Electronic Supplementary Material (ESI) for RSC Advances.

Visible Light Photocatalytic One Pot Synthesis of Z-Arylvinyl Halides from E-Arylvinyl Acids with N-Halosuccinimide

Qiong Yu,[a] Kun Yi Yu,[a] Cai Feng Xu[a] and Man-Kin Wong*[ab]

[a] The Hong Kong Polytechnic University Shenzhen Research Institute, Shenzhen, 518057, China

[b] State Key Laboratory of Chemical Biology and Drug Discovery, Department of Applied Biology and Chemical Technology, TheHong Kong Polytechnic University, Hung Hum, Hong Kong, China

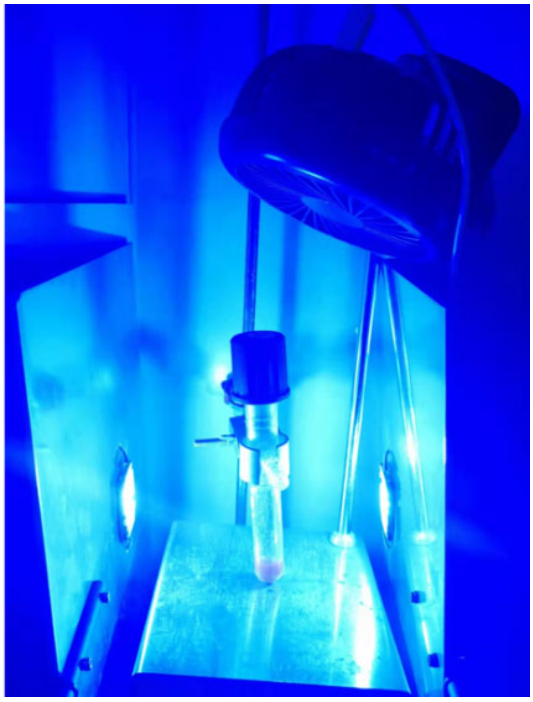
SUPPORTING INFORMATION

General procedure

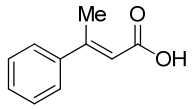
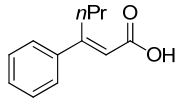
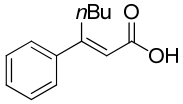
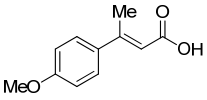
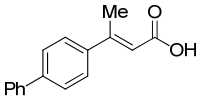
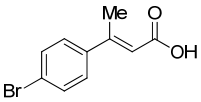
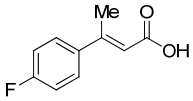
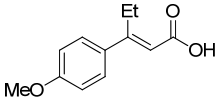
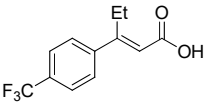
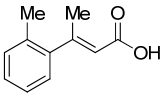
All reagents were commercially available and used without further purification. Flash column chromatography was performed using silica gel 60 (230-400 mesh ASTM) with ethyl acetate/ petroleum or methanol/dichloromethane as eluent. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker DPX-400 spectrometer. All chemical shifts are quoted on the scale in ppm using TMS or residual solvent as the internal standard. Coupling constants (J) are reported in Hertz (Hz) with the following splitting abbreviations: s = singlet, br s = broad singlet, d = doublet, dd = double doublet, t = triplet and m = multiplet. High resolution mass spectra were obtained on an Agilent 6540 UHD Accurate-Mass QTOF LC/MS system equipped with an ion spray source in the positive ion mode. For ESI–MS/MS analysis, collision energy was set at 10, 15 or 20 eV.

Photocatalytic reactions were set up in light bath which are described below.

The 30 W blue LEDs was placed ~5 cm from the reaction tubes and a fan attached to the apparatus was used to maintain the temperature no more than 5 °C above room temperature.



Literature references:

 *E*-**1a**	T. Fukuyama, M. Arai, H. Matsubara, and I. Ryu, *J. Org. Chem.* 2004, **69**, 8105–8107.
 *E*-**1b**	J. B. Metternich and Ryan Gilmour, *J. Am. Chem. Soc.* 2016, **138**, 1040–1045.
 *E*-**1c**	J. B. Metternich, D. G. Artiukhin, M. C. Holland, M. v. Bremen-Kühne, J. Neugebauer and R. Gilmour, *J. Org. Chem.* 2017, **82**, 9955-9977.
 *E*-**1d**	J. Gao, J. Zhang, S. Fang, J. Feng, T. Lu and D. Du, *Org. Lett.* 2020, 22, 19, 7725–7729.
 *E*-**1e**	J. Gao, J. Zhang, S. Fang, J. Feng, T. Lu, and D. Du, *Org. Lett.* 2020, **22**, 7725–7729.
 *E*-**1f**	T. Brégent, J. -P. Bouillon and T. Poisson, *Org. Lett.* 2020, **22**, 7688–7693.
 *E*-**1g**	T. Brégent, J.-P. Bouillon and T. Poisson, *Org. Lett.* 2020, **22**, 7688–7693.
 *E*-**1j**	J. B. Metternich and Ryan Gilmour, *J. Am. Chem. Soc.* 2016, **138**, 1040–1045.
 *E*-**1k**	A. Pesyan and M. F. Balandrin, *U. S. Pat. Appl. Publ.* 2021, US 20210130285.
 *E*-**1n**	T. Brégent, J.-P. Bouillon and T. Poisson, *Org. Lett.* 2020, **22**, 7688–7693.

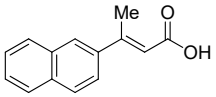
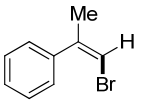
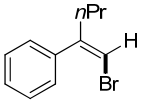
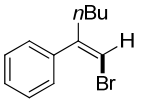
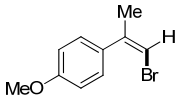
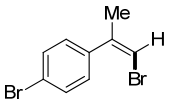
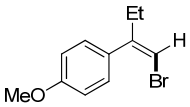
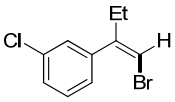
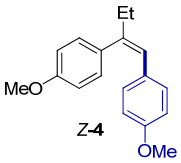
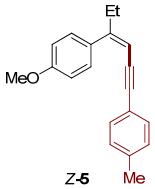
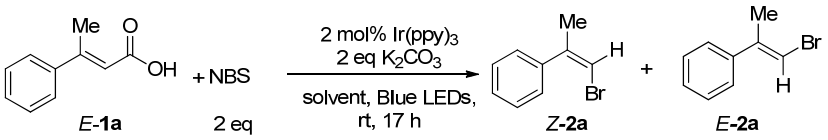
 *E*-**1o**	J. B. Metternich and Ryan Gilmour, *J. Am. Chem. Soc.* 2016, **138**, 1040–1045.
 *Z*-**2a**	H. Zhang, Q. Xu, L. Yu and S. Yu, *Eur. J. Org. Chem.* 2020, 1472.
 *Z*-**2b**	H. Zhang, Q. Xu, L. Yu and S. Yu, *Eur. J. Org. Chem.* 2020, 1472.
 *Z*-**2c**	H. Zhang, Q. Xu, L. Yu and S. Yu, *Eur. J. Org. Chem.* 2020, 1472.
 *Z*-**2d**	H. Zhang, Q. Xu, L. Yu and S. Yu, *Eur. J. Org. Chem.* 2020, 1472.
 *Z*-**2f**	H. Zhang, Q. Xu, L. Yu and S. Yu, *Eur. J. Org. Chem.* 2020, 1472.
 *Z*-**2j** [b]	H. Zhang, Q. Xu, L. Yu and S. Yu, *Eur. J. Org. Chem.* 2020, 1472.
 *Z*-**2m**	H. Zhang, Q. Xu, L. Yu and S. Yu, *Eur. J. Org. Chem.* 2020, 1472.
 *Z*-**4**	H. Zhang, Q. Xu, L. Yu and S. Yu, *Eur. J. Org. Chem.* 2020, 1472.
 *Z*-**5**	H. Zhang, Q. Xu, L. Yu and S. Yu, *Eur. J. Org. Chem.*2020,1472.

Table S1 Solvent effect

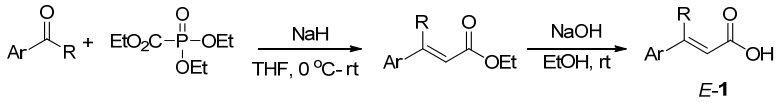


E-**1a** *Z*-**2a** *E*-**2a**

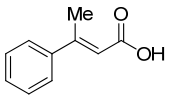
Entry	solvent	SM%	Yield%	Z/E
1	H_2O	0	59	75/25
2	MeOH: H_2O =1:1	0	29	93/7
3	EtOH	40	36	6/94
4	*n*BuOH	0	47	89/11
5	dioxane	37	0	-
6	THF	34	Trace	-
7	CH_3CN	0	84	2/98
8	DMF	2	0	-
9	DMSO	29	4	75/25

[a] Reaction conditions: Treatment of *E*-**1a** (0.2 mmol), K_2CO_3 (0.4 mmol), NBS (0.4 mmol) and $Ir(ppy)_3$ (2 mol%) in 2 mL of solvent under N_2 and blue LEDs light for 17 hours at room temperature. [b] Yield was determined by ^1H NMR using dibromomethane as internal standard. [c]The Z/E ratio was determined by ^1H NMR spectroscopy.

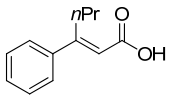
Table S2 Synthetic routes of α,β-unsaturated arylvinyl acids *E*-**1a to** *E*-**1o**



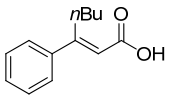
E-**1**



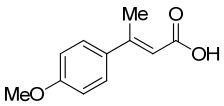
E-**1a**
30% yield



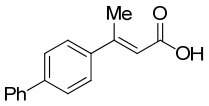
E-**1b**
29% yield



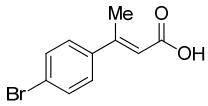
E-**1c**
24% yield



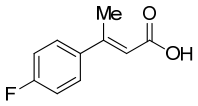
E-**1d**
31% yield



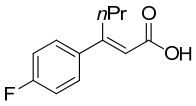
E-**1e**
35% yield



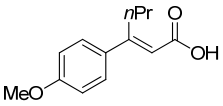
E-**1f**
41% yield



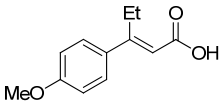
E-**1g**
38% yield



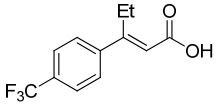
E-**1h**
28% yield



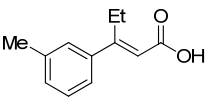
E-**1i**
33% yield



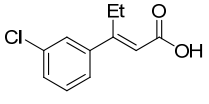
E-**1j**
40% yield



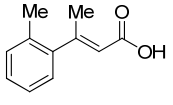
E-**1k**
27% yield



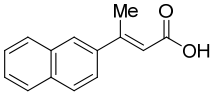
E-**1l**
31% yield



E-**1m**
38% yield



E-**1n**
36% yield



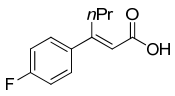
E-**1o**
33% yield

General procedure for synthesis of α,β-unsaturated arylvinyl acids *E*-1

(1) To a suspension of NaH (480 mg, 60% in mineral oil, 12 mmol) in THF (10 mL), a solution of triethyl phosphonoacetate (2.5 mL, 12 mmol) in THF (5 mL) was slowly added. The mixture was stirred at room temperature for 30 min. Then, ketone (10 mmol) in THF (5 mL) was added at 0 °C, and the mixture was stirred at room temperature. After confirmation of consumption of ketone by TLC, a solution of saturated aqueous sodium bicarbonate (15 mL) was added. The mixture was extracted with EtOAc (3 x 25 mL), washed with brine (15 mL) and dried over Mg_2SO_4. After concentration of the organic phase, the residue was purified by silica-gel column chromatography (Petroleum ether/EtOAc as eluent).

(2) The α,β-unsaturated ester was placed in a 50 mL round-bottom flask, then EtOH (0.5M) was added, the reaction mixture was stirred, and NaOH (5 equiv.) was added. The reaction mixture was stirred at room temperature until no starting material was detected by TLC. Then the pH was adjusted to 1.0 with HCl (1 M). The mixture was extracted with EtOAc. The combined organic layer was washed with saturated NaCl solution, dried over $MgSO_4$, and concentrated in vacuum. If needed, the crude residue was subjected to flash chromatography (Petroleum ether/EtOAc) or recrystallize.

E-3-(4-fluorophenyl)-2-hexenoic acid ***E*-1h**



E-**1h**

Colorless solid, 28% yield for two steps

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.36 (m, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 6.04 (s, 1H), 3.09 (t, *J* =

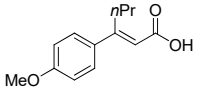
8.0 Hz, 2H), 1.56 – 1.37 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.17, 163.31(d, *J* = 248 Hz), 162.38, 137.13 (d, *J* = 3.5 Hz), 128.55 (d, *J* = 8.4 Hz), 116.75, 115.53 (d, *J* = 21.7 Hz), 32.90, 22.25, 13.91.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.10.

HRMS (ESI) calcd for$C_{12}H_{12}FO_2^-$ (M - H)$^-$ 207.0827, found 207.0822.

E-3-(4-methoxyphenyl)-2-hexenoic acid ***E*-1i**



E-**1i**

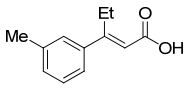
Colorless solid, 33% yield for two steps

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dt, *J* = 8.0, 2.0 Hz, 2H), 6.91 (dt, *J* = 8.0, 2.0 Hz, 2H), 6.06 (s, 1H), 3.84 (s, 2H), 3.10 (t, *J* = 8.0 Hz, 1H), 1.65 – 1.26 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.35, 162.90, 160.56, 133.16, 128.11, 114.95, 113.91, 55.27, 32.55, 22.52, 14.01.

HRMS (ESI) calcd for $C_{13}H_{15}O_3^-$ (M - H)$^-$ 219.1027, found 219.1023.

E-3-(3-methylphenyl)-2-pentenoic acid ***E*-1l**



E-**1l**

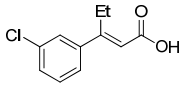
Colorless solid, 31% yield for two steps

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.22 (m, 3H), 7.21-7.13(m, 1H), 6.05 (s, 1H), 3.12 (q, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.09 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.29, 165.26, 140.90, 138.15, 129.94, 128.42, 127.43, 123.86, 115.89, 24.56, 21.41, 13.60.

HRMS (ESI) calcd for $C_{12}H_{13}O_2^-$ (M - H)$^-$ 189.0921, found 189.0915.

E-3-(3-chlorophenyl)-2-pentenoic acid ***E*-1m**



E-**1m**

Colorless solid, 38% yield for two steps

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.39 – 7.29 (m, 3H), 6.04 (s, 1H), 3.10 (q, J = 7.5 Hz, 2H), 1.09 (t, J = 7.5 Hz, 3H).

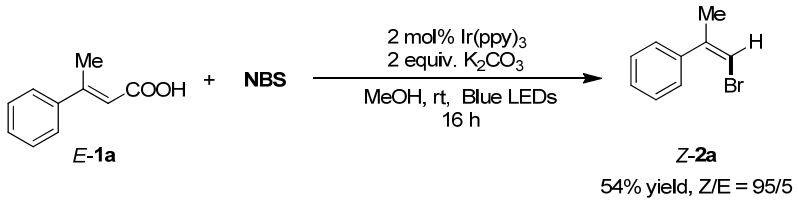
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.83, 163.38, 142.76, 134.59, 129.82, 129.14, 126.90, 124.93, 117.04, 24.53, 13.43.

HRMS (ESI) calcd for $C_{11}H_{10}ClO_2^-$ (M - H)$^-$ 209.0375, found 209.0370.

2. General procedure forsynthesis of α,β-unsaturated arylvinyl halides *Z*-2

The specified *E*-arylvinyl acids ***E*-1** (0.2 mmol, 1.0 eq.), NXS (0.4 mmol, 2.0 eq), K_2CO_3 (0.4 mmol, 2.0 eq) and fac-Ir(ppy)$_3$ (2.6 mg, 0.004 mmol, 0.02 eq.) were added in a 10-mL reaction tube. The tube was evacuated and backfilled with nitrogen 3 times. Methanol (2.0 mL) was then added via syringe under nitrogen. The mixture was then irradiated by 30 W blue LEDs. After the reaction was completed, H_2O (5 mL) was added. The mixture was extracted with CH_2Cl_2 (3 x 15 mL), washed with brine (10 mL) and dried over Mg_2SO_4. After concentration of the organic phase, the residue was purified by silica-gel column chromatography (Petroleum ether as eluent) to afford the desired product. The Z/E ratio of the mixture was determined by the ^{1}H NMR spectra.

