Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A combined DFT-predictive and experimental exploration of the sensitivity towards nucleofuge variation in zwitterionic intermediates relating to mechanistic models for unimolecular chemical generation and trapping of free C_2 and alternative bimolecular pathways involving no free C_2.

Henry S. Rzepa,* Miki Arita,[†] Kazunori Miyamoto,[†,*] Masanobu Uchiyama[†,‡,*]
Department of Chemistry, Molecular Sciences Research Hub, Imperial College London, White City Campus, Wood Lane, London W12 OBZ, UK.
[†] Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.
[‡] Research Initiative for Supra-Materials (RISM), Shinshu University, Ueda, 386-8567.

1. General Information

Instructions.

NMR spectra were obtained either on a BRUKER AVANCE III HD 500 or Avance III HD 400 MHz spectrometer. Chemical shifts were reported in ppm on the δ scale relative to tetramethylsilane (δ = 0 ppm for ^{1}H NMR). GCMS: Mass spectra (MS) were obtained on either an Agilent 7890A/5975C or 7890B/5977A spectrometers with VF-5ms (agilent) or CP-PoraPLOT Q column (GL science). APCI mass spectra were measured on a Bruker compact spectrometer. Raman spectra were obtained on either a NRS-4500 spectrometer.

Substrates. Iodoalkyne **1a**, alkynyl(aryl)-λ^3-iodane **1b**, *N*-alkynylpyridinium salt **1c**, and *S*-alkynylsulfonium salt **1d** were prepared according to the reported procedures.[S1–S4] All of these starting materials used were greater than 99% purity, which was confirmed by ^{1}H NMR. ^{1}H NMR spectra of **1a**–**d** were shown in section 4, Copies of ^{1}H NMR spectra and GCMS chart. Tetrabutylammonium fluoride trihydrate (≥98%), 9,10-dihydroanthracene (>98.0%(GC)), galvinoxyl free radical, iodobenzene (>99.0%(GC)), 4-phenylpyridine (>98.0%(GC)), and dibenzothiophene (>98.0%(GC)) were purchased from Tokyo Kasei Co. The purity of these reagents (except for galvinoxyl free radical) was also confirmed by ^{1}H NMR (NMR spectra were shown in section 4, Copies of ^{1}H NMR spectra and GCMS chart) prior to use. The purity of galvinoxyl free radical was confirmed by GC/GCMS and was determined to be >99%. Dichloromethane (>99.5%(GC)) was purchased from Kanto Chemical Co., Inc., degassed by purging with argon, and dried with a solvent purification system containing a one-meter column of activated alumina.

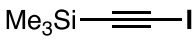
All trapping reactions were carried out either in a two-necked flask or connected flasks under an argon atmosphere.

2. Experimental Details

General procedure. To a stirred solution of C_2-precursor **1** (0.065 mmol) and trapping agent (50 equivalent for 9,10-dihydroanthracene and 1.2 equivalent for galvinoxyl radical) in dichloromethane (1.3 mL), tetrabutylammonium fluoride trihydrate (1.2 equivalent) was added in one portion at –78 °C and the solution was gradually warmed to room temperature for 3–72 h (disappearance of starting material was monitored by ^{1}H NMR, except for **1a**). After concentration of the reaction mixture under a reduced pressure, the resulting residue was then analyzed by ^{1}H NMR (ethyl acetate as an internal standard) and APCIMS. For the trapping reaction with galvinoxyl radical, excess 1,4-cyclohexadiene was added (in order to quench remaining galvinoxyl radical) prior to ^{1}H NMR measurement. The formation of acetylene was confirmed by GCMS with PLOT column (Rt-U-Bond, 0.25 mm x 30 m, 30 °C) or silver nitrate testing.

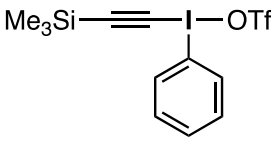
Solvent-free connected flask experiment. *S*-(trimethylsilylethynyl)-dibenzothiophenium salt **1d** (33 mg, 0.077 mmol) and cesium fluoride (35.0 mg, 0.231 mmol) was placed in one of a pair of connected flasks (Flask A), and galvinoxyl radical (97 mg, 0.231 mmol) was placed in the other flask (Flask B). The reaction mixture in Flask A was vigorously stirred at room temperature for 48 hours under argon. The contents of Flask B were directly analyzed by APCI mass spectrometry. The contents of Flask A were analyzed by ^{1}H NMR (ethyl acetate was an internal standard).

