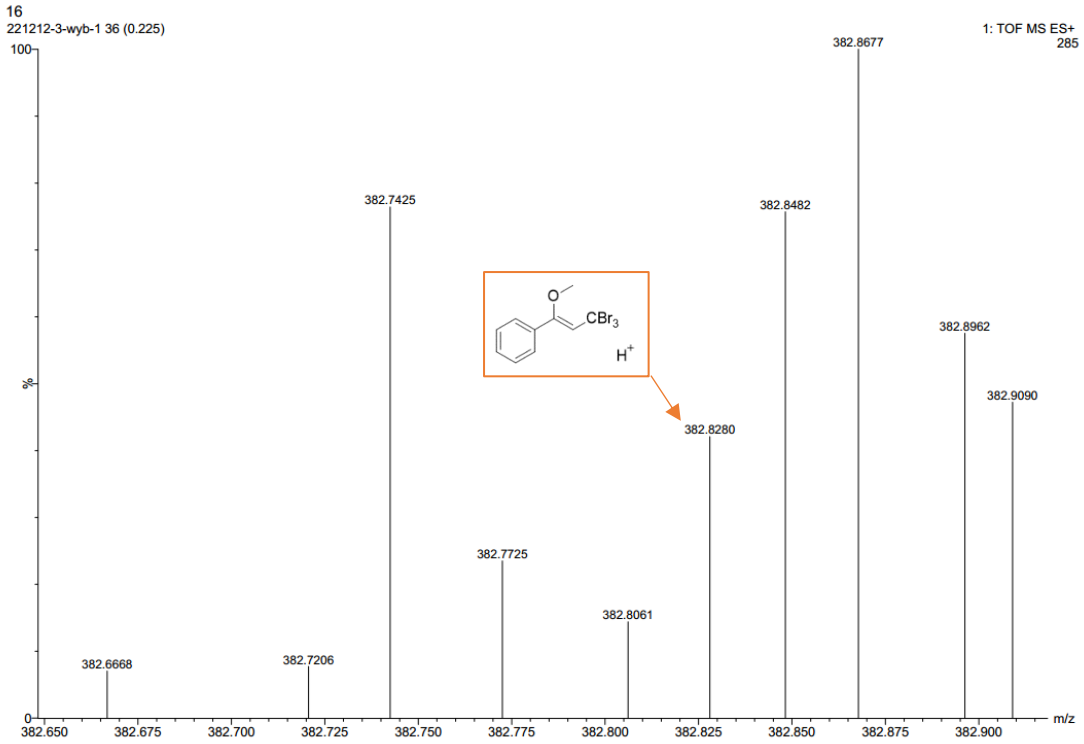


Figure S7. HRMS Spectra of **4** (top) and intermediate **12** (bottom).

8. UV-vis spectra experiments for CBr_4

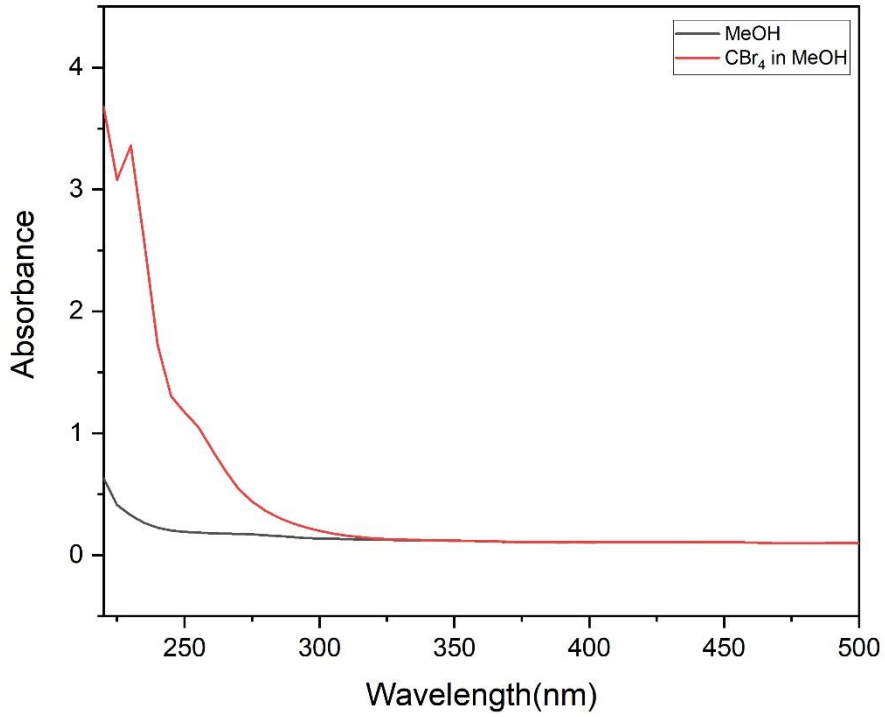


Figure S8. UV-vis spectra experiments: (a) MeOH (black curve); (b) CBr_4 (5.0×10^{-4} mol/L) in MeOH.

9. GC Spectra for detecting CH_4

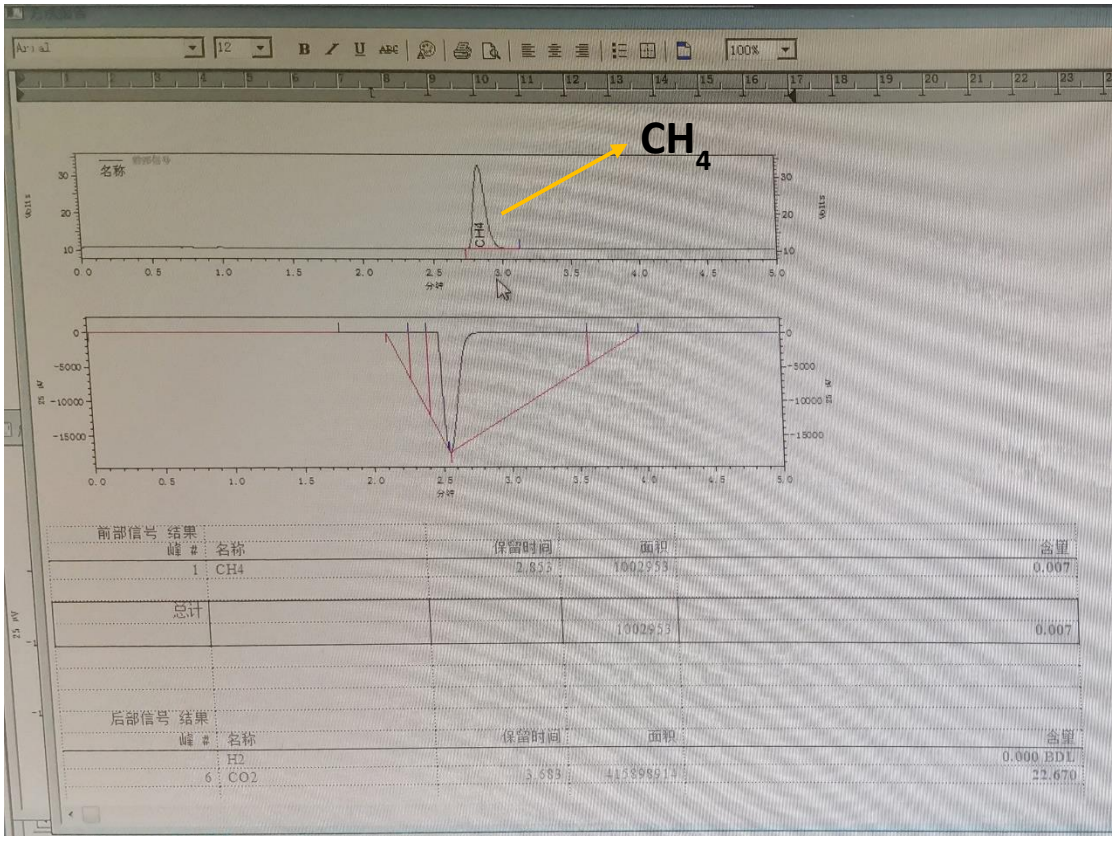


Figure S9. GC Spectra for detecting CH_4

10. Evaluation of Green Chemistry metrics of the thermal method[3]

$$\text{Atom economy (\%) (AE)} = \frac{\text{Molecular mass of desired product}}{\text{Molecular mass of all reactants}} \times 100\%$$

$$\text{Reaction mass efficiency (\%) (RME)} = \frac{\text{Mass of desired product}}{\text{Mass of all reactants}} \times 100\%$$

Reactant **1**	Phenylacetylene	0.51g	5.0 mmol	FW 102.13
Reactant **2**	Tetrabromomethane	1.69g	5.1 mmol	FW 331.62
Reactant **3**	water	4 ml, 4.0 g		FW 18
Oxidant	Potassium persulfate	2.7g	10 mmol	FW 270.32
Solvent	EtOH	1 ml, 0.79g		
Product	3,3-dibromo-1-phenylprop-2-en-1-one	1.02g	3.52 mmol	FW 289.95

Product yield = 71%

$$\text{E-factor} = \frac{0.51 + 1.69 + 4.0 + 2.7 + 0.79 - 1.02}{1.02} = 8.5 \text{ Kg waste/ 1 Kg product}$$

$$\text{Atom economy} = \frac{289.95}{465.79} \times 100 = 64.2\%$$

$$\text{Atom efficiency} = \frac{71\% \times 64.2\%}{100} = 45.6\%$$

$$\text{Carbon efficiency} = \frac{9}{8 + 1} \times 100 = 100\%$$

$$\text{Reaction mass efficiency} = \frac{1.02\text{g}}{0.51\text{g} + 1.69\text{g}} \times 100 = 46.4\%$$

Figure S10. Green chemistry metrics for the synthesis of **2a**

11. The NMR spectra data for *gem*-dihaloenones

3,3-dibromo-1-phenylprop-2-en-1-one (**2a**)[3]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), yellow oil (**1**: 84%, 96.7 mg; **2**: 86%, 99.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 7.2 Hz, 2H), 7.85 (s, 1H), 7.63–7.60 (m, 1H), 7.52–7.48 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.7, 135.4, 132.8, 131.6, 127.9, 127.7, 102.3.

3,3-dibromo-1-(o-tolyl)prop-2-en-1-one (**2b**)[3]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), yellow oil (**1**: 81%, 97.8 mg; **2**: 64%, 77.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.61 (d, J = 7.2 Hz, 1H), 7.42 (t, J = 7.2 Hz, 1H), 7.31–7.27 (m, 2H), 2.53 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 139.2, 136.6, 135.3, 132.2, 132.1, 129.5, 125.9, 102.9, 21.0.

3,3-dibromo-1-(m-tolyl)prop-2-en-1-one (**2c**)[3]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), yellow oil (**1**: 85%, 102.6 mg; B: 88%, 106.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.74–7.12 (m, 2H), 7.43–7.36 (m, 2H), 2.43 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.9, 137.8, 135.4, 133.6, 131.8, 128.1, 127.7, 124.9, 101.9, 20.3.

3,3-dibromo-1-(p-tolyl)prop-2-en-1-one (**2d**)[3]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 30:1), yellow oil (**1**: 90%, 108.6 mg; **2**: 81%, 97.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 8.4 Hz, 2H), 7.81 (s, 1H), 7.29 (d, J = 7.6 Hz, 2H), 2.43 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.4, 144.0, 132.8, 131.9, 128.6, 127.8, 101.5, 20.8.

3,3-dibromo-1-(4-ethylphenyl)prop-2-en-1-one (**2e**)[3]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), yellow oil (**1**: 88%, 111.2 mg; **2**: 84%, 106.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.0 Hz, 2H), 7.81 (s, 1H), 7.32 (d, J = 8.0 Hz, 2H), 2.72 (q, J = 7.6 Hz, 2H), 1.27 (t, J=7.6 Hz, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.5, 150.1, 133.1, 131.9, 128.0, 127.4, 101.5, 28.0, 14.1.

3,3-dibromo-1-(4-(tert-butyl)phenyl)prop-2-en-1-one (**2f**)[4]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 30:1), yellow oil (**1**: 87%, 119.6 mg; **2**: 75%, 103.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.4 Hz, 2H), 7.83 (s, 1H), 7.51 (d, J = 8.4 Hz, 2H), 1.35 (s, 9H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 157.9, 133.8, 132.9, 128.7, 125.9, 102.6, 35.3, 31.1; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{14}Br_2O$ $[M + H]^+$ 344.9484, found 344.9492.

3,3-dibromo-1-(4-pentylphenyl)prop-2-en-1-one (**2g**): Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 30:1), yellow oil (**1**: 81%, 115.9 mg; **2**: 77%, 110.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J=8.4 Hz, 2H), 7.82 (s, 1H), 7.29 (d, J = 8.0 Hz, 2H), 2.69–2.65 (m, 2H), 1.67–1.59 (m, 2H), 1.37–1.29 (m, 4H), 0.89 (t, J = 6.4 Hz, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.5, 149.9, 134.1, 132.9, 129.0, 128.9, 102.5, 36.1, 31.4, 30.7, 22.5, 14.0; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{16}Br_2O$ $[M + H]^+$ 358.9641, found 358.9647.

3,3-dibromo-1-(4-ethoxyphenyl)prop-2-en-1-one (**2h**)[3]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), yellow oil (**1**: 59%, 78.3 mg; **2**: 0%, 0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.8 Hz, 2H), 7.76 (s, 1H), 6.94 (d, J = 8.4 Hz, 2H), 4.11 (q, J = 6.8 Hz, 2H), 1.44 (t, J = 6.8 Hz, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.6, 163.7, 133.2, 131.2, 129.0, 114.6, 101.5, 63.9, 14.7.

3,3-dibromo-1-(4-methoxyphenyl)prop-2-en-1-one (**2i**)[3]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), yellow oil (**1**: 69%, 87.7 mg; **2**: trace, 0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 9.2 Hz, 2H), 7.76 (s, 1H), 6.96 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.6, 164.2, 133.14, 131.2, 129.2, 114.2, 101.6, 55.6.

2-(4-(3,3-dibromoacryloyl)phenyl)acetonitrile (**2j**): Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 30:1), white solid (**1**: 51%, 66.6 mg; **2**: 45%, 58.8 mg); M.P. = 108.2−108.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.4 Hz, 2H), 7.83 (s, 1H), 7.48 (d, J = 8.0 Hz, 2H), 3.84 (s, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.9, 136.3, 135.8, 132.1, 129.5, 128.5, 116.9, 104.3, 23.8; HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_7Br_2NO$ $[M + H]^+$ 327.8967, found 327.8972.

3,3-dibromo-1-(4-fluorophenyl)prop-2-en-1-one (**2k**)[3]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), colorless oil (**1**: 81%, 99.1 mg; **2**: 86%, 105.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, J = 8.0, 5.2 Hz, 2H), 7.79 (s, 1H), 7.17 (t, J = 8.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.3, 165.2 (d, J = 255 Hz, C-F), 131.7 (d, J = 3.0 Hz, C-F), 131.3, 130.4 (d, J = 9.0 Hz, C-F), 115.1 (d, J =22 Hz, C-F), 102.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -103.3.

3,3-dibromo-1-(4-chlorophenyl)prop-2-en-1-one (**2l**)[3]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), white solid (**1**: 64%, 82.3 mg; **2**: 71%, 91.4 mg); M.P. = 67.2−68.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.4 Hz, 2H), 7.80 (s, 1H), 7.47 (d, J = 8.4 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.6, 140.5, 134.7, 132.1, 130.1, 129.3, 104.1.

3,3-dibromo-1-(4-bromophenyl)prop-2-en-1-one (**2m**)[3]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 30:1), yellow solid (**1**: 35%, 51.2 mg; **2**: 55%, 80.4 mg); M.P. = 89.2−90.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.79 (m, 3H), 7.64 (d, J = 8.4 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.7, 134.1, 131.2, 131.0, 129.1, 128.2, 103.2.

3,3-dibromo-1-(3-fluorophenyl)prop-2-en-1-one (**2n**): Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), colorless oil (**1**: 82%, 100.3 mg; **2**: 84%, 102.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 9.2 Hz, 1H), 7.48 (dd, J = 13.6, 8.0 Hz, 1H), 7.33–7.28 (m, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.5, 163.1 (d, J = 147 Hz, C-F), 138.7 (d, J = 6.0 Hz, C-F), 132.1, 130.7 (d, J=8.0 Hz, C-F), 124.5 (d, J = 3.0 Hz, C-F), 121.3 (d, J = 22 Hz, C-F), 115.5 (d, J = 23 Hz, C-F), 104.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -111.0; HRMS (ESI-TOF) *m/z* calcd for $C_9H_5Br_2FO$ $[M + H]^+$ 306.8764, found 306.8769.

3,3-dibromo-1-(3-chlorophenyl)prop-2-en-1-one (**2o**)[4]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), yellow oil (**1**: 55%, 70.8 mg; **2**: 69%, 88.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 1.2 Hz, 1H), 7.81–7.80 (m, 2H), 7.58 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 6.4 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.4, 138.0, 135.3, 133.7, 131.9, 130.2, 128.6, 126.7, 104.9; HRMS (ESI-TOF) *m/z* calcd for $C_9H_5Br_2ClO$ $[M + H]^+$ 322.8468, found 322.8470.

3,3-dibromo-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (**2p**)[3]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 30:1), yellow white (**1**: 52%, 74.0 mg; **2**: 61%, 86.8 mg); M.P. = 59.2−59.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.0 Hz, 2H), 7.86 (s, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 6.4 Hz, 1H), ppm; ^{13}C NMR (100

MHz, $CDCl_3$): δ 186.6, 139.2, 134.9 (d, J = 33 Hz, C-F), 131.7, 128.9, 131.9, 125.9 (q, J = 3.7 Hz, C-F), 105.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.2.

4-(3,3-dibromoacryloyl)benzaldehyde (**2q**): Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 20:1), yellow solid (**1**: 22%, 27.7 mg; **2**: 14%, 17.6 mg); M.P. = 93.6−94.1 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 10.1 (s, 1H), 8.04 (dd, J = 28.4, 8.0 Hz, 4H), 7.88 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 186.9, 140.8, 139.4, 131.8, 130.0, 129.1, 15.7; HRMS (ESI-TOF) *m/z* calcd for $C_{10}H_6Br_2O_2$ $[M + H]^+$ 316.8807, found 316.8811.

1-(4-acetylphenyl)-3,3-dibromoprop-2-en-1-one (**2r**): Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 15:1), yellow solid (**1**: 47%, 62.0 mg; **2**: 38%, 50.1 mg); M.P. = 60.8−61.5 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (dd, J = 20, 8.4 Hz, 4H), 7.87 (s, 1H), 2.65 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 187.0, 140.6, 139.7, 131.9, 128.8, 128.7, 105.2, 26.9; HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_8Br_2O_2$ $[M + H]^+$ 330.8964, found 330.8969.

1-([1,1'-biphenyl]-4-yl)-3,3-dibromoprop-2-en-1-one (**2s**)[3]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 20:1), white solid (**1**: 52%, 75.6 mg; **2**: 47%, 68.4 mg); M.P. = 107.0−107.8 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.4 Hz, 2H), 7.88 (s, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.67–7.63 (m, 2H), 7.50–7.40 (m, 3H) , ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.3, 146.6, 139.6, 135.1, 132.7, 129.3, 129.1, 128.5, 127.5, 127.3, 103.2.

methyl 4-(3,3-dibromoacryloyl)benzoate (**2t**)[3]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 20:1), light yellow solid (**1**: 33%, 45.6 mg; **2**: 25%, 34.5 mg); M.P. = 92.6−92.8 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.4 Hz, 2H), 7.87 (s, 1H), 3.96 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.1, 166.0, 139.8, 134.5, 132.0, 130.1, 128.5, 105.1, 52.6.

3,3-dibromo-1-(naphthalen-1-yl)prop-2-en-1-one (**2v**): Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), colorless oil (**1**: 79%, 106.7 mg; **2**: 70%, 94.6 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 7.6 Hz, 2H), 7.79 (s, 1H), 7.64 (t, J = 7.2 Hz, 1H), 7.58–7.52 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 135.6, 134.3, 134.0, 133.9, 130.4, 129.6, 128.6, 128.5, 126.8, 125.5, 124.5, 103.2; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_8Br_2O$ $[M + H]^+$ 338.9015, found 338.9016.

3,3-dibromo-1-(thiophen-2-yl)prop-2-en-1-one (**2w**)[3]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 20:1), white solid (**1**: 41%, 48.1 mg; **2**: 35%, 41.1 mg); M.P. = 85.2−85.8 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.74–7.71 (m, 2H), 7.18–7.15 (m, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.3, 143.2, 134.2, 131.5, 130.2, 127.4, 103.8.

3,3-dibromo-1-(thiophen-3-yl)prop-2-en-1-one (**2x**)[3]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 20:1), white solid (**1**: 55%, 64.6 mg; **2**: 38%, 44.6 mg); M.P. = 92.6−92.9 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.09–8.08 (m, 1H), 7.80 (s, 1H), 7.57 (d, J=5.2 Hz, 1H), 7.36 (dd, J = 5.2, 2.8 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.9, 141.9, 133.2, 132.4, 127.1, 127.0, 104.1.

1,1-dibromohept-1-en-3-one (**2aa**)[4]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 20:1), colorless oil (**1**: 17%, 18.2 mg; **2**: 32%, 34.2 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.29 (s, 1H), 2.50 (t, J = 7.6 Hz, 2H), 1.61 (dd, J = 14.8, 7.2 Hz, 2H), 1.38–1.29 (m, 2H), 0.92 (t, J = 7.6 Hz, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 134.1, 103.3, 43.9, 25.7, 22.2, 13.8; HRMS (ESI-TOF) *m/z* calcd for $C_7H_{10}Br_2O$ $[M + Na]^+$ 290.8991, found

290.9001.

3,3-dibromo-2-methyl-1-phenylprop-2-en-1-one (**2ab**): Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), colorless oil (**1**: 68%, 82.1 mg; **2**: 57%, 68.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 7.2 Hz, 2H), 7.64 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 2.09 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.0, 142.4, 134.3, 133.6, 129.6, 129.1, 88.7, 22.3; HRMS (ESI-TOF) *m/z* calcd for $C_{10}H_8Br_2O$ $[M + H]^+$ 302.9015, found 302.9020.

2-(dibromomethylene)-1-phenylbutan-1-one (**2ac**): Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), colorless oil (**1**: 56%, 70.7 mg; **2**: 44%, 55.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 2.46 (q, J = 7.6 Hz, 2H), 1.01 (t, J = 7.6 Hz, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.8, 147.6, 134.3, 134.2, 129.6, 129.0, 88.2, 30.1, 11.4; HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{10}Br_2O$ $[M + H]^+$ 316.9171, found 316.9167.

3,3-dibromo-1,2-diphenylprop-2-en-1-one (**2ad**): Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), colorless oil (**1**: 15%, 21.8 mg; **2**: 8%, 11.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 7.6 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.52–7.48 (m, 4H), 7.39–7.33 (m, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.8, 146.7, 135.6, 134.9, 134.3, 134.0, 130.0, 129.1, 128.8, 128.2, 90.9; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{10}Br_2O$ $[M + H]^+$ 364.9171, found 364.9176.

3,3-dichloro-1-phenylprop-2-en-1-one (**3a**)[4]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), yellow oil (**1**: 77%, 61.5 mg; **2**: 78%, 62.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.0 Hz, 2H), 7.61 (t, J = 6.8 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.27 (s, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.7, 137.0, 135.6, 133.7, 128.9, 128.5, 124.1; HRMS (ESI-TOF) *m/z* calcd for $C_9H_6Cl_2O$ $[M + H]^+$ 200.9868, found 200.9874.

1-(4-(tert-butyl)phenyl)-3,3-dichloroprop-2-en-1-one (**3b**)[4]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), yellow oil (**1**: 85%, 87.0 mg; **2**: 72%, 73.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.26 (s, 1H), 1.35 (s, 9H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.3, 157.7, 134.9, 134.3, 128.5, 125.8, 124.3, 35.3, 31.1; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{14}Cl_2O$ $[M + H]^+$ 257.0494, found 257.0495.

3,3-dichloro-1-(4-pentylphenyl)prop-2-en-1-one (**3c**): Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), yellow oil (**1**: 80%, 86.4 mg; **2**: 65%, 70.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.25 (s, 1H), 2.67 (t, J = 7.6 Hz, 2H), 1.67–1.59 (m, 2H), 1.36–1.32 (m, 4H), 0.89 (t, J = 6.0 Hz, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.4, 149.7, 134.8, 134.6, 128.9, 128.7, 124.3, 36.0, 31.4, 30.7, 22.5, 13.9; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{16}Cl_2O$ $[M + H]^+$ 271.0651, found 271.0655.

3,3-dichloro-1-(4-ethylphenyl)prop-2-en-1-one (**3d**)[4]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), yellow oil (**1**: 83%, 75.6 mg; **2**: 71%, 64.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.25 (s, 1H), 2.72 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.4, 150.9, 134.9, 134.6, 128.8, 128.4, 124.3, 29.0, 15.1; HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{10}Cl_2O$ $[M + H]^+$ 229.0181, found 229.0188.

3,3-dichloro-1-(4-methoxyphenyl)prop-2-en-1-one (**3e**)[4]: Following the general conditions **1** and

2, purification by flash chromatography (petroleum/EtOAc = 50:1), yellow oil (**1**: 72%, 66.2 mg; **2**: <5%, 0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.8 Hz, 2H), 7.20 (s, 1H), 7.36 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.4, 164.1, 134.1, 131.0, 129.8, 124.4, 114.1, 55.6; HRMS (ESI-TOF) *m/z* calcd for $C_{10}H_8Cl_2O_2$ $[M + H]^+$ 230.9974, found 230.9979.

3,3-dichloro-1-(m-tolyl)prop-2-en-1-one (**3f**): Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), yellow oil (**1**: 65%, 55.6 mg; **2**: 58%, 49.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–7.73 (m, 2H), 7.43–7.36 (m, 2H), 7.25 (s, 1H), 2.43 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.9, 138.8, 136.9, 135.2, 134.5, 129.0, 128.7, 125.8, 124.3, 21.4; HRMS (ESI-TOF) *m/z* calcd for $C_{10}H_8Cl_2O$ $[M + H]^+$ 215.0025, found 215.0027.

3,3-dichloro-1-(4-fluorophenyl)prop-2-en-1-one (**3g**)[4]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), yellow oil (**1**: 76%, 66.2 mg; **2**: 69%, 60.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96–7.94 (m, 2H), 7.22 (s, 1H), 7.17 (t, J = 8.4 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.2, 166.1 (d, J = 255 Hz, C-F), 135.7, 133.3 (d, J = 3.0 Hz, C-F), 131.2 (d, J =9.0 Hz, C-F), 123.8, 116.1 (d, J = 22 Hz, C-F); ^{19}F NMR (376 MHz, $CDCl_3$): δ -103.6; HRMS (ESI-TOF) *m/z* calcd for $C_9H_5Cl_2FO$ $[M + H]^+$ 218.9774, found 218.9770.

3,3-dichloro-1-(4-chlorophenyl)prop-2-en-1-one (**3h**)[4]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 30:1), white solid (**1**: 71%, 66.4 mg; **2**: 76%, 71.1 mg); M.P. = 43.2−43.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 7.22 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.4, 140.3, 136.3, 135.3, 129.9, 129.2, 123.6; HRMS (ESI-TOF) *m/z* calcd for $C_9H_5Cl_3O$ $[M + H]^+$ 234.9479, found 234.9483.

1-(4-bromophenyl)-3,3-dichloroprop-2-en-1-one (**3i**): Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 30:1), white solid (**1**: 75%, 83.3 mg; **2**: 70%, 77.8 mg); M.P. = 67.4−68.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 7.22 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.6, 136.4, 135.7, 132.2, 129.9, 129.1, 123.5; HRMS (ESI-TOF) *m/z* calcd for $C_9H_5BrCl_2O$ $[M + H]^+$ 278.8974, found 278.8965.

3,3-dichloro-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (**3j**): Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 30:1), semi-solid (**1**: 55%, 58.9 mg; **2**: 27%, 28.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.27 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.6, 139.7, 137.4, 134.9 (d, J = 33 Hz, C-F), 128.7, 125.9 (q, J = 4.0 Hz, C-F), 123.3, 122.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.2; HRMS (ESI-TOF) *m/z* calcd for $C_{10}H_5Cl_2F_3O$ $[M + H]^+$ 268.9742, found 268.9750.

1-([1,1'-biphenyl]-4-yl)-3,3-dichloroprop-2-en-1-one (**3k**)[4]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 20:1), white solid (**1**: 54%, 59.6 mg; **2**: 60%, 66.2 mg); M.P. = 91.3−91.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.49 (t, J = 8.0 Hz, 2H), 7.44–7.40 (m, 1H), 7.31 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 146.5, 139.6, 135.6, 135.4, 129.2, 129.0, 128.5, 127.5, 127.3, 124.1; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{10}Cl_2O$ $[M + H]^+$ 277.0181, found 277.0186.

methyl 4-(3,3-dichloroacryloyl)benzoate (**3l**)[4]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 20:1), white solid (**1**: 35%, 36.1 mg; **2**: 26%, 26.8 mg); M.P. = 87.3−88.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.22 (s, 1H), 3.89 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.0, 166.2, 140.3, 137.0, 134.4, 130.1, 128.4, 123.6, 52.6; HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_8Cl_2O_3$ $[M + H]^+$ 258.9923, found 258.9931.

3,3-dichloro-1-(thiophen-3-yl)prop-2-en-1-one (**3m**): Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 20:1), grey solid (**1**: 65%, 53.5 mg; **2**: 23%, 18.9 mg); M.P. = 62.3−62.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 1.6 Hz, 1H), 7.57–7.56 (m, 2H), 7.36 (dd, J = 5.2, 3.2 Hz, 1H), 7.20 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.9, 141.3, 134.9, 131.9, 126.0, 125.9, 123.1; HRMS (ESI-TOF) *m/z* calcd for $C_7H_4Cl_2OS$ $[M + H]^+$ 206.9433, found 206.9432.

3,3-dichloro-1-(naphthalen-1-yl)prop-2-en-1-one (**3n**): Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), colorless oil (**1**: 70%, 69.9 mg; **2**: 59%, 58.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.88 (dd, J = 17.6, 8.0 Hz, 2H), 7.63 (t, J = 8.0 Hz, 1H), 7.57–7.20 (m, 2H), 7.19 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 135.3, 135.1, 133.9, 133.6, 130.3, 129.1, 128.6, 128.3, 127.3, 126.8, 125.4, 124.5; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_8Cl_2O$ $[M + H]^+$ 251.0025, found 251.0029.

1,1-dichlorooct-1-en-3-one (**3o**): Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 100:1), colorless oil (**1**: 28%, 20.1 mg; **2**: 15%, 10.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.65 (d, J = 0.8 Hz, 1H), 2.53 (t, J = 8.0 Hz, 2H), 1.63–1.58 (m, 2H), 1.31–1.29 (m, 4H), 0.89 (t, J = 6.0 Hz, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 133.1, 125.4, 76.3, 75.9, 75.7, 43.2, 30.2, 22.4, 21.4, 12.9. HRMS (ESI-TOF) *m/z* calcd for $C_8H_{12}Cl_2O$ $[M + H]^+$ 195.0338, found 195.0350.

3,3-dichloro-2-methyl-1-phenylprop-2-en-1-one (**3p**)[4]: Following the general conditions **1** and **2**, purification by flash chromatography (petroleum/EtOAc = 50:1), colorless oil (**1**: 53%, 45.3 mg; **2**: 58%, 49.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.89 (m, 2H), 7.65–7.61 (m, 1H), 7.53–7.49 (m, 2H), 2.12 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.4, 135.1, 134.3, 134.2, 129.5, 129.0, 120.0, 19.1; HRMS (ESI-TOF) *m/z* calcd for $C_{10}H_8Cl_2O$ $[M + H]^+$ 215.0025, found 215.0029.

(Z)-(1,3,3,3-tetrabromoprop-1-en-1-yl)benzene (**5**): Purification by flash chromatography (petroleum), colorless oil (42%, 72.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.50 (m, 2H), 7.41–7.35 (m, 3H), 6.80 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 129.4, 129.2, 128.3, 121.4, 103.0; HRMS (ESI-TOF) *m/z* calcd for $C_9H_6Br_4$ $[M + Na]^+$ 452.7095, found 452.7106.

(E)-(1,3,3,3-tetrabromoprop-1-en-1-yl)benzene (**6**): Purification by flash chromatography (petroleum), colorless oil (5%, 8.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.49 (m, 2H), 7.36–7.35 (m, 3H), 7.06 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 131.2, 129.4, 128.6, 127.7, 108.8; HRMS (ESI-TOF) *m/z* calcd for $C_9H_6Br_4$ $[M + H]^+$ 430.7276, found 430.7284.

Reference

1. S. Guha; I. Kazi; D. Sathish; G. Sekar, *J. Org. Chem.* **2022**, *87*, 5424-5429.

2. S. Kumar; M. Patel; A. K. Verma, *Asian J. Org. Chem.* **2021**, *10*, 2365-2369.

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

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

12. The NMR and HRMS spectra for *gem*-dihaloenones

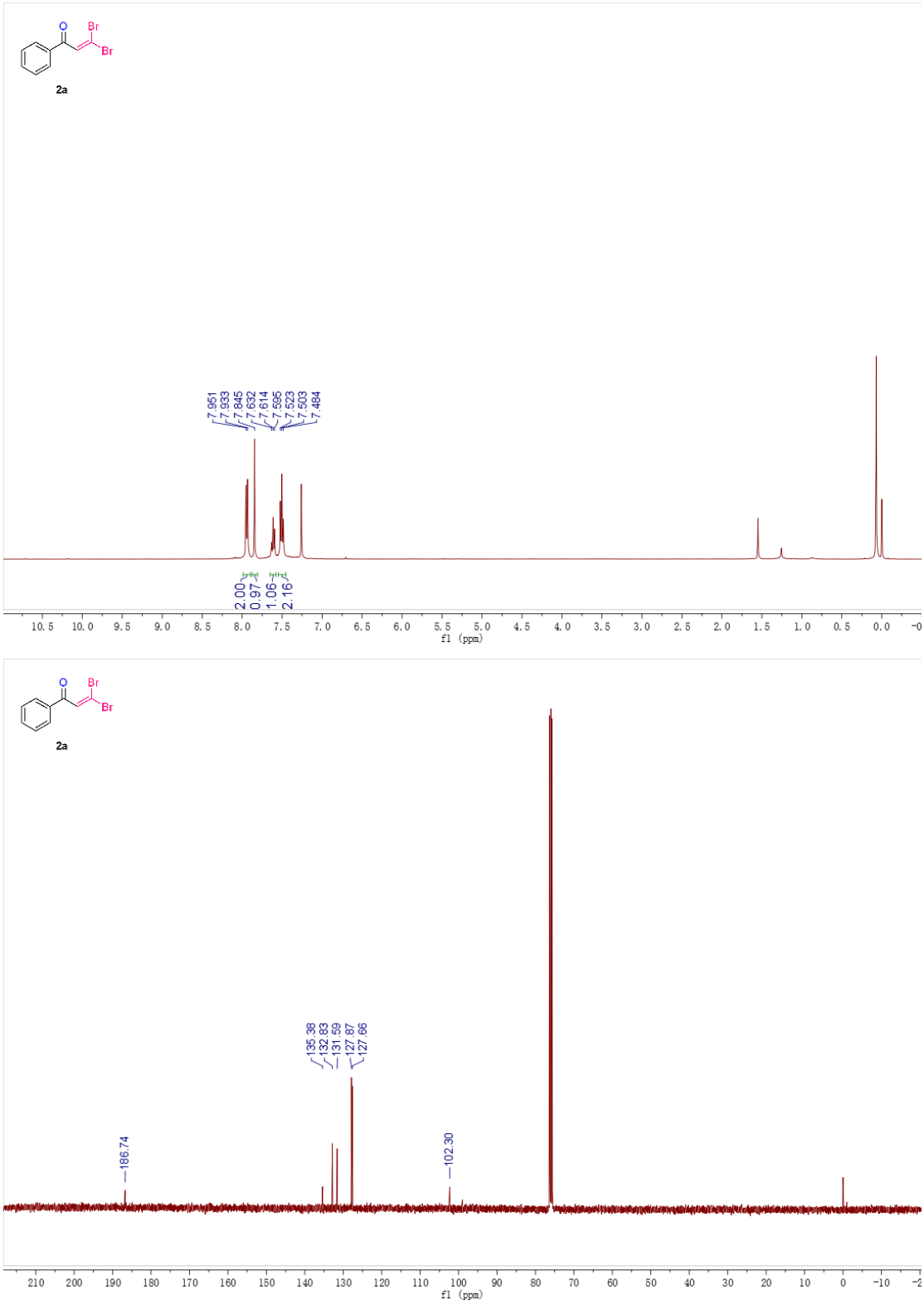


Figure S11. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2a**.