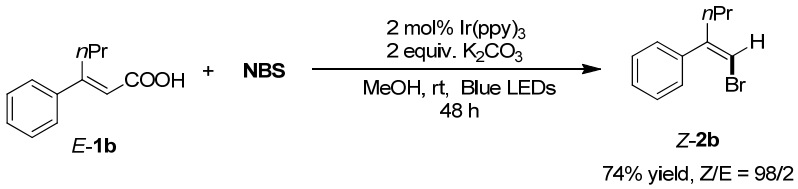
***Z*-(1-bromoprop-1-en-2-yl)benzene (*Z*-2a)**



Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 7.37 – 7.29 (m, 3H), 6.24 (d, *J* = 1.1 Hz, 1H), 2.14 (d, *J* = 1.1 Hz, 3H).

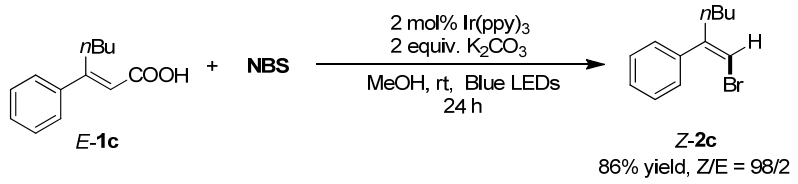
***Z*-(1-bromopent-1-en-2-yl)benzene (*Z*-2b)**



Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.29 (dt, *J* = 4.8, 2.0 Hz, 1H), 7.25 – 7.18 (m, 2H), 6.20 (s, 1H), 2.39 (td, *J* = 7.6, 1.1 Hz, 2H), 1.37-1.29 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

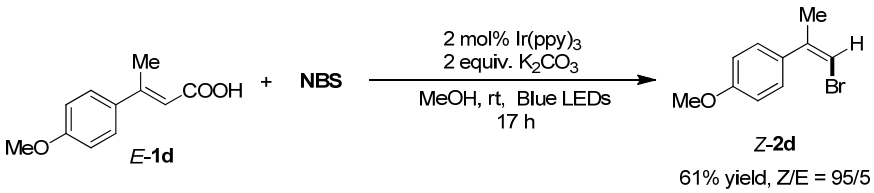
***Z*-(1-bromohex-1-en-2-yl)benzene (*Z*-2c)**



Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ7.40-7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.26 – 7.22 (m, 2H), 6.22 (t, *J* = 1.2 Hz, 1H), 2.43 (td, *J* = 7.2, 1.1 Hz, 2H), 1.35 – 1.24 (m, 4H), 0.85 (t, *J* = 7.0 Hz, 3H).

***Z*-(1-bromoprop-1-en-2-yl)-4-methylbenzene (*Z*-2d)**



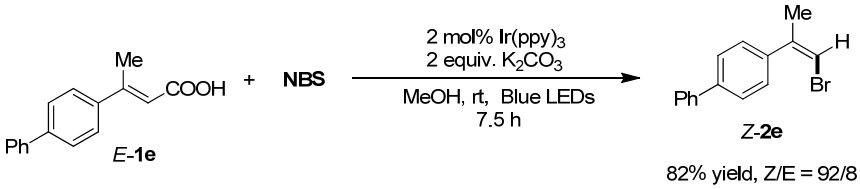
Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.10 (s, 1H), 3.74 (s, 3H), 2.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.91, 140.78, 132.22, 128.94, 113.45, 100.79, 55.17, 24.91.

HRMS (ESI) calcd for $C_{10}H_{12}BrO^+$ $(M+H)^+$ 227.0066, found 227.0066.

***Z*-(1-bromoprop-1-en-2-yl)-4-phenylbenzene (*Z*-2e)**



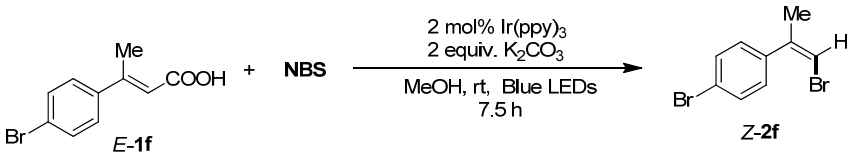
Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.58 (m, 4H), 7.52 – 7.43 (m, 4H), 7.39 (t, *J* = 7.3 Hz, 1H), 6.30 (s, 1H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.96, 140.62, 140.39, 138.92, 128.73, 128.11 127.33, 127.02, 126.81, 101.58, 24.87.

HRMS (ESI) calcd for $C_{15}H_{14}Br^+$ $(M+H)^+$ 273.0273, found 273.0272.

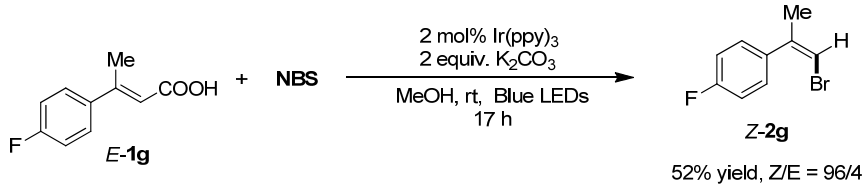
***Z*-(1-bromoprop-1-en-2-yl)-4-bromobenzene (*Z*-2f)**



Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.25 (d, *J* = 1.4 Hz, 1H), 2.10 (d, *J* = 1.4 Hz, 3H).

***Z*-(1-bromoprop-1-en-2-yl)-4-fluorobenzene (*Z*-2g)**



Colorless oil

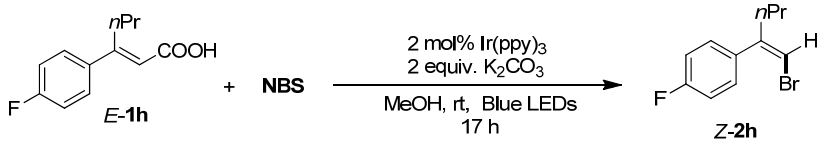
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.12 – 7.03 (m, 2H), 6.24 (d, *J* = 1.4 Hz, 1H), 2.12 (d, *J* = 1.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ162.02 (d, *J* = 246.7 Hz), 140.52, 135.95 (d, *J* = 3.2 Hz), 129.45 (d, *J* = 8.0 Hz), 115.11 (d, *J* = 21.6 Hz), 101.86, 24.93.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.03.

HRMS (ESI) calcd for $C_9H_9BrF^+$ $(M + H)^+$ 214.9866, found 214.9866.

***Z*-(1-bromopent-1-en-2-yl)-4-fluorobenzene (*Z*-2h)**



57% yield, Z/E = 94/6

Colorless oil

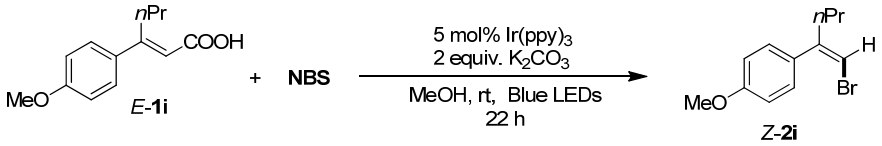
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 2H), 7.15 – 7.03 (m, 2H), 6.25 (t, *J* = 1.2 Hz, 1H), 2.42 (td, *J* = 4, 1.6 Hz, 2 H), 1.43 – 1.26 (m, 4H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.02 (d, *J* = 246.4 Hz), 145.41, 135.21 (d, *J* = 3.5 Hz), 129.77 (d, *J* = 8.1 Hz), 115.16 (d, *J* = 21.6 Hz), 102.39, 40.86, 20.76, 13.33.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.38.

HRMS (ESI) calcd for $C_{11}H_{13}BrF^{+}$(M + H)$^{+}$ 243.0179, found 243.0171.

***Z*-(1-bromopent-1-en-2-yl)-4-methoxylbenzene (*Z*-2i)**



85% yield, Z/E>99/1

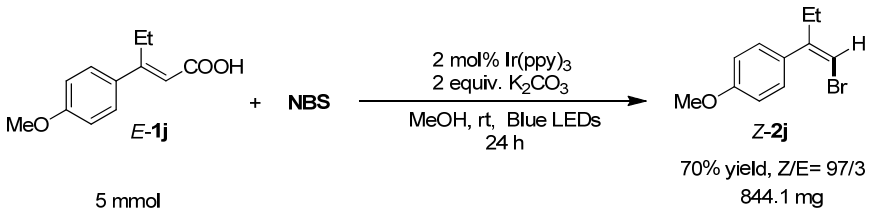
Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dt, *J* = 8.8, 2.4 Hz,2H), 6.92 (dt, *J* = 8.8, 2.4 Hz, 2H), 6.19 (s, 1H), 3.83 (s, 3H), 2.41 (td, *J* = 8.0, 1.2 Hz, 2H), 1.35 (q, *J* = 7.5 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.82, 145.76, 131.46, 129.25, 113.49, 101.47, 55.15, 40.84, 20.86, 13.34.

HRMS (ESI) calcd for $C_{12}H_{16}BrO^{+}$ (M + H)$^{+}$ 255.0379, found 255.0382.

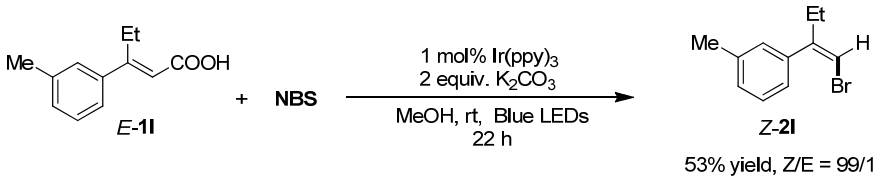
***Z*-(1-bromobut-1-en-2-yl)-4-methoxylbenzene (*Z*-2j)**



Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (dt,*J* = 8.8, 2.4 Hz, 2H), 6.91 (dt,*J* = 8.8, 2.4 Hz, 2H), 6.19 (s, 1H), 3.83 (s, 3H), 2.44 (qd, *J* = 7.4, 1.3 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

***Z*-(1-bromobut-1-en-2-yl)-3-methylbenzene (*Z*-2l)**



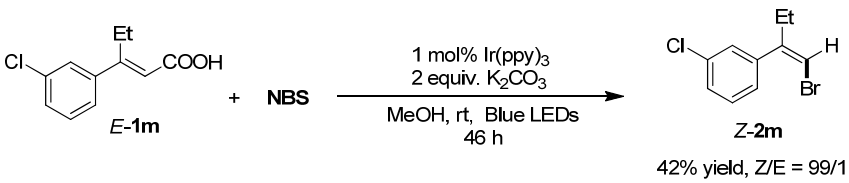
Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.1 Hz, 2H), 6.23 (s, 1H), 2.47 (q, *J* = 7.4 Hz, 2H), 2.40 (s, 3H), 1.03 (t, *J* = 7.4 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.14, 139.56, 137.71, 128.46, 128.21, 128.01, 125.05, 101.30, 32.12, 1.44, 12.68.

HRMS (ESI) calcd for $C_{11}H_{14}Br^+$ $(M + H)^+$ 225.0273, found 225.0272.

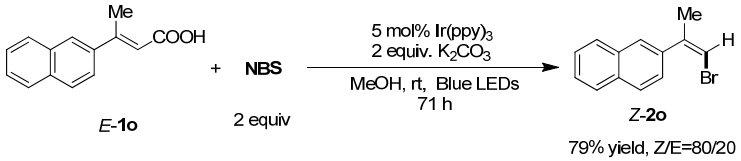
***Z*-(1-bromobut-1-en-2-yl)-3-chlorobenzene (*Z*-2m)**



Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.23 (s, 1H), 7.12 (d, *J* = 6.7 Hz, 1H), 6.25 (s, 1H), 2.43 (q, *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).

(*Z*-(1-bromoprop-1-en-2-yl)naphthalene (*Z*-2o)



E-**1o** *Z*-**2o**

79% yield, Z/E=80/20

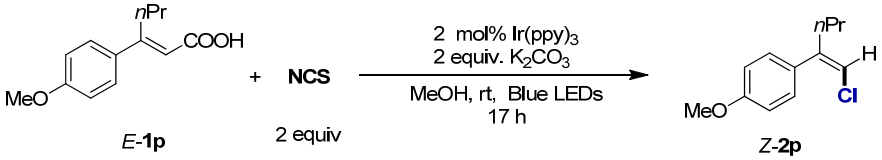
Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 3H), 7.83 (s, 1H), 7.56 – 7.47 (m, 3H), 7.28 (s, 1H), 6.35 (d, *J* = 1.4 Hz, 1H), 2.25 (d, *J* = 1.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.53, 137.63, 133.10, 132.68, 128.04, 127.74, 127.68, 126.69, 126.13, 125.74, 101.90, 25.04.

HRMS (ESI) calcd for $C_{13}H_{12}Br^+$ $(M + H)^+$ 247.0117, found 247.0116.

(*Z*-(1-chloropent-1-en-2-yl)-4-methoxylbenzene (*Z*-2p)



E-**1p** *Z*-**2p**

26% yield, Z/E = 96/4

Colorless oil

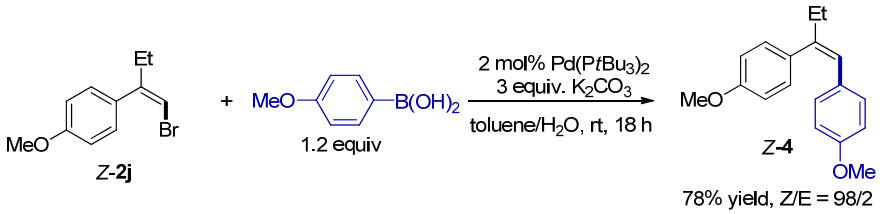
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.09 (s, 1H), 3.85 (s, 4H), 2.40 (t, *J* = 6.9 Hz, 2H), 1.40-1.32 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ158.82, 142.36, 129.95, 129.42, 113.52, 112.39, 55.17, 39.30, 20.93, 13.37.

HRMS (ESI) calcd for $C_{12}H_{16}ClO^+$ $(M + H)^+$ 211.0884, found 211.0887.

3. Derivatization of *Z*-2j

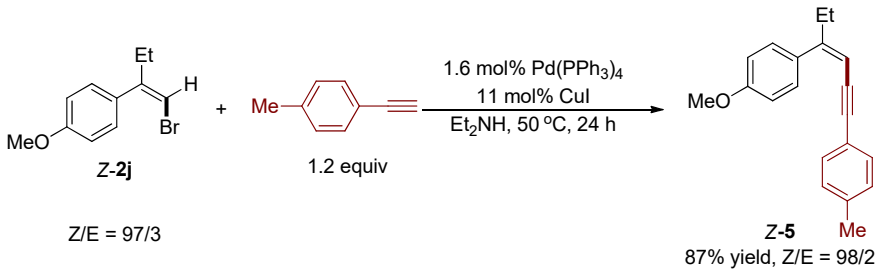
***Z*-4,4'-(but-1-ene-1,2-diyl)bis(methoxybenzene) (*Z*-4)**



To a 10-mL reaction tube was added 4-methoxyphenylboronic acid (18.2 mg, 0.12 mmol, 1.2 eq.), K_2CO_3 (41.5 mg, 0.3 mmol, 3 eq.) and $Pd(PtBu_3)_2$ (1.0 mg, 0.002 mmol, 0.02 eq.). The tube was sealed and degassed with nitrogen for 3 times. Next, *Z*-**2j** (24.1 mg, 0.1 mmol, 1.0 eq.) (Z/E = 97/3) in 1.0 mL toluene and 0.1 mL H_2O was added via syringe. The resulting solution was allowed to stir at rt for 21 h. After the reaction was completed, H_2O (3 mL) was added. The mixture was extracted with CH_2Cl_2 (3 x 10 mL), washed with brine (10 mL) and dried over Mg_2SO_4. After concentration of the organic phase, the crude residue was purified by column chromatography to yield *Z*-**4** as a colourless oil (21 mg, 78%, Z/E = 98/2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, J = 8.7 Hz, 2H), 6.91-6.83 (m,4H), 6.65 (d, J = 8.8 Hz, 2H), 6.34 (s, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 2.47 (qd, J = 7.4, 1.0 Hz, 2H), 1.06 (t, J = 7.4 Hz, 3H).

***Z*-1-methoxy-4-(6-phenylhex-3-en-5-yn-3-yl)benzene (*Z*-5)**



To a 10-mL round bottom flask was added *Z*-**2j** (48.2 mg, 0.2 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (3.7 mg, 0.003 mmol, 0.016 eq.) and copper(I) iodide (4.2 mg, 0.022mmol, 0.11 eq.). The flask was sealed, degassed with nitrogen for 3 times, and 1.0 mL Et_2NH was added via syringe. Phenylacetylene (25.6 mg, 0.22mmol, 1.1 eq.) in 1.0 mL Et_2NH was added. Then, the temperature was raised to 50 ^oC and the resulting solution was allowed to stir for 18 h. After the reaction was completed (as monitored by TLC analysis), the reaction mixture was diluted with H_2O (5 mL) and the pH was adjusted to 7.0 with HCl (1 M). The mixture was extracted with CH_2Cl_2 (3 x 15 mL), washed with brine (15 mL), dried over Mg_2SO_4 and concentrated in vacuo. The crude residue was purified by column chromatography to yield ***Z*-5** as a colorless oil (48.5 mg, 88%, Z/E = 98/2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.76 (s, 1H), 3.85 (s, 3H), 2.57 (qd, *J* = 7.3, 0.8 Hz, 1H), 2.34 (s, 3H), 1.09 (t, *J* = 7.4 Hz, 3H).