2-1. Starting materials



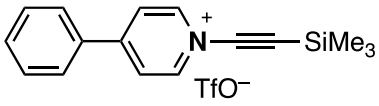
1a

1-Iodo-2-(trimethylsilyl)acetylene (1a):[S1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.17 (s, 9H); EIMS *m/z* (relative intensity) 224 (16%, M^+), 209 (100), 155 (6), 127 (21), 97 (16).



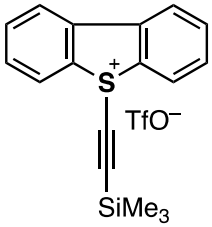
1b

[2-(Trimethylsilyl)ethynyl](phenyl)(triflato)-λ^3-iodane (1b):[S2] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.7 Hz, 2H), 7.71 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.59 (dd, *J* = 8.7, 7.5 Hz, 2H), 0.28 (s, 9H).



1c

***N*-[2-(Trimethylsilyl)ethynyl]-4-phenylpyridinium triflate (1c)**:[S3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.83 (d, *J* = 7.0 Hz, 2H), 8.44 (d, *J* = 7.0 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.51 (dd, *J* = 8.2, 7.2 Hz, 2H), 0.28 (s, 9H).

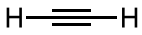


1d

***S*-[2-(Trimethylsilyl)ethynyl]dibenzothiophenium triflate (1d)**:[S4] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (d, *J* = 8.0 Hz, 2H), 8.10 (dd, *J* = 7.9, 0.9 Hz, 2H), 7.89 (td, *J* = 7.7, 0.9 Hz, 2H), 7.77 (td, *J* = 7.7, 0.9 Hz, 2H), 0.26 (s, 9H).

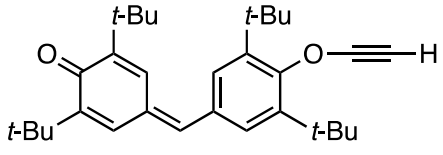
2-2. Products

The formation of acetylene was confirmed by GCMS with CP-PoraPLOT Q column (GL science, 0.25 mm x 25 m) or Raman spectroscopy.



Acetylene:[S5] Raman (ν): 1974 cm^{-1}; EIMS *m/z* (relative intensity): 26 (100%, M^+), 25 (22), 24 (6).

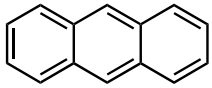
The formation of **4a** was confirmed by ^{1}H NMR and APCI mass analyses of the reaction mixture. The product was purified by preparative TLC (hexane:ethyl acetate = 14:1, using a PLC plate pre-developed with dichloromethane:triethylamine = 5:1).[S6]



4a

4a:[S6] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, *J* = 2.2 Hz, 1H), 7.41 (s, 2H), 7.15 (s, 1H), 7.01 (d, *J* = 2.2 Hz, 1H), 1.78 (s, 1H), 1.40–1.25 (m, 36H). APCIMS *m/z* (positive ion mode): 447 $[M+H]^+$.

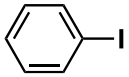
The formation of anthracene (**5**) was confirmed by ^{1}H NMR and GCMS analyses of the reaction mixture. The product was purified by column chromatography using hexane as an eluent.



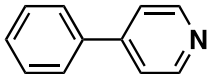
5

Anthracene (5):[S7] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (s, 2H), 8.02–8.00 (m, 4H), 7.46–7.44 (m, 4H); EIMS *m/z* (relative intensity) 178 (100%, M^+), 176 (19), 152 (11), 151 (9), 77 (9), 76 (11).

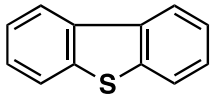
The ^{1}H NMR data of following products were in agreement with those obtained by commercially available authentic samples. See section 4, Copies of ^{1}H NMR spectra and GCMS chart.