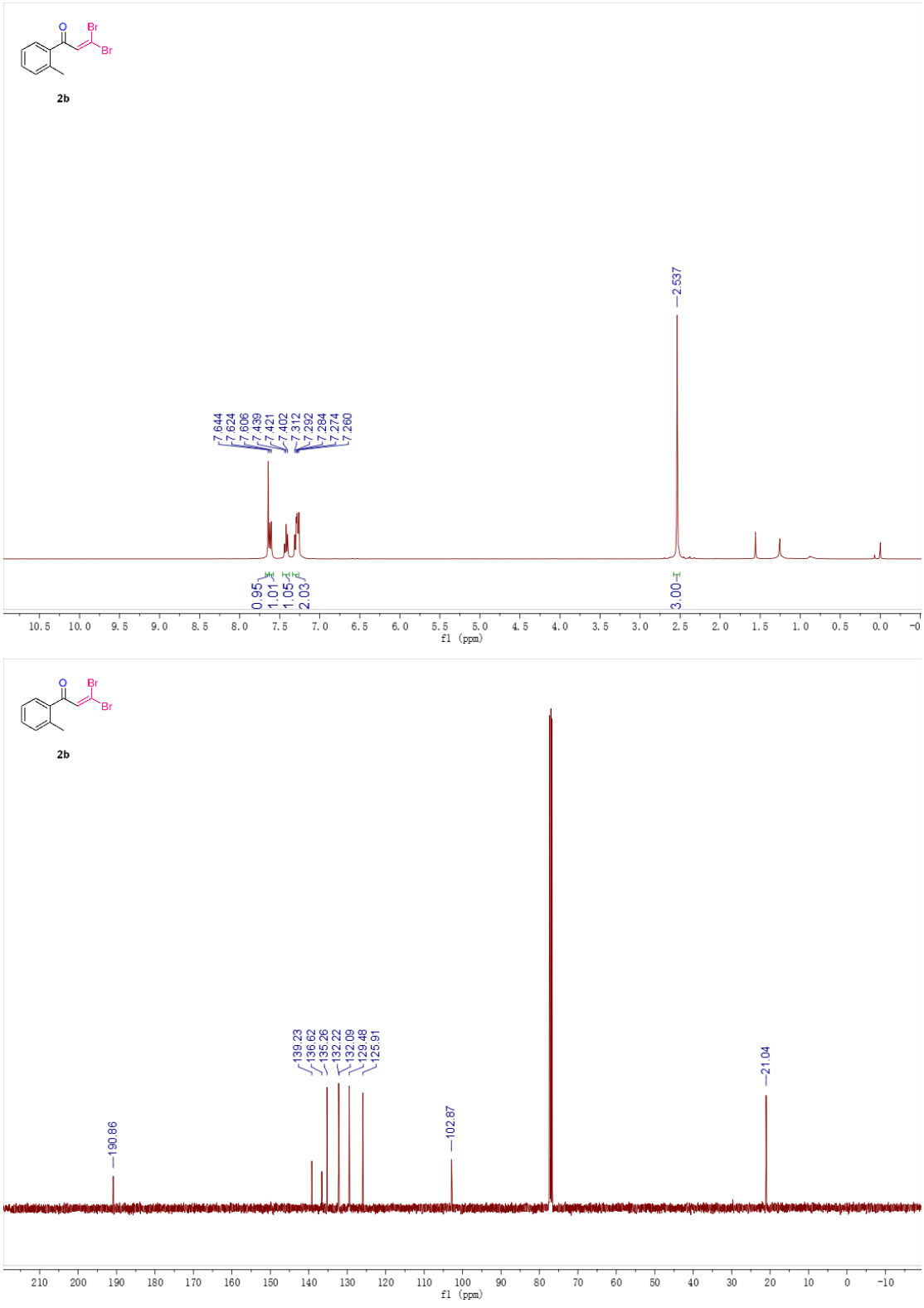


Figure S12. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2b**.

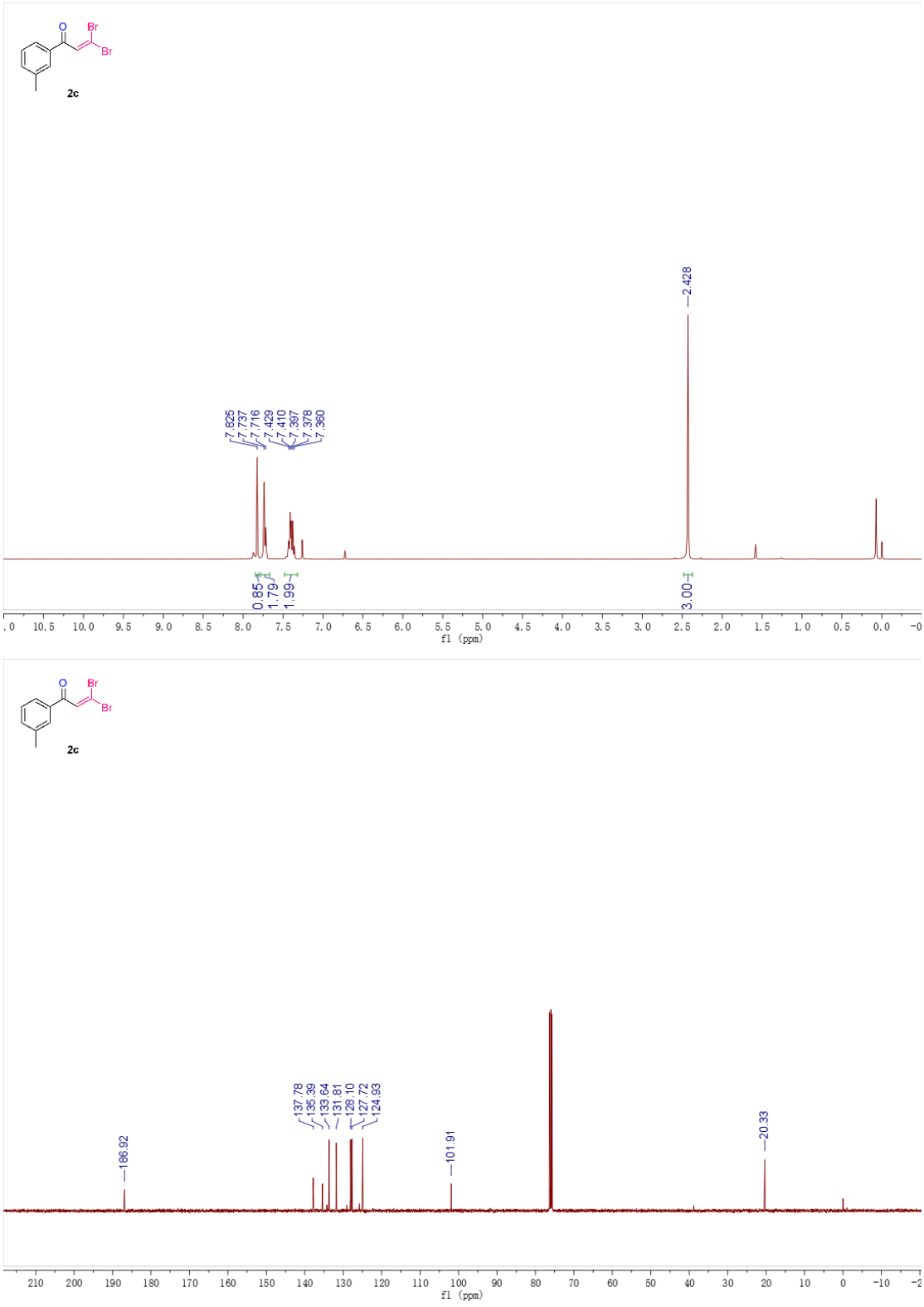


Figure S13. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2c**.

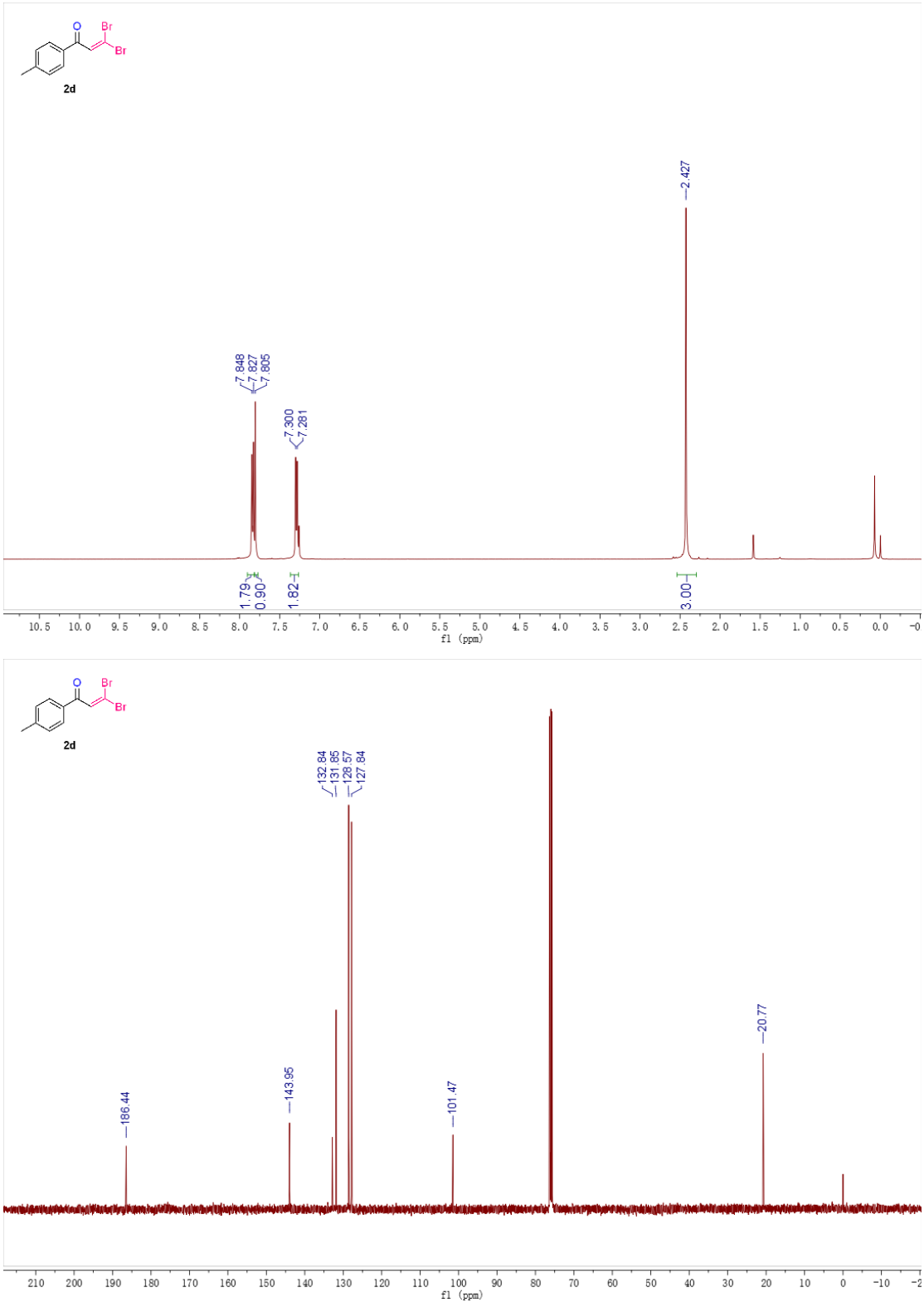


Figure S14. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2d**.

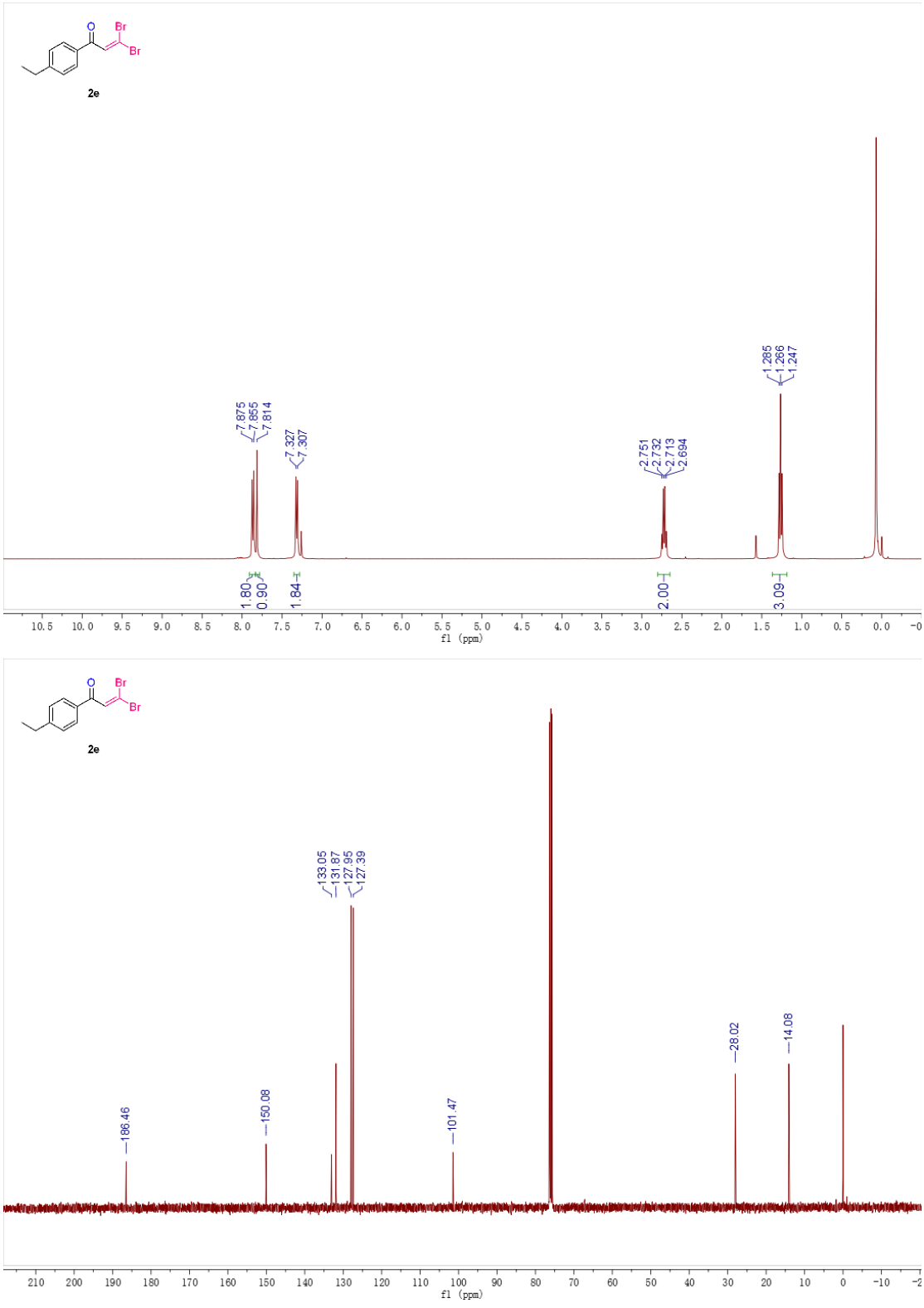


Figure S15. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2e**.

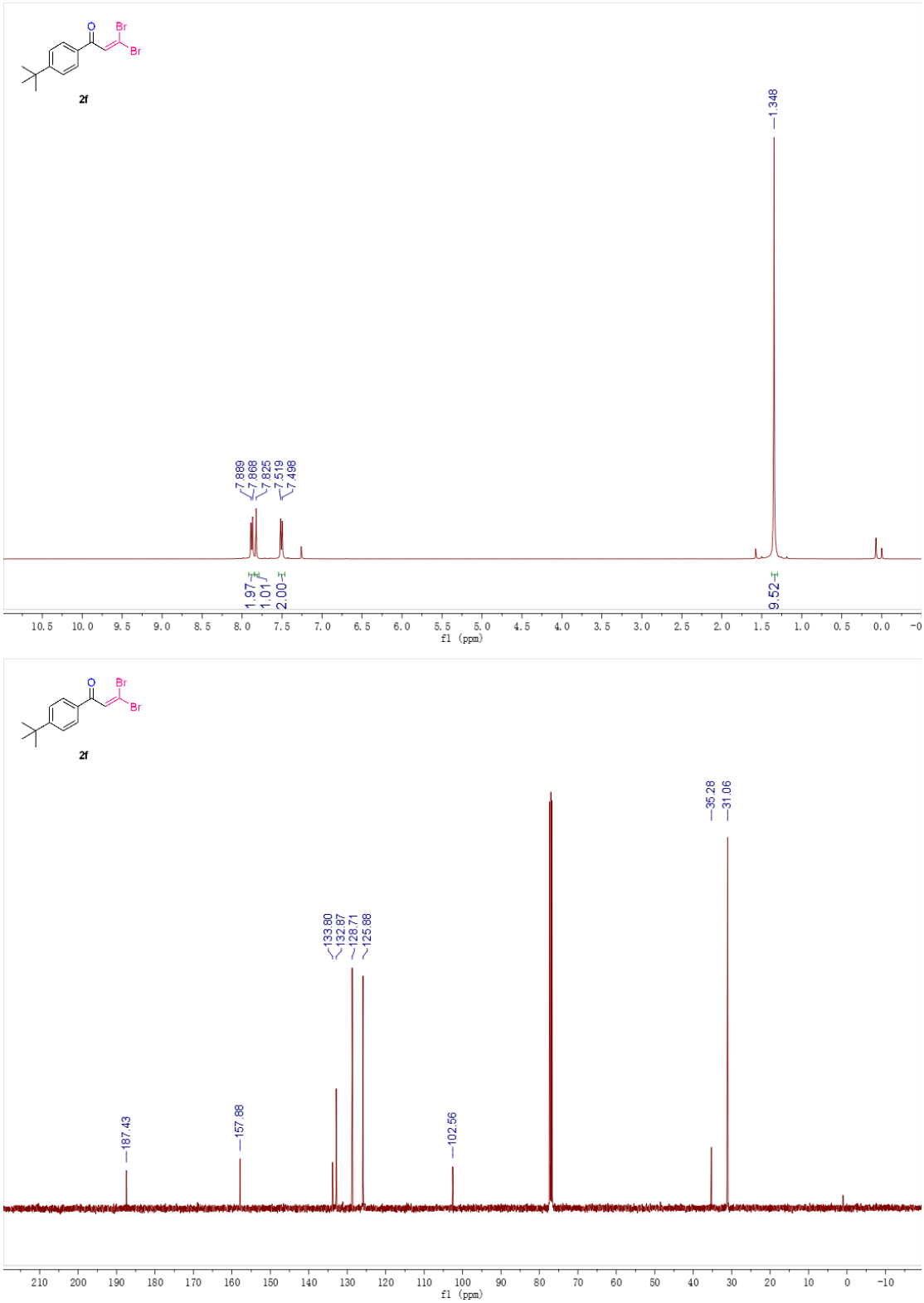


Figure S16. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2f**.

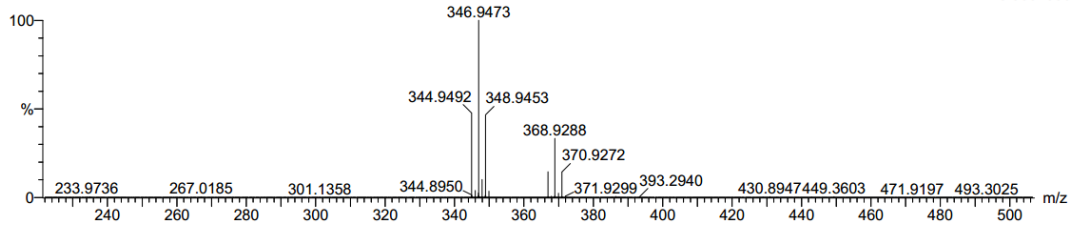
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
261 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 13-13 H: 0-60 N: 0-6 O: 0-20 Si: 0-3 Br: 2-3

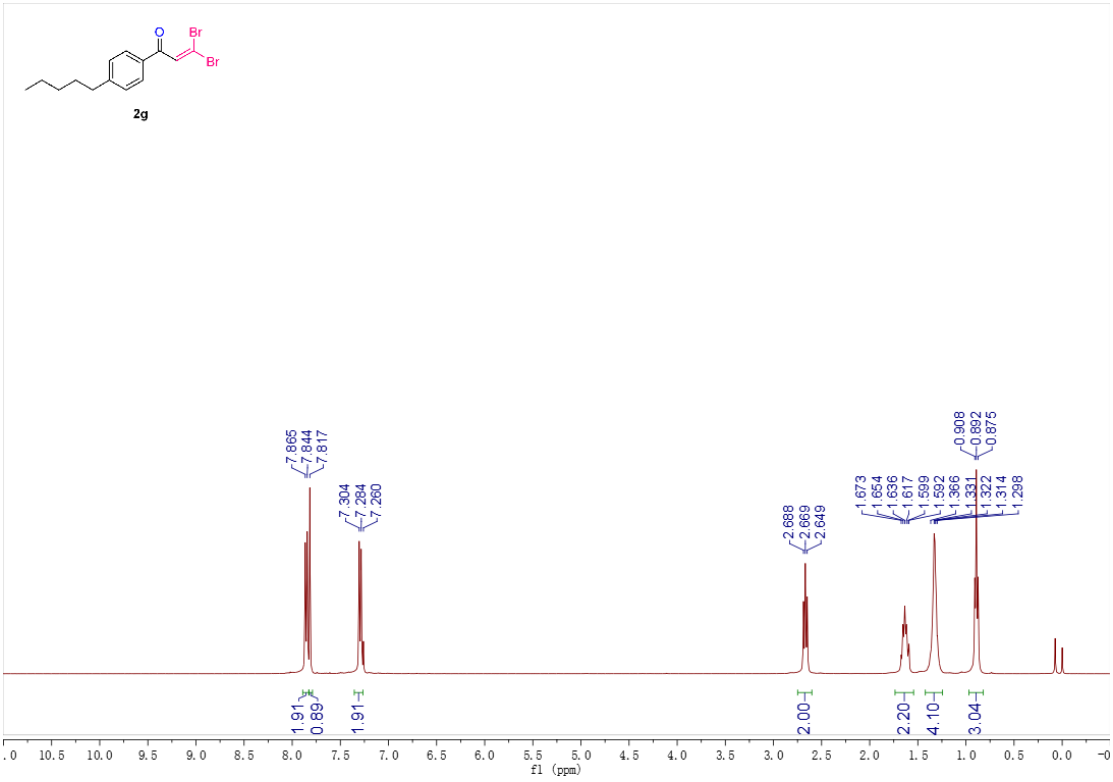
12
0521-1-3 111 (0.663)

1: TOF MS ES+
5.36e+006



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
344.9492	344.9490	0.2	0.6	5.5	1378.5	n/a	n/a	C13 H15 O Br2

Figure S17. HRMS Spectra of **2f**.



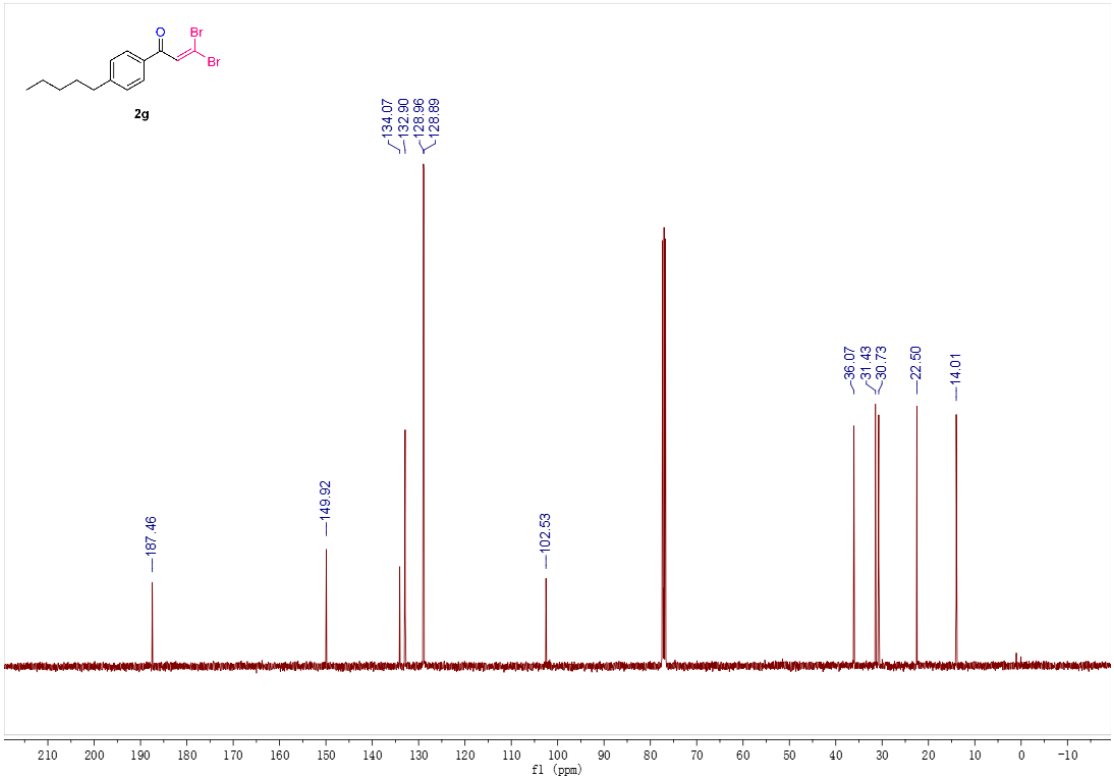


Figure S18. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2g**.

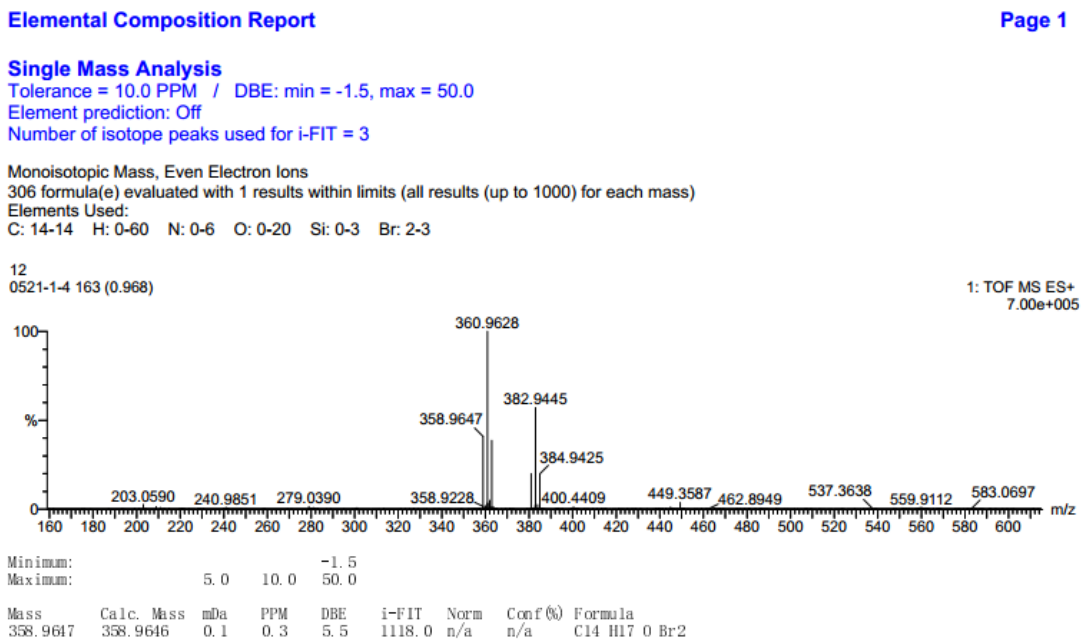


Figure S19. HRMS Spectra of **2g**.

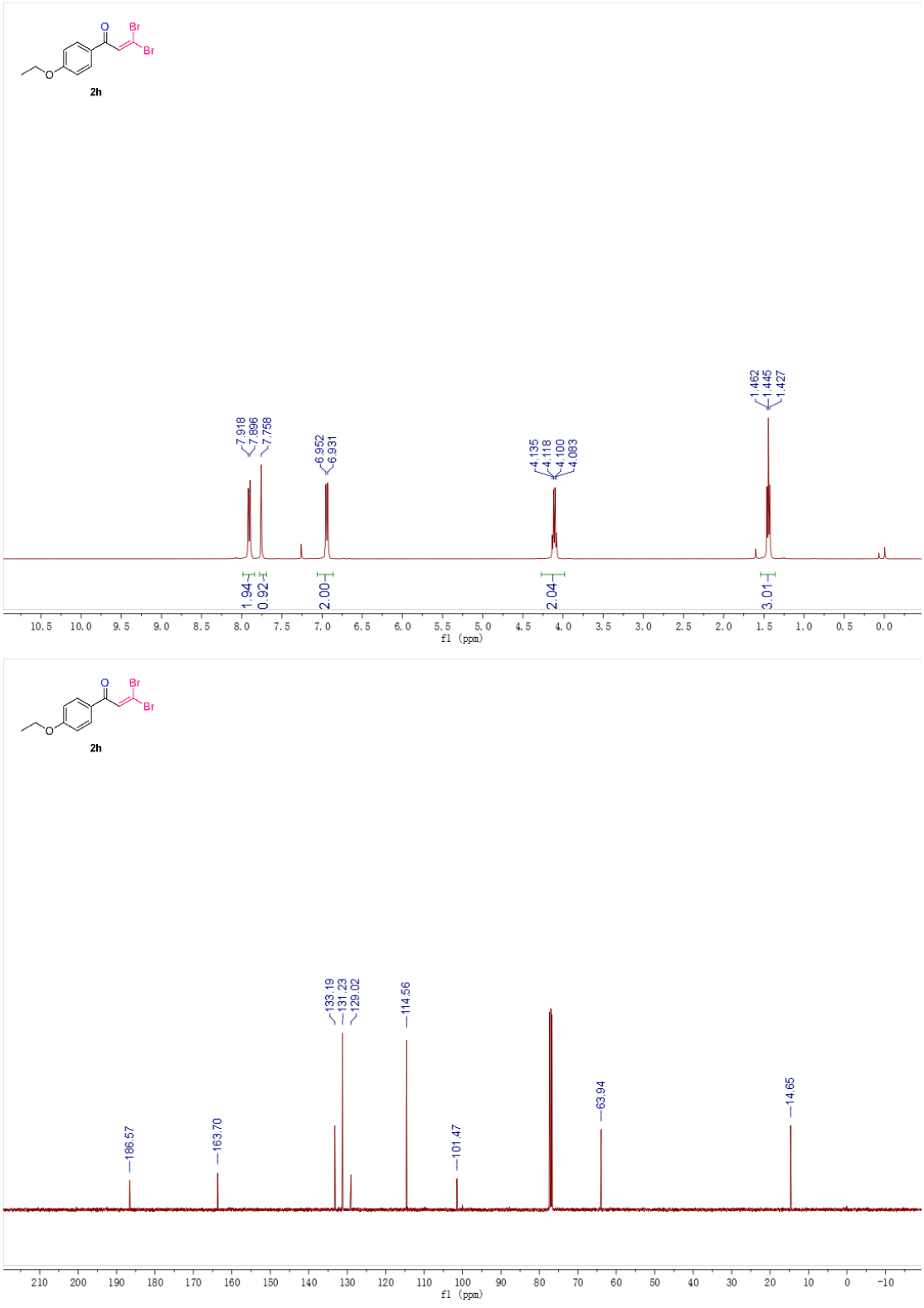


Figure S20. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2h**.

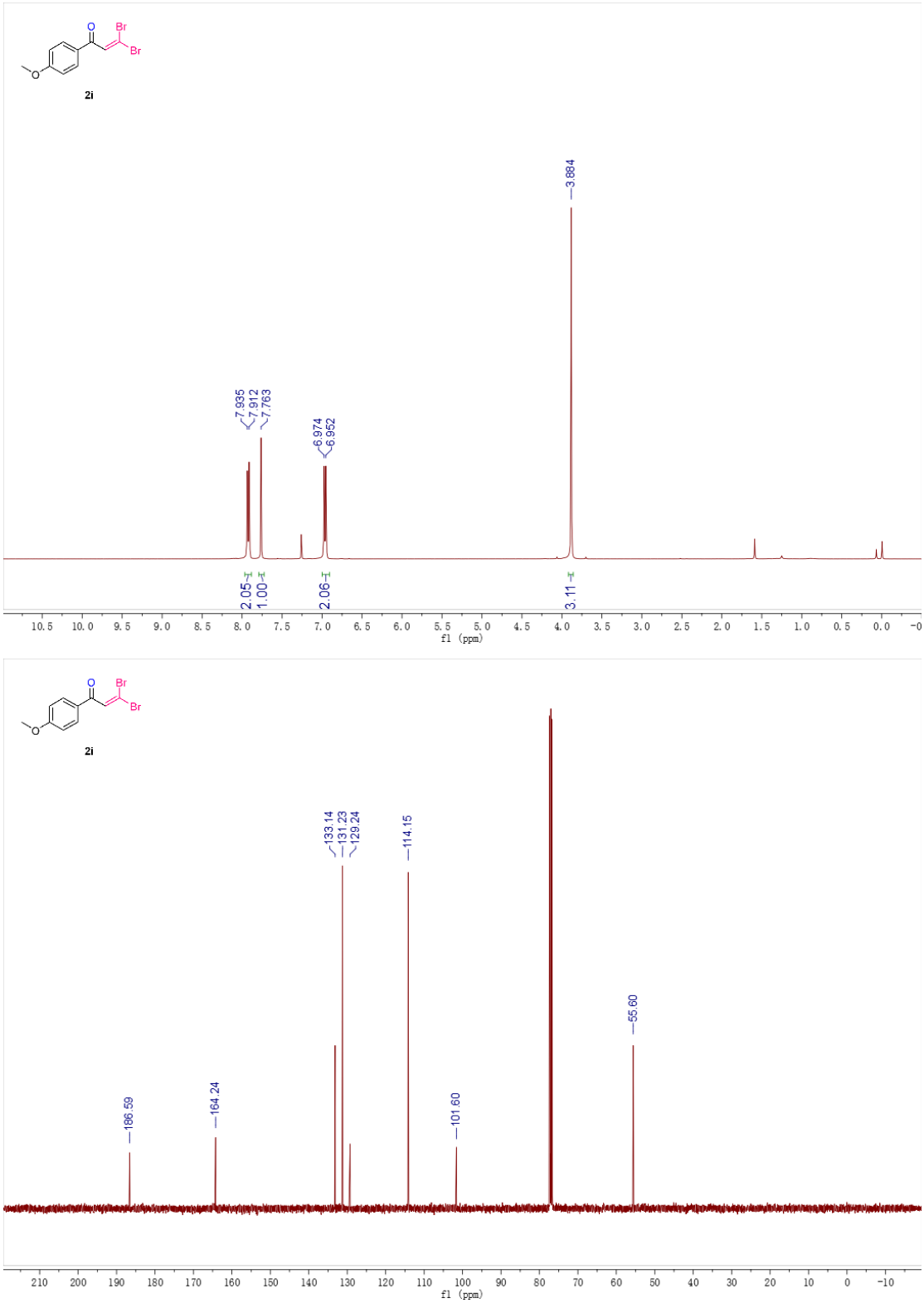


Figure S21. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2i**.

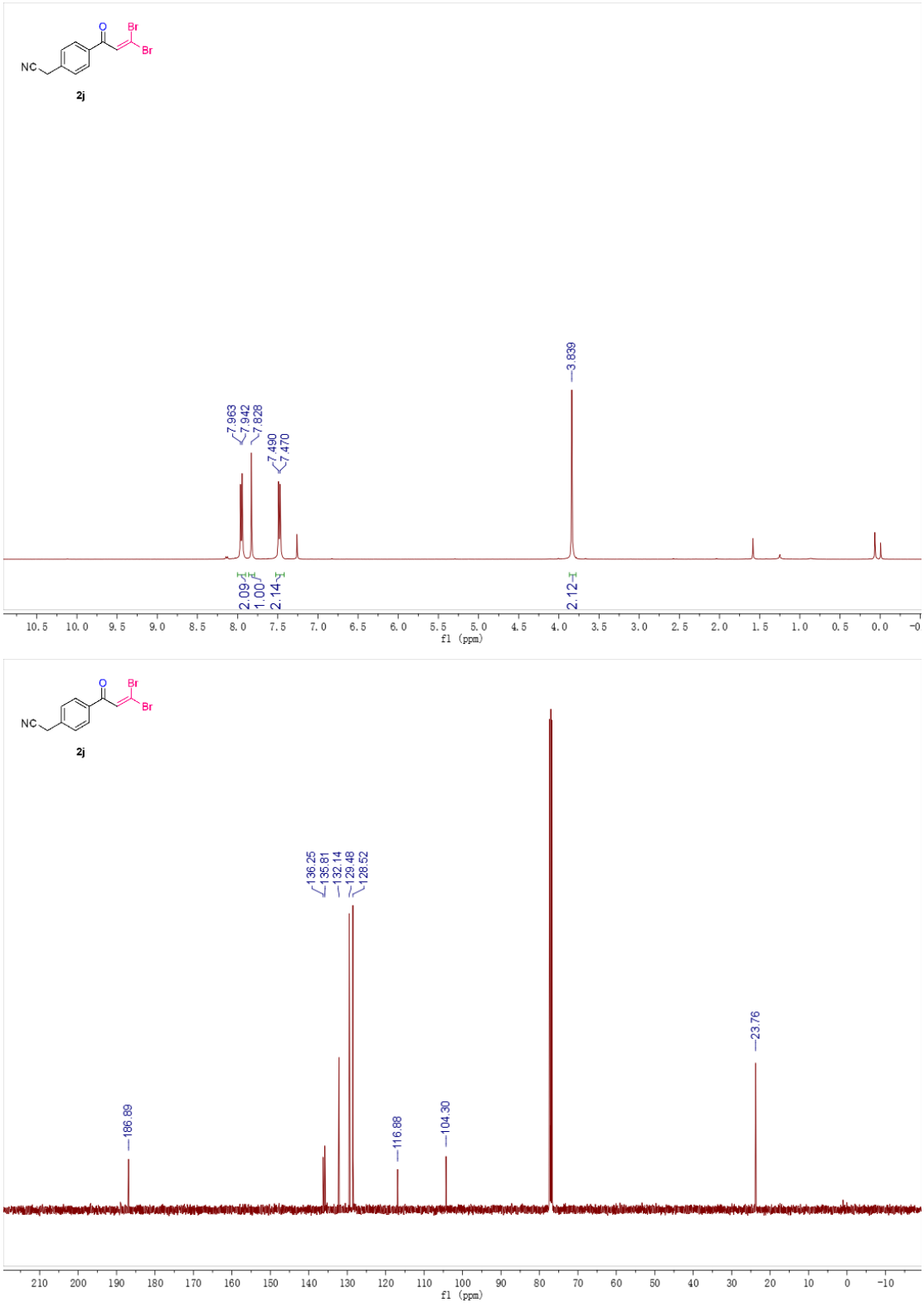


Figure S22. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2j**.