UV/visible absorption spectra of quinolizinium compounds

The UV-Vis absorption spectra of photocatalysts **3a**-**3f** were reported in *Chem. Sci.*, 2017, **8**, 7537–7544. The UV-Vis absorption spectrum of photocatalyst **3h** was reported in *Org. Biomol. Chem.*, 2021, **19**, 8507–8515. The UV-Vis absorption spectra of photocatalysts **3g** and **3i** were measured by Jenway 6850 UV-Vis Spectrophotometer, and the final concentration of each quinolizinium compound in CH_2Cl_2 was 1×10^{-5} M.

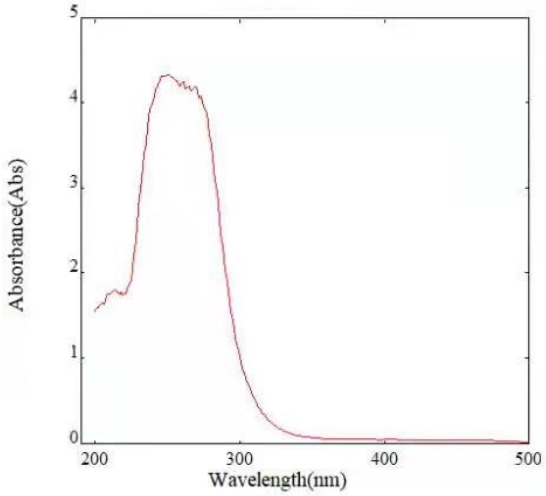


Figure S1 Absorption spectrum of compound **3g**.

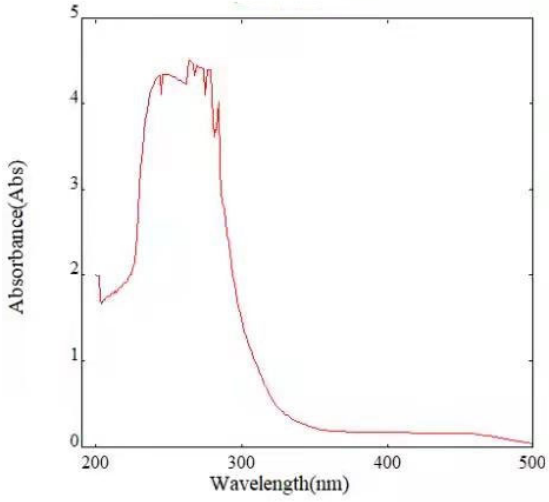
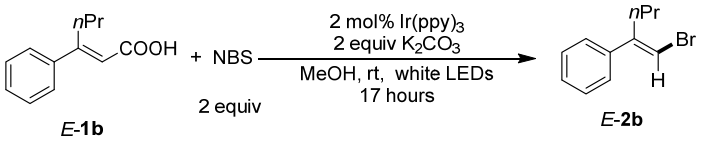


Figure S2 Absorption spectrum of compound **3i**.

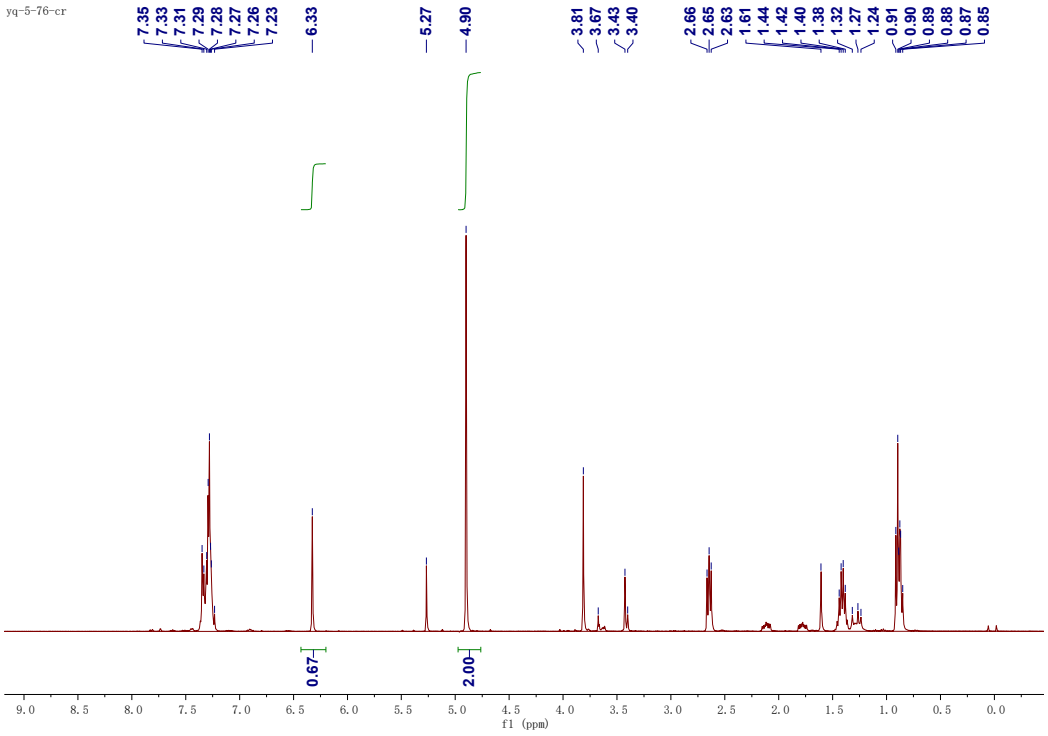
Use of white LEDs light source

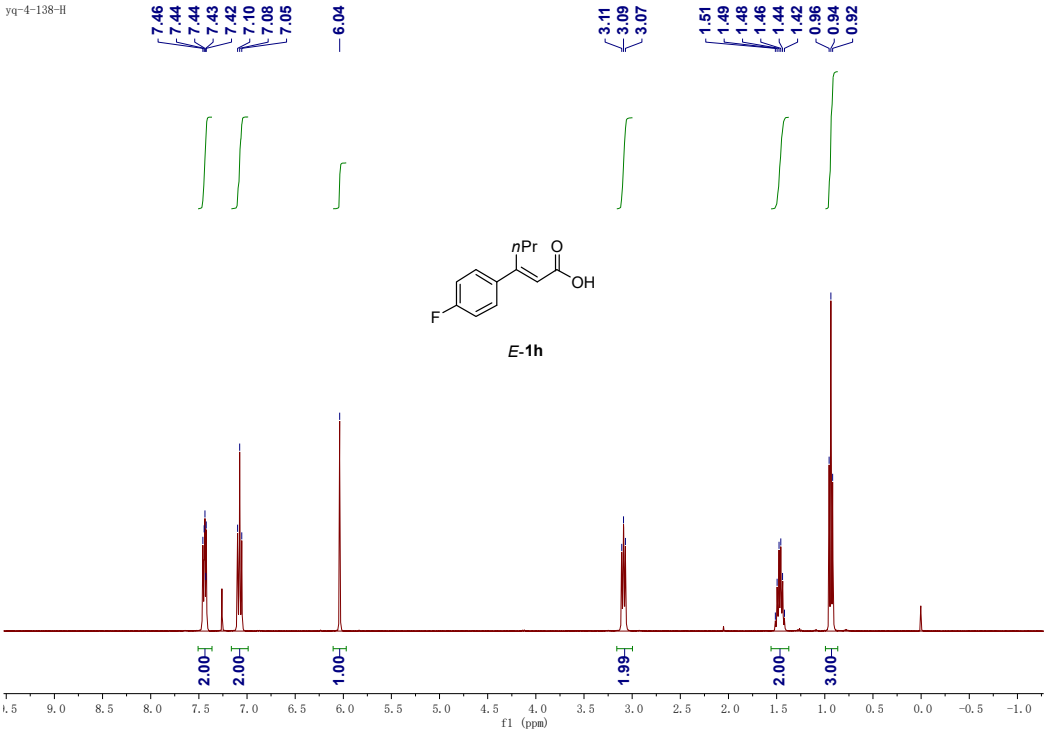
We conducted the experiment by changing the blue LEDs light to white LEDs light. Only *E*-arylvinyl halide was obtained through decarboxylation/halogenations.

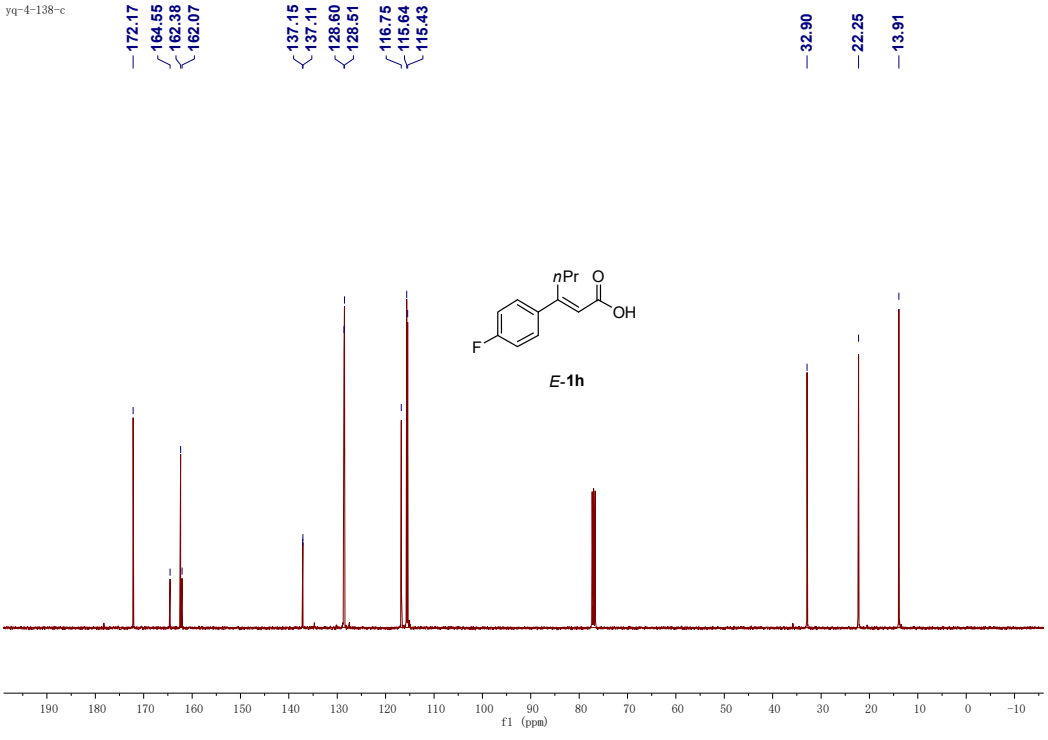


E-**1b** *E*-**2b**

67% NMR Yield

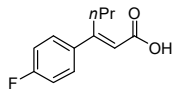



yq-4-138-H
7.46
7.44
7.44
7.43
7.42
7.10
7.08
7.05
6.04
3.11
3.09
3.07
1.51
1.49
1.48
1.46
1.44
1.42
0.96
0.94
0.92
nPr
O
OH
F
E-1h
2.00
2.00
1.00
1.99
2.00
3.00
f1 (ppm)

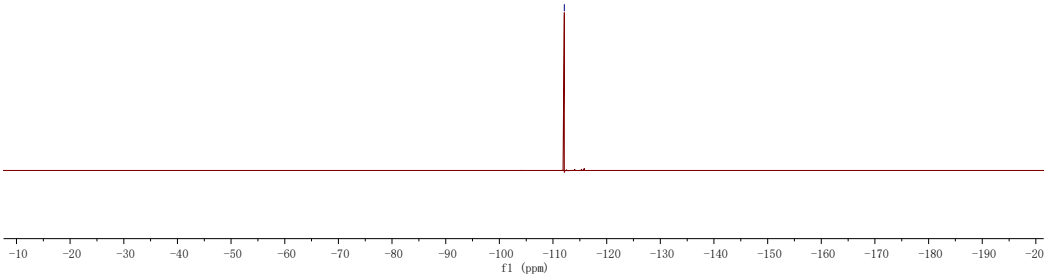

yq-4-138-c
172.17
164.55
162.38
162.07
137.15
137.11
128.60
128.51
116.75
115.64
115.43
32.90
22.25
13.91
nPr
O
OH
F
E-1h
f1 (ppm)