Iodobenzene:[S8] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 8.1, 1.1 Hz, 2H), 7.33 (tt, *J* = 7.5, 1.1 Hz, 1H), 7.11 (dd, *J* = 8.1, 7.5 Hz, 2H).



4-Phenylpyridine:[S9] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66 (dd, *J* = 6.1, 2.8 Hz, 2H), 7.65 (br d, *J* = 8.0 Hz, 2H), 7.54–7.47 (m, 4H), 7.44 (tt, *J* = 7.2, 1.1 Hz, 1H).



Dibenzothiophene:[S10] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20–8.13 (m, 2H), 7.90–7.82 (m, 2H), 7.50–7.42 (m, 4H).

References

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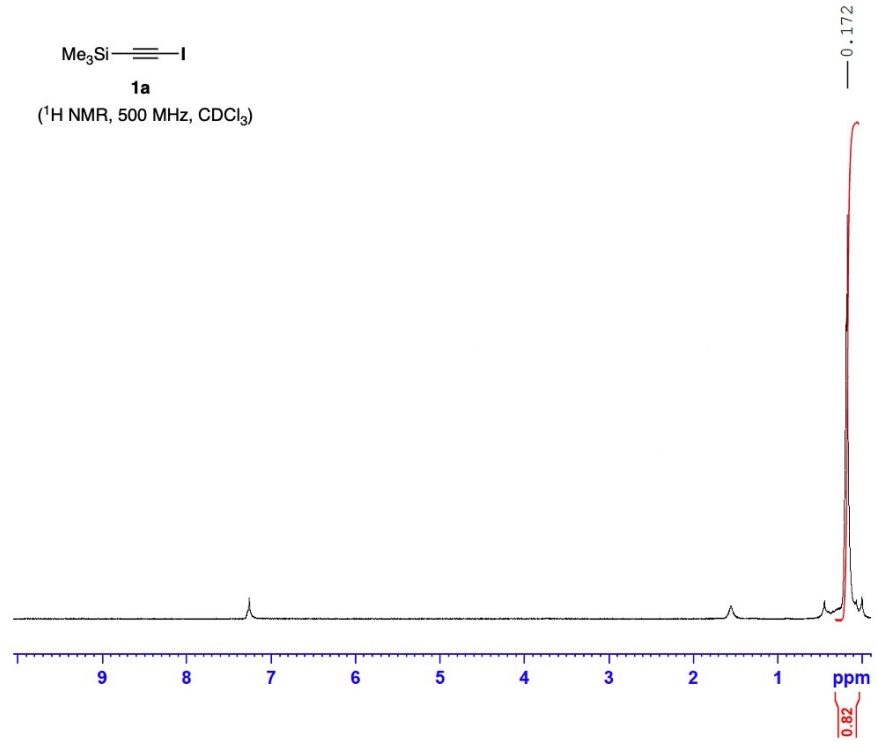
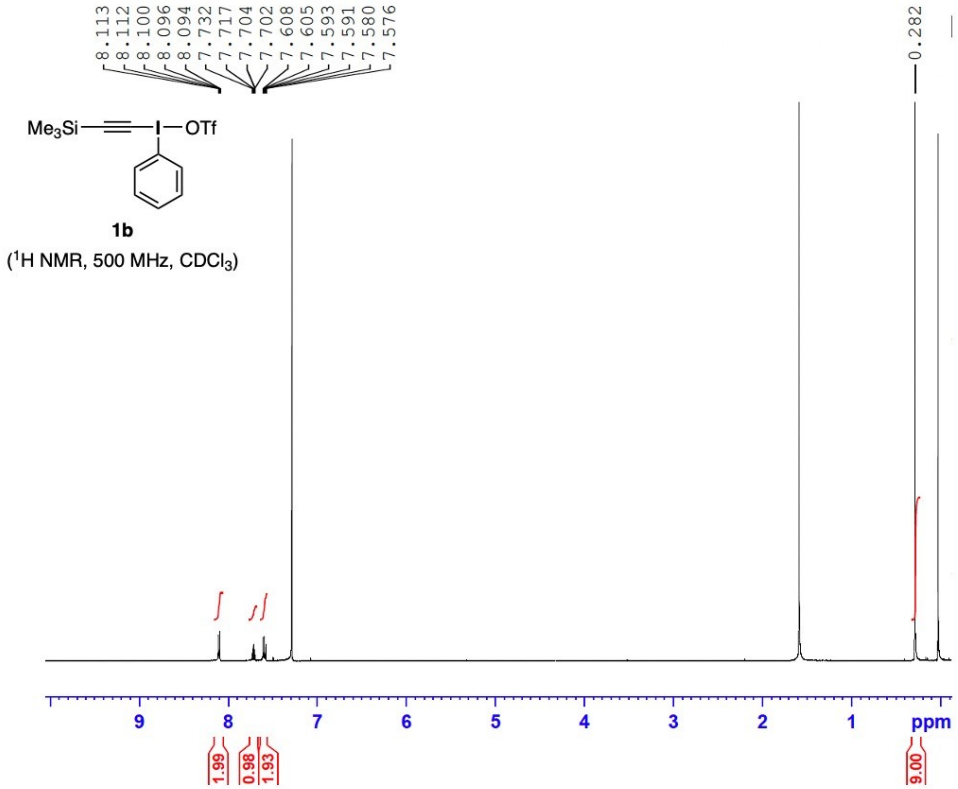
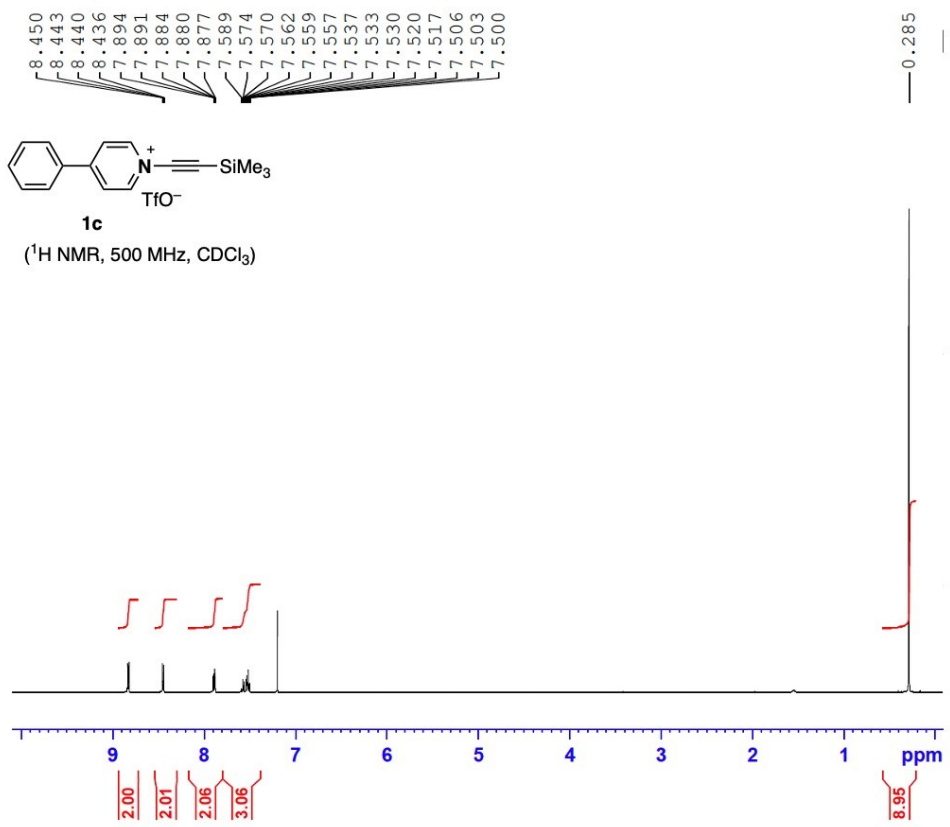
S10 G. K. S. Prakash, C. Weber, S. Chacko, G. A. Olah, *Org. Lett.* **2007**, *9*, 1863–1866.