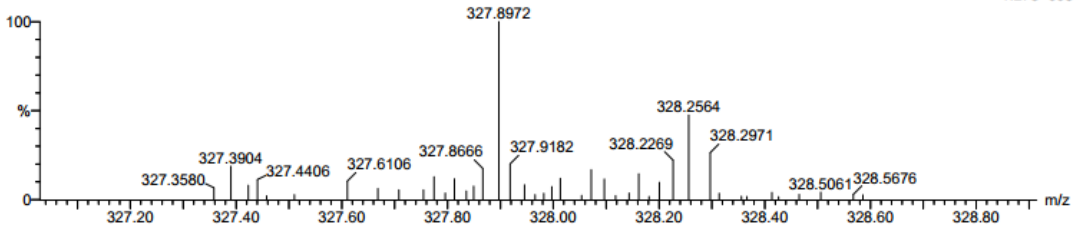
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
83 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 11-11 H: 0-60 N: 0-6 O: 0-20 Br: 2-3

12
0521-1-8 56 (0.343)

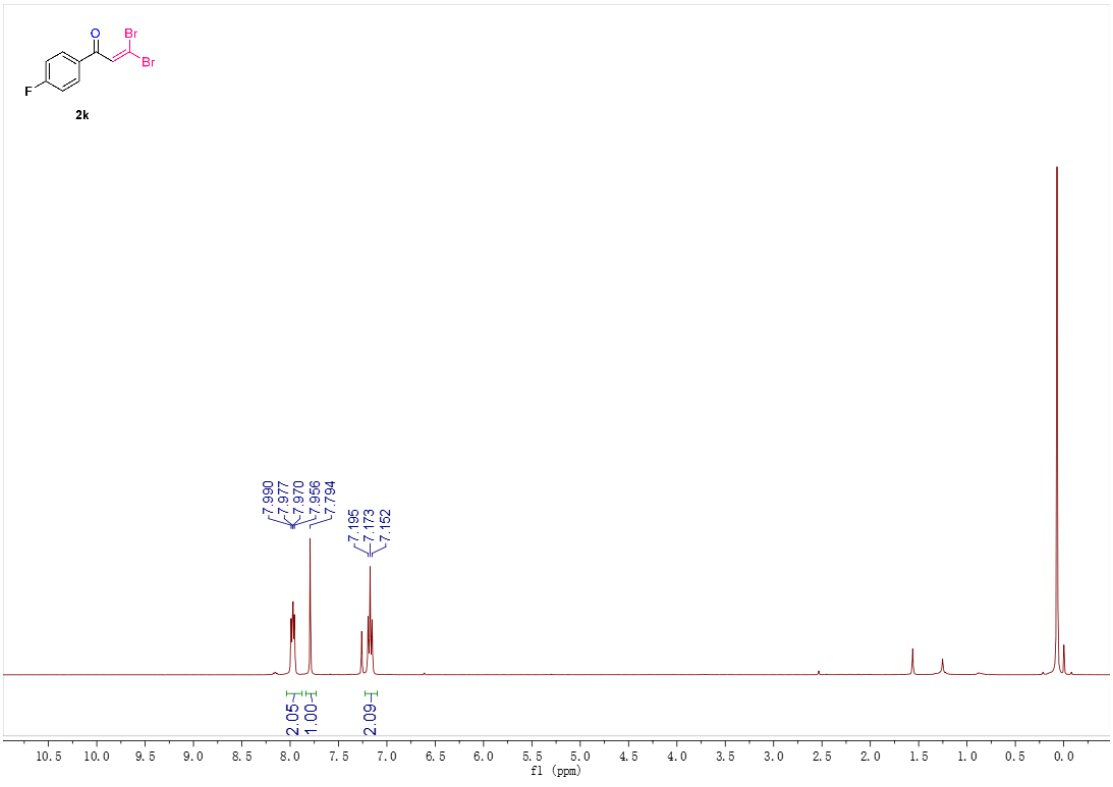
1: TOF MS ES+
1.27e+003

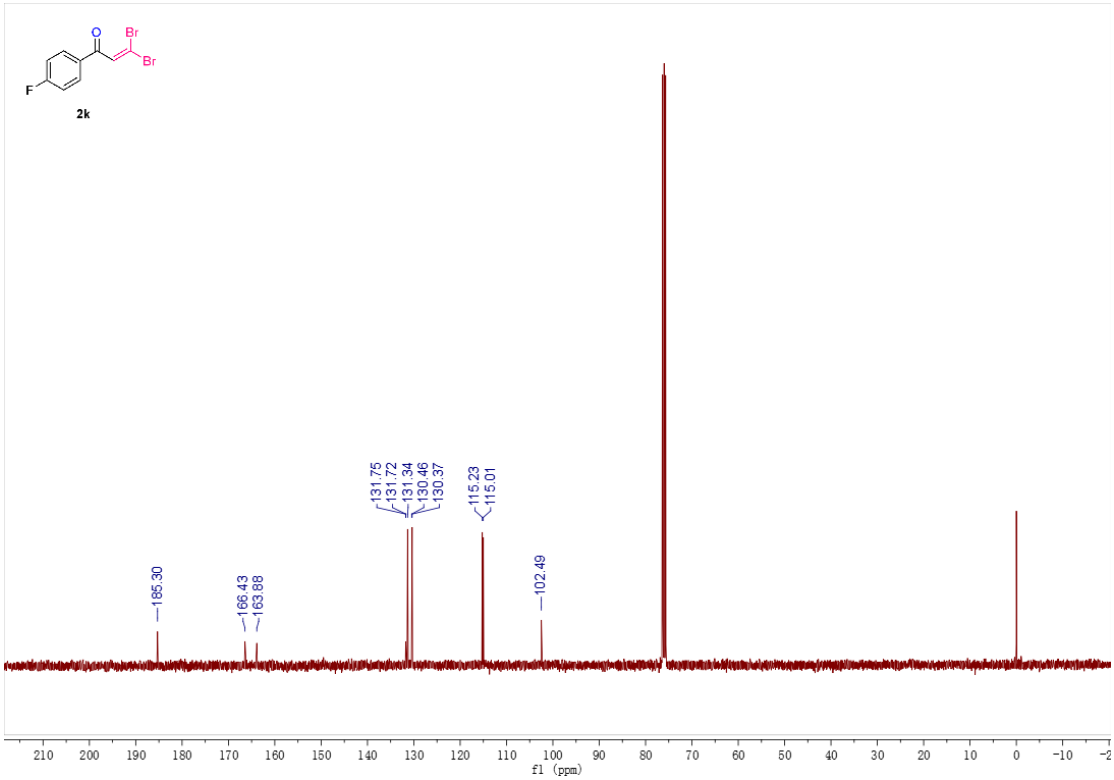


Minimum:			-1.5	
Maximum:		5.0	10.0	50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
327.8972	327.8973	-0.1	-0.3	7.5	247.0	n/a	n/a	C11 H8 N O Br2

Figure S23. HRMS Spectra of **2j**.





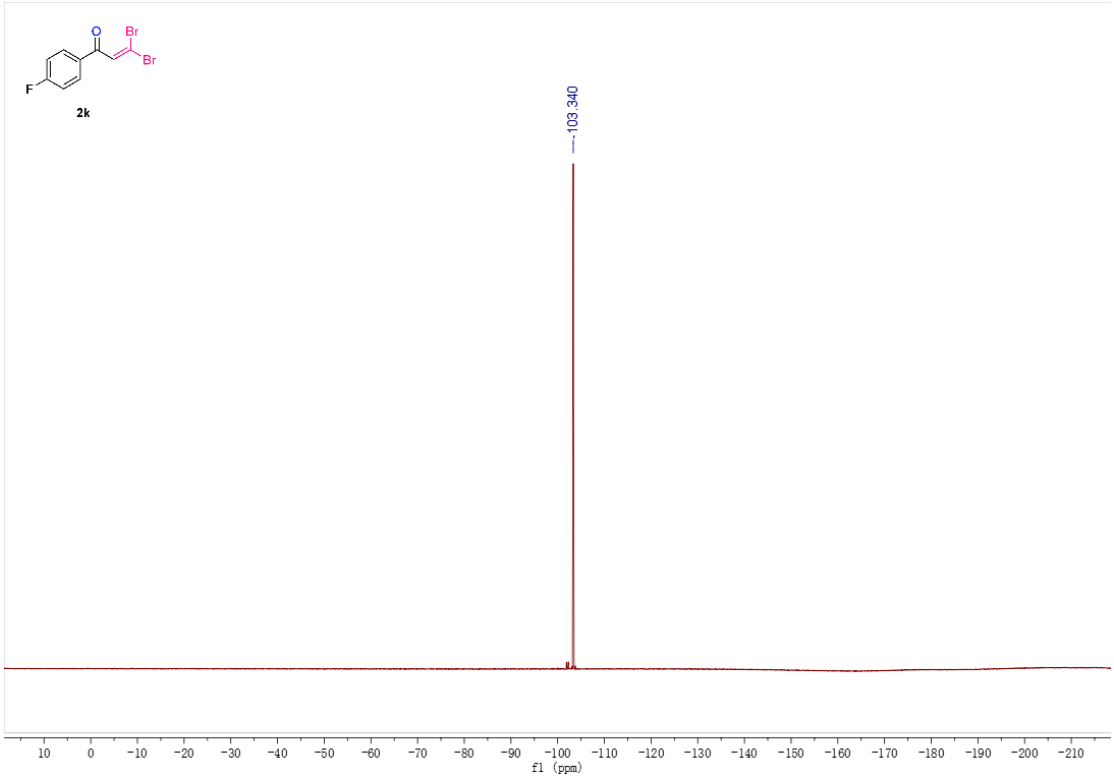
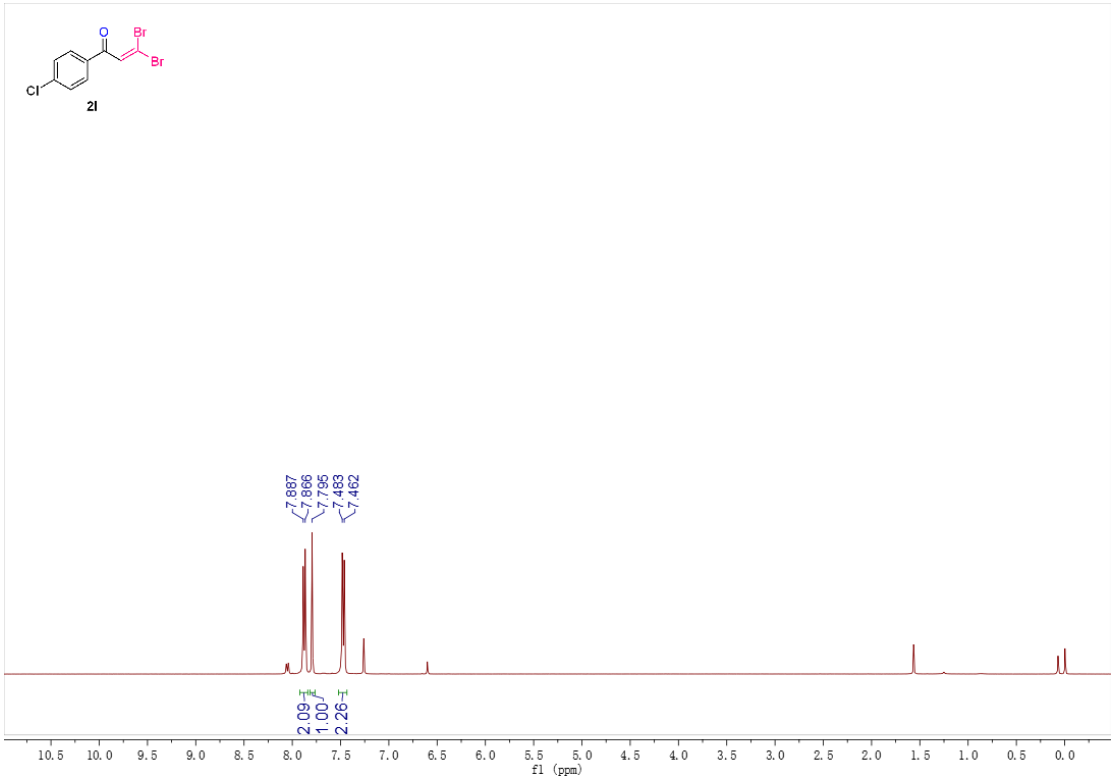


Figure S24. ^{1}H NMR and ^{13}C{^{1}H} NMR and ^{19}F NMR of **2k**.



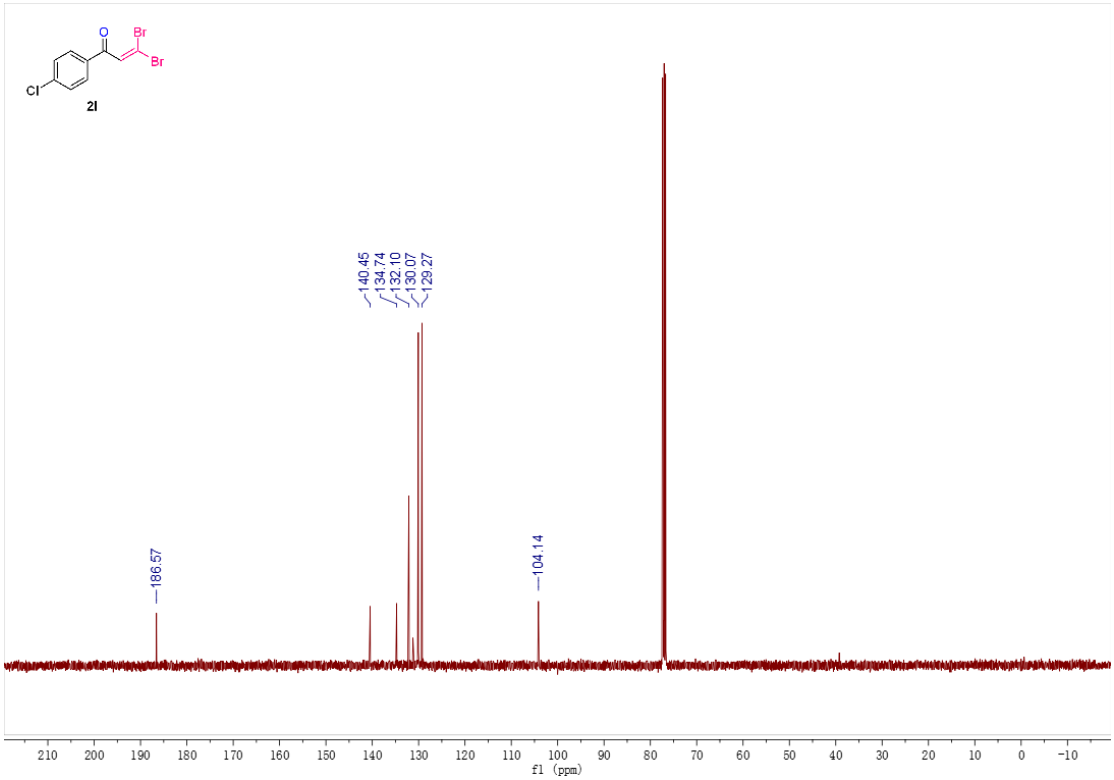
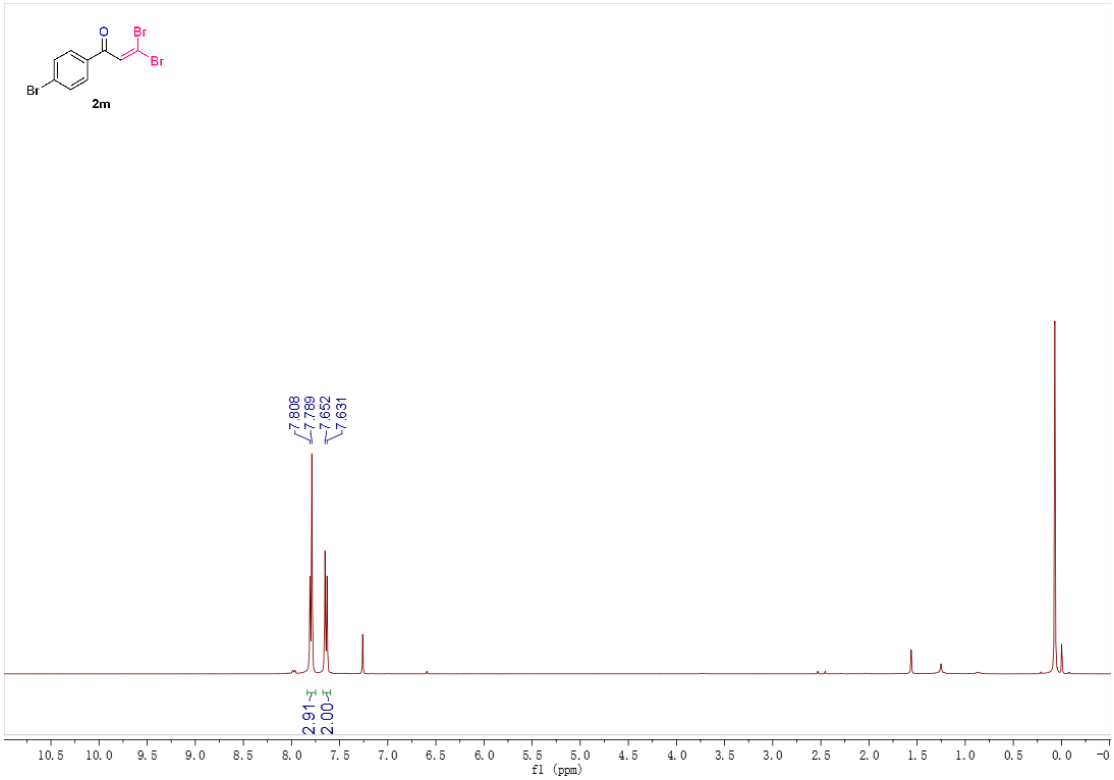


Figure S25. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2l**.



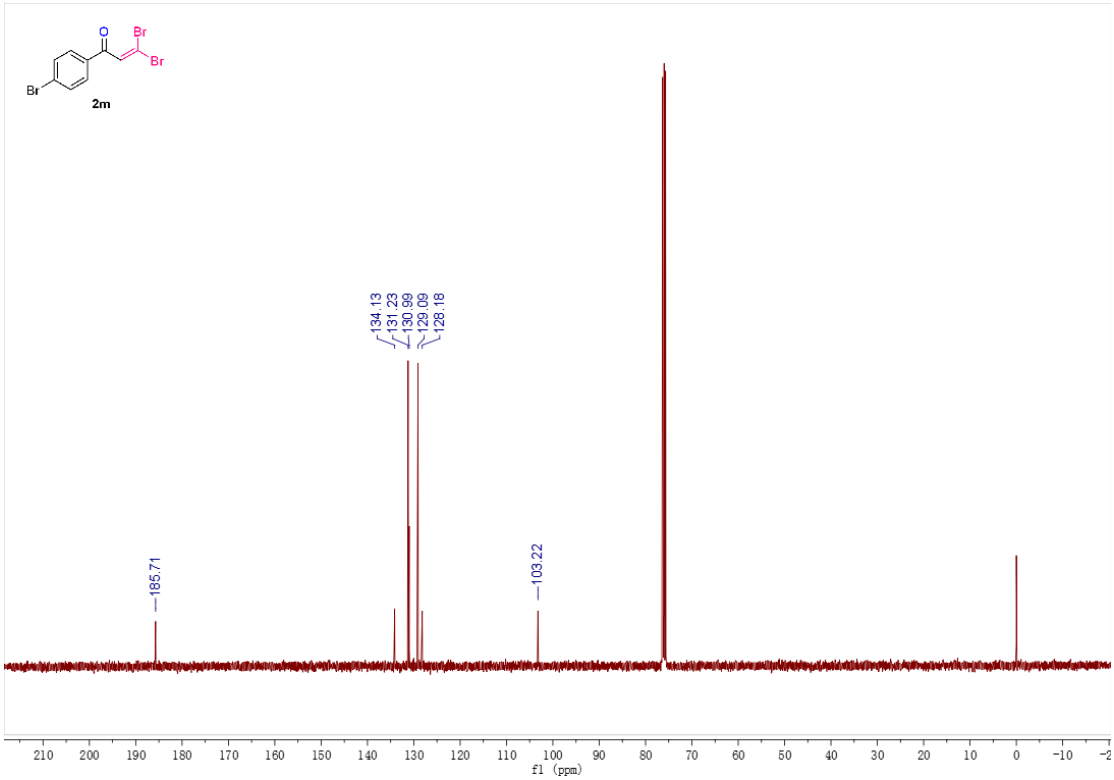
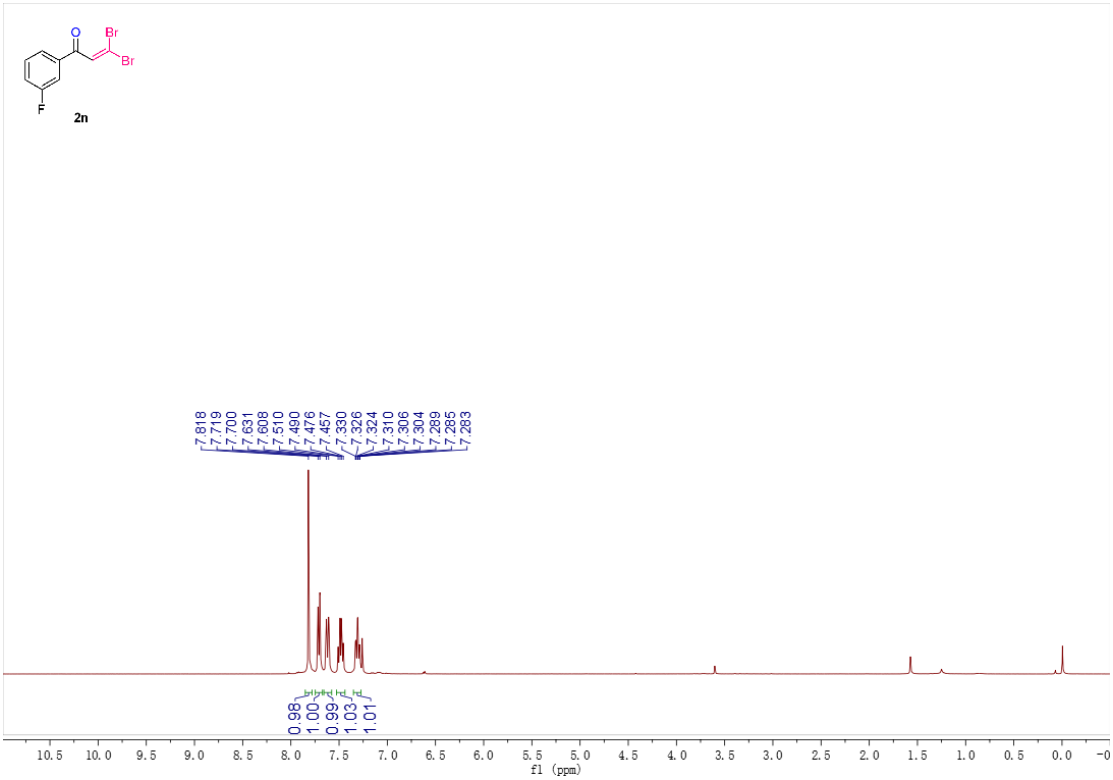
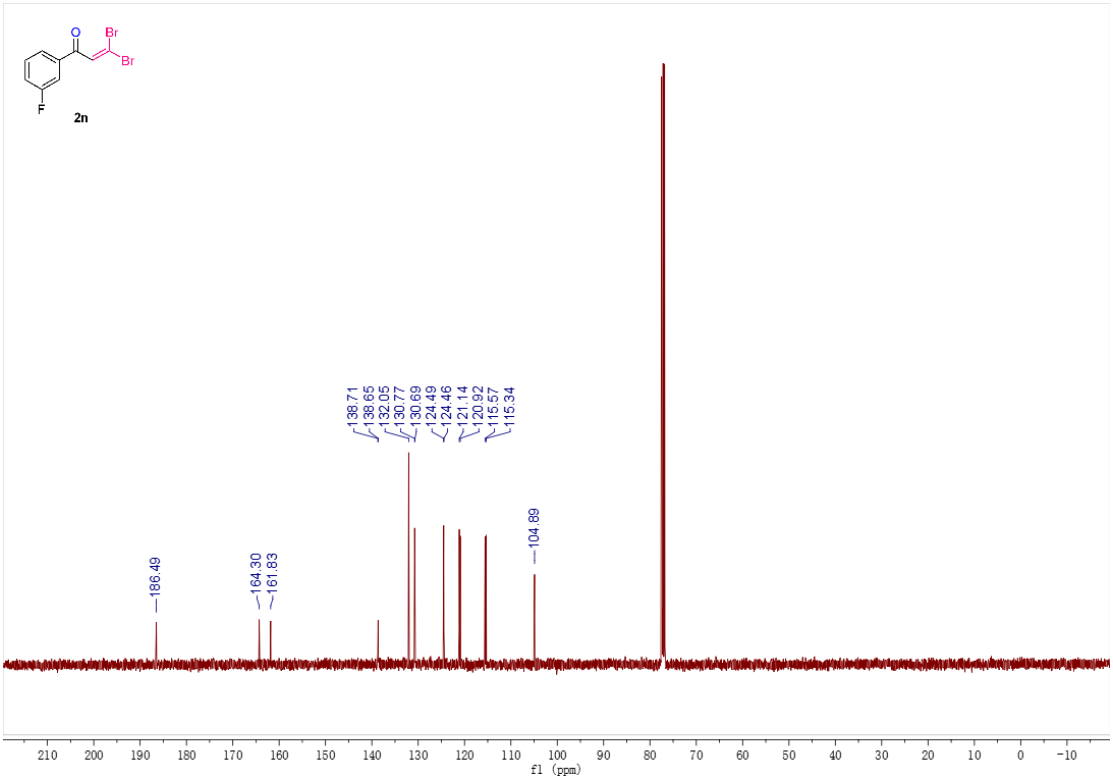


Figure S26. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2m**.


2n
7.818
7.719
7.700
7.631
7.608
7.510
7.490
7.476
7.457
7.330
7.326
7.324
7.310
7.306
7.304
7.289
7.285
7.283
0.98
1.00
0.99
1.03
1.01
f1 (ppm)


2n
138.71
138.65
132.05
130.77
130.69
124.49
124.46
121.14
120.92
115.57
115.34
186.49
164.30
161.83
104.89
f1 (ppm)

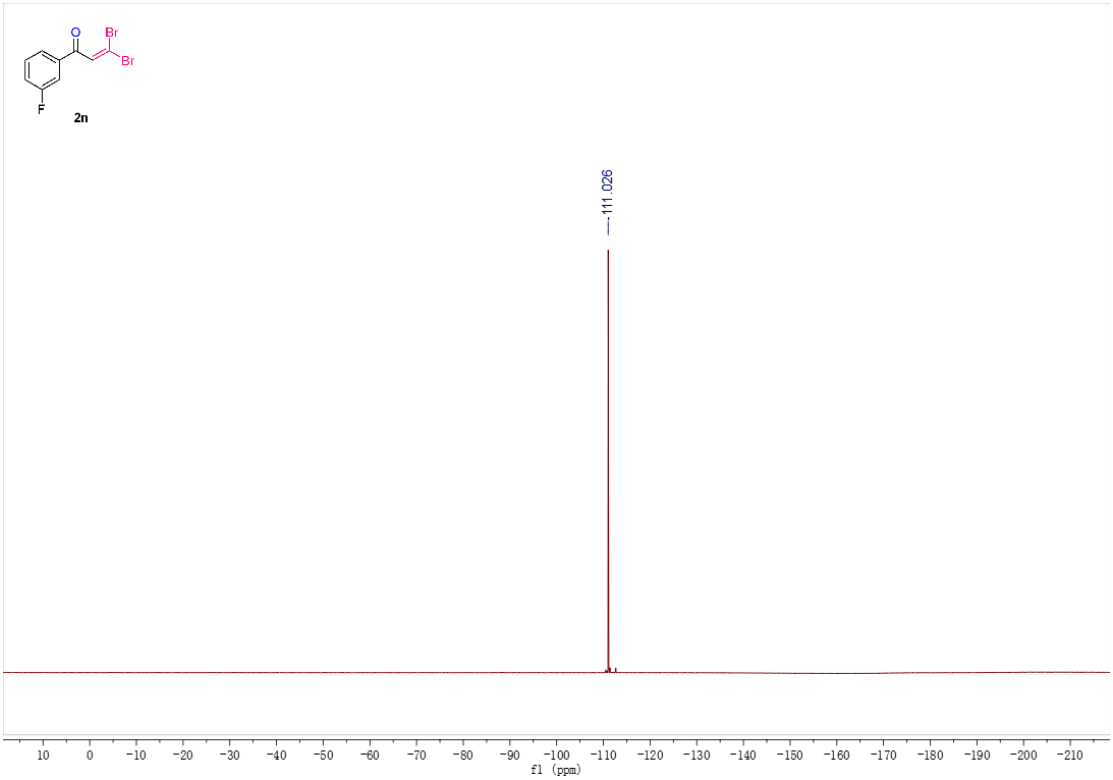


Figure S27. ^{1}H NMR and ^{13}C{^{1}H} NMR and ^{19}F NMR of **2n**.

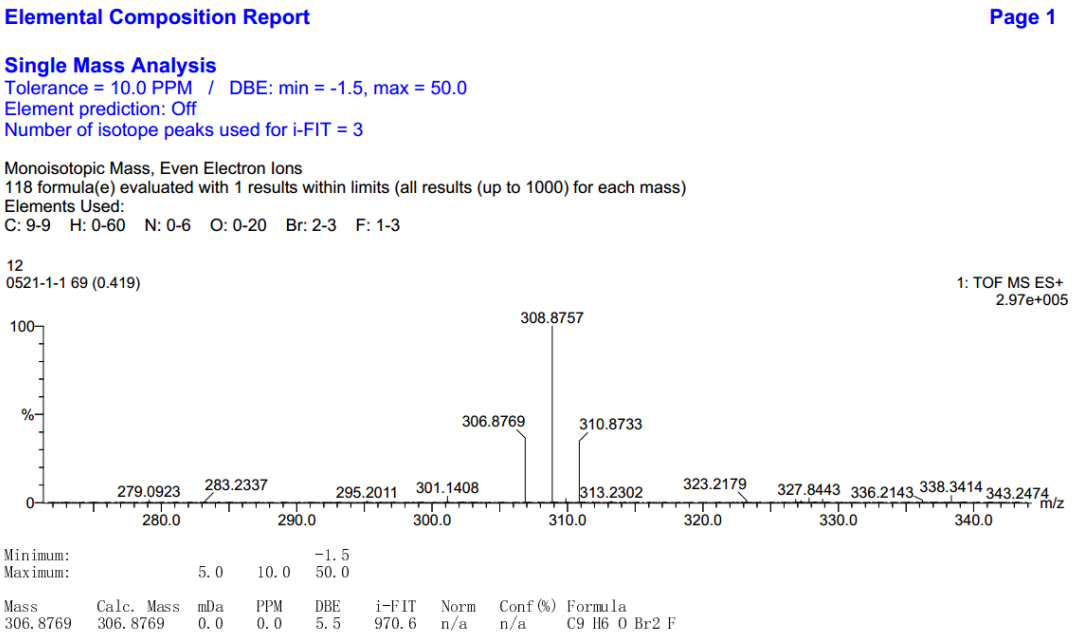


Figure S28. HRMS Spectra of **2n**.

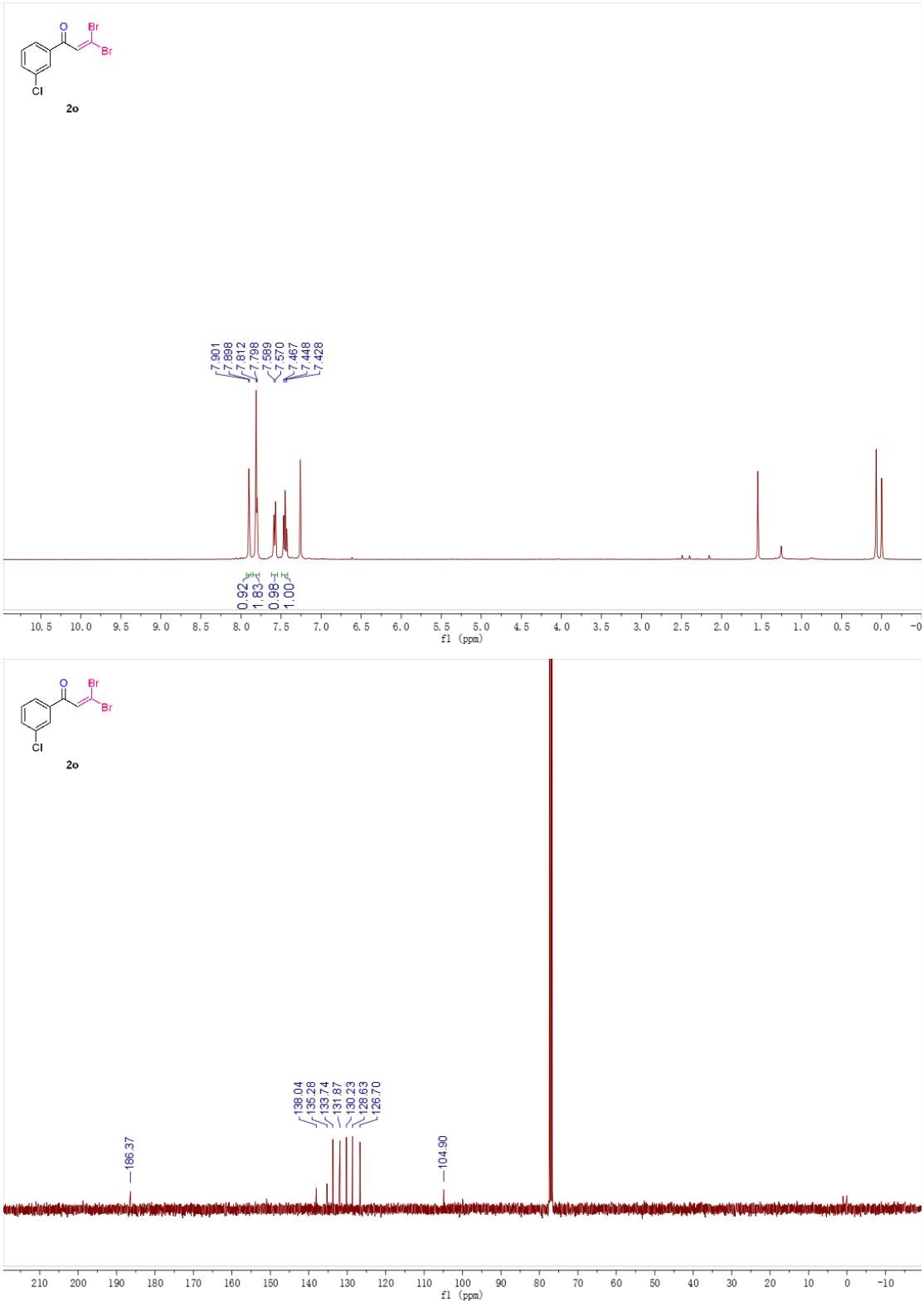


Figure S29. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2o**.

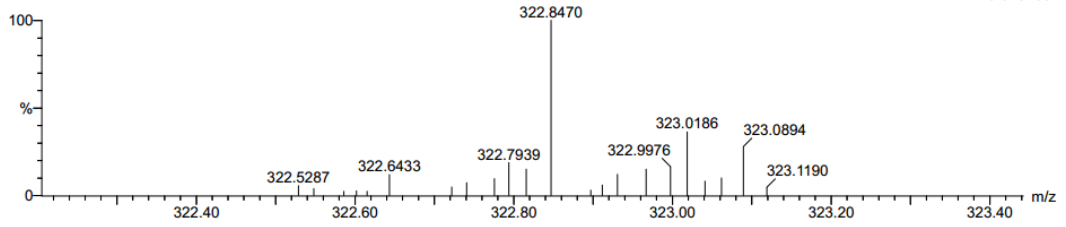
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
182 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 9-9 H: 0-60 N: 0-6 O: 0-20 Si: 0-3 Cl: 1-3 Br: 2-3

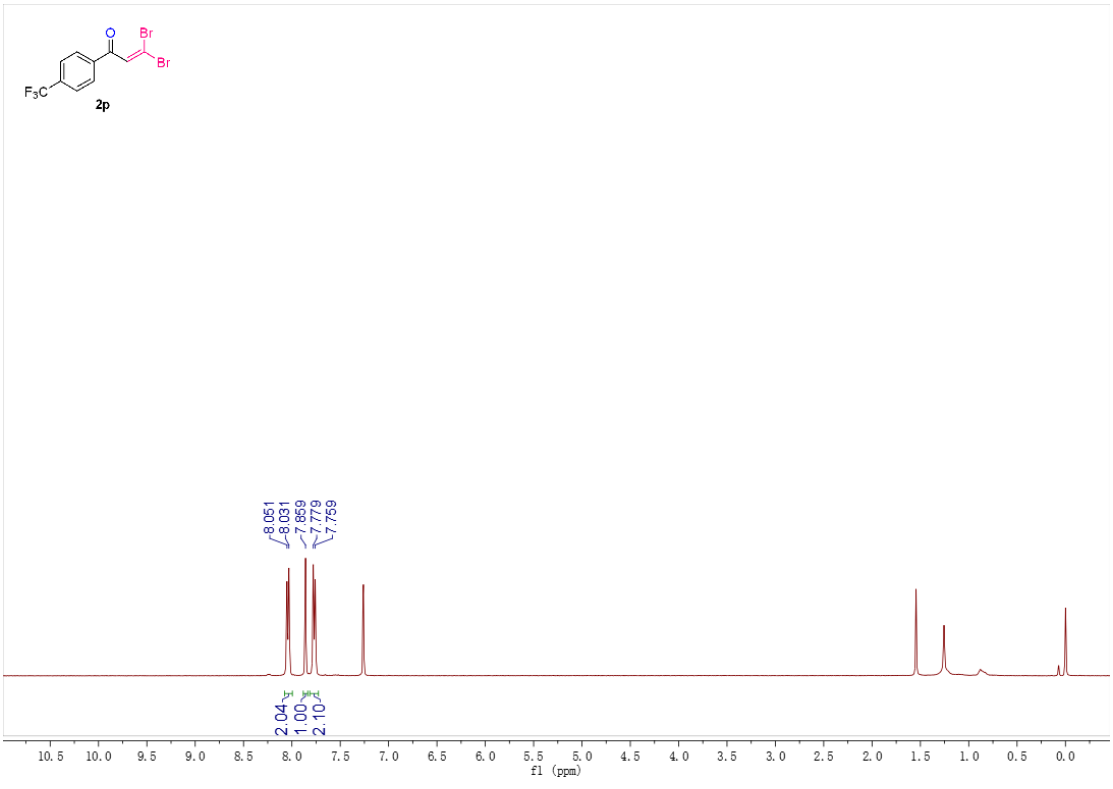
12
0521-1-5 79 (0.480)

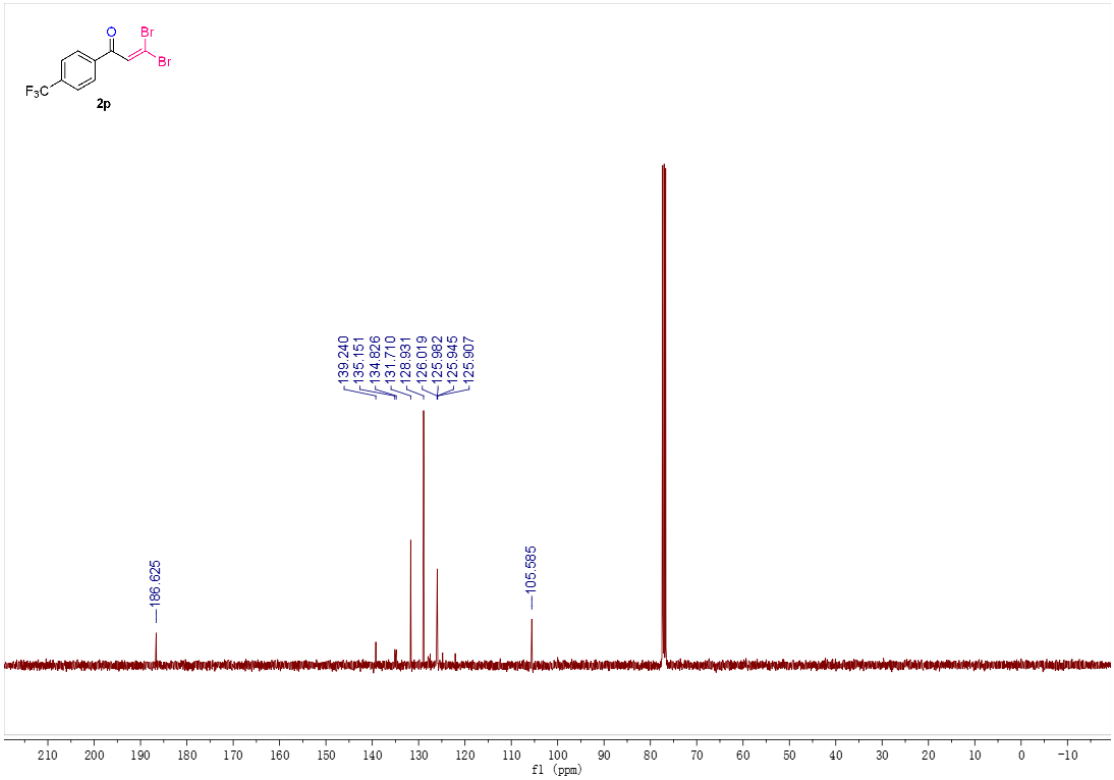
1: TOF MS ES+
9.07e+002



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
322.8470	322.8474	-0.4	-1.2	5.5	116.5	n/a	n/a	C9 H6 O Cl Br2

Figure S30. HRMS Spectra of **2o**.