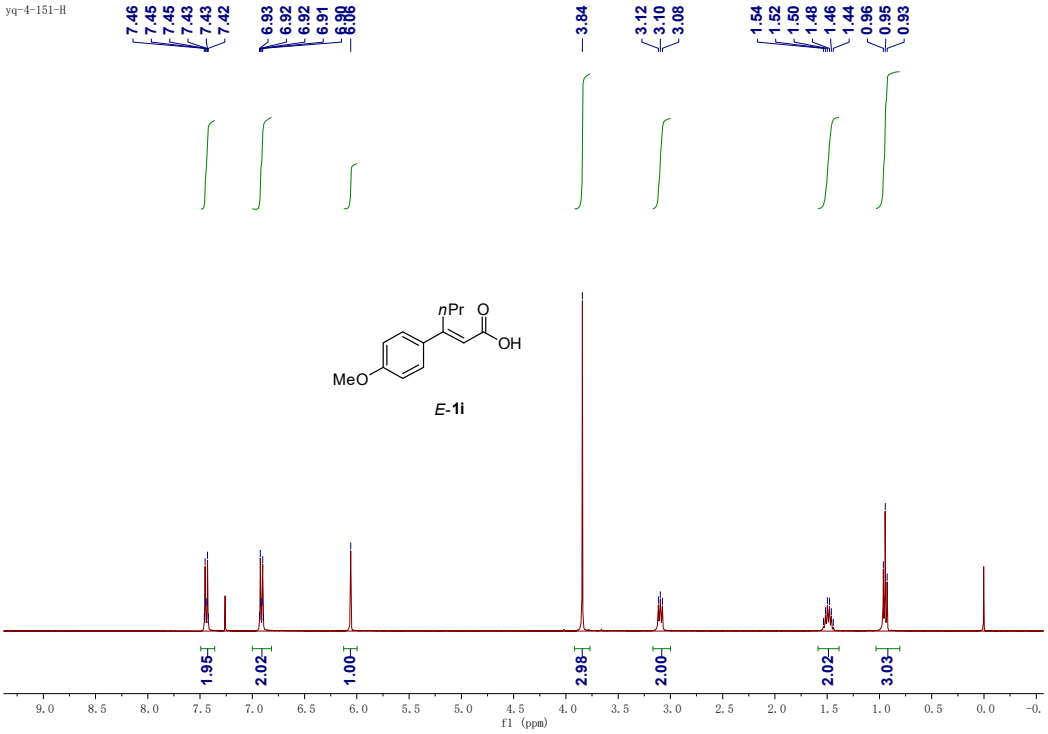
yq-4-138-f

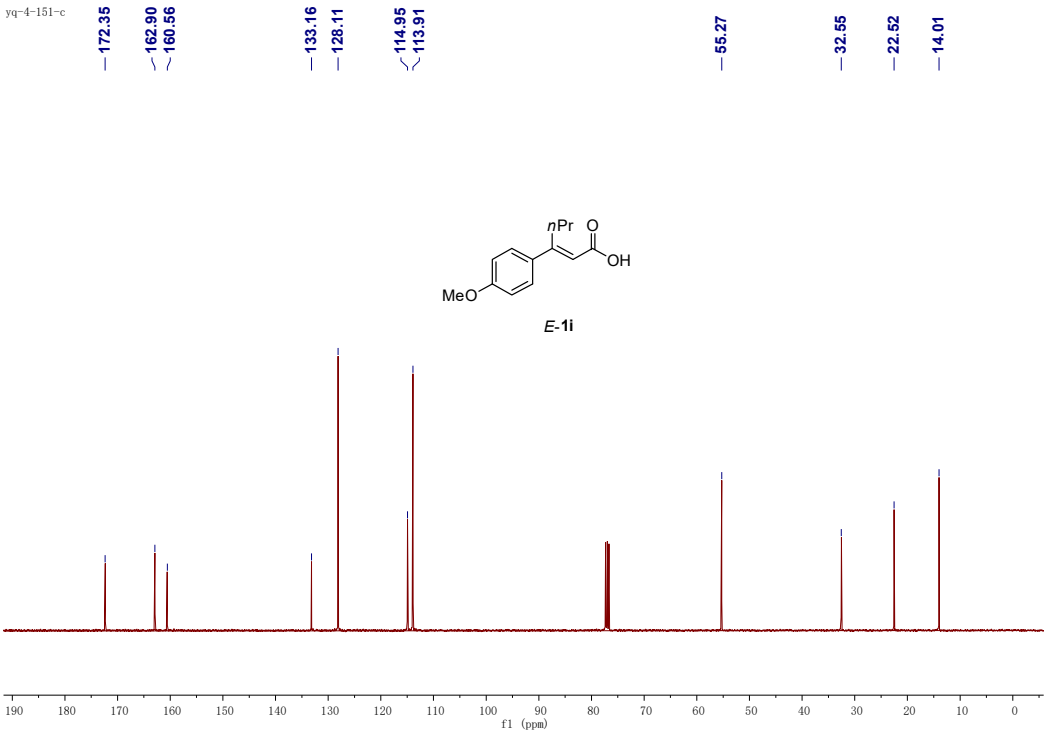
-112.10

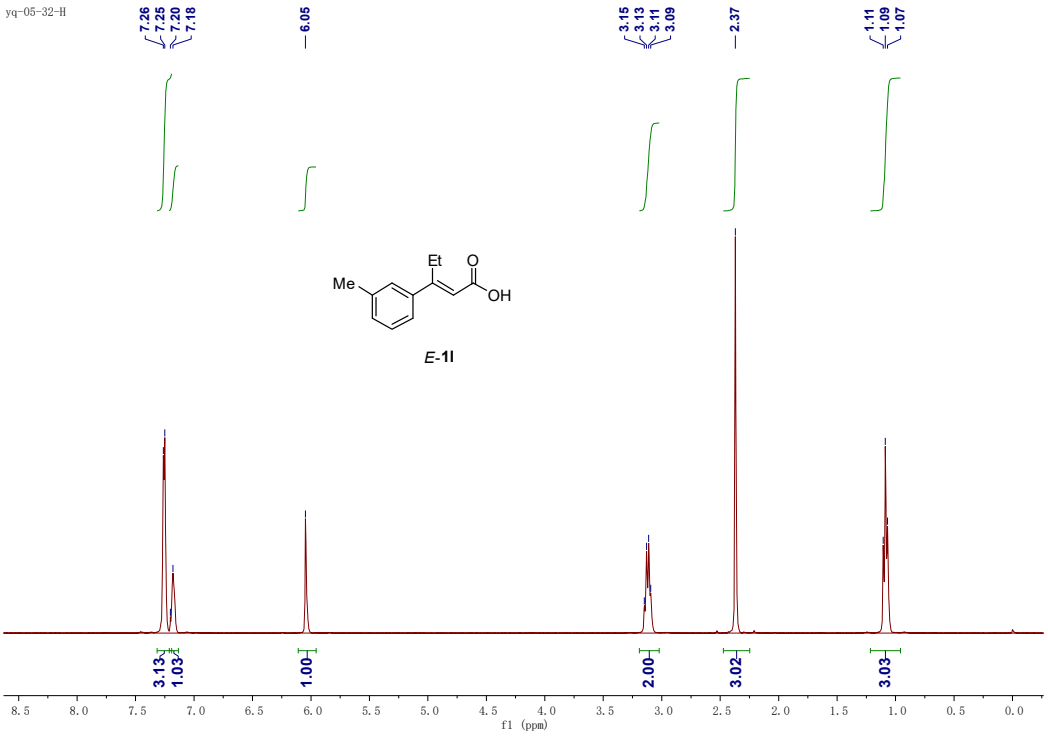


E-**1h**

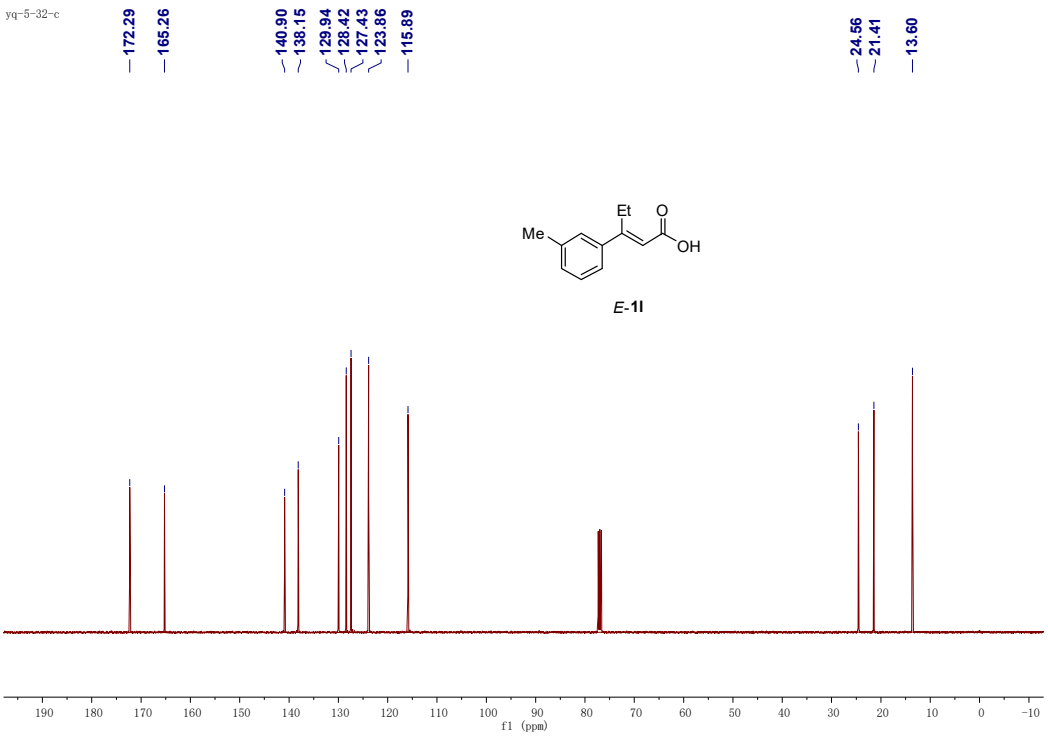



yq-4-151-H
7.46
7.45
7.45
7.43
7.43
7.42
6.93
6.92
6.92
6.91
6.88
6.88
3.84
3.12
3.10
3.08
1.54
1.52
1.50
1.48
1.46
1.44
0.96
0.95
0.93
nPr
O
OH
MeO
E-1i
1.95
2.02
1.00
2.98
2.00
2.02
3.03
f1 (ppm)

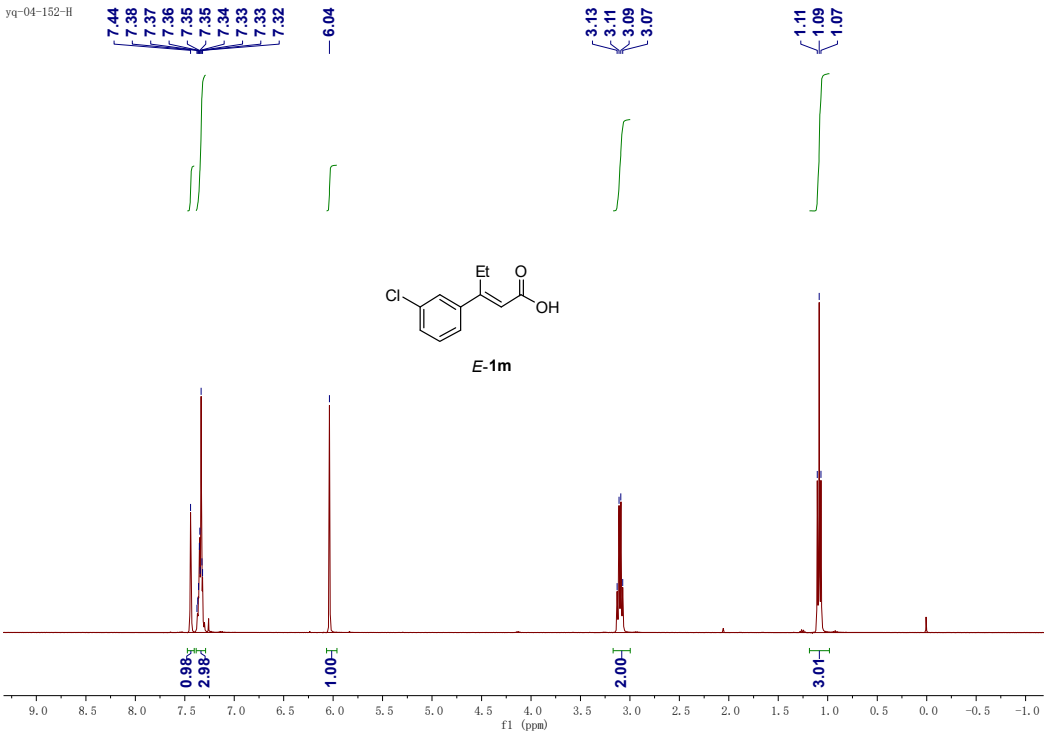

yq-4-151-c
172.35
162.90
160.56
133.16
128.11
114.95
113.91
55.27
32.55
22.52
14.01
nPr
O
OH
MeO
E-1i
f1 (ppm)

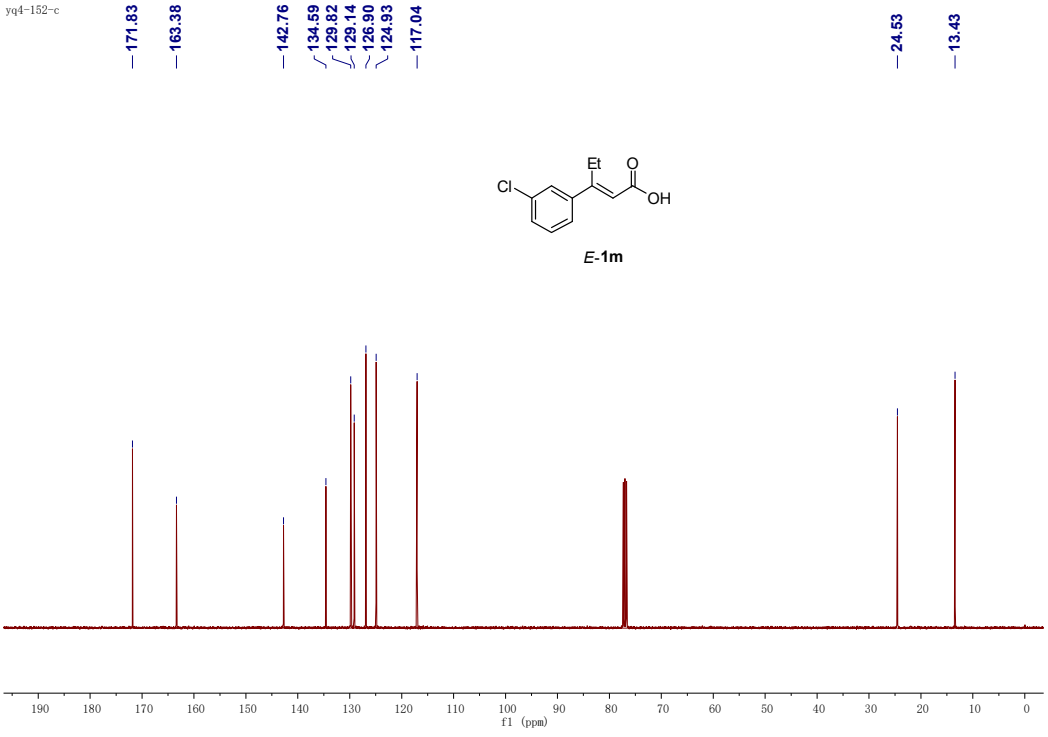

yq-05-32-H
7.26
7.25
7.20
7.18
6.05
3.15
3.13
3.11
3.09
2.37
1.11
1.09
1.07
Et
O
Me
OH
3.13
1.03
1.00
2.00
3.02
3.03
f1 (ppm)

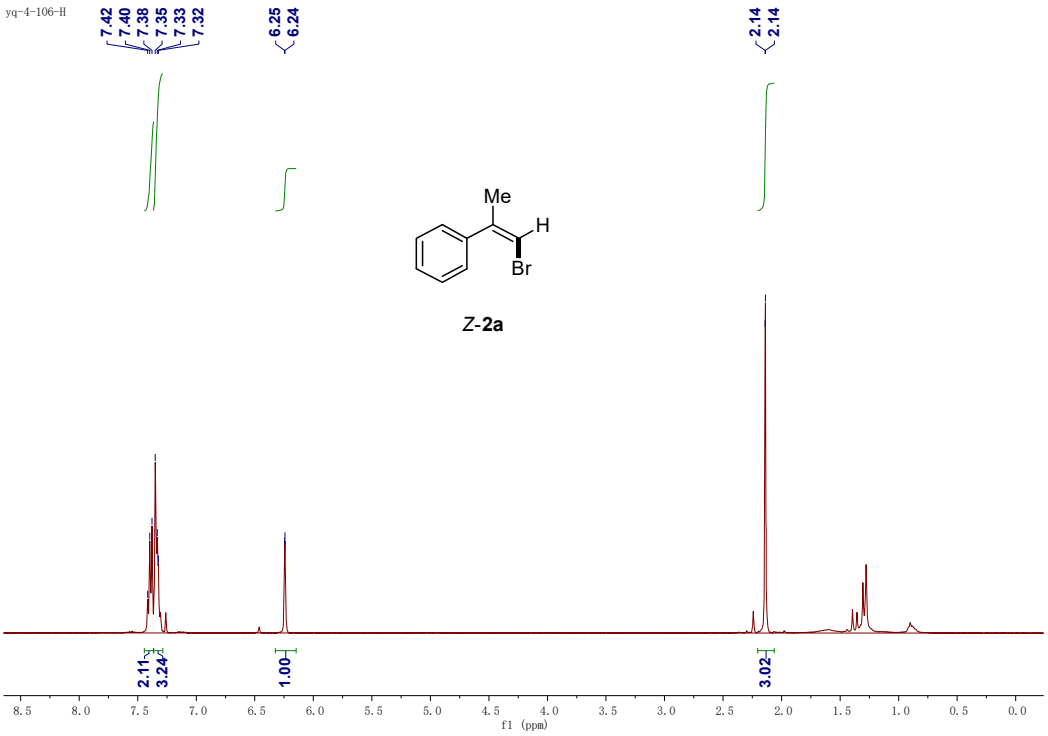
E-**1l**


yq-5-32-c
172.29
165.26
140.90
138.15
129.94
128.42
127.43
123.86
115.89
24.56
21.41
13.60
Et
O
Me
OH
f1 (ppm)

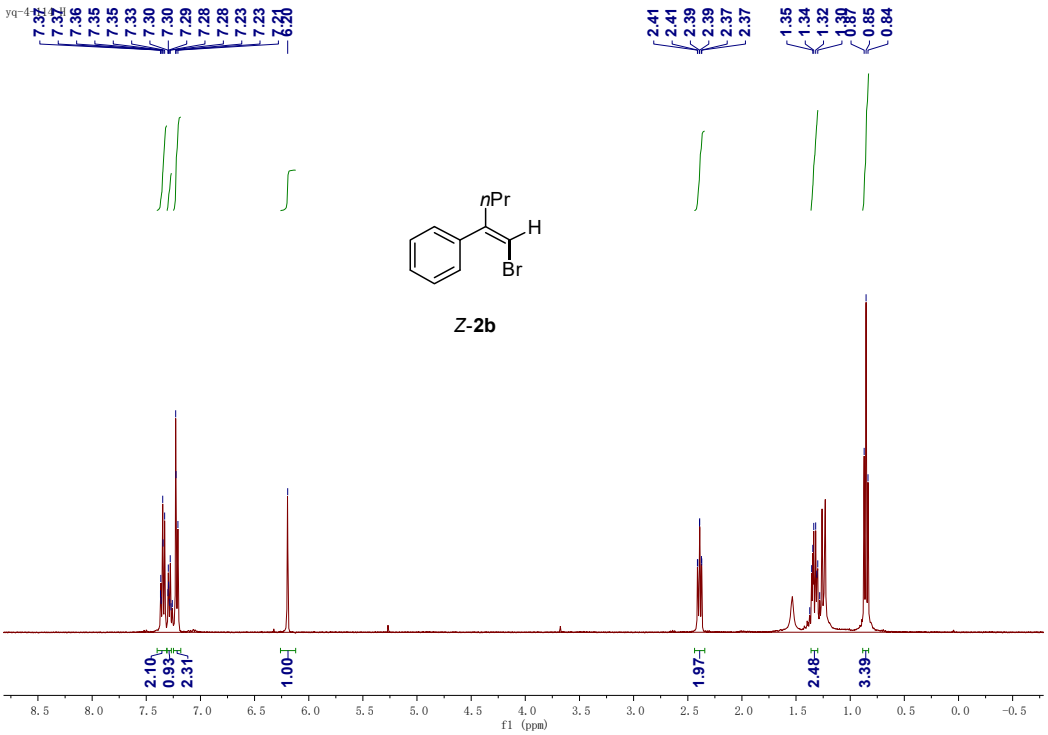
E-**1l**


yq-04-152-H
7.44
7.38
7.37
7.36
7.35
7.35
7.34
7.33
7.33
7.32
6.04
3.13
3.11
3.09
3.07
1.11
1.09
1.07
Et
O
Cl
OH
E-1m
0.98
2.98
1.00
2.00
3.01
f1 (ppm)