3. Copies of ^{1}H NMR spectra and GCMS chart

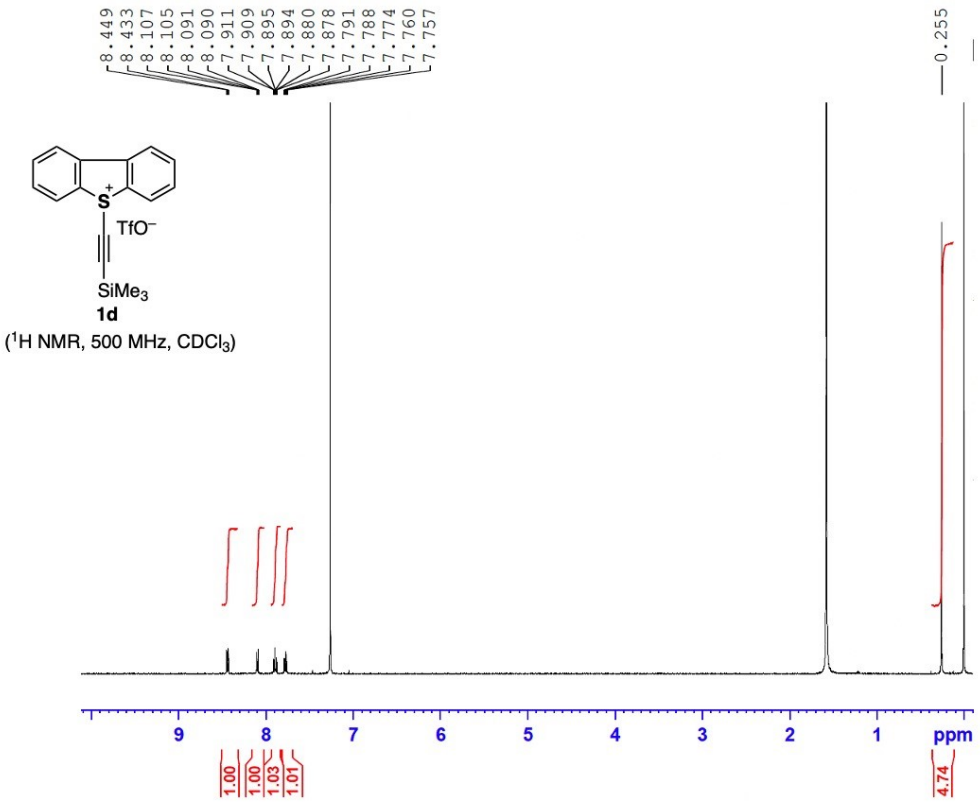






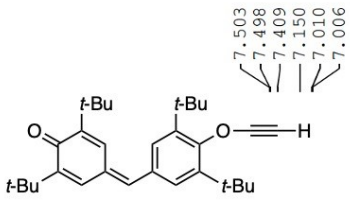
1c

(^{1}H NMR, 500 MHz, $CDCl_3$)



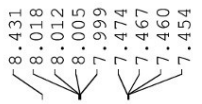
1d

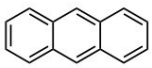
(^{1}H NMR, 500 MHz, $CDCl_3$)



4a

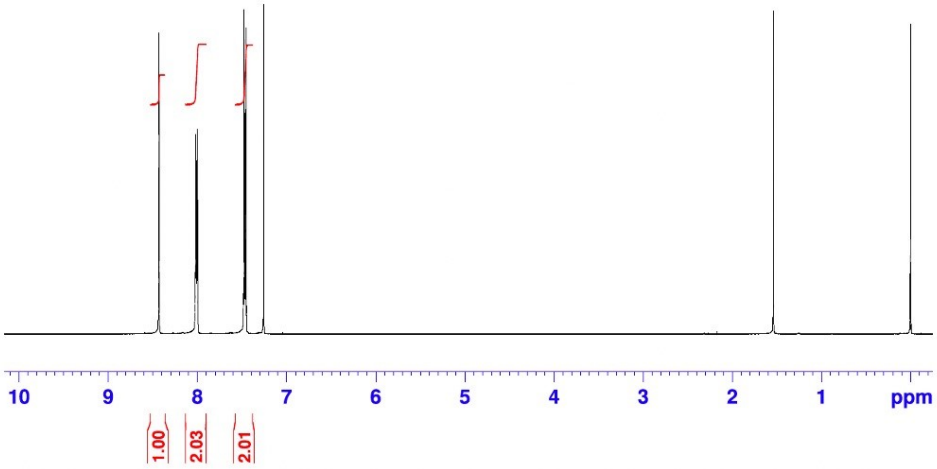
(^{1}H NMR, 500 MHz, $CDCl_3$)