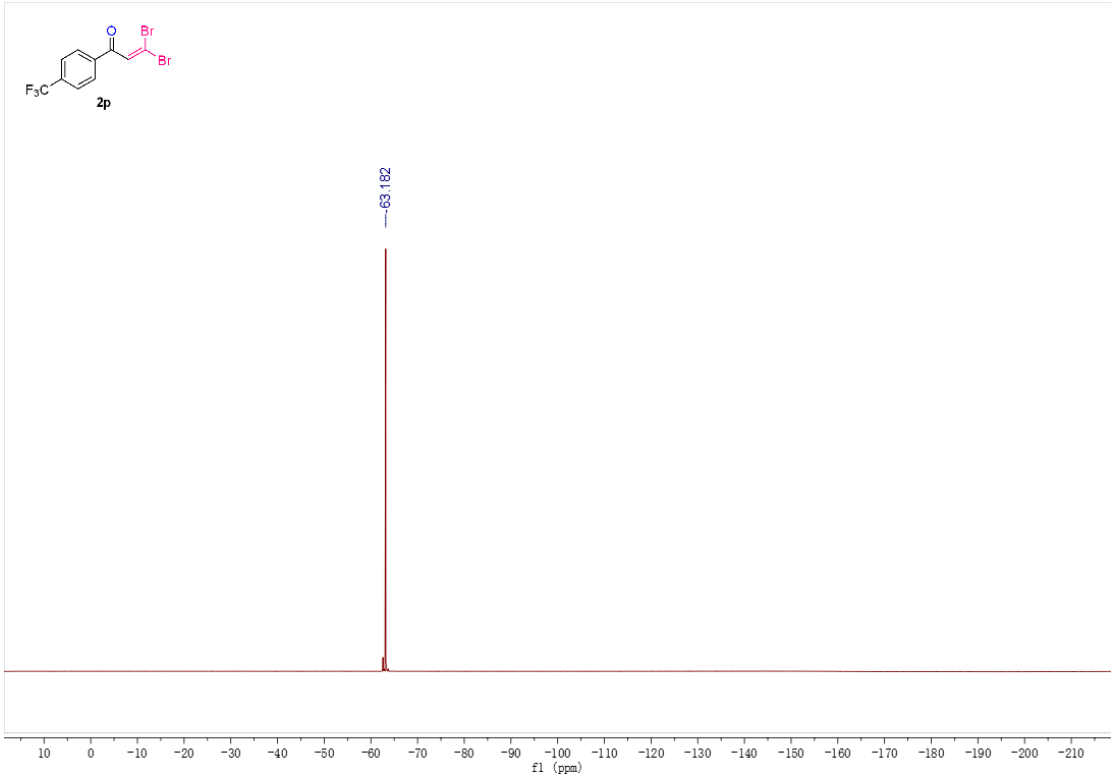


Figure S31. ^{1}H NMR and ^{13}C{^{1}H} NMR and ^{19}F NMR of **2p**.

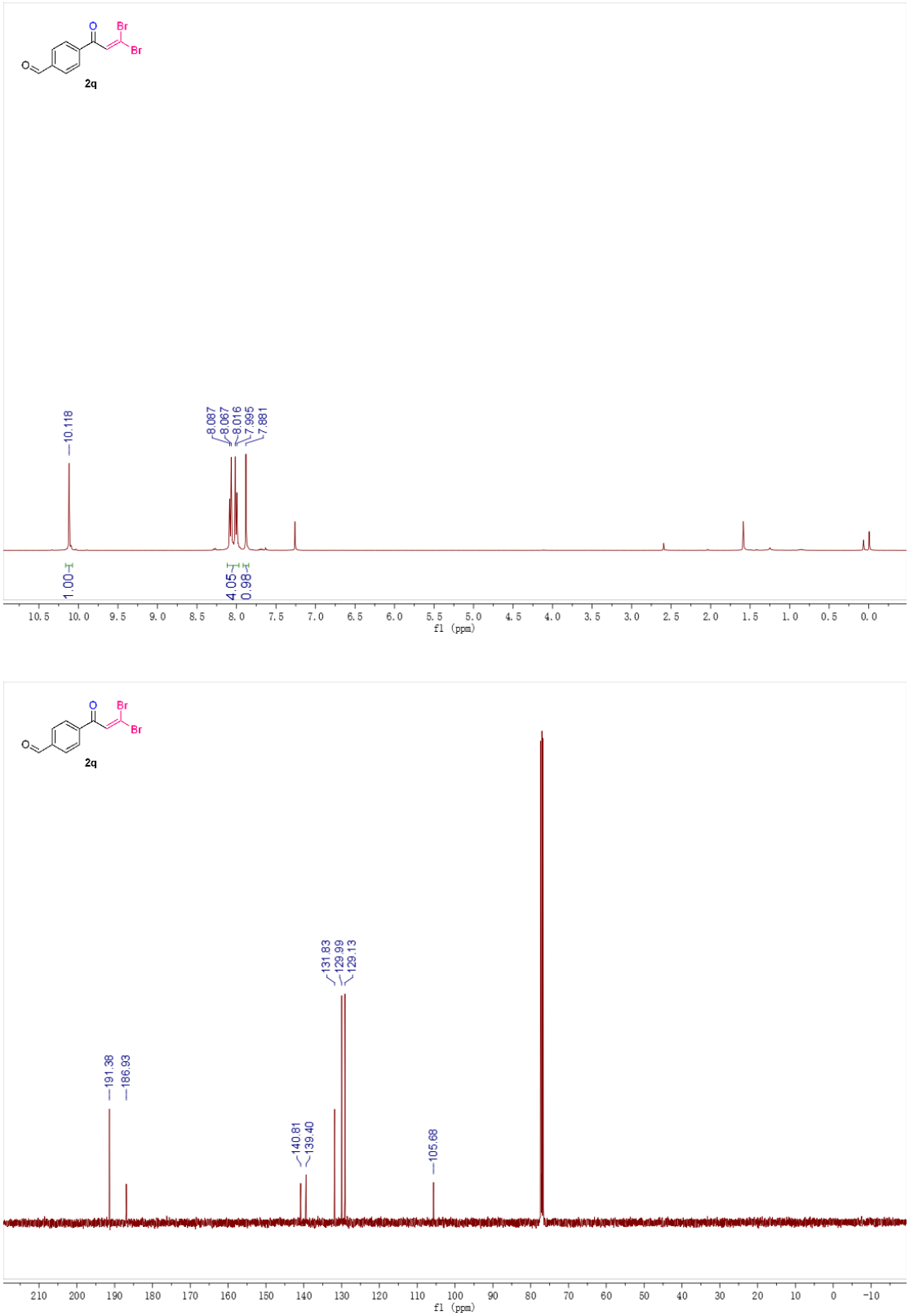


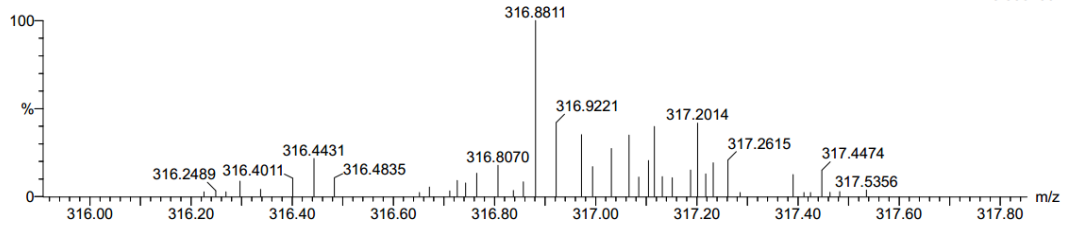
Figure S32. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2q**.

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

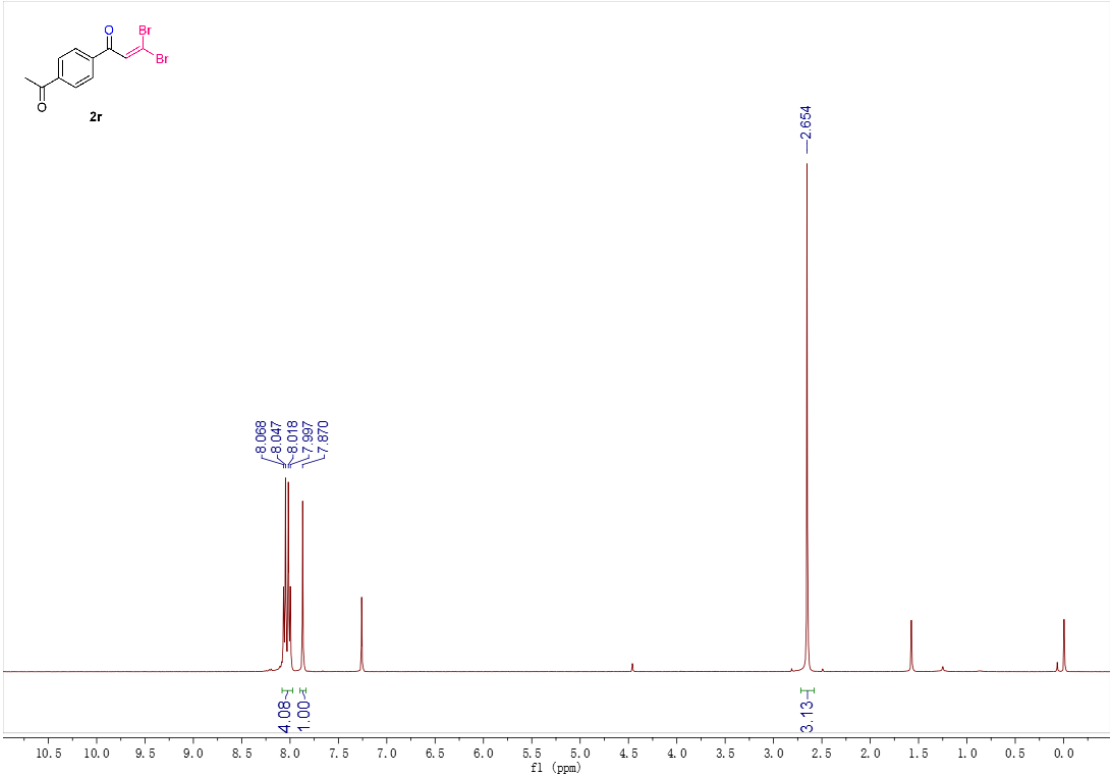
Monoisotopic Mass, Even Electron Ions
175 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 10-10 H: 0-60 N: 0-6 O: 0-20 Si: 0-3 Br: 2-3

12
0521-1-2 61 (0.377)



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
316.8811	316.8813	-0.2	-0.6	6.5	238.9	n/a	n/a	C10 H7 O2 Br2

Figure S33. HRMS Spectra of **2q**.



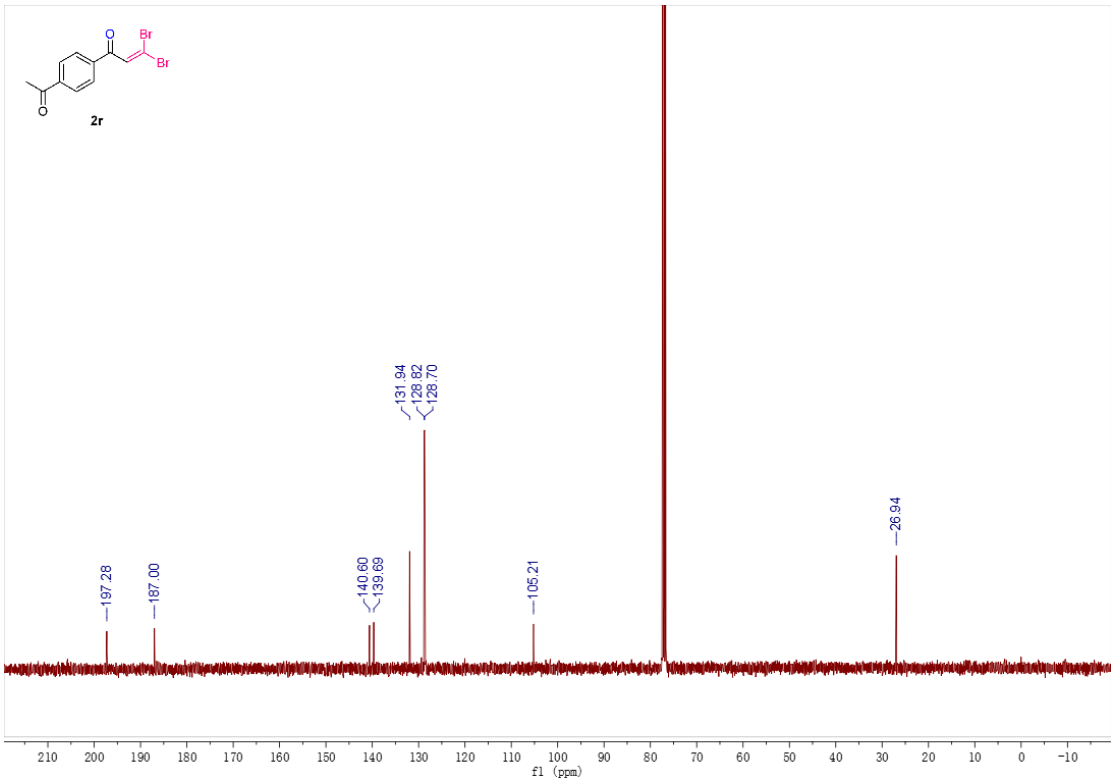


Figure S34. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2r**.

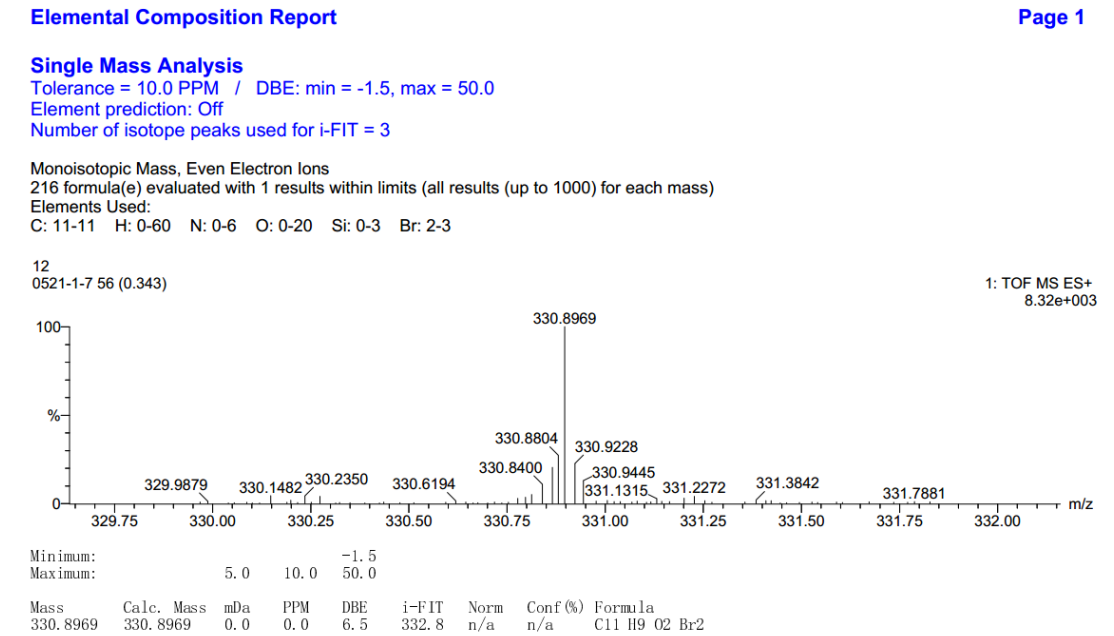


Figure S35. HRMS Spectra of **2r**.

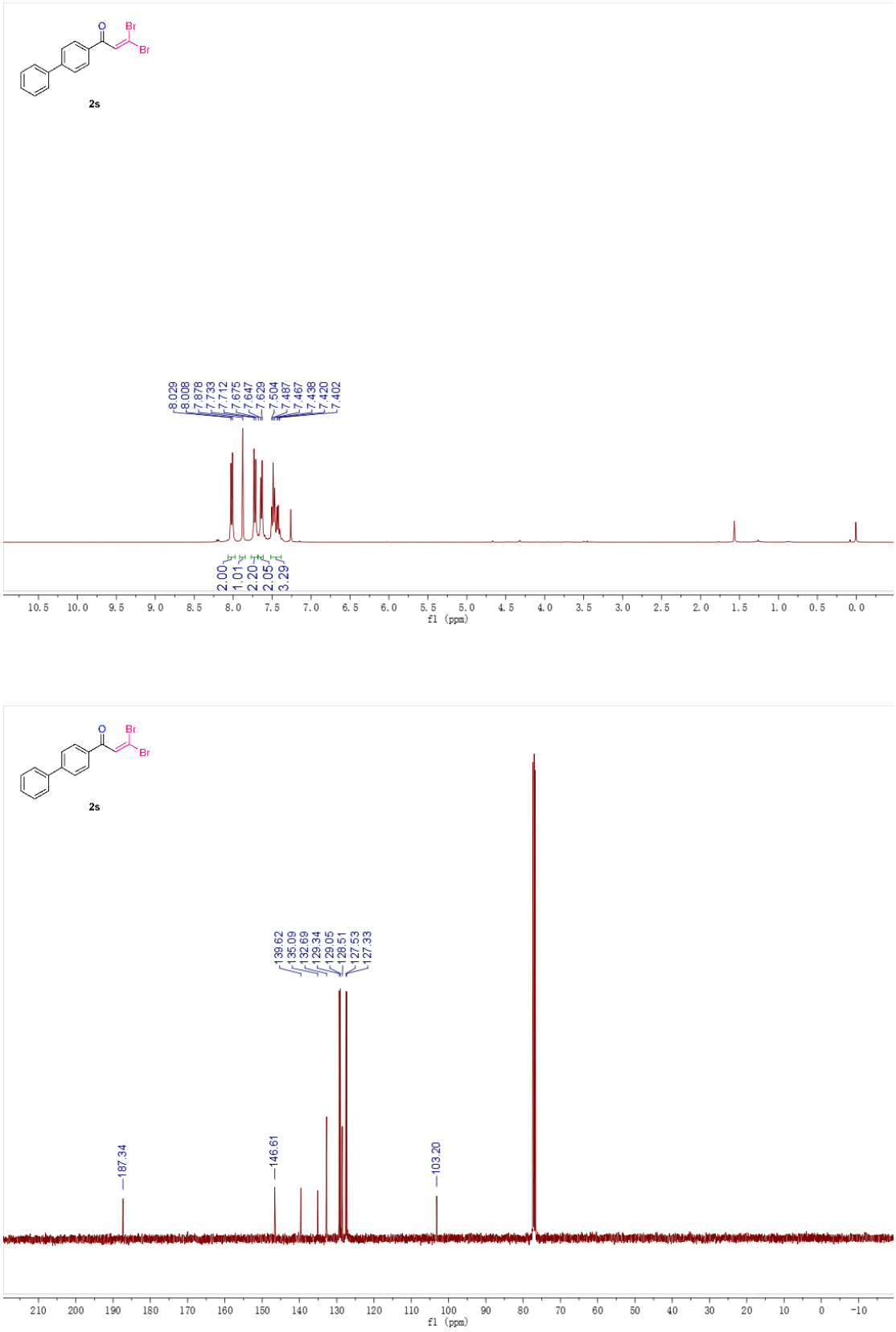


Figure S36. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2s**.

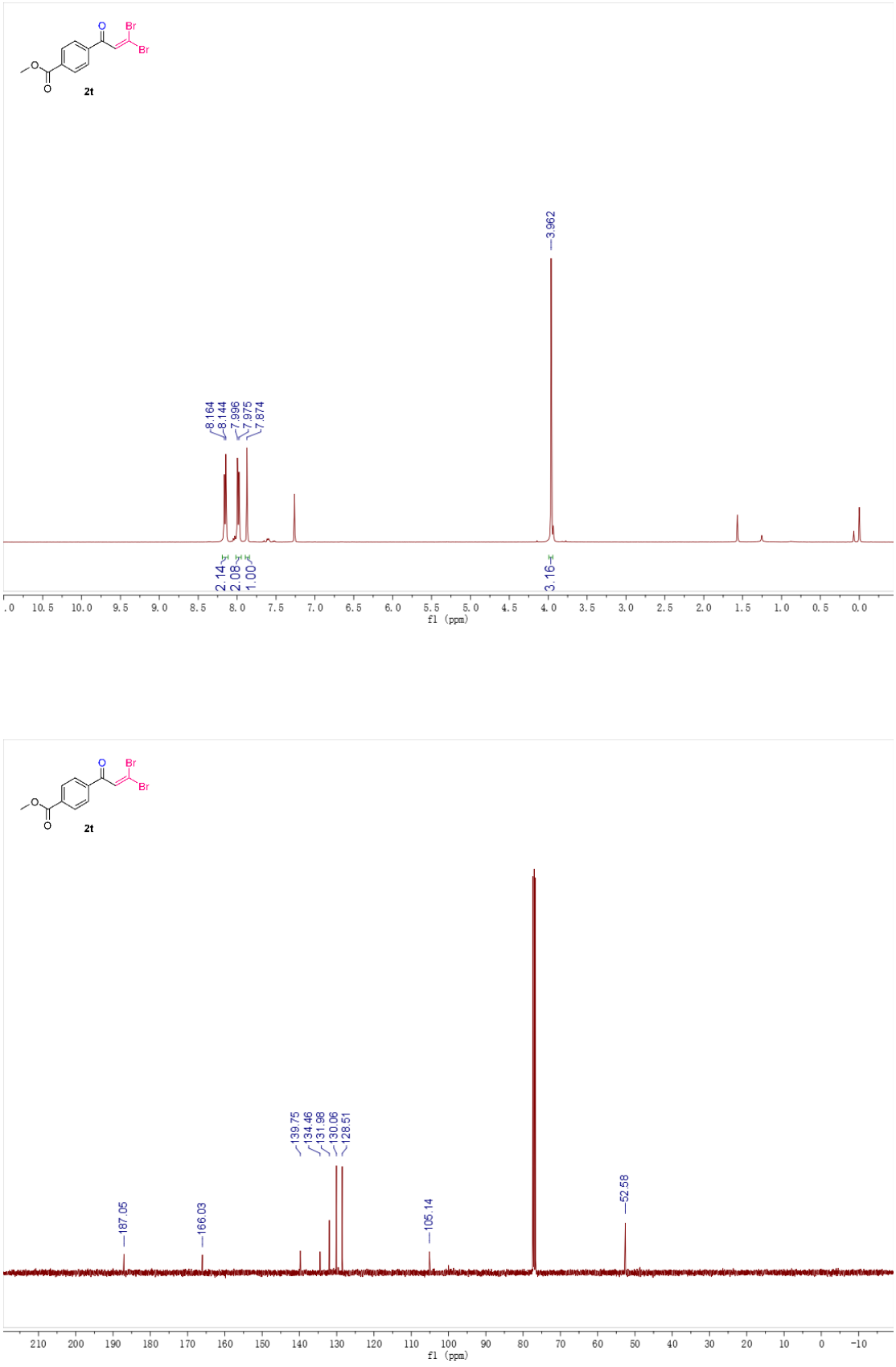


Figure S37. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2t**.

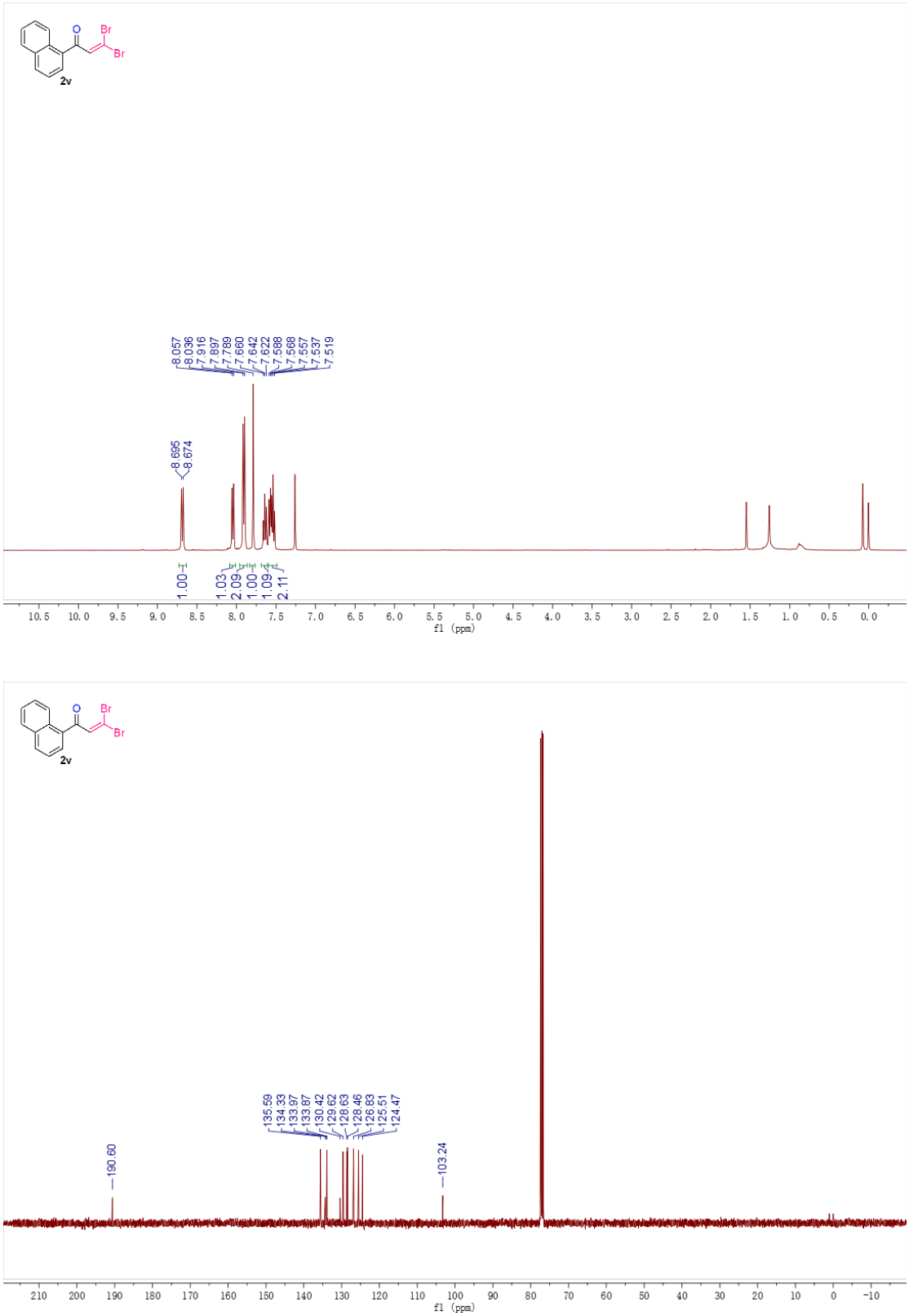


Figure S38. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2v**.

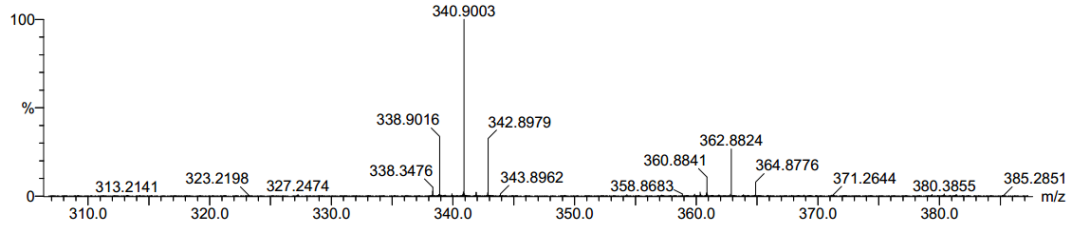
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
241 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 13-13 H: 0-60 N: 0-6 O: 0-20 Si: 0-3 Br: 2-3

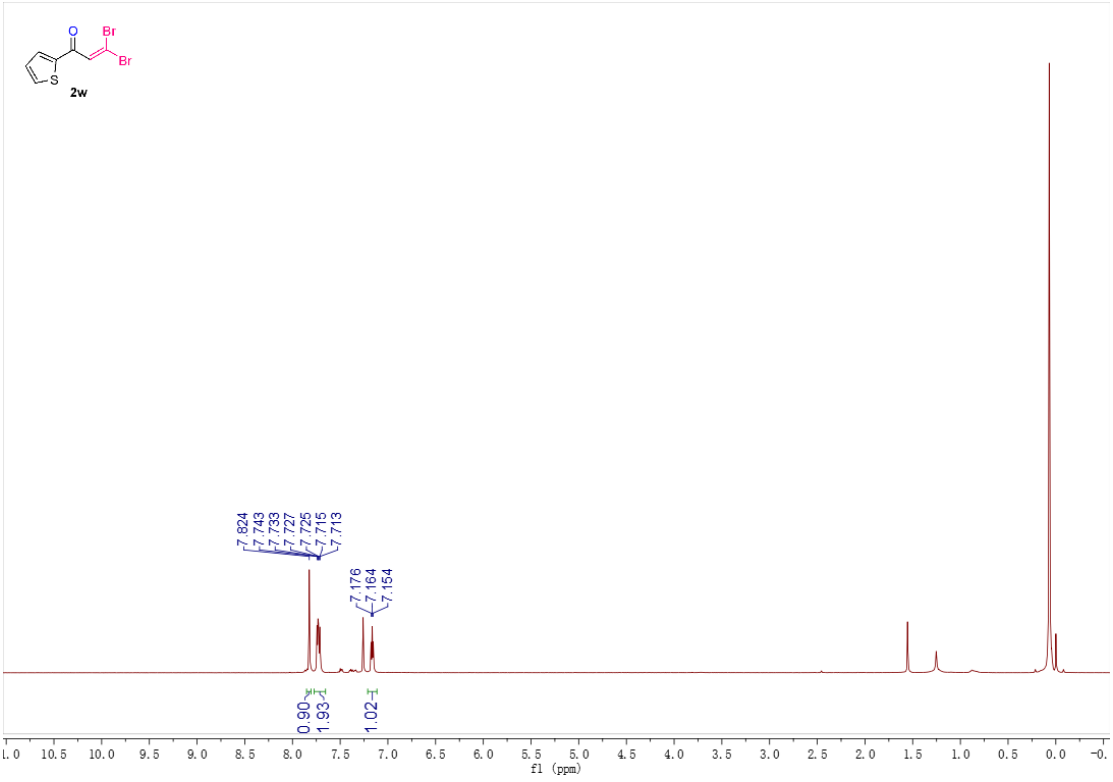
12
0521-1-6 84 (0.506)

1: TOF MS ES+
2.50e+005



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
338.9016	338.9020	-0.4	-1.2	8.5	1085.8	n/a	n/a	C13 H9 O Br2

Figure S39. HRMS Spectra of **2v**.



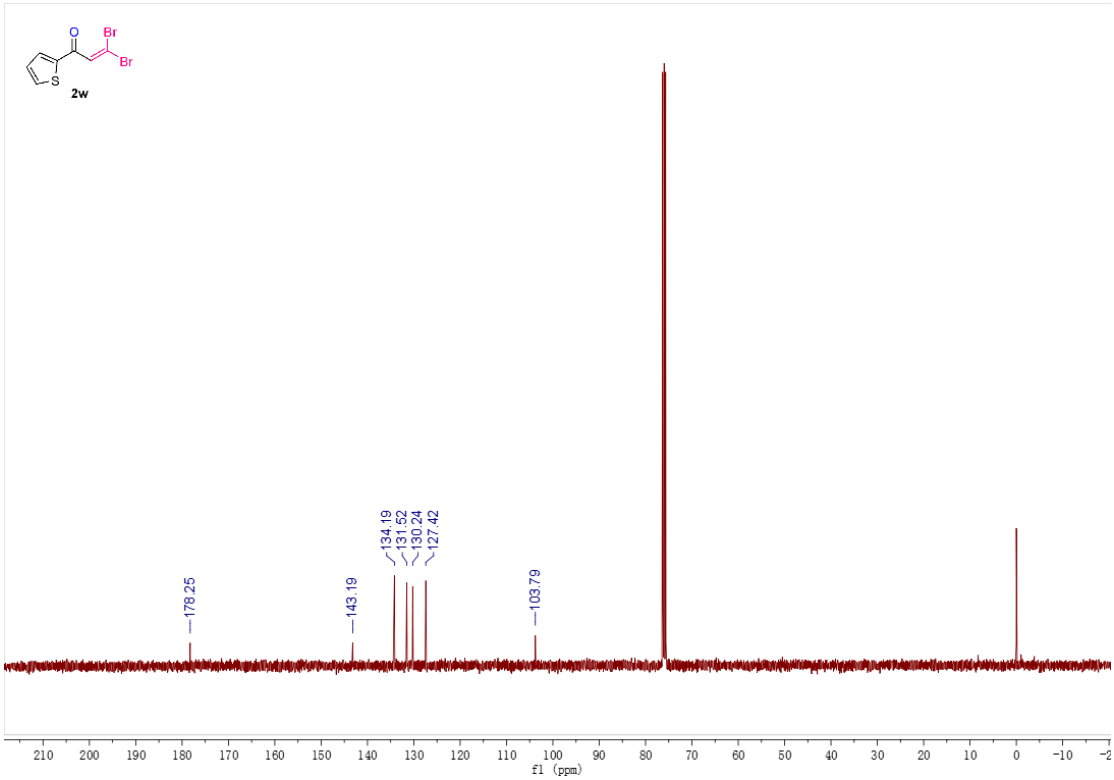
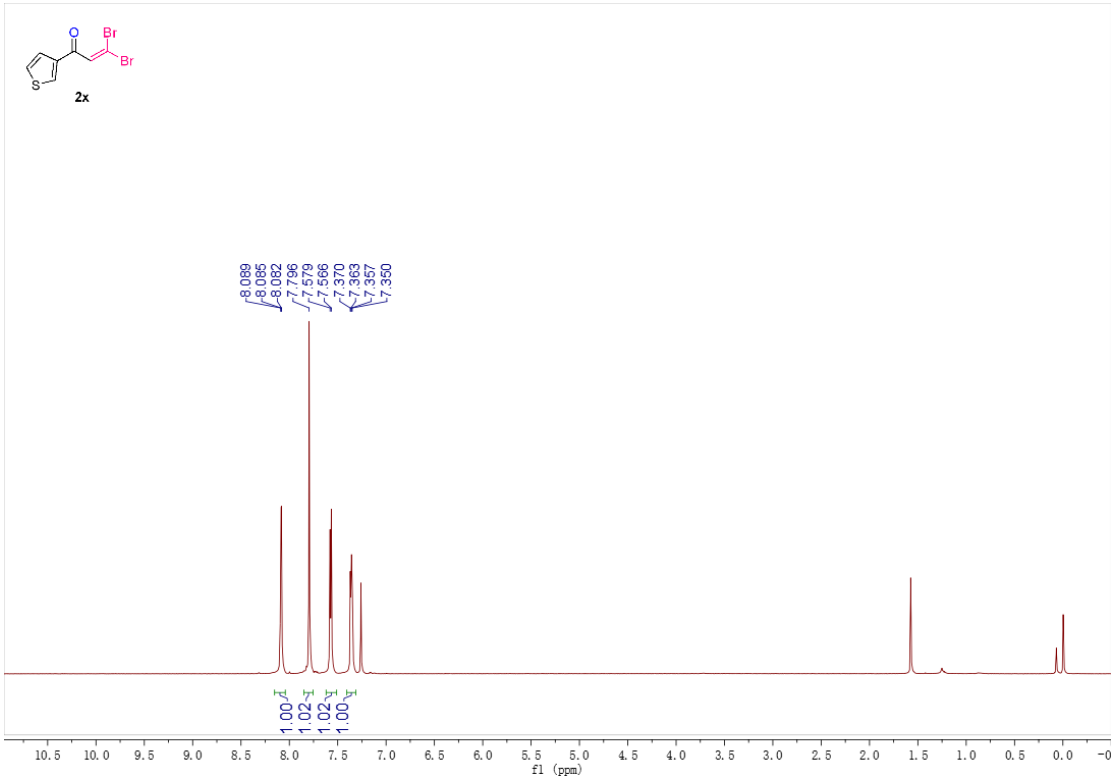


Figure S40. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of **2w**.