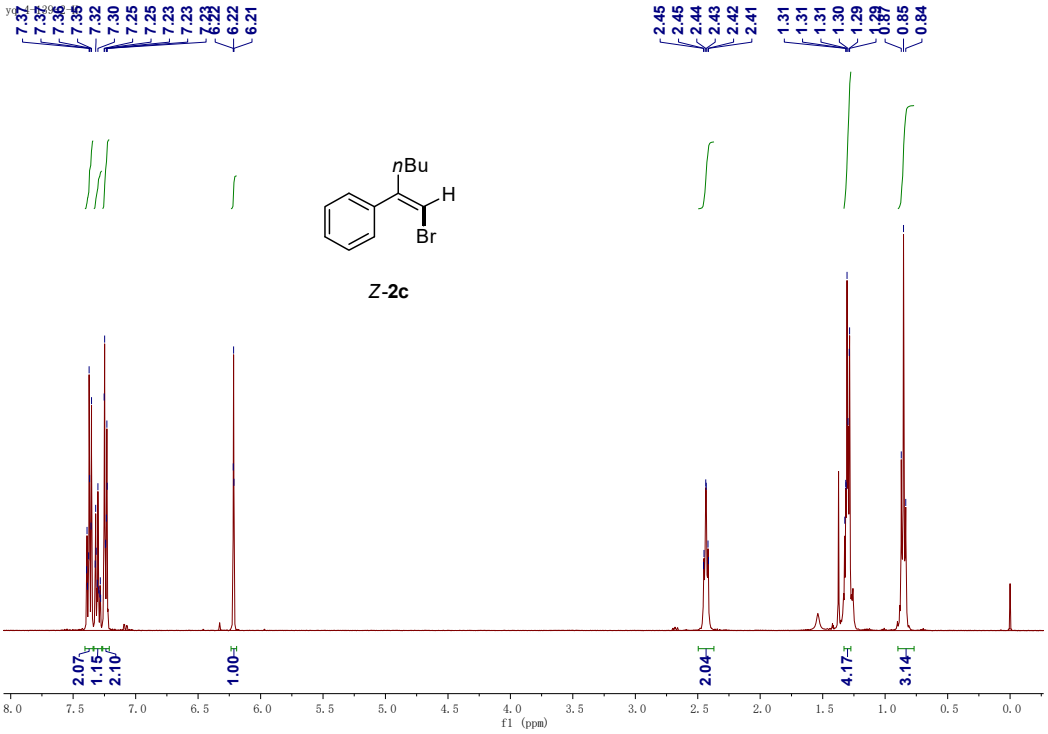

yq4-152-c
171.83
163.38
142.76
134.59
129.82
129.14
126.90
124.93
117.04
24.53
13.43
Et
O
Cl
OH
E-1m
f1 (ppm)


yq-4-106-H
7.42
7.40
7.38
7.35
7.33
7.32
6.25
6.24
2.14
2.14
Me
H
Br
2.11
3.24
1.00
3.02
f1 (ppm)

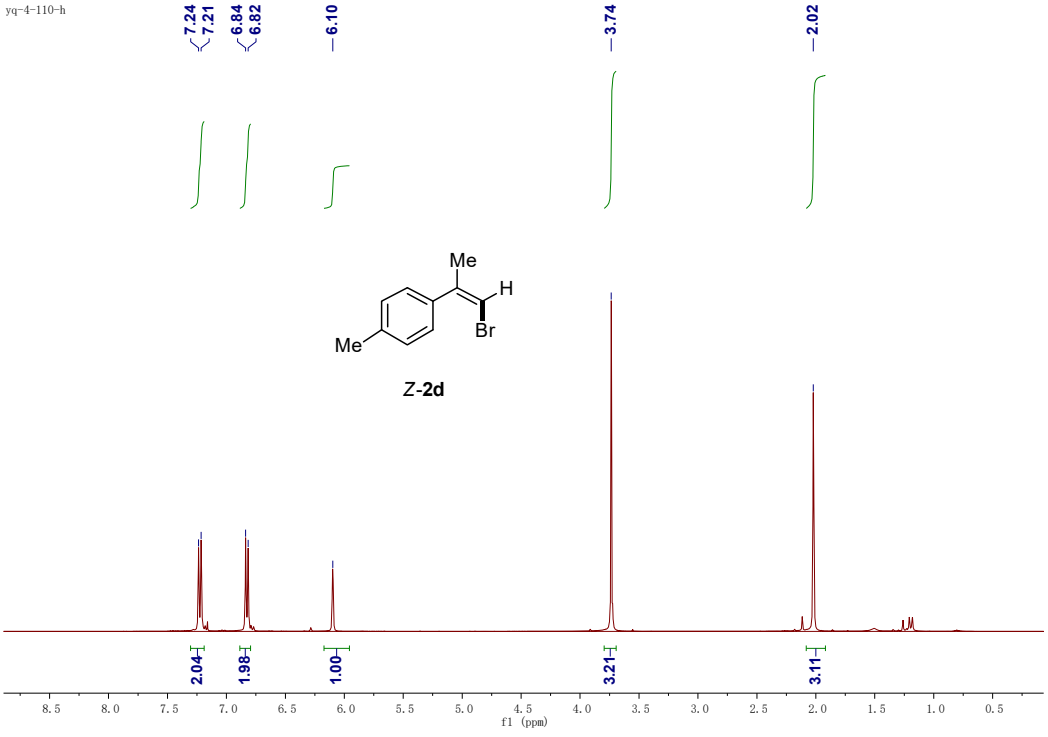
Z-**2a**


7.37
7.36
7.35
7.33
7.30
7.29
7.28
7.23
6.20
2.41
2.39
2.37
1.35
1.34
1.32
0.85
0.84
nPr
H
Br
2.10
0.93
2.31
1.00
1.97
2.48
3.39
f1 (ppm)

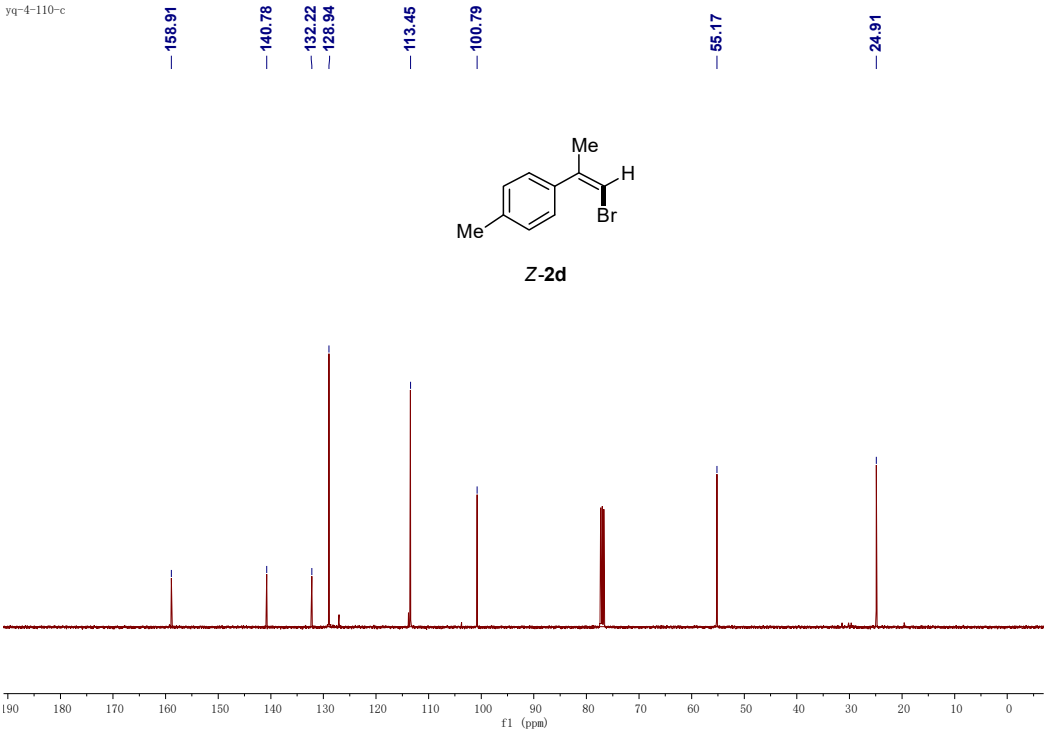
Z-**2b**


7.37
7.33
7.36
7.35
7.32
7.30
7.25
7.25
7.23
7.23
6.22
6.21
2.45
2.45
2.44
2.43
2.42
2.41
1.31
1.31
1.31
1.30
1.29
0.87
0.85
0.84
nBu
H
Br
2.07
1.15
2.10
1.00
2.04
4.17
3.14
f1 (ppm)

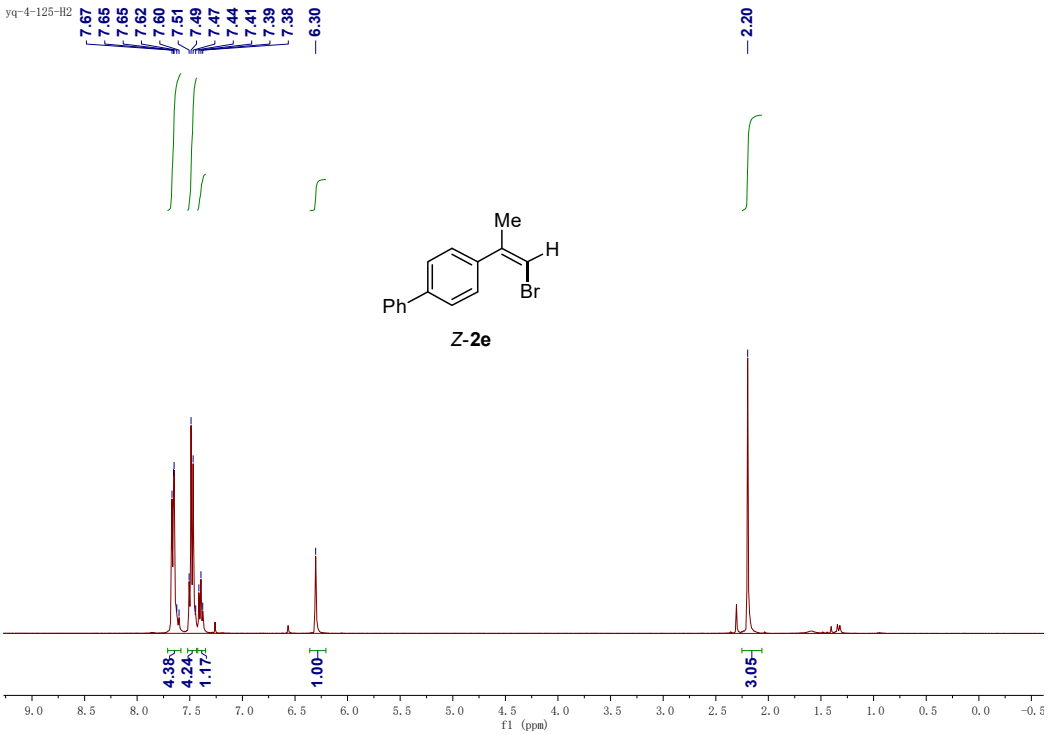
Z-**2c**


yq-4-110-h
7.24
7.21
6.84
6.82
6.10
3.74
2.02
Me
H
Br
Me
2.04
1.98
1.00
3.21
3.11
f1 (ppm)

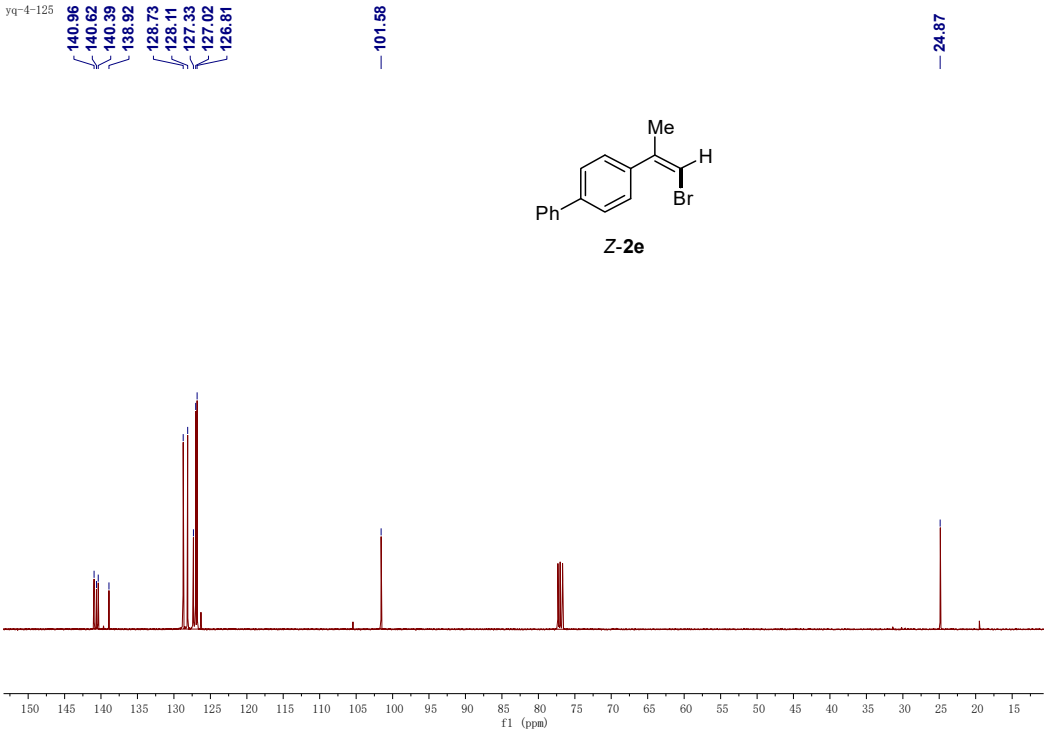
Z-**2d**


yq-4-110-c
158.91
140.78
132.22
128.94
113.45
100.79
55.17
24.91
Me
H
Br
Me
f1 (ppm)

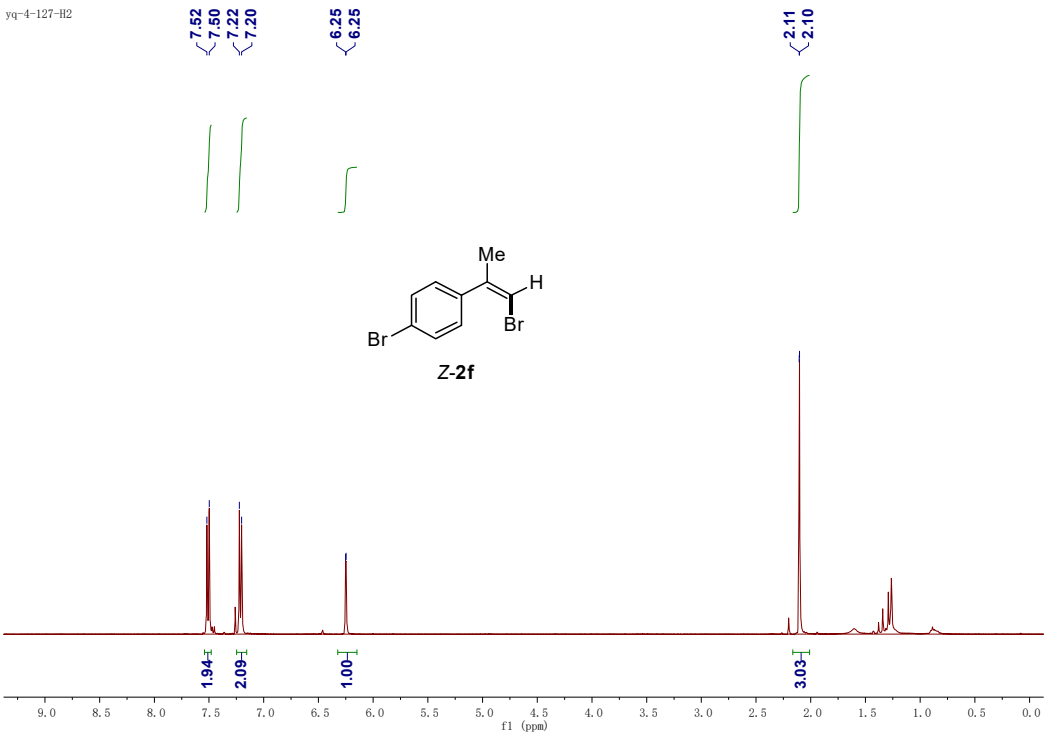
Z-**2d**


yq-4-125-H2
7.67
7.65
7.65
7.62
7.60
7.51
7.49
7.47
7.44
7.41
7.39
7.38
6.30
2.20
Me
H
Br
Ph
4.38
4.24
1.17
1.00
3.05
f1 (ppm)