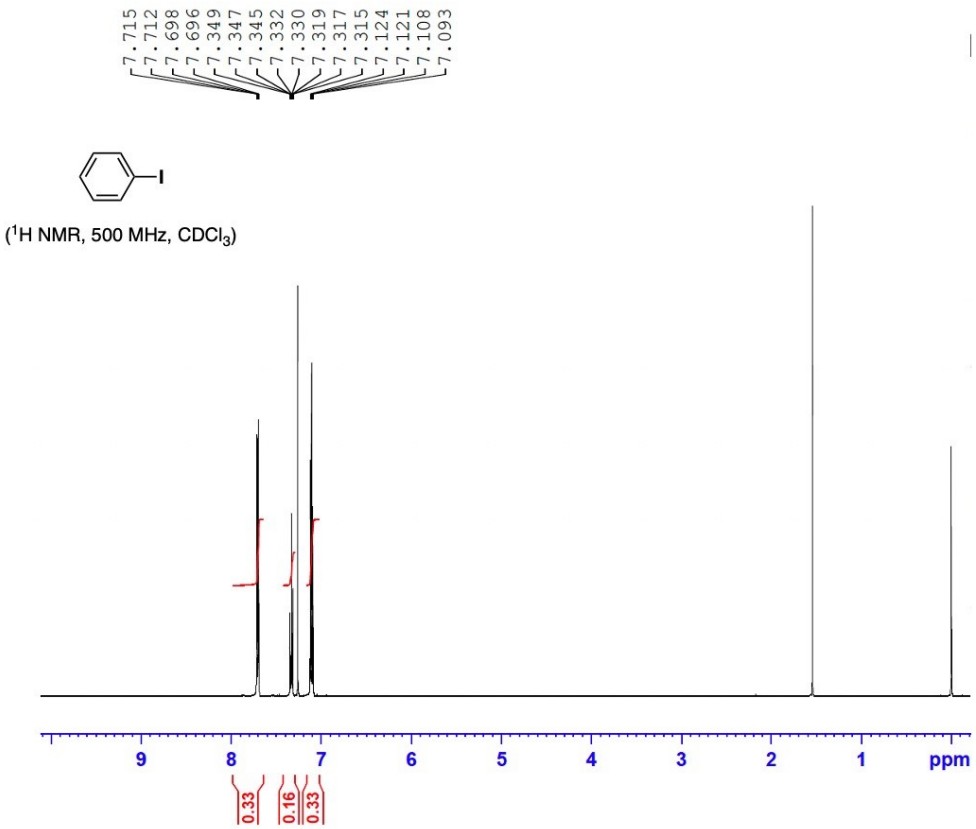




5

(^{1}H NMR, 500 MHz, $CDCl_3$)