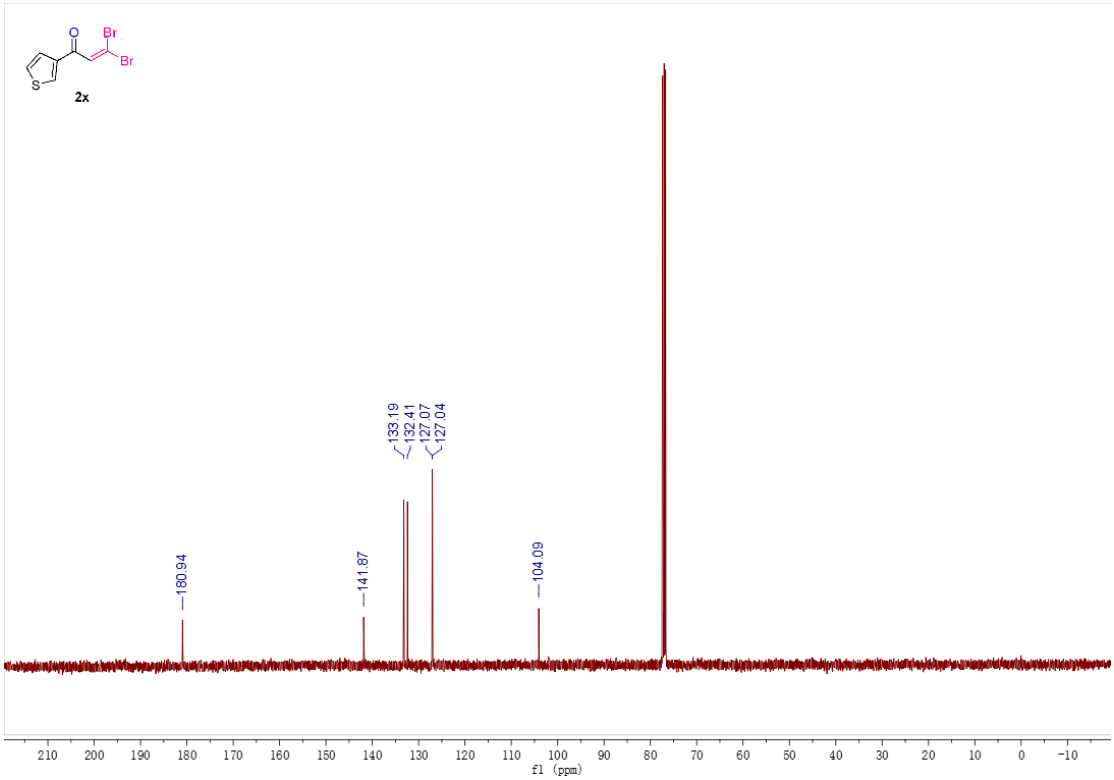
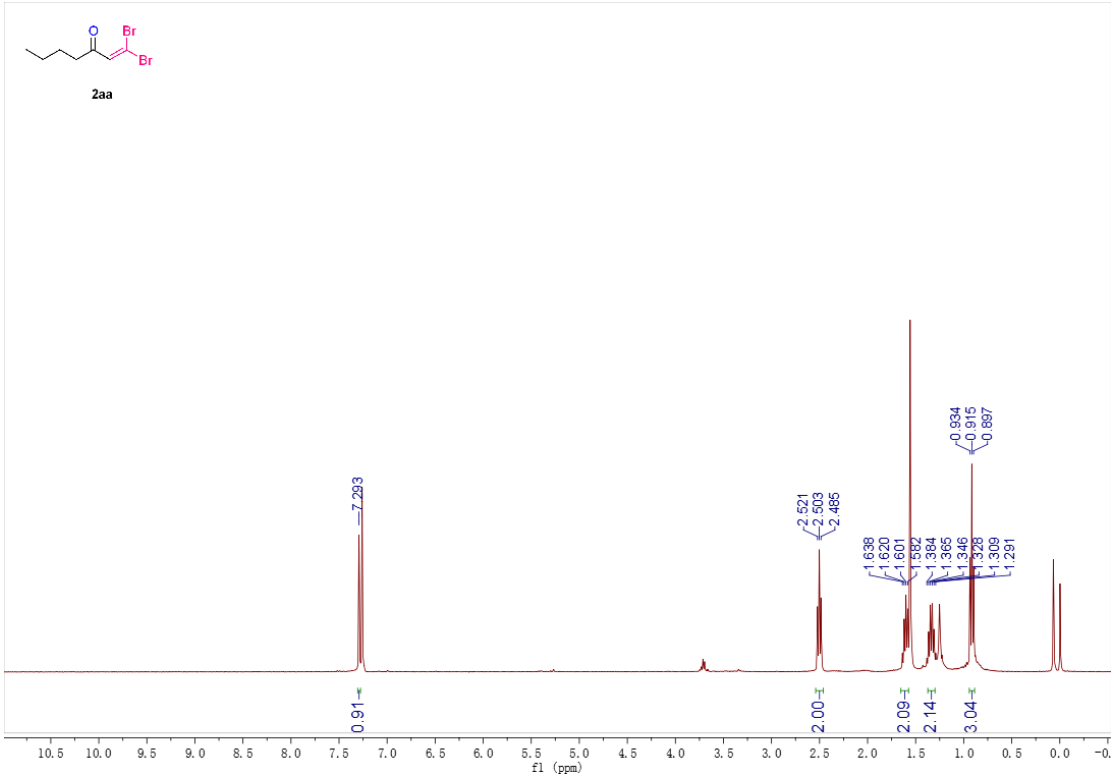


Figure S41. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2x**.



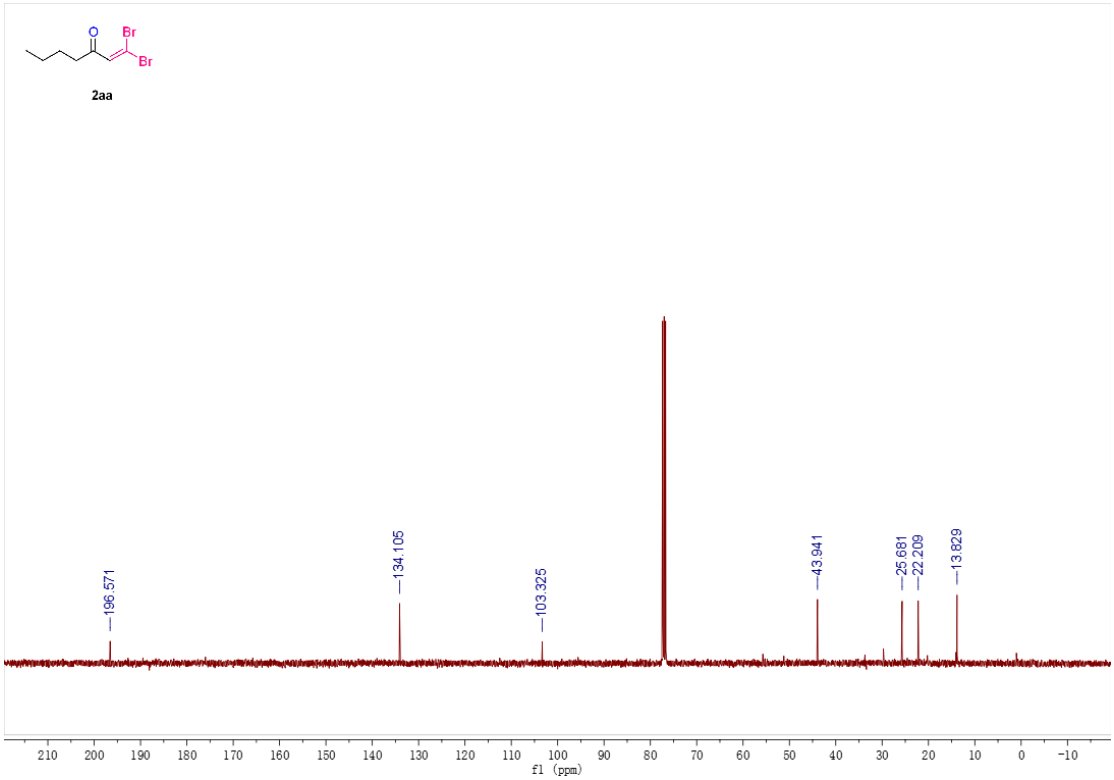


Figure S42. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2aa**.

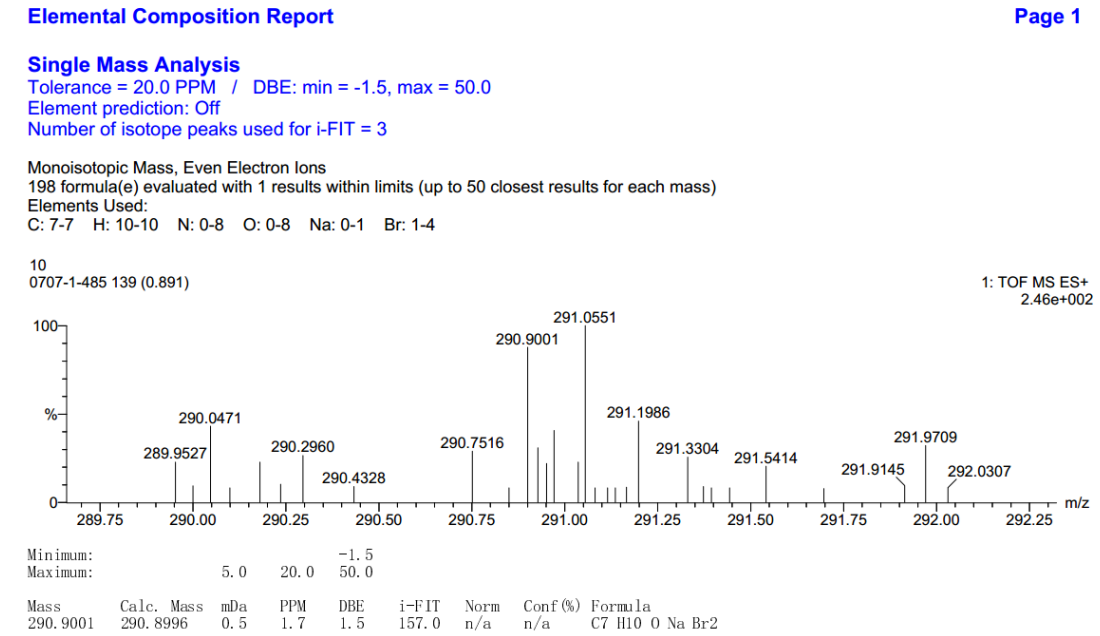
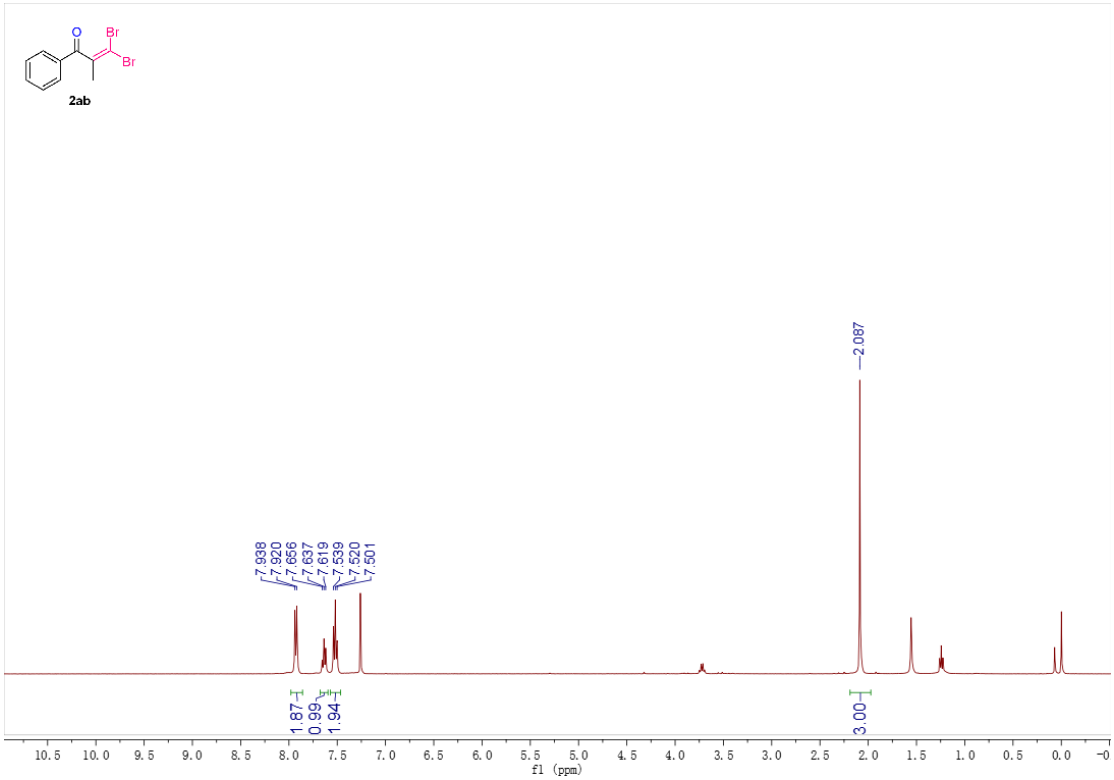


Figure S43. HRMS Spectra of **2aa**.



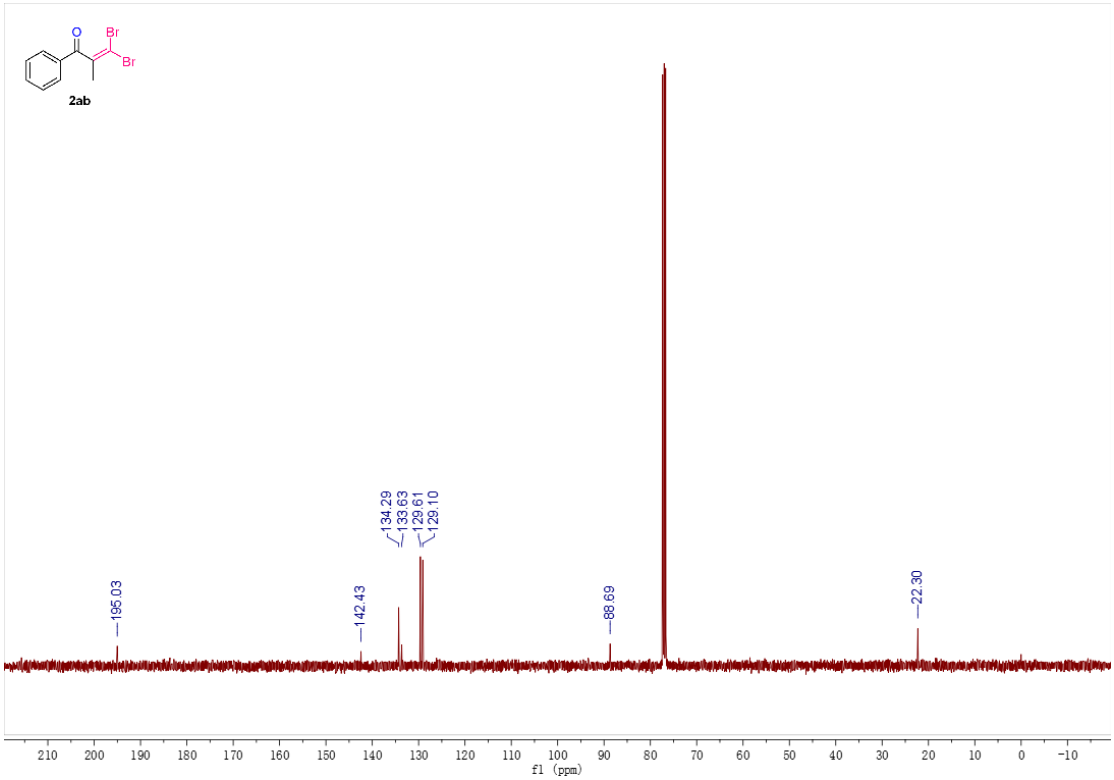


Figure S44. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2ab**.

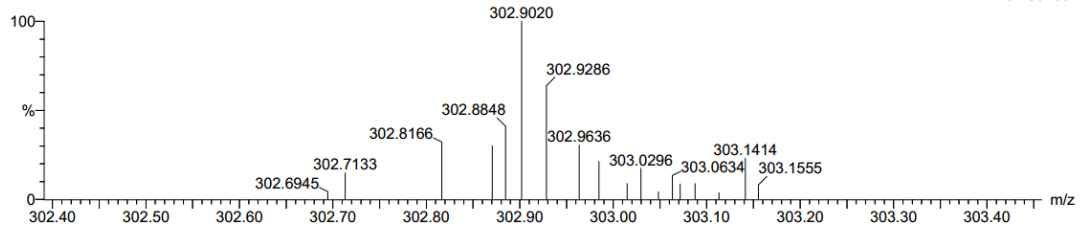
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
62 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 10-10 H: 0-60 N: 0-6 O: 0-20 Br: 2-3

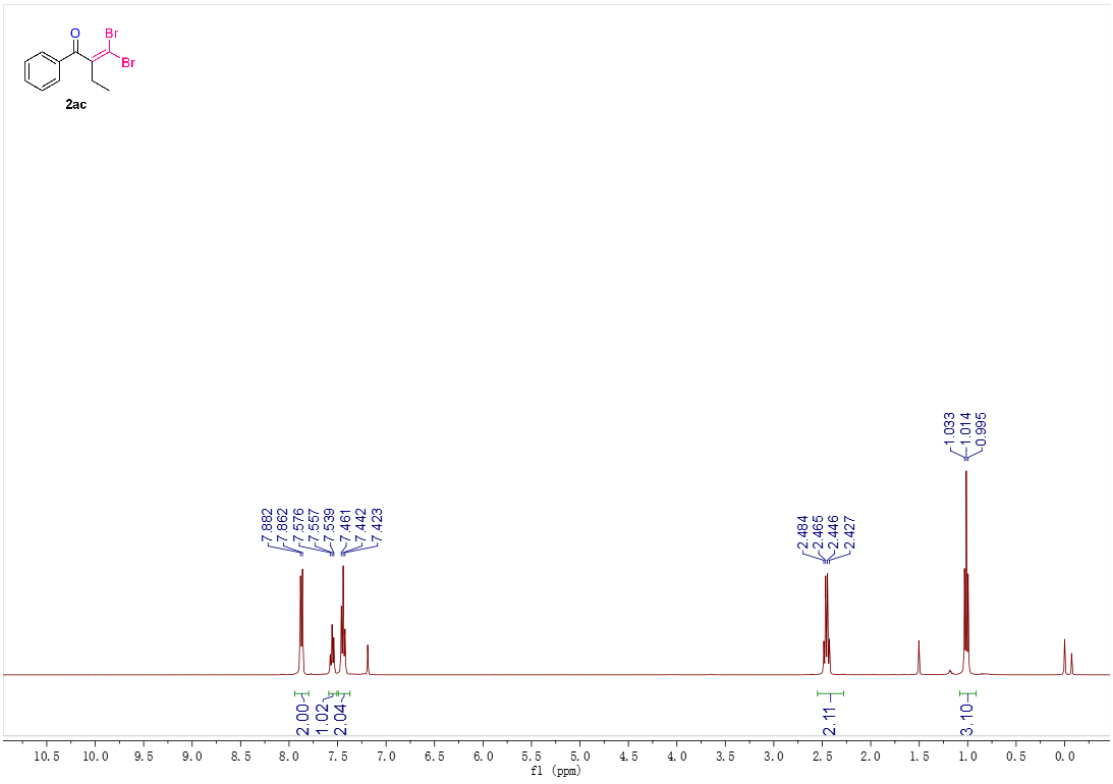
12
0521-1-9 65 (0.398)

1: TOF MS ES+
6.13e+002



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
302.9020	302.9020	0.0	0.0	5.5	128.5	n/a	n/a	C10 H9 O Br2

Figure S45. HRMS Spectra of **2ab**.



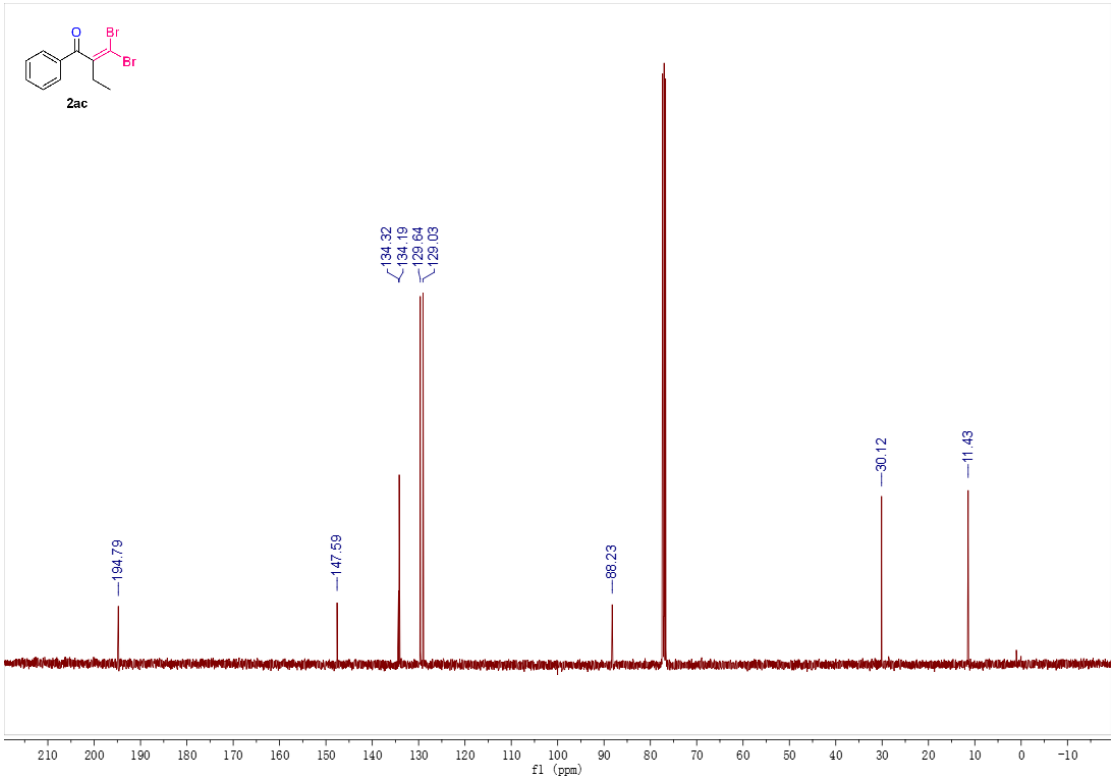


Figure S46. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2ac**.

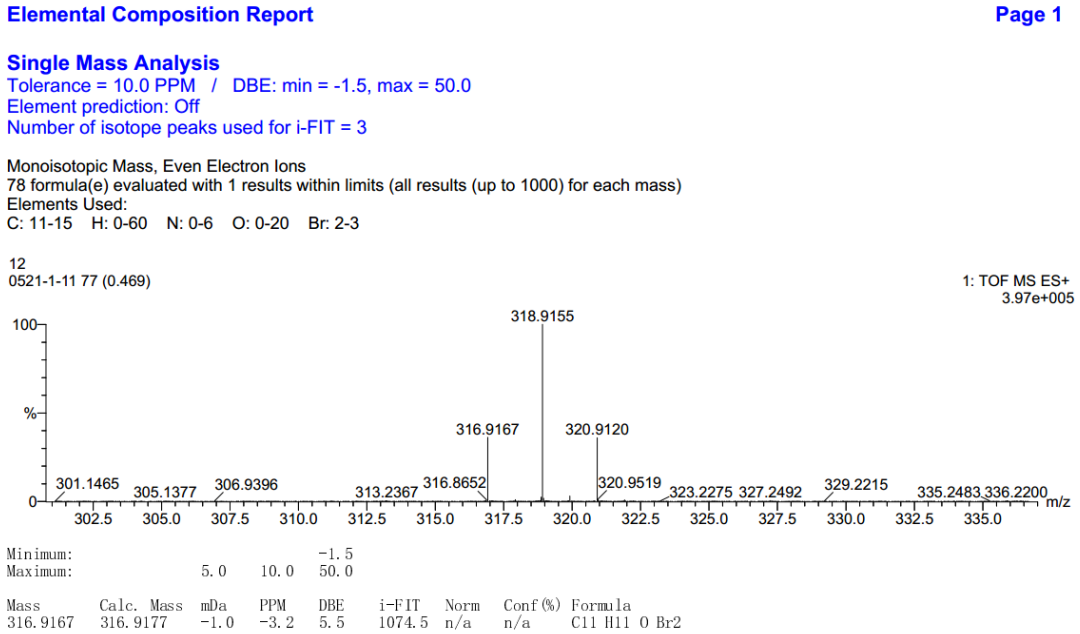


Figure S47. HRMS Spectra of **2ac**.

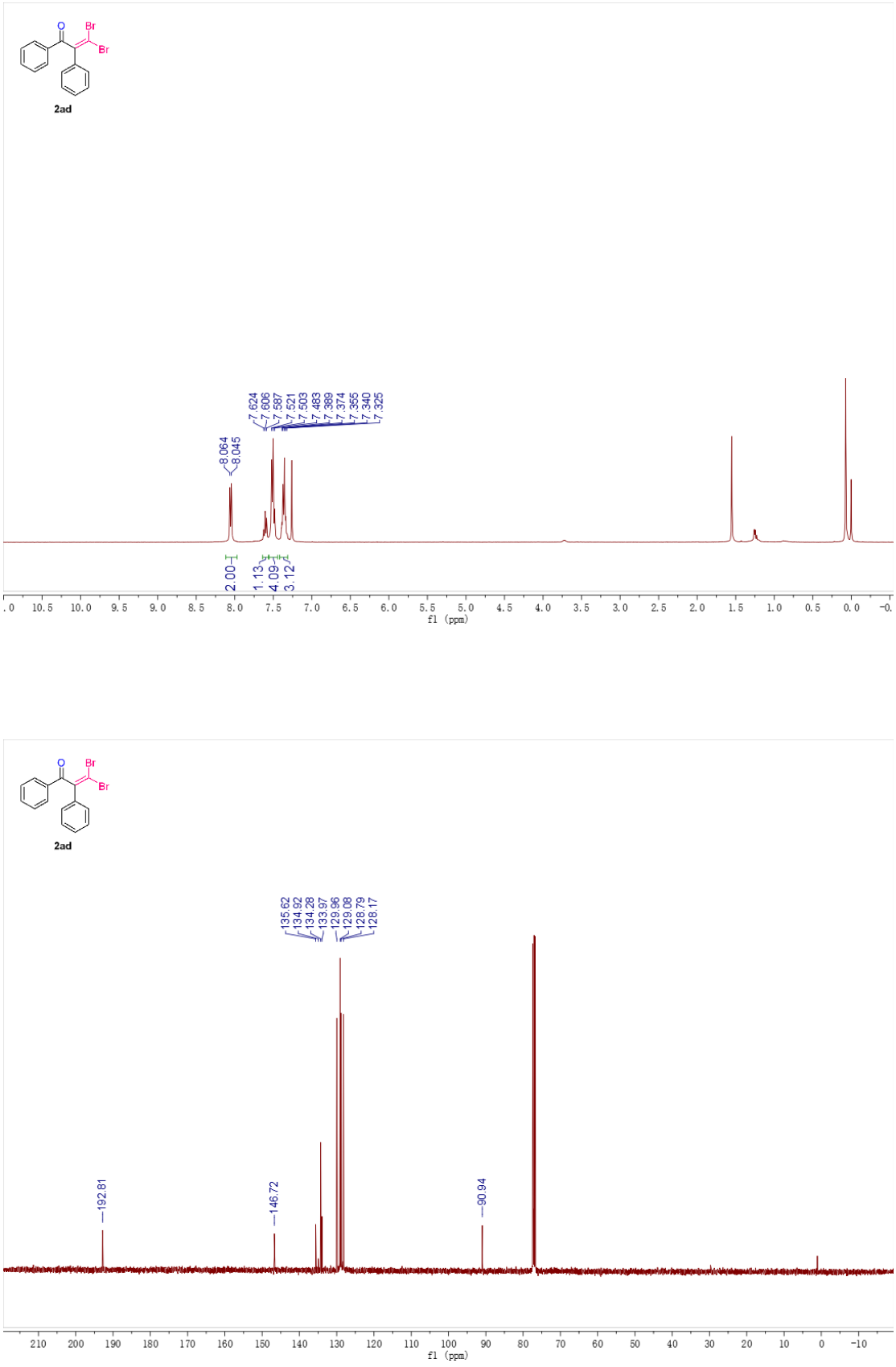


Figure S48. ^{1}H NMR and ^{13}C{^{1}H} NMR of **2ad**.

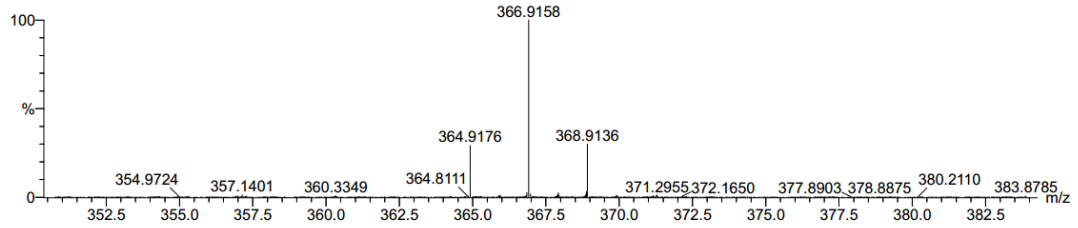
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
116 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 15-15 H: 0-60 N: 0-6 O: 0-20 Br: 2-3

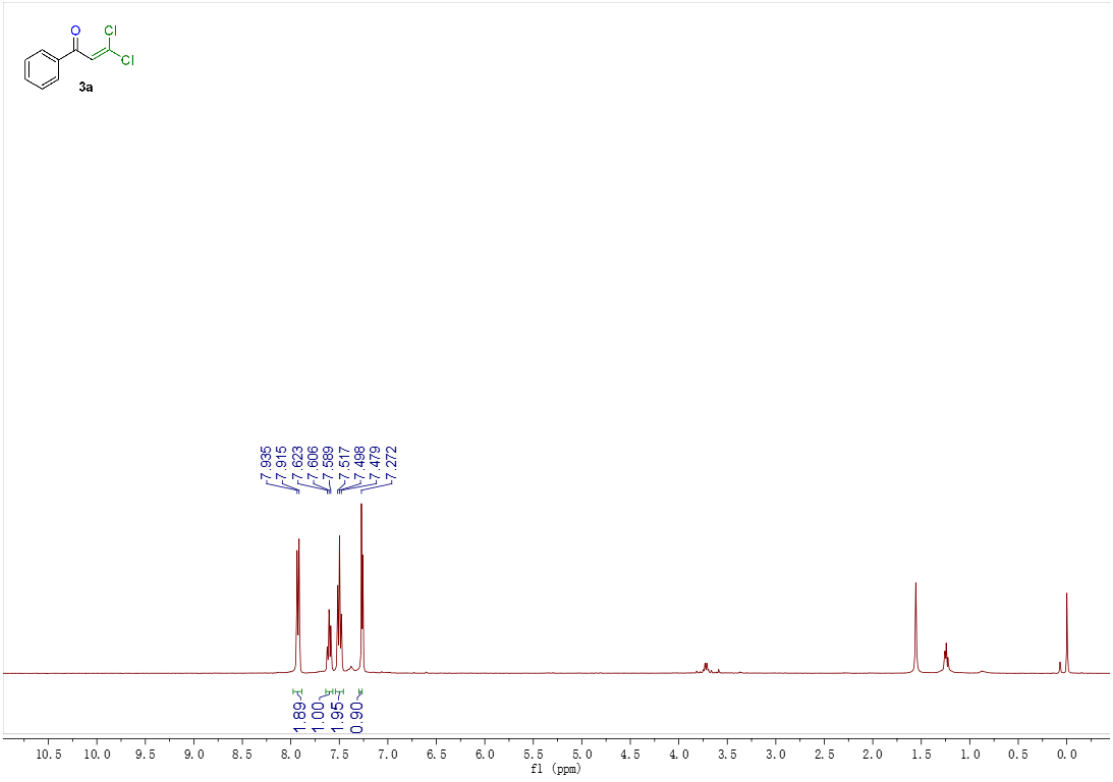
12
0521-1-10 82 (0.495)

1: TOF MS ES+
1.90e+005



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
364.9176	364.9177	-0.1	-0.3	9.5	953.4	n/a	n/a	C15 H11 O Br2

Figure S49. HRMS Spectra of **2ad**.



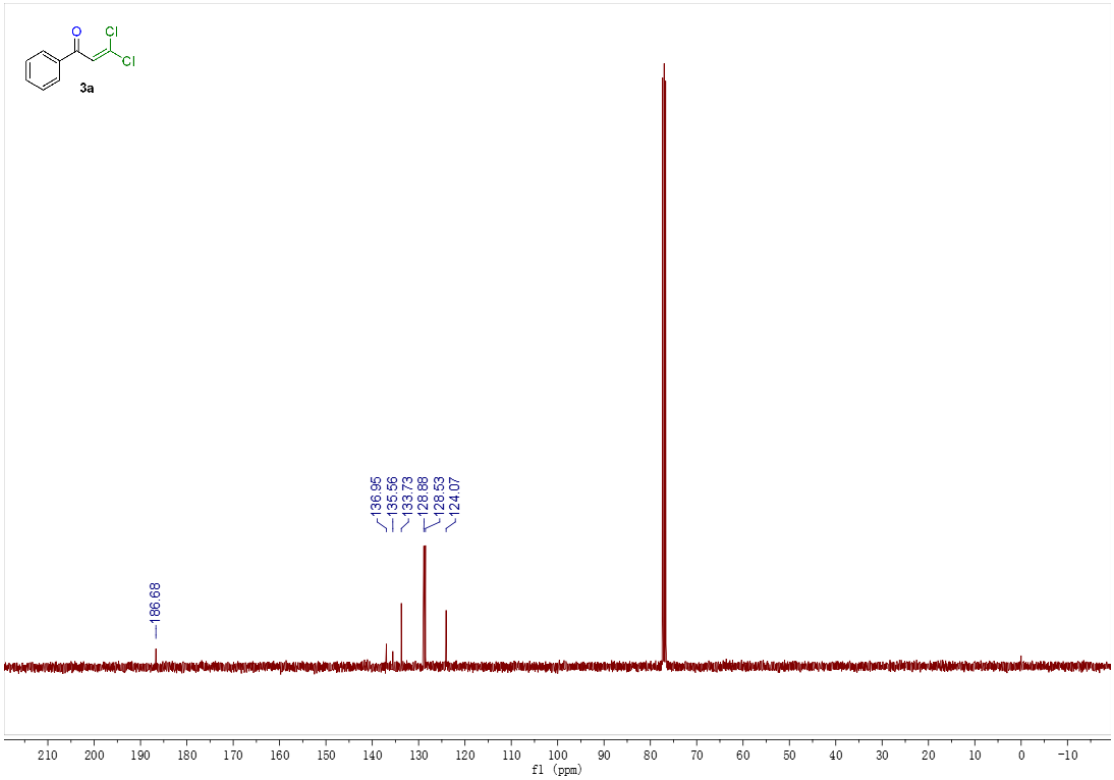


Figure S50. ^{1}H NMR and ^{13}C{^{1}H} NMR of **3a**.

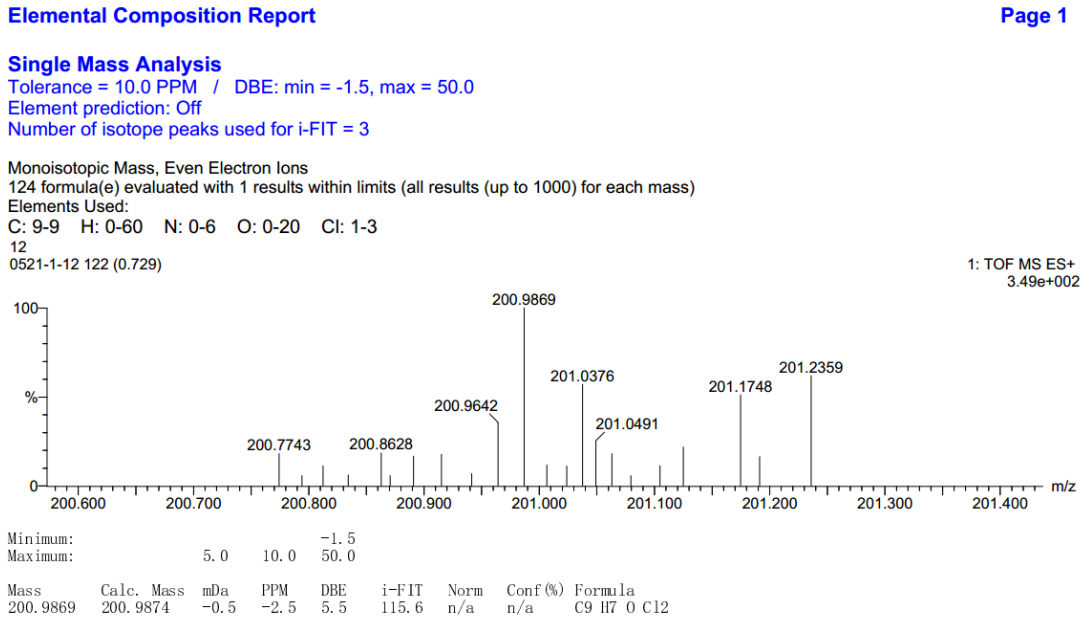
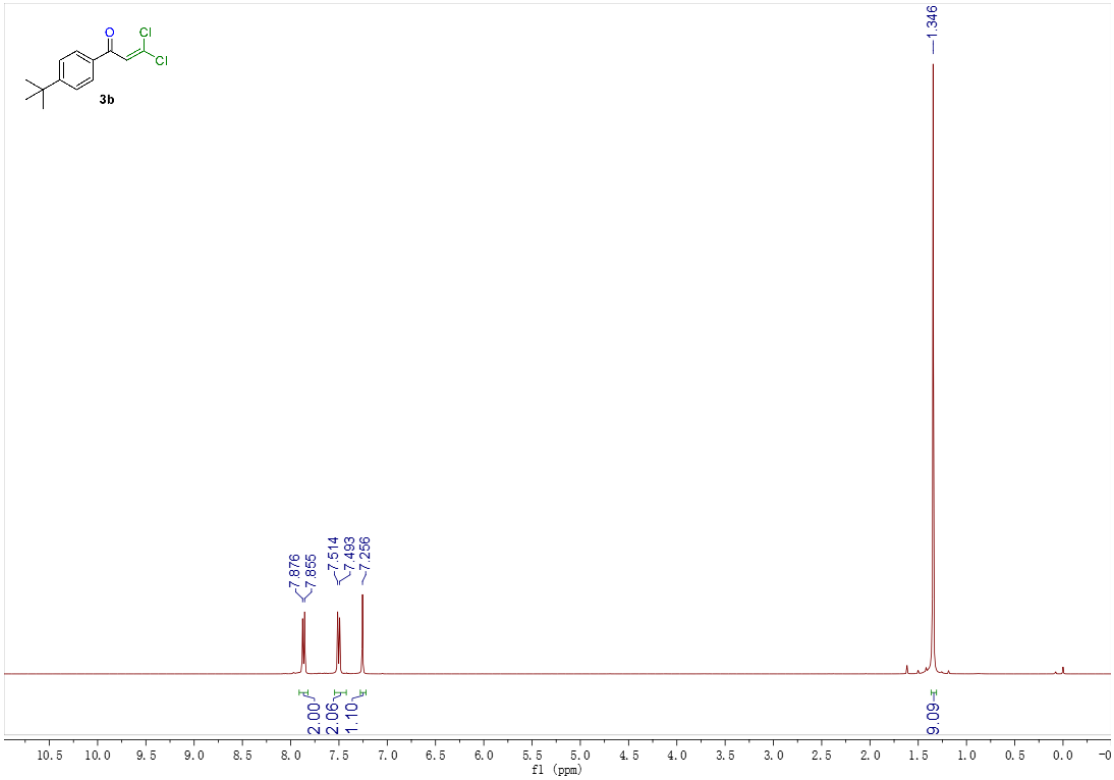


Figure S51. HRMS Spectra of **3a**.