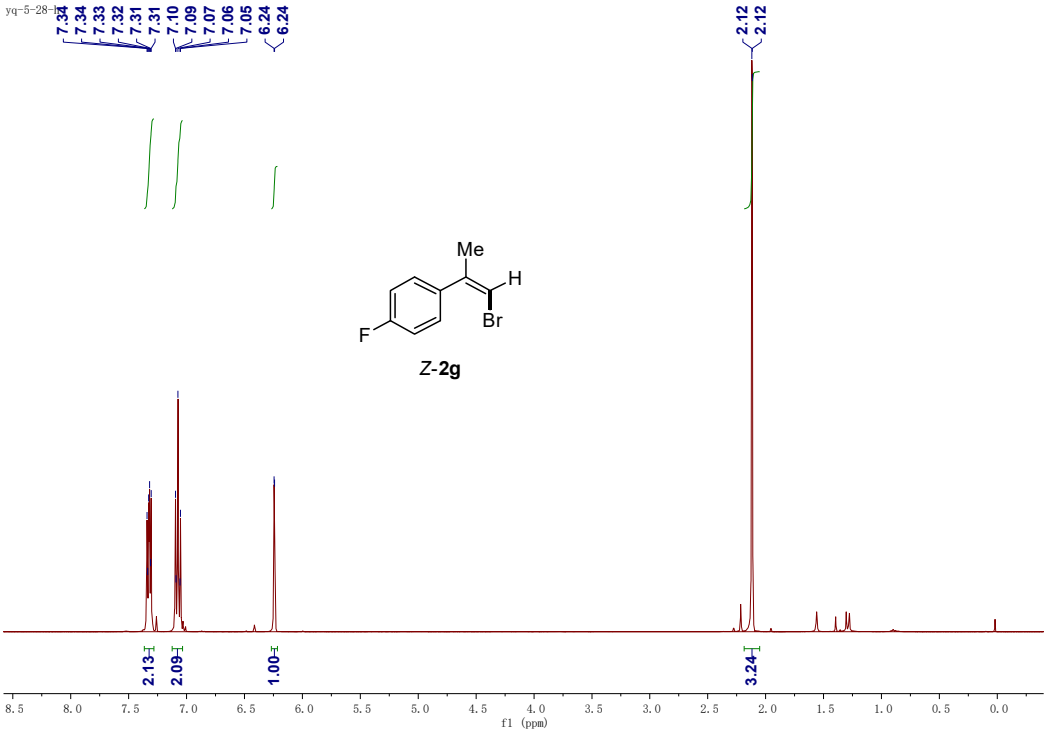
Z-**2e**


yq-4-125
140.96
140.62
140.39
138.92
128.73
128.11
127.33
127.02
126.81
101.58
24.87
Me
H
Br
Ph
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)

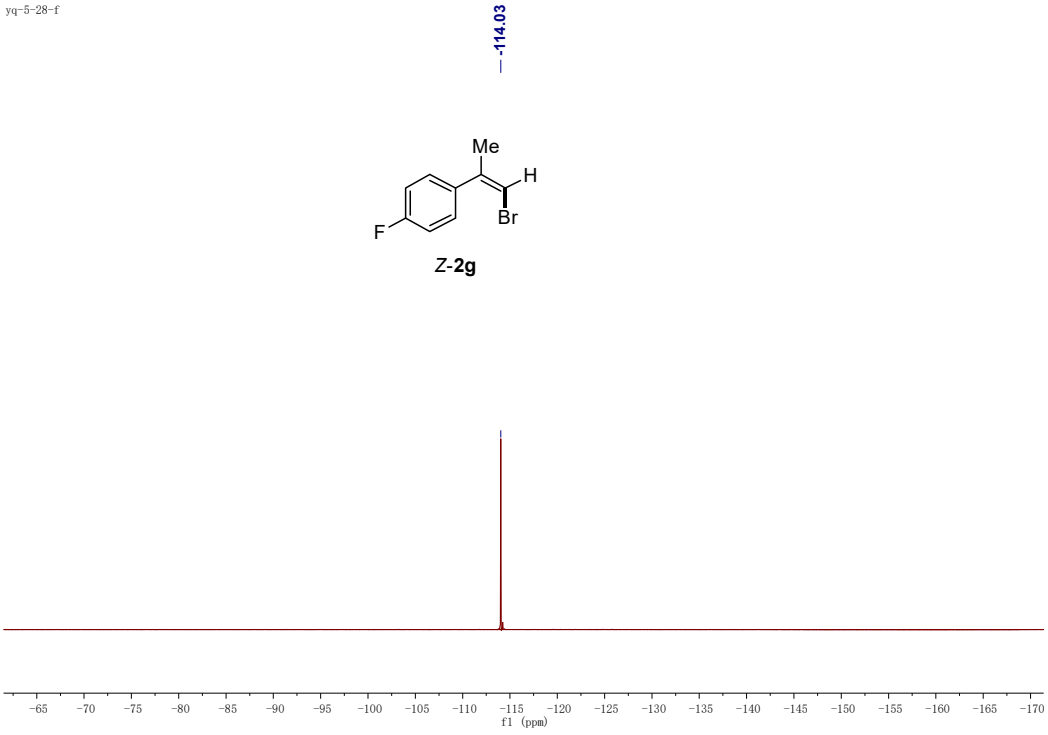
Z-**2e**


yq-4-127-H2
7.52
7.50
7.22
7.20
6.25
6.25
2.11
2.10
Me
H
Br
Br
1.94
2.09
1.00
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

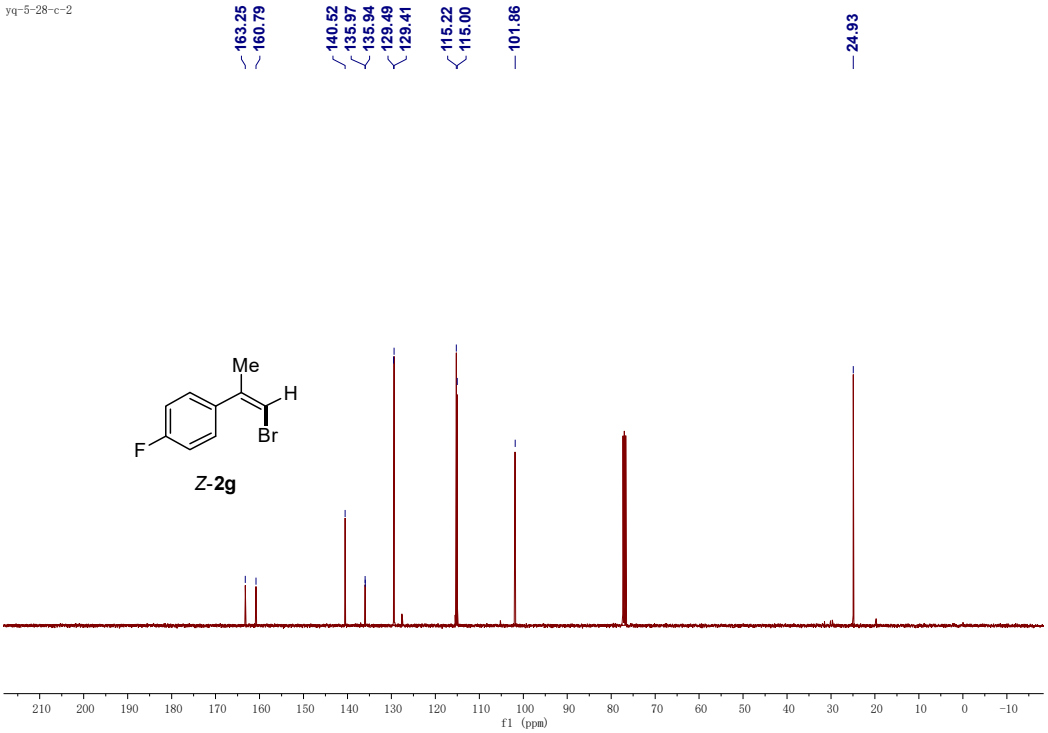
Z-**2f**

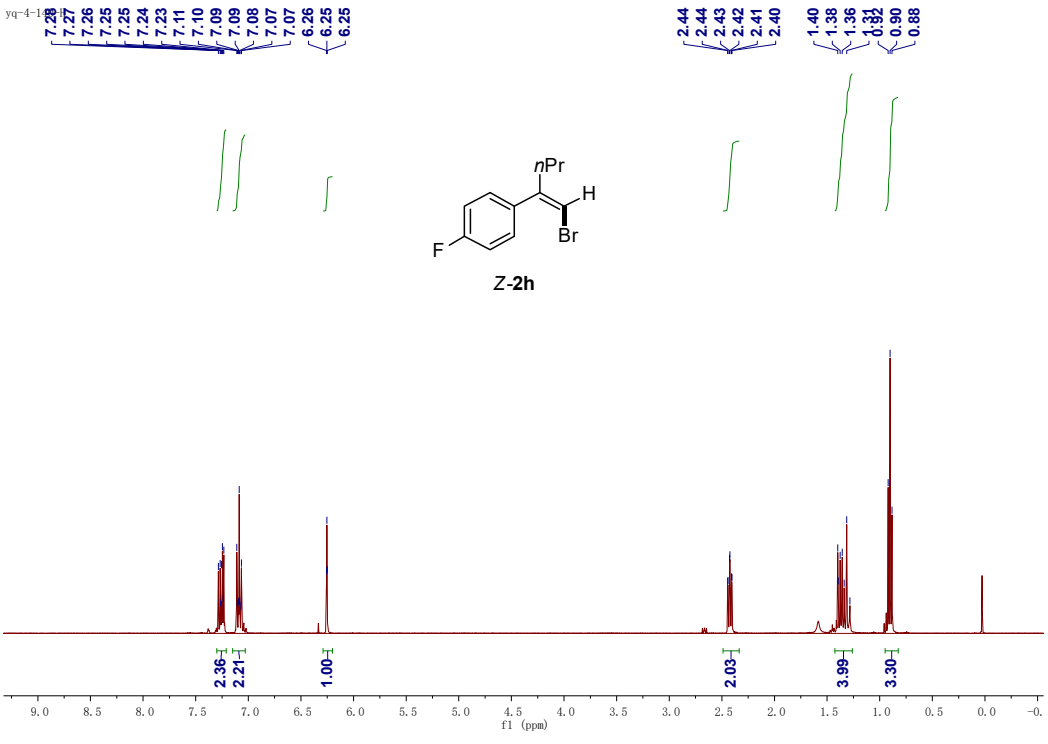

yq-5-28-h
7.34
7.34
7.33
7.32
7.31
7.31
7.10
7.09
7.07
7.06
7.05
6.24
6.24
2.12
2.12
Me
H
Br
F
2.13
2.09
1.00
3.24
f1 (ppm)

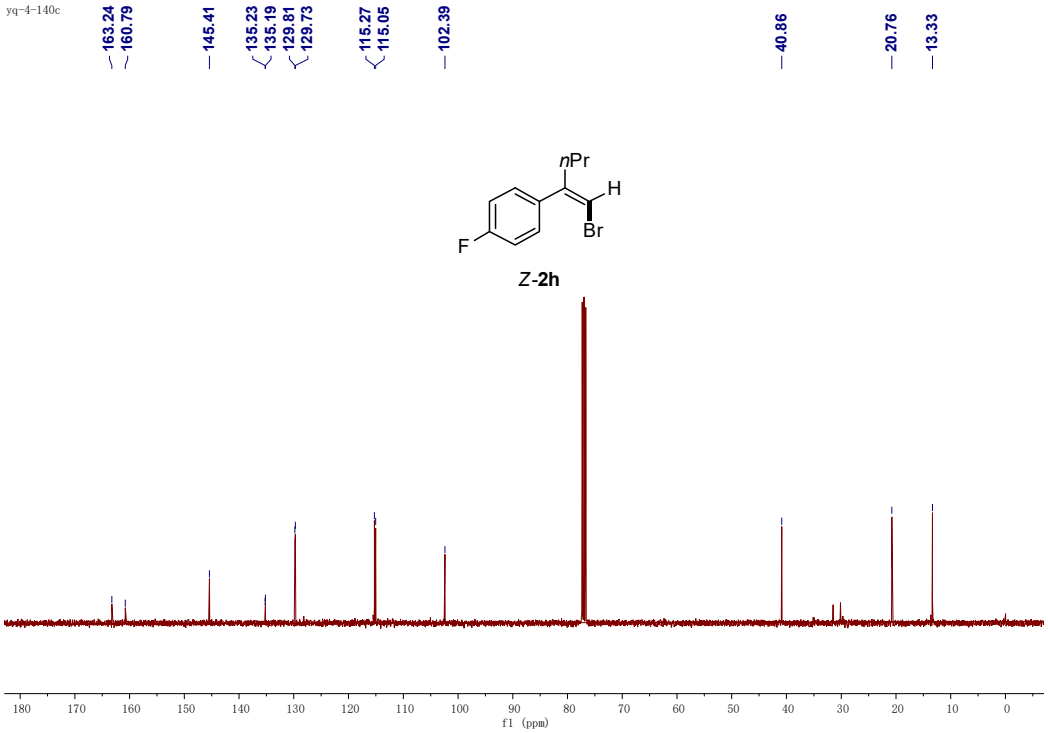
Z-**2g**

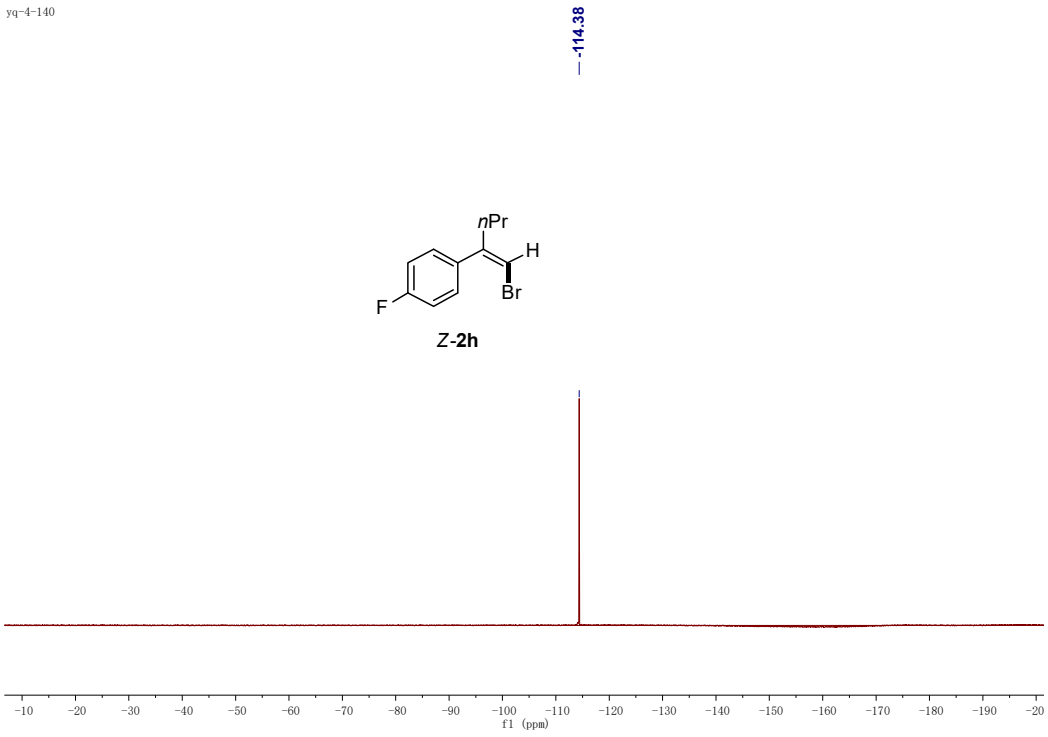

yq-5-28-f
-114.03
Me
H
Br
F
f1 (ppm)