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7.121
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7.093
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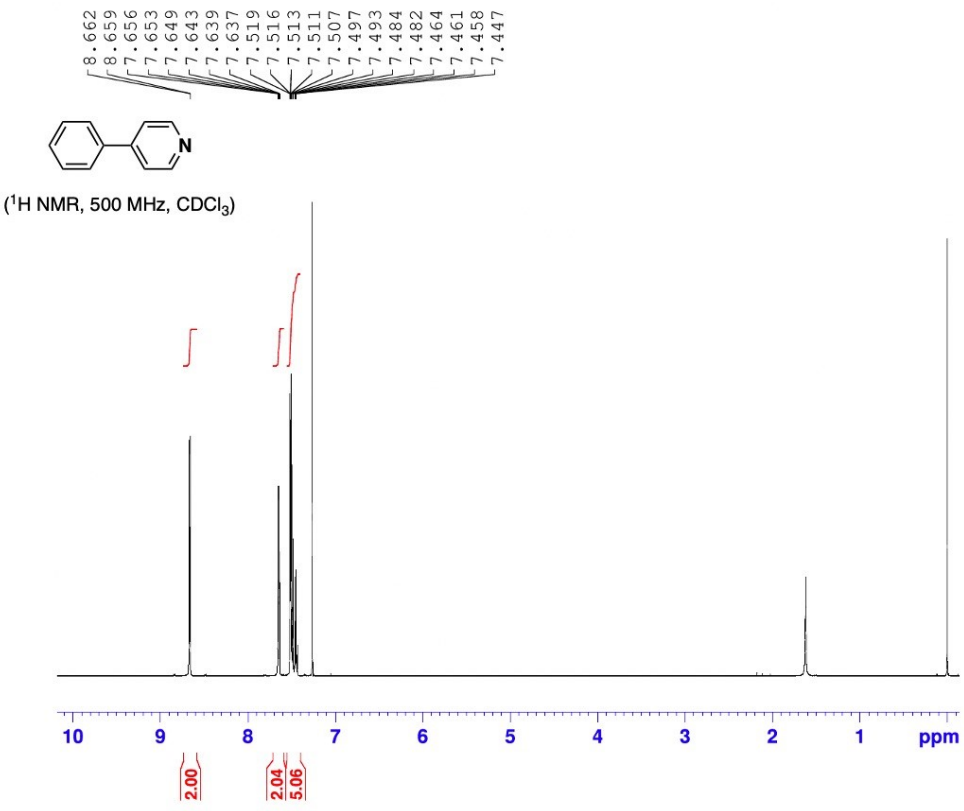
0.16
0.33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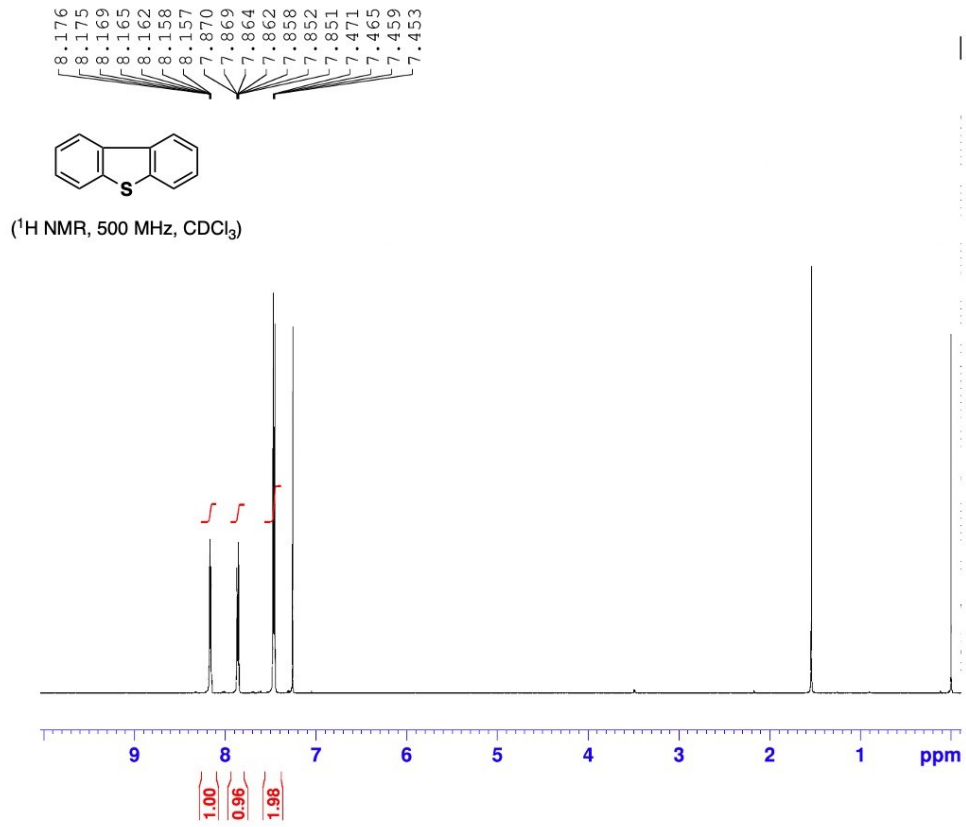