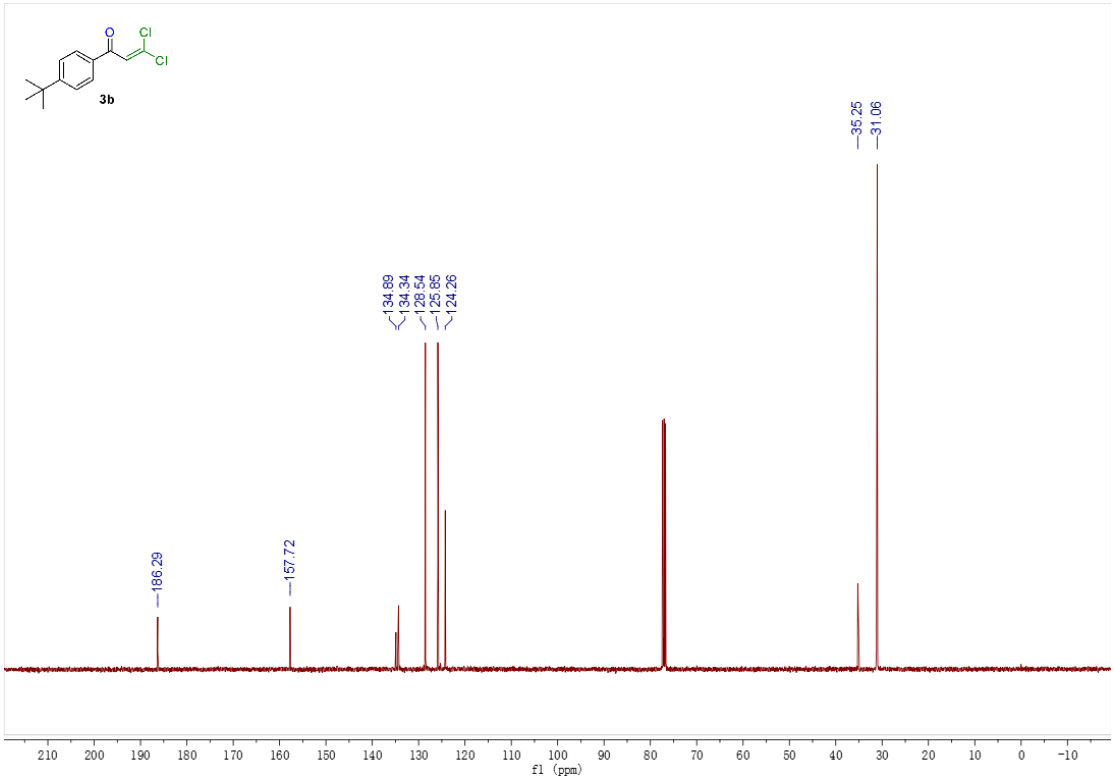
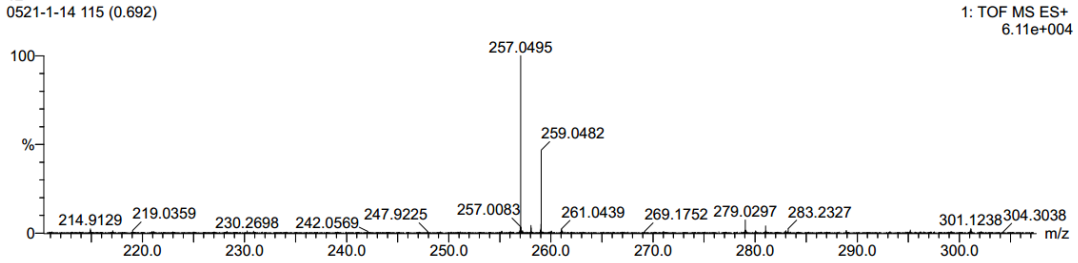


Figure S52. ^{1}H NMR and ^{13}C{^{1}H} NMR of **3b**.

Elemental Composition Report **Page 1**

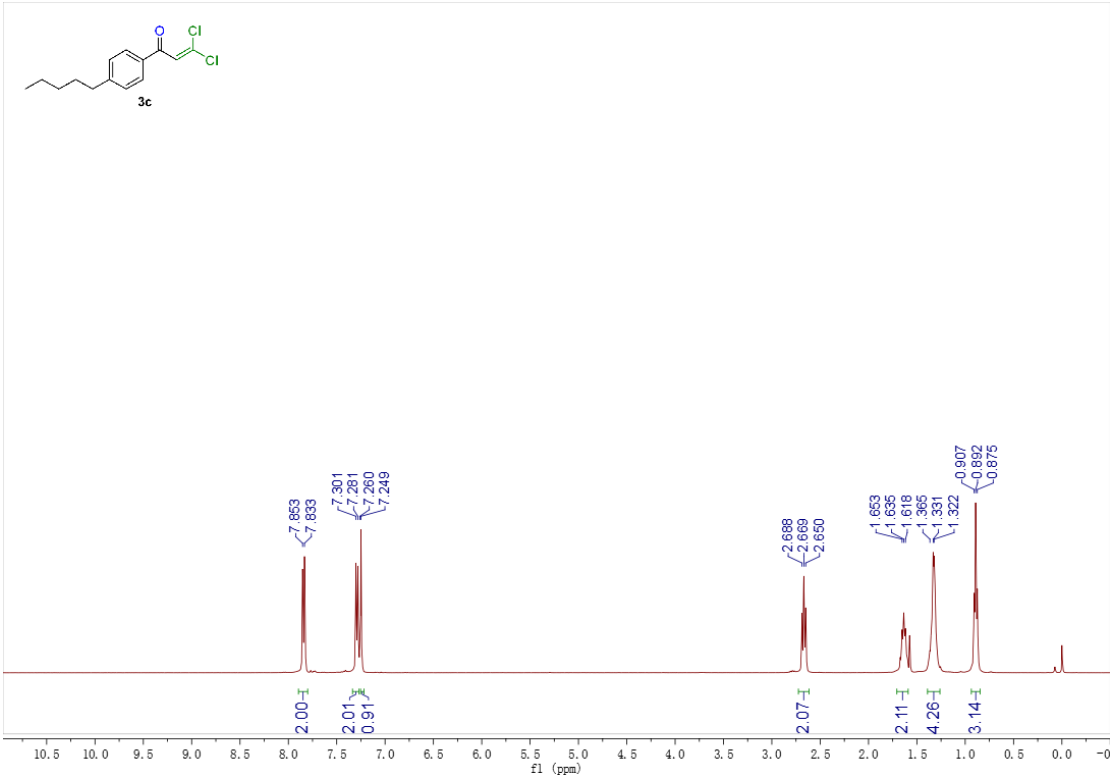
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
199 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 13-13 H: 0-60 N: 0-6 O: 0-20 Cl: 1-3
12
0521-1-14 115 (0.692)



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
257.0495	257.0500	-0.5	-1.9	5.5	1010.0	n/a	n/a	C13 H15 O Cl2

Figure S53. HRMS Spectra of **3b**.



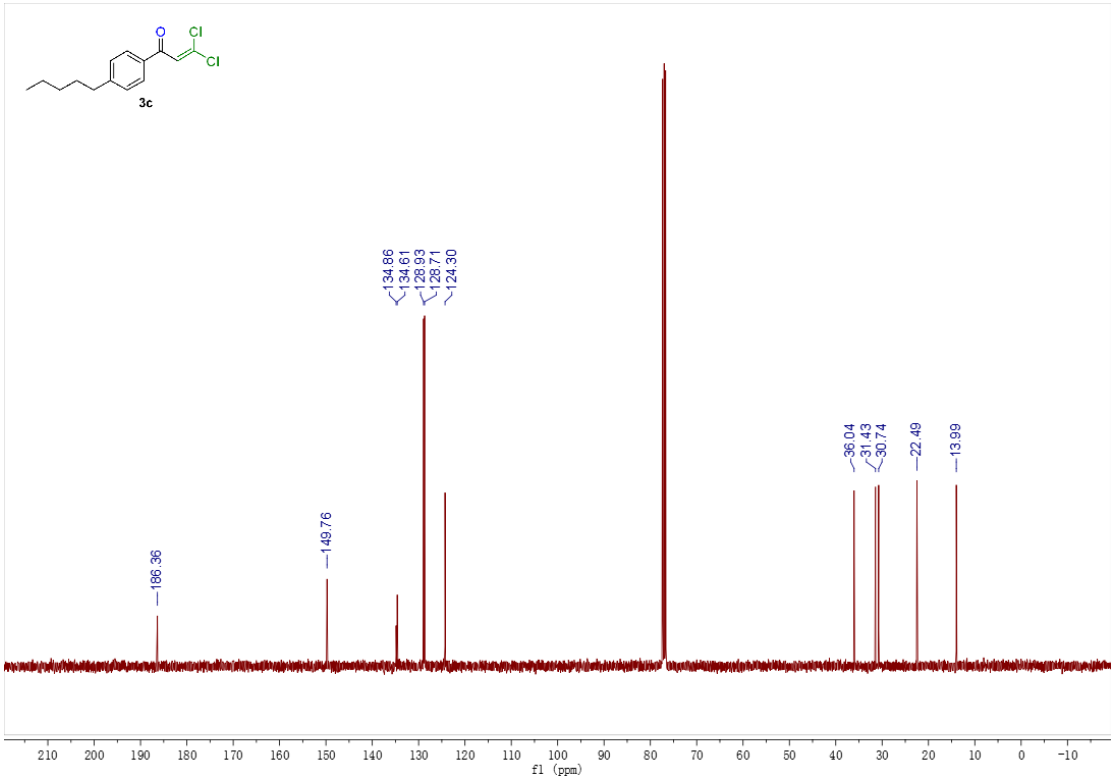


Figure S54. ^{1}H NMR and ^{13}C{^{1}H} NMR of **3c**.

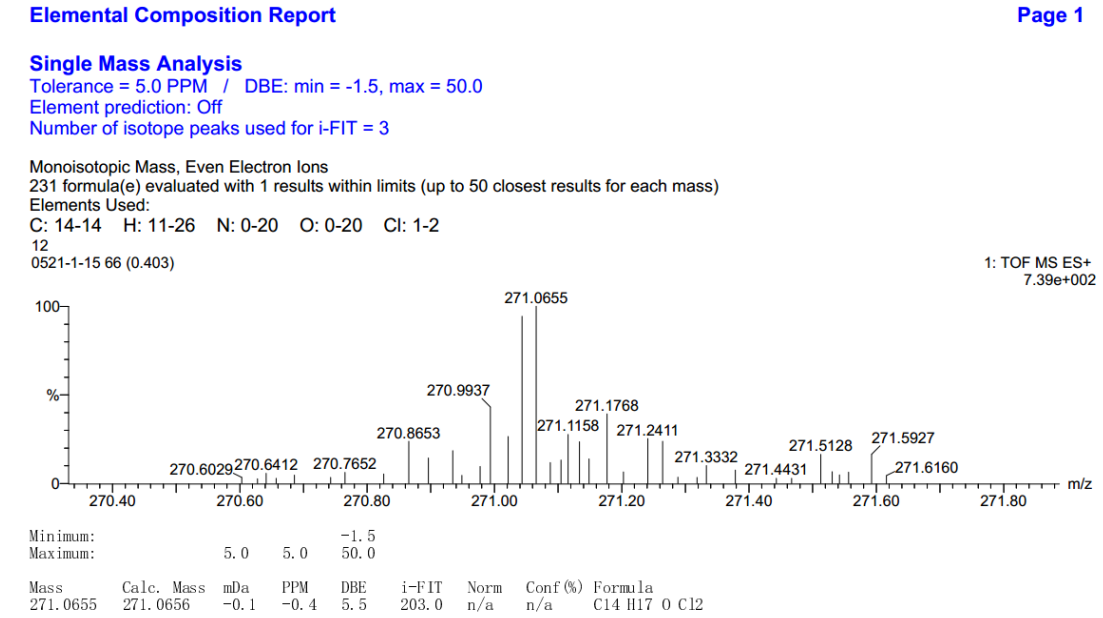


Figure S55. HRMS Spectra of **3c**.

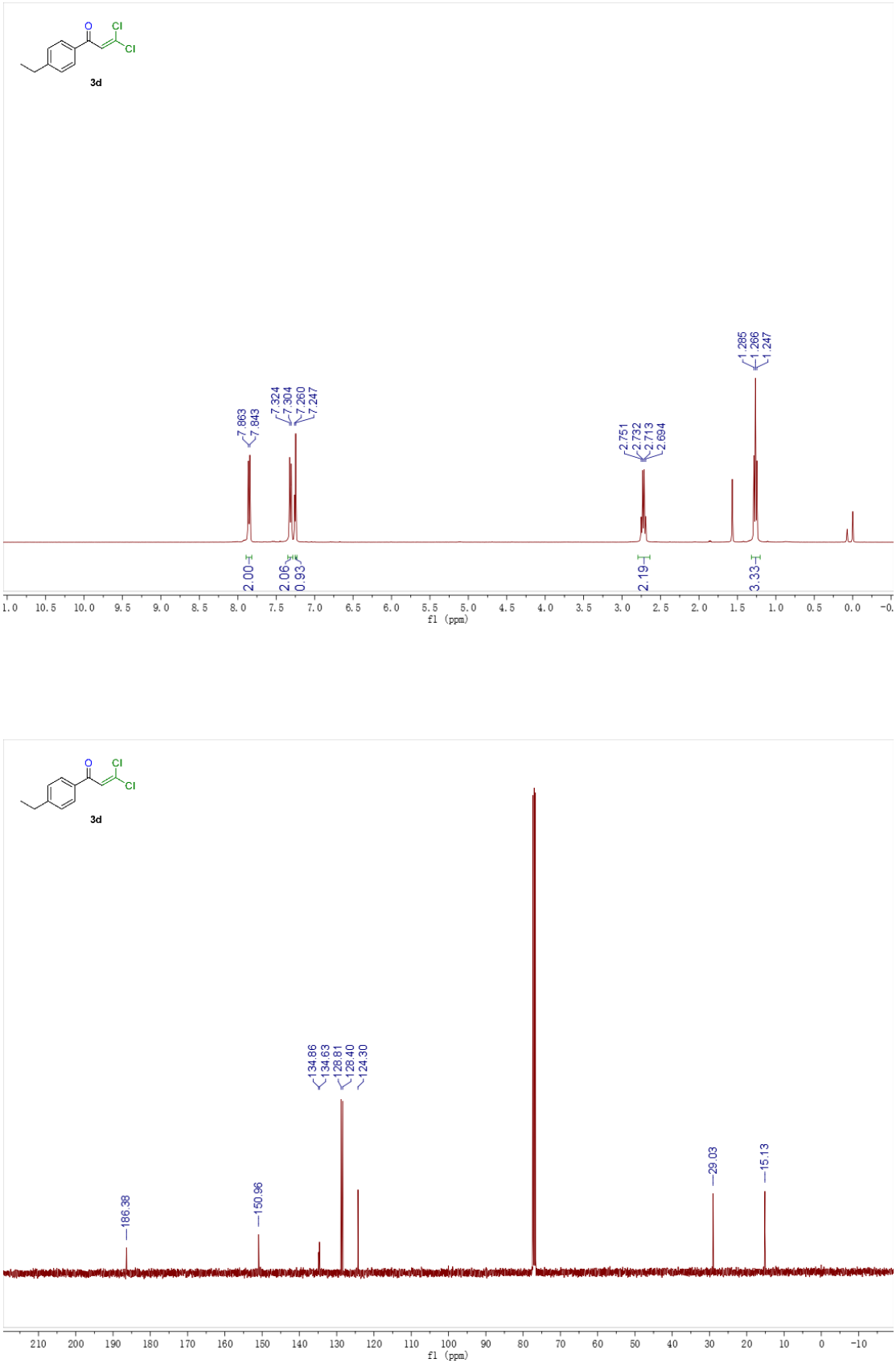
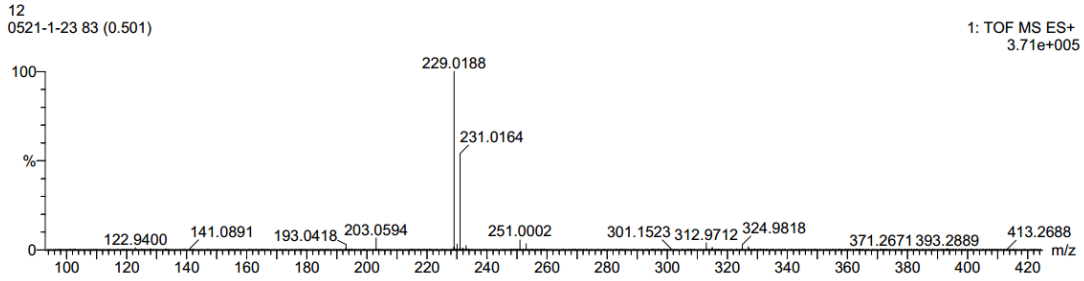


Figure S56. ^{1}H NMR and ^{13}C{^{1}H} NMR of **3d**.

Elemental Composition Report **Page 1**

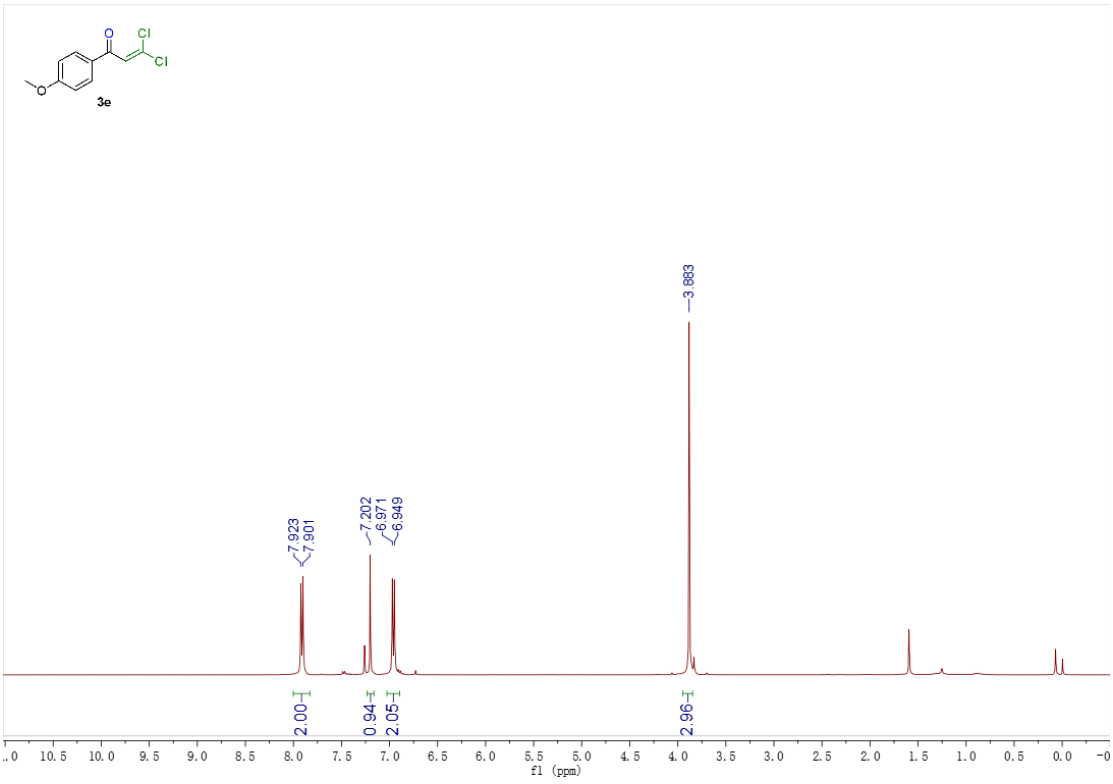
Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
202 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 11-11 H: 0-26 N: 0-20 O: 0-20 Cl: 1-3
12
0521-1-23 83 (0.501)



Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
229.0188	229.0187	0.1	0.4	5.5	1154.3	n/a	n/a	C11 H11 O Cl2

Figure S57. HRMS Spectra of **3d**.



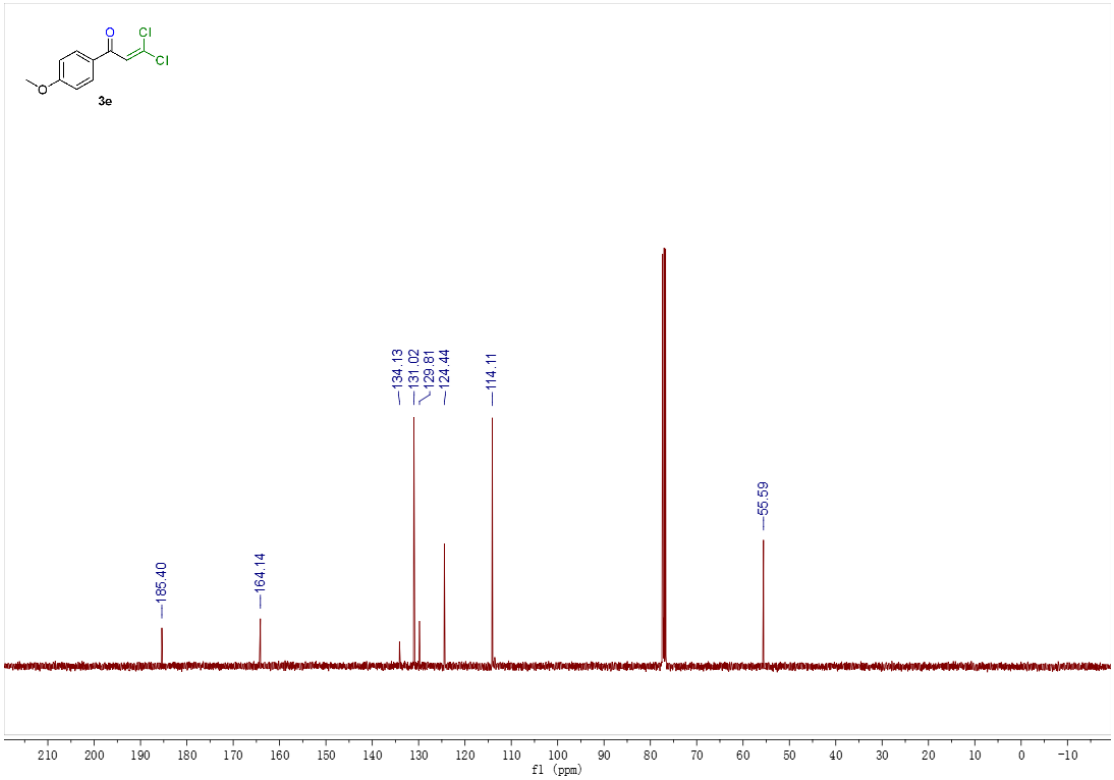


Figure S58. ^{1}H NMR and ^{13}C{^{1}H} NMR of **3e**.

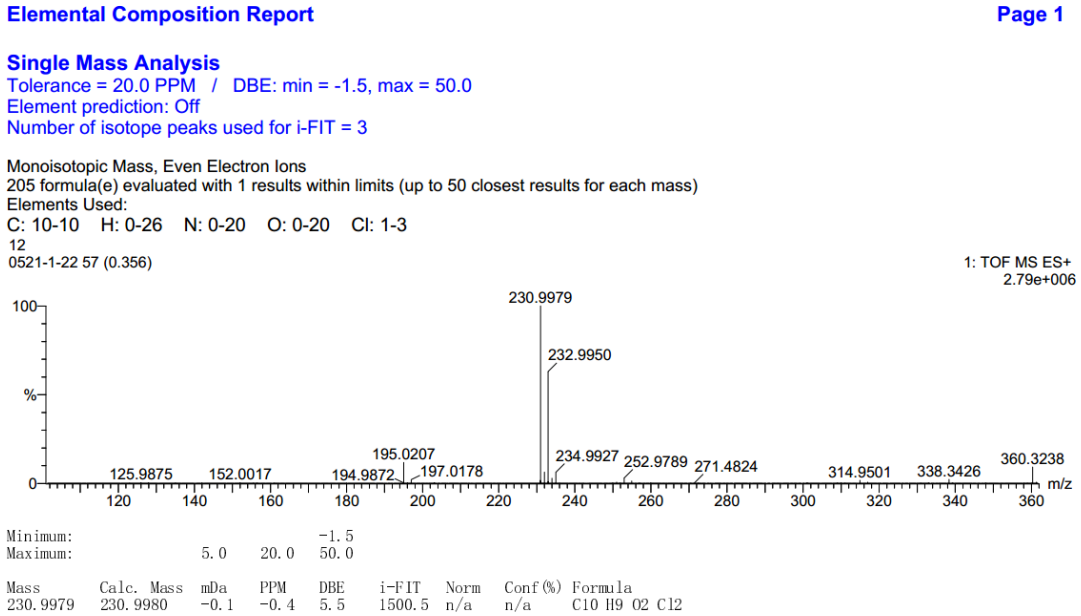
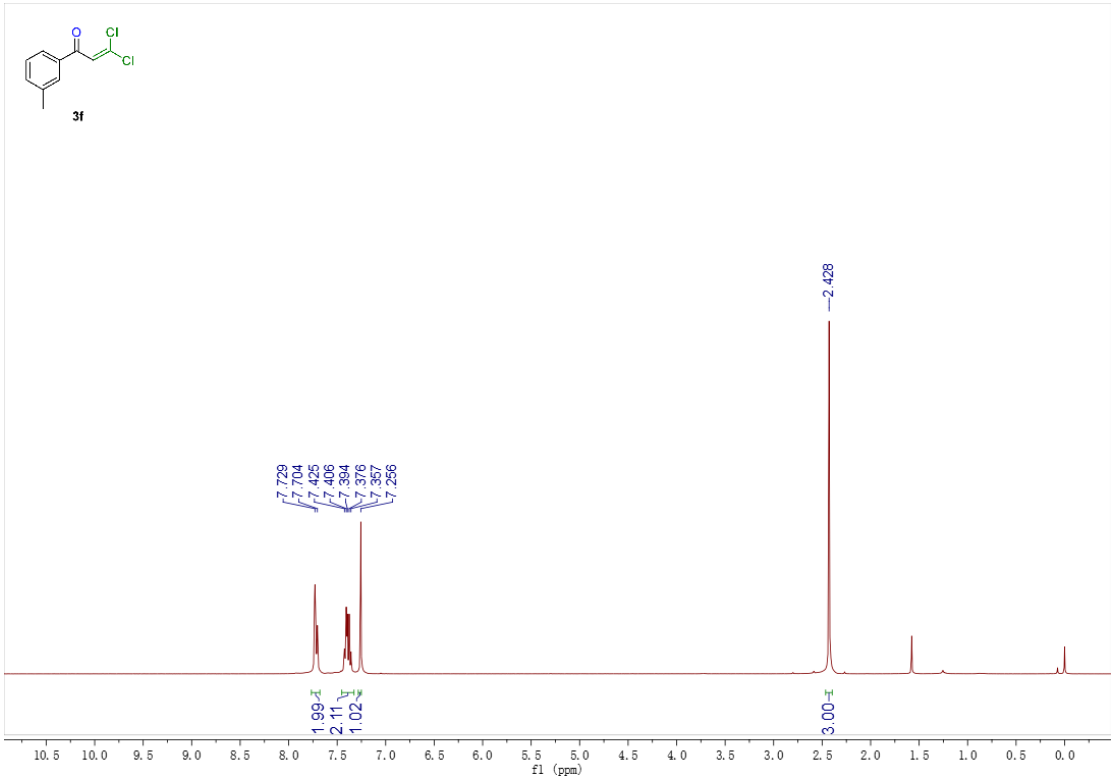


Figure S59. HRMS Spectra of **3e**.



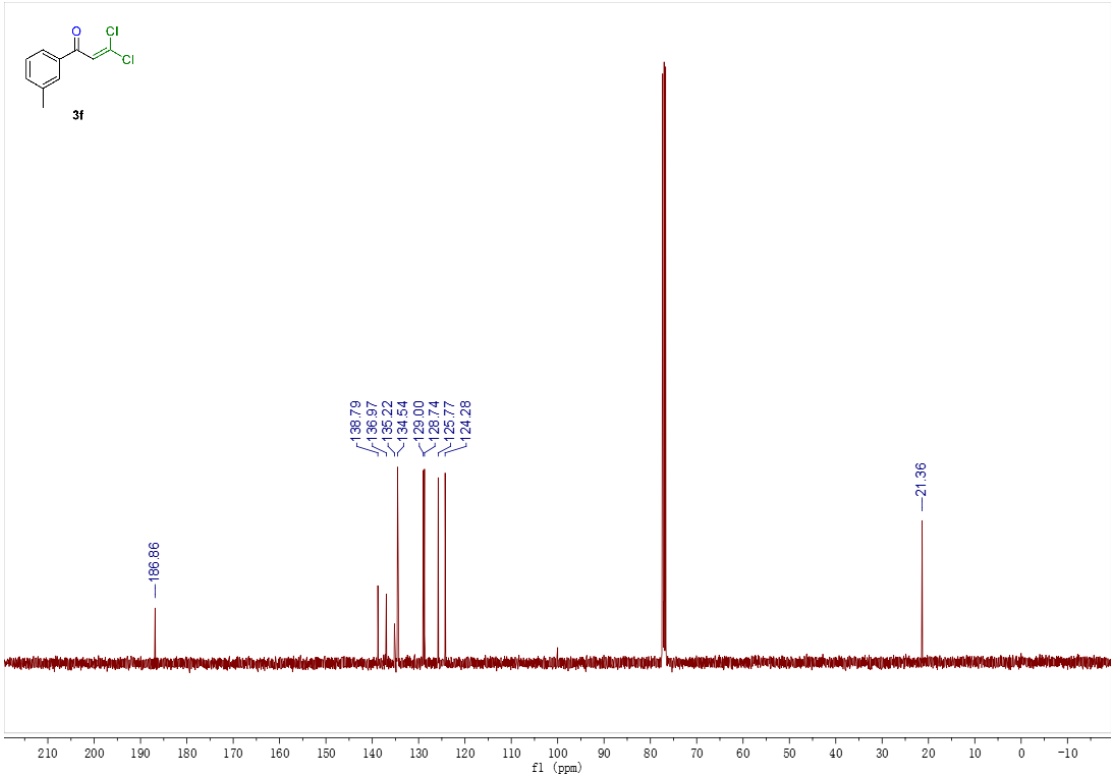
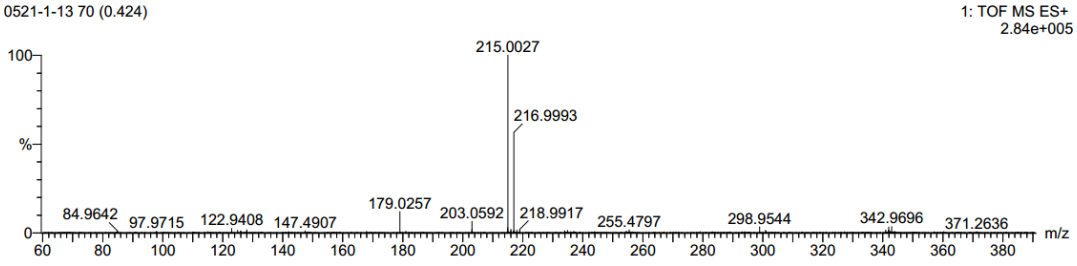


Figure S60. ^{1}H NMR and ^{13}C{^{1}H} NMR of **3f**.

Elemental Composition Report **Page 1**

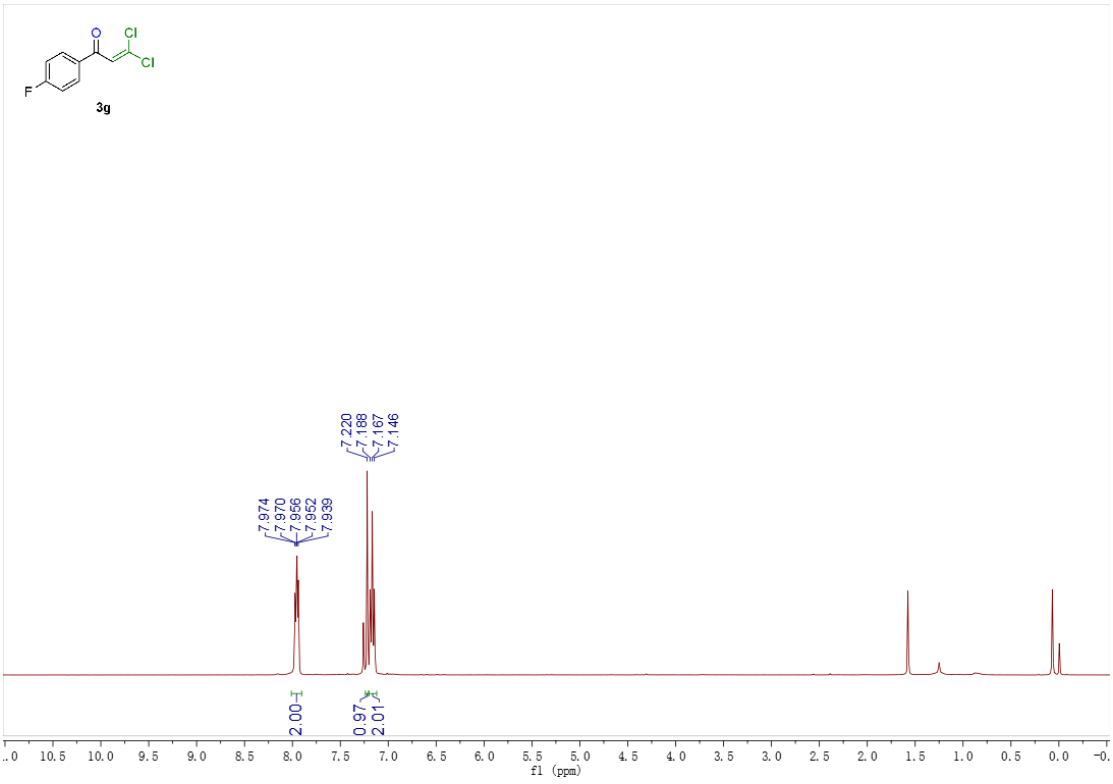
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

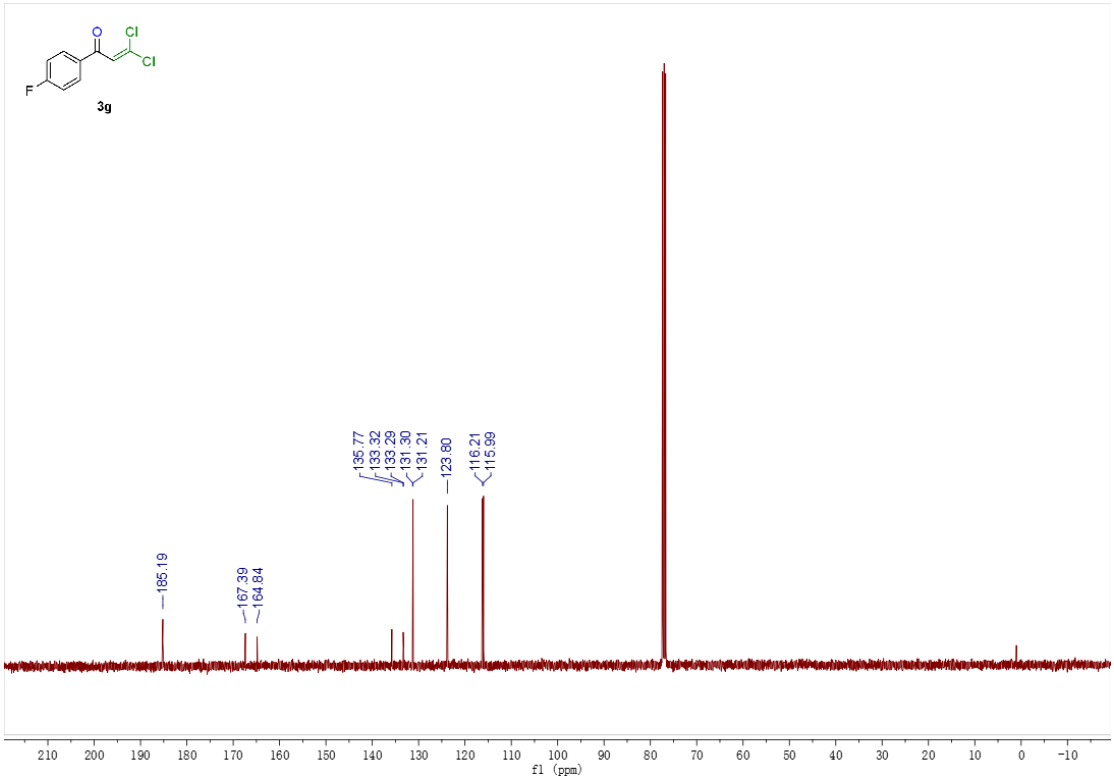
Monoisotopic Mass, Even Electron Ions
143 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 10-10 H: 0-60 N: 0-6 O: 0-20 Cl: 1-3
12
0521-1-13 70 (0.424)



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
215.0027	215.0030	-0.3	-1.4	5.5	1124.7	n/a	n/a	C10 H9 O Cl2

Figure S61. HRMS Spectra of **3f**.