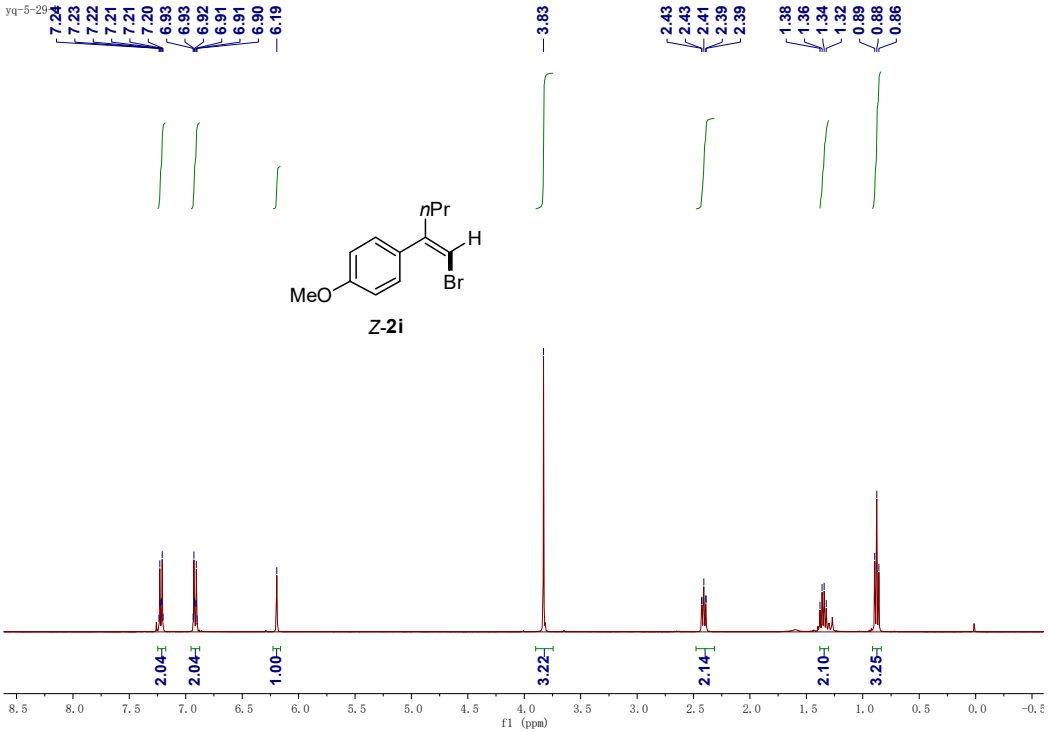
Z-**2g**

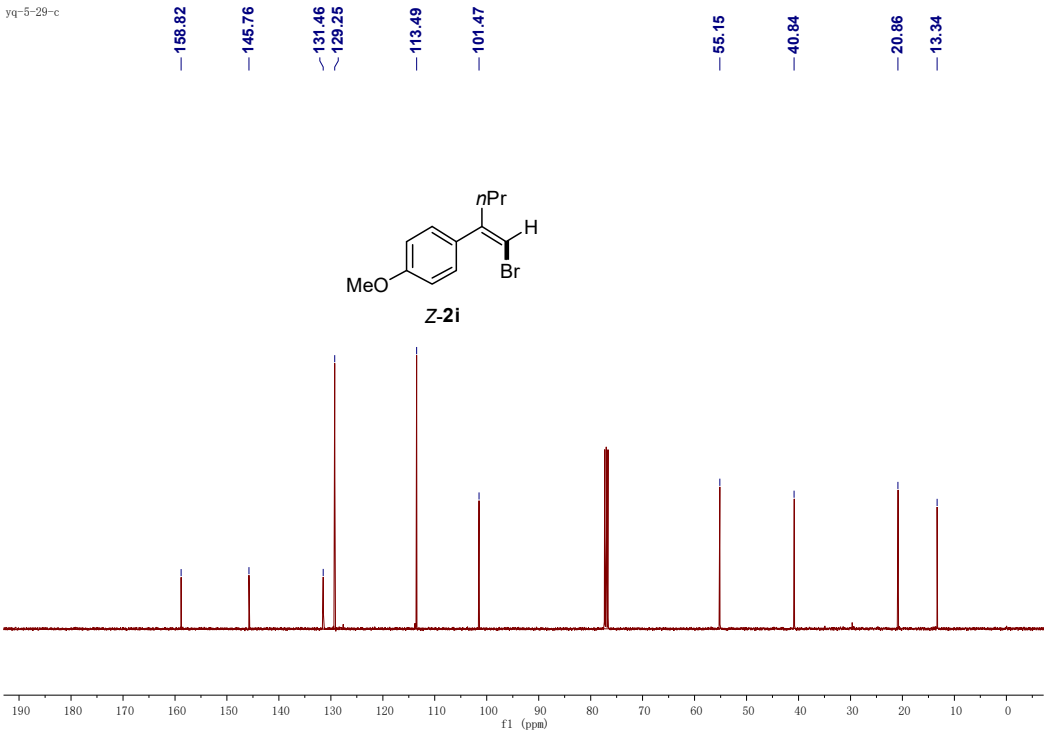

yq-5-28-c-2
163.25
160.79
140.52
135.97
135.94
129.49
129.41
115.22
115.00
101.86
24.93
Me
H
Br
F
Z-2g
f1 (ppm)

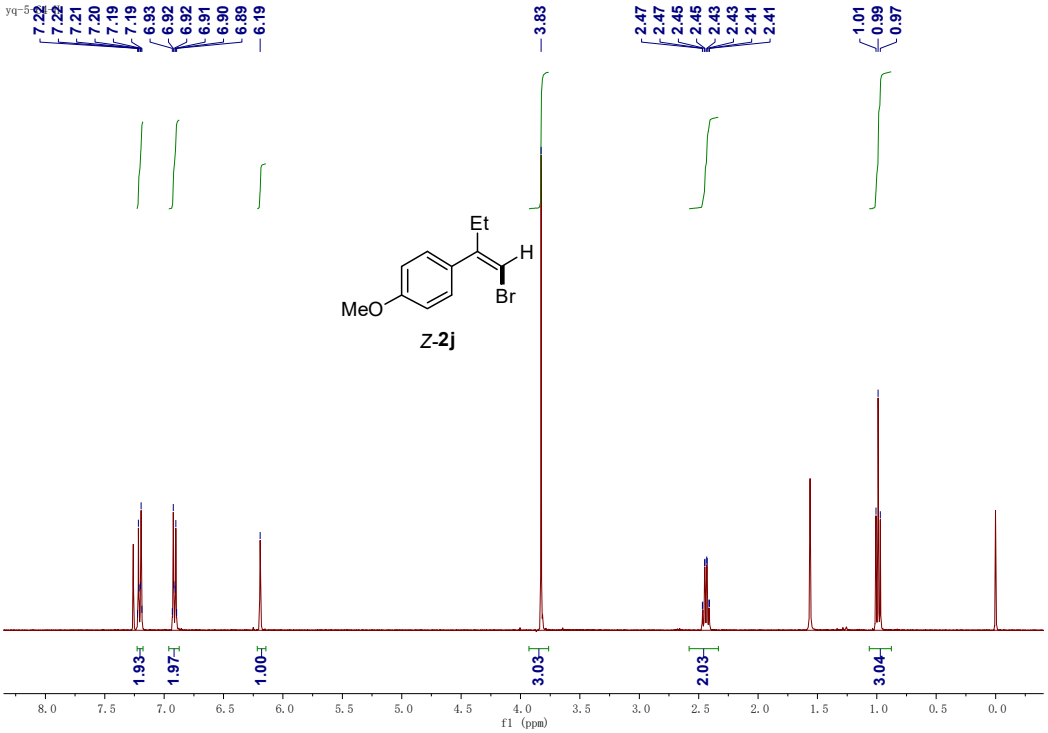

7.28
7.27
7.26
7.25
7.25
7.24
7.23
7.11
7.10
7.09
7.09
7.08
7.07
7.07
6.26
6.25
6.25
2.44
2.44
2.43
2.42
2.41
2.40
1.40
1.38
1.36
1.31
0.92
0.90
0.88
nPr
H
Br
F
Z-2h
2.36
2.21
1.00
2.03
3.99
3.30
f1 (ppm)

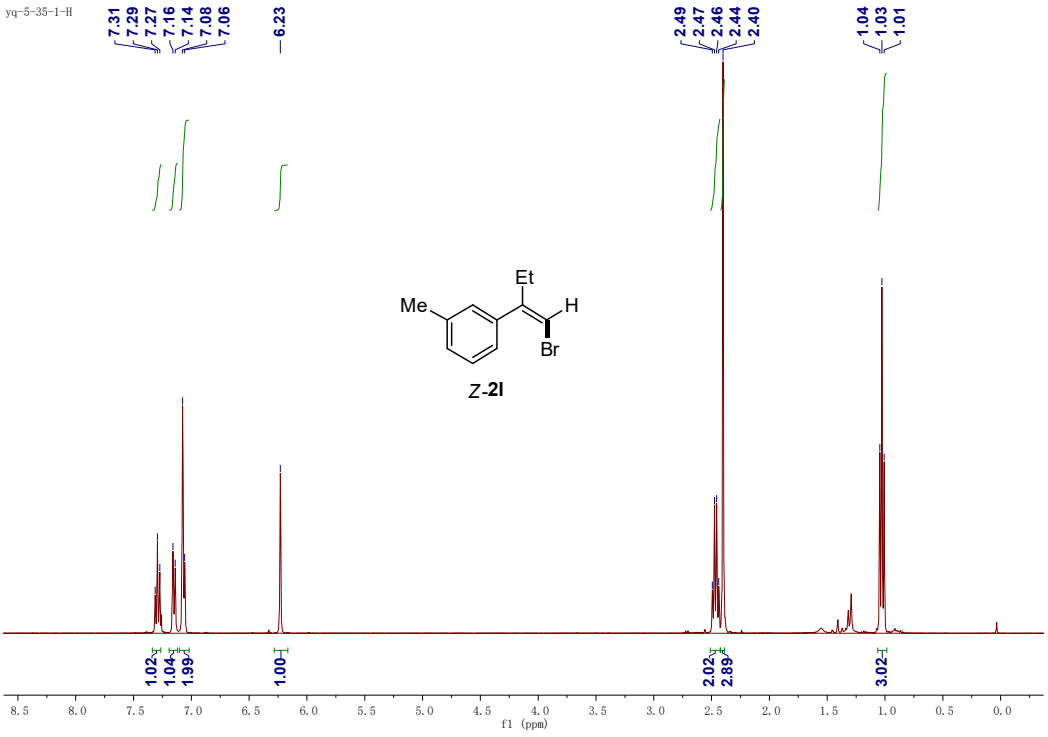

yq-4-140c
163.24
160.79
145.41
135.23
135.19
129.81
129.73
115.27
115.05
102.39
40.86
20.76
13.33
nPr
H
Br
F
Z-2h
f1 (ppm)

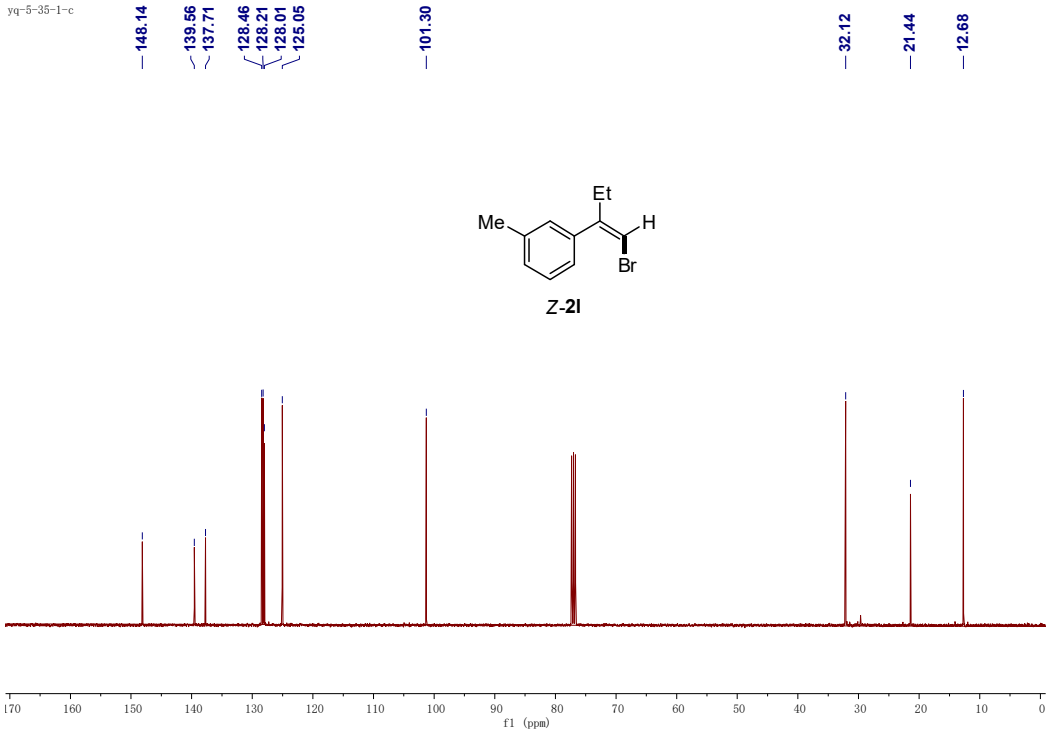

yq-4-140
-114.38
nPr
H
Br
F
Z-2h
f1 (ppm)


yq-5-29
7.24
7.23
7.22
7.21
7.21
7.20
6.93
6.93
6.92
6.91
6.91
6.90
6.19
3.83
2.43
2.43
2.41
2.39
2.39
1.38
1.36
1.34
1.32
0.89
0.88
0.86
nPr
H
Br
MeO
Z-2i
2.04
2.04
1.00
3.22
2.14
2.10
3.25
f1 (ppm)

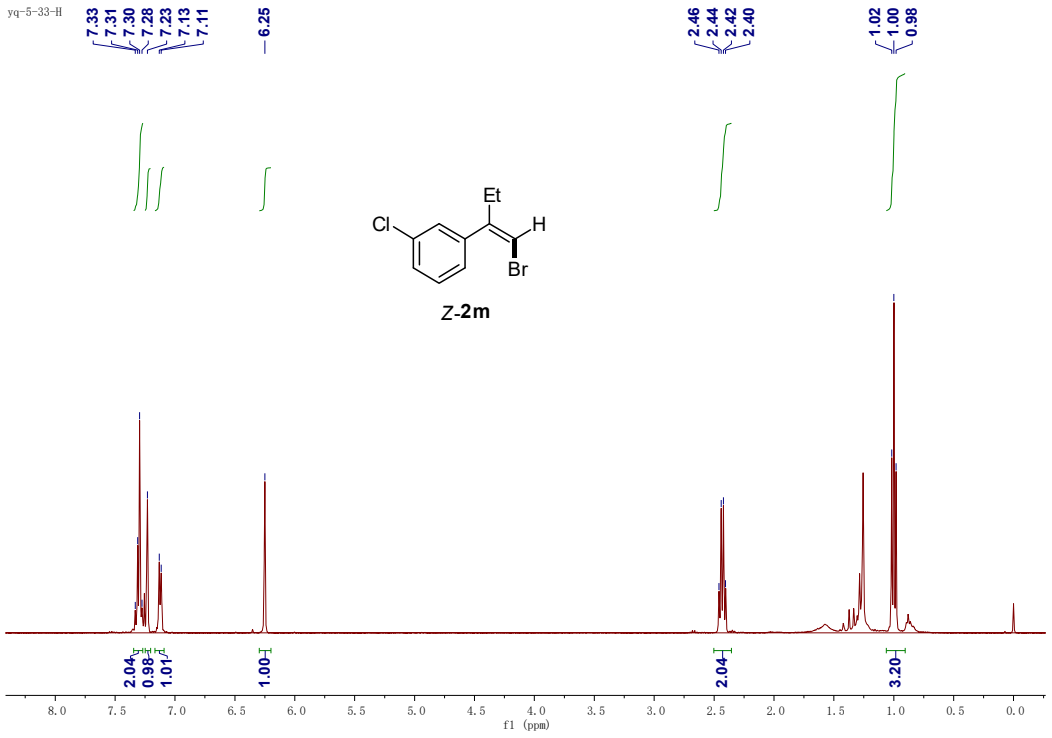

yq-5-29-c
158.82
145.76
131.46
129.25
113.49
101.47
55.15
40.84
20.86
13.34
nPr
H
Br
MeO
Z-2i
f1 (ppm)


7.24
7.22
7.21
7.20
7.19
7.19
6.93
6.92
6.92
6.91
6.90
6.89
6.19
3.83
2.47
2.47
2.45
2.45
2.43
2.43
2.41
2.41
1.01
0.99
0.97
Et
H
Br
MeO
Z-2j
1.93
1.97
1.00
3.03
2.03
3.04
f1 (ppm)