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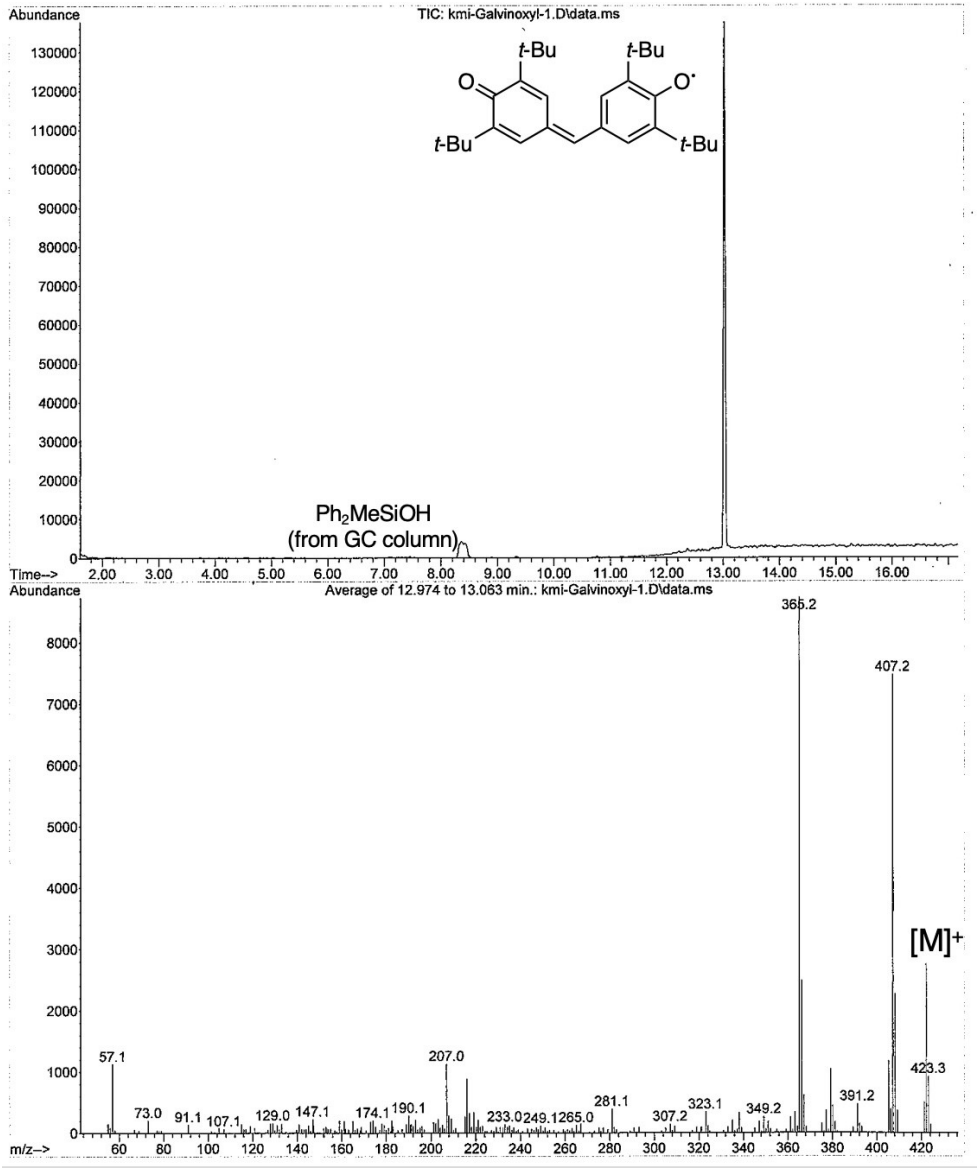

GCMS chromatograms (TIC chromatogram and MS spectrum) of galvinoxyl free radical. $Ph_2MeSiOH$ is a decomposed product of liquid stationary phases of GC column.