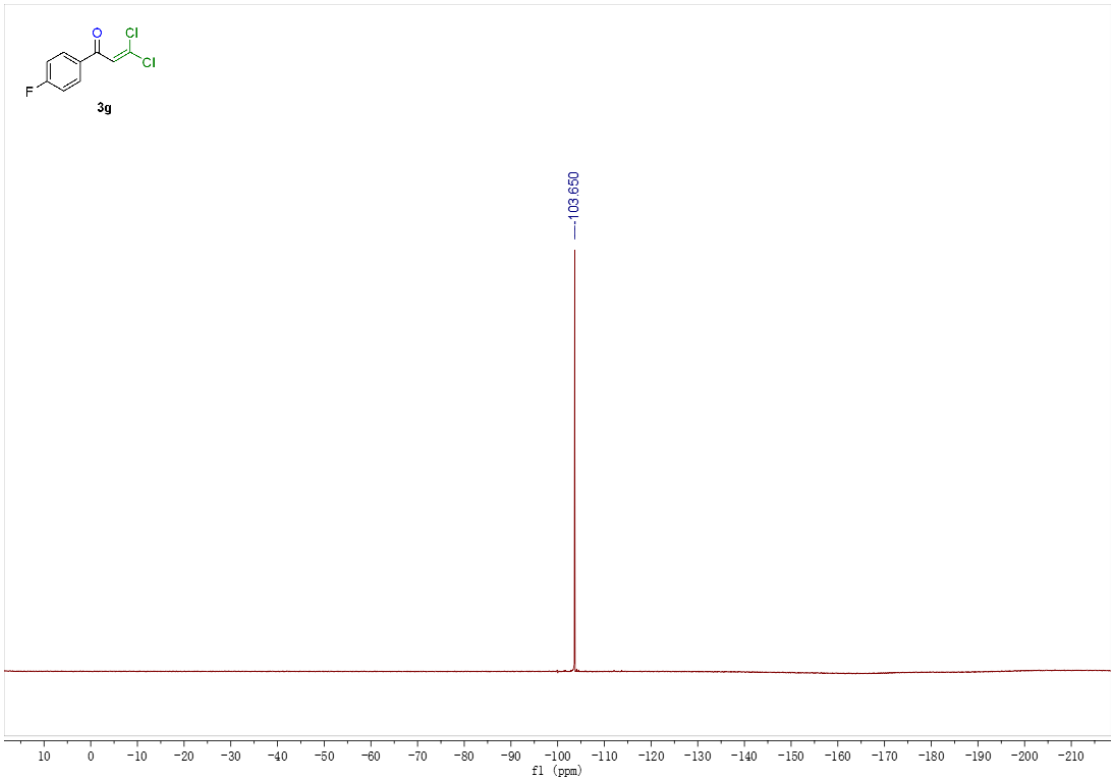


Figure S62. ^{1}H NMR and ^{13}C{^{1}H} NMR and ^{19}F NMR of **3g**.

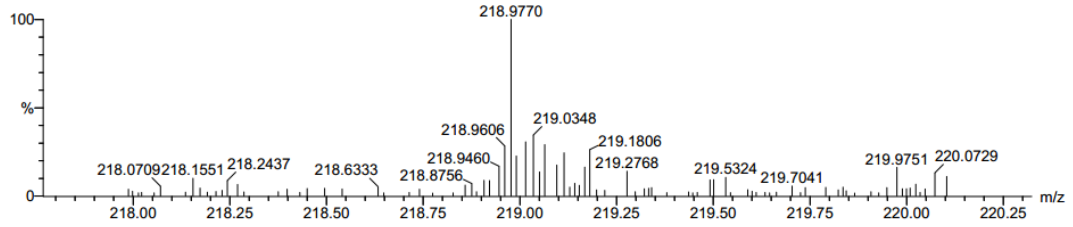
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
335 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 9-9 H: 0-26 N: 0-20 O: 0-20 Cl: 1-3 F: 1-3

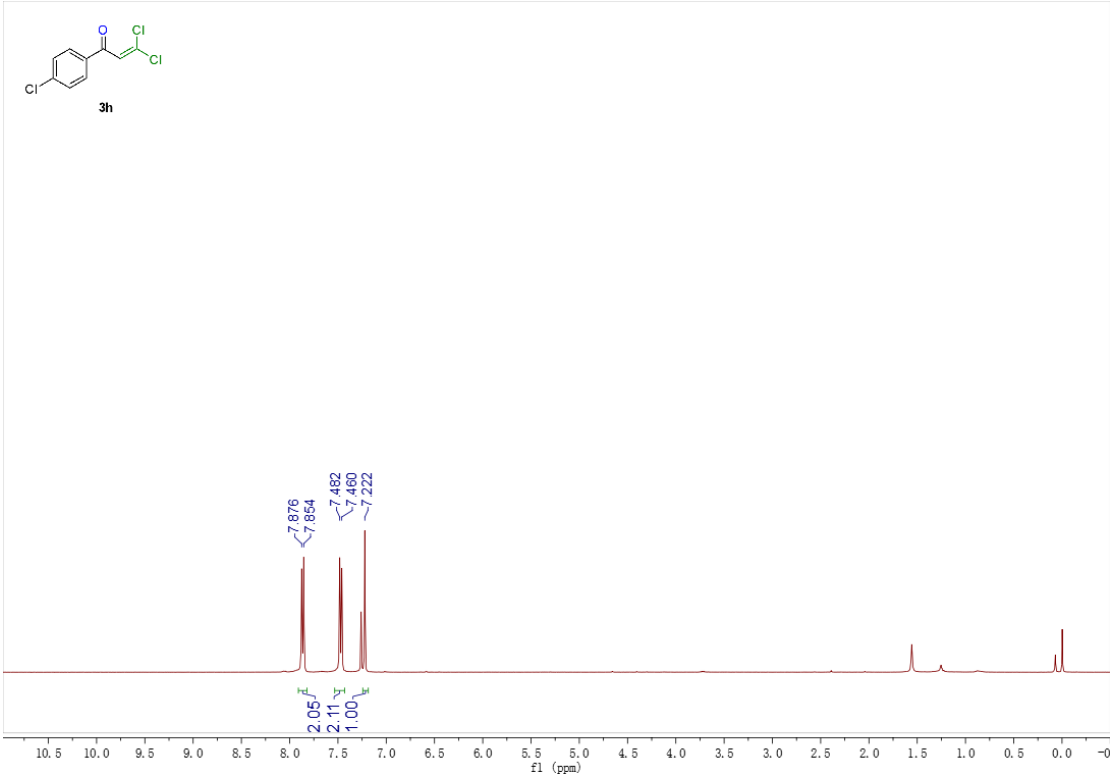
12
0521-1-21 60 (0.372)

1: TOF MS ES+
1.22e+003



Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
218.9770	218.9780	-1.0	-4.6	5.5	457.8	n/a	n/a	C9 H6 O Cl2 F

Figure S63. HRMS Spectra of **3g**.



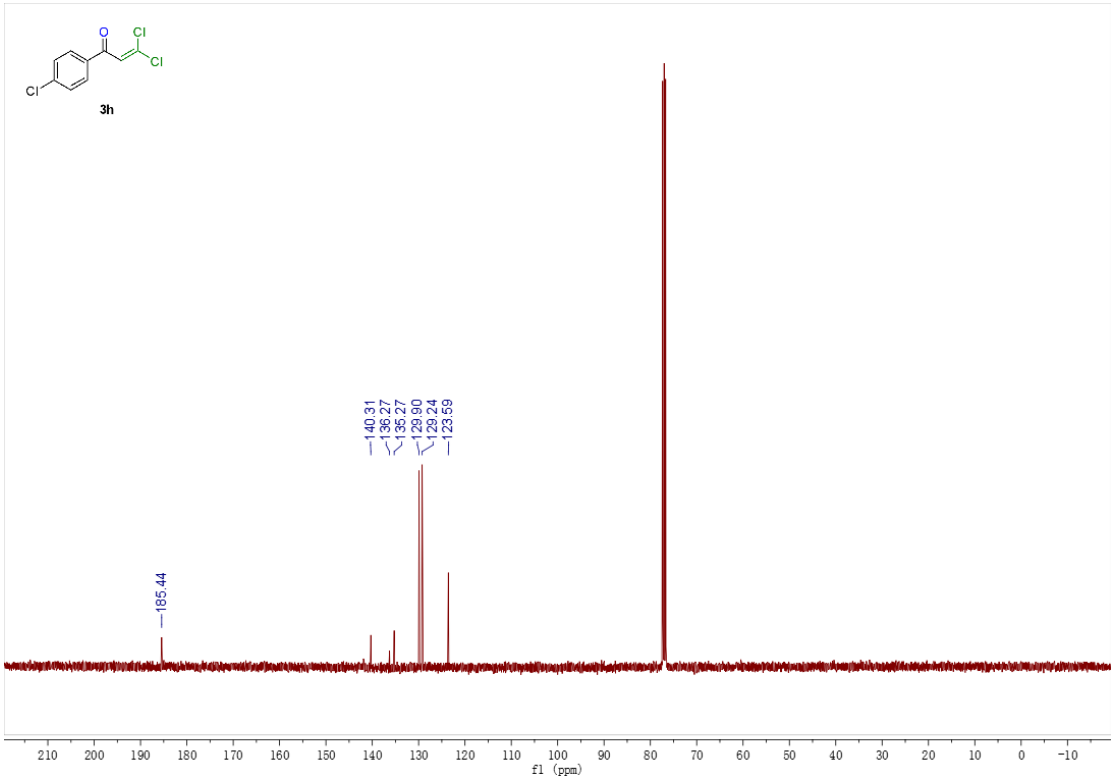


Figure S64. ^{1}H NMR and ^{13}C{^{1}H} NMR of **3h**.

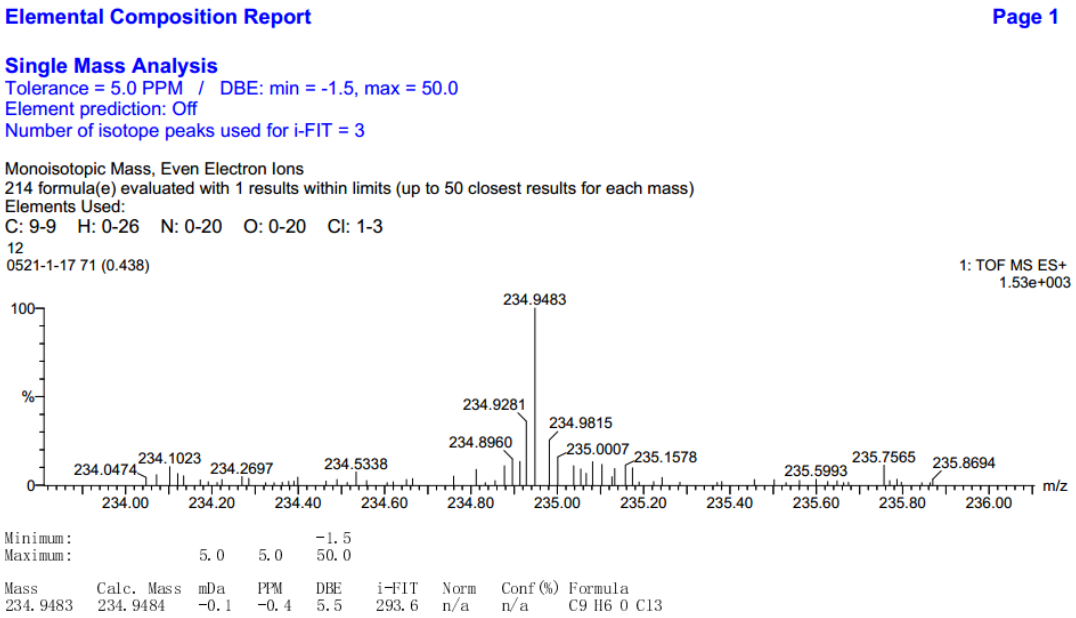


Figure S65. HRMS Spectra of **3h**.

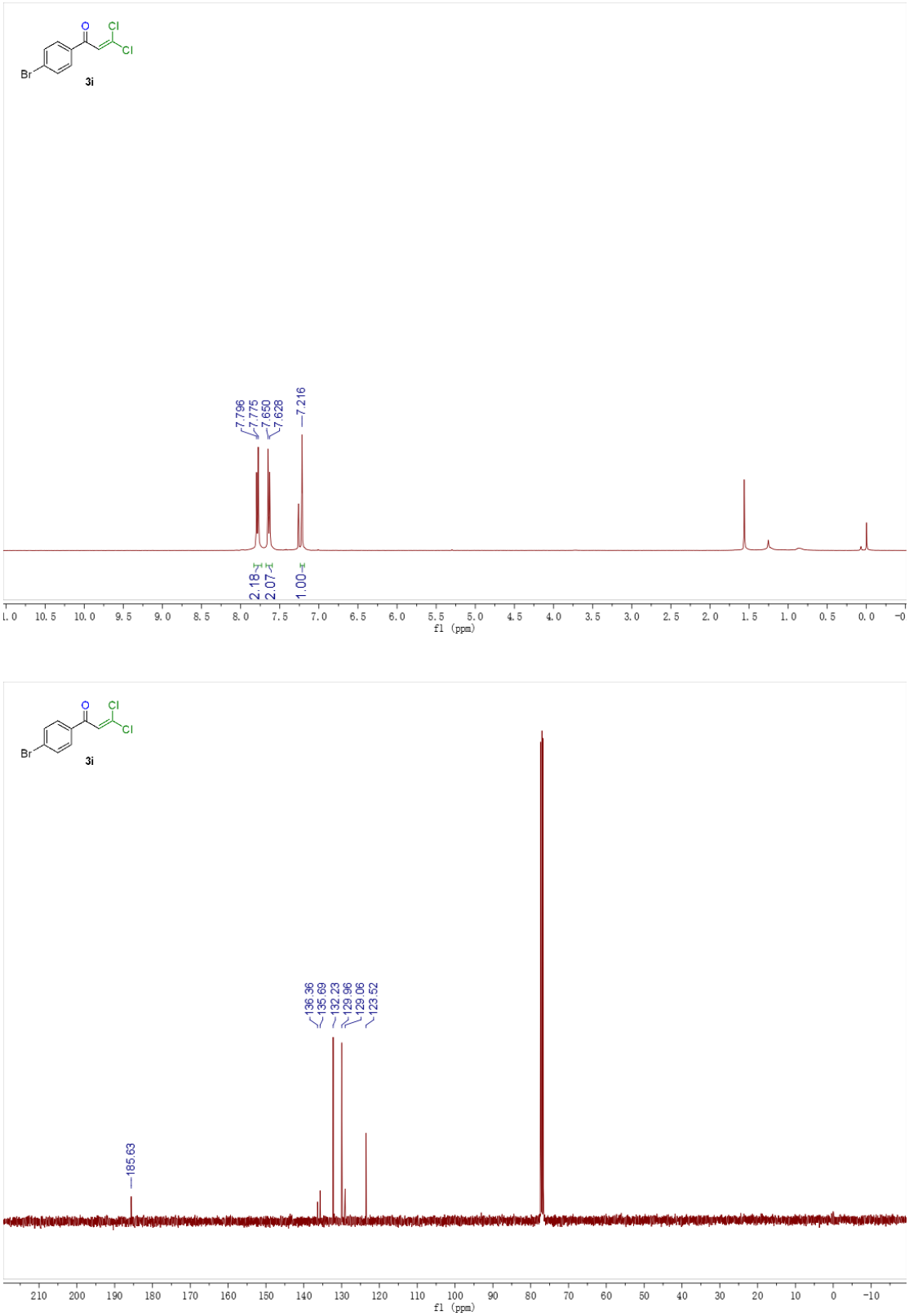


Figure S66. ^{1}H NMR and ^{13}C{^{1}H} NMR of **3i**.

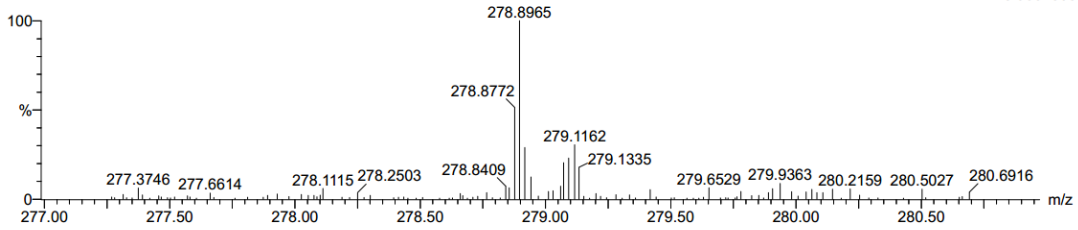
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
179 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 9-9 H: 0-26 N: 0-20 O: 0-20 Cl: 1-3 Br: 1-3

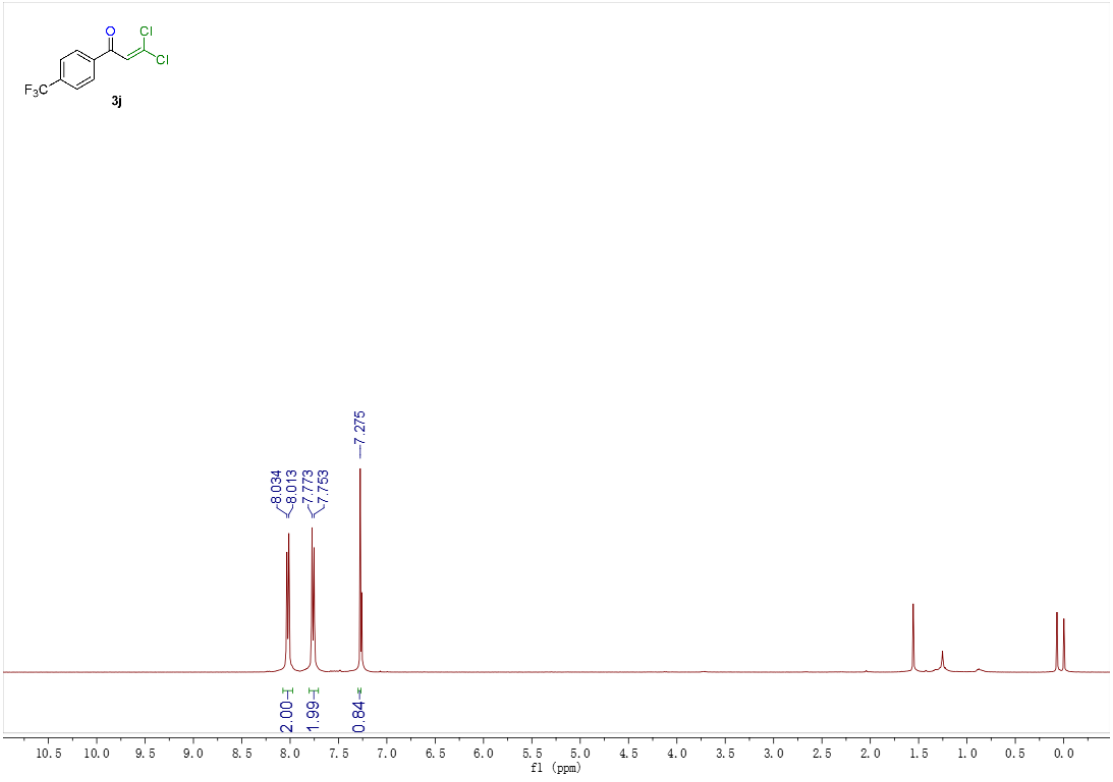
12
0521-1-19 77 (0.469)

1: TOF MS ES+
3.96e+003



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
278.8965	278.8979	-1.4	-5.0	5.5	540.8	n/a	n/a	C9 H6 O Cl2 Br

Figure S67. HRMS Spectra of **3i**.



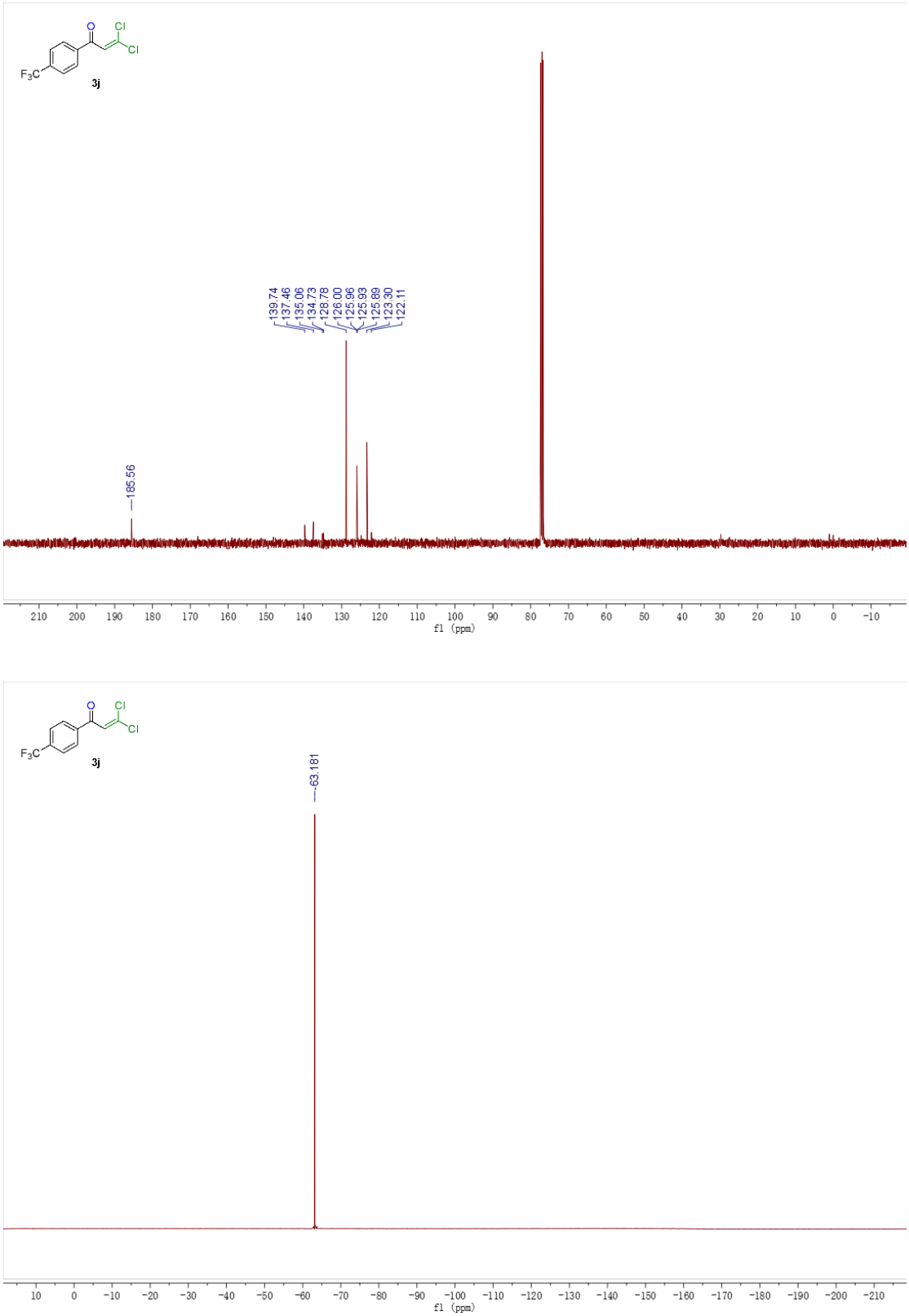


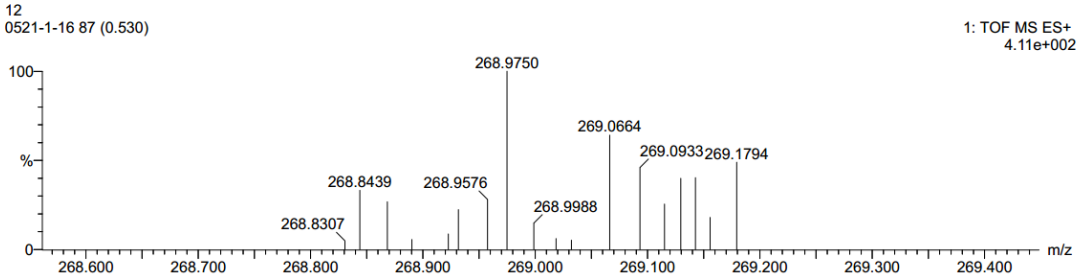
Figure S68. ^{1}H NMR and ^{13}C{^{1}H} NMR and ^{19}F NMR of **3j**.

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

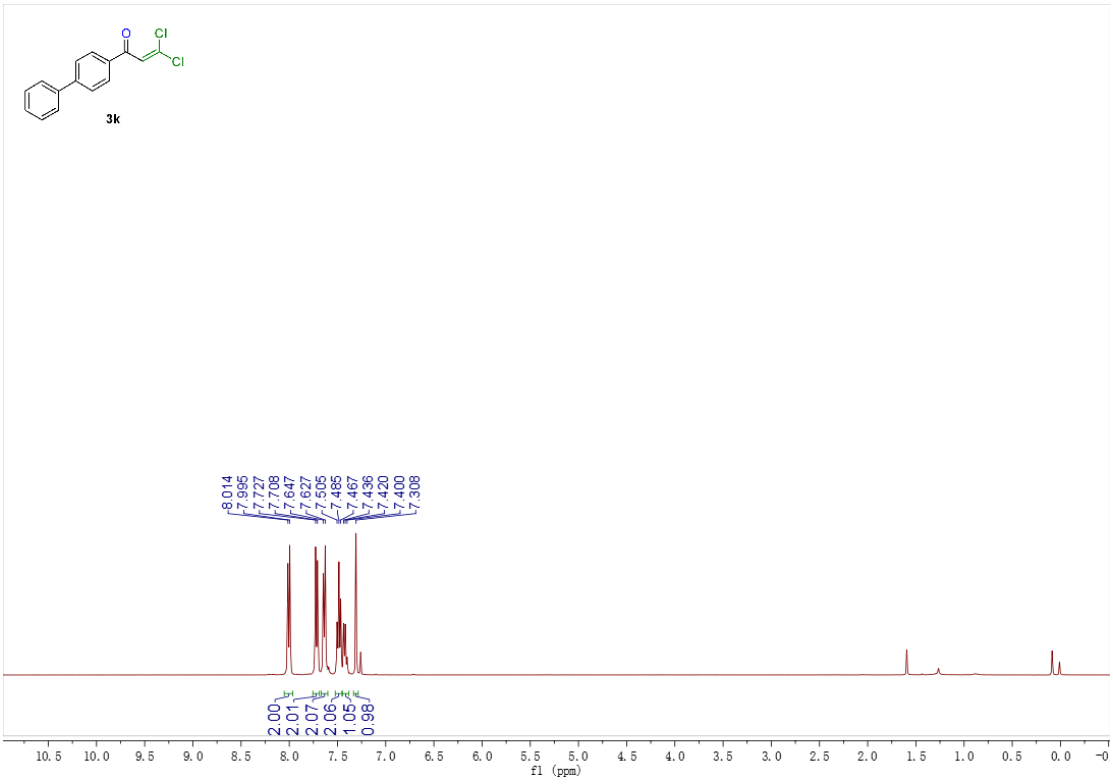
Monoisotopic Mass, Even Electron Ions
296 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 10-10 H: 0-26 N: 0-20 O: 0-20 Cl: 1-2 F: 2-3

12
0521-1-16 87 (0.530)



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
268.9750	268.9748	0.2	0.7	5.5	113.9	n/a	n/a	C10 H6 O Cl2 F3

Figure S69. HRMS Spectra of **3j**.



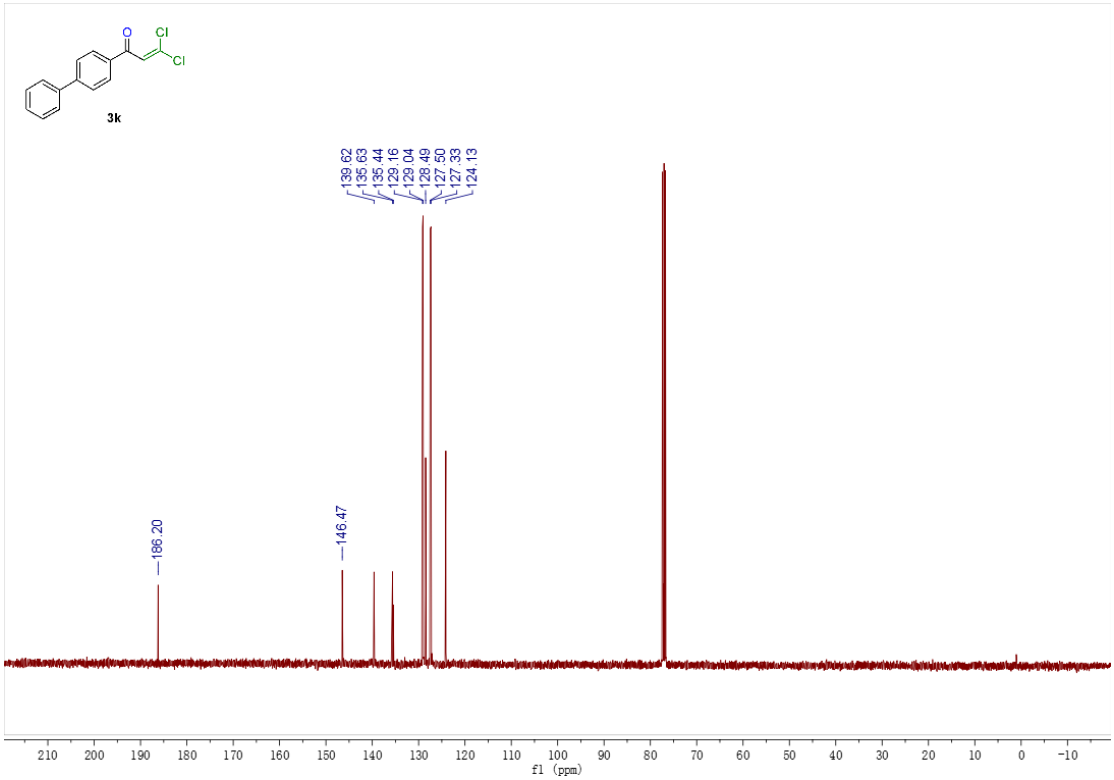


Figure S70. ^{1}H NMR and ^{13}C{^{1}H} NMR of **3k**.

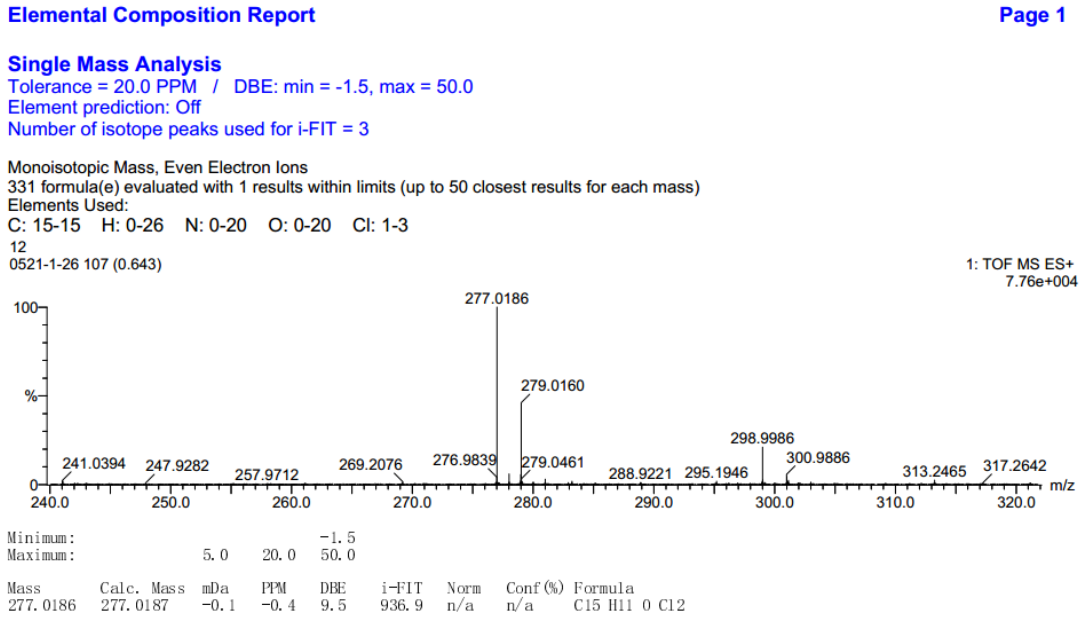


Figure S71. HRMS Spectra of **3k**.

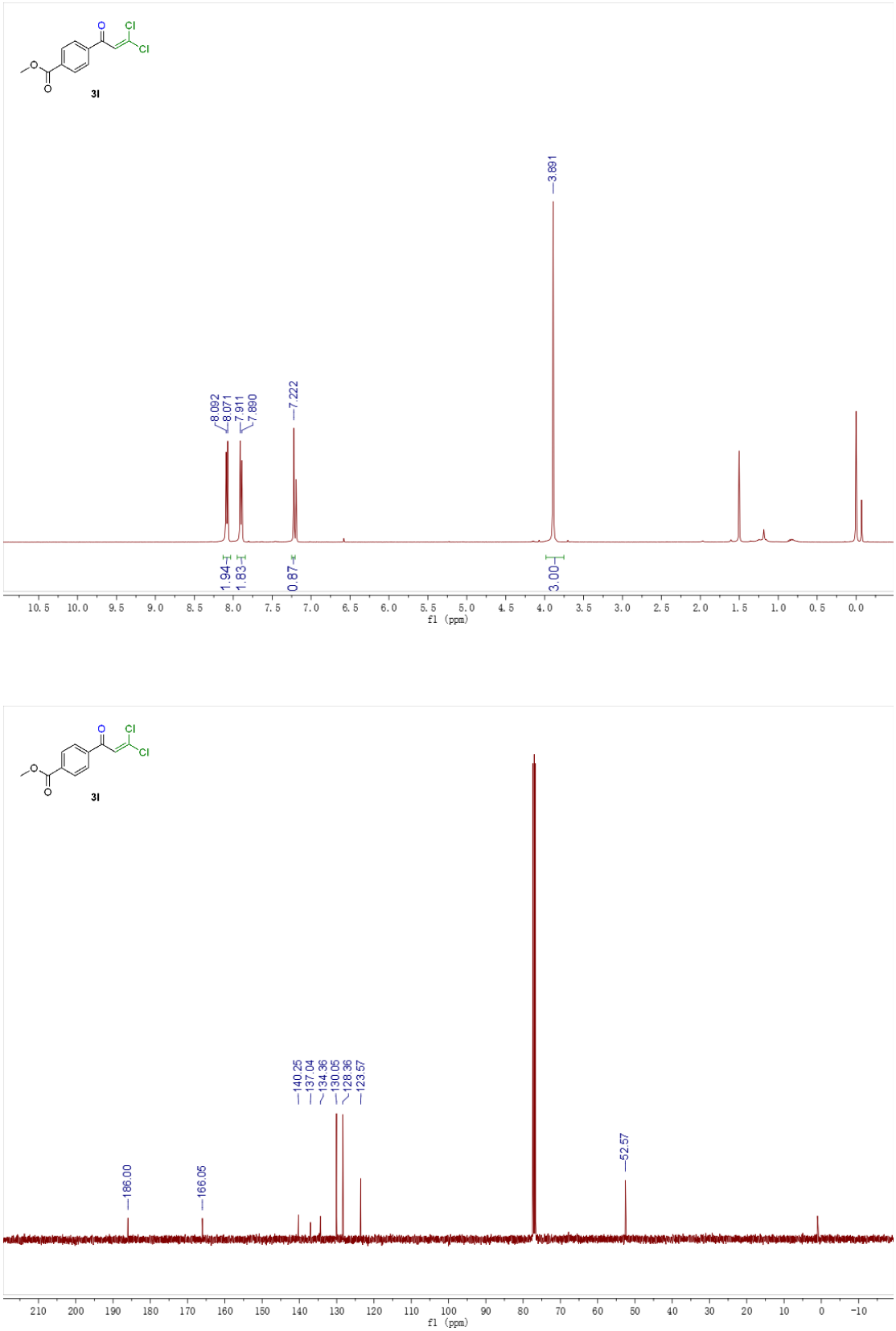


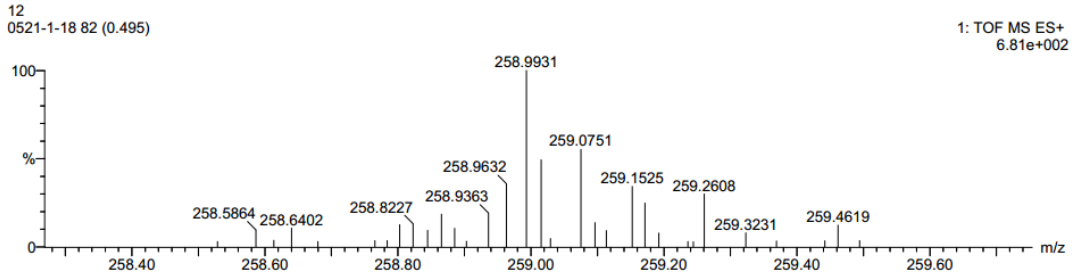
Figure S72. ^{1}H NMR and ^{13}C{^{1}H} NMR of **3l**.

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

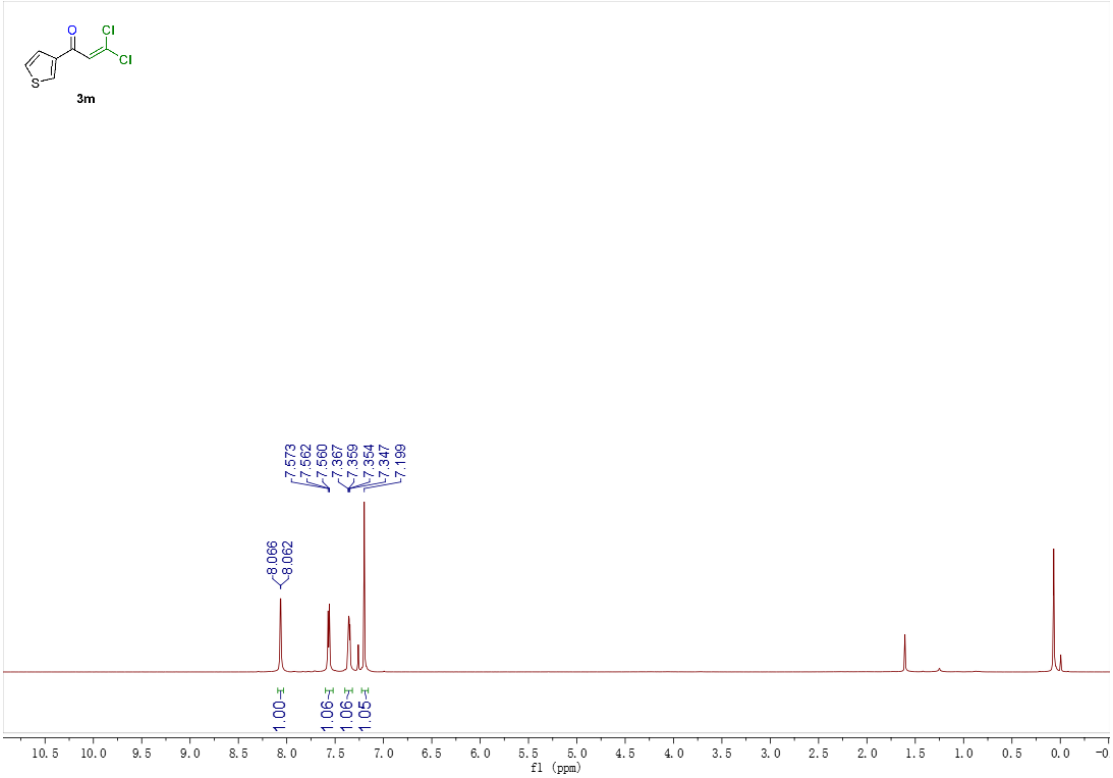
Monoisotopic Mass, Even Electron Ions
272 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 11-11 H: 0-26 N: 0-20 O: 0-20 Cl: 1-3

12
0521-1-18 82 (0.495)



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
258.9931	258.9929	0.2	0.8	6.5	159.2	n/a	n/a	C11 H9 O3 Cl2

Figure S73. HRMS Spectra of **3l**.