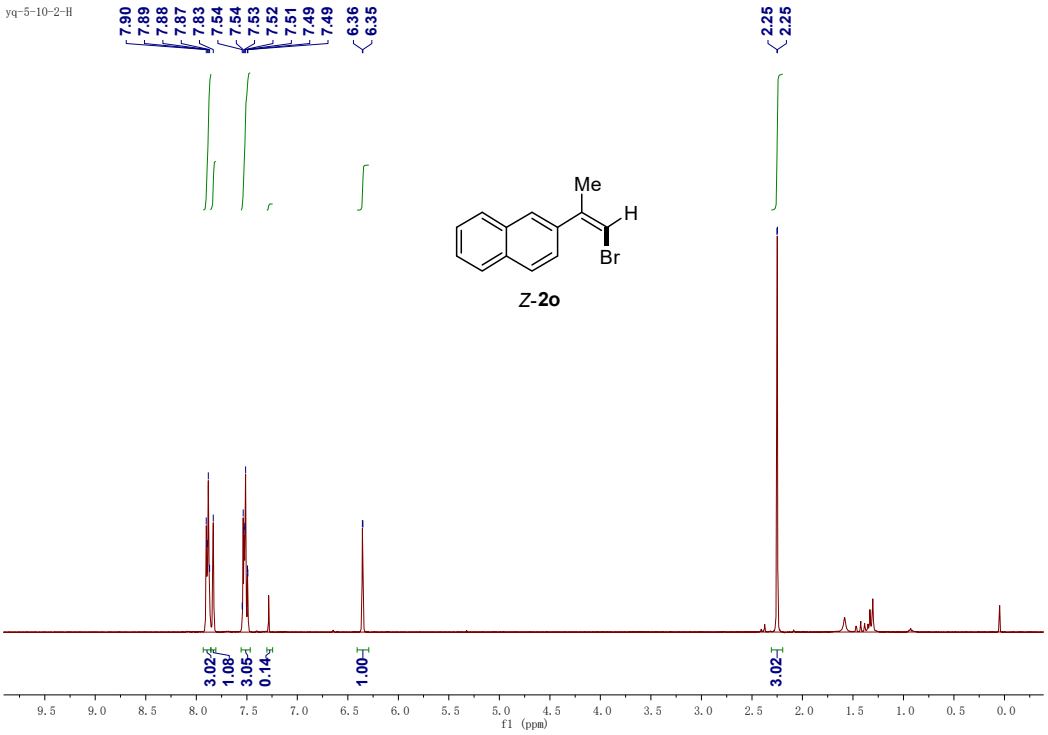

yq-5-35-1-H
7.31
7.29
7.27
7.16
7.14
7.08
7.06
6.23
2.49
2.47
2.46
2.44
2.40
1.04
1.03
1.01
Et
H
Br
Me
Z-2l
1.02
1.04
1.99
1.00
2.02
2.89
3.02
f1 (ppm)


yq-5-35-1-c
148.14
139.56
137.71
128.46
128.21
128.01
125.05
101.30
32.12
21.44
12.68
Et
Me
H
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

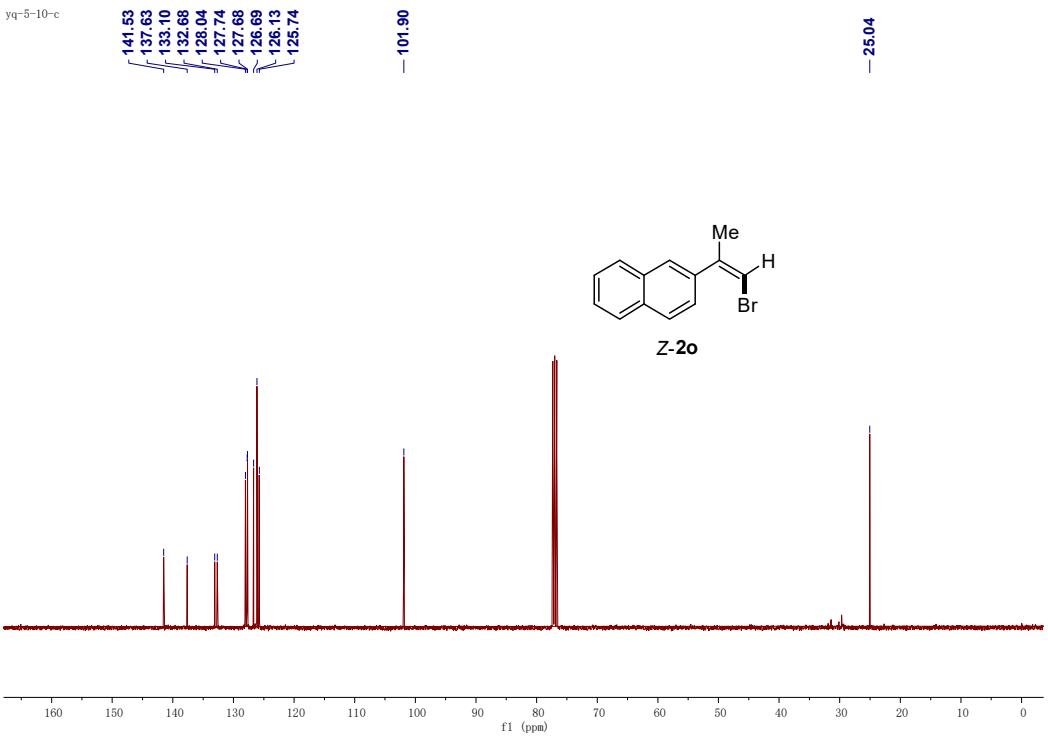
Z-**2l**


yq-5-33-H
7.33
7.31
7.30
7.28
7.23
7.13
7.11
6.25
2.46
2.44
2.42
2.40
1.02
1.00
0.98
Et
Cl
H
Br
2.04
0.98
1.01
1.00
2.04
3.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

Z-**2m**

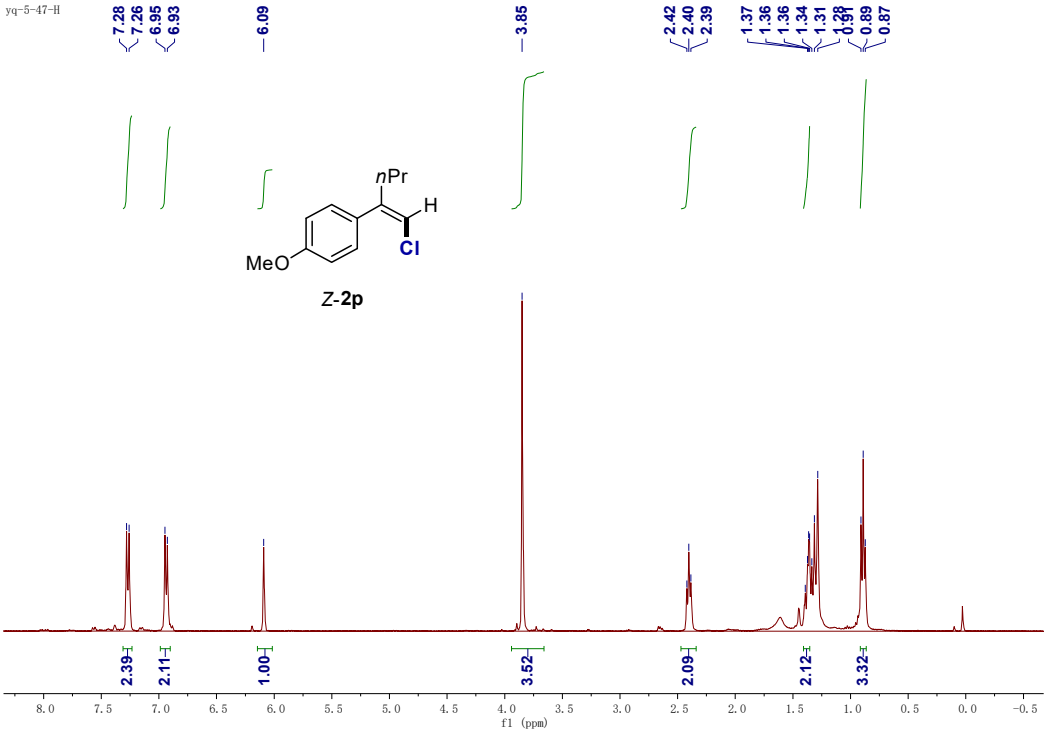

yq-5-10-2-H
7.90
7.89
7.88
7.87
7.83
7.54
7.54
7.53
7.52
7.51
7.49
7.49
6.36
6.35
2.25
2.25
Me
H
Br
3.02
1.08
3.05
0.14
1.00
3.02
f1 (ppm)

Z-**2o**

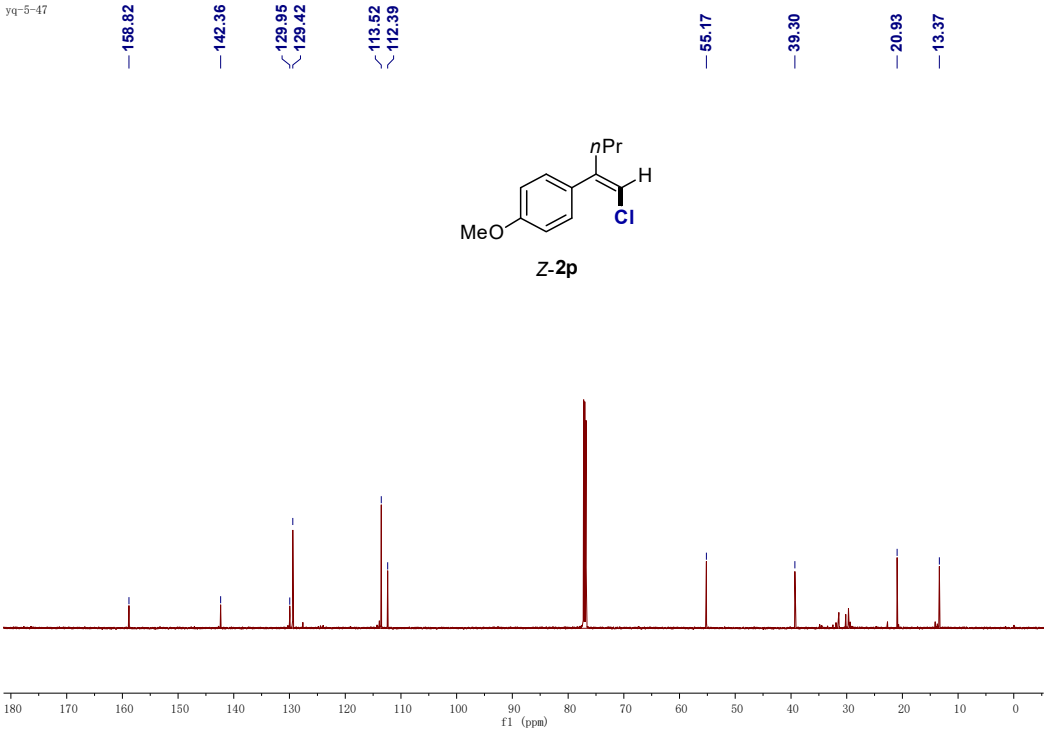

yq-5-10-c
141.53
137.63
133.10
132.68
128.04
127.74
127.68
126.69
126.13
125.74
101.90
25.04
f1 (ppm)

Me
H
Br

Z-**2o**

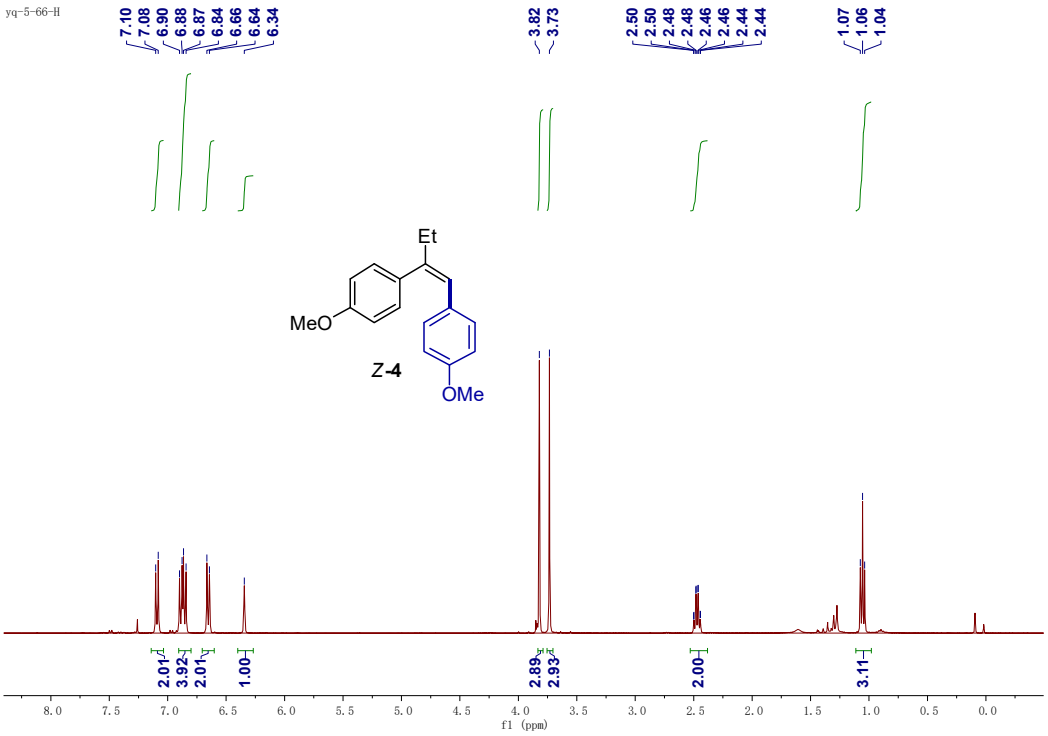

yq-5-47-H
7.28
7.26
6.95
6.93
6.09
3.85
2.42
2.40
2.39
1.37
1.36
1.36
1.34
1.31
1.28
0.91
0.89
0.87
nPr
H
Cl
MeO
2.39
2.11
1.00
3.52
2.09
2.12
3.32
f1 (ppm)

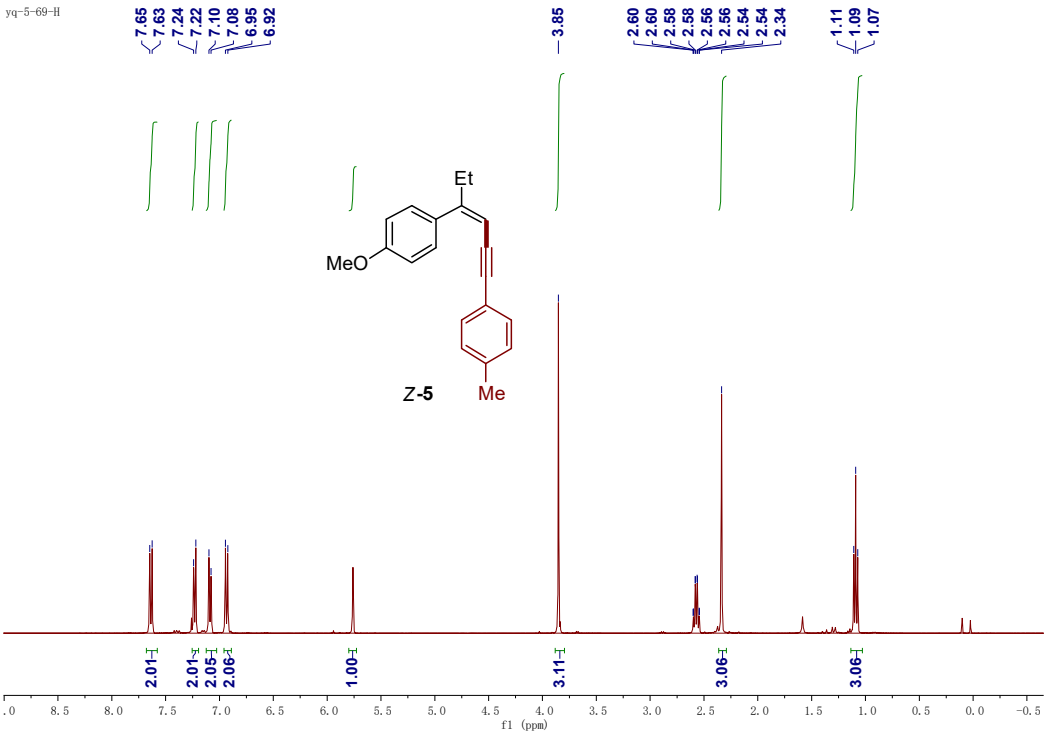
Z-**2p**


yq-5-47
158.82
142.36
129.95
129.42
113.52
112.39
55.17
39.30
20.93
13.37
f1 (ppm)

nPr
H
Cl
MeO

Z-**2p**


yq-5-66-H
7.10
7.08
6.90
6.88
6.87
6.84
6.66
6.64
6.34
3.82
3.73
2.50
2.50
2.48
2.48
2.46
2.46
2.44
2.44
1.07
1.06
1.04
Et
MeO
OMe
Z-4
2.01
3.92
2.01
1.00
2.89
2.93
2.00
3.11
f1 (ppm)


yq-5-69-H
7.65
7.63
7.24
7.22
7.10
7.08
6.95
6.92
3.85
2.60
2.60
2.58
2.58
2.56
2.56
2.54
2.54
2.34
1.11
1.09
1.07
Et
MeO
Me
Z-5
2.01
2.01
2.05
2.06
1.00
3.11
3.06
3.06
f1 (ppm)