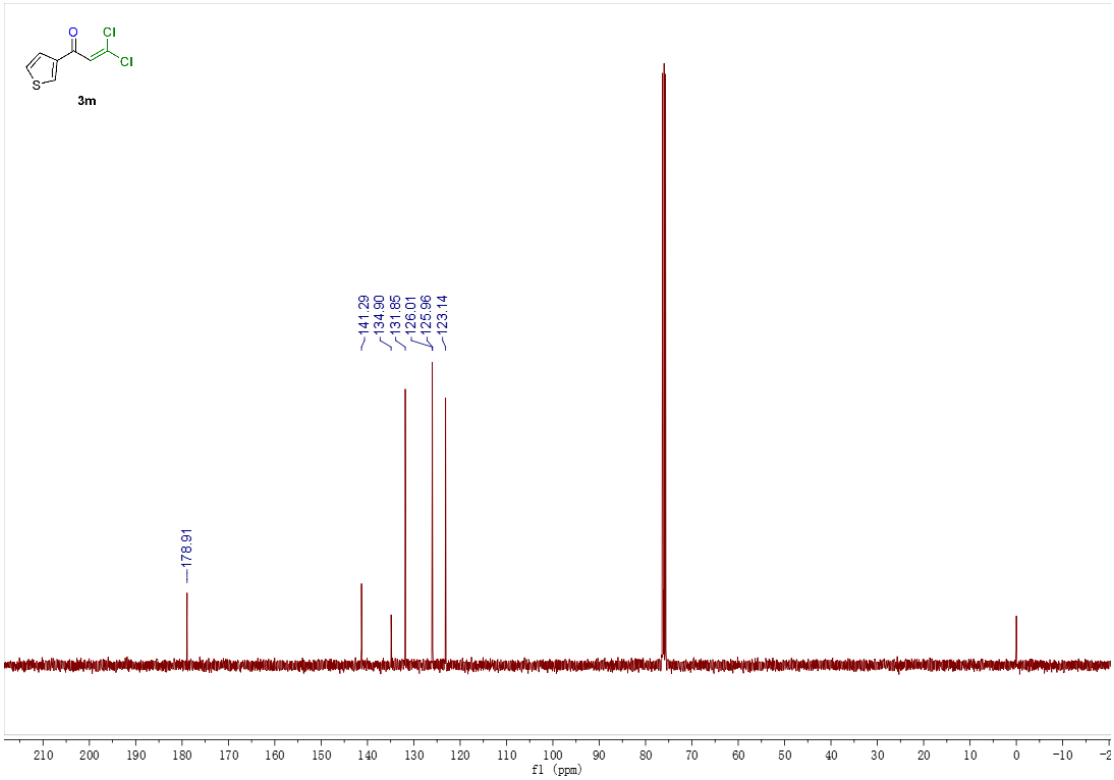


Figure S74. ^{1}H NMR and ^{13}C{^{1}H} NMR of **3m**.

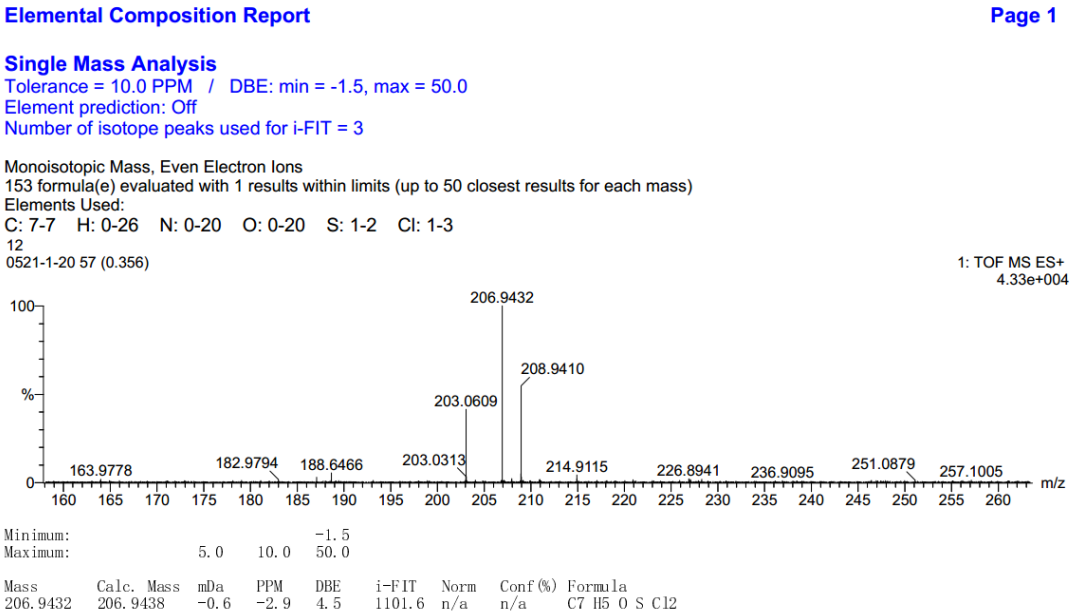
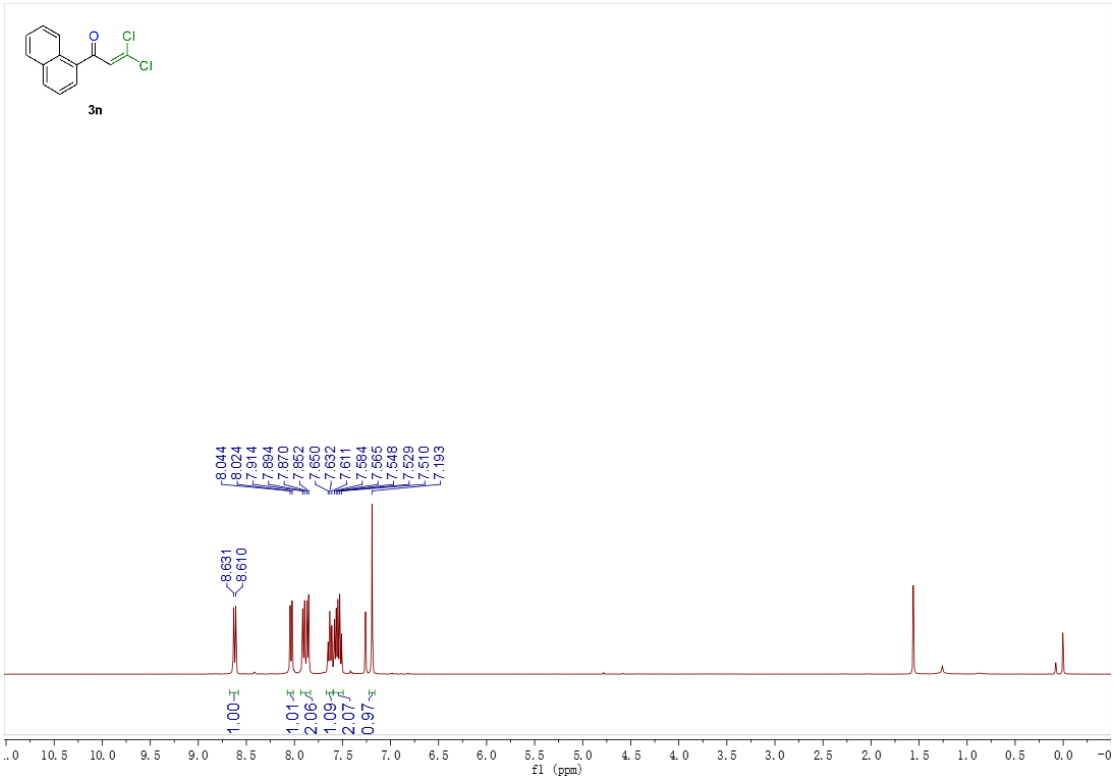


Figure S75. HRMS Spectra of **3m**.



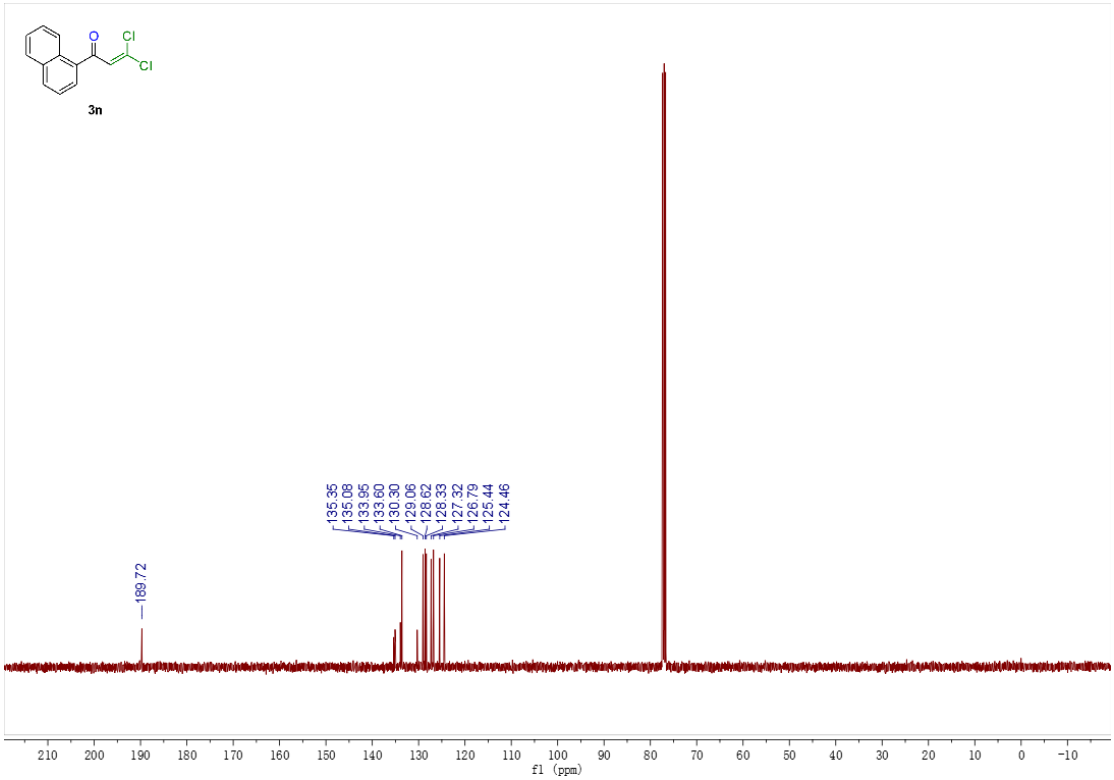
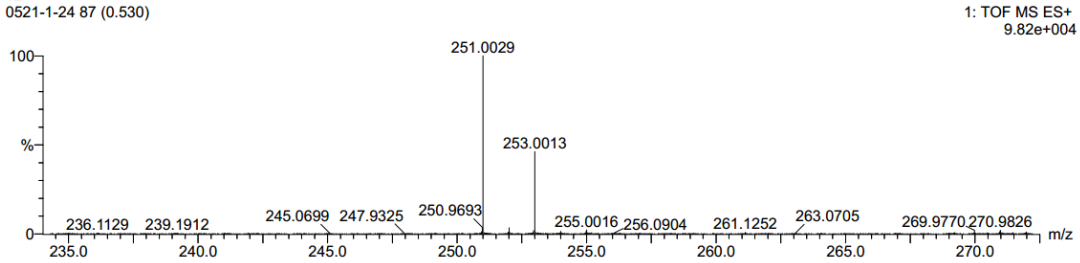


Figure S76. ^{1}H NMR and ^{13}C{^{1}H} NMR of **3n**.

Elemental Composition Report **Page 1**

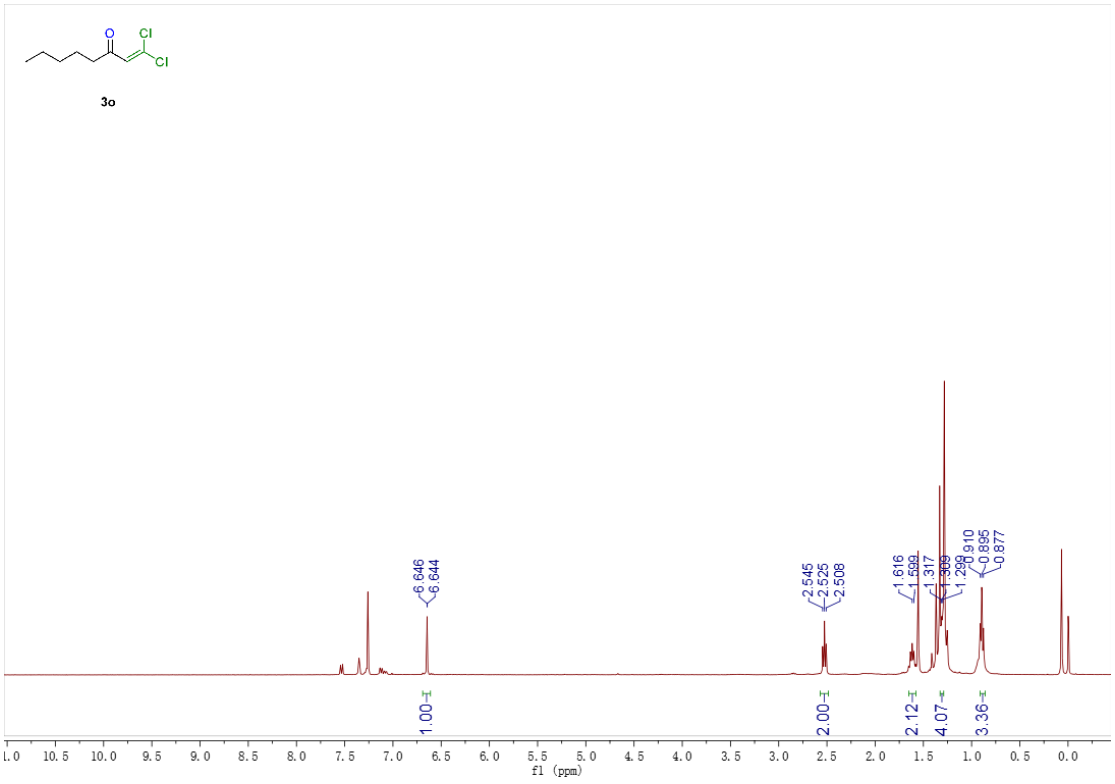
Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
257 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 13-13 H: 0-26 N: 0-20 O: 0-20 Cl: 1-3
12
0521-1-24 87 (0.530)



Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
251.0029	251.0030	-0.1	-0.4	8.5	958.5	n/a	n/a	C13 H9 O Cl2

Figure S77. HRMS Spectra of **3n**.



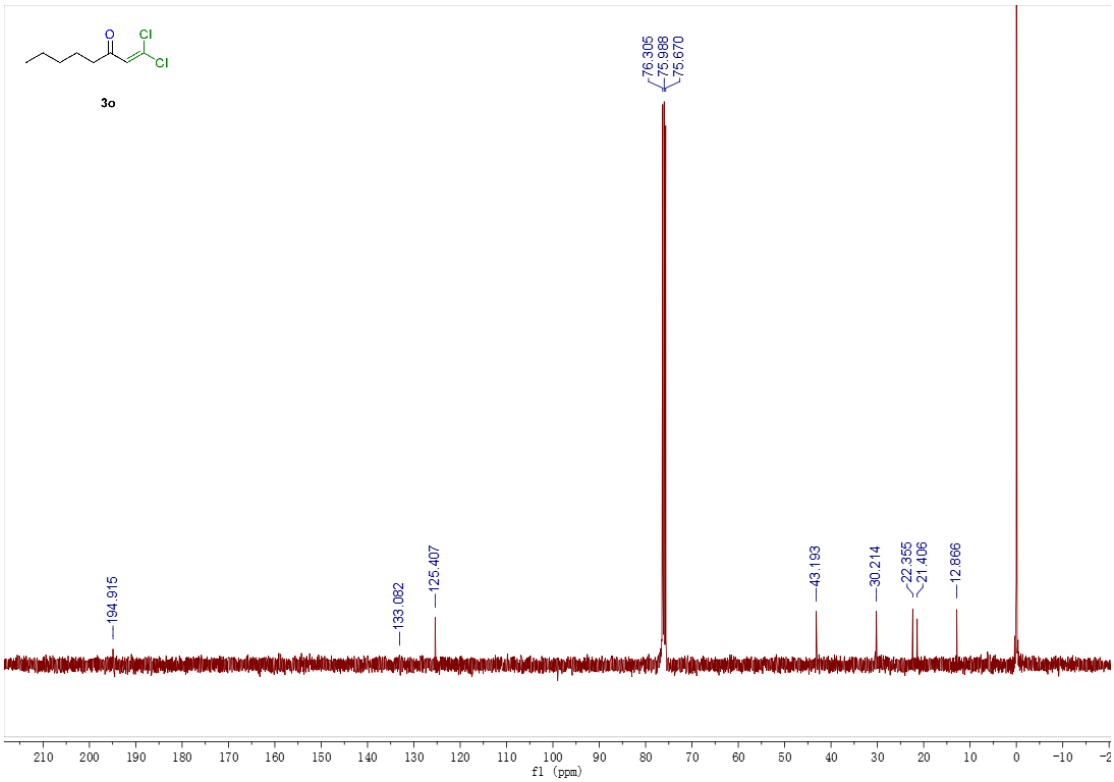


Figure S78. ^{1}H NMR and ^{13}C{^{1}H} NMR of **3o**.

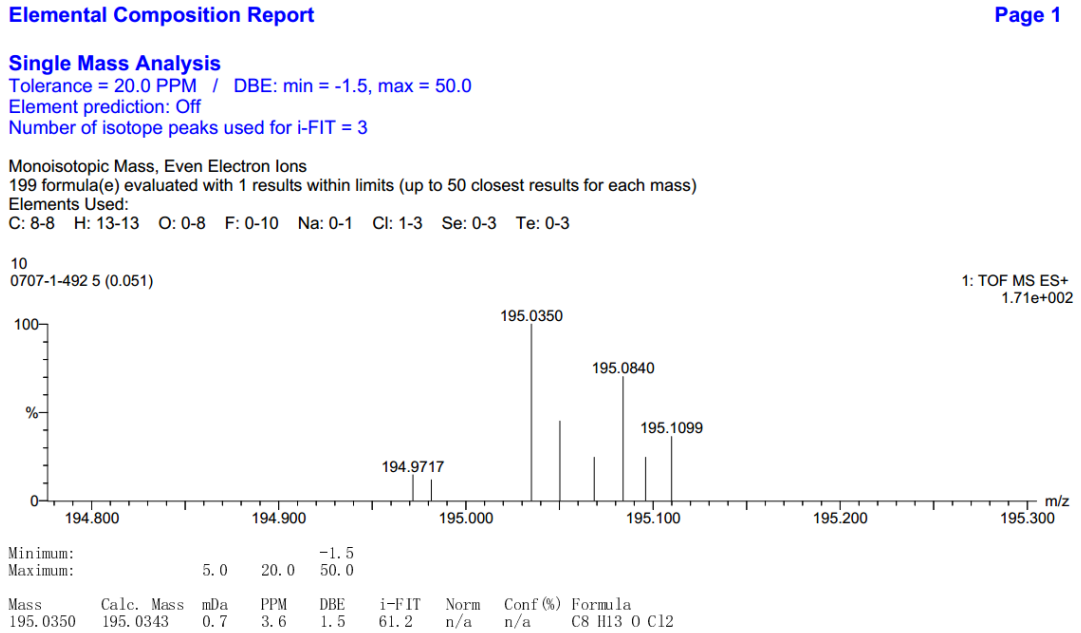


Figure S79. HRMS Spectra of **3o**.

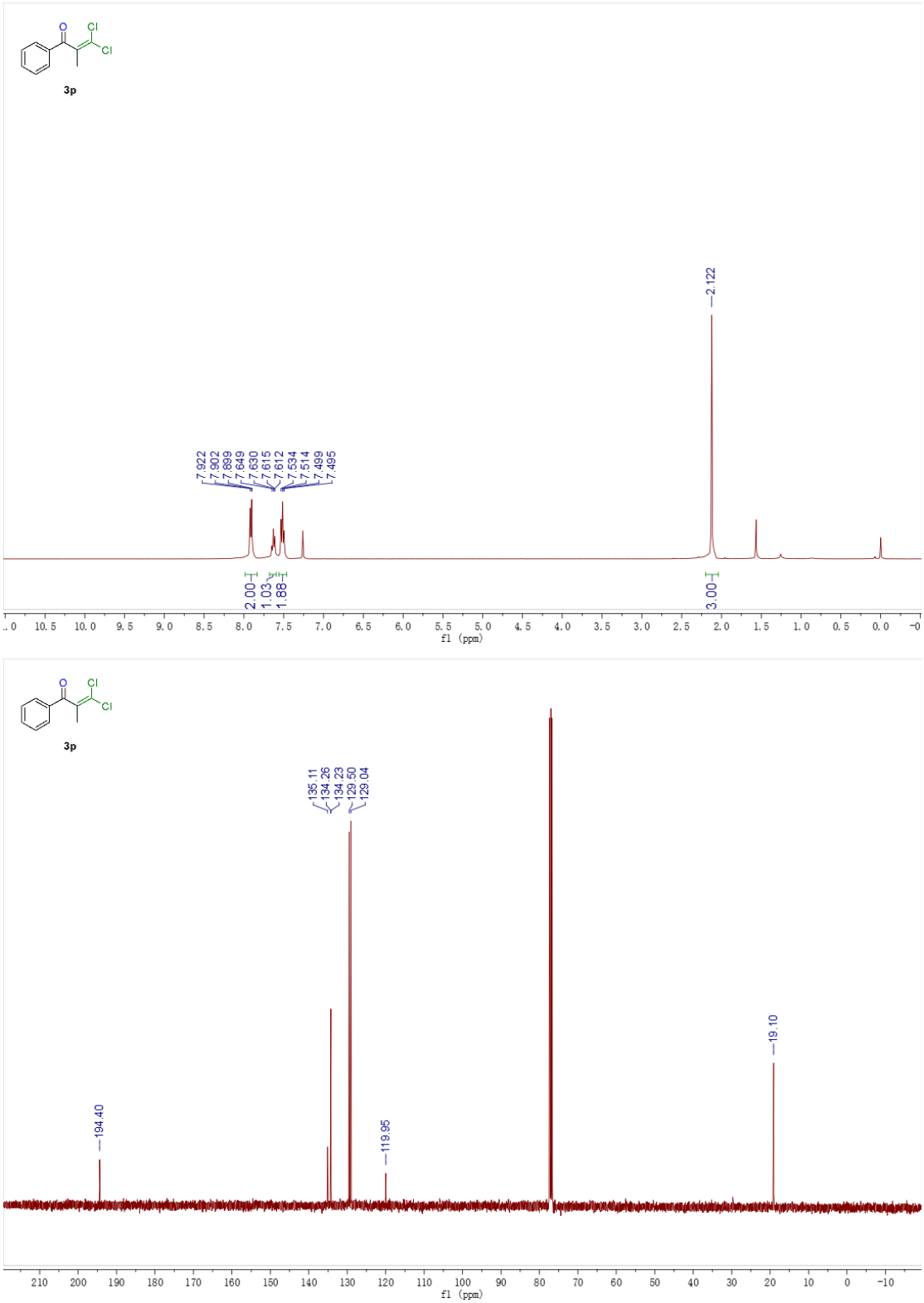
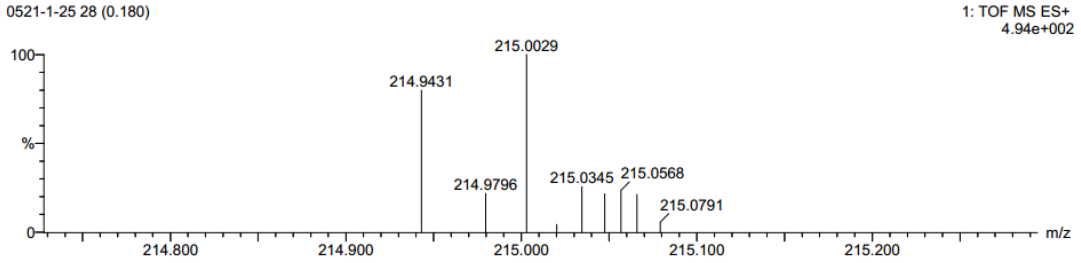


Figure S80. ^{1}H NMR and ^{13}C{^{1}H} NMR of **3p**.

Elemental Composition Report **Page 1**

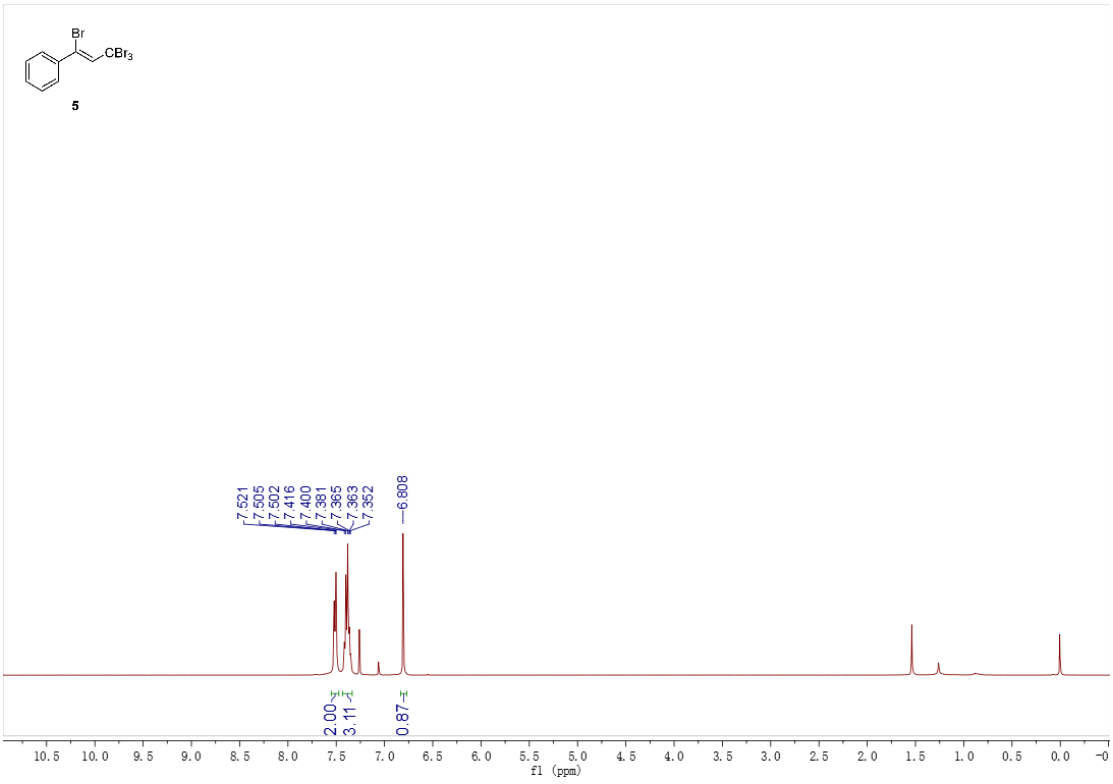
Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
171 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 10-10 H: 0-26 N: 0-20 O: 0-20 Cl: 1-3
12
0521-1-25 28 (0.180)



Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
215.0029	215.0030	-0.1	-0.5	5.5	72.9	n/a	n/a	C10 H9 0 C12

Figure S81. HRMS Spectra of **3p**.



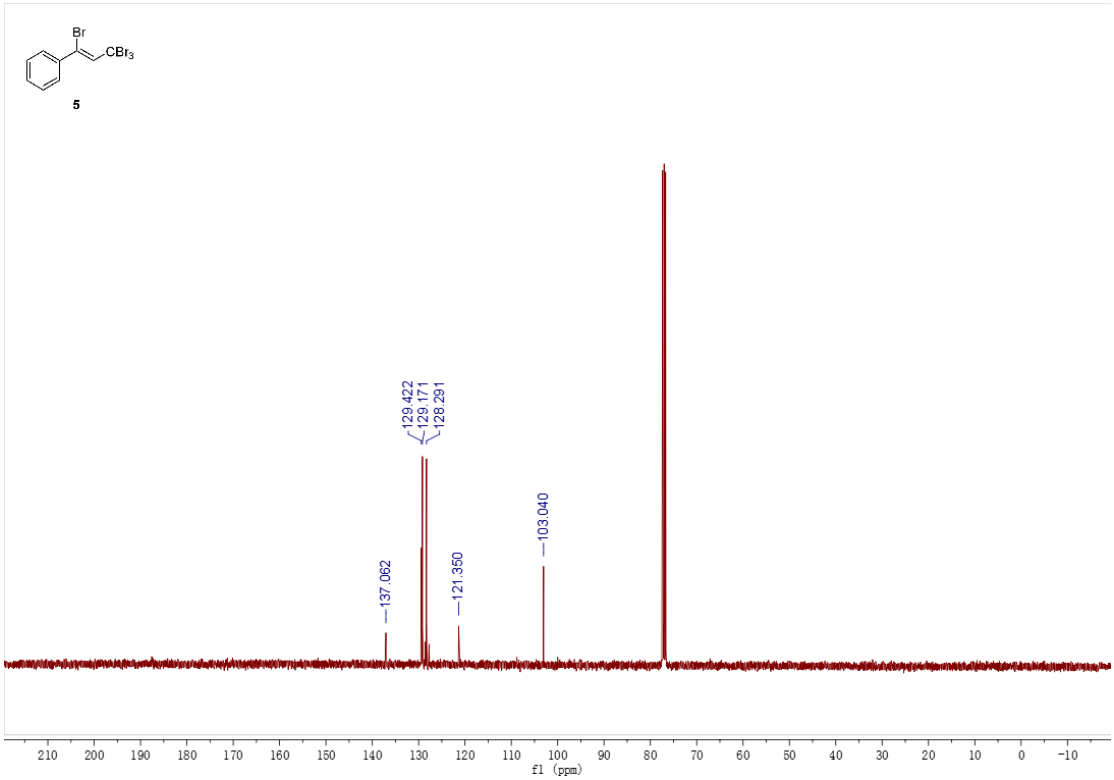


Figure S82. ^{1}H NMR and ^{13}C{^{1}H} NMR of **5**.

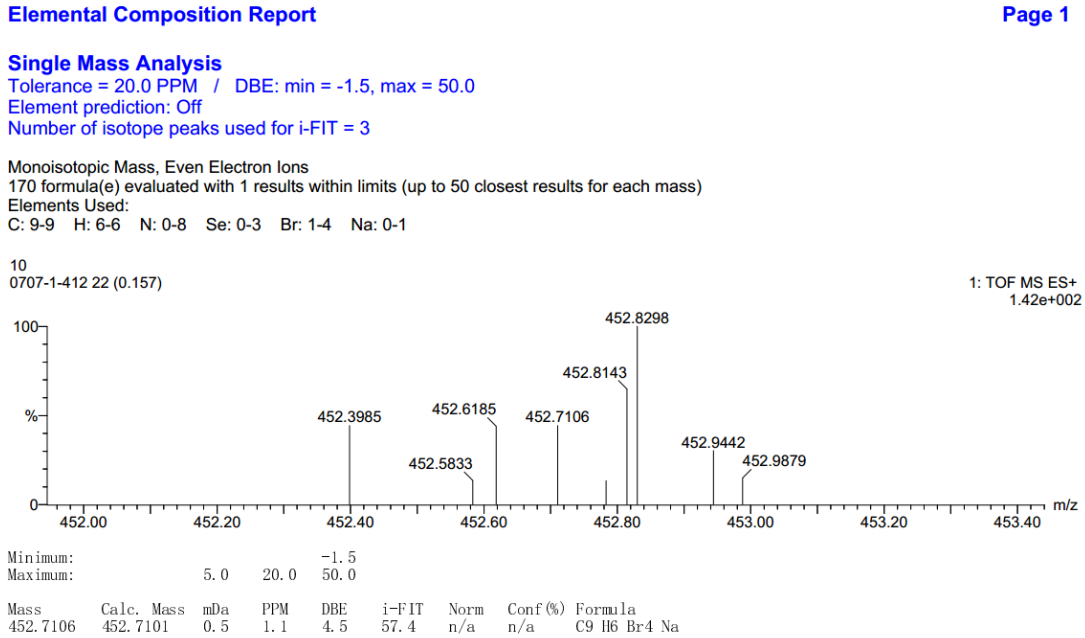


Figure S83. HRMS Spectra of **5**.

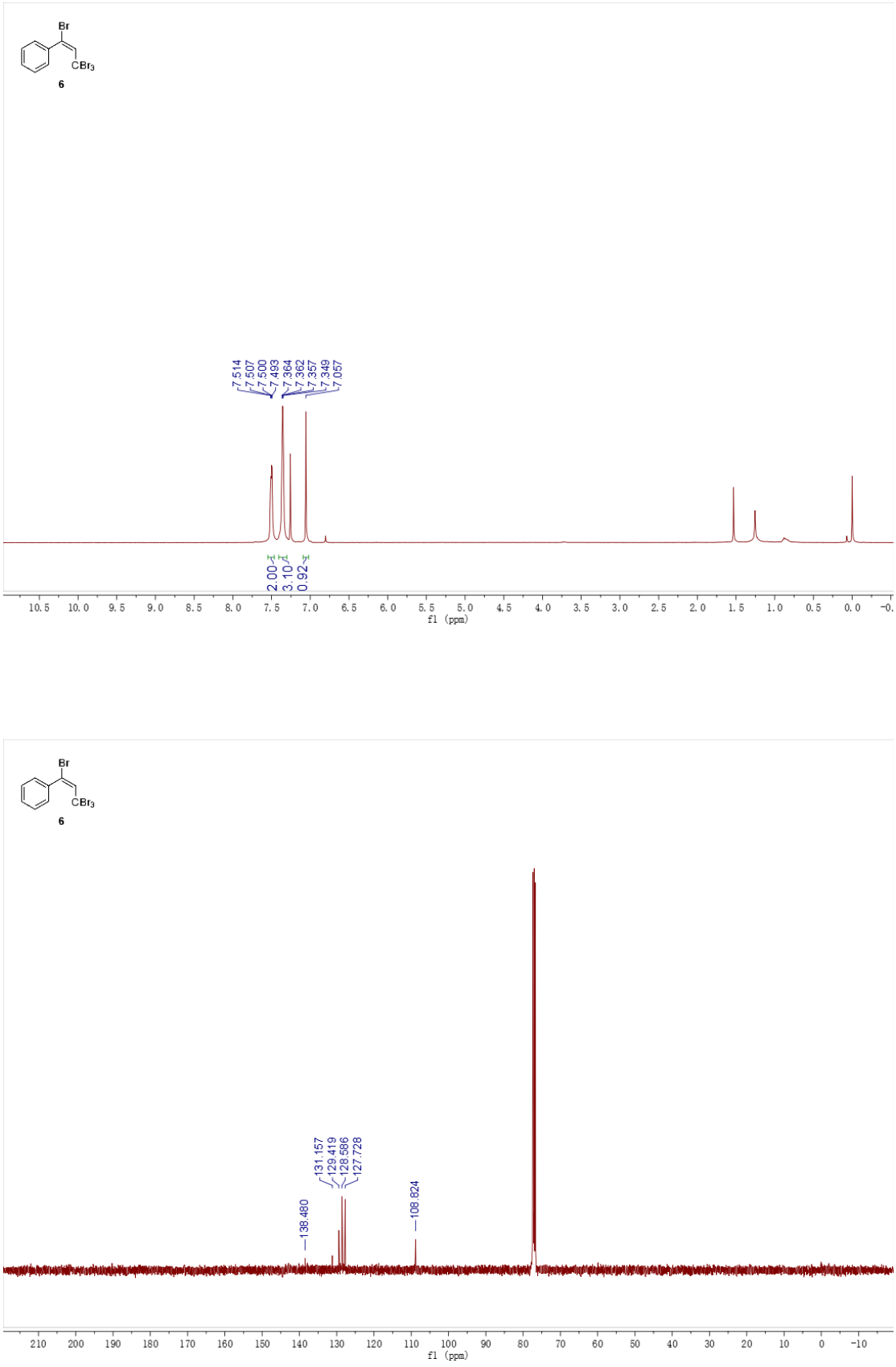


Figure S84. ^{1}H NMR and ^{13}C{^{1}H} NMR of **6**.

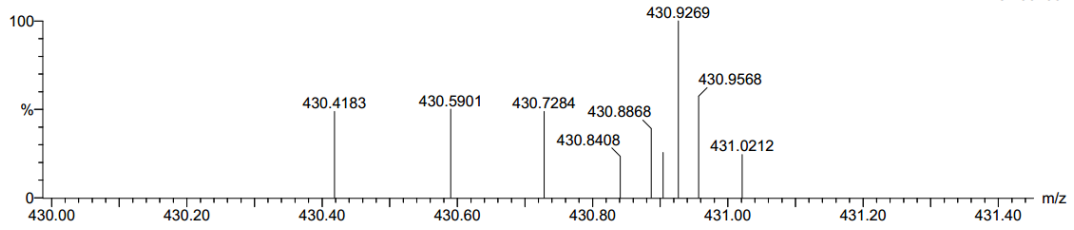
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
87 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 9-9 H: 7-7 N: 0-8 Se: 0-3 Br: 1-4

10
0707-1-438 15 (0.112)

1: TOF MS ES+
8.20e+001



Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
430.7284	430.7281	0.3	0.7	4.5	59.4	n/a	n/a	C9 H7 Br4

Figure S85. HRMS Spectra of **6